Electronic Supplementary Information (ESI) for

Stable group 8 metal porphyrin mono- and bis(dialkylcarbene) complexes. Synthesis, characterization, and catalytic activity

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I. Abbreviations

Por: porphyrinato(2–)

TPFPP: 5,10,15,20-tetrakis(pentafluorophenyl)porphyrinato(2–)

TTP: 5,10,15,20-tetra(*p*-tolyl)porphyrinato(2–)

TFSPP: 5,10,15,20-tetrakis(2,3,5,6-tetrafluoro-4-(methylthio)phenyl)porphyrinato(2–)

TFOPP: 5,10,15,20-tetrakis(2,3,5,6-tetrafluoro-4-methoxyphenyl)porphyrinato(2–)

4-F-TPP: 5,10,15,20-tetrakis(4-fluorophenyl)porphyrinato(2–)

C_6F_5: pentafluorophenyl

$C_6H_4CH_3$: *p*-tolyl

C_6F_4SMe: 2,3,5,6-tetrafluoro-4-(methylthio)phenyl

C_6F_4OMe: 2,3,5,6-tetrafluoro-4-methoxyphenyl

C_6H_4F: 4-fluorophenyl

Ad: 2-adamantylidene

L: axial ligand

Py: pyridine

NMe_2Py: 4-dimethylaminopyridine

CNPy: 4-cyanoyridine

MeIm: 1-methylimidazole

ArNC: 2,6-dimethylphenyl isocyanide

NHC: N-heterocyclic carbene

Fc: ferrocene

XANES: X-ray absorption near edge structure

TGA: thermogravimetric analysis

DFT: density functional theory

MO: molecular orbital

II. Experimental section

General

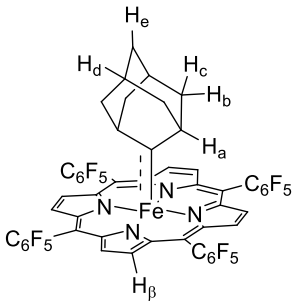
All reactions were performed using the standard Schlenk technique under an argon atmosphere unless indicated otherwise. [Fe(Por)Cl] and [Fe(Por)],[1] [Ru(Por)(CO)],[2] [Os(Por)(CO)],[3] and aziadamantane[4] were synthesized according to literature procedures. Other reagents were obtained commercially and used without further purification. All solvents used in the reactions were dried and freshly distilled. UV irradiations in photochemical reactions were provided by SJMAEA-UV4D LED light source (λ = 365 nm). Flash chromatography was performed using Merck silica gel under air unless stated otherwise. NMR spectra were measured on a Bruker DPX-500, DPX-400, or DPX-300 spectrometer at 298 K. Chemical shifts (δ ppm) were determined with tetramethylsilane (TMS) as internal reference. XANES spectroscopy was performed in the BL14W1 XAFS Beamline at Shanghai Synchrotron Radiation Facility (SSRF). Mössbauer spectrum was recorded at 298 K on a WissEl model using a radiation source of ^{57}Co(Pd). Infrared spectra were recorded as a KBr disc on a Nicolet 20 SXC FT-IR spectrophotometer. UV-vis spectra were recorded on a Cary 8454 UV-vis spectrophotometer (Agilent Technologies). Resonance Raman spectrum was measured using 416 nm excitation wavelength which is the first Stokes hydrogen Raman-shifted laser line produced from the third harmonic of Nd: YAG laser (power = 12 mW). Cyclic voltammetry was conducted on a Princeton Applied Research Model 273A Potentiostat, with glassy carbon as working electrode, SCE (DMF) or Ag/AgCl (DCM) as reference electrode, and platinum wire as counter electrode. Spectroelectrochemistry was performed by using Honeycomb Spectroelectrochemical Cell Kit (Pine Research), with platinum honeycomb electrode (an effective path length of 1.7 mm) and Ag/AgCl reference electrode. Thermal analyses were performed on a TGA Q50 (TA Instruments).

Synthesis and characterization of Fe, Ru, and Os porphyrin dialkylcarbene complexes

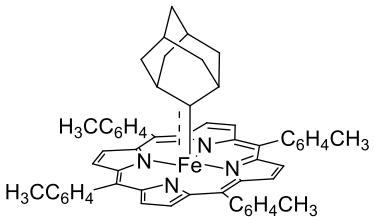
Method A: A DCM solution (1 mL) of [M(Por)] (M = Fe, Ru(CO), or Os(CO), 0.01 mmol) and aziadamantane (0.03 mmol) were irradiated by UV light (λ = 365 nm) at room temperature. After removing the volatiles at reduced pressure, the crude product was redissolved in hexane and purified by column chromatography with hexane/DCM (5:1 v/v) as eluent, and evaporation of solvent afforded the product as a red powder.

Method B: A DCM solution (1 mL) of [Fe^{III}(Por)Cl] (0.01 mmol) and aziadamantane (0.1 mmol) were irradiated by UV light (λ = 365 nm) for 30 min at 40 °C. Work-up procedure was the same as Method A.

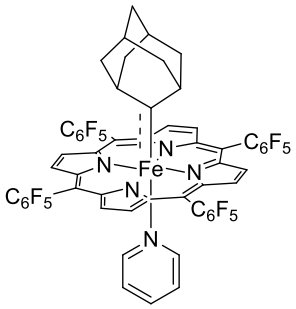
Method C: A DCM or $CDCl_3$ solution of **1a**·L was obtained by adding excess ligand into a DCM or $CDCl_3$ solution (0.5 mL) of **1a** (0.005 mmol) until no more spectral change was observed by UV-vis or ^{1}H NMR.



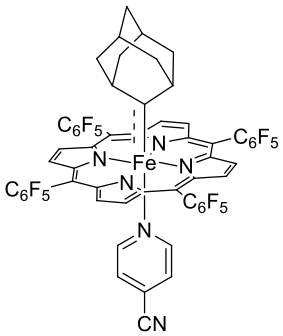
[Fe(TPFPP)(Ad)] (1a). Prepared by Method A (93% yield) or Method B (85% yield), purified by silica gel or neutral alumina column. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (s, H_β, 8H), 0.71 (s, H_e, 2H), 0.27 (s, H_d, 2H), -0.26 (d, *J* = 11.5 Hz, H_c, 4H), -1.30 (s, H_a, 2H), -1.52 (d, *J* = 11.5 Hz, H_b, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 413.57 (Fe=C), 147.71, 147.68, 147.34, 147.28, 146.86, 145.32, 145.22, 144.88, 144.80, 143.42, 143.33, 143.27, 143.19, 140.91, 140.78, 140.66, 139.08, 138.96, 138.82, 138.71, 136.61, 136.42, 136.30, 136.15, 132.73, 115.89, 115.85, 115.69, 115.65, 115.49, 104.88, 65.52, 35.12, 34.32, 25.93; ^{19}F NMR (376 MHz, $CDCl_3$) δ -136.82 (d, *J* = 18.9 Hz, 4F), -137.63 (d, *J* = 20.8 Hz, 4F), -152.19 (t, *J* = 20.2 Hz, 4F), -161.39 (s, 4F), -161.84 (s, 4F). UV-vis (DCM) λ_{max}/nm (log ε): 401 (5.12), 517 (4.03), 549 (4.18). HRMS (*m*/*z*): $[M]^+$ calcd. for $C_{54}H_{22}F_{20}N_4Fe$, 1162.0875; found, 1162.0778. Elemental analysis: Found (%): C, 57.33; H, 2.58; N, 4.52. Calcd for $C_{54}H_{22}F_{20}N_4Fe{\cdot}C_6H_{14}$: C, 57.71; H, 2.91; N, 4.49.



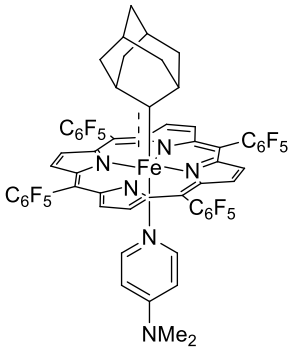
[Fe(TTP)(Ad)] (1b). Prepared by Method A (67% yield) or Method B (40% yield), purified by neutral or basic alumina column under an argon atmosphere. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 8H), 7.95 (s, 4H), 7.74 (s, 4H), 7.45 (s, 8H), 2.63 (s, 12H), 0.71 (s, 2H), 0.29 (s, 2H), -0.29 (d, *J* = 11.2 Hz, 4H), -1.34 (s, 2H), -1.50 (d, *J* = 11.6 Hz, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 394.92 (Fe=C), 146.81, 139.33, 137.02, 133.60, 132.28, 127.53, 120.77, 63.80, 33.77, 29.85, 26.29, 21.62. UV-vis (DCM) λ_{max}/nm (log ε): 413 (5.27), 520 (4.32), 549 (3.87). HRMS (*m*/*z*): $[M]^+$ calcd. for $C_{58}H_{50}N_4Fe$, 858.3385; found, 858.3197.



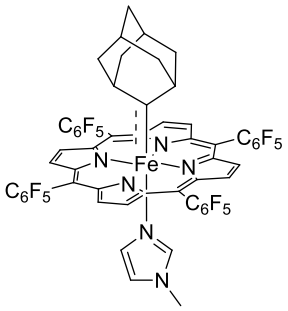
[Fe(TPFPP)(Ad)(Py)] (1a·Py**)**. Prepared by Method C with pyridine as ligand; solid sample obtained by slow evaporation of its hexane/$CDCl_3$ solution. ^{1}H NMR (400 MHz, $CDCl_3$, with excess pyridine) δ 8.22 (s, 8H), 0.60 (s, 2H), 0.15 (s, 2H), -0.34 (d, *J* = 11.5 Hz, 4H), -1.14 (s, 2H), -1.56 (d, *J* = 11.4 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 433.58 (Fe=C); ^{19}F NMR (376 MHz, $CDCl_3$) δ -137.40 (dd, *J* = 24.4, 7.9 Hz, 4F), -137.71 (dd, *J* = 24.3, 8.0 Hz, 4F), -153.00 (t, *J* = 20.9 Hz, 4F), -162.27 (td, *J* = 25.9, 8.4 Hz, 8F). UV-vis (DCM) λ_{max}/nm (log ε): 419 (5.07), 530 (4.03), 550 (sh).



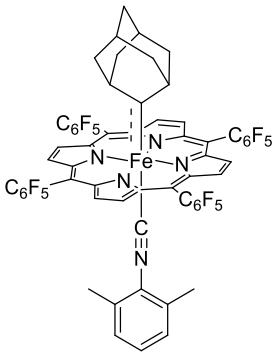
[Fe(TPFPP)(Ad)(CNPy)] (1a·CNPy**)**. Prepared by Method C with 4-cyanopyridine as ligand. ^{1}H NMR (400 MHz, $CDCl_3$, with excess 4-cyanopyridine) δ 8.36 (s, 8H), 0.69 (s, 2H), 0.24 (s, 2H), -0.26 (d, *J* = 11.6 Hz, 4H), -1.13 (s, 2H), -1.52 (d, *J* = 11.1 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 433.85 (Fe=C); ^{19}F NMR (376 MHz, $CDCl_3$) δ -137.50 (dd, *J* = 24.3, 7.6 Hz, 4F), -137.99 (dd, *J* = 24.2, 7.6 Hz, 4F), -152.68 (t, *J* = 20.9 Hz, 4F), -162.01 (dd, *J* = 30.1, 14.3 Hz, 8F). UV-vis (DCM) λ_{max}/nm (log ε): 417 (5.09), 528 (4.17), 550 (sh).



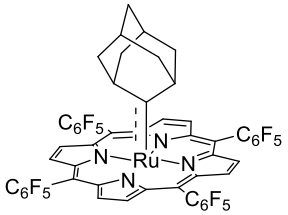
[Fe(TPFPP)(Ad)(NMe$_2$Py)] (1a·NMe$_2$Py**)**. Prepared by Method C with 4-dimethylaminopyridine as ligand. ^{1}H NMR (500 MHz, $CDCl_3$, with excess 4-dimethylaminopyridine) δ 8.26 (s, 8H), 0.69 (s, 2H), 0.24 (s, 2H), -0.26 (d, *J* = 10.8 Hz, 4H), -1.02 (s, 2H), -1.46 (d, *J* = 10.8 Hz, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 433.39 (Fe=C); ^{19}F NMR (376 MHz, $CDCl_3$) δ -136.91 – -137.94 (m, 8F), -153.35 (t, *J* = 21.0 Hz, 4F), -162.07 – -162.88 (m, 8F). UV-vis (DCM) λ_{max}/nm (log ε): 425 (5.08), 533 (4.10), 558 (sh).



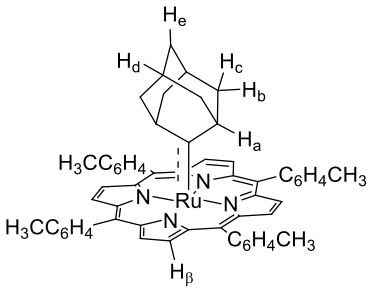
[Fe(TPFPP)(Ad)(MeIm)] (1a·MeIm**)**. Prepared by Method C with 1-methylimidazole as ligand. ^{1}H NMR (400 MHz, $CDCl_3$, with excess 1-methylimidazole) δ 8.25 (s, 8H), 0.70 (s, 2H), 0.23 (s, 2H), -0.25 (d, *J* = 11.8 Hz, 4H), -1.02 (s, 2H), -1.50 (d, *J* = 11.1 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 433.36 (Fe=C); ^{19}F NMR (376 MHz, $CDCl_3$) δ -137.28 (dd, *J* = 24.4, 7.9 Hz, 4F), -137.84 (dd, *J* = 24.3, 8.0 Hz, 4F), -153.30 (t, *J* = 20.8 Hz, 4F), -161.84 – -162.91 (m, 8F). UV-vis (DCM) λ_{max}/nm (log ε): 414 (5.08), 528 (4.08), 575 (sh).



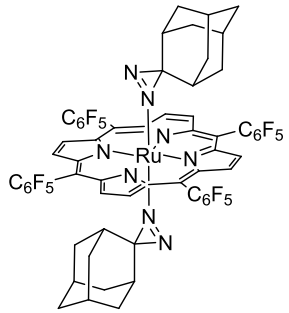
[Fe(TPFPP)(Ad)(ArNC)] (1a·ArNC**)**. Prepared by Method C with 2,6-dimethylphenyl isocyanide as ligand. ^{1}H NMR (400 MHz, $CDCl_3$, with excess 2,6-dimethylphenyl isocyanide) δ 8.37 (s, 8H), 0.66 (s, 2H), 0.20 (s, 2H), -0.24 (d, *J* = 11.5 Hz, 4H), -1.06 (s, 2H), -1.61 (d, *J* = 11.5 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 444.78 (Fe=C); ^{19}F NMR (376 MHz, $CDCl_3$) δ -137.34 (dd, *J* = 23.8, 9.7 Hz, 8F), -153.18 (t, *J* = 20.8 Hz, 4F), -162.37 (td, *J* = 29.0, 8.2 Hz, 8F). UV-vis (DCM) λ_{max}/nm (log ε): 434 (5.11), 542 (4.22).



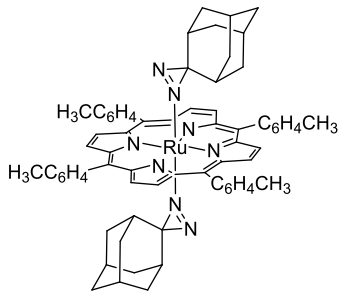
[Ru(TPFPP)(Ad)] (2a). Prepared by Method A in 88% yield, purified by silica gel column. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 8H), 0.57 (s, 2H), 0.18 (s, 2H), -0.32 (d, *J* = 11.6 Hz, 4H), -1.55 (d, *J* = 11.9 Hz, 4H), -1.79 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 369.55 (Ru=C), 147.85, 147.40, 145.40, 144.89, 143.30, 140.76, 138.93, 136.35, 131.93, 115.97, 115.81, 115.61, 106.15, 61.21, 34.89, 34.47, 25.49; ^{19}F NMR (376 MHz, $CDCl_3$) δ -137.12 (dd, *J* = 23.9, 7.8 Hz, 4F), -137.68 (dd, *J* = 24.2, 7.6 Hz, 4F), -152.40 (t, *J* = 20.9 Hz, 4F), -161.57 (td, *J* = 23.0, 8.3 Hz, 4F), -161.94 (td, *J* = 23.6, 8.5 Hz, 4F). UV-vis (DCM) λ_{max}/nm (log ε): 393 (5.00), 412 (5.16), 511 (4.20), 541 (4.27). HRMS (*m*/*z*): $[M]^+$ calcd. for $C_{54}H_{22}F_{20}N_4Ru$, 1208.0569; found, 1208.0411. Elemental analysis: Found (%): C, 55.29; H, 2.44; N, 4.67. Calcd for $C_{54}H_{22}F_{20}N_4Ru{\cdot}C_6H_{14}$: C, 55.69; H, 2.80; N, 4.33.



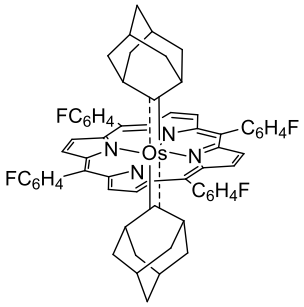
[Ru(TTP)(Ad)] (2b). Prepared by Method A in 95% yield, purified by silica gel column. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (s, H_β, 8H), 7.98 (d, *J* = 7.5 Hz, $C_6H_4CH_3$, 4H), 7.83 (d, *J* = 7.5 Hz, $C_6H_4CH_3$, 4H), 7.46 (dd, *J* = 14.5, 7.7 Hz, $C_6H_4CH_3$, 8H), 2.64 (s, $C_6H_4CH_3$, 12H), 0.56 (s, H_e, 2H), 0.17 (s, H_d, 2H), -0.37 (d, *J* = 11.3 Hz, H_c, 4H), -1.60 (d, *J* = 11.6 Hz, H_b, 4H), -1.81 (s, H_a, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 353.72 (Ru=C), 144.94, 139.61, 136.92, 134.07, 133.55, 131.54, 127.51, 127.26, 122.54, 59.54, 35.24, 33.88, 29.86, 25.75, 21.64. UV-vis (DCM) λ_{max}/nm (log ε): 400 (sh), 423 (5.00), 517 (4.02), 538 (sh). HRMS (*m*/*z*): $[M]^+$ calcd. for $C_{58}H_{50}N_4Ru$, 904.3079; found, 904.3061. Elemental analysis: Found (%): C, 77.04; H, 6.42; N, 5.81. Calcd for $C_{58}H_{50}N_4Ru{\cdot}0.5C_6H_{14}$: C, 77.35; H, 6.07; N, 5.91.



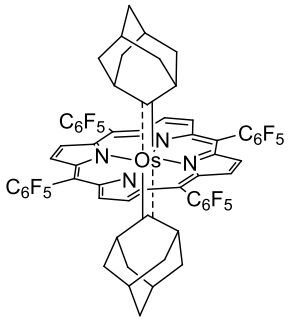
[Ru(TPFPP)(AdN_2)$_2$] (2az). Prepared by Method A in 5% yield, purified by silica gel column. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (s, 8H), 0.95 – 0.84 (m, 8H), 0.53 (d, *J* = 12.8 Hz, 4H), 0.39 – 0.23 (m, 8H), -1.59 (d, *J* = 12.2 Hz, 4H), -2.76 (s, 4H); ^{13}C NMR (126 MHz, CD_2Cl_2) δ 147.92, 147.90, 145.97, 145.95, 144.56, 143.53, 143.42, 143.32, 141.50, 141.43, 141.40, 141.36, 141.28, 139.27, 139.16, 139.04, 137.27, 137.16, 137.03, 132.64, 116.76, 116.73, 116.60, 116.57, 116.44, 105.54, 44.21, 36.11, 34.19, 32.73, 32.70, 30.25, 26.86, 26.10; ^{19}F NMR (376 MHz, $CDCl_3$) δ -137.24 (dd, *J* = 24.2, 8.2 Hz, 8F), -152.71 (t, *J* = 21.0 Hz, 4F), -162.08 (td, *J* = 23.5, 23.0, 8.3 Hz, 8F). UV-vis (DCM) λ_{max}/nm (log ε): 393 (4.63), 412 (5.26), 511 (4.11).



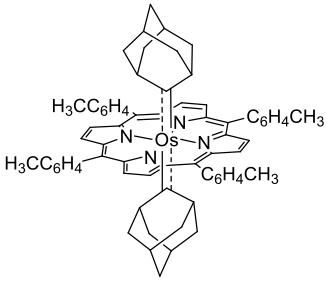
[Ru(TTP)(AdN_2)$_2$] (2bz). Prepared by Method A in 2% yield, purified by silica gel column. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (s, 8H), 7.91 (d, *J* = 7.8 Hz, 8H), 7.46 (d, *J* = 7.8 Hz, 8H), 2.66 (s, 12H), 0.99 (s, 8H), 0.51 (d, *J* = 12.5 Hz, 4H), 0.33 (d, *J* = 11.1 Hz, 8H), -1.43 (d, *J* = 12.1 Hz, 4H), -2.85 (s, 4H).



[Os(4-F-TPP)(Ad)$_2$] (3a). Prepared by Method A in 30% yield, purified by neutral alumina column. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 8H), 7.96 (dd, *J* = 8.5, 5.5 Hz, 8H), 7.36 (t, *J* = 8.6 Hz, 8H), 0.45 (s, 4H), -0.01 (s, 4H), -0.55 (d, *J* = 12.0 Hz, 8H), -1.72 (d, *J* = 11.9 Hz, 8H), -1.78 (s, 4H); ^{13}C NMR (101 MHz, C_6D_6) δ 351.28 (Os=C), 164.24, 161.79, 145.06, 138.47, 135.57, 135.49, 131.81, 113.98, 113.77, 53.28, 33.54, 32.62, 30.21, 26.07; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.68 (p, *J* = 6.1 Hz, 4F). UV-vis (DCM) λ_{max}/nm (log ε): 377 (sh), 412 (4.50), 534 (3.45), 564 (sh). HRMS (*m*/*z*): $[M+H]^+$ calcd. for $C_{64}H_{53}F_4N_4Os$, 1145.3821; found, 1145.3735. Elemental analysis: Found (%): C, 68.62; H, 5.47; N, 4.61. Calcd for $C_{64}H_{52}F_4N_4Os \cdot 1.5C_6H_{14}$: C, 68.90; H, 5.78; N, 4.40.



[Os(TPFPP)(Ad)$_2$] (3b). Prepared by Method A in 26% yield, purified by neutral alumina column. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 8H), 0.48 (s, 4H), -0.01 (s, 4H), -0.46 (d, *J* = 11.3 Hz, 8H), -1.49 (s, 4H), -1.57 (d, *J* = 12.1 Hz, 8H); ^{13}C NMR (126 MHz, C_6D_6) δ 367.36 (Os=C), 147.98, 146.92, 146.04, 145.29, 144.08, 143.03, 140.94, 138.84, 136.84, 136.84, 132.65, 132.07, 53.55, 34.26, 34.02, 27.43; ^{19}F NMR (376 MHz, $CDCl_3$) δ -137.50 (dd, *J* = 24.2, 8.2 Hz, 8F), -152.82 (t, *J* = 20.8 Hz, 4F), -162.07 (td, *J* = 23.7, 8.2 Hz, 8F). UV-vis (DCM) λ_{max}/nm (log ε): 393 (4.55), 447 (3.84), 473 (4.10). HRMS (*m*/*z*): $[M+H]^+$ calcd. for $C_{64}H_{37}F_{20}N_4Os$, 1433.2314; found, 1433.2195.



[Os(TTP)(Ad)$_2$] (3c). Prepared by Method A in 12% yield, purified by neutral alumina column. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 8H), 7.90 (d, *J* = 7.8 Hz, 8H), 7.46 (d, *J* = 7.7 Hz, 8H), 2.65 (s, 12H), 0.43 (s, 4H), -0.03 (s, 4H), -0.58 (d, *J* = 10.9 Hz, 8H), -1.71 (d, *J* = 11.9 Hz, 8H), -1.79 (s, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 350.39 (Os=C), 144.35, 139.69, 136.65, 134.07, 131.08, 127.20, 122.30, 52.60, 32.20, 29.84, 25.67, 21.63. UV-vis

(DCM) λ_{max}/nm (log ε): 400 (4.51), 428 (sh), 456 (4.20). HRMS (*m*/*z*): $[M+H]^+$ calcd. for $C_{68}H_{65}N_4Os$, 1129.4826; found, 1129.4802.

Single-crystal X-ray diffraction analysis

Diffraction-quality crystals were obtained by the following methods: **1b** by slow evaporation of its pentane/$CDCl_3$ solution; **1a**·Py by slow evaporation of a hexane/DCM/pyridine solution of **1a**; **2b**·MeOH by layering of MeOH over a DCM solution of **2b**; **2az** by slow evaporation of its hexane/DCM solution; **3a** by slow evaporation of its THF solution. The crystal data and structural refinement are summarized in Tables S1-S5. The CCDC numbers of **1b**, **1a**·Py, **2b**·MeOH, **2az**, and **3a** are CCDC 1854830, 1943318, 1854823, 1943319, and 1943321.

Measurement of binding constants between 1a/2b and pyridine

A DCM solution of **1a** ([**1a**] = 5×10^{-5} M) was titrated with pyridine at 298 K, during which the absorbance change (ΔA) of the Soret band (419 nm) was recorded by UV-vis spectrometry. A nonlinear plot of ΔA vs [Py] was fitted with the following equation and the binding constant K_{py} was determined accordingly:

$$\Delta A = \frac{\Delta\varepsilon[\mathbf{1a}][\mathrm{Py}]}{\frac{1}{K_{py}} + [Py]}$$

in which

$$\Delta\varepsilon = \varepsilon(\mathbf{1a}\cdot\mathrm{Py}) - \varepsilon(\mathbf{1a})$$

The binding constant of **2b** was measured similarly by monitoring at 423 nm.

UV-vis spectroelectrochemistry

Spectroelectrochemistry was performed with a DMF solution of **1a** (10^{-5} M) containing 0.1 M $(Bu_4N)PF6$ as electrolyte. When a voltage of 0.6 V or –1.1 V (V vs Ag/AgCl, same as below) was applied to the solution, its UV-vis spectra were recorded until no more changes were observed for 30 s. To test the reversibility, 0 V was then applied and UV-vis spectra were recorded until no more changes.

Oxidation at 0.6 V. Isosbestic points observed at 293, 317, 399, 429, 511 and 563 nm; irreversible; when holding the voltage at 0.6 V, the oxidized species decomposed after 2–3 min.

Reduction at –1.1 V. Isosbestic points observed at 400, 428, 555 and 561 nm; reversible.

General procedures for studies on stoichiometric carbene transfer reactions of 1a and 2a

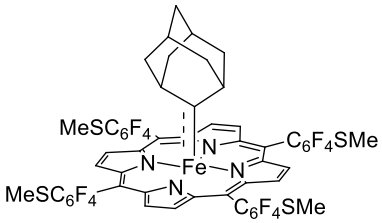
Thermal reactions. Complex **1a** or **2a** (0.005 mmol) was added into a DCE (0.5 mL) solution containing substrate (0.5 mmol) with or without axial ligand (0.01 mmol; for binding to the complex), and the resulting solution was stirred at 80 °C for 24 h. The reaction mixture was analyzed by TLC, ^{1}H NMR, and GC-MS.

For substrates styrene, 1-octene, 1,4-cyclohexadiene, benzene, $PhNH_2$, PhSH, PhNO, PhSMe, PPh_3, and axial ligands pyridine, 1-methylimidazole, no conversion of **1a** or **2a** and no formation of new product were observed.

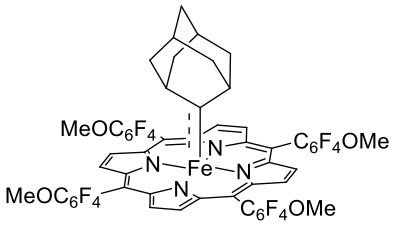
Photochemical reactions. Complex **1a** or **2a** (0.005 mmol) was added into a benzene (0.5 mL) solution of styrene (0.5 mmol), and the resulting solution was stirred at room temperature, 50 °C, or 80 °C for 24 h under UV irradiation (λ > 360 nm). No conversion of **1a** or **2a** and no formation of new product were observed according to TLC, ^{1}H NMR, or GC-MS analysis.

Procedure for intermolecular reactions between 1a and anionic nucleophiles

A DCE solution (1 mL) of **1a** (0.005 mmol) and NaXMe (X = S or O, 0.1 mmol) were refluxed for 24 h. After **1a** was fully consumed according to TLC analysis, the solution was filtered and volatiles were removed at reduced pressure. The crude product was redissolved in hexane and loaded onto a silica gel column. The bright red band was collected with hexane/DCM (3:1 v/v) as eluent, and evaporation of solvent afforded the product (**1c** or **1d**) as a red powder.



[Fe(TFSPP)(Ad)] (1c). 91% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 8H), 2.80 (s, 12H), 0.70 (s, 2H), 0.26 (s, 2H), -0.27 (d, *J* = 11.8 Hz, 4H), -1.29 (s, 2H), -1.51 (d, *J* = 11.9 Hz, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 413.04 (Fe=C), 147.27, 146.62, 145.27, 144.91, 132.67, 120.00, 119.84, 119.69, 117.69, 117.54, 117.39, 105.66, 65.31, 35.21, 34.24, 25.99, 17.87; ^{19}F NMR (376 MHz, $CDCl_3$) δ -135.14 (dd, *J* = 24.7, 11.8 Hz, 4F), -135.63 (dd, *J* = 25.1, 11.9 Hz, 4F), -137.46 (dd, *J* = 24.7, 11.9 Hz, 4F), -138.15 (dd, *J* = 25.1, 11.8 Hz, 4F). UV-vis (DCM) λ_{max}/nm (log ε): 405 (5.24), 518 (4.16), 550 (4.22). HRMS (*m*/*z*): $[M]^+$ calcd. for $C_{58}H_{34}F_{16}N_4S_4Fe$, 1274.0760; found, 1274.0672.



[Fe(TFOPP)(Ad)] (1d). 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 8H), 4.37 (s, 12H), 0.69 (s, 2H), 0.25 (s, 2H), -0.29 (d, *J* = 11.4 Hz, 4H), -1.31 (s, 2H), -1.52 (d, *J* = 11.6 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 411.48 (Fe=C), 147.96, 147.58, 147.00, 145.41, 145.13, 142.12, 141.99, 141.85, 139.53, 139.17, 132.60, 114.12, 113.93, 113.73, 105.49, 65.12, 35.25, 34.14, 29.85, 26.01; ^{19}F NMR (376 MHz, $CDCl_3$) δ -138.93 (dd, *J* = 23.1, 8.0 Hz, 4F), -139.66 (dd, *J* = 23.3, 7.9 Hz, 4F), -158.02 (dd, *J* = 23.2, 8.4 Hz, 4F), -158.45 (dd, *J* = 23.5, 8.5 Hz, 4F). UV-vis (DCM) λ_{max}/nm (log ε): 404 (5.26), 517 (4.23), 549 (4.31). HRMS (*m*/*z*): $[M]^+$ calcd. for $C_{58}H_{34}F_{16}N_4O_4Fe$, 1210.1674; found, 1210.1581.

General procedure for studies on stoichiometric carbene transfer reactions of 3a

Complex **3a** (0.005 mmol) was stirred in neat substrate (for liquid reagents) or a DCE (0.5 mL) solution of substrate (0.5 mmol) at certain temperature for 24 h. When conversion of **3a** was detected, the reaction mixture was analyzed by ^{1}H NMR and GC-MS.

Procedures for carbene substitution experiments

Starting from M=CPh$_2$ complexes. A DCM (1 mL) solution of [Fe(TPFPP)(CPh_2)] or [Os(TPFPP)(CPh_2)$_2$] (0.005 mmol) and aziadamantane (0.05 mmol) was stirred at room temperature under UV irradiation (λ = 365 nm) for 2 h. The crude mixture was analyzed by TLC, ^{1}H NMR, and GC-MS.

Starting from M=Ad complexes. A DCM (1 mL) solution of **1a** or **3a** (0.005 mmol) and Ph_2CN_2 (0.05 mmol) was stirred at room temperature or 40 °C for 12 h. No conversion of **1a** or **3a** and no formation of [Fe(TPFPP)(CPh_2)] or [Os(TPFPP)(CPh_2)$_2$] were observed by TLC or ^{1}H NMR. Formation of the azine product was detected by GC-MS in the reaction of **1a**.

Experimental procedures for catalytic intermolecular donor-donor carbene transfer reactions

Typical procedure for cyclopropanation and X–H (X = S, N, O) insertion reactions of CAr_2 carbenes. To a DCM (0.5 mL) solution containing 2 mmol of substrate and 0.004 mmol of **1a** was added a DCM (0.5 mL) solution of Ar_2CN_2 (0.2 mmol) in one portion. The reaction mixture was stirred at 40 °C for 12 h, during which time Ar_2CN_2 was fully consumed according to TLC monitoring, and all the volatiles were removed under reduced pressure. Product yield and recovery of **1a** were determined by ^{1}H NMR with PhTMS as internal standard. The carbene transfer product was purified by silica gel column and the spectroscopic data matched the literature data (cyclopropanation;[5] S–H insertion;[6] N–H insertion;[7] O–H insertion[8]).

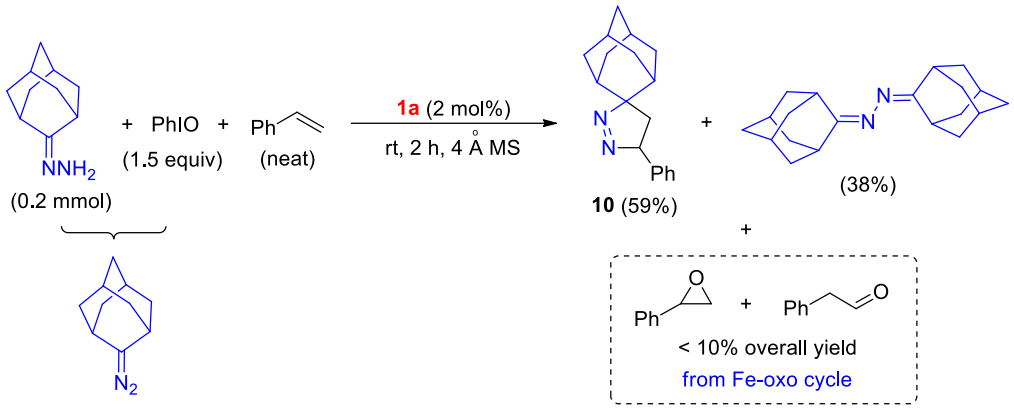
Experimental procedure for C–H insertion reactions of CPh_2 carbene. To a DCE (0.5 mL) solution containing 2 mmol of substrate and 0.01 mmol of **1a** was added a DCE (0.5 mL) solution of Ph_2CN_2 (0.2 mmol) dropwise over 3 h. The solution was stirred at 80 °C until Ph_2CN_2 was fully consumed according to TLC monitoring, and all the volatiles were removed under reduced pressure. Product yield and recovery of **1a** were determined by ^{1}H NMR with PhTMS as internal standard. The carbene transfer product was purified by silica gel column and the spectroscopic data matched the literature data.[9]

Typical procedure of catalyst screening for the cyclopropanation of CPh_2 carbene with styrene. To a DCM (0.5 mL) solution containing 2 mmol of styrene and 0.004 mmol of catalyst was added a DCM (0.5 mL) solution of Ph_2CN_2 (0.2 mmol) in one portion. The reaction mixture was stirred at 40 °C for 12 h, during which time Ph_2CN_2 was fully consumed according to TLC monitoring. In a control experiment where no catalyst was added, prolonged reaction time (36 h) was required for the full conversion of diazo compound. Yield of **5a** was determined by ^{1}H NMR with PhTMS as internal standard.

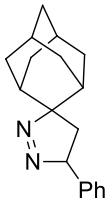
Typical Procedure for Cyclopropanation of $C(Ph)CF_3$ Carbene with Styrene. To a DCM (0.5 mL) solution containing 2 mmol of styrene and 0.004 mmol of **1a** was added a DCM (0.5 mL) solution of $N_2C(Ph)CF_3$ (0.2 mmol) in one portion. The reaction mixture was stirred at 40 °C for 12 h, during which time $N_2C(Ph)CF_3$ was fully consumed according to TLC monitoring, and all the volatiles were removed under reduced pressure. Product yield, dr ratio, and recovery of **1a** were determined by ^{1}H NMR with PhTMS as internal standard. The carbene transfer product was purified by silica gel column and the spectroscopic data matched the literature data.[10]

Typical procedure for cyclopropanation of C(Ph)Me carbene with syrene. To a DCM (0.5 mL) solution containing 2 mmol of styrene, 0.004 mmol of **1a**, and acetophenone hydrazone (0.2 mmol) was added Ag_2O (0.3 mmol) in one portion. The reaction mixture was stirred at 40 °C for 2 h, during which time acetophenone hydrazone was fully consumed according to TLC monitoring, and all the volatiles were removed under reduced pressure. Product yield, dr ratio, and recovery of **1a** were determined by ^{1}H NMR with PhTMS as internal standard. The carbene transfer product was purified by silica gel column and the spectroscopic data matched the literature data.[11]

Experimental procedures for the studies on catalytic intermolecular dialkylcarbene transfer reactions



To a styrene (1 mL) solution containing 0.004 mmol of **1a**, 0.2 mmol of 2-adamantanone hydrazine,[12] and 500 mg of 4 Å molecular sieves was added 0.3 mmol of PhIO in one portion. The reaction mixture was stirred at room temperature for 2 h, during which time 2-adamantanone hydrazone was fully consumed according to TLC monitoring, and all the volatiles were removed under reduced pressure. Product yield and recovery of **1a** were determined by ^{1}H NMR with PhTMS as internal standard, and the major product **10** was purified by silica gel column.



5'-Phenyl-4',5'-dihydrospiro[adamantane-2,3'-pyrazole (10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 8.1, 6.6 Hz, 2H), 7.33 – 7.27 (m, 1H), 7.27 – 7.17 (m, 2H), 5.38 (t, *J* = 9.1 Hz, 1H), 3.04 (d, *J* = 12.5 Hz, 1H), 2.62 (d, *J* = 12.6 Hz, 1H), 2.31 (dd, *J* = 13.0, 9.0 Hz, 1H), 2.13 (t, *J* = 3.2 Hz, 1H), 1.91 (s, 1H), 1.90 – 1.63 (m, 10H), 1.23 (dd, *J* = 13.0, 9.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.17, 128.86, 127.62, 127.29, 98.61, 90.14, 38.39, 38.17, 38.09, 36.50, 36.00, 35.11, 34.49, 33.98, 28.00, 27.17. HRMS (*m*/*z*): $[M+H]^+$ calcd. for $C_{18}H_{23}N_2$, 267.1861; found, 267.1855.

Computational details

All calculations were performed using the G09 program package.[13] The real vibrational frequencies of optimized structures were computed to confirm that all the optimized structures are potential energy minima. For the calculation of small free carbene molecules, hybrid B3LYP[14] functional and large Weigend's def2-TZVPP[15] basis set were employed, using the same method as that reported in the literature (the MOs of NHC and CAAC free carbenes have been used for comparison).[16]

For the calculation of relatively large Fe porphyrin carbene systems, inclusion of non-covalent interactions is important. Therefore, we used the hybrid functional B3LYP,[14] with dispersion corrections in revision three (D3)[17] due to its accuracy and wide applications in describing dispersion interactions.[18] The DFT-D3 method has been proved to provide reliable computed interaction energies as compared to the spin-component-scaled (SCS)-MP2 method for large complexes.[19] The valence atomic orbital of Os was described by LANL2DZ basis set and the effective core potentials (ECPs) proposed by Hay and Wadt were employed.[20] The 6-31G* basis set[21] was used for iron, hydrogen, carbon, oxygen, and nitrogen atoms. Solvent effects were taken into account using the Solvation Model based on Density (SMD) with CH_2Cl_2 as solvent.[22]

The initial geometry guess used for the optimization on complex **1b**/**3a** was directly obtained from its X-ray crystal structure. For the comparison among Fe porphyrins with Ad, CPh_2, $C(Ph)CO_2Et$, CMe_2, or C^iPr_2 as the carbene ligand, we utilized a commonly used simplification of the porphyrin ligand, i.e., with the *meso*-substituents of porphyrins replaced by hydrogens.[23] The optimized structure of the triplet/quintuplet for free/metal carbene complex was obtained by performing an unrestricted DFT (UDFT) calculation. Gibbs free energies and enthalpies were calculated under standard conditions (p = 1 atm, T = 298 K) and are unscaled. The PEC (potential energy curve) was obtained from a relax scan by fixing the angel of the carbene group.

To calculate the absorption spectra, TDDFT method with functional M06 has been used at the calculation level of M06/LanL2DZ for Os and 6-31g* for other atoms/SMD(CH_2Cl_2). First 30 excited states have been included in the simulated spectra. Gaussian functions have been adopted to simulate the absorption spectrum according to the equation:[24]

$$\varepsilon\left(\vartheta^{'}\right) = \frac{2.175.10^{8} L.mol^{-1}cm^{-2}}{\Delta_{1/2}\vartheta^{'}} f.\exp[-2.772(\frac{\vartheta^{'} - \vartheta^{'}_{i\to f}}{\Delta_{1/2}\vartheta^{'}})^{2}]$$

where the values of f and $\vartheta'_{i\to f}$ are derived from a quantum mechanical calculation. $\Delta_{1/2}\vartheta'$, which is the full-width half-maximum (FWHM) of the band, was set as 3000 cm^{-1} when convoluting the spectra.

III. Tables and figures

Table S1 Crystal data and structure refinement for **1b**

$C_{58}H_{50}FeN_4 \cdot CDCl_3$
$M_r = 979.24$
Triclinic, $P\overline{1}$
$a = 11.3588$ (11) Å
$b = 13.5043$ (14) Å
$c = 16.5422$ (15) Å
$\alpha = 85.786$ (3)°
$\beta = 84.240$ (3)°
$\gamma = 70.986$ (3)°
$V = 2384.6$ (4) Å^3

$Z = 2$
$F(000) = 1020$
$D_x = 1.364$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 445 reflections
$\theta = 2.8$–$22.5°$
$\mu = 0.53$ mm^{-1}
$T = 150$ K
Rod, red
0.31 × 0.14 × 0.08 mm

Data collection

Bruker D8 VENTURE FIXED-CHI PHOTON 100 CMOS diffractometer
Radiation source: IμS HB micro-focus sealed tube
Detector resolution: 1024 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan *SADABS* 2014/5 (Sheldrick, 2014)
$T_{min} = 0.654$, $T_{max} = 0.745$

35866 measured reflections
8671 independent reflections
6460 reflections with $I > 2\sigma(I)$
$R_{int} = 0.066$
$\theta_{max} = 25.4°$, $\theta_{min} = 2.3°$
$h = -13 \rightarrow 13$
$k = -16 \rightarrow 16$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.131$
$S = 1.03$
8671 reflections
572 parameters
0 restraints

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0275P)^2 + 5.0744P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.36$ e Å^{-3}
$\Delta\rho_{min} = -0.46$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Table S2 Crystal data and structure refinement for **1a**·Py

$C_{59}H_{27}F_{20}FeN_5$	$Z = 2$
$M_r = 1241.70$	$F(000) = 1244$
Triclinic, $P\bar{1}$	$D_x = 1.635$ Mg m^{-3}
$a = 10.5317$ (15) Å	Ga $K\alpha$ radiation, $\lambda = 1.34138$ Å
$b = 14.347$ (2) Å	Cell parameters from 1213 reflections
$c = 17.434$ (3) Å	$\theta = 3.1$–$53.2°$
$\alpha = 76.710$ (5)°	$\mu = 2.36$ mm^{-1}
$\beta = 80.147$ (4)°	$T = 173$ K
$\gamma = 84.826$ (4)°	Plate, red
$V = 2522.4$ (6) Å^3	0.22 × 0.19 × 0.11 mm

Data collection

'Bruker D8 VENTURE KAPPA goniometer PHOTON II CPAD' diffractometer	$T_{min} = 0.398$, $T_{max} = 0.750$
Radiation source: Excillum MetalJet D2	56653 measured reflections
Detector resolution: 10.24 pixels mm^{-1}	17368 independent reflections
φ and ω scans	11105 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan *SADABS2014*/5 - Bruker AXS area detector scaling and absorption correction	$R_{int} = 0.086$
	$\theta_{max} = 53.3°$, $\theta_{min} = 2.3°$
	$h = -12 \rightarrow 12$
	$k = -17 \rightarrow 17$
	$l = -20 \rightarrow 20$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.090$	$w = 1/[\sigma^2(F_o^2) + (0.1507P)^2 + 1.4068P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.278$	$(\Delta/\sigma)_{max} = 0.004$
$S = 1.08$	$\Delta\rho_{max} = 0.62$ e Å^{-3}
17368 reflections	$\Delta\rho_{min} = -0.58$ e Å^{-3}
1350 parameters	Absolute structure: Refined as an inversion twin.
2893 restraints	Absolute structure parameter: 0.450 (12)

Table S3 Crystal data and structure refinement for **2b**·MeOH

$C_{59}H_{54}N_4ORu \cdot CH_4O \cdot CH_2CL_2$	$F(000) = 2192$
$M_r = 1053.10$	$D_x = 1.402$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 11.5545$ (10) Å	Cell parameters from 531 reflections
$b = 17.3432$ (16) Å	$\theta = 2.8–22.5°$
$c = 25.028$ (2) Å	$\mu = 0.47$ mm^{-1}
$\beta = 95.757$ (2)°	$T = 150$ K
$V = 4990.1$ (8) Å^3	Plate, purple
$Z = 4$	0.34 × 0.22 × 0.03 mm

Data collection

Bruker D8 VENTURE FIXED-CHI PHOTON 100 CMOS diffractometer	148426 measured reflections
	9219 independent reflections
	7352 reflections with $I > 2\sigma(I)$
Radiation source: IμS HB micro-focus sealed tube	$R_{int} = 0.122$
Detector resolution: 10.24 pixels mm^{-1}	$\theta_{max} = 25.5°$, $\theta_{min} = 2.2°$
φ and ω scans	$h = -13 \rightarrow 13$
Absorption correction: multi-scan *SADABS* 2014/5 (Sheldrick, 2014)	$k = -20 \rightarrow 20$
	$l = -29 \rightarrow 30$
$T_{min} = 0.381$, $T_{max} = 0.490$	

Refinement

Refinement on F^2	Hydrogen site location: mixed
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.049$	$w = 1/[\sigma^2(F_o^2) + (0.0207P)^2 + 12.8644P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.098$	$(\Delta/\sigma)_{max} = 0.001$
$S = 1.06$	$\Delta\rho_{max} = 0.89$ e Å^{-3}
9219 reflections	$\Delta\rho_{min} = -0.53$ e Å^{-3}
615 parameters	
0 restraints	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Table S4 Crystal data and structure refinement for **2az**

$C_{64}H_{36}F_{20}N_8Ru \cdot 0.25(C_6H_{14})$	$F(000) = 5700$
$M_r = 1419.62$	$D_x = 1.537$ Mg m^{-3}
Monoclinic, $C2/c$	Ga $K\alpha$ radiation, $\lambda = 1.34138$ Å
$a = 24.815$ (6) Å	Cell parameters from 817 reflections
$b = 20.891$ (5) Å	$\theta = 3.1–53.2°$
$c = 24.043$ (5) Å	$\mu = 2.03$ mm^{-1}
$\beta = 100.174$ (7)°	$T = 149$ K
$V = 12268$ (5) Å^3	Ribbon, red
$Z = 8$	0.33 × 0.10 × 0.02 mm

Data collection

'Bruker D8 VENTURE KAPPA goniometer PHOTON II CPAD' diffractometer	$T_{min} = 0.045$, $T_{max} = 0.171$
Radiation source: Excillum MetalJet D2	69230 measured reflections
Detector resolution: 10.24 pixels mm^{-1}	10731 independent reflections
φ and ω scans	7204 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan *SADABS2014*/5 - Bruker AXS area detector scaling and absorption correction	$R_{int} = 0.177$
	$\theta_{max} = 53.2°$, $\theta_{min} = 2.4°$
	$h = -28 \rightarrow 29$
	$k = -24 \rightarrow 22$
	$l = -20 \rightarrow 28$

Refinement

Refinement on F^2	H-atom parameters constrained
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.2P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.109$	$(\Delta/\sigma)_{max} = 0.001$
$wR(F^2) = 0.325$	$\Delta\rho_{max} = 1.57$ e Å^{-3}
$S = 1.19$	$\Delta\rho_{min} = -1.96$ e Å^{-3}
10731 reflections	Extinction correction: *SHELXL2014*/7 (Sheldrick 2014, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
839 parameters	Extinction coefficient: 0.00057 (8)
6 restraints	
Hydrogen site location: inferred from neighbouring sites	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Table S5 Crystal data and structure refinement for **3a**

$C_{64}H_{52}F_4N_4Os$	$Z = 1$
$M_r = 1143.29$	$F(000) = 576$
Triclinic, $P\overline{1}$	$D_x = 1.487$ Mg m^{-3}
$a = 11.0536$ (7) Å	Ga $K\alpha$ radiation, $\lambda = 1.34138$ Å
$b = 11.1353$ (7) Å	Cell parameters from 1172 reflections
$c = 11.8926$ (7) Å	$\theta = 2.8$–$66.1°$
$\alpha = 97.460$ (3)°	$\mu = 3.50$ mm^{-1}
$\beta = 108.927$ (4)°	$T = 173$ K
$\gamma = 107.647$ (3)°	Ribbon, red
$V = 1276.53$ (14) Å^3	0.06 × 0.03 × 0.01 mm

Data collection

'Bruker D8 VENTURE KAPPA goniometer PHOTON II CPAD' diffractometer	$T_{min} = 0.502$, $T_{max} = 0.751$
Radiation source: Excillum MetalJet D2	8354 measured reflections
Detector resolution: 7.3910 pixels mm^{-1}	4387 independent reflections
φ and ω scans	4011 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan	$R_{int} = 0.052$
SADABS2014/5 - Bruker AXS area detector scaling and absorption correction	$\theta_{max} = 53.0°$, $\theta_{min} = 3.5°$
	$h = -12 \rightarrow 13$
	$k = -13 \rightarrow 13$
	$l = -14 \rightarrow 13$

Refinement

Refinement on F^2	Secondary atom site location: diff
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.052$	H-atom parameters constrained
$wR(F^2) = 0.132$	$w = 1/[\sigma^2(F_o^2) + (0.0432P)^2 + 2.5115P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.11$	$(\Delta/\sigma)_{max} < 0.001$
4387 reflections	$\Delta\rho_{max} = 1.56$ e Å^{-3}
362 parameters	$\Delta\rho_{min} = -2.15$ e Å^{-3}
141 restraints	
Primary atom site location: dual	

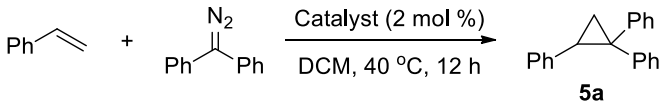
Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Table S6 Comparison of XANES spectra of iron porphyrin complexes

Complexes	Pre-edge peak (eV)	Rising edge peak (eV)	Ref
[Fe(TPFPP)(Ad)] (**1a**)	7113.0	7136.6	This work
[Fe(TPFPP)(CPh_2)]	7113.0	7137.2	
[Fe(TPFPP)Cl]	7114.0	7136.0	
[Fe(TPFPP)(CPh_2)]	7112.9	Not available	1
[Fe(TPP)(CCl_2)]	7112.9		
[Fe(TPP)(CS)]	7112.9		
[Fe(TPP)Cl]	7113.9		

Table S7 Catalyst screening for the cyclopropanation reaction of styrene and Ph_2CN_2



5a

Catalyst	Yield of **5a** (%)[a]
1a	90
2a	92
[Fe(TPFPP)]	48
[Fe(TPFPP)Cl]	56
$[Rh_2(esp)_2]$	10
CuI	1
[Ru(TTP)(CO)]	56
[Ir(TTP)Me]	2
No catalyst	37[b]

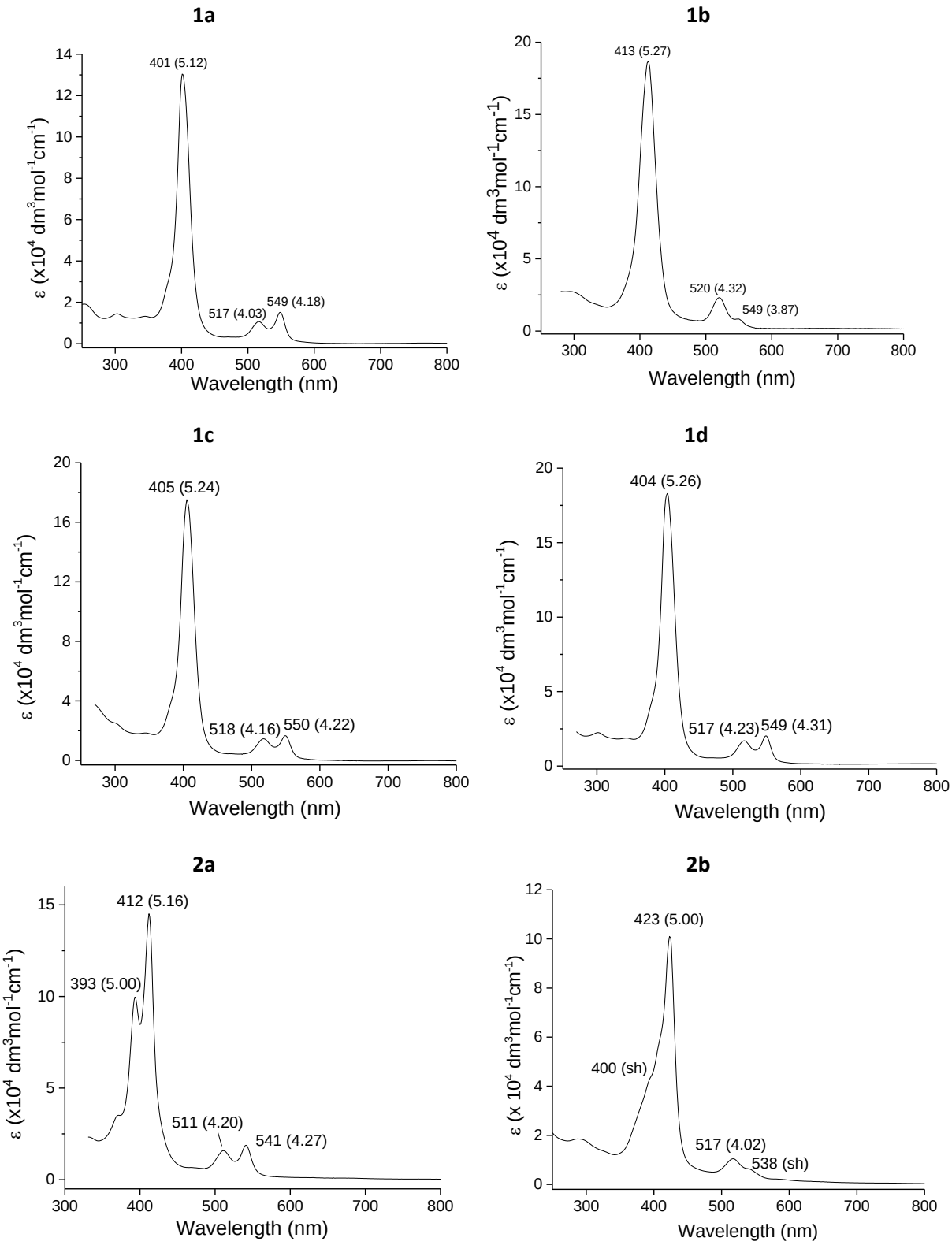
[a] Azine was the major byproduct as revealed by GC-MS. [b] The reaction time was 36 h.

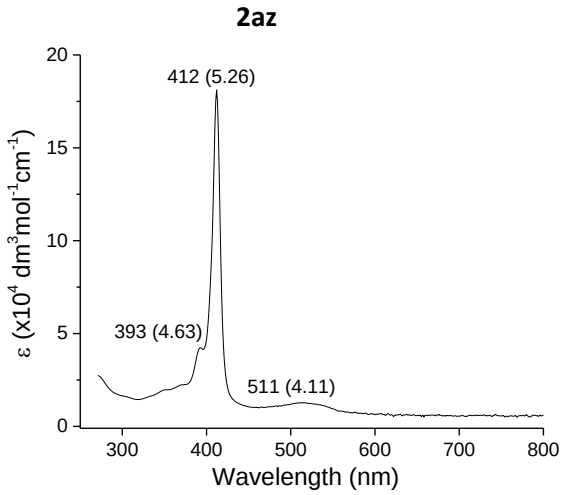
Table S8 First oxidation potentials (E_{o1}) of group 8 metal porphyrin carbene complexes

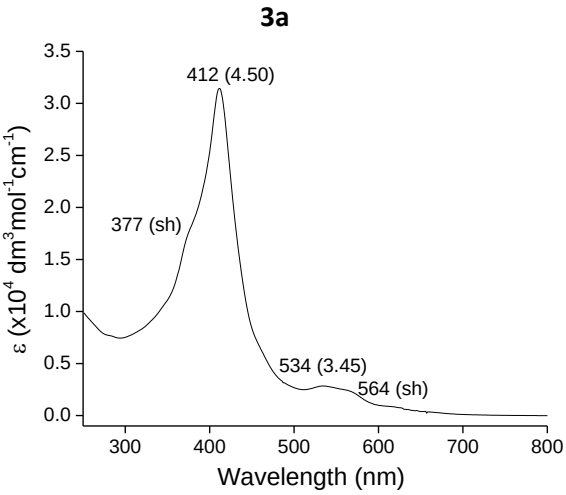
Fe-mono(carbene) complexes	E_{O1} (V vs $Fc^{+/0}$)
[Fe(Por)(Ad)]	–0.18 to 0.01
$[Fe(Por)(CPh_2)(L)]^{a,b}$	0.13 to 0.35
Ru-mono(carbene) complexes	**E_{O1} (V vs $Fc^{+/0}$)**
$[Ru(Por)(NHC)_2]^{c}$	–0.27 to –0.20
[Ru(Por)(Ad)]	–0.03 to 0.18
$[Ru(Por)(CPh_2)(L)]^{a,b}$	0.19 to 0.52
$[Ru(Por)(C(Ph)CO_2R)(L)]^{a,b}$	0.32 to 0.65
Os-bis(carbene) complexes	**E_{O1} (V vs $Fc^{+/0}$)**
$[Os(Por)(Ad)_2]$	–0.17 to 0.04
$[Os(TPFPP)(CPh_2)_2]$	0.30

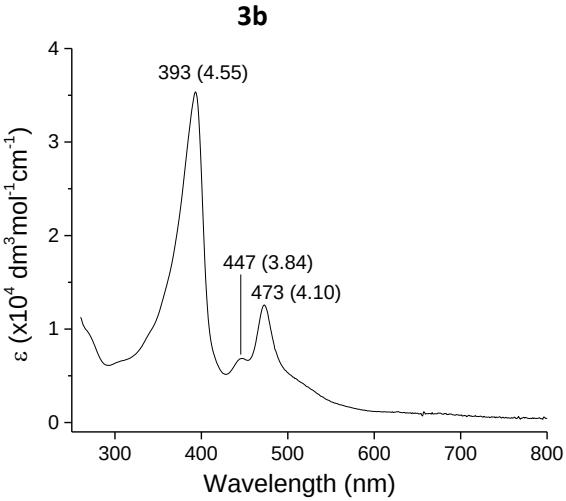
[a] Ref 25. [b] L = none, MeIm, EtSH, Et_2S, or MeOH. [c] Ref 26.

Fig. S1 UV-vis spectra in DCM




2az
412 (5.26)
393 (4.63)
511 (4.11)
ε (x10^4 dm^3mol^-1cm^-1)
Wavelength (nm)


3a
412 (4.50)
377 (sh)
534 (3.45)
564 (sh)
ε (x10^4 dm^3mol^-1cm^-1)
Wavelength (nm)


3b
393 (4.55)
447 (3.84)
473 (4.10)
ε (x10^4 dm^3mol^-1cm^-1)
Wavelength (nm)

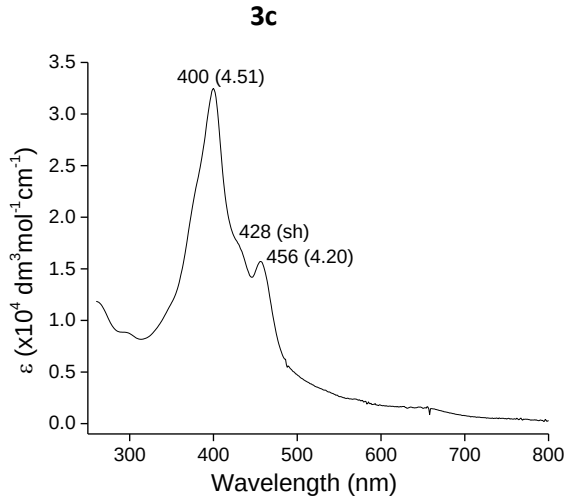
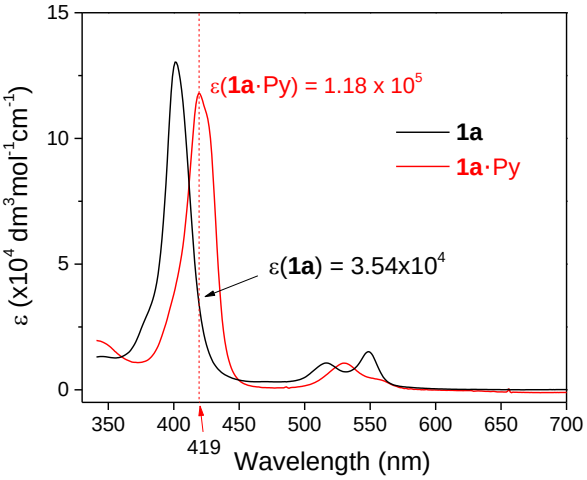
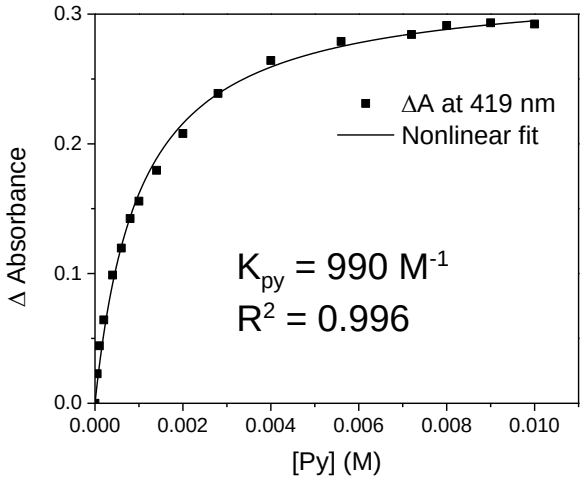

3c
400 (4.51)
428 (sh)
456 (4.20)
ε (x10^4 dm^3mol^-1cm^-1)
Wavelength (nm)

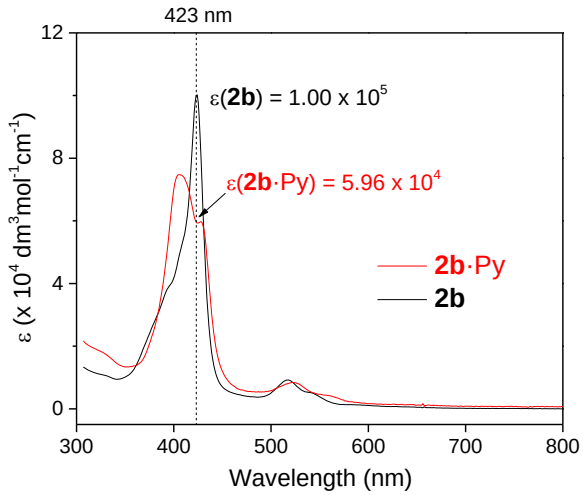
Fig. S2 Titration curves for the addition of pyridine into **1a**/**2b** (determination of binding constants)

1a





2b



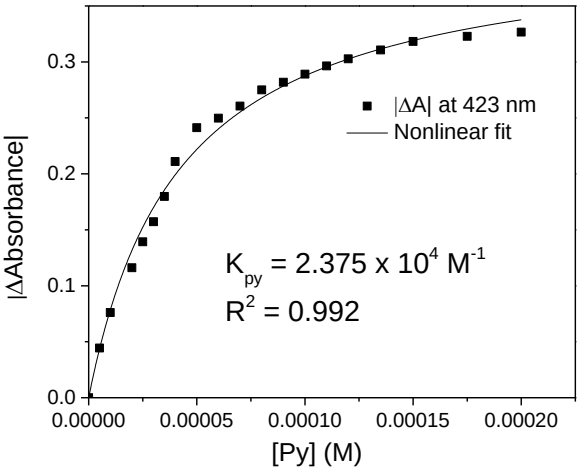
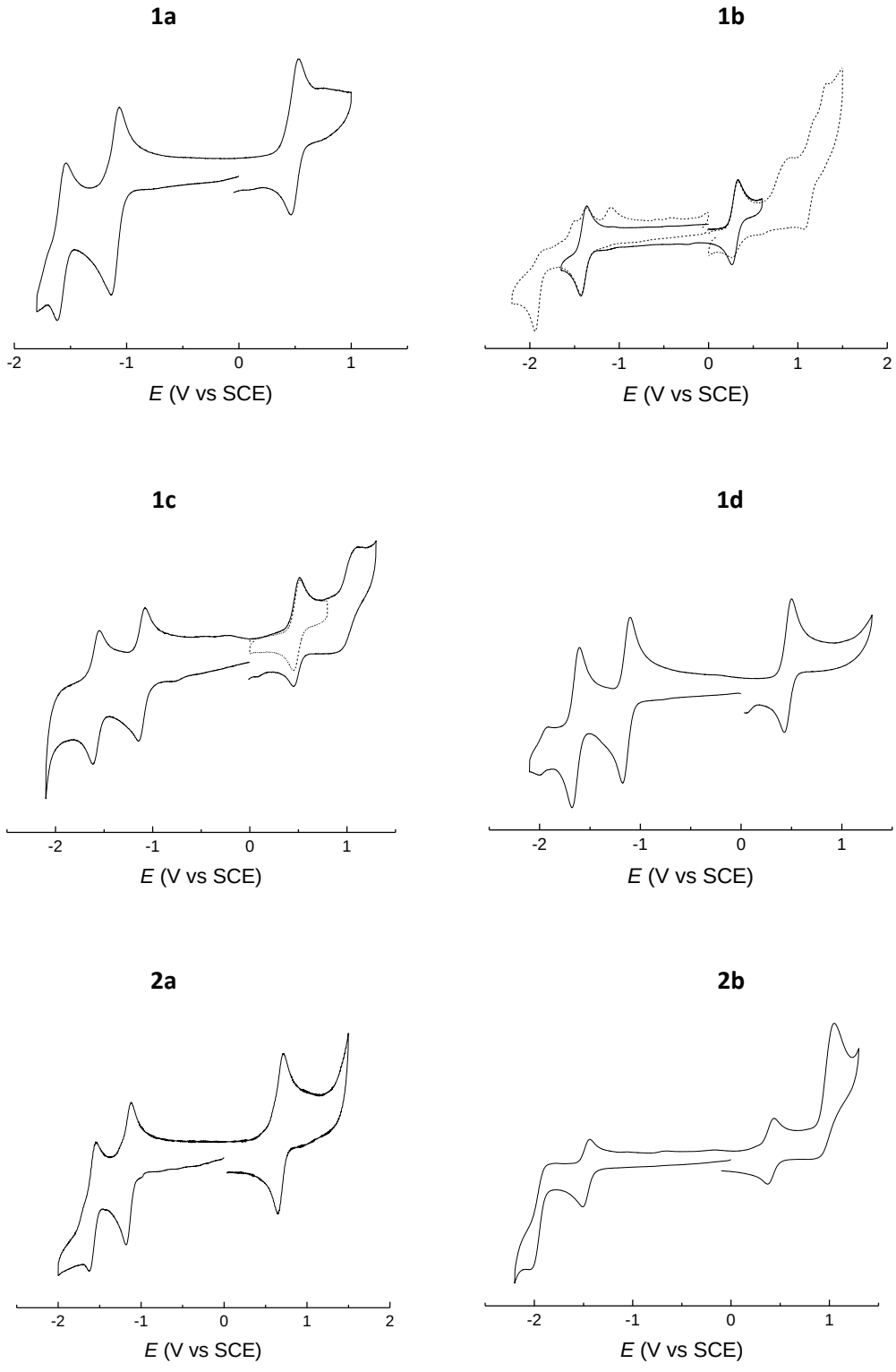
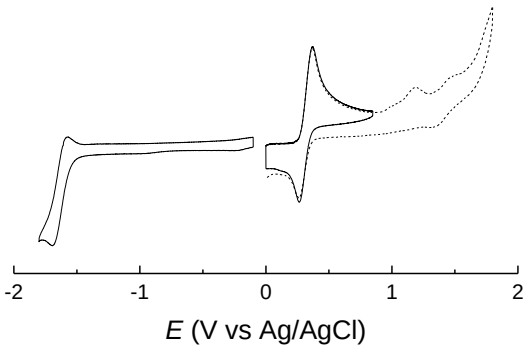


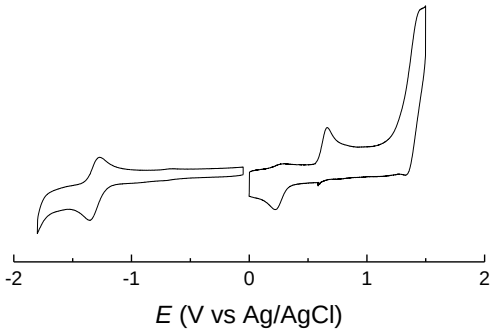
Fig. S3 Cyclic voltammograms



3a



3b



3c

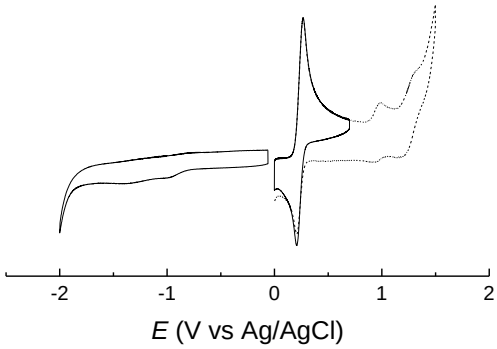
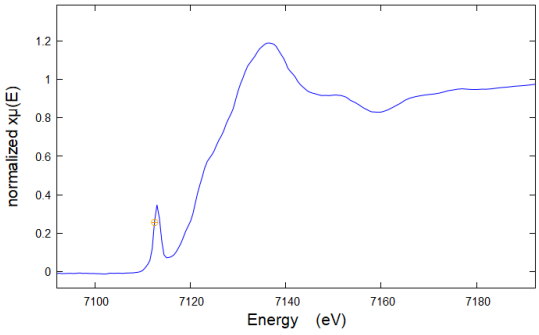
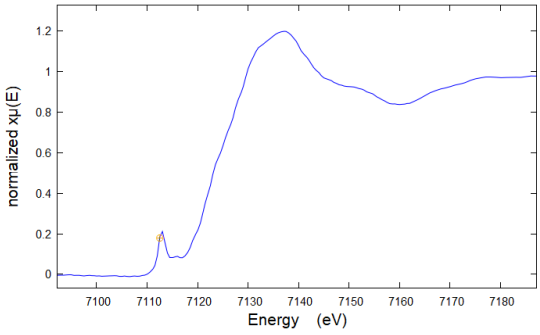


Fig. S4 XANES spectra

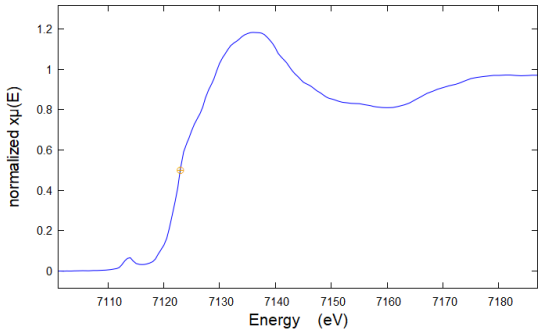
1a



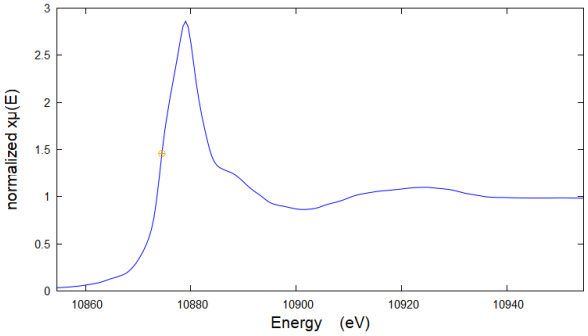
[Fe(TPFPP)(CPh_2)]



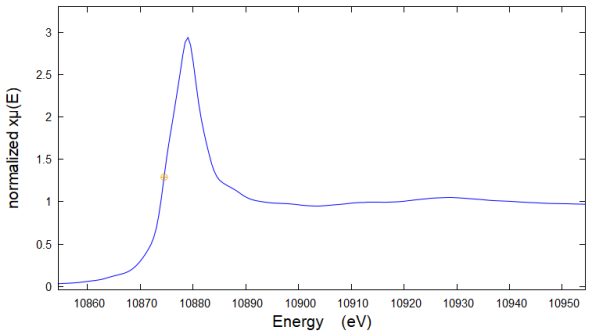
[Fe(TPFPP)Cl]



3a



[Os(4-F-TPP)(CO)]



trans-dioxo [Os(TTP)O_2]

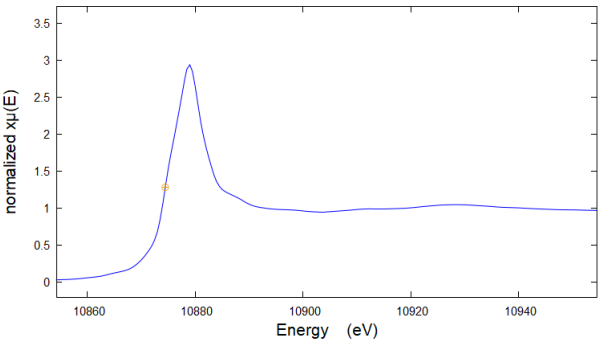
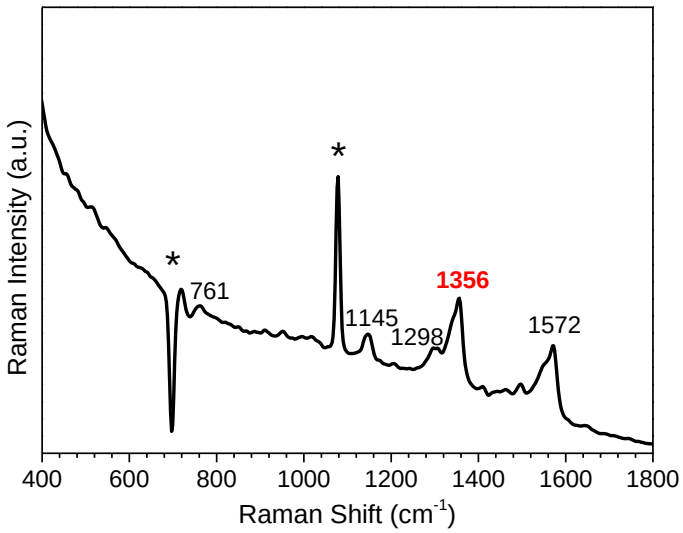


Fig. S5 Resonance Raman spectra of **1a**

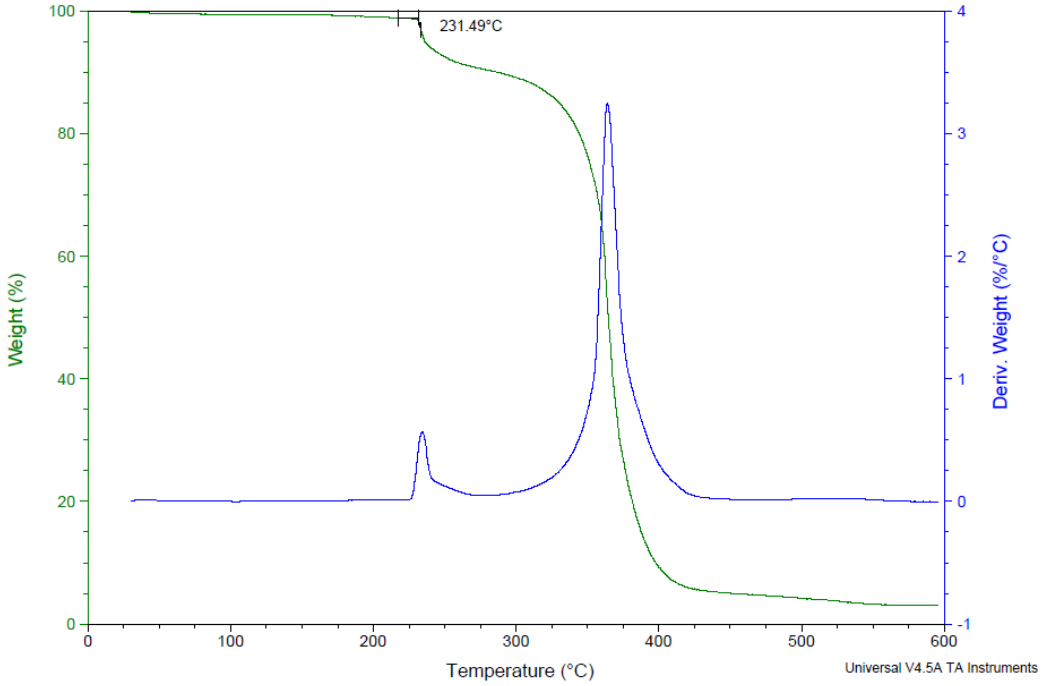


Band A assignable to iron porphyrin is highlighted in red.[27]

Stars (*) refer to the solvent subtraction artifacts.

Fig. S6 TGA curves under air (green) and first derivatives (blue)

1a



2a

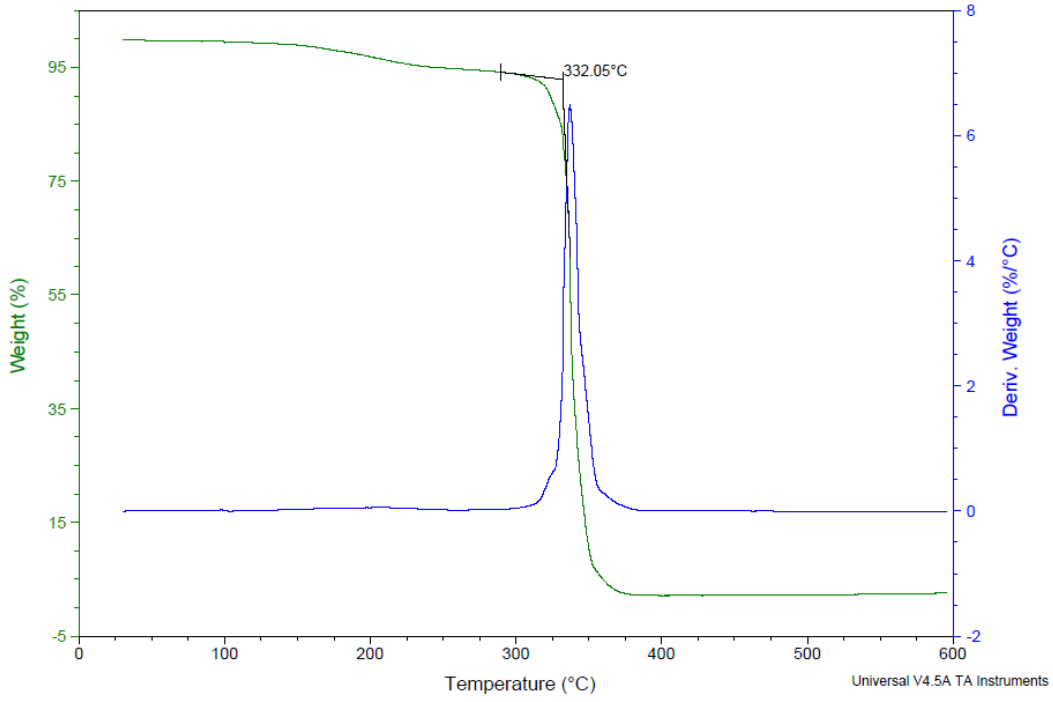
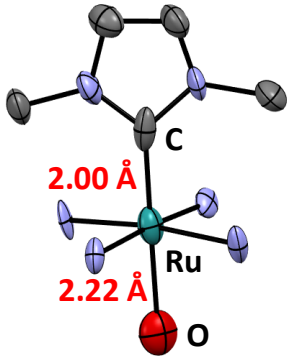
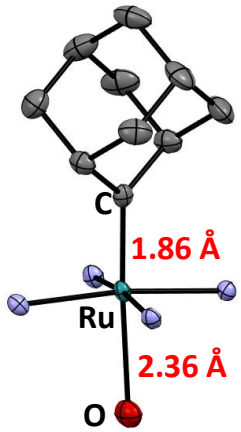


Fig. S7 Comparison of truncated crystal structures of [Ru(TTP)(Ad)(MeOH)] (**2b**·MeOH) and [Ru(TPP)(IMe_2)(THF)]



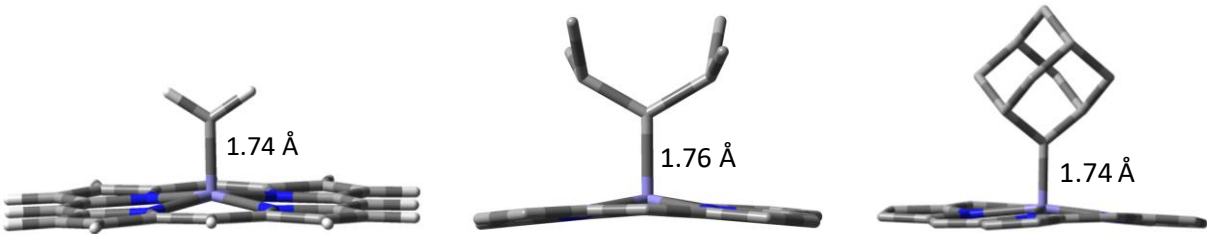
[Ru(TPP)(IMe_2)(THF)]

(ref 26)

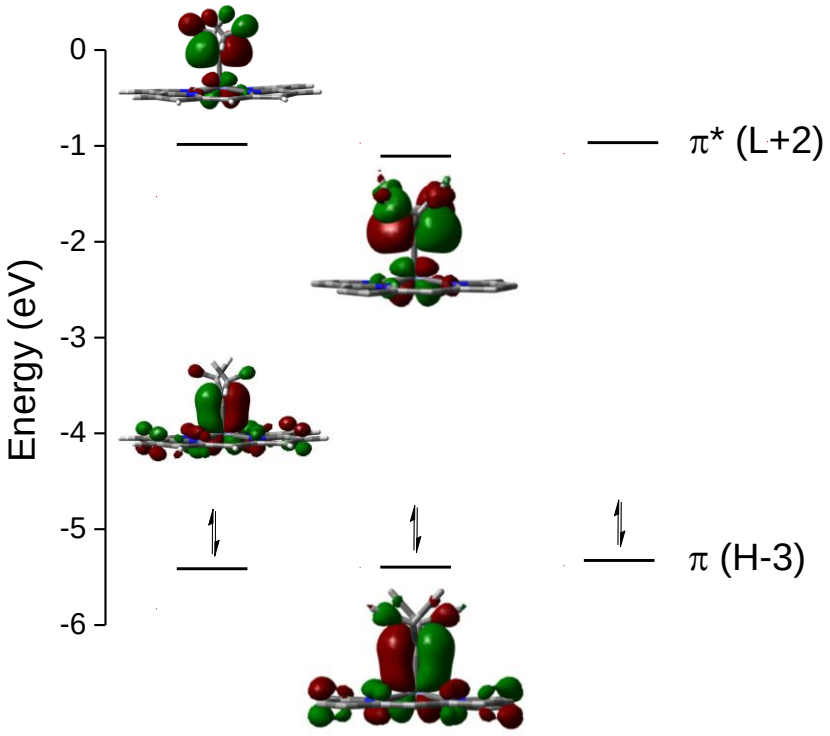


2b·MeOH

Fig. S8 Comparison of DFT-optimized structures and calculated Fe=C π orbitals among [Fe(Por)(CMe_2)], [Fe(Por)(C^iPr_2)], and [Fe(Por)(Ad)]

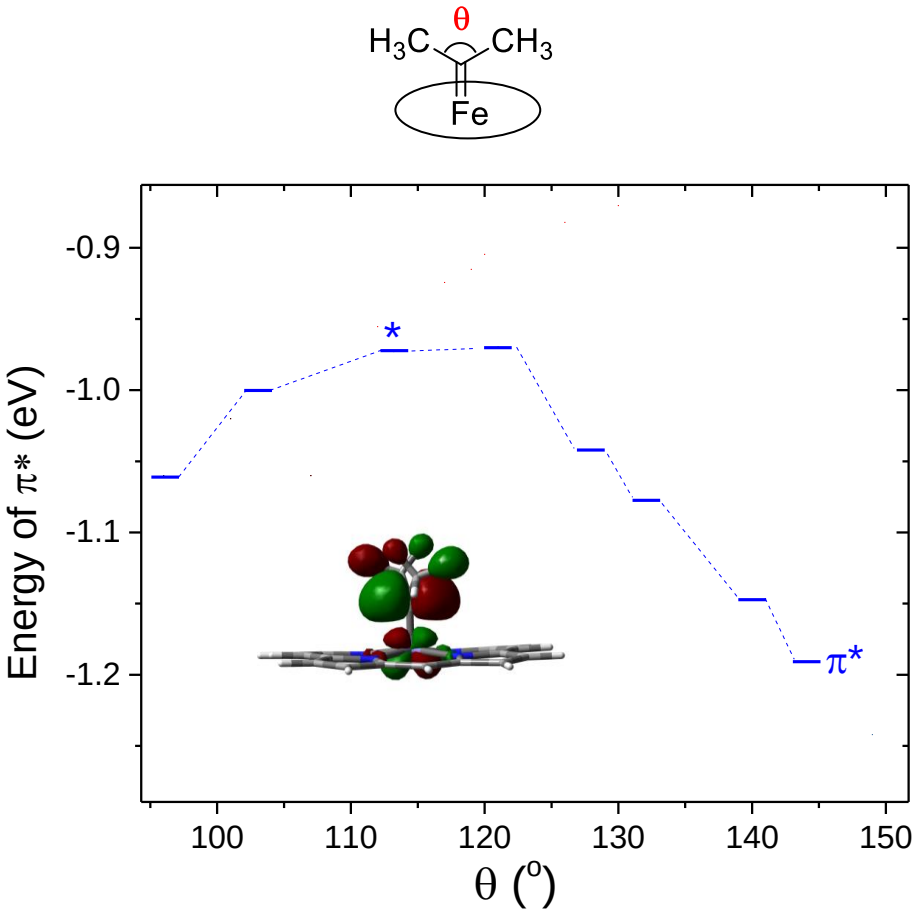


[Fe(Por)(CMe_2)] **[Fe(Por)(C^iPr_2)]** **[Fe(Por)(Ad)]**



[Fe(Por)(CMe_2)] **[Fe(Por)(C^iPr_2)]** **[Fe(Por)(Ad)]**

Fig. S9 Effect of angle of carbene (θ) on the energy level of π*(Fe=C) in [Fe(Por)(CMe_2)]



* Represents the optimized angle without constraints

Fig. S10 Calculated MO diagram of [Fe(Por)(Ad)(CPh_2)] (**4b**)

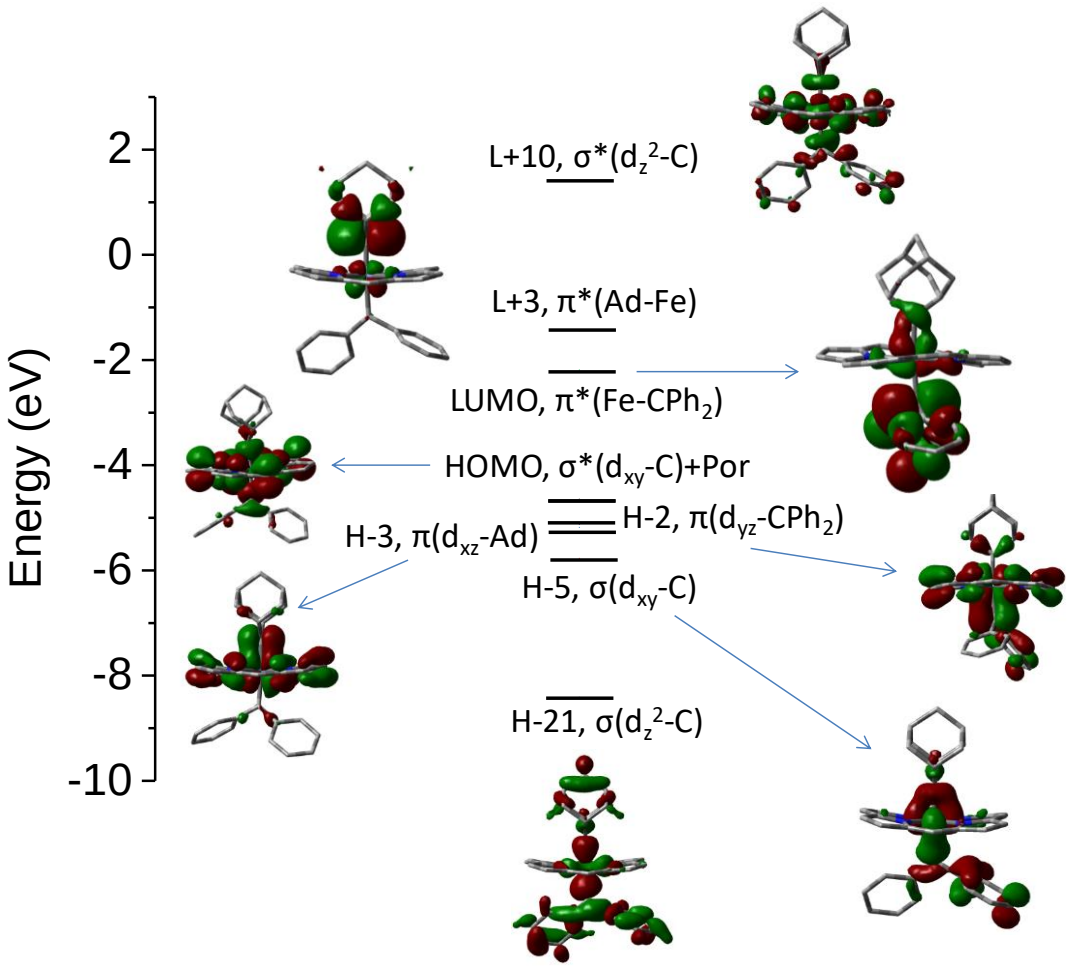
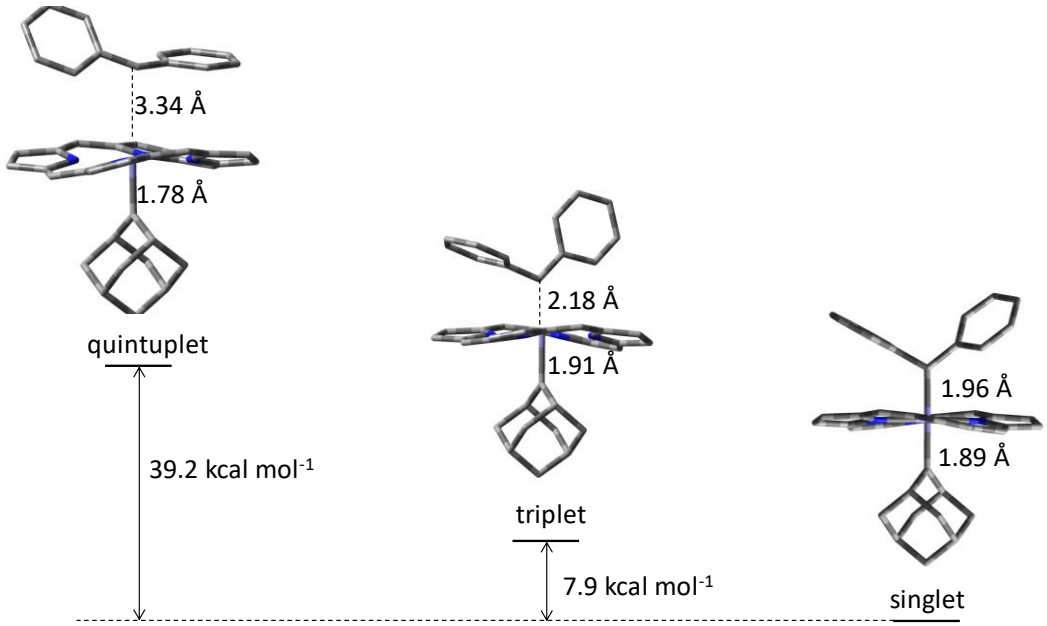


Fig. S11 Comparison of calculated geometry and energy among different spin states of **4b**



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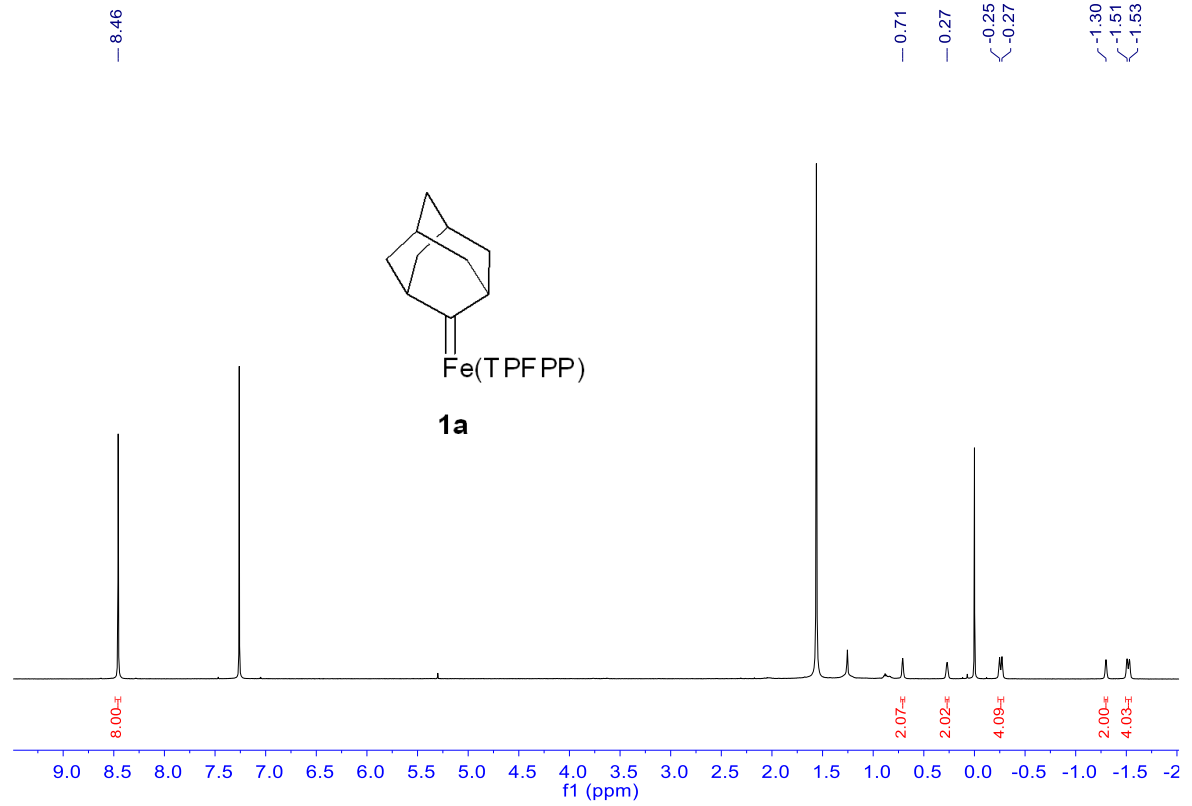
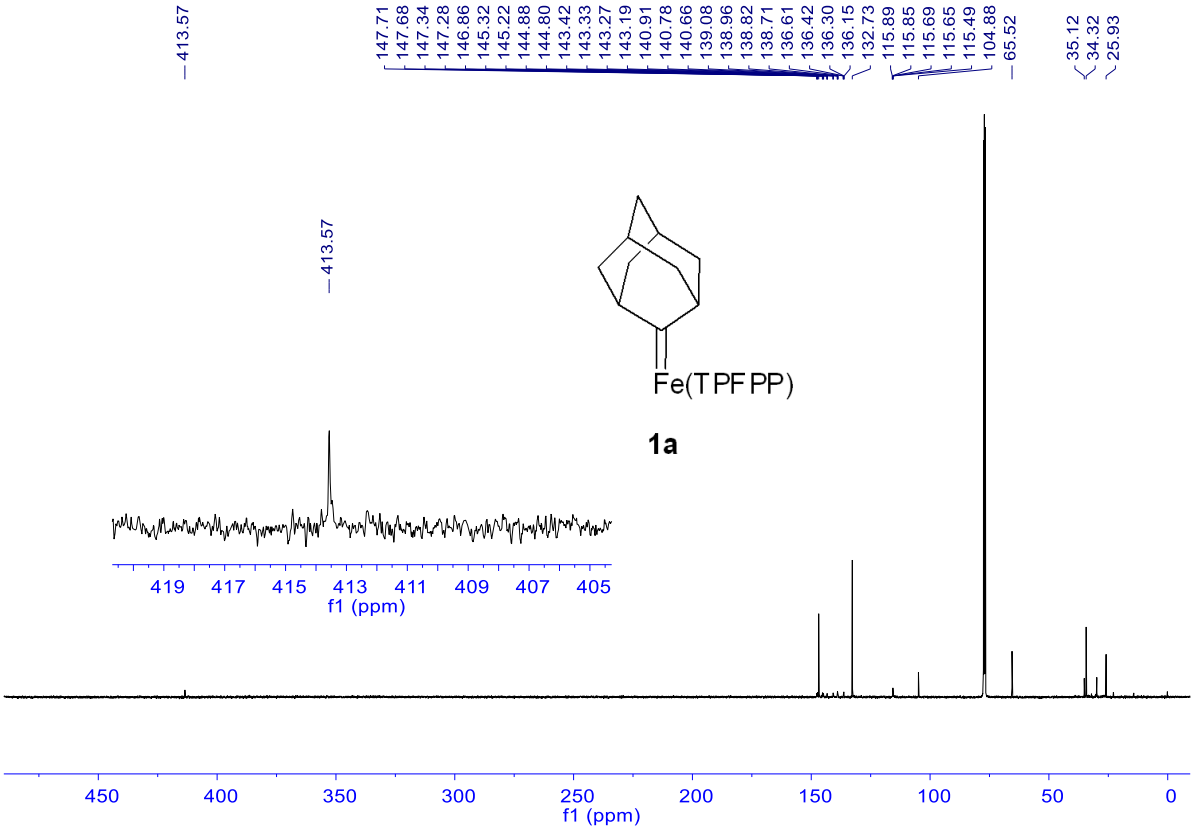
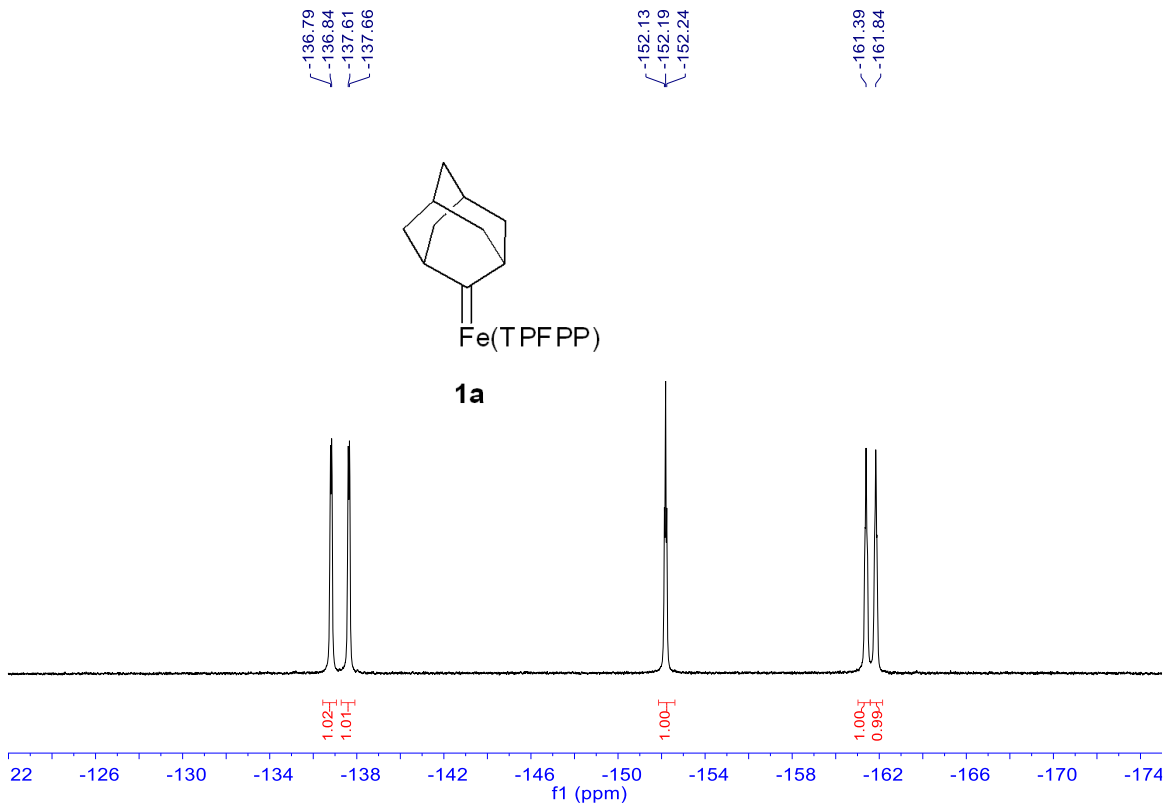
V. NMR spectra



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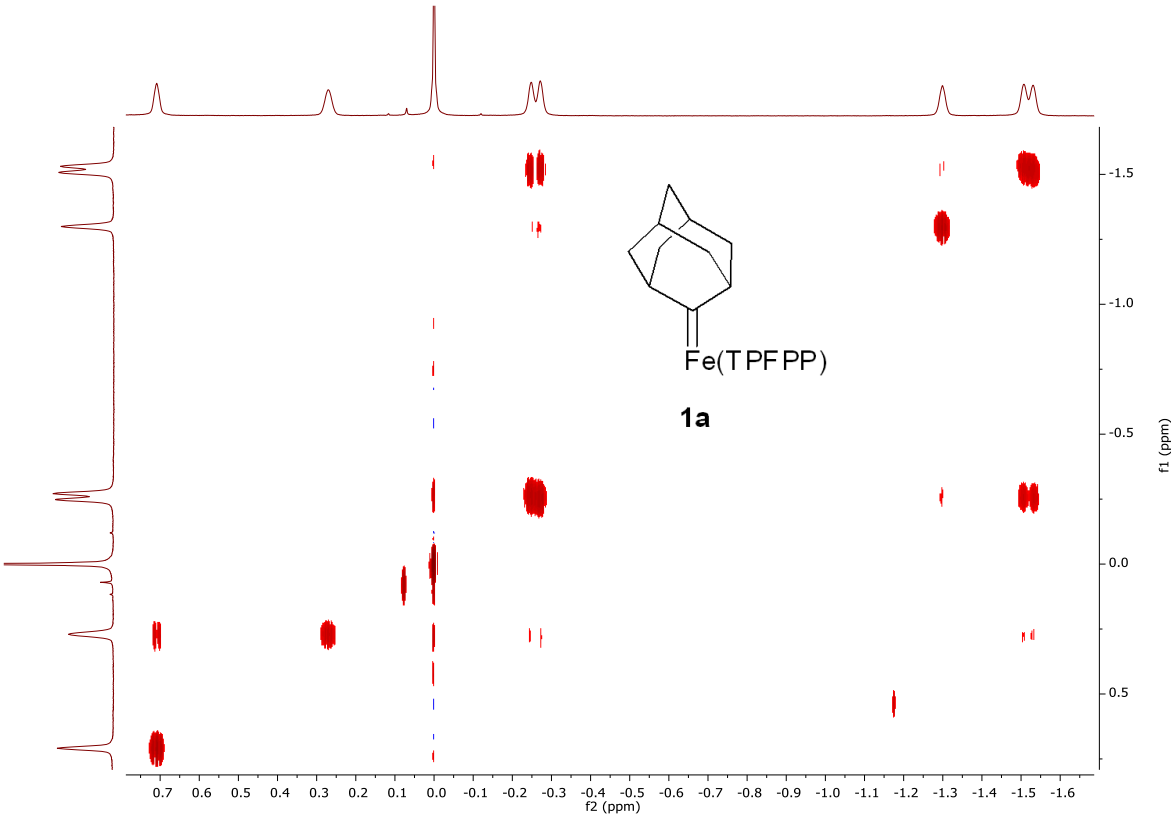
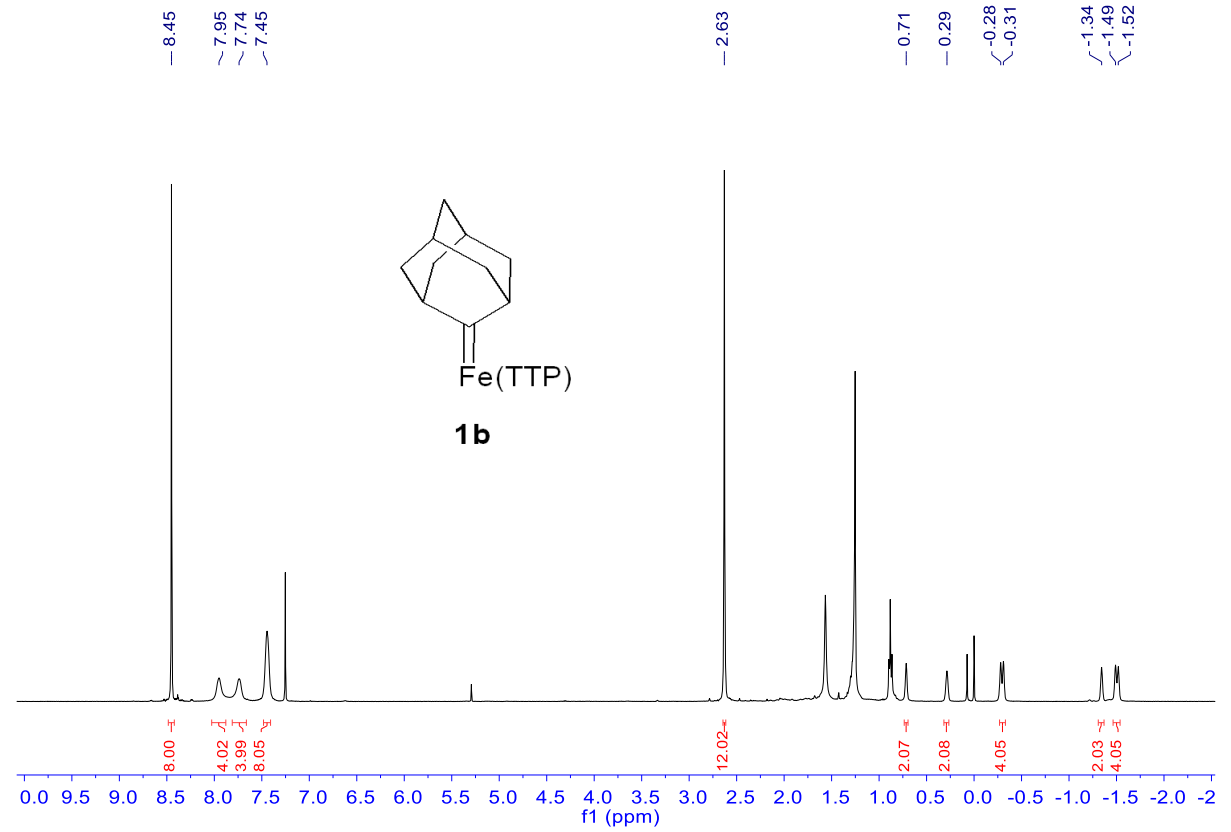
-136.84
-137.61
-137.66
-152.13
-152.19
-152.24
-161.39
-161.84
Fe(TPFPP)
1a
1.02
1.01
1.00
1.00
0.99
22 -126 -130 -134 -138 -142 -146 -150 -154 -158 -162 -166 -170 -174
f1 (ppm)

H-H COSY


Fe(TPFPP)
1a
-1.5
-1.0
-0.5
0.0
0.5
f1 (ppm)
0.7 0.6 0.5 0.4 0.3 0.2 0.1 0.0 -0.1 -0.2 -0.3 -0.4 -0.5 -0.6 -0.7 -0.8 -0.9 -1.0 -1.1 -1.2 -1.3 -1.4 -1.5 -1.6
f2 (ppm)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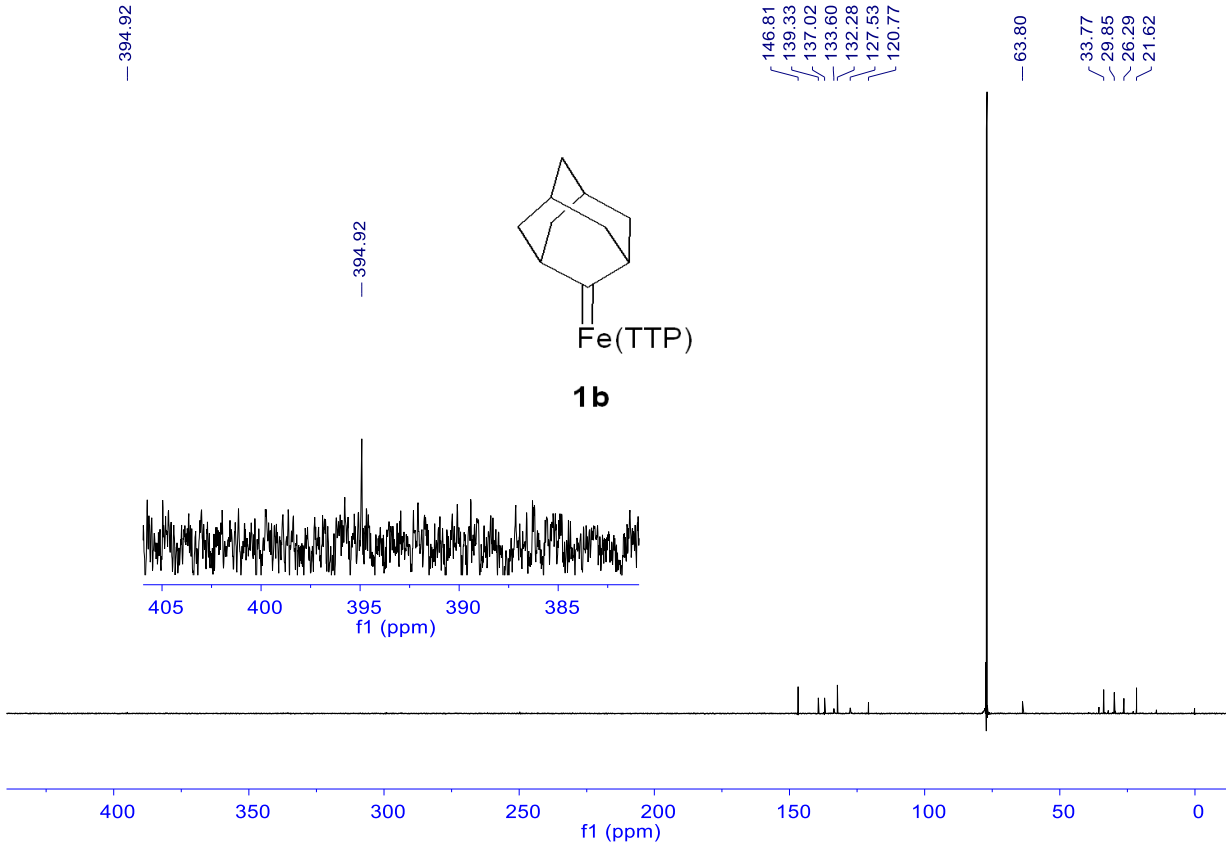
7.95
7.74
7.45
2.63
0.71
0.29
-0.28
-0.31
-1.34
-1.49
-1.52
Fe(TTP)
1b
8.00
4.02
3.99
8.05
12.02
2.07
2.08
4.05
2.03
4.05
f1 (ppm)


394.92
146.81
139.33
137.02
133.60
132.28
127.53
120.77
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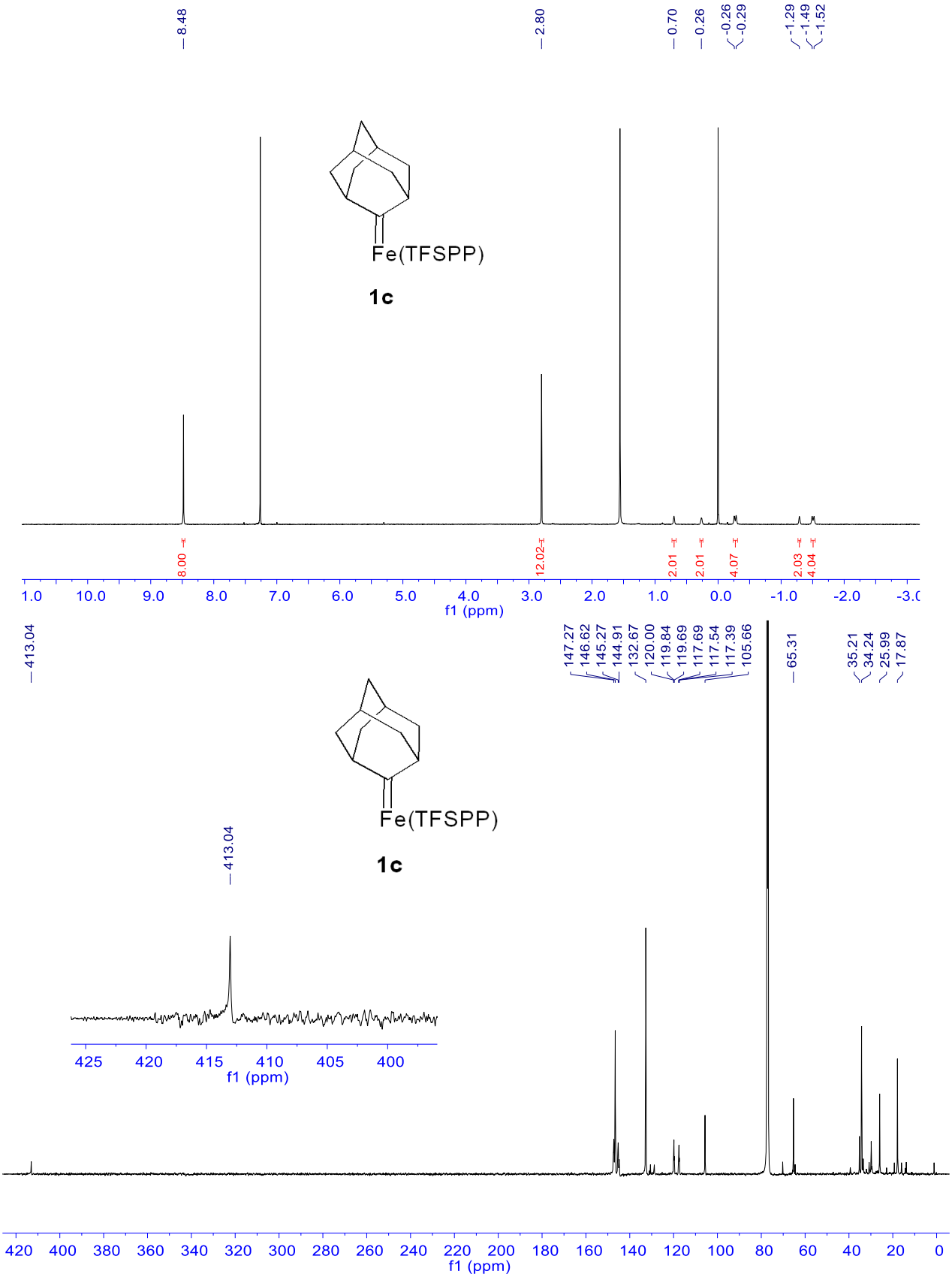
33.77
29.85
26.29
21.62
Fe(TTP)
1b
f1 (ppm)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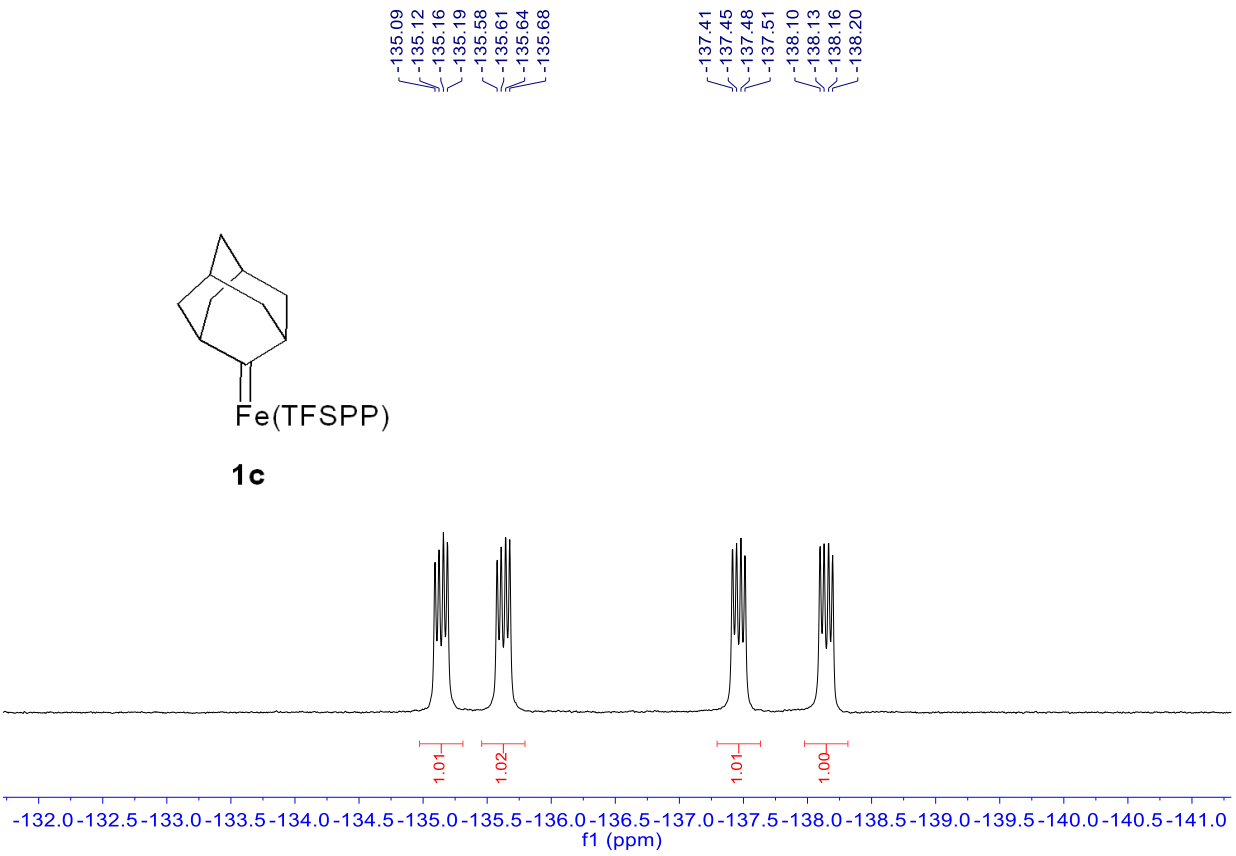
2.80
0.70
0.26
-0.26
-0.29
-1.29
-1.49
-1.52
Fe(TFSPP)
1c
8.00
12.02
2.01
2.01
4.07
2.03
4.04
f1 (ppm)
413.04
147.27
146.62
145.27
144.91
132.67
120.00
119.84
119.69
117.69
117.54
117.39
105.66
65.31
35.21
34.24
25.99
17.87
Fe(TFSPP)
1c
413.04
f1 (ppm)
f1 (ppm)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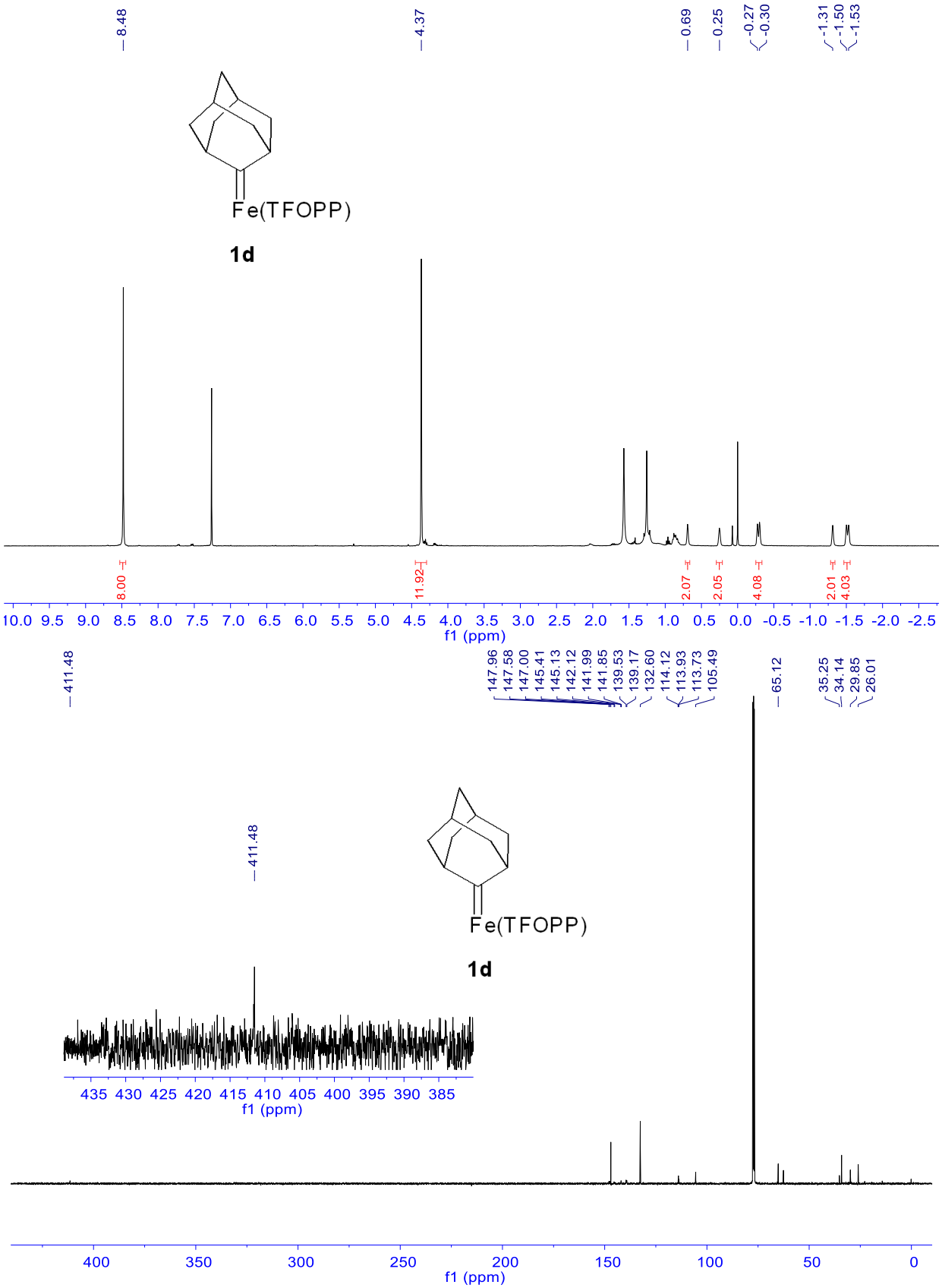
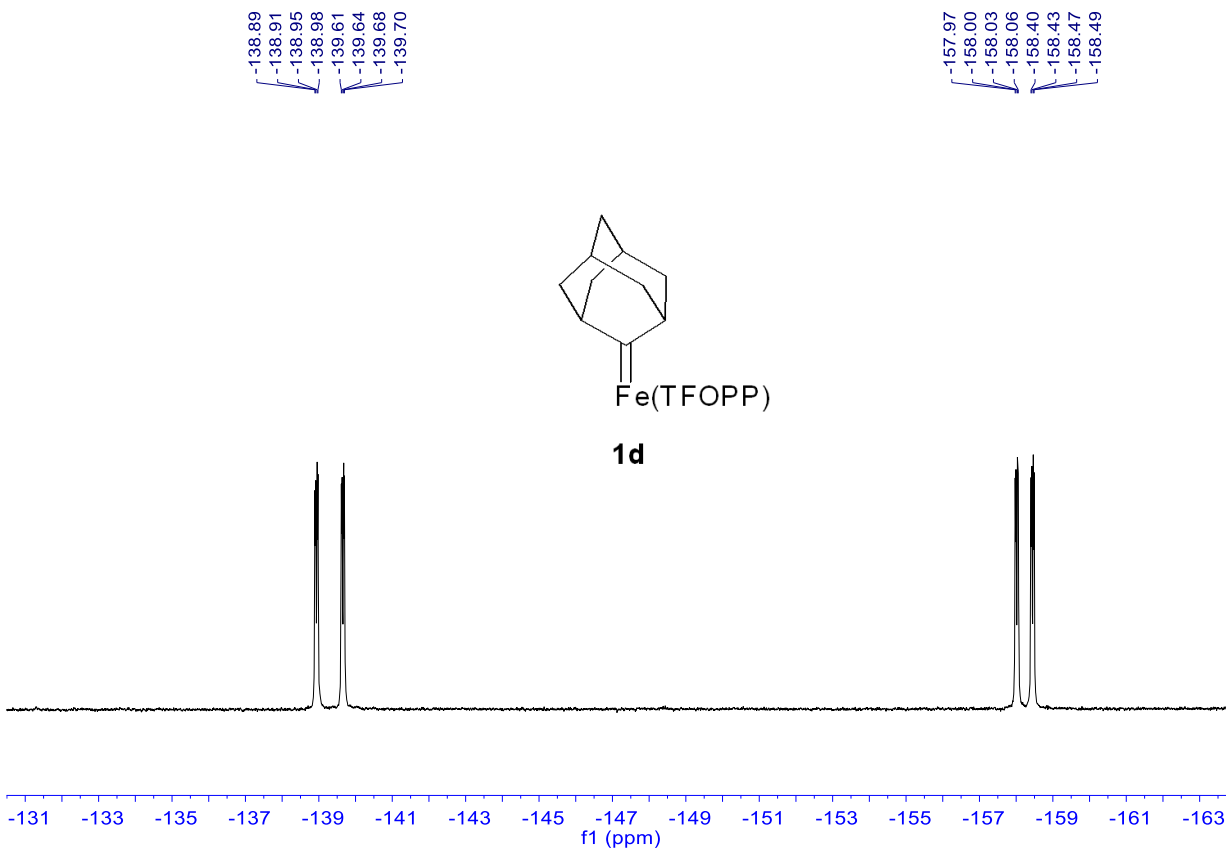
-135.19
-135.58
-135.61
-135.64
-135.68
-137.41
-137.45
-137.48
-137.51
-138.10
-138.13
-138.16
-138.20
Fe(TFSPP)
1c
1.01
1.02
1.01
1.00
-132.0 -132.5 -133.0 -133.5 -134.0 -134.5 -135.0 -135.5 -136.0 -136.5 -137.0 -137.5 -138.0 -138.5 -139.0 -139.5 -140.0 -140.5 -141.0
f1 (ppm)


8.48
4.37
0.69
0.25
-0.27
-0.30
-1.31
-1.50
-1.53
Fe(TFOPP)
1d
8.00
11.92
2.07
2.05
4.08
2.01
4.03
f1 (ppm)
411.48
147.96
147.58
147.00
145.41
145.13
142.12
141.99
141.85
139.53
139.17
132.60
114.12
113.93
113.73
105.49
65.12
35.25
34.14
29.85
26.01
411.48
Fe(TFOPP)
1d
f1 (ppm)
f1 (ppm)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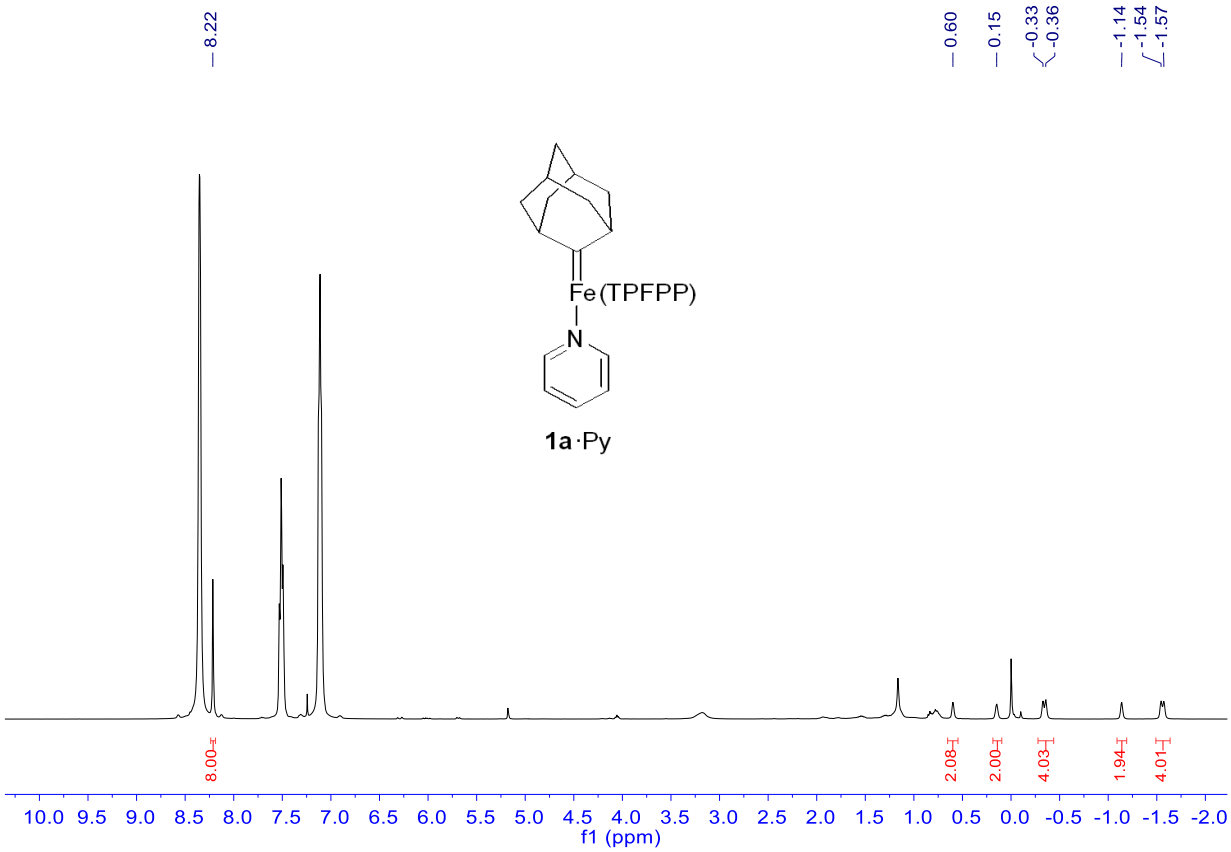
-158.03
-158.06
-158.40
-158.43
-158.47
-158.49
Fe(TFOPP)
1d
-131
-133
-135
-137
-139
-141
-143
-145
-147
-149
-151
-153
-155
-157
-159
-161
-163
f1 (ppm)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0.60
0.15
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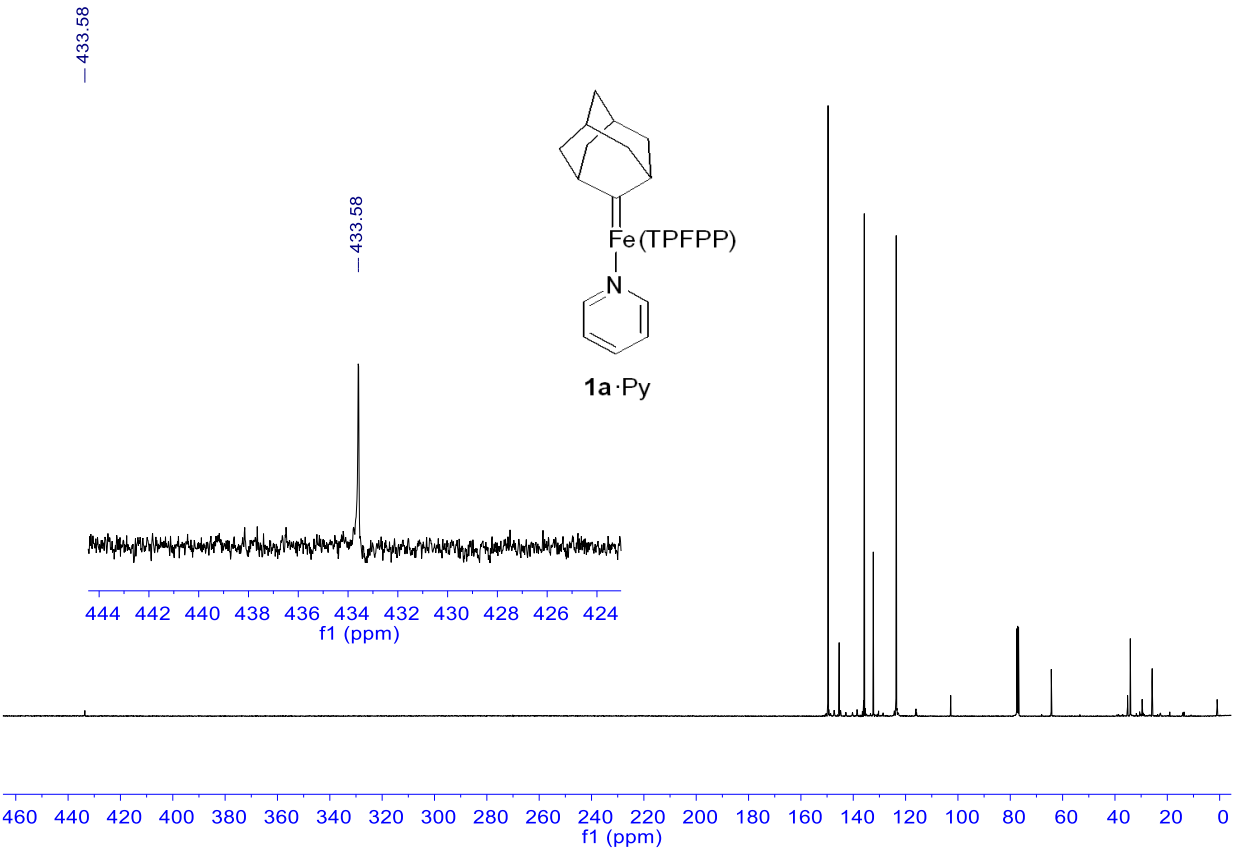
-1.57
Fe(TPFPP)
N
1a·Py
8.00
2.08
2.00
4.03
1.94
4.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)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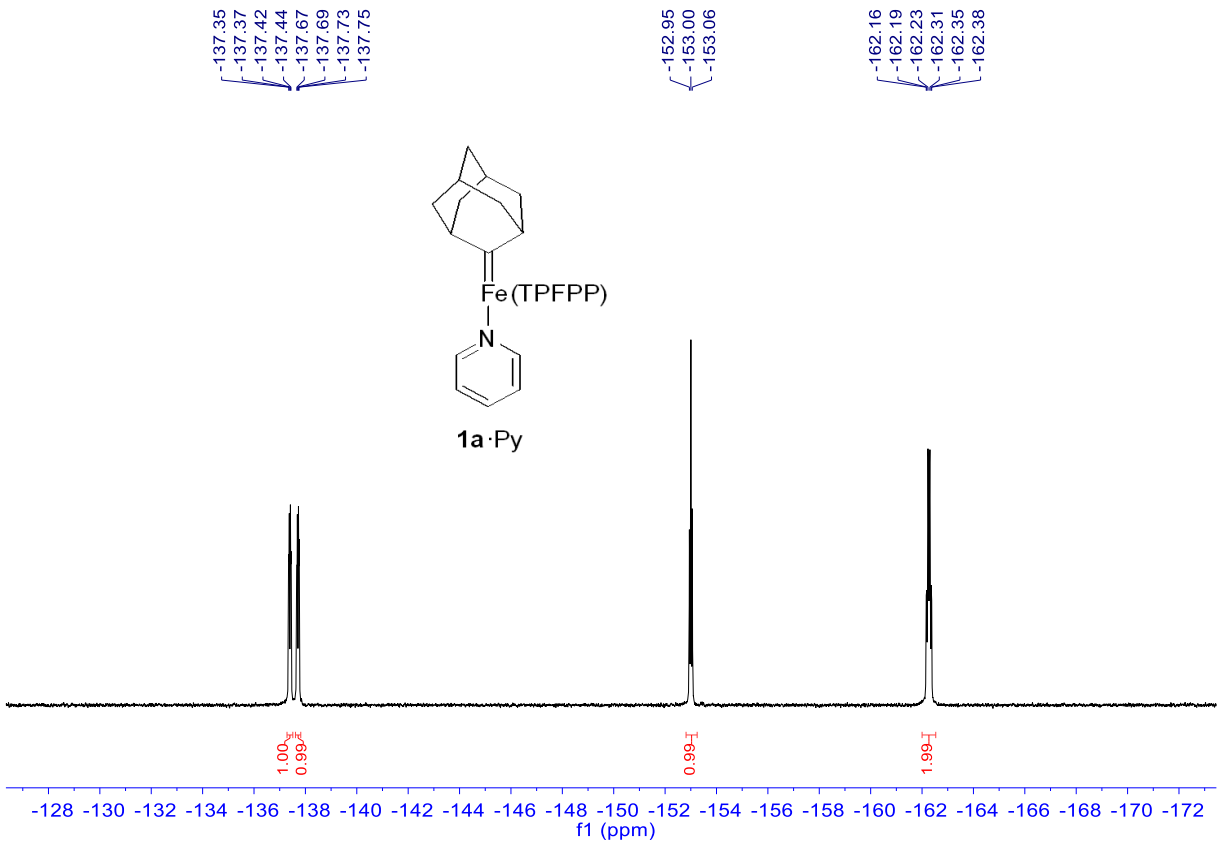
433.58
Fe(TPFPP)
N
1a·Py
444 442 440 438 436 434 432 430 428 426 424
f1 (ppm)
460 440 420 400 380 360 340 320 300 280 260 240 220 200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)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-137.44
-137.67
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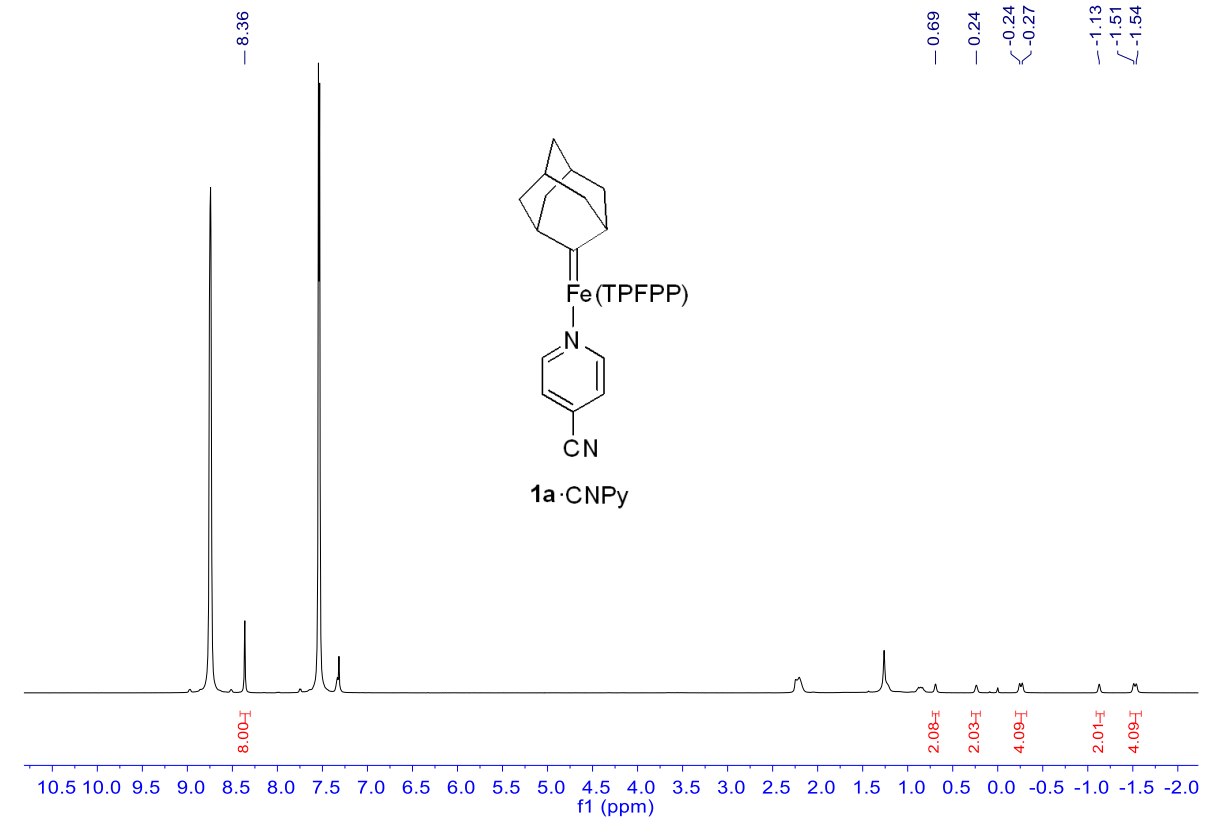
-137.73
-137.75
-152.95
-153.00
-153.06
-162.16
-162.19
-162.23
-162.31
-162.35
-162.38
Fe(TPFPP)
N
1a·Py
1.00
0.99
0.99
1.99
-128 -130 -132 -134 -136 -138 -140 -142 -144 -146 -148 -150 -152 -154 -156 -158 -160 -162 -164 -166 -168 -170 -172
f1 (ppm)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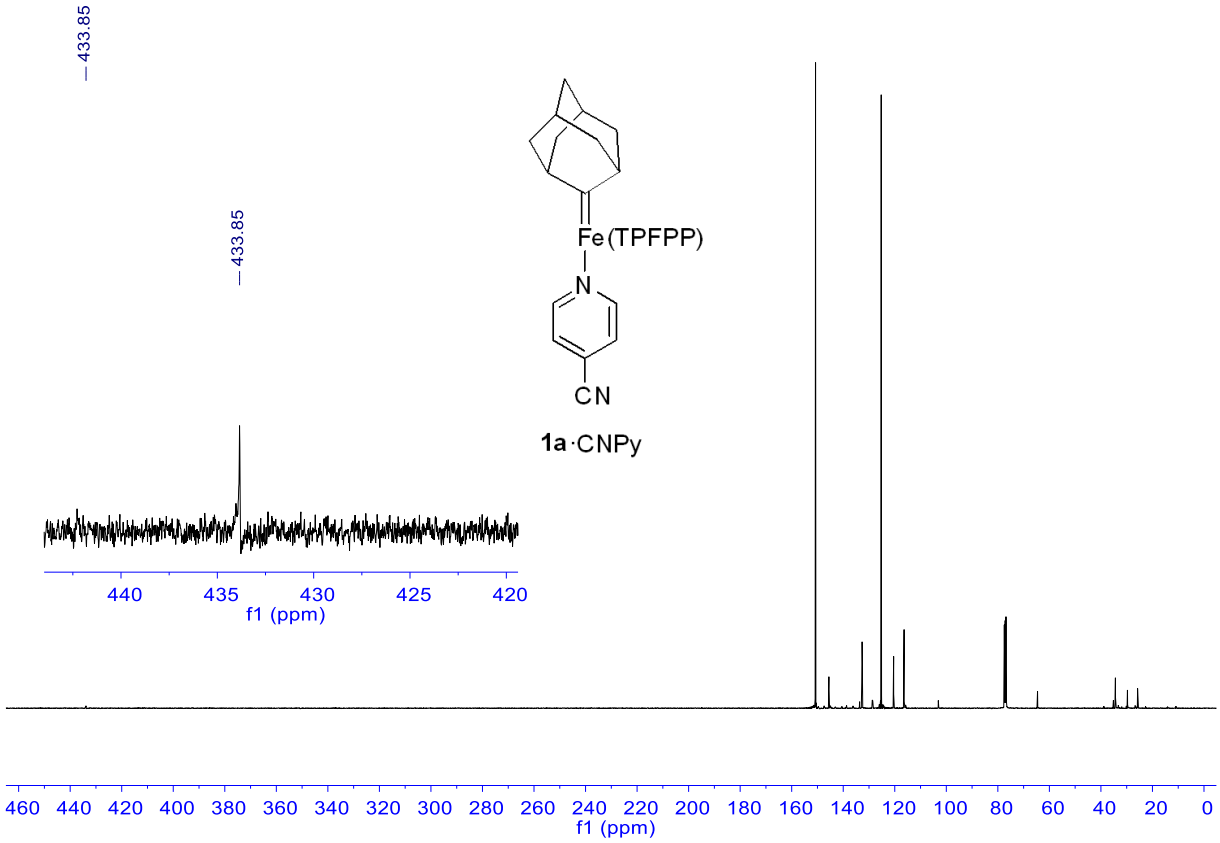
0.69
0.24
-0.24
-0.27
-1.13
-1.51
-1.54
Fe(TPFPP)
N
CN
1a·CNPy
8.00
2.08
2.03
4.09
2.01
4.09
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)


433.85
433.85
Fe(TPFPP)
N
CN
1a·CNPy
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f1 (ppm)
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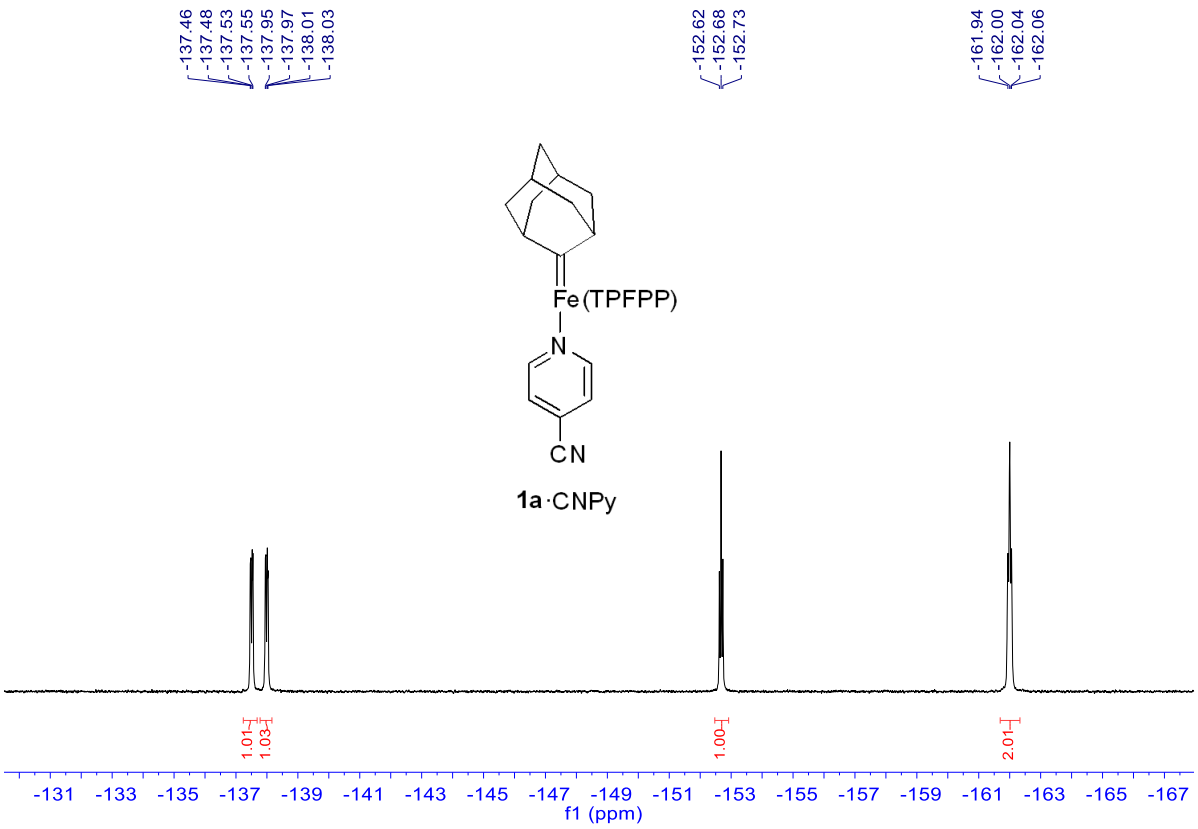
f1 (ppm)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-138.01
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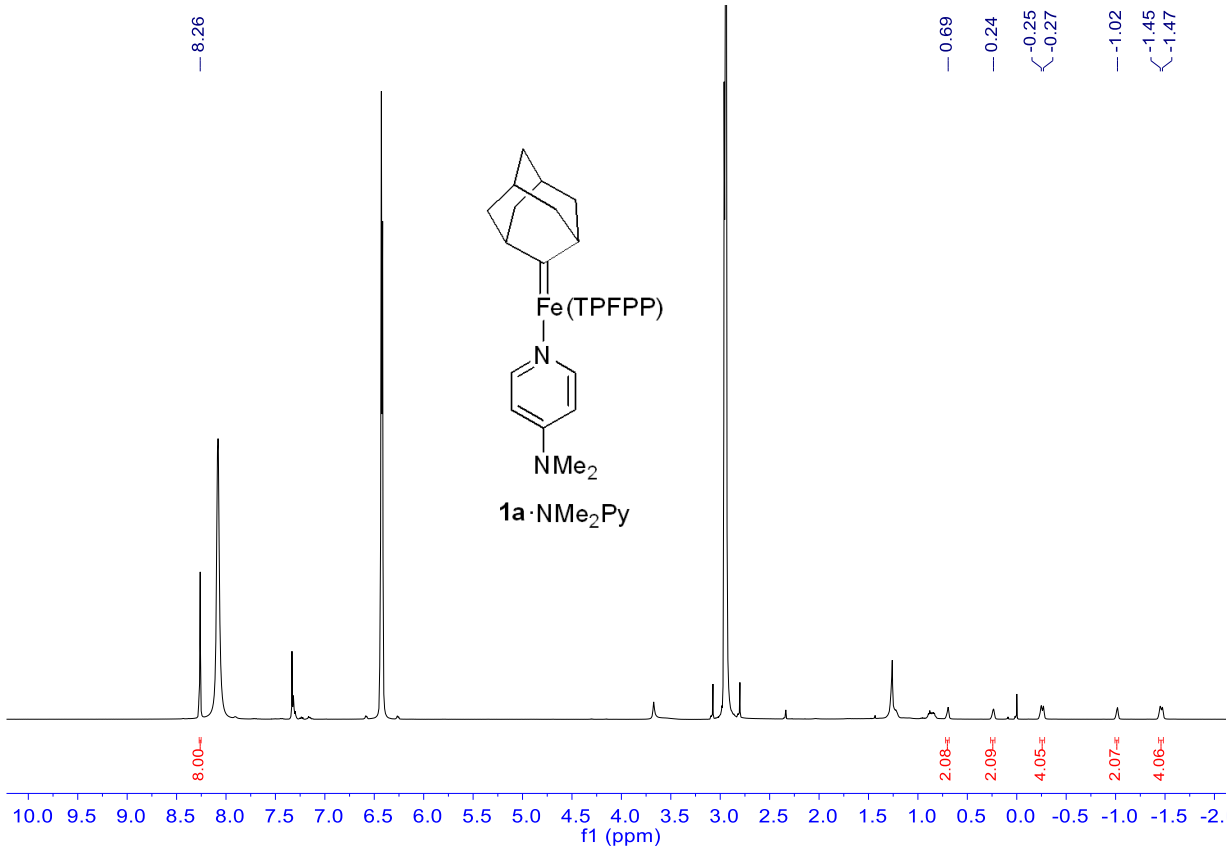
-152.62
-152.68
-152.73
-161.94
-162.00
-162.04
-162.06
Fe(TPFPP)
N
CN
1a·CNPy
1.01
1.03
1.00
2.01
-131 -133 -135 -137 -139 -141 -143 -145 -147 -149 -151 -153 -155 -157 -159 -161 -163 -165 -167
f1 (ppm)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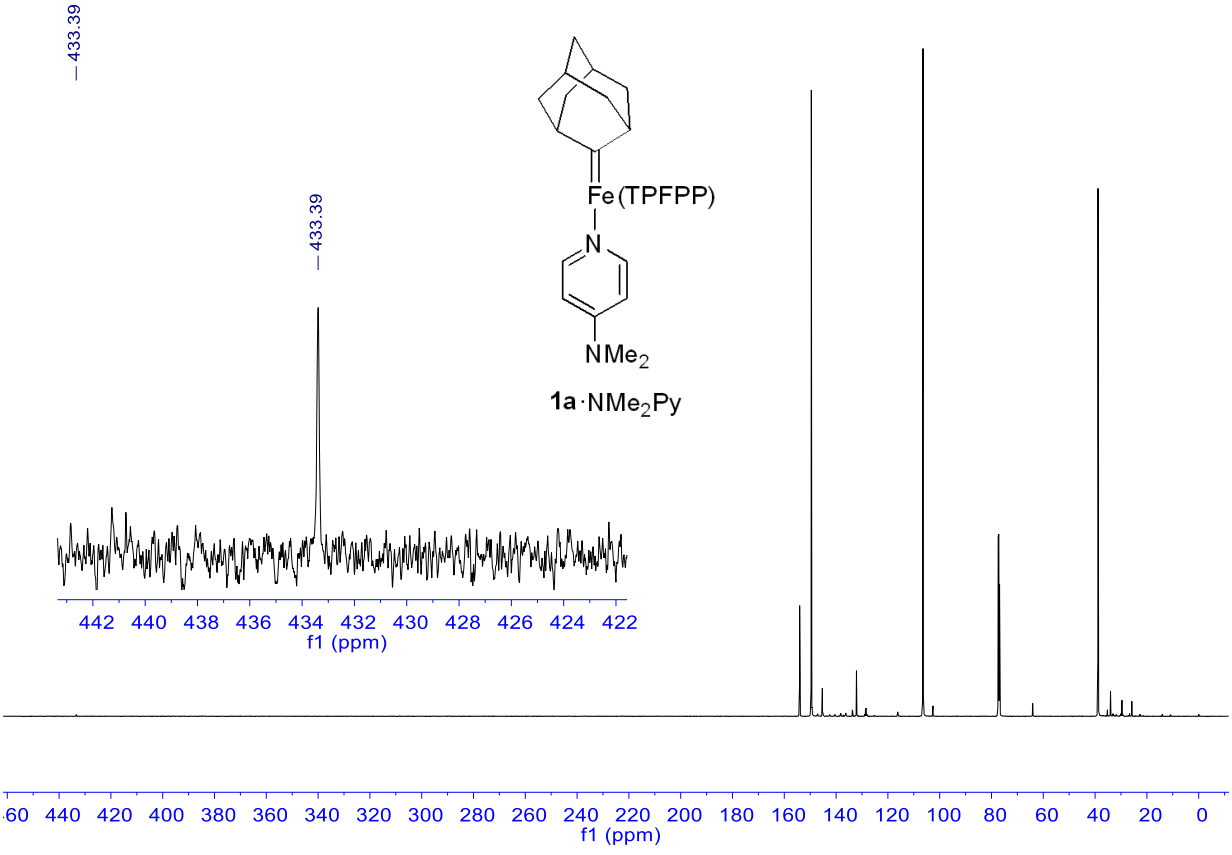
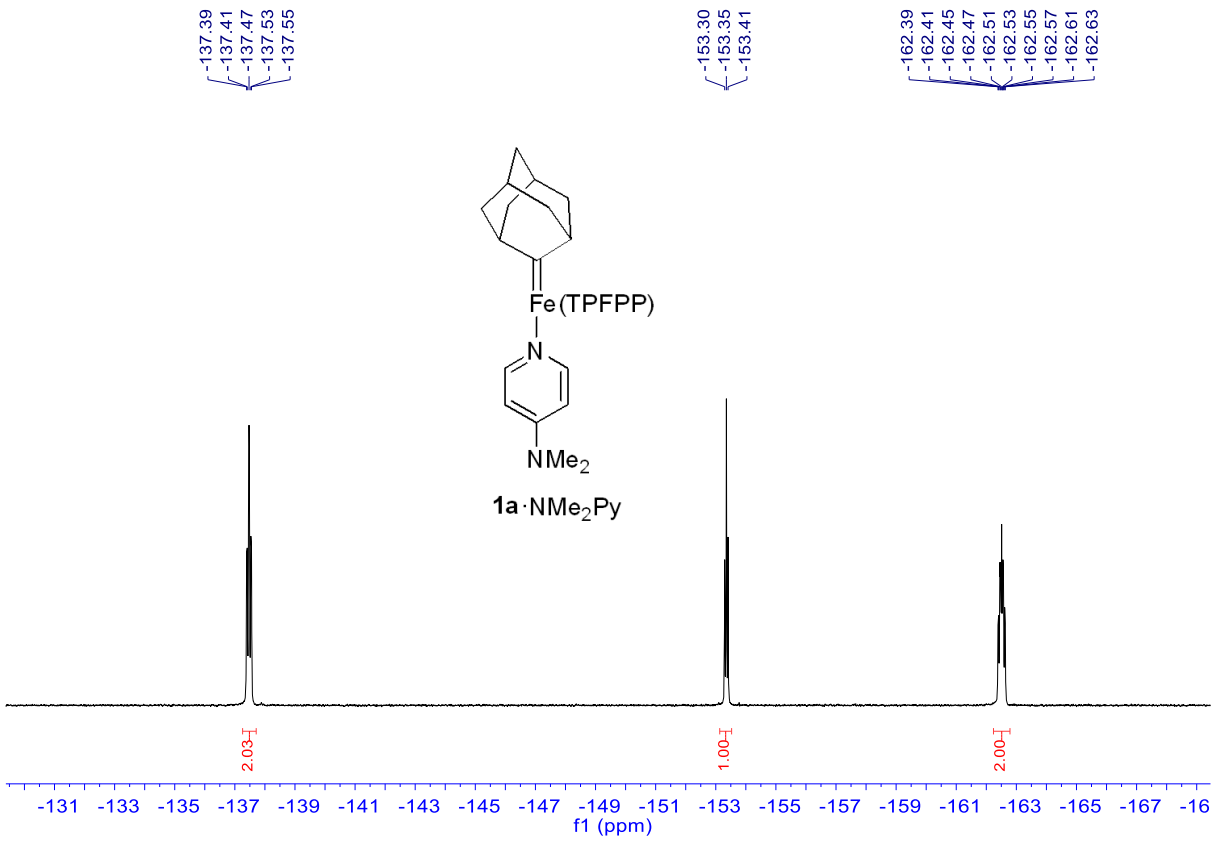
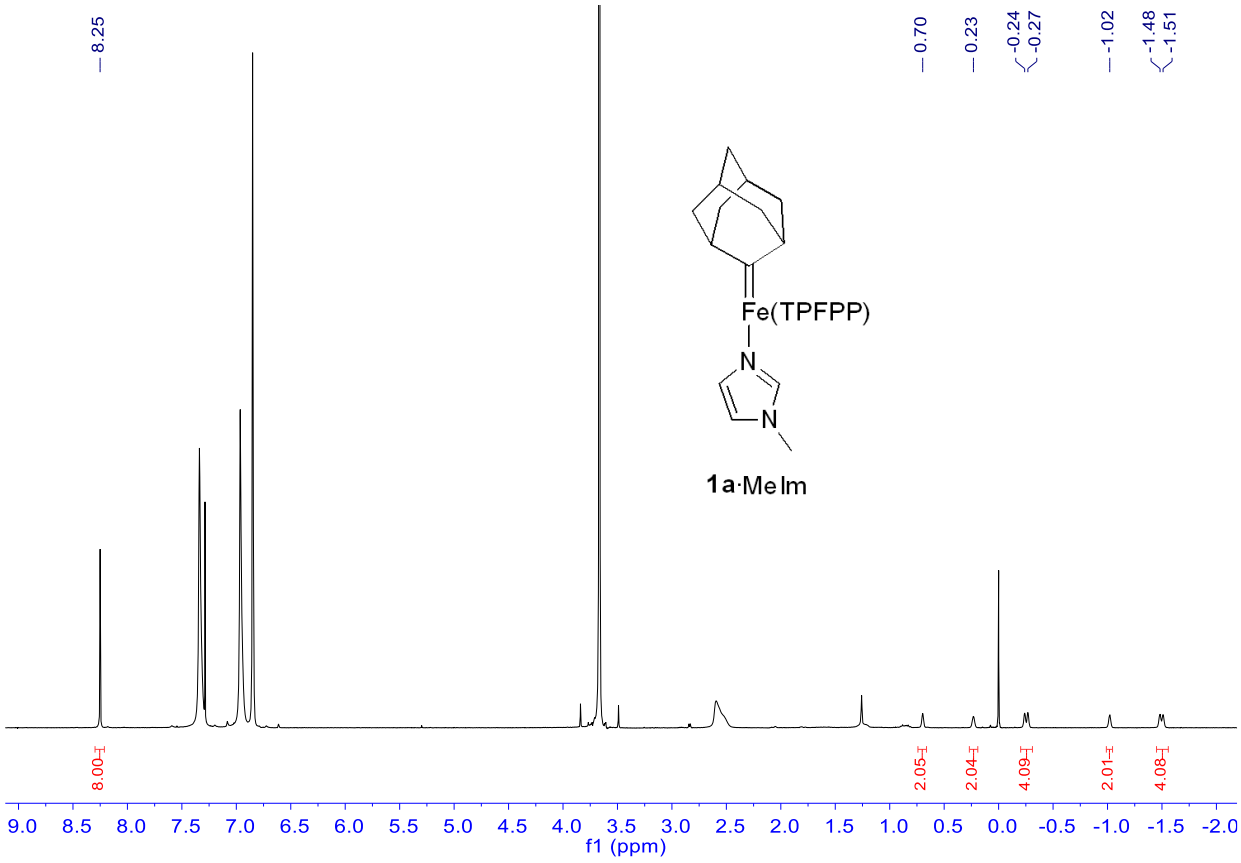
0.69
0.24
-0.25
-0.27
-1.02
-1.45
-1.47
Fe(TPFPP)
N
NMe2
1a·NMe2Py
8.00
2.08
2.09
4.05
2.07
4.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.
f1 (ppm)


433.39
433.39
Fe(TPFPP)
N
NMe2
1a·NMe2Py
442 440 438 436 434 432 430 428 426 424 422
f1 (ppm)
60 440 420 400 380 360 340 320 300 280 260 240 220 200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)


-137.39
-137.41
-137.47
-137.53
-137.55
-153.30
-153.35
-153.41
-162.39
-162.41
-162.45
-162.47
-162.51
-162.53
-162.55
-162.57
-162.61
-162.63
Fe(TPFPP)
N
NMe2
1a·NMe2Py
2.03
1.00
2.00
-131 -133 -135 -137 -139 -141 -143 -145 -147 -149 -151 -153 -155 -157 -159 -161 -163 -165 -167 -16
f1 (ppm)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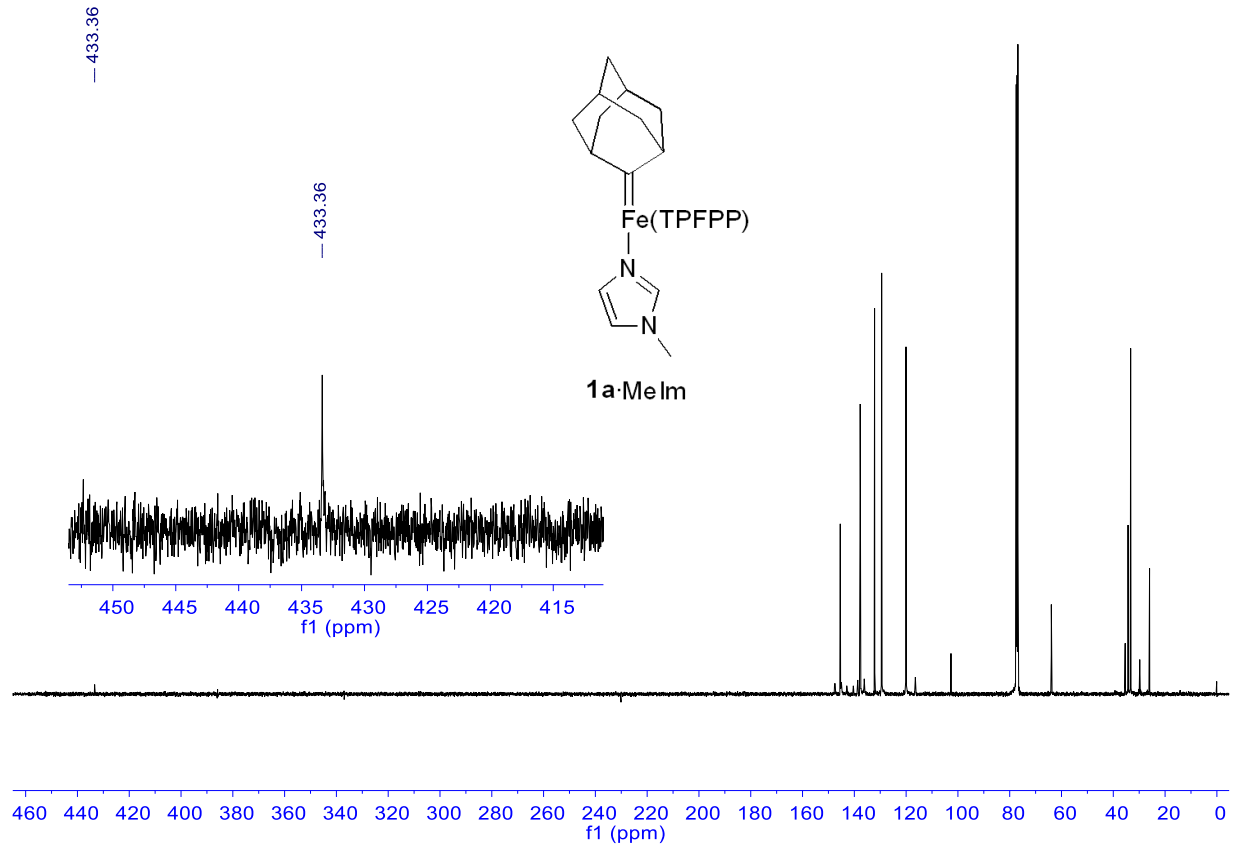
0.70
0.23
-0.24
-0.27
-1.02
-1.48
-1.51
Fe(TPFPP)
N
N
1a·MeIm
8.00
2.05
2.04
4.09
2.01
4.08
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)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433.36
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N
N
1a·MeIm
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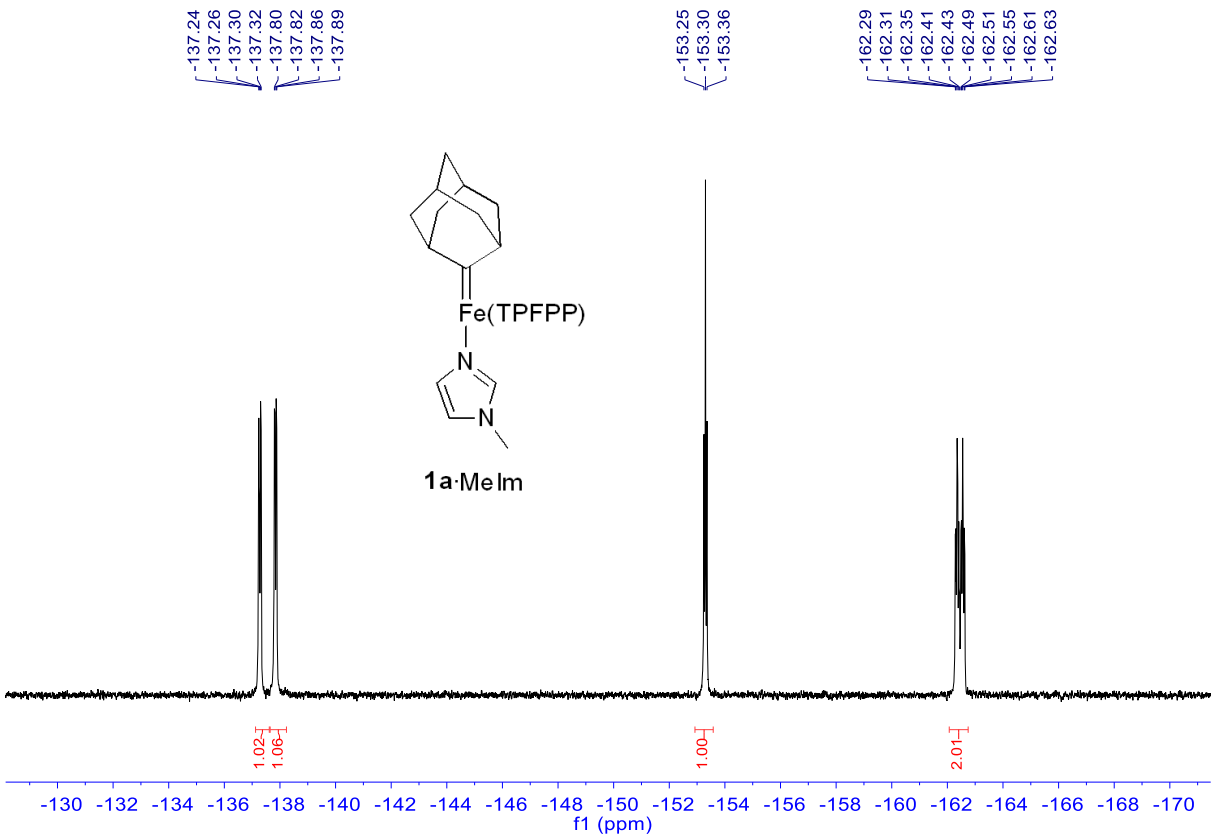
f1 (ppm)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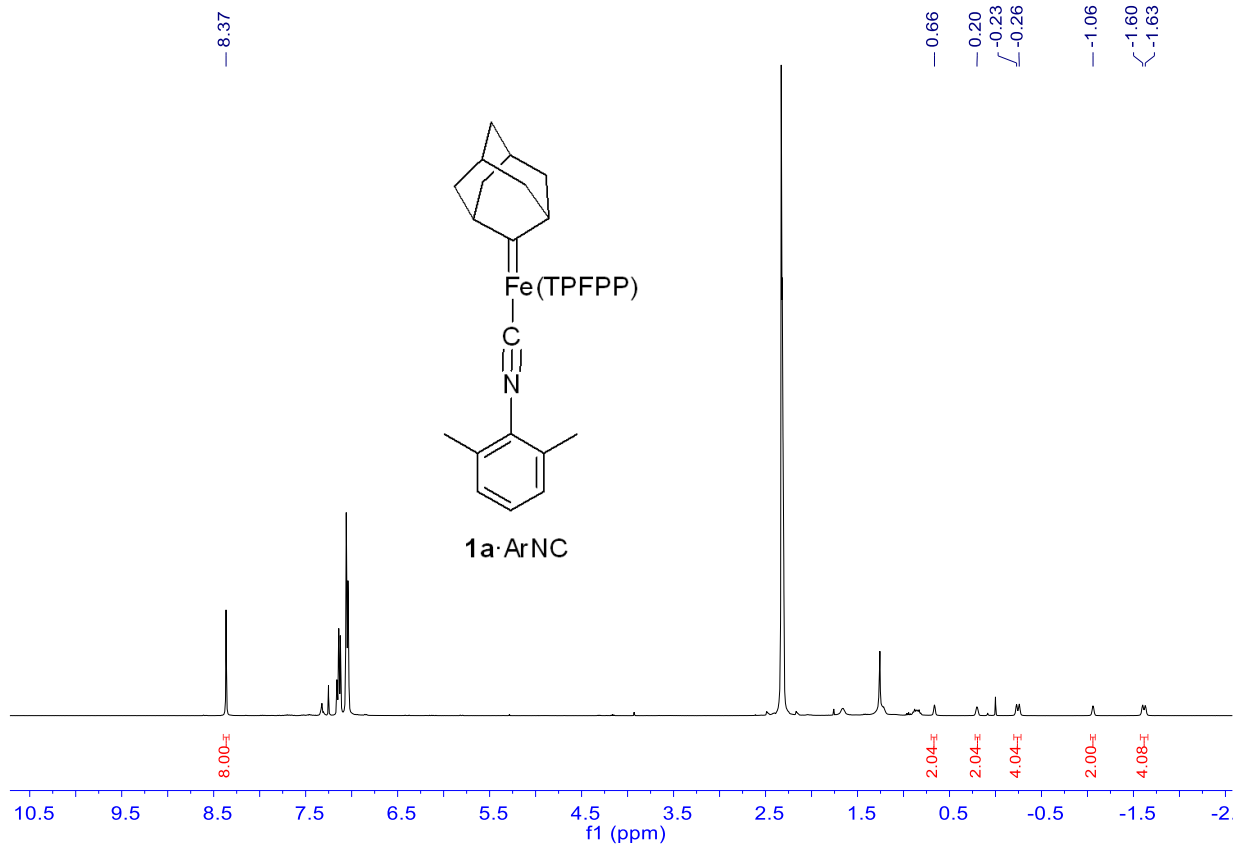
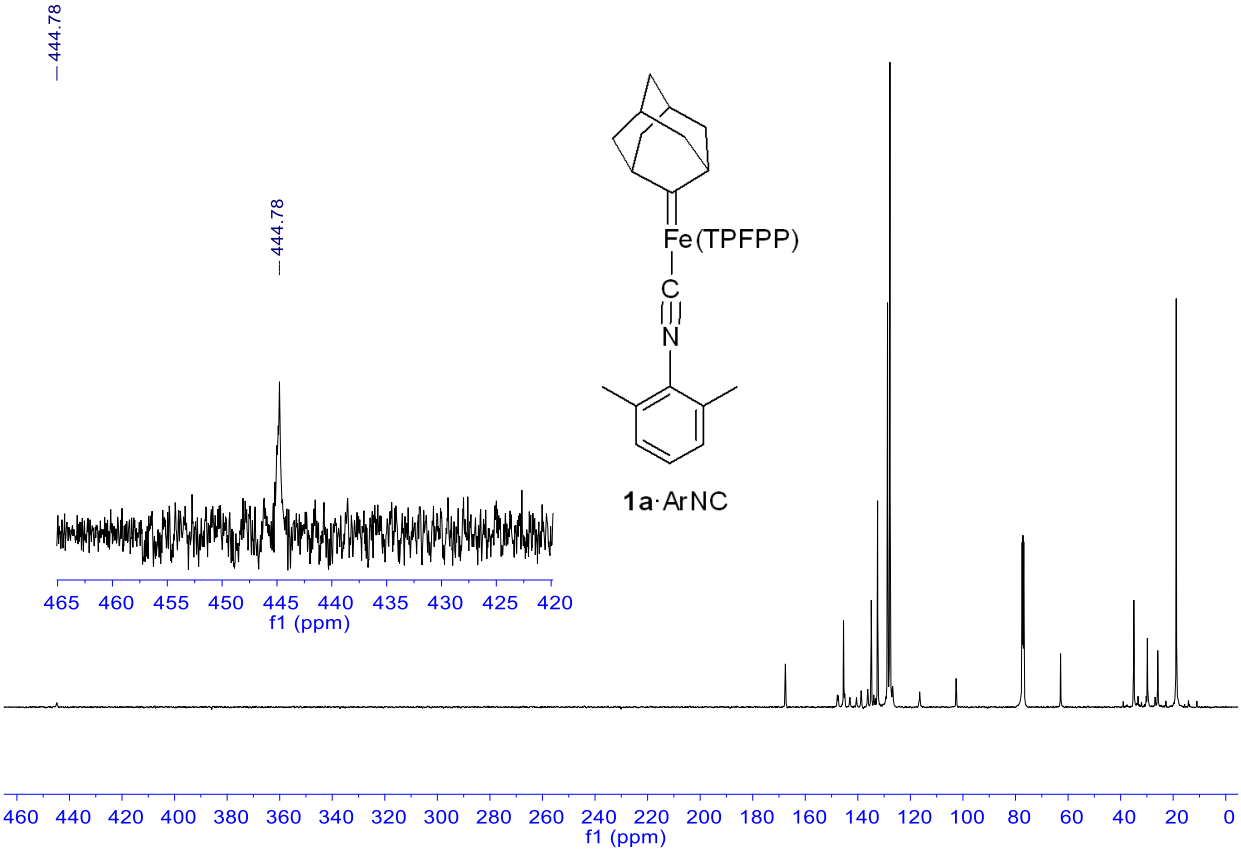
-137.89
-153.25
-153.30
-153.36
-162.29
-162.31
-162.35
-162.41
-162.43
-162.49
-162.51
-162.55
-162.61
-162.63
Fe(TPFPP)
N
N
1a·MeIm
1.02
1.06
1.00
2.01
-130 -132 -134 -136 -138 -140 -142 -144 -146 -148 -150 -152 -154 -156 -158 -160 -162 -164 -166 -168 -170
f1 (ppm)


8.37
0.66
0.20
-0.23
-0.26
-1.06
-1.60
-1.63
Fe(TPFPP)
C
N
1a·ArNC
8.00
2.04
2.04
4.04
2.00
4.08
10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5 -1.5 -2.
f1 (ppm)


444.78
444.78
Fe(TPFPP)
C
N
1a·ArNC
465 460 455 450 445 440 435 430 425 420
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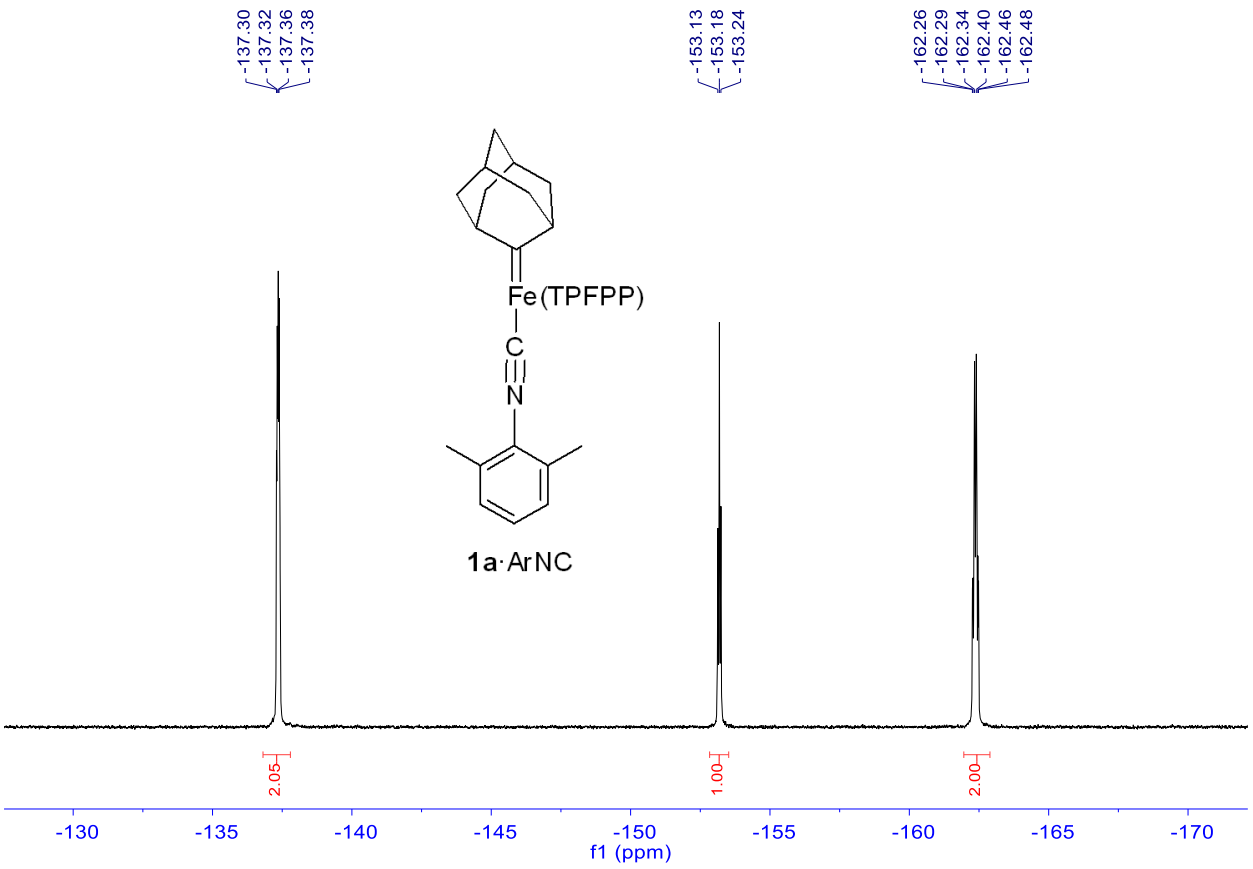
f1 (ppm)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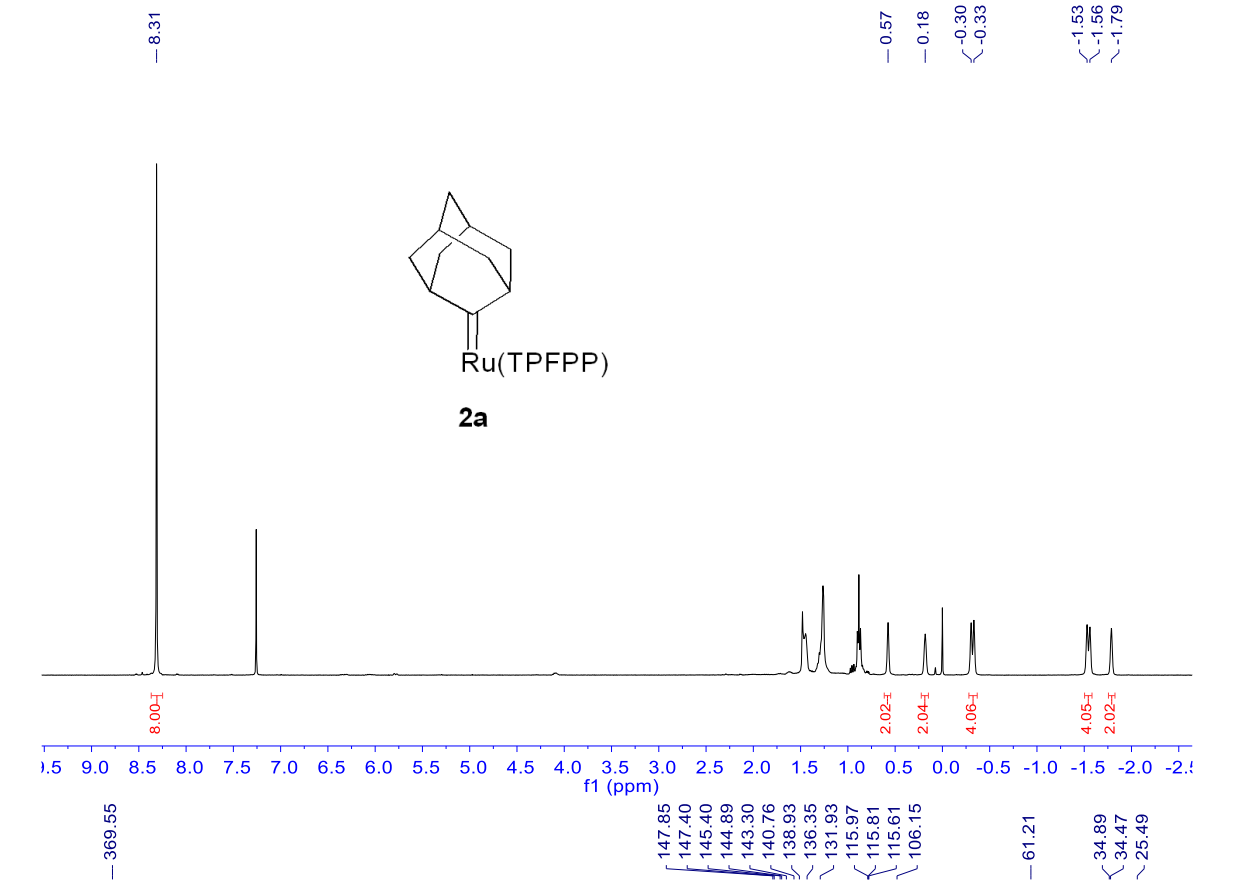
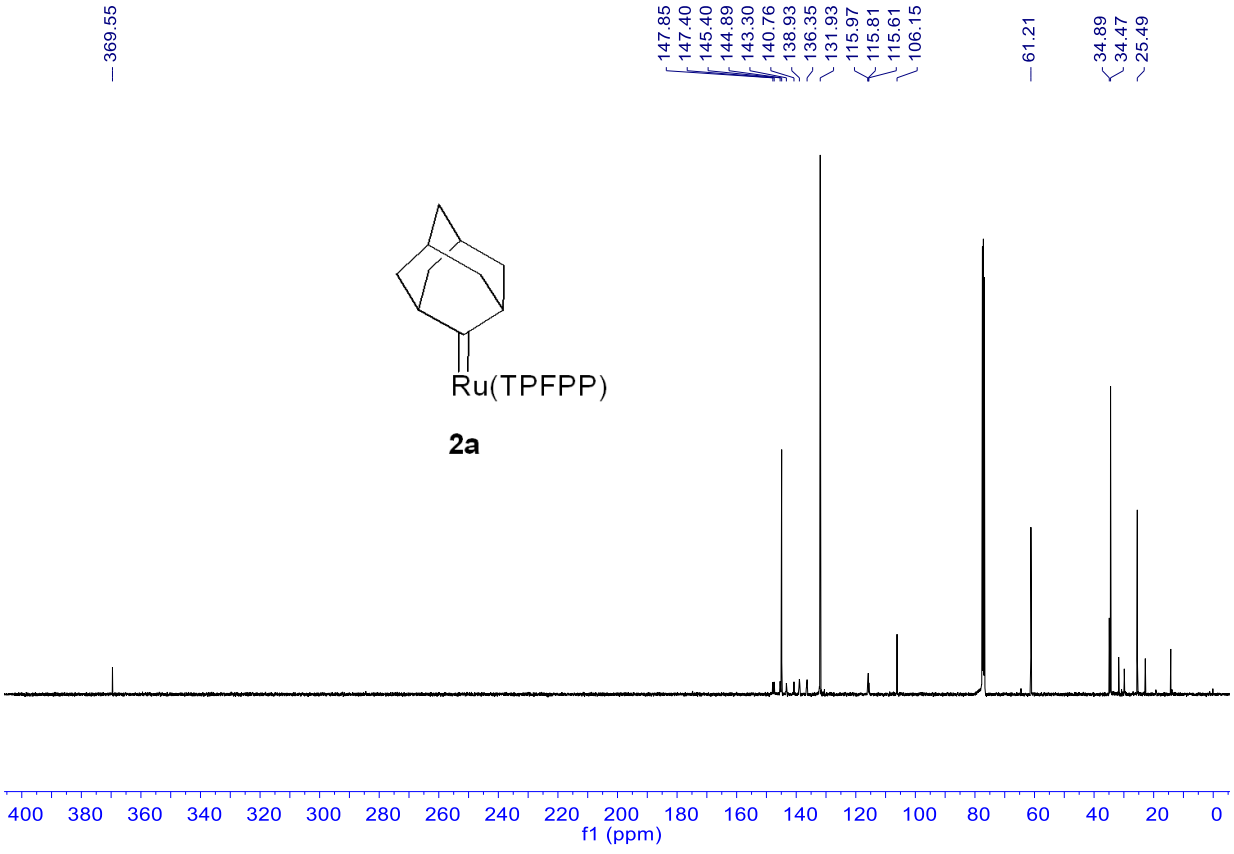
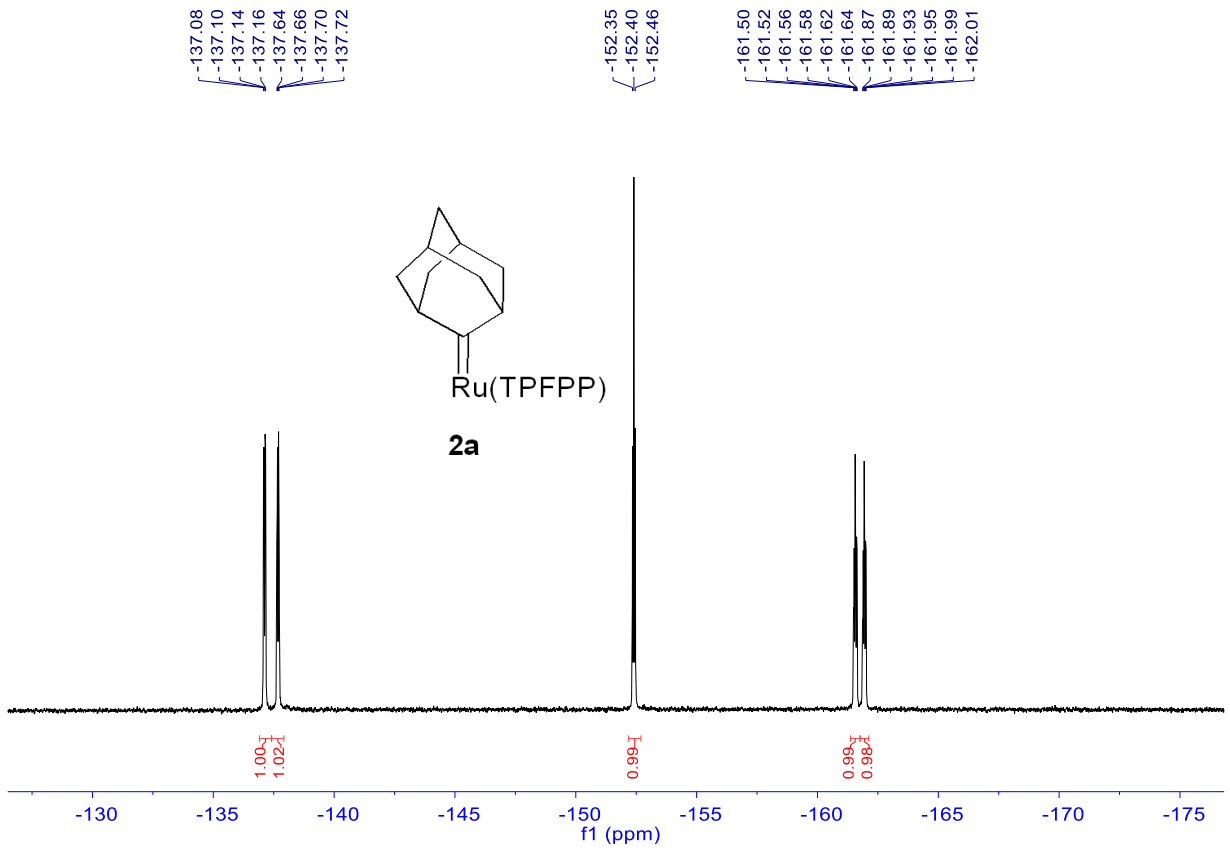
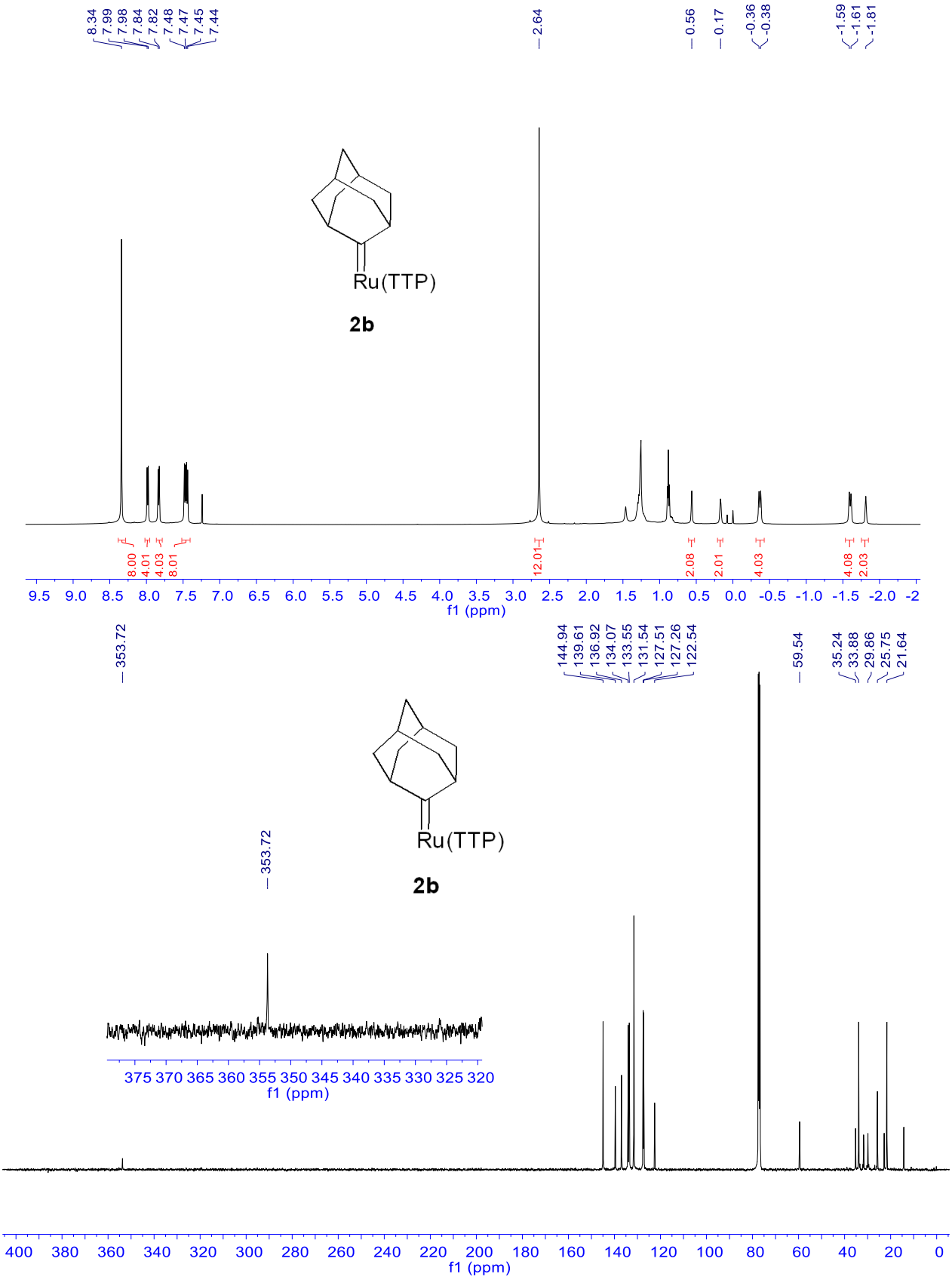
-153.13
-153.18
-153.24
-162.26
-162.29
-162.34
-162.40
-162.46
-162.48
Fe(TPFPP)
C
N
1a·ArNC
2.05
1.00
2.00
-130
-135
-140
-145
-150
-155
-160
-165
-170
f1 (ppm)

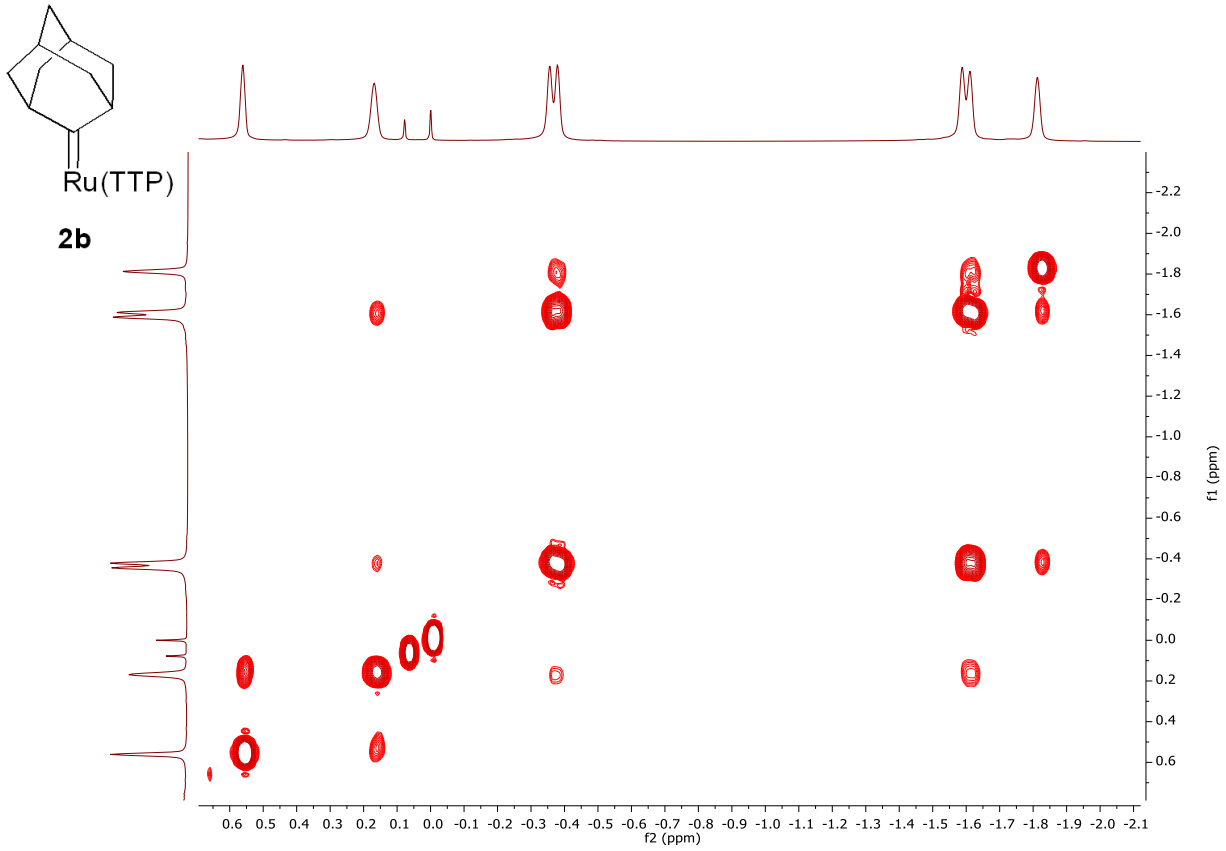

8.31
0.57
0.18
-0.30
-0.33
-1.53
-1.56
-1.79
Ru(TPFPP)
2a
8.00
2.02
2.04
4.06
4.05
2.02
f1 (ppm)

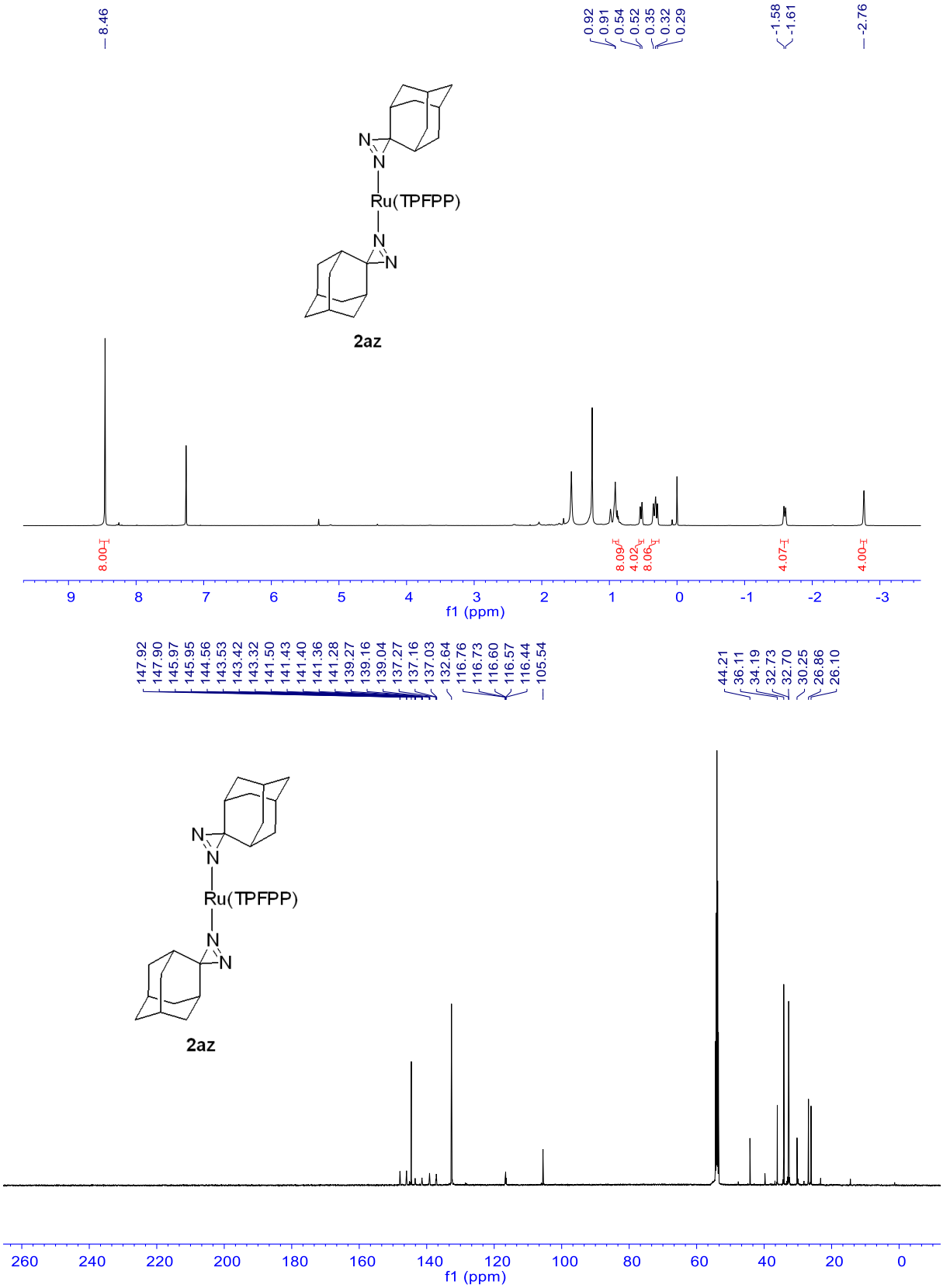

369.55
147.85
147.40
145.40
144.89
143.30
140.76
138.93
136.35
131.93
115.97
115.81
115.61
106.15
61.21
34.89
34.47
25.49
Ru(TPFPP)
2a
f1 (ppm)

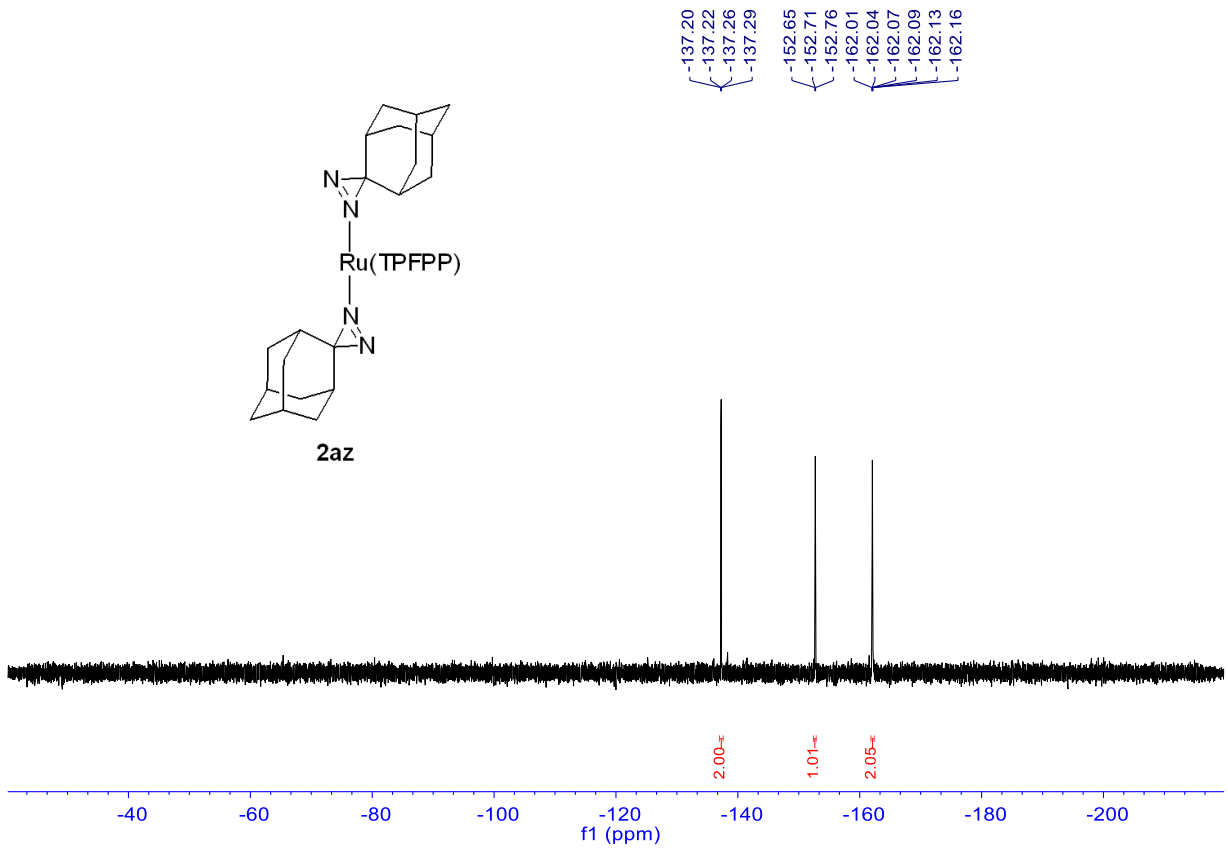

-137.08
-137.10
-137.14
-137.16
-137.64
-137.66
-137.70
-137.72
-152.35
-152.40
-152.46
-161.50
-161.52
-161.56
-161.58
-161.62
-161.64
-161.87
-161.89
-161.93
-161.95
-161.99
-162.01
Ru(TPFPP)
2a
1.00
1.02
0.99
0.99
0.98
-130
-135
-140
-145
-150
-155
-160
-165
-170
-175
f1 (ppm)

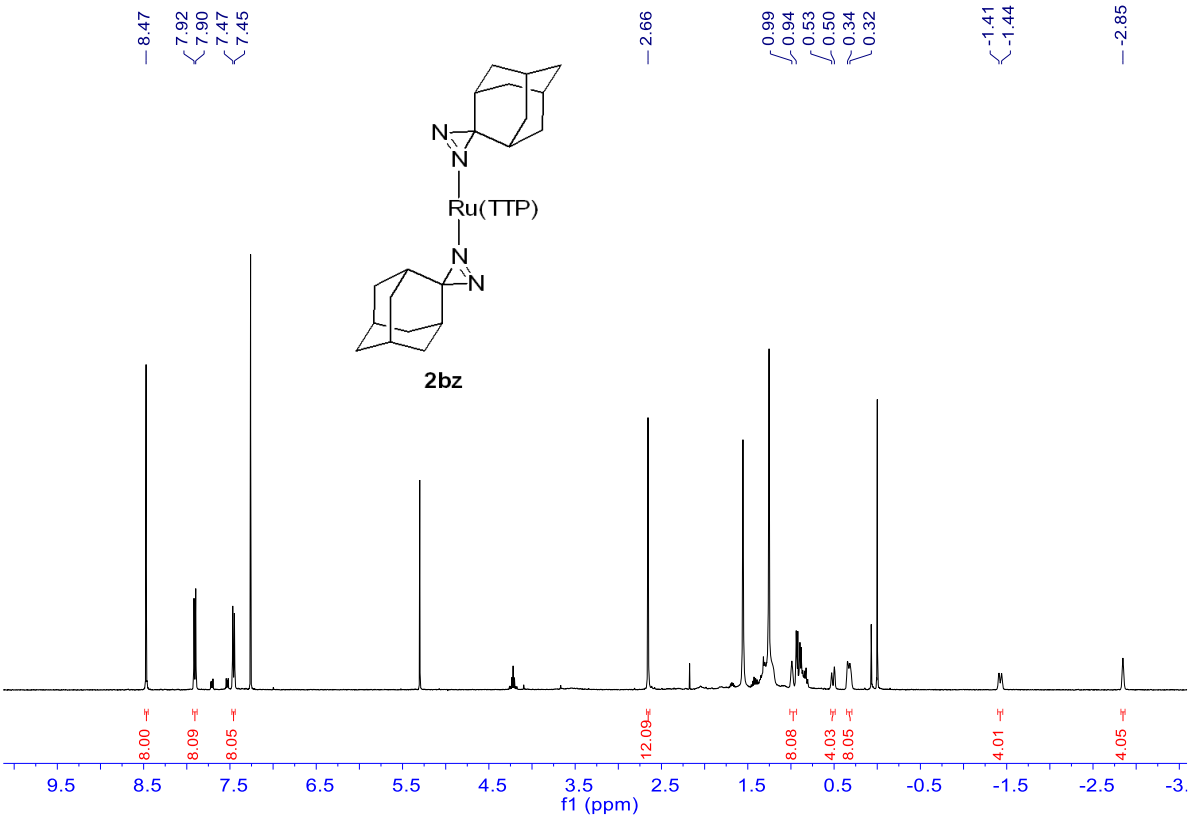

8.34
7.99
7.98
7.84
7.82
7.48
7.47
7.45
7.44
2.64
0.56
0.17
-0.36
-0.38
-1.59
-1.61
-1.81
Ru(TTP)
2b
8.00
4.01
4.03
8.01
12.01
2.08
2.01
4.03
4.08
2.03
f1 (ppm)
353.72
144.94
139.61
136.92
134.07
133.55
131.54
127.51
127.26
122.54
59.54
35.24
33.88
29.86
25.75
21.64
Ru(TTP)
2b
353.72
f1 (ppm)
f1 (ppm)

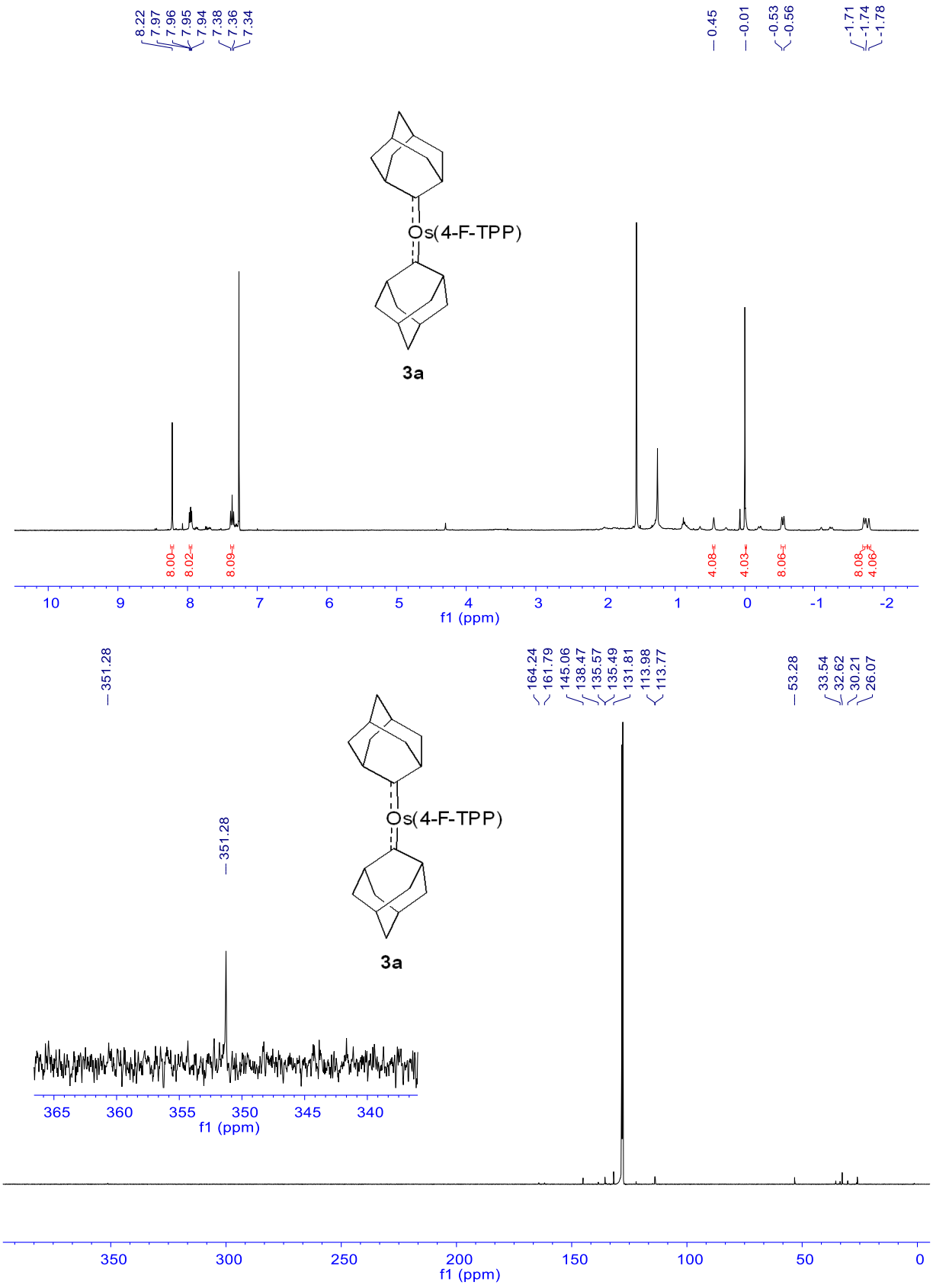
H-H COSY

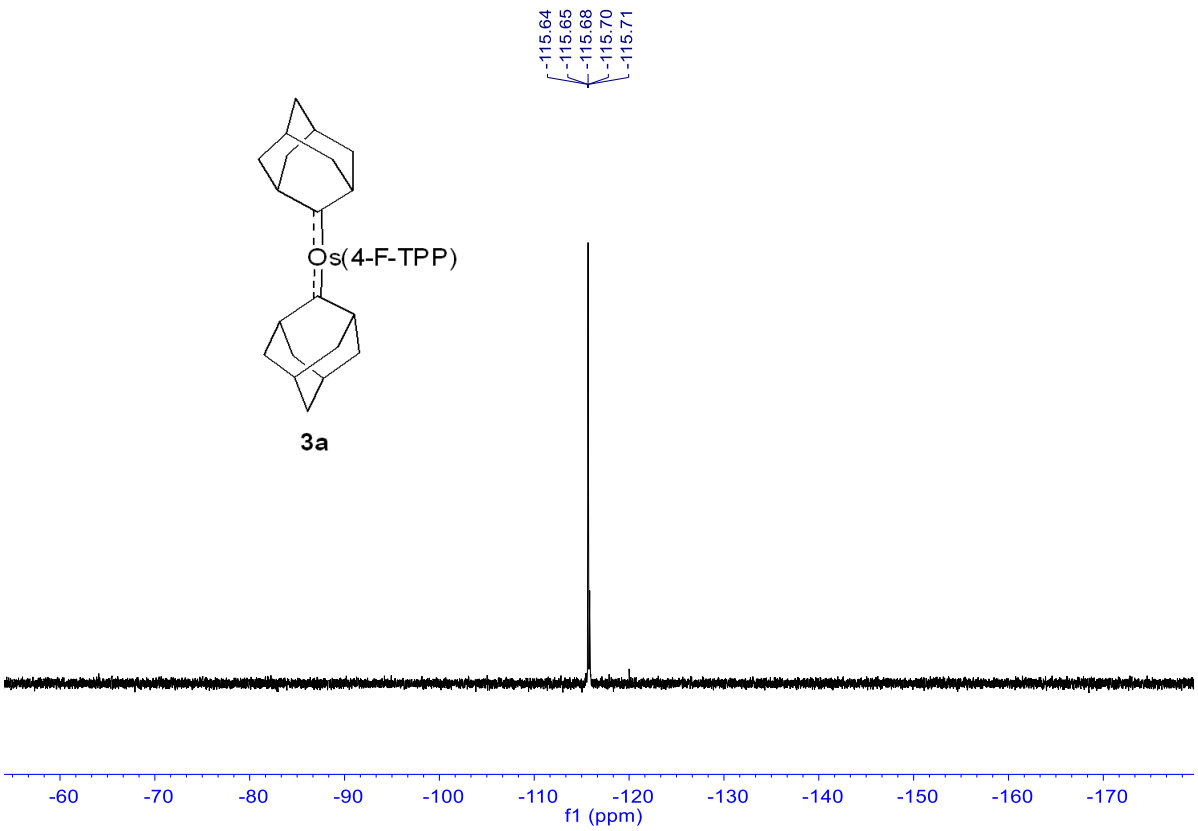


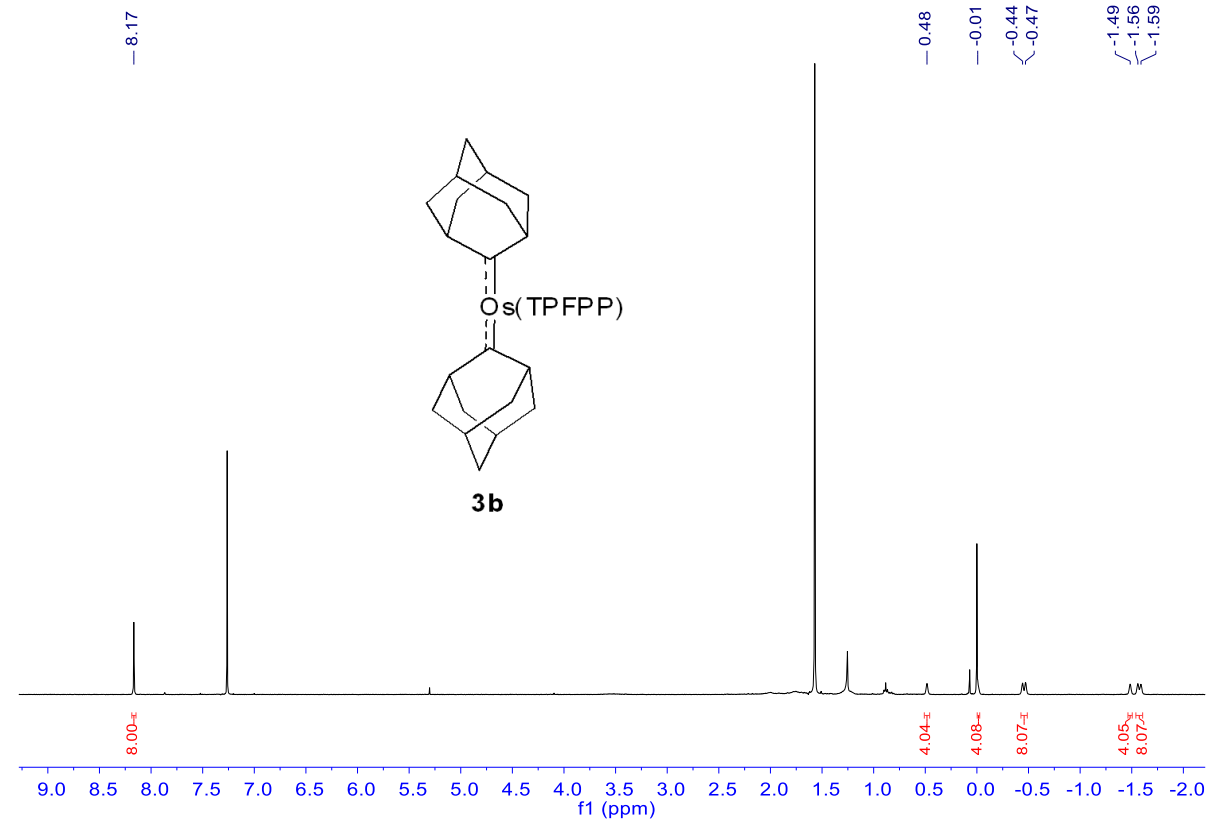

8.46
0.92
0.91
0.54
0.52
0.35
0.32
0.29
-1.58
-1.61
-2.76
N
N
Ru(TPFPP)
N
N
2az
8.00
8.09
4.02
8.06
4.07
4.00
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)
147.92
147.90
145.97
145.95
144.56
143.53
143.42
143.32
141.50
141.43
141.40
141.36
141.28
139.27
139.16
139.04
137.27
137.16
137.03
132.64
116.76
116.73
116.60
116.57
116.44
105.54
44.21
36.11
34.19
32.73
32.70
30.25
26.86
26.10
N
N
Ru(TPFPP)
N
N
2az
260
240
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

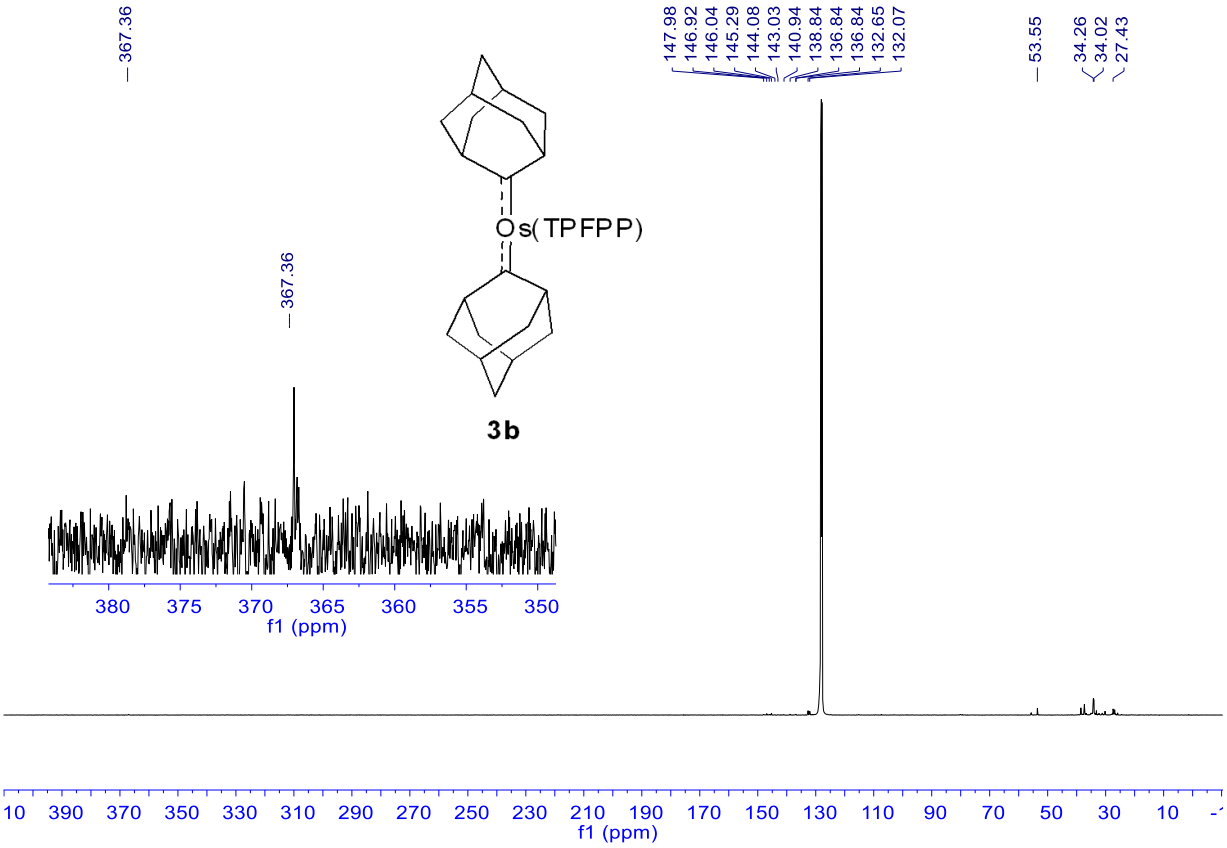

-137.20
-137.22
-137.26
-137.29
-152.65
-152.71
-152.76
-162.01
-162.04
-162.07
-162.09
-162.13
-162.16
N
N
Ru(TPFPP)
N
N
2az
2.00
1.01
2.05
-40
-60
-80
-100
-120
-140
-160
-180
-200
f1 (ppm)

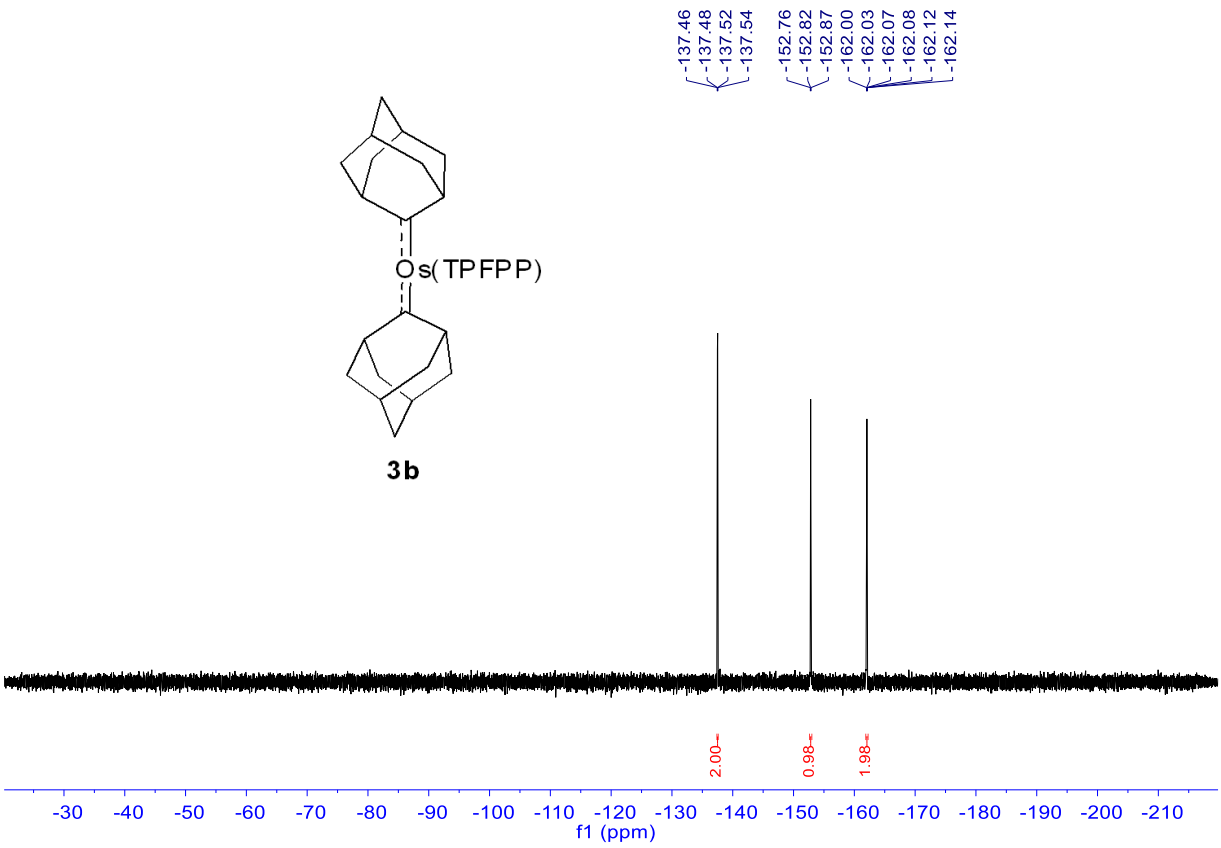

8.47
7.92
7.90
7.47
7.45
2.66
0.99
0.94
0.53
0.50
0.34
0.32
-1.41
-1.44
-2.85
N
N
Ru(TTP)
N
N
2bz
8.00
8.09
8.05
12.09
8.08
4.03
8.05
4.01
4.05
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
-2.5
f1 (ppm)

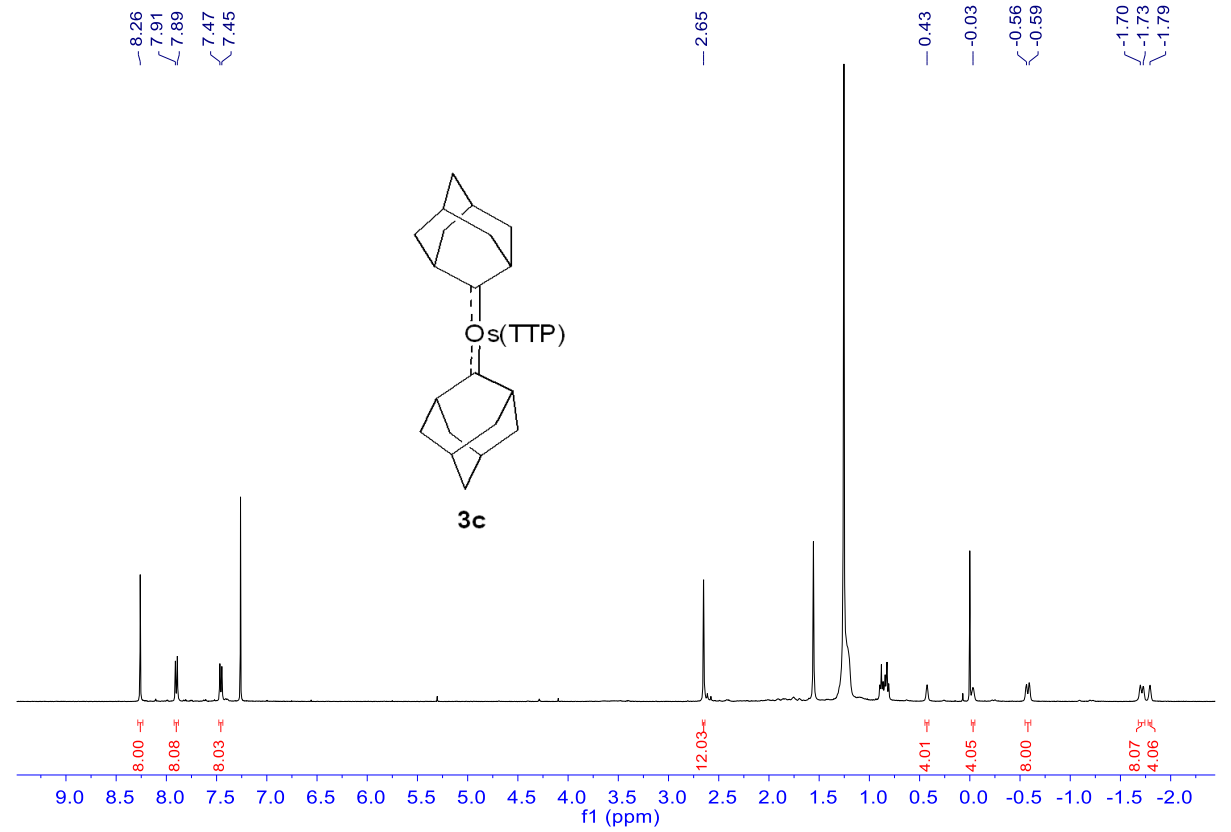

8.22
7.97
7.96
7.95
7.94
7.38
7.36
7.34
0.45
-0.01
-0.53
-0.56
-1.71
-1.74
-1.78
Os(4-F-TPP)
3a
8.00
8.02
8.09
4.08
4.03
8.06
8.08
4.06
f1 (ppm)
351.28
164.24
161.79
145.06
138.47
135.57
135.49
131.81
113.98
113.77
53.28
33.54
32.62
30.21
26.07
Os(4-F-TPP)
3a
351.28
f1 (ppm)
f1 (ppm)

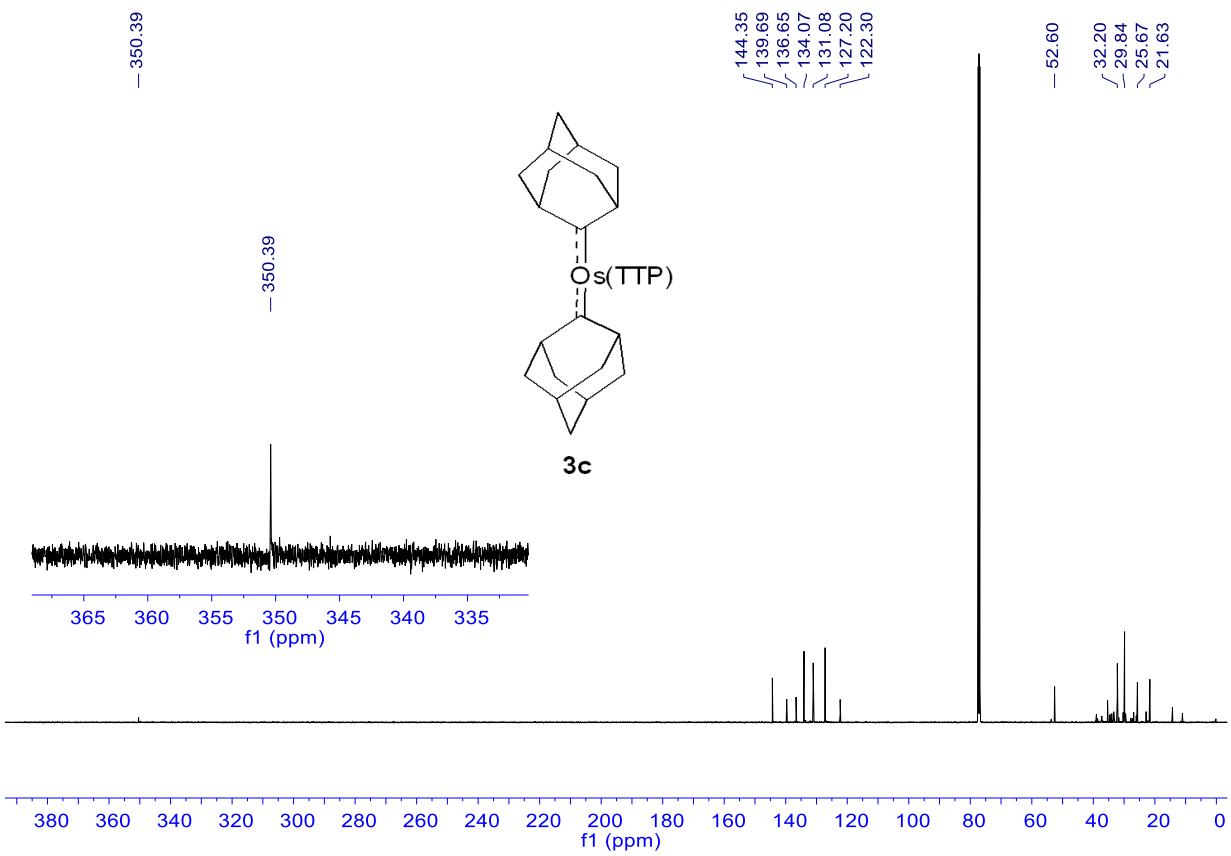

-115.64
-115.65
-115.68
-115.70
-115.71
Os(4-F-TPP)
3a
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

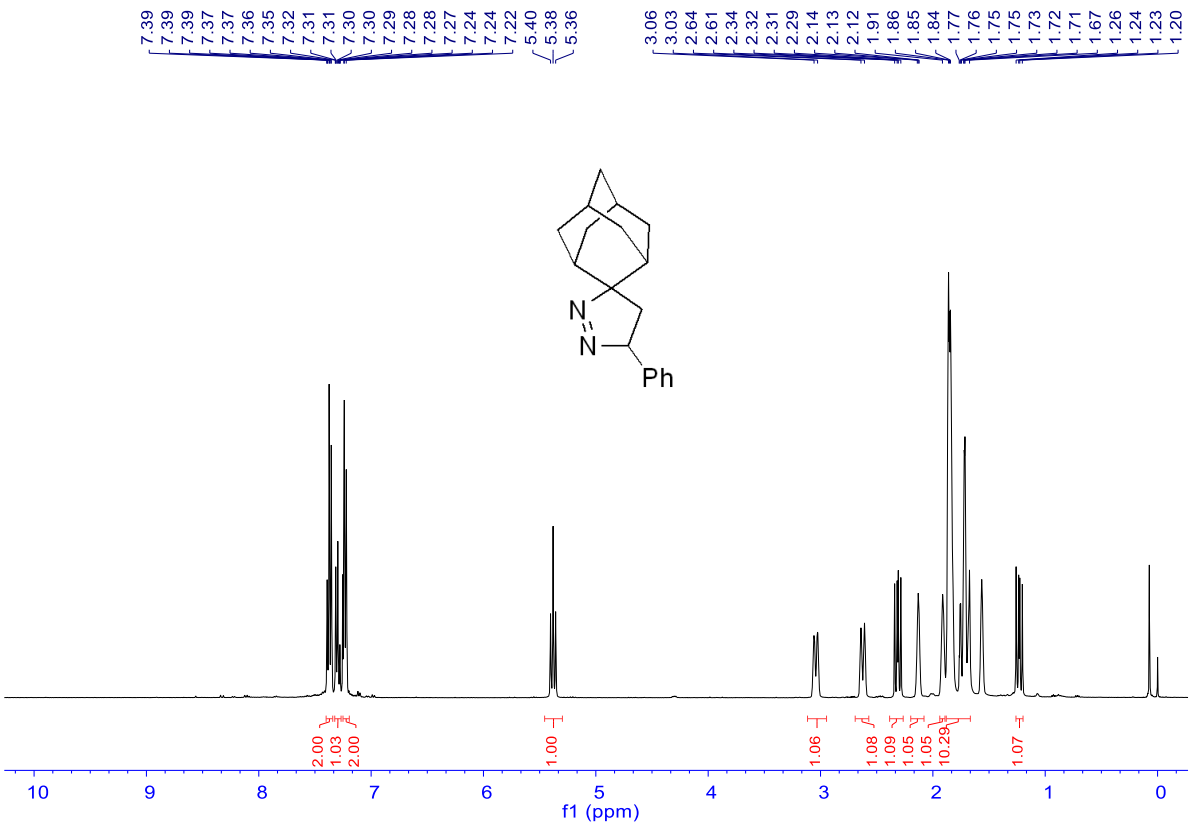

8.17
0.48
-0.01
-0.44
-0.47
-1.49
-1.56
-1.59
Os(TPFPP)
3b
8.00
4.04
4.08
8.07
4.05
8.07
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)

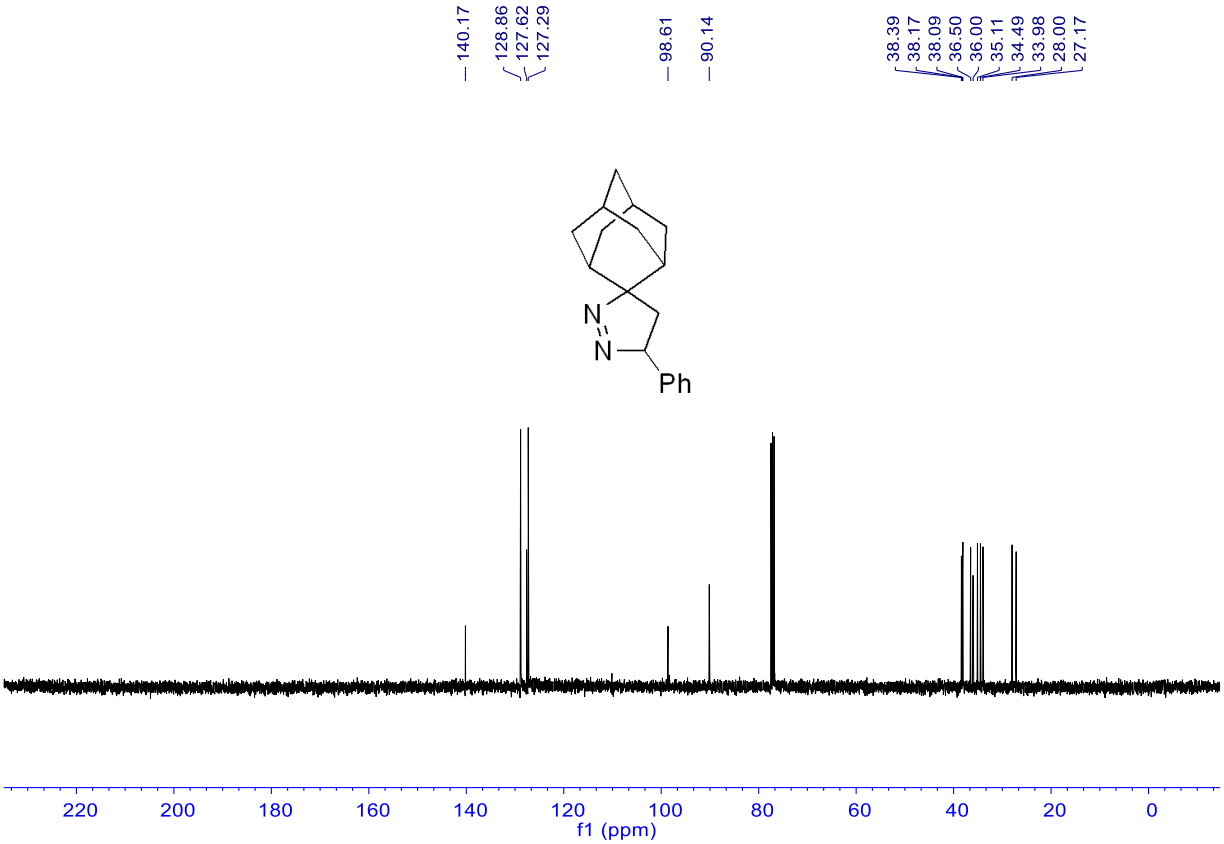

367.36
147.98
146.92
146.04
145.29
144.08
143.03
140.94
138.84
136.84
136.84
132.65
132.07
53.55
34.26
34.02
27.43
Os(TPFPP)
3b
380 375 370 365 360 355 350
f1 (ppm)
10 390 370 350 330 310 290 270 250 230 210 190 170 150 130 110 90 70 50 30 10
f1 (ppm)


-137.46
-137.48
-137.52
-137.54
-152.76
-152.82
-152.87
-162.00
-162.03
-162.07
-162.08
-162.12
-162.14
Os(TPFPP)
3b
2.00
0.98
1.98
-30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


8.26
7.91
7.89
7.47
7.45
2.65
0.43
-0.03
-0.56
-0.59
-1.70
-1.73
-1.79
Os(TTP)
3c
8.00
8.08
8.03
12.03
4.01
4.05
8.00
8.07
4.06
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 -0.5 -1.0 -1.5 -2.0
f1 (ppm)


350.39
144.35
139.69
136.65
134.07
131.08
127.20
122.30
52.60
32.20
29.84
25.67
21.63
350.39
Os(TTP)
3c
365 360 355 350 345 340 335
f1 (ppm)
380 360 340 320 300 280 260 240 220 200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)


7.39
7.39
7.39
7.37
7.37
7.36
7.35
7.32
7.31
7.31
7.30
7.30
7.29
7.28
7.28
7.27
7.24
7.24
7.22
5.40
5.38
5.36
3.06
3.03
2.64
2.61
2.34
2.32
2.31
2.29
2.14
2.13
2.12
1.91
1.86
1.85
1.84
1.77
1.76
1.75
1.75
1.73
1.72
1.71
1.67
1.26
1.24
1.23
1.20
N
N
Ph
2.00
1.03
2.00
1.00
1.06
1.08
1.09
1.05
1.05
10.29
1.07
10
9
8
7
6
5
4
3
2
1
0
f1 (ppm)


140.17
128.86
127.62
127.29
98.61
90.14
38.39
38.17
38.09
36.50
36.00
35.11
34.49
33.98
28.00
27.17
N
N
Ph
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

VI. Cartesian coordinates from DFT calculations

1b

Fe	0.00935900	-0.00708500	-0.40991900
N	-0.00747700	1.96979700	-0.64385900
N	-1.98339000	-0.01036700	-0.61097700
N	0.01247000	-1.98525900	-0.63106800
N	1.98988900	0.00407000	-0.62611300
C	1.06654100	2.81133400	-0.88332600
C	0.62899700	4.18680700	-0.90456800
H	1.26517800	5.04126200	-1.07836600
C	-0.70389300	4.18039800	-0.64833900
H	-1.37377200	5.02645600	-0.59303800
C	-1.10166400	2.80302100	-0.49360200
C	-2.42166500	2.39378800	-0.28849200
C	-2.82718200	1.06150900	-0.38068300
C	-4.20036100	0.62614600	-0.34994400
H	-5.05220400	1.26658300	-0.17278200
C	-4.19076200	-0.70933400	-0.60204500
H	-5.03361800	-1.38252800	-0.66966800
C	-2.81282700	-1.10206700	-0.75136500
C	-2.40152600	-2.42435900	-0.93847500
C	-1.06481600	-2.82515100	-0.86934700
C	-0.62370700	-4.19862200	-0.93644300
H	-1.26487100	-5.04728400	-1.12672900
C	0.71610000	-4.19700200	-0.70706900
H	1.39290700	-5.03968300	-0.67725500
C	1.10897100	-2.82009800	-0.54797700
C	2.43070700	-2.40955400	-0.37159000
C	2.83317100	-1.08010700	-0.46053100
C	4.20992300	-0.66121800	-0.49536200
H	5.06142300	-1.31767300	-0.38532300
C	4.20545500	0.67496600	-0.73807300
H	5.05995400	1.32235900	-0.86491900
C	2.82389700	1.09295800	-0.79094800
C	2.40854500	2.41492600	-0.97188100
C	-3.45622200	3.43547600	-0.00955200
C	-4.34461500	3.88454000	-0.99649000
H	-4.26176700	3.48882000	-2.00493500
C	-5.31632200	4.83550600	-0.69612600
H	-5.99323700	5.17576000	-1.47668100
C	-5.44682600	5.35478400	0.59980500
C	-4.55966100	4.90053500	1.58291900

H	-4.64308500	5.28318600	2.59736500
C	-3.57177500	3.96238000	1.28206800
H	-2.89134700	3.61593400	2.05566700
C	-6.53959500	6.34452500	0.92538100
H	-6.54695600	7.18440800	0.22043800
H	-6.42693600	6.75526100	1.93431200
H	-7.53191900	5.87934700	0.87050800
C	-3.47084400	-3.43851000	-1.20534700
C	-4.09580100	-3.48138600	-2.46086700
H	-3.77686800	-2.78965000	-3.23490400
C	-5.12117800	-4.38901700	-2.71237800
H	-5.58944300	-4.41282700	-3.69352900
C	-5.57229600	-5.26576000	-1.71492600
C	-4.95819100	-5.20861600	-0.46034400
H	-5.30655100	-5.86274500	0.33453100
C	-3.91803700	-4.31093300	-0.20741900
H	-3.46490600	-4.27003600	0.77900800
C	-6.68036000	-6.24675800	-2.01281700
H	-7.62215300	-5.73575600	-2.24897400
H	-6.86622200	-6.91957600	-1.16951300
H	-6.43547500	-6.86378300	-2.88579100
C	3.46565900	-3.45745300	-0.12006600
C	3.53960900	-4.06098300	1.14335000
H	2.84356100	-3.75238400	1.91909300
C	4.49604400	-5.03679600	1.41127600
H	4.54165200	-5.48410300	2.40153800
C	5.40178900	-5.45020400	0.42461400
C	5.31203300	-4.85635300	-0.84093700
H	6.00483700	-5.15791900	-1.62311900
C	4.35782700	-3.87483100	-1.11230300
H	4.31241400	-3.41511700	-2.09558800
C	6.48626000	-6.45051600	0.74323300
H	6.13840900	-7.21600900	1.44557500
H	7.34614900	-5.95452300	1.21258300
H	6.85226700	-6.95549800	-0.15703500
C	3.44729700	3.45716200	-1.22513300
C	4.49833100	3.65971700	-0.31648400
H	4.54553800	3.04614700	0.57864800
C	5.47590000	4.62029500	-0.55951000
H	6.27978100	4.75945700	0.15946400
C	5.43944300	5.41910400	-1.71151900
C	4.39530400	5.21101200	-2.61943800
H	4.34978500	5.80601000	-3.52859300
C	3.41659100	4.24514300	-2.38370700

H	2.62555900	4.08947600	-3.11167700
C	6.47237800	6.49327600	-1.94567600
H	6.21405700	7.41229200	-1.40350200
H	6.55186700	6.76035500	-3.00504600
H	7.46449000	6.18469800	-1.59869000
C	0.02458600	0.01136600	1.33239400
C	-0.77308100	-0.94460800	2.18414800
H	-1.36660100	-1.61565500	1.56376900
C	-1.70694700	-0.13207800	3.12645800
H	-2.41977300	0.44605800	2.52597400
H	-2.29182200	-0.83496700	3.73737800
C	-0.85988400	0.79339900	4.01899400
H	-1.51728100	1.36381900	4.68907600
C	0.13872200	-0.04091900	4.85544900
H	-0.40928500	-0.72419300	5.51930100
H	0.73312800	0.62593200	5.49574100
C	1.06831200	-0.84788300	3.92246900
H	1.77433000	-1.43873200	4.52370800
C	1.84657700	0.11689900	3.01031200
H	2.51805000	-0.43305800	2.33931400
H	2.46885500	0.80230600	3.60285100
C	0.85218100	0.95435100	2.16425300
H	1.41275500	1.63958400	1.52941100
C	0.21110100	-1.78223900	3.04879800
H	-0.37308800	-2.47131200	3.67422300
H	0.84709500	-2.39610200	2.39946300
C	-0.07881000	1.76242000	3.11504700
H	0.53998400	2.44340400	3.71606500
H	-0.76505900	2.38239900	2.52347900

3a

Os	0.00091500	0.00168200	0.00036200
N	0.04279800	2.07694400	-0.00137200
N	-2.07479800	0.04362800	0.00291000
C	2.49172900	2.39864100	-0.20536500
C	1.16237900	2.86164100	-0.15427700
C	0.74673400	4.24903200	-0.21985100
H	1.40751800	5.09097000	-0.36588700
C	-0.60675000	4.27520700	-0.06722700
H	-1.25191500	5.14179600	-0.06841100
C	-1.05309400	2.90315500	0.07164700
C	-2.39624600	2.49334200	0.19715300
C	-2.85935400	1.16378000	0.15217700

C	-4.24656200	0.74824900	0.22125800
H	-5.08838500	1.40943600	0.36614200
C	-4.27275100	-0.60581500	0.07332200
H	-5.13929200	-1.25102500	0.07793500
C	-2.90085700	-1.05255600	-0.06609300
C	-0.00533700	-0.00416700	-2.00215300
C	-0.89131000	0.87061800	-2.85262100
H	-1.51724900	1.51045600	-2.22746700
C	0.86785700	-0.89163900	-2.85244300
H	1.50436700	-1.52048800	-2.22672700
C	-1.79797200	-0.03053000	-3.73451200
H	-2.43859200	-0.64753800	-3.09113400
H	-2.45789200	0.60796400	-4.33777300
C	-0.00313200	1.76068100	-3.76314100
H	-0.65078400	2.41155200	-4.36653100
H	0.62583100	2.41039500	-3.14115700
C	-0.03493700	-1.79709300	-3.73327000
H	0.60305100	-2.45749900	-4.33664800
H	-0.65292000	-2.43682700	-3.09025800
C	1.75959300	-0.00561800	-3.76398400
H	2.41066700	0.62211800	-3.14174200
H	2.40962900	-0.65426400	-4.36708600
C	-0.92184500	-0.91968300	-4.63278700
H	-1.56061000	-1.55727100	-5.25804900
C	0.86879100	0.86850200	-4.66259200
H	1.49701500	1.49543200	-5.30896500
C	-0.03392100	-0.03296800	-5.53218300
H	-0.66392400	0.58714800	-6.18441100
H	0.58504500	-0.66381300	-6.18468800
N	-0.04120600	-2.07422300	0.00593100
N	2.07640100	-0.04056200	-0.00816900
C	-2.49107700	-2.39621600	-0.18760500
C	-1.16144200	-2.85931000	-0.14096500
C	-0.74559600	-4.24676600	-0.20595100
C	0.60849900	-4.27243600	-0.05748500
H	1.25385600	-5.13888900	-0.05925300
C	1.05512000	-2.89999300	0.07665200
C	2.39878700	-2.48946900	0.19476300
C	2.86157700	-1.16012400	0.14191300
C	4.24915100	-0.74451600	0.20270400
H	5.09163300	-1.40529400	0.34560900
C	4.27472500	0.60898000	0.05050400
H	5.14129100	1.25417500	0.04892600
C	2.90219800	1.05536000	-0.08333000

C	0.00661700	0.00570200	2.00338500
C	-0.86805500	-0.87546600	2.85872400
H	-1.50401800	-1.50882700	2.23740300
C	0.88927300	0.88843800	2.84934500
H	1.51903900	1.52078200	2.22029400
C	0.03238700	-1.77139100	3.75223200
H	0.65431200	-2.41541900	3.11699600
H	-0.60643100	-2.42822200	4.35855400
C	-1.76431800	0.01821200	3.75758200
H	-2.41548000	-0.62583900	4.36446300
H	-2.41356700	0.63920100	3.12714600
C	1.79364900	-0.00354500	3.74262800
H	2.44946000	0.64202500	4.34296500
H	2.43812900	-0.62561500	3.10827800
C	-0.00297300	1.78616200	3.74886700
H	-0.62999400	2.42961900	3.11812300
H	0.64144000	2.44358000	4.34852800
C	0.91485900	-0.88449300	4.64655800
H	1.55145400	-1.51572200	5.28044200
C	-0.87833700	0.90136800	4.65217300
H	-1.50960100	1.53395700	5.29003200
C	0.02193900	0.00935400	5.53384400
H	-0.59911500	-0.61630300	6.18937500
H	0.64833100	0.63612700	6.18319100
C	3.42058900	-3.56940700	0.35175300
C	4.36145100	-3.83049800	-0.65712100
C	3.44960900	-4.35240500	1.51702800
C	5.31179900	-4.84148100	-0.51145900
H	4.34466300	-3.23642700	-1.56586000
C	4.39195300	-5.36824000	1.67929800
H	2.72651200	-4.15966900	2.30411600
C	5.30852600	-5.59294900	0.65828600
H	6.04052600	-5.05465000	-1.28638500
H	4.42609500	-5.97622300	2.57717200
C	-3.41714000	3.57418600	0.35413600
C	-3.44101600	4.36179500	1.51640800
C	-4.36187200	3.83188000	-0.65200800
C	-4.38214200	5.37875000	1.67857900
H	-2.71474300	4.17187300	2.30124500
C	-5.31108300	4.84396800	-0.50638900
H	-4.34906400	3.23427800	-1.55848400
C	-5.30269400	5.59997100	0.66044000
H	-4.41229200	5.99025500	2.57420800
H	-6.04282600	5.05455200	-1.27916600

C	3.57183300	3.41990900	-0.36496700
C	4.35486800	3.44583300	-1.53026900
C	3.83330600	4.36302800	0.64170000
C	5.37104800	4.38738400	-1.69484400
H	4.16196100	2.72086000	-2.31557400
C	4.84465800	5.31265100	0.49371000
H	3.23922200	4.34863400	1.55046300
C	5.59610500	5.30630500	-0.67606300
H	5.97904500	4.41911500	-2.59280500
H	5.05812000	6.04316300	1.26686400
F	6.22627900	-6.57611200	0.80722800
F	6.57963800	6.22330000	-0.82724200
F	-6.21930300	6.58421800	0.80930400
H	-1.40654500	-5.08914600	-0.34841200
C	-3.57216200	-3.41717600	-0.34242500
C	-3.83401100	-4.35623100	0.66802900
C	-4.35609200	-3.44679900	-1.50711000
C	-4.84634500	-5.30544800	0.52433100
H	-3.23964100	-4.33875500	1.57654400
C	-5.37321500	-4.38809500	-1.66743600
H	-4.16294100	-2.72508800	-2.29536100
C	-5.59848500	-5.30292200	-0.64499200
H	-5.06009100	-6.03270500	1.30048000
H	-5.98179700	-4.42271500	-2.56488700
F	-6.58298300	-6.21956400	-0.79198900

Free Ad carbene, triplet:

C	-0.00002267	-0.00018724	-1.72957155
C	1.26970418	0.00038190	-0.97255088
H	2.14781410	0.00083745	-1.62150955
C	1.26572521	-1.26568642	-0.06881217
H	1.29490380	-2.16187319	-0.69150260
H	2.16133204	-1.27452504	0.56037910
C	0.00050450	-1.25976457	0.81018565
H	0.00090068	-2.14999582	1.44460843
C	0.00002622	0.00016109	1.69414194
H	0.87840032	0.00055828	2.34595729
H	-0.87832576	-0.00011375	2.34598666
C	-0.00048369	1.25994051	0.80997595
H	-0.00086862	2.15027191	1.44426676
C	-1.26572085	1.26567997	-0.06898022
H	-1.29493890	2.16171745	-0.69187643
H	-2.16131298	1.27458203	0.56021630

C	-1.26973212	-0.00057621	-0.97252328
H	-2.14785695	-0.00104733	-1.62146077
C	1.26479624	1.26658010	-0.06882514
H	2.16034964	1.27594685	0.56042791
H	1.29349862	2.16266580	-0.69164375
C	-1.26480438	-1.26658226	-0.06859662
H	-2.16034342	-1.27588550	0.56069369
H	-1.29350838	-2.16282038	-0.69120516

Free Ad carbene, singlet:

C	-0.49141800	0.00023100	-1.72689000
C	-0.14015500	1.22443800	-0.96817500
H	-0.27179600	2.11937100	-1.58083800
C	1.24772600	1.23868900	-0.28701500
H	2.03158900	1.25721800	-1.04833700
H	1.35553000	2.15876000	0.29570600
C	1.40061500	-0.00028500	0.60072200
H	2.38707100	-0.00053100	1.07166600
C	0.31203400	-0.00023500	1.68723300
H	0.42256800	0.87821900	2.32908800
H	0.42221900	-0.87890800	2.32885000
C	-1.08046900	0.00009900	1.03442300
H	-1.85166200	0.00022600	1.80978400
C	-1.24986200	-1.23826700	0.14945900
H	-2.24261900	-1.25623100	-0.30216500
H	-1.12978800	-2.16569900	0.71437600
C	-0.14060800	-1.22421000	-0.96833000
H	-0.27262200	-2.11899500	-1.58112300
C	-1.24938900	1.23869200	0.14968500
H	-1.12888500	2.16596800	0.71477000
H	-2.24217000	1.25717900	-0.30187000
C	1.24729800	-1.23907200	-0.28722400
H	1.35479800	-2.15928500	0.29533700
H	2.03113700	-1.25776900	-1.04856800

Free CPh_2 carbene, singlet:

C	0.00005024	-1.27653314	0.00008591
C	-1.23424775	-0.56295128	0.03682880
C	-2.36566985	-1.13535928	-0.59314539
C	-1.41828410	0.65294920	0.74203278
C	-3.58914291	-0.49230439	-0.58200472
H	-2.23905959	-2.08492756	-1.09485063

C	-2.66662432	1.24845735	0.81753010
H	-0.57689435	1.09284650	1.25926833
C	-3.74818461	0.69218227	0.13873559
H	-4.43452115	-0.92689390	-1.09907883
H	-2.79848704	2.15755899	1.38996461
H	-4.71777397	1.17071290	0.18375143
C	1.23431467	-0.56294160	-0.03644313
C	1.41796376	0.65321516	-0.74136684
C	2.36600776	-1.13535224	0.59306704
C	2.66627586	1.24872430	-0.81740125
H	0.57625341	1.09318471	-1.25802069
C	3.58941870	-0.49229008	0.58143688
H	2.23961597	-2.08496605	1.09476552
C	3.74815005	0.69230753	-0.13927010
H	2.79788424	2.15797172	-1.38966855
H	4.43506224	-0.92686976	1.09809085
H	4.71775514	1.17075961	-0.18473604

Free CPh_2 carbene, triplet:

C	-0.00000229	0.82097114	-0.00004742
C	-1.32574197	0.38478228	0.01280167
C	-1.69162102	-0.86502235	0.58682250
C	-2.36703054	1.19458153	-0.51278829
C	-3.01140484	-1.27385128	0.60847644
H	-0.92113143	-1.49138950	1.01488401
C	-3.68161022	0.77159706	-0.47832922
H	-2.11110937	2.15228462	-0.94504928
C	-4.01591346	-0.46376077	0.07808536
H	-3.26583116	-2.23004255	1.04755709
H	-4.45716253	1.40533772	-0.88849302
H	-5.04701921	-0.78924505	0.10218249
C	1.32574587	0.38474136	-0.01286436
C	1.69166661	-0.86501911	-0.58688660
C	2.36696321	1.19457114	0.51278061
C	3.01146080	-1.27381998	-0.60847982
H	0.92120380	-1.49140059	-1.01497712
C	3.68157101	0.77162096	0.47839333
H	2.11099512	2.15226169	0.94503933
C	4.01591801	-0.46372181	-0.07799460
H	3.26593866	-2.23000201	-1.04754823
H	4.45707979	1.40537042	0.88862254
H	5.04702926	-0.78919563	-0.10203547

[Fe(Por)(Ad)]

Fe	0.04788900	-0.00030300	-0.85954700
N	1.45362800	-1.41986100	-1.01760400
N	1.47675300	1.39612500	-1.01772000
N	-1.33927000	1.41874900	-1.13622200
N	-1.36243700	-1.39651800	-1.13636000
C	1.26726900	-2.78194600	-1.13504600
C	2.53187000	-3.47628700	-1.08844800
H	2.64520000	-4.55043700	-1.16929900
C	3.49450700	-2.52672800	-0.93060900
H	4.56765700	-2.65433700	-0.85829900
C	2.81875000	-1.25169200	-0.89724700
C	3.46734600	-0.02824700	-0.81137000
C	2.83894900	1.20565200	-0.89726900
C	3.53541900	2.46952700	-0.93005700
H	4.61050600	2.57959500	-0.85761400
C	2.58834600	3.43469700	-1.08740700
H	2.71918700	4.50688900	-1.16771100
C	1.31259600	2.76111500	-1.13455500
C	0.09180500	3.41170700	-1.24522500
C	-1.14435700	2.78121400	-1.23383500
C	-2.40869700	3.47603900	-1.27768000
H	-2.51552700	4.55067100	-1.36081000
C	-3.38070200	2.52645400	-1.19554600
H	-4.45617400	2.65468400	-1.20127700
C	-2.70968500	1.25082900	-1.11876300
C	-3.36316600	0.02751200	-1.08105800
C	-2.72986300	-1.20632000	-1.11866100
C	-3.42161900	-2.47080800	-1.19524600
H	-4.49905200	-2.58138600	-1.20075600
C	-2.46525200	-3.43613600	-1.27777400
H	-2.58965500	-4.50887400	-1.36090900
C	-1.18973900	-2.76200600	-1.23412400
C	0.03604000	-3.41248700	-1.24591100
C	-0.03118100	0.00033500	0.88133000
C	-0.06831500	1.24945800	1.72316000
H	-0.02007600	2.14229700	1.10094400
C	1.13725000	1.23801600	2.70293600
H	2.07534200	1.24640600	2.13410600
H	1.11038100	2.15615300	3.30557400
C	1.06456200	-0.00934900	3.60005200
H	1.91708300	-0.01668900	4.29182800
C	-0.25511700	0.00146300	4.40044200
H	-0.29015600	0.88550000	5.05197200

H	-0.30501000	-0.88242200	5.05119100
C	-1.45929600	0.01202700	3.43419200
H	-2.39484600	0.01993300	4.00886700
C	-1.41298300	-1.23752600	2.53792300
H	-2.26872500	-1.24997800	1.85177600
H	-1.46219900	-2.15376500	3.14211700
C	-0.08954200	-1.24817300	1.72301600
H	-0.05630400	-2.14131600	1.10021300
C	-1.39184600	1.26064300	2.53797000
H	-1.42601500	2.17755300	3.14214200
H	-2.24716600	1.28715900	1.85165200
C	1.11618600	-1.25747000	2.70249200
H	1.07390000	-2.17532900	3.30467400
H	2.05395400	-1.28143800	2.13358100
H	-4.44893100	0.03637800	-1.06964800
H	0.03046100	-4.49552400	-1.32353800
H	4.54935900	-0.03711700	-0.72087100
H	0.10375700	4.49473000	-1.32243600

[Fe(Por)(CPh_2)]

Fe	0.04034700	0.13566600	-0.88471700
N	-1.07249000	-1.45383800	-1.37108600
N	-1.60489000	1.28321200	-0.98880300
N	1.15715300	1.78937300	-0.98117000
N	1.68926400	-0.96192600	-1.19969000
C	0.67040600	-3.18881000	-1.31782100
C	-0.64752300	-2.76813600	-1.42398500
C	-1.76615900	-3.65367200	-1.63018200
C	-2.87823800	-2.87062400	-1.70821200
C	-2.44249300	-1.50873800	-1.52800300
C	-3.30493800	-0.42698700	-1.42887600
C	-2.91032300	0.87120600	-1.14883400
C	-3.81930900	1.97853000	-0.97395400
C	-3.05616800	3.07225300	-0.70206900
C	-1.68092000	2.63467100	-0.72885000
C	-0.58858500	3.47737900	-0.58682400
C	0.73180900	3.08527800	-0.75215100
C	1.85153200	3.99279500	-0.75276300
C	2.96368100	3.24615700	-1.00091100
C	2.52821100	1.87794800	-1.12495000
C	3.39166700	0.80086600	-1.25456700
C	2.99594000	-0.52749800	-1.25779100
C	3.90336400	-1.64803400	-1.31999400

C	3.13794900	-2.77343800	-1.29749800
C	1.76307500	-2.33826200	-1.24248900
H	0.86287800	-4.25664200	-1.35767400
H	-4.36743000	-0.61867900	-1.54240700
H	-0.78209700	4.52828800	-0.39471100
H	4.45423100	1.01242700	-1.32330900
C	-0.01291500	-0.09894000	0.84608300
C	1.18390900	-0.24756100	1.70788600
C	1.39536900	-1.47122600	2.37488800
C	2.51876500	-1.65893800	3.17721000
C	3.43060600	-0.61539700	3.36734000
C	3.21087200	0.61259600	2.74013100
C	2.10662300	0.79221100	1.90568200
C	-1.29279700	-0.21313400	1.59530500
C	-1.75898100	0.90622600	2.30878100
C	-2.95303200	0.84444100	3.02547200
C	-3.68867300	-0.34414700	3.06788400
C	-3.22133500	-1.46620100	2.38130000
C	-2.03765900	-1.40144000	1.64287500
H	0.67897700	-2.27762300	2.24684800
H	2.67618200	-2.61720500	3.66584500
H	4.30030600	-0.75840800	4.00319100
H	3.90610400	1.43474200	2.89033000
H	1.94450700	1.74612300	1.42001800
H	-1.18735700	1.82963900	2.28044800
H	-3.30677400	1.72484200	3.55615200
H	-4.61699400	-0.39340400	3.63087000
H	-3.78298100	-2.39665200	2.40854800
H	-1.69136300	-2.27287900	1.09852200
H	-1.68762200	-4.73055400	-1.71450600
H	-3.90799100	-3.16805300	-1.86348200
H	-4.89657700	1.90616600	-1.05765500
H	-3.37153700	4.09211800	-0.51928600
H	1.77345700	5.06213300	-0.59987500
H	3.99355700	3.57064200	-1.08462300
H	4.98132900	-1.56135600	-1.37758700
H	3.45253200	-3.80895700	-1.33844900

[Fe(Por)(C(Ph)CO_2Et)]

Fe	-0.17023400	0.19841000	-0.79354200
N	1.76857000	0.21738100	-1.31470900
N	-0.26248900	-1.72615800	-1.33711500
N	-2.18017400	0.22943100	-0.68717100

N	-0.16775100	2.19029400	-0.81855800
C	2.26073500	2.57745500	-0.88215500
C	2.63860000	1.27750500	-1.18381200
C	3.98535800	0.87582100	-1.51211200
C	3.92323900	-0.43237300	-1.88355300
C	2.54353300	-0.83526200	-1.75500400
C	2.07363600	-2.11399400	-2.01083100
C	0.76576700	-2.52780800	-1.80192700
C	0.30788000	-3.88073000	-1.98639700
C	-1.00480600	-3.90725800	-1.62213800
C	-1.35773300	-2.56594900	-1.23536100
C	-2.63947200	-2.17273900	-0.87670900
C	-3.02600700	-0.86071500	-0.64946000
C	-4.38999900	-0.43934100	-0.44194600
C	-4.37537200	0.92122800	-0.38791700
C	-3.00115800	1.32915800	-0.54659600
C	-2.56977100	2.64604600	-0.56022300
C	-1.24582700	3.03905300	-0.67299000
C	-0.80206100	4.40610200	-0.56158500
C	0.55812700	4.38294100	-0.59797600
C	0.94723800	3.00413300	-0.75854800
H	3.04212000	3.32734600	-0.80748400
H	2.78477700	-2.85364400	-2.36543300
H	-3.40593000	-2.93997600	-0.82878200
H	-3.31741000	3.42393800	-0.44134200
C	0.09764400	0.11878000	0.94282400
C	1.32486700	-0.26401400	1.65756700
C	2.00326700	-1.45943800	1.35393600
C	3.15967700	-1.81489000	2.04323500
C	3.67784400	-0.97217200	3.03134600
C	3.01553200	0.21890500	3.34347700
C	1.84004500	0.56288500	2.68044300
H	1.59759400	-2.11224700	0.59287000
H	3.66283800	-2.74784500	1.80327700
H	4.58884000	-1.24317600	3.55813900
H	3.41139800	0.87904100	4.11064000
H	1.32734600	1.48647300	2.92923100
H	4.84568100	1.53302700	-1.48446200
H	4.72276400	-1.08178300	-2.21815600
H	0.92798100	-4.69181300	-2.34760200
H	-1.69325100	-4.74327100	-1.62832300
H	-5.23618100	-1.11228800	-0.37832900
H	-5.20646500	1.60431000	-0.26376800
H	-1.46435600	5.25638400	-0.45637800

H	1.25360000	5.21086200	-0.53686200
C	-0.94147100	0.67402100	1.87315200
O	-1.76064500	-0.19066600	2.50081700
O	-1.04503800	1.86337300	2.10838000
C	-1.53785500	-1.62218900	2.38106700
H	-0.73168100	-1.89960000	3.06865600
H	-1.22562800	-1.86395100	1.36296400
C	-2.83736200	-2.31172500	2.73864000
H	-2.70740100	-3.39777900	2.67398700
H	-3.14449500	-2.05890200	3.75924500
H	-3.63226300	-2.01264800	2.04862000

[Fe(Por)(CMe_2)]

Fe	-0.00000400	-0.00000400	-0.07609500
N	-1.54575900	-1.25825100	-0.29977800
N	1.25682400	-1.54489200	-0.30653900
N	1.54576000	1.25821500	-0.29984300
N	-1.25684600	1.54486200	-0.30659500
C	-2.88376900	-0.94163000	-0.41257500
C	-3.69214400	-2.13729900	-0.42522500
H	-4.77150900	-2.14676200	-0.51453800
C	-2.83647600	-3.18969100	-0.30941400
H	-3.06243500	-4.24877000	-0.28791100
C	-1.50516300	-2.63696800	-0.24115100
C	-0.34783400	-3.39985400	-0.18348300
C	0.93959400	-2.88694300	-0.24259100
C	2.13260600	-3.69627000	-0.30664900
H	2.14110500	-4.77907200	-0.28105800
C	3.18265000	-2.83794600	-0.42374600
H	4.23825900	-3.06459100	-0.51017100
C	2.63181300	-1.50409200	-0.41574400
C	3.39531400	-0.34640400	-0.47409600
C	2.88377900	0.94160700	-0.41262700
C	3.69213200	2.13728700	-0.42530100
H	4.77149800	2.14675400	-0.51460700
C	2.83645600	3.18966700	-0.30943800
H	3.06239900	4.24874900	-0.28793800
C	1.50514600	2.63692300	-0.24120200
C	0.34782000	3.39981400	-0.18350500
C	-0.93960800	2.88691000	-0.24259400
C	-2.13261600	3.69624700	-0.30667200
H	-2.14110700	4.77904800	-0.28107300
C	-3.18266300	2.83793200	-0.42378000

H	-4.23827100	3.06458000	-0.51022000
C	-2.63183400	1.50407400	-0.41579200
C	-3.39532100	0.34637600	-0.47408800
H	0.45817000	4.47917500	-0.14017100
H	-4.47230800	0.45759200	-0.55608900
H	-0.45817700	-4.47921700	-0.14017700
H	4.47229900	-0.45765200	-0.55607700
C	0.00003900	0.00007900	1.66695900
C	1.25013500	-0.03203900	2.49190500
H	2.13374300	-0.34260400	1.93468100
H	1.43458100	0.98565900	2.87201000
H	1.12842600	-0.67801300	3.37371400
C	-1.25005400	0.03224000	2.49194000
H	-2.13371000	0.34255000	1.93466100
H	-1.43433300	-0.98538300	2.87231600
H	-1.12839100	0.67842100	3.37360200

[Fe(Por)(C^iPr_2)]

Fe	0.00004500	-0.00004900	-0.46900900
N	0.85412400	1.80222000	-0.72479200
N	-1.79676800	0.85677900	-0.75609200
N	-0.85408400	-1.80228900	-0.72464900
N	1.79683100	-0.85683900	-0.75585500
C	2.19979400	2.08957700	-0.83145400
C	2.41829300	3.51595900	-0.84394500
H	3.39006900	3.98648600	-0.92905700
C	1.19295600	4.10066500	-0.74571800
H	0.94280300	5.15441800	-0.73460300
C	0.22613600	3.03100800	-0.68427600
C	-1.14718500	3.22449200	-0.67072700
C	-2.08638400	2.20692300	-0.74993600
C	-3.50813200	2.42525900	-0.86299300
H	-3.97888900	3.40042700	-0.88372600
C	-4.08727400	1.19653600	-0.95056300
H	-5.13546900	0.94602700	-1.05853200
C	-3.01972000	0.22843800	-0.88148700
C	-3.21347100	-1.14512300	-0.91287300
C	-2.19973400	-2.08964900	-0.83146200
C	-2.41823700	-3.51603400	-0.84386700
H	-3.39000500	-3.98656300	-0.92905900
C	-1.19291600	-4.10073700	-0.74544700
H	-0.94276900	-5.15449100	-0.73418600
C	-0.22609400	-3.03107900	-0.68400400

C	1.14722400	-3.22455500	-0.67052700
C	2.08642200	-2.20699100	-0.74986600
C	3.50816000	-2.42534000	-0.86299300
H	3.97889700	-3.40051400	-0.88386200
C	4.08731900	-1.19661900	-0.95049100
H	5.13551500	-0.94611800	-1.05846300
C	3.01979400	-0.22850900	-0.88125700
C	3.21354400	1.14505200	-0.91266100
C	-0.00003600	0.00005700	1.29365400
H	1.51171100	-4.24715500	-0.65607700
H	4.23341900	1.50742500	-0.99849800
H	-1.51166700	4.24709300	-0.65625900
H	-4.23333600	-1.50749400	-0.99882900
C	-1.27539400	-0.34161000	2.04912500
H	-1.95333700	-0.79187700	1.32545400
C	1.27520400	0.34182000	2.04922200
H	1.95320800	0.79208700	1.32559700
C	-2.00508900	0.92417900	2.56582000
H	-2.03206600	1.71216400	1.80964300
H	-3.04053900	0.66059100	2.81427000
H	-1.54019300	1.33042400	3.46742100
C	-1.12541800	-1.37208600	3.18510000
H	-0.62895600	-2.28480100	2.83952000
H	-0.56696700	-0.97717100	4.03886500
H	-2.12399800	-1.65189900	3.54421500
C	1.12513700	1.37237000	3.18514700
H	0.62852200	2.28497600	2.83950700
H	0.56682100	0.97747300	4.03900500
H	2.12370800	1.65235200	3.54415600
C	2.00496200	-0.92390300	2.56604100
H	1.54007100	-1.33015900	3.46764000
H	2.03202500	-1.71192600	1.80990900
H	3.04037500	-0.66019800	2.81451200

4b, singlet

Fe	-0.06971300	-0.05157600	0.11315500
N	-0.11476500	1.73114600	1.03525300
N	0.22490300	0.86395000	-1.65941500
N	-0.08737700	-1.83731600	-0.81416200
N	-0.44391300	-0.96842500	1.86386200
C	-0.14949600	1.95578500	2.38654000
C	-0.15235300	3.37970600	2.65313100
H	-0.17225700	3.82057400	3.64237800

C	-0.14546800	4.00520300	1.44345800
H	-0.14956700	5.06734700	1.23100100
C	-0.10803500	2.96559800	0.43567200
C	-0.02168100	3.19382700	-0.93435800
C	0.17378200	2.21109400	-1.90278300
C	0.45096600	2.46955500	-3.29939200
H	0.46815200	3.45394200	-3.75098700
C	0.69576100	1.26187500	-3.88337300
H	0.94506900	1.04842700	-4.91572300
C	0.53721000	0.25894000	-2.85140000
C	0.61110400	-1.11766100	-3.05557100
C	0.26764600	-2.08741700	-2.11541600
C	0.12345000	-3.49907700	-2.40588800
H	0.34686500	-3.95691400	-3.36189000
C	-0.36173600	-4.08479200	-1.27570900
H	-0.61008600	-5.12550600	-1.10623200
C	-0.48116300	-3.03835600	-0.28181400
C	-0.87847800	-3.23937600	1.03890400
C	-0.82101800	-2.27805300	2.04515500
C	-1.04916300	-2.53655500	3.45074900
H	-1.35390700	-3.49253700	3.85888200
C	-0.79072400	-1.37325200	4.11197000
H	-0.84980300	-1.17262300	5.17484800
C	-0.43723400	-0.39143300	3.10863100
C	-0.24499800	0.96555600	3.36206800
C	-1.92678000	0.07752200	-0.18760900
C	-2.60209700	-0.18515900	-1.50200000
H	-1.87698400	-0.47292100	-2.26085200
C	-3.35377300	1.09442500	-1.97230900
H	-2.63732000	1.90975900	-2.12512400
H	-3.82052600	0.88146700	-2.94337000
C	-4.40575500	1.49038400	-0.92521400
H	-4.92853800	2.39920200	-1.25079800
C	-5.41993500	0.34208800	-0.74421900
H	-5.94400100	0.15438300	-1.69130800
H	-6.17948800	0.62624000	-0.00318400
C	-4.68948600	-0.93643800	-0.28454800
H	-5.41301700	-1.75230700	-0.15701200
C	-3.96734200	-0.67279300	1.04507800
H	-3.46110200	-1.58031600	1.39257700
H	-4.67494300	-0.37105000	1.82886100
C	-2.92892800	0.47294700	0.85994600
H	-2.43762400	0.66857700	1.81182500
C	-3.63460100	-1.33811800	-1.32637700

H	-4.09560100	-1.53515800	-2.30344700
H	-3.11913400	-2.25438100	-1.01623300
C	-3.67788300	1.75911800	0.40041100
H	-4.38439800	2.04326700	1.19183600
H	-2.96461100	2.58375600	0.28699200
H	-1.17907200	-4.24344300	1.32304400
H	-0.26820100	1.28730600	4.39907700
H	-0.02864600	4.22684200	-1.26896400
H	0.86964400	-1.46006900	-4.05325300
C	1.88654300	-0.11600000	0.22107900
C	2.73541100	-1.30976400	0.17272000
C	2.39879100	-2.44696000	0.93938100
C	3.90234800	-1.38203900	-0.62905900
C	3.18603600	-3.59444500	0.91565600
H	1.53326000	-2.39892200	1.58192900
C	4.65263300	-2.55129600	-0.69923800
H	4.20430000	-0.52432000	-1.21905100
C	4.30309600	-3.66063200	0.07876000
H	2.91516300	-4.44515100	1.53537300
H	5.52418200	-2.59382800	-1.34725800
H	4.90209100	-4.56658500	0.03683800
C	2.67467000	1.13904900	0.17675300
C	3.11895800	1.75649000	-1.00532200
C	2.99654000	1.74497600	1.40650400
C	3.85095500	2.94477400	-0.95748900
H	2.87879600	1.31275500	-1.96477000
C	3.72751400	2.93125600	1.44852100
H	2.65235800	1.28777900	2.32920000
C	4.15749000	3.54141900	0.26636200
H	4.17576200	3.40516000	-1.88758200
H	3.95535600	3.38326900	2.41082400
H	4.72176900	4.46964400	0.30061100

4b, triplet

Fe	-0.12105100	-0.11204200	0.00903800
N	0.00301000	1.32027000	1.39386700
N	0.01717800	1.26728000	-1.42902500
N	-0.26900500	-1.55471900	-1.37200600
N	-0.28185400	-1.50057800	1.44115100
C	0.15791200	1.13844700	2.74477800
C	0.21485800	2.41996300	3.40978800
H	0.33842400	2.55180200	4.47759300
C	0.06955300	3.37312100	2.44602600

H	0.05960500	4.45028800	2.55555200
C	-0.04223300	2.67808600	1.18605500
C	-0.10549600	3.29796800	-0.05646700
C	-0.03106700	2.63146000	-1.27449000
C	0.09414100	3.27736600	-2.55905100
H	0.08488500	4.34942400	-2.71063100
C	0.25105000	2.28775400	-3.48362100
H	0.38671100	2.37807100	-4.55426800
C	0.18742700	1.03303500	-2.77020500
C	0.21545200	-0.22043600	-3.37401200
C	-0.05462600	-1.41945000	-2.72066400
C	-0.30342600	-2.67666000	-3.38739800
H	-0.19228900	-2.83886900	-4.45237700
C	-0.72068900	-3.55571600	-2.43219700
H	-1.00927600	-4.59309800	-2.54705100
C	-0.68620100	-2.85061400	-1.17356800
C	-0.94713900	-3.42490500	0.06738700
C	-0.69734700	-2.80395500	1.28775900
C	-0.74349700	-3.46056200	2.57192300
H	-1.03292100	-4.49295200	2.72374400
C	-0.33554400	-2.54566700	3.49701200
H	-0.23472200	-2.66738800	4.56840100
C	-0.08071100	-1.31443300	2.78576900
C	0.18088300	-0.09109900	3.39624300
C	-2.01762400	0.07212800	-0.01087700
C	-2.83307000	0.14900800	-1.25786900
H	-2.20955200	0.05189900	-2.14502500
C	-3.56494900	1.52806800	-1.28854900
H	-2.82765000	2.33784100	-1.31793600
H	-4.14671100	1.57673800	-2.21786700
C	-4.46691200	1.66275900	-0.05360100
H	-4.97160900	2.63718100	-0.07372500
C	-5.51460200	0.53043900	-0.04131400
H	-6.15363200	0.60193200	-0.93143500
H	-6.16546000	0.63199400	0.83725200
C	-4.80376400	-0.83800500	-0.01351100
H	-5.54849100	-1.64419600	-0.00439800
C	-3.91838800	-0.94438400	1.23599100
H	-3.41977200	-1.91929800	1.27418800
H	-4.50702000	-0.83817100	2.15610200
C	-2.84944300	0.19158200	1.22235600
H	-2.23740300	0.12513600	2.12033800
C	-3.90220400	-0.98670600	-1.24704600
H	-4.47883300	-0.91183900	-2.17778200

H	-3.40364800	-1.96237500	-1.24554600
C	-3.58163300	1.57047400	1.19713100
H	-4.17577700	1.64967500	2.11649200
H	-2.84511200	2.38139000	1.20958100
H	-1.27280800	-4.46001200	0.08520400
H	0.31394200	-0.08579500	4.47342000
H	-0.13048000	4.38271600	-0.07702300
H	0.36006300	-0.25585100	-4.44917100
C	2.05568500	-0.17928600	0.01005100
C	2.94824500	-1.30083000	0.00651200
C	2.49068900	-2.65417900	0.04342500
C	4.37791400	-1.14614000	-0.03538500
C	3.35845300	-3.73678000	0.03676500
H	1.43122700	-2.83405900	0.08150500
C	5.24106500	-2.23360300	-0.04324700
H	4.79792700	-0.14661900	-0.06430700
C	4.74745100	-3.54601700	-0.00785900
H	2.94909200	-4.74474200	0.06708900
H	6.31507700	-2.06014300	-0.07712800
H	5.42638600	-4.39475200	-0.01371300
C	2.72041300	1.14509700	0.00739500
C	3.05765200	1.79842600	-1.19458900
C	3.06471200	1.79278800	1.21041300
C	3.67446000	3.05039500	-1.19537400
H	2.82395400	1.31350700	-2.13765100
C	3.68050700	3.04501200	1.21403000
H	2.83526200	1.30356600	2.15237100
C	3.98150100	3.68832600	0.00990400
H	3.91030900	3.53140700	-2.14238500
H	3.92105100	3.52192200	2.16191400
H	4.45452700	4.66731800	0.01084900

4b, quintuplet

Fe	-0.33810200	0.08239200	0.12454200
N	0.22212900	-1.13763200	-1.33562200
N	-0.39512200	-1.47874400	1.35665900
N	-0.55205800	1.33057100	1.65741900
N	-0.01263600	1.66557900	-1.04522700
C	0.73719900	-0.77515300	-2.57434800
C	0.94231500	-1.96103400	-3.37850000
H	1.35623900	-1.94856800	-4.37941400
C	0.50648500	-3.02244400	-2.65410700
H	0.50177400	-4.07087700	-2.92565100

C	0.07289200	-2.51783000	-1.36862300
C	-0.32428000	-3.29939800	-0.31156900
C	-0.49169700	-2.81420900	0.99836400
C	-0.61391700	-3.62239100	2.15913700
H	-0.68579000	-4.70298100	2.14919800
C	-0.56998500	-2.77186000	3.24965600
H	-0.62625300	-3.02158700	4.30210300
C	-0.45387600	-1.45136200	2.74245800
C	-0.50809300	-0.27957100	3.51867300
C	-0.60256400	0.99035200	3.00668700
C	-0.91262300	2.16645600	3.79082500
H	-0.98625900	2.17004800	4.87157700
C	-1.11200900	3.19223400	2.92465000
H	-1.36915400	4.22147600	3.14325100
C	-0.87506500	2.68285000	1.59130400
C	-0.85223800	3.44556800	0.44925400
C	-0.38343000	2.97766300	-0.79279700
C	-0.07031300	3.79602600	-1.91005700
H	-0.24077300	4.86461800	-1.95533400
C	0.52302200	2.97860700	-2.85480400
H	0.89967000	3.24530800	-3.83460600
C	0.53482000	1.66422100	-2.31945100
C	0.92505100	0.50979300	-3.02137100
C	-2.07775100	0.00495800	-0.26478200
C	-3.13998400	-0.11670400	0.77381800
H	-2.71651800	-0.14701600	1.77658800
C	-3.94656100	-1.42431300	0.50246700
H	-3.28783300	-2.29213400	0.61712600
H	-4.72989800	-1.49698500	1.26742400
C	-4.54924500	-1.37602000	-0.90968300
H	-5.10854400	-2.30111500	-1.09938200
C	-5.49060400	-0.16036600	-1.03662500
H	-6.31642400	-0.25267700	-0.31883300
H	-5.93320400	-0.13308400	-2.04120700
C	-4.70569400	1.14121600	-0.77190800
H	-5.37637800	2.00520400	-0.86015800
C	-3.56113000	1.27594000	-1.78785400
H	-3.00090900	2.20288600	-1.62337700
H	-3.94037300	1.29497100	-2.81733800
C	-2.59976100	0.05576200	-1.66002000
H	-1.79223000	0.14837500	-2.38392900
C	-4.09784900	1.10895200	0.63903800
H	-4.87530600	1.00941400	1.40702800
H	-3.54488500	2.03236500	0.84306000

C	-3.40135400	-1.25806800	-1.92378200
H	-3.77965800	-1.21670300	-2.95291500
H	-2.72854700	-2.11957800	-1.85139900
H	-1.10524200	4.49784700	0.52985300
H	1.32526100	0.64564000	-4.02112500
H	-0.38937000	-4.37183200	-0.46300600
H	-0.57443600	-0.39877500	4.59550400
C	2.93501200	-0.04491000	0.79980500
C	3.46754000	1.21958700	0.50509000
C	2.72103500	2.40673000	0.75257800
C	4.78856500	1.36045700	-0.02132900
C	3.25735600	3.65478000	0.46788500
H	1.71842800	2.31415500	1.15134100
C	5.30692300	2.61742400	-0.30276200
H	5.38369100	0.46957800	-0.19764300
C	4.54942600	3.77296100	-0.06336900
H	2.66234500	4.54488900	0.65510700
H	6.31238100	2.70218100	-0.70793600
H	4.96226000	4.75291600	-0.28638700
C	3.13834500	-1.40196200	0.48822900
C	2.81238600	-2.42435300	1.42084900
C	3.63850300	-1.79546500	-0.78827400
C	2.99992600	-3.76257600	1.09999900
H	2.39834200	-2.14389900	2.38414300
C	3.82415000	-3.13777700	-1.09112900
H	3.85538400	-1.03035700	-1.52678900
C	3.50890500	-4.12984000	-0.15239200
H	2.73749600	-4.52743700	1.82595300
H	4.20184700	-3.41780700	-2.07119100
H	3.64832800	-5.17866400	-0.39969700