Monomeric M(II) (M = Fe, Co, Ni) complexes supported by bulky aryloxide ligands tethered to an arene functionality; synthesis, electrochemistry and study of the M(II)-arene interaction.

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General Considerations

All manipulations were performed using either Schlenk-techniques or in a nitrogen filled MBraun glovebox with O_2 and H_2O levels ≤0.5 ppm, unless otherwise stated. Pentane, n-hexane, THF, Et_2O and PhMe were refluxed using Na/benzophenone (THF, Et_2O until a persistent red solution is observed) or molten potassium (THF, toluene) under N_2. The solvents were distilled under N_2 and stored over activated 4 Å molecular sieves. Absolute EtOH was purchased from Fischer and used as received. C_6D_6, d^8-toluene (C_7D_8) and d^8-THF (C_4D_8O) were purchased from Deutero GmBh, freeze-pump-thaw-degassed, dried over molten K for at least two days, vacuum-transferred over activated 4 Å molecular sieves and stored inside the glovebox in a Young's ampoule. 1,2-Difluorobenzene was passed through basic-alumina, distilled over CaH_2, degassed and stored inside the glovebox over activated 3 Å molecular sieves prior to use. $[N(n\text{-}Bu)_4]PF_6$ ($TBAPF_6$) was purchased from TCI Chemicals and recrystallised twice from absolute ethanol and dried ($4x10^{-3}$ mbar) prior to use. Ferrocene (Fc) was sublimed and finally recrystallised twice from n-hexane prior to use. $[Fe(N_2'')]$,[1] $[Co(N_2'')]$[2] and $[Ni(N_2'')]$[3] (N'' = $N(SiMe_3)_2$) were prepared according to literature procedures. 2,4-bis-^{t}Bu-phenol, α,α'-Dihydroxy-1,4-diisopropylbenzene, p-TSA.H_2O, Na_2CO_3 were purchased from commercial suppliers and used as received.

All glassware and glass microfibre filter paper (Sativa GF/D 25 mm circles) were dried prior to use in a high-temperature oven (typically T>110 °C) overnight.

NMR spectroscopy: NMR spectra were recorded on a 400 MHz Bruker Avance III at 27 °C unless otherwise stated. ^{1}H NMR spectra of all paramagnetic compounds were recorded

between -300 to +300 ppm with a minimum of 100 scans (depending on the concentration of the sample), using the spectrometers default pulse sequence parameters. The spectra were referenced internally to the residual proton signals (^{1}H) or the ^{13}C signals of the deuterated solvent. In the case of paramagnetic compounds, their assignment was done on the basis of the observed peaks' integrations. Evan's measurements were conducted as per the paper by Mazzanti *et.al.* [4], using hexamethylbenzene as the shift standard, and data corrected for diamagnetic contributions using tabulated Pascal constants. [5]

IR Spectroscopy: IR spectra were recorded as neat solids in an Ar filled glovebox on an ATR setup with a Bruker Alpha spectrometer from 400 – 4000 cm^{-1}.

UV-Vis Spectroscopy: UV-Vis spectra were recorded on an Agilent Carry 17D spectrometer at RT in custom made air-tight Young's tap quartz cuvettes (l = 1 cm).

Elemental analyses were performed by the Elemental Analysis Laboratory of the Catalysis Research Centre at the Technical University of Munich using a Eurovector EA3000 CHNS combustion analyser.

Synthetic Details:

Synthesis of p-^{t}Bu$_2$O$_2$H$_2$ (LH_2) The synthesis is conducted in air following a slight modification of the procedure reported by Cloke *et al.* [6]

A 250 ml 2-neck RBF flask was charged with 20 g (96.93 mmol) of 2,4-bis-^{t}Bu-phenol and 0.06 g (0.35 mmol) of p-TSA.H_2O. The mixture was heated at 100 °C until the formation of an orange-brown melt. 2 g (10,2 mmol) of α,α'-Dihydroxy-1,4-diisopropylbenzene were added to this mixture in portions of *ca* 160 mg every *ca* 15 minutes. After the addition was complete the mixture was left to stir for another 2 h at this temperature resulting in the precipitation of a white crystalline solid. 0.24 g (2.26 mmol) of Na_2CO_3 were then added at 100 °C to neutralize the p-TSA.H_2O and the excess 2,4-bis-^{t}Bu-phenol was removed by vacuum distillation (10^{-2} mbar) between 100 - 120 °C leaving an off-white solid (it is important that the temperature does not exceed 140 °C as it leads to un-identified decomposition products). The residue was washed multiple times with EtOH, until the filtrate was colorless and the remaining solids were dissolved in *ca* 150 mL of toluene and filtered. Insoluble material was discarded and toluene was removed from the filtrate on a rotary evaporator to afford ligand LH_2 as a white solid. It was further dried at 80°C under vacuum (10^{-2} mbar) overnight to afford **LH_2** as a crystalline powder which was stored in the glovebox. Yield: 2.24 g (*ca.* 38%).

^{1}H NMR (δ(C_6D_6)): 7.54 (2H C-$H_{aromatic}$ of phenol arm), 7.50 (s, 2H C-$H_{aromatic}$ of phenol arm), 7.05(s, 4H C-$H_{aromatic}$ of central arene), 4.53 (s, 2H O*H*), 1.52-3.00 (s, 30H CH_3 bridgeheads and C(CH_3)$_3$), 1.45 (s, 18H, C(CH_3)$_3$); $^{13}C\{^{1}H\}$ NMR (δ(C_6D_6)): 151.19, 147.50, 141.97, 137.78, 127.36, 123.10, 1231.02, 42.00, 35.50, 34.82, 32.09, 90.28, 29.77.

Anal Calcd. for $C_{40}H_{58}O_2$: C, 84.15; H, 10.24. Found C: 84.26; H: 10.35.

Synthesis of $K_2(THF)_x$(p-tBu2O2) (2-K_2): To a suspension of KH (42.15 mg, 1.05 mmol) in THF (20 ml) kept at -20°C was added dropwise a THF (20 ml) solution of LH_2 (300 mg, 0.525 mmol). After the addition was complete, the mixture was left to equilibrate RT and stirred overnight. The blurry colorless solution was filtered using a filter canula and the filtrate stripped to dryness to afford a white solid that was washed twice with n-hexane (2x10 ml) and once with n-pentane (1x10 ml) and dried in vacuum to yield $K_2(p\text{-}^tBu_2O_2)(THF)_x$; typically x = 0.2-0.5 resulting in yields of *ca.* 55%

^{1}H NMR (δ(C_7D_8) with a few drops of d_8-THF): 7.79 (very broad s, 4H C-$H_{aromatic}$ anchor), 7.43 (s, 2H C-$H_{aromatic}$ of the phenoxide arm), 7.28 (s, 2H C-$H_{aromatic}$ of the phenoxide arm), 3.56 (t, varied integral THF), 1.84 (broad s, 12H, bridge head Me), 1.42 (18H ^{t}Bu), 1.33 (18H ^{t}Bu); ^{13}C{^{1}H} NMR (δ(C_7D_8) with a few drops of d_8-THF): 166.34, 157.72, 153.04, 136.30, 122.75, 122.54 (aromatic), 68.10 (THF), 43.09, 35.84, 34.72, 32.93, 31.56, 26.20 (THF)

NOTE: One aromatic carbon in the ^{13}C{^{1}H} NMR spectrum could not be observed.

Synthesis of [Fe(p-^{t}Bu_2O_2)] (2-Fe): To a yellow-green toluene solution (*ca* 5 ml) of [FeN''$_2$] (132 mg, 0.35 mmol) in a 50 ml J-Young ampule cooled at -78°C, was added dropwise an RT toluene solution (*ca* 10 ml) of **p-^{t}$Bu_2O_2H_2$** (**LH_2**) (200 mg, 0.35 mmol) *via* canula. Upon completion an immediate color change to intense golden-yellow was observed and the solution was allowed to warm to RT overnight with stirring. Careful and slow removal of volatiles with no stirring (ampule placed parallel to bench) at RT afforded golden-yellow crystals of the title compound suitable for SC-XRD studies. The crystals were separated from the supernatant and its volume was further reduced (*ca* 1-2 ml) followed by storage in a -30 °C glovebox freezer to afford a second crop of crystalline (**2-Fe**) as an extremely air and moisture sensitive solid. Combined yield: 92 mg, 42%.

^{1}H NMR (δ(C_6D_6)): 54.00 (s, 2H C-$H_{aromatic}$ of the phenoxide arm), 47.14 (s, 2H C-$H_{aromatic}$ of the phenoxide arm), 27.87 (s, 12H, CH_3 bridgeheads), 5.08 (s, 18H, C(CH_3)$_3$), -0.81 (s, 18H, C(CH_3)$_3$), -146.79 (broad s, 4H C-$H_{aromatic}$ of the anchor arene); μ_{eff} = 4.20 μ_B.

Anal Calcd. for $C_{40}H_{56}FeO_2$: C, 76.90; H, 9.04. Found C: 76.70; H: 9.39.

Note: *Upon work-up and subsequent crystallisation of (**2-Fe**), we often observed the formation of a dark purple/black veneer on the surface of crystals. Nevertheless, the EA results indicate over 95% of purity and ^{1}H-NMR spectra of different batches were identical.*

Synthesis of [Co(p-^{t}Bu_2O_2)] (2-Co): This was prepared in a similar manner as above, starting from 350 mg (0.92 mmol) of [CoN''$_2$] and 520 mg (1 mol eq.) of LH_2. Upon warming the reaction mixture overnight to RT a change to forest-green was observed. Work-up and crystallization similar to (**2-Fe**) resulted in a combined yield of 289 mg (*ca.* 50%).

^{1}H NMR (δ(C_6D_6)): 66.48 (s, 2H C-$H_{aromatic}$ of phenoxide arm), 52.70 (s, 2H C-$H_{aromatic}$ of phenoxide arm), 41.42 (s, 12H, CH_3 bridgeheads), 7.59 (s, 18H, C(CH_3)$_3$), 9.04 (s, 18H, C(CH_3)$_3$), -136.76 (broad s, 4H C-$H_{aromatic}$ of the anchor arene); μ_{eff} = 3.40 μ_B.

Anal Calcd. for $C_{40}H_{56}CoO_2$: C, 76.53; H, 8.99. Found C: 76.44; H: 9.19.

Synthesis of [Ni(p-^{t}Bu$_2$O$_2$)] (2-Ni): In a similar manner as above, starting from 150 mg of freshly prepared [NiN''$_2$] (0.39 mmol) and 226 mg (1 mol equiv.) of LH_2. Upon completion of the addition the color changed to red and the reaction mixture was left to slowly warm up to RT with overnight stirring. Volatiles were removed under reduced pressure and the residue extracted in n-hexane, filtered and its volume reduced to *ca* 2 ml. Refrigeration at -45 °C afforded a small amount of red crystals suitable for X-ray analysis that were isolated by careful filtration at -45 °C and dried in vacuum. The crystals rapidly decompose at RT forming white solids (presumably **LH_2**) and combined with their small yield no other spectroscopic or analytical data could be obtained.

Synthesis of [Fe(p-^{t}Bu$_2$O$_2$)(THF)] (2-Fe.THF): In a 50 ml J-Young ampule charged with (**2-Fe**) (70 mg, 0.11 mmol) was added 5 ml of THF at RT forming a light yellow solution. The solution was stripped to dryness and the resulting pale yellow powder was dissolved in the minimum amount of n-hexane and cooled to -30ºC in a glovebox freezer inducing the formation of (**2-Fe.THF**) as a yellow crystalline powder after 24 hours. Yield: 65 mg (*ca* 84%). Crystals suitable for SC-XRD studies were obtained after storing a 2 ml solution of (**2-Fe.THF**) (*ca.* 30 mg) in a 4:1 THF/n-hexane mixture at -30 °C for 3 days.

^{1}H-NMR (δ(C_6D_6)): 53.08 (s, 2H C-H$_{aromatic}$ of the phenoxide arm), 46.59 (s, 2H C-H$_{aromatic}$ of the phenoxide arm), 27.90 (s, 12H, C*H$_3$* bridgeheads), 6.02 (s, 18H, C(C*H$_3$*)$_3$), 0.92 (s, 4H, THF), -0.93 (s, 4H, THF), -6.01 (s, 18H, C(C*H$_3$*)$_3$)), -101.57 (broad s, 4H C-H$_{aromatic}$ of the anchor arene); ^{1}H-NMR (δ(C_4D_8O): 52.37 (s, 2H C-H$_{aromatic}$ of the phenoxide arm), 46.09 (s, 2H C-H$_{aromatic}$ of the phenoxide arm), 27.91 (s, 12H, C*H$_3$* bridgeheads), 6.19 (s, 18H, C(C*H$_3$*)$_3$), -9.77 (s, 18H, C(C*H$_3$*)$_3$)), -78.01 (broad s, 4H C-H$_{aromatic}$ of the anchor arene); μ_{eff} = 4.79 μ_B.

Anal Calcd for $C_{44}H_{64}FeO_3$ 3(C_4H_8O): C: 73.66; H: 9.71; T Found: C: 73.34; H: 9.08.

Synthesis of [Co(p-^{t}Bu$_2$O$_2$)(THF)] (2-Co.THF): THF (*ca* 5 ml) was added to a 50 ml J-Young ampule containing 50 mg (**2-Co**) (0.079 mmol) resulting in an immediate color change from forest-green to red-brown. The solution was stripped to dryness, to afford a brown red powder which was dissolved in the minimum amount of n-pentane (*ca* 5 ml) with a few drops of THF and refrigerated at -30ºC to give (**2-Co.THF**) as single crystals, suitable for SC-XRD studies. The crystals were isolated from the supernatant *via* careful decantation of the supernatant followed by drying in vacuum. Yield: 43 mg (*ca.* 77%)

^{1}H-NMR (δ(C_6D_6)): 65.06 (s, 2H, C-H$_{aromatic}$ of the phenoxide arm), 54.62 (s, 2H, C-H$_{aromatic}$ of the phenoxide arm), 44.60 (s, 12H, C*H$_3$* bridgeheads), 8.68 (s, 18H C(C*H$_3$*)$_3$), -7.28 (s, 4H, THF), -11.12 (two broad overlapping s, 22H, THF and C(C*H$_3$*)$_3$), -123.99 (broad s, 4H C-H$_{aromatic}$ of the anchor arene); ^{1}H-NMR (δ(C_4D_8O): 61.68 (s, 2H, C-H$_{aromatic}$ of the phenoxide arm), 54.65 (s, 2H, C-H$_{aromatic}$ of the phenoxide arm), 9.15 (s, 18H C(C*H$_3$*)$_3$), -13.37 (s, 18H C(C*H$_3$*)$_3$), -106.41 (broad s, 4H C-H$_{aromatic}$ of the anchor arene); μ_{eff} = 3.70 μ_B.

Anal Calcd for $C_{44}H_{64}CoO_3$.C_4H_8O: C: 74.68, H: 9.40; Found: C: 74.07, H: 9.13.

NMR SPECTRA OF COMPOUNDS

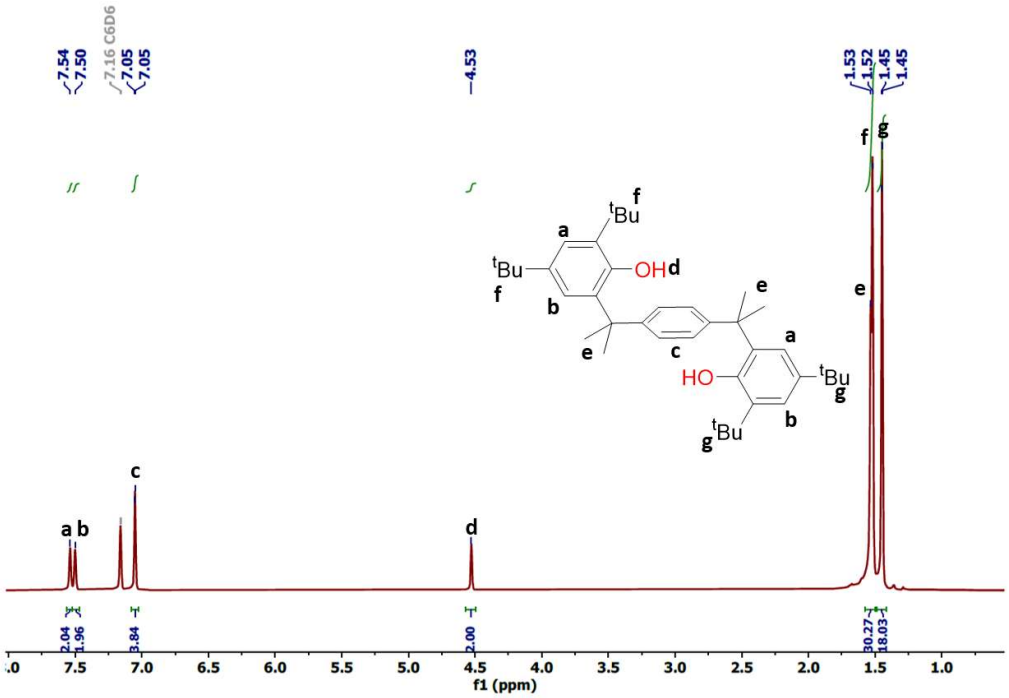


Figure S1: The ^{1}H NMR spectrum of **LH_2** measured in C_6D_6.

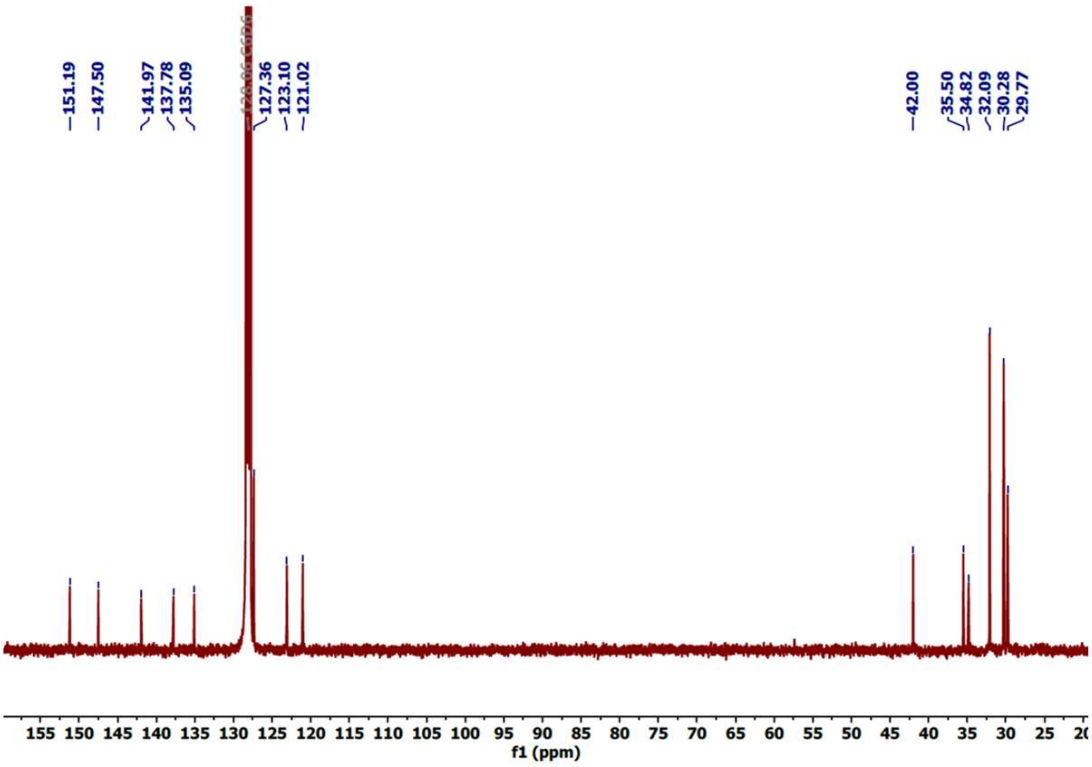


Figure S2: $^{13}C\{H\}$ NMR spectrum of **LH_2** measured in C_6D_6.

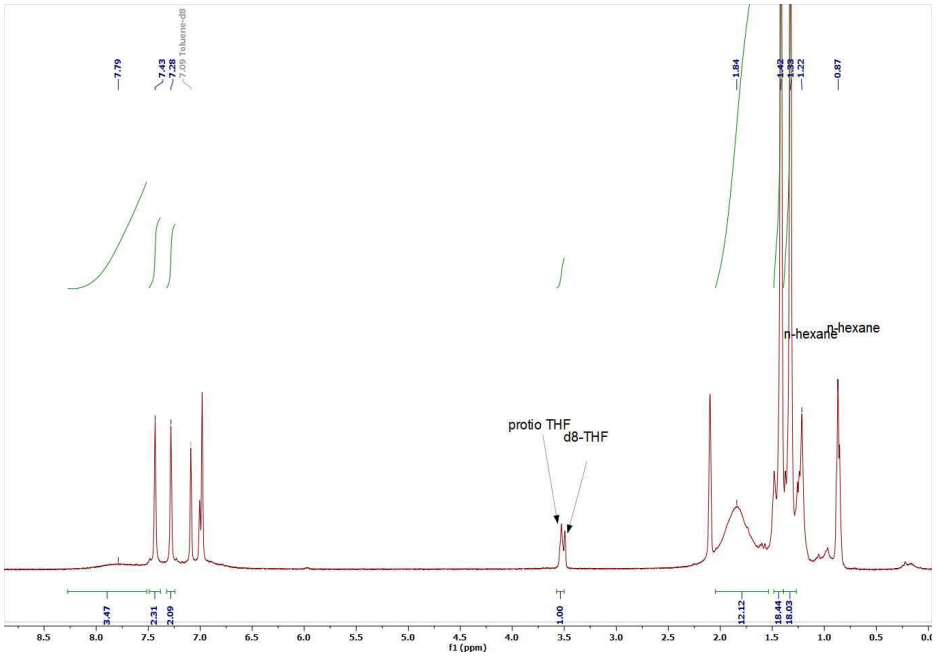


Figure S3: The ^{1}H NMR spectrum of **(2-K_2)** measured in C_7D_8 with a few drops of d^8-THF.

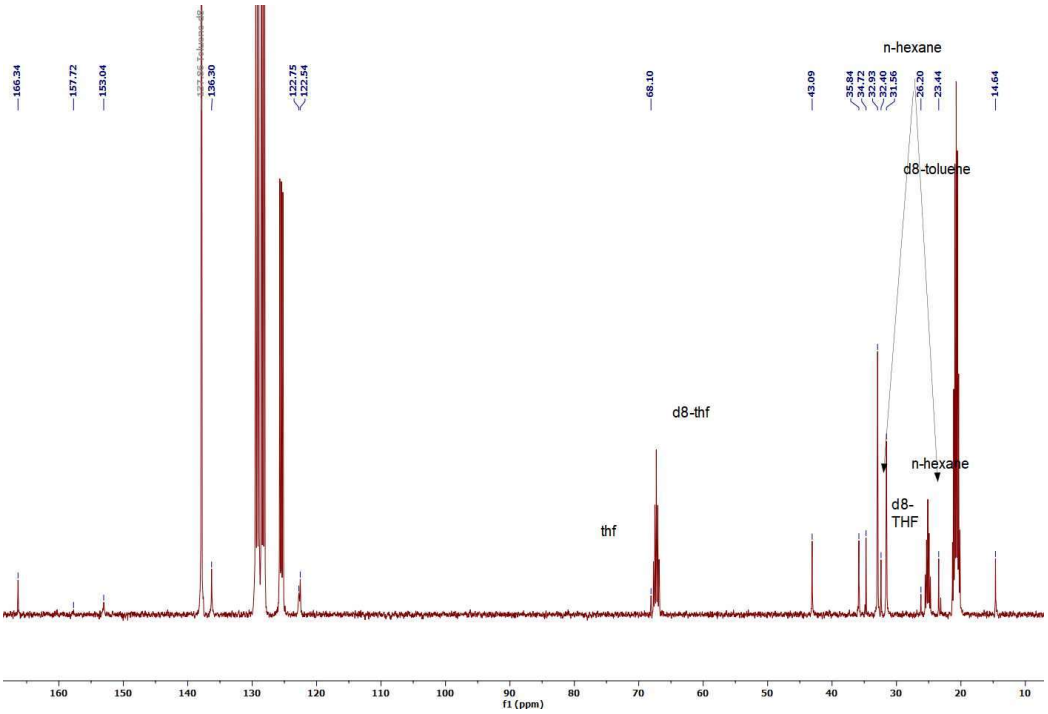


Figure S4: The $^{13}C\{^{1}H\}$ NMR spectrum of **(2-K_2)** measured in d^8-toluene with a few drops of d^8-THF.

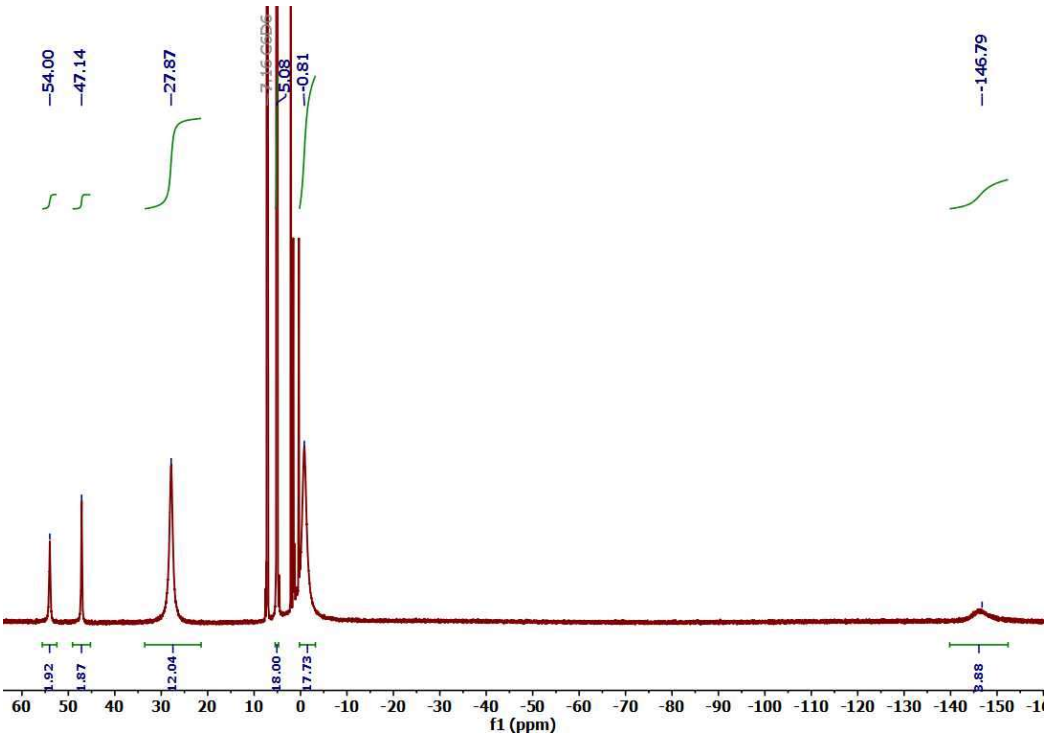


Figure S5: The ^{1}H NMR spectrum ($\delta(C_6D_6)$) of (**2-Fe**) in the region between -150 to 60 ppm.

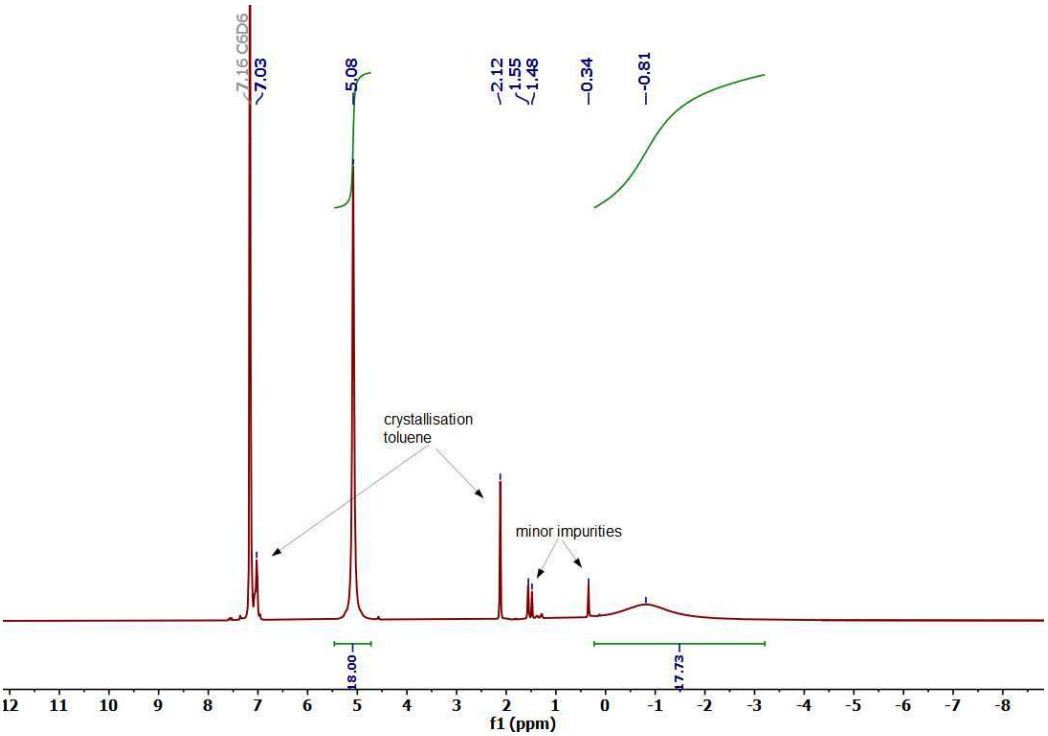


Figure S6: The ^{1}H NMR spectrum ($\delta(C_6D_6)$) of (**2-Fe**) in the region between -8 to 12 ppm.

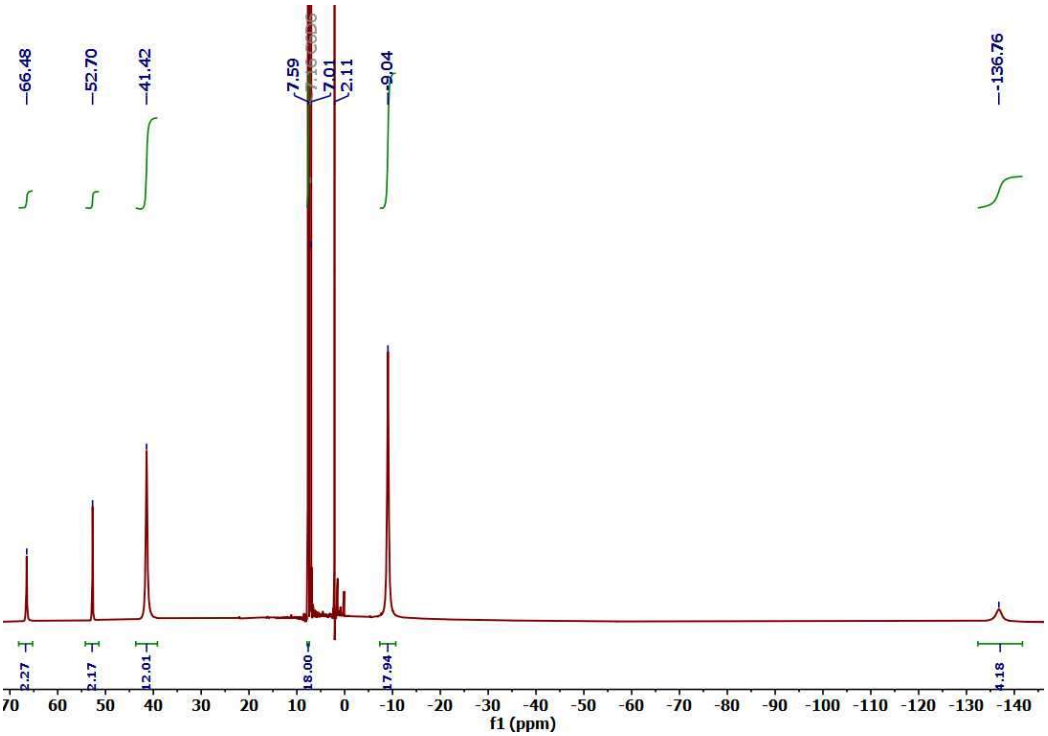


Figure S7: The ^{1}H NMR spectrum (δ(C_6D_6)) of (**2-Co**) in the region between -140 to 70 ppm.

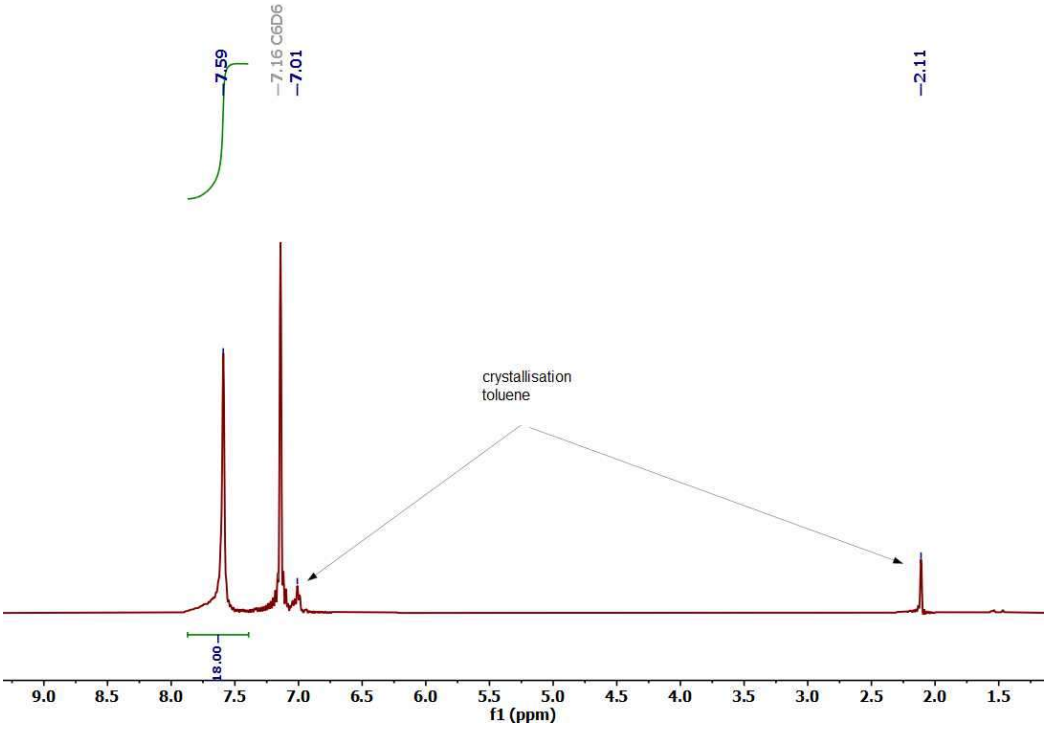


Figure S8: The ^{1}H NMR spectrum (δ(C_6D_6)) of (**2-Co**) in the region between 1.5-9.0 ppm

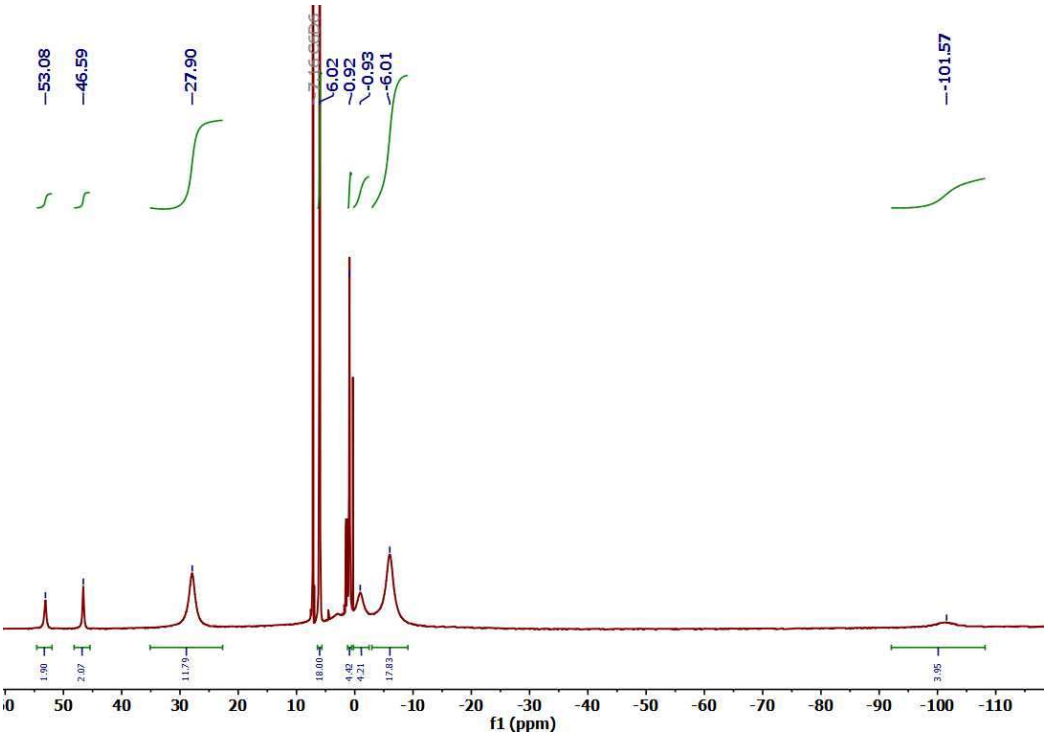


Figure S9: The ^{1}H NMR spectrum ($\delta(C_6D_6)$) of (**2-Fe.THF**) in the region between -110 to 60 ppm.

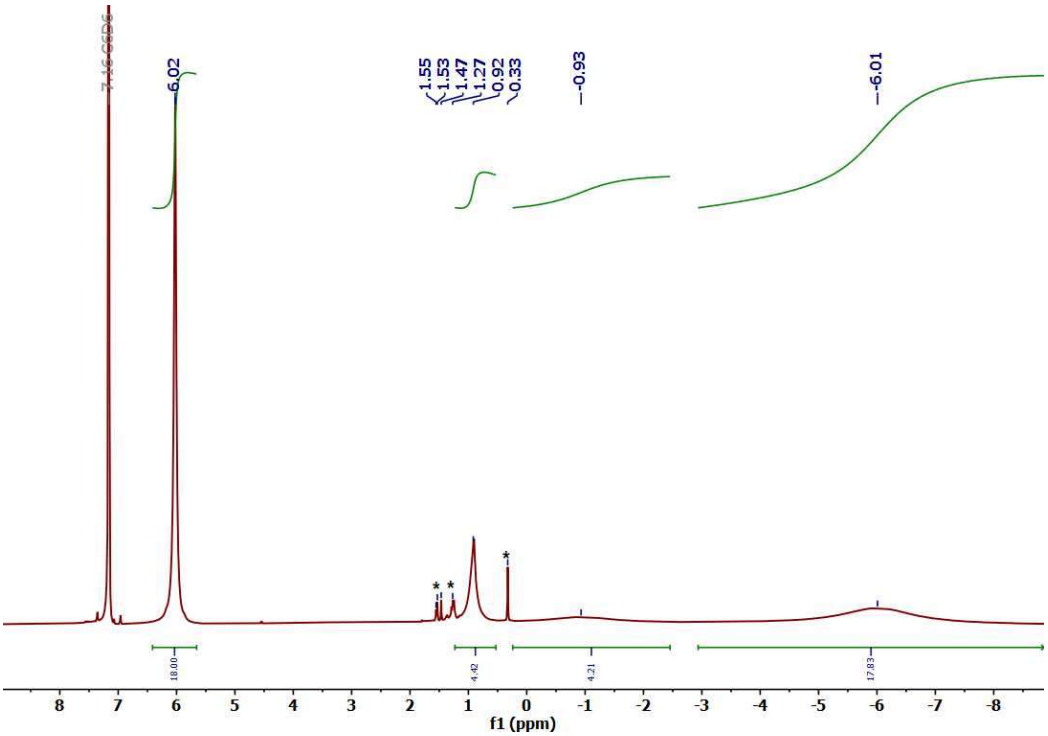


Figure S10: The ^{1}H NMR spectrum ($\delta(C_6D_6)$) of (**2-Fe.THF**) in the region between -8 to 8 ppm.; * denotes minor impurities.

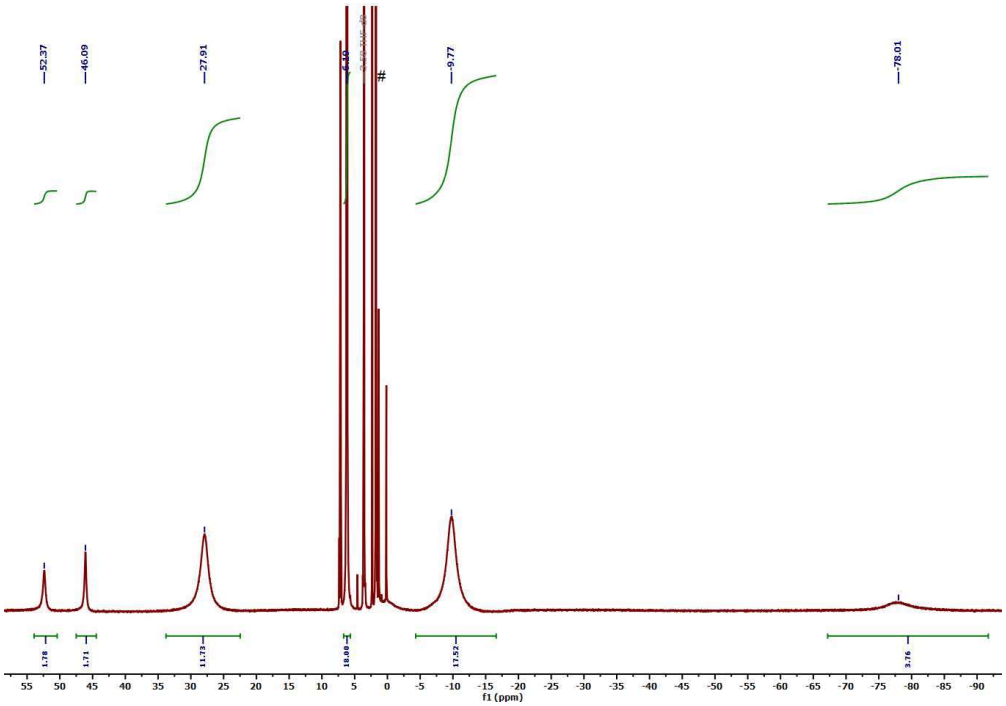


Figure S11: The ^{1}H NMR spectrum (δ(d^{8}-THF)) of (**2-Fe.THF**) in the region between -90 to 55 ppm.

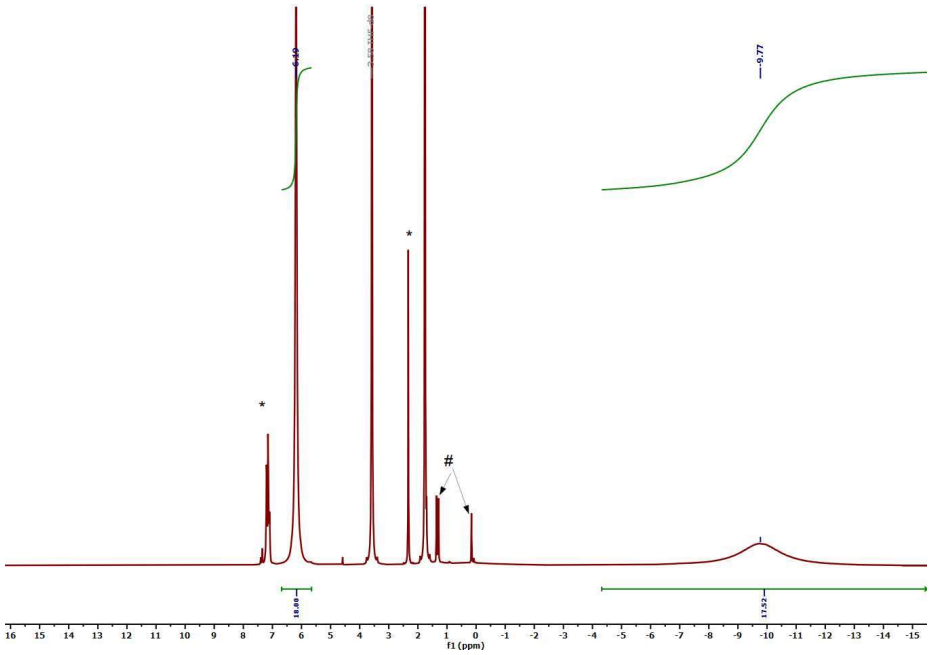


Figure S12: The ^{1}H NMR spectrum (δ(d^{8}-THF)) of (**2-Fe.THF**) in the region between -15 to 16 ppm; * denotes toluene, # denotes minor impurities.

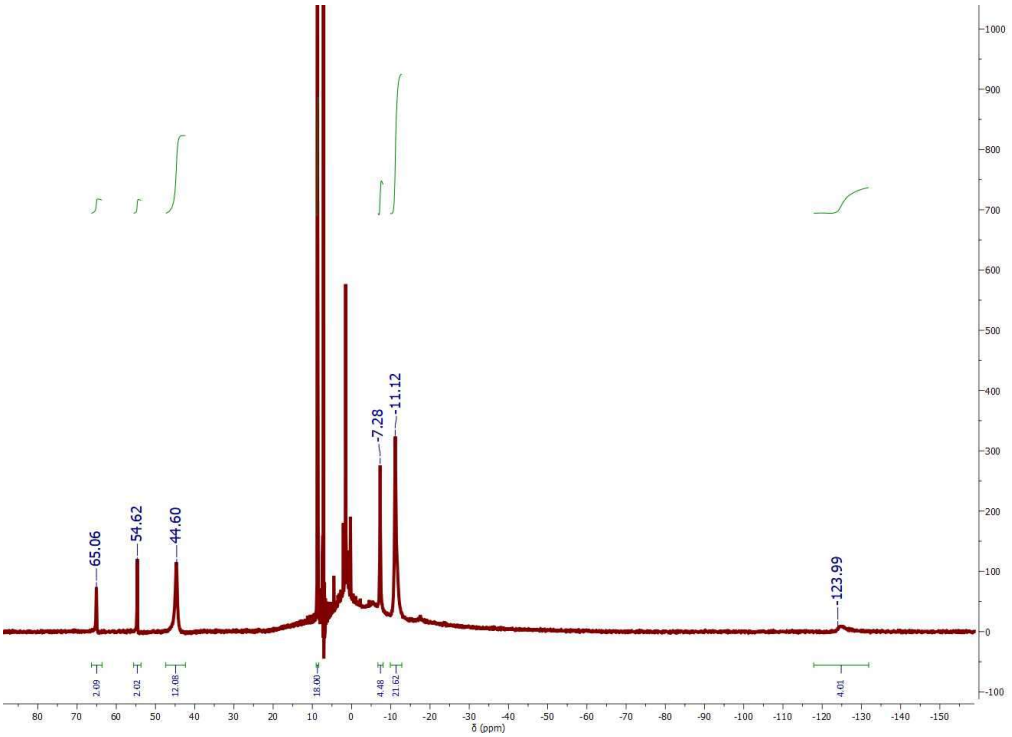


Figure S13: The ^{1}H NMR (δ(C_6D_6) of (**2-Co.THF**) in the region between -160 to 80 ppm

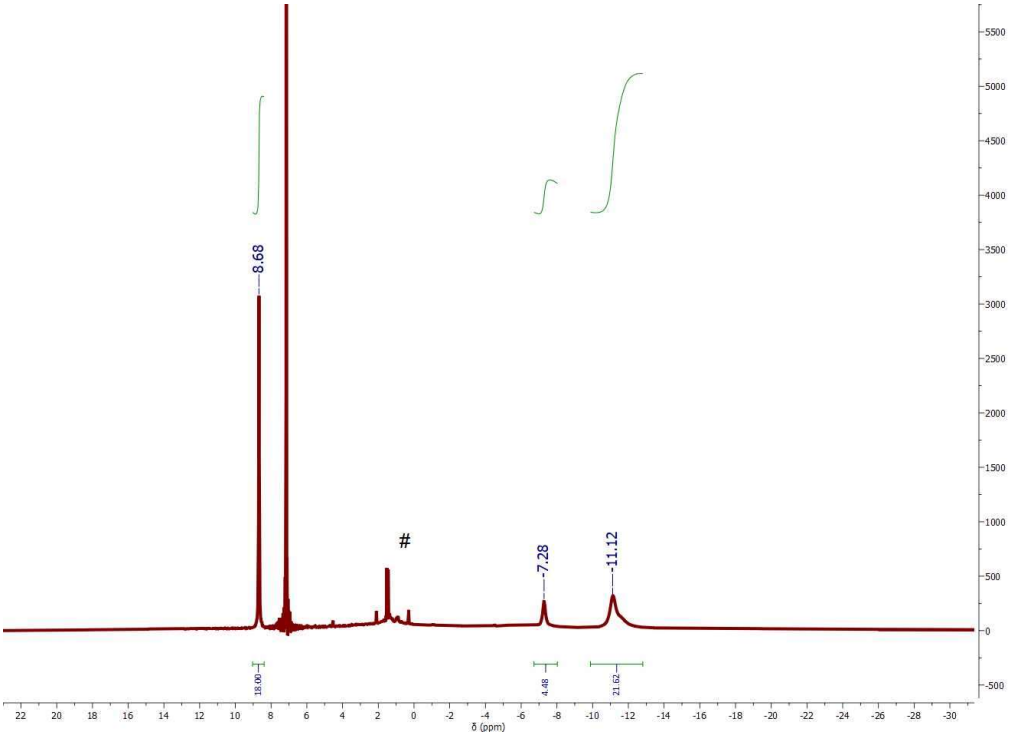


Figure S14: The ^{1}H NMR (δ(C_6D_6) of (**2-Co.THF**) in the region between -30 to 22 ppm; # denotes minor impurities.

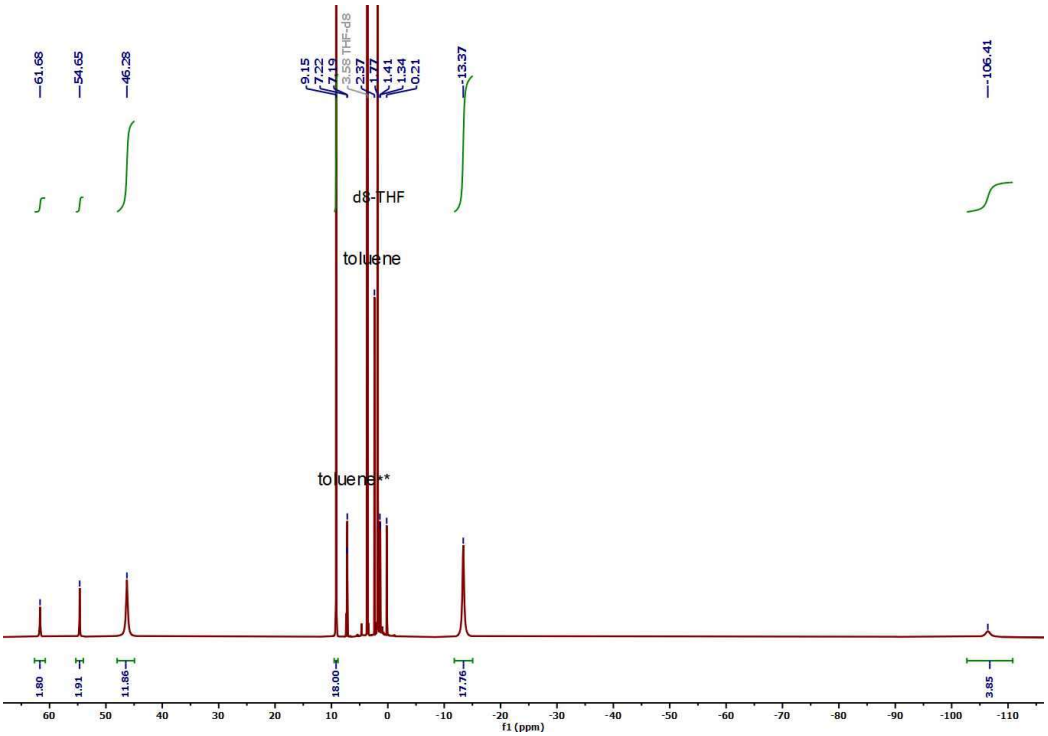


Figure S15: The ^{1}H NMR spectrum (δ(d^{8}-THF)) of (**2-Co.THF**) in the region between -110 to 70 ppm.

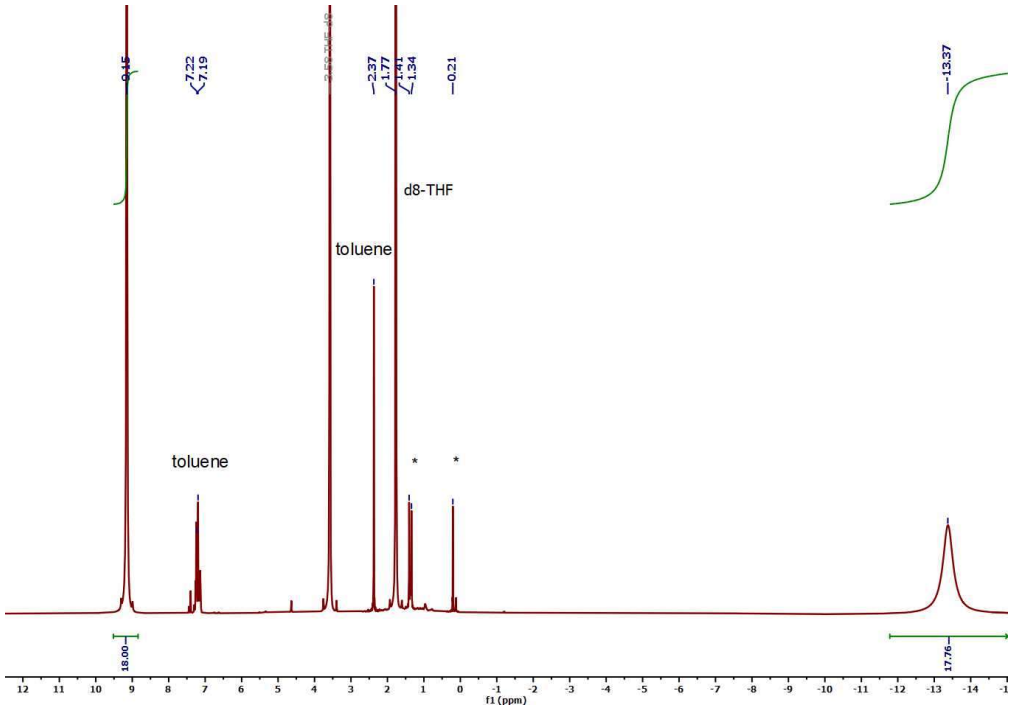


Figure S15: The ^{1}H NMR spectrum (δ(d^{8}-THF)) of (**2-Co.THF**) in the region between -15 to 12 ppm; * denotes minor impurities.

IR Spectra

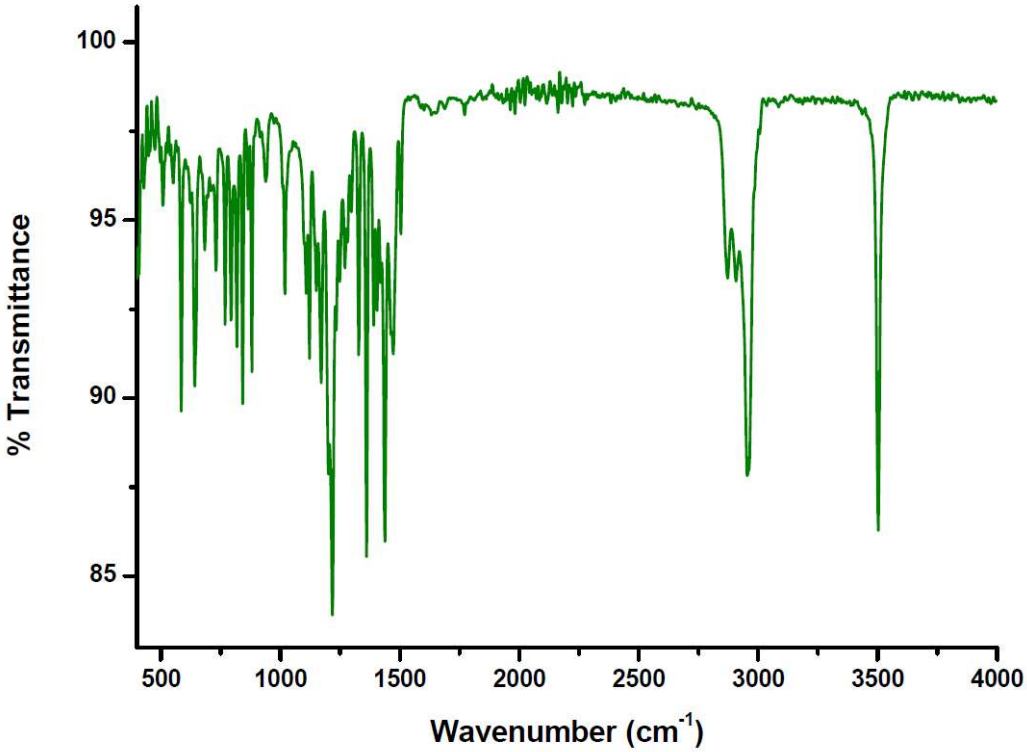


Figure S16a: The solid state IR spectrum **LH_2**.

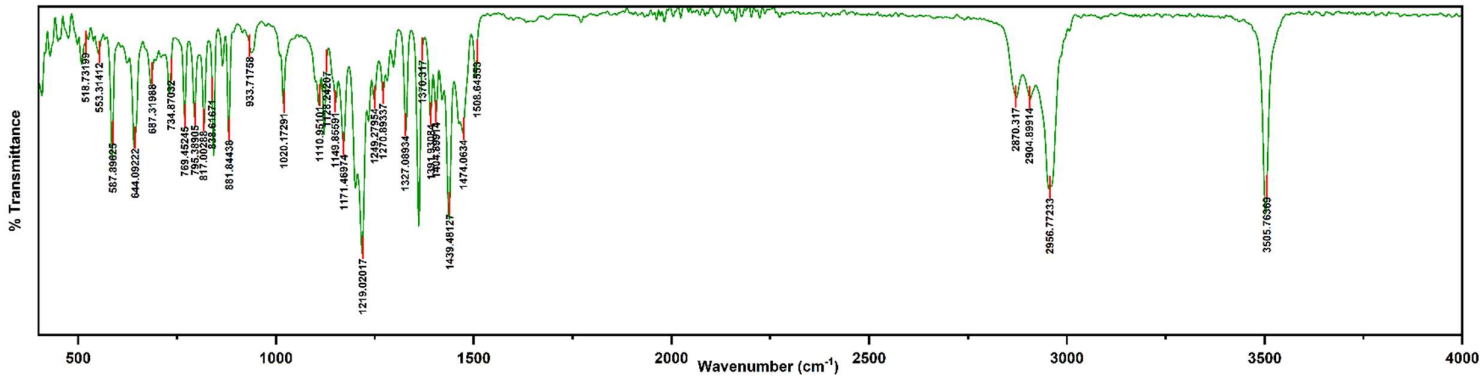


Figure S16b: Peak picked solid state IR spectrum **LH_2**.

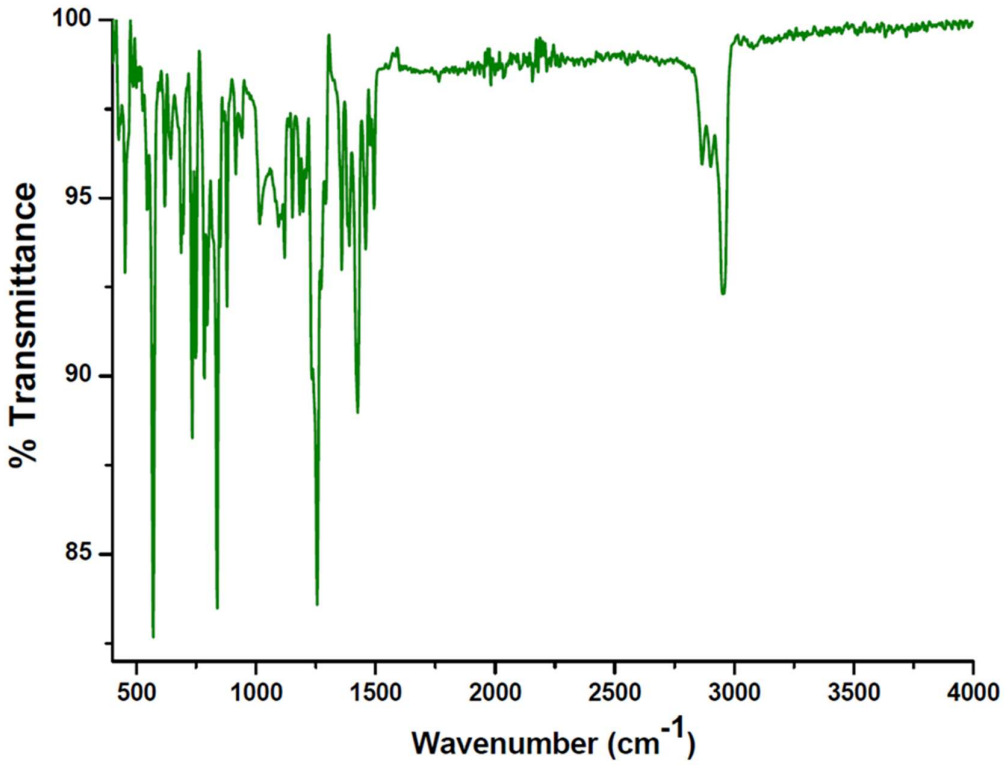


Figure S17a: The solid state IR spectrum of (**2-Fe**).

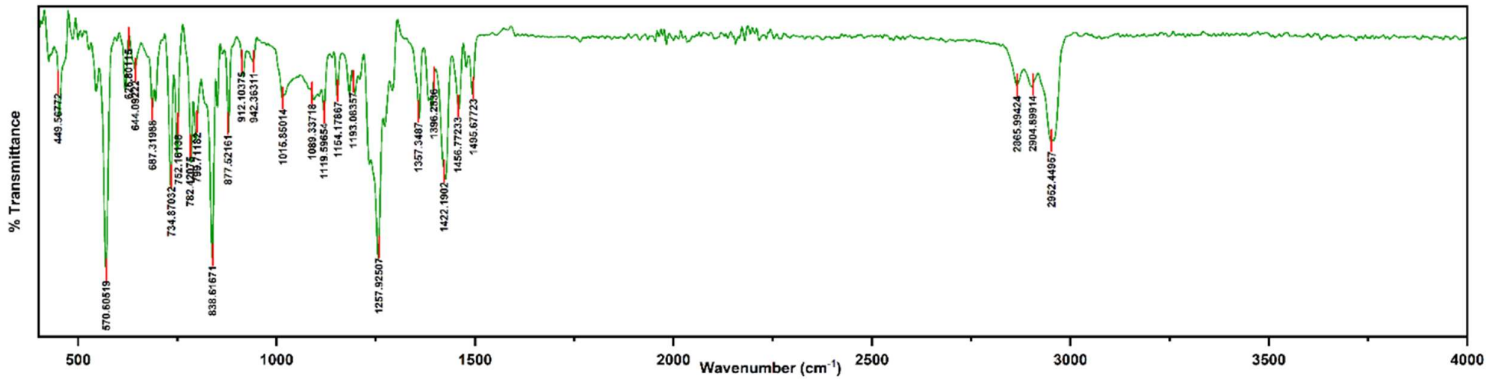


Figure S17b: Peak picked solid state IR spectrum of (**2-Fe**).

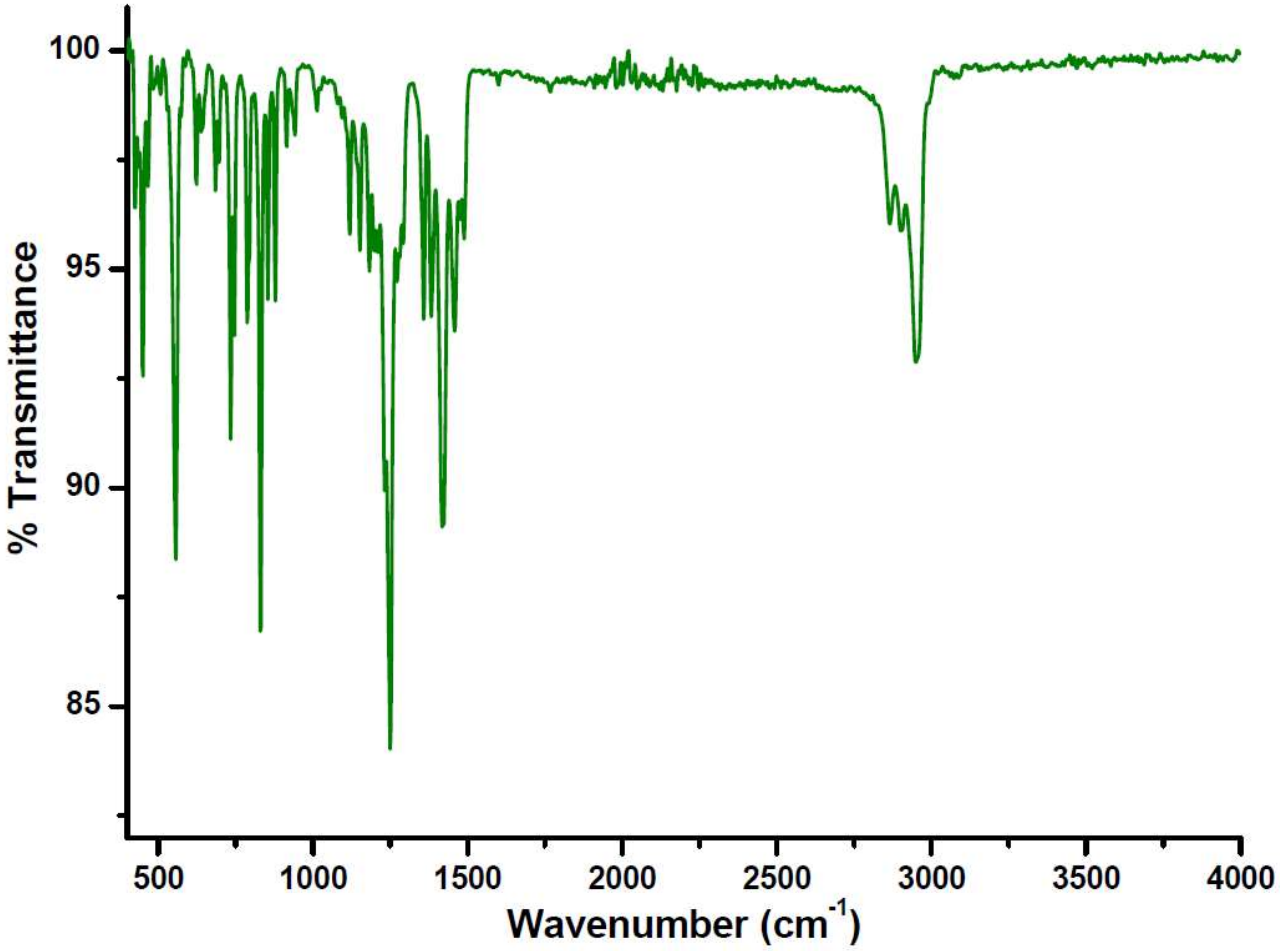


Figure S18a: The solid state IR spectrum of (**2-Co**).

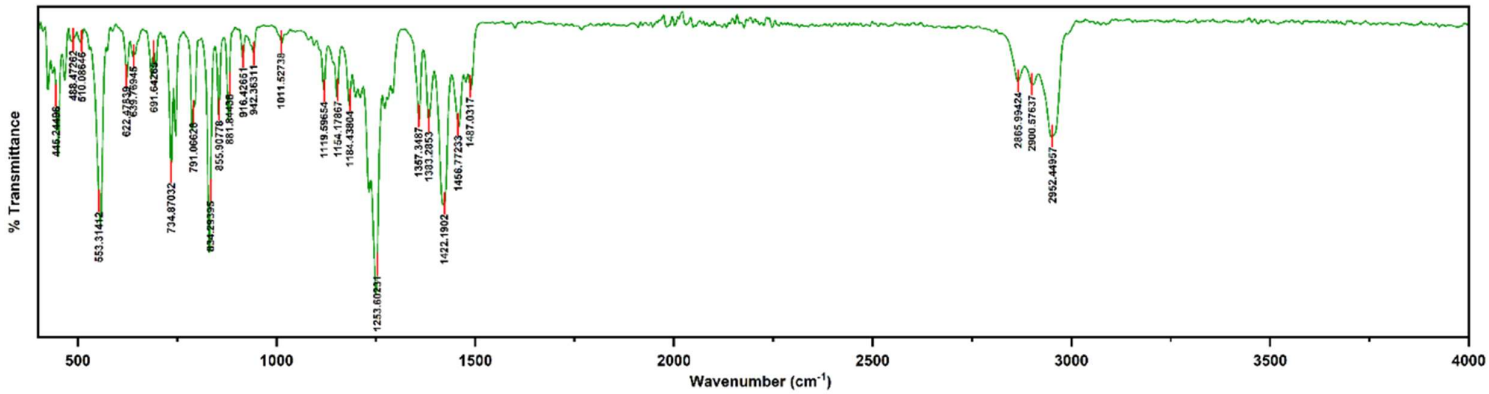


Figure S18b: Peak picked solid state IR spectrum of (**2-Co**).

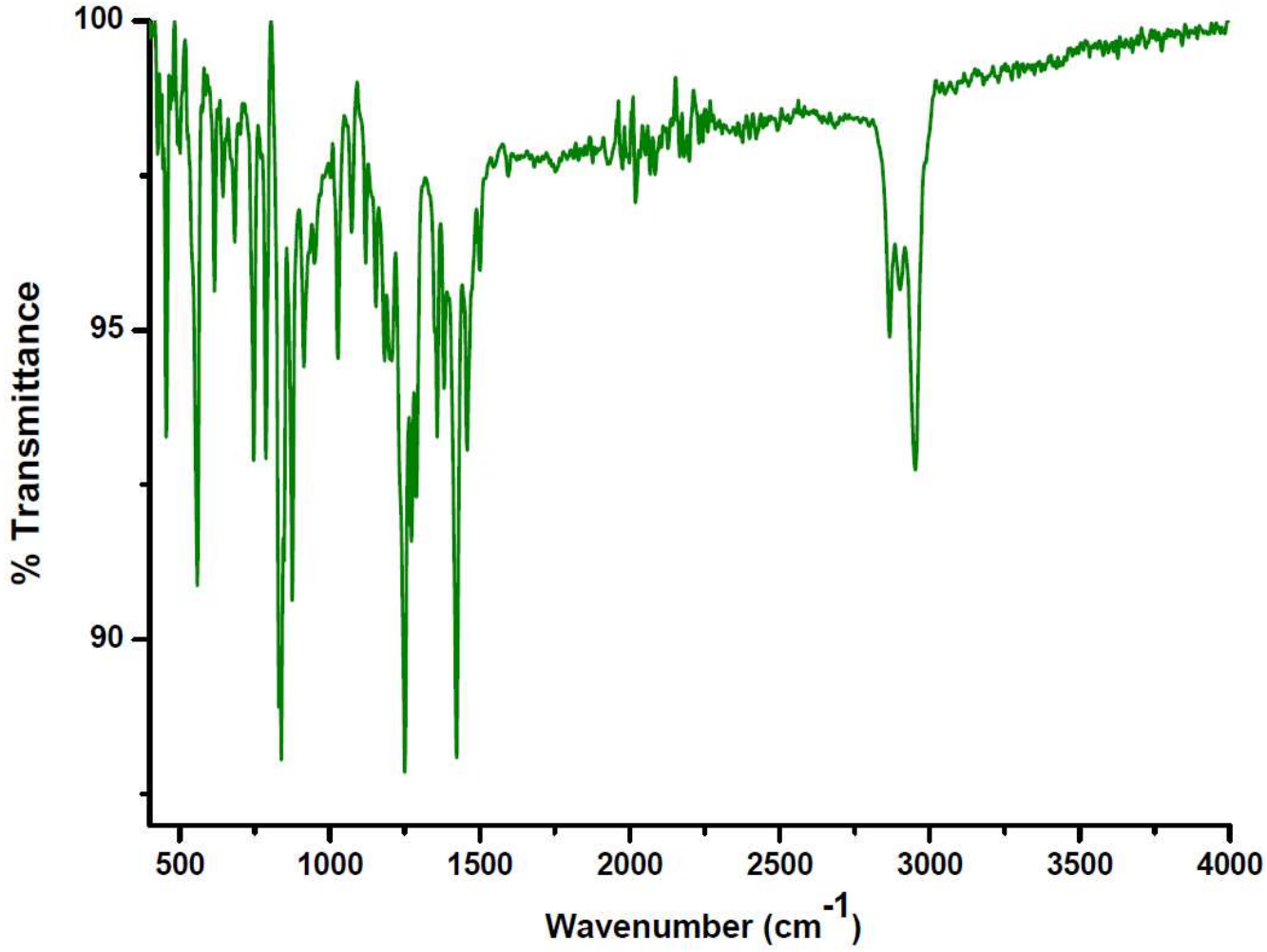


Figure S19a: The solid state IR spectrum of the (**2-Fe.THF**).

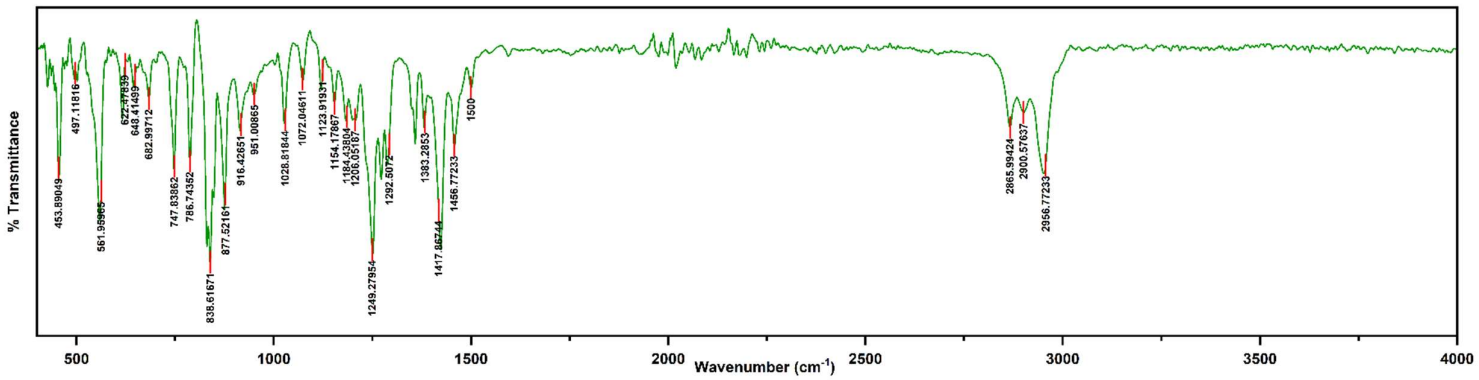


Figure S19b: Peak picked solid state IR spectrum of the (**2-Fe.THF**).

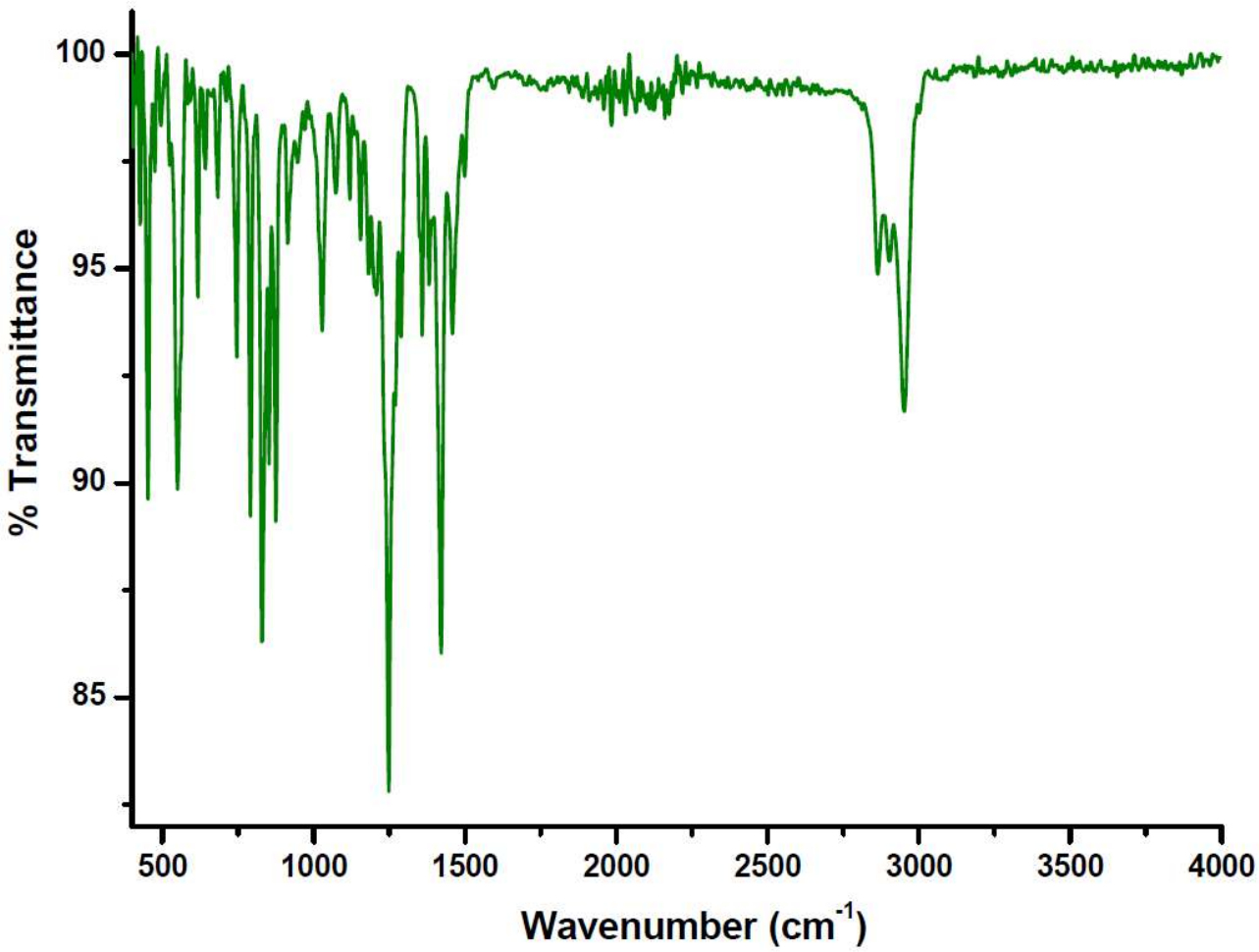


Figure S20a: The solid state IR spectrum of (**2-Co.THF**).

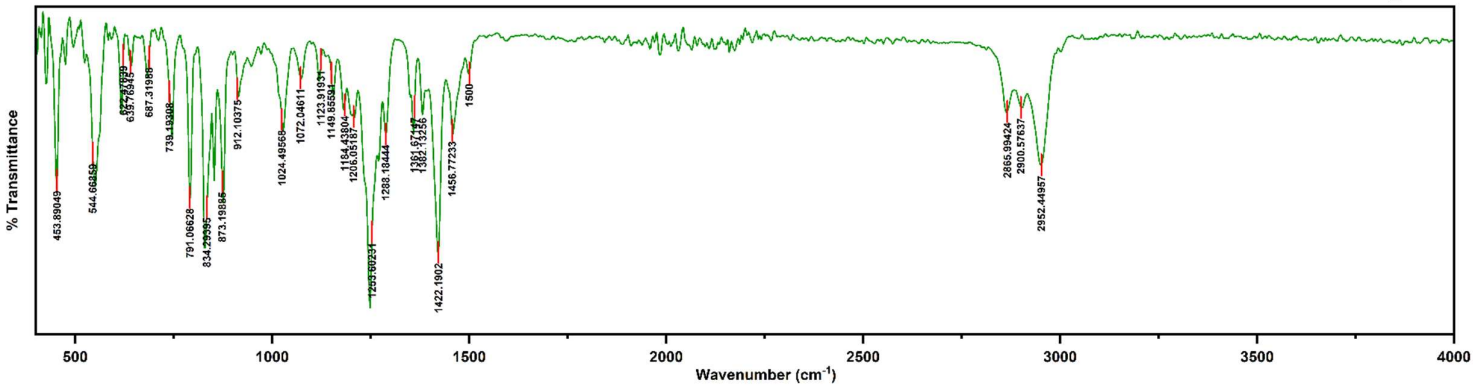


Figure S20b: Peak picked solid state IR spectrum of (**2-Co.THF**)

UV-Vis Spectra

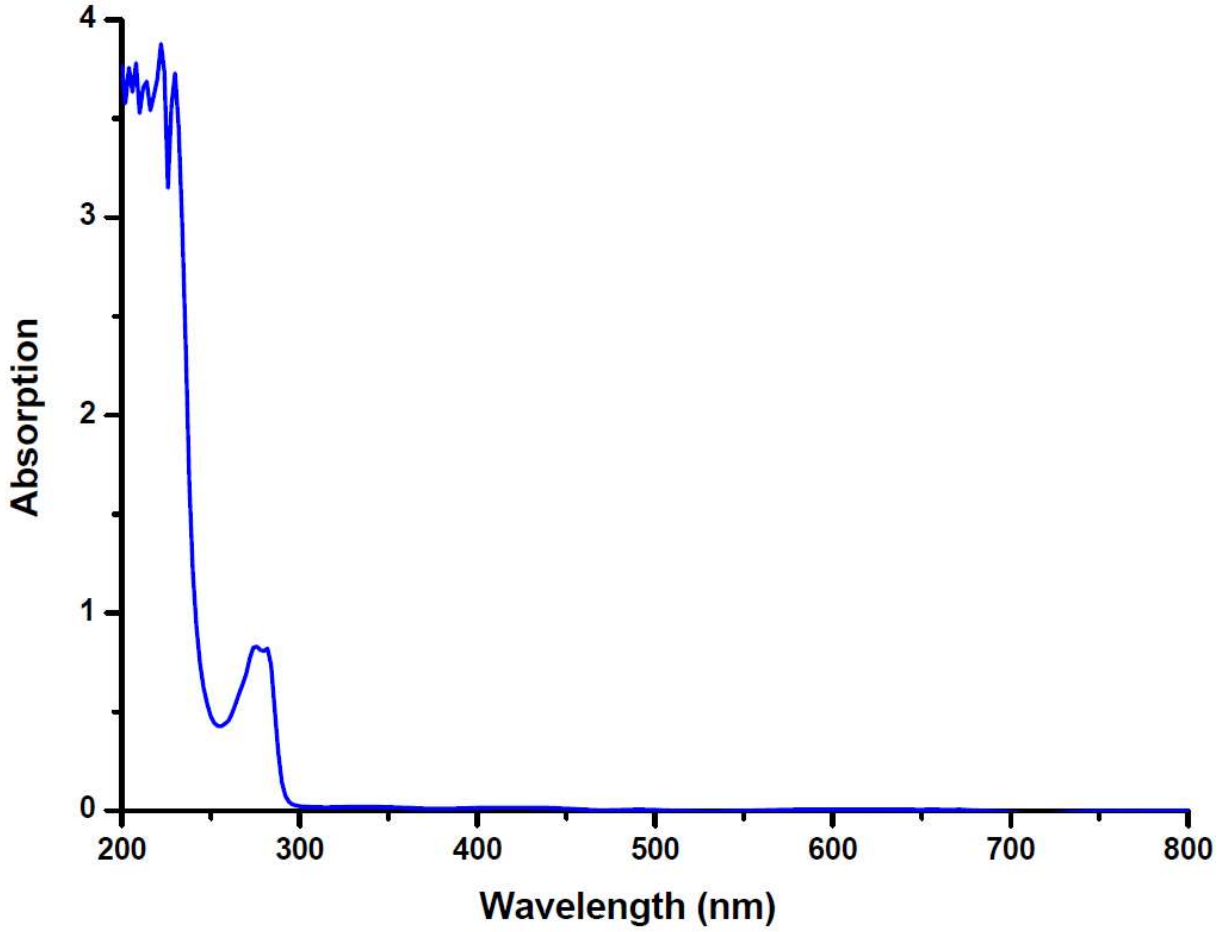


Figure S21: UV-Vis spectrum of L$\mathbf{H_2}$ measured as a 44 µM THF solution; λ=276 nm, ε = 18509.6 $cm^{-1}M^{-1}$.

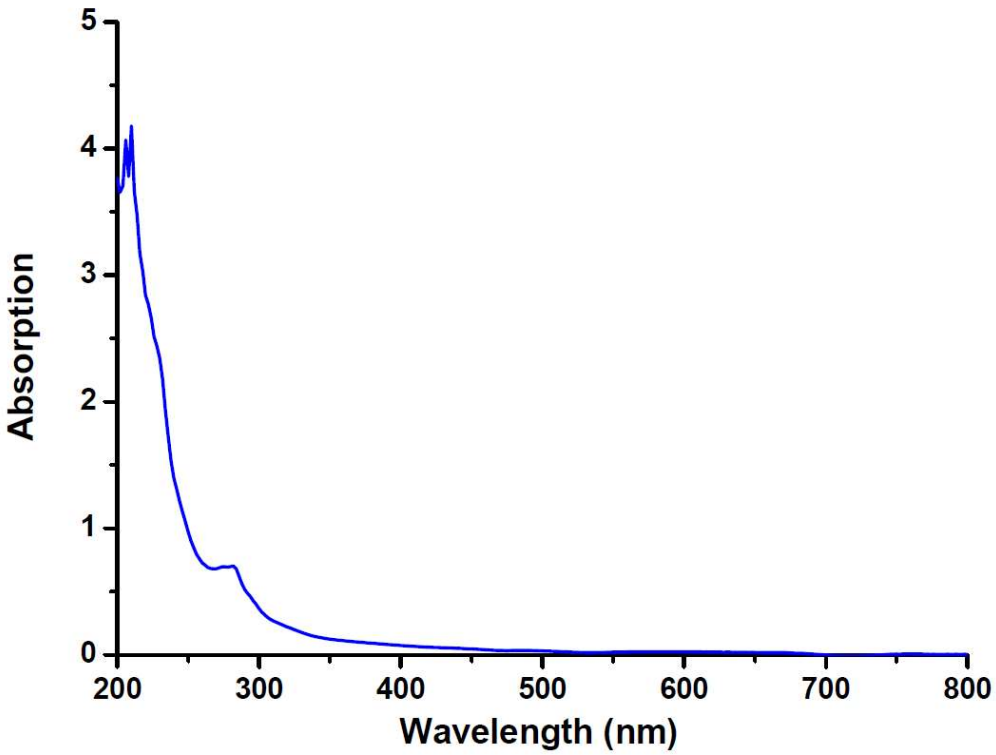


Figure S22: UV-Vis spectrum of (**2-Fe**) measured as a 80µM n-hexane solution; λ= 282 nm, ε = 8937.5 $cm^{-1}M^{-1}$

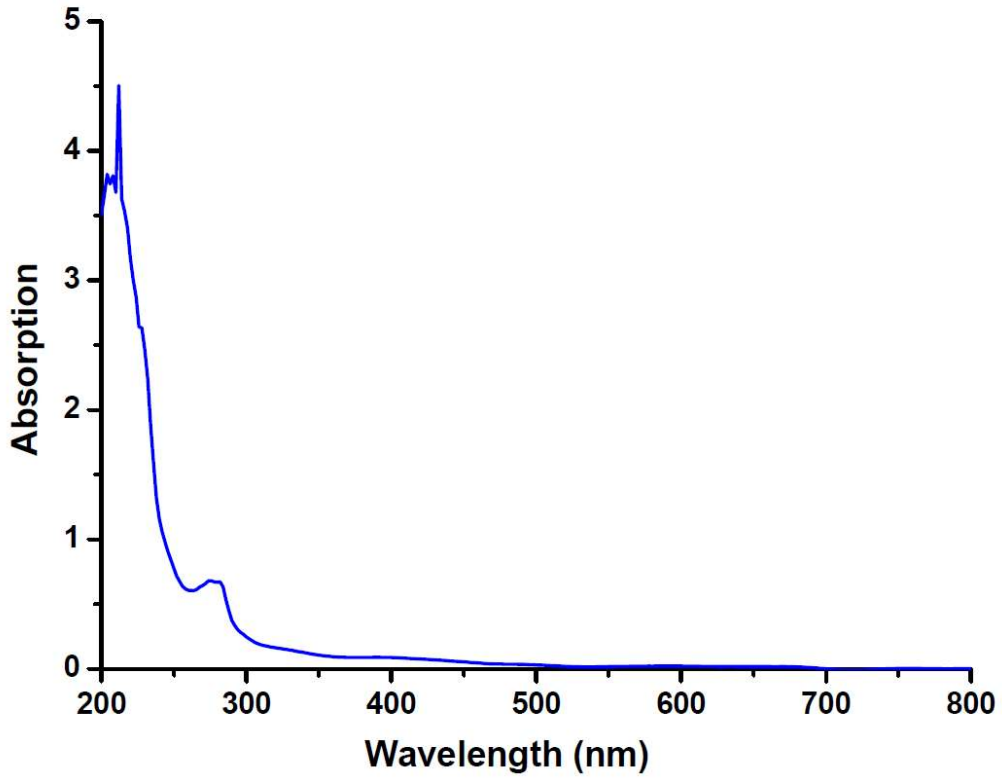


Figure S23: UV-Vis spectrum of (**2-Co**) measured as a 79 µM n-hexane solution; λ= 282 nm, ε = 14500 $cm^{-1}M^{-1}$.

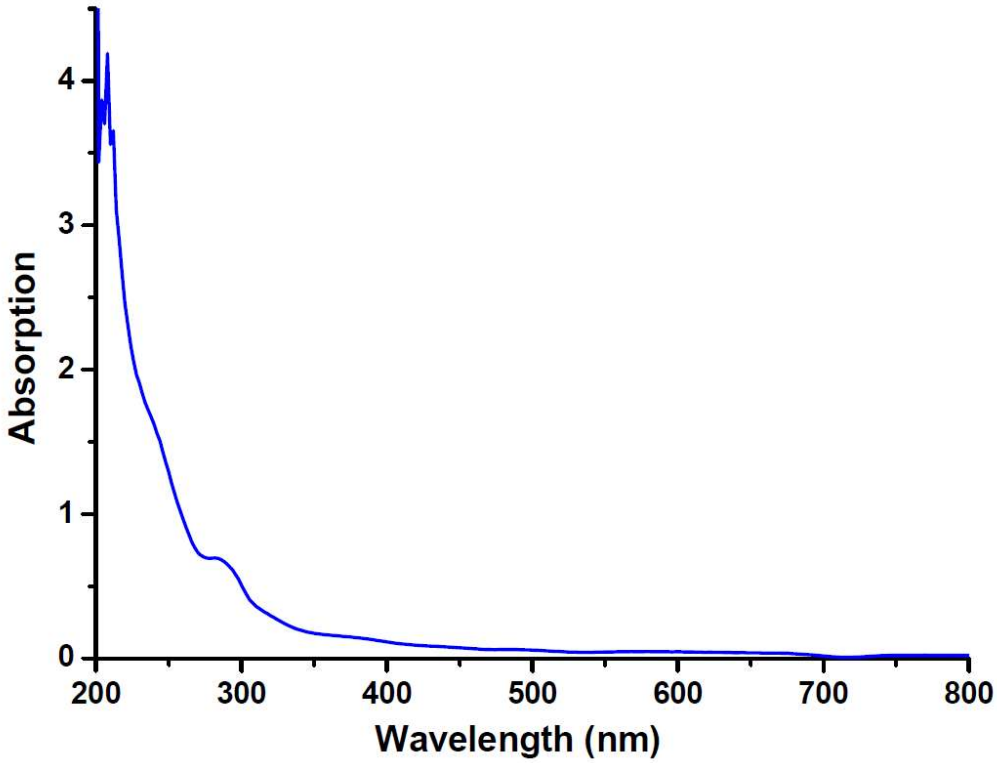
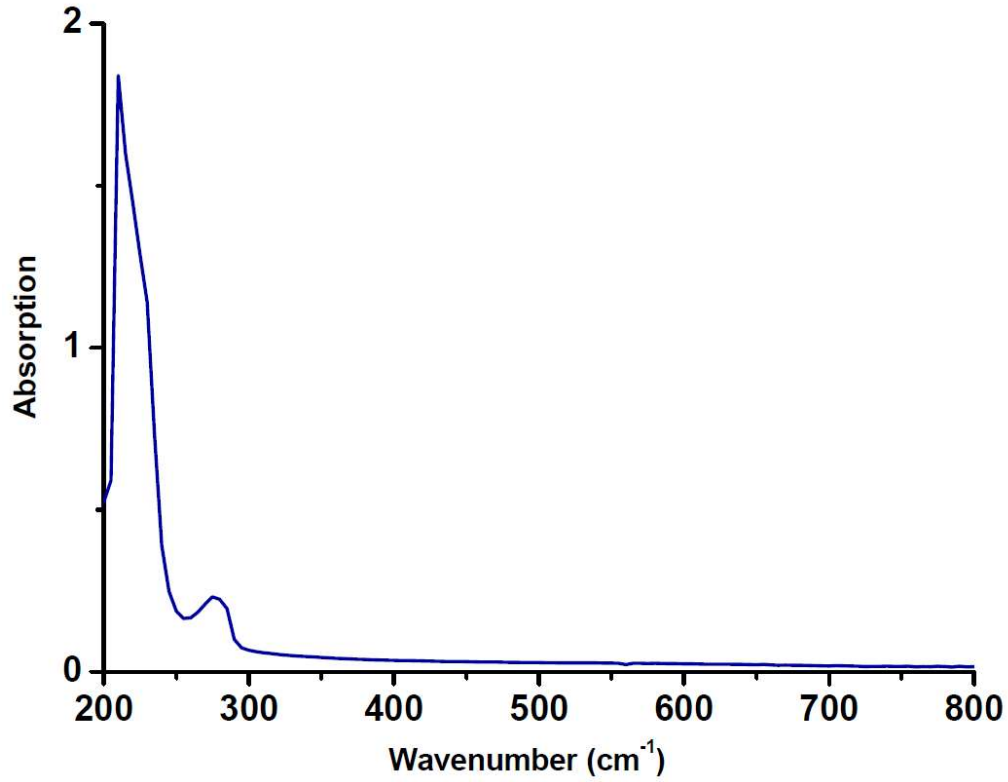


Figure S24: UV-Vis spectrum of (**2-Fe.THF**) measured as a 48 µM THF solution; λ= 282 nm, ε = 14500 $cm^{-1}M^{-1}$.

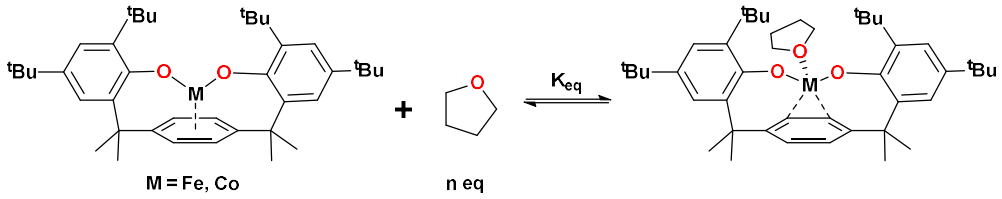


:

Figure S25: UV-Vis spectrum of (**2-Co.THF**) measured as a 45 µM THF solution; . λ= 275 nm, ε = 5133 $cm^{-1}M^{-1}$.

Calculation of THF binding constant

For the calculation of the THF binding constant in **(2-Fe.THF)** and **(2-Co.THF)** it is reasonable to assume the 1:1 equilibrium shown in Scheme S1. We base this on the different chemical shifts observed for the ^{1}H-NMR resonances of **(2-Fe)** and **(2-Co)** in C_6D_6 and d_8-THF, as well as the isolation of **(2-Fe.THF)** and **(2-Co.THF)** adducts in the presence of THF.



Scheme S1

$$(\mathbf{2-M}) + \mathbf{THF} \rightleftharpoons (\mathbf{2-M.THF}) \text{ (eq. 1)}$$

The association constant K_{eq} is defined by the following equation (2):

$$\boldsymbol{K_{eq}} = \frac{[(\mathbf{2-M.THF})]}{[(\mathbf{2-M})][\mathbf{THF}]} \quad (2)$$

The variable chemical shifts of the protons of the ^{t}Bu- groups, phenolate wingtips, benzylic methyls and the anchor arene resonances were plotted against the equivalents of THF added and Bindfit [7,8] was used to fit the binding curves to the data points using equation (3):

$$\boldsymbol{\Delta\delta = \delta_{\Delta HG}\left(\frac{[(2-M.THF)]}{[(2-M)]_0}\right)} \quad (3)$$

where H = **(2-M)**, G = (THF) and **[(2-M)]$_0$** is the initial concentration of **(2-M)** before the addition of any THF equivalents.

Procedure for (**2-Fe.THF**): 10.1 mg of (**2-Fe**) (0.016 mmol) were added to J-Young's NMR tube in an Ar glovebox and dissolved in 0.509 g of C_6D_6. Increasing equivalents of protonated THF (from ca 1 to 299) were added incrementally *via* microsyringe to the NMR tube and the ^{1}H NMR spectra were recorded at 291 K. Data were corrected for

the density of C_6D_6 at 291K. After fitting, the *Keq* value of **63,54 (± 4,91%)** M^{-1} was obtained. ***Note:*** The spectra no 20, 21 & 22 (Figure S26) were not included in the fitting process due to the significant broadening of peaks.

Procedure for (**2-Co.THF**): 10.7 mg of (**2-Co**) (0.017 mmol) were added to J-Young's NMR tube in an Ar glovebox and dissolved in 0.508 g of C_6D_6. Increasing equivalents of protonated THF (from ca 0.65 to 239) were added incrementally *via* a microsyringe to the NMR tube and the ^1H NMR spectra were recorded at 291 K Data were corrected for the density of C_6D_6 at 291 K. After fitting, *Keq* value of **216,77 (± 7,15%)** M^{-1} was obtained. ***Note:*** The spectra no 20, 21 & 22 (Figure S28) were not included in the fitting process due to the significant broadening of the peaks.

In both cases fittings were attempted for the coordination of 2 THF solvent molecules to the metal centres, but the errors in the fitting curves were extremely high (3 orders of magnitude higher for the first constant and one order of magnitude for the second)

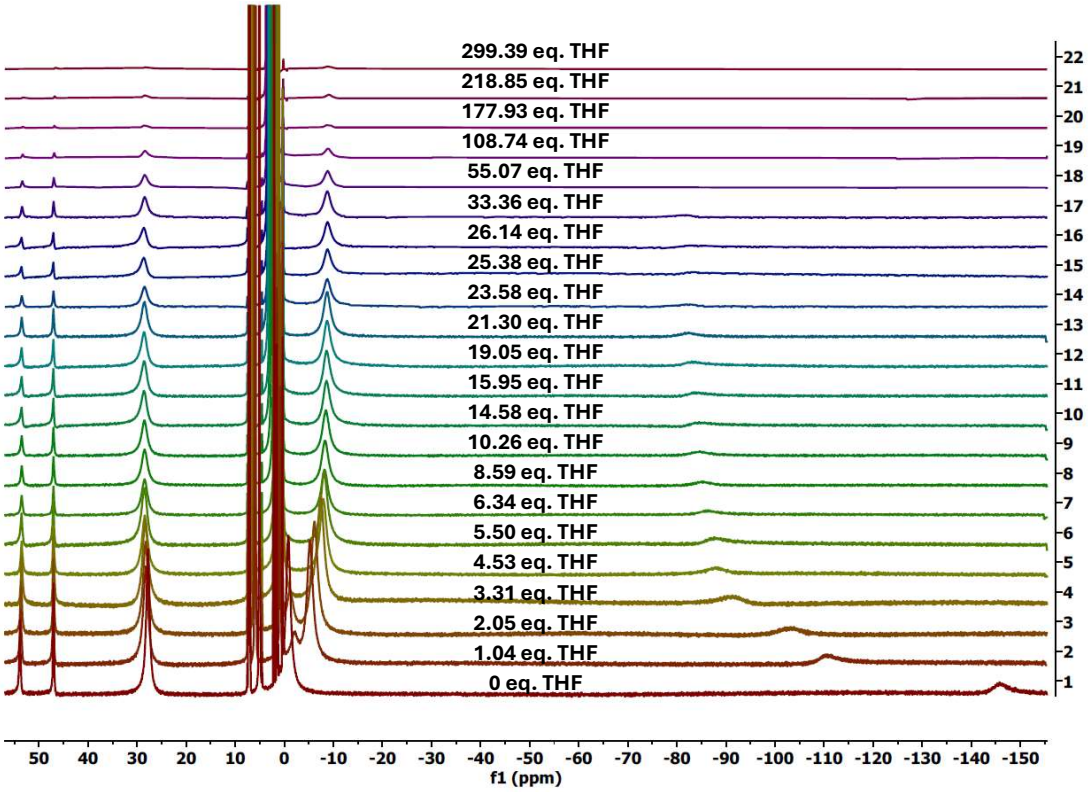


Figure S26: NMR THF titration experiment on the **(2-Fe)** complex measured at 16°C.

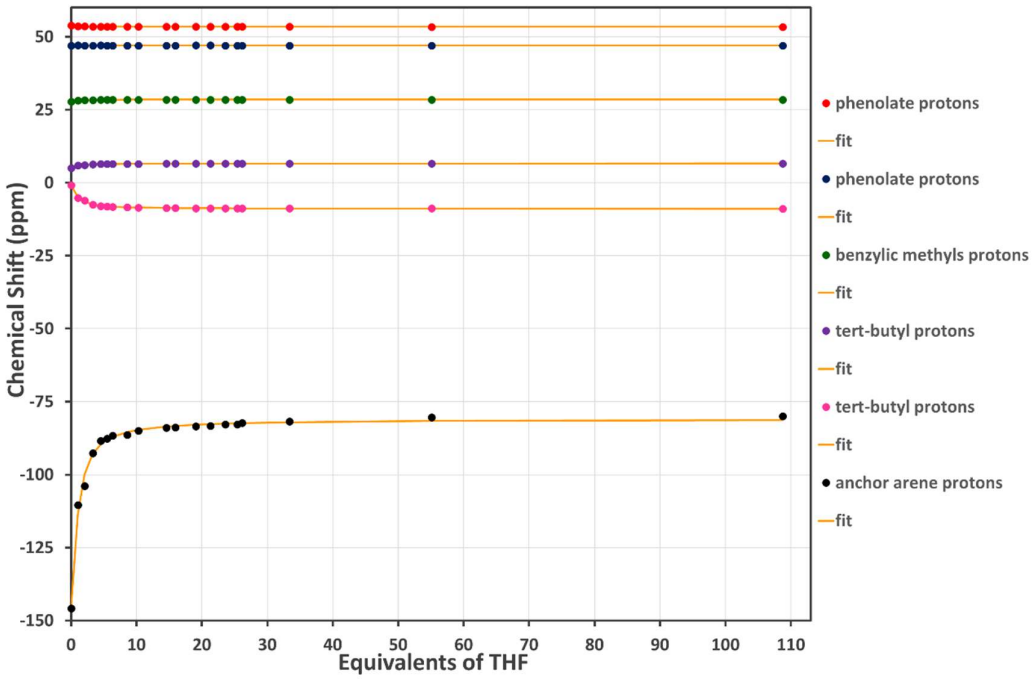


Figure S27: Binding curve from the ^{1}H-NMR spectrum of 0.0280 M **(2-Fe)** upon incremental addition of THF.

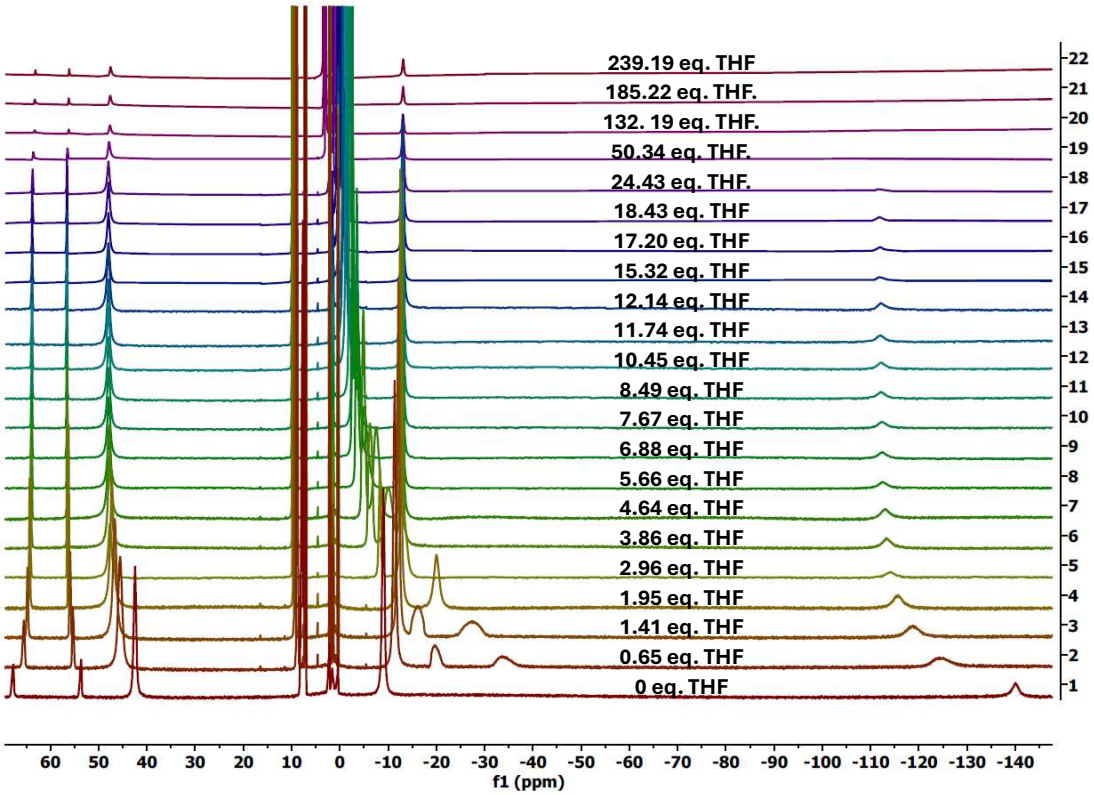


Figure S28: NMR titration experiment on the **(2-Co)** complex measured at 16°C.

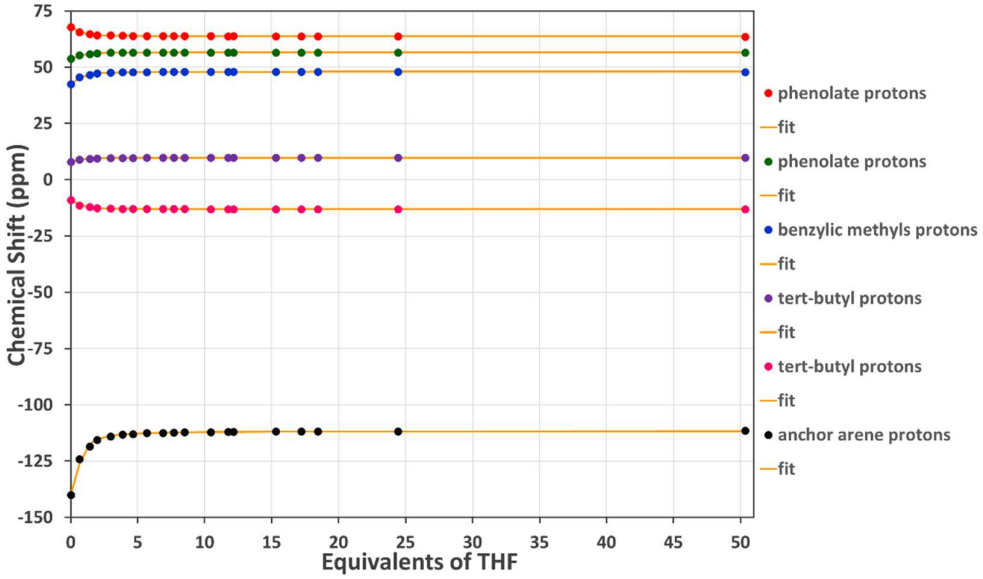


Figure S29: Binding curve from the ^{1}H-NMR spectrum of 0.0285 M **(2-Co)** upon incremental addition of THF.

Single Crystal X-Ray Crystallography:

Data for **LH_2**, (**2-Co**) and (**2-Fe**) were collected at the NKUA X-ray core facility on a dual source (IμS Diamond Cu/Kα & Mo/Kα) Bruker D8-Venture SC-XRD instrument equipped with a Photon-III area detector at 100K using an Oxford Cryosystems 100 cryostream. In the case of **LH_2** and (**2-Co**), data were collected using Cu/Kα to a resolution of 0.83 and 0.79 Å respectively. In the case of (**2-Fe**) data were collected using Mo/Kα to a resolution of 0.60 Å.

Data were collected using ϕ and ω scans to fill the Ewald sphere using a 4-circle kappa goniometer. Data collection and subsequent processing were handled by the APEX4 software package. A multi-scan absorption correction (SADABS 2016/2) was applied in both cases.

In the case of (**2-Ni**) data were collected using a Rigaku AFC11 diffractometer equipped with a Highflux-007 VHF Cu/Kα rotating anode, a Saturn-924 CCD area detector and a ¼ chi 4 circle kappa goniometer at 100K, to a resolution of 0.84 Å. Data were collected using ω scans to fill the Ewald sphere. Diffractometer control, data acquisition and subsequent processing were handled by the ChrysAlis software package (Rigaku Oxford Diffraction, 2015).

Data for complexes (**2-M.THF**) (M = Fe, Co) were collected at the SC-XRD laboratory of the Catalysis Research Center at TUM using a Bruker D8-Venture three-circle diffractometer equipped with a Mo/Kα TXS rotating anode and a Photon-III area detector at 100K using an Oxford Cryosystems low temperature device to a resolution of 0.75 Å (M = Fe) and 0.83 Å (M = Co). Crystals were mounted on Kapton micro-sampler stages from Fomblin oil. Data were collected using ϕ and ω scans to fill the Ewald sphere. Data collection and subsequent processing were handled by the APEX4 software package. A multi-scan absorption correction (SADABS 2016/2) was applied in both cases with spherical harmonics.

In all the above cases, crystals were mounted on Mitigen cryo-crystallography loops from either dried vacuum-pump oil or Fomblin that were stored in a N_2 filled glovebox over activated 4Å molecular sieves.

For the datasets of the compounds listed above data solution (ShelXT[9]) and subsequent model refinement (ShelXL[10]) were achieved using the graphic interface of the Olex2-1.5 software package[11] or SHEXLE.[12] In the case of (**2-Ni**) data solution was achieved using DirDIFF.[13] For the graphics of the molecular structures ORTEP-III was used.[14]

All atoms were refined anisotropically and hydrogen atoms were added using the riding model, unless otherwise stated.

Special Refinement Details:

LH_2: Data collected for this compound were processed as a non-merohedral two-component twin using TWINABS.[15] Initial solution and model refinement were performed using the hkl4 file and at the final stages of the model refinement using the hkl5 file with a BASF value for the two domains of 0.396 (*ie ca* 60:40 two-component twin).

(2-Co): The ^{t}Bu substituent *para* to the O functionality in one of the aryloxy pendant arms, displays occupational disorder over two positions of all its three methyls. This was successfully

modelled using the PART command with the occupancy of each site let to refine freely and converging to a value of *ca* 84:16. Furthermore SADI restraints had to be used while atoms C40, C40A, C38A and C39A of this disordered ^{t}Bu group had to be refined isotropically, using the ISOR command for the refinement to converge.

(2-Ni): Half a molecule of crystallization solvent (n-hexane) is present in the asymmetric unit showing significant disorder. Despite our best efforts, this was best modelled, using the FragmentDB functionality in Olex2-1.5 and the PART -1 command and finally refining it as a rigid body using the RIGU command. Checkcif returns the PLATON alert: 'PLAT029_ALERT_3_C _diffrn_measured_fraction_theta_full value Low . 0.973'; this is due to partial X-ray damage of the crystal resulting in frames with very little data, that were excluded from the data processing.

(2-Co.THF): Checkcif returns a PLATON alert (PLAT_601) that the Unit Cell Contains Solvent Accessible VOIDS of 106 Å^3; Examination of the electron difference map indicated the presence of a disordered tetrahydrofuran (THF) molecule positioned on the inversion center. The electron density was insufficient for a whole THF molecule however, and could not be modelled reasonably, suggesting a partial occupancy of the cavity. This may be attributed to solvent evaporation from the crystal during sample preparation and is further supported by the PLATON/SQUEEZE routine, which found only 7 electrons (per unit cell) within the solvent-accessible void.

(2-Fe.THF): Half a molecule of crystallization solvent (THF) is found in the unit cell positioned on the inversion centre. This was successfully modelled using RIGU and SADI restraints.

All other crystal collection data and final refinement details are given in Tables S1 & S2 below.

Compound	**LH_2**	**(2-Fe)**	**(2-Co)**
Colour, habit	Colorless/Plate	Yellow/Plate	Green/Plate
Size/mm	0.04x0.04x0.02	0.19x0.12x0.039	0.040x0.035x0.020
Empirical formula	$C_{40}H_{58}O_2$	$C_{80}H_{116}Fe_2O_4$. C_7H_8	$C_{80}H_{116}Co_2O_4$. C_7H_8
FW	570.86	1341.52	1347.68
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	*P2₁/c*	*C2/c*	*C2/c*
a/Å	18.3294(7)	37.508(2)	38.2316(15)
b/Å	8.3314(4)	11.0766(7)	10.9254(4)
c/Å	11.9719(6)	19.8485(12)	19.6425(8)
α/°	90	90	90
β/°	104.643(3)	110.908(2)	111.610(2)
γ/°	90	90	90
V/Å^3	1768.84(14)	7703.3(8)	7627.9(5)
Z	2	4	4
μ/mm^{-1}	0.480	0.425	3.771
T/K	100	100	100
$\vartheta_{min/max/full}$ (°)	2.491/68.247/67.679	2.087/36.438/25.242	2.486/77.668/67.679
Completeness to $\vartheta_{max/full}$ (%)	99.0 and 98.8	99.6 and 99.9	99.1 and 99.9
Reflections Total/ Independent	3195/2695	231950/18745	104099/8070
Parameters/restraints	203/0	438/0	467/27
R_{int}	N/A	0.0548	0.0553
Final *R*1, *wR*2	0.0437, 0.0994	0.0405, 0.1220	0.0516, 0.1529
Goof	1.058	1.044	1.055
Largest peak, hole / e.Å^{-3}	0.2 and -0.2	0.8 and -0.3	0.9 and -0.5
ρ_{calc}/g.cm^{-3}	1.072	1.157	1.174
CCDC reference	2413653	2413654	2413658

Table S1: Crystal data and final refinement details

Compound	**(2-Ni)**	**(2-Fe.THF)**	**(2-Co.THF)**
Colour, habit	Red/Plate	Yellow/Plate	Pink/Plate
Size/mm	0.05x0.03x0.01	0.050×0.122×0.378	0.013×0.079×0.156
Empirical formula	$C_{40}H_{56}NiO_2$. 0.5 (C_6H_{14})	$C_{44}H_{66}FeO_3$. 0.5(C_4H_8O)	$C_{44}H_{64}CoO_3$
FW	670.64	732.85	699.88
Crystal system	Triclinic	Triclinic	Triclinic
Space group	*P-1*	*P-1*	*P-1*
a/Å	10.5754(10)	11.7580(11)	11.7146(8)
b/Å	13.2838(10)	13.5926(11)	13.4105(10)
c/Å	14.3962(12)	14.6117(9)	14.5881(10)
α/°	84.035(7)	108.448(3)	109.675(2)
β/°	84.047(7)	106.081(2)	105.668(2)
γ/°	72.058(8)	98.129(3)	98.353(2)
V/Å^3	1908.1(3)	2060.3(3)	2006.0(2)
Z	2	2	2
μ/mm^{-1}	0.972	0.405	0.464
T/K	100	100	100
$\vartheta_{min/max/full}$ (°)	4.407/67.071/67.071	2.490/28.295/25.242	2.159/25.429/25.242
Completeness to $\vartheta_{max/full}$ (%)	97.3 and 97.3	99.8/99.9	99.5/99.9
Reflections Total/ Independent	23356/6630	47187/10220	81229/7381
Parameters/restraints	444/85	494/72	480/0
R_{int}	0.0867	0.0319	0.0976
Final *R*1, *wR*2	0.0699, 0.2068	0.0333, 0.0897	0.0414, 0.1089
Goof	1.066	1.029	1.074
Largest peak, hole / e.Å^{-3}	0.6 and -0.8	0.6 and -0.3	0.7 and -0.4
ρ_{calc}/g.cm^{-3}	1.167	1.181	1.159
CCDC reference	2413655	2413656	2413657

Table S2: Crystal Data and final refinement details

Electrochemistry

Cyclic voltammetry (CV) measurements were carried out at room temperature under an argon atmosphere with a PalmSens4 potentiostat. A 3 mm disc electrode with glassy carbon tip was used as working electrode, a silver wire as a pseudo-reference electrode and a platinum rod as a counter electrode. $[N(n\text{-}Bu)_4]PF_6$ ($TBAPF_6$) was used as supporting electrolyte throughout. Ferrocene (Fc) was added as an internal standard at the end of each measurement to reference the CV's *vs* the Fc/Fc^+ redox couple. Two sweeps over the selected voltage range were recorded per cyclic voltammogram, both anodically and cathodically, to exclude any abnormal electrochemical behavior of the analyte between scans.

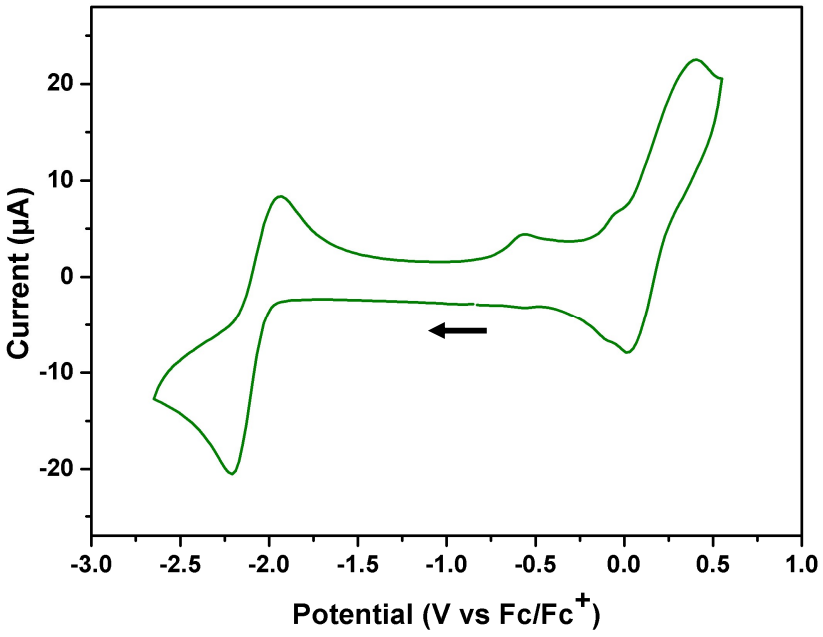


Figure S30a: The Cyclic voltammogram (one scan) of (**2-Fe**) measured cathodically with a scan rate of 200 mV/s; 5 mg of (**2-Fe**) (2.7 mM) and 121 mg of $TBAPF_6$ (*ca* 0.1M) in 3 ml of 1,2-difluorobenzene.

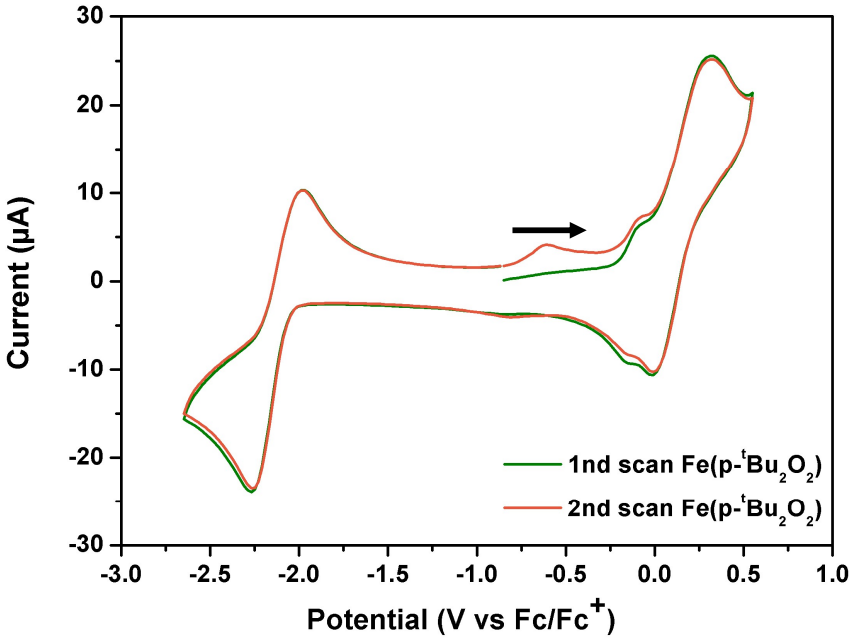


Figure S30b: The Cyclic voltammogram (two scans) of (**2-Fe**) measured anodically with a scan rate of 200 mV/s; 5 mg of (**2-Fe**) (2.7 mM) and 121 mg of $TBAPF_6$ (0.1M) in 3 ml of 1,2-difluorobenzene.

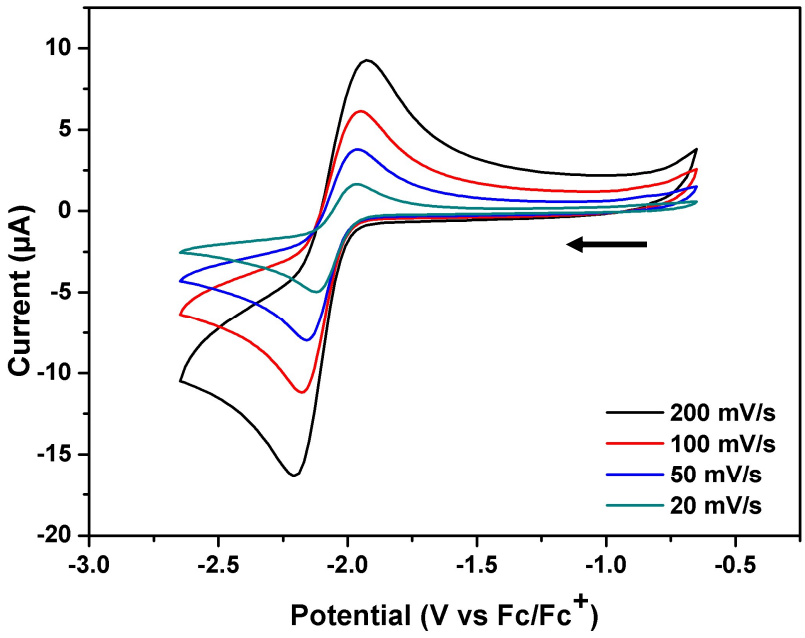


Figure S30c: Overlayed CV's (one scan/CV) with different scan rates of the process at $E_{1/2}$ = -2.13 V *vs* Fc^+/Fc. Data have been collected both anodically and cathodically with no effect on the position of the peaks, their separation or current responses. A slight decrease of the current responses compared to Figures S30a and S30b is

probably due to some partial sample decomposition during measurement. Conditions: 5 mg of (**2-Fe**) (*ca* 2.7 mM) and 121 mg of $TBAPF_6$ (*ca* 0.1M) in 3 ml of 1,2-difluorobenzene.

			Wave 1			
$i_{pa,1}$ (µA)	$i_{pc,1}$(µA)	$\lvert i_{pa,1}/i_{pc,1}\rvert$	$E_{pa,1}$(V)	$E_{pc,1}$(V)	$E_{1/2}$(V)	$\lvert E_{pa,1}\text{-}E_{pc,1}\rvert$(V)
12.54	-20.81	0.60	-2.00	-2.27	-2.13	0.26
			Wave 2			
$i_{pa,2}$ (µA)	$i_{pc,2}$(µA)	$\lvert i_{pa,2}/i_{pc,2}\rvert$	$E_{pa,2}$(V)	$E_{pc,2}$(V)	$E_{1/2}$(V)	$\lvert E_{pa.2}\text{-}E_{pc,2}\rvert$(V)
16.32	-10.73	1.52	+0.29	+0.030	0.16	0.26

Table S3a: Parameters derived from the cyclic voltammogram of (**2-Fe**) in Figure S30b (200 mV/s scan rate); Wave 1 corresponds to the process at $E_{1/2}$ = -2.13 V and Wave 2 to the process at $E_{1/2}$ = 0.16 V.

Scan Rate	$i_{pc,1}$ (µA)	$i_{pa,1}$(µA)	$\lvert i_{pc,1}/i_{pa,1}\rvert$	$E_{pc,1}$(V)	$E_{pa,1}$(V)	$E_{1/2}$(V)	$\lvert E_{pa,1}\text{-}E_{pc,1}\rvert$(V)
200 mV/s	-15,105	10,70	0,71	-2.21	-2,27	-2.13	0,26
100 mV/s	-10,53	7,59	0,72	-1,96	-2,18	-2.07	0,22
50 mV/s	-7,44	5,13	0,69	-1,97	-2,16	-2.06	0,19
20 mV/s	-4,56	2,80	0,61	-1,97	-2,12	-2.04	0,15

Table S3b: Scan rate dependence of the wave characteristics corresponding to the process at $E_{1/2}$ = -2.13 V.

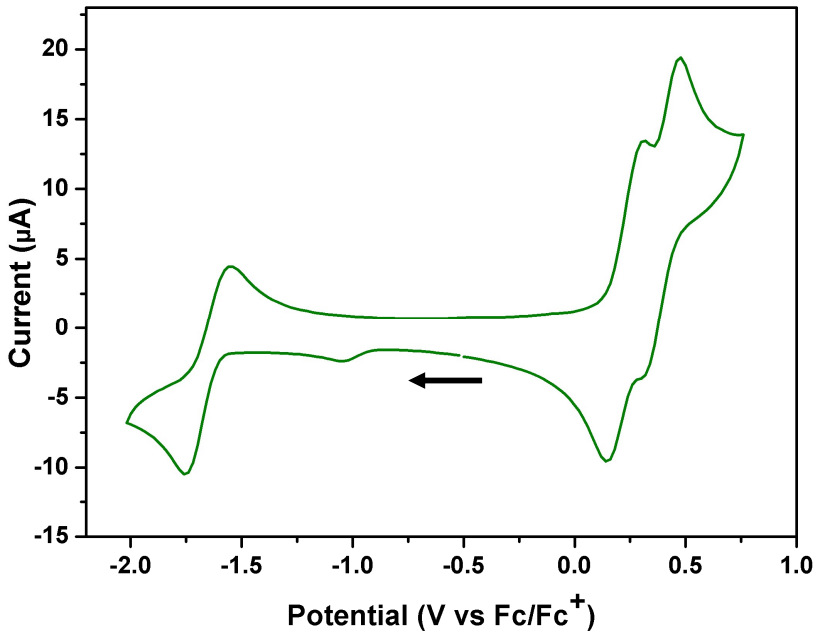


Figure S31a: The CV (one scan) of **(2-Co)** measured cathodically with a scan rate of 200 mV/s; Conditions: 5 mg of (**2-Co**) (1.5 mM) and 121 mg of $TBAPF_6$ (0.06 M) in 5 ml of 1,2-difluorobenzene.

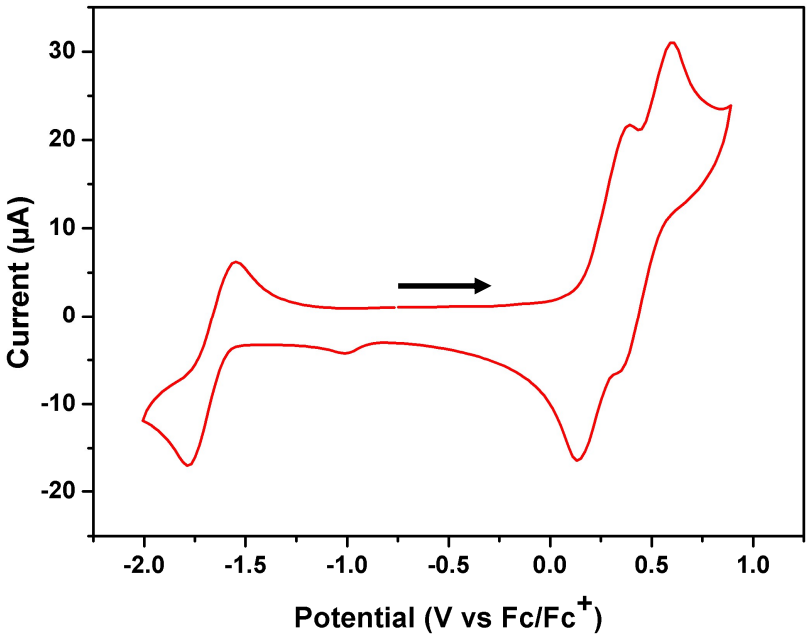


Figure 31b: The CV (1 scan) of **(2-Co)** measured anodically with a scan rate of 200 mV/s; Conditions: 5 mg of (**2-Co**) (1.5 mM) and 121 mg of $TBAPF_6$ (0.06 M) in 5 ml of 1,2-difluorobenzene.

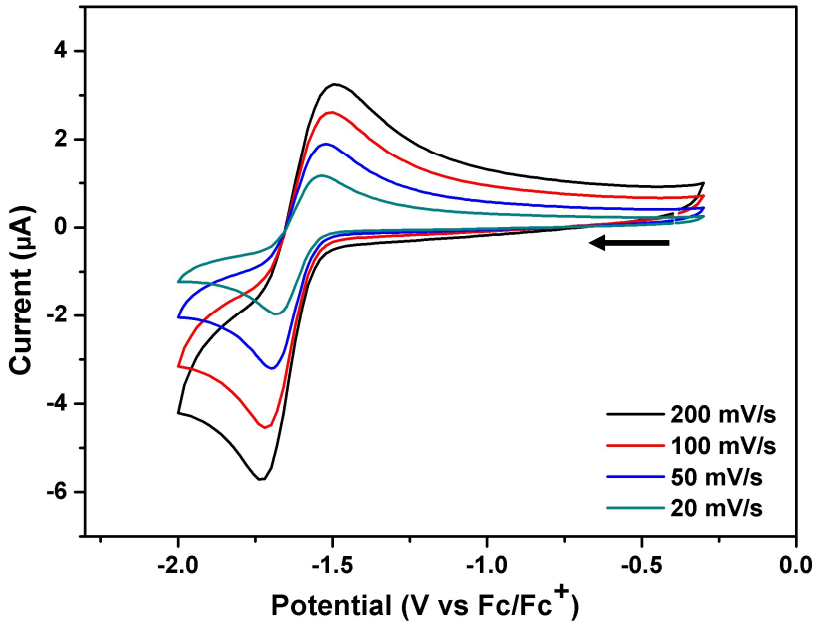


Figure 31c: Overlayed CV's (2^{nd} scan) with different scan rates at $E_{1/2}$ = -1.67 V *vs* Fc^+/Fc. Data have been collected both anodically and cathodically with no effect on the position of the peaks, their separation or current responses. The slight decrease

in the current responses (Table S4b) during these scan-rate dependence studies is due to some partial sample decomposition during the experiment. Conditions: 5 mg of (**2-Co**) (1.5 mM) and 121 mg of $TBAPF_6$ (0.06 M) in 5 ml of 1,2-difluorobenzene.

$i_{pa,1}$ (µA)	$i_{pc,1}$(µA)	$\lvert i_{pc,1}/i_{p1,1}\rvert$	$E_{pa,1}$(V)	$E_{pc,1}$(V)	$E_{1/2}$(V)	$\lvert E_{pa,1}$-$E_{pc,1}\rvert$(V)
9.106(1)	-12.84	1.41	-1.57	-1.77	-1.67	0,20

Table S4a: Parameters of process at $E_{1/2}$ = -1.67 V *vs* Fc^+/Fc (scan rate 200 $mV.s^{-1}$) derived from the CV in Figure 31b.

Scan Rate	$i_{pc,1}$ (µA)	$i_{pa,1}$(µA)	$\lvert i_{pc,1}/i_{pa,1}\rvert$	$E_{pc,1}$(V)	$E_{pa,1}$(V)	$E_{1/2}$(V)	$\lvert E_{pa,1}$- $E_{pc,1}\rvert$(V)
200 mV/s	-4.59	3.53	1.29	-1.77	-1.57	-1.67	0.2
100 mV/s	-3.93	3.03	1.29	-1.72	-1.52	-1.62	0.2
50 mV/s	-2.95	2.29	1.29	-1.69	-1.54	-1.62	0.16
20 mV/s	-1.83	1.47	1.24	-1.68	-1.54	-1.61	0.14

Table S4b: Scan rate dependence of the wave corresponding to the process at $E_{1/2}$ = -1.67 V.

NOTE: There are two more processes but they have current responses very close to each other to be able to deconvolute which one belongs to which. The irreversible process at *ca* -1.0 V that does not have an oxidation current response has no effect on the other processes observed in the CV of (**2-Co**) when studied in isolation from this peak.

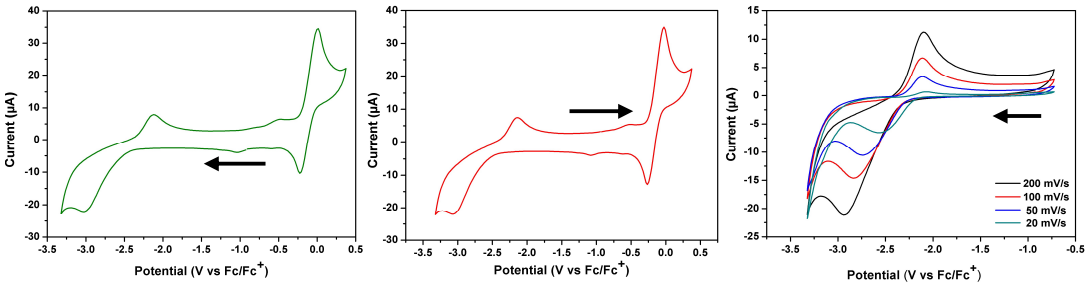


Figure 32a: *left*) The Cyclic voltammogram (2nd scan) of **(2-Fe.THF)** complex measured cathodically with a scan rate of 200 mV/s; *middle*) The Cyclic voltammogram(1st scan) of **(2-Fe.THF)** complex measured anodically with a scan rate of 200 mV/s; *right*) Scan rate dependence (2nd scans) of the reduction event at -2.61 V *vs* Fc^+/Fc **(2-Fe.THF)**; Conditions: 5 mg of **(2-Fe)** (2.67 mM (**2-Fe.THF**)) and 193 mg of $TBAPF_6$ (0.17M) in 3 ml of THF.

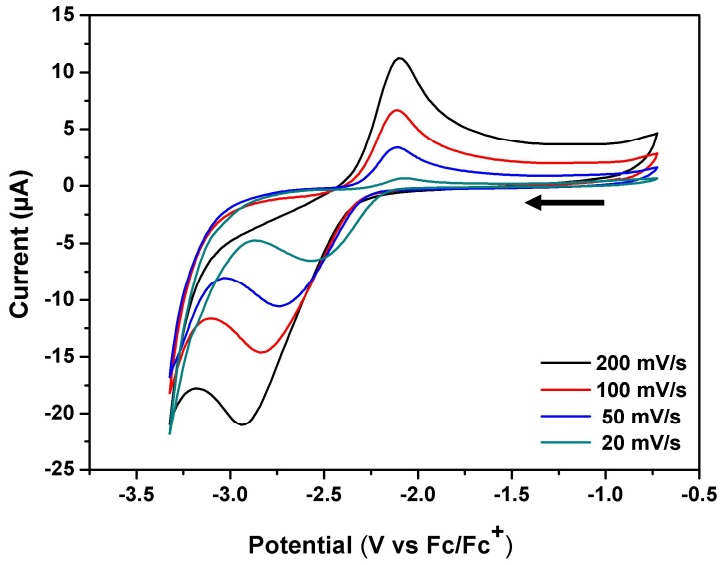


Figure S32b: Expanded picture of the scan rate dependence of the process at *ca* -2.61 V *vs* Fc^+/Fc observed for complex (**2-Fe.THF**).

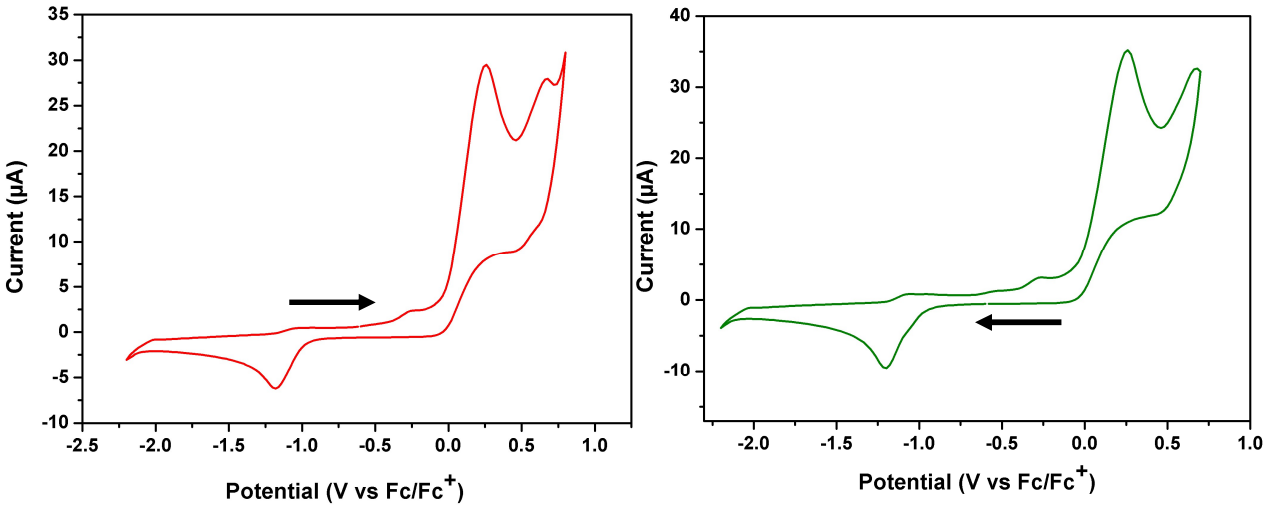


Figure S33: *left*) The Cyclic voltammogram (1st scan) of (**2-Co.THF**) complex measured anodically with a scan rate of 200 mV/s; *right*) The Cyclic voltammogram (2nd scan) of (**2-Co.THF**) complex measured cathodically with a scan rate of 200 mV/s; Conditions used: 5 mg of (**2-Co**) (2.66 mM (**2-Co**) and 193 mg of $TBAPF_6$ (0.17M) in 3 ml of THF.

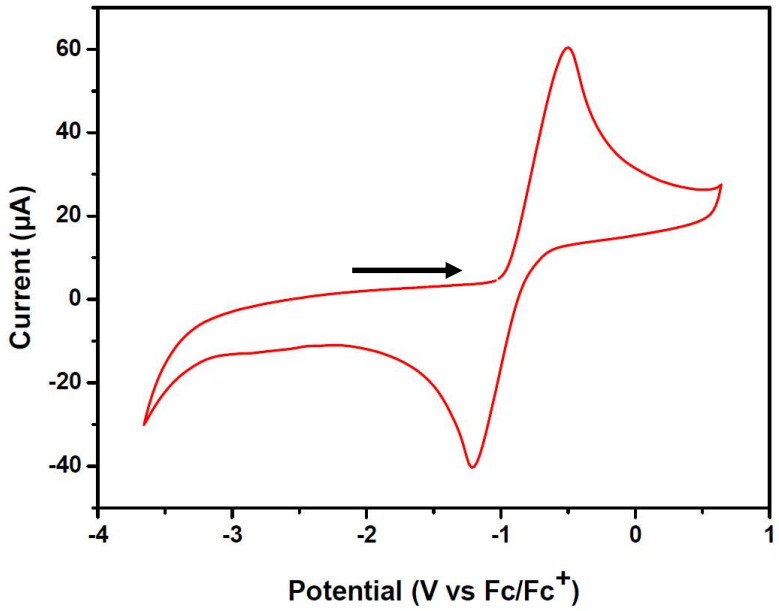


Figure S34: The Cyclic voltammogram (2nd scan) of **(2-K$_2$)** salt measured anodically with a scan rate of 200 mV/s. Conditions: 5 mg of **(2-K$_2$)** (*ca* 7.7 mM) and 193 mg of $TBAPF_6$ (0.17 M) in 3 ml of THF.

i_{pc} (µA)	i_{pa}(µA)	$\lvert i_{pc}/i_{pa} \rvert$	E_{pc}(V)	E_{pa}(V)	$E_{1/2}$(V)	$\lvert E_{pa}-E_{pc} \rvert$(V)
0.055(1)	0.05	1.10	-0.50	-1.22	-0.86	0.72

Table S6: Key parameters of the process observed at $E_{1/2}$ = -0.858 V *vs* Fc^+/Fc for the (**2-K$_2$**) salt.

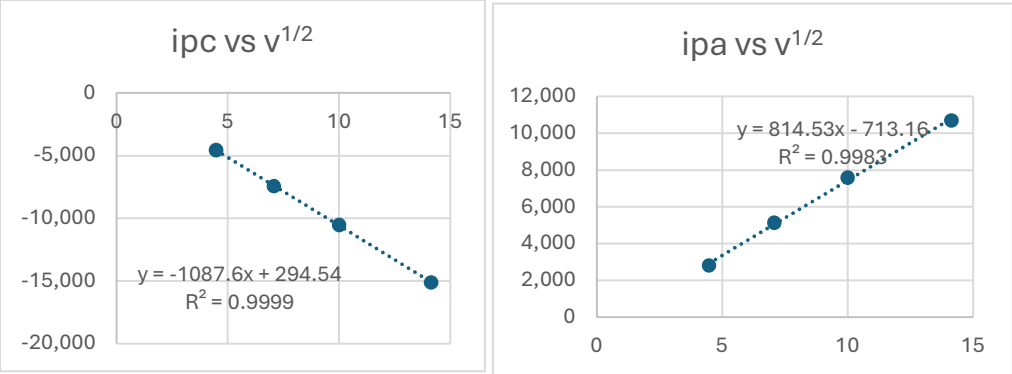


Figure S35: Plots of i_{pa} and i_{pc} *vs* $v^{1/2}$ for the process at $E_{1/2}$ = -2.13 V in (**2-Fe**)

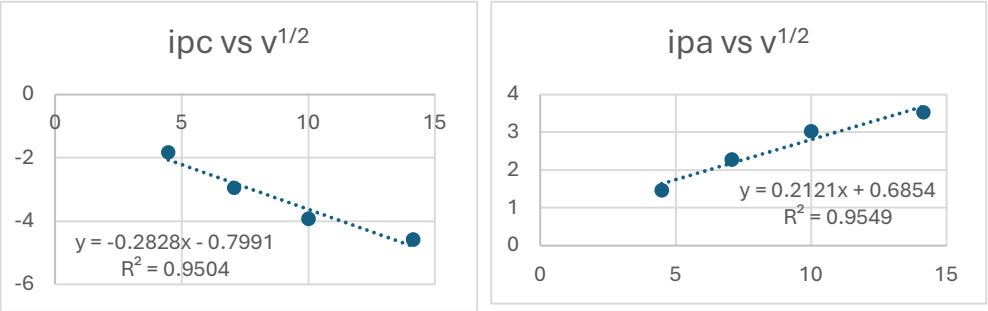


Figure S36: Plots of i_{pa} and i_{pc} *vs* $v^{1/2}$ for the process at $E_{1/2}$ = -1.67 V in (**2-Co**)

Quantum Chemical Calculations

All DFT calculations were carried out using Gaussian 09 software package.[16] Optimizations, frequency calculations and population analyses were performed using the B3PW91 functional.[17,18] Fe, Co and Ni atoms were treated with a Stuttgart effective core potential [19,20]and the associated basis set. The 6-31G** basis set [21,22] was employed for C, O and H atoms.

(2-Fe) (S = 2)

Fe	21.117451000	7.026140000	7.378588000
O	20.494449000	5.642669000	8.449474000
O	21.411616000	8.859486000	7.448252000
C	22.791489000	9.789390000	5.721637000
C	21.966704000	9.077220000	4.634388000
C	18.433736000	4.566149000	9.025375000
C	23.857015000	10.619077000	5.376790000
H	24.136495000	10.702250000	4.331789000
C	21.542657000	4.920741000	5.962315000
C	24.172662000	11.238002000	7.652595000
H	24.704060000	11.808368000	8.402770000
C	22.781095000	5.587939000	6.002263000
H	23.636014000	5.117706000	6.475304000
C	24.576190000	11.355187000	6.322146000
C	19.947191000	3.578523000	7.360324000
C	22.424359000	9.666443000	7.091174000
C	18.077217000	5.656258000	10.053206000
C	17.843619000	2.451714000	7.902559000
C	19.640802000	4.620936000	8.273535000
C	19.040331000	2.526887000	7.193413000
H	19.283331000	1.740647000	6.489719000
C	21.301277000	3.565665000	6.627945000
C	22.720168000	10.360986000	9.560924000
C	21.821601000	7.595268000	4.982164000
C	20.614264000	6.886099000	4.836895000
H	19.744803000	7.375191000	4.411711000
C	23.116870000	10.420765000	8.073896000
C	25.746120000	12.242688000	5.874913000
C	17.579964000	3.483750000	8.810599000
H	16.658257000	3.437867000	9.379743000
C	22.630187000	9.130639000	3.242095000
H	22.688891000	10.158228000	2.870495000
H	22.030244000	8.556378000	2.528626000
H	23.639061000	8.706449000	3.250986000
C	20.484560000	5.574067000	5.305370000
H	19.518181000	5.080751000	5.250100000
C	16.841983000	1.301045000	7.733323000
C	21.367842000	2.513903000	5.500260000
H	20.568496000	2.647135000	4.764710000

H	21.302971000	1.498204000	5.901714000
H	22.325243000	2.599959000	4.976064000
C	22.918046000	6.890981000	5.511110000
H	23.866039000	7.408504000	5.627975000
C	20.601969000	9.787810000	4.537297000
H	20.048498000	9.703549000	5.475755000
H	19.988942000	9.393670000	3.718553000
H	20.771658000	10.849160000	4.336367000
C	22.393203000	3.220142000	7.660189000
H	23.379931000	3.108881000	7.195671000
H	22.143950000	2.264061000	8.128605000
H	22.447694000	3.977615000	8.446020000
C	19.176521000	5.749421000	11.131189000
H	19.258158000	4.803042000	11.677151000
H	18.927411000	6.534700000	11.854919000
H	20.147785000	5.975970000	10.690228000
C	26.822883000	11.371737000	5.197590000
H	27.210743000	10.619875000	5.893177000
H	27.663985000	11.989434000	4.860797000
H	26.427708000	10.844837000	4.323225000
C	16.755637000	5.359750000	10.781182000
H	15.900910000	5.329137000	10.096492000
H	16.562236000	6.154551000	11.509415000
H	16.792477000	4.413419000	11.331474000
C	25.242346000	13.299244000	4.872013000
H	24.800228000	12.838675000	3.983021000
H	26.068434000	13.938620000	4.538656000
H	24.480101000	13.938167000	5.330036000
C	17.903249000	7.018625000	9.352192000
H	18.825043000	7.344311000	8.866221000
H	17.622181000	7.787226000	10.081711000
H	17.113391000	6.967905000	8.594491000
C	21.246267000	10.782494000	9.731919000
H	21.102417000	11.815411000	9.396025000
H	20.959280000	10.729736000	10.789070000
H	20.579852000	10.138803000	9.156758000
C	26.402856000	12.980028000	7.050111000
H	25.697938000	13.646026000	7.559051000
H	27.231132000	13.595673000	6.683016000
H	26.812251000	12.284026000	7.790068000
C	22.934113000	8.939547000	10.118779000
H	22.313722000	8.204838000	9.602125000
H	22.672796000	8.906611000	11.183084000
H	23.982446000	8.636823000	10.019210000
C	16.666008000	0.568787000	9.078371000
H	17.618615000	0.153547000	9.423638000
H	15.950376000	-0.255839000	8.977414000
H	16.293347000	1.238846000	9.859065000
C	23.564322000	11.309948000	10.427982000
H	24.628360000	11.049176000	10.416673000

H	23.223254000	11.243273000	11.466620000
H	23.461179000	12.354636000	10.115530000
C	15.480071000	1.861746000	7.278183000
H	15.073210000	2.575907000	8.000402000
H	14.749668000	1.052141000	7.162931000
H	15.571808000	2.376909000	6.316042000
C	17.304439000	0.274712000	6.689883000
H	17.424484000	0.726898000	5.699267000
H	16.559384000	-0.523016000	6.599169000
H	18.254214000	-0.193123000	6.970969000

(2-Co) (S = 3/2)

Co	9.375231000	4.025579000	11.264079000
O	9.311024000	2.151524000	11.090620000
O	9.851957000	5.268407000	9.932854000
C	6.468109000	-0.115985000	10.706332000
H	5.956105000	-0.658443000	9.922676000
C	5.989116000	-0.231367000	12.011936000
C	7.796241000	1.258215000	12.720111000
C	6.684844000	0.466912000	13.002588000
H	6.348856000	0.383160000	14.031119000
C	8.055944000	0.711523000	8.887054000
C	8.243457000	1.387952000	11.372133000
C	4.764753000	-1.077445000	12.386557000
C	9.082387000	6.077878000	12.497322000
C	8.759965000	3.417731000	13.520809000
C	7.573898000	0.664982000	10.348542000
C	8.587350000	1.936931000	13.853533000
C	9.356705000	7.399898000	11.783669000
C	10.811461000	6.199917000	10.046393000
C	10.144438000	5.400137000	13.129295000
H	11.127180000	5.862595000	13.138833000
C	10.659033000	7.273143000	10.972683000
C	7.826011000	5.438435000	12.490904000
H	6.977777000	5.919433000	12.017249000
C	11.963458000	6.161133000	9.215636000
C	7.669083000	4.140033000	12.996712000
H	6.711374000	3.638372000	12.892758000
C	11.661728000	8.234679000	11.081759000
H	11.537890000	9.042597000	11.795930000
C	12.146202000	5.065339000	8.149793000
C	9.990119000	4.098125000	13.625705000
H	10.858973000	3.585013000	14.022037000
C	7.956850000	2.145201000	8.329056000
H	6.929164000	2.519742000	8.398367000
H	8.247886000	2.159757000	7.272156000
H	8.616309000	2.832918000	8.860327000
C	8.223546000	7.785094000	10.812729000
H	8.082914000	7.015484000	10.049746000

H	8.496457000	8.716259000	10.308860000
H	7.275133000	7.961040000	11.334359000
C	3.688606000	-0.173778000	13.020608000
H	4.057464000	0.323799000	13.923224000
H	2.806924000	-0.761677000	13.302322000
H	3.368763000	0.603253000	12.318115000
C	12.818766000	8.204799000	10.298634000
C	9.938530000	1.211124000	13.997576000
H	9.748053000	0.152905000	14.195743000
H	10.528772000	1.600529000	14.835613000
H	10.519518000	1.286207000	13.075273000
C	9.512871000	0.212819000	8.802370000
H	10.173729000	0.821478000	9.420806000
H	9.866059000	0.254533000	7.765000000
H	9.582467000	-0.827436000	9.139627000
C	5.175237000	-2.164595000	13.399633000
H	5.935706000	-2.827104000	12.973252000
H	4.309583000	-2.775960000	13.681359000
H	5.587327000	-1.731940000	14.316673000
C	7.866348000	1.879351000	15.216528000
H	6.866904000	2.323570000	15.175851000
H	8.448619000	2.427717000	15.964339000
H	7.771063000	0.846774000	15.565396000
C	12.926910000	7.164335000	9.374902000
H	13.805755000	7.127051000	8.745021000
C	12.227786000	3.675682000	8.812400000
H	13.048623000	3.638260000	9.537673000
H	12.415441000	2.906041000	8.054515000
H	11.299217000	3.415496000	9.322506000
C	7.212729000	-0.186510000	7.966635000
H	7.244997000	-1.237900000	8.272232000
H	7.612351000	-0.129262000	6.948545000
H	6.164260000	0.128993000	7.923842000
C	10.970630000	5.106583000	7.152368000
H	10.016614000	4.965221000	7.661814000
H	11.086268000	4.317645000	6.399365000
H	10.945536000	6.069225000	6.629416000
C	4.141304000	-1.775321000	11.169663000
H	3.795843000	-1.055597000	10.419889000
H	3.273753000	-2.364238000	11.486485000
H	4.846215000	-2.460730000	10.687253000
C	9.428200000	8.479047000	12.883969000
H	8.497944000	8.478239000	13.461518000
H	9.544347000	9.475767000	12.448191000
H	10.256401000	8.307504000	13.578606000
C	13.438495000	5.251794000	7.337477000
H	13.457687000	6.209284000	6.805693000
H	13.504503000	4.458749000	6.584986000
H	14.336551000	5.185074000	7.961726000
C	13.890574000	9.290346000	10.467742000

C	13.278710000	10.673181000	10.167919000
H	12.899306000	10.716732000	9.141695000
H	14.030450000	11.462484000	10.287555000
H	12.446162000	10.903513000	10.840251000
C	15.083287000	9.084910000	9.523399000
H	15.583977000	8.126999000	9.700491000
H	14.781282000	9.123360000	8.471391000
H	15.821917000	9.877931000	9.682971000
C	14.420697000	9.273144000	11.915166000
H	13.622917000	9.457756000	12.641562000
H	15.183599000	10.048007000	12.056082000
H	14.872206000	8.304330000	12.154037000

(2-Co) (S = 1/2)

Co	9.242027000	4.237026000	11.730244000
O	9.051334000	2.571581000	10.932694000
O	10.052308000	4.927475000	10.209745000
C	6.391063000	0.108666000	10.610508000
H	5.846317000	-0.385353000	9.817170000
C	6.072077000	-0.208550000	11.931794000
C	7.801233000	1.374463000	12.642164000
C	6.800082000	0.446836000	12.926747000
H	6.581953000	0.218003000	13.964724000
C	7.656046000	1.328276000	8.764034000
C	8.096649000	1.698096000	11.283064000
C	4.986950000	-1.224568000	12.314466000
C	9.021966000	6.124863000	12.555032000
C	8.751464000	3.478137000	13.593507000
C	7.369957000	1.039482000	10.248938000
C	8.637329000	1.969494000	13.790998000
C	9.311796000	7.359400000	11.705592000
C	10.909846000	5.957139000	10.243987000
C	10.097939000	5.483013000	13.232779000
H	11.083099000	5.935934000	13.176536000
C	10.651409000	7.158626000	10.971038000
C	7.744669000	5.513374000	12.623097000
H	6.891848000	5.972055000	12.137516000
C	12.116835000	5.857040000	9.492516000
C	7.623062000	4.201971000	13.112493000
H	6.691911000	3.663421000	12.965123000
C	11.589934000	8.189596000	10.952016000
H	11.383987000	9.092487000	11.517423000
C	12.441287000	4.598172000	8.667429000
C	9.964652000	4.191209000	13.767230000
H	10.846604000	3.687299000	14.143654000
C	7.391058000	2.815067000	8.449103000
H	6.346469000	3.073143000	8.661283000
H	7.572045000	3.009668000	7.385152000
H	8.043349000	3.467413000	9.030852000

C	8.220226000	7.590255000	10.641743000
H	8.123114000	6.721847000	9.985515000
H	8.508164000	8.447554000	10.027396000
H	7.245706000	7.820345000	11.088434000
C	3.907610000	-0.532391000	13.170378000
H	4.326546000	-0.110849000	14.089707000
H	3.127137000	-1.246629000	13.458415000
H	3.433259000	0.283794000	12.615075000
C	12.781475000	8.113332000	10.227963000
C	10.018621000	1.283781000	13.770115000
H	9.872072000	0.203694000	13.855239000
H	10.650590000	1.594933000	14.610362000
H	10.541720000	1.479630000	12.830554000
C	9.118373000	0.970534000	8.430671000
H	9.812393000	1.561347000	9.028643000
H	9.319476000	1.163160000	7.370073000
H	9.306627000	-0.092349000	8.621038000
C	5.618614000	-2.372733000	13.126415000
H	6.384779000	-2.889511000	12.539124000
H	4.856385000	-3.106625000	13.414202000
H	6.092064000	-2.008565000	14.043633000
C	8.011015000	1.757573000	15.184395000
H	6.989830000	2.147581000	15.240919000
H	8.613272000	2.273059000	15.940050000
H	7.990638000	0.697204000	15.451163000
C	13.002999000	6.938407000	9.507812000
H	13.915081000	6.852398000	8.932744000
C	12.528025000	3.364004000	9.588605000
H	13.306415000	3.504171000	10.348333000
H	12.792365000	2.476673000	9.000911000
H	11.576747000	3.172902000	10.086332000
C	6.760818000	0.500005000	7.827487000
H	6.914282000	-0.577679000	7.952335000
H	7.008251000	0.746382000	6.789541000
H	5.696115000	0.716718000	7.969710000
C	11.355672000	4.379973000	7.594451000
H	10.375763000	4.240989000	8.051566000
H	11.591469000	3.491369000	6.996753000
H	11.308737000	5.239083000	6.915446000
C	4.300038000	-1.834079000	11.084942000
H	3.802934000	-1.071448000	10.476276000
H	3.536573000	-2.551033000	11.405784000
H	5.009977000	-2.371412000	10.447351000
C	9.312739000	8.562237000	12.671254000
H	8.363227000	8.597442000	13.215957000
H	9.411936000	9.505525000	12.126723000
H	10.122059000	8.500812000	13.405727000
C	13.788540000	4.713908000	7.935090000
H	13.804188000	5.547339000	7.224000000
H	13.962608000	3.795542000	7.364347000

H	14.630413000	4.833103000	8.626464000
C	13.774497000	9.283449000	10.250976000
C	13.085406000	10.560343000	9.729918000
H	12.736043000	10.422731000	8.701350000
H	13.782605000	11.406581000	9.743128000
H	12.219989000	10.835754000	10.341069000
C	15.006097000	9.019469000	9.374144000
H	15.568197000	8.142932000	9.713428000
H	14.732256000	8.864898000	8.325122000
H	15.681485000	9.880851000	9.415888000
C	14.257403000	9.521572000	11.695510000
H	13.425457000	9.757305000	12.366770000
H	14.963822000	10.359368000	11.733899000
H	14.762199000	8.632881000	12.089104000

(2-Ni) (S = 0)

C	5.639841000	5.880171000	4.332414000
C	5.068370000	4.920492000	3.460083000
H	5.515402000	4.714041000	2.495218000
C	5.077669000	6.023488000	5.635119000
H	5.550882000	6.718072000	6.322872000
C	3.859318000	5.430089000	5.973214000
H	3.411455000	5.635835000	6.937685000
C	3.123766000	4.762041000	4.962525000
C	3.800238000	4.414691000	3.756542000
H	3.252337000	3.852685000	3.006047000
C	6.808637000	6.778185000	3.931718000
C	8.079784000	6.125470000	4.511842000
H	8.976643000	6.666233000	4.196391000
H	8.168610000	5.098550000	4.141715000
H	8.064943000	6.090755000	5.605756000
C	6.963550000	6.868327000	2.400468000
H	7.771006000	7.569511000	2.172631000
H	6.046863000	7.243362000	1.939221000
H	7.232633000	5.904475000	1.952689000
C	6.547475000	8.196864000	4.467720000
C	7.547006000	8.877216000	5.167502000
H	8.478310000	8.364515000	5.374152000
C	7.389844000	10.193296000	5.597820000
C	6.171374000	10.812895000	5.297494000
H	6.031678000	11.839284000	5.617300000
C	5.122401000	10.189257000	4.622310000
C	5.305374000	8.838831000	4.192317000
C	8.477795000	10.964609000	6.356175000
C	7.925917000	11.445095000	7.712987000
H	7.613536000	10.596536000	8.330949000
H	7.060180000	12.102782000	7.589918000
H	8.692177000	12.003842000	8.263313000
C	9.721207000	10.105873000	6.626693000

H	10.190940000	9.763768000	5.698149000
H	9.484999000	9.226669000	7.236349000
H	2.058373000	8.790628000	0.236358000
H	2.321580000	7.045362000	0.099827000
H	2.648035000	7.881425000	1.637042000
C	0.520104000	7.595005000	1.203666000
C	0.047210000	8.726609000	2.138125000
H	0.123484000	9.693228000	1.625967000
H	0.652991000	8.763772000	3.043484000
H	-1.000849000	8.578216000	2.422644000
C	-0.343750000	7.661421000	-0.066320000
H	-0.218000000	8.645557000	-0.530091000
H	-1.410989000	7.536736000	0.148426000
H	-0.050548000	6.911188000	-0.809397000
C	0.400999000	6.240204000	1.922349000
C	1.115666000	5.973898000	3.125799000
C	0.945343000	4.703947000	3.757654000
C	0.110321000	3.749830000	3.182817000
H	-0.000586000	2.787465000	3.672279000
C	-0.600207000	3.987748000	2.002305000
C	-0.434752000	5.240615000	1.411048000
H	-0.976664000	5.452729000	0.499084000
C	-2.193084000	3.339627000	0.119642000
H	-1.465272000	3.581733000	-0.662116000
H	-2.832874000	4.214884000	0.273741000
H	-2.826705000	2.530115000	-0.258541000
C	-1.507683000	2.896417000	1.419594000
C	-0.671303000	1.638238000	1.112093000
H	-0.189852000	1.240595000	2.011124000
H	0.114709000	1.861178000	0.382747000
H	-1.305247000	0.845655000	0.697147000
C	-2.605033000	2.538617000	2.441749000
H	-2.180611000	2.170020000	3.381028000
H	-3.262668000	1.756242000	2.044455000
H	-3.219722000	3.414032000	2.675841000
C	1.568561000	2.943786000	5.532843000
H	0.536681000	2.645477000	5.739540000
H	2.141953000	2.801423000	6.454958000
H	1.977617000	2.269768000	4.773475000
C	1.640578000	4.422485000	5.101020000
C	0.957274000	5.280655000	6.184347000
H	-0.111523000	5.050120000	6.190615000
H	1.075656000	6.344657000	5.966706000
H	1.343386000	5.066245000	7.187834000
O	4.334617000	8.233073000	3.495133000
O	1.881128000	6.929993000	3.669415000
Ni	3.667351000	6.590416000	4.043695000

(2-Co.THF) (S = 3/2)

Co	8.872751000	4.287416000	10.939227000
O	9.206900000	2.415416000	11.132805000
O	9.726012000	5.577661000	9.855303000
C	6.675001000	-0.205903000	10.829212000
H	6.244326000	-0.841046000	10.065968000
C	6.148303000	-0.270260000	12.119720000
C	7.867917000	1.333857000	12.813507000
C	6.800405000	0.484892000	13.099673000
H	6.470477000	0.392983000	14.129599000
C	8.368157000	0.514457000	9.061791000
C	8.283885000	1.500772000	11.454759000
C	4.953227000	-1.155470000	12.497608000
C	9.332235000	6.079290000	12.700364000
C	8.928270000	3.434836000	13.690984000
C	7.742947000	0.626515000	10.467246000
C	8.690643000	1.954825000	13.962805000
C	9.615838000	7.445615000	12.073458000
C	10.790234000	6.368176000	10.051918000
C	10.394295000	5.315520000	13.217496000
H	11.401947000	5.717631000	13.158146000
C	10.813280000	7.320117000	11.114924000
C	8.039174000	5.537837000	12.820220000
H	7.179030000	6.112627000	12.493493000
C	11.898948000	6.306260000	9.160872000
C	7.845309000	4.239023000	13.316296000
H	6.843429000	3.817871000	13.330334000
C	11.916270000	8.160325000	11.257626000
H	11.921178000	8.881697000	12.067775000
C	11.940401000	5.299697000	7.995824000
C	10.196504000	4.031032000	13.710609000

H	11.061513000	3.456628000	14.021851000
C	8.195349000	1.808798000	8.248521000
H	7.133077000	2.045045000	8.118037000
H	8.635797000	1.690207000	7.251168000
H	8.686438000	2.651841000	8.735090000
C	8.412125000	8.008377000	11.294439000
H	8.111720000	7.332754000	10.491875000
H	8.698846000	8.963390000	10.845201000
H	7.552903000	8.197226000	11.948989000
C	3.831397000	-0.278480000	13.088345000
H	4.168523000	0.264934000	13.976701000
H	2.971105000	-0.892846000	13.379904000
H	3.487754000	0.460067000	12.355825000
C	13.017471000	8.117886000	10.399820000
C	10.012507000	1.165473000	14.038984000
H	9.787227000	0.105934000	14.189213000
H	10.636377000	1.494340000	14.878607000
H	10.580216000	1.266856000	13.110516000
C	9.870903000	0.195318000	9.205580000
H	10.384187000	0.976663000	9.768159000
H	10.335989000	0.113198000	8.215746000
H	10.011711000	-0.759084000	9.724664000
C	5.386192000	-2.197672000	13.547913000
H	6.182068000	-2.838789000	13.154799000
H	4.540757000	-2.836932000	13.829480000
H	5.760987000	-1.723361000	14.460193000
C	7.995983000	1.847765000	15.335780000
H	7.006925000	2.316753000	15.336349000
H	8.606404000	2.352910000	16.091208000
H	7.883374000	0.804661000	15.647121000
C	12.971065000	7.181632000	9.367260000

H	13.809225000	7.126182000	8.685859000
C	11.927901000	3.860318000	8.546357000
H	12.806932000	3.682220000	9.175742000
H	11.952458000	3.136983000	7.722455000
H	11.037204000	3.662044000	9.143397000
C	7.740157000	-0.620703000	8.235429000
H	7.832233000	-1.591709000	8.733236000
H	8.260610000	-0.692650000	7.274308000
H	6.680407000	-0.444087000	8.018552000
C	10.740691000	5.520158000	7.052561000
H	9.798597000	5.406787000	7.588731000
H	10.770096000	4.795891000	6.229235000
H	10.773839000	6.525650000	6.617696000
C	4.379871000	-1.910520000	11.290408000
H	4.035832000	-1.225905000	10.507577000
H	3.520735000	-2.512836000	11.605117000
H	5.114692000	-2.592205000	10.849050000
C	9.880670000	8.407585000	13.251559000
H	9.012713000	8.410270000	13.919157000
H	10.031417000	9.433315000	12.900295000
H	10.753389000	8.112065000	13.841513000
C	13.211791000	5.440111000	7.141120000
H	13.295926000	6.431989000	6.683536000
H	13.177539000	4.705916000	6.328848000
H	14.123930000	5.246517000	7.716158000
C	14.198739000	9.073529000	10.617789000
C	13.710826000	10.532161000	10.513290000
H	13.287983000	10.731598000	9.523011000
H	14.541182000	11.229713000	10.676524000
H	12.938270000	10.755796000	11.255745000
C	15.313091000	8.871219000	9.581901000

H	15.727374000	7.858183000	9.621912000
H	14.959009000	9.056025000	8.562119000
H	16.132444000	9.571291000	9.778423000
C	14.802179000	8.840392000	12.017202000
H	14.068210000	9.013972000	12.810548000
H	15.646028000	9.518693000	12.191654000
H	15.165482000	7.812199000	12.118018000
H	7.245045000	4.553616000	7.887549000
O	6.984391000	4.537336000	9.947929000
C	5.750547000	3.879934000	10.324343000
C	4.792041000	4.106822000	9.157660000
C	5.335570000	5.388902000	8.518688000
C	6.835743000	5.200332000	8.672166000
H	5.962470000	2.825818000	10.521974000
H	5.388299000	4.353869000	11.244447000
H	3.754127000	4.193149000	9.489528000
H	4.850440000	3.275252000	8.447539000
H	5.000565000	6.271963000	9.074333000
H	5.036844000	5.508912000	7.474014000
H	7.421313000	6.119314000	8.709886000

(2-Co.THF) (S = ½)

Co	9.587727000	4.021355000	11.613013000
O	9.550268000	2.310450000	10.884432000
O	10.524752000	4.676128000	10.150342000
C	7.024455000	-0.272131000	10.437615000
H	6.575491000	-0.824284000	9.622749000
C	6.594002000	-0.540227000	11.738014000
C	8.193197000	1.140145000	12.526578000
C	7.203972000	0.186567000	12.762536000

H	6.900249000	-0.006688000	13.786306000
C	8.423950000	0.903193000	8.659613000
C	8.602108000	1.414257000	11.185967000
C	5.515238000	-1.580405000	12.070692000
C	9.206235000	5.929213000	12.317239000
C	8.963271000	3.324891000	13.458419000
C	8.001604000	0.677594000	10.123293000
C	8.897685000	1.821766000	13.715011000
C	9.516627000	7.129717000	11.426012000
C	11.325250000	5.749377000	10.215362000
C	10.245345000	5.372192000	13.117683000
H	11.211173000	5.868123000	13.125545000
C	10.934147000	6.969338000	10.846416000
C	7.950693000	5.268426000	12.311316000
H	7.106540000	5.664727000	11.754214000
C	12.608774000	5.675047000	9.600464000
C	7.850137000	3.976193000	12.852867000
H	6.956413000	3.391102000	12.658336000
C	11.820479000	8.044909000	10.869216000
H	11.513350000	8.962606000	11.360165000
C	13.079325000	4.392107000	8.891522000
C	10.122465000	4.102649000	13.705738000
H	10.988346000	3.661983000	14.184738000
C	8.139030000	2.359410000	8.238820000
H	7.071413000	2.587503000	8.343163000
H	8.409171000	2.503735000	7.185676000
H	8.713092000	3.066193000	8.838679000
C	8.533899000	7.226279000	10.241137000
H	8.584439000	6.325457000	9.624215000
H	8.824586000	8.078365000	9.619927000
H	7.499052000	7.380839000	10.564055000

C	4.341913000	-0.897186000	12.800281000
H	4.665152000	-0.420293000	13.730994000
H	3.566225000	-1.629674000	13.053734000
H	3.888163000	-0.125217000	12.169552000
C	13.085187000	7.995608000	10.278650000
C	10.303918000	1.202736000	13.844068000
H	10.199498000	0.120921000	13.963005000
H	10.844493000	1.578391000	14.720818000
H	10.896659000	1.388668000	12.944809000
C	9.924505000	0.591391000	8.491222000
H	10.531282000	1.234420000	9.128969000
H	10.225927000	0.749331000	7.448660000
H	10.131308000	-0.454193000	8.746931000
C	6.113972000	-2.669643000	12.983029000
H	6.948871000	-3.176583000	12.488148000
H	5.357476000	-3.422952000	13.233871000
H	6.489494000	-2.250486000	13.921881000
C	8.159001000	1.638203000	15.056140000
H	7.122172000	1.985219000	15.005204000
H	8.669486000	2.210364000	15.838099000
H	8.157829000	0.589454000	15.366724000
C	13.437603000	6.800648000	9.649640000
H	14.410991000	6.734901000	9.181740000
C	13.132174000	3.219995000	9.893206000
H	13.829403000	3.442196000	10.710033000
H	13.488070000	2.313194000	9.389185000
H	12.147434000	3.012743000	10.313726000
C	7.657807000	-0.007712000	7.686057000
H	7.831420000	-1.070488000	7.887994000
H	8.003609000	0.191440000	6.666107000
H	6.577446000	0.175821000	7.706705000

C	12.123610000	4.049314000	7.731086000
H	11.110451000	3.881667000	8.096354000
H	12.465621000	3.141806000	7.219199000
H	12.103317000	4.862872000	6.996878000
C	4.958667000	-2.265559000	10.815173000
H	4.490338000	-1.547554000	10.133474000
H	4.195096000	-2.996958000	11.101629000
H	5.738716000	-2.801141000	10.264174000
C	9.347053000	8.385752000	12.303766000
H	8.342403000	8.394538000	12.739307000
H	9.453615000	9.298572000	11.710670000
H	10.072658000	8.418971000	13.122914000
C	14.487045000	4.540031000	8.291193000
H	14.533689000	5.329862000	7.533172000
H	14.764875000	3.600759000	7.801192000
H	15.246439000	4.747402000	9.053592000
C	14.010579000	9.218008000	10.342972000
C	13.326848000	10.421308000	9.663478000
H	13.112779000	10.204572000	8.611733000
H	13.972409000	11.306823000	9.705147000
H	12.380375000	10.677860000	10.149554000
C	15.351722000	8.973550000	9.637370000
H	15.906672000	8.146487000	10.092838000
H	15.217901000	8.750501000	8.573535000
H	15.976809000	9.870138000	9.710489000
C	14.304110000	9.567244000	11.815583000
H	13.387625000	9.795044000	12.369296000
H	14.958558000	10.444679000	11.881836000
H	14.801425000	8.733110000	12.321992000

H	4.699105000	4.577563000	9.805553000
O	5.082453000	6.233286000	10.990751000
C	3.994910000	6.748037000	11.762133000
C	2.726334000	6.171283000	11.140075000
C	3.125853000	6.082319000	9.665267000
C	4.593498000	5.670829000	9.766455000
H	4.138205000	6.456654000	12.808558000
H	3.995505000	7.847238000	11.710750000
H	1.846116000	6.794951000	11.318285000
H	2.523264000	5.171996000	11.541412000
H	3.034089000	7.063652000	9.186246000
H	2.527378000	5.368879000	9.092578000
H	5.206700000	6.042879000	8.939063000

(2-Fe.THF) (S = 2)

C	17.515023000	6.689633000	6.145085000
O	18.563935000	7.640100000	6.412875000
C	18.058642000	8.949464000	6.115633000
C	16.626849000	8.904413000	6.624808000
C	16.190129000	7.468059000	6.276923000
Fe	20.673470000	7.186574000	6.989924000
C	20.884810000	5.474733000	5.081261000
C	21.850356000	4.855917000	5.888798000
C	23.099281000	5.486869000	5.990364000
C	23.320991000	6.739237000	5.427471000
C	22.313025000	7.421465000	4.728468000
C	21.110334000	6.734420000	4.508277000
C	21.512112000	3.549812000	6.602929000
C	22.527851000	3.229123000	7.719013000
C	22.558673000	8.861690000	4.276014000
C	21.285782000	9.548711000	3.748467000

O	20.586434000	5.763508000	8.237520000
C	19.816344000	4.667753000	8.181583000
C	18.706649000	4.519537000	9.066921000
C	17.855437000	3.429280000	8.871741000
C	18.058060000	2.450740000	7.891815000
C	19.225698000	2.552258000	7.136511000
C	20.126222000	3.613392000	7.277483000
C	18.497216000	5.471872000	10.262012000
C	18.162033000	6.903164000	9.805822000
C	17.050107000	1.305006000	7.727045000
C	17.445122000	0.339565000	6.601012000
O	21.243137000	8.971995000	6.830878000
C	22.375518000	9.678259000	6.708381000
C	23.089044000	9.672626000	5.473901000
C	24.247077000	10.437756000	5.352635000
C	24.746078000	11.225539000	6.393421000
C	24.025579000	11.218021000	7.587065000
C	22.857597000	10.471449000	7.784655000
C	26.029333000	12.043714000	6.192442000
C	26.410973000	12.847017000	7.443337000
C	22.133692000	10.518116000	9.144099000
C	22.800234000	11.491971000	10.130947000
C	23.559479000	8.791006000	3.103606000
C	19.778594000	5.492185000	11.121441000
C	17.348066000	5.012008000	11.174205000
C	21.613144000	2.434459000	5.540498000
C	20.677903000	10.992874000	8.965309000
C	22.162873000	9.126128000	9.804992000
C	27.198719000	11.095948000	5.859168000
C	25.834650000	13.036927000	5.029787000
C	16.959480000	0.497542000	9.037174000

C	15.660891000	1.883200000	7.392100000
H	24.783446000	10.422908000	4.409669000
H	24.386833000	11.821485000	8.408917000
H	23.890062000	5.034024000	6.577895000
H	19.454818000	1.773003000	6.420215000
H	20.314542000	7.197891000	3.934941000
H	16.994524000	3.326541000	9.523327000
H	23.737094000	9.780452000	2.670258000
H	23.148096000	8.153278000	2.314445000
H	24.522367000	8.368348000	3.405541000
H	19.922914000	4.986767000	4.943036000
H	20.862584000	2.547926000	4.751777000
H	21.499022000	1.442337000	5.988192000
H	22.600519000	2.472341000	5.069265000
H	24.271235000	7.238105000	5.597888000
H	20.516514000	9.598175000	4.521105000
H	20.881516000	9.037352000	2.866476000
H	21.532943000	10.571958000	3.451091000
H	23.532945000	3.054240000	7.318464000
H	22.215925000	2.316875000	8.235066000
H	22.570579000	4.039985000	8.450587000
H	19.997502000	4.490623000	11.507520000
H	19.645382000	6.162615000	11.979051000
H	20.636042000	5.834847000	10.540470000
H	27.367908000	10.383878000	6.673906000
H	28.124490000	11.663302000	5.704973000
H	27.006543000	10.520113000	4.948387000
H	16.378011000	5.027162000	10.664422000
H	17.275987000	5.692568000	12.029411000
H	17.514433000	4.004052000	11.568631000
H	25.601073000	12.524033000	4.091550000

H	26.745662000	13.625704000	4.868819000
H	25.014096000	13.729910000	5.243335000
H	18.957028000	7.323805000	9.189703000
H	18.027216000	7.553496000	10.678641000
H	17.229044000	6.920186000	9.231312000
H	20.652500000	12.000968000	8.536623000
H	20.168590000	11.025258000	9.936086000
H	20.127949000	10.323493000	8.303627000
H	25.630356000	13.563776000	7.719760000
H	27.328506000	13.414526000	7.253523000
H	26.597675000	12.195718000	8.303823000
H	21.673851000	8.369605000	9.188327000
H	21.649107000	9.151275000	10.773459000
H	23.195056000	8.802953000	9.978420000
H	17.933351000	0.071563000	9.300023000
H	16.243038000	-0.326157000	8.933403000
H	16.631731000	1.119034000	9.876075000
H	23.827797000	11.200375000	10.373169000
H	22.233147000	11.495425000	11.068145000
H	22.813322000	12.519228000	9.750734000
H	15.307725000	2.565549000	8.171499000
H	14.921504000	1.079518000	7.292831000
H	15.686500000	2.438797000	6.448283000
H	17.517779000	0.850351000	5.634603000
H	16.688682000	-0.446685000	6.503571000
H	18.403697000	-0.150921000	6.801635000
H	17.624983000	5.875175000	6.863785000
H	18.712599000	9.669056000	6.608252000
H	18.094926000	9.117250000	5.029008000
H	15.993008000	9.664779000	6.160847000
H	16.614629000	9.062586000	7.707046000

H	15.636688000	7.443596000	5.333596000
H	15.543968000	7.040640000	7.047433000
H	17.646007000	6.290291000	5.130968000

(2-Fe.THF) (S = 0)

C	17.019634000	7.285206000	2.887035000
O	17.753408000	7.873241000	3.965979000
C	16.848637000	8.410796000	4.934217000
C	15.515350000	7.717676000	4.679082000
C	15.540738000	7.574939000	3.155091000
C	20.778961000	6.832618000	4.842761000
C	22.019717000	7.524336000	4.924821000
C	23.151387000	6.780285000	5.332604000
C	23.019420000	5.460370000	5.825874000
C	21.757282000	4.806010000	5.854749000
C	20.666586000	5.486883000	5.266179000
Fe	21.609839000	6.644621000	6.709835000
O	21.967480000	8.183851000	7.658982000
C	22.827344000	9.149103000	7.305901000
C	23.019805000	9.571521000	5.954044000
C	23.961072000	10.563036000	5.679970000
C	24.725556000	11.181399000	6.671039000
C	24.496511000	10.774010000	7.986314000
C	23.574499000	9.785330000	8.340222000
C	22.130841000	9.039976000	4.812657000
C	20.756971000	9.728830000	4.940804000
C	21.498979000	3.541718000	6.664983000
C	22.643688000	3.245844000	7.655799000
C	25.755198000	12.254480000	6.291065000
C	26.493401000	12.813440000	7.514856000
C	23.374288000	9.404580000	9.818868000

C	24.277804000	10.221397000	10.757653000
O	20.748191000	5.980224000	8.202847000
C	19.965808000	4.895844000	8.251458000
C	18.835254000	4.931249000	9.127343000
C	17.993512000	3.822721000	9.167147000
C	18.191655000	2.665418000	8.403918000
C	19.315526000	2.642184000	7.583903000
C	20.209116000	3.714901000	7.491409000
C	18.554402000	6.156052000	10.017165000
C	18.325738000	7.412272000	9.151950000
C	17.198171000	1.500454000	8.500930000
C	17.583342000	0.328016000	7.588449000
C	22.689570000	9.334292000	3.405539000
C	19.739501000	6.384024000	10.977019000
C	17.297112000	5.970401000	10.883048000
C	21.431129000	2.381867000	5.649892000
C	21.915469000	9.685025000	10.233346000
C	23.713041000	7.916991000	10.045449000
C	26.803317000	11.646973000	5.337470000
C	25.045870000	13.426707000	5.584522000
C	17.150340000	0.980159000	9.951189000
C	15.793978000	1.985226000	8.088673000
H	24.103275000	10.870033000	4.649175000
H	25.066016000	11.242133000	8.777823000
H	23.870378000	5.018078000	6.330307000
H	19.513085000	1.756719000	6.993141000
H	19.861147000	7.358781000	4.596040000
H	17.132969000	3.858361000	9.825230000
H	22.688766000	10.406641000	3.189598000
H	22.055479000	8.850654000	2.655172000
H	23.709528000	8.956544000	3.281574000

H	19.672362000	5.063186000	5.370486000
H	20.571485000	2.475348000	4.978947000
H	21.374475000	1.411461000	6.151419000
H	22.339116000	2.379700000	5.037592000
H	24.084425000	7.306806000	5.508907000
H	20.293821000	9.502851000	5.904959000
H	20.067476000	9.438664000	4.141185000
H	20.904779000	10.810975000	4.884085000
H	23.589178000	3.031243000	7.143355000
H	22.379040000	2.360748000	8.240566000
H	22.792925000	4.075404000	8.352343000
H	19.880431000	5.512237000	11.626117000
H	19.542310000	7.252337000	11.616827000
H	20.662814000	6.562676000	10.425948000
H	27.330225000	10.814805000	5.816293000
H	27.546417000	12.400562000	5.050539000
H	26.344000000	11.266794000	4.419546000
H	16.391482000	5.840368000	10.279623000
H	17.153921000	6.865647000	11.497453000
H	17.383615000	5.117162000	11.564910000
H	24.532174000	13.101239000	4.674512000
H	25.770029000	14.199315000	5.299820000
H	24.299889000	13.884155000	6.242723000
H	19.202925000	7.641741000	8.546202000
H	18.112965000	8.275109000	9.794611000
H	17.462633000	7.267957000	8.490732000
H	21.680064000	10.748655000	10.111970000
H	21.768292000	9.426230000	11.288735000
H	21.217611000	9.101262000	9.632827000
H	25.806873000	13.292965000	8.220630000
H	27.219012000	13.569203000	7.195030000

H	27.043723000	12.032427000	8.050068000
H	23.065388000	7.268569000	9.454655000
H	23.584807000	7.661582000	11.104322000
H	24.757150000	7.715542000	9.777626000
H	18.134577000	0.620196000	10.268731000
H	16.438865000	0.150370000	10.039451000
H	16.839863000	1.760380000	10.652650000
H	25.342625000	10.053912000	10.560423000
H	24.085000000	9.915162000	11.791319000
H	24.079115000	11.296965000	10.693494000
H	15.440127000	2.796032000	8.732591000
H	15.068106000	1.166010000	8.154773000
H	15.796422000	2.355537000	7.057823000
H	17.611645000	0.624352000	6.534154000
H	16.845209000	-0.475345000	7.685668000
H	18.560600000	-0.089567000	7.853944000
H	17.219321000	6.204572000	2.870577000
H	17.260495000	8.223762000	5.930266000
H	16.759593000	9.499306000	4.796697000
H	14.660418000	8.290132000	5.049003000
H	15.501047000	6.732519000	5.158693000
H	15.241876000	8.517183000	2.682254000
H	14.883633000	6.786520000	2.778167000
H	17.370770000	7.708822000	1.938438000

(**2-Fe**) S multiplicity	ΔH (kcal/mol)	ΔG (kcal/mol)
Singlet	40.76	45.14
Triplet	26.40	28.99
Quintet	0.0	0.0

OPTIMISED STRUCTURES FOR (2-Fe)

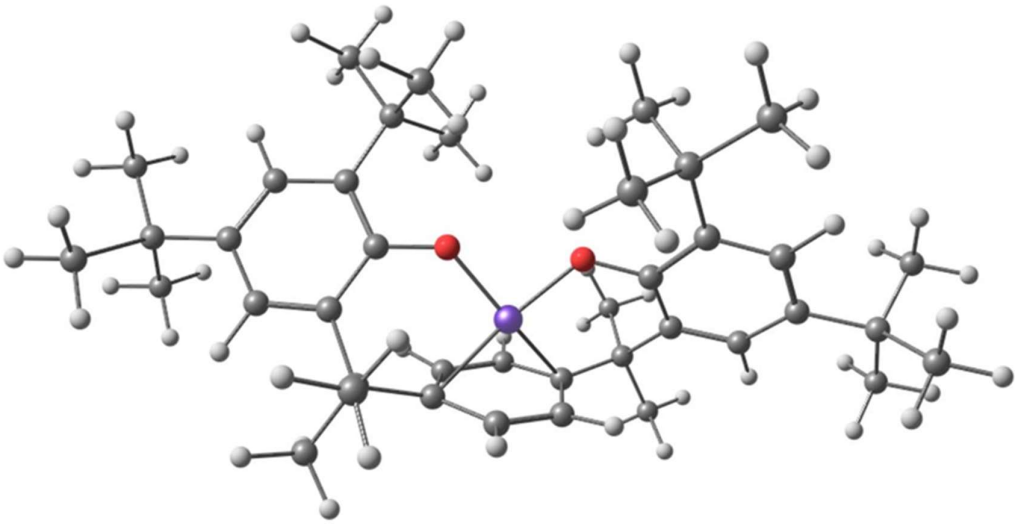


Figure S37: Optimised structure for S = 0 **(2-Fe**)

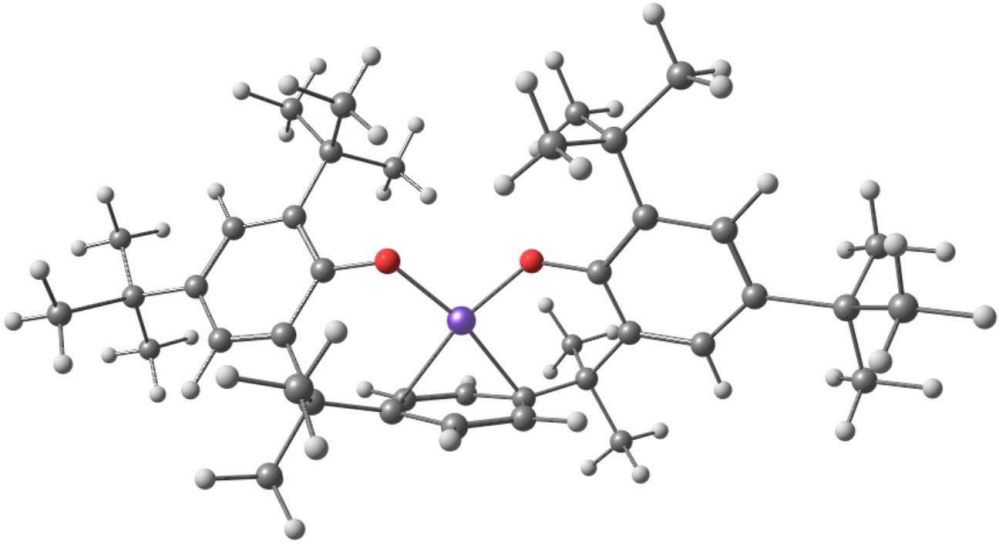


Figure S38: Optimised structure for S = 1 (**2-Fe**)

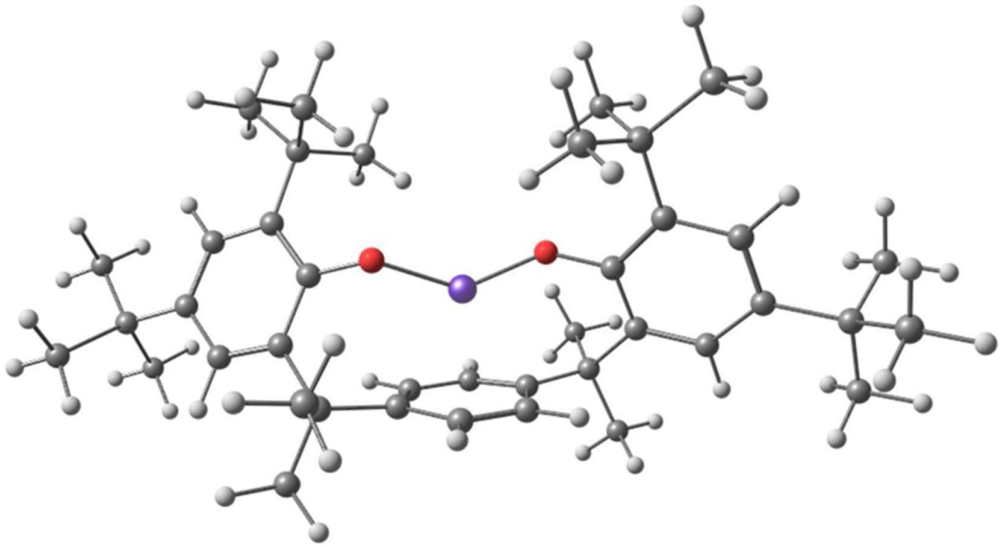


Figure S39: Optimised structure for S = 2 (**2-Fe**)

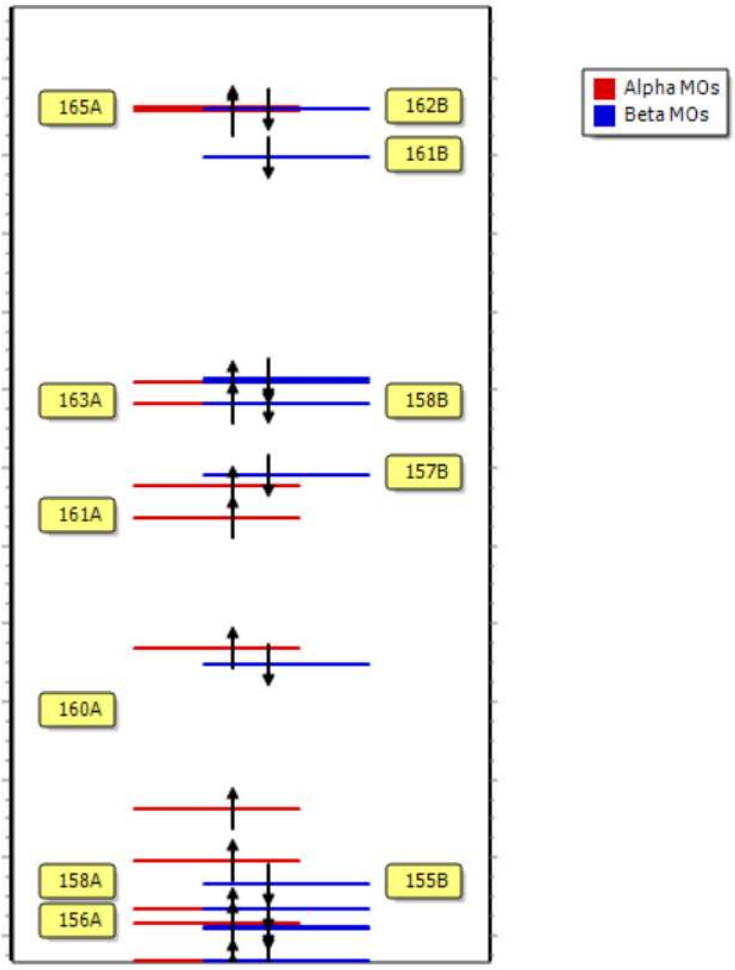
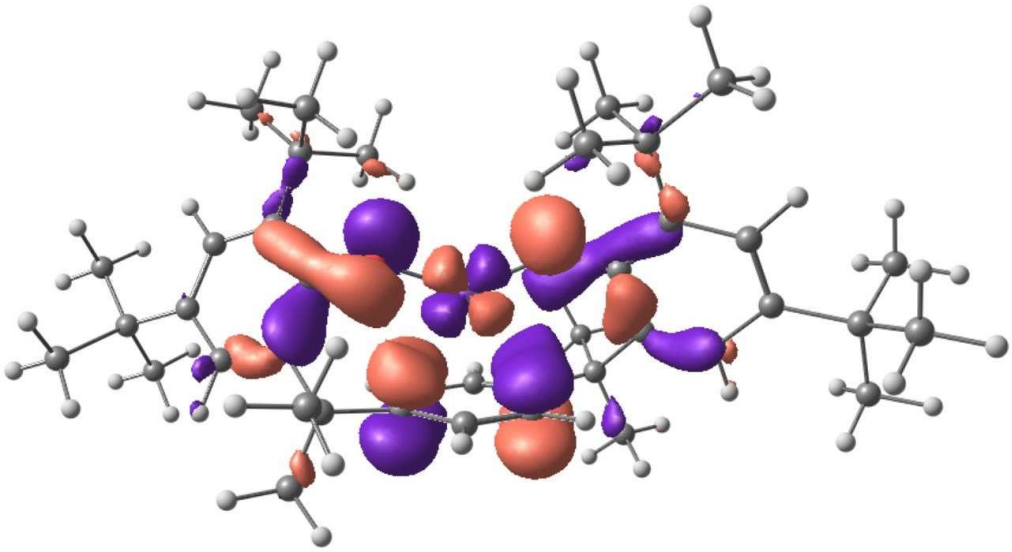
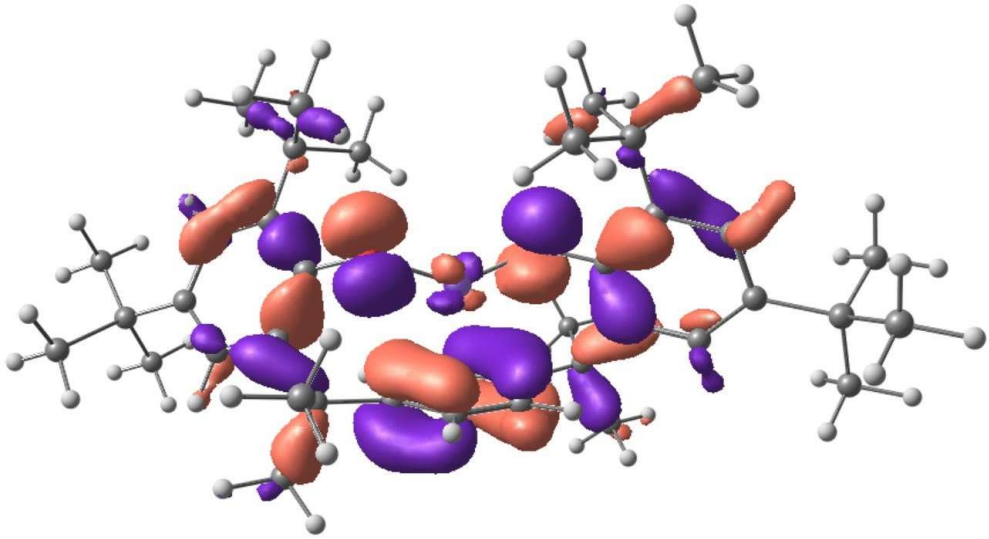


Figure 40: MO energy diagram for (**2-Fe**) (S = 2)

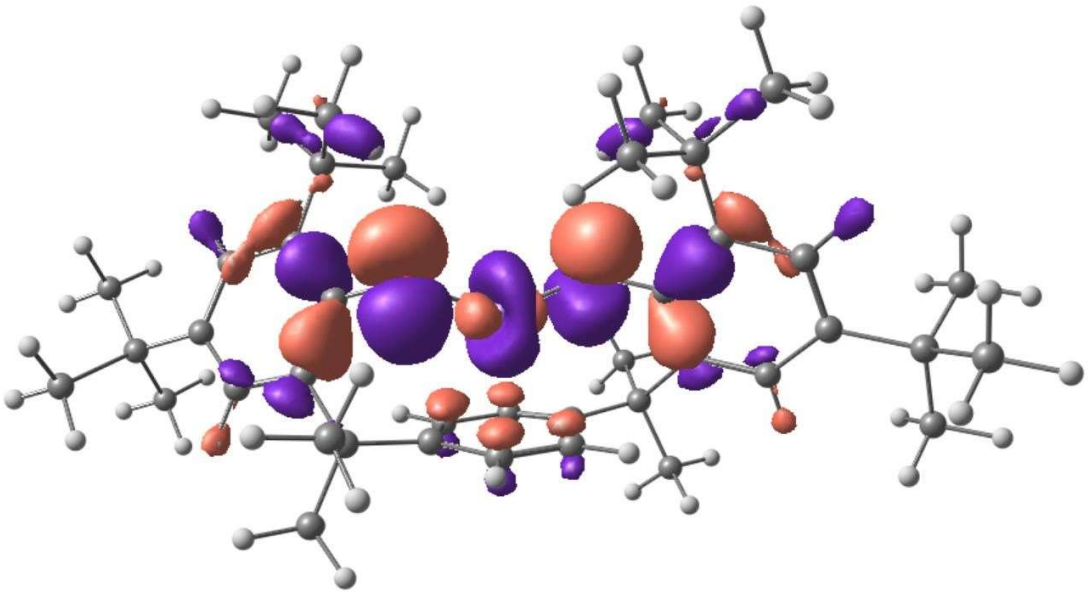
Alpha MO's (**2-Fe**) (S = 2):



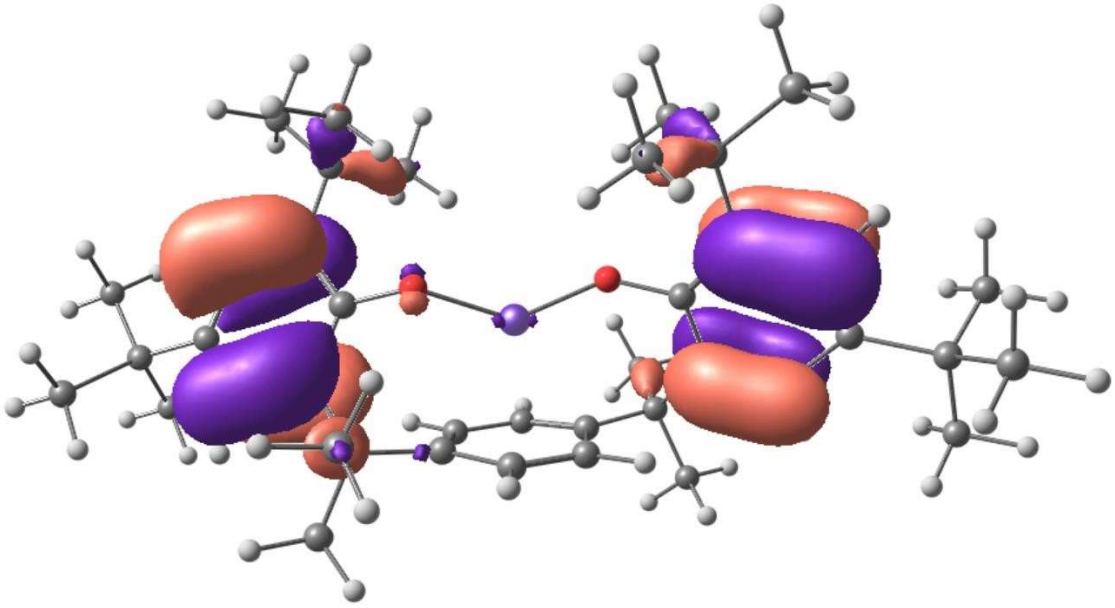
MO 160A - -HOMO-6



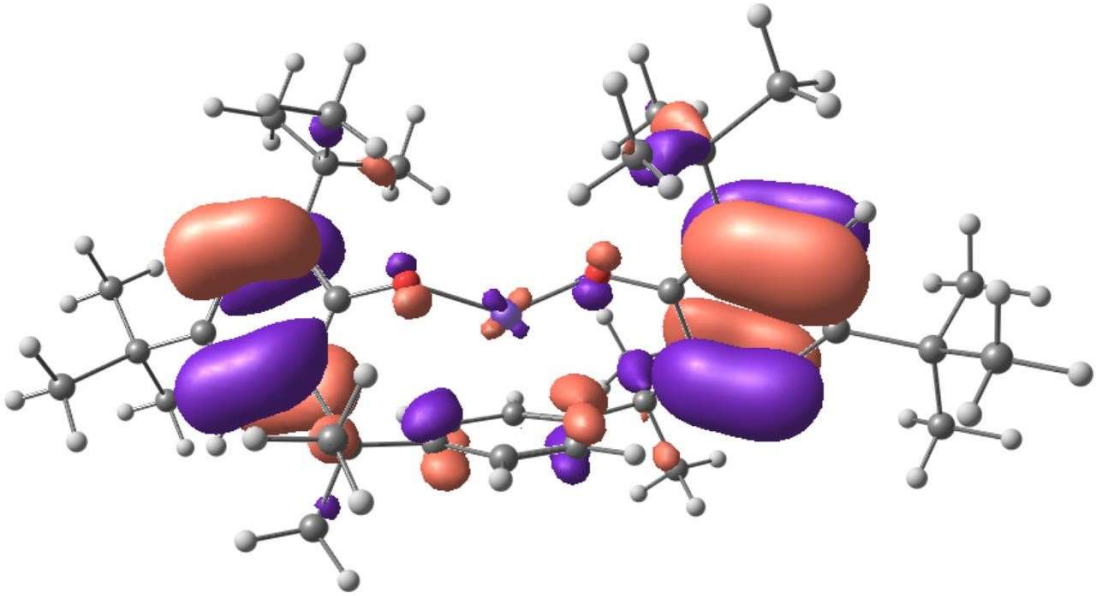
MO 161A – HOMO-5



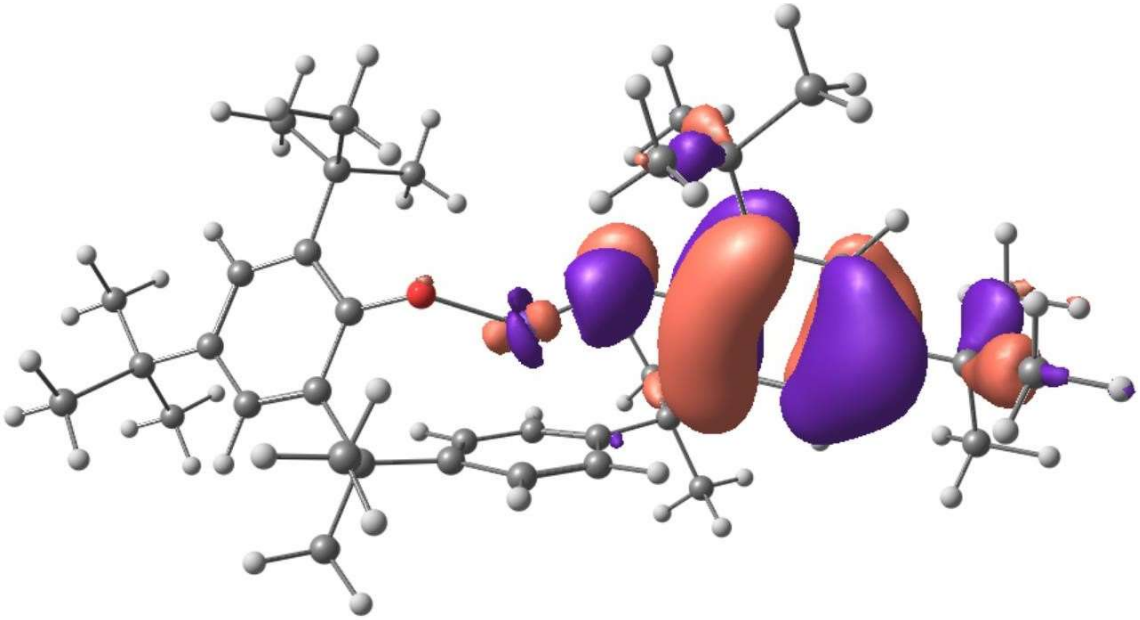
MO 162A – HOMO-4



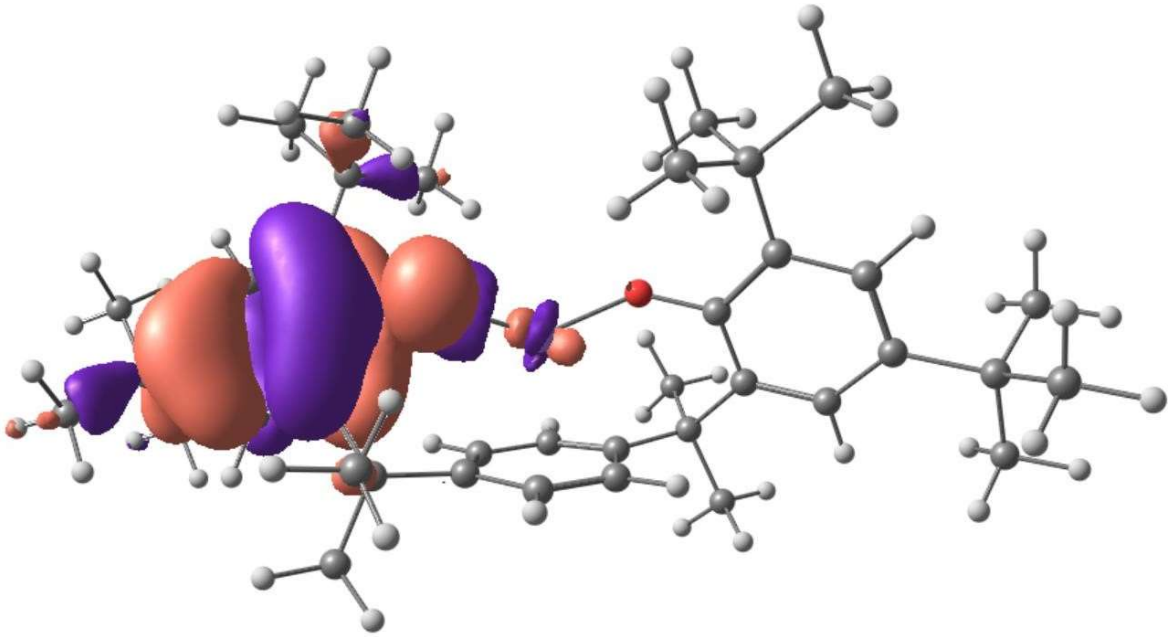
MO163A – HOMO-3



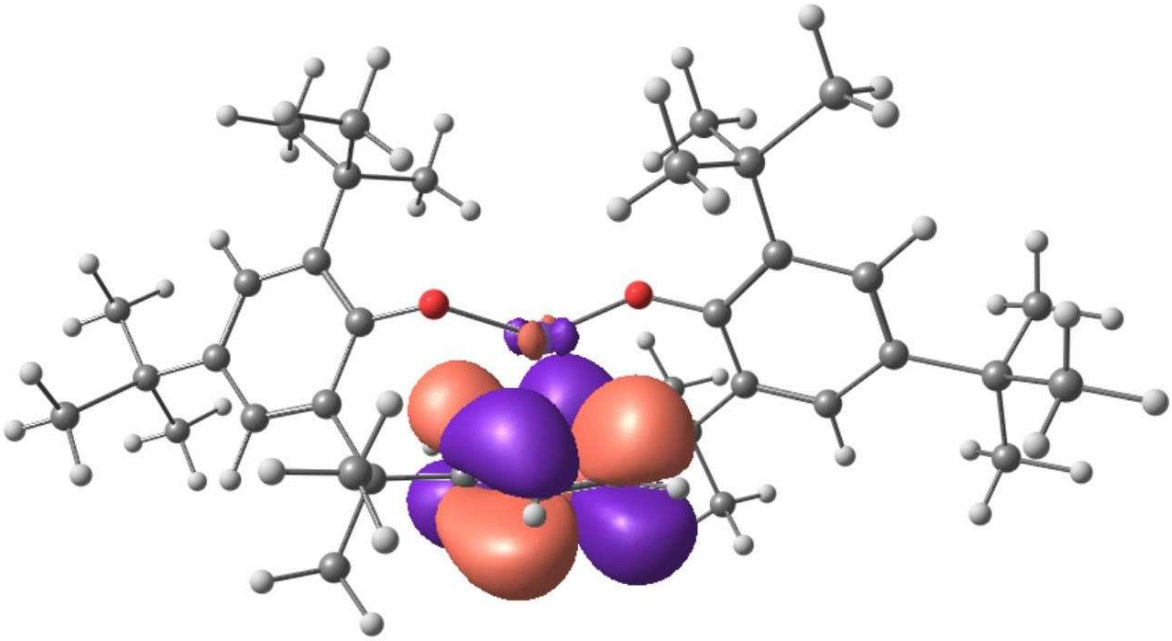
MO164A – HOMO-2



MO165A – HOMO-1

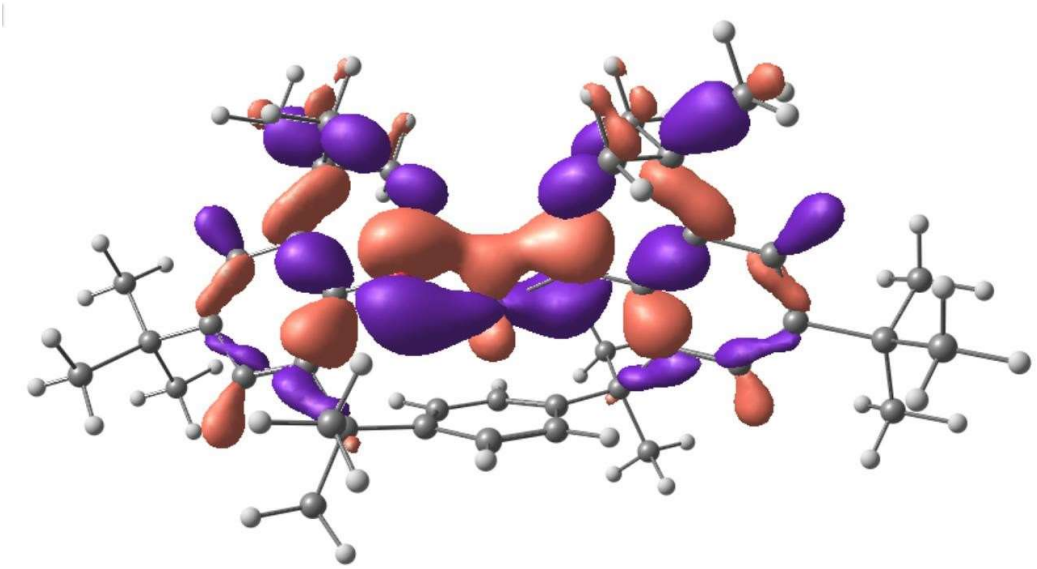


MO166A - HOMO

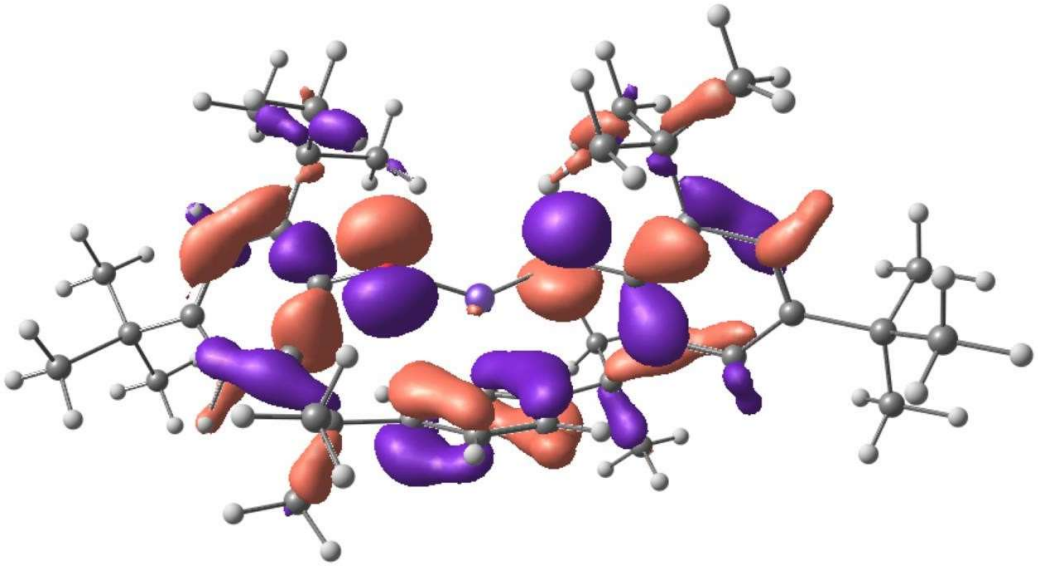


MO167A - LUMO

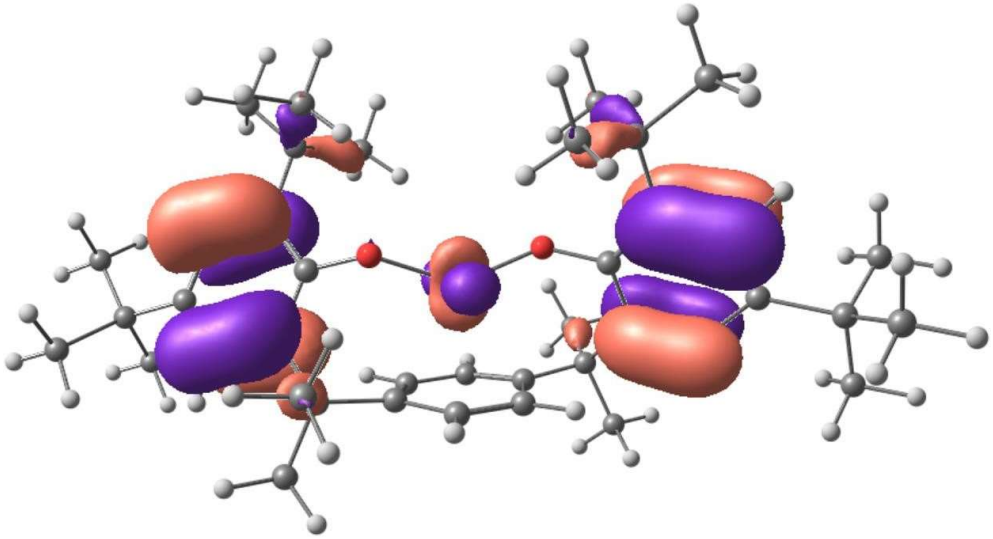
MO's (**2-Fe**) (S = 2):



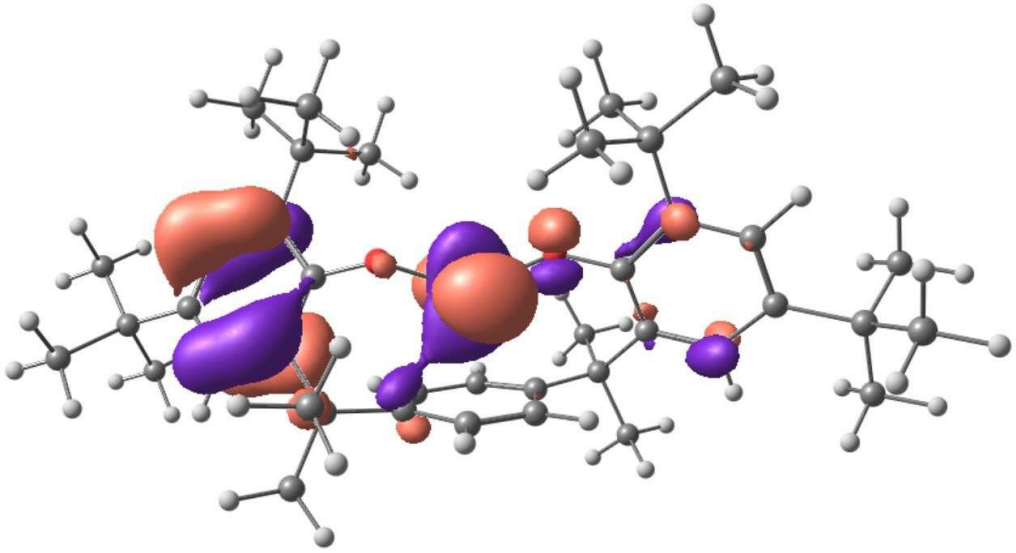
MO156B – HOMO-6



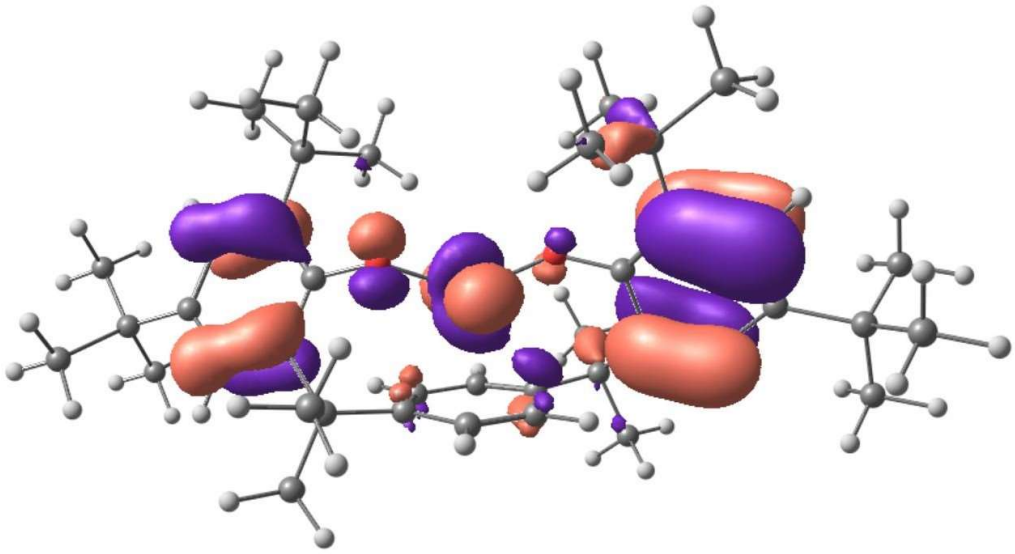
MO157B – HOMO-5



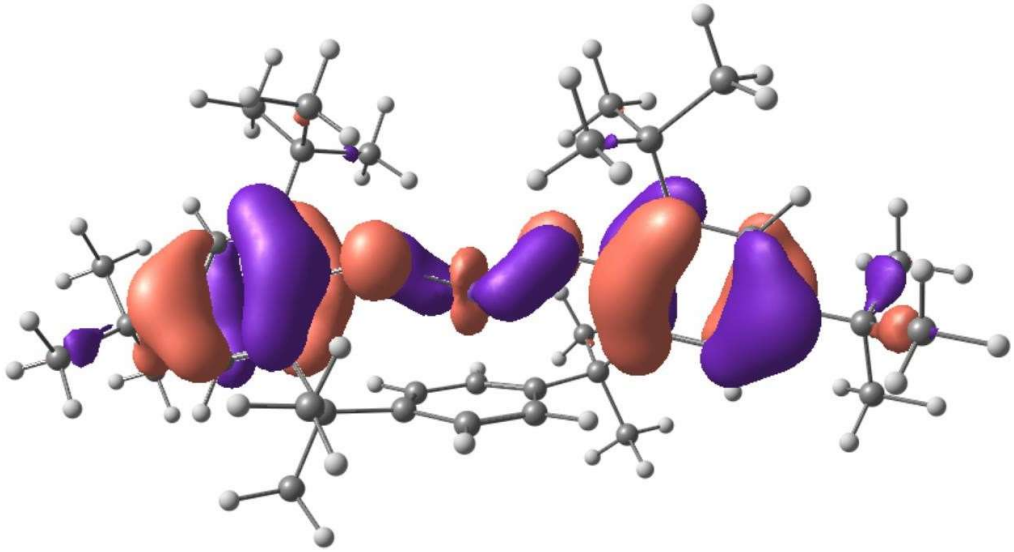
MO158B – HOMO-4



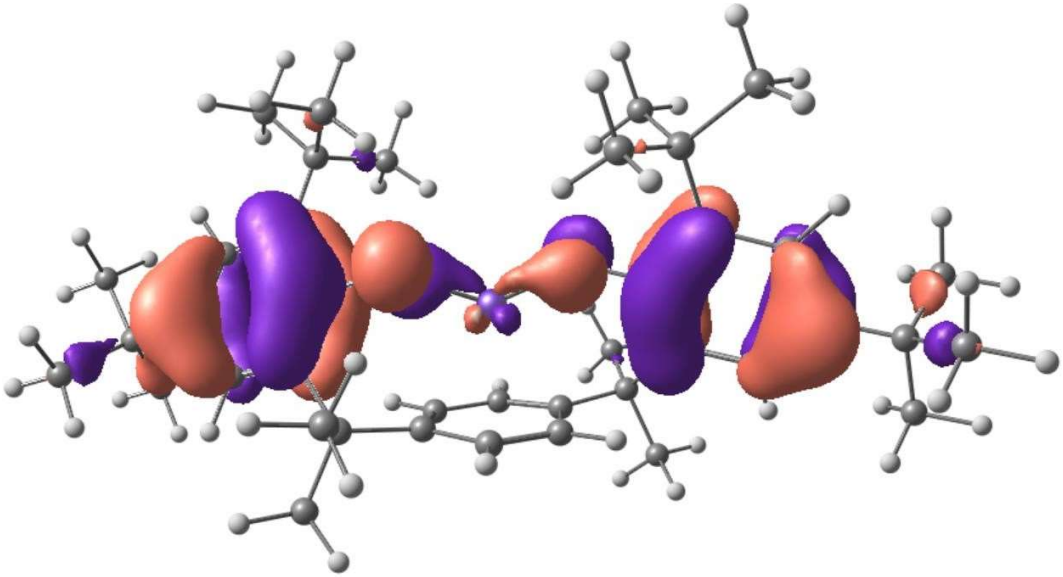
MO159B – HOMO-3



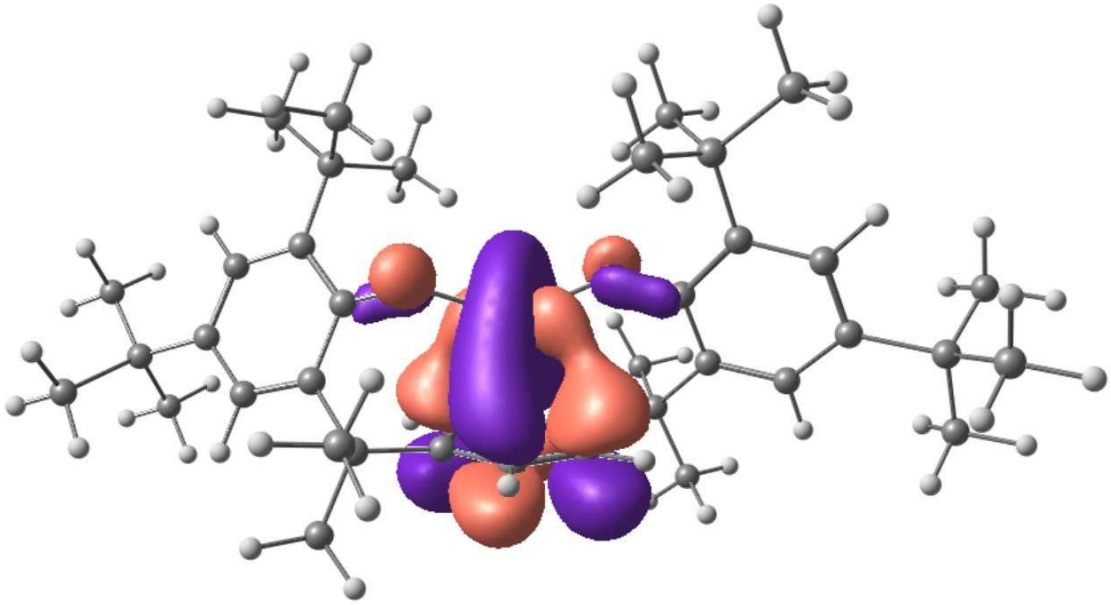
MO160B – HOMO-2



MO161B – HOMO-1



MO162B - HOMO

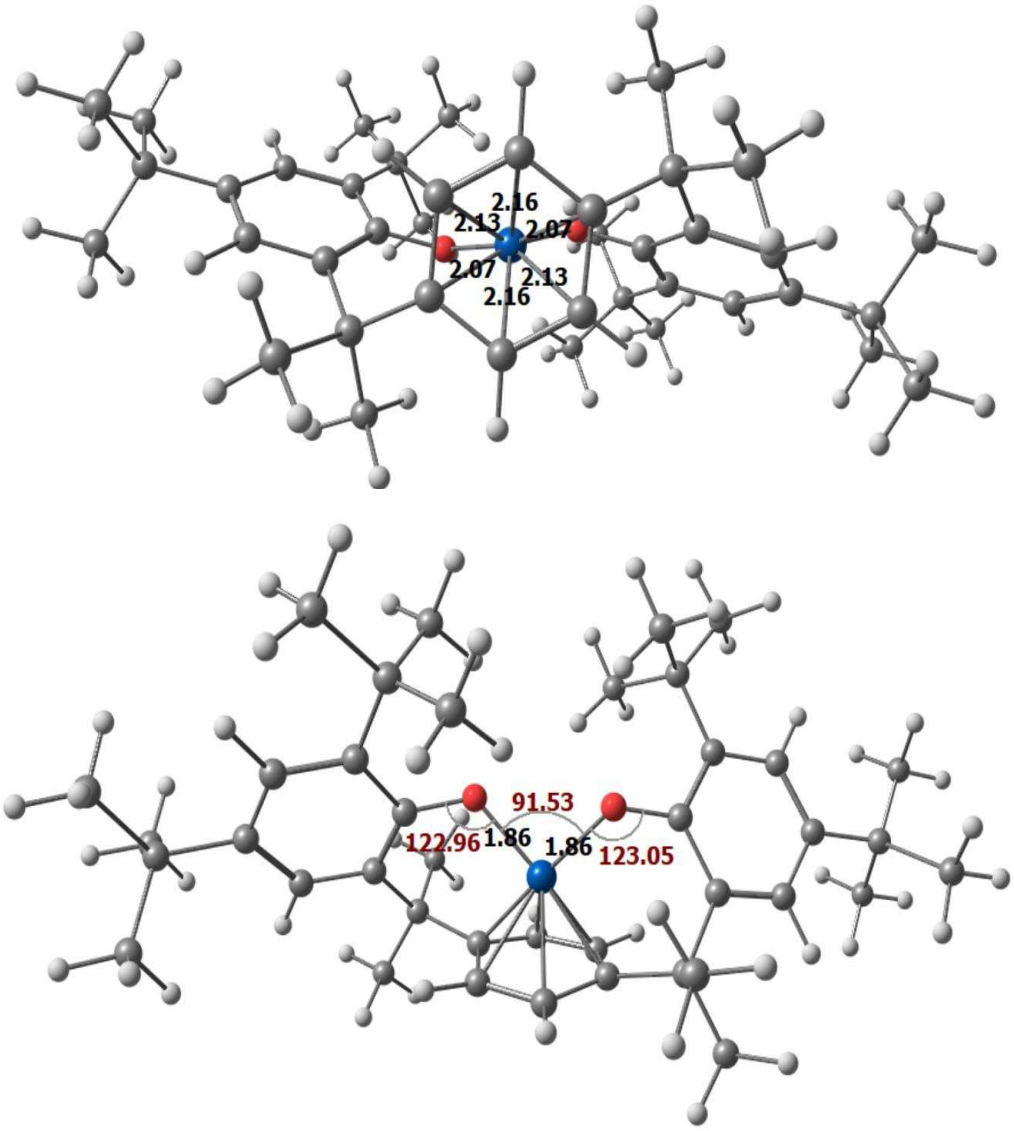


MO163B - LUMO

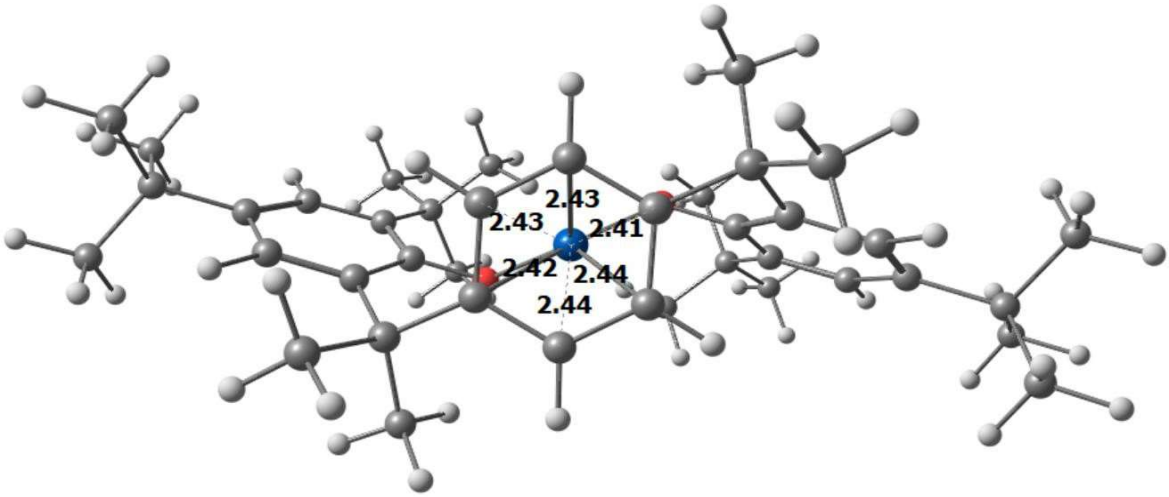
(**2-Co**)

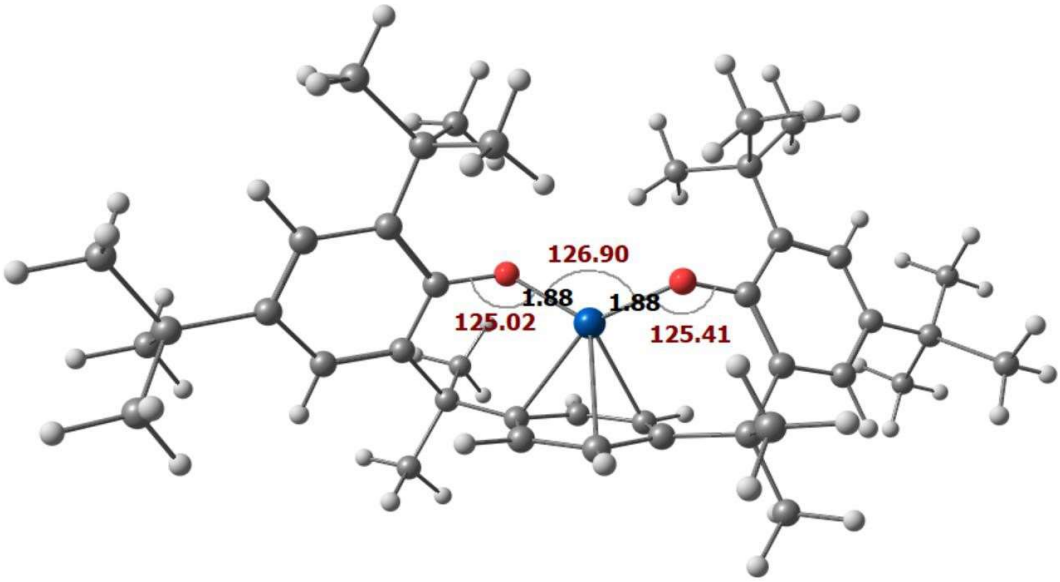
(**2-Co**) S multiplicity	ΔH (kcal/mol)	ΔG (kcal/mol)
Doublet	16.63	18.55
Quartet	0.0	0.0

Calculated Structural Parameters for (2-Co) (S = ½)



Calculated Structural Parameters for (2-Co) (S = 3/2)





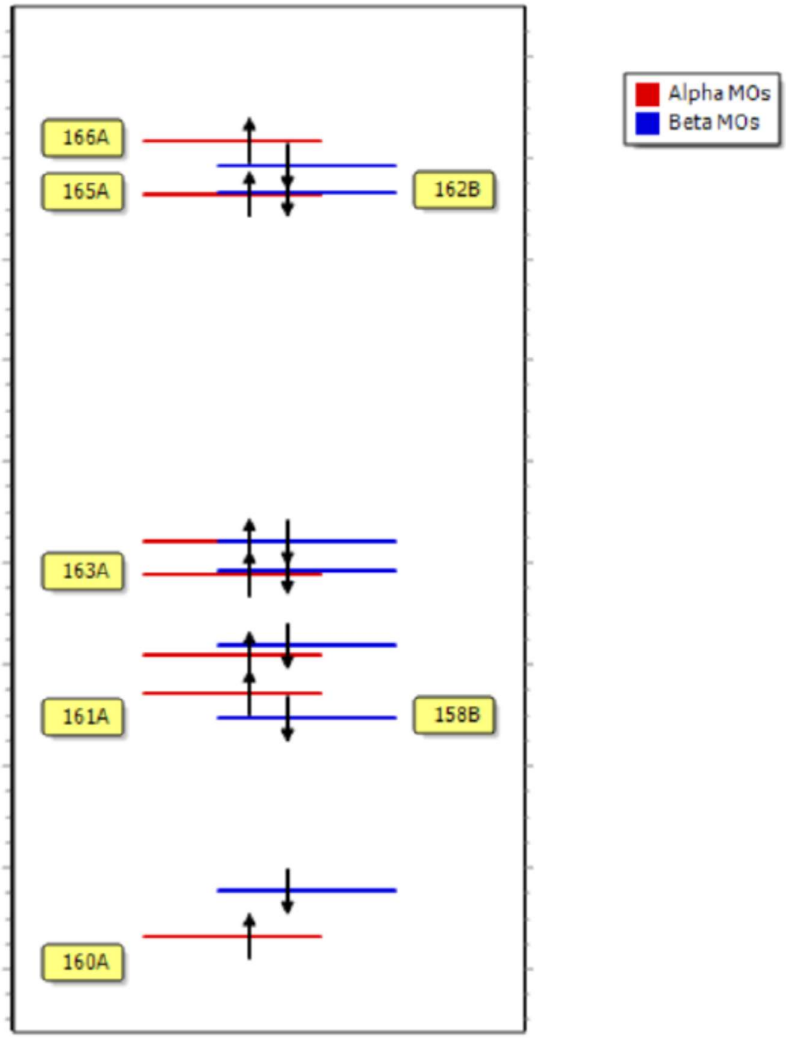
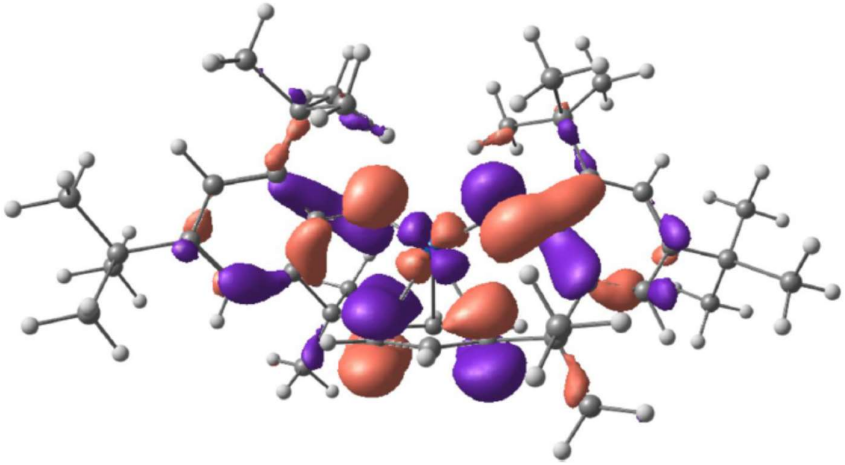
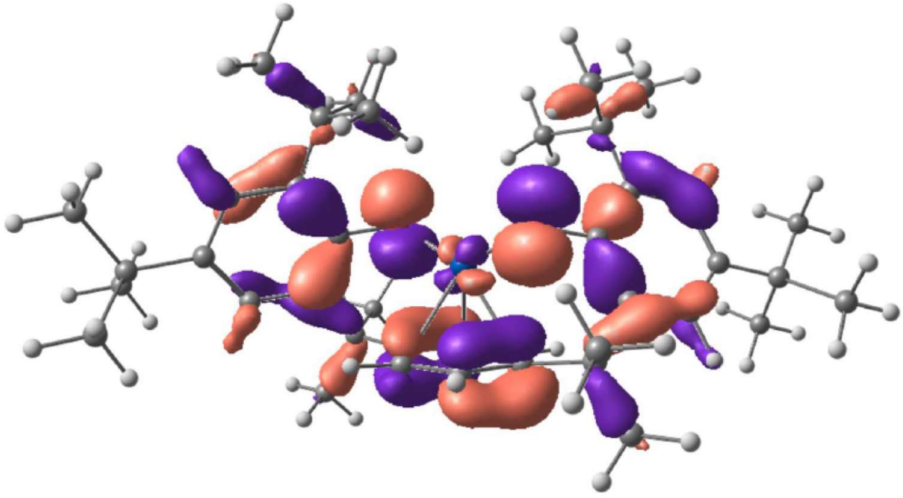


Figure 40: MO energy diagram for (**2-Co**) (S = 3/2)

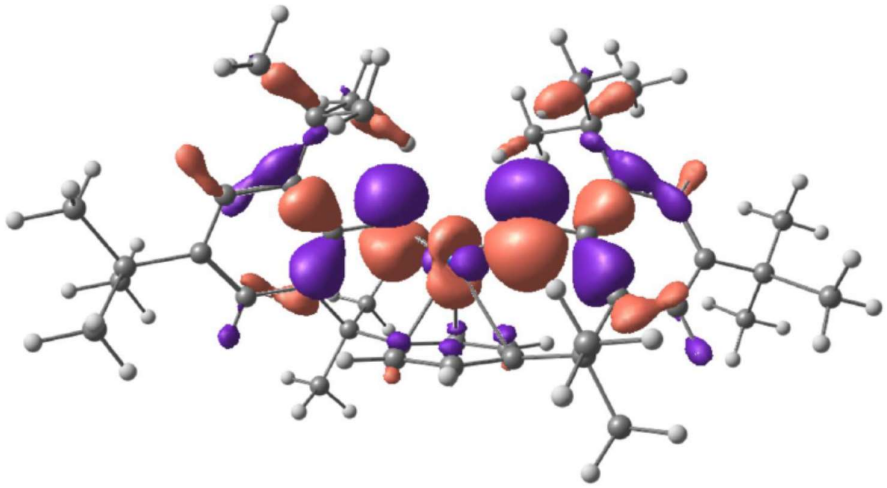
Alpha MO's (2-Co) (S = 3/2)



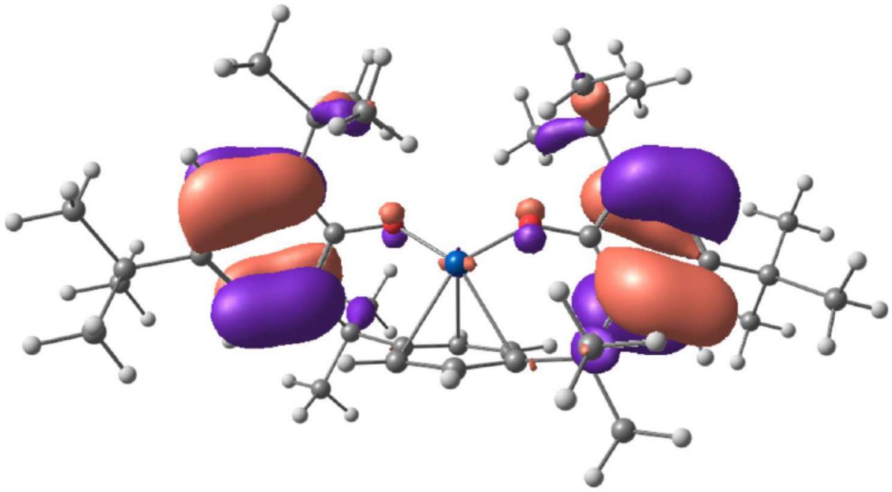
MO 160A HOMO - 6



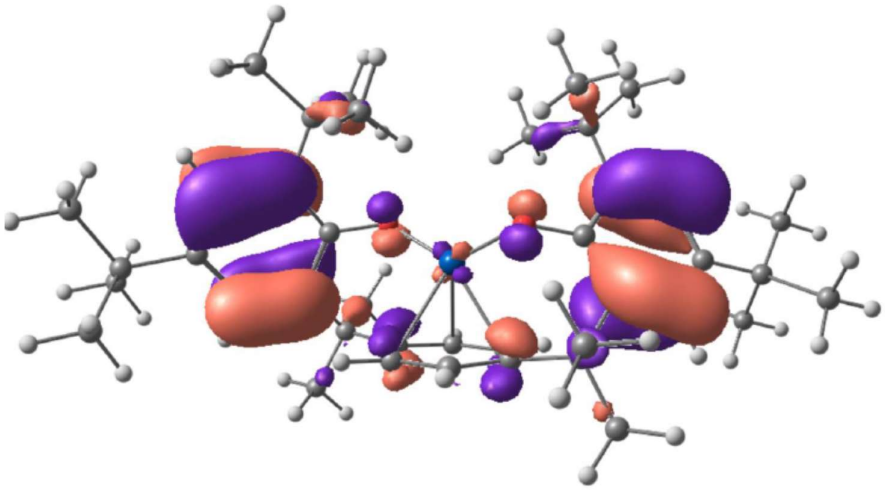
MO 161A HOMO - 5



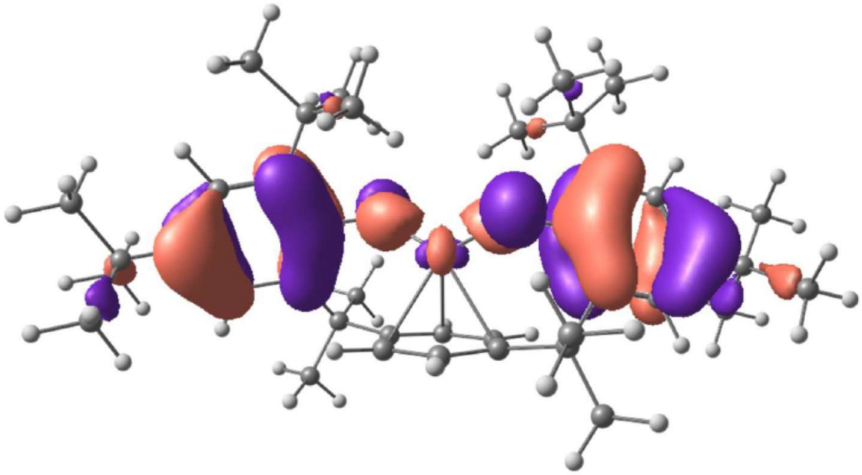
MO 162A HOMO - 4



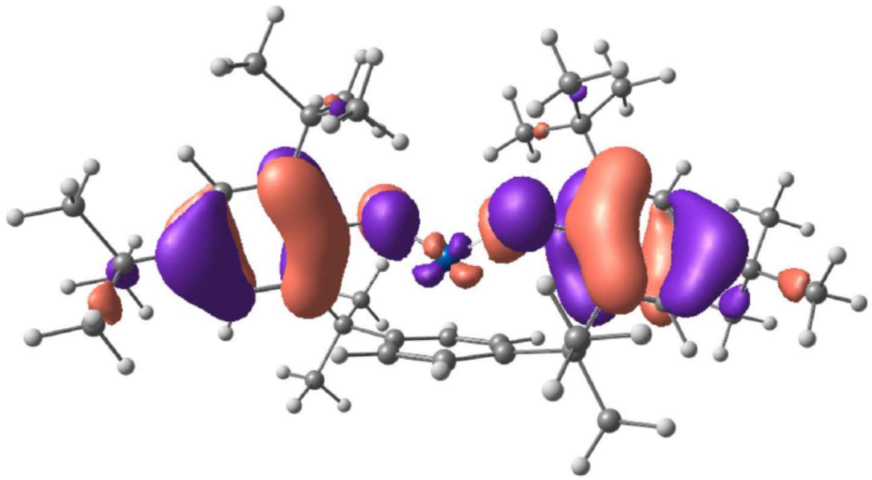
MO 163A HOMO - 3



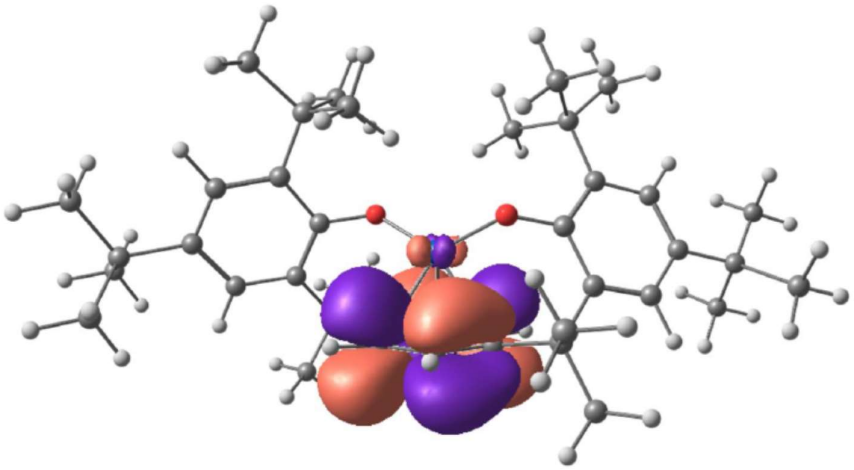
MO 164A HOMO - 2



MO 165A HOMO - 1

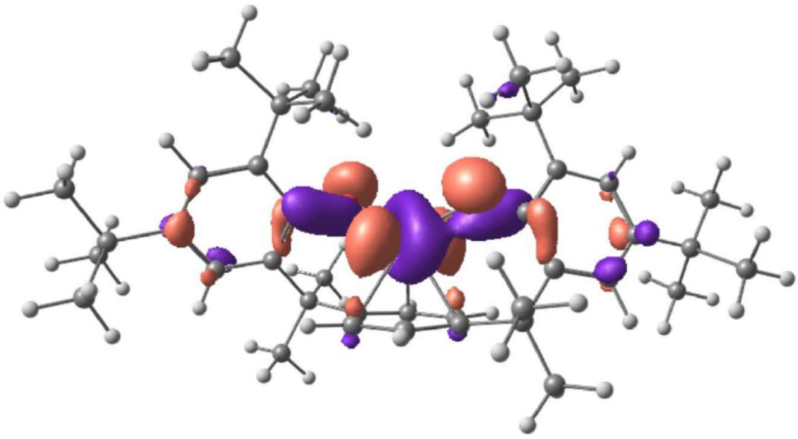


MO 166A HOMO

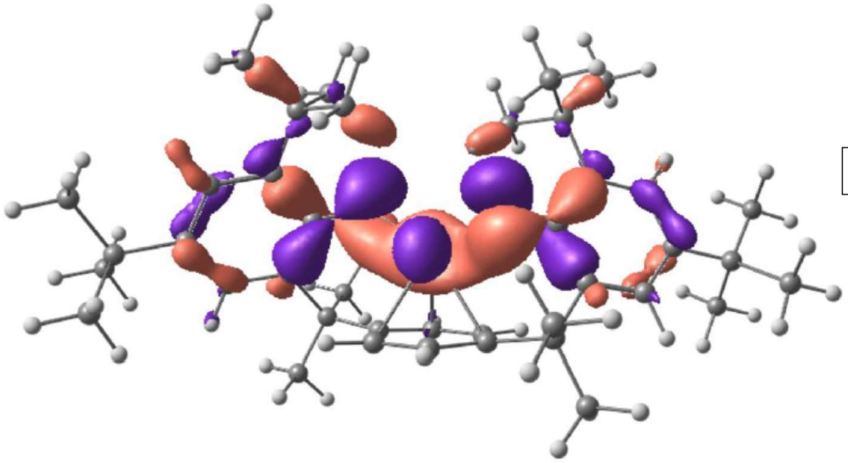


MO 167A LUMO

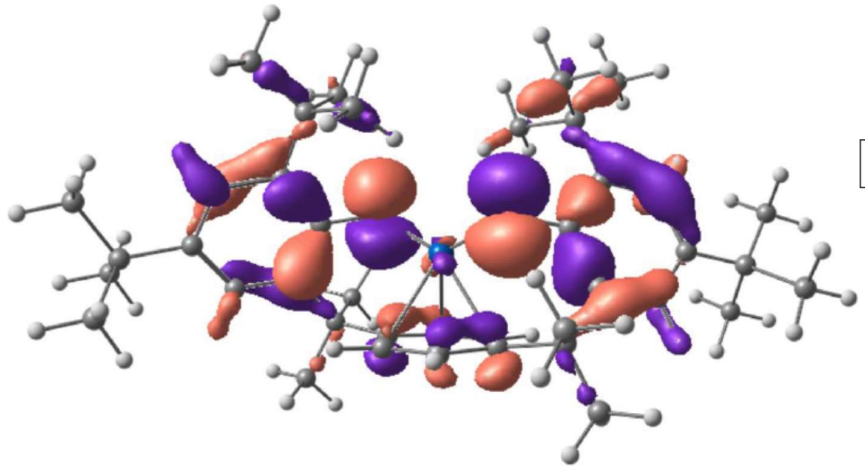
Beta MO's for (2-Co) (S = 3/2)



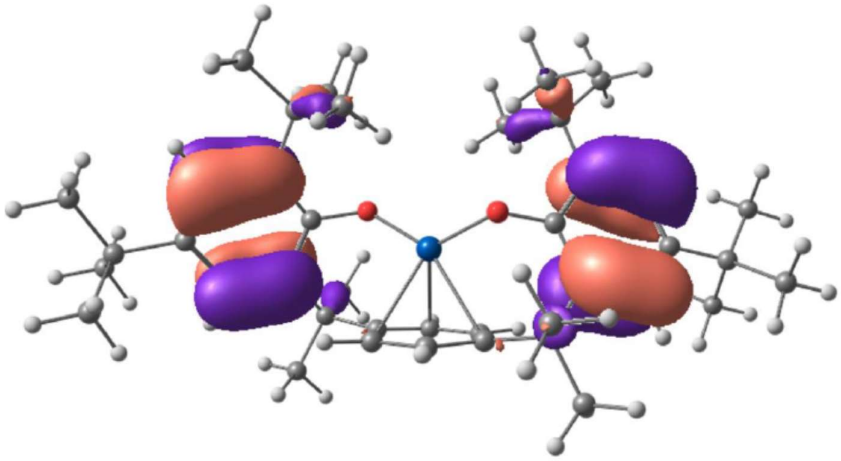
MO 157B HOMO - 6



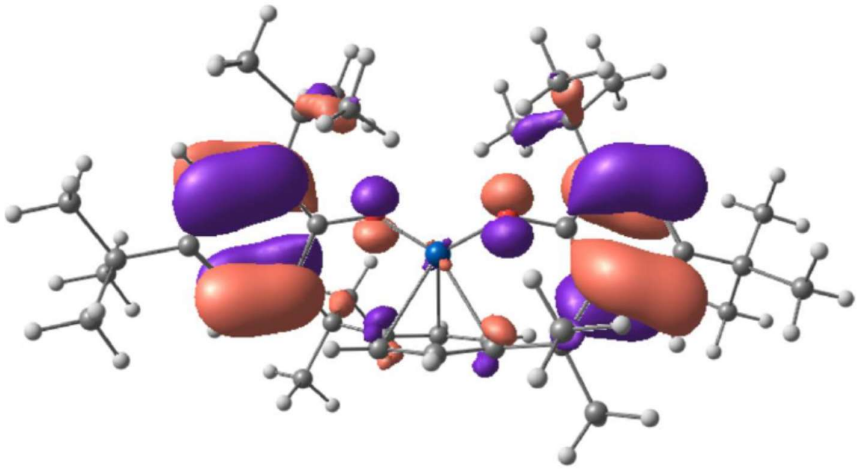
MO 158B HOMO - 5



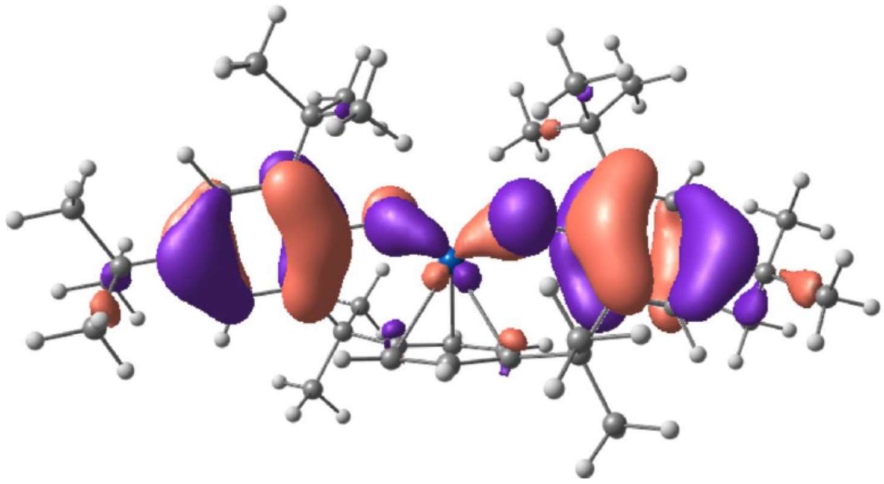
MO 159B HOMO - 4



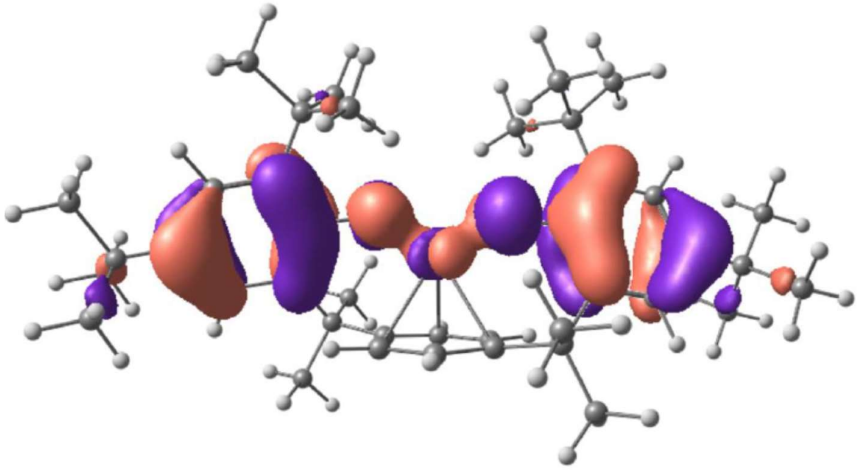
MO 160B HOMO - 3



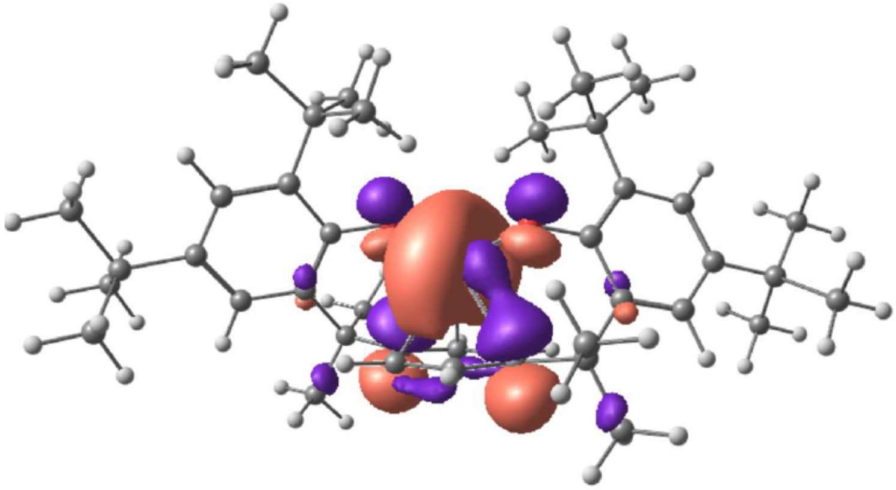
MO 161B HOMO - 2



MO 162B HOMO - 1



MO 163B HOMO



MO 164B LUMO

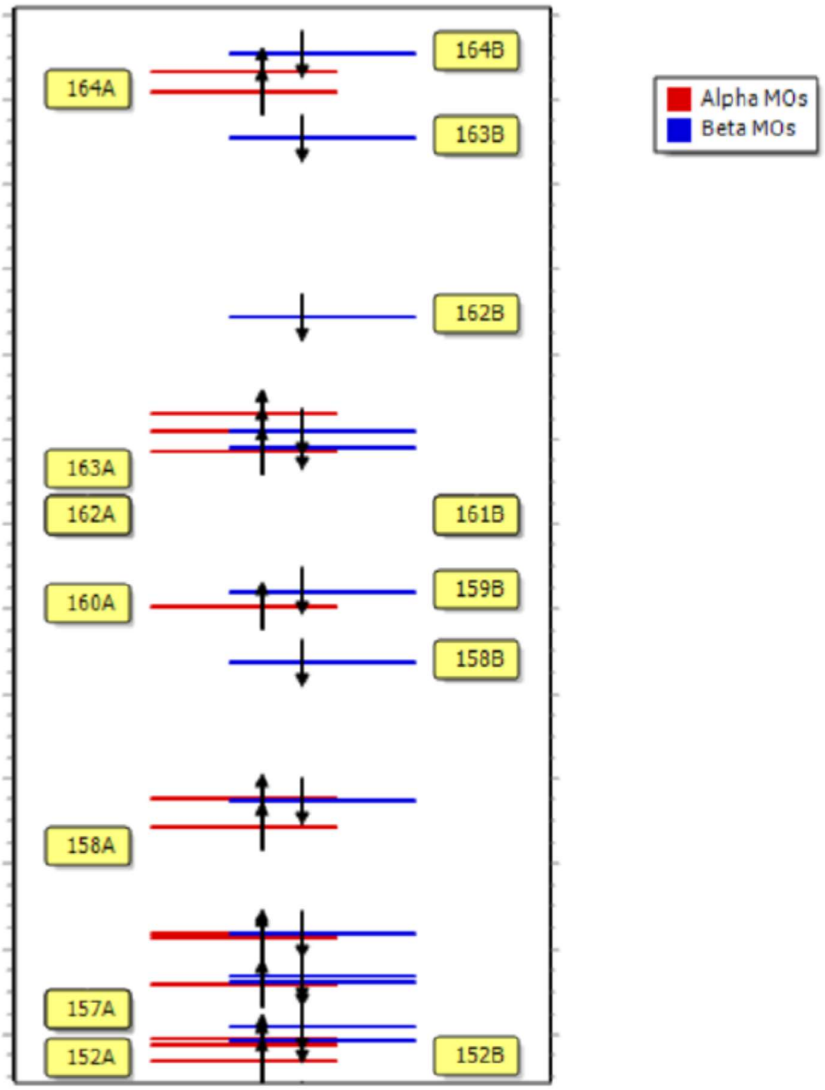
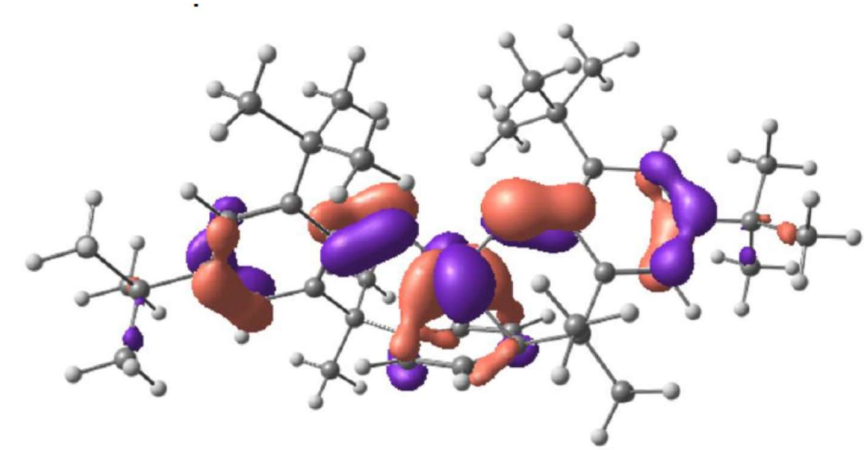
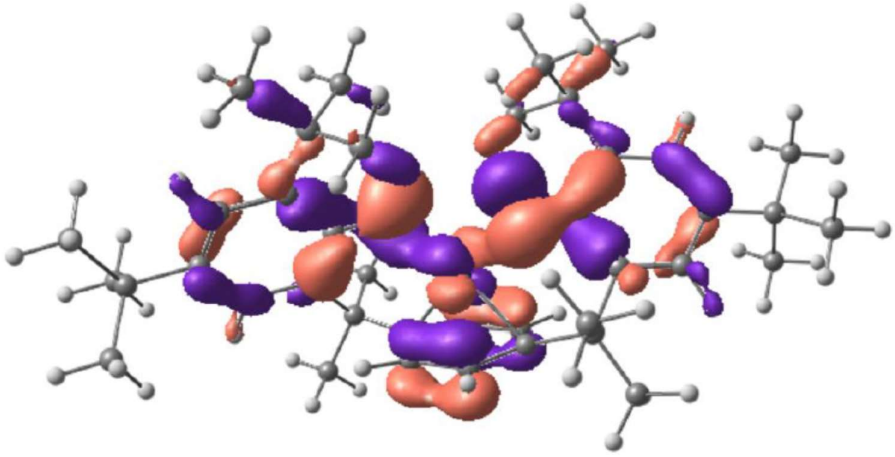


Figure 41: MO energy diagram for (**2-Co**) (S = 1/2)

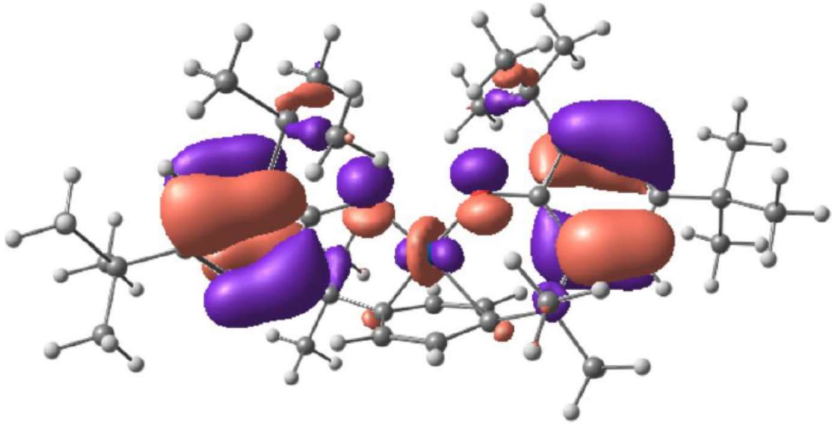
Alpha MO's (2-Co) (S = 1/2)



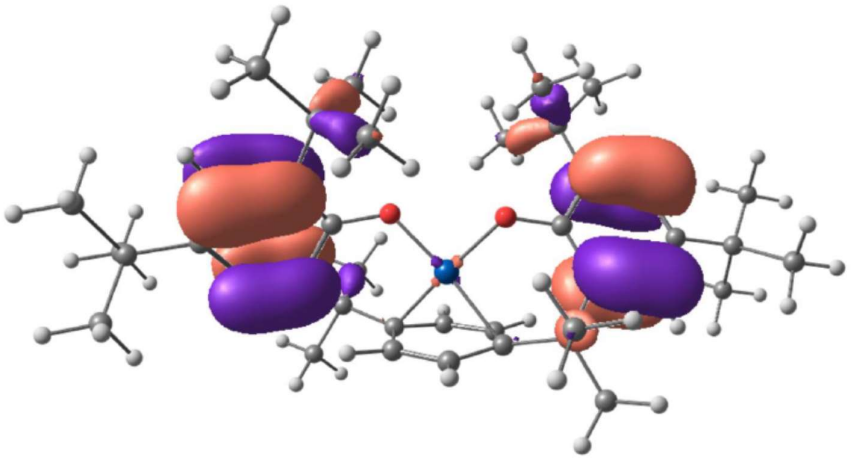
MO 159A HOMO - 6



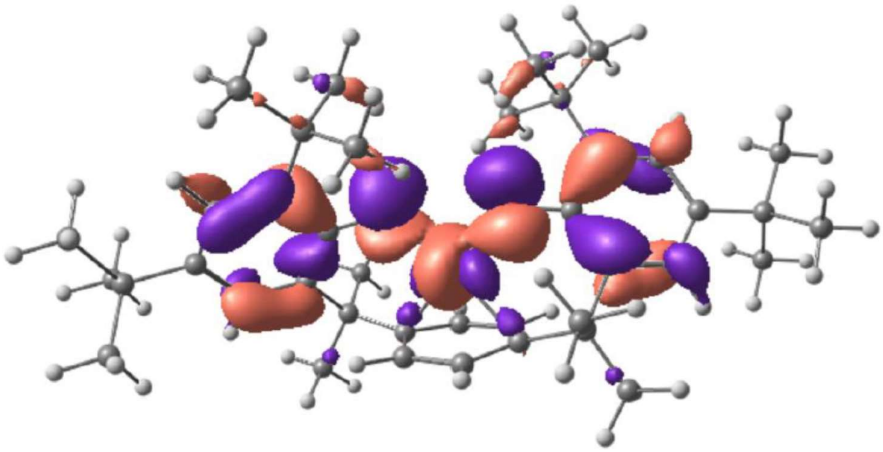
MO 160A HOMO - 5



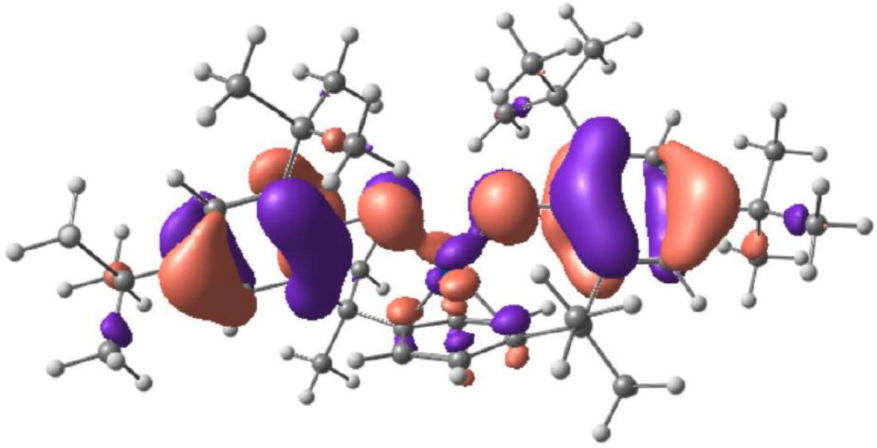
MO 161A HOMO - 4



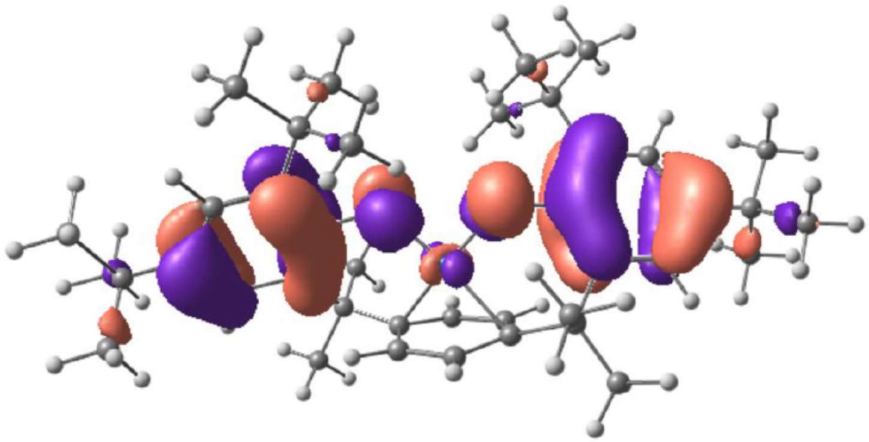
MO 162A HOMO - 3



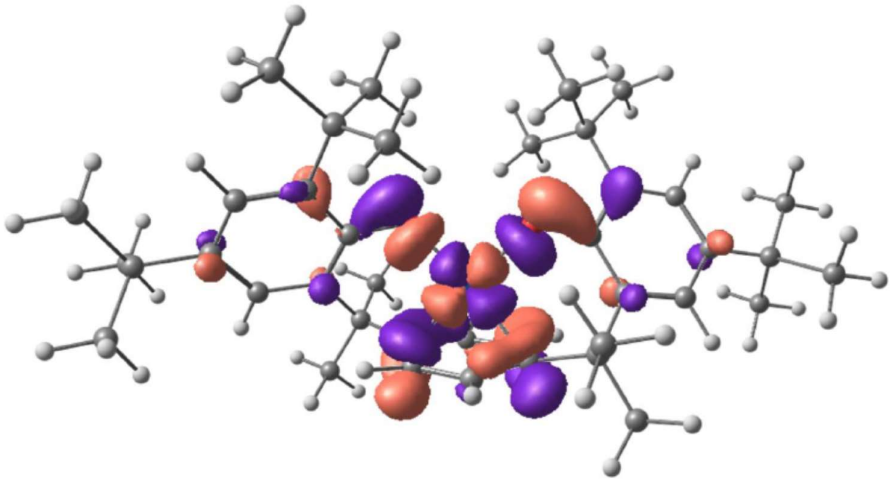
MO 163A HOMO - 2



MO 164A HOMO - 1

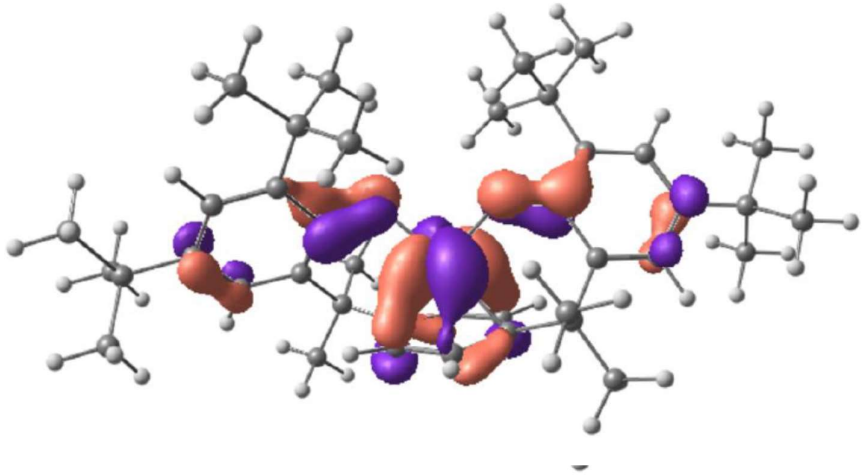


MO 165A HOMO

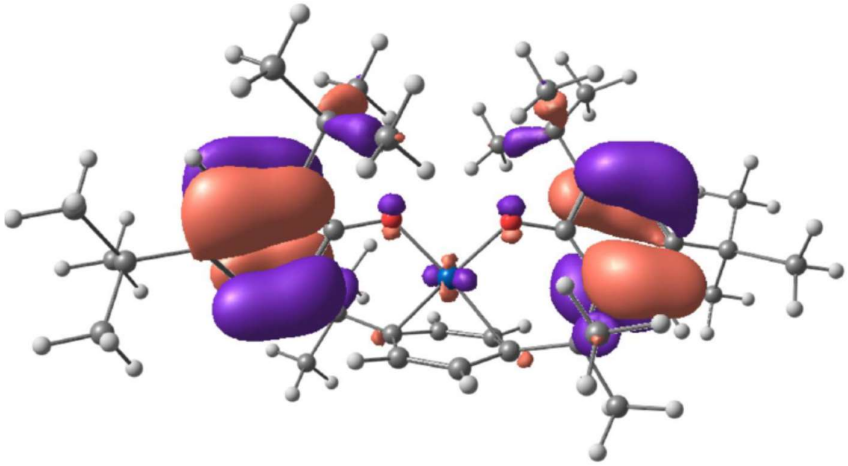


MO 166A LUMO

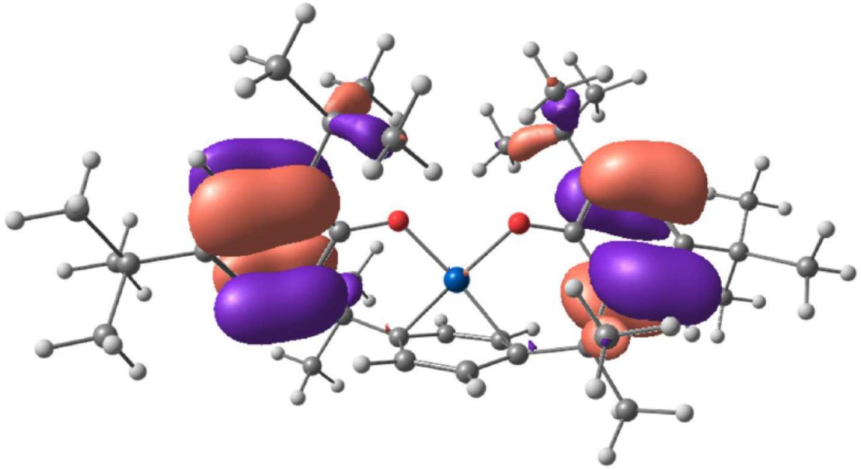
Beta MO's for (2-Co) (S = ½)



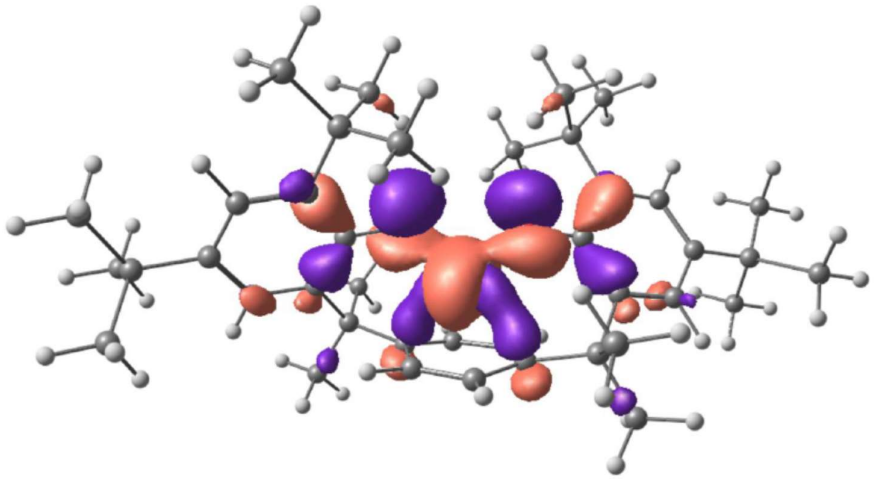
MO 159B HOMO - 5



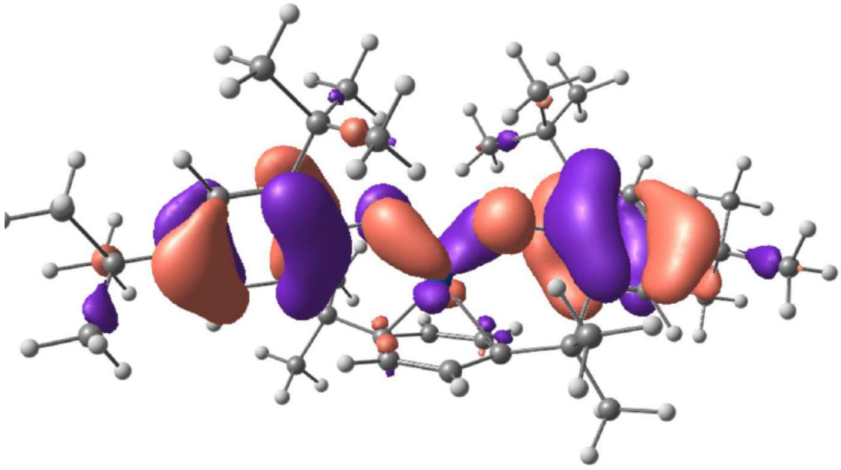
MO 160B HOMO - 4



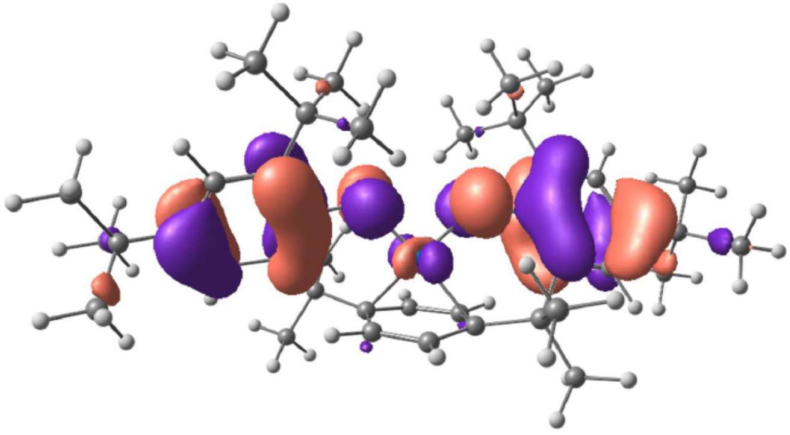
MO 161B HOMO - 3



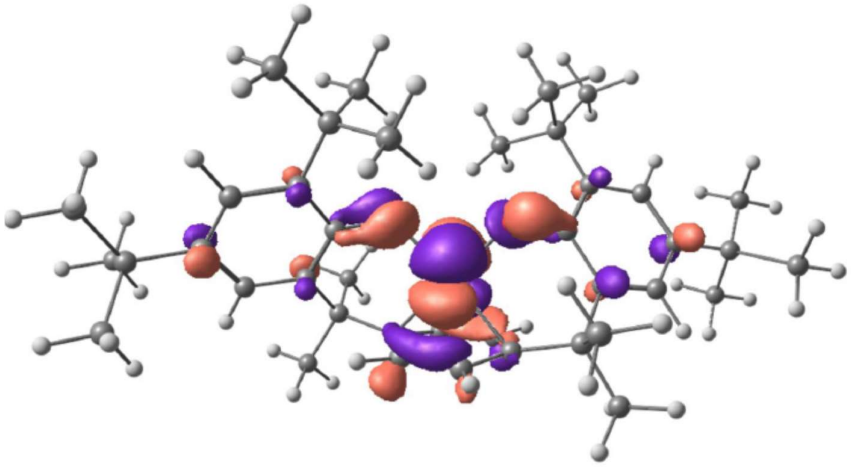
MO 162B HOMO - 2



MO 163B HOMO - 1

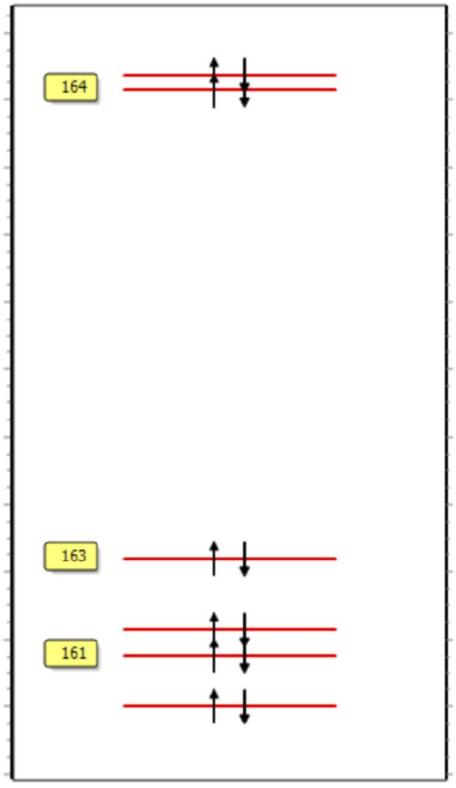


MO 164B HOMO



MO 165B LUMO

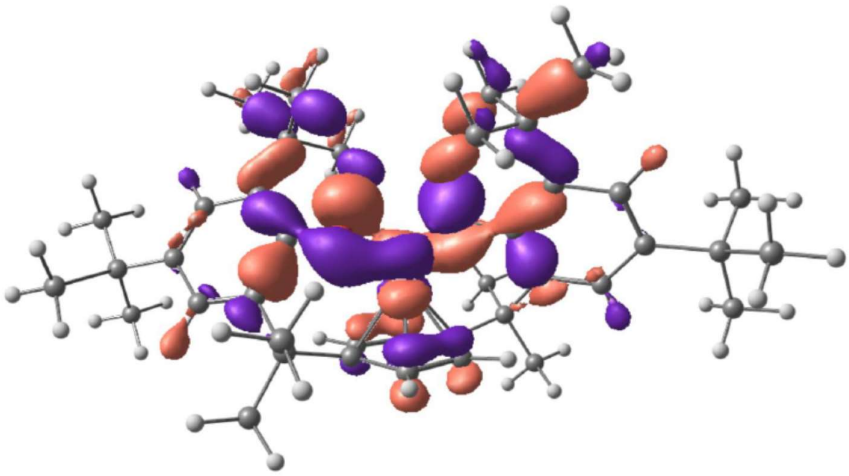
(2-Ni)



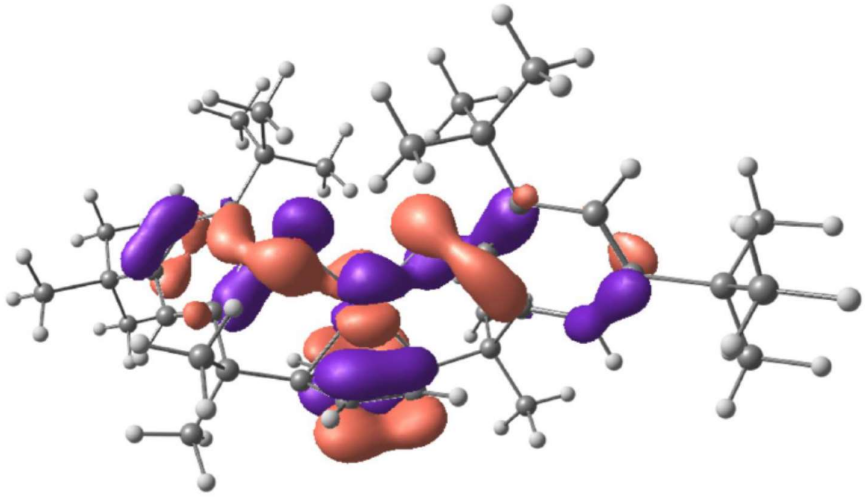
MO energies (A.U.)

MO num	Energy	Occupancy
159	-0.25936	Occupied
160	-0.23501	Occupied
161	-0.2312	Occupied
162	-0.22929	Occupied
163	-0.22405	Occupied
164	-0.18927	Occupied
165	-0.18816	Occupied
166	-0.09333	Unoccupied
167	-0.05464	Unoccupied
168	-0.05103	Unoccupied
169	-0.00294	Unoccupied

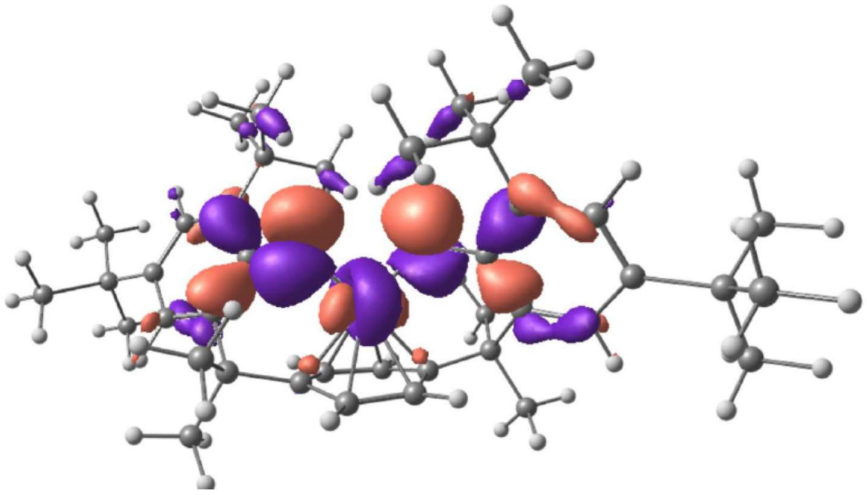
Figure 42: MO energy diagram for (**2-Ni**) (S = 0)



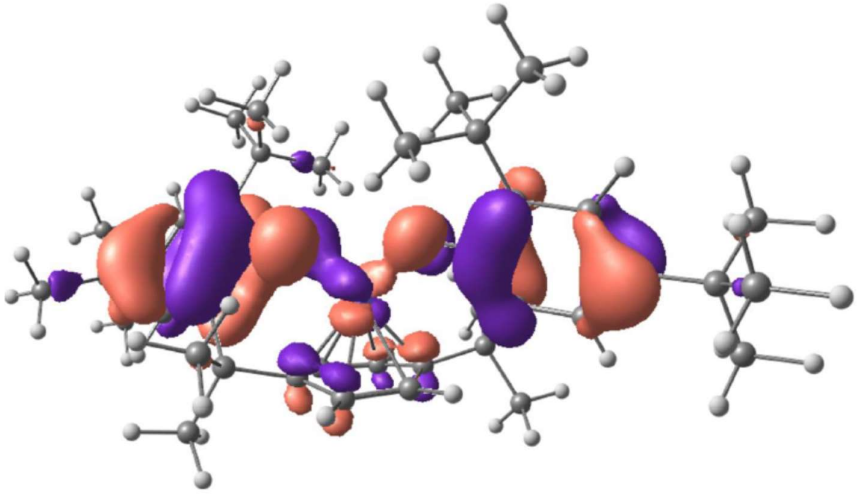
MO 159 HOMO - 6



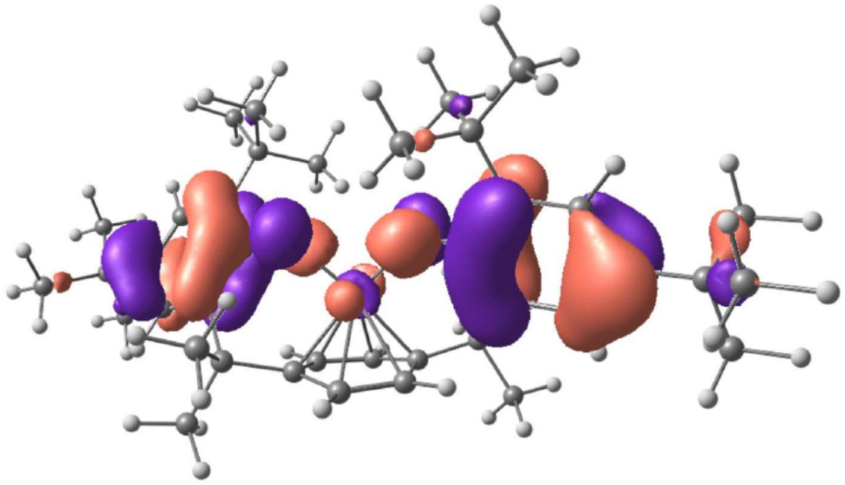
MO 160 HOMO - 5



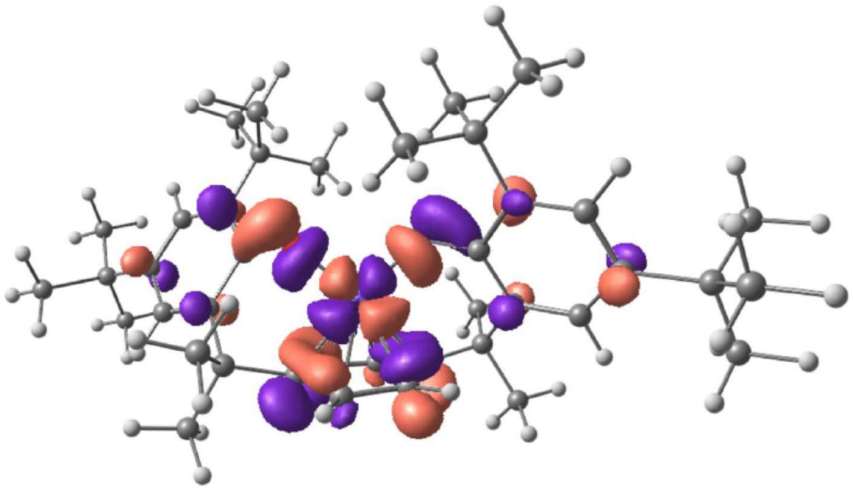
MO 163 HOMO - 2



MO 164 HOMO - 1



MO 165 HOMO



MO 166 LUMO

(2-Fe.THF)

(2-Fe.THF) spin multiplicity	ΔH (kcal/mol)	ΔG (kcal/mol)
Singlet	43.84	43.95
Quintet	0.0	0.0

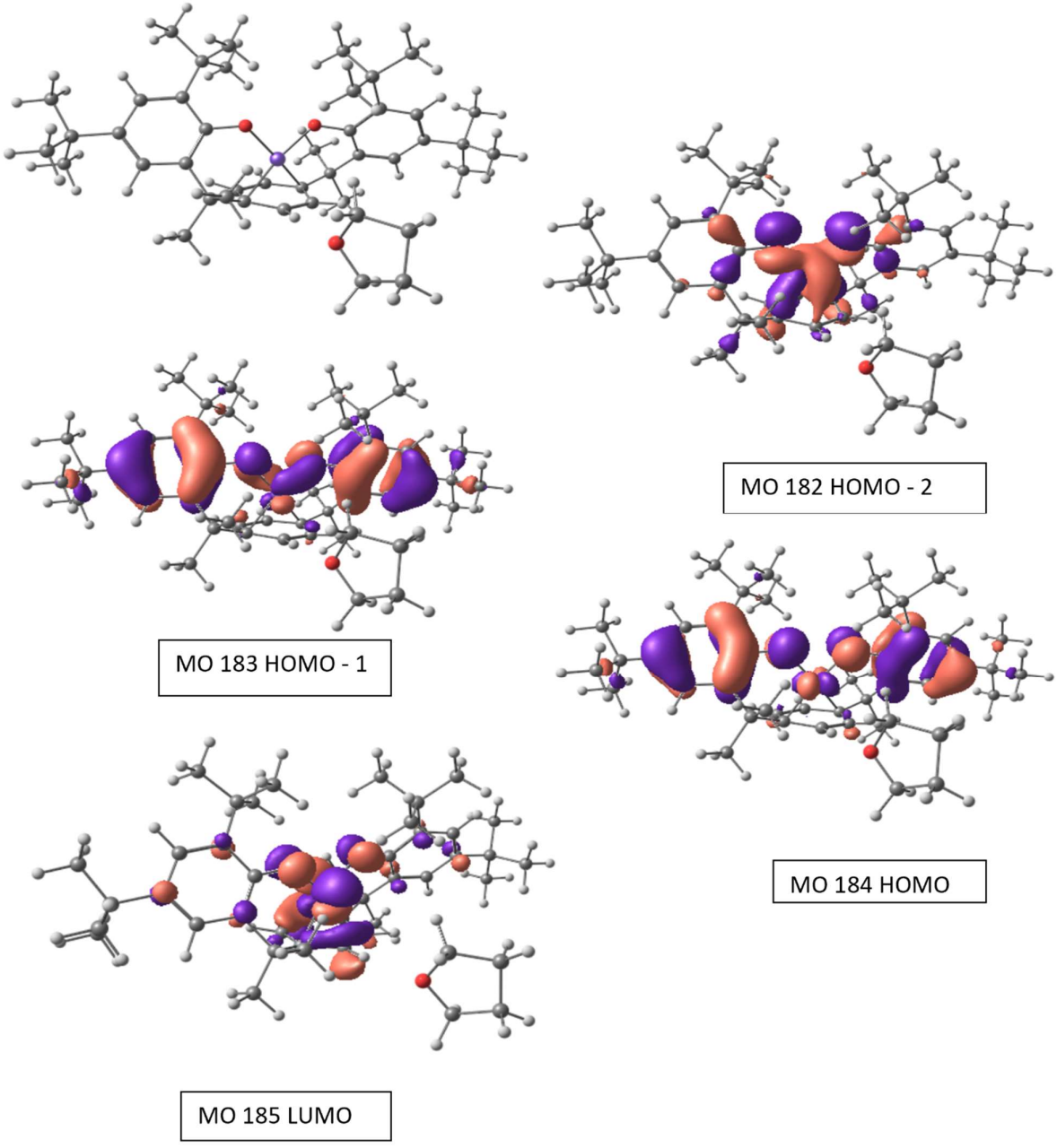
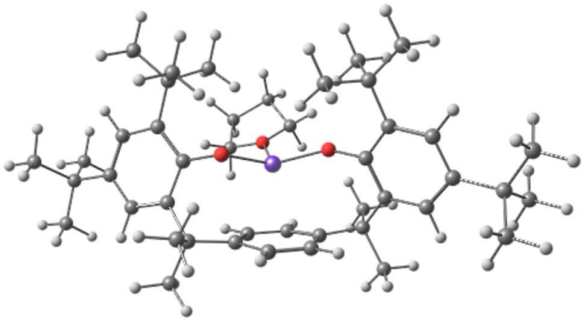
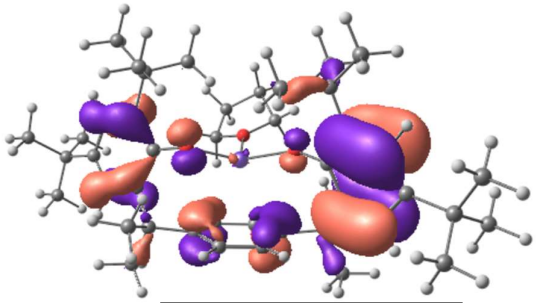
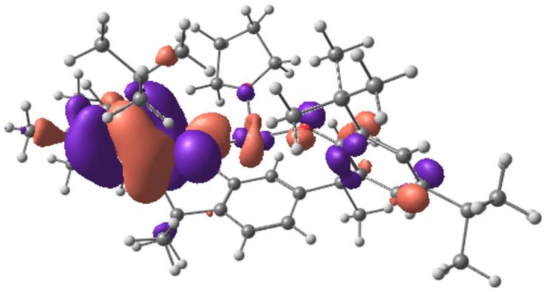


Figure 43: Calculated MO's for (**2-Fe.THF**) (S = 0)

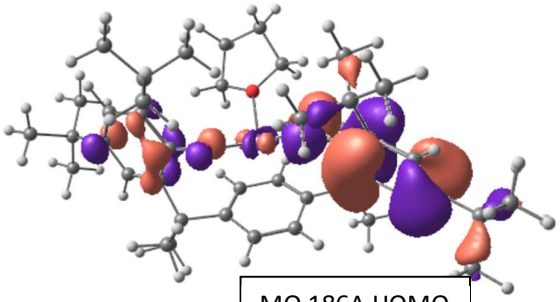




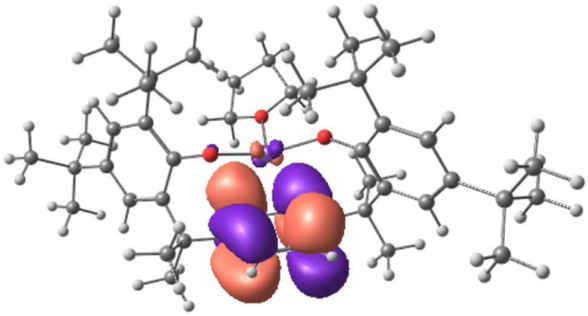
MO 184A HOMO - 2



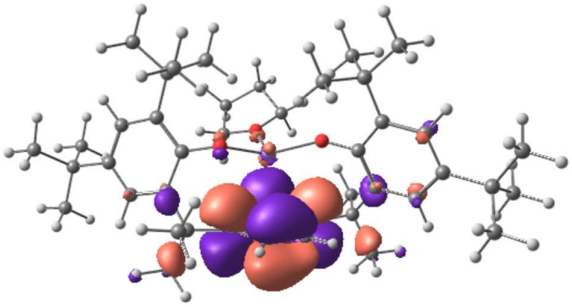
MO 185A HOMO - 1



MO 186A HOMO

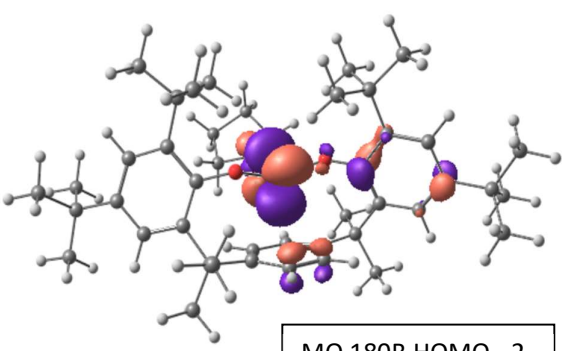


MO 187A LUMO

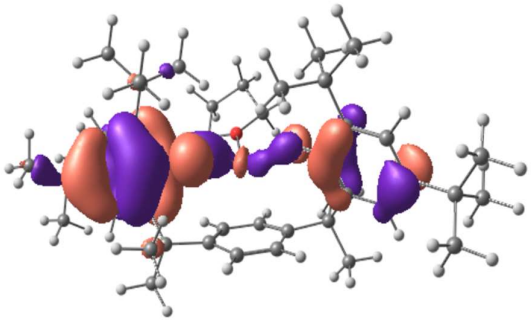


MO 188A LUMO + 1

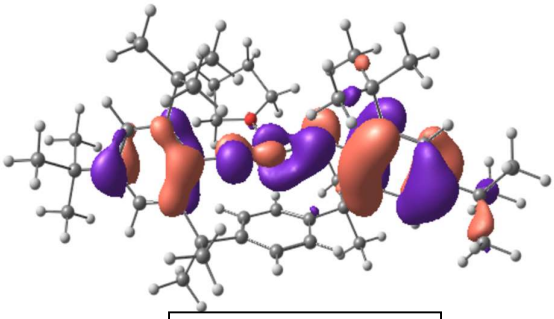
Figure 44: Alpha MO's for (**2-Fe.THF**) (S = 2)



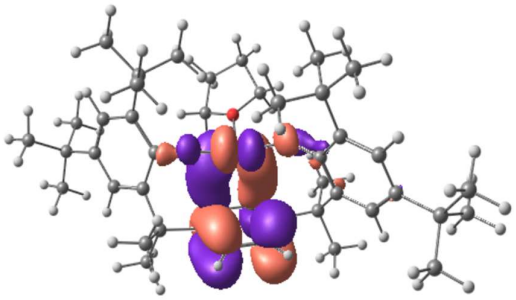
MO 180B HOMO - 2



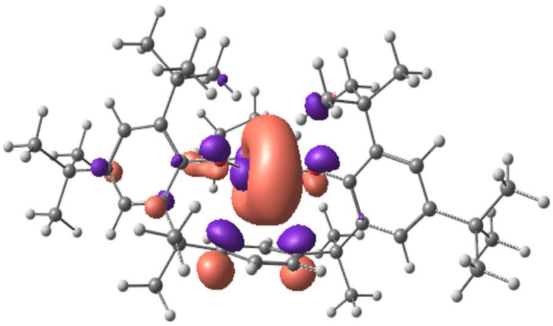
MO 181B HOMO - 1



MO 182B HOMO



MO 183B LUMO



MO 184B LUMO + 1

Figure 45: Beta MO's for (**2-Fe.THF**) (S = 2)

(2-Co.THF)

(2-Co.THF) spin multiplicity	ΔH (kcal/mol)	ΔG (kcal/mol)
Doublet	21.40	18.68
Quartet	0.0	0.0

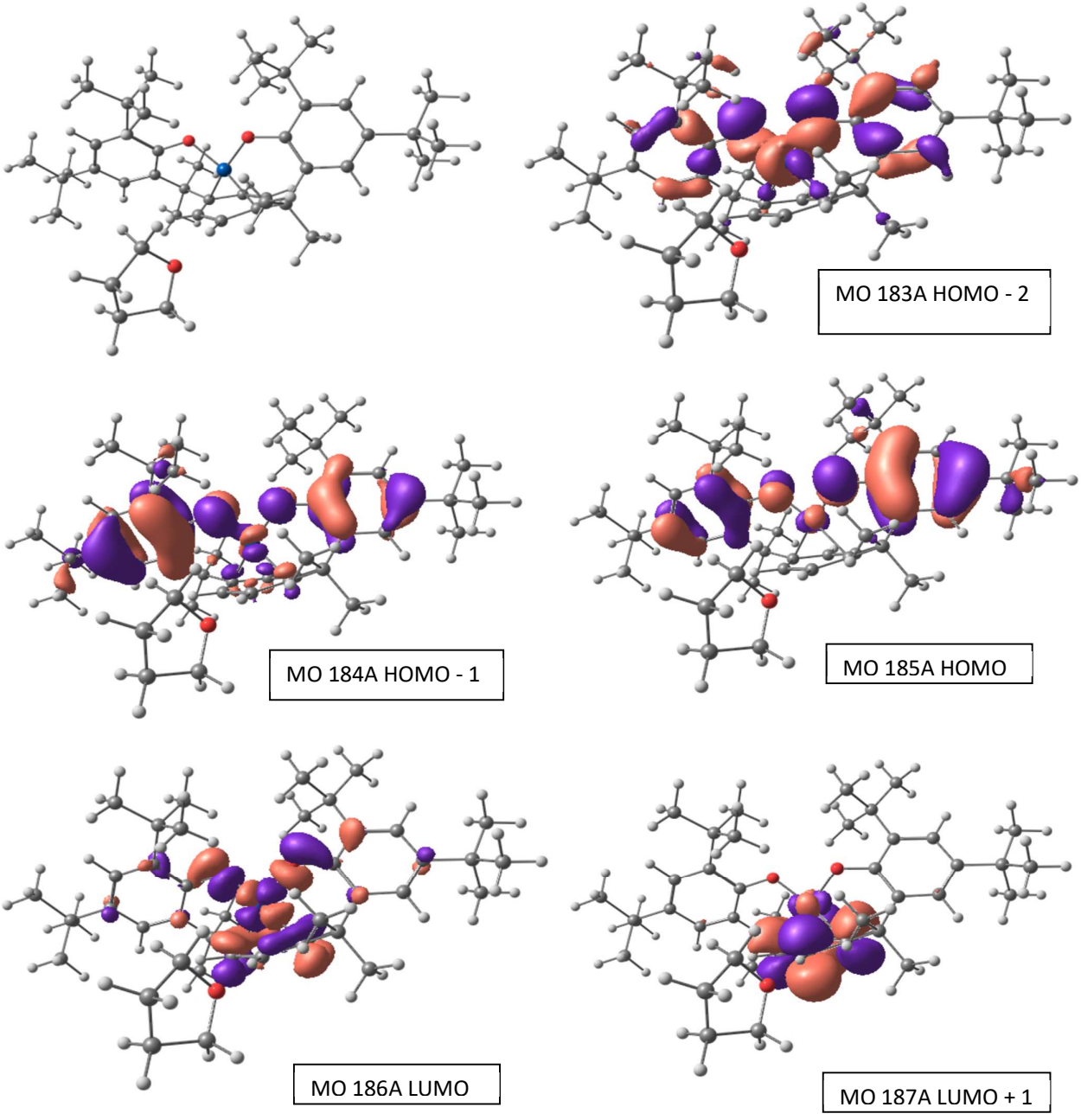


Figure 46: Alpha MO's for (**2-Co.THF**) (S = ½)

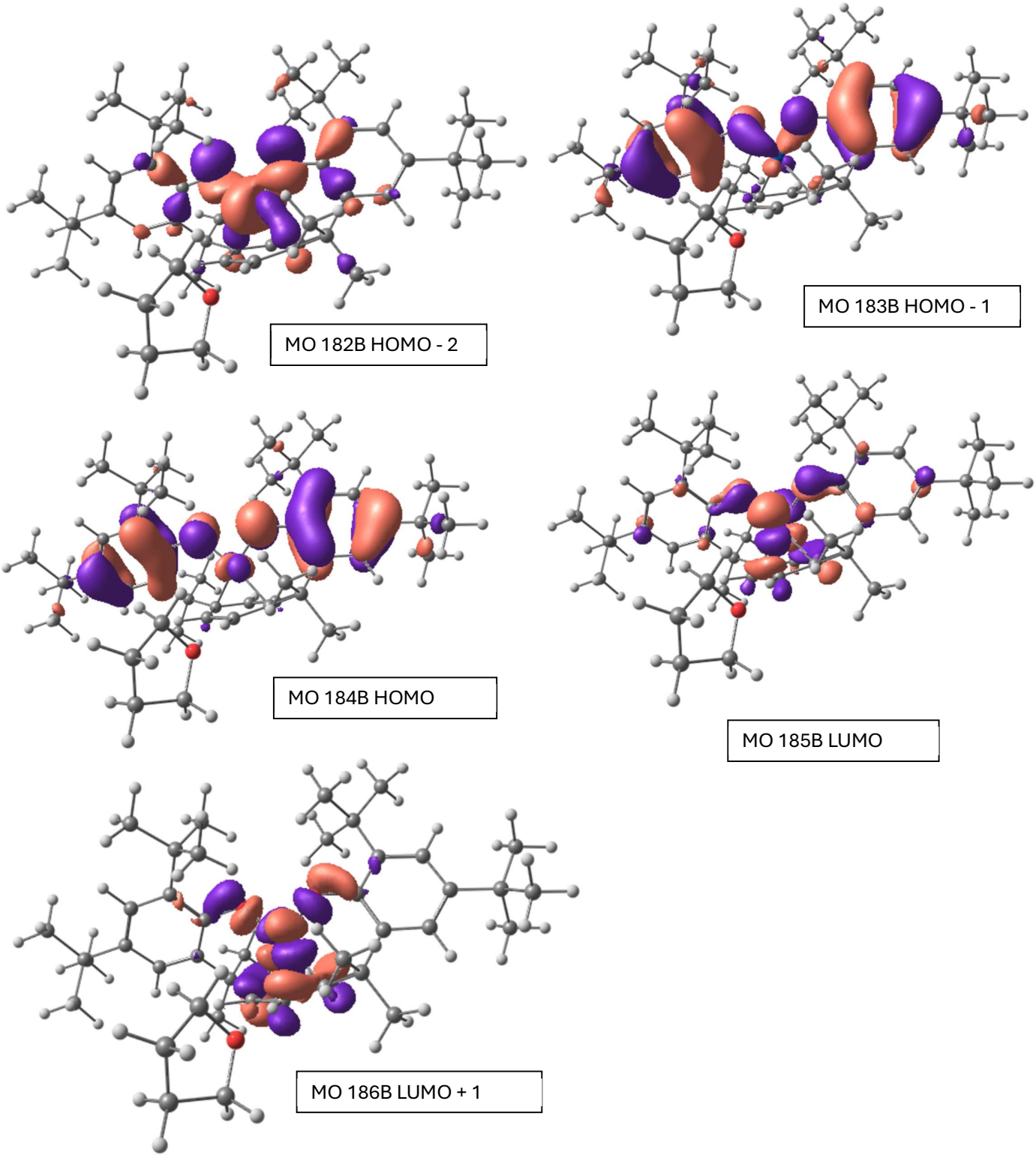


Figure 47: Beta MO's for (**2-Co.THF**) (S = ½)

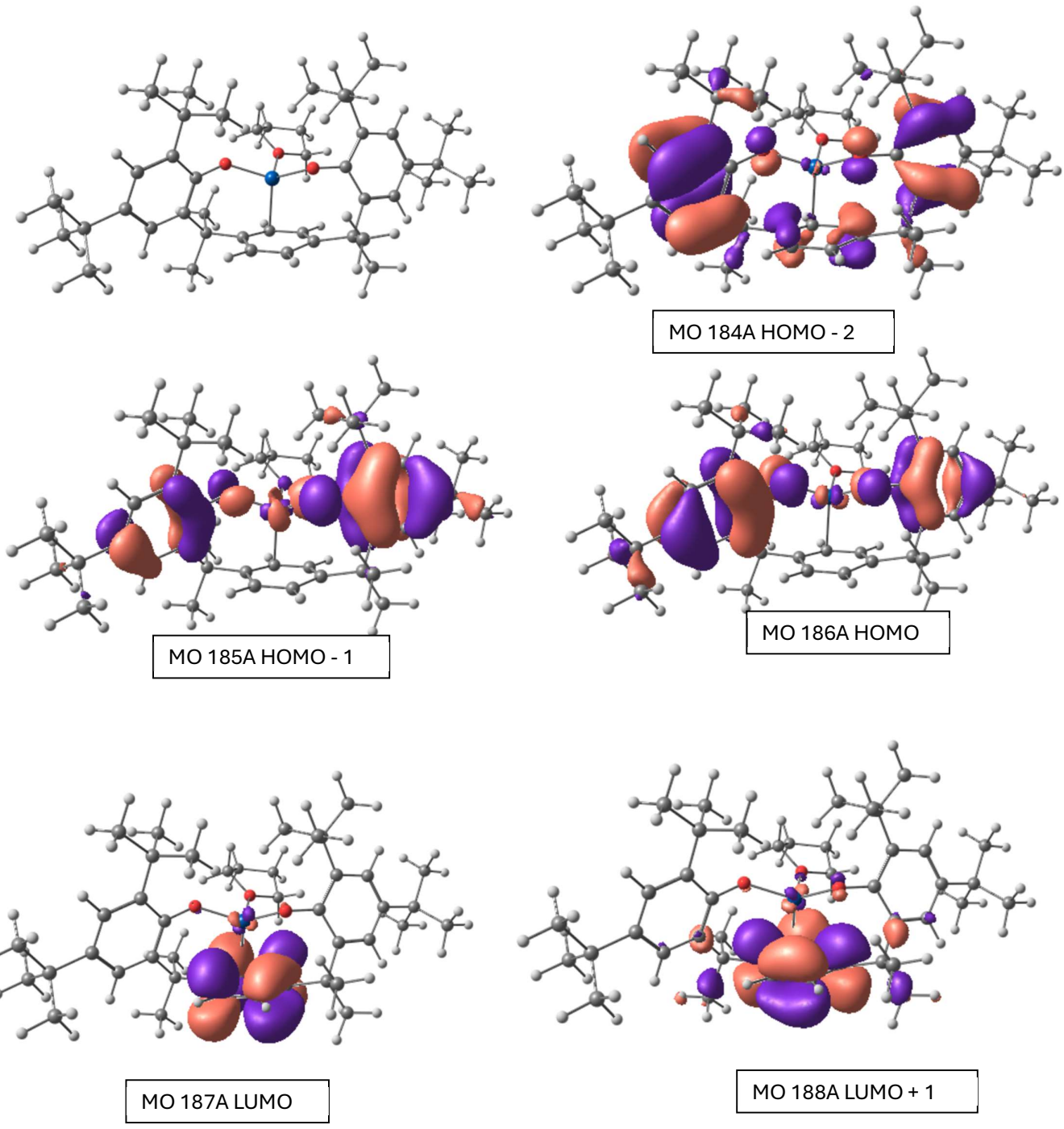


Figure 48: Alpha MO's for (**2-Co.THF**) (S = 3/2)

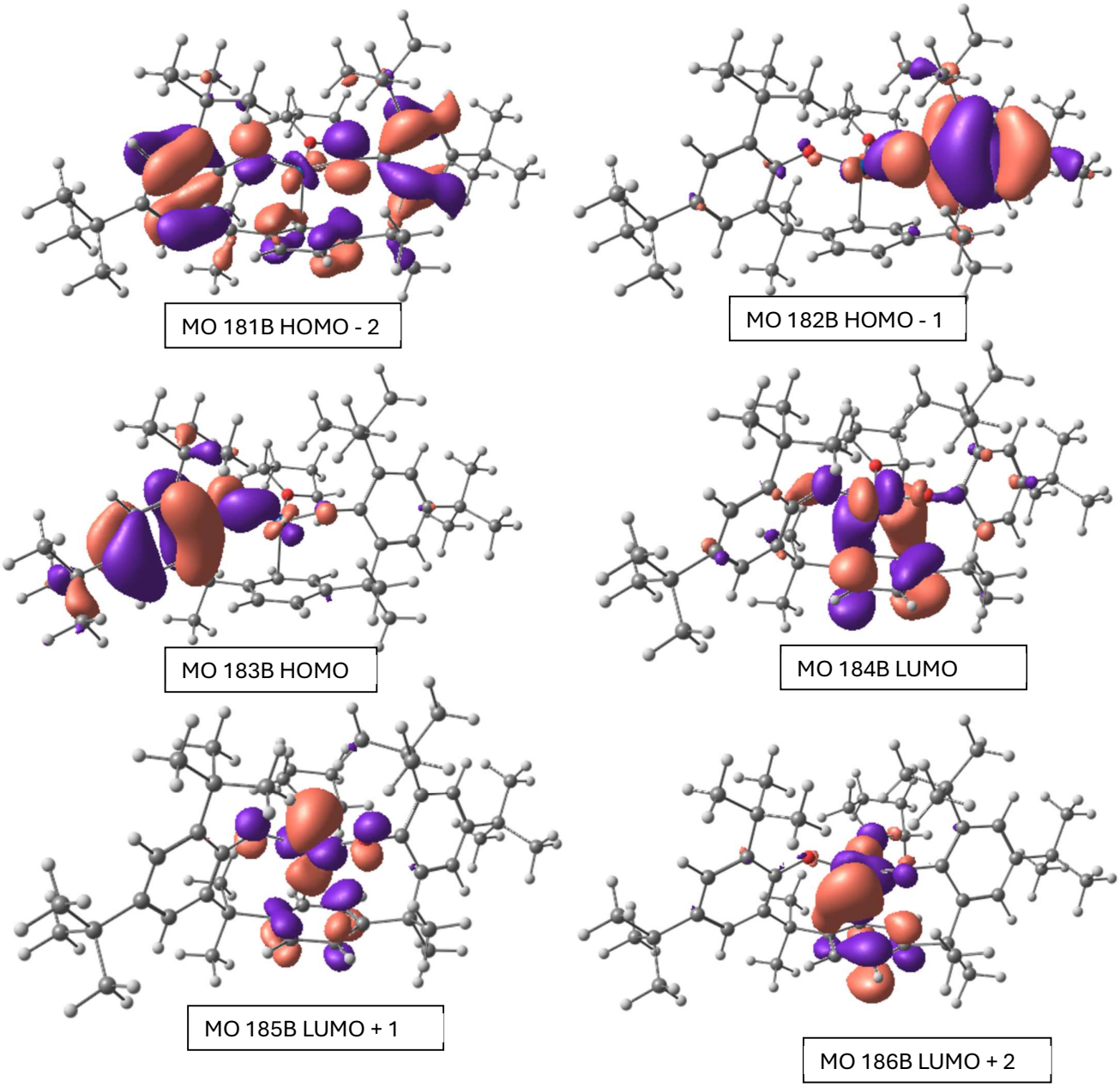


Figure 49: Beta MO's for (**2-Co.THF**) (S = 3/2)

Calculated IR C-C stretches:

(**2-Fe**): 1495 cm^{-1}

(**2-Co**): 1484 cm^{-1}

(**2-Ni**): 1433 cm^{-1}

(**2-Co.THF**): 1497 cm^{-1}

(**2-Fe.THF**): 1502 cm^{-1}

References

1 D. L. J. Broere, I. Čorić, A. Brosnahan and P. L. Holland, *Inorg Chem*, 2017, **56**, 3140–3143.

2 A. M. Bryan, G. J. Long, F. Grandjean and P. P. Power, *Inorg Chem*, 2013, **52**, 12152–12160.

3 M. Faust, A. M. Bryan, A. Mansikkamäki, P. Vasko, M. M. Olmstead, H. M. Tuononen, F. Grandjean, G. J. Long and P. P. Power, *Angewandte Chemie*, 2015, **127**, 13106–13109.

4 R. A. Keerthi Shivaraam, M. Keener, D. K. Modder, T. Rajeshkumar, I. Živković, R. Scopelliti, L. Maron and M. Mazzanti, *Angewandte Chemie - International Edition*, DOI:10.1002/anie.202304051.

5 G. A. Bain and J. F. Berry, *J Chem Educ*, 2008, **85**, 532–436.

6 C. J. Inman, A. S. P. Frey, A. F. R. Kilpatrick, F. G. N. Cloke and S. M. Roe, *Organometallics*, 2017, **36**, 4539–4545.

7 D. Brynn Hibbert and P. Thordarson, *Chemical Communications*, 2016, **52**, 12792–12805.

8 P. Thordarson, *Chem Soc Rev*, 2011, **40**, 1305–1323.

9 G. M. Sheldrick, *Acta Crystallogr A*, 2015, **71**, 3–8.

10 G. M. Sheldrick, *Acta Crystallogr C Struct Chem*, 2015, **71**, 3–8.

11 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J Appl Crystallogr*, 2009, **42**, 339–341.

12 C. B. Hübschle, G. M. Sheldrick and B. Dittrich, *J Appl Crystallogr*, 2011, **44**, 1281–1284.

13 J.M.M. Smits, C. Smykalla, P.T. Beurskens, W.P. Bosman and S. Garcia-Granda, *Journal Applied Crystallography*, 1994, **27**, 661–665.

14 L. J. Farrugia, *J Appl Crystallogr*, 2012, **45**, 849–854.

15 M. Sevvana, M. Ruf, I. Uson, G. M. Sheldrick and R. Herbst-Irmer, *Acta Crystallogr D Struct Biol*, 2019, **75**, 1040–1050.

16 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken and C. Adamo, 2013, preprint.

17 A. D. Becke, *J Chem Phys*, 1993, **98**, 5648–5652.

18 J. F. Dobson, M. P. Das and G. Vignale, *Electronic Density Functional Theory*, Springer US, Boston, MA, 1998.

19 X. Cao, M. Dolg and H. Stoll, *Journal of Chemical Physics*, 2003, **118**, 487–496.

20 W. Küchle, M. Dolg, H. Stoll and H. Preuss, *J Chem Phys*, 1994, **100**, 7535–7542.

21 P. C. Hariharan and J. A. Pople, *The Influence of Polarization Functions on Molecular Orbital Hydrogenation Energies*, Springer-Verlag, 1973, vol. 28.

22 W. J. Hehre, K. Ditchfield and J. A. Pople, *J Chem Phys*, 1972, **56**, 2257–2261.