Supplementary Information

‘Oxygen-consuming complexes’– Catalytic effects of iron salen-complexes with dioxygen

Katarzyna Rydel-Ciszek[1]*, Tomasz Pacześniak[1], Anna Miłaczewska[2], Paweł Chmielarz[1], Andrzej Sobkowiak[1]

[1] Department of Physical Chemistry, Faculty of Chemistry, Rzeszów University of Technology, Al. Powstańców Warszawy 6, 35-959 Rzeszów, Poland
[2] Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, 30- 239 Kraków, Poland
* Correspondence: kasiar@prz.edu.pl

Table S1. Oxidation of 1 M cyclohexene by air in acetonitrile at room temperature (23±1 °C) catalyzed by the iron-salen complex at various concentrations. Reaction time 24 h.

Catalyst, mM	Ketone, mM	Alcohol, mM	Epoxide, mM
0.5	35.9	15.7	0.6
1	53.6	26.1	0.9
2.5	55.8	38.2	0.7
5	42.3	33.8	0.3
7.5	0.0	0.0	0.0
10	0.0	0.0	0.0

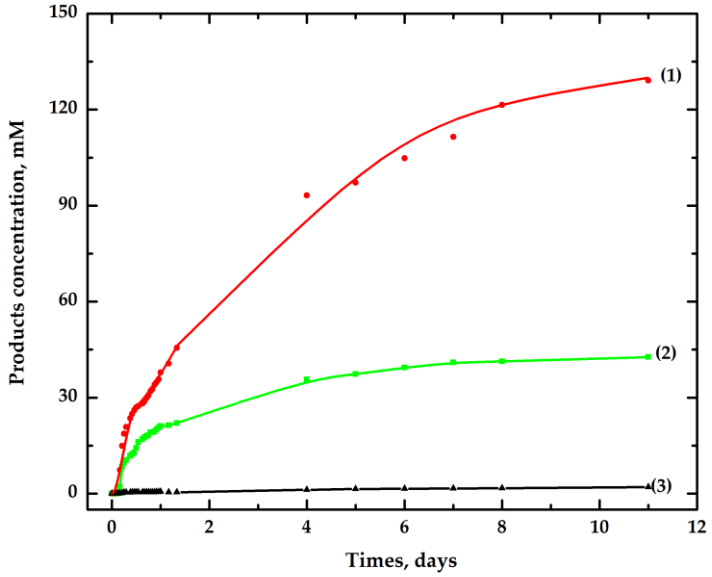


Figure S1. Dependence of product concentration for (1) ketone, (2) alcohol, (3) epoxide on time during oxidation of 1 M cyclohexene by air (p_{O2} = 0.2 atm) catalyzed by 1 mM $[(salen)Fe^{II}]_{MeCN}$ in acetonitrile, room temperature 23 ± 1 °C.

Table S2. Concentrations of products for the oxidation of 1 M cyclohexene with dioxygen in acetonitrile catalyzed by different Fe-salen complexes (1 mM) after 24 h at room temperature (23 ± 1 °C).

Catalyst, mM	Ketone, mM	Alcohol, mM	Epoxide, mM	TON
[(salen)Fe^{II}]	27.8	12.6	0.4	40.8
[(salen)Fe^{III}]ClO_4	11.7	2.7	0.3	14.7
[(salen)Fe^{III}]Cl	0.0	0.0	0.0	0.0

TON – product molecules per catalyst molecule

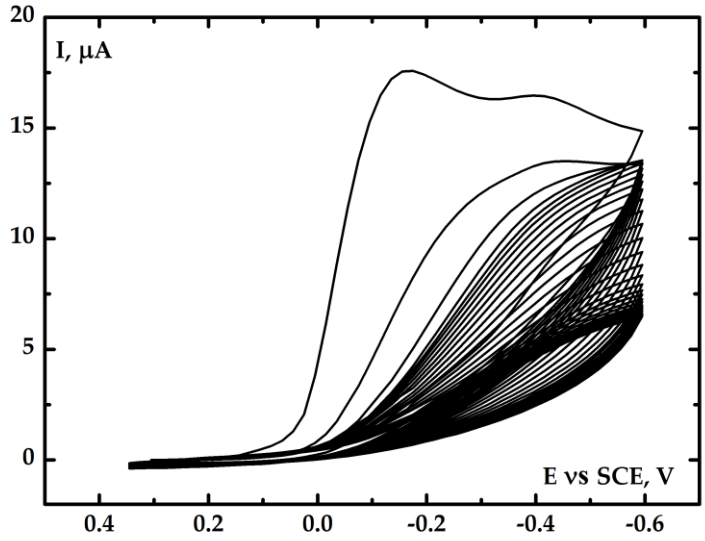


Figure S2. Cyclic voltammograms in acetonitrile (0.1 M Et_4NClO_4) for 5 mM [(salen)Fe^{III}]$^{+}{}_{MeCN}$ in an air atmosphere. Scan rate, 0.1 Vs^{-1}, GCE (0.008 cm^2); SCE *vs.* NHE, +0.242 V, cathodic scans.

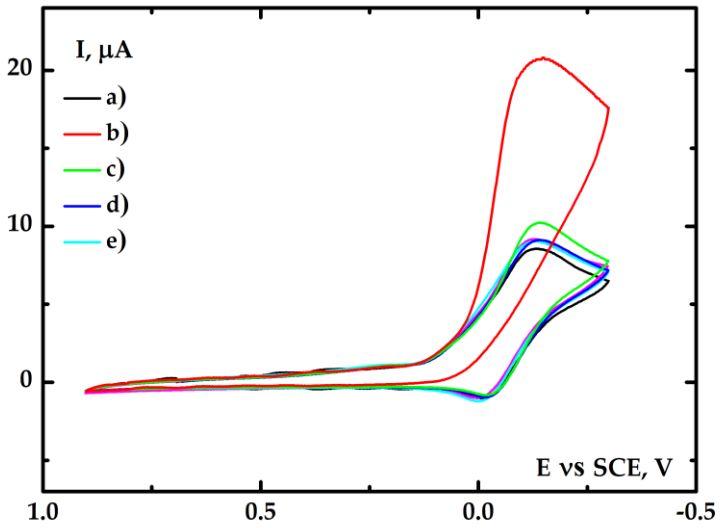


Figure S3. Cyclic voltammograms in acetonitrile (0.1 M Et_4NClO_4) for 5 mM $[(salen)Fe^{III}](ClO_4)_{MeCN}$ in: a) argon atmosphere, b) air atmosphere, and after oxygen removal from previously oxygenated catalyst solution after c) 5 min, d) 10 min, and e) 15 min of purging with Ar. Scan rate, 0.1 Vs^{-1}, GCE (0.008 cm^2); SCE *vs.* NHE, +0.242 V, cathodic scans.

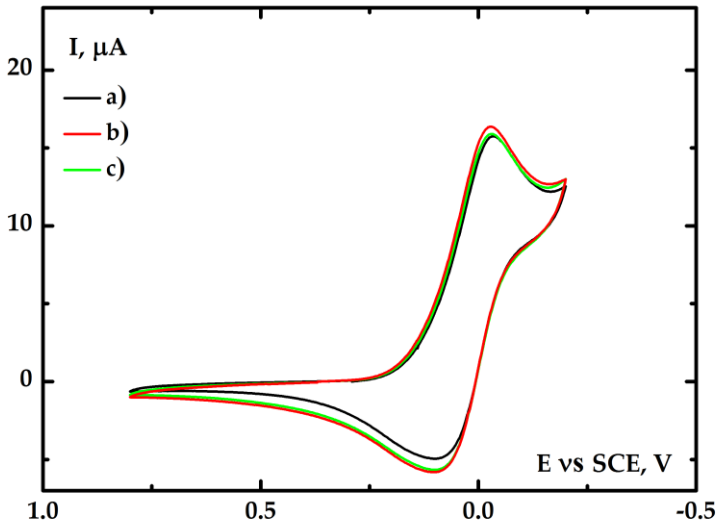


Figure S4. Cyclic voltammograms in acetonitrile (0.1 M Et_4NClO_4) for 5 mM $[(salen)Fe^{III}]Cl_{MeCN}$ in: a) argon atmosphere, b) air atmosphere, and after deoxidation of previously oxygenated catalyst solution after c) 5 min of deoxidation by use of Ar atmosphere. Scan rate, 0.1 Vs^{-1}, GCE (0.008 cm^2); SCE *vs.* NHE, +0.242 V, cathodic scans.

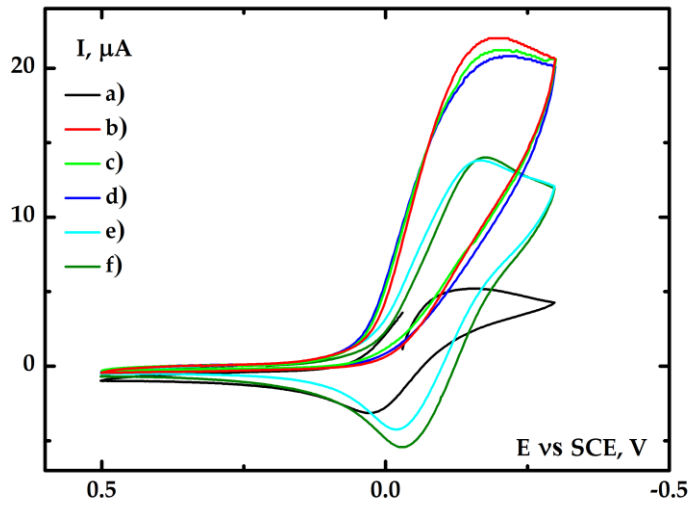
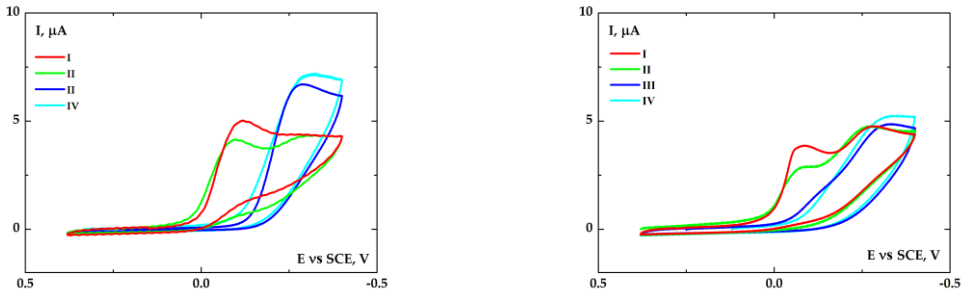
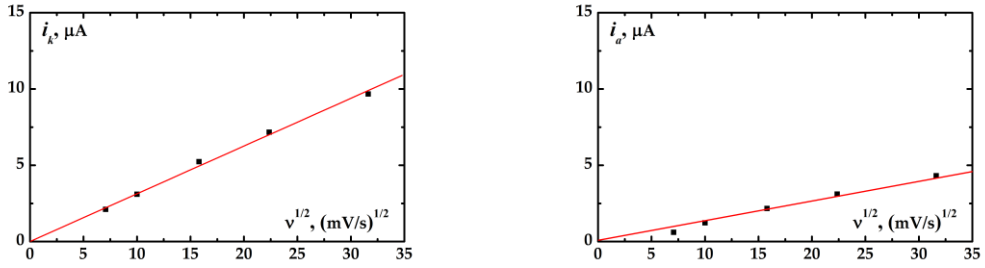


Figure S5. Cyclic voltammograms in acetonitrile (0.1 M Et_4NClO_4) for 5 mM $[(salen)Fe^{II}]_{MeCN}$ in: a) an argon atmosphere, b) an air atmosphere, and after oxygen removal of the previously oxygenated catalyst solution after c) 5 min, d) 10 min, e) 15 min, and f) 45 min of purging with Ar. Scan rate, 0.1 Vs^{-1}, GCE (0.008 cm^2); SCE *vs.* NHE, +0.242 V, cathodic scans.



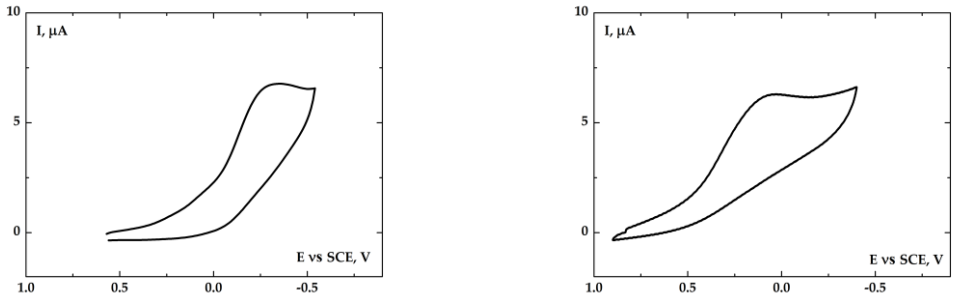
a) air (p_{O2} = 0.2 atm) **b)** dioxygen (p_{O2} = 1 atm)

Figure S6. Cyclic voltammograms in acetonitrile (0.1 M Et_4NClO_4) for iron species formed in a reaction of 1 mM $[(salen)Fe^{II}]_{MeCN}$ with O_2 and 1 M cyclohexene, a) air (p_{O2} = 0.2 atm) atmosphere, b) dioxygen (p_{O2} = 1 atm) atmosphere. Scan rate, 0.1 Vs^{-1}, GCE (0.008 cm^2); SCE *vs.* NHE, +0.242 V, cathodic scans. Oxygenated catalyst with 1 M of cyclohexene in time after: I – 0 min (immediately after aeration), II – 30 min, III – 3 hours, IV – 12 hours.



a) **b)**

Figure S7. Dependence of i (μA) on $\nu^{1/2}$ $(mV/s)^{1/2}$ registered in acetonitrile (0.1 M Et_4NClO_4) for 1 mM $[(salen)Fe^{II}]_{MeCN}$ in an argon atmosphere for **a)** cathodic (–0.1 V) and **b)** anodic (~0 V) peaks.



a) **b)**

Figure S8. Cyclic voltammograms in acetonitrile (0.1 M Et_4NClO_4) for 1 mM $[(salen)Fe^{II}]_{MeCN}$ under Ar atmosphere a) with 15 mM PhIO, b) with 15 mM PhIO and 30 mM $HClO_4$. Scan rate, 0.1 Vs^{-1}, GCE (0.008 cm^2); SCE *vs.* NHE, +0.242 V, cathodic scans.

Table S3. Energies (with and without zero point correction), enthalpies, free energies (G), and respective relative values for different catalyst molecules calculated with Def2SVP.

Molecules	**Electronic Energy**	Sum of electronic and zero-point **Energies**	Sum of electronic and thermal **Energies**	Sum of electronic and thermal **Enthalpies**	Sum of electronic and thermal **Free Energies**	Relative **Electronic Energy**	Relative **Gibbs Free Energy**
	[a.u.]	[a.u.]	[a.u.]	[a.u.]	[a.u.]	[kJ/mol]	[kJ/mol]
	ε_0	ε_0+ZPE	ε_0+E*tot*	ε_0+H*corr*	ε_0+G*corr*	$\Delta(\varepsilon_0$+ZPE)	ΔG
^{1}[Fe(salen)]	–2141.17542	–2140.903345	–2140.886871	–2140.885927	–2140.947783	**125.4**	**132.9**
^{3}[Fe(salen)]	–2141.22141	–2140.949504	–2140.932864	–2140.931919	–2140.994995	**4.2**	**9.0**
^{5}[Fe(salen)]	–2141.22126	–2140.951113	–2140.933768	–2140.932823	–2140.998419	**0**	**0**
^{2}[Fe(salen)]Cl	–2601.310640	–2601.036897	–2601.018524	–2601.017580	–2601.084465	**71.7**	**78.5**
^{4}[Fe(salen)]Cl	–2601.324835	–2601.051553	–2601.032948	–2601.032004	–2601.100260	**33.3**	**37.1**
^{6}[Fe(salen)]Cl	–2601.336367	–2601.064225	–2601.045185	–2601.044240	–2601.114376	**0**	**0**
^{2}[Fe(salen)]ClO_4	–2901.579156	–2901.289455	–2901.267576	–2901.266632	–2901.341353	**55.1**	**66.1**
^{4}[Fe(salen)]ClO_4	–2901.595051	–2901.305953	–2901.283688	–2901.282744	–2901.359557	**11.8**	**18.3**
^{6}[Fe(salen)]ClO_4	–2901.598191	–2901.310444	–2901.287609	–2901.286664	–2901.366543	**0**	**0**
^{1}[Fe(salen)]=O	–2216.298160	–2216.022514	–2216.004831	–2216.003887	–2216.068037	**96.1**	**98.5**
^{3}[Fe(salen)]=O	–2216.334670	–2216.05911	–2216.041401	–2216.040457	–2216.105569	**0**	**0**
^{5}[Fe(salen)]=O	–2216.330210	–2216.056267	–2216.037977	–2216.037033	–2216.104402	**7.5**	**3.1**
^{1}(Cl)[(salen)Fe]=O	–2676.459913	–2676.184429	–2676.164950	–2676.164006	–2676.231918	**125.0**	**131.7**
^{3}(Cl)[(salen)Fe]=O	–2676.506008	–2676.230404	–2676.210984	–2676.210040	–2676.278808	**4.3**	**8.6**
^{5}(Cl)[(salen)Fe]=O	–2676.506696	–2676.232035	–2676.211998	–2676.211053	–2676.282069	**0**	**0**
^{1}(ClO_4)[(salen)Fe]=O	–2976.768910	–2976.478225	–2976.454921	–2976.453977	–2976.530777	**84.4**	**87.5**
^{3}(ClO_4)[(salen)Fe]=O	–2976.326108	–2976.510369	–2976.487186	–2976.486241	–2976.564120	**0**	**0**
^{5}(ClO_4)[(salen)Fe]=O	–2976.798832	–2976.508500	–2976.484871	–2976.483927	–2976.563259	**4.9**	**2.3**
^{2}[Fe(salen)]OH	–2216.97619	–2216.689958	–2216.671640	–2216.670696	–2216.736837	**58.4**	**66.2**
^{4}[Fe(salen)]OH	–2216.98108	–2216.696433	–2216.677536	–2216.676592	–2216.744959	**41.4**	**44.8**
^{6}[Fe(salen)]OH	–2216.99564	–2216.712218	–2216.692834	–2216.691890	–2216.762041	**0**	**0**
^{2}(Cl)[Fe(salen)]OH	–2677.15741	–2676.871028	–2676.851020	–2676.850076	–2676.919545	**28.8**	**37.0**
^{4}(Cl)[Fe(salen)]OH	–2677.15142	–2676.866041	–2676.845332	–2676.844388	–2676.916353	**41.9**	**45.4**
^{6}(Cl)[Fe(salen)]OH	–2677.16515	–2676.882005	–2676.860763	–2676.859819	–2676.933651	**0**	**0**

Table S3 (cont). Energies (with and without zero point correction), enthalpies, free energies (G), and respective relative values for different catalyst molecules calculated with Def2SVP.

Molecules	**Electronic Energy**	Sum of electronic and zero-point **Energies**	Sum of electronic and thermal **Energies**	Sum of electronic and thermal **Enthalpies**	Sum of electronic and thermal **Free Energies**	Relative **Electronic Energy**	Relative **Gibbs Free Energy**
	[a.u.]	[a.u.]	[a.u.]	[a.u.]	[a.u.]	[kJ/mol]	[kJ/mol]
	ε_0	ε_0+ZPE	ε_0+E*tot*	ε_0+H*corr*	ε_0+G*corr*	$\Delta(\varepsilon_0$+ZPE)	ΔG
^{2}(ClO$_4$)[Fe(salen)]OH	–2977.450727	–2977.148087	–2977.124479	–2977.123535	–2977.201457	**34.2**	**42.9**
^{4}(ClO$_4$)[Fe(salen)]OH	–2977.435956	–2977.135490	–2977.111165	–2977.110221	–2977.190547	**67.3**	**71.6**
^{6}(ClO$_4$)[Fe(salen)]OH	–2977.460724	–2977.161117	–2977.136214	–2977.135270	–2977.217812	**0**	**0**
^{1}[Fe(salen)]OO$^{\cdot}$	–2291.40266	–2291.123793	–2291.104859	–2291.103915	–2291.170717	**93.6**	**107.1**
^{3}[Fe(salen)]OO$^{\cdot}$	–2291.43199	–2291.154694	–2291.135149	–2291.134205	–2291.203523	**12.4**	**20.9**
^{5}[Fe(salen)]OO$^{\cdot}$	–2291.43570	–2291.159426	–2291.138974	–2291.138030	–2291.211499	**0**	**0**
^{1}(Cl)[Fe(salen)]OO$^{\cdot}$	–2751.58556	–2751.306537	–2751.285913	–2751.284968	–2751.355271	**114.3**	**127.4**
^{3}(Cl)[Fe(salen)]OO$^{\cdot}$	–2751.61077	–2751.332789	–2751.311578	–2751.310634	–2751.385114	**45.3**	**49.0**
^{5}(Cl)[Fe(salen)]OO$^{\cdot}$	–2751.62539	–2751.350054	–2751.327699	–2751.326755	–2751.403779	**0**	**0**
^{1}(ClO$_4$)[Fe(salen)]OO$^{\cdot}$	–3051.876855	–3051.581933	–3051.557545	–3051.556601	–3051.635635	**91.3**	**106.5**
^{3}(ClO$_4$)[Fe(salen)]OO$^{\cdot}$	–3051.905139	–3051.610874	–3051.586226	–3051.585281	–3051.666001	**15.3**	**26.7**
^{5}(ClO$_4$)[Fe(salen)]OO$^{\cdot}$	–3051.909204	–3051.616701	–3051.590789	–3051.589845	–3051.676183	**0**	**0**
^{2}[Fe(salen)]OOH	–2292.053783	–2291.764237	–2291.744507	–2291.743563	–2291.812828	**48.4**	**55.6**
^{4}[Fe(salen)]OOH	–2292.057796	–2291.769253	–2291.748993	–2291.748049	–2291.819396	**35.2**	**38.4**
^{6}[Fe(salen)]OOH	–2292.070061	–2291.782663	–2291.761923	–2291.760979	–2291.834006	**0**	**0**
^{2}(ClO$_4$)[Fe(salen)]OOH	–3052.535504	–3052.228737	–3052.204117	–3052.203173	–3052.283296	**25.6**	**34.9**
^{4}(ClO$_4$)[Fe(salen)]OOH	–3052.526124	–3052.220882	–3052.195272	–3052.194328	–3052.278456	**46.2**	**47.6**
^{6}(ClO$_4$)[Fe(salen)]OOH	–3052.542459	–3052.238470	–3052.212574	–3052.211630	–3052.296591	**0**	**0**
^{2}(Cl)[Fe(salen)]OOH	–2752.243878	–2751.953274	–2751.932313	–2751.931369	–2752.002879	**26.9**	**35.9**
^{4}(Cl)[Fe(salen)]OOH	–2752.236502	–2751.947496	–2751.925723	–2751.924779	–2751.999193	**42.1**	**45.6**
^{6}(Cl)[Fe(salen)]OOH	–2752.251290	–2751.963518	–2751.941330	–2751.940386	–2752.016568	**0**	**0**
H atom	–0.501259	–0.501259	–0.499843	–0.498898	–0.511913	**0**	**0**

Table S4. Energies (with and without zero point correction), enthalpies, free energies (G) calculated with Def2TZVP, and the MeCN model for the best multiplicity of different catalyst molecules determined on the basis of the data presented in Table S3.

Molecules	**Electronic Energy** [a.u.] ε_0	Sum of electronic and zero-point **Energies** [a.u.] ε_0+ZPE	Sum of electronic and thermal **Energies** [a.u.] ε_0+E*tot*	Sum of electronic and thermal **Enthalpies** [a.u.] ε_0+H*corr*	Sum of electronic and thermal **Free Energies** [a.u.] ε_0+G*corr*
^{5}[Fe(salen)]=O	–2217.57376422	–2217.299821	–2217.281531	–2217.280587	**–2217.347956**
^{5}(Cl)[(salen)Fe]=O	–2677.98328079	–2677.70862	–2677.688583	–2677.687638	**–2677.758654**
^{5}(ClO_4)[(salen)Fe]=O	–2979.20757813	–2978.917246	–2978.893617	–2978.892673	**–2978.972005**
^{6}[Fe(salen)]OH	–2218.24122624	–2217.957804	–2217.93842	–2217.937476	**–2218.007627**
^{6}(Cl)[Fe(salen)]OH	–2678.64435036	–2678.361205	–2678.339963	–2678.339019	**–2678.412851**
^{6}(ClO_4)[Fe(salen)]OH	–2979.87400023	–2979.574393	–2979.54949	–2979.548546	**–2979.631088**
^{5}[Fe(salen)]OO··	–2292.76399083	–2292.487717	–2292.467265	–2292.466321	**–2292.539790**
^{5}(Cl)[Fe(salen)]OO·	–2753.18349700	–2752.908161	–2752.885806	–2752.884862	**–2752.961886**
^{5}(ClO_4)[Fe(salen)]OO··	–3053.92676551	–3053.634263	–3053.608351	–3053.607407	**–3053.693745**
^{6}[Fe(salen)]OOH	–2293.40590815	–2293.11851	–2293.09777	–2293.096826	**–2293.169853**
^{6}(ClO_4)[Fe(salen)]OOH	–3054.56666259	–3054.262674	–3054.236778	–3054.235834	**–3054.320795**
^{6}(Cl)[Fe(salen)]OOH	–2753.81628125	–2753.528509	–2753.506321	–2753.505377	**–2753.581559**
H atom	–0.502175248866	–0.502175249	–0.500759249	–0.499815249	**–0.512829249**

Table S5. Relative energies and Gibbs free energies and values of ε_0, ZPE, E_{corr}, H_{corr}, G_{corr} of the singlet (**1**), triplet (**3**), and quintet (**5**) for the reaction of cyclohexene oxidation catalyzed by [(salen)Fe^{IV}=O] to alcohol and [(salen)Fe^{II}]. Calculated relative energies with ZPE correction as well as Gibbs free energies are given in reference to substrate ^{3}S.

	Molecules	**Electronic Energy** [a.u.] ε_0	Zero-point correction [a.u.] ZPE	Thermal correction to **Energy** [a.u.] *Ecorr*	Thermal correction to **Enthalpy** [a.u.] *Hcorr*	Thermal correction to **Gibbs Free Energy** [a.u.] *Gcorr*	$\Delta(\varepsilon_0$+ZPE) [kJ/mol]	ΔG [kJ/mol]
Singlet	**S**	–2452.336645	0.4223	0.4476	0.4485	0.3655	**38.5**	**41.2**
	TSI	–2452.302722	0.4153	0.4399	0.4408	0.3607	**109.0**	**117.7**
	PI	–2452.351274	0.4199	0.4455	0.4464	0.3628	**–6.2**	**–4.1**
	TSII	–2452.332251	0.4189	0.4438	0.4448	0.3643	**41.1**	**49.7**
	PII	–2452.383649	0.4242	0.4488	0.4498	0.3701	**–80.0**	**–70.1**
Triplet	**S**	–2452.351325	0.4223	0.4476	0.4486	0.3644	**0.0**	**0.0**
	TSI	–2452.325403	0.4151	0.4400	0.4409	0.3582	**49.0**	**51.7**
	PI	–2452.356759	0.4179	0.4442	0.4452	0.3580	**–26.0**	**–31.3**
	TSII	–2452.344534	0.4183	0.4435	0.4445	0.3617	**7.3**	**10.8**
	PII	–2452.402102	0.4239	0.4486	0.4496	0.3681	**–129.2**	**–123.7**
Quintet	**S**	–2452.344787	0.4207	0.4466	0.4476	0.3615	**13.0**	**9.4**
	TSI	–2452.333866	0.4157	0.4410	0.4420	0.3581	**28.4**	**29.2**
	PI	–2452.370296	0.4166	0.4434	0.4443	0.3547	**–65.0**	**–75.5**
	TSII	–2452.359409	0.4172	0.4430	0.4439	0.3591	**–34.7**	**–35.3**
	PII	–2452.406779	0.4219	0.4475	0.4485	0.3637	**–146.8**	**–147.5**

S – substrates: [(salen)Fe=O)]+H-C_6H_9,

TSI – [(salen)Fe---O----H-C_6H_9],

PI – products1: [(salen)Fe-OH)]+C_6H_9,

TSII – [(salen)Fe---O(H)---C_6H_9],

PII – products2: [(salen)Fe]+C_6H_9OH.

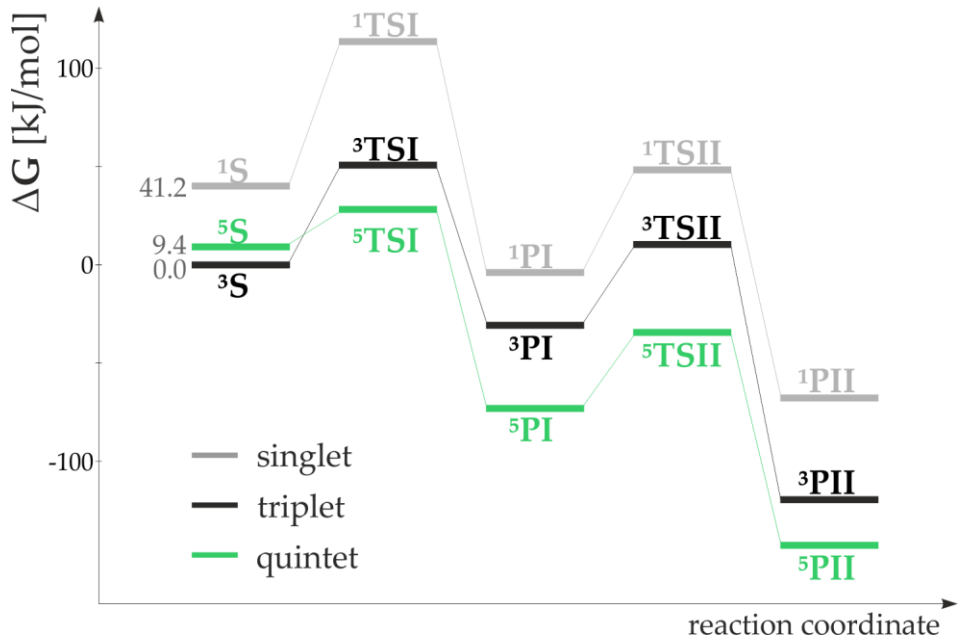


Figure S9. Relative Gibbs free enthalpies (**Table S5**) of the singlet (**1, gray**), triplet (**3, black**), and quintet (**5, green**) for reaction of cyclohexene oxidation catalysed by [(salen)Fe^{IV}=O] to alcohol. For the initial complexes **S** (in three various spin states) the values of starting relatives Gibbs free enthalpies are given next to the respective line. The legend of used symbols: S – substrates: [(salen)Fe=O)]+H-C_6H_9, TSI – [(salen)Fe---O----H-C_6H_9], PI – products1: [(salen)Fe-OH)]+C_6H_9, TSII – [(salen)Fe---O(H)---C_6H_9], PII – products2: [(salen)Fe]+C_6H_9OH.