Supporting Information

The Valence Bond Way: Reactivity Patterns of Cytochrome P450 Enzymes and Synthetic Analogs

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Part I. Alkane Hydroxylation

Methods

Technical Details: The DFT calculations for L-Cpd I + cyclohexane were carried out with the Gaussian 03. As previously,[14,16,23] UB3LYP hybrid density functional method was used throughout, the geometries were optimized with the double-ζ LACVP basis set (B1), followed by single-point energy correction with larger basis set B2, LACV3P+* for iron and 6-311+G* for the rest. Transition states and optimized minima were characterized by the UB3LYP/B1 frequency calculations as having one and zero imaginary vibrational modes, respectively.

Different alkanes + Cpd I P450: The computations were described in the original literature (Ref. 14 in the text: *J. Am. Chem. Soc.* **2008**, *130*, 10128–10140).

Cyclohexane + L-Cpd I: The computations were described in the original work (Ref. 16 in the text: *Chem. Eur. J.* **2009**, *15*, 10039–10046). The data for L = SH is new and single-point energy correction with B2 were carried out for other ligands (L = OAc, Cl, CF_3SO_3) on the optimized geometry taken from previous calculations.

Table S1. Bond dissociation energies (*BDE*) of FeO–H.[a]

	L	B1		B2	
		ΔE	ΔE + ZPE	ΔE	ΔE + ZPE
HS	OAc	91.11	83.66	96.46	89.00
	Cl	87.40	80.27	94.70	87.57
	CF_3SO_3	85.68	78.10	88.94	81.36
	SH	88.64	81.83	96.11	89.29
LS	OAc	91.55	84.04	96.68	89.17
	Cl	87.66	80.47	94.85	87.67
	CF_3SO_3	85.89	78.25	89.04	81.40
	SH	88.58	81.80	96.04	89.26

[a] The LS/HS BDEs are different since in one case the dissociation of triplet FeO–H leads to the doublet (LS) Cpd I, in the other to quartet (HS) Cpd I. All data are in kcal/mol and calculated with basis set B1, B2. ZPE data calculated with basis set B1.

Table S2. Activation energies for C–H cleavage of cyclohexane by $[(Por)^{+\bullet}Fe^{IV}(O)(L)]$ in doublet (LS) and quartet (HS) states.[a]

	L	B1		B2	
		$\Delta E^{\ddagger}$	$\Delta E^{\ddagger}$ + ZPE‡	$\Delta E^{\ddagger}$	$\Delta E^{\ddagger}$ + ZPE‡
HS	OAc	20.33	16.16	22.23	18.06
	Cl	21.36	16.97	22.65	18.26
	CF_3SO_3	22.19	19.42	22.30	19.54
	SH	19.12	15.57	18.22	14.68
LS	OAc	17.52	13.94	19.67	16.08
	Cl	19.06	15.11	20.26	16.31
	CF_3SO_3	17.50	13.97	21.23	17.69
	SH	19.08	15.57	20.16	16.65

[a] All data are in kcal/mol and calculated with basis set B1, B2. ZPE data calculated with basis set B1.

Table S3. DFT calculated BDE_{FeO-H}, $|RE_{FeO}|$, D_{FeO-H}, BDE_{C-H}, $|RE_{R\bullet}|$, D_{C-H}, and barrier for hydroxylation.[a]

substrate	L	BDE_{FeO-H}	$\|RE_{FeO}\|$	D_{FeO-H}	BDE_{C-H}	$\|RE_{R\bullet}\|$	D_{C-H}	$\Delta E^{\ddagger}_{HS}$	$\Delta E^{\ddagger}_{LS}$
Methane (**1**)	SH	89.28	14.94	104.22	101.62	6.79	108.41	22.91	22.34
Ethane (**2**)					96.87	7.00	103.87	17.41	15.30
i-Propane (**3**)					93.03	7.21	100.24	15.80	13.85
n-Propane (**4**)					97.49	6.87	104.36	17.48	15.19
Propene (**5**)					82.80	16.69	99.49	12.95	12.82
(**6**) *trans*-methyl phenylcyclopropane					93.62	8.30	101.92	14.53	13.13
(**7**) *trans*-*i*-propyl-phenylcyclopropane					86.60	8.60	95.20	13.46	12.27
N,*N*-DMA (**8**)					86.08	7.94	94.02	5.54	4.99
Toluene (**9**)					85.80	12.27	98.07	12.43	12.05
Phenylethane (**10**)					82.45	18.38	100.83	12.55	11.47
Camphor (**11**)					93.89	7.61	101.50	14.51	15.88
p-CN-DMA (**12**)					85.98	9.09	95.07	10.10	9.47
p-NO_2-DMA (**13**)					85.94	9.76	95.70	10.82	10.31
p-Cl-DMA (**14**)					85.42	8.57	93.99	7.17	6.49
Cyclohexane (**15**)					93.05	7.15	100.20	15.57	14.82
Cyclohexane	OAc(**16**)	89.09	10.79	99.88	93.05	7.15	100.20	18.06	16.08
Cyclohexane	Cl(**17**)	87.62	8.81	96.43	93.05	7.15	100.20	18.26	16.31
Cyclohexane	CF_3SO_3(**18**)	81.38	12.69	94.07	93.05	7.15	100.20	19.54	17.69

[a] All data are the values at the B2 level with ZPE correction. BDE_{C-H}, $RE_{R\bullet}$, $\Delta E^{\ddagger}_{HS}$, and $\Delta E^{\ddagger}_{LS}$ for substrates **1-11** taken from Ref. 14; **12-14** taken from Ref. 23; **15-18** are calculated in the present work. BDE_{FeO-H} and RE_{FeO} are the average of the HS and LS values.

Table S4. Average DFT calculated barriers ($\Delta E^{\ddagger}_{av}$), $\Delta E^{\ddagger}_{VB}$ Values, and corresponding deviations from the DFT values ($\Delta\Delta E^{\ddagger}_{VB}$).[a]

substrate	L	$\Delta E^{\ddagger}_{av}$ [b]	$\Delta E^{\ddagger}_{VB}(1)$ [c]	$\Delta E^{\ddagger}_{VB}(2)$ [d]	$\Delta\Delta E^{\ddagger}_{VB}(1)$	$\Delta\Delta E^{\ddagger}_{VB}(2)$
Methane (**1**)		22.63	18.27	23.18	-4.36	0.55
Ethane (**2**)		16.36	15.54	19.44	-0.82	3.08
i-Propane (**3**)		14.83	13.36	16.43	-1.47	1.60
n-Propane (**4**)		16.34	15.84	19.90	-0.50	3.56
Propene (**5**)		12.89	12.91	11.09	0.02	-1.8
(**6**) *trans*-methyl phenylcyclopropane		13.83	14.37	17.23	0.54	3.40
(**7**) *trans*-*i*-propyl-phenylcyclopropane	SH	12.87	10.34	11.71	-2.53	-1.16
N,*N*-DMA (**8**)		5.27	9.63	11.09	4.36	5.82
Toluene (**9**)		12.24	12.06	12.17	-0.18	-0.07
Phenylethane (**10**)		12.01	13.72	11.32	1.71	-0.69
Camphor (**11**)		15.20	14.12	17.24	-1.08	2.04
p-CN-DMA (**12**)		9.79	10.26	11.36	0.47	1.57
p-NO_2-DMA (**13**)		10.57	10.64	11.53	0.07	0.96
p-Cl-DMA (**14**)		6.83	9.61	10.75	2.78	3.92
Cyclohexane (**15**)		15.67	13.34	16.43	-2.33	0.76
Cyclohexane	OAc(**16**)	17.07	–	15.22		-1.85
Cyclohexane	Cl(**17**)	17.29	–	14.92		-2.37
Cyclohexane	CF_3SO_3(**18**)	18.62	–	17.34		-1.28

[a] All data are in kcal/mol.

[b] The average barriers (at the B2 level with ZPE correction) for the quartet and doublet H-abstraction steps.

[c] $\Delta E^{\ddagger}_{VB}(1)=0.6D_{CH} - 46.78$; corresponding to eq. 6 in the text.

[d] $\Delta E^{\ddagger}_{VB}(2)= 0.3(D_{CH} + D_{OH}) + 0.5\Delta E_{rp} - 46.78$; corresponding to eq. 11 in the text.

Comments on Table S5: Starting from eq. 2 in the text, neglecting the quadratic term, and setting the $G_0 = D_{CH} + D_{FeO-H}$ (Eq. 11), we can derive the following expressions for the barrier:
(a) $\Delta E^{\ddagger}_{VB}(3) = 0.3(BDE_{CH} + BDE_{FeO-H}) + 0.5\Delta E_{rp} - B$. This is a *BDE*-only version of equation 11, where *B* given by $B = 0.5BDE_{W}$. Here 'W' means the weaker of the C–H and FeO–H bonds.
(b) $\Delta E^{\ddagger}_{av} = f_0(D_{CH} + D_{FeO-H}) + 0.5\Delta E_{rp} - 46.78$. Here $B = 46.78$ kcal/mol. f_0 values that match $\Delta E^{\ddagger}_{av}$ values are then found, and the spread of f_0 is then assessed. As can be seen from the table below, there is a spread though not a wide one.
(c) Using the average f_0 value from (b), we compute VB barrier using: $\Delta E^{\ddagger}_{VB}(4) = 0.298(D_{CH} + D_{FeO-H}) + 0.5\Delta E_{rp} - 46.78$.
(d) Using the expressions $\Delta E^{\ddagger}_{av} \approx f_0[D_{CH} + D_{FeO-H}] + 0.5\Delta E_{rp} - B$ and $f_0 = 0.3$ we can get the spread in the *B* values needed to reproduce the DFT barriers. As can be seen, $B = 47.38 \pm 2.96$ kcal/mol with **8**, **14** excluded. The latter two reactions should have greater B values due to the mixture of the charge transfer state into the TS.

Table S5. Estimated f_0, *B*(kcal/mol), and barriers (kcal/mol) modeled by VB theory along with corresponding deviations vis-à-vis the DFT calculated values.

substrate	L	$\Delta E^{\ddagger}_{VB}(3)^a$	$\Delta\Delta E^{\ddagger}_{VB}(3)$	$f_0{}^b$	$\Delta E^{\ddagger}_{VB}(4)^c$	$\Delta\Delta E^{\ddagger}_{VB}(4)$	B^d
Methane (**1**)		18.80	-3.83	0.297	22.75	0.12	47.33
Ethane (**2**)		15.00	-1.36	0.285	19.03	2.67	49.87
i-Propane (**3**)		11.93	-2.90	0.292	16.02	1.19	48.39
n-Propane (**4**)		15.50	-0.84	0.283	19.48	3.14	50.34
Propene (**5**)		6.98	-5.91	0.309	10.69	-2.2	44.99
(**6**) *trans*-methyl phenylcyclopropane		12.40	-1.43	0.283	16.82	2.99	50.18
(**7**) *trans*-*i*-propyl-phenylcyclopropane	SH	8.12	-4.75	0.306	11.31	-1.56	45.62
N,*N*-DMA (**8**)		7.97	2.70	0.271	10.70	5.43	52.61
Toluene (**9**)		7.88	-4.36	0.300	11.76	-0.48	46.71
Phenylethane (**10**)		6.88	-5.13	0.303	10.91	-1.10	46.09
Camphor (**11**)		12.62	-2.58	0.290	16.83	1.63	48.83
p-CN-DMA (**12**)		7.94	-1.85	0.292	10.96	1.17	48.35
p-NO_2-DMA (**13**)		7.93	-2.64	0.295	11.13	0.56	47.74
p-Cl-DMA (**14**)		7.77	0.94	0.280	10.36	3.53	50.70
Cyclohexane (**15**)		11.94	-3.73	0.296	16.02	0.35	47.55
Cyclohexane	OAc(**16**)	12.08	-4.99	0.309	14.82	-2.25	44.93
Cyclohexane	Cl(**17**)	13.11	-4.18	0.312	14.53	-2.76	44.42
Cyclohexane	CF_3SO_3(**18**)	17.47	-1.15	0.307	16.95	-1.67	45.50

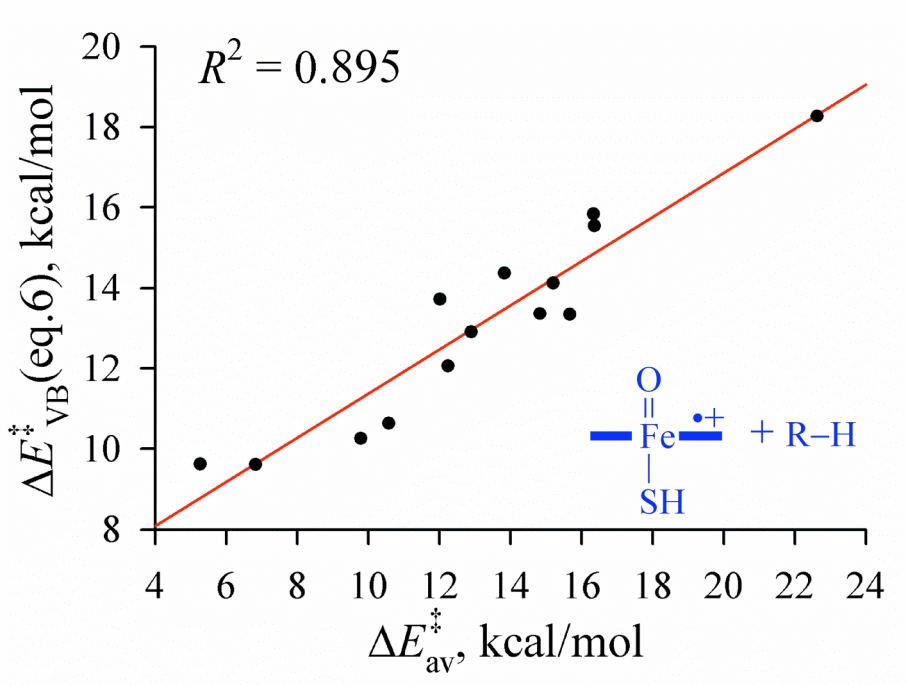

Figure S1. VB barriers (eq. 6) for the 14 alkanes (with **7** excluded) plotted against average DFT barriers.

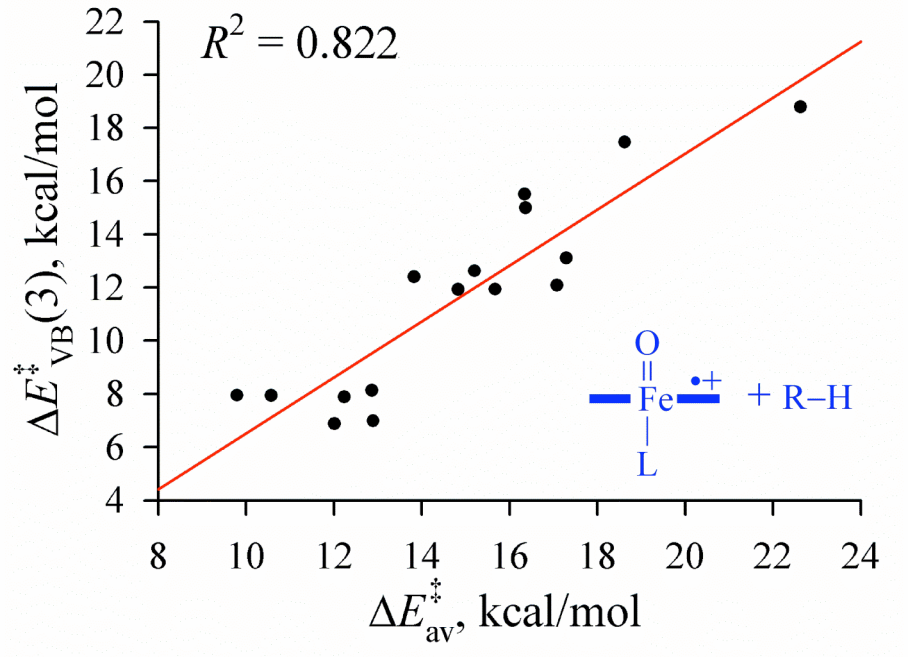

Figure S2. VB barriers [$\Delta E^{\ddagger}_{VB}(3) = 0.3(BDE_S + BDE_W) + 0.5\Delta E_{rp} - 0.5BDE_W$] plotted against average DFT barriers.

Cartesian coordinates of various species with L=SH.

^{3}Fe-OH

Fe	-0.03078800	-0.07712700	-0.02991100	H	-1.37275900	-0.00251300	5.04365300
N	-0.01891600	-0.10367300	1.98681700	H	5.05848800	-0.01741200	-1.38095800
N	1.99800900	0.01990000	-0.02983200	H	1.33380000	0.06717100	5.04232700
N	-2.03294600	-0.12152800	-0.02598500	H	5.05707900	0.09511500	1.32348200
N	-0.01643100	-0.23959500	-2.03438500	H	-5.09264600	-0.10018300	1.32538800
C	-1.12896800	-0.08189600	2.81777600	H	1.34023300	-0.35533100	-5.08930100
C	2.83118400	-0.03720400	-1.13933700	H	-5.09014400	-0.20078900	-1.38044000
C	1.09214700	-0.02410600	2.81657900	H	-1.36662700	-0.41268000	-5.08822900
C	2.82984100	0.05447300	1.08168600	C	-2.45124100	-0.08208500	2.40365500
C	-2.86344200	-0.09612100	1.08241100	C	2.41603600	-0.15307900	-2.45586500
C	1.09544200	-0.24598200	-2.86432100	C	-2.44751700	-0.26273200	-2.45232300
C	-2.86157200	-0.17841600	-1.13458800	C	2.41294500	0.04360300	2.40299600
C	-1.12494900	-0.29427200	-2.86354200	H	-3.21782900	-0.06398100	3.17018000
C	-0.70187500	-0.02420700	4.19734400	H	3.18145900	-0.17926700	-3.22335000
C	4.21086700	0.00595600	-0.71175200	H	-3.21308200	-0.30776300	-3.21869600
C	0.66398100	0.01118600	4.19669700	H	3.17719500	0.08754700	3.17094800
C	4.21018400	0.06274700	0.65370700	O	-0.09414500	1.73332500	-0.07993500
C	-4.24592500	-0.11701700	0.65490900	H	0.79210000	2.15210300	-0.13210800
C	0.66906200	-0.33034900	-4.24333100	S	0.09384200	-2.42344800	-0.05336700
C	-4.24463900	-0.16762000	-0.70907700	H	0.10047100	-2.63161400	1.31205900
C	-0.69652300	-0.35935200	-4.24278100				

^{2}Cpd I

Fe	0.00865800	0.04340500	0.00168100	C	-0.69057900	-0.23561300	-4.22724400
N	0.02541100	-0.04304200	2.00987400	H	-1.30692300	-0.09454200	5.08167300
N	2.02581800	0.00907200	-0.01631800	H	5.07626800	0.16696100	-1.39098400
N	-1.99475400	-0.20330900	0.01033700	H	1.39482400	0.09431900	5.06378500
N	0.00501400	-0.17727400	-2.01138200	H	5.09114800	0.24944300	1.31543000
C	-1.07035700	-0.10620800	2.84969600	H	-5.04786000	-0.36924500	1.38359100
C	2.85183300	0.03319000	-1.12608900	H	1.33677500	-0.17909500	-5.08994700
C	1.13289400	0.04511600	2.83520800	H	-5.06371900	-0.36238600	-1.32294700
C	2.86413700	0.10105900	1.08368100	H	-1.36542100	-0.27699500	-5.06959300
C	-2.82250200	-0.24303900	1.12344400	C	-2.39372200	-0.20387400	2.43909000
C	1.10940000	-0.13601300	-2.85948300	C	2.42603700	-0.03634900	-2.44735000
C	-2.83502600	-0.24408700	-1.08953500	C	-2.42510900	-0.23639700	-2.41482300
C	-1.10968400	-0.22005100	-2.84302300	C	2.45031000	0.11536000	2.40653900
C	-0.64197800	-0.05797400	4.23127900	H	-3.15301900	-0.24544900	3.21287900
C	4.23524600	0.13383300	-0.71396400	H	3.18895100	-0.00503800	-3.21806900
C	0.72008300	0.03762300	4.22224000	H	-3.19762400	-0.26330800	-3.17587300
C	4.24266600	0.17566600	0.65107100	H	3.21927300	0.18496000	3.16876000
C	-4.20676200	-0.32001200	0.70771000	O	-0.07348200	1.68821900	-0.06686200
C	0.67333100	-0.18718800	-4.23755200	S	-0.04648100	-2.54198600	-0.25218600
C	-4.21478500	-0.31555300	-0.65682400	H	1.16753500	-2.70810500	-0.89321100

^{4}Cpd I

Fe	0.00747100	0.04203600	-0.00389900	C	-0.69043000	-0.24163100	-4.22787700
N	0.02469100	-0.04563800	2.00900400	H	-1.30729800	-0.08844500	5.08100400
N	2.02579300	0.01023900	-0.01995900	H	5.07732300	0.17388800	-1.39199400
N	-1.99505400	-0.19922300	0.00735100	H	1.39504100	0.09236000	5.06236300
N	0.00449100	-0.16885100	-2.01206300	H	5.09050700	0.24410600	1.31474100
C	-1.07081900	-0.10500700	2.84870500	H	-5.04700700	-0.37289200	1.38250000
C	2.85271800	0.03846500	-1.12879700	H	1.33708400	-0.18636900	-5.09026300
C	1.13247100	0.04028500	2.83360600	H	-5.06462500	-0.36618700	-1.32399000
C	2.86357800	0.09692600	1.08126000	H	-1.36509700	-0.28879500	-5.07004500
C	-2.82221300	-0.24172800	1.12134300	C	-2.39392000	-0.20253300	2.43715000
C	1.10917800	-0.13215500	-2.86034400	C	2.42611100	-0.02995100	-2.44974200
C	-2.83616500	-0.24275100	-1.09178000	C	-2.42566500	-0.23589400	-2.41682900
C	-1.10989500	-0.21958800	-2.84399100	C	2.44985700	0.10690400	2.40415300
C	-0.64229400	-0.05541600	4.23051700	H	-3.15378200	-0.24445900	3.21038300
C	4.23590400	0.13783300	-0.71562800	H	3.18813700	0.00137300	-3.22132700
C	0.71994000	0.03596000	4.22109200	H	-3.19750600	-0.26570700	-3.17845100
C	4.24243400	0.17328200	0.64953900	H	3.21935800	0.17269900	3.16620100
C	-4.20643500	-0.32157200	0.70612100	O	-0.06245500	1.69148000	-0.03137000
C	0.67333700	-0.19083700	-4.23809000	S	-0.04460200	-2.52918900	-0.23101700
C	-4.21539200	-0.31719500	-0.65842100	H	1.16105600	-2.69972900	-0.88645100

^{2}TS$_H$ for C-H Cleavage of Cyclohexane

Fe	0.08907900	0.02246400	-0.09063900	H	1.23121400	-0.51870200	-5.19793100
N	0.15115400	0.05703200	1.93167000	H	-5.04601700	-0.20408200	-1.22966300
N	2.09247800	0.05394400	-0.18310400	H	-1.47070900	-0.45300500	-5.07483100
N	-1.93557800	-0.12663200	0.01412100	C	-2.25686700	-0.01056700	2.44850700
N	0.02426600	-0.18986300	-2.08838100	C	2.42804400	-0.24416400	-2.60385500
C	-0.91686400	0.06691900	2.81036900	C	-2.42652300	-0.21301000	-2.39482600
C	2.89399300	-0.07483600	-1.30637800	C	2.58756800	0.24722000	2.22603200
C	1.28756800	0.19383600	2.70891600	H	-2.98997300	0.01085400	3.24826400
C	2.96125300	0.16642600	0.89157400	H	3.16684600	-0.34076900	-3.39273800
C	-2.73110000	-0.08912800	1.14980900	H	-3.22002900	-0.25266800	-3.13408000
C	1.09076900	-0.29147800	-2.96915300	H	3.38406200	0.34115000	2.95732300
C	-2.80507800	-0.16749400	-1.06185800	O	-0.18350000	1.78449100	-0.09755300
C	-1.12232500	-0.24884400	-2.86710700	H	2.50888200	6.03277200	-0.61850800
C	-0.43775000	0.19409900	4.17149600	C	3.12760100	5.13342300	-0.75238600
C	4.29075000	-0.01625700	-0.93098300	C	2.34720100	3.89109500	-0.23020400
C	0.92412500	0.27458500	4.10883200	C	3.48718200	4.97435900	-2.24325900
C	4.33234200	0.13791800	0.42563600	H	4.03420700	5.27651200	-0.14977200
C	-4.13082300	-0.12651900	0.77346000	C	1.13695000	3.64569800	-1.10851800
C	0.60244900	-0.41859900	-4.32520000	H	2.04914800	4.03799600	0.81383600
C	-4.17671100	-0.17012700	-0.58919100	H	3.01682200	3.02092600	-0.26097800
C	-0.76138900	-0.38393400	-4.26292600	C	2.23738800	4.70184300	-3.10337500
H	-1.07169000	0.22171700	5.04580800	H	4.00212800	5.87460500	-2.60461600
H	5.11689100	-0.09453300	-1.62275800	H	4.19441100	4.13867400	-2.35642300
H	1.62802800	0.37967500	4.92161900	C	1.44761400	3.46431000	-2.57889500
H	5.19980400	0.20944200	1.06563300	H	0.52026700	2.51043200	-0.63958600
H	-4.95464900	-0.11506900	1.47222000	H	0.30174600	4.32704300	-0.91167200

H	1.57972600	5.58302100	-3.08278000	H	2.06688900	2.56848700	-2.72459600
H	2.51830500	4.53730700	-4.15207600	S	-0.02884800	-2.43283500	-0.08465700
H	0.53039900	3.32648400	-3.16229700	H	-0.69217500	-2.60421400	1.11532400

$^{4}TS_{H}$ for C-H Cleavage of Cyclohexane

Fe	-0.09347500	-0.05539500	-0.06690300	C	-2.46891100	-0.12539100	2.39099800
N	-0.05146800	-0.00018700	1.93334100	C	2.33418400	-0.32040200	-2.51707700
N	1.95315500	-0.02541500	-0.09958800	C	-2.52789800	-0.29852000	-2.46335200
N	-2.08079000	-0.16578400	-0.04076300	C	2.38048500	0.24739900	2.30798000
N	-0.09695000	-0.29155300	-2.07976000	H	-3.22415900	-0.13732200	3.16921100
C	-1.14293900	-0.02813900	2.78492500	H	3.09088000	-0.40425900	-3.28992000
C	2.77097200	-0.15498000	-1.21115900	H	-3.30496400	-0.34974000	-3.21833100
C	1.06723400	0.17269100	2.74181400	H	3.14879500	0.37412300	3.06325200
C	2.79361200	0.13511700	0.98667600	O	-0.15242200	1.69417600	-0.19384000
C	-2.90012800	-0.17441800	1.07660300	H	2.93632400	5.78818300	-1.01249200
C	1.00748200	-0.37642400	-2.91606000	C	3.32844300	4.86712000	-1.46814900
C	-2.92579800	-0.22699600	-1.14041300	C	2.64629800	3.63597300	-0.80138800
C	-1.20918300	-0.34317800	-2.89707700	C	3.06646800	4.89448500	-2.98758200
C	-0.70043800	0.10955300	4.15548000	H	4.40712400	4.84381400	-1.26359600
C	4.15909400	-0.07052500	-0.80718100	C	1.16975400	3.61912600	-1.14849700
C	0.65859800	0.23983900	4.12822500	H	2.79629400	3.66265800	0.28410500
C	4.17294200	0.11419500	0.54679100	H	3.13182000	2.72435500	-1.17488200
C	-4.28855400	-0.23162800	0.66745700	C	1.55863700	4.85409400	-3.30633100
C	0.56789300	-0.49544200	-4.28997400	H	3.52084400	5.79072800	-3.43113900
C	-4.30441400	-0.25773600	-0.69611600	H	3.55805900	4.02743000	-3.45464600
C	-0.79798200	-0.47024700	-4.27881100	C	0.87488300	3.62642400	-2.63791500
H	-1.35753100	0.11423200	5.01287800	H	0.58825700	2.48876100	-0.65154800
H	4.99946200	-0.14731900	-1.48179100	H	0.57711200	4.34785900	-0.58170900
H	1.33647700	0.36878000	4.95950900	H	1.08267500	5.77535600	-2.93967700
H	5.02683600	0.21720500	1.20056000	H	1.39504300	4.82045200	-4.39167600
H	-5.12640700	-0.24856100	1.34909200	H	-0.20519800	3.64521500	-2.82213400
H	1.22996600	-0.58329400	-5.13910800	H	1.26805100	2.71006900	-3.10072500
H	-5.15807200	-0.30400800	-1.35653600	S	0.18198200	-2.43124700	-0.05684700
H	-1.47679500	-0.53519400	-5.11666200	H	0.85424400	-2.53729800	1.14595300

Part II. Thioanisole sulfoxidation by Cpd I.

Methods.

Cpd I P450 + *p*-X-Thioanisoles: The methods used here were described in the original literature (Ref 5: *Faraday Discuss.*, **2010**, *145*, 49–70). The geometries were optimized with the LACVP**(Fe)/6-31G**(H, C, N, O, S, F) basis set (B1). Single-point energy correction with larger basis set B2 which was LACV3P++** for iron, 6-311++G** for rest atoms.

Cpd I (L) + Thioanisole: The same methods as above. The calculations, except for L = SH, were done for the present paper.

Energies and $BDE_{Fe=O}$

Table S6. Energies (a.u.) and relative energies compared to reactants Δ*E* (kcal/mol) for the key species in sulfoxidation of thioanisole by Cpd I [$(Por)^{+\bullet}Fe^{IV}(O)(L)$] with L = CF_3SO_3, Cl, OAc and OH.

L		B1	B2	B2+ZPE	Δ*E* (B2+ZPE)
	^{2}RC	-2818.202991	-2818.810685	-2818.374472	0.00
CF_3SO_3	$^2TS_{SO}$	-2818.185846	-2818.798977	-2818.362724	7.37
	^{2}PC	-2818.244572	-2818.855475	-2818.416256	-26.22
	^{2}RC	-2316.996325	-2317.414580	-2317.005878	0.00
Cl	$^2TS_{SO}$	-2316.979719	-2317.404180	-2316.995220	6.69
	^{2}PC	-2317.039120	-2317.462791	-2317.051556	-28.66
	^{2}RC	-2085.261959	-2085.720650	-2085.262470	0.00
OAc	$^2TS_{SO}$	-2085.246017	-2085.708740	-2085.250509	7.51
	^{2}PC	-2085.311536	-2085.771742	-2085.310193	-29.95
	^{2}RC	-1932.580661	-1932.998048	-1932.577985	0.00
OH	$^2TS_{SO}$	-1932.574934	-1932.995939	-1932.574372	2.27
	^{2}PC	-1932.645460	-1933.060962	-1932.637173	-37.14

Table S7. $BDE_{Fe=O}$ (kcal/mol) of [$(Por)^{+\bullet}Fe^{IV}(O)(L)$] with L = SH, CF_3SO_3, Cl, OAc or OH.

L	B1	B1+ZPE	B2	B2+ZPE
SH	48.10	45.16	37.57	34.63
CF_3SO_3	49.54	48.48	40.48	39.42
Cl	44.32	42.41	33.05	31.14
OAc	42.10	40.53	33.40	31.83
OH	33.62	31.27	25.64	23.30

Cartesian coordinates of various species.

A. L = CF_3SO_3

^{2}RC

Fe	-0.12466000	0.11134800	-0.01683000	C	-2.49079800	-0.39979400	-2.42831500
N	-0.13193100	0.13314900	2.00805100	C	2.24283500	0.58547900	2.39914300
N	1.88626000	0.32618500	-0.00725400	H	-3.27094700	-0.42362600	3.16236100
N	-2.11183600	-0.27222100	-0.01484800	H	3.08935100	0.12816800	-3.16594500
N	-0.09563200	-0.10208600	-2.02804600	H	-3.24209300	-0.53367700	-3.20003900
C	-1.21663800	-0.05801500	2.83178900	H	2.98569100	0.76294900	3.16896100
C	2.71768600	0.31344700	-1.08224600	O	-0.37338300	1.71749700	-0.11435500
C	0.92585000	0.35714200	2.82793600	S	1.93522500	4.05488000	2.75681800
C	2.68570300	0.54678300	1.08609300	C	0.15190600	3.95641600	2.38147500
C	-2.92762400	-0.37627900	1.06580600	H	-0.33981500	3.80033300	3.34414600
C	1.00971800	-0.06578000	-2.84233100	H	-0.19536900	4.89618600	1.94648600
C	-2.92511600	-0.40420400	-1.11518300	H	-0.08037300	3.12162900	1.71666700
C	-1.16020700	-0.28330000	-2.85017500	C	2.67916100	4.42529800	1.17914500
C	-0.81672300	0.04834000	4.21422600	C	3.95664100	5.01003800	1.20343600
C	4.08385600	0.53450100	-0.67336400	C	2.07410800	4.13413600	-0.05234900
C	0.51870100	0.31308700	4.21249900	C	4.61902900	5.29691200	0.01219300
C	4.06253200	0.68836100	0.67905900	H	4.42115400	5.25023500	2.15582400
C	-4.29613200	-0.57929100	0.65666900	C	2.74389900	4.43948300	-1.23911800
C	0.61931200	-0.23181500	-4.22236600	H	1.10251600	3.65475100	-0.09916400
C	-4.29522900	-0.59043100	-0.70408300	C	4.01369400	5.01797600	-1.21609100
C	-0.73523000	-0.36170800	-4.22777300	H	5.60469000	5.75280400	0.04455200
H	-1.48033200	-0.07197200	5.05986200	H	2.26365800	4.21498500	-2.18756900
H	4.93231800	0.56832100	-1.34323500	H	4.52633700	5.25306600	-2.14423100
H	1.18022200	0.45803700	5.05581800	O	0.32866900	-1.88749700	0.12285800
H	4.88957500	0.87192700	1.35117600	S	-0.59158800	-3.10263900	0.04040300
H	-5.13076700	-0.70526700	1.33278400	C	0.69896600	-4.43443900	0.17045400
H	1.30298300	-0.24819400	-5.06042100	F	1.58446700	-4.33630200	-0.83130600
H	-5.12857000	-0.73006500	-1.37913300	F	0.11361900	-5.63734300	0.10575700
H	-1.39625100	-0.51161500	-5.07058200	F	1.35856100	-4.34237200	1.33328200
C	-2.50926300	-0.29343000	2.40021600	O	-1.20658900	-3.28236200	-1.28217300
C	2.31140000	0.12195200	-2.40869800	O	-1.44546700	-3.27012400	1.22449300

^{2}TS$_{SO}$

Fe	0.14693700	-0.01304100	0.01706900	C	0.85399800	-0.14612400	4.21273000
N	0.15144600	-0.05798000	2.01760200	C	4.37516500	-0.20074000	0.65559200
N	2.16655500	-0.15475500	-0.00901800	C	-4.06987100	-0.12608700	0.70319800
N	-1.86608100	-0.02610700	0.02833700	C	0.80450100	-0.10531500	-4.22267000
N	0.13850200	-0.09895000	-2.01447500	C	-4.06914500	-0.01873500	-0.65401800
C	-0.93846800	-0.16014900	2.85094800	C	-0.54976300	0.01485400	-4.21270000
C	2.97563200	-0.24410200	-1.10691500	H	-1.17168600	-0.29074900	5.07486600
C	1.25604100	-0.07290600	2.82997000	H	5.19883000	-0.36118200	-1.38267600
C	2.99587000	-0.12650500	1.07800700	H	1.53736100	-0.17569000	5.05128700
C	-2.68902000	-0.12826100	1.11884800	H	5.22555200	-0.20317000	1.32446100
C	1.22671000	-0.16721100	-2.84333300	H	-4.91506900	-0.20375200	1.37412500
C	-2.68793400	0.02779500	-1.06742800	H	1.47207600	-0.15616300	-5.07231100
C	-0.95608600	0.01382500	-2.82687500	H	-4.91381500	0.00161700	-1.32971600
C	-0.50765000	-0.20772400	4.22467700	H	-1.22853900	0.07915200	-5.05259500
C	4.36171200	-0.28128000	-0.70210500	C	-2.26278600	-0.19891100	2.43983500

C	2.54652100	-0.26034500	-2.42855900	C	2.44452600	4.26649000	3.66960200
C	-2.27267400	0.08125500	-2.39185800	H	0.82694500	2.85058900	3.80251900
C	2.57913400	-0.06924300	2.40065000	C	2.52078200	5.60500400	1.65873000
H	-3.02391100	-0.28426800	3.20848100	H	0.98173200	5.24264600	0.20816600
H	3.30723200	-0.33410600	-3.19857600	C	3.05739800	5.26013100	2.90140400
H	-3.04542900	0.13159300	-3.15199700	H	2.85717000	3.99156800	4.63564900
H	3.34863000	-0.07180500	3.16597600	H	2.99617200	6.37189700	1.05448100
O	0.25313700	1.61650500	-0.13944500	H	3.94845100	5.76079000	3.26737700
S	-0.68640400	3.09010200	1.46585900	O	0.10639600	-2.02337900	0.15105700
C	-1.28882900	3.97685500	0.00423100	S	-0.05244000	-3.11197600	-0.91396100
H	-2.21668500	3.47650600	-0.27644300	C	-0.04940100	-4.58211700	0.22570000
H	-1.48612300	5.02399700	0.24270200	F	-0.18846200	-5.70532500	-0.49170100
H	-0.57191300	3.87242100	-0.81129400	F	1.10193700	-4.65155200	0.90739500
C	0.75604500	3.97865900	1.95636900	F	-1.06091900	-4.50834800	1.10199500
C	1.30100000	3.62383600	3.20525200	O	-1.37400100	-3.11431300	-1.55315900
C	1.37748900	4.96895800	1.17889400	O	1.13193100	-3.27871500	-1.76455400

^{2}PC

Fe	0.11802300	-0.14431100	-0.04438900	C	-2.42190900	0.07842800	-2.29889700
N	0.21501600	-0.16084000	1.97925100	C	2.65391000	-0.33462900	2.22247100
N	2.12081800	-0.19190200	-0.17436300	H	-2.90008000	-0.23812400	3.34025800
N	-1.89134500	-0.00230900	0.10083200	H	3.12596700	-0.09026600	-3.41806800
N	0.01859500	-0.04804700	-2.04815100	H	-3.23096800	0.11967500	-3.02077000
C	-0.83033700	-0.22282200	2.87189400	H	3.46389800	-0.43037300	2.93825200
C	2.88843800	-0.17831700	-1.31197900	O	0.27117100	1.84315500	-0.11041700
C	1.36131400	-0.28581400	2.72658600	S	-0.44951100	2.69651100	0.97955900
C	2.99610000	-0.29398400	0.87710800	C	-1.17319600	4.02586300	-0.03523600
C	-2.66234600	-0.08048800	1.23746800	H	-1.97468700	3.56694300	-0.61712700
C	1.05996500	-0.03364400	-2.94261200	H	-1.57151700	4.80218700	0.62186500
C	-2.76989700	0.04056900	-0.95499600	H	-0.39740600	4.42260700	-0.69215700
C	-1.12734400	0.03810500	-2.79637200	C	0.88093400	3.62691700	1.77877800
C	-0.32745800	-0.35349100	4.21598300	C	0.58877800	4.35973400	2.93156100
C	4.28580000	-0.26615800	-0.96943000	C	2.17108800	3.56349500	1.25395400
C	1.03128000	-0.39096500	4.12616700	C	1.61408900	5.07258400	3.55374200
C	4.35334000	-0.34095900	0.38785300	H	-0.41641100	4.37135200	3.34487600
C	-4.06012800	-0.05483800	0.88962400	C	3.18811500	4.27573200	1.89228800
C	0.55649600	0.05669700	-4.29108300	H	2.36298400	2.95262000	0.37839200
C	-4.12704900	0.02292400	-0.46899600	C	2.91041200	5.03112900	3.03361300
C	-0.79987200	0.09991900	-4.20075700	H	1.40268300	5.64931800	4.44894200
H	-0.94657700	-0.42000500	5.10105800	H	4.19907300	4.23454300	1.49840000
H	5.09462400	-0.28116400	-1.68789900	H	3.70703000	5.58078100	3.52600100
H	1.75659800	-0.49445600	4.92260200	O	-0.04441400	-2.03683300	0.06058300
H	5.23010900	-0.42814300	1.01613200	S	0.19169400	-3.10936200	-1.03509900
H	-4.87249900	-0.10361600	1.60290600	C	0.09040800	-4.58541900	0.09573200
H	1.17545600	0.07436600	-5.17821800	F	0.25913000	-5.70011200	-0.62750300
H	-5.00590800	0.04834300	-1.09985000	F	1.04700700	-4.53104200	1.02991100
H	-1.52809700	0.16013600	-4.99875000	F	-1.10158200	-4.64124600	0.69953900
C	-2.17596700	-0.17597400	2.53448000	O	-0.93951900	-3.23264900	-1.95694800
C	2.40411500	-0.09104300	-2.60843400	O	1.55270300	-3.11460000	-1.57605000

B. L = Cl

^{2}RC

Fe	-0.04070000	0.02623100	-0.00434200	H	-1.39247900	-0.27994600	-5.07047700
N	-0.03660600	-0.02200500	2.01776900	C	-2.44627100	-0.16940800	2.41496500
N	1.98009900	0.00740700	-0.00388100	C	2.37641500	-0.10325800	-2.41450600
N	-2.05672300	-0.14923500	0.00019600	C	-2.45110400	-0.19782500	-2.41327300
N	-0.03784000	-0.11868000	-2.02166400	C	2.37412200	0.12858200	2.40694000
C	-1.12637000	-0.08926200	2.84343800	H	-3.21221100	-0.21652000	3.18318600
C	2.80508700	-0.03664000	-1.09342400	H	3.14459800	-0.13080100	-3.18135300
C	1.05047000	0.05634000	2.83889400	H	-3.21841600	-0.24240700	-3.18024200
C	2.80309400	0.08231900	1.08355000	H	3.13987800	0.19726000	3.17213600
C	-2.87690300	-0.19680900	1.09074200	O	-0.10699400	1.66218900	-0.04409400
C	1.05237700	-0.13969400	-2.84400100	S	2.54613500	3.75237400	2.75741900
C	-2.87988700	-0.19984700	-1.08966300	C	0.74413700	3.77345500	2.46159700
C	-1.12810300	-0.17310000	-2.84378500	H	0.28562000	3.60986500	3.43952000
C	-0.71430700	-0.05586000	4.22645900	H	0.43494500	4.74756600	2.07619800
C	4.18906800	0.00606500	-0.68347200	H	0.43157200	2.97999800	1.77911100
C	0.64345200	0.03940800	4.22373800	C	3.23446500	4.12847800	1.15307800
C	4.18775500	0.08567100	0.67382600	C	4.51658300	4.70111600	1.12931000
C	-4.25935900	-0.28112900	0.68280400	C	2.57969700	3.84782800	-0.05522900
C	0.64318200	-0.20918300	-4.22695300	C	5.13659900	4.98493400	-0.08587400
C	-4.26136600	-0.28016900	-0.67783800	H	5.01928500	4.93359600	2.06403300
C	-0.71733000	-0.22694300	-4.22694800	C	3.20587500	4.15235100	-1.26598100
H	-1.38646700	-0.10318500	5.07276400	H	1.60142400	3.37847800	-0.06651300
H	5.03404900	-0.01741000	-1.35821300	C	4.48172100	4.71757900	-1.29065500
H	1.31987300	0.08743200	5.06639700	H	6.12772300	5.43032700	-0.08968700
H	5.03061200	0.14124300	1.34909900	H	2.68657500	3.93689100	-2.19592000
H	-5.10132300	-0.33626200	1.35974000	H	4.96048100	4.95103600	-2.23725800
H	1.31944300	-0.24346300	-5.07057000	Cl	0.04344300	-2.37287700	0.04624000
H	-5.10516600	-0.33581400	-1.35242700				

$^2TS_{SO}$

Fe	-0.00502300	0.00404000	0.01282300	H	1.35274500	-0.07642600	5.08100200
N	0.00231000	-0.00937500	2.02939800	H	5.05542200	-0.07066400	1.34640900
N	1.99562500	0.01245800	0.01157500	H	-5.07780600	-0.13875000	1.38433900
N	-2.03331100	-0.13328400	0.01745300	H	1.32075400	-0.14273900	-5.06310900
N	-0.02071300	-0.12869300	-2.00712600	H	-5.08485600	-0.31366300	-1.32120700
C	-1.09539500	-0.00796000	2.84916200	H	-1.38459400	-0.33020100	-5.04544500
C	2.81114100	0.00895700	-1.09043100	C	-2.42041000	-0.02188600	2.43196100
C	1.09531900	-0.03993900	2.85324600	C	2.38773900	-0.00585100	-2.41379200
C	2.82802300	-0.02923600	1.10417400	C	-2.43674000	-0.28131900	-2.39364500
C	-2.84949200	-0.08792300	1.11343200	C	2.41798900	-0.05308500	2.42894200
C	1.06713400	-0.08245300	-2.83327200	H	-3.18354400	-0.01180700	3.20377000
C	-2.85576300	-0.22403400	-1.07213400	H	3.15515800	0.00564800	-3.18109200
C	-1.11601300	-0.22782500	-2.81946700	H	-3.20373600	-0.36080600	-3.15735000
C	-0.68189800	-0.02257000	4.23243800	H	3.18936800	-0.08500900	3.19150300
C	4.19543800	-0.00812200	-0.68388200	O	-0.20198200	1.63459800	-0.08900100
C	0.67885000	-0.04867700	4.23491900	S	1.36863900	3.27107800	0.76684100
C	4.20532000	-0.03654300	0.67786500	C	-0.15256800	4.11103900	1.28436600
C	-4.23517200	-0.15136200	0.70562700	H	-0.45209400	3.61982100	2.21110300
C	0.64929300	-0.15539000	-4.21477500	H	0.03148100	5.17196500	1.46679500
C	-4.23864000	-0.24089700	-0.65085200	H	-0.93254900	3.95422900	0.53836300
C	-0.70692100	-0.25091500	-4.20567700	C	1.86571300	4.12804100	-0.69461600
H	-1.35887900	-0.02825700	5.07657200	C	3.12512600	3.77584800	-1.21618300
H	5.03611600	-0.01997600	-1.36521400	C	1.08790200	5.09575000	-1.34955000

C	3.59801400	4.39671800	-2.36813400	H	4.57217100	4.12180000	-2.76166400
H	3.72421100	3.01938200	-0.71766800	H	0.96970900	6.46080100	-3.00116800
C	1.57603900	5.71102700	-2.50139400	H	3.20116300	5.85206900	-3.91207100
H	0.10951000	5.36909100	-0.97266600	Cl	0.02180700	-2.34889500	0.05752600
C	2.82854000	5.36810700	-3.01450200				

^{2}PC

Fe	-0.08974800	-0.19965300	-0.11914500	H	-1.73010700	-0.66434700	-5.08100800
N	0.05167100	0.03895600	1.88597900	C	-2.34869000	0.15889300	2.40616800
N	1.92676600	-0.20185200	-0.21152700	C	2.17824500	-0.41841800	-2.64653100
N	-2.09787100	-0.10161300	-0.02389100	C	-2.65424300	-0.37234700	-2.39453400
N	-0.21903000	-0.33881800	-2.12071900	C	2.48254300	-0.12252200	2.17773100
C	-1.00466600	0.13489400	2.75973700	H	-3.07190500	0.24393100	3.21118800
C	2.67723000	-0.32935100	-1.35376400	H	2.89962600	-0.51331800	-3.45186900
C	1.18600900	-0.00855800	2.66191500	H	-3.46490800	-0.45738200	-3.11093300
C	2.81899500	-0.21180600	0.83382200	H	3.29027900	-0.14991000	2.90196200
C	-2.84654300	0.03523300	1.11495000	O	-0.14673900	1.81738300	-0.38041100
C	0.83308000	-0.43471100	-2.99221500	S	0.78300800	2.72756800	0.46839600
C	-2.99039500	-0.21771800	-1.05684500	C	-0.38991300	3.70624600	1.46786100
C	-1.35577200	-0.42608100	-2.88141600	H	-0.83609500	3.01326200	2.18351100
C	-0.52039900	0.18181700	4.11828900	H	0.15665900	4.49742600	1.98634400
C	4.08036900	-0.39248800	-1.02143800	H	-1.15144600	4.12105700	0.80513600
C	0.83757800	0.08737200	4.05711700	C	1.30752600	4.01539100	-0.69034800
C	4.16782200	-0.32441500	0.33541400	C	2.33172300	4.88536700	-0.30933600
C	-4.25471800	0.01638100	0.78983300	C	0.71042100	4.09113800	-1.94815500
C	0.34639600	-0.57526000	-4.34585200	C	2.74408000	5.87477500	-1.20265000
C	-4.34361500	-0.14466600	-0.55803500	H	2.80768200	4.79097200	0.66334100
C	-1.01225700	-0.57331100	-4.27633700	C	1.13866200	5.08089800	-2.83476000
H	-1.15127200	0.25844100	4.99440400	H	-0.05822200	3.37403600	-2.21656300
H	4.87971900	-0.48950700	-1.74453000	C	2.14737500	5.97234400	-2.46231800
H	1.54956500	0.07409200	4.87206800	H	3.53736500	6.55981200	-0.91930100
H	5.05350000	-0.35264100	0.95664500	H	0.68522600	5.15189800	-3.81887700
H	-5.05466800	0.10630400	1.51322400	H	2.47688900	6.73844700	-3.15783000
H	0.97754100	-0.67047400	-5.21982300	Cl	-0.14375200	-2.45034700	0.09563900
H	-5.23141500	-0.21188600	-1.17307700				

C. L = OAc

^{2}RC

Fe	0.04640500	0.01314700	-0.09514400	C	4.27809400	0.06909800	-0.75308900
N	0.04719300	-0.04801800	1.92886200	C	0.71256800	0.01722800	4.13581700
N	2.06974800	0.05879100	-0.08458300	C	4.26892900	0.21443000	0.60019200
N	-1.96161300	-0.18771800	-0.10677100	C	-4.16272800	-0.37215300	0.56324400
N	0.05170800	-0.08583300	-2.11014900	C	0.74386900	-0.12451600	-4.31332700
C	-1.03742300	-0.22487600	2.74411600	C	-4.16749700	-0.21556700	-0.78802600
C	2.89658700	-0.01854600	-1.16535300	C	-0.61390200	-0.03795900	-4.31853600
C	1.12200300	0.09395300	2.75347300	H	-1.30136500	-0.31260700	4.97241000
C	2.88321200	0.19377300	1.00579800	H	5.12735400	0.03462800	-1.42216600
C	-2.77806100	-0.33381600	0.97561300	H	1.37872100	0.10339000	4.98372700
C	1.14886500	-0.13467000	-2.92637600	H	5.10850600	0.31990400	1.27376600
C	-2.78622500	-0.11028100	-1.19588100	H	-5.00421200	-0.49253600	1.23234500
C	-1.03155500	-0.02314200	-2.93596100	H	1.42128400	-0.16765500	-5.15566900
C	-0.63346400	-0.19322200	4.12972600	H	-5.01369300	-0.19050500	-1.46136800

H	-1.28461500	-0.00468300	-5.16656500	C	2.55169600	3.86914000	-0.07674400
C	-2.34787700	-0.37580900	2.30179900	C	5.05577400	5.11897500	-0.02622900
C	2.46901600	-0.12777600	-2.48951200	H	4.84665200	5.11099200	2.11762500
C	-2.35788700	0.01121500	-2.51099200	C	3.21581000	4.17522300	-1.26663700
C	2.44384600	0.24619200	2.32519200	H	1.59705900	3.35446800	-0.11775100
H	-3.11272100	-0.50199000	3.06237100	C	4.46590500	4.79588800	-1.25067800
H	3.24040900	-0.17417000	-3.25245700	H	6.02575500	5.60802100	0.00110900
H	-3.12287500	0.07451200	-3.27860400	H	2.74780900	3.91545300	-2.21233800
H	3.20040400	0.36104600	3.09403100	H	4.97484400	5.02897600	-2.18153400
O	-0.06109400	1.65069200	-0.12032000	O	0.30163700	-1.96025200	0.05065600
S	2.40124200	3.83115400	2.73276500	C	-0.32091800	-2.90350200	-0.58770900
C	0.61068900	3.80262900	2.37141300	O	-1.21804300	-2.77142100	-1.42060300
H	0.12195500	3.63889300	3.33464500	C	0.17456800	-4.30293800	-0.20174200
H	0.29231700	4.76479000	1.96412300	H	1.24809300	-4.38156700	-0.39867100
H	0.34218500	2.99438400	1.68741600	H	0.02929600	-4.46131700	0.87135100
C	3.14048900	4.20683200	1.15093700	H	-0.36385300	-5.06611200	-0.76527200
C	4.39619100	4.83535300	1.16813300				

$^2TS_{SO}$

Fe	-0.00016000	0.01678800	0.06228500	C	-2.40322500	0.02957400	-2.36615300
N	-0.01953300	-0.06624900	2.08985000	C	2.38603700	0.07629000	2.50549200
N	2.00883500	0.05298100	0.08237200	H	-3.20561500	-0.35355600	3.21194400
N	-2.02702000	-0.12775900	0.04384600	H	3.20160300	-0.08969100	-3.08880400
N	0.01007600	-0.04249400	-1.95303700	H	-3.16256500	0.07612500	-3.14045500
C	-1.11688900	-0.18689700	2.89537800	H	3.14792100	0.10578900	3.27847300
C	2.84137200	-0.00772800	-1.00047000	O	-0.20169600	1.65497100	0.06520800
C	1.05994500	-0.00706900	2.92312100	S	1.51173600	3.47099000	0.25601600
C	2.82229200	0.07816000	1.18626100	C	-0.01272300	4.40416500	0.56461300
C	-2.85375400	-0.21913100	1.12757900	H	-0.34072700	4.09873600	1.55866900
C	1.10768700	-0.06315900	-2.76755600	H	0.17642100	5.47980600	0.54870500
C	-2.84059400	-0.05492900	-1.05118300	H	-0.78186800	4.11708800	-0.15369500
C	-1.07624300	0.00283200	-2.77978900	C	2.07426700	4.08478600	-1.30272100
C	-0.71997900	-0.19927300	4.28430500	C	3.34532900	3.64705000	-1.72538800
C	4.22124700	0.00100300	-0.57488500	C	1.33333300	4.94111800	-2.13416400
C	0.63645200	-0.08128600	4.30197100	C	3.86306900	4.07300100	-2.94479000
C	4.20884000	0.06234100	0.78584400	H	3.92125100	2.97956100	-1.09108300
C	-4.23758400	-0.21952700	0.70510400	C	1.86473100	5.36113600	-3.35310300
C	0.70460300	-0.04691300	-4.15514000	H	0.34695900	5.27924100	-1.83951900
C	-4.22856500	-0.10592200	-0.64940100	C	3.12828700	4.93382700	-3.76509800
C	-0.65431800	0.00535300	-4.16169800	H	4.84778200	3.73412300	-3.25428900
H	-1.40064900	-0.28789900	5.12073500	H	1.28273200	6.02632300	-3.98481700
H	5.07316400	-0.04469700	-1.24055100	H	3.53566900	5.26607100	-4.71508600
H	1.30081600	-0.05597000	5.15562700	O	0.16985400	-1.94900300	0.16438000
H	5.04834600	0.07752700	1.46830600	C	-0.45799500	-2.89100700	-0.48106000
H	-5.08656700	-0.29366800	1.37170800	O	-1.32571900	-2.76135200	-1.34008800
H	1.38490600	-0.06667900	-4.99610200	C	0.01380000	-4.28717800	-0.05197500
H	-5.06896200	-0.07422400	-1.32998200	H	1.08945700	-4.38693100	-0.22747400
H	-1.32482600	0.02930600	-5.01037200	H	-0.15281100	-4.42123400	1.02142300
C	-2.43431900	-0.26788500	2.45246300	H	-0.52569900	-5.05399500	-0.60993500
C	2.42653600	-0.05950400	-2.32934400				

^2PC

Fe	-0.05243100	-0.18206800	-0.07899400	N	1.97983800	-0.18069700	-0.08375900
N	0.00270400	-0.00938100	1.94452700	N	-2.05145300	-0.04519500	-0.06429900

N	-0.08141800	-0.21010000	-2.08401800	H	-3.17619400	0.09421900	3.13816400
C	-1.08854800	0.03160000	2.77597100	H	3.08589700	-0.48762500	-3.28119400
C	2.77917600	-0.32476800	-1.19074100	H	-3.27042100	-0.00660600	-3.23267800
C	1.10498600	-0.06317100	2.76250200	H	3.19738400	-0.19781600	3.09016400
C	2.82133100	-0.22166800	1.00212000	O	-0.09153500	1.87225400	-0.25076700
C	-2.85190400	0.02297500	1.04524800	S	0.93445400	2.73047700	0.53227000
C	1.00583700	-0.32231200	-2.91066600	C	-0.11336500	4.06321000	1.20652400
C	-2.89209200	-0.00836200	-1.14589300	H	-0.73710400	3.60431400	1.97592300
C	-1.18071300	-0.15402900	-2.90129200	H	0.52130200	4.83941400	1.64004100
C	-0.66213100	0.03538400	4.15500800	H	-0.72988800	4.46172500	0.39894900
C	4.16314900	-0.42504600	-0.79464600	C	1.80841600	3.68132100	-0.74027400
C	0.69894500	-0.02402100	4.14634900	C	2.90008000	4.47047400	-0.37037000
C	4.18922700	-0.36062200	0.56570500	C	1.40268000	3.56675100	-2.06886100
C	-4.24118300	0.09468100	0.65221700	C	3.57964100	5.18659700	-1.35616300
C	0.57961000	-0.34033100	-4.29143100	H	3.22331100	4.52350000	0.66617500
C	-4.26461700	0.08118500	-0.70773600	C	2.09679000	4.28339100	-3.04593400
C	-0.77668100	-0.22885600	-4.28467800	H	0.57101300	2.91593900	-2.31761100
H	-1.32973000	0.06784100	5.00638900	C	3.17734800	5.09359900	-2.69132400
H	4.99309100	-0.53890400	-1.47994700	H	4.42815900	5.80675500	-1.08331800
H	1.37792500	-0.04920900	4.98888300	H	1.79398600	4.20277500	-4.08562200
H	5.04482800	-0.41124600	1.22664500	H	3.71457700	5.64604000	-3.45653800
H	-5.07356800	0.15018600	1.34171700	O	0.01938900	-2.01770400	0.13869000
H	1.24578100	-0.42809600	-5.13991700	C	-0.68827500	-2.95107400	-0.47601400
H	-5.12034900	0.12022400	-1.36885200	O	-1.53568300	-2.79120300	-1.33927900
H	-1.45676900	-0.20942700	-5.12616400	C	-0.30765700	-4.33859000	0.03863000
C	-2.41590300	0.05275700	2.36443500	H	0.75858900	-4.51945400	-0.12856200
C	2.33394100	-0.38333700	-2.50538400	H	-0.48090600	-4.39755700	1.11755000
C	-2.49525000	-0.04108500	-2.47417500	H	-0.89881300	-5.09789300	-0.47527200
C	2.42268200	-0.15471300	2.33111800				

D. L = OH

^{2}RC

Fe	0.04253100	0.00713800	0.02958600	H	-1.40216700	0.05673000	5.09181900
N	-0.00051100	0.07058400	2.05748400	H	5.12276900	0.24981500	-1.24593700
N	2.05001100	0.14301100	0.05791700	H	1.28937400	0.38645600	5.11923100
N	-1.97234700	-0.28168400	0.00720800	H	5.06325300	0.50170200	1.45233200
N	0.07703500	-0.16247600	-1.99621800	H	-5.03698100	-0.50471000	1.31657800
C	-1.10262800	-0.01886600	2.86555800	H	1.48935700	-0.29053800	-5.02021800
C	2.89187900	0.10638200	-1.01512200	H	-4.98903000	-0.60321500	-1.39166800
C	1.06284700	0.23983300	2.88837000	H	-1.21441000	-0.47592700	-5.06151600
C	2.84534200	0.30077800	1.15561500	C	-2.40598700	-0.19355900	2.41586200
C	-2.81207400	-0.30717500	1.08501200	C	2.49099200	-0.02805100	-2.34223700
C	1.17974000	-0.14681700	-2.79765600	C	-2.32025900	-0.39448000	-2.41505900
C	-2.77344700	-0.38983800	-1.09729500	C	2.39010100	0.36765900	2.46963100
C	-0.99480600	-0.30050800	-2.83055900	H	-3.18522900	-0.23906200	3.17110300
C	-0.71845800	0.09861600	4.25430100	H	3.27568000	-0.03734200	-3.09298600
C	4.26583700	0.24493900	-0.58583500	H	-3.07306100	-0.49396300	-3.19161200
C	0.63258700	0.26321200	4.26856000	H	3.13821700	0.50442300	3.24340000
C	4.23634900	0.37172700	0.76741400	O	-0.16057800	1.65417100	-0.07787900
C	-4.18233900	-0.45290000	0.65517900	S	2.18095800	3.93342500	2.69851000
C	0.79869000	-0.27398500	-4.18760000	C	0.39343900	3.80626300	2.34666100
C	-4.15826900	-0.50186000	-0.70604000	H	-0.07892500	3.60880200	3.31181000
C	-0.55811500	-0.36627300	-4.20840300	H	0.02089000	4.75239000	1.94775500

H	0.16723200	2.98822000	1.65645600	H	1.39421000	3.36288000	-0.13836800
C	2.89307900	4.32340000	1.10839600	C	4.17563200	4.94383300	-1.30727800
C	4.11215600	5.02084600	1.11036000	H	5.69197000	5.86393100	-0.07651900
C	2.31876700	3.93189100	-0.11043800	H	2.50642500	3.95233000	-2.24678500
C	4.75085300	5.32087900	-0.09120700	H	4.66748800	5.18924300	-2.24422000
H	4.54972900	5.33618300	2.05351600	O	0.27755900	-1.87997100	0.11422000
C	2.96200400	4.25401900	-1.30747800	H	-0.59310700	-2.29076500	0.19994900

$^{2}TS_{SO}$

Fe	-0.02673000	0.02455300	0.02099300	H	-1.49377100	-0.17163900	-5.00179200
N	-0.00260600	-0.03836400	2.05637200	C	-2.42151600	0.00992300	2.49806600
N	1.97084700	0.07085600	-0.00890700	C	2.33630400	-0.02259600	-2.43627400
N	-2.07033700	0.01831500	0.06954100	C	-2.50533200	-0.05054000	-2.34191500
N	-0.07187400	-0.04494400	-1.98938500	C	2.42102300	0.06768200	2.40874700
C	-1.09018600	-0.00877900	2.89356200	H	-3.17335500	0.02087400	3.28038600
C	2.77199700	0.04160500	-1.12094800	H	3.09208200	-0.04039700	-3.21421800
C	1.10823000	0.01848000	2.85757900	H	-3.28372100	-0.07569600	-3.09750000
C	2.80892500	0.08398100	1.07654000	H	3.20590300	0.09534700	3.15734900
C	-2.86717700	0.02342400	1.18338400	O	-0.23163100	1.71180200	0.06988300
C	1.00673400	-0.06759300	-2.83060300	S	1.76323500	3.60230400	-0.02506700
C	-2.90584300	-0.00367400	-1.01384400	C	0.38148600	4.59395800	0.63890900
C	-1.18893200	-0.07821300	-2.78183600	H	0.30945300	4.35354800	1.70131600
C	-0.64834500	0.02731400	4.26686800	H	0.57627000	5.66064100	0.50863800
C	4.15987400	0.06295600	-0.72572800	H	-0.54509000	4.30018200	0.14565500
C	0.71319400	0.04582600	4.24467200	C	1.67763300	4.02393200	-1.76707300
C	4.18279200	0.08980600	0.63425500	C	2.71211000	4.77049400	-2.34486700
C	-4.25685600	0.01630900	0.78944300	C	0.60775900	3.57826400	-2.55529000
C	0.56037200	-0.12683300	-4.20212700	C	2.66953200	5.08076600	-3.70579000
C	-4.28075000	-0.00081500	-0.57127200	H	3.54048900	5.10829200	-1.72974200
C	-0.80021700	-0.13273300	-4.17199700	C	0.56878900	3.90137400	-3.91169600
H	-1.30887400	0.04509100	5.12384200	H	-0.16709300	2.96843000	-2.10221100
H	4.99366000	0.04933800	-1.41518100	C	1.59668900	4.65166500	-4.48892100
H	1.40102200	0.08124500	5.07928500	H	3.47231500	5.66218200	-4.15048100
H	5.03941300	0.10341100	1.29512600	H	-0.25913500	3.55089200	-4.52108900
H	-5.09085300	0.01600800	1.47895500	H	1.56384000	4.89654200	-5.54682900
H	1.21739200	-0.15629100	-5.06123300	O	-0.05695400	-1.79067400	-0.00733000
H	-5.13860500	-0.01877500	-1.23057800	H	-0.16291800	-2.11234300	0.90015000

^{2}PC

Fe	0.00727900	-0.06633400	-0.00872800	C	-0.62953900	-0.25268900	4.22836300
N	0.00984300	-0.06643500	2.01612700	C	4.22673000	-0.05012900	-0.74065800
N	2.02239900	-0.04489600	-0.05015200	C	0.73096200	-0.24763100	4.20273100
N	-2.01897600	0.05518400	0.04090900	C	4.23097500	-0.10467500	0.61942700
N	-0.00095200	0.07048600	-2.02270900	C	-4.22169600	-0.04561100	0.72900400
C	-1.07095300	-0.14690400	2.85605900	C	0.63483700	0.16425700	-4.24176600
C	2.84156000	-0.01175400	-1.14968800	C	-4.22903300	0.04267300	-0.63012300
C	1.12093000	-0.14343400	2.81424200	C	-0.72551900	0.19206400	-4.21183300
C	2.84849600	-0.10140800	1.04208800	H	-1.28771200	-0.32632200	5.08441200
C	-2.83662500	-0.04547800	1.13820800	H	5.07073800	-0.03649500	-1.41808600
C	1.07807200	0.09068200	-2.86851500	H	1.42117500	-0.31718500	5.03354800
C	-2.84727900	0.09024800	-1.05192100	H	5.08001500	-0.14564800	1.28949100
C	-1.11388200	0.13280900	-2.82047600	H	-5.06490200	-0.11285600	1.40430400

H	1.29137400	0.19136200	-5.10175200
H	-5.07969900	0.05956700	-1.29930900
H	-1.41690200	0.24547300	-5.04293300
C	-2.40180700	-0.13416900	2.45573600
C	2.40903700	0.04878700	-2.46941700
C	-2.43266600	0.14437700	-2.37877000
C	2.43803000	-0.14646700	2.36991000
H	-3.15906700	-0.21115500	3.22972100
H	3.16704700	0.06601200	-3.24619800
H	-3.20774500	0.17998500	-3.13837300
H	3.21535500	-0.20244900	3.12579400
O	0.13157700	2.03424300	-0.02030300
S	-0.81166500	2.86913900	0.86263400
C	-1.81474000	3.81188800	-0.33947400
H	-2.45816800	3.08357600	-0.83673900
H	-2.41381600	4.55489400	0.19214300
H	-1.14399400	4.28642100	-1.05808100
C	0.22635400	4.22703900	1.46905400
C	-0.28879900	5.11101600	2.42024000
C	1.53857900	4.32995100	1.01033500
C	0.52357500	6.14057800	2.89618800
H	-1.30396900	4.99765300	2.79225400
C	2.34333400	5.36072100	1.50016400
H	1.90810800	3.60161400	0.29580400
C	1.83702300	6.26573600	2.43538200
H	0.13488500	6.83690400	3.63322000
H	3.36802800	5.45297600	1.15254400
H	2.46844800	7.06385900	2.81446300
O	-0.07769900	-1.84698000	-0.02821300
H	0.55688700	-2.15368700	-0.69361200

Part III. VB modeling of the two reviewed reaction families.

Table S8. *f*, *B*(kcal/mol), promotion gaps G_r and G_p (kcal/mol) modeled by VB theory for alkane hydroxylation and thioether sulfoxidation.

substrate	L	*f*	*B*	G_r [c]	G_p [d]
hydroxylation[a]					
Methane (**1**)				216.82	
Ethane (**2**)				207.74	
i-Propane (**3**)				200.48	
n-Propane (**4**)				208.72	
Propene (**5**)				198.98	
(**6**) *trans*-methyl phenylcyclopropane				203.84	
(**7**) *trans*-*i*-propyl-phenylcyclopropane	SH	0.3	46.78	190.40	208.44
N,*N*-DMA (**8**)				188.04	
Toluene (**9**)				196.14	
Phenylethane (**10**)				201.66	
Camphor (**11**)				203.00	
p-CN-DMA (**12**)				190.14	
p-NO_2-DMA (**13**)				191.40	
p-Cl-DMA (**14**)				187.98	
Cyclohexane (**15**)				200.40	
Cyclohexane	OAc(**16**)			200.40	199.76
Cyclohexane	Cl(**17**)			200.40	192.86
Cyclohexane	CF_3SO_3(**18**)			200.40	188.14
sulfoxidation[b]					
p-MeO-thioanisole	SH	0.2	13.5	96.0/124.9	-
p-Me-thioanisole				103.5/132.4	-
thioanisole				108.8/137.7	-
p-NO_2-thioanisole				124.2/153.1	-

[a] $G_r \approx 2D_{C\text{-}H}$; $G_p \approx 2D_{FeO\text{-}H}$. Data for substrates **1-11** taken from Ref. 14; **12-14** taken from Ref. 23; **15-18** are calculated in the present work.

[b] Data taken from Ref. 5.

[c] G_r in sulfoxidation given in the order G_r (LS)/G_r (HS).

[d] For G_p in sulfoxidation, see discussion Ref. 5.