

Supporting information for “Alternative mechanisms for O₂ release and O–O bond formation in the oxygen evolving complex of photosystem II.”

Xichen Li^{a,b} and Per E M Siegbahn^{b,*}

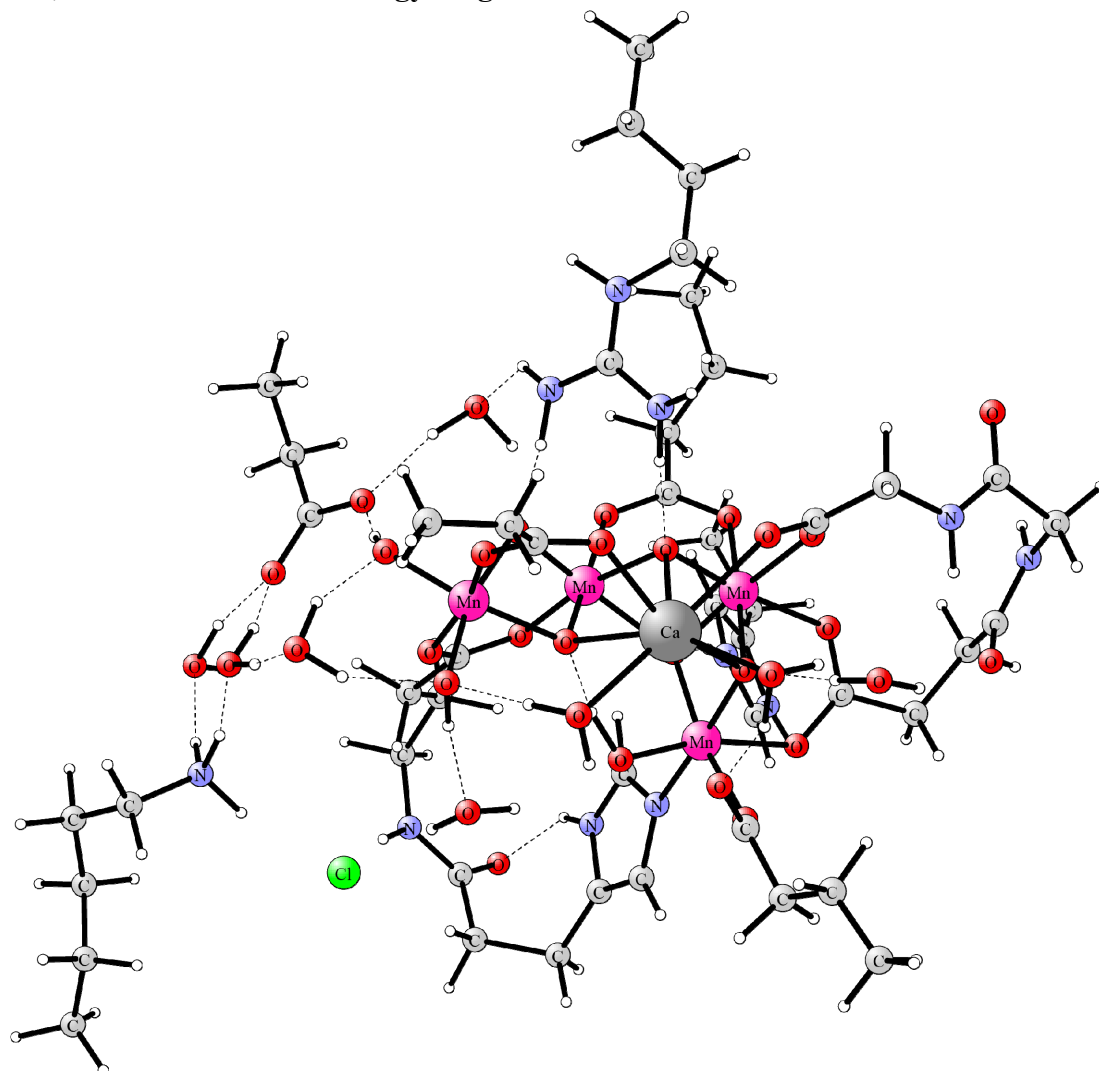
a. College of Chemistry, Beijing Normal University, 100875, Beijing, China.

b. Department of Organic Chemistry, Arrhenius Laboratory, Stockholm University, SE-106 91, Stockholm, Sweden.

- 1. Structures to build the energy diagram.**
- 2. Table S1. Energies to build the energy diagram.**
- 3. Structure of the alternative TS(O-O) (Figure 6 D).**
- 4. Table S2. Energy of the alternative TS(O-O) (Figure 6 D).**

Structures to build the diagram

S_3^{-1} , 0.0 kcal/mol on the energy diagram

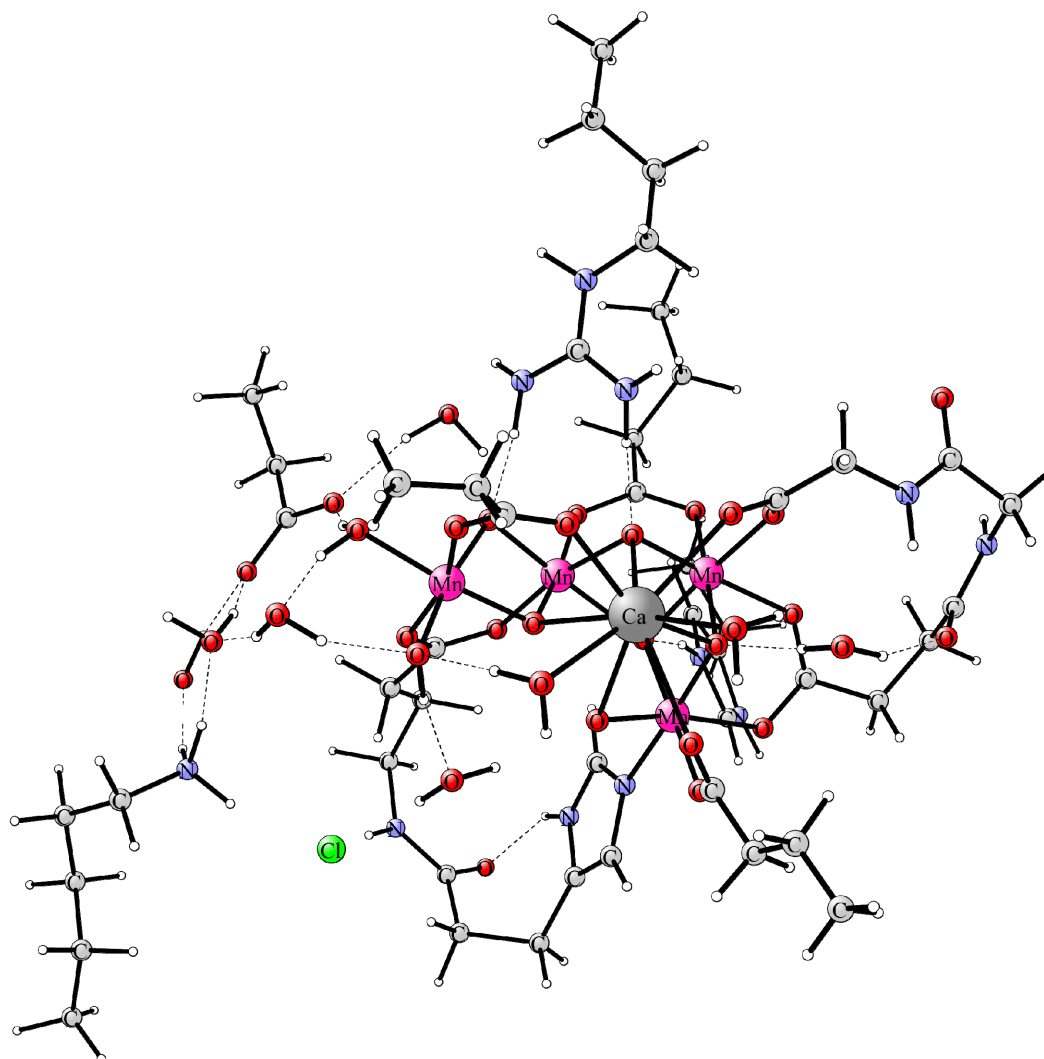


Mn1	3.04066500	-1.46515400	3.73137500	O19	2.50573000	0.34846600	3.15837700
Mn2	4.60411800	-1.64433200	8.78861500	C20	1.05826000	1.18299700	13.45631300
Mn3	5.36904900	-1.56791600	5.29652700	H21	0.37022400	0.36013900	13.58246300
Mn4	6.57524500	-0.12777400	7.42807600	H22	0.73364700	2.12912700	13.86357900
O5	3.65806700	-1.14987600	5.58850600	H23	1.93973000	0.90371200	14.05401000
O6	5.85375400	0.14717700	5.82946700	C24	1.47650300	1.22277200	11.98197900
O7	5.01699000	0.11482500	8.35744700	H25	2.34952300	1.87271600	11.84219800
O8	5.96955700	-1.90810100	7.41956300	H26	0.67593900	1.62250900	11.34915800
Ca9	3.53443900	1.14366100	6.66025700	C27	1.81719400	-0.21173000	11.54515900
C10	0.66754600	1.95150900	1.70634700	H28	0.89031000	-0.79592400	11.44600300
H11	1.22518400	1.90580300	0.78257800	H29	2.42065300	-0.70830700	12.31183500
H12	-0.32439000	2.36864200	1.61432400	C30	2.55572800	-0.31549700	10.22416700
H13	0.47832000	0.89465400	1.93999500	O31	2.25207500	0.38538400	9.25188000
C14	1.48936500	2.52097400	2.87115100	O32	3.51287100	-1.20618500	10.25773700
H15	0.82513600	2.85001700	3.68164300	C33	2.78445000	-7.86080800	8.62574400
H16	2.06331700	3.41260300	2.58932200	H34	2.33753200	-8.81589300	8.93134700
C17	2.47950200	1.56031100	3.56929800	H35	2.01729700	-7.30640800	8.07771100
O18	3.17050700	2.02833100	4.50450800	C36	3.98592200	-8.15336700	7.72174400

O37	5.09814900	-8.44952500	8.20828000	O100	7.35425000	-1.94099700	4.88800400
C38	3.22290000	-7.10552900	9.91345500	O101	8.33302200	-0.76810100	6.55446300
H39	3.89930500	-7.75335800	10.48338800	C102	10.81872400	4.22856800	-0.81502100
H40	2.34283800	-6.91828900	10.53591100	H103	11.54036400	3.48392200	-0.51313100
C41	3.89954300	-5.79894200	9.60887500	H104	11.20109300	5.23062600	-0.68822300
N42	4.97214400	-5.78367700	8.73528800	H105	10.66568500	4.09810800	-1.89383600
H43	5.40687100	-6.64011600	8.38468900	C106	9.49016200	4.00639900	-0.07751000
C44	3.64988600	-4.47137200	9.88090800	H107	9.04271100	3.07930600	-0.46476700
H45	2.89381200	-4.02142800	10.50581100	H108	8.78333600	4.81094300	-0.32251900
C46	5.28851600	-4.51320600	8.45273800	C109	9.65257600	3.90925000	1.44585800
H47	5.96133300	-4.22382800	7.66812700	H110	10.08656100	4.84298600	1.82661000
N48	4.53482000	-3.68727300	9.16018800	H111	10.36339900	3.10902300	1.69213600
N49	3.79961200	-7.95120300	6.40655000	C112	8.34707400	3.66213500	2.21273300
H50	2.86365400	-7.64880400	6.10090700	H113	7.64028100	4.48409900	2.01967500
C51	4.91725300	-7.84634500	5.46886600	H114	8.55232100	3.64658300	3.28766200
H52	4.65049000	-8.38516900	4.55034300	N115	7.74741900	2.37547200	1.86194800
H53	5.77580300	-8.34561900	5.92096900	H116	7.76742400	2.09538400	0.89135600
C54	5.25312700	-6.36874800	5.13862400	C117	6.93125000	1.64629900	2.66031400
H55	6.12123200	-6.35153000	4.46601300	N118	6.54214700	2.13401200	3.84791600
H56	5.57205100	-5.87559000	6.06083500	H119	6.12314300	1.50334600	4.53877700
C57	4.08800100	-5.57828900	4.51319500	H120	6.41615800	3.12333400	4.00074300
H58	3.13089800	-5.82841600	4.99034800	N121	6.53330600	0.44108400	2.27525600
H59	3.95822200	-5.82051600	3.45103600	H122	7.08454000	-0.21410500	1.70931000
C60	4.17672500	-4.06023100	4.58286700	H123	5.82453800	-0.06783000	2.83476300
O61	3.23154500	-3.42531100	4.03820500	C124	11.84239800	-5.39309000	7.24925500
O62	5.15270400	-3.51725200	5.20218900	H125	11.25220200	-5.97246100	6.55470800
C63	9.15951200	0.11915800	11.44782300	H126	12.79646300	-5.85244900	7.46174200
H64	9.79980200	-0.16033900	10.60430300	H127	12.01645800	-4.39296800	6.84033200
H65	9.75701800	0.00823000	12.36288400	C128	11.16983600	-5.34423700	8.63620200
C66	7.93813400	-0.78950700	11.52733000	H129	11.86576400	-4.88095300	9.35062600
H67	7.23998200	-0.42574300	12.28762500	H130	11.02060200	-6.37441500	8.98854000
H68	8.23474700	-1.79927300	11.83900400	C131	9.87102900	-4.61386000	8.70721900
C69	7.15721500	-0.91484600	10.22271800	N132	9.07086300	-4.63348600	9.84601400
O70	7.61302600	-0.33376100	9.19828100	C133	9.22558500	-3.78380700	7.83501100
O71	6.12182100	-1.64414700	10.25642900	H134	9.48629000	-3.49451100	6.83416500
C72	8.76804900	1.59307200	11.33128600	C135	7.99513400	-3.85109300	9.66369000
O73	7.64331700	2.00688000	11.62650800	H136	7.19384800	-3.66889300	10.36328700
N74	9.77464000	2.42716800	10.96175300	N137	8.08317700	-3.31953300	8.45031900
H75	10.61008200	2.02290400	10.56061800	H138	7.33339500	-2.70026300	8.01556600
C76	9.56777800	3.85881500	10.76518900	C139	6.09893600	-4.23518800	-1.22219700
H77	10.51308000	4.37903800	10.92878700	H140	5.38336300	-4.56843400	-1.95928700
H78	8.83300900	4.19062100	11.50235800	H141	7.10941700	-4.13018100	-1.58867200
C79	9.10756400	4.16461900	9.32465800	H142	5.79434800	-3.22429500	-0.92803900
O80	9.91058800	4.51953600	8.46779000	C143	6.03505200	-5.13266000	0.03255000
N81	7.77665300	3.98672100	9.10584300	H144	5.95688800	-6.19234100	-0.23144900
H82	7.20564200	3.56978400	9.83281900	H145	6.94955500	-4.99027400	0.62219800
C83	7.19218700	4.06722200	7.78269100	C146	4.85531900	-4.70480100	0.91484700
H84	6.43342300	4.85441600	7.73461700	O147	4.91340100	-3.51609300	1.34765900
H85	8.00437200	4.31775900	7.09255500	O148	3.90549900	-5.51139200	1.14363000
C86	6.52310300	2.75780500	7.33720600	C149	-1.82887500	-11.98671700	4.24856800
O87	5.42095900	2.81071800	6.77219200	H150	-2.35869300	-12.71809500	3.65630000
O88	7.20240800	1.68796300	7.59368200	H151	-2.32840600	-11.78325000	5.18423400
C89	11.58166200	-0.61708300	3.48089900	H152	-0.85212800	-12.41724300	4.50706400
H90	12.44417500	-1.21809300	3.72840300	C153	-1.64420000	-10.65203200	3.48039500
H91	11.83042700	0.38213700	3.15520800	H154	-2.52191000	-10.47985400	2.84100800
H92	11.11563300	-1.10083700	2.61091700	H155	-1.62962500	-9.82386700	4.19993400
C93	10.52635100	-0.45179100	4.58310100	C156	-0.36517900	-10.58954400	2.62535900
H94	9.83650100	0.33967300	4.26388500	H157	0.50523900	-10.49628100	3.29086600
H95	10.97144700	-0.09812900	5.51987000	H158	-0.23636100	-11.54638800	2.09942900
C96	9.71147700	-1.72762000	4.82964600	C159	-0.34518200	-9.48229900	1.55318900
H97	10.29707400	-2.41204400	5.45771700	H160	0.56900300	-9.57446800	0.95123000
H98	9.51339100	-2.24329600	3.88572800	H161	-1.18098300	-9.66276600	0.86274100
C99	8.35906400	-1.45103400	5.47965200	C162	-0.47325100	-8.02049600	2.00473300

H163	-0.68522300	-7.39709500	1.13163800	H183	5.14770500	1.45902900	9.62063800
H164	-1.29056000	-7.87943200	2.71716800	H184	5.79319200	2.15574800	10.84721500
N165	0.76111800	-7.43913400	2.62348400	O185	2.89560300	-1.87148200	2.00609200
H166	0.84983100	-6.41075900	2.31466800	H186	3.59711800	-2.55392200	1.78539400
H167	0.75529500	-7.44841300	3.66429000	H187	0.95486300	-4.43580600	6.21265100
H168	1.63981900	-7.87267500	2.26487400	O188	3.15716900	-1.94042100	7.84686600
C169	0.83583900	-6.81915400	5.76508000	O189	1.11552800	-5.09771300	1.45362000
O170	1.31174900	-1.62548400	4.35081800	H190	2.09183200	-4.99890900	1.39532800
H171	0.26426300	-2.29785800	2.83366500	H191	0.74258100	-4.20672100	1.69313400
O172	4.98819700	-1.31539200	3.61650400	O192	0.22282900	-2.54747300	1.88664200
O173	7.34526000	-2.18293000	1.78423000	H193	1.09656300	-2.20054300	1.60213800
H174	7.26026500	-2.20519800	2.75444300	O194	3.24696000	-8.11409600	1.42447100
H175	6.49572900	-2.60743700	1.50150000	H195	3.54611300	-7.19820400	1.17345900
O176	1.23583300	0.28112300	6.38463700	H196	3.98443600	-8.47751000	1.93557900
H177	1.15936600	-0.35172900	5.61745800	O197	1.00521100	-3.47608400	6.40826500
H178	0.99339700	-0.23792600	7.16908700	H198	1.26701300	-2.39532600	4.97899400
O179	2.91193600	2.84665400	8.38510200	H199	1.73898300	-3.35428600	7.03602800
H180	3.69269100	3.05290200	8.93654100	H200	3.30997200	-1.71572900	6.85206400
H181	2.37714800	2.26611700	8.96277400	H201	9.25369400	-5.17045500	10.68360800
O182	5.13379100	2.29133400	10.14277900				

S₄⁰ RE(O–O) with the outer oxo bridge and the inner oxyl radical, ¹⁴A

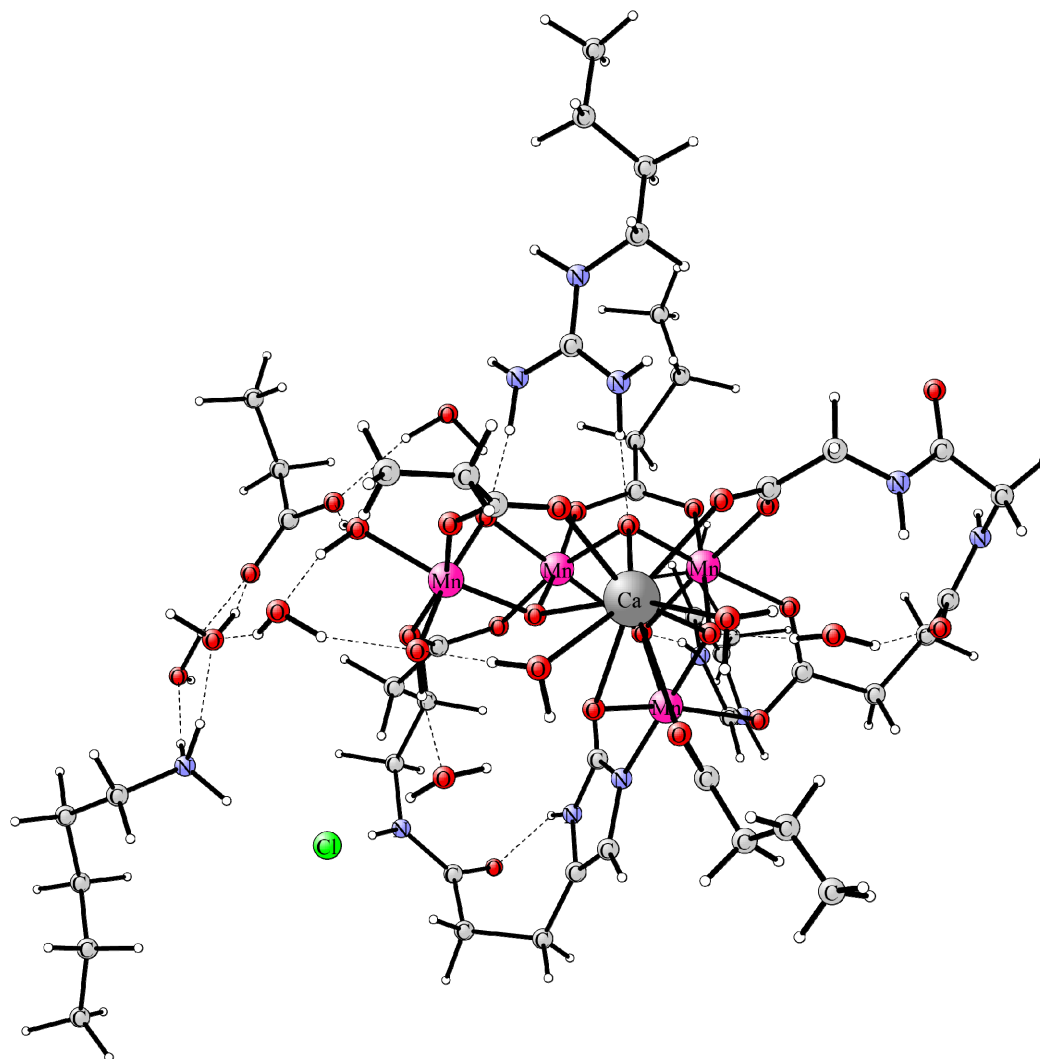


Mn1	3.03972900	-1.43456500	3.81275700	H22	0.73357700	2.12912900	13.86352600
Mn2	4.65571500	-1.56787000	8.73254700	H23	1.94156000	0.90871500	14.05369500
Mn3	5.33169100	-1.54706500	5.32926000	C24	1.47490400	1.24488300	11.98271000
Mn4	6.58626800	-0.05754900	7.40117300	H25	2.28461200	1.97056500	11.83566800
O5	3.57554500	-1.19496700	5.56166400	H26	0.63897300	1.56074200	11.34785900
O6	5.76407000	0.17514100	5.83485700	C27	1.95203300	-0.14893300	11.56087700
O7	5.08922000	0.19624000	8.41014700	H28	1.11411500	-0.86210200	11.59392900
O8	5.94017400	-1.85602900	7.38027900	H29	2.69604200	-0.53220200	12.26839000
Ca9	3.35366800	1.04441900	6.85039400	C30	2.54495000	-0.24516300	10.17217600
C10	0.66760800	1.95146100	1.70637800	O31	2.27199100	0.54319000	9.26690000
H11	1.22515600	1.90588600	0.78257300	O32	3.35563600	-1.27934500	10.05000100
H12	-0.32440200	2.36857900	1.61443100	C33	2.78448100	-7.86076200	8.62573900
H13	0.46695200	0.89320700	1.92796900	H34	2.39636400	-8.82290000	8.98290400
C14	1.48826300	2.50344800	2.88635500	H35	1.98394100	-7.36945100	8.06480300
H15	0.82450300	2.89344600	3.66806100	C36	3.99107700	-8.12436300	7.72536100
H16	2.11695400	3.35497700	2.59582300	O37	5.11189400	-8.37959200	8.21265600
C17	2.41619400	1.52755400	3.65040700	C38	3.19220700	-7.01998000	9.87145400
O18	2.98983500	1.94495600	4.67430400	H39	3.88024000	-7.61669600	10.48139800
O19	2.53432600	0.32888200	3.18132800	H40	2.30301500	-6.82319400	10.47706200
C20	1.05839900	1.18293600	13.45628300	C41	3.84272500	-5.71410600	9.50903300
H21	0.37022600	0.36015400	13.58241400	N42	4.94792700	-5.71395600	8.67546200

H43	5.40039400	-6.57906700	8.36626600	C106	9.48700400	4.01312800	-0.07958700
C44	3.56018300	-4.38183100	9.71708000	H107	9.04432800	3.07750800	-0.45321200
H45	2.78147000	-3.92246500	10.30555500	H108	8.77935700	4.81091300	-0.34301000
C46	5.25539500	-4.45159200	8.35299900	C109	9.64095500	3.94675800	1.44711600
H47	5.96568400	-4.17921400	7.59579400	H110	10.08220900	4.88397800	1.80925000
N48	4.45759600	-3.61023700	8.99458300	H111	10.34266900	3.14599800	1.71651500
N49	3.80011000	-7.94030900	6.40672600	C112	8.32924000	3.73597200	2.21564200
H50	2.86647100	-7.64625500	6.09579700	H113	7.63288800	4.55981100	1.99889400
C51	4.91726000	-7.84632400	5.46885700	H114	8.53093900	3.74109300	3.29172700
H52	4.65049300	-8.39112800	4.55458900	N115	7.71072600	2.44856500	1.88665400
H53	5.77517500	-8.34009000	5.92709300	H116	7.77954300	2.12902700	0.93009200
C54	5.26259500	-6.37125500	5.12183500	C117	6.87361200	1.74683900	2.67881300
H55	6.13647200	-6.36878800	4.45693600	N118	6.44856600	2.26052200	3.84376300
H56	5.57631100	-5.86742300	6.03917000	H119	6.00062200	1.65446200	4.53512700
C57	4.10739000	-5.57819400	4.47542100	H120	6.38537000	3.25636800	3.99156800
H58	3.14148600	-5.83287800	4.93358800	N121	6.47212300	0.53365500	2.31118800
H59	3.99650400	-5.82820600	3.41346300	H122	7.01155000	-0.11851600	1.73576200
C60	4.18087400	-4.05792700	4.55782300	H123	5.76400500	0.03572600	2.86942900
O61	3.23902800	-3.41905800	3.99764400	C124	11.84238000	-5.39307400	7.24925300
O62	5.13166400	-3.50932500	5.20318300	H125	11.25221000	-5.97248800	6.55472300
C63	9.15938800	0.11919500	11.44783900	H126	12.79648000	-5.85245200	7.46172900
H64	9.82459500	-0.16046400	10.62390400	H127	12.01999600	-4.39322400	6.84097000
H65	9.72769700	0.00262300	12.37996600	C128	11.17784900	-5.34398400	8.64037700
C66	7.93320400	-0.78972100	11.49265900	H129	11.87809300	-4.88325700	9.35171200
H67	7.22444100	-0.43552800	12.24756700	H130	11.02552000	-6.37296500	8.99351100
H68	8.22304800	-1.80406200	11.79593000	C131	9.88198400	-4.61023000	8.71762300
C69	7.16749600	-0.90117500	10.17935700	N132	9.05057800	-4.68023000	9.83156400
O70	7.64276100	-0.34069400	9.15318800	C133	9.26301900	-3.73892500	7.86629700
O71	6.11018800	-1.61257500	10.20204000	H134	9.55647400	-3.39218500	6.89276400
C72	8.76744800	1.59212600	11.32047200	C135	7.98050400	-3.89007700	9.65949200
O73	7.62707700	1.99405100	11.57145400	H136	7.16394500	-3.73837200	10.34806100
N74	9.77809600	2.43046900	10.98295400	N137	8.10248300	-3.30600000	8.47142400
H75	10.64301700	2.03316400	10.64193400	H138	7.37982900	-2.67770800	8.04580400
C76	9.56774000	3.85878700	10.76514800	C139	6.09883400	-4.23516400	-1.22212100
H77	10.51495900	4.38048100	10.90841000	H140	5.38340000	-4.56850100	-1.95931000
H78	8.84133100	4.20878200	11.50238300	H141	7.10939600	-4.13018100	-1.58861700
C79	9.09543900	4.12930300	9.31848500	H142	5.79573000	-3.22082800	-0.93807000
O80	9.89576500	4.40783800	8.43371900	C143	6.02765300	-5.12258400	0.03892000
N81	7.75079000	4.00504900	9.12375800	H144	6.02863800	-6.18705500	-0.21433500
H82	7.17233900	3.64488400	9.87362500	H145	6.89568400	-4.91232600	0.67492400
C83	7.14729700	4.08676800	7.80961300	C146	4.77345500	-4.75333000	0.82812300
H84	6.38701800	4.87303600	7.77371300	O147	4.73427000	-3.57161400	1.27114500
H85	7.95197300	4.33722200	7.11048100	O148	3.83393400	-5.60378900	0.96278100
C86	6.47484200	2.77874400	7.36509600	C149	-1.82882600	-11.98664800	4.24855400
O87	5.33886200	2.79502500	6.87774100	H150	-2.35871200	-12.71804600	3.65626700
O88	7.20901600	1.71705900	7.54045100	H151	-2.32839800	-11.78327900	5.18423700
C89	11.58170000	-0.61714500	3.48091200	H152	-0.84826100	-12.41068000	4.50202600
H90	12.44423300	-1.21806300	3.72839100	C153	-1.66401000	-10.64946600	3.49168500
H91	11.83038900	0.38213300	3.15519200	H154	-2.58263700	-10.44246900	2.92405800
H92	11.11875500	-1.09760900	2.60737300	H155	-1.57434300	-9.83752100	4.22514300
C93	10.52696200	-0.46040200	4.58780500	C156	-0.45365400	-10.60091600	2.54461600
H94	9.89120000	0.39527400	4.32804600	H157	0.46983500	-10.55622100	3.14030000
H95	10.98473200	-0.20708200	5.55032400	H158	-0.39533100	-11.53821200	1.97471900
C96	9.62629300	-1.69360600	4.72852600	C159	-0.49439400	-9.45023600	1.52244000
H97	10.16009900	-2.48500400	5.27299900	H160	0.38273100	-9.50106500	0.86302800
H98	9.38480400	-2.10749300	3.74513100	H161	-1.36975400	-9.59756600	0.87587000
C99	8.29919900	-1.40527800	5.41816500	C162	-0.60830000	-8.02312400	2.07084300
O100	7.27378500	-1.90662800	4.86743800	H163	-0.89573900	-7.34870500	1.25957800
O101	8.29498700	-0.70720400	6.48200200	H164	-1.36891000	-7.94016500	2.85011700
C102	10.81872400	4.22856600	-0.81502900	N165	0.67431000	-7.47121200	2.64020900
H103	11.54037600	3.48391700	-0.51315900	H166	0.83143400	-6.51014500	2.25933500
H104	11.20108900	5.23062800	-0.68819800	H167	0.67172300	-7.37574200	3.68471700
H105	10.66522000	4.09781100	-1.89329000	H168	1.52426700	-7.99262000	2.33953500

C1169	0.86954700	-6.64004900	5.68256900	H186	3.48239100	-2.61997500	1.65466200
O170	1.28143500	-1.63959000	4.28829200	H187	1.03539300	-4.26319600	6.26142000
H171	0.35764400	-2.21311900	2.74770300	O188	3.18464500	-1.57853500	7.70810100
O172	4.93694700	-1.29218200	3.63858600	O189	1.26196000	-5.08756900	1.29591400
O173	7.17425100	-2.14466800	1.77406100	H190	2.26989900	-5.13844200	1.26709800
H174	7.08495200	-2.17982400	2.74294900	H191	0.99838800	-5.13506500	0.36250300
H175	6.33218200	-2.56058900	1.47532700	O192	0.35698100	-2.48940000	1.80257300
O176	1.04406700	0.24689700	6.35779700	H193	0.52355900	-3.45730400	1.81158700
H177	1.01900300	-0.33458000	5.55499200	H194	1.90894100	-2.07116500	1.67850300
H178	0.70725200	-0.32221100	7.06834300	O195	3.12396100	-8.18018000	1.49396700
O179	2.88427600	2.99629600	8.35421900	H196	3.51725400	-7.32196900	1.19809800
H180	3.70882300	3.23854100	8.81769900	H197	3.86043300	-8.79912000	1.59246900
H181	2.35045500	2.56635900	9.04636300	O198	1.06329800	-3.29607200	6.42505300
O182	5.11437000	2.39864200	10.17243500	H199	1.21023500	-2.36496300	4.97478700
H183	5.16331500	1.57293400	9.64574900	H200	1.90171300	-3.09798700	6.87983600
H184	5.78576900	2.27865300	10.86883300	H201	9.21552200	-5.25256800	10.65029300
O185	2.87922800	-1.84322400	1.87969400				

S₄⁰ RE(O–O) with the outer oxo bridge and the inner oxyl radical, ¹²A

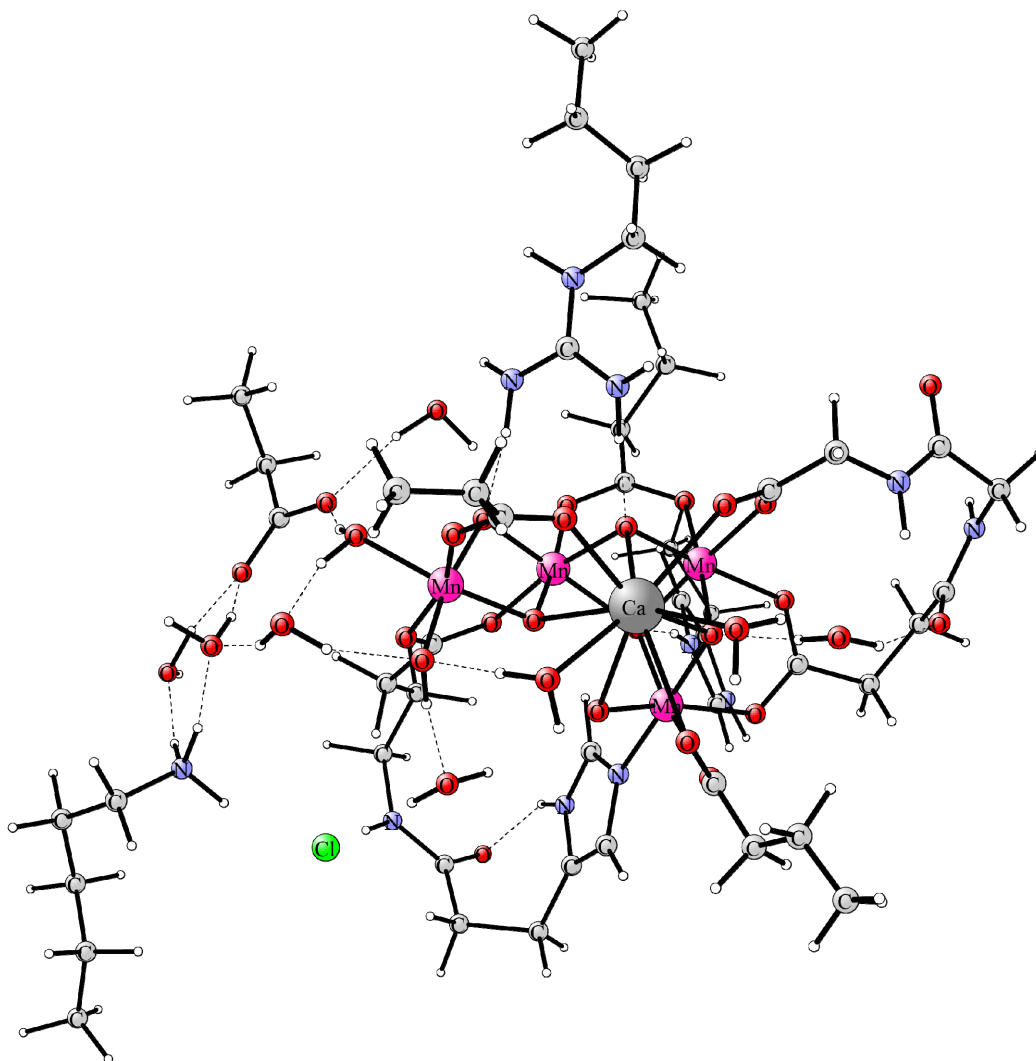


Mn1	3.04308000	-1.43976300	3.89960400	H22	0.73364700	2.12912700	13.86357900
Mn2	4.59808600	-1.53296600	8.65785200	H23	1.94108400	0.90637000	14.05278000
Mn3	5.39023300	-1.51639700	5.33459400	C24	1.47589100	1.24090900	11.98275900
Mn4	6.61307800	-0.03733100	7.39988400	H25	2.31871500	1.93032600	11.84528900
O5	3.64878200	-1.13297400	5.62371200	H26	0.65655500	1.60311900	11.35103100
O6	5.83395600	0.19914300	5.80435700	C27	1.88524800	-0.17293400	11.54405400
O7	5.08939100	0.22476500	8.35940300	H28	0.99439400	-0.81731400	11.49656900
O8	5.96540700	-1.82845400	7.35358000	H29	2.55395400	-0.62439800	12.28387800
Ca9	3.41539900	1.14614700	6.81799900	C30	2.56066100	-0.25657600	10.19037000
C10	0.66754600	1.95151000	1.70634700	O31	2.22577500	0.46095000	9.23908900
H11	1.22518400	1.90580300	0.78257800	O32	3.50526900	-1.16351200	10.15713100
H12	-0.32439000	2.36864100	1.61432400	C33	2.78445000	-7.86080800	8.62574400
H13	0.46696700	0.89332400	1.92900100	H34	2.42273900	-8.82713100	8.99876000
C14	1.48525900	2.50357400	2.88895200	H35	1.97102500	-7.40227400	8.05570200
H15	0.81415200	2.87830700	3.67284200	C36	3.99755700	-8.10721000	7.72914600
H16	2.10227100	3.36554500	2.60660100	O37	5.12309600	-8.33535500	8.21929900
C17	2.42641200	1.53966600	3.65407900	C38	3.16287700	-6.98690900	9.85841600
O18	3.07199400	1.99596600	4.61889800	H39	3.85580500	-7.55784500	10.48728300
O19	2.47078300	0.31126600	3.25950400	H40	2.26328800	-6.79763300	10.45084100
C20	1.05826000	1.18299700	13.45631400	C41	3.79322600	-5.67567100	9.48031500
H21	0.37022400	0.36013900	13.58246300	N42	4.91834800	-5.67301100	8.67412600

H43	5.38612700	-6.53761800	8.38526600	C106	9.48386200	4.01401300	-0.08729400
C44	3.48572600	-4.34410900	9.65817900	H107	9.04829500	3.07269600	-0.45484300
H45	2.69220700	-3.88676500	10.22859000	H108	8.77489800	4.80606700	-0.36428800
C46	5.21474600	-4.41194000	8.33720100	C109	9.62601100	3.96432200	1.44077900
H47	5.94175000	-4.13971200	7.59642200	H110	10.06202400	4.90657300	1.79616500
N48	4.38839200	-3.57178900	8.94251700	H111	10.32694100	3.16801400	1.72493500
N49	3.80275800	-7.94146300	6.40848300	C112	8.30792400	3.75957900	2.19880800
H50	2.86191100	-7.67736200	6.08878200	H113	7.61324800	4.58124300	1.96882600
C51	4.91725300	-7.84634500	5.46886600	H114	8.50008000	3.77421000	3.27651900
H52	4.64276800	-8.38160400	4.55145000	N115	7.69226600	2.46937300	1.87613300
H53	5.77324900	-8.35213800	5.91793200	H116	7.76331700	2.14276500	0.92215600
C54	5.27926800	-6.37286700	5.13470100	C117	6.85417000	1.77476600	2.67384200
H55	6.14921700	-6.37395600	4.46492900	N118	6.43107900	2.29933900	3.83334400
H56	5.60550000	-5.88288600	6.05533500	H119	5.98978700	1.69751700	4.53149700
C57	4.12900100	-5.56290500	4.50236900	H120	6.36558300	3.29606000	3.97331600
H58	3.16108800	-5.82426800	4.95116800	N121	6.45171300	0.55819100	2.31705500
H59	4.01897100	-5.79185200	3.43496500	H122	6.99061600	-0.09780200	1.74463100
C60	4.21205700	-4.04479100	4.60645100	H123	5.74355100	0.06512100	2.87898700
O61	3.24556200	-3.40304400	4.08461000	C124	11.84239800	-5.39309000	7.24925500
O62	5.18041300	-3.49929100	5.21971100	H125	11.25220200	-5.97246100	6.55470800
C63	9.15951200	0.11915800	11.44782300	H126	12.79646300	-5.85244900	7.46174200
H64	9.83664200	-0.15708400	10.63238600	H127	12.01860100	-4.39215400	6.84316600
H65	9.71403200	-0.00028300	12.38783200	C128	11.17242200	-5.34931200	8.63899800
C66	7.93204000	-0.79330900	11.47312700	H129	11.86870200	-4.88896100	9.35449900
H67	7.21785100	-0.44512900	12.22591200	H130	11.02223400	-6.38007400	8.98790700
H68	8.22243900	-1.80826600	11.77384200	C131	9.87380400	-4.61890100	8.71544900
C69	7.16708500	-0.90159900	10.15519500	N132	9.04515600	-4.68274100	9.83212000
O70	7.64132000	-0.30498900	9.14219600	C133	9.25193100	-3.75237600	7.86166600
O71	6.12838700	-1.62897600	10.15287900	H134	9.54118800	-3.41436500	6.88424100
C72	8.76717300	1.59205200	11.32059000	C135	7.97568200	-3.89134100	9.65997800
O73	7.62969300	1.99696400	11.58036800	H136	7.16219800	-3.73093100	10.35050200
N74	9.77608500	2.42909000	10.97389100	N137	8.09391800	-3.31424700	8.46826900
H75	10.63823200	2.03127000	10.62665500	H138	7.37788200	-2.67522600	8.04712500
C76	9.56777800	3.85881500	10.76518900	C139	6.09893600	-4.23518800	-1.22219700
H77	10.51539600	4.37863400	10.91356100	H140	5.38336300	-4.56843400	-1.95928700
H78	8.84134500	4.20411700	11.50455100	H141	7.10941700	-4.13018100	-1.58867200
C79	9.09762900	4.14196200	9.32149600	H142	5.79761700	-3.21666700	-0.94910800
O80	9.89836700	4.43212700	8.44039100	C143	6.01581400	-5.10489500	0.05031900
N81	7.75326500	4.02098500	9.12509500	H144	6.01194400	-6.17285000	-0.18791600
H82	7.17609200	3.64586500	9.86886400	H145	6.88306400	-4.89118200	0.68623800
C83	7.15322600	4.11457300	7.81083700	C146	4.76177400	-4.72333800	0.83782400
H84	6.38395900	4.89217700	7.78324700	O147	4.72559000	-3.53862500	1.27532100
H85	7.95700000	4.38372000	7.11746200	O148	3.82246300	-5.57161000	0.98522100
C86	6.49720200	2.80595200	7.34650300	C149	-1.82887600	-11.98671800	4.24856800
O87	5.37235500	2.82476100	6.83119100	H150	-2.35869300	-12.71809500	3.65630100
O88	7.22703600	1.74559200	7.53726400	H151	-2.32840600	-11.78325000	5.18423400
C89	11.58166200	-0.61708300	3.48089900	H152	-0.85027700	-12.41406600	4.50463200
H90	12.44417500	-1.21809300	3.72840300	C153	-1.65412800	-10.65668000	3.48212300
H91	11.83042700	0.38213700	3.15520800	H154	-2.57379100	-10.44322600	2.91856000
H92	11.11751100	-1.09810800	2.60827700	H155	-1.54759100	-9.83851700	4.20652600
C93	10.53001800	-0.45489300	4.58403000	C156	-0.44910900	-10.64026800	2.52638600
H94	9.86990300	0.37388200	4.29829600	H157	0.47777800	-10.57960100	3.11531100
H95	10.98233600	-0.15886100	5.53679500	H158	-0.39639300	-11.59667000	1.98851600
C96	9.66757400	-1.70896800	4.76843400	C159	-0.48915500	-9.52836900	1.46264400
H97	10.22054700	-2.45234400	5.35785000	H160	0.38756500	-9.60537000	0.80537600
H98	9.44709200	-2.17219100	3.80251200	H161	-1.36490900	-9.69874500	0.82213300
C99	8.33447600	-1.40604300	5.43292200	C162	-0.60235400	-8.08003200	1.95049800
O100	7.30935800	-1.88079600	4.85302200	H163	-0.85571800	-7.43752100	1.10258600
O101	8.32664900	-0.71465300	6.49885700	H164	-1.38504100	-7.95655000	2.70249600
C102	10.81872500	4.22856900	-0.81502100	N165	0.66678100	-7.51803600	2.53588100
H103	11.54036400	3.48392200	-0.51313100	H166	0.78738000	-6.53098600	2.21451200
H104	11.20109300	5.23062600	-0.68822400	H167	0.67771200	-7.48221900	3.58254300
H105	10.66947300	4.09812300	-1.89414300	H168	1.52912400	-7.99112500	2.18524800

C1169	0.87438400	-6.75844700	5.59715300	H186	3.48631200	-2.60563900	1.72804800
O170	1.29652400	-1.65818600	4.41396000	H187	1.00334400	-4.44055700	6.18627300
H171	0.35460000	-2.19738400	2.85945900	O188	3.20847700	-1.53572900	7.67697600
O172	4.93048400	-1.28857600	3.65131500	O189	1.24340000	-5.05581100	1.32662100
O173	7.17371700	-2.10888600	1.76083300	H190	2.24993900	-5.11115200	1.29725700
H174	7.10935700	-2.15229400	2.73126000	H191	0.98002400	-5.05027500	0.39192100
H175	6.32479300	-2.52081900	1.47781800	O192	0.35889400	-2.46841900	1.91310300
O176	1.10461800	0.34546000	6.38583400	H193	0.51253200	-3.43857900	1.91415700
H177	1.05222000	-0.31459800	5.64689000	H194	1.90213700	-2.06284300	1.78333800
H178	0.79444000	-0.13395400	7.17105900	O195	3.06763300	-8.17772700	1.26393500
O179	2.90344900	2.95878900	8.45591700	H196	3.46556000	-7.29730000	1.04874800
H180	3.69509100	3.14588900	9.00088400	H197	3.80881700	-8.75670000	1.49076000
H181	2.31996800	2.47293200	9.06774100	O198	1.05187300	-3.48559900	6.41240800
O182	5.12610800	2.37692500	10.17001600	H199	1.22474300	-2.42126600	5.05750700
H183	5.18696100	1.54764100	9.65010400	H200	1.88554500	-3.35020700	6.89252900
H184	5.78083300	2.26719200	10.88396000	H201	9.21217500	-5.25053300	10.65361900
O185	2.87725200	-1.83754600	1.97685800				

S_4^0 RE(O-O) with the outer oxo bridge and the inner oxyl radical, 6A

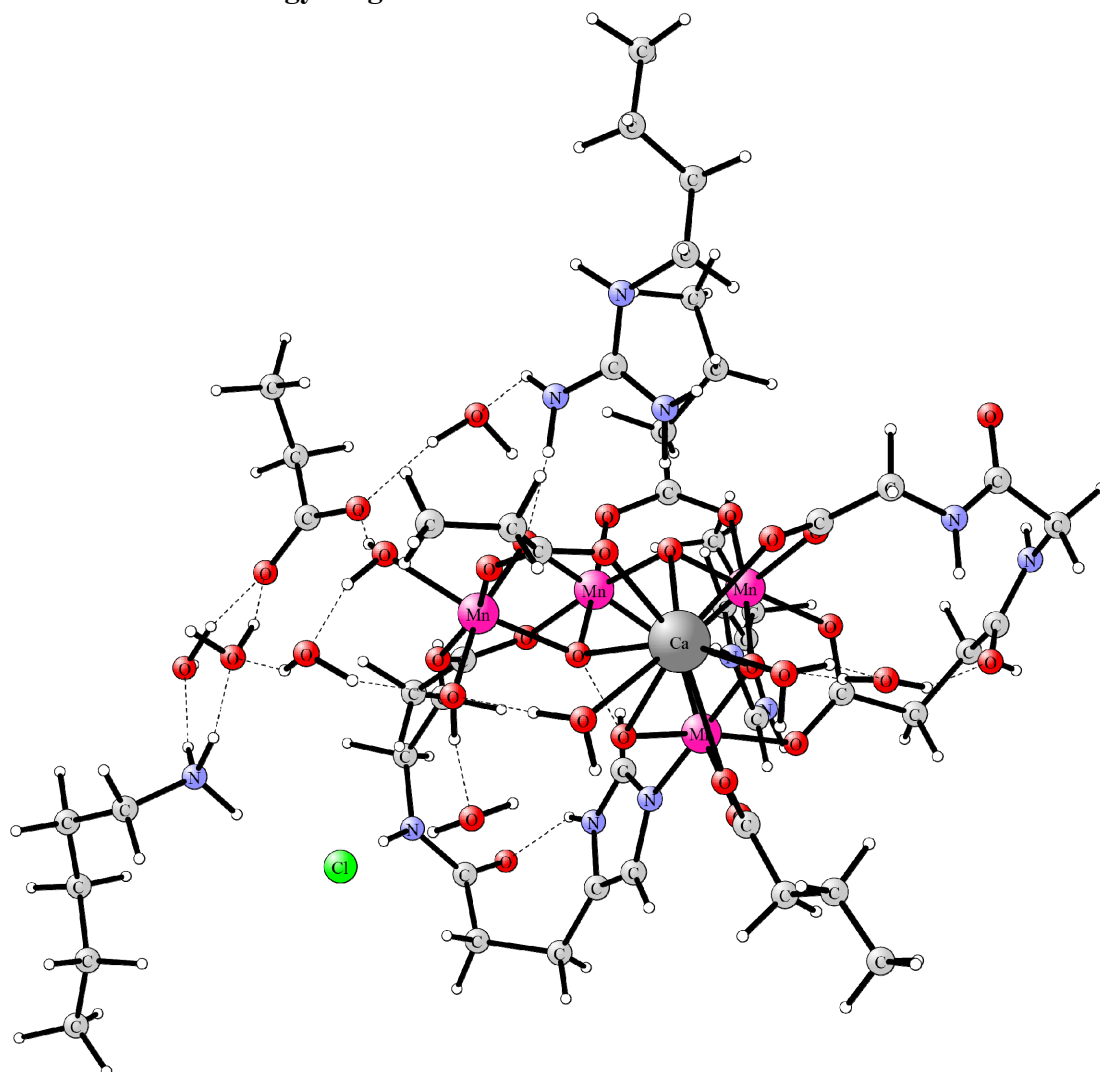


Mn1	3.03730100	-1.44024500	3.86867000	H22	0.73364700	2.12912700	13.86357900
Mn2	4.60364800	-1.52129800	8.66436200	H23	1.94044200	0.90641600	14.05384400
Mn3	5.38187500	-1.52299100	5.33956400	C24	1.47720900	1.23940800	11.98404200
Mn4	6.61600800	-0.03708600	7.39948500	H25	2.32106500	1.92753900	11.84651900
O5	3.63681200	-1.18458600	5.61225900	H26	0.65928100	1.60088600	11.35017300
O6	5.81562200	0.19717900	5.81627700	C27	1.88524600	-0.17595800	11.54931900
O7	5.10326000	0.23312000	8.37271700	H28	0.99348900	-0.81890600	11.50110500
O8	5.95975300	-1.82799500	7.35484700	H29	2.55285700	-0.62692600	12.29030600
Ca9	3.42367000	1.13050500	6.81087100	C30	2.56142300	-0.25809100	10.19707300
C10	0.66754600	1.95151000	1.70634700	O31	2.22325800	0.45620800	9.24519100
H11	1.22518400	1.90580300	0.78257800	O32	3.51259900	-1.15901600	10.16479800
H12	-0.32439000	2.36864100	1.61432400	C33	2.78445000	-7.86080800	8.62574400
H13	0.46619000	0.89351800	1.92829000	H34	2.42932900	-8.82715700	9.00484900
C14	1.48643100	2.50120600	2.88847800	H35	1.96757400	-7.41051600	8.05381400
H15	0.81719600	2.87230100	3.67577100	C36	3.99820100	-8.10419600	7.72952400
H16	2.10363900	3.36375700	2.60837400	O37	5.12501600	-8.32428500	8.22075800
C17	2.42592400	1.52894600	3.64263600	C38	3.15908400	-6.97738200	9.85274500
O18	3.08064800	1.97160200	4.60741400	H39	3.85409500	-7.54157700	10.48540700
O19	2.45703300	0.30406800	3.23681700	H40	2.25861600	-6.78843700	10.44403400
C20	1.05826000	1.18299700	13.45631400	C41	3.78472100	-5.66515000	9.46888400
H21	0.37022400	0.36013900	13.58246300	N42	4.90735300	-5.66136500	8.65875000

H43	5.37689500	-6.52549600	8.37081500	C106	9.48726800	4.01390500	-0.08040700
C44	3.47636500	-4.33379100	9.64691600	H107	9.04122100	3.08114200	-0.45706500
H45	2.68433100	-3.87693400	10.21975600	H108	8.78196300	4.81511900	-0.33964600
C46	5.20199600	-4.40022600	8.32114200	C109	9.64472600	3.94082800	1.44509600
H47	5.92856900	-4.12633000	7.58028400	H110	10.09368600	4.87349700	1.80949900
N48	4.37647100	-3.56077500	8.92866400	H111	10.34148700	3.13405800	1.70947300
N49	3.80325800	-7.94143600	6.40905300	C112	8.33402500	3.73631800	2.21554000
H50	2.86149600	-7.68367500	6.08791700	H113	7.64346900	4.56677100	2.00531000
C51	4.91725300	-7.84634500	5.46886600	H114	8.53889600	3.73421500	3.29098000
H52	4.64343800	-8.38627000	4.55403000	N115	7.70427000	2.45550200	1.88236000
H53	5.77424400	-8.34906500	5.91965400	H116	7.76450000	2.13962100	0.92402500
C54	5.27743500	-6.37485000	5.12828400	C117	6.86011500	1.76484600	2.67673100
H55	6.14803300	-6.37905100	4.45931000	N118	6.45091800	2.28398300	3.84369000
H56	5.60275100	-5.87953700	6.04632300	H119	6.00277700	1.68281700	4.53837700
C57	4.12710700	-5.56998500	4.49107000	H120	6.39968600	3.28025100	3.99273600
H58	3.15959400	-5.82974600	4.94190000	N121	6.43731700	0.55794100	2.30904400
H59	4.01679800	-5.80586800	3.42538000	H122	6.96995200	-0.10594300	1.73877300
C60	4.20885900	-4.05063500	4.58667500	H123	5.72966000	0.07143300	2.87534300
O61	3.24483500	-3.41538400	4.05606700	C124	11.84239800	-5.39309000	7.24925500
O62	5.17750600	-3.50675000	5.20363200	H125	11.25220200	-5.97246100	6.55470800
C63	9.15951200	0.11915800	11.44782300	H126	12.79646300	-5.85244900	7.46174200
H64	9.83838100	-0.15588400	10.63354900	H127	12.01920600	-4.39269100	6.84203500
H65	9.71318200	0.00084300	12.38852400	C128	11.17327500	-5.34703700	8.63949500
C66	7.93441700	-0.79608300	11.47175800	H129	11.86965500	-4.88382300	9.35299300
H67	7.21775300	-0.44873600	12.22264900	H130	11.02553800	-6.37717000	8.99104400
H68	8.22597100	-1.81033600	11.77361000	C131	9.87238000	-4.62011700	8.71709000
C69	7.17345300	-0.90658600	10.15263500	N132	9.02825700	-4.71522300	9.82012400
O70	7.64963700	-0.31252300	9.13936500	C133	9.26124400	-3.73093800	7.87891800
O71	6.13421300	-1.63413300	10.14936500	H134	9.56596800	-3.36091000	6.91794400
C72	8.76631400	1.59178700	11.32101000	C135	7.95970700	-3.92105900	9.65460500
O73	7.62954200	1.99651200	11.58367100	H136	7.13823700	-3.77954400	10.33953500
N74	9.77466500	2.42860000	10.97177100	N137	8.09367600	-3.31191100	8.48058900
H75	10.63591700	2.03040400	10.62287600	H138	7.37948500	-2.67013200	8.06313800
C76	9.56777800	3.85881500	10.76518900	C139	6.09893600	-4.23518800	-1.22219700
H77	10.51521700	4.37811900	10.91626700	H140	5.38336300	-4.56843400	-1.95928700
H78	8.83970700	4.20295200	11.50347200	H141	7.10941700	-4.13018100	-1.58867200
C79	9.10011300	4.14405500	9.32116100	H142	5.79751300	-3.21724800	-0.94746200
O80	9.90174000	4.43788100	8.44223700	C143	6.01479500	-5.10835700	0.04770900
N81	7.75658300	4.01974900	9.12171300	H144	6.01121300	-6.17562800	-0.19345900
H82	7.17715700	3.64487000	9.86388800	H145	6.88062500	-4.89682300	0.68642400
C83	7.15931600	4.11327500	7.80622200	C146	4.75864200	-4.72814700	0.83197700
H84	6.39000400	4.89086100	7.77695100	O147	4.72204600	-3.54403700	1.27154800
H85	7.96451900	4.38236400	7.11455600	O148	3.81731300	-5.57492400	0.97367000
C86	6.50353600	2.80461200	7.34182600	C149	-1.82887600	-11.98671800	4.24856800
O87	5.37889200	2.82282500	6.82687200	H150	-2.35869300	-12.71809500	3.65630100
O88	7.23365300	1.74378700	7.53248000	H151	-2.32840600	-11.78325000	5.18423400
C89	11.58166200	-0.61708300	3.48089900	H152	-0.85028300	-12.41430000	4.50443200
H90	12.44417500	-1.21809300	3.72840300	C153	-1.65371700	-10.65700600	3.48168900
H91	11.83042700	0.38213700	3.15520800	H154	-2.57489600	-10.44182500	2.92120500
H92	11.11856900	-1.09775300	2.60752300	H155	-1.54290700	-9.83901700	4.20559700
C93	10.52938400	-0.45835400	4.58410300	C156	-0.45201200	-10.64352100	2.52160200
H94	9.87398100	0.37639700	4.30521300	H157	0.47713500	-10.58272300	3.10693700
H95	10.98189400	-0.17329100	5.54007400	H158	-0.40224000	-11.60097100	1.98528200
C96	9.65945200	-1.70925000	4.75519700	C159	-0.49475000	-9.53352600	1.45609800
H97	10.20692200	-2.46464300	5.33472200	H160	0.37863600	-9.61385800	0.79468200
H98	9.43643200	-2.16083500	3.78433600	H161	-1.37386200	-9.70321000	0.82000200
C99	8.32740400	-1.40654100	5.42160000	C162	-0.60204000	-8.08412500	1.94225000
O100	7.30085700	-1.87652900	4.84177500	H163	-0.85681000	-7.44189700	1.09452700
O101	8.32178600	-0.71843800	6.49008700	H164	-1.38150300	-7.95745100	2.69711900
C102	10.81872500	4.22856900	-0.81502100	N165	0.67084400	-7.52548100	2.52236700
H103	11.54036400	3.48392200	-0.51313100	H166	0.78990800	-6.53708700	2.20515800
H104	11.20109300	5.23062600	-0.68822400	H167	0.68618800	-7.49506500	3.56924500
H105	10.66622500	4.09804400	-1.89353600	H168	1.53140900	-7.99770800	2.16511600

C1169	0.87019800	-6.77850300	5.58839400	H186	3.47096300	-2.61926100	1.70468700
O170	1.29404100	-1.65966100	4.41083400	H187	0.99320400	-4.45612300	6.17333400
H171	0.34980800	-2.20653900	2.86010200	O188	3.21409000	-1.48498300	7.68326800
O172	4.90379500	-1.27223300	3.66628400	O189	1.23800300	-5.05989700	1.31723400
O173	7.16124600	-2.10622200	1.75664200	H190	2.24442400	-5.11345300	1.28773700
H174	7.10675500	-2.15530000	2.72741100	H191	0.97439000	-5.05383000	0.38263700
H175	6.31537600	-2.52726200	1.47675600	O192	0.34294600	-2.47630300	1.91291500
O176	1.11112000	0.34485300	6.37153500	H193	0.49924000	-3.44578000	1.91121600
H177	1.05901200	-0.31896000	5.63504800	H194	1.88682500	-2.07231500	1.76296800
H178	0.78572800	-0.12645700	7.15535200	O195	3.07256300	-8.18361100	1.24951200
O179	2.91019700	2.94733100	8.44304400	H196	3.46777900	-7.30118800	1.03669500
H180	3.69952400	3.14339600	8.98806500	H197	3.81410200	-8.75649800	1.49036900
H181	2.32649100	2.46542000	9.05756800	O198	1.04849600	-3.50331000	6.40629800
O182	5.13258500	2.39172800	10.16996900	H199	1.22880000	-2.42100800	5.05516300
H183	5.19613400	1.56095800	9.65262100	H200	1.88510000	-3.37927200	6.88355200
H184	5.78178700	2.28146800	10.88890700	H201	9.18510000	-5.30430800	10.62852500
O185	2.86339600	-1.84849300	1.94936000				

S₄⁰ TS(O-O) between the outer oxo bridge and the inner oxyl radical, 9.1 kcal/mol on the energy diagram

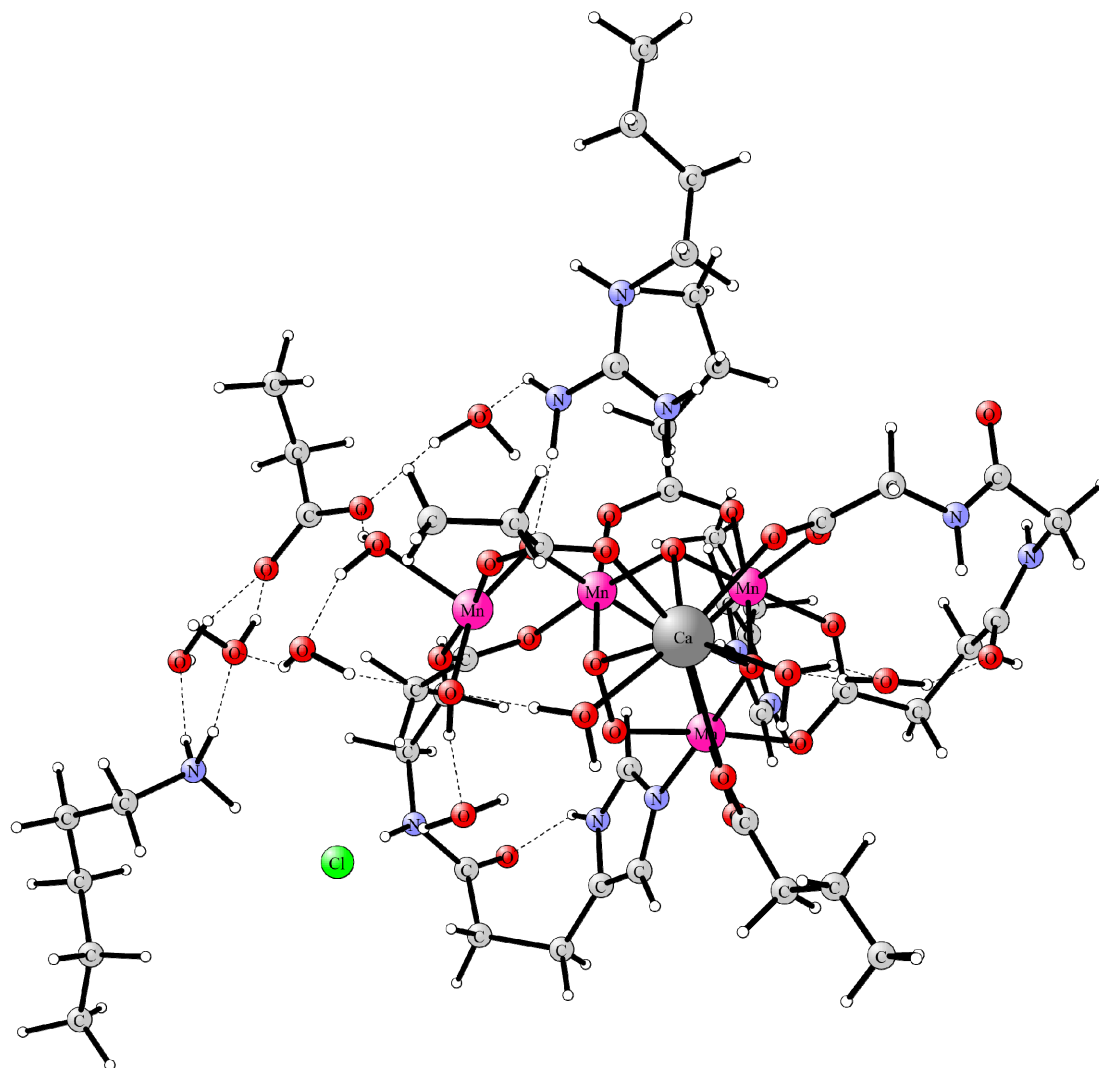


Mn1	2.93461200	-1.43865700	3.96046400	H21	0.37022400	0.36013900	13.58246300
Mn2	4.60750700	-1.51171900	8.63779300	H22	0.73364700	2.12912700	13.86357900
Mn3	5.40308400	-1.51925900	5.43015300	H23	1.94583300	0.90479600	14.04442900
Mn4	6.62572800	-0.00113400	7.42631100	C24	1.46433100	1.25538500	11.97499400
O5	3.63637800	-1.17800200	5.86796900	H25	2.31437900	1.93721400	11.84349500
O6	5.83765300	0.21491400	5.84621000	H26	0.64384100	1.64401000	11.36046100
O7	5.08970100	0.24893200	8.36569000	C27	1.85148200	-0.15264500	11.49233000
O8	6.01236900	-1.80741900	7.37659100	H28	0.95065600	-0.78135100	11.42619200
Ca9	3.40766000	1.23718700	6.85381100	H29	2.51029200	-0.63768000	12.22009400
C10	0.66754600	1.95151000	1.70634700	C30	2.53572100	-0.21826700	10.13764600
H11	1.22518400	1.90580300	0.78257800	O31	2.25155100	0.55142500	9.20928900
H12	-0.32439000	2.36864100	1.61432400	O32	3.43070100	-1.17054200	10.07197700
H13	0.47166700	0.89527300	1.93790600	C33	2.78445000	-7.86080800	8.62574400
C14	1.47666500	2.52304900	2.88628700	H34	2.43785100	-8.82692300	9.01304700
H15	0.80038300	2.93133500	3.64909600	H35	1.96403700	-7.42297900	8.04938700
H16	2.11512900	3.36480300	2.59164300	C36	4.00110700	-8.10036800	7.73205700
C17	2.38016800	1.55361900	3.68275500	O37	5.12961000	-8.31014800	8.22498300
O18	3.06090300	2.01349300	4.62506100	C38	3.14833600	-6.96364000	9.84704300
O19	2.35139300	0.31291900	3.34271800	H39	3.83654500	-7.52191900	10.49240700
C20	1.05826000	1.18299700	13.45631400	H40	2.24190600	-6.76952900	10.42745600

C41	3.78010600	-5.65385100	9.46276700	H104	11.20109300	5.23062600	-0.68822400
N42	4.91890300	-5.65594200	8.67595400	H105	10.67008800	4.09923600	-1.89428100
H43	5.38611700	-6.52420400	8.39450800	C106	9.48348400	4.00434700	-0.08702700
C44	3.47281900	-4.32060600	9.63178100	H107	9.03645600	3.07781300	-0.47795400
H45	2.67137600	-3.85910300	10.18752400	H108	8.77994600	4.81016100	-0.33650600
C46	5.22491800	-4.39632000	8.34197300	C109	9.63365700	3.90781500	1.43817700
H47	5.96647100	-4.12879600	7.61382400	H110	10.08755300	4.83251700	1.81678900
N48	4.39006700	-3.55175200	8.93009300	H111	10.32464300	3.09357900	1.69497700
N49	3.80518900	-7.94789800	6.41079500	C112	8.32041800	3.70540100	2.20564900
H50	2.86071000	-7.70043600	6.08863000	H113	7.62874800	4.53197800	1.98360600
C51	4.91725300	-7.84634500	5.46886600	H114	8.52377800	3.71816400	3.28124600
H52	4.63609200	-8.37071400	4.54747200	N115	7.68949100	2.41822800	1.89358200
H53	5.77358300	-8.35976700	5.90898700	H116	7.75119600	2.08268400	0.94184000
C54	5.28269900	-6.37133100	5.14883800	C117	6.82883900	1.75928600	2.69878700
H55	6.14945200	-6.36839500	4.47489500	N118	6.42649900	2.31517200	3.85217100
H56	5.61521700	-5.89226100	6.07302500	H119	5.95982900	1.73925300	4.55392000
C57	4.12969400	-5.55599600	4.53079500	H120	6.38073600	3.31561300	3.97139700
H58	3.16230900	-5.83575700	4.96920500	N121	6.38388200	0.55111400	2.36396900
H59	4.02531500	-5.76451300	3.45843400	H122	6.89788900	-0.14158900	1.80734100
C60	4.19285100	-4.03845700	4.66291800	H123	5.66890300	0.09807800	2.94721600
O61	3.20290000	-3.40691500	4.18336600	C124	11.84239800	-5.39309000	7.24925500
O62	5.17682000	-3.49483300	5.26229600	H125	11.25220200	-5.97246100	6.55470800
C63	9.15951200	0.11915800	11.44782300	H126	12.79646300	-5.85244900	7.46174200
H64	9.82740400	-0.16047800	10.62626900	H127	12.02098400	-4.39350500	6.84064400
H65	9.72218600	-0.00079500	12.38291500	C128	11.17670400	-5.34317300	8.64089400
C66	7.92740100	-0.78835000	11.48641500	H129	11.88057000	-4.89070200	9.35395300
H67	7.22476300	-0.44115400	12.25028100	H130	11.01688500	-6.37225500	8.99009100
H68	8.21666900	-1.80673500	11.77629200	C131	9.88554800	-4.60013900	8.72308200
C69	7.15076600	-0.88052500	10.17445300	N132	9.03660200	-4.69699300	9.82210800
O70	7.63783500	-0.28897300	9.16347200	C133	9.28764000	-3.69530200	7.89177300
O71	6.09617200	-1.58522300	10.17259200	H134	9.60095900	-3.31631400	6.93660700
C72	8.76919700	1.59274700	11.32248200	C135	7.97659100	-3.89064900	9.65969500
O73	7.63438400	1.99953300	11.59110000	H136	7.15072800	-3.75218000	10.34014600
N74	9.77593300	2.42837900	10.96729700	N137	8.12111800	-3.27188300	8.49218800
H75	10.63663600	2.03077800	10.61633100	H138	7.40705000	-2.62892000	8.07179500
C76	9.56777800	3.85881500	10.76518900	C139	6.09893600	-4.23518800	-1.22219700
H77	10.51437000	4.37840600	10.92165900	H140	5.38336300	-4.56843400	-1.95928700
H78	8.83779900	4.19914300	11.50317700	H141	7.10941700	-4.13018100	-1.58867200
C79	9.10545500	4.14852800	9.32164900	H142	5.79621200	-3.21786000	-0.94530500
O80	9.91224400	4.41610900	8.43928700	C143	6.02431800	-5.11016500	0.04831500
N81	7.75827600	4.05970200	9.12624600	H144	6.02471500	-6.17669100	-0.19649900
H82	7.17430600	3.69056100	9.86768600	H145	6.89545300	-4.89732100	0.67941100
C83	7.16425500	4.15010900	7.80947200	C146	4.77402500	-4.74346300	0.85084000
H84	6.39656000	4.92888800	7.77547100	O147	4.73606000	-3.57151400	1.32086600
H85	7.97146000	4.41390700	7.11803100	O148	3.83461500	-5.59510700	0.97918200
C86	6.50922700	2.83998500	7.35123700	C149	-1.82887600	-11.98671800	4.24856800
O87	5.38889800	2.85594900	6.82627700	H150	-2.35869300	-12.71809500	3.65630100
O88	7.23392600	1.77920700	7.55992000	H151	-2.32840600	-11.78325000	5.18423400
C89	11.58166200	-0.61708300	3.48089900	H152	-0.85096900	-12.41554200	4.50524300
H90	12.44417500	-1.21809300	3.72840300	C153	-1.65036700	-10.65891700	3.48006000
H91	11.83042700	0.38213700	3.15520800	H154	-2.57266500	-10.43898200	2.92330400
H92	11.11729700	-1.09664200	2.60777300	H155	-1.53115800	-9.84085700	4.20252300
C93	10.53506400	-0.46285100	4.59156400	C156	-0.45278200	-10.65549300	2.51487200
H94	9.91090400	0.40698000	4.35175300	H157	0.47905900	-10.60199900	3.09661300
H95	10.99818900	-0.23702400	5.55819100	H158	-0.41291100	-11.61370700	1.97902900
C96	9.61699800	-1.68442700	4.70679100	C159	-0.48998100	-9.54572100	1.44901600
H97	10.13477500	-2.50099100	5.22915200	H160	0.38189900	-9.63224900	0.78638100
H98	9.36134400	-2.06974000	3.71547100	H161	-1.37134700	-9.70887500	0.81433300
C99	8.30846500	-1.37323300	5.41261600	C162	-0.58530800	-8.09606600	1.93587600
O100	7.26499300	-1.84144000	4.84998100	H163	-0.82768100	-7.45016100	1.08728000
O101	8.33005000	-0.69201300	6.48145000	H164	-1.36807800	-7.96208600	2.68604900
C102	10.81872500	4.22856900	-0.81502100	N165	0.68934800	-7.55252900	2.52497400
H103	11.54036400	3.48392200	-0.51313100	H166	0.81698000	-6.56180800	2.21541900

H167	0.69946800	-7.52896500	3.57177400	O185	2.81340300	-1.86245400	1.96374100
H168	1.54683400	-8.02911000	2.16821700	H186	3.41887100	-2.62738700	1.73430200
C1169	0.86585500	-6.81854300	5.59456900	H187	0.96854100	-4.50990300	6.22420500
O170	1.20450600	-1.66385700	4.54545800	O188	3.27194400	-1.56249400	7.52624600
H171	0.29799000	-2.23836700	2.96156600	O189	1.26307400	-5.07350400	1.36837400
O172	4.80678400	-1.20244700	3.82795200	H190	2.26838000	-5.13073000	1.31898000
O173	7.11456600	-2.09360400	1.80766200	H191	0.98154800	-5.02685800	0.44032300
H174	7.07379600	-2.16510100	2.77758500	O192	0.27219700	-2.53031900	2.02205100
H175	6.28374900	-2.54442200	1.52191000	H193	0.46588800	-3.49133400	2.03801500
O176	1.11110800	0.40095900	6.43416700	H194	1.84848900	-2.10476600	1.78904400
H177	1.02442000	-0.28670300	5.72118100	O195	3.09180900	-8.20379900	1.25322800
H178	0.80044200	-0.03707400	7.24277400	H196	3.48830500	-7.32151800	1.04264900
O179	2.94271000	3.06231100	8.49259900	H197	3.83534700	-8.79334700	1.44100900
H180	3.73828500	3.22280400	9.04103800	O198	1.01986200	-3.56787200	6.49925800
H181	2.34799700	2.58379700	9.09938700	H199	1.14268900	-2.43571800	5.17663500
O182	5.15137900	2.41221800	10.17808400	H200	1.88502600	-3.44986700	6.92400600
H183	5.19501100	1.58007200	9.66139200	H201	9.18414400	-5.29628400	10.62480800
H184	5.81018600	2.29405700	10.88759100				

S₄⁰ peroxide formed by the outer oxo bridge and the inner oxyl radical, -1.0 kcal/mol on the energy diagram

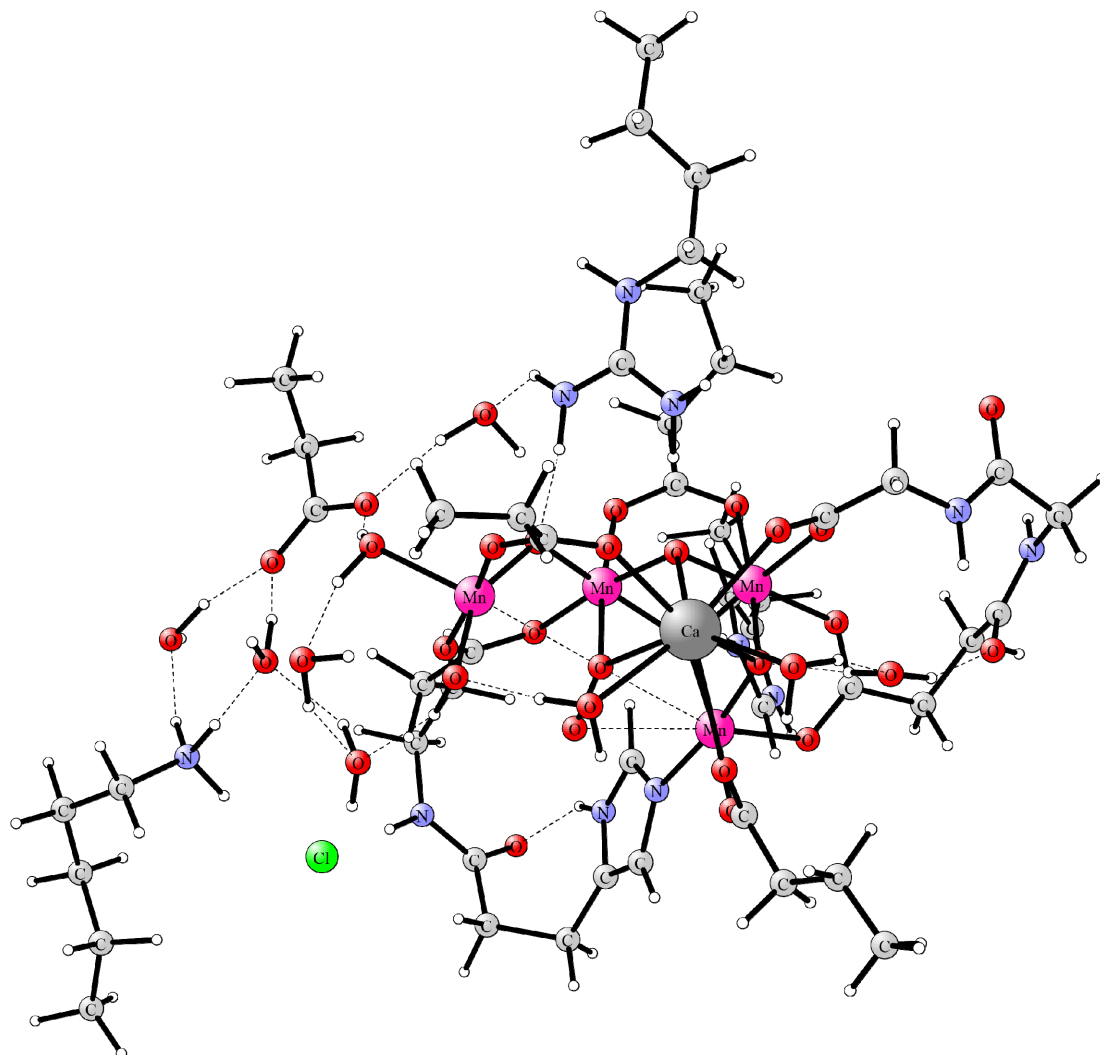


Mn1	2.81979800	-1.45766400	3.84557600	H21	0.37022300	0.36013900	13.58246400
Mn2	4.65293400	-1.57341000	8.74076200	H22	0.73364600	2.12912700	13.86357900
Mn3	5.36812100	-1.55761700	5.51066100	H23	1.94699300	0.90444100	14.04220800
Mn4	6.60628600	-0.01625900	7.47092000	C24	1.46103500	1.24697500	11.96923300
O5	3.66805600	-1.16035000	6.24932700	H25	2.32237000	1.91339700	11.83324300
O6	5.81573400	0.19925400	5.91349600	H26	0.64306200	1.64889900	11.35958400
O7	5.03626300	0.18519300	8.40830500	C27	1.82164400	-0.16987700	11.48376500
O8	6.06859600	-1.83625300	7.46375700	H28	0.90963500	-0.78326100	11.42756900
Ca9	3.39968500	1.31087800	6.86744500	H29	2.47570500	-0.66399400	12.20972800
C10	0.66755700	1.95149800	1.70635000	C30	2.49824400	-0.26768000	10.12393800
H11	1.22517900	1.90580900	0.78257600	O31	2.24302000	0.49794900	9.18533800
H12	-0.32439000	2.36864500	1.61432600	O32	3.35447400	-1.25818700	10.05932100
H13	0.48017200	0.89817000	1.95044300	C33	2.78444700	-7.86079900	8.62574900
C14	1.47287000	2.55019000	2.87311900	H34	2.40139500	-8.82826400	8.97405900
H15	0.79989700	2.98307100	3.62510900	H35	1.98182200	-7.37943700	8.05861200
H16	2.11945500	3.37907500	2.55904600	C36	3.99839400	-8.11050300	7.72890500
C17	2.35442800	1.56956000	3.66744700	O37	5.12574300	-8.33238000	8.22141900
O18	3.02435500	2.00718700	4.63414800	C38	3.16457900	-7.02229100	9.88141100
O19	2.32601600	0.34304300	3.30119200	H39	3.84108300	-7.61864800	10.50449200
C20	1.05826200	1.18299600	13.45631100	H40	2.26152900	-6.83233800	10.46844700

C41	3.82081800	-5.71280800	9.54348700	H104	11.20109200	5.23062700	-0.68821900
N42	4.96008500	-5.71088500	8.75759300	H105	10.67283700	4.10068500	-1.89486000
H43	5.41021300	-6.58186200	8.45228000	C106	9.48053300	3.99110700	-0.09138300
C44	3.52972700	-4.38095800	9.74518600	H107	9.02569300	3.07984700	-0.50859900
H45	2.73083800	-3.92234000	10.30685400	H108	8.78190600	4.80858200	-0.31519700
C46	5.28106800	-4.44942800	8.45165300	C109	9.62889000	3.84583000	1.43082700
H47	6.02423600	-4.17705100	7.72681400	H110	10.09324100	4.75420800	1.83582500
N48	4.45680500	-3.60803500	9.06136000	H111	10.31240200	3.01803800	1.66356100
N49	3.80311100	-7.95961600	6.40857700	C112	8.31661100	3.63799600	2.20084500
H50	2.85702300	-7.72139800	6.08199000	H113	7.62053400	4.45967600	1.97414500
C51	4.91726400	-7.84633900	5.46888000	H114	8.52363100	3.66207800	3.27539300
H52	4.64302500	-8.36749100	4.54393300	N115	7.68507700	2.34407700	1.91059000
H53	5.77685500	-8.35449300	5.90853000	H116	7.73932500	1.99272000	0.96392600
C54	5.26484900	-6.36299800	5.16555700	C117	6.82842300	1.70312200	2.73657400
H55	6.14255800	-6.33972100	4.50626400	N118	6.44609000	2.28720500	3.88577400
H56	5.57289100	-5.88817800	6.10090500	H119	5.96423400	1.72886700	4.59040300
C57	4.10988700	-5.55739600	4.53726600	H120	6.37446900	3.29014900	3.96728500
H58	3.13882100	-5.86662600	4.94687400	N121	6.37443500	0.48950800	2.44163100
H59	4.03403900	-5.74578800	3.45871900	H122	6.86314100	-0.21964400	1.88040300
C60	4.13293600	-4.04152100	4.69605700	H123	5.65314900	0.06286300	3.03857100
O61	3.14641000	-3.41457700	4.22094500	C124	11.84240200	-5.39308200	7.24925000
O62	5.10233500	-3.49438500	5.33207900	H125	11.25219900	-5.97246100	6.55471100
C63	9.15950900	0.11915700	11.44782000	H126	12.79646000	-5.85245500	7.46174400
H64	9.79578600	-0.16923100	10.60468800	H127	12.01998900	-4.39236300	6.84331700
H65	9.75837900	0.00941900	12.36169700	C128	11.19070000	-5.34945300	8.64668500
C66	7.93140900	-0.78141100	11.53964500	H129	11.90759200	-4.91304600	9.35685900
H67	7.24765200	-0.42259500	12.31507900	H130	11.02151700	-6.37988500	8.98749400
H68	8.22265200	-1.79844300	11.83115200	C131	9.91221100	-4.59085500	8.74726300
C69	7.13946700	-0.87176400	10.24269000	N132	9.07667500	-4.68114600	9.85616200
O70	7.61219500	-0.28748300	9.22614500	C133	9.31427900	-3.67864200	7.92387200
O71	6.07862700	-1.57331200	10.26368900	H134	9.62017800	-3.30116700	6.96494300
C72	8.76873800	1.59307900	11.32034600	C135	8.02263000	-3.86475500	9.70559300
O73	7.63239500	2.00040500	11.58326000	H136	7.20249400	-3.72730800	10.39288900
N74	9.77639700	2.42860800	10.96975800	N137	8.15911200	-3.24518600	8.53782500
H75	10.64039200	2.03166400	10.62601100	H138	7.43165300	-2.60867600	8.11409300
C76	9.56777600	3.85881200	10.76518700	C139	6.09892200	-4.23517900	-1.22218800
H77	10.51591200	4.37742500	10.91570200	H140	5.38336700	-4.56843600	-1.95928900
H78	8.84263000	4.20252000	11.50633900	H141	7.10941900	-4.13018700	-1.58867400
C79	9.09867800	4.14210600	9.32400200	H142	5.79223800	-3.22730000	-0.91900200
O80	9.90081600	4.38376100	8.43057600	C143	6.05316900	-5.15100400	0.02308300
N81	7.74755800	4.07722400	9.14449500	H144	6.06171600	-6.20826700	-0.25906200
H82	7.17216300	3.71929000	9.89757300	H145	6.93338700	-4.95011100	0.64550500
C83	7.14373100	4.15309300	7.83172000	C146	4.81576200	-4.82465000	0.85837300
H84	6.37978100	4.93516300	7.79256600	O147	4.78141800	-3.67532500	1.38052400
H85	7.94687300	4.40392100	7.13071100	O148	3.87766000	-5.68148400	0.96192200
C86	6.48166100	2.84021000	7.39448000	C149	-1.82885500	-11.98670600	4.24856200
O87	5.36549300	2.86194600	6.85838800	H150	-2.35869900	-12.71809500	3.65630400
O88	7.18863100	1.77656000	7.63125000	H151	-2.32841400	-11.78325300	5.18423400
C89	11.58165400	-0.61710300	3.48090000	H152	-0.85146000	-12.41667000	4.50569800
H90	12.44418200	-1.21808400	3.72840400	C153	-1.64678100	-10.66349600	3.47481900
H91	11.83042400	0.38213900	3.15521000	H154	-2.57848900	-10.42906300	2.93995400
H92	11.11496900	-1.09687800	2.60929400	H155	-1.49480200	-9.84593000	4.19160400
C93	10.53585300	-0.46288000	4.60020400	C156	-0.47342700	-10.68780400	2.48041200
H94	9.94224400	0.43547200	4.39072900	H157	0.47305600	-10.64122100	3.03861200
H95	11.00884200	-0.28350900	5.57195900	H158	-0.46018600	-11.65290300	1.95559900
C96	9.57225900	-1.65289800	4.68021400	C159	-0.51943500	-9.59105600	1.40174500
H97	10.06394500	-2.51462500	5.15510300	H160	0.33610200	-9.69884200	0.72116300
H98	9.29109700	-1.98623000	3.67675000	H161	-1.41715200	-9.74861500	0.78888200
C99	8.27516000	-1.35309600	5.41945700	C162	-0.58214600	-8.13486100	1.87260200
O100	7.22795000	-1.84867300	4.88590200	H163	-0.81508300	-7.49308000	1.01817000
O101	8.31041200	-0.66868300	6.48771100	H164	-1.35766800	-7.97657900	2.62576100
C102	10.81871500	4.22855200	-0.81502400	N165	0.70578100	-7.61372800	2.45048700
H103	11.54037000	3.48392700	-0.51313000	H166	0.83896500	-6.61788000	2.15808500

H167	0.72749100	-7.61049300	3.49708700	O185	2.80558500	-1.91173900	1.75889900
H168	1.55322500	-8.09110900	2.06927100	H186	1.85573600	-2.16601500	1.58444400
C1169	0.85049400	-6.92409600	5.53349900	H187	3.40425200	-2.68623800	1.58798000
O170	1.10399800	-1.65051300	4.48635800	O188	3.39704500	-1.87879100	7.41101100
H171	1.02808900	-2.45319400	5.07151600	O189	1.31076300	-5.12559800	1.34661500
O172	4.69873700	-1.15591300	3.97942900	H190	2.31506300	-5.19649300	1.30560100
O173	7.09548000	-2.14149500	1.87224100	H191	1.03823500	-5.06060700	0.41701000
H174	7.05207200	-2.21950800	2.84167800	O192	0.22144000	-2.59505400	1.93217600
H175	6.28465800	-2.62414800	1.57589700	H193	0.45636400	-3.54264500	2.00553500
O176	1.13856800	0.36796200	6.43897100	H194	0.25185100	-2.24728900	2.85117600
H177	1.01587400	-0.28958200	5.70177300	O195	3.07425100	-8.28485300	1.12015500
H178	0.79400600	-0.07433700	7.23067000	H196	3.48642600	-7.40147600	0.94718200
O179	2.92619400	3.05571500	8.57631800	H197	3.80487300	-8.87482100	1.35330800
H180	3.71656400	3.18508900	9.14233600	O198	0.90142500	-3.65935500	6.37685500
H181	2.31434500	2.56897500	9.15837100	H199	1.78373200	-3.58930000	6.77435000
O182	5.10120000	2.34652100	10.23477200	H200	0.82279300	-4.59250500	6.07872000
H183	5.15001500	1.52078500	9.70915700	H201	9.22818600	-5.28356400	10.65575900
H184	5.80693700	2.25635400	10.90230000				

S₄⁰ TS(O₂-release), 10.0 kcal/mol on the energy diagram

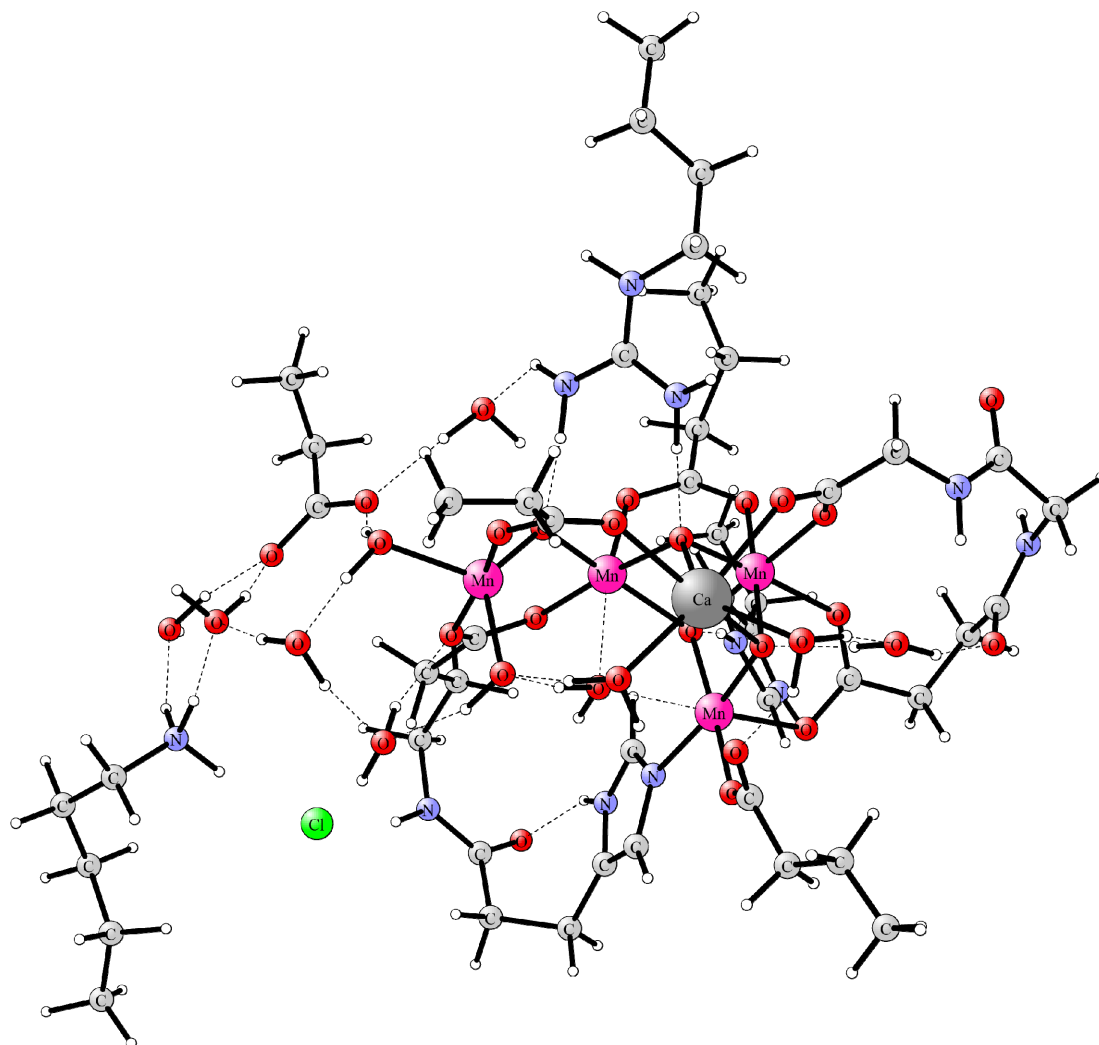


Mn1	2.84584800	-1.46831900	3.69035900	H22	0.73364500	2.12913100	13.86358000
Mn2	4.63810700	-1.58298700	8.85413300	H23	1.95677200	0.90178900	14.02419900
Mn3	5.33357500	-1.59646100	5.52942200	C24	1.42538800	1.26650600	11.96076900
Mn4	6.52995200	-0.03047400	7.52582900	H25	2.32270500	1.88239400	11.81901600
O5	3.55017000	-1.29215400	6.37247300	H26	0.61799700	1.73757200	11.38741800
O6	5.65236500	0.16730900	5.98329500	C27	1.67781100	-0.15538300	11.42928300
O7	5.00206200	0.20405100	8.48324100	H28	0.72024000	-0.69241900	11.35438400
O8	6.00881800	-1.85026200	7.48192900	H29	2.28908900	-0.72060100	12.14017000
Ca9	3.39951000	1.33506600	6.89787400	C30	2.35353200	-0.26625500	10.07303400
C10	0.66755700	1.95150000	1.70636100	O31	2.13277500	0.52155000	9.13868100
H11	1.22517900	1.90580900	0.78257200	O32	3.15802800	-1.28898400	9.98638100
H12	-0.32439200	2.36864200	1.61432400	C33	2.78443800	-7.86074700	8.62575000
H13	0.47437700	0.89695100	1.94167700	H34	2.40750700	-8.83285500	8.96854200
C14	1.48352200	2.52635700	2.87434300	H35	1.97943000	-7.38947300	8.05336900
H15	0.82269400	2.92678900	3.65370000	C36	4.00267500	-8.09870500	7.73017700
H16	2.11559600	3.37109200	2.57192700	O37	5.13604200	-8.28324900	8.22669800
C17	2.38846000	1.52175500	3.60793400	C38	3.14505200	-7.01947700	9.88095000
O18	3.00463800	1.89760000	4.63077800	H39	3.83924400	-7.59816400	10.50099300
O19	2.43946200	0.33383700	3.12077400	H40	2.23964100	-6.85201600	10.47109400
C20	1.05826700	1.18297700	13.45630700	C41	3.76367200	-5.69874100	9.52830700
H21	0.37022000	0.36014300	13.58246800	N42	4.90846500	-5.68181900	8.74894000

H43	5.38004700	-6.54860900	8.46148000	C106	9.48439700	3.98514800	-0.08096000
C44	3.42303300	-4.37556500	9.68620300	H107	9.02052900	3.08360300	-0.50924000
H45	2.60729700	-3.92698200	10.23097100	H108	8.78727400	4.80965100	-0.28230500
C46	5.18612200	-4.42302700	8.40537700	C109	9.64830800	3.81064500	1.43782500
H47	5.93417600	-4.14188200	7.68986100	H110	10.12108100	4.70979600	1.85350500
N48	4.32509000	-3.59184100	8.98119200	H111	10.33233200	2.97703400	1.64717700
N49	3.80549600	-7.97359100	6.40903200	C112	8.34680200	3.59378900	2.22635100
H50	2.84772200	-7.82600700	6.05957900	H113	7.64507100	4.41469600	2.01500900
C51	4.91718800	-7.84635300	5.46878900	H114	8.57257800	3.61383200	3.29738600
H52	4.65173100	-8.38153200	4.54995600	N115	7.71215300	2.29923000	1.94126200
H53	5.78842300	-8.33278600	5.91038200	H116	7.75874800	1.95093800	0.99290900
C54	5.23469000	-6.36116600	5.15557300	C117	6.84873200	1.66294500	2.76481100
H55	6.09971200	-6.32516500	4.48032700	N118	6.47551900	2.23664800	3.92195200
H56	5.55050900	-5.87774600	6.08352800	H119	5.97619700	1.68160500	4.61819700
C57	4.05889800	-5.57458100	4.54482500	H120	6.44885200	3.23906600	4.03038900
H58	3.10324400	-5.87318400	4.99711600	N121	6.37442300	0.45928800	2.45809200
H59	3.94994700	-5.79095500	3.47518400	H122	6.85138300	-0.24945200	1.88721000
C60	4.10496000	-4.05659000	4.66839000	H123	5.65709600	0.03164200	3.06079400
O61	3.15005200	-3.41528100	4.14920000	C124	11.84239000	-5.39309100	7.24925300
O62	5.06955900	-3.52126000	5.32065900	H125	11.25220400	-5.97246400	6.55470600
C63	9.15950700	0.11916400	11.44783400	H126	12.79646600	-5.85244700	7.46174200
H64	9.76693800	-0.16895400	10.58315600	H127	12.02026200	-4.39328300	6.84090300
H65	9.79972900	0.02738400	12.33598800	C128	11.18103600	-5.34435300	8.64131600
C66	7.95650200	-0.78957800	11.59209500	H129	11.88634600	-4.89077900	9.35233600
H67	7.28150900	-0.42141900	12.37116800	H130	11.02393900	-6.37374900	8.99107600
H68	8.26611200	-1.79575600	11.90193600	C131	9.88974300	-4.60384600	8.72767600
C69	7.14273500	-0.92489100	10.31922100	N132	9.05817200	-4.69193100	9.83970700
O70	7.56491400	-0.33618800	9.27505600	C133	9.27533400	-3.71166500	7.89399400
O71	6.11753900	-1.66355900	10.38673900	H134	9.57220100	-3.34455800	6.92802000
C72	8.76194800	1.59141300	11.32162800	C135	7.99260800	-3.89197000	9.68326200
O73	7.62812000	1.99992100	11.59269400	H136	7.18055100	-3.74281500	10.37835400
N74	9.76849500	2.42658800	10.96290100	N137	8.11572500	-3.28575900	8.50686300
H75	10.63101600	2.02694300	10.61882000	H138	7.38650400	-2.64430700	8.09227000
C76	9.56778700	3.85881200	10.76519600	C139	6.09893700	-4.23519500	-1.22217300
H77	10.52045300	4.37088400	10.90890300	H140	5.38336300	-4.56843300	-1.95929000
H78	8.85123600	4.20480900	11.51391100	H141	7.10941800	-4.13018000	-1.58868200
C79	9.08544400	4.15288200	9.33093200	H142	5.79022200	-3.22942600	-0.91443900
O80	9.87537900	4.42653600	8.43554300	C143	6.06357400	-5.15667500	0.01665400
N81	7.73540200	4.05877400	9.15877200	H144	6.10823100	-6.21176800	-0.26983000
H82	7.17152500	3.68104500	9.91104500	H145	6.92755900	-4.93148800	0.65329800
C83	7.12176900	4.14406800	7.85232000	C146	4.80433200	-4.87386700	0.82921800
H84	6.35926000	4.92825900	7.82208100	O147	4.72583400	-3.72532600	1.35843000
H85	7.91960900	4.39946900	7.14649700	O148	3.89329100	-5.75657300	0.91089100
C86	6.45237500	2.83763700	7.40888300	C149	-1.82887600	-11.98671000	4.24860400
O87	5.34832100	2.87780600	6.84528100	H150	-2.35868500	-12.71809000	3.65628700
O88	7.13380900	1.76358500	7.66158400	H151	-2.32841500	-11.78325600	5.18423100
C89	11.58166100	-0.61708500	3.48090800	H152	-0.85427500	-12.42256200	4.50791000
H90	12.44417800	-1.21809300	3.72840000	C153	-1.63037000	-10.68757600	3.44408700
H91	11.83042700	0.38213800	3.15520500	H154	-2.58818000	-10.39823000	2.98734400
H92	11.11045400	-1.09799800	2.61257800	H155	-1.35268200	-9.87147300	4.12341000
C93	10.53695300	-0.45144800	4.60744900	C156	-0.55738500	-10.83320300	2.34991700
H94	9.96799700	0.46551300	4.41091100	H157	0.43698100	-10.82308100	2.81955100
H95	11.01777900	-0.29604000	5.57959200	H158	-0.65095800	-11.82220400	1.88056000
C96	9.53902400	-1.61435900	4.67762600	C159	-0.62538700	-9.79460300	1.21612900
H97	10.00945600	-2.49662800	5.13642300	H160	0.16783100	-9.99449400	0.48255600
H98	9.24909300	-1.92771400	3.67007200	H161	-1.57460900	-9.92417100	0.67892400
C99	8.24034800	-1.31450700	5.42383800	C162	-0.56027700	-8.31793900	1.60944500
O100	7.20065600	-1.83761300	4.89617100	H163	-0.72655400	-7.69725600	0.72410600
O101	8.25539000	-0.62029600	6.48203800	H164	-1.32075000	-8.05762000	2.35032300
C102	10.81871900	4.22856600	-0.81502400	N165	0.75920500	-7.89683600	2.18238500
H103	11.54036700	3.48392300	-0.51312900	H166	0.88948100	-6.86142400	2.07741300
H104	11.20109500	5.23062800	-0.68822300	H167	0.82437400	-8.06273000	3.21220300
H105	10.66717300	4.10029700	-1.89375300	H168	1.58118300	-8.30326100	1.68012800

C1169	0.81215800	-7.42792100	5.28785300	H186	1.72303700	-2.53614900	1.62876300
O170	1.12191200	-1.58468500	4.34677000	H187	3.31002600	-2.85996100	1.52290000
H171	0.91639000	-2.51658400	4.60075600	O188	2.87582800	-2.29528100	6.84030000
O172	4.67853400	-1.18358700	3.97169000	O189	1.47802800	-5.25462800	1.86463400
O173	7.04051700	-2.18185300	1.88086700	H190	2.41134200	-5.32008100	1.49622700
H174	6.99650900	-2.25019100	2.85106900	H191	0.99474600	-4.58941000	1.34686500
H175	6.22863500	-2.66262500	1.58584100	O192	-0.10702300	-2.77750700	2.02636700
O176	1.16525800	0.33588800	6.40499200	H193	-0.27317500	-3.42717100	2.74568500
H177	1.04220900	-0.32756200	5.67506300	H194	0.00084600	-1.95741400	2.54741400
H178	0.81968800	-0.08942100	7.20539000	O195	3.07592600	-8.36977100	0.67223100
O179	2.91711600	3.06663500	8.60771000	H196	3.47690900	-7.46682100	0.62845100
H180	3.69897200	3.19385900	9.18721400	H197	3.80464500	-8.96168400	0.90813700
H181	2.29662700	2.57203700	9.17458400	O198	0.36379300	-4.32934400	4.27441400
O182	5.08874400	2.37472400	10.26364900	H199	1.07511200	-4.62418900	3.66775800
H183	5.14428600	1.54512900	9.74218700	H200	0.18458700	-5.13371700	4.80543800
H184	5.78700800	2.28643500	10.93903200	H201	9.22079900	-5.28126300	10.64673800
O185	2.62637900	-2.14286100	1.66882500				

S₀⁰ RE(H⁺-transfer), 5.5 kcal/mol on the energy diagram

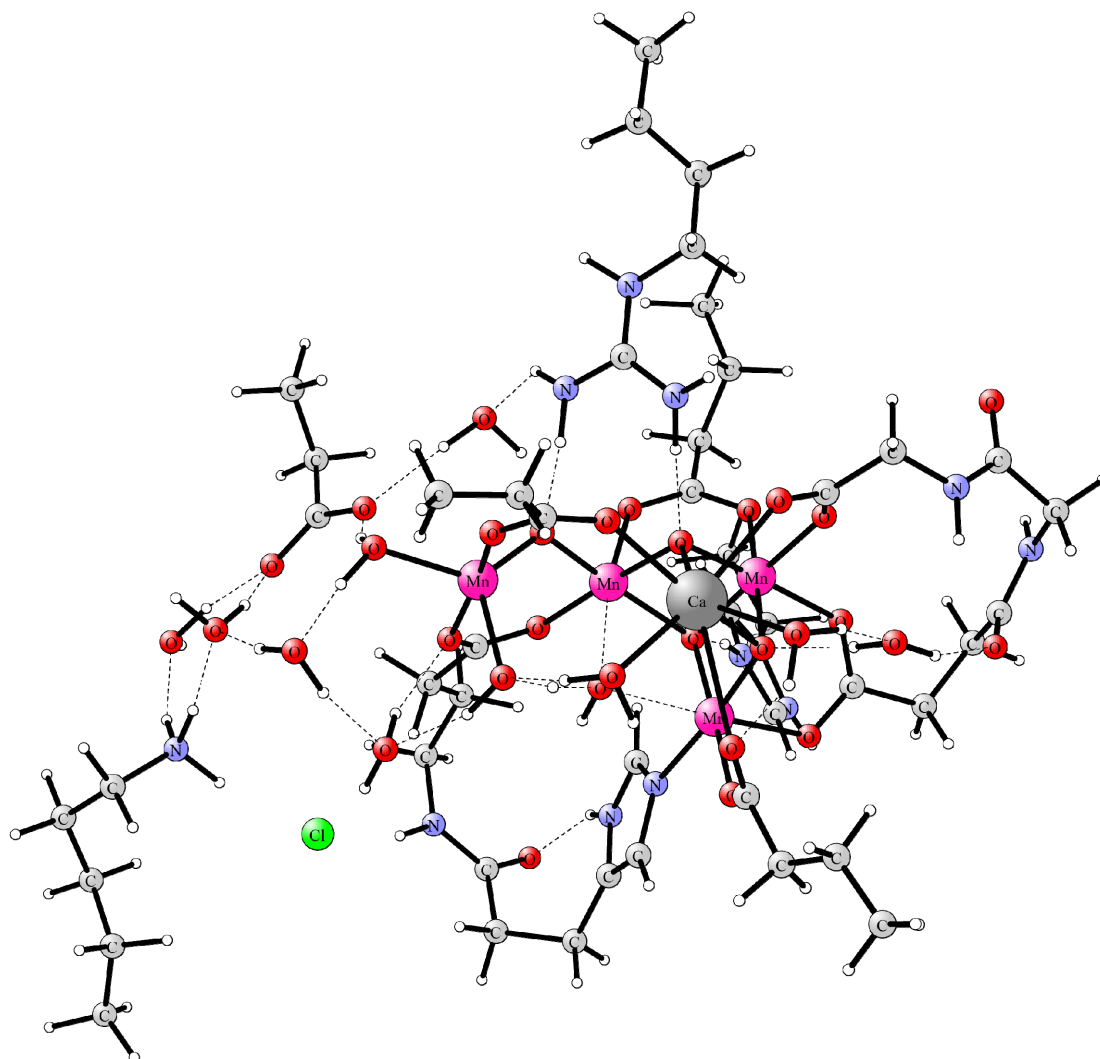


Mn1	2.97404169	-1.39253563	3.62218143	H22	0.73364676	2.12912702	13.86357874
Mn2	4.61256379	-1.44401955	8.70702888	H23	1.96463418	0.90825616	14.01445998
Mn3	5.46102261	-1.56808713	5.48690847	C24	1.41106720	1.29303197	11.96309944
Mn4	6.61960549	0.03953125	7.48182343	H25	2.28094006	1.94808885	11.82331216
O5	3.33693907	-1.78255509	6.70259656	H26	0.58532345	1.74092496	11.39735522
O6	5.73865162	0.24135485	5.93800966	C27	1.71756721	-0.10602465	11.41156163
O7	5.05245124	0.32785414	8.40485107	H28	0.78599011	-0.68837592	11.33746646
O8	6.07222787	-1.77707993	7.44775387	H29	2.36562578	-0.65820941	12.10152047
Ca9	3.69874121	1.57944144	6.75115667	C30	2.37661618	-0.14364020	10.04488502
C10	0.66754610	1.95150824	1.70634800	O31	2.17266557	0.72332359	9.17882616
H11	1.22518343	1.90580284	0.78257762	O32	3.14311058	-1.18280059	9.87343279
H12	-0.32438961	2.36864195	1.61432411	C33	2.78445007	-7.86080811	8.62574398
H13	0.52917320	0.91223570	2.02470326	H34	2.52870366	-8.82386683	9.08394906
C14	1.51415928	2.56551959	2.83863984	H35	1.92980060	-7.55620700	8.01351744
H15	0.87573386	2.93296713	3.65319870	C36	4.01466069	-8.06002047	7.74535403
H16	2.10751751	3.43139951	2.51842647	O37	5.14713516	-8.21841758	8.24645949
C17	2.48575809	1.58315840	3.52524950	C38	3.05976753	-6.89197872	9.81368999
O18	3.18798469	1.98450216	4.47512708	H39	3.72332244	-7.40741922	10.51839824
O19	2.48585735	0.37291188	3.07231920	H40	2.12076802	-6.69791177	10.33964091
C20	1.05825996	1.18299629	13.45631309	C41	3.68534681	-5.59060541	9.41139514
H21	0.37022395	0.36013904	13.58246292	N42	4.88178829	-5.59855358	8.71395453

H43	5.37462580	-6.47008676	8.48377766	C106	9.49096266	3.99672762	-0.07283026
C44	3.32859259	-4.26573611	9.48895391	H107	9.02604433	3.08715013	-0.48288462
H45	2.48248609	-3.80003506	9.97023448	H108	8.79056569	4.81759733	-0.27955866
C46	5.17677019	-4.35121284	8.34054112	C109	9.67863418	3.84592491	1.44518315
H47	5.97861488	-4.09486491	7.67655471	H110	10.14574525	4.75565060	1.84478969
N48	4.26984779	-3.50195434	8.81264093	H111	10.37413336	3.02129346	1.65299654
N49	3.81750955	-7.94046151	6.42219017	C112	8.38809748	3.61549703	2.24313682
H50	2.87047846	-7.81034544	6.05915804	H113	7.69307548	4.45366730	2.08105285
C51	4.91725307	-7.84634434	5.46886579	H114	8.62755088	3.58095840	3.31085926
H52	4.59815318	-8.35177396	4.55110937	N115	7.73978539	2.34517849	1.90016107
H53	5.77949649	-8.38378247	5.87007141	H116	7.73437604	2.06711950	0.92805994
C54	5.29302212	-6.37805544	5.13680754	C117	6.92026401	1.65064818	2.72023636
H55	6.18158801	-6.38803185	4.49213306	N118	6.60473901	2.13893721	3.92739625
H56	5.59442352	-5.87753969	6.06071588	H119	6.17553918	1.52131845	4.62496234
C57	4.16080446	-5.57842365	4.45861481	H120	6.57804567	3.12954667	4.11590028
H58	3.18149124	-5.86482043	4.86242144	N121	6.42686554	0.47076946	2.35051065
H59	4.08982059	-5.80905790	3.38751691	H122	6.90030437	-0.20911022	1.74900945
C60	4.23417626	-4.06165263	4.56990271	H123	5.72251473	0.01704129	2.95464901
O61	3.25944155	-3.40165004	4.07939687	C124	11.84239763	-5.39308953	7.24925489
O62	5.21183115	-3.53170128	5.18739705	H125	11.25220231	-5.97246126	6.55470795
C63	9.15951156	0.11915813	11.44782285	H126	12.79646291	-5.85244915	7.46174208
H64	9.77555945	-0.15932138	10.58699873	H127	12.01595349	-4.39184023	6.84352773
H65	9.77706204	-0.00687676	12.34765105	C128	11.17279016	-5.35812088	8.64200963
C66	7.93555792	-0.77159979	11.57357678	H129	11.87433891	-4.90898247	9.35984858
H67	7.26930917	-0.39589013	12.35702713	H130	11.01817049	-6.39176474	8.98201043
H68	8.22520524	-1.78650288	11.87514998	C131	9.88108668	-4.61479810	8.73312815
C69	7.12125888	-0.86981000	10.29378263	N132	9.12606305	-4.56795438	9.90183973
O70	7.56381430	-0.24320507	9.27958157	C133	9.20975692	-3.82021550	7.84741588
O71	6.09470635	-1.60752193	10.32220011	H134	9.42813279	-3.59253448	6.82031483
C72	8.77160544	1.59719531	11.35317159	C135	8.05738261	-3.77348200	9.73002528
O73	7.64979880	2.00592193	11.66927962	H136	7.28804836	-3.53905762	10.45101175
N74	9.77378964	2.42930882	10.97273026	N137	8.10391016	-3.30128363	8.48893154
H75	10.61557104	2.02695095	10.58188029	H138	7.38420446	-2.64274226	8.07142854
C76	9.56777761	3.85881471	10.76518874	C139	6.09893605	-4.23518876	-1.22219710
H77	10.48457095	4.39273743	11.02489079	H140	5.38336325	-4.56843395	-1.95928725
H78	8.76293235	4.17139651	11.43242070	H141	7.10941696	-4.13018081	-1.58867205
C79	9.25768342	4.12981458	9.28466163	H142	5.80028579	-3.20631645	-0.97668744
O80	10.15786530	4.24498897	8.46057146	C143	6.02581086	-5.11220116	0.04398744
N81	7.92978764	4.19282156	8.98324767	H144	6.12085065	-6.17406425	-0.20518216
H82	7.25047867	3.89412479	9.67545951	H145	6.84199754	-4.83338074	0.72028962
C83	7.46795716	4.22254407	7.61249868	C146	4.70088389	-4.84224671	0.75595162
H84	6.80688348	5.07641092	7.43479175	O147	4.56928824	-3.69838035	1.27556664
H85	8.35688119	4.31749391	6.97921428	O148	3.79211884	-5.74000476	0.75107361
C86	6.69881856	2.95112046	7.23484821	C149	-1.82887465	-11.98671726	4.24856859
O87	5.62158388	3.05816737	6.62112071	H150	-2.35869354	-12.71809503	3.65630028
O88	7.26013624	1.84631508	7.59881973	H151	-2.32840671	-11.78325026	5.18423368
C89	11.58166190	-0.61708344	3.48089927	H152	-0.85965051	-12.42982056	4.51601170
H90	12.44417524	-1.21809272	3.72840284	C153	-1.62030853	-10.69347723	3.43429020
H91	11.83042704	0.38213700	3.15520804	H154	-2.58036513	-10.40209956	2.98254583
H92	11.07378253	-1.11489469	2.64466918	H155	-1.33047181	-9.87092867	4.09936132
C93	10.58146972	-0.36941240	4.61657110	C156	-0.55575445	-10.86504595	2.33258362
H94	9.80128228	0.29165092	4.21651097	H157	0.44311808	-10.73144110	2.77151804
H95	11.04987436	0.18978858	5.43459620	H158	-0.58072887	-11.89896422	1.96198268
C96	9.91555915	-1.63822866	5.17619171	C159	-0.72557142	-9.95931791	1.10033985
H97	10.50782378	-2.00933004	6.02062211	H160	0.04275610	-10.20305076	0.35253529
H98	9.86581449	-2.41965447	4.41075441	H161	-1.68986302	-10.19113931	0.62728186
C99	8.49262781	-1.33919582	5.62701578	C162	-0.71779177	-8.44707857	1.32826168
O100	7.55190913	-1.86928865	4.97670728	H163	-0.98557864	-7.93722353	0.39790191
O101	8.36113672	-0.55173729	6.62900836	H164	-1.43848292	-8.14563232	2.09342295
C102	10.81872437	4.22856835	-0.81502146	N165	0.61269000	-7.89536634	1.75112751
H103	11.54036435	3.48392235	-0.51313097	H166	0.70421766	-6.90478980	1.43570049
H104	11.20109296	5.23062594	-0.68822340	H167	0.73176499	-7.87437423	2.79042939
H105	10.67344020	4.10334260	-1.89518561	H168	1.44105531	-8.35588923	1.31120152

C1169	0.86393947	-7.22277414	4.79048355	H187	0.31137630	-4.91646772	4.64130200
O170	1.52811316	-1.41218730	5.02646831	O188	1.18634101	-5.38500641	0.63569596
H171	0.01807778	-3.39778463	2.73759090	H189	2.18787736	-5.38422289	0.78075794
O172	4.74188750	-1.08988645	3.89560096	H190	1.08466436	-5.38381272	-0.32978185
O173	7.00062407	-2.19324932	1.76040168	O191	0.08161722	-3.12367360	1.79354565
H174	7.09392966	-2.27880936	2.72497678	H192	0.31037330	-3.95795759	1.32866013
H175	6.13856064	-2.62866480	1.56211843	H193	1.54671243	-2.43582249	1.67480829
O176	1.40810224	0.79291520	6.53175909	O194	3.03994687	-8.36716363	0.44613040
H177	1.12698918	0.52519343	7.42469651	H195	3.44895127	-7.46636346	0.46922875
H178	1.20489895	0.03496460	5.91947885	H196	3.74569837	-8.97632745	0.70785718
O179	3.14600045	3.18380470	8.53414637	O197	0.54367869	-3.99742791	4.38608000
H180	3.90928632	3.31428681	9.13897044	H198	1.49437544	-4.05890805	4.16412536
H181	2.52407082	2.65000757	9.06667529	H199	0.92593797	-2.18577743	4.98872669
O182	5.35307014	2.58262018	10.10209252	H200	3.30714938	-2.73514587	6.89473952
H183	5.36085130	1.72594275	9.62202547	H201	2.48187486	-1.62475138	6.07881194
H184	5.97211283	2.45087141	10.84646453	H202	9.34233932	-5.06109644	10.75914823
O185	2.49071433	-2.07616403	1.72365566				
H186	3.13687171	-2.80458040	1.50464847				

S₀⁰ TS(H⁺-transfer), 4.0 kcal/mol on the energy diagram



Mn1	2.99442546	-1.41364879	3.58183833	H22	0.73364676	2.12912702	13.86357874
Mn2	4.59385503	-1.42472656	8.69549697	H23	1.96463418	0.90825616	14.01445998
Mn3	5.42698033	-1.55188765	5.53048455	C24	1.40821205	1.31140267	11.96100443
Mn4	6.62633379	0.04885775	7.49243403	H25	2.30943591	1.92552820	11.83491164
O5	3.37477272	-1.68601012	6.69242033	H26	0.60433495	1.82032087	11.41569863
O6	5.73660651	0.25411931	5.95321946	C27	1.63731400	-0.08350902	11.35763893
O7	5.06588986	0.34327004	8.42389894	H28	0.67002545	-0.59065642	11.22235898
O8	6.07544546	-1.76765476	7.45754581	H29	2.21775647	-0.70748778	12.04543680
Ca9	3.66635416	1.53636108	6.78830509	C30	2.35080146	-0.10878120	10.01565923
C10	0.66754609	1.95150825	1.70634799	O31	2.17689315	0.76566457	9.14717579
H11	1.22518343	1.90580284	0.78257762	O32	3.12872435	-1.14019858	9.86884286
H12	-0.32438961	2.36864195	1.61432411	C33	2.78445007	-7.86080811	8.62574398
H13	0.52917320	0.91223570	2.02470326	H34	2.52870366	-8.82386683	9.08394906
C14	1.51503860	2.55605766	2.84473623	H35	1.92980060	-7.55620700	8.01351744
H15	0.87536708	2.92836570	3.65609724	C36	4.01659788	-8.05578810	7.74665300
H16	2.12009199	3.41575623	2.53027450	O37	5.14968715	-8.20605703	8.24821376
C17	2.47291142	1.56132763	3.53586801	C38	3.05440347	-6.88723168	9.81157746
O18	3.18019210	1.95223370	4.48475280	H39	3.72353580	-7.39613903	10.51583249
O19	2.44854234	0.34722199	3.08636538	H40	2.11474673	-6.70057121	10.33912200
C20	1.05825996	1.18299629	13.45631310	C41	3.66881609	-5.58033357	9.40727378
H21	0.37022395	0.36013904	13.58246292	N42	4.86256121	-5.58098083	8.70526353

H43	5.36243456	-6.44798990	8.47601196	C106	9.49299335	3.99800409	-0.06804836
C44	3.30758709	-4.25647252	9.49004056	H107	9.02603069	3.08753103	-0.47384667
H45	2.46056698	-3.79623662	9.97528630	H108	8.79189405	4.81852382	-0.27364951
C46	5.15163829	-4.33083064	8.33605559	C109	9.68832308	3.85169807	1.44989428
H47	5.95144419	-4.06873711	7.67203764	H110	10.16121933	4.76123575	1.84296243
N48	4.24398369	-3.48631719	8.81407801	H111	10.38243231	3.02570511	1.65694252
N49	3.81867118	-7.94191081	6.42286826	C112	8.40275545	3.62963652	2.25840793
H50	2.87132541	-7.81551735	6.05956327	H113	7.70790975	4.46746443	2.09341431
C51	4.91725307	-7.84634434	5.46886579	H114	8.64925252	3.60375543	3.32491329
H52	4.59815318	-8.35177396	4.55110937	N115	7.75067347	2.35739470	1.92955255
H53	5.77949649	-8.38378247	5.87007141	H116	7.75468807	2.06341524	0.96216409
C54	5.29593777	-6.37815557	5.13864724	C117	6.91460199	1.68391513	2.75036968
H55	6.18515630	-6.38917257	4.49475819	N118	6.59110216	2.19176179	3.94690507
H56	5.59646410	-5.87833759	6.06326432	H119	6.14544014	1.58917885	4.64606450
C57	4.16619895	-5.57687794	4.45940611	H120	6.58302080	3.18449255	4.12464748
H58	3.18732062	-5.86111904	4.86617008	N121	6.41070318	0.50528502	2.39029576
H59	4.09249772	-5.81085382	3.38931758	H122	6.87806260	-0.18699373	1.79683070
C60	4.23984921	-4.06008981	4.56828784	H123	5.70232083	0.06427177	2.99719902
O61	3.27462560	-3.40409128	4.04701743	C124	11.84239763	-5.39308953	7.24925489
O62	5.19916088	-3.52572006	5.20358632	H125	11.25220231	-5.97246126	6.55470795
C63	9.15951156	0.11915813	11.44782285	H126	12.79646291	-5.85244915	7.46174208
H64	9.77555945	-0.15932138	10.58699873	H127	12.01595349	-4.39184023	6.84352773
H65	9.77706204	-0.00687676	12.34765105	C128	11.16835764	-5.35828343	8.63997053
C66	7.93513241	-0.77179825	11.57380250	H129	11.86678041	-4.90965565	9.36123667
H67	7.26967476	-0.39679970	12.35816717	H130	11.01289840	-6.39229384	8.97870414
H68	8.22536665	-1.78700836	11.87409300	C131	9.87520997	-4.61597789	8.72793375
C69	7.11995013	-0.86845105	10.29371297	N132	9.11994681	-4.56801664	9.89665939
O70	7.57255528	-0.24609061	9.27976158	C133	9.20317627	-3.82243455	7.84157237
O71	6.08903020	-1.59817980	10.32056379	H134	9.42161892	-3.59400728	6.81450702
C72	8.77119732	1.59709594	11.35299747	C135	8.05087913	-3.77407638	9.72392884
O73	7.64979452	2.00572065	11.66961333	H136	7.28177238	-3.53824460	10.44484977
N74	9.77338254	2.42933046	10.97139418	N137	8.09680461	-3.30379134	8.48243458
H75	10.61392771	2.02641913	10.57853557	H138	7.37844840	-2.64116456	8.06736453
C76	9.56777761	3.85881471	10.76518874	C139	6.09893605	-4.23518876	-1.22219710
H77	10.48457095	4.39273743	11.02489079	H140	5.38336325	-4.56843395	-1.95928725
H78	8.76293235	4.17139651	11.43242070	H141	7.10941696	-4.13018081	-1.58867205
C79	9.24858892	4.13459504	9.28657677	H142	5.80028579	-3.20631645	-0.97668744
O80	10.14240941	4.25868866	8.45695217	C143	6.00795425	-5.09625166	0.05344777
N81	7.91792973	4.19338727	8.99539710	H144	6.10457367	-6.16221149	-0.17668730
H82	7.24537922	3.88600923	9.69058932	H145	6.81345717	-4.80821618	0.73883771
C83	7.44262984	4.22692819	7.62894713	C146	4.67072122	-4.81385320	0.74048039
H84	6.77341294	5.07671822	7.46269879	O147	4.52553735	-3.65944557	1.23429232
H85	8.32450231	4.33147102	6.98754006	O148	3.76586672	-5.71526302	0.74306901
C86	6.67991091	2.95021431	7.25382491	C149	-1.82887465	-11.98671726	4.24856859
O87	5.59176545	3.04574557	6.65924496	H150	-2.35869354	-12.71809503	3.65630028
O88	7.26414291	1.85129594	7.60166987	H151	-2.32840671	-11.78325026	5.18423368
C89	11.58166190	-0.61708344	3.48089927	H152	-0.85965051	-12.42982056	4.51601170
H90	12.44417524	-1.21809272	3.72840284	C153	-1.61937344	-10.69613511	3.43052593
H91	11.83042704	0.38213700	3.15520804	H154	-2.57823833	-10.40595105	2.97587772
H92	11.07378253	-1.11489469	2.64466918	H155	-1.33042586	-9.87111084	4.09292235
C93	10.57674722	-0.37135102	4.61373988	C156	-0.55220676	-10.87153553	2.33134599
H94	9.80769374	0.30444019	4.21665068	H157	0.44575087	-10.73816422	2.77228806
H95	11.04527625	0.17089726	5.44296997	H158	-0.57772441	-11.90662966	1.96426936
C96	9.89000549	-1.63898927	5.14818101	C159	-0.71870972	-9.96803142	1.09695414
H97	10.48049854	-2.03952816	5.98044692	H160	0.05078319	-10.21330759	0.35111355
H98	9.82428486	-2.40289101	4.36655998	H161	-1.68201112	-10.19995906	6.22239818
C99	8.47267367	-1.33217867	5.61486192	C162	-0.71141791	-8.45549113	1.32277055
O100	7.52219125	-1.85661822	4.97514873	H163	-0.97695384	-7.94700654	0.39100131
O101	8.35793771	-0.54771016	6.62204402	H164	-1.43308149	-8.15273843	2.08640541
C102	10.81872437	4.22856835	-0.81502146	N165	0.61785218	-7.90341526	1.74734040
H103	11.54036435	3.48392235	-0.51313097	H166	0.70006011	-6.90707604	1.44761362
H104	11.20109296	5.23062594	-0.68822340	H167	0.74416357	-7.89948291	2.78561533
H105	10.67344020	4.10334260	-1.89518561	H168	1.44579205	-8.35141004	1.29372365

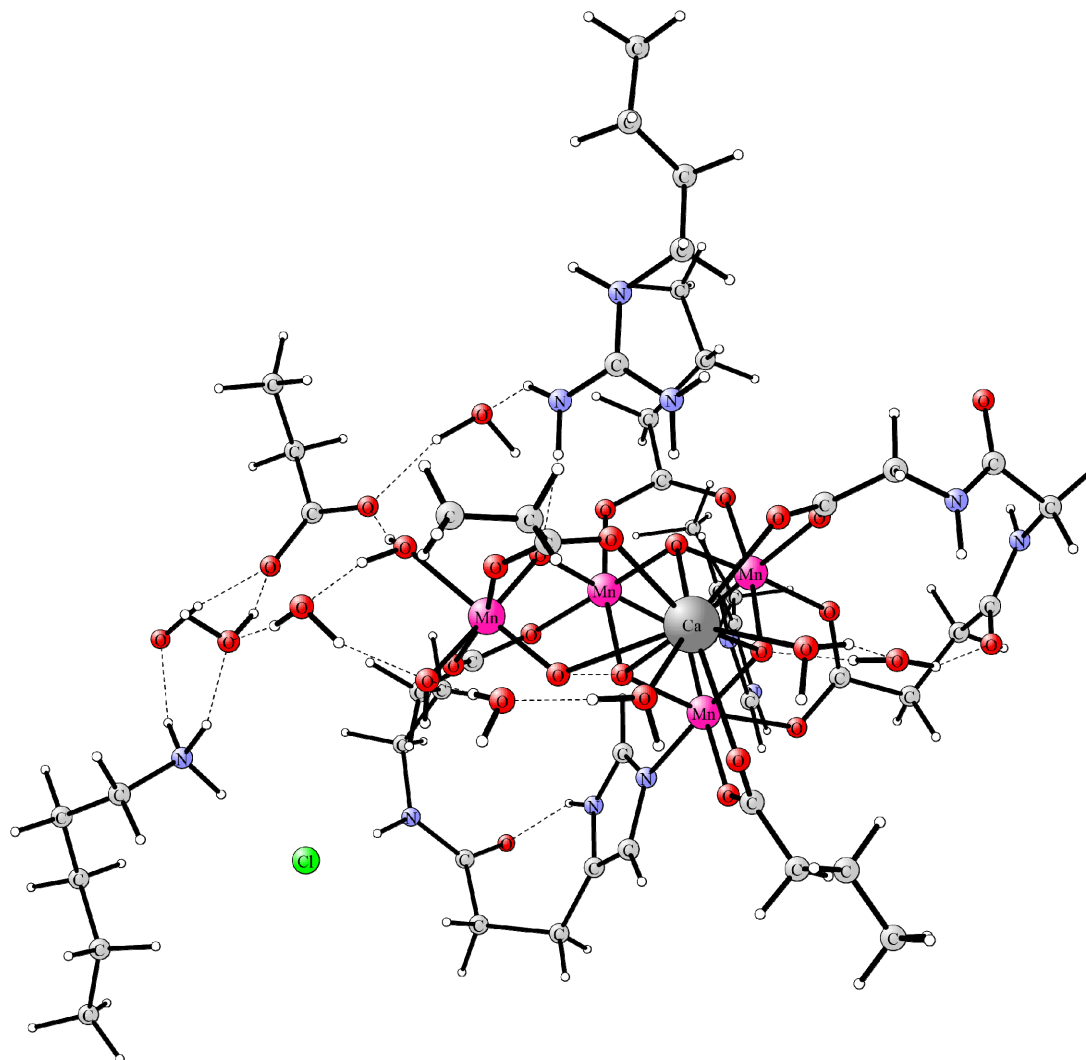
C1169	0.87880431	-7.25213976	4.79302910	H187	0.36549542	-4.94259923	4.74220856
O170	1.56782080	-1.43047668	5.13281221	O188	1.15915565	-5.36137400	0.67293768
H171	-0.00569028	-3.42944883	2.85527497	H189	2.16357335	-5.36385307	0.79949975
O172	4.72260305	-1.06856083	3.92168647	H190	1.03841421	-5.33533981	-0.28993049
O173	6.96237903	-2.15517986	1.77440053	O191	0.02796491	-3.16179328	1.90809084
H174	7.04815228	-2.25207847	2.73900949	H192	0.25616440	-3.99405288	1.43839920
H175	6.10207876	-2.58601016	1.56164548	H193	1.47430763	-2.46114734	1.71776708
O176	1.32084232	0.86955387	6.52540652	O194	3.03099097	-8.34163371	0.41043415
H177	1.02922563	0.63379739	7.42280609	H195	3.43575401	-7.43924382	0.44459555
H178	1.14469598	0.08106315	5.95211509	H196	3.74269031	-8.95245300	0.64925370
O179	3.14854302	3.22645518	8.51754271	O197	0.59313365	-4.01899109	4.49684971
H180	3.92343685	3.34984305	9.10832689	H198	1.52752054	-4.08539231	4.21403560
H181	2.52490137	2.71525334	9.06837619	H199	0.99528378	-2.22939060	5.12271163
O182	5.34957459	2.60415208	10.10610131	H200	3.33032427	-2.63354585	6.90786994
H183	5.36142599	1.74364420	9.63213292	H201	2.40797055	-1.56520848	5.99192009
H184	5.95054438	2.47165167	10.86451085	H202	9.33629505	-5.06013036	10.75456208
O185	2.41703359	-2.09107285	1.72842838				
H186	3.06722313	-2.81184188	1.48582474				

Table S1. Energies to build the energy diagram.

		Energy	ZPE	Solvation	Energy	VDW	Sum	Sum'
		B3LYP	B3LYP	B3LYP	B3LYP*	D2		(no ZPE)
		lacvp*	lacvp*	lacvp*	cc-pvtz(-f)/lacv3p+			
H ₂ O	¹ A	-76.407002	0.021131		-76.417655		-76.418834	-76.439965
O ₂	³ A	-150.316623	0.003775		-150.304632		-150.319980	-150.323755
S ₃ ⁻¹	¹³ A	-5851.626273	1.639543	-0.110373	-5850.687813	-0.407863	-5849.566506	-5851.206049
S ₄ ⁰ RE(O-O)	¹⁴ A	-5851.405693	1.640667	-0.127515	-5850.457476	-0.404542	-5849.348867	-5850.989534
	¹² A	-5851.419345	1.640821	-0.126868	-5850.474186	-0.405500	-5849.365733	-5851.006554
	⁶ A	-5851.421262	1.640866	-0.127167	-5850.475836	-0.405475	-5849.367612	-5851.008478
S ₄ ⁰ TS(O-O)	⁶ A	-5851.411180	1.639692	-0.128522	-5850.462537	-0.405005	-5849.356372	-5850.996064
S ₄ ⁰ O ₂ ²⁻	⁶ A	-5851.439270	1.640796	-0.130171	-5850.481900	-0.401059	-5849.372334	-5851.013130
S ₄ ⁰ TS(O ₂)	⁶ A	-5851.431681	1.639456	-0.126148	-5850.462088	-0.402893	-5849.351672	-5850.991128
S ₀ ⁰ RE(H ⁺)	¹⁶ A	-5777.568224	1.659663	-0.125665	-5776.599913	-0.398662	-5775.464577	-5777.124240
S ₀ ⁰ TS(H ⁺)	¹⁶ A	-5777.569945	1.656919	-0.124173	-5776.601116	-0.398618	-5775.466988	-5777.123907

Alternative TS(O-O) as shown in Figure 6 D.

S_4^0 TS(O-O) between the outer oxyl radical and inner oxo bridge, +1.1 kcal/mol higher than S_4^0 TS(O-O) between the inner oxyl radical and outer oxo bridge.



Mn1	2.66407300	-1.44162300	4.08842100	O18	3.13325200	1.87308400	4.53343800
Mn2	4.64499600	-1.45971800	8.58162600	O19	2.15096900	0.23406400	3.34217700
Mn3	5.30069500	-1.50146700	5.69401900	C20	1.05826500	1.18289500	13.45621700
Mn4	6.65096200	0.10400600	7.50006900	H21	0.37021000	0.36015900	13.58249700
O5	3.83294200	-1.35311500	6.84852100	H22	0.73366100	2.12914400	13.86359100
O6	5.74174800	0.26089700	5.98135500	H23	1.95117700	0.90708800	14.03694600
O7	5.12578400	0.32105000	8.46419700	C24	1.45168600	1.27375200	11.96547300
O8	6.16408900	-1.74943200	7.48933500	H25	2.24743700	2.01675400	11.82741600
Ca9	3.42223700	1.33634300	6.85737900	H26	0.59865100	1.60710800	11.36212200
C10	0.66765300	1.95117500	1.70645900	C27	1.94083500	-0.09310700	11.45758700
H11	1.22513700	1.90593300	0.78254000	H28	1.12372500	-0.82883200	11.50906000
H12	-0.32435100	2.36874600	1.61430400	H29	2.72828100	-0.48606200	12.11165400
H13	0.45739200	0.89753600	1.92861800	C30	2.48359400	-0.14459700	10.03368600
C14	1.47332400	2.49229600	2.89591900	O31	2.22673600	0.71365900	9.17865200
H15	0.79271700	2.87130400	3.66963900	O32	3.22525900	-1.19578400	9.79961900
H16	2.12482400	3.33351700	2.63304100	C33	2.78434400	-7.86067400	8.62583600
C17	2.34317000	1.47397600	3.65495600	H34	2.49869200	-8.81976800	9.07453000

H35	1.94107200	-7.52321500	8.01526200	H98	9.13455200	-1.73712200	3.53264400
C36	4.02102800	-8.07284300	7.74597800	C99	8.19395200	-1.24124500	5.36294300
O37	5.16076200	-8.17646600	8.25654400	O100	7.11676700	-1.74577000	4.89540500
C38	3.06849600	-6.86238200	9.78918700	O101	8.29034900	-0.54231800	6.41739900
H39	3.73287800	-7.35540500	10.50882500	C102	10.81873400	4.22853500	-0.81501400
H40	2.12915400	-6.65430300	10.30963400	H103	11.54037000	3.48392900	-0.51313100
C41	3.69721600	-5.56231600	9.36480400	H104	11.20108300	5.23063200	-0.68823000
N42	4.90846700	-5.58376300	8.69417600	H105	10.67558600	4.10239600	-1.89537900
H43	5.38212200	-6.47124200	8.46911000	C106	9.47634700	3.97927700	-0.09532400
C44	3.35798900	-4.22906000	9.43735400	H107	8.99953400	3.09986400	-0.55363100
H45	2.50469200	-3.75291100	9.89347000	H108	8.79344600	4.82104700	-0.27262400
C46	5.23156000	-4.33962600	8.33263300	C109	9.62762100	3.75244800	1.41780600
H47	6.04904100	-4.09365100	7.68348600	H110	10.14205100	4.61651500	1.85802700
N48	4.33035200	-3.47886300	8.79027300	H111	10.27191900	2.88275500	1.60555700
N49	3.82472700	-8.01169300	6.42271700	C112	8.31806600	3.58228900	2.20474000
H50	2.86006600	-7.95790900	6.05426900	H113	7.64626500	4.42589800	1.98424700
C51	4.91755300	-7.84623300	5.46887900	H114	8.54603900	3.60841200	3.27523700
H52	4.63456000	-8.35895000	4.54369400	N115	7.63155000	2.30748100	1.94521500
H53	5.81163200	-8.32403600	5.87385900	H116	7.67739600	1.92084600	1.01174100
C54	5.20648100	-6.33890700	5.18983900	C117	6.71434700	1.76126200	2.77765600
H55	6.02099000	-6.27388900	4.45664800	N118	6.36112000	2.41750600	3.89368900
H56	5.59286500	-5.89683200	6.11162600	H119	5.82217600	1.93814600	4.61099300
C57	3.99136100	-5.52132200	4.69595600	H120	6.40917200	3.42267000	3.95660000
H58	3.06320400	-5.85339800	5.17922500	N121	6.17132900	0.57333600	2.51729600
H59	3.82516800	-5.68081100	3.62283100	H122	6.64079500	-0.19613200	2.01101800
C60	4.03815200	-4.00102800	4.87988000	H123	5.43676300	0.22130800	3.13927200
O61	3.00267700	-3.37276500	4.48920800	C124	11.84244700	-5.39311800	7.24929500
O62	5.06293400	-3.46038100	5.40854700	H125	11.25217800	-5.97244000	6.55469900
C63	9.15949800	0.11914400	11.44782200	H126	12.79646100	-5.85244700	7.46172300
H64	9.79003200	-0.16288100	10.59876100	H127	12.02109500	-4.39279700	6.84295600
H65	9.76291900	-0.00422500	12.35751300	C128	11.18947700	-5.34932900	8.64557100
C66	7.92757800	-0.77458600	11.53739700	H129	11.90948500	-4.92422200	9.35940500
H67	7.24846500	-0.41396800	12.31608900	H130	11.00768600	-6.37908600	8.98129100
H68	8.21260100	-1.79505900	11.82307600	C131	9.91984600	-4.57651400	8.74648500
C69	7.13521200	-0.85022700	10.23874900	N132	9.05555700	-4.70372700	9.82933900
O70	7.63495700	-0.24134000	9.23672500	C133	9.35848600	-3.61643900	7.95131000
O71	6.07798500	-1.54597600	10.23923100	H134	9.69488600	-3.19436000	7.02013000
C72	8.77896500	1.59649000	11.34849300	C135	8.01909400	-3.86285500	9.69272900
O73	7.66666900	2.01262600	11.68826300	H136	7.18489000	-3.73852500	10.36590300
N74	9.77096500	2.42481200	10.93981400	N137	8.19559100	-3.19403800	8.55842000
H75	10.60755000	2.02272200	10.53900900	H138	7.48895800	-2.52991900	8.15110800
C76	9.56769600	3.85878600	10.76514600	C139	6.09855600	-4.23516900	-1.22214400
H77	10.51583800	4.37370000	10.93037100	H140	5.38344900	-4.56843900	-1.95933800
H78	8.83999900	4.18517700	11.51106100	H141	7.10947000	-4.13021100	-1.58863200
C79	9.10729900	4.17428700	9.32772100	H142	5.79325100	-3.22307800	-0.92797200
O80	9.91942400	4.40810300	8.44062300	C143	6.06497200	-5.13755000	0.03501100
N81	7.75584900	4.14943900	9.13932000	H144	6.05638000	-6.19660500	-0.24033700
H82	7.15887300	3.78409800	9.87282400	H145	6.96315500	-4.94509200	0.63365400
C83	7.16761100	4.25110400	7.82140300	C146	4.85373900	-4.80686000	0.90956800
H84	6.39386200	5.02380500	7.79206000	O147	4.86886600	-3.68226800	1.49069300
H85	7.97501900	4.52945800	7.13561100	O148	3.89762600	-5.64137200	0.99302700
C86	6.52808400	2.94236400	7.34055300	C149	-1.82881200	-11.98640500	4.24869900
O87	5.44731400	2.95698300	6.74102600	H150	-2.35863300	-12.71815900	3.65628000
O88	7.22784200	1.87755600	7.61752600	H151	-2.32848200	-11.78331600	5.18422000
C89	11.58174700	-0.61712300	3.48092100	H152	-0.85443800	-12.42134800	4.50974900
H90	12.44418600	-1.21807000	3.72839500	C153	-1.62859500	-10.68116400	3.45257200
H91	11.83037600	0.38213900	3.15519200	H154	-2.57899400	-10.40622500	2.97128800
H92	11.11660700	-1.09676500	2.60866700	H155	-1.37873900	-9.86518200	4.14170900
C93	10.53957800	-0.47583600	4.61343200	C156	-0.52135900	-10.79805100	2.38853300
H94	10.04398700	0.49674900	4.51225200	H157	0.45694100	-10.73007800	2.88475100
H95	11.02016900	-0.45513700	5.59782500	H158	-0.55813700	-11.79705100	1.93220200
C96	9.45303200	-1.55788200	4.56465800	C159	-0.61267700	-9.78189900	1.23587400
H97	9.84035600	-2.52658000	4.91725000	H160	0.19041200	-9.96818200	0.50885500

H161	-1.55354800	-9.95406800	0.69555000	O182	5.24991900	2.47395200	10.26585600
C162	-0.60247100	-8.29528200	1.59929900	H183	5.28144600	1.64050500	9.74975800
H163	-0.84452300	-7.70313100	0.71151000	H184	5.91576000	2.35445800	10.96999100
H164	-1.33891600	-8.05952200	2.37186400	O185	3.00658500	-1.89895300	2.14270000
N165	0.71983600	-7.79440400	2.10044600	H186	3.62948100	-2.66456900	1.97946200
H166	0.79830900	-6.77345200	1.91962600	H187	-0.03159000	-0.46105300	4.50617200
H167	0.83497600	-7.93158300	3.14431600	O188	2.31398300	-0.94420400	5.74503100
H168	1.53862100	-8.19249300	1.58852100	O189	1.28355500	-5.20838200	1.04678300
C169	0.92453100	-7.79938200	5.17178400	H190	2.28308000	-5.23260100	1.14883600
O170	0.82536900	-1.90415900	3.92845500	H191	1.15164400	-5.32695300	0.09152400
H171	0.37464900	-2.29575100	2.19916700	O192	0.61328100	-2.49949000	1.26566000
O172	4.47927500	-1.10492800	4.20787100	H193	0.71624400	-3.47765400	1.24679200
O173	7.03901500	-2.00356300	1.96154700	H194	2.13349500	-2.08683100	1.66292200
H174	6.97882300	-2.11018300	2.92882700	O195	3.04860200	-8.21829600	0.57118500
H175	6.29697300	-2.56984400	1.63331400	H196	3.48423200	-7.33164500	0.62663800
O176	0.97147700	1.54839000	6.83981300	H197	3.73689000	-8.85651400	0.80878400
H177	0.42614100	1.12234000	6.12429000	O198	-0.45150800	0.36620100	4.85591500
H178	0.69723400	1.12653000	7.66975500	H199	-1.37960900	0.14591900	5.02271400
O179	3.16423400	3.20141600	8.53368400	H200	0.70492300	-2.67419800	4.51258000
H180	3.92250200	3.27137100	9.15070200	H201	9.17785700	-5.34564700	10.60281300
H181	2.45825800	2.82590300	9.08802100				

Table S2. Energy of the alternative TS(O-O) (Figure 6 D).

		Energy	ZPE	Solvation	Energy	VDW	Sum
		B3LYP	B3LYP	B3LYP	B3LYP*	D2	
		lacvp*	lacvp*	lacvp*	cc-pvtz(-f)/lacv3p+		
S ₄ ⁰ TS(O-O)	⁶ A	-5851.404946	1.639222	-0.134399	-5850.461065	-0.398394	-5849.354636