SUPPORTING INFORMATION

A quantum mechanical study of Compound I (Cpd I) of microperoxidase-5 (MP5) and its reactivity toward styrene.

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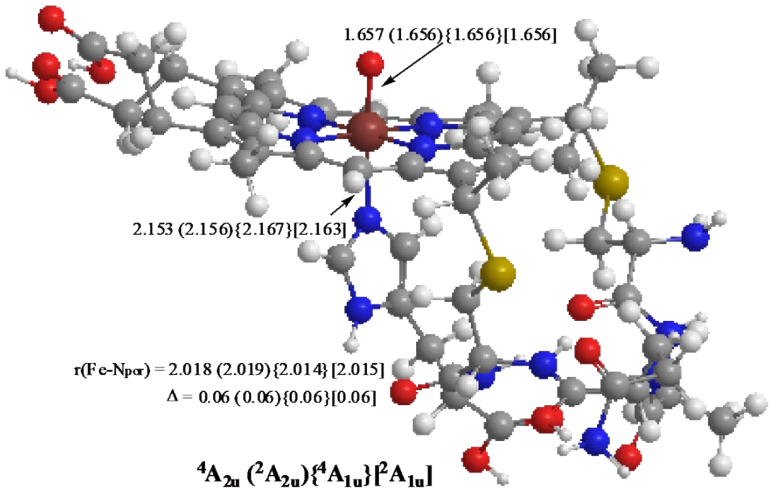
Figure S1: LACVP optimized geometries of Cpd I of MP5 in $^{4,2}A_{2u}$ and $^{4,2}A_{1u}$ states. The distances are in Å.

MP5 CpdI



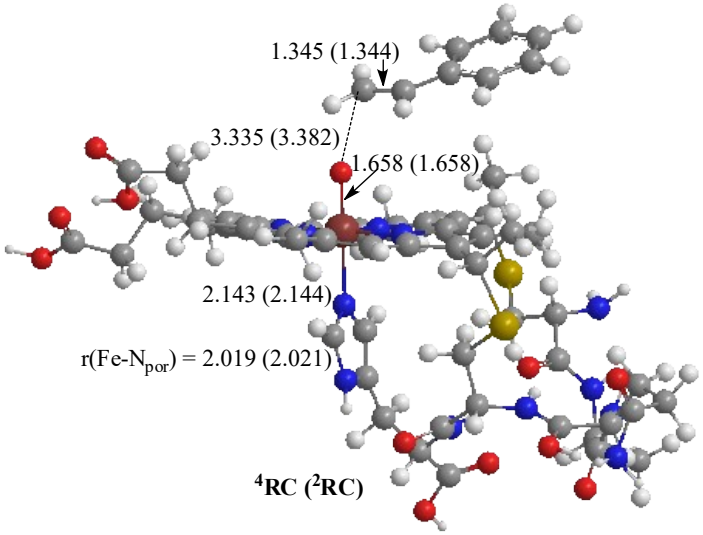
Orbitals:

$^4A_{2u}$: $\delta^{\uparrow\downarrow}\ \pi^*_{xz}{}^{\uparrow}\ \pi^*_{yz}{}^{\uparrow}\ a_{2u}{}^{\uparrow}\ a_{1u}{}^{\uparrow\downarrow}\ \sigma^*_{z^2}{}^{0}\ \sigma^*_{xy}{}^{0}$
$^2A_{2u}$: $\delta^{\uparrow\downarrow}\ \pi^*_{xz}{}^{\uparrow}\ \pi^*_{yz}{}^{\uparrow}\ a_{2u}{}^{\downarrow}\ a_{1u}{}^{\uparrow\downarrow}\ \sigma^*_{z^2}{}^{0}\ \sigma^*_{xy}{}^{0}$
$^4A_{1u}$: $\delta^{\uparrow\downarrow}\ \pi^*_{xz}{}^{\uparrow}\ \pi^*_{yz}{}^{\uparrow}\ a_{1u}{}^{\uparrow}\ a_{2u}{}^{\uparrow\downarrow}\ \sigma^*_{z^2}{}^{0}\ \sigma^*_{xy}{}^{0}$
$^2A_{1u}$: $\delta^{\uparrow\downarrow}\ \pi^*_{xz}{}^{\uparrow}\ \pi^*_{yz}{}^{\uparrow}\ a_{1u}{}^{\downarrow}\ a_{2u}{}^{\uparrow\downarrow}\ \sigma^*_{z^2}{}^{0}\ \sigma^*_{xy}{}^{0}$

Table S1: Relative energies in kcal/mol, group spin densities and group charges of different states of Cpd I of MP5. A_{2u} and A_{1u} represents sum of spin densities and charges on atoms involved in a_{2u} orbital and a_{1u} respectively.

	ΔE	Spin Density						Charges					
		ρ_{Fe}	ρ_O	ρ_{por}		ρ_{Im}	ρ_{rest}	Q_{Fe}	Q_O	Q_{por}		Q_{Im}	Q_{rest}
				A_{2u}	A_{1u}					A_{2u}	A_{1u}		
$^2A_{2u}$	0.00	1.02	1.05	-0.87	-0.17	-0.03	-0.01	0.65	-0.25	-2.36	2.59	0.22	1.16
$^2A_{1u}$	1.09	1.02	1.05	-0.39	-0.64	-0.02	-0.02	0.65	-0.25	-2.43	2.67	0.22	1.16
$^4A_{2u}$	0.71	0.99	1.05	1.29	-0.35	0.01	0.01	0.64	-0.25	-2.33	2.58	0.23	1.14
$^4A_{1u}$	2.40	1.02	1.04	-0.16	1.09	-0.01	0.02	0.65	-0.26	-2.50	2.72	0.21	1.18

Figure S2 LACVP optimized geometries of reactant complex of Cpd I of MP5 with styrene, ^{4,2}RC. The distances are in Å.



Orbitals: **^{4}RC:** $\delta^{\uparrow\downarrow}\ \pi^*_{xz}{}^{\uparrow}\ \pi^*_{yz}{}^{\uparrow}\ a_{2u}{}^{\uparrow}\ a_{1u}{}^{\uparrow\downarrow}\ \sigma^*_{z^2}{}^{0}\ \sigma^*_{xy}{}^{0}$
^{2}RC: $\delta^{\uparrow\downarrow}\ \pi^*_{xz}{}^{\uparrow}\ \pi^*_{yz}{}^{\uparrow}\ a_{2u}{}^{\downarrow}\ a_{1u}{}^{\uparrow\downarrow}\ \sigma^*_{z^2}{}^{0}\ \sigma^*_{xy}{}^{0}$

Table S2: Relative energies in kcal/mol, group spin densities and group charges of different states of reactant complex of Cpd I of MP5 with styrene, ^{4,2}RC.

		Spin Density						Charges					
	ΔE^a	ρ_{Fe}	ρ_O	ρ_{por}	ρ_{Im}	ρ_{rest}	ρ_{St}	Q_{Fe}	Q_O	Q_{por}	Q_{Im}	Q_{rest}	Q_{St}
^{4}RC	0.00	1.01	1.04	0.89	0.01	0.00	0.06	0.64	-0.27	0.19	0.23	1.12	0.08
^{2}RC	0.23	1.03	1.04	-1.03	-0.03	-0.01	-0.01	0.64	-0.26	0.23	0.23	1.14	0.03

[a] with respect to ^{4}RC.

Figure S3 Variation of LACVP energy with C-O bond distance for C=O bond activation scan for styrene by Cpd I of MP5.

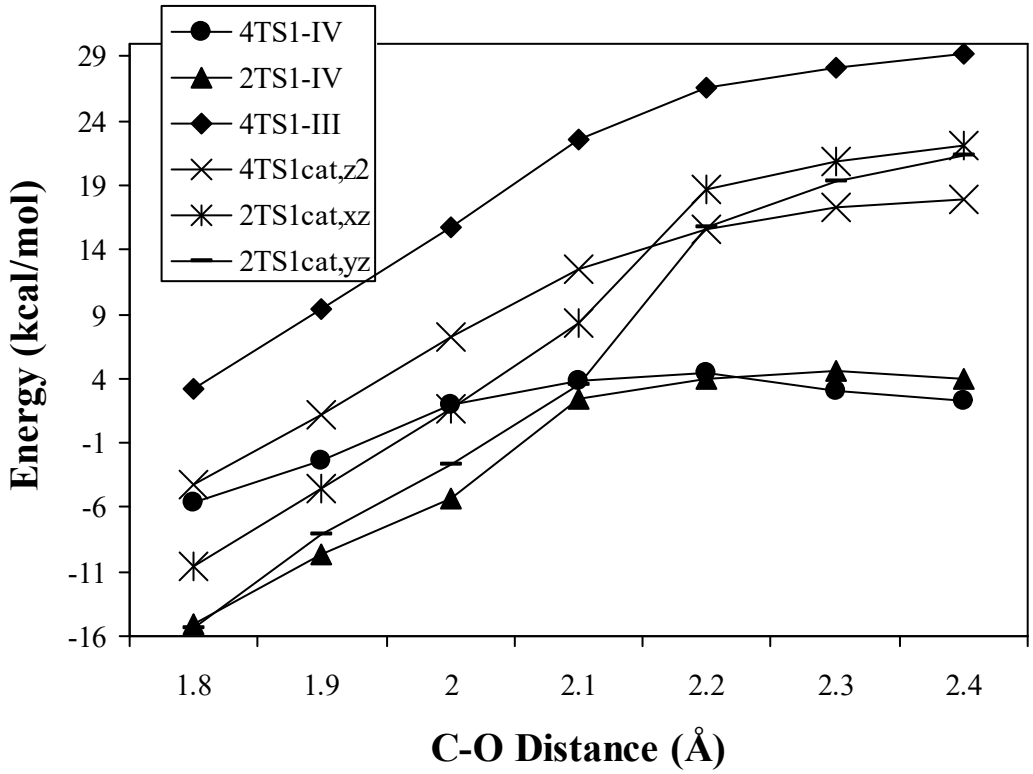
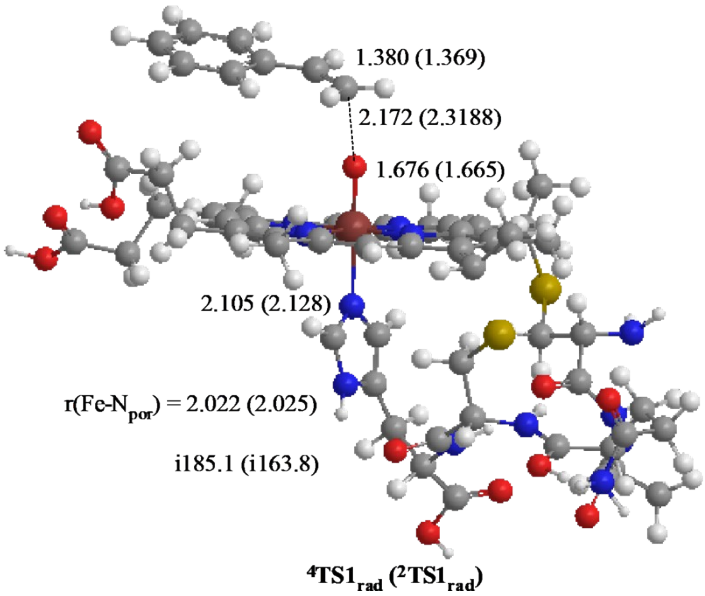


Figure S4 LACVP optimized geometries of C=O bond activation transition states, $^{4,2}TS1_{rad}$. The distances are in Å and frequencies are in cm^{-1}.



Orbitals: $^4\mathbf{TS1_{rad}}$: $\delta^{\uparrow\downarrow}\,\pi^{*\uparrow}_{xz}\,\pi^{*\uparrow}_{yz}\,(a_{2u}+\phi_{st})^{\uparrow}\,a_{1u}^{\uparrow\downarrow}\,\sigma^{*0}_{z^2}\,\sigma^{*0}_{xy}$

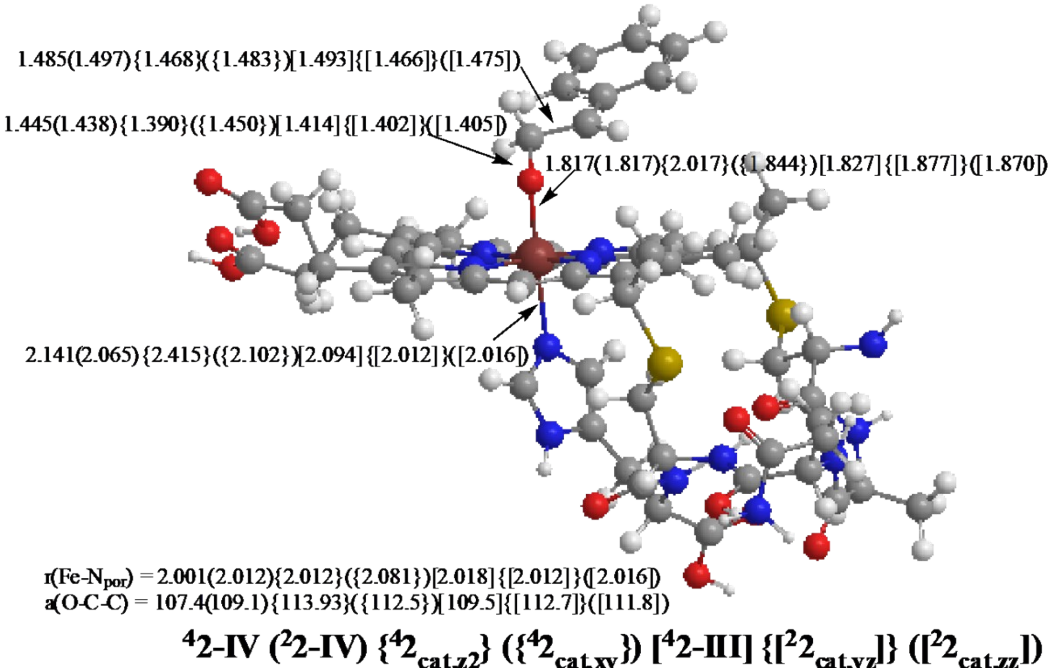
$^2\mathbf{TS1_{rad}}$: $\delta^{\uparrow\downarrow}\,\pi^{*\uparrow}_{xz}\,\pi^{*\uparrow}_{yz}\,(a_{2u}+\phi_{st})^{\downarrow}\,a_{1u}^{\uparrow\downarrow}\,\sigma^{*0}_{z^2}\,\sigma^{*0}_{xy}$

Table S3: Relative energies in kcal/mol, group spin densities and group charges of bond activation transition states, $^{4,2}TS1_{rad}$.

		Spin Density						Charges					
	ΔE^a	ρ_{Fe}	ρ_O	ρ_{por}	ρ_{Im}	ρ_{rest}	ρ_{St}	Q_{Fe}	Q_O	Q_{por}	Q_{Im}	Q_{rest}	Q_{St}
^{4}TS1	4.06	1.25	0.92	0.22	0.02	0.00	0.59	0.67	-0.33	-0.09	0.26	0.96	0.54
^{2}TS1	3.94	1.12	0.85	-0.50	-0.03	0.00	-0.44	0.65	-0.30	-0.02	0.24	0.98	0.45

[a] Energy is kcal/mol with respect to ^{4}RC.

Figure S5 LACVP optimized geometries of different electromers of intermediate, $^{4,2}2$. The distances are in Å.



Orbitals:

^{4}2 : $\delta^{\uparrow\downarrow}\ \pi^*_{xz}{}^{\uparrow}\ \pi^*_{yz}{}^{\uparrow}\ \phi_{st}{}^{\uparrow}\ a_{2u}{}^{\uparrow\downarrow}\ a_{1u}{}^{\uparrow\downarrow}\ \sigma^*_{z^2}{}^{0}\ \sigma^*_{xy}{}^{0}$

^{4}2-III : : $\delta^{\uparrow\downarrow}\ \pi^*_{xz}{}^{\uparrow\downarrow}\ \pi^*_{yz}{}^{\uparrow}\ \phi_{st}{}^{\uparrow}\ a_{2u}{}^{\uparrow}\ a_{1u}{}^{\uparrow\downarrow}\ \sigma^*_{z^2}{}^{0}\ \sigma^*_{xy}{}^{0}$

^{4}2$_{cat,z2}$: $\delta^{\uparrow\downarrow}\ \pi^*_{xz}{}^{\uparrow}\ \pi^*_{yz}{}^{\uparrow}\ \sigma^*_{z^2}{}^{\uparrow}\ a_{2u}{}^{\uparrow\downarrow}\ a_{1u}{}^{\uparrow\downarrow}\ \phi_{st}{}^{0}\ \sigma^*_{xy}{}^{0}$

^{4}2$_{cat,xy}$: $\delta^{\uparrow\downarrow}\ \pi^*_{xz}{}^{\uparrow}\ \pi^*_{yz}{}^{\uparrow}\ \sigma^*_{xy}{}^{\uparrow}\ a_{2u}{}^{\uparrow\downarrow}\ a_{1u}{}^{\uparrow\downarrow}\ \phi_{st}{}^{0}\ \sigma^*_{z^2}{}^{0}$

^{2}2 : $\delta^{\uparrow\downarrow}\ \pi^*_{xz}{}^{\uparrow}\ \pi^*_{yz}{}^{\uparrow}\ \phi_{st}{}^{\downarrow}\ a_{2u}{}^{\uparrow\downarrow}a_{1u}{}^{\uparrow\downarrow}\ \sigma^*_{z^2}{}^{0}\ \sigma^*_{xy}{}^{0}$

^{2}2$_{cat,yz}$: $\delta^{\uparrow\downarrow}\ \pi^*_{xz}{}^{\uparrow\downarrow}\ \pi^*_{yz}{}^{\uparrow}\ \phi_{st}{}^{0}\ a_{2u}{}^{\uparrow\downarrow}\ a_{1u}{}^{\uparrow\downarrow}\ \sigma^*_{z^2}{}^{0}\ \sigma^*_{xy}{}^{0}$

^{2}2$_{cat,xz}$: $\delta^{\uparrow\downarrow}\ \pi^*_{xz}{}^{\uparrow}\ \pi^*_{yz}{}^{\uparrow\downarrow}\ \phi_{st}{}^{0}\ a_{2u}{}^{\uparrow\downarrow}a_{1u}{}^{\uparrow\downarrow}\ \sigma^*_{z^2}{}^{0}\ \sigma^*_{xy}{}^{0}$

Table S4: Relative energies in kcal/mol, group spin densities and group charges of of different electromers of intermediate, $^{4,2}2$.

		Spin Density						Charges					
	ΔE^a	ρ_{Fe}	ρ_O	ρ_{por}	ρ_{Im}	ρ_{rest}	ρ_{St}	Q_{Fe}	Q_O	Q_{por}	Q_{Im}	Q_{rest}	Q_{St}
^{4}2	-8.51	2.14	0.19	-0.07	0.02	0.00	0.72	0.81	-0.48	-0.19	0.25	1.00	0.61
^{4}2-III	-3.19	0.90	0.19	0.92	0.01	0.00	0.98	0.67	-0.49	0.18	0.23	1.06	0.33
^{4}2$_{Cat,z2}$	-12.09	2.72	0.16	-0.11	0.06	0.00	0.17	0.86	-0.54	-0.29	0.18	0.94	0.86
^{4}2$_{Cat,xy}$	3.04	2.92	-0.11	0.08	-0.03	0.00	0.13	0.81	-0.48	-0.35	0.25	0.90	0.88
^{2}2	-4.03	1.29	0.26	0.08	-0.01	0.01	-0.64	0.72	-0.46	-0.19	0.27	1.02	0.64
^{2}2 $_{Cat,yz}$	-18.40	0.99	0.06	-0.05	-0.01	0.00	0.01	0.69	-0.51	-0.28	0.25	0.90	0.94
^{2}2 $_{Cat,xz}$	-16.58	0.99	0.07	0.03	-0.01	0.00	-0.08	0.70	-0.52	-0.29	0.25	0.89	0.98

[a] with respect to ^{4}RC.

Figure S6 Variation of LACVP energy with O-C-C angle (ring closure) for rebound scan for styrene.

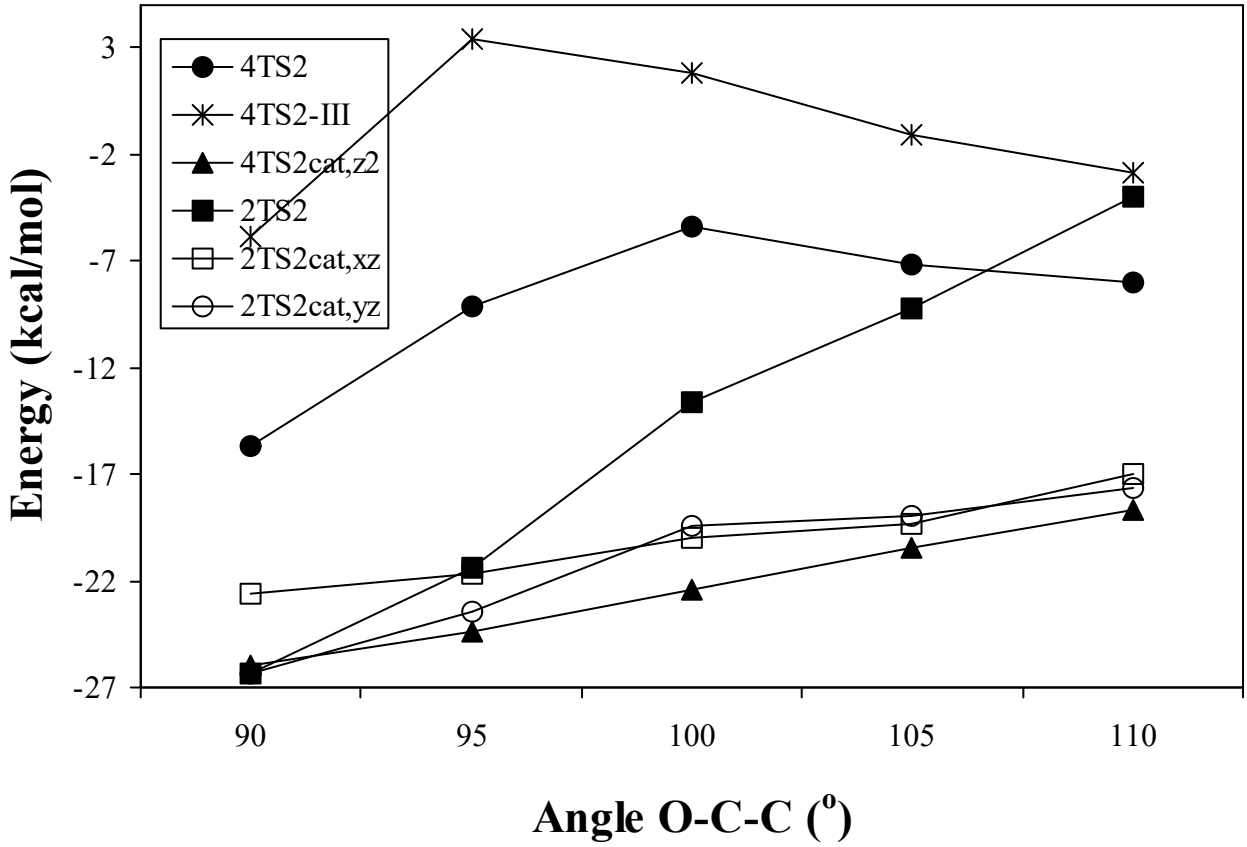
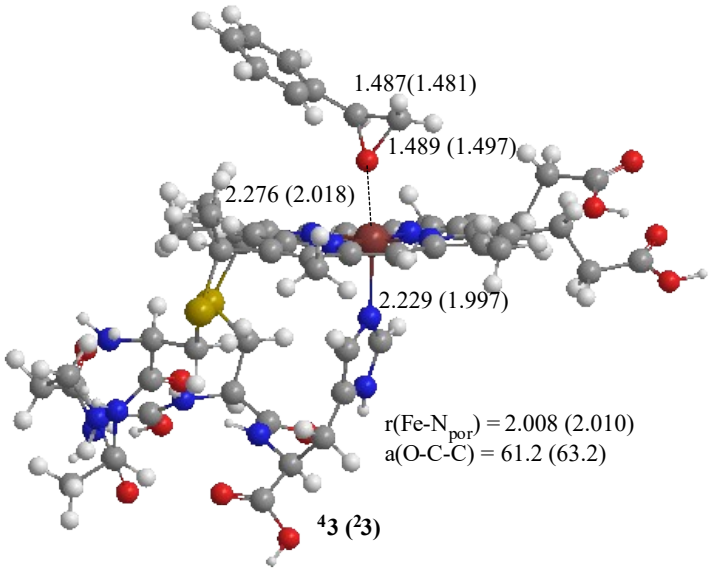


Figure S7 LACVP optimized geometries of styrene epoxide product, ^{4,2}3. The distances are in Å.



Orbitals ^{4}**3** : $\delta^{\uparrow\downarrow}\ \pi^*_{xz}{}^{\uparrow}\ \pi^*_{yz}{}^{\uparrow}\ \sigma^*_{z2}{}^{\uparrow}\ a_{2u}{}^{\uparrow\downarrow}\ a_{1u}{}^{\uparrow\downarrow}\ \phi_{st}{}^{0}\ \sigma^*_{xy}{}^{0}$

^{2}**3** : $\delta^{\uparrow\downarrow}\ \pi^*_{xz}{}^{\uparrow\downarrow}\ \pi^*_{yz}{}^{\uparrow}\ \phi_{st}{}^{0}\ a_{2u}{}^{\uparrow\downarrow}\ a_{1u}{}^{\uparrow\downarrow}\ \sigma^*_{z2}{}^{0}\ \sigma^*_{xy}{}^{0}$

Table S5: Relative energies in kcal/mol, group spin densities and group charges of of of styrene epoxide product, ^{4,2}3.

	ΔE^a	Spin Density						Charges					
		ρ_{Fe}	ρ_O	ρ_{por}	ρ_{Im}	ρ_{rest}	ρ_{St}	Q_{Fe}	Q_O	Q_{por}	Q_{Im}	Q_{rest}	Q_{St}
^{4}3	-30.56	2.85	0.02	0.01	0.10	0.00	0.03	0.94	-0.49	-0.29	0.20	1.01	0.65
^{2}3	-33.39	1.03	-0.01	-0.02	-0.01	0.00	0.00	0.78	-0.47	-0.31	0.28	0.99	0.72

[a] with respect to ^{4}RC.

Table S6: Relative energies in kcal/mol, group spin densities and group charges of LAC3P+*// LACVP species.

	ΔE^a	Spin Density						Charges					
		ρ_{Fe}	ρ_O	ρ_{por}		ρ_{Im}	ρ_{rest}	Q_{Fe}	Q_O	Q_{por}		Q_{Im}	Q_{rest}
				A_{2u}	A_{1u}					A_{2u}	A_{1u}		
$^4A_{2u}$	1.80	1.06	0.99	1.00	-0.06	0.00	0.01	0.57	-0.13	-0.78	0.96	0.26	1.12
$^2A_{2u}$	0.93	1.10	0.99	-0.64	-0.41	-0.02	-0.01	0.57	-0.12	-0.90	1.06	0.26	1.13
$^4A_{1u}$	1.61	1.07	0.99	-0.09	1.02	-0.01	0.02	0.59	-0.13	-0.98	1.11	0.25	1.17
$^2A_{1u}$	1.04	1.11	0.99	-0.32	-0.73	-0.03	-0.02	0.59	-0.14	-0.91	1.07	0.25	1.14
	ΔE^a	ρ_{Fe}	ρ_O	ρ_{por}	ρ_{Im}	ρ_{rest}	ρ_{St}	Q_{Fe}	Q_O	Q_{por}	Q_{Im}	Q_{rest}	Q_{St}
^{4}RC	0.00	2.92	0.00	-0.03	0.08	0.01	0.03	0.91	-0.03	-0.37	0.18	1.02	0.30
^{4}TS1	4.40	1.33	0.87	0.17	0.01	0.00	0.62	0.58	-0.12	-0.11	0.32	0.91	0.43
^{4}2	-15.01	2.26	0.14	-0.11	0.01	0.00	0.70	0.67	-0.14	-0.20	0.27	1.03	0.38
^{4}2-III	-7.06	-7.06	0.88	0.19	0.93	0.01	0.00	0.61	-0.16	0.14	0.22	1.09	0.09
^{4}2$_{Cat,z2}$	-20.66	2.80	0.13	-0.13	0.04	0.00	0.16	0.88	-0.28	-0.31	0.16	0.92	0.64
^{4}2$_{Cat,xy}$	12.56	3.13	-0.26	.08	-0.05	0.00	0.09	0.88	-0.19	-0.51	0.22	0.90	0.71
^{4}3	-44.61	2.92	0.00	-0.03	0.08	0.01	0.03	0.91	-0.03	-0.37	0.18	1.02	0.30
^{2}RC	-0.02	1.12	0.97	-1.05	-0.03	0.00	0.00	0.50	-0.11	0.25	0.24	1.13	-0.01
^{2}TS1	5.55	1.20	0.79	-0.50	-0.03	0.00	-0.48	0.60	-0.05	-0.15	0.26	0.98	0.38
^{2}2	-10.55	1.33	0.22	0.04	-0.01	0.01	-0.59	0.61	-0.15	-0.17	0.26	1.01	0.43
^{2}2$_{yz}$	-24.53	1.00	0.05	-0.06	-0.01	0.00	0.01	0.67	-0.23	-0.33	0.22	0.92	0.75
^{2}2 $_{xz}$	-23.29	1.01	0.06	0.01	-0.01	0.00	-0.06	0.67	-0.23	-0.33	0.23	0.91	0.75
^{2} 3	-40.63	1.05	-0.01	-0.03	-0.01	0.00	0.00	0.72	-0.04	-0.39	0.25	1.00	0.46

[a] with respect to ^{4}RC.

Table S7: Relative energies in kcal/mol, group spin densities and group charges in dielectric medium (ε = 5.708)..

	ΔE^a	Spin Density						Charges					
		ρ_{Fe}	ρ_O	ρ_{por}		ρ_{Im}	ρ_{rest}	Q_{Fe}	Q_O	Q_{por}		Q_{Im}	Q_{rest}
				A_{2u}	A_{1u}					A_{2u}	A_{1u}		
$^4A_{2u}$	-3.59	0.99	1.05	1.29	-2.33	0.01	0.01	0.64	-0.25	-0.35	2.58	0.23	1.14
$^2A_{2u}$	-3.12	1.11	0.97	-0.89	-0.16	-0.03	-0.01	0.65	-0.33	-2.33	2.58	0.23	-0.01
$^4A_{1u}$	-2.78	1.05	1.00	-0.15	1.08	-0.01	0.02	0.65	-0.31	-2.48	2.72	0.22	1.21
$^2A_{1u}$	-2.65	1.10	0.97	-0.48	-0.56	-0.02	-0.01	0.64	-0.33	-2.40	2.66	0.23	1.20
	ΔE^a	ρ_{Fe}	ρ_O	ρ_{por}	ρ_{Im}	ρ_{rest}	ρ_{St}	Q_{Fe}	Q_O	Q_{por}	Q_{Im}	Q_{rest}	Q_{St}
^{4}RC	0.00	1.05	1.00	0.94	0.01	0.00	0.01	0.64	-0.30	0.28	0.24	1.11	0.02
^{4}TS1	7.81	1.23	0.90	0.34	0.03	0.00	0.48	0.66	-0.33	-0.03	0.26	0.99	0.45
^{4}2	5.25	2.41	0.12	-0.11	0.04	0.00	0.53	0.82	-0.52	-0.22	0.23	0.05	0.74
^{4}2-III	3.40	0.89	0.20	0.92	0.01	0.00	0.98	0.67	-0.49	0.19	0.24	0.32	1.07
^{4}2$_{Cat,z2}$	0.38	2.73	0.18	-0.09	0.06	0.00	0.11	0.84	-0.57	-0.29	0.18	0.90	0.93
^{4}2$_{Cat,xy}$	0.46	2.41	0.12	-0.11	0.04	0.00	0.53	0.80	-0.50	-0.37	0.26	0.88	0.94
^{4}3	3.01	2.85	0.03	0.00	0.10	0.00	0.02	0.93	-0.49	-0.30	0.20	1.02	0.65
^{2}RC	0.26	1.08	1.00	-1.04	-0.03	-0.01	0.00	0.64	-0.30	0.28	0.24	1.12	0.02
^{2}TS1	3.83	1.09	0.90	-0.77	-0.04	0.00	-0.19	0.64	-0.31	0.12	0.25	1.06	0.24
^{2}2	2.83	0.94	0.11	-0.06	-0.01	0.00	0.02	0.68	-0.52	-0.28	0.25	0.83	1.04
^{2}2$_{yz}$	2.74	0.97	0.07	-0.05	0.00	0.00	0.02	0.68	-0.51	-0.28	0.25	0.85	1.01
^{2}2$_{xz}$	3.01	0.98	0.07	-0.05	-0.01	0.00	0.01	0.69	-0.52	-0.29	0.25	0.83	1.04
^{2}3	4.98	1.03	0.00	-0.02	-0.01	0.00	0.00	0.78	-0.47	-0.30	0.29	0.98	0.72

[a] with respect to ^{4}RC.