SUPPORTING INFORMATION

Experimental and theoretical insights into the oxodiperoxomolybdenum-catalysed sulphide oxidation using hydrogen peroxide in ionic liquids

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Fig. S1. Selected structural parameters of the optimised transition structures **TS(1-2)**, **TS(1-8)**, **TS(3-9)** and **TS'(3-9)**.

Fig. S2. Reaction profile and structures of the intermediates and transition states for the oxidation of dimethylsulfide to dimethylsulfoxide with hydrogen peroxide catalysed by $[Mo(O)(O_2)_2(dmpz)]$ (relative Gibbs free energy in kcal·mol^{-1}).

Fig. S3. Reaction profile and structures of the intermediates and transition states for the oxidation of dimethylsulfide to dimethylsulfoxide with hydrogen peroxide catalysed by $[Mo(O)(O_2)_2(H_2O)]$ (relative Gibbs free energy in kcal·mol^{-1}).

Fig. S4. Reaction profile for the oxidation of methylphenylsulfide to methylphenylsulfoxide with hydrogen peroxide catalysed by $[Mo(O)(O_2)_2(Mepz)]$ (relative Gibbs free energy in kcal·mol^{-1}).

Fig. S5. Selected structural parameters of the optimised transition state structures concerning the oxidation of methylphenylsulfide catalysed by $[Mo(O)(O_2)_2(Mepz)]$.

Fig. S6 Evolution of the intermediate $[Mo(O)_2(O_2)(dmpz)]$, **3b**, under catalytic conditions: oxidation of **3b** with hydrogen peroxide *versus* oxidation of the dimetylsulfoxide substrate with **3b**.

Fig. S7 Evolution of the intermediate $[Mo(O)_2(O_2)(H2O)]$, **3c**, under catalytic conditions: oxidation of **3c** with hydrogen peroxide *versus* oxidation of the dimetylsulfoxide substrate with **3c**.

Fig. S8 Reaction profile and structures of the new intermediates and transition states for the oxidation of dimethylsulfoxide to dimethylsulfone with hydrogen peroxide catalysed by $[Mo(O)(O_2)_2(dmpz)]$ (relative Gibbs free energy in kcal·mol^{-1}).

Fig. S9 Reaction profile and structures of the new intermediates and transition states for the oxidation of dimethylsulfoxide to dimethylsulfone with hydrogen peroxide catalysed by $[Mo(O)(O_2)_2(H_2O)]$ (relative Gibbs free energy in kcal·mol^{-1}).

Fig. S10 Reaction profile and structures of the new intermediates and transition states for the oxidation of dimethylsulfoxide with $[Mo(O)(O_2)_2(dmpz)]$ (relative Gibbs free energy in kcal·mol^{-1}).

Fig. S11 Reaction profile and structures of the new intermediates and transition states for the oxidation of dimethylsulfoxide with $[Mo(O)(O_2)_2(H_2O)]$ (relative Gibbs free energy in kcal·mol^{-1}).

Table S1 Coordinates of the optimised molybdenum complexes.

Table S2 Energies of the optimised complexes involved in the Sharpless-type mechanism.

Table S3 Energies of the optimised complexes involved in the Thiel-type mechanism (with the co-ligand type **b**).

Table S4 Energies of the optimised reagents, products and ligands.

Table S5 Selected bond lengths [Å] and angles [°] for $[HMepz]_4[Mo_8O_{26}(Mepz)_2]\cdot 2H_2O$, **1**.

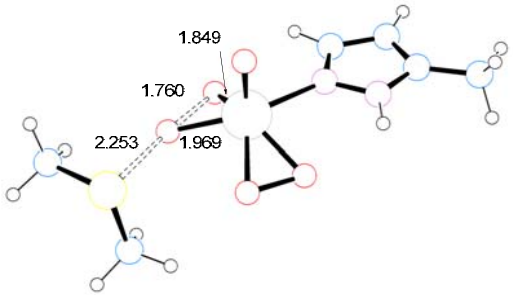
Table S6 Selected bond lengths [Å] and angles [°] for $[Hdmpz]_4[Mo_8O_{26}(dmpz)_2]\cdot 2dmpz$, **2**.

Table S7 Selected bond lengths [Å] and angles [°] for $[Hpz]_4[Mo_8O_{22}(O_2)_4(pz)_2]\cdot 3H_2O$, **3**.

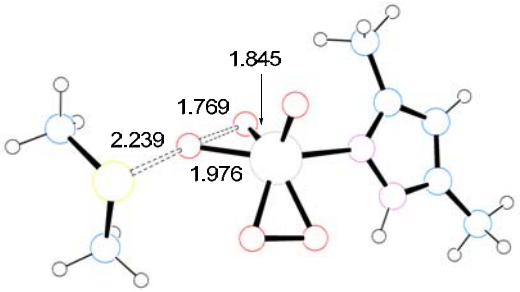
Table S8 Selected bond lengths [Å] and angles [°] for $[Him]_4[Mo_8O_{24}(O_2)_2(im)_2]\cdot 3H_2O$, **4**.

Table S9 Crystallographic data for compounds $[HMepz]_4[Mo_8O_{26}(Mepz)_2]\cdot 2H_2O$, **1**, $[Hdmpz]_4[Mo_8O_{26}(dmpz)_2]\cdot 2dmpz$, **2**, $[Hpz]_4[Mo_8O_{22}(O_2)_4(pz)_2]\cdot 3H_2O$, **3**, and $[Him]_4[Mo_8O_{24}(O_2)_2(im)_2]\cdot 3H_2O$, **4**.

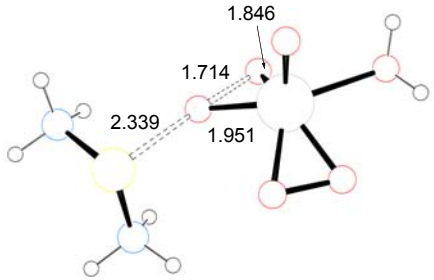
Fig. S1. Selected structural parameters of the optimised transition structures **TS(1-2)**, **TS(1-8)**, **TS(3-9)** and **TS'(3-9)**.



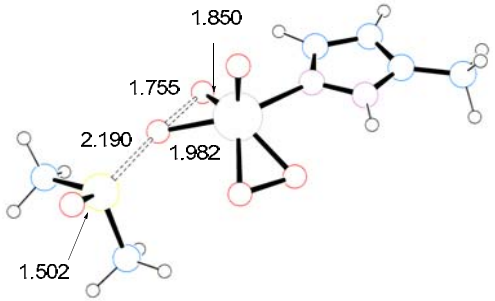
TS(1a-2a)



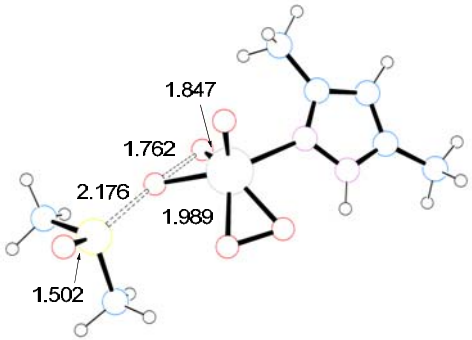
TS(1b-2b)



TS(1c-2c)



TS(1a-8a)



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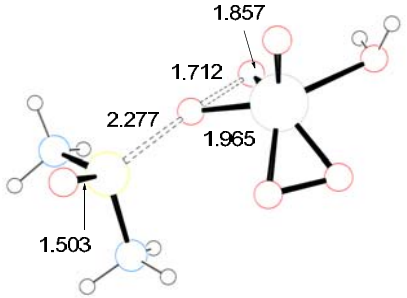

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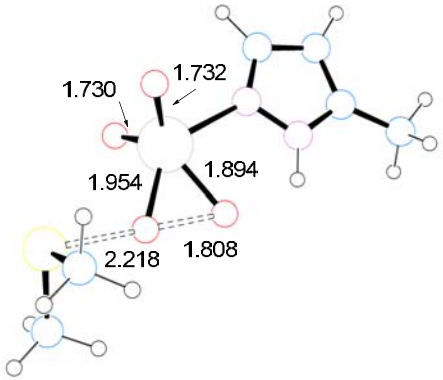

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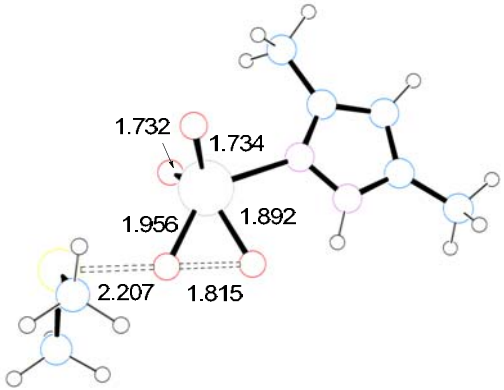

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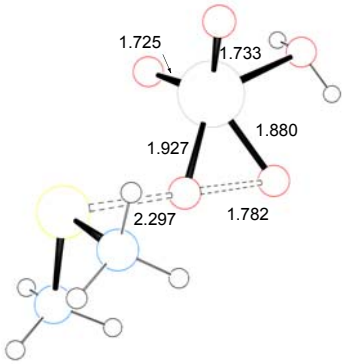

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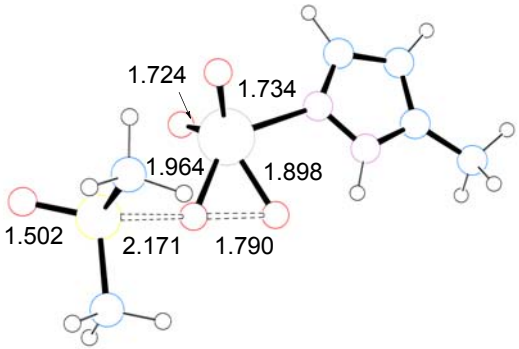

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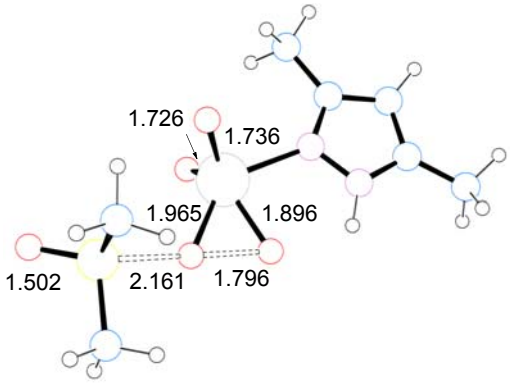

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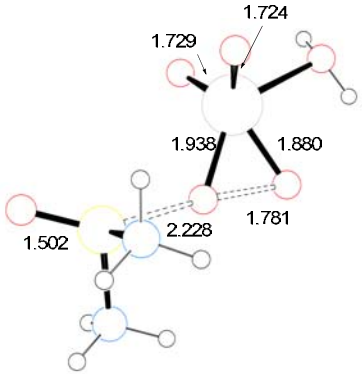
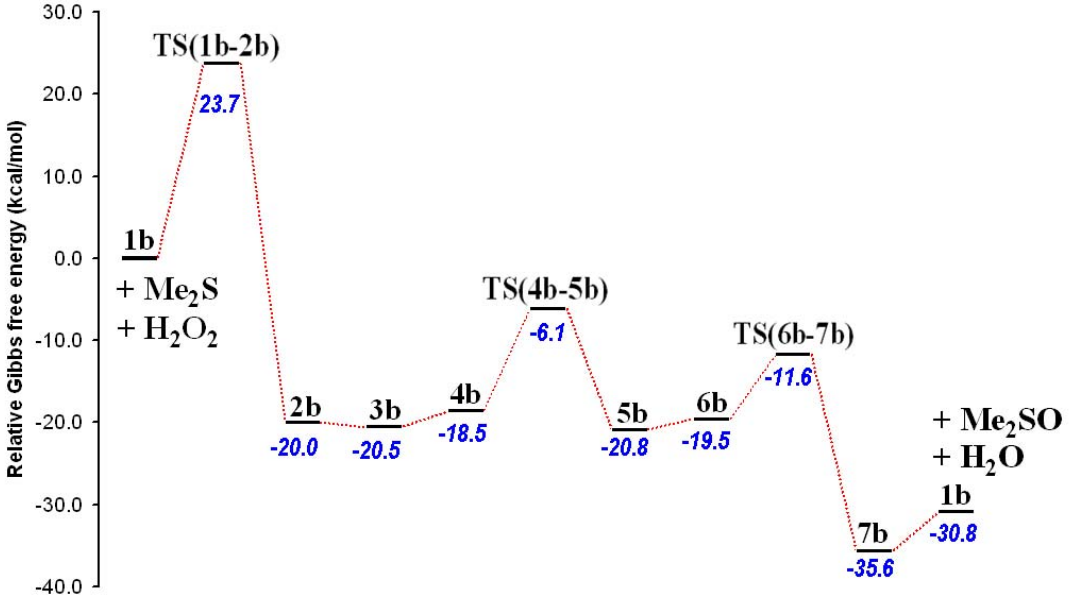


TS'(3c-9c)

Fig. S2. Reaction profile and structures of the intermediates and transition states for the oxidation of dimethylsulfide to dimethylsulfoxide with hydrogen peroxide catalysed by [Mo(O)(O_2)$_2$(dmpz)] (relative Gibbs free energy in kcal·mol^{-1}).



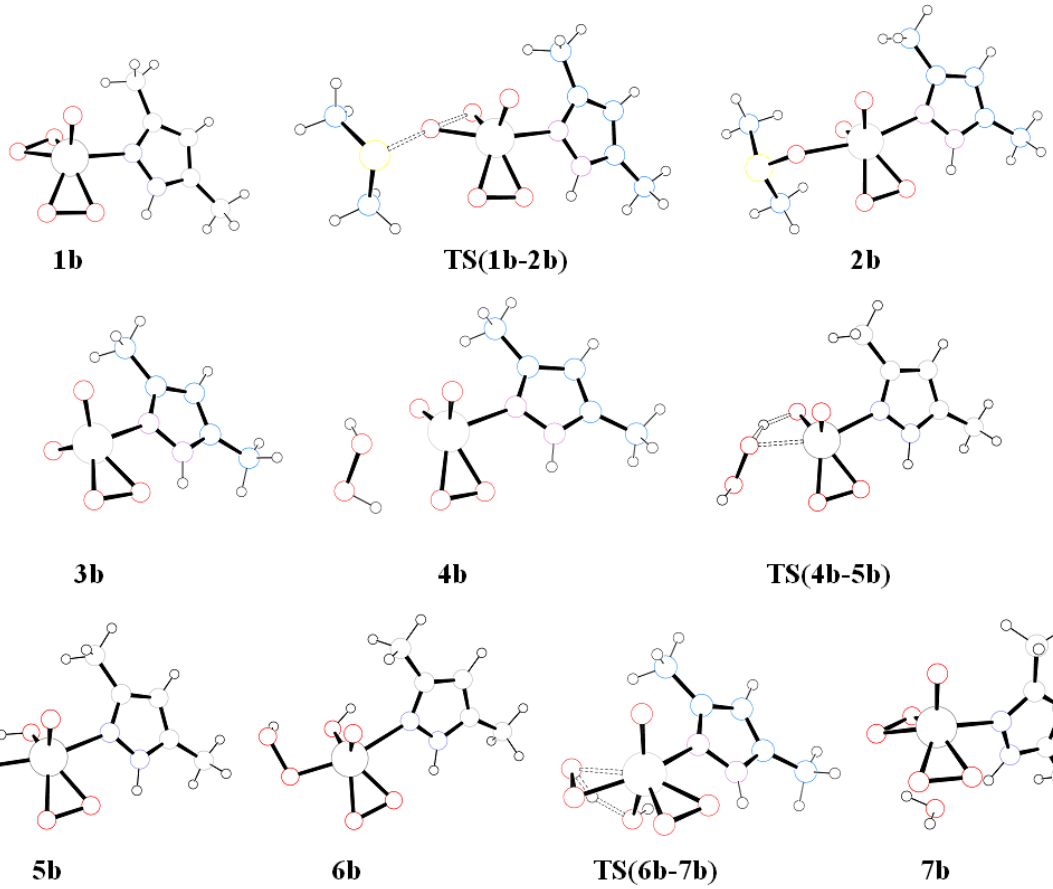
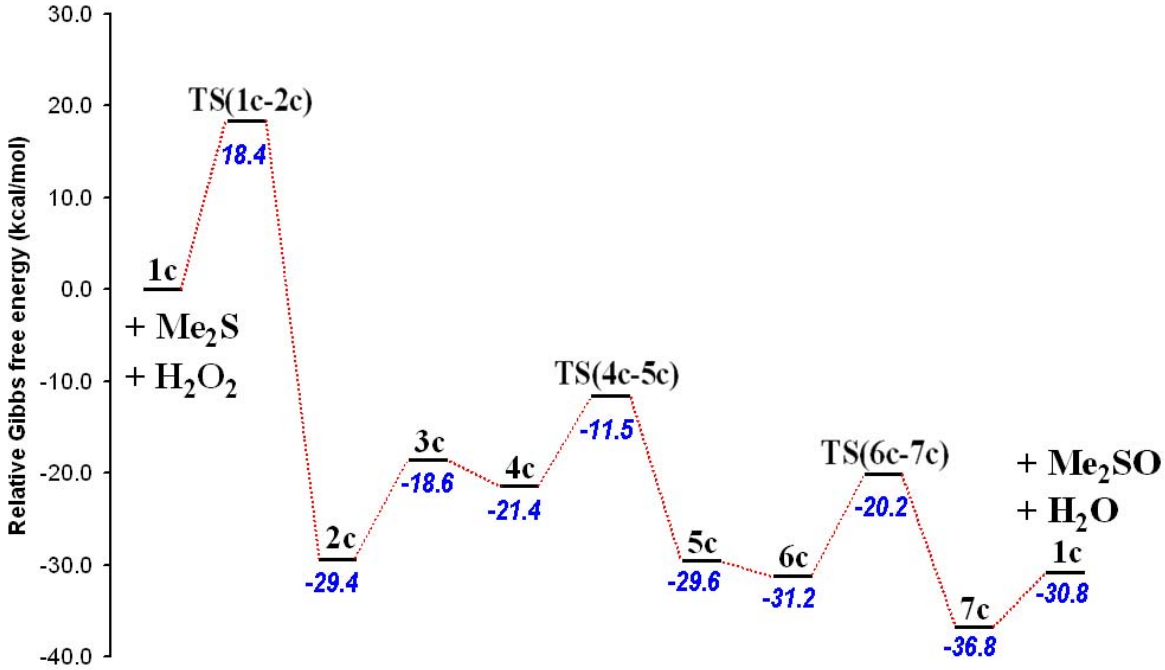
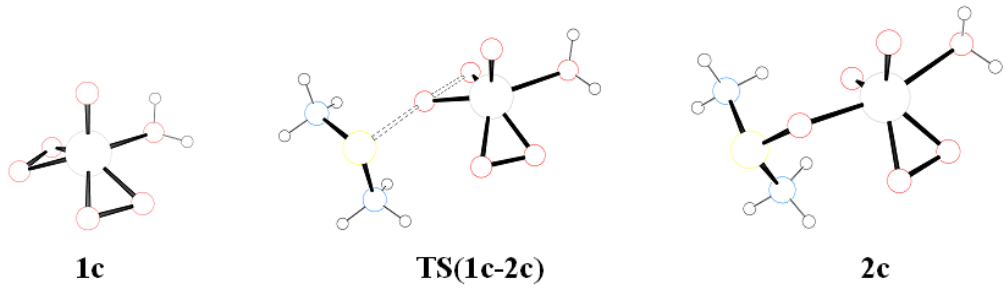
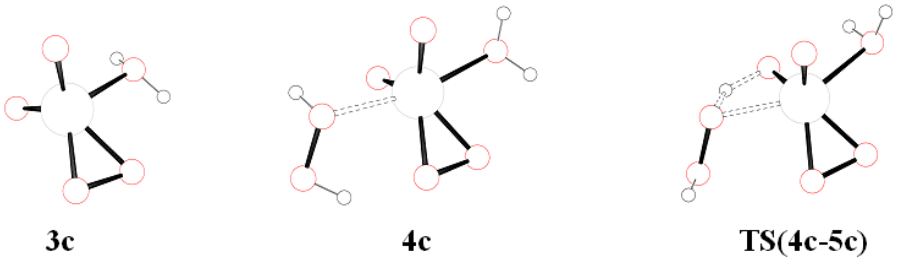


Fig. S3. Reaction profile and structures of the intermediates and transition states for the oxidation of dimethylsulfide to dimethylsulfoxide with hydrogen peroxide catalysed by $[Mo(O)(O_2)_2(H_2O)]$ (relative Gibbs free energy in kcal·mol^{-1}).







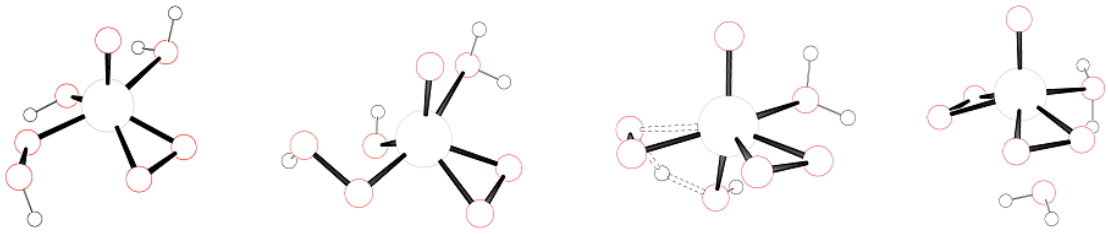


Fig. S4 Reaction profile for the oxidation of methylphenylsulfide to methylphenylsulfoxide with hydrogen peroxide catalysed by $[Mo(O)(O_2)_2(Mepz)]$ (relative Gibbs free energy in $kcal \cdot mol^{-1}$).

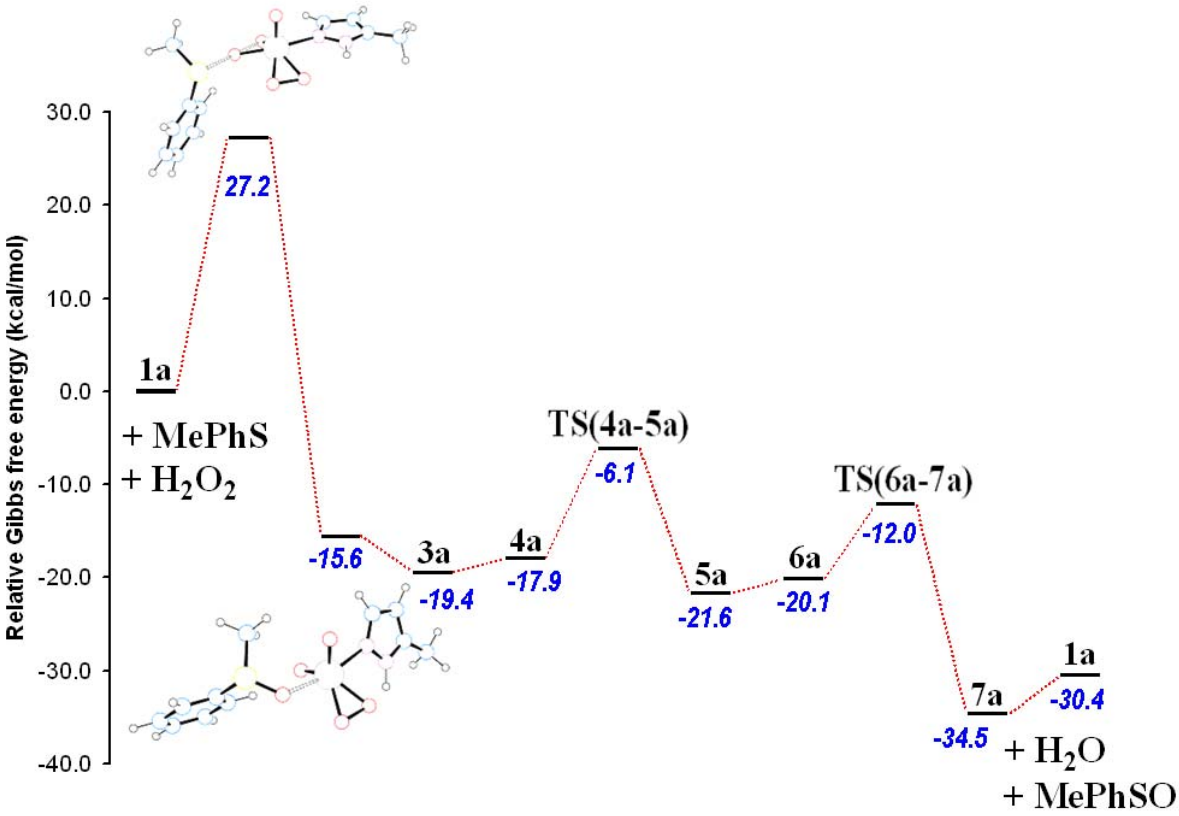


Fig. S5. Selected structural parameters of the optimised transition state structures concerning the oxidation of methylphenylsulfide catalysed by $[Mo(O)(O_2)_2(Mepz)]$.

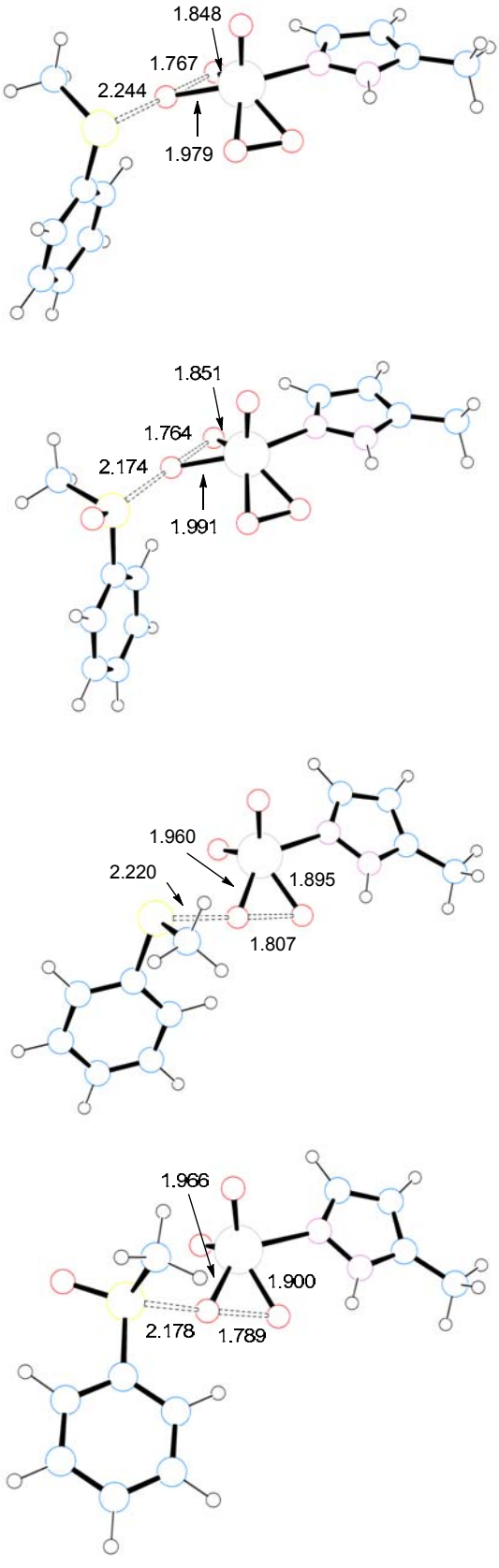


Fig. S6 Evolution of the intermediate [Mo(O)$_2$(O$_2$)(dmpz)], **3b**, under catalytic conditions: oxidation of **3b** with hydrogen peroxide *versus* oxidation of the dimetylsulfoxide substrate with **3b**.

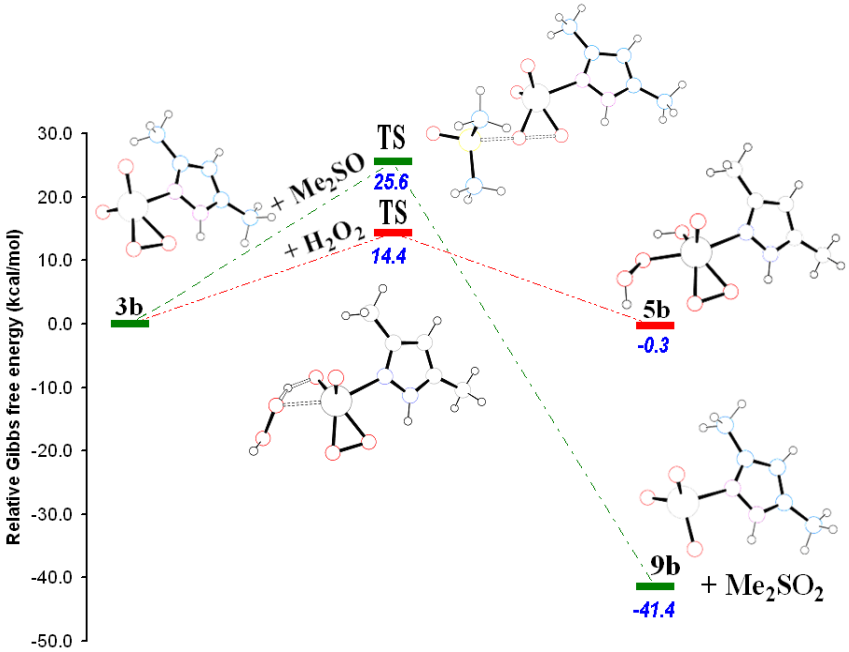


Fig. S7 Evolution of the intermediate [Mo(O)$_2$(O$_2$)(H2O)], **3c**, under catalytic conditions: oxidation of **3c** with hydrogen peroxide *versus* oxidation of the dimetylsulfoxide substrate with **3c**.

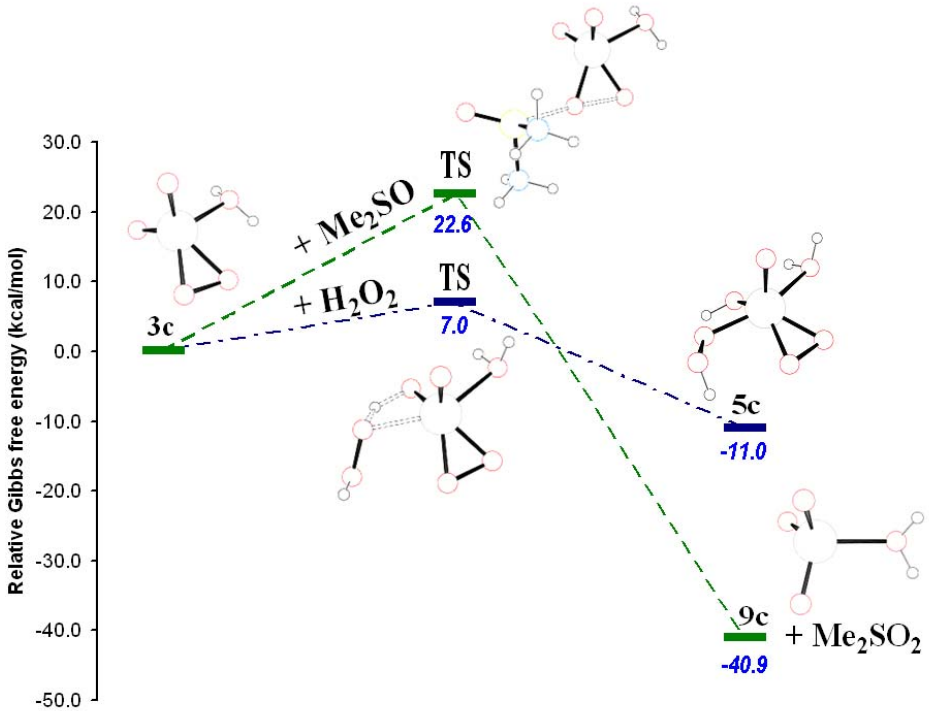
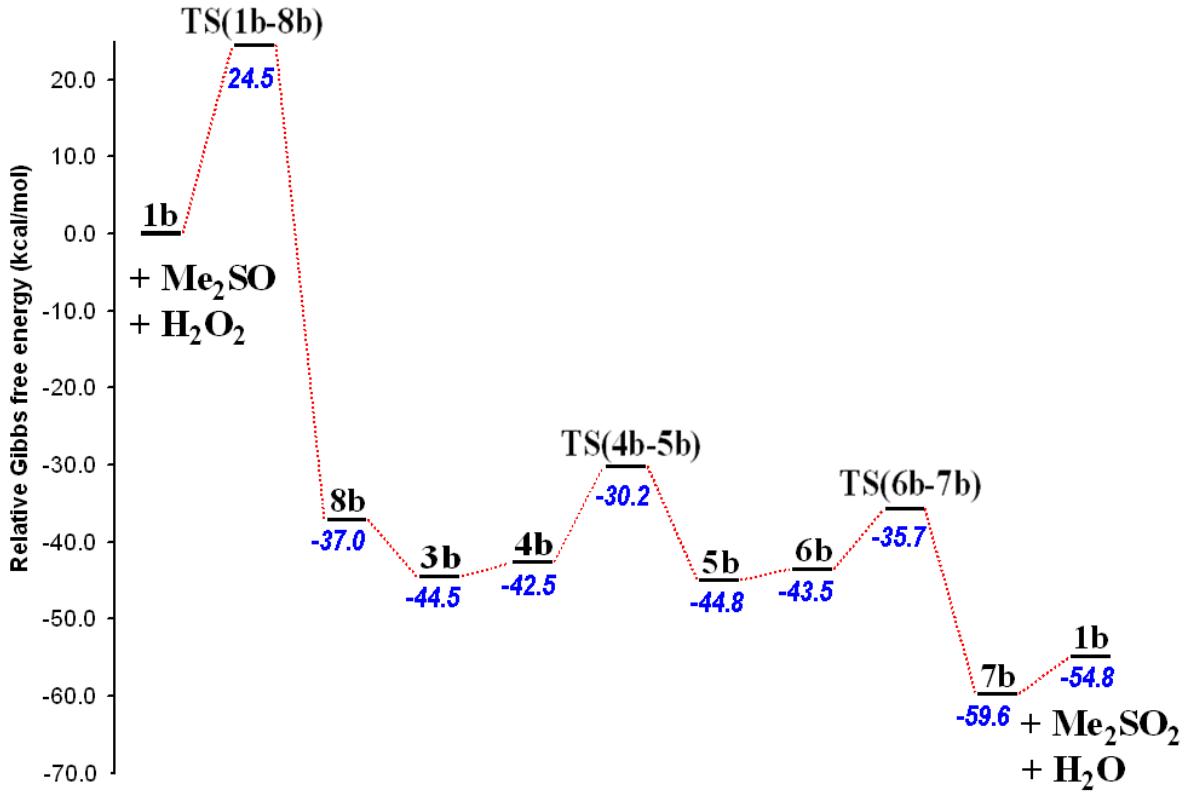
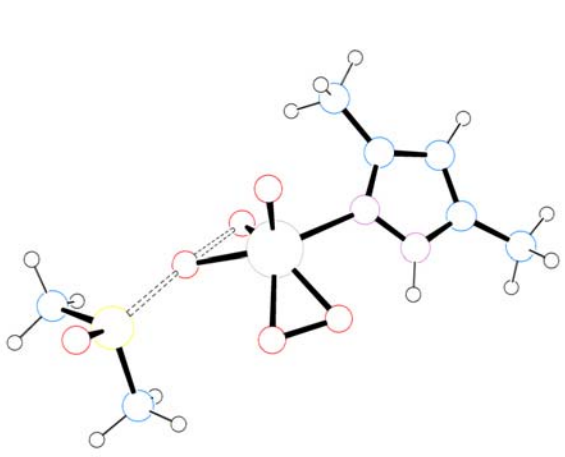
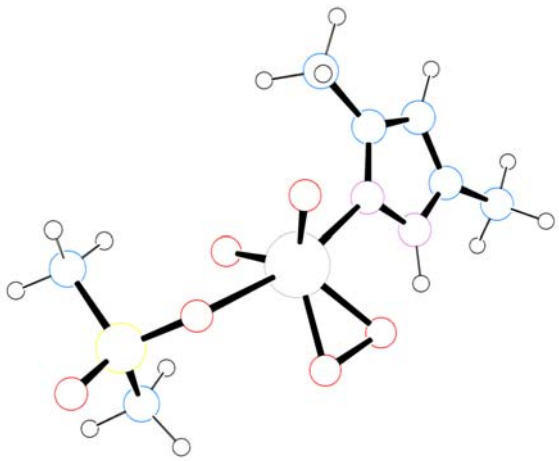


Fig. S8 Reaction profile and structures of the new intermediates and transition states for the oxidation of dimethylsulfoxide to dimethylsulfone with hydrogen peroxide catalysed by $[Mo(O)(O_2)_2(dmpz)]$ (relative Gibbs free energy in kcal·mol^{-1}).



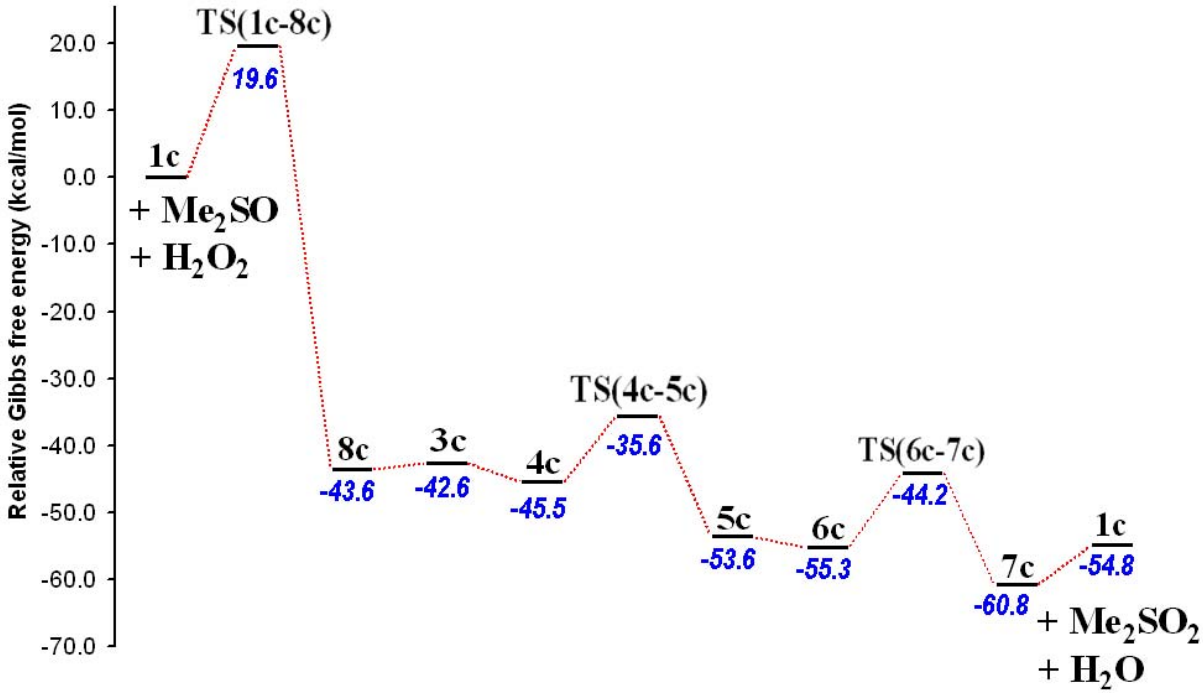


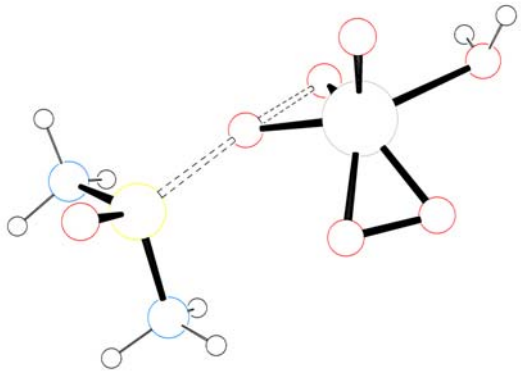
TS(1b-8b)



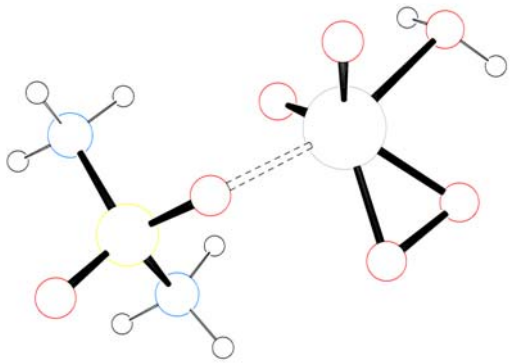
8b

Fig. S9 Reaction profile and structures of the new intermediates and transition states for the oxidation of dimethylsulfoxide to dimethylsulfone with hydrogen peroxide catalysed by $[Mo(O)(O_2)_2(H_2O)]$ (relative Gibbs free energy in kcal·mol^{-1}).



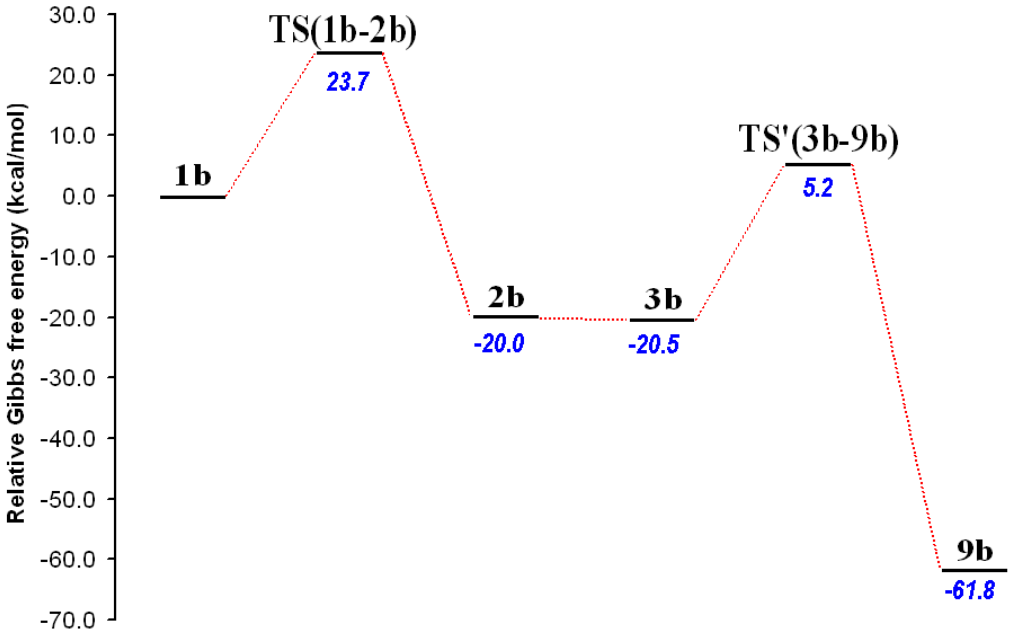


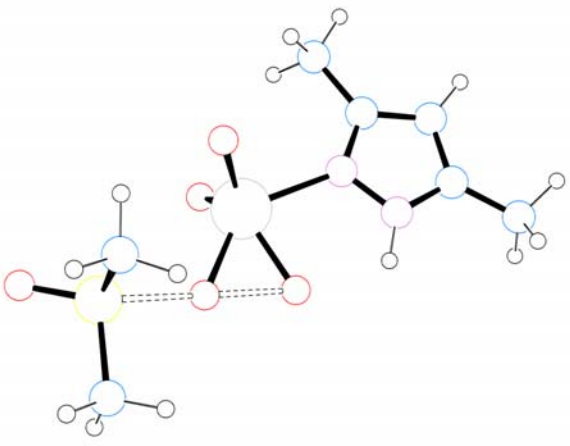
TS(1c-8c)



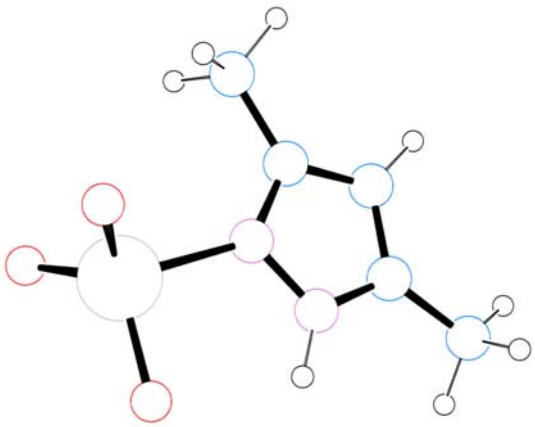
8c

Fig. S10 Reaction profile and structures of the new intermediates and transition states for the oxidation of dimethylsulfoxide with [Mo(O)(O_2)$_2$(dmpz)] (relative Gibbs free energy in kcal·mol^{-1}).



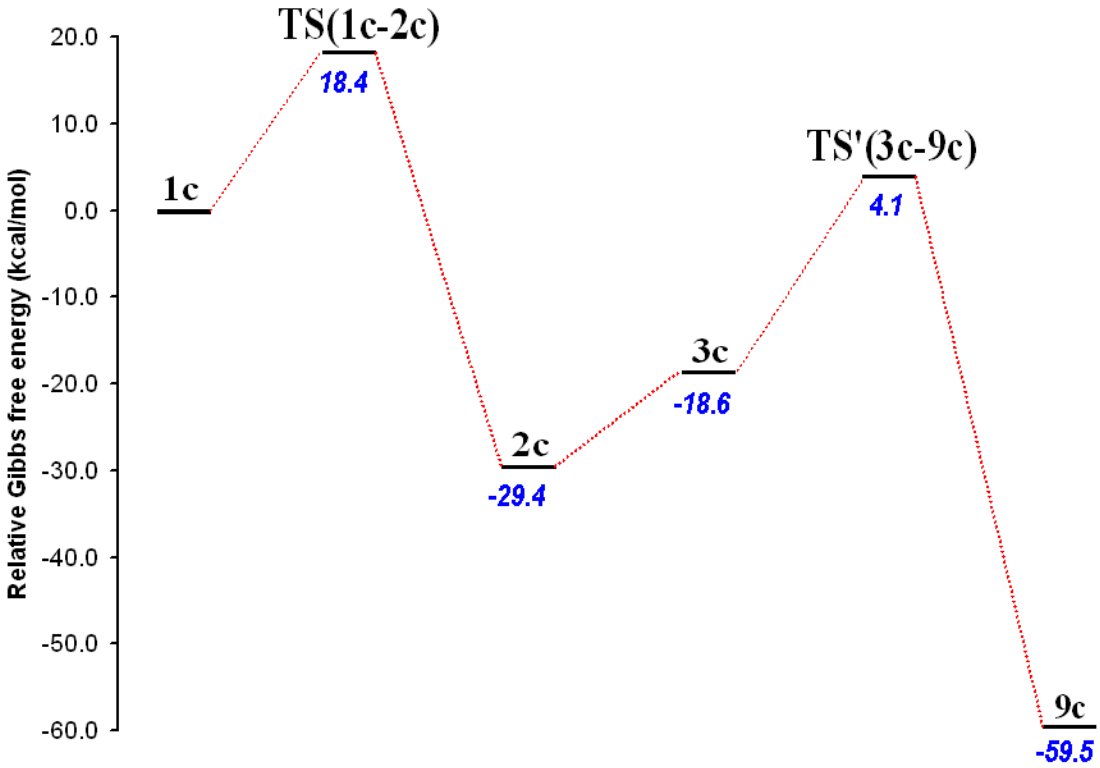


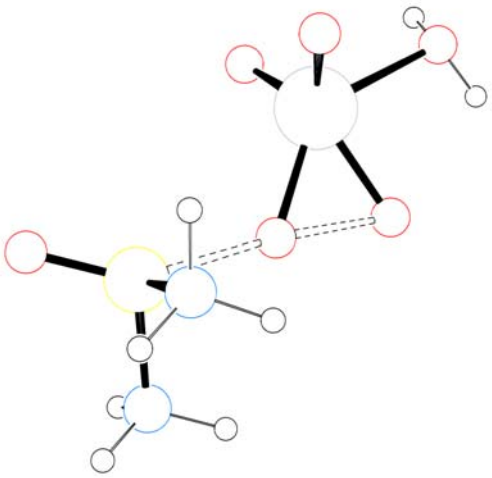
TS'(3b-9b)



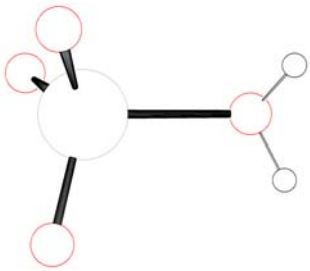
9b

Fig. S11 Reaction profile and structures of the new intermediates and transition states for the oxidation of dimethylsulfoxide with $[Mo(O)(O_2)_2(H_2O)]$ (relative Gibbs free energy in kcal·mol^{-1}).





TS'(3c-9c)



9c

Table S1a Coordinates of the optimised complexes containing the methylpyrazol ligand (type **a**).

1a

H	-4.338900	1.792600	0.397700
H	-1.114100	-2.469100	0.453200
N	-0.947500	-0.406300	0.108200
C	-1.637700	-1.541700	0.273100
H	-1.517500	1.504500	-0.287100
H	-5.231500	0.369000	-0.158800
N	-1.861900	0.567500	-0.102900
H	-3.818900	-1.991300	0.257700
C	-3.009200	-1.283500	0.168700
C	-3.122900	0.083200	-0.079300
C	-4.319500	0.950800	-0.302100
H	-4.332900	1.357400	-1.319100
O	1.587700	-0.357200	1.728500
O	0.501200	1.849100	0.026300
Mo	1.200400	0.034000	0.128200
O	1.269300	-1.533300	-0.999300
O	1.893300	1.797400	-0.353500
O	2.515900	-0.802300	-1.043300

TS(1a-2a)

H	-5.546100	1.422600	0.779800
N	-2.037300	-0.412600	-0.131000
C	-2.693800	-1.518500	-0.487300
H	-2.647300	1.491200	0.231600
H	-6.315100	0.395300	-0.438400
N	-2.968100	0.557900	0.000700
H	-4.854300	-1.932900	-0.858700
C	-4.066200	-1.246700	-0.588900
C	-4.212300	0.100900	-0.272100
C	-5.420800	0.979100	-0.213600
H	-5.357600	1.795800	-0.940900
H	-2.140200	-2.431500	-0.651300
O	-0.096800	-0.346100	2.011700
O	-0.520000	1.734600	-0.172500
Mo	0.104000	-0.049000	0.345000
O	0.344500	-1.602000	-0.628600
O	0.888200	1.750200	0.126100
O	1.845100	-0.787900	-0.201600
S	3.744500	0.349200	0.217300
C	3.722600	1.085200	-1.443700
H	3.355700	0.344700	-2.157400
H	3.015100	1.914400	-1.396000
H	4.714700	1.445800	-1.726500
C	4.702900	-1.163500	-0.090600
H	5.708500	-0.921600	-0.443400
H	4.769700	-1.697700	0.858900
H	4.170900	-1.782900	-0.815700

2a

H	5.340600	1.788400	0.294000
N	1.938900	-0.432500	-0.081000
C	2.691600	-1.530900	-0.098600
H	2.343900	1.503000	0.346300
H	5.974400	0.484500	1.307100

N	2.732000	0.566600	0.356000
H	4.833300	-1.898800	0.419600
C	3.995400	-1.224700	0.327900
C	3.993100	0.137900	0.604900
C	5.077200	1.058000	1.067200
H	4.779500	1.611900	1.963900
H	2.256400	-2.465500	-0.420100
O	-0.134700	-1.508000	-1.469900
O	0.641500	1.601600	-1.014900
Mo	-0.235500	-0.090400	-0.489300
O	-0.528500	-0.340500	1.213000
O	-0.776300	1.657900	-1.205800
O	-2.462800	-0.289700	-0.785300
S	-3.598400	0.002600	0.224900
C	-3.470300	-1.251900	1.542500
H	-2.447400	-1.258000	1.922800
H	-4.202300	-1.010600	2.318100
H	-3.717400	-2.210400	1.082600
C	-3.140800	1.480400	1.193200
H	-2.960600	2.277800	0.470500
H	-3.987900	1.729600	1.837700
H	-2.234300	1.281200	1.765200

3a

O	-1.862400	-1.275300	-1.086100
O	-0.684000	1.720100	-0.468900
O	-2.108200	1.649600	-0.229600
Mo	-1.326900	-0.094400	0.045300
O	-1.582800	-0.600900	1.670100
H	4.081200	1.848500	-0.623600
H	5.048400	0.514300	0.022900
H	3.732900	-1.920500	-0.237300
H	1.048100	-2.526600	-0.330300
C	2.894600	-1.246300	-0.153200
C	4.115500	1.067300	0.142900
C	1.534600	-1.571000	-0.201500
C	2.953200	0.135700	0.021700
N	0.800000	-0.459400	-0.066600
N	1.673300	0.563600	0.072400
H	1.286500	1.499500	0.157700
H	4.133500	1.556500	1.122500

4a

O	0.753100	-0.631100	1.784000
O	0.218900	1.657300	-0.469500
O	1.602600	1.658700	-0.106000
Mo	0.829000	-0.137000	0.139300
O	1.114200	-1.444200	-0.962900
H	-4.267300	-1.814400	-0.516600
C	-3.426100	-1.161600	-0.341400
C	-2.065400	-1.497700	-0.370900
C	-3.477800	0.197800	-0.044900
N	-1.327500	-0.416100	-0.108500
N	-2.193700	0.600200	0.094600
H	-1.803200	1.523800	0.249000
C	-4.632800	1.134200	0.107500
H	-4.646700	1.594700	1.100900
H	-4.596400	1.938000	-0.635700
H	-5.570300	0.592100	-0.027100
H	-1.578000	-2.440500	-0.569600

H	3.303100	-1.211100	-0.230300
O	3.252900	-0.386000	0.287400
O	3.974700	0.527400	-0.591800
H	3.268500	1.190800	-0.754700

TS(4a-5a)

O	-0.765000	0.000400	1.962100
O	-0.262000	-1.687700	-0.562900
O	-1.655200	-1.733600	-0.276400
Mo	-0.891300	-0.017600	0.264300
O	-1.091500	1.667500	-0.422800
H	4.057800	2.029600	-0.501600
C	3.276300	1.303600	-0.338300
C	1.896000	1.538400	-0.266300
C	3.442500	-0.067100	-0.160700
N	1.252400	0.387100	-0.056600
N	2.199800	-0.575900	0.010500
H	1.899700	-1.537000	0.116400
H	1.322000	2.448400	-0.360100
C	4.668600	-0.921700	-0.138800
H	4.801000	-1.405700	0.834800
H	4.623700	-1.706300	-0.901600
H	5.550800	-0.309900	-0.334500
H	-2.301500	1.470600	-0.289800
O	-3.026300	0.563300	0.093100
O	-3.564400	0.048200	-1.155900
H	-3.469900	-0.911300	-1.016700

5a

O	-0.851400	-0.050900	1.787500
O	-0.248000	-1.595300	-0.693500
O	-1.664200	-1.666300	-0.536500
Mo	-0.939300	0.046600	0.097500
O	-0.818500	1.859700	-0.553800
H	-1.705500	2.237600	-0.685500
O	-2.823500	0.631700	-0.215100
H	4.199900	1.894100	-0.188000
C	3.368700	1.208000	-0.131700
C	2.001400	1.518300	-0.173200
C	3.443000	-0.175500	-0.003800
N	1.278100	0.400500	-0.078500
N	2.163700	-0.616300	0.029300
H	1.801400	-1.560900	0.072200
H	1.491600	2.464300	-0.271800
C	4.613500	-1.100900	0.087800
H	4.624200	-1.640500	1.040900
H	4.602400	-1.842400	-0.718200
H	5.542200	-0.532800	0.011200
O	-3.833100	-0.341700	0.091700
H	-3.848700	-0.863900	-0.729200

6a

O	-1.109300	-0.728400	-1.582100
O	-0.125200	1.797200	-0.375100
O	-1.529400	2.025600	-0.254000
Mo	-1.057000	0.126100	-0.114800
O	-0.848200	-0.769000	1.607500
H	-0.063500	-1.329800	1.677300
O	-2.950800	0.132400	0.361200
H	4.096800	-1.931900	-0.737600

C	3.294600	-1.268300	-0.453000
C	1.914600	-1.467600	-0.625200
C	3.422800	-0.023200	0.151900
N	1.232200	-0.423600	-0.148800
N	2.159600	0.437100	0.326800
H	1.842700	1.348800	0.634000
H	1.383500	-2.293500	-1.076600
C	4.627500	0.757200	0.570300
H	4.668600	1.729300	0.067300
H	4.634800	0.937500	1.650600
H	5.534300	0.206700	0.313800
O	-3.211300	-1.280700	0.472100
H	-2.807600	-1.463300	1.345500

TS(6a-7a)

O	-1.196800	-0.707700	-1.697300
O	-0.322500	1.830000	-0.503400
O	-1.752800	1.897700	-0.373100
Mo	-1.116100	0.080100	-0.197700
O	-2.862800	-0.318800	0.560800
H	4.023400	-1.849300	-0.773000
C	3.196000	-1.213000	-0.498800
C	1.827600	-1.455400	-0.698500
C	3.274600	0.029100	0.121800
N	1.106000	-0.438500	-0.221900
N	1.995500	0.447900	0.283700
H	1.641400	1.348100	0.588200
C	4.447800	0.845800	0.559100
H	4.512500	1.783000	-0.004500
H	4.388600	1.097400	1.623200
H	5.371200	0.288400	0.393300
H	1.330200	-2.295800	-1.161000
O	-0.638200	-0.114400	1.933500
H	0.214400	-0.508400	2.156800
O	-2.140500	-1.522200	0.881100
H	-1.480500	-1.048800	1.734100

7a

O	-1.626200	-1.919200	-0.000300
O	-0.856800	0.259000	-1.842100
Mo	-1.161400	-0.292300	-0.000000
O	-0.856700	0.258400	1.842200
O	-2.163800	0.671300	-1.381700
O	-2.163700	0.670900	1.382000
N	1.005800	-0.600300	-0.000100
C	1.787400	-1.686300	-0.000200
H	1.392400	1.394400	0.000200
N	1.830700	0.470700	0.000000
H	4.000600	-1.940400	-0.000300
C	3.132900	-1.298800	-0.000200
C	3.127900	0.094700	0.000000
C	4.247900	1.085000	0.000100
H	4.211500	1.728600	-0.885200
H	4.211200	1.728700	0.885300
H	5.206100	0.562500	0.000300
H	1.341600	-2.670200	-0.000400
O	-0.271300	2.351800	0.000300
H	-0.853900	2.437600	-0.770900
H	-0.854000	2.437400	0.771500

TS(1a-8a)

H	5.756900	-1.561700	0.647800
N	2.265500	0.405100	-0.080700
C	2.952300	1.528800	-0.301100
H	2.828000	-1.544500	0.055800
H	6.516100	-0.476600	-0.525400
N	3.170900	-0.598400	-0.063000
H	5.123700	1.928000	-0.615400
C	4.317200	1.235100	-0.430900
C	4.427600	-0.143900	-0.275500
C	5.614100	-1.052500	-0.311300
H	5.508800	-1.818900	-1.086600
H	2.424000	2.469300	-0.356900
O	0.323200	0.125400	2.034700
O	0.684700	-1.670900	-0.398000
Mo	0.120700	0.050500	0.346400
O	-0.073000	1.722300	-0.422300
O	-0.723800	-1.671500	-0.110000
O	-1.602300	0.923000	-0.100400
S	-3.540800	-0.089500	0.006600
C	-3.532100	-1.053300	-1.540800
H	-3.053500	-0.458600	-2.320600
H	-2.938300	-1.946800	-1.345700
H	-4.561100	-1.311700	-1.800800
C	-4.444700	1.386300	-0.560800
H	-5.433300	1.087400	-0.916600
H	-4.539100	2.044300	0.304300
H	-3.862200	1.878600	-1.340200
O	-4.389500	-0.806600	1.017900

8a

O	0.060531	-1.277283	-1.616552
O	0.917109	1.746219	-0.789239
Mo	0.031990	0.006636	-0.466661
O	-0.305086	-0.463845	1.178973
N	2.169320	-0.419577	-0.120999
C	2.887747	-1.534986	-0.252762
H	2.638909	1.457107	0.480330
N	3.000078	0.514277	0.387045
H	5.024389	-2.008108	0.185438
C	4.205589	-1.305100	0.173073
C	4.249978	0.026907	0.571715
O	-0.501889	1.825175	-0.954119
O	-2.297913	-0.102476	-0.759830
S	-3.378644	-0.065529	0.278160
C	-3.241470	-1.580608	1.236872
H	-2.218278	-1.648892	1.611964
H	-3.982921	-1.559330	2.037343
H	-3.456021	-2.393576	0.540487
C	-2.988245	1.251651	1.440886
H	-2.909387	2.164257	0.847399
H	-3.802262	1.323997	2.163506
H	-2.031596	1.020660	1.912120
O	-4.752648	0.094716	-0.205665
C	5.368332	0.866666	1.100008
H	5.573632	1.719125	0.443405
H	5.140562	1.257999	2.097296
H	6.279054	0.269438	1.171621
H	2.420428	-2.423035	-0.651310

9a

O	2.178100	-0.475700	1.439500
O	1.070400	1.788600	-0.011200
Mo	1.388400	0.071600	0.000200
O	2.178900	-0.494700	-1.431200
H	-3.627200	-1.982200	-0.005800
C	-2.795300	-1.295000	-0.002900
C	-1.434100	-1.609800	0.005200
C	-2.867700	0.098900	-0.008000
N	-0.703900	-0.484500	0.003600
N	-1.594100	0.541800	-0.004500
H	-1.213200	1.484400	-0.010500
C	-4.039500	1.026400	0.005200
H	-3.893000	1.864800	-0.682200
H	-4.942600	0.492000	-0.294700
H	-4.205600	1.436200	1.007500
H	-0.944600	-2.572800	0.009000

TS(3a-9a)

O	0.286600	-1.539800	1.359600
O	-0.059600	1.328200	-0.022300
O	1.630900	0.689000	-0.058600
Mo	0.125500	-0.556800	-0.056700
O	0.209500	-1.484600	-1.514600
H	-5.309500	-0.992500	0.079200
C	-4.313600	-0.576900	0.057100
C	-3.097900	-1.272800	0.026700
C	-3.976300	0.776200	0.053000
N	-2.080700	-0.404800	0.005400
N	-2.628000	0.826500	0.021400
H	-1.963400	1.603300	0.009600
H	-2.902600	-2.335000	0.018700
C	-4.826000	2.006300	0.077000
H	-4.626500	2.612600	0.967000
H	-4.646400	2.633000	-0.802800
H	-5.881700	1.729300	0.085800
S	3.711000	-0.079500	-0.047300
C	4.030200	0.742200	1.540800
H	3.425300	1.649100	1.599500
H	3.715900	0.048800	2.322800
H	5.093600	0.966600	1.654700
C	4.192000	1.229300	-1.211200
H	5.252400	1.470900	-1.104700
H	4.003200	0.845000	-2.215000
H	3.566000	2.106500	-1.036900

TS'(3a-9a)

O	0.272600	-1.367100	1.273200
O	-0.313700	1.346900	-0.367600
O	1.378000	0.761300	-0.391500
Mo	-0.089000	-0.530100	-0.201500
O	-0.097000	-1.581500	-1.568100
H	-5.448200	-1.065300	0.571600
C	-4.477600	-0.630900	0.386400
C	-3.244200	-1.291400	0.331800
C	-4.198800	0.715700	0.152500
N	-2.269500	-0.408700	0.082000
N	-2.863500	0.797400	-0.024300
H	-2.240700	1.585500	-0.209000
C	-5.094100	1.910300	0.073400

H	-4.742000	2.717800	0.723400
H	-5.147100	2.300800	-0.948700
H	-6.104700	1.639800	0.384400
H	-3.007100	-2.337400	0.458500
S	3.446200	0.212800	-0.023800
C	3.412800	0.197100	1.798700
H	2.770400	1.008900	2.142800
H	2.984400	-0.760900	2.096200
H	4.434800	0.298500	2.171200
C	4.048900	1.907000	-0.309600
H	5.026600	2.023200	0.163100
H	4.136900	2.026000	-1.390600
H	3.316100	2.611400	0.085100
O	4.493600	-0.754200	-0.496800

Table S1b Coordinates of the optimised complexes containing the 3,5-dimethylpyrazol ligand (type **b**).

1b

H	-4.108800	-2.256900	-0.442700
N	-0.907400	0.196700	-0.059000
C	-1.686700	1.290400	-0.144700
H	-1.309900	-1.783900	0.183300
H	-5.106400	-0.951100	0.214600
N	-1.734500	-0.864900	0.109100
H	-3.897400	1.537500	-0.063600
C	-3.030500	0.894800	-0.031300
C	-3.029500	-0.487000	0.131100
C	-4.147400	-1.463000	0.310200
H	-4.111200	-1.934100	1.298300
C	-1.115500	2.656900	-0.351800
H	-0.340300	2.873300	0.388200
H	-0.657500	2.738400	-1.343200
H	-1.902700	3.408900	-0.271700
O	1.615900	0.676000	-1.568900
O	0.670200	-1.935100	-0.413000
Mo	1.261400	-0.104000	-0.108200
O	1.243900	1.145300	1.366300
O	2.060900	-1.885600	-0.029800
O	2.534900	0.506800	1.238900

TS(1b-2b)

H	5.192100	-2.322800	0.207700
N	1.983600	0.186900	0.014200
C	2.816000	1.228100	-0.143200
H	2.243800	-1.825800	-0.086700
H	5.990700	-1.248800	-0.949300
N	2.718300	-0.934200	-0.176700
H	4.994500	1.326000	-0.606600
C	4.104900	0.740000	-0.430700
C	4.010200	-0.646800	-0.445800
C	5.036200	-1.707600	-0.685300
H	4.742300	-2.373300	-1.503800
C	2.343500	2.640400	-0.011600
H	1.554300	2.847600	-0.740300
H	1.922400	2.815800	0.983300
H	3.172300	3.333100	-0.172000
O	-0.166300	1.058000	1.770500
O	0.373300	-1.773600	0.765100

Mo	-0.213700	0.063800	0.385100
O	-0.305200	1.029600	-1.183800
O	-1.060500	-1.673800	0.747100
O	-1.885600	0.545300	-0.552300
S	-3.865000	-0.192800	0.189000
C	-3.863500	-1.548100	-1.021000
H	-3.412900	-1.194000	-1.950400
H	-3.235000	-2.333300	-0.598300
H	-4.875800	-1.922900	-1.191500
C	-4.694900	1.112300	-0.764600
H	-5.707500	0.807500	-1.040200
H	-4.742000	1.994800	-0.124100
H	-4.097900	1.340600	-1.649900

2b

H	-5.281800	-2.001400	0.087900
N	-1.856700	0.227400	-0.050300
C	-2.604300	1.333900	0.067500
H	-2.249200	-1.744400	0.221200
H	-5.876100	-0.838600	1.281100
N	-2.655000	-0.816500	0.270400
H	-4.742500	1.628400	0.632800
C	-3.907400	0.965800	0.460200
C	-3.908200	-0.417600	0.580000
C	-4.991400	-1.382100	0.944000
H	-4.678600	-2.053200	1.751000
C	-2.049200	2.700900	-0.174900
H	-1.360700	2.982400	0.629300
H	-1.484000	2.727100	-1.109500
H	-2.857400	3.434800	-0.212000
O	0.200400	1.092500	-1.719500
O	-0.490700	-1.892300	-0.738500
Mo	0.324900	-0.105300	-0.483900
O	0.636900	0.481800	1.130100
O	0.930600	-1.927700	-0.895000
O	2.560600	0.098000	-0.835700
S	3.704800	0.017000	0.202400
C	3.560100	1.490000	1.269100
H	2.540100	1.546200	1.652200
H	4.302300	1.410100	2.068100
H	3.784100	2.351900	0.638100
C	3.276300	-1.265500	1.428600
H	3.106700	-2.184100	0.864700
H	4.129000	-1.379700	2.103100
H	2.368000	-0.978500	1.958400

3b

O	1.827300	1.161100	-1.131400
O	0.855600	-1.881800	-0.425600
O	2.273100	-1.707900	-0.199800
Mo	1.377900	-0.015700	0.043400
O	1.628400	0.560500	1.646700
H	-3.778700	1.493500	-0.066900
C	-2.899400	0.867700	-0.041300
C	-1.562700	1.297300	-0.076100
C	-2.872700	-0.522400	0.034400
N	-0.763700	0.213700	-0.029600
N	-1.571000	-0.872800	0.042300
H	-1.128300	-1.785700	0.082600
C	-1.009400	2.683900	-0.134600

H	-0.557600	2.959700	0.824700
H	-0.229500	2.761400	-0.897500
H	-1.804400	3.397500	-0.359200
C	-3.974100	-1.531700	0.073700
H	-3.762900	-2.327300	0.794600
H	-4.911400	-1.051700	0.360700
H	-4.118900	-1.996500	-0.907900

4b

O	-0.843900	0.739000	1.704200
O	-0.390400	-1.831000	-0.325600
O	-1.763800	-1.722300	0.059900
Mo	-0.900300	0.044100	0.131100
O	-1.154500	1.213000	-1.121400
H	4.324100	1.377400	-0.225300
C	3.429000	0.778400	-0.151700
C	2.102600	1.246800	-0.141000
C	3.364700	-0.606500	-0.046400
N	1.275000	0.192300	-0.042500
N	2.052700	-0.915500	0.019800
H	1.585400	-1.811800	0.106800
C	1.595000	2.650700	-0.201500
H	0.850800	2.760300	-0.995000
H	1.107700	2.921500	0.741200
H	2.420700	3.342300	-0.379600
C	4.436500	-1.648100	-0.015300
H	4.402300	-2.282600	-0.907700
H	5.417400	-1.171300	0.022600
H	4.339900	-2.296700	0.861600
H	-3.354900	1.175000	-0.362700
O	-3.350300	0.402900	0.232400
O	-4.089300	-0.560600	-0.575900
H	-3.404100	-1.259100	-0.662000

TS(4b-5b)

O	-1.077100	0.939700	1.625900
O	-0.372300	-1.870400	0.515800
O	-1.786700	-1.751800	0.390100
Mo	-0.955600	-0.014500	0.216100
O	-0.977600	0.954600	-1.337000
H	4.241200	1.459900	-0.261000
C	3.368200	0.830200	-0.177600
C	2.039900	1.253300	0.012200
C	3.338700	-0.558200	-0.241200
N	1.244700	0.171600	0.069600
N	2.044300	-0.910700	-0.087200
H	1.611000	-1.826100	-0.094000
C	1.494600	2.639400	0.128900
H	0.807300	2.844900	-0.697600
H	0.932400	2.759700	1.060100
H	2.307300	3.368100	0.109800
C	4.428200	-1.566200	-0.419000
H	4.181700	-2.288500	-1.203900
H	5.356700	-1.065600	-0.699200
H	4.610700	-2.124200	0.506100
H	-2.202700	0.950100	-1.231700
O	-3.025100	0.566200	-0.416100
O	-3.803800	-0.487800	-1.024500
H	-4.408400	-0.692000	-0.293500

5b

O	1.186600	0.857200	-1.507600
O	0.394300	-1.829300	-0.452900
O	1.801800	-1.811600	-0.229300
Mo	1.024300	-0.021400	-0.066200
O	0.657600	1.073000	1.481600
H	1.496200	1.328600	1.906500
O	2.803800	0.353300	0.775800
H	-4.249500	1.430300	-0.060900
C	-3.366700	0.809300	-0.032500
C	-2.031100	1.236500	-0.160600
C	-3.328200	-0.569100	0.136400
N	-1.223200	0.167600	-0.081300
N	-2.021400	-0.910200	0.105500
H	-1.581100	-1.820100	0.169000
C	-1.500500	2.620800	-0.348900
H	-0.933200	2.929700	0.533700
H	-0.823600	2.664300	-1.207200
H	-2.322000	3.321600	-0.510700
C	-4.417400	-1.578600	0.309500
H	-4.253000	-2.198500	1.197000
H	-5.378100	-1.073400	0.423500
H	-4.487000	-2.245000	-0.557400
O	3.913900	-0.180800	0.036900
H	4.022000	-1.049300	0.460400

6b

O	1.152100	0.818000	-1.464400
O	0.254300	-1.871200	-0.601700
O	1.664700	-2.063000	-0.500500
Mo	1.125100	-0.215300	-0.115300
O	0.940900	0.482700	1.699900
H	0.090700	0.906900	1.877700
O	3.022200	-0.222800	0.350700
H	-4.150100	1.640500	-0.192700
C	-3.300100	0.984100	-0.080800
C	-1.940300	1.331900	-0.211700
C	-3.334000	-0.373300	0.209000
N	-1.182900	0.242600	-0.003200
N	-2.042600	-0.772300	0.260000
H	-1.656000	-1.705100	0.343200
C	-1.343700	2.668400	-0.529000
H	-0.828300	3.095000	0.339200
H	-0.611400	2.583600	-1.335500
H	-2.127600	3.367100	-0.828500
C	-4.475700	-1.312300	0.433100
H	-4.417700	-1.788200	1.417800
H	-5.420800	-0.769500	0.375100
H	-4.494700	-2.105700	-0.321900
O	3.272400	1.167400	0.633000
H	2.850200	1.244400	1.513300

TS(6b-7b)

O	1.211500	0.925400	-1.521400
O	0.471900	-1.829300	-0.850900
O	1.904100	-1.851300	-0.721800
Mo	1.178700	-0.137400	-0.197700
O	2.918700	0.212300	0.606500
H	-4.076700	1.550700	-0.121300
C	-3.200000	0.923400	-0.060900

C	-1.858700	1.332700	-0.199300
C	-3.176400	-0.447300	0.161600
N	-1.058700	0.263800	-0.058600
N	-1.870400	-0.799400	0.174000
H	-1.444800	-1.719800	0.197500
C	-1.316100	2.704200	-0.451500
H	-0.802800	3.097800	0.432800
H	-0.593200	2.689300	-1.270900
H	-2.128600	3.388500	-0.703300
C	-4.277600	-1.441700	0.343900
H	-4.123900	-2.052200	1.239600
H	-5.233700	-0.925100	0.444900
H	-4.348200	-2.118200	-0.515000
O	0.766900	-0.406100	1.934600
H	-0.111100	-0.146000	2.239600
O	2.138800	1.286900	1.162800
H	1.539000	0.622900	1.911800

7b

H	-3.856000	-2.356000	-0.875600
N	-0.974600	0.366900	0.000600
C	-1.882700	1.359600	-0.000300
H	-1.112400	-1.667100	0.000500
H	-4.997700	-1.311300	-0.016300
N	-1.661500	-0.803100	0.000700
H	-4.107700	1.319700	-0.002000
C	-3.167300	0.789500	-0.001100
C	-2.992500	-0.590900	-0.000400
C	-3.982400	-1.711300	0.000400
H	-3.877400	-2.335600	0.894000
C	-1.497000	2.804600	0.000900
H	-0.911900	3.057700	0.889900
H	-0.885100	3.052700	-0.871000
H	-2.393700	3.427200	-0.014100
O	1.586300	1.890400	0.000000
O	0.936500	-0.337500	-1.837000
Mo	1.210800	0.240700	-0.000100
O	0.937800	-0.338200	1.836900
O	2.270200	-0.662700	-1.382900
O	2.271100	-0.663000	1.381900
O	0.567100	-2.529900	0.000100
H	1.158700	-2.513200	-0.769400
H	1.159300	-2.512700	0.769100

TS(1b-8b)

H	5.381300	-2.384100	0.201600
N	2.200000	0.168500	0.022300
C	3.055200	1.198500	-0.087600
H	2.426100	-1.846300	-0.140200
H	6.186400	-1.313500	-0.953900
N	2.916300	-0.960500	-0.194400
H	5.241300	1.268300	-0.513800
C	4.338000	0.694200	-0.371200
C	4.217400	-0.689400	-0.433200
C	5.227800	-1.761600	-0.686800
H	4.919700	-2.418100	-1.507300
C	2.610500	2.615400	0.084000
H	1.840800	2.866400	-0.651800
H	2.174600	2.766500	1.076500
H	3.457200	3.294000	-0.036800

O	0.062200	1.030300	1.785800
O	0.538500	-1.779300	0.687000
Mo	0.006400	0.085300	0.370100
O	-0.055600	1.103500	-1.169600
O	-0.889600	-1.638600	0.652600
O	-1.651200	0.653900	-0.571500
S	-3.648600	-0.050000	-0.071300
C	-3.687000	-1.617400	-1.001000
H	-3.156200	-1.477700	-1.944100
H	-3.162900	-2.352900	-0.389700
H	-4.727600	-1.909800	-1.158700
C	-4.445900	1.045400	-1.288400
H	-5.447800	0.669700	-1.508200
H	-4.507300	2.030900	-0.824200
H	-3.822300	1.093500	-2.181700
O	-4.555000	-0.174100	1.120500

8b

H	-5.549700	-1.953200	0.046600
N	-2.089400	0.221700	-0.049900
C	-2.824900	1.341200	0.040300
H	-2.513300	-1.744300	0.237800
H	-6.140700	-0.776500	1.228000
N	-2.906200	-0.810000	0.268000
H	-4.967000	1.667200	0.561800
C	-4.137600	0.992300	0.412500
C	-4.158400	-0.390100	0.548900
C	-5.260800	-1.335500	0.904100
H	-4.967500	-2.007500	1.717300
C	-2.250500	2.697700	-0.211600
H	-1.544700	2.968400	0.581100
H	-1.700300	2.715400	-1.155500
H	-3.047300	3.444100	-0.236800
O	0.001600	1.057500	-1.698600
O	-0.745500	-1.924400	-0.699100
Mo	0.056200	-0.128200	-0.450400
O	0.408700	0.482100	1.145300
O	0.677300	-1.940200	-0.841100
O	2.412000	0.044800	-0.774600
S	3.495400	0.054400	0.258800
C	3.351300	1.605800	1.157000
H	2.326100	1.685300	1.524400
H	4.089000	1.619600	1.961100
H	3.566500	2.391400	0.430100
C	3.114500	-1.215000	1.477100
H	3.032500	-2.151400	0.922400
H	3.932000	-1.256800	2.198100
H	2.160000	-0.966900	1.944000
O	4.871300	-0.117400	-0.217000

9b

O	2.184200	0.452300	-1.413100
O	1.272400	-1.955000	-0.044900
Mo	1.439200	-0.218500	-0.000200
O	2.161700	0.371600	1.459100
H	-3.630700	1.613400	0.011300
C	-2.777600	0.952000	0.006100
C	-1.424800	1.324900	-0.006500
C	-2.810800	-0.441200	0.010500
N	-0.669500	0.210400	-0.009100

N	-1.525500	-0.847100	0.004000
H	-1.119800	-1.777400	-0.006800
C	-0.799000	2.682300	0.000900
H	-0.366700	2.905800	0.982400
H	0.005400	2.745500	-0.738800
H	-1.543800	3.446700	-0.228100
C	-3.955300	-1.402100	-0.003900
H	-3.781700	-2.240600	0.677200
H	-4.872300	-0.896500	0.303600
H	-4.114400	-1.810400	-1.008000

TS(3b-9b)

O	0.314000	-1.437800	1.340200
O	0.180900	1.477500	0.016500
O	1.829200	0.719500	-0.034100
Mo	0.234800	-0.412500	-0.055500
O	0.255000	-1.316800	-1.532200
H	-5.191300	-0.547400	0.074100
C	-4.175700	-0.181200	0.053100
C	-3.000100	-0.953200	0.024500
C	-3.774700	1.152700	0.049300
N	-1.944200	-0.123500	0.005300
N	-2.426800	1.137500	0.018900
H	-1.725200	1.879200	0.015500
C	-2.823800	-2.437200	0.008900
H	-2.370200	-2.761800	-0.933500
H	-2.155900	-2.753500	0.816000
H	-3.787500	-2.936900	0.126100
C	-4.565100	2.421600	0.074200
H	-4.346800	3.046000	-0.798700
H	-5.632900	2.195200	0.069900
H	-4.346900	3.011700	0.970800
S	3.843300	-0.183800	-0.046900
C	4.236800	0.622100	1.532300
H	3.699100	1.570400	1.589700
H	3.880200	-0.042000	2.321500
H	5.314700	0.769800	1.635000
C	4.399900	1.081900	-1.224500
H	5.476300	1.247300	-1.134700
H	4.168800	0.707700	-2.223200
H	3.840700	2.002200	-1.045500

TS'(3b-9b)

O	0.307700	-1.264600	1.224800
O	-0.077500	1.512100	-0.369700
O	1.578800	0.817000	-0.382600
Mo	0.024300	-0.376600	-0.239200
O	-0.043000	-1.407600	-1.622200
H	-5.343200	-0.654000	0.429900
C	-4.348600	-0.258400	0.287900
C	-3.154700	-0.994000	0.190600
C	-3.999800	1.084900	0.164700
N	-2.135600	-0.133900	0.019400
N	-2.661400	1.110800	0.006400
H	-1.997900	1.875000	-0.120800
C	-2.925500	-2.469400	0.250800
H	-2.457100	-2.824400	-0.672900
H	-2.250600	-2.722400	1.074800
H	-3.871000	-2.996300	0.393000
C	-4.832900	2.326200	0.170100

H	-5.848900	2.092300	0.493200
H	-4.423900	3.080200	0.850100
H	-4.889900	2.771400	-0.829300
S	3.594000	0.135700	0.000100
C	3.531400	0.116800	1.821400
H	2.947300	0.974000	2.159300
H	3.026300	-0.806700	2.107500
H	4.552200	0.138500	2.209900
C	4.314100	1.785500	-0.272600
H	5.289900	1.835800	0.215600
H	4.427100	1.898900	-1.351800
H	3.623900	2.537100	0.111600
O	4.579800	-0.899600	-0.460700

Table S1c Coordinates of the optimised complexes containing the water ligand (type **c**).

1c

O	0.090000	0.299900	1.773800
O	1.575600	-0.844900	-0.550600
Mo	-0.040300	-0.038700	0.118600
O	-1.585200	0.817100	-0.634500
O	0.578000	-1.845700	-0.260600
O	-1.854600	-0.568800	-0.326000
O	1.044900	1.811600	-0.546900
H	0.900100	2.600000	-0.002800
H	2.001200	1.670200	-0.619900

TS(1c-2c)

O	-1.454600	-0.786900	1.579900
O	-1.608300	1.745500	-0.071200
Mo	-1.020400	-0.097000	0.081000
O	-0.646100	-1.374700	-1.197500
O	-0.221600	1.675600	0.314500
O	0.748000	-0.749400	-0.420900
S	2.641000	0.208600	0.563100
C	2.882300	1.267000	-0.895500
H	2.573500	0.723600	-1.791000
H	2.228800	2.130200	-0.760600
H	3.922700	1.591700	-0.974600
C	3.587600	-1.264700	0.072600
H	4.639000	-1.013300	-0.087500
H	3.507600	-1.982800	0.890700
H	3.147700	-1.695700	-0.829200
O	-3.186700	-0.317600	-0.626400
H	-3.612000	-1.056800	-0.166100
H	-3.672400	0.485800	-0.383000

2c

O	1.397200	-1.181800	-1.306900
O	1.825200	1.565200	0.224700
Mo	0.831800	-0.085400	-0.092400
O	0.078300	-0.802800	1.298900
O	0.588300	1.832800	-0.451100
O	-1.095700	-0.060800	-1.096000
S	-2.505300	0.103100	-0.453000
C	-2.833200	-1.428400	0.475200
H	-1.993700	-1.621000	1.145600
H	-3.775600	-1.300900	1.014900

H	-2.931400	-2.225500	-0.263700
C	-2.363800	1.273600	0.936800
H	-1.896400	2.174300	0.535300
H	-3.376600	1.486700	1.288300
H	-1.739500	0.846400	1.722200
O	2.883000	-0.745800	0.862100
H	3.163900	-1.368500	0.171600
H	3.470700	0.022000	0.789900

3c

O	0.458700	-1.206800	-1.330300
O	-1.267300	1.260500	-0.089000
O	-1.880100	-0.027800	0.175800
Mo	0.019400	-0.228300	0.007600
O	0.786100	-0.743000	1.461200
O	1.412800	1.449700	-0.279000
H	2.150900	1.431800	0.349700
H	0.950800	2.297600	-0.179700

4c

O	0.694500	-1.127900	-1.352000
O	0.668800	1.802000	0.065700
O	-0.678600	1.572100	-0.359500
Mo	0.266600	-0.121700	-0.016300
O	0.054100	-0.989100	1.455100
H	-2.043900	-1.508400	0.177100
O	-1.936800	-0.716200	-0.381300
O	-2.875600	0.188500	0.279700
H	-2.330900	1.007700	0.290100
O	2.505900	-0.050400	0.342000
H	2.829500	0.838800	0.127800
H	2.891600	-0.658700	-0.308600

TS(4c-5c)

O	-0.720200	-0.324100	1.721900
O	-0.709700	1.777300	-0.500400
O	0.662400	1.686900	-0.114800
Mo	-0.251300	0.004800	0.113200
O	-0.007400	-1.490300	-0.913400
H	1.169300	-1.464800	-0.486000
O	1.780400	-0.806400	0.322800
O	2.792300	-0.078000	-0.402600
H	3.177300	0.446700	0.318500
O	-2.374900	-0.427400	-0.577400
H	-2.953900	-0.622900	0.175300
H	-2.219800	-1.265400	-1.049200

5c

O	-0.375300	-0.057900	1.746800
O	-0.499300	1.761000	-0.564500
O	0.906600	1.526400	-0.474300
Mo	-0.157600	-0.016500	0.063200
O	-0.713400	-1.619900	-0.859100
H	0.017000	-2.178400	-1.169200
O	1.568200	-0.946200	-0.138800
O	2.747000	-0.220400	0.222200
H	2.943000	0.255800	-0.603800
O	-2.488400	-0.005000	-0.086500
H	-2.629700	-0.895900	-0.451200
H	-2.873100	0.007200	0.802500

6c

O	-0.167700	-0.360500	1.687800
O	-1.429700	1.312000	-0.320800
O	-0.165900	1.986600	-0.306100
Mo	-0.023600	0.065000	0.043900
O	0.183000	-1.193700	-1.394000
H	-0.376100	-1.983100	-1.330900
O	1.847300	0.568800	-0.071500
O	2.358200	-0.739300	0.262200
H	2.425600	-1.146100	-0.624000
H	-2.267900	-1.336700	1.019900
H	-2.835700	-0.713400	-0.280500
O	-2.119600	-1.267500	0.064000

TS(6c-7c)

O	0.364800	-0.099000	1.781000
O	1.535400	-0.975800	-0.737400
O	0.431300	-1.885800	-0.579900
Mo	0.018000	-0.135500	0.120000
O	-1.829800	-0.678400	0.016000
O	-0.585000	1.208600	-1.429800
H	-0.166800	2.080500	-1.438700
O	-1.979600	0.710600	0.339500
H	-1.582200	1.195800	-0.714100
O	1.644700	1.645400	0.157100
H	2.415800	1.341400	-0.346300
H	1.923200	1.669900	1.086200

7c

O	1.889500	-0.096000	0.764100
O	-0.245900	1.848500	0.252800
Mo	0.357200	0.005400	0.059300
O	-0.163400	-1.818900	-0.396400
O	0.283700	1.587900	-1.065100
O	0.353000	-1.104900	-1.539500
O	-2.218400	0.059400	-0.435400
H	-2.252300	0.954700	-0.804200
H	-2.242200	-0.559800	-1.179300
O	-0.891600	-0.358000	1.888600
H	-0.781700	-1.247300	2.257600
H	-1.780600	-0.318500	1.483400

TS(1c-8c)

O	-1.635800	-0.225900	1.749200
O	-1.700200	1.748100	-0.532200
Mo	-1.237800	-0.012000	0.106600
O	-1.031700	-1.617000	-0.803900
O	-0.297300	1.665600	-0.210800
O	0.449600	-0.948200	-0.266300
S	2.459500	0.000300	0.228600
C	2.726600	1.081300	-1.216200
H	2.328500	0.586300	-2.103900
H	2.169900	1.999600	-1.027200
H	3.795300	1.286100	-1.312100
C	3.378000	-1.469900	-0.332700
H	4.420000	-1.196200	-0.513600
H	3.316800	-2.202400	0.473600
H	2.900100	-1.864300	-1.230500
O	3.174900	0.586600	1.413000

O	-3.408200	-0.451400	-0.434900
H	-3.396200	-1.345300	-0.815100
H	-3.939200	-0.495500	0.375800

8c

O	1.419100	-0.872200	-1.633900
O	2.132800	1.521200	0.289700
Mo	1.071600	-0.051300	-0.170200
O	0.447900	-1.042500	1.135900
O	0.817400	1.890300	-0.141400
O	-1.025100	0.156500	-0.883700
S	-2.309200	0.047700	-0.094800
C	-2.502200	-1.684400	0.338100
H	-1.590900	-2.005100	0.847400
H	-3.393800	-1.791800	0.958400
H	-2.629000	-2.214200	-0.608100
C	-2.077700	0.910200	1.466500
H	-1.773500	1.926800	1.209800
H	-3.031100	0.907500	1.996700
H	-1.288600	0.405500	2.026100
O	-3.508100	0.541800	-0.771000
O	3.067400	-0.893900	0.631400
H	2.749800	-1.439400	1.369400
H	3.567000	-0.159300	1.020400

9c

O	-1.020400	-0.012500	1.488000
O	-0.442500	-1.426100	-0.934500
Mo	-0.145300	-0.000100	0.000800
O	-0.435100	1.446100	-0.905300
O	2.031900	-0.003800	0.337700
H	2.517100	0.773000	0.021900
H	2.513500	-0.796600	0.058500

TS(3c-9c)

O	1.200600	1.734600	-0.587000
O	0.782200	-0.478900	1.645400
O	-0.667000	-0.246200	0.635300
Mo	1.073200	0.077200	-0.126600
O	1.384300	-1.013700	-1.436600
S	-2.565900	0.091800	-0.611700
C	-3.137700	1.290300	0.629800
H	-2.727200	1.019200	1.604300
H	-2.747900	2.265500	0.332600
H	-4.229500	1.325900	0.656900
C	-3.246600	-1.450200	0.068800
H	-4.337700	-1.405200	0.105700
H	-2.937700	-2.256500	-0.598700
H	-2.825600	-1.620700	1.061600
O	3.214400	-0.199900	0.537700
H	3.623800	-0.866100	-0.036300
H	3.151900	-0.580900	1.429400

TS'(3c-9c)

O	-1.230000	-1.362400	1.187700
O	-1.091400	1.692900	0.340300
O	0.405100	0.799100	-0.025400
Mo	-1.290300	-0.140400	-0.027500
O	-1.658100	-0.765600	-1.597200
S	2.405200	-0.169500	-0.178900

C	2.728700	-0.283500	1.610800
H	2.266000	0.573000	2.103200
H	2.262700	-1.208100	1.955400
H	3.807600	-0.317700	1.778400
C	3.230500	1.413000	-0.539600
H	4.286900	1.335200	-0.273000
H	3.125100	1.581100	-1.612400
H	2.726100	2.205600	0.014200
O	3.144200	-1.273600	-0.879700
O	-3.459000	0.419600	0.214100
H	-3.935000	0.196400	-0.601100
H	-3.473600	1.386600	0.307200

Table S2a Energies of the optimised complexes involved in the Sharpless-type mechanism (with the methylpyrazol ligand, **a**).

	1a	**TS(1a-2a)**	**2a**	**3a**	**4a**	**TS(4a-5a)**
E	-709.113882441	-1187.118153300	-1187.192564500	-633.972890786	-785.534475889	-785.511666768
Eo	-708.996993000	-1186.924823000	-1186.996778000	-633.859177000	-785.390876000	-785.372908000
Et	-708.984250000	-1186.906084000	-1186.978349000	-633.847402000	-785.375631000	-785.358198000
H	-708.983305000	-1186.905140000	-1186.977405000	-633.846458000	-785.374687000	-785.357254000
G	-709.038376000	-1186.974591000	-1187.044986000	-633.899089000	-785.435134000	-785.416291000

	5a	**6a**	**TS(6a-7a)**	**7a**	**TS(1a-8a)**	**8a**
E	-785.540582935	-785.537294895	-785.521820420	-785.560397052	-1262.290111620	-1262.394121070
Eo	-785.397907000	-785.394873000	-785.382849000	-785.417941000	-1262.093106000	-1262.193204000
Et	-785.382871000	-785.379788000	-785.368688000	-785.402624000	-1262.073476000	-1262.174872000
H	-785.381927000	-785.378844000	-785.367744000	-785.401680000	-1262.072531000	-1262.173928000
G	-785.441127000	-785.438624000	-785.425798000	-785.461626000	-1262.144209000	-1262.241257000

	TS(3a-9a)	**TS'(3a-9a)**	**9a**
E	-1111.972936890	-1187.144454870	-558.825378955
Eo	-1111.783377000	-1186.951369000	-558.715018000
Et	-1111.765398000	-1186.932390000	-558.704077000
H	-1111.764453000	-1186.931446000	-558.703132000
G	-1111.833741000	-1187.003570000	-558.754652000

Sum of electronic and zero-point Energies = Eo; Sum of electronic and thermal Energies = Et;
Sum of electronic and thermal Enthalpies = H; Sum of electronic and thermal Free Energies = G.

Table S2b Energies of the optimised complexes involved in the Sharpless-type mechanism (with the 3,5-dimethylpyrazol ligand, **b**).

	1b	**TS(1b-2b)**	**2b**	**3b**	**4b**	**TS(4b-5b)**
E	-748.439678015	-1226.442542080	-1226.516586250	-673.299398493	-824.859701256	-824.835423960
Eo	-748.295129000	-1226.221741000	-1226.293272000	-673.158143000	-824.688619000	-824.669539000
Et	-748.280672000	-1226.201186000	-1226.273071000	-673.144622000	-824.671558000	-824.652838000
H	-748.279728000	-1226.200242000	-1226.272126000	-673.143677000	-824.670614000	-824.651894000
G	-748.338349000	-1226.273921000	-1226.343599000	-673.200042000	-824.735423000	-824.715703000

	5b	**6b**	**TS(6b-7b)**	**7b**	**TS(1b-8b)**	**8b**
E	-824.862941018	-824.861467534	-824.846725846	-824.885072205	-1301.614615740	-1301.718569380
Eo	-824.692769000	-824.691373000	-824.679956000	-824.715115000	-1301.390162000	-1301.489993000
Et	-824.675882000	-824.674586000	-824.664136000	-824.697909000	-1301.368704000	-1301.469046000
H	-824.674938000	-824.673642000	-824.663192000	-824.696965000	-1301.367760000	-1301.468102000
G	-824.739085000	-824.736988000	-824.724459000	-824.762643000	-1301.443614000	-1301.541614000

	TS(3b-9b)	**TS'(3b-9b)**	**9b**
E	-1151.298876860	-1226.470622290	-598.151909581
Eo	-1151.081680000	-1226.249933000	-598.014200000
Et	-1151.061969000	-1226.229208000	-598.001328000
H	-1151.061025000	-1226.228264000	-598.000383000
G	-1151.133806000	-1226.303533000	-598.056777000

Sum of electronic and zero-point Energies = Eo; Sum of electronic and thermal Energies = Et;
Sum of electronic and thermal Enthalpies = H; Sum of electronic and thermal Free Energies = G.

Table S2c Energies of the optimised complexes involved in the Sharpless-type mechanism (with the water ligand, **c**).

	1c	**TS(1c-2c)**	**2c**	**3c**	**4c**	**TS(4c-5c)**
E	-519.985058114	-997.995018922	-998.077112623	-444.841218390	-596.410248580	-596.389924474
Eo	-519.944560000	-997.877966000	-997.957158000	-444.803592000	-596.342472000	-596.327174000
Et	-519.936528000	-997.863086000	-997.942926000	-444.795817000	-596.331418000	-596.316559000
H	-519.935584000	-997.862142000	-997.941981000	-444.794873000	-596.330474000	-596.315615000
G	-519.977522000	-997.921533000	-997.997832000	-444.836179000	-596.379251000	-596.363466000

	5c	**6c**	**TS(6c-7c)**	**7c**	**TS(1c-8c)**	**8c**
E	-596.422360067	-596.425286664	-596.389924474	-596.433836130	-1073.166645110	-1073.274412870
Eo	-596.355858000	-596.358889000	-596.342227000	-596.367284000	-1073.045916000	-1073.149272000
Et	-596.344841000	-596.347905000	-596.332177000	-596.356124000	-1073.030246000	-1073.134318000
H	-596.343896000	-596.346960000	-596.331232000	-596.355180000	-1073.029302000	-1073.133374000
G	-596.392223000	-596.394867000	-596.377230000	-596.403706000	-1073.090546000	-1073.191356000

	TS(3c-9c)	**TS'(3c-9c)**	**9c**
E	-922.848038003	-998.018095902	-369.693058777
Eo	-922.734181000	-997.900636000	-369.659144000
Et	-922.720291000	-997.885819000	-369.651907000
H	-922.719347000	-997.884875000	-369.650963000
G	-922.776777000	-997.944459000	-369.692169000

Sum of electronic and zero-point Energies = Eo; Sum of electronic and thermal Energies = Et;
Sum of electronic and thermal Enthalpies = H; Sum of electronic and thermal Free Energies = G.

Table S3 Energies of the optimised complexes involved in the Thiel-type mechanism (with the co-ligand type **b**).

	1b	**10b**	**TS(10b-11b)**	**11b**	**TS(11b-12b)**	**12b**
E	-748.439678015	-900.007690948	-899.972900435	-899.989583873	-1377.995568620	-1378.076115430
Eo	-748.295129000	-899.833203000	-899.800483000	-899.815588000	-1377.744605000	-1377.824055000
Et	-748.280672000	-899.815398000	-899.783663000	-899.797671000	-1377.721581000	-1377.800387000
H	-748.279728000	-899.814453000	-899.782719000	-899.796727000	-1377.720637000	-1377.799443000
G	-748.338349000	-899.880821000	-899.845822000	-899.864158000	-1377.797821000	-1377.880332000

	13b	**14b**	**TS(14b-7b)**	**7b**
E	-824.858895879	-824.864917970	-824.837620909	-824.885072205
Eo	-824.688153000	-824.694456000	-824.668883000	-824.715115000
Et	-824.671589000	-824.677931000	-824.653317000	-824.697909000
H	-824.670645000	-824.676987000	-824.652373000	-824.696965000
G	-824.733507000	-824.739645000	-824.712770000	-824.762643000

Sum of electronic and zero-point Energies = Eo; Sum of electronic and thermal Energies = Et;
Sum of electronic and thermal Enthalpies = H; Sum of electronic and thermal Free Energies = G.

Table S4 Energies of the optimised reagents, products and ligands.

	Me_2S	Me_2SO	Me_2SO_2	H_2O_2	H_2O
E	-478.022305101	-553.195518554	-628.409519802	-151.543190814	-76.419736619
Eo	-477.946315000	-553.115973000	-628.324192000	-151.516799000	-76.398367000
Et	-477.941408000	-553.110311000	-628.317986000	-151.513538000	-76.395532000
H	-477.940464000	-553.109367000	-628.317042000	-151.512594000	-76.394588000
G	-477.973398000	-553.144308000	-628.353521000	-151.538486000	-76.416678000

	MePhS	MePhSO	$MePhSO_2$	5-Methylpyrazol	3,5-Dimethylpyrazol
E	-669.761672284	-744.934909603	-820.147838310	-265.530442261	-304.853972188
Eo	-669.632217000	-744.801950000	-820.009212000	-265.431407000	-304.727472000
Et	-669.624561000	-744.793360000	-819.999997000	-265.425893000	-304.720175000
H	-669.623616000	-744.792416000	-819.999053000	-265.424949000	-304.719231000
G	-669.665646000	-744.835882000	-820.044128000	-265.460643000	-304.759296000

Sum of electronic and zero-point Energies = Eo; Sum of electronic and thermal Energies = Et;
Sum of electronic and thermal Enthalpies = H; Sum of electronic and thermal Free Energies = G.

Table S5 Selected bond lengths [Å] and angles [°] for $[HMepz]_4[Mo_8O_{26}(Mepz)_2]\cdot 2H_2O$, **1**.

Mo(1)-O(2)	1.693(3)	Mo(5)-O(18)	1.701(3)
Mo(1)-O(1)	1.702(3)	Mo(5)-O(17)	1.719(3)
Mo(1)-O(3)	1.948(3)	Mo(5)-O(4)	1.899(3)
Mo(1)-O(4)	1.975(3)	Mo(5)-O(21)	2.063(3)
Mo(1)-O(7)	2.235(3)	Mo(5)-N(3)	2.209(4)
Mo(1)-O(19)	2.298(3)	Mo(5)-O(19)	2.215(3)
Mo(2)-O(5)	1.698(3)	Mo(6)-O(20)	1.681(3)
Mo(2)-O(6)	1.714(3)	Mo(6)-O(8)	1.758(3)
Mo(2)-O(3)	1.946(3)	Mo(6)-O(19)	1.904(3)
Mo(2)-O(10)	1.949(3)	Mo(6)-O(12)	1.960(3)
Mo(2)-O(7)	2.178(3)	Mo(6)-O(21)	2.157(3)
Mo(2)-O(8)	2.393(3)	Mo(6)-O(7)	2.454(3)
Mo(3)-O(9)	1.698(3)	Mo(7)-O(22)	1.700(3)
Mo(3)-O(11)	1.748(3)	Mo(7)-O(23)	1.719(3)
Mo(3)-O(15)	1.869(3)	Mo(7)-O(24)	1.938(3)
Mo(3)-O(7)	1.973(3)	Mo(7)-O(21)	1.939(3)
Mo(3)-O(10)	2.168(3)	Mo(7)-O(12)	2.189(3)
Mo(3)-O(12)	2.453(3)	Mo(7)-O(11)	2.380(3)
Mo(4)-O(13)	1.699(3)	Mo(8)-O(26)	1.686(3)
Mo(4)-O(14)	1.723(3)	Mo(8)-O(25)	1.704(3)
Mo(4)-O(16)	1.906(3)	Mo(8)-O(16)	1.964(3)
Mo(4)-O(10)	2.056(3)	Mo(8)-O(24)	1.966(3)
Mo(4)-N(1)	2.216(4)	Mo(8)-O(12)	2.209(3)
Mo(4)-O(15)	2.261(3)	Mo(8)-O(15)	2.282(3)
O(2)-Mo(1)-O(1)	105.07(16)	O(11)-Mo(3)-O(15)	103.98(14)
O(2)-Mo(1)-O(3)	101.18(14)	O(9)-Mo(3)-O(7)	103.90(15)
O(1)-Mo(1)-O(3)	96.13(14)	O(11)-Mo(3)-O(7)	97.33(13)
O(2)-Mo(1)-O(4)	96.49(14)	O(15)-Mo(3)-O(7)	139.65(13)
O(1)-Mo(1)-O(4)	100.27(14)	O(9)-Mo(3)-O(10)	93.75(13)
O(3)-Mo(1)-O(4)	151.83(14)	O(11)-Mo(3)-O(10)	161.52(12)
O(2)-Mo(1)-O(7)	93.05(14)	O(15)-Mo(3)-O(10)	75.83(12)
O(1)-Mo(1)-O(7)	160.49(14)	O(7)-Mo(3)-O(10)	73.40(11)
O(3)-Mo(1)-O(7)	72.89(12)	O(9)-Mo(3)-O(12)	178.92(14)
O(4)-Mo(1)-O(7)	84.49(12)	O(11)-Mo(3)-O(12)	76.60(12)
O(2)-Mo(1)-O(19)	163.39(13)	O(15)-Mo(3)-O(12)	75.46(12)
O(1)-Mo(1)-O(19)	89.62(13)	O(7)-Mo(3)-O(12)	76.76(11)
O(3)-Mo(1)-O(19)	84.55(12)	O(10)-Mo(3)-O(12)	85.61(10)
O(4)-Mo(1)-O(19)	72.88(12)	O(13)-Mo(4)-O(14)	105.05(16)
O(7)-Mo(1)-O(19)	73.59(11)	O(13)-Mo(4)-O(16)	100.62(14)
O(5)-Mo(2)-O(6)	104.89(16)	O(14)-Mo(4)-O(16)	98.94(14)
O(5)-Mo(2)-O(3)	96.20(14)	O(13)-Mo(4)-O(10)	96.75(15)
O(6)-Mo(2)-O(3)	102.47(14)	O(14)-Mo(4)-O(10)	153.29(15)
O(5)-Mo(2)-O(10)	96.25(13)	O(16)-Mo(4)-O(10)	91.88(12)
O(6)-Mo(2)-O(10)	103.27(14)	O(13)-Mo(4)-N(1)	93.40(14)
O(3)-Mo(2)-O(10)	147.35(13)	O(14)-Mo(4)-N(1)	83.40(14)
O(5)-Mo(2)-O(7)	102.68(14)	O(16)-Mo(4)-N(1)	164.58(14)
O(6)-Mo(2)-O(7)	152.43(14)	O(10)-Mo(4)-N(1)	80.03(12)
O(3)-Mo(2)-O(7)	74.25(12)	O(13)-Mo(4)-O(15)	166.22(14)
O(10)-Mo(2)-O(7)	73.61(12)	O(14)-Mo(4)-O(15)	88.69(14)
O(5)-Mo(2)-O(8)	174.21(14)	O(16)-Mo(4)-O(15)	75.77(12)
O(6)-Mo(2)-O(8)	80.79(14)	O(10)-Mo(4)-O(15)	70.33(12)
O(3)-Mo(2)-O(8)	81.28(12)	N(1)-Mo(4)-O(15)	89.09(12)
O(10)-Mo(2)-O(8)	83.37(11)	O(18)-Mo(5)-O(17)	104.91(15)
O(7)-Mo(2)-O(8)	71.64(11)	O(18)-Mo(5)-O(4)	101.06(14)
O(9)-Mo(3)-O(11)	104.10(15)	O(17)-Mo(5)-O(4)	100.04(14)
O(9)-Mo(3)-O(15)	103.54(15)	O(18)-Mo(5)-O(21)	92.54(14)

O(17)-Mo(5)-O(21)	157.60(13)	O(23)-Mo(7)-O(24)	103.64(13)
O(4)-Mo(5)-O(21)	90.03(12)	O(22)-Mo(7)-O(21)	96.88(14)
O(18)-Mo(5)-N(3)	96.17(14)	O(23)-Mo(7)-O(21)	103.18(14)
O(17)-Mo(5)-N(3)	83.20(15)	O(24)-Mo(7)-O(21)	145.59(13)
O(4)-Mo(5)-N(3)	160.93(14)	O(22)-Mo(7)-O(12)	103.50(14)
O(21)-Mo(5)-N(3)	81.03(13)	O(23)-Mo(7)-O(12)	152.13(13)
O(18)-Mo(5)-O(19)	163.11(13)	O(24)-Mo(7)-O(12)	73.81(12)
O(17)-Mo(5)-O(19)	91.96(13)	O(21)-Mo(7)-O(12)	72.37(12)
O(4)-Mo(5)-O(19)	76.22(12)	O(22)-Mo(7)-O(11)	174.60(14)
O(21)-Mo(5)-O(19)	70.92(12)	O(23)-Mo(7)-O(11)	81.04(13)
N(3)-Mo(5)-O(19)	84.91(12)	O(24)-Mo(7)-O(11)	81.37(11)
O(20)-Mo(6)-O(8)	103.82(15)	O(21)-Mo(7)-O(11)	81.93(11)
O(20)-Mo(6)-O(19)	103.94(15)	O(12)-Mo(7)-O(11)	71.12(11)
O(8)-Mo(6)-O(19)	102.93(14)	O(26)-Mo(8)-O(25)	105.22(17)
O(20)-Mo(6)-O(12)	102.70(15)	O(26)-Mo(8)-O(16)	95.77(14)
O(8)-Mo(6)-O(12)	99.60(13)	O(25)-Mo(8)-O(16)	100.69(14)
O(19)-Mo(6)-O(12)	139.53(13)	O(26)-Mo(8)-O(24)	101.61(14)
O(20)-Mo(6)-O(21)	94.86(13)	O(25)-Mo(8)-O(24)	95.41(14)
O(8)-Mo(6)-O(21)	161.05(13)	O(16)-Mo(8)-O(24)	152.28(14)
O(19)-Mo(6)-O(21)	75.18(12)	O(26)-Mo(8)-O(12)	93.13(14)
O(12)-Mo(6)-O(21)	72.70(12)	O(25)-Mo(8)-O(12)	160.05(14)
O(20)-Mo(6)-O(7)	179.07(13)	O(16)-Mo(8)-O(12)	84.88(12)
O(8)-Mo(6)-O(7)	77.10(12)	O(24)-Mo(8)-O(12)	72.85(12)
O(19)-Mo(6)-O(7)	75.93(11)	O(26)-Mo(8)-O(15)	163.64(14)
O(12)-Mo(6)-O(7)	76.94(11)	O(25)-Mo(8)-O(15)	89.56(13)
O(21)-Mo(6)-O(7)	84.22(10)	O(16)-Mo(8)-O(15)	74.20(12)
O(22)-Mo(7)-O(23)	104.35(15)	O(24)-Mo(8)-O(15)	83.58(12)
O(22)-Mo(7)-O(24)	96.95(14)	O(12)-Mo(8)-O(15)	73.41(11)

Table S6 Selected bond lengths [Å] and angles [°] for $[Hdmpz]_4[Mo_8O_{26}(dmpz)_2]\cdot 2dmpz$, **2**.

Mo(1)-O(1)	1.708(17)	Mo(3)-O(10)	1.711(15)
Mo(1)-O(2)	1.654(17)	Mo(3)-O(11)	1.797(17)
Mo(1)-O(3)	1.883(16)	Mo(3)-O(4)	1.904(15)
Mo(1)-O(4)	2.243(16)	Mo(3)-O(9)#1	1.915(16)
Mo(1)-O(5)	2.142(16)	Mo(3)-O(5)	2.157(16)
Mo(1)-N(1)	2.23(2)	Mo(3)-O(9)	2.446(14)
Mo(2)-O(3)	1.983(17)	Mo(4)-O(12)	1.690(16)
Mo(2)-O(4)	2.235(15)	Mo(4)-O(13)	1.724(16)
Mo(2)-O(6)	1.658(17)	Mo(4)-O(5)#1	1.923(16)
Mo(2)-O(7)	1.707(16)	Mo(4)-O(8)	1.968(16)
Mo(2)-O(8)	1.955(16)	Mo(4)-O(9)	2.242(16)
Mo(2)-O(9)	2.264(15)	Mo(4)-O(11)	2.293(16)
O(2)-Mo(1)-O(1)	105.4(8)	O(3)-Mo(1)-O(4)	74.2(6)
O(2)-Mo(1)-O(3)	99.6(8)	O(5)-Mo(1)-O(4)	71.2(6)
O(1)-Mo(1)-O(3)	100.7(8)	N(1)-Mo(1)-O(4)	85.4(7)
O(2)-Mo(1)-O(5)	161.6(7)	O(6)-Mo(2)-O(7)	108.2(8)
O(1)-Mo(1)-O(5)	88.8(7)	O(6)-Mo(2)-O(8)	93.3(8)
O(3)-Mo(1)-O(5)	88.8(6)	O(7)-Mo(2)-O(8)	101.8(7)
O(2)-Mo(1)-N(1)	87.5(8)	O(6)-Mo(2)-O(3)	102.0(8)
O(1)-Mo(1)-N(1)	96.4(8)	O(7)-Mo(2)-O(3)	97.3(7)
O(3)-Mo(1)-N(1)	158.9(8)	O(8)-Mo(2)-O(3)	150.4(7)
O(5)-Mo(1)-N(1)	79.3(7)	O(6)-Mo(2)-O(4)	90.9(7)
O(2)-Mo(1)-O(4)	95.3(7)	O(7)-Mo(2)-O(4)	160.2(7)
O(1)-Mo(1)-O(4)	159.3(7)	O(8)-Mo(2)-O(4)	82.1(6)

O(3)-Mo(2)-O(4)	72.6(6)	O(4)-Mo(3)-O(9)	75.2(6)
O(6)-Mo(2)-O(9)	161.0(6)	O(9)#1-Mo(3)-O(9)	77.3(6)
O(7)-Mo(2)-O(9)	88.8(7)	O(5)-Mo(3)-O(9)	84.2(5)
O(8)-Mo(2)-O(9)	74.4(6)	O(12)-Mo(4)-O(13)	103.7(8)
O(3)-Mo(2)-O(9)	83.7(6)	O(12)-Mo(4)-O(5)#1	95.6(8)
O(4)-Mo(2)-O(9)	73.3(5)	O(13)-Mo(4)-O(5)#1	103.5(8)
O(10)-Mo(3)-O(11)	100.6(7)	O(12)-Mo(4)-O(8)	97.4(7)
O(10)-Mo(3)-O(4)	106.8(7)	O(13)-Mo(4)-O(8)	103.5(8)
O(11)-Mo(3)-O(4)	101.7(7)	O(5)#1-Mo(4)-O(8)	146.2(7)
O(10)-Mo(3)-O(9)#1	102.1(7)	O(12)-Mo(4)-O(9)	99.9(7)
O(11)-Mo(3)-O(9)#1	96.0(7)	O(13)-Mo(4)-O(9)	156.4(7)
O(4)-Mo(3)-O(9)#1	142.4(6)	O(5)#1-Mo(4)-O(9)	72.4(6)
O(10)-Mo(3)-O(5)	98.8(7)	O(8)-Mo(4)-O(9)	74.7(6)
O(11)-Mo(3)-O(5)	159.8(6)	O(12)-Mo(4)-O(11)	172.0(7)
O(4)-Mo(3)-O(5)	77.7(6)	O(13)-Mo(4)-O(11)	84.3(7)
O(9)#1-Mo(3)-O(5)	74.5(6)	O(5)#1-Mo(4)-O(11)	81.7(6)
O(10)-Mo(3)-O(9)	176.7(7)	O(8)-Mo(4)-O(11)	81.2(6)
O(11)-Mo(3)-O(9)	76.3(6)	O(9)-Mo(4)-O(11)	72.1(5)

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+1,-z+1

Table S7 Bond lengths [Å] and angles [°] for $[Hpz]_4[Mo_8O_{22}(O_2)_4(pz)_2]\cdot 3H_2O$, **3**.

Mo(1)-O(1)	1.783(6)	Mo(3)-O(11)	1.703(4)
Mo(1)-O(2)	1.875(7)	Mo(3)-O(12)	1.908(3)
Mo(1)-O(3)	1.699(4)	Mo(3)-O(5)	1.957(3)
Mo(1)-O(4)	2.064(3)	Mo(3)-O(6)	2.285(3)
Mo(1)-O(5)	1.928(3)	Mo(3)-O(9)	2.347(3)
Mo(1)-O(6)	2.250(4)	Mo(4)-O(13)	1.695(4)
Mo(1)-N(1)	2.220(4)	Mo(4)-O(14)	1.867(5)
Mo(2)-O(6)	1.871(3)	Mo(4)-O(15)	1.893(5)
Mo(2)-O(7)	1.689(3)	Mo(4)-O(12)	1.970(3)
Mo(2)-O(8)	1.774(3)	Mo(4)-O(4)#1	1.978(3)
Mo(2)-O(9)#1	1.966(3)	Mo(4)-O(9)	2.149(3)
Mo(2)-O(4)	2.103(3)	Mo(4)-O(8)	2.273(3)
Mo(2)-O(9)	2.444(3)	O(1)-O(2)	1.099(9)
Mo(3)-O(10)	1.700(4)	O(14)-O(15)	1.317(7)

O(3)-Mo(1)-O(1)	105.4(2)	O(3)-Mo(1)-O(6)	90.87(15)
O(3)-Mo(1)-O(2)	104.5(3)	O(1)-Mo(1)-O(6)	158.2(2)
O(1)-Mo(1)-O(2)	34.8(3)	O(2)-Mo(1)-O(6)	153.8(2)
O(3)-Mo(1)-O(5)	99.33(16)	O(5)-Mo(1)-O(6)	74.39(13)
O(1)-Mo(1)-O(5)	88.5(3)	O(4)-Mo(1)-O(6)	69.30(13)
O(2)-Mo(1)-O(5)	122.4(3)	N(1)-Mo(1)-O(6)	87.04(15)
O(3)-Mo(1)-O(4)	154.39(16)	O(7)-Mo(2)-O(8)	102.20(17)
O(1)-Mo(1)-O(4)	98.2(2)	O(7)-Mo(2)-O(6)	103.98(16)
O(2)-Mo(1)-O(4)	89.2(2)	O(8)-Mo(2)-O(6)	102.51(15)
O(5)-Mo(1)-O(4)	90.98(14)	O(7)-Mo(2)-O(9)#1	103.14(15)
O(3)-Mo(1)-N(1)	82.52(17)	O(8)-Mo(2)-O(9)#1	97.28(15)
O(1)-Mo(1)-N(1)	109.1(3)	O(6)-Mo(2)-O(9)#1	141.93(15)
O(2)-Mo(1)-N(1)	74.4(3)	O(7)-Mo(2)-O(4)	98.00(15)
O(5)-Mo(1)-N(1)	161.33(16)	O(8)-Mo(2)-O(4)	159.40(15)
O(4)-Mo(1)-N(1)	80.48(15)	O(6)-Mo(2)-O(4)	76.16(14)

O(9)#1-Mo(2)-O(4)	74.04(13)	O(13)-Mo(4)-O(14)	105.3(2)
O(7)-Mo(2)-O(9)	176.70(14)	O(13)-Mo(4)-O(15)	105.8(2)
O(8)-Mo(2)-O(9)	74.53(14)	O(14)-Mo(4)-O(15)	41.0(2)
O(6)-Mo(2)-O(9)	77.39(13)	O(13)-Mo(4)-O(12)	96.89(17)
O(9)#1-Mo(2)-O(9)	77.04(14)	O(14)-Mo(4)-O(12)	83.9(2)
O(4)-Mo(2)-O(9)	85.23(12)	O(15)-Mo(4)-O(12)	123.9(2)
O(10)-Mo(3)-O(11)	105.66(18)	O(13)-Mo(4)-O(4)#1	93.71(16)
O(10)-Mo(3)-O(12)	99.16(17)	O(14)-Mo(4)-O(4)#1	123.0(2)
O(11)-Mo(3)-O(12)	102.14(17)	O(15)-Mo(4)-O(4)#1	82.4(2)
O(10)-Mo(3)-O(5)	100.72(16)	O(12)-Mo(4)-O(4)#1	147.06(14)
O(11)-Mo(3)-O(5)	94.45(16)	O(13)-Mo(4)-O(9)	98.56(16)
O(12)-Mo(3)-O(5)	149.52(14)	O(14)-Mo(4)-O(9)	149.72(19)
O(10)-Mo(3)-O(6)	91.11(16)	O(15)-Mo(4)-O(9)	146.11(19)
O(11)-Mo(3)-O(6)	160.88(16)	O(12)-Mo(4)-O(9)	74.85(13)
O(12)-Mo(3)-O(6)	83.73(14)	O(4)#1-Mo(4)-O(9)	72.77(13)
O(5)-Mo(3)-O(6)	73.05(13)	O(13)-Mo(4)-O(8)	170.80(16)
O(10)-Mo(3)-O(9)	161.47(16)	O(14)-Mo(4)-O(8)	83.58(19)
O(11)-Mo(3)-O(9)	92.10(15)	O(15)-Mo(4)-O(8)	82.44(19)
O(12)-Mo(3)-O(9)	71.37(13)	O(12)-Mo(4)-O(8)	81.36(13)
O(5)-Mo(3)-O(9)	82.75(13)	O(4)#1-Mo(4)-O(8)	83.25(13)
O(6)-Mo(3)-O(9)	72.34(12)	O(9)-Mo(4)-O(8)	72.25(12)

Symmetry transformations used to generate equivalent atoms: #1 -x+3/2,-y+3/2,-z+1.

Table S8 Selected bond lengths [Å] and angles [°] for $[Him]_4[Mo_8O_{24}(O_2)_2(im)_2]\cdot 3H_2O$, **4**.

Mo(1)-O(2)	1.709(3)	Mo(3)-O(9)	1.879(3)
Mo(1)-O(1)	1.735(3)	Mo(3)-O(10)	1.914(4)
Mo(1)-O(14)#1	1.926(2)	Mo(3)-O(4)	1.942(2)
Mo(1)-O(4)	2.117(2)	Mo(3)-O(8)	1.977(2)
Mo(1)-N(1)	2.189(3)	Mo(3)-O(7)	2.142(2)
Mo(1)-O(3)	2.200(2)	Mo(3)-O(6)#1	2.275(2)
Mo(2)-O(5)	1.689(2)	Mo(4)-O(13)	1.717(2)
Mo(2)-O(6)	1.760(2)	Mo(4)-O(12)	1.732(2)
Mo(2)-O(3)	1.906(2)	Mo(4)-O(8)	1.895(2)
Mo(2)-O(7)	1.963(2)	Mo(4)-O(14)	1.950(2)
Mo(2)-O(4)	2.116(2)	Mo(4)-O(3)#1	2.248(2)
Mo(2)-O(7)#1	2.462(2)	Mo(4)-O(7)	2.304(2)
Mo(3)-O(11)	1.696(2)	O(9)-O(10)	1.287(6)
O(2)-Mo(1)-O(1)	105.06(15)	O(14)#1-Mo(1)-O(3)	75.52(9)
O(2)-Mo(1)-O(14)#1	100.21(11)	O(4)-Mo(1)-O(3)	70.17(9)
O(1)-Mo(1)-O(14)#1	104.5(2)	N(1)-Mo(1)-O(3)	83.53(9)
O(2)-Mo(1)-O(4)	156.49(12)	O(5)-Mo(2)-O(6)	104.10(11)
O(1)-Mo(1)-O(4)	93.85(14)	O(5)-Mo(2)-O(3)	103.77(11)
O(14)#1-Mo(1)-O(4)	88.15(9)	O(6)-Mo(2)-O(3)	100.72(11)
O(2)-Mo(1)-N(1)	86.39(11)	O(5)-Mo(2)-O(7)	103.43(10)
O(1)-Mo(1)-N(1)	93.8(2)	O(6)-Mo(2)-O(7)	98.37(10)
O(14)#1-Mo(1)-N(1)	158.02(10)	O(3)-Mo(2)-O(7)	141.59(10)
O(4)-Mo(1)-N(1)	78.42(9)	O(5)-Mo(2)-O(4)	98.51(10)
O(2)-Mo(1)-O(3)	90.53(11)	O(6)-Mo(2)-O(4)	157.24(9)
O(1)-Mo(1)-O(3)	164.02(13)	O(3)-Mo(2)-O(4)	76.01(10)

O(7)-Mo(2)-O(4)	73.57(9)	O(11)-Mo(3)-O(6)#1	171.43(11)
O(5)-Mo(2)-O(7)#1	179.40(10)	O(9)-Mo(3)-O(6)#1	85.51(12)
O(6)-Mo(2)-O(7)#1	75.47(9)	O(10)-Mo(3)-O(6)#1	85.56(14)
O(3)-Mo(2)-O(7)#1	75.93(8)	O(4)-Mo(3)-O(6)#1	82.56(9)
O(7)-Mo(2)-O(7)#1	77.08(9)	O(8)-Mo(3)-O(6)#1	79.99(9)
O(4)-Mo(2)-O(7)#1	81.94(8)	O(7)-Mo(3)-O(6)#1	73.43(8)
O(11)-Mo(3)-O(9)	101.34(13)	O(13)-Mo(4)-O(12)	104.94(12)
O(11)-Mo(3)-O(10)	102.99(15)	O(13)-Mo(4)-O(8)	99.63(12)
O(9)-Mo(3)-O(10)	39.67(18)	O(12)-Mo(4)-O(8)	100.18(11)
O(11)-Mo(3)-O(4)	98.01(11)	O(13)-Mo(4)-O(14)	99.58(12)
O(9)-Mo(3)-O(4)	121.17(15)	O(12)-Mo(4)-O(14)	95.89(11)
O(10)-Mo(3)-O(4)	81.98(16)	O(8)-Mo(4)-O(14)	150.77(10)
O(11)-Mo(3)-O(8)	95.34(11)	O(13)-Mo(4)-O(3)#1	93.29(10)
O(9)-Mo(3)-O(8)	85.15(16)	O(12)-Mo(4)-O(3)#1	160.51(10)
O(10)-Mo(3)-O(8)	123.97(16)	O(8)-Mo(4)-O(3)#1	83.16(9)
O(4)-Mo(3)-O(8)	147.01(10)	O(14)-Mo(4)-O(3)#1	73.94(9)
O(11)-Mo(3)-O(7)	98.47(10)	O(13)-Mo(4)-O(7)	165.12(10)
O(9)-Mo(3)-O(7)	153.02(14)	O(12)-Mo(4)-O(7)	89.12(10)
O(10)-Mo(3)-O(7)	149.25(15)	O(8)-Mo(4)-O(7)	72.59(9)
O(4)-Mo(3)-O(7)	73.38(9)	O(14)-Mo(4)-O(7)	83.48(9)
O(8)-Mo(3)-O(7)	74.89(9)	O(3)#1-Mo(4)-O(7)	73.45(8)

Symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+1,-z+1

Table S9 Crystallographic data for compounds $[HMepz]_4[Mo_8O_{26}(Mepz)_2]\cdot 2H_2O$, **1**, $[Hdmpz]_4[Mo_8O_{26}(dmpz)_2]\cdot 2dmpz$, **2**, $[Hpz]_4[Mo_8O_{22}(O_2)_4(pz)_2]\cdot 3H_2O$, **3**, and $[Him]_4[Mo_8O_{24}(O_2)_2(im)_2]\cdot 3H_2O$, **4**.

Complex	**1**	**2**	**3**	**4**
empirical formula	$C_{24}H_{40}Mo_8N_{12}O_{28}$	$C_{40}H_{70}Mo_8N_{16}O_{26}$	$C_{18}H_{34}Mo_8N_{12}O_{33}$	$C_{18}H_{34}Mo_8N_{12}O_{31}$
fw	1716.23	1956.62	1714.09	1682.09
cryst syst	Monoclinic	Monoclinic	Monoclinic	Triclinic
space group	*C c*	*P 2₁/c*	*C 2/c*	$P\bar{1}$
a (Å)	19.1767(5)	11.7737(5)	20.1800(14)	10.6258(7)
b (Å)	11.3151(4)	13.2676(6)	10.0629(7)	10.6937(8)
c (Å)	23.0147(7)	21.7757(11)	22.8645(16)	11.2851(8)
α (º)	90	90	90	93.182(2)
β (º)	98.482(2)	102.197(2)	105.041(2)	117.554(2)
γ (º)	90	90	90	101.937(2)
V (Å^3)	4939.3(3)	3324.8(3)	4484.0(5)	1095.26(13)
Z	4	2	4	1
ρ (calculated, Mg·m^{-3})	2.308	1.954	2.539	2.550
abs coeff (mm^{-1})	2.061	1.544	2.278	2.326
F(000)	3328	1928	3304	810
crystal size (mm^3)	0.50 x 0.45 x 0.45	0.50 x 0.45 x 0.40	0.50 x 0.45 x 0.40	0.20 x 0.19 x 0.17
reflns collected	25228	25601	41624	39873
independent reflns	6510	5894	4061	6695
no. of param.	692	414	321	339
$R_1(F)$ [$F^2>2\sigma(F^2)$] [a]	0.0173	0.0647	0.0323	0.0330
$wR_2(F^2)$ [b] (all data)	0.0453	0.1926	0.0769	0.0883
S [c] (all data)	1.035	1.057	1.146	1.054

[a] $R_1(F) = \sum(\left|Fo\right| - \left|Fc\right|)/\sum\left|Fo\right|$ for the observed reflections [$F^2>2\sigma(F^2)$]. [b] $wR_2(F^2) = \{\sum [w(F_o^2 - F_c^2)^2]/ \sum w(F_o^2)^2\}^{1/2}$. [c] $S = \{\sum [w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$; (n = number of reflections, p = number of parameters).