Electronic Supplementary Material (ESI) for Dalton Transactions.

Supplementary data

Straightforward synthesis of iron cyclopentadienone N-heterocyclic carbene complexes

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SUMMARY

Imidazolium salts employed in this work

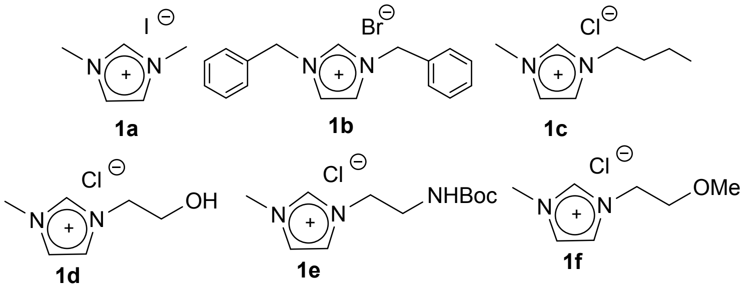


Chart S1. Imidazolium salts precursors of NHC ligands.

Crystal Structure of 5

The crystal structure of **5** closely resembles those previously reported for other Fe(CO)$_3$-cyclopentadienone complexes.[1] The X-ray crystal structure clearly illustrates the η^4 character of the bonding of the cyclopentadienone ligand. The average bonding distance from the iron to the tetracyclone ring carbons C(4)-C(7) is 2.11 Å and is markedly shorter than the distance to the ketonic carbon Fe(1)-C(3) [2.4074(19) Å].

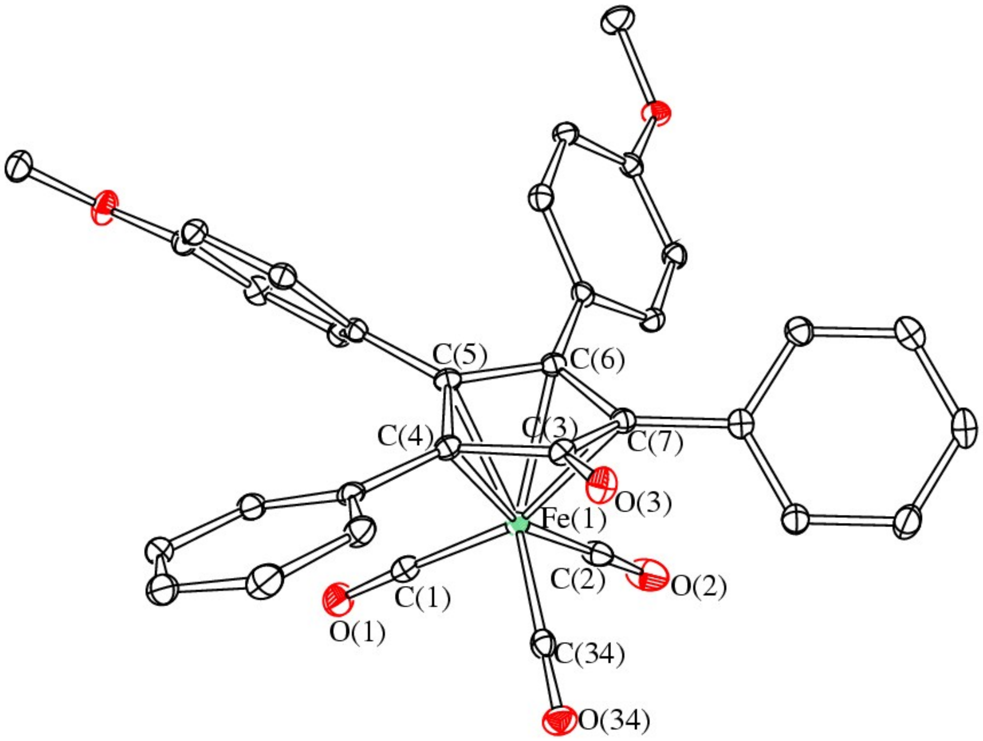


Figure S1. ORTEP drawing of **5**. Displacement ellipsoids are at the 30% probability level. H-atoms have been omitted for clarity. Selected bond lengths (Å): Fe(1)-C(1) 1.807(2), Fe(1)-C(2) 1.800(2), Fe(1)-C(34) 1.809(2), Fe(1)-C(3) 2.4074(19), Fe(1)-C(4) 2.1257(19), Fe(1)-C(5) 2.1065(19), Fe(1)-C(6) 2.1016(19), Fe(1)-C(7) 2.1027(19), C(3)-O(3) 1.230(2).

Crystal Structure of 7b and 7c

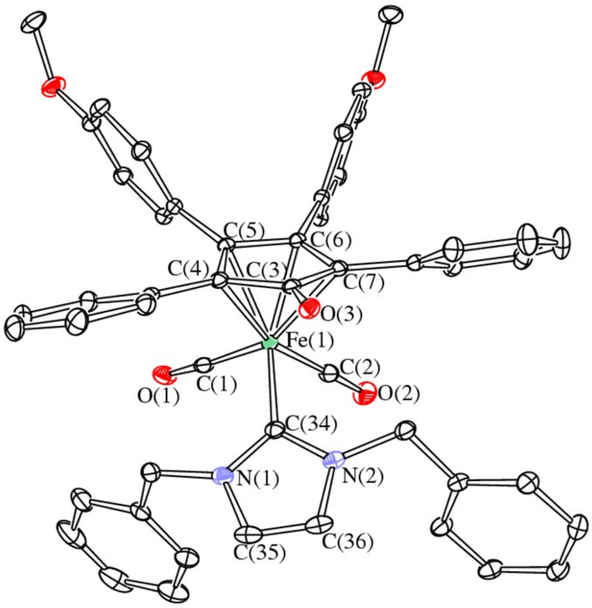


Figure S2. ORTEP drawing of **7b**. Displacement ellipsoids are at the 30% probability level. H-atoms have been omitted for clarity. Selected bond lengths (Å): Fe(1)-C(1) 1.7678(18), Fe(1)-C(2) 1.7671(17), Fe(1)-C(3) 2.3784(16), Fe(1)-C(4) 2.1442(15), Fe(1)-C(5) 2.0912(15), Fe(1)-C(6) 2.0766(15), Fe(1)-C(7) 2.1758(16), Fe(1)-C(34) 2.0138(17), C(3)-O(3) 1.2444(19).

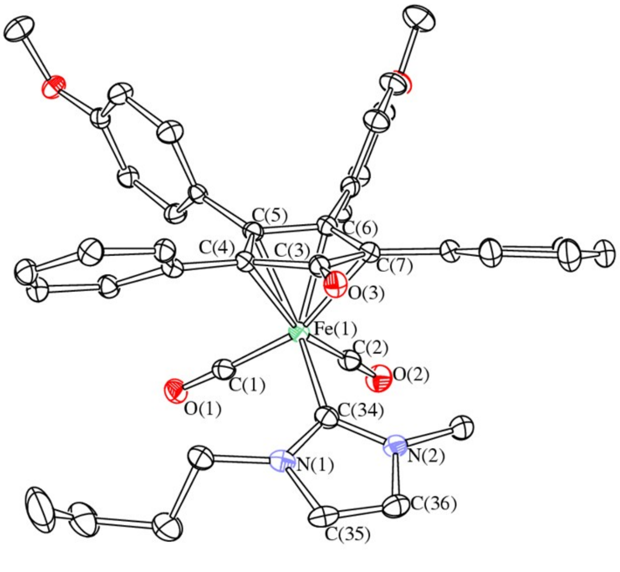


Figure S3. ORTEP drawing of **7c**. Displacement ellipsoids are at the 30% probability level. H-atoms have been omitted for clarity. Selected bond lengths (Å): Fe(1)-C(1) 1.764(3), Fe(1)-C(2) 1.766(4), Fe(1)-C(3) 2.392(3), Fe(1)-C(4) 2.161(3), Fe(1)-C(5) 2.079(3), Fe(1)-C(6) 2.082(3), Fe(1)-C(7) 2.168(3), Fe(1)-C(34) 2.000(3), C(3)-O(3) 1.240(4).

General: materials and procedures

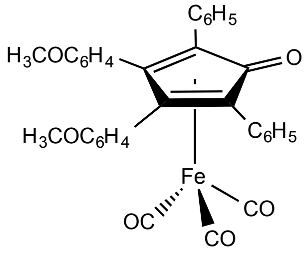
Solvents: dichloromethane (CH_2Cl_2), tetrahydrofuran (THF), diethyl ether (Et_2O), petroleum ether referring to a fraction of bp 60-80 °C, acetonitrile (CH_3CN) were dried and distilled prior to use. Acetone has been degassed and stored under inert atmosphere on molecular sieves. Other solvents such as ethylacetate (EtOAc), chloroform, ethanol (EtOH), methanol (MeOH), heptane, toluene, $CDCl_3$, D_2O, CD_3CN (Sigma Aldrich) have been employed without further purification. Reagents: $Fe_2(CO)_9$ (Strem), methyl iodide, chloridric acid, silver oxide, 1-methylimidazole, 1,3 diphenylacetone, benzyl bromide, 4,4'dimethoxybenzil (Alfa Aesar) have been employed as purchased.

1,3-dimethylimidazolium iodide (**1a**),[2] 1,3-dibenzylimidazolium bromide (**1b**),[3] 1-methyl-3-butyl-imidazolium chloride, 1-methyl-3-(2-hydroxyethyl)imidazolium chloride (**1d**),[4] 1-(2-BocNH-ethyl)-3-methylimidazolium iodide (**1e**)[5] 1-methyl-3-(2-methoxyethyl)imidazolium chloride (**1f**), 1,3-bis(2,6-diisopropylphenyl)imidazolium bromide,[6] 1,3-dimethylimidazol-2-ylidene silver iodide (**2a**),[7] 1,3-dibenzylimidazol-2-ylidene silver bromide (**2b**),[8] 1-methyl-3-(2-hydroxyethyl)imidazol-2-ylidene silver chloride (**2d**),[9] 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene silver bromide,[10] 3,4-Bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone,[11] have been prepared following procedures reported in the literature.

The prepared derivatives were characterized by spectroscopic methods. The NMR spectra were recorded using Varian Inova 300 (^{1}H, 300.1; ^{13}C, 75.5 MHz), Varian Mercury Plus VX 400 (^{1}H, 399.9; ^{13}C, 100.6 MHz), Varian Inova 600 (^{1}H, 599.7; ^{13}C, 150.8 MHz) spectrometers at 298 K; chemical shifts were referenced internally to residual solvent peaks. Full ^{1}H- and ^{13}C-NMR assignments were done, when necessary, by gHSQC and gHMBC NMR experiments using standard Varian pulse sequences. Infrared spectra were recorded at 298 K on a Perkin-Elmer Spectrum 2000 FT-IR spectrophotometer. ESI-MS spectra were recorded on Waters Micromass ZQ 4000 with samples dissolved in MeOH or CH_3CN. Elemental analyses were performed on a Thermo-Quest Flash 1112 Series EA instrument.

Synthesis and characterization of iron complexes

Triscarbonyl-(η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylciclopenta-2,4-dienone)iron (5)

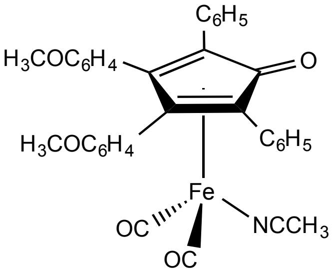


5

In a 75 mL Teflon tube equipped with magnetic stirrer, 3,4-Bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone 0.53 g (1.2 mmol) and $Fe_2(CO)_9$ 0.728 g (2 mmol) were dissolved in 40 mL of toluene. The container is closed with a cap, equipped with a temperature sensor, and placed into microwave. The reaction is heated to 140 °C for 70 min. Upon removal of the solvent, the crude was purified to afford the yellow triscarbonyl-η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)iron complex (**5**) by neutral alumina column chromatography using dichloromethane/ethyl acetate (100/0 to 0/100). Yield = 50%

Suitable crystals of **5** for X-Ray diffraction were obtained by slow diffusion (CH_2Cl_2/Hexane). **5** has been analyzed by IR, ^{1}H-NMR, ^{13}C-NMR, ESI-MS and X-Ray diffraction. ^{1}H-NMR (399.9 MHz, $CDCl_3$): δ (ppm) 7.55-6.69 (m, 18H, C_{aryl}), 3.76 (s, 6H, -OCH_3). ^{13}C-NMR (150.8 MHz, $CDCl_3$, g-HSQC, g-HMBC): δ (ppm) 208.58 (CO), 169.75 (C=O, Cp), 159.58 (-*C*OCH_3), 133.05-121.56 (C_{aryl}), 113.40 (CH_{aryl}), 103.44 ($C_{2,5}$, Cp), 82.75 ($C_{3,4}$, Cp), 55.12 (-OCH_3). IR (CH_2Cl_2, cm^{-1}): (ν_{CO}) 2067, 2013, 1997; ($\nu_{C=O}$) 1636; ($\nu_{C=C}$) 1609, 1518. ESI-MS (m/z) (+): 585 $[M+H]^+$; 607 $[M + Na]^+$; 623 $[M+K]^+$. Anal. Calcd (%) for $C_{34}H_{24}O_6Fe$: C, 69.88; H, 4.14. Found: C, 68.97; H, 3.93.

Dicarbonyl-(η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)(acetronitrile)iron (6)



6

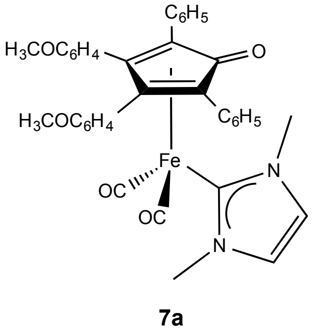
In a dried 15 mL Schlenk flask, triscarbonyl-(η^4-3,4-bis(4methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)iron (**5**) 0.145 g (0.249 mmol) and trimethylamine-N-oxide 0.028 g (0.374 mmol) were dissolved in 3 mL of anhydrous acetonitrile. Reaction mixture was stirred at room temperature and protected from light for 3 hours. A yellow precipitate appeared. The solid was filtered and washed with diethyl ether and hexane. Yield : 54%

5 has been analyzed by IR, ^{1}H-NMR, ^{13}C-NMR, ESI-MS. ^{1}H-NMR (399.9 MHz, C_7D_8): δ (ppm) 8.24-6.433 (m, 18H, CH_{aryl}); 3.10 (s, 6H, $-OCH_3$); 0.72 (s, 3H, $-NCCH_3$). ^{13}C-NMR (150.8 MHz, C_7D_8, g-HSQC, g-HMBC): δ (ppm) 214.21 (CO), 169.74 (C=O, Cp), 159.56 (-*C*OCH$_3$), 134.99-124.45 (C_{aryl}), 113.44 (CH_{aryl}), 101.41 ($C_{2,5}$, Cp), 81.31 ($C_{3,4}$, Cp), 54.32 ($-OCH_3$), 2.48 (CH_3, CH_3CN). IR (CH_2Cl_2, cm^{-1}): (ν_{CO}) 2008, 1954; ($\nu_{C=O}$) 1636; ($\nu_{C=C}$) 1608, 1515. ESI-MS (m/z) (+): 557 $[M-CH_3CN]^+$, 583 $[M-CH_3]^+$, 598 $[M+H]^+$. Anal. Calcd (%) for $C_{35}H_{27}NO_5Fe$: C, 70.36; H, 4.56. Found: C, 70.75; H, 4.35.

General procedure for the synthesis of dicarbonyl-η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)(NHC)iron complexes (7)

Imidazolium salts (**1**), silver oxide (1.2 eq.), tryscarbonyl-η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone) iron precursor (**5**) and trimethylammine-N-oxide (1.5 eq.) were reacted in CH_3CN under inert atmosphere and with protection from light. After stirring the reaction for the time and at the temperature required in order to reach complete conversion to silver complexes (**2**), the solvent was removed under vacuo, then the solid dissolved in toluene. The reaction mixture was stirred for 1 hour at 110 °C. Upon removal of the solvent, the crude was purified to afford the dicarbonyl-η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)(NHC)iron complexes (**7**) by neutral alumina column chromatography using dichloromethane/ethyl acetate (100/0 to 0/100). Formation of the iron complexes (**7**) was verified by IR, ^{1}H-NMR, ^{13}C-NMR, ESI-MS and X-Ray crystal structure, when suitable crystals were available.

Dicarbonyl-(η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)(1,3-dimethyl-ilidene)iron (7a)

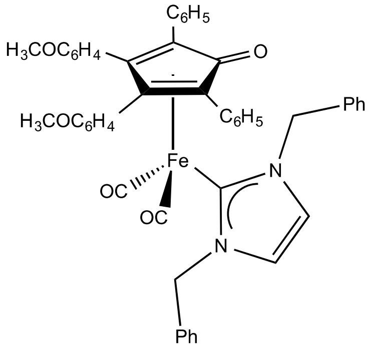


7a

Triscarbonyl-(η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)iron (**5**) 0.150 g, (0.256 mmol), trimethylammine-N-oxide 0.029 g (0.384 mmol), 1,3-dimethylimidazolium iodide (**1a**) 0.057 g (0.256 mmol) and silver oxide 0.071 g (0.307 mmol), room temperature, 3h. Yield: 60%.

Suitable crystals of **7a** for X-Ray diffraction were obtained by slow diffusion (THF/Hexane). **7a** has been analyzed by IR, ^{1}H-NMR, ^{13}C-NMR, ESI-MS and X-Ray diffraction. ^{1}H-NMR (399.9 MHz, C_7D_8): δ (ppm) 8.33-6.50 (m, 18H, CH_{aryl}), 5.88 (s, 2H, CH_{NHC}) 3.10 (s, 6H, -OCH_3), 2.93 (s. 6H, -NCH_{3NHC}). ^{13}C-NMR (150.8 MHz, C_7D_8, g-HSQC, g-HMBC): δ (ppm) 218.11 (CO), 182.41 ($C_{carbene}$), 166.57 (C=O, Cp), 159.30 (-$COCH_3$), 123.96 (CH_{NHC}), 136.44-125.66 (CH_{aryl}), 113.39 (CH_{aryl}), 100.73 ($C_{2,5}$, Cp), 79.76 ($C_{3,4}$, Cp), 54.28 (-OCH_3) 38.18 (-NCH_3). IR (CH_2Cl_2, cm^{-1}): (ν_{CO}) 1988, 1930; ($\nu_{C=O}$) 1585; ($\nu_{C=C}$) 1603, 1518. ESI-MS (m/z) (+): 653 $[M+H]^+$; 675 $[M + Na]^+$; 691 $[M+K]^+$. Anal. Calcd (%) for $C_{38}H_{32}N_2O_5Fe$: C, 69.95; H, 4.94. Found: C, 69.33; H, 4.63.

Synthesis of dicarbonyl-(η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)(1,3-dibenzylimidazole)iron (7b)

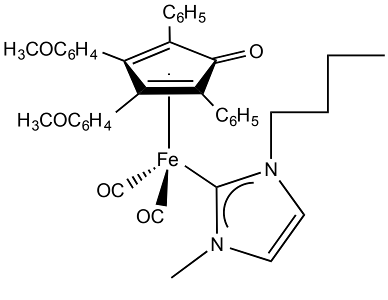


7b

Triscarbonyl-(η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)iron (**5**) 0.030 g (0.005 mmol), trimethylammine-N-oxide 0.006 g (0.080 mmol), 1,3-dibenzylimidazolium bromide (**1b**) 0.016 g (0.005 mmol), and silver oxide 0.014 g (0.016 mmol), 80 °C, 3h. Yield : 70 %.

Suitable crystals of **7b** for X-Ray diffraction were obtained by slow diffusion (Toluene/Hexane). **7b** has been analyzed by IR, ^{1}H-NMR, ^{13}C-NMR, ESI-MS and X-Ray diffraction. ^{1}H-NMR (399.9 MHz, C_7D_8) δ (ppm): 8.43-6.46 (m, 28H, CH_{aryl}), 6.06 (s, 2H, -CH_{NHC}), 5.15 (m, -CH_2), 4.50 (m, -CH_2) 3.06 (s, 6H, -OCH_3). ^{13}C-NMR (150.8 MHz, C_7D_8, g-HSQC, g-HMBC) δ (ppm): 217.43 (CO), 184.99 ($C_{carbene}$), 167.37 (C=O, Cp), 159.27 (-$COCH_3$), 137.34-123.15 (C_{aryl}), 127.78 (CH_{NHC}), 113.36 (CH_{aryl}), 101.31 ($C_{2,5}$, Cp), 80.08 ($C_{3,4}$, Cp), 54.57 (-CH_2), 54.22 (-OCH_3). IR (CH_2Cl_2, cm^{-1}): (ν_{CO}) 1989, 1933; ($\nu_{C=O}$) 1586; ($\nu_{C=C}$) 1603, 1518. ESI-MS (m/z) (+): 805 $[M+H]^+$; 827 $[M + Na]^+$; 843 $[M+K]^+$. Anal. Calcd (%) for $C_{50}H_{40}N_2O_5Fe$: C, 74.63; H, 5.01. Found: C, 74.19; H, 4.65.

Dicarbonyl-(η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)(1-methyl-3-butyl-imidazol-ylidene)iron (7c)

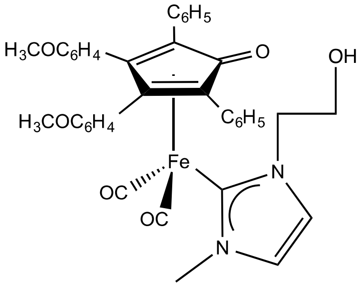


7c

Triscarbonyl-(η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)iron (**5**) 0.030 g (0.005 mmol), trimethylammine-N-oxide 0.006 g (0.075 mmol), 1-methyl-3-butyl-imidazolium bromide (**1c**) 0.011 g (0.005mmol) and silver oxide 0.014 g (0.006 mmol), 80 °C, 3 hours. Yield : 50 %.

Suitable crystals of **7c** for X-Ray diffraction were obtained by slow diffusion (Toluene/Hexane). **7c** has been analyzed by IR, ^{1}H-NMR, ^{13}C-NMR, ESI-MS and X-Ray diffraction. ^{1}H-NMR (399.9 C_7D_8) δ (ppm): 8.97-7.13 (m, 18H, CH_{aryl}), 6.85 (d, H, $-CH_{NHC}$), 6.69 (d, H, $-CH_{NHC}$), 4.19 (m, 2H, $CH_{2\ NHC}$), 3.73 (s, 6H, $-OCH_3$), 3.60 (s. 6H, $-CH_{3\ NHC}$), 2.73 (m, 2H, $CH_{2\ NHC}$), 1.53 (t, 2H, $CH_{2\ NHC}$), 1.36 (t, 3H, $CH_{3\ NHC}$). ^{13}C-NMR (150.8 MHz, C_7D_8, g-HSQC, g-HMBC) δ (ppm): 216.04 (CO), 182.41 ($C_{carbene}$), 166.83 (C=O, Cp), 159.29 ($-COCH_3$), 129.18-121.65 (C_{aryl}), 124.54 (CH_{NHC}), 113.40 (CH_{aryl}), 100.87 ($C_{2,5}$, Cp), 80.26 ($C_{3,4}$, Cp), 54.27 ($-OCH_3$), 50.39 ($-NCH_2-$), 38.22 ($-NCH_3$), 33.63 ($-CH_2-$), 25.83 ($-CH_2-$), 13.99($-CH_3$). IR (CH_2Cl_2, cm^{-1}): (ν_{CO}) 1987, 1931; ($\nu_{C=O}$) 1587; ($\nu_{C=C}$) 1607, 1518. ESI-MS (m/z) (+): 695 $[M+H]^+$; 717 $[M + Na]^+$; 733 $[M+K]^+$. Anal. Calcd (%) for $C_{41}H_{38}N_2O_5Fe$: C, 70.90; H, 5.51. Found: C, 69.19; H, 5.13.

Dicarbonyl-(η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)[1-(2-hydroxyethyl)-3-methylilidene]iron (7d)

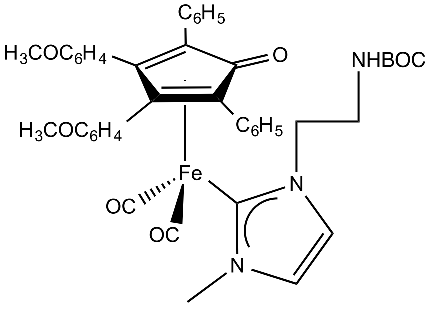


7d

Triscarbonyl-(η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)iron 0.060 g (0.103 mmol), trimethylammine-N-oxide 0.012 g (0.155 mmol), 13-(2-hydroxyethyl)-1-methylimidazole chloride (**1d**) 0.016 g (0.103 mmol) and silver oxide 0.029 g (0.124 mmol), room temperature, 3 h. Chromatography eluent: dichloromethane/ethyl acetate/MeOH (100/0/0 to 0/0/100). Yield : 18 %.

7d has been analyzed by IR, ^{1}H-NMR, ^{13}C-NMR, ESI-MS. ^{1}H-NMR (399.9 MHz, C_7D_8) δ (ppm): 8.10 (m, 18H, CH_{aryl}), 6.63 (s, 1H, CH_{NHC}), 6.07 (s, 1H, CH_{NHC}), (CH_2 not visible), 3.10 (s, 6H, -OCH_3), 2.90 (s, 3H, -NCH_3). ^{13}C-NMR (150.8 MHz, C_7D_8, g-HSQC, g-HMBC) δ (ppm): 218.60 (CO), 181.69 ($C_{carbene}$), 163.0 (C=O, Cp), 159.46 (-$COCH_3$) 134.80-125.37 (CH_{aryl}), 124.48 (CH_{NHC}), 121.99 (CH_{NHC}), 113.47 (CH_{aryl}), (not visible $C_{3,4}$, Cp), (not visible $C_{2,5}$, Cp), 59.24 (-CH_2), 53.30 (-OCH_3), 52.40 (-CH_2), 37.92 (-NCH_3). IR (CH_2Cl_2, cm^{-1}) (ν_{CO}) 1991, 1935; ($\nu_{C=O}$) 1576 (broad); ($\nu_{C=C}$) 1604, 1517. ESI-MS (m/z) (+): 683 $[M+H]^+$, 705 $[M+Na]^+$. Anal. Calcd (%) for $C_{39}H_{34}N_2O_6Fe$: C, 68.63; H, 5.02. Found: C, 68.35; H, 4.69.

Dicarbonyl-(η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)[1-(2-Boc-NH-ethyl)-3-methylilidene]iron (7e)

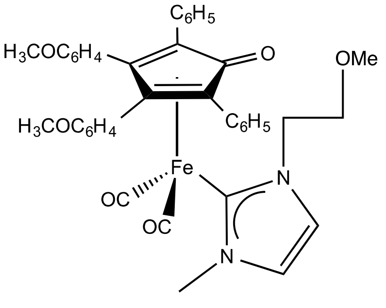


7e

Triscarbonyl-(η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)iron (**5**) 0.150 g (0.257 mmol), trimethylammine-N-oxide 0.029 g (0.386 mmol), 1-(2-BocNH-ethyl-)-3-methylimidazolium iodide (**1e**) 0.091 g (0.257 mmol) and silver oxide 0.071 g (0.308 mmol), room temperature,1 h. Yield : 53 %.

7e has been analyzed by IR, ^{1}H-NMR, ^{13}C-NMR, ESI-MS. ^{1}H-NMR (399.9 MHz, C_7D_8) δ (ppm): 8.10-6.48 (m, 18H, CH_{aryl}), 6.68 (s, H, CH_{NHC}), 5.98 (s, H, CH_{NHC}), 3.12 (s, 2H, -CH_2), 3.11 (s, 6H, OCH_3), 2.96 (s, 2H, CH_2), 2.79 (s, 3H, NCH_3), 1.45 (s. 9H, -$CH_{3\ BOC}$). ^{13}C-NMR (150.8 MHz, C_7D_8, g-HSQC, g-HMBC) δ (ppm): 217.63 (CO), 182.44 ($C_{carbene}$), 164.51 (C=O, Cp), 159.43(-$COCH_3$), 156.86 (C=O, BOC), 137.68-121.84 (C_{aryl}), 125.41 (CH_{NHC}), 121.84 (CH_{NHC}), 113.46 (CH_{Aryl}), 98.92 ($C_{2,5}$, Cp), 88.59 ($C_{3,4}$, Cp), 77.94 ($C_,$ BOC), 58.32 (CH_2), 54.38 (-OCH_3), 49.33 (NCH_2), 37.82(NCH_3), 28.66 (-$CH_{3,}$ BOC). IR (CH_2Cl_2, cm^{-1}): (ν_{CO}) 1991, 1935; ($\nu_{C=O}$) 1576 (broad); ($\nu_{C=C}$) 1604, 1517. ESI-MS (m/z) (+) = 782[M+H]$^+$, 804 [M+Na]$^+$. Anal. Calcd (%) for $C_{44}H_{43}N_3O_7Fe$: C, 67.61; H, 5.54. Found: C, 66.95; H, 5.06.

Dicarbonyl-(η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)[1-(2-methoxyethyl)-3-methylilidene]iron (7f)

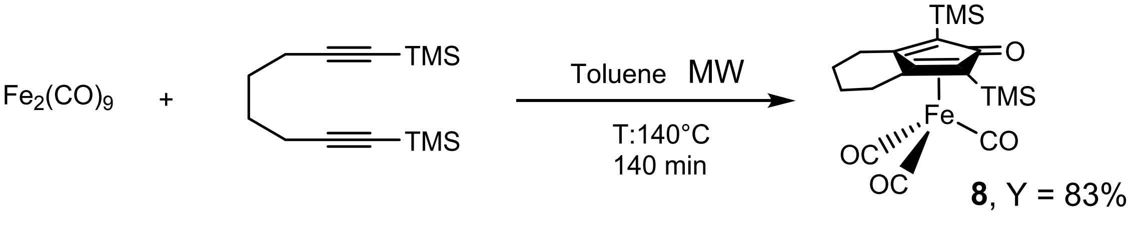


7f

Triscarbonyl-(η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)iron (**5**) 0.060 g (0.100 mmol), trimethylammine-N-oxide 0.012 g (0.150 mmol), 3-(2-methoxyethyl)-1-methylimidazole chloride (**1f**) 0.016 g (0.103 mmol) and silver oxide 0.028 g (0.120 mmol, room temperature,1 h. Yield : 55 %.

7f has been analyzed by IR, ^{1}H-NMR, ^{13}C-NMR, ESI-MS. ^{1}H-NMR (399.9 MHz, C_7D_8) δ (ppm): 8.29-6.49 (m, 18H, CH_{aryl}), 6.95 (s, 1H, CH_{NHC}), 6.00 (s, 1H, CH_{NHC}), 3.86 (br, 2H, CH_2), 3.09 (s, 6H, -OCH_3), 2.92 (s, 3H, -NCH_3) 2.88 (s, 3H, -OCH_3), 2.08 (br, 2H, CH_2). ^{13}C-NMR (150.8 MHz, C_7D_8, g-HSQC, g-HMBC) δ (ppm): 218.05 (CO), 182.42 ($C_{carbene}$), 166.72 (C=O, Cp), 159.34 (-$COCH_3$), 136.23-125.61 (CH_{aryl}), 124.24 (CH_{NHC}), 123.53 (CH_{NHC}), 113.41 (CH_{aryl}), 100.83 ($C_{3,4}$, Cp), 79.97 ($C_{2,5}$, Cp), 72.72 (-CH_2), 58.17 (-OCH_3), 54.30 (-OCH_3), 50.73 (CH_2), 38.14 (-NCH_3). IR (CH_2Cl_2, cm^{-1}): (ν_{CO}) 1987, 1931; ($\nu_{C=O}$) 1586 (broad); ($\nu_{C=C}$) 1518. ESI-MS (m/z) (+) = 697 [M+H]$^+$, 719 [M+Na]$^+$. Anal. Calcd (%) for $C_{40}H_{36}N_2O_6Fe$: C, 68.97; H, 5.21. Found: C, 68.80; H, 4.99.

Triscarbonyl-(2,4-bis(trimethylsilyl)bicyclo[3.3.0]nona-1,4-dien-3-one)iron (8)

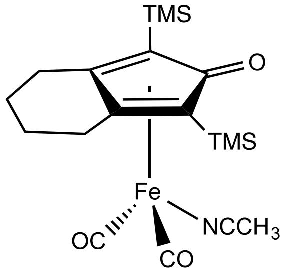


Scheme S1 Microwave assisted synthesis of triscarbonyl-(η^4-2,4-bis(trimethylsilil)biciclo[3.3.0]nona 1,4-dien-3-one)4-methoxyphenyl)iron (**8**).

In a 75 mL Teflon tube equipped with magnetic stirrer, 1,7-octadiyne 0.027 g (0.11 mmol) and $Fe_2(CO)_9$ 0.039 g (0.11 mmol) were dissolved in 40 mL of toluene. The container is closed with a cap, equipped with a temperature sensor, and placed into microwave reactor. The reaction is heated to 140 °C for 140 min. Upon removal of the solvent, the crude was purified to afford the yellow triscarbonyl-(2,4-bis(trimethylsilyl)bicyclo[3.3.0]nona-1,4-dien-3-one)iron (**8**) by neutral alumina column chromatography using dichloromethane/ethyl acetate (100/0 to 0/100). Yield = 83%

8 has been analyzed by IR, ^{1}H-NMR. ^{1}H-NMR (399.9 MHz, $CDCl_3$): δ (ppm) 2.56 (m, 4H, CH_2), 1.82 (m, 4H, CH_2), 0.27 (s, 18H, CH_3, TMS). IR (CH_2Cl_2, cm^{-1}): (ν_{CO}) 2063, 2004, 1987.

Dicarbonyl-(2,4-bis(trimethylsilyl)bicyclo[3.3.0]nona-1,4-dien-3-one)[acetonitrile]iron (9)



9

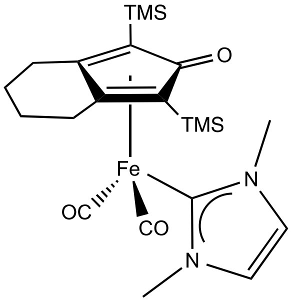
In a dried 15 mL Schlenk flask, triscarbonyl-(2,4-bis(trimethylsilyl)bicyclo[3.3.0]nona-1,4-dien-3-one)iron (**8**) 0.039 g (0.094 mmol) and trimethylamine-N-oxide 0.011 g (0.14 mmol) were dissolved in 3 mL of anhydrous acetonitrile. Reaction mixture was stirred at room temperature and protected from light for 3 hours. A yellow precipitate appeared. The solid was filtered and washed with diethyl ether and hexane. Yield : 78%.

9 has been analyzed by IR, ^{1}H-NMR. ^{1}H-NMR (399.9 MHz, $CDCl_3$): δ (ppm) 2.28 (m, 4H, CH_2), 2.23 (s, 3H, CH_3), 1.56 (m, 4H, CH_2), 0.24 (s, 18H, CH_3, TMS). IR (CH_2Cl_2, cm^{-1}): (ν_{CO}) 1999, 1938.

General procedure for the synthesis of dicarbonyl-(2,4-bis(trimethylsilyl)bicyclo[3.3.0]nona-1,4-dien-3-one)(NHC)iron complexes (10)

Same general procedure for complex **7**. Precursor is triscarbonyl-(2,4-bis(trimethylsilyl)bicyclo[3.3.0]nona-1,4-dien-3-one)iron (**8**).

Dicarbonyl-(2,4-bis(trimethylsilyl)bicyclo[3.3.0]nona-1,4-dien-3-one)[1,3-dimethyl-ilidene]iron (10a)

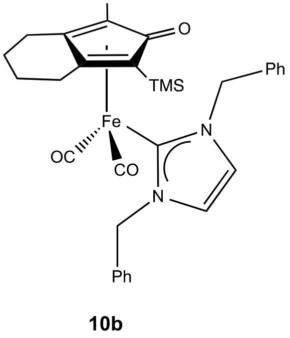


10a

Triscarbonyl-(2,4-bis(trimethylsilyl)bicyclo[3.3.0]nona-1,4-dien-3-one)iron (**8)** 0.035 g (0.084 mmol), trimethylammine-N-oxide 0.009 g (0.12 mmol), 1,3-dimethylimidazolium iodide 0.019 g (0.084 mmol) and silver oxide 0.035 g (0.084 mmol), room temperature, 3 h. Yield : 86 %

Suitable crystals of **10a** for X-Ray diffraction were obtained by slow diffusion (Toluene/Hexane). **10a** has been analyzed by IR, ^{1}H-NMR, ^{13}C-NMR, ESI-MS and X-Ray diffraction. ^{1}H-NMR (399.9 CDCl$_3$) δ (ppm): 6.98 (s, 2H, CH$_{NHC}$), 3.91 (s, 6H, CH$_3$), 2.45 (t, 4H, CH$_2$), 1.85-1.87 (m, 4H, CH$_2$), 0.174 (s, 18H, CH$_{3,}$ TMS). ^{13}C-NMR (150.8 MHz, C$_7$D$_8$, g-HSQC, g-HMBC) δ (ppm): 217.00 (CO), 182.00 (C$_{carbene}$), (C=O, Cp) (not visible), 123.79 (CH$_{NHC}$), 103.72 (C$_{3,4q}$), 65.00 (C$_{2,5q}$), 39.94 (CH$_3$), 24.52 (CH$_2$), 22.55 (CH$_2$), 0.23 (CH$_3$, TMS). IR (CH$_2$Cl$_2$, cm^{-1}): (ν_{CO}) 1983, 1922. ESI-MS (m/z): 487 [M+H]$^+$, 509 [M+Na]$^+$, 525 [M+K]$^+$. Anal. Calcd (%) for C$_{22}$H$_{34}$N$_2$O$_3$Si$_2$Fe: C, 54.31; H, 7.04. Found: C, 54.82; H, 6.72.

Dicarbonyl-(2,4-bis(trimethylsilyl)bicyclo[3.3.0]nona-1,4-dien-3-one)[1,3-dibenzylimidazol-lilidene]iron (10b)

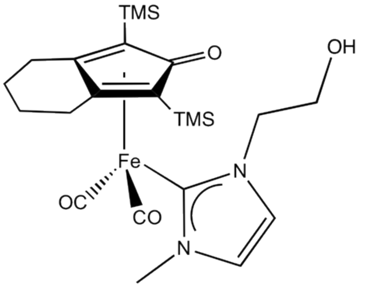


10b

Triscarbonyl-(2,4-bis(trimethylsilyl)bicyclo[3.3.0]nona-1,4-dien-3-one)iron (**8**) 0.077 g (0.018 mmol), trimethylammine-N-oxide 0.021 g (0.28 mmol), 1,3-dibenzylimidazolium bromide 0.060 g (0.018 mmol) and silver oxide 0.051 g (0.022 mmol), 80 °C 3 h. Yield : 61%.

10b has been analyzed by IR, ^{1}H-NMR, ^{13}C-NMR, ESI-MS. ^{1}H-NMR (399.9 $CDCl_3$) δ (ppm): 7.42-7.18 (10H, CH_{aryl}), 6.82 (s, 2H, CH_{NHC}), 5.6 (br, 4H, NCH_2), 2.49 (m, 4H, CH_2), 1.78-1.72 (m, 4H, CH_2), 0.19 (s, 18H, CH_3, TMS). ^{13}C-NMR (150.8 MHz, C_7D_8, g-HSQC, g-HMBC) δ (ppm): 216.14 (CO), 186.32 ($C_{carbene}$), 177.02 (C=O, Cp), 136.30 (C_{aryl}), 128.75 (CH_{aryl}), 127.88 (CH_{aryl}), 126.81(CH_{aryl}), 123.30 (CH_{aryl}), 103.91 ($C_{3,4q}$), 70.12 ($C_{2,5q}$), 55.15 (-NCH_2-), 23.94 (CH_2), 22.04 (CH_2), 0.98 (CH_3, TMS). IR (CH_2Cl_2, cm^{-1}): (ν_{CO}) 1986, 1924. ESI-MS (m/z): 639 $[M+H]^+$, 661 $[M+Na]^+$, 677 $[M+K]^+$. Anal. Calcd (%) for $C_{34}H_{42}N_2O_3Si_2Fe$: C, 63.93; H, 6.63. Found: C, 64.22; H, 6.21.

Dicarbonyl-(2,4-bis(trimethylsilyl)bicyclo[3.3.0]nona-1,4-dien-3-one)[1-(2-hydroxyethyl))-3-methylilidene]iron (10d)

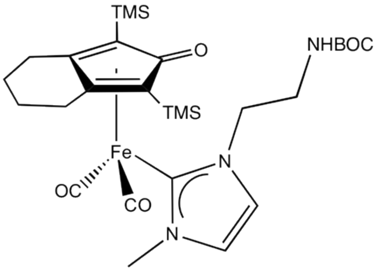


10d

Triscarbonyl-(2,4-bis(trimethylsilyl)bicyclo[3.3.0]nona-1,4-dien-3-one)iron (**8**) 0.048 g (0.103 mmol), trimethylammine-N-oxide 0.012 g (0.155 mmol), 3-(2-hydroxyethyl)-1-methylimidazole chloride 0.020 g (0.103 mmol) and silver oxide 0.037 g (0.160 mmol), room temperature, 3 h. Chromatography eluent: dichloromethane/ethyl acetate/MeOH (100/0/0 to 0/0/100). Yield = 13 %

10c has been analyzed by IR, ^{1}H-NMR, ^{13}C-NMR, ESI-MS. ^{1}H-NMR (399.9 $CDCl_3$) δ (ppm): 7.27 (d, 1H, -CH_{NHC}), 7.04 (d, 1H, -CH_{NHC}), 4.33 (t, CH_2, NHC), 4.00 (t. 2H, -CH_2, NHC), 3.83 (s, 3H, -NCH_3), 2.52-2.45 (m, 4H, CH_2), 1.85-1.75 (m, 4H, CH_2), 0.18 (s, 18H, CH_3, TMS). ^{13}C-NMR (150.8 MHz, C_7D_8, g-HSQC, g-HMBC) δ (ppm): 217.68 (CO), 183.60 ($C_{carbene}$), 171.22 (C=O, Cp), 126.63 ($C_{3,4}$, Cp), 124.28 (CH_{NHC}), 120.91 (CH_{NHC}), 75.27 ($C_{2,5}$, Cp), 59.06 (-CH_2-), 52.66 (-CH_2-), 40.24 (-NCH_3), 25.01 (-CH_2-, Cp), 22.43 (-CH_2-, Cp), 0.21 (CH_3, TMS). IR (CH_2Cl_2, cm^{-1}): (ν_{CO}) 1986, 1926. ESI-MS (m/z): 517 $[M+H]^+$, 539 $[M+Na]^+$. Anal. Calcd (%) for $C_{23}H_{36}N_2O_4Si_2Fe$: C, 53.48; H, 7.02. Found: C, 53.54; H, 6.67.

Dicarbonyl-(2,4-bis(trimethylsilyl)bicyclo[3.3.0]nona-1,4-dien-3-one)[1-(2-BocNH-ethyl)-3-methylilidene]iron (10e)



10e

Triscarbonyl-(η^4-3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone)iron 0.082 g (0.197 mmol), trimethylammine-N-oxide 0.022 g (0.296 mmol), 1-(2-BocNH-ethyl-)-3-methylimidazolium iodide 0.070 g (0.197 mmol) and silver oxide 0.055 g (0.236 mmol), room temperature, 1 h. Yield = 52 %.

10e has been analyzed by IR, ^{1}H-NMR, ^{13}C-NMR, ESI-MS. ^{1}H-NMR (399.9 $CDCl_3$) δ (ppm): 7.19 (s, 1H, $-CH_{NHC}$), 6.98 (s, 1H, $-CH_{NHC}$), 6.41 (br, 1H, NH), 4.33 (t, CH_2, NHC), 3.85 (s, 6H, $-NCH_3$), 3.65 (t. 2H, $-CH_2$, NHC), 2.47 (t, 4H, CH_2), 1.83-1.77 (m, 4H, CH_2), 1.35 (s, 9H, CH_3, BOC), 0.17 (s, 18H, CH_3, TMS). ^{13}C-NMR (150.8 MHz, C_7D_8, g-HSQC, g-HMBC) δ (ppm): 217.61 (CO), 184.56 ($C_{carbene}$), 174.08 (C=O, Cp), 156.66 (C=O, BOC), 123.91 (CH_{NHC}), 121.17 (CH_{NHC}), 103.26 ($C_{3,4}$, Cp), 78.80 (Cq, BOC), 73.31 ($C_{2,5}$, Cp), 49.55 ($-NCH_2-$), 40.16 ($-NCH_3$), 38.73 ($-NCH_2-$), 28.32 (CH_3, BOC), 24.87 ($-CH_2$), 22.47 ($-CH_2$), 0.29 ($CH_{3,}$ TMS) IR (CH_2Cl_2, cm^{-1}): (ν_{CO}) 1982, 1922. ESI-MS (m/z): 638 $[M+Na]^+$, 654 $[M+K]^+$. Anal. Calcd (%) for $C_{28}H_{46}N_3O_5Si_2Fe$: C, 54.53; H, 7.52. Found: C, 54.53; H, 7.10.

X-ray Crystallography.

Crystal data and collection details for **$5{\cdot}0.5C_6H_{14}$**, **$7a{\cdot}thf{\cdot}C_6H_{14}$**, **7b**, **7c** and **10a** are reported in Table X. The diffraction experiments were carried out on a Bruker APEX II diffractometer equipped with a CCD detector using Mo–Kα radiation. Data were corrected for Lorentz polarization and absorption effects (empirical absorption correction SADABS).[12] Structures were solved by direct methods and refined by full-matrix least-squares based on all data using F^2.[13] All hydrogen atoms were fixed at calculated positions and refined by a riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters.

The C_6H_{14} molecule of **$5{\cdot}0.5C_6H_{14}$** is located on an inversion center.

The C_6H_{14} and THF molecules of **$7a{\cdot}thf{\cdot}C_6H_{14}$** are disordered and, therefore, they have been split into two positions each and refined isotropically using one occupancy parameter per disordered group. The disordered molecules have been restrained to have similar geometries (SAME line in SHELXTL; s.u. 0.02) and similar *U* parameters (SIMU line in SHELXTL; s.u. 0.01). Restraints to bond distances were applied as follow (s.u. 0.02): 1.53 Å for C–C and 1.43 Å for C–O in THF and C_6H_{14}.

Table S1

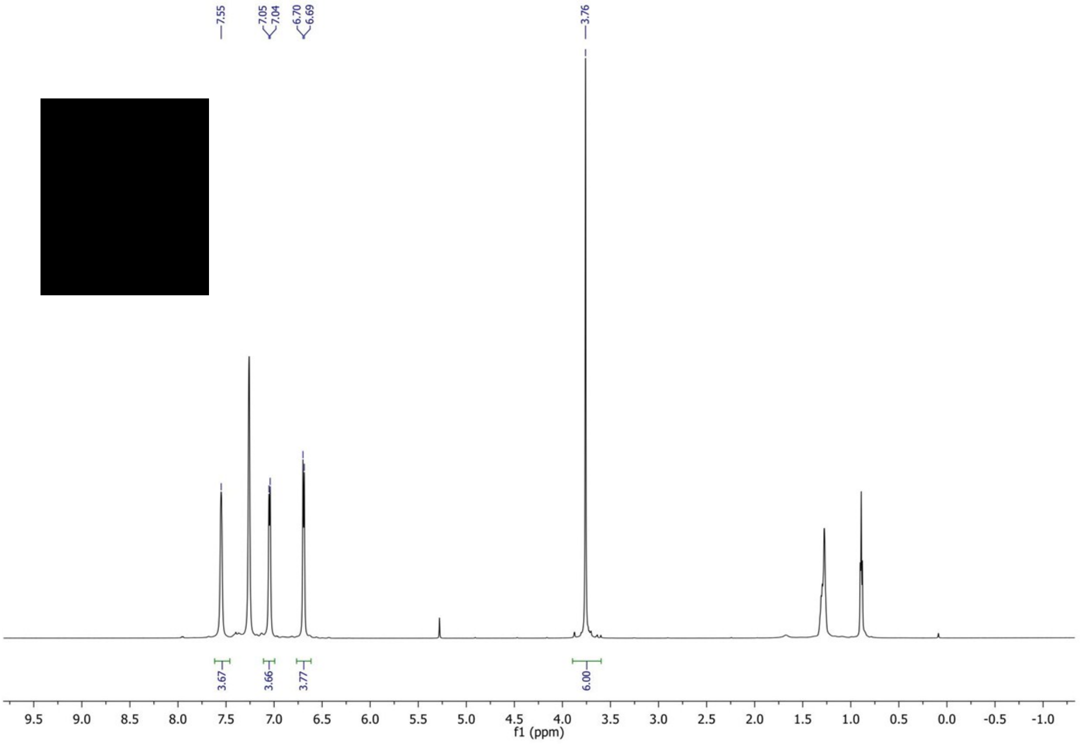
Crystal data and experimental details for ***$5{\cdot}0.5C_6H_{14}$****,* ***$7a{\cdot}thf{\cdot}C_6H_{14}$****,* ***7b****,* ***7c*** *and* ***10a****.*

	$5{\cdot}0.5C_6H_{14}$	**$7a{\cdot}thf{\cdot}C_6H_{14}$**
Formula	$C_{37}H_{31}FeO_6$	$C_{48}H_{54}FeN_2O_6$
Fw	627.47	810.78
T, K	100(2)	100(2)
λ, Å	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a, Å	14.3553(2)	9.4831(7)
b, Å	11.8026(2)	23.5286(19)
c, Å	17.6616(3)	19.2990(16)
α, °	90	90
β, °	90.0710(10)	103.518(4)
γ, °	90	90
Cell Volume, Å^3	2992.40(8)	4186.8(6)
Z	4	4

D_c, g cm^{-3}	1.393	1.286
μ, mm^{-1}	0.552	0.412
F(000)	1308	1720
Crystal size, mm	0.22×0.18×0.14	0.25×0.21×0.16
θ limits, °	1.83–25.03	1.73–26.00
Reflections collected	42504	64046
Independent reflections	5268 [R_{int}= 0.0285]	8231 [R_{int}= 0.0740]
Data / restraints /parameters	5268 / 0 / 397	8231/ 121 / 505
Goodness on fit on F^2	1.024	1.023
R_1 (I> 2σ(I))	0.0335	0.0641
wR_2 (all data)	0.0881	0.1870
Largest diff. peak and hole, e Å^{-3}	1.714 / –0.278	1.401 / –0.827

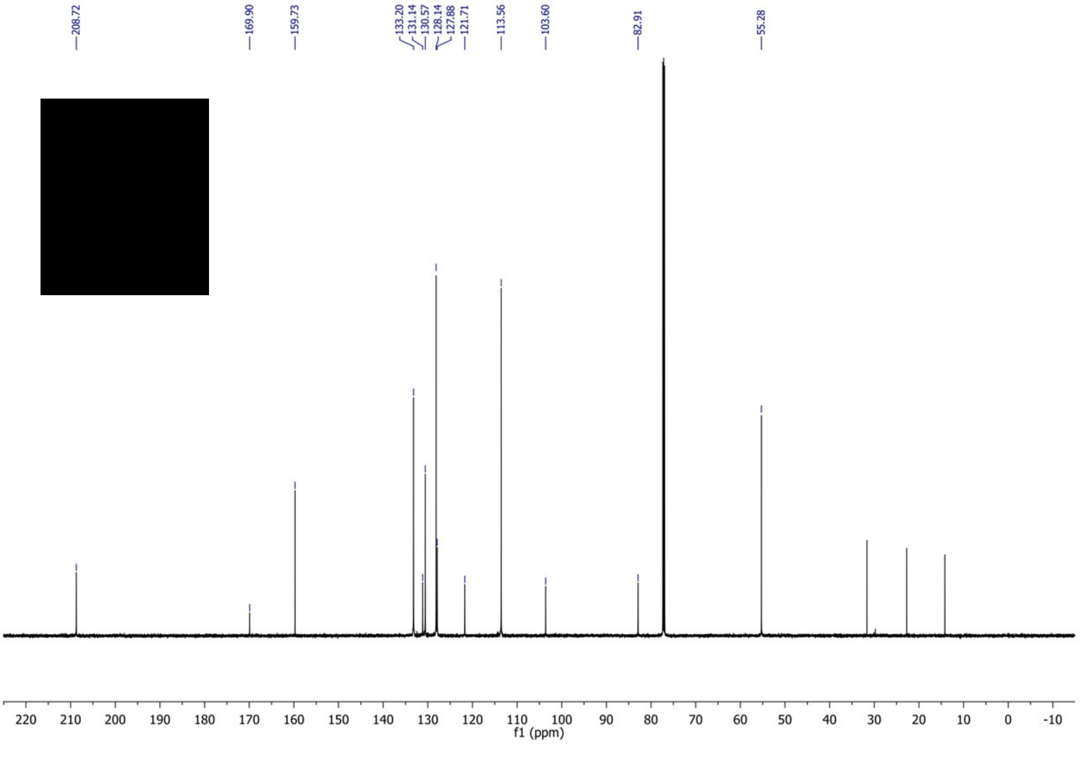
	7b	**7c**	**10a**
Formula	$C_{50}H_{40}FeN_2O_5$	$C_{41}H_{38}FeN_2O_5$	$C_{22}H_{34}FeN_2O_3Si_2$
Fw	804.69	694.58	486.54
T, K	100(2)	100(2)	100(2)
λ, Å	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$
a, Å	14.8500(8)	12.7360(4)	8.3374(2)
b, Å	15.3813(8)	17.9148(5)	10.1477(3)
c, Å	17.4682(10)	15.2500(4)	15.9325(4)
α, °	90	90	75.869(2)
β, °	101.570(3)	95.190(2)	77.444(2)
γ, °	90	90	76.216(2)
Cell Volume, Å^3	3908.9(4)	3465.22(17)	1251.27(6)
Z	4	4	2
D_c, g cm^{-3}	1.367	1.331	1.291
μ, mm^{-1}	0.439	0.483	0.723
F(000)	1680	1896	516
Crystal size, mm	0.19×0.15×0.12	0.16×0.13×0.10	0.18×0.16×0.11

θ limits, °	1.65–27.00	1.76–26.00	1.34–27.00
Reflections collected	64623	39892	21430
Independent reflections	8525 [R_{int}= 0.0444]	6797 [R_{int}= 0.0844]	5441 [R_{int}= 0.0497]
Data / restraints /parameters	8525 / 0 / 523	6797 / 18 / 442	5441 / 0 / 279
Goodness on fit on F^2	1.015	1.040	1.016
R_1 ($I > 2\sigma(I)$)	0.0336	0.0472	0.0399
wR_2 (all data)	0.0866	0.1309	0.0987
Largest diff. peak and hole, e Å^{-3}	0.370 / –0.428	0.584 / –0.488	0.281 / –0.232



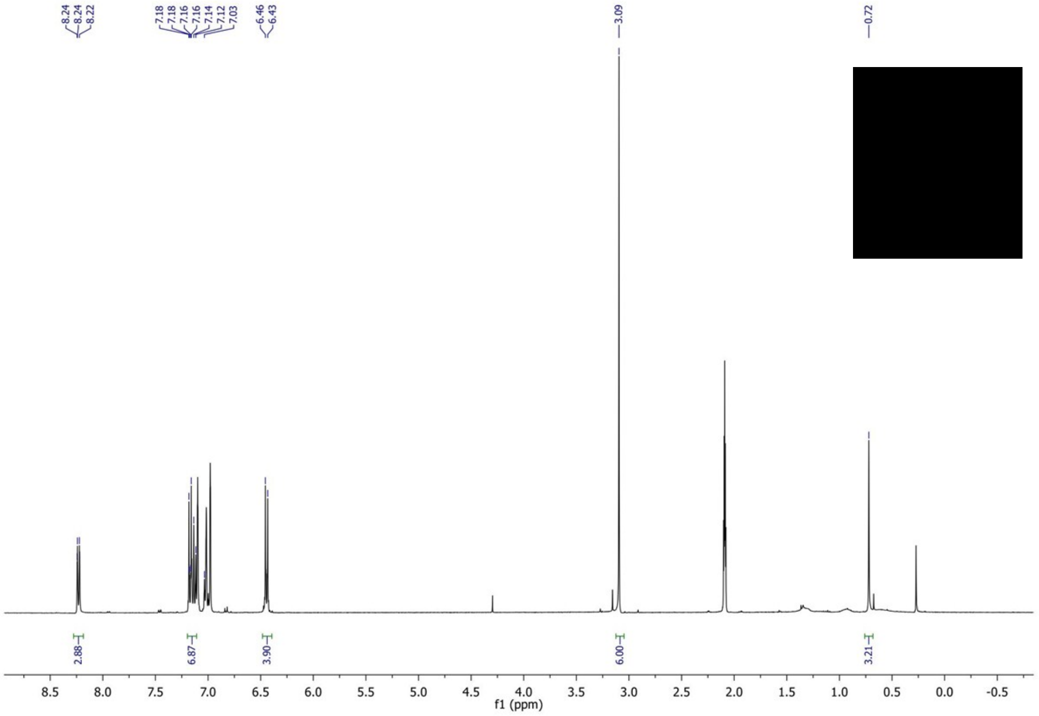
[redacted]

Figure S4. ^{1}H-NMR spectrum of **5** in CDCl$_3$.



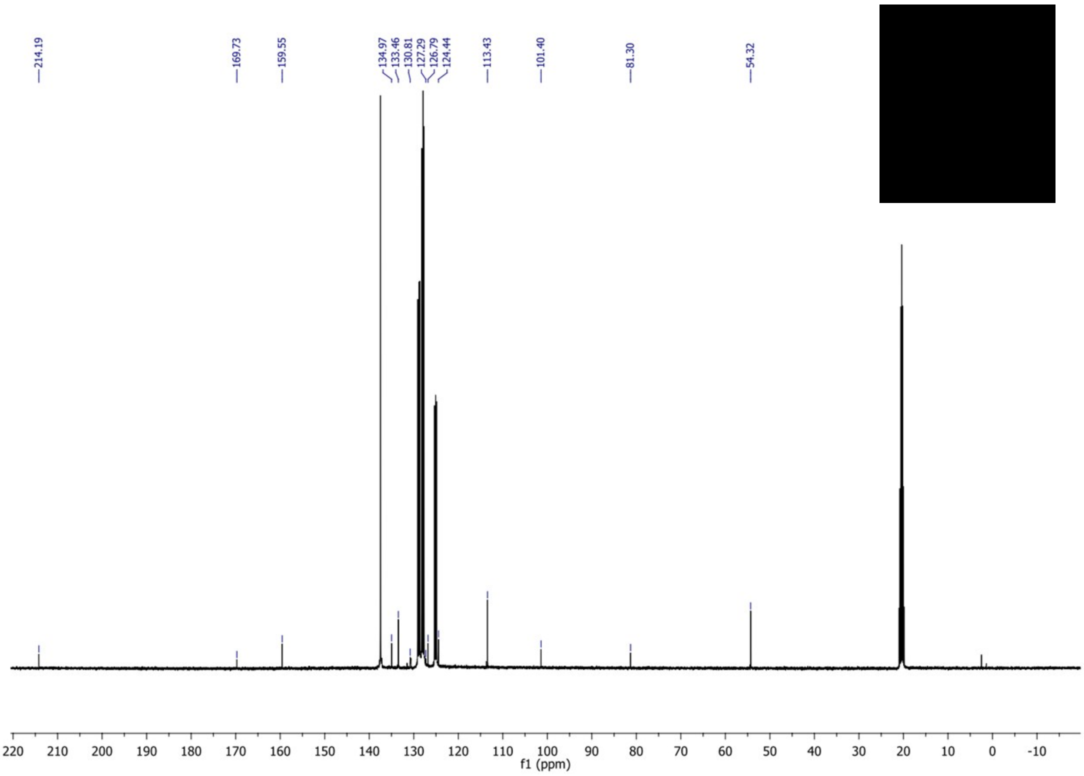
[redacted]

Figure S5. ^{13}C-NMR spectrum of **5** in CDCl$_3$.



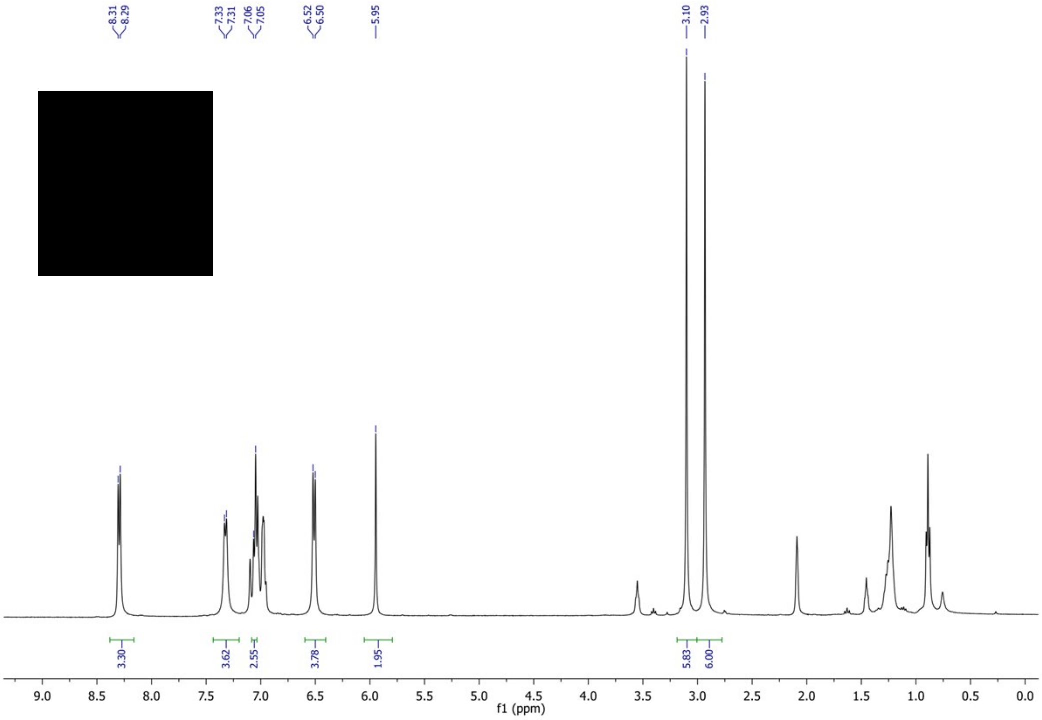
[redacted]

Figure S6. ^{1}H-NMR spectrum of **6** in C_7D_8.



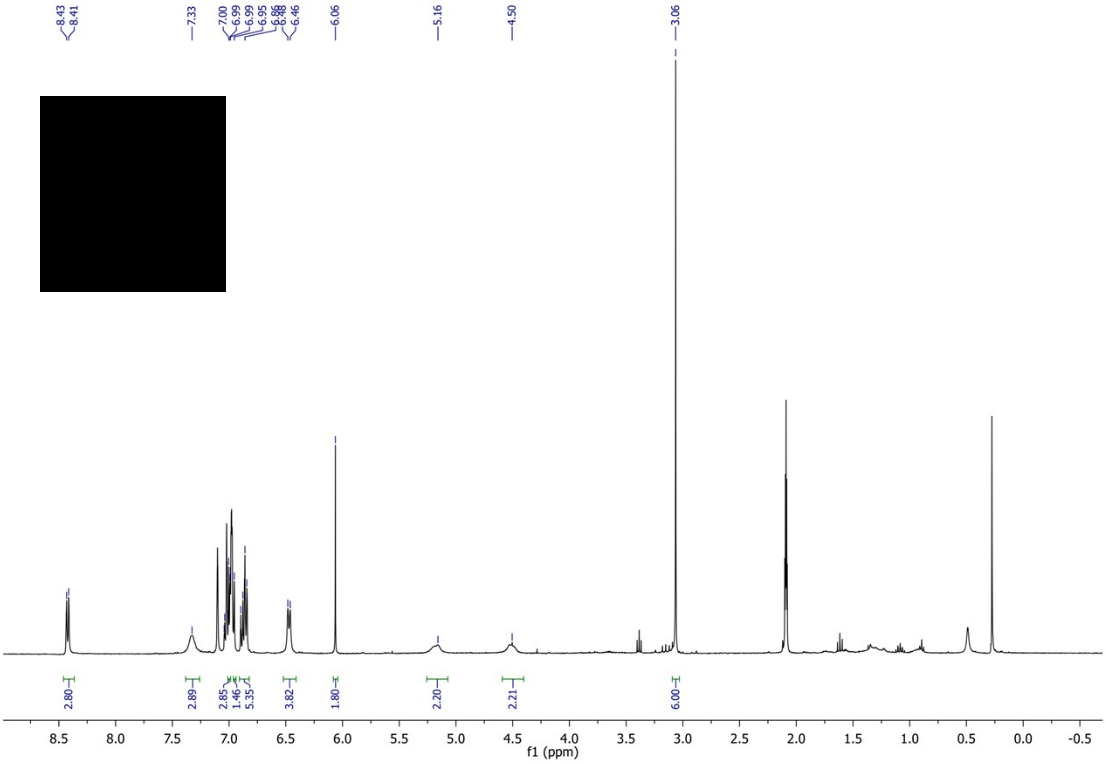
[redacted]

Figure S7. ^{13}C-NMR spectrum of **6** in C_7D_8.



[redacted]

Figure S8. ^{1}H-NMR spectrum of **7a** in C_7D_8.



[redacted]

Figure S9. ^{13}C-NMR spectrum of **7a** in C_7D_8.

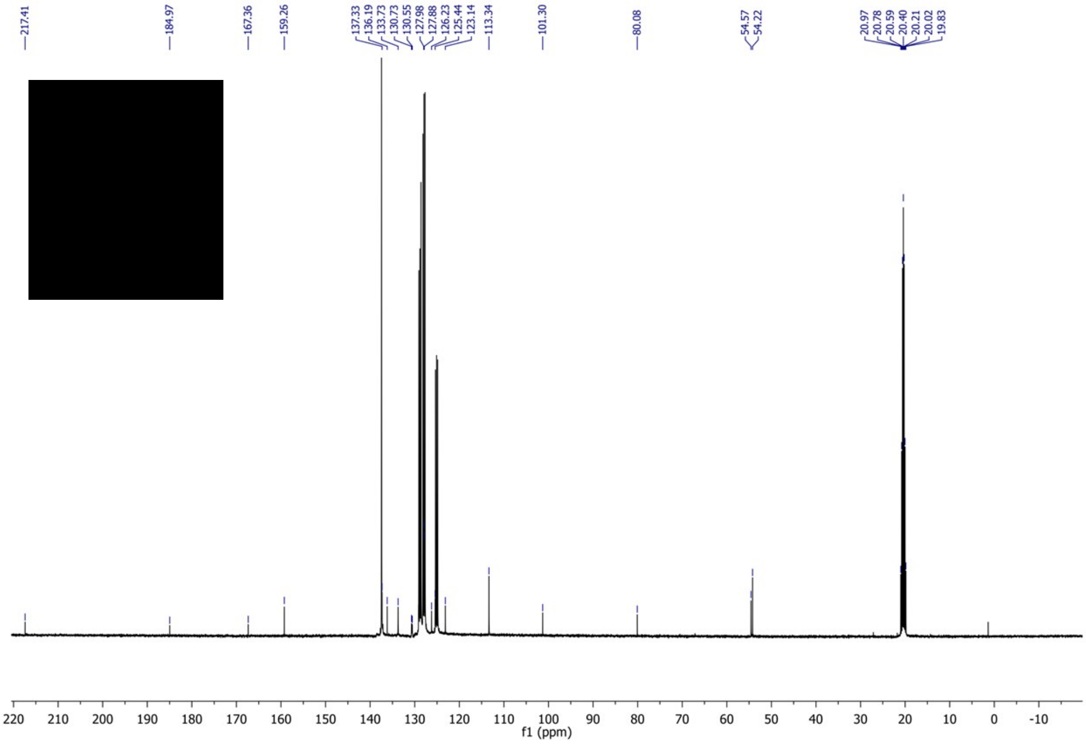

[redacted]

Figure S10. ^{1}H-NMR spectrum of **7b** in C_7D_8.

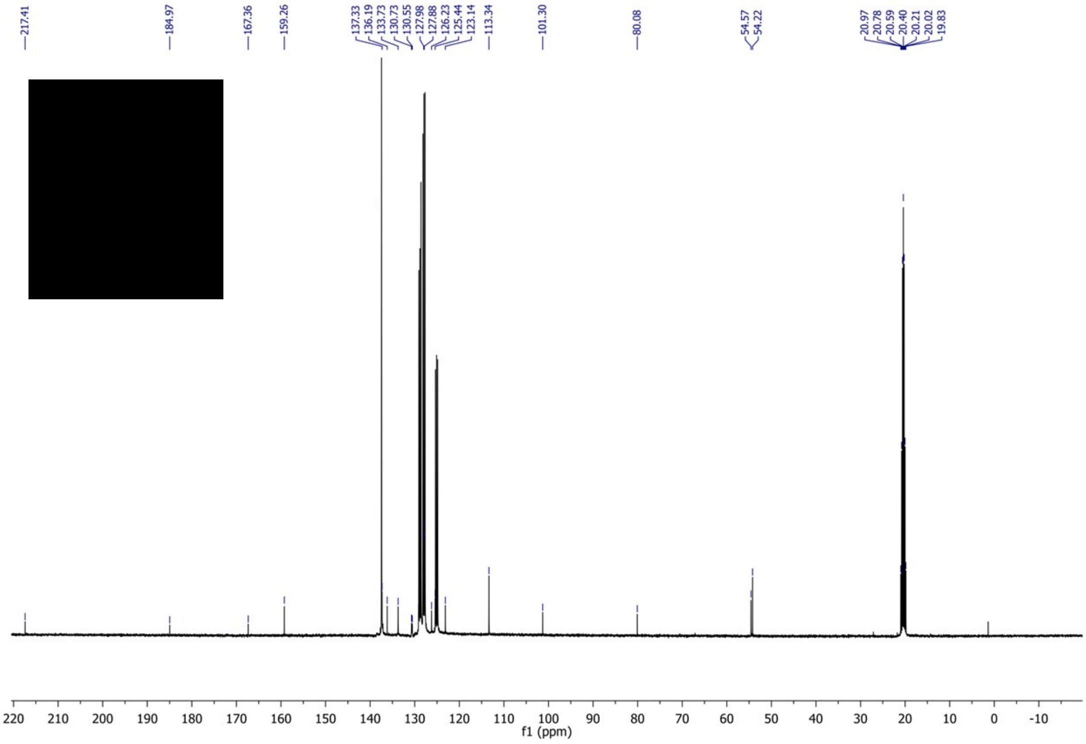

[redacted]

Figure S11. ^{13}C-NMR spectrum of **7b** in C_7D_8.

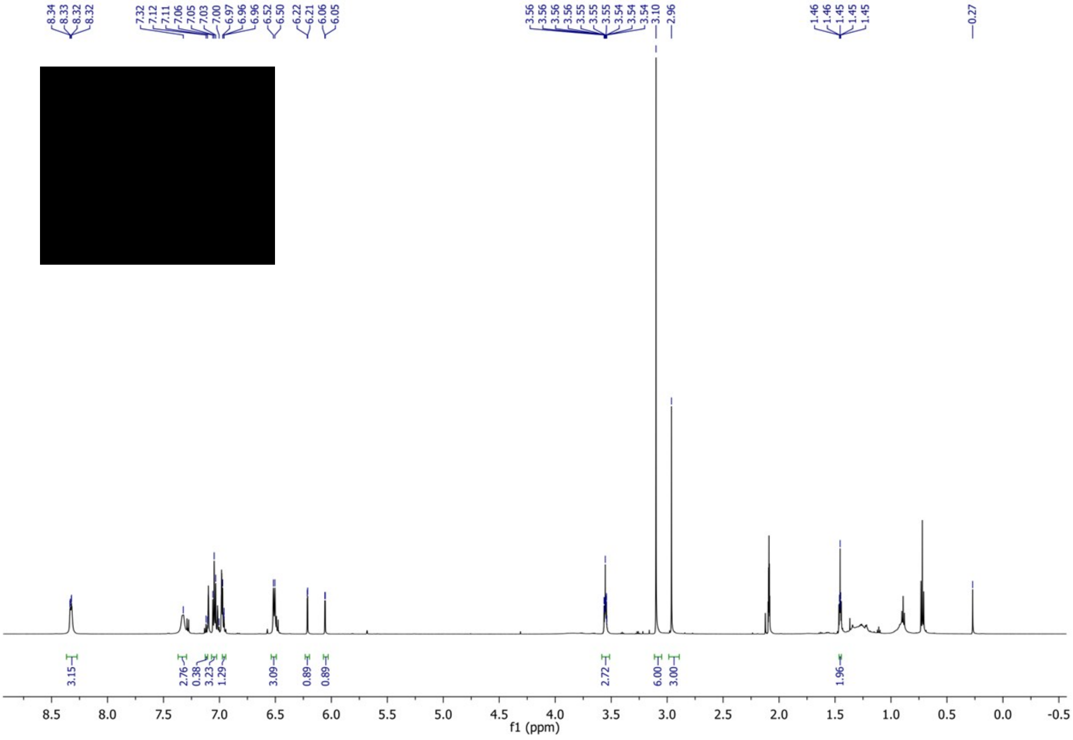

[redacted]

Figure S12. ^{1}H-NMR spectrum of **7c** in C_7D_8.

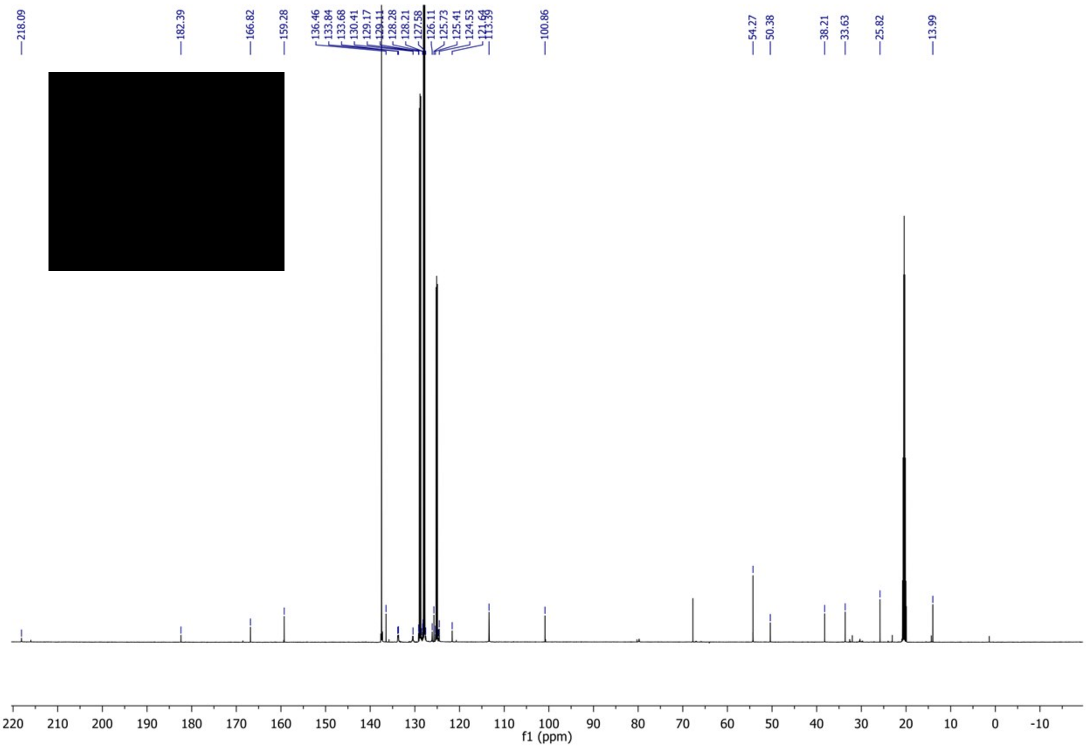
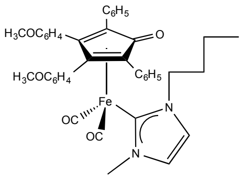

[redacted]

Figure S13. ^{13}C-NMR spectrum of **7c** in C_7D_8.



7c

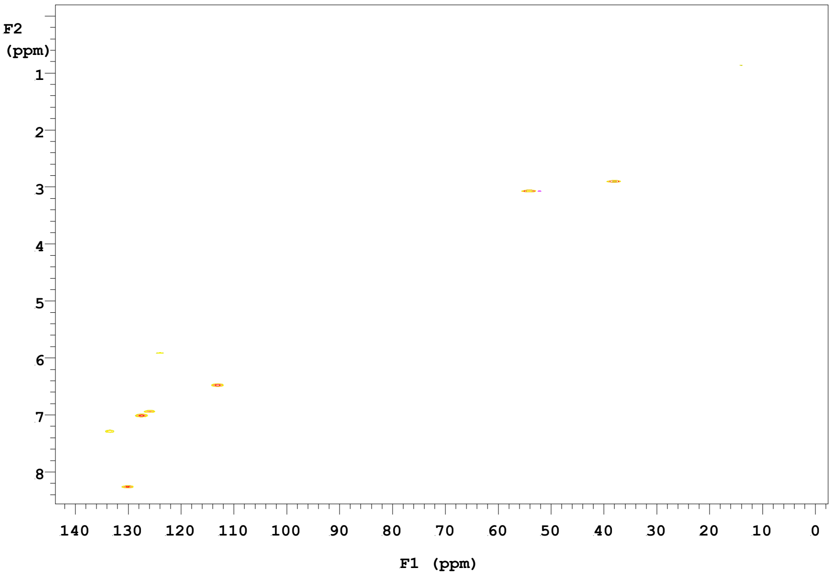
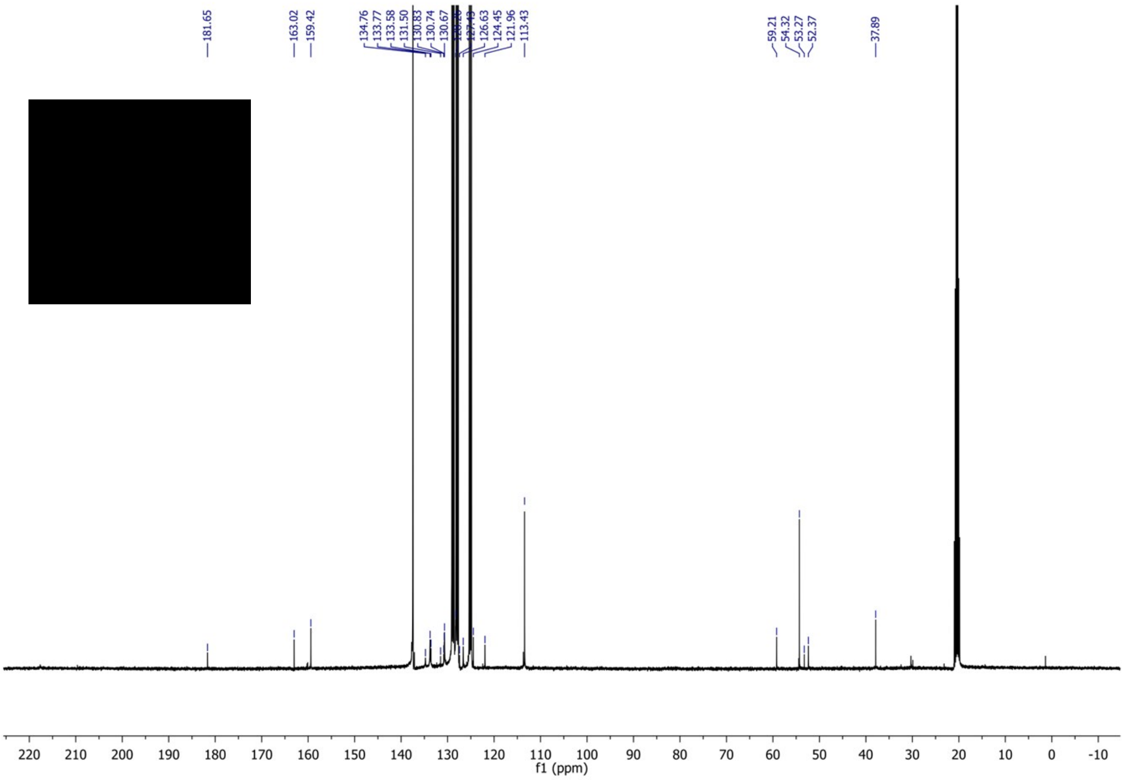


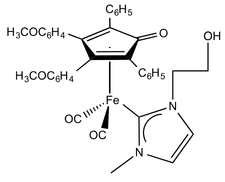
Figure S14. HSQC-NMR spectrum of **7c** in C_7D_8.



[redacted]

Figure S15. ^{1}H-NMR spectrum of **7d** in C_7D_8.

Figure S16. ^{13}C-NMR spectrum of **7d** in C_7D_8.



7d

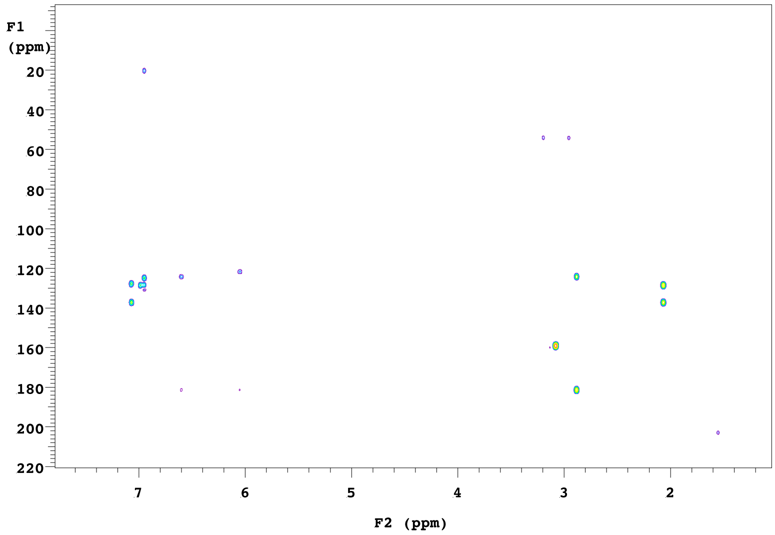
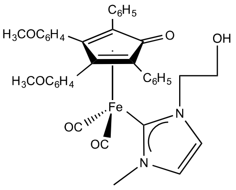


Figure S17. HMBC-NMR spectrum of **7d** in C_7D_8.



7d

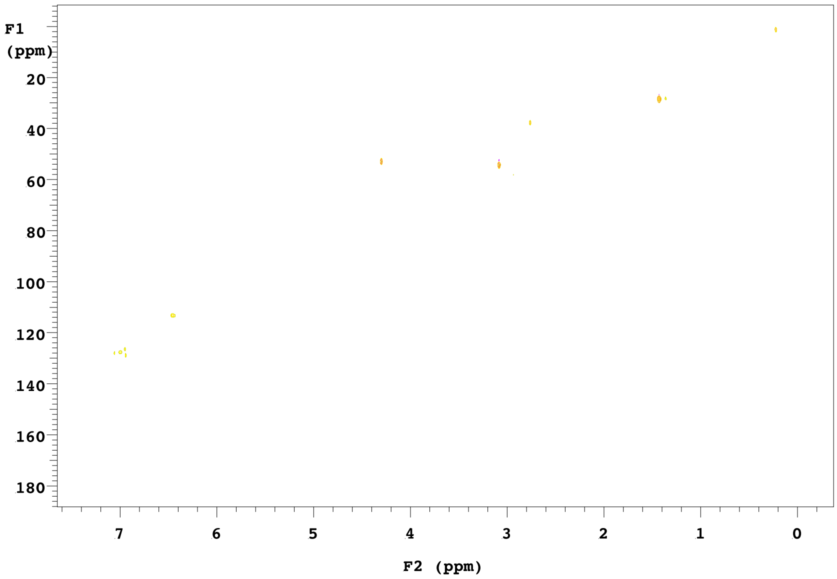


Figure S18. HMBC-NMR spectrum of **7d** in C_7D_8.

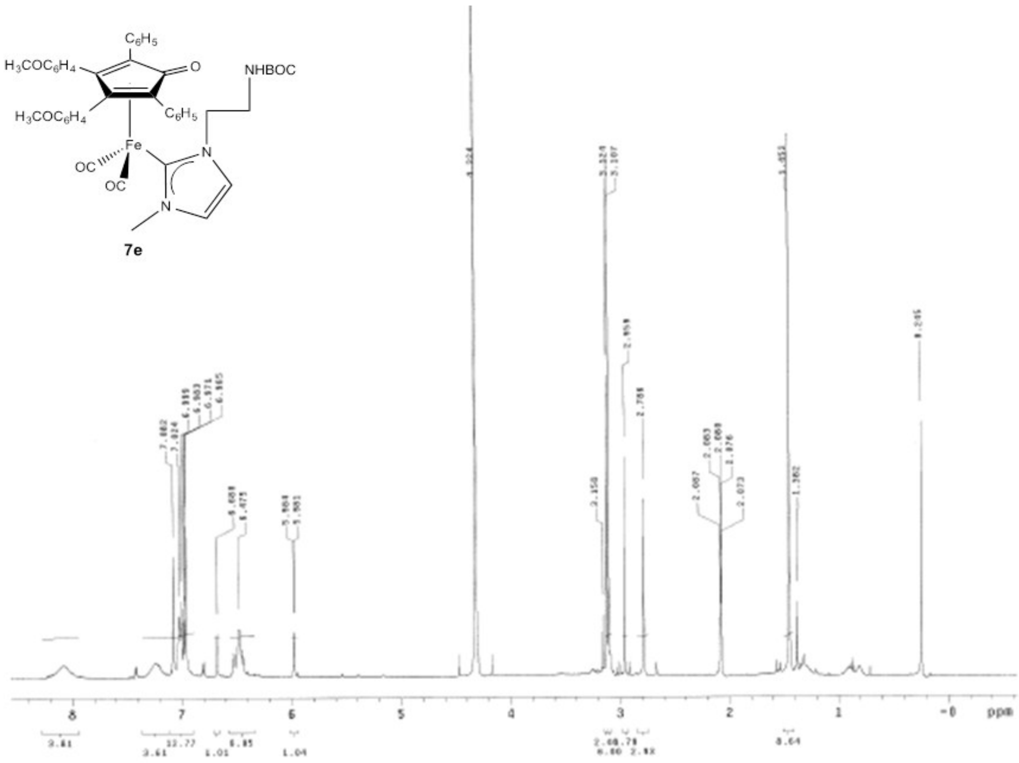


Figure S19. ^{1}H-NMR spectrum of **7e** in C_7D_8.

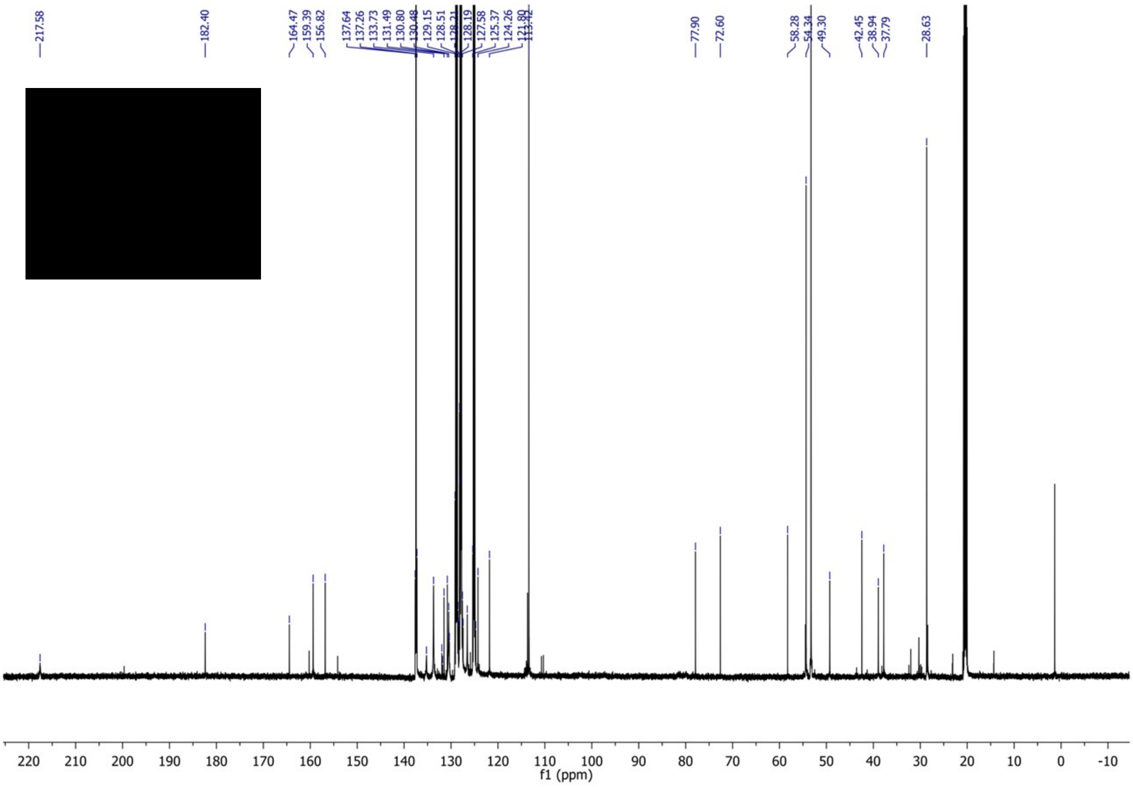


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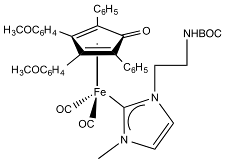
Figure S20. ^{13}C-NMR spectrum of **7e** in C_7D_8.



7e

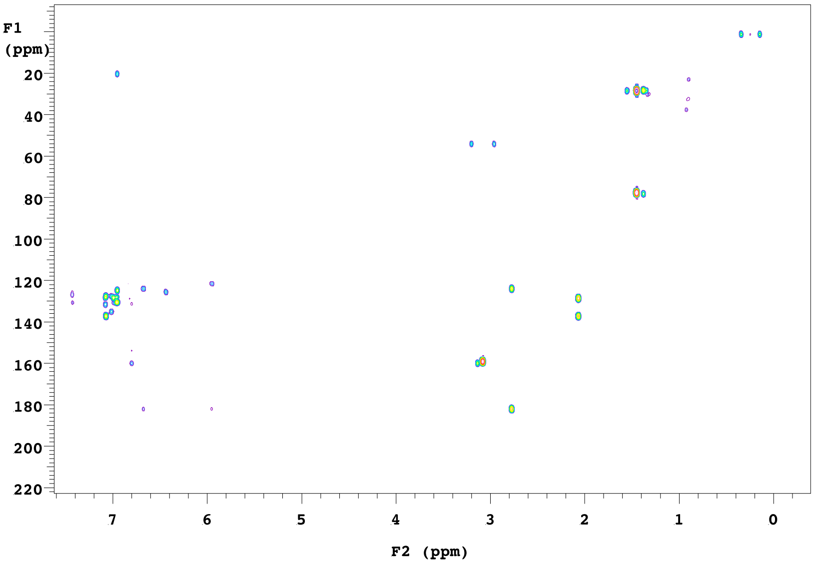


Figure S21. HMBC-NMR spectrum of **7e** in C_7D_8.

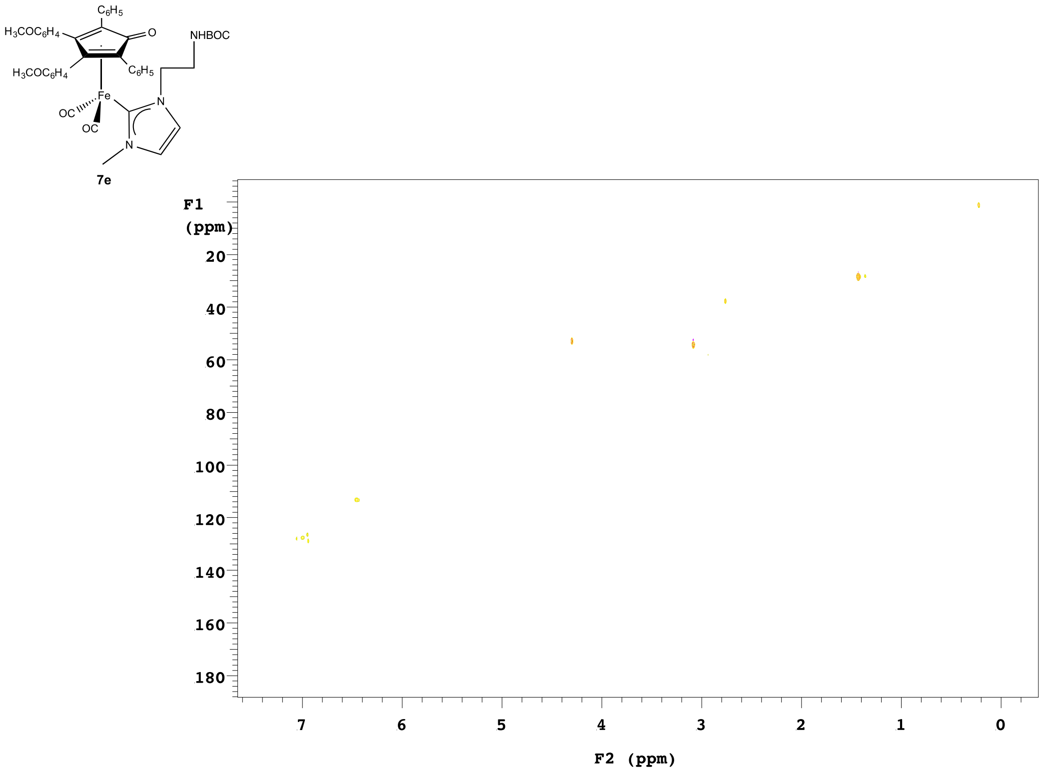


Figure S22. HSQC-NMR spectrum of **7e** in C_7D_8.

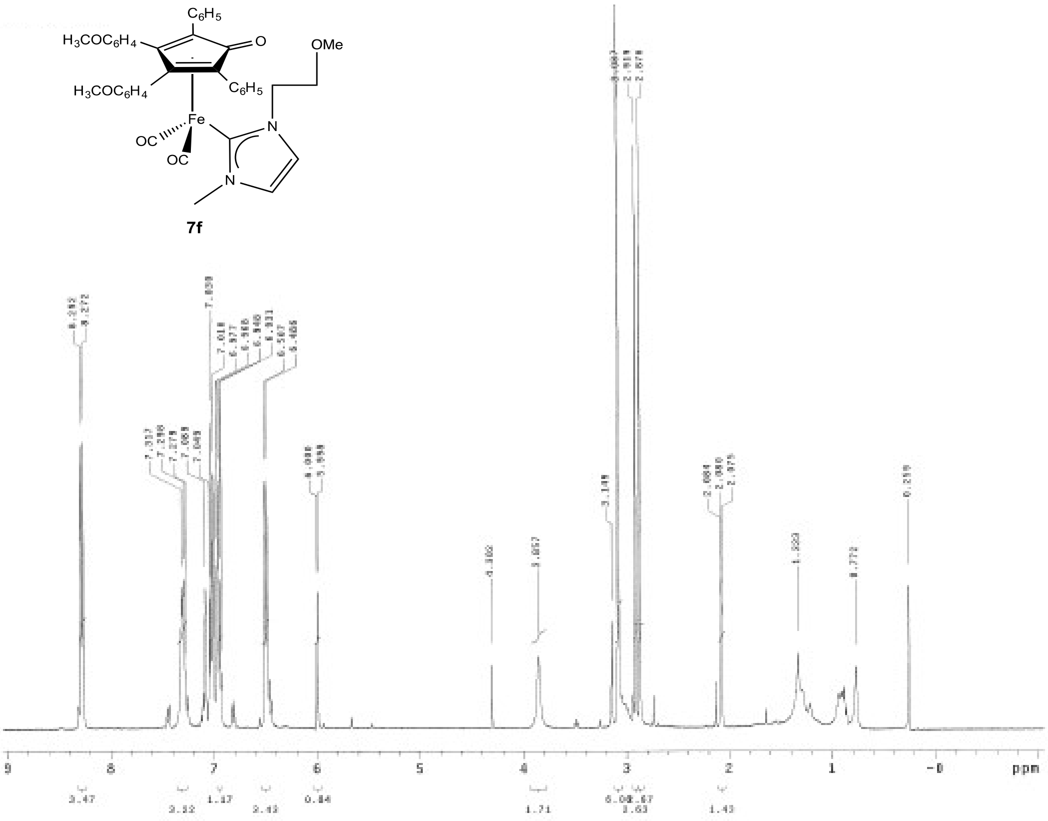


Figure S23. ^{1}H-NMR spectrum of **7f** in C_7D_8.

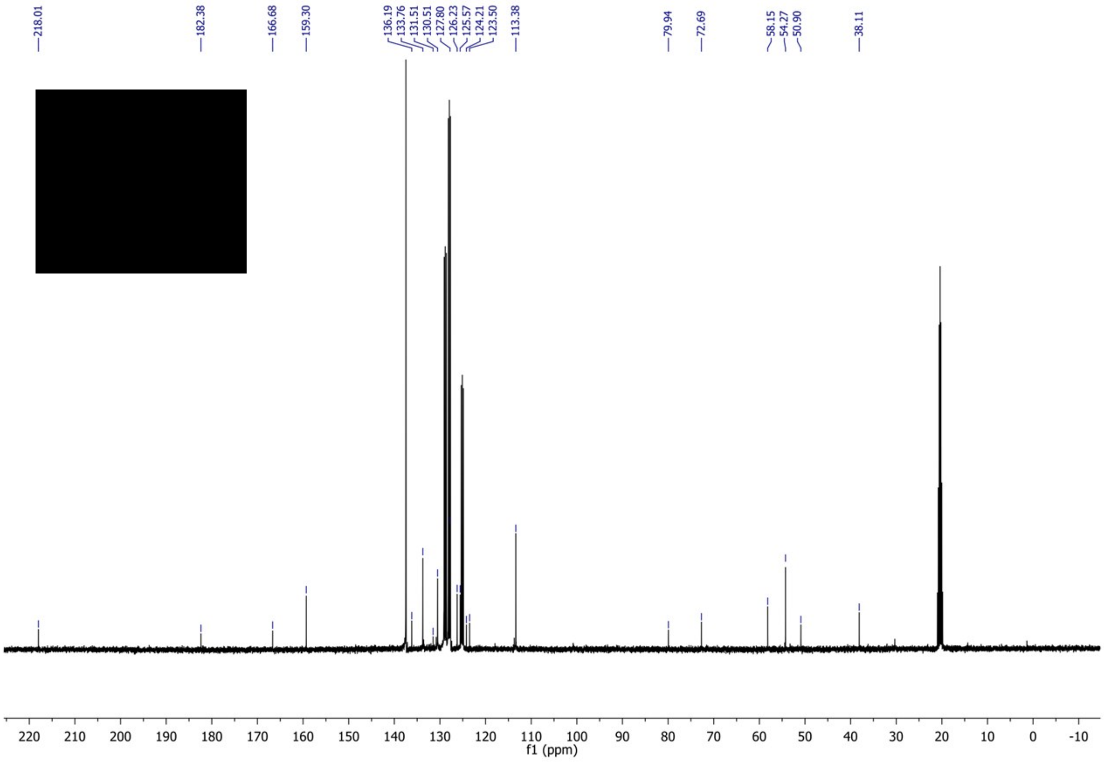


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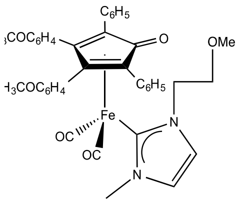
Figure S24. ^{13}C-NMR spectrum of **7f** in C_7D_8.



7f

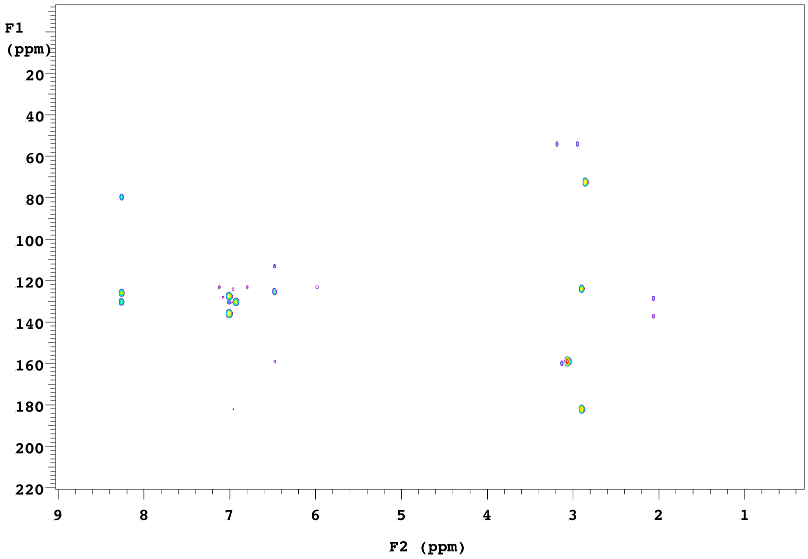
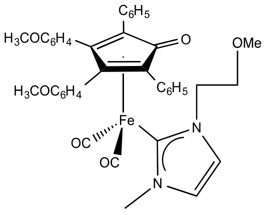


Figure S25. HMBC-NMR spectrum of **7f** in C_7D_8.



7f

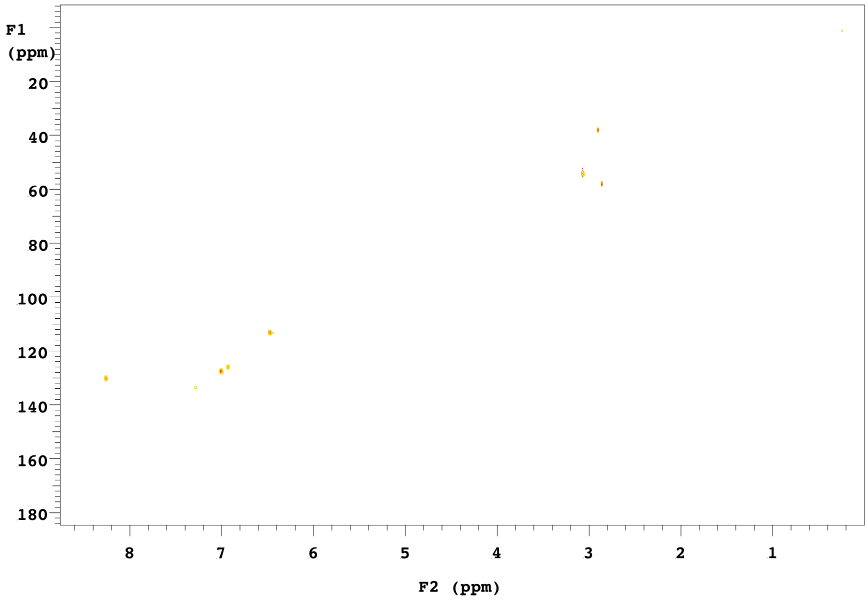


Figure S26. HSQC-NMR spectrum of **7f** in C_7D_8.

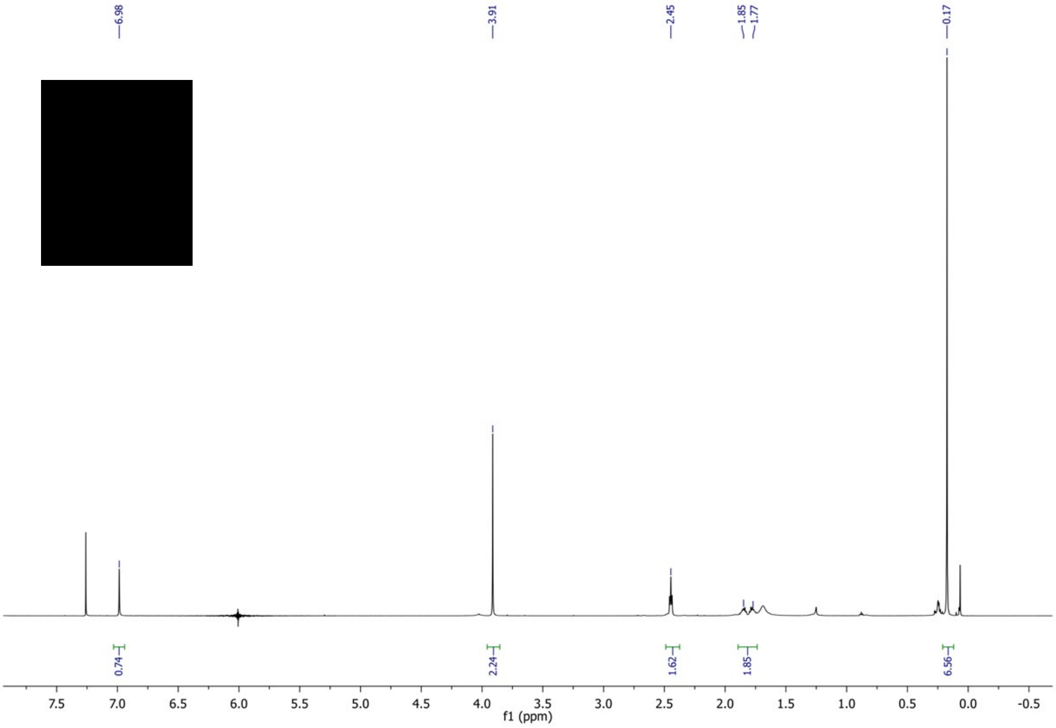


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Figure S27. ^{1}H-NMR spectrum of **10a** in $CDCl_3$.

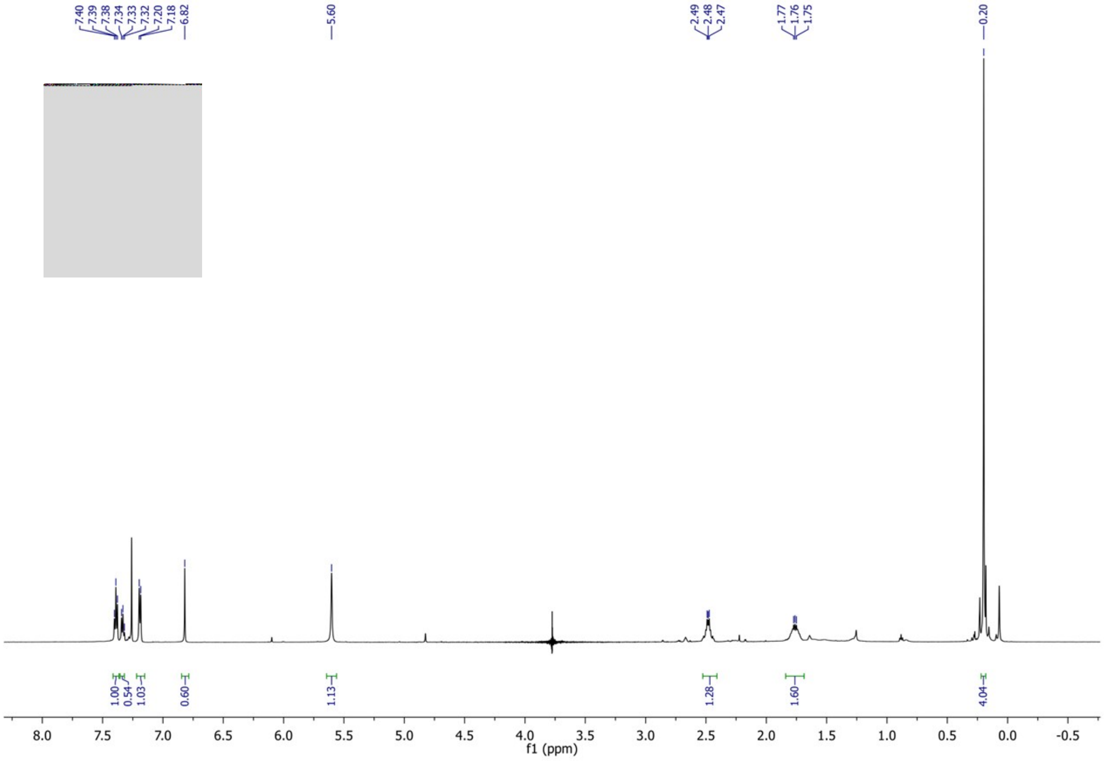
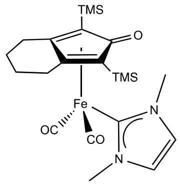


Figure S28. ^{13}C-NMR spectrum of **10a** in CDCl$_3$.



10a

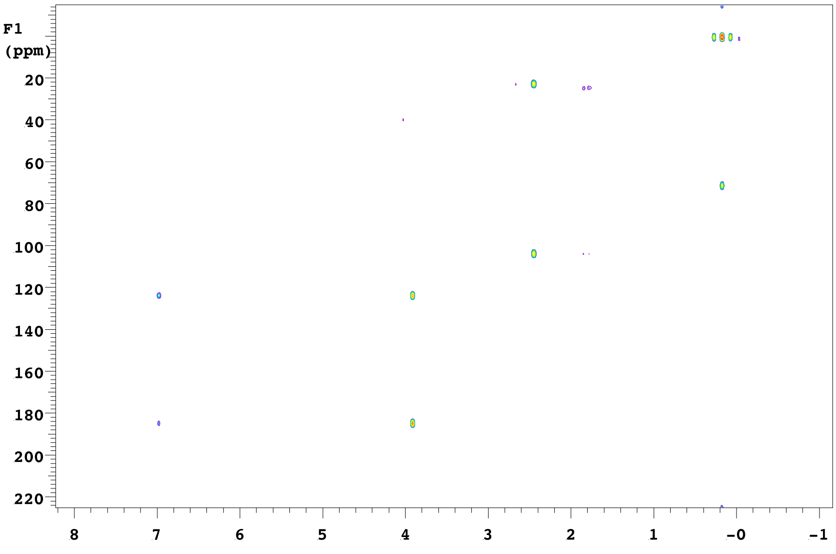


Figure S29. HMBC-NMR spectrum of **10a** in CDCl$_3$.

[redacted]

Figure S30. ^{1}H-NMR spectrum of **10b** in $CDCl_3$.

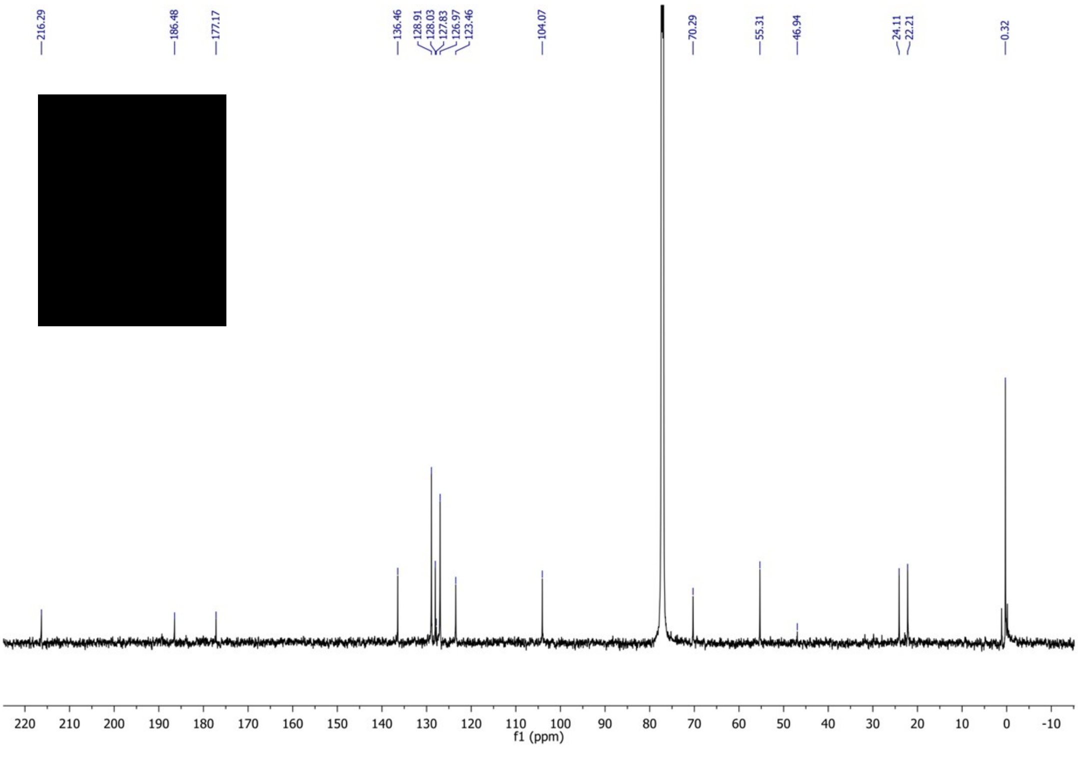


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Figure S31. ^{13}C-NMR spectrum of **10b** in $CDCl_3$.

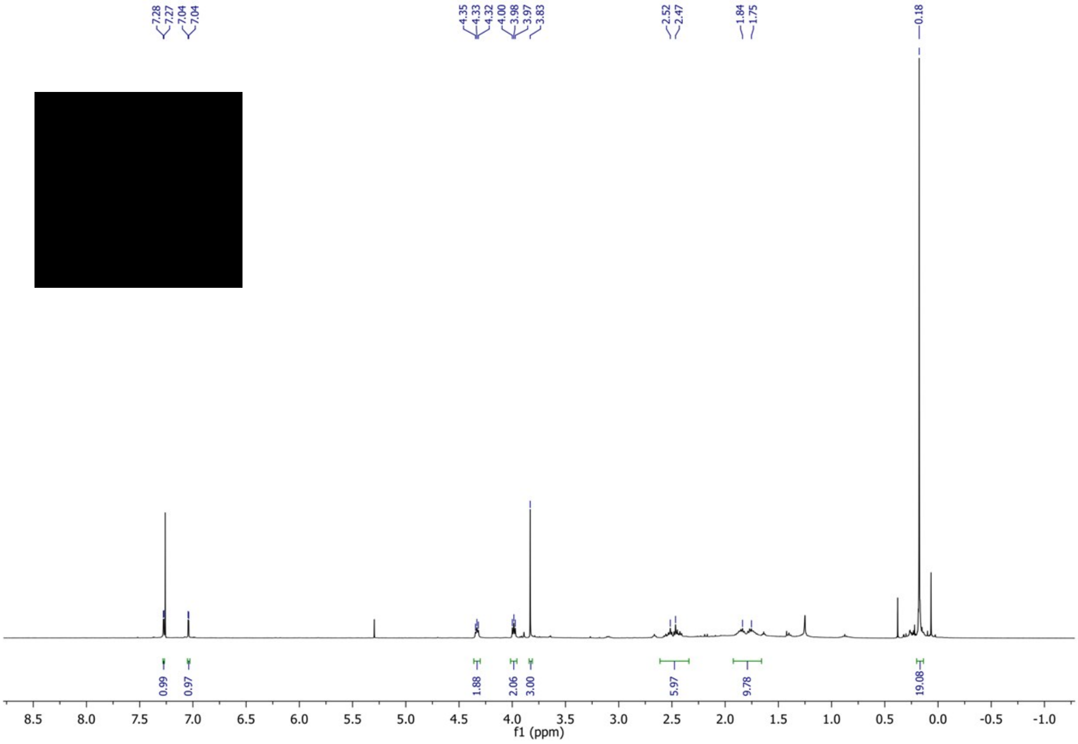
[redacted]

Figure S32. ^{1}H-NMR spectrum of **10d** in CDCl$_3$.

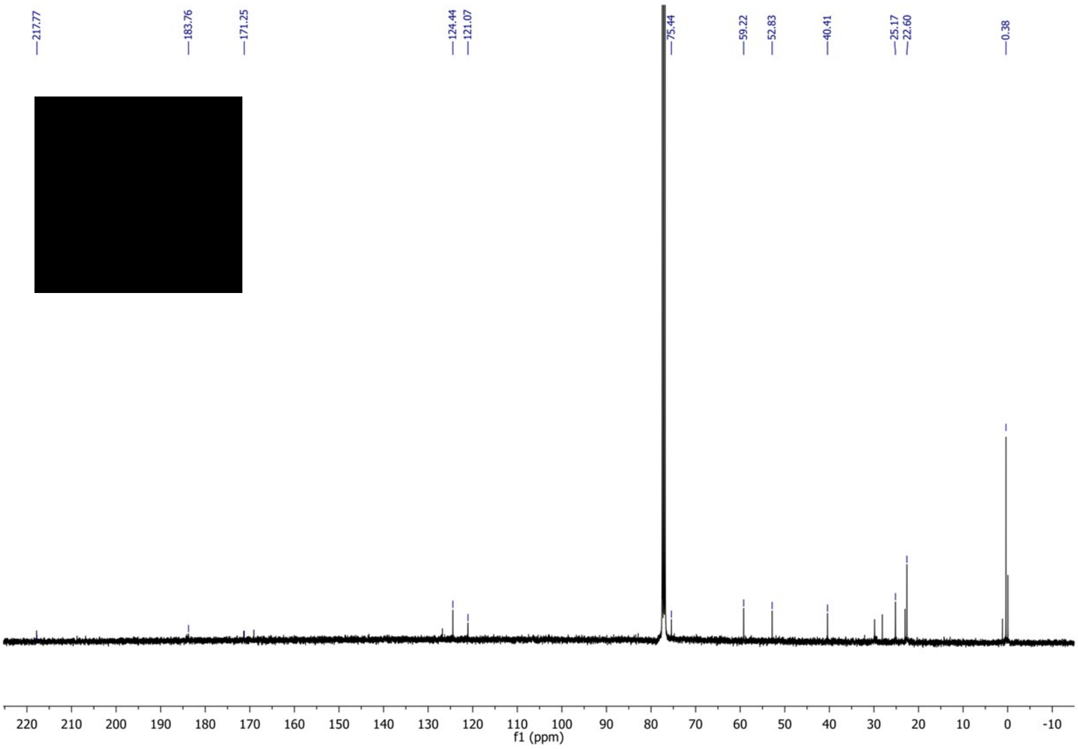
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Figure S33. ^{13}C-NMR spectrum of **10d** in CDCl$_3$.

[redacted]

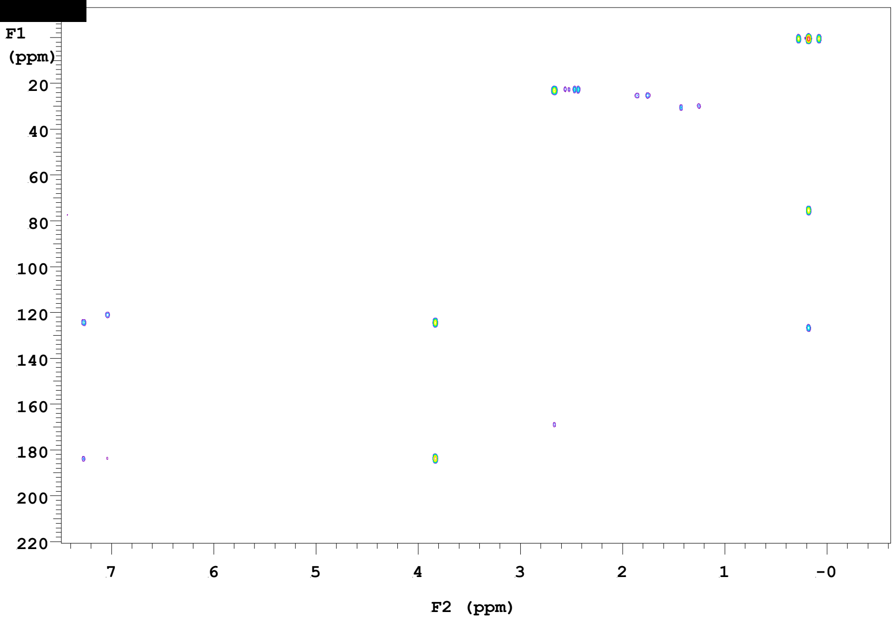

Figure S34. HMBC-NMR spectrum of **10d** in $CDCl_3$.

[redacted]

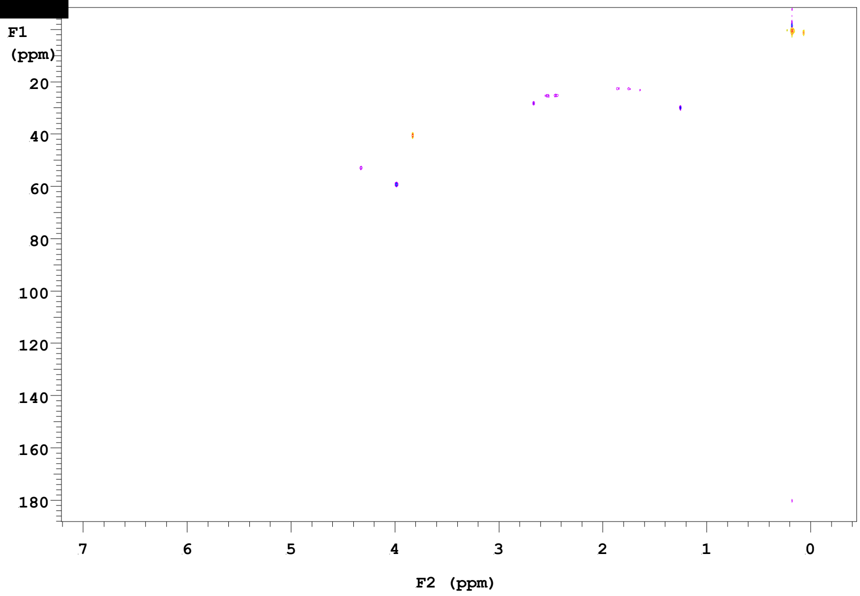

Figure S35. HSQC-NMR spectrum of **10d** in $CDCl_3$.

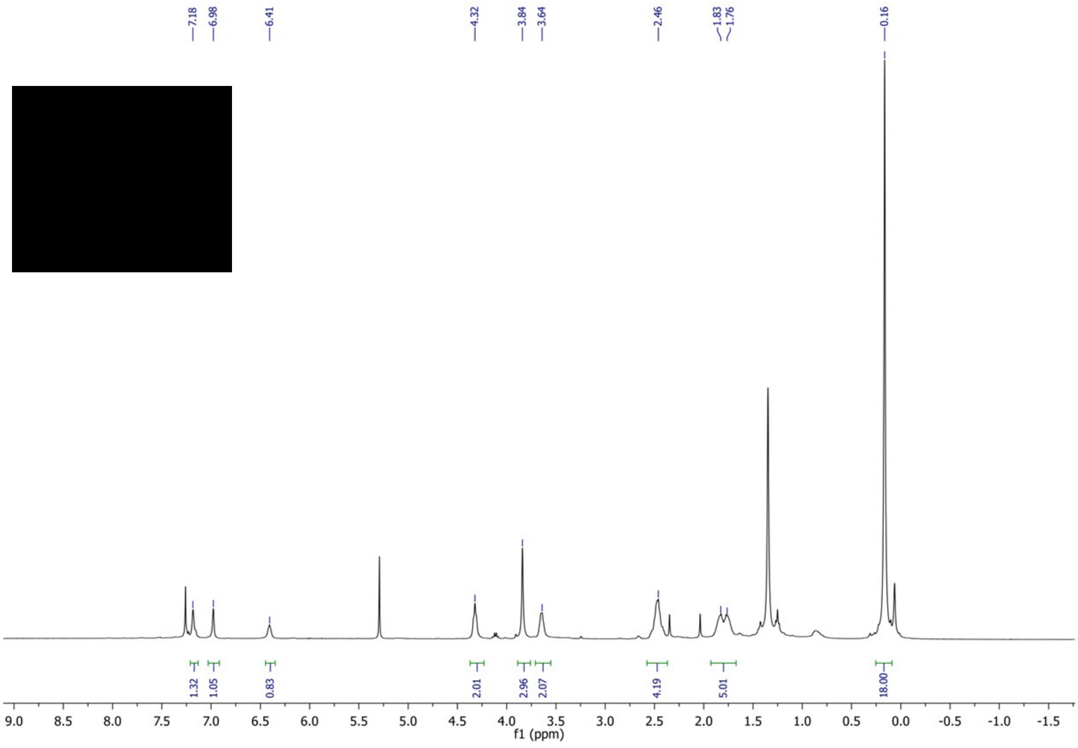
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Figure S36. ^{1}H-NMR spectrum of **10e** in CDCl$_3$.

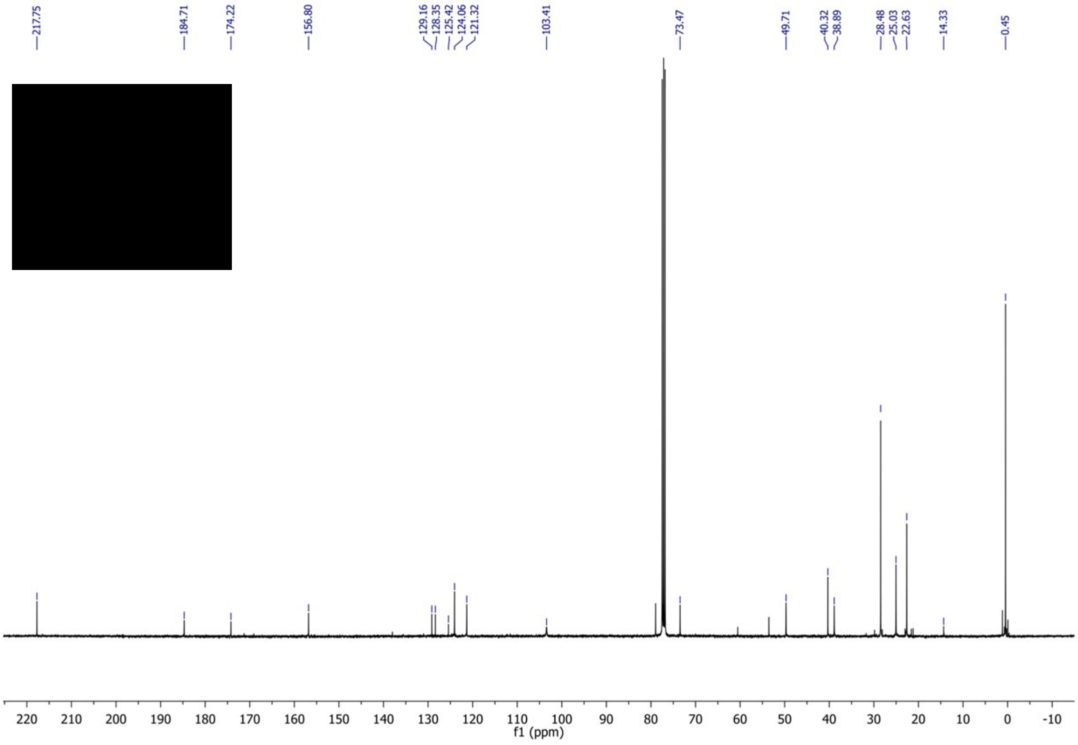
[redacted]

Figure S37. ^{13}C-NMR spectrum of **10e** in CDCl$_3$.

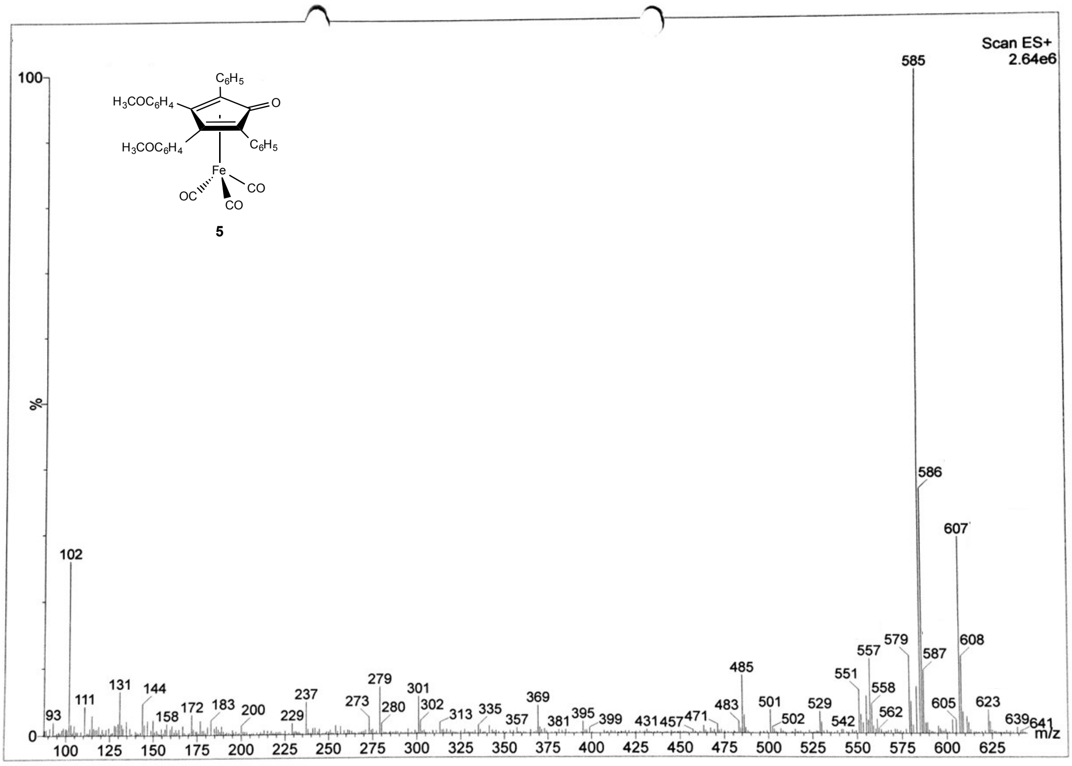

Figure S38. ESI-MS spectrum of **5** in CH_3CN.

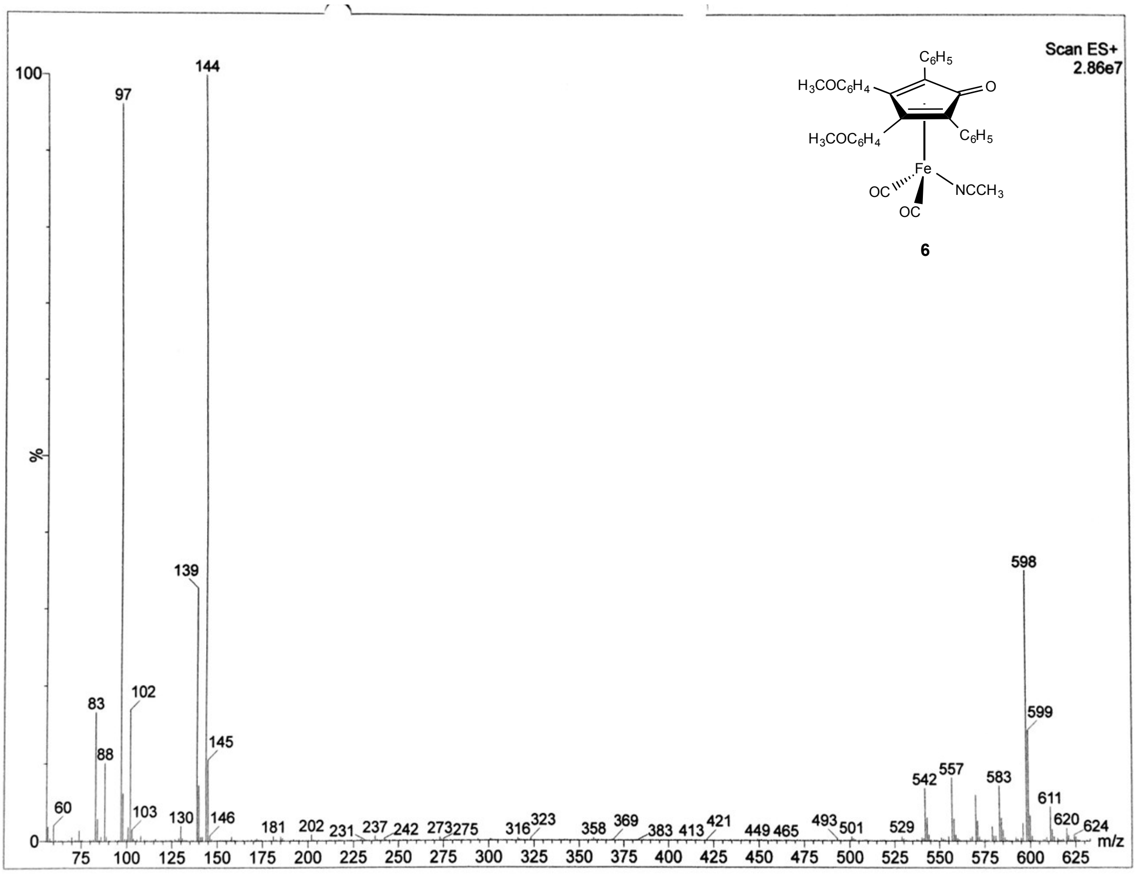

Figure S39. ESI-MS spectrum of **6** in CH_3CN.

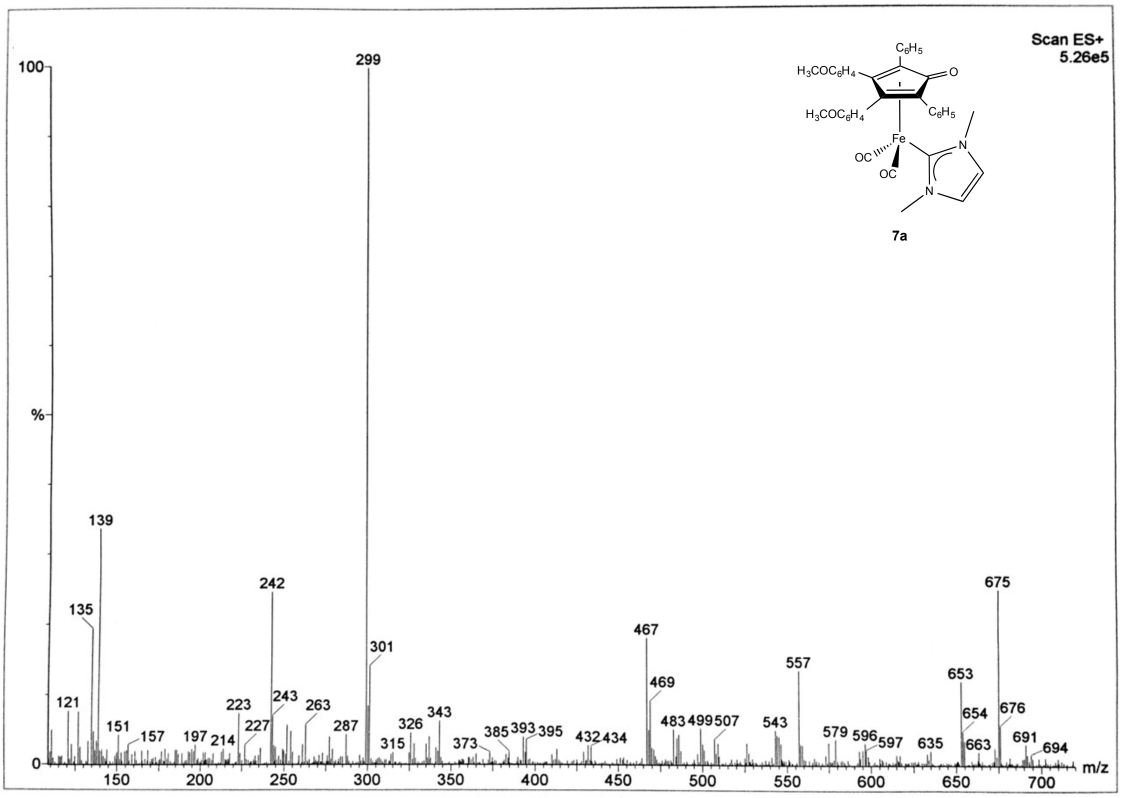

Figure S40. ESI-MS spectrum of **7a** in CH_3CN.

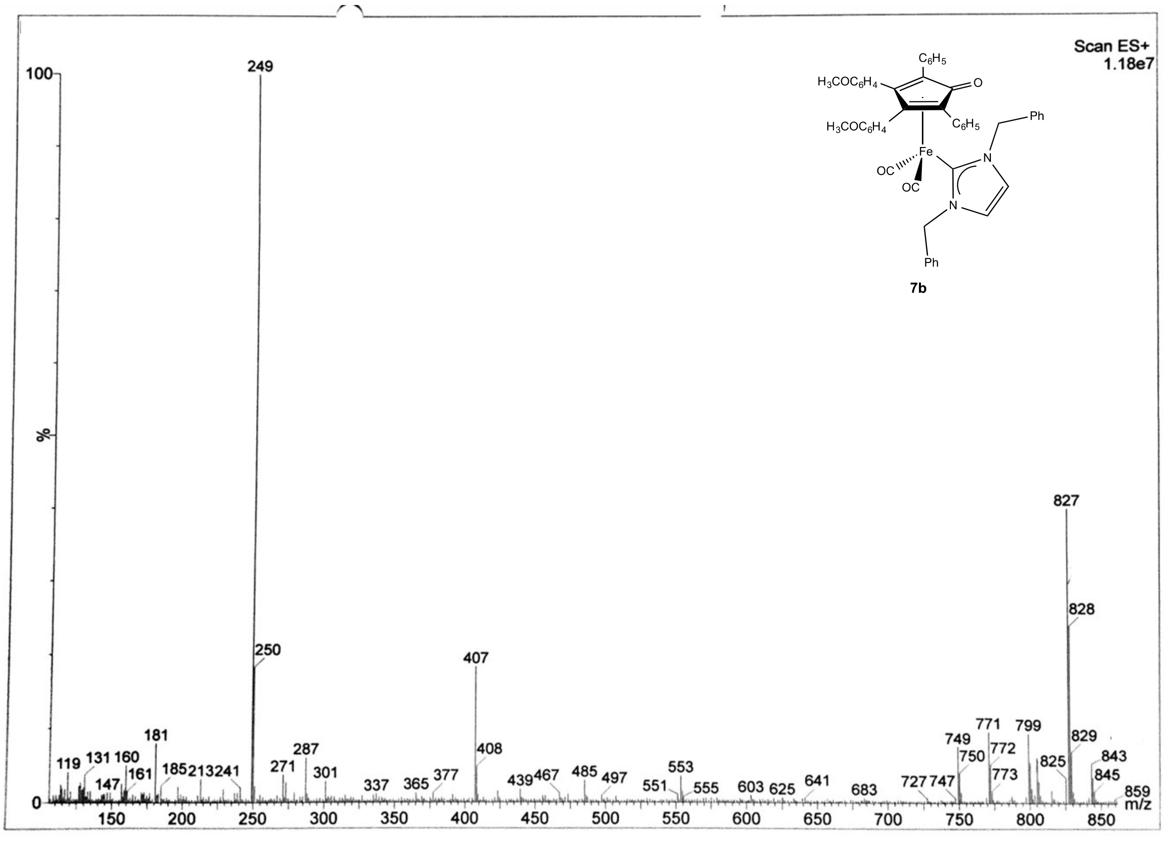

Figure S41. ESI-MS spectrum of **7b** in CH_3CN.

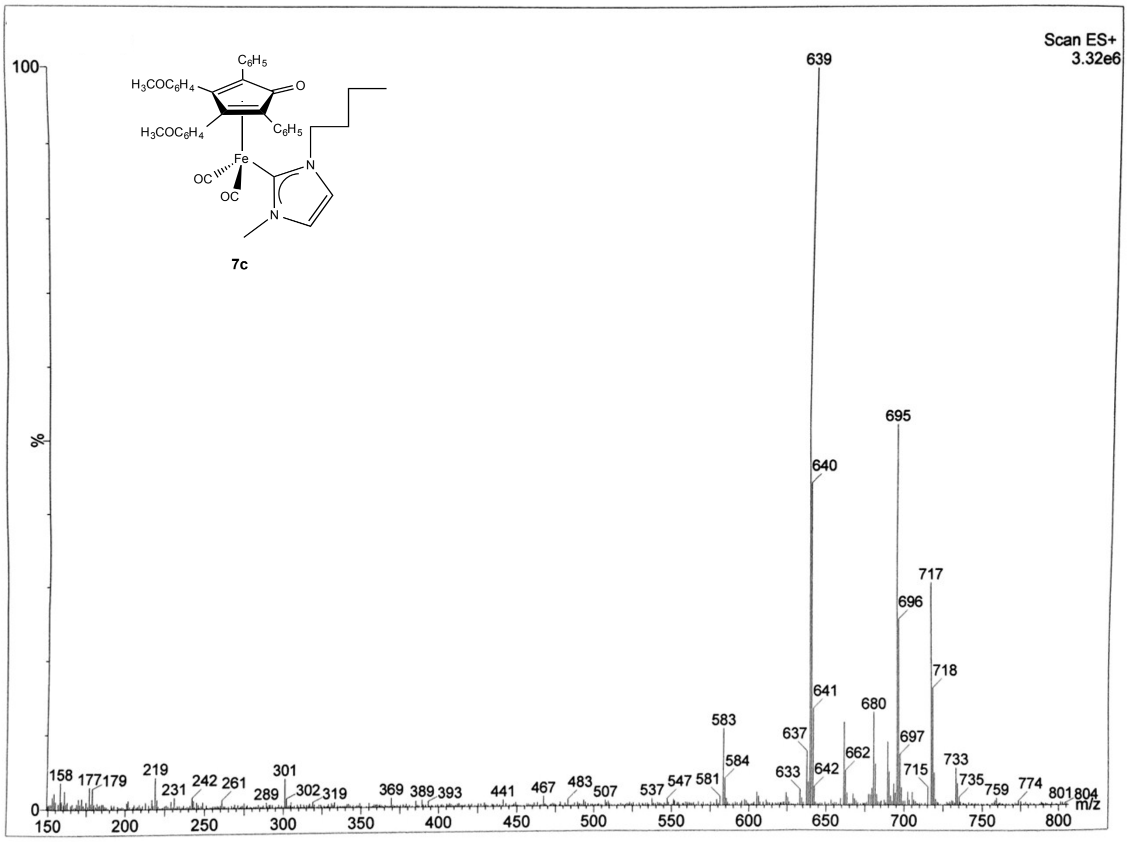

Figure S42. ESI-MS spectrum of **7c** in CH_3CN.

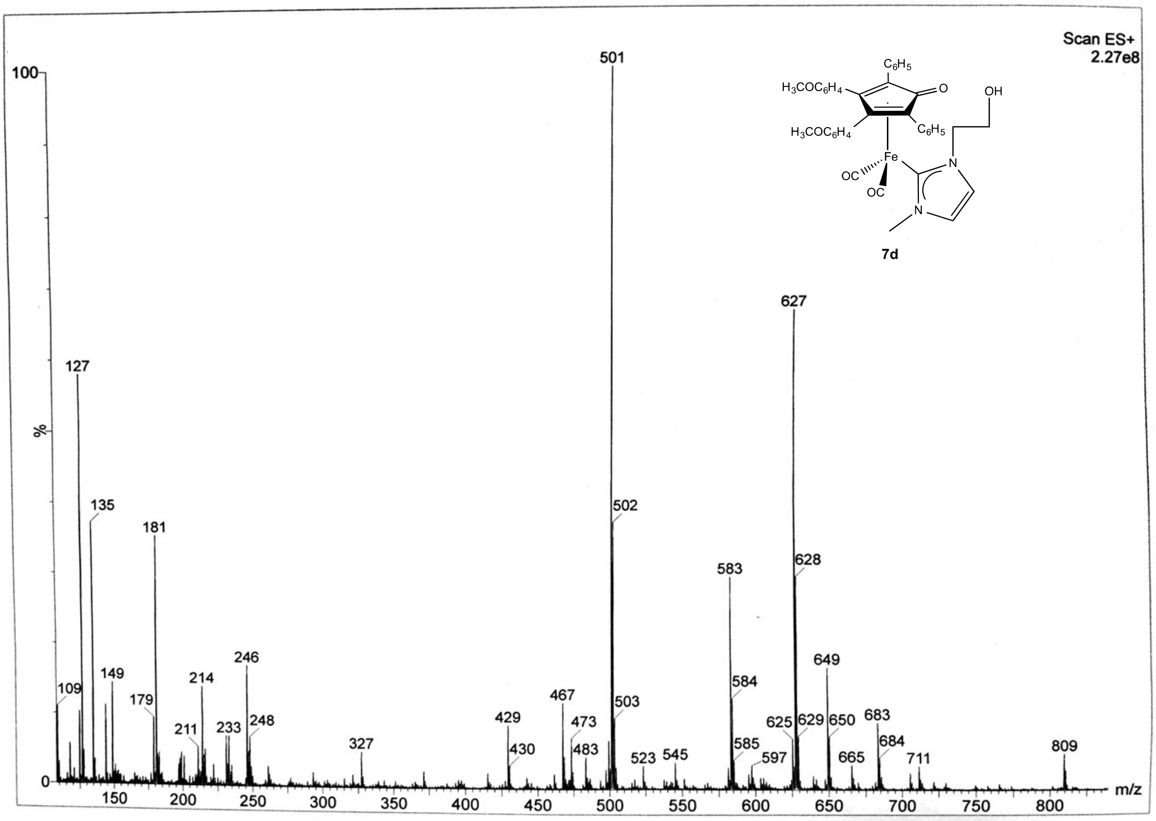

Figure S43. ESI-MS spectrum of **7d** in CH_3CN.

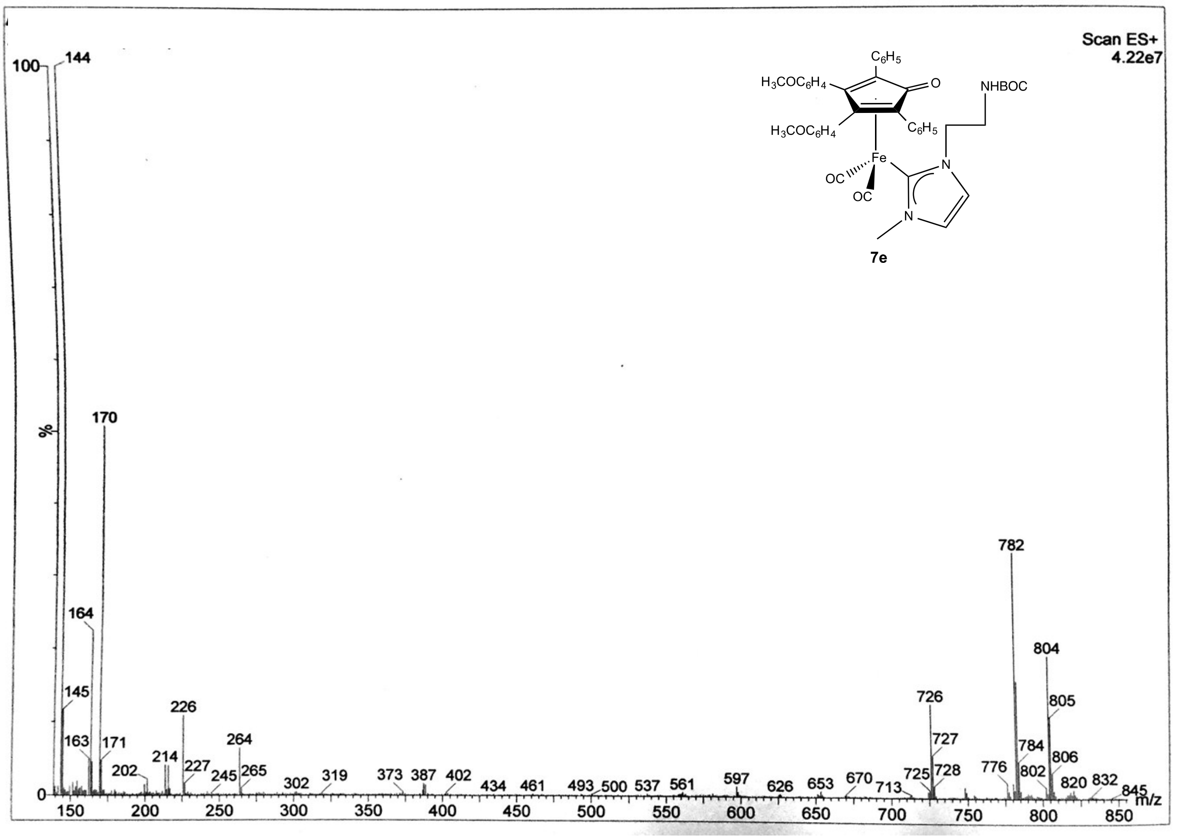

Figure S44. ESI-MS spectrum of **7e** in CH_3CN.

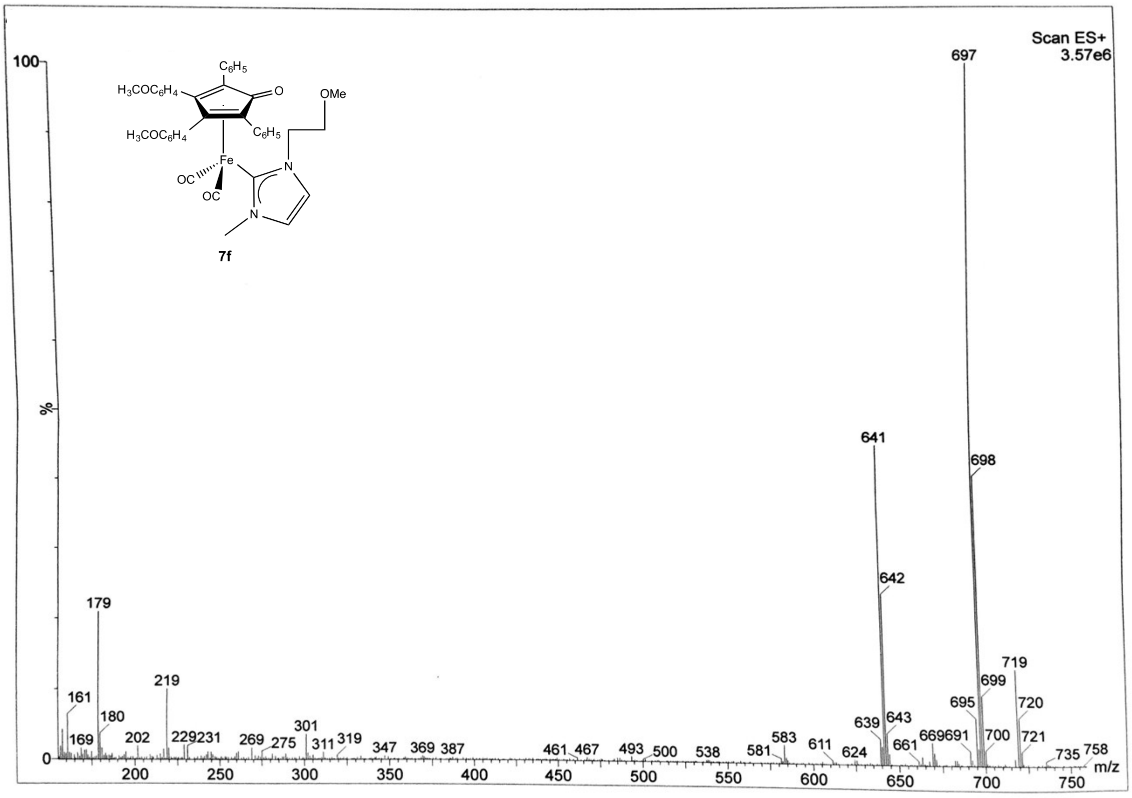

Figure S45. ESI-MS spectrum of **7f** in CH_3CN.

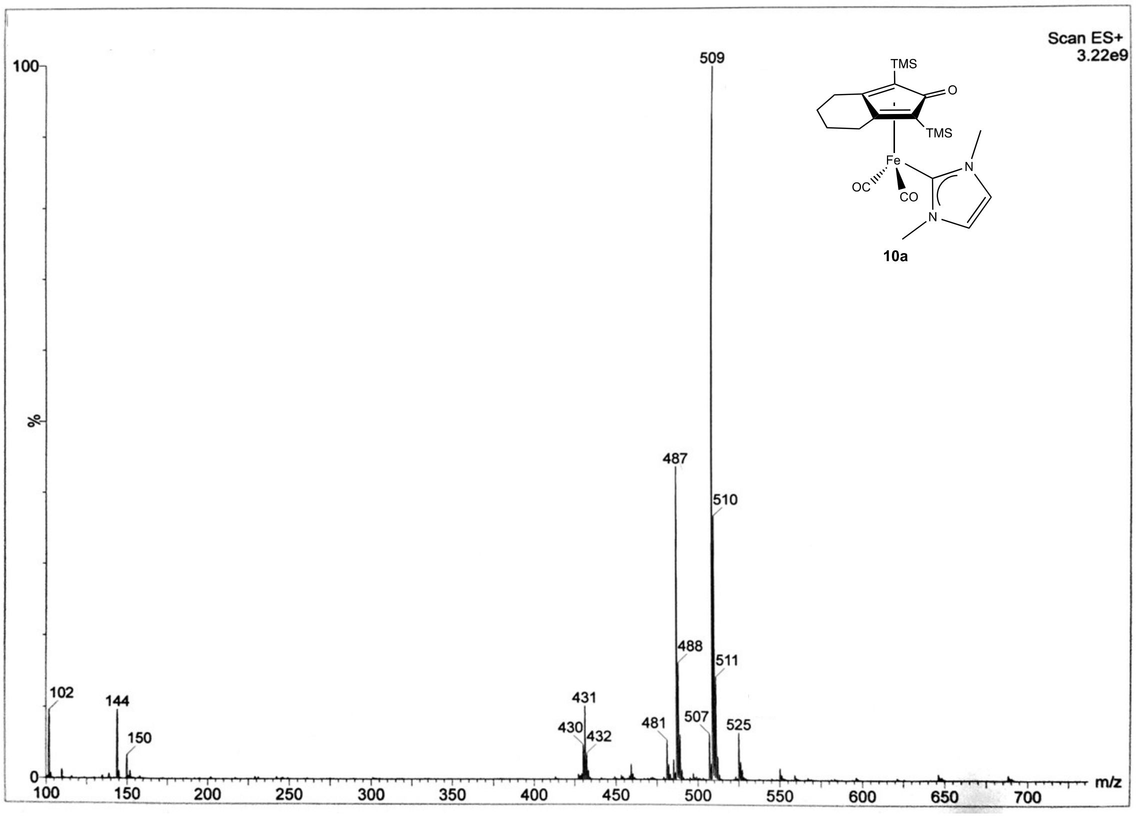

Figure S46. ESI-MS spectrum of **10a** in CH_3CN.

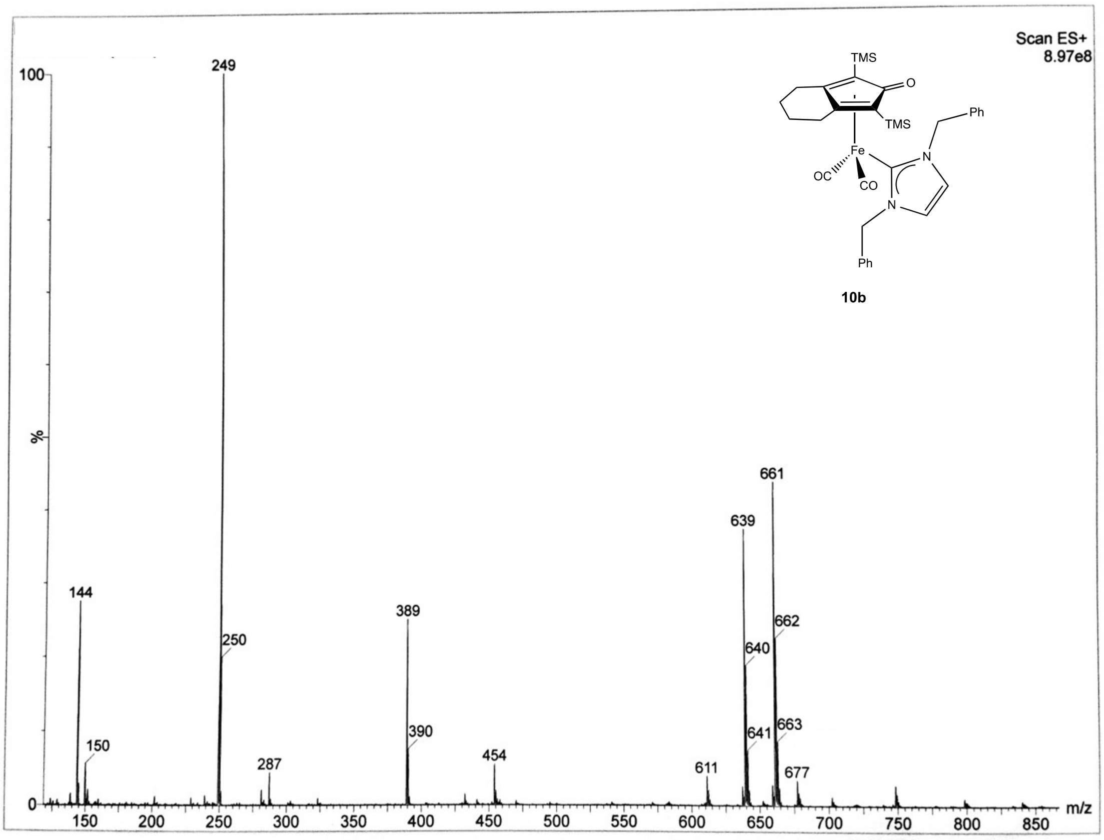

Figure S47. ESI-MS spectrum of **10b** in CH_3CN.

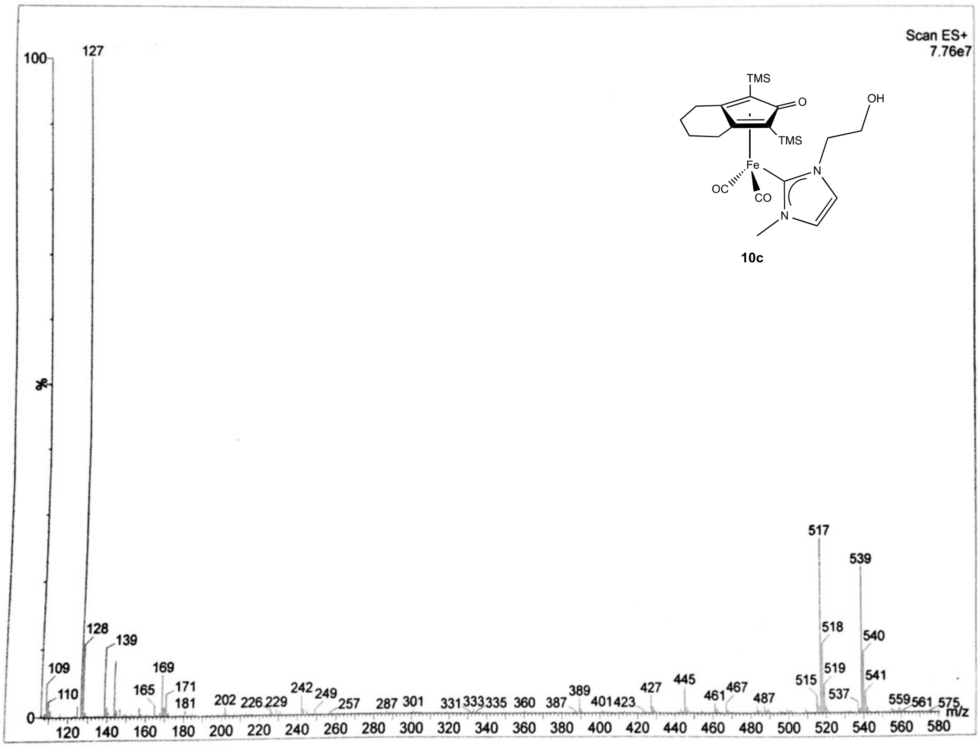

Figure S48. ESI-MS spectrum of **10d** in CH_3CN.

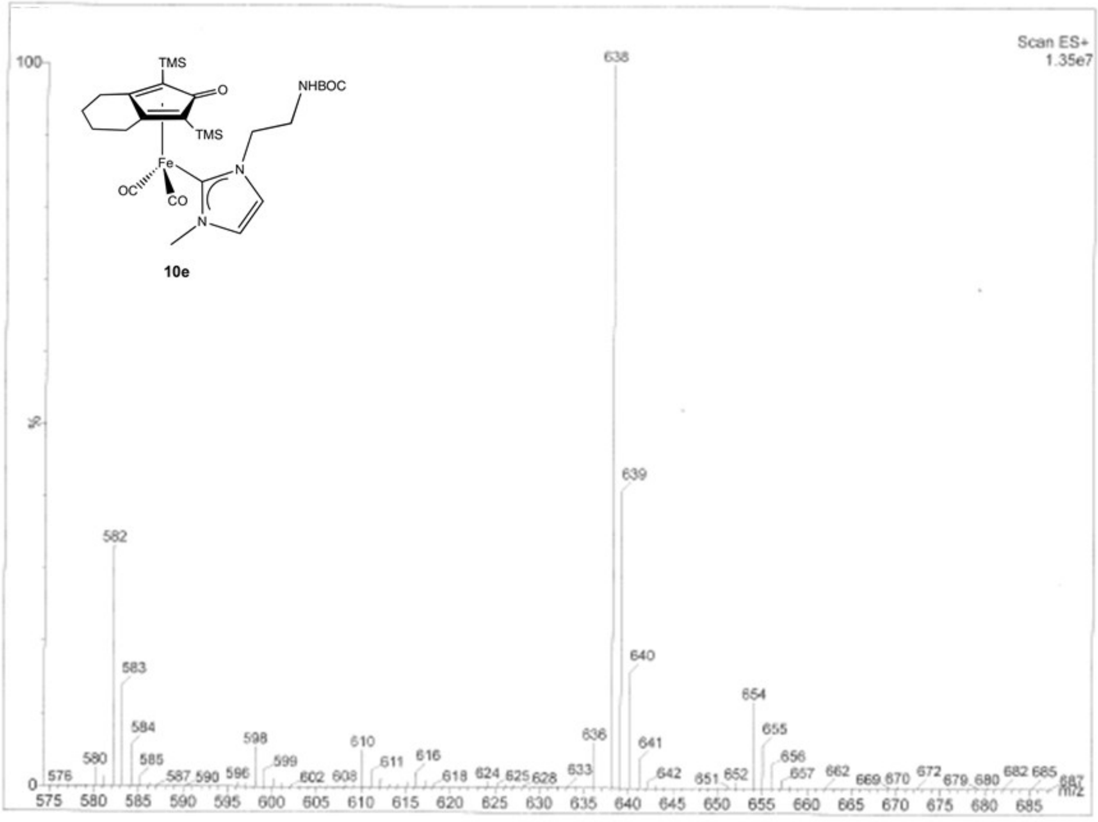

Figure S49. ESI-MS spectrum of **10e** in CH_3CN.

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