Iodine-promoted insertion of the oxygen atom from water in η⁴-vinylketene[Fe(CO)₃] complexes

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SUPPORTING INFORMATION

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. Methyllithium (1.6 M in diethyl ether) was purchased from Aldrich and its concentration tested by a literature procedure.[1] Enneacarbonyldiiron(0) was prepared by a published procedure.[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 FTIR, using ATR technique. NMR spectra were measured at room temperature on Bruker 300 (300.52 MHz ^1H, 75.56 MHz, ^{13}C) spectrometer, using $CDCl_3$ as solvent. Mass spectra were recorded on a JEOL JMS-AX505 instrument by using EI and FAB (matrix-*m*-nitrobenzylalcohol) techniques.

Structure Determination by X-ray Crystallography.

Suitable X-ray-quality crystals of **3g** and **4f** were grown by slow evaporation of a mixture of dichloromethane/ hexane at room temperature and diethyl ether at -5°C, respectively. The crystals of each compound were mounted on a glass fiber at room temperature. The crystals of **3g** and **4f** were then placed on a Rigaku Oxford Diffraction GEMINI EOS equipped with Mo-Kα radiation; decay was negligible in all cases. Details of crystallographic data collected for compounds **3g** and **4f** are provided in Table 3 of main manuscript. Systematic absences and intensity statistics were used in space group determinations. The structures were solved by the Integrated Space-Group and Crystal-Structure software (SHELXt)[3] and refined

[1] E. Juaristi, A. Martínez-Richa, A. Garcia-Rivera and J. S. Cruz-Sánchez, *J. Org. Chem.,* 1983, **48**, 2603-2606.
[2] H. E. Braye and W. Hubel, *Inorg. Synth.,* 1966, **8**, 168.
[3] G. M. Sheldrick, *Acta Crystallogr.* 2015, **A71**, 3-8.

by least-squares procedures on F2 using SHELXL-2015.[4] All H atoms attached to carbon were introduced in calculation in idealized positions and treated as riding models. The drawing of the molecules was realized with the help of ORTEP32.[5]

2. General procedure for obtaining chalcones 1a-h

The synthesis of compounds **1a-h** had been previously described.[6] An ethanolic solution (25mL) of NaOH (3 eq) was added the substituted aldehyde (1.2 eq) and a solution of acetylferrocene (1eq) in 5 mL of ethanol was added, the mixture was stirred at room temperature and was monitored by TLC. 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 Hexane/Ethyl acetate (9:1) as the mobile phase gave the expected deep purple crystalline solid products.

***(E)*-3-(4-chlorophenyl)-1-ferrocenyl-2-propen-1-one (1a)**

Purple crystals (94 %, yield), mp: 155-156 °C (lit[6] 51% yield, mp 155-156°C). ATR-FTIR (cm^{-1}): *ν*(CO) 1650. ^{1}H-NMR ($CDCl_3$, 300 MHz): *δ* (ppm) 7.74 (d, 1H, *J* = 15.6 Hz), 7.58 (d, 2H, Ph), 7.40 (d, 2H, Ph), 7.08 (d, 1H, *J* = 15.6 Hz), 4.91 (s, 2H, Cp), 4.60 (s, 2H, Cp), 4.22 (s, 5H, Cp). ^{13}C-NMR ($CDCl_3$, 75 MHz): *δ* (ppm) 192.7 (CO), 139.4 (CH), 136.0 (C_{para}), 133.7 (C_{ipso}), 129.4 (2CH, Ph), 129.2 (2CH, Ph), 124.0 (CH), 80.5 (C, Cp), 73.0 (2CH, Cp), 70.2 (5CH, Cp), 69.8 (2CH, Cp). **MS-EI** [*m/z*, (%)]: 350 [M^+] (100%); 352 [M^++ 2] (34%); 316 [M^+-Cl] (5%); 285 [(M^+-Cp)] (10%); 165 [M^+-(CpFeCp)] (14%); 121 [FeCp]$^+$ (9%).

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[4] G. M. Sheldrick, *Acta Crystallogr.* 2015, **C71**, 3-8

[5] L. J. Farrugia, ORTEP-3 for Windows, *J. Appl. Cryst*. 1997, **30**, 565. b) M.N. Burnett and C.K. Johnson, ORTEPIII. Report ORNL-6895, 1996, Oak Ridge National Laboratory, Tennessee, USA.

[6] a) Q. Jiang, T. Guo, Q. Wang, P. Wu, and Z. Yu, *Adv. Synth. Catal*, 2013, **355**, 1874. b) H. Parveen, F. Hayat, A. Salahuddin and A. Azam, *Eur. J. Med. Chem*., 2010, **45**, 3497, c) X. Wu, E. R.T. Tiekink, I. Kostetski, N. Kocherginsky, A. L.C. Tan, S. B. Khoo, P. Wilairat and M, L. Go, *Eur. J. Pharm. Science*, 2006, **27**, 175.

(*E*)-3-(4-fluorophenyl)-1-ferrocenyl-2-propen-1-one (1b)

Purple crystals (92 %, yield), mp 151-152 °C (lit[6b,c] 50% yield, mp 148-149°C). ATR-FTIR (cm^{-1}): *v*(CO) 1651. ^{1}H-NMR ($CDCl_3$, 300 MHz): *δ* (ppm) 7.75 (d, 1H, *J* = 15.6 Hz), 7.63 (m, 2H, Ph), 7.10 (m, 2H, Ph), 7.05 (d, 1H, *J* = 15.6 Hz), 4.91 (s, 2H, Cp), 4.59 (s, 2H, Cp), 4.21 (s, 5H, Cp). ^{13}C-NMR ($CDCl_3$, 75 MHz): *δ* (ppm) 192.8 (CO), 163.8 (C_{para}), 139.6 (CH), 131.4 (C_{ipso}), 130.1 (2CH, Ph), 122.7 (CH), 116.1 (2CH, Ph), 80.5 (C, Cp), 72.9 (2CH, Cp), 70.2 (5CH, Cp), 69.8 (2CH, Cp). **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%).

(*E*)-3-(4-trifluoromethylphenyl)-1-ferrocenyl-2-propen-1-one (1c)

Purple crystals (71 %, yield), mp 171-172 °C (lit[6b,c] 40% yield, mp 171-172°C). ATR-FTIR (cm^{-1}): *v*(CO) 1651. ^{1}H-NMR ($CDCl_3$, 300 MHz): *δ* (ppm) 7.79 (d, 1H, *J* = 15.6 Hz), 7.71 (m, 4H, Ph), 7.16 (d, 1H, *J* = 15.6 Hz), 4.92 (s, 2H, Cp), 4.63 (s, 2H, Cp), 4.22 (s, 5H, Cp). ^{13}C-NMR ($CDCl_3$, 75 MHz): *δ* (ppm) 192.5 (CO), 138.7 (C_{ipso}), 131.5 (C_{para}), 128.4 (2CH, Ph), 125.9 (2CH, Ph), 125.2 (CH), 123,9 (C, CF_3), 125.2 (CH), 80.3 (C, Cp), 73.1 (2CH, Cp), 70.2 (5CH, Cp), 69.8 (2CH, Cp). MS-EI [*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%).

(*E*)-3-(phenyl)-1-ferrocenyl-2-propen-1-one (1d)

Purple crystals (95 %, yield), mp 134-135 °C (lit[6b,c] 68% yield, mp 130-131°C). ATR-FTIR (cm^{-1}): *v*(CO) 1648. ^{1}H-NMR ($CDCl_3$, 300 MHz): *δ* (ppm) 7.80 (d, 1H, *J* = 15.6 Hz), 7.66 (d, 2H, Ph), 7.42 (s, 3H, Ph), 7.13 (d, 1H, *J* = 15.6 Hz), 4.91 (s, 2H, Cp), 4.59 (s, 2H, Cp), 4.22 (s, 5H, Cp). ^{13}C-NMR ($CDCl_3$, 75 MHz): *δ* (ppm) 193.0 (CO), 140.8 (CH), 135.3 (C_{ipso}), 130.2 (CH), 129.0 (2CH, Ph), 128.3 (2CH, Ph), 123.1 (CH), 80.5 (C, Cp), 72.8 (2CH, Cp), 70.2 (5CH, Cp), 69.8 (2CH, Cp). MS-EI [*m/z*, (%)]: 316 [M+] (100%); 251 [M^+-Cp] (16%); 121 [Cp-Fe]$^+$ (9%).

(*E*)-3-(4-methylphenyl)-1-ferrocenyl-2-propen-1-one (1e)

Purple crystals (97 %, yield), mp 163-165 °C (lit[6b,c] 57% yield, mp 169-170°C). ATR-FTIR (cm^{-1}): *v*(CO) 1645. ^{1}H-NMR ($CDCl_3$, 300 MHz): *δ* (ppm) 7.78 (d, 1H, *J* = 15.6 Hz), 7.55 (d, 2H, *J* =

7.5 Hz, Ph), 7.23 (d, 2H, *J* = 7.5 Hz, Ph), 7.09 (d, 1H, *J* = 15.6 Hz), 4.91 (s, 2H, Cp), 4.58 (s, 2H, Cp), 4.21 (s, 5H, Cp), 2.40 (s, 3H, Me). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ (ppm) 193.1 (CO), 140.9 (CH), 140.6 (C_{para}), 132.5 (C_{ipso}), 129.7 (2CH, Ph), 128.3 (2CH, Ph), 122.0 (CH), 80.7 (C, Cp), 72.7 (2CH, Cp), 70.1 (5CH, Cp), 69.7 (2CH, Cp), 21.6 (CH, Me). MS-IE [m/z, (%)]: 330 [M+] (100%); 265 [M^+-Cp] (22%); 237 [M^+-(Cp-CO)] (5%); 157 [M^+-(C_4H_4FeCp)] (10%); 121 $[FeCp]^+$ (12%).

(*E*)-3-(4-methoxyphenyl)-1-ferrocenyl-2-propen-1-one (1f)

Purple crystals (92 %, yield), mp 149-150 °C (lit[6b,c] 51% yield, mp 122-123°C). ATR-FTIR (cm^{-1}): *v*(CO) 1645. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ (ppm) 7.76 (d, 1H, *J* = 15.6 Hz), 7.60 (d, 2H, Ph), 7.02 (d, 1H, *J* = 15.6 Hz), 6.94 (d, 2H, Ph), 4.90 (s, 2H, Cp), 4.56 (s, 2H, Cp), 4.2 (s, 5H, Cp), 3.8 (s, 3H, Me). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ (ppm) 193.1 (CO), 161.4 (C_{para}), 140.7 (CH), 130.0 (2CH, Ph), 127.9 (C_{ipso}), 120.8 (CH), 114.4 (2CH, Ph), 80.6 (C, Cp), 72.6 (2CH, Cp), 70.1 (5CH, Cp), 69.7 (2CH, Cp), 55.5 (CH, Me). **MS-EI** [*m/z*, (%)]: 346 [M^+] (100%); 331 [M^+-CH_3] (4%); 281 [M^+-Cp] (17%); 121 [CpFe] (11%)

(*E*)-3-(4-chlorophenyl)-1-phenyl-2-propen-1-one (1g)

White crystals (94 %, yield), mp 101-102 °C. (lit[6a] 75% yield, mp 116 °C). ATR-FTIR (cm^{-1}): *v*(CO) 1656. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ (ppm) 7.79 (d, 1H, *J* = 15 Hz), 7.59 (d, 1H, *J* = 15 Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ (ppm) 190.3 (CO), 143.4 (CH), 138 (C, Ph), 136.5 (C_{para}), 132.9 (C_{ipso}), 122.4 (CH). MS-EI [*m/z*, (%)]:242 $[M]^+$ (100)

(*E*)-3-(4-chlorophenyl)-1-(thiophen-2-yl)-propen-1-one (1h)[6a]

White crystals (90 %, yield), mp 135 °C. ATR-FTIR (cm^{-1}): *v*(CO) 1656. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ (ppm) 7.86 (d, 1H, *J* = 4 Hz), 7.7 (d, 2H, *J* = 4 Hz), 7.58 (d, 2H, *J* = 8.7 Hz), 7.4 (d, 2H, *J* = 8.7 Hz), 7.2 (t, 1H, thiophen). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ (ppm) 181.8 (CO), 145.4 (C, thiophen), 142.6 (CH), 129.7 (2CH, Ph), 129.3 (2CH, Ph), 136.5 (C_{para}), 134.3 (CH, thiophen), 133.2 (C_{ipso}), 132.0 (CH, thiophen), 128.3 (CH, thiophen), 122.0 (CH). MS-EI [*m/z*, (%)]: 214[M^+]

3. General procedure for obtaining complexes 2

A solution of **1** (0.4 g, 1 equiv.) in anhydrous dichloromethane (30 mL) was treated with $Fe_2(CO)_9$ (1.25 equiv.) was stirred at room temperature for 2.5-4 h, under inert atmosphere. After the reaction was completed, the solvent was evaporated under reduced pressure using a rotary evaporator. This reaction mixture was purified through a neutral alumina/celite flash column (about 5 cm per phase) using a solution of Hexane/CH_2Cl_2 (7:3) as eluent. The solvent was evaporated in vacuum.

η^2-[(*E*)-3-(4-chlorophenyl)-1-ferrocenyl-2-propen-1-one]tetracarbonyliron(0) (2a)

Red crystals (98 %, yield), mp 152-153 °C. ATR-FTIR (cm^{-1}): *v*(CO) 2088, 2028, 2007, 1996, 1650. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ (ppm) 7.41 - 7.28 (m, 4H, Ph), 5.22 (d, 1H, *J* = 11.1 Hz), 4.95 (s, 2H, Cp), 4.73 (d, 1H, *J* = 11.4 Hz), 4.60 (s, 2H, Cp), 4.27 (s, 5H, Cp). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ (ppm) 207.2 (CO), 141.3 (C_{ipso}), 132.0 (C_{para}), 129.2 (2CH, Ph), 127.1 (2CH, Ph), 79.3 (C, Cp), 72.5 (CH, Cp), 72.4 (CH, Cp), 70.1 (5CH, Cp), 68.7 (2CH, Cp), 55.4 (CH), 49.7 (CH). 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%). MStation-FAB [M – 3CO]$^+$Calcd for $C_{20}H_{15}Fe_2O_2Cl$: 433.9459. Found: 433.9471, Error (ppm): +2.7.

η^2-[(*E*)-3-(4-fluorophenyl)-1-ferrocenyl-2-propen-1-one]tetracarbonyliron(0) (2b)

Red crystal in 97% yield, mp 151-152 °C. ATR-FTIR (cm^{-1}): *v*(CO) 2089, 1999, 1979, 1954, 1600. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ (ppm) 7.56 (s, 2H, Ph), 7.45 (s, 2H, Ph), 5.23 (d, 1H, *J* = 10.8 Hz), 4.96 (s, 2H, Cp), 4.75 (d, 1H, *J* = 10.8 Hz), 4.62 (s, 2H, Cp), 4.27 (s, 5H, Cp). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ (ppm) 207.4 (CO), 161.4 (d, C_{para}, $J_{C\text{-}F}$ = 244.5 Hz), 128.3 (C_{ipso}), 127.4 (d, CH, $J_{C\text{-}F}$ = 8.25 Hz), 116.0 (d, CH, $J_{C\text{-}F}$ = 21.75 Hz), 79.3 (C, Cp), 72.5 (CH, Cp), 72.4 (CH, Cp), 70.1 (5CH, Cp), 69.8 (CH, Cp), 68.7 (CH, Cp), 56.0 (CH), 50.2 (CH). 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%). MStation-FAB [M + H]$^+$Calcd for $C_{23}H_{16}Fe_2O_5F$: 502.9681. Found: 502.9685, Error (ppm): +0.9.

η²-[(*E*)-3-(4-(trifluoromethyl)phenyl)-1-ferrocenyl-2-propen-1-one]tetracarbonyliron (0) (2c)

Red crystals (98 % yield), mp 144-146 °C. ATR-FTIR (cm^{-1}): *ν*(CO) 2091, 2033, 2012, 1989, 1617. ^{1}H-NMR ($CDCl_3$, 300 MHz): *δ* (ppm) 7.57 (d, 2H, *J* = 7.2 Hz, Ph), 7.44 (d, 2H, *J* = 7.2 Hz, Ph), 5.22 (d, 1H, *J* = 10.8 Hz), 4.97 (s, 2H, Cp), 4.75 (d, 1H, *J* = 11.1 Hz), 4.62 (s, 2H, Cp), 4.27 (s, 5H, Cp). ^{13}C-NMR ($CDCl_3$, 75 MHz): *δ* (ppm) 206.8 (CO), 147.0 (C_{ipso}), 128.1 (C_{para}, J_{C-F} = 32.3 Hz), 122.3 (2CH, Ph, J_{C-F} = 3.8 Hz), 79.2 (C, Cp), 72.6 (CH, Cp), 72.5 (CH, Cp), 70.11 (5CH, Cp), 69.8 (CH, Cp), 68.8 (CH, Cp), 54.3 (CH), 49.3 (CH). 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%). MStation-FAB [M + H]$^+$Calcd for $C_{24}H_{16}Fe_2O_5F_3$: 552.9649 Found: 552.9649, Error (ppm): +0.1.

η²-[(*E*)-3-(phenyl)-1-ferrocenyl-2-propen-1-one]tetracarbonyliron(0) (2d)

Red crystal in 92% yield, mp 134-135 °C. ATR-FTIR (cm^{-1}): *ν*(CO) 2090, 2025, 2010, 1980, 1624. ^{1}H-NMR ($CDCl_3$, 300 MHz): *δ* (ppm) 7.42 - 7.32 (m, 4H, Ph), 7.19 - 7.15 (m, 1H, Ph), 5.31 (d, 1H, *J* = 11.4 Hz), 4.96 (s, 2H, Cp), 4.82 (d, 1H, *J* = 11.4 Hz), 4.60 (s, 2H, Cp), 4.28 (s, 5H, Cp). ^{13}C-NMR ($CDCl_3$, 75 MHz): *δ* (ppm) 207.5 (CO), 142.5(C_{ipso}), 129.0 (2CH, Ph), 126.7 (CH, Ph), 126.0 (2CH, Ph), 79.6 (C, Cp), 72.5 (CH, Cp), 72.3 (CH, Cp), 70.1 (5CH, Cp), 68.7 (2CH, Cp), 57.1 (CH), 49.9 (CH). 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%). MStation-FAB [M + H]$^+$Calcd for $C_{23}H_{17}Fe_2O_5$: 484.9775. Found: 484.9767, Error (ppm): -1.6.

η²-[(*E*)-3-(4-methylphenyl)-1-ferrocenyl-2-propen-1-one]tetracarbonyliron(0) (2e)

Red crystals (99 % yield), mp 127-129 °C. ATR-FTIR (cm^{-1}): *ν*(CO) 2091, 2026, 2012, 1981, 1646. ^{1}H-NMR ($CDCl_3$, 300 MHz): *δ* (ppm) 7.26 (s, 2H, Ph), 7.13 (s, 2H, Ph), 5.31 (d, 1H, *J* = 10.8 Hz), 4.96 (s, 2H, Cp), 4.83 (d, 1H, *J* = 11.1 Hz), 4.59 (s, 2H, Cp), 4.27 (s, 5H, Cp), 2.32 (s, 3H, Me). ^{13}C-NMR ($CDCl_3$, 75 MHz): *δ* (ppm) 207.7 (CO), 139.3 (C_{ipso}), 136.3 (C_{para}), 129.7 (2CH, Ph), 129.5 (2CH, Ph), 79.5 (C, Cp), 72.4 (CH, Cp), 72.3 (CH, Cp), 70.1 (5CH, Cp), 68.7

(2CH, Cp), 57.6 (CH), 50.1 (CH), 21.2 (C, Me). 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%). MStation-FAB [M–3CO]$^+$Calcd for $C_{21}H_{18}Fe_2O_2$: 414.0001. Found: 414.0001, Error (ppm): -1.1.

η²-[(*E*)-3-(4-methoxyphenyl)-1-ferrocenyl-2-propen-1-one]tetracarbonyliron(0) (2f)

Red crystals (95 % yield), mp 149-150 °C. ATR-FTIR (cm^{-1}): *v*(CO) 2089, 2023, 2012, 1987, 1647. ^{1}H-NMR ($CDCl_3$, 300 MHz): *δ* (ppm) 7.31 (s, 2H, Ph), 6.87 (s, 2H, Ph), 5.33 (s, 1H), 4.96 (s, 2H, Cp), 4.82 (s, 1H), 4.59 (s, 2H, Cp), 4.27 (s, 5H, Cp), 3.82 (s, 3H, Me). ^{13}C-NMR ($CDCl_3$, 75 MHz): *δ* (ppm) 207.9 (CO), 158.4 (C_{para}), 130.0 (C_{ipso}), 127.2 (2CH, Ph), 114.4 (2CH, Ph), 79.6 (C, Cp), 72.4 (CH, Cp), 72.3 (CH, Cp), 70.11 (5CH, Cp), 68.7 (2CH, Cp), 58.0 (CH), 50.4 (CH). 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%). MStation-FAB [M^+–3CO]$^+$Calcd for $C_{21}H_{18}Fe_2O_3$: 429.9955. Found: 429.9955, Error (ppm): -1.1.

η²-[(*E*)-3-(4-chlorophenyl)-1-phenyl-2-propen-1-one]tetracarbonyliron(0) (2g)

Yellow crystals (94 % yield), mp 81-82 °C. ATR-FTIR (cm^{-1}): *v*(CO) 2093, 2026, 2012, 1988, 1638. ^{1}H-NMR ($CDCl_3$, 300 MHz): *δ* (ppm) 8.16-7.29 (m, 9H, Ph), 5.32 (d, 1H, *J* = 12 Hz), 5.02 (d, 1H, *J* = 12 Hz).^{13}C-NMR ($CDCl_3$, 75 MHz): *δ* (ppm) 206.8 (CO), 140.9 (C_{para}), 137.2 (C_{ipso}), 129.1-127.4 (9CH, Ph), 82.1 (C_{ipso}),56.4 (CH), 47.9 (CH). MS-FAB [*m/z*, (%)]: 411 [M+1]$^+$ (18), 383 [M+1]$^+$ -CO (16), 355 [M+1]$^+$ -2CO (25), 326 [M^+ -3CO] (45), 298 [M^+ -4CO] (25), 243 [M^+–$Fe(CO)_4$] (22). MStation-FAB [M + H]$^+$Calcd for $C_{19}H_{11}ClFeO_5$: 411.9644. Found: 429.9955, Error (ppm): -1.1.

η²-[(*E*)-3-(4-chlorophenyl)-1-(thiophen-2-yl)-propen-1-one]tetracarbonyliron(0) (2h)

Yellow crystals (90 % yield), p. decomp.: 72-74 °C. ATR-FTIR (cm^{-1}): *v*(CO) 2094, 2021, 2010, 1981, 1644. ^{1}H-NMR ($CDCl_3$, 300 MHz): *δ* (ppm) 7.95-7.27 (m, 7H, CH), 5.23 (s, 1H), 4.92 (s, 1H).^{13}C-NMR ($CDCl_3$, 75 MHz): *δ* (ppm) 206.7 (CO), 143.8 (C_{para}), 140.8 (C, thiophen), 134.0 (C_{ipso}), 132.6 (CH, thiophen), 130.7 (CH, thiophen), 129.1 (2CH, Ph), 128.3 (CH, thiophen),

127.3 (2CH, Ph), 55.7 (CH), 48.53 (CH). MS-FAB [*m/z*, (%)]: 383 $[M+1]^+$ (5), 298 $[M^+ -3CO]$ (15). MStation-FAB$^+$ $[M - 3CO]^+$Calcd for $C_{14}H_{10}FeO_2S$: 297.9751. Found: 297.9748, Error (ppm): -1.1.

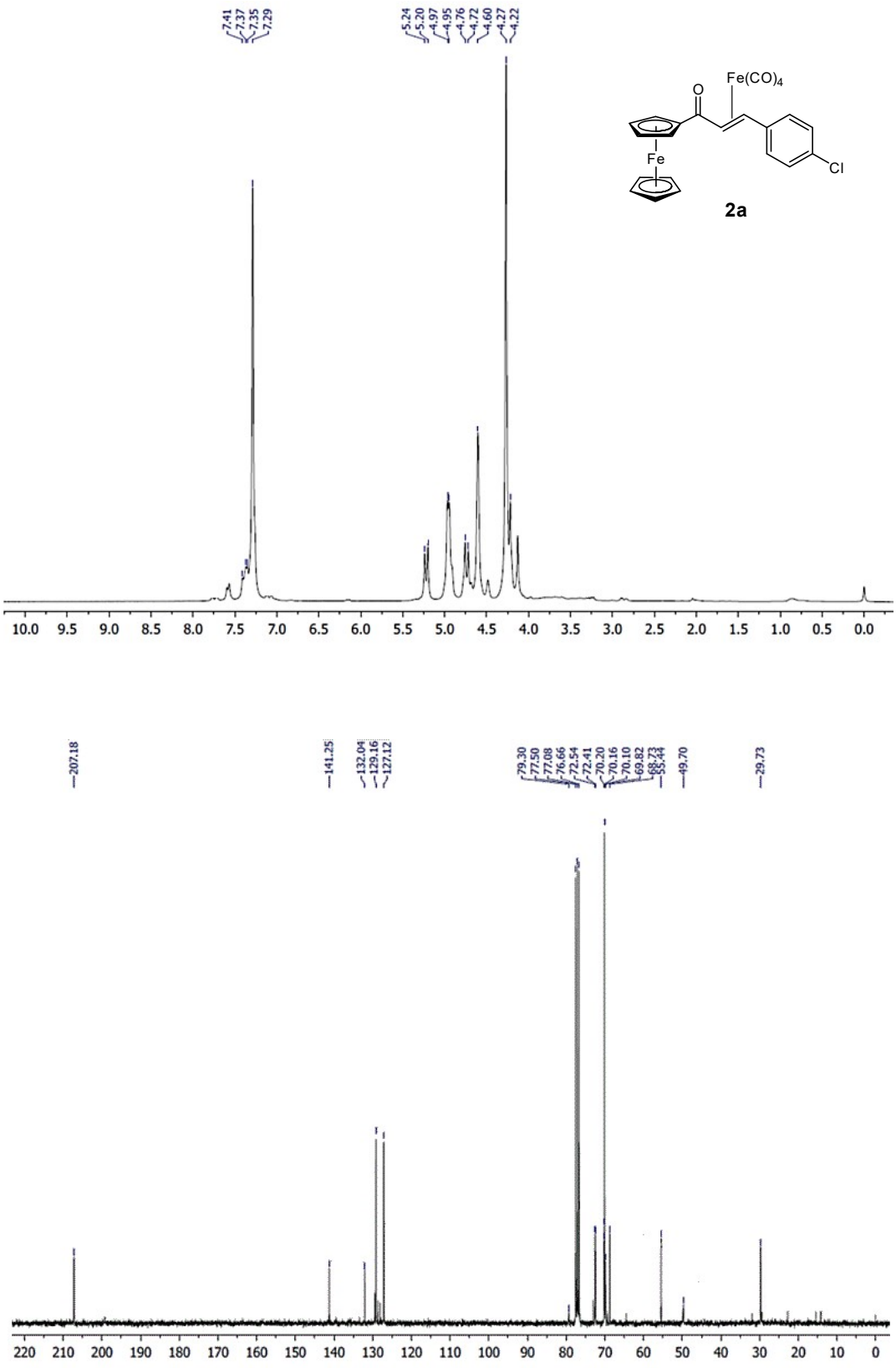


Figure S1. NMR spectra of complex **2a**

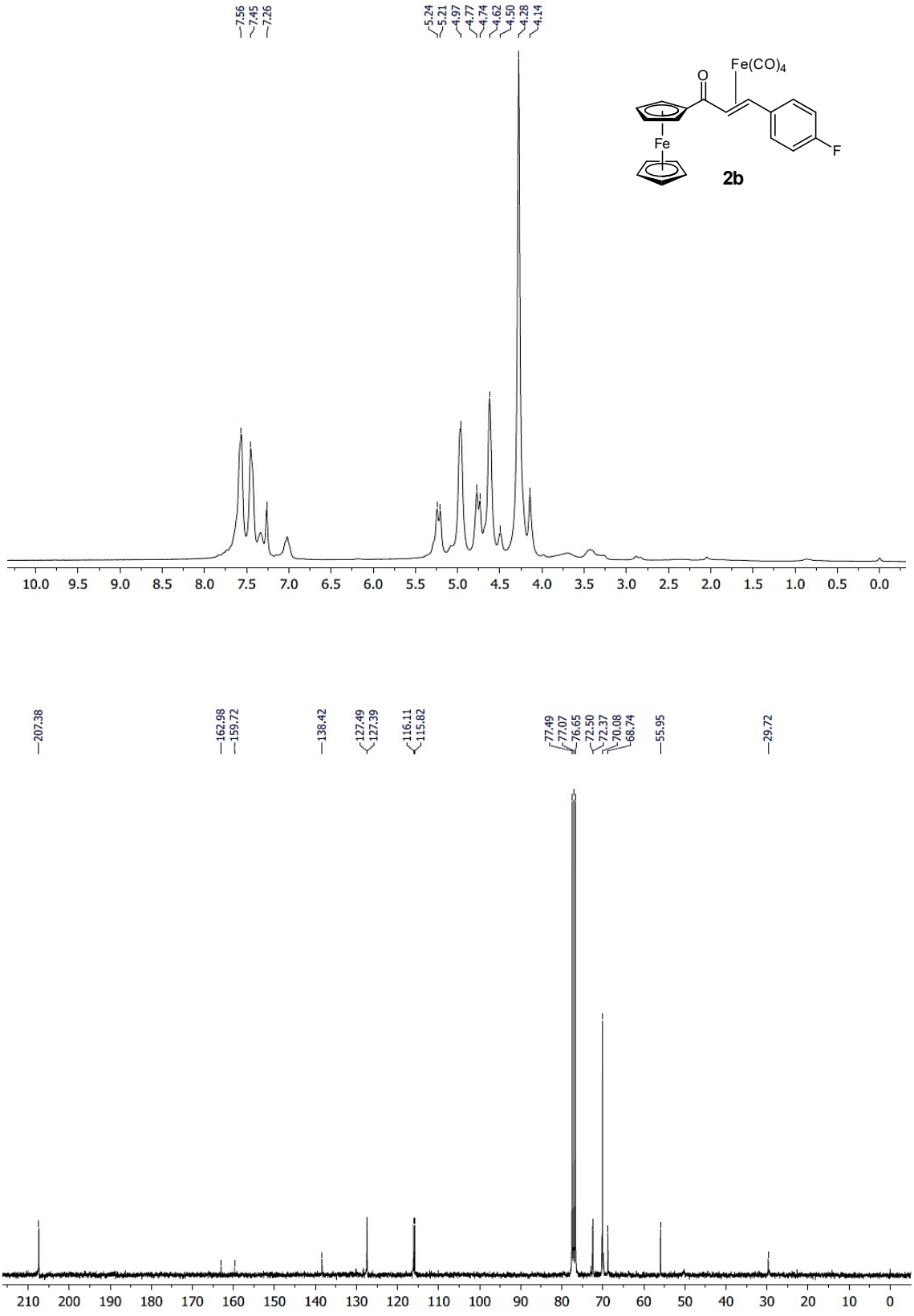


Figure S2. NMR spectra of complex **2b**

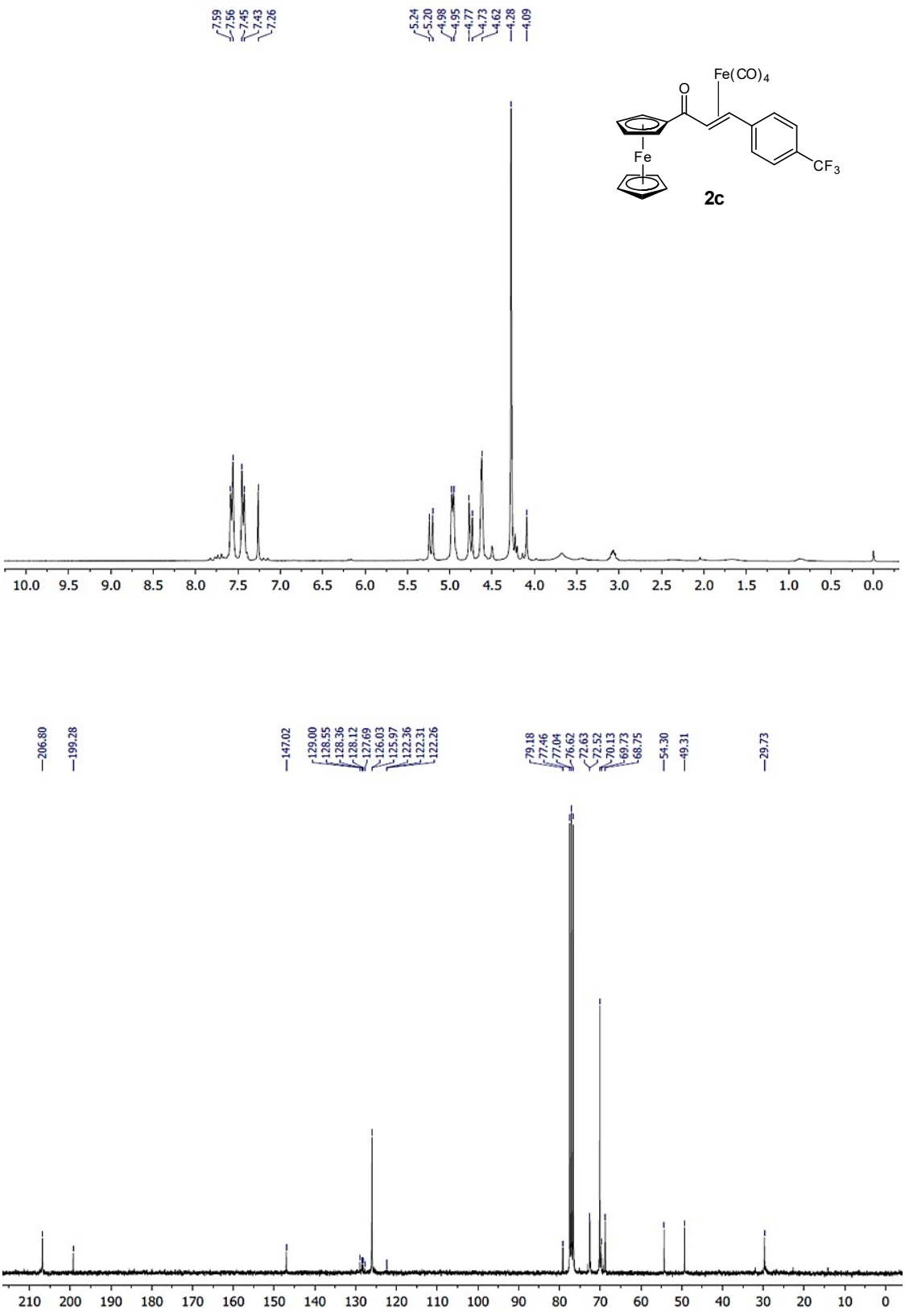


Figure S3. NMR Spectra of complex **2c**

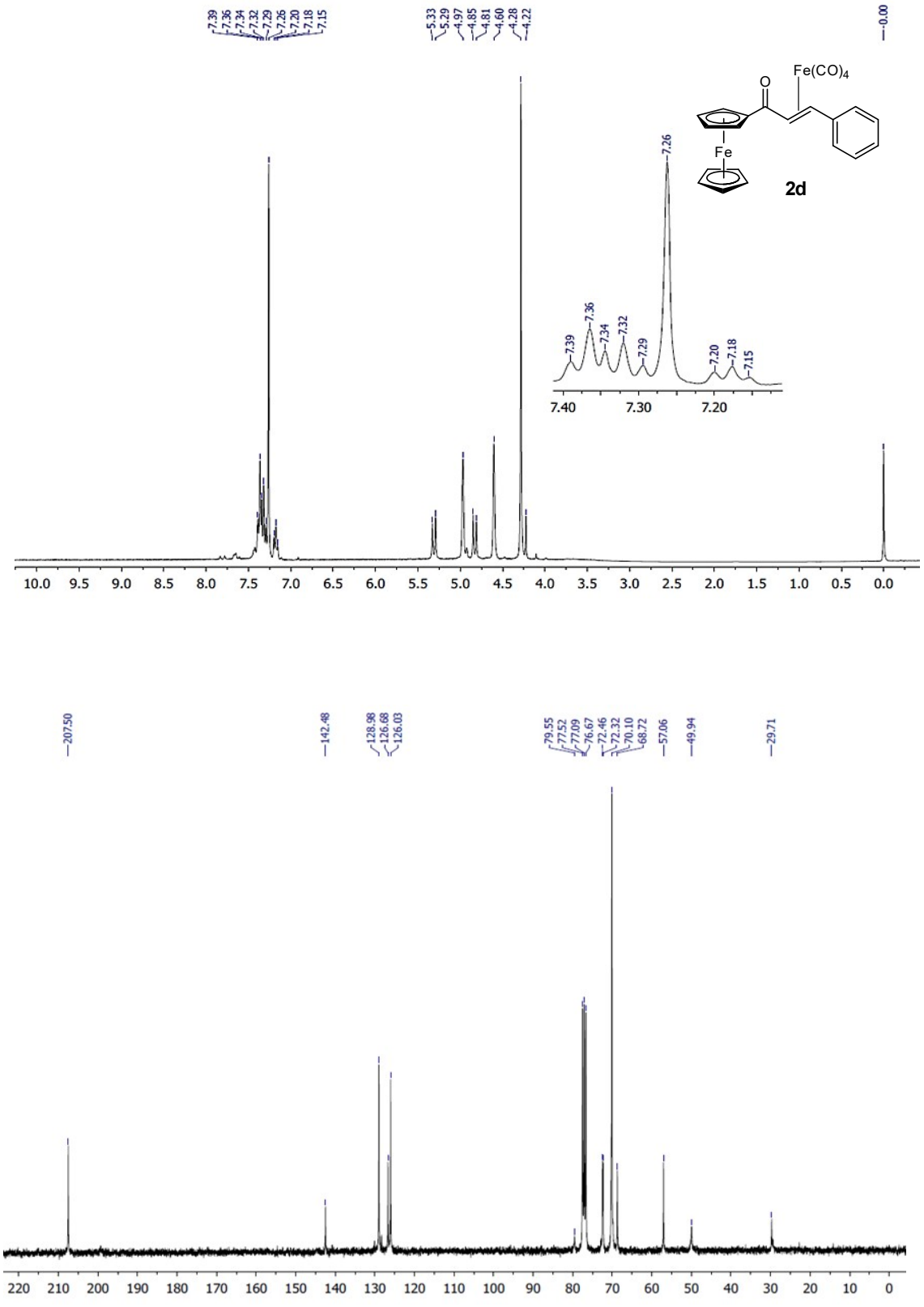
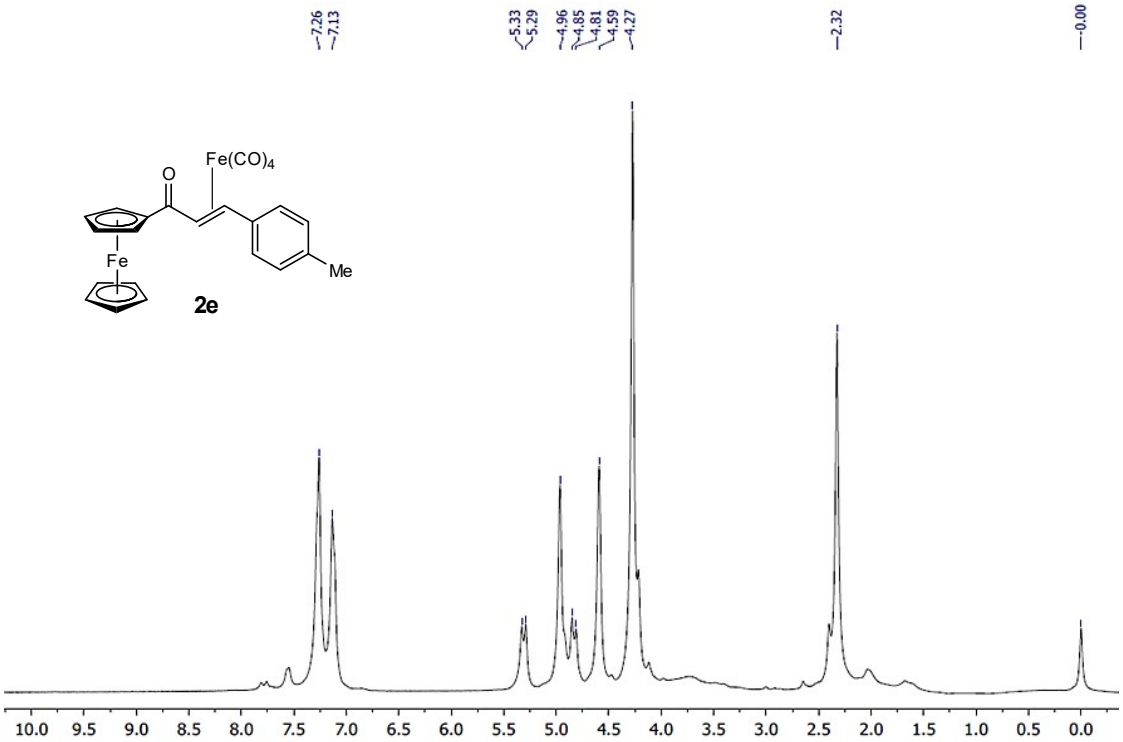


Figure S4. NMR spectra of complex **2d**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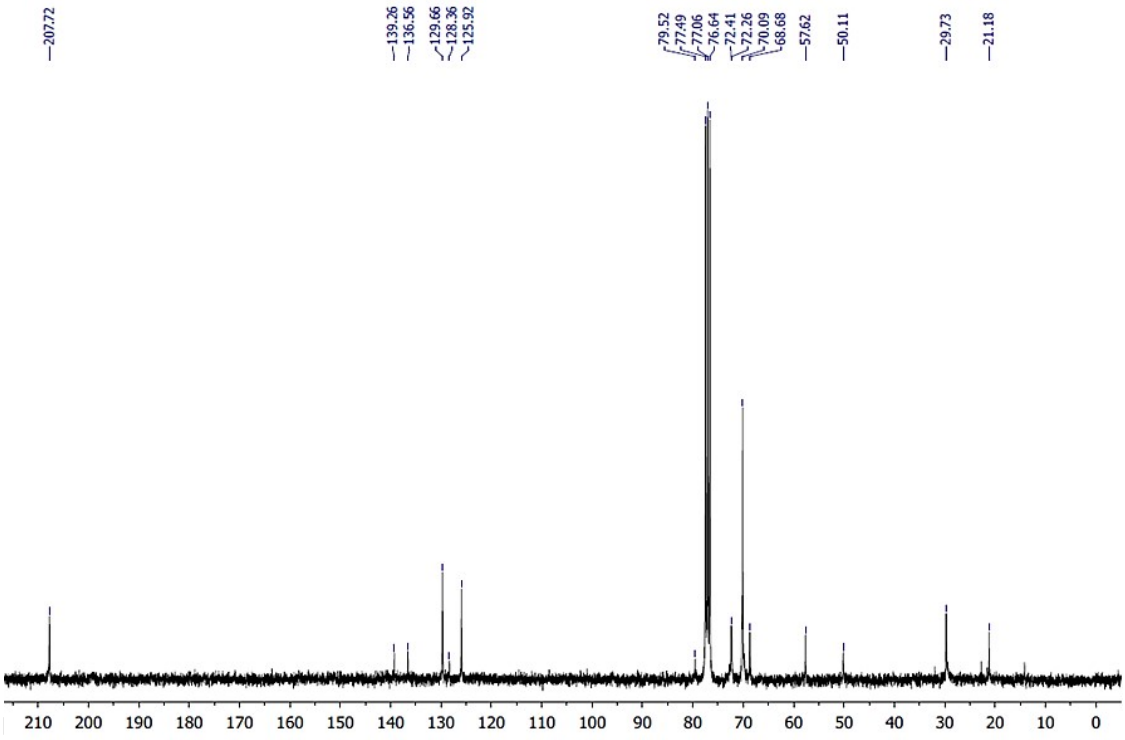
7.13
5.33
5.29
4.96
4.85
4.81
4.59
4.27
2.32
0.00
Fe(CO)4
O
Fe
Me
2e
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


207.72
139.26
136.56
129.66
128.36
125.92
79.52
77.49
77.06
76.64
72.41
72.26
70.09
68.68
57.62
50.11
29.73
21.18
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

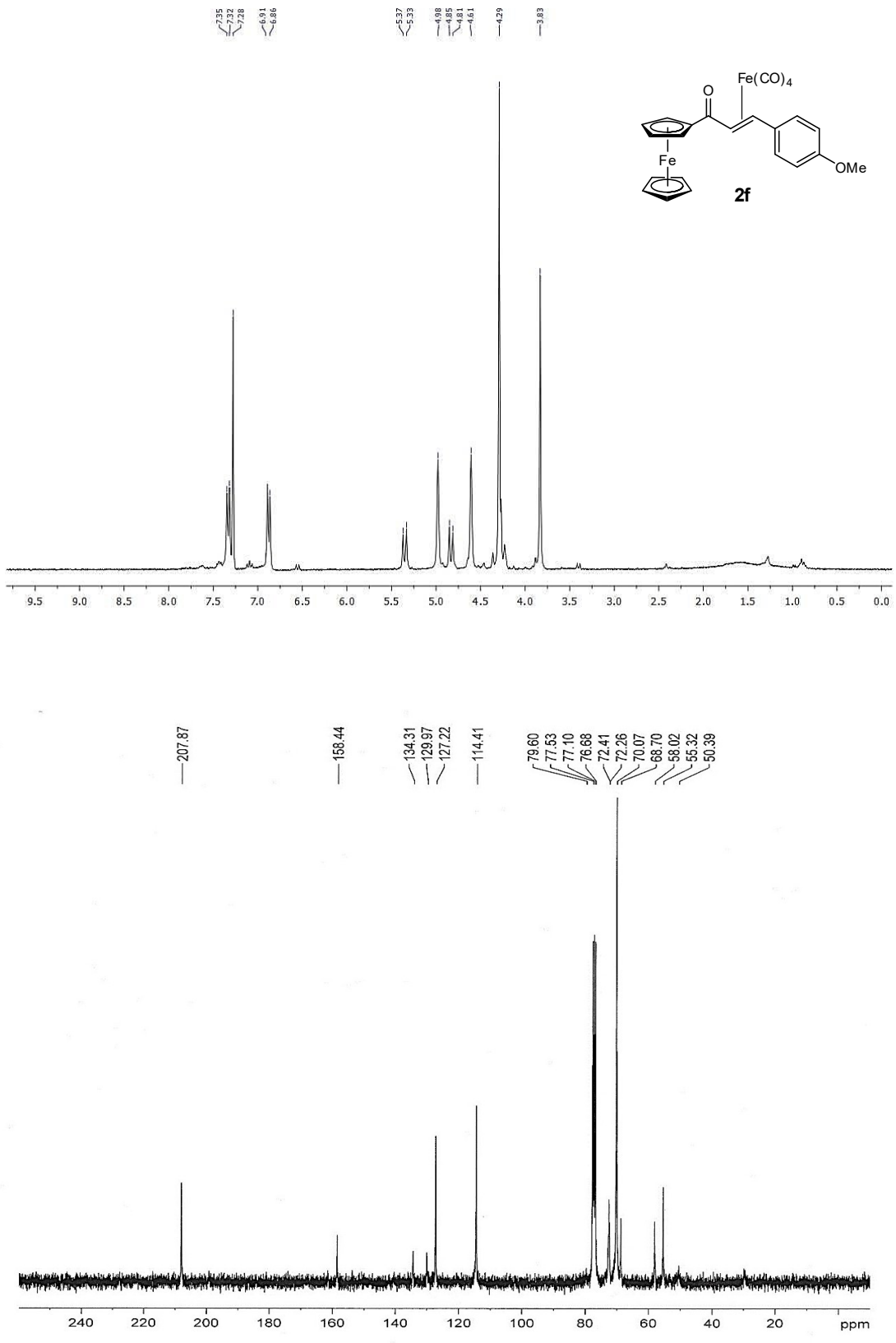


Figure S6. NMR spectra of complex **2f**

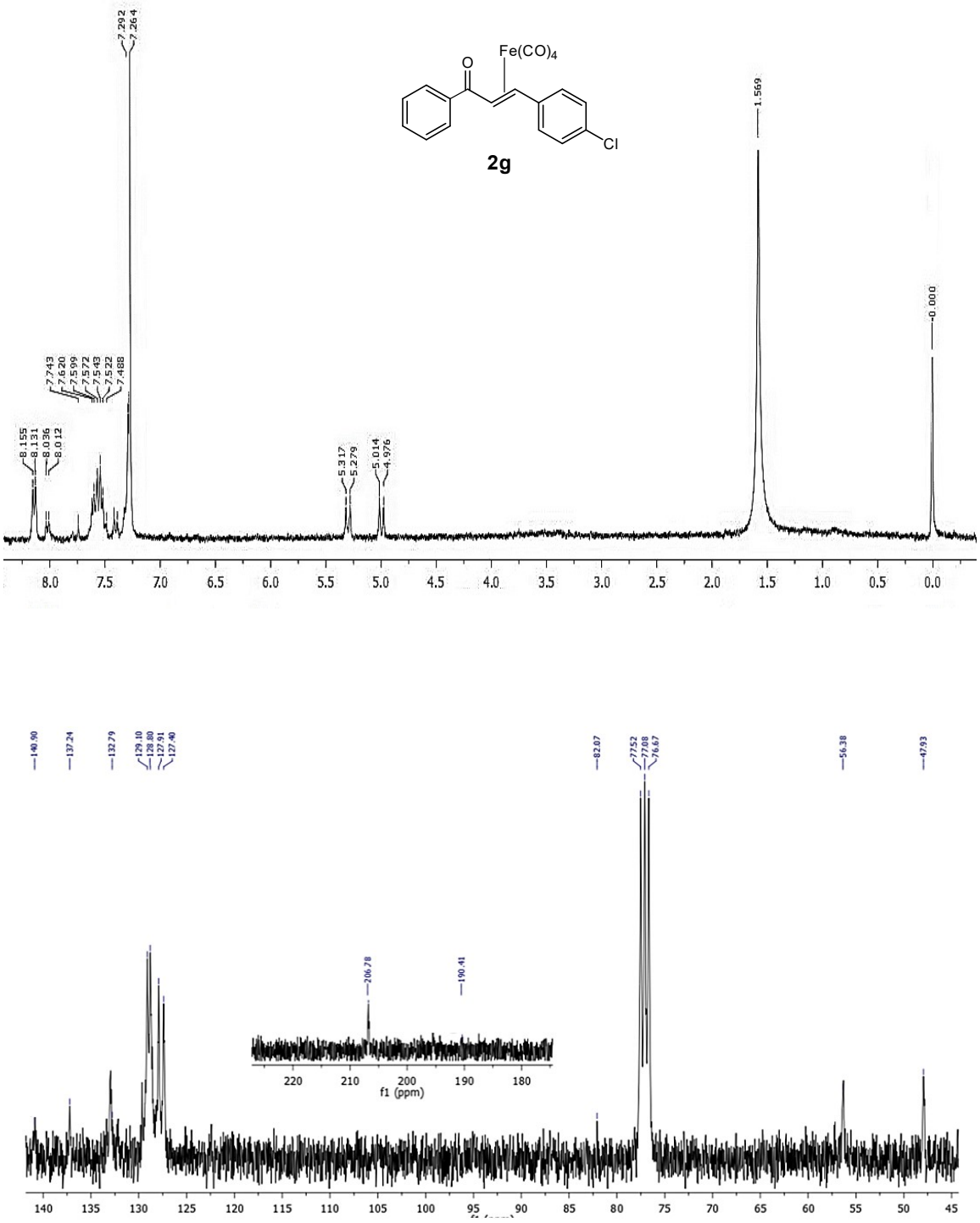


Figure S7. NMR Spectra of complex **2g**

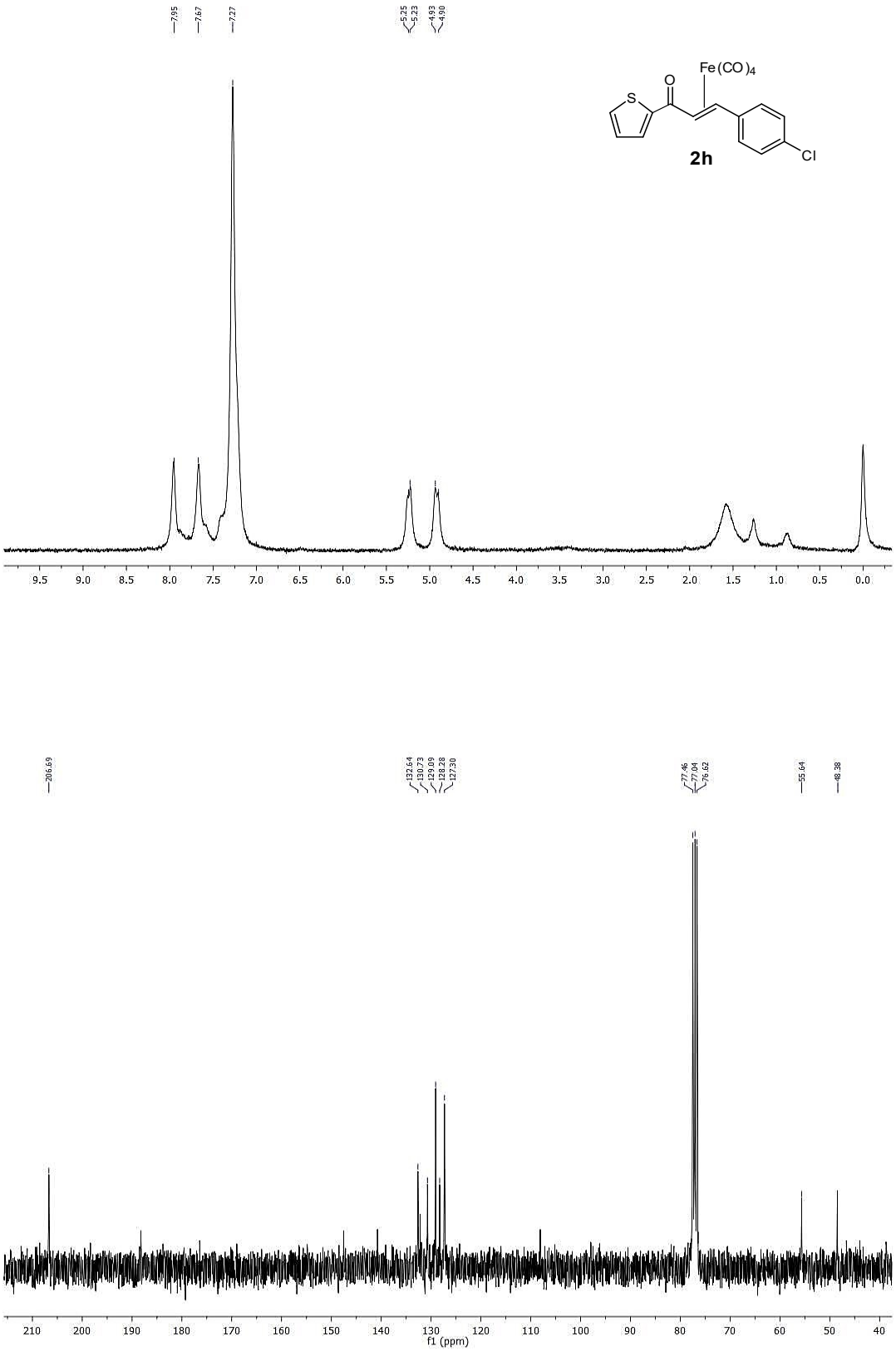


Figure S8. NMR Spectra of complex **2h**

4. General procedure for obtaining complexes 3

In a solution of **2** (1 equiv.) in anhydrous dichloromethane (20 mL) was added dropwise MeLi (1.1 equiv., 1.6 M) at −78 °C under argon atmosphere. The reaction mixture was stirred for 30 min at this temperature. After this time, inert atmosphere was changed for CO at atmospheric pressure and the mixture was stirred for another 3.5 h at room temperature. The reaction mixture was passed through a Celite/Neutral Alumina/Na_2SO_4 column, and the solvent was evaporated under vacuum. The crude was concentrated and purified by preparative silica TLC using gradient of hexane/dichloromethane as eluent.

η^4-[(*E*)-4-(4-chlorophenyl)-2-ferrocenyl-1,3-butadien-1-one]tricarbonyliron(0) (3a)

Red crystals (50 % yield), mp 116-117 °C.ATR-FTIR (cm^{-1}): *ν*(CO) 2061, 2001, 1715. ^{1}H-NMR ($CDCl_3$, 300 MHz): *δ* (ppm) 7.38 – 7.36 (m, 4H, Ph), 6.56 (d, 1H, *J* = 9.18 Hz), 4.63 (s, 1H, Cp), 4.45 (s, 1H, Cp), 4.34 (m, 2H, Cp), 4.25 (s, 5H, Cp), 3.33 (d, 1H, *J* = 9.18 Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz): *δ* (ppm) 233.8 (CO), 137.3(C_{para}), 133.3 (C_{ipso}), 129.5 (2CH, Ph), 127.8 (2CH, Ph), 90.8 (CH), 75.5 (C, Cp), 70.6 (CH, Cp), 70.3 (CH, Cp), 69.9 (5CH, Cp), 69.3 (CH, Cp), 65.5 (CH, Cp), 57.8 (CH), 54.4 (C). 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%). MStation-FAB [M – 3CO]$^+$Calcd for $C_{20}H_{15}Fe_2OCl$: 417.9510. Found: 417.9514, Error (ppm): +0.9.

η^4-[(*E*)-4-(4-fluorophenyl)-2-ferrocenyl-1,3-butadien-1-one]tricarbonyliron(0) (3b)

Red crystals (62 % yield), mp 100-101 °C. ATR-FTIR (cm^{-1}): *ν*(CO) 2055, 1996, 1972, 1733. ^{1}H-NMR ($CDCl_3$, 300 MHz): *δ* (ppm) 7.41 (m, 2H, Ph), 7.07 (m, 2H, Ph), 6.54 (d, 1H, *J* = 9.3 Hz), 4.63 (s, 1H, Cp), 4.44 (s, 1H, Cp), 4.34 (m, 2H, Cp), 4.25 (s, 5H, Cp), 3.38 (d, 1H, *J* = 9.3 Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz): *δ* (ppm) 233.9 (CO), 162.1 (C_{para}, $J_{C\text{-}F}$ = 246.75 Hz), 134.4 (C_{ipso}, $J_{C\text{-}F}$ = 3.75 Hz), 128.1 (d, 2CH, Ph $J_{C\text{-}F}$ = 7.5 Hz), 116.3 (d, 2CH, Ph, $J_{C\text{-}F}$ = 21.75 Hz), 90.7 (CH), 75.6 (C, Cp), 70.5 (CH, Cp), 70.1 (CH, Cp), 69.8 (5CH, Cp), 69.2 (CH, Cp), 65.5 (CH, Cp), 58.4 (CH), 54.0 (C). 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%). MStation-FAB [M]$^+$Calcd for $C_{23}H_{15}Fe_2O_4F$: 485.9653. Found: 485.9657, Error (ppm): +0.8.

η^4-[(*E*)-4-(4-(trifluoromethyl)phenyl)-2-ferrocenyl-1,3-butadien-1-one]tricarbonyliron (0) (3c)

Red crystals (61 % yield), mp 118-120 °C. ATR-FTIR (cm^{-1}): *ν*(CO) 2063, 2007, 1973, 1736. ^{1}H-NMR ($CDCl_3$, 300 MHz): *δ* (ppm) 7.61 (d, 2H, *J* = 7.2 Hz, Ph), 7.52 (d, 2H, *J* = 7.2 Hz, Ph), 6.62 (d, 1H, *J* = 9 Hz), 4.65 (s, 1H, Cp), 4.47 (s, 1H, Cp), 4.35 (s, 2H, Cp), 4.26 (s, 5H, Cp), 3.29 (d, 1H, *J* = 8.7 Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz): *δ* (ppm) 233.3 (CO), 142.9 (C_{ipso}), 129.1 (C_{para}, J_{C-F} = 32.25 Hz), 126.6 (2CH, Ph), 126.1 (q, 2CH, Ph, J_{C-F} = 3.8 Hz), 124.1 (s, CF_3, J_{C-F} = 207 Hz), 91.1 (CH), 75.1 (C, Cp), 70.7 (CH, Cp), 70.3 (CH, Cp), 69.9 (5CH, Cp), 69.3 (CH, Cp), 65.5 (CH, Cp), 56.1 (CH), 54.8 (C). 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%). MStation-FAB [M]$^+$Calcd for $C_{24}H_{15}Fe_2O_4F_3$: 535.9621. Found: 535.9621, Error (ppm): 0.0.

η^4-[(*E*)-4-(phenyl)-2-ferrocenyl-1,3-butadien-1-one]tricarbonyliron(0) (3d)

Red crystals (78 % yield), p. decomp.: 109-110 °C.ATR-FTIR (cm^{-1}): *ν*(CO) 2051, 1992, 1969, 1737. ^{1}H-NMR ($CDCl_3$, 300 MHz): *δ* (ppm) 7.43 – 7.29 (m, 5H, Ph), 6.61 (d, 1H, *J* = 8.4 Hz, Ph), 4.64 (s, 1H, Cp), 4.44 (s, 1H, Cp), 4.34 (s, 2H, Cp), 4.25 (s, 5H, Cp), 3.41 (d, 1H, *J* = 8.4 Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz): *δ* (ppm) 234.2 (CO), 138.4 (C, Ph), 129.2 (2CH, Ph), 127.6 (C_{ipso}), 126.7 (2CH, Ph), 91.0 (CH), 75.8 (C, Cp), 70.4 (CH, Cp), 70.1 (CH, Cp), 69.8 (5CH, Cp), 69.2 (CH, Cp), 65.5 (CH, Cp), 59.5 (CH), 54.0 (C). 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%). MStation-FAB [M + OH]$^+$ Found for $C_{23}H_{17}Fe_2O_5$: 484.9769, Error (ppm): -1.2.

η^4-[(*E*)-4-(4-methylphenyl)-2-ferrocenyl-1,3-butadien-1-one]tricarbonyliron(0) (3e)

Red crystals (66 % yield), mp 97-99 °C. ATR-FTIR (cm^{-1}): *ν*(CO) 2050, 1989, 1971, 1981, 1737. ^{1}H-NMR ($CDCl_3$, 300 MHz): *δ* (ppm) 7.34 (d, 2H, *J* = 8.1 Hz, Ph), 7.17 (d, 2H, *J* = 8.1 Hz, Ph), 6.58 (d, 1H, *J* = 9.6 Hz), 4.63 (s, 1H, Cp), 4.43 (s, 1H, Cp), 4.34 (d, 2H, Cp), 4.24 (s, 5H, Cp), 3.44 (d, 1H, *J* = 9.3 Hz), 2.34 (s, 3H, Me). ^{13}C-NMR ($CDCl_3$, 75 MHz): *δ* (ppm) 234.3 (CO), 137.7 (C_{para}), 135.2 (C_{ipso}), 130.0 (2CH, Ph), 127.0 (2CH, Ph), 90.7 (CH), 76.0 (C, Cp), 70.4 (CH, Cp), 70.0 (CH, Cp), 69.8 (5CH, Cp), 69.2 (CH, Cp), 65.5 (CH, Cp), 60.3 (CH), 53.7 (C), 21.3 (C, Me).

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^+–$Fe(CO)_4$]. MStation-FAB [M]$^+$Calcd for $C_{24}H_{18}Fe_2O_4$: 481.9904. Found: 481.9904, Error (ppm): +1.9.

η^4-[(*E*)-4-(4-methoxyphenyl)-2-ferrocenyl-1,3-butadien-1-one]tricarbonyliron(0) (3f)

Red crystals (59 % yield), mp 113-114 °C. ATR-FTIR (cm^{-1}): *ν*(CO) 2047, 1987, 1968, 1735. ^{1}H-NMR ($CDCl_3$, 300 MHz): *δ* (ppm) 7.40 (d, 2H, *J* = 8.4 Hz, Ph), 6.91 (d, 2H, *J* = 8.4 Hz, Ph), 6.53 (d, 1H, *J* = 9.3 Hz), 4.62 (s, 1H, Cp), 4.42 (s, 1H, Cp), 4.33 (m, 2H, Cp), 4.24 (s, 5H, Cp), 3.83 (s, 3H, Me), 3.50 (d, 1H, *J* = 9.3 Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz): *δ* (ppm) 234.5 (CO), 159.3 (C_{para}), 130.5 (C_{ipso}), 128.0 (2CH, Ph), 114.8 (2CH, Ph), 90.2 (CH), 76.1 (C, Cp), 70.3 (CH, Cp), 69.9 (CH, Cp), 69.8 (5CH, Cp), 69.2 (CH, Cp), 65.4 (CH, Cp), 61.1 (CH), 55.4 (C, Me), 53.5 (C). MS-FAB [*m/z*, (%)]: 498 [M^+] (3%); 470 [M^+–CO] (3%); 442 [M^+–2CO] (1%); 414 [M^+–3CO] (12%); 386 [M^+–4CO] (8%). MStation-FAB [M]$^+$Calcd for $C_{24}H_{18}Fe_2O_5$: 497.9853. Found: 497.9840, Error (ppm): -2.6.

η^4-[(*E*)-4-(4-chlorophenyl)-2-phenyl-1,3-butadien-1-one]tricarbonyliron(0) (3g)

Yellow crystals (53 % yield), mp 103-104 °C. ATR-FTIR (cm^{-1}): *ν*(CO) 2055, 1983, 1949, 1729. ^{1}H-NMR ($CDCl_3$, 300 MHz): *δ* (ppm) 7.71 (m, 9H, Ph), 6.83 (d, 1H, *J* = 9 Hz), 3.42 (d, 1H, *J* = 9 Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz): *δ* (ppm) 232.7 (CO), 136.7 (C_{para}), 133.32 (C_{ipso}) 132.5 (CH, Ph), 129.5 (2CH, Ph), 129.4 (2CH, Ph), 127.8 (2CH, Ph), 91.3 (CH), 68.2 (C_{ipso}, Ph), 59.1 (CH), 50.0 (C). MS-FAB [*m/z*, (%)]: 366[M^++1](8), 339 [M^++1-CO], 310 [M^+-2CO] (22), 282 [M^+-3CO] (10). MStation-FAB [M]$^+$Calcd for $C_{18}H_{11}ClFeO_4$: 365.9746 Found: 365.9753, Error (ppm): +1.9.

η^4-[(*E*)-4-(4-chlorophenyl)-2-(thiopen-2-yl)-1,3-butadien-1-one]tricarbonyliron(0) (3h)

Yellow crystals (59 % yield), p. decomp.: 84-85 °C. ATR-FTIR (cm^{-1}): *ν*(CO) 2059, 2000, 1981, 1730. ^{1}H-NMR ($CDCl_3$, 300 MHz): *δ* (ppm) 7.87-6.93 (m, 7H, CH), 6.75 (d, 1H, *J* = 9 Hz), 3.45 (d, 1H, *J* = 9 Hz). ^{13}C-NMR ($CDCl_3$, 75 MHz): *δ* (ppm) 232.5 (CO), 136.6 (C, thiophene), 142.6 (C_{para}), 134.1 (C_{ipso}), 131.2 (CH, thiophene), 129.5 (2CH, Ph), 128.3 (CH, thiophene), 127.8

(2CH, Ph), 122.0 (CH, thiophene), 91.2 (CH), 58.4 (CH), 47.8 (C). MS-FAB [*m/z*, (%)]: 331[M^++1](5), 303 [M^++1-CO], 275 [M^+-2CO] (15), 247 [M^+-3CO] (8). MStation-FAB $[M]^+$Calcd for $C_{14}H_{10}FeO_4S$: 330.1373. Found: 330.1368, Error (ppm): -1.8.

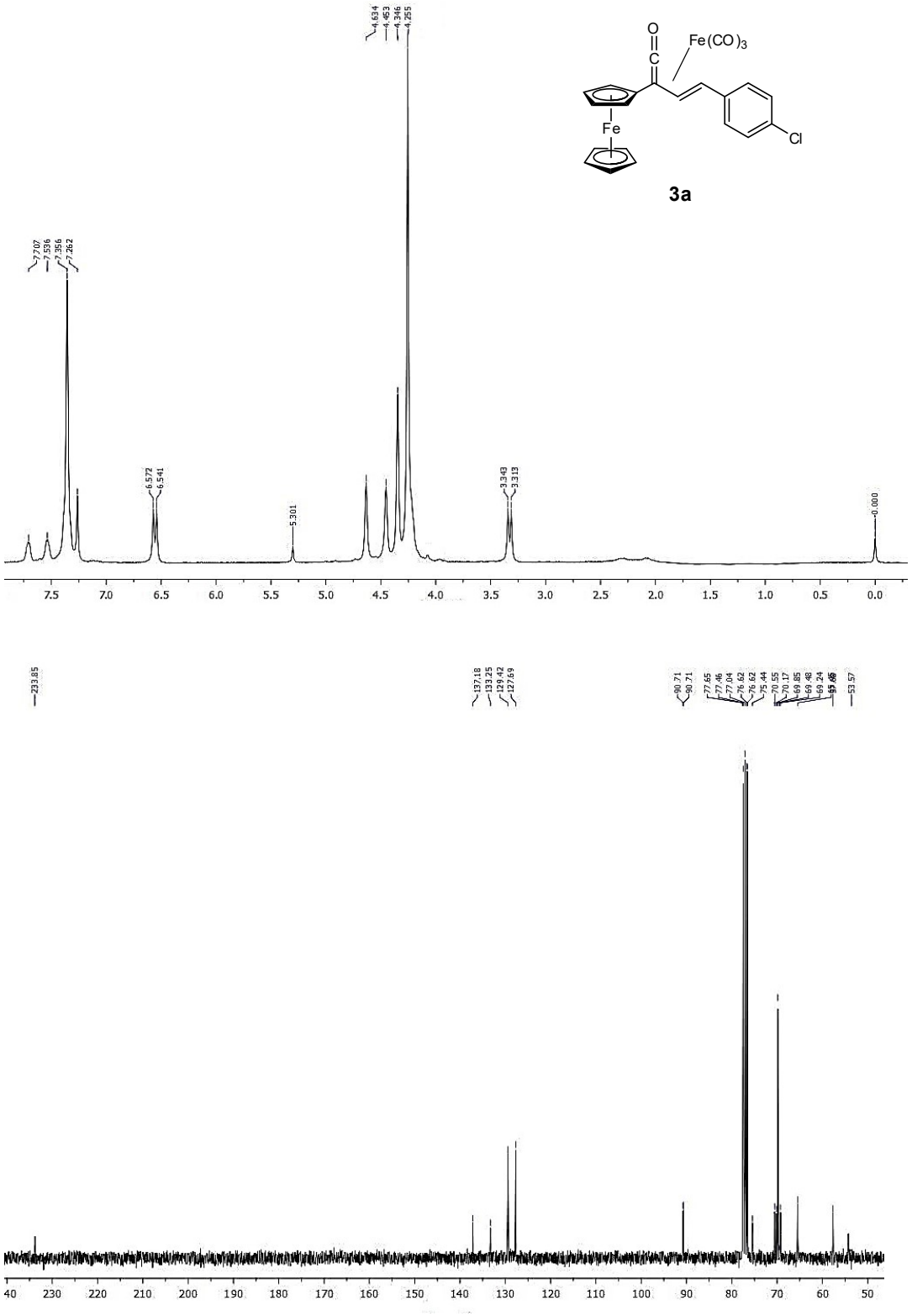


Figure S9. NMR spectra of complex **3a**

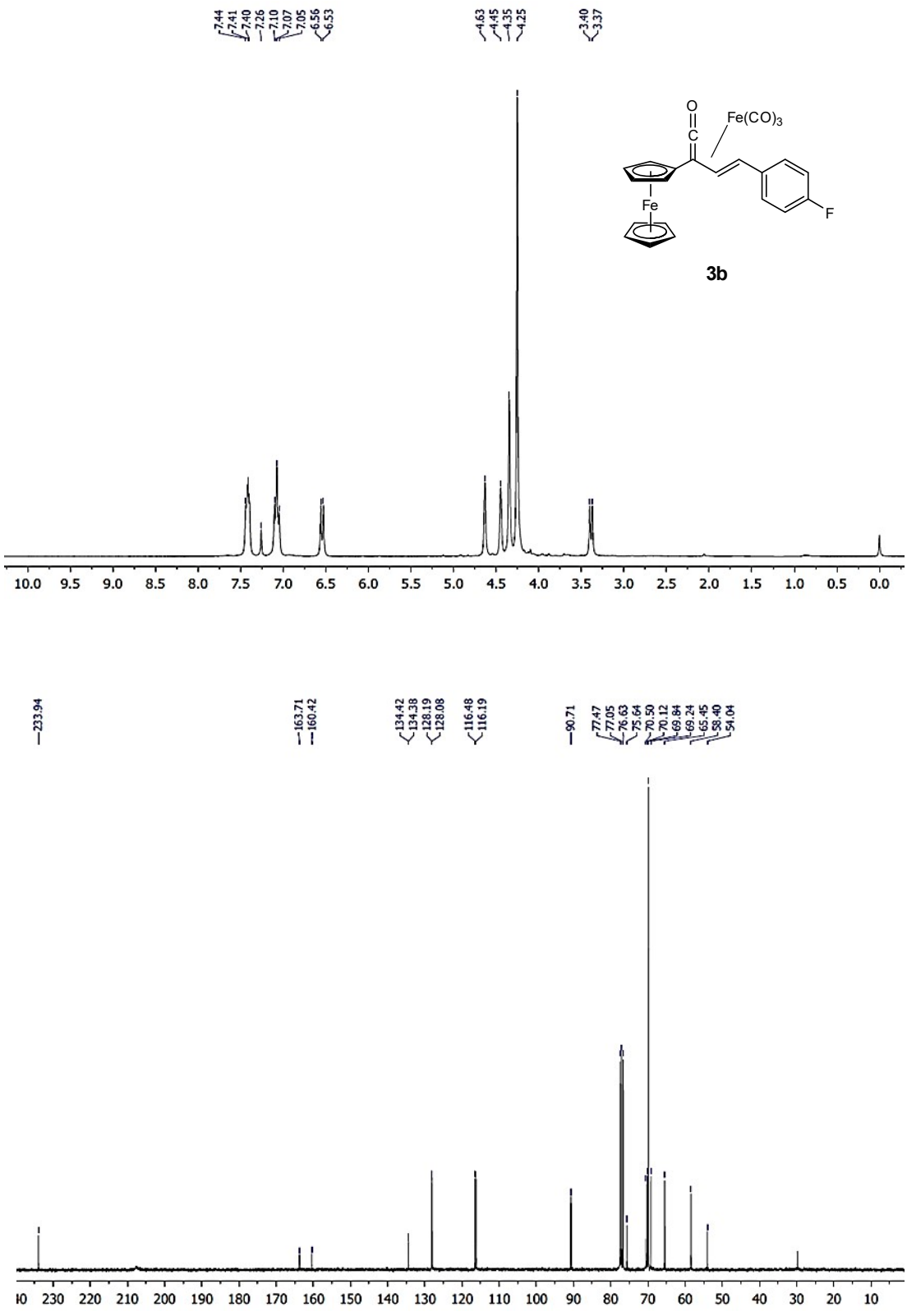


Figure S10. NMR spectra of complex **3b**

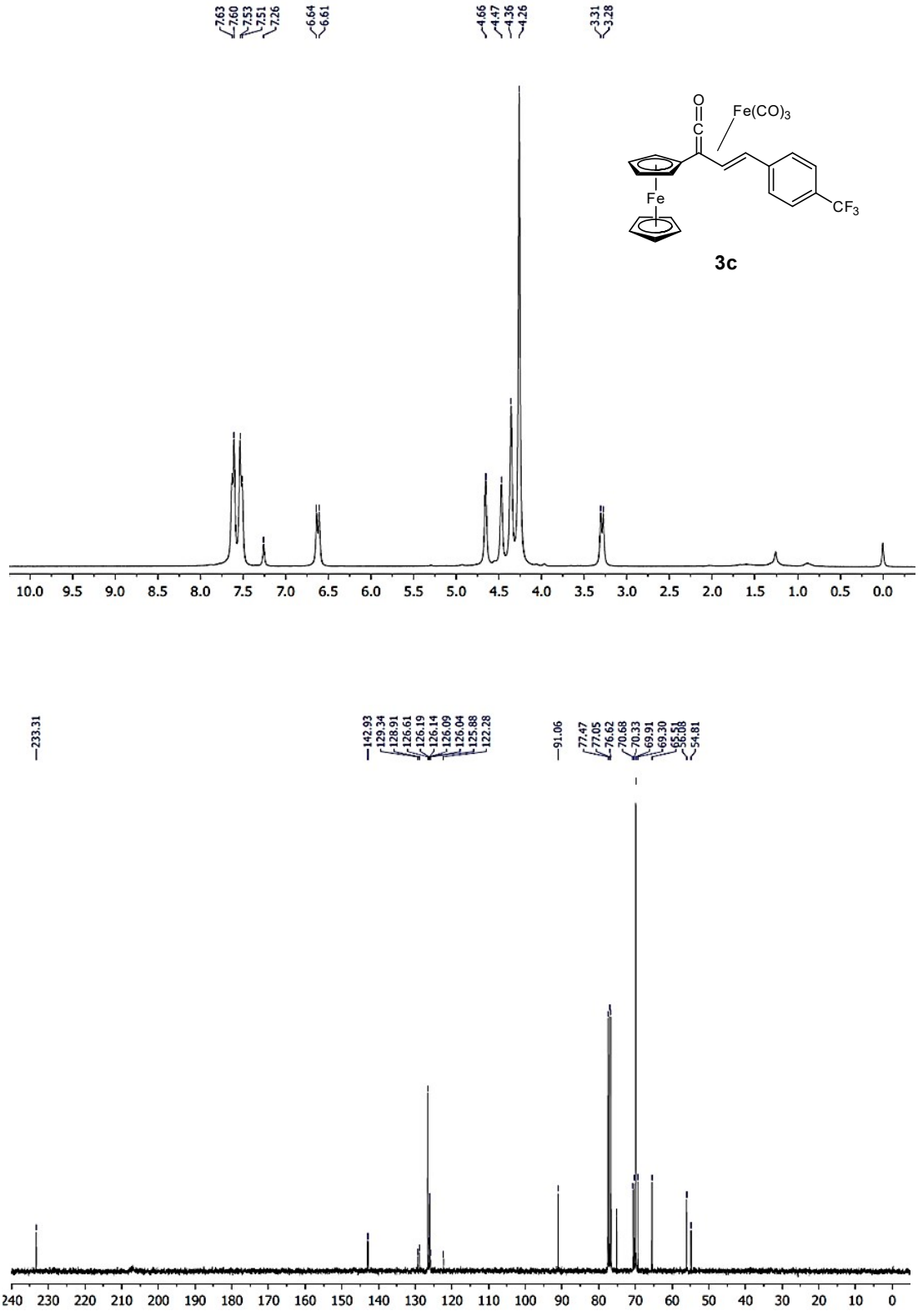
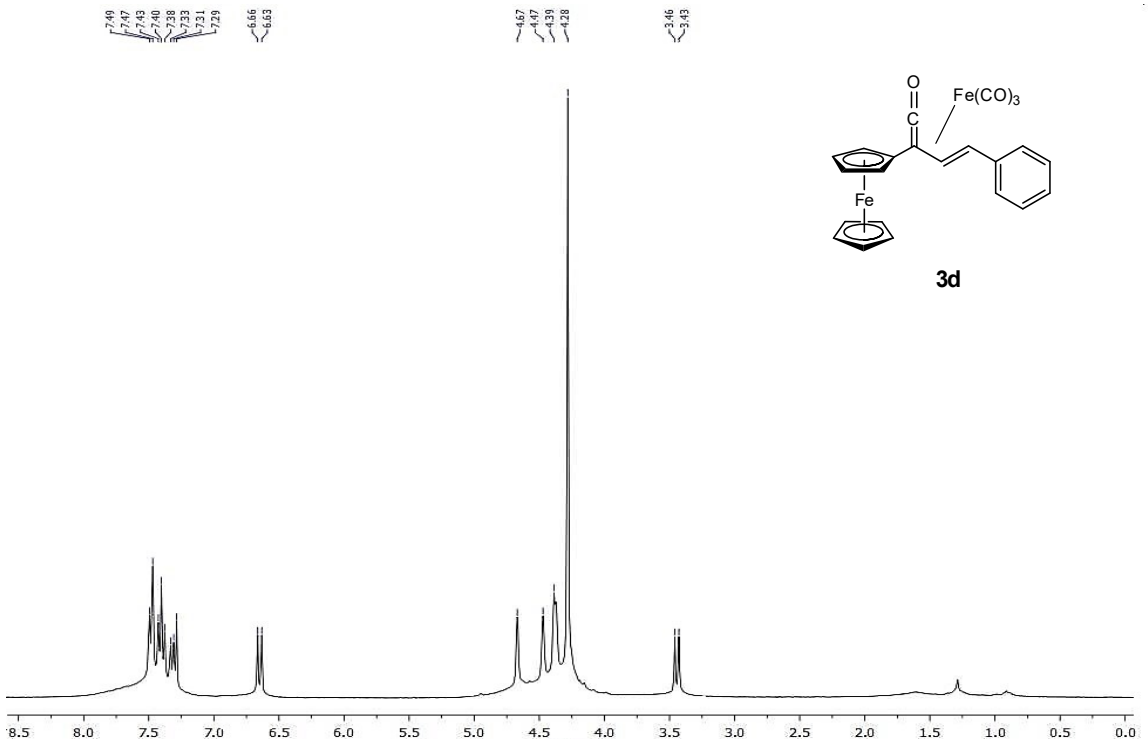


Figure S11. NMR spectra of complex **3c**



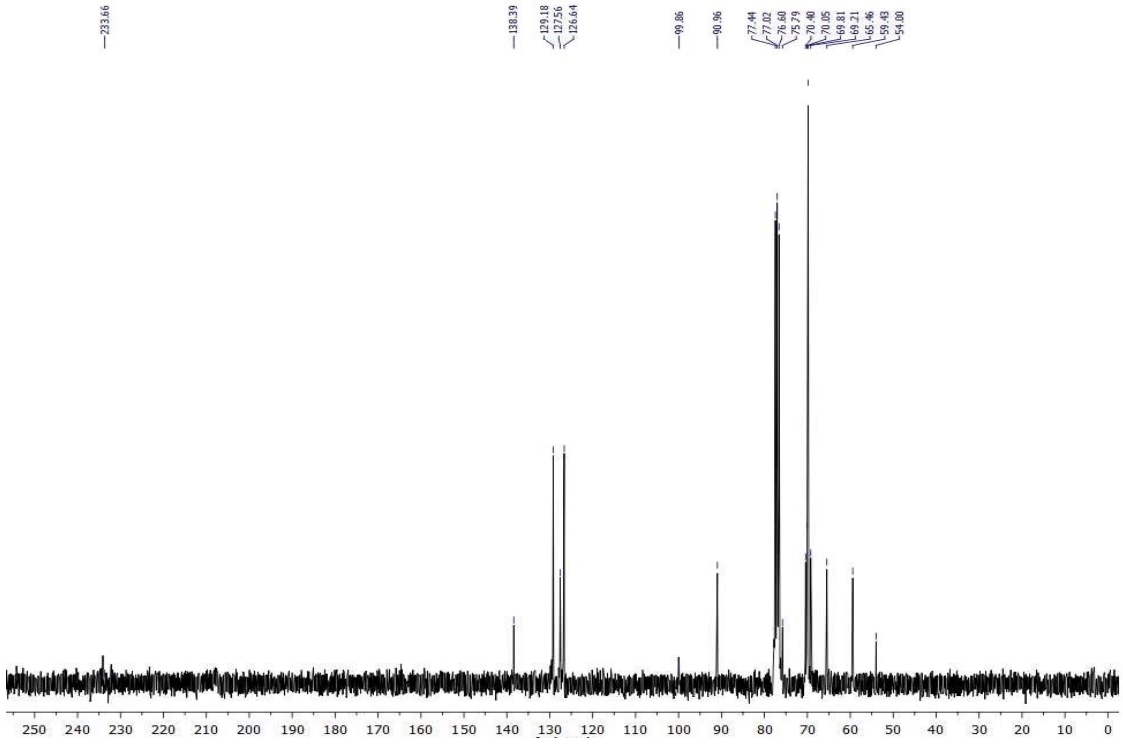


Figure S12. NMR spectra of complex **3d**

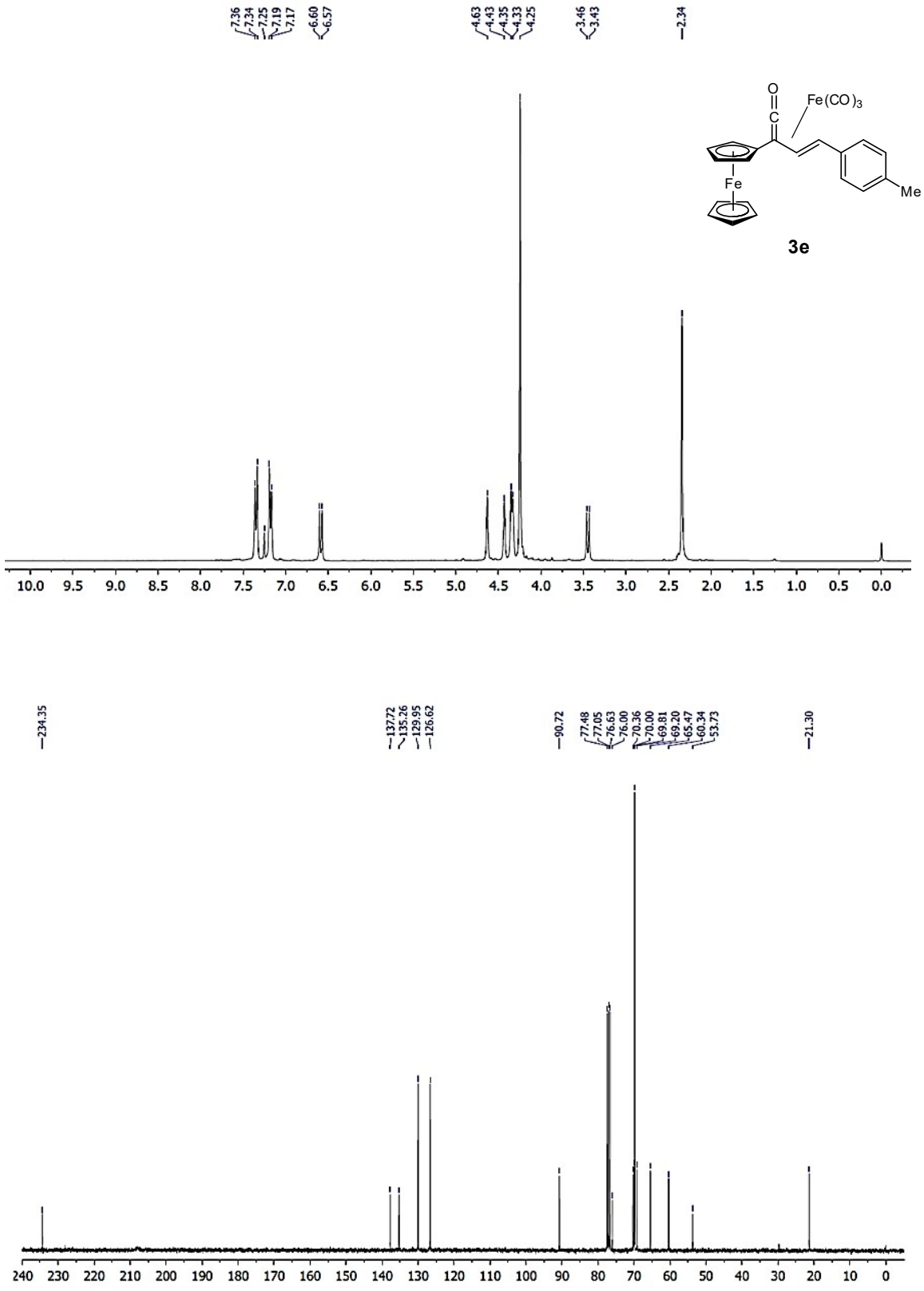


Figure S13. NMR spectra of complex **3e**

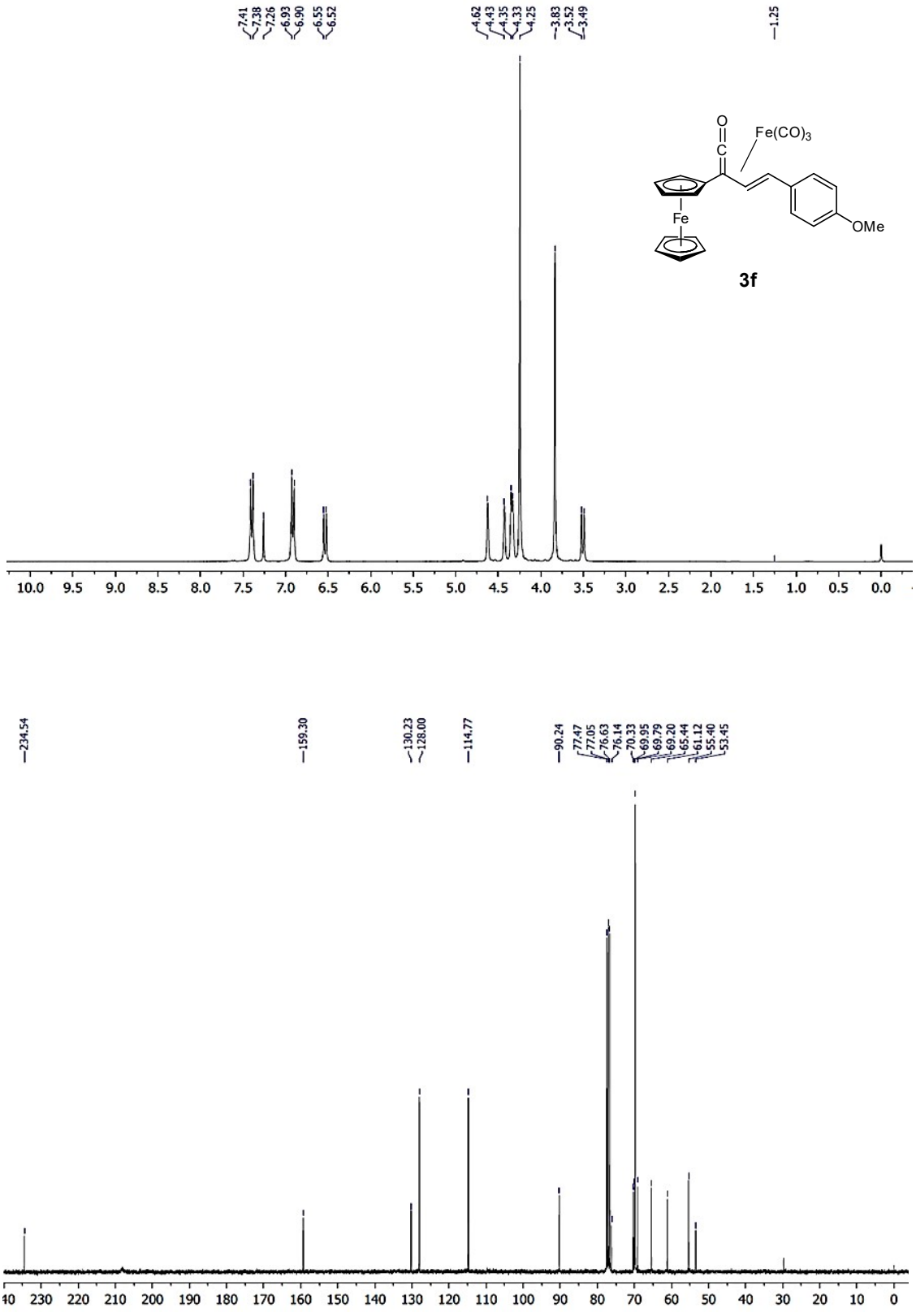
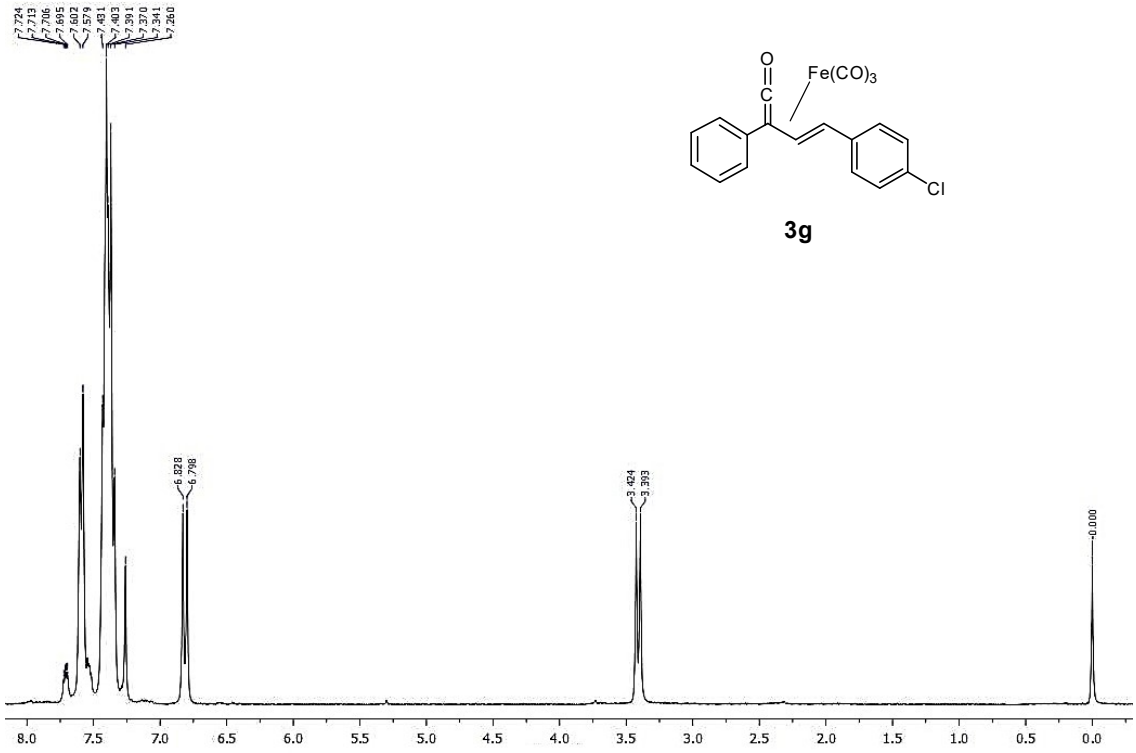


Figure S14. NMR spectra of complex **3f**



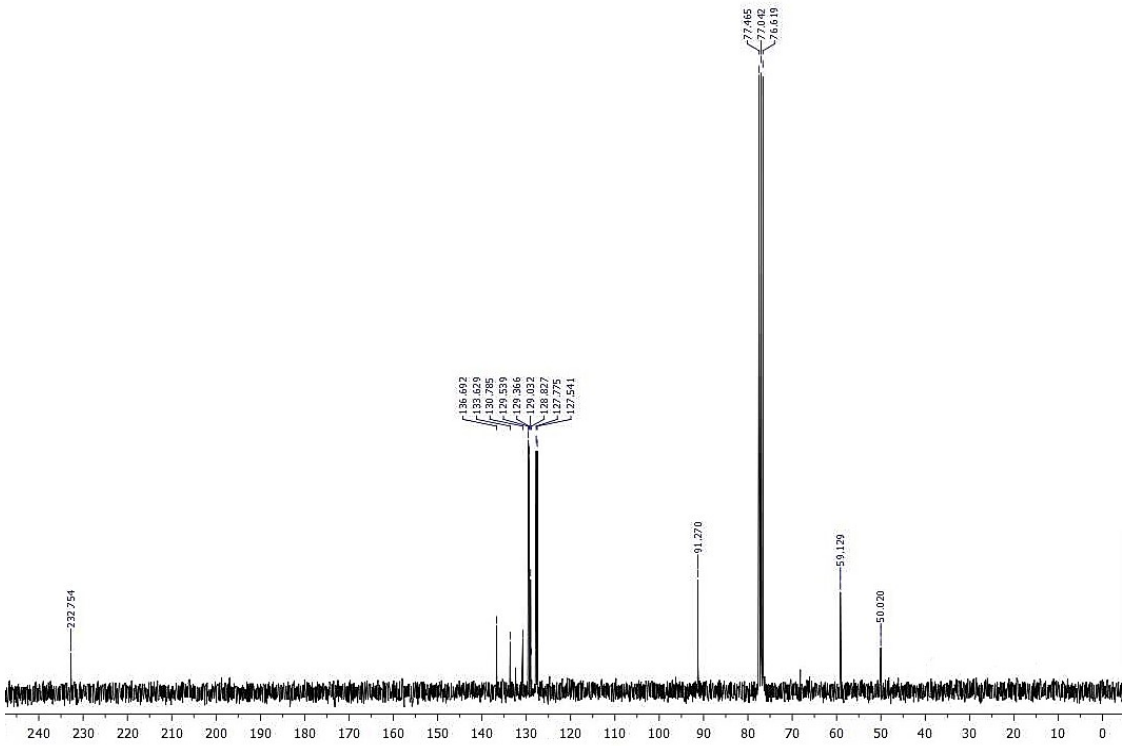


Figure S15. NMR spectra of complex **3g**

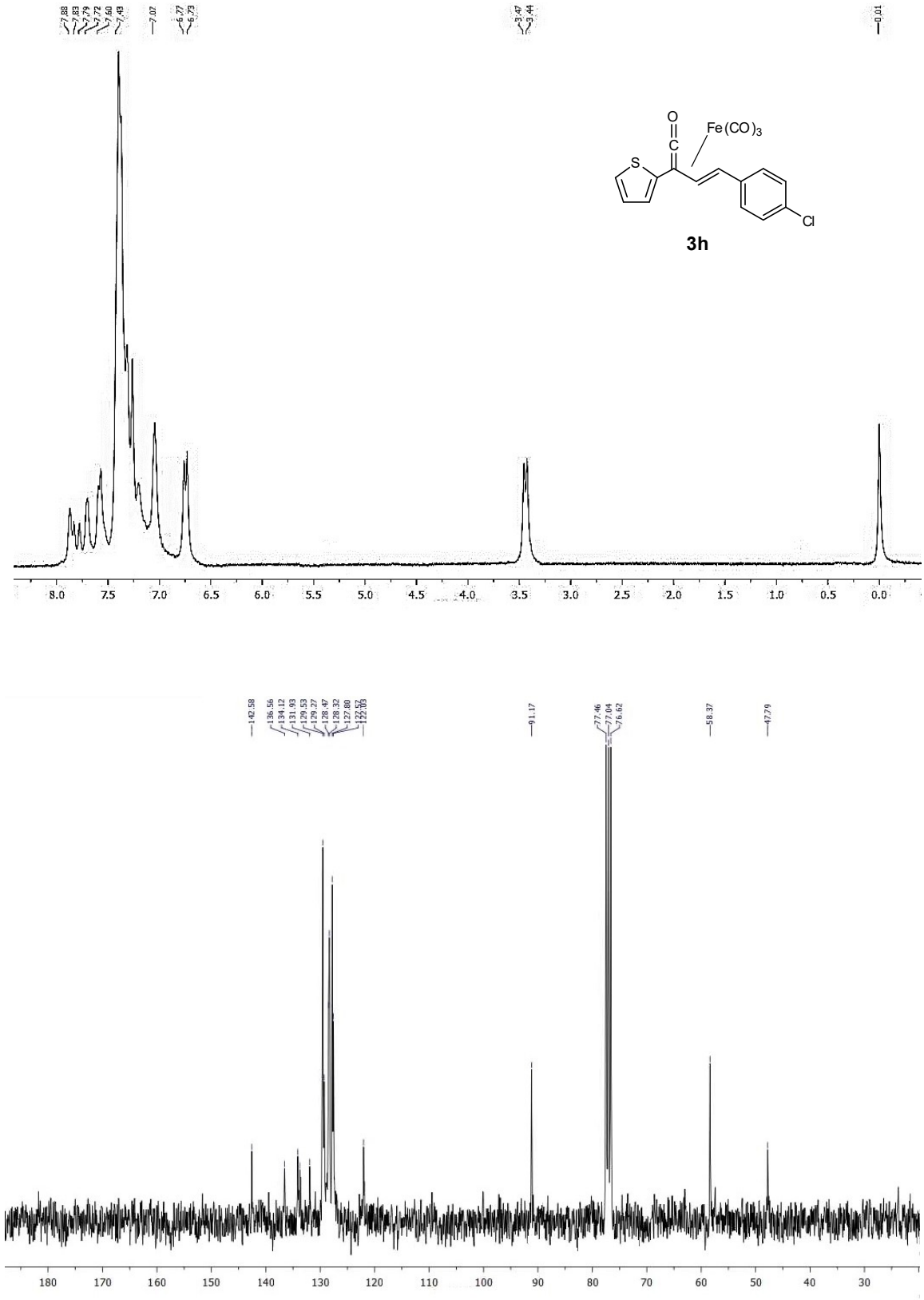


Figure S16. NMR spectra of complex **3h**

5. General procedure of synthesis of lactones 4a-h

A solution of η^4-vinylketene[Fe(CO)$_3$] (0.2 g, 1 equiv.) in 20 mL of ethyl ether and 25 µL of water was stirred at 15 °C. On the other hand, an iodine solution (1 equiv.) in 30 mL of ethyl ether was added to the reaction mixture and was stirred for 40 min at 15 °C and followed of this time at room temperature for 6-8 h (TLC indicated consumption of the starting material). The reaction mixture was filtered through a mixture of celite, neutral alumina and activated carbon (about 3/2/1 cm per phase). The solvent was removed under reduced pressure using a rotary evaporator. The crude was purified by preparative silica TLC using gradient of hexane/dichloromethane as eluent.

3-ferrocenyl-5-(4-chlorophenyl)furan-2(5*H*)-one (4a)

Orange crystals (86 % yield), mp 124 °C. ATR-FTIR (cm^{-1}): *ν*(CO) 1757 (vs), 1641 (sh). ^{1}H-NMR ($CDCl_3$, 300 MHz): *δ* (ppm) 7.28 (t, 2H, Ph), 7.23 (s, H), 7.10 (t, 2H, Ph), 5.83 (s, H), 4.85 (s, 2H, Cp), 4.39 (s, 2H, Cp), 4.15 (s, 5H, Cp). ^{13}C-NMR ($CDCl_3$, 75 MHz): *δ* (ppm) 171.5 (CO), 142.1 (CH), 135.2 (C_{para}), 133.9 (C_{ipso}), 132.0 (OC=), 128.5 (2CH, Ph), 126.0 (2CH, Ph), 81.5 (CH), 72.9 (C, Cp), 70.2 (2CH, Cp), 69.9 (5CH, Cp), 67.6 (2CH, Cp). MStation-FAB [M]$^+$ Calcd for $C_{20}H_{15}ClFeO_2$: 378.0110. Found: 378.0118, Error (ppm): 2.1.

3-ferrocenyl-5-(4-fluorophenyl)furan-2(5*H*)-one (4b)

Orange crystals (94 % yield), m. p.: 122-123°C. ATR-FTIR (cm^{-1}): *ν*(CO) 1760 (vs), 1722 (sh). ^{1}H-NMR ($CDCl_3$, 300 MHz): *δ* (ppm) 7.28 (t, 2H, Ph), 7.22 (s, H), 7.10 (t, 2H, Ph), 5.84 (s, H), 4.86 (s, 2H, Cp), 4.38 (s, 2H, Cp), 4.16 (s, 5H, Cp). ^{13}C-NMR ($CDCl_3$, 75 MHz): *δ* (ppm) 171.5 (CO), 161.5 (C_{para}), 142.1 (OC=), 132.0 (CH), 131.1 (C_{ipso}), 128.5 (2CH, Ph), 116.1 (2CH, Ph), 81.5 (CH), 72.9 (C, Cp), 70.0 (2CH, Cp), 69.7 (5CH, Cp), 67.6 (2CH, Cp). HRMS-ESI [M + 1]$^+$ Calcd for $C_{20}H_{16}FFeO_2$: 363.0483. Found: 363.0484, Error (ppm): 0.12.

3-ferrocenyl-5-(4-(trifluoromethyl)phenyl)furan-2(5*H*)-one (4c)

Orange crystals (43 % yield), mp 120 °C. ATR-FTIR (cm^{-1}): *ν*(CO) 1759 (vs), 1723 (sh). ^{1}H-NMR [$(CD_3)_2CO$, 300 MHz]: *δ* (ppm) 8.36 (d, 1H, *J* = 11.1 Hz), 7.91-7.68 (m, 4H, Ph), 4.91 (d, 1H, *J*

= 11.1 Hz), 4.75 (d, 1H, Cp), 4.38 (d, 1H, Cp), 4.05 (s, 2H, Cp), 3.86 (s, 5H, Cp). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ (ppm) 167.9 (CO), 160.7 (CH), 132.5 (OC=), 131.0 (2CH, Ph), 128.9 (2CH, Ph), 127.6 (CF_3), 125.9 (C_{para}), 125.6 (C_{ipso}), 76.4 (CH), 69.8 (2CH, Cp), 69.7 (2CH, Cp), 68.3 (5CH, Cp). MStation-FAB $[M - 1]^+$ Calcd for $C_{21}H_{14}F_3FeO_2$: 411.0295. Found: 411.0301, Error (ppm): 0.12.

3-ferrocenyl-5-(phenyl)furan-2(5*H*)-one(4d)

Orange crystals (95 % yield), p. decomp.: 119 °C. ATR-FTIR (cm^{-1}): *ν*(CO) 1741 (vs), 1640 (s). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ (ppm) 7.42 (t, 2H, Ph), 7.40 (s, H), 7.33-7.24 (m, 2H, Ph), 5.87 (s, H), 4.86 (d, 2H, Cp), 4.38 (s, 2H, Cp), 4.16 (s, 5H, Cp). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ (ppm) 171.8 (CO), 142.6 (CH) 135.3 (OC=), 131.6 (C_{ipso}), 129.2 (CH, Ph), 129.1 (2CH, Ph), 126.6 (2CH, Ph), 82.3 (CH), 73.1 (C, Cp), 69.9 (2CH, Cp), 69.7 (5CH, Cp), 67.6 (2CH, Cp). MStation-FAB $[M]^+$ Calcd for $C_{20}H_{16}FeO_2$: 344.0500. Found: 344.0495, Error (ppm): -1.4.

3-ferrocenyl-5-(4-methylphenyl)furan-2(5*H*)-one (4e)

Orange crystals (90 % yield), m. p.: 128-129°C. ATR-FTIR (cm^{-1}): *ν*(CO) 1759 (vs), 1640 (m). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ (ppm) 7.26-7.20 (m, 5H), 5.83 (s, H), 4.88 (s, H, Cp), 4.84 (s, H, Cp), 4.38 (s, 2H, Cp), 4.16 (s, 5H, Cp), 2.37 (s, 3H, Me). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ (ppm) 171.9 (CO), 142.9 (CH), 139.3 (C_{ipso}), 132.3 (C_{para}), 131.5 (OC=), 129.8 (d, 2CH, Ph), 126.7 (d, 2CH, Ph), 82.3 (CH), 73.3 (C, Cp), 70.0 (CH, Cp), 69.9 (CH, Cp), 69.8 (5CH, Cp), 67.7 (CH, Cp), 67.6 (CH, Cp), 21.4 (C, Me). MStation-FAB $[M]^+$ Calcd for $C_{21}H_{18}FeO_2$: 358.0656. Found: 358.0649, Error (ppm): -2.0.

3-ferrocenyl-5-(4-methoxyphenyl)furan-2(5*H*)-one (4f)

Orange crystals (96 % yield), mp 106 °C.ATR-FTIR (cm^{-1}): *ν*(CO) 1739 (vs), 1645 (m). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ (ppm) 7.37 (t, 2CH, Ph), 7.26-7.20 (m, 3H), 5.83 (s, H), 4.88 (s, CH, Cp), 4.84 (s, CH, Cp), 4.38 (s, 2CH, Cp), 4.16 (s, 5CH, Cp), 2.37 (s, 3H, Me). ^{13}C-NMR ($CDCl_3$, 75 MHz): δ (ppm) 171.9 (CO), 142.9 (CH), 139.3 (C_{ipso}), 132.3 (C_{para}), 131.5 (OC=), 129.8 (2C, Ph), 126.7 (2C, Ph), 82.3 (CH), 73.3 (C, Cp), 70.0 (CH, Cp), 69.9 (CH, Cp), 69.8 (5CH, Cp), 67.7 (CH,

Cp), 67.6 (CH, Cp), 21.4 (C, Me). MStation-FAB $[M]^+$ Calcd for $C_{21}H_{18}FeO_3$: 374.0605. Found: 374.0600, Error (ppm): -1.4.

-phenyl-5-(4-chlorophenyl)furan-2(5*H*)-one (4g)

White crystals (77 % yield), mp 192-193 °C. ATR-FTIR (cm^{-1}): *ν*(CO) 1759 (vs), 1493 (m). ^{1}H-NMR ($CDCl_3$, 300 MHz): *δ* (ppm) 7.89 (s, 1H), 7.83-7.32 (m, 9H, Ph), 5.3 (s, H). ^{13}C-NMR ($CDCl_3$, 75 MHz): *δ* (ppm) 146.8 (CO), 133.3 (CH), 131.3 (C_{ipso}), 130.6 (C_{para}), 129.7 (OC=), 129.3 (2CH, Ph), 128.8 (2CH, Ph), 128.4 (C), 128.0 (2CH, Ph), 127.2 (2CH, Ph), 80.8 (CH). MStation-FAB $[M]^+$ Calcdfor $C_{16}H_{11}ClO_2$: 271.0525. Found: 271.0528, Error (ppm): +0.8.

3-(thiophen-2-yl)-5-(4-chlorophenyl)furan-2(5*H*)-one (4h)

White crystals (67 % yield), mp 115-116 °C. ATR-FTIR (cm^{-1}): *ν*(CO) 1754 (vs), 1655 (m). ^{1}H-NMR [$(CD_3)_2CO$, 300 MHz]: *δ* (ppm) 8.06 (s, 1H), 7.65-7.01 (m, 7H), 7,43 (s, H). ^{13}C-NMR ($CDCl_3$, 75 MHz): *δ* (ppm) 142.7 (CO), 141.7 (C), 141.0 (OC=), 130.1 (C), 129.7 (C), 129.3 (C), 128.8-128.0 (7C, CH), 89.5 (CH). MStation-FAB $[M]^+$ Calcd for $C_{21}H_{18}FeO_3$: 374.0605. Found: 374.0600, Error (ppm): -1.4.

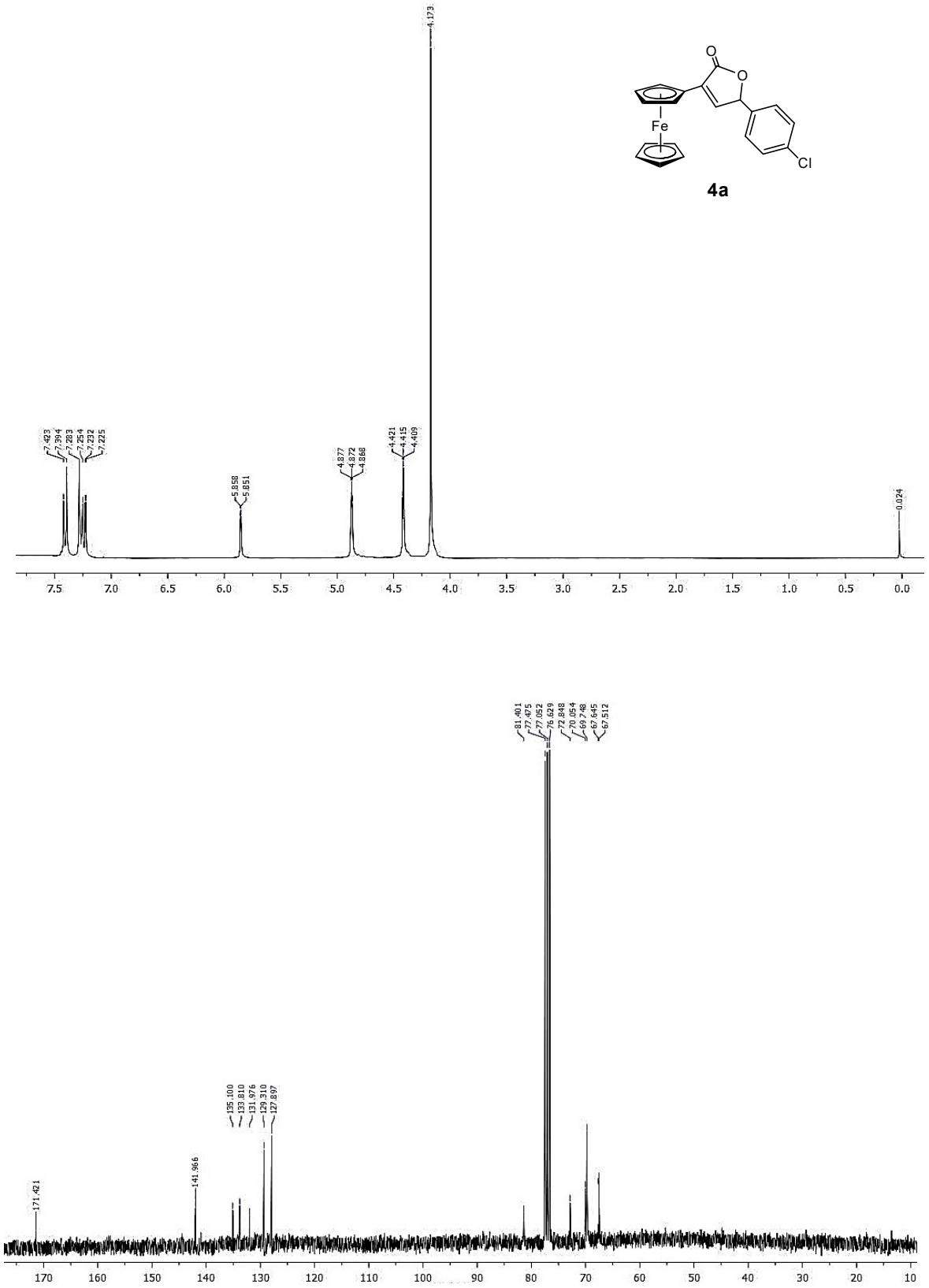


Figure S17. NMR Spectra of compound **4a**

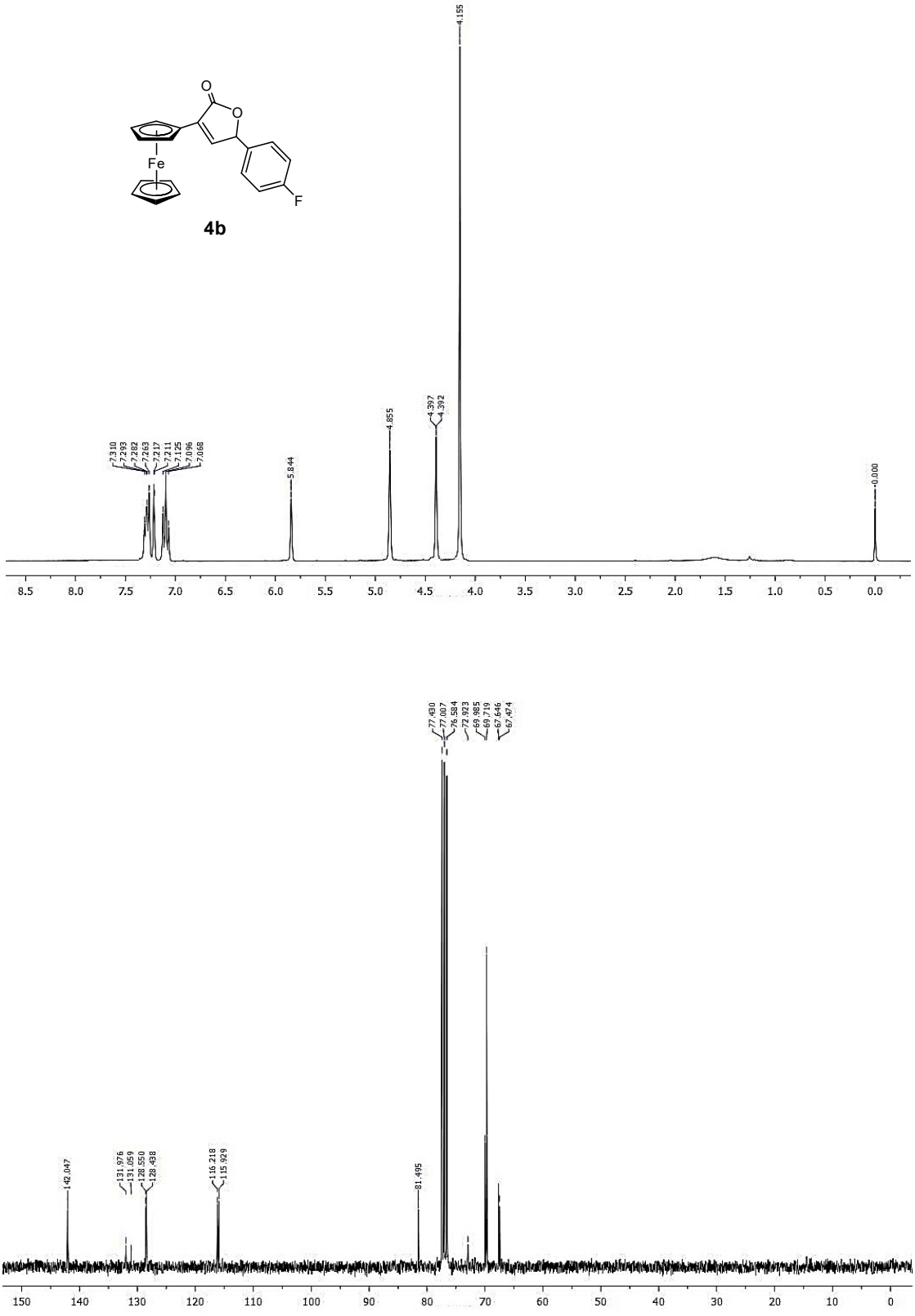


Figure S18. NMR Spectra of compound **4b**

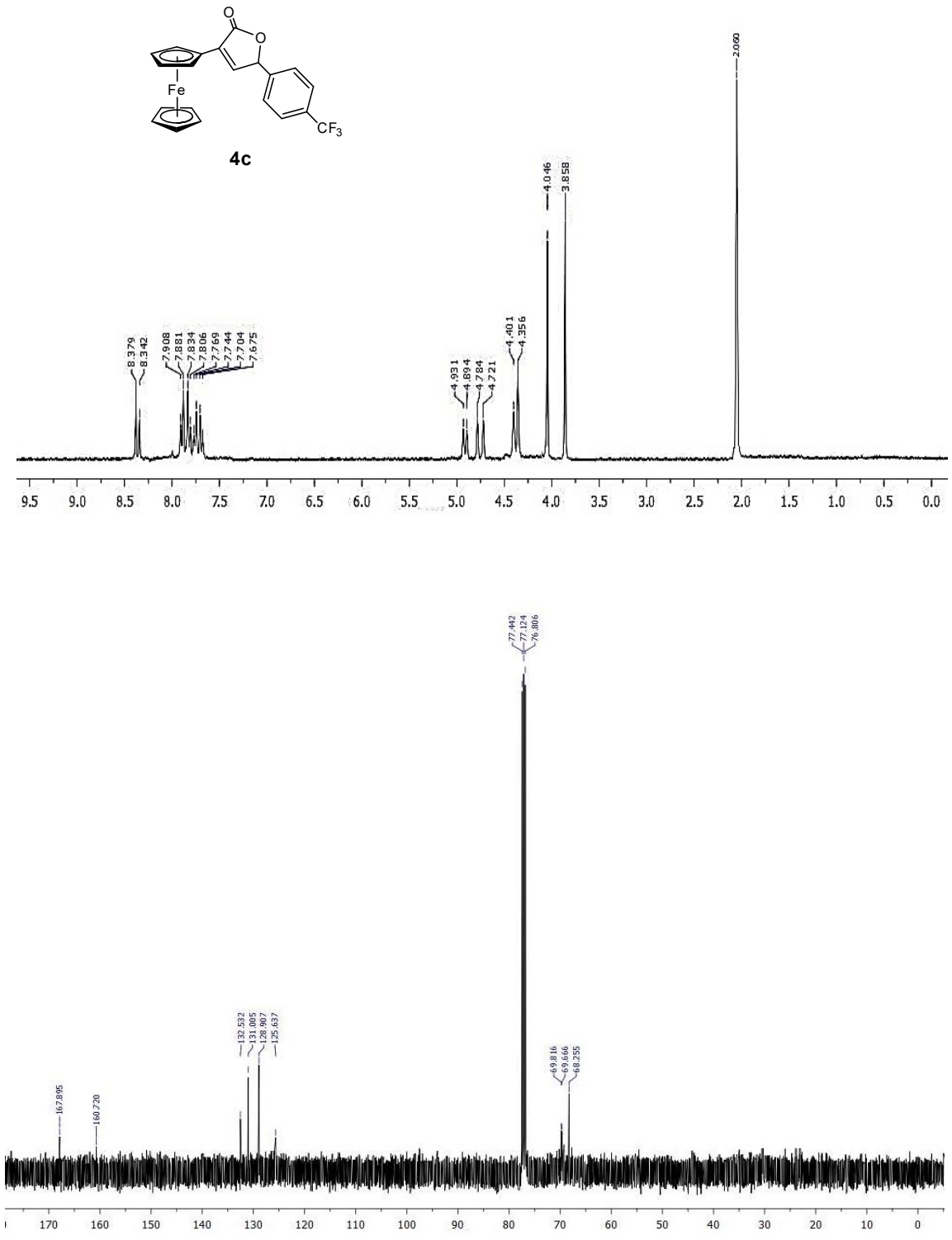


Figure S19. NMR Spectra of compound **4c**

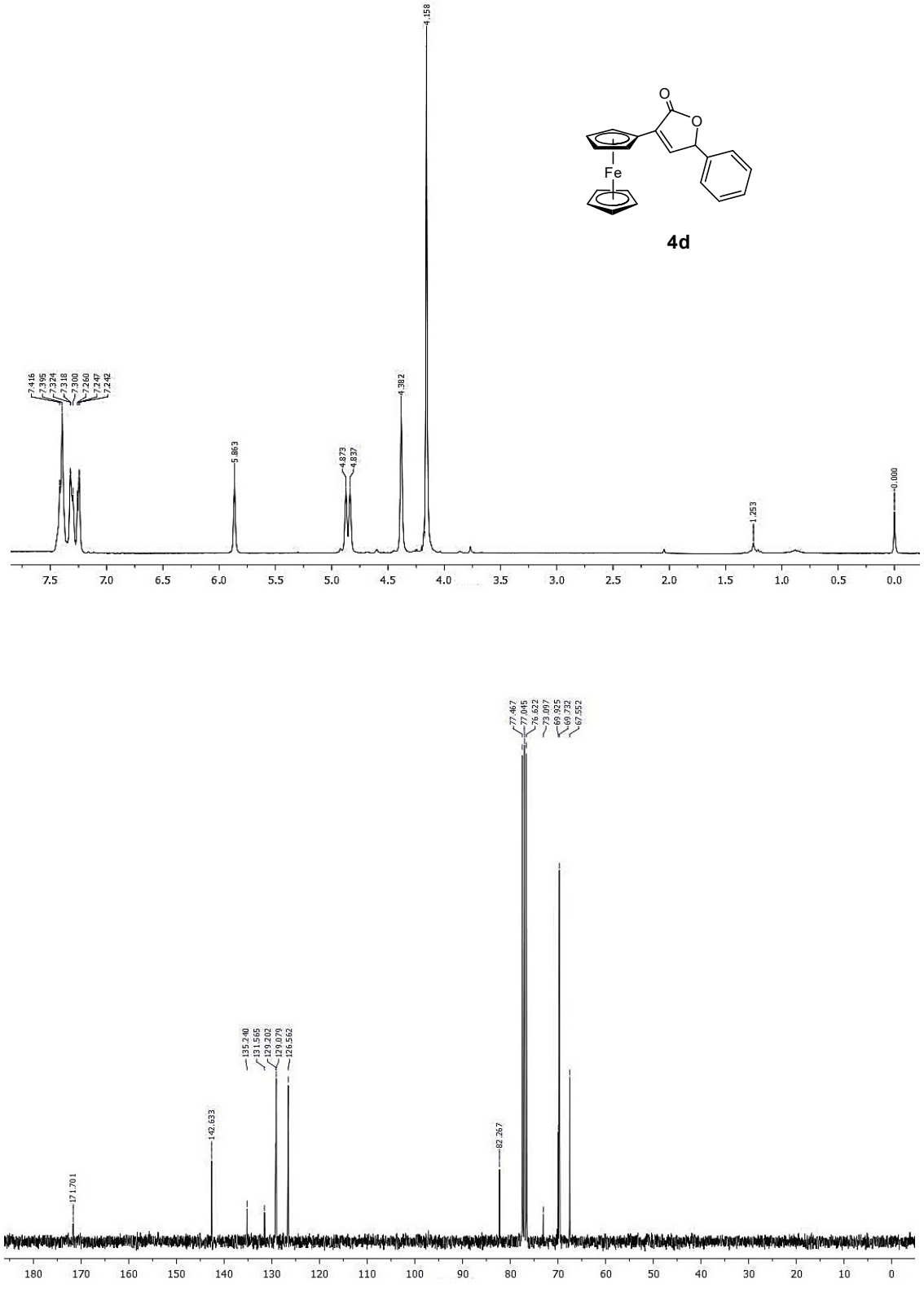


Figure S20. NMR Spectra of compound **4d**

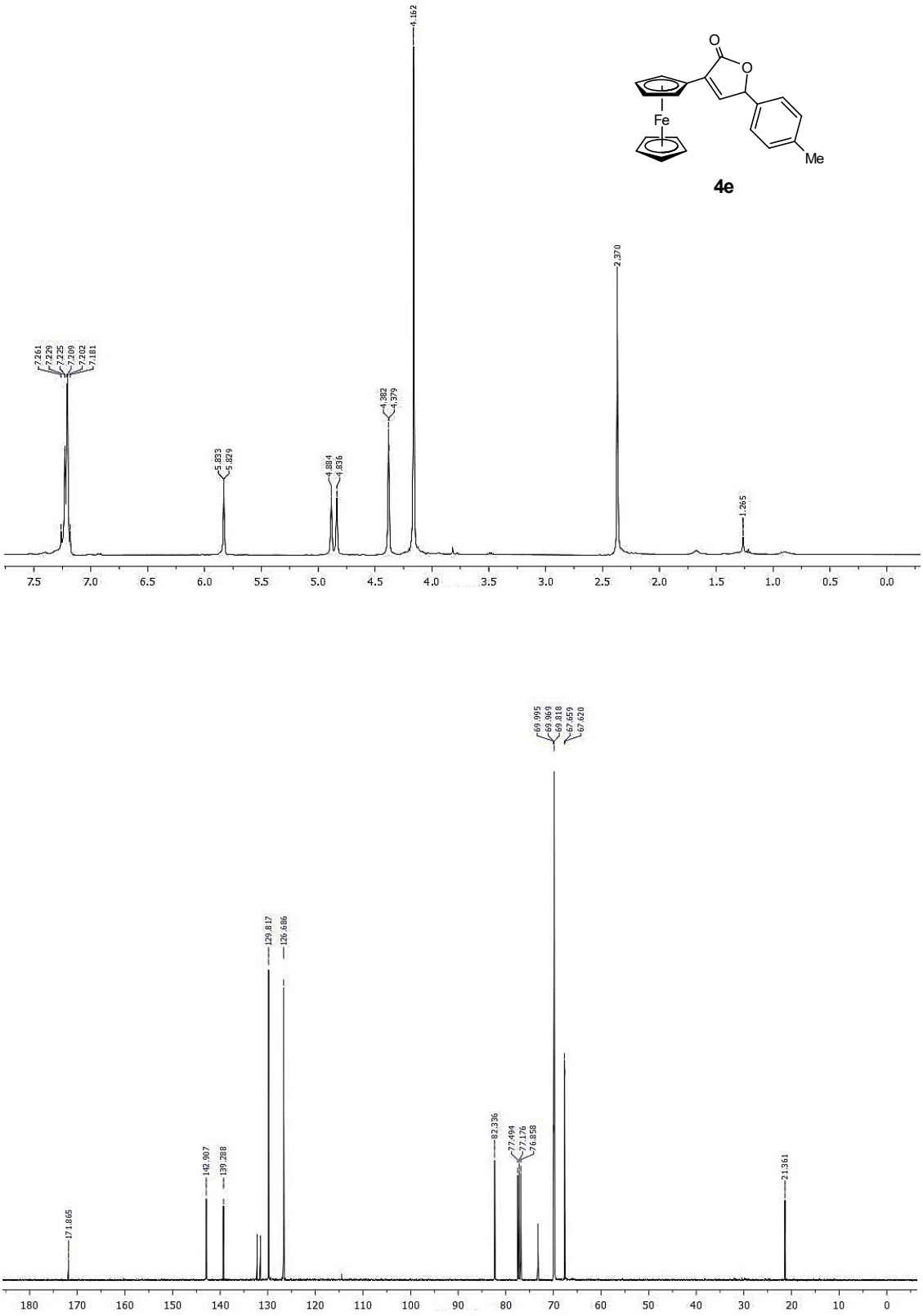


Figure S21. NMR Spectra of compound **4e**

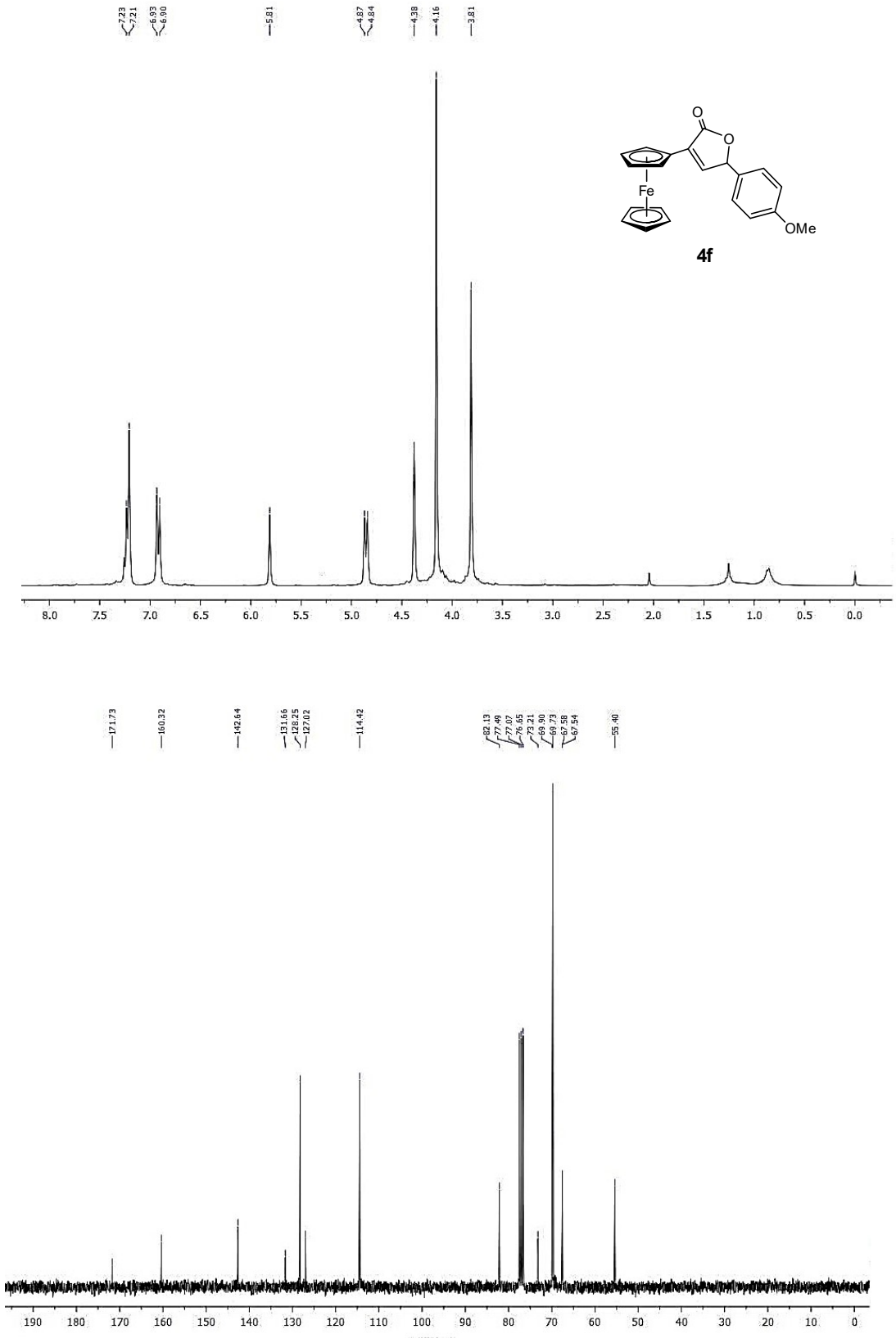


Figure S22. NMR Spectra of compound **4f**

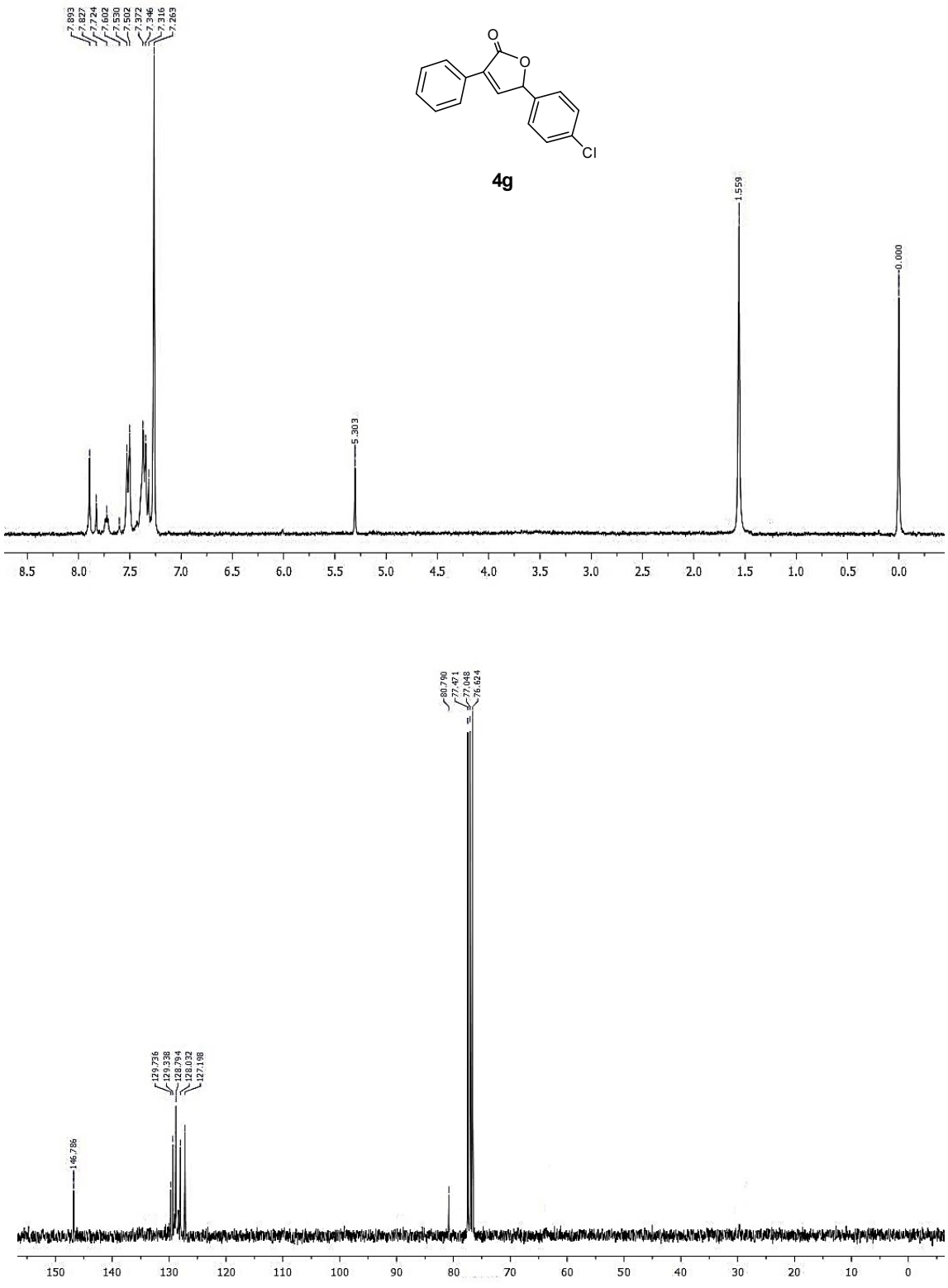


Figure S23. NMR Spectra of compound **4g**

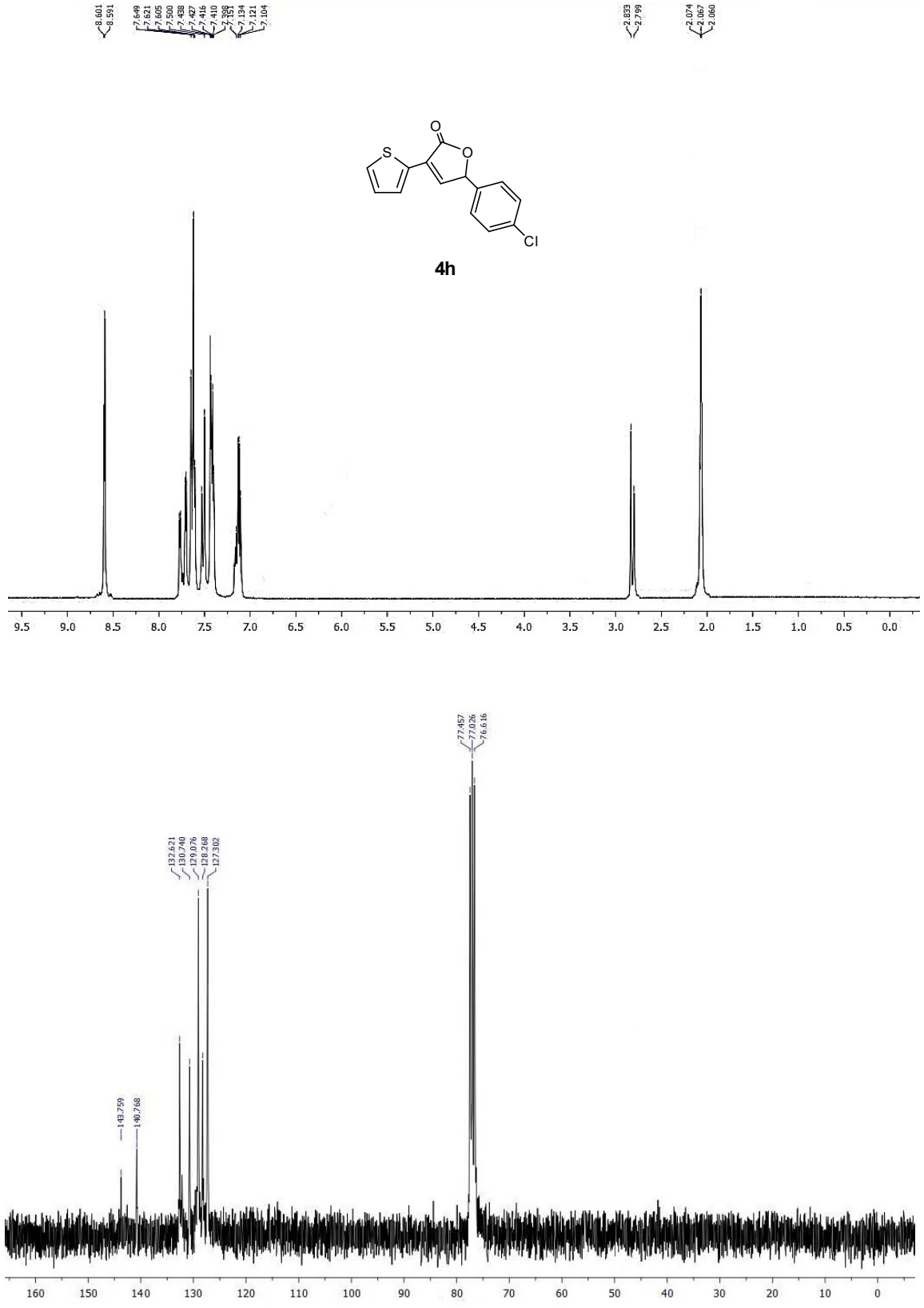


Figure S24. NMR Spectra of compound **4h**

6. General procedure of synthesis of (5*H*)-pyrrol-2-ones 5-6.

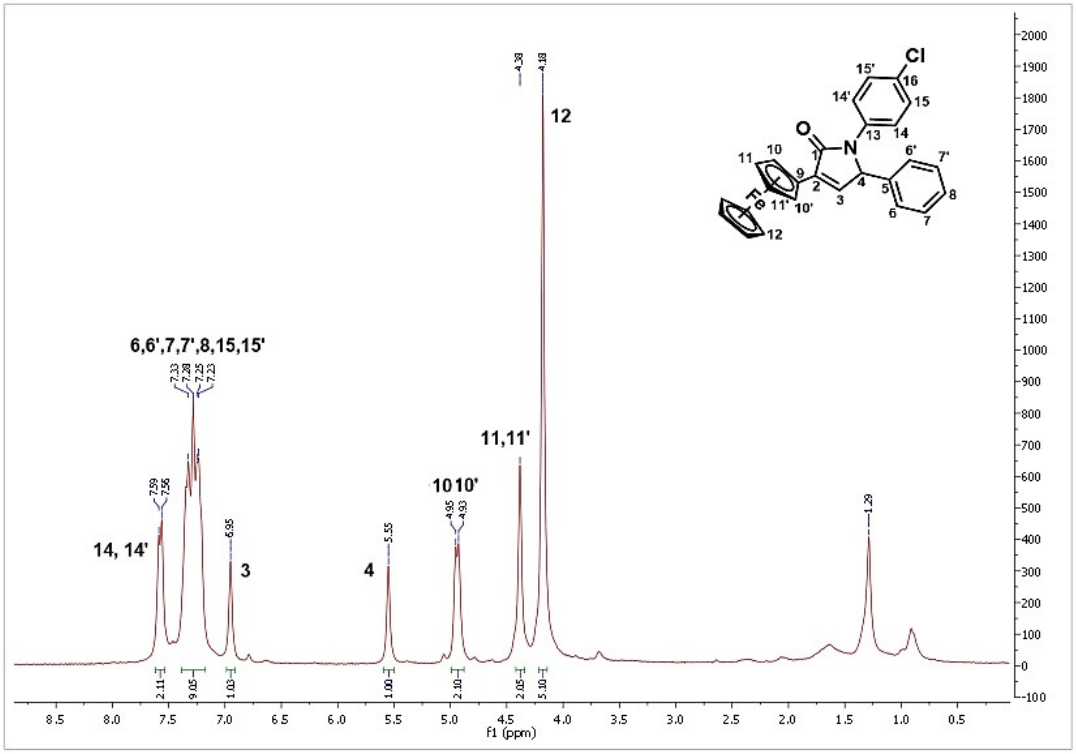
In a 50 mL two-neck round-bottom flask equipped with a condenser was put a solution of η^4-vinylketene[$Fe(CO)_3$] (0.15 g, 0,32 mmol, 1 equiv) in 5 mL of anhydrous benzene. The solution was purged with argon. Then, a freshly anhydrous benzene solution (5 mL) of iodine (80mg, 0.32mmol) was added by canula followed of an anhydrous benzene solution (5mL) of the corresponding aniline (0.96mmol, 3 equiv). The mixture is heated at 90 ºC for the time included in table 3. After that, the reaction was cooled at room temperature and then filtered through a mixture of celite, neutral alumina and activated carbon (about 3/2/1 cm per phase). The solvent was removed under reduced pressure using a rotary evaporator. The crude was purified by preparative silica TLC using gradient of hexane/ethyl acetate (95:5) as eluent.

3-ferrocenyl-5-phenyl-*N*-(4-tolyl)-(5*H*)-pyrrol-2-one (5)

Orange solid (Yield 31%). mp 189-190°C. ATR-FTIR ν(cm^{-1}): 810 (=C-H), 1268 (C-N), 1513 (C=C), 1620 (C=O), 3335 (-CH-), 3417 (N-C). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 2.29 (s,3H), 4.18 (s,5H), 4.37 (s,2H), 4.96 (d,2H), 5.57 (s, 1H), 6.94 (d, 1H), 7.12 (d, J=9Hz, 2H), 7.28 (m, 5H), 7.47 (d, J= 9Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 20.8, 65.4, 67.5, 69.5, 69.7, 75.1, 121.6, 126.8, 128.3, 129.2, 129.4, 134.2, 135.2, 135.3, 136.2, 136.8, 169.3. MS (EI^+, 70eV) m/z (%): 433 (100) $[M]^{+\cdot}$,368 (22) [M^+-Cp], 340 (10) [-CH_3 ,-O]. MS-HR (FAB^+) *m/z* for $C_{27}H_{23}FeNO$: calc. 433.1129, found 433.1125

3-ferrocenyl-5-phenyl-*N*-(4-chlorophenyl)-(5*H*)-pyrrol-2-one (6)

Orange solid (Yield 37%) mp 186-188°C. ATR-FTIR ν(cm^{-1}):824 (=C-H), 1094 (C-Cl), 1362 (C-N), 1493 (C=C), 1694 (C=O), 2924 (-CH-), 3090 (Cl-Ar). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 4.18 (s,5H), 4.39 (s,2H), 4.94 (d,2H), 5.55 (s, 1H), 6.95 (d, 1H), 7.28 (m, 7H), 7.58 (d, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 65.2, 67.4, 67.4, 69.6, 69.5, 74.7, 122.3, 126.6, 128.5, 128.9, 129.3, 129.6, 135.2, 135.1, 136.3, 136.9, 169.2. MS (EI^+, 70eV) m/z (%): (453 (100). HR-MS (FAB^+) *m/z* for $C_{26}H_{20}ClFeNO$: calc 453.0583, found 453.0579.



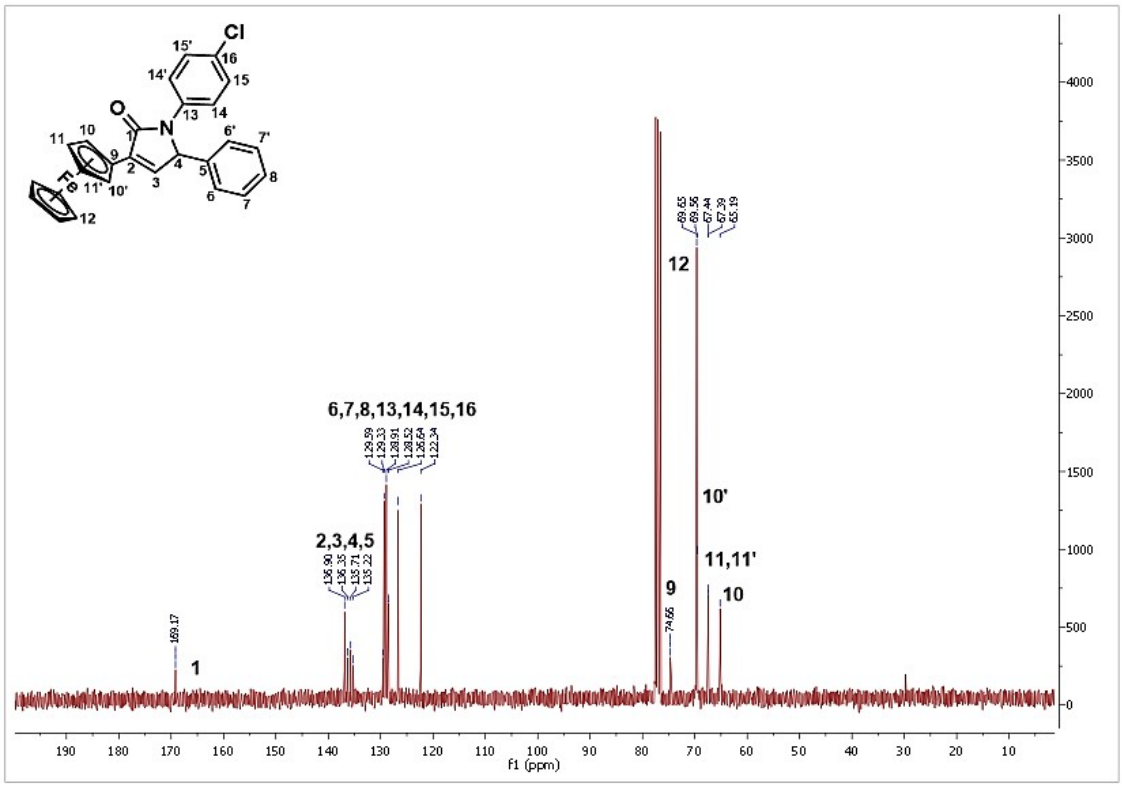
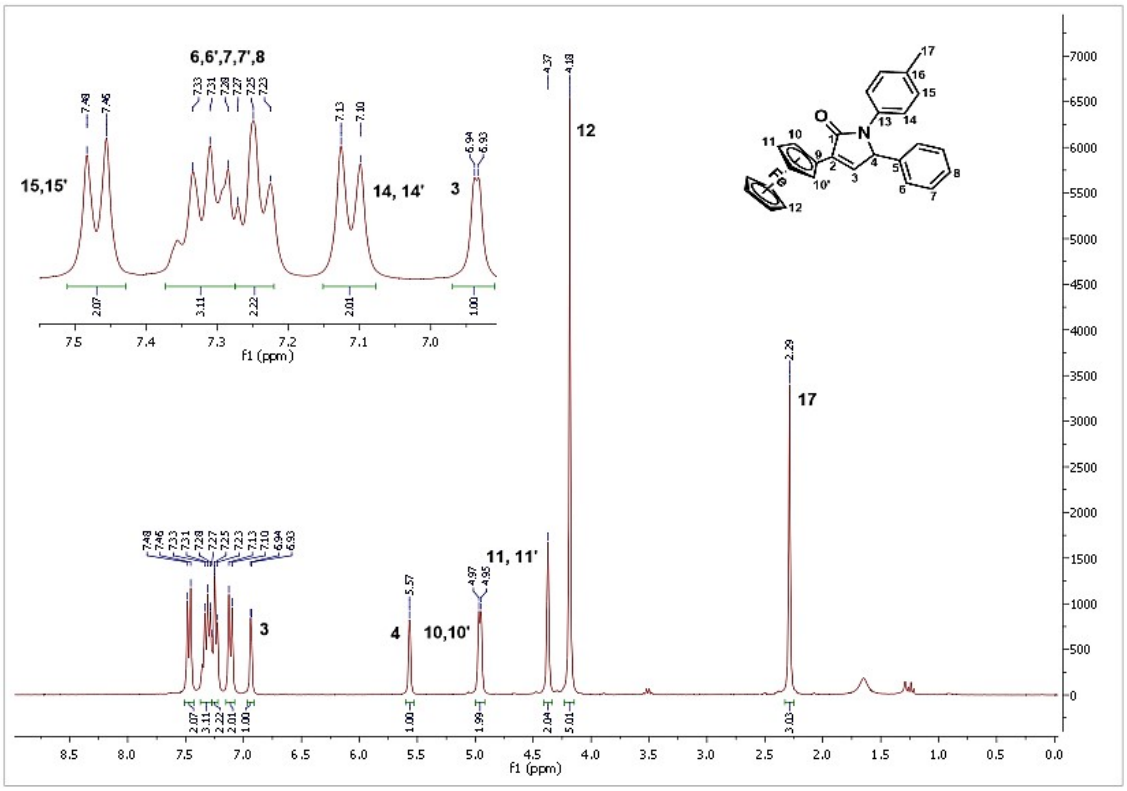


Figure S25. NMR Spectra of compound **5**



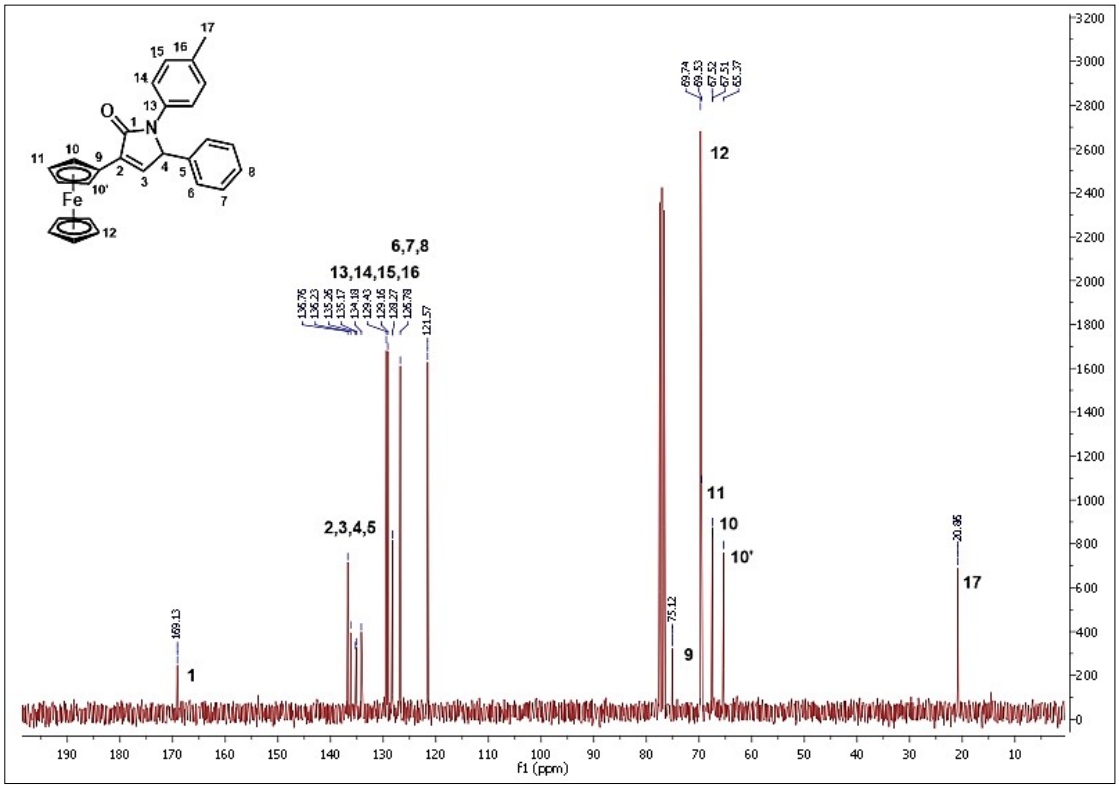


Figure S26. NMR Spectra of compound **6**

7. DFT Calculations

Cartesian coordinates [Å] of the studied complexes and their absolute Energies with ZPE correction (Hartree) optimized at M06/Def2TZP level of theory.

Fe0CO3 E+ZPE=-2295.298299

Fe	0.05218400	0.97251800	0.29359700
O	-1.44954500	1.71327300	-2.17701900
O	1.20391900	0.08245400	2.89826200
O	-1.97109200	2.64613900	1.59532800
O	1.89634100	3.08604600	-0.54984700
C	-1.01824200	1.01843700	-1.32208100
C	-1.21698400	-0.32146400	-0.78491800
C	0.00327000	-0.95803700	-0.49902300
C	1.20445800	-0.37816400	-0.95402300
C	0.76995900	0.39638400	1.89763800
C	-1.18040200	1.99033400	1.10808600
C	1.18151100	2.28228700	-0.18286900
H	0.00683000	-1.82451100	0.15613200
H	1.18310200	0.11295600	-1.92264800
C	2.77984600	-1.77496500	0.43322100
C	-2.54415100	-0.84931200	-0.45055600
C	-3.65728500	-0.01071600	-0.40457900
H	-3.54131800	1.04979600	-0.59972700
C	-4.90864700	-0.51549800	-0.11010300
H	-5.76010700	0.15377300	-0.07520100
C	-5.07712100	-1.86776900	0.13900900
C	-3.98262800	-2.71277900	0.08149900
H	-4.10534000	-3.77481200	0.25916600
C	-2.72888200	-2.21037100	-0.21428300
H	-1.88763900	-2.89050800	-0.28584900
C	2.54489600	-0.83123600	-0.56580200
C	3.64554600	-0.29777400	-1.23525800
H	3.47911400	0.43840900	-2.01608300
C	4.93285900	-0.68899100	-0.92086800
H	5.77148300	-0.25777600	-1.45486800
C	5.14962000	-1.63034600	0.07113400
H	6.15733100	-1.94067700	0.32000500
C	4.06672500	-2.17205700	0.74396700
H	4.22545000	-2.91054700	1.52114600
H	-6.05969500	-2.26217600	0.36867200
H	1.95093700	-2.21046500	0.98077100

I2 E+ZPE=-595.556903

I	0.00000000	0.00000000	1.33991500
I	0.00000000	0.00000000	-1.33991500

H2O E+ZPE=-76.400576

O	0.00000000	0.11641800	0.00000000
H	0.76130000	-0.46567400	0.00000000
H	-0.76130000	-0.46567400	0.00000000

OMe2 E+ZPE=-154.904396

H	1.20661000	-0.83839500	0.88898500
H	-1.20676900	-0.83815600	0.88915100
C	1.15497100	-0.19243800	-0.00000100
C	-1.15497100	-0.19243800	0.00000100
O	0.00000000	0.58930600	0.00000000
H	2.01759100	0.47395700	0.00017000
H	-2.01759100	0.47395700	-0.00017100
H	1.20676800	-0.83815600	-0.88915000
H	-1.20660900	-0.83839600	-0.88898500

HI E+ZPE=-298.360446

I	0.00000000	0.00000000	0.02996100
H	0.00000000	0.00000000	-1.58795500

TS1_1 E+ZPE=-2890.823636

Fe	-1.13562700	-0.09846900	1.02068300
O	0.96231000	2.48580300	-0.98082500
O	-3.97484700	0.08758000	1.79367100
O	-0.24832100	1.72539200	3.14303400
O	-0.52998700	-2.60775600	2.41082400
C	0.21415600	1.63539900	-0.79792100
C	-1.11908200	1.21296300	-0.68298000
C	-1.67601200	-0.09179700	-0.94967000
C	-1.04141000	-1.31726700	-0.86950700
C	-2.88913100	0.02952100	1.46327600
C	-0.56851900	0.99821000	2.32900800
C	-0.72734200	-1.61914100	1.88362800
H	-2.74112800	-0.06152800	-1.15633600

H	0.02630400	-1.37634800	-1.02946000
C	-3.12287900	-2.73814400	-0.88216400
C	-2.03123000	2.40004200	-0.83155600
C	-2.01687900	3.42507800	0.10686000
H	-1.33885300	3.37061100	0.95232800
C	-2.86256700	4.50978600	-0.02823800
H	-2.84534300	5.29917000	0.71344000
C	-3.73376700	4.58240300	-1.10277000
C	-3.74598400	3.57159200	-2.04745500
H	-4.41617900	3.62769300	-2.89693500
C	-2.89213300	2.48970300	-1.91915600
H	-2.88703300	1.71381500	-2.67721700
C	-1.73775500	-2.60236800	-0.96680100
C	-0.96742500	-3.75194100	-1.13034000
H	0.11323000	-3.65800600	-1.18039600
C	-1.55975400	-4.99751600	-1.22344900
H	-0.94239300	-5.87875000	-1.35034400
C	-2.93663900	-5.11634900	-1.15140400
H	-3.40446500	-6.09094000	-1.22238800
C	-3.71490500	-3.98205700	-0.97907900
H	-4.79301400	-4.06941800	-0.91365200
H	-4.40009400	5.43034900	-1.20570900
H	-3.75257200	-1.86748000	-0.73077400
I	4.40196500	0.18391500	-0.66382000
I	1.74917000	-0.16949600	0.54880700

TS1_2 E+ZPE=-2890.810782

Fe	1.50181400	-0.72745300	0.95348900
O	1.64142100	-2.03846700	-1.79553800
O	0.03542000	0.09462800	3.37882800
O	4.12731600	-0.28982100	2.22007200
O	1.44574100	-3.64889500	1.28517300
C	1.69191500	-1.12985500	-1.05213400
C	2.16170200	0.17573300	-0.80378800
C	1.25701500	1.05093400	-0.11509000
C	-0.09215200	1.23861400	-0.58860200
C	0.58365100	-0.24022900	2.44163200
C	3.11081400	-0.44040300	1.73864600
C	1.46371800	-2.51845000	1.18572800
H	1.69620500	1.89683000	0.40609100
H	-0.28347800	0.95136000	-1.61771800
C	-0.75193600	2.91147400	1.13581900
C	3.57342600	0.50297800	-1.08682300

C	4.52018900	-0.49391300	-1.31935400
H	4.23104700	-1.53822400	-1.26346000
C	5.82971800	-0.16601900	-1.60573100
H	6.55211900	-0.95439700	-1.78027600
C	6.22211000	1.16219700	-1.66509600
C	5.28988100	2.15878100	-1.44261300
H	5.58305300	3.20058100	-1.49658300
C	3.97451500	1.83415300	-1.15882500
H	3.24811600	2.62555200	-1.01540800
C	-0.98279600	2.25273200	-0.07626900
C	-2.12379500	2.57830900	-0.81732900
H	-2.32467100	2.04814100	-1.74236200
C	-2.99959900	3.54457900	-0.36795500
H	-3.88423900	3.78024300	-0.94619600
C	-2.75121000	4.19730200	0.82801100
H	-3.44024600	4.95391900	1.18424800
C	-1.62742500	3.87863100	1.57877500
H	-1.44146800	4.38535500	2.51786500
H	7.25119100	1.41722300	-1.88742300
H	0.11410200	2.65776300	1.73630000
I	-4.11574200	-0.79393700	-0.82587400
I	-1.25117300	-0.98786400	0.06270300

FeIICO3I2a E+ZPE=-2890.870884

Fe	-0.44773700	0.71310400	1.10124000
O	2.36871500	-1.48866700	0.70289200
O	-0.10543200	3.62243700	1.02738400
O	1.05217000	0.52239900	3.63427500
O	-3.23892400	0.98941600	2.04813500
C	1.68830900	-1.03073500	-0.14118000
C	1.19483000	0.37906100	-0.22262200
C	0.04141400	0.81130800	-0.94045800
C	-1.19701000	0.19133400	-0.93845700
C	-0.23460700	2.49621000	1.03790100
C	0.46719000	0.57816200	2.66637600
C	-2.16546100	0.86195800	1.71350300
H	0.09506600	1.82203900	-1.33780600
H	-1.23933300	-0.88074500	-0.79012700
C	-2.55371300	2.11841800	-1.83342400
C	2.37996000	1.29953200	-0.26305100
C	3.19050600	1.51014200	0.84814400
H	2.97047500	1.00128900	1.77851200
C	4.28369700	2.35251000	0.77163100

H	4.89838400	2.51065900	1.64985500
C	4.59441300	2.99093100	-0.41805400
C	3.81202500	2.76870000	-1.53629400
H	4.05807100	3.24465900	-2.47820400
C	2.71831100	1.92333300	-1.46082800
H	2.13069300	1.72570500	-2.35182800
C	-2.43077300	0.77946200	-1.46357200
C	-3.55207700	-0.04200600	-1.56168900
H	-3.46744500	-1.08193500	-1.26109000
C	-4.75727500	0.45310900	-2.02431500
H	-5.61758700	-0.20188800	-2.09283200
C	-4.86295900	1.78175000	-2.39618600
H	-5.80569000	2.17350200	-2.75892100
C	-3.75660900	2.61203900	-2.29810300
H	-3.83419400	3.65419600	-2.58476500
H	5.45120900	3.65168400	-0.47429100
H	-1.70443000	2.78989900	-1.75820000
I	1.33903200	-2.22467600	-1.97005100
I	-0.96294400	-1.87203600	1.76797600

FeIICO3I2b E+ZPE=-2890.862708

Fe	-0.66061600	1.40753100	0.63011600
O	-1.71278100	0.41981200	-2.69449700
O	1.63686600	2.29934800	2.22345200
O	-2.12079200	0.69185600	3.06260200
O	-2.27363000	3.87265300	0.22259000
C	-1.46980900	0.11923000	-1.62286700
C	-1.38605400	-0.33364700	-0.34588000
C	-0.12086600	-0.52593700	0.36939900
C	1.15340100	-0.89572200	-0.30288000
C	0.74897200	1.97444700	1.59731000
C	-1.56916900	0.95968200	2.10741700
C	-1.64840400	2.93891600	0.37263400
H	-0.29236800	-1.12869700	1.25984400
H	1.31305700	-0.33512200	-1.22197900
C	2.37892900	-1.32814700	1.85672500
C	-2.68055000	-0.95651000	0.09318200
C	-3.87952100	-0.25737300	-0.00205300
H	-3.87977800	0.75919000	-0.38500300
C	-5.06316100	-0.83851200	0.41112400
H	-5.98979900	-0.28229100	0.33562300
C	-5.06026300	-2.12055700	0.93601000
C	-3.87063100	-2.82114000	1.03083300

H	-3.86266300	-3.82690700	1.43388400
C	-2.68514900	-2.24963700	0.60126200
H	-1.75924000	-2.81281800	0.64791100
C	2.35686200	-0.79387400	0.57178800
C	3.47951600	-0.11952100	0.10852300
H	3.46966300	0.30171500	-0.89130800
C	4.59314800	0.03545800	0.91633800
H	5.45741600	0.57143700	0.54232800
C	4.59954100	-0.48688400	2.19696000
H	5.46926300	-0.36415600	2.83146000
C	3.48949000	-1.17401800	2.66351000
H	3.49192200	-1.59543200	3.66193800
H	-5.98589800	-2.57240300	1.27167100
H	1.52477500	-1.88731100	2.22551600
I	0.99052300	-2.96856000	-1.08377900
I	0.77899900	2.43177000	-1.40610900

TS2 E+ZPE=-2967.234472

Fe	1.01402600	1.11526100	0.61777100
O	1.01580600	-2.56286200	0.96660900
O	2.95802200	2.71414000	-0.89315700
O	2.91933600	0.82939900	2.84786900
O	-0.47895000	3.54764600	1.41220800
C	0.98116600	-1.82037600	0.10846600
C	1.43709000	-0.60750500	-0.50603900
C	0.54732200	0.26007100	-1.24487700
C	-0.74007500	0.55832200	-0.85747600
C	2.20576100	2.08371700	-0.32769800
C	2.15456200	0.94118100	2.02012400
C	0.09402400	2.61117500	1.14425300
H	0.98369800	0.78298800	-2.09090700
H	-1.26541200	-0.13751100	-0.20516300
C	-1.07918200	2.61189400	-2.26163700
C	2.81650900	-0.87749200	-1.04613400
C	3.86551900	-1.16319200	-0.17763200
H	3.68471400	-1.19424200	0.89206600
C	5.13409800	-1.40867700	-0.66666800
H	5.94138600	-1.62561400	0.02227500
C	5.37312000	-1.37181000	-2.03084700
C	4.33292900	-1.10513100	-2.90262800
H	4.50813400	-1.09054300	-3.97160500
C	3.05847200	-0.87157000	-2.41524400
H	2.24690700	-0.69124100	-3.11234500

C	-1.57621400	1.59778300	-1.44106300
C	-2.93472600	1.58429600	-1.12781800
H	-3.31937000	0.78135900	-0.50487700
C	-3.77786600	2.55572500	-1.63560900
H	-4.83298300	2.53087900	-1.39194500
C	-3.27579600	3.55166000	-2.45427200
H	-3.93635100	4.31360200	-2.85101900
C	-1.92302200	3.57926200	-2.76550900
H	-1.52810300	4.36355400	-3.40023400
H	6.36898300	-1.55885000	-2.41369300
H	-0.02006800	2.65832400	-2.49819000
I	-2.94099300	-2.38886400	-0.46877300
I	-0.59020200	0.06982300	2.51375700
O	0.15574300	-2.81026000	-1.35709700
H	-0.80414800	-2.91560200	-1.02968400
H	0.03949500	-2.30520000	-2.17250600

FeIICO3IOHa E+ZPE=-2668.931701

Fe	-0.03345400	-0.18527700	0.72989900
O	2.31447000	-1.69659500	-1.65851200
O	0.76792700	2.11508600	2.35668800
O	1.84378500	-1.93936500	2.18630300
O	-2.53792600	-0.44518200	2.28032000
C	1.46503500	-0.85902400	-1.77389700
C	1.31807400	0.33011200	-0.88205200
C	0.15868200	1.15708600	-0.87743700
C	-1.15306900	0.70973400	-0.96273900
C	0.46041300	1.23787900	1.70732600
C	1.11333800	-1.28210100	1.62447900
C	-1.57268200	-0.38323100	1.69201800
H	0.30904100	2.18614000	-0.56160600
H	-1.34566100	-0.20548000	-1.50767100
C	-2.29376400	2.81150900	-0.15686200
C	2.62356100	0.97873300	-0.54328700
C	3.64600800	0.27333700	0.08890400
H	3.50657700	-0.77428700	0.32001300
C	4.84141100	0.89075100	0.40488400
H	5.61849600	0.32166500	0.90158000
C	5.04925500	2.22411900	0.09271800
C	4.05276700	2.93076600	-0.55405100
H	4.20689800	3.96871800	-0.82496400
C	2.85604600	2.31189300	-0.87300900
H	2.10288800	2.87609900	-1.41228700

C	-2.33821000	1.53635000	-0.71970800
C	-3.58328600	0.99670000	-1.03700000
H	-3.62785700	-0.00214800	-1.46041800
C	-4.74679700	1.70825800	-0.80977300
H	-5.70439300	1.26902600	-1.06293100
C	-4.68705700	2.97592100	-0.25824300
H	-5.59637100	3.53660000	-0.07798300
C	-3.45557600	3.52365300	0.06742100
H	-3.40151200	4.51451600	0.50290000
H	5.98664100	2.70565300	0.34441800
H	-1.34332700	3.25941700	0.11505000
I	-0.88297300	-2.62068500	-0.14074700
O	0.57703800	-0.86768100	-2.78062700
H	0.70868400	-1.70719700	-3.24539800

TS3 E+ZPE=-2668.882619

Fe	-0.96758500	-0.65726800	-0.85755200
O	1.22334600	0.30422100	1.95435500
O	-1.98593600	1.20956200	-2.85723500
O	-3.68506100	-1.59233400	-0.20471700
O	-0.02194400	-2.52716800	-2.93994100
C	0.03622100	0.56350700	1.77949200
C	-0.48094900	0.84820900	0.42387400
C	0.62169400	0.63116000	-0.51621900
C	1.79424500	0.02645200	0.05174300
C	-1.59162200	0.49457600	-2.06506600
C	-2.62563400	-1.25979300	-0.45158500
C	-0.39821400	-1.81885900	-2.13578800
H	0.80911900	1.41188000	-1.24918000
H	1.74538000	-1.02570600	0.32329600
C	3.39936100	1.85118100	-0.50596700
C	-1.31734500	2.08955500	0.37292000
C	-2.67903500	2.05429200	0.66988600
H	-3.15840300	1.09690800	0.85626500
C	-3.43960100	3.21098100	0.68197200
H	-4.49712900	3.15498100	0.91193200
C	-2.85790300	4.42832800	0.37377100
C	-1.50840600	4.47960600	0.06947700
H	-1.04222600	5.42828900	-0.17037500
C	-0.74548200	3.32512800	0.08287600
H	0.31734300	3.38169800	-0.12817900
C	3.13643000	0.53674100	-0.11428100
C	4.20736200	-0.31673200	0.15782500

H	3.99879000	-1.33212700	0.47720500
C	5.50821500	0.12354000	0.02327900
H	6.33345900	-0.54634300	0.23117800
C	5.75283200	1.42768800	-0.37554700
H	6.77345200	1.77738000	-0.47966700
C	4.69884500	2.29196400	-0.63682000
H	4.89784200	3.31280000	-0.93950500
H	-3.45446200	5.33252700	0.36586900
H	2.57619400	2.52921400	-0.69921200
I	-0.29831800	-2.69160200	0.80516700
O	-0.74910300	0.65727600	2.83003900
H	-1.64779300	0.88477000	2.54782900

Fe0CO3IOH E+ZPE=-2668.902548

Fe	1.25602800	-0.10025500	0.80540600
O	-1.13354100	-0.80388900	-1.53027100
O	1.20070000	1.97011900	2.86073600
O	3.99319400	0.67153100	-0.04381500
O	1.51236200	-2.16721700	2.87296400
C	-0.43857900	0.27412400	-1.57245500
C	-0.18250300	0.90500400	-0.32979500
C	-0.75544300	-0.01327100	0.65425300
C	-1.48531300	-1.08512800	-0.12569500
C	1.21176400	1.17938700	2.04217400
C	2.95182200	0.35216900	0.27994800
C	1.43944600	-1.37399600	2.06153600
H	-1.30224400	0.37374500	1.50916400
H	-1.09587200	-2.09180300	0.05254300
C	-3.70911100	0.06112900	-0.34793200
C	-0.11284400	2.38500100	-0.30479400
C	0.90234300	3.06861800	-0.97523000
H	1.71916700	2.50859700	-1.42698400
C	0.93116500	4.45239400	-1.00157500
H	1.73087300	4.96264100	-1.52544200
C	-0.03763500	5.17985000	-0.33199100
C	-1.03492800	4.51244500	0.35905600
H	-1.79181100	5.07402500	0.89423000
C	-1.07962300	3.12947100	0.36458700
H	-1.87366200	2.61399100	0.89529500
C	-2.97538600	-1.06405900	0.01186900
C	-3.63492500	-2.16068400	0.54402700
H	-3.06530600	-3.04257500	0.81829300
C	-5.00844800	-2.13492200	0.72343000

H	-5.51390300	-2.99725000	1.14170200
C	-5.73216500	-1.01406500	0.35988400
H	-6.80733800	-0.99444400	0.49343300
C	-5.08017400	0.08418700	-0.18056500
H	-5.64537500	0.96178300	-0.47164800
H	-0.00736500	6.26257300	-0.33696200
H	-3.20236300	0.92427800	-0.76960300
I	1.76009400	-2.20299700	-0.83223600
O	-0.13005100	0.68670000	-2.75946400
H	0.35538700	1.52604800	-2.69170000

TS4 E+ZPE=-2668.881808

Fe	1.18586700	0.03021000	0.93513500
O	-0.90693600	-1.21120000	-1.33641500
O	0.66490400	1.99480500	3.01368700
O	3.60524500	1.56248500	0.13855400
O	1.66665100	-2.00589700	3.00505600
C	-0.26129600	-0.06169700	-1.49334700
C	-0.34100700	0.76271300	-0.29127100
C	-0.86408900	-0.11871000	0.71008000
C	-1.42298400	-1.32829500	0.00603200
C	0.86421500	1.23819100	2.18855300
C	2.69606600	0.94982300	0.43486200
C	1.49878500	-1.21257600	2.20541500
H	-1.43750900	0.23336100	1.56067400
H	-1.03317000	-2.27634000	0.39183800
C	-3.65427500	-0.35781200	-0.61806700
C	-0.46507200	2.23388400	-0.38441500
C	0.32546300	2.97134100	-1.26536900
H	1.05059900	2.45662600	-1.88514800
C	0.18786700	4.34300700	-1.35283400
H	0.81077700	4.89876100	-2.04412500
C	-0.73318800	5.00957800	-0.55956300
C	-1.52387000	4.28766600	0.31565200
H	-2.25263700	4.79525500	0.93691500
C	-1.39656200	2.91133500	0.39707400
H	-2.03681700	2.35402700	1.07337000
C	-2.92297100	-1.36973900	-0.00640100
C	-3.59483000	-2.39925100	0.63317100
H	-3.02637600	-3.19400500	1.10589500
C	-4.97971100	-2.42133300	0.66660400
H	-5.49466400	-3.23218100	1.16821400
C	-5.70130900	-1.41408700	0.05237200

H	-6.78461200	-1.43169600	0.07227800
C	-5.03551100	-0.38299000	-0.59297400
H	-5.59756300	0.40610600	-1.07844900
H	-0.83363900	6.08633500	-0.62598600
H	-3.13856000	0.45362300	-1.12232000
I	2.22406600	-1.82523100	-0.87653900
O	0.42101300	0.09100900	-2.51031600
H	1.40480600	-0.89397900	-2.16809300

Fe0CO3O-HI E+ZPE= -2668.88878

Fe	1.24458500	0.11828400	0.86585500
O	-0.85138300	-1.19379000	-1.43546300
O	0.72123900	2.14898000	2.87755400
O	3.55011500	1.72226500	-0.09936700
O	1.78788300	-1.77295700	3.05921900
C	-0.30776300	0.03696000	-1.61405100
C	-0.34404000	0.77775100	-0.32890200
C	-0.79439500	-0.15404700	0.64462400
C	-1.28669300	-1.38085800	-0.08611600
C	0.91829900	1.36522400	2.07823500
C	2.67932300	1.08800400	0.26268400
C	1.59795600	-1.04300700	2.20398100
H	-1.36006400	0.13296200	1.52426000
H	-0.83021600	-2.31177200	0.27101100
C	-3.60303200	-0.60085500	-0.67586500
C	-0.58198300	2.23843200	-0.36308900
C	0.17290900	3.06941700	-1.18959700
H	0.94657900	2.63413400	-1.81145400
C	-0.06585000	4.42955400	-1.22646500
H	0.53081400	5.05961100	-1.87596400
C	-1.05776500	4.99007400	-0.43663900
C	-1.81718300	4.17444900	0.38245000
H	-2.60164900	4.59919600	0.99809200
C	-1.58637800	2.80956500	0.41301500
H	-2.20212600	2.17587300	1.04347100
C	-2.78225500	-1.50879600	-0.01759500
C	-3.35783300	-2.50534800	0.75483200
H	-2.71941500	-3.22093600	1.26390200
C	-4.73502300	-2.59754400	0.87295200
H	-5.17382700	-3.38344800	1.47649600
C	-5.54684000	-1.69336700	0.21211900
H	-6.62465200	-1.76673200	0.29713900
C	-4.97750700	-0.69599100	-0.56463400

H	-5.60981600	0.01152700	-1.08811700
H	-1.23876900	6.05809100	-0.46325900
H	-3.16399000	0.18086200	-1.28762100
I	2.22786300	-1.86371700	-0.79857500
O	0.14090300	0.35542400	-2.67958100
H	1.67743400	-1.34480500	-2.24620200

Fe0CO3OMe2 E+ZPE=-2525.440467

Fe	1.43711300	-0.77675800	0.59006300
O	-1.10854700	-0.94542000	-1.66493000
O	1.64293500	0.99906100	2.88186800
O	4.16200000	0.06422200	-0.24109600
O	1.65787300	-3.04291100	2.47559600
C	-0.18732400	0.05054900	-1.74350200
C	0.12806900	0.53668300	-0.37180800
C	-0.57709900	-0.31904800	0.51896400
C	-1.51467700	-1.16276100	-0.31708200
C	1.56637600	0.31659700	1.97579200
C	3.11797300	-0.28355900	0.04634400
C	1.57120400	-2.17781300	1.73865500
H	-0.97582300	0.01691900	1.47042100
H	-1.43722800	-2.23764200	-0.11872800
C	-3.44473400	0.40636300	-0.71260200
C	0.39523700	1.98390800	-0.20426700
C	1.39046100	2.61959600	-0.94465200
H	1.97797000	2.03841100	-1.64668600
C	1.62522200	3.97259800	-0.79603000
H	2.40298800	4.44877900	-1.38191400
C	0.87674600	4.71959300	0.10080000
C	-0.11690600	4.10135200	0.83769300
H	-0.71470700	4.67596100	1.53585300
C	-0.36090100	2.74723700	0.68003300
H	-1.15851500	2.27574700	1.24549800
C	-2.94241200	-0.73768900	-0.10672200
C	-3.75081400	-1.45426600	0.76307100
H	-3.36295100	-2.35322800	1.23336100
C	-5.04412500	-1.03691400	1.02823100
H	-5.66790800	-1.60803700	1.70599900
C	-5.54074200	0.10238200	0.41932200
H	-6.55464900	0.42834200	0.61940100
C	-4.73854400	0.82104000	-0.45254000
H	-5.12440200	1.71093400	-0.93603300
H	1.06716900	5.77954700	0.22117000

H	-2.82420000	0.96949600	-1.40161900
O	0.23581900	0.41898100	-2.79942900
H	1.52735000	-2.32951800	-3.10043700
H	0.25151300	-3.72719400	-1.80818800
C	2.10395100	-1.98373600	-2.23762200
O	1.33155200	-2.14318800	-1.05699400
H	2.31648600	-0.92652900	-2.37442600
C	0.86562900	-3.47143600	-0.93856400
H	0.25993100	-3.55103500	-0.03882700
H	3.03640300	-2.55444700	-2.15961200
H	1.70703200	-4.17083000	-0.86807200

Lactone E+ZPE=-766.874041

O	1.06997300	2.54270100	0.74734700
C	0.48099000	1.71211300	0.12776300
C	0.93845000	0.38425200	-0.37122100
C	-0.08871700	-0.15488300	-1.02696700
C	-1.27071900	0.74877200	-0.97663500
H	-0.12168900	-1.10756500	-1.53859200
H	-1.54163800	1.09236800	-1.98440500
C	-3.56869800	-0.23988900	-1.11521600
C	2.27417000	-0.16217600	-0.14632200
C	3.35201300	0.66593600	0.16137500
H	3.18827500	1.73039300	0.26614700
C	4.61600700	0.13174300	0.33902600
H	5.44464500	0.78909200	0.57512500
C	4.82511100	-1.23059600	0.22030700
C	3.75793100	-2.06469900	-0.07513600
H	3.91005000	-3.13450700	-0.15806600
C	2.49614400	-1.53535300	-0.25451000
H	1.66265600	-2.19737700	-0.46359800
C	-2.47805600	0.11619000	-0.33871000
C	-2.49251200	-0.15454300	1.02317000
H	-1.64292000	0.12894300	1.63554000
C	-3.58907400	-0.76799900	1.59821000
H	-3.59730600	-0.96820100	2.66318900
C	-4.67633300	-1.12718400	0.81615500
H	-5.53521600	-1.60828200	1.26906600
C	-4.66462000	-0.86391100	-0.54153800
H	-5.51466300	-1.13516800	-1.15644900
H	5.81590000	-1.64531600	0.36445600
H	-3.56393400	-0.01791700	-2.17798600
O	-0.81705800	1.87316000	-0.23896300

Fe0CO3OMe22 E+ZPE=-1913.447574

Fe	-0.02328100	0.38573100	-0.01971300
O	-2.39181200	1.98702400	-0.50372600
O	1.18161700	1.45625000	-2.46463000
O	0.35030900	1.81995200	2.51076000
C	-1.44659800	1.36742600	-0.31004900
C	0.68033400	0.95860100	-1.55566400
C	0.17704600	1.18108200	1.57023400
H	2.27160500	-1.37579300	-1.59907900
H	3.22907300	0.28071000	-0.05079500
C	1.82038600	-1.86880800	-0.72989000
C	2.80185800	-0.34682700	0.73981000
O	1.58743100	-0.93429400	0.30802500
H	0.86272900	-2.30081700	-1.00893900
H	2.59310200	0.26778900	1.61230800
H	2.49028700	-2.65729500	-0.37164000
H	3.51623200	-1.13245400	1.00626200
H	-2.48054500	-2.77858400	-0.97017300
H	-2.06474600	-2.89885900	1.33958500
C	-2.11691000	-1.74403600	-0.96398300
C	-1.66498500	-1.87751100	1.32522400
H	-1.64129000	-1.51425500	-1.91705500
O	-1.15239900	-1.56637100	0.04871000
H	-2.46080300	-1.17573100	1.60494800
H	-2.97070800	-1.07050900	-0.81915600
H	-0.84758800	-1.79324300	2.03906400

FeIICO3Oa E+ZPE=-2370.502839

Fe	-1.17441500	-1.42509100	-0.04517500
O	2.37345500	-1.77603800	-1.83116700
O	-0.64138300	-0.63996100	2.69387300
O	-1.55430400	-4.40786900	0.33184900
O	-4.04635600	-0.81168400	0.25844600
C	1.57369700	-1.29022300	-1.07106300
C	1.75820100	0.06414400	-0.47163800
C	0.67445700	0.83592800	-0.27727500
C	-0.69811800	0.47821600	-0.62130600
C	-0.88279800	-0.95677100	1.63195300
C	-1.45531600	-3.29933500	0.16053100
C	-2.94387100	-1.03802300	0.13411100
H	0.81492900	1.81951100	0.16668300

H	-0.77885200	0.05596300	-1.64285100
C	-1.78879600	2.26149000	0.76920200
C	3.11940400	0.51383500	-0.15582100
C	4.10841900	-0.40279400	0.20132200
H	3.88053100	-1.46147600	0.19772100
C	5.37467400	0.02222600	0.55506500
H	6.12484200	-0.70819300	0.83512300
C	5.68907300	1.37067600	0.54572000
C	4.72459000	2.29173900	0.17299300
H	4.96477300	3.34822500	0.14035800
C	3.45675300	1.86737400	-0.17558600
H	2.72238200	2.59744000	-0.49740900
C	-1.72462100	1.52195300	-0.41161500
C	-2.68379900	1.76901400	-1.39217000
H	-2.64332600	1.20907900	-2.32233100
C	-3.67598800	2.71324900	-1.20051800
H	-4.40802500	2.88959100	-1.98000400
C	-3.73105700	3.43357900	-0.01975900
H	-4.50834300	4.17228000	0.13419900
C	-2.78133600	3.20386100	0.96323100
H	-2.81608600	3.76254900	1.89135700
H	6.68528700	1.70168000	0.81482300
H	-1.05859800	2.08663200	1.55349600
O	0.47782000	-1.93716400	-0.72060700