Supplementary material for the paper

Comparison of heme and honheme iron-based 1-aminocyclopropane-1-carboxylic acid oxidase mimics: kinetic, mechanistic and computational studies

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Analytical and physical measurements

UV-vis spectra were recorded on an Agilent 8453 diode-array spectrophotometer using quartz cells. GC analyses were performed on a Hewlett Packard 5890 gas chromatograph equipped with a flame ionization detector and a 30 m Supelcowax column.

Determination of products

Catalytic oxidations

A respective amino acid (ACCH, ACBH, ACPH, ACHH, AIBH) was dissolved in 10 mL of DMF/H_2O mixture (3/1) in a sealable tube of 20 mL. With MeCN (10 μl) as inner standard, NH_4OH and the catalyst were then added to the mixture. Hydrogen peroxide was added through the septum with a syringe and the evolved ethylene, cyclobutanone, cyclopentanone, cyclohexanone or acetone was measured by removing 0.25 mL of the headspace with a gastight syringe and the sample was injected into a gas chromatograph. The reactions were performed in DMF/D_2O mixture, in DMF/pH=7.5 buffer in H_2O mixture and in DMF/pH=7.5 buffer in D_2O because the solvent isotope effect.

Stoichiometric oxidations

These reactions were carried out in the absence of base.

Table S1. Kinetic data for the oxidation of ACCH catalyzed by $[Fe^{II}(N_4Py)(CH_3CN)](ClO_4)_2$ and $[Fe^{III}(tpp)Cl]$ with H_2O_2 in DMF/water (3/1) at 35°C. $[S]_0 = 3.6 \times 10^{-2}$ M, $[catalyst]_0 = 7.2 \times 10^{-6}$ M, $[NH_4OH]_0 = 3.6 \times 10^{-2}$ M.

N_0	S	Fe	Solvent	T (K)	$[S]_0$ (10^{-2} M)	$[Fe]_0$ (10^{-6} M)	$[H_2O_2]_0$ (10^{-2} M)	v (10^{-5} M s^{-1})
1	ACCH	1	DMF/H_2O	308	3.6	7.2	3.6	3.63
2	ACCH	1	DMF/H_2O	308	3.6	7.2	5.4	5.73
3	ACCH	1	DMF/H_2O	308	3.6	7.2	7.2	7.94
4	ACCH	1	DMF/H_2O	308	0.36	7.2	3.6	0.55
5	ACCH	1	DMF/H_2O	308	0.54	7.2	3.6	0.95
6	ACCH	1	DMF/H_2O	308	0.72	7.2	3.6	1.22
7	ACCH	1	DMF/H_2O	308	1.26	7.2	3.6	2.19
8	ACCH	1	DMF/H_2O	308	1.8	7.2	3.6	2.48
9	ACCH	1	DMF/H_2O	308	2.7	7.2	3.6	3.19
10	ACCH	2	DMF/H_2O	308	3.6	7.2	1.8	1.28
11	ACCH	2	DMF/H_2O	308	3.6	7.2	3.6	2.52
12	ACCH	2	DMF/H_2O	308	3.6	7.2	5.4	3.51
13	ACCH	2	DMF/H_2O	308	3.6	7.2	7.2	4.99
14	ACCH	2	DMF/H_2O	308	3.6	14.4	3.6	13.2
15	ACCH	2	DMF/H_2O	308	3.6	21.6	3.6	21.5
16	ACCH	2	DMF/H_2O	308	3.6	36	3.6	33.9
17	ACCH	2	DMF/H_2O	308	0.36	7.2	3.6	0.34
18	ACCH	2	DMF/H_2O	308	0.54	7.2	3.6	0.58
19	ACCH	2	DMF/H_2O	308	0.72	7.2	3.6	0.74
20	ACCH	2	DMF/H_2O	308	1.8	7.2	3.6	1.23
21	ACCH	2	DMF/H_2O	308	3.6	7.2	3.6	2.60[A]
22	ACCH	2	DMF/H_2O	308	3.6	7.2	3.6	1.66[B]

[A] 3.6×10^{-2} M $NaHCO_3$ was added to the reaction mixture in presence of base.

[B] 3.6×10^{-2} M $NaHCO_3$ was added to the reaction mixture in absence of base.

Table S2. Kinetic data for the oxidation of ACCH catalyzed by $[Fe^{II}(N_4Py)(CH_3CN)](ClO_4)_2$ and $[Fe^{III}(tpp)Cl]$ with H_2O_2 in DMF/pH=7.5 buffer in water or in DMF/pH=7.5 buffer in D_2O at 35°C. $[S]_0 = 3.6 \times 10^{-2}$ M, $[catalyst]_0 = 7.2 \times 10^{-6}$ M, $[NH_4OH]_0 = 3.6 \times 10^{-2}$ M.

N_0	S	Fe	Solvent	T (K)	$[S]_0$ (10^{-2} M)	$[Fe]_0$ (10^{-6} M)	$[H_2O_2]_0$ (10^{-2} M)	v (10^{-8} M s^{-1})	SIE
1	ACCH	1	DMF/pH=7.5 buffer in H_2O	308	3.6	7.2	3.6	2.71	
2	ACCH	1	DMF/pH=7.5 buffer in H_2O	308	3.6	7.2	3.6	1.26	2.15
3	ACCH	2	DMF/pH=7.5 buffer in H_2O	308	3.6	7.2	3.6	2.03	
4	ACCH	2	DMF/pH=7.5 buffer in H_2O	308	3.6	7.2	3.6	1.10	1.85

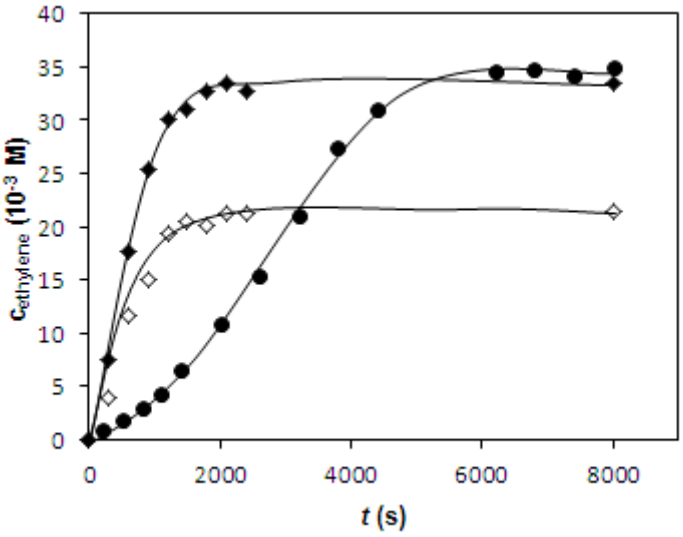

Figure S1. Formation of ethylene versus time in the oxidation reaction of ACCH with ● $[Fe^{II}(N_4Py)(CH_3CN)](ClO_4)_2$, with ♦$[Fe^{II}(N_4Py)(CH_3CN)](ClO_4)_2$ in presence of $NaHCO_3$ and NH_4OH and with ◊$[Fe^{II}(N_4Py)(CH_3CN)](ClO_4)_2$ in presence of $NaHCO_3$ without NH_4OH in DMF/water (3 / 1) at 35 °C. $[S]_0 = 3.6 \times 10^{-2}$ M, $[[Fe^{II}(N_4Py)(CH_3CN)](ClO_4)_2]_0$, $[[Fe^{III}(tpp)]Cl]_0 = 7.2 \times 10^{-6}$ M, $[NH_4OH]_0 = 3.6 \times 10^{-2}$ M, $[NaHCO_3]_0 = 3.6 \times 10^{-2}$ M.

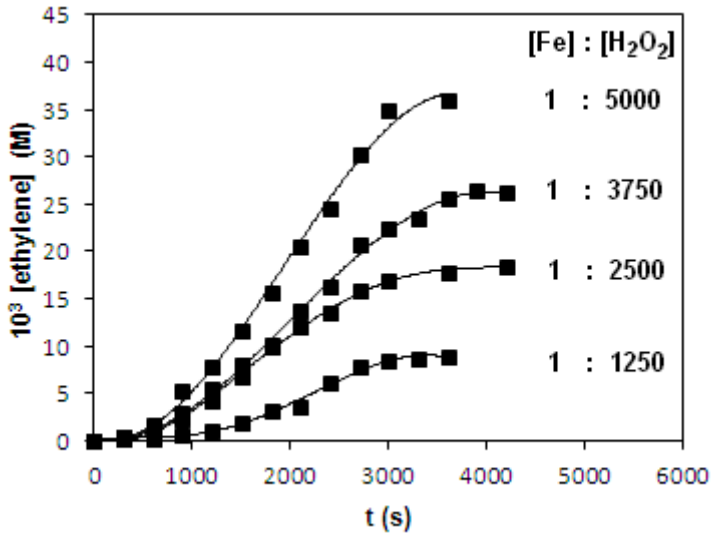

Figure S2. Formation of ethylene versus time in the oxidation reaction of ACCH with $[Fe^{II}(N_4Py)(CH_3CN)](ClO_4)_2$ in DMF/water (3 / 1) at 35 °C. $[S]_0 = 3.6 \times 10^{-2}$ M, $[[Fe^{II}(N_4Py)(CH_3CN)](ClO_4)_2]_0 = 7.2 \times 10^{-6}$ M, $[NH_4OH]_0 = 3.6 \times 10^{-2}$ M.

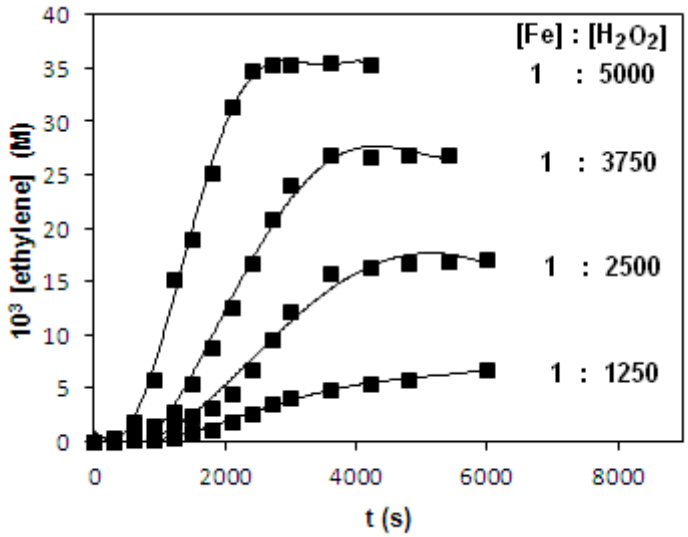

Figure S3. Formation of ethylene versus time in the oxidation reaction of ACCH with $[Fe^{III}(tpp)Cl]$ in DMF/water (3 / 1) at 35 °C. $[S]_0 = 3.6 \times 10^{-2}$ M, $[[Fe^{III}(tpp)Cl]]_0 = 7.2 \times 10^{-6}$ M, $[NH_4OH]_0 = 3.6 \times 10^{-2}$ M.

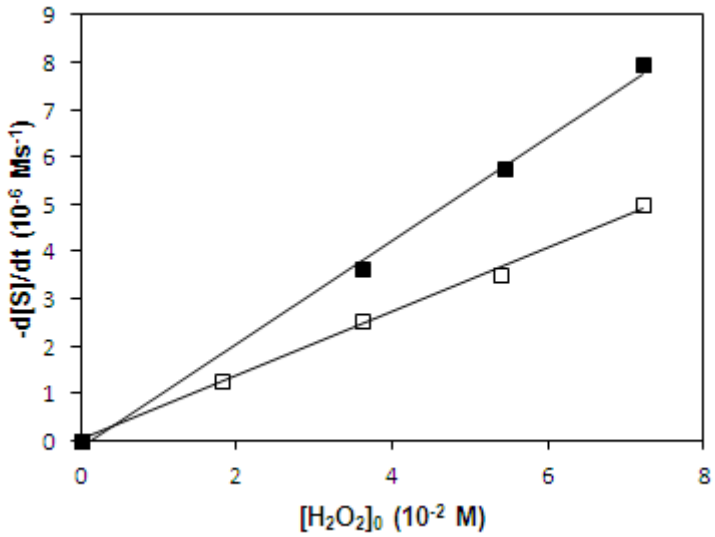

Figure S4. Hydrogen peroxide dependence of amino acid oxidation reactions in DMF/water (3 / 1) at 35 °C. $[ACCH]_0 = 3.6 \times 10^{-2}$, $[catalyst]_0 = 7.2 \times 10^{-6}$ M, $[NH_4OH]_0 = 3.6 \times 10^{-2}$ M. ■ $[Fe^{III}(tpp)Cl]$ +ACCH, □ $[Fe^{II}(N_4Py)(CH_3CN)](ClO_4)_2$ + ACCH.

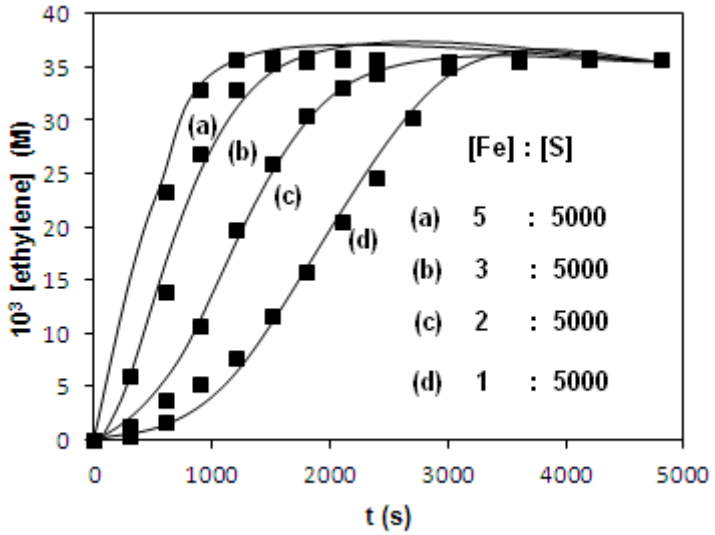

Figure S5. Formation of ethylene versus time in the oxidation reaction of ACCH with $[Fe^{II}(N_4Py)(CH_3CN)](ClO_4)_2$ in DMF/water (3 / 1) at 35 °C. $[S]_0 = 3.6 \times 10^{-2}$ M, $[[Fe^{II}(N_4Py)(CH_3CN)](ClO_4)_2]_0 = 7.2 \times 10^{-6}$ M, $[H_2O_2]_0 = 3.6 \times 10^{-2}$ M, $[NH_4OH]_0 = 3.6 \times 10^{-2}$ M.

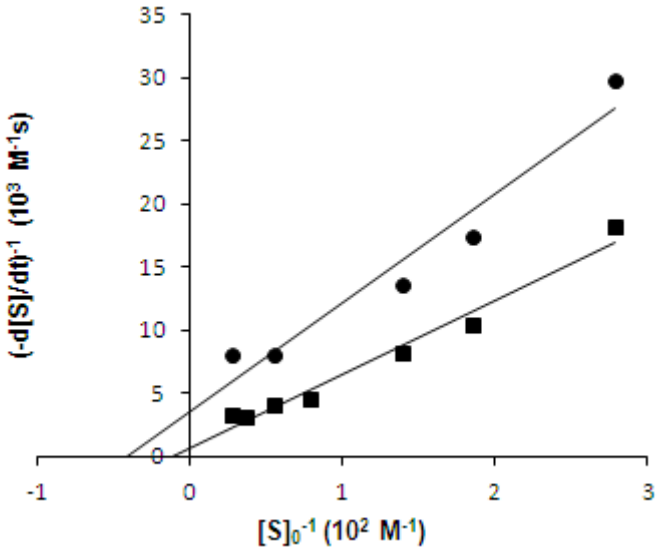

Figure S6. *Lineweaver-Burk* plot of ● ACCH + $[Fe^{III}(tpp)]Cl$ and ■ ACCH + $[Fe^{II}(N_4Py)(CH_3CN)](ClO_4)_2$]
$[catalyst]_0 = 7.2 \times 10^{-6}$ M, $[H_2O_2]_0 = 3.6 \times 10^{-2}$ M, $[NH_4OH]_0 = 3.6 \times 10^{-2}$ M, DMF/water (3/1), T=35°C.

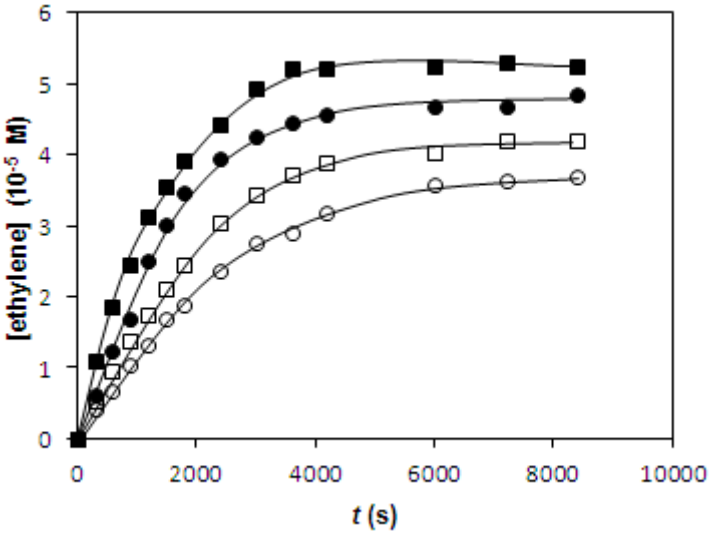

Figure S7. Formation of ethylene versus time in the oxidation reaction of ■ ACCH with $[Fe^{III}(tpp)Cl]$ in DMF/pH=7.5 buffer in water (3/1), ● ACCH with $[Fe^{II}(N_4Py)(CH_3CN)](ClO_4)_2$ in DMF/pH=7.5 buffer in water (3 / 1), □ ACCH with $[Fe^{III}(tpp)Cl]$ in DMF/pH=7.5 buffer in D_2O (3/1),○ACCH with $[Fe^{II}(N_4Py)(CH_3CN)](ClO_4)_2$ in DMF/pH=7.5 buffer in D_2O (3 / 1) at 35 °C. $[S]_0 = 3.6 \times 10^{-2}$ M, $[[Fe^{II}(N_4Py)(CH_3CN)](ClO_4)_2]_0$, $[Fe^{III}(tpp)Cl]_0 = 7.2 \times 10^{-6}$ M, $[H_2O_2]_0 = 3.6 \times 10^{-2}$ M, $[NH_4OH]_0 = 3.6 \times 10^{-2}$ M.

	K_M (10^{-3} M)	k_{cat} (s^{-1})	k_{cat}/K_M (M^{-1} s^{-1})	v_{max} (10^{-3} Ms^{-1})
ACCH + 2	13.66	0.58	42.46	0.58
ACCH + 1	2.41	0.28	116.01	27.93

Table S3. Calculated K_M, k_{cat}, v_{max} values for ACCH oxidation with $[Fe^{II}(N_4Py)(CH_3CN)](ClO_4)_2$ and $[Fe^{III}(tpp)]Cl$ in DMF/water (3/1) at 35 °C. $[catalyst]_0$ = 7.2×10^{-6} M, $[H_2O_2]_0 = 3.6 \times 10^{-2}$ M, $[NH_4OH]_0 = 3.6 \times 10^{-2}$ M.

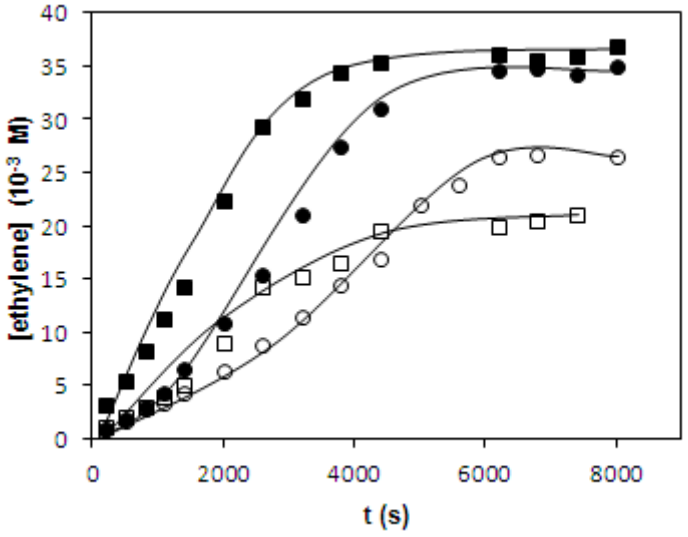

Figure S8. Formation of product (ethylene) versus time in the oxidation reaction of ACCH with ● $[Fe^{II}(N_4Py)(CH_3CN)](ClO_4)_2$ in DMF/water (3/1), ○ $[Fe^{II}(N_4Py)(CH_3CN)](ClO_4)_2$ in DMF/D_2O (3/1), ■ $[Fe^{III}(tpp)]Cl$ in DMF/water (3/1) and □ $[Fe^{III}(tpp)]Cl$ in DMF/D_2O (3/1) at 35 °C. $[ACCH]_0 = 3.6 \times 10^{-2}$ M, $[[Fe^{III}(tpp)]Cl]_0$, $[[Fe^{II}(N_4Py)(CH_3CN)](ClO_4)_2]_0$ = 7.2×10^{-6} M, $[H_2O_2]_0 = 3.6 \times 10^{-2}$ M, $[NH_4OH]_0 = 3.6 \times 10^{-2}$ M.

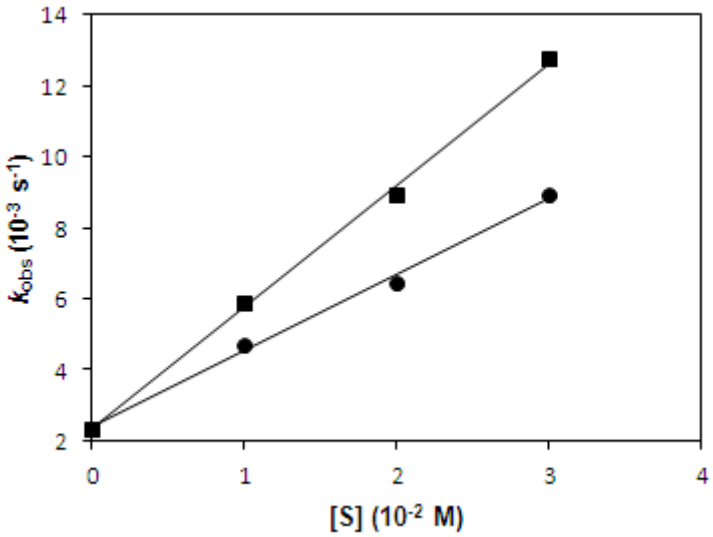

Figure S9. The calculated k_{obs} values for different concentrations of ● ACCH and ■ AIBH with $[Fe^{II}(N_4Py)(CH_3CN)](ClO_4)_2$ in DMF/water (3/1) at 25°C. $[[Fe^{II}(N_4Py)(CH_3CN)](ClO_4)_2]_0$ = 1.00×10^{-3} M, $[H_2O_2]_0 = 1 \times 10^{-2}$ M.

Table S4. Kinetic data for the oxidation of ACCH, ACBH, ACPH, ACHH and AIBH catalyzed by $[Fe^{II}(N_4Py)(CH_3CN)](ClO_4)_2$ with H_2O_2 in DMF/water (3/1) at 25°C. $[[Fe^{II}(N_4Py)(CH_3CN)](ClO_4)_2]_0 = 1.00 \times 10^{-3}$ M, $[H_2O_2]_0 = 1 \times 10^{-2}$ M.

N_0	S	T (K)	Solvent	$[Fe]_0$ (10^{-3} M)	$[S]_0$ (10^{-2} M)	k_{ox} (10^{-3} M^{-1} s^{-1})	k_{obs} [A] (10^{-3} s^{-1})	SIE [B]
1	-	298	DMF/H_2O	1	0	0	2.35	
2	ACCH	298	DMF/H_2O	1	1	0.23	4.68	
3	ACCH	298	DMF/H_2O	1	2	0.205	6.45	
4	ACCH	298	DMF/H_2O	1	3	0.22	8.95	
5	ACCH	303	DMF/H_2O	1	1	0.33	5.63	
6	ACCH	308	DMF/H_2O	1	1	0.45	6.86	
7	ACCH	313	DMF/H_2O	1	1	0.63	8.64	
8	-	298	DMF/D_2O	1	0	0	1.32	
9	ACCH	298	DMF/D_2O	1	1	0.139	2.71	1.68
10	ACCH	298	DMF/D_2O	1	2	0.119	3.69	1.73
11	ACCH	298	DMF/D_2O	1	3	0.128	5.17	1.71
12	AIBH	298	DMF/H_2O	1	1	0.35	5.86	
13	AIBH	298	DMF/H_2O	1	2	0.33	8.94	
14	AIBH	298	DMF/H_2O	1	3	0.35	12.75	
15	AIBH	303	DMF/H_2O	1	1	0.497	7.32	
16	AIBH	308	DMF/H_2O	1	1	0.713	9.48	
17	AIBH	313	DMF/H_2O	1	1	0.917	11.52	
18	ACBH	313	DMF/H_2O	1	1	0.66	8.95	
15	ACPH	313	DMF/H_2O	1	1	0.75	9.87	
16	ACHH	313	DMF/H_2O	1	1	0.78	10.14	
17	ACCH	298	DMF/pH=7.5 buffer in H_2O	1	0	0	3.49	
18	ACCH	298	DMF/pH=7.5 buffer in H_2O	1	1	0.9	12.5	
19	ACCH	298	DMF/pH=7.5 buffer in D_2O	1	0	0	0.56	
20	ACCH	298	DMF/pH=7.5 buffer in D_2O	1	1	0.49	5.49	1.83

[A] $k_{obs} = k_0 + k_{ox}$ [S]
[B] SIE = k_{ox}(H) / k_{ox}(D)

Table S5. Calculated values E_A, $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ for AIBH and ACCH oxidation with $[Fe^{II}(N_4Py)(CH_3CN)](ClO_4)_2$ in DMF/water (3/1) at 25 °C. $[S]_0 = 1.00 \times 10^{-2}$ M, $[[Fe^{II}(N_4Py)(CH_3CN)](ClO_4)_2]_0 = 1.00 \times 10^{-3}$ M, $[H_2O_2]_0 = 3.6 \times 10^{-2}$ M.

	E_A (kJ/mol)	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J mol^{-1} K^{-1})
ACCH	51	48	-112
AIBH	25	22	-90

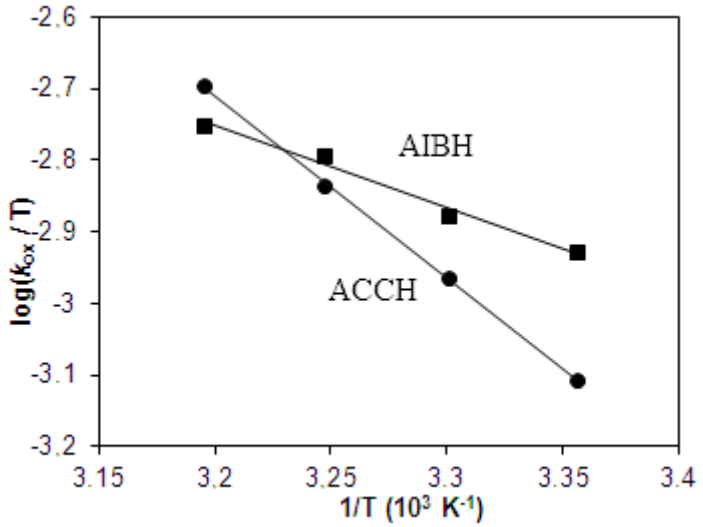

Figure S10. Eyring plot of ● ACCH and ■ AIBH
$[S]_0 = 1.00 \times 10^{-2}$ M, $[[Fe^{II}(N_4Py)(CH_3CN)](ClO_4)_2]_0 = 1.00 \times 10^{-3}$ M, $[H_2O_2]_0 = 1.00 \times 10^{-2}$ M, T = 25°C, 30°C, 35°C and 40°C.

	TON	yield (%)
AIBH	0.866111	42
ACCH	0.285	15
ACBH (cyclobutanone)	0.1896	7
ACBH (butyronitrile)	0.1896	7
ACBH (dehydroproline)	0.0542	2
ACPH	0.122778	15
ACHH	0.62	35

Table S6. Calculated yield and TON values for AIBH, ACCH, ACBH, ACPH and ACHH oxidation with $[Fe^{II}(N_4Py)(CH_3CN)](ClO_4)_2$ in DMF/water (3/1) at 35 °C. $[S]_0 = 1.8 \times 10^{-2}$ M, $[[Fe^{II}(N_4Py)(CH_3CN)](ClO_4)_2]_0 = 1.8 \times 10^{-3}$ M, $[H_2O_2]_0 = 1.8 \times 10^{-2}$ M, $[NH_4OH]_0 = 1.8 \times 10^{-2}$ M.

Computational methods

Starting geometries were constructed in Spartan 06 [1] as follows. The aminoacids and their degradation products were built by hand. For the N_4Py complexes the crystal structure for $N_4PyFe^{2+}MeCN$ [2] was used and the MeCN ligand was replaced by oxygen. For the porphyrin (P) equivalents, the starting models were built in Spartan using a porphyrin iron, with oxygen and ACC as axial ligands. Separately, another model was built using tetraphenylporphyrin instead of porphyrin and partitioned for QM/MM calculations with the four phenyl rings in the MM region and the rest of the model optimized by DFT.

All computations were performed in Gaussian 09 using the M06L functional and the 6-31G(d,p) basis set [3], or M06L/6-31G(d,p)//UFF in the case of the QM/MM calculations. Test runs showed no significant differences for the QM/MM models compared to the smaller models so they were not used further because of increased computational cost. The M06L functional was employed due to the fact that is has been designed for transition metal systems, thermochemistry and reaction barriers and was tested against suitable benchmarks [4]. Solvent effects were accounted for by using the CPCM solvation model as employed in Gaussian 09 using water [3]. All geometries were confirmed as stationary points by vibrational analysis. Preliminary calculations showed that the lowest energy spin states are S=1 for the Fe(IV)O models and S=3/2 for the Fe(V)O models so only these were used further. Also, in the case of the porphyrins models, the binding of the aminoacid to iron is preferred through the carboxyl oxygen compared to the nitrogen, so this mode of binding was used further. Scans were performed along the relevant coordinates for the reaction paths, followed by a transition state search on the maximum points of the scan. Transition states were confirmed by IRC calculations. Thermochemistry information was extracted from the vibrational analysis and all values given contain ZPE, thermal corrections and entropies (298.15K). Single point energy calculations were further performed by using the larger 6-311++G(d,p) basis set on all atoms except for Fe, for which the 6-311++G(2df,p) basis set was employed The given free energies contain electronic energies with the higher basis set, solvent corrections and dispersion corrections (calculated with the DFT-D3 software [5]). Spin densities were obtained from Mulliken population analysis.

Results of scans along the relevant reaction coordinates

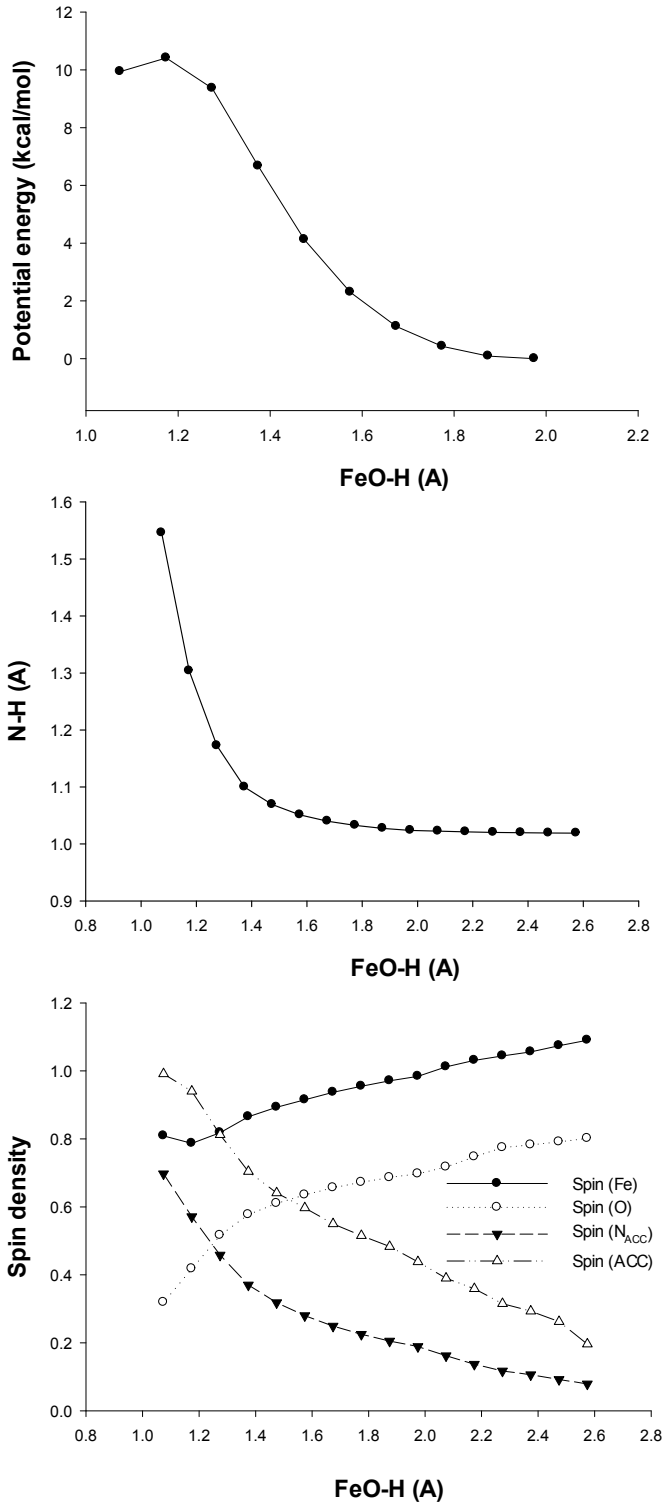

Figure S8. [Fe(IV)(O)(N_4Py)] barrier for hydrogen atom abstraction from the nitrogen of ACC; N-H bond length along the reaction coordinate; evolution of spin densities on ACC nitrogen, the whole ACC, Fe and ferryl O along the reaction coordinate

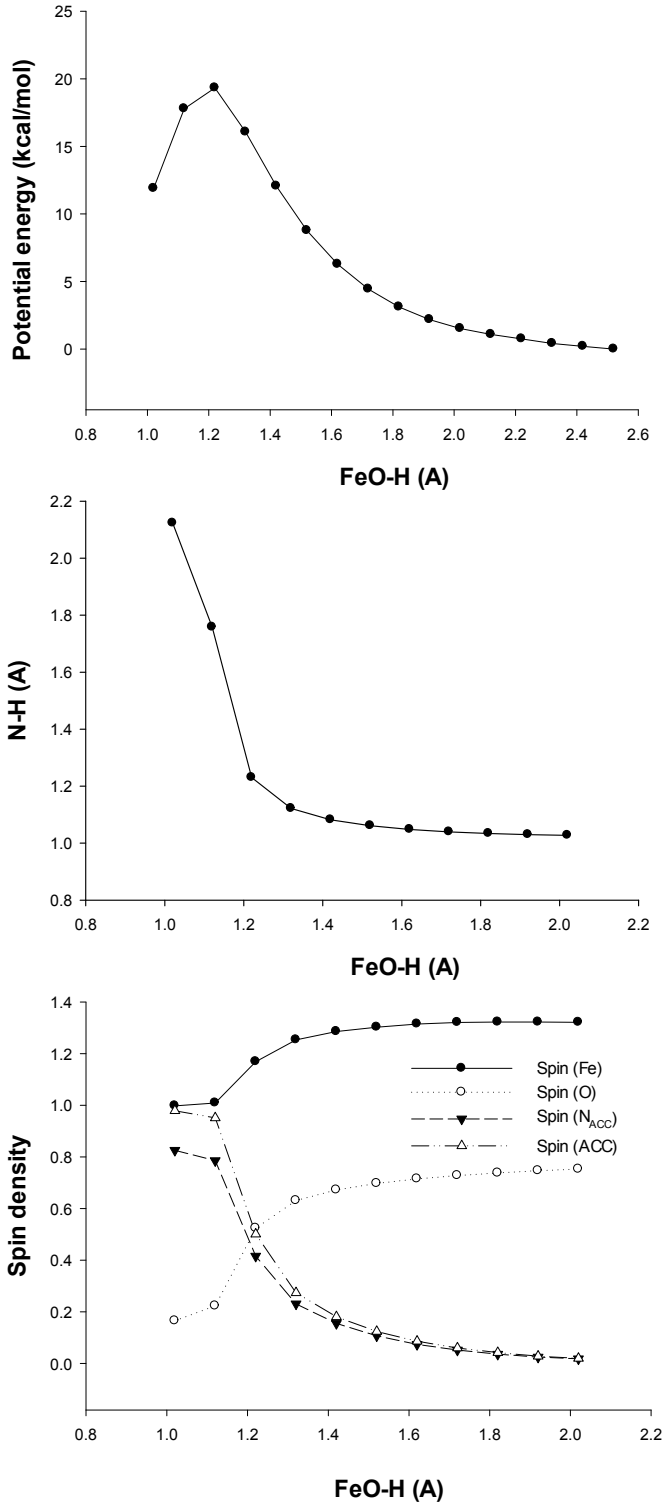

Figure S9. [Fe(IV)(O)(P)(ACC)] barrier for hydrogen atom abstraction from the nitrogen of ACC; N-H bond length along the reaction coordinate; evolution of spin densities on ACC nitrogen, the whole ACC, Fe and ferryl O along the reaction coordinate.

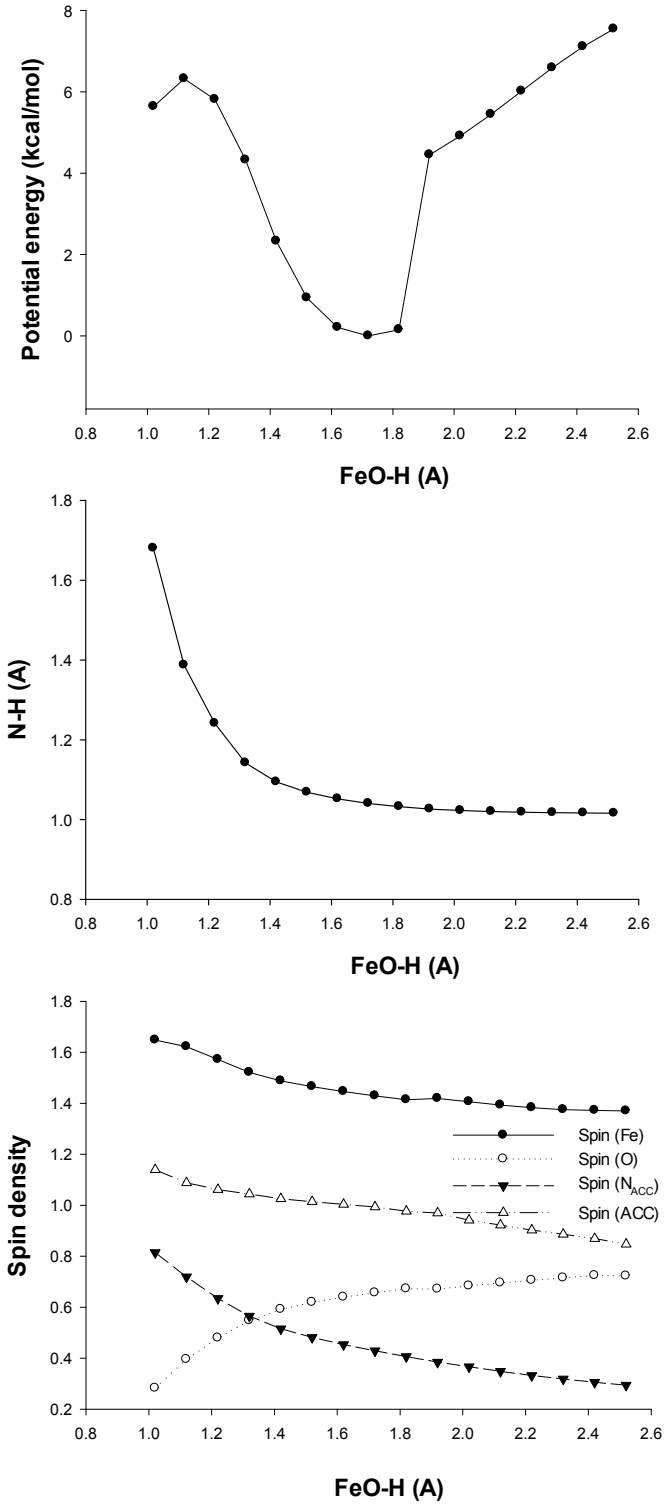

Figure S10. [Fe(V)(O)(P$^{\cdot+}$)(ACC)] barrier for hydrogen atom abstraction from the nitrogen of ACC; N-H bond length along the reaction coordinate; evolution of spin densities on ACC nitrogen, the whole ACC, Fe and ferryl O along the reaction coordinate.

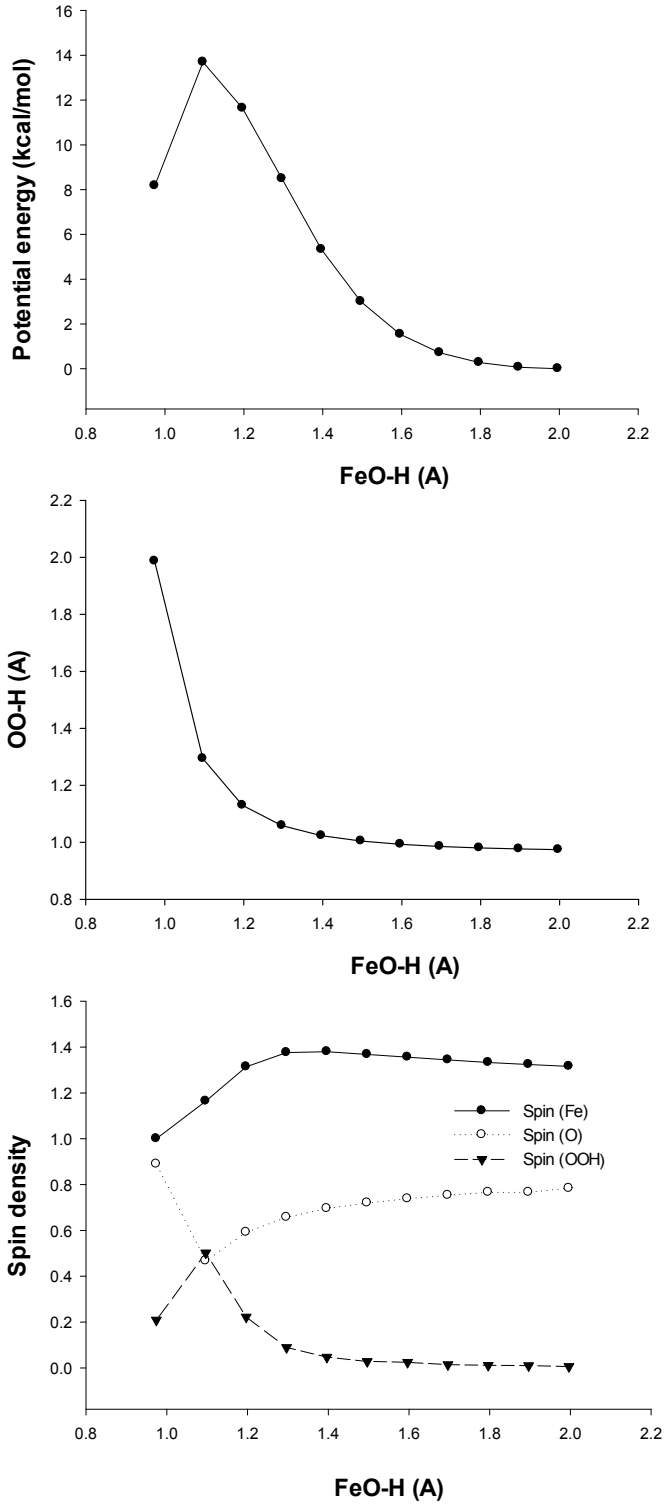

Figure S11. [Fe(IV)(O)(N_4Py)] barrier for hydrogen atom abstraction from H_2O_2; OO-H bond length along the reaction coordinate; evolution of spin densities on Fe, ferryl O and substrate along the reaction coordinate.

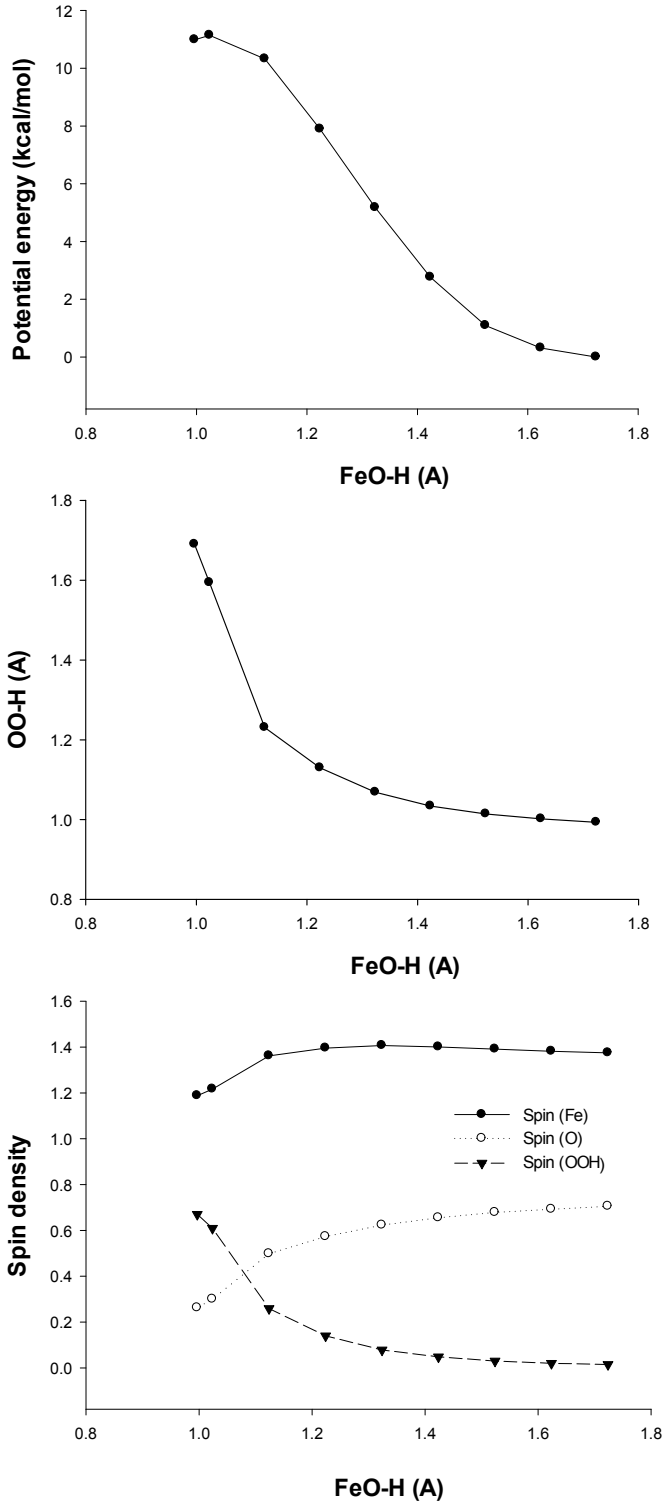

Figure S12. [Fe(IV)(O)(P)(ACC)] barrier for hydrogen atom abstraction from H_2O_2; OO-H bond length along the reaction coordinate; evolution of spin densities on Fe, ferryl O and substrate along the reaction coordinate.

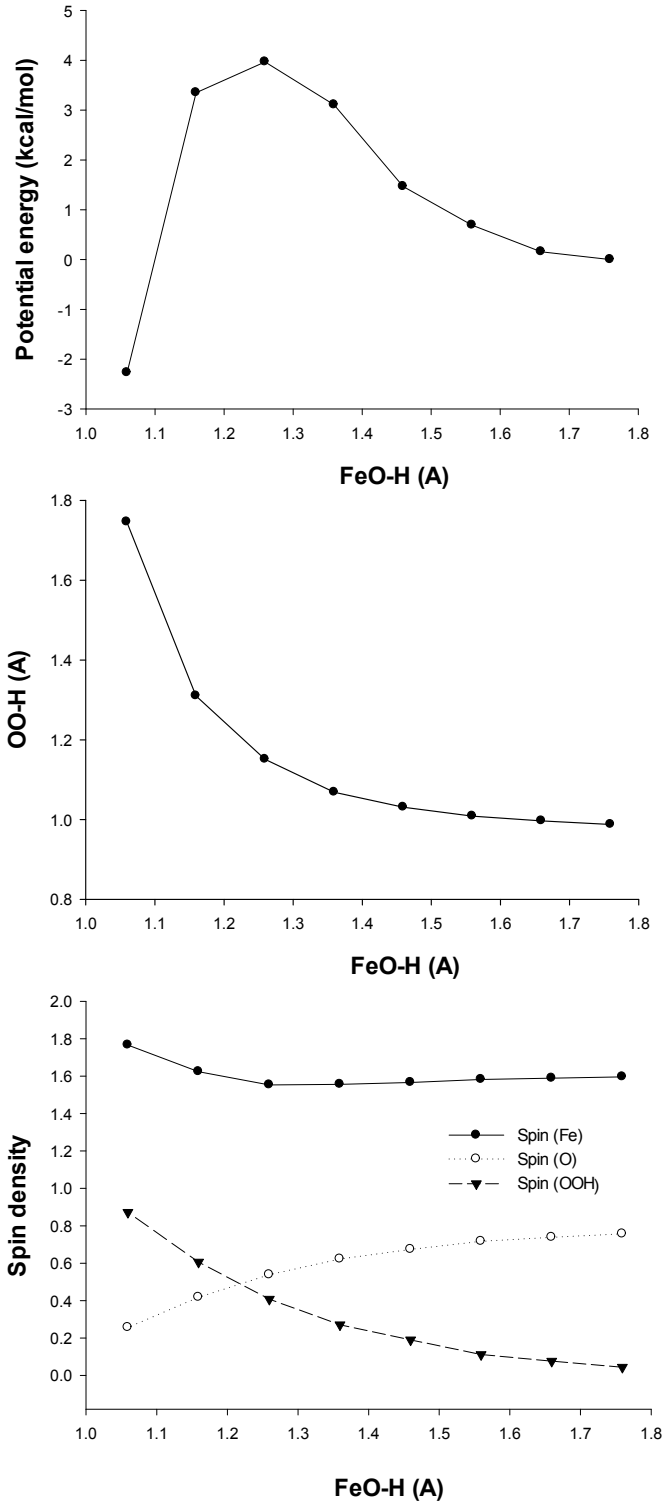

Figure S13. [Fe(V)(O)($P^{\cdot+}$)(ACC)] barrier for hydrogen atom abstraction from H_2O_2; OO-H bond length along the reaction coordinate; evolution of spin densities on Fe, ferryl O and substrate along the reaction coordinate.

Cartesian coordinates, absolute energies and imaginary frequencies

[Fe(IV)(O)(N_4Py)]
E(SCF)= -2501.12184540
No imaginary frequencies

	X	Y	Z
Fe	-0.06294	-9.5E-05	-0.67179
N	0.116124	-0.00011	1.399573
N	-1.43275	1.376671	-0.31283
N	-1.43283	-1.37673	-0.31283
N	1.376722	-1.35535	-0.49441
N	1.376506	1.355416	-0.49436
C	-0.51532	1.242197	1.926809
H	-0.94114	1.067753	2.92035
H	0.266509	1.999157	2.059801
C	-1.55127	1.773425	0.974443
C	-2.53365	2.675589	1.3601
H	-2.61259	2.975171	2.40049
C	-3.39953	3.187892	0.398726
H	-4.17283	3.89461	0.681446
C	-3.26194	2.780185	-0.92504
H	-3.91617	3.156345	-1.70303
C	-2.27126	1.865419	-1.2457
H	-2.11262	1.494733	-2.2543
C	-0.51512	-1.24254	1.926731
H	0.266794	-1.99942	2.059655
H	-0.94093	-1.06823	2.920306
C	-1.5511	-1.77377	0.974397
C	-2.53336	-2.67606	1.360027
H	-2.6121	-2.9759	2.400359
C	-3.39945	-3.18815	0.398708
H	-4.17264	-3.89498	0.681433
C	-3.26217	-2.78008	-0.92497
H	-3.91657	-3.15602	-1.70292
C	-2.27154	-1.86525	-1.24562
H	-2.11308	-1.49438	-2.25418
C	1.622916	0.000011	1.445057
H	2.018973	0.000029	2.468021
C	2.071793	-1.21177	0.65834
C	3.113883	-2.05938	0.992463
H	3.651086	-1.92655	1.926292
C	3.451423	-3.07863	0.100578
H	4.265175	-3.75776	0.332651
C	2.73874	-3.21257	-1.08682
H	2.982159	-3.98731	-1.8047

C	1.696983	-2.3325	-1.35492
H	1.104737	-2.37612	-2.26381
C	2.071598	1.211907	0.658385
C	3.11348	2.059738	0.992584
H	3.650711	1.926959	1.926405
C	3.450768	3.079155	0.100795
H	4.264363	3.758458	0.332928
C	2.73804	3.213047	-1.08658
H	2.98125	3.987924	-1.80438
C	1.696503	2.332739	-1.35476
H	1.104248	2.376307	-2.26365
O	-0.20474	-0.00015	-2.29387

[Fe(IV)(O)(N_4Py)]+ACC, TS1
E(SCF)= -2862.55792882
i647.55

	X	**Y**	**Z**
Fe	0.508486	0.111027	-0.19466
N	1.88033	-0.02198	1.317983
N	1.110834	1.996025	-0.28007
N	-0.72667	0.620624	1.239631
N	0.19693	-1.77848	0.30296
N	2.041385	-0.50616	-1.25919
C	2.813101	1.130062	1.199103
H	3.225262	1.404246	2.177028
H	3.663924	0.817917	0.582387
C	2.139555	2.305411	0.538373
C	2.571464	3.614934	0.695802
H	3.397575	3.838402	1.36401
C	1.928643	4.625791	-0.01436
H	2.247436	5.657395	0.095344
C	0.872462	4.296594	-0.85722
H	0.344957	5.057246	-1.42151
C	0.483141	2.968358	-0.96002
H	-0.33602	2.619015	-1.58507
C	1.153697	-0.05122	2.619353
H	1.08945	-1.09361	2.952707
H	1.727825	0.479235	3.387537
C	-0.23883	0.509436	2.495425
C	-1.0193	0.81725	3.599621
H	-0.59985	0.729527	4.597479
C	-2.34294	1.206389	3.406799
H	-2.97466	1.428486	4.260669
C	-2.84495	1.29402	2.114142
H	-3.87905	1.533929	1.894598
C	-1.99814	1.013593	1.051438

H	-2.3225	1.086604	0.01726
C	2.464141	-1.35475	0.905984
H	3.265107	-1.69773	1.574784
C	1.29937	-2.32017	0.879157
C	1.314032	-3.6056	1.389905
H	2.216881	-4.00215	1.844818
C	0.139702	-4.35878	1.324466
H	0.117047	-5.36892	1.720769
C	-0.99984	-3.78324	0.777553
H	-1.94664	-4.31104	0.740574
C	-0.94391	-2.48596	0.274901
H	-1.84585	-1.99615	-0.10623
C	2.941922	-1.1864	-0.51488
C	4.106516	-1.70066	-1.06023
H	4.812225	-2.23969	-0.43583
C	4.338221	-1.51016	-2.42202
H	5.240766	-1.90067	-2.88068
C	3.401513	-0.81814	-3.18417
H	3.548709	-0.66242	-4.2467
C	2.25758	-0.32449	-2.57022
H	1.473552	0.213357	-3.09519
O	-0.55112	0.345783	-1.56303
C	-3.75422	1.220529	-2.37109
C	-4.74872	0.209188	-2.83118
C	-3.61535	-0.18752	-1.87259
H	-4.67043	-0.17307	-3.84304
H	-4.10454	1.964056	-1.66331
H	-5.74015	0.231713	-2.39129
C	-4.14964	-0.53955	-0.42095
O	-3.74695	-1.62328	0.048368
O	-4.86187	0.359589	0.064124
H	-3.00764	1.544603	-3.09082
N	-2.53558	-0.93232	-2.3147
H	-1.36471	-0.35499	-1.95352
H	-2.70567	-1.9021	-2.03623

[Fe(III)(OH)(N_4Py)]

E(SCF)= -2501.75200274

No imaginary frequencies

	X	**Y**	**Z**
Fe	-0.04704	-0.00913	-0.62769
N	0.144063	-0.01911	1.38206
N	-1.47641	1.311353	-0.30649
N	-1.3792	-1.42102	-0.29321
N	1.446335	-1.3168	-0.52266
N	1.320222	1.407452	-0.46854
C	-0.54507	1.190152	1.92861

H	-0.95689	0.980321	2.920979
H	0.204518	1.977494	2.069327
C	-1.60902	1.686214	0.985846
C	-2.6264	2.539018	1.391106
H	-2.71513	2.820577	2.435835
C	-3.51729	3.027224	0.4392
H	-4.31949	3.695465	0.734724
C	-3.36686	2.644841	-0.89022
H	-4.04014	3.004895	-1.65953
C	-2.33801	1.777108	-1.22708
H	-2.16526	1.427876	-2.24115
C	-0.42177	-1.29502	1.91597
H	0.392517	-2.02347	2.001477
H	-0.81102	-1.14877	2.928606
C	-1.47201	-1.838	0.989889
C	-2.43743	-2.75397	1.383031
H	-2.49449	-3.06901	2.420101
C	-3.3188	-3.25777	0.430457
H	-4.08054	-3.97542	0.716756
C	-3.21448	-2.82376	-0.88782
H	-3.8856	-3.18857	-1.65676
C	-2.2376	-1.89573	-1.21471
H	-2.10916	-1.49783	-2.21704
C	1.656614	0.043422	1.428602
H	2.048512	0.036841	2.453039
C	2.150426	-1.13839	0.623391
C	3.223403	-1.94364	0.966248
H	3.760461	-1.77489	1.894441
C	3.587814	-2.97266	0.098288
H	4.425684	-3.61893	0.337475
C	2.856572	-3.16648	-1.06932
H	3.105034	-3.96122	-1.76333
C	1.786251	-2.32406	-1.34312
H	1.172609	-2.44655	-2.23177
C	2.044359	1.28761	0.667718
C	3.035452	2.193908	1.003786
H	3.597451	2.077726	1.925073
C	3.285498	3.252931	0.129444
H	4.056337	3.980214	0.362007
C	2.536757	3.369217	-1.03828
H	2.709408	4.179048	-1.73763
C	1.550058	2.428796	-1.30725
H	0.926589	2.459313	-2.19567
O	-0.25989	0.086819	-2.40098
H	0.444943	-0.31123	-2.93009

[Fe(IV)(O)(P)(ACC)]
E(SCF)= -2688.42011323
No imaginary frequencies.

	X	Y	Z
N	-0.90033	2.021645	-0.35223
Fe	0.063782	0.296839	-0.78967
N	1.001206	-1.46541	-1.04006
N	1.819766	1.171727	-0.35036
N	-1.72374	-0.62883	-1.03503
C	-1.93279	-1.94827	-1.31493
C	-2.96059	-0.05741	-0.95038
C	-2.24847	2.236308	-0.37419
C	-0.33144	3.212437	-0.00402
C	2.024456	2.477187	-0.00722
C	3.056666	0.600852	-0.42635
C	2.34849	-1.68153	-1.02427
C	0.427451	-2.66987	-1.3306
C	1.440745	-3.67797	-1.49864
C	-0.93473	-2.90242	-1.45469
C	-3.34175	-2.21969	-1.42029
C	-3.20991	1.274669	-0.65242
C	2.637138	-3.05984	-1.3132
C	3.309982	-0.72163	-0.75247
C	4.073713	1.569218	-0.11502
C	-2.54115	3.60438	-0.03948
C	1.029499	3.430173	0.157596
C	3.431037	2.737194	0.150667
C	-3.98225	-1.04131	-1.19358
C	-1.34661	4.212993	0.19111
H	-3.53853	4.024572	0.014631
H	-5.04668	-0.83912	-1.17928
H	5.136392	1.35908	-0.09803
H	-3.76697	-3.19387	-1.63079
H	-1.15133	5.240602	0.474002
H	3.633549	-3.48355	-1.35168
H	3.850896	3.696284	0.430198
H	1.240335	-4.7181	-1.72613
H	4.349557	-1.03861	-0.77221
H	1.343179	4.43295	0.437784
H	-4.2502	1.589405	-0.62106
H	-1.2463	-3.91972	-1.67899
C	-1.71653	-1.8012	2.925114
C	-1.58934	-0.46333	3.578893
C	-0.34972	-1.22867	3.217932
H	-1.82689	-0.39719	4.637409
H	-2.02369	-1.824	1.883719

H	-1.80766	0.411181	2.974206
C	0.45761	-0.78342	2.00863
O	1.654303	-1.09373	1.960351
O	-0.24444	-0.13704	1.145428
O	0.19454	0.678442	-2.38713
H	-2.02349	-2.63862	3.544398
N	0.386627	-1.83265	4.308706
H	1.112956	-2.37876	3.845059
H	0.927551	-1.08033	4.732621

[Fe(IV)(O)(P)(ACC)]+ACC, TS3
E(SCF)=-3049.5698690
i1393.86

	X	**Y**	**Z**
N	0.524295	-1.65689	0.348615
Fe	-0.30625	0.021559	-0.34349
N	-1.22276	1.699447	-0.97494
N	-1.6428	-1.08033	-1.41519
N	0.902059	1.108769	0.833356
C	0.970287	2.471495	0.89725
C	1.940801	0.644413	1.593768
C	1.615432	-1.75472	1.167321
C	0.204464	-2.94329	-0.00034
C	-1.696	-2.44337	-1.4967
C	-2.67151	-0.61367	-2.18538
C	-2.30861	1.796927	-1.79916
C	-0.88401	2.981494	-0.64826
C	-1.76804	3.915354	-1.29402
C	0.139746	3.346183	0.210037
C	2.059404	2.876615	1.743689
C	2.273238	-0.68992	1.76259
C	-2.66077	3.178109	-2.00568
C	-2.98817	0.728546	-2.36232
C	-3.39097	-1.70773	-2.77245
C	2.002789	-3.12987	1.335882
C	-0.8317	-3.31389	-0.84002
C	-2.77945	-2.8507	-2.34313
C	2.669332	1.738364	2.17265
C	1.116349	-3.86983	0.62081
H	2.875505	-3.44187	1.894015
H	3.568021	1.619912	2.765034
H	-4.25233	-1.60123	-3.42289
H	2.326904	3.907763	1.945531
H	1.079851	-4.94548	0.487178
H	-3.49017	3.515438	-2.61769
H	-3.03159	-3.88123	-2.56807
H	-1.70566	4.992777	-1.18866

H	-3.84256	0.959488	-2.99553
H	-0.97564	-4.37918	-1.01015
H	3.171766	-0.91875	2.325698
H	0.303247	4.410584	0.365668
C	-3.53588	-1.63515	2.636
C	-4.293	-1.28127	1.395293
C	-3.71061	-0.19326	2.264499
H	-5.37465	-1.38176	1.419118
H	-2.53928	-2.04646	2.51349
H	-3.80641	-1.45954	0.440622
C	-2.53043	0.573602	1.673248
O	-2.56112	1.809602	1.756875
O	-1.65099	-0.18989	1.137314
O	0.829316	0.121883	-1.64916
H	-4.10884	-1.98938	3.490091
N	-4.64987	0.579188	3.058397
H	-4.15688	0.798681	3.92375
H	-4.65116	1.488183	2.591257
C	4.74154	0.901741	-2.04381
C	3.738526	1.472883	-1.12173
C	4.049622	-0.01667	-1.01739
H	2.746015	1.713344	-1.49502
H	5.789382	1.098073	-1.83134
H	4.115736	2.051227	-0.28382
C	4.940117	-0.46503	0.166517
O	4.785424	-1.66486	0.525585
O	5.715726	0.404873	0.634591
H	4.465175	0.734565	-3.08171
N	3.087634	-0.90768	-1.52435
H	3.177226	-1.73064	-0.91744
H	1.867126	-0.42953	-1.59638

[Fe(III)(OH)(P)(ACC)]
E(SCF)= -2689.04909694
No imaginary frequencies

	X	**Y**	**Z**
N	-1.28851	1.694747	-0.53034
Fe	-0.05922	0.106775	-0.76612
N	1.168794	-1.47959	-0.88381
N	1.525362	1.322597	-0.68283
N	-1.65289	-1.11399	-0.84032
C	-1.6436	-2.47937	-0.90336
C	-2.97053	-0.75535	-0.77519
C	-2.6546	1.67866	-0.5169
C	-0.92342	3.000202	-0.3579
C	1.520172	2.679123	-0.47954
C	2.846676	0.971088	-0.78571

C	2.53176	-1.46229	-0.97396
C	0.802598	-2.79485	-0.9502
C	1.964343	-3.6305	-1.06651
C	-0.50395	-3.26581	-0.94592
C	-2.98861	-2.99651	-0.89959
C	-3.4418	0.540247	-0.63854
C	3.042085	-2.79788	-1.09078
C	3.31798	-0.31896	-0.94996
C	3.688621	2.130948	-0.66379
C	-3.16701	3.006898	-0.33417
C	0.386948	3.461416	-0.32473
C	2.864603	3.192139	-0.46426
C	-3.81582	-1.92228	-0.82366
C	-2.0869	3.831607	-0.231
H	-4.21978	3.259649	-0.28841
H	-4.89869	-1.8994	-0.78929
H	4.770981	2.110608	-0.70896
H	-3.24325	-4.04892	-0.94278
H	-2.0647	4.905195	-0.0851
H	4.093042	-3.04974	-1.1688
H	3.121717	4.234399	-0.31573
H	1.940282	-4.71203	-1.12841
H	4.39459	-0.45177	-1.02334
H	0.535437	4.528107	-0.17332
H	-4.52018	0.675691	-0.59837
H	-0.64226	-4.34344	-0.99427
C	-1.06763	-1.34754	3.55457
C	-1.17933	0.125756	3.778252
C	0.159305	-0.47345	3.454535
H	-1.31788	0.469498	4.799776
H	-1.45966	-1.74578	2.623283
H	-1.646	0.719357	2.998349
C	0.731618	-0.26523	2.062267
O	1.957978	-0.29451	1.919888
O	-0.18794	-0.11579	1.169451
O	-0.11441	0.262233	-2.58273
H	-1.11933	-1.99467	4.424999
N	1.110233	-0.56303	4.541702
H	1.886546	-1.10127	4.157288
H	1.522481	0.364326	4.631204
H	0.639254	0.814991	-2.82642

[Fe(IV)(O)(P$^{\cdot+}$)(ACC)]

E(SCF)= -2688.30994541

No imaginary frequencies

	X	**Y**	**Z**
N	-1.66475	1.364675	-0.42516

Fe	-0.21632	0.065984	-0.8316
N	1.249398	-1.23831	-1.01645
N	1.114239	1.522857	-0.82825
N	-1.52604	-1.41057	-0.61289
C	-1.24004	-2.72656	-0.38738
C	-2.88665	-1.31201	-0.68483
C	-3.00909	1.143632	-0.52289
C	-1.5089	2.66341	-0.03435
C	0.931441	2.801898	-0.3799
C	2.384304	1.460509	-1.32712
C	2.504767	-0.98539	-1.49456
C	1.199336	-2.57571	-0.73472
C	2.470256	-3.18107	-1.02339
C	0.043864	-3.26255	-0.38525
C	-2.45799	-3.48365	-0.30515
C	-3.58322	-0.10887	-0.71118
C	3.266326	-2.20209	-1.53073
C	3.013704	0.286134	-1.71756
C	3.021326	2.741691	-1.20152
C	-3.72657	2.346759	-0.20413
C	-0.28512	3.320645	0.043709
C	2.133756	3.563663	-0.57969
C	-3.47932	-2.61057	-0.52458
C	-2.79542	3.280896	0.13292
H	-4.80459	2.440022	-0.205
H	-4.54298	-2.80892	-0.54087
H	4.033604	2.958729	-1.51621
H	-2.50976	-4.54988	-0.12771
H	-2.95098	4.305808	0.443694
H	4.292664	-2.27478	-1.86545
H	2.256712	4.602372	-0.30211
H	2.698652	-4.22901	-0.87961
H	4.034809	0.360838	-2.07971
H	-0.29994	4.362128	0.351935
H	-4.6677	-0.16096	-0.74447
H	0.135367	-4.33103	-0.2112
C	-0.31663	-1.15219	3.742381
C	-0.4116	0.328998	3.913618
C	0.840581	-0.27236	3.336477
H	-0.3237	0.72514	4.919796
H	-0.89488	-1.60566	2.944306
H	-1.05459	0.875022	3.231743
C	1.069257	-0.10995	1.835452
O	2.228624	-0.05432	1.419687
O	-0.0293	-0.06282	1.161411
O	-0.44419	0.166348	-2.45746

H	-0.15851	-1.75366	4.631218
N	1.991286	-0.293	4.187717
H	2.647017	-0.97379	3.815215
H	2.472878	0.597147	4.098246

[Fe(IV)(O)(P$^{\cdot+}$)(ACC)]+ACC, TS5
E(SCF)= -3049.5936874
i474.3

	X	**Y**	**Z**
N	-0.5212	1.658375	0.370116
Fe	0.387172	0.056835	-0.44068
N	1.374287	-1.53293	-1.15874
N	1.718021	1.28261	-1.35812
N	-0.83275	-1.15072	0.587827
C	-0.89496	-2.51409	0.49668
C	-1.83896	-0.78101	1.440579
C	-1.57921	1.652787	1.238981
C	-0.26728	2.973705	0.086678
C	1.695893	2.649038	-1.36819
C	2.815442	0.910478	-2.08227
C	2.511257	-1.52773	-1.91967
C	1.018461	-2.84428	-1.01033
C	1.948485	-3.68959	-1.70239
C	-0.0538	-3.30588	-0.26545
C	-1.96224	-3.01555	1.317159
C	-2.17703	0.520363	1.76943
C	2.884216	-2.87261	-2.25682
C	3.199061	-0.39819	-2.33466
C	3.50858	2.073237	-2.56109
C	-2.0171	2.99453	1.49705
C	0.758758	3.439528	-0.71982
C	2.806954	3.154776	-2.12412
C	-2.54822	-1.94036	1.906154
C	-1.20218	3.81492	0.78121
H	-2.87295	3.240466	2.11068
H	-3.41773	-1.8977	2.547834
H	4.411564	2.047267	-3.15845
H	-2.22195	-4.06312	1.406738
H	-1.22051	4.895557	0.711344
H	3.751521	-3.13715	-2.84893
H	3.013178	4.20623	-2.28283
H	1.88684	-4.77027	-1.73325
H	4.095916	-0.55086	-2.92906
H	0.852207	4.516355	-0.83168
H	-3.0352	0.665001	2.417298
H	-0.21918	-4.37931	-0.23904
C	3.17716	1.261364	3.084346

C	4.153929	0.909596	2.012102
C	3.29503	-0.16755	2.632919
H	5.206054	0.881778	2.276934
H	2.277756	1.793832	2.793285
H	3.914141	1.203919	0.994828
C	2.202498	-0.74863	1.759073
O	1.999861	-1.96168	1.774517
O	1.601357	0.160319	1.050832
O	-0.67318	0.084704	-1.7875
H	3.572398	1.479639	4.071998
N	3.956061	-1.07788	3.537558
H	3.254226	-1.37684	4.211818
H	4.119071	-1.92649	2.998026

[Fe(IV)(OH)(P)(ACC)]

E(SCF)= -2688.96167485

No imaginary frequencies

	X	**Y**	**Z**
N	-1.43309	1.688629	-0.2658
Fe	-0.09113	0.242976	-0.69953
N	1.245318	-1.20476	-1.032
N	1.386494	1.578388	-0.49916
N	-1.57864	-1.0832	-0.91277
C	-1.45858	-2.43438	-1.1087
C	-2.92296	-0.82663	-0.83479
C	-2.79671	1.56756	-0.28603
C	-1.16895	2.97719	0.115197
C	1.279027	2.878402	-0.06783
C	2.725272	1.352112	-0.6989
C	2.598929	-1.04897	-1.18365
C	0.991568	-2.53721	-1.22072
C	2.216613	-3.24105	-1.47029
C	-0.26319	-3.12188	-1.23263
C	-2.75664	-3.04044	-1.1686
C	-3.4953	0.405974	-0.57009
C	3.211466	-2.31503	-1.46169
C	3.29037	0.141878	-1.05969
C	3.470553	2.54148	-0.41968
C	-3.40654	2.813378	0.081587
C	0.095103	3.532251	0.230071
C	2.576186	3.484004	-0.01467
C	-3.6655	-2.04078	-1.00871
C	-2.39587	3.685765	0.340327
H	-4.47468	2.978343	0.13843
H	-4.7457	-2.10438	-0.99276
H	4.546024	2.622562	-0.50629
H	-2.93186	-4.09802	-1.31708

H	-2.45649	4.72103	0.64977
H	4.272612	-2.45915	-1.61731
H	2.761291	4.505309	0.291955
H	2.283989	-4.30716	-1.64362
H	4.366747	0.112994	-1.19648
H	0.162045	4.567086	0.551147
H	-4.57938	0.455738	-0.53992
H	-0.31555	-4.19514	-1.38693
C	-0.83948	-2.13579	2.981772
C	-1.08187	-0.82553	3.645862
C	0.310914	-1.17258	3.18767
H	-1.22908	-0.82542	4.720639
H	-1.20357	-2.26794	1.967214
H	-1.61094	-0.06201	3.085942
C	0.855069	-0.50387	1.952841
O	2.057044	-0.34839	1.793975
O	-0.10361	-0.1419	1.121253
O	-0.19162	0.633936	-2.44368
H	-0.81309	-3.02329	3.60432
N	1.257501	-1.51613	4.210195
H	2.030397	-2.00217	3.763146
H	1.673091	-0.65586	4.557498
H	0.178929	1.515194	-2.58957

[Fe(IV)(O)(N_4Py)]+H2O2 TS2

E(SCF)= -2652.64615860

I1305.60,i15.86

	X	**Y**	**Z**
Fe	-0.01512	0.040073	0.39316
N	0.447549	0.383273	-1.56639
N	-1.70823	-0.7004	-0.34862
N	-0.83471	1.831391	0.27606
N	1.793195	0.847157	0.637363
N	0.923735	-1.65967	-0.00598
C	-0.45431	-0.44788	-2.41566
H	-0.63835	0.043794	-3.37645
H	0.060517	-1.38764	-2.64603
C	-1.74093	-0.75518	-1.70345
C	-2.884	-1.14014	-2.38948
H	-2.87706	-1.16646	-3.47468
C	-4.02213	-1.49272	-1.67059
H	-4.92481	-1.79831	-2.18947
C	-3.9805	-1.44136	-0.28271
H	-4.84091	-1.70774	0.319922
C	-2.81382	-1.03175	0.347185
H	-2.73651	-0.98475	1.431815
C	0.317115	1.844231	-1.84689

H	1.303969	2.307224	-1.73041
H	0.019996	2.01007	-2.88738
C	-0.6406	2.49128	-0.88785
C	-1.24031	3.720242	-1.12679
H	-1.07341	4.228889	-2.07109
C	-2.04595	4.283211	-0.14185
H	-2.52268	5.243371	-0.30923
C	-2.23202	3.600308	1.056296
H	-2.85048	4.006046	1.848609
C	-1.61668	2.370325	1.230102
H	-1.72039	1.782427	2.137037
C	1.876412	-0.10638	-1.52896
H	2.372284	-0.0314	-2.50413
C	2.570205	0.706698	-0.45995
C	3.861391	1.202999	-0.51488
H	4.461384	1.079479	-1.41098
C	4.362975	1.86046	0.609625
H	5.371255	2.261383	0.600981
C	3.560879	1.993464	1.738613
H	3.925457	2.490388	2.630388
C	2.271285	1.474427	1.720238
H	1.596688	1.527418	2.569348
C	1.81000	-1.53014	-1.02162
C	2.576663	-2.59442	-1.46309
H	3.27588	-2.46446	-2.28301
C	2.423663	-3.82795	-0.82854
H	3.010883	-4.68179	-1.14987
C	1.511479	-3.95228	0.214119
H	1.371198	-4.89728	0.72612
C	0.767987	-2.84445	0.603835
H	0.038352	-2.87831	1.41061
O	-0.19154	-0.14055	2.085129
O	-1.89931	-1.35477	3.260437
H	-0.96703	-0.70498	2.612823
O	-1.62485	-2.69705	3.056331
H	-1.32106	-2.99063	3.934549

[Fe(IV)(O)(P)(ACC)]+H_2O_2, TS4

E(SCF)= -2839.95598317

i594.76, i10.37

	X	**Y**	**Z**
N	-2.01617	0.553913	-1.00454
Fe	-0.06737	0.217436	-0.5642
N	1.818864	-0.13856	-0.01494
N	0.152923	2.167687	-0.12616
N	-0.33994	-1.76433	-0.85908
C	0.576785	-2.76197	-0.68243

C	-1.49431	-2.37635	-1.25978
C	-2.93525	-0.37563	-1.3973
C	-2.67428	1.749525	-0.97923
C	-0.79273	3.148287	-0.21915
C	1.309577	2.790287	0.245204
C	2.750711	0.797871	0.340842
C	2.455041	-1.34784	0.039797
C	3.827607	-1.17045	0.427725
C	1.881284	-2.57464	-0.25689
C	-0.00911	-4.03826	-0.98733
C	-2.69743	-1.7363	-1.52082
C	4.011202	0.167561	0.610899
C	2.525887	2.159667	0.447203
C	1.088786	4.200672	0.404508
C	-4.20879	0.250796	-1.63728
C	-2.1111	2.96094	-0.60844
C	-0.2226	4.424027	0.121673
C	-1.29813	-3.79764	-1.34887
C	-4.04644	1.574816	-1.37598
H	-5.10101	-0.27398	-1.95745
H	-2.0625	-4.50504	-1.64753
H	1.850288	4.911454	0.701905
H	0.513911	-4.98483	-0.92606
H	-4.7762	2.373351	-1.43628
H	4.908687	0.694472	0.91092
H	-0.77128	5.358136	0.13173
H	4.541141	-1.97658	0.548207
H	3.368419	2.780885	0.738571
H	-2.75221	3.838433	-0.63213
H	-3.53193	-2.35938	-1.83266
H	2.510873	-3.45566	-0.16639
C	-1.11303	-2.29122	3.065461
C	-2.23181	-1.32613	3.283648
C	-0.81454	-0.86543	3.466939
H	-2.8203	-1.43692	4.190151
H	-0.88234	-2.57352	2.042652
H	-2.75394	-0.95517	2.40759
C	-0.18191	0.012125	2.402355
O	0.760719	0.741086	2.72257
O	-0.72582	-0.13851	1.238955
O	0.367889	0.48163	-2.21573
H	-0.93884	-3.043	3.829017
N	-0.36963	-0.65901	4.827572
H	0.634571	-0.50173	4.748431
H	-0.70916	0.261664	5.101153
O	3.451562	-0.02587	-2.80559

H	3.758521	-0.37104	-1.94862
O	2.302814	-0.80271	-3.04086
H	1.212802	-0.04614	-2.5853

[Fe(IV)(O)($P^{\cdot+}$)(ACC)]+H_2O_2 TS

E(SCF)= -2839.84837687

i1172.02

	X	**Y**	**Z**
N	0.604665	1.921512	-0.0622
Fe	-0.05653	0.107938	-0.62212
N	-0.7688	-1.72061	-0.99032
N	1.694052	-0.69832	-0.09002
N	-1.84606	0.899525	-1.01686
C	-3.00352	0.223271	-1.27442
C	-2.15242	2.231257	-1.11644
C	-0.0175	3.118566	-0.26002
C	1.769716	2.199823	0.594303
C	2.719013	-0.08354	0.559218
C	2.114014	-1.9815	-0.34766
C	-0.04367	-2.86693	-1.12278
C	-2.07067	-2.06031	-1.24552
C	-2.1698	-3.46808	-1.51515
C	-3.11937	-1.16138	-1.34098
C	-4.06959	1.146363	-1.5432
C	-1.28923	3.269164	-0.80158
C	-0.9052	-3.9641	-1.46446
C	1.320772	-2.97911	-0.87773
C	3.454026	-2.16087	0.130189
C	0.78092	4.187678	0.273072
C	2.742406	1.263201	0.91273
C	3.821033	-0.99176	0.720064
C	-3.53502	2.394816	-1.46749
C	1.883684	3.613046	0.824283
H	0.507554	5.234157	0.242718
H	-4.02434	3.349658	-1.60798
H	4.015419	-3.08246	0.05127
H	-5.08747	0.860047	-1.77332
H	2.712434	4.09054	1.330314
H	-0.57102	-4.98168	-1.61894
H	4.751263	-0.74839	1.217693
H	-3.09283	-3.98831	-1.73503
H	1.77568	-3.95376	-1.02611
H	3.627745	1.624117	1.429658
H	-1.66967	4.281233	-0.90645
H	-4.10343	-1.56662	-1.55895
C	-2.18105	0.299204	3.558811
C	-0.82917	0.82427	3.909401

C	-0.98973	-0.61427	3.47024
H	-0.59948	0.966484	4.959936
H	-2.62211	0.624442	2.622724
H	-0.35398	1.507404	3.212415
C	-0.4493	-0.95957	2.094042
O	0.136127	-2.02793	1.925479
O	-0.66177	-0.022	1.220868
O	0.501804	0.306238	-2.19997
H	-2.86891	0.098163	4.37347
N	-0.87057	-1.61219	4.493496
H	-1.44738	-2.40656	4.230493
H	0.078968	-1.97355	4.458681
O	2.863612	-0.00061	-2.55947
H	1.717814	0.190881	-2.4275
O	3.414007	1.211293	-2.10581
H	4.318292	0.927036	-1.90101

ACC deprotonated radical

E(SCF)= -360.58063605

No imaginary frequencies

	X	**Y**	**Z**
C	1.458275	-0.5184	-0.73529
C	1.458582	-0.51818	0.735268
C	0.419452	0.347981	0.000042
H	2.242919	0.021512	1.257925
H	1.014487	-1.3768	-1.23122
H	1.015016	-1.37646	1.231634
C	-1.03317	-0.20092	0.00005
O	-1.91522	0.694633	0.000092
O	-1.14415	-1.45115	-1.2E-05
H	2.24257	0.021079	-1.25825
N	0.639932	1.720052	-0.00013
H	-0.33839	2.059542	-0.00028

ACC deprotonated radical ring opening, TS7

E(SCF)= -360.56944602

i595.33

	X	**Y**	**Z**
C	1.495921	-0.39984	-0.64561
C	1.590164	-0.57138	0.809314
C	0.345419	0.456073	-0.2035
H	2.185474	0.111816	1.403848
H	1.167834	-1.28841	-1.18289
H	0.992948	-1.33778	1.287117
C	-1.03596	-0.24149	-0.03328
O	-1.97945	0.556928	0.182845
O	-1.03449	-1.49335	-0.13702

H	2.310842	0.150841	-1.11741
N	0.504586	1.762021	-0.07131
H	-0.45089	2.060639	0.180362

ACC deprotonated radical ring opening, product

E(SCF)= -360.58459429

No imaginary frequencies

	X	**Y**	**Z**
C	1.49099	0.180684	-0.54081
C	2.112932	-0.58361	0.568947
C	0.097684	0.65338	-0.15627
H	2.562345	-0.04133	1.400496
H	1.379069	-0.4776	-1.41177
H	1.724894	-1.5788	0.766332
C	-0.99781	-0.44269	-0.02945
O	-2.13532	0.001879	0.260764
O	-0.60922	-1.61934	-0.23527
H	2.092919	1.056728	-0.81398
N	-0.12745	1.891403	0.070409
H	-1.13365	1.894336	0.307588

Cyclopropanonimine

E(SCF)= -171.99593768

No imaginary frequencies

	X	**Y**	**Z**
C	-0.90111	-0.75563	0.000049
C	-0.87337	0.78749	0.000044
C	0.352109	-0.01838	-0.00014
H	-1.1687	1.30113	0.911854
H	-1.21713	-1.25622	-0.91173
H	-1.16916	1.3011	-0.91164
H	-1.21694	-1.2567	0.911615
N	1.610112	-0.13776	0.000025
H	2.035314	0.794073	0.000005

ACB deprotonated radical

E(SCF)= -399.88372504

No imaginary frequencies

	X	**Y**	**Z**
C	-0.17466	-0.2774	-0.28525
C	-1.21036	0.7724	-0.71705
C	-0.94256	-0.38098	1.087826
C	-2.14436	0.272395	0.393664
H	-2.72027	1.014761	0.964587
H	-2.83926	-0.48716	0.016493
H	-1.06798	-1.38793	1.502636
H	-0.49574	0.265845	1.852156

H	-1.56749	0.697376	-1.75038
H	-0.81993	1.776916	-0.52803
C	1.35114	0.242952	0.047652
O	1.526713	1.457619	-0.14785
O	2.069993	-0.66396	0.50205
N	-0.14545	-1.42311	-1.07312
H	0.479948	-2.04349	-0.54031

ACB deprotonated radical ring opening, TS8

E(SCF)= -399.86660078

i633.04

	X	**Y**	**Z**
C	0.058063	0.471265	-0.34036
C	1.207305	-0.30154	-0.98198
C	1.0607	-0.21289	1.291358
C	2.128732	-0.30097	0.235311
H	2.812936	-1.16138	0.321658
H	2.736897	0.61131	0.243522
H	1.13778	0.503969	2.106788
H	0.517318	-1.12616	1.523544
H	1.614351	0.174834	-1.88311
H	0.852638	-1.30927	-1.2168
C	-1.31595	-0.28914	-0.03502
O	-1.33678	-1.48899	-0.38333
O	-2.17405	0.43626	0.507828
N	0.054977	1.782253	-0.45122
H	-0.80324	2.05245	0.051157

ACB deprotonated radical ring opening, product

E(SCF)= -399.89451212

No imaginary frequencies

	X	**Y**	**Z**
C	0.335472	0.740452	0.176793
C	-0.98811	0.577438	0.88028
C	-1.96885	-1.06793	-0.75639
C	-2.12237	0.251524	-0.09708
H	-3.09229	0.308289	0.432819
H	-2.17076	1.061561	-0.84647
H	-2.6853	-1.39639	-1.50774
H	-1.10903	-1.6896	-0.51366
H	-1.23028	1.51028	1.404555
H	-0.89484	-0.23763	1.605862
C	1.289476	-0.48658	0.087006
O	0.857741	-1.55453	0.595361
O	2.378336	-0.24952	-0.48852
N	0.636367	1.87104	-0.34501
H	1.56561	1.689209	-0.75872

ACB deprotonated radical ring closing, TS9
E(SCF)= -399.86796993
i548.06

	X	Y	Z
C	0.153633	-0.00666	-0.38936
C	-0.76585	1.162957	-0.24998
C	-2.0893	-0.78817	0.58743
C	-2.18327	0.596807	0.027083
H	-2.74097	1.285545	0.682113
H	-2.74635	0.550082	-0.91432
H	-2.87449	-1.5004	0.342828
H	-1.68534	-0.89644	1.593821
H	-0.78462	1.815628	-1.13361
H	-0.37911	1.791691	0.562059
C	1.618604	0.04035	0.05007
O	2.074903	1.187762	0.281457
O	2.169997	-1.09125	0.126261
N	-0.47982	-1.1395	-0.59776
H	0.207533	-1.87344	-0.36177

ACB deprotonated radical ring closing, product
E(SCF)= -399.90694778
No imaginary frequencies

	X	Y	Z
C	0.140473	0.103046	-0.30575
C	-0.77424	1.254475	-0.04281
C	-1.86882	-0.8516	0.335331
C	-2.16803	0.60382	-0.0294
H	-2.88233	1.0766	0.65596
H	-2.60716	0.636345	-1.03481
H	-2.66156	-1.54673	0.020715
H	-1.77071	-0.94419	1.436342
H	-0.70274	2.066186	-0.78226
H	-0.5308	1.726646	0.923633
C	1.597546	0.019669	-0.01106
O	2.190727	1.120045	0.154632
O	2.050551	-1.16642	0.059738
N	-0.61788	-1.08289	-0.36617
H	-0.01139	-1.84015	-0.04931

Cyclobutanonimine
E(SCF)=-211.32752136
No imaginary frequencies

	X	Y	Z
C	-0.64353	-0.02423	0.053597
C	0.431041	-1.08416	0.102522

C	0.386357	1.092817	0.108666
C	1.467246	0.027169	-0.17338
H	2.351241	0.046195	0.467282
H	1.795716	0.038293	-1.21525
H	0.270054	1.915647	-0.60413
H	0.466473	1.525452	1.112471
H	0.341742	-1.90445	-0.61477
H	0.529134	-1.51999	1.102862
N	-1.89689	-0.13748	-0.09411
H	-2.32282	0.791619	-0.13813

ACP deprotonated radical

E(SCF)= -439.22197291

No imaginary frequencies

	X	**Y**	**Z**
C	-1.97485	-0.45387	-0.35845
C	-0.97213	0.388618	-1.1652
C	0.197633	0.687818	-0.2245
C	-0.49107	0.733846	1.165017
C	-1.48338	-0.42152	1.106989
H	-2.99295	-0.04808	-0.43859
H	-2.00987	-1.48399	-0.72543
H	-1.41761	1.343208	-1.4788
H	-0.62028	-0.13302	-2.05866
H	0.24539	0.654896	1.971242
H	-1.01612	1.697221	1.26587
H	-0.95677	-1.35529	1.33254
H	-2.30493	-0.32543	1.829071
C	1.201081	-0.63426	-0.08202
O	0.79536	-1.63795	-0.69721
O	2.177026	-0.43021	0.659463
N	0.961874	1.796043	-0.59575
H	1.697249	1.819687	0.123918

ACP deprotonated radical ring opening, TS10

E(SCF)= -439.19371885

i514.34

	X	**Y**	**Z**
C	2.070084	-0.26142	-0.77905
C	0.755436	-0.7315	-1.29951
C	-0.32928	-0.45651	0.574585
C	0.825769	0.228366	1.277841
C	1.800491	0.819543	0.269274
H	2.611276	-1.09694	-0.3112
H	2.725814	0.126655	-1.57787
H	0.602693	-1.78666	-1.50861
H	0.198734	-0.05624	-1.94404

H	0.418534	1.021578	1.914993
H	1.32896	-0.50967	1.918845
H	1.304981	1.672988	-0.20853
H	2.72856	1.176689	0.738474
C	-1.39203	0.469774	-0.14271
O	-1.14515	1.696513	-0.0665
O	-2.34169	-0.14851	-0.66964
N	-0.69384	-1.64507	1.001253
H	-1.55074	-1.82651	0.455623

ACP deprotonated radical ring opening, product

E(SCF)= -439.20454693

No imaginary frequencies

	X	**Y**	**Z**
C	2.214134	-0.24272	0.555066
C	1.241363	-0.94628	1.427489
C	-0.5469	0.827742	-0.10072
C	0.623897	0.970719	-1.03772
C	1.714789	-0.09076	-0.88353
H	2.451395	0.74744	0.974727
H	3.179579	-0.7853	0.535136
H	1.09676	-0.6633	2.465879
H	0.568395	-1.68299	0.998056
H	0.244337	0.909514	-2.06635
H	1.052936	1.972258	-0.89143
H	1.300058	-1.04533	-1.2231
H	2.559304	0.164233	-1.54129
C	-1.44816	-0.43373	-0.22301
O	-1.06577	-1.29607	-1.05681
O	-2.44408	-0.43429	0.539605
N	-0.78995	1.757923	0.747919
H	-1.63899	1.411049	1.225111

Cyclopentanonimine

E(SCF)= -250.66695807

No imaginary frequencies

	X	**Y**	**Z**
C	-1.39634	-0.70439	-0.25419
C	-0.01732	-1.22505	0.141679
C	0.899597	-0.02816	0.007985
C	0.034254	1.21793	-0.10889
C	-1.38033	0.747301	0.228623
H	-1.50592	-0.72789	-1.3461
H	-2.22122	-1.2884	0.162883
H	0.344964	-2.07805	-0.43662
H	-0.01724	-1.53844	1.194603
H	0.404069	2.036355	0.51706

H	0.081881	1.573237	-1.14763
H	-1.53222	0.776228	1.314849
H	-2.16325	1.363579	-0.22184
N	2.168496	-0.13633	-0.00551
H	2.590313	0.791914	-0.0899

References

[1] SPARTAN '06 for Windows, *Wavefunction Inc.*, 18401 Von Karman Avenue, Suite 370 Irvine, CA 92612.

[2] J.-U. Rohde, S. Torelli, X. Shan, M.H. Lim, E.J. Klinker, J. Kaizer, K. Chen, W. Nam, L. Que, Journal of the American Chemical Society, 126 (2004) 16750-16761.

[3] Gaussian 09, Revision C.01, 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.J. 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. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, 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, D.J. Fox, Gaussian, Inc., Wallingford CT, 2009.

[4] Y. Zhao, D. Truhlar, Theor Chem Account, 120 (2008) 215-241.

[5] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, J. Chem. Phys., 132 (2010).