Supporting Information

The Thiolate *Trans* Effect in Heme {FeNO}^{6} Complexes and Beyond: Insight into the Nature of the Push Effect

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Table of Contents

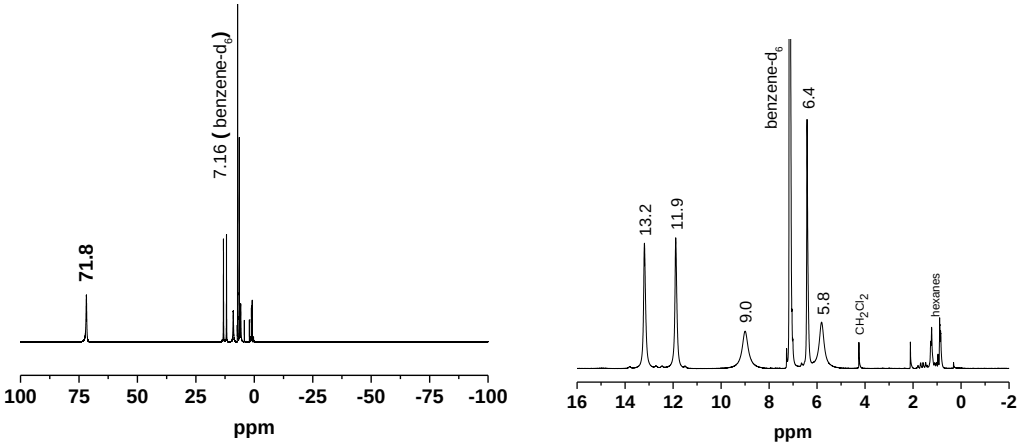

Figure S1. ^{1}H-NMR spectrum of [Fe(TPP)($SPhF_4CF_3$)] in benzene-d_6 at room temperature.

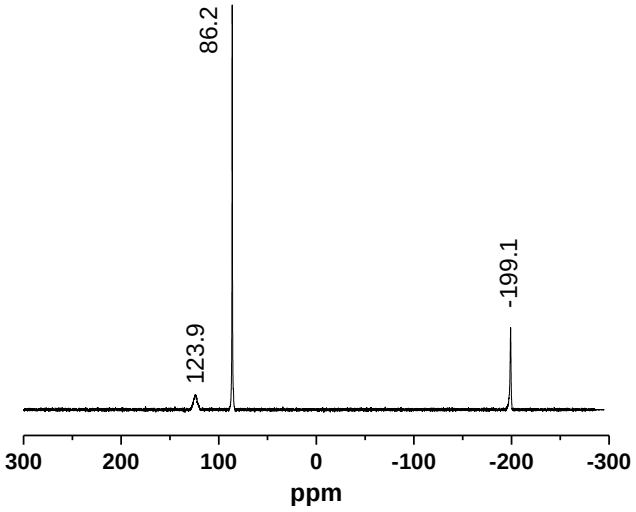

Figure S2. ^{19}F-NMR spectrum of Fe(TPP)($SPhF_4CF_3$)] in benzene-d_6 at room temperature.

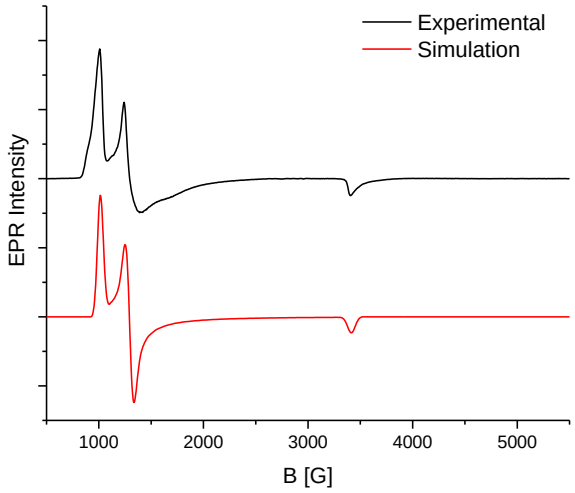

Figure S3. EPR spectrum of [Fe(TPP)($SPhF_4CF_3$)] (black) in 1:1 CH_2Cl_2:toluene, recorded at 4 K ($g_{eff,\,x}$ = 6.6, $g_{eff,\,y}$ = 5.1, and $g_{eff,\,z}$ = 1.95). The simulated spectrum was generated using the program SpinCount. Fit parameters are g_x = 1.945, g_y = 1.96, g_z = 1.975, g_x-strain = 0.045, g_y-strain = 0.05, g_z-strain = 0.02, D = 7 cm^{-1}, E/D = 0.03, E/D-strain = 0.03.

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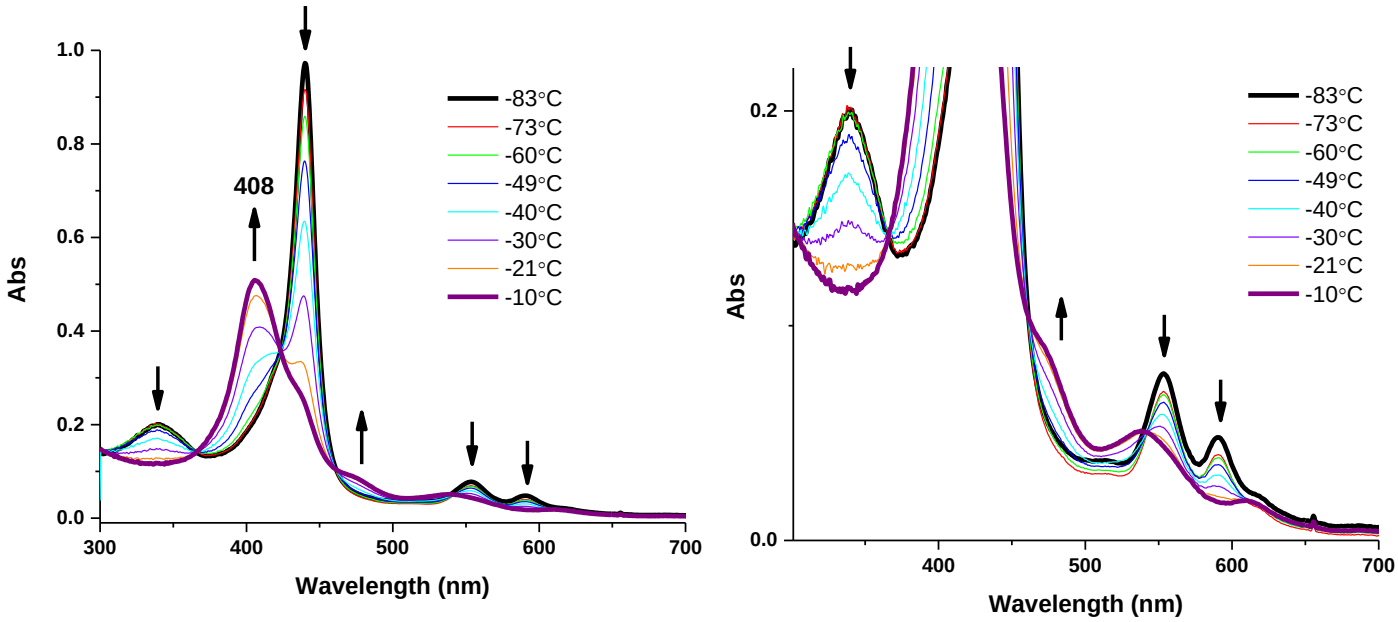

Figure S4. UV-Vis spectral changes observed upon allowing a solution of *in situ* generated [Fe(TPP)($SPhF_4CF_3$)(NO)] (black) to warm up from -80 °C to -10 °C. Arrows indicate the direction of spectral changes over time.

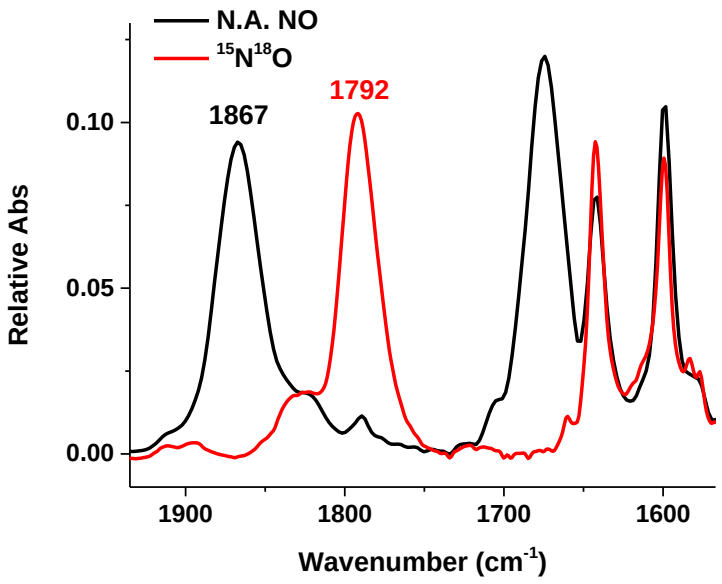

Figure S5. Overlay of the first scans from the solution IR measurements (Figures 7 and 8) of [Fe(TPP)($SPhF_4CF_3$)(NO)], prepared with natural abundance isotopes (n.a.i.) NO (black) and isotopically labeled $^{15}N^{18}O$ (red).

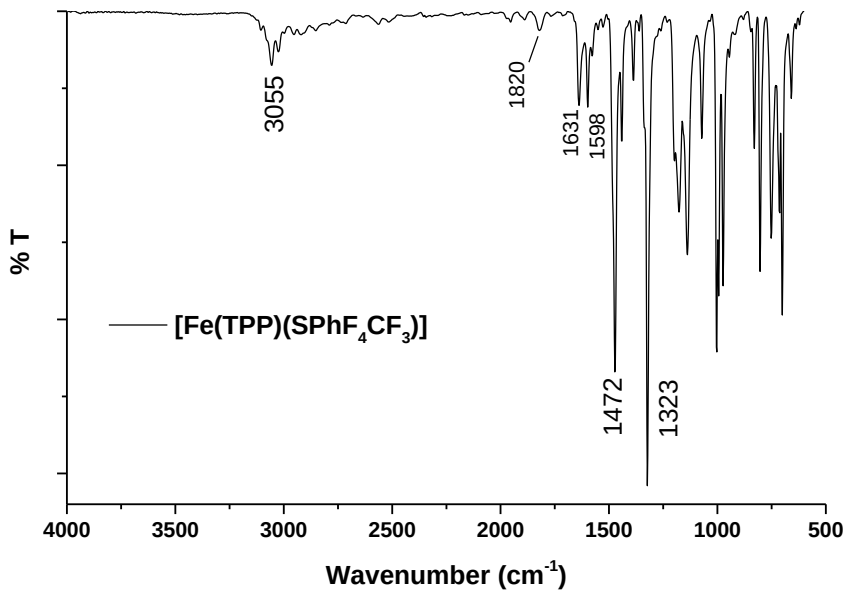

Figure S6. ATF-FTIR of solid [Fe(TPP)($SPhF_4CF_3$)] at room temperature. The 1820 cm^{-1} aromatic overtone band of [Fe(TPP)] complexes is labeled, as well as the 1631 and 1598 cm^{-1} bands which are seen in the low temperature solution IR spectra, showing that these are signals originating from the TPP^{2-} ligand.

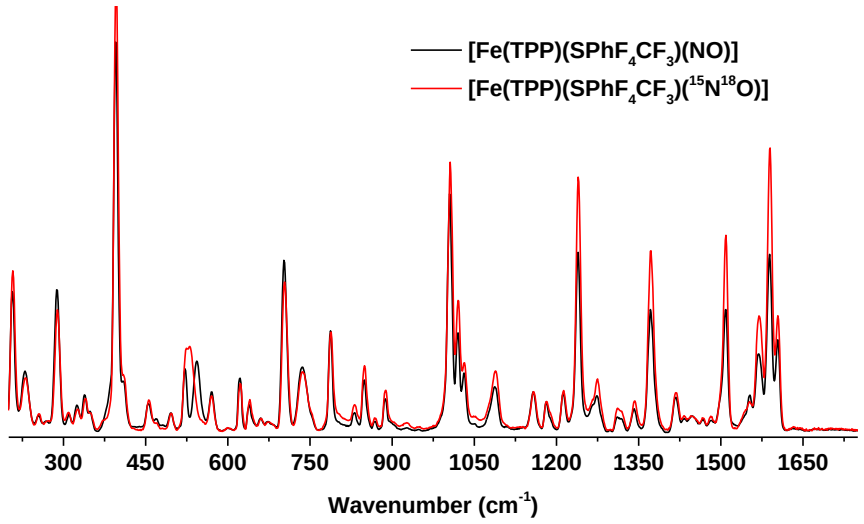

Figure S7. Overlay of the resonance Raman spectra (458 nm excitation) of n.a.i. [Fe(TPP)($SPhF_4CF_3$)(NO)] and [Fe(TPP)($SPhF_4CF_3$)($^{15}N^{18}O$)], prepared in a 1:1 mixture of CH_2Cl_2:toluene, and collected at 77 K (liquid N_2).

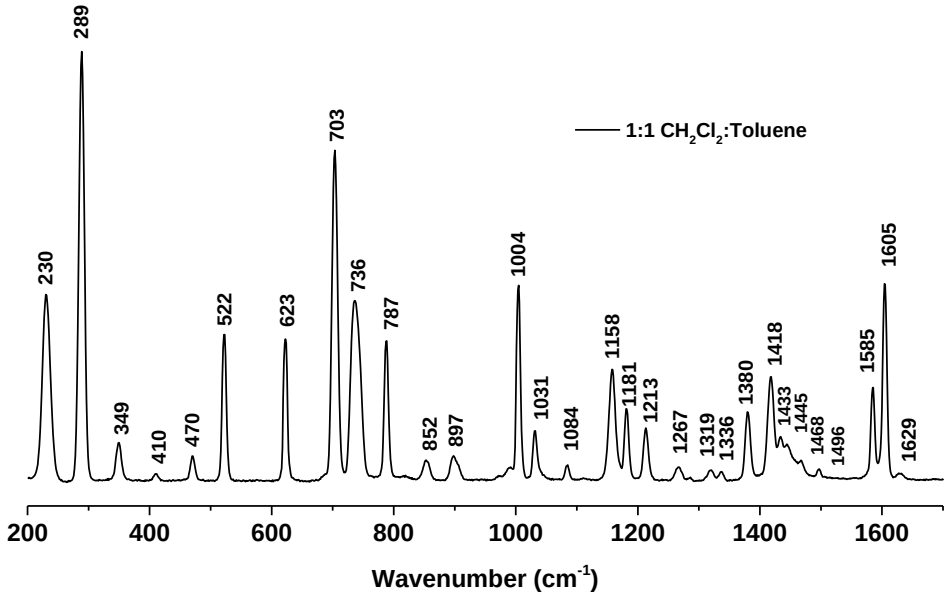

Figure S8. Resonance Raman spectrum (458 nm excitation) of a 1:1 mixture of CH_2Cl_2 and toluene as a frozen glass, recorded at 77 K (liquid N_2). This solvent mixture was used as the solvent for all rRaman samples.

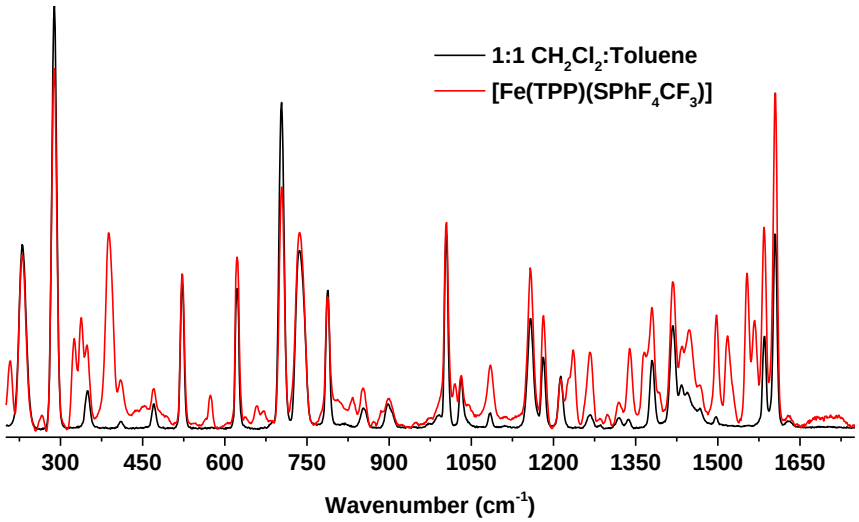

Figure S9. Resonance Raman spectrum (458 nm excitation) of [Fe(TPP)($SPhF_4CF_3$)] overlaid with the spectrum of the 1:1 mixture of CH_2Cl_2 and toluene, recorded at 77 K.

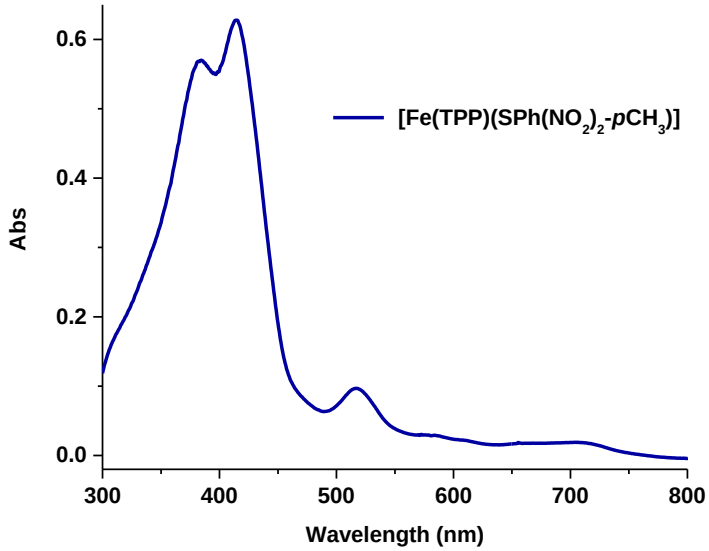

Figure S10. UV-Vis spectrum of [Fe(TPP)($SPh(NO_2)_2$-*p*CH_3)] in toluene at room temperature.

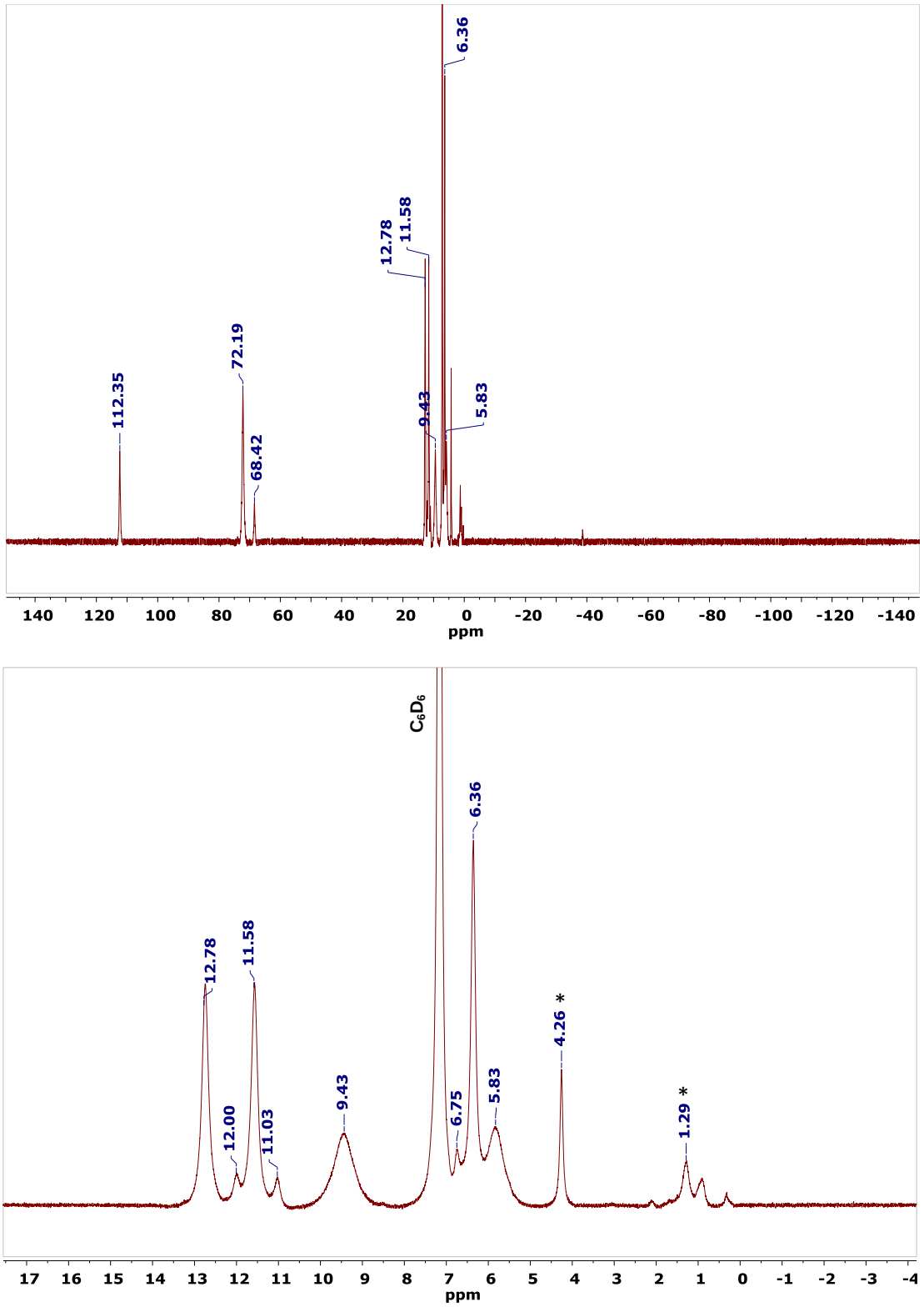

Figure S11. ^{1}H-NMR spectrum of [Fe(TPP)(SPh(NO_2)$_2$-*p*CH_3)] in benezene-d_6 at room temperature. The asterisk denotes residual CH_2Cl_2 (4.26) and hexanes (1.29) in the NMR sample. A minor amount of the unidentified decomposition product can be seen at 12.0, 11.0, 6.5, and -39 ppm; see below.

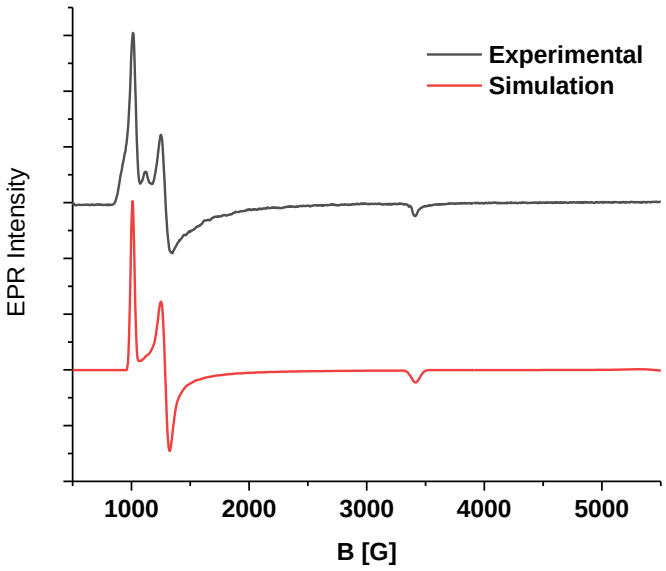

Figure S12. EPR spectrum of [Fe(TPP)(SPh(NO_2)$_2$-*p*CH_3)] in 1:1 CH_2Cl_2:toluene, collected at 4 K. The simulated spectrum was generated using the program SpinCount. Fit parameters are g_x = 1.977, g_y = 1.97, g_z = 1.98, g_x-strain = 0.04, g_y-strain = 0.025, g_z-strain = 0.02, D = 7 cm^{-1}, E/D = 0.031, E/D-strain = 0.01.

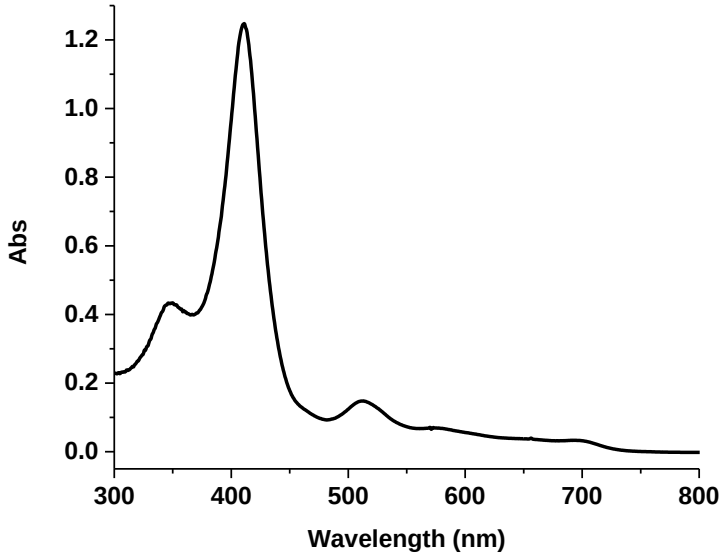

Figure S13. UV-Vis spectrum of the [Fe(TPP)(SPh(NO_2)$_2$-*p*CH_3)] decomposition product shown in Figure S14 (diluted in CH_2Cl_2). λ_{max} = 346, 411, 512, 574, 695 nm.

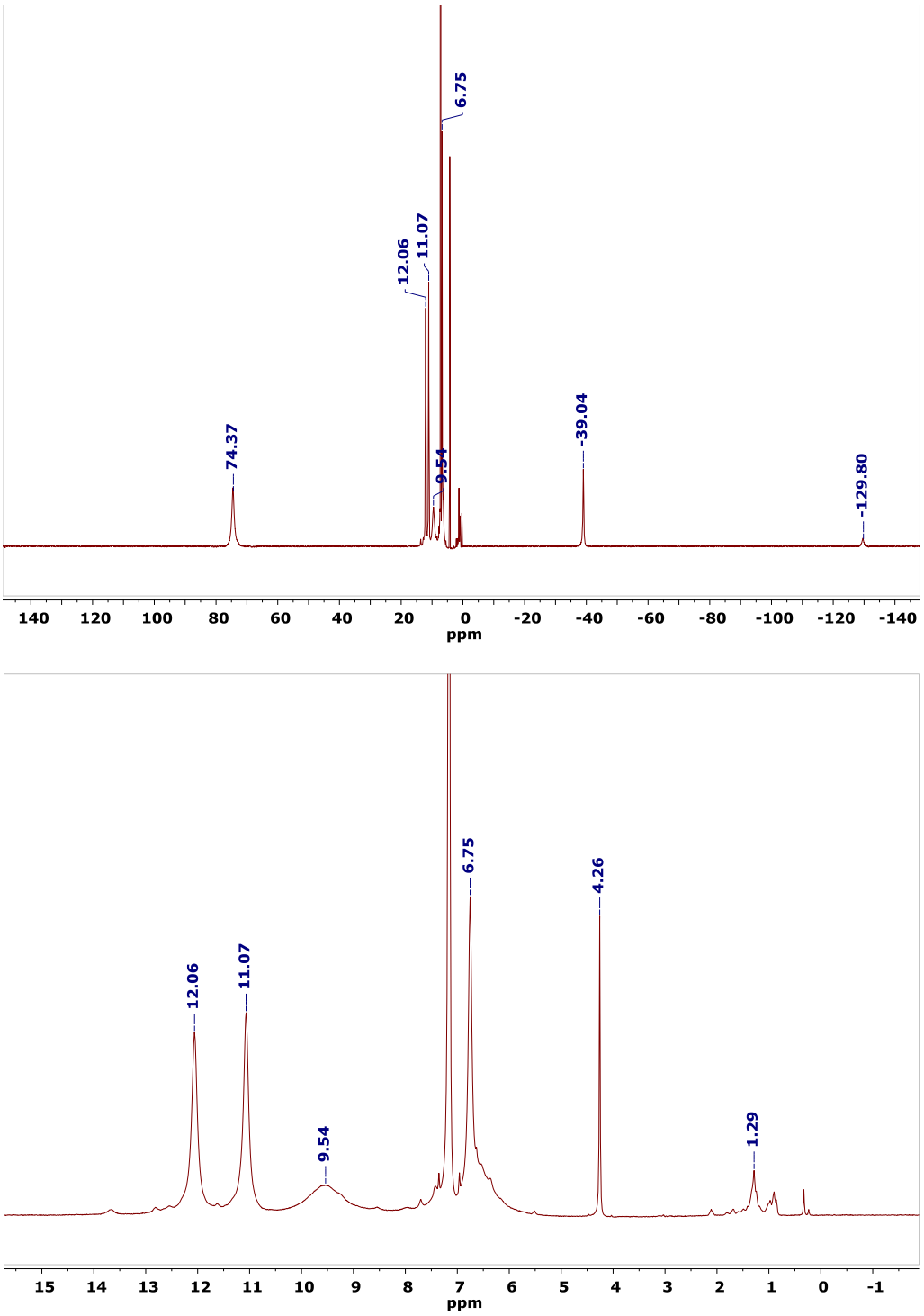

Figure S14. ^{1}H-NMR spectrum of the same sample of [Fe(TPP)(SPh(NO_2)$_2$-*p*CH_3)] shown in Figure S11, 24 hr after the sample was dissolved in benezene-d_6. Decomposition of [Fe(TPP)(SPh(NO_2)$_2$-*p*CH_3)] is observed, generating a new, unidentified high-spin ferric heme complex with chemical shifts of 74.4 (beta pyrrole-H), 12.06 and 11.07 (*m*-Ph TPP), 9.54(*o*-Ph TPP), 6.75 (*p*-Ph TPP), -39.0, and -129.8 ppm. Due to this decomposition, all solutions of [Fe(TPP)(SPh(NO_2)$_2$-*p*CH_3)] were prepared immediately before measurements were conducted, and used within one hour for the preparation of the {FeNO}^{6} complex.

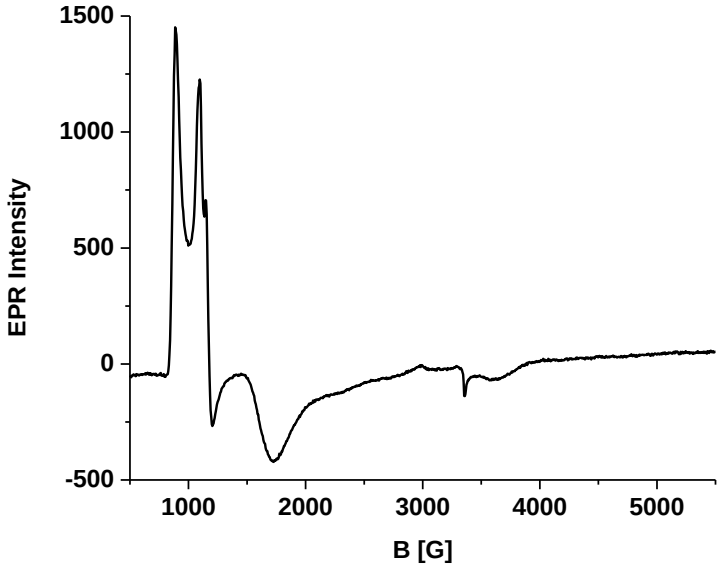

Figure S15. EPR spectrum of the decomposition product of [Fe(TPP)(SPh(NO_2)$_2$-*p*CH_3)] in 1:1 CH_2Cl_2:toluene, collected at 4 K. The EPR spectrum suggests multiple products, but confirms the high-spin nature of the major product characterized by ^{1}H-NMR in Figure S14.

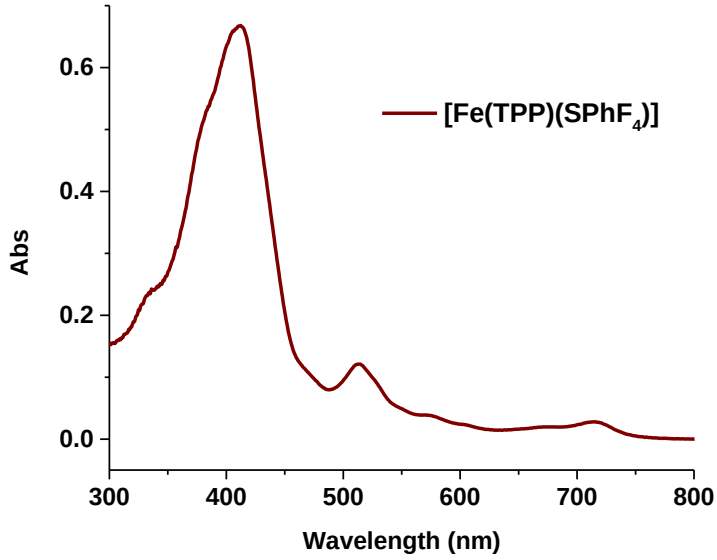

Figure S16. UV-Vis spectrum of [Fe(TPP)($SPhF_4$)] in toluene at room temperature.

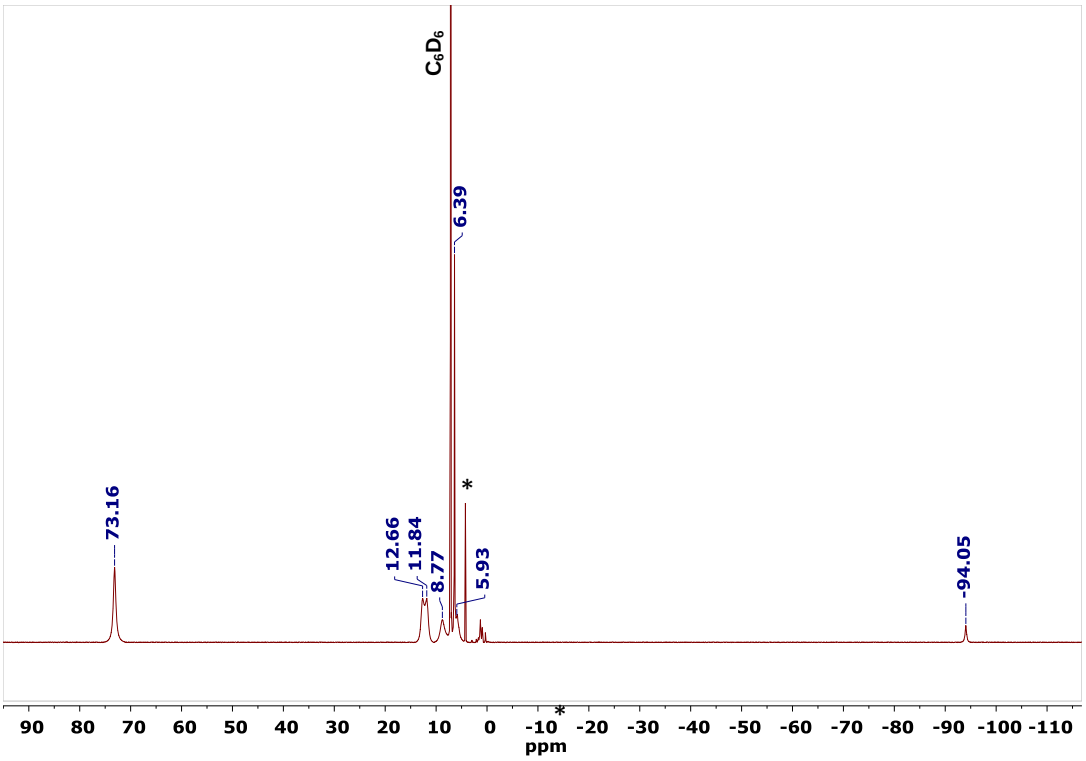

Figure S17. ^{1}H-NMR spectrum of [Fe(TPP)($SPhF_4$)] in benezene-d_6 at room temperature. The asterisk denotes residual CH_2Cl_2 in the NMR sample.

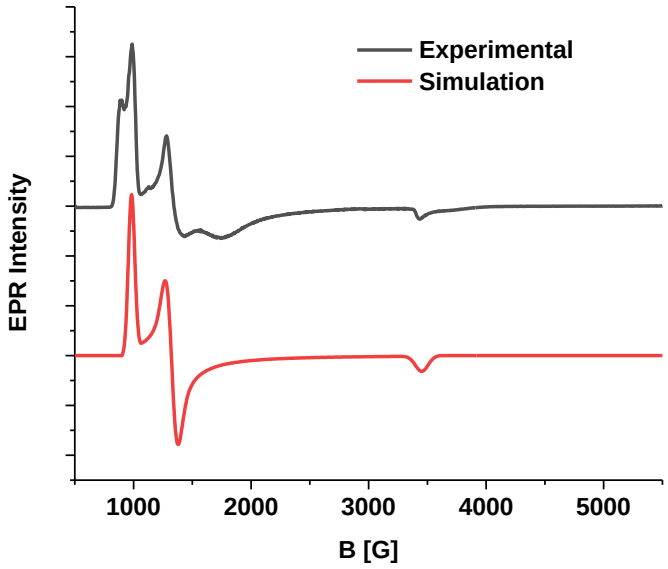

Figure S18. EPR spectrum of [Fe(TPP)($SPhF_4$)] in 1:1 CH_2Cl_2:toluene, collected at 4 K. The dominant species was fit (the red spectrum) using the program SpinCount. Fit parameters are g_x = 1.971, g_y = 1.971, g_z = 1.97, g_x-strain = 0.06, g_y-strain = 0.05, g_z-strain = 0.03, D = 7 cm^{-1}, E/D = 0.038, D-strain = 1, E/D-strain = 0.001.

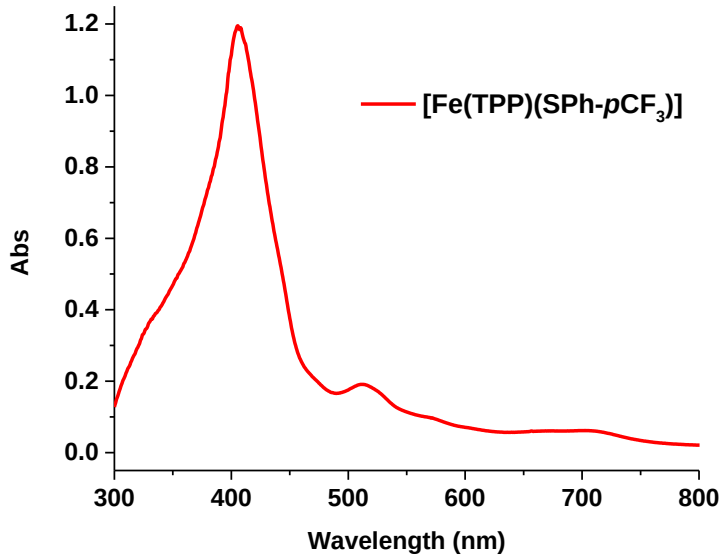

Figure S19. UV-Vis spectrum of [Fe(TPP)(SPh-*p*CF_3)] in toluene at room temperature.

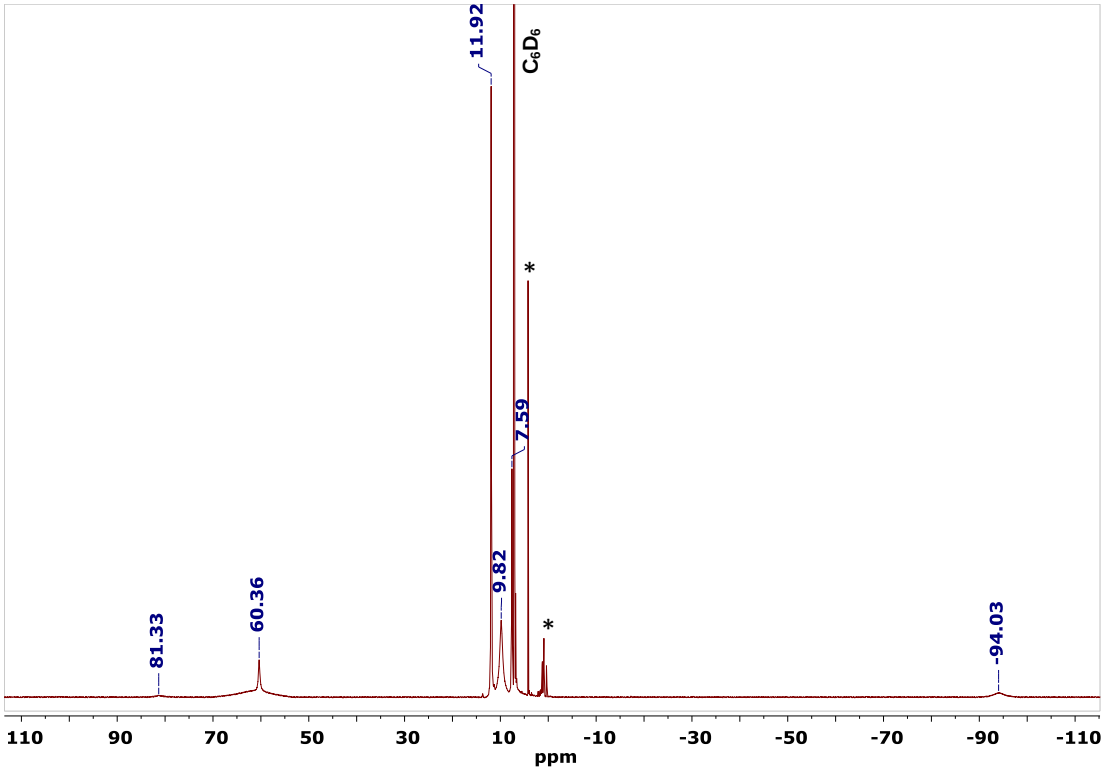

Figure S20. ^{1}H-NMR spectrum of [Fe(TPP)(SPh-*p*CF_3)] in benezene-d_6 at room temperature. The asterisk denotes residual CH_2Cl_2 and hexanes in the NMR sample.

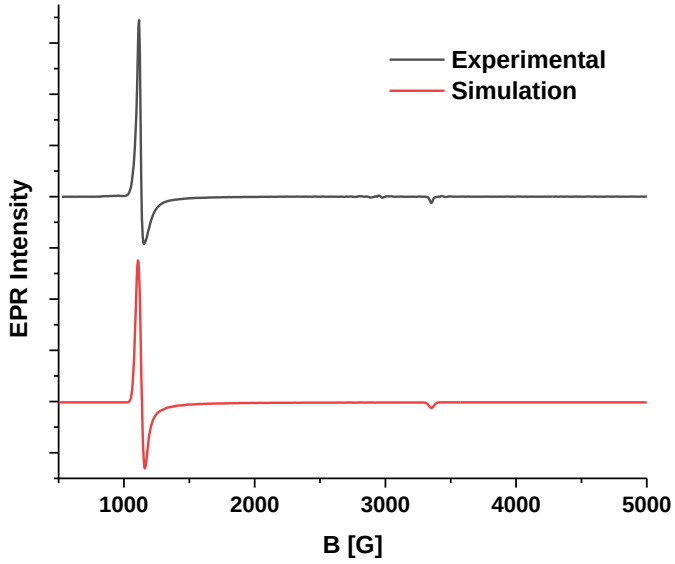

Figure S21. EPR spectrum of [Fe(TPP)(SPh-*p*CF_3)] in 1:1 CH_2Cl_2:toluene, collected at 4 K. The simulated spectrum was generated using the program SpinCount. Fit parameters are g_x = 1.976, g_y = 1.976, g_z = 1.98, g_x-strain = 0.37, g_y-strain = 0.05, g_z-strain = 0.01, D = 7 cm^{-1}, E/D = 0.

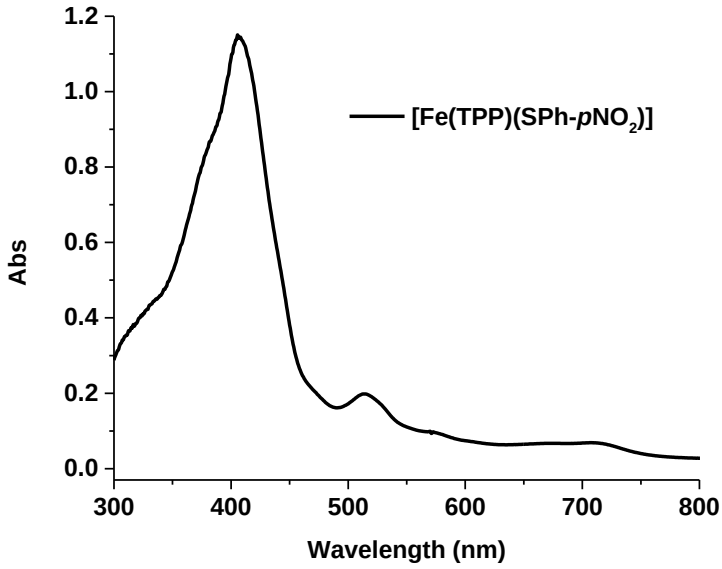

Figure S22. UV-Vis spectrum of [Fe(TPP)(SPh-*p*NO_2)] in toluene at room temperature.

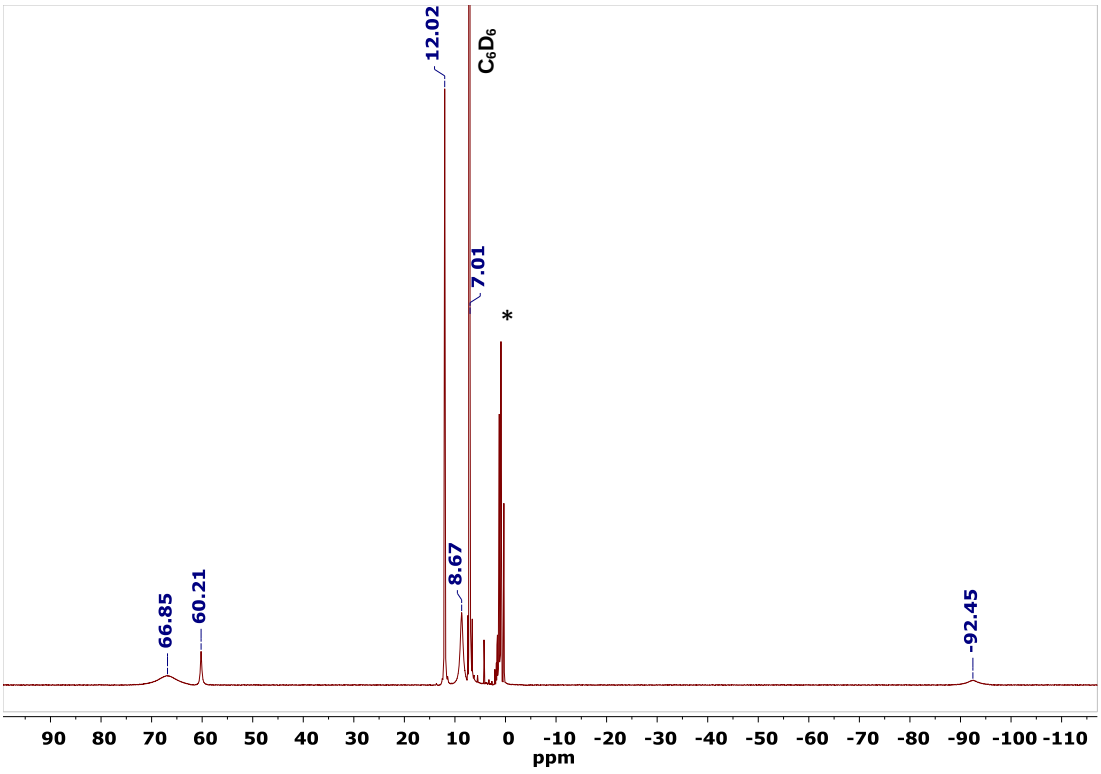

Figure S23. ^{1}H-NMR spectrum of [Fe(TPP)(SPh-*p*NO_2)] in benezene-d_6 at room temperature. The asterisk denotes residual hexanes in the NMR sample.

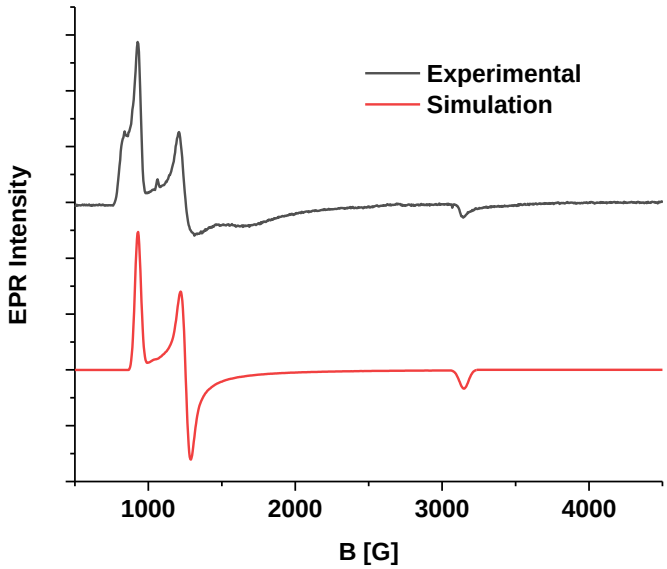

Figure S24. EPR spectrum of [Fe(TPP)(SPh-*p*NO_2)] in 1:1 CH_2Cl_2:toluene, collected at 4 K. The dominant species was fit (the red spectrum) using the program SpinCount. Fit parameters are g_x = 2.1, g_y = 2.15, g_z = 2.2, g_x-strain = 0.04, g_y-strain = 0.04, g_z-strain = 0.02, D = 7 cm^{-1}, E/D = 0.035, E/D-strain = 0.02.

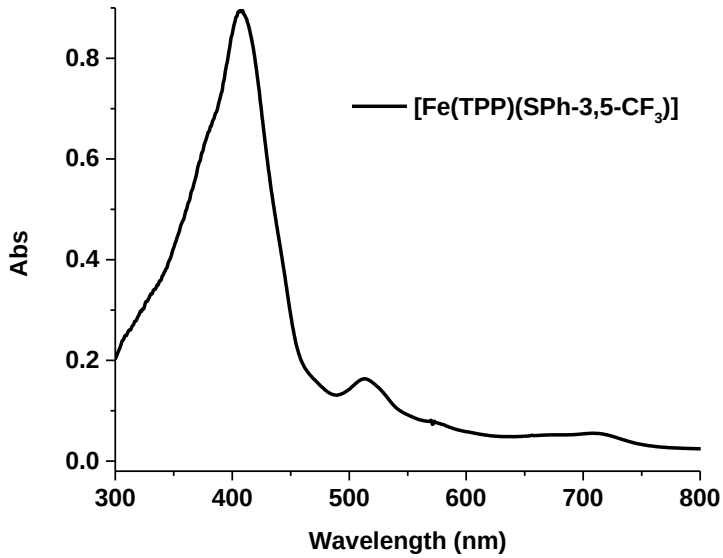

Figure S25. UV-Vis spectrum of [Fe(TPP)(SPh-3,5-CF_3)] in toluene at room temperature.

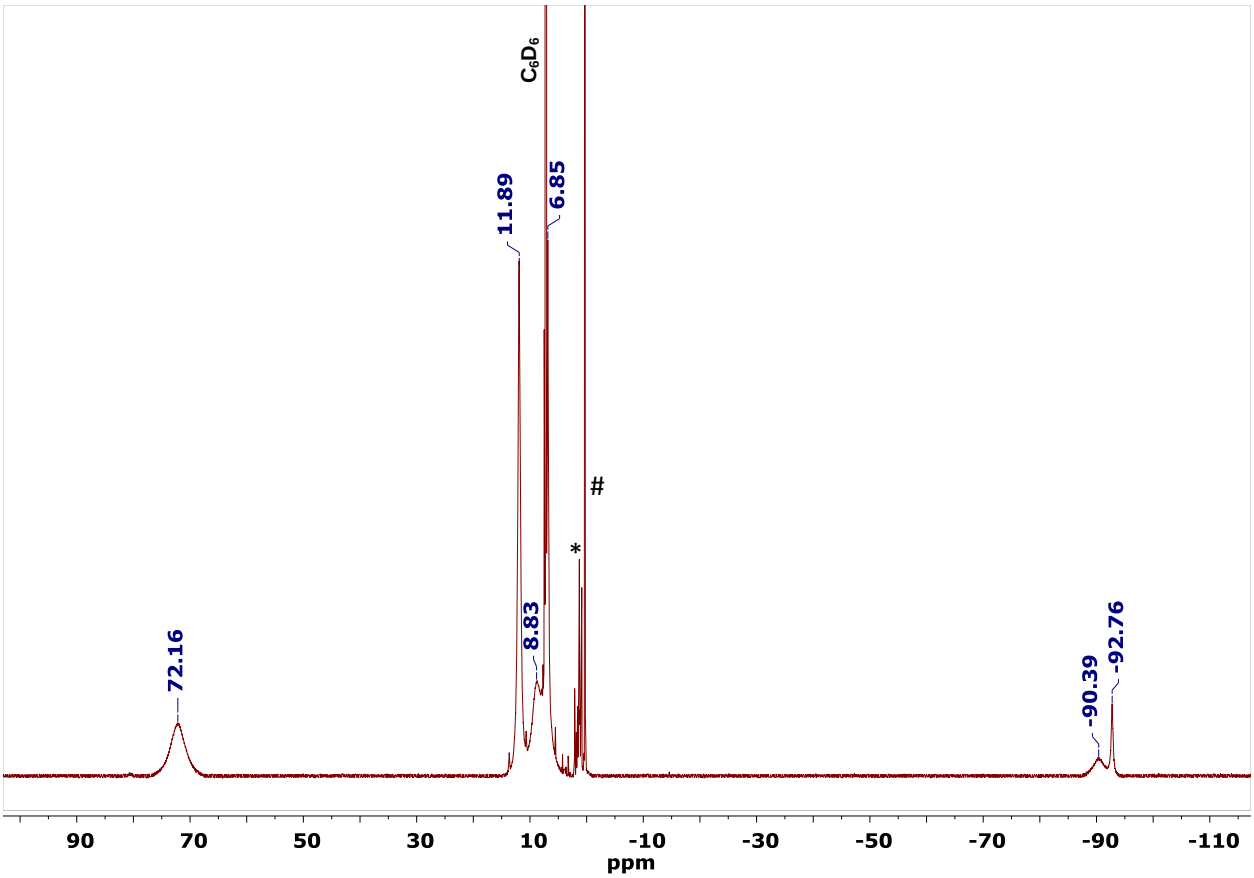

Figure S26. ^{1}H-NMR spectrum of [Fe(TPP)(SPh-3,5-CF_3)] in benezene-d_6 at room temperature. The asterisk denotes residual hexanes (0.89 and 1.24) in the NMR sample. The large peak to the right of this feature, denoted with '#', is believed to be a grease impurity that was also present in the stock 3,5-bis(trifluoromethyl)benzenethiol received from the commercial vendor. This heme-thiolate complex is quite soluble in methanol and hexanes, and thus successful recrystallization conditions could not be identified to remove the 0.32 ppm impurity. Note that silicone grease has a reported chemical shift of 0.29 ppm.

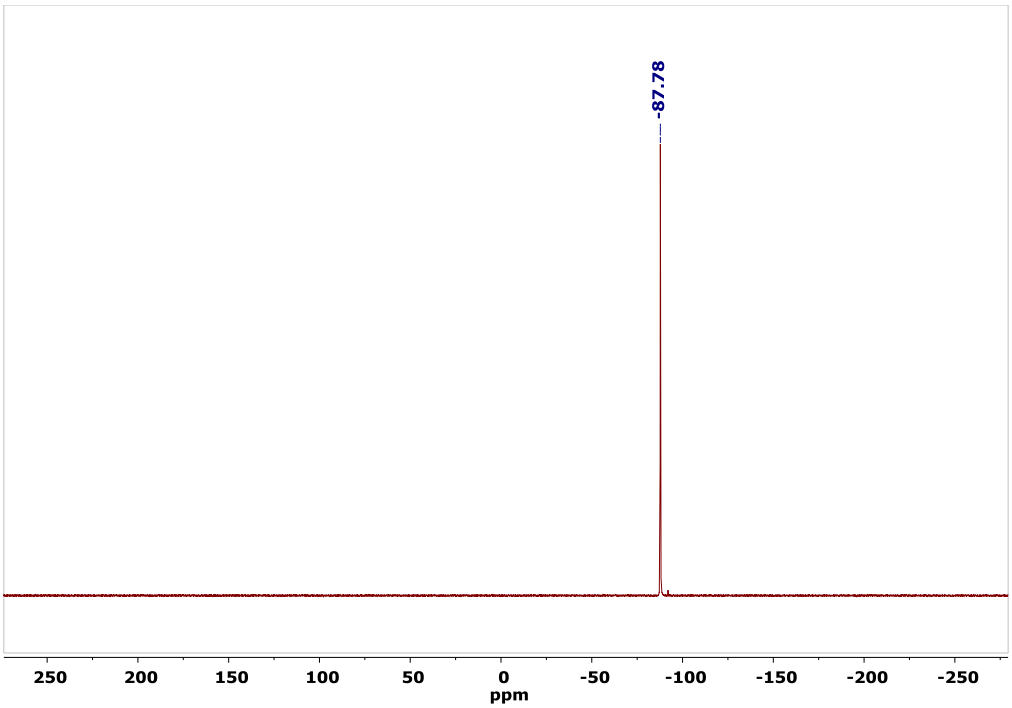

Figure S27. ^{19}F-NMR spectrum of [Fe(TPP)(SPh-3,5-CF_3)] in benezene-d_6 at room temperature.

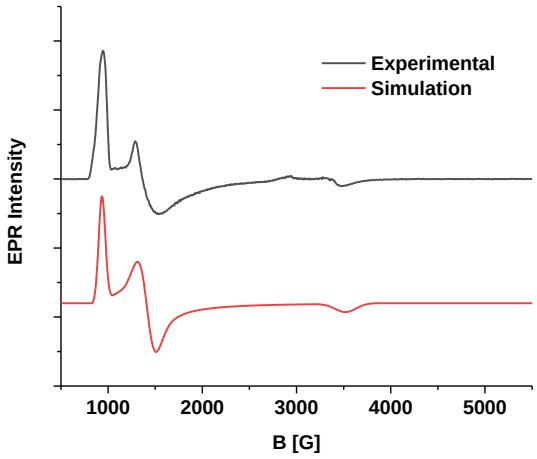

Figure S28. EPR spectrum of [Fe(TPP)(SPh-3,5-CF_3)] in 1:1 CH_2Cl_2:toluene, collected at 4 K. The simulated spectrum was generated using the program SpinCount. Fit parameters are g_x = 1.98, g_y = 1.98, g_z = 1.97, g_x-strain = 0.1, g_y-strain = 0.05, g_z-strain = 0.06, D = 7 cm^{-1}, E/D = 0.053, D-strain =0.5, E/D-strain = 0.1.

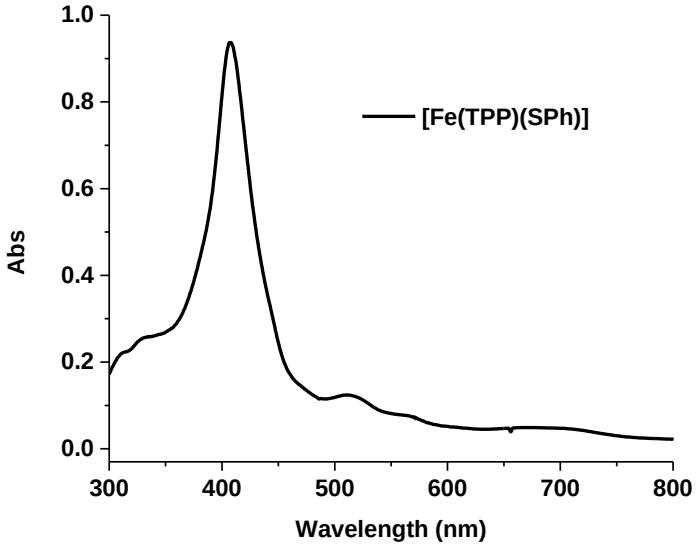

Figure S29. UV-Vis spectrum of [Fe(TPP)(SPh)] in toluene at room temperature.

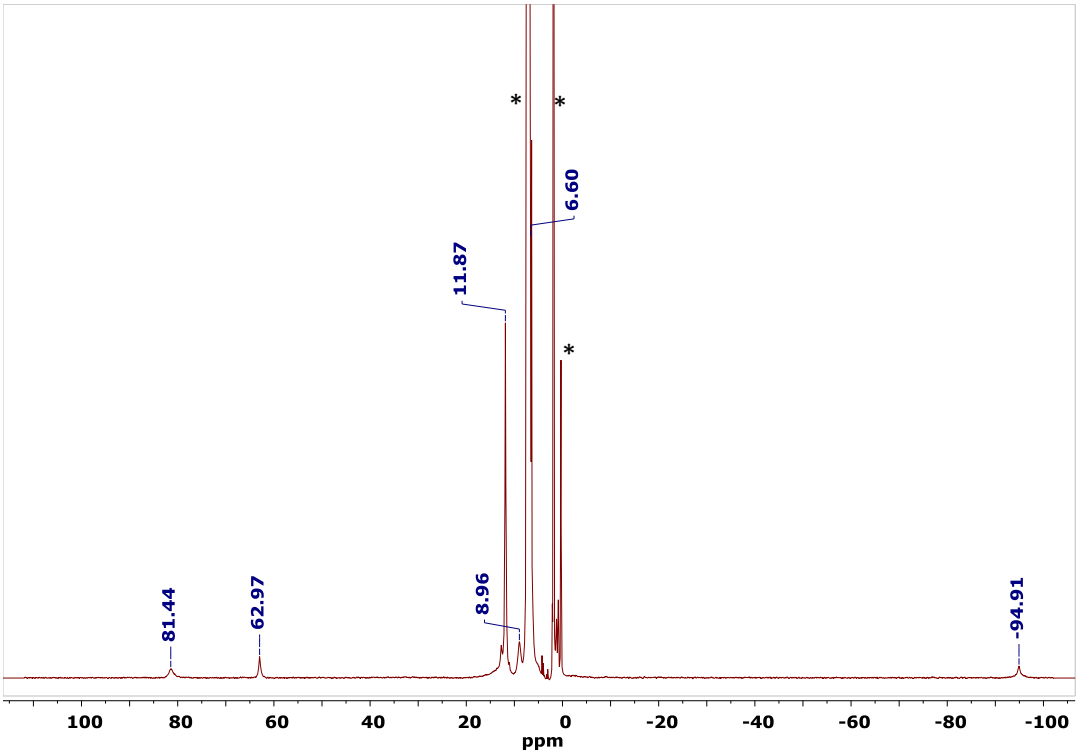

Figure S30. ^{1}H-NMR spectrum of [Fe(TPP)(SPh)] in benezene-d_6 at room temperature. The asterisks denote residual toluene and hexanes in the NMR sample from the synthesis of this complex, by reaction of [Fe(TPP)] with diphenyl disulfide in toluene followed by recrystallization by layering with hexanes.

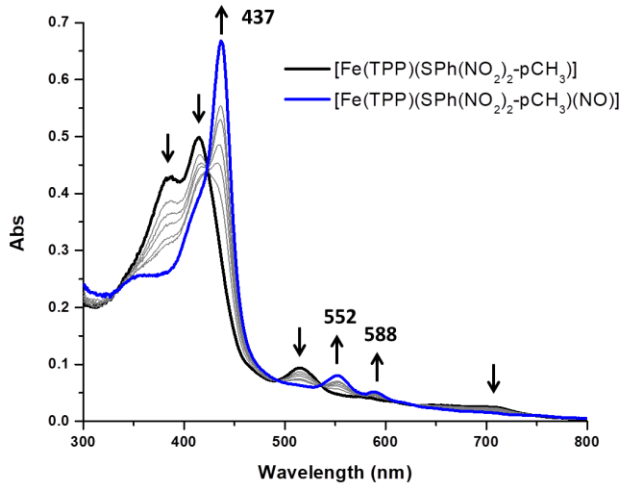

Figure S31. UV-Vis spectra monitoring the reaction between [Fe(TPP)(SPh(NO)$_2$-*p*CH$_3$)] (black) and NO(g) at -80 °C in toluene. Arrows indicate the direction of spectral changes over time.

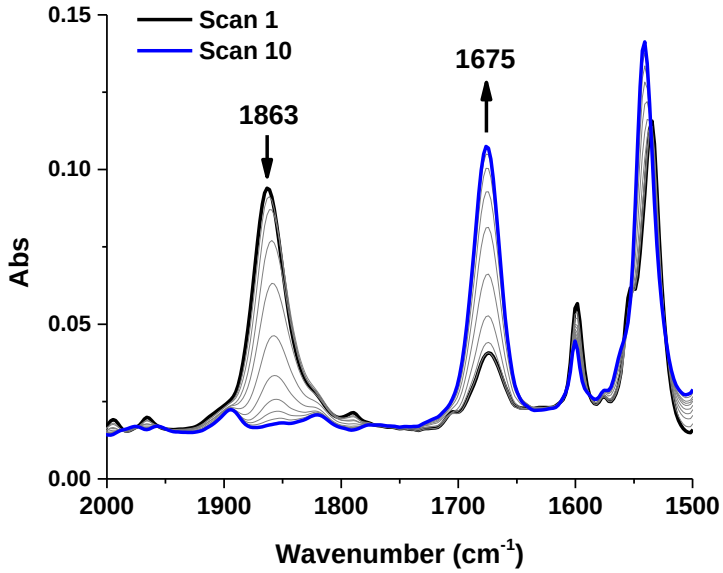

Figure S32. Solution IR spectra of [Fe(TPP)(SPh(NO)$_2$-*p*CH$_3$)(NO)] (black, Scan 1) in CH_2Cl_2. The ν(N-O) band of the complex is observed at 1863 cm^{-1}. As the solution warmed naturally in the spectrometer, [Fe(TPP)(SPh(NO)$_2$-*p*CH$_3$)(NO)] is observed to decompose to [Fe(TPP)(NO)] (ν(N-O) = 1675 cm^{-1}).

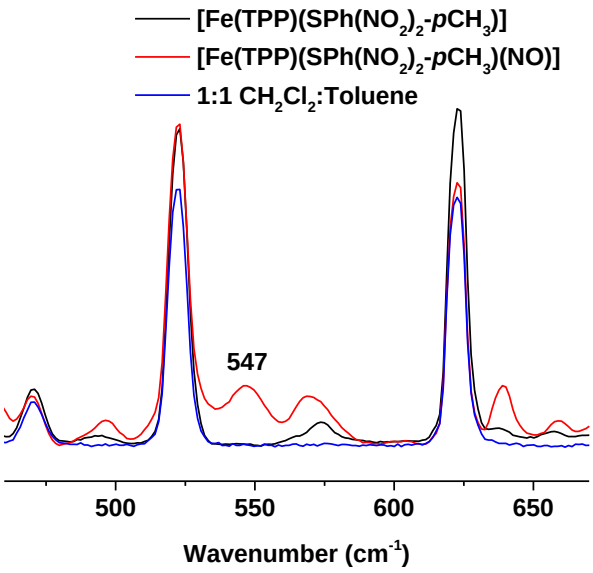

Figure S33. Resonance Raman spectra (458 nm excitation) of [Fe(TPP)(SPh(NO)$_2$-*p*CH$_3$)] (black) and of [Fe(TPP)(SPh(NO)$_2$-*p*CH$_3$)(NO)] (red), prepared in a 1:1 mixture of CH_2Cl_2:toluene (blue), and collected at 77 K. The ν(Fe-NO) band of the latter complex is observed at 547 cm^{-1}.

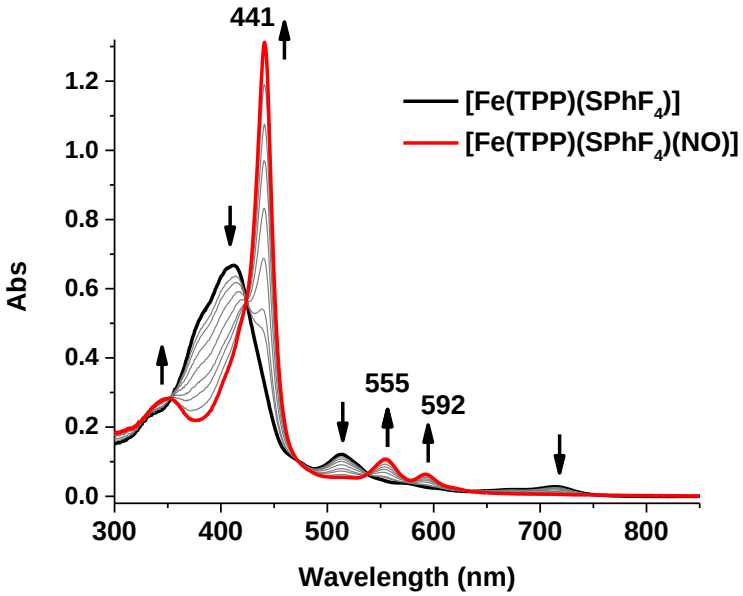

Figure S34. UV-Vis spectra monitoring the reaction between [Fe(TPP)(SPhF$_4$)] (black) and NO(g) at -80 °C in toluene. Arrows indicate the direction of spectral changes over time.

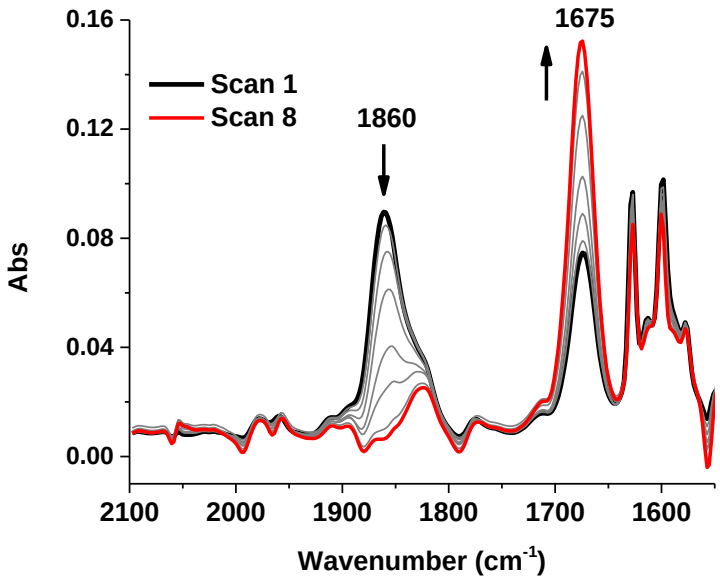

Figure S35. Solution IR spectra of [Fe(TPP)($SPhF_4$)(NO)] (black, Scan 1) in CH_2Cl_2.

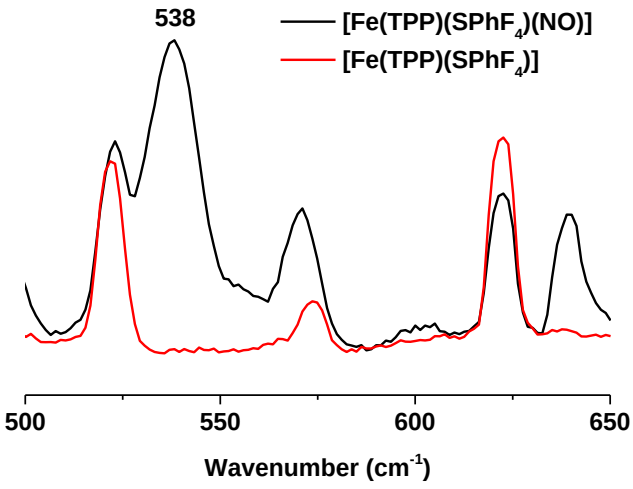

Figure S36. Resonance Raman spectra (458 nm excitation) of [Fe(TPP)($SPhF_4$)] (red) and of [Fe(TPP)($SPhF_4$)(NO)] (black), prepared in a 1:1 mixture of CH_2Cl_2:toluene, and collected at 77 K (liquid N_2). The ν(Fe-NO) band of the latter complex is observed at 538 cm^{-1}.

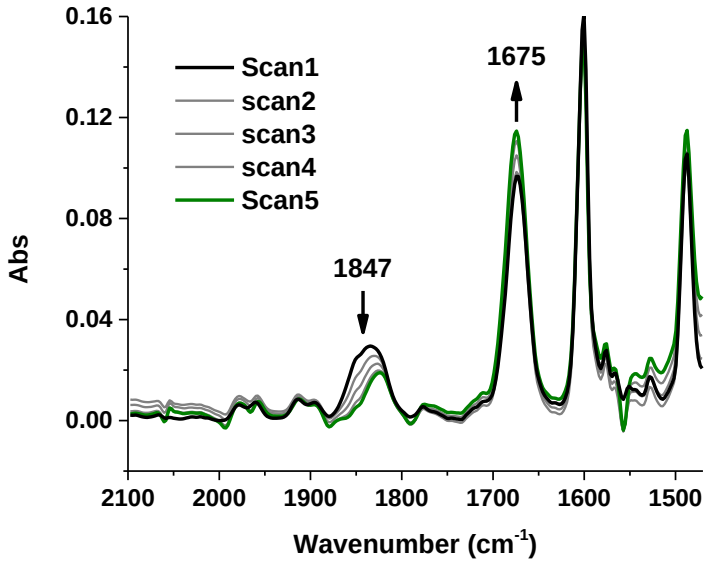

Figure S37. Solution IR spectra of [Fe(TPP)(SPh-*p*CF_3)(NO)] (black, Scan 1) in CH_2Cl_2.

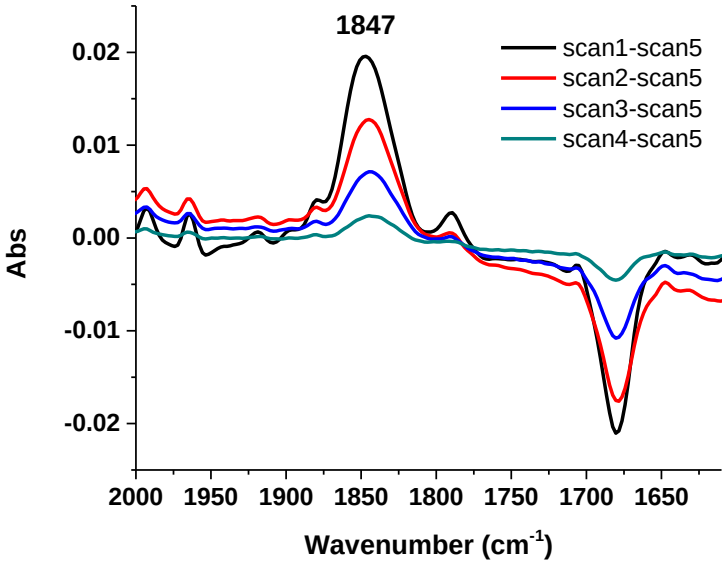

Figure S38. Difference spectra of the IR data shown in Figure S37 for [Fe(TPP)(SPh-*p*CF_3)(NO)]. Difference spectra were generated by subtraction of the fifth spectrum from the previous four, to determine the N-O stretching frequency without interference of a TPP^{2-} aromatic overtone band observed in this region at ~1820 cm^{-1} (see Figure S6). This feature can be seen in the final scans of all solution IR experiments.

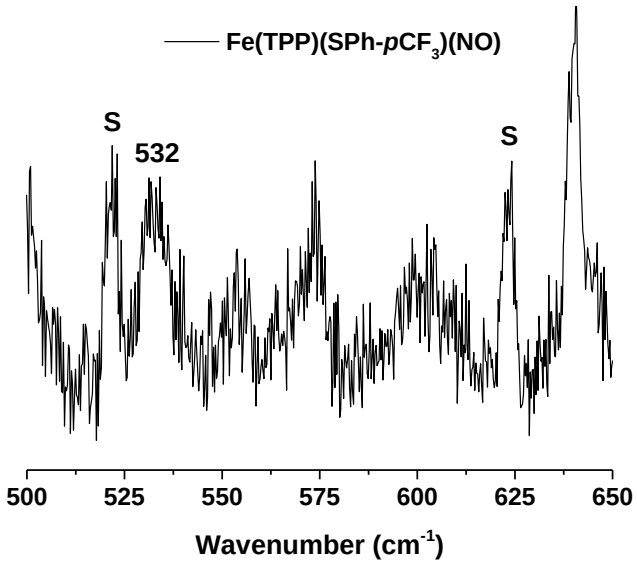

Figure S39. Resonance Raman spectrum (457 nm excitation) of [Fe(TPP)(SPh-*p*CF_3)(NO)], prepared in a 1:1 mixture of CH_2Cl_2:toluene, and collected at 77 K (liquid N_2).

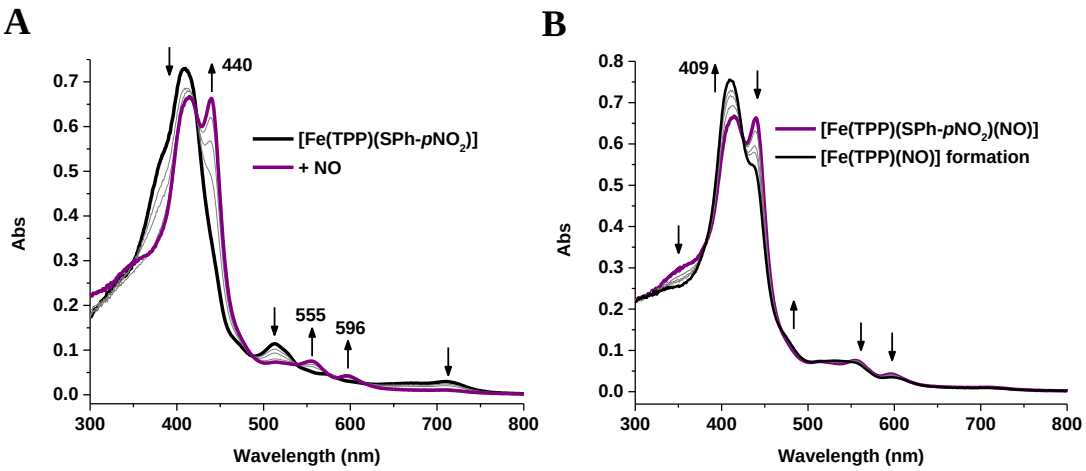

Figure S40. UV-Vis spectra monitoring the reaction between [Fe(TPP)(SPh-*p*NO_2)] and NO(g) at -80 °C in toluene. A) Initial spectral changes observed for the reaction with ~1 equivalent of NO(g) added to the solution. B) Changes observed upon addition of more NO(g) to the solution. Arrows indicate the direction of the spectral changes over time.

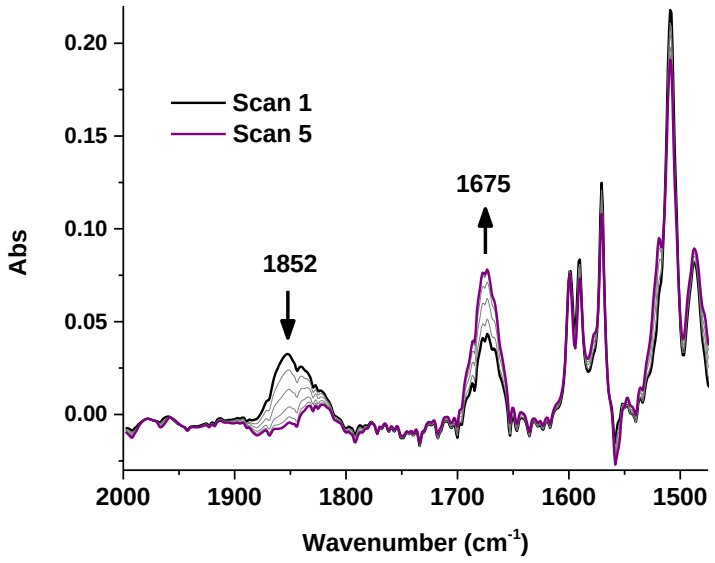

Figure S41. Solution IR spectra of [Fe(TPP)(SPh-*p*NO_2)(NO)] (black, Scan 1) in CH_2Cl_2.

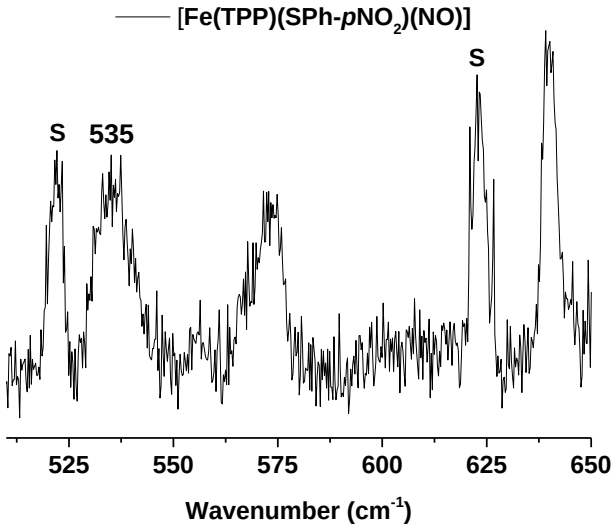

Figure S42. Resonance Raman spectrum (457 nm excitation) of [Fe(TPP)(SPh-*p*NO_2)(NO)] (black), prepared in a 1:1 mixture of CH_2Cl_2:toluene, and collected at 77 K (liquid N_2).

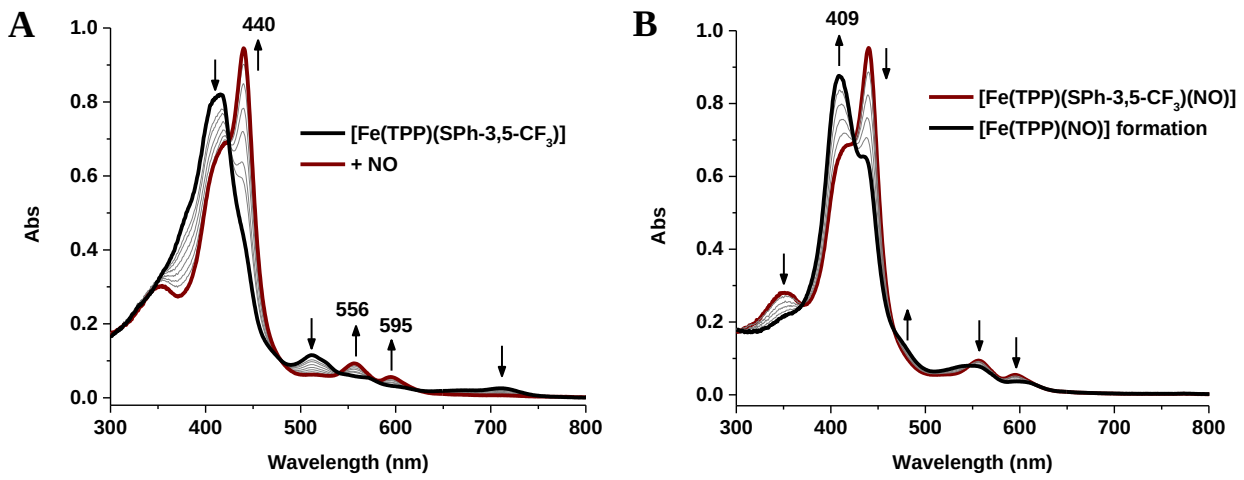

Figure S43. UV-Vis spectra monitoring the reaction between [Fe(TPP)(SPh-3,5-CF_3)] (black) and NO(g) at -80 °C in toluene. A) Initial spectral changes observed for the reaction with ~1 equivalent of NO(g) added to the solution. B) Changes observed upon addition of more NO(g). Arrows indicate the direction of the spectral changes over time.

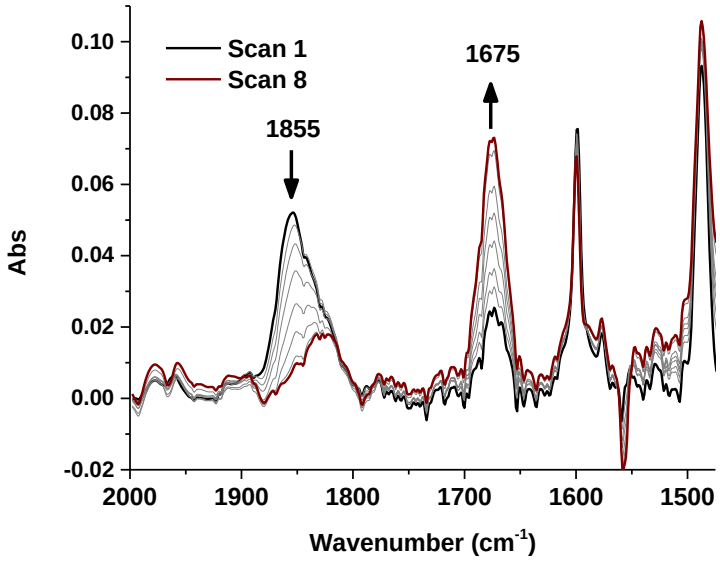

Figure S44. Solution IR spectra of [Fe(TPP)(SPh-3,5-CF_3)(NO)] (black, Scan 1) in CH_2Cl_2.

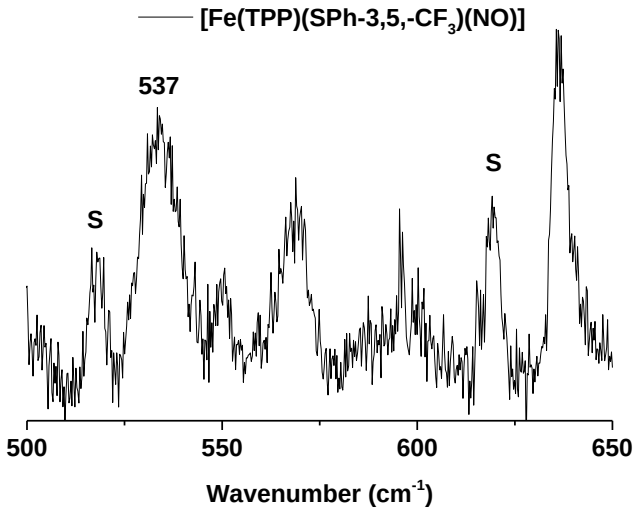

Figure S45. Resonance Raman spectrum (457 nm excitation) of [Fe(TPP)(SPh-3,5-CF_3)(NO)] (black), prepared in a 1:1 mixture of CH_2Cl_2:toluene, and collected at 77 K (liquid N_2).

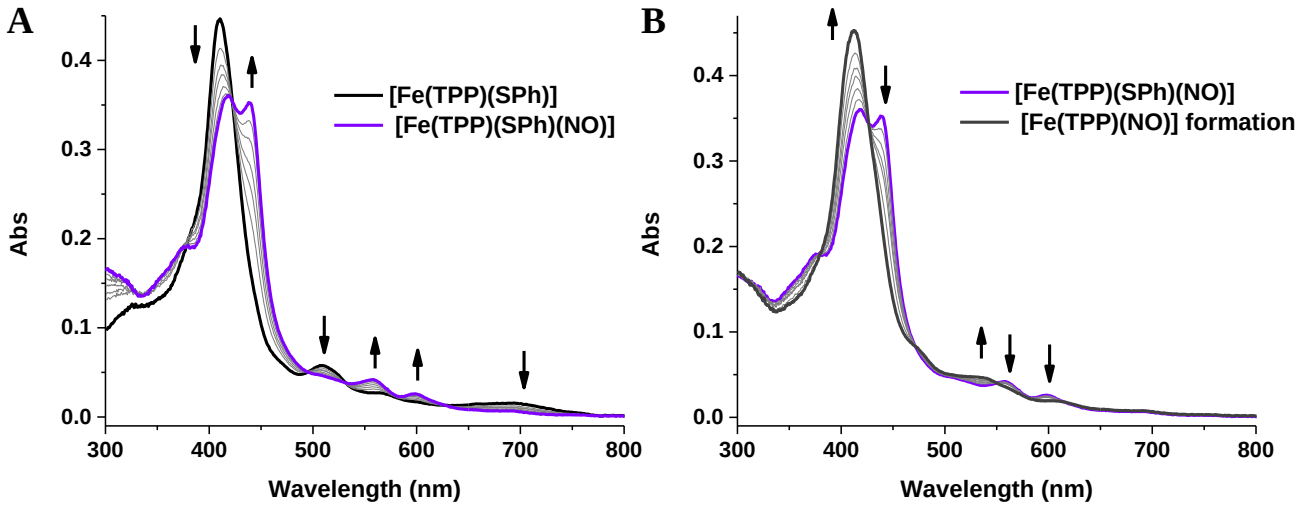

Figure S46. UV-Vis spectra monitoring the reaction between [Fe(TPP)(SPh)] (black) and NO(g) at -80 °C in toluene. A) Initial spectral changes observed upon addition of 1 equivalent of NO. B) Additional spectral changes of the reaction mixture over time, demonstrating the formation of [Fe(TPP)(NO)] at -80 °C.

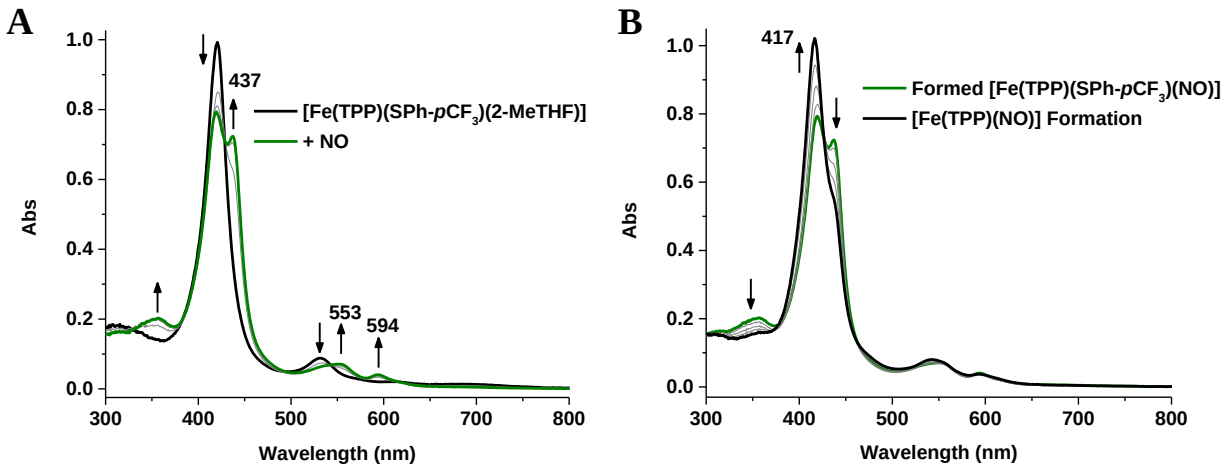

Figure S47. UV-Vis spectra monitoring the reaction between [Fe(TPP)(SPh-*p*CF_3)(2-MeTHF)] and NO(g) at -125 °C in 2-MeTHF. A) Initial changes observed upon addition of ~ 1 equivalent of NO, showing formation of a new species consistent with [Fe(TPP)(SPh-*p*CF_3)(NO)]. B) Additional spectral changes of the reaction mixture over time, showing the formation of a species with a Soret band at 417 nm, consistent with [Fe(TPP)(NO)(2-MeTHF)] at -125 °C. Note that this species then converts to the spectrum of [Fe(TPP)(NO)] (Soret band = 409 nm) upon warming to room temperature.

Table S1. Comparison of the DFT optimized bond lengths, calculated ν(Fe-NO) and ν(N-O) stretching frequencies, and the total NO σ* contribution to the MO shown in Figure 12 (bottom left) for each structure of [Fe(P)(Cl)(NO)] at the listed Fe-Cl distance. All calculations were performed at the BP86/TZVP level in the gas phase. The total NO σ* (N+O) contribution is the sum of the N(s), N(p_z), O(s) and O(p_z) orbitals in this MO. The population of the Cl(p_z) donor orbital is also given. The fully optimized structure, without constraint of the Fe-Cl bond, was calculated to have a Fe-Cl distance of 2.257 Å (listed as 2.26). All other Fe-Cl distances were fixed at the stated distance and the structures were reoptimized. The Fe-N-O angle was calculated to be 180° for all structures.

Fe-Cl (Å)	**Fe-NO (Å)**	**N-O (Å)**	**ν(N-O) [cm^{-1}]**	**ν(Fe-NO) [cm^{-1}]**	**NO σ* (N+O)**	**Cl (p_z)**
1.90	1.692	1.159	1863.6	518.7	6.8	67.8
2.00	1.678	1.1577	1872	574	5.9	65.5
2.10	1.667	1.1597	1878	626	5.0	64.8
2.26	1.654	1.15669	1883.6	630	3.8	61
2.40	1.646	1.15668	1885.9	639.6	2.9	53.2

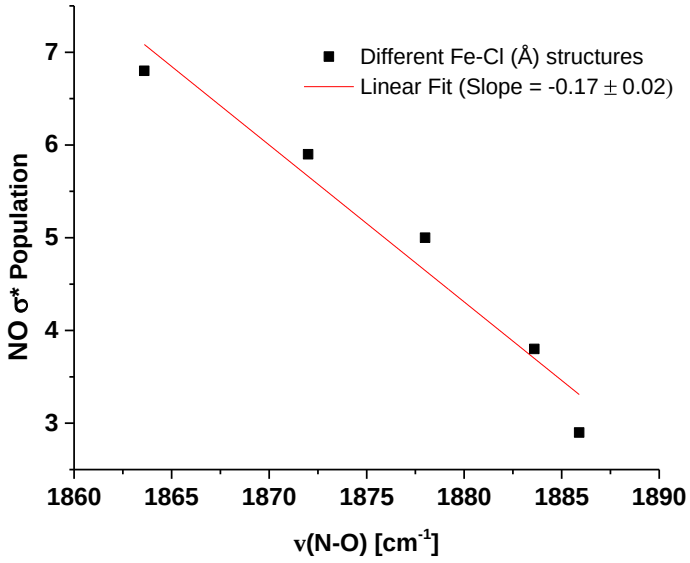

Figure S48. Correlation plot of the calculated N-O stretching frequencies for the [Fe(P)(Cl)(NO)] complexes with varied Fe-Cl distances (Table S1) versus the admixture of the NO σ* orbital in the MO shown in Figure 12 (bottom left). As the admixture of the NO σ* orbital is increased, the N-O stretching frequency is decreased.

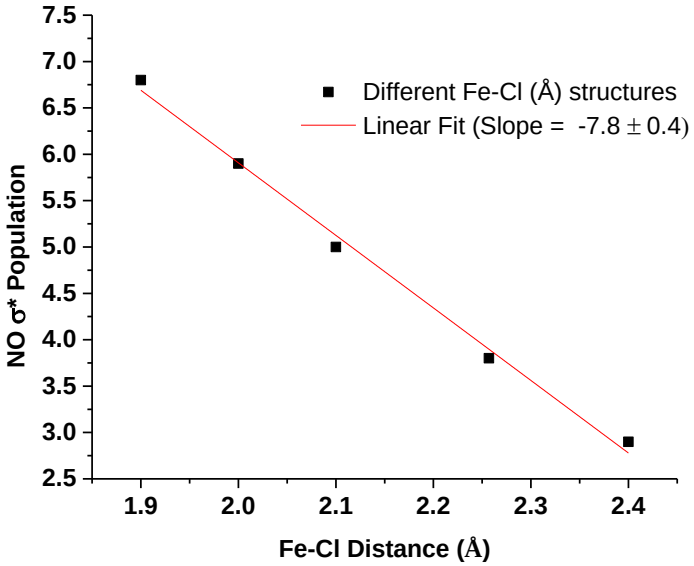

Figure S49. Correlation plot of the Fe-Cl bond distances (Å) of the [Fe(P)(Cl)(NO)] complexes versus the admixture of the NO σ* orbital in the MO shown in Figure 12 (bottom left). Here, a decrease in the Fe-Cl distances causes an increase in the population of NO σ* orbital.

Table S2. Loewdin reduced orbital populations of MO 127 shown in Figure 14, for the calculated structure of [Fe(P)(SPh)(OOH_2)] (BP86/TZVP).

Orbital	Fe	S	O(-Fe)	O(H_2)
d_{z2}	20.2	-	-	-
d_{xz}	9.1	-	-	-
d_{x2-y2}	14.8	-	-	-
s	-	0.4	0.3	0
p_z	-	8.8	3.2	0
p_x	-	0.5	0.2	1.1
Total	44.1	9.7	3.7	1.1

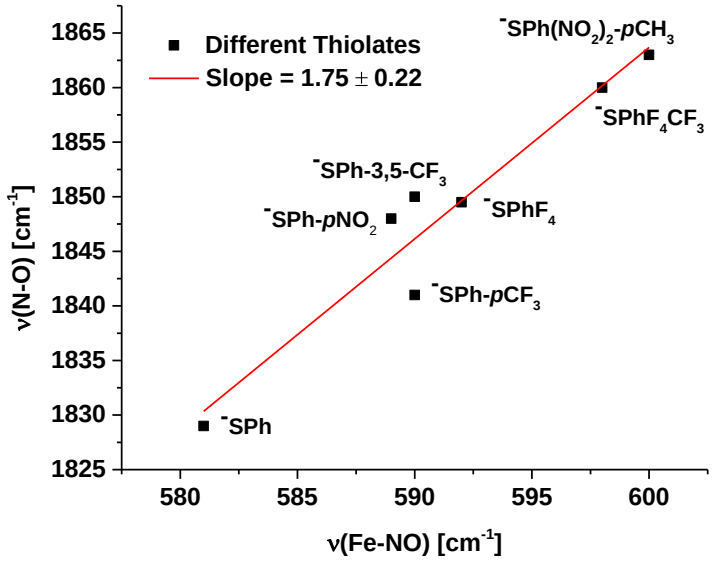

Figure S50. Correlation plot of the DFT-calculated (BP86/TZVP) ν(Fe-NO) and ν(N-O) stretching frequencies for the different{FeNO}^{6} [Fe(P)(SPh*)(NO)] complexes investigated here.

DFT Optimized Coordinates

[Fe(PPIX)(SCH_2CH_3)(NO)]_0H-B

C	0.34915300	0.70244600	3.18539700
S	1.48689000	-0.28564300	2.11296400
C	-3.89877000	-2.77945700	0.48717900
C	5.96778400	-2.90987400	-0.43450400
C	3.74241300	4.80584200	-0.46369500
N	-0.36886600	-1.55297000	0.08142600
C	6.94831500	-2.18326100	0.13482300
C	4.85270200	5.52301300	-0.19774800
N	2.48982100	-1.55785700	-0.23754000
N	-0.33399000	1.31211800	0.13738500
C	1.04445000	-3.54964200	-0.09254400
C	4.47081600	-0.14148800	-0.53406000
C	1.10042900	3.30309000	-0.04797800
C	-1.62669800	-5.09281200	0.22073800
C	3.70282900	-5.11369900	-0.27079400
C	6.01243200	2.52210800	-0.87349500
C	-1.54366700	4.86665400	0.32864900
C	-1.71702000	-1.35014100	0.24427800
C	2.28100700	-2.92085700	-0.20738200
C	3.84884700	1.10192100	-0.49083400
C	-0.12767700	2.67451400	0.12253400
C	-2.41479700	-2.62781400	0.32694100
C	3.54161000	-3.62589800	-0.31114200
C	4.55008000	2.36817100	-0.60016300
C	-1.38942400	3.37697300	0.29214500

C	-1.45626000	-3.60499200	0.20376700
C	4.53154100	-2.66214000	-0.37421600
C	3.59709400	3.35851600	-0.43301000
C	-2.36462800	2.41047200	0.39278700
C	-0.18159500	-2.91472900	0.05155800
C	3.84730700	-1.37044700	-0.35858500
C	2.32060600	2.66708400	-0.24938700
C	-1.69001300	1.12586400	0.28781700
N	2.50291600	1.30852700	-0.28679800
Fe	1.06717700	-0.12204900	-0.15845000
N	0.68879400	-0.10167800	-1.80209700
O	0.16257100	-0.09004800	-2.83973200
H	1.01322000	1.13498900	3.95168300
H	-0.05593700	1.54185100	2.60514700
H	-4.27885100	-2.06654800	1.23501600
H	-4.12891000	-3.78371900	0.87632300
H	6.26056600	-3.81494100	-0.98070800
H	2.83991300	5.36575100	-0.73466100
H	6.74314100	-1.30912100	0.75545400
H	7.99408500	-2.47520400	0.02354300
H	4.84229000	6.61162600	-0.27431300
H	5.78752000	5.06358800	0.12502000
H	1.04178600	-4.64026500	-0.10041500
H	5.54565600	-0.15963900	-0.70757000
H	1.10179500	4.39286700	-0.02264900
H	-2.67426400	-5.37111700	0.40116300
H	-1.01838300	-5.56323600	1.01019300
H	-1.32669400	-5.54849800	-0.73738900

H	3.51022800	-5.51317100	0.73913300
H	4.72406400	-5.41049700	-0.54631600
H	3.00930400	-5.61926200	-0.96100700
H	6.20138300	3.43351600	-1.46112900
H	6.59997800	2.60804000	0.05687700
H	6.41357300	1.66694500	-1.43631300
H	-2.57832700	5.15328700	0.56282600
H	-0.89242300	5.32558300	1.08975900
H	-1.28652700	5.32718800	-0.63976600
C	-4.66598800	-2.56750100	-0.84395900
H	-4.41116000	-1.57796500	-1.25782600
H	-4.37277600	-3.31978700	-1.58767000
C	-4.59039700	2.54280300	-0.82769300
H	-4.44385400	1.56964100	-1.31277400
H	-4.17867700	3.31939000	-1.49220700
C	-0.76243800	-0.11619800	3.84204500
H	-1.34644100	0.51474400	4.53451500
H	-1.45236700	-0.52738200	3.09207700
H	-0.34643000	-0.95719400	4.41630200
C	-3.84649300	2.60183200	0.53508600
H	-4.05194100	3.57415100	1.00664300
H	-4.26937700	1.83715700	1.20703700
C	-2.33269500	-0.10725500	0.34237900
H	-3.41353300	-0.09707100	0.49021400
C	-6.08191000	2.76665500	-0.69713200
C	-6.17294100	-2.63056700	-0.70485800
O	-6.95537100	1.97162700	-0.98737600
O	-6.92171000	-3.32152500	-1.36903800

O	-6.36304500	4.01084900	-0.18965400
H	-7.34064800	4.06478000	-0.13421600
O	-6.62508100	-1.78489100	0.27392100
H	-7.60345300	-1.84712500	0.25900700

[Fe(PPIX)(SCH_2CH_3)(NO)]_1H-B

C	0.14007400	0.46573000	2.96844200
S	1.32063000	0.03314000	1.60844800
N	3.36424000	-2.83150200	2.14816400
C	4.73257100	-2.38836600	1.89768300
C	-3.70419400	-3.11420300	-0.12956800
C	5.75454300	-0.97702200	-2.15102700
C	2.25553000	5.88943500	0.11747500
N	-0.52835800	-1.14662800	-0.48028700
C	6.69001100	-0.18194000	-1.59769900
C	3.25441200	6.73365500	0.44361600
N	2.20257200	-0.48710900	-1.09310400
N	-1.01054800	1.59015900	0.22364200
C	1.18550400	-2.72731800	-1.24667400
C	3.80574000	1.35715600	-1.31765300
C	0.00950600	3.82076000	0.41173800
C	-1.09635000	-4.81885000	-1.05216800
C	3.99768600	-3.60644500	-2.17313300
C	4.78345100	4.28740400	-1.13890200
C	-2.80510900	4.69275900	1.35807200
C	-1.86042300	-1.26077000	-0.16906100

C	2.24944300	-1.83860300	-1.36864100
C	2.99407700	2.39729900	-0.87802000
C	-1.05508200	2.93460200	0.52240200
C	-2.29491500	-2.64263700	-0.32072700
C	3.57045400	-2.21454000	-1.82683700
C	3.43660200	3.77292700	-0.74114700
C	-2.39396000	3.31190500	0.94808400
C	-1.19709900	-3.35881200	-0.73492900
C	4.33957900	-1.06412500	-1.80629100
C	2.36859900	4.47593200	-0.21022400
C	-3.16321000	2.17287900	0.87930700
C	-0.09996000	-2.40602800	-0.83336800
C	3.45412200	0.01425500	-1.37017100
C	1.27897600	3.51092100	-0.06373300
C	-2.28391800	1.10545900	0.42635500
N	1.68619800	2.26512100	-0.46781700
Fe	0.56816200	0.56861100	-0.52916200
N	-0.01811100	0.81722900	-2.08437900
O	-0.63756900	0.86117200	-3.06614400
H	4.86285300	-2.18336000	0.82059700
H	5.37986200	-3.23903100	2.15428500
H	2.61056600	-2.14948100	2.01543500
H	0.79075300	0.86240600	3.76449000
H	-0.48698600	1.29830700	2.62503400
H	-4.15579500	-2.63707300	0.75478000
H	-3.71867400	-4.19872400	0.05845300
H	6.08298000	-1.67628000	-2.92935600
H	1.24012200	6.30150700	0.09486900

H	6.47097100	0.49385500	-0.76914000
H	7.72506500	-0.21943200	-1.94157100
H	3.04762800	7.78468800	0.65226900
H	4.29132500	6.40995500	0.53999200
H	1.37952900	-3.76883500	-1.50484100
H	4.81477700	1.60994000	-1.63895800
H	-0.17636900	4.85265000	0.70962500
H	-2.04109100	-5.33820700	-0.84004300
H	-0.30768200	-5.31120600	-0.46135900
H	-0.86006700	-4.98916100	-2.11557500
H	4.08202600	-4.23801000	-1.27312800
H	4.98060400	-3.61049900	-2.66349800
H	3.28248400	-4.09526400	-2.85298500
H	4.71180700	5.32989700	-1.48464300
H	5.49659500	4.27299200	-0.29680300
H	5.22404500	3.69103300	-1.95077700
H	-3.83234800	4.70035500	1.74835000
H	-2.14965100	5.09498700	2.14696200
H	-2.76911600	5.39965000	0.51247000
C	-4.57984800	-2.80626400	-1.37653700
H	-4.53515900	-1.73049700	-1.59975300
H	-4.19857700	-3.35958100	-2.24470500
C	-5.48735400	2.06339800	-0.11794600
H	-5.16990000	1.28950700	-0.83644200
H	-5.36117000	3.02168900	-0.64717400
C	5.09474900	-1.14320900	2.71043600
H	6.12313300	-0.82387600	2.48042600
H	4.41809400	-0.30602800	2.47921500

H	5.03224800	-1.34757500	3.78992800
C	-0.70590300	-0.69491700	3.49583500
H	-1.34105900	-0.35193800	4.33028400
H	-1.36244000	-1.10102800	2.71379800
H	-0.07165100	-1.51237700	3.86863200
C	-4.62963900	2.01693900	1.16090000
H	-4.96691500	2.80972400	1.84564600
H	-4.82831800	1.07151500	1.68935400
C	-2.67847200	-0.21666200	0.24993700
H	-3.71672600	-0.45818700	0.48120400
C	3.05335900	-4.11248900	2.51340300
O	3.89605700	-5.00758900	2.64576100
C	-6.96064100	1.85935600	0.15948100
C	-6.02293700	-3.21853600	-1.16045800
O	-7.46009900	1.59299300	1.23605700
O	-6.53954000	-4.24973600	-1.54481100
O	-7.70475600	2.01265300	-0.98050600
H	-8.63712900	1.85829000	-0.71856200
O	-6.70127000	-2.28555600	-0.41630100
H	-7.60220500	-2.64734100	-0.27656100
C	1.57267500	-4.36651000	2.77401400
H	1.42603300	-4.52066100	3.85376600
H	0.92268800	-3.54529300	2.43954200
H	1.28011200	-5.29768700	2.26997200

[Fe(PPIX)(SCH_2CH_3)(NO)]_2H-B

C	-4.32592300	-3.51565000	1.88402000
C	-3.20244000	-2.72478200	2.01250700
C	-5.34129100	-2.67570000	1.30239100
C	-4.75986100	-1.38137800	1.10198500
C	-6.68209600	-2.88819900	0.92312300
C	-5.48763800	-0.32361000	0.54035800
C	-7.40474700	-1.83653100	0.36133800
C	-6.81215700	-0.56706200	0.17297600
C	0.46509200	-0.20576200	2.81101300
S	-0.53808500	0.55985800	1.44044500
N	-1.85492300	3.81722000	2.10653300
C	-3.26507500	3.70928800	1.74328400
C	5.27199500	2.64313400	0.14064600
C	-4.16749800	3.05166700	-2.67596000
C	-2.41387800	-4.70476200	-1.41697100
N	1.71295200	1.55397300	-0.34144300
C	-5.31489100	2.36108400	-2.53212100
C	-3.57620800	-5.38249600	-1.49545800
N	-1.01001000	1.62369900	-1.26305400
N	1.50224800	-1.28107900	-0.00784600
C	0.45579100	3.57692500	-0.93224000
C	-2.85921100	0.23149600	-2.07333900
C	0.01691700	-3.22524600	-0.27372500
C	3.15810600	5.01585500	-0.49791000
C	-1.98830500	5.19614600	-1.88761300
C	-4.34190300	-2.41443800	-2.67093600
C	2.40263800	-4.81548700	0.89556900

C	3.02112700	1.30689300	-0.00301900
C	-0.75267900	2.97977000	-1.27513500
C	-2.34665900	-1.01397600	-1.72774700
C	1.20641900	-2.62105000	0.11859800
C	3.78484400	2.54591400	-0.01662100
C	-1.89253400	3.70565900	-1.79339100
C	-3.03482800	-2.27019000	-1.96156000
C	2.35911800	-3.34169100	0.63048200
C	2.89946200	3.54992600	-0.33382800
C	-2.85271300	2.76100100	-2.11645700
C	-2.23379700	-3.26064200	-1.41948800
C	3.36777700	-2.41494100	0.77127900
C	1.60887700	2.91069800	-0.54145600
C	-2.26826500	1.45865900	-1.79999300
C	-1.05538100	-2.58314300	-0.88103200
C	2.81960900	-1.13205300	0.36653100
N	-1.15263800	-1.22633700	-1.07168000
Fe	0.29307700	0.16036800	-0.73734600
N	0.97610200	-0.01149100	-2.25363500
O	1.64393500	-0.09591500	-3.19671300
H	-2.21670400	-2.98031700	2.39284700
H	-7.15130300	-3.86424400	1.07127400
H	-8.44563700	-1.98923000	0.06755300
H	-5.03571000	0.65984800	0.40122400
H	-7.40578400	0.24192200	-0.25888500
H	-3.35649700	3.55124500	0.65400300
H	-3.71630100	4.68492500	1.97336700
H	-1.27515600	2.97775000	2.00794900

H	-0.29682000	-0.52068500	3.54194100
H	0.92898800	-1.11921400	2.41725900
H	5.62105100	2.14441400	1.05772800
H	5.54641900	3.70240600	0.24827700
H	-4.21199200	3.97592700	-3.26432000
H	-1.49243800	-5.29532000	-1.35405500
H	-5.39730100	1.46267500	-1.91841000
H	-6.23050800	2.70847700	-3.01385500
H	-3.58057500	-6.47378600	-1.51696100
H	-4.54625500	-4.88525700	-1.51069800
H	0.51334900	4.66189900	-1.02353800
H	-3.81679100	0.24963500	-2.58978500
H	-0.05746100	-4.30412600	-0.13699000
H	4.18447300	5.27522900	-0.20435800
H	2.47694700	5.62046200	0.12154000
H	3.02164100	5.33982900	-1.54300400
H	-2.08777600	5.65575100	-0.88996600
H	-2.86351600	5.50392300	-2.47547300
H	-1.09613500	5.63317800	-2.36285300
H	-4.38699600	-3.37662500	-3.20338400
H	-5.18845400	-2.38663200	-1.96366800
H	-4.49878000	-1.61216600	-3.40625500
H	3.33996100	-5.10222900	1.39273100
H	1.57283500	-5.13743800	1.54442500
H	2.33338800	-5.40108500	-0.03634000
C	6.03289900	2.04916000	-1.08209400
H	5.77039724	0.99594237	-1.24269785
H	5.72966752	2.59964254	-1.99031962

C	5.67583600	-2.95262100	-0.09415100
H	5.61520400	-2.11730700	-0.80884700
H	5.32115300	-3.86668000	-0.58844300
N	-3.45715900	-1.44170000	1.55747700
H	-2.73014400	-0.72398700	1.45695500
C	-3.96592300	2.57778400	2.49697300
H	-5.01759700	2.49722800	2.18397700
H	-3.47987200	1.60923000	2.30795000
H	-3.94556300	2.75881800	3.58217500
C	1.50615800	0.69625900	3.48770900
H	2.00620100	0.14139900	4.29895600
H	2.27391500	1.02624000	2.77459900
H	1.03596100	1.58841600	3.92628100
C	-4.45821000	-4.96045200	2.24453800
H	-5.27167000	-5.13086400	2.96990200
H	-4.67700400	-5.58117900	1.35920200
H	-3.53003600	-5.34424800	2.69317900
C	4.79599700	-2.65607700	1.15732400
H	4.85669100	-3.50849900	1.85261100
H	5.20976300	-1.78662900	1.69093500
C	3.52972900	0.06404600	0.35684100
H	4.57068300	0.02868800	0.67797300
C	-1.27277000	4.99497500	2.48618900
O	-1.88096500	6.07065700	2.53698400
C	7.12351000	-3.10816900	0.28664300
C	7.54610123	2.14489970	-1.04442273
O	8.06963933	-2.56523998	-0.28062604
O	8.24029906	2.44841353	-2.00465787

O	7.31814891	-3.89434667	1.37324049
H	8.28590759	-3.90900965	1.54054856
O	8.04332058	1.89255228	0.18950976
H	9.04571634	1.98673093	0.17603976
C	0.19586200	4.88909000	2.88142800
H	0.27468600	4.99089200	3.97454000
H	0.66277900	3.94113500	2.57843100
H	0.74401400	5.73006900	2.43583600

[Fe(TPP)(SPhF$_4$CF$_3$)(NO)]

Fe	1.00790700	0.02813400	-0.78989700
S	0.54699900	-0.15404700	1.53204900
O	2.08552600	-0.31054400	-3.36667800
N	0.49304900	-1.93557500	-0.91476400
N	2.82835600	-0.49601600	-0.05770700
N	1.48055300	1.98173400	-0.52984000
N	-0.87352900	0.54869500	-1.27814000
N	1.59174300	-0.05836800	-2.34852500
C	-0.74199700	-2.45118400	-1.25094000
C	-0.70698100	-3.89365600	-1.16715700
C	0.55978300	-4.24225100	-0.80360100
C	1.31064900	-3.01718900	-0.65057000
C	2.65251500	-2.96948700	-0.25132200
C	3.34399000	-1.77908000	0.01169900
C	4.72577800	-1.72204200	0.42288700
C	5.03509700	-0.40678700	0.61614600
C	3.84901400	0.35858600	0.31681700

C	3.78000400	1.75753000	0.38195000
C	2.65350100	2.49319100	-0.00773700
C	2.56721700	3.93404800	0.06773200
C	1.35276700	4.28898200	-0.43904700
C	0.67779900	3.06754800	-0.81392300
C	-0.62005100	3.02429400	-1.33823200
C	-1.32418200	1.83110000	-1.54902200
C	-2.65844600	1.77411900	-2.09337400
C	-3.01511900	0.45851700	-2.14896500
C	-1.89879500	-0.30723400	-1.64981100
C	-1.87342400	-1.70942000	-1.61843200
C	-1.19196200	-0.08725200	1.86741600
C	-1.91325300	-1.24720800	2.21782200
C	-3.25850700	-1.19353000	2.57957500
C	-3.96908100	0.01997200	2.61553900
C	-3.25637400	1.18381900	2.28411500
C	-1.90540900	1.12324000	1.93035600
H	3.34132400	4.57852400	0.47293600
H	0.92585100	5.28298700	-0.53192900
H	5.98423400	0.02211400	0.92292800
H	5.36959000	-2.58815400	0.54242500
H	0.95854500	-5.23619000	-0.62464600
H	-1.55829100	-4.54322400	-1.34585300
H	-3.94217500	0.02914600	-2.51605200
H	-3.23575200	2.64054000	-2.40099800
F	-1.31385100	-2.45000700	2.21550200
F	-1.28471100	2.28733500	1.66666500
F	-3.83946200	2.40044000	2.30674800

F	-3.88671600	-2.34574800	2.89629100
C	-5.43259800	-0.00842800	3.00895000
F	-6.01385500	1.21281400	2.99573900
F	-6.15240200	-0.80187100	2.15811200
F	-5.59729400	-0.51947600	4.26254800
C	-3.10669100	-2.45281000	-2.02639000
C	-3.12264300	-3.21880000	-3.20660000
C	-4.27183600	-2.40191200	-1.24062100
C	-4.27352200	-3.91438100	-3.58991900
H	-2.22605700	-3.25871600	-3.82941100
C	-5.42125500	-3.10128700	-1.62174600
H	-4.27097400	-1.81704600	-0.31859100
C	-5.42593700	-3.85880000	-2.79801000
H	-4.27013700	-4.49897300	-4.51275900
H	-6.31285400	-3.05648800	-0.99274300
H	-6.32401400	-4.40407300	-3.09624300
C	-1.30199300	4.32038700	-1.65027600
C	-0.88253500	5.10642900	-2.73844500
C	-2.37098600	4.77670800	-0.85788000
C	-1.52097500	6.31607900	-3.03149600
H	-0.05514100	4.75851100	-3.36125500
C	-3.00565100	5.98825300	-1.14959200
H	-2.69372700	4.18209500	-0.00097400
C	-2.58452000	6.76019900	-2.23801100
H	-1.18763900	6.91128000	-3.88472600
H	-3.82982500	6.33123500	-0.52008200
H	-3.08209300	7.70533700	-2.46621900
C	4.97713000	2.50032700	0.88889000

C	5.33363300	2.43300500	2.24785200
C	5.76587600	3.27610400	0.02046800
C	6.45002500	3.12654400	2.72618100
H	4.72120000	1.84006300	2.93081300
C	6.88436900	3.96616900	0.49897800
H	5.50099000	3.32921100	-1.03802600
C	7.22904700	3.89405100	1.85321000
H	6.70869300	3.07021100	3.78596700
H	7.49010300	4.55937000	-0.18989400
H	8.10134200	4.43469800	2.22696700
C	3.37937700	-4.26580600	-0.06048400
C	3.77752500	-5.03574900	-1.16738800
C	3.67289600	-4.73521800	1.23228300
C	4.45818900	-6.24437500	-0.98627400
H	3.55567100	-4.67692700	-2.17509900
C	4.35090000	-5.94510700	1.41242900
H	3.35563600	-4.14855900	2.09731900
C	4.74710000	-6.70200000	0.30404600
H	4.76645300	-6.82800500	-1.85671800
H	4.56599400	-6.29932900	2.42313400
H	5.27793800	-7.64596100	0.44559300

[Fe(P)(SPh)(OOH_2)]

Fe	0.54114800	-0.00016300	0.38239900
S	-0.21308800	0.00036600	-1.73554100
N	-0.71865500	1.40656500	1.00371400
N	1.94832600	1.41144200	-0.13498300
N	1.94727400	-1.41256000	-0.13449300
N	-0.71966100	-1.40559100	1.00395100
C	-1.97345900	1.23242600	1.54643000
C	-2.56181100	2.51408500	1.87309900
C	-1.64430600	3.46425600	1.53208200
C	-0.49610300	2.76604200	0.98802900
C	0.64282100	3.40473100	0.50199000
H	0.64371900	4.49647600	0.52435600
C	1.75377600	2.78622000	-0.06119600
C	2.83205100	3.47328700	-0.72392800
C	3.66141600	2.51714800	-1.24874500
C	3.10325800	1.23636700	-0.89958700
C	3.64711600	-0.00129600	-1.24025300
H	4.55975100	-0.00178800	-1.83860600
C	3.10250800	-1.23843700	-0.89882200
C	3.66012300	-2.51969800	-1.24721800
C	2.83013200	-3.47514500	-0.72215900
C	1.75201200	-2.78715900	-0.06009700
C	0.64050500	-3.40483600	0.50292700
H	0.64070400	-4.49657200	0.52561400
C	-0.49816600	-2.76527200	0.98835600
C	-1.64707100	-3.46256700	1.53208400
C	-2.56395800	-2.51168500	1.87276400

C	-1.97452700	-1.23048900	1.54628900
C	-2.57271600	0.00120500	1.78585500
H	-3.57448000	0.00162300	2.21853600
C	-2.00569200	0.00019400	-1.80750800
C	-2.71599800	1.21266000	-1.88177500
C	-4.10753000	1.20972200	-2.01862900
C	-4.80907400	-0.00000900	-2.08474000
C	-4.10741200	-1.20961700	-2.01812600
C	-2.71585700	-1.21235300	-1.88126800
H	4.57030900	-2.66182500	-1.82597000
H	2.92196800	-4.55696800	-0.79388500
H	4.57150200	2.65854800	-1.82783300
H	2.92438700	4.55502600	-0.79630800
H	-1.71973900	4.54520500	1.63071800
H	-3.54737700	2.64854700	2.31305900
H	-3.54976100	-2.64538100	2.31242600
H	-1.72341100	-4.54345400	1.63070000
H	-4.64540000	-2.15911000	-2.07552900
H	-4.64564000	2.15912100	-2.07643100
H	-2.16740000	2.15525600	-1.83386200
H	-2.16721800	-2.15491300	-1.83296300
H	-5.89579200	-0.00009200	-2.19579600
O	1.26574000	-0.00003100	2.16838200
O	2.72486800	0.00022100	2.02255100
H	2.81305100	-0.76677400	1.40971700
H	2.81230600	0.76628400	1.40844500