Supporting Information for

Mechanism of $[\gamma\text{-}H_2SiV_2W_{10}O_{40}]^{4-}$-Catalyzed Epoxidation of Alkenes with Hydrogen Peroxide

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1. Rate law derivation for the mechanism in Scheme 1

$$\mathbf{I} + H_2O_2 \xrightarrow{k_1} \mathbf{II} + H_2O \quad (1)$$

$$\mathbf{II} + H_2O \xrightarrow{k_2} \mathbf{I} + H_2O_2 \quad (2)$$

$$\mathbf{II} \xrightarrow{k_3} \mathbf{III} + H_2O \quad (3)$$

$$\mathbf{III} + H_2O \xrightarrow{k_4} \mathbf{II} \quad (4)$$

$$\mathbf{III} + \text{alkene} \xrightarrow{k_5} \mathbf{I} + \text{epoxide} \quad (5)$$

($k_1 - k_5$; rate constants)

From Eqs. (1)-(5), $d[\mathbf{II}]/dt$, $d[\mathbf{III}]/dt$, and alkene epoxidation rate were obtained as follows;

$$\frac{d}{dt}[\mathbf{II}] = k_1[\mathbf{I}][H_2O_2] - k_2[\mathbf{II}][H_2O] - k_3[\mathbf{II}] + k_4[\mathbf{III}][H_2O] \quad (6)$$

$$\frac{d}{dt}[\mathbf{III}] = k_3[\mathbf{II}] - k_4[\mathbf{III}][H_2O] - k_5[\mathbf{III}][\text{alkene}] \quad (7)$$

$$rate = \frac{d}{dt}[\text{product}] = k_5[\mathbf{III}][\text{alkene}] \quad (8).$$

At steady state (d[**II**]/dt = 0 and d[**III**]/dt = 0), Eqs. (9) – (11) were obtained.

$$[\mathbf{III}] = \frac{k_3[\mathbf{II}]}{k_4[\mathrm{H_2O}] + k_5[\mathrm{alkene}]} \tag{9}$$

$$[\mathbf{II}] = \frac{k_1[\mathbf{I}][\mathrm{H_2O_2}](k_4[\mathrm{H_2O}] + k_5[\mathrm{alkene}])}{k_2 k_4[\mathrm{H_2O}]^2 + (k_2[\mathrm{H_2O}] + k_3)k_5[\mathrm{alkene}]} \tag{10}$$

$$[\mathbf{I}] = [\mathrm{catalyst}] - [\mathbf{II}] - [\mathbf{III}] \cong [\mathrm{catalyst}] \tag{11}$$

From (9)-(11), rate was obtained as follows;

$$rate = \frac{k_1 k_3 k_5[\mathrm{catalyst}][\mathrm{H_2O_2}][\mathrm{alkene}]}{k_2 k_4[\mathrm{H_2O}]^2 + (k_2[\mathrm{H_2O}] + k_3)k_5[\mathrm{alkene}]} \tag{12}$$

Upon [substrate] → ∞ , Eqs. (13) and (14) were obtained.

$$(rate)_{\mathrm{inf}} = \frac{k_1 k_3[\mathrm{catalyst}][\mathrm{H_2O_2}]}{(k_2[\mathrm{H_2O}] + k_3)} \tag{13}$$

$$[\mathbf{II}]_{\mathrm{inf}} = \frac{k_1[\mathrm{catalyst}][\mathrm{H_2O_2}]}{(k_2[\mathrm{H_2O}] + k_3)} \tag{14}$$

From (13) and (14), Eq. (15) was obtained.

$$k_3 = \frac{(rate)_{\mathrm{inf}}}{[\mathbf{II}]_{\mathrm{inf}}} \tag{15}$$

When [substrate] = 0, Eqs. (16) and (17) were obtained.

$$[\mathbf{II}]_0 = \frac{k_1[\mathrm{catalyst}][\mathrm{H_2O_2}]}{k_2[\mathrm{H_2O}]} \tag{16}$$

$$[\mathbf{III}]_0 = \frac{k_1 k_3[\mathrm{catalyst}][\mathrm{H_2O_2}]}{k_2 k_4[\mathrm{H_2O}]^2} \tag{17}$$

From (16) and (17), Eq. (18) was obtained.

$$k_4 = \frac{k_3[\mathbf{II}]_0}{[\mathbf{III}]_0[\mathrm{H_2O}]} \tag{18}$$

From (14) and (16), Eq. (19) was obtained.

$$k_2 = \frac{k_3[\mathbf{II}]_{\mathrm{inf}}}{[\mathrm{H_2O}]([\mathbf{II}]_0 - [\mathbf{II}]_{\mathrm{inf}})} \tag{19}$$

From (16), Eq. (20) was obtained.

$$k_1 = \frac{k_2[\mathbf{II}]_0[\mathrm{H_2O}]}{[\mathrm{catalyst}][\mathrm{H_2O_2}]} \tag{20}$$

From (12), Eq. (21) was obtained.

$$\frac{\partial(1/rate)}{\partial(1/[\mathrm{alkene}])} = \frac{k_2 k_4 [\mathrm{H_2O}]^2}{k_1 k_3 k_5 [\mathrm{catalyst}][\mathrm{H_2O_2}]} \tag{21}$$

Experimental data:

(rate)$_{\mathrm{inf}}$ = 0.571 mM min^{-1}

∂(1/rate)/ ∂(1/[alkene]) = 18.9 min

[**II**]$_{\mathrm{inf}}$ = 0.010 [catalyst] = 0.0167 mM

[**II**]$_0$ = 0.018 [catalyst] = 0.0301 mM

[**III**]$_0$ = 0.0026 [catalyst] = 0.00434 mM

(alkene, 1-octene; [catalyst], 1.67 mM; [H_2O_2], 33.3 mM; [H_2O], 140 mM; temp., 293 K)

From experimental data and Eqs. (15) and (18) - (21), k_1-k_5 were obtained as follows;

$k_1 = 0.022$ mM^{-1} min^{-1}

$k_2 = 0.291$ mM^{-1} min^{-1}

$k_3 = 34.2$ min^{-1}

$k_4 = 1.69$ mM^{-1} min^{-1}

$k_5 = 12.2$ mM^{-1} min^{-1}.

Table S1. Calculated Cartesian coordinates of $[\gamma\text{-}H_2SiV_2W_{10}O_{40}]^{4-}$ with B3LYP

Atom	X/Å	Y/Å	Z/Å
O	-1.360765	0	1.165703
O	1.360765	0	1.165703
O	0	1.353847	-0.708406
O	0	-1.353847	-0.708406
O	-1.393391	2.861404	1.205674
O	1.393391	2.861404	1.205674
O	-2.820748	1.604991	-0.684123
O	2.820748	1.604991	-0.684123
O	1.393391	-2.861404	1.205674
O	-1.393391	-2.861404	1.205674
O	2.820748	-1.604991	-0.684123
O	-2.820748	-1.604991	-0.684123
O	-1.760127	0	-2.564117
O	1.760127	0	-2.564117
O	-3.908082	0	1.222475
O	3.908082	0	1.222475
O	-1.275519	3.550228	-1.349429
O	1.275519	3.550228	-1.349429
O	-1.275519	-3.550228	-1.349429
O	1.275519	-3.550228	-1.349429
O	0	2.036785	-3.154702
O	0	-2.036785	-3.154702
O	-2.577876	1.333881	3.101896
O	2.577876	1.333881	3.101896
O	2.577876	-1.333881	3.101896
O	-2.577876	-1.333881	3.101896

O	-4.25114	2.783652	1.419009
O	4.25114	2.783652	1.419009
O	4.25114	-2.783652	1.419009
O	-4.25114	-2.783652	1.419009
O	-2.794988	-2.468025	-3.432792
O	-2.794988	2.468025	-3.432792
O	0	5.254385	0.540195
O	0	-5.254385	0.540195
O	2.794988	2.468025	-3.432792
O	2.794988	-2.468025	-3.432792
Si	0	0	0.254912
W	-2.944673	1.673879	1.225167
W	2.944673	1.673879	1.225167
W	2.944673	-1.673879	1.225167
W	-2.944673	-1.673879	1.225167
W	-1.699205	-1.890048	-2.23298
W	-1.699205	1.890048	-2.23298
W	1.699205	1.890048	-2.23298
W	1.699205	-1.890048	-2.23298
W	0	3.584584	0.108194
W	0	-3.584584	0.108194
V	1.615932	0	3.798923
V	-1.615932	0	3.798923
O	0	1.200174	3.751041
O	0	-1.200174	3.751041
O	1.963858	0	5.345917
O	-1.963858	0	5.345917
H	0	1.862984	3.041746
H	0	-1.862984	3.041746

Table S2. Calculated Cartesian coordinates of [γ-$HSiV_2W_{10}O_{39}(OOH)$]$^{4-}$

Atom	X/Å	Y/Å	Z/Å
O	0.131468	-1.348141	1.143243
O	0.007836	1.391791	1.098968
O	-1.424395	-0.068954	-0.623993
O	1.273757	0.035694	-0.841096
O	-2.701155	-1.478740	1.434136
O	-2.828699	1.307041	1.381025
O	-1.561764	-2.902680	-0.532844
O	-1.800943	2.748173	-0.631235
O	2.876074	1.504528	0.950247
O	3.006653	-1.278171	0.934947
O	1.415884	2.854296	-0.873890
O	1.637846	-2.778650	-0.800707
O	-0.159501	-1.805288	-2.553491
O	-0.306003	1.712747	-2.606439
O	0.243026	-3.881071	1.257545

O	-0.082993	3.928134	1.127209
O	-3.612001	-1.442303	-1.057941
O	-3.719982	1.103564	-1.101886
O	3.458952	-1.162748	-1.655817
O	3.353863	1.391132	-1.675886
O	-2.307895	-0.144846	-3.007123
O	1.749203	0.020623	-3.335115
O	-0.987525	-2.572370	3.227599
O	-1.228305	2.596466	3.137944
O	1.439720	2.710093	2.929405
O	1.674760	-2.471235	3.000954
O	-2.495610	-4.327730	1.685130
O	-2.854704	4.171748	1.528006
O	2.694284	4.365107	1.093718
O	3.041220	-4.112549	1.223905
O	2.264383	-2.767227	-3.607381
O	-2.643775	-2.958958	-3.199604
O	-5.200861	-0.204872	0.950832
O	5.259763	0.220799	0.070075
O	-2.882366	2.618292	-3.297786
O	2.036239	2.819458	-3.690835
Si	0.002029	0.004386	0.230594
W	-1.454349	-2.987863	1.374261
W	-1.712570	2.905398	1.268159
W	1.620680	3.017203	1.017702
W	1.879389	-2.843778	1.106689
W	1.749174	-1.676588	-2.375090
W	-2.014721	-1.818512	-2.069345
W	-2.165446	1.573218	-2.128380
W	1.600242	1.720268	-2.435569
W	-3.574247	-0.144809	0.380828
W	3.562292	0.143583	-0.226260
V	0.196310	1.748986	3.771235
V	0.365644	-1.579320	3.807970
O	-0.862864	0.030608	3.813797
O	1.377374	0.145335	3.561749
O	0.311858	2.151532	5.302216
O	0.527882	-1.916065	5.350175
H	-1.583408	-0.011816	3.164270
O	2.790898	0.265164	3.749115
H	3.044434	0.569262	2.853161

Table S3. Calculated Cartesian coordinates of $[\gamma\text{-SiV}_2W_{10}O_{38}(O_2)]^{4-}$

Atom	X/Å	Y/Å	Z/Å
O	0	1.375283	1.145024
O	0	-1.375283	1.145024
O	1.355177	0	-0.709284

O	-1.355177	0	-0.709284
O	2.872500	1.408360	1.185946
O	2.872500	-1.408360	1.185946
O	1.609065	2.832018	-0.690254
O	1.609065	-2.832018	-0.690254
O	-2.872500	-1.408360	1.185946
O	-2.872500	1.408360	1.185946
O	-1.609065	-2.832018	-0.690254
O	-1.609065	2.832018	-0.690254
O	0	1.766031	-2.559645
O	0	-1.766031	-2.559645
O	0	3.899002	1.235957
O	0	-3.899002	1.235957
O	3.544087	1.272705	-1.360844
O	3.544087	-1.272705	-1.360844
O	-3.544087	1.272705	-1.360844
O	-3.544087	-1.272705	-1.360844
O	2.024433	0	-3.166366
O	-2.024433	0	-3.166366
O	1.355060	2.588546	3.126187
O	1.355060	-2.588546	3.126187
O	-1.355060	-2.588546	3.126187
O	-1.355060	2.588546	3.126187
O	2.774672	4.245678	1.409121
O	2.774672	-4.245678	1.409121
O	-2.774672	-4.245678	1.409121
O	-2.774672	4.245678	1.409121
O	-2.466730	2.790656	-3.443816
O	2.466730	2.790656	-3.443816
O	5.250123	0	0.532051
O	-5.250123	0	0.532051
O	2.466730	-2.790656	-3.443816
O	-2.466730	-2.790656	-3.443816
Si	0	0	0.26023
W	1.672679	2.933597	1.208626
W	1.672679	-2.933597	1.208626
W	-1.672679	-2.933597	1.208626
W	-1.672679	2.933597	1.208626
W	-1.891678	1.696384	-2.241643
W	1.891678	1.696384	-2.241643
W	1.891678	-1.696384	-2.241643
W	-1.891678	-1.696384	-2.241643
W	3.578080	0	0.111164
W	-3.578080	0	0.111164
V	0	-1.836335	3.942727
V	0	1.836335	3.942727
O	0.747903	0	4.170375
O	-0.747903	0	4.170375

O	0	-2.431080	5.418709
O	0	2.431080	5.418709

Table S4. Calculated Cartesian coordinates and the displacement vectors of the imaginary frequency mode of the transition state for the reaction of $[\gamma\text{-SiV}_2W_{10}O_{38}(O_2)]^{4-}$ with ethene

Atom	Cartesian coordinates			displacement vectors of the imaginary frequency mode		
	X/Å	Y/Å	Z/Å	X	Y	Z
O	0.241231	-1.379201	1.037940	0.00	0.00	-0.01
O	0.240173	1.380194	1.036729	0.00	0.00	-0.01
O	-1.552842	-0.000743	-0.385466	0.00	0.00	0.00
O	1.064392	-0.000133	-1.096726	0.00	0.00	0.00
O	-2.519875	-1.410361	1.844713	0.00	0.00	0.00
O	-2.521592	1.409799	1.843329	0.00	0.00	0.00
O	-1.793760	-2.833675	-0.297385	0.00	0.00	0.00
O	-1.796254	2.832241	-0.299266	0.00	0.00	0.00
O	3.027077	1.401861	0.339681	0.01	-0.01	0.01
O	3.028493	-1.398856	0.340901	0.01	0.01	0.01
O	1.316808	2.828418	-1.138137	0.00	0.00	0.00
O	1.319009	-2.828285	-1.135133	0.00	0.00	0.00
O	-0.731301	-1.767226	-2.524894	0.00	0.00	0.00
O	-0.732814	1.765177	-2.526087	0.00	0.00	0.00
O	0.268557	-3.900374	1.142914	0.00	0.00	-0.01
O	0.264859	3.901409	1.139579	0.00	0.00	-0.01
O	-3.837749	-1.273847	-0.434351	0.00	0.00	0.00
O	-3.839042	1.269954	-0.435378	0.00	0.00	0.00
O	3.011531	-1.276611	-2.298132	0.00	0.00	0.00
O	3.010223	1.277143	-2.299291	0.00	0.00	0.00
O	-2.845083	-0.002039	-2.577264	0.00	0.00	0.00
O	1.070654	-0.001456	-3.634464	0.00	0.00	0.00
O	-0.545636	-2.582405	3.315521	0.01	-0.01	-0.01
O	-0.547672	2.584207	3.313512	0.01	0.01	-0.01
O	2.064505	2.573370	2.612816	0.00	-0.04	-0.02
O	2.066717	-2.569027	2.615139	0.00	0.04	-0.02
O	-2.364038	-4.248550	2.036074	0.00	0.00	0.00
O	-2.367685	4.247885	2.033835	0.00	0.00	0.00
O	2.994024	4.234975	0.594278	0.01	0.00	0.00
O	2.998311	-4.231589	0.598444	0.01	0.00	0.00
O	1.416466	-2.795608	-4.016703	0.00	0.00	0.00
O	-3.345026	-2.792761	-2.726726	0.00	0.00	0.00
O	-4.985145	-0.001883	1.841187	0.00	0.00	0.00
O	5.152172	0.002070	-0.915100	0.01	0.00	0.01
O	-3.347356	2.788752	-2.727869	0.00	0.00	0.00
O	1.413824	2.792062	-4.020178	0.00	0.00	0.00
Si	0.009260	0.000044	0.192511	0.00	0.00	0.00

W	-1.353137	-2.936004	1.554096	0.00	0.00	0.00
W	-1.355557	2.935779	1.553270	0.00	0.00	0.00
W	1.871559	2.926572	0.686408	0.00	0.00	0.01
W	1.874620	-2.924209	0.690016	0.00	0.00	0.01
W	1.174742	-1.700754	-2.706175	0.00	0.00	0.00
W	-2.475567	-1.697763	-1.717033	0.00	0.00	0.00
W	-2.476919	1.695500	-1.717132	0.00	0.00	0.00
W	1.172917	1.698467	-2.708452	0.00	0.00	0.00
W	-3.481965	-0.001452	0.996448	0.00	0.00	0.00
W	3.425990	0.001203	-0.903297	0.00	0.00	0.00
V	0.952386	1.774595	3.736986	-0.04	-0.09	0.00
V	0.952463	-1.770695	3.738568	-0.04	0.09	0.00
O	1.318361	2.301143	5.197879	0.01	0.04	-0.01
O	1.318898	-2.295251	5.200081	0.01	0.04	-0.01
O	0.318400	0.001775	3.849310	0.06	0.00	-0.05
O	2.089127	0.002767	3.757974	0.72	0.00	0.02
C	4.122049	0.003628	3.061321	-0.36	0.00	-0.08
C	4.062999	0.004370	4.421390	-0.40	0.00	0.03
H	4.041718	-0.922168	4.987173	-0.17	-0.01	0.01
H	4.131511	0.926938	2.493569	-0.21	0.01	-0.06
H	4.132494	-0.920319	2.494616	-0.21	-0.01	-0.06
H	4.040689	0.931526	4.986119	-0.17	0.01	0.01

Table S5. Calculated Cartesian coordinates of the transition state for the reaction of peracetic acid with ethene

Atom	X/Å	Y/Å	Z/Å
C	-3.007002	-0.016129	0.000200
H	-3.389145	0.502556	0.881820
H	-3.389219	0.500206	-0.882774
H	-3.343592	-1.051166	0.001539
C	-1.492754	0.080171	-0.000023
O	-0.869655	-1.046620	0.000308
O	0.927372	-0.519366	-0.000101
H	3.027577	-0.725338	-1.244408
C	2.710442	0.142323	-0.682991
C	2.710461	0.143506	0.683181
H	2.473994	1.035864	-1.247149
H	2.473798	1.037960	1.245820
H	3.027294	-0.723330	1.246067
O	-0.921050	1.181883	-0.000547
H	0.499068	0.396848	-0.000405

Table S6. Calculated Cartesian coordinates of the transition state for the reaction of dimethyldioxirane with ethene

Atom	X/Å	Y/Å	Z/Å
C	-1.166622	-1.283072	-0.717487
C	-0.911642	-0.000056	0.071433
O	0.447853	-0.000139	0.710658
O	-1.327496	-0.000322	1.333819
C	-1.166780	1.283306	-0.716908
H	-2.236270	-1.350767	-0.943442
H	-0.885719	-2.146582	-0.110326
H	-0.623409	-1.303663	-1.669050
H	-0.885381	2.146543	-0.109591
H	-2.236548	1.351273	-0.942190
H	-0.624108	1.304142	-1.668774
C	2.114986	0.686532	-0.166539
C	2.115261	-0.686330	-0.166311
H	2.536642	1.250396	0.657100
H	1.771551	1.250302	-1.026327
H	1.772067	-1.250520	-1.025914
H	2.537095	-1.249713	0.657563

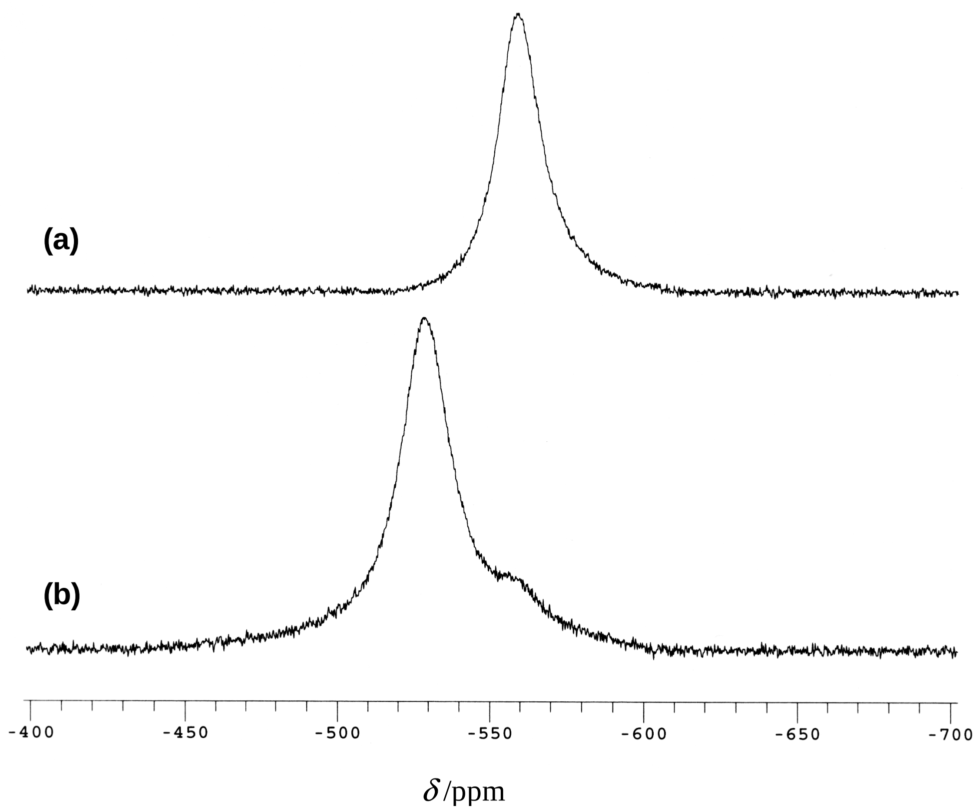

Figure S1. ^{51}V NMR spectra of (a) **I** (2.5 mM) in 1,2-$C_2D_4Cl_2$ and (b) **I** (2.5 mM) in 1,2-$C_2D_4Cl_2$ treated with 20 equiv. H_2O_2 (95% aq.) with respect to **I** at 253 K for 2 h.

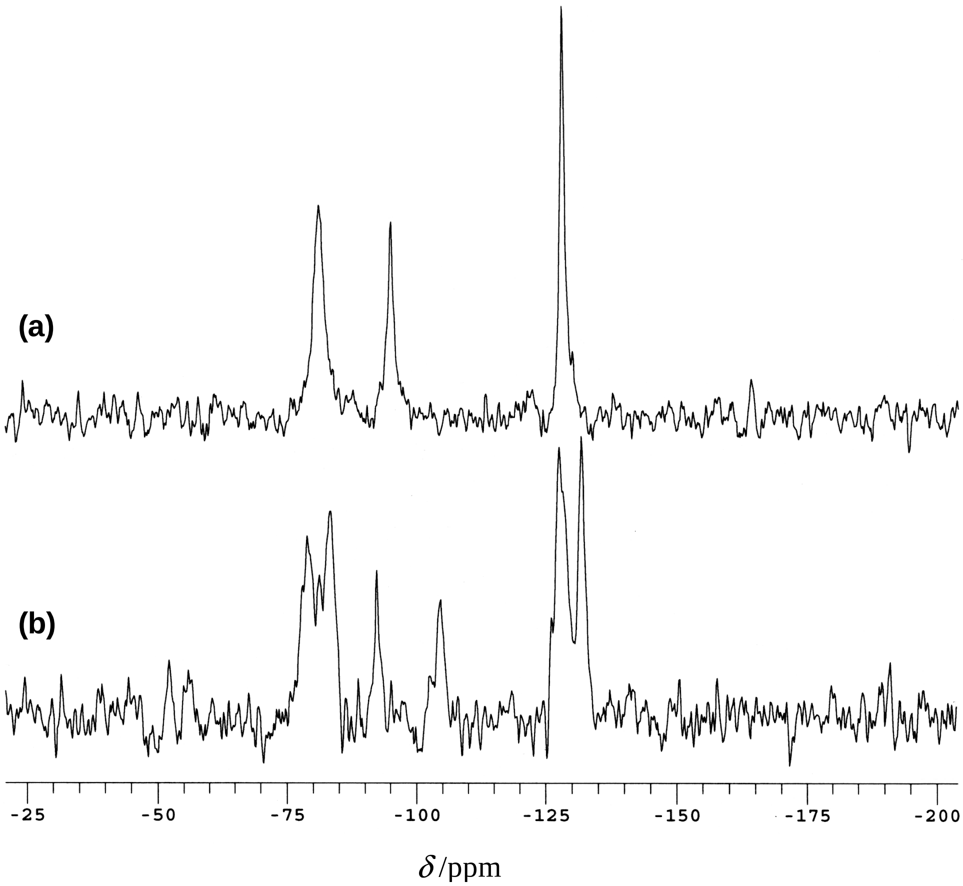

Figure S2. ^{183}W NMR spectra of (a) tetra-*n*-decylammonium salt of **I** (TDA-**I,** 0.1 M) in 1,2-$C_2D_4Cl_2$ and (b) TDA-**I** (0.1 M) in 1,2-$C_2D_4Cl_2$ treated with 15 equiv. H_2O_2 (95% aq.) with respect to TDA-**I** at 253 K for 2 h.

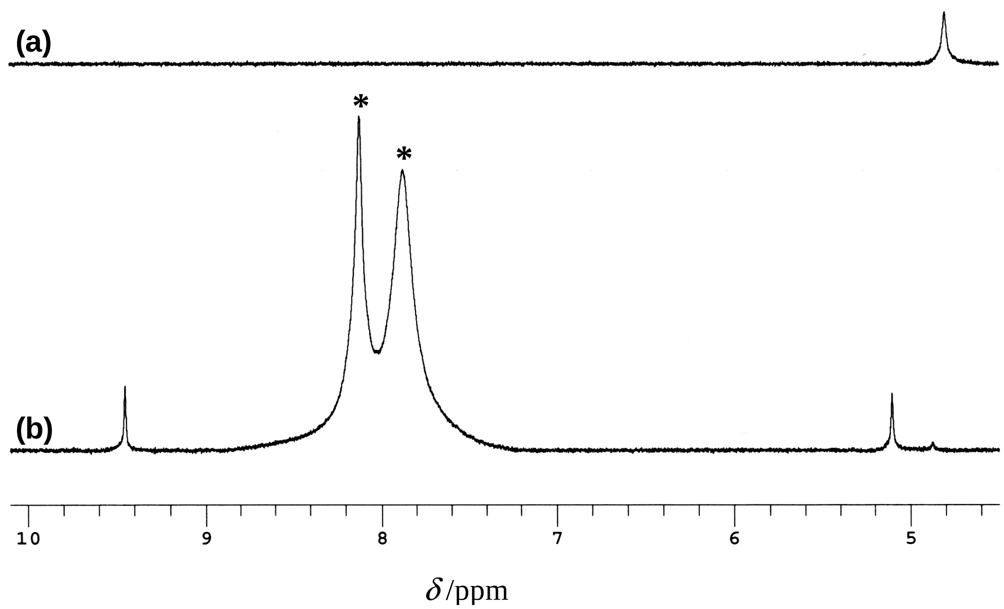

Figure S3. ¹H NMR spectra of (a) **I** (2.5 mM) in 1,2-$C_2D_4Cl_2$ and (b) **I** (2.5 mM) in 1,2-$C_2D_4Cl_2$ treated with 20 equiv. H_2O_2 (95% aq.) with respect to **I** at 253 K for 2 h. Asterisks are assigned the signals of H_2O_2 in organic and aqueous phases.

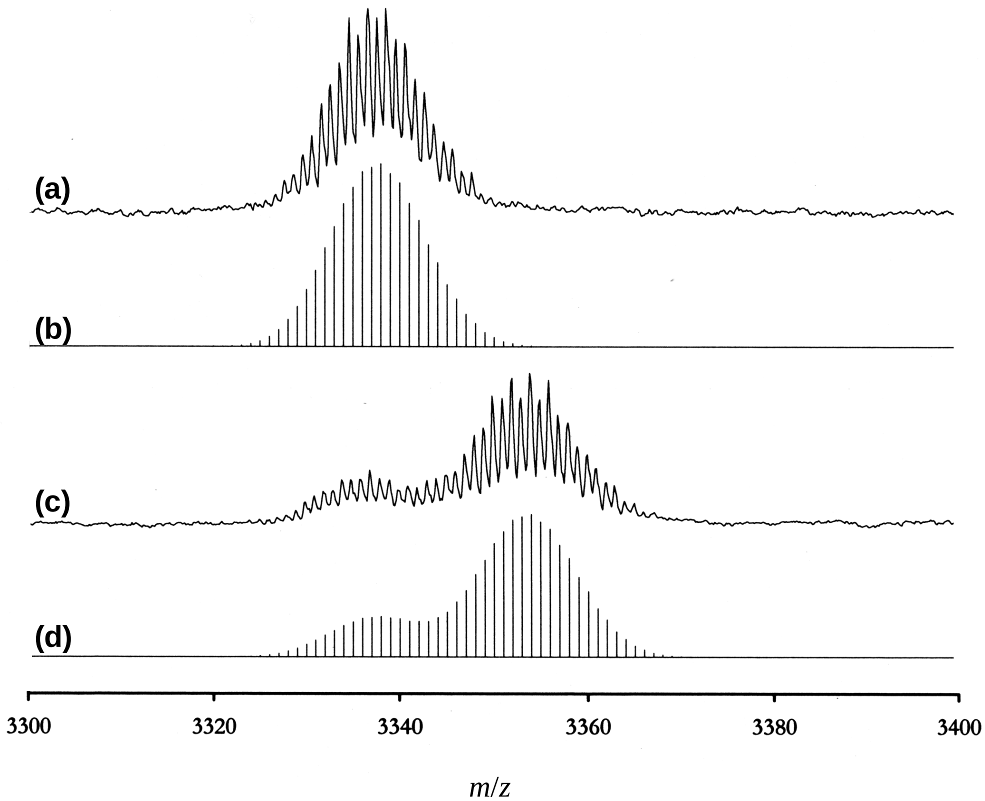

Figure S4. CSI-MS (anion mode, *m/z* 3300–3400) spectra of (a) **I (**0.14 mM) in 1,2-$C_2H_4Cl_2$ and (c) **I** (0.14 mM) in 1,2-$C_2H_4Cl_2$ treated with 350 equiv. H_2O_2 (96% aq.) with respect to **I** (253 K, 2 h). The lines in (b) are the calculated pattern of $[(TBA)_3H_2SiV_2W_{10}O_{40}]^-$. The lines in (d) are the calculated pattern of a mixture of $[(TBA)_3H_2SiV_2W_{10}O_{40}]^-$ (22%) and $[(TBA)_3HSiV_2W_{10}O_{39}(OOH)]^-$ (78%). An increase in the content of $[(TBA)_3H_2SiV_2W_{10}O_{40}]^-$ in comparison with those of Figures S1 and S2 is probably caused by the slight increase in the temperature at the inlet of the injection of the CSI-MS spectrometer.

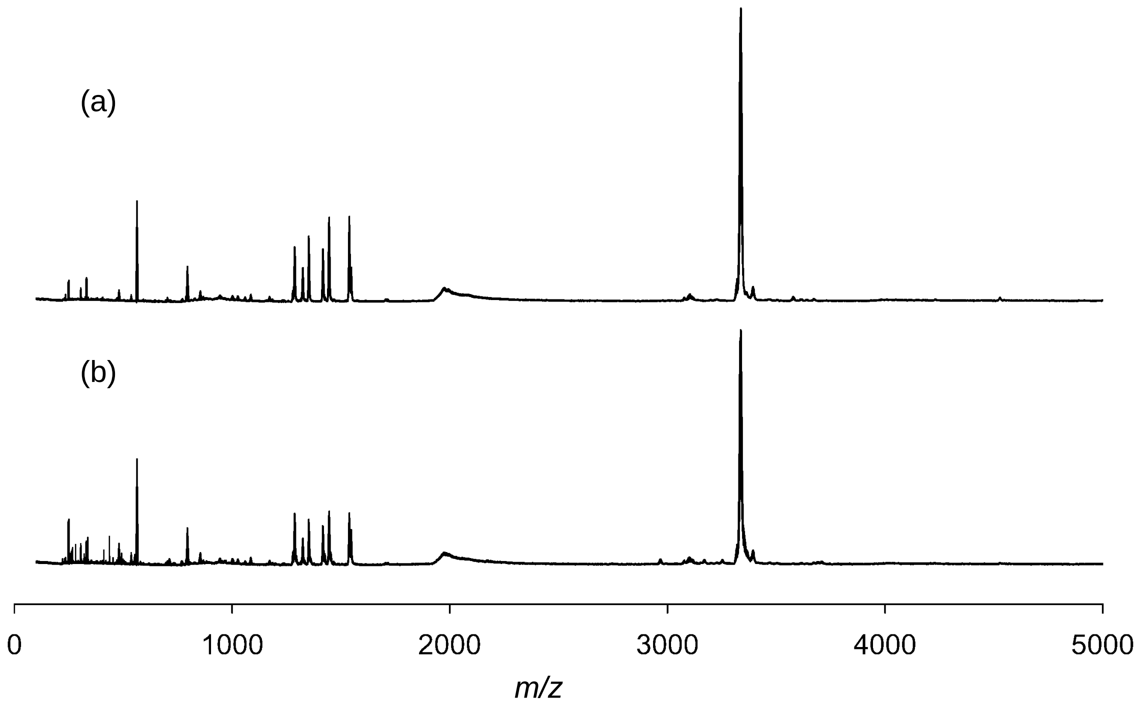

Figure S5. CSI-MS spectra (anion mode, *m*/*z* 100 - 5000) of (a) **I** (0.14 mM) in MeCN/*t*-BuOH (*v*/*v* = 1/1) and (b) treated with 240 equiv. of H_2O_2 (95% aq.) at room temperature for 3 min.

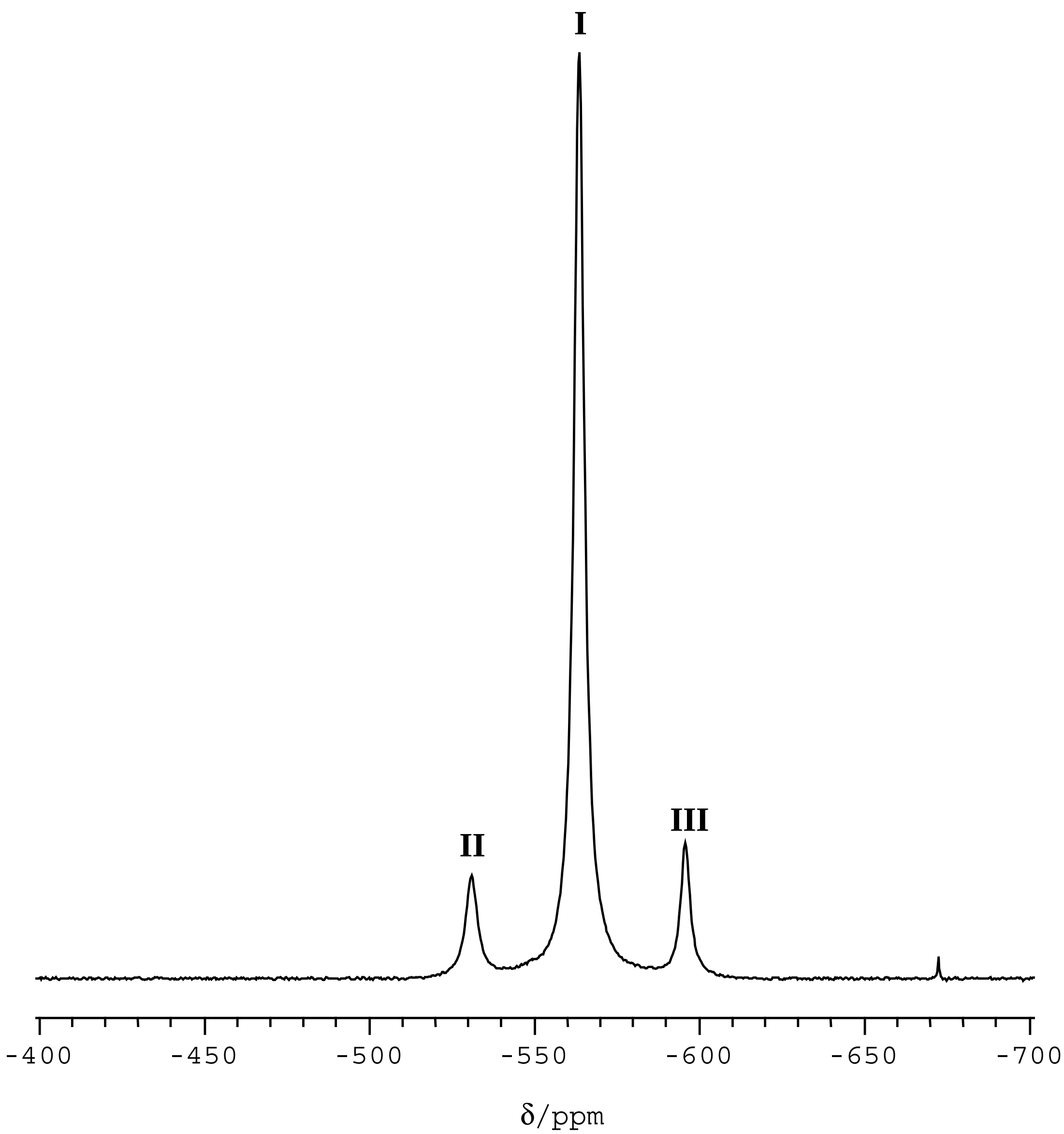

Figure S6. ^{51}V NMR spectrum of **I** (3.3 mM) treated with 10 equiv. of H_2O_2 (95% aq.) in MeCN/tBuOH (*v*/*v* = 1) at room temperature.

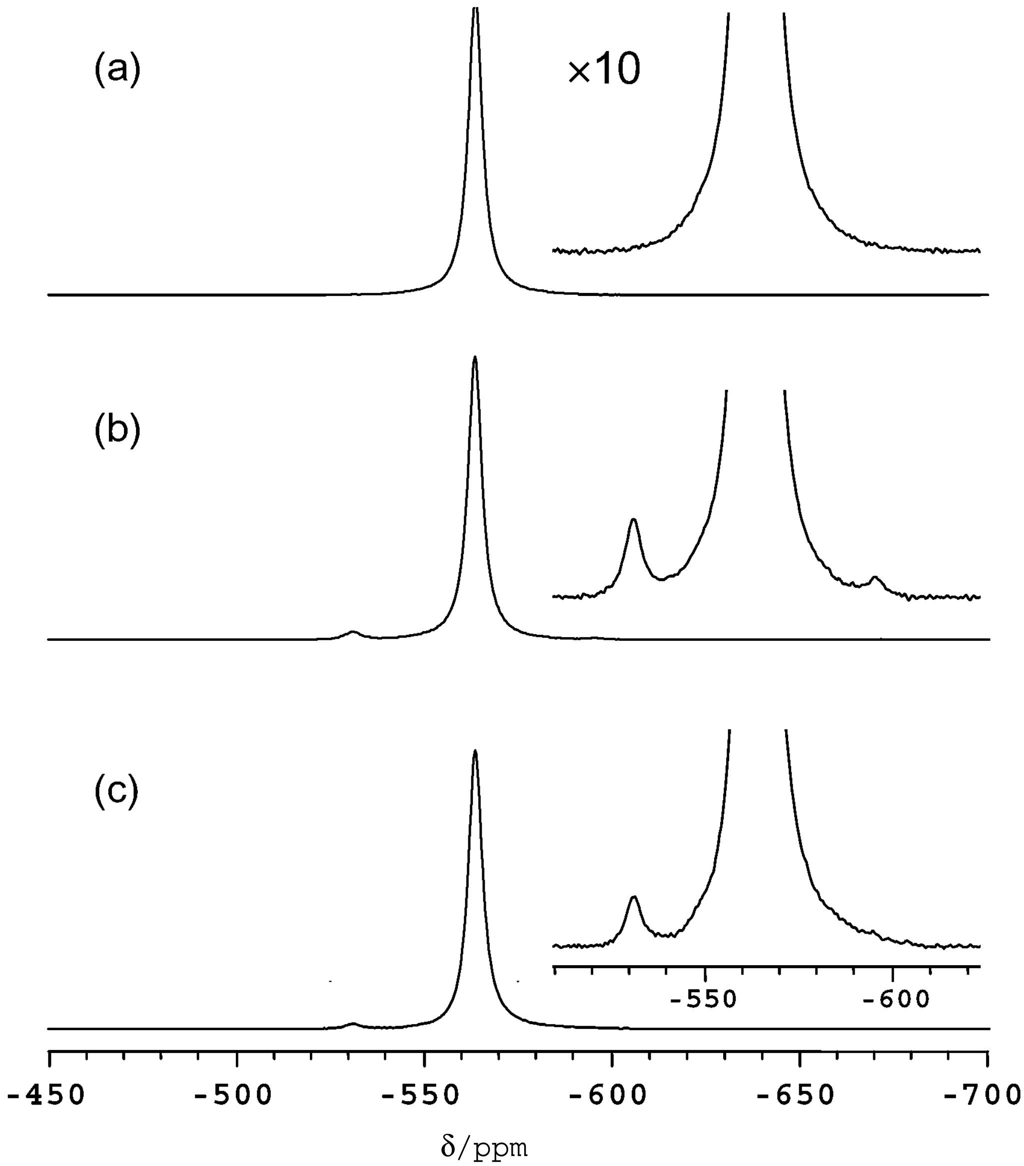

Figure S7. [51]V NMR spectra of (a) **I** (3.3 mM) in MeCN/*t*-BuOH (*v*/*v* = 1) and **I** (3.3 mM) treated with (b) 10 equiv. of H_2O_2 (30% aq.) and (c) 10 equiv. of 1-octene and 10 equiv. of H_2O_2 (30% aq.) at 293 K for 1.5 min.

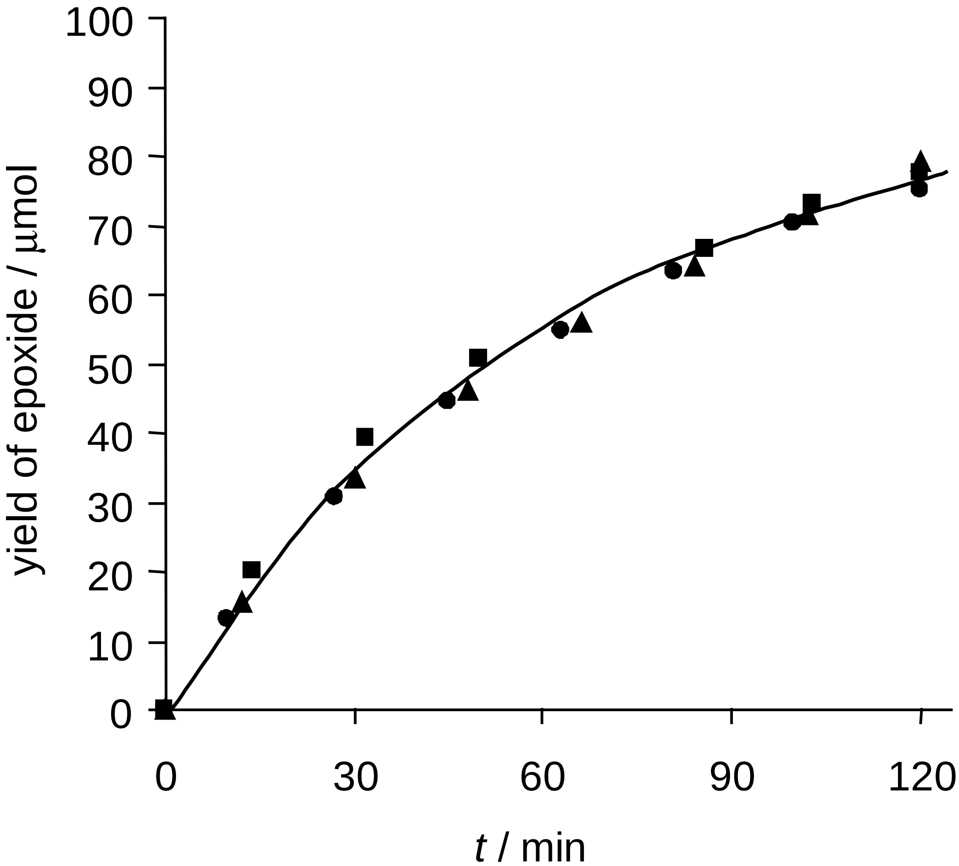

Figure S8. Time course of epoxidation of C8-alkenes catalyzed by **I**. Conditions: alkene (● , 1-octene; ■ , cyclooctene; ▲ , *cis*-2-octene) (500 µmol), **I** (5 µmol), H_2O_2 (30% aq., 100 µmol), MeCN (1.5 mL), *t*-BuOH (1.5 mL), 293 K.