

Supplemental Data

**ENZYME REACTIVATION BY HYDROGEN PEROXIDE IN HEME-BASED  
TRYPTOPHAN DIOXYGENASE**

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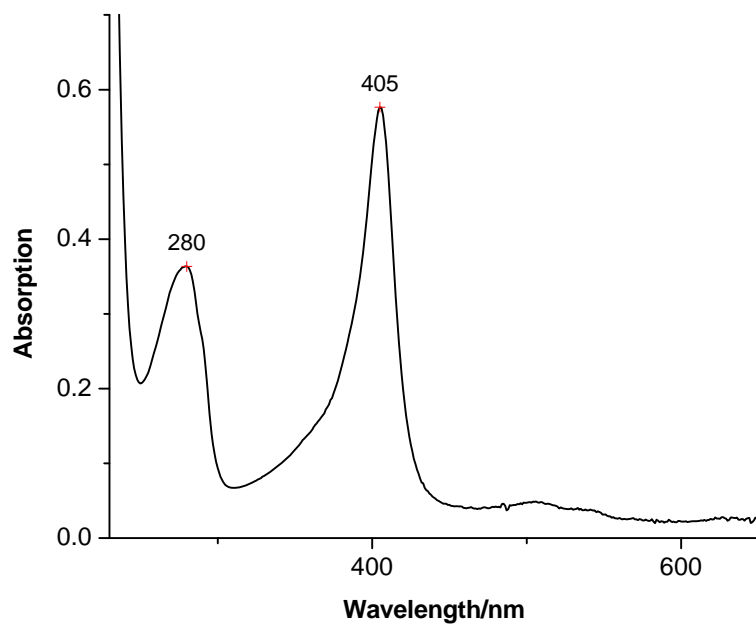
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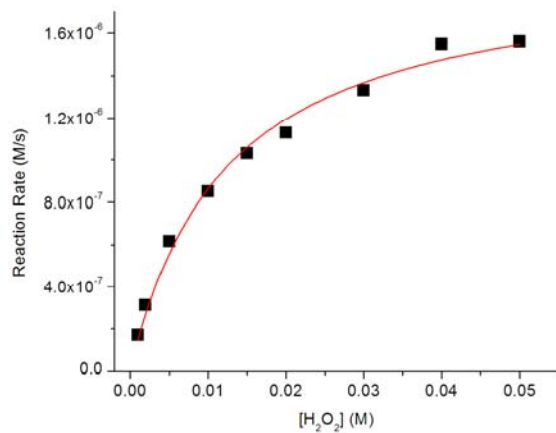
*Engineering, Stevens Institute of Technology, Castle Point on Hudson, Hoboken, New Jersey*

*07030*

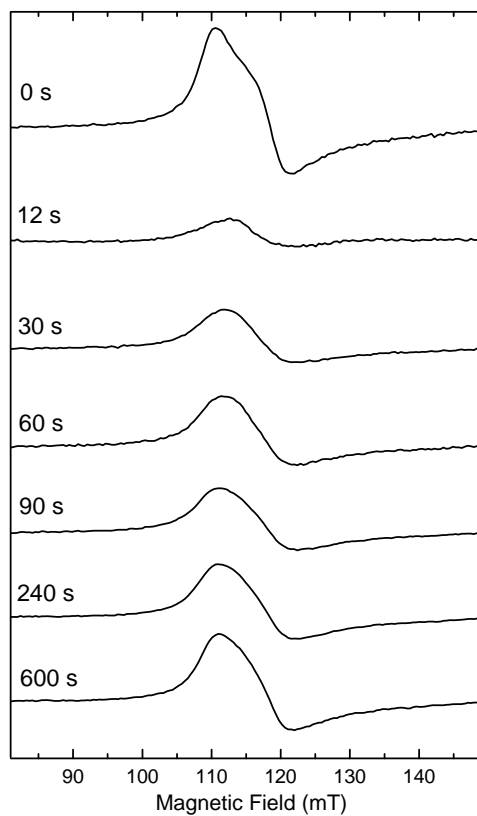
1. Figure S1 – S10 .....	2 - 11
2. Computational Details .....	12 - 13
3. Table S1 –S14 .....	14 - 37



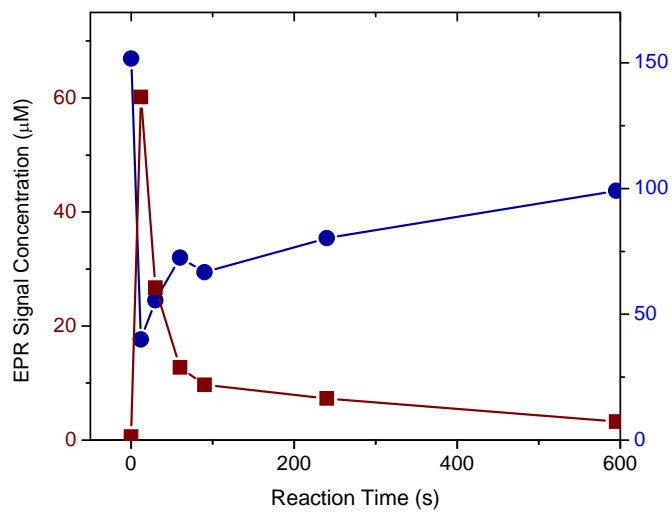
**Figure S1.** UV-Vis spectrum of as-isolated *Cupriavidus metallidurans* TDO (CmTDO).



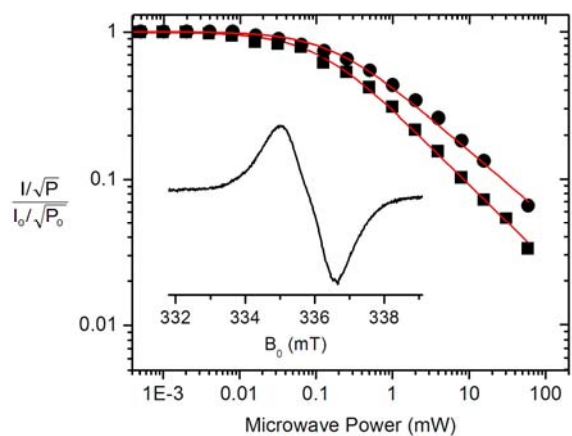
**Figure S2.** Top Panel: Saturation curve showing the relation between the concentration of H<sub>2</sub>O<sub>2</sub> and rate of the catalase-like activity of ferric TDO. Three repeating experiments were carried out and similar results were observed.



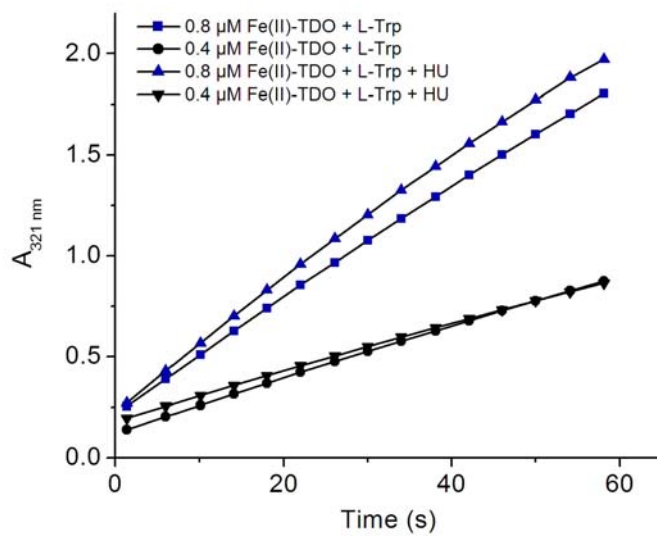
**Figure S3.** EPR spectra of the high-spin ferric heme ( $150\ \mu\text{M}$ ) taken during the reaction with  $\text{H}_2\text{O}_2$  ( $900\ \mu\text{M}$ ). EPR parameters: recording temperature, 10 K; microwave power, 1 mW; microwave frequency, 9.44 GHz; modulation amplitude, 0.8 mT.



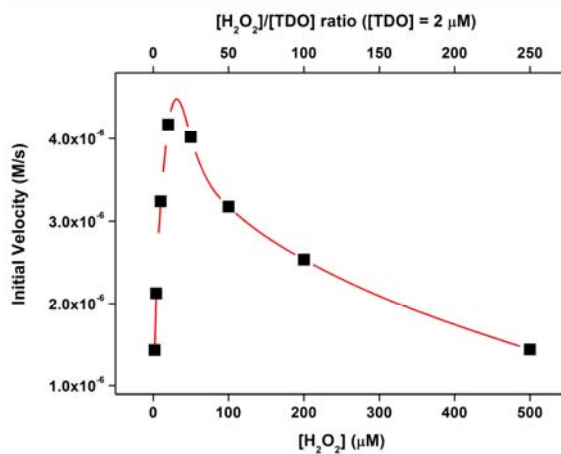
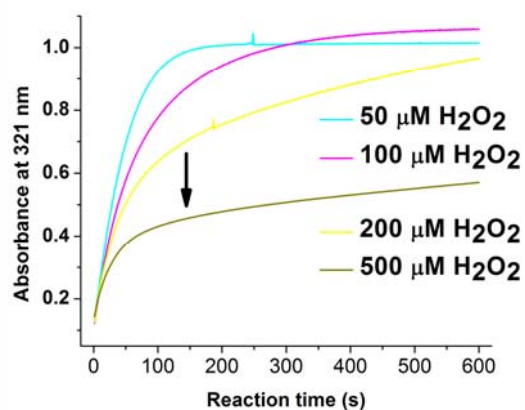
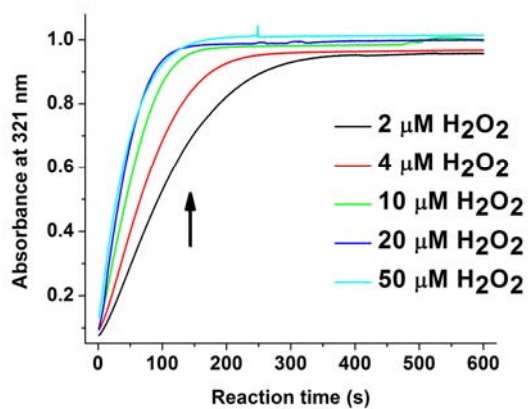
**Figure S4.** EPR signal intensity as a function of reaction time for the  $g = 2.0028$  (wine trace, ■) and  $g = 6$  (navy, ●) resonances, respectively. The initial heme concentration was 150  $\mu\text{M}$ .



**Figure S5.** The  $g = 2.0028$  free radical (inset) and its relaxation properties. The power saturation of the 10 K (■) and 100 K (●) and the fit to Eq. 2 are shown, where  $I$  is the EPR signal amplitude and  $P$  is the microwave power.

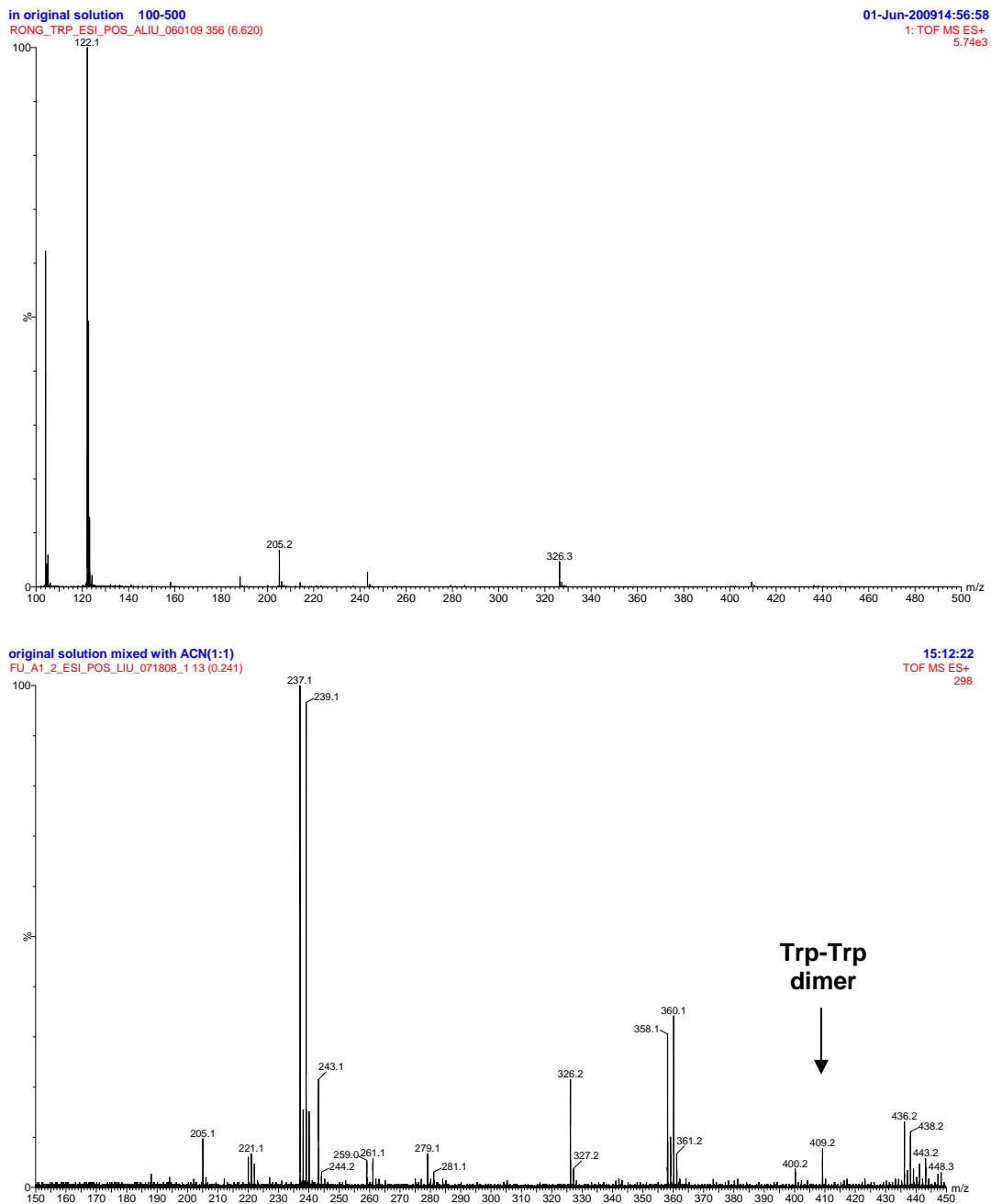


**Figure S6.** The effect of hydroxyurea (HU) on the enzymatic activity of ferrous TDO. Ferric TDO was treated with 2 equivalents of sodium dithionite and purged with argon for 15 min under anaerobic conditions. The reactions were conducted in O<sub>2</sub>-saturated buffer containing 5 mM L-Trp in the absence or presence of hydroxyurea (5 mM).

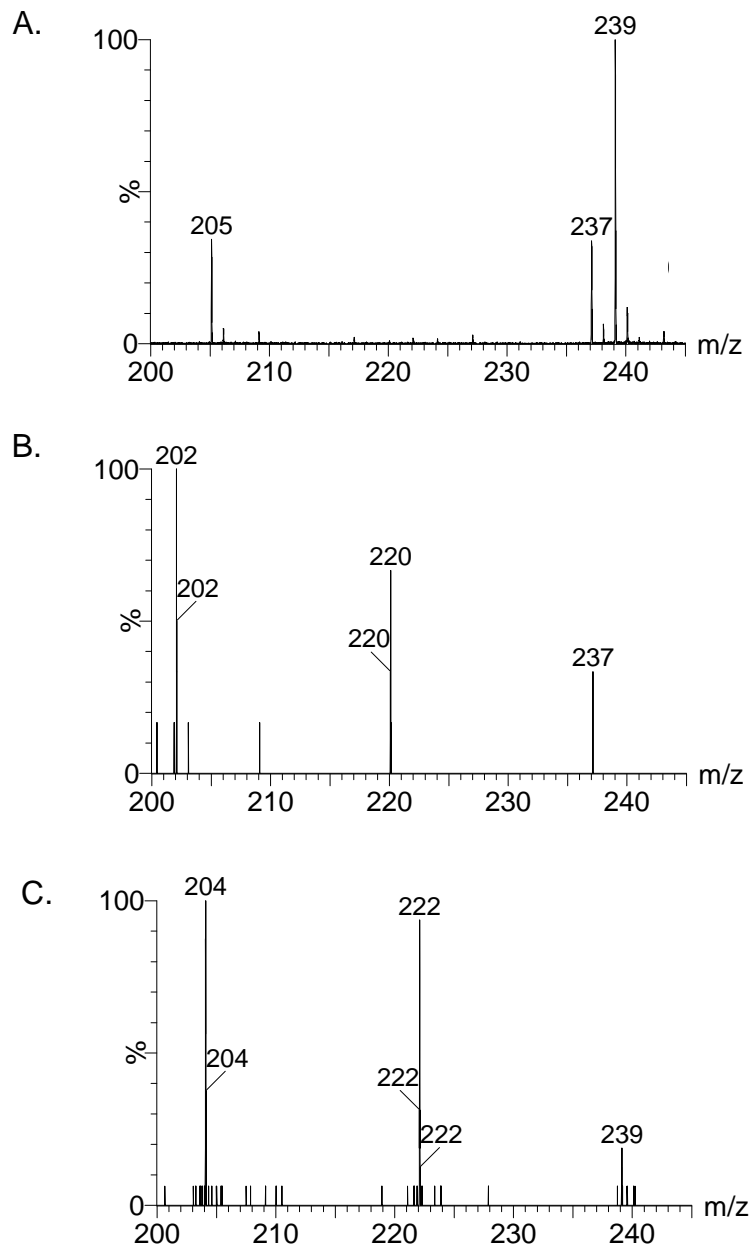


**Figure S7.** Optical spectra of TDO (2 μM) and L-Trp (5 mM) taken from the reaction with H<sub>2</sub>O<sub>2</sub> (Panel A: 2 – 50 μM, Panel B: 50 – 500 μM) under aerobic conditions. Panel C shows the Initial velocity as a function peroxide concentrations. Initial velocity of each set of experiment was counted within 20 - 40 s. High concentration of peroxide can inhibit the enzyme reactivation due to the oxidation of the newly generated ferrous TDO.

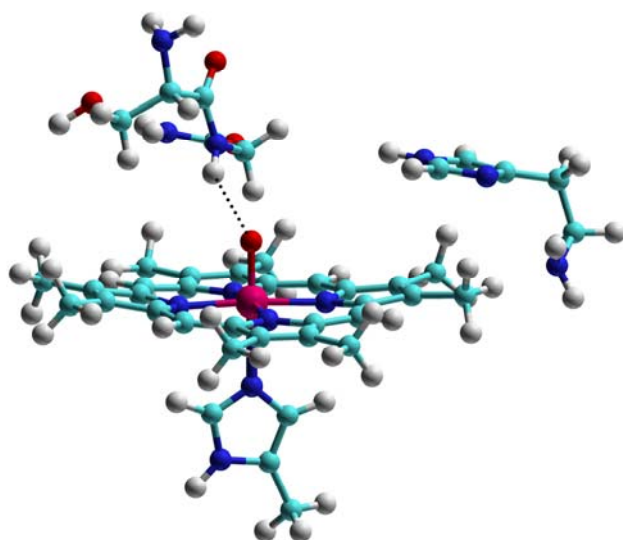




**Figure S8.** (A) 5 mM L-Trp in 50 mM Tris pH 7.4, (B) After reaction with H<sub>2</sub>O<sub>2</sub> (4 mM) in the presence of TDO (100 μM). The experimental details are described below. All the reagents were prepared using anaerobic 50 mM Tris-HCl pH 7.4 buffer in H<sub>2</sub><sup>18</sup>O (75% <sup>18</sup>O) which was bubbled and purged with argon for hours prior to the experiments. The reactions were performed on ice with stirring using septum-sealed reaction vials. Ferric TDO (100 μM) was allowed to react with H<sub>2</sub>O<sub>2</sub> in the presence of 5 mM L-Trp, in which H<sub>2</sub><sup>16</sup>O<sub>2</sub> was added to a total of 4 mM with a stepwise addition. After 20 minutes of reaction, TDO was removed from the reaction system using a Centriprep-10 at 3000×g for 10 min, and the filtrate was collected for electrospray ionization-mass spectrometry (ESI-MS) analysis.



**Figure S9.** MS/MS analysis of  $m/z$  220 and  $m/z$  222 ion peaks. (A) ESI-MS spectrum of the TDO reaction in  $\text{H}_2^{18}\text{O}$  solvent. MS/MS characterization of ion peaks of  $m/z$  237 (B) and  $m/z$  239 (C) of the spectrum A, respectively.



**Figure S10.** An active site structural model. Color schemes are as follows: Fe – pink, O – red, N – blue, C – cyan, and H – grey. The dashed lines connect the oxo group to the hydrogen atoms in Gly125 (*Cm*TDO amino acid numbering).

## Computational Details:

The  $^{57}\text{Fe}$  quadrupole splitting arises from the non-spherical nuclear charge distribution in the  $I^*=3/2$  excited state in the presence of an electric field gradient at the  $^{57}\text{Fe}$  nucleus, while the isomer shift arises from differences in the electron density at the nucleus between the absorber (the molecule or system of interest) and a reference compound (usually  $\alpha\text{-Fe}$  at 300K). The former effect is related to the components of the electric field gradient tensor at the nucleus as follows:<sup>1</sup>

$$\Delta E_Q = \frac{1}{2} eQV_{zz} \left( 1 + \frac{\eta^2}{3} \right)^{1/2} \quad (1)$$

where  $e$  is the electron charge,  $Q$  is the quadrupole moment of the  $E^*=14.4$  keV excited state, and the principal components of the EFG tensor are labeled according to the convention:

$$|V_{zz}| > |V_{yy}| > |V_{xx}| \quad (2)$$

with the asymmetry parameter being given by:

$$\eta = \frac{V_{xx} - V_{yy}}{V_{zz}} \quad (3)$$

The isomer shift in  $^{57}\text{Fe}$  Mössbauer spectroscopy is given by:<sup>1</sup>

$$\delta_{\text{Fe}} = E_A - E_{\text{Fe}} = \frac{2\pi}{3} Ze^2 \left( \langle R^2 \rangle^* - \langle R^2 \rangle \right) \left( |\psi(0)|_{\text{A}}^2 - |\psi(0)|_{\text{Fe}}^2 \right) \quad (4)$$

where  $Z$  represents the atomic number of the nucleus of interest (iron) and  $R$ ,  $R^*$  are average nuclear radii of the ground and excited states of  $^{57}\text{Fe}$ . Since  $|\psi(0)|_{\text{Fe}}^2$  is a constant, the isomer shift (from Fe) can be written as:

$$\delta_{\text{Fe}} = \alpha [ \rho(0) - c ] \quad (5)$$

where  $\alpha$  is the so-called calibration constant and  $\rho(0)$  is the computed charge density at the iron nucleus. Both  $\alpha$  and  $c$  can be obtained from the correlation between experimental  $\delta_{\text{Fe}}$  values and the corresponding computed  $\rho(0)$  data in a training set. Then, one can use equation (5) to predict  $\delta_{\text{Fe}}$  for a new molecule from its computed  $\rho(0)$ , basically as described in detail elsewhere for a wide variety of heme and other model systems.<sup>2</sup>

The hybrid functional B3LYP<sup>3</sup> with a Wachter's basis (62111111/3311111/3111) for Fe,<sup>4</sup> 6-311G\* for all the other heavy atoms and 6-31G\* for hydrogens in the *Gaussian 03* program<sup>5</sup> was used to predict Mössbauer quadrupole splittings and isomer shifts, the same approach used in the previous work for various iron-containing proteins and models.<sup>2,6</sup> To calculate  $\Delta E_Q$ , we first evaluated the principal components of the electric field gradient tensor at the  $^{57}\text{Fe}$  nucleus ( $V_{ii}$ ), then we used equation (1) to deduce  $\Delta E_Q$ , using a precise recent determination of  $Q = 0.16 (\pm 5\%) \times 10^{-28} \text{m}^2$ ,<sup>7</sup> a value previously found to permit excellent accord between theory and experiment in a broad range of systems.<sup>2,6</sup> In order to calculate  $\delta_{\text{Fe}}$  values, we read the wavefunctions from the *Gaussian 03* calculations into the AIM 2000 program,<sup>8</sup> to evaluate the charge density at the iron nucleus,  $\rho(0)$ . Then, we evaluated the isomer shifts by using the equation derived previously:<sup>2</sup>

$$\delta_{\text{Fe}} = -0.404 [ \rho(0) - 11614.16 ] \quad (6)$$

We considered numerous structural models pertaining to the axial ligands based on the examination of the X-ray crystal structures of TDO: 1) the His ligand in the substrate-free TDO structure (PDB ID: 2NW7) is twisted from a normal perpendicular position with respect to the heme ring; 2) the Ser124-Gly125 residues (*Cm*TDO amino acid numbering) are adjacent to the Fe center, and the amide proton of Gly125 is within hydrogen bonding distance to the Fe-oxo

with an H–oxo distance of ca. 2.2 Å; 3) the distal His residue is in the vicinity of the presumed oxo position; 4) the proximal His group has a water molecule hydrogen bonded to the N<sub>δ</sub> position in the substrate-bound TDO structure (PDB ID: 2NW8).

In all of these models, the heme group is represented by a porphyrin with original eight β substituents replaced by methyl groups and the axial His group is truncated to be 5-methylimidazole. Geometries of all of the structural models investigated in this work were first optimized (see Table S1-14 for the optimized coordinates) with the terminal atoms fixed at the x-ray crystal structure positions to mimic the protein environment effect, using the DFT method BPW91<sup>9</sup> with the Wachters' basis for Fe, 6-311G\* for other heavy atoms and 6-31G\* for hydrogens, which is the same approach used previously to investigate other oxoferryl species.<sup>6e</sup> Then, the Mössbauer properties of these optimized structures were calculated using above methods.

#### References cited in this supporting information:

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- (8) (a) AIM2000, Version 1.0, written by Biegler-König F, University of Applied Science, Bielefeld, Germany. (b) Bader RFW (1990) *Atoms in Molecules: A Quantum Theory*; Oxford Univ. Press, Oxford.
- (9) (a) Becke AD (1988) *Phys. Rev. A* 38:3098-3100. (b) Perdew JP, Burke K, Wang Y (1996) *Phys. Rev. B* 54:16533-16539.

**Table S1.** Cartesian coordinates of model **1A**:  $\text{Fe}^{\text{IV}}(\text{Por})^{2-}(\text{His})^0(\text{O})^{2-}$ 

C	0.9697073605	-1.443107041	5.3149774343
C	0.423302732	-0.9158325501	4.0038868075
N	-0.6622375381	-0.044044849	3.9714858185
C	0.8399921705	-0.9746954072	2.6846263664
C	-0.8558118333	0.3693917604	2.684803842
N	0.0415942555	-0.1758558336	1.8773328397
H	0.1608397914	-1.6998089826	5.9984526489
H	1.6137985698	-2.3072903699	5.1511308963
H	-1.2255767929	0.2322583145	4.7719063027
H	1.667592403	-1.5387990973	2.261187464
H	-1.6525386162	1.0421801856	2.3782206034
H	1.5758318392	-0.6492182632	5.7521304107
Fe	0.0049112317	0.1542539873	-0.4388669808
C	-3.3903161248	-0.4989645372	-0.3991561766
C	-0.6833570639	3.4879632012	-0.1194490713
C	3.3799427938	0.8522833846	-0.471560272
C	0.6430876805	-3.1548267593	-0.7510056356
N	-1.6939060915	1.2678013851	-0.2347494395
C	-2.9906257137	0.8280502718	-0.3795436203
C	-3.9108717466	1.9371448649	-0.4865316378
C	-3.151512656	3.0859373687	-0.3827812574
C	-1.7764440837	2.64181624	-0.2375868866
C	-3.6009963362	4.5332324035	-0.3873523143
C	-5.4119730826	1.8474115729	-0.5796091478
N	1.123538615	1.8121259126	-0.2057772211
C	0.6471804839	3.0986276162	-0.1020046927
C	1.7339103083	4.0552332368	-0.0422169616
C	2.8894830645	3.3223985758	-0.1470908069
C	2.4962304961	1.9186550924	-0.2695144857
C	1.5476356543	5.5457368159	0.1417719067
C	4.2830482948	3.8674723874	-0.0880567121
N	1.7221415039	-0.9492582626	-0.5239436414
C	3.0262055436	-0.4917714026	-0.625619992
C	3.945820408	-1.6086309957	-0.9036021464
C	3.1429996818	-2.7289200618	-0.9494796206
C	1.7610620004	-2.3074907372	-0.7339819162
C	5.4839203791	-1.5721042207	-1.0784311675
C	3.6325156844	-4.1184838812	-1.2518534294
N	-1.1589644386	-1.509502538	-0.449067873
C	-0.7049173106	-2.7935556278	-0.6187677534
C	-1.8413279894	-3.7143100317	-0.6707484242
C	-2.9881509778	-2.9687565919	-0.5184885326
C	-2.5348018016	-1.589899841	-0.4170716543
C	-1.7578934421	-5.2004827227	-0.8234389615
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H	2.5200274769	6.0284512599	0.2361483279
H	1.0103106226	5.9740077747	-0.7048920149
H	0.9723664381	5.7038407994	1.0544999381
H	4.2149728015	4.9386691891	0.1002094273
H	5.8916728492	-2.5691272422	-1.2455359781
H	5.7558766835	-0.9244945951	-1.9114104838
H	5.8897253189	-1.1639189927	-0.1523662829
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H	-2.7624432938	-5.6219892233	-0.7792930061
H	-1.2860238576	-5.4840919242	-1.7639690866
H	-1.1669015247	-5.5820968604	0.0086645197
H	-5.1173613174	-2.5814274453	-0.5242299236
H	-4.5623921087	-4.0302502677	-1.4669210748
O	-0.0407272249	0.304186238	-2.0850143381
H	-5.8249157534	1.2316715362	-1.3790918292
H	4.8170638732	3.3877570936	0.7325202794
H	4.8204917941	3.6967218307	-1.0208416458
H	3.8967319419	-4.1268197414	-2.3095316805
H	2.900300782	-4.879544885	-0.9793603375
H	-4.6957517738	-4.132191538	0.2407021791

**Table S2.** Cartesian coordinates of model **1B**:  $\text{Fe}^{\text{IV}}(\text{Por})^{2-}(\text{His})^0(\text{O})^{2-}$  with twisted His

C	1.0059512525	-1.4204213067	5.3076174758
C	0.4222564286	-1.028706359	3.9874350065
N	-0.7490837237	-1.5671250942	3.499377107
C	0.8694081276	-0.1743536476	3.0343815962
C	-0.9735278737	-1.0198597851	2.2716283294
N	-0.0016322933	-0.1876292812	1.9354234683
H	0.2044793601	-1.698814778	5.9913139587
H	1.672602856	-2.2671702025	5.1429847112
H	-1.3549931726	-2.2236750182	3.9844516647
H	1.7700877232	0.4350753285	3.0277495331
H	-1.845861001	-1.2652310053	1.675571225
H	1.5910657289	-0.6110188759	5.7449477336
Fe	-0.0018368872	0.1851691006	-0.5810321971
C	-3.3832481619	-0.5772190429	-0.5288986039
C	-0.7804755635	3.4716866974	-0.1727365191
C	3.3526028371	0.9478380808	-0.5256023029
C	0.72306951	-3.1280706628	-0.8134412666
N	-1.7240470488	1.2283005609	-0.3601020729
C	-3.0105969319	0.7561171974	-0.4825772511
C	-3.9657286857	1.838460419	-0.5188899908
C	-3.2374050366	3.003902726	-0.405780727
C	-1.8468839998	2.5960394438	-0.3079791653
C	-3.723941873	4.4360862542	-0.3892202619
C	-5.4633185974	1.7034015388	-0.5821862084
N	1.0692324138	1.8491840551	-0.2888181596
C	0.5595983868	3.1206844738	-0.1583871802
C	1.6211987161	4.1014575614	-0.0622337591
C	2.7962185064	3.3996675312	-0.1680378168
C	2.4405441923	1.9903203617	-0.3281211113
C	1.3963491334	5.5841544909	0.1381395148
C	4.1750963127	3.9789751285	-0.0938913618
N	1.7357997911	-0.8869036771	-0.6104729735

C	3.031191854	-0.4033599421	-0.6852488998
C	3.9825561007	-1.5014022502	-0.928469153
C	3.2092711248	-2.6410212186	-0.9727420338
C	1.8135743629	-2.2478470753	-0.7938125357
C	5.5189924284	-1.4263727724	-1.0879166633
C	3.7355216947	-4.0207452434	-1.2619500614
N	-1.1262674503	-1.5228324877	-0.6077134809
C	-0.6361754039	-2.8026917807	-0.7141183966
C	-1.7437722972	-3.7579295781	-0.7070071702
C	-2.9126555	-3.0407455221	-0.5696004952
C	-2.5020550829	-1.646693526	-0.5595857795
C	-1.6241733319	-5.2452149393	-0.8317010808
C	-4.3544097303	-3.5533423039	-0.5661145707
H	-4.4534258569	-0.7897014743	-0.5606447321
H	-1.0035175892	4.5373487159	-0.1010709578
H	4.4112131182	1.2188524291	-0.5752190475
H	0.9560858718	-4.1890355889	-0.9384625587
H	-2.8697960069	5.107976418	-0.3054978205
H	-4.2611544916	4.6453246657	-1.3139817931
H	-4.3904985869	4.5872025519	0.4595618136
H	-5.851247152	1.3578163376	0.3761813125
H	-5.8103494744	2.7022220756	-0.8462337527
H	2.3556741042	6.0923731047	0.2323490735
H	0.8474840536	5.9985327251	-0.7080352918
H	0.8175273845	5.7264737934	1.051219248
H	4.0787934531	5.0478906287	0.0950171155
H	5.9529009283	-2.412165679	-1.2557760066
H	5.7733289181	-0.7713297066	-1.9206498331
H	5.9142914273	-1.0081116238	-0.1618036503
H	4.6333171792	-4.170382722	-0.6627123014
H	-2.6171993076	-5.6931751985	-0.787338734
H	-1.1454076991	-5.5157155561	-1.7726074975
H	-1.0229013548	-5.6115247292	-0.000084494
H	-5.0516142758	-2.716123146	-0.5294689219
H	-4.4589521531	-4.1492296236	-1.4732392501
O	-0.0210415896	0.3384575031	-2.2220778661
H	-5.8602022666	1.077398724	-1.3818322733
H	4.7220018557	3.5130975892	0.7261686637
H	4.7164307434	3.8230241544	-1.0270180026
H	3.9993690119	-4.0214972291	-2.3197529862
H	3.0238258853	-4.8010636564	-0.9895583412
H	-4.5887658104	-4.2556171892	0.2343860309

**Table S3.** Cartesian coordinates of model **2A**:  $\text{Fe}^{\text{IV}}(\text{Por})^{2-}(\text{His})^0(\text{OH})^{1-}$

C	1.533529	-0.556007	5.278315
C	0.8165978811	-0.4515489376	3.9391045097
N	-0.5665495937	-0.3031151853	3.8728108196
C	1.2228939511	-0.3338934702	2.6182711948
C	-0.9423995919	-0.113012733	2.5813618603
N	0.1245828234	-0.1233802233	1.7852113863
H	0.994082	-1.202694	5.969758
H	2.555073	-0.913232	5.146597
H	-1.2026665152	-0.3337243985	4.6671489241
H	2.2302555843	-0.3793892415	2.2142297554



H	-1.9718920469	0.0145607047	2.261199767
H	1.579777	0.453708	5.687076
Fe	-0.0438365304	0.0450975961	-0.4004994897
C	-2.4822304287	-2.4011216804	-0.4287836308
C	-2.4877917381	2.432720137	-0.2920679243
C	2.3634390095	2.5295900051	-0.5439374962
C	2.3557793544	-2.3427795207	-0.6885000199
N	-2.0586279203	0.0205788855	-0.3309393394
C	-2.8932803422	-1.0811944523	-0.4675152851
C	-4.2694741911	-0.6806070949	-0.6343075564
C	-4.2888285931	0.7085487311	-0.5731391969
C	-2.9121115189	1.1195080141	-0.3927895606
C	-5.481983	1.648299	-0.641833
C	-5.467612	-1.595257	-0.738618
N	-0.0472370077	2.0521161907	-0.2704807847
C	-1.1684080664	2.8560860231	-0.2450780342
C	-0.8089845268	4.2578284237	-0.253913605
C	0.5639688261	4.2988799488	-0.3304672707
C	1.0331925606	2.9151997271	-0.36508652
C	-1.803068	5.394151	-0.144114
C	1.406897	5.537281	-0.309983
N	1.992870399	0.0986491916	-0.5439651089
C	2.8286562615	1.2158628458	-0.6626122338
C	4.2115628032	0.8018962663	-0.9185465783
C	4.1786291692	-0.5887973616	-0.9276495848
C	2.804121181	-1.0141954238	-0.7102126653
C	5.475931	1.68647	-1.101277
C	5.378156	-1.463985	-1.184337
N	-0.0652853162	-1.9784632197	-0.4013556059
C	1.037767596	-2.7920698075	-0.5528855502
C	0.613048175	-4.189186893	-0.6066001742
C	-0.7607604532	-4.2139930421	-0.4818997252
C	-1.1617415373	-2.8205849642	-0.3952428284
C	1.517912	-5.37504	-0.722894
C	-1.698726	-5.418059	-0.526556
H	-3.2615376502	-3.1613443744	-0.4931251917
H	-3.2474218536	3.2145138966	-0.3100927602
H	3.1016420501	3.3300696235	-0.6378379481
H	3.1155972745	-3.1153182563	-0.8281800027
H	-5.127335	2.677133	-0.580708
H	-6.02673	1.506914	-1.575012
H	-6.143203	1.440642	0.199138
H	-5.628758	-2.067067	0.230822
H	-6.292748	-0.950221	-1.040072
H	-1.271824	6.342402	-0.066228
H	-2.470016	5.421363	-1.006328
H	-2.387106	5.228364	0.761656
H	0.745041	6.390048	-0.160732
H	6.376652	1.086525	-1.231696
H	5.354927	2.350184	-1.956879
H	5.562681	2.279129	-0.190168
H	6.20141	-1.087408	-0.577742
H	0.92275	-6.286699	-0.664602
H	2.087492	-5.371924	-1.652012
H	2.20336	-5.333953	0.123138
H	-2.738035	-5.089132	-0.522464
H	-1.445333	-6.002594	-1.411427

O	-0.1683143273	0.1010026051	-2.1945620502
H	-5.446403	-2.359784	-1.515715
H	2.100552	5.464917	0.528023
H	1.967176	5.670768	-1.235379
H	5.623882	-1.353449	-2.240729
H	5.194083	-2.496586	-0.885246
H	-1.534715	-6.111671	0.298622
H	0.7372566012	0.1835432645	-2.5641065109

**Table S4.** Cartesian coordinates of model **2B**:  $\text{Fe}^{\text{IV}}(\text{Por})^{2-}(\text{His})^0(\text{OH})^{1-}$  with twisted His

C	0.575756	-1.675977	5.258536
C	0.12433	-1.130059	3.941262
N	-1.154291	-1.307612	3.457801
C	0.794699	-0.438478	2.987063
C	-1.2328435387	-0.7385373784	2.2340428586
N	-0.0596361447	-0.2267930856	1.8763483225
H	-0.269257	-1.71343	5.94545
H	0.969908	-2.678389	5.09023
H	-1.9247825222	-1.741268076	3.9616448483
H	1.8319269213	-0.1163843704	2.9669073092
H	-2.1532669105	-0.7180308275	1.6641782242
H	1.370731	-1.070108	5.694066
Fe	0.0503750964	0.1465862236	-0.4228821699
C	-3.4154375289	0.4008664423	-0.4952536772
C	0.2487044581	3.5289075087	-0.1234863289
C	3.4930423652	-0.0801857583	-0.5084986258
C	-0.21100502	-3.2241842472	-0.8139155526
N	-1.3041074682	1.6427560433	-0.2753840757
C	-2.6731856128	1.5666850686	-0.434173342
C	-3.2701804988	2.8799182625	-0.5157393041
C	-2.2309257621	3.791042159	-0.4046364632
C	-1.0248475534	3.0010947478	-0.2556711272
C	-2.290987	5.305986	-0.412311
C	-4.743878	3.1898	-0.600237
N	1.5544084494	1.4259650547	-0.2069407181
C	1.4303394619	2.8065157991	-0.1101095013
C	2.7253566512	3.4423653229	-0.0779025676
C	3.6549588799	2.4286177732	-0.1906814905
C	2.9161221738	1.1747979745	-0.2921940487
C	2.945112	4.931011	0.093863
C	5.143504	2.594638	-0.151712
N	1.4059122189	-1.3678852883	-0.5690066452
C	2.7953554729	-1.279659379	-0.6720456696
C	3.3794202718	-2.5932393324	-0.9696654505
C	2.3035651673	-3.4661616093	-1.0169416644
C	1.0858107848	-2.6981150751	-0.791155395
C	4.871258	-2.966669	-1.156541
C	2.416012	-4.937745	-1.325216
N	-1.5146774162	-1.1496546669	-0.5601255707
C	-1.4151304799	-2.520265725	-0.7005761414
C	-2.7493032955	-3.1123591294	-0.729803088
C	-3.6671787355	-2.0866277706	-0.5863854897
C	-2.8759204608	-0.8733715081	-0.5340633722
C	-3.067619	-4.569093	-0.872821

C	-5.194475	-2.163724	-0.593821
H	-4.4994037637	0.5059775008	-0.5514895361
H	0.3461574157	4.6139426713	-0.0794167756
H	4.5822390458	-0.1182833524	-0.5900452264
H	-0.2960837743	-4.3024494562	-0.9678726651
H	-1.279309	5.703499	-0.33168
H	-2.748865	5.662928	-1.334537
H	-2.882556	5.640702	0.439497
H	-5.211107	2.968415	0.359488
H	-4.78984	4.246794	-0.861855
H	4.010463	5.141488	0.184373
H	2.53541	5.487602	-0.749538
H	2.435286	5.23192	1.009579
H	5.359597	3.64565	0.038597
H	5.002489	-4.035265	-1.327191
H	5.300084	-2.410742	-1.989768
H	5.373797	-2.681819	-0.231769
H	3.235102	-5.34067	-0.730021
H	-4.147366	-4.712458	-0.824559
H	-2.690609	-4.963911	-1.816046
H	-2.593952	-5.094697	-0.044161
H	-5.621128	-1.161374	-0.553377
H	-5.469598	-2.702392	-1.501032
O	0.046762209	0.3488717209	-2.2063307119
H	-5.307222	2.706182	-1.398728
H	5.536408	1.989346	0.665536
H	5.613428	2.291504	-1.087324
H	2.664362	-5.012132	-2.384155
H	1.510944	-5.480849	-1.050454
H	-5.617883	-2.770566	0.207042
H	0.9671443454	0.2512831082	-2.5329263154

**Table S5.** Cartesian coordinates of model **3A**:  $\text{Fe}^{\text{IV}}(\text{Por})^{2-}(\text{His})^0(\text{O}^{\cdots}\text{HB})^{2-}$

C	4.6467444549	-2.3139949355	4.1871423285
C	3.6998253758	-1.4561690903	3.3700956126
N	3.4594243173	-0.1262491666	3.7064657079
C	3.034052734	-1.6175738225	2.1661305165
C	2.6847228838	0.4409673691	2.7367530897
N	2.4093671992	-0.437320982	1.7834854499
H	4.5098526067	-2.1434874333	5.2546107419
H	4.5174978927	-3.3711530279	3.9542816537
H	3.7956016074	0.3438824183	4.5434288333
H	2.964768327	-2.5076800832	1.5457069844
H	2.3374897766	1.4703274843	2.7650139032
H	5.6589498165	-2.0272493838	3.9008447657
Fe	0.9652858093	0.0571025214	0.0001876037
C	-1.2796002293	1.3775280666	2.2641081208
C	2.315647476	3.1790383057	-0.4098907001
C	3.2490534406	-1.2127018542	-2.2597828824
C	-0.3436453578	-3.0230151755	0.469031508
N	0.6305911985	1.8991766635	0.8121255936
C	-0.4258552822	2.2593257121	1.61846861
C	-0.5273551321	3.6956673217	1.7346546279
C	0.5152675582	4.2235203787	0.9976828524

C	1.2109917507	3.0863332806	0.4235925007
C	0.9160492985	5.6728023143	0.8081612187
C	-1.5101959676	4.4557470781	2.5864591298
N	2.5321546778	0.8036725656	-1.0339086442
C	2.9235930731	2.1231637822	-1.0704731366
C	4.0489500563	2.3121377929	-1.9634715986
C	4.319589784	1.0769442669	-2.498224734
C	3.3526997505	0.1414961073	-1.9231877369
C	4.7539342764	3.63462393	-2.1801521468
C	5.4323992392	0.7572236376	-3.4498481151
N	1.4230053617	-1.7942739934	-0.7339432973
C	2.3253424076	-2.1211692189	-1.7351794731
C	2.1687452655	-3.5307217643	-2.133135982
C	1.1561268311	-4.0175072867	-1.3326834521
C	0.6919652663	-2.9298330494	-0.4737245308
C	2.9729382408	-4.331452721	-3.1884030643
C	0.5997166585	-5.412171397	-1.4159216216
N	-0.4469103638	-0.689203226	1.2433856282
C	-0.8766764891	-1.9944345224	1.2601396467
C	-2.0189676901	-2.1259613071	2.1688201883
C	-2.2552132414	-0.8853482754	2.7174128171
C	-1.2828797334	0.0009510047	2.0976131497
C	-2.7736733912	-3.3844467332	2.4466349489
C	-3.3607114469	-0.4670578971	3.6841278581
H	-2.0340665647	1.8154470738	2.9205089859
H	2.7252096689	4.171770197	-0.6025229068
H	3.9394073668	-1.5869442613	-3.0211639491
H	-0.8223278573	-4.0005479164	0.5725099109
H	1.7817210255	5.7249650955	0.1479320877
H	0.0905347468	6.2327361084	0.3693424964
H	1.1707958581	6.1018107623	1.7769857342
H	-1.2584206044	4.3106076761	3.6371397285
H	-1.410851271	5.4922424732	2.2645865972
H	5.6092244888	3.4922277417	-2.8402036433
H	4.0715967117	4.3615514179	-2.6217015497
H	5.0977480269	4.0005830467	-1.2122316801
H	6.0109788052	1.6673057738	-3.6064916313
H	2.6417908474	-5.3686477851	-3.2414012031
H	2.8752393416	-3.8686938039	-4.169994685
H	4.0160483982	-4.2985833354	-2.8726028062
H	1.4436712232	-6.1007667095	-1.4489547612
H	-3.5273171517	-3.1859392893	3.2090999494
H	-3.2544158747	-3.7952673222	1.5590510891
H	-2.0480972417	-4.100843062	2.8308387375
H	-3.3388521766	0.611161953	3.8433042612
H	-4.308583735	-0.8127324841	3.2706871666
O	-0.1542882519	0.3341429665	-1.1973314016
H	-2.5686420372	4.2431233722	2.4337729241
H	6.0717307774	-0.0082666666	-3.009478068
H	5.0472145759	0.4033614062	-4.4061447722
H	0.045810287	-5.4697225909	-2.3531721707
H	0.0017027855	-5.6658378103	-0.5397722288
H	-3.2954674666	-0.9769008219	4.645750141
N	-4.9360952513	2.0881911205	-3.6525907086
C	-3.941807631	1.6497276208	-2.6944169835
C	-4.2234233484	0.1941862061	-2.3106476104
O	-5.2353205788	-0.399470944	-2.6856820382

C	-3.8590706865	2.6179357438	-1.5149757477
O	-5.0723249673	2.6463573741	-0.7872668355
H	-5.8567955848	1.8361444009	-3.3216521235
H	-2.9678404479	1.6236532381	-3.1827826792
H	-3.0458130911	2.317505276	-0.8540494149
H	-3.6725890114	3.6182568627	-1.9067451237
H	-4.9668008481	3.2793020398	0.0434393162
N	-3.294742946	-0.3857030168	-1.5058540625
C	-3.5657063648	-1.7191370183	-1.0186822548
C	-4.7231462731	-1.8011575637	-0.0437137995
O	-5.10992843	-2.8901643526	0.3761192349
H	-2.3615149377	0.0184302451	-1.3631816137
H	-3.7357692988	-2.4109074421	-1.8442628259
H	-2.6668146014	-1.9895660379	-0.46436128
N	-5.2626288251	-0.6458456061	0.3259101401
H	-4.8733103444	0.2131703226	-0.0345531103
H	-6.0505352642	-0.6263816107	0.9577286236
H	-4.7651869456	1.6426530864	-4.542810463

**Table S6.** Cartesian coordinates of model **3B**:  $\text{Fe}^{\text{IV}}(\text{Por})^{2-}(\text{His})^0(\text{O}^{\cdot\cdot}\text{HB})^{2-}$  with twisted His

C	4.6435191289	-2.496052237	4.083895294
C	3.6121955792	-1.6912314745	3.3588730351
N	2.3426839589	-1.4837139366	3.8542614861
C	3.6521419917	-1.0703556977	2.1542604194
C	1.6611833345	-0.737744767	2.9412265217
N	2.4073830992	-0.4852564021	1.8772992582
H	4.4818489587	-2.4112307862	5.1581248214
H	4.5431975692	-3.53466205	3.7680832597
H	1.9938521641	-1.7928166687	4.7578410601
H	4.4689097622	-1.0156543858	1.438443972
H	0.6407123524	-0.4115369613	3.1080495848
H	5.6542818456	-2.1664991458	3.8420224128
Fe	0.9136574148	0.1568483978	-0.0991545753
C	-1.4109284721	1.2334511816	2.2236220087
C	2.2466976976	3.2924214919	-0.1633793746
C	3.3186341767	-0.9196304851	-2.327212807
C	-0.2802864803	-3.0107381444	0.178894961
N	0.5241881347	1.8947003176	0.8592124918
C	-0.5423841938	2.1692041331	1.68424276
C	-0.6361926657	3.581736403	1.965184808
C	0.4131309742	4.1831121864	1.3014532913
C	1.1179362636	3.1121410489	0.6206935677
C	0.7971481637	5.6455199648	1.2475662439
C	-1.6348643624	4.2434489505	2.8753699617
N	2.5143707497	0.9855456497	-0.9839748223
C	2.8915584729	2.3070652717	-0.8922473662
C	4.0512993564	2.5799808364	-1.7163369941
C	4.3605981904	1.3958153619	-2.3394175375
C	3.3825318351	0.4067505371	-1.8875948498
C	4.7387031646	3.926191113	-1.8055635395
C	5.5078894442	1.1703106972	-3.2770765707
N	1.4553432363	-1.6387100944	-0.9116941763
C	2.401474451	-1.8813578695	-1.895280851
C	2.3090192489	-3.2709653028	-2.3753938056

C	1.2951578252	-3.8386586469	-1.6342613331
C	0.7676233639	-2.8167186779	-0.7318527285
C	3.1614066941	-3.9748865718	-3.4584402024
C	0.7793735087	-5.2394738409	-1.8248671423
N	-0.5271094398	-0.7200757677	1.0407966653
C	-0.8788735224	-2.0509208849	1.007100456
C	-1.9970498383	-2.2905706155	1.9218977931
C	-2.2868246497	-1.0951470284	2.5444472434
C	-1.3898774288	-0.1238246928	1.943683541
C	-2.7147923836	-3.5879460962	2.1088374507
C	-3.3928816072	-0.7877671275	3.553258701
H	-2.169738935	1.6044134599	2.9153100616
H	2.656544452	4.3003753197	-0.2412896105
H	4.0462726528	-1.2265250931	-3.0838812032
H	-0.7048947224	-4.0168330463	0.2288624656
H	1.6741653908	5.7669004704	0.6118630457
H	-0.0322611992	6.2197782579	0.8354139401
H	1.02292848	6.0039990137	2.251598624
H	-1.4004595126	4.0232497701	3.9169805835
H	-1.5530839021	5.3035434724	2.635984162
H	5.609812705	3.8533992209	-2.4562059214
H	4.0486200686	4.6701851813	-2.2046025689
H	5.0549771348	4.2237995902	-0.8053615749
H	6.0683537808	2.1019345638	-3.3512230368
H	2.8552924392	-5.0117727079	-3.5977319957
H	3.072352408	-3.4401054155	-4.4035811702
H	4.197095861	-3.944104761	-3.1188972307
H	1.6394199153	-5.9052483488	-1.8925316307
H	-3.4875989469	-3.4649328964	2.8680309494
H	-3.16847581	-3.9393917945	1.1823660427
H	-1.9806086227	-4.3161003909	2.452439733
H	-3.3989383766	0.2752119799	3.7949438942
H	-4.3242718869	-1.1207940817	3.0944655073
O	-0.1602692629	0.4983402042	-1.3141809693
H	-2.6849470483	4.0205977049	2.6843367836
H	6.1558957471	0.3870470576	-2.8830817708
H	5.1497575433	0.8829792499	-4.2656468418
H	0.2454119477	-5.2365224121	-2.7753614035
H	0.170292412	-5.5726099177	-0.9836504212
H	-3.334793673	-1.3686387545	4.4741973227
N	-4.8824960606	2.2905906025	-3.5981980364
C	-3.8973617943	1.8010311424	-2.6554377208
C	-4.1554685543	0.3147952321	-2.3895176899
O	-5.1491921521	-0.2674328936	-2.8260268861
C	-3.8600356895	2.6770806525	-1.4038395354
O	-5.0876518564	2.6233863612	-0.7021063454
H	-5.8034680884	1.9941469629	-3.307219184
H	-2.913668322	1.8335082858	-3.1235033013
H	-3.0531962661	2.3441276502	-0.7506761231
H	-3.6889565396	3.7083656622	-1.7138139747
H	-5.0130070565	3.1925903363	0.1766780358
N	-3.2288499154	-0.3053462098	-1.6126616844
C	-3.4768302933	-1.6780524201	-1.2349030252
C	-4.6509646849	-1.8596823962	-0.2939582966
O	-5.0207641872	-2.9858200098	0.0329337398
H	-2.3021701024	0.1026077617	-1.4369684488
H	-3.6147326068	-2.3076707571	-2.1144567198

H	-2.5829961256	-1.971056119	-0.6838864074
N	-5.224003823	-0.7480862484	0.1514506731
H	-4.847545644	0.1442785309	-0.1338129596
H	-6.0243810128	-0.7942158379	0.7659735896
H	-4.6839763514	1.9186967199	-4.5160705031

**Table S7.** Cartesian coordinates of model **4A**:  $\text{Fe}^{\text{IV}}(\text{Por})^{2-}(\text{His}\cdots\text{H}_2\text{O})^0(\text{O})^{2-}$

C	1.533529	-0.556007	5.278315
C	0.8105759718	-0.4684933491	3.9479550391
N	-0.5759040858	-0.3923899936	3.8857756198
C	1.2220129624	-0.3029716269	2.634204452
C	-0.9361617834	-0.1960757186	2.5875270631
N	0.1285080162	-0.1339795667	1.7958543626
H	0.994082	-1.202694	5.969758
H	2.555073	-0.913232	5.146597
H	-1.2344806814	-0.4800229134	4.6770897493
H	2.2336925269	-0.2905123257	2.2356673693
H	-1.9668679517	-0.1155351901	2.2524089984
H	1.579777	0.453708	5.687076
Fe	-0.0363269135	0.0530925707	-0.5093193129
C	-2.4812061559	-2.3934803224	-0.4682856173
C	-2.4872654976	2.4314523475	-0.3264302641
C	2.3614596534	2.5257799666	-0.5772410949
C	2.3536769481	-2.3324170831	-0.7137694108
N	-2.0753618655	0.0248965944	-0.363294168
C	-2.8966487967	-1.0713138459	-0.4961149735
C	-4.2782264541	-0.6748013511	-0.6464399146
C	-4.2975679936	0.7045103253	-0.5823367103
C	-2.9140212321	1.1141499608	-0.4159991396
C	-5.481983	1.648299	-0.641833
C	-5.467612	-1.595257	-0.738618
N	-0.0493817773	2.059859551	-0.3437852704
C	-1.1683220643	2.8577791621	-0.2913565185
C	-0.8080958702	4.2614026235	-0.2710399324
C	0.561428601	4.3019158998	-0.3477497571
C	1.0273052203	2.9165930755	-0.4132431282
C	-1.803068	5.394151	-0.144114
C	1.406897	5.537281	-0.309983
N	2.0049762953	0.1036556769	-0.5620442283
C	2.8274441678	1.2115530337	-0.6825365617
C	4.220695349	0.796824163	-0.9249333662
C	4.1866962181	-0.5815613962	-0.9308929733
C	2.8028088773	-1.0033723706	-0.7258548597
C	5.475931	1.68647	-1.101277
C	5.378156	-1.463985	-1.184337
N	-0.0667367888	-1.9775739026	-0.4695996328
C	1.0332008303	-2.7877983366	-0.5948709354
C	0.611034599	-4.1891627584	-0.62118557
C	-0.7593719047	-4.2128897794	-0.4979975203
C	-1.1606191114	-2.8153483268	-0.4416055643
C	1.517912	-5.37504	-0.722894
C	-1.698726	-5.418059	-0.526556
H	-3.2615304278	-3.15485076	-0.5260177954
H	-3.2486391999	3.2134881785	-0.3328115883

H	3.1024395353	3.3259160344	-0.663230678
H	3.1178138727	-3.1037630304	-0.8438482215
H	-5.127335	2.677133	-0.580708
H	-6.02673	1.506914	-1.575012
H	-6.143203	1.440642	0.199138
H	-5.628758	-2.067067	0.230822
H	-6.292748	-0.950221	-1.040072
H	-1.271824	6.342402	-0.066228
H	-2.470016	5.421363	-1.006328
H	-2.387106	5.228364	0.761656
H	0.745041	6.390048	-0.160732
H	6.376652	1.086525	-1.231696
H	5.354927	2.350184	-1.956879
H	5.562681	2.279129	-0.190168
H	6.20141	-1.087408	-0.577742
H	0.92275	-6.286699	-0.664602
H	2.087492	-5.371924	-1.652012
H	2.20336	-5.333953	0.123138
H	-2.738035	-5.089132	-0.522464
H	-1.445333	-6.002594	-1.411427
O	-0.1188545434	0.1066242888	-2.1622596494
H	-5.446403	-2.359784	-1.515715
H	2.100552	5.464917	0.528023
H	1.967176	5.670768	-1.235379
H	5.623882	-1.353449	-2.240729
H	5.194083	-2.496586	-0.885246
H	-1.534715	-6.111671	0.298622
O	-2.5660558174	-0.6295303846	5.9515228391
H	-3.1120705022	0.156495828	6.1307389735
H	-3.1835223321	-1.3772130147	5.8628243672

**Table S8.** Cartesian coordinates of model **4B**:  $\text{Fe}^{\text{IV}}(\text{Por})^{2-}(\text{His}\cdots\text{H}_2\text{O})^0(\text{O})^{2-}$  with twisted His

C	-1.6468201872	-1.9594391404	5.0168727972
C	-1.3815184223	-1.2250940377	3.7412446603
N	-2.340565573	-0.4703071976	3.1004468381
C	-0.2710090333	-1.1590846885	2.966224646
C	-1.7645821814	0.0345886341	1.9720004612
N	-0.5077780469	-0.3653625606	1.8400883389
H	-2.3986648961	-1.423228123	5.5954650962
H	-2.0067044308	-2.9565897813	4.7626693538
H	-3.3034563293	-0.2795025675	3.4200831982
H	0.6989669572	-1.6264979141	3.1256259335
H	-2.300172109	0.6841240333	1.2859779039
H	-0.7409631219	-2.0700183882	5.6134659476
Fe	0.4389361017	0.1182283384	-0.682090596
C	-1.9009401083	2.6605042894	-0.9342931314
C	2.7805376654	2.4317414082	0.2083755986
C	2.757626354	-2.3961956874	-0.2905220516
C	-1.9674681226	-2.1605277711	-1.3926828271
N	0.4300335015	2.1256262407	-0.3746755007
C	-0.5899403117	3.0063156157	-0.6558072439
C	-0.1348929853	4.3756836758	-0.5985249881
C	1.2009088417	4.3279781284	-0.2585075066
C	1.5263029701	2.9180949832	-0.1266489286



C	2.1750714502	5.4686415236	-0.0518961469
C	-0.9828167175	5.6059570436	-0.786208089
N	2.3373871627	0.020683409	-0.0411565348
C	3.1459604638	1.0965414706	0.2523115328
C	4.4960781721	0.670321983	0.5613758247
C	4.5033944806	-0.6952020757	0.4192965091
C	3.1526779307	-1.0914618894	0.021613433
C	5.614153896	1.6045712283	0.9753717508
C	5.6735426315	-1.5976824933	0.6686292522
N	0.4094797258	-1.9148175237	-0.7832366917
C	1.4774246551	-2.790745089	-0.6902257988
C	1.0591617835	-4.1599319295	-1.0389507865
C	-0.2875414463	-4.0621192346	-1.3127471564
C	-0.6785828537	-2.6619006373	-1.1688340023
C	1.915453843	-5.4473649688	-1.0830805027
C	-1.1499730025	-5.2028915853	-1.7796361717
N	-1.5640997319	0.2363189565	-1.026755709
C	-2.3871766852	-0.8257693171	-1.3180186793
C	-3.7515414244	-0.3478578258	-1.5355949183
C	-3.7486126684	1.0188846815	-1.3548578083
C	-2.3637025696	1.3621582285	-1.0804620923
C	-4.9353108719	-1.1942408277	-1.890708216
C	-4.9025002249	2.0087641932	-1.5340906795
H	-2.6078508148	3.480692283	-1.073341156
H	3.565962096	3.1567299522	0.4272790308
H	3.5248109848	-3.1736115603	-0.2311548112
H	-2.7323117037	-2.8906610305	-1.6712604571
H	3.1579507329	5.0652105494	0.1914785947
H	2.2415497161	6.0612666787	-0.9639701163
H	1.827768474	6.0995290584	0.7659910405
H	-1.6320611279	5.7438929854	0.0785307511
H	-0.2617984519	6.4138255054	-0.9099978663
H	6.5085581424	1.0278105669	1.2098197057
H	5.836016727	2.308272206	0.1725249234
H	5.2922758739	2.1535444446	1.8607904577
H	6.5024714536	-0.9827390968	1.0182518015
H	1.3218969863	-6.3130079312	-1.3773769681
H	2.7400502753	-5.3176037733	-1.7835068628
H	2.3115315908	-5.602371212	-0.0791682395
H	-0.9310942794	-6.0692890167	-1.155901897
H	-5.8187074076	-0.5615776583	-1.9812770554
H	-4.7675714637	-1.7203402057	-2.8302321463
H	-5.0877470191	-1.9187095092	-1.0913092978
H	-4.5443226559	3.0307269034	-1.409487076
H	-5.3078885282	1.8227941953	-2.5290605401
O	0.8429271886	0.2817873165	-2.2697157527
H	-1.5776455631	5.6549611294	-1.6986527963
H	5.4113376244	-2.3248758087	1.4374027926
H	5.9685543162	-2.1205658854	-0.2410872114
H	-0.840189207	-5.4049358597	-2.8052730622
H	-2.2142619365	-4.9859545115	-1.6803835592
H	-5.7518274205	1.8388587143	-0.871783158
O	-5.0710341719	0.218912933	3.7455082575
H	-5.695442885	-0.0773254667	3.0591668248
H	-5.2172088177	1.1762899079	3.8492128059

**Table S9.** Cartesian coordinates of model **5A**:  $\text{Fe}^{\text{IV}}(\text{Por})^{2-}(\text{His}\cdots\text{H}_2\text{O})^0(\text{O}\cdots\text{HB})^{2-}$ 

C	4.638732	-2.308075	4.165615
C	3.6864552546	-1.4499445376	3.3511988624
N	3.4061311982	-0.1388410649	3.7182971811
C	3.0481758194	-1.6064791528	2.1296570619
C	2.6357926722	0.4243408339	2.7481066109
N	2.3974413788	-0.4351363429	1.7627615704
H	4.504074	-2.135747	5.233075
H	4.508289	-3.365517	3.934721
H	3.7084375587	0.3324288379	4.5870242255
H	3.0148683016	-2.4843771346	1.4889379897
H	2.2572413456	1.4419780066	2.7922058094
H	5.650567	-2.022499	3.87685
Fe	0.9682866346	0.0536032572	0.0038289564
C	-1.2816660572	1.3824026815	2.2563283938
C	2.3073966096	3.1778857753	-0.4296762469
C	3.2330200278	-1.217334304	-2.2749682786
C	-0.354947075	-3.0209880305	0.4638858473
N	0.6283994939	1.9023370203	0.8046803838
C	-0.4286590197	2.2636809728	1.6084346113
C	-0.533827347	3.7007021851	1.7164402472
C	0.5076691855	4.2266330774	0.976276006
C	1.2057069239	3.0875236237	0.4085090531
C	0.906904	5.675856	0.781115
C	-1.516659	4.463371	2.566179
N	2.5248716765	0.8006271071	-1.0469940807
C	2.9135514124	2.1203086707	-1.0894851373
C	4.0336983354	2.3081334994	-1.9896162583
C	4.3026600471	1.071963646	-2.5223434553
C	3.3398612012	0.1370043888	-1.9391310911
C	4.737443	3.630171	-2.211492
C	5.411391	0.75025	-3.477873
N	1.4116777103	-1.796660395	-0.743503132
C	2.309423883	-2.1243875699	-1.7476892148
C	2.148305302	-3.5337111371	-2.1463983332
C	1.1370655378	-4.0183633317	-1.3433096361
C	0.6790102399	-2.9300697285	-0.4809916757
C	2.948915	-4.336279	-3.203329
C	0.578459	-5.412474	-1.424407
N	-0.4507864343	-0.6881336698	1.2410563183
C	-0.8842132756	-1.991308422	1.2563860174
C	-2.0297178088	-2.1189431249	2.162285501
C	-2.2631874116	-0.8777140437	2.7098693006
C	-1.2864121846	0.005436078	2.0919342551
C	-2.785862	-3.376154	2.441537
C	-3.368419	-0.45636	3.67547
H	-2.0367648894	1.8211177559	2.9117389597
H	2.7142365749	4.1704299703	-0.6298755554
H	3.9193510386	-1.5921657687	-3.0397139146
H	-0.8364098401	-3.99712273	0.5673790955
H	1.771302	5.726347	0.119089
H	0.080911	6.235656	0.343026
H	1.163868	6.106251	1.748738
H	-1.262904	4.319753	3.616592
H	-1.417232	5.499275	2.242434

H	5.591325	3.486111	-2.873004
H	4.054738	4.35686	-2.652864
H	5.083428	3.997453	-1.244847
H	5.990291	1.659673	-3.637134
H	2.616942	-5.373326	-3.253994
H	2.849593	-3.875038	-4.185473
H	3.992671	-4.303628	-2.889649
H	1.421867	-6.101711	-1.457997
H	-3.537855	-3.175889	3.20517
H	-3.268647	-3.788073	1.555572
H	-2.060024	-4.092436	2.825461
H	-3.345494	0.6221	3.832858
H	-4.317348	-0.802041	3.264466
O	-0.1576457558	0.334591523	-1.1903547757
H	-2.575553	4.25124	2.415933
H	6.051061	-0.014975	-3.037532
H	5.024066	0.395112	-4.432832
H	0.022657	-5.471153	-2.360465
H	-0.017994	-5.664306	-0.546666
H	-3.301624	-0.964694	4.637784
N	-4.956557	2.088129	-3.662238
C	-3.960678	1.65052	-2.705327
C	-4.2429846783	0.1959727299	-2.3178770175
O	-5.2571933431	-0.3967378825	-2.6885698529
C	-3.874932	2.620575	-1.52762
O	-5.086722	2.65102	-0.797557
H	-5.876775	1.837261	-3.32907
H	-2.987699	1.622977	-3.195578
H	-3.060576	2.320645	-0.86782
H	-3.688531	3.620131	-1.921375
H	-4.979112	3.285232	0.031914
N	-3.3125521005	-0.3837467993	-1.5152728734
C	-3.5836	-1.715894	-1.024894
C	-4.739163	-1.79553	-0.047505
O	-5.12587	-2.883587	0.374854
H	-2.3799912306	0.0213568146	-1.3713229357
H	-3.755779	-2.408878	-1.849017
H	-2.6838	-1.986054	-0.471917
N	-5.277109	-0.639246	0.321318
H	-4.887908	0.218914	-0.041304
H	-6.063749	-0.618211	0.954663
H	-4.787723	1.641034	-4.552073
O	4.1443884752	1.256223103	6.1158211834
H	3.4354337253	1.5050671085	6.7348683073
H	4.7548296022	2.0134524821	6.0761292962

**Table S10.** Cartesian coordinates of model **5B**:  $\text{Fe}^{\text{IV}}(\text{Por})^{2-}(\text{His}\cdots\text{H}_2\text{O})^0(\text{O}\cdots\text{HB})^{2-}$  with twisted His

C	4.8196830949	-3.4327028229	2.8483196269
C	3.7482832393	-2.4705157351	2.4441887399
N	2.4920540856	-2.4699624377	3.0116577786
C	3.7350677809	-1.4975681784	1.5000637035
C	1.7695419877	-1.5002597083	2.3986613819
N	2.4694326405	-0.8932334098	1.448438715
H	4.6923450678	-3.6991780486	3.8971655902

H	4.730296125	-4.3192856662	2.2202328166
H	2.1498709449	-3.075695103	3.776146572
H	4.5271228781	-1.1930883643	0.8194316696
H	0.7486767905	-1.2748356235	2.6842780808
H	5.8147685089	-3.0129044563	2.6989116274
Fe	0.9235264528	0.2829525457	-0.1509364325
C	-1.3593797728	0.5044382972	2.437331075
C	2.1732069005	3.324877036	0.7421140993
C	3.2572413431	0.0555015941	-2.6800899338
C	-0.2150542171	-2.8303163711	-0.8868221233
N	0.5198318952	1.6214851375	1.3148908446
C	-0.5273801645	1.5884210445	2.2056452409
C	-0.6484182155	2.838776048	2.9170179537
C	0.3650328073	3.6517223764	2.453512704
C	1.0755582667	2.8706977239	1.4566919468
C	0.7133727496	5.0680432604	2.8558558389
C	-1.6333452574	3.1478954312	4.0117889789
N	2.4649892636	1.4063504369	-0.7750413891
C	2.8133845285	2.6424427114	-0.279223414
C	3.9323087099	3.2032400693	-1.0092038857
C	4.2448291608	2.2890965374	-1.9850465902
C	3.3093422303	1.1738751428	-1.8412682983
C	4.5851554232	4.5300176319	-0.6843942716
C	5.3613500278	2.4104976806	-2.9772163902
N	1.4601289491	-1.1349407596	-1.5220885056
C	2.3745504549	-1.0207348177	-2.5560080894
C	2.2890836673	-2.1831867842	-3.4575562211
C	1.3125102307	-2.9874516402	-2.9113275678
C	0.7988444016	-2.3257244228	-1.7129586727
C	3.1167656197	-2.4777657995	-4.7318254212
C	0.8173451602	-4.2679739184	-3.5278135969
N	-0.4769254508	-0.9454414427	0.6715449924
C	-0.804855679	-2.2027877825	0.219697857
C	-1.8912114845	-2.7518053191	1.0336970414
C	-2.1835104663	-1.8263733074	2.0129229265
C	-1.3218595858	-0.6908780234	1.7362327561
C	-2.5765209667	-4.0609774972	0.8137987561
C	-3.263509599	-1.8881059473	3.092798495
H	-2.1058841285	0.6152676607	3.226355746
H	2.5572224879	4.318848709	0.9758880759
H	3.9624453594	0.0295909089	-3.5157093562
H	-0.6204439067	-3.8100836187	-1.1528117105
H	1.5659286334	5.4119220667	2.2702741313
H	-0.141038653	5.7182814231	2.6694863649
H	0.9651900404	5.0949149616	3.9157764018
H	-1.3597129941	2.6147696425	4.9224418839
H	-1.5815124533	4.2310084044	4.1212097498
H	5.4353149794	4.6944960404	-1.3459400245
H	3.8668992579	5.3411173649	-0.8076830098
H	4.9285242683	4.5031699712	0.3501980026
H	5.899677842	3.3337536364	-2.7642817908
H	2.8276181129	-3.4251263053	-5.1869535264
H	2.9851103035	-1.6728889271	-5.4543574889
H	4.1623834215	-2.5253800809	-4.4263691957
H	1.68819732	-4.8512584127	-3.8259900397
H	-3.3258556644	-4.2094534187	1.5917379301
H	-3.0536138125	-4.1127635488	-0.1646652116

H	-1.8163804987	-4.8380880693	0.8885121448
H	-3.2834031936	-0.958052707	3.6611105994
H	-4.2026651612	-2.0857559405	2.5752987655
O	-0.1995468427	0.9618747479	-1.1670665643
H	-2.6844123776	2.9658139277	3.7861029948
H	6.0382038643	1.5625236799	-2.8701788486
H	4.976333543	2.4421144626	-3.9964564409
H	0.2519201051	-3.9787489576	-4.4139324488
H	0.243765682	-4.8698125645	-2.8218379075
H	-3.1626555312	-2.7298857165	3.778473601
N	-5.0548621745	3.2601114231	-2.6626759333
C	-4.0288326323	2.5259262517	-1.9505027347
C	-4.2466472302	1.0252947862	-2.165696914
O	-5.2419368115	0.5817851917	-2.7400710418
C	-3.9677151875	2.9586920664	-0.4861494737
O	-5.1697857221	2.6473284996	0.1924041637
H	-5.9592657353	2.8587664023	-2.4584382306
H	-3.0622369802	2.7354304089	-2.4083181132
H	-3.1327674987	2.4596876058	0.0061183686
H	-3.8284211302	4.0396780019	-0.4550425079
H	-5.0775268682	2.9091639136	1.2047070076
N	-3.281828475	0.2182498976	-1.651409564
C	-3.4892976613	-1.209985076	-1.725428974
C	-4.6272813102	-1.7170987692	-0.8624174694
O	-4.962618785	-2.8993493629	-0.9027663745
H	-2.3596134113	0.5760516461	-1.3732716537
H	-3.6435443871	-1.5307300746	-2.7561479262
H	-2.5716657518	-1.6359919137	-1.3193748226
N	-5.2079017809	-0.8229695996	-0.0713288529
H	-4.8596942141	0.1247315927	-0.066304782
H	-5.9861388826	-1.0864902879	0.516271689
H	-4.8795462869	3.2059266625	-3.6559194059
O	1.2697888594	-4.0978320658	5.0343406332
H	0.5618835649	-4.649689384	4.6558999243
H	0.8782517535	-3.6406512167	5.7998152179

**Table S11.** Cartesian coordinates of model **6A**:  $\text{Fe}^{\text{IV}}(\text{Por})^{2-}(\text{His})^0(\text{OH}\cdots\text{HB})^{1-}$

C	4.640732866	-2.3180776843	4.1622179739
C	3.7064556897	-1.4498808338	3.3427022903
N	3.5370481946	-0.1009386748	3.6390901408
C	2.9903494675	-1.6238960666	2.1727700018
C	2.7617722886	0.4764252898	2.6853276667
N	2.4110636295	-0.4213037133	1.7681141885
H	4.5077219342	-2.1472702356	5.2301287734
H	4.5097558401	-3.3751622198	3.9299932932
H	3.9370886425	0.3816422418	4.4406441073
H	2.8734683212	-2.5358753312	1.5924514725
H	2.4736066552	1.5236409068	2.7006176804
H	5.6521791183	-2.0322587064	3.8723336265
Fe	1.0402259857	0.0440414357	0.0587282659
C	-1.2443661237	1.3826314002	2.2976589547
C	2.3254390656	3.1827406756	-0.4250615152
C	3.2562221028	-1.234246335	-2.2640394481
C	-0.3352168858	-3.0357812558	0.4949040618

N	0.6653045319	1.8922786752	0.8413270101
C	-0.3977612727	2.2562867603	1.6458886125
C	-0.525998702	3.690290378	1.7396906498
C	0.51419679	4.2219922436	0.9924150679
C	1.2303579953	3.0891728317	0.4280061487
C	0.9051754243	5.6713816502	0.7949216067
C	-1.5158924637	4.4567341406	2.5819002532
N	2.5435755197	0.7921037453	-1.0102358564
C	2.9315924479	2.1236363644	-1.0667106711
C	4.0346164067	2.310383644	-1.9741867167
C	4.3036423206	1.0666410795	-2.5131279913
C	3.3636366893	0.1183950767	-1.9248562751
C	4.7308203246	3.6293664024	-2.2064393565
C	5.4023470462	0.7511635804	-3.4780022089
N	1.4523951324	-1.7999493448	-0.7124632861
C	2.3336220659	-2.1352567258	-1.7293931296
C	2.1527958911	-3.5350360416	-2.1448763377
C	1.1363296724	-4.0200310355	-1.3386377377
C	0.6929739532	-2.9409759453	-0.4542134489
C	2.9394025136	-4.3353328864	-3.2070822042
C	0.5714560337	-5.4136908063	-1.4261289558
N	-0.400195464	-0.7041142221	1.2920287962
C	-0.8580427143	-2.0053665968	1.2929780883
C	-2.0206559764	-2.1313145597	2.1748256299
C	-2.2497852654	-0.8810604139	2.7307115028
C	-1.2546397847	0.0029341647	2.1378386527
C	-2.7866502222	-3.3823837068	2.4478472685
C	-3.3668282431	-0.4642767479	3.6868813881
H	-1.9907885312	1.8306925251	2.9559256261
H	2.7206747828	4.1727972579	-0.6536863137
H	3.9345553097	-1.6156140914	-3.0315773401
H	-0.8256200102	-4.0070125077	0.5964770235
H	1.768578474	5.7226810125	0.1316605589
H	0.0786174684	6.2319568076	0.3588942149
H	1.1636798313	6.1003327384	1.7627754484
H	-1.2605717778	4.3115536746	3.6317188948
H	-1.4167752551	5.4930880567	2.2595029983
H	5.5836742296	3.4861160389	-2.8694517468
H	4.0475743397	4.3568104503	-2.6457255314
H	5.0783331379	3.9951906388	-1.2397896183
H	5.9811637749	1.6607162006	-3.6368250493
H	2.6071722673	-5.3722483459	-3.2587434915
H	2.8386734562	-3.8726550746	-4.1884067458
H	3.9836381182	-4.3033152821	-2.8949368971
H	1.4146919525	-6.1030237716	-1.4619930459
H	-3.537450762	-3.1830936206	3.2129073393
H	-3.2708484588	-3.792937998	1.5620200609
H	-2.0603564872	-4.0993451243	2.8296352721
H	-3.3434767636	0.6139505748	3.8457934983
H	-4.3164389736	-0.8091996214	3.2768160752
O	-0.2086447826	0.3182888599	-1.1978558734
H	-2.5750498082	4.2450030061	2.4329520372
H	6.0425497976	-0.0148075235	-3.0397375504
H	5.0135140996	0.3974735533	-4.4328857885
H	0.0142266228	-5.4709204605	-2.3614277412
H	-0.0237107095	-5.6666890325	-0.5478503862
H	-3.2986643983	-0.974013233	4.6483571643

N	-4.9656347904	2.0910935207	-3.6447259177
C	-3.9683838727	1.651929749	-2.6899583699
C	-4.2861792983	0.2003307033	-2.2912669338
O	-5.3172197668	-0.3783650129	-2.6337913297
C	-3.8806849257	2.620265971	-1.5109813925
O	-5.0913624002	2.649863975	-0.7790402084
H	-5.885390839	1.8399025186	-3.3105272812
H	-2.9961533777	1.6249281031	-3.181722104
H	-3.0653828078	2.3192419453	-0.8528501503
H	-3.6947062006	3.6203581809	-1.9035728031
H	-4.9823855231	3.2828573414	0.0511828648
N	-3.3524458237	-0.3743003428	-1.4883637438
C	-3.5893482057	-1.7169755584	-1.0149672961
C	-4.743443329	-1.797825759	-0.0359449836
O	-5.1296999327	-2.8864257363	0.3854258621
H	-2.4395083706	0.0266966106	-1.3825403231
H	-3.7628961589	-2.4087374745	-1.8398295336
H	-2.6887587962	-1.988089865	-0.4637452207
N	-5.2806283679	-0.641983653	0.3353638538
H	-4.8918273858	0.216632758	-0.0266062749
H	-6.066304474	-0.6217290109	0.9699295758
H	-4.7982267818	1.6452566287	-4.5354611254
H	0.2219573571	0.5045439314	-2.0802794331

**Table S12.** Cartesian coordinates of model **7A**:  $\text{Fe}^{\text{IV}}(\text{Por})^{2-}(\text{His})^0(\text{O}\cdots\text{HB})^{2-}(\text{distalHis})\text{-1}$

C	1.5208647814	-4.9646429406	4.7043908972
C	1.7329190448	-4.0452571656	3.5165142725
N	2.9188803908	-4.0712565805	2.7865386943
C	0.9232252476	-3.1796831009	2.799280843
C	2.7888426772	-3.2507083284	1.7038905733
N	1.5866477629	-2.6938830208	1.6795534753
H	2.4184144618	-5.0272146929	5.3190374192
H	0.6730909279	-4.6376351663	5.3067673648
H	3.750424491	-4.6061216834	3.0252053502
H	-0.0988360994	-2.8764128287	3.0125895876
H	3.5787341963	-3.0760857402	0.9781910441
H	1.2875853796	-5.9505744403	4.3015648821
Fe	0.9853368802	-1.0728049782	0.0857013418
C	3.969141182	0.5467547578	0.6940378919
C	2.4993811348	-2.8116767408	-2.4497070108
C	-1.9704582	-2.7468850597	-0.5516742017
C	-0.4690741487	0.6031394048	2.6340243138
N	2.8731028707	-1.1656504262	-0.6830184179
C	3.9186461443	-0.3197619305	-0.3874593745
C	4.9907575058	-0.4617017845	-1.3449401819
C	4.5957153557	-1.4432572695	-2.2336227427
C	3.2703432986	-1.8535775635	-1.808226894
C	5.3499592249	-2.0291913218	-3.4101447973
C	6.3217435217	0.2427490082	-1.3067771601
N	0.4095812463	-2.5516524084	-1.1670393138
C	1.1867766506	-3.1339652855	-2.1434913412
C	0.4359077938	-4.12100362	-2.8927293139
C	-0.8332627248	-4.1087628281	-2.3689705255
C	-0.8446507677	-3.1103469938	-1.2992800372

C	1.018469397	-4.9803190474	-3.9954566956
C	-1.9658964663	-4.9937644926	-2.7932692669
N	-0.8801661797	-1.1156963936	0.9155546873
C	-2.0065935726	-1.7885702602	0.4649868274
C	-3.2029301099	-1.3588508511	1.210627787
C	-2.7415083842	-0.4203395804	2.1103160686
C	-1.3003767446	-0.2699173533	1.9160668153
C	-4.6645938815	-1.8478596386	1.0579959682
C	-3.6168106045	0.3521556187	3.0589724977
N	1.6725647019	0.2173188314	1.4847634127
C	0.9003805106	0.8363236202	2.4379563672
C	1.7052307104	1.8267301193	3.1574968293
C	2.9802095024	1.77811326	2.6394049253
C	2.9252647245	0.7905878539	1.5734768167
C	1.2205888914	2.7131087409	4.2574037526
C	4.1889072119	2.6363228069	3.0042675794
H	4.8949912422	1.1089657156	0.8300208382
H	2.941882047	-3.3371845403	-3.2974279507
H	-2.9133058604	-3.2408916756	-0.8027267472
H	-0.9484968291	1.2044652191	3.4111467211
H	4.7276270135	-2.776448546	-3.9024051547
H	5.60132816	-1.2414267486	-4.1199353549
H	6.2652273939	-2.4980521393	-3.049563721
H	6.9084636135	-0.1471551973	-0.4748395156
H	6.7713062147	0.0362362792	-2.2778795634
H	0.2674628108	-5.6873012027	-4.3470691804
H	1.3486529875	-4.3576281698	-4.8274476016
H	1.8708380947	-5.5260993883	-3.5897530814
H	-1.591487282	-5.6741895102	-3.5577171449
H	-5.327334847	-1.3556641623	1.7698660587
H	-5.0228072319	-1.6684328192	0.0447328178
H	-4.6515059611	-2.9202014052	1.2549752618
H	-4.2914925739	-0.3586635931	3.5354746365
H	2.0590090205	3.2960065834	4.6395278062
H	0.4250074481	3.3865949571	3.9393495375
H	0.8474890949	2.055735961	5.0422314853
H	5.0227914831	2.4224609958	2.33548275
H	3.87507909	3.6798409686	2.9659562758
O	0.5847996902	0.1732272569	-0.941574852
H	6.3058806338	1.3320131337	-1.2611478526
H	-2.3133479885	-5.5683535384	-1.934333374
H	-2.7927362949	-4.4113693252	-3.1997674426
H	-4.193095081	1.0500692358	2.4512095627
H	-3.0375312825	0.8353903827	3.8467063551
H	4.5085263248	2.4990172596	4.0376623778
N	1.0903006178	4.9416312774	-3.9183591642
C	1.2493065928	3.8879503108	-2.9368152168
C	0.5971426824	4.324182508	-1.6216697291
O	0.1441310085	5.4583042555	-1.4583688301
C	2.7145340001	3.4696995183	-2.8205013335
O	3.5158985189	4.5326404557	-2.3405789735
H	1.3581035298	5.8258670339	-3.5095245678
H	0.6713223294	3.0199325476	-3.2534733198
H	2.7972760856	2.6183426827	-2.1446202154
H	3.0711156967	3.1949416709	-3.8136068763
H	4.5043895963	4.1995850693	-2.2231630479
N	0.5702590758	3.3823400223	-0.6429212241



C	0.076579366	3.7775973151	0.6564174597
C	0.9653755609	4.763965727	1.3872229606
O	0.6132834881	5.2433223544	2.4633476727
H	0.7561202948	2.3885409973	-0.8267977489
H	-0.9336096964	4.1818913452	0.5848954672
H	0.0853981046	2.8550272906	1.2371039325
N	2.1241523643	5.0520379688	0.8069991216
H	2.3625392273	4.5964531552	-0.0619227282
H	2.7574625757	5.7168739729	1.2280469381
H	0.1247763195	4.9855391239	-4.211684803
N	-8.479965677	-1.2429662237	0.1882586408
C	-8.9768613705	0.010462575	0.7550306767
C	-8.9461751589	1.152563719	-0.2819620922
C	-7.6273517637	1.3438828282	-0.9733519033
N	-7.311608663	0.6242037605	-2.1164118885
C	-6.5740750858	2.1724977786	-0.6328064118
C	-6.0912877614	1.0053218749	-2.453640479
N	-5.5974673134	1.9427777553	-1.5860212864
H	-8.6745284186	-1.2964158195	-0.7911740878
H	-8.3453607956	0.2965597994	1.6198437446
H	-9.7051719588	0.9452784174	-1.0587818297
H	-9.2538977441	2.0851447581	0.221876704
H	-6.4305998039	2.8892548744	0.1725011621
H	-5.5209093733	0.6456663417	-3.3093761851
H	-4.6869648236	2.394291506	-1.6312452637
H	-8.6859000879	-2.0207386657	0.782111352
H	-10.0228605808	-0.0515804954	1.137482256

**Table S13.** Cartesian coordinates of model **8A**:  $\text{Fe}^{\text{IV}}(\text{Por})^{2-}(\text{His})^0(\text{O}^{\cdots}\text{HB})^{2-}(\text{distalHis})\text{-2}$

C	0.3564838628	-4.8437282878	4.9680408791
C	0.7326109186	-4.0595641549	3.7236429794
N	1.857374009	-4.3928688994	2.9727066987
C	0.1189680789	-3.0682984646	2.9745029928
C	1.8853968128	-3.6209207224	1.8494267159
N	0.8413285142	-2.8040795446	1.8169708189
H	1.2373979508	-5.0928412001	5.5590012216
H	-0.3613178707	-4.2916377742	5.5750571361
H	2.5521164144	-5.0921320667	3.2239305969
H	-0.798506318	-2.5271330314	3.1918378057
H	2.6702079776	-3.6650371527	1.1004466836
H	-0.1244504202	-5.7616519232	4.6291199222
Fe	0.5786333305	-1.1987404643	0.1630195728
C	3.8947916064	-0.3009544636	0.5897184643
C	1.5280044256	-3.3559288794	-2.3067948523
C	-2.7133904635	-2.1165638752	-0.2876770226
C	-0.3163391464	0.9313188659	2.6465343677
N	2.3630034965	-1.7643098216	-0.6491757465
C	3.5924378247	-1.1812490153	-0.4378382411
C	4.5541058136	-1.6212876958	-1.4221818139
C	3.8963462551	-2.5189977311	-2.2416529908
C	2.5327982102	-2.5806889154	-1.7475077251
C	4.4367666842	-3.3236977621	-3.4084338745
C	6.0153150061	-1.2571829203	-1.46731703
N	-0.3827790909	-2.5532043359	-0.9672476275

C	0.1910656536	-3.3426336681	-1.9405346869
C	-0.8085978471	-4.1379013714	-2.6225728394
C	-2.01569264	-3.7918193112	-2.0643303001
C	-1.7415968067	-2.7849476409	-1.0403988182
C	-0.4993722324	-5.1578039607	-3.6984960195
C	-3.3456900476	-4.3869899889	-2.4115633422
N	-1.201654017	-0.7275170372	1.0521716102
C	-2.4753694341	-1.1271184924	0.6701983656
C	-3.4990683698	-0.3720131301	1.4129833905
C	-2.7883569767	0.4683443276	2.2452710974
C	-1.362928909	0.2495423637	2.00721272
C	-5.0417041177	-0.4967144103	1.3302572302
C	-3.4111181156	1.4766860606	3.1711004802
N	1.6172450642	-0.0248725414	1.4604784095
C	1.0586917661	0.813142434	2.3967387018
C	2.1087153623	1.6134418314	3.0329252596
C	3.3115997536	1.2301545576	2.4827833693
C	2.9749394162	0.2313179202	1.4807515536
C	1.8988690205	2.6457028315	4.0920822413
C	4.7057219841	1.7889107504	2.7599246791
H	4.9314196323	0.0332166331	0.6630593805
H	1.7935856127	-4.0049369093	-3.1424857595
H	-3.7570514285	-2.3703215198	-0.4926734978
H	-0.6036927522	1.6709447266	3.3984049183
H	3.6324528184	-3.9201276211	-3.8389703171
H	4.8407554087	-2.6560002495	-4.1690488508
H	5.2261833762	-3.9830196778	-3.0483215339
H	6.52500881	-1.7373135293	-0.6318095049
H	6.3606299016	-1.6135593527	-2.4376507155
H	-1.4128261709	-5.6771216412	-3.9872468618
H	-0.0639191774	-4.6751046778	-4.5739136566
H	0.2123959384	-5.8741659694	-3.2871378503
H	-3.1789032937	-5.17420781	-3.1464179407
H	-5.5356609421	0.175714517	2.0317463558
H	-5.38823295	-0.2848277645	0.3192009421
H	-5.2794553698	-1.5292266276	1.5877098729
H	-4.2167559286	0.975170957	3.7067723155
H	2.8684196843	3.025031948	4.4158382167
H	1.2766455538	3.4762177142	3.7592534761
H	1.411460678	2.137557057	4.9236578419
H	5.4345677132	1.3465970817	2.080575342
H	4.6515916146	2.87430417	2.6711720584
O	0.4188457094	0.046665382	-0.9414997707
H	6.2646361842	-0.1958603553	-1.4835455016
H	-3.7851502766	-4.8175863785	-1.5115036462
H	-4.0239065077	-3.6414021473	-2.8265455149
H	-3.8269816703	2.2635219471	2.5414102456
H	-2.6998466574	1.8421047932	3.912832954
H	5.0258379555	1.6281889592	3.7897830531
N	1.9671945495	4.4406468553	-4.1904230907
C	1.9083347639	3.4287031443	-3.1553093522
C	1.439718329	4.0753156726	-1.8503021506
O	1.2814409473	5.2903475242	-1.7338032816
C	3.232929709	2.672865183	-3.0577839313
O	4.2864669645	3.5309937127	-2.6627792757
H	2.4573190804	5.2519460112	-3.8406965921
H	1.1252518225	2.7129982269	-3.4049903048

H	3.1361158147	1.8606795864	-2.3370540051
H	3.4707070531	2.2719179646	-4.043483816
H	5.1694394115	2.9736644978	-2.5552116038
N	1.2238161337	3.2160967348	-0.8177494443
C	0.8954304109	3.780849643	0.4708188329
C	2.0257892545	4.5556790184	1.1180331126
O	1.8452074683	5.1577636374	2.1747640765
H	1.1865247215	2.1995119493	-0.9445072111
H	0.0105323465	4.4146904837	0.4056099042
H	0.7057698458	2.9130416701	1.1027588555
N	3.1944440543	4.5249164833	0.4889793587
H	3.2792098629	3.983537298	-0.3590385276
H	3.9865299414	5.0353825088	0.8528397498
H	1.0293525866	4.7037577933	-4.4576871676
N	-5.5048620434	1.7580019271	-5.912651369
C	-5.4060831614	2.6349330078	-4.7363291812
C	-3.9455429894	3.0784783092	-4.525561877
C	-3.0537822043	1.9900787834	-3.9945718194
N	-2.9717624672	0.7471091404	-4.6078370642
C	-2.2224433633	2.0141670675	-2.8876375916
C	-2.1080071469	0.0491034646	-3.8822407909
N	-1.6220618892	0.7697691498	-2.8307019681
H	-4.820022817	0.9982102943	-5.7914438686
H	-5.7711637761	2.1794528952	-3.7859612868
H	-3.5659410994	3.4405751822	-5.4997839128
H	-3.9188791516	3.9338987145	-3.8283595513
H	-2.0082851447	2.7866026527	-2.1526723841
H	-1.8002987121	-0.9778041333	-4.0741107408
H	-0.9407264034	0.4436224455	-2.1216156328
H	-6.4358338242	1.328102664	-5.9410766125
H	-6.0263121132	3.5334147842	-4.9172762323

**Table S14.** Cartesian coordinates of model **9A**:  $\text{Fe}^{\text{IV}}(\text{Por})^{2-}(\text{His})^0(\text{O}^{\cdots}\text{HB})^{2-}(\text{distalHis})\text{-3}$

C	-4.8457473236	-5.0107966615	-2.112084197
C	-4.0628076602	-3.9961204967	-1.2976482027
N	-4.3292430885	-3.7962275871	0.05487814
C	-2.9427330201	-3.21438533	-1.5313214175
C	-3.4034935162	-2.9343719922	0.56588859
N	-2.5428839495	-2.5617807357	-0.3709023751
H	-5.9094496857	-4.9664446301	-1.8799825338
H	-4.6859200467	-4.8596110831	-3.1798436093
H	-5.0939864752	-4.2171805242	0.5770657975
H	-2.3933935869	-3.0804041588	-2.4598662294
H	-3.395062334	-2.5974152172	1.5989260542
H	-4.4578791152	-5.9953413047	-1.8494454744
Fe	-0.8533426493	-0.9881195881	0.0407859166
C	-3.2261408013	1.0520217928	1.5070515507
C	-0.1591086183	-2.3089349862	3.1262368266
C	1.5021925283	-3.0784355782	-1.3740922428
C	-1.5844764677	0.3146422452	-2.9893065347
N	-1.5892285062	-0.7297458333	1.9295773833
C	-2.4609174498	0.2537392188	2.3433565226
C	-2.5038976809	0.3404847505	3.7844796433
C	-1.6507828619	-0.6360958727	4.2622653535

C	-1.0856801258	-1.2779157657	3.0895710215
C	-1.3451955823	-1.022120206	5.6956765345
C	-3.3915731642	1.2452850379	4.5995719536
N	0.3327260473	-2.4768976098	0.7139441745
C	0.4836418539	-2.8609517813	2.0292781189
C	1.4825349817	-3.9015557616	2.1587842483
C	1.9655961809	-4.1244068044	0.8919394207
C	1.2518148868	-3.2163157399	-0.0043720795
C	1.8385483433	-4.5846010182	3.4627291373
C	2.9942399393	-5.1449538413	0.5127703836
N	-0.1948839308	-1.3761075578	-1.8509340819
C	0.85482107	-2.195541503	-2.2426539708
C	1.1588532332	-1.9980636158	-3.6697762951
C	0.2526742609	-1.0512995808	-4.1011077184
C	-0.5712229267	-0.6558880553	-2.9617570103
C	2.2313735448	-2.7053506335	-4.5348330133
C	0.2031514799	-0.4905866007	-5.4955408435
N	-2.2364724746	0.3349573414	-0.6171986746
C	-2.3567690275	0.7744964195	-1.9138028866
C	-3.3799289075	1.8192123785	-1.9876732487
C	-3.8839429847	1.9954623516	-0.7183558522
C	-3.1292924392	1.0822903687	0.1248199235
C	-3.8110294012	2.5340850335	-3.2265136603
C	-4.9245680472	3.0060216519	-0.2391289325
H	-3.92589329	1.7382500257	1.9875600195
H	0.1273262488	-2.7010509602	4.1031026237
H	2.3024854315	-3.6934872579	-1.7943055583
H	-1.7788339387	0.7902685932	-3.9542613526
H	-0.6114039562	-1.8280321547	5.7038484627
H	-0.9471922439	-0.163267316	6.2356089894
H	-2.2624133046	-1.3600840222	6.177399597
H	-4.4234493909	0.9045712271	4.5127874393
H	-3.0033678093	1.1715624714	5.6152764311
H	2.5600976659	-5.3797387091	3.2767489566
H	2.2611141846	-3.8685448092	4.1681904156
H	0.9262299179	-5.0110806971	3.8808130692
H	3.2518458825	-5.710035694	1.4082382377
H	2.1961648841	-2.3684972899	-5.5709465086
H	3.2259611706	-2.5248040366	-4.1281250334
H	2.0084106669	-3.7717939614	-4.4915296264
H	0.2686734504	-1.3270074051	-6.190969567
H	-4.6225245517	3.2190308217	-2.9794066229
H	-2.9929149975	3.0901935125	-3.6838146356
H	-4.1722497937	1.7798489894	-3.9250441305
H	-5.0190835004	2.9681041348	0.8462291149
H	-4.6143048334	3.9866791005	-0.6009765616
O	0.2908316571	0.2068624301	0.2647603607
H	-3.3424946607	2.3134165514	4.3862262944
H	2.5669514219	-5.8179731974	-0.230946948
H	3.8921509856	-4.6782817638	0.1077247997
H	1.0847017547	0.1418689157	-5.6024619961
H	-0.734080965	0.0305817711	-5.6944978045
H	-5.9047750374	2.8596324644	-0.6937479622
N	2.7013535081	4.9202003372	2.3868641266
C	1.8341250179	3.9601616432	1.7052795535
C	1.5311194217	4.3590602566	0.2304092006
O	1.9921230781	5.3891433202	-0.2589401711

C	0.5279234507	3.8036090056	2.4871618807
O	-0.2550127923	5.00365023	2.285996956
H	2.2442726664	5.8377298866	2.3182930219
H	2.3320822919	2.9733274632	1.7120523997
H	-0.0337039574	2.9117670499	2.1515170217
H	0.7808764881	3.6831272156	3.5560347695
H	-0.9920524505	4.9894934058	2.923139801
N	0.6782719229	3.5306138123	-0.4564582318
C	0.1497017156	3.9101817169	-1.7555638856
C	-1.0870793397	4.8317236613	-1.7542771504
O	-1.6576133728	5.0869623243	-2.816154441
H	0.3867220407	2.6350121295	-0.0581554101
H	0.9327505149	4.4484420797	-2.3142321866
H	-0.1156053064	3.006882263	-2.3243006661
N	-1.4850004709	5.3219689644	-0.5474056558
H	-0.9443278523	5.2020690128	0.3161058333
H	-2.213715913	6.0315259942	-0.5653090491
H	3.5609153719	5.0225962753	1.8354025429
N	8.170992297	-0.580650599	0.0589055854
C	7.5806545625	0.1305288261	-1.0852497972
C	6.5743977697	1.187402324	-0.5917851517
C	5.286824227	0.6029522498	-0.079417086
N	5.2670969486	-0.3918094534	0.88928803
C	3.9891231715	0.9103227254	-0.4519753232
C	3.9847734111	-0.6674182182	1.0889992464
N	3.1687170137	0.0944730154	0.3047567057
H	7.3958303702	-0.9359636894	0.6365447485
H	7.0609019767	-0.5269965552	-1.8211197086
H	7.0716678789	1.7716582743	0.2055486018
H	6.345402953	1.8890124186	-1.412687486
H	3.5835376901	1.6213473576	-1.1679628171
H	3.5939608956	-1.409611008	1.783408423
H	2.1333680445	0.0621294028	0.2719073705
H	8.6974716122	-1.3936320453	-0.2790147171
H	8.3935098341	0.6428603227	-1.6343899986