

Supplementary Information for

A comprehensive experimental, multivariate statistical, and DFT computational analysis of the catalytic oxidation of benzyl alcohols mediated by Mn(III) and Fe(III) metalloporphyrins

Larissa Chimilouski^a, Sheetal Ranaut^b, William Henrique Slominski^a, Patrícia Salvador Tessaro^c, Gilson DeFreitas-Silva^c, Edmar Martendal^a, Claudio Nazari Verani^d, Shivnath Mazumder^{b}, Fernando Roberto Xavier^{a*}*

^a*Departamento de Química, Universidade do Estado de Santa Catarina (UDESC), 89.219-710, Joinville – SC, Brazil.*

^b*Department of Chemistry, Indian Institute of Technology Jammu (IIT Jammu), Jammu 181221, India.*

^c*Departamento de Química, Universidade Federal de Minas Gerais (UFMG), 31270-901, Belo Horizonte – MG, Brazil.*

^d*Department of Chemistry and Biochemistry, University of Windsor, 401 Sunset Avenue, Windsor, Ontario N9B 3P4, Canada.*

*fernando.xavier@udesc.br (corresponding author)

Table of Contents	Page
Experimental section	S3
Table S1. Calibration parameters obtained for product quantification using High-performance liquid chromatography with a diode array detector (HPLC-DAD) analysis. LOD = 0.16%, LOQ = 0.5%	S5
Table S2. Wavelength of the analytes used for quantification using High-performance liquid chromatography with a diode array detector (HPLC-DAD).	S5
Table S3. Comparison of the DFT-calculated results with experimental findings.	S6
Figure S1. Reaction monitoring of the catalytic oxidation of BnOH to form BA (top) and BzA (bottom), mediated by 2 . At 0.10 mol%, the conversion values for BzA were not quantified.	S7
Figure S2. Residual graph obtained by modeling the % yield as a function of catalyst concentration (1 , top; 2 , bottom) and reaction time with a 10-coefficient quadratic regression equation, for BA formation. $R^2 = 0.97$ for 1 and 0.98 for 2 .	S8
Figure S3. Residual graph obtained by modeling the % yield as a function of catalyst concentration (1 , top; 2 , bottom) and reaction time with a 10-coefficient quadratic regression equation, for BzA formation. $R^2 = 0.97$ for 1 and 0.98 for 2 .	S9
Figure S4. Energetics of the oxygen rebound step and subsequent dehydration pathway to carbonyl product in presence of Mn-porphyrin (A) and Fe-porphyrin (B) systems.	S10
Figure S5. Energetics of the acetate addition to Mn-porphyrin (A) and Fe-porphyrin (B).	S11
Table S4. XYZ coordinates of the DFT-optimized geometries.	S12

Experimental Section

Chemicals and instrumentation

Benzyl alcohol, *p*-nitrobenzyl alcohol, *p*-methoxybenzyl alcohol, *p*-chlorobenzyl alcohol, benzaldehyde, anisaldehyde, *p*-chlorobenzaldehyde, *p*-nitrobenzaldehyde, benzoic acid, *p*-methoxybenzoic acid, *p*-chlorobenzoic acid, *p*-nitrobenzoic acid, acetonitrile grade HPLC, iron(III) chloride, (diacetoxy)iodobenzene (DAIB) and dichloromethane were purchased from Sigma-Aldrich (St. Louis, MO, USA). The chemicals benzyl alcohol and benzaldehyde were distilled under reduced pressure prior to use. All other chemicals were used as received.

Metalloporphyrin complexes

The complex chlorido-5,10,15,20-tetraphenylporphyrin-21,23-diido manganese(III) - [Mn^{III}(TPP)Cl] (**1**) was prepared according to previously described procedures^{1,2} and chlorido-5,10,15,20-tetraphenylporphyrin-21,23-diido iron(III) - [Fe^{III}(TPP)Cl] (**2**) was purchased from Sigma-Aldrich (St. Louis, MO, USA). The [Fe^{III}(TPP)Cl] was passed through an alumina column using a mixture of dichloromethane and methanol (10:1) as eluent. The solvent was eliminated in a rotary evaporator, and the complex was dried in Abderhalden's drying pistol. The two complexes presented characterization data consistent with the literature.³

Catalytic assays

For the calibration curves, stock solutions were prepared containing benzyl alcohol (15 g L⁻¹), *p*-nitrobenzyl alcohol (15 g L⁻¹), *p*-methoxybenzyl alcohol (14.5 g L⁻¹), *p*-chlorobenzyl alcohol (14.5 g L⁻¹), benzaldehyde (10.2 g L⁻¹), anisaldehyde (10.2 g L⁻¹), *p*-chlorobenzaldehyde (10.2 g L⁻¹), *p*-nitrobenzaldehyde (10.2 g L⁻¹), benzoic acid (11.5 g L⁻¹), *p*-methoxybenzoic acid (11.5 g L⁻¹), *p*-chlorobenzoic acid (11.5 g L⁻¹) and *p*-nitrobenzoic acid (11.5 g L⁻¹) using acetonitrile as solvent. Seven diluted solutions were prepared from the stock solutions with concentrations ranging from 5.7 to 98 mg L⁻¹ for substrate, 0.5 to 91 mg L⁻¹ for aldehydes, and 0.6 to 92 mg L⁻¹ for acids using acetonitrile as solvent. Calibration curves were constructed by injecting 10 µL aliquots of the analyte's solutions into the high-performance liquid chromatography with a diode-array detection (HPLC-DAD) using toluene as an internal standard (81 mg L⁻¹) to correct instrumental variations. All measurements were made in triplicates. The concentration range was calculated based on different yield ranges for the compounds: substrates 5-100%, aldehydes 0.5-55% and acids 0.5-55%. Calibration parameters obtained for product quantification were extracted from the HPLC-DAD analysis and are summarized in **Table S1**.

Oxidation reactions were carried out in 4.5 mL amber screw-capped glass vials with a PTFE-coated silicone septum obtained from Sigma-Aldrich, where the catalysts (**1**) or (**2**), oxidant (DAIB) and substrate (benzyl alcohol) solutions were added. The solvent (dichloromethane) was added until the final volume mark of 2.5 mL was reached. The reactions were maintained under constant magnetic stirring at a temperature of 20 °C. The amount of substrate added in each reaction was fixed at 20 µmol (equivalent to a mass of 2.16

mg for substrate), and the amount of catalyst (mol%) was calculated from this value, and the oxidant was fixed in excess (equivalent to an average mass of 60 mg for DAIB – 182.6 µmol).

After the completion of each reaction time required by the experimental design, 80 µL of the reaction mixture was added into a 2.0 mL screw-capped glass vial with a PTFE-coated silicone septum with 89 µL of toluene (internal standard) to obtain a final concentration of 81 mg L⁻¹ in 1331 µL of acetonitrile (solvent). Injections were made into the liquid chromatograph for the quantification of the products using the areas obtained from the calibration curves previously prepared.

The oxidation reactions with the *p*-substituted benzyl alcohol substrates were carried out in 4.5 mL PTFE septum flasks (Sigma Aldrich), in which 2.45 mol% of catalyst (**1**) or (**2**), excess oxidant DAIB – 182.6 µmol, 20 µmol of the substrates (benzyl alcohol, *p*-methoxybenzyl alcohol, *p*-chlorobenzyl alcohol, *p*-nitrobenzyl alcohol), and dichloromethane solvent were added to 2.5 mL (final reaction volume). The reaction was carried out for 60 minutes. These conditions were chosen in order to evaluate the catalytic activity of (**1**) and (**2**). The reactions were carried out in triplicate, maintained under magnetic stirring, and at a temperature of 20°C. After completion, each reaction was diluted in acetonitrile (80 µL of sample, 89 µL of internal standard for a final volume of 1500 µL) and injected into the HPLC-DAD for product quantification. The control reactions with benzaldehyde substrate were carried out in presence of FeCl₃·6H₂O without adding catalysts (**1**) or (**2**) in the same way as described above for the *p*-substituted benzyl alcohol.

Separation and quantification of the substrates and products

The separation and quantification of *p*-substituted benzyl alcohol substrates and their oxidation products were performed using a high-performance liquid chromatograph with a diode array detector, model LC 2050C 3D (Shimadzu, Kyoto, Japan). The stationary phase used was a Shim Pack Velox C18 packed column (Shimadzu, Kyoto, Japan) which is 150 mm long and 4.6 mm in diameter with a particle thickness of 2.7 µm. The separation was carried out at 30°C using gradient elution. Phase A consisted of ultrapure water acidified with HPLC-grade phosphoric acid at pH = 2.30. Phase B consisted of HPLC-grade acetonitrile. Separation began with a phase A to phase B ratio of 90:10 (v/v), which changed to 80:20 in 30 min. The mobile phase flow rate was 0.500 mL min⁻¹. The volume of the sample injected was 10 µL. **Table S2** shows the wavelengths for each compound analyzed.

Multivariate analysis

The experimental design and the variables chosen for the multivariate optimization were based on preliminary studies and literature.⁴ A set of eleven experiments were carried out, considering catalyst load (complexes (**1**) or (**2**) in mol%), oxidant (DAIB) and time (min). An initial catalyst concentration of 0.1 mol% was selected, which corresponds to a ratio of 1:1000 with respect to the substrate. The highest level, 5 mol% was chosen, with a center point at 2.45 mol%. The proportion of DAIB used was set at 9.1 excess with

oxidant in relation to the substrate (equivalent to a mass of 60 mg for DAIB). During the preliminary studies for monitoring the reaction, aliquots were collected in every 2-120 minutes and, based on the results, the following was determined for the multivariate analysis. The reaction time was evaluated in the range of 5 to 120 min, with the center point at 62.5 min. The temperature was kept constant at 20 °C.

The regression model generated by the three-level full factorial design had 8 coefficients: the intercept, 2 linear (1L and 2L) coefficients for each variable, 1 linear-interaction coefficient between the two variables (1Lx2L), 2 quadratic (1Q and 2Q) coefficients and 2 linear-quadratic interaction coefficients (1Lx2Q and 2Lx1Q). The generated models are initially validated by analyzing the coefficient of determination R^2 , which should be greater than 0.9, and by analyzing the residuals, which are the differences between the values predicted by the model and the values experimentally obtained. Residuals were randomly distributed, indicating that the mathematical model used for the regression was adequate. Residual plots for all models can be visualized in **Figures S1-S2**.

The significance of the regression model coefficients was statistically evaluated using Pareto charts. The x-axis value on the Pareto chart represents the calculated t-value, which was obtained by the ratio between the coefficient value and its standard error estimated by the software. If the calculated t-value obtained was greater than the critical t, the coefficient was considered statistically significant for the mathematical model. The critical t-value was tabulated as a function of the number of degrees of freedom and the statistical significance chosen for analysis (95%). The number of degrees of freedom for a regression model was the difference between the number of experiments performed and the number of coefficients in the model. The greater the number of degrees of freedom, the better the estimation of the coefficients where a minimum of 3 degrees of freedom is required. In the present work, all the models generated were validated with a few degrees of freedom greater than or equal to 3.

Computational details

All calculations were carried out using Density Functional Theory (DFT) as implemented in Gaussian16 (revision C.01) suit of package.⁵ The functional used is BP86-D3 where D3 denotes the third-generation dispersion correction by Grimme and co-workers.^{6,7,8} The basis set chosen is def2SVP for geometry optimization in solvent dichloromethane.^{9,10} Implicit SMD solvation model was employed.¹¹ The initial coordinates for the DFT optimization were taken from the X-ray coordinates of the crystal structure. The energies of the optimized structures were re-evaluated by additional single point calculations in dichloromethane solvent on each optimized geometry using triple-zeta def2TZVP basis set.^{9,10} A systematic benchmarking study was performed in order to evaluate the performance of our chosen DFT methodology in reproducing the experimental results. The details can be found in **Table S3**. Gratifyingly, our methodology is in agreement with the experimental findings. It correctly predicts the diamagnetic low-spin ($S = 0$) ground state for manganese(V)-oxo porphyrin and paramagnetic quartet ($S =$

$3/2$) ground state for iron(IV)-oxo porphyrin radical complex. Frequency calculations at the BP86-D3/def2SVP level of theory were performed to identify all the stationary points as minima (zero imaginary frequency) or transition states (one imaginary frequency). The SCF energy calculated at the BP86-D3/def2TZVP level of theory was used for calculations of the free energy. The zero-point and thermal corrections were included. To locate the transition states, the potential energy surface was first explored approximately using the linear synchronous transit (LST) method,¹² followed by a free transition state search using the LST geometry as an initial guess. A keyword TS was used that requests optimization to a transition state rather than a local minimum using the Berny algorithm. Intrinsic reaction coordinate¹³ (IRC) scans were performed to verify that the transition states connect to appropriate reactants and products. All of the transition state structures had only one imaginary frequency. GaussView 6¹⁴ was used to visualize isodensity plots of the spin populations (isovalue = 0.004 au) and corresponding biorthogonal orbitals¹⁵ (isovalue = 0.05 au).

Table S1. Calibration parameters obtained for product quantification using High-performance liquid chromatography with a diode array detector (HPLC-DAD) analysis. LOD = 0.16%, LOQ = 0.5%.

Compound	Linear range (%conversion)	R²
Benzaldehyde	0.5-55%	0.9994
Benzoic acid	0.1-55%	0.9996
Anisaldehyde	0.5-55%	0.9991
<i>p</i> -methoxybenzoic acid	0.5-55%	0.9995
<i>p</i> -chlorobenzaldehyde	0.5-55%	0.9999
<i>p</i> -chlorobenzoic acid	0.5-55%	0.9976
<i>p</i> -nitrobenzaldehyde	0.5-55%	0.9979
<i>p</i> -nitrobenzoic acid	0.5-55%	0.9995

Table S2. Wavelength of the analytes used for quantification using High-performance liquid chromatography with a diode array detector (HPLC-DAD).

Analytes	Wavelength (nm)
Toluene	197
Benzaldehyde	248
Benzoic acid	229
Anisaldehyde	281
<i>p</i> -methoxybenzoic acid	255
<i>p</i> -chlorobenzaldehyde	255
<i>p</i> -chlorobenzoic acid	239
<i>p</i> -nitrobenzaldehyde	266
<i>p</i> -nitrobenzoic acid	262

Table S3. Comparison of the DFT-calculated results with experimental findings.

Molecular System	BP86-D3 / def2SVP (GO) / def2TZVP (SP) results		Experimental Findings
[Mn(V)-Oxo-Cl-(TPP)]	Spin states	ΔG (kcal/mol)	Diamagnetic low-spin ($S = 0$) ground state ^a
	Singlet ($S=0$)	0.0	
	Triplet ($S=1$)	+2.0	
[Fe(IV)-Oxo-Cl-(TPP ^{•+})]	Spin states	ΔG (kcal/mol)	A triradicaloid ($S = 3/2$) quartet ground state ^b
	Doublet ($S=1/2$)	0.0	
	Quartet ($S=3/2$)	-0.7	
	Hextet ($S=5/2$)	+19.8	

^aSong, W. J.; Seo, M. S.; DeBeer George, S.; Ohta, T.; Song, R.; Kang, M.-J.; Tosha, T.; Kitagawa, T.; Solomon, E. I.; Nam, W. Synthesis, Characterization, and Reactivities of Manganese(V)-Oxo Porphyrin Complexes. *J. Am. Chem. Soc.* 2007, 129, 1268–1277.

^bBoso, B.; Lang, G.; McMurry, T. J.; Groves, J. T. Mossbauer Effect Study of Tight Spin Coupling in Oxidized Chloro-5,10,15,20-tetra(mesityl)porphyrinatoiron(III). *J. Chem. Phys.* 1983, 79, 1122-1126.

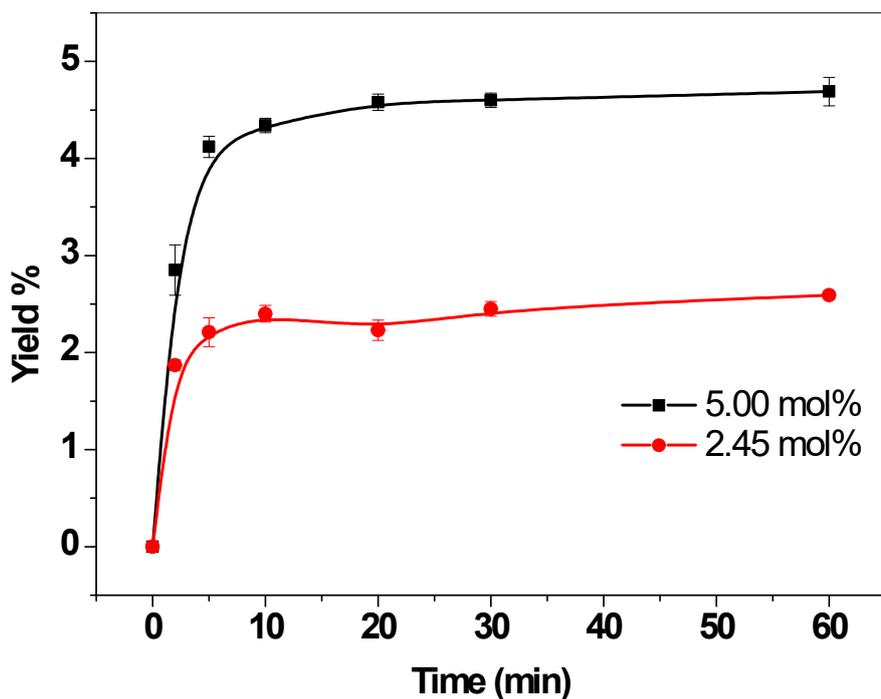
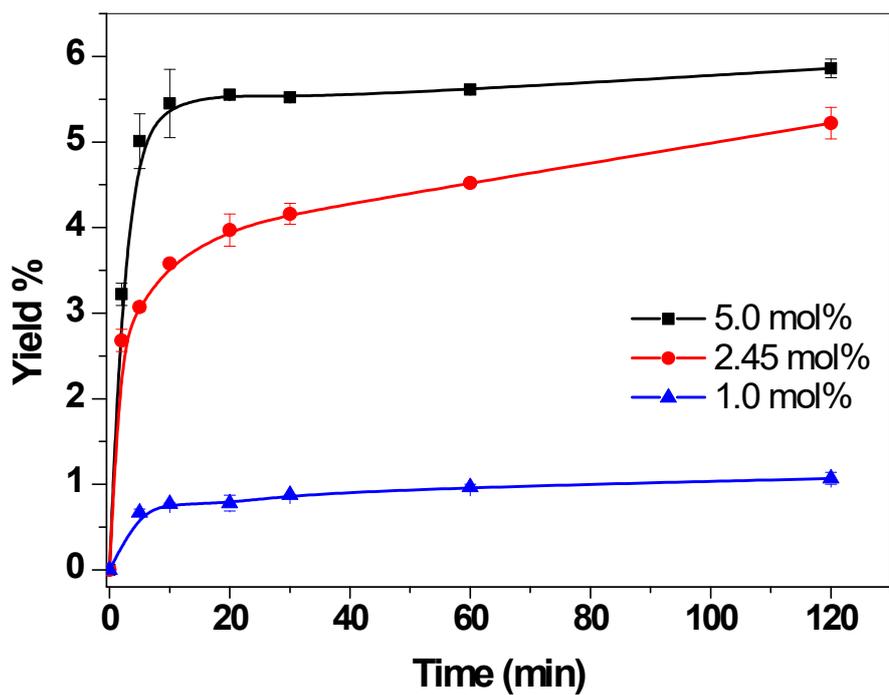


Figure S1. Reaction monitoring of the catalytic oxidation of BnOH to form BA (top) and BzA (bottom), mediated by **2**. At 0.10 mol%, the conversion values for BzA were not quantified.

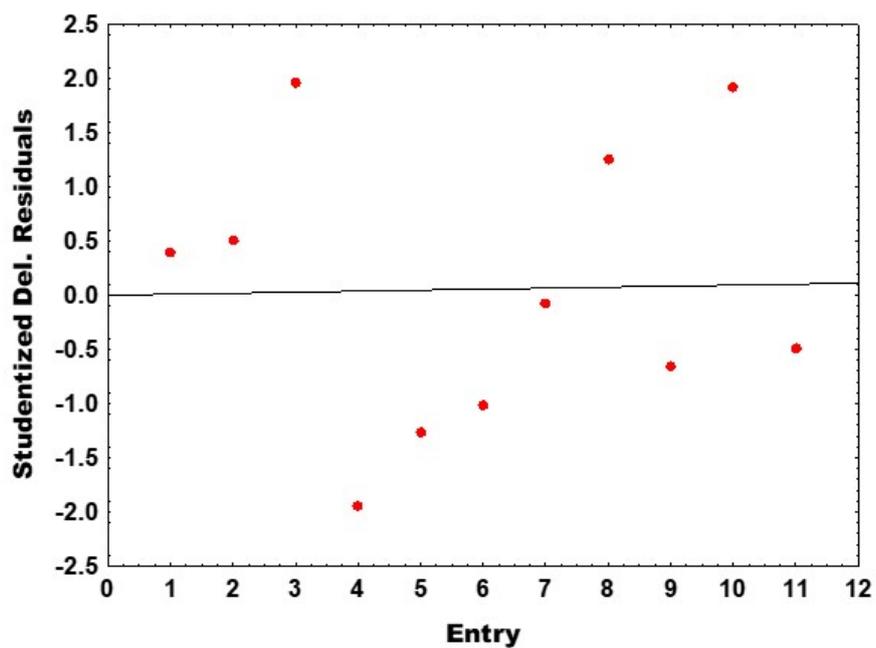
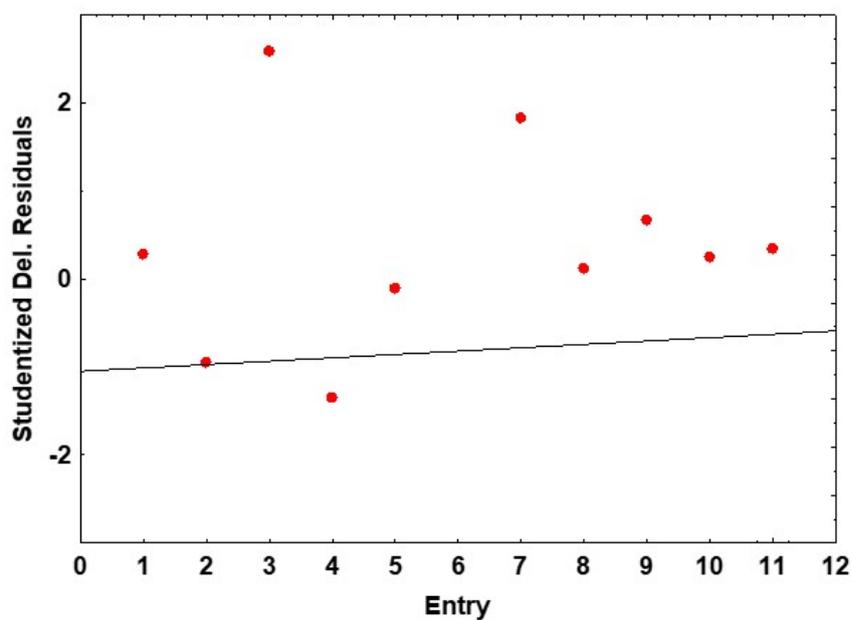


Figure S2. Residual graph obtained by modeling the % yield as a function of catalyst concentration (**1**, top; **2**, bottom) and reaction time with a 10-coefficient quadratic regression equation, for BA formation. $R^2 = 0.97$ for **1** and 0.98 for **2**.



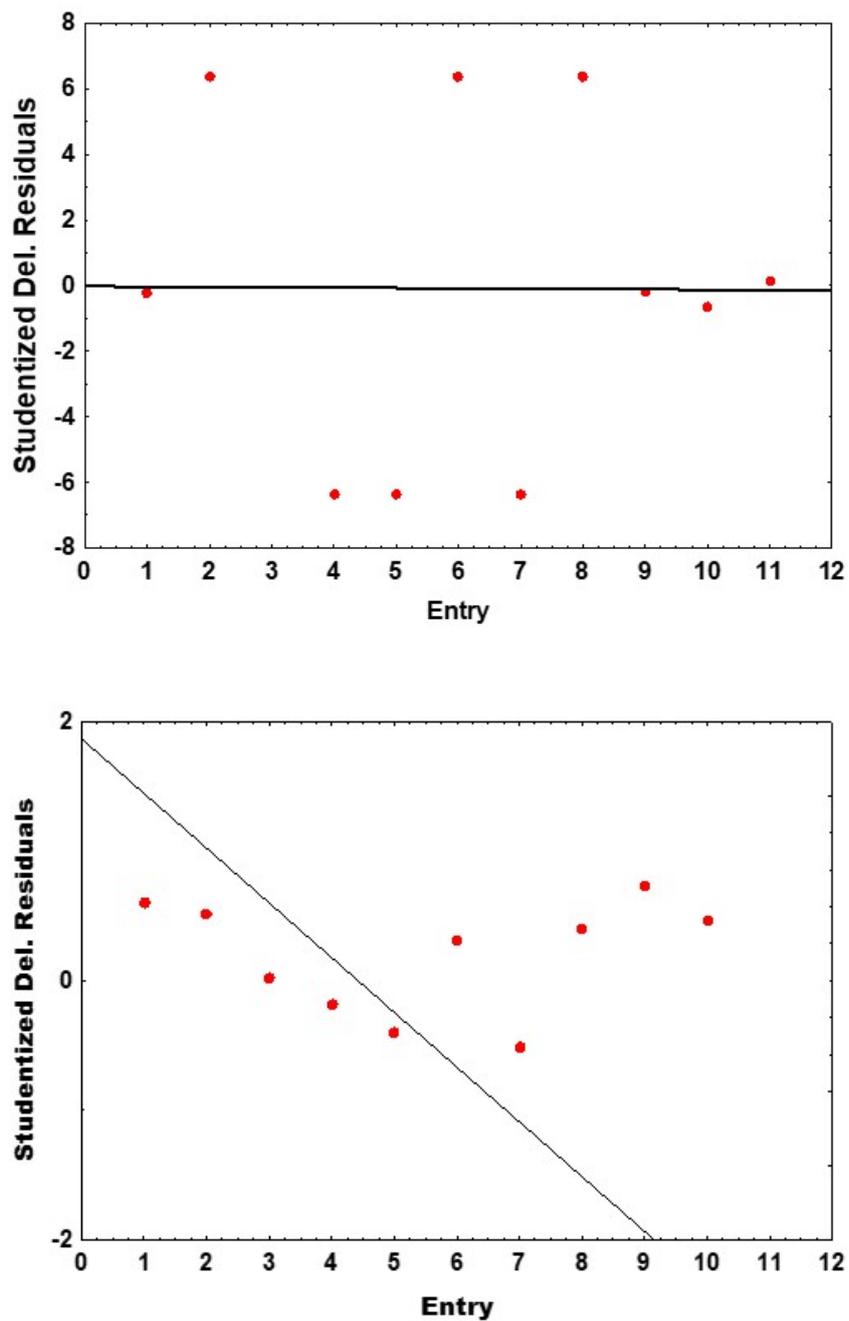


Figure S3. Residual graph obtained by modeling the % yield as a function of catalyst concentration (**1**, top; **2**, bottom) and reaction time with a 10-coefficient quadratic regression equation, for BzA formation. $R^2 = 0.97$ for **1** and 0.98 for **2**.

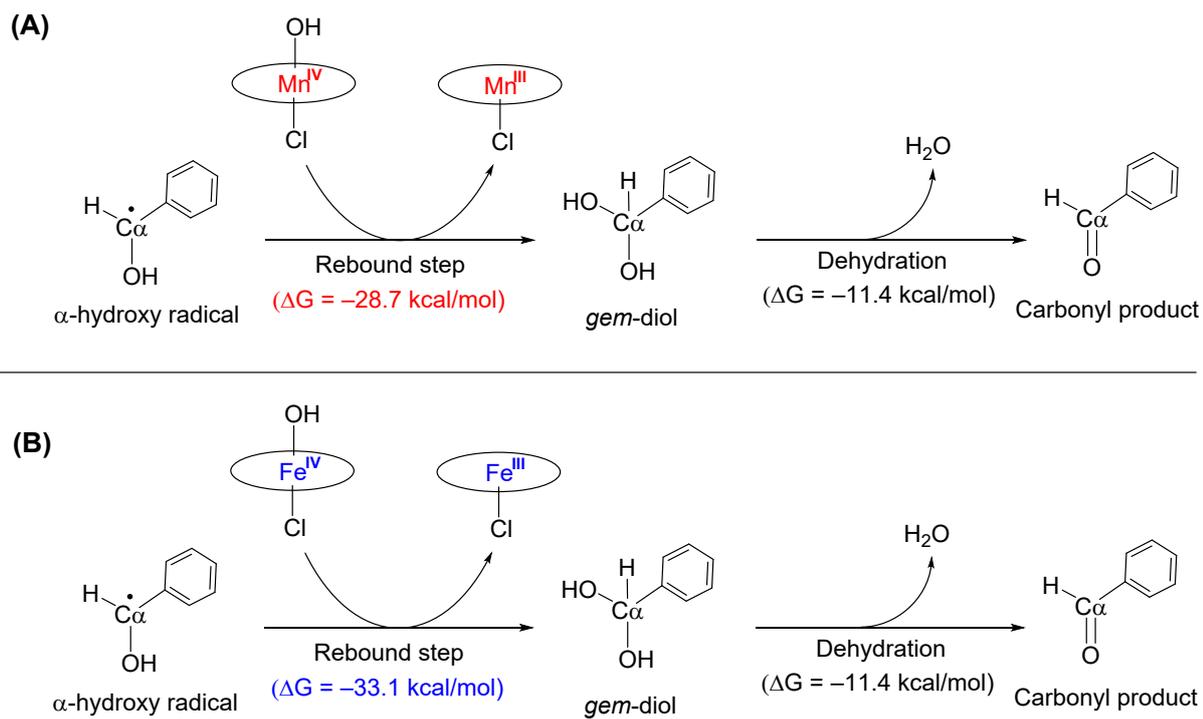


Figure S4. Energetics of the oxygen rebound step and subsequent dehydration pathway to carbonyl product in presence of Mn-porphyrin **(A)** and Fe-porphyrin **(B)** systems.

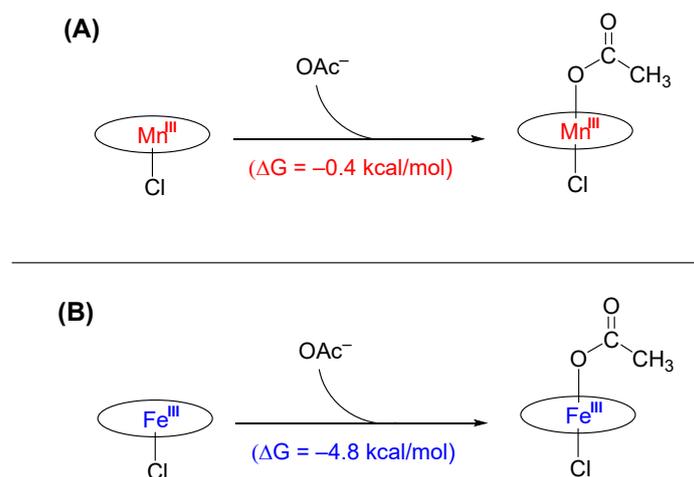


Figure S5. Energetics of the acetate addition to Mn-porphyrin (A) and Fe-porphyrin (B).

The $[(\text{TPP})(\text{Cl})\text{Fe}^{\text{III}}]^0$ intermediate can bind with an acetate ion from the solution and this step is energetically more favorable than the corresponding acetate binding step by $[(\text{TPP})(\text{Cl})\text{Mn}^{\text{III}}]^0$. The resulting six-coordinate intermediate $[(\text{TPP})(\text{Cl})(\text{OAc})\text{Fe}^{\text{III}}]^-$ is unproductive for having a catalytic turnover.

Table S4. XYZ coordinates of the DFT-optimized geometries**(i)**

C	-3.618297000	-1.552339000	-1.372019000	C	2.980859000	-1.653277000	6.209866000
C	-3.154539000	-0.934716000	-2.508327000	H	2.790103000	-0.918919000	7.008859000
C	-1.716081000	-0.830811000	-2.382909000	C	3.794108000	-2.774054000	6.459850000
C	-2.469711000	-1.798972000	-0.529157000	H	4.239347000	-2.922944000	7.456645000
N	-1.315285000	-1.372973000	-1.165066000	C	4.036271000	-3.704171000	5.432119000
C	-2.538224000	-2.363657000	0.759720000	H	4.668014000	-4.586694000	5.622271000
C	-1.410912000	-2.481422000	1.593149000	C	3.470172000	-3.514402000	4.159711000
N	-0.100252000	-2.173026000	1.249812000	H	3.655495000	-4.243497000	3.355110000
C	0.655352000	-2.345586000	2.409319000	C	-3.866277000	-2.796479000	1.295633000
C	-1.477577000	-2.873499000	2.982790000	C	-4.881331000	-1.851289000	1.571466000
C	-0.203674000	-2.782033000	3.488227000	C	-6.122508000	-2.267588000	2.082503000
C	2.044945000	-2.183080000	2.547690000	H	-6.902511000	-1.519517000	2.297023000
C	2.900946000	-1.854743000	1.474301000	C	-6.366349000	-3.632064000	2.324926000
N	2.503840000	-1.613503000	0.181104000	H	-7.340106000	-3.957396000	2.724838000
C	4.808328000	-1.438764000	0.324933000	C	-5.360787000	-4.579114000	2.056944000
C	4.342241000	-1.728617000	1.583506000	H	-5.544911000	-5.649443000	2.242914000
C	2.597889000	-0.704812000	-2.706872000	C	-4.118146000	-4.165076000	1.547583000
N	1.278721000	-0.803002000	-2.317590000	H	-3.330613000	-4.905621000	1.336045000
C	0.517663000	-0.365704000	-3.373774000	C	-1.557826000	0.243444000	-4.623440000
C	1.379325000	0.042169000	-4.470472000	C	-2.248371000	1.474095000	-4.536600000
C	2.669320000	-0.198472000	-4.067856000	C	-2.874815000	2.020397000	-5.669936000
C	-0.893337000	-0.330239000	-3.409944000	H	-3.405266000	2.982788000	-5.589186000
C	3.725784000	-0.979876000	-1.904802000	C	-2.822596000	1.343258000	-6.902236000
C	3.649507000	-1.359917000	-0.547608000	H	-3.314838000	1.771683000	-7.790016000
H	-4.651022000	-1.821975000	-1.124896000	C	-2.140385000	0.116134000	-6.996188000
H	-3.733291000	-0.603151000	-3.377699000	H	-2.100619000	-0.422809000	-7.956424000
H	-2.393651000	-3.165572000	3.508402000	C	-1.510912000	-0.431059000	-5.864841000
H	0.133435000	-2.999351000	4.507920000	H	-0.981280000	-1.394216000	-5.935757000
H	5.843464000	-1.259946000	0.013088000	C	5.087502000	-0.807689000	-2.502719000
H	4.918014000	-1.842515000	2.508800000	C	5.564326000	0.474393000	-2.861495000
H	1.035745000	0.447652000	-5.428606000	C	6.849019000	0.628703000	-3.409704000
H	3.593287000	-0.033436000	-4.633125000	H	7.209739000	1.634494000	-3.678717000
C	2.651393000	-2.391515000	3.900669000	C	7.673400000	-0.494313000	-3.608338000
C	2.411221000	-1.462847000	4.939230000	H	8.680270000	-0.372074000	-4.038772000
				C	7.207768000	-1.773483000	-3.252489000
				H	7.846802000	-2.657761000	-3.406720000
				C	5.924645000	-1.929981000	-2.700782000

H	5.558770000	-2.930777000	-2.421636000	H	5.817404000	-1.560700000	-0.094887000
H	1.776599000	-0.584842000	4.740117000	H	4.890752000	-1.531286000	2.462049000
H	4.921608000	1.353526000	-2.696879000	H	1.080016000	0.788632000	-5.241323000
H	-2.286308000	2.002844000	-3.571031000	H	3.534334000	-0.248114000	-4.729411000
H	-4.686447000	-0.782488000	1.390137000	C	2.549796000	-1.769466000	3.954784000
O	0.830238000	-3.019055000	-1.183594000	C	2.110817000	-0.760125000	4.843754000
Cl	0.587677000	0.601689000	0.134617000	C	2.609338000	-0.702662000	6.156046000
Mn	0.560506000	-1.636359000	-0.532476000	H	2.265570000	0.093783000	6.835336000
(ii)				C	3.544143000	-1.656148000	6.599949000
C	-3.552683000	-1.671474000	-1.471338000	H	3.932246000	-1.611854000	7.630147000
C	-3.132840000	-0.802844000	-2.452190000	C	3.978283000	-2.669125000	5.725003000
C	-1.706049000	-0.604754000	-2.261622000	H	4.701446000	-3.425401000	6.069985000
C	-2.399061000	-1.949899000	-0.634773000	C	3.486100000	-2.726623000	4.410110000
N	-1.298426000	-1.297518000	-1.145386000	H	3.814038000	-3.528441000	3.730200000
C	-2.414483000	-2.665492000	0.588012000	C	-3.672975000	-3.333454000	1.033627000
C	-1.317392000	-2.677266000	1.482657000	C	-4.854804000	-2.595282000	1.280010000
N	-0.058624000	-2.169340000	1.223686000	C	-6.020264000	-3.244876000	1.719684000
C	0.624071000	-2.133713000	2.421526000	H	-6.930657000	-2.656367000	1.916588000
C	-1.419022000	-3.007018000	2.892500000	C	-6.023257000	-4.638153000	1.917484000
C	-0.229510000	-2.639780000	3.478623000	H	-6.938852000	-5.145917000	2.260655000
C	1.994909000	-1.816422000	2.568904000	C	-4.850817000	-5.379440000	1.681396000
C	2.860997000	-1.640543000	1.467025000	H	-4.845248000	-6.470410000	1.835201000
N	2.468443000	-1.630976000	0.137263000	C	-3.681500000	-4.732385000	1.248275000
C	4.775613000	-1.597683000	0.243503000	H	-2.762521000	-5.310714000	1.063166000
C	4.305214000	-1.574791000	1.536929000	C	-1.531284000	0.812986000	-4.290667000
C	2.575128000	-0.896349000	-2.774584000	C	-2.226371000	1.998643000	-3.954701000
N	1.293335000	-0.797965000	-2.288131000	C	-2.878336000	2.747101000	-4.949170000
C	0.541928000	-0.136715000	-3.237955000	H	-3.408484000	3.673270000	-4.675001000
C	1.397541000	0.228195000	-4.355051000	C	-2.854396000	2.316171000	-6.288440000
C	2.641746000	-0.296381000	-4.096035000	H	-3.368973000	2.901641000	-7.067142000
C	-0.862778000	0.028645000	-3.208055000	C	-2.175934000	1.131272000	-6.628982000
C	3.687079000	-1.351187000	-2.022762000	H	-2.164226000	0.781113000	-7.673573000
C	3.620294000	-1.592040000	-0.630499000	C	-1.517694000	0.383455000	-5.638058000
H	-4.558917000	-2.078786000	-1.322568000	H	-1.002092000	-0.553245000	-5.901540000
H	-3.723376000	-0.373339000	-3.269625000	C	5.030086000	-1.444287000	-2.670280000
H	-2.309097000	-3.423501000	3.377930000	C	5.689947000	-0.299297000	-3.175302000
H	0.058199000	-2.726767000	4.532666000	C	6.962907000	-0.412100000	-3.759130000

H	7.468760000	0.489201000	-4.140832000	H	-4.482744000	1.266234000	1.261272000
C	7.593390000	-1.667084000	-3.847213000	H	-2.927116000	3.493234000	1.478280000
H	8.590988000	-1.753696000	-4.306764000	C	-3.164454000	-0.834333000	-0.226455000
C	6.948186000	-2.809720000	-3.339533000	N	-1.232449000	-1.383697000	-1.678594000
H	7.436454000	-3.795353000	-3.403073000	C	-1.022529000	-2.234910000	-2.742911000
C	5.677795000	-2.699806000	-2.749484000	C	-2.227241000	-3.013661000	-2.974318000
H	5.171881000	-3.593081000	-2.350271000	C	-3.122680000	-2.672237000	-1.987311000
H	1.380359000	-0.014774000	4.491421000	C	-2.505487000	-1.615147000	-1.205456000
H	5.206787000	0.686178000	-3.087159000	H	-2.360873000	-3.751967000	-3.772813000
H	-2.243438000	2.332395000	-2.905143000	H	-4.129179000	-3.074731000	-1.826759000
H	-4.847890000	-1.502565000	1.144503000	C	0.213231000	-2.430273000	-3.404149000
O	0.535151000	-3.054879000	-1.220123000	O	0.337209000	-1.122387000	0.385805000
Cl	0.439282000	0.657961000	0.211467000	H	1.037998000	-0.538126000	1.497210000
Mn	0.626120000	-1.592525000	-0.543146000	C	1.449881000	-0.142388000	2.558473000
(ii-TS)				H	2.266741000	0.569697000	2.325547000
Mn	0.098231000	-0.063693000	-0.903729000	C	0.268071000	0.509748000	3.225219000
C	1.070897000	2.555044000	0.244317000	C	-1.006444000	-0.096009000	3.161992000
C	2.306029000	3.235344000	0.572095000	C	-2.099982000	0.483972000	3.823896000
C	3.334047000	2.343234000	0.351340000	C	-1.935659000	1.682605000	4.543667000
C	2.743003000	1.139869000	-0.193588000	C	-0.673547000	2.300932000	4.596358000
N	1.368212000	1.291814000	-0.241007000	C	0.424869000	1.715813000	3.941311000
H	2.382693000	4.264766000	0.939208000	H	-1.137032000	-1.003625000	2.550865000
H	4.408914000	2.506376000	0.491255000	H	-3.094056000	0.015552000	3.754296000
C	3.482536000	0.063558000	-0.736331000	H	-2.798311000	2.144884000	5.049570000
C	3.656323000	-1.814154000	-2.455760000	H	-0.543482000	3.247171000	5.145406000
C	2.743797000	-2.398898000	-3.303698000	H	1.416807000	2.194598000	3.982490000
C	1.434032000	-1.884928000	-2.939007000	Cl	-0.317160000	1.231975000	-2.820446000
N	1.576524000	-0.957819000	-1.930435000	O	2.013392000	-1.230809000	3.234950000
C	2.917549000	-0.881216000	-1.623724000	H	1.281758000	-1.771456000	3.607108000
H	4.737832000	-1.985673000	-2.411040000	C	-4.522809000	-1.241609000	0.248794000
H	2.929063000	-3.155358000	-4.075165000	C	-5.649018000	-1.214341000	-0.605294000
C	-0.231930000	3.034744000	0.510658000	C	-4.694810000	-1.632910000	1.596978000
N	-1.396883000	0.902856000	-0.007943000	C	-6.917369000	-1.579105000	-0.121641000
C	-2.651962000	0.392953000	0.253184000	C	-5.963371000	-1.999706000	2.077873000
C	-3.447643000	1.402113000	0.927918000	C	-7.077935000	-1.974390000	1.219383000
C	-2.667960000	2.531266000	1.022119000	H	-5.526174000	-0.888616000	-1.650115000
C	-1.375077000	2.203042000	0.451083000	H	-3.819532000	-1.653352000	2.265306000

H	-7.787748000	-1.547365000	-0.796576000	C	0.995027000	2.632872000	0.182089000
H	-6.080574000	-2.308137000	3.129171000	C	2.243647000	3.230255000	0.610022000
H	-8.073176000	-2.259795000	1.596238000	C	3.195626000	2.235382000	0.588180000
C	4.939744000	0.001662000	-0.414072000	C	2.552056000	1.041835000	0.075980000
C	5.335373000	-0.260013000	0.919419000	N	1.218060000	1.309948000	-0.158897000
C	5.934085000	0.219201000	-1.395232000	H	2.375754000	4.277612000	0.903952000
C	6.697517000	-0.312741000	1.260251000	H	4.258050000	2.314554000	0.846033000
C	7.295616000	0.168996000	-1.050161000	C	3.246771000	-0.132738000	-0.303460000
C	7.680890000	-0.098640000	0.276618000	C	3.440006000	-2.171316000	-1.813119000
H	4.562047000	-0.437936000	1.683893000	C	2.605708000	-2.735437000	-2.750697000
H	5.631884000	0.445708000	-2.429717000	C	1.324616000	-2.063281000	-2.638842000
H	6.991750000	-0.525376000	2.300571000	N	1.409456000	-1.077727000	-1.678897000
H	8.060734000	0.347004000	-1.822798000	C	2.698009000	-1.099226000	-1.176405000
H	8.748912000	-0.138000000	0.544527000	H	4.475057000	-2.448609000	-1.584029000
C	-0.426609000	4.446301000	0.959706000	H	2.818774000	-3.571683000	-3.426666000
C	0.124415000	4.932324000	2.167931000	C	-0.274422000	3.252686000	0.235013000
C	-1.207925000	5.320284000	0.166289000	N	-1.579280000	1.223397000	-0.368718000
C	-0.095603000	6.260758000	2.569559000	C	-2.902516000	0.847471000	-0.245056000
C	-1.423920000	6.649043000	0.568328000	C	-3.664391000	1.954177000	0.300463000
C	-0.868419000	7.123686000	1.770940000	C	-2.790393000	3.006912000	0.454952000
H	0.709834000	4.252667000	2.803572000	C	-1.479721000	2.533975000	0.053662000
H	-1.639472000	4.947009000	-0.775925000	H	-4.741238000	1.935619000	0.504442000
H	0.334343000	6.621178000	3.517916000	H	-3.005349000	4.011372000	0.837770000
H	-2.028961000	7.318284000	-0.064221000	C	-3.473549000	-0.339777000	-0.759679000
H	-1.039959000	8.165211000	2.086873000	N	-1.410723000	-1.178508000	-1.866501000
C	0.280225000	-3.351526000	-4.579900000	C	-1.147961000	-2.115053000	-2.847557000
C	0.023513000	-4.736804000	-4.456025000	C	-2.387637000	-2.760885000	-3.235103000
C	0.640956000	-2.832450000	-5.845562000	C	-3.375143000	-2.260146000	-2.417948000
C	0.113712000	-5.580660000	-5.576130000	C	-2.764872000	-1.234793000	-1.593397000
C	0.726634000	-3.678003000	-6.964753000	H	-2.486749000	-3.527870000	-4.011363000
C	0.461837000	-5.053679000	-6.833703000	H	-4.434745000	-2.538488000	-2.400757000
H	-0.231245000	-5.152571000	-3.468576000	C	0.141313000	-2.501611000	-3.279563000
H	0.846580000	-1.754786000	-5.944783000	O	-0.171996000	-0.912420000	0.527274000
H	-0.082661000	-6.659048000	-5.463425000	H	-0.156434000	-0.282630000	1.281574000
H	1.001083000	-3.258036000	-7.945788000	Cl	0.006961000	1.294568000	-2.954290000
H	0.530960000	-5.716656000	-7.711038000	C	0.285150000	-3.511979000	-4.371874000
(iii)				C	0.924045000	-3.142951000	-5.579035000

C	-0.169382000	-4.842444000	-4.217152000	H	-5.554702000	-0.190275000	-2.553235000
C	1.089857000	-4.079684000	-6.613346000	H	-4.627114000	-0.965485000	1.615663000
C	0.000524000	-5.777908000	-5.251948000	H	-7.987944000	-0.552208000	-2.082917000
C	0.627364000	-5.398877000	-6.453491000	H	-7.060824000	-1.324310000	2.094004000
H	1.284383000	-2.109237000	-5.701649000	H	-8.750162000	-1.122502000	0.243344000
H	-0.642373000	-5.144653000	-3.269635000	Mn	-0.091571000	0.061432000	-1.015250000
H	1.583061000	-3.775743000	-7.550620000	(iv)			
H	-0.352668000	-6.812592000	-5.114832000	C	-3.522757000	-1.707232000	-1.496128000
H	0.759451000	-6.133573000	-7.263915000	C	-3.117939000	-0.790097000	-2.438022000
C	4.664676000	-0.267893000	0.149844000	C	-1.692650000	-0.591309000	-2.246144000
C	4.947660000	-0.397645000	1.530136000	C	-2.363384000	-2.002902000	-0.674188000
C	5.740952000	-0.234301000	-0.767784000	N	-1.264253000	-1.332340000	-1.170068000
C	6.274383000	-0.508310000	1.979654000	C	-2.378107000	-2.726172000	0.542739000
C	7.066959000	-0.341330000	-0.315364000	C	-1.295367000	-2.684735000	1.456828000
C	7.337550000	-0.482036000	1.058402000	N	-0.066228000	-2.119876000	1.203317000
H	4.114447000	-0.418443000	2.250424000	C	0.610007000	-2.060166000	2.401161000
H	5.531267000	-0.104458000	-1.841053000	C	-1.398378000	-3.012066000	2.867215000
H	6.478210000	-0.617092000	3.057025000	C	-0.229671000	-2.590615000	3.459108000
H	7.894983000	-0.306468000	-1.041486000	C	1.978726000	-1.729338000	2.552082000
H	8.377812000	-0.566569000	1.411472000	C	2.854083000	-1.604320000	1.447774000
C	-0.376545000	4.696683000	0.604153000	N	2.457945000	-1.619732000	0.126134000
C	-0.929267000	5.613532000	-0.321261000	C	4.766773000	-1.660846000	0.225966000
C	0.042347000	5.170678000	1.869422000	C	4.303161000	-1.580370000	1.518527000
C	-1.046374000	6.974685000	0.007059000	C	2.550981000	-0.949742000	-2.776853000
C	-0.079013000	6.531957000	2.196204000	N	1.272755000	-0.816888000	-2.278921000
C	-0.620548000	7.438004000	1.265611000	C	0.543948000	-0.115830000	-3.215795000
H	-1.259106000	5.248506000	-1.306828000	C	1.401408000	0.237152000	-4.332733000
H	0.450027000	4.459552000	2.604944000	C	2.626323000	-0.339237000	-4.092189000
H	-1.471355000	7.678069000	-0.726880000	C	-0.856510000	0.080079000	-3.171839000
H	0.245506000	6.885497000	3.188084000	C	3.658259000	-1.433021000	-2.038573000
H	-0.714209000	8.505233000	1.522959000	C	3.600244000	-1.647946000	-0.638714000
C	-4.929566000	-0.570828000	-0.503032000	H	-4.523879000	-2.130939000	-1.360329000
C	-5.887178000	-0.453558000	-1.536829000	H	-3.716624000	-0.329035000	-3.231967000
C	-5.368483000	-0.878966000	0.805474000	H	-2.273004000	-3.466923000	3.346311000
C	-7.252387000	-0.652050000	-1.268600000	H	0.057325000	-2.663274000	4.514462000
C	-6.734206000	-1.078773000	1.070692000	H	5.806961000	-1.664413000	-0.119419000
C	-7.679482000	-0.967392000	0.034551000	H	4.892744000	-1.522202000	2.440077000

H	1.097901000	0.821504000	-5.208221000	H	8.519659000	-2.063496000	-4.355687000
H	3.513453000	-0.317199000	-4.734341000	C	6.847618000	-3.036182000	-3.351801000
C	2.511853000	-1.621629000	3.940365000	H	7.298081000	-4.040597000	-3.397351000
C	2.026455000	-0.591448000	4.781240000	C	5.588440000	-2.866055000	-2.752639000
C	2.500201000	-0.466965000	6.097606000	H	5.053791000	-3.730364000	-2.328109000
H	2.122628000	0.346013000	6.738196000	Fe	0.603346000	-1.552971000	-0.558026000
C	3.452593000	-1.375515000	6.595345000	H	1.282644000	0.117887000	4.385294000
H	3.820258000	-1.279779000	7.629517000	H	5.241837000	0.528277000	-3.160936000
C	3.929728000	-2.410652000	5.769974000	H	-2.227228000	2.357592000	-2.726515000
H	4.664756000	-3.133574000	6.158542000	H	-4.870784000	-1.670339000	1.070530000
C	3.465387000	-2.533892000	4.449757000	O	0.670986000	-3.110389000	-1.118909000
H	3.824015000	-3.355963000	3.811047000	Cl	0.498970000	0.687374000	0.229537000
C	-3.612367000	-3.446249000	0.969219000	(iv-TS)			
C	-4.829670000	-2.762780000	1.200992000	C	1.000148000	2.665250000	0.037784000
C	-5.969345000	-3.465944000	1.625087000	C	2.240925000	3.246391000	0.519738000
H	-6.907808000	-2.919754000	1.811690000	C	3.170252000	2.231777000	0.550482000
C	-5.911278000	-4.858283000	1.820594000	C	2.516207000	1.049872000	0.017678000
H	-6.807336000	-5.407950000	2.150430000	N	1.211395000	1.338969000	-0.287129000
C	-4.702834000	-5.544732000	1.600524000	H	2.380472000	4.293953000	0.808645000
H	-4.649194000	-6.634448000	1.753697000	H	4.220536000	2.284856000	0.859482000
C	-3.558294000	-4.844304000	1.185421000	C	3.192193000	-0.157432000	-0.297749000
H	-2.610946000	-5.379330000	1.014057000	C	3.403507000	-2.183383000	-1.812327000
C	-1.523127000	0.924607000	-4.205373000	C	2.589344000	-2.723733000	-2.778996000
C	-2.215122000	2.089015000	-3.794656000	C	1.309394000	-2.045725000	-2.682212000
C	-2.865397000	2.899323000	-4.740035000	N	1.369760000	-1.077627000	-1.702648000
H	-3.391015000	3.809127000	-4.408594000	C	2.653535000	-1.113707000	-1.179954000
C	-2.846035000	2.550519000	-6.103133000	H	4.432069000	-2.468111000	-1.564134000
H	-3.360161000	3.184284000	-6.843340000	H	2.812289000	-3.547647000	-3.466828000
C	-2.173616000	1.385737000	-6.517286000	C	-0.259379000	3.305235000	0.051399000
H	-2.167650000	1.099147000	-7.581079000	N	-1.575637000	1.287633000	-0.560666000
C	-1.514156000	0.577145000	-5.576506000	C	-2.881132000	0.902829000	-0.378597000
H	-1.005911000	-0.345139000	-5.898139000	C	-3.641486000	2.007585000	0.178383000
C	4.987783000	-1.585639000	-2.698690000	C	-2.770503000	3.073731000	0.281632000
C	5.685303000	-0.476820000	-3.233553000	C	-1.471852000	2.600333000	-0.158714000
C	6.948264000	-0.650170000	-3.823737000	H	-4.712634000	1.984860000	0.410754000
H	7.484695000	0.223321000	-4.227596000	H	-2.982339000	4.082425000	0.654252000
C	7.530165000	-1.929737000	-3.890000000	C	-3.444468000	-0.323945000	-0.811437000

N	-1.400817000	-1.137706000	-1.954310000	C	4.572432000	-0.334954000	0.243955000
C	-1.149173000	-2.080429000	-2.928437000	C	4.746229000	-0.499907000	1.637914000
C	-2.387124000	-2.743412000	-3.295683000	C	5.712059000	-0.310195000	-0.592562000
C	-3.363860000	-2.256033000	-2.459404000	C	6.032503000	-0.650953000	2.182077000
C	-2.750816000	-1.213408000	-1.657665000	C	6.997892000	-0.456118000	-0.044274000
H	-2.489560000	-3.515021000	-4.066803000	C	7.161784000	-0.629450000	1.342686000
H	-4.417975000	-2.551545000	-2.418229000	H	3.859330000	-0.519410000	2.289751000
C	0.140863000	-2.463822000	-3.359403000	H	5.584748000	-0.156672000	-1.675564000
O	-0.242051000	-0.747618000	0.412190000	H	6.151458000	-0.788495000	3.268888000
H	-0.556926000	0.029772000	1.454116000	H	7.878609000	-0.427561000	-0.705758000
C	-0.883837000	0.727756000	2.477361000	H	8.170986000	-0.744803000	1.769520000
H	-0.631369000	1.752915000	2.123496000	C	-0.356706000	4.738746000	0.452765000
C	0.027068000	0.242968000	3.535822000	C	-0.885718000	5.686538000	-0.454644000
C	-0.397738000	-0.665947000	4.535193000	C	0.033575000	5.166998000	1.743607000
C	0.509974000	-1.136735000	5.497501000	C	-1.002978000	7.036735000	-0.083966000
C	1.853823000	-0.714252000	5.477214000	C	-0.091151000	6.516633000	2.112913000
C	2.285659000	0.186614000	4.482218000	C	-0.605511000	7.455498000	1.199298000
C	1.384937000	0.655535000	3.515136000	H	-1.195931000	5.355425000	-1.458310000
H	-1.449375000	-0.990161000	4.552563000	H	0.417970000	4.427783000	2.464023000
H	0.166154000	-1.839650000	6.273722000	H	-1.407439000	7.766455000	-0.803569000
H	2.562946000	-1.084425000	6.234812000	H	0.208778000	6.835075000	3.124135000
H	3.332968000	0.528425000	4.463984000	H	-0.701411000	8.513959000	1.489747000
H	1.726241000	1.354050000	2.733355000	C	-4.854052000	-0.608889000	-0.410622000
O	-2.239137000	0.547381000	2.751713000	C	-5.916989000	-0.618930000	-1.342518000
H	-2.754312000	1.054073000	2.084758000	C	-5.134019000	-0.846066000	0.956541000
Cl	0.053297000	1.297004000	-3.060020000	C	-7.231525000	-0.873652000	-0.915410000
C	0.300027000	-3.447337000	-4.471605000	C	-6.448778000	-1.104224000	1.378457000
C	0.956367000	-3.044755000	-5.658703000	C	-7.500459000	-1.120520000	0.443586000
C	-0.152730000	-4.782355000	-4.356704000	H	-5.709719000	-0.405890000	-2.402775000
C	1.139012000	-3.953803000	-6.714383000	H	-4.305117000	-0.828870000	1.682260000
C	0.036468000	-5.690193000	-5.412484000	H	-8.052848000	-0.871455000	-1.649899000
C	0.678718000	-5.278093000	-6.594805000	H	-6.651569000	-1.294715000	2.444549000
H	1.315278000	-2.007184000	-5.748317000	H	-8.531945000	-1.320817000	0.774990000
H	-0.636736000	-5.111027000	-3.423785000	Fe	-0.097543000	0.064452000	-1.101809000
H	1.644429000	-3.624356000	-7.636353000	(v)			
H	-0.314108000	-6.729398000	-5.306760000	C	0.979146000	2.609529000	0.255890000
H	0.824976000	-5.991411000	-7.421689000	C	2.225432000	3.229708000	0.655802000

C	3.202586000	2.266591000	0.551488000	C	-0.018562000	-5.940671000	-5.037295000
C	2.563652000	1.075972000	0.028898000	C	0.607495000	-5.615419000	-6.254885000
N	1.216115000	1.304507000	-0.139437000	H	1.282711000	-2.300690000	-5.642471000
H	2.338574000	4.269802000	0.981304000	H	-0.655654000	-5.221124000	-3.082729000
H	4.273161000	2.364269000	0.765011000	H	1.568000000	-4.044142000	-7.421015000
C	3.274169000	-0.078840000	-0.377400000	H	-0.377676000	-6.966649000	-4.856815000
C	3.456364000	-2.145390000	-1.819841000	H	0.733696000	-6.383785000	-7.034461000
C	2.606234000	-2.773710000	-2.697013000	C	4.713007000	-0.179843000	0.016591000
C	1.317055000	-2.122256000	-2.573567000	C	5.060967000	-0.311843000	1.381513000
N	1.396557000	-1.092426000	-1.660955000	C	5.745841000	-0.112097000	-0.947734000
C	2.708733000	-1.063533000	-1.208136000	C	6.409027000	-0.389142000	1.770700000
H	4.504840000	-2.385479000	-1.611385000	C	7.093292000	-0.185766000	-0.555975000
H	2.814135000	-3.635559000	-3.341537000	C	7.428893000	-0.327220000	0.803298000
C	-0.289240000	3.221587000	0.343724000	H	4.261892000	-0.359928000	2.138280000
N	-1.593091000	1.226159000	-0.378640000	H	5.483931000	0.015084000	-2.009857000
C	-2.923617000	0.881041000	-0.309619000	H	6.663630000	-0.499691000	2.837036000
C	-3.687641000	1.972638000	0.261811000	H	7.886663000	-0.124712000	-1.318189000
C	-2.799341000	2.994586000	0.501459000	H	8.485843000	-0.385419000	1.108969000
C	-1.487270000	2.511393000	0.115539000	C	-0.391054000	4.650267000	0.769187000
H	-4.770490000	1.961525000	0.431227000	C	-0.934393000	5.607814000	-0.119859000
H	-3.004055000	3.982413000	0.929988000	C	0.024622000	5.070242000	2.054517000
C	-3.502368000	-0.288841000	-0.850231000	C	-1.047447000	6.954698000	0.264094000
N	-1.400010000	-1.185940000	-1.847759000	C	-0.092547000	6.417223000	2.437268000
C	-1.137891000	-2.168499000	-2.790000000	C	-0.626059000	7.363586000	1.542831000
C	-2.377557000	-2.790695000	-3.206225000	H	-1.260842000	5.285980000	-1.121452000
C	-3.381223000	-2.228765000	-2.454648000	H	0.428215000	4.327725000	2.760732000
C	-2.774604000	-1.196546000	-1.640250000	H	-1.465561000	7.689782000	-0.442232000
H	-2.465195000	-3.581112000	-3.959912000	H	0.229266000	6.727932000	3.444274000
H	-4.449888000	-2.469677000	-2.473530000	H	-0.716545000	8.419593000	1.843897000
C	0.141663000	-2.589607000	-3.199195000	C	-4.972142000	-0.494237000	-0.653199000
O	-0.177752000	-0.848401000	0.546524000	C	-5.885737000	-0.322284000	-1.718413000
H	0.013316000	-0.196173000	1.259496000	C	-5.467827000	-0.835671000	0.626109000
Cl	0.038040000	1.304533000	-2.880453000	C	-7.264462000	-0.498414000	-1.509645000
C	0.280814000	-3.641449000	-4.252291000	C	-6.847007000	-1.012285000	0.832340000
C	0.917097000	-3.326376000	-5.475843000	C	-7.748649000	-0.845456000	-0.234812000
C	-0.180576000	-4.961892000	-4.041960000	H	-5.507006000	-0.038076000	-2.712863000
C	1.075885000	-4.306259000	-6.470606000	H	-4.760544000	-0.965058000	1.460680000

H	-7.965495000	-0.357265000	-2.347961000	O	-0.210688000	-0.670137000	0.437894000
H	-7.218593000	-1.283477000	1.833622000	H	-0.537742000	0.151726000	1.493127000
H	-8.829713000	-0.982970000	-0.072215000	C	-0.860928000	0.856020000	2.486091000
Fe	-0.101311000	0.038309000	-1.018023000	H	-0.632112000	1.878939000	2.107621000
(iv-TS)Fe-OMe							
C	1.002771000	2.735747000	-0.016977000	C	-0.316138000	-0.466808000	4.577227000
C	2.242547000	3.338061000	0.442094000	C	0.603600000	-0.908682000	5.540277000
C	3.181841000	2.333177000	0.483493000	C	1.948369000	-0.466645000	5.482855000
C	2.533948000	1.134933000	-0.020168000	C	2.345845000	0.423932000	4.450766000
N	1.223819000	1.405872000	-0.319229000	C	1.423562000	0.851200000	3.497324000
H	2.374287000	4.392259000	0.709889000	H	-1.360733000	-0.810391000	4.625194000
H	4.234340000	2.401711000	0.781903000	H	0.267792000	-1.594757000	6.330691000
C	3.217461000	-0.073400000	-0.312003000	H	3.392157000	0.765014000	4.426435000
C	3.432616000	-2.137868000	-1.772462000	H	1.747350000	1.534457000	2.695099000
C	2.612932000	-2.716028000	-2.712265000	O	-2.213229000	0.660325000	2.780109000
C	1.328205000	-2.045643000	-2.623856000	H	-2.740135000	1.119983000	2.089156000
N	1.391019000	-1.045167000	-1.677545000	Cl	0.041214000	1.290220000	-3.082600000
C	2.679706000	-1.055215000	-1.166125000	C	0.313977000	-3.516662000	-4.354689000
H	4.466343000	-2.405617000	-1.526626000	C	0.955879000	-3.155126000	-5.562602000
H	2.836056000	-3.559507000	-3.375969000	C	-0.128769000	-4.849383000	-4.186108000
C	-0.261360000	3.365703000	-0.003955000	C	1.134818000	-4.101993000	-6.585300000
N	-1.568216000	1.328034000	-0.568207000	C	0.055606000	-5.795011000	-5.209147000
C	-2.871022000	0.939485000	-0.372660000	C	0.684160000	-5.423671000	-6.412158000
C	-3.634264000	2.049995000	0.169659000	H	1.307115000	-2.119444000	-5.694567000
C	-2.768556000	3.122075000	0.249706000	H	-0.602528000	-5.145514000	-3.237121000
C	-1.469840000	2.647605000	-0.189810000	H	1.629510000	-3.804241000	-7.523765000
H	-4.704117000	2.025975000	0.407907000	H	-0.287764000	-6.831546000	-5.061501000
H	-2.983437000	4.136183000	0.605646000	H	0.826986000	-6.166328000	-7.213446000
C	-3.430016000	-0.297497000	-0.778588000	C	4.600269000	-0.230374000	0.230560000
N	-1.385992000	-1.131236000	-1.907957000	C	4.776477000	-0.363955000	1.627627000
C	-1.131965000	-2.103224000	-2.852253000	C	5.739143000	-0.217733000	-0.607077000
C	-2.368252000	-2.781747000	-3.197131000	C	6.063935000	-0.495579000	2.174172000
C	-3.345754000	-2.271251000	-2.375819000	C	7.026327000	-0.344672000	-0.056888000
C	-2.734663000	-1.203091000	-1.606425000	C	7.192437000	-0.486398000	1.333437000
H	-2.468830000	-3.577259000	-3.943850000	H	3.890643000	-0.373419000	2.281318000
H	-4.399023000	-2.568331000	-2.324466000	H	5.610142000	-0.089241000	-1.693171000
C	0.157568000	-2.494162000	-3.277085000	H	6.184024000	-0.608159000	3.263789000

H	7.906378000	-0.325968000	-0.719665000	H	4.183148000	2.200562000	0.969679000
H	8.202688000	-0.586651000	1.761667000	C	3.116089000	-0.250651000	-0.135569000
C	-0.366365000	4.806923000	0.368311000	C	3.330251000	-2.277894000	-1.654598000
C	-0.904280000	5.732573000	-0.556484000	C	2.539780000	-2.780133000	-2.661482000
C	0.026066000	5.264814000	1.648203000	C	1.276807000	-2.065511000	-2.605285000
C	-1.028896000	7.089530000	-0.213666000	N	1.328344000	-1.114015000	-1.612094000
C	-0.105072000	6.621241000	1.989707000	C	2.587411000	-1.193612000	-1.039051000
C	-0.628978000	7.537648000	1.058878000	H	4.339357000	-2.596262000	-1.369940000
H	-1.216229000	5.378589000	-1.551795000	H	2.765846000	-3.601871000	-3.350851000
H	0.418353000	4.543183000	2.382146000	C	-0.266204000	3.289983000	0.077767000
H	-1.440791000	7.801529000	-0.946724000	N	-1.595730000	1.275070000	-0.506106000
H	0.197402000	6.962679000	2.992666000	C	-2.903846000	0.893976000	-0.314569000
H	-0.730174000	8.601408000	1.327431000	C	-3.654286000	2.000393000	0.249512000
C	-4.836035000	-0.581882000	-0.363723000	C	-2.780798000	3.065063000	0.338165000
C	-5.904800000	-0.618118000	-1.288245000	C	-1.486337000	2.588086000	-0.112604000
C	-5.106922000	-0.791189000	1.009788000	H	-4.722943000	1.978790000	0.493943000
C	-7.215379000	-0.870953000	-0.847748000	H	-2.986321000	4.075978000	0.708602000
C	-6.417725000	-1.046529000	1.445701000	C	-3.473549000	-0.316307000	-0.780284000
C	-7.474996000	-1.089060000	0.517969000	N	-1.430420000	-1.133049000	-1.916850000
H	-5.705122000	-0.427456000	-2.354235000	C	-1.177154000	-2.046974000	-2.918216000
H	-4.273574000	-0.754530000	1.729739000	C	-2.422311000	-2.667911000	-3.332771000
H	-8.041044000	-0.889707000	-1.577151000	C	-3.404727000	-2.189223000	-2.497027000
H	-6.613073000	-1.214517000	2.516995000	C	-2.783221000	-1.192829000	-1.644846000
H	-8.503396000	-1.287447000	0.860010000	H	-2.527620000	-3.405923000	-4.135690000
Fe	-0.082617000	0.100604000	-1.091967000	H	-4.467781000	-2.455092000	-2.488184000
O	2.920811000	-0.830421000	6.357249000	C	0.117032000	-2.444880000	-3.325038000
C	2.596910000	-1.732559000	7.417669000	O	-0.307184000	-0.786451000	0.465219000
H	2.243862000	-2.713869000	7.029076000	H	-0.645867000	-0.013082000	1.484156000
H	3.532991000	-1.885970000	7.987810000	C	-1.034931000	0.624436000	2.537020000
H	1.823828000	-1.308346000	8.096886000	H	-1.011815000	1.686283000	2.208050000
(iv-TS)Fe-NO2				C	0.041604000	0.279741000	3.474478000
C	0.986205000	2.635332000	0.082989000	C	-0.031174000	-0.857940000	4.321488000
C	2.236377000	3.201973000	0.557375000	C	1.063963000	-1.232473000	5.104090000
C	3.137441000	2.164226000	0.643115000	C	2.245593000	-0.466252000	5.043164000
C	2.462100000	0.981112000	0.142369000	C	2.336131000	0.683789000	4.231994000
N	1.172044000	1.293754000	-0.196603000	C	1.239091000	1.045228000	3.451940000
H	2.401147000	4.255286000	0.809395000	H	-0.956745000	-1.452100000	4.346589000

H	1.028517000	-2.117968000	5.753985000	H	0.294156000	6.933178000	3.001921000
H	3.265876000	1.268453000	4.218266000	H	-0.673148000	8.546439000	1.334882000
H	1.301808000	1.933220000	2.804086000	C	-4.897360000	-0.592758000	-0.423071000
O	-2.303700000	0.164092000	2.887880000	C	-5.941658000	-0.456120000	-1.365160000
H	-2.941517000	0.565690000	2.259332000	C	-5.207978000	-0.974721000	0.902587000
Cl	0.072029000	1.265585000	-2.994234000	C	-7.272647000	-0.701734000	-0.986169000
C	0.290193000	-3.405077000	-4.453187000	C	-6.539508000	-1.222800000	1.276575000
C	1.020314000	-2.998105000	-5.595423000	C	-7.574574000	-1.086549000	0.333324000
C	-0.220501000	-4.723171000	-4.397779000	H	-5.704521000	-0.141652000	-2.393530000
C	1.216470000	-3.884968000	-6.666994000	H	-4.391465000	-1.090969000	1.633012000
C	-0.015192000	-5.609421000	-5.468452000	H	-8.080083000	-0.585950000	-1.726828000
C	0.698961000	-5.192147000	-6.606900000	H	-6.767613000	-1.526798000	2.310668000
H	1.423542000	-1.973972000	-5.638283000	H	-8.618828000	-1.278828000	0.627208000
H	-0.759340000	-5.057879000	-3.497792000	Fe	-0.133528000	0.044907000	-1.029063000
H	1.777784000	-3.551931000	-7.554625000	N	3.419399000	-0.889426000	5.812948000
H	-0.409482000	-6.636462000	-5.408431000	O	3.301831000	-1.852592000	6.584358000
H	0.857071000	-5.888659000	-7.445793000	O	4.481912000	-0.264625000	5.647504000
C	4.461171000	-0.465709000	0.473525000	Mn^{III}(Cl)(TPP)			
C	4.551666000	-0.607766000	1.877680000	C	0.969769000	2.619019000	0.319582000
C	5.645477000	-0.496871000	-0.298101000	C	2.210722000	3.269138000	0.681466000
C	5.797300000	-0.786598000	2.500881000	C	3.219923000	2.363795000	0.454080000
C	6.891769000	-0.673086000	0.327716000	C	2.604304000	1.169278000	-0.083469000
C	6.971259000	-0.819955000	1.725591000	N	1.230763000	1.343921000	-0.165063000
H	3.630334000	-0.584890000	2.477455000	H	2.298739000	4.291938000	1.064373000
H	5.586024000	-0.359162000	-1.389006000	H	4.295988000	2.501437000	0.609111000
H	5.839517000	-0.892422000	3.596615000	C	3.331485000	0.038229000	-0.513762000
H	7.809350000	-0.686563000	-0.282108000	C	3.489554000	-2.148571000	-1.770597000
H	7.950893000	-0.955742000	2.211286000	C	2.611725000	-2.881114000	-2.533946000
C	-0.353250000	4.734498000	0.433512000	C	1.322935000	-2.229460000	-2.439344000
C	-0.916820000	5.646092000	-0.491148000	N	1.420265000	-1.110431000	-1.627225000
C	0.079150000	5.213241000	1.693170000	C	2.750689000	-1.021650000	-1.241005000
C	-1.024037000	7.009188000	-0.169561000	H	4.549805000	-2.351834000	-1.583157000
C	-0.037655000	6.575645000	2.014091000	H	2.808805000	-3.804922000	-3.089797000
C	-0.584510000	7.477667000	1.082512000	C	-0.308715000	3.184352000	0.508270000
H	-1.259085000	5.276116000	-1.470466000	N	-1.608081000	1.245152000	-0.370978000
H	0.487314000	4.503964000	2.430154000	C	-2.958663000	0.930048000	-0.389453000
H	-1.453544000	7.710188000	-0.902976000	C	-3.718315000	1.985907000	0.246086000

C	-2.819668000	2.955935000	0.621757000	C	-0.961670000	5.611640000	0.306173000
C	-1.505520000	2.488317000	0.233980000	C	0.008800000	4.836756000	2.402233000
H	-4.806788000	1.987057000	0.373886000	C	-1.075432000	6.906915000	0.839326000
H	-3.024013000	3.902774000	1.134323000	C	-0.108196000	6.132196000	2.934140000
C	-3.543509000	-0.188597000	-1.017449000	C	-0.649163000	7.170926000	2.154087000
N	-1.423005000	-1.189514000	-1.866621000	H	-1.292085000	5.403260000	-0.723733000
C	-1.141118000	-2.243267000	-2.725010000	H	0.422997000	4.021283000	3.016008000
C	-2.374971000	-2.844832000	-3.184849000	H	-1.497723000	7.715764000	0.221675000
C	-3.402689000	-2.184457000	-2.554811000	H	0.220480000	6.329462000	3.967206000
C	-2.805326000	-1.134527000	-1.757413000	H	-0.740234000	8.186448000	2.571745000
H	-2.445502000	-3.684160000	-3.885500000	C	-5.032761000	-0.337777000	-0.941753000
H	-4.477892000	-2.379844000	-2.635560000	C	-5.845507000	-0.071183000	-2.066960000
C	0.145121000	-2.733744000	-3.032009000	C	-5.645358000	-0.736024000	0.268155000
Cl	0.046663000	1.428345000	-3.201235000	C	-7.242292000	-0.205307000	-1.983966000
C	0.280869000	-3.877597000	-3.986971000	C	-7.042467000	-0.869483000	0.349017000
C	0.931383000	-3.682159000	-5.227714000	C	-7.844237000	-0.605243000	-0.776570000
C	-0.214548000	-5.163473000	-3.669466000	H	-5.372647000	0.248326000	-3.009069000
C	1.072956000	-4.746556000	-6.134271000	H	-5.016281000	-0.943157000	1.148447000
C	-0.069536000	-6.227153000	-4.576570000	H	-7.864233000	0.009288000	-2.867853000
C	0.572351000	-6.021419000	-5.811817000	H	-7.506724000	-1.184156000	1.297522000
H	1.320053000	-2.682557000	-5.479045000	H	-8.939216000	-0.709750000	-0.712373000
H	-0.707498000	-5.327180000	-2.698190000	Mn	-0.079556000	0.199226000	-1.218179000
H	1.575671000	-4.577154000	-7.100048000	Fe^{III}(Cl)(TPP)			
H	-0.456160000	-7.224883000	-4.313537000	C	0.966803000	2.611412000	0.293414000
H	0.684237000	-6.855695000	-6.522801000	C	2.206767000	3.264615000	0.648342000
C	4.803041000	0.006089000	-0.244354000	C	3.212584000	2.352053000	0.438180000
C	5.284291000	-0.069138000	1.083556000	C	2.591444000	1.156187000	-0.086429000
C	5.735293000	0.068511000	-1.306456000	N	1.217393000	1.328216000	-0.180113000
C	6.665556000	-0.089886000	1.341973000	H	2.295950000	4.292929000	1.015892000
C	7.115919000	0.050832000	-1.045697000	H	4.289024000	2.485346000	0.594743000
C	7.585009000	-0.030195000	0.278519000	C	3.319131000	0.020430000	-0.492526000
H	4.563881000	-0.117041000	1.915538000	C	3.466912000	-2.159087000	-1.744987000
H	5.367425000	0.142862000	-2.341923000	C	2.592380000	-2.877675000	-2.524199000
H	7.025431000	-0.155458000	2.381327000	C	1.310105000	-2.215040000	-2.436324000
H	7.829728000	0.106673000	-1.883248000	N	1.399091000	-1.100355000	-1.614895000
H	8.667814000	-0.044512000	0.481853000	C	2.730045000	-1.029982000	-1.220707000
C	-0.414783000	4.562261000	1.080952000	H	4.523235000	-2.371255000	-1.545745000

C	2.577845000	-2.777983000	-2.513201000	C	5.699402000	0.318077000	-1.520129000
C	1.277120000	-2.141043000	-2.394002000	C	6.689565000	0.163466000	1.104902000
N	1.389631000	-0.958172000	-1.690560000	C	7.086177000	0.310194000	-1.290717000
C	2.729410000	-0.820432000	-1.377147000	C	7.586270000	0.232347000	0.022463000
H	4.553175000	-2.126281000	-1.732152000	H	4.600836000	0.113287000	1.722648000
H	2.769536000	-3.741858000	-2.998963000	H	5.308507000	0.388576000	-2.547550000
C	-0.341760000	3.347089000	0.435434000	H	7.071726000	0.099297000	2.136655000
N	-1.658430000	1.457300000	-0.501925000	H	7.780735000	0.371700000	-2.144238000
C	-3.011408000	1.202615000	-0.612870000	H	8.673513000	0.226747000	0.202173000
C	-3.774399000	2.301080000	-0.044627000	C	-0.431607000	4.692850000	1.085888000
C	-2.862229000	3.230463000	0.393663000	C	-0.848627000	5.827523000	0.352954000
C	-1.545027000	2.693383000	0.101343000	C	-0.109576000	4.846885000	2.454460000
H	-4.868456000	2.358698000	-0.005803000	C	-0.936963000	7.086891000	0.972150000
H	-3.060128000	4.194874000	0.875785000	C	-0.198096000	6.105914000	3.073192000
C	-3.600619000	0.094541000	-1.260731000	C	-0.611247000	7.230065000	2.333717000
N	-1.484047000	-1.031374000	-1.931141000	H	-1.100649000	5.713846000	-0.713493000
C	-1.201180000	-2.174984000	-2.652157000	H	0.203537000	3.961638000	3.030153000
C	-2.433433000	-2.787504000	-3.120949000	H	-1.259256000	7.962586000	0.385595000
C	-3.465357000	-2.017322000	-2.642437000	H	0.052625000	6.208375000	4.141576000
C	-2.861582000	-0.917675000	-1.910018000	H	-0.680551000	8.217198000	2.818801000
H	-2.499594000	-3.697386000	-3.728442000	C	-5.096686000	0.013308000	-1.288722000
H	-4.541683000	-2.178456000	-2.773242000	C	-5.812577000	0.217891000	-2.491210000
C	0.083511000	-2.710273000	-2.892925000	C	-5.821934000	-0.261825000	-0.106123000
Cl	-0.013689000	1.424893000	-3.086535000	C	-7.216331000	0.143693000	-2.511493000
C	0.193760000	-3.968140000	-3.698739000	C	-7.225832000	-0.334187000	-0.126119000
C	0.811918000	-3.952825000	-4.971286000	C	-7.927671000	-0.132757000	-1.329105000
C	-0.303230000	-5.196639000	-3.203222000	H	-5.255753000	0.441754000	-3.414992000
C	0.926624000	-5.131624000	-5.728474000	H	-5.271678000	-0.422209000	0.834738000
C	-0.189473000	-6.375418000	-3.960684000	H	-7.757974000	0.308871000	-3.457053000
C	0.425587000	-6.347013000	-5.226195000	H	-7.774509000	-0.553016000	0.804363000
H	1.201256000	-3.000666000	-5.365560000	H	-9.028090000	-0.189943000	-1.345002000
H	-0.776688000	-5.221004000	-2.208844000	O	-0.237243000	-0.784135000	0.490806000
H	1.407567000	-5.099109000	-6.719606000	C	-0.295591000	-0.437887000	1.756936000
H	-0.578917000	-7.323817000	-3.556204000	O	-0.351749000	0.705004000	2.219907000
H	0.515371000	-7.271206000	-5.819685000	C	-0.286606000	-1.671087000	2.669965000
C	4.787825000	0.246423000	-0.440317000	H	-1.138135000	-2.337422000	2.417806000
C	5.302821000	0.170936000	0.875582000	H	0.642438000	-2.255979000	2.503338000

H	-0.351167000	-1.368837000	3.733229000	C	0.837711000	-3.435447000	-5.378954000
Mn	-0.138431000	0.268089000	-1.106530000	C	-0.236231000	-4.973135000	-3.829338000
Fe^{III}(OAc)(Cl)(TPP)				C	0.987098000	-4.477716000	-6.310338000
C	0.953347000	2.797993000	0.098751000	C	-0.087651000	-6.015109000	-4.761250000
C	2.195805000	3.408061000	0.534922000	C	0.523026000	-5.770764000	-6.005464000
C	3.160946000	2.433631000	0.455030000	H	1.198104000	-2.421999000	-5.617247000
C	2.516887000	1.248808000	-0.085948000	H	-0.700675000	-5.169106000	-2.849967000
N	1.176428000	1.493612000	-0.300253000	H	1.466962000	-4.276921000	-7.282002000
H	2.309473000	4.445163000	0.870749000	H	-0.444812000	-7.027049000	-4.509908000
H	4.226304000	2.515037000	0.700960000	H	0.639948000	-6.588143000	-6.735310000
C	3.222272000	0.078852000	-0.443943000	C	4.651845000	-0.031831000	-0.016500000
C	3.408161000	-2.045938000	-1.807612000	C	4.970744000	-0.147792000	1.357397000
C	2.551427000	-2.717854000	-2.645971000	C	5.709384000	0.002425000	-0.955923000
C	1.265101000	-2.050991000	-2.547373000	C	6.308597000	-0.238018000	1.779147000
N	1.351084000	-0.971394000	-1.692702000	C	7.047167000	-0.088053000	-0.533882000
C	2.660147000	-0.933019000	-1.249062000	C	7.351529000	-0.210422000	0.834726000
H	4.457487000	-2.277528000	-1.591562000	H	4.153514000	-0.169973000	2.095875000
H	2.753857000	-3.613453000	-3.245080000	H	5.473171000	0.114326000	-2.025881000
C	-0.302954000	3.427407000	0.165844000	H	6.537180000	-0.333006000	2.853118000
N	-1.609307000	1.431672000	-0.520705000	H	7.857944000	-0.054533000	-1.279712000
C	-2.953857000	1.121387000	-0.495955000	H	8.400526000	-0.280633000	1.164979000
C	-3.716920000	2.250341000	0.008783000	C	-0.387897000	4.851340000	0.616072000
C	-2.816899000	3.259893000	0.251229000	C	-0.819029000	5.859655000	-0.276765000
C	-1.503782000	2.731202000	-0.067354000	C	-0.066141000	5.212245000	1.945498000
H	-4.806147000	2.270277000	0.132590000	C	-0.916717000	7.196908000	0.146497000
H	-3.014970000	4.267677000	0.634700000	C	-0.163357000	6.549346000	2.367963000
C	-3.547686000	-0.053121000	-1.006032000	C	-0.587624000	7.546230000	1.469387000
N	-1.456588000	-1.037909000	-1.919075000	H	-1.074902000	5.584052000	-1.312277000
C	-1.194830000	-2.087578000	-2.778927000	H	0.251433000	4.426702000	2.649352000
C	-2.435277000	-2.730616000	-3.176042000	H	-1.249870000	7.971457000	-0.563298000
C	-3.443590000	-2.097599000	-2.490528000	H	0.087520000	6.813002000	3.408311000
C	-2.826750000	-1.018724000	-1.738789000	H	-0.664333000	8.594419000	1.800905000
H	-2.519796000	-3.576057000	-3.868168000	C	-5.025926000	-0.218274000	-0.832410000
H	-4.515463000	-2.325648000	-2.510081000	C	-5.913873000	-0.112379000	-1.928507000
C	0.086836000	-2.547359000	-3.144130000	C	-5.563371000	-0.458057000	0.454095000
Cl	-0.014275000	1.364673000	-3.108493000	C	-7.300457000	-0.253175000	-1.744407000
C	0.219161000	-3.667277000	-4.127658000	C	-6.950124000	-0.597344000	0.638188000

C	-7.823262000	-0.497452000	-0.460831000	C	3.687079000	-1.351187000	-2.022762000
H	-5.506661000	0.093402000	-2.931085000	C	3.620294000	-1.592040000	-0.630499000
H	-4.879094000	-0.535323000	1.314060000	H	-4.558917000	-2.078786000	-1.322568000
H	-7.977570000	-0.163641000	-2.609399000	H	-3.723376000	-0.373339000	-3.269625000
H	-7.350412000	-0.787143000	1.647376000	H	-2.309097000	-3.423501000	3.377930000
H	-8.910387000	-0.606266000	-0.316739000	H	0.058199000	-2.726767000	4.532666000
Fe	-0.137358000	0.242377000	-1.110937000	H	5.817404000	-1.560700000	-0.094887000
O	-0.234949000	-0.811482000	0.484382000	H	4.890752000	-1.531286000	2.462049000
C	-0.303970000	-0.383404000	1.725882000	H	1.080016000	0.788632000	-5.241323000
O	-0.364263000	0.782646000	2.126045000	H	3.534334000	-0.248114000	-4.729411000
C	-0.294165000	-1.564021000	2.708487000	C	2.549796000	-1.769466000	3.954784000
H	-1.112604000	-2.273155000	2.465141000	C	2.110817000	-0.760125000	4.843754000
H	0.660073000	-2.123516000	2.610647000	C	2.609338000	-0.702662000	6.156046000
H	-0.406769000	-1.202515000	3.749024000	H	2.265570000	0.093783000	6.835336000
Mn^V-Oxo(Cl)(TPP) – Triplet							
C	-3.552683000	-1.671474000	-1.471338000	C	3.544143000	-1.656148000	6.599949000
C	-3.132840000	-0.802844000	-2.452190000	H	3.932246000	-1.611854000	7.630147000
C	-1.706049000	-0.604754000	-2.261622000	C	3.978283000	-2.669125000	5.725003000
C	-2.399061000	-1.949899000	-0.634773000	H	4.701446000	-3.425401000	6.069985000
N	-1.298426000	-1.297518000	-1.145386000	C	3.486100000	-2.726623000	4.410110000
C	-2.414483000	-2.665492000	0.588012000	H	3.814038000	-3.528441000	3.730200000
C	-1.317392000	-2.677266000	1.482657000	C	-3.672975000	-3.333454000	1.033627000
N	-0.058624000	-2.169340000	1.223686000	C	-4.854804000	-2.595282000	1.280010000
C	0.624071000	-2.133713000	2.421526000	C	-6.020264000	-3.244876000	1.719684000
C	-1.419022000	-3.007018000	2.892500000	H	-6.930657000	-2.656367000	1.916588000
C	-0.229510000	-2.639780000	3.478623000	C	-6.023257000	-4.638153000	1.917484000
C	1.994909000	-1.816422000	2.568904000	H	-6.938852000	-5.145917000	2.260655000
C	2.860997000	-1.640543000	1.467025000	C	-4.850817000	-5.379440000	1.681396000
N	2.468443000	-1.630976000	0.137263000	H	-4.845248000	-6.470410000	1.835201000
C	4.775613000	-1.597683000	0.243503000	C	-3.681500000	-4.732385000	1.248275000
C	4.305214000	-1.574791000	1.536929000	H	-2.762521000	-5.310714000	1.063166000
C	2.575128000	-0.896349000	-2.774584000	C	-1.531284000	0.812986000	-4.290667000
N	1.293335000	-0.797965000	-2.288131000	C	-2.226371000	1.998643000	-3.954701000
C	0.541928000	-0.136715000	-3.237955000	C	-2.878336000	2.747101000	-4.949170000
C	1.397541000	0.228195000	-4.355051000	H	-3.408484000	3.673270000	-4.675001000
C	2.641746000	-0.296381000	-4.096035000	C	-2.854396000	2.316171000	-6.288440000
C	-0.862778000	0.028645000	-3.208055000	H	-3.368973000	2.901641000	-7.067142000
				C	-2.175934000	1.131272000	-6.628982000

H	-2.164226000	0.781113000	-7.673573000	C	2.579201000	-0.816226000	-2.741883000
C	-1.517694000	0.383455000	-5.638058000	N	1.286371000	-0.769745000	-2.275878000
H	-1.002092000	-0.553245000	-5.901540000	C	0.531045000	-0.172241000	-3.263787000
C	5.030086000	-1.444287000	-2.670280000	C	1.387311000	0.208083000	-4.373938000
C	5.689947000	-0.299297000	-3.175302000	C	2.649179000	-0.243062000	-4.074246000
C	6.962907000	-0.412100000	-3.759130000	C	-0.875503000	-0.043028000	-3.262822000
H	7.468760000	0.489201000	-4.140832000	C	3.696935000	-1.249751000	-1.990094000
C	7.593390000	-1.667084000	-3.847213000	C	3.622148000	-1.537657000	-0.608607000
H	8.590988000	-1.753696000	-4.306764000	H	-4.574950000	-2.047816000	-1.287622000
C	6.948186000	-2.809720000	-3.339533000	H	-3.721135000	-0.462758000	-3.329341000
H	7.436454000	-3.795353000	-3.403073000	H	-2.344303000	-3.319828000	3.408006000
C	5.677795000	-2.699806000	-2.749484000	H	0.081486000	-2.784912000	4.532327000
H	5.171881000	-3.593081000	-2.350271000	H	5.823674000	-1.495041000	-0.082268000
H	1.380359000	-0.014774000	4.491421000	H	4.901858000	-1.641763000	2.475097000
H	5.206787000	0.686178000	-3.087159000	H	1.059212000	0.728864000	-5.280039000
H	-2.243438000	2.332395000	-2.905143000	H	3.552443000	-0.169173000	-4.689428000
H	-4.847890000	-1.502565000	1.144503000	C	2.581997000	-1.917767000	3.951752000
O	0.535151000	-3.054879000	-1.220123000	C	2.173778000	-0.926072000	4.875042000
Cl	0.439282000	0.657961000	0.211467000	C	2.689391000	-0.916706000	6.181706000
Mn	0.626120000	-1.592525000	-0.543146000	H	2.370731000	-0.133113000	6.887579000
Fe^{IV}Oxo(Cl)(TPP•⁺) Doublet				C	3.609001000	-1.901934000	6.586501000
C	-3.566267000	-1.656648000	-1.459668000	H	4.009705000	-1.895786000	7.612776000
C	-3.137492000	-0.852329000	-2.487495000	C	4.012079000	-2.897560000	5.677385000
C	-1.710007000	-0.658378000	-2.300411000	H	4.723066000	-3.678405000	5.991433000
C	-2.412500000	-1.897538000	-0.612060000	C	3.504971000	-2.905887000	4.367166000
N	-1.298654000	-1.293264000	-1.151699000	H	3.809856000	-3.692605000	3.659571000
C	-2.443004000	-2.572874000	0.630213000	C	-3.712849000	-3.205102000	1.092795000
C	-1.338058000	-2.595579000	1.512420000	C	-4.877195000	-2.434870000	1.324836000
N	-0.062196000	-2.147579000	1.232711000	C	-6.055682000	-3.048266000	1.780975000
C	0.636040000	-2.180615000	2.421656000	H	-6.951727000	-2.435074000	1.967898000
C	-1.439857000	-2.943005000	2.917206000	C	-6.090167000	-4.436904000	2.006589000
C	-0.221810000	-2.659942000	3.486743000	H	-7.016310000	-4.916375000	2.361862000
C	2.015617000	-1.914793000	2.570993000	C	-4.936030000	-5.210015000	1.782309000
C	2.873934000	-1.717845000	1.468045000	H	-4.955688000	-6.297688000	1.956702000
N	2.470366000	-1.637216000	0.147482000	C	-3.752907000	-4.599124000	1.335112000
C	4.784806000	-1.573188000	0.257615000	H	-2.848164000	-5.202236000	1.159654000
C	4.318418000	-1.640795000	1.547874000	C	-1.545510000	0.694333000	-4.375887000

C	-2.266498000	1.877041000	-4.087038000	C	-0.215492000	-2.894603000	3.540936000
C	-2.917616000	2.581268000	-5.113623000	C	2.072642000	-2.425726000	2.506824000
H	-3.467223000	3.506274000	-4.876438000	C	2.942072000	-2.027401000	1.450214000
C	-2.868380000	2.107645000	-6.437736000	N	2.558776000	-1.699712000	0.171974000
H	-3.382946000	2.658180000	-7.241479000	C	4.839294000	-1.378836000	0.379466000
C	-2.164485000	0.924928000	-6.731045000	C	4.378174000	-1.829134000	1.593240000
H	-2.132757000	0.541547000	-7.763474000	C	2.599772000	-0.568642000	-2.681749000
C	-1.505220000	0.222128000	-5.708526000	N	1.285550000	-0.785317000	-2.341728000
H	-0.968082000	-0.712084000	-5.935166000	C	0.515178000	-0.428111000	-3.421866000
C	5.043065000	-1.301766000	-2.633274000	C	1.376707000	0.045412000	-4.496700000
C	5.675070000	-0.132353000	-3.118179000	C	2.670278000	-0.058240000	-4.044026000
C	6.952591000	-0.203718000	-3.698106000	C	-0.908004000	-0.478543000	-3.482879000
H	7.437376000	0.716123000	-4.062423000	C	3.725882000	-0.807646000	-1.842387000
C	7.614041000	-1.441196000	-3.805305000	C	3.685198000	-1.300644000	-0.505910000
H	8.614904000	-1.495188000	-4.262695000	H	-4.714925000	-1.731824000	-1.072114000
C	6.995576000	-2.608145000	-3.319906000	H	-3.806371000	-0.836821000	-3.462326000
H	7.507913000	-3.580271000	-3.399430000	H	-2.429590000	-2.997917000	3.642853000
C	5.721833000	-2.539712000	-2.731378000	H	0.118655000	-3.221794000	4.531698000
H	5.236940000	-3.451602000	-2.348739000	H	5.864369000	-1.093549000	0.117920000
Fe	0.618900000	-1.557754000	-0.522891000	H	4.955083000	-1.981361000	2.512213000
H	1.455124000	-0.155806000	4.553608000	H	1.038608000	0.418601000	-5.469742000
H	5.166511000	0.838949000	-3.016623000	H	3.588492000	0.189492000	-4.587902000
H	-2.304299000	2.243847000	-3.049178000	C	2.715494000	-2.786288000	3.805597000
H	-4.845689000	-1.345936000	1.164655000	C	2.465363000	-2.021864000	4.970478000
O	0.581190000	-3.028614000	-1.225684000	C	3.084671000	-2.356130000	6.185779000
Cl	0.469933000	0.669266000	0.223435000	H	2.890564000	-1.745334000	7.081870000
Fe^{IV}Oxo(Cl)(TPP•⁺) Hextet				C	3.951566000	-3.462378000	6.258121000
C	-3.682539000	-1.485414000	-1.343992000	H	4.433253000	-3.725490000	7.213415000
C	-3.221567000	-1.031249000	-2.556419000	C	4.203164000	-4.229949000	5.105740000
C	-1.777441000	-0.886285000	-2.429761000	H	4.876893000	-5.100183000	5.156175000
C	-2.520640000	-1.618249000	-0.475299000	C	3.595959000	-3.891777000	3.885353000
N	-1.389081000	-1.249857000	-1.162633000	H	3.790884000	-4.492238000	2.983016000
C	-2.560931000	-2.105776000	0.863217000	C	-3.909291000	-2.398118000	1.434639000
C	-1.433838000	-2.344954000	1.702177000	C	-4.856303000	-1.359489000	1.602580000
N	-0.118135000	-2.162146000	1.350614000	C	-6.123346000	-1.633928000	2.142533000
C	0.650108000	-2.481177000	2.444886000	H	-6.846399000	-0.814036000	2.279315000
C	-1.508461000	-2.793853000	3.085766000	C	-6.467096000	-2.948469000	2.508996000

H	-7.463377000	-3.162864000	2.927658000
C	-5.534307000	-3.988372000	2.338655000
H	-5.799700000	-5.021052000	2.615901000
C	-4.261419000	-3.716416000	1.811273000
H	-3.532623000	-4.530178000	1.672363000
C	-1.548927000	-0.073529000	-4.769226000
C	-2.417715000	1.043135000	-4.816079000
C	-3.017851000	1.426042000	-6.026631000
H	-3.682161000	2.304585000	-6.051178000
C	-2.770327000	0.693363000	-7.202395000
H	-3.246280000	0.991929000	-8.150103000
C	-1.913567000	-0.422410000	-7.163530000
H	-1.721452000	-1.005037000	-8.078618000
C	-1.301146000	-0.801283000	-5.957862000
H	-0.634978000	-1.677522000	-5.924948000
C	5.074372000	-0.484800000	-2.397107000
C	5.412697000	0.844937000	-2.744598000
C	6.687992000	1.143646000	-3.251348000
H	6.942497000	2.184834000	-3.506065000
C	7.637271000	0.119942000	-3.428645000
H	8.635555000	0.355675000	-3.830737000
C	7.308029000	-1.205421000	-3.088855000
H	8.044756000	-2.012402000	-3.229471000
C	6.038433000	-1.506770000	-2.569496000
H	5.778660000	-2.543448000	-2.303836000
Fe	0.584911000	-1.590331000	-0.538507000
H	1.793229000	-1.151678000	4.910572000
H	4.671690000	1.646150000	-2.597840000
H	-2.607553000	1.617817000	-3.896086000
H	-4.584448000	-0.330836000	1.318622000
O	0.569029000	-3.132135000	-1.118869000
Cl	0.609938000	0.619623000	0.291042000

References

- 1 T. P. Wijesekera and D. Dolphin, *ChemInform*, 1995, **26**, chin.199534281.
- 2 V. V. Borovkov, *Synlett*, 1999, **1999**, 61–62.
- 3 S. D. Gokakakar, P. A. Pavaskar and A. V. Salker, *SN Appl. Sci.*, 2020, **2**, 294.
- 4 G. R. Karimipour, H. A. Shadegan and R. Ahmadpour, *Journal of Chemical Research*, 2007, **2007**, 252–256.
- 5 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. A. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Milliam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyey, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. Fox, 2019.
- 6 A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098–3100.
- 7 J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822–8824.
- 8 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *The Journal of Chemical Physics*, 2010, **132**, 154104.
- 9 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297.
- 10 F. Weigend, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1057.
- 11 A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 6378–6396.
- 12 T. A. Halgren and W. N. Lipscomb, *Chemical Physics Letters*, 1977, **49**, 225–232.
- 13 K. Fukui, 1981, **14**, 363–368.
- 14 R. Dennington, T. Keith, and J. M. Milliam, 2016.
- 15 F. Neese, *Journal of Physics and Chemistry of Solids*, 2004, **65**, 781–785.