

# **Propene Activation by the Oxo–Iron Active Species of Taurine/α–Ketoglutarate Dioxygenase (TauD) Enzyme. How Does the Catalysis Compare to Heme–Enzymes?**

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## **Full Reference 31:**

Gaussian 98, Revision A.7, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, Jr., J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A., Gaussian Inc., Pittsburgh, PA, 1998.

**Estimation of the ZPE contribution for  ${}^4\mathbf{4}$  with a polyoxometallate catalyst (POM):**

The difference between  $\Delta E$  and  $\Delta(E+ZPE)$  is compared for different catalysts, whereby  $\Delta E$  the energy difference between reactants and hydroxylation intermediate is. In all cases propene hydroxylation by an oxo-iron catalyst was studied.

		$\Delta E$	$\Delta(E+ZPE)$	difference
$\alpha$ KGD	${}^5\mathbf{4}$	-6.33	-9.35	3.02
P450	${}^4\mathbf{4}$	-1.57	-2.57	1.00
P450	${}^2\mathbf{4}$	-1.60	-2.54	0.94
HRP	${}^4\mathbf{4}$	-0.55	-1.31	0.76
HRP	${}^2\mathbf{4}$	-0.81	-1.35	0.54
CpdICl	${}^4\mathbf{4}$	-0.55	-1.31	0.76
CpdICl	${}^2\mathbf{4}$	-0.81	-1.35	0.54
Average:				1.08

Thus, ZPE correction on the data gives an average lowering of the exothermicity of the hydroxylation intermediate by  $1.08 \text{ kcal mol}^{-1}$ . Based on this the estimated  $\Delta(E+ZPE)$  for  ${}^4\mathbf{4}$  (POM) is  $-5.01 - 1.08 = -6.09 \text{ kcal mol}^{-1}$ .

**Table S1.** Group spin densities and charges of optimized geometries of intermediates in the epoxidation reaction of <sup>5</sup>Cpd I with propene as calculated with UB3LYP/LACVP in Jaguar 6.0.

**(a) Group Spin Densities ( $\rho$ ).**

	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	O	CH <sub>2</sub>	CH	CH <sub>3</sub>
<sup>5</sup> Cpd I	2.95	0.09	-0.01	0.05	0.00	0.14	0.78	0.00	0.00	0.00
<sup>5</sup> <b>TS1</b>	3.67	0.08	0.03	0.12	0.00	0.16	0.19	0.06	-0.31	0.00
<sup>5</sup> <b>2</b>	4.00	0.09	0.05	0.17	0.00	0.19	0.36	0.07	-0.93	0.00
<sup>5</sup> <b>TS2</b>	3.93	0.07	0.05	0.13	0.00	0.15	0.35	0.05	-0.73	0.00
<sup>5</sup> <b>3</b>	3.76	0.04	0.04	0.07	0.00	0.06	0.02	0.01	0.00	0.00

**(b) Group Charges ( $Q$ ).**

	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	O	CH <sub>2</sub>	CH	CH <sub>3</sub>
<sup>5</sup> Cpd I	0.82	0.18	0.23	-0.50	0.02	-0.43	-0.32	-0.07	0.07	0.00
<sup>5</sup> <b>TS1</b>	0.82	0.16	0.19	-0.42	0.00	-0.50	-0.44	0.08	0.11	0.00
<sup>5</sup> <b>2</b>	0.91	0.15	0.19	-0.44	0.00	-0.51	-0.61	0.24	0.07	0.00
<sup>5</sup> <b>TS2</b>	0.88	0.13	0.17	-0.48	0.00	-0.55	-0.57	0.26	0.12	0.04
<sup>5</sup> <b>3</b>	0.84	0.09	0.13	-0.59	0.02	-0.58	-0.50	0.28	0.25	0.06

**(c) Absolute energies (in au) and relative energies (in kcal mol<sup>-1</sup>).**

	<i>E</i>	$\Delta E$
<sup>5</sup> Cpd I	-1414.239857	0.00
<sup>5</sup> <b>TS1</b>	-1414.228790	6.94
<sup>5</sup> <b>2</b>	-1414.254489	-9.18
<sup>5</sup> <b>TS2</b>	-1414.252019	-7.63
<sup>5</sup> <b>3</b>	-1414.295041	-34.63

**Table S2.** Group spin densities and charges of optimized geometries of intermediates in the hydroxylation reaction of <sup>5</sup>Cpd I with propene as calculated with UB3LYP/LACVP in Jaguar 6.0.

(a) Group Spin Densities ( $\rho$ ).

	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	OH	CH <sub>2</sub>	CH	CH <sub>2</sub>
<sup>5</sup> <b>TS3</b>	3.73	0.08	0.04	0.14	0.00	0.19	0.20	-0.20	0.11	-0.29
<sup>5</sup> <b>4</b>	4.03	0.09	0.06	0.19	0.00	0.24	0.38	-0.65	0.29	-0.63
<sup>5</sup> <b>TS4</b>	4.01	0.09	0.06	0.17	0.00	0.20	0.37	-0.59	0.28	-0.59
<sup>5</sup> <b>5</b>	3.77	0.04	0.03	0.07	0.00	0.07	0.02	0.00	0.00	0.00

(b) Group Charges ( $Q$ ).

	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	OH	CH <sub>2</sub>	CH	CH <sub>2</sub>
<sup>5</sup> <b>TS3</b>	0.87	0.17	0.20	-0.42	0.00	-0.48	-0.24	-0.03	0.10	-0.17
<sup>5</sup> <b>4</b>	0.89	0.16	0.19	-0.43	-0.01	-0.50	-0.34	0.00	0.09	-0.05
<sup>5</sup> <b>TS4</b>	0.89	0.16	0.19	-0.44	0.00	-0.51	-0.32	-0.04	0.02	0.05
<sup>5</sup> <b>5</b>	0.81	0.13	0.13	-0.59	0.04	-0.58	-0.25	-0.04	0.08	0.27

(c) Absolute energies (in au) and relative energies (in kcal mol<sup>-1</sup>).

	<i>E</i>	$\Delta E$
<sup>5</sup> Cpd I	-1414.239857	0.00
<sup>5</sup> <b>TS3</b>	-1414.224685	9.52
<sup>5</sup> <b>4</b>	-1414.249931	-6.32
<sup>5</sup> <b>TS4</b>	-1414.245253	-3.39
<sup>5</sup> <b>5</b>	-1414.325154	-53.52

**Table S3.** Group spin densities and charges of single point UB3LYP/LACV3P+\* calculations on UB3LYP/LACVP optimized geometries of intermediates in the epoxidation reaction of <sup>5</sup>Cpd I with propene as calculated with Jaguar 6.0.

**(a) Group Spin Densities ( $\rho$ ).**

	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	O	CH <sub>2</sub>	CH	CH <sub>3</sub>
<sup>5</sup> Cpd I	3.08	0.08	-0.02	0.03	0.00	0.11	0.72	0.00	0.00	0.00
<sup>5</sup> <b>TS1</b>	3.79	0.06	0.02	0.10	0.00	0.13	0.15	0.04	-0.29	0.00
<sup>5</sup> <b>2</b>	4.15	0.07	0.04	0.14	0.00	0.17	0.32	0.05	-0.93	-0.01
<sup>5</sup> <b>TS2</b>	4.08	0.06	0.04	0.11	0.00	0.12	0.31	0.04	-0.75	-0.01
<sup>5</sup> <b>3</b>	3.81	0.03	0.03	0.06	0.01	0.05	0.00	0.01	0.00	0.00

**(b) Group Charges ( $Q$ ).**

	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	O	CH <sub>2</sub>	CH	CH <sub>3</sub>
<sup>5</sup> Cpd I	0.44	0.27	0.27	-0.45	0.05	-0.38	-0.16	-0.11	0.07	0.00
<sup>5</sup> <b>TS1</b>	0.56	0.22	0.16	-0.42	-0.03	-0.45	-0.09	-0.01	0.06	0.00
<sup>5</sup> <b>2</b>	0.76	0.23	0.16	-0.43	-0.02	-0.51	-0.22	0.05	0.00	-0.02
<sup>5</sup> <b>TS2</b>	0.71	0.19	0.11	-0.40	-0.03	-0.58	-0.15	0.09	0.03	0.03
<sup>5</sup> <b>3</b>	0.79	0.14	0.13	-0.60	0.00	-0.62	-0.11	0.12	0.12	0.03

**(c) Absolute energies (in au) and relative energies (in kcal mol<sup>-1</sup>).**

	<i>E</i>	$\Delta E$
<sup>5</sup> Cpd I	-1415.002833	0.00
<sup>5</sup> <b>TS1</b>	-1414.993890	5.61
<sup>5</sup> <b>2</b>	-1415.027604	-15.54
<sup>5</sup> <b>TS2</b>	-1415.023109	-12.72
<sup>5</sup> <b>3</b>	-1415.067632	-40.66

**Table S4.** Group spin densities and charges of single point UB3LYP/LACV3P+\* calculations on UB3LYP/LACVP optimized geometries of intermediates in the hydroxylation reaction of <sup>5</sup>Cpd I with propene as calculated with Jaguar 6.0.

(a) Group Spin Densities ( $\rho$ ).

	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	OH	CH <sub>2</sub>	CH	CH <sub>2</sub>
<sup>5</sup> <b>TS3</b>	3.87	0.07	0.03	0.11	0.00	0.15	0.15	-0.19	0.09	-0.28
<sup>5</sup> <b>4</b>	4.19	0.08	0.05	0.16	0.00	0.17	0.34	-0.62	0.24	-0.61
<sup>5</sup> <b>TS4</b>	4.17	0.07	0.04	0.14	0.00	0.17	0.33	-0.58	0.24	-0.58
<sup>5</sup> <b>5</b>	3.83	0.03	0.03	0.06	0.01	0.04	0.00	0.00	0.00	0.00

(b) Group Charges ( $Q$ ).

	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	OH	CH <sub>2</sub>	CH	CH <sub>2</sub>
<sup>5</sup> <b>TS3</b>	0.70	0.18	0.16	-0.33	0.02	-0.44	-0.08	-0.06	0.09	-0.24
<sup>5</sup> <b>4</b>	0.77	0.22	0.14	-0.38	-0.01	-0.46	-0.24	-0.03	0.10	-0.11
<sup>5</sup> <b>TS4</b>	0.73	0.28	0.16	-0.37	-0.04	-0.54	-0.17	-0.05	0.02	-0.02
<sup>5</sup> <b>5</b>	0.78	0.23	0.03	-0.63	0.06	-0.60	0.08	-0.06	0.05	0.06

(c) Absolute energies (in au) and relative energies (in kcal mol<sup>-1</sup>).

	<i>E</i>	$\Delta E$
<sup>5</sup> Cpd I	-1415.002833	0.00
<sup>5</sup> <b>TS3</b>	-1414.988084	9.26
<sup>5</sup> <b>4</b>	-1415.022970	-12.64
<sup>5</sup> <b>TS4</b>	-1415.017990	-9.51
<sup>5</sup> <b>5</b>	-1415.088922	-54.02

**Table S5.** Group spin densities and charges of single point calculations in a dielectric constant of  $\epsilon = 5.7$  on UB3LYP/LACVP optimized geometries of intermediates in the epoxidation reaction of <sup>5</sup>Cpd I with propene as calculated with Jaguar 6.0.

(a) Group Spin Densities ( $\rho$ ).

	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	O	CH <sub>2</sub>	CH	CH <sub>3</sub>
<sup>5</sup> Cpd I	2.95	0.10	-0.01	0.05	0.00	0.13	0.78	0.00	0.00	0.00
<sup>5</sup> <b>TS1</b>	3.67	0.08	0.04	0.12	0.00	0.15	0.19	0.05	-0.30	0.00
<sup>5</sup> <b>2</b>	4.00	0.10	0.06	0.16	0.00	0.18	0.36	0.07	-0.93	0.00
<sup>5</sup> <b>TS2</b>	3.93	0.07	0.05	0.12	0.00	0.15	0.35	0.05	-0.72	0.00
<sup>5</sup> <b>3</b>	3.76	0.04	0.04	0.07	0.01	0.06	0.02	0.00	0.00	0.00

(b) Group Charges ( $Q$ ).

	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	O	CH <sub>2</sub>	CH	CH <sub>3</sub>
<sup>5</sup> Cpd I	0.81	0.21	0.27	-0.51	0.02	-0.46	-0.35	-0.07	0.08	0.00
<sup>5</sup> <b>TS1</b>	0.81	0.19	0.21	-0.44	0.00	-0.52	-0.44	0.07	0.12	0.00
<sup>5</sup> <b>2</b>	0.90	0.18	0.21	-0.46	0.00	-0.53	-0.61	0.24	0.07	0.00
<sup>5</sup> <b>TS2</b>	0.86	0.16	0.20	-0.50	-0.01	-0.57	-0.57	0.26	0.13	0.04
<sup>5</sup> <b>3</b>	0.82	0.11	0.15	-0.60	0.01	-0.58	-0.52	0.29	0.26	0.06

(c) Solvation energies (in kcal mol<sup>-1</sup>) and relative energies (in kcal mol<sup>-1</sup>).

	$E_{\text{solv}}$	$\Delta E$
<sup>5</sup> Cpd I	-22.1644	0.00
<sup>5</sup> <b>TS1</b>	-21.4256	7.68
<sup>5</sup> <b>2</b>	-21.5325	-8.55
<sup>5</sup> <b>TS2</b>	-21.8096	-7.28
<sup>5</sup> <b>3</b>	-19.9973	-32.46

**Table S6.** Group spin densities and charges of single point calculations in a dielectric constant of  $\epsilon = 5.7$  on UB3LYP/LACVP optimized geometries of intermediates in the hydroxylation reaction of <sup>5</sup>Cpd I with propene as calculated with Jaguar 6.0.

**(a) Group Spin Densities ( $\rho$ ).**

	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	OH	CH <sub>2</sub>	CH	CH <sub>2</sub>
<sup>5</sup> <b>TS3</b>	3.74	0.09	0.04	0.13	0.00	0.18	0.20	-0.20	0.11	-0.29
<sup>5</sup> <b>4</b>	4.04	0.11	0.06	0.18	0.00	0.20	0.38	-0.64	0.29	-0.62
<sup>5</sup> <b>TS4</b>	4.02	0.10	0.06	0.16	0.00	0.19	0.37	-0.59	0.28	-0.59
<sup>5</sup> <b>5</b>	3.77	0.04	0.04	0.07	0.00	0.06	0.02	0.00	0.00	0.00

**(b) Group Charges ( $Q$ ).**

	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	OH	CH <sub>2</sub>	CH	CH <sub>2</sub>
<sup>5</sup> <b>TS3</b>	0.86	0.20	0.23	-0.43	-0.01	-0.67	-0.24	-0.03	0.26	-0.17
<sup>5</sup> <b>4</b>	0.88	0.19	0.21	-0.45	-0.01	-0.52	-0.35	0.00	0.09	-0.04
<sup>5</sup> <b>TS4</b>	0.88	0.18	0.21	-0.45	0.00	-0.53	-0.32	-0.05	0.03	0.05
<sup>5</sup> <b>5</b>	0.79	0.14	0.15	-0.60	0.04	-0.57	-0.26	-0.04	0.08	0.27

**(c) Solvation energies (in kcal mol<sup>-1</sup>) and relative energies (in kcal mol<sup>-1</sup>).**

	$E_{\text{solv}}$	$\Delta E$
<sup>5</sup> Cpd I	-22.1644	0.00
<sup>5</sup> <b>TS3</b>	-22.1931	9.49
<sup>5</sup> <b>4</b>	-23.0364	-7.19
<sup>5</sup> <b>TS4</b>	-22.2290	-3.45
<sup>5</sup> <b>5</b>	-20.0685	-51.43

**Table S7.** Group spin densities and charges of single point calculations in a dielectric constant of  $\epsilon = 10.65$  on UB3LYP/LACVP optimized geometries of intermediates in the epoxidation reaction of <sup>5</sup>Cpd I with propene as calculated with Jaguar 6.0.

(a) Group Spin Densities ( $\rho$ ).

	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	O	CH <sub>2</sub>	CH	CH <sub>3</sub>
<sup>5</sup> Cpd I	2.96	0.10	-0.01	0.05	0.00	0.13	0.77	0.00	0.00	0.00
<sup>5</sup> <b>TS1</b>	3.67	0.08	0.04	0.11	0.00	0.16	0.19	0.05	-0.30	0.00
<sup>5</sup> <b>2</b>	4.00	0.10	0.06	0.16	0.00	0.18	0.36	0.07	-0.93	0.00
<sup>5</sup> <b>TS2</b>	3.93	0.07	0.05	0.12	0.00	0.15	0.35	0.05	-0.72	0.00
<sup>5</sup> <b>3</b>	3.76	0.04	0.04	0.07	0.01	0.06	0.02	0.00	0.00	0.00

(b) Group Charges ( $Q$ ).

	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	O	CH <sub>2</sub>	CH	CH <sub>3</sub>
<sup>5</sup> Cpd I	0.82	0.21	0.28	-0.51	0.02	-0.47	-0.36	-0.07	0.08	0.00
<sup>5</sup> <b>TS1</b>	0.80	0.19	0.22	-0.44	0.00	-0.53	-0.44	0.07	0.12	0.01
<sup>5</sup> <b>2</b>	0.89	0.18	0.21	-0.46	0.00	-0.53	-0.61	0.24	0.08	0.00
<sup>5</sup> <b>TS2</b>	0.86	0.16	0.20	-0.50	-0.01	-0.57	-0.58	0.26	0.14	0.04
<sup>5</sup> <b>3</b>	0.82	0.11	0.15	-0.61	0.01	-0.55	-0.52	0.29	0.24	0.06

(c) Solvation energies (in kcal mol<sup>-1</sup>) and relative energies (in kcal mol<sup>-1</sup>).

	$E_{\text{solv}}$	$\Delta E$
<sup>5</sup> Cpd I	-25.7393	0.00
<sup>5</sup> <b>TS1</b>	-24.8770	7.81
<sup>5</sup> <b>2</b>	-25.0614	-8.50
<sup>5</sup> <b>TS2</b>	-25.3899	-7.28
<sup>5</sup> <b>3</b>	-23.1253	-32.01

**Table S8.** Group spin densities and charges of single point calculations in a dielectric constant of  $\epsilon = 10.65$  on UB3LYP/LACVP optimized geometries of intermediates in the hydroxylation reaction of <sup>5</sup>Cpd I with propene as calculated with Jaguar 6.0.

**(a) Group Spin Densities ( $\rho$ ).**

	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	OH	CH <sub>2</sub>	CH	CH <sub>2</sub>
<sup>5</sup> <b>TS3</b>	3.74	0.09	0.04	0.13	0.00	0.18	0.20	-0.20	0.11	-0.29
<sup>5</sup> <b>4</b>	4.04	0.11	0.07	0.18	0.00	0.20	0.37	-0.64	0.29	-0.62
<sup>5</sup> <b>TS4</b>	4.02	0.10	0.06	0.16	0.00	0.19	0.37	-0.59	0.28	-0.59
<sup>5</sup> <b>5</b>	3.77	0.04	0.04	0.07	0.00	0.06	0.02	0.00	0.00	0.00

**(b) Group Charges ( $Q$ ).**

	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	OH	CH <sub>2</sub>	CH	CH <sub>2</sub>
<sup>5</sup> <b>TS3</b>	0.85	0.21	0.23	-0.44	-0.01	-0.52	-0.24	-0.02	0.10	-0.16
<sup>5</sup> <b>4</b>	0.88	0.19	0.22	-0.45	-0.01	-0.52	-0.35	-0.01	0.09	-0.04
<sup>5</sup> <b>TS4</b>	0.88	0.19	0.22	-0.45	0.00	-0.55	-0.32	-0.05	0.03	0.05
<sup>5</sup> <b>5</b>	0.79	0.14	0.15	-0.60	0.04	-0.57	-0.26	-0.04	0.08	0.27

**(c) Solvation energies (in kcal mol<sup>-1</sup>) and relative energies (in kcal mol<sup>-1</sup>).**

	$E_{\text{solv}}$	$\Delta E$
<sup>5</sup> Cpd I	-25.7393	0.00
<sup>5</sup> <b>TS3</b>	-25.7995	9.46
<sup>5</sup> <b>4</b>	-26.4375	-7.02
<sup>5</sup> <b>TS4</b>	-25.7310	-3.38
<sup>5</sup> <b>5</b>	-23.1284	-50.91

**Table S9.** Group spin densities and charges of optimized geometries of intermediates in the epoxidation reaction of <sup>3</sup>Cpd I with propene as calculated with UB3LYP/LACVP in Jaguar 6.0.

**(a) Group Spin Densities ( $\rho$ ).**

	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	O	CH <sub>2</sub>	CH	CH <sub>3</sub>
<sup>3</sup> Cpd I	2.84	0.11	0.01	-0.01	0.00	0.02	-0.97	0.00	0.00	0.00
<sup>3</sup> <b>TS1</b>	2.98	0.09	0.01	0.01	0.00	0.02	-0.83	0.11	-0.39	0.00
<sup>3</sup> <b>2</b>	2.84	0.07	-0.01	0.05	0.00	0.03	-0.07	0.04	-0.95	0.00
<sup>3</sup> <b>TS2</b>	2.31	0.05	-0.03	0.02	0.00	0.04	0.19	0.03	-0.61	0.00
<sup>3</sup> <b>3</b>	1.97	0.03	-0.03	0.02	0.00	0.02	-0.01	0.00	0.00	0.00

**(b) Group Charges ( $Q$ ).**

	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	O	CH <sub>2</sub>	CH	CH <sub>3</sub>
<sup>3</sup> Cpd I	0.85	0.17	0.22	-0.51	-0.46	0.03	-0.30	0.00	0.00	0.00
<sup>3</sup> <b>TS1</b>	0.87	0.14	0.20	-0.52	0.01	-0.51	-0.36	0.05	0.13	-0.01
<sup>3</sup> <b>2</b>	0.86	0.15	0.25	-0.51	0.00	-0.53	-0.52	0.24	0.07	-0.01
<sup>3</sup> <b>TS2</b>	0.77	0.11	0.23	-0.55	0.01	-0.54	-0.50	0.26	0.16	0.05
<sup>3</sup> <b>3</b>	0.69	0.10	0.20	-0.57	0.00	-0.57	-0.48	0.31	0.27	0.05

**(c) Absolute energies (in au) and relative energies (in kcal mol<sup>-1</sup>).**

	<i>E</i>	$\Delta E$
<sup>3</sup> Cpd I	-1414.220698	12.02
<sup>3</sup> <b>TS1</b>	-1414.211543	17.77
<sup>3</sup> <b>2</b>	-1414.235611	2.66
<sup>3</sup> <b>TS2</b>	-1414.229292	6.63
<sup>3</sup> <b>3</b>	-1414.262768	-14.38

**Table S10.** Group spin densities and charges of optimized geometries of intermediates in the hydroxylation reaction of <sup>3</sup>Cpd I with propene as calculated with UB3LYP/LACVP in Jaguar 6.0.

**(a) Group Spin Densities ( $\rho$ ).**

	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	OH	CH <sub>2</sub>	CH	CH <sub>2</sub>
<sup>3</sup> <b>TS3</b>	2.89	0.11	0.01	0.01	0.01	-0.02	-0.53	-0.25	0.15	-0.38
<sup>3</sup> <b>4</b>	2.80	0.09	-0.01	0.01	0.00	0.04	0.06	-0.65	0.30	-0.64
<sup>3</sup> <b>TS4</b>	2.77	0.09	-0.01	0.01	0.00	0.03	0.08	-0.64	0.29	-0.62
<sup>3</sup> <b>5</b>	1.98	0.04	-0.01	0.00	0.00	0.00	-0.01	0.00	0.00	0.00

**(b) Group Charges ( $Q$ ).**

	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	OH	CH <sub>2</sub>	CH	CH <sub>2</sub>
<sup>3</sup> <b>TS3</b>	0.86	0.15	0.21	-0.51	0.02	-0.50	-0.17	-0.02	0.10	-0.14
<sup>3</sup> <b>4</b>	0.85	0.16	0.22	-0.51	0.00	-0.50	-0.23	-0.04	0.07	-0.02
<sup>3</sup> <b>TS4</b>	0.85	0.15	0.21	-0.52	0.03	-0.48	-0.25	-0.06	0.05	0.02
<sup>3</sup> <b>5</b>	0.68	0.11	0.18	-0.57	0.03	-0.52	-0.24	-0.02	0.07	0.28

**(c) Absolute energies (in au) and relative energies (in kcal mol<sup>-1</sup>).**

	<i>E</i>	$\Delta E$
<sup>3</sup> Cpd I	-1414.220698	12.02
<sup>3</sup> <b>TS3</b>	-1414.205472	21.58
<sup>3</sup> <b>4</b>	-1414.239286	0.36
<sup>3</sup> <b>TS4</b>	-1414.235748	2.58
<sup>3</sup> <b>5</b>	-1414.297902	-36.42

**Table S11.** Group spin densities and charges of single point UB3LYP/LACV3P+\* calculations on UB3LYP/LACVP optimized geometries of intermediates in the epoxidation reaction of <sup>3</sup>Cpd I with propene as calculated with Jaguar 6.0.

(a) Group Spin Densities ( $\rho$ ).

	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	O	CH <sub>2</sub>	CH	CH <sub>3</sub>
<sup>3</sup> Cpd I	2.92	0.10	0.00	-0.03	0.00	-0.02	-0.97	0.00	0.00	0.00
<sup>3</sup> <b>TS1</b>	3.04	0.08	0.00	-0.01	0.01	-0.01	-0.81	0.08	-0.38	0.00
<sup>3</sup> <b>2</b>	2.92	0.05	-0.02	0.04	0.00	0.01	-0.07	0.03	-0.95	-0.01
<sup>3</sup> <b>TS2</b>	2.39	0.04	-0.03	0.01	0.00	0.02	0.17	0.02	-0.62	0.00
<sup>3</sup> <b>3</b>	1.99	0.03	-0.04	0.01	0.00	0.03	-0.02	0.00	0.00	0.00

(b) Group Charges ( $Q$ ).

	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	O	CH <sub>2</sub>	CH	CH <sub>3</sub>
<sup>3</sup> Cpd I	0.54	0.22	0.18	-0.42	0.09	-0.48	-0.12	-0.13	0.13	-0.01
<sup>3</sup> <b>TS1</b>	0.58	0.25	0.24	-0.50	-0.01	-0.55	-0.06	-0.06	0.11	0.00
<sup>3</sup> <b>2</b>	0.59	0.30	0.26	-0.52	-0.01	-0.58	-0.10	0.05	0.02	-0.01
<sup>3</sup> <b>TS2</b>	0.66	0.21	0.19	-0.56	-0.01	-0.62	-0.06	0.07	0.08	0.04
<sup>3</sup> <b>3</b>	0.77	0.13	0.11	-0.59	0.00	-0.66	-0.01	0.08	0.15	0.02

(c) Absolute energies (in au) and relative energies (in kcal mol<sup>-1</sup>).

	<i>E</i>	$\Delta E$
<sup>3</sup> Cpd I	-1414.977305	16.02
<sup>3</sup> <b>TS1</b>	-1414.967347	22.27
<sup>3</sup> <b>2</b>	-1415.001684	0.72
<sup>3</sup> <b>TS2</b>	-1414.993222	6.03
<sup>3</sup> <b>3</b>	-1415.032800	-18.80

**Table S12.** Group spin densities and charges of single point UB3LYP/LACV3P+\* calculations on UB3LYP/LACVP optimized geometries of intermediates in the hydroxylation reaction of <sup>3</sup>Cpd I with propene as calculated with Jaguar 6.0.

(a) Group Spin Densities ( $\rho$ ).

	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	OH	CH <sub>2</sub>	CH	CH <sub>2</sub>
<sup>3</sup> <b>TS3</b>	2.95	0.09	-0.01	-0.01	0.00	0.01	-0.58	-0.25	0.13	-0.33
<sup>3</sup> <b>4</b>	2.88	0.07	-0.02	0.00	0.01	0.02	0.05	-0.63	0.25	-0.63
<sup>3</sup> <b>TS4</b>	2.86	0.08	-0.03	0.00	0.01	0.00	0.06	-0.62	0.25	-0.61
<sup>3</sup> <b>5</b>	2.00	0.03	-0.02	-0.01	0.01	0.01	-0.02	0.00	0.00	0.00

(b) Group Charges ( $Q$ ).

	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	OH	CH <sub>2</sub>	CH	CH <sub>2</sub>
<sup>3</sup> <b>TS3</b>	0.60	0.19	0.23	-0.47	0.10	-0.53	-0.30	-0.04	0.08	0.14
<sup>3</sup> <b>4</b>	0.55	0.31	0.16	-0.44	0.01	-0.49	-0.04	-0.07	0.09	-0.08
<sup>3</sup> <b>TS4</b>	0.64	0.22	0.20	-0.46	0.01	-0.52	-0.03	-0.07	0.06	-0.05
<sup>3</sup> <b>5</b>	0.76	0.15	0.07	-0.61	0.02	-0.61	0.14	-0.04	0.05	0.07

(c) Absolute energies (in au) and relative energies (in kcal mol<sup>-1</sup>).

	<i>E</i>	$\Delta E$
<sup>3</sup> <b>TS3</b>	-1414.960526	26.55
<sup>3</sup> <b>4</b>	-1415.004820	-1.25
<sup>3</sup> <b>TS4</b>	-1414.998913	2.46
<sup>3</sup> <b>5</b>	-1415.057427	-34.26

**Table S13.** Group spin densities and charges of single point calculations in a dielectric constant of  $\epsilon = 5.7$  on UB3LYP/LACVP optimized geometries of intermediates in the epoxidation reaction of <sup>3</sup>Cpd I with propene as calculated with Jaguar 6.0.

**(a) Group Spin Densities ( $\rho$ ).**

	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	O	CH <sub>2</sub>	CH	CH <sub>3</sub>
<sup>3</sup> Cpd I	2.83	0.12	0.01	-0.01	0.00	0.02	-0.97	0.00	0.00	0.00
<sup>3</sup> <b>TS1</b>	2.97	0.10	0.01	0.01	0.00	0.03	-0.83	0.10	-0.39	0.00
<sup>3</sup> <b>2</b>	2.83	0.08	-0.01	0.05	0.00	0.02	-0.06	0.04	-0.95	0.00
<sup>3</sup> <b>TS2</b>	2.30	0.05	-0.03	0.02	0.00	0.04	0.19	0.03	-0.60	0.00
<sup>3</sup> <b>3</b>	1.97	0.03	-0.03	0.02	0.00	0.02	-0.01	0.00	0.00	0.00

**(b) Group Charges ( $Q$ ).**

	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	O	CH <sub>2</sub>	CH	CH <sub>3</sub>
<sup>3</sup> Cpd I	0.84	0.19	0.25	-0.52	0.03	-0.47	-0.32	-0.08	0.09	-0.01
<sup>3</sup> <b>TS1</b>	0.86	0.16	0.23	-0.54	0.01	-0.51	-0.38	0.05	0.12	0.00
<sup>3</sup> <b>2</b>	0.85	0.17	0.28	-0.53	0.00	-0.53	-0.53	0.24	0.06	-0.01
<sup>3</sup> <b>TS2</b>	0.76	0.13	0.25	-0.57	0.01	-0.56	-0.51	0.27	0.16	0.06
<sup>3</sup> <b>3</b>	0.68	0.12	0.22	-0.59	0.01	-0.60	-0.50	0.32	0.27	0.07

**(c) Solvation energies (in kcal mol<sup>-1</sup>) and relative energies (in kcal mol<sup>-1</sup>).**

	$E_{\text{solv}}$	$\Delta E$
<sup>3</sup> Cpd I	-21.4288	12.76
<sup>3</sup> <b>TS1</b>	-19.9468	19.98
<sup>3</sup> <b>2</b>	-21.4589	3.37
<sup>3</sup> <b>TS2</b>	-20.5775	8.22
<sup>3</sup> <b>3</b>	-20.3591	-12.57

**Table S14.** Group spin densities and charges of single point calculations in a dielectric constant of  $\epsilon = 5.7$  on UB3LYP/LACVP optimized geometries of intermediates in the hydroxylation reaction of  $^3\text{Cpd I}$  with propene as calculated with Jaguar 6.0.

(a) Group Spin Densities ( $\rho$ ).

	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	OH	CH <sub>2</sub>	CH	CH <sub>2</sub>
$^3\text{TS3}$	2.88	0.11	0.00	0.01	0.00	0.00	-0.56	-0.26	0.15	-0.33
$^3\text{4}$	2.80	0.10	-0.01	0.01	0.00	0.03	0.06	-0.65	0.30	-0.64
$^3\text{TS4}$	2.78	0.10	-0.01	0.01	0.00	0.01	0.08	-0.64	0.29	-0.62
$^3\text{5}$	1.98	0.04	-0.01	0.00	0.00	0.00	-0.01	0.00	0.00	0.00

(b) Group Charges ( $Q$ ).

	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	OH	CH <sub>2</sub>	CH	CH <sub>2</sub>
$^3\text{TS3}$	0.85	0.17	0.24	-0.52	0.02	-0.50	-0.52	-0.01	0.10	0.17
$^3\text{4}$	0.84	0.19	0.26	-0.53	0.00	-0.51	-0.26	-0.04	0.07	-0.02
$^3\text{TS4}$	0.84	0.17	0.24	-0.53	0.03	-0.49	-0.26	-0.06	0.05	0.01
$^3\text{5}$	0.67	0.13	0.20	-0.59	0.03	-0.53	-0.25	-0.02	0.07	0.29

(c) Solvation energies (in kcal mol<sup>-1</sup>) and relative energies (in kcal mol<sup>-1</sup>).

	$E_{\text{solv}}$	$\Delta E$
$^3\text{Cpd I}$	-21.4288	12.76
$^3\text{TS3}$	-22.4258	21.32
$^3\text{4}$	-23.4055	-0.88
$^3\text{TS4}$	-20.6478	4.10
$^3\text{5}$	-19.8336	-34.09

**Table S15.** Group spin densities and charges of single point calculations in a dielectric constant of  $\epsilon = 10.65$  on UB3LYP/LACVP optimized geometries of intermediates in the epoxidation reaction of <sup>3</sup>Cpd I with propene as calculated with Jaguar 6.0.

**(a) Group Spin Densities ( $\rho$ ).**

	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	O	CH <sub>2</sub>	CH	CH <sub>3</sub>
<sup>3</sup> Cpd I	2.83	0.12	0.01	-0.01	0.00	0.01	-0.96	0.00	0.00	0.00
<sup>3</sup> <b>TS1</b>	2.97	0.10	0.01	0.01	0.00	0.02	-0.82	0.10	-0.39	0.00
<sup>3</sup> <b>2</b>	2.83	0.08	-0.01	0.05	0.00	0.02	-0.06	0.04	-0.95	0.00
<sup>3</sup> <b>TS2</b>	2.30	0.05	-0.03	0.02	0.00	0.03	0.19	0.03	-0.59	0.00
<sup>3</sup> <b>3</b>	1.97	0.03	-0.03	0.02	0.00	0.02	-0.01	0.00	0.00	0.00

**(b) Group Charges ( $Q$ ).**

	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	O	CH <sub>2</sub>	CH	CH <sub>3</sub>
<sup>3</sup> Cpd I	0.84	0.20	0.26	-0.52	0.03	-0.48	-0.33	-0.08	0.09	-0.01
<sup>3</sup> <b>TS1</b>	0.85	0.16	0.24	-0.54	0.01	-0.52	-0.38	0.06	0.12	0.00
<sup>3</sup> <b>2</b>	0.84	0.17	0.29	-0.53	0.00	-0.52	-0.54	0.24	0.06	-0.01
<sup>3</sup> <b>TS2</b>	0.75	0.13	0.25	-0.57	0.01	-0.57	-0.51	0.27	0.17	0.07
<sup>3</sup> <b>3</b>	0.68	0.12	0.22	-0.59	0.00	-0.59	-0.50	0.32	0.27	0.07

**(c) Solvation energies (in kcal mol<sup>-1</sup>) and relative energies (in kcal mol<sup>-1</sup>).**

	$E_{\text{solv}}$	$\Delta E$
<sup>3</sup> Cpd I	-25.2210	12.54
<sup>3</sup> <b>TS1</b>	-23.3553	20.15
<sup>3</sup> <b>2</b>	-25.1081	3.30
<sup>3</sup> <b>TS2</b>	-23.3355	9.03
<sup>3</sup> <b>3</b>	-22.9615	-11.60

**Table S16.** Group spin densities and charges of single point calculations in a dielectric constant of  $\epsilon = 10.65$  on UB3LYP/LACVP optimized geometries of intermediates in the hydroxylation reaction of <sup>3</sup>Cpd I with propene as calculated with Jaguar 6.0.

(a) Group Spin Densities ( $\rho$ ).

	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	OH	CH <sub>2</sub>	CH	CH <sub>2</sub>
<sup>3</sup> <b>TS3</b>	2.87	0.11	0.00	0.01	0.00	0.02	-0.56	-0.27	0.15	-0.33
<sup>3</sup> <b>4</b>	2.80	0.10	-0.01	0.01	0.00	0.03	0.06	-0.65	0.30	-0.64
<sup>3</sup> <b>TS4</b>	2.78	0.10	-0.01	0.01	0.00	0.01	0.08	-0.64	0.29	-0.62
<sup>3</sup> <b>5</b>	1.98	0.04	-0.01	0.00	0.00	0.00	-0.01	0.00	0.00	0.00

(b) Group Charges ( $Q$ ).

	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	OH	CH <sub>2</sub>	CH	CH <sub>2</sub>
<sup>3</sup> <b>TS3</b>	0.85	0.17	0.25	-0.53	0.02	-0.49	-0.53	-0.01	0.10	0.17
<sup>3</sup> <b>4</b>	0.84	0.19	0.26	-0.53	0.00	-0.50	-0.27	-0.04	0.07	-0.02
<sup>3</sup> <b>TS4</b>	0.83	0.18	0.24	-0.53	0.03	-0.49	-0.26	-0.06	0.05	0.01
<sup>3</sup> <b>5</b>	0.66	0.13	0.20	-0.59	0.03	-0.52	-0.25	-0.02	0.07	0.29

(c) Solvation energies (in kcal mol<sup>-1</sup>) and relative energies (in kcal mol<sup>-1</sup>).

	$E_{\text{solv}}$	$\Delta E$
<sup>3</sup> Cpd I	-25.2210	12.54
<sup>3</sup> <b>TS3</b>	-26.1257	21.19
<sup>3</sup> <b>4</b>	-26.8367	-0.74
<sup>3</sup> <b>TS4</b>	-24.0627	4.26
<sup>3</sup> <b>5</b>	-22.8622	-33.55

**Table S17.** Group spin densities and charges of optimized geometries of intermediates in the epoxidation reaction of <sup>7</sup>Cpd I with propene as calculated with UB3LYP/LACVP in Jaguar 6.0.

**(a) Group Spin Densities ( $\rho$ ).**

	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	O	CH <sub>2</sub>	CH	CH <sub>3</sub>
<sup>7</sup> Cpd I	3.97	0.10	0.09	0.23	0.00	0.24	1.37	0.00	0.00	0.00
<sup>7</sup> <b>TS1</b>	3.96	0.09	0.09	0.22	0.00	0.14	1.23	-0.06	0.33	0.00
<sup>7</sup> <b>2</b>	4.01	0.09	0.09	0.18	0.00	0.16	0.51	-0.03	0.99	0.00
<sup>7</sup> <b>3'</b>	3.76	0.06	0.04	0.09	0.00	0.07		0.01(CH <sub>2</sub> O)	1.97(CH <sub>3</sub> CH)	

**(b) Group Charges ( $Q$ ).**

	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	O	CH <sub>2</sub>	CH	CH <sub>3</sub>
<sup>7</sup> Cpd I	1.03	0.15	0.16	-0.49	0.00	-0.38	-0.47	0.00	0.00	0.00
<sup>7</sup> <b>TS1</b>	1.00	0.15	0.15	-0.50	0.00	-0.54	-0.45	0.06	0.13	0.00
<sup>7</sup> <b>2</b>	1.08	0.16	0.15	-0.53	0.01	-0.55	-0.62	0.24	0.09	-0.03
<sup>7</sup> <b>3'</b>	0.84	0.11	0.14	-0.58	-0.02	-0.59		0.07(CH <sub>2</sub> O)	0.03(CH <sub>3</sub> CH)	

**(c) Absolute energies (in au) and relative energies (in kcal mol<sup>-1</sup>).**

	<i>E</i>	$\Delta E$
<sup>7</sup> Cpd I	-1414.229597	6.44
<sup>7</sup> <b>TS1</b>	-1414.225227	9.18
<sup>7</sup> <b>2</b>	-1414.252338	-7.83
<sup>7</sup> <b>3'</b>	-1414.170759	43.36

**Table S18.** Group spin densities and charges of optimized geometries of intermediates in the hydroxylation reaction of <sup>7</sup>Cpd I with propene as calculated with UB3LYP/LACVP in Jaguar 6.0.

(a) Group Spin Densities ( $\rho$ ).

	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	OH	CH <sub>2</sub>	CH	CH <sub>2</sub>
<sup>7</sup> <b>TS3</b>	3.98	0.10	0.09	0.24	0.00	0.19	1.03	0.19	-0.11	0.29
<sup>7</sup> <b>4</b>	4.04	0.10	0.10	0.21	0.00	0.16	0.41	0.65	-0.29	0.62
<sup>7</sup> <b>5</b>	3.77	0.04	0.03	0.07	0.00	0.16	0.01	0.00	0.91	1.01

(b) Group Charges ( $Q$ ).

	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	OH	CH <sub>2</sub>	CH	CH <sub>2</sub>
<sup>7</sup> <b>TS3</b>	1.02	0.16	0.16	-0.48	0.00	-0.53	-0.23	-0.03	0.10	-0.17
<sup>7</sup> <b>4</b>	1.05	0.17	0.17	-0.50	-0.01	-0.55	-0.35	-0.02	0.06	-0.02
<sup>7</sup> <b>5</b>	0.81	0.11	0.13	-0.59	0.03	-0.86	-0.10	0.30	0.17	0.00

(c) Absolute energies (in au) and relative energies (in kcal mol<sup>-1</sup>).

	<i>E</i>	$\Delta E$
<sup>7</sup> Cpd I	-1414.229597	6.44
<sup>7</sup> <b>TS3</b>	-1414.220468	12.17
<sup>7</sup> <b>4</b>	-1414.255322	-9.70
<sup>7</sup> <b>5</b>	-1414.216364	14.74

**Table S19.** Group spin densities and charges of single point UB3LYP/LACV3P+\* calculations on UB3LYP/LACVP optimized geometries of intermediates in the epoxidation reaction of <sup>7</sup>Cpd I with propene as calculated with Jaguar 6.0.

**(a) Group Spin Densities ( $\rho$ ).**

	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	O	CH <sub>2</sub>	CH	CH <sub>3</sub>
<sup>7</sup> Cpd I	4.13	0.09	0.07	0.20	0.00	0.21	1.30	0.00	0.00	0.00
<sup>7</sup> <b>TS1</b>	4.12	0.07	0.07	0.19	0.00	0.11	1.15	-0.04	0.32	0.01
<sup>7</sup> <b>2</b>	4.18	0.07	0.07	0.15	0.00	0.12	0.43	-0.01	0.98	0.01
<sup>7</sup> <b>3'</b>	3.85	0.04	0.03	0.07	0.00	0.06		-0.03 (CH <sub>2</sub> O)	1.98(CH <sub>3</sub> CH)	

**(b) Group Charges ( $Q$ ).**

	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	O	CH <sub>2</sub>	CH	CH <sub>3</sub>
<sup>7</sup> Cpd I	0.73	0.23	0.18	-0.48	0.02	-0.46	-0.22	0.00	0.00	0.00
<sup>7</sup> <b>TS1</b>	0.80	0.14	0.15	-0.45	0.00	-0.54	-0.17	-0.04	0.11	0.00
<sup>7</sup> <b>2</b>	0.82	0.18	0.21	-0.55	-0.01	-0.56	-0.19	0.08	0.05	-0.03
<sup>7</sup> <b>3'</b>	0.53	0.20	0.13	-0.59	-0.01	-0.61		0.33 (CH <sub>2</sub> O)	0.02(CH <sub>3</sub> CH)	

**(c) Absolute energies (in au) and relative energies (in kcal mol<sup>-1</sup>).**

	<i>E</i>	$\Delta E$
<sup>7</sup> Cpd I	-1414.989954	8.08
<sup>7</sup> <b>TS1</b>	-1414.985286	11.01
<sup>7</sup> <b>2</b>	-1415.020831	-11.29
<sup>7</sup> <b>3'</b>	-1414.943407	37.29

**Table S20.** Group spin densities and charges of single point UB3LYP/LACV3P+\* calculations on UB3LYP/LACVP optimized geometries of intermediates in the hydroxylation reaction of <sup>7</sup>Cpd I with propene as calculated with Jaguar 6.0.

(a) Group Spin Densities ( $\rho$ ).

	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	OH	CH <sub>2</sub>	CH	CH <sub>2</sub>
<sup>7</sup> <b>TS3</b>	4.14	0.08	0.08	0.21	0.00	0.14	0.96	0.19	-0.09	0.29
<sup>7</sup> <b>4</b>	4.19	0.08	0.08	0.17	0.00	0.12	0.36	0.64	-0.25	0.61
<sup>7</sup> <b>5</b>	3.82	0.02	0.03	0.05	0.01	0.05	0.06	0.02	0.93	1.01

(b) Group Charges ( $Q$ ).

	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	OH	CH <sub>2</sub>	CH	CH <sub>2</sub>
<sup>7</sup> <b>TS3</b>	0.78	0.11	0.17	-0.38	0.02	-0.51	0.00	-0.05	0.08	-0.22
<sup>7</sup> <b>4</b>	0.88	0.20	0.18	-0.45	0.01	-0.62	-0.17	-0.04	0.08	-0.07
<sup>7</sup> <b>5</b>	0.91	0.24	0.05	-0.66	0.01	-0.63	-0.04	-0.04	0.18	-0.02

(c) Absolute energies (in au) and relative energies (in kcal mol<sup>-1</sup>).

	<i>E</i>	$\Delta E$
<sup>7</sup> Cpd I	-1414.989954	8.08
<sup>7</sup> <b>TS3</b>	-1414.980108	14.26
<sup>7</sup> <b>4</b>	-1415.024770	-13.77
<sup>7</sup> <b>5</b>	-1414.980698	13.89

**Table S21.** Group spin densities and charges of single point calculations in a dielectric constant of  $\epsilon = 5.7$  on UB3LYP/LACVP optimized geometries of intermediates in the epoxidation reaction of <sup>7</sup>Cpd I with propene as calculated with Jaguar 6.0.

**(a) Group Spin Densities ( $\rho$ ).**

	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	O	CH <sub>2</sub>	CH	CH <sub>3</sub>
<sup>7</sup> Cpd I	3.98	0.11	0.10	0.23	0.00	0.24	1.34	0.00	0.00	0.00
<sup>7</sup> <b>TS1</b>	3.97	0.09	0.09	0.21	0.00	0.16	1.21	-0.06	0.33	0.00
<sup>7</sup> <b>2</b>	4.02	0.09	0.10	0.17	0.00	0.16	0.50	-0.03	0.99	0.00
<sup>7</sup> <b>3'</b>	3.76	0.06	0.04	0.09	0.00	0.07		0.01(CH <sub>2</sub> O)	1.97(CH <sub>3</sub> CH)	

**(b) Group Charges ( $Q$ ).**

	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	O	CH <sub>2</sub>	CH	CH <sub>3</sub>
<sup>7</sup> Cpd I	1.03	0.18	0.19	-0.50	0.00	-0.49	-0.41	0.00	0.00	0.00
<sup>7</sup> <b>TS1</b>	1.00	0.17	0.18	-0.53	0.00	-0.55	-0.47	0.06	0.13	0.01
<sup>7</sup> <b>2</b>	1.07	0.18	0.17	-0.56	0.01	-0.54	-0.63	0.24	0.08	-0.02
<sup>7</sup> <b>3'</b>	0.83	0.12	0.15	-0.60	-0.02	-0.58		0.08(CH <sub>2</sub> O)	0.02(CH <sub>3</sub> CH)	

**(c) Solvation energies (in kcal mol<sup>-1</sup>) and relative energies (in kcal mol<sup>-1</sup>).**

	$E_{\text{solv}}$	$\Delta E$
<sup>7</sup> Cpd I	-22.8861	5.72
<sup>7</sup> <b>TS1</b>	-21.6413	9.70
<sup>7</sup> <b>2</b>	-20.3092	-5.98
<sup>7</sup> <b>3</b>	-20.0637	45.46

**Table S22.** Group spin densities and charges of single point calculations in a dielectric constant of  $\epsilon = 5.7$  on UB3LYP/LACVP optimized geometries of intermediates in the hydroxylation reaction of <sup>7</sup>Cpd I with propene as calculated with Jaguar 6.0.

**(a) Group Spin Densities ( $\rho$ ).**

	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	OH	CH <sub>2</sub>	CH	CH <sub>2</sub>
<sup>7</sup> <b>TS3</b>	3.99	0.11	0.10	0.23	0.00	0.18	1.00	0.20	-0.11	0.30
<sup>7</sup> <b>4</b>	4.04	0.11	0.11	0.20	0.00	0.16	0.40	0.65	-0.29	0.62
<sup>7</sup> <b>5</b>	3.77	0.04	0.04	0.07	0.00	0.07	0.09	0.00	0.91	1.01

**(b) Group Charges ( $Q$ ).**

	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	OH	CH <sub>2</sub>	CH	CH <sub>2</sub>
<sup>7</sup> <b>TS3</b>	1.01	0.19	0.19	-0.51	-0.01	-0.53	-0.26	-0.02	0.10	-0.16
<sup>7</sup> <b>4</b>	1.04	0.19	0.19	-0.53	-0.01	-0.52	-0.37	-0.02	0.06	-0.03
<sup>7</sup> <b>5</b>	0.79	0.13	0.15	-0.60	0.03	-0.60	-0.23	0.30	0.03	0.00

**(c) Solvation energies (in kcal mol<sup>-1</sup>) and relative energies (in kcal mol<sup>-1</sup>).**

	$E_{\text{solv}}$	$\Delta E$
<sup>7</sup> Cpd I	-22.8861	5.72
<sup>7</sup> <b>TS3</b>	-22.6588	11.67
<sup>7</sup> <b>4</b>	-22.4964	-10.04
<sup>7</sup> <b>5</b>	-19.7010	17.21

**Table S23.** Group spin densities and charges of single point calculations in a dielectric constant of  $\epsilon = 10.65$  on UB3LYP/LACVP optimized geometries of intermediates in the epoxidation reaction of <sup>7</sup>Cpd I with propene as calculated with Jaguar 6.0.

**(a) Group Spin Densities ( $\rho$ ).**

	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	O	CH <sub>2</sub>	CH	CH <sub>3</sub>
<sup>7</sup> Cpd I	3.99	0.11	0.10	0.23	0.00	0.23	1.34	0.00	0.00	0.00
<sup>7</sup> <b>TS1</b>	3.97	0.09	0.09	0.20	0.00	0.16	1.22	-0.06	0.33	0.00
<sup>7</sup> <b>2</b>	4.02	0.10	0.10	0.17	0.00	0.15	0.50	-0.03	0.99	0.00
<sup>7</sup> <b>3'</b>	3.76	0.06	0.04	0.09	0.00	0.07		0.01(CH <sub>2</sub> O)	1.97(CH <sub>3</sub> CH)	

**(b) Group Charges ( $Q$ ).**

	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	O	CH <sub>2</sub>	CH	CH <sub>3</sub>
<sup>7</sup> Cpd I	1.03	0.19	0.20	-0.51	0.00	-0.49	-0.42	0.00	0.00	0.00
<sup>7</sup> <b>TS1</b>	0.99	0.18	0.18	-0.53	0.00	-0.56	-0.46	0.06	0.13	0.01
<sup>7</sup> <b>2</b>	1.07	0.19	0.17	-0.56	0.01	-0.55	-0.63	0.24	0.08	-0.02
<sup>7</sup> <b>3'</b>	0.83	0.13	0.16	-0.60	-0.02	-0.60		0.08(CH <sub>2</sub> O)	0.02(CH <sub>3</sub> CH)	

**(c) Solvation energies (in kcal mol<sup>-1</sup>) and relative energies (in kcal mol<sup>-1</sup>).**

	$E_{\text{solv}}$	$\Delta E$
<sup>7</sup> Cpd I	-26.4244	5.75
<sup>7</sup> <b>TS1</b>	-24.3365	10.58
<sup>7</sup> <b>2</b>	-23.6927	-5.79
<sup>7</sup> <b>3</b>	-23.2987	45.80

**Table S24.** Group spin densities and charges of single point calculations in a dielectric constant of  $\epsilon = 10.65$  on UB3LYP/LACVP optimized geometries of intermediates in the hydroxylation reaction of <sup>7</sup>Cpd I with propene as calculated with Jaguar 6.0.

**(a) Group Spin Densities ( $\rho$ ).**

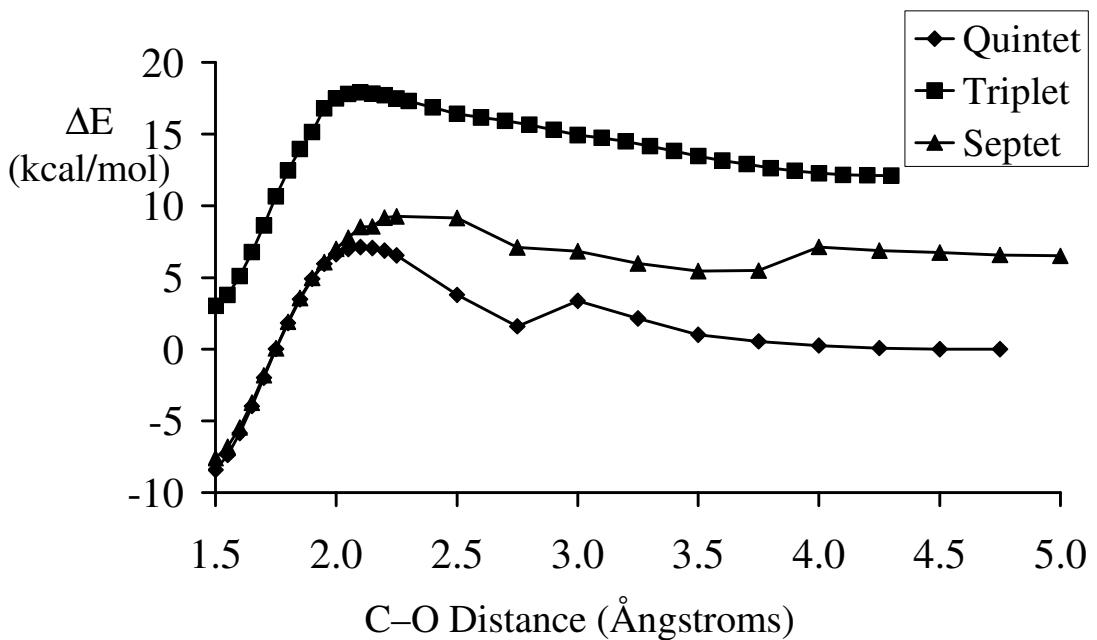
	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	OH	CH <sub>2</sub>	CH	CH <sub>2</sub>
<sup>7</sup> <b>TS3</b>	3.99	0.11	0.10	0.23	0.00	0.18	1.00	0.20	-0.11	0.30
<sup>7</sup> <b>4</b>	4.04	0.11	0.11	0.20	0.00	0.16	0.40	0.65	-0.29	0.62
<sup>7</sup> <b>5</b>	3.77	0.04	0.04	0.07	0.00	0.07	0.09	0.00	0.91	1.01

**(b) Group Charges ( $Q$ ).**

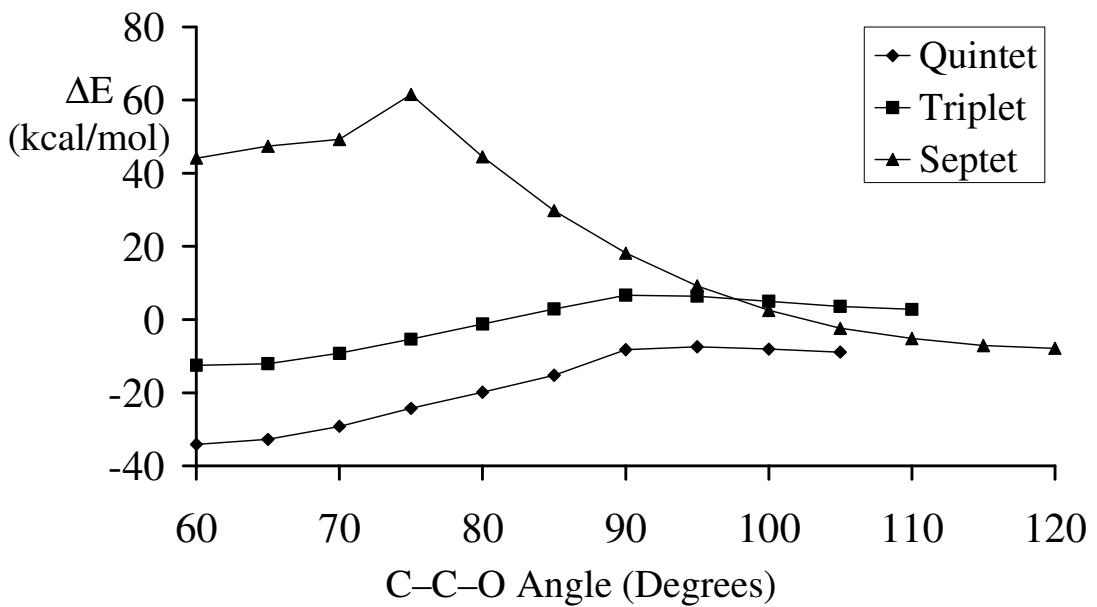
	Fe	His <sub>255</sub>	His <sub>99</sub>	Asp <sub>101</sub> <sup>-</sup>	CO <sub>2</sub>	Succ <sup>-</sup>	OH	CH <sub>2</sub>	CH	CH <sub>2</sub>
<sup>7</sup> <b>TS3</b>	1.01	0.19	0.19	-0.51	0.00	-0.54	-0.26	-0.02	0.10	-0.16
<sup>7</sup> <b>4</b>	1.04	0.20	0.19	-0.53	-0.01	-0.54	-0.36	-0.02	0.06	-0.03
<sup>7</sup> <b>5</b>	0.79	0.13	0.15	-0.60	0.03	-0.60	-0.23	0.30	0.03	0.00

**(c) Solvation energies (in kcal mol<sup>-1</sup>) and relative energies (in kcal mol<sup>-1</sup>).**

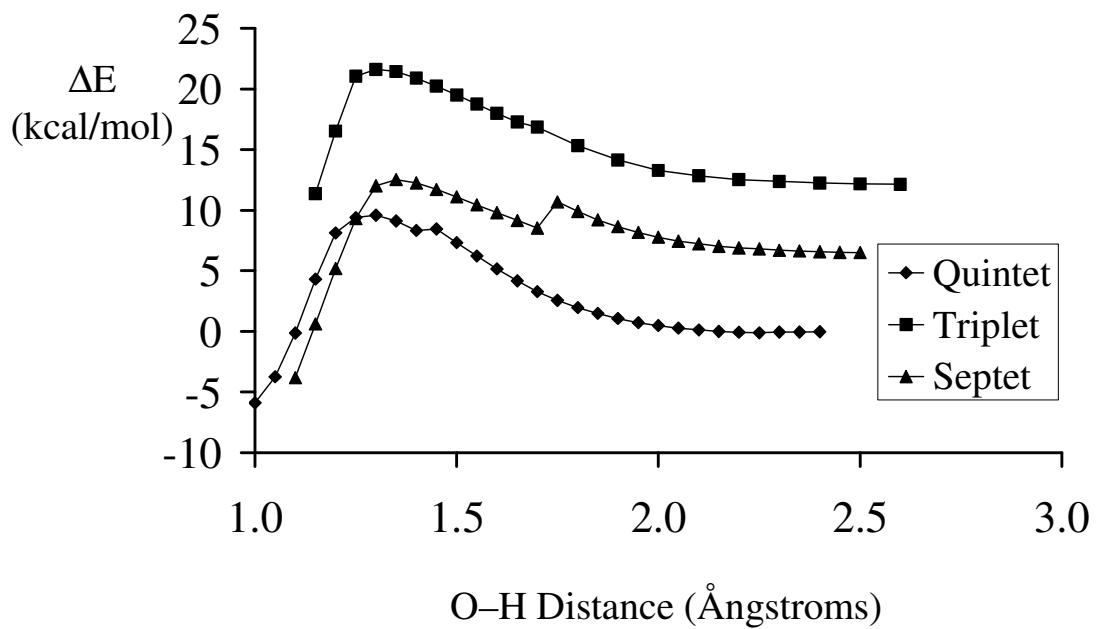
	$E_{\text{solv}}$	$\Delta E$
<sup>7</sup> Cpd I	-26.4244	5.75
<sup>7</sup> <b>TS3</b>	-26.1202	11.79
<sup>7</sup> <b>4</b>	-25.5568	-9.52
<sup>7</sup> <b>5</b>	-22.5434	17.94



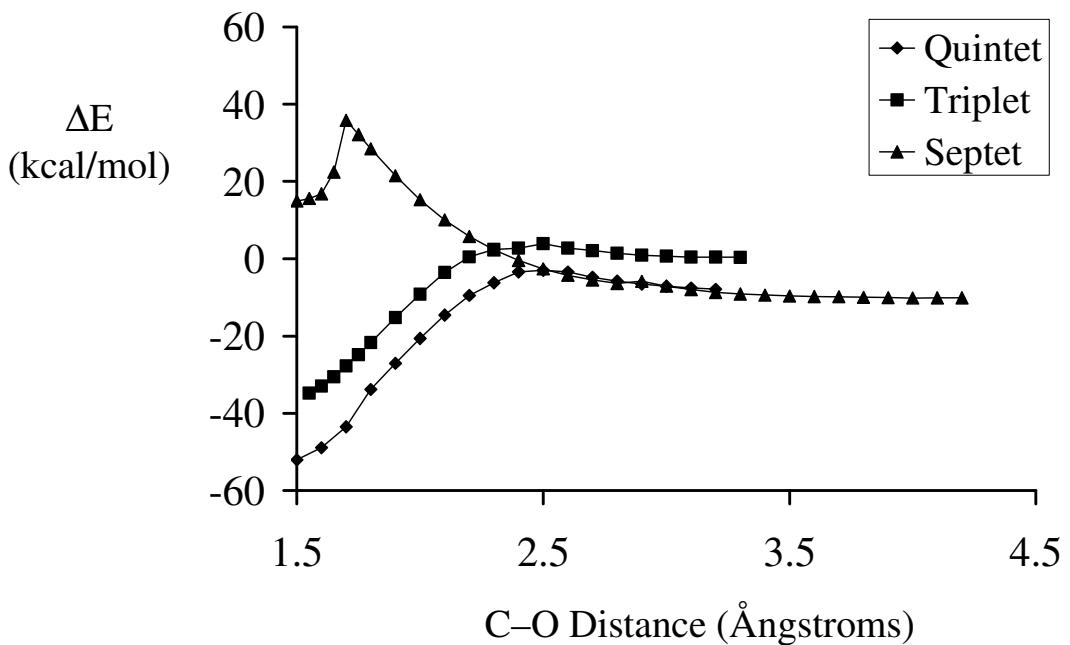
**Figure S1.** Geometry scans for the C–O bond activation process in the epoxidation mechanism on the quintet, triplet and septet spin surfaces. All energies are in kcal mol<sup>-1</sup> relative to <sup>5</sup>Cpd I + propene. Each data point corresponds to a full UB3LYP/LACVP optimization in Jaguar 6.0 with one degree of freedom (C–O bond) fixed. The maxima in the figures were used as starting point for the <sup>3,5,7</sup>TS1 transition state optimizations.



**Figure S2.** Geometry scans for the C–C–O ring closure process in the epoxidation mechanism on the quintet, triplet and septet spin surfaces. All energies are in kcal mol<sup>-1</sup> relative to <sup>5</sup>Cpd I + propene. Each data point corresponds to a full UB3LYP/LACVP optimization in Jaguar 6.0 with one degree of freedom (C–C–O angle) fixed. The maxima in the figures were used as starting point for the <sup>3,5</sup>TS2 transition state optimizations. The maximum point on the septet spin surface is 61.5 kcal mol<sup>-1</sup> above <sup>5</sup>Cpd I + propene.



**Figure S3.** Geometry scans for the hydrogen transfer process in the hydroxylation mechanism on the quintet, triplet and septet spin surfaces. All energies are in kcal mol<sup>-1</sup> relative to <sup>5</sup>Cpd I + propene. Each data point corresponds to a full UB3LYP/LACVP optimization in Jaguar 6.0 with one degree of freedom (O–H distance) fixed. The maxima in the figures were used as starting point for the <sup>3,5,7</sup>TS3 transition state optimizations.



**Figure S4.** Geometry scans for the radical rebound process in the hydroxylation mechanism on the quintet, triplet and septet spin surfaces. All energies are in  $\text{kcal mol}^{-1}$  relative to  ${}^5\text{Cpd I} + \text{propene}$ . Each data point corresponds to a full UB3LYP/LACVP optimization in Jaguar 6.0 with one degree of freedom (C–O distance) fixed. The maxima in the figures were used as starting point for the  ${}^{3,5}\text{TS4}$  transition state optimizations. The maximum point on the septet spin surface is 35.8  $\text{kcal mol}^{-1}$  above  ${}^5\text{Cpd I} + \text{propene}$ .