The open-cubane oxo-oxyl coupling mechanism dominates photosynthetic oxygen evolution: A comprehensive DFT investigation on O-O bond formation in the S_4 state

Yu Guo, Hui Li, Lan-Lan He, Dong-Xia Zhao*, Li-Dong Gong, and Zhong-Zhi Yang*

School of Chemistry and Chemical Engineering, Liaoning Normal University, Dalian 116029, People's Republic of China

*Corresponding author: Tel: (86) 411-82159607 Fax: (86) 411-82158977

E-mail: zzyang@lnnu.edu.cn; zhaodxchem@lnnu.edu.cn

Electronic Supplementary Information

Contents: Presentations of additional remarks, diagrammatic sketches, computed absolute and relative Gibbs free energies of stationary points, calculated barrier heights, driving forces and Mulliken spin populations on relevant atomic sites for all the determined pathways in all spin states, with typical structures shown in optimized Cartesian coordinates, and animations for representative reaction scenarios uploaded as 'video_open/closed-cubane.zip'.

Abbreviated drawings

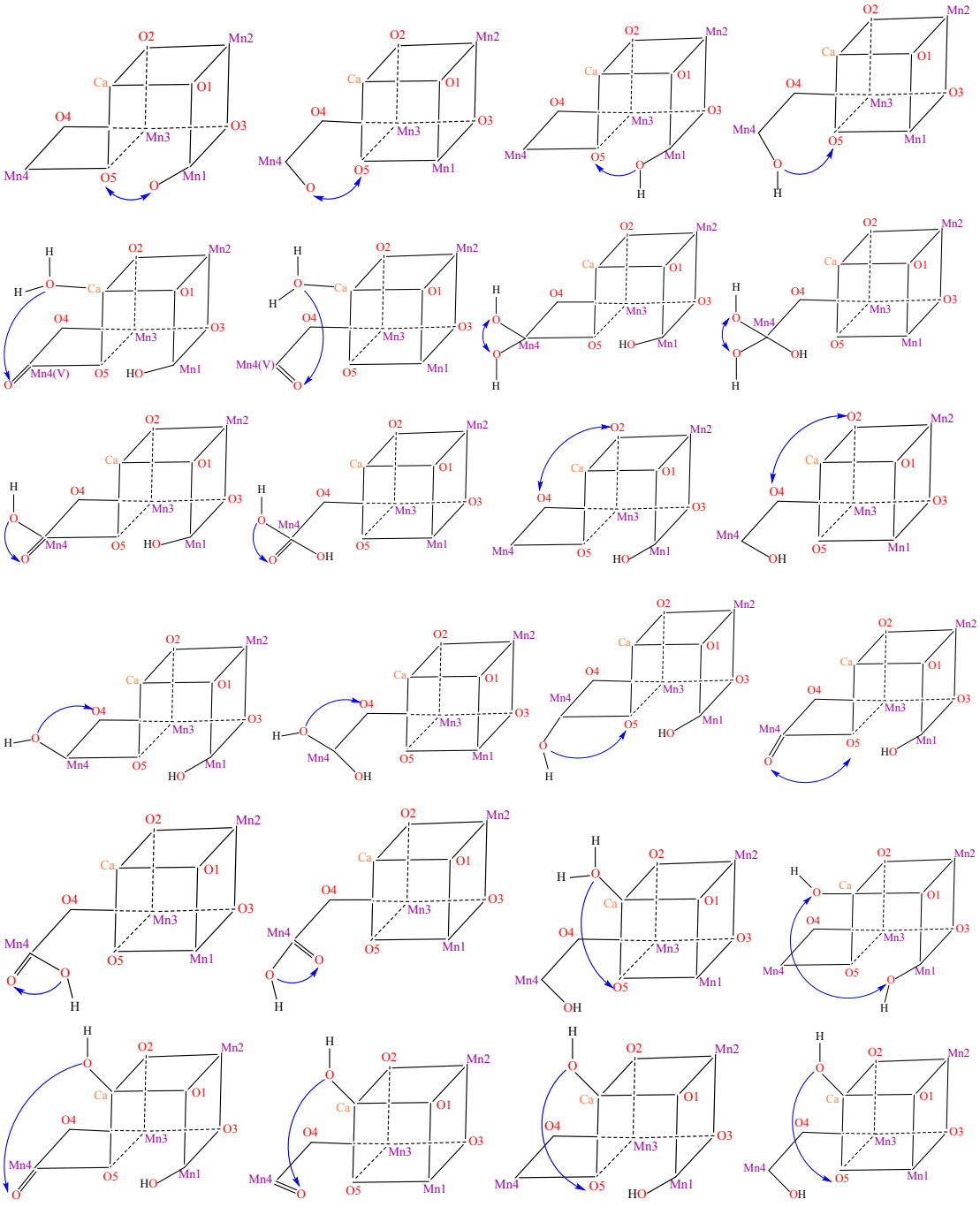

Fig. S1 Abbreviated drawings of O-O bond formation reactions exemplified in partial proton states explored in this paper.

Wx (oxyl/hydroxyl)-O5 (oxo)

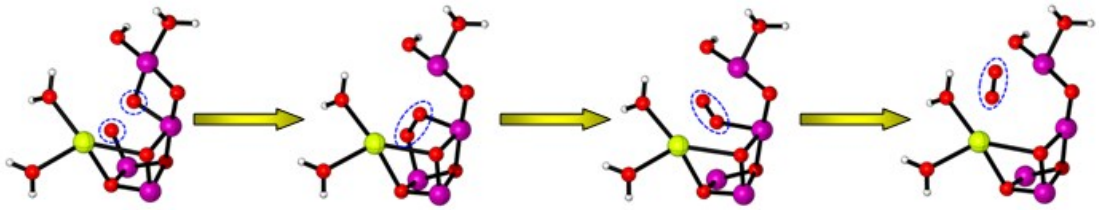

Fig. S2 Pictorial exhibitions for the open-cubane Wx (oxyl)-O5 (oxo) coupling and O_2 release. All the protein residues are not shown for clarity. The blue dotted circle stands for the two coupling oxygen atoms, the same below.

Table S1 Reaction parameters for the open-cubane Wx (oxyl)-O5 (oxo) coupling:

Spin state	Spin topology (Mn1~Mn4-O10)	Gibbs Free energy (a.u.)				
		Rea	TS-OO	Pro-O_2^{2-}	Int-$O_2^{\cdot-}$	Pro-O_2
doublet	ααββα	-3366.2127	-3366.1920	-3366.2050	-3366.2307	-3366.2360
	αβαβα	-3366.2133	-3366.1932	-3366.2061	-3366.2304	-3366.2237
	αββαα	-3366.2144	-3366.2076	-3366.2481	-3366.2259	-3366.2232
	βααβα	-3366.2261	-3366.2021	-3366.2058	-3366.1811	-3366.2391
	βαβαα	-3366.2247	-3366.2153	-3366.2486	-3366.2307	-3366.2422
	ββααα	-3366.2240	-3366.2164	-3366.2481	-3366.2245	-3366.2188
sextet	αααββ	-3366.2265	-3366.2180	-3366.2503	-3366.2301	-3366.2363
	ααβαβ	-3366.2279	-3366.2025	-3366.2069	-3366.1925	-3366.2398
	αβααβ	-3366.2247	-3366.2034	-3366.2069	-3366.1856	-3366.1968
	βαααβ	-3366.2126	-3366.1942	-3366.2059	-3366.2333	-3366.2382
octet	αααβα	-3366.2122	-3366.1941	-3366.2075	-3366.1852	-3366.2227
	ααβαα	-3366.2132	-3366.2071	-3366.2493	-3366.2260	-3366.2223
	αβααα	-3366.2120	-3366.2057	-3366.2500	-3366.2300	-3366.2392
	βαααα	-3366.2249	-3366.2167	-3366.2493	-3366.2266	-3366.2202
12-et	ααααβ	-3366.2259	-3366.2022	-3366.2076	-3366.1844	-3366.1927
14-et	ααααα	-3366.2125	-3366.2084	-3366.2514	-3366.2265	-3366.2368

Spin state	Spin topology (Mn1~Mn4-O10)	Relative Gibbs Free energy (kcal/mol)				
		$\Delta G^{\neq}$(Rea-TS)	ΔG(Rea-Pro-O_2^{2-})	ΔG(Rea)	ΔG(Pro-O_2^{2-})	ΔG(Pro-O_2)
doublet	ααββα	13.0	4.8	9.5	29.1	3.9
	αβαβα	12.6	4.5	9.2	28.4	11.6
	αββαα	4.3	-21.1	8.5	2.1	11.9
	βααβα	15.1	12.7	1.1	28.6	1.9
	βαβαα	5.9	-15.0	2.0	1.8	0.0
	ββααα	4.8	-15.1	2.4	2.1	14.7
sextet	αααββ	5.3	-14.9	0.9	0.7	3.7

	ααβαβ	15.9	13.2	0.0	27.9	1.5
	αβααβ	13.4	11.2	2.0	27.9	28.5
	βαααβ	11.5	4.2	9.6	28.6	2.5
octet	αααβα	11.4	2.9	9.9	27.5	12.2
	ααβαα	3.8	-22.7	9.2	1.3	12.5
	αβααα	4.0	-23.8	10.0	0.9	1.9
	βαααα	5.1	-15.3	1.9	1.3	13.8
12-et	ααααβ	14.9	11.5	1.3	27.5	31.1
14-et	αααααα	2.6	-24.4	9.7	0.0	3.4

Spin state	Spin topology (Mn1~Mn4-O10)		Mulliken spin density				
			Rea	TS-OO	Pro-O_2^{2-}	Int-$O_2^{\cdot-}$	Pro-O_2
doublet	α	Mn1	2.81	2.95	2.94	3.88	3.84
	α	Mn2	2.93	2.93	2.93	2.97	2.94
	β	Mn3	-2.88	-2.80	-2.83	-2.93	-3.81
	β	Mn4	-2.87	-2.42	-1.95	-3.86	-3.90
		O4	-0.12	-0.16	-0.19	-0.13	-0.11
	α	O5	-0.03	0.09	0.07	0.62	1.00
		O10	0.89	0.37	-0.01	0.42	1.00
	α	Mn1	2.81	2.92	2.93	3.88	3.85
	β	Mn2	-2.91	-2.90	-2.92	-2.91	-2.89
	α	Mn3	2.86	2.85	2.84	2.80	3.78
	β	Mn4	-2.83	-2.44	-1.94	-3.83	-3.83
		O4	0.03	0.06	0.13	0.12	-0.02
	α	O5	-0.05	0.02	-0.03	0.55	0.01
		O10	0.90	0.43	-0.04	0.32	0.00
	α	Mn1	2.80	2.89	2.96	3.86	3.85
	β	Mn2	-2.93	-2.93	-2.93	-2.92	-2.95
	β	Mn3	-2.89	-2.85	-2.83	-2.81	-3.80
	α	Mn4	2.86	3.33	3.87	3.82	3.83
		O4	-0.02	-0.09	-0.13	0.09	0.03
	α	O5	0.10	0.01	0.05	-0.57	0.01
		O10	0.89	0.57	-0.02	-0.31	0.00
	β	Mn1	-2.79	-2.74	-2.92	-3.86	-3.85
	α	Mn2	2.93	2.93	2.93	2.91	2.95
	α	Mn3	2.90	2.95	2.84	2.84	3.80
	β	Mn4	-2.84	-2.36	-1.95	-1.88	-3.83
		O4	0.01	0.03	0.11	0.04	0.03
	α	O5	-0.04	-0.04	-0.05	0.57	1.00
		O10	0.69	0.16	0.02	0.29	1.00
	β	Mn1	-2.80	-2.82	-2.96	-3.87	-3.85
	α	Mn2	2.91	2.91	2.92	2.92	2.89
	β	Mn3	-2.87	-2.81	-2.85	-2.93	-3.77
	α	Mn4	2.86	3.40	3.87	3.82	3.83

		O4	-0.02	-0.11	-0.14	-0.08	0.02
	α	O5	0.13	0.00	0.07	0.67	1.00
		O10	0.69	0.39	0.06	0.47	0.99
	β	Mn1	-2.80	-2.83	-2.94	-3.87	-3.84
	β	Mn2	-2.94	-2.94	-2.94	-2.97	-2.94
	α	Mn3	2.87	2.88	2.85	2.87	3.81
	α	Mn4	2.90	3.40	3.90	3.89	3.90
		O4	0.13	0.13	0.15	0.17	0.11
	α	O5	0.09	-0.06	-0.02	0.58	-0.01
		O10	0.69	0.41	0.02	0.32	0.01
sextet	α	Mn1	2.82	2.84	2.97	3.87	3.85
	α	Mn2	2.95	2.95	2.94	2.97	3.00
	α	Mn3	2.91	2.86	2.89	2.98	3.80
	β	Mn4	-2.86	-3.40	-3.87	-3.82	-3.83
		O4	0.01	0.10	0.12	0.07	-0.03
	β	O5	-0.13	0.00	-0.06	-0.66	-1.00
		O10	-0.67	-0.38	-0.05	-0.47	-1.00
	α	Mn1	2.81	2.74	2.94	2.03	3.85
	α	Mn2	2.94	2.93	2.93	2.91	2.94
	β	Mn3	-2.87	-2.93	-2.81	-2.76	-3.77
	α	Mn4	2.84	2.37	1.95	3.82	3.83
		O4	-0.01	-0.03	-0.12	-0.10	0.03
	β	O5	0.06	0.04	0.06	-0.64	-1.00
		O10	-0.66	-0.14	-0.01	-0.32	-1.00
	α	Mn1	2.80	2.78	2.93	3.86	3.89
	β	Mn2	-2.91	-2.91	-2.91	-2.91	-2.89
	α	Mn3	2.88	2.81	2.85	3.16	3.87
	α	Mn4	2.87	2.35	1.96	1.95	1.92
		O4	0.14	0.19	0.21	0.13	0.13
	β	O5	-0.01	-0.04	-0.04	-0.69	-1.01
		O10	-0.68	-0.19	-0.04	-0.50	-0.99
	β	Mn1	-2.80	-2.93	-2.92	-3.88	-3.84
	α	Mn2	2.93	2.92	2.93	2.92	2.95
	α	Mn3	2.91	2.84	2.86	2.96	3.84
	α	Mn4	2.87	2.42	1.95	3.85	3.90
		O4	0.12	0.16	0.18	0.12	0.11
	β	O5	0.02	-0.09	-0.06	-0.61	-1.00
		O10	-0.89	-0.36	0.01	-0.41	-1.00
octet	α	Mn1	2.82	2.95	2.96	3.86	3.85
	α	Mn2	2.94	2.95	2.94	2.97	3.00
	α	Mn3	2.90	2.88	2.88	3.06	3.81
	β	Mn4	-2.82	-2.37	-1.93	-1.87	-3.83
	α	O4	0.02	0.08	0.12	0.01	-0.03
		O5	-0.05	0.02	-0.03	-0.67	0.00

		O10	0.90	0.39	-0.03	-0.48	-0.01
	α	Mn1	2.81	2.90	2.98	3.86	3.85
	α	Mn2	2.93	2.93	2.94	2.97	2.94
	β	Mn3	-2.86	-2.81	-2.80	-2.77	-3.77
	α	Mn4	2.86	3.33	3.87	3.82	3.83
		O4	-0.02	-0.10	-0.14	-0.10	0.03
	α	O5	0.11	0.02	0.06	-0.56	0.00
		O10	0.89	0.58	-0.01	-0.31	0.00
	α	Mn1	2.81	2.89	2.98	3.89	3.85
	β	Mn2	-2.91	-2.91	-2.92	-2.88	-2.89
	α	Mn3	2.88	2.88	2.89	2.80	3.83
	α	Mn4	2.91	3.37	3.91	3.87	3.90
		O4	0.13	0.14	0.16	0.12	0.12
	α	O5	0.08	-0.05	-0.03	0.60	-1.00
		O10	0.90	0.61	-0.05	0.31	-1.00
	β	Mn1	-2.78	-2.82	-2.93	-3.87	-3.84
	α	Mn2	2.93	2.93	2.93	2.92	2.95
	α	Mn3	2.90	2.91	2.88	2.92	3.84
	α	Mn4	2.90	3.40	3.90	3.89	3.90
		O4	0.13	0.13	0.14	0.15	0.11
	α	O5	0.10	-0.05	-0.01	0.59	0.00
		O10	0.70	0.42	0.02	0.32	0.01
	α	Mn1	2.82	2.79	2.95	3.86	3.90
	α	Mn2	2.95	2.94	2.94	2.98	3.00
	α	Mn3	2.92	2.85	2.89	3.18	3.89
12-et	α	Mn4	2.87	2.37	1.96	1.93	1.92
		O4	0.13	0.18	0.20	0.11	0.13
	β	O5	-0.01	-0.05	-0.04	-0.68	-1.00
		O10	-0.67	-0.18	-0.04	-0.49	-1.00
	α	Mn1	2.83	2.90	3.00	3.85	3.85
	α	Mn2	2.95	2.95	2.95	2.90	3.00
	α	Mn3	2.92	2.92	2.93	2.94	3.86
14-et	α	Mn4	2.91	3.37	3.90	3.88	3.90
		O4	0.12	0.13	0.14	0.13	0.11
	α	O5	0.08	-0.06	-0.02	0.65	-0.99
		O10	0.90	0.61	-0.04	0.40	-1.00

Optimized Cartesian coordinates of reactant (Rea), transition state (TS) and product (Pro) structures exemplified by a certain spin state for structural similarities, the same below:

Rea:

Ca	-2.70854800	0.54568200	-0.74851800	Mn	-1.37097500	-0.93388900	2.05105100
Mn	-0.26397600	-1.73469500	-0.27778000	Mn	0.23898700	0.87190500	0.74821100

Mn	0.50616600	3.46700900	-1.21267400	N	3.60672000	-2.93356500	-1.40507800
O	-1.90885400	-1.58594100	0.44914000	H	4.51414300	-3.31291500	-1.12844200
O	0.37143800	-0.98678800	1.29609100	C	2.48227000	-2.99462000	-0.65570600
O	-1.45458700	0.74089100	1.39794500	H	2.31827600	-3.68255000	0.16073200
O	-0.23450500	0.00139600	-0.83176400	C	4.50572700	-1.53498400	-3.34759200
O	-0.00673800	2.52497900	0.20164900	H	4.29620400	-2.03337100	-4.30637600
O	-5.06809300	0.08352700	-1.50363300	H	4.41414300	-0.45852500	-3.54553900
H	-5.36440000	-0.19482900	-0.61344400	C	5.97274300	-1.87421400	-2.96122100
H	-4.83277900	-0.73568600	-1.98311300	H	6.15259100	-2.95094100	-3.05641600
O	-2.16748400	1.17302300	-3.10021100	H	6.64583800	-1.36810800	-3.66668900
H	-1.91196800	0.34983000	-3.54886400	C	6.28861700	-1.50133200	-1.51549300
H	-1.33434900	1.70582300	-3.03142900	O	6.21650000	-2.33980200	-0.60948400
O	1.11330500	4.39783000	-2.70891800	N	6.56852300	-0.18980600	-1.28111000
H	2.03201100	4.09076000	-2.84403600	H	6.56152600	0.44161200	-2.07299000
O	0.90920400	5.03345300	0.25719900	C	6.47372200	0.39385900	0.06071400
H	0.10013700	5.54608300	0.05381400	H	6.89706800	-0.33494500	0.75837900
H	0.66033100	4.46327900	1.01523800	H	7.10602100	1.29092000	0.08111500
O	-2.73227300	2.93093400	-0.87695800	C	5.02114700	0.71913400	0.45712500
C	-2.36534800	4.08165700	-1.14303200	H	4.43345200	-0.20560500	0.44228600
O	-1.13326400	4.47327600	-1.32533600	H	5.01049100	1.07830200	1.49579900
C	-3.37941300	5.21316400	-1.30628800	C	4.37045900	1.75724800	-0.46096300
H	-3.06519400	6.04304900	-0.65651200	H	4.54886900	1.50017400	-1.51728200
H	-3.26993600	5.58958900	-2.33392800	H	4.80366800	2.75652700	-0.31846000
C	-4.82249600	4.79868700	-1.02189500	C	2.85076200	1.89331200	-0.34519400
H	-4.93756700	4.44591200	0.01020900	O	2.21695900	0.99179600	0.26393200
H	-5.13478200	3.98409300	-1.68527800	O	2.38480600	2.92608300	-0.93739600
H	-5.50077300	5.64827200	-1.17256700	O	-0.08901800	-3.53350200	0.69087700
O	-0.96004800	-2.59062300	-1.87100200	C	-0.51615800	-3.71137300	1.88268900
C	-2.13665800	-2.47220400	-2.39735400	O	-1.04158400	-2.83911100	2.64083600
O	-2.89794200	-1.49430100	-2.24030100	C	-0.39233400	-5.13154000	2.42623000
C	-2.53927100	-3.64614700	-3.28512800	H	0.59766600	-5.50865500	2.13517200
H	-1.72947200	-3.79963200	-4.01451000	H	-1.11679700	-5.73998100	1.86271300
H	-2.52884300	-4.54566900	-2.65032400	H	-6.32362200	-0.30411700	2.63608600
C	-3.88863000	-3.49152900	-3.99087200	C	-0.62509800	-5.26809700	3.93114300
H	-3.88499000	-2.56615700	-4.58375700	H	-0.53253700	-6.31827500	4.23628900
H	-4.67856000	-3.36565200	-3.23687500	H	0.10490300	-4.67945100	4.49990600
C	-4.21822700	-4.68788000	-4.89061500	H	-1.62271300	-4.91120700	4.20889000
H	-3.46066900	-4.81735400	-5.67636000	O	-4.30845300	-0.03829600	1.11057000
H	-5.19027800	-4.55768500	-5.38349500	C	-4.20759000	-0.52206000	2.25639000
H	-4.25891600	-5.62263900	-4.31392400	O	-3.10599200	-0.91158000	2.81995400
N	1.61200300	-2.08621400	-1.06843000	C	-5.43597200	-0.70936100	3.12938000
C	2.20289500	-1.39348200	-2.10446100	H	-5.28293500	-0.21152300	4.09434500
H	1.68339300	-0.57382800	-2.58327500	H	-5.57914100	-1.77785500	3.33530900
C	3.45985500	-1.90291600	-2.32890000	O	-0.50653300	-0.19667600	3.69330800

C	0.35035700	0.74578700	3.66275200	H	2.84882500	0.36065100	4.85464200
O	0.80735500	1.32980800	2.62600200	C	2.90498100	1.86543200	6.41287900
C	0.87524500	1.23393800	5.00586200	H	2.50246600	2.86521000	6.62869500
H	0.42777100	2.22450900	5.18591000	H	4.00043300	1.93556700	6.43163800
H	0.50046900	0.55901700	5.78406000	H	2.59912300	1.20097500	7.23285700
C	2.40745800	1.34769300	5.05932500	O	0.23460600	2.28850200	-2.45732000
H	2.74187600	2.01213600	4.25217500				

TS:

Ca	2.78758700	-0.65602900	-0.60169500	H	2.53914000	4.22485900	-3.00954300
Mn	0.26152700	1.62539800	-0.44867400	C	3.95528100	3.10241600	-4.23037200
Mn	1.36279400	1.04746800	1.97034000	H	3.98629300	2.13549900	-4.75216800
Mn	-0.24710500	-0.93062300	0.95857200	H	4.72742500	3.05082900	-3.44975700
Mn	-0.54872100	-3.27196700	-1.07572900	C	4.28426600	4.23458400	-5.20981900
O	1.89859700	1.49500600	0.29957800	H	3.54499800	4.28803500	-6.02135600
O	-0.35725000	0.99206000	1.19971900	H	5.27123400	4.08894700	-5.66743300
O	1.45661400	-0.70835500	1.53517500	H	4.29129800	5.21060900	-4.70457100
O	0.23228600	-0.36378300	-0.79123400	N	-1.60811600	1.85604700	-1.29310900
O	-0.13168200	-2.63174900	0.56234900	C	-2.21708900	1.03586200	-2.22186100
O	5.13912900	-0.22432800	-1.39705800	H	-1.71931000	0.14264900	-2.57949300
H	5.43265300	0.12912600	-0.53306400	C	-3.46120700	1.54077500	-2.51986500
H	4.89963100	0.55030900	-1.94389000	N	-3.57965300	2.69818900	-1.75607200
O	2.36235600	-1.45268400	-2.94487800	H	-4.47543300	3.14179100	-1.54429300
H	2.36720700	-0.61230200	-3.43556000	C	-2.45441600	2.83812000	-1.01973100
H	1.40879500	-1.69929500	-2.84402200	H	-2.26889300	3.63313000	-0.31185500
O	-1.04748100	-3.96842800	-2.68910700	C	-4.52028700	1.05531700	-3.47427600
H	-1.98327000	-3.71962900	-2.81535300	H	-4.29659900	1.39545500	-4.49683700
O	-1.06844600	-5.05544600	0.06727700	H	-4.46276000	-0.04104400	-3.50627800
H	-0.28155200	-5.55915500	-0.22684600	C	-5.97624800	1.49432300	-3.14919500
H	-0.80325300	-4.64516200	0.91822000	H	-6.12370900	2.54861000	-3.40887400
O	2.75671600	-3.01297300	-0.46867300	H	-6.66498900	0.90632400	-3.77109600
C	2.31105800	-4.07876700	-0.91167200	C	-6.30080700	1.35636500	-1.66449000
O	1.07665800	-4.30914000	-1.25920100	O	-6.20377000	2.32137600	-0.89733000
C	3.22258800	-5.28958400	-1.10918900	N	-6.61410600	0.10412100	-1.23094300
H	2.81723100	-6.11336600	-0.50193100	H	-6.62379500	-0.64085900	-1.91710700
H	3.10682300	-5.61067000	-2.15392400	C	-6.50419300	-0.27123600	0.18286100
C	4.68823400	-5.02405300	-0.76819000	H	-6.90864400	0.55947600	0.76878500
H	4.80222000	-4.72044300	0.27907600	H	-7.14466900	-1.14718400	0.34786000
H	5.09607200	-4.21966100	-1.39141200	C	-5.04680800	-0.54885900	0.59888900
H	5.28871100	-5.92773600	-0.93381000	H	-4.45407600	0.35661400	0.42566100
O	0.98693400	2.28854300	-2.12918400	H	-5.01335000	-0.73623800	1.68067400
C	2.18236900	2.17050000	-2.60520300	C	-4.42768700	-1.72742800	-0.15910700
O	2.96655400	1.23089100	-2.34246000	H	-4.69759900	-1.69574000	-1.22465400
C	2.58473000	3.27945400	-3.57227200	H	-4.80920100	-2.69010800	0.21184500
H	1.79113300	3.35791800	-4.33064000	C	-2.90127000	-1.81099500	-0.13427000

O	-2.25695900	-0.96536800	0.53495700	H	5.24959600	0.56068300	4.15475700
O	-2.43138900	-2.76712300	-0.84435400	H	5.53022700	2.07036300	3.28352100
O	0.06809600	3.54672500	0.38924600	O	0.51137600	0.51914200	3.70199800
C	0.50159100	3.80804200	1.55787800	C	-0.33249300	-0.42558300	3.80017000
O	1.04297900	2.99030500	2.36959300	O	-0.79422000	-1.13551000	2.84413400
C	0.36981500	5.25804400	2.01765500	C	-0.84418900	-0.75671100	5.19357000
H	-0.65034400	5.58391600	1.77063800	H	-0.41720300	-1.73368000	5.46993500
H	1.03268900	5.84912000	1.36711600	H	-0.44277400	-0.01144600	5.88987500
H	6.32293600	0.56382100	2.71828100	C	-2.37815400	-0.82719500	5.27796700
C	0.69290600	5.50402800	3.49146400	H	-2.73889400	-1.56499000	4.54978200
H	0.58214700	6.56916800	3.73241900	H	-2.80017500	0.14333400	4.97651200
H	0.02301700	4.93194200	4.14452400	C	-2.86558700	-1.18792500	6.68504500
H	1.71860900	5.19917200	3.72625500	H	-2.48235800	-2.16898200	6.99921400
O	4.34874700	0.10890000	1.18541500	H	-3.96189800	-1.22915700	6.72552800
C	4.21179200	0.70179100	2.27648200	H	-2.53190600	-0.44859700	7.42629700
O	3.09251700	1.12894500	2.76671400	O	-0.15599600	-1.77781700	-1.96142800
C	5.41524700	0.98628200	3.15770300				

Pro-O_2^{2-}:

Ca	-2.84567900	0.62618900	-0.54129300	H	-3.24439900	5.76802100	-1.70868500
Mn	-0.28571800	-1.85532400	-0.53227800	C	-4.80216500	4.95930400	-0.40926100
Mn	-1.25121200	-1.04381700	1.89583600	H	-4.90013100	4.51400900	0.58759900
Mn	0.29057100	1.02552200	0.92832500	H	-5.19805400	4.23778700	-1.13366700
Mn	0.47660000	3.40449800	-0.98848500	H	-5.42365000	5.86310600	-0.44756400
O	-1.87987300	-1.51774600	0.27085200	O	-1.11316900	-2.46224100	-2.18562200
O	0.38453600	-0.92995300	1.00544700	C	-2.30461100	-2.23974400	-2.63173900
O	-1.38941100	0.73209900	1.51142100	O	-2.99099000	-1.22664800	-2.36281800
O	-0.30169800	0.76097600	-0.87892800	C	-2.83466100	-3.31599700	-3.57391400
O	0.20073100	2.76425000	0.68926700	H	-2.09844400	-3.43011000	-4.38445900
O	-5.18659500	0.13019900	-1.29639500	H	-2.80370800	-4.26829300	-3.02271500
H	-5.44706500	-0.24305500	-0.42971300	C	-4.23226800	-3.05701200	-4.14147000
H	-4.93998200	-0.62731000	-1.86383900	H	-4.24383100	-2.08303800	-4.65034800
O	-2.48749100	1.47350900	-2.88638300	H	-4.95058500	-2.97589700	-3.31279800
H	-2.45540400	0.62477900	-3.36352600	C	-4.68418800	-4.15723600	-5.10830800
H	-1.55657100	1.78674500	-2.82499800	H	-4.00235900	-4.23881900	-5.96645200
O	0.85959600	4.15068100	-2.59719000	H	-5.68917200	-3.95329500	-5.49950900
H	1.81198100	4.00657300	-2.75322300	H	-4.71112400	-5.13806400	-4.61327800
O	1.02475600	5.17920900	0.11183700	N	1.56716900	-2.02971500	-1.42763200
H	0.21062300	5.67009400	-0.12556800	C	2.14453700	-1.24679900	-2.40701400
H	0.82649000	4.75567000	0.97578400	H	1.60243800	-0.42615000	-2.85890100
O	-2.81689100	2.97812500	-0.35659900	C	3.43158500	-1.67643300	-2.63174200
C	-2.40681500	4.09596300	-0.69015800	N	3.61151300	-2.75175300	-1.76872300
O	-1.19063200	4.38776400	-1.05382200	H	4.53148100	-3.11663200	-1.50943100
C	-3.34543100	5.30193100	-0.71865500	C	2.47857100	-2.91646500	-1.05075900
H	-2.95367000	6.04107000	-0.00285600	H	2.33198000	-3.65731600	-0.27728300

C	4.47762800	-1.19072700	-3.60115900	H	-0.97276600	-5.89347500	1.75889700
H	4.26724300	-1.57787600	-4.60962100	H	-6.19338100	-0.61955700	2.91573500
H	4.38550400	-0.09860900	-3.67654000	C	-0.55630800	-5.31624400	3.81730400
C	5.94561700	-1.56775600	-3.26013600	H	-0.45630500	-6.34922500	4.17522000
H	6.11836300	-2.63359600	-3.44721900	H	0.14520200	-4.68811900	4.37963400
H	6.61203100	-1.00736900	-3.92994900	H	-1.56756300	-4.96393200	4.04819200
C	6.28485700	-1.31600000	-1.79350000	O	-4.31778100	-0.16035800	1.26860200
O	6.21355400	-2.22403400	-0.95618900	C	-4.10576900	-0.73616800	2.36090700
N	6.58619300	-0.03286500	-1.45640800	O	-2.95579400	-1.12091200	2.79819600
H	6.58246100	0.66225200	-2.19297400	C	-5.26148800	-1.04546300	3.29775500
C	6.52312900	0.43629700	-0.06798300	H	-5.04637100	-0.64418700	4.29516700
H	6.96517800	-0.34556100	0.55686200	H	-5.36564900	-2.13322500	3.40194100
H	7.15337100	1.33139600	0.01088300	O	-0.35036100	-0.53797800	3.62887900
C	5.07928800	0.71982900	0.38743400	C	0.51249100	0.38153700	3.71972800
H	4.49484100	-0.20354800	0.30498500	O	0.94361200	1.11367600	2.76128600
H	5.08895300	0.98524500	1.45355100	C	1.11295300	0.65888400	5.08851100
C	4.40754500	1.83166300	-0.42298600	H	0.82266500	1.68165200	5.37352400
H	4.59006100	1.69243300	-1.49966300	H	0.65947900	-0.03349800	5.80690300
H	4.82163900	2.82000000	-0.17833200	C	2.64762900	0.54184700	5.10175000
C	2.88833600	1.92898600	-0.28616400	H	3.06065500	1.23037200	4.35299500
O	2.27432200	1.04231600	0.35655000	H	2.93377600	-0.47321200	4.78772500
O	2.38128500	2.93350800	-0.89823800	C	3.24055800	0.84194800	6.48224100
O	0.00922300	-3.71599700	0.50338800	H	2.99376800	1.86240000	6.80745400
C	-0.40393600	-3.85533600	1.69425100	H	4.33451400	0.74991800	6.47157200
O	-0.92926600	-2.94612500	2.41699300	H	2.85474100	0.14881600	7.24252000
C	-0.27908200	-5.24438000	2.31556100	O	0.03700800	1.82220700	-1.78939800
H	0.72678400	-5.61559000	2.07416800				

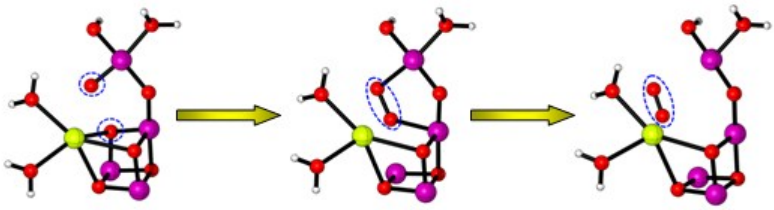

Fig. S3 Pictorial exhibitions for the closed-cubane Wx (oxyl)-O5 (oxo) coupling.

Table S2 Reaction parameters for the closed-cubane Wx (oxyl)-O5 (oxo) coupling:

Spin state	Spin topology (Mn1~Mn4-O10)	Gibbs Free energy (a.u.)			
		Rea	TS	Pro-O_2^{2-}	Pro-O_2
doublet	ααββα	-3366.2464	-3366.2049	-3366.2247	-3366.2353
	αβαβα	-3366.2522	-3366.2041	-3366.2279	-3366.2212
	αββαα	-3366.2179	-3366.2028	-3366.2303	-3366.1892
	βααβα	-3366.2541	-3366.1894	-3366.1939	-3366.1777
	βαβαα	-3366.2164	-3366.1947	-3366.2278	-3366.1750

	ββααα	-3366.2144	-3366.1815	-3366.1882	-3366.2191
sextet	αααββ	-3366.2181	-3366.1863	-3366.1921	-3366.2416
	ααβαβ	-3366.2554	-3366.1901	-3366.1937	-3366.2394
	αβααβ	-3366.2497	-3366.1876	-3366.1914	-3366.1899
	βαααβ	-3366.2473	-3366.2064	-3366.2296	-3366.2354
octet	αααβα	-3366.2549	-3366.2076	-3366.2287	-3366.2258
	ααβαα	-3366.2181	-3366.2016	-3366.2293	-3366.2394
	αβααα	-3366.2141	-3366.1982	-3366.2291	-3366.1985
	βαααα	-3366.2173	-3366.1814	-3366.2296	-3366.2239
12-et	ααααβ	-3366.2514	-3366.1878	-3366.1900	-3366.1907
14-et	ααααα	-3366.2169	-3366.2002	-3366.2270	-3366.2340

Spin state	Spin topology (Mn1~Mn4-O10)	Relative Gibbs Free energy (kcal/mol)				
		$\Delta G^{\neq}$(Rea-TS)	ΔG(Rea-Pro-O_2^{2-})	ΔG(Rea)	ΔG(Pro-O_2^{2-})	ΔG(Pro-O_2)
doublet	ααββα	26.0	13.6	5.6	3.1	4.0
	αβαβα	30.2	15.2	2.0	1.1	12.8
	αββαα	9.5	-7.8	23.5	-0.4	32.9
	βααβα	40.6	37.8	0.8	22.4	40.1
	βαβαα	13.6	-7.2	24.5	1.1	41.8
	ββααα	20.6	16.4	25.7	26.0	14.1
sextet	αααββ	20.0	16.3	23.4	23.5	0.0
	ααβαβ	41.0	38.7	0.0	22.5	1.4
	αβααβ	39.0	36.6	3.6	24.0	32.4
	βαααβ	25.7	11.1	5.1	0.0	3.9
octet	αααβα	29.7	16.4	0.3	0.6	9.9
	ααβαα	10.4	-7.0	23.4	0.2	1.4
	αβααα	10.0	-9.4	25.9	0.3	27.0
	βαααα	22.5	-7.7	23.9	0.0	11.1
12-et	ααααβ	39.9	38.5	2.5	24.8	31.9
14-et	ααααα	10.5	-6.3	24.2	1.6	4.8

Spin state	Spin topology (Mn1~Mn4-O10)		Mulliken spin density			
			Rea	TS	Pro-O-O	Pro-O_2
doublet	α	Mn1	2.93	3.42	3.88	3.84
	α	Mn2	2.94	2.95	2.97	2.94
	β	Mn3	-2.90	-2.80	-2.87	-3.81
	β	Mn4	-1.87	-2.78	-2.88	-3.90
	α	O4	-0.05	-0.19	-0.18	-0.11
		O5	0.01	0.00	0.02	1.00
		O10	-0.15	0.35	-0.01	1.00
	α	Mn1	2.93	3.37	3.89	3.85
	β	Mn2	-2.93	-2.93	-2.91	-2.90
	α	Mn3	2.88	2.83	2.81	3.78

	β	Mn4	-1.81	-2.72	-2.80	-3.81
		O4	-0.03	0.04	0.00	-0.03
	α	O5	0.03	-0.08	-0.05	0.00
		O10	-0.11	0.41	-0.01	0.00
	α	Mn1	2.92	3.38	3.88	3.85
	β	Mn2	-2.93	-2.92	-2.91	-2.91
	β	Mn3	-2.82	-2.78	-2.83	-1.87
	α	Mn4	2.64	2.76	2.82	3.83
		O4	0.06	-0.03	-0.03	-0.03
	α	O5	0.02	-0.04	0.03	-1.00
		O10	0.85	0.57	0.01	-1.00
	β	Mn1	-2.91	-2.46	-2.01	-3.88
	α	Mn2	2.92	2.93	2.90	2.94
	α	Mn3	2.89	2.88	2.83	3.80
	β	Mn4	-1.81	-2.68	-2.80	-1.86
		O4	-0.04	0.02	0.02	-0.09
	α	O5	-0.01	-0.01	-0.04	0.02
		O10	-0.11	0.23	0.01	0.01
	β	Mn1	-2.92	-2.84	-3.88	-3.84
	α	Mn2	2.93	2.94	2.92	2.92
	β	Mn3	-2.81	-2.72	-2.80	-1.89
	α	Mn4	2.64	3.39	3.84	3.84
		O4	0.05	-0.17	-0.19	-0.04
	α	O5	-0.02	0.13	0.48	0.02
		O10	0.85	0.24	0.62	0.03
	β	Mn1	-2.92	-2.53	-2.02	-3.84
	β	Mn2	-2.94	-2.92	2.91	-2.94
	α	Mn3	2.86	2.84	2.85	3.81
	α	Mn4	2.70	2.92	2.88	3.90
		O4	0.24	0.20	0.20	0.11
	α	O5	-0.02	0.03	-0.02	0.01
		O10	0.82	0.39	-0.01	0.00
sextet	α	Mn1	2.92	2.54	2.03	3.85
	α	Mn2	2.92	2.91	2.90	3.00
	α	Mn3	2.82	2.76	2.80	3.82
	β	Mn4	-2.61	-2.86	-2.81	-3.83
		O4	-0.14	0.01	-0.02	-0.03
	β	O5	0.04	-0.07	-0.05	-1.00
		O10	-0.87	-0.37	0.00	-1.00
	α	Mn1	2.92	2.49	2.03	3.85
	α	Mn2	2.93	2.93	2.92	2.94
	β	Mn3	-2.86	-2.84	-2.79	-3.77
	α	Mn4	1.81	2.68	2.81	3.83
		O4	0.03	-0.03	-0.03	0.03

	β	O5	0.02	0.00	0.03	-1.00
		O10	0.11	-0.22	0.00	-1.00
	α	Mn1	2.92	2.49	2.03	3.85
	β	Mn2	2.93	2.93	2.92	2.94
	α	Mn3	-2.86	-2.84	-2.79	-3.77
	α	Mn4	1.81	2.68	2.81	2.83
		O4	0.03	-0.03	-0.03	0.03
	β	O5	0.02	0.01	0.03	-1.00
		O10	0.11	-0.22	0.00	-1.00
	β	Mn1	-2.91	-3.39	-3.88	-3.84
	α	Mn2	2.93	2.93	2.91	2.95
	α	Mn3	2.94	2.84	2.89	3.84
	α	Mn4	1.87	2.79	2.87	3.90
		O4	0.04	0.18	0.15	0.11
	β	O5	0.00	0.01	-0.03	-1.00
		O10	0.15	-0.36	0.01	-1.00
octet	α	Mn1	2.93	3.41	3.89	3.85
	α	Mn2	2.92	2.95	2.97	3.00
	α	Mn3	2.89	2.87	2.85	3.81
	β	Mn4	-1.81	-2.72	-2.79	-3.83
		O4	-0.04	0.03	-0.01	-0.03
	α	O5	0.05	-0.07	-0.04	0.00
		O10	-0.11	0.40	0.00	0.00
	α	Mn1	2.93	3.41	3.89	3.85
	α	Mn2	2.94	2.95	2.97	2.94
	β	Mn3	-2.79	-2.75	-2.80	-3.77
	α	Mn4	2.64	2.76	2.82	3.83
		O4	0.05	-0.03	-0.03	0.03
	α	O5	0.03	-0.03	0.03	-1.00
		O10	0.85	0.56	0.02	-1.00
	α	Mn1	2.93	3.41	3.89	3.89
	β	Mn2	-2.93	-2.93	-2.91	-2.89
	α	Mn3	2.89	2.90	2.88	3.80
	α	Mn4	2.72	2.81	2.89	-1.83
		O4	0.20	0.78	0.16	-0.08
	α	O5	0.03	-0.13	-0.03	0.99
		O10	0.83	0.61	0.01	1.00
	β	Mn1	2.91	-2.50	-3.88	-3.84
	α	Mn2	2.93	2.91	2.91	2.95
	α	Mn3	2.89	2.86	2.89	3.84
	α	Mn4	2.72	2.91	2.87	3.90
		O4	0.20	0.17	0.15	0.11
	α	O5	0.00	0.02	-0.03	0.00
		O10	0.82	0.40	0.01	0.00

	α	Mn1	2.92	2.49	2.03	3.85
	α	Mn2	2.93	2.91	2.90	2.96
	α	Mn3	2.94	2.80	2.87	1.94
12-et	α	Mn4	1.87	2.79	2.87	2.89
		O4	0.04	0.17	0.17	0.16
	β	O5	0.05	-0.06	-0.04	-1.00
		O10	0.15	-0.26	-0.02	-1.00
	α	Mn1	2.93	3.42	3.89	3.85
	α	Mn2	2.93	2.95	2.97	3.00
	α	Mn3	2.92	2.94	2.93	3.85
14-et	α	Mn4	2.71	2.82	2.89	3.90
		O4	0.22	0.19	0.18	0.11
	α	O5	0.05	-0.10	-0.02	-1.01
		O10	0.83	0.59	0.02	-0.99

Rea:

Ca	-2.70854800	0.54568200	-0.74851800	H	-5.13478200	3.98409300	-1.68527800
Mn	-0.26397600	-1.73469500	-0.27778000	H	-5.50077300	5.64827200	-1.17256700
Mn	-1.37097500	-0.93388900	2.05105100	O	-0.96004800	-2.59062300	-1.87100200
Mn	0.23898700	0.87190500	0.74821100	C	-2.13665800	-2.47220400	-2.39735400
Mn	0.50616600	3.46700900	-1.21267400	O	-2.89794200	-1.49430100	-2.24030100
O	-1.90885400	-1.58594100	0.44914000	C	-2.53927100	-3.64614700	-3.28512800
O	0.37143800	-0.98678800	1.29609100	H	-1.72947200	-3.79963200	-4.01451000
O	-1.45458700	0.74089100	1.39794500	H	-2.52884300	-4.54566900	-2.65032400
O	-0.23450500	0.00139600	-0.83176400	C	-3.88863000	-3.49152900	-3.99087200
O	-0.00673800	2.52497900	0.20164900	H	-3.88499000	-2.56615700	-4.58375700
O	-5.06809300	0.08352700	-1.50363300	H	-4.67856000	-3.36565200	-3.23687500
H	-5.36440000	-0.19482900	-0.61344400	C	-4.21822700	-4.68788000	-4.89061500
H	-4.83277900	-0.73568600	-1.98311300	H	-3.46066900	-4.81735400	-5.67636000
O	-2.16748400	1.17302300	-3.10021100	H	-5.19027800	-4.55768500	-5.38349500
H	-1.91196800	0.34983000	-3.54886400	H	-4.25891600	-5.62263900	-4.31392400
H	-1.33434900	1.70582300	-3.03142900	N	1.61200300	-2.08621400	-1.06843000
O	1.11330500	4.39783000	-2.70891800	C	2.20289500	-1.39348200	-2.10446100
H	2.03201100	4.09076000	-2.84403600	H	1.68339300	-0.57382800	-2.58327500
O	0.90920400	5.03345300	0.25719900	C	3.45985500	-1.90291600	-2.32890000
H	0.10013700	5.54608300	0.05381400	N	3.60672000	-2.93356500	-1.40507800
H	0.66033100	4.46327900	1.01523800	H	4.51414300	-3.31291500	-1.12844200
O	-2.73227300	2.93093400	-0.87695800	C	2.48227000	-2.99462000	-0.65570600
C	-2.36534800	4.08165700	-1.14303200	H	2.31827600	-3.68255000	0.16073200
O	-1.13326400	4.47327600	-1.32533600	C	4.50572700	-1.53498400	-3.34759200
C	-3.37941300	5.21316400	-1.30628800	H	4.29620400	-2.03337100	-4.30637600
H	-3.06519400	6.04304900	-0.65651200	H	4.41414300	-0.45852500	-3.54553900
H	-3.26993600	5.58958900	-2.33392800	C	5.97274300	-1.87421400	-2.96122100
C	-4.82249600	4.79868700	-1.02189500	H	6.15259100	-2.95094100	-3.05641600
H	-4.93756700	4.44591200	0.01020900	H	6.64583800	-1.36810800	-3.66668900

C	6.28861700	-1.50133200	-1.51549300	H	-0.53253700	-6.31827500	4.23628900
O	6.21650000	-2.33980200	-0.60948400	H	0.10490300	-4.67945100	4.49990600
N	6.56852300	-0.18980600	-1.28111000	H	-1.62271300	-4.91120700	4.20889000
H	6.56152600	0.44161200	-2.07299000	O	-4.30845300	-0.03829600	1.11057000
C	6.47372200	0.39385900	0.06071400	C	-4.20759000	-0.52206000	2.25639000
H	6.89706800	-0.33494500	0.75837900	O	-3.10599200	-0.91158000	2.81995400
H	7.10602100	1.29092000	0.08111500	C	-5.43597200	-0.70936100	3.12938000
C	5.02114700	0.71913400	0.45712500	H	-5.28293500	-0.21152300	4.09434500
H	4.43345200	-0.20560500	0.44228600	H	-5.57914100	-1.77785500	3.33530900
H	5.01049100	1.07830200	1.49579900	O	-0.50653300	-0.19667600	3.69330800
C	4.37045900	1.75724800	-0.46096300	C	0.35035700	0.74578700	3.66275200
H	4.54886900	1.50017400	-1.51728200	O	0.80735500	1.32980800	2.62600200
H	4.80366800	2.75652700	-0.31846000	C	0.87524500	1.23393800	5.00586200
C	2.85076200	1.89331200	-0.34519400	H	0.42777100	2.22450900	5.18591000
O	2.21695900	0.99179600	0.26393200	H	0.50046900	0.55901700	5.78406000
O	2.38480600	2.92608300	-0.93739600	C	2.40745800	1.34769300	5.05932500
O	-0.08901800	-3.53350200	0.69087700	H	2.74187600	2.01213600	4.25217500
C	-0.51615800	-3.71137300	1.88268900	H	2.84882500	0.36065100	4.85464200
O	-1.04158400	-2.83911100	2.64083600	C	2.90498100	1.86543200	6.41287900
C	-0.39233400	-5.13154000	2.42623000	H	2.50246600	2.86521000	6.62869500
H	0.59766600	-5.50865500	2.13517200	H	4.00043300	1.93556700	6.43163800
H	-1.11679700	-5.73998100	1.86271300	H	2.59912300	1.20097500	7.23285700
H	-6.32362200	-0.30411700	2.63608600	O	0.23460600	2.28850200	-2.45732000
C	-0.62509800	-5.26809700	3.93114300				

TS:

Ca	2.78758700	-0.65602900	-0.60169500	H	-0.28155200	-5.55915500	-0.22684600
Mn	0.26152700	1.62539800	-0.44867400	H	-0.80325300	-4.64516200	0.91822000
Mn	1.36279400	1.04746800	1.97034000	O	2.75671600	-3.01297300	-0.46867300
Mn	-0.24710500	-0.93062300	0.95857200	C	2.31105800	-4.07876700	-0.91167200
Mn	-0.54872100	-3.27196700	-1.07572900	O	1.07665800	-4.30914000	-1.25920100
O	1.89859700	1.49500600	0.29957800	C	3.22258800	-5.28958400	-1.10918900
O	-0.35725000	0.99206000	1.19971900	H	2.81723100	-6.11336600	-0.50193100
O	1.45661400	-0.70835500	1.53517500	H	3.10682300	-5.61067000	-2.15392400
O	0.23228600	-0.36378300	-0.79123400	C	4.68823400	-5.02405300	-0.76819000
O	-0.13168200	-2.63174900	0.56234900	H	4.80222000	-4.72044300	0.27907600
O	5.13912900	-0.22432800	-1.39705800	H	5.09607200	-4.21966100	-1.39141200
H	5.43265300	0.12912600	-0.53306400	H	5.28871100	-5.92773600	-0.93381000
H	4.89963100	0.55030900	-1.94389000	O	0.98693400	2.28854300	-2.12918400
O	2.36235600	-1.45268400	-2.94487800	C	2.18236900	2.17050000	-2.60520300
H	2.36720700	-0.61230200	-3.43556000	O	2.96655400	1.23089100	-2.34246000
H	1.40879500	-1.69929500	-2.84402200	C	2.58473000	3.27945400	-3.57227200
O	-1.04748100	-3.96842800	-2.68910700	H	1.79113300	3.35791800	-4.33064000
H	-1.98327000	-3.71962900	-2.81535300	H	2.53914000	4.22485900	-3.00954300
O	-1.06844600	-5.05544600	0.06727700	C	3.95528100	3.10241600	-4.23037200

H	3.98629300	2.13549900	-4.75216800	O	-2.25695900	-0.96536800	0.53495700
H	4.72742500	3.05082900	-3.44975700	O	-2.43138900	-2.76712300	-0.84435400
C	4.28426600	4.23458400	-5.20981900	O	0.06809600	3.54672500	0.38924600
H	3.54499800	4.28803500	-6.02135600	C	0.50159100	3.80804200	1.55787800
H	5.27123400	4.08894700	-5.66743300	O	1.04297900	2.99030500	2.36959300
H	4.29129800	5.21060900	-4.70457100	C	0.36981500	5.25804400	2.01765500
N	-1.60811600	1.85604700	-1.29310900	H	-0.65034400	5.58391600	1.77063800
C	-2.21708900	1.03586200	-2.22186100	H	1.03268900	5.84912000	1.36711600
H	-1.71931000	0.14264900	-2.57949300	H	6.32293600	0.56382100	2.71828100
C	-3.46120700	1.54077500	-2.51986500	C	0.69290600	5.50402800	3.49146400
N	-3.57965300	2.69818900	-1.75607200	H	0.58214700	6.56916800	3.73241900
H	-4.47543300	3.14179100	-1.54429300	H	0.02301700	4.93194200	4.14452400
C	-2.45441600	2.83812000	-1.01973100	H	1.71860900	5.19917200	3.72625500
H	-2.26889300	3.63313000	-0.31185500	O	4.34874700	0.10890000	1.18541500
C	-4.52028700	1.05531700	-3.47427600	C	4.21179200	0.70179100	2.27648200
H	-4.29659900	1.39545500	-4.49683700	O	3.09251700	1.12894500	2.76671400
H	-4.46276000	-0.04104400	-3.50627800	C	5.41524700	0.98628200	3.15770300
C	-5.97624800	1.49432300	-3.14919500	H	5.24959600	0.56068300	4.15475700
H	-6.12370900	2.54861000	-3.40887400	H	5.53022700	2.07036300	3.28352100
H	-6.66498900	0.90632400	-3.77109600	O	0.51137600	0.51914200	3.70199800
C	-6.30080700	1.35636500	-1.66449000	C	-0.33249300	-0.42558300	3.80017000
O	-6.20377000	2.32137600	-0.89733000	O	-0.79422000	-1.13551000	2.84413400
N	-6.61410600	0.10412100	-1.23094300	C	-0.84418900	-0.75671100	5.19357000
H	-6.62379500	-0.64085900	-1.91710700	H	-0.41720300	-1.73368000	5.46993500
C	-6.50419300	-0.27123600	0.18286100	H	-0.44277400	-0.01144600	5.88987500
H	-6.90864400	0.55947600	0.76878500	C	-2.37815400	-0.82719500	5.27796700
H	-7.14466900	-1.14718400	0.34786000	H	-2.73889400	-1.56499000	4.54978200
C	-5.04680800	-0.54885900	0.59888900	H	-2.80017500	0.14333400	4.97651200
H	-4.45407600	0.35661400	0.42566100	C	-2.86558700	-1.18792500	6.68504500
H	-5.01335000	-0.73623800	1.68067400	H	-2.48235800	-2.16898200	6.99921400
C	-4.42768700	-1.72742800	-0.15910700	H	-3.96189800	-1.22915700	6.72552800
H	-4.69759900	-1.69574000	-1.22465400	H	-2.53190600	-0.44859700	7.42629700
H	-4.80920100	-2.69010800	0.21184500	O	-0.15599600	-1.77781700	-1.96142800
C	-2.90127000	-1.81099500	-0.13427000				

Pro-O_2^{2-}:

Ca	-2.84567900	0.62618900	-0.54129300	O	0.20073100	2.76425000	0.68926700
Mn	-0.28571800	-1.85532400	-0.53227800	O	-5.18659500	0.13019900	-1.29639500
Mn	-1.25121200	-1.04381700	1.89583600	H	-5.44706500	-0.24305500	-0.42971300
Mn	0.29057100	1.02552200	0.92832500	H	-4.93998200	-0.62731000	-1.86383900
Mn	0.47660000	3.40449800	-0.98848500	O	-2.48749100	1.47350900	-2.88638300
O	-1.87987300	-1.51774600	0.27085200	H	-2.45540400	0.62477900	-3.36352600
O	0.38453600	-0.92995300	1.00544700	H	-1.55657100	1.78674500	-2.82499800
O	-1.38941100	0.73209900	1.51142100	O	0.85959600	4.15068100	-2.59719000
O	-0.30169800	0.76097600	-0.87892800	H	1.81198100	4.00657300	-2.75322300

O	1.02475600	5.17920900	0.11183700	C	6.52312900	0.43629700	-0.06798300
H	0.21062300	5.67009400	-0.12556800	H	6.96517800	-0.34556100	0.55686200
H	0.82649000	4.75567000	0.97578400	H	7.15337100	1.33139600	0.01088300
O	-2.81689100	2.97812500	-0.35659900	C	5.07928800	0.71982900	0.38743400
C	-2.40681500	4.09596300	-0.69015800	H	4.49484100	-0.20354800	0.30498500
O	-1.19063200	4.38776400	-1.05382200	H	5.08895300	0.98524500	1.45355100
C	-3.34543100	5.30193100	-0.71865500	C	4.40754500	1.83166300	-0.42298600
H	-2.95367000	6.04107000	-0.00285600	H	4.59006100	1.69243300	-1.49966300
H	-3.24439900	5.76802100	-1.70868500	H	4.82163900	2.82000000	-0.17833200
C	-4.80216500	4.95930400	-0.40926100	C	2.88833600	1.92898600	-0.28616400
H	-4.90013100	4.51400900	0.58759900	O	2.27432200	1.04231600	0.35655000
H	-5.19805400	4.23778700	-1.13366700	O	2.38128500	2.93350800	-0.89823800
H	-5.42365000	5.86310600	-0.44756400	O	0.00922300	-3.71599700	0.50338800
O	-1.11316900	-2.46224100	-2.18562200	C	-0.40393600	-3.85533600	1.69425100
C	-2.30461100	-2.23974400	-2.63173900	O	-0.92926600	-2.94612500	2.41699300
O	-2.99099000	-1.22664800	-2.36281800	C	-0.27908200	-5.24438000	2.31556100
C	-2.83466100	-3.31599700	-3.57391400	H	0.72678400	-5.61559000	2.07416800
H	-2.09844400	-3.43011000	-4.38445900	H	-0.97276600	-5.89347500	1.75889700
H	-2.80370800	-4.26829300	-3.02271500	H	-6.19338100	-0.61955700	2.91573500
C	-4.23226800	-3.05701200	-4.14147000	C	-0.55630800	-5.31624400	3.81730400
H	-4.24383100	-2.08303800	-4.65034800	H	-0.45630500	-6.34922500	4.17522000
H	-4.95058500	-2.97589700	-3.31279800	H	0.14520200	-4.68811900	4.37963400
C	-4.68418800	-4.15723600	-5.10830800	H	-1.56756300	-4.96393200	4.04819200
H	-4.00235900	-4.23881900	-5.96645200	O	-4.31778100	-0.16035800	1.26860200
H	-5.68917200	-3.95329500	-5.49950900	C	-4.10576900	-0.73616800	2.36090700
H	-4.71112400	-5.13806400	-4.61327800	O	-2.95579400	-1.12091200	2.79819600
N	1.56716900	-2.02971500	-1.42763200	C	-5.26148800	-1.04546300	3.29775500
C	2.14453700	-1.24679900	-2.40701400	H	-5.04637100	-0.64418700	4.29516700
H	1.60243800	-0.42615000	-2.85890100	H	-5.36564900	-2.13322500	3.40194100
C	3.43158500	-1.67643300	-2.63174200	O	-0.35036100	-0.53797800	3.62887900
N	3.61151300	-2.75175300	-1.76872300	C	0.51249100	0.38153700	3.71972800
H	4.53148100	-3.11663200	-1.50943100	O	0.94361200	1.11367600	2.76128600
C	2.47857100	-2.91646500	-1.05075900	C	1.11295300	0.65888400	5.08851100
H	2.33198000	-3.65731600	-0.27728300	H	0.82266500	1.68165200	5.37352400
C	4.47762800	-1.19072700	-3.60115900	H	0.65947900	-0.03349800	5.80690300
H	4.26724300	-1.57787600	-4.60962100	C	2.64762900	0.54184700	5.10175000
H	4.38550400	-0.09860900	-3.67654000	H	3.06065500	1.23037200	4.35299500
C	5.94561700	-1.56775600	-3.26013600	H	2.93377600	-0.47321200	4.78772500
H	6.11836300	-2.63359600	-3.44721900	C	3.24055800	0.84194800	6.48224100
H	6.61203100	-1.00736900	-3.92994900	H	2.99376800	1.86240000	6.80745400
C	6.28485700	-1.31600000	-1.79350000	H	4.33451400	0.74991800	6.47157200
O	6.21355400	-2.22403400	-0.95618900	H	2.85474100	0.14881600	7.24252000
N	6.58619300	-0.03286500	-1.45640800	O	0.03700800	1.82220700	-1.78939800
H	6.58246100	0.66225200	-2.19297400				

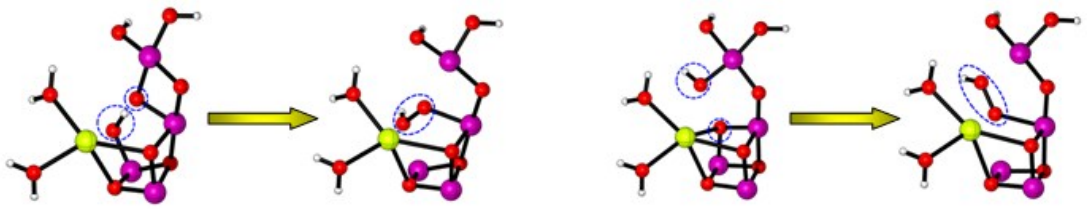

Fig. S4 Pictorial exhibitions for the open (left) and closed-cubane (right) Wx (hydroxyl)-O5 (oxo) nucleophilic attack.

Table S3 Reaction parameters for the open-cubane Wx (hydroxyl)-O5 (oxo) nucleophilic attack:

Spin state	Spin topology (Mn1~Mn4-O5/O10)	Gibbs Free energy (a.u.)		
		Rea	TS	Pro
doublet	ααββα	-3366.2139	-3366.1928	-3366.2195
	αβαβα	-3366.2152	-3366.1908	-3366.2207
	αββαα	-3366.2130	-3366.1956	-3366.2219
	βααβα	-3366.2175	-3366.1878	-3366.1895
	βαβαα	-3366.2168	-3366.1887	-3366.1890
	ββααα	-3366.2149	-3366.1876	-3366.1880
sextet	αααββ	-3366.2185	-3366.1915	-3366.1917
	ααβαβ	-3366.2182	-3366.1889	-3366.1899
	αβααβ	-3366.2209	-3366.1877	-3366.1879
	βαααβ	-3366.2177	-3366.1956	-3366.2223
octet	αααβα	-3366.2141	-3366.1899	-3366.2214
	ααβαα	-3366.2130	-3366.1962	-3366.2217
	αβααα	-3366.2167	-3366.1928	-3366.2216
	βαααα	-3366.2166	-3366.1887	-3366.1892
12-et	αααaβ	-3366.2219	-3366.1898	-3366.1902
14-et	αααaα	-3366.2166	-3366.1926	-3366.2211

Spin state	Spin topology (Mn1~Mn4-O5/O10)	Relative Gibbs Free energy (kcal/mol)			
		$\Delta G^{\neq}$(Rea-TS)	ΔG(Rea-Pro)	ΔG(Rea)	ΔG(Pro)
doublet	ααββα	13.9	-3.7	5.0	1.8
	αβαβα	16.0	-3.6	4.2	1.0
	αββαα	11.4	-5.9	5.6	0.3
	βααβα	19.5	18.4	2.8	20.6
	βαβαα	18.5	18.3	3.2	20.9
	ββααα	18.0	17.7	4.4	21.5
sextet	αααββ	17.8	17.6	2.1	19.2
	ααβαβ	19.3	18.6	2.3	20.3
	αβααβ	21.8	21.7	0.6	21.6
	βαααβ	14.5	-3.0	2.6	0.0
octet	αααβα	15.9	-4.8	4.9	0.6

	ααβαα	11.0	-5.7	5.6	0.4
	αβααα	15.7	-3.2	3.3	0.4
	βαααα	18.3	18.0	3.3	20.8
12-et	αααaβ	21.1	20.8	0.0	20.1
14-et	ααααα	15.8	-3.0	3.3	0.8

Spin state	Spin topology (Mn1~Mn4-O5/O10)		Mulliken spin density		
			Rea	TS	Pro
doublet	α	Mn1	2.93	3.37	3.90
	α	Mn2	2.94	2.95	2.98
	β	Mn3	-2.86	-2.85	-2.83
	β	Mn4	-2.94	-2.92	-2.94
	α	O5	0.57	0.37	0.05
		O10	0.40	0.17	0.01
	α	Mn1	2.92	3.37	3.89
	β	Mn2	-2.92	-2.91	-2.91
	α	Mn3	2.79	2.82	2.80
	β	Mn4	-2.90	-2.86	-2.88
	α	O5	0.59	0.36	-0.01
		O10	0.29	0.13	0.02
	α	Mn1	2.90	3.30	3.89
	β	Mn2	-2.92	-2.92	-2.91
	β	Mn3	-2.87	-2.84	-2.82
	α	Mn4	2.87	2.92	2.88
	α	O5	0.53	0.35	0.01
		O10	0.39	0.17	0.01
	β	Mn1	-2.91	-2.35	-2.01
	α	Mn2	2.92	2.93	2.92
	α	Mn3	2.83	2.91	2.85
	β	Mn4	-2.90	-2.85	-2.86
	α	O5	0.52	0.16	-0.01
		O10	0.36	0.10	0.02
	β	Mn1	-2.92	-2.38	-2.01
	α	Mn2	2.91	2.92	2.93
	β	Mn3	-2.86	-2.76	-2.78
	α	Mn4	2.87	2.93	2.88
	α	O5	0.51	0.20	0.02
		O10	0.41	0.11	0.02
	β	Mn1	-2.93	-2.41	-2.05
	β	Mn2	-2.95	-2.94	-2.95
	α	Mn3	2.83	2.92	2.86
	α	Mn4	2.91	2.99	2.94
	α	O5	0.52	0.14	0.19
		O10	0.33	0.11	0.02

sextet	α	Mn1	2.94	2.39	2.05
	α	Mn2	2.94	2.93	2.94
	α	Mn3	2.89	2.80	2.81
	β	Mn4	-2.87	-2.93	-2.88
	β	O5	-0.50	-0.19	-0.03
		O10	-0.41	-0.11	-0.02
	α	Mn1	2.94	2.38	2.04
	α	Mn2	2.95	2.94	2.95
	β	Mn3	-2.79	-2.88	-2.81
	α	Mn4	2.90	2.85	2.86
	β	O5	-0.53	-0.17	0.01
		O10	-0.34	-0.10	-0.02
	α	Mn1	2.92	2.31	2.00
	β	Mn2	-2.91	-2.92	-2.93
	α	Mn3	2.86	2.81	2.82
	α	Mn4	2.94	2.91	2.93
	β	O5	-0.54	-0.22	-0.05
		O10	-0.41	-0.10	-0.02
	β	Mn1	-2.90	-3.35	-3.89
	α	Mn2	2.92	2.92	2.91
	α	Mn3	2.89	2.88	2.87
	α	Mn4	2.94	2.92	2.94
	β	O5	-0.56	-0.34	-0.04
		O10	-0.34	-0.16	-0.01
octet	α	Mn1	2.95	3.40	3.90
	α	Mn2	2.95	2.96	2.98
	α	Mn3	2.85	2.86	2.85
	β	Mn4	-2.90	-2.86	-2.88
	α	O5	0.57	0.35	-0.01
		O10	0.32	0.13	0.02
	α	Mn1	2.93	3.34	3.90
	α	Mn2	2.94	2.95	2.98
	β	Mn3	-2.84	-2.81	-2.79
	α	Mn4	2.87	2.92	2.88
	α	O5	0.54	0.34	0.01
		O10	0.39	0.18	0.01
	α	Mn1	2.96	3.33	3.89
	β	Mn2	-2.92	-2.91	-2.90
	α	Mn3	2.85	2.86	2.84
	α	Mn4	2.86	2.98	2.94
	α	O5	0.51	0.34	0.01
		O10	0.42	0.20	0.01
	β	Mn1	-2.91	-2.39	-2.02
	α	Mn2	2.92	2.93	2.92

	α	Mn3	2.86	2.97	2.90
	α	Mn4	2.92	2.99	2.93
	α	O5	0.51	0.16	-0.03
		O10	0.36	0.11	0.02
12-et	α	Mn1	2.95	2.33	2.04
	α	Mn2	2.94	2.93	2.93
	α	Mn3	2.90	2.84	2.86
	α	Mn4	2.94	2.91	2.92
	β	O5	-0.53	-0.21	-0.05
		O10	-0.41	-0.10	-0.02
14-et	α	Mn1	2.98	3.37	3.90
	α	Mn2	2.94	2.96	2.98
	α	Mn3	2.89	2.90	2.89
	α	Mn4	2.86	2.98	2.94
	α	O5	0.51	0.32	0.01
		O10	0.42	0.19	0.02

Rea:

Ca	-2.74814800	0.17542200	-1.02002700	H	-3.65635000	6.37549700	-1.32408600
Mn	0.20493900	-1.73046100	-0.47580900	H	-3.36276300	6.12622900	0.40573100
Mn	-1.19500700	-0.88291100	1.76340600	H	-4.98123600	6.59015500	-0.16169500
Mn	0.04117300	1.42297100	0.82567900	O	-0.25120200	-2.88208900	-1.96424000
Mn	-0.35296500	3.38178200	-1.17765800	C	-1.40400900	-2.93131300	-2.56310000
O	-1.48602300	-1.59792700	0.08476200	O	-2.28061400	-2.04726800	-2.51083800
O	0.48288800	-0.59672800	0.97114300	C	-1.60241500	-4.20024800	-3.38910000
O	-1.61940600	0.78433300	1.32365100	H	-0.74758000	-4.27955900	-4.07778800
O	-0.59396600	1.40255700	-0.87257800	H	-1.49868500	-5.05357200	-2.70165700
O	-0.21583400	3.14850500	0.65739900	C	-2.92646100	-4.27246200	-4.15346200
O	-4.73534700	-0.94307100	-2.06586300	H	-3.01887700	-3.39128200	-4.80373400
H	-5.10127000	-1.22743500	-1.20418200	H	-3.76081800	-4.21303700	-3.43991300
H	-4.22043800	-1.70472800	-2.40660600	C	-3.05096800	-5.55275100	-4.98703100
O	-1.74578700	0.69146600	-3.24278100	H	-2.24731500	-5.62292100	-5.73343300
H	-2.07460600	0.44899900	-4.12215500	H	-2.99290000	-6.44910700	-4.35384700
H	-1.37829400	1.64000700	-3.28054200	H	-4.00795700	-5.58504800	-5.52349100
O	-0.65923100	3.04092900	-2.99052900	N	2.26045900	-1.91453100	-0.84161300
H	-0.73440900	3.89298700	-3.45278800	C	2.94880900	-1.61906500	-1.99754700
O	0.07138800	5.11937500	-1.35135700	H	2.42165500	-1.37608200	-2.90896700
H	-0.70006700	5.59857600	-0.99016000	C	4.30014600	-1.66536800	-1.74947600
O	-3.62000800	2.34235800	-1.04361600	N	4.41032200	-2.01262400	-0.40713500
C	-3.33999800	3.54400400	-0.86208900	H	5.26740100	-1.89788500	0.14144900
O	-2.16780500	4.07040800	-0.91986800	C	3.16416200	-2.13125900	0.10257800
C	-4.47903500	4.51321900	-0.54132500	H	2.94636100	-2.33668600	1.14017500
H	-5.23590100	4.37278100	-1.32625400	C	5.47270200	-1.42369800	-2.66349000
H	-4.94213200	4.13752100	0.38297000	H	5.63359700	-2.29515400	-3.31615500
C	-4.09571700	5.98559100	-0.39740800	H	5.20854500	-0.59470800	-3.33462200

C	6.82291300	-1.11647000	-1.96372100	H	0.03344500	-6.16135600	4.11862000
H	7.24161600	-2.03069300	-1.52844900	H	0.42830500	-4.45809700	4.44066700
H	7.53412100	-0.76221800	-2.72241600	H	-1.21213600	-4.90015900	3.95462400
C	6.69553100	-0.11579100	-0.81567500	O	-4.25479100	-0.78968300	0.65919200
O	6.63215800	-0.50028300	0.36019600	C	-4.09051200	-1.17760200	1.83775600
N	6.59218600	1.19259900	-1.15879400	O	-2.95669600	-1.27417800	2.44676700
H	6.60937900	1.43618000	-2.14151700	C	-5.28677500	-1.57102300	2.68735100
C	6.22076200	2.23003700	-0.18918100	H	-5.41378900	-0.83129700	3.48854500
H	6.82596600	2.07231100	0.71006000	H	-5.10879100	-2.54115500	3.16552100
H	6.50815500	3.19517700	-0.62496000	H	-6.19590600	-1.60571300	2.08065600
C	4.72891700	2.21613000	0.18489900	O	-0.54279400	-0.26315600	3.51785900
H	4.49166800	1.27233700	0.68728200	C	0.16602400	0.78586400	3.66696500
H	4.55722900	3.01502500	0.92026800	O	0.57313000	1.54721100	2.73647800
C	3.79997200	2.40945100	-1.01868100	C	0.53786500	1.17717100	5.08852900
H	3.96137400	1.60379700	-1.75178200	H	1.43356700	1.80854600	5.03774600
H	3.99268300	3.35796400	-1.53568100	H	-0.27828400	1.82380100	5.45129700
C	2.31458800	2.36970600	-0.67616400	C	0.73127400	-0.00358900	6.04873600
O	1.95259800	1.64444400	0.29743200	H	1.53926600	-0.64787600	5.67078900
O	1.56438800	3.05544300	-1.43593900	H	-0.17783900	-0.61778400	6.04770000
O	0.50202300	-3.34055500	0.61062400	C	1.06054400	0.45677100	7.47285900
C	-0.01087900	-3.56253800	1.76599500	H	1.98238000	1.05467100	7.49910300
O	-0.68337700	-2.74325600	2.44085400	H	1.20012900	-0.40113500	8.14336200
C	0.23357300	-4.95748000	2.32737400	H	0.25261500	1.07600900	7.88742000
H	1.29064000	-5.20074100	2.15329100	O	0.34671800	-0.31201100	-1.73729600
H	-0.33577900	-5.64940200	1.68773500	H	-0.35667700	-0.21887800	-2.42962700
C	-0.15265600	-5.12904100	3.79653600				

TS:

Ca	-2.71248700	0.29148100	-1.03787800	H	-0.45314500	4.02133600	-3.34189500
Mn	0.14479700	-1.75077800	-0.54443900	O	0.39876200	5.13314300	-1.13556500
Mn	-1.25557900	-0.96120400	1.70888900	H	-0.37850600	5.62613000	-0.80588000
Mn	0.07263500	1.33194800	0.91286300	O	-3.42686000	2.51448100	-0.98325100
Mn	-0.10763000	3.41080900	-1.08046700	C	-3.09809900	3.70804300	-0.84321100
O	-1.55760700	-1.60600100	0.02427800	O	-1.90689900	4.18609500	-0.94370600
O	0.43848500	-0.65585300	1.00117100	C	-4.19325100	4.73129800	-0.53801700
O	-1.61443400	0.75123400	1.28374500	H	-4.94861600	4.62311400	-1.32977700
O	-0.44843500	1.39829900	-0.87744600	H	-4.68235400	4.38148300	0.38275000
O	-0.13935300	3.07463400	0.72804200	C	-3.74349900	6.18501700	-0.39720600
O	-4.77705900	-0.61536800	-2.14546800	H	-3.27731800	6.54996400	-1.32079200
H	-5.15273700	-0.91958900	-1.29391400	H	-3.01326400	6.29579400	0.41333500
H	-4.31741600	-1.39004600	-2.53038700	H	-4.60218500	6.83100200	-0.17247500
O	-1.66048400	0.95470500	-3.25107700	O	-0.33881800	-2.69736100	-2.16888800
H	-1.95960300	0.74787400	-4.15005900	C	-1.50724900	-2.69950800	-2.73911900
H	-1.22534300	1.88210100	-3.24803600	O	-2.35359200	-1.78959700	-2.64087400
O	-0.32183100	3.14823900	-2.93397000	C	-1.76740500	-3.93658100	-3.59392400

H	-0.93156000	-4.02607200	-4.30440300	C	2.47758700	2.28636300	-0.42771400
H	-1.67539900	-4.81003000	-2.93041900	O	2.03501300	1.53429500	0.48613700
C	-3.11055300	-3.94665900	-4.32762800	O	1.79571800	3.00562500	-1.22510300
H	-3.18979100	-3.04650300	-4.95333100	O	0.42960000	-3.45880800	0.56443100
H	-3.92523800	-3.87954500	-3.59232100	C	-0.11907700	-3.66434300	1.69763200
C	-3.29637600	-5.20031000	-5.18979800	O	-0.79630100	-2.82278800	2.35510100
H	-2.51323500	-5.27689200	-5.95709000	C	0.05765400	-5.05965900	2.28814700
H	-3.25268200	-6.11399500	-4.58076100	H	1.10793400	-5.34639700	2.14050700
H	-4.26627800	-5.18808500	-5.70339200	H	-0.52489200	-5.73895200	1.64655100
N	2.16973700	-1.92779100	-0.99582000	C	-0.36502100	-5.19872000	3.75081700
C	2.86196300	-1.48389500	-2.10336000	H	-0.22585300	-6.23320900	4.09001200
H	2.34390700	-1.07292000	-2.95816300	H	0.22784100	-4.54216700	4.39910400
C	4.21130000	-1.64174600	-1.89416800	H	-1.41770300	-4.92662400	3.88361400
N	4.31653800	-2.20946300	-0.62944000	O	-4.29741000	-0.67327300	0.56643000
H	5.18598200	-2.23313300	-0.08829200	C	-4.16887500	-1.12854500	1.72662500
C	3.07321000	-2.34506900	-0.11937000	O	-3.05333600	-1.29401800	2.35075900
H	2.85241800	-2.72228000	0.86783300	C	-5.39544200	-1.53271100	2.52745500
C	5.38592100	-1.32012800	-2.78106900	H	-5.47415300	-0.89167500	3.41469700
H	5.48591000	-2.08130400	-3.56956700	H	-5.28703100	-2.56479800	2.88193600
H	5.16443000	-0.37886000	-3.30287400	H	-6.30172200	-1.43360600	1.92364100
C	6.76092200	-1.20927900	-2.06994200	O	-0.66849200	-0.36570700	3.51643800
H	7.12766800	-2.20438500	-1.79452000	C	0.05021800	0.66139400	3.71384800
H	7.48331100	-0.78055000	-2.77786200	O	0.50273700	1.44435300	2.81439100
C	6.70349500	-0.39788300	-0.77660600	C	0.39179900	1.02534800	5.15018600
O	6.61327500	-0.95930600	0.32388300	H	1.36121200	1.54013600	5.14151100
N	6.68681900	0.95261100	-0.90747000	H	-0.35071000	1.77994000	5.45858300
H	6.71826600	1.34535800	-1.84039800	C	0.38507500	-0.15159500	6.13247300
C	6.34254000	1.84063000	0.20951200	H	1.12215100	-0.89965400	5.80517900
H	6.89612200	1.49240700	1.08772100	H	-0.59255700	-0.64787200	6.09100800
H	6.71024900	2.84204000	-0.04745200	C	0.69633200	0.29084700	7.56639600
C	4.83613400	1.86562300	0.52158800	H	1.68407500	0.76814800	7.63466300
H	4.51832900	0.86605700	0.83766800	H	0.69137500	-0.56498000	8.25379800
H	4.67491500	2.53049900	1.38169600	H	-0.04650800	1.01477100	7.93009400
C	3.98469300	2.33162900	-0.66258400	O	0.21273300	-0.04308300	-1.64107200
H	4.16887600	1.69203600	-1.53976600	H	-0.33815500	0.05190300	-2.47252500
H	4.23419200	3.35667900	-0.96689700				

Pro:

Ca	-2.72016100	0.26508700	-1.10634800	O	-1.60297700	0.70514800	1.25664200
Mn	0.16157300	-1.79710700	-0.55581800	O	-0.39256800	1.30190300	-0.93854100
Mn	-1.29693700	-1.04717100	1.65064900	O	-0.14869400	2.96456700	0.77118800
Mn	0.09475100	1.23744500	0.97886300	O	-4.78816100	-0.58013400	-2.25186600
Mn	-0.08559500	3.39873000	-0.99613000	H	-5.16968000	-0.91235200	-1.41343900
O	-1.57527200	-1.60839500	-0.04138700	H	-4.32684400	-1.34027000	-2.66199200
O	0.42586500	-0.71860600	1.01193700	O	-1.67884600	1.12663200	-3.28492800

H	-1.92551100	0.90783900	-4.19696000	O	6.63555800	-0.88520700	0.46889100
H	-1.28472300	2.06881200	-3.25921900	N	6.72385600	0.96974800	-0.84206000
O	-0.29084900	3.25349800	-2.86081800	H	6.77138900	1.32568900	-1.78893300
H	-0.36047600	4.15723800	-3.21340700	C	6.37522600	1.90144900	0.23769500
O	0.41423800	5.11897800	-0.96175400	H	6.94499800	1.60597100	1.12502600
H	-0.36699200	5.59027300	-0.60942100	H	6.72041600	2.89629600	-0.07045000
O	-3.38708100	2.49444300	-0.95866200	C	4.87230900	1.91451100	0.56797700
C	-3.07507100	3.68395500	-0.76187300	H	4.57656200	0.92741800	0.93908100
O	-1.88772500	4.17624500	-0.83423000	H	4.71071600	2.62136700	1.39409100
C	-4.18259900	4.68018700	-0.41705600	C	3.99920000	2.30322900	-0.62843700
H	-4.93456200	4.59693400	-1.21500000	H	4.18121800	1.61495700	-1.46868900
H	-4.66986400	4.28575600	0.48650900	H	4.23110300	3.31236200	-0.99244400
C	-3.75031600	6.13174700	-0.21311900	C	2.49657200	2.24771500	-0.37155800
H	-3.28534900	6.54094300	-1.11860500	O	2.06431100	1.46491100	0.51973400
H	-3.02433400	6.21665800	0.60435900	O	1.80532500	2.99145000	-1.14173200
H	-4.61724400	6.75759800	0.03542500	O	0.41488400	-3.61085900	0.59973800
O	-0.28763100	-2.53725800	-2.30445900	C	-0.19573000	-3.77003700	1.69497300
C	-1.43181400	-2.52986700	-2.91155200	O	-0.88670200	-2.88303200	2.30025200
O	-2.31791000	-1.66182700	-2.76051000	C	-0.12367100	-5.14801300	2.34849500
C	-1.62685500	-3.68654300	-3.88778800	H	0.89502400	-5.52807000	2.19446500
H	-0.77260500	-3.67623700	-4.58218100	H	-0.77760400	-5.80220700	1.75021700
H	-1.51386100	-4.61605100	-3.30904100	C	-0.52719500	-5.19320000	3.82301800
C	-2.95108700	-3.67894000	-4.65487200	H	-0.47030400	-6.22115300	4.20404700
H	-3.05440000	-2.72611000	-5.19317100	H	0.13351000	-4.56562800	4.43413600
H	-3.78444400	-3.71559400	-3.93848200	H	-1.54924200	-4.82483100	3.96182300
C	-3.06558600	-4.84920200	-5.63822800	O	-4.33055300	-0.69674000	0.46402700
H	-2.26265000	-4.82033700	-6.38825900	C	-4.21845900	-1.16401000	1.62160100
H	-2.99739600	-5.81521800	-5.11877700	O	-3.11389700	-1.33077300	2.26304800
H	-4.02325800	-4.82570200	-6.17403500	C	-5.45567900	-1.59497900	2.39194600
N	2.19004800	-1.92279900	-0.96190000	H	-5.48980200	-1.07173500	3.35512500
C	2.91688200	-1.56185000	-2.07647700	H	-5.39697900	-2.66914400	2.60898000
H	2.42561100	-1.25647600	-2.99012600	H	-6.36224600	-1.38033100	1.81939000
C	4.26071400	-1.65933900	-1.80001800	O	-0.74478800	-0.44776200	3.51188500
N	4.32532300	-2.11123000	-0.48708400	C	-0.00395600	0.54666300	3.72989800
H	5.17693200	-2.09936100	0.08252100	O	0.49311800	1.33014400	2.83887100
C	3.06631100	-2.23702700	-0.01680800	C	0.34691700	0.90621000	5.16472000
H	2.81187600	-2.53276800	0.99027100	H	1.40351800	1.20753700	5.18020300
C	5.46466700	-1.36597400	-2.65838000	H	-0.22486200	1.81800300	5.40195200
H	5.58445900	-2.14837400	-3.42272300	C	0.06000300	-0.19158400	6.19363400
H	5.26668800	-0.43768800	-3.21260800	H	0.63133800	-1.09304100	5.93001900
C	6.81801200	-1.24220400	-1.91010200	H	-0.99830100	-0.47544400	6.13200600
H	7.16216700	-2.22893600	-1.58088500	C	0.40876700	0.24964500	7.61939200
H	7.56689200	-0.85399500	-2.61396500	H	1.47238500	0.51166900	7.71056500
C	6.74069900	-0.37376200	-0.65459300	H	0.19947500	-0.54974400	8.34185900

H	-0.17564000	1.13101200	7.91907600	H	-0.17580400	0.48723200	-2.61040700
O	0.39322200	0.41309400	-1.79078200				

Table S4 Reaction parameters for the closed-cubane Wx (hydroxyl)-O5 (oxo) nucleophilic attack:

Spin state	Spin topology (Mn1~Mn4-O5/O10)	Gibbs Free energy (a.u.)		
		Rea	TS	Pro
doublet	αααββα	-3366.2116	-3366.1901	-3366.2043
	αβαβα	-3366.2011	-3366.1891	-3366.2048
	αββαα	-3366.2144	-3366.1922	-3366.2126
	βααβα	-3366.2028	-3366.1730	-3366.1802
	βαβαα	-3366.2051	-3366.1736	-3366.1828
	ββαααα	-3366.2045	-3366.1720	-3366.1790
sextet	αααββ	-3366.2088	-3366.1783	-3366.1854
	ααβαβ	-3366.2113	-3366.1802	-3366.1803
	αβααβ	-3366.2063	-3366.1690	-3366.1701
	βαααβ	-3366.2144	-3366.1934	-3366.2065
octet	αααβα	-3366.2050	-3366.1947	-3366.2083
	ααβαα	-3366.2154	-3366.1926	-3366.2114
	αβααα	-3366.2129	-3366.1899	-3366.2077
	βαααα	-3366.2063	-3366.1750	-3366.1811
12-et	ααααβ	-3366.2057	-3366.1764	-3366.1719
14-et	ααααα	-3366.2154	-3366.1911	-3366.2077

Spin state	Spin topology (Mn1~Mn4-O5/O10)	Relative Gibbs Free energy (kcal/mol)			
		$\Delta G^{\neq}$ (Rea-TS)	ΔG(Rea-Pro)	ΔG(Rea)	ΔG(Pro)
doublet	αααββα	13.5	4.6	2.4	5.2
	αβαβα	7.5	-2.3	9.0	4.9
	αββαα	13.9	1.1	0.6	0.0
	βααβα	18.7	14.2	7.9	20.3
	βαβαα	19.8	14.0	6.5	18.7
	ββαααα	20.4	16.0	6.8	21.1
sextet	αααββ	19.1	14.7	4.1	17.1
	ααβαβ	19.5	19.5	2.6	20.3
	αβααβ	23.4	22.7	5.7	27.4
	βαααβ	13.2	5.0	0.6	3.8
octet	αααβα	6.5	-2.1	6.5	2.7
	ααβαα	14.3	2.5	0.0	0.8
	αβαααα	14.4	3.3	1.6	3.1
	βαααα	19.6	15.8	5.7	19.8
12-et	ααααβ	18.4	21.2	6.1	25.5
14-et	ααααα	15.2	4.8	0.0	3.1

Spin state	Spin	Mulliken spin density

	topology (Mn1~Mn4-O5/O10)		Rea	TS	Pro
doublet	α	Mn1	2.93	3.48	3.88
	α	Mn2	2.94	2.95	2.97
	β	Mn3	-2.89	-2.78	-2.84
	β	Mn4	-2.91	-2.90	-2.87
	α	O5	0.61	-0.04	-0.06
		O10	0.46	0.39	0.02
	α	Mn1	2.94	3.41	3.88
	β	Mn2	-2.95	-2.93	2.92
	α	Mn3	2.73	2.77	2.79
	β	Mn4	-2.84	-2.84	-2.83
	α	O5	0.33	0.04	-0.04
		O10	0.58	0.43	0.02
	α	Mn1	2.92	3.45	3.87
	β	Mn2	-2.93	-2.92	-2.91
	β	Mn3	-2.83	-2.77	-2.80
	α	Mn4	2.74	2.81	-2.81
	α	O5	0.57	0.07	0.05
		O10	0.48	0.37	-0.01
	β	Mn1	-2.86	-2.35	-2.00
	α	Mn2	2.94	2.92	2.89
	α	Mn3	2.79	2.82	2.79
	β	Mn4	-2.83	-2.81	-2.81
	α	O5	0.44	0.04	-0.02
		O10	0.48	0.28	0.02
	β	Mn1	-2.92	-2.35	-2.01
	α	Mn2	2.93	2.92	2.91
	β	Mn3	-2.82	-2.74	-2.75
	α	Mn4	2.74	2.82	2.81
	α	O5	0.53	0.06	0.05
		O10	0.52	0.25	0.00
	β	Mn1	-2.92	-2.35	-2.02
	β	Mn2	-2.94	-2.92	-2.91
	α	Mn3	2.87	2.82	2.80
	α	Mn4	2.83	2.88	2.87
	α	O5	0.55	0.08	0.07
		O10	0.51	0.24	0.00
sextet	α	Mn1	2.92	2.36	2.03
	α	Mn2	2.93	2.90	2.90
	α	Mn3	2.84	2.77	2.79
	β	Mn4	-2.74	-2.82	-2.81
	β	O5	-0.53	-0.06	-0.05
		O10	-0.52	-0.23	0.00

	α	Mn1	2.90	2.25	2.04
	α	Mn2	2.96	2.95	2.95
	β	Mn3	-2.70	-2.74	-2.76
	α	Mn4	2.85	2.83	2.83
	β	O5	-0.42	-0.03	0.02
		O10	-0.48	-0.19	-0.04
	α	Mn1	2.89	2.17	2.00
	β	Mn2	-2.96	-2.93	-2.93
	α	Mn3	2.79	2.82	2.83
	α	Mn4	2.89	2.85	2.84
	β	O5	-0.50	-0.08	-0.04
		O10	-0.45	-0.13	-0.02
	β	Mn1	-2.92	-3.42	-3.88
	α	Mn2	2.93	2.93	2.92
	α	Mn3	2.91	2.81	2.87
	α	Mn4	2.91	2.90	2.87
	β	O5	-0.61	0.04	0.06
		O10	-0.47	-0.41	-0.02
	α	Mn1	2.95	3.47	3.88
	α	Mn2	2.92	2.94	2.96
	α	Mn3	2.76	2.82	2.82
	β	Mn4	-2.83	-2.84	-2.82
	α	O5	0.34	0.04	-0.03
		O10	0.59	0.39	0.04
	α	Mn1	2.93	3.49	3.88
octet	α	Mn2	2.94	2.96	2.97
	β	Mn3	-2.80	-2.73	-2.77
	α	Mn4	2.73	2.81	2.81
	α	O5	0.57	0.07	0.05
		O10	0.48	0.37	0.00
	α	Mn1	2.93	3.43	2.88
	β	Mn2	-2.93	-2.93	-2.91
	α	Mn3	2.89	2.85	2.87
	α	Mn4	2.83	2.87	2.87
	α	O5	0.58	0.11	0.07
		O10	0.47	0.40	0.00
	β	Mn1	-2.91	-2.34	-2.01
	α	Mn2	2.93	2.91	2.89
	α	Mn3	2.90	2.86	2.84
	α	Mn4	2.83	2.87	2.87
	α	O5	0.55	0.08	0.07
		O10	0.51	0.25	0.00
12-et	α	Mn1	2.92	2.33	2.04
	α	Mn2	2.93	2.90	2.92

	α	Mn3	2.82	2.81	2.88
	α	Mn4	2.89	2.86	2.83
	β	O5	-0.37	-0.09	-0.04
		O10	-0.55	-0.22	-0.02
14-et	α	Mn1	2.93	3.48	3.89
	α	Mn2	2.93	2.95	2.97
	α	Mn3	2.92	2.90	2.91
	α	Mn4	2.83	2.87	2.87
	α	O5	0.59	0.11	0.06
		O10	0.47	0.39	0.00

Rea:

Ca	-2.49040900	0.06765000	-1.17200600	C	-1.01460800	-3.70142800	-3.86309800
Mn	0.21164200	-1.71337100	-0.34619200	H	-0.12120900	-3.48457100	-4.46843600
Mn	-1.37283700	-1.21467600	1.79520500	H	-0.80249500	-4.66112800	-3.36704100
Mn	0.06159600	0.89923900	0.78104100	C	-2.25945300	-3.80316400	-4.74760300
Mn	0.00872700	3.60627300	-1.04415700	H	-2.46092400	-2.82252200	-5.20023600
O	-1.52164600	-1.88214100	0.11477400	H	-3.13080900	-4.03397200	-4.11851500
O	0.44769100	-0.92229900	1.32392900	C	-2.11343800	-4.86672400	-5.84160300
O	-1.65511600	0.44234500	1.14915200	H	-1.26751400	-4.64230500	-6.50663100
O	0.01384700	0.02611100	-0.87401400	H	-3.01737100	-4.92478500	-6.46168000
O	-0.42791900	2.51117600	0.23392300	H	-1.93980300	-5.86305600	-5.41105300
O	-4.59460100	-0.71353900	-2.33619800	N	2.26196600	-1.76458300	-0.65470900
H	-4.98783100	-1.07066600	-1.51434500	C	3.00606200	-1.43173400	-1.76436800
H	-4.13139100	-1.46235300	-2.76382400	H	2.52583600	-1.15254600	-2.69240200
O	-2.25643900	0.94981100	-3.52913800	C	4.34571300	-1.53486200	-1.46303600
H	-3.05507300	1.49550200	-3.63121300	N	4.38468100	-1.96126900	-0.14078800
H	-1.52120400	1.60576200	-3.41735600	H	5.22750400	-1.95571300	0.44163400
O	0.49130900	4.56066000	-2.71783600	C	3.11677900	-2.06587500	0.31131800
H	-0.38382200	4.90269800	-3.00042800	H	2.84488100	-2.32966300	1.32250300
O	0.44751400	4.96201500	0.04037700	C	5.56958200	-1.26658400	-2.30261900
H	0.14786100	4.70529500	0.93412700	H	5.69658000	-2.06152600	-3.05256800
O	-3.04127300	2.41335100	-1.19765100	H	5.39185900	-0.34554200	-2.87556600
C	-2.90117900	3.64632400	-1.23412300	C	6.91129300	-1.14333900	-1.53076700
O	-1.77456400	4.29304900	-1.29887500	H	7.24917800	-2.12979400	-1.19471300
C	-4.11629700	4.57284600	-1.20075900	H	7.67214800	-0.75577200	-2.22202900
H	-4.09075000	5.08089400	-0.22463900	C	6.81141500	-0.27432400	-0.27729500
H	-3.95925800	5.36498900	-1.94532400	O	6.70036400	-0.78563500	0.84564000
C	-5.45239400	3.85979000	-1.40638100	N	6.77108500	1.06922900	-0.46471100
H	-5.60918400	3.09030200	-0.64223800	H	6.82242600	1.42543700	-1.41145200
H	-5.49567800	3.36486000	-2.38505300	C	6.34200000	1.98354600	0.60099500
H	-6.28137800	4.57678200	-1.35222100	H	6.86952300	1.69409700	1.51553400
O	-0.00097400	-2.53459900	-2.06712300	H	6.67635800	2.99004100	0.32027800
C	-1.09120600	-2.63906500	-2.77217800	C	4.82139600	1.95190300	0.84294000
O	-2.11381300	-1.95020600	-2.61295100	H	4.53151100	0.95340500	1.18742600

H	4.58908600	2.64698800	1.66212000	O	-3.18547700	-1.52864700	2.26365500
C	4.01886500	2.32839100	-0.40508100	C	-5.53069900	-1.77250500	2.18824300
H	4.29245400	1.66357700	-1.23960800	H	-5.62502700	-1.29526300	3.17087600
H	4.23904500	3.35184400	-0.73410900	H	-5.50692000	-2.85705000	2.35534100
C	2.50113100	2.21385800	-0.27589700	O	-0.92412400	-0.39820300	3.55460500
O	2.02477200	1.40549400	0.56711200	C	-0.24523800	0.67634000	3.66923900
O	1.86068100	2.94721400	-1.10252900	O	0.25822000	1.36478000	2.72351000
O	0.50001400	-3.50805900	0.61159600	C	-0.01142500	1.17660500	5.08660200
C	-0.07887300	-3.80801500	1.70813500	H	0.65238500	0.45085500	5.58195000
O	-0.82383500	-3.05042500	2.40740600	H	0.52156800	2.13292500	5.03201400
C	0.13993600	-5.23143300	2.21032500	C	-1.31352800	1.31042500	5.89566700
H	1.18103300	-5.50172600	1.99018000	H	-1.82739300	0.34081400	5.89926100
H	-0.47728700	-5.87821900	1.56684500	H	-1.98316900	2.01859900	5.38512300
H	-6.38862400	-1.51322300	1.56194000	C	-1.05874200	1.78283900	7.33062800
C	-0.20510900	-5.45404200	3.68357600	H	-0.41609600	1.07570200	7.87385700
H	-0.04111600	-6.50389400	3.95809000	H	-1.99969600	1.87481700	7.88844600
H	0.41733200	-4.82897500	4.33590800	H	-0.56301200	2.76347400	7.34820000
H	-1.25118600	-5.19987100	3.88492900	O	-0.23932300	2.53273600	-2.69555300
O	-4.24085700	-0.84667100	0.37859900	H	0.64955200	2.15468500	-2.84722200
C	-4.23575500	-1.33477800	1.52683900				

TS:

Ca	2.64691700	-0.17735700	-1.09125600	C	3.65507000	-4.81336000	-1.46814700
Mn	-0.07457300	1.74559600	-0.33333600	H	3.46101600	-5.42221100	-0.57172400
Mn	1.39069900	0.96597400	1.83035200	H	3.46177900	-5.47997200	-2.31934100
Mn	-0.11649500	-1.09590300	0.79211800	C	5.09183900	-4.29201700	-1.46998100
Mn	-0.34654300	-3.43180500	-1.35729900	H	5.27884700	-3.65194200	-0.60048600
O	1.64732800	1.68251900	0.18786200	H	5.30072200	-3.69623700	-2.36781200
O	-0.39584900	0.79603500	1.25114200	H	5.80247700	-5.12782800	-1.44477400
O	1.61465600	-0.69989700	1.16180600	O	0.30791100	2.55606200	-2.04036700
O	0.07351900	-0.26415500	-0.95355600	C	1.45300100	2.65810000	-2.65340200
O	0.13090600	-2.72313400	0.25005100	O	2.42494000	1.90330300	-2.47470000
O	4.82893800	0.51487400	-2.13318800	C	1.51392000	3.80023700	-3.66097200
H	5.21465200	0.83482500	-1.29347000	H	0.66296400	3.67532900	-4.34796200
H	4.43925200	1.29755400	-2.57257000	H	1.30591500	4.73007500	-3.10930200
O	2.33058700	-0.88716300	-3.53434900	C	2.82907100	3.90352200	-4.43683400
H	2.86425600	-1.69863300	-3.58349300	H	3.02114700	2.95049300	-4.94872500
H	1.41088300	-1.21069700	-3.39977000	H	3.65672100	4.04119600	-3.72658900
O	-0.81566900	-3.81362100	-3.08114100	C	2.82045800	5.05207600	-5.45179100
H	-0.11347200	-4.40143400	-3.41908900	H	2.02111500	4.92235600	-6.19499700
O	-0.84834100	-4.97812900	-0.61745400	H	3.77289600	5.10903900	-5.99450500
H	-0.56467200	-4.89710200	0.31578500	H	2.65904400	6.02111700	-4.95874300
O	2.89889900	-2.53261200	-1.26375000	N	-2.09515400	1.90245700	-0.77046600
C	2.58993700	-3.71853900	-1.47723200	C	-2.81822100	1.48021600	-1.86570300
O	1.40109900	-4.16289000	-1.73490700	H	-2.32598000	1.06978000	-2.73721900

C	-4.15930100	1.69665300	-1.64095200	C	0.15398600	5.05052300	2.53561100
N	-4.22087800	2.28560600	-0.38466200	H	-0.86372500	5.41093300	2.33531200
H	-5.08628100	2.40169700	0.15317400	H	0.82100800	5.71168900	1.96009800
C	-2.96831500	2.37210400	0.10994800	H	6.43599100	1.01163200	1.91996700
H	-2.71777100	2.75853800	1.08647700	C	0.49332400	5.11029900	4.02561000
C	-5.36514500	1.39362900	-2.49546200	H	0.39693800	6.13861800	4.39686600
H	-5.40226700	2.08264000	-3.35225400	H	-0.17862300	4.47087400	4.61151100
H	-5.23129600	0.39167700	-2.92682400	H	1.51695400	4.76709900	4.20952000
C	-6.74417600	1.46834700	-1.78459800	O	4.34053900	0.53092000	0.56785300
H	-7.01765000	2.51172600	-1.59244000	C	4.28302200	0.95118700	1.74306200
H	-7.50175600	1.05132700	-2.46205400	O	3.19797200	1.15972200	2.41696800
C	-6.76287300	0.75954500	-0.43076000	C	5.55345400	1.27412600	2.50964300
O	-6.63018300	1.39725900	0.62356300	H	5.56109700	0.72724400	3.46002000
N	-6.84666600	-0.59496300	-0.44793700	H	5.57249600	2.34453600	2.75145400
H	-6.90957500	-1.06048900	-1.34535100	O	0.83769200	0.15547200	3.56881000
C	-6.48766000	-1.39879500	0.72802300	C	0.10821400	-0.88063800	3.65065000
H	-6.96144100	-0.93408500	1.59814000	O	-0.39135000	-1.53687400	2.67504500
H	-6.92740600	-2.39472300	0.59232800	C	-0.21632100	-1.38967500	5.04563800
C	-4.96382900	-1.48221200	0.93847700	H	-0.91187000	-0.66523700	5.49807800
H	-4.57119000	-0.47082700	1.09261700	H	-0.74783700	-2.34350500	4.95019500
H	-4.76692000	-2.03516900	1.86722100	C	1.02846900	-1.52982200	5.93858500
C	-4.24712600	-2.15380400	-0.23400000	H	1.54461900	-0.56235600	5.97913900
H	-4.58467600	-1.72932000	-1.19146400	H	1.72799100	-2.23898000	5.47161000
H	-4.48131900	-3.22634500	-0.28888400	C	0.67605900	-2.00521800	7.35172700
C	-2.72383600	-2.04425900	-0.25963500	H	0.00131500	-1.29705600	7.85308100
O	-2.14192100	-1.32861800	0.60081300	H	1.57737400	-2.10227700	7.97062300
O	-2.18584800	-2.69472300	-1.21602600	H	0.17684600	-2.98404200	7.33332800
O	-0.28884900	3.51104000	0.77273400	O	0.01977800	-1.54023300	-2.22323900
C	0.28204900	3.66864000	1.90057900	H	-0.88871800	-1.33314200	-2.52191000
O	0.95712700	2.79800500	2.53695300				

Pro:

Ca	2.62766600	-0.20858900	-1.12168600	O	2.26007500	-0.91074300	-3.56787200
Mn	0.00495700	2.03811700	-0.29373400	H	2.77287800	-1.73835200	-3.55616400
Mn	1.34543200	0.84818900	1.77922600	H	1.33414800	-1.21709200	-3.46756900
Mn	-0.20580600	-1.16647800	0.69343500	O	-0.78071900	-3.96020400	-3.08707600
Mn	-0.43034500	-3.60984400	-1.34231400	H	-0.13438000	-4.63069500	-3.37653300
O	1.70394700	1.66256900	0.21137800	O	-1.02072200	-5.11955100	-0.61048500
O	-0.39358200	0.75711500	1.09399900	H	-0.76613000	-5.04217500	0.33180300
O	1.52211800	-0.81606800	1.05849200	O	2.71748000	-2.59262700	-1.38005400
O	0.07863000	-0.52769900	-1.15006500	C	2.48559800	-3.81502800	-1.40108600
O	-0.02476200	-2.83497200	0.23708600	O	1.32359400	-4.36504000	-1.56534100
O	4.84788800	0.39783300	-2.11988100	C	3.61464600	-4.83073900	-1.24301200
H	5.23234800	0.65548500	-1.25756000	H	3.45440900	-5.31895700	-0.26958700
H	4.50910000	1.22033400	-2.52803700	H	3.46533500	-5.61953000	-1.99259500

C	5.01735400	-4.22925700	-1.32445100	H	-4.94932700	-2.03303600	1.58532200
H	5.16785000	-3.47236600	-0.54631800	C	-4.34515500	-2.07629000	-0.49495200
H	5.19045500	-3.74500900	-2.29395600	H	-4.61384500	-1.57820900	-1.44004100
H	5.77606300	-5.01154400	-1.19609400	H	-4.64034500	-3.12691100	-0.62004000
O	0.51686700	2.84338700	-1.97482400	C	-2.81858000	-2.04996600	-0.44456500
C	1.66712100	2.81304200	-2.58271900	O	-2.24449400	-1.31286200	0.40015700
O	2.51624700	1.91134000	-2.45758500	O	-2.26070500	-2.77191900	-1.34277100
C	1.90432700	3.99280500	-3.51879200	O	-0.18165200	3.64739700	1.10495000
H	1.06180300	4.01996600	-4.22699400	C	0.40582000	3.59781900	2.22728100
H	1.80461400	4.90924700	-2.91713900	O	1.03004300	2.59172800	2.69979500
C	3.23981500	3.96787900	-4.26570100	C	0.37946200	4.86008200	3.08470100
H	3.32115700	3.02754900	-4.82813400	H	-0.63421700	5.27779000	3.01553100
H	4.06161200	3.95975800	-3.53522100	H	1.03230200	5.58700500	2.57647200
C	3.40269900	5.16181200	-5.21307200	H	6.39804400	0.55014300	2.01845100
H	2.61139100	5.17685800	-5.97579200	C	0.81312800	4.67075300	4.53869300
H	4.36743200	5.12528900	-5.73544000	H	0.78274300	5.62850400	5.07416900
H	3.35428200	6.11505000	-4.66801000	H	0.15401000	3.96576300	5.06025600
N	-1.98923800	2.27627500	-0.77991700	H	1.83125200	4.27088500	4.59626400
C	-2.69301800	1.91907600	-1.91131600	O	4.32461100	0.31615600	0.56852600
H	-2.18158500	1.59542400	-2.80825400	C	4.25387500	0.67759000	1.76632900
C	-4.04154100	2.06831600	-1.67805800	O	3.16761500	0.89330700	2.42580300
N	-4.12930900	2.54989900	-0.37854000	C	5.52444300	0.91651000	2.56495000
H	-5.00310800	2.60044700	0.15735500	H	5.45309600	0.42357600	3.54104900
C	-2.88334300	2.64248700	0.12986700	H	5.63549500	1.99310400	2.75113200
H	-2.64772100	2.95860400	1.13550200	O	0.74709300	-0.00493300	3.50071700
C	-5.23176500	1.78931400	-2.56242000	C	-0.06165200	-0.97447000	3.55067900
H	-5.25405700	2.50620700	-3.39637500	O	-0.58562400	-1.57315200	2.54766800
H	-5.09158200	0.80155300	-3.02419200	C	-0.48254100	-1.47732500	4.92278500
C	-6.62232700	1.83866300	-1.87560500	H	-1.24946000	-0.77788300	5.29358300
H	-6.88002100	2.87036000	-1.61127000	H	-0.96939000	-2.45165400	4.79701400
H	-7.37238100	1.48941800	-2.59829400	C	0.67534100	-1.55235800	5.93000800
C	-6.68736800	1.02816800	-0.58147400	H	1.15135200	-0.56615000	5.99664600
O	-6.54309400	1.57426700	0.52182300	H	1.44169000	-2.24201500	5.54637400
N	-6.83468800	-0.31497800	-0.70537400	C	0.20898100	-2.01438600	7.31439700
H	-6.91660300	-0.70819600	-1.63505500	H	-0.53495600	-1.32319300	7.73524300
C	-6.57422700	-1.22305200	0.41913600	H	1.05087800	-2.06574600	8.01682100
H	-7.05400700	-0.79239800	1.30354100	H	-0.25114900	-3.01153900	7.27171100
H	-7.06901300	-2.17600800	0.19372000	O	-0.06981600	-1.55586000	-2.18879200
C	-5.06980400	-1.41959800	0.68160500	H	-1.01691300	-1.47581800	-2.43861600
H	-4.61819000	-0.44687500	0.90609200				

W3 (water)-W2 (oxyl)

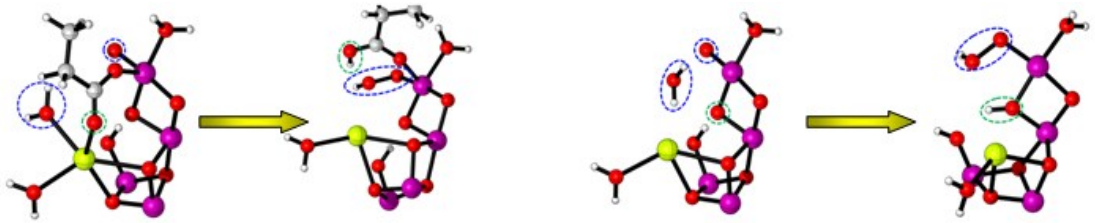

Fig. S5 Pictorial exhibitions for the open-cubane water (W3/crystal or solvent water)-W2 (oxyl) nucleophilic attack with Ca-bound O of Asp170 (left) and O5 (right) as the proton acceptors. The green dotted circle stands for the proton acceptor, the same below.

Table S5 Reaction parameters for the open-cubane W3 (hydroxyl)-W2 (oxyl) nucleophilic attack with Ca-bound O of Asp170 as the proton acceptor:

Spin state	Spin topology (Mn1~Mn4-O7)	Gibbs Free energy (a.u.)		
		Rea	TS	Pro
doublet	ααββα	-3366.2094	-3366.1457	-3366.1458
	αβαβα	-3366.2095	-3366.1461	-3366.1464
	αββαα	-3366.2028	-3366.1477	-3366.1873
	βααβα	-3366.2111	-3366.1464	-3366.1465
	βαβαα	-3366.2022	-3366.1462	-3366.1882
	ββααα	-3366.2014	-3366.1446	-3366.1837
sextet	αααββ	-3366.2048	-3366.1506	-3366.1895
	ααβαβ	-3366.2103	-3366.1477	-3366.1479
	αβααβ	-3366.2109	-3366.1462	-3366.1463
	βαααβ	-3366.2111	-3366.1464	-3366.1468
octet	αααβα	-3366.2125	-3366.1477	-3366.1478
	ααβαα	-3366.2037	-3366.1474	-3366.1896
	αβααα	-3366.2028	-3366.1446	-3366.1862
	βαααα	-3366.2031	-3366.1448	-3366.1867
12-et	ααααβ	-3366.2116	-3366.1471	-3366.1475
14-et	ααααα	-3366.2036	-3366.1453	-3366.1871

Spin state	Spin topology (Mn1~Mn4-O7)	Relative Gibbs Free energy (kcal/mol)			
		$\Delta G^{\neq}$ (Rea-TS)	ΔG(Rea-Pro)	ΔG(Rea)	ΔG(Pro)
doublet	ααββα	40.0	39.9	1.9	27.5
	αβαβα	39.8	39.6	1.9	27.1
	αββαα	34.6	9.7	6.1	1.4
	βααβα	40.6	40.5	0.9	27.0
	βαβαα	35.1	8.8	6.5	0.9

	ββααα	35.6	11.1	7.0	3.7
sextet	αααββ	34.0	9.6	4.8	0.1
	ααβαβ	39.3	39.2	1.4	26.2
	αβααβ	40.6	40.5	1.0	27.2
	βαααβ	40.6	40.3	0.9	26.9
octet	αααβα	40.7	40.6	0.0	26.2
	ααβαα	35.3	8.8	5.5	0.0
	αβααα	36.5	10.4	6.1	2.1
	βαααα	36.6	10.3	5.9	1.8
12-et	ααααβ	40.5	40.2	0.6	26.4
14-et	ααααα	36.6	10.4	5.6	1.6

Spin state	Spin topology (Mn1~Mn4-O7)		Mulliken spin density		
			Rea	TS	Pro
doublet	α	Mn1	2.96	2.94	2.94
	α	Mn2	2.94	2.94	2.94
	β	Mn3	-2.88	-2.85	-2.84
	β	Mn4	-2.68	-2.05	-1.96
	α	O7	0.74	-0.02	-0.04
		O8	0.00	0.11	0.03
	α	Mn1	2.95	2.93	2.93
	β	Mn2	-2.91	-2.91	-2.91
	α	Mn3	2.87	2.89	2.91
	β	Mn4	-2.64	-2.03	-1.97
	α	O7	0.78	-0.03	-0.04
		O8	0.00	0.10	0.03
	α	Mn1	2.94	2.93	2.93
	β	Mn2	-2.93	-2.93	-2.92
	β	Mn3	-2.91	-2.86	-2.84
	α	Mn4	2.74	3.27	3.84
	α	O7	1.01	0.36	0.01
		O8	0.00	0.30	0.02
	β	Mn1	-2.94	-2.92	-2.92
	α	Mn2	2.93	2.93	2.93
	α	Mn3	2.91	2.91	2.92
	β	Mn4	-2.65	-2.01	-1.96
	α	O7	0.79	-0.03	-0.04
		O8	0.00	0.09	0.04
	β	Mn1	-2.94	-2.93	-2.93
	α	Mn2	-2.91	2.92	2.92
	β	Mn3	-2.89	-2.84	-2.82
	α	Mn4	2.74	3.27	3.84
	α	O7	1.01	0.36	0.01
		O8	0.00	0.30	0.02

	β	Mn1	-2.95	-2.94	-2.94
	β	Mn2	-2.94	-2.94	-2.93
	α	Mn3	2.89	2.91	2.92
	α	Mn4	2.80	3.32	3.85
	α	O7	1.01	0.35	0.01
		O8	0.00	0.30	0.02
sextet	α	Mn1	2.96	2.96	2.95
	α	Mn2	2.96	2.95	2.94
	α	Mn3	2.92	2.87	2.84
	β	Mn4	-2.74	-3.27	-3.84
	β	O7	-1.01	-0.36	-0.01
		O8	0.00	-0.30	-0.02
	α	Mn1	2.96	2.94	2.94
	α	Mn2	2.94	2.93	2.93
	β	Mn3	-2.87	-2.89	-2.93
	α	Mn4	2.64	2.03	1.97
	β	O7	-0.78	0.03	0.04
		O8	0.00	-0.10	-0.03
	α	Mn1	2.95	-2.93	2.93
	β	Mn2	-2.91	-2.92	-2.92
	α	Mn3	2.88	2.85	2.84
	α	Mn4	2.68	2.05	1.96
	β	O7	-0.74	0.02	0.04
		O8	0.00	-0.11	-0.03
	β	Mn1	-2.94	-2.92	-2.92
	α	Mn2	2.93	2.93	2.93
	α	Mn3	2.91	2.88	2.87
	α	Mn4	2.68	2.05	1.96
	β	O7	-0.74	0.03	0.04
		O8	0.00	-0.10	-0.03
octet	α	Mn1	2.96	2.95	2.95
	α	Mn2	2.96	2.95	2.95
	α	Mn3	2.91	2.92	2.93
	β	Mn4	-2.65	-2.02	-1.96
	α	O7	0.79	-0.03	-0.04
		O8	0.00	0.09	0.03
	α	Mn1	2.96	2.94	2.94
	α	Mn2	2.94	2.94	2.94
	β	Mn3	-2.89	-2.83	-2.81
	α	Mn4	2.74	3.27	3.84
	α	O7	1.01	0.36	0.01
		O8	0.00	0.30	0.02
	α	Mn1	2.95	2.93	2.93
	β	Mn2	-2.91	-2.91	-2.91

	α	Mn3	2.89	2.91	2.92
	α	Mn4	2.80	3.31	3.85
	α	O7	1.01	0.35	0.01
		O8	0.00	0.30	0.02
	β	Mn1	-2.94	-2.93	-2.92
	α	Mn2	2.93	2.93	2.93
	α	Mn3	2.92	2.94	2.95
	α	Mn4	2.80	3.32	3.85
	α	O7	1.01	0.35	0.01
		O8	0.00	0.30	0.02
12-et	α	Mn1	2.97	2.95	2.95
	α	Mn2	2.96	2.95	2.95
	α	Mn3	2.92	2.87	2.88
	α	Mn4	2.68	2.05	1.96
	β	O7	-0.74	0.03	0.04
		O8	0.00	-0.10	-0.03
14-et	α	Mn1	2.97	2.95	2.95
	α	Mn2	2.96	2.95	2.95
	α	Mn3	2.93	2.95	2.95
	α	Mn4	2.80	3.32	3.85
	α	O7	1.01	0.35	0.01
		O8	0.00	0.30	0.02

Rea:

Ca	2.36535900	-0.21295000	-1.30529900	C	3.20396800	-3.62765600	-0.71009300
Mn	-0.10820400	1.89356000	-0.57334400	O	2.02289300	-4.14173800	-0.57457700
Mn	1.21130900	0.98364100	1.68526200	C	4.34608100	-4.59595100	-0.41538300
Mn	-0.13177100	-1.33664200	0.91212600	H	5.24440600	-4.20173300	-0.90604800
Mn	0.26002100	-3.46455800	-0.71005700	H	4.52837100	-4.52973300	0.66907700
O	1.56435900	1.70115700	0.05834900	C	4.07879200	-6.05116700	-0.81248600
O	-0.45976000	0.69176000	0.84571600	H	3.90915600	-6.14253700	-1.89299700
O	1.52721700	-0.74339200	1.28555400	H	3.19083800	-6.43880200	-0.30259300
O	0.42433500	-1.72137100	-0.80422800	H	4.93759500	-6.68164000	-0.54941100
O	0.03488500	-3.10645500	1.07147800	O	0.51274000	3.17264500	-1.88870800
O	4.83073200	-0.34547900	-2.01259300	C	1.64594600	3.04561900	-2.53213200
H	5.10057500	0.12207900	-1.19314800	O	2.29567800	1.99104000	-2.64611400
H	4.84983900	-1.28794600	-1.74380200	C	2.13150700	4.34399400	-3.16666800
O	1.79371700	-1.43866900	-3.40938600	H	1.25939400	4.87515500	-3.57318000
H	1.26875300	-2.24397000	-3.14818500	H	2.50061400	4.97409900	-2.34070700
H	2.50972500	-1.77552100	-3.97207500	C	3.22183000	4.15988800	-4.22597100
O	0.50073100	-3.78656400	-2.53303000	H	2.83745000	3.51991400	-5.03338100
O	-0.32961700	-5.48133100	-0.11599200	H	4.06217100	3.61068500	-3.78254300
H	-1.26170900	-5.43771700	-0.40686200	C	3.70546900	5.49429400	-4.80410900
H	-0.35367300	-5.25766100	0.83865500	H	2.88361800	6.04819600	-5.27987200
O	3.44774200	-2.44853500	-1.02320700	H	4.12743300	6.13943800	-4.02037300

H	4.48459700	5.33883300	-5.56174300	C	0.05688600	3.66402400	1.74541600
N	-2.13720100	2.07615100	-1.08526000	O	0.77197800	2.83811600	2.37528600
C	-2.75733200	1.59237600	-2.21726200	C	-0.17099600	5.04080400	2.35711000
H	-2.18256500	1.18320900	-3.03538500	H	-1.23675200	5.28001500	2.23744600
C	-4.11945900	1.69836400	-2.07770300	H	0.36367700	5.75400400	1.71099500
N	-4.31131300	2.26888700	-0.82390700	C	0.27852000	5.17917500	3.81165200
H	-5.20083500	2.23982300	-0.32050300	H	0.09863700	6.20103500	4.16925900
C	-3.09745700	2.46110200	-0.25750000	H	-0.26692900	4.48580300	4.46315100
H	-2.93947100	2.85104000	0.73688400	H	1.34589000	4.95620300	3.91613000
C	-5.22781600	1.34876900	-3.03443500	O	4.09805900	0.51067800	0.44263300
H	-5.32180600	2.12742300	-3.80671600	C	4.07786200	0.98248800	1.59856000
H	-4.93540900	0.43400000	-3.56838700	O	3.01599000	1.23626000	2.29443000
C	-6.63028300	1.15687700	-2.40244200	C	5.37403900	1.32081400	2.31685100
H	-7.04462900	2.12448500	-2.09747100	H	6.23786500	1.03221500	1.71144500
H	-7.30235100	0.74208500	-3.16614400	H	5.40604700	0.80712200	3.28518200
C	-6.60742900	0.28299300	-1.15089400	H	5.40854300	2.39884100	2.51939000
O	-6.56715200	0.78414200	-0.02030000	O	0.56156300	0.45315300	3.49269600
N	-6.57424200	-1.06045700	-1.35398300	C	-0.27996400	-0.47661600	3.68732500
H	-6.58290000	-1.40560900	-2.30563400	O	-0.76912000	-1.23146200	2.78832600
C	-6.34399900	-2.01201700	-0.26327900	C	-0.72737800	-0.73841300	5.11771500
H	-6.96852300	-1.70101300	0.58128700	H	-1.72482800	-1.19468700	5.07781700
H	-6.70245200	-2.99140500	-0.60534200	H	-0.05023300	-1.51284300	5.51486500
C	-4.87635200	-2.08401100	0.18907700	C	-0.70570400	0.49263000	6.03173900
H	-4.56721300	-1.10123200	0.56004800	H	-1.37731400	1.26016400	5.61908600
H	-4.81777600	-2.77392700	1.04362700	H	0.30081600	0.92889800	6.01954300
C	-3.91249000	-2.53971200	-0.91314300	C	-1.12289300	0.15675400	7.46757000
H	-3.99680800	-1.87121800	-1.78455500	H	-2.13979200	-0.25901200	7.50445000
H	-4.14151000	-3.55291800	-1.26829900	H	-1.10517700	1.05094100	8.10409600
C	-2.44534100	-2.49392700	-0.49920200	H	-0.44612300	-0.58448800	7.91569600
O	-2.08704200	-1.60631700	0.31200000	O	0.00670600	0.59290300	-1.85133600
O	-1.68754300	-3.37800900	-1.04836700	H	0.23285800	1.02324200	-2.69700900
O	-0.50032500	3.45679400	0.61395700				

TS:

Ca	2.22977500	0.55952400	-1.18631500	H	4.95167900	0.33337100	-1.13017000
Mn	-0.58303300	1.99074400	-0.56756200	H	4.67558300	-0.97619900	-1.98911100
Mn	0.87512400	1.27294700	1.66587400	O	2.43139600	-2.79802700	-3.56534700
Mn	0.15842700	-1.31008900	0.69248600	H	2.58922800	-3.52530200	-4.19751700
Mn	1.14235900	-3.29523600	-0.85648200	H	3.27739400	-2.78737200	-2.89475300
O	1.07119500	2.19051000	0.10319700	O	1.45660800	-3.92305700	-2.52154800
O	-0.66931000	0.69489900	0.75403300	O	0.94252500	-5.41153000	-0.06993200
O	1.60060500	-0.28215600	1.14584000	H	-0.01183800	-5.44441000	-0.28671300
O	0.91802200	-1.51763900	-0.98081700	H	0.96393900	-5.09577100	0.85719200
O	0.76355100	-2.93666700	0.93684700	O	4.39150400	-2.70615800	-2.03138500
O	4.45940100	-0.01260200	-1.90046100	C	4.25648100	-3.22537300	-0.85879200

O	3.16341900	-3.54086500	-0.32980000	C	-4.25560000	-2.99677700	0.22235800
C	5.54187900	-3.44408000	-0.06867200	H	-4.10294800	-1.94945200	0.50427400
H	6.20258500	-4.05820300	-0.69781500	H	-4.02818900	-3.59706800	1.11559000
H	6.04093500	-2.46525100	0.00511500	C	-3.28694100	-3.36496000	-0.90853700
C	5.34882500	-4.06508700	1.31403600	H	-3.54825700	-2.80641700	-1.82170400
H	4.88056000	-5.05340100	1.23787800	H	-3.33848800	-4.43143400	-1.16367600
H	4.70040100	-3.44045400	1.93884900	C	-1.82811500	-3.01598000	-0.61193800
H	6.31594500	-4.17971800	1.82001400	O	-1.62822500	-1.97105900	0.07930900
O	-0.17456300	3.39014800	-1.89819300	O	-0.93949400	-3.77691600	-1.10365800
C	0.98245100	3.50360000	-2.48708600	O	-1.30618000	3.39009900	0.63633600
O	1.84434900	2.60229600	-2.58351100	C	-0.83695600	3.64909700	1.80157200
C	1.23242700	4.88141800	-3.09046700	O	0.00383300	2.95437400	2.43034800
H	0.28986300	5.24052300	-3.52673200	C	-1.36155300	4.92406900	2.45043600
H	1.43903600	5.55558600	-2.24286700	H	-2.45335500	4.93105900	2.32454300
C	2.37802200	4.93654600	-4.10490300	H	-0.99063400	5.75651100	1.83311700
H	2.16010900	4.24973500	-4.93582000	C	-0.96271800	5.10814200	3.91447500
H	3.29267200	4.55617200	-3.63222500	H	-1.36144900	6.05502200	4.30027500
C	2.61056200	6.35111800	-4.64705900	H	-1.34999000	4.29251000	4.53675000
H	1.71442200	6.74102700	-5.15039900	H	0.12693400	5.11755100	4.02670700
H	2.86544300	7.05117900	-3.83877900	O	3.86778700	1.35896600	0.46998000
H	3.43387500	6.36750700	-5.37310200	C	3.72519600	1.77505100	1.64404700
N	-2.58626600	1.73080300	-1.14134400	O	2.60986200	1.87984500	2.28830000
C	-3.05739200	1.04853400	-2.24347500	C	4.94266700	2.19979800	2.44934000
H	-2.38885300	0.72509800	-3.02772200	H	5.82358500	2.27541200	1.80543300
C	-4.40895300	0.84407300	-2.11694100	H	5.12911300	1.45621200	3.23570100
N	-4.75167700	1.42913000	-0.90307100	H	4.75177100	3.15789400	2.94568800
H	-5.61491000	1.21130100	-0.39916300	O	0.36067500	0.51101900	3.40453500
C	-3.62646900	1.93086900	-0.34411000	C	-0.27607700	-0.58696600	3.51477300
H	-3.58126400	2.40428000	0.62520900	O	-0.57436900	-1.36498300	2.56163900
C	-5.38670900	0.18557600	-3.05282200	C	-0.69234700	-1.00722100	4.91651000
H	-5.64736000	0.87200600	-3.87293100	H	-1.47108900	-1.77384000	4.82144200
H	-4.87748400	-0.66531200	-3.52609000	H	0.18472700	-1.50057000	5.36682200
C	-6.71550400	-0.29381300	-2.41471300	C	-1.14857500	0.15225800	5.81307200
H	-7.34656200	0.56580900	-2.16163800	H	-2.01725900	0.64491900	5.35078300
H	-7.26228900	-0.89023100	-3.15784800	H	-0.35173900	0.90530900	5.85263900
C	-6.50629700	-1.07595100	-1.12018600	C	-1.51107900	-0.31421400	7.22694400
O	-6.57433100	-0.51702400	-0.01811700	H	-2.32458200	-1.05321700	7.21049700
N	-6.19119600	-2.39059900	-1.25716900	H	-1.83861200	0.52828100	7.84994100
H	-6.11485900	-2.77063500	-2.19247400	H	-0.64947900	-0.78147700	7.72447300
C	-5.73622400	-3.21212700	-0.13149700	O	-0.13859000	0.76395500	-1.88508500
H	-6.36030000	-2.95300500	0.73024900	H	-0.11956500	1.28475100	-2.70835400
H	-5.93522300	-4.26025400	-0.39036000				

Pro:

Ca	2.12578800	0.75105300	-1.20578800	Mn	-0.76670800	1.95850600	-0.50391000

Mn	0.73013500	1.21253600	1.69438600	C	-4.50462000	0.59180600	-2.09507600
Mn	0.22829700	-1.36566100	0.57536900	N	-4.89758800	1.15033000	-0.88376300
Mn	1.40741900	-3.10602900	-1.10156300	H	-5.74838400	0.87246600	-0.38869900
O	0.86808200	2.22873200	0.18228600	C	-3.81224200	1.71999000	-0.31065200
O	-0.75890100	0.58199200	0.73810400	H	-3.80751000	2.19263900	0.66005200
O	1.58491700	-0.23971700	1.10836900	C	-5.42902100	-0.12231200	-3.04411100
O	0.95670600	-1.34587200	-1.08765600	H	-5.72881400	0.55200400	-3.86102900
O	1.01560400	-2.93407800	0.69751200	H	-4.86025700	-0.93328600	-3.51963200
O	4.50263700	0.46757600	-1.70578600	C	-6.72748900	-0.69483900	-2.42039100
H	4.77299600	0.89691700	-0.86208800	H	-7.41600000	0.11849800	-2.16400800
H	4.95199000	-0.40056800	-1.75146300	H	-7.22846300	-1.31939100	-3.17272200
O	2.76299200	-1.96096400	-3.22200400	C	-6.47313500	-1.47371900	-1.13184000
H	2.76380300	-2.02616700	-4.19495400	O	-6.58500600	-0.93054200	-0.02555800
H	4.16002900	-2.29750300	-2.46122000	N	-6.07066200	-2.76300900	-1.28166700
O	2.01490800	-3.19494900	-2.89779000	H	-5.95321700	-3.11931400	-2.22215200
O	1.40944400	-5.25222900	-0.75973700	C	-5.54178800	-3.55815300	-0.16907700
H	0.43243700	-5.29591000	-0.87674100	H	-6.15247400	-3.32444600	0.70909400
H	1.53996200	-5.22908400	0.20901000	H	-5.69837100	-4.61595400	-0.41860100
O	5.01542900	-2.33599300	-1.91347600	C	-4.06287300	-3.26937800	0.13616500
C	4.80397200	-3.00132200	-0.76219500	H	-3.95201900	-2.21422100	0.40860200
O	3.70779300	-3.41835400	-0.41635100	H	-3.77750600	-3.85095700	1.02504600
C	6.06565600	-3.16626300	0.05702400	C	-3.11203700	-3.59671500	-1.02131900
H	6.80031700	-3.68719000	-0.57446200	H	-3.43091000	-3.06408900	-1.93215300
H	6.48446500	-2.16183500	0.22127800	H	-3.11817400	-4.66713500	-1.26699600
C	5.83871000	-3.89624000	1.37993300	C	-1.65860400	-3.17529000	-0.78257000
H	5.45372100	-4.90812900	1.20867300	O	-1.49594000	-2.15708200	-0.03497600
H	5.10969300	-3.36492100	2.00213400	O	-0.75167900	-3.83450400	-1.36582700
H	6.78055900	-3.97512100	1.93595200	O	-1.59053900	3.23530100	0.76831200
O	-0.43395200	3.47548800	-1.74389700	C	-1.14747500	3.45907400	1.95143900
C	0.71580300	3.69495900	-2.31253300	O	-0.26387900	2.79086700	2.54688300
O	1.63089400	2.85415100	-2.46937200	C	-1.76708700	4.65428100	2.66613700
C	0.89236600	5.12572500	-2.81147700	H	-2.85698500	4.58134300	2.54341700
H	-0.07165900	5.47200100	-3.20910600	H	-1.46724500	5.54458000	2.09264000
H	1.07994000	5.74182200	-1.91650700	C	-1.37619500	4.79249600	4.13730300
C	2.02021200	5.31393000	-3.82988000	H	-1.84641800	5.68315500	4.57344600
H	1.82302000	4.68425800	-4.71003000	H	-1.69382800	3.91681800	4.71579500
H	2.95781300	4.94184400	-3.39724100	H	-0.29003100	4.88225700	4.24840100
C	2.17958800	6.77556800	-4.26269900	O	3.69850500	1.63866600	0.53354900
H	1.25944400	7.16039100	-4.72494200	C	3.52535600	1.97474800	1.73256100
H	2.41250800	7.42212900	-3.40475800	O	2.41201800	1.93967200	2.37624300
H	2.99128500	6.88752200	-4.99350400	C	4.70611100	2.46610700	2.55548300
N	-2.75243400	1.58878500	-1.09637600	H	5.58055900	2.63290500	1.91974700
C	-3.16726900	0.88101900	-2.20544400	H	4.94765400	1.71715700	3.32133000
H	-2.46694400	0.59957600	-2.97803700	H	4.43870000	3.39094000	3.07915000

O	0.27030100	0.33166900	3.38745100	H	-0.60962500	0.58096800	5.80330900
C	-0.25236300	-0.83136100	3.44668400	C	-1.58326100	-0.83287700	7.13489700
O	-0.47664900	-1.58965700	2.46159700	H	-2.26527400	-1.69372500	7.09002500
C	-0.61699200	-1.34438100	4.83257300	H	-2.05576200	-0.06564900	7.76222000
H	-1.26012200	-2.22411200	4.70935000	H	-0.66709000	-1.16276900	7.64494900
H	0.32023000	-1.69338800	5.29602900	O	-0.25096100	0.87177800	-1.91452400
C	-1.27342200	-0.28999400	5.73590700	H	-0.27912500	1.46533700	-2.68665700
H	-2.20166400	0.06296800	5.26154300				

Table S6 Reaction parameters for the open-cubane crystal or solvent water-W2 (oxyl) nucleophilic attack with O5 as the proton acceptor:

Spin state	Spin topology (Mn1~Mn4-O7)	Gibbs Free energy (a.u.)		
		Rea	TS	Pro
doublet	ααββα	-3366.2184	-3366.1729	-3366.1852
	αβαβα	-3366.2187	-3366.1734	-3366.1856
	αββαα	-3366.2084	-3366.1620	-3366.2210
	βααβα	-3366.2189	-3366.1732	-3366.1853
	βαβαα	-3366.2086	-3366.1624	-3366.2211
	ββααα	-3366.2082	-3366.1601	-3366.2216
sextet	αααββ	-3366.2099	-3366.1635	-3366.2236
	ααβαβ	-3366.2198	-3366.1747	-3366.1870
	αβααβ	-3366.2195	-3366.1739	-3366.1859
	βαααβ	-3366.2196	-3366.1737	-3366.1857
octet	αααβα	-3366.2206	-3366.1747	-3366.1867
	ααβαα	-3366.2106	-3366.1638	-3366.2226
	αβααα	-3366.2091	-3366.1612	-3366.2226
	βαααα	-3366.2088	-3366.1611	-3366.2224
12-et	ααααβ	-3366.2208	-3366.1746	-3366.1865
14-et	ααααα	-3366.2100	-3366.1619	-3366.2231

Spin state	Spin topology (Mn1~Mn4-O7)	Relative Gibbs Free energy (kcal/mol)			
		$\Delta G^{\neq}$(Rea-TS)	ΔG(Rea-Pro)	ΔG(Rea)	ΔG(Pro)
doublet	ααββα	28.6	20.8	1.5	24.1
	αβαβα	28.4	20.8	1.3	23.8
	αββαα	29.1	-7.9	7.8	1.6
	βααβα	28.7	21.1	1.2	24.0
	βαβαα	29.0	-7.8	7.7	1.6
	ββααα	30.2	-8.4	7.9	1.3
sextet	αααββ	29.1	-8.6	6.8	0.0
	ααβαβ	28.3	20.6	0.6	23.0
	αβααβ	28.6	21.1	0.8	23.7
	βαααβ	28.8	21.3	0.8	23.8

octet	ααaβα	28.8	21.3	0.1	23.2
	ααβαα	29.4	-7.5	6.4	0.6
	αβααα	30.1	-8.5	7.3	0.6
	βαααα	29.9	-8.5	7.5	0.8
12-et	αααaβ	29.0	21.5	0.0	23.3
14-et	ααααα	30.2	-8.2	6.8	0.3

Spin state	Spin topology (Mn1~Mn4-O7)		Mulliken spin density		
			Rea	TS	Pro
doublet	α	Mn1	2.96	2.96	2.95
	α	Mn2	2.94	2.95	2.95
	β	Mn3	-2.88	-2.79	-2.83
	β	Mn4	-2.69	-2.47	-1.94
	α	O7	0.73	0.03	-0.06
		O8	0.00	0.44	-0.02
	α	Mn1	2.96	2.95	2.95
	β	Mn2	-2.92	-2.92	-2.93
	α	Mn3	2.88	2.78	2.80
	β	Mn4	-2.66	-2.47	-1.93
	α	O7	0.77	0.02	-0.04
		O8	0.00	0.43	-0.02
	α	Mn1	2.96	2.95	2.95
	β	Mn2	-2.94	-2.93	-2.93
	β	Mn3	-2.91	-2.86	-2.85
	α	Mn4	2.75	3.32	3.92
	α	O7	1.03	0.45	-0.04
		O8	0.01	0.24	0.00
	β	Mn1	-2.96	-2.95	-2.95
	α	Mn2	2.94	2.94	2.94
	α	Mn3	2.90	2.82	2.84
	β	Mn4	-2.66	-2.47	-1.92
	α	O7	0.77	0.02	-0.04
		O8	0.00	0.43	-0.02
	β	Mn1	-2.96	-2.95	-2.95
	α	Mn2	2.92	2.92	2.93
	β	Mn3	-2.88	-2.82	-2.81
	α	Mn4	2.75	3.31	3.92
	α	O7	1.03	0.46	-0.04
		O8	0.01	0.24	0.00
	β	Mn1	-2.96	-2.96	-2.95
	β	Mn2	-2.94	-2.94	-2.94
	α	Mn3	2.89	2.89	2.84
	α	Mn4	2.79	3.32	3.95
	α	O7	1.03	0.48	-0.02

		O8	0.01	0.26	0.00
sextet	α	Mn1	2.97	2.97	2.96
	α	Mn2	2.96	2.95	2.95
	α	Mn3	2.91	2.86	2.86
	β	Mn4	-2.75	-3.30	-3.92
	β	O7	-1.03	-0.46	0.04
		O8	-0.01	-0.24	0.00
	α	Mn1	2.97	2.96	2.96
	α	Mn2	2.94	2.95	2.95
	β	Mn3	-2.87	-2.78	-2.80
	α	Mn4	2.66	2.47	1.93
	β	O7	-0.77	-0.03	0.04
		O8	0.00	-0.43	0.02
	α	Mn1	2.96	2.95	2.95
	β	Mn2	-2.92	-2.92	-2.93
	α	Mn3	2.88	2.79	2.83
	α	Mn4	2.69	2.47	1.94
	β	O7	-0.73	0.00	0.06
		O8	0.00	-0.44	0.02
	β	Mn1	-2.95	-2.95	-2.95
	α	Mn2	2.94	2.94	2.94
	α	Mn3	2.91	2.83	2.87
	α	Mn4	2.69	2.47	1.94
	β	O7	-0.73	0.00	0.06
		O8	0.00	-0.44	0.02
octet	α	Mn1	2.97	2.96	2.96
	α	Mn2	2.96	2.96	2.96
	α	Mn3	2.91	2.83	2.85
	β	Mn4	-2.66	-2.47	-1.93
	α	O7	0.77	0.02	-0.04
		O8	0.00	0.43	-0.02
	α	Mn1	2.97	2.96	2.96
	α	Mn2	2.94	2.94	2.95
	β	Mn3	-2.88	-2.82	-2.81
	α	Mn4	2.75	3.32	3.92
	α	O7	1.03	0.45	-0.04
		O8	0.01	0.24	0.00
	α	Mn1	2.96	2.96	2.95
	β	Mn2	-2.92	-2.92	-2.92
	α	Mn3	2.89	2.88	2.84
	α	Mn4	2.79	3.33	3.95
	α	O7	1.03	0.47	-0.02
		O8	0.01	0.26	0.00
	β	Mn1	-2.95	-2.95	-2.94

	α	Mn2	2.94	2.93	2.93
	α	Mn3	2.92	2.92	2.88
	α	Mn4	2.79	3.33	3.95
	α	O7	1.03	0.47	-0.02
		O8	0.01	0.26	0.00
12-et	α	Mn1	2.97	2.96	2.96
	α	Mn2	2.96	2.96	2.96
	α	Mn3	2.92	2.84	2.88
	α	Mn4	2.69	2.47	1.94
	β	O7	-0.73	0.00	0.06
		O8	0.00	-0.43	0.02
14-et	α	Mn1	2.97	2.97	2.96
	α	Mn2	2.96	2.95	2.95
	α	Mn3	2.93	2.93	2.89
	α	Mn4	2.79	3.34	3.94
	α	O7	1.03	0.46	-0.02
		O8	0.01	0.25	0.00

Rea:

Ca	2.28609300	0.66174400	-1.27110800	C	5.93340100	-1.56863300	-3.82499200
Mn	-0.43969500	1.88817300	0.25669300	H	6.28688500	-1.04821000	-2.92689500
Mn	1.48790500	0.71297500	1.85812300	H	5.52835800	-0.81352400	-4.50829400
Mn	0.53504900	-1.56655300	0.47403600	H	6.79552300	-2.04535400	-4.30822300
Mn	0.93222700	-2.92587900	-1.83412900	O	-0.61744900	3.75959600	-0.33568800
O	1.33179900	2.01410200	0.59166700	C	-0.31618000	4.35981100	-1.43408400
O	-0.21453600	0.25704600	1.13602300	O	0.07786700	3.79196600	-2.48546800
O	2.06677800	-0.64925900	0.80703200	C	-0.50387700	5.87294200	-1.39569800
O	0.68782900	-1.23642900	-1.33597100	H	-1.56816800	6.05805500	-1.18234200
O	1.18823500	-3.13813200	-0.01359100	H	0.03756600	6.24803900	-0.51446800
O	2.46716400	2.53631500	-2.79292700	C	-0.06912400	6.60632400	-2.66735700
H	3.23287400	3.11258300	-2.94147100	H	-0.60879700	6.18847800	-3.52751300
H	1.66248200	3.11610800	-2.78725500	H	0.99584600	6.40750900	-2.85450600
O	-1.54775700	-0.63092900	-3.17219000	C	-0.30723900	8.11775400	-2.57788500
H	-0.94439300	-1.28250700	-3.58075100	H	-1.37148300	8.34565500	-2.42456900
H	-0.98552700	-0.23547100	-2.47435200	H	0.24942000	8.56277600	-1.74114000
O	0.56018200	-2.80453200	-3.62747700	H	0.01227100	8.62456900	-3.49765200
O	1.34315700	-5.04880200	-1.82208300	N	-2.47784600	1.59400200	-0.04195200
H	2.25062700	-4.98968000	-2.18408700	C	-3.11501100	1.31466300	-1.23418500
H	1.45408200	-5.10221400	-0.84902900	H	-2.58236000	1.28017400	-2.17320100
O	3.48926700	-0.81636000	-2.66123600	C	-4.43695600	1.03868400	-0.98794200
C	3.62947200	-2.04196200	-2.80763100	N	-4.58969700	1.17181100	0.38786800
O	2.77773200	-2.94841100	-2.42984900	H	-5.39083900	0.80414600	0.90760800
C	4.87555500	-2.61408200	-3.47509900	C	-3.38708600	1.48699200	0.91884400
H	5.28279000	-3.38543400	-2.80559300	H	-3.19409700	1.61941000	1.97273400
H	4.53582600	-3.15144400	-4.37325900	C	-5.53865200	0.67629400	-1.94734000

H	-5.87889900	1.57171000	-2.48911200	C	-0.02062700	3.37070300	5.52854400
H	-5.10577400	0.01391700	-2.70934200	H	-0.37982300	4.08985600	6.27554500
C	-6.79184900	0.01414600	-1.32023000	H	-0.23014200	2.35926100	5.89745100
H	-7.37194800	0.75316800	-0.75589500	H	1.06665600	3.47078900	5.44246600
H	-7.43397700	-0.35294600	-2.13252600	O	4.13176300	1.32323100	0.15592800
C	-6.44893600	-1.10492400	-0.34059100	C	4.23438000	1.42437300	1.39517900
O	-6.41418900	-0.89970800	0.88036600	O	3.28735100	1.22574900	2.26195000
N	-6.13095300	-2.30800400	-0.88520000	C	5.56047900	1.81129000	2.02761100
H	-6.11864700	-2.39042900	-1.89455900	H	6.31305800	1.99150100	1.25533600
C	-5.54362900	-3.38931700	-0.08969200	H	5.89623400	1.00769000	2.69495500
H	-6.09099000	-3.42814100	0.85779500	H	5.42929400	2.71001500	2.64272900
H	-5.72728500	-4.32914300	-0.62614900	O	1.38165400	-0.51712300	3.40739800
C	-4.04411000	-3.19453700	0.18930300	C	0.81907100	-1.65563300	3.37209900
H	-3.90170500	-2.26248700	0.74727200	O	0.31918200	-2.19763100	2.33815900
H	-3.71116700	-4.00931400	0.84870300	C	0.71635000	-2.42215100	4.68070500
C	-3.18955300	-3.17483200	-1.08178800	H	1.33418200	-1.90843600	5.42650700
H	-3.50984200	-2.37244500	-1.76510200	H	-0.33103300	-2.34534500	5.01467900
H	-3.26301000	-4.11646700	-1.64100900	C	1.10545000	-3.90373200	4.55310100
C	-1.71889700	-2.88468700	-0.84534100	H	2.14598400	-3.97361600	4.20274200
O	-1.38216100	-2.18636000	0.14550400	H	0.48447000	-4.36691000	3.77598100
O	-0.92311400	-3.37832400	-1.72443600	C	0.95333700	-4.65889500	5.87749000
O	-0.98564300	2.69247700	2.01202700	H	1.58553600	-4.22255800	6.66336700
C	-0.25510600	2.69686000	3.05863500	H	1.23985500	-5.71269900	5.76611400
O	0.79779800	2.01948500	3.22429400	H	-0.08600900	-4.63129700	6.23436300
C	-0.70297700	3.62104800	4.18342000	O	-0.12004500	1.31659800	-1.46206200
H	-1.79561100	3.53883600	4.26000600	H	-0.19886200	2.13133500	-2.02842200
H	-0.50798300	4.64553800	3.83000200				

TS:

Ca	2.48395000	-0.48435500	-0.96701800	O	-0.25142300	-2.36043800	-3.65894900
Mn	0.42902800	1.92379500	0.17982900	O	-0.83397400	-5.07988200	-2.09418700
Mn	1.38903800	0.07270000	1.99480000	H	0.08871700	-5.40455600	-2.16808300
Mn	-0.33712600	-1.58833200	0.45804600	H	-1.08976000	-5.21864100	-1.16082300
Mn	-0.24036200	-2.97639500	-1.89035700	O	3.04106600	-2.34425800	-2.30285100
O	2.00407500	1.25783500	0.74092400	C	2.68299200	-3.52247800	-2.52681300
O	-0.22743600	0.42700500	1.06546700	O	1.49916600	-3.98612500	-2.32502800
O	1.41276900	-1.43190400	1.00314700	C	3.68116600	-4.53502900	-3.08554300
O	0.15202800	-1.29473400	-1.30078700	H	3.64691700	-5.42064600	-2.43483100
O	-0.31452500	-3.27162400	-0.04667400	H	3.28569300	-4.86859900	-4.05680800
O	3.63715700	1.03848300	-2.46711700	C	5.10857100	-4.00804500	-3.22586300
H	4.59666600	1.14363900	-2.56282900	H	5.51089600	-3.69474200	-2.25498300
H	3.23858200	1.94693900	-2.49072300	H	5.14321200	-3.13953600	-3.89385500
O	-0.68437000	-0.62058100	-3.56637600	H	5.76643000	-4.78517600	-3.63591100
H	0.11125000	-0.34998500	-4.06499600	O	1.17846800	3.67545000	-0.38682000
H	-0.40225900	-0.58426500	-2.56630600	C	1.90204200	4.03411200	-1.38589000

O	2.16539700	3.31459200	-2.38686100	H	-4.83357500	-2.62640300	-1.41823700
C	2.44032900	5.45880400	-1.29934500	C	-2.87357400	-1.93382300	-0.93936300
H	1.59000800	6.11631800	-1.06584200	O	-2.27628400	-1.35430700	0.02650300
H	3.09093700	5.50072000	-0.41156900	O	-2.34198500	-2.65918400	-1.82384900
C	3.18715600	5.94280300	-2.54505800	O	0.09174200	2.97319800	1.85502900
H	2.52044200	5.87581600	-3.41589900	C	0.59532600	2.68861500	2.99476500
H	4.02271800	5.26068600	-2.75377300	O	1.19653600	1.62004300	3.28853700
C	3.70750900	7.37632500	-2.39185100	C	0.45915300	3.76213600	4.06780200
H	2.88507700	8.08344300	-2.21396500	H	-0.56078300	4.16518900	4.00226700
H	4.40390900	7.46099900	-1.54568600	H	1.12230900	4.58588500	3.76133500
H	4.23895500	7.70434300	-3.29463000	C	0.79057800	3.29442700	5.48509600
N	-1.50060100	2.51655200	-0.37535000	H	0.69062100	4.12723800	6.19279500
C	-2.12587000	2.29270300	-1.58433500	H	0.11757600	2.48942400	5.80432000
H	-1.57768500	1.88764900	-2.42290700	H	1.81415500	2.90882300	5.54221900
C	-3.45606900	2.62391800	-1.47931800	O	4.24081300	-0.63446900	0.68657000
N	-3.61671000	3.06900800	-0.17273600	C	4.20736000	-0.53509600	1.93074300
H	-4.52874400	3.15808500	0.28576900	O	3.16551700	-0.24993400	2.64930900
C	-2.42616100	2.96978000	0.45920400	C	5.46616200	-0.76264900	2.75111400
H	-2.25644400	3.20809500	1.49839000	H	6.32586000	-0.92310300	2.09494300
C	-4.56219400	2.57456100	-2.50161700	H	5.32530400	-1.63912800	3.39650200
H	-4.43334000	3.38531100	-3.23449000	H	5.64507000	0.09788400	3.40691300
H	-4.45824600	1.64016600	-3.07062300	O	0.56615600	-0.91186400	3.49608000
C	-6.00607000	2.68402400	-1.94585200	C	-0.39866400	-1.72889500	3.36994700
H	-6.19390500	3.69685900	-1.57150600	O	-0.95828200	-2.04864100	2.27666900
H	-6.70762600	2.50693200	-2.77251500	C	-0.94381400	-2.36271500	4.63971500
C	-6.27065300	1.72923200	-0.78358300	H	-0.28149700	-2.09097800	5.46986600
O	-6.16053700	2.10514100	0.39139600	H	-1.92468100	-1.90056100	4.83506500
N	-6.56707100	0.44538400	-1.11365100	C	-1.10929500	-3.88759700	4.53107100
H	-6.58872900	0.19981600	-2.09597600	H	-0.13023800	-4.34143700	4.31749500
C	-6.51431100	-0.64287500	-0.13084000	H	-1.75035300	-4.11280600	3.66939300
H	-6.97201600	-0.26779800	0.78992400	C	-1.69634300	-4.49961600	5.80705700
H	-7.13888200	-1.46113400	-0.51187400	H	-1.05553800	-4.30333800	6.67800800
C	-5.07801500	-1.11778500	0.15250500	H	-1.80261700	-5.58792500	5.71010800
H	-4.49865200	-0.27837100	0.55286100	H	-2.69052300	-4.08503400	6.02663700
H	-5.11219100	-1.87783600	0.94601600	O	0.68890200	1.23908900	-1.52044800
C	-4.37595200	-1.68542600	-1.08413600	H	1.09715500	1.99568400	-2.02054100
H	-4.46889400	-0.98725900	-1.93123200				

Pro:

Ca	2.31062800	-1.05905500	-1.02657500	O	-0.06255200	0.59722400	1.02764200
Mn	0.91303900	1.87183400	0.09557500	O	1.07696000	-1.61485000	1.00254100
Mn	1.44710000	-0.11763600	1.92977400	O	-0.12125300	-1.23459000	-1.33371100
Mn	-0.67159400	-1.38124800	0.49681700	O	-1.01918100	-3.02071900	0.08131300
Mn	-1.11383400	-3.05286200	-1.83216200	O	3.66918200	0.12576300	-2.64055500
O	2.29214200	0.83590400	0.61770800	H	4.60859600	0.01042800	-2.85161600

H	3.46999600	1.09547800	-2.70969100	H	-6.01220900	4.04605300	-2.60100800
O	-1.44585900	-1.61811300	-4.06503100	C	-5.70510600	3.12216200	-0.65167900
H	-0.56114300	-1.35681600	-4.38876900	O	-5.48125000	3.41981600	0.53021300
H	-0.33393200	-0.34390300	-1.68668500	N	-6.29100900	1.95048500	-1.00679500
O	-1.17292200	-2.97985100	-3.67277100	H	-6.40754100	1.75181200	-1.99293200
O	-2.04714100	-5.13654900	-1.29509700	C	-6.49108300	0.85796000	-0.04771700
H	-1.17622000	-5.55761400	-1.44751800	H	-6.85321400	1.30703200	0.88261100
H	-2.03040500	-4.88804500	-0.34844900	H	-7.28526900	0.21339000	-0.44550600
O	2.26005400	-3.09914800	-2.19713500	C	-5.20432900	0.05912700	0.22333100
C	1.66648400	-4.20318600	-2.26033300	H	-4.44467100	0.73565500	0.63026200
O	0.41694700	-4.38673100	-2.02875900	H	-5.41602000	-0.68193100	1.00761500
C	2.43996100	-5.46279200	-2.64810100	C	-4.65572500	-0.64401600	-1.02182600
H	2.20672200	-6.23380200	-1.89996400	H	-4.57257100	0.07285700	-1.85506800
H	2.00066400	-5.82610800	-3.58954800	H	-5.32327900	-1.44228200	-1.37058200
C	3.94910600	-5.26839500	-2.78813600	C	-3.25913100	-1.24556100	-0.87519300
H	4.39326100	-4.92878000	-1.84441900	O	-2.48556100	-0.71165800	-0.00959700
H	4.17970100	-4.51624000	-3.55166800	O	-2.96999100	-2.18484700	-1.66512800
H	4.43395500	-6.21043600	-3.07534900	O	0.92623100	3.01257600	1.73545500
O	2.05056300	3.34553900	-0.58386000	C	1.37974600	2.63705700	2.87042300
C	2.76811400	3.47665200	-1.64227200	O	1.68994500	1.45589300	3.18232900
O	2.76102700	2.68789400	-2.62561800	C	1.56940500	3.73653500	3.90746400
C	3.66007900	4.71356800	-1.65267900	H	0.70379000	4.40906000	3.83710500
H	3.01783500	5.57957900	-1.43349400	H	2.43244500	4.32968100	3.56709200
H	4.33579700	4.62892600	-0.78730400	C	1.78322100	3.23634400	5.33637200
C	4.45153500	4.92802100	-2.94549900	H	1.93570600	4.08412100	6.01623900
H	3.75340300	4.98996200	-3.79153100	H	0.91677800	2.66433000	5.69014600
H	5.07809600	4.04593500	-3.13723000	H	2.65758000	2.57946600	5.39590500
C	5.32437400	6.18677000	-2.89140500	O	4.01347000	-1.54039700	0.61123900
H	4.71617000	7.08841800	-2.73288800	C	4.03024600	-1.39811600	1.85132100
H	6.05432400	6.13297600	-2.07143400	O	3.10213800	-0.84604200	2.57102300
H	5.88320300	6.32252100	-3.82639400	C	5.21115000	-1.90031300	2.66454600
N	-0.84291100	2.90923000	-0.39281200	H	5.99907800	-2.27164100	2.00380700
C	-1.52879700	2.87996600	-1.58926300	H	4.87640700	-2.70730300	3.32897400
H	-1.08543600	2.43888800	-2.47068500	H	5.59701200	-1.09486000	3.30071100
C	-2.77108600	3.44412200	-1.41946700	O	0.42448700	-0.82180800	3.47702100
N	-2.81293500	3.83121500	-0.08619000	C	-0.71409700	-1.37177000	3.38877100
H	-3.67953200	4.07233200	0.40672000	O	-1.35246200	-1.58889200	2.30839800
C	-1.64690100	3.47631200	0.49660600	C	-1.39000900	-1.80887800	4.67675200
H	-1.41315100	3.61457800	1.54139900	H	-0.72328500	-1.57012500	5.51321800
C	-3.89693700	3.64746500	-2.40088200	H	-2.30345100	-1.20470300	4.78929300
H	-3.62618200	4.43040200	-3.12499900	C	-1.76333200	-3.30251600	4.67147600
H	-4.00909100	2.72503700	-2.98791200	H	-0.85065600	-3.90083300	4.53341300
C	-5.26824100	4.03931100	-1.79274600	H	-2.40320100	-3.50322000	3.80264600
H	-5.22564000	5.05454900	-1.38188500	C	-2.47020500	-3.72690800	5.96268300

H	-1.83543700	-3.55393700	6.84283600	O	0.88317600	1.09342800	-1.58096800
H	-2.72473900	-4.79439000	5.93958600	H	1.42032300	1.69751100	-2.16096800
H	-3.40277700	-3.16387400	6.10941500				

W3 (water)-Wx (oxo/oxyl)

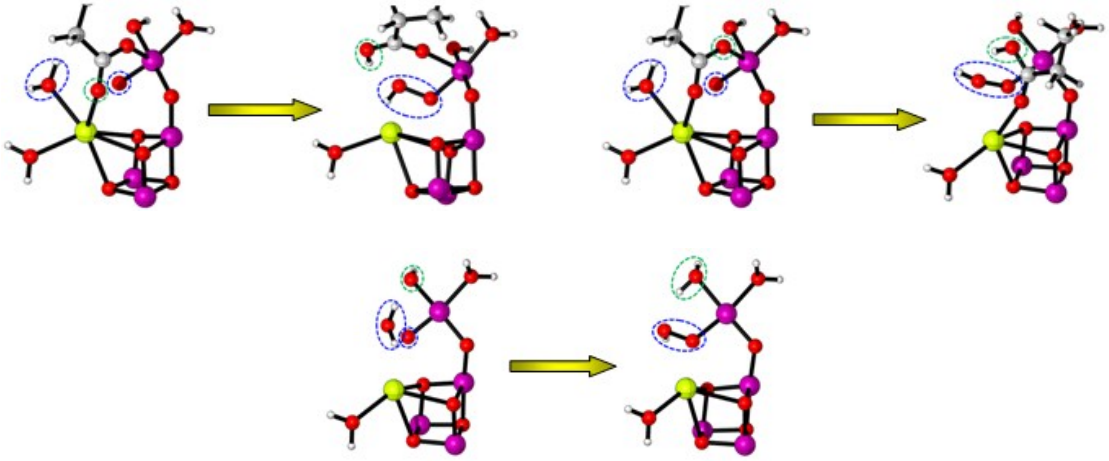

Fig. S6 Pictorial exhibitions for the closed-cubane water (W3/crystal or solvent water)-Wx (oxo/oxyl) nucleophilic attack with Ca/Mn4-bound O of Asp170 (upper) and W2 (lower) as the proton acceptors.

Table S7 Reaction parameters for the closed-cubane W3 (water)-Wx (oxo/oxyl) nucleophilic attack with Ca-bound O of Asp170 as the proton acceptor:

Spin state	Spin topology (Mn1~Mn4-O10)	Gibbs Free energy (a.u.)		
		Rea	TS	Pro
doublet	ααββα	-3366.2428	-3366.1588	-3366.1590
	αβαβα	-3366.2428	-3366.1588	-3366.1590
	αββαα	-3366.2091	-3366.1697	-3366.2115
	βααβα	-3366.2416	-3366.1593	-3366.1597
	βαβαα	-3366.2081	-3366.1691	-3366.2085
	ββααα	-3366.1899	-3366.1696	-3366.2085
sextet	αααββ	-3366.2111	-3366.1718	-3366.2132
	ααβαβ	-3366.2425	-3366.1605	-3366.1607
	αβααβ	-3366.2430	-3366.1592	-3366.1594
	βαααβ	-3366.2443	-3366.1600	-3366.1602
octet	αααβα	-3366.2440	-3366.1617	-3366.1619
	ααβαα	-3366.2103	-3366.1712	-3366.2127
	αβααα	-3366.1907	-3366.1702	-3366.2091
	βαααα	-3366.1914	-3366.1710	-3366.2118
12-et	ααααβ	-3366.2455	-3366.1616	-3366.1618
14-et	ααααα	-3366.1933	-3366.1729	-3366.2136

Spin state	Spin topology (Mn1~Mn4-O10)	Relative Gibbs Free energy (kcal/mol)			
		$\Delta G^{\neq}$(Rea-TS)	ΔG(Rea-Pro)	ΔG(Rea)	ΔG(Pro)
doublet	ααββα	52.7	52.6	1.7	34.3
	αβαβα	52.7	52.6	1.7	34.3
	αββαα	24.7	-1.5	22.8	1.3
	βααβα	51.6	51.4	2.4	33.8
	βαβαα	24.5	-0.3	23.5	3.2
	ββααα	12.7	-11.7	34.9	3.2
sextet	αααββ	24.7	-1.3	21.6	0.3
	ααβαβ	51.5	51.3	1.9	33.2
	αβααβ	52.6	52.5	1.6	34.0
	βαααβ	52.9	52.8	0.8	33.5
octet	αααβα	51.6	51.5	0.9	32.4
	ααβαα	24.5	-1.5	22.1	0.6
	αβααα	12.9	-11.5	34.4	2.8
	βαααα	12.8	-12.8	33.9	1.1
12-et	ααααβ	52.6	52.5	0.0	32.5
14-et	ααααα	12.8	-12.7	32.8	0.0

Spin state	Spin topology (Mn1~Mn4-O10)		Mulliken spin density		
			Rea	TS	Pro
doublet	α	Mn1	2.92	2.93	2.92
	α	Mn2	2.93	2.95	2.95
	β	Mn3	-2.93	-2.84	-2.83
	β	Mn4	-1.85	-2.02	-1.96
	α	O10	-0.16	0.00	0.00
		O8	0.00	0.08	0.03
	α	Mn1	2.92	2.93	2.92
	β	Mn2	2.93	2.95	2.95
	α	Mn3	-2.93	-2.84	-2.83
	β	Mn4	-1.85	-2.02	-1.96
	α	O10	-0.16	0.00	0.00
		O8	0.00	0.08	0.03
	α	Mn1	2.92	2.92	2.92
	β	Mn2	-2.93	-2.93	-2.93
	β	Mn3	-2.82	-2.82	-2.82
	α	Mn4	2.61	3.25	3.82
	α	O10	0.85	0.26	0.02
		O8	0.00	0.41	0.01
	β	Mn1	-2.92	-2.92	-2.92
	α	Mn2	2.93	2.93	2.93
	α	Mn3	2.91	2.80	2.79

	β	Mn4	-1.80	-2.00	-1.92
	α	O10	-0.15	0.01	0.00
		O8	0.00	0.09	0.02
	β	Mn1	-2.94	-2.94	-2.93
	α	Mn2	2.94	2.95	2.95
	β	Mn3	-2.81	-2.81	-2.80
	α	Mn4	2.62	3.25	3.82
	α	O10	0.85	0.26	0.02
		O8	0.00	0.41	0.01
	β	Mn1	-2.92	-2.92	-2.93
	β	Mn2	-2.95	-2.95	-2.95
	α	Mn3	2.84	2.83	2.86
	α	Mn4	2.76	3.30	3.88
	α	O10	0.89	0.26	0.03
		O8	0.00	0.41	0.01
sextet	α	Mn1	2.94	2.94	2.93
	α	Mn2	2.93	2.93	2.93
	α	Mn3	2.84	2.84	2.83
	β	Mn4	-2.61	-3.26	-3.82
	β	O10	-0.84	-0.26	-0.02
		O8	0.00	-0.41	-0.01
	α	Mn1	2.92	2.92	2.92
	α	Mn2	2.93	2.96	2.96
	β	Mn3	-2.89	-2.76	-2.75
	α	Mn4	1.79	2.00	1.92
	β	O10	0.15	-0.01	0.00
		O8	0.00	-0.09	-0.02
	α	Mn1	2.94	2.94	2.94
	β	Mn2	-2.93	-2.95	-2.95
	α	Mn3	2.95	2.86	2.86
	α	Mn4	1.86	2.02	1.96
	β	O10	0.16	-0.01	0.00
		O8	0.00	-0.08	-0.03
	β	Mn1	-2.91	-2.92	-2.92
	α	Mn2	2.93	2.94	2.94
	α	Mn3	2.96	2.88	2.88
	α	Mn4	1.85	2.02	1.96
	β	O10	0.16	-0.01	0.00
		O8	0.00	-0.08	-0.03
octet	α	Mn1	2.93	2.94	2.94
	α	Mn2	2.3	2.93	2.93
	α	Mn3	2.87	2.81	2.81
	β	Mn4	-1.82	-2.00	-1.93
	α	O10	-0.13	0.01	0.00

		O8	0.00	0.09	0.03
	α	Mn1	2.93	2.92	2.93
	α	Mn2	2.95	2.95	2.96
	β	Mn3	-2.79	-2.78	-2.78
	α	Mn4	2.61	3.25	3.82
	α	O10	0.85	0.26	0.02
		O8	0.00	0.41	0.01
	α	Mn1	2.94	2.94	2.93
	β	Mn2	-2.94	-2.94	-2.94
	α	Mn3	2.86	2.85	2.88
	α	Mn4	2.76	3.30	3.88
	α	O10	0.89	0.26	0.02
		O8	0.00	0.41	0.01
	β	Mn1	-2.92	-2.92	-2.92
	α	Mn2	2.93	2.93	2.94
	α	Mn3	2.88	2.88	2.90
	α	Mn4	2.76	3.29	3.88
	α	O10	0.89	0.26	0.03
		O8	0.00	0.41	0.01
12-et	α	Mn1	2.94	2.94	2.94
	α	Mn2	2.93	2.93	2.93
	α	Mn3	2.96	2.90	2.90
	α	Mn4	1.85	2.02	1.96
	β	O10	0.16	0.00	0.00
		O8	0.00	-0.08	-0.03
14-et	α	Mn1	2.94	2.94	2.94
	α	Mn2	2.93	2.93	2.93
	α	Mn3	2.89	2.89	2.91
	α	Mn4	2.76	3.30	3.88
	α	O10	0.89	0.26	0.02
		O8	0.00	0.41	0.01

Rea:

Ca	-2.50123800	-0.97394600	-0.86224400	H	-3.36096300	-3.11389100	-2.48961500
Mn	0.77340000	-1.68394200	-0.44621300	O	-4.56938500	0.09098100	-1.30429300
Mn	-0.63855300	-1.93183300	1.83920100	H	-5.24905400	-0.37746100	-1.81283100
Mn	-0.24488100	0.62853100	0.88053200	H	-4.63365600	1.06205100	-1.53119200
Mn	-1.74904600	3.01999700	-0.87746100	O	-1.90754300	4.03059700	-2.37533100
O	-0.72458900	-2.51809200	0.11524600	H	-1.20658300	3.75408000	-2.99536900
O	0.87623100	-0.95042000	1.25219500	O	-1.16420500	4.67646600	0.48341200
O	-1.59994600	-0.48571700	1.38250700	H	-0.22506900	4.78002200	0.24511300
O	-0.12387200	-0.14025100	-0.79552300	H	-1.16743000	4.15302600	1.30990700
O	-1.41263700	1.89269600	0.52964100	O	-4.98639800	2.67710500	-1.74880900
O	-4.07414600	-2.70244800	-1.96464900	C	-4.59496500	3.53071500	-0.94896800
H	-4.13871200	-3.20666800	-1.12781300	O	-3.44416500	3.53408000	-0.31758400

C	-5.47274900	4.73673000	-0.61733200	C	3.63147200	3.56184100	0.02502200
H	-5.21805900	5.50261800	-1.36729500	H	3.84879900	2.68657000	0.64570000
H	-6.51185000	4.44242200	-0.80744700	H	3.18398800	4.31643400	0.68964200
C	-5.29378000	5.31400300	0.79018400	C	2.64198900	3.18099500	-1.08454500
H	-4.25794900	5.63149400	0.94999400	H	3.07042500	2.37448900	-1.69836500
H	-5.54186100	4.57107200	1.55939500	H	2.44477700	4.03030900	-1.75104500
H	-5.95158500	6.18116900	0.93362200	C	1.29302000	2.65893700	-0.58664000
O	0.73106500	-2.36895500	-2.25238800	O	1.30497700	1.85231000	0.39215100
C	-0.30564300	-2.56216900	-3.00409600	O	0.28223200	3.10173200	-1.22089200
O	-1.47286000	-2.21194500	-2.73205400	O	1.78455900	-3.30827500	0.28893500
C	0.00945900	-3.26293700	-4.32291100	C	1.49361500	-3.85184900	1.40474400
H	0.63129400	-2.56861500	-4.91124700	O	0.61802500	-3.45438000	2.23811700
H	0.66070300	-4.11982700	-4.09849900	C	2.27257500	-5.11572700	1.75441000
C	-1.21636700	-3.69253900	-5.13297600	H	3.31433000	-4.95386600	1.44724400
H	-1.85817400	-2.81861700	-5.30607600	H	1.88676300	-5.90459700	1.08968500
H	-1.81433200	-4.39832100	-4.53742900	H	-3.71745600	-5.07040900	2.65860800
C	-0.83667100	-4.34108600	-6.46876700	C	2.17439100	-5.54890200	3.21769900
H	-0.26685400	-3.64589600	-7.10141100	H	2.74400300	-6.47293800	3.37980300
H	-1.72980200	-4.64493000	-7.02968300	H	2.57500600	-4.77805200	3.88758800
H	-0.21642800	-5.23587700	-6.31841600	H	1.13286500	-5.72598100	3.50663200
N	2.67370400	-0.95418200	-0.86249500	O	-3.54104200	-2.66908000	0.70599800
C	3.26840100	-0.60999600	-2.05508400	C	-3.23433400	-3.15271700	1.81368000
H	2.73689500	-0.71847500	-2.99046500	O	-2.12287500	-2.93955100	2.44958900
C	4.54799300	-0.16239200	-1.81419600	C	-4.18444800	-4.08365800	2.54552500
N	4.71366600	-0.27232700	-0.43793200	H	-5.12624500	-4.17784400	1.99825100
H	5.48844000	0.13938700	0.08768700	H	-4.37451000	-3.69769500	3.55417200
C	3.56033900	-0.73054200	0.09571300	O	-0.32207500	-1.06291900	3.61558600
H	3.37535600	-0.86165000	1.15214900	C	-0.08788700	0.18157600	3.75152900
C	5.60084400	0.36141300	-2.75684600	O	0.01523000	1.05058200	2.82124000
H	6.05502300	-0.46642800	-3.32165300	C	0.08406900	0.69392400	5.17401700
H	5.09770700	0.98868700	-3.50608400	H	-0.79171100	1.32313500	5.39774600
C	6.75725400	1.16160700	-2.09974900	H	0.05665100	-0.16566700	5.85346600
H	7.45954200	0.48085800	-1.60660800	C	1.36836000	1.51683700	5.37191200
H	7.31198000	1.68413800	-2.89111100	H	1.37096300	2.34793900	4.65484800
C	6.28984000	2.13821800	-1.02030500	H	2.23935900	0.88991900	5.12749400
O	6.42592900	1.87358800	0.18163300	C	1.50243500	2.04979500	6.80212700
N	5.65672100	3.26187400	-1.44272900	H	0.65942900	2.70515300	7.06251300
H	5.53635600	3.40743100	-2.43759000	H	2.42657300	2.62989500	6.92311900
C	4.94916500	4.14926300	-0.51367000	H	1.52400400	1.23068900	7.53420100
H	5.62289400	4.36230000	0.32361200	O	-2.06982000	1.53722600	-1.70288800
H	4.76547000	5.09028100	-1.04704300				

TS:

Ca	2.31679500	1.06385600	-0.99804600	Mn	0.64276100	1.93166500	1.83655500
Mn	-0.89710400	1.64491100	-0.35353800	Mn	0.27330200	-0.64571900	0.90835400

Mn	1.82272500	-2.72443900	-1.01815200	N	-4.72978400	-0.04314000	-0.17223400
O	0.60890900	2.52942100	0.11232500	H	-5.42693200	-0.56236300	0.36579000
O	-0.87994600	0.92153600	1.34170000	C	-3.57924500	0.46706500	0.32124100
O	1.61762100	0.51639100	1.32303900	H	-3.32725100	0.53010500	1.37026400
O	0.02447700	0.13608500	-0.76711500	C	-5.73004500	-0.55580100	-2.47697400
O	1.42769900	-1.91683600	0.58445300	H	-6.29061700	0.27751600	-2.92666000
O	3.79884800	2.79650600	-2.13110100	H	-5.23499200	-1.06517500	-3.31566700
H	3.97499600	3.27676200	-1.29702700	C	-6.76519100	-1.51050900	-1.82550500
H	3.05663900	3.25265000	-2.57272000	H	-7.48045600	-0.94174100	-1.22155800
O	3.86860500	-0.39119100	-2.29685200	H	-7.33468600	-2.00452900	-2.62472800
H	3.69838900	-0.35456100	-3.25695700	C	-6.14138100	-2.53749700	-0.88056900
H	4.70130100	-1.67844800	-2.03332100	O	-6.20941600	-2.39757200	0.34758200
O	2.19305300	-3.89752900	-2.36496800	N	-5.45564400	-3.55957400	-1.45310500
H	2.13458600	-3.40604400	-3.20390500	H	-5.40176300	-3.60435400	-2.46319500
O	1.55002600	-4.53501400	0.38453300	C	-4.63300200	-4.48213900	-0.66339400
H	0.67448300	-4.86523200	0.11686700	H	-5.24343200	-4.84393300	0.17174900
H	1.38138800	-3.86942600	1.08940500	H	-4.40321500	-5.33893500	-1.30899200
O	5.30884200	-2.49134600	-1.85591700	C	-3.34272600	-3.84891300	-0.11300300
C	4.83327500	-3.22314000	-0.88167100	H	-3.60247900	-3.05219400	0.59116600
O	3.76342000	-2.98592800	-0.29362700	H	-2.81788700	-4.62333000	0.46660100
C	5.69592100	-4.40589700	-0.50571600	C	-2.41960500	-3.29458700	-1.20612200
H	5.60994700	-5.11234900	-1.34668600	H	-2.94284500	-2.50518200	-1.76699100
H	6.74331800	-4.07588700	-0.49652500	H	-2.13264000	-4.07153000	-1.92541800
C	5.28563000	-5.07741000	0.80513800	C	-1.13988200	-2.64891000	-0.67286700
H	4.23417500	-5.38160300	0.77079000	O	-1.22762000	-1.94781100	0.37181600
H	5.40850700	-4.39415100	1.65451200	O	-0.09932800	-2.89900900	-1.38098400
H	5.90650300	-5.96338300	0.98644800	O	-1.91157000	3.24151600	0.44465900
O	-1.00085600	2.35829600	-2.15770300	C	-1.56485200	3.79458900	1.53929500
C	-0.02742100	2.63965000	-2.96033200	O	-0.62163200	3.43015000	2.31209500
O	1.17130200	2.33303400	-2.78275400	C	-2.36339700	5.03066200	1.94285500
C	-0.45831700	3.39124800	-4.21790900	H	-3.41923700	4.82373500	1.72283900
H	-1.09133100	2.70237000	-4.80071900	H	-2.06589600	5.82813100	1.24398000
H	-1.12570000	4.20708300	-3.90525900	H	3.83006300	5.01572700	2.53652500
C	0.69058700	3.91559900	-5.08289600	C	-2.16573500	5.48137400	3.39062200
H	1.35166000	3.08036900	-5.35006000	H	-2.75814100	6.38299200	3.59308200
H	1.30218200	4.61077200	-4.48901900	H	-2.47836400	4.70081700	4.09514900
C	0.19452800	4.62098200	-6.35003800	H	-1.11245100	5.70330900	3.59333400
H	-0.39218300	3.93937600	-6.98213000	O	3.51776800	2.62259500	0.56833000
H	1.03388800	4.99281700	-6.95174100	C	3.25633500	3.12520500	1.68249200
H	-0.44687900	5.47933400	-6.10568700	O	2.15778500	2.96418500	2.34935300
N	-2.78449000	0.83737900	-0.67122600	C	4.26598500	4.02113100	2.37911000
C	-3.43526200	0.53857300	-1.84662600	H	5.18099500	4.10343000	1.78621800
H	-2.98192900	0.76506300	-2.80165300	H	4.49877600	3.60988100	3.36892200
C	-4.65519700	-0.03074000	-1.56093000	O	0.45169400	1.06673000	3.63023400

C	0.23249300	-0.17984100	3.78231100	H	-1.99831000	-1.00723600	5.25957200
O	0.09135400	-1.05219200	2.86263100	C	-1.12643500	-2.10735900	6.90934200
C	0.14134000	-0.68523100	5.21524100	H	-0.23661200	-2.71055800	7.13830600
H	1.06111300	-1.25937800	5.41011900	H	-2.00925800	-2.73931900	7.07226800
H	0.14672300	0.18189100	5.88582500	H	-1.16555200	-1.28487900	7.63705700
C	-1.08242500	-1.57980000	5.47150300	O	2.23299400	-1.22239000	-1.97693300
H	-1.06528200	-2.41547500	4.76028400				

Pro:

Ca	2.38035500	1.13242000	-0.73202000	H	-0.59988200	4.58695000	-3.61846700
Mn	-0.82676600	1.66072500	-0.34822500	C	1.23645300	4.23477700	-4.74565100
Mn	0.53395800	1.75998200	1.98149500	H	1.83732400	3.36993700	-5.05819600
Mn	0.20080700	-0.74251100	0.83505500	H	1.87553200	4.82293000	-4.07120900
Mn	1.80517600	-2.64774500	-1.19606500	C	0.85759600	5.08033000	-5.96669900
O	0.63409600	2.49057300	0.31085800	H	0.24485700	4.50548200	-6.67543000
O	-0.95014500	0.81678100	1.29170500	H	1.75088100	5.42516100	-6.50337600
O	1.53053100	0.37484100	1.43802600	H	0.27970800	5.96865000	-5.67519000
O	0.10404800	0.16108000	-0.79961500	N	-2.69451500	0.93768900	-0.88050600
O	1.38858600	-1.96425400	0.42186400	C	-3.20370500	0.54252500	-2.09661800
O	4.23596200	2.48603700	-1.67333500	H	-2.60930700	0.61509800	-2.99717600
H	4.38937000	3.00357200	-0.85644700	C	-4.49464800	0.09433700	-1.92636300
H	3.71347100	3.05358200	-2.27169600	N	-4.75438200	0.25445300	-0.56990800
O	3.47838800	-1.15655500	-2.92943500	H	-5.56076200	-0.14608600	-0.08356900
H	2.93514900	-1.92040000	-3.32326300	C	-3.64310200	0.74169900	0.02274600
H	4.72206700	-1.92549000	-2.21442800	H	-3.53302700	0.91247000	1.08366800
O	2.01942400	-3.22572500	-2.96074900	C	-5.48108100	-0.47046400	-2.91691700
H	1.14023200	-3.33925100	-3.36361300	H	-5.88231500	0.33093700	-3.55518900
O	1.42725900	-4.66181200	-0.28534900	H	-4.93246400	-1.14012700	-3.59429700
H	0.47193600	-4.65120100	-0.49066500	C	-6.69357600	-1.22673600	-2.30990100
H	1.49029900	-4.34651600	0.63824900	H	-7.41461300	-0.51639000	-1.89101500
O	5.49479600	-2.36543900	-1.72315200	H	-7.20282300	-1.76975300	-3.11791000
C	5.07352500	-3.20690000	-0.79427800	C	-6.31475300	-2.16969900	-1.16758900
O	3.89174500	-3.44782300	-0.53983200	O	-6.50706900	-1.85008700	0.01328400
C	6.21526100	-3.87613100	-0.05232600	N	-5.69464300	-3.32776200	-1.50924600
H	6.82942100	-4.39387400	-0.80375600	H	-5.51787300	-3.50916600	-2.48982300
H	6.85692100	-3.07830000	0.34889900	C	-5.01623400	-4.16457300	-0.51236600
C	5.75755300	-4.83278200	1.04714600	H	-5.70032000	-4.29104400	0.33333700
H	5.12463900	-5.62822500	0.63706300	H	-4.85985500	-5.14909500	-0.97110400
H	5.17311100	-4.30494500	1.81003800	C	-3.68415300	-3.56895200	-0.01943500
H	6.62392500	-5.29550200	1.53586800	H	-3.88031000	-2.63528700	0.51791600
O	-0.72688800	2.50840100	-2.09208000	H	-3.25431300	-4.26729400	0.71373600
C	0.32089100	2.86710700	-2.76235300	C	-2.68643900	-3.31489900	-1.15369100
O	1.49943300	2.54524900	-2.49729000	H	-3.12257300	-2.60832500	-1.87686100
C	0.01029500	3.74287400	-3.97293900	H	-2.46707200	-4.23706500	-1.70866900
H	-0.65414900	3.16103300	-4.63103400	C	-1.34679100	-2.69624400	-0.74153500

O	-1.35211700	-1.91585300	0.26122400	H	5.08142300	3.90062900	2.42570600
O	-0.35404100	-3.01584600	-1.46606000	H	4.19802100	3.43342500	3.91701600
O	-1.88841500	3.20811900	0.49011800	O	0.20494300	0.77791900	3.68370600
C	-1.61804500	3.68228900	1.64313600	C	-0.01027000	-0.47888100	3.73056700
O	-0.74867400	3.24565700	2.46243300	O	-0.07975700	-1.28285300	2.74458900
C	-2.42049000	4.91108500	2.06073300	C	-0.18958400	-1.08415800	5.11582500
H	-3.45497700	4.75688400	1.72618300	H	0.73994600	-1.62868000	5.34731400
H	-2.03481400	5.74649700	1.45539800	H	-0.27588000	-0.26445800	5.83862200
H	3.67243400	4.84678900	2.99826000	C	-1.38424900	-2.04570800	5.21705900
C	-2.35178400	5.24948000	3.55044000	H	-1.27174200	-2.83122300	4.45904300
H	-2.93629900	6.15388300	3.76288000	H	-2.30751000	-1.50128000	4.96708900
H	-2.75243300	4.43162700	4.16210100	C	-1.51368700	-2.66728600	6.61154800
H	-1.31738300	5.42000900	3.86756100	H	-0.61616900	-3.24497000	6.87404800
O	3.50737000	2.54771400	0.96213900	H	-2.37484800	-3.34622500	6.66395500
C	3.15947900	2.96986800	2.08811500	H	-1.64891000	-1.89659900	7.38314400
O	2.02372700	2.74578700	2.66513200	O	2.73309200	-1.01653000	-1.67665300
C	4.09985600	3.84001000	2.90377400				

Table S8 Reaction parameters for the closed-cubane W3 (water)-Wx (oxo/oxyl) nucleophilic attack with Mn4-bound O of Asp170 as the proton acceptor:

Spin state	Spin topology (Mn1~Mn4-O10)	Gibbs Free energy (a.u.)		
		Rea	TS	Pro
doublet	ααββα	-3366.2421	-3366.1662	-3366.1678
	αβαβα	-3366.2409	-3366.1659	-3366.1671
	αββαα	-3366.2112	-3366.1730	-3366.2255
	βααβα	-3366.2424	-3366.1661	-3366.1674
	βαβαα	-3366.2105	-3366.1743	-3366.2222
	ββααα	-3366.2113	-3366.1752	-3366.2243
sextet	αααββ	-3366.2163	-3366.1764	-3366.2254
	ααβαβ	-3366.2438	-3366.1676	-3366.1687
	αβααβ	-3366.2417	-3366.1667	-3366.1686
	βαααβ	-3366.2437	-3366.1679	-3366.1658
octet	αααβα	-3366.2451	-3366.1691	-3366.1698
	ααβαα	-3366.2128	-3366.1766	-3366.2260
	αβααα	-3366.2113	-3366.1753	-3366.2258
	βαααα	-3366.2127	-3366.1765	-3366.2259
12-et	αααaβ	-3366.2452	-3366.1698	-3366.1712
14-et	ααααα	-3366.2144	-3366.1782	-3366.2283

Spin state	Spin topology (Mn1~Mn4-O10)	Relative Gibbs Free energy (kcal/mol)			
		$\Delta G^{\neq}$ (Rea-TS)	ΔG(Rea-Pro)	ΔG(Rea)	ΔG(Pro)
doublet	ααββα	47.6	46.6	1.9	38.0

	αβαβα	47.1	46.3	2.7	38.4
	αββαα	24.0	-9.0	21.3	1.8
	βααβα	47.9	47.1	1.8	38.2
	βαβαα	22.7	-7.3	21.8	3.8
	ββαaα	22.7	-8.2	21.3	2.5
sextet	αααββ	25.0	-5.7	18.1	1.8
	ααβαβ	47.8	47.1	0.9	37.4
	αβααβ	47.1	45.9	2.2	37.5
	βαααβ	47.6	48.9	0.9	39.2
octet	αααβα	47.7	47.3	0.1	36.7
	ααβαα	22.7	-8.3	20.3	1.4
	αβααα	22.6	-9.1	21.3	1.6
	βαααα	22.7	-8.3	20.4	1.5
12-et	ααααβ	47.3	46.4	0.0	35.8
14-et	ααααα	22.7	-8.7	19.3	0.0

Spin state	Spin topology (Mn1~Mn4-O10)		Mulliken spin density		
			Rea	TS	Pro
doublet	α	Mn1	2.92	2.93	2.93
	α	Mn2	2.93	2.95	2.95
	β	Mn3	-2.90	-2.84	-2.84
	β	Mn4	-1.88	-2.05	-1.93
	α	O10	-0.12	-0.02	-0.03
		O8	0.00	0.14	0.02
	α	Mn1	2.92	2.94	2.94
	β	Mn2	-2.92	-2.95	-2.95
	α	Mn3	2.89	2.79	2.79
	β	Mn4	-1.81	-2.02	-1.89
	α	O10	-0.11	-0.02	-0.03
		O8	0.00	0.14	0.02
	α	Mn1	2.92	2.92	3.05
	β	Mn2	-2.92	-2.93	-2.93
	β	Mn3	-2.81	-2.80	-2.86
	α	Mn4	2.62	2.89	3.87
	α	O10	0.88	0.40	-0.03
		O8	0.01	0.53	0.03
	β	Mn1	-2.91	-2.92	-2.92
	α	Mn2	2.92	2.93	2.93
	α	Mn3	2.89	2.80	2.78
	β	Mn4	-1.81	-2.02	-1.89
	α	O10	-0.12	-0.02	-0.03
		O8	0.00	0.14	0.02
	β	Mn1	-2.92	-2.93	-2.87
	α	Mn2	2.93	2.94	2.94

	β	Mn3	-2.81	-2.80	-2.83
	α	Mn4	2.62	2.89	3.91
	α	O10	0.88	0.40	-0.02
		O8	0.01	0.53	0.03
	β	Mn1	-2.92	-2.93	-2.89
	β	Mn2	-2.94	-2.94	-2.94
	α	Mn3	2.87	2.88	2.82
	α	Mn4	2.70	2.98	3.92
	α	O10	0.84	0.39	-0.02
		O8	0.01	0.55	0.03
sextet	α	Mn1	2.92	2.93	2.88
	α	Mn2	2.93	2.93	2.93
	α	Mn3	2.83	2.82	2.87
	β	Mn4	-2.62	-2.89	-3.91
	β	O10	-0.88	-0.40	0.02
		O8	-0.01	-0.52	-0.03
	α	Mn1	2.92	2.93	2.93
	α	Mn2	2.93	2.95	2.95
	β	Mn3	-2.87	-2.76	-2.75
	α	Mn4	1.81	2.02	1.89
	β	O10	0.12	0.01	0.02
		O8	0.00	-0.14	-0.02
	α	Mn1	2.92	2.94	2.94
	β	Mn2	-2.92	-2.94	-2.94
	α	Mn3	2.92	2.88	2.88
	α	Mn4	1.88	2.05	1.93
	β	O10	0.12	0.01	0.01
		O8	0.00	-0.14	-0.03
	β	Mn1	-2.91	-2.92	-2.92
	α	Mn2	2.92	2.94	2.94
	α	Mn3	2.93	2.88	2.8
	α	Mn4	1.88	2.05	1.93
	β	O10	0.11	0.01	0.02
		O8	0.00	-0.14	-0.01
octet	α	Mn1	2.92	2.93	2.93
	α	Mn2	2.92	2.93	2.93
	α	Mn3	2.90	2.82	2.81
	β	Mn4	-1.81	-2.02	-1.89
	α	O10	-0.12	-0.01	0.00
		O8	0.00	0.14	0.02
	α	Mn1	2.93	2.92	3.05
	α	Mn2	2.94	2.95	2.95
	β	Mn3	-2.78	-2.77	-2.83
	α	Mn4	2.62	2.89	3.87

	α	O10	0.88	0.40	-0.03
		O8	0.01	0.53	0.03
	α	Mn1	2.93	2.93	3.04
	β	Mn2	-2.93	-2.93	-2.94
	α	Mn3	2.90	2.90	2.84
	α	Mn4	2.70	2.98	3.88
	α	O10	0.85	0.38	-0.02
		O8	0.01	0.55	0.03
	β	Mn1	-2.91	-2.92	-2.88
	α	Mn2	2.93	2.93	2.93
	α	Mn3	2.91	2.91	2.85
	α	Mn4	2.70	2.98	3.92
	α	O10	0.84	0.39	-0.02
		O8	0.01	0.55	0.03
12-et	α	Mn1	2.92	2.93	2.94
	α	Mn2	2.92	2.93	2.94
	α	Mn3	2.93	2.91	2.91
	α	Mn4	1.88	2.05	1.93
	β	O10	0.12	0.02	0.02
		O8	0.00	-0.13	-0.02
14-et	α	Mn1	2.93	2.93	3.03
	α	Mn2	2.93	2.93	2.94
	α	Mn3	2.92	2.93	2.87
	α	Mn4	2.70	2.98	3.88
	α	O10	0.84	0.38	-0.02
		O8	0.01	0.55	0.03

Rea:

Ca	2.68254900	-0.25683800	-0.86668700	H	-0.08496800	-4.88978600	-3.07586700
Mn	0.06721600	1.74809200	-0.31129600	O	-0.53642300	-5.36043400	0.13644600
Mn	1.33031600	1.08581900	1.98960900	H	-0.72851900	-5.88329500	-0.67325000
Mn	-0.11147500	-0.89184000	0.74410400	H	-1.41887800	-5.10298200	0.46921000
Mn	-0.19019000	-3.59752400	-1.11493000	O	3.02642200	-2.65422700	-0.98880000
O	1.73445000	1.78350300	0.37571300	C	2.72865600	-3.85387200	-1.09381500
O	-0.43323500	0.93574400	1.29082700	O	1.55381900	-4.33278700	-1.39166300
O	1.57216200	-0.57787100	1.33077300	C	3.78031100	-4.94260500	-0.89052200
O	0.20561800	0.01655900	-0.85620400	H	3.47954500	-5.49815600	0.01076000
O	0.32948200	-2.49323800	0.15674900	H	3.68832300	-5.65855600	-1.71918400
O	4.96962800	0.30467700	-1.76558200	C	5.20876700	-4.41592300	-0.75786300
H	5.30087800	0.59360100	-0.89083400	H	5.29693000	-3.72934500	0.09167600
H	4.64326200	1.11520000	-2.20800200	H	5.51679600	-3.86776400	-1.65682700
O	2.10461400	-1.08188600	-3.18669400	H	5.91004700	-5.24635600	-0.60620700
H	1.22033400	-1.50135300	-3.03232300	O	0.62800700	2.62358400	-1.93090400
H	2.69583100	-1.84376300	-3.31174300	C	1.79916800	2.62539400	-2.49402900
O	-0.82620800	-4.72746600	-2.46358100	O	2.71348900	1.81549900	-2.25405800

C	1.97608600	3.72922600	-3.53159300	H	-4.50307000	-3.31613900	0.01649500
H	1.15701700	3.62496500	-4.25935200	C	-2.64041400	-2.27331700	-0.12194000
H	1.79221600	4.68768200	-3.02226900	O	-2.07508600	-1.23819500	0.31665300
C	3.33348900	3.73478700	-4.23846200	O	-2.09340300	-3.33260100	-0.58742900
H	3.49691600	2.75682000	-4.71176500	O	-0.26456900	3.52416700	0.67156500
H	4.13030200	3.84935500	-3.48976900	C	0.17881400	3.74758400	1.84639900
C	3.44236500	4.84880500	-5.28564100	O	0.81114500	2.93253600	2.59233700
H	2.67584900	4.73960300	-6.06579100	C	-0.03296300	5.14389300	2.42270000
H	4.42308000	4.83583400	-5.77874000	H	0.91465900	5.68289200	2.26463300
H	3.31116400	5.84063900	-4.83031200	H	-0.14300300	5.03834600	3.50880200
N	-1.85749200	1.88257300	-1.03860800	H	6.34638800	0.95663700	2.33777000
C	-2.39817900	1.09749900	-2.03571100	C	-1.19459500	5.92686800	1.80849700
H	-1.80381600	0.32990700	-2.51349900	H	-1.25311100	6.93097500	2.24703600
C	-3.71274000	1.45127500	-2.22389400	H	-1.07178300	6.02832200	0.72463100
N	-3.94740100	2.48385100	-1.32007200	H	-2.15364200	5.42532100	1.99619200
H	-4.88260000	2.76438700	-1.01961600	O	4.30257400	0.48611700	0.90333700
C	-2.81297700	2.69556300	-0.61453100	C	4.20476300	0.96829300	2.05033800
H	-2.70387900	3.42001700	0.17927600	O	3.09724700	1.24462100	2.66785000
C	-4.74243100	0.93117100	-3.19107800	C	5.44752300	1.29734600	2.85889000
H	-4.62738800	1.41984300	-4.17061300	H	5.38369400	0.82648000	3.84690000
H	-4.53012500	-0.13265100	-3.36248200	H	5.50064300	2.38198900	3.01904100
C	-6.22477700	1.10765400	-2.75802800	O	0.61750500	0.24593900	3.65782100
H	-6.53495900	2.15186200	-2.87724800	C	-0.13870300	-0.77894600	3.65061600
H	-6.85707700	0.50243800	-3.42198000	O	-0.57566800	-1.39943900	2.62561400
C	-6.44580000	0.74919400	-1.29137800	C	-0.55390800	-1.32558300	5.00871700
O	-6.44599600	1.62054300	-0.41382400	H	-1.31295700	-2.10105600	4.85162900
N	-6.56180700	-0.57748700	-1.00806800	H	0.33356300	-1.81721500	5.43817900
H	-6.50132300	-1.23096700	-1.77959700	C	-1.05509900	-0.23992800	5.97499700
C	-6.37181900	-1.09855800	0.34867800	H	-1.92952000	0.26077800	5.53244800
H	-6.84145300	-0.38557700	1.03286700	H	-0.27720200	0.52683800	6.07840900
H	-6.91527000	-2.04959000	0.42276800	C	-1.42607100	-0.81033900	7.34774400
C	-4.88425200	-1.27135900	0.70889600	H	-2.21977900	-1.56646600	7.26771800
H	-4.38386700	-0.29958600	0.63102300	H	-1.78484600	-0.02012700	8.02001100
H	-4.80997600	-1.57768200	1.76221600	H	-0.55998000	-1.28832600	7.82673600
C	-4.16804300	-2.28952000	-0.18263100	O	-0.19675000	-2.34910700	-2.32869500
H	-4.39881800	-2.10094800	-1.24350400				

TS:

Ca	2.59890400	0.19892200	-1.21206900	O	1.74797000	-0.69636200	0.90605300
Mn	-0.12037200	1.77981300	0.03336200	O	0.07251700	0.26112300	-0.92625800
Mn	1.45467700	0.74031000	1.96916700	O	0.52931900	-2.38867600	-0.62364400
Mn	0.04664200	-1.03575400	0.41366700	O	4.65174700	1.29873900	-2.18293700
Mn	-0.16942300	-3.12455100	-2.07837600	H	5.05168200	1.44076400	-1.30039700
O	1.61188300	1.82647000	0.53008300	H	4.17805200	2.12572300	-2.40264400
O	-0.35792300	0.57482900	1.43097800	O	1.97444700	-0.93537300	-3.29693700

H	1.60330300	-0.62846700	-4.14141500	C	-6.65377700	0.45609000	-0.45144900
H	2.49726500	-2.41706300	-3.09964900	O	-6.58854600	1.03253300	0.64067800
O	-0.55645800	-4.36348800	-3.41062900	N	-6.64540500	-0.90067100	-0.56331200
H	-0.27590400	-4.01477900	-4.27386900	H	-6.65888900	-1.29925800	-1.49430900
O	0.14614600	-5.17268600	-1.14226600	C	-6.24219300	-1.76416300	0.55048600
H	-0.08689100	-5.50443700	-2.04446300	H	-6.68254700	-1.34370700	1.45953800
H	-0.62961700	-5.34104000	-0.57856100	H	-6.68546400	-2.75449400	0.38443000
O	3.74046200	-1.99387400	-1.17514700	C	-4.71159200	-1.85166600	0.70175600
C	3.41774100	-3.11675800	-1.56542200	H	-4.31326600	-0.84725600	0.88416800
O	2.74430300	-3.32520300	-2.69520700	H	-4.47819800	-2.44723500	1.59564100
C	3.73128200	-4.38832300	-0.81208000	C	-4.03032700	-2.46150100	-0.52587000
H	2.76710600	-4.88631000	-0.63425400	H	-4.39947300	-1.98412600	-1.44731400
H	4.28878900	-5.05041900	-1.49130800	H	-4.25808100	-3.53047000	-0.63322900
C	4.48639400	-4.14861800	0.49419000	C	-2.51309400	-2.29938800	-0.59049300
H	3.91113600	-3.49181300	1.15681700	O	-1.95390300	-1.45605500	0.14180300
H	5.45555400	-3.66902000	0.31175000	O	-1.96978700	-3.06690500	-1.47343400
H	4.66425100	-5.09966200	1.01180800	O	-0.45121200	3.25071500	1.44842700
O	0.15272800	3.06041400	-1.38905800	C	0.11587000	3.23823800	2.58921200
C	1.18750000	3.21055000	-2.15163400	O	0.88272600	2.33195800	3.05071900
O	2.11877200	2.38867700	-2.27978800	C	-0.10721700	4.44052200	3.50131400
C	1.18247200	4.51558500	-2.94377500	H	0.78023800	5.08143800	3.37811800
H	0.27735300	4.50839600	-3.57117600	H	-0.07751800	4.07956400	4.53656300
H	1.02984800	5.33425900	-2.22491900	H	6.44962700	1.29216100	1.83483700
C	2.42877400	4.75840500	-3.79829100	C	-1.37929600	5.24036900	3.21549200
H	2.57022100	3.90978400	-4.48146300	H	-1.44144100	6.11086600	3.88060800
H	3.31537200	4.77762500	-3.14787400	H	-1.39769900	5.59328100	2.17858600
C	2.34610600	6.06513300	-4.59529900	H	-2.27739900	4.63011500	3.38193300
H	1.48630800	6.06099000	-5.28007300	O	4.31949000	0.87793500	0.51177800
H	3.25056900	6.22070900	-5.19749300	C	4.30973100	1.00996000	1.75022600
H	2.23449700	6.93313200	-3.93040800	O	3.26080000	0.92854700	2.51353000
N	-2.13906100	1.91015300	-0.40807400	C	5.59172200	1.29484500	2.51266300
C	-2.76539400	1.40773400	-1.52889600	H	5.73106000	0.53989200	3.29569900
H	-2.19499400	0.90163300	-2.29646200	H	5.51273600	2.26922200	3.01145800
C	-4.11557100	1.65339900	-1.44176100	O	1.00841400	-0.54018600	3.43778100
N	-4.28472100	2.33372600	-0.23975500	C	0.34628800	-1.61283600	3.25093300
H	-5.18399800	2.41737200	0.23821400	O	-0.15170700	-2.02381500	2.15156700
C	-3.07624000	2.44744600	0.35720700	C	0.14077100	-2.50023600	4.47047400
H	-2.90254000	2.90878000	1.31819400	H	-0.56271100	-3.29758600	4.20267000
C	-5.23927700	1.33829300	-2.39364700	H	1.11087400	-2.97639200	4.68486800
H	-5.28899500	2.09683000	-3.18962200	C	-0.33513100	-1.72886500	5.71220500
H	-4.99514300	0.39364700	-2.89819700	H	-1.29470500	-1.23936900	5.48661400
C	-6.65529400	1.24208100	-1.75954900	H	0.38128000	-0.92541400	5.92411800
H	-7.03629300	2.24229800	-1.52495200	C	-0.49346400	-2.63720200	6.93582900
H	-7.33817500	0.79816700	-2.49677100	H	-1.22377800	-3.43755000	6.75072600

H	-0.83725800	-2.06753800	7.80899400	O	0.18420600	-1.93558900	-3.26402000
H	0.46018200	-3.11395800	7.20282900				

Pro:

Ca	-2.44562800	0.27900400	-1.33995100	H	-1.46123700	-4.67279800	-6.49261200
Mn	-0.04813800	-1.76049600	-0.24961200	H	-3.23136500	-4.64277800	-6.59832100
Mn	-1.66511600	-0.89120900	1.72565400	H	-2.42965300	-5.70817900	-5.42893200
Mn	0.03520800	0.98396400	0.58102200	N	1.99339000	-2.06016400	-0.49737500
Mn	0.31460900	3.35292400	-1.65692700	C	2.78235600	-1.72718400	-1.57588400
O	-1.81274200	-1.69182600	0.09462400	H	2.34701800	-1.29772900	-2.46808100
O	0.18546900	-0.86031300	1.34656500	C	4.09528400	-2.02218000	-1.28885900
O	-1.73875700	0.71985100	0.93657600	N	4.07318900	-2.55720100	-0.00511800
O	-0.02109600	-0.08502800	-0.93898500	H	4.90260500	-2.65540000	0.58492800
O	-0.36476000	2.52857800	-0.16464300	C	2.79592700	-2.54115400	0.43870700
O	-4.46113100	-0.29030100	-2.72208500	H	2.48257400	-2.86161400	1.42125300
H	-4.98980500	-0.53953500	-1.93556200	C	5.34452600	-1.87368400	-2.11792300
H	-4.06630100	-1.12006700	-3.05923900	H	5.41032800	-2.68654100	-2.85703200
O	-1.35367400	1.76879600	-3.21352800	H	5.25282700	-0.94801800	-2.70296400
H	-1.23988900	1.51354200	-4.14717100	C	6.68172300	-1.86087200	-1.32794400
H	-1.90321800	3.32710500	-2.72451400	H	6.93069100	-2.87112100	-0.98468600
O	0.77028500	4.62654200	-2.93565900	H	7.48409000	-1.54045500	-2.00660000
H	1.24932200	4.21038800	-3.67145800	C	6.62488700	-0.98113500	-0.08082200
O	0.70867400	5.15994500	-0.50179500	O	6.42722800	-1.47013300	1.03848400
H	1.01344600	5.52253400	-1.37446300	N	6.72731900	0.35941200	-0.28197600
H	1.52140100	4.91655200	-0.02312000	H	6.83347700	0.69117100	-1.23299700
O	-3.35463600	2.61662400	-1.11542300	C	6.33795800	1.32931500	0.74696100
C	-2.67502500	3.62560000	-0.99402900	H	6.74802100	0.97724200	1.69877900
O	-1.82239900	4.00808700	-1.99406000	H	6.82417200	2.28183100	0.49986100
C	-2.70901000	4.58332200	0.16117300	C	4.81195100	1.49871700	0.86564800
H	-1.67442300	4.88426700	0.36337300	H	4.36702700	0.55063200	1.18697100
H	-3.22774200	5.48873800	-0.19507400	H	4.60734800	2.22653000	1.66417600
C	-3.38931200	3.99205700	1.39615400	C	4.16012400	1.95607500	-0.44239200
H	-2.87263900	3.07766500	1.70889200	H	4.40571500	1.24572600	-1.24747600
H	-4.43604500	3.73806900	1.19134800	H	4.53996300	2.93466400	-0.76503400
H	-3.36407600	4.71555300	2.22030700	C	2.63313700	2.02972000	-0.42719500
O	-0.28989600	-2.70495500	-1.94195800	O	2.01597800	1.28152600	0.38148800
C	-1.23379100	-2.57201500	-2.80991800	O	2.14536200	2.84487200	-1.27829900
O	-2.06504800	-1.63482200	-2.84776100	O	-0.01050500	-3.48735000	0.86084500
C	-1.26754200	-3.67769800	-3.86331100	C	-0.67748200	-3.61897300	1.94132900
H	-0.30359900	-3.64587500	-4.39528200	O	-1.37786100	-2.72777100	2.51602700
H	-1.27008300	-4.63834200	-3.32756700	C	-0.63421700	-5.00151800	2.58583600
C	-2.43130200	-3.59805600	-4.85405300	H	0.39556300	-5.37311000	2.49765800
H	-2.41818000	-2.61817900	-5.35105600	H	-1.24077600	-5.65736900	1.94166800
H	-3.38095300	-3.64702300	-4.30147900	H	-5.96733100	-2.16021300	2.03396500
C	-2.38669000	-4.71673700	-5.90113500	C	-1.13255700	-5.05564300	4.03045100

H	-1.08858400	-6.08440700	4.41060200	C	-0.19725600	1.64717900	4.86321200
H	-0.52103800	-4.42226000	4.68493100	H	0.58883200	2.40768900	4.78640100
H	-2.16623800	-4.70082400	4.10300000	H	-1.13115900	2.16361700	5.13665000
O	-4.39800000	-0.44620500	0.04182500	C	0.14057800	0.60294700	5.93981200
C	-4.51341700	-0.79601900	1.23585900	H	1.06334100	0.07581100	5.65336400
O	-3.54316900	-0.95824400	2.07927600	H	-0.65547600	-0.15184800	5.96067400
C	-5.88533300	-1.08615300	1.82095600	C	0.31451800	1.23110200	7.32643000
H	-6.67238400	-0.79081500	1.12151800	H	1.12258400	1.97618500	7.33149400
H	-6.00641100	-0.55620100	2.77267200	H	0.55867300	0.46923400	8.07830300
O	-1.20131300	0.03730100	3.43054500	H	-0.60531900	1.73765900	7.65121100
C	-0.41279200	1.04101800	3.48218000	O	0.11750800	1.98763300	-2.83871000
O	0.20106500	1.59045900	2.51241800				

Table S9 Reaction parameters for the closed-cubane crystal or solvent water-Wx (oxo/oxyl) nucleophilic attack with W2 as the proton acceptor:

Spin state	Spin topology (Mn1~Mn4-O10)	Gibbs Free energy (a.u.)		
		Rea	TS	Pro
doublet	ααββα	-3366.2435	-3366.1804	-3366.1818
	αβαβα	-3366.2419	-3366.1804	-3366.1817
	αββαα	-3366.2147	-3366.1741	-3366.2167
	βααβα	-3366.2469	-3366.1803	-3366.1819
	βαβαα	-3366.2139	-3366.1732	-3366.2159
	ββααα	-3366.2110	-3366.1730	-3366.2155
sextet	αααββ	-3366.2167	-3366.1761	-3366.2187
	ααβαβ	-3366.2442	-3366.1812	-3366.1829
	αβααβ	-3366.2433	-3366.1803	-3366.1817
	βαααβ	-3366.2445	-3366.1816	-3366.1830
octet	αααβα	-3366.2453	-3366.1833	-3366.1846
	ααβαα	-3366.2157	-3366.1754	-3366.2182
	αβααα	-3366.2119	-3366.1734	-3366.2151
	βαααα	-3366.2124	-3366.1746	-3366.2168
12-et	aaaaβ	-3366.2463	-3366.1828	-3366.1843
14-et	aaaaa	-3366.2143	-3366.1760	-3366.2178

Spin state	Spin topology (Mn1~Mn4-O10)	Relative Gibbs Free energy (kcal/mol)			
		$\Delta G^{\neq}$ (Rea-TS)	ΔG(Rea-Pro)	ΔG(Rea)	ΔG(Pro)
doublet	ααββα	39.6	38.7	2.1	23.2
	αβαβα	38.6	37.8	3.1	23.2
	αββαα	25.5	-1.3	20.2	1.3
	βααβα	41.8	40.8	0.0	23.1
	βαβαα	25.5	-1.3	20.7	1.8
	ββααα	23.8	-2.8	22.5	2.0

sextet	αααββ	25.5	-1.3	19.0	0.0
	ααβαβ	39.5	38.5	1.7	22.5
	αβααβ	39.5	38.7	2.3	23.2
	βαααβ	39.5	38.6	1.5	22.4
octet	αααβα	38.9	38.1	1.0	21.4
	ααβαα	25.3	-1.6	19.6	0.3
	αβααα	24.2	-2.0	22.0	2.3
	βαααα	23.7	-2.8	21.6	1.2
12-et	αααaβ	39.8	38.9	0.4	21.6
14-et	ααααα	24.0	-2.2	20.5	0.6

Spin state	Spin topology (Mn1~Mn4-O10)		Mulliken spin density		
			Rea	TS	Pro
doublet	α	Mn1	2.92	2.93	2.92
	α	Mn2	2.93	2.95	2.95
	β	Mn3	-2.93	-2.86	-2.84
	β	Mn4	-1.86	-2.28	-1.99
	α	O10	-0.15	0.00	-0.03
		O8	0.00	0.27	0.02
		O7	0.05	0.01	0.01
	α	Mn1	2.94	2.95	2.94
	β	Mn2	-2.92	-2.94	-2.95
	α	Mn3	2.91	2.86	2.87
	β	Mn4	-1.80	-2.23	-1.95
	α	O10	-0.14	0.01	-0.04
		O8	0.00	0.28	0.02
		O7	0.06	0.01	0.01
	α	Mn1	2.94	2.92	2.92
	β	Mn2	-2.93	-2.93	-2.93
	β	Mn3	-2.84	-2.82	-2.83
	α	Mn4	2.64	3.47	3.79
	α	O10	0.87	0.26	0.09
		O8	0.00	0.22	0.01
		O7	0.30	-0.01	-0.02
	β	Mn1	-2.92	-2.91	-2.91
	α	Mn2	2.93	2.93	2.93
	α	Mn3	2.89	2.87	2.88
	β	Mn4	-1.81	-2.23	-1.95
	α	O10	-0.12	0.01	-0.04
		O8	0.00	0.28	0.02
		O7	0.06	0.01	0.01
	β	Mn1	-2.94	-2.93	-2.92
	α	Mn2	2.94	2.95	2.94
	β	Mn3	-2.82	-2.80	-2.81

	α	Mn4	2.64	3.47	3.79
	α	O10	0.87	0.26	0.09
		O8	0.00	0.22	0.01
		O7	0.30	-0.01	-0.02
	β	Mn1	-2.94	-2.93	-2.92
	β	Mn2	-2.94	-2.95	-2.95
	α	Mn3	2.88	2.85	2.88
	α	Mn4	2.69	3.54	3.93
	α	O10	0.85	0.26	-0.04
		O8	0.00	0.21	0.01
		O7	0.37	0.00	-0.01
	α	Mn1	2.94	2.93	2.93
	α	Mn2	2.93	2.93	2.93
	α	Mn3	2.85	2.83	2.84
	β	Mn4	-2.64	-3.47	-3.80
	β	O10	-0.87	-0.26	-0.09
		O8	0.00	-0.22	-0.01
		O7	-0.29	0.01	0.02
	α	Mn1	2.92	2.91	2.92
	α	Mn2	2.93	2.95	2.95
	β	Mn3	-2.89	-2.83	-2.83
	α	Mn4	1.80	2.23	1.94
	β	O10	0.14	-0.01	0.04
sextet		O8	0.00	-0.28	-0.02
		O7	-0.01	-0.01	-0.01
	α	Mn1	2.94	2.93	2.93
	β	Mn2	-2.92	-2.94	-2.95
	α	Mn3	2.95	2.88	2.87
	α	Mn4	1.86	2.28	1.99
	β	O10	0.15	0.00	0.03
		O8	0.00	-0.28	-0.02
		O7	-0.05	-0.01	-0.01
	β	Mn1	-2.92	-2.92	-2.92
	α	Mn2	2.92	2.93	2.93
	α	Mn3	2.95	2.90	2.89
	α	Mn4	1.86	2.27	1.99
	β	O10	0.15	0.00	0.03
		O8	0.00	-0.28	-0.02
		O7	-0.05	-0.01	-0.01
	α	Mn1	2.93	2.95	2.94
	α	Mn2	2.92	2.93	2.93
octet	α	Mn3	2.92	2.89	2.91
	β	Mn4	-1.80	-2.23	-1.95
	α	O10	-0.14	0.01	-0.04

		O8	0.00	0.28	0.02
		O7	0.06	0.01	0.01
	α	Mn1	2.95	2.93	2.92
	α	Mn2	2.95	2.95	2.95
	β	Mn3	-2.80	-2.78	-2.79
	α	Mn4	2.63	3.47	3.79
	α	O10	0.87	0.26	0.09
		O8	0.00	0.22	0.01
		O7	0.30	-0.01	-0.02
	α	Mn1	2.95	2.93	2.92
	β	Mn2	-2.94	-2.94	-2.94
	α	Mn3	2.90	2.87	2.89
	α	Mn4	2.69	3.54	3.94
	α	O10	0.85	0.26	-0.04
		O8	0.00	0.21	0.01
		O7	0.37	0.01	-0.01
	β	Mn1	-2.93	-2.92	-2.92
	α	Mn2	2.93	2.94	2.93
	α	Mn3	2.93	2.90	2.92
	α	Mn4	2.69	3.54	3.93
	α	O10	0.85	0.26	-0.04
		O8	0.00	0.21	0.01
		O7	0.37	0.00	-0.01
12-et	α	Mn1	2.93	2.93	2.93
	α	Mn2	2.92	2.93	2.93
	α	Mn3	2.96	2.92	2.91
	α	Mn4	1.86	2.27	1.99
	β	O10	0.14	0.00	0.03
		O8	0.00	-0.28	-0.02
		O7	-0.05	-0.01	-0.01
14-et	α	Mn1	2.95	2.93	2.92
	α	Mn2	2.93	2.93	2.93
	α	Mn3	2.93	2.90	2.93
	α	Mn4	2.69	3.54	3.93
	α	O10	0.85	0.26	-0.04
		O8	0.00	0.21	0.01
		O7	0.37	0.00	-0.01

Rea:

Ca	-2.55748500	-0.39452000	1.00052300	O	0.48673400	1.50976600	-0.67914000
Mn	0.36691200	1.29913700	1.16017600	O	-1.79056600	0.53940200	-1.13094300
Mn	-1.27475000	2.21922200	-0.77443300	O	-0.08579700	-0.41887500	0.67970400
Mn	-0.16680500	-0.28167200	-1.17744600	O	-0.98168500	-1.81474700	-1.51272000
Mn	-0.91024200	-3.41929100	-0.73071500	O	-4.40914800	-0.19604600	2.67453000
O	-1.34108900	1.85908200	1.00393100	H	-4.80082900	0.60583400	2.27415800

H	-3.84987400	0.10535600	3.41686000	H	7.43429600	0.48403800	1.42527800
O	1.51999300	-2.32846100	2.09416400	H	7.63665700	-1.21966000	1.84688800
H	0.98811200	-1.65018900	1.62233600	C	6.62849900	-0.80481900	-0.03865000
H	0.94240500	-3.10677800	2.00001500	O	6.61318900	0.09117000	-0.89386500
O	-0.71384000	-5.03994000	0.17029500	N	6.31851500	-2.09232900	-0.33774400
H	-1.62332900	-5.36483200	0.32245300	H	6.28468700	-2.77126800	0.41298000
O	-0.61900800	-4.19843900	-2.75604100	C	5.79469400	-2.47120000	-1.65337400
H	0.35063000	-4.31153500	-2.71871400	H	6.40959800	-1.96661100	-2.40617500
H	-0.75665400	-3.33106800	-3.19085700	H	5.94276500	-3.55297100	-1.76455600
O	-3.80461200	-2.11842500	-0.03980500	C	4.31780600	-2.09336000	-1.86004900
C	-3.79820000	-3.17692900	-0.68721000	H	4.20723900	-1.00827900	-1.76163600
O	-2.74345500	-3.85518800	-1.03128100	H	4.05120900	-2.34348600	-2.89817000
C	-5.11961300	-3.76508800	-1.17669100	C	3.36876700	-2.80680100	-0.89149900
H	-5.88226900	-3.48750400	-0.43872500	H	3.61520700	-2.56466600	0.15379300
H	-5.37236800	-3.21360900	-2.09639100	H	3.43534000	-3.89766900	-0.99039800
C	-5.11731200	-5.27092700	-1.44969500	C	1.90248900	-2.41344300	-1.02318800
H	-4.88930300	-5.83955900	-0.53856200	O	1.63933300	-1.20269600	-1.28145100
H	-4.36915300	-5.53496900	-2.20481500	O	1.07825300	-3.37338800	-0.83583600
H	-6.10261000	-5.59489400	-1.80847600	O	0.85787200	3.26437500	1.34578100
O	0.29436200	0.99179900	3.05572500	C	0.33640300	4.17996600	0.62627600
C	-0.66803900	0.47071800	3.75033600	O	-0.48483800	4.01710200	-0.33094500
O	-1.72793400	0.00524000	3.28236500	C	0.74301700	5.60759000	0.97394900
C	-0.39604000	0.44092700	5.24986900	H	1.82496000	5.60169600	1.16265800
H	0.43378400	-0.26777000	5.40209000	H	0.27546100	5.82915100	1.94597700
H	0.00014500	1.42481500	5.53882800	H	-6.19110000	2.90929500	0.01233100
C	-1.59710400	0.04758800	6.11362500	C	0.35601900	6.65992200	-0.06558900
H	-1.97803900	-0.92588400	5.77747400	H	0.66781500	7.65722000	0.27000600
H	-2.41185200	0.76928300	5.95226700	H	0.83473100	6.45855900	-1.03175200
C	-1.24916900	-0.01042300	7.60520900	H	-0.72673900	6.67098700	-0.23114400
H	-0.45970500	-0.74955900	7.80089100	O	-4.14686000	1.47000700	0.46661700
H	-2.12405600	-0.29088900	8.20585000	C	-4.08526000	2.49903100	-0.23490600
H	-0.89047700	0.96180600	7.97139300	O	-3.02897100	2.93709100	-0.85235500
N	2.40763600	0.97896200	1.25409500	C	-5.30730600	3.37958000	-0.42725100
C	3.14908100	0.19276600	2.10861900	H	-5.46984100	3.56356600	-1.49564300
H	2.67543000	-0.40415000	2.87425600	H	-5.13192300	4.35392000	0.04721600
C	4.47379200	0.26198100	1.75006300	O	-0.91824800	2.42045300	-2.74031800
N	4.51485800	1.13853700	0.67004600	C	-0.39557200	1.50459900	-3.45277300
H	5.32378500	1.26213800	0.05688800	O	0.00798600	0.35769800	-3.05693100
C	3.25234400	1.52752500	0.39057900	C	-0.25433400	1.78984700	-4.94135300
H	2.97057200	2.16468300	-0.43500700	H	0.45633200	1.06748600	-5.36111700
C	5.67074800	-0.44692800	2.32678300	H	-1.23583300	1.57267700	-5.39423700
H	5.96691000	0.01355300	3.28124200	C	0.15400700	3.23387100	-5.26697700
H	5.35707700	-1.47002500	2.57639300	H	1.12740500	3.44725500	-4.80024900
C	6.93214300	-0.48966000	1.42513000	H	-0.56703700	3.91934900	-4.80479600

C	0.23768300	3.48675700	-6.77589700	H	-0.73229000	3.31289600	-7.26278600
H	0.97246300	2.82431200	-7.25473400	O	-1.08259900	-2.86115400	0.89580400
H	0.53524900	4.52208000	-6.98666100				

TS:

Ca	-2.66659700	-0.34710000	0.81681600	C	-2.00077200	0.85387700	7.45509800
Mn	0.31147900	1.27774500	1.11115100	H	-1.21535100	0.19846200	7.85718100
Mn	-1.18308100	2.11062200	-0.97914300	H	-2.93053600	0.62685500	7.99248500
Mn	-0.05601100	-0.40703900	-1.19917900	H	-1.72153000	1.88974700	7.69404500
Mn	-0.84809200	-3.42105700	-0.41091000	N	2.35247400	0.96947200	1.36781400
O	-1.37362800	1.83468700	0.80937900	C	3.05543400	0.20685200	2.27341900
O	0.55656700	1.41998000	-0.72118200	H	2.54823800	-0.31725300	3.07229400
O	-1.68502200	0.41684100	-1.28138000	C	4.39926800	0.27075500	1.97824400
O	-0.06305600	-0.46078600	0.69554000	N	4.48516400	1.11873900	0.88050400
O	-0.78608900	-1.97855800	-1.50679600	H	5.32566800	1.24406500	0.30957700
O	-4.63886300	-0.04618600	2.33691300	C	3.23606300	1.49715500	0.53387700
H	-4.98050600	0.73863100	1.86369600	H	2.99099400	2.10748900	-0.32314600
H	-4.11401300	0.29102900	3.08996500	C	5.58306200	-0.40317500	2.62514500
O	-0.33883300	-2.56810200	2.35586200	H	5.80082100	0.06137300	3.59838500
H	0.07714800	-1.84887900	1.78877900	H	5.29816700	-1.44056600	2.85072300
H	-0.10107400	-3.46972000	1.95655500	C	6.90188900	-0.39535800	1.80579000
O	-0.41808200	-4.78872700	0.78735900	H	7.36149000	0.59858900	1.83411000
H	-1.25749100	-5.16483200	1.11157000	H	7.60602500	-1.09361000	2.27872900
O	-0.01019700	-4.54587500	-2.18828400	C	6.70759400	-0.72917900	0.32634300
H	0.88108900	-4.68048600	-1.81519500	O	6.69946600	0.16368700	-0.53218400
H	0.05206000	-3.73117500	-2.72769000	N	6.47102600	-2.02852100	0.01423500
O	-3.77793400	-2.15795500	-0.35130700	H	6.44758800	-2.71042800	0.76261600
C	-3.68393800	-3.27912500	-0.88021100	C	5.98712700	-2.42769300	-1.31315900
O	-2.62335600	-4.02469100	-0.89214300	H	6.62179300	-1.93723200	-2.05882500
C	-4.89148900	-3.85764400	-1.61815500	H	6.13956100	-3.51088900	-1.39912300
H	-5.78633700	-3.49833500	-1.09540600	C	4.51329500	-2.05520000	-1.56149300
H	-4.89887000	-3.36962600	-2.60561800	H	4.40966500	-0.96532600	-1.54818100
C	-4.90069700	-5.37906800	-1.77904800	H	4.24805300	-2.38123000	-2.57775200
H	-4.91272500	-5.88125300	-0.80331200	C	3.56031700	-2.68082800	-0.54003400
H	-4.01229600	-5.72293600	-2.31944400	H	3.85786500	-2.38156700	0.47713000
H	-5.79260700	-5.69763000	-2.33404200	H	3.60754600	-3.77816800	-0.56156700
O	0.09806300	1.06627900	3.01753000	C	2.08658100	-2.28247600	-0.65727700
C	-0.98662700	0.75178100	3.65972600	O	1.81559300	-1.17082700	-1.20583900
O	-2.02496200	0.29724700	3.14161300	O	1.26554000	-3.10689800	-0.14950800
C	-0.89183100	0.96943800	5.16659300	O	0.79973000	3.25485000	1.24440300
H	-0.05633900	0.35051500	5.52955400	C	0.33172100	4.13824000	0.45025500
H	-0.57407300	2.01034900	5.32845000	O	-0.42036400	3.93547800	-0.55356900
C	-2.17155400	0.65507300	5.94489900	C	0.71502300	5.58060100	0.76543300
H	-2.47764600	-0.37834500	5.73330800	H	1.77521700	5.58269300	1.05198500
H	-2.98508900	1.29719100	5.57705600	H	0.16162900	5.85013100	1.67863600

H	-6.13761500	2.94937200	-0.62049700	O	0.21635900	0.14755300	-3.08627100
C	0.42956800	6.58246100	-0.35386700	C	0.06640300	1.48546200	-5.04909900
H	0.71425700	7.59481200	-0.03971400	H	0.78938700	0.73694900	-5.39537700
H	0.99316600	6.33463500	-1.26179500	H	-0.89275900	1.25445500	-5.54107600
H	-0.63346300	6.58536600	-0.61784700	C	0.50707100	2.90824900	-5.42235700
O	-4.17567200	1.49307500	0.07392800	H	1.45756900	3.13590200	-4.91665800
C	-4.03024100	2.47770500	-0.67851700	H	-0.22904700	3.62181600	-5.03197100
O	-2.91652100	2.85551900	-1.22628300	C	0.67107900	3.08652300	-6.93537000
C	-5.21158100	3.36687600	-1.02500800	H	1.42186200	2.39491300	-7.34288100
H	-5.29021800	3.47254300	-2.11341700	H	0.99067000	4.10770200	-7.18041100
H	-5.04584200	4.37057200	-0.61251400	H	-0.27448000	2.89735800	-7.46285300
O	-0.70512100	2.22855200	-2.91903600	O	-1.70116100	-2.58052800	1.14730000
C	-0.15498900	1.27477100	-3.55807300				

Pro:

Ca	-2.66113000	-0.45102700	0.72762100	H	-5.76939100	-5.80128800	-2.28689100
Mn	0.29068300	1.21837400	1.20092500	O	0.04516000	0.84559000	3.07182800
Mn	-1.16498300	2.22117700	-0.84135800	C	-1.05540400	0.49495000	3.67177000
Mn	-0.01695900	-0.25399200	-1.24110000	O	-2.09559600	0.11861500	3.10279000
Mn	-0.78460300	-3.26872300	-0.70976500	C	-0.97077300	0.56649800	5.19300300
O	-1.38723500	1.79772100	0.90881100	H	-0.14378200	-0.09204400	5.50145700
O	0.58050400	1.50895800	-0.61241900	H	-0.64616900	1.58435200	5.45673600
O	-1.64306800	0.55192500	-1.29514900	C	-2.26050200	0.19048200	5.92608800
O	-0.07476400	-0.47145700	0.62255800	H	-2.57237900	-0.81511500	5.61319200
O	-0.75137400	-1.80780500	-1.70075200	H	-3.06509200	0.87178500	5.61374800
O	-4.67852500	-0.23677100	2.21343000	C	-2.10280400	0.24191700	7.44983200
H	-5.00188200	0.57620900	1.77615900	H	-1.32656900	-0.45595400	7.79428500
H	-4.16761300	0.05649000	2.99394700	H	-3.03955300	-0.02742600	7.95459900
O	-0.52962200	-2.75213600	2.01962200	H	-1.81777400	1.24759600	7.78978300
H	-0.01785800	-1.96411000	1.70612500	N	2.32506000	0.87572900	1.47084700
H	-0.33569200	-4.40499900	1.31351000	C	2.99621700	0.03681700	2.33168800
O	-0.54394500	-4.97011600	0.51456800	H	2.46340700	-0.53362600	3.08051900
H	-1.48044400	-5.21925700	0.63934300	C	4.34652100	0.09717600	2.06776700
O	-0.02837000	-4.51484500	-2.64651500	N	4.46942900	1.02024300	1.03596400
H	0.90948700	-4.42071300	-2.39985700	H	5.32325400	1.17036300	0.49167500
H	-0.20953400	-3.75104200	-3.22728900	C	3.23393800	1.44583500	0.69421200
O	-3.77251500	-2.08537300	-0.65564100	H	3.01654500	2.12082000	-0.12086700
C	-3.65840900	-3.21327000	-1.16829500	C	5.50510700	-0.63931100	2.69149700
O	-2.55597000	-3.89273000	-1.25932100	H	5.70439800	-0.24961300	3.70087500
C	-4.88610600	-3.87742700	-1.78989600	H	5.20208000	-1.68627100	2.83420100
H	-5.76610100	-3.48825500	-1.26381900	C	6.84347300	-0.59058100	1.90678300
H	-4.95053900	-3.49484400	-2.82126900	H	7.31044600	0.39477900	2.01176500
C	-4.86603900	-5.40818600	-1.80262000	H	7.53006900	-1.32538800	2.34916600
H	-4.83103800	-5.81242100	-0.78206000	C	6.68232800	-0.82486000	0.40470200
H	-3.99012100	-5.78457600	-2.34200500	O	6.69943000	0.12163300	-0.39390900

N	6.44656000	-2.09976600	0.00282200	H	1.03638900	6.44095800	-0.74956600
H	6.40692700	-2.83026200	0.70301900	H	-0.60812400	6.64601700	-0.13509700
C	6.00472800	-2.40957200	-1.36209400	O	-4.15287500	1.47371000	0.09552400
H	6.66599000	-1.87731900	-2.05415200	C	-4.01311400	2.51903800	-0.56747800
H	6.15351300	-3.48616200	-1.51283700	O	-2.89489900	2.96220700	-1.06065300
C	4.54285900	-2.00956700	-1.63477500	C	-5.20231100	3.41534100	-0.86474100
H	4.44391400	-0.92284900	-1.54613200	H	-5.27012900	3.59518700	-1.94421000
H	4.31244200	-2.26061500	-2.68047100	H	-5.05566600	4.38995500	-0.38157400
C	3.54927200	-2.69951200	-0.69595000	O	-0.64293900	2.49626000	-2.76033100
H	3.81161700	-2.47572400	0.35020000	C	-0.06595600	1.60355100	-3.45968800
H	3.58714100	-3.79230200	-0.79758900	O	0.30719200	0.44496400	-3.06925800
C	2.08931400	-2.26850800	-0.84146400	C	0.18998900	1.93399800	-4.92307000
O	1.85150200	-1.09485600	-1.24238800	H	0.93852100	1.22941600	-5.30556400
O	1.23763400	-3.15646700	-0.49623600	H	-0.75025800	1.72136300	-5.45804200
O	0.77841900	3.17823200	1.49928900	C	0.60752000	3.39012700	-5.17380200
C	0.32382300	4.12242500	0.77086400	H	1.53880100	3.59793900	-4.62560500
O	-0.41186700	4.00077200	-0.25882200	H	-0.15472900	4.05592500	-4.75058900
C	0.69965300	5.53516400	1.20543900	C	0.80714100	3.68815200	-6.66350000
H	1.75112200	5.51200900	1.52139000	H	1.58400700	3.04587000	-7.10173100
H	0.12017200	5.73618600	2.12017000	H	1.10961200	4.73163100	-6.82047100
H	-6.12668000	2.95734300	-0.50255900	H	-0.11964200	3.52074400	-7.23018300
C	0.44688100	6.62023900	0.15807500	O	-1.67606300	-2.65240400	1.08853700
H	0.72293800	7.60489000	0.55657700				

W1 (hydroxyl)-W2 (hydroxyl/oxyl)

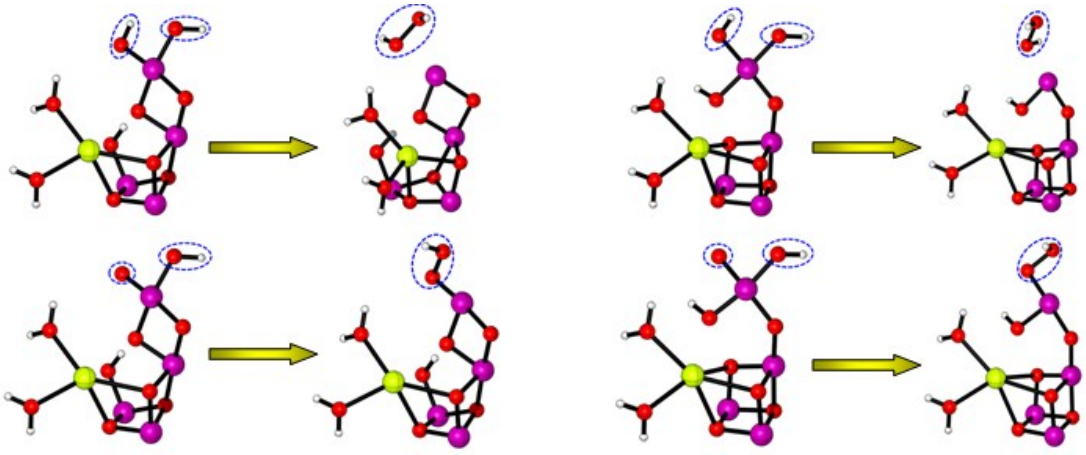

Fig. S7 Pictorial exhibitions for the open (left) and closed-cubane (right) W1 (hydroxyl)-W2 (hydroxyl) coupling (upper) and W1 (hydroxyl)-W2 (oxyl) nucleophilic attack (lower).

Table S10 Reaction parameters for the open-cubane W1 (hydroxyl)-W2 (hydroxyl) coupling:

Spin state	Spin topology (Mn1~Mn4-O6/O7)	Gibbs Free energy (a.u.)		
		Rea	TS	Pro

doublet	ααββα	-3366.2131	-3366.1597	-3366.1651
	αβαβα	-3366.2125	-3366.1571	-3366.1855
	αββαα	-3366.2142	-3366.1685	-3366.2084
	βααβα	-3366.2127	-3366.1581	-3366.1870
	βαβαα	-3366.2148	-3366.1687	-3366.2081
	ββααα	-3366.2136	-3366.1546	-3366.1882
sextet	αααββ	-3366.2155	-3366.1702	-3366.2111
	ααβαβ	-3366.2136	-3366.1602	-3366.1871
	αβααβ	-3366.2131	-3366.1596	-3366.1690
	βααβ	-3366.2132	-3366.1604	-3366.1703
octet	αααβα	-3366.2143	-3366.1596	-3366.1876
	ααβαα	-3366.2163	-3366.1698	-3366.2089
	αβααα	-3366.2162	-3366.1547	-3366.1871
	βαααα	-3366.2153	-3366.1560	-3366.1900
12-et	ααααβ	-3366.2149	-3366.1619	-3366.1704
14-et	ααααα	-3366.2161	-3366.1570	-3366.1898

Spin state	Spin topology (Mn1~Mn4-O6/O7)	Relative Gibbs Free energy (kcal/mol)			
		$\Delta G^{\neq}$ (Rea-TS)	ΔG(Rea-Pro)	ΔG(Rea)	ΔG(Pro)
doublet	ααββα	33.5	30.1	2.0	27.5
	αβαβα	34.8	16.9	2.4	14.7
	αββαα	28.7	3.6	1.3	0.3
	βααβα	34.3	16.1	2.3	13.7
	βαβαα	28.9	4.2	0.9	0.5
	ββααα	37.0	15.9	1.7	13.0
sextet	αααββ	28.4	2.8	0.5	1.4
	ααβαβ	33.5	16.6	1.7	13.7
	αβααβ	33.6	27.7	2.0	25.0
	βααβ	33.1	26.9	1.9	24.2
octet	αααβα	34.3	16.8	1.3	13.4
	ααβαα	29.2	4.6	0.0	0.0
	αβααα	38.6	18.3	0.1	13.7
	βαααα	37.2	15.9	0.6	11.9
12-et	ααααβ	33.3	27.9	0.9	24.2
14-et	ααααα	37.1	16.5	0.1	12.0

Spin state	Spin topology (Mn1~Mn4-O6/O7)		Mulliken spin density		
			Rea	TS	Pro
doublet	α	Mn1	2.96	2.95	2.95
	α	Mn2	2.95	2.96	2.96
	β	Mn3	-2.91	-2.89	-2.89
	β	Mn4	-2.95	-2.39	-1.95
	α	O6	0.55	0.33	0.00

		O7	0.54	0.09	0.00
	α	Mn1	2.95	2.95	2.91
	β	Mn2	-2.92	-2.91	-2.88
	α	Mn3	2.88	3.48	3.81
	β	Mn4	-2.90	-2.66	-2.68
	α	O6	0.55	0.16	0.00
		O7	0.55	0.28	0.00
	α	Mn1	2.94	2.94	2.94
	β	Mn2	-2.94	-2.95	-2.94
	β	Mn3	-2.90	-2.88	-2.86
	α	Mn4	2.80	3.29	3.83
	α	O6	0.54	0.37	0.00
		O7	0.53	0.30	-0.01
	β	Mn1	-2.94	-2.90	-2.90
	α	Mn2	2.94	2.95	2.95
	α	Mn3	2.91	3.51	3.85
	β	Mn4	-2.90	-2.67	-2.68
	α	O6	0.55	0.16	0.00
		O7	0.55	0.28	0.00
	β	Mn1	-2.95	-2.95	-2.94
	α	Mn2	2.92	2.94	2.94
	β	Mn3	-2.88	-2.86	-2.83
	α	Mn4	2.80	3.28	3.82
	α	O6	0.54	0.38	0.00
		O7	0.53	0.30	-0.01
	β	Mn1	-2.96	-2.92	-2.91
	β	Mn2	-2.95	-2.93	-2.92
	α	Mn3	2.91	3.54	3.86
	α	Mn4	2.84	2.78	2.68
	α	O6	0.53	0.24	0.00
		O7	0.54	0.26	0.00
	α	Mn1	2.97	2.96	2.96
	α	Mn2	2.96	2.97	2.96
	α	Mn3	2.91	2.89	2.87
	β	Mn4	-2.80	-3.28	-3.83
	β	O6	-0.54	-0.38	0.00
		O7	-0.53	-0.30	0.01
sextet	α	Mn1	2.96	2.91	2.91
	α	Mn2	2.95	2.93	2.91
	β	Mn3	-2.88	-3.47	-3.81
	α	Mn4	2.90	2.67	2.68
	β	O6	-0.56	-0.15	0.00
		O7	-0.54	-0.28	0.00
	α	Mn1	2.94	2.94	2.94

	β	Mn2	-2.92	-2.94	-2.93
	α	Mn3	2.91	2.89	2.86
	α	Mn4	2.95	2.39	2.01
	β	O6	-0.55	-0.33	0.00
		O7	-0.54	-0.09	0.00
	β	Mn1	-2.94	-2.94	-2.94
	α	Mn2	2.94	2.95	2.94
	α	Mn3	2.94	2.92	2.88
	α	Mn4	2.95	2.40	1.99
	β	O6	-0.55	-0.33	0.00
		O7	-0.54	-0.10	0.00
octet	α	Mn1	2.97	2.97	2.95
	α	Mn2	2.96	2.96	2.96
	α	Mn3	2.92	3.52	3.85
	β	Mn4	-2.90	-2.67	-2.67
	α	O6	0.55	0.16	0.00
		O7	0.55	0.28	0.00
	α	Mn1	2.96	2.96	2.97
	α	Mn2	2.95	2.96	2.96
	β	Mn3	-2.87	-2.85	-2.83
	α	Mn4	2.80	3.30	3.82
	α	O6	0.54	0.37	0.00
		O7	0.53	0.29	-0.01
	α	Mn1	2.95	2.96	2.93
	β	Mn2	-2.92	-2.91	-2.90
	α	Mn3	2.91	3.54	3.87
	α	Mn4	2.85	2.79	2.68
	α	O6	0.54	0.24	0.00
		O7	0.54	0.26	0.00
	β	Mn1	-2.94	-2.91	-2.90
	α	Mn2	2.94	2.95	2.95
	α	Mn3	2.94	3.56	3.89
	α	Mn4	2.85	2.79	2.68
	α	O5	0.53	0.24	0.00
		O10	0.54	0.26	0.00
12-et	α	Mn1	2.97	2.96	2.96
	α	Mn2	2.97	2.97	2.97
	α	Mn3	2.95	2.93	2.89
	α	Mn4	2.95	2.40	2.00
	β	O6	-0.55	-0.33	0.00
		O7	-0.55	-0.10	0.00
14-et	α	Mn1	2.97	2.97	2.95
	α	Mn2	2.96	2.97	2.97
	α	Mn3	2.95	3.58	3.90

	α	Mn4	2.85	2.79	2.69
	α	O6	0.54	0.24	0.00
		O7	0.54	0.26	0.00

Rea:

Ca	2.38126600	-0.08633400	-1.43464700	H	2.21978300	7.25948600	-4.00634800
Mn	0.03121500	1.95823100	-0.06910200	H	3.39607200	7.45418200	-2.69480900
Mn	1.41742400	0.38409300	1.74761900	H	3.94201300	6.96370600	-4.30927700
Mn	-0.18716200	-1.53658800	0.50786500	N	-2.00862300	2.35863300	-0.29495800
Mn	-0.19529100	-3.20312400	-1.62178300	C	-2.75896100	2.26282600	-1.44740100
O	1.72598400	1.49744700	0.34183500	H	-2.27788800	2.11647100	-2.40426200
O	-0.33046900	0.44386100	1.00645400	C	-4.09386700	2.36519700	-1.13319200
O	1.55275900	-1.17135300	0.84141400	N	-4.12845800	2.54287000	0.24496300
O	0.12814300	-1.44201500	-1.31735700	H	-4.97371200	2.43058200	0.81298600
O	-0.16271700	-3.28725200	0.15558200	C	-2.85990400	2.51413500	0.70896400
O	4.48555600	1.07080200	-2.20573500	H	-2.58641500	2.58248000	1.75095600
H	4.93673500	0.92060200	-1.34964300	C	-5.31525000	2.32247600	-2.01506600
H	4.14276200	1.98818100	-2.17013700	H	-5.39674100	3.25545600	-2.59275900
O	1.66434200	0.67431600	-3.75309000	H	-5.17070100	1.52536900	-2.75789100
H	2.17004500	1.50777200	-3.79359900	C	-6.67001600	2.11222600	-1.29001800
H	0.81441200	0.96804800	-3.35098200	H	-6.94561900	3.01437700	-0.73229400
O	-0.37322600	-3.35856000	-3.56436300	H	-7.44619600	1.95042300	-2.05048300
H	-1.34024200	-3.31081600	-3.71389100	C	-6.64560600	0.96890600	-0.27685300
O	-0.74204400	-4.99039000	-2.16759400	O	-6.45888000	1.18559500	0.92822600
H	0.12277100	-5.40539800	-2.37379500	N	-6.77538800	-0.28788200	-0.77357500
O	3.02628200	-2.23298900	-2.12909000	H	-6.90670900	-0.40343700	-1.77078600
C	2.74049100	-3.43873900	-2.06533600	C	-6.53355400	-1.47943900	0.04774400
O	1.56596400	-3.93526900	-1.83778100	H	-7.04130600	-1.32724000	1.00609100
C	3.85201000	-4.47201900	-2.24582900	H	-7.01351000	-2.32633300	-0.45865100
H	4.44770100	-4.13562200	-3.10487900	C	-5.04025900	-1.75314400	0.29560200
H	4.50776500	-4.36234100	-1.36863500	H	-4.60564600	-0.90585000	0.83657100
C	3.40865300	-5.92581300	-2.40861600	H	-4.95659900	-2.62615100	0.95828300
H	2.77172800	-6.05007100	-3.29397800	C	-4.24993000	-2.00269800	-0.99320100
H	2.84475800	-6.26930900	-1.53355500	H	-4.38942300	-1.15680200	-1.68569900
H	4.28216700	-6.57932900	-2.52969600	H	-4.59557400	-2.90275400	-1.51728100
O	0.55642200	3.55744000	-1.00423700	C	-2.74360400	-2.12891500	-0.79269900
C	1.61383500	3.71571800	-1.74073300	O	-2.20691000	-1.49559200	0.15531500
O	2.39249100	2.81072600	-2.09797300	O	-2.13919200	-2.85458900	-1.65434500
C	1.84212400	5.16834700	-2.15783400	O	-0.14723100	3.14844100	1.52884100
H	0.88495800	5.56469200	-2.52685900	C	0.49399100	3.00252800	2.62457200
H	2.05617700	5.73611800	-1.23846200	O	1.18350700	1.99614800	2.94392100
C	2.95659800	5.36974100	-3.18783200	C	0.41322700	4.16630400	3.60412600
H	2.73352800	4.77562500	-4.08567900	H	-0.62139700	4.53469700	3.59325600
H	3.89719300	4.96871500	-2.78634700	H	1.01845100	4.97498300	3.16546700
C	3.13882000	6.84249300	-3.57101800	C	0.88586400	3.84301900	5.02184900

H	0.82027200	4.73582000	5.65643400	C	-0.37798500	-2.08455200	4.75976100
H	0.27205500	3.05474300	5.47470300	H	-0.82740500	-1.28165000	5.36390600
H	1.92318800	3.49159700	5.01978100	H	-1.13624000	-2.86145800	4.60946600
O	4.22561300	0.02865900	0.27990900	C	0.85332900	-2.64644200	5.49452800
C	4.27303400	0.16708400	1.52017100	H	1.59891500	-1.84721500	5.59482800
O	3.25187000	0.32665200	2.29922300	H	1.31330300	-3.43088900	4.87563200
C	5.60537700	0.14488200	2.24927600	C	0.49567500	-3.21623300	6.87083500
H	5.65484000	-0.75400700	2.87747600	H	0.06013200	-2.44384400	7.52038600
H	5.68638500	1.01207200	2.91498100	H	1.38559300	-3.61391800	7.37558400
H	6.43373800	0.13375800	1.53549300	H	-0.23472200	-4.03314200	6.78887700
O	0.85634700	-0.57721900	3.38963000	O	-0.04009000	1.09766200	-1.68529000
C	-0.02386700	-1.49304700	3.40674000	H	-0.41595800	0.18789700	-1.58214900
O	-0.62820000	-1.95043200	2.38692700				

TS:

Ca	-2.66324700	-0.51632600	-1.15517000	O	0.82875600	-3.39754200	-1.33645600
Mn	0.65907800	-1.80677600	-0.28829800	C	0.00975000	-4.03464900	-2.11989200
Mn	-1.10022800	-1.00287400	1.71624900	O	-1.15229700	-3.70465200	-2.40664000
Mn	-0.40732600	1.45433200	0.60036300	C	0.63030600	-5.30714400	-2.70253500
Mn	-1.19003500	3.06184500	-1.41670100	H	1.58706200	-5.02683700	-3.16839700
O	-1.09835900	-1.97516400	0.16247700	H	0.89997200	-5.95527000	-1.85414300
O	0.48406700	-0.35240100	0.93002200	C	-0.26765400	-6.05107700	-3.69381800
O	-1.87141800	0.47489300	1.01721800	H	-0.52978000	-5.37630500	-4.52049700
O	-0.81939200	1.29132600	-1.21581300	H	-1.21628900	-6.30355900	-3.20122200
O	-1.17032000	3.05821000	0.35964600	C	0.39382900	-7.31995700	-4.24288900
O	-3.62796500	-2.72982500	-1.74317100	H	1.33067700	-7.08807000	-4.76924600
H	-4.01821900	-2.90585300	-0.86665500	H	0.63532300	-8.02671100	-3.43627100
H	-2.82950000	-3.30224000	-1.81735000	H	-0.26650200	-7.83686200	-4.95138600
O	-1.68734400	-1.07386500	-3.36778900	N	2.71481300	-1.41850700	-0.44180400
H	-1.79338000	-2.04136100	-3.45644200	C	3.39780700	-1.00792800	-1.56535600
H	-0.74457700	-1.00841300	-3.06573400	H	2.90920800	-0.99905600	-2.52939200
O	-1.00411500	3.71289600	-3.40097300	C	4.67423500	-0.63725600	-1.21323800
H	-0.04233100	3.91899400	-3.42155500	N	4.74818100	-0.85044600	0.15886500
O	-1.34667900	5.02675500	-2.32769500	H	5.48254300	-0.46255000	0.75756200
H	-2.32109400	4.95877400	-2.47531700	C	3.54603900	-1.30076500	0.58266800
O	-4.10019600	1.21946300	-1.79524600	H	3.29878900	-1.50639300	1.61299300
C	-4.17362800	2.45921400	-1.92552500	C	5.81301200	-0.12346400	-2.05533700
O	-3.18357800	3.27589900	-1.81538100	H	6.24788000	-0.94354900	-2.64648400
C	-5.53892400	3.07521400	-2.22834800	H	5.40076200	0.58419000	-2.78836000
H	-5.97454200	2.48552100	-3.04643900	C	6.97578500	0.55169100	-1.28285400
H	-6.16707400	2.86610200	-1.34930200	H	7.55712000	-0.20107900	-0.73861400
C	-5.54578700	4.56864400	-2.55395200	H	7.65116100	1.01832000	-2.01306200
H	-4.94814900	4.78379700	-3.44951000	C	6.50485800	1.56669100	-0.24254200
H	-5.13816300	5.15766500	-1.72358900	O	6.40214700	1.25827600	0.95223800
H	-6.56949500	4.91505300	-2.74528200	N	6.15170800	2.79312700	-0.70648600

H	6.23321900	2.97689200	-1.69875000	O	-4.11669800	-1.42022300	0.61762500
C	5.47098200	3.78043300	0.13823200	C	-3.92255800	-1.66638900	1.82770900
H	5.98943300	3.80026600	1.10280600	O	-2.77775000	-1.63237200	2.42504100
H	5.60331300	4.76082400	-0.33683200	C	-5.08967700	-2.02684700	2.73005800
C	3.98153200	3.46920000	0.36291900	H	-5.38940000	-1.12831500	3.28683900
H	3.88894100	2.50726800	0.87810000	H	-4.79634100	-2.78765600	3.46082800
H	3.57262500	4.23099300	1.04211200	H	-5.94065400	-2.36843800	2.13366600
C	3.16407800	3.43830500	-0.93347900	O	-0.75483900	-0.01852900	3.41875400
H	3.59669200	2.69897500	-1.62679800	C	-0.29761000	1.16333400	3.47247000
H	3.17933100	4.40798600	-1.44750200	O	-0.02258300	1.89867000	2.47008800
C	1.70461300	3.03050700	-0.74654600	C	-0.04752700	1.74861600	4.85222900
O	1.44329300	2.19019000	0.16418800	H	0.80053300	1.19922800	5.29022800
O	0.86278800	3.54257800	-1.55032800	H	0.25833700	2.79428000	4.73232000
O	1.28736600	-3.01066100	1.20996300	C	-1.26830800	1.62737600	5.78127500
C	0.68402400	-3.20175200	2.31419500	H	-1.55969000	0.57126800	5.84502900
O	-0.29318400	-2.52306300	2.73899100	H	-2.11767400	2.16063100	5.32925600
C	1.18396000	-4.35870500	3.16939200	C	-0.98986000	2.18862600	7.17929100
H	2.27723900	-4.39106500	3.07393500	H	-0.16354500	1.65181600	7.66643000
H	0.81634000	-5.27544500	2.68200000	H	-1.87352700	2.09630900	7.82386400
C	0.74032100	-4.31142200	4.63221800	H	-0.71677100	3.25225100	7.13755300
H	1.11466100	-5.19089200	5.17121300	O	0.49723200	-0.85934300	-1.82906600
H	1.12302600	-3.41415700	5.13436800	H	0.30609700	0.09379500	-1.62807300
H	-0.35185000	-4.29210500	4.71054800				

Pro:

Ca	2.68408100	0.24926200	-1.03097300	O	3.71408000	-1.89300700	-1.42842800
Mn	-0.58574000	1.87504200	-0.43535500	C	3.91644400	-3.12492800	-1.51077600
Mn	1.04976300	1.14329700	1.69722500	O	2.95342400	-3.99862800	-1.45038700
Mn	0.28176800	-1.36129100	0.75297600	C	5.33389700	-3.65236300	-1.65485700
Mn	1.17628000	-3.08505900	-1.09296800	H	5.89617500	-2.92006500	-2.24761000
O	1.16313400	1.96759100	0.06567600	H	5.76892900	-3.61737700	-0.64308300
O	-0.53907400	0.50439800	0.91067600	C	5.45529400	-5.06398100	-2.23309000
O	1.77185300	-0.41614200	1.16298100	H	5.05193200	-5.11319300	-3.25326900
O	0.66862400	-1.29107900	-1.02801400	H	4.91232000	-5.79009400	-1.61820800
O	1.14182600	-2.95228500	0.66264500	H	6.50835200	-5.36806600	-2.27697000
O	3.77717000	2.35526200	-1.76144900	O	-0.60956400	3.39705000	-1.58810000
H	4.13712800	2.59625800	-0.88760300	C	0.26955100	3.87641500	-2.41840000
H	3.00474400	2.94915800	-1.92006800	O	1.41185700	3.43853800	-2.62994200
O	1.84634800	0.69117900	-3.31811600	C	-0.25101900	5.10359700	-3.17167300
H	2.05229900	1.62426000	-3.51868800	H	-1.15862300	4.79490200	-3.71334800
H	0.89035900	0.75589100	-3.05304200	H	-0.59505100	5.83036200	-2.42038600
O	0.83377700	-3.49172800	-3.20290700	C	0.76481400	5.73693900	-4.12520400
H	-0.08610300	-3.81766500	-3.05724200	H	1.09840700	4.98201500	-4.85008800
O	1.51191900	-4.73064300	-3.60126900	H	1.66103300	6.02449600	-3.55841200
H	2.26466700	-4.70073500	-2.95348100	C	0.19580000	6.95577600	-4.85992200

H	-0.68397100	6.68602500	-5.46139700	O	-1.20758500	3.21439200	0.95023700
H	-0.11500600	7.73969000	-4.15474200	C	-0.62740800	3.47016500	2.05303900
H	0.94019400	7.39397300	-5.53751900	O	0.30568200	2.78608300	2.56183800
N	-2.65348000	1.54903400	-0.62290400	C	-1.09693600	4.71423500	2.79566700
C	-3.31264100	1.06331100	-1.73073700	H	-2.18597800	4.77963300	2.67227800
H	-2.80647200	0.99831500	-2.68335800	H	-0.68384400	5.57146500	2.24111200
C	-4.58882300	0.69436600	-1.37751400	C	-0.68536000	4.77506500	4.26727800
N	-4.68942700	0.98747600	-0.02204700	H	-1.03553100	5.71064000	4.72147100
H	-5.43001500	0.62533700	0.58574000	H	-1.11305800	3.93863300	4.83395900
C	-3.50091900	1.48033600	0.39326100	H	0.40341900	4.72143200	4.37276000
H	-3.27185400	1.74488500	1.41440700	O	4.15117400	1.18937600	0.70009400
C	-5.69986500	0.10515700	-2.20720700	C	3.92225800	1.58709400	1.86579500
H	-6.11392700	0.86935500	-2.88217800	O	2.75533200	1.73841400	2.39401400
H	-5.26526100	-0.66419600	-2.86111300	C	5.07965500	1.92348400	2.79034300
C	-6.88897200	-0.50163000	-1.41995200	H	5.28499000	1.04741400	3.42111800
H	-7.47144000	0.29404000	-0.94164300	H	4.82195200	2.75708200	3.45140200
H	-7.55376100	-1.00551500	-2.13503100	H	5.97828800	2.15121900	2.20935100
C	-6.46419200	-1.45403200	-0.30312100	O	0.59728700	0.31808800	3.46068000
O	-6.36611100	-1.06402400	0.86819800	C	0.09471900	-0.84009200	3.59400600
N	-6.15470300	-2.72419900	-0.67047300	O	-0.17762700	-1.64549100	2.64712400
H	-6.24037600	-2.98188800	-1.64562700	C	-0.22160200	-1.29721700	5.00888700
C	-5.56202100	-3.68534600	0.26636900	H	-1.07754300	-0.69939300	5.35993300
H	-6.11651900	-3.60895600	1.20801200	H	-0.54276500	-2.34443800	4.96763200
H	-5.73271400	-4.68813700	-0.14567800	C	0.95979800	-1.11326300	5.97695000
C	-4.06812700	-3.43803100	0.53230300	H	1.26908100	-0.06048900	5.96031100
H	-3.94208600	-2.43328700	0.94878800	H	1.81733400	-1.69771500	5.61183500
H	-3.73794100	-4.14335000	1.30856500	C	0.61127600	-1.54367200	7.40537500
C	-3.18681800	-3.59117000	-0.71246900	H	-0.22460700	-0.95296500	7.80624100
H	-3.57577000	-2.95204500	-1.52248600	H	1.46806700	-1.40829100	8.07811000
H	-3.18989100	-4.62126000	-1.09148900	H	0.31937800	-2.60239900	7.44557200
C	-1.73337500	-3.16603600	-0.50996600	O	-0.43624100	0.83135200	-1.90867500
O	-1.51826800	-2.22927300	0.31572400	H	-0.29973200	-0.11170900	-1.61269000
O	-0.85425300	-3.76185000	-1.21734500				

Table S11 Reaction parameters for the closed-cubane W1 (hydroxyl)-W2 (hydroxyl) coupling:

Spin state	Spin topology (Mn1~Mn4-O6/O7)	Gibbs Free energy (a.u.)		
		Rea	TS	Pro
doublet	ααββα	-3366.2140	-3366.1577	-3366.1748
	αβαβα	-3366.2151	-3366.1602	-3366.1770
	αββαα	-3366.2169	-3366.1789	-3366.2272
	βααβα	-3366.2153	-3366.1600	-3366.1748
	βαβαα	-3366.2156	-3366.1778	-3366.2259
	ββααα	-3366.2156	-3366.1753	-3366.2031

sextet	ααααββ	-3366.2186	-3366.1811	-3366.2289
	ααβαβ	-3366.2102	-3366.1606	-3366.1783
	αβααβ	-3366.2154	-3366.1595	-3366.1763
	βαααβ	-3366.2161	-3366.1668	-3366.2024
octet	αααβα	-3366.2185	-3366.1622	-3366.1804
	ααβαα	-3366.2178	-3366.1802	-3366.2285
	αβααα	-3366.2164	-3366.1759	-3366.2037
	βαααα	-3366.2175	-3366.1771	-3366.2044
12-et	αααaβ	-3366.2186	-3366.1635	-3366.1790
14-et	ααααα	-3366.2193	-3366.1786	-3366.2065

Spin state	Spin topology (Mn1~Mn4-O6/O7)	Relative Gibbs Free energy (kcal/mol)			
		$\Delta G^{\neq}$(Rea-TS)	ΔG(Rea-Pro)	ΔG(Rea)	ΔG(Pro)
doublet	ααββα	35.3	24.6	3.3	33.9
	αβαβα	34.5	23.9	2.6	32.6
	αββαα	23.8	-6.5	1.5	1.1
	βααβα	34.7	25.4	2.5	33.9
	βαβαα	23.7	-6.5	2.3	1.9
	ββααα	25.3	7.8	2.3	16.2
sextet	αααββ	23.5	-6.5	0.4	0.0
	ααβαβ	31.1	20.0	5.7	31.8
	αβααβ	35.1	24.5	2.4	33.0
	βαααβ	30.9	8.6	2.0	16.6
octet	αααβα	35.3	23.9	0.5	30.4
	ααβαα	23.6	-6.7	0.9	0.3
	αβααα	25.4	8.0	1.8	15.8
	βαααα	25.4	8.2	1.1	15.4
12-et	αααaβ	34.6	24.8	0.4	31.3
14-et	ααααα	25.5	8.0	0.0	14.1

Spin state	Spin topology (Mn1~Mn4-O6/O7)		Mulliken spin density		
			Rea	TS	Pro
doublet	α	Mn1	2.93	2.93	2.93
	α	Mn2	2.94	2.95	2.95
	β	Mn3	-2.86	-2.87	-2.79
	β	Mn4	-2.94	-2.99	-1.98
	α	O6	0.55	0.54	0.01
		O7	0.54	0.55	-0.01
	α	Mn1	2.92	2.92	2.92
	β	Mn2	-2.94	-2.93	-2.95
	α	Mn3	2.80	2.95	2.95
	β	Mn4	-2.85	-2.30	-1.96
	α	O6	0.55	0.16	0.01

		O7	0.55	0.24	0.00
	α	Mn1	2.92	2.92	2.93
	β	Mn2	-2.93	-2.93	-2.93
	β	Mn3	-2.81	-2.78	-2.82
	α	Mn4	2.76	3.41	3.84
	α	O6	0.54	0.23	0.00
		O7	0.52	0.20	0.02
	β	Mn1	-2.92	-2.92	-2.93
	α	Mn2	2.93	2.94	2.93
	α	Mn3	2.83	2.96	2.95
	β	Mn4	-2.85	-2.31	-1.94
	α	O6	0.55	0.17	0.01
		O7	0.55	0.25	0.00
	β	Mn1	-2.92	-2.92	-2.92
	α	Mn2	2.94	2.95	2.94
	β	Mn3	-2.80	-2.76	-2.80
	α	Mn4	2.76	3.41	3.84
	α	O6	0.54	0.23	0.00
		O7	0.52	0.20	0.02
	β	Mn1	-2.93	-2.93	-2.93
	β	Mn2	-2.94	-2.94	-2.94
	α	Mn3	2.86	2.88	2.90
	α	Mn4	2.85	3.47	3.84
	α	O6	0.54	0.27	0.00
		O7	0.53	0.23	-0.01
	α	Mn1	2.92	2.93	2.92
	α	Mn2	2.93	2.93	2.93
	α	Mn3	2.82	2.80	2.83
	β	Mn4	-2.76	-3.41	-3.84
	β	O6	-0.54	-0.23	0.00
		O7	-0.52	-0.20	-0.02
	α	Mn1	2.93	2.87	2.93
	α	Mn2	2.94	2.88	2.95
	β	Mn3	-2.79	-3.59	-2.87
sextet	α	Mn4	2.84	2.70	1.93
	β	O6	-0.55	-0.11	-0.01
		O7	-0.54	-0.14	0.00
	α	Mn1	2.92	2.93	2.92
	β	Mn2	-2.94	-2.94	-2.96
	α	Mn3	2.88	2.88	2.80
	α	Mn4	2.94	2.97	1.98
	β	O6	-0.56	-0.54	-0.01
		O7	-0.53	-0.55	0.00
	β	Mn1	-2.92	-3.56	-3.89

	α	Mn2	2.93	2.89	2.90
	α	Mn3	2.91	2.91	2.95
	α	Mn4	2.93	2.79	2.74
	β	O6	-0.55	-0.25	0.00
		O7	-0.54	-0.19	0.02
octet	α	Mn1	2.92	2.93	2.92
	α	Mn2	2.93	2.93	2.94
	α	Mn3	2.82	2.98	3.08
	β	Mn4	-2.85	-2.31	-2.01
	α	O6	0.55	0.18	0.00
		O7	0.55	0.25	0.00
	α	Mn1	2.93	2.93	2.94
	α	Mn2	2.94	2.95	2.94
	β	Mn3	-2.78	-2.74	-2.78
	α	Mn4	2.76	3.41	3.84
	α	O6	0.54	0.23	0.00
		O7	0.52	0.20	0.02
	α	Mn1	2.92	2.92	2.92
	β	Mn2	-2.93	-2.94	-2.93
	α	Mn3	2.87	2.89	2.92
	α	Mn4	2.85	3.47	3.84
	α	O6	0.54	0.27	0.00
		O7	0.53	0.23	-0.01
	β	Mn1	-2.92	-2.92	-2.92
	α	Mn2	2.93	2.93	2.93
	α	Mn3	2.90	2.92	2.94
	α	Mn4	2.85	3.46	3.84
	α	O5	0.54	0.27	0.00
		O10	0.53	0.23	-0.01
12-et	α	Mn1	2.92	2.93	2.93
	α	Mn2	2.93	2.93	2.93
	α	Mn3	2.91	2.92	2.86
	α	Mn4	2.93	2.99	1.97
	β	O6	-0.55	-0.54	-0.01
		O7	-0.53	-0.55	0.01
14-et	α	Mn1	2.93	2.93	2.92
	α	Mn2	2.93	2.93	2.93
	α	Mn3	2.90	2.92	2.95
	α	Mn4	2.84	3.46	3.84
	α	O6	0.54	0.27	0.00
		O7	0.53	0.23	-0.01

Rea:

Ca	2.38126600	-0.08633400	-1.43464700	Mn	1.41742400	0.38409300	1.74761900
Mn	0.03121500	1.95823100	-0.06910200	Mn	-0.18716200	-1.53658800	0.50786500

Mn	-0.19529100	-3.20312400	-1.62178300	H	-4.97371200	2.43058200	0.81298600
O	1.72598400	1.49744700	0.34183500	C	-2.85990400	2.51413500	0.70896400
O	-0.33046900	0.44386100	1.00645400	H	-2.58641500	2.58248000	1.75095600
O	1.55275900	-1.17135300	0.84141400	C	-5.31525000	2.32247600	-2.01506600
O	0.12814300	-1.44201500	-1.31735700	H	-5.39674100	3.25545600	-2.59275900
O	-0.16271700	-3.28725200	0.15558200	H	-5.17070100	1.52536900	-2.75789100
O	4.48555600	1.07080200	-2.20573500	C	-6.67001600	2.11222600	-1.29001800
H	4.93673500	0.92060200	-1.34964300	H	-6.94561900	3.01437700	-0.73229400
H	4.14276200	1.98818100	-2.17013700	H	-7.44619600	1.95042300	-2.05048300
O	1.66434200	0.67431600	-3.75309000	C	-6.64560600	0.96890600	-0.27685300
H	2.17004500	1.50777200	-3.79359900	O	-6.45888000	1.18559500	0.92822600
H	0.81441200	0.96804800	-3.35098200	N	-6.77538800	-0.28788200	-0.77357500
O	-0.37322600	-3.35856000	-3.56436300	H	-6.90670900	-0.40343700	-1.77078600
H	-1.34024200	-3.31081600	-3.71389100	C	-6.53355400	-1.47943900	0.04774400
O	-0.74204400	-4.99039000	-2.16759400	H	-7.04130600	-1.32724000	1.00609100
H	0.12277100	-5.40539800	-2.37379500	H	-7.01351000	-2.32633300	-0.45865100
O	3.02628200	-2.23298900	-2.12909000	C	-5.04025900	-1.75314400	0.29560200
C	2.74049100	-3.43873900	-2.06533600	H	-4.60564600	-0.90585000	0.83657100
O	1.56596400	-3.93526900	-1.83778100	H	-4.95659900	-2.62615100	0.95828300
C	3.85201000	-4.47201900	-2.24582900	C	-4.24993000	-2.00269800	-0.99320100
H	4.44770100	-4.13562200	-3.10487900	H	-4.38942300	-1.15680200	-1.68569900
H	4.50776500	-4.36234100	-1.36863500	H	-4.59557400	-2.90275400	-1.51728100
C	3.40865300	-5.92581300	-2.40861600	C	-2.74360400	-2.12891500	-0.79269900
H	2.77172800	-6.05007100	-3.29397800	O	-2.20691000	-1.49559200	0.15531500
H	2.84475800	-6.26930900	-1.53355500	O	-2.13919200	-2.85458900	-1.65434500
H	4.28216700	-6.57932900	-2.52969600	O	-0.14723100	3.14844100	1.52884100
O	0.55642200	3.55744000	-1.00423700	C	0.49399100	3.00252800	2.62457200
C	1.61383500	3.71571800	-1.74073300	O	1.18350700	1.99614800	2.94392100
O	2.39249100	2.81072600	-2.09797300	C	0.41322700	4.16630400	3.60412600
C	1.84212400	5.16834700	-2.15783400	H	-0.62139700	4.53469700	3.59325600
H	0.88495800	5.56469200	-2.52685900	H	1.01845100	4.97498300	3.16546700
H	2.05617700	5.73611800	-1.23846200	C	0.88586400	3.84301900	5.02184900
C	2.95659800	5.36974100	-3.18783200	H	0.82027200	4.73582000	5.65643400
H	2.73352800	4.77562500	-4.08567900	H	0.27205500	3.05474300	5.47470300
H	3.89719300	4.96871500	-2.78634700	H	1.92318800	3.49159700	5.01978100
C	3.13882000	6.84249300	-3.57101800	O	4.22561300	0.02865900	0.27990900
H	2.21978300	7.25948600	-4.00634800	C	4.27303400	0.16708400	1.52017100
H	3.39607200	7.45418200	-2.69480900	O	3.25187000	0.32665200	2.29922300
H	3.94201300	6.96370600	-4.30927700	C	5.60537700	0.14488200	2.24927600
N	-2.00862300	2.35863300	-0.29495800	H	5.65484000	-0.75400700	2.87747600
C	-2.75896100	2.26282600	-1.44740100	H	5.68638500	1.01207200	2.91498100
H	-2.27788800	2.11647100	-2.40426200	H	6.43373800	0.13375800	1.53549300
C	-4.09386700	2.36519700	-1.13319200	O	0.85634700	-0.57721900	3.38963000
N	-4.12845800	2.54287000	0.24496300	C	-0.02386700	-1.49304700	3.40674000

O	-0.62820000	-1.95043200	2.38692700	C	0.49567500	-3.21623300	6.87083500
C	-0.37798500	-2.08455200	4.75976100	H	0.06013200	-2.44384400	7.52038600
H	-0.82740500	-1.28165000	5.36390600	H	1.38559300	-3.61391800	7.37558400
H	-1.13624000	-2.86145800	4.60946600	H	-0.23472200	-4.03314200	6.78887700
C	0.85332900	-2.64644200	5.49452800	O	-0.04009000	1.09766200	-1.68529000
H	1.59891500	-1.84721500	5.59482800	H	-0.41595800	0.18789700	-1.58214900
H	1.31330300	-3.43088900	4.87563200				

TS:

Ca	-2.66324700	-0.51632600	-1.15517000	C	-0.26765400	-6.05107700	-3.69381800
Mn	0.65907800	-1.80677600	-0.28829800	H	-0.52978000	-5.37630500	-4.52049700
Mn	-1.10022800	-1.00287400	1.71624900	H	-1.21628900	-6.30355900	-3.20122200
Mn	-0.40732600	1.45433200	0.60036300	C	0.39382900	-7.31995700	-4.24288900
Mn	-1.19003500	3.06184500	-1.41670100	H	1.33067700	-7.08807000	-4.76924600
O	-1.09835900	-1.97516400	0.16247700	H	0.63532300	-8.02671100	-3.43627100
O	0.48406700	-0.35240100	0.93002200	H	-0.26650200	-7.83686200	-4.95138600
O	-1.87141800	0.47489300	1.01721800	N	2.71481300	-1.41850700	-0.44180400
O	-0.81939200	1.29132600	-1.21581300	C	3.39780700	-1.00792800	-1.56535600
O	-1.17032000	3.05821000	0.35964600	H	2.90920800	-0.99905600	-2.52939200
O	-3.62796500	-2.72982500	-1.74317100	C	4.67423500	-0.63725600	-1.21323800
H	-4.01821900	-2.90585300	-0.86665500	N	4.74818100	-0.85044600	0.15886500
H	-2.82950000	-3.30224000	-1.81735000	H	5.48254300	-0.46255000	0.75756200
O	-1.68734400	-1.07386500	-3.36778900	C	3.54603900	-1.30076500	0.58266800
H	-1.79338000	-2.04136100	-3.45644200	H	3.29878900	-1.50639300	1.61299300
H	-0.74457700	-1.00841300	-3.06573400	C	5.81301200	-0.12346400	-2.05533700
O	-1.00411500	3.71289600	-3.40097300	H	6.24788000	-0.94354900	-2.64648400
H	-0.04233100	3.91899400	-3.42155500	H	5.40076200	0.58419000	-2.78836000
O	-1.34667900	5.02675500	-2.32769500	C	6.97578500	0.55169100	-1.28285400
H	-2.32109400	4.95877400	-2.47531700	H	7.55712000	-0.20107900	-0.73861400
O	-4.10019600	1.21946300	-1.79524600	H	7.65116100	1.01832000	-2.01306200
C	-4.17362800	2.45921400	-1.92552500	C	6.50485800	1.56669100	-0.24254200
O	-3.18357800	3.27589900	-1.81538100	O	6.40214700	1.25827600	0.95223800
C	-5.53892400	3.07521400	-2.22834800	N	6.15170800	2.79312700	-0.70648600
H	-5.97454200	2.48552100	-3.04643900	H	6.23321900	2.97689200	-1.69875000
H	-6.16707400	2.86610200	-1.34930200	C	5.47098200	3.78043300	0.13823200
C	-5.54578700	4.56864400	-2.55395200	H	5.98943300	3.80026600	1.10280600
H	-4.94814900	4.78379700	-3.44951000	H	5.60331300	4.76082400	-0.33683200
H	-5.13816300	5.15766500	-1.72358900	C	3.98153200	3.46920000	0.36291900
H	-6.56949500	4.91505300	-2.74528200	H	3.88894100	2.50726800	0.87810000
O	0.82875600	-3.39754200	-1.33645600	H	3.57262500	4.23099300	1.04211200
C	0.00975000	-4.03464900	-2.11989200	C	3.16407800	3.43830500	-0.93347900
O	-1.15229700	-3.70465200	-2.40664000	H	3.59669200	2.69897500	-1.62679800
C	0.63030600	-5.30714400	-2.70253500	H	3.17933100	4.40798600	-1.44750200
H	1.58706200	-5.02683700	-3.16839700	C	1.70461300	3.03050700	-0.74654600
H	0.89997200	-5.95527000	-1.85414300	O	1.44329300	2.19019000	0.16418800

O	0.86278800	3.54257800	-1.55032800	H	-5.94065400	-2.36843800	2.13366600
O	1.28736600	-3.01066100	1.20996300	O	-0.75483900	-0.01852900	3.41875400
C	0.68402400	-3.20175200	2.31419500	C	-0.29761000	1.16333400	3.47247000
O	-0.29318400	-2.52306300	2.73899100	O	-0.02258300	1.89867000	2.47008800
C	1.18396000	-4.35870500	3.16939200	C	-0.04752700	1.74861600	4.85222900
H	2.27723900	-4.39106500	3.07393500	H	0.80053300	1.19922800	5.29022800
H	0.81634000	-5.27544500	2.68200000	H	0.25833700	2.79428000	4.73232000
C	0.74032100	-4.31142200	4.63221800	C	-1.26830800	1.62737600	5.78127500
H	1.11466100	-5.19089200	5.17121300	H	-1.55969000	0.57126800	5.84502900
H	1.12302600	-3.41415700	5.13436800	H	-2.11767400	2.16063100	5.32925600
H	-0.35185000	-4.29210500	4.71054800	C	-0.98986000	2.18862600	7.17929100
O	-4.11669800	-1.42022300	0.61762500	H	-0.16354500	1.65181600	7.66643000
C	-3.92255800	-1.66638900	1.82770900	H	-1.87352700	2.09630900	7.82386400
O	-2.77775000	-1.63237200	2.42504100	H	-0.71677100	3.25225100	7.13755300
C	-5.08967700	-2.02684700	2.73005800	O	0.49723200	-0.85934300	-1.82906600
H	-5.38940000	-1.12831500	3.28683900	H	0.30609700	0.09379500	-1.62807300
H	-4.79634100	-2.78765600	3.46082800				

Pro:

Ca	2.68408100	0.24926200	-1.03097300	C	5.45529400	-5.06398100	-2.23309000
Mn	-0.58574000	1.87504200	-0.43535500	H	5.05193200	-5.11319300	-3.25326900
Mn	1.04976300	1.14329700	1.69722500	H	4.91232000	-5.79009400	-1.61820800
Mn	0.28176800	-1.36129100	0.75297600	H	6.50835200	-5.36806600	-2.27697000
Mn	1.17628000	-3.08505900	-1.09296800	O	-0.60956400	3.39705000	-1.58810000
O	1.16313400	1.96759100	0.06567600	C	0.26955100	3.87641500	-2.41840000
O	-0.53907400	0.50439800	0.91067600	O	1.41185700	3.43853800	-2.62994200
O	1.77185300	-0.41614200	1.16298100	C	-0.25101900	5.10359700	-3.17167300
O	0.66862400	-1.29107900	-1.02801400	H	-1.15862300	4.79490200	-3.71334800
O	1.14182600	-2.95228500	0.66264500	H	-0.59505100	5.83036200	-2.42038600
O	3.77717000	2.35526200	-1.76144900	C	0.76481400	5.73693900	-4.12520400
H	4.13712800	2.59625800	-0.88760300	H	1.09840700	4.98201500	-4.85008800
H	3.00474400	2.94915800	-1.92006800	H	1.66103300	6.02449600	-3.55841200
O	1.84634800	0.69117900	-3.31811600	C	0.19580000	6.95577600	-4.85992200
H	2.05229900	1.62426000	-3.51868800	H	-0.68397100	6.68602500	-5.46139700
H	0.89035900	0.75589100	-3.05304200	H	-0.11500600	7.73969000	-4.15474200
O	0.83377700	-3.49172800	-3.20290700	H	0.94019400	7.39397300	-5.53751900
H	-0.08610300	-3.81766500	-3.05724200	N	-2.65348000	1.54903400	-0.62290400
O	1.51191900	-4.73064300	-3.60126900	C	-3.31264100	1.06331100	-1.73073700
H	2.26466700	-4.70073500	-2.95348100	H	-2.80647200	0.99831500	-2.68335800
O	3.71408000	-1.89300700	-1.42842800	C	-4.58882300	0.69436600	-1.37751400
C	3.91644400	-3.12492800	-1.51077600	N	-4.68942700	0.98747600	-0.02204700
O	2.95342400	-3.99862800	-1.45038700	H	-5.43001500	0.62533700	0.58574000
C	5.33389700	-3.65236300	-1.65485700	C	-3.50091900	1.48033600	0.39326100
H	5.89617500	-2.92006500	-2.24761000	H	-3.27185400	1.74488500	1.41440700
H	5.76892900	-3.61737700	-0.64308300	C	-5.69986500	0.10515700	-2.20720700

H	-6.11392700	0.86935500	-2.88217800	C	-0.68536000	4.77506500	4.26727800
H	-5.26526100	-0.66419600	-2.86111300	H	-1.03553100	5.71064000	4.72147100
C	-6.88897200	-0.50163000	-1.41995200	H	-1.11305800	3.93863300	4.83395900
H	-7.47144000	0.29404000	-0.94164300	H	0.40341900	4.72143200	4.37276000
H	-7.55376100	-1.00551500	-2.13503100	O	4.15117400	1.18937600	0.70009400
C	-6.46419200	-1.45403200	-0.30312100	C	3.92225800	1.58709400	1.86579500
O	-6.36611100	-1.06402400	0.86819800	O	2.75533200	1.73841400	2.39401400
N	-6.15470300	-2.72419900	-0.67047300	C	5.07965500	1.92348400	2.79034300
H	-6.24037600	-2.98188800	-1.64562700	H	5.28499000	1.04741400	3.42111800
C	-5.56202100	-3.68534600	0.26636900	H	4.82195200	2.75708200	3.45140200
H	-6.11651900	-3.60895600	1.20801200	H	5.97828800	2.15121900	2.20935100
H	-5.73271400	-4.68813700	-0.14567800	O	0.59728700	0.31808800	3.46068000
C	-4.06812700	-3.43803100	0.53230300	C	0.09471900	-0.84009200	3.59400600
H	-3.94208600	-2.43328700	0.94878800	O	-0.17762700	-1.64549100	2.64712400
H	-3.73794100	-4.14335000	1.30856500	C	-0.22160200	-1.29721700	5.00888700
C	-3.18681800	-3.59117000	-0.71246900	H	-1.07754300	-0.69939300	5.35993300
H	-3.57577000	-2.95204500	-1.52248600	H	-0.54276500	-2.34443800	4.96763200
H	-3.18989100	-4.62126000	-1.09148900	C	0.95979800	-1.11326300	5.97695000
C	-1.73337500	-3.16603600	-0.50996600	H	1.26908100	-0.06048900	5.96031100
O	-1.51826800	-2.22927300	0.31572400	H	1.81733400	-1.69771500	5.61183500
O	-0.85425300	-3.76185000	-1.21734500	C	0.61127600	-1.54367200	7.40537500
O	-1.20758500	3.21439200	0.95023700	H	-0.22460700	-0.95296500	7.80624100
C	-0.62740800	3.47016500	2.05303900	H	1.46806700	-1.40829100	8.07811000
O	0.30568200	2.78608300	2.56183800	H	0.31937800	-2.60239900	7.44557200
C	-1.09693600	4.71423500	2.79566700	O	-0.43624100	0.83135200	-1.90867500
H	-2.18597800	4.77963300	2.67227800	H	-0.29973200	-0.11170900	-1.61269000
H	-0.68384400	5.57146500	2.24111200				

Table S12 Reaction parameters for the open-cubane W1 (hydroxyl)-W2 (oxo) coupling:

Spin state	Spin topology (Mn1~Mn4-O7)	Gibbs Free energy (a.u.)		
		Rea	TS	Pro
doublet	ααββα	-3365.7489	-3365.7025	-3365.7086
	αβαβα	-3365.7507	-3365.7060	-3365.7322
	αββαα	-3365.7430	-3365.7133	-3365.7537
	βααβα	-3365.7500	-3365.7059	-3365.7333
	βαβαα	-3365.7428	-3365.7130	-3365.7535
	ββααα	\	\	\
sextet	αααββ	-3365.7441	-3365.7143	-3365.7554
	ααβαβ	-3365.7509	-3365.7066	-3365.7350
	αβααβ	-3365.7496	-3365.7025	-3365.7102
	βαααβ	-3365.7498	-3365.7026	-3365.7100
octet	αααβα	-3365.7518	-3365.7071	-3365.7353
	ααβαα	-3365.7440	-3365.7143	-3365.7558

	αβααα	\	\	\
	βαααα	\	\	\
12-et	aaaaβ	-3365.7517	-3365.7049	-3365.7105
14-et	ααααα	\	\	\

Spin state	Spin topology (Mn1~Mn4-O7)	Relative Gibbs Free energy (kcal/mol)			
		$\Delta G^{\neq}$(Rea-TS)	ΔG(Rea-Pro)	ΔG(Rea)	ΔG(Pro)
doublet	ααββα	29.1	25.3	1.8	29.6
	αβαβα	28.0	11.6	0.7	14.8
	αββαα	18.6	-6.7	5.5	1.3
	βααβα	27.7	10.5	1.1	14.1
	βαβαα	18.7	-6.7	5.6	1.4
	ββααα	\	\	\	\
sextet	αααββ	18.7	-7.1	4.8	0.3
	ααβαβ	27.8	10.0	0.6	13.1
	αβααβ	29.6	24.7	1.4	28.6
	βααaβ	29.6	25.0	1.3	28.7
octet	αααβα	28.0	10.4	0.0	12.9
	ααβαα	18.6	-7.4	4.9	0.0
	αβααα	\	\	\	\
	βαααα	\	\	\	\
12-et	aaaaβ	29.4	25.9	0.1	28.4
14-et	ααααα	\	\	\	\

Spin state	Spin topology (Mn1~Mn4-O7)		Mulliken spin density		
			Rea	TS	Pro
doublet	α	Mn1	2.93	2.94	2.94
	α	Mn2	2.95	2.95	2.95
	β	Mn3	-2.80	-2.81	-2.84
	β	Mn4	-2.28	-2.55	-1.99
		O6	0.03	0.40	0.00
	α	O7	0.15	0.14	-0.02
	α	Mn1	2.93	2.93	2.93
	β	Mn2	-2.93	-2.92	-2.81
	α	Mn3	2.82	2.92	3.81
	β	Mn4	-2.33	-2.53	-2.74
		O6	-0.01	0.39	0.01
	α	O7	0.36	0.16	-0.01
	α	Mn1	2.92	2.93	2.93
	β	Mn2	-2.94	-2.94	-2.93
	β	Mn3	-2.85	-2.83	-2.82
	α	Mn4	2.72	2.86	3.88
		O6	0.27	0.44	0.01
	α				

		O7	0.95	0.69	-0.04
	β	Mn1	-2.92	-2.93	-2.88
	α	Mn2	2.94	2.93	2.97
	α	Mn3	2.86	2.93	3.81
	β	Mn4	-2.37	-2.51	-2.75
		O6	-0.01	0.38	0.01
	α	O7	0.41	0.15	-0.01
	β	Mn1	-2.93	-2.93	-2.93
	α	Mn2	2.93	2.93	2.93
	β	Mn3	-2.81	-2.80	-2.79
	α	Mn4	2.72	2.86	3.88
		O6	0.27	0.44	0.01
	α	O7	0.95	0.69	-0.04
	β	Mn1	\	\	\
	β	Mn2	\	\	\
	α	Mn3	\	\	\
	α	Mn4	\	\	\
		O6	\	\	\
	α	O7	\	\	\
	α	Mn1	2.95	2.95	2.95
	α	Mn2	2.96	2.96	2.95
	α	Mn3	2.85	2.84	2.82
	β	Mn4	-2.72	-2.86	-3.88
		O6	-0.27	-0.44	-0.01
	β	O7	-0.95	-0.69	0.04
	α	Mn1	2.94	2.94	2.92
	α	Mn2	2.95	2.94	2.82
	β	Mn3	-2.82	-2.93	-3.80
	α	Mn4	2.34	2.57	2.75
		O6	0.01	-0.39	-0.01
	β	O7	-0.38	-0.18	0.01
sextet	α	Mn1	2.93	2.93	2.93
	β	Mn2	-2.92	-2.93	-2.93
	α	Mn3	2.80	2.81	2.84
	α	Mn4	2.29	2.56	1.99
		O6	-0.03	-0.40	0.00
	β	O7	-0.15	-0.15	0.02
	β	Mn1	-2.92	-2.92	-2.92
	α	Mn2	2.93	2.93	2.93
	α	Mn3	2.84	2.85	2.88
	α	Mn4	2.31	2.55	1.99
		O6	-0.02	-0.40	0.00
	β	O7	-0.18	-0.15.	0.02
octet	α	Mn1	2.95	2.95	2.91

	α	Mn2	2.96	2.96	2.97
	α	Mn3	2.86	2.93	3.82
	β	Mn4	-2.36	-2.51	-2.74
		O6	-0.01	0.38	0.01
	α	O7	0.40	0.14	-0.01
	α	Mn1	2.94	2.95	2.94
	α	Mn2	2.95	2.95	2.95
	β	Mn3	-2.81	-2.79	-2.78
	α	Mn4	2.72	2.87	3.88
		O6	0.27	0.44	0.01
	α	O7	0.95	0.69	-0.04
	α	Mn1	\	\	\
	β	Mn2	\	\	\
	α	Mn3	\	\	\
	α	Mn4	\	\	\
		O6	\	\	\
	α	O7	\	\	\
	β	Mn1	\	\	\
	α	Mn2	\	\	\
	α	Mn3	\	\	\
	α	Mn4	\	\	\
		O6	\	\	\
	α	O7	\	\	\
12-et	α	Mn1	2.95	2.95	2.95
	α	Mn2	2.96	2.96	2.95
	α	Mn3	2.84	2.85	2.88
	α	Mn4	2.31	2.55	1.99
		O6	-0.03	-0.40	0.00
	β	O7	-0.17	-0.15	0.02
14-et	α	Mn1	\	\	\
	α	Mn2	\	\	\
	α	Mn3	\	\	\
	α	Mn4	\	\	\
		O6	\	\	\
	α	O7	\	\	\

‘\’ denotes TSs for some spin states do not exist due to the failure of IRC verification on reactants concerning W1 returning back to Mn4.

Rea:

Ca	2.57709900	0.80882000	-1.16354000	O	-0.46468500	0.28305800	1.00245100
Mn	-0.71493700	1.80636700	-0.01666500	O	1.96085400	-0.48928500	0.91955700
Mn	1.12649100	0.81882200	1.79769800	O	0.90875700	-1.03815700	-1.38398400
Mn	0.56262400	-1.54538000	0.33706900	O	1.30499900	-3.03921200	-0.07656300
Mn	1.31651500	-2.78232200	-2.00381200	O	3.38465900	3.19919200	-1.29433900
O	1.03969800	2.01562000	0.38604800	H	3.71903500	3.14368700	-0.37831900

H	2.53341000	3.69535000	-1.25359900	C	-6.39366100	-1.88294500	-0.42495600
O	1.49520000	1.83074900	-3.17072100	O	-6.36843600	-1.78587300	0.80874400
H	1.45963400	2.78675200	-2.95349200	N	-5.92954000	-2.97632400	-1.08477400
H	0.58180200	1.54507300	-2.91327300	H	-5.89007300	-2.93775800	-2.09626100
O	1.31274000	-2.33672200	-3.71711500	C	-5.16492000	-4.03160700	-0.40920300
O	1.56191100	-4.47101600	-2.68849500	H	-5.66558500	-4.22475600	0.54540100
H	2.53598100	-4.53723100	-2.74461200	H	-5.24807200	-4.93690200	-1.02535200
O	4.11160700	-0.67756700	-2.10587800	C	-3.69387600	-3.66351500	-0.16090900
C	4.23510700	-1.92322200	-2.08447900	H	-3.64647600	-2.78212900	0.48785100
O	3.30511100	-2.78727100	-1.92704500	H	-3.22652100	-4.48721100	0.39831400
C	5.65129000	-2.49409300	-2.22562000	C	-2.89737800	-3.39519000	-1.44226100
H	6.11379200	-1.97433300	-3.07616100	H	-3.37862900	-2.59297300	-2.02452300
H	6.20674000	-2.16031900	-1.33605800	H	-2.85000900	-4.27957200	-2.09021500
C	5.74791400	-4.01126600	-2.38427500	C	-1.46502200	-2.92418200	-1.18431100
H	5.22497400	-4.34757700	-3.28910400	O	-1.26867200	-2.22898900	-0.14411300
H	5.29550900	-4.52546900	-1.52850700	O	-0.61569800	-3.24667700	-2.06463200
H	6.79753800	-4.32756100	-2.46336700	O	-1.35683100	2.82857400	1.63334600
O	-1.03417000	3.54085600	-0.88509300	C	-0.72133200	2.89180500	2.73382600
C	-0.30128600	4.39385800	-1.51158200	O	0.29367800	2.21301200	3.04555300
O	0.89853200	4.27802400	-1.83625100	C	-1.24318800	3.90841300	3.74898500
C	-1.05738100	5.68293700	-1.86860600	H	-2.34036000	3.88882500	3.70307900
H	-2.01172300	5.39337100	-2.33315400	H	-0.94666000	4.89950900	3.37118300
H	-1.33064000	6.17008100	-0.91878600	C	-0.73202300	3.70220000	5.17541900
C	-0.27884200	6.64777800	-2.76535500	H	-1.11924300	4.48532300	5.84146900
H	-0.01241000	6.13561500	-3.70055700	H	-1.04660400	2.72823900	5.57102200
H	0.67497000	6.89595600	-2.28141600	H	0.36259100	3.72576300	5.20351800
C	-1.06274200	7.92812700	-3.07579000	O	4.10847200	1.51588800	0.70405700
H	-2.00887300	7.70431000	-3.58994700	C	3.93988900	1.56138400	1.94472400
H	-1.31196700	8.47733400	-2.15598800	O	2.81879000	1.44860500	2.56198700
H	-0.48579100	8.60480300	-3.72114600	C	5.14893600	1.74918300	2.85261100
N	-2.78349600	1.34824400	-0.17553900	H	5.52065000	0.75579900	3.14058400
C	-3.45731200	1.07096700	-1.34184000	H	4.87452300	2.28500100	3.76717000
H	-2.97791700	1.23312200	-2.29709300	H	5.94810100	2.27364200	2.31897700
C	-4.69754000	0.55826100	-1.04550400	O	0.86260600	-0.35541900	3.38108200
N	-4.76228600	0.54535000	0.34535300	C	0.44034500	-1.55480300	3.29282400
H	-5.45573400	0.02310800	0.88325400	O	0.15796100	-2.17249500	2.22958100
C	-3.58088300	1.01025600	0.82248700	C	0.23800300	-2.29961500	4.60942800
H	-3.32163700	1.06318900	1.86956000	H	0.71811200	-1.72336800	5.40983100
C	-5.80574300	0.10273000	-1.95763300	H	-0.84517100	-2.30202600	4.81521300
H	-6.29236600	0.96958600	-2.43128400	C	0.75423600	-3.74519700	4.57062100
H	-5.35429400	-0.46795600	-2.78199100	H	1.83450000	-3.73583900	4.36302700
C	-6.92172700	-0.74194600	-1.29521200	H	0.28593100	-4.26279600	3.72447000
H	-7.53413100	-0.11416800	-0.63797400	C	0.48482100	-4.50052700	5.87633800
H	-7.58081300	-1.12870000	-2.08536900	H	0.96644400	-4.00757500	6.73335400

H	0.86609100	-5.52951400	5.82639000	O	-0.57875200	1.05833600	-1.65776000
H	-0.59282000	-4.55422600	6.09006800	H	-0.22862200	0.11750000	-1.59963200

TS:

Ca	2.64764800	0.92744400	-0.97979200	H	-0.67648000	8.58061500	-3.74625400
Mn	-0.82290200	1.77482300	-0.05595000	N	-2.86215000	1.23193300	-0.32461000
Mn	0.95021500	0.84280500	1.85085000	C	-3.45232500	0.88399400	-1.51733400
Mn	0.57712800	-1.52859500	0.34040300	H	-2.92133000	1.02992000	-2.44755600
Mn	1.58491100	-2.61918300	-1.93134200	C	-4.68880400	0.33473300	-1.27556400
O	0.89743300	2.04785400	0.44708300	N	-4.83890200	0.37294200	0.10788300
O	-0.56429400	0.24581100	0.95638700	H	-5.54403000	-0.15657600	0.62351100
O	1.89312900	-0.41351500	1.01008800	C	-3.70754200	0.90154400	0.63620600
O	1.01336800	-0.97051100	-1.37489500	H	-3.51779100	1.00752600	1.69392800
O	1.45614800	-2.95682400	-0.03698700	C	-5.72106300	-0.20076600	-2.23233100
O	3.26938000	3.37356300	-1.03601200	H	-6.21097500	0.62639600	-2.76932000
H	3.54094500	3.33609600	-0.09892100	H	-5.19842100	-0.78417700	-3.00392900
H	2.38614300	3.81187600	-1.05615300	C	-6.84194400	-1.06441600	-1.60277100
O	1.59465200	1.88242200	-3.03037800	H	-7.51774800	-0.43711900	-1.01039000
H	1.52503000	2.84252600	-2.84561600	H	-7.43539800	-1.50921500	-2.41409200
H	0.67454400	1.58103900	-2.81182100	C	-6.32261600	-2.14687000	-0.65561800
O	1.81400200	-2.81717800	-3.65148200	O	-6.37194800	-1.99709900	0.57225500
O	2.18639800	-4.38779200	-2.68970100	N	-5.78053200	-3.24654100	-1.24100900
H	3.14966600	-4.19130400	-2.64594000	H	-5.68293200	-3.24427100	-2.24938800
O	4.40156700	-0.33045700	-1.87110400	C	-4.99854000	-4.23142500	-0.48359500
C	4.62129100	-1.57119300	-1.92219900	H	-5.51848100	-4.38247200	0.46808300
O	3.76257900	-2.49139800	-1.74862700	H	-5.03442300	-5.17534700	-1.04408100
C	6.06957200	-2.00348700	-2.19099100	C	-3.54760400	-3.79464800	-0.22608300
H	6.42034100	-1.42037900	-3.05410500	H	-3.54655600	-2.87509000	0.36946000
H	6.66448700	-1.65054800	-1.33483600	H	-3.06422300	-4.56535500	0.39205900
C	6.27933200	-3.50108200	-2.41400000	C	-2.73115900	-3.57340500	-1.50361500
H	5.72205000	-3.85051300	-3.29309700	H	-3.22840100	-2.82632000	-2.14353400
H	5.93088100	-4.07904200	-1.54993200	H	-2.64154300	-4.49277900	-2.09678400
H	7.34259500	-3.72837700	-2.57628200	C	-1.31513500	-3.03816400	-1.25917500
O	-1.16410800	3.49790200	-0.92829300	O	-1.17183200	-2.29231600	-0.23175100
C	-0.43908700	4.37422100	-1.53335300	O	-0.43725100	-3.34028500	-2.10209900
O	0.78351100	4.31865900	-1.77493100	O	-1.59694900	2.75286700	1.55865300
C	-1.24355000	5.60334700	-1.98349500	C	-1.03456000	2.82547700	2.69821200
H	-2.09704400	5.24109800	-2.57678200	O	-0.01752900	2.17932500	3.06525300
H	-1.68592400	6.05206100	-1.08022900	C	-1.65657000	3.80986700	3.68789400
C	-0.43462600	6.64001800	-2.76569600	H	-2.74737500	3.74864300	3.57499700
H	0.00379700	6.16085500	-3.65183400	H	-1.37688800	4.81559000	3.33692700
H	0.41700400	6.96719100	-2.15418200	C	-1.22504700	3.60814300	5.14100500
C	-1.27655300	7.85014700	-3.18634500	H	-1.68262000	4.36844400	5.78852200
H	-2.11784700	7.54937700	-3.82770800	H	-1.52439100	2.61854100	5.50856600
H	-1.69954300	8.36681100	-2.31235400	H	-0.13595700	3.67415100	5.23614400

O	3.97220500	1.70610000	0.99506600	H	0.39168400	-1.76707500	5.39872800
C	3.70968500	1.71349200	2.21949500	H	-1.04563700	-2.48866800	4.65531900
O	2.55149800	1.53130700	2.74561500	C	0.70901700	-3.75716000	4.54316200
C	4.83566500	1.93755900	3.22049300	H	1.79670700	-3.63436100	4.43375800
H	5.24504900	0.95728000	3.50214400	H	0.37179200	-4.30255400	3.65315600
H	4.46462600	2.42325400	4.12883200	C	0.40423800	-4.56120400	5.81140500
H	5.63839900	2.52561600	2.76410500	H	0.75596300	-4.03914900	6.71311600
O	0.64144100	-0.36967000	3.40112200	H	0.89161200	-5.54520400	5.78450000
C	0.29183000	-1.58575200	3.26785000	H	-0.67685000	-4.72743200	5.92708100
O	0.11406500	-2.20021400	2.17775900	O	-0.57662200	1.05258300	-1.70027300
C	0.04546800	-2.37163400	4.55163600	H	-0.20314700	0.12787700	-1.63000900

Pro:

Ca	2.78060200	0.42865700	-0.83334200	C	-0.13740500	5.67831600	-2.23670800
Mn	-0.52229900	1.94207100	-0.13835500	H	-0.94350500	5.42333100	-2.94280700
Mn	0.96313700	0.78752400	1.88988000	H	-0.63000500	6.21844300	-1.41408100
Mn	0.29138400	-1.53079600	0.40534700	C	0.91821500	6.55384500	-2.91488000
Mn	1.22597400	-2.87502400	-1.75387700	H	1.40333400	5.97723700	-3.71373600
O	1.19066600	1.93241000	0.45512800	H	1.71285400	6.78536200	-2.19210100
O	-0.57748300	0.40955800	0.92244600	C	0.33236100	7.85173000	-3.48280200
O	1.73194700	-0.62750800	1.13924100	H	-0.44297800	7.64492500	-4.23493700
O	0.81289600	-1.06130400	-1.26514500	H	-0.13158800	8.46118100	-2.69348300
O	1.06403100	-3.06282200	0.10712600	H	1.10707600	8.46453000	-3.96407300
O	3.84513600	2.71778000	-0.95275700	N	-2.61326000	1.71500700	-0.50273100
H	4.05564500	2.66957300	0.00003300	C	-3.17819800	1.35031000	-1.70293300
H	3.05255000	3.30012000	-1.03488600	H	-2.58266400	1.35723300	-2.60501900
O	2.05052800	1.47173300	-2.97924700	C	-4.48283600	0.96899800	-1.50094600
H	2.14927300	2.43569400	-2.83338700	N	-4.70078100	1.12854900	-0.13545300
H	1.07888100	1.36020700	-2.80876600	H	-5.49334500	0.72816500	0.36985900
O	1.34695100	-2.76543900	-3.60602600	C	-3.54328800	1.55966100	0.42411800
O	1.55275800	-4.21003300	-3.60319700	H	-3.39760100	1.72119700	1.48177500
H	2.51577700	-4.24762900	-3.39479400	C	-5.51537800	0.47912200	-2.48168600
O	4.13229100	-1.37152300	-1.50427100	H	-5.84698100	1.30445000	-3.13080500
C	4.25501600	-2.60987900	-1.68509300	H	-5.03213400	-0.24677500	-3.15160600
O	3.29684100	-3.45007200	-1.77630700	C	-6.78625600	-0.15619700	-1.86690700
C	5.68096400	-3.16477900	-1.77921700	H	-7.39006400	0.60982900	-1.36691100
H	6.25777900	-2.47468100	-2.40984400	H	-7.39493700	-0.57215300	-2.68231900
H	6.11190400	-3.07415200	-0.76994000	C	-6.49245800	-1.22592500	-0.81431700
C	5.79456900	-4.60512700	-2.27965900	O	-6.56904800	-0.97027000	0.39456600
H	5.40883500	-4.70058000	-3.30356200	N	-6.11996400	-2.44480700	-1.28602700
H	5.21605500	-5.28585000	-1.64503900	H	-5.97867800	-2.54074500	-2.28459300
H	6.84238600	-4.93682700	-2.28320700	C	-5.55461400	-3.48191300	-0.41454100
O	-0.49922900	3.68268300	-1.03836400	H	-6.12016800	-3.44531600	0.52220700
C	0.40126700	4.35705100	-1.66574300	H	-5.74986900	-4.45190400	-0.89196900
O	1.59741900	4.05287200	-1.84908800	C	-4.05618200	-3.29224700	-0.13120500

H	-3.90116100	-2.32196400	0.35323100	O	2.62463200	1.23786700	2.84265800
H	-3.74690900	-4.05584000	0.59783400	C	4.91758800	1.24653000	3.43367000
C	-3.16823000	-3.38285200	-1.37683500	H	5.13830100	0.22187600	3.76436800
H	-3.52336900	-2.67672200	-2.14564800	H	4.59167900	1.82185700	4.30619000
H	-3.19695500	-4.38296200	-1.82863800	H	5.83139900	1.67177500	3.00594300
C	-1.69752900	-3.01921000	-1.13052300	O	0.38652500	-0.30822500	3.45046000
O	-1.49715400	-2.14760100	-0.21523100	C	-0.12658400	-1.46855200	3.33394200
O	-0.83770900	-3.56179300	-1.86450600	O	-0.34181300	-2.08963300	2.25658000
O	-1.21770400	3.07397700	1.42108600	C	-0.54368900	-2.15555500	4.63199600
C	-0.70469100	3.09272600	2.58494800	H	-0.08824100	-1.61376200	5.47007900
O	0.17685400	2.30391700	3.01901300	H	-1.63582000	-2.03451000	4.72352700
C	-1.20327900	4.19550200	3.51858600	C	-0.18904000	-3.64865900	4.66993300
H	-2.28287600	4.30882400	3.35114500	H	0.90094400	-3.76217900	4.57439200
H	-0.74652100	5.13114900	3.15961900	H	-0.62400300	-4.13586800	3.78862500
C	-0.87980700	3.97186300	4.99637100	C	-0.67040100	-4.33453100	5.95293600
H	-1.23635300	4.81617400	5.60213700	H	-0.22589400	-3.87334900	6.84688600
H	-1.35425700	3.05591000	5.37054700	H	-0.40230700	-5.39984900	5.95951300
H	0.19966800	3.86247800	5.14575800	H	-1.76335600	-4.26503700	6.05559100
O	4.14212100	1.06385600	1.17242700	O	-0.32161600	1.16213500	-1.75231900
C	3.81989700	1.18030800	2.37882600	H	-0.09947700	0.18465900	-1.62379600

Table S13 Reaction parameters for the closed-cubane W1 (hydroxyl)-W2 (oxo) coupling:

Spin state	Spin topology (Mn1~Mn4-O7)	Gibbs Free energy (a.u.)		
		Rea	TS	Pro
doublet	ααββα	-3365.7378	-3365.7022	-3365.7141
	αβαβα	-3365.7390	-3365.7026	-3365.7149
	αββαα	\	\	\
	βααβα	-3365.7417	-3365.7061	-3365.7159
	βαβαα	\	\	\
	ββαaα	\	\	\
sextet	αααββ	\	\	\
	ααβαβ	-3365.7407	-3365.7051	-3365.7168
	αβααβ	-3365.7367	-3365.7002	-3365.7246
	βααaβ	-3365.7389	-3365.7045	-3365.7166
octet	αααβα	-3365.7433	-3365.7063	-3365.7182
	ααβαα	\	\	\
	αβααα	\	\	\
	βαααα	\	\	\
12-et	αααaβ	-3365.7417	-3365.7053	-3365.7176
14-et	ααααα	\	\	\

Spin state	Spin topology (Mn1~Mn4-O7)	Relative Gibbs Free energy (kcal/mol)			
		$\Delta G^{\neq}$ (Rea-TS)	ΔG(Rea-Pro)	ΔG(Rea)	ΔG(Pro)

doublet	ααββα	22.3	14.9	3.5	6.6
	αβαβα	22.8	15.1	2.7	6.1
	αββαα	\	\	\	\
	βααβα	22.3	16.2	1.0	5.5
	βαβαα	\	\	\	\
	ββααα	\	\	\	\
sextet	αααββ	\	\	\	\
	ααβαβ	22.3	15.0	1.6	4.9
	αβααβ	22.9	7.6	4.1	0.0
	βαααβ	21.6	14.0	2.8	5.0
octet	αααβα	23.2	15.8	0.0	4.0
	ααβαα	\	\	\	\
	αβααα	\	\	\	\
	βαααα	\	\	\	\
12-et	ααααβ	22.8	15.1	1.0	4.4
14-et	ααααα	\	\	\	\

Spin state	Spin topology (Mn1~Mn4-O7)		Mulliken spin density		
			Rea	TS	Pro
doublet	α	Mn1	2.93	2.94	2.93
	α	Mn2	2.95	2.95	2.95
	β	Mn3	-2.72	-2.74	-2.79
	β	Mn4	-2.51	-2.56	-1.95
		O6	-0.06	0.42	-0.01
	α	O7	0.53	0.16	-0.03
	α	Mn1	2.91	2.92	2.92
	β	Mn2	-2.94	-2.95	-2.95
	α	Mn3	2.74	2.73	2.73
	β	Mn4	-2.58	-2.55	-1.91
		O6	-0.05	0.43	0.00
	α	O7	0.65	0.19	0.00
	α	Mn1	\	\	\
	β	Mn2	\	\	\
	β	Mn3	\	\	\
	α	Mn4	\	\	\
		O6	\	\	\
	α	O7	\	\	\
	β	Mn1	-2.92	-2.92	-2.92
	α	Mn2	2.92	2.92	2.92
	α	Mn3	2.74	2.74	2..74
	β	Mn4	-2.57	-2.57	-1.92
		O6	-0.05	0.43	0.00
	α	O7	0.64	0.20	0.00
	β	Mn1	\	\	\
					\

	α	Mn2	\	\	
	β	Mn3	\	\	\
	α	Mn4	\	\	\
		O6	\	\	\
	α	O7	\	\	\
	β	Mn1	\	\	\
	β	Mn2	\	\	\
	α	Mn3	\	\	\
	α	Mn4	\	\	\
		O6	\	\	\
	α	O7	\	\	\
	α	Mn1	\	\	\
	α	Mn2	\	\	\
	α	Mn3	\	\	\
	β	Mn4	\	\	\
		O6	\	\	\
	β	O7	\	\	\
	α	Mn1	2.93	2.92	2.93
	α	Mn2	2.95	2.95	2.95
	β	Mn3	-2.71	-2.71	-2.70
	α	Mn4	2.59	2.55	1.91
		O6	0.05	-0.44	0.00
	β	O7	-0.66	-0.19	0.01
sextet	α	Mn1	2.91	2.91	2.82
	β	Mn2	-2.94	-2.95	-3.82
	α	Mn3	2.76	2.77	2.79
	α	Mn4	2.49	2.48	2.82
		O6	0.06	-0.37	0.00
	β	O7	-0.50	-0.14	0.02
	β	Mn1	-2.91	-2.94	-2.91
	α	Mn2	2.92	2.93	2.93
	α	Mn3	2.77	2.80	2.85
	α	Mn4	2.51	2.56	1.95
		O6	0.07	-0.42	0.01
	β	O7	-0.53	-0.17	0.03
	α	Mn1	2.92	2.93	2.92
	α	Mn2	2.92	2.93	2.92
	α	Mn3	2.78	2.77	2.77
	β	Mn4	-2.59	-2.55	-1.91
octet		O6	-0.05	0.43	0.00
	α	O7	0.66	0.19	-0.01
	α	Mn1	\	\	\
	α	Mn2	\	\	\
	β	Mn3	\	\	\

	α	Mn4	\	\	\
		O6	\	\	\
	α	O7	\	\	\
	α	Mn1	\	\	\
	β	Mn2	\	\	\
	α	Mn3	\	\	\
	α	Mn4	\	\	\
		O6	\	\	\
	α	O7	\	\	\
	β	Mn1	\	\	\
	α	Mn2	\	\	\
	α	Mn3	\	\	\
	α	Mn4	\	\	\
		O6	\	\	\
	α	O7	\	\	\
12-et	α	Mn1	2.92	2.92	2.92
	α	Mn2	2.93	2.92	2.92
	α	Mn3	2.82	2.82	2.81
	α	Mn4	2.76	2.47	1.96
		O6	-0.03	-0.38	0.01
	β	O7	-0.70	-0.12	0.06
14-et	α	Mn1	\	\	\
	α	Mn2	\	\	\
	α	Mn3	\	\	\
	α	Mn4	\	\	\
		O6	\	\	\
	α	O7	\	\	\

‘\’ denotes TSs for some spin states do not exist due to the failure of IRC verification on reactants concerning W1 returning back to Mn4.

Rea:

Ca	-2.53281700	0.15490400	-1.33882900	H	-2.90091400	2.29061700	-3.11675100
Mn	0.32949200	-1.54522100	-0.75955000	H	-1.37649200	2.27541600	-2.85429100
Mn	-1.43064400	-1.85025400	1.24964400	O	-0.01542700	5.27161300	-0.97593800
Mn	-0.29732400	0.66878100	0.98693200	O	-0.61329000	4.57370400	1.42377100
Mn	-0.45212500	3.84761500	-0.25200300	H	-0.93404600	3.79578300	1.92404000
O	-1.37278600	-2.05673300	-0.55629100	O	-3.51992600	2.30050100	-0.91563200
O	0.33795100	-1.26026600	1.06021200	C	-3.41163400	3.52188400	-0.65962900
O	-1.93965300	-0.16157700	1.04074800	O	-2.34621500	4.22872700	-0.58721700
O	-0.08033900	0.22779800	-0.84286500	C	-4.71075500	4.30762600	-0.42018600
O	-1.00625400	2.19667800	0.73477100	H	-5.39001300	4.06649100	-1.25089400
O	-4.43697400	-0.61944100	-2.89130700	H	-5.16981100	3.85917100	0.47432200
H	-4.74066700	-1.22983700	-2.18744600	C	-4.55013400	5.81763900	-0.24583100
H	-3.76536100	-1.11713400	-3.40366700	H	-4.12249200	6.27612900	-1.14572700
O	-2.11618600	1.74098400	-3.28906800	H	-3.86985900	6.04206100	0.58301600

H	-5.52245700	6.29051000	-0.04502900	C	3.47561200	2.79775500	1.28002600
O	0.30340400	-1.92614300	-2.68135200	H	3.99362800	3.06819900	0.34805800
C	-0.72464600	-1.91694800	-3.46597400	H	3.45552400	3.71713500	1.88301400
O	-1.82071900	-1.37477100	-3.22458800	C	2.02453100	2.51090100	0.86699100
C	-0.52044100	-2.65730100	-4.78817400	O	1.54435700	1.38540200	1.21313000
H	-0.55457200	-3.73632600	-4.56454600	O	1.48853700	3.43701400	0.20467900
H	-1.37409800	-2.42912200	-5.43857000	O	0.88533400	-3.47937400	-0.30882500
C	0.80693000	-2.32943800	-5.48782400	C	0.30204600	-4.14648900	0.61383200
H	1.63029100	-2.54290600	-4.79449400	O	-0.62554300	-3.75351500	1.37918600
H	0.84640900	-1.24984900	-5.69670900	C	0.79245500	-5.58691500	0.78145800
C	0.99466500	-3.11250700	-6.79188100	H	1.89035000	-5.55386000	0.83389100
H	0.99030900	-4.19692600	-6.60838600	H	0.55821800	-6.10943400	-0.15848100
H	1.94810200	-2.86017000	-7.27613600	H	-5.70285900	-2.98291900	2.03983900
H	0.18970400	-2.89595300	-7.50875700	C	0.20333300	-6.33058500	1.97998100
N	2.36878800	-1.14420700	-1.02281300	H	0.59353100	-7.35658900	2.02685400
C	2.90548100	-0.03524500	-1.63967400	H	0.45142100	-5.82269100	2.91968700
H	2.26407700	0.73066200	-2.05532200	H	-0.88952400	-6.37549600	1.91437900
C	4.27750000	-0.10522500	-1.58968000	O	-4.21983300	-1.48040800	-0.32156400
N	4.55837900	-1.30171500	-0.93436700	C	-4.21857100	-2.27944500	0.63811900
H	5.46072800	-1.51404500	-0.50770100	O	-3.22285100	-2.53984900	1.41883500
C	3.37981000	-1.87938100	-0.59343400	C	-5.47875800	-3.06915400	0.97010000
H	3.27941600	-2.80722600	-0.04913900	H	-5.30651000	-4.13272700	0.75721100
C	5.32713900	0.83051200	-2.12737100	H	-6.32540600	-2.70986400	0.37774900
H	5.48282400	0.65612600	-3.20339600	O	-1.24120600	-1.51828000	3.21553700
H	4.93256500	1.85244300	-2.04751800	C	-0.79736800	-0.41382700	3.67987300
C	6.71844200	0.74912900	-1.44098400	O	-0.35497100	0.57913800	3.02807300
H	7.25353600	-0.15038600	-1.76585700	C	-0.82399400	-0.27299000	5.20028900
H	7.31513000	1.61698900	-1.75514700	H	-0.21094300	0.59446100	5.47350500
C	6.61419000	0.66859900	0.08073500	H	-1.86381000	-0.03474000	5.47807300
O	6.72596800	-0.41342800	0.67026900	C	-0.37160100	-1.53541100	5.94721500
N	6.32746500	1.83555800	0.72065600	H	0.66292400	-1.77459100	5.65736400
H	6.15121900	2.64489000	0.13619700	H	-0.98744600	-2.38063800	5.61554500
C	5.72676100	1.85184700	2.06094800	C	-0.45713600	-1.37896500	7.46938300
H	6.19511600	1.03831300	2.62284300	H	0.17045800	-0.54850900	7.82360500
H	6.00107900	2.80111200	2.54073300	H	-0.12496700	-2.29112900	7.98389800
C	4.19949600	1.66516800	2.01455200	H	-1.48848300	-1.17200000	7.78976800
H	3.97395700	0.70741100	1.53114900	O	-0.21735900	2.80216800	-1.80001000
H	3.81927800	1.58412800	3.04218000	H	0.06161300	1.91156300	-1.48988100

TS:

Ca	-2.50756900	0.11970600	-1.48367300	O	-1.59047600	-1.98600400	-0.28839500
Mn	0.16174100	-1.69500000	-0.52838600	O	0.18004900	-1.09813800	1.21170900
Mn	-1.64046900	-1.45368900	1.45115900	O	-1.96433900	0.21844900	0.93432900
Mn	-0.24231600	0.85000200	0.78666100	O	-0.06756300	0.06733900	-0.93718700
Mn	-0.03443600	3.64819300	-1.01222500	O	-0.74937700	2.39595000	0.27527900

O	-4.45519500	-0.73415300	-2.93137300	H	7.21426300	-1.15310800	-1.37707100
H	-4.82494900	-1.17917000	-2.14049400	H	7.46781400	0.56760200	-1.69654700
H	-3.83163200	-1.37493900	-3.33310400	C	6.60757900	0.06825400	0.24454500
O	-1.86723300	1.42103100	-3.57774200	O	6.57545900	-0.88421900	1.03354500
H	-2.52511400	2.10849200	-3.36102200	N	6.44146500	1.36113200	0.63712600
H	-1.01082500	1.86086900	-3.28475400	H	6.38002600	2.05798900	-0.09635600
O	0.42239300	5.14917800	-1.72208200	C	5.82680600	1.70485300	1.92579200
O	0.05620400	5.63558500	-0.11492100	H	6.19879800	0.97770900	2.65378500
H	-0.86255300	5.88059300	-0.34712200	H	6.19368100	2.69840800	2.21701400
O	-3.34203200	2.39068300	-1.41160100	C	4.28911200	1.66739900	1.86726100
C	-3.06216000	3.57278800	-1.09765900	H	3.96833100	0.65826100	1.58441500
O	-1.94892400	4.17412100	-1.29875500	H	3.89181400	1.84294000	2.87693100
C	-4.17765800	4.40433700	-0.45209000	C	3.69660100	2.68698000	0.89036000
H	-5.03300700	4.38781800	-1.14365800	H	4.24857100	2.68910000	-0.06232000
H	-4.50215700	3.83647300	0.43193500	H	3.77315200	3.71236800	1.27754900
C	-3.80620300	5.83682100	-0.06985700	C	2.23104600	2.46084700	0.49437500
H	-3.49106000	6.41326500	-0.94859000	O	1.68185700	1.39196700	0.89902500
H	-2.97908900	5.84665300	0.65122200	O	1.75685200	3.37405900	-0.23812400
H	-4.66119300	6.35267400	0.38947900	O	0.50172900	-3.57426900	0.27615800
O	0.12838700	-2.41178300	-2.35418200	C	-0.16411500	-3.99975100	1.28110700
C	-0.87340500	-2.43337000	-3.16969600	O	-1.05078900	-3.37909900	1.93753500
O	-1.90934400	-1.74553000	-3.07130900	C	0.15293200	-5.43493600	1.71072700
C	-0.72534200	-3.41300500	-4.33466600	H	1.24739800	-5.53309800	1.74364000
H	-0.90594500	-4.42348000	-3.93214000	H	-0.17689000	-6.08728700	0.88754100
H	-1.52280200	-3.20109900	-5.05789800	H	-6.01407000	-2.01417300	2.31422100
C	0.65364600	-3.37844100	-5.00947500	C	-0.48364300	-5.86550300	3.03221200
H	1.42115600	-3.56282300	-4.24723000	H	-0.22363900	-6.90744300	3.26466900
H	0.83817400	-2.36620100	-5.39950500	H	-0.14198600	-5.23150400	3.85943900
C	0.77893300	-4.39809100	-6.14687200	H	-1.57491700	-5.77917400	2.98698000
H	0.62995700	-5.42385400	-5.77906700	O	-4.36611200	-1.11890900	-0.24272100
H	1.77115300	-4.35326200	-6.61668700	C	-4.45421400	-1.71810300	0.84986700
H	0.03054100	-4.21714700	-6.93173600	O	-3.49910600	-1.91552500	1.69553400
N	2.23892900	-1.54807300	-0.77202000	C	-5.78928600	-2.31165000	1.28325000
C	2.90788100	-0.62744300	-1.54853900	H	-5.72013900	-3.40768600	1.26728700
H	2.36424400	0.09661000	-2.14104800	H	-6.59091200	-1.98642800	0.61354900
C	4.26292000	-0.79786500	-1.39196300	O	-1.43247100	-0.80388400	3.33360800
N	4.39690900	-1.86278900	-0.50432100	C	-0.86050900	0.30453200	3.61208100
H	5.25290200	-2.06294200	0.01406500	O	-0.30590100	1.11378800	2.81055500
C	3.15356500	-2.26513700	-0.14253100	C	-0.86563300	0.69995400	5.08727100
H	2.93904500	-3.05603800	0.56153300	H	-0.18218100	1.54787800	5.21651600
C	5.42138500	-0.07280900	-2.02345500	H	-1.88103400	1.06219900	5.31644800
H	5.60119900	-0.44981000	-3.04232700	C	-0.50963100	-0.45454500	6.03475800
H	5.12980300	0.97930600	-2.14507100	H	0.49990000	-0.82079100	5.79329500
C	6.76944900	-0.15864200	-1.25737600	H	-1.19451700	-1.29017500	5.84392400

C	-0.56900600	-0.04348500	7.50996000	H	-1.57752300	0.29617900	7.78696100
H	0.12654700	0.78042700	7.72544000	O	0.27368900	2.39402200	-2.32604200
H	-0.30696500	-0.88235000	8.16936800	H	0.35553900	1.52529900	-1.86476700

Pro:

Ca	-2.54529300	0.01410500	-1.36644200	H	2.07347600	-3.02196100	-7.18320100
Mn	0.37171200	-1.56025600	-0.71875300	H	0.31915900	-3.14706200	-7.41607800
Mn	-1.37021900	-1.81427600	1.31341200	N	2.42147500	-1.16731700	-0.94992500
Mn	-0.28010400	0.71238100	0.93063500	C	2.99773100	-0.16750500	-1.69991100
Mn	-0.60038800	3.62435800	-0.50403600	H	2.38970500	0.49021200	-2.30627400
O	-1.31949900	-2.09708100	-0.48509800	C	4.36019400	-0.18118800	-1.51337400
O	0.38540100	-1.20015000	1.08671800	N	4.59473700	-1.23460300	-0.63404600
O	-1.90965600	-0.14393700	1.03346200	H	5.46372800	-1.35935000	-0.11271300
O	-0.06988700	0.19589400	-0.87824700	C	3.39864000	-1.78226800	-0.30681700
O	-1.01847200	2.24939100	0.70150000	H	3.26305200	-2.60043700	0.38514700
O	-4.42538000	-0.93937100	-2.86922400	C	5.44063100	0.68640200	-2.10384400
H	-4.68869200	-1.52626700	-2.13053100	H	5.65346100	0.38192000	-3.14034600
H	-3.72842700	-1.42151200	-3.36121000	H	5.04853100	1.71063700	-2.17202900
O	-2.27603700	1.52313700	-3.35421200	C	6.79266700	0.69507900	-1.34116200
H	-3.04487600	2.08189700	-3.14226500	H	7.33058300	-0.24528800	-1.50628400
H	-1.49769700	2.07098300	-2.98482500	H	7.41597500	1.50482700	-1.74592500
O	-0.33836800	5.39004100	-1.00760500	C	6.62039500	0.83623700	0.17072200
O	-0.75788800	5.58844800	0.38662700	O	6.70838100	-0.14746500	0.91656900
H	-1.73666800	5.59990000	0.26565400	N	6.30792800	2.08045800	0.62370100
O	-3.71722900	2.07645500	-0.96023700	H	6.15156800	2.79799000	-0.07496300
C	-3.63689400	3.28537900	-0.63258600	C	5.67980600	2.28807300	1.93552600
O	-2.58883900	4.01623400	-0.65110700	H	6.17031000	1.60064300	2.63129100
C	-4.93929000	3.97179100	-0.19419100	H	5.90628800	3.31483100	2.25305200
H	-5.64819000	3.87267400	-1.02983800	C	4.16250100	2.03139700	1.90666100
H	-5.35494700	3.35650800	0.61672800	H	3.98135200	0.99163000	1.61109300
C	-4.81293900	5.43194700	0.24053100	H	3.76869900	2.13194500	2.92790300
H	-4.40479600	6.05184300	-0.56722500	C	3.40922100	2.97328900	0.96399500
H	-4.14316600	5.52839700	1.10502700	H	3.90524800	3.02255400	-0.01790000
H	-5.79202500	5.84197600	0.52640100	H	3.40157800	4.00389200	1.34544800
O	0.37572000	-2.01053300	-2.62310900	C	1.95356900	2.59497400	0.65789700
C	-0.64923700	-2.07139900	-3.41060500	O	1.55526700	1.45742200	1.07222600
O	-1.76714400	-1.56797000	-3.19015300	O	1.31939300	3.45250700	-0.00752300
C	-0.40846000	-2.84750400	-4.70599800	O	0.95492500	-3.47861500	-0.18624000
H	-0.39287000	-3.91850100	-4.44500200	C	0.37885100	-4.11593300	0.75937200
H	-1.27006900	-2.68135400	-5.36458500	O	-0.54111300	-3.69743300	1.52205300
C	0.90411300	-2.48305600	-5.41543500	C	0.85624400	-5.55664500	0.96151500
H	1.73464700	-2.63425200	-4.71426000	H	1.95146900	-5.55759400	0.87240400
H	0.89385200	-1.41073100	-5.66214700	H	0.48839400	-6.12903900	0.09559000
C	1.13143300	-3.30121000	-6.69137300	H	-5.61266200	-2.99700000	2.20632000
H	1.17671500	-4.37763700	-6.47025000	C	0.40011700	-6.20577800	2.26854400

H	0.76061900	-7.24174000	2.33215200	C	-0.72583100	-0.08498600	5.19032600
H	0.78164800	-5.65468700	3.13710500	H	-0.11975200	0.79957800	5.42092300
H	-0.69285900	-6.20973400	2.34134300	H	-1.76382800	0.14934800	5.47785000
O	-4.17756100	-1.62054300	-0.25365700	C	-0.24333400	-1.31369600	5.97379100
C	-4.14906500	-2.35607100	0.75431900	H	0.78927500	-1.54961200	5.67442100
O	-3.14205100	-2.53689900	1.54259300	H	-0.85312600	-2.17823000	5.68324000
C	-5.38455800	-3.15773300	1.14595000	C	-0.30453800	-1.10439500	7.49079100
H	-5.17929900	-4.22862100	1.01497600	H	0.31800400	-0.25394300	7.80428500
H	-6.24112400	-2.87026600	0.52915800	H	0.04850600	-1.99335800	8.03144200
O	-1.17069800	-1.40445100	3.26105600	H	-1.33286800	-0.89917900	7.82191300
C	-0.72317600	-0.28122500	3.67546500	O	-0.33013000	2.71587500	-2.11499800
O	-0.29519900	0.68652300	2.98002500	H	0.23972800	1.95243700	-1.89575900

O2 (oxo)-O4 (oxo/oxyl)

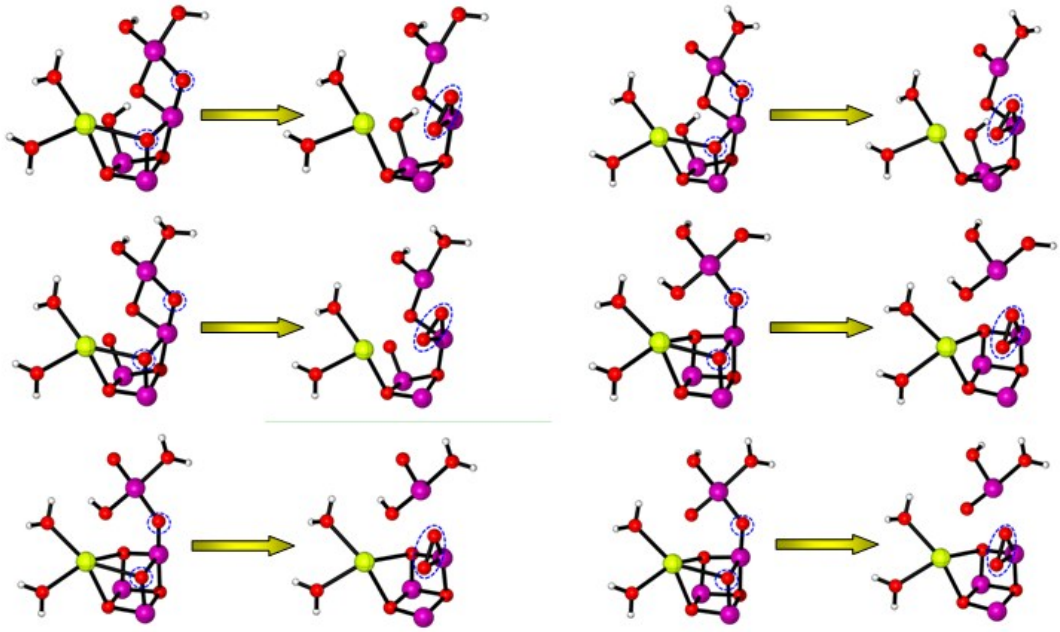

Fig. S8 Pictorial exhibitions for O2 (oxo)-O4 (oxo/oxyl) coupling in the open and closed-cubane structures with previous deprotonation sites of W1, W2 and Wx.

Table S14 Reaction parameters for the open-cubane O2 (oxo)-O4 (oxo/oxyl) coupling with deprotonated W1:

Spin state	Spin topology (Mn1~Mn4/O4)	Gibbs Free energy (a.u.)		
		Rea	TS	Pro-O-O
doublet	ααββα	-3366.2250	-3366.1806	-3366.2157
	αβαβα	-3366.2168	-3366.1543	-3366.1707
	αββαα	-3366.2232	-3366.1517	-3366.1755
	βααβα	-3366.2177	-3366.1813	-3366.2147
	βαβαα	-3366.2222	-3366.1817	-3366.2164

	ββααα	-3366.2158	-3366.1542	-3366.1737
sextet	αααββ	-3366.2239	-3366.1538	-3366.1751
	ααβαβ	-3366.2177	-3366.1559	-3366.2235
	αβααβ	-3366.2244	-3366.1781	-3366.2172
	βαααβ	-3366.2246	-3366.1530	-3366.1766
octet	αααβα	-3366.2178	-3366.1794	-3366.2141
	ααβαα	-3366.2234	-3366.1826	-3366.2168
	αβααα	-3366.2154	-3366.1544	-3366.1724
	βαααα	-3366.2159	-3366.1836	-3366.2156
12-et	ααααβ	-3366.2267	-3366.1529	-3366.1755
14-et	ααααα	-3366.2159	-3366.1829	-3366.2148

Spin state	Spin topology (Mn1~Mn4-O4/O10)	Relative Gibbs Free energy (kcal/mol)			
		$\Delta G^{\neq}$(Rea-TS)	ΔG(Rea-Pro)	ΔG(Rea)	ΔG(Pro)
doublet	αααββα	27.9	5.8	1.1	4.9
	αβαβα	39.2	28.9	6.2	33.1
	αββαα	44.9	29.9	2.2	30.1
	βααβα	22.8	1.9	5.6	5.5
	βαβαα	25.4	3.6	2.8	4.5
	ββαααα	38.7	26.4	6.8	31.2
sextet	αααββ	44.0	30.6	1.8	30.4
	αααβα	38.8	-3.6	5.6	0.0
	αβααβ	29.1	4.5	1.4	4.0
	βαααβ	44.9	30.1	1.3	29.4
octet	αααβα	24.1	2.3	5.6	5.9
	αααβα	25.6	4.1	2.1	4.2
	αβαααα	38.3	27.0	7.1	32.1
	βαααα	20.3	0.2	6.8	5.0
12-et	ααααβ	46.3	32.1	0.0	30.1
14-et	ααααα	20.7	0.7	6.8	5.5

Spin state	topology	Spin (Mn1~Mn4-O4)	Mulliken spin density		
			Rea	TS	Pro-O-O
doublet	α	Mn1	2.92	2.97	2.97
	α	Mn2	2.94	3.56	3.85
	β	Mn3	-2.73	-2.94	-3.07
	β	Mn4	-2.90	-2.93	-2.94
	α	O2	-0.02	-0.10	0.11
		O4	0.77	0.56	0.15
	α	Mn1	2.94	2.97	2.97
	β	Mn2	-2.91	-2.40	-1.93
	α	Mn3	2.84	3.01	3.04
	β	Mn4	-2.86	-2.90	-2.90

	α	O2	0.03	0.02	-0.08
		O4	0.87	0.33	-0.06
	α	Mn1	2.93	2.94	2.95
	β	Mn2	-2.93	-2.39	-1.98
	β	Mn3	-2.70	-2.91	-2.97
	α	Mn4	2.84	2.91	2.92
	α	O2	-0.06	0.00	0.06
		O4	0.73	0.40	0.06
	β	Mn1	-2.93	-2.93	-2.91
	α	Mn2	2.93	3.49	3.85
	α	Mn3	2.84	2.86	3.02
	β	Mn4	-2.86	-2.91	-2.90
	α	O2	0.10	-0.04	-0.07
		O4	0.85	0.49	-0.06
	β	Mn1	-2.94	-2.95	-2.93
	α	Mn2	2.91	3.52	3.84
	β	Mn3	-2.65	-2.92	-3.02
	α	Mn4	2.84	2.87	3.90
	α	O2	-0.02	-0.08	0.07
		O4	0.67	0.49	0.06
	β	Mn1	-2.96	-2.95	-2.94
	β	Mn2	-2.95	-2.46	-1.98
	α	Mn3	2.83	3.02	3.11
	α	Mn4	2.87	2.93	2.94
	α	O2	0.03	0.02	-0.12
		O4	0.62	0.28	-0.15
		O5	0.45	0.06	0.07
	α	Mn1	2.96	2.97	2.95
	α	Mn2	2.96	2.43	1.99
	α	Mn3	2.73	2.92	3.01
	β	Mn4	-2.84	-2.91	-2.91
	β	O2	0.06	-0.01	-0.06
		O4	-0.73	-0.39	-0.04
	α	Mn1	2.95	2.94	2.95
	α	Mn2	2.4	2.91	3.07
sextet	β	Mn3	-2.83	-3.46	2.95
	α	Mn4	2.86	2.88	-3.82
		O2	-0.03	-0.07	-0.08
	β	O4	-0.84	-0.24	-0.10
	α	Mn1	2.94	2.95	2.93
	β	Mn2	-2.90	-3.52	-3.84
	α	Mn3	2.73	2.95	3.09
	α	Mn4	2.90	2.92	2.94
	β	O2	0.03	0.10	-0.10

		O4	-0.75	-0.54	-0.14
	β	Mn1	-2.93	-2.94	-2.95
	α	Mn2	2.93	2.40	1.99
	α	Mn3	2.76	2.92	3.02
	α	Mn4	2.90	2.92	2.94
	β	O2	0.07	-0.01	-0.10
		O4	-0.79	-0.46	-0.14
octet	α	Mn1	2.96	2.99	2.98
	α	Mn2	2.95	3.53	3.86
	α	Mn3	2.87	2.86	3.02
	β	Mn4	-2.86	-2.90	-2.90
	α	O2	0.09	-0.04	-0.06
		O4	0.88	0.50	-0.04
	α	Mn1	2.95	2.97	2.97
	α	Mn2	2.94	3.55	3.85
	β	Mn3	-2.67	-2.92	-3.02
	α	Mn4	2.84	2.87	2.91
	α	O2	-0.01	-0.08	0.07
		O4	0.70	0.50	0.07
	α	Mn1	2.94	2.97	2.97
	β	Mn2	-2.91	-2.41	-1.93
	α	Mn3	2.84	3.02	3.10
	α	Mn4	2.85	2.93	2.94
	α	O2	0.08	0.02	-0.11
		O4	0.84	0.29	-0.14
	β	Mn1	-2.93	-2.93	-2.91
	α	Mn2	2.92	3.49	3.85
	α	Mn3	2.85	2.89	3.07
	α	Mn4	2.87	2.90	2.93
	α	O2	0.09	-0.03	-0.10
		O4	0.62	0.45	-0.14
		O5	0.44	0.08	0.08
12-et	α	Mn1	2.97	2.97	2.94
	α	Mn2	2.96	2.44	1.99
	α	Mn3	2.78	2.93	3.07
	α	Mn4	2.90	2.92	2.94
	β	O2	0.07	-0.01	-0.09
		O4	-0.78	-0.44	-0.13
14-et	α	Mn1	2.97	2.99	2.99
	α	Mn2	2.96	3.53	3.86
	α	Mn3	2.87	2.89	3.07
	α	Mn4	2.85	2.90	2.94
	α	O2	0.11	-0.03	-0.09
		O4	0.87	0.46	-0.12

Rea:

Ca	2.46171800	0.20655500	-1.41545100	N	-1.92900400	2.45431000	-0.04296800
Mn	0.08170600	1.94290100	0.19508000	C	-2.62612200	2.55138500	-1.22843900
Mn	1.36093400	0.12206800	1.87957800	H	-2.10562100	2.49818300	-2.17423200
Mn	-0.17845400	-1.58557700	0.32093200	C	-3.96667500	2.69592900	-0.95934000
Mn	-0.13563300	-2.83018400	-2.23268900	N	-4.05936000	2.69809100	0.42816300
O	1.73724100	1.37498800	0.62776800	H	-4.93465500	2.55430700	0.93969000
O	-0.35140400	0.28162700	1.06381900	C	-2.81835100	2.53230100	0.93673300
O	1.51022200	-1.34564400	0.81701400	H	-2.59257800	2.45220300	1.98929800
O	0.23866900	-1.19559500	-1.37569300	C	-5.14277300	2.84972300	-1.88809500
O	-0.28143500	-3.25591500	-0.23288000	H	-5.17159000	3.87064000	-2.29791500
O	4.71118100	1.14671600	-2.02280200	H	-4.98055400	2.18821900	-2.75043000
H	5.08785300	0.95614800	-1.13941100	C	-6.53604700	2.56325900	-1.26880800
H	4.41768500	2.07975400	-1.99441300	H	-6.82763300	3.37849900	-0.59716500
O	1.57256300	0.31924400	-3.73147200	H	-7.27566400	2.53070600	-2.08045000
H	0.82726100	0.92816600	-3.57346600	C	-6.57426100	1.28393900	-0.43480900
H	1.14563300	-0.55368900	-3.92171400	O	-6.45531600	1.32011300	0.79730900
O	0.15775300	-2.06629500	-3.84470500	N	-6.67889900	0.11586000	-1.11875300
H	-0.05281000	-2.74751100	-4.51061800	H	-6.74548400	0.15086600	-2.12849900
O	-0.67081100	-4.42521400	-2.89838300	C	-6.48507200	-1.18712200	-0.47349300
H	0.07002500	-5.04444700	-2.75563500	H	-7.04109600	-1.17326900	0.46992000
O	3.07640300	-1.98960900	-2.12447900	H	-6.94196100	-1.94301500	-1.12459300
C	2.77373000	-3.17794300	-1.96668300	C	-5.00850700	-1.51740800	-0.19490300
O	1.56378900	-3.66606600	-1.98031400	H	-4.60138400	-0.78222600	0.50758900
C	3.87224900	-4.21016200	-1.71878800	H	-4.96695100	-2.49260900	0.31059400
H	4.67424600	-3.98394500	-2.43419400	C	-4.15187700	-1.55255600	-1.46460800
H	4.28362500	-3.96965700	-0.72658000	H	-4.19516500	-0.57735500	-1.97482200
C	3.45546300	-5.67944100	-1.78746300	H	-4.51119800	-2.30214700	-2.18101000
H	3.06192200	-5.93666000	-2.77919400	C	-2.66965400	-1.82824900	-1.22663600
H	2.67878500	-5.90645200	-1.04844800	O	-2.17380600	-1.46854600	-0.11646300
H	4.31823000	-6.32823300	-1.58920800	O	-2.05833300	-2.37653700	-2.19517600
O	0.73992800	3.59384500	-0.51184600	O	-0.13701200	2.92411500	1.94222000
C	1.81293000	3.72394800	-1.23951100	C	0.46512900	2.62973500	3.02626000
O	2.54363200	2.79945000	-1.63700800	O	1.11593600	1.56738500	3.24031300
C	2.11320200	5.17865200	-1.59703200	C	0.39369100	3.66403000	4.14184900
H	1.25603200	5.55117600	-2.17951300	H	-0.62951800	4.06308300	4.15383500
H	2.10389100	5.75929400	-0.66287500	H	1.03250300	4.50115100	3.81954900
C	3.41999300	5.39008900	-2.36553500	C	0.82026200	3.15445800	5.51889800
H	3.40739100	4.77471500	-3.27524500	H	0.76183800	3.96393400	6.25742300
H	4.25999500	5.02136600	-1.75914800	H	0.17427100	2.33484300	5.85655800
C	3.65188400	6.86092200	-2.72925000	H	1.84764000	2.77550000	5.49716400
H	2.84224600	7.24733400	-3.36431200	O	4.20358800	0.01026700	0.41995600
H	3.69806400	7.49342700	-1.83153400	C	4.22237700	-0.03255900	1.66672000
H	4.59449100	6.98982000	-3.27673000	O	3.18361600	-0.03205000	2.44265500

C	5.54253500	-0.07906200	2.41801300	C	-0.66405400	-4.16828100	4.31789600
H	5.52844700	-0.89634800	3.14833700	H	0.34805000	-4.52058700	4.06913400
H	5.67466500	0.85558600	2.97872200	H	-1.29991900	-4.41863200	3.45940800
H	6.37547300	-0.21022700	1.72165800	C	-1.16445200	-4.88212000	5.57772600
O	0.71469400	-1.01991600	3.36882100	H	-0.52634300	-4.66130800	6.44478500
C	-0.18482600	-1.90929200	3.23251200	H	-1.17133000	-5.97074100	5.43729100
O	-0.74327400	-2.22893400	2.13873800	H	-2.18802500	-4.57149600	5.83114000
C	-0.63742500	-2.63976400	4.48643900	O	0.04484000	1.32990600	-1.51109900
H	0.01680100	-2.34052300	5.31358300	H	-0.27420400	0.38782200	-1.51183100
H	-1.65212700	-2.27995200	4.72063300				

TS:

Ca	2.47454100	0.07362500	-1.60640100	C	3.11783400	4.89981800	-1.20659800
Mn	0.50350900	1.93321100	0.28674400	H	2.38105500	5.44341200	-1.81944300
Mn	1.23874400	-0.22768000	1.87403200	H	3.12247700	5.41277800	-0.23419600
Mn	-0.82580500	-1.27168800	0.33793900	C	4.49911900	4.94447000	-1.86523600
Mn	-0.37164400	-2.75908600	-2.02660900	H	4.46122900	4.40285600	-2.81972000
O	1.93455100	0.89657400	0.61762800	H	5.21830800	4.40178000	-1.23431800
O	-0.35587200	0.41760200	1.07932400	C	4.99094400	6.37825200	-2.09249300
O	0.65032300	-2.17447400	0.84471700	H	4.30697500	6.93520100	-2.74829300
O	-0.10584100	-1.03373500	-1.30803100	H	5.06501400	6.93169000	-1.14583000
O	-0.50496700	-3.08292400	0.00101000	H	5.98291300	6.38682800	-2.56224300
O	4.92889700	0.43631400	-1.89344200	N	-1.38002600	2.83900900	0.11086600
H	5.14704500	-0.06100800	-1.07752200	C	-1.98029800	3.23572600	-1.06449500
H	4.94159400	1.38243800	-1.65305100	H	-1.39758100	3.35640600	-1.96662300
O	1.47863100	0.10709700	-3.86095700	C	-3.33283400	3.37389200	-0.86378400
H	0.75436100	0.75513800	-3.88512500	N	-3.53361500	3.06894800	0.47735900
H	1.02455300	-0.77493200	-3.94394900	H	-4.45444200	2.88147800	0.88847500
O	-0.06764300	-2.14668200	-3.71429500	C	-2.34119200	2.73647800	1.01936200
H	-0.25695900	-2.89155500	-4.31444900	H	-2.20604900	2.38657600	2.03227600
O	-0.99630600	-4.39251800	-2.49789500	C	-4.42609900	3.74602800	-1.83228400
H	-0.27700600	-5.02052500	-2.29486000	H	-4.30997000	4.79539100	-2.14159100
O	2.82863200	-2.10313700	-2.43938100	H	-4.29150600	3.14990000	-2.74636400
C	2.51255000	-3.24972100	-2.08930700	C	-5.87898200	3.57737000	-1.32450900
O	1.30685900	-3.65753400	-1.84891700	H	-6.08685300	4.29965500	-0.52666600
C	3.60264000	-4.29909600	-1.88582600	H	-6.55933300	3.80773700	-2.15590300
H	4.25715200	-4.23961400	-2.76635600	C	-6.18242000	2.19632300	-0.74240100
H	4.20518700	-3.92689200	-1.04358400	O	-6.11056000	1.98631900	0.47663300
C	3.13276200	-5.73103800	-1.63090300	N	-6.48993000	1.21441100	-1.62739800
H	2.55366300	-6.11760300	-2.47940100	H	-6.54809200	1.44724600	-2.61067300
H	2.49823900	-5.78671800	-0.73920800	C	-6.70803700	-0.17819600	-1.21462400
H	3.99484100	-6.39421100	-1.48261000	H	-7.40359100	-0.17057300	-0.36714600
O	1.47658700	3.47994400	-0.27326400	H	-7.20324500	-0.68614800	-2.05155000
C	2.56138800	3.49470400	-0.98977100	C	-5.41970900	-0.90648100	-0.80076800
O	3.12221300	2.49852300	-1.48348500	H	-4.96232000	-0.36116700	0.03041000

H	-5.69958400	-1.89725100	-0.41466900	C	5.13411900	-1.83273700	2.13279200
C	-4.39633900	-1.06340300	-1.93375300	H	4.86617200	-2.76067100	2.65224300
H	-4.25187800	-0.09422100	-2.43889100	H	5.49493900	-1.12931100	2.89412800
H	-4.72377900	-1.78036700	-2.69562100	H	5.92561200	-2.02859400	1.40393700
C	-3.01232400	-1.47903500	-1.44781000	O	0.21129400	-1.19714000	3.28998800
O	-2.62383700	-0.96315800	-0.34420700	C	-0.96400100	-1.66664600	3.17509700
O	-2.34940300	-2.26833500	-2.17223200	O	-1.66218700	-1.67259400	2.10864200
O	0.54872200	2.77816400	2.13682600	C	-1.60066900	-2.27569700	4.41289700
C	1.10095900	2.29051100	3.16988600	H	-0.90523700	-2.16215400	5.25255200
O	1.48384500	1.08534700	3.31254200	H	-2.50868900	-1.69686400	4.64138800
C	1.33391500	3.23962800	4.33801300	C	-1.97916800	-3.75424900	4.20505100
H	0.44399600	3.87817500	4.41569700	H	-1.07408700	-4.32399400	3.94875600
H	2.15117600	3.90777200	4.02434800	H	-2.64968500	-3.82836000	3.33928200
C	1.66589300	2.56246000	5.66820000	C	-2.64177800	-4.36313300	5.44479500
H	1.83299900	3.31884000	6.44533900	H	-1.97580100	-4.31897100	6.31789100
H	0.84844600	1.90890300	5.99603200	H	-2.90048100	-5.41643600	5.27561900
H	2.56690700	1.94553800	5.58325000	H	-3.56681200	-3.82919500	5.70498500
O	3.91596400	-1.00993200	0.22540000	O	0.34483900	1.46606200	-1.45582500
C	3.90462500	-1.25651600	1.45012000	H	-0.15631900	0.59975800	-1.50087700
O	2.90539800	-1.06908800	2.25219900				

Pro:

Ca	2.65521500	0.14778300	-1.48918700	C	3.66414300	-4.35496500	-1.60590300
Mn	0.42845700	1.84977200	0.26536000	H	4.39619500	-4.27521700	-2.42235200
Mn	1.34061900	-0.11993800	1.96791600	H	4.18958800	-4.00425000	-0.70551100
Mn	-0.64854600	-1.48115400	0.39049600	C	3.17894000	-5.79369900	-1.43086900
Mn	-0.25443200	-2.80780900	-2.13248100	H	2.68841000	-6.16281700	-2.34016600
O	1.97158700	1.04565400	0.70765600	H	2.45924700	-5.87057200	-0.60795500
O	-0.27639400	0.25827400	1.04881400	H	4.02596900	-6.45641300	-1.21120200
O	0.42178400	-2.98529100	0.67567300	O	1.25817000	3.47031900	-0.33838200
O	0.17172600	-1.23808900	-1.18259900	C	2.36413000	3.57439400	-1.01089500
O	-0.67717300	-3.32962100	-0.12874000	O	3.03619600	2.62861200	-1.46581200
O	5.03974000	0.76435600	-1.91226500	C	2.79799300	5.02245800	-1.22969700
H	5.33930600	0.39048100	-1.05767000	H	2.00973700	5.50772600	-1.82658200
H	4.92063900	1.72290900	-1.76325300	H	2.77444100	5.52728100	-0.25291400
O	1.76149500	0.15501000	-3.78253300	C	4.16208700	5.18713500	-1.90442600
H	1.04889300	0.81777100	-3.75875300	H	4.15820000	4.65041100	-2.86270700
H	1.28141800	-0.71121400	-3.88798700	H	4.93206900	4.70303500	-1.28620500
O	0.15706600	-2.03610600	-3.72942900	C	4.52881500	6.65853200	-2.12788500
H	-0.07001700	-2.69975400	-4.40706300	H	3.79198100	7.16008100	-2.77101100
O	-0.89063500	-4.34722900	-2.83982200	H	4.56842700	7.21043300	-1.17824800
H	-0.20615900	-5.02438600	-2.67953000	H	5.51040300	6.75350200	-2.60983000
O	2.93042400	-2.12619500	-2.07280500	N	-1.50356600	2.61340800	-0.04169900
C	2.59269200	-3.30383100	-1.88817200	C	-2.07900200	2.93284200	-1.25185100
O	1.37617000	-3.75671700	-1.91292700	H	-1.48130000	2.96450300	-2.15184700

C	-3.42662300	3.14267600	-1.07699800	C	0.70783500	3.39579700	4.32342700
N	-3.64846800	2.95502600	0.28234800	H	-0.22747500	3.96605200	4.25008000
H	-4.57719100	2.83466700	0.69862800	H	1.51105300	4.11519000	4.09935000
C	-2.47341400	2.62160100	0.86125800	C	0.89782000	2.79066900	5.71487200
H	-2.35700800	2.36542400	1.90381100	H	0.90585400	3.58239500	6.47451600
C	-4.49715800	3.50492900	-2.07438700	H	0.08771300	2.09230200	5.95864400
H	-4.35767500	4.54173300	-2.41532000	H	1.84082100	2.23724900	5.77841000
H	-4.35920900	2.87815800	-2.96701700	O	4.22477000	-0.59901500	0.32875900
C	-5.96001500	3.37779900	-1.57953300	C	4.16171400	-0.84539300	1.55117500
H	-6.17761100	4.15207200	-0.83515600	O	3.07072000	-0.90207200	2.24684200
H	-6.62828600	3.55111200	-2.43421300	C	5.42410900	-1.13129800	2.34531900
C	-6.26500300	2.03815700	-0.91028900	H	5.31144400	-2.07379400	2.89410100
O	-6.24329500	1.91867600	0.32259400	H	5.56904700	-0.33937800	3.09194800
N	-6.50058900	0.98594000	-1.73426200	H	6.29630100	-1.18228700	1.68763300
H	-6.48903000	1.14122300	-2.73457500	O	0.50443300	-1.40464600	3.21685700
C	-6.60686900	-0.39043200	-1.23557300	C	-0.68691500	-1.85896200	3.19530100
H	-7.29491300	-0.38356600	-0.38278400	O	-1.45186600	-1.85249900	2.18027900
H	-7.06511200	-0.98742000	-2.03388600	C	-1.21668600	-2.43557200	4.49712600
C	-5.25895100	-0.98696200	-0.79785400	H	-0.40193300	-3.02717800	4.93780400
H	-4.85497800	-0.38693000	0.02385700	H	-1.36487500	-1.58479200	5.18223200
H	-5.44735500	-1.99209000	-0.39384000	C	-2.50153300	-3.26014100	4.37442700
C	-4.22711800	-1.06765700	-1.92956000	H	-2.33293000	-4.08717400	3.67071400
H	-4.10639900	-0.07490800	-2.39238600	H	-3.28953100	-2.63883900	3.92859500
H	-4.53662400	-1.75944400	-2.72209500	C	-2.96647800	-3.81024000	5.72739100
C	-2.83379300	-1.47802800	-1.46578700	H	-2.20436200	-4.46100200	6.17865000
O	-2.44482000	-1.03109800	-0.33846000	H	-3.88586000	-4.40002200	5.61933900
O	-2.16838100	-2.20695100	-2.25716300	H	-3.17261300	-2.99913200	6.44036800
O	0.25853900	2.79267900	2.06407000	O	0.39532000	1.29021700	-1.46298300
C	0.71688000	2.39135500	3.17811500	H	-0.02722500	0.38478100	-1.47143300
O	1.18999200	1.23511000	3.40852900				

Table S15 Reaction parameters for the open-cubane O2 (oxo)-O4 (oxo/oxyl) coupling with deprotonated W2:

Spin state	Spin topology (Mn1~Mn4-O4/O7)	Gibbs Free energy (a.u.)		
		Rea	TS	Pro-O-O
doublet	ααββα	-3366.2166	-3366.1591	-3366.1950
	αβαβα	-3366.2133	-3366.1298	-3366.1566
	αββαα	-3366.2030	-3366.1312	-3366.1553
	βααβα	-3366.2179	-3366.1643	-3366.2010
	βαβαα	-3366.2026	-3366.1599	-3366.1963
	ββααα	-3366.1942	-3366.1330	-3366.1537
sextet	αααββ	-3366.2040	-3366.1324	-3366.1469
	ααβαβ	-3366.2159	-3366.1361	-3366.1666

	αβααβ	-3366.2181	-3366.1607	-3366.1968
	βαααβ	-3366.2175	-3366.1374	-3366.1661
octet	αααβα	-3366.2188	-3366.1604	-3366.1957
	ααβαα	-3366.2036	-3366.1607	-3366.1970
	αβααα	-3366.1949	-3366.1335	-3366.1517
	βαααα	-3366.1952	-3366.1612	-3366.1967
12-et	aaaaβ	-3366.2164	-3366.1337	-3366.1551
14-et	aaaaa	-3366.1957	-3366.1607	-3366.1952

Spin state	Spin topology (Mn1~Mn4-O4/O10)	Relative Gibbs Free energy (kcal/mol)			
		$\Delta G^{\neq}$(Rea-TS)	ΔG(Rea-Pro)	ΔG(Rea)	ΔG(Pro)
doublet	ααββα	36.1	13.6	1.4	3.8
	αβαβα	52.4	35.6	3.5	27.9
	αββαα	45.1	29.9	9.9	28.7
	βααβα	33.6	10.6	0.6	0.0
	βαβαα	26.8	4.0	10.2	2.9
	ββαaα	38.4	25.4	15.4	29.7
sextet	aaaββ	44.9	35.8	9.3	33.9
	aaβaβ	50.1	30.9	1.8	21.6
	aβaaβ	36.0	13.4	0.4	2.6
	βaaaβ	50.3	32.3	0.8	21.9
octet	aaaβa	36.6	14.5	0.0	3.3
	aaβaa	26.9	4.1	9.5	2.5
	aβaaa	38.5	27.1	15.0	30.9
	βaaaa	21.3	-0.9	14.8	2.7
12-et	aaaaβ	51.9	38.5	1.5	28.8
14-et	aaaaa	22.0	0.3	14.5	3.6

Spin state	topology	Spin (Mn1~Mn4-O4/O7)	Mulliken spin density		
			Rea	TS	Pro-O-O
doublet	α	Mn1	2.96	2.97	2.97
	α	Mn2	2.94	3.57	3.85
	β	Mn3	-2.88	-2.96	-3.09
	β	Mn4	-2.72	-2.69	-2.70
	α	O2	-0.02	-0.14	0.08
		O4	-0.12	0.54	0.12
		O7	0.78	-0.31	-0.31
	α	Mn1	2.94	2.94	2.97
	β	Mn2	-2.92	-2.48	-1.92
	α	Mn3	2.86	2.93	3.02
	β	Mn4	-2.69	-2.66	-2.61
	α	O2	0.01	0.02	-0.06
		O4	0.04	0.40	-0.04

		O7	0.80	-0.28	-0.35
	α	Mn1	2.93	2.94	2.95
	β	Mn2	-2.93	-2.35	-1.98
	β	Mn3	-2.73	-2.93	-2.99
	α	Mn4	2.61	2.66	2.67
	α	O2	-0.07	-0.04	0.07
		O4	0.74	0.41	0.07
		O7	0.34	0.33	0.32
	β	Mn1	-2.94	-2.93	-2.91
	α	Mn2	2.94	3.49	3.85
	α	Mn3	2.90	2.89	3.05
	β	Mn4	-2.71	-2.65	-2.66
	α	O2	0.05	-0.05	-0.07
		O4	-0.01	0.52	-0.06
		O7	0.83	-0.33	-0.32
	β	Mn1	-2.94	-2.95	-2.93
	α	Mn2	2.90	3.52	3.83
	β	Mn3	-2.68	-2.95	-3.06
	α	Mn4	2.61	2.64	2.66
	α	O2	-0.04	-0.10	0.07
		O4	0.69	0.49	0.07
		O7	0.34	0.33	0.32
	β	Mn1	-2.95	-2.95	-2.95
	β	Mn2	-2.94	-2.42	-1.98
	α	Mn3	2.85	3.03	3.13
	α	Mn4	2.63	2.70	2.70
	α	O2	0.07	0.01	-0.09
		O4	0.88	0.33	-0.12
		O7	0.37	0.31	0.31
	α	Mn1	2.96	2.97	2.92
	α	Mn2	2.96	2.39	1.98
	α	Mn3	2.75	2.94	3.05
	β	Mn4	-2.61	-2.66	-2.67
	β	O2	0.07	0.03	-0.07
		O4	-0.73	-0.39	-0.05
		O7	-0.34	-0.33	-0.31
sextet	α	Mn1	2.96	2.97	2.97
	α	Mn2	2.95	3.85	3.86
	β	Mn3	-2.86	-2.90	-3.07
	α	Mn4	2.68	1.46	0.98
	β	O2	0.00	0.11	0.08
		O4	-0.05	0.08	0.09
		O7	-0.76	-0.34	0.00
	α	Mn1	2.94	2.95	2.93

	β	Mn2	-2.91	-3.53	-3.83
	α	Mn3	2.88	2.97	3.10
	α	Mn4	2.73	2.70	2.70
	β	O2	0.03	0.14	-0.08
		O4	0.13	-0.52	-0.11
		O7	-0.78	0.31	0.31
	β	Mn1	-2.93	-2.90	-2.91
	α	Mn2	2.94	3.85	3.85
	α	Mn3	2.91	2.95	3.07
	α	Mn4	2.72	2.22	1.06
	β	O2	0.06	-0.40	-0.08
		O4	0.11	-0.10	-0.09
		O7	-0.78	-0.68	-0.02
	α	Mn1	2.96	2.99	2.99
	α	Mn2	2.96	3.49	3.86
	α	Mn3	2.91	2.86	3.00
	β	Mn4	-2.69	-2.75	-2.69
	α	O2	0.05	-0.03	-0.06
		O4	0.02	0.53	-0.04
		O7	0.80	-0.17	-0.25
	α	Mn1	2.96	2.97	2.97
	α	Mn2	2.94	3.56	3.85
	β	Mn3	-2.69	-2.95	-3.04
	α	Mn4	2.61	3.65	2.67
	α	O2	-0.04	-0.10	0.07
		O4	0.71	0.50	0.07
octet		O7	0.34	0.33	0.32
	α	Mn1	2.94	2.96	2.96
	β	Mn2	-2.90	-2.37	-1.93
	α	Mn3	2.86	3.03	3.12
	α	Mn4	2.63	2.71	2.71
	α	O2	0.07	0.01	-0.09
		O4	0.89	0.34	-0.11
		O7	0.37	0.31	0.31
	β	Mn1	-2.93	-2.93	-2.91
	α	Mn2	2.93	3.48	3.85
	α	Mn3	2.86	2.91	3.09
	α	Mn4	2.63	2.69	2.70
	α	O2	0.12	-0.02	-0.07
		O4	0.88	0.50	-0.10
		O7	0.37	0.31	0.31
	α	Mn1	2.97	2.99	2.95
12-et	α	Mn2	2.97	3.86	2.00
	α	Mn3	2.91	2.95	3.07

	α	Mn4	2.70	1.56	2.71
	β	O2	0.06	-0.23	-0.07
		O4	0.11	0.05	-0.10
		O7	-0.72	-0.38	0.31
14-et	α	Mn1	2.97	2.99	2.99
	α	Mn2	2.96	3.52	3.87
	α	Mn3	2.88	2.91	3.09
	α	Mn4	2.63	2.69	2.71
	α	O2	0.11	-0.02	-0.07
		O4	0.90	0.50	-0.09
		O7	0.37	0.31	0.31

Rea:

Ca	2.40213400	0.15818500	-1.40870600	O	2.61151200	2.72499200	-1.66605600
Mn	0.09510200	1.97976200	0.14929800	C	2.18354600	5.10156200	-1.78025000
Mn	1.31608400	0.20884700	1.91787000	H	1.33830000	5.42781400	-2.40631900
Mn	-0.23227200	-1.55620000	0.42633600	H	2.15210700	5.74537200	-0.88907200
Mn	-0.07145300	-2.77664000	-2.12275300	C	3.50560800	5.26503100	-2.53406100
O	1.73222900	1.39952100	0.62836100	H	3.51117400	4.59064600	-3.40095600
O	-0.38293600	0.35897500	1.06643200	H	4.33354100	4.93935700	-1.88769700
O	1.44562900	-1.32007900	0.93890000	C	3.74288100	6.70899300	-2.99026400
O	0.24800300	-1.21500300	-1.30424200	H	2.94558200	7.04995900	-3.66567000
O	-0.31849600	-3.23733100	-0.03113300	H	3.77005300	7.40004200	-2.13592900
O	4.69196300	0.97377100	-2.06812500	H	4.69617200	6.80402900	-3.52622800
H	5.05667000	0.77460700	-1.18049600	N	-1.89901400	2.49889700	-0.16953200
H	4.43108500	1.91711300	-2.04054700	C	-2.55590500	2.54530800	-1.38113200
O	1.97011800	-0.29145000	-3.82189300	H	-2.00260700	2.46023000	-2.30626300
H	2.75210500	-0.77746000	-4.13569700	C	-3.90560300	2.68845900	-1.16180800
H	1.24166300	-0.97562400	-3.86475300	N	-4.04509300	2.74399600	0.22075400
O	0.18060500	-2.36306700	-3.71485300	H	-4.93666700	2.61784400	0.70833000
O	-0.55699800	-4.76828900	-2.81933200	C	-2.82088500	2.60801600	0.77663200
H	-0.52578200	-4.48728100	-3.75789500	H	-2.62958000	2.56915900	1.83844100
H	0.33192900	-5.13921700	-2.63821400	C	-5.05062600	2.79069400	-2.13554300
O	3.18952200	-2.10307600	-1.83062000	H	-5.06261900	3.78682100	-2.60302900
C	2.82763600	-3.28437100	-1.72736000	H	-4.86270600	2.08151300	-2.95366000
O	1.60084600	-3.70782800	-1.80384700	C	-6.46459700	2.54222600	-1.54830200
C	3.87445000	-4.36530900	-1.46161300	H	-6.77020000	3.38942000	-0.92399700
H	4.74478300	-4.12001000	-2.08426600	H	-7.17819100	2.47829400	-2.38114400
H	4.20137200	-4.21358200	-0.42153100	C	-6.54315300	1.30242400	-0.65925800
C	3.42480400	-5.81165200	-1.67265700	O	-6.45906900	1.39246100	0.57305600
H	3.11488800	-5.98588800	-2.71200600	N	-6.64759900	0.10555900	-1.29207100
H	2.58167300	-6.06370300	-1.01898200	H	-6.68399300	0.09475500	-2.30387800
H	4.24641900	-6.50468300	-1.45078500	C	-6.49675800	-1.16830800	-0.58057400
O	0.80347900	3.59164600	-0.60174500	H	-7.07368900	-1.09575300	0.34741900
C	1.87920900	3.67328900	-1.33212400	H	-6.95553900	-1.94584800	-1.20449200

C	-5.03401900	-1.51264900	-0.25110000	O	3.13466000	0.04466800	2.48586900
H	-4.62387600	-0.73976200	0.40775600	C	5.49339400	-0.00899700	2.45597600
H	-5.02381400	-2.45096700	0.32159300	H	5.64645900	0.95908000	2.95121500
C	-4.15387200	-1.65337200	-1.49644900	H	6.32094600	-0.20117100	1.76726000
H	-4.19838500	-0.73020100	-2.09602400	H	5.46657500	-0.77481800	3.23946100
H	-4.49421500	-2.46701500	-2.14996000	O	0.61840800	-0.85668500	3.45072600
C	-2.67161400	-1.88453200	-1.21615100	C	-0.31406000	-1.71163300	3.33904200
O	-2.20716100	-1.45045100	-0.11737000	O	-0.86517500	-2.06486100	2.24910300
O	-2.02397400	-2.46529400	-2.14171600	C	-0.82523000	-2.36302000	4.61376000
O	-0.15209900	3.02567500	1.85503000	H	-0.19253300	-2.03204500	5.44550300
C	0.43693400	2.76937300	2.95550400	H	-1.83980700	-1.97275800	4.79238000
O	1.07982100	1.71207300	3.21608200	C	-0.87690100	-3.89793500	4.52661100
C	0.35971900	3.84486200	4.03097300	H	0.13560700	-4.28147700	4.33147700
H	-0.66440100	4.24184400	4.02363100	H	-1.48944600	-4.18269000	3.66183400
H	0.99795000	4.67055400	3.67955700	C	-1.43246600	-4.53298900	5.80535700
C	0.78118500	3.38893800	5.42819400	H	-0.81853300	-4.27708300	6.68015400
H	0.71788600	4.22569900	6.13529900	H	-1.45674700	-5.62735900	5.72359800
H	0.13547100	2.58121100	5.79384400	H	-2.45721000	-4.19013300	6.00715700
H	1.80945800	3.01169500	5.42543700	O	0.10499300	1.31137100	-1.53306200
O	4.15125600	0.02064500	0.45885400	H	-0.31776900	0.41878900	-1.54927700
C	4.17200700	0.01634900	1.70516100				

TS:

Ca	2.41217500	-0.07897300	-1.52927700	O	1.32855900	-3.75735200	-1.59948000
Mn	0.49842000	1.98423900	0.18674400	C	3.55211400	-4.63528400	-1.59694400
Mn	1.20417500	-0.04841500	1.94394800	H	4.30751700	-4.53895100	-2.38803200
Mn	-0.82394900	-1.24072300	0.45483300	H	4.08249600	-4.43284600	-0.65403100
Mn	-0.29885900	-2.74413500	-1.88872400	C	2.93969400	-6.03612900	-1.57488800
O	1.91892700	0.97507100	0.62101700	H	2.43225200	-6.26469400	-2.52238100
O	-0.37764000	0.52031600	1.05607100	H	2.20961400	-6.13590700	-0.76335700
O	0.65266900	-2.06304600	1.06088800	H	3.71925300	-6.79452000	-1.42729200
O	-0.03755800	-1.09559200	-1.22172200	O	1.51253000	3.46576300	-0.46638600
O	-0.49439200	-3.03977200	0.27782500	C	2.59578000	3.39565600	-1.18399700
O	4.86446000	0.23601500	-1.95031000	O	3.13849200	2.34982400	-1.58469000
H	5.09585800	-0.18413300	-1.09503600	C	3.17409200	4.76631800	-1.52731200
H	4.86697000	1.19993600	-1.78963200	H	2.43630500	5.27096900	-2.17113900
O	1.77243700	-0.49424400	-3.89660200	H	3.20667200	5.35863500	-0.60149500
H	2.49748100	-1.04051100	-4.24753300	C	4.54362200	4.72757900	-2.21002300
H	1.01499600	-1.14886000	-3.83797200	H	4.47718700	4.10880600	-3.11483500
O	-0.05429200	-2.47960700	-3.51202500	H	5.26400200	4.22515200	-1.54798500
O	-0.91892800	-4.78303300	-2.36596400	C	5.05795100	6.12685600	-2.56613700
H	-0.94420400	-4.60924500	-3.32887900	H	4.37219100	6.64035900	-3.25470200
H	-0.02860800	-5.15815700	-2.19980500	H	5.16024500	6.75647300	-1.67104100
O	3.02329700	-2.34623900	-2.04797600	H	6.04096100	6.07601000	-3.05197100
C	2.57730200	-3.47366300	-1.77849000	N	-1.37966400	2.87487800	-0.11647600

C	-1.95024400	3.14046400	-1.34320600	O	1.40142100	1.37699900	3.28679500
H	-1.34441600	3.16011300	-2.23823500	C	1.21356100	3.60347200	4.13863800
C	-3.30695200	3.29754200	-1.19171600	H	0.31898100	4.24025000	4.14273700
N	-3.54164700	3.14065800	0.16948200	H	2.03580700	4.25071800	3.79563400
H	-4.47211900	2.99353000	0.57429400	C	1.51264900	3.03412300	5.52591300
C	-2.36292700	2.87100800	0.77380500	H	1.65587800	3.84957100	6.24604100
H	-2.25295600	2.63654500	1.82248000	H	0.68943200	2.40293000	5.88204500
C	-4.37410400	3.56199900	-2.22245400	H	2.41806700	2.41793100	5.51288600
H	-4.25215500	4.57442700	-2.63528700	O	3.92091400	-0.88535800	0.40668500
H	-4.21250900	2.87559500	-3.06596800	C	3.89725800	-1.03521600	1.64470900
C	-5.83999000	3.43941600	-1.73951200	O	2.87251800	-0.83385300	2.41474700
H	-6.07069100	4.23788800	-1.02479900	C	5.13940600	-1.49119000	2.39239900
H	-6.49791700	3.58144600	-2.60791900	H	5.48725100	-0.68194300	3.04783300
C	-6.15666200	2.12326700	-1.02923400	H	5.93345000	-1.76303600	1.69120200
O	-6.11142200	2.03489800	0.20574600	H	4.89513600	-2.34538900	3.03471400
N	-6.44812400	1.05777400	-1.81871100	O	0.13137400	-0.91148200	3.40984300
H	-6.48172300	1.19051100	-2.82154700	C	-1.04014000	-1.38213200	3.29784700
C	-6.67627300	-0.28583300	-1.27231600	O	-1.70468600	-1.48356400	2.21078800
H	-7.37528100	-0.18969700	-0.43329700	C	-1.72936000	-1.87697900	4.55804100
H	-7.17093200	-0.87201300	-2.05692900	H	-1.07769600	-1.66682700	5.41400700
C	-5.39338700	-0.97496300	-0.78145000	H	-2.65698200	-1.29809700	4.68331400
H	-4.93065200	-0.34434100	-0.01610100	C	-2.07207900	-3.37697500	4.48130100
H	-5.67970300	-1.91445700	-0.28686600	H	-1.14576500	-3.94936700	4.32709100
C	-4.37306400	-1.26402900	-1.89059600	H	-2.69758900	-3.55101200	3.59625700
H	-4.23717900	-0.36511800	-2.51441200	C	-2.78532200	-3.87401100	5.74267700
H	-4.69869800	-2.06990500	-2.55900900	H	-2.16430700	-3.72896500	6.63765900
C	-2.98154700	-1.60389800	-1.37066400	H	-3.01767800	-4.94427700	5.66787300
O	-2.60302300	-0.98585800	-0.31958500	H	-3.73083300	-3.33682600	5.90344000
O	-2.29346600	-2.43466400	-2.02681800	O	0.38066600	1.40704100	-1.52870400
O	0.48972500	2.96743600	1.96058500	H	-0.20174200	0.60637800	-1.56811800
C	1.01721300	2.56418200	3.04289800				

Pro:

Ca	2.56361400	0.11935900	-1.42398500	H	4.78374600	1.70342600	-1.86471000
Mn	0.34074600	1.92330500	0.20489500	O	2.14354300	-0.35919700	-3.80371300
Mn	1.27731200	0.07819400	2.02643400	H	2.90385400	-0.85673600	-4.15009100
Mn	-0.59950800	-1.46571000	0.50003200	H	1.39962400	-1.03562800	-3.80247500
Mn	-0.04717600	-2.75063100	-1.99866400	O	0.29870800	-2.30242700	-3.56453500
O	1.89447000	1.19256000	0.72074500	O	-0.61879000	-4.70076100	-2.77675900
O	-0.32361900	0.33567700	1.04507500	H	-0.55939300	-4.39158500	-3.70440700
O	0.50960400	-2.89265000	0.90318900	H	0.25031100	-5.11476800	-2.59424100
O	0.29136100	-1.24085000	-1.08624000	O	3.16982800	-2.20281600	-1.67709600
O	-0.56738600	-3.31121900	0.09189900	C	2.78075900	-3.37691400	-1.57852800
O	4.94150400	0.74195200	-1.95229900	O	1.55045200	-3.77217600	-1.68472200
H	5.24754900	0.44108100	-1.07083200	C	3.79673500	-4.47838000	-1.28279100

H	4.69366500	-4.24807300	-1.87258300	H	-4.80266900	-0.52902000	-0.05624700
H	4.08803600	-4.33963500	-0.23033000	H	-5.34756900	-2.18022200	-0.33162800
C	3.32487500	-5.91414200	-1.51705500	C	-4.14239800	-1.36279300	-1.93784400
H	3.04883100	-6.07718200	-2.56772000	H	-4.06506800	-0.42214800	-2.50701200
H	2.45336800	-6.14966700	-0.89555800	H	-4.41472800	-2.14723200	-2.65454100
H	4.12312100	-6.62545800	-1.26910000	C	-2.73158600	-1.65106100	-1.43683200
O	1.15937100	3.51571800	-0.47124200	O	-2.38389900	-1.10968100	-0.33942900
C	2.26381900	3.58201900	-1.15460600	O	-2.00323700	-2.37617200	-2.17774100
O	2.95246400	2.61464600	-1.52907900	O	0.09490500	2.94834900	1.94540400
C	2.66958300	5.01505300	-1.49250800	C	0.54611400	2.62619400	3.08827100
H	1.86476000	5.43870700	-2.11339300	O	1.05070100	1.50110800	3.39224800
H	2.65232000	5.59499900	-0.55808600	C	0.48221500	3.69337900	4.17338400
C	4.02083400	5.14647400	-2.19939800	H	-0.48077800	4.20996300	4.06604800
H	4.01066800	4.53562600	-3.11220600	H	1.24789300	4.43902100	3.90804200
H	4.80762900	4.72440500	-1.55746000	C	0.69647400	3.18074400	5.59792800
C	4.35984600	6.60093200	-2.54448800	H	0.66005000	4.01463200	6.31021900
H	3.60537800	7.03840100	-3.21339100	H	-0.07724600	2.45625100	5.88038400
H	4.40421100	7.22705900	-1.64224500	H	1.66658400	2.68167600	5.69536800
H	5.33258700	6.67264900	-3.04804500	O	4.19470400	-0.34926500	0.46068600
N	-1.60410800	2.60774300	-0.19225200	C	4.12388200	-0.54738200	1.68906300
C	-2.15407700	2.81306700	-1.43920300	O	3.02240200	-0.63122900	2.37132100
H	-1.53032700	2.79673500	-2.32215400	C	5.38320700	-0.73479400	2.51643000
C	-3.51259900	2.98421500	-1.31646400	H	5.47190100	0.09188400	3.23355300
N	-3.76845400	2.89235300	0.04702000	H	6.26921500	-0.76436400	1.87614600
H	-4.70372100	2.76373000	0.44494100	H	5.30962600	-1.66045900	3.09953300
C	-2.59981600	2.64815900	0.68131100	O	0.43977500	-1.15233100	3.34418500
H	-2.50521400	2.47755400	1.74346500	C	-0.72951900	-1.65165700	3.30739100
C	-4.56419500	3.22870100	-2.36788400	O	-1.45409400	-1.74296100	2.26324100
H	-4.45981100	4.24559200	-2.77500800	C	-1.30629500	-2.15320100	4.62023700
H	-4.36796300	2.55058800	-3.21052000	H	-0.46690500	-2.53315000	5.21756500
C	-6.03576000	3.06753500	-1.91002400	H	-1.68021600	-1.26617400	5.15852400
H	-6.31258700	3.88072600	-1.22946600	C	-2.41850400	-3.19896500	4.48379100
H	-6.68207500	3.14966400	-2.79470200	H	-2.03341400	-4.06260900	3.92317800
C	-6.30387400	1.76548900	-1.15662300	H	-3.23339200	-2.78191600	3.87811400
O	-6.31346000	1.73220000	0.08164400	C	-2.95240000	-3.65632200	5.84560600
N	-6.47433300	0.64963500	-1.91073100	H	-2.15735700	-4.10395800	6.45835100
H	-6.43746800	0.73517500	-2.91878100	H	-3.74430300	-4.40720700	5.72762200
C	-6.54442000	-0.69087200	-1.31768300	H	-3.37326800	-2.81436000	6.41369100
H	-7.24326800	-0.64408400	-0.47512500	O	0.35532600	1.28763800	-1.49733900
H	-6.97417300	-1.35749300	-2.07592900	H	-0.11921100	0.41979700	-1.50615000
C	-5.18427000	-1.21037200	-0.82350600				

Table S16 Reaction parameters for the open-cubane O2 (oxo)-O4 (oxo/oxyl) coupling with deprotonated Wx:

Spin state	Spin topology (Mn1~Mn4-O4/O10)	Gibbs Free energy (a.u.)		
		Rea	TS	Pro-O-O
doublet	ααββα	-3366.1933	-3366.1487	-3366.1788
	αβαβα	-3366.2133	-3366.1313	-3366.1815
	αββαα	-3366.1799	-3366.1383	-3366.1730
	βααβα	-3366.2249	-3366.1550	-3366.1813
	βαβαα	-3366.2263	-3366.1447	-3366.1783
	ββααα	-3366.2254	-3366.1360	-3366.1894
sextet	αααββ	-3366.2275	-3366.1588	-3366.1808
	ααβαβ	-3366.2279	-3366.1397	-3366.1495
	αβααβ	-3366.2247	-3366.1584	-3366.1866
	βαααβ	-3366.2111	-3366.1260	-3366.1415
octet	αααβα	-3366.2122	-3366.1507	-3366.1768
	ααβαα	-3366.2149	-3366.1478	-3366.1795
	αβααα	-3366.2141	-3366.1284	-3366.1785
	βαααα	-3366.2235	-3366.1427	-3366.1838
12-et	ααααβ	-3366.2260	-3366.1379	-3366.1481
14-et	ααααα	-3366.2278	-3366.1567	-3366.1839

Spin state	Spin topology (Mn1~Mn4-O4/O10)	Relative Gibbs Free energy (kcal/mol)			
		$\Delta G^{\neq}$(Rea-TS)	ΔG(Rea-Pro)	ΔG(Rea)	ΔG(Pro)
doublet	ααββα	28.0	9.1	21.7	6.7
	αβαβα	51.5	20.0	9.2	5.0
	αββαα	26.1	4.3	30.1	10.3
	βααβα	43.9	27.4	1.9	5.1
	βαβαα	51.2	30.1	1.0	7.0
	ββααα	56.1	22.6	1.6	0.0
sextet	αααββ	43.1	29.3	0.3	5.4
	ααβαβ	55.3	49.2	0.0	25.0
	αβααβ	41.6	23.9	2.0	1.8
	βαααβ	53.4	43.7	10.5	30.1
octet	αααβα	38.6	22.2	9.9	7.9
	ααβαα	42.1	22.2	8.2	6.2
	αβααα	53.8	22.3	8.7	6.8
	βαααα	50.7	24.9	2.8	3.5
12-et	ααααβ	55.3	48.9	1.2	25.9
14-et	ααααα	44.6	27.5	0.1	3.5

Spin state	topology	Spin (Mn1~Mn4-O4/O10)	Mulliken spin density		
			Rea	TS	Pro-O-O
doublet	α	Mn1	2.67	2.68	2.71

	α	Mn2	2.92	3.50	3.82
	β	Mn3	-2.65	-2.90	-2.99
	β	Mn4	-2.85	-2.92	-2.93
		O2	-0.09	-0.09	0.09
	α	O4	0.68	0.46	0.13
		O10	0.37	0.37	0.34
	α	Mn1	2.81	2.80	2.79
	β	Mn2	-2.91	-3.84	-3.83
	α	Mn3	2.86	3.23	3.85
	β	Mn4	-2.83	-2.66	-2.73
		O2	0.00	0.39	-0.06
	α	O4	0.03	0.10	-0.06
		O10	0.90	0.88	0.87
	α	Mn1	2.79	2.80	2.75
	β	Mn2	-2.93	-3.43	-3.83
	β	Mn3	-2.70	-2.82	-3.03
	α	Mn4	3.81	3.84	3.85
		O2	-0.05	0.01	0.10
	α	O4	-0.78	-0.51	0.10
		O5	-0.35	0.11	0.04
		O10	0.85	0.84	0.85
	β	Mn1	-2.78	-2.78	-2.77
	α	Mn2	2.93	3.52	3.84
	α	Mn3	2.89	2.86	2.96
	β	Mn4	-2.83	-3.80	-3.81
		O2	0.05	-0.05	-0.05
	α	O4	0.01	0.43	0.00
		O10	0.70	0.52	0.46
	β	Mn1	-2.79	-2.68	-2.66
	α	Mn2	2.91	3.81	3.81
	β	Mn3	-2.87	-2.92	-2.92
	α	Mn4	2.86	2.78	2.89
		O2	0.00	-0.31	0.06
	α	O4	-0.02	-0.11	0.01
		O10	0.69	0.15	-0.34
	β	Mn1	-2.80	-2.80	-2.82
	β	Mn2	-2.93	-3.86	-3.84
	α	Mn3	2.88	3.39	3.91
	α	Mn4	2.90	2.96	2.92
		O2	0.00	0.39	-0.03
	α	O4	0.13	0.14	0.02
		O10	0.69	0.70	0.69
sextet	α	Mn1	2.82	2.86	2.86
	α	Mn2	2.95	3.56	3.86

	α	Mn3	2.91	2.80	2.91
	β	Mn4	-2.86	-3.89	-3.91
		O2	0.05	-0.05	-0.06
	β	O4	0.01	0.42	0.00
		O5	-0.13	-0.12	-0.13
		O10	-0.68	-0.54	-0.58
	α	Mn1	2.81	2.82	2.82
	α	Mn2	2.94	3.85	3.84
	β	Mn3	-2.87	-2.97	-3.05
	α	Mn4	2.84	2.48	1.92
		O2	0.01	-0.43	0.06
	β	O4	-0.01	-0.08	0.07
		O10	-0.66	-0.63	-0.55
	α	Mn1	2.80	2.80	2.80
	β	Mn2	-2.91	-3.53	-3.82
	α	Mn3	2.88	2.92	3.03
	α	Mn4	2.87	3.81	3.83
		O2	0.01	0.05	-0.10
	β	O4	0.14	-0.47	-0.15
		O10	-0.68	-0.35	-0.35
	β	Mn1	-2.80	-2.78	-2.64
	α	Mn2	2.93	3.84	2.95
	α	Mn3	2.92	2.94	2.04
	α	Mn4	2.87	2.47	2.95
		O2	0.06	-0.34	-0.04
	β	O4	0.13	-0.13	-0.09
		O10	-0.89	-0.86	-0.38
	α	Mn1	2.82	2.69	2.71
	α	Mn2	2.94	3.56	3.85
	α	Mn3	2.90	2.86	2.96
	β	Mn4	-2.82	-2.87	-2.88
		O2	0.05	-0.01	-0.05
	α	O4	0.05	0.38	0.00
		O10	0.90	0.36	0.34
	α	Mn1	2.81	2.68	2.71
octet	α	Mn2	2.93	3.49	3.83
	β	Mn3	-2.86	-2.88	-2.89
	α	Mn4	2.86	2.90	2.91
		O2	0.01	-0.05	0.06
	α	O4	-0.02	0.43	0.02
		O10	0.89	0.35	0.34
	α	Mn1	2.81	2.79	2.79
	β	Mn2	-2.91	-3.84	-3.83
	α	Mn3	2.88	3.37	3.92

	α	Mn4	2.91	2.95	2.91
		O2	0.01	0.43	-0.02
	α	O4	0.13	0.15	0.03
		O10	0.90	0.89	0.88
	β	Mn1	-2.79	-2.71	-2.77
	α	Mn2	2.93	3.84	2.84
	α	Mn3	2.91	2.89	3.91
	α	Mn4	2.91	2.79	2.90
		O2	0.06	-0.26	-0.03
	α	O4	0.14	-0.14	0.03
		O10	0.70	0.26	-0.81
	α	Mn1	2.82	2.85	2.85
	α	Mn2	2.95	3.86	3.85
	α	Mn3	2.92	2.96	3.12
12-et	α	Mn4	2.87	2.45	1.91
		O2	0.07	-0.35	-0.09
	β	O4	0.13	-0.13	-0.09
		O10	-0.67	-0.59	-0.50
	α	Mn1	2.82	2.83	2.84
	α	Mn2	2.95	3.53	3.86
	α	Mn3	2.91	2.86	3.02
14-et	α	Mn4	2.86	3.84	3.82
		O2	0.05	0.00	-0.09
	α	O4	0.01	0.35	-0.13
		O10	0.69	-0.33	-0.32

Rea:

Ca	-2.25862100	-0.15255500	-1.64928300	O	0.35831300	5.30998700	-1.57396700
Mn	0.12743200	-1.85889900	-0.23014800	H	-0.58410700	5.54472600	-1.70596100
Mn	-1.46212400	-0.54517800	1.71655800	H	0.52412400	5.45693800	-0.62187800
Mn	-0.02830700	1.53354700	0.68726000	O	-3.10986400	2.07224500	-2.02749400
Mn	-0.01954300	3.14349800	-1.55436700	C	-2.94385700	3.27707600	-1.82409000
O	-1.62475100	-1.55005200	0.26942800	O	-1.80021400	3.85119600	-1.55022600
O	0.31359200	-0.24631400	1.08818800	C	-4.14406900	4.22108100	-1.86181300
O	-1.69546500	1.11658900	0.90899200	H	-4.73078600	3.93230900	-2.74371600
O	-0.26971200	1.46662800	-1.17304200	H	-4.76373300	3.95313500	-0.99282000
O	0.05527900	3.32824400	0.32542600	C	-3.83858700	5.71921300	-1.86499200
O	-4.36236300	-1.13962000	-2.60943700	H	-3.22640300	5.99903400	-2.73228000
H	-4.82220600	-1.10788300	-1.74507500	H	-3.30413600	6.01969600	-0.95540400
H	-3.98354300	-2.04067100	-2.67487100	H	-4.76997500	6.29753700	-1.91316400
O	-1.01176700	0.34318000	-3.78144900	O	-0.35560000	-3.48592800	-1.08610300
H	-0.25126000	-0.12735500	-3.37569100	C	-1.36058100	-3.60188400	-1.90323700
H	-0.74890700	1.29452800	-3.75981700	O	-2.14242500	-2.69467800	-2.24309300
O	-0.04419700	3.02680700	-3.37295200	C	-1.51248600	-5.01994200	-2.45379500
H	0.88234400	3.03935100	-3.67942500	H	-0.60800500	-5.23433800	-3.04463100

H	-1.47668700	-5.71486800	-1.60233500	C	2.55861000	2.29355400	-0.67853800
C	-2.76973300	-5.24511200	-3.29723800	O	2.05536000	1.72961700	0.32173800
H	-2.78428600	-4.52074600	-4.12268900	O	1.92081200	2.96298500	-1.57558300
H	-3.65852900	-5.03000700	-2.68633700	O	0.43129800	-3.05534400	1.50205800
C	-2.85534100	-6.67236800	-3.84955300	C	-0.27351300	-3.01405900	2.54330800
H	-1.99385400	-6.90377500	-4.49189400	O	-1.10634800	-2.08892000	2.83925900
H	-2.87200200	-7.41530100	-3.03959700	C	-0.16153800	-4.16727100	3.53467200
H	-3.76434000	-6.81233800	-4.44901100	H	0.86949500	-4.54046400	3.48761800
N	2.16815500	-2.15317800	-0.46270500	H	-0.79278700	-4.97423300	3.12970600
C	2.88675600	-1.88216400	-1.60695100	C	-0.58079500	-3.83398900	4.96796100
H	2.37146200	-1.57699900	-2.50689100	H	-0.49618200	-4.72239700	5.60686300
C	4.22712700	-2.05728300	-1.35941500	H	0.05390300	-3.04649200	5.39378100
N	4.30011400	-2.45536800	-0.02769400	H	-1.61558300	-3.47713100	5.00004900
H	5.15577500	-2.42172500	0.52878200	O	-4.17573000	-0.39131400	0.03066000
C	3.04388900	-2.48183500	0.47544900	C	-4.29598300	-0.59160500	1.25578500
H	2.79296200	-2.72558000	1.49682700	O	-3.33156900	-0.63042200	2.12271200
C	5.41958600	-1.92605200	-2.26875600	C	-5.66771200	-0.83453300	1.86530100
H	5.52724700	-2.82809000	-2.89038000	H	-6.45433200	-0.61861600	1.13672500
H	5.21873600	-1.10480100	-2.97054400	H	-5.79823400	-0.21427200	2.75934500
C	6.78113600	-1.68857400	-1.56305800	H	-5.74076600	-1.88334500	2.18252000
H	7.13182400	-2.61418600	-1.09305800	O	-1.09237200	0.46839700	3.46656100
H	7.52447000	-1.40792600	-2.32188100	C	-0.30982800	1.45244900	3.54465600
C	6.70092700	-0.64488600	-0.45190700	O	0.29452000	2.00871500	2.56066900
O	6.58102700	-0.97700200	0.73319700	C	-0.05480800	2.08098800	4.90785400
N	6.70269900	0.65707700	-0.84611300	H	0.99712800	2.39642600	4.93585300
H	6.77302500	0.86144400	-1.83520800	H	-0.64721300	3.01029900	4.93679100
C	6.38624500	1.75131500	0.07521500	C	-0.40610600	1.18948100	6.10313500
H	6.91125100	1.55038600	1.01498900	H	0.18691100	0.26506900	6.05067000
H	6.80214100	2.67182600	-0.35438600	H	-1.45592100	0.88020600	6.02425100
C	4.88055100	1.90227200	0.35311600	C	-0.15840000	1.89246900	7.44229600
H	4.51073000	0.99203500	0.83748000	H	0.89503300	2.18605700	7.55399300
H	4.74587800	2.71950200	1.07592500	H	-0.41259300	1.23711200	8.28538400
C	4.06117700	2.18419000	-0.91028100	H	-0.76684600	2.80344700	7.53366900
H	4.18876000	1.36325500	-1.63322800	O	0.10405200	-0.98023700	-1.65127800
H	4.38820300	3.10309400	-1.41523600				

TS:

Ca	2.33568100	-0.27087700	-1.62682900	O	-0.04026100	-1.48217600	-1.01347300
Mn	0.32430900	1.91719900	-0.37261000	O	-0.25952000	-3.08563000	0.84041500
Mn	1.30151700	0.41611900	1.82903500	O	4.75309600	0.12138000	-2.17865900
Mn	-0.68989400	-1.17930100	0.75316900	H	5.04376100	-0.10215200	-1.27057100
Mn	-0.19959100	-3.22162500	-1.08117000	H	4.66374300	1.09535700	-2.20763000
O	1.87748900	1.14713900	0.31393900	O	0.98667000	-0.87166200	-3.66320300
O	-0.42401100	0.58783500	0.94832700	H	0.27238900	-0.30513000	-3.30187100
O	0.87295500	-1.80334000	1.30561700	H	0.66759900	-1.79482800	-3.52358800

O	-0.14913800	-3.44666800	-2.89269600	N	-6.54610000	0.13207900	-1.74720000
H	-1.07295800	-3.43582500	-3.20723900	H	-6.63566000	0.00354500	-2.74696500
O	-0.66613800	-5.35216100	-0.64550500	C	-6.67246300	-1.03358800	-0.86658200
H	0.27365600	-5.61808900	-0.72955500	H	-7.34985000	-0.76339600	-0.04788500
H	-0.81806000	-5.29600500	0.31878200	H	-7.15121900	-1.83006400	-1.45018400
O	2.92364800	-2.56404500	-1.96977500	C	-5.33478300	-1.50087600	-0.27165700
C	2.67833100	-3.66235600	-1.46495700	H	-4.89191600	-0.66751200	0.28231000
O	1.53154100	-4.00393500	-0.94345600	H	-5.54412000	-2.29483000	0.45982600
C	3.77146800	-4.72371700	-1.38600600	C	-4.32999900	-2.00994400	-1.31477500
H	4.28530800	-4.70515500	-2.35594400	H	-4.26741900	-1.29027500	-2.14772900
H	4.50168100	-4.34514000	-0.65493800	H	-4.62403800	-2.97566000	-1.74338300
C	3.32492700	-6.13935000	-1.01949600	C	-2.91030000	-2.12410800	-0.77832900
H	2.60342400	-6.53069800	-1.74909800	O	-2.53797500	-1.25422900	0.05909700
H	2.86155700	-6.16628700	-0.02559100	O	-2.18658700	-3.07345700	-1.23563100
H	4.18572000	-6.81982300	-1.00640800	O	0.18536300	3.28567200	1.25145600
O	1.25603700	3.34331100	-1.23206100	C	0.80376600	3.20542800	2.34644100
C	2.32338500	3.20411000	-1.95301600	O	1.36828900	2.15266800	2.80098400
O	2.91467000	2.13154600	-2.19296900	C	0.91365900	4.46895700	3.19527500
C	2.83055000	4.52246700	-2.53617900	H	-0.01626600	5.03573600	3.05773400
H	2.10002100	4.83316200	-3.30056300	H	1.70600600	5.07684700	2.73041900
H	2.77279600	5.28546200	-1.74742500	C	1.22161800	4.23306500	4.67497300
C	4.23511400	4.45430700	-3.14142200	H	1.30849200	5.19016900	5.20535400
H	4.25755600	3.67097200	-3.91057900	H	0.42847900	3.64740000	5.15687100
H	4.94896300	4.14179100	-2.36486400	H	2.15913100	3.68008900	4.79694400
C	4.67919400	5.79306100	-3.74129900	O	3.93507800	-0.74695400	0.33153400
H	4.00060400	6.11443100	-4.54411700	C	4.00481200	-0.58325400	1.56628800
H	4.69227200	6.58792600	-2.98224800	O	3.02818900	-0.23883100	2.34658800
H	5.68852400	5.72217500	-4.16729300	C	5.32257600	-0.78637800	2.29791100
N	-1.59539900	2.59494400	-0.80193600	H	6.08178500	-1.18927600	1.62151900
C	-2.22753100	2.43971900	-2.01558000	H	5.17695000	-1.46415000	3.14721600
H	-1.65777200	2.17330300	-2.89447700	H	5.66314500	0.17466700	2.70505200
C	-3.57854800	2.62879100	-1.85760100	O	0.39021600	-0.28555800	3.51490200
N	-3.74918200	2.91952400	-0.50739100	C	-0.73135400	-0.86163500	3.57133400
H	-4.65014000	2.87380500	-0.02658700	O	-1.42884100	-1.24189200	2.56384200
C	-2.53490300	2.87080400	0.09056200	C	-1.31879900	-1.17438500	4.93884000
H	-2.36362500	3.00329600	1.14871400	H	-2.41002700	-1.22954800	4.83449300
C	-4.69050100	2.58077000	-2.87186800	H	-0.98136600	-2.19327400	5.19220800
H	-4.65420600	3.47377700	-3.51427700	C	-0.90566200	-0.19694500	6.04588800
H	-4.50625800	1.72714900	-3.53945600	H	-1.23992600	0.81579800	5.77609200
C	-6.12898700	2.48893200	-2.30575300	H	0.18944600	-0.15441400	6.09346500
H	-6.39904200	3.42764100	-1.80828800	C	-1.48379500	-0.58787300	7.41010600
H	-6.82249100	2.35832200	-3.14802800	H	-2.58255200	-0.61181700	7.39010600
C	-6.31763500	1.38483400	-1.26753100	H	-1.18016200	0.12601600	8.18664400
O	-6.22851500	1.61956000	-0.05619300	H	-1.13657400	-1.58393300	7.71929900

O	0.25655000	0.98209300	-1.76033600				

Pro:

Ca	-2.32930300	0.09105100	-1.72170000	H	-3.85979200	-6.95396400	-3.23205300
Mn	-0.17896500	-1.86270500	-0.36265100	H	-4.77831300	-6.20787600	-4.55338200
Mn	-1.50281900	-0.62941000	1.80500200	N	1.82932500	-2.32590200	-0.68843800
Mn	0.50981100	1.38211600	0.88632600	C	2.50799400	-2.12528500	-1.86964000
Mn	0.12802800	3.27812200	-1.18303500	H	1.96888100	-1.83621500	-2.76077900
O	-1.86857900	-1.38365300	0.23127800	C	3.85164500	-2.32989800	-1.66887500
O	0.24396600	-0.36786400	0.98753200	N	3.96874300	-2.67163100	-0.32474400
O	-0.81106200	2.59075300	1.38199800	H	4.84922000	-2.65151800	0.19265500
O	-0.16104600	1.59296600	-0.87877300	C	2.73230800	-2.64031400	0.22762700
O	0.24868600	3.35138700	0.84032400	H	2.51571000	-2.82858700	1.26862400
O	-4.60333400	-0.51436400	-2.57879800	C	5.00257000	-2.27636100	-2.63840000
H	-5.01129100	-0.36030100	-1.70152500	H	5.00121400	-3.17240800	-3.27774700
H	-4.40641500	-1.47218500	-2.62475400	H	4.83726100	-1.42789400	-3.31734200
O	-0.97220700	0.75070500	-3.72098700	C	6.41466800	-2.16792500	-2.00975100
H	-0.25145100	0.20554100	-3.33654500	H	6.68548900	-3.11118100	-1.52192500
H	-0.68092900	1.68346700	-3.58243600	H	7.14188600	-1.99931800	-2.81604900
O	0.09551000	3.31105300	-3.00201100	C	6.51986000	-1.08414600	-0.93997700
H	1.02610000	3.28867200	-3.29733200	O	6.41344800	-1.35325400	0.26231500
O	0.60168200	5.42458500	-0.97123600	N	6.68096800	0.19160200	-1.38527400
H	-0.33469000	5.70393200	-1.04740900	H	6.76176700	0.35193100	-2.38132200
H	0.80890700	5.50471800	-0.01963200	C	6.63819200	1.34508900	-0.48274400
O	-2.91094500	2.42112300	-1.92381400	H	7.27134300	1.11652900	0.38211200
C	-2.74465300	3.55931600	-1.48356900	H	7.08884000	2.19196100	-1.01567500
O	-1.59694800	4.04536300	-1.07785800	C	5.22153400	1.68498300	0.00857600
C	-3.93017600	4.51021100	-1.35596700	H	4.82010600	0.82276800	0.55046800
H	-4.50955500	4.40296400	-2.28233800	H	5.29904200	2.50857700	0.73320200
H	-4.56285500	4.08891400	-0.56012600	C	4.25561300	2.07385200	-1.11825900
C	-3.60570100	5.97642700	-1.06800500	H	4.26179600	1.29152200	-1.89462300
H	-2.98436800	6.41076600	-1.86240000	H	4.54141100	3.01476600	-1.60468600
H	-3.07417000	6.08735300	-0.11518100	C	2.80686000	2.18338600	-0.66698500
H	-4.52937600	6.56578000	-1.00862100	O	2.40506700	1.38771500	0.22392000
O	-0.86408100	-3.38322200	-1.28766200	O	2.09132900	3.07272500	-1.25260000
C	-1.89897000	-3.36000000	-2.06859000	O	0.08841200	-3.20302700	1.27301700
O	-2.58672700	-2.35932900	-2.35533800	C	-0.57401000	-3.30012100	2.34820500
C	-2.22953500	-4.73084700	-2.65904600	O	-1.32090900	-2.39155800	2.83330800
H	-1.39286200	-5.00513300	-3.32115200	C	-0.47663500	-4.62231000	3.10565900
H	-2.20612700	-5.46293500	-1.83930400	H	0.55671800	-4.98204000	3.01276400
C	-3.55615500	-4.79559000	-3.41990300	H	-1.09156400	-5.34186300	2.54224600
H	-3.55210700	-4.03927900	-4.21623600	C	-0.92565100	-4.56499700	4.56644900
H	-4.37625300	-4.52028400	-2.74068200	H	-0.85438100	-5.55728300	5.03077300
C	-3.82204100	-6.18306000	-4.01464300	H	-0.30222100	-3.87238700	5.14629600
H	-3.03276400	-6.47090300	-4.72353900	H	-1.96138400	-4.21710600	4.64380100

O	-4.12680900	0.37425400	-0.00226500	H	1.80718400	1.26096600	5.11195800
C	-4.26207500	0.25593200	1.23635500	H	0.35273000	2.22407900	5.33799200
O	-3.30297800	0.07914500	2.08055300	C	0.16610200	0.19725800	6.09956100
C	-5.64704300	0.32339600	1.86050500	H	0.51886700	-0.80860600	5.82862900
H	-6.39671600	0.61376000	1.11882800	H	-0.92759200	0.16693600	6.02073400
H	-5.64655600	1.03492800	2.69460100	C	0.58846600	0.52784900	7.53496000
H	-5.90304300	-0.66041300	2.27589000	H	1.68251200	0.53746900	7.64108400
O	-0.82249400	0.38715200	3.43761600	H	0.19160700	-0.21140000	8.24259000
C	0.28477400	0.95547900	3.65038300	H	0.21742300	1.51588400	7.84237500
O	1.09003000	1.38286000	2.74520800	O	-0.13260400	-0.90921400	-1.73886300
C	0.71088000	1.21166400	5.08681000				

Table S17 Reaction parameters for the closed-cubane O2 (oxo)-O4 (oxo/oxyl) coupling with deprotonated W1:

Spin state	Spin topology (Mn1~Mn4-O4/O10)	Gibbs Free energy (a.u.)		
		Rea	TS	Pro-O-O
doublet	ααββα	-3366.2057	-3366.1670	-3366.1945
	αβαβα	-3366.1984	-3366.1467	-3366.1860
	αββαα	-3366.2062	-3366.1389	-3366.1564
	βααβα	-3366.2008	-3366.1782	-3366.2081
	βαβαα	-3366.2078	-3366.1686	-3366.2013
	ββαaα	-3366.1967	-3366.1477	-3366.1892
sextet	αααββ	-3366.2082	-3366.1398	-3366.1587
	ααβαβ	-3366.2043	-3366.1484	-3366.1753
	αβααβ	-3366.2212	-3366.1803	-3366.2119
	βαααβ	-3366.2117	-3366.1332	-3366.1778
octet	αααβα	-3366.2049	-3366.1708	-3366.1998
	ααβαα	-3366.2083	-3366.1702	-3366.2022
	αβααα	-3366.1966	-3366.1397	-3366.1579
	βαααα	-3366.1980	-3366.1706	-3366.2024
12-et	ααααβ	-3366.2230	-3366.1532	-3366.1698
14-et	ααααα	-3366.1998	-3366.1704	-3366.2004

Spin state	Spin topology (Mn1~Mn4-O4/O10)	Relative Gibbs Free energy (kcal/mol)			
		$\Delta G^{\neq}$(Rea-TS)	ΔG(Rea-Pro)	ΔG(Rea)	ΔG(Pro)
doublet	ααββα	23.9	6.9	10.9	10.9
	αβαβα	31.9	7.7	15.4	16.3
	αββαα	41.6	30.8	10.5	34.8
	βααβα	14.0	-4.5	13.9	2.4
	βαβαα	24.2	4.0	9.5	6.7
	ββαaα	30.3	4.6	16.5	14.2
sextet	αααββ	42.2	30.6	9.3	33.4

	ααβαβ	34.5	17.9	11.7	23.0
	αβααβ	25.3	5.7	1.1	0.0
	βαααβ	48.5	20.9	7.1	21.4
octet	αααβα	21.1	3.1	11.4	7.6
	ααβαα	23.5	3.8	9.2	6.1
	αβααα	35.1	23.9	16.6	33.9
	βαααα	16.9	-2.7	15.7	6.0
12-et	αααaβ	43.1	32.9	0.0	26.4
14-et	ααααα	18.2	-0.4	14.6	7.2

Spin state	topology	Spin (Mn1~Mn4-O4/O10)	Mulliken spin density		
			Rea	TS	Pro-O-O
doublet	α	Mn1	2.93	2.93	2.94
	α	Mn2	2.94	3.46	3.86
	β	Mn3	-2.78	-2.91	-3.04
	β	Mn4	-2.88	-2.88	-2.91
	α	O2	-0.01	-0.02	0.11
		O4	0.76	0.51	0.14
	α	Mn1	2.93	2.94	2.95
	β	Mn2	-2.92	-2.82	-2.96
	α	Mn3	2.82	3.36	3.84
	β	Mn4	-2.84	-2.87	-2.90
	α	O2	0.07	0.05	0.05
		O4	0.83	0.35	0.07
	α	Mn1	2.92	2.91	2.91
	β	Mn2	-2.93	-2.46	-1.92
	β	Mn3	-2.85	-2.94	-3.02
	α	Mn4	2.82	2.95	2.90
	α	O2	-0.03	0.07	0.07
		O4	0.62	0.37	0.03
	β	Mn1	-2.91	-2.90	-2.88
	α	Mn2	2.93	3.46	3.86
	α	Mn3	2.82	2.85	3.00
	β	Mn4	-2.85	-2.87	-2.90
	α	O2	0.07	-0.04	-0.07
		O4	0.83	0.46	-0.03
	β	Mn1	-2.93	-2.92	-2.91
	α	Mn2	2.93	3.46	3.84
	β	Mn3	-2.84	-2.94	-3.04
	α	Mn4	2.83	2.88	2.90
	α	O2	-0.02	-0.06	0.07
		O4	0.61	0.45	0.05
	β	Mn1	-2.92	-2.90	-2.89
	β	Mn2	-2.94	-2.83	-2.97

	α	Mn3	2.81	3.32	3.82
	α	Mn4	2.83	2.92	2.92
	α	O2	0.05	0.05	0.05
		O4	0.85	0.32	0.03
sextet	α	Mn1	2.93	2.89	2.95
	α	Mn2	2.93	2.48	1.96
	α	Mn3	2.85	2.90	3.02
	β	Mn4	-2.83	-2.93	-2.90
	β	O2	0.06	-0.08	-0.05
		O4	-0.62	-0.30	-0.02
	α	Mn1	2.85	2.78	2.79
	α	Mn2	2.88	2.91	2.87
	β	Mn3	-3.83	-3.84	-3.98
	α	Mn4	2.91	2.95	2.95
		O2	0.06	-0.01	0.09
	β	O4	0.03	0.01	0.05
	α	Mn1	2.93	2.93	2.91
	β	Mn2	-2.93	-3.46	-3.85
	α	Mn3	2.83	2.94	3.04
	α	Mn4	2.87	2.89	2.91
	β	O2	0.02	0.05	-0.07
		O4	-0.61	-0.49	-0.11
	β	Mn1	-2.92	-2.89	-2.88
	α	Mn2	2.93	3.85	3.87
	α	Mn3	2.90	2.97	3.02
	α	Mn4	2.92	2.17	1.05
	β	O2	0.03	-0.18	-0.08
		O4	0.18	-0.02	-0.04
octet	α	Mn1	2.93	2.95	2.97
	α	Mn2	2.93	3.51	3.87
	α	Mn3	2.81	2.87	3.02
	β	Mn4	-2.80	-2.87	-2.90
	α	O2	0.06	-0.02	-0.06
		O4	0.09	0.45	-0.02
	α	Mn1	2.93	2.94	2.95
	α	Mn2	2.94	3.49	3.86
	β	Mn3	-2.82	-2.93	-3.04
	α	Mn4	2.82	2.88	2.90
	α	O2	0.00	-0.04	0.08
		O4	0.62	0.45	0.05
	α	Mn1	2.93	2.93	2.93
	β	Mn2	-2.92	-2.49	-1.92
	α	Mn3	2.82	2.92	3.05
	α	Mn4	2.83	2.96	2.90

	α	O2	0.07	0.09	-0.08
		O4	0.85	0.35	-0.09
	β	Mn1	-2.91	-2.91	-2.88
	α	Mn2	2.93	3.45	3.86
	α	Mn3	2.84	2.85	3.03
	α	Mn4	2.83	2.89	2.91
	α	O2	0.07	-0.02	-0.09
		O4	0.85	0.44	-0.09
12-et	α	Mn1	2.93	2.91	2.96
	α	Mn2	2.92	2.46	1.96
	α	Mn3	2.91	2.91	3.03
	α	Mn4	2.93	2.89	2.90
	β	O2	0.06	-0.06	-0.06
		O4	-0.63	-0.37	-0.08
14-et	α	Mn1	2.93	2.95	2.97
	α	Mn2	2.93	3.49	3.87
	α	Mn3	2.84	2.86	3.03
	α	Mn4	2.83	2.89	2.90
	α	O2	0.10	-0.01	-0.07
		O4	0.85	0.42	-0.08

Rea:

Ca	-2.57960100	0.20713400	-1.09886100	C	-2.99454400	4.86150600	-1.18666000
Mn	-0.06670200	-1.85851800	-0.08791700	H	-3.94556300	5.01407100	-0.66542200
Mn	-1.46943500	-0.85226800	2.00310200	H	-2.17406500	5.26491200	-0.57992800
Mn	0.25197800	0.85825200	0.72162600	C	-2.99209900	5.55916500	-2.56009500
Mn	0.14950100	3.29796500	-1.73576500	H	-3.79349000	5.17463100	-3.20498100
O	-1.77975500	-1.68993900	0.42975500	H	-2.03472000	5.41167600	-3.07260100
O	0.35819700	-0.91034900	1.46496700	H	-3.15371200	6.63662700	-2.43061700
O	-1.50715200	0.74648000	1.14905200	O	-0.46889900	-2.82556300	-1.68133000
O	-0.02772800	-0.16285400	-0.81587900	C	-1.59642500	-2.87248400	-2.33803500
O	0.07300000	2.46957500	0.02722700	O	-2.52583500	-2.05990300	-2.21497900
O	-4.76789000	-0.46981200	-2.14283100	C	-1.68061800	-4.03800300	-3.31619200
H	-5.21857000	-0.61981800	-1.28826900	H	-0.80380000	-3.97054100	-3.97817800
H	-4.43454700	-1.34454600	-2.42789600	H	-1.53636800	-4.96235000	-2.73596800
O	-1.80631100	0.60671400	-3.45554500	C	-2.97443100	-4.09507400	-4.13173200
H	-0.91030400	1.04535600	-3.31727300	H	-3.09965600	-3.14777600	-4.67384900
H	-2.33894700	1.30498900	-3.87215000	H	-3.83025600	-4.17118200	-3.44604300
O	0.49592900	4.14964800	-3.28514200	C	-2.99258400	-5.26968200	-5.11621800
H	0.73885000	3.42183700	-3.89154500	H	-2.16440400	-5.20064800	-5.83553600
O	0.02922600	4.92115200	-0.94640400	H	-3.92897400	-5.29261200	-5.68848100
H	0.22681300	5.57473000	-1.64416700	H	-2.89735500	-6.23202700	-4.59369500
O	-3.61760300	2.53514400	-0.95846700	N	1.93369100	-2.18950600	-0.48831900
C	-2.77561600	3.37575900	-1.30551100	C	2.62103800	-1.94361600	-1.65605300
O	-1.67199000	2.91004800	-1.87578600	H	2.10080900	-1.65020000	-2.55772800

C	3.96679900	-2.12793800	-1.43786000	C	-0.48680600	-4.95755700	2.89661000
N	4.06798800	-2.51229600	-0.10591000	H	0.50442600	-5.38281800	2.69165400
H	4.94805300	-2.53623600	0.41860900	H	-1.20209000	-5.59846600	2.35729900
C	2.82947000	-2.51601500	0.43168100	H	-5.71354400	-1.81512200	2.96416700
H	2.61029500	-2.72711500	1.46791800	C	-0.80032200	-4.94205600	4.39339700
C	5.14253500	-1.97296000	-2.36914000	H	-0.75396800	-5.95991800	4.80071700
H	5.14567100	-2.78562400	-3.11065900	H	-0.08256300	-4.32060000	4.94297500
H	5.00035900	-1.04750800	-2.94483600	H	-1.79981400	-4.53606100	4.58195900
C	6.54330200	-1.95520900	-1.70218500	O	-4.32375800	-0.35441400	0.60701300
H	6.80419400	-2.95539500	-1.33857500	C	-4.32848900	-0.63580000	1.81830100
H	7.28411400	-1.68260800	-2.46625600	O	-3.27146700	-0.82779000	2.55515400
C	6.62938200	-1.02152000	-0.49602800	C	-5.63079800	-0.78987600	2.58161500
O	6.51699200	-1.45559100	0.65886300	H	-6.48182500	-0.56359300	1.93379200
N	6.76292500	0.30435400	-0.75609500	H	-5.63156600	-0.11847400	3.44862000
H	6.82030000	0.60550200	-1.72121900	O	-0.83890200	0.09373200	3.63966200
C	6.56707800	1.31780200	0.28646700	C	0.01162600	1.04212000	3.60856200
H	7.12176300	0.99165100	1.17244000	O	0.60457300	1.49854700	2.57469600
H	7.02012200	2.24984800	-0.07350700	C	0.33749000	1.72752500	4.92336100
C	5.08566800	1.52284100	0.65197000	H	-0.06298800	1.11958700	5.74285500
H	4.67756600	0.57979300	1.03098000	H	1.43127900	1.77283700	5.02207300
H	5.03090000	2.24916400	1.47543000	C	-0.24149100	3.15666400	4.97090000
C	4.24344300	2.01208200	-0.53187200	H	-1.33226000	3.10565200	4.83953100
H	4.38123000	1.33754100	-1.39165200	H	0.15234900	3.72618100	4.11880200
H	4.54073500	3.01641500	-0.85536200	C	0.08978900	3.87104900	6.28488200
C	2.73544700	2.02102700	-0.27996000	H	-0.31650800	3.32804200	7.14952100
O	2.23911800	1.03508900	0.34950800	H	-0.33219300	4.88419800	6.29779800
O	2.11261300	3.01429400	-0.75998500	H	1.17608200	3.95926400	6.42672500
O	0.01684800	-3.52085200	1.07111000	O	0.53183000	1.70928400	-2.70262600
C	-0.54843500	-3.59533600	2.21559700	H	0.62169600	0.94860300	-2.08344700
O	-1.16100700	-2.66322200	2.82377600				

TS:

Ca	-2.51783700	0.31737000	-1.16459000	O	-1.84416000	0.63008100	-3.54644500
Mn	-0.09892000	-1.95049400	-0.06387500	H	-0.95640300	1.07965200	-3.36889100
Mn	-1.40051900	-0.79408100	2.06846300	H	-2.38581400	1.32657100	-3.95423400
Mn	0.59356100	0.65449500	0.67332400	O	0.38843500	4.18915200	-3.01792700
Mn	0.07295300	3.20221700	-1.54182900	H	0.68518200	3.51406300	-3.66098200
O	-1.77148400	-1.50540100	0.45512500	O	-0.09261700	4.73008200	-0.59219700
O	0.45996400	-1.04028000	1.46037300	H	0.32464700	5.42605300	-1.13575300
O	-1.16435500	1.08725900	0.87706700	O	-3.78031100	2.57803400	-0.94709100
O	0.18505800	-0.31865100	-0.84335100	C	-2.89472700	3.37199300	-1.29524000
O	-0.16235000	2.30251600	0.30642800	O	-1.77217800	2.84540400	-1.76323000
O	-4.75213600	-0.32201700	-2.14101400	C	-3.07038100	4.86904800	-1.28487700
H	-5.19384400	-0.39498500	-1.27207500	H	-4.04851200	5.08406200	-0.84100100
H	-4.46750300	-1.22732400	-2.37721600	H	-2.28008500	5.28181700	-0.64489300

C	-2.94857400	5.47762500	-2.69470800	H	5.19038600	2.49537700	1.15168800
H	-3.71488600	5.07316100	-3.37006800	C	4.27669600	2.24750300	-0.80012800
H	-1.96076000	5.27260500	-3.12275100	H	4.44221600	1.62411000	-1.69466500
H	-3.08746900	6.56514400	-2.64500000	H	4.51109300	3.28001400	-1.08312100
O	-0.58796000	-2.91599000	-1.63169500	C	2.77403200	2.15466800	-0.54305600
C	-1.71713000	-2.88514500	-2.28564000	O	2.38869400	1.10456600	0.08888500
O	-2.57512800	-1.99577600	-2.17856700	O	2.05859600	3.07161600	-1.01866700
C	-1.90065900	-4.06094500	-3.23748800	O	-0.22337900	-3.60307000	1.10022500
H	-1.02699700	-4.07530800	-3.90704500	C	-0.72183400	-3.59281000	2.27040500
H	-1.82289900	-4.98158600	-2.63900400	O	-1.19650600	-2.58196200	2.88551600
C	-3.20165000	-4.03423300	-4.04313000	C	-0.77842800	-4.93339900	2.99323100
H	-3.25965600	-3.08976500	-4.60113000	H	0.13492600	-5.48300300	2.73179800
H	-4.05538400	-4.03406600	-3.35049700	H	-1.60662800	-5.49159500	2.52876200
C	-3.31619700	-5.22125200	-5.00601700	H	-5.66379100	-1.30400600	3.09627400
H	-2.49118100	-5.22713800	-5.73222000	C	-0.97483000	-4.84187700	4.50736200
H	-4.25636300	-5.18343800	-5.57119600	H	-1.02260500	-5.84757800	4.94338600
H	-3.28919300	-6.17884200	-4.46702700	H	-0.14670800	-4.30239600	4.98345400
N	1.88375500	-2.46315400	-0.44924900	H	-1.90047500	-4.31092100	4.75358500
C	2.54375700	-2.30265800	-1.64759600	O	-4.24056900	-0.12776700	0.59898400
H	1.99577700	-2.14979900	-2.56717600	C	-4.24468600	-0.30220400	1.82893200
C	3.90091100	-2.34315300	-1.42857500	O	-3.18432400	-0.47035100	2.56887400
N	4.04176100	-2.56205400	-0.06407300	C	-5.54255400	-0.32584400	2.61362800
H	4.92542900	-2.44820200	0.44487600	H	-6.39155500	-0.12598200	1.95468900
C	2.81031700	-2.60553900	0.48878200	H	-5.50355700	0.42682400	3.41030600
H	2.61727000	-2.69049400	1.54841400	O	-0.68376800	0.23559400	3.58279600
C	5.05113300	-2.15990500	-2.38598100	C	0.33199900	1.00794000	3.54704400
H	5.09666100	-3.00809700	-3.08492200	O	1.02801900	1.28930400	2.51848400
H	4.84160300	-1.27554800	-3.00447800	C	0.71169100	1.68981100	4.84679600
C	6.45791000	-2.01562300	-1.75092100	H	0.65618000	0.94856300	5.65525500
H	6.76713700	-2.96412500	-1.29690600	H	1.74309800	2.05282100	4.76690400
H	7.17233100	-1.79235900	-2.55513300	C	-0.24572600	2.86222400	5.15231100
C	6.53836700	-0.96333700	-0.64486600	H	-1.27272900	2.47552200	5.20013300
O	6.41686300	-1.27840700	0.54786100	H	-0.21363100	3.57648100	4.31722100
N	6.70012400	0.32698500	-1.03299200	C	0.11183900	3.57280000	6.46140200
H	6.78904400	0.53158800	-2.02040100	H	0.06229100	2.88333200	7.31575900
C	6.60738300	1.44079500	-0.08081000	H	-0.58036000	4.40132300	6.65916600
H	7.19987600	1.17099800	0.80014100	H	1.12852600	3.98810100	6.42533400
H	7.07889300	2.31225500	-0.55192300	O	0.39890000	1.68332500	-2.64487400
C	5.16183500	1.74586300	0.34784400	H	0.63924400	0.88383000	-2.12723000
H	4.72813300	0.83689800	0.77704600				

Pro:

Ca	-2.55537600	0.55929300	-1.15876700	Mn	0.61269600	0.58946700	0.77876800
Mn	-0.14222000	-1.86534200	-0.29120900	Mn	0.26834500	3.37047200	-1.23044400
Mn	-1.48780800	-1.10542300	1.98852800	O	-1.79576000	-1.40665700	0.23596900

O	0.37672300	-1.16810800	1.36384500	H	2.49851800	-2.88829800	1.29991000
O	-1.11663100	1.37842300	0.81470700	C	5.09025700	-2.01791200	-2.46948700
O	0.24913900	-0.16218400	-0.84235400	H	5.12807200	-2.78445300	-3.25757800
O	-0.08862000	2.32613700	0.57987100	H	4.93789400	-1.06236800	-2.99137500
O	-4.82670000	-0.00476200	-2.06216200	C	6.47779700	-2.00544600	-1.77813400
H	-5.18885200	-0.13574600	-1.16137600	H	6.73397200	-3.01124100	-1.42586200
H	-4.57307500	-0.89130200	-2.38611200	H	7.22900200	-1.72291200	-2.52841500
O	-1.74242300	1.07079100	-3.45758300	C	6.55793300	-1.08914400	-0.55702100
H	-0.83932900	1.45984000	-3.22292600	O	6.38635500	-1.53195300	0.58785500
H	-2.22586000	1.81677400	-3.85031300	N	6.77530400	0.23014100	-0.79037900
O	0.67460900	4.48022400	-2.58558300	H	6.90510600	0.54158700	-1.74477900
H	0.95886500	3.85618700	-3.28405600	C	6.68579400	1.23173800	0.27939800
O	0.13974800	4.79848500	-0.13208200	H	7.24137900	0.84501000	1.14060600
H	0.60559000	5.52903100	-0.58230100	H	7.19790900	2.13457200	-0.07605700
O	-3.65561700	2.89029400	-0.89518100	C	5.23680600	1.53451900	0.69845000
C	-2.70682500	3.66195700	-1.09783400	H	4.76419800	0.59912700	1.01476600
O	-1.57512700	3.11390400	-1.51217200	H	5.26150100	2.19207200	1.57921300
C	-2.80966900	5.16002700	-0.96980100	C	4.40417100	2.18368000	-0.41343600
H	-3.79273100	5.38947300	-0.54469800	H	4.57698300	1.65179700	-1.36404500
H	-2.02475000	5.48035600	-0.27287600	H	4.68195900	3.23056900	-0.58201400
C	-2.60729700	5.86967900	-2.32264700	C	2.89101400	2.12273100	-0.21434700
H	-3.36645900	5.55719800	-3.05255500	O	2.45022200	1.05582000	0.34935000
H	-1.61440100	5.65112300	-2.73203200	O	2.22360100	3.08577700	-0.66983800
H	-2.69727900	6.95538400	-2.19094600	O	-0.34326100	-3.66900300	0.59435700
O	-0.61020200	-2.57305900	-1.99931800	C	-0.88889600	-3.87144200	1.72712000
C	-1.74402700	-2.47739300	-2.63941700	O	-1.40270600	-2.98926800	2.48719700
O	-2.61780400	-1.62561500	-2.41651000	C	-0.95179300	-5.31937000	2.19597200
C	-1.91165000	-3.52216800	-3.73644600	H	0.01280300	-5.78243400	1.94924400
H	-1.04807700	-3.42311700	-4.41205000	H	-1.69209300	-5.81607200	1.54970700
H	-1.80119500	-4.51158800	-3.26683000	H	-6.04407500	-1.59072000	2.32088100
C	-3.22450200	-3.42412600	-4.51687800	C	-1.31018000	-5.50522800	3.67092300
H	-3.31443800	-2.41596100	-4.94360000	H	-1.34755400	-6.57348600	3.91860400
H	-4.06777200	-3.53796700	-3.82076600	H	-0.56815300	-5.02869500	4.32317700
C	-3.32363200	-4.47616800	-5.62709600	H	-2.28461200	-5.06035400	3.89928700
H	-2.50983400	-4.36388300	-6.35733400	O	-4.18743800	0.02203400	0.63776100
H	-4.27293500	-4.38970500	-6.17133800	C	-4.29812200	-0.46402000	1.78660900
H	-3.26417800	-5.49548800	-5.22001800	O	-3.33205600	-0.93350400	2.50384700
N	1.84531300	-2.40331100	-0.67941300	C	-5.66887400	-0.56403700	2.43506400
C	2.55385700	-2.13525100	-1.82966800	H	-6.37012100	0.12527500	1.95585600
H	2.04496200	-1.85936200	-2.74318300	H	-5.60107900	-0.35631300	3.50802900
C	3.90019700	-2.25717300	-1.57519000	O	-0.84551100	-0.14392100	3.57734300
N	3.98387900	-2.63542700	-0.24129700	C	0.17637900	0.61489700	3.67318400
H	4.85219000	-2.61878800	0.30465300	O	0.90473200	1.01977200	2.71075400
C	2.73189400	-2.69025900	0.26370200	C	0.52824800	1.10451800	5.06529700

H	0.65282900	0.22212100	5.70982600	H	-0.11972700	1.64863300	7.75347400
H	1.48332400	1.63997900	5.01955300	H	-1.03935700	3.13628600	7.45546800
C	-0.57719100	2.00911400	5.64748700	H	0.69164000	3.07357300	7.07464000
H	-1.52258600	1.45103300	5.65132200	O	0.54520700	1.95357500	-2.46294900
H	-0.72100600	2.87289200	4.98214400	H	0.74913600	1.10341600	-2.01315600
C	-0.24159700	2.49365800	7.06138000				

Table S18 Reaction parameters for the closed-cubane O2 (oxo)-O4 (oxo/oxyl) coupling with deprotonated W2:

Spin state	Spin topology (Mn1~Mn4-O4)	Gibbs Free energy (a.u.)		
		Rea	TS	Pro-O-O
doublet	ααββα	-3366.2332	-3366.1768	-3366.2005
	αβαβα	-3366.2325	-3366.1464	-3366.1669
	αββαα	-3366.2026	-3366.1326	-3366.1525
	βααβα	-3366.2200	-3366.1668	-3366.1969
	βαβαα	-3366.2041	-3366.1593	-3366.1958
	ββααα	-3366.1938	-3366.1429	-3366.1821
sextet	αααββ	-3366.2034	-3366.1353	-3366.1431
	ααβαβ	-3366.2507	-3366.1472	-3366.1656
	αβααβ	-3366.2166	-3366.1694	-3366.1985
	βαααβ	-3366.2453	-3366.1635	-3366.1519
octet	αααβα	-3366.2218	-3366.1673	-3366.1874
	ααβαα	-3366.2027	-3366.1649	-3366.1956
	αβααα	-3366.1944	-3366.1279	-3366.1506
	βαααα	-3366.2039	-3366.1602	-3366.1965
12-et	ααααβ	-3366.2533	-3366.1472	-3366.1547
14-et	ααααα	-3366.1892	-3366.1659	-3366.1945

Spin state	Spin topology (Mn1~Mn4-O4/O10)	Relative Gibbs Free energy (kcal/mol)			
		$\Delta G^{\neq}$(Rea-TS)	ΔG(Rea-Pro)	ΔG(Rea)	ΔG(Pro)
doublet	ααββα	35.4	20.5	12.6	0.0
	αβαβα	54.0	41.2	13.1	21.1
	αββαα	43.9	31.4	31.8	30.1
	βααβα	33.4	14.5	20.9	2.3
	βαβαα	28.1	5.2	30.9	2.9
	ββααα	31.9	7.3	37.3	11.5
sextet	αααββ	42.7	37.8	31.3	36.0
	ααβαβ	64.9	53.4	1.6	21.9
	αβααβ	29.6	11.4	23.0	1.3
	βαααβ	51.3	58.6	5.0	30.5
octet	αααβα	34.2	21.6	19.8	8.2
	ααβαα	23.7	4.5	31.8	3.1

	αβααα	41.7	27.5	37.0	31.3
	βαααα	27.4	4.6	31.0	2.5
12-et	αααaβ	66.6	61.9	0.0	28.7
14-et	ααααα	14.6	-3.3	40.2	3.8

Spin state	topology	Spin (Mn1~Mn4-O4)	Mulliken spin density		
			Rea	TS	Pro-O-O
doublet	α	Mn1	2.92	2.93	2.94
	α	Mn2	2.93	3.60	3.86
	β	Mn3	-2.90	-2.90	-2.98
	β	Mn4	-1.91	-2.80	-2.98
	α	O2	0.03	-0.12	0.07
		O4	-0.01	0.32	0.07
		O7	-0.10	-0.02	0.03
	α	Mn1	2.92	2.92	2.92
	β	Mn2	-2.93	-3.75	-3.84
	α	Mn3	2.89	2.91	3.08
	β	Mn4	-1.83	-1.24	-0.83
	α	O2	0.00	0.28	-0.07
		O4	-0.02	-0.12	-0.06
		O7	-0.09	-0.07	-0.21
	α	Mn1	2.91	2.90	2.89
	β	Mn2	-2.93	-2.42	-1.92
	β	Mn3	-2.84	-2.88	-3.01
	α	Mn4	2.86	2.84	2.83
	α	O2	-0.03	0.06	0.08
		O4	0.54	0.33	0.05
		O7	0.02	0.15	0.16
	β	Mn1	-2.93	-2.91	-2.89
	α	Mn2	2.93	3.59	3.85
	α	Mn3	2.83	2.88	3.00
	β	Mn4	-2.64	-2.59	-2.72
	α	O2	0.03	-0.14	-0.06
		O4	0.07	0.37	-0.03
		O7	0.70	-0.28	-0.24
	β	Mn1	-2.93	-2.90	-2.91
	α	Mn2	2.94	3.84	3.85
	β	Mn3	-2.81	-2.94	-3.02
	α	Mn4	2.74	2.33	2.83
	α	O2	-0.02	0.45	0.07
		O4	-0.02	-0.02	0.05
		O7	1.04	0.19	0.17
	β	Mn1	-2.91	-2.90	-2.88
	β	Mn2	-2.93	-2.75	-3.01

	α	Mn3	2.87	3.25	3.81
	α	Mn4	2.84	2.82	2.85
	α	O2	0.03	0.04	0.05
		O4	0.61	0.34	0.06
		O7	0.09	0.18	0.16
	α	Mn1	2.92	2.89	2.95
	α	Mn2	2.93	2.43	1.97
	α	Mn3	2.85	2.88	3.01
	β	Mn4	-2.86	-2.85	-2.83
	β	O2	0.06	-0.05	-0.06
		O4	-0.54	-0.31	-0.03
		O7	-0.02	-0.15	-0.16
	α	Mn1	2.92	2.94	2.95
	α	Mn2	2.93	3.76	3.86
	β	Mn3	-2.86	-2.89	-3.01
	α	Mn4	1.78	1.16	1.28
	β	O2	0.02	-0.24	0.08
		O4	0.04	0.15	0.07
sextet		O7	-0.02	0.10	-0.32
	α	Mn1	2.92	2.92	2.91
	β	Mn2	-2.94	-3.54	-3.85
	α	Mn3	2.84	2.93	3.03
	α	Mn4	2.58	2.66	2.75
	β	O2	0.02	0.14	-0.06
		O4	0.14	-0.42	-0.09
		O7	-0.59	0.28	0.27
	β	Mn1	-2.91	-2.90	-2.91
	α	Mn2	2.93	3.83	1.93
	α	Mn3	2.94	2.92	3.02
	α	Mn4	1.83	1.05	2.87
	β	O2	0.03	-0.26	-0.07
		O4	0.03	0.04	-0.06
		O7	0.18	0.21	0.05
	α	Mn1	2.93	2.95	2.97
	α	Mn2	2.93	3.56	3.88
	α	Mn3	2.84	2.87	3.00
	β	Mn4	-2.64	-2.65	-2.70
	α	O2	0.05	-0.08	-0.06
octet		O4	0.08	0.41	-0.02
		O7	0.70	-0.26	-0.25
	α	Mn1	2.92	2.93	2.95
	α	Mn2	2.94	3.48	3.86
	β	Mn3	-2.81	-2.92	-3.02
	α	Mn4	2.86	2.82	2.83

	α	O2	0.01	-0.04	0.08
		O4	0.54	0.47	0.06
		O7	0.02	0.17	0.17
	α	Mn1	2.92	2.93	2.92
	β	Mn2	-2.92	-3.80	-1.92
	α	Mn3	2.90	3.54	3.02
	α	Mn4	2.84	2.74	2.84
	α	O2	0.05	0.22	-0.04
		O4	0.61	0.15	-0.05
		O7	0.09	0.40	0.16
	β	Mn1	-2.92	-2.89	-2.88
	α	Mn2	2.93	3.83	3.86
	α	Mn3	2.87	2.88	3.00
	α	Mn4	2.79	2.39	2.83
	α	O2	0.04	0.38	-0.07
		O4	0.16	0.07	-0.06
		O7	1.06	0.22	0.17
12-et	α	Mn1	2.93	2.96	2.97
	α	Mn2	2.93	3.74	1.95
	α	Mn3	2.94	2.91	3.03
	α	Mn4	1.83	1.13	2.76
	β	O2	0.05	-0.22	-0.06
		O4	0.04	0.18	-0.07
		O7	0.17	0.12	0.26
14-et	α	Mn1	2.93	2.95	2.97
	α	Mn2	2.93	3.48	3.87
	α	Mn3	2.82	2.87	3.01
	α	Mn4	2.79	2.81	2.82
	α	O2	0.12	-0.01	-0.05
		O4	0.88	0.47	-0.05
		O7	0.18	0.19	0.18

Rea:

Ca	-2.71220600	-0.05760000	-0.91494200	H	-4.54232800	-2.06424400	-1.60697500
Mn	0.19739900	-1.78197700	-0.14073300	O	-3.88456200	0.37203100	-3.23079000
Mn	-0.99269700	-0.73500200	2.06145600	H	-4.72112100	0.75037500	-2.91084300
Mn	0.31253100	0.99132700	0.37978600	H	-3.25902700	1.12628200	-3.31663700
Mn	-0.77646500	3.10800900	-2.11958400	O	0.14546300	3.15720600	-3.44324900
O	-1.43620300	-1.73490600	0.61477200	O	-0.09978300	5.05769700	-1.52694100
O	0.72096000	-0.65582600	1.26835000	H	-0.73821300	5.23383800	-0.80920700
O	-1.34488800	0.74568100	1.07993100	H	0.74538700	4.80648600	-1.09214800
O	-0.03691900	-0.19252300	-0.99885400	O	-3.75183400	2.14443400	-0.81769800
O	-0.12189700	2.54025400	-0.40190800	C	-3.53104600	3.36025300	-0.95044400
O	-4.97281700	-1.28055300	-1.21458200	O	-2.42921900	3.88585000	-1.39528300
H	-5.06051100	-1.45051400	-0.25546100	C	-4.59665400	4.38863200	-0.57340600

H	-4.17315500	5.00637500	0.23306400	H	4.70942100	0.94947100	0.42439600
H	-4.71671300	5.06898300	-1.42872500	H	5.06231400	2.53366000	1.11707600
C	-5.93275100	3.78072400	-0.14893600	C	4.10075600	2.60645800	-0.82647000
H	-5.80535200	3.11424500	0.71152900	H	4.20679800	2.12164500	-1.80936500
H	-6.37341500	3.18742900	-0.95945000	H	4.31346700	3.67351700	-0.96055400
H	-6.64539600	4.56976300	0.12365100	C	2.62380000	2.43997500	-0.46234700
O	-0.32134500	-2.96481800	-1.55195100	O	2.23352500	1.27545700	-0.13806700
C	-1.49552200	-3.08975000	-2.09558500	O	1.89521500	3.46568300	-0.54976300
O	-2.42381300	-2.26641500	-1.99798500	O	0.65240900	-3.31679100	1.12763600
C	-1.65433800	-4.36245600	-2.92089300	C	0.27153700	-3.33718600	2.34689500
H	-0.89180500	-4.32822000	-3.71484800	O	-0.36565400	-2.42439800	2.95937400
H	-1.36637800	-5.20880700	-2.27958200	C	0.60327500	-4.60503800	3.12691400
C	-3.04777500	-4.56882300	-3.51974200	H	1.61445400	-4.91667400	2.83274000
H	-3.31776800	-3.68855100	-4.11823000	H	-0.07047700	-5.38547100	2.73965500
H	-3.78644600	-4.62277300	-2.70671100	H	-4.87556100	-0.34890600	4.23535100
C	-3.13228300	-5.83626800	-4.37754800	C	0.46891700	-4.48177500	4.64513800
H	-2.42755500	-5.79529900	-5.22007800	H	0.70494400	-5.43943500	5.12633900
H	-4.13984000	-5.96682700	-4.79295700	H	1.15148000	-3.72090600	5.04328500
H	-2.89402000	-6.73472000	-3.79082200	H	-0.54856100	-4.19104300	4.92754200
N	2.13883200	-1.94330400	-0.84650200	O	-4.05746800	-0.62420600	1.20155200
C	2.61836400	-1.45597000	-2.04203200	C	-3.83159800	-0.81332500	2.41069800
H	1.94958200	-1.01522300	-2.76801600	O	-2.65452400	-0.84235000	2.95737400
C	3.98361500	-1.60805800	-2.08122200	C	-4.96646600	-1.04433800	3.39262200
N	4.31514500	-2.21817700	-0.87614700	H	-4.89470900	-2.06056200	3.80150200
H	5.26528200	-2.24684000	-0.49798800	H	-5.93297700	-0.91150900	2.89897100
C	3.18144800	-2.38182100	-0.15766400	O	-0.25288300	0.42185800	3.50346700
H	3.13745400	-2.79931800	0.83732300	C	0.45576700	1.45622900	3.26922400
C	4.97923500	-1.24385900	-3.15146500	O	0.81968300	1.88664100	2.12879500
H	4.94059700	-1.97651400	-3.97173300	C	0.89843100	2.25827600	4.48461100
H	4.66446300	-0.28782700	-3.59214700	H	1.58717900	3.04249600	4.14877800
C	6.46015200	-1.14360900	-2.69763200	H	0.00047500	2.75558000	4.88414100
H	6.86806400	-2.14318100	-2.50962600	C	1.53287200	1.39112200	5.58480500
H	7.04395500	-0.70292300	-3.51730900	H	2.41743000	0.87971200	5.17569800
C	6.63860600	-0.35351500	-1.40383100	H	0.82154200	0.60509200	5.86781700
O	6.71940100	-0.92654600	-0.30964800	C	1.93411000	2.21306000	6.81396200
N	6.63757400	1.00188100	-1.51262600	H	2.66287300	2.99394100	6.55483000
H	6.53389700	1.41210700	-2.43255900	H	2.38759100	1.57599500	7.58441100
C	6.50771900	1.86845800	-0.33805700	H	1.06173600	2.70916200	7.26207600
H	7.15196800	1.45436900	0.44420400	O	-1.58844200	1.50487600	-2.60117200
H	6.89623900	2.85806200	-0.60996300	H	-0.97510800	1.08868400	-3.23378400
C	5.06093700	1.95803700	0.18025800				

TS:

Ca	2.60880100	0.18626900	-1.28515700	Mn	1.16059700	0.59929300	1.99131300
Mn	-0.33463600	1.81155900	0.03087700	Mn	-0.52083900	-0.92371900	0.51876800

Mn	0.68068100	-3.05001700	-1.95505200	H	-5.37377600	1.33370000	0.61850500
O	1.37906800	1.59725600	0.43088200	C	-3.30661600	1.79911600	0.70572400
O	-0.68887900	0.69130700	1.49164800	H	-3.08522300	1.63177700	1.75024900
O	1.41632600	-0.88396100	0.69744400	C	-5.56728600	1.80032400	-2.18985900
O	-0.44462500	0.19893600	-0.89040600	H	-5.79443500	2.79967300	-2.59027700
O	0.65675200	-2.26673800	0.16262900	H	-5.23795200	1.20323100	-3.05208100
O	4.64751800	1.56390600	-1.83312400	C	-6.89292600	1.21671100	-1.63785900
H	4.90254000	1.70245600	-0.89967000	H	-7.35769000	1.92485000	-0.94254400
H	4.17961100	2.36702000	-2.12844800	H	-7.58636800	1.08594200	-2.47998100
O	3.08865800	-0.24466000	-3.80606800	C	-6.72303400	-0.09044200	-0.86306600
H	3.80406200	-0.89162100	-3.66788200	O	-6.66161800	-0.09497200	0.37447700
H	2.27593300	-0.79735100	-3.83099800	N	-6.59045200	-1.22523900	-1.59525600
O	0.50650900	-4.06633700	-3.18293000	H	-6.64621400	-1.16333600	-2.60415000
O	0.17744100	-4.75589700	-0.38002000	C	-6.26187300	-2.51848200	-0.98189200
H	1.07198100	-5.12412600	-0.52388200	H	-6.94194800	-2.66971800	-0.13583200
H	0.28310900	-4.18832700	0.41238800	H	-6.47642200	-3.29216500	-1.72946700
O	3.79547500	-1.91658400	-1.52257700	C	-4.80826600	-2.60810000	-0.48733700
C	3.59114000	-3.13087800	-1.32859100	H	-4.64672000	-1.83204100	0.26719100
O	2.45448500	-3.73241300	-1.46259900	H	-4.67994300	-3.57510900	0.01973300
C	4.73456500	-4.05552500	-0.91340300	C	-3.77168500	-2.46518100	-1.60726900
H	4.41336100	-4.58416900	-0.00403600	H	-3.99826400	-1.56862000	-2.20750400
H	4.82036800	-4.83207600	-1.68781400	H	-3.78224200	-3.31930100	-2.29507000
C	6.06733500	-3.34076100	-0.69465300	C	-2.33327900	-2.27013300	-1.13942300
H	5.98120000	-2.57740700	0.08749600	O	-2.19223500	-1.66570500	-0.00534300
H	6.39844900	-2.83508000	-1.60909200	O	-1.41326200	-2.65411300	-1.89257100
H	6.84301400	-4.05773900	-0.39622900	O	-0.38147500	3.33903800	1.34000200
O	-0.10182000	2.96732800	-1.47219000	C	0.27222700	3.31134200	2.43406000
C	0.95628700	3.12800500	-2.21313800	O	0.94280300	2.33592400	2.90055800
O	1.92646400	2.35223000	-2.25924900	C	0.25527200	4.59575900	3.25481900
C	0.90830800	4.38114400	-3.08161200	H	-0.75514900	5.01720100	3.17497300
H	0.04496400	4.27042600	-3.75701800	H	0.91556100	5.30159700	2.72678200
H	0.65748600	5.22892600	-2.42709400	H	5.30295400	0.04065300	3.55114600
C	2.18368700	4.65424200	-3.88284500	C	0.69081000	4.43753300	4.71219700
H	2.42528000	3.77118600	-4.48893800	H	0.66387500	5.40872700	5.22227300
H	3.02553600	4.78685500	-3.18725800	H	0.02840200	3.74944700	5.25168300
C	2.05682900	5.89166700	-4.77832800	H	1.70792000	4.03682800	4.77913400
H	1.24408200	5.77329900	-5.50878600	O	4.11856000	0.63666500	0.65105100
H	2.98336800	6.07113400	-5.33859400	C	4.05257000	0.63985100	1.89752700
H	1.84283300	6.79426600	-4.18866500	O	2.96620900	0.55201900	2.59270700
N	-2.40574300	2.05209900	-0.23325300	C	5.31337900	0.77172400	2.73499900
C	-3.08089400	2.10912100	-1.43206400	H	5.33893700	1.76988500	3.19265100
H	-2.55209800	2.29962600	-2.35580300	H	6.20268500	0.63489900	2.11348700
C	-4.42012900	1.88147100	-1.21561700	O	0.62404300	-0.51400400	3.52252500
N	-4.53988200	1.71110000	0.15808400	C	-0.23127600	-1.45359000	3.40936300

O	-0.80137300	-1.81180800	2.33077000	C	-1.21033500	-2.09855900	7.14256600
C	-0.57925800	-2.21878400	4.67567600	H	-2.07013000	-2.76830500	7.00158800
H	-1.41326000	-2.89429300	4.45187800	H	-1.44365800	-1.42757600	7.97936900
H	0.29397900	-2.84316100	4.92328800	H	-0.35240200	-2.71760000	7.44027700
C	-0.90443600	-1.30425900	5.86867600	O	1.00571200	-1.34208700	-2.51612800
H	-1.76621100	-0.66971200	5.61184000	H	0.18451900	-0.82886600	-2.32965500
H	-0.05702600	-0.62746200	6.03546900				

Pro:

Ca	-2.59508500	0.29871700	-1.23811600	C	-2.14100800	-2.88737600	-5.27671400
Mn	0.39257800	-1.65071700	-0.60097100	H	-2.44931700	-1.85487400	-5.48764100
Mn	-1.11713600	-1.67060200	1.59121800	H	-2.94140900	-3.32591300	-4.66236600
Mn	0.43858400	0.67795600	0.93266300	C	-2.00664400	-3.67579200	-6.58427700
Mn	-0.65104400	3.59607300	-0.80266800	H	-1.23639900	-3.23885200	-7.23545600
O	-1.42119600	-1.65507500	-0.13983800	H	-2.95104600	-3.67995100	-7.14368700
O	0.64428100	-1.18866500	1.22914600	H	-1.72551400	-4.72166900	-6.39575900
O	-1.45665300	0.92894000	1.00204600	N	2.42077900	-1.66629700	-0.94980600
O	0.38256800	0.18190900	-0.79809300	C	3.08573100	-1.24593600	-2.07972900
O	-0.72142500	2.14732400	0.95093000	H	2.54757000	-1.06632500	-3.00005500
O	-4.60346500	-0.81474600	-2.27225300	C	4.42636800	-1.11243900	-1.79956200
H	-4.85133300	-1.31665800	-1.47194000	N	4.55730500	-1.49393200	-0.46989400
H	-4.07597300	-1.41285500	-2.83659700	H	5.39900100	-1.33823100	0.09385000
O	-3.06113600	1.56433400	-3.46931700	C	3.32962600	-1.79655800	0.00737900
H	-3.76239300	2.13671000	-3.10866200	H	3.11872900	-2.05456900	1.03559500
H	-2.23810000	2.07835700	-3.31176200	C	5.56601400	-0.63898700	-2.66599600
O	-0.42435300	4.95281300	-1.62842600	H	5.77845700	-1.38163900	-3.44936400
O	-0.21988800	4.70084600	1.25027500	H	5.23567700	0.26506500	-3.19726800
H	-1.08053100	5.15873200	1.18227700	C	6.90283100	-0.34535600	-1.93756800
H	-0.40685600	3.93095600	1.82574800	H	7.36802100	-1.28052800	-1.60620500
O	-3.78122700	2.36482700	-0.77145000	H	7.58898000	0.12260700	-2.65683700
C	-3.58653200	3.48077800	-0.25008000	C	6.75015600	0.52129000	-0.68701800
O	-2.45071300	4.09501500	-0.18544100	O	6.71847800	0.01179400	0.44247700
C	-4.74616300	4.26103500	0.36811400	N	6.59193600	1.85479200	-0.87871800
H	-4.44603600	4.54106500	1.38837600	H	6.60755800	2.21585600	-1.82451300
H	-4.82522800	5.20997700	-0.18298800	C	6.22566400	2.76080400	0.21773500
C	-6.07665400	3.50957400	0.36966500	H	6.89700400	2.55407500	1.05854500
H	-6.00148800	2.57523300	0.93832800	H	6.42355400	3.78247500	-0.12940500
H	-6.38266400	3.24755600	-0.64970900	C	4.76551400	2.60093400	0.67611700
H	-6.86531800	4.12635900	0.81958100	H	4.62041900	1.57926700	1.04132800
O	0.17900600	-2.12660800	-2.46329300	H	4.60197000	3.26897400	1.53378000
C	-0.89632300	-2.05297700	-3.17906400	C	3.74858300	2.90786100	-0.42700700
O	-1.90440900	-1.37077500	-2.90365000	H	3.99688200	2.32985200	-1.33218800
C	-0.84065200	-2.86828300	-4.46943000	H	3.76132200	3.96555400	-0.71802800
H	-0.01926500	-2.45374100	-5.07540700	C	2.30047000	2.54069400	-0.11547300
H	-0.52044500	-3.88696900	-4.20483300	O	2.12432700	1.59178700	0.74068200

O	1.40973900	3.15125900	-0.74771400	H	-6.18354700	-1.78389000	1.55858500
O	0.53287800	-3.62778400	-0.09355300	O	-0.80884500	-0.90196400	3.42951000
C	-0.00090800	-4.13292100	0.92441500	C	-0.04142900	0.06079800	3.74727600
O	-0.71816600	-3.49569500	1.79074200	O	0.54902500	0.84831400	2.93718700
C	0.16041100	-5.62306300	1.17554200	C	0.16273600	0.32572500	5.23164200
H	1.06386600	-5.94436600	0.64452000	H	1.00841600	1.01448000	5.34481000
H	-0.68929400	-6.10841500	0.66955300	H	-0.73589400	0.85822400	5.58363500
H	-5.34939900	-1.77530700	3.14506400	C	0.36037000	-0.94895700	6.06613400
C	0.18990300	-6.02352500	2.65419700	H	1.25200800	-1.48267700	5.70349900
H	0.29044000	-7.11176000	2.74679600	H	-0.49249800	-1.61822500	5.89694100
H	1.03751800	-5.55949800	3.17425700	C	0.51238200	-0.64763300	7.56073200
H	-0.72803900	-5.71363400	3.16442300	H	1.37527400	0.00510100	7.75334900
O	-4.10270900	-0.88487300	0.41447600	H	0.65711400	-1.57059000	8.13706400
C	-4.03439900	-1.56979700	1.45389900	H	-0.38002500	-0.14319000	7.95715800
O	-2.94603900	-1.87767800	2.08745800	O	-0.97699400	2.16754900	-1.88473300
C	-5.29545200	-2.11512600	2.10360500	H	-0.16710300	1.60429100	-1.83968400
H	-5.25591300	-3.21184500	2.12395600				

Table S19 Reaction parameters for the closed-cubane O2 (oxo)-O4 (oxo/oxyl) coupling with deprotonated Wx:

Spin state	Spin topology (Mn1~Mn4-O2/O4/O7)	Gibbs Free energy (a.u.)		
		Rea	TS	Pro-O-O
doublet	ααββα	-3366.2469	-3366.1697	-3366.1991
	αβαβα	-3366.2503	-3366.1572	-3366.1609
	αββαα	-3366.2147	-3366.1415	-3366.1659
	βααβα	-3366.2511	-3366.1775	-3366.2002
	βαβαα	-3366.2009	-3366.1675	-3366.2034
	ββααα	-3366.2115	-3366.1393	-3366.1650
sextet	αααββ	-3366.2170	-3366.1410	-3366.1644
	ααβαβ	-3366.2459	-3366.1707	-3366.1728
	αβααβ	-3366.2436	-3366.1699	-3366.1999
	βαααβ	-3366.2498	-3366.1654	-3366.1703
octet	αααβα	-3366.2541	-3366.1709	-3366.1958
	ααβαα	-3366.1947	-3366.1686	-3366.2040
	αβααα	-3366.2151	-3366.1359	-3366.1489
	βαααα	-3366.1968	-3366.1653	-3366.2041
12-et	αααaβ	-3366.2493	-3366.1572	-3366.1745
14-et	ααααα	-3366.1875	-3366.1637	-3366.2023

Spin state	Spin topology (Mn1~Mn4-O4/O10)	Relative Gibbs Free energy (kcal/mol)			
		$\Delta G^{\neq}$(Rea-TS)	ΔG(Rea-Pro)	ΔG(Rea)	ΔG(Pro)
doublet	ααββα	48.4	30.0	4.5	3.1

	αβαβα	58.4	56.1	2.4	27.1
	αββαα	45.9	30.6	24.7	24.0
	βααβα	46.2	31.9	1.9	2.4
	βαβαα	21.0	-1.6	33.4	0.4
	ββαaα	45.3	29.2	26.7	24.5
sextet	ααaββ	47.7	33.0	23.3	24.9
	ααβαβ	47.2	45.9	5.1	19.6
	αβααβ	46.2	27.4	6.6	2.6
	βαααβ	53.0	49.9	2.7	21.2
octet	αααβα	52.2	36.6	0.0	5.2
	ααβαα	16.4	-5.8	37.3	0.1
	αβααα	49.7	41.5	24.5	34.6
	βαααα	19.8	-4.6	36.0	0.0
12-et	αααaβ	57.8	46.9	3.0	18.6
14-et	ααααα	14.9	-9.3	41.8	1.1

Spin state	topology	Spin (Mn1~Mn4-O2/O4/O7)	Mulliken spin density		
			Rea	TS	Pro-O-O
doublet	α	Mn1	2.92	2.94	2.96
	α	Mn2	2.94	3.56	3.86
	β	Mn3	-2.90	-2.92	-3.02
	β	Mn4	-1.87	-2.58	-2.67
	α	O2	0.01	-0.09	0.08
		O4	-0.06	0.37	0.09
		O10	-0.14	-0.30	-0.30
	α	Mn1	2.93	2.93	2.93
	β	Mn2	-2.93	-3.78	-1.91
	α	Mn3	2.88	2.91	3.02
	β	Mn4	-1.81	-1.20	-2.65
	α	O2	0.01	0.25	-0.04
		O4	-0.04	-0.08	-0.03
		O10	-0.12	-0.12	-0.32
	α	Mn1	2.92	2.89	2.89
	β	Mn2	-2.93	-3.80	-3.85
	β	Mn3	-2.83	-2.91	-2.98
	α	Mn4	2.64	3.47	3.79
	α	O2	-0.03	0.30	0.07
		O4	0.07	-0.02	0.04
		O10	0.86	0.71	0.82
	β	Mn1	-2.92	-2.91	-2.89
	α	Mn2	2.93	3.53	3.86
	α	Mn3	2.90	2.85	2.98
	β	Mn4	-1.80	-2.59	-2.65
	α	O2	0.04	-0.10	-0.07

		O4	-0.05	0.40	-0.03
		O10	-0.15	-0.33	-0.34
	β	Mn1	-2.85	-2.90	-2.91
	α	Mn2	3.80	3.84	3.85
	β	Mn3	-2.85	-2.92	-3.01
	α	Mn4	1.82	2.25	2.64
	α	O2	0.36	0.48	0.07
		O4	0.05	0.05	0.05
		O10	0.13	0.23	0.33
	β	Mn1	-2.92	-2.95	-2.95
	β	Mn2	-2.94	-3.79	-3.85
	α	Mn3	2.87	2.91	3.01
	α	Mn4	2.71	3.49	3.79
	α	O2	-0.01	0.26	-0.06
		O4	0.20	-0.05	-0.07
		O7	0.38	0.47	0.29
	α	Mn1	2.92	2.95	2.96
	α	Mn2	2.93	3.80	3.87
	α	Mn3	2.84	2.92	2.99
	β	Mn4	-2.64	-3.49	-3.79
	β	O2	0.06	-0.27	-0.06
		O4	-0.07	0.05	-0.03
		O10	-0.86	-0.71	-0.82
	α	Mn1	2.92	2.95	2.95
	α	Mn2	2.94	3.81	3.85
	β	Mn3	-2.86	-2.88	-3.06
	α	Mn4	1.82	1.18	0.92
	β	O2	0.00	-0.24	0.11
		O4	0.04	0.05	0.07
sextet		O10	0.09	0.13	0.11
	α	Mn1	2.93	2.94	2.92
	β	Mn2	-2.93	-3.53	-3.84
	α	Mn3	2.93	2.94	3.04
	α	Mn4	1.86	2.57	2.66
	β	O2	0.02	0.10	-0.07
		O4	0.06	-0.37	-0.09
		O10	0.14	0.30	0.30
	β	Mn1	-2.91	-2.89	-2.89
	α	Mn2	2.93	3.83	3.85
	α	Mn3	2.94	2.91	3.03
	α	Mn4	1.88	1.05	0.82
	β	O2	0.02	-0.25	-0.09
		O4	0.05	0.04	-0.07
		O10	0.14	0.19	0.25

	α	Mn1	2.93	2.96	2.98
	α	Mn2	2.92	3.56	3.87
	α	Mn3	2.89	2.87	2.99
	β	Mn4	-1.82	-2.59	-2.66
	α	O2	0.07	-0.07	-0.06
		O4	-0.04	0.36	-0.03
		O10	-0.11	-0.30	-0.31
	α	Mn1	2.92	2.94	2.95
	α	Mn2	3.81	3.86	3.86
	β	Mn3	-2.80	-2.91	-3.00
	α	Mn4	1.80	2.24	2.65
	α	O2	0.65	0.50	0.08
		O4	0.06	0.05	0.06
octet		O10	0.13	0.23	0.33
	α	Mn1	2.94	2.93	2.93
	β	Mn2	-2.93	-2.48	-1.94
	α	Mn3	2.89	3.01	3.03
	α	Mn4	2.71	2.83	2.84
	α	O2	0.02	0.03	-0.04
		O4	0.19	0.33	-0.05
		O10	0.83	0.01	0.01
	β	Mn1	-2.82	-2.88	-2.88
	α	Mn2	3.83	3.84	3.86
	α	Mn3	2.81	2.87	3.01
	α	Mn4	1.87	2.31	2.65
	α	O2	0.75	0.47	-0.06
		O4	0.08	0.09	-0.08
		O10	0.13	0.21	0.33
		O5	0.29	0.01	0.04
	α	Mn1	2.92	2.97	2.98
	α	Mn2	2.92	3.81	3.87
	α	Mn3	2.94	2.93	3.03
12-et	α	Mn4	1.87	1.16	0.81
	β	O2	0.07	-0.24	-0.07
		O4	0.04	0.07	-0.06
		O10	0.16	0.12	0.25
	α	Mn1	2.94	2.96	2.98
	α	Mn2	3.87	3.85	3.87
	α	Mn3	2.81	2.88	3.02
14-et	α	Mn4	1.86	2.30	2.65
	α	O2	0.79	0.47	-0.05
		O4	0.08	0.13	-0.07
		O10	0.12	0.21	0.33
		O5	0.38	0.04	0.04

Rea:

Ca	-2.44462700	0.18356100	-1.32010800	H	-2.46218500	-6.08616800	-5.06824900
Mn	0.02104300	-1.80511000	-0.26279700	N	2.03888900	-1.99241100	-0.65312300
Mn	-1.58788500	-1.04559700	1.77519200	C	2.74749200	-1.30746100	-1.61768500
Mn	0.06927000	0.86911900	0.71802200	H	2.24934400	-0.59674000	-2.26392900
Mn	0.43612000	3.42847200	-1.27502100	C	4.07038100	-1.67584900	-1.55177100
O	-1.73591500	-1.79898800	0.14234800	N	4.13773700	-2.61479600	-0.52646700
O	0.26706400	-0.94299400	1.37135600	H	5.00708500	-2.86778900	-0.05273400
O	-1.69645400	0.59212600	1.03197200	C	2.89969500	-2.75872600	-0.00151300
O	-0.00040600	-0.08567600	-0.88031800	H	2.65063100	-3.40319100	0.82867500
O	-0.23486200	2.47574500	0.05738700	C	5.25371900	-1.25523500	-2.38251200
O	-4.57667100	-0.41394000	-2.53388600	H	5.28299700	-1.82822000	-3.32180200
H	-5.04058500	-0.65926100	-1.70762900	H	5.09949700	-0.20852600	-2.67759100
H	-4.19185500	-1.24512700	-2.88040200	C	6.64384800	-1.40908800	-1.70420500
O	-1.61930600	0.87095400	-3.61007400	H	6.94052500	-2.46362600	-1.67884200
H	-2.22628700	1.58564900	-3.86863000	H	7.38894600	-0.87588300	-2.31038500
H	-0.78448200	1.35238600	-3.37940200	C	6.64107400	-0.91903400	-0.25891500
O	1.17781900	4.39021400	-2.69070100	O	6.48209500	-1.70550200	0.68221600
H	2.13290000	4.18136100	-2.67468300	N	6.74161000	0.42658200	-0.07973500
O	0.43845000	5.06095000	0.18346400	H	6.82300700	1.00749300	-0.90536500
H	-0.37648000	5.48509400	-0.15519700	C	6.34832400	1.07127600	1.17716300
H	0.13411100	4.48408300	0.91559400	H	6.71182300	0.43693400	1.99119400
O	-2.75627000	2.56127200	-1.62548300	H	6.87175400	2.03427000	1.23706400
C	-2.46727900	3.76846800	-1.68265900	C	4.82295500	1.25187300	1.29302000
O	-1.27106700	4.27113200	-1.66865200	H	4.34394300	0.26726700	1.25104100
C	-3.59389300	4.79274400	-1.83727800	H	4.59139200	1.66958500	2.28301400
H	-3.91674600	4.73527400	-2.88876300	C	4.24554800	2.15281600	0.19825700
H	-4.44042100	4.42254700	-1.24514800	H	4.62536600	1.84538800	-0.78917300
C	-3.24328000	6.23684000	-1.47482100	H	4.55280200	3.19937600	0.32688600
H	-2.41136000	6.60724500	-2.08412500	C	2.72308900	2.13277900	0.05211400
H	-2.95719600	6.32392400	-0.41727600	O	2.08335000	1.19549200	0.59480300
H	-4.10754700	6.89366400	-1.63583900	O	2.26992100	3.09039300	-0.66676800
O	-0.27299400	-2.72594200	-1.92578100	O	0.16580200	-3.54374700	0.81098500
C	-1.34529700	-2.76492300	-2.65995400	C	-0.46861300	-3.72729800	1.90562300
O	-2.29027900	-1.95825500	-2.59299200	O	-1.20404800	-2.88707200	2.51061700
C	-1.35449000	-3.90967800	-3.66747900	C	-0.33359700	-5.11492600	2.52488800
H	-0.43545500	-3.82207700	-4.26674400	H	0.71638100	-5.42044500	2.42111500
H	-1.24245700	-4.84535300	-3.09842700	H	-0.90496900	-5.79630200	1.87523200
C	-2.58914000	-3.95976200	-4.57040400	H	-5.89668700	-2.29381800	2.11088500
H	-2.68580300	-3.00268700	-5.10117900	C	-0.81095300	-5.22278400	3.97348300
H	-3.48920800	-4.05587400	-3.94657700	H	-0.69608200	-6.25231300	4.33597800
C	-2.53031900	-5.11417200	-5.57706200	H	-0.23399600	-4.56111100	4.63112900
H	-1.65551100	-5.02457200	-6.23645900	H	-1.86465500	-4.93739300	4.06233800
H	-3.42526900	-5.13290400	-6.21254800	O	-4.33671600	-0.46684100	0.20773800

C	-4.43187900	-0.90913500	1.37055900	H	0.38384300	2.35874000	4.91188500
O	-3.44216400	-1.16806900	2.16937000	C	-1.39699500	1.50101700	5.85315400
C	-5.79314500	-1.20939400	1.97370100	H	-1.88200600	0.51775500	5.89231800
H	-6.59105700	-0.84492000	1.32085400	H	-2.10603100	2.17764100	5.35286200
H	-5.87420300	-0.74759700	2.96445500	C	-1.10872600	2.00955800	7.26943100
O	-1.13430800	-0.16859500	3.51415700	H	-0.42727200	1.33272300	7.80396800
C	-0.36966500	0.84656500	3.60237900	H	-2.03253400	2.08497300	7.85754900
O	0.22111500	1.44348500	2.64304800	H	-0.64197600	3.00450600	7.25234500
C	-0.12150100	1.38971700	5.00289400	O	0.50162000	2.20247900	-2.49734900
H	0.58485900	0.69897400	5.49112800				

TS:

Ca	2.36964900	0.31847600	-1.32238300	O	1.96360400	2.54927100	-2.32328300
Mn	-0.30860400	1.93239800	-0.04193100	C	0.82996500	4.49064900	-3.21003100
Mn	1.29970100	1.10819700	2.04497700	H	-0.07415400	4.36477100	-3.82519100
Mn	-0.28273600	-0.79881300	0.56130700	H	0.61761100	5.34933800	-2.55488700
Mn	0.41417600	-3.40938900	-1.53890000	C	2.05297900	4.75760400	-4.09057900
O	1.42441700	1.92691900	0.41252200	H	2.25555900	3.86941400	-4.70446000
O	-0.53484400	0.82958800	1.44881000	H	2.93619100	4.89468100	-3.45040100
O	1.53921000	-0.88990000	0.71800100	C	1.86886400	5.98608800	-4.98854700
O	-0.17650900	0.28952800	-0.89085100	H	1.01062400	5.86169400	-5.66385800
O	0.79702400	-2.20640800	-0.02243600	H	2.75751800	6.16056400	-5.60885800
O	4.45033800	1.37849400	-2.29578400	H	1.69305400	6.89409800	-4.39451900
H	4.84774700	1.52098700	-1.41278700	N	-2.35664800	1.93626300	-0.43198400
H	3.99122500	2.21061800	-2.52630700	C	-2.96602600	1.50893800	-1.59063600
O	1.84932200	-0.38393000	-3.66888400	H	-2.37965600	1.24717600	-2.46060500
H	2.66074900	-0.88957300	-3.85545200	C	-4.32688600	1.46789200	-1.40034400
H	1.16735000	-1.09712900	-3.54703900	N	-4.52441900	1.89999100	-0.09330200
O	0.00777900	-4.51996700	-3.06199400	H	-5.39502400	1.75770200	0.42556700
H	-0.95966300	-4.46784200	-3.19180500	C	-3.31431000	2.15034300	0.45678600
O	0.69584100	-4.92002100	-0.01351200	H	-3.15787000	2.45910700	1.48011400
H	1.64395500	-5.04881500	-0.23657600	C	-5.43566900	1.07845900	-2.34312400
H	0.70107600	-4.31643200	0.75800800	H	-5.60170000	1.87642400	-3.08252900
O	3.40160600	-1.81463400	-1.77534400	H	-5.09879900	0.20537000	-2.91916500
C	3.43345000	-3.06123200	-1.72382300	C	-6.80793500	0.76879900	-1.68932400
O	2.40148700	-3.83061300	-1.65552300	H	-7.27113300	1.69235600	-1.32390300
C	4.79492800	-3.75777100	-1.78097900	H	-7.47221200	0.35495000	-2.46035300
H	5.18125300	-3.58701100	-2.79775900	C	-6.70518300	-0.16891700	-0.48875900
H	5.46617700	-3.19868800	-1.11537300	O	-6.65763300	0.27223500	0.66700100
C	4.79836300	-5.25157000	-1.45488200	N	-6.60696700	-1.49704800	-0.76095100
H	4.13103000	-5.80428200	-2.12572900	H	-6.62194800	-1.79362200	-1.72887800
H	4.46698400	-5.43579500	-0.42386900	C	-6.23285800	-2.47211200	0.26807600
H	5.80998000	-5.66540300	-1.55586800	H	-6.80310400	-2.22933900	1.17069300
O	-0.11684900	3.03651100	-1.59889000	H	-6.55597900	-3.46092500	-0.08136900
C	0.94123200	3.25872600	-2.31880900	C	-4.72800200	-2.45494700	0.58882000

H	-4.45153200	-1.45060600	0.92737700	C	4.17195500	1.19428100	1.61439600
H	-4.54566900	-3.13737000	1.43167000	O	3.16462600	1.19536200	2.43266800
C	-3.84914100	-2.85541600	-0.60307600	C	5.49141400	1.57419100	2.26290800
H	-4.14254900	-2.27083300	-1.49041300	H	6.31924300	1.44243200	1.56086600
H	-3.96793200	-3.91484700	-0.85990100	H	5.65609400	0.96296600	3.15802700
C	-2.35986000	-2.57493000	-0.42196500	O	0.91629800	-0.17986800	3.50133900
O	-2.06349900	-1.47779300	0.16046500	C	0.14813900	-1.19638100	3.44308900
O	-1.55324900	-3.42223300	-0.89095100	O	-0.43220700	-1.64865100	2.40449500
O	-0.66025600	3.51541000	1.11710700	C	-0.10253500	-1.93121300	4.75162500
C	-0.12791500	3.72799800	2.27063800	H	-0.77591300	-1.29586700	5.34909400
O	0.61259600	2.93633100	2.90916000	H	-0.64181900	-2.85994000	4.53031000
C	-0.44891800	5.09183300	2.87652600	C	1.18066700	-2.20647100	5.55305300
H	-1.52795400	5.26082000	2.75555200	H	1.69881400	-1.25510900	5.72631500
H	0.03761400	5.83994700	2.23193600	H	1.85964600	-2.82502200	4.94690300
H	5.44645900	2.62134400	2.58969900	C	0.89419100	-2.90741000	6.88495500
C	-0.01245600	5.26003100	4.33171200	H	0.24411800	-2.29428800	7.52486500
H	-0.26170300	6.26673400	4.69097500	H	1.82294200	-3.09761500	7.43816500
H	-0.51025500	4.53039800	4.98192400	H	0.39320900	-3.87351400	6.73145200
H	1.06767400	5.11053700	4.43796700	O	0.12290200	-2.28786900	-2.82710000
O	4.11821600	0.91435100	0.40037600				

Pro:

Ca	2.42036100	0.38617100	-1.34572200	O	2.63527300	-3.69765200	-1.73238900
Mn	-0.35323600	1.84976200	-0.03839100	C	5.03561000	-3.51898600	-1.63235900
Mn	1.26333500	1.18968000	2.10451600	H	5.55673800	-3.28339200	-2.57252900
Mn	-0.30028400	-0.87252000	0.58896300	H	5.56894700	-2.95136200	-0.85684400
Mn	0.48306000	-3.32625000	-1.75800500	C	5.08182400	-5.02096600	-1.35203800
O	1.38336300	1.88451600	0.41225400	H	4.54974100	-5.58477300	-2.12710900
O	-0.51788200	0.76534000	1.47782100	H	4.61731300	-5.26089800	-0.38629900
O	1.56432600	-1.23589400	0.46974400	H	6.11984300	-5.37688900	-1.31913300
O	-0.19415500	0.20435900	-0.86383400	O	-0.20988300	2.93407200	-1.61027900
O	0.74918000	-2.33069300	0.04514600	C	0.84417900	3.24529300	-2.30478200
O	4.46708200	1.58977500	-2.19092400	O	1.91876400	2.61967000	-2.28545800
H	4.84167600	1.71148400	-1.29583700	C	0.65404200	4.46712600	-3.19551500
H	3.99234000	2.41574500	-2.40864700	H	-0.21953000	4.26795500	-3.83496900
O	1.87104200	-0.27985900	-3.68105900	H	0.35291000	5.30245900	-2.54494000
H	2.61793600	-0.90065200	-3.77617000	C	1.87382900	4.83768700	-4.04250700
H	1.09313500	-0.88951400	-3.55934600	H	2.16517200	3.97164200	-4.65209600
O	0.05038700	-4.18687800	-3.32508000	H	2.72539900	5.04463200	-3.37864200
H	-0.92197100	-4.20258600	-3.41325500	C	1.61218700	6.05036600	-4.94264000
O	0.83352500	-5.06716800	-0.53354000	H	0.78555000	5.85793300	-5.64097000
H	1.80939700	-5.01122000	-0.67470000	H	2.49946200	6.30016800	-5.53861300
H	0.67279300	-4.72480700	0.36680500	H	1.34607600	6.93838300	-4.35193000
O	3.55856000	-1.65762300	-1.88134500	N	-2.39951500	1.79393300	-0.41418300
C	3.63917500	-2.90546100	-1.75011700	C	-2.99837800	1.31476400	-1.55842500

H	-2.40325700	1.00616200	-2.40688500	O	0.51062400	2.99862300	2.90263600
C	-4.36114800	1.29013200	-1.38072200	C	-0.63037300	5.11005500	2.77736700
N	-4.57023800	1.78294500	-0.09703500	H	-1.70873300	5.24452500	2.61559000
H	-5.44634300	1.66493400	0.41908700	H	-0.14286800	5.85138300	2.12552700
C	-3.36526700	2.05336000	0.45380500	H	5.40098800	2.77252100	2.56499900
H	-3.21914700	2.41270500	1.46189200	C	-0.24655400	5.33589900	4.23967400
C	-5.46334900	0.86702600	-2.31665500	H	-0.53470000	6.34595400	4.55772300
H	-5.61992500	1.63563800	-3.08848700	H	-0.74604600	4.61389800	4.89713200
H	-5.12440500	-0.02919500	-2.85462400	H	0.83310600	5.22040100	4.38512300
C	-6.84161700	0.58841900	-1.66118700	O	4.07717200	0.93793600	0.47165700
H	-7.30592300	1.52737500	-1.33902200	C	4.13347900	1.28872200	1.66737000
H	-7.50081700	0.14267200	-2.41862800	O	3.12737000	1.33078900	2.48545800
C	-6.74638200	-0.29773800	-0.42139500	C	5.45254100	1.71118400	2.28889100
O	-6.70998400	0.19218600	0.71515900	H	6.27853200	1.55051800	1.59076900
N	-6.63904800	-1.63482500	-0.63884800	H	5.62612600	1.14569200	3.21200500
H	-6.63407300	-1.96645900	-1.59555600	O	0.99649000	-0.17163500	3.50993200
C	-6.24303800	-2.56397100	0.42424200	C	0.26335000	-1.21651600	3.47072300
H	-6.81007400	-2.29451300	1.32125800	O	-0.31556000	-1.69257700	2.44519200
H	-6.55519000	-3.56960100	0.11506700	C	0.07252700	-1.95719900	4.78480700
C	-4.73540700	-2.51540400	0.72930200	H	-0.56260300	-1.32106800	5.42152300
H	-4.47210800	-1.50158000	1.04983900	H	-0.48103200	-2.88203000	4.58505400
H	-4.53441000	-3.18154400	1.58109300	C	1.39605400	-2.24555700	5.51455100
C	-3.86115200	-2.91909400	-0.46510100	H	1.92690100	-1.29790600	5.66964700
H	-4.15286600	-2.32814500	-1.34854300	H	2.03821600	-2.86175500	4.86741300
H	-3.99092900	-3.97704300	-0.72412500	C	1.17660300	-2.95788100	6.85308700
C	-2.36516300	-2.66281600	-0.28921200	H	0.56385600	-2.34829800	7.53194000
O	-2.07394700	-1.53933900	0.28577300	H	2.13241300	-3.15697800	7.35458000
O	-1.55290100	-3.50096500	-0.72818000	H	0.66417400	-3.92045300	6.71677000
O	-0.75422100	3.46111000	1.07543500	O	-0.02934700	-1.95328300	-2.77228100
C	-0.25115000	3.73903000	2.22553300				

W1 (hydroxyl)-O4 (oxo)

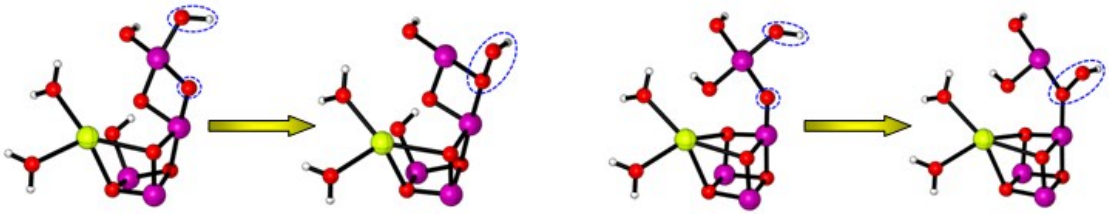

Fig. S9 Pictorial exhibitions for W1 (hydroxyl)-O4 (oxo) nucleophilic attack in the open (left) and closed-cubane (right) structures.

Table S20 Reaction parameters for the open-cubane W1 (hydroxyl)-O4 (oxo) nucleophilic attack:

Spin state	Spin	Gibbs Free energy (a.u.)

	topology (Mn1~Mn4-O4/O5/O6)	Rea	TS	Pro
doublet	ααββα	\	\	\
	αβαβα	-3366.2122	-3366.1888	-3366.2154
	αββαα	\	\	\
	βααβα	-3366.2146	-3366.1883	-3366.2155
	βαβαα	\	\	\
	ββααα	-3366.2133	-3366.1881	-3366.2132
sextet	αααββ	\	\	\
	ααβαβ	-3366.2143	-3366.1919	-3366.2154
	αβααβ	\	\	\
	βααaβ	\	\	\
octet	αααβα	-3366.2178	-3366.1885	-3366.2204
	ααβαα	\	\	\
	αβααα	-3366.2132	-3366.1880	-3366.2154
	βαααα	-3366.2146	-3366.1900	-3366.2157
12-et	αααaβ	\	\	\
14-et	ααααα	-3366.2137	-3366.1899	-3366.2231

Spin state	Spin topology (Mn1~Mn4-O4/O10)	Relative Gibbs Free energy (kcal/mol)			
		$\Delta G^{\neq}$(Rea-TS)	ΔG(Rea-Pro)	ΔG(Rea)	ΔG(Pro)
doublet	ααββα	\	\	\	\
	αβαβα	14.7	-2.0	3.5	4.8
	αββαα	\	\	\	\
	βααβα	16.5	-0.6	2.0	4.8
	βαβαα	\	\	\	\
	ββααα	15.8	0.1	2.8	6.2
sextet	αααββ	\	\	\	\
	ααβαβ	14.1	-0.7	2.2	4.8
	αβααβ	\	\	\	\
	βααaβ	\	\	\	\
octet	αααβα	18.4	-1.6	0.0	1.7
	ααβαα	\	\	\	\
	αβααα	15.8	-1.4	2.9	4.8
	βαααα	15.4	-0.7	2.0	4.6
12-et	αααaβ	\	\	\	\
14-et	ααααα	14.9	-2.9	2.6	0.0

Spin state	Spin topology (Mn1~Mn4- O4/O5/O6)		Mulliken spin density		
			Rea	TS	Pro
doublet	α	Mn1	\	\	\
	α	Mn2	\	\	\

	β	Mn3	\	\	\
	β	Mn4	\	\	\
		O4	\	\	\
	α	O6	\	\	\
		O5	\	\	\
	α	Mn1	2.94	2.95	2.95
	β	Mn2	-2.91	-2.91	-2.91
	α	Mn3	2.87	3.41	3.82
	β	Mn4	-2.43	-2.88	-2.81
		O4	0.29	0.06	0.00
	α	O6	0.07	0.45	0.01
		O5	0.07	-0.10	-0.12
	α	Mn1	\	\	\
	β	Mn2	\	\	\
	β	Mn3	\	\	\
	α	Mn4	\	\	\
		O4	\	\	\
	α	O6	\	\	\
		O5	\	\	\
	β	Mn1	-2.93	-2.92	-2.90
	α	Mn2	2.93	2.93	2.94
	α	Mn3	2.86	3.41	3.83
	β	Mn4	-2.62	-2.88	-2.81
		O4	0.42	0.06	0.00
	α	O6	0.03	0.46	0.01
		O5	0.16	-0.10	-0.12
	β	Mn1	\	\	\
	α	Mn2	\	\	\
	β	Mn3	\	\	\
	α	Mn4	\	\	\
		O4	\	\	\
	α	O6	\	\	\
		O5	\	\	\
	β	Mn1	-2.96	-2.94	-2.92
	β	Mn2	-2.95	-2.93	-2.93
	α	Mn3	2.82	3.41	3.85
	α	Mn4	2.86	2.86	2.89
		O4	0.62	0.09	0.00
	α	O6	0.08	0.48	0.00
		O5	0.46	0.05	0.12
sextet	α	Mn1	\	\	\
	α	Mn2	\	\	\
	α	Mn3	\	\	\
	β	Mn4	\	\	\

		O4	\	\	\
	β	O6	\	\	\
		O5	\	\	\
	α	Mn1	2.95	2.94	2.92
	α	Mn2	2.94	2.94	2.94
	β	Mn3	-2.85	-3.39	-3.80
	α	Mn4	2.53	2.89	2.81
		O4	-0.34	-0.06	0.00
	β	O6	-0.05	-0.46	-0.01
		O5	-0.11	0.10	0.12
	α	Mn1	\	\	\
	β	Mn2	\	\	\
	α	Mn3	\	\	\
	α	Mn4	\	\	\
		O4	\	\	\
	β	O6	\	\	\
		O5	\	\	\
	β	Mn1	\	\	\
	α	Mn2	\	\	\
	α	Mn3	\	\	\
	α	Mn4	\	\	\
		O4	\	\	\
	β	O6	\	\	\
		O5	\	\	\
	α	Mn1	2.96	2.97	2.97
	α	Mn2	2.95	2.96	2.96
	α	Mn3	2.87	3.43	3.85
	β	Mn4	-2.86	-2.88	-2.81
		O4	0.88	0.06	0.00
	α	O6	-0.05	0.46	0.01
		O5	0.04	-0.10	-0.12
	α	Mn1	\	\	\
octet	α	Mn2	\	\	\
	β	Mn3	\	\	\
	α	Mn4	\	\	\
		O4	\	\	\
	α	O6	\	\	\
		O5	\	\	\
	α	Mn1	2.94	2.95	2.95
	β	Mn2	-2.91	-2.90	-2.91
	α	Mn3	2.84	3.43	3.87
	α	Mn4	2.86	2.87	2.90
	α	O4	0.65	0.09	0.00
		O6	0.08	0.48	0.01

		O5	0.45	0.05	0.12
	β	Mn1	-2.93	-2.92	-2.90
	α	Mn2	2.92	2.93	2.94
	α	Mn3	2.85	3.43	3.87
	α	Mn4	2.86	2.87	2.89
		O4	0.62	0.09	0.00
	α	O6	0.08	0.49	0.00
		O5	0.46	0.05	0.12
12-et	α	Mn1	\	\	\
	α	Mn2	\	\	\
	α	Mn3	\	\	\
	α	Mn4	\	\	\
		O4	\	\	\
	β	O6	\	\	\
		O5	\	\	\
14-et	α	Mn1	2.97	2.97	2.97
	α	Mn2	2.95	2.96	2.97
	α	Mn3	2.88	3.45	3.89
	α	Mn4	2.86	2.87	2.90
		O4	0.66	0.09	0.00
	α	O6	0.08	0.50	0.01
		O5	0.45	0.04	0.10

‘\’ denotes TSs for some spin states do not exist due to the failure of IRC verification on reactants concerning W1 returning back to Mn4.

Rea:

Ca	2.55662900	-0.04542100	-1.15682300	H	-1.43421900	-4.91285500	-2.27587600
Mn	-0.00847500	1.91641400	-0.16955800	O	3.16045100	-2.31852300	-1.49046500
Mn	1.23741600	0.49273400	1.89320100	C	2.94593800	-3.53575800	-1.44852200
Mn	-0.18941400	-1.49204700	0.58136200	O	1.78604500	-4.11873800	-1.54437000
Mn	0.03704300	-3.36999900	-1.54897400	C	4.08631000	-4.53767400	-1.27389700
O	1.62667300	1.55531100	0.47785500	H	3.93065500	-5.01864500	-0.29668900
O	-0.45080400	0.40538700	0.96247900	H	3.95144700	-5.33394200	-2.01846300
O	1.49976100	-1.07429200	1.04785600	C	5.47587300	-3.90722900	-1.36198000
O	0.20849300	-1.48773700	-1.16502800	H	5.60282200	-3.12684800	-0.60343200
O	0.07223000	-3.30071100	0.19963300	H	5.64050100	-3.44235200	-2.34156800
O	4.24756400	0.60381500	-2.93152500	H	6.24942800	-4.67085900	-1.20962800
H	4.01718900	1.55563300	-2.91441200	O	0.63227800	3.42494200	-1.13953000
H	3.66714600	0.23748800	-3.63116100	C	1.73710400	3.44615600	-1.83419000
O	1.73115000	-0.39285100	-3.56593700	O	2.50442200	2.48559500	-2.01237400
H	1.01403300	0.26393800	-3.46147100	C	2.02752100	4.81925500	-2.43666900
H	1.27310200	-1.28004200	-3.52383200	H	1.12593000	5.14255100	-2.97789100
O	0.34863200	-2.72799600	-3.28119000	H	2.13119000	5.52384700	-1.59706000
H	0.66723600	-3.51021400	-3.77211600	C	3.26080000	4.87055000	-3.34179500
O	-0.46215600	-4.96657900	-2.16882300	H	3.13766100	4.15020200	-4.16328900

H	4.13969300	4.53795100	-2.77269300	O	-1.96203100	-3.05336800	-1.63128600
C	3.50797500	6.27151500	-3.91238800	O	-0.40659100	3.16923300	1.34454300
H	2.65393600	6.61603800	-4.51243900	C	0.10555800	3.09854200	2.51267500
H	3.66664900	7.00656100	-3.11086700	O	0.76970800	2.12636200	2.96776500
H	4.39592400	6.28553500	-4.55750600	C	-0.10907700	4.30958800	3.41096500
N	-2.02117600	2.24775600	-0.64174400	H	-1.15252100	4.63007300	3.28673500
C	-2.64682000	2.00046600	-1.84560900	H	0.50008300	5.11863600	2.97882300
H	-2.06640800	1.75103300	-2.72268900	C	0.24410300	4.08879800	4.88194000
C	-4.00766900	2.11712900	-1.68634100	H	0.08346200	5.01206500	5.45278700
N	-4.18730700	2.45996900	-0.35134900	H	-0.37507500	3.29926000	5.32481400
H	-5.08627800	2.40072900	0.13617500	H	1.29114000	3.78742700	4.99389400
C	-2.97458500	2.50950100	0.24177700	O	4.16445200	0.20900400	0.65357200
H	-2.81181300	2.71236300	1.28928700	C	4.09835700	0.40436100	1.87709500
C	-5.12997400	1.94770400	-2.67761700	O	3.00191300	0.54847200	2.57163500
H	-5.16440600	2.80967000	-3.36075400	C	5.35728900	0.49300900	2.72155900
H	-4.89717700	1.07831400	-3.30834600	H	5.35855400	-0.31645000	3.46255300
C	-6.54969200	1.78345800	-2.07448400	H	5.36938600	1.44021100	3.27444700
H	-6.89738500	2.73563300	-1.65813400	H	6.24335400	0.41606800	2.08608500
H	-7.23950600	1.51209900	-2.88529700	O	0.57894900	-0.45694400	3.51459400
C	-6.61016600	0.76651200	-0.93614300	C	-0.20829300	-1.45312200	3.48978600
O	-6.55174500	1.12640200	0.24737600	O	-0.71532700	-1.96674600	2.44318700
N	-6.66668700	-0.54283400	-1.29184200	C	-0.56333100	-2.10808100	4.81562300
H	-6.68788000	-0.77601500	-2.27689800	H	-1.56155000	-2.55235400	4.71031800
C	-6.47650300	-1.62251100	-0.31724400	H	0.13540100	-2.95285700	4.93452500
H	-7.05277900	-1.36146400	0.57640700	C	-0.48154300	-1.18373300	6.03597800
H	-6.91324400	-2.53247000	-0.74806500	H	-1.17473800	-0.34077000	5.89797000
C	-5.00210500	-1.84013400	0.06537400	H	0.52360400	-0.74707600	6.08791500
H	-4.61212700	-0.92526200	0.52448000	C	-0.81049100	-1.91753300	7.34059600
H	-4.95834200	-2.62123300	0.83757000	H	-1.82443400	-2.34140700	7.31928200
C	-4.12519900	-2.23576800	-1.12592200	H	-0.75087900	-1.23898700	8.20136800
H	-4.21877800	-1.48661600	-1.92849200	H	-0.10976300	-2.74520300	7.51963500
H	-4.43634400	-3.19489200	-1.56051200	O	0.12285100	0.97143300	-1.72212500
C	-2.63068300	-2.32269200	-0.82633200	H	-0.25166100	0.06098400	-1.59466000
O	-2.17404300	-1.65556000	0.14140100				

TS:

Ca	2.48225900	0.14855500	-1.19775600	O	0.13502900	-3.51741400	-0.04275600
Mn	-0.10102500	1.95464300	0.03272500	O	3.97163300	0.91382300	-3.09818600
Mn	1.20461100	0.41803000	1.93101100	H	3.72844400	1.85839900	-3.00471500
Mn	-0.13473500	-1.61685000	0.52553500	H	3.33857500	0.57308900	-3.76484900
Mn	0.25349400	-3.08083700	-1.85772000	O	1.45539400	-0.12859700	-3.66908000
O	1.56520600	1.58396600	0.59580000	H	0.74476300	0.47800600	-3.37486700
O	-0.47553300	0.40652700	1.05241800	H	1.02288200	-1.02106300	-3.73571300
O	1.51278700	-1.10871800	1.01000600	O	0.29093500	-2.74112900	-3.67239800
O	0.39655700	-1.43092200	-1.28173200	H	1.04133800	-3.23885100	-4.04714400

O	-0.18900900	-4.98323800	-0.94759700	H	-6.99181200	-1.84060500	0.18570500
H	-1.16254300	-4.94305200	-0.84006500	H	-6.73459500	-2.74737600	-1.31651700
O	3.39766600	-2.01719000	-1.65648200	C	-4.90132400	-2.11578600	-0.30262900
C	3.17866700	-3.22330600	-1.80028500	H	-4.58116900	-1.27653400	0.32392100
O	2.00351800	-3.76011000	-2.00465300	H	-4.84909300	-3.01552700	0.32748700
C	4.30195400	-4.25250400	-1.75552400	C	-3.95251500	-2.26010000	-1.49695900
H	4.12164000	-4.86904400	-0.86200800	H	-4.04518800	-1.38210000	-2.15645400
H	4.17282000	-4.93115900	-2.61011600	H	-4.19335400	-3.13716200	-2.11148000
C	5.69955900	-3.63469200	-1.72716200	C	-2.47517100	-2.33617000	-1.12774600
H	5.81799500	-2.97314400	-0.86203000	O	-2.08558700	-1.74762900	-0.08196000
H	5.88744700	-3.03540800	-2.62615800	O	-1.73694800	-2.98060100	-1.95034600
H	6.46218000	-4.42194800	-1.67228300	O	-0.46045400	3.11633100	1.61454200
O	0.47820100	3.53606900	-0.89833600	C	0.07182700	2.95866300	2.76518400
C	1.55192400	3.62155600	-1.62666500	O	0.75274900	1.96113000	3.13377200
O	2.33593600	2.68822600	-1.88154100	C	-0.13615100	4.09529100	3.75725700
C	1.79841100	5.02860600	-2.16818100	H	-1.17536800	4.43549800	3.65437200
H	0.86535100	5.37339100	-2.63788400	H	0.48450800	4.92956400	3.39487500
H	1.94504800	5.68548300	-1.29662800	C	0.20882500	3.75254800	5.20681500
C	2.97822500	5.14599300	-3.13613700	H	0.05720600	4.62878100	5.84973200
H	2.81422000	4.47404600	-3.99113700	H	-0.42199700	2.93796000	5.58327100
H	3.89004400	4.78964200	-2.63775100	H	1.25151900	3.42979300	5.29681600
C	3.18331500	6.58023200	-3.63653800	O	4.11030600	0.32023700	0.60966700
H	2.29422700	6.95072800	-4.16614400	C	4.07134800	0.40293500	1.84828900
H	3.38205900	7.26867400	-2.80316800	O	2.99343200	0.44921900	2.58139400
H	4.03315400	6.64120300	-4.32863000	C	5.35351200	0.45462200	2.66193500
N	-2.13039500	2.26467200	-0.37555100	H	5.40389200	-0.42180000	3.32061700
C	-2.75642800	2.18716500	-1.60114900	H	5.35278900	1.34409300	3.30371200
H	-2.17563200	2.12645200	-2.51079700	H	6.22201900	0.46939700	1.99822600
C	-4.11928900	2.18506700	-1.41942200	O	0.55407900	-0.66894100	3.49649500
N	-4.30107800	2.28159400	-0.04449000	C	-0.19461500	-1.68302700	3.40662600
H	-5.18613600	2.07833000	0.42857600	O	-0.66929900	-2.16466100	2.32115500
C	-3.08406600	2.30778900	0.54343500	C	-0.56900300	-2.42363300	4.68087500
H	-2.91933800	2.32975800	1.61033300	H	-1.62994800	-2.69913100	4.60028600
C	-5.24046300	2.11417700	-2.42319900	H	-0.01358600	-3.37534300	4.65556700
H	-5.34457000	3.07831700	-2.94332800	C	-0.28246600	-1.66954500	5.98277600
H	-4.95612200	1.38824100	-3.19779300	H	-0.83821400	-0.72094900	5.98155800
C	-6.63635900	1.74597000	-1.85707800	H	0.78019100	-1.39738000	6.01498200
H	-7.04377500	2.58345200	-1.27955100	C	-0.65676100	-2.49223600	7.22064600
H	-7.31670300	1.57296500	-2.70214200	H	-1.72489500	-2.75205000	7.22325100
C	-6.61428200	0.54459800	-0.91383900	H	-0.44720700	-1.93525200	8.14292600
O	-6.56824600	0.69557800	0.31434700	H	-0.08795100	-3.43182400	7.26257400
N	-6.58849200	-0.68409000	-1.49190500	O	0.00721900	1.08476600	-1.58747500
H	-6.61511400	-0.74702100	-2.50198600	H	-0.38632400	0.19033000	-1.49459700
C	-6.36905800	-1.90698000	-0.71288000				

Pro:

Ca	-2.53167200	0.37103600	-0.87225700	N	2.03475700	-1.99177500	-1.35686400
Mn	0.04583600	-1.87290100	-0.70614400	C	2.61014900	-1.34602700	-2.43085000
Mn	-1.09263400	-1.26612800	1.71860600	H	1.99475600	-0.84989100	-3.16846400
Mn	0.23090600	1.17238200	1.19054300	C	3.97894100	-1.45282700	-2.34938200
Mn	-0.18883200	3.67529400	-0.71900500	N	4.21561300	-2.20114600	-1.20223300
O	-1.57591600	-1.77560400	0.05581200	H	5.12654300	-2.25595100	-0.73785900
O	0.55261900	-0.95487000	0.83735200	C	3.02520500	-2.48606400	-0.62846500
O	-1.40981900	0.49620300	1.46816700	H	2.90557400	-3.01528900	0.30505100
O	-0.46290100	2.00977100	-0.33664600	C	5.06020700	-0.92798100	-3.25758200
O	0.11510300	4.36996600	0.98531900	H	5.11566700	-1.53720600	-4.17232800
O	-4.23509400	0.40691800	-2.76664300	H	4.76587700	0.07782600	-3.58822900
H	-4.04446400	-0.51108300	-3.05118100	C	6.48871100	-0.87773800	-2.65410000
H	-3.61016500	0.93571600	-3.30780000	H	6.89526000	-1.89106100	-2.55974300
O	-1.68036000	1.38708200	-3.18045300	H	7.13841400	-0.33124100	-3.35130100
H	-1.01962600	0.66212900	-3.15155700	C	6.53785500	-0.26231900	-1.25694100
H	-1.14830300	2.21580800	-3.02587900	O	6.51887700	-0.97300100	-0.24329500
O	-0.23329900	3.67035500	-2.57612200	N	6.54392400	1.09459500	-1.18865000
H	-0.91203900	4.31887400	-2.84175100	H	6.54265000	1.62323000	-2.05213300
O	0.45444300	5.53361200	0.17836600	C	6.36330000	1.81124800	0.07793300
H	1.42869500	5.43234800	0.09130700	H	6.95626100	1.28833300	0.83528900
O	-3.33711400	2.62348100	-0.54694600	H	6.78688500	2.81568000	-0.05008800
C	-3.10564100	3.83562000	-0.54644000	C	4.89455000	1.88104200	0.53196400
O	-1.93242500	4.39145200	-0.72164700	H	4.51804600	0.86272100	0.67937300
C	-4.21508200	4.86074400	-0.33388900	H	4.85891700	2.37135900	1.51488800
H	-3.98425200	5.38329900	0.60657200	C	3.99942400	2.62849000	-0.45876100
H	-4.12247100	5.62212200	-1.12119000	H	4.08698000	2.18359100	-1.46254300
C	-5.61639500	4.25179500	-0.30010800	H	4.30341700	3.67880300	-0.57070000
H	-5.70372800	3.51146000	0.50283700	C	2.50651300	2.61214800	-0.14167600
H	-5.85040200	3.74162900	-1.24201600	O	2.08486100	1.78467800	0.71658000
H	-6.36743800	5.03484300	-0.13501400	O	1.80699200	3.43809100	-0.81745300
O	-0.63110100	-2.86194900	-2.21676500	O	0.42627900	-3.61161400	0.18688200
C	-1.75764000	-2.62346700	-2.81958800	C	-0.01192100	-3.93456400	1.34438000
O	-2.51488300	-1.66236700	-2.58829800	O	-0.61807400	-3.17237100	2.14833800
C	-2.10295800	-3.66173900	-3.88555900	C	0.21650700	-5.38239100	1.75875400
H	-1.22731800	-3.76648400	-4.54344300	H	1.22434200	-5.66558300	1.42668100
H	-2.19699100	-4.63072300	-3.37110600	H	-0.47514500	-5.98391600	1.14851700
C	-3.36481600	-3.35494300	-4.69552100	C	0.00878700	-5.66275600	3.24742100
H	-3.25308800	-2.37609000	-5.18377700	H	0.16574200	-6.72822000	3.45783400
H	-4.21839900	-3.25891500	-4.01044800	H	0.71018300	-5.08510500	3.86197500
C	-3.65999800	-4.42930800	-5.74818700	H	-1.00476800	-5.39060400	3.56055800
H	-2.83281900	-4.52459500	-6.46580700	O	-4.06679500	-0.55005500	0.78260500
H	-3.80833700	-5.41388100	-5.28273300	C	-3.95877300	-1.15997200	1.85939100
H	-4.56813000	-4.18937900	-6.31626900	O	-2.84396800	-1.54200300	2.41835300

C	-5.19273500	-1.53322200	2.66397200	C	0.36368400	-0.83732700	6.26507900
H	-5.14512200	-1.05799400	3.65192200	H	0.88729200	-1.73575100	5.90948000
H	-5.21642200	-2.61799000	2.82594100	H	-0.70787200	-1.06290500	6.18852300
H	-6.09688100	-1.21223800	2.14008000	C	0.74164500	-0.55360700	7.72318100
O	-0.34330800	-0.87264700	3.55604100	H	1.81759200	-0.35409700	7.82820400
C	0.33162100	0.14442100	3.88033600	H	0.49699800	-1.40772800	8.36763700
O	0.74607900	1.05061100	3.07486600	H	0.20365800	0.32218900	8.11272700
C	0.69737900	0.33896200	5.34345600	O	-0.13950100	-0.33471300	-1.73013000
H	1.76872200	0.58502800	5.38027800	H	0.35414800	0.40868600	-1.33334400
H	0.17634900	1.25211100	5.67323100				

Table S21 Reaction parameters for the closed-cubane W1 (hydroxyl)-O4 (oxo) nucleophilic attack:

Spin state	Spin topology (Mn1~Mn4-O4/O6/O7)	Gibbs Free energy (a.u.)		
		Rea	TS	Pro
doublet	ααββα	-3366.2156	-3366.1865	-3366.1882
	αβαβα	-3366.2101	-3366.1868	-3366.2034
	αββαα	-3366.2189	-3366.1871	-3366.1881
	βααβα	-3366.2098	-3366.1853	-3366.2005
	βαβαα	-3366.2190	-3366.1846	-3366.1870
	ββααα	-3366.2131	-3366.1860	-3366.2008
sextet	αααββ	-3366.2177	-3366.1862	-3366.1879
	ααβαβ	-3366.2063	-3366.1850	-3366.1994
	αβααβ	-3366.2155	-3366.1851	-3366.1867
	βαααβ	-3366.2167	-3366.1875	-3366.1899
octet	αααβα	-3366.2146	-3366.1899	-3366.2060
	ααβαα	-3366.2185	-3366.1865	-3366.1891
	αβααα	-3366.2082	-3366.1851	-3366.2007
	βαααα	-3366.2089	-3366.1861	-3366.2002
12-et	aaaaβ	-3366.2228	-3366.1887	-3366.1888
14-et	aaaaa	-3366.2112	-3366.1879	-3366.2024

Spin state	Spin topology (Mn1~Mn4-O4/O10)	Relative Gibbs Free energy (kcal/mol)			
		$\Delta G^{\neq}$(Rea-TS)	ΔG(Rea-Pro)	ΔG(Rea)	ΔG(Pro)
doublet	ααββα	18.3	17.2	4.5	11.2
	αβαβα	14.6	4.2	8.0	1.6
	αββαα	20.0	19.3	2.4	11.2
	βααβα	15.4	5.8	8.2	3.5
	βαβαα	21.6	20.1	2.4	11.9
	ββααα	17.0	7.7	6.1	3.3
sextet	αααββ	19.8	18.7	3.2	11.4
	ααβαβ	13.4	4.3	10.4	4.1

	αβααβ	19.1	18.1	4.6	12.1
	βαααβ	18.3	16.8	3.8	10.1
octet	αααβα	15.5	5.4	5.1	0.0
	ααβαα	20.1	18.4	2.7	10.6
	αβααα	14.5	4.7	9.2	3.3
	βαααα	14.3	5.5	8.7	3.6
12-et	αααββ	21.4	21.3	0.0	10.8
14-et	ααααα	14.6	5.5	7.3	2.3

Spin state	Spin topology (Mn1~Mn4- O4/O6/O7)		Mulliken spin density		
			Rea	TS	Pro
doublet	α	Mn1	2.93	2.96	2.97
	α	Mn2	2.94	2.94	2.93
	β	Mn3	-2.81	-2.25	-1.99
	β	Mn4	-2.93	-2.91	-2.91
	α	O4	0.49	0.06	-0.01
		O6	0.37	0.23	0.02
	α	Mn1	2.93	2.93	2.89
	β	Mn2	-2.94	-2.93	-2.88
	α	Mn3	2.86	3.48	3.88
	β	Mn4	-2.92	-2.90	-2.90
	α	O4	0.47	0.34	0.00
		O6	0.62	-0.06	0.01
	α	Mn1	-2.92	2.97	2.98
	β	Mn2	-2.92	-2.93	-2.94
	β	Mn3	-2.84	-2.15	-2.02
	α	Mn4	2.84	2.90	2.91
	α	O4	0.43	0.03	0.00
		O6	0.47	0.14	0.03
	β	Mn1	-2.92	-2.93	-2.93
	α	Mn2	2.93	2.94	2.95
	α	Mn3	2.89	3.51	3.87
	β	Mn4	-2.92	-2.90	-2.90
	α	O4	0.47	0.12	0.01
		O6	0.61	-0.06	0.01
	β	Mn1	-2.92	-2.92	-2.92
	α	Mn2	2.94	2.95	2.94
	β	Mn3	-2.82	-2.12	-2.01
	α	Mn4	2.84	2.90	2.91
	α	O4	0.42	0.02	0.00
		O6	0.47	0.12	0.03
	β	Mn1	-2.93	-2.94	-2.93
	β	Mn2	-2.94	-2.94	-2.92
	α	Mn3	2.87	3.49	3.0

	α	Mn4	2.85	2.88	3.04
	α	O4	0.54	0.13	-0.02
		O6	0.56	0.33	0.00
sextet	α	Mn1	2.93	2.92	2.93
	α	Mn2	2.92	2.94	2.94
	α	Mn3	2.84	2.22	1.98
	β	Mn4	-2.82	-2.88	-2.90
	β	O4	-0.49	-0.05	-0.01
		O6	-0.41	-0.22	-0.01
	α	Mn1	2.93	2.93	2.94
	α	Mn2	2.94	2.94	2.93
	β	Mn3	-2.84	-3.47	-3.83
	α	Mn4	2.89	2.89	2.90
	β	O4	-0.42	-0.35	-0.01
		O6	-0.66	0.07	-0.02
	α	Mn1	2.92	2.92	2.94
	β	Mn2	-2.93	-2.93	-2.91
	α	Mn3	2.83	2.25	1.98
	α	Mn4	2.93	2.91	2.91
	β	O4	-0.49	-0.06	0.01
		O6	-0.37	-0.22	-0.02
	β	Mn1	-2.92	-2.96	-2.99
	α	Mn2	2.93	2.93	2.93
	α	Mn3	2.85	2.28	2.01
	α	Mn4	2.93	2.91	2.91
	β	O4	-0.50	-0.07	0.00
		O6	-0.37	-0.23	-0.02
octet	α	Mn1	2.93	3.93	2.92
	α	Mn2	2.93	2.94	2.95
	α	Mn3	2.89	3.49	3.89
	β	Mn4	-2.92	-2.90	-2.90
	α	O4	0.47	0.13	0.01
		O6	0.61	0.35	0.01
	α	Mn1	2.93	2.96	2.97
	α	Mn2	2.94	2.93	2.92
	β	Mn3	-2.79	-2.21	-1.97
	α	Mn4	2.82	2.88	2.90
	α	O4	0.48	0.05	0.01
		O6	0.42	0.23	0.01
	α	Mn1	2.92	2.92	2.92
	β	Mn2	-2.93	-2.93	-2.91
	α	Mn3	2.88	3.49	3.87
	α	Mn4	2.84	2.87	2.94
	α	O4	0.50	0.11	0.00

		O6	0.62	0.37	0.02
	β	Mn1	-2.92	-2.92	-2.92
	α	Mn2	2.92	2.94	2.94
	α	Mn3	2.91	3.51	3.86
	α	Mn4	2.83	2.87	2.93
	α	O4	0.62	0.11	0.00
		O6	0.50	0.37	0.02
12-et	α	Mn1	2.93	2.92	2.93
	α	Mn2	2.92	2.93	2.94
	α	Mn3	2.87	2.15	2.02
	α	Mn4	2.95	2.91	2.91
	β	O4	-0.51	-0.04	-0.01
		O6	-0.40	-0.12	-0.02
14-et	α	Mn1	2.92	2.93	2.93
	α	Mn2	2.93	2.94	2.94
	α	Mn3	2.91	3.51	3.89
	α	Mn4	2.84	2.87	2.94
	α	O4	0.49	0.11	0.00
		O6	0.61	0.37	0.02

Rea:

Ca	-2.70440500	0.40908000	-0.82922100	H	-4.32473400	4.74260700	-1.07091800
Mn	-0.16030400	-1.76329300	-0.21265000	H	-3.03720800	5.95971400	-1.29423900
Mn	-1.40255200	-0.95230400	2.05010800	C	-3.71613900	5.04262500	-3.14301600
Mn	0.21770800	0.89492000	0.81005200	H	-4.08572100	4.07361100	-3.50133400
Mn	0.48596100	3.36942100	-1.43113600	H	-2.81052300	5.29665200	-3.70669400
O	-1.83927600	-1.64878500	0.43142800	H	-4.48005400	5.80164700	-3.35340000
O	0.37040900	-0.95749400	1.37515000	O	-0.72853600	-2.65074200	-1.82717500
O	-1.51061100	0.70413900	1.36216900	C	-1.87860900	-2.58705000	-2.42272800
O	-0.15802700	-0.02871600	-0.80574600	O	-2.70185300	-1.65808800	-2.29588000
O	-0.13918200	2.46153100	0.11181800	C	-2.15661500	-3.76548400	-3.35072400
O	-5.00534500	-0.20937500	-1.64116100	H	-1.30530500	-3.84554600	-4.04385200
H	-5.33036900	-0.47517300	-0.75777500	H	-2.11203400	-4.67666500	-2.73453100
H	-4.72624400	-1.03016400	-2.09190600	C	-3.47952400	-3.68769500	-4.11673400
O	-2.33194100	1.06832900	-3.20966900	H	-3.51180500	-2.75282600	-4.69370600
H	-2.14383900	0.28603800	-3.75401800	H	-4.31011000	-3.62997800	-3.39895800
H	-1.48623000	1.59786800	-3.18908100	C	-3.68493700	-4.88540900	-5.05084200
O	1.18711000	4.50751200	-2.62877800	H	-2.88487100	-4.94815900	-5.80175200
H	2.13848700	4.29421200	-2.68229400	H	-4.63969700	-4.81063900	-5.58695000
O	0.93777200	4.33603400	0.22800000	H	-3.68893300	-5.83190900	-4.49228100
H	0.08947300	4.73451800	0.51114800	N	1.78087800	-2.08551200	-0.86376100
O	-2.72822600	2.78473400	-0.96277100	C	2.42430000	-1.47973800	-1.92285100
C	-2.37684000	3.91322600	-1.33639100	H	1.91131900	-0.76411000	-2.55094300
O	-1.15554200	4.31203300	-1.56128500	C	3.72344200	-1.92718100	-1.98132800
C	-3.41637600	4.98782600	-1.63340800	N	3.84226400	-2.83407100	-0.93385600

H	4.74190100	-3.13436900	-0.54953700	H	0.65603800	-5.49171700	2.25237200
C	2.66161700	-2.88305100	-0.27775100	H	-1.05139900	-5.73693600	1.94980300
H	2.46708100	-3.48285400	0.59875200	H	-5.40234400	-0.25884400	3.92926600
C	4.83699100	-1.60002500	-2.94195800	C	-0.60399900	-5.24249700	4.02275800
H	4.71647800	-2.17514000	-3.87244300	H	-0.51052300	-6.28910000	4.33912300
H	4.73165300	-0.54499900	-3.22874100	H	0.11062600	-4.64414100	4.60093500
C	6.27904300	-1.85970500	-2.42232100	H	-1.60944700	-4.89009900	4.27663600
H	6.49488700	-2.93396200	-2.41836200	O	-4.33311300	-0.19100300	0.98972500
H	6.98803800	-1.38735100	-3.11578900	C	-4.25593100	-0.63850600	2.15122400
C	6.47912600	-1.36606500	-0.99188500	O	-3.16027900	-0.98441700	2.75499600
O	6.36678900	-2.13677700	-0.03001200	C	-5.50220300	-0.82756400	2.99678200
N	6.69859700	-0.03285900	-0.83724000	H	-5.60434600	-1.88489200	3.27175400
H	6.73135800	0.53996100	-1.67195900	H	-6.39005600	-0.49535200	2.45213500
C	6.47731400	0.63960800	0.44827200	O	-0.64564700	-0.15048800	3.71452800
H	6.89859900	-0.00391900	1.22638000	C	0.17289400	0.82380600	3.70009500
H	7.04768900	1.57708500	0.43674500	O	0.66121700	1.39475500	2.66695300
C	4.98252200	0.89088800	0.72360300	C	0.63018700	1.36846900	5.04337400
H	4.46081300	-0.07281100	0.73843500	H	0.09100500	0.83068400	5.83174800
H	4.87262300	1.31728800	1.73003200	H	1.70004300	1.12825800	5.14487800
C	4.33798100	1.81749600	-0.31076300	C	0.43419700	2.88976000	5.17078800
H	4.64094700	1.53766700	-1.33070700	H	-0.63255700	3.12697600	5.04360900
H	4.66701700	2.85814600	-0.17810400	H	0.96523800	3.38500300	4.34803800
C	2.80954000	1.84135800	-0.33915400	C	0.92541000	3.42502900	6.51959800
O	2.18643600	1.07502600	0.44987600	H	0.38934200	2.95660900	7.35673500
O	2.32317700	2.63134000	-1.20842400	H	0.77384900	4.50975100	6.59129400
O	0.01191400	-3.52782100	0.78962600	H	1.99764400	3.22750300	6.65925100
C	-0.46718600	-3.70533000	1.96345500	O	0.08395500	2.02822900	-2.59745300
O	-1.04225000	-2.83706800	2.68710400	H	0.15183000	1.19769200	-2.06140100
C	-0.34147600	-5.11879700	2.52148500				

TS:

Ca	-2.71914100	0.51294200	-0.69564400	H	-2.30771800	0.31926700	-3.55666900
Mn	-0.25813900	-1.70022100	-0.26151000	H	-1.50635000	1.61044900	-3.15767700
Mn	-1.38545000	-0.91445900	2.07547300	O	1.32071500	4.54162400	-2.55520100
Mn	0.27818900	0.87166600	0.87254000	H	2.25809700	4.28886400	-2.66474900
Mn	0.58133400	3.33751800	-1.46642400	O	0.72568900	3.88339900	0.69113500
O	-1.91279600	-1.55054600	0.45503200	H	-0.08484500	4.39106000	0.90596400
O	0.35422900	-0.98037200	1.33295200	O	-2.63406900	2.90275300	-0.85243200
O	-1.44100900	0.77003500	1.43975400	C	-2.26308700	3.99161400	-1.30682900
O	-0.22446700	0.03271400	-0.82703300	O	-1.02761500	4.32784800	-1.58501400
O	0.00190300	2.57023200	0.17900000	C	-3.26769100	5.08456100	-1.64448600
O	-5.06332400	0.02158900	-1.47383900	H	-4.17874300	4.89395300	-1.06579900
H	-5.36816100	-0.24766300	-0.58364900	H	-2.85463400	6.05812800	-1.35229700
H	-4.82518800	-0.79967700	-1.94741100	C	-3.57667100	5.08086300	-3.15377200
O	-2.39608800	1.18207200	-3.11537100	H	-3.97179800	4.10651500	-3.46698400

H	-2.66965800	5.28908400	-3.73370000	C	4.41221300	1.71359300	-0.41745300
H	-4.32350900	5.84872100	-3.39071300	H	4.64628300	1.41129100	-1.44981100
O	-0.91139100	-2.56644500	-1.87640800	H	4.79950900	2.73681500	-0.31193000
C	-2.06721500	-2.44556300	-2.43848400	C	2.88733500	1.79778000	-0.36350600
O	-2.84615400	-1.47741700	-2.28381400	O	2.25708600	1.00493200	0.37357400
C	-2.43222000	-3.60133900	-3.36637200	O	2.40512000	2.69494600	-1.14794300
H	-1.59570100	-3.73669900	-4.06861800	O	-0.11996200	-3.51407600	0.70049400
H	-2.44082400	-4.51402000	-2.75060000	C	-0.57513400	-3.70364400	1.87984500
C	-3.75596400	-3.43867300	-4.11740700	O	-1.08992600	-2.83346600	2.64657600
H	-3.73543200	-2.50330200	-4.69439100	C	-0.50445100	-5.13845400	2.39520200
H	-4.57310700	-3.32791900	-3.39063200	H	0.45514800	-5.56025200	2.06718500
C	-4.04863400	-4.61997200	-5.04920700	H	-1.27704700	-5.69887700	1.84550300
H	-3.26267500	-4.73370000	-5.80906000	H	-5.29542700	-0.17601100	4.12785200
H	-5.00272400	-4.48414600	-5.57459700	C	-0.70092600	-5.28964500	3.90414900
H	-4.10676800	-5.56460000	-4.49044800	H	-0.65509000	-6.34834200	4.19000800
N	1.66263700	-2.08920500	-0.97364600	H	0.07520900	-4.75018600	4.46085400
C	2.30970900	-1.50779300	-2.04325900	H	-1.66971700	-4.88532100	4.21632400
H	1.81206300	-0.77388200	-2.66269800	O	-4.33558000	-0.02112900	1.13868000
C	3.59052400	-2.00256900	-2.12636600	C	-4.22879500	-0.50098000	2.28744700
N	3.69434600	-2.91414400	-1.08145600	O	-3.12728800	-0.89163300	2.84390100
H	4.58666100	-3.25402500	-0.71559100	C	-5.45467900	-0.67871700	3.16641300
C	2.52348300	-2.91892300	-0.40462200	H	-5.60093700	-1.74542500	3.37936300
H	2.32148800	-3.51147300	0.47519900	H	-6.34324300	-0.27294300	2.67510900
C	4.69646200	-1.71881000	-3.10919500	O	-0.53492300	-0.20673100	3.73881400
H	4.53393500	-2.28528800	-4.03871300	C	0.32473400	0.73681200	3.74229600
H	4.63036000	-0.65927300	-3.39182800	O	0.78965300	1.35064000	2.72896400
C	6.13666200	-2.04000200	-2.62074900	C	0.85901800	1.16028700	5.10387200
H	6.30537300	-3.12265500	-2.61949400	H	0.22818200	0.70285100	5.87508700
H	6.85056500	-1.59996400	-3.33041300	H	1.86416100	0.71906100	5.20345300
C	6.39251300	-1.55537300	-1.19609400	C	0.94892400	2.68325700	5.28547200
O	6.27603700	-2.32003700	-0.23069700	H	-0.05527100	3.11898000	5.17220400
N	6.67169600	-0.23182400	-1.04847700	H	1.56184600	3.10094800	4.47677100
H	6.70671900	0.34046800	-1.88332300	C	1.52909800	3.07355700	6.64889700
C	6.53172700	0.44454200	0.24572700	H	0.91572800	2.68281900	7.47279800
H	6.95674000	-0.21892900	1.00491800	H	1.58037100	4.16459200	6.75988700
H	7.14068100	1.35703100	0.21269300	H	2.54636000	2.67680500	6.77657700
C	5.06244600	0.75788600	0.58598900	O	0.16890400	1.97277700	-2.52834100
H	4.49983900	-0.18176400	0.62119300	H	0.14383700	1.14236200	-1.94544200
H	5.01492700	1.18558900	1.59694000				

Pro:

Ca	-2.71929600	0.55608600	-0.65660200	Mn	0.61166500	3.36978400	-1.43464000
Mn	-0.28997400	-1.69643400	-0.29089600	O	-1.93533800	-1.53399900	0.44751100
Mn	-1.37805000	-0.93160400	2.07199100	O	0.35251800	-1.01730000	1.31044300
Mn	0.30260800	0.83518300	0.88280300	O	-1.41211000	0.76371500	1.45955600

O	-0.23814500	0.04566200	-0.83203600	H	4.47325300	-2.29098200	-4.10946000
O	0.05632900	2.62857800	0.23169500	H	4.58846200	-0.67225400	-3.44752300
O	-5.07712900	0.11542500	-1.42253000	C	6.08679100	-2.07369700	-2.69981700
H	-5.37688500	-0.16440300	-0.53379500	H	6.24459500	-3.15798000	-2.70691100
H	-4.85506500	-0.70091600	-1.91232000	H	6.79981300	-1.63620500	-3.41196700
O	-2.40636300	1.25999400	-3.07124600	C	6.35920100	-1.60131400	-1.27407700
H	-2.34128400	0.39306200	-3.50928100	O	6.24308500	-2.37106500	-0.31275100
H	-1.50545600	1.66242900	-3.11108900	N	6.65431500	-0.28191300	-1.11987900
O	1.35054100	4.58239200	-2.51310000	H	6.68969600	0.29609600	-1.95072200
H	2.29070200	4.33819600	-2.61917500	C	6.54029100	0.38532600	0.18142900
O	0.71337800	3.80846500	0.85820200	H	6.96502300	-0.29084700	0.92950100
H	-0.08686700	4.31419000	1.11325700	H	7.16208400	1.28915200	0.14851800
O	-2.59185900	2.95127700	-0.77737200	C	5.08040300	0.71704700	0.54353100
C	-2.22386900	4.04038200	-1.23324200	H	4.50333800	-0.21391000	0.57457600
O	-0.99009300	4.37152700	-1.52820400	H	5.05236200	1.13362600	1.55994100
C	-3.22778100	5.13931600	-1.55186000	C	4.43207700	1.69450800	-0.43994400
H	-4.13446700	4.94608500	-0.96725400	H	4.64535700	1.39729000	-1.47865700
H	-2.80909100	6.10882600	-1.25399000	H	4.83840100	2.70973300	-0.33111200
C	-3.54956800	5.15125700	-3.05850700	C	2.90966600	1.80010600	-0.36335900
H	-3.94944000	4.18091600	-3.37798900	O	2.27327600	0.98120600	0.33660400
H	-2.64704600	5.36329900	-3.64399400	O	2.43408600	2.74606600	-1.09677500
H	-4.29664400	5.92308900	-3.28128100	O	-0.16951000	-3.52789600	0.63838400
O	-0.97286700	-2.52922700	-1.91490800	C	-0.61692600	-3.73084000	1.81860400
C	-2.13043500	-2.37917300	-2.46422900	O	-1.10934500	-2.86668500	2.60617700
O	-2.89130400	-1.39948300	-2.28771700	C	-0.56610200	-5.17615600	2.30674000
C	-2.52538800	-3.51337700	-3.40667300	H	0.38113100	-5.60939200	1.95840700
H	-1.69799800	-3.65296500	-4.11884400	H	-1.35616300	-5.71207600	1.75741900
H	-2.54515800	-4.43532200	-2.80513000	H	-5.25553200	-0.17803800	4.18147500
C	-3.85271600	-3.31497100	-4.14261300	C	-0.74590600	-5.35131700	3.81518400
H	-3.82048400	-2.37102400	-4.70491000	H	-0.71629400	-6.41572300	4.08141200
H	-4.66110400	-3.20109800	-3.40658000	H	0.04733000	-4.83655400	4.37120800
C	-4.17535300	-4.47577400	-5.09016100	H	-1.70277100	-4.93470500	4.14732500
H	-3.39848200	-4.59159500	-5.85900300	O	-4.32680000	0.02206900	1.18275600
H	-5.13154100	-4.31442900	-5.60443500	C	-4.21365700	-0.47871900	2.32232700
H	-4.24558500	-5.42798800	-4.54584300	O	-3.11217600	-0.89272000	2.86044600
N	1.62181600	-2.10089400	-1.02618800	C	-5.43313000	-0.65581200	3.21062300
C	2.26658500	-1.51761600	-2.09593400	H	-5.59489100	-1.72462600	3.40079600
H	1.76964300	-0.77781900	-2.70891600	H	-6.32007900	-0.22479600	2.73820500
C	3.54433800	-2.01865700	-2.18839200	O	-0.50006900	-0.26666800	3.73646800
N	3.64864900	-2.93622800	-1.14880700	C	0.37884500	0.66085500	3.75079800
H	4.54064900	-3.28435400	-0.79014200	O	0.84355300	1.28874400	2.74804600
C	2.48109300	-2.93805500	-0.46602300	C	0.93465700	1.03622500	5.11872100
H	2.28087000	-3.53341600	0.41233900	H	0.27847700	0.60431100	5.88363200
C	4.64653800	-1.73508500	-3.17549000	H	1.91174100	0.53447300	5.21313800

C	1.11362800	2.54765800	5.32369400	H	1.83199600	3.96727800	6.81962300
H	0.13644500	3.04307800	5.21904900	H	2.70957800	2.42561100	6.81141600
H	1.74867000	2.94168000	4.52020300	O	0.17992000	1.99388400	-2.46129900
C	1.71704000	2.88290200	6.69175600	H	0.14135900	1.15171300	-1.88264600
H	1.08302600	2.51578100	7.51088800				

W2 (hydroxyl/oxyl)-O5 (oxo)

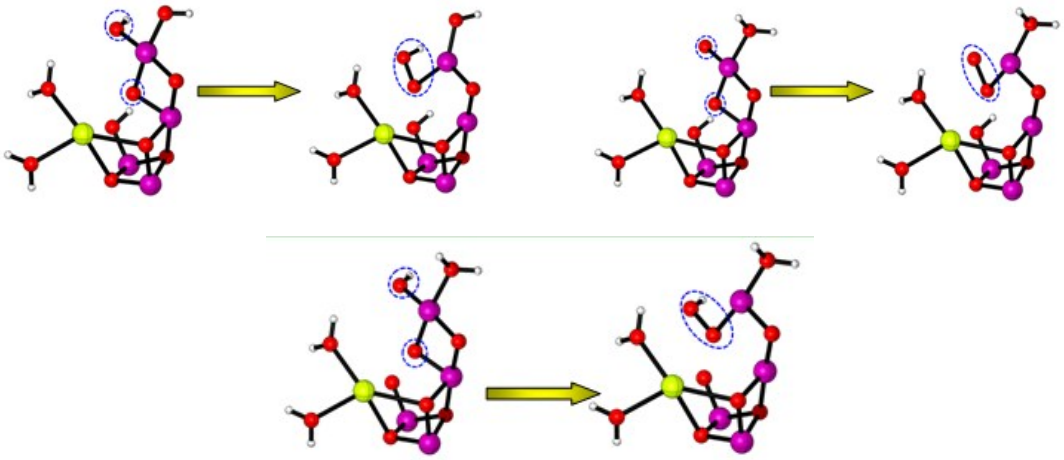

Fig. S10 Pictorial exhibitions for the open-cubane W2 (hydroxyl/oxyl)-O5 (oxo) nucleophilic attack with previous deprotonation sites of W1, W2 and Wx.

Table S22 Reaction parameters for the open-cubane W2 (hydroxyl/oxyl)-O5 (oxo) nucleophilic attack with deprotonated W1:

Spin state	Spin topology (Mn1~Mn4-OX)	Gibbs Free energy (a.u.)		
		Rea	TS	Pro
doublet	ααββα	\	\	\
	αβαβα	-3366.2100	-3366.1845	-3366.2030
	αββαα	\	\	\
	βααβα	-3366.2088	-3366.1834	-3366.1917
	βαβαα	\	\	\
	ββααα	-3366.2230	-3366.1822	-3366.2159
sextet	αααββ	\	\	\
	ααβαβ	-3366.2099	-3366.1852	-3366.1941
	αβααβ	\	\	\
	βαααβ	\	\	\
octet	αααβα	-3366.2098	-3366.1853	-3366.1940
	ααβαα	\	\	\
	αβααα	-3366.2249	-3366.1856	-3366.2166
	βαααα	-3366.2169	-3366.1845	-3366.2061
12-et	aaaaβ	\	\	\
14-et	aaaaa	-3366.2165	-3366.1852	-3366.2028

Spin state	Spin topology (Mn1~Mn4-OX)	Relative Gibbs Free energy (kcal/mol)			
		$\Delta G^{\neq}$(Rea-TS)	ΔG(Rea-Pro)	ΔG(Rea)	ΔG(Pro)
doublet	ααββα	\	\	\	\
	αβαβα	16.0	4.4	9.3	8.5
	αββαα	\	\	\	\
	βααβα	15.9	10.7	10.1	15.6
	βαβαα	\	\	\	\
	ββααα	25.6	4.5	1.2	0.4
sextet	αααββ	\	\	\	\
	ααβαβ	15.5	9.9	9.4	14.1
	αβααβ	\	\	\	\
	βαααβ	\	\	\	\
octet	αααβα	15.4	9.9	9.5	14.2
	ααβαα	\	\	\	\
	αβααα	24.7	5.2	0.0	0.0
	βαααα	20.3	6.8	5.0	6.6
12-et	ααααβ	\	\	\	\
14-et	ααααα	19.6	8.6	5.3	8.7

Spin state	Spin topology (Mn1~Mn4-OX)		Mulliken spin density		
			Rea	TS	Pro
doublet	α	Mn1	\	\	\
	α	Mn2	\	\	\
	β	Mn3	\	\	\
	β	Mn4	\	\	\
	α	O7	\	\	\
	α	Mn1	2.94	2.94	2.93
	β	Mn2	-2.92	-2.91	-2.88
	α	Mn3	2.88	3.49	3.81
	β	Mn4	-2.29	-2.85	-2.77
	α	O7	0.14	0.37	0.00
		O4	0.10	-0.07	-0.12
		O6	0.11	-0.02	-0.02
	α	Mn1	\	\	\
	β	Mn2	\	\	\
	β	Mn3	\	\	\
	α	Mn4	\	\	\
	α	O7	\	\	\
	β	Mn1	-2.93	-2.93	-2.91
	α	Mn2	2.93	2.96	2.95
	α	Mn3	2.89	3.51	3.81
	β	Mn4	-2.34	-2.84	-2.76

	α	O7	0.13	0.36	0.00
		O4	0.13	-0.09	-0.13
		O1	-0.01	-0.02	-0.10
	β	Mn1	\	\	\
	α	Mn2	\	\	\
	β	Mn3	\	\	\
	α	Mn4	\	\	\
	α	O7	\	\	\
	β	Mn1	-2.96	-2.95	-2.93
	β	Mn2	-2.91	-2.93	-2.91
	α	Mn3	2.73	3.55	3.86
	α	Mn4	2.92	2.89	2.91
	α	O7	0.06	0.38	0.00
		O2	0.59	-0.01	-0.04
		O5	0.41	0.04	0.01
		O4	0.17	0.04	0.08
	α	Mn1	\	\	\
	α	Mn2	\	\	\
	α	Mn3	\	\	\
	β	Mn4	\	\	\
	β	O7	\	\	\
	α	Mn1	2.95	2.95	2.92
	α	Mn2	2.94	2.93	2.89
	β	Mn3	-2.87	-3.47	-3.79
	α	Mn4	2.33	2.84	2.77
	β	O7	-0.13	-0.37	0.00
sextet		O4	-0.13	0.08	0.13
		O1	0.04	0.05	0.10
	α	Mn1	\	\	\
	β	Mn2	\	\	\
	α	Mn3	\	\	\
	α	Mn4	\	\	\
	β	O7	\	\	\
	β	Mn1	\	\	\
	α	Mn2	\	\	\
	α	Mn3	\	\	\
	α	Mn4	\	\	\
	β	O7	\	\	\
	α	Mn1	2.96	2.97	2.95
	α	Mn2	2.96	2.98	2.96
	α	Mn3	2.90	3.52	3.83
octet	β	Mn4	-2.28	-2.85	-2.76
	α	O7	0.14	0.37	0.00
		O4	0.10	-0.08	-0.13

	α	Mn1	\	\	\
	α	Mn2	\	\	\
	β	Mn3	\	\	\
	α	Mn4	\	\	\
	α	O7	\	\	\
	α	Mn1	2.95	2.94	2.94
	β	Mn2	-2.87	-2.91	-2.89
	α	Mn3	2.73	3.57	3.88
	α	Mn4	2.92	2.88	2.90
	α	O7	0.06	0.38	0.00
		O2	0.60	-0.01	-0.03
		O4	0.18	0.05	0.09
		O5	0.40	0.04	0.01
	β	Mn1	-2.93	-2.93	-2.92
	α	Mn2	2.92	2.96	2.96
	α	Mn3	2.85	3.60	3.89
	α	Mn4	2.87	2.88	2.90
	α	O7	0.05	0.38	0.00
		O4	0.62	0.04	0.08
		O5	0.45	0.03	0.00
12-et	α	Mn1	\	\	\
	α	Mn2	\	\	\
	α	Mn3	\	\	\
	α	Mn4	\	\	\
	β	O7	\	\	\
14-et	α	Mn1	2.96	2.97	2.95
	α	Mn2	2.96	2.98	2.95
	α	Mn3	2.87	3.61	3.90
	α	Mn4	2.85	2.88	2.90
	α	O7	0.05	0.38	0.00
		O4	0.87	0.05	0.14
		O5	0.13	0.04	0.00
		O2	0.11	0.05	0.05

'\' denotes TSs for some spin states do not exist due to the failure of IRC verification on reactants concerning W2 returning back to Mn4. 'X' denotes atypism for the ascription of spin center.

Rea:

Ca	2.46768200	0.31356100	-1.55276700	O	0.28207500	-1.12060600	-1.26866600
Mn	0.16405700	1.95921300	0.31528200	O	-0.54064200	-3.23262400	-0.33673700
Mn	1.33546600	-0.03762500	1.79389600	O	4.77215100	1.17131400	-2.02091200
Mn	-0.51086200	-1.61486600	0.28630100	H	5.12446200	0.84059100	-1.16882400
Mn	-0.11172900	-2.85213900	-2.15336600	H	4.54818800	2.11181800	-1.87449300
O	1.81267700	1.25005100	0.63918500	O	1.57686400	0.27618900	-3.83276400
O	-0.37248700	0.34371100	1.13090000	H	0.80895000	0.86953200	-3.89062300
O	1.30263300	-1.50533100	0.72912500	H	1.19045300	-0.64197300	-3.94123800

O	0.31046700	-2.07796800	-3.77373300	H	-6.72316100	0.66297900	-2.37345100
H	0.10384800	-2.73370900	-4.46357800	C	-6.56480200	-0.95939900	-0.97641500
O	-0.64877200	-4.39963100	-2.88961400	H	-7.19987800	-1.08402200	-0.09210200
H	-0.03374900	-5.08536500	-2.56582500	H	-6.99751800	-1.55593700	-1.78914800
O	3.01527800	-1.91897500	-2.17143700	C	-5.13682600	-1.42390400	-0.64607500
C	2.76875500	-3.11607000	-1.96551500	H	-4.75699700	-0.83512600	0.19506800
O	1.59024400	-3.65646800	-1.89181700	H	-5.19024700	-2.46731700	-0.30386200
C	3.92769900	-4.09054300	-1.75479900	C	-4.16793500	-1.31558300	-1.82994000
H	4.63996500	-3.90114200	-2.56987200	H	-4.16815600	-0.28338100	-2.21551600
H	4.43326500	-3.75468700	-0.83701500	H	-4.45640200	-1.97107400	-2.66053500
C	3.56473700	-5.57262400	-1.66417700	C	-2.71959800	-1.62889000	-1.47467400
H	3.08415200	-5.92151100	-2.58688000	O	-2.31902900	-1.24991300	-0.31895000
H	2.87251200	-5.76050000	-0.83560100	O	-2.01860200	-2.18901400	-2.36001800
H	4.46710800	-6.17692900	-1.50352200	O	0.10382200	2.86096100	2.11342800
O	0.87229200	3.62888200	-0.33032900	C	0.68865000	2.42452200	3.15537700
C	1.93356000	3.77444700	-1.06602200	O	1.25690300	1.29621800	3.26156300
O	2.63886600	2.85535200	-1.52455700	C	0.71747500	3.35373300	4.36095300
C	2.26606400	5.23735400	-1.35482600	H	-0.26566100	3.83915200	4.42190100
H	1.42264700	5.65039900	-1.93047900	H	1.42783100	4.15607400	4.10725500
H	2.25497200	5.77659500	-0.39642400	C	1.10435000	2.68492900	5.68056100
C	3.58481300	5.45981500	-2.09946000	H	1.12362300	3.42641900	6.48910700
H	3.57163900	4.88680700	-3.03638800	H	0.38835100	1.89989000	5.95298700
H	4.41151500	5.04895800	-1.50170600	H	2.09306300	2.21889400	5.61113900
C	3.84694500	6.94118200	-2.39317800	O	4.15429100	-0.19984200	0.28140200
H	3.05144400	7.37074400	-3.01831300	C	4.18159500	-0.39329100	1.51364100
H	3.89423600	7.53121200	-1.46709200	O	3.15084900	-0.41945300	2.29974100
H	4.79773000	7.07764400	-2.92438400	C	5.50224300	-0.61611800	2.23175700
N	-1.81213000	2.56714700	0.15424300	H	5.70359100	0.23585300	2.89444600
C	-2.49061000	2.88992700	-1.00065700	H	6.31823500	-0.72132900	1.51129300
H	-1.95681600	3.03719500	-1.92886900	H	5.43839900	-1.50994300	2.86301800
C	-3.83876500	2.94129600	-0.73689900	O	0.63311400	-1.25729400	3.24770100
N	-3.95464500	2.65565600	0.61907300	C	-0.41210700	-1.97122800	3.14810200
H	-4.83715600	2.40040500	1.07388900	O	-1.08542600	-2.16275700	2.08448800
C	-2.71861200	2.41883500	1.11013500	C	-0.91247800	-2.66168300	4.40650800
H	-2.50988800	2.11027000	2.12371600	H	-0.22098500	-2.43209500	5.22512000
C	-5.00197200	3.23677300	-1.64810100	H	-1.88885400	-2.21720500	4.65492000
H	-5.01737000	4.30656400	-1.90507500	C	-1.07577200	-4.18144200	4.22222300
H	-4.83415200	2.70590700	-2.59579100	H	-0.10244900	-4.61797000	3.95403700
C	-6.40570500	2.87695100	-1.09826500	H	-1.74451200	-4.36428000	3.37173000
H	-6.68519600	3.56595800	-0.29317700	C	-1.61793200	-4.86116000	5.48356300
H	-7.13627800	3.01033700	-1.90784800	H	-0.94914800	-4.70736500	6.34189700
C	-6.49243700	1.46975200	-0.50810800	H	-1.72296000	-5.94315400	5.33211800
O	-6.37796300	1.28004000	0.71094500	H	-2.60605900	-4.46429500	5.75627800
N	-6.64319500	0.44767600	-1.38751400	O	0.07910800	1.43519200	-1.42058200

H	-0.27146300	0.51120800	-1.44157500

TS:

Ca	-2.59957700	0.39225500	-1.17620400	H	-6.04623400	-5.73478900	-3.50720100
Mn	-0.50164400	-1.96122700	0.07829100	N	1.37595000	-2.77893200	-0.38697000
Mn	-1.29343900	-0.05554600	1.90897700	C	1.97982600	-2.86855800	-1.62298700
Mn	0.57679700	1.38323700	0.45089800	H	1.41014200	-2.69983300	-2.52634300
Mn	0.61777500	3.25467700	-1.71019700	C	3.31174700	-3.17298800	-1.46144000
O	-2.00464100	-1.17077100	0.65636300	N	3.49221500	-3.28383100	-0.08841600
O	0.33644900	-0.52338200	1.01569000	H	4.41052800	-3.29446600	0.36761000
O	-1.20180700	1.38147500	0.83626100	C	2.31358000	-3.02264500	0.51773300
O	-0.02354500	1.45655400	-1.61132400	H	2.16922500	-2.98731700	1.58703100
O	0.71443200	3.17867300	0.02512000	C	4.40547800	-3.36702500	-2.48070800
O	-4.98983900	-0.11882500	-1.75890500	H	4.24314000	-4.30500100	-3.03241900
H	-5.30390100	0.01060500	-0.84144400	H	4.32359500	-2.56516000	-3.22832700
H	-4.84726700	-1.08167900	-1.86238400	C	5.85387600	-3.40551200	-1.92852300
O	-2.02987300	-0.02468500	-3.58374300	H	6.01689000	-4.32657400	-1.35747000
H	-1.52249700	-0.82347700	-3.33396600	H	6.54537000	-3.42577000	-2.78198000
H	-1.33460600	0.64566900	-3.76308700	C	6.18140000	-2.24856200	-0.98523600
O	0.15505800	1.75024800	-3.31815900	O	6.09322900	-2.37975800	0.24344500
H	1.07408500	1.41859300	-3.40396200	N	6.51304400	-1.06512600	-1.56133900
O	1.36652700	4.73194600	-2.37024600	H	6.56593600	-1.01356400	-2.57098200
H	0.68230600	5.42874200	-2.37232500	C	6.64070300	0.17184900	-0.78173800
O	-2.72088500	2.68396400	-1.77853300	H	7.22243300	-0.06277700	0.11609500
C	-2.28447300	3.84224700	-1.78839500	H	7.22207500	0.87890400	-1.38662200
O	-1.03200500	4.19278000	-1.83649800	C	5.28506600	0.77199500	-0.37177000
C	-3.27220800	5.00794400	-1.74670600	H	4.74642100	0.04708600	0.24761000
H	-4.05231400	4.77919300	-2.48551000	H	5.47539600	1.64936100	0.26247900
H	-3.76682500	4.94072900	-0.76571800	C	4.41611300	1.17627200	-1.56779400
C	-2.69003800	6.40470200	-1.96207400	H	4.31572600	0.32024300	-2.25570100
H	-2.21221300	6.49005900	-2.94623100	H	4.86444300	1.99536200	-2.14345400
H	-1.93822000	6.64231600	-1.20059800	C	2.99285500	1.58726400	-1.20376700
H	-3.48405700	7.16050800	-1.90607500	O	2.44865000	1.02653000	-0.20810200
O	-1.47025100	-3.38840300	-0.74866500	O	2.44622900	2.43846500	-1.97949400
C	-2.59642600	-3.25025400	-1.39132800	O	-0.36852800	-3.10556800	1.69440400
O	-3.15026400	-2.17189200	-1.66730900	C	-0.80221000	-2.77488800	2.85285900
C	-3.20602100	-4.58626500	-1.81251500	O	-1.21270000	-1.63013800	3.18228200
H	-2.45885500	-5.10435700	-2.43336600	C	-0.82298400	-3.88488900	3.89519800
H	-3.30686700	-5.20232000	-0.90636900	H	0.12124000	-4.43898600	3.80375300
C	-4.54142100	-4.47316400	-2.55199400	H	-1.60785800	-4.58805300	3.57607600
H	-4.41503800	-3.82469700	-3.42966100	C	-1.06522000	-3.41153000	5.32856500
H	-5.27210900	-3.96880900	-1.90356700	H	-1.08876800	-4.26942900	6.01232600
C	-5.08793700	-5.83903000	-2.98220700	H	-0.27305600	-2.72948000	5.66046200
H	-4.39107300	-6.35265500	-3.65950800	H	-2.01625500	-2.87431100	5.41004600
H	-5.25144300	-6.49596000	-2.11630300	O	-4.18864200	0.68326400	0.72995100

C	-4.08695100	0.64567300	1.97324100	H	1.17669400	1.31306700	5.41125800
O	-3.00143100	0.40219900	2.63571000	C	2.46921300	2.88652400	4.61721300
C	-5.29799700	0.89408200	2.85615600	H	2.39279600	3.69306300	3.87614500
H	-5.50680800	-0.00210800	3.45413000	H	3.24487900	2.20386400	4.24279300
H	-6.17072500	1.14716400	2.24793500	C	2.88645200	3.45727400	5.97734500
H	-5.08167100	1.70870900	3.55769700	H	2.14050400	4.16926700	6.35779300
O	-0.43488700	0.87925800	3.43071000	H	3.84546100	3.98672300	5.90680300
C	0.63962000	1.56231800	3.37112600	H	2.99842100	2.66308800	6.72919900
O	1.30417200	1.78775900	2.31853700	O	-0.47999800	-1.13879400	-1.56471500
C	1.13318700	2.14225400	4.68954500	H	0.16669000	-0.40343600	-1.56161800
H	0.33515500	2.80660400	5.05581000				

Pro:

Ca	-2.51096000	0.15609400	-1.23314800	O	-2.60733800	-2.40854200	-1.93996900
Mn	-0.19298900	-1.99961400	0.07609000	C	-2.28568800	-4.77768600	-2.30749900
Mn	-1.38399000	-0.37119100	1.92876400	H	-1.41908700	-5.13803000	-2.88292400
Mn	0.40003100	1.29365200	0.65407800	H	-2.38412900	-5.47817700	-1.46426900
Mn	0.21358800	3.47605100	-1.58461600	C	-3.54958700	-4.77760000	-3.17082100
O	-1.82695200	-1.50746200	0.55484900	H	-3.43626500	-4.04129500	-3.97828900
O	0.38193200	-0.60107000	1.22429900	H	-4.40053100	-4.43559000	-2.56474100
O	-1.41620700	1.06169900	0.87419400	C	-3.85565000	-6.15963800	-3.75873100
O	-0.25946400	1.76884200	-2.18438600	H	-3.03399800	-6.51292300	-4.39778200
O	0.19337300	3.03616700	0.08720800	H	-4.00345900	-6.90791400	-2.96730100
O	-4.74190500	-0.64356600	-2.06478100	H	-4.76677900	-6.13716100	-4.37043300
H	-5.13365300	-0.66155800	-1.16822600	N	1.81599300	-2.47919200	-0.30026500
H	-4.43494300	-1.55581900	-2.24314100	C	2.48631600	-2.67143200	-1.48873300
O	-1.80573600	-0.18212800	-3.64906300	H	1.94736000	-2.76286200	-2.42238900
H	-1.11265300	-0.78531900	-3.31099000	C	3.84096200	-2.72288300	-1.24751800
H	-1.31274400	0.61702000	-3.92406300	N	3.96603900	-2.57827700	0.12830400
O	-0.07136000	2.13028100	-3.58855100	H	4.85189600	-2.39542300	0.61071400
H	0.89607700	1.99584600	-3.69193200	C	2.73317700	-2.41518600	0.65419300
O	0.85278100	5.10033700	-1.96743400	H	2.53099200	-2.21497000	1.69616500
H	0.11080200	5.73406700	-1.93644100	C	5.00402700	-2.88415100	-2.19366500
O	-2.96317200	2.48338800	-1.57039200	H	5.01287200	-3.90249100	-2.60976900
C	-2.70946600	3.69307200	-1.63606200	H	4.84328800	-2.21529300	-3.05140000
O	-1.52478300	4.23430800	-1.71169200	C	6.41010000	-2.62025200	-1.59540800
C	-3.86617200	4.69255700	-1.63490400	H	6.68539700	-3.42501800	-0.90466200
H	-4.57899400	4.34023700	-2.39344400	H	7.13982100	-2.63251900	-2.41662100
H	-4.37519800	4.55620100	-0.66895900	C	6.50771400	-1.31952600	-0.79771700
C	-3.50229100	6.16095100	-1.85312400	O	6.42492300	-1.31932900	0.43833500
H	-3.01071600	6.31021300	-2.82243800	N	6.62395700	-0.16999400	-1.50917300
H	-2.82182400	6.52091100	-1.07254500	H	6.68155400	-0.22439400	-2.51846700
H	-4.40581100	6.78397400	-1.83168100	C	6.52017300	1.14993400	-0.87614300
O	-0.81718200	-3.44633500	-1.01750600	H	7.15737800	1.14383100	0.01499900
C	-1.91185600	-3.41629300	-1.72456600	H	6.93328700	1.88044900	-1.58255700

C	5.08376700	1.52579600	-0.47290800	O	-3.18871800	-0.21377300	2.52877700
H	4.72173200	0.81339800	0.27611200	C	-5.54273800	-0.08030100	2.58548500
H	5.11605400	2.51267300	0.01056400	H	-5.65707400	-1.03334300	3.11746100
C	4.11185900	1.56170400	-1.66253200	H	-6.39709800	0.08013400	1.92217200
H	4.09927400	0.57193800	-2.14504000	H	-5.50323000	0.71133100	3.34331200
H	4.42265400	2.30243900	-2.40883400	O	-0.76447700	0.61279000	3.51859300
C	2.67480300	1.86971200	-1.25482800	C	0.21635600	1.43438600	3.58957600
O	2.15659600	1.12674500	-0.36036400	O	0.94861800	1.78761700	2.62483300
O	2.11079900	2.82475500	-1.87569000	C	0.48126500	2.00559200	4.97692900
O	-0.04358000	-3.26092000	1.57940500	H	-0.45658400	2.47441900	5.31144100
C	-0.58749500	-3.07676900	2.72796200	H	0.63625700	1.15165900	5.65399000
O	-1.17005500	-2.02815800	3.10887000	C	1.64702300	2.99424500	5.06122900
C	-0.50901000	-4.26087500	3.68303300	H	1.46844300	3.82256100	4.36251200
H	0.51920200	-4.64611500	3.64239300	H	2.56638900	2.50131600	4.71592900
H	-1.13608600	-5.05203100	3.24404000	C	1.84500400	3.53672300	6.48121300
C	-0.94086500	-3.95321200	5.11681300	H	0.94818700	4.06356200	6.83667100
H	-0.87406600	-4.85721500	5.73533800	H	2.68390400	4.24368500	6.52195800
H	-0.30419900	-3.18140600	5.56585500	H	2.05622300	2.72713300	7.19440400
H	-1.97229200	-3.58557200	5.14717200	O	-0.18076700	-0.88441000	-1.42353100
O	-4.26320700	0.00475700	0.54822300	H	0.64232000	-0.36231000	-1.43471100
C	-4.24699900	-0.09291500	1.79206500				

Table S23 Reaction parameters for the open-cubane W2 (hydroxyl/oxyl)-O5 (oxo) nucleophilic attack with deprotonated W2:

Spin state	Spin topology (Mn1~Mn4-O7)	Gibbs Free energy (a.u.)		
		Rea	TS	Pro
doublet	ααββα	-3366.2136	-3366.1462	-3366.1662
	αβαβα	-3366.2144	-3366.1790	-3366.2124
	αββαα	-3366.2050	-3366.1492	-3366.1663
	βααβα	-3366.2141	-3366.1776	-3366.2104
	βαβαα	-3366.2047	-3366.1626	-3366.2037
	ββαaα	-3366.2036	-3366.1696	-3366.2117
sextet	αααββ	-3366.2060	-3366.1647	-3366.2042
	ααβαβ	-3366.2172	-3366.1863	-3366.2197
	αβααβ	-3366.2180	-3366.1554	-3366.1649
	βααaβ	-3366.2166	-3366.1554	-3366.1900
octet	αααβα	-3366.2188	-3366.1791	-3366.2125
	ααβαα	-3366.2067	-3366.1506	-3366.1674
	αβααα	-3366.2053	-3366.1705	-3366.2130
	βαaαa	-3366.2050	-3366.1793	-3366.2112
12-et	αααaβ	-3366.2196	-3366.1492	-3366.1903
14-et	αααaα	-3366.2062	-3366.1705	-3366.2123

Spin state	Spin topology (Mn1~Mn4-O7)	Relative Gibbs Free energy (kcal/mol)			
		$\Delta G^{\neq}$(Rea-TS)	ΔG(Rea-Pro)	ΔG(Rea)	ΔG(Pro)
doublet	ααββα	42.3	29.7	3.8	33.6
	αβαβα	22.2	1.3	3.3	4.6
	αββαα	35.0	24.3	9.2	33.5
	βααβα	22.9	2.3	3.5	5.8
	βαβαα	26.4	0.6	9.3	10.0
	ββααα	21.3	-5.1	10.0	5.0
sextet	αααββ	25.9	1.1	8.5	9.7
	ααβαβ	19.4	-1.6	1.5	0.0
	αβααβ	39.3	33.3	1.0	34.4
	βαααβ	38.4	16.7	1.9	18.6
octet	αααβα	24.9	4.0	0.5	4.5
	ααβαα	35.2	24.7	8.1	32.8
	αβααα	21.8	-4.8	9.0	4.2
	βαααα	20.1	-3.9	9.2	5.3
12-et	ααααβ	44.2	18.4	0.0	18.4
14-et	ααααα	22.4	-3.8	8.4	4.6

Spin state	Spin topology (Mn1~Mn4-O7)		Mulliken spin density		
			Rea	TS	Pro
doublet	α	Mn1	2.96	2.97	3.01
	α	Mn2	2.94	2.97	2.93
	β	Mn3	-2.89	-2.46	-1.95
	β	Mn4	-2.71	-2.77	-2.85
	α	O7	0.76	0.32	0.00
	α	Mn1	2.96	2.96	2.97
	β	Mn2	-2.91	-2.91	-2.89
	α	Mn3	2.88	3.52	3.81
	β	Mn4	-2.68	-2.80	-2.84
	α	O7	0.80	0.45	0.02
	α	Mn1	2.95	2.98	2.96
	β	Mn2	-2.94	-2.94	-2.93
	β	Mn3	-2.92	-2.35	-1.97
	α	Mn4	2.75	2.95	2.91
	α	O7	1.01	0.40	0.01
	β	Mn1	-2.95	-2.96	-2.94
	α	Mn2	2.94	2.96	2.96
	α	Mn3	2.91	3.55	3.83
	β	Mn4	-2.68	-2.81	-2.83
	α	O7	0.80	0.44	0.02
	β	Mn1	-2.96	-2.96	-2.95

	α	Mn2	2.91	2.93	2.93
	β	Mn3	-2.89	-2.79	-2.73
	α	Mn4	2.75	3.13	3.80
	α	O7	1.01	0.66	-0.03
	β	Mn1	-2.96	-2.97	-2.95
	β	Mn2	-2.94	-2.93	-2.91
	α	Mn3	2.90	3.48	3.85
	α	Mn4	2.80	2.84	2.90
	α	O7	1.02	0.58	0.00
	α	Mn1	2.97	2.97	2.97
	α	Mn2	2.96	2.98	2.96
	α	Mn3	2.92	2.82	2.77
	β	Mn4	-2.75	-3.12	-3.79
	β	O7	-1.01	-0.65	0.03
	α	Mn1	2.97	2.96	2.94
	α	Mn2	2.94	2.93	2.90
	β	Mn3	-2.88	-3.49	-3.80
	α	Mn4	2.67	2.81	2.84
sextet	β	O7	-0.78	-0.46	-0.03
	α	Mn1	2.96	2.95	2.95
	β	Mn2	-2.91	-2.92	-2.92
	α	Mn3	2.89	2.38	1.95
	α	Mn4	2.71	2.88	2.85
	β	O7	-0.75	-0.45	0.01
	β	Mn1	-2.95	-2.97	-2.94
	α	Mn2	2.94	2.93	2.94
	α	Mn3	2.92	2.40	3.90
	α	Mn4	2.71	2.87	1.92
	β	O7	-0.75	-0.44	-0.49
	α	Mn1	2.96	2.98	2.97
	α	Mn2	2.96	2.97	2.97
	α	Mn3	2.91	3.56	3.84
	β	Mn4	-2.69	-2.81	-2.84
	α	O7	0.80	0.44	0.03
	α	Mn1	2.96	2.99	2.97
octet	α	Mn2	2.94	2.95	2.93
	β	Mn3	-2.89	-2.31	-1.93
	α	Mn4	2.75	2.95	2.92
	α	O7	1.01	0.41	0.02
	α	Mn1	2.96	2.96	2.96
	β	Mn2	-2.91	-2.91	-2.89
	α	Mn3	2.90	3.49	3.86
	α	Mn4	2.80	2.84	2.89
	α	O7	1.01	0.58	0.00

	β	Mn1	-2.95	-2.96	-2.94
	α	Mn2	2.94	2.96	2.97
	α	Mn3	2.92	3.52	3.88
	α	Mn4	2.80	2.84	2.89
	α	O7	1.02	0.57	0.00
12-et	α	Mn1	2.98	2.97	2.94
	α	Mn2	2.96	2.91	2.94
	α	Mn3	2.93	2.44	3.90
	α	Mn4	2.71	2.79	1.90
	β	O7	-0.75	-0.29	-0.49
14-et	α	Mn1	2.98	2.98	2.97
	α	Mn2	2.96	2.98	2.97
	α	Mn3	2.93	3.53	3.89
	α	Mn4	2.80	2.84	2.89
	α	O7	1.02	-0.57	0.01

Rea:

Ca	2.18086400	0.43712100	-1.52923400	H	5.79135800	-1.71405200	-3.92980900
Mn	-0.48287800	1.88973900	0.05549800	H	6.89702000	-2.99461800	-3.38043500
Mn	1.46394900	0.77384000	1.67673100	O	-0.61571600	3.73295700	-0.60865700
Mn	0.36534100	-1.55329400	0.53411400	C	-0.21611400	4.27288200	-1.71248400
Mn	0.69483600	-3.09886800	-1.66129100	O	0.13066900	3.63508100	-2.73585800
O	1.30295800	1.96225600	0.30554700	C	-0.19663900	5.79628200	-1.69748400
O	-0.28527100	0.31226100	1.04807100	H	-1.13918500	6.13591300	-1.24454400
O	1.94869700	-0.69812100	0.73597400	H	0.59246300	6.09467200	-0.98861000
O	0.50926900	-1.37713900	-1.29220800	C	0.03178500	6.44649000	-3.06492300
O	0.89315700	-3.21175000	0.15746600	H	-0.75924300	6.12342000	-3.75639100
O	2.36214600	2.06721100	-3.37744800	H	0.97335500	6.07316800	-3.48882000
H	1.75722900	2.83307900	-3.25899400	C	0.06211300	7.97664000	-2.98338600
H	1.89480200	1.48559900	-4.01579000	H	-0.88312900	8.37608700	-2.58936700
O	0.80672600	-0.17242700	-3.79126900	H	0.86876200	8.32561900	-2.32337500
H	0.04243100	0.01475900	-3.20645800	H	0.22551900	8.42282100	-3.97289500
H	0.79987000	-1.16093500	-3.86514300	N	-2.54284700	1.59953300	-0.13002400
O	0.57893300	-2.97744100	-3.50997100	C	-3.23124000	1.23424700	-1.26717500
O	0.89359100	-5.25080300	-1.53859100	H	-2.72626900	1.17799100	-2.22092300
H	1.82382200	-5.27860600	-1.84468600	C	-4.53957600	0.96446100	-0.94272600
H	0.94824100	-5.26870800	-0.55968100	N	-4.62622800	1.18755900	0.42677400
O	3.51868500	-1.32917000	-2.39932900	H	-5.39966300	0.85298200	1.00840800
C	3.55833100	-2.56614300	-2.41517700	C	-3.40369000	1.54874100	0.87658400
O	2.56554100	-3.35782000	-2.11491600	H	-3.16116900	1.75006300	1.90918100
C	4.83027700	-3.31178900	-2.80592000	C	-5.69869700	0.55041200	-1.81200300
H	5.06181900	-4.01257800	-1.99046500	H	-6.04565800	1.40675100	-2.40968800
H	4.58142200	-3.93943800	-3.67471000	H	-5.33301400	-0.18916700	-2.53805500
C	6.01819200	-2.39828400	-3.10431600	C	-6.93365300	-0.02114100	-1.06877000
H	6.27505100	-1.78762100	-2.23108500	H	-7.45087600	0.77561700	-0.52230100

H	-7.63683400	-0.41208300	-1.81682900	H	-0.06702200	2.75443400	5.64488600
C	-6.57100100	-1.09025200	-0.04069700	H	1.24386400	3.78914600	5.06524100
O	-6.43566200	-0.80855500	1.15735000	O	4.03801500	1.17054700	-0.14190600
N	-6.34392100	-2.33998200	-0.52216700	C	4.19532600	1.36456700	1.07633500
H	-6.44254800	-2.49872100	-1.51729800	O	3.27775000	1.24999100	1.99459100
C	-5.73629000	-3.39266400	0.29825300	C	5.55178900	1.76757400	1.62802500
H	-6.23490200	-3.37920700	1.27317800	H	6.26148500	1.92235100	0.81108300
H	-5.96136400	-4.35240400	-0.18382400	H	5.92205200	0.98001600	2.29686700
C	-4.22145400	-3.20852800	0.49281600	H	5.45527400	2.68249500	2.22483700
H	-4.04027200	-2.26386200	1.01658800	O	1.35191200	-0.32006600	3.33103300
H	-3.85995900	-4.00870800	1.15440400	C	0.74068600	-1.43031100	3.41281000
C	-3.43680500	-3.22722100	-0.82301500	O	0.18219400	-2.03625200	2.44570800
H	-3.84367000	-2.47254600	-1.51495200	C	0.66406900	-2.07555600	4.78673600
H	-3.51333600	-4.19490200	-1.33508500	H	-0.01406400	-1.45934000	5.39788000
C	-1.95802200	-2.89017900	-0.67729700	H	0.20524700	-3.06503000	4.67689200
O	-1.59273400	-2.15576200	0.27417400	C	2.03333800	-2.16886600	5.48220100
O	-1.20467200	-3.38766200	-1.59319100	H	2.46930200	-1.16348700	5.53925200
O	-0.95964900	2.80993500	1.78269600	H	2.71265800	-2.76950800	4.85924700
C	-0.18083900	2.88793100	2.79002200	C	1.93230000	-2.78589700	6.88081500
O	0.87358900	2.21319400	2.95602800	H	1.28323600	-2.18605400	7.53437000
C	-0.56470300	3.90251100	3.85927400	H	2.91949900	-2.84718400	7.35679700
H	-1.65571600	3.85862300	3.97772600	H	1.51653000	-3.80250200	6.84219300
H	-0.35367300	4.89288200	3.42653900	O	-0.26775000	1.24201600	-1.64520000
C	0.15807100	3.72949300	5.19551200	H	-0.20937300	2.07137800	-2.20346400
H	-0.15322200	4.51154500	5.89958300				

TS:

Ca	2.31159800	-0.12538800	-1.46131300	H	0.48863100	-5.62803900	-1.74345800
Mn	0.05014200	1.97457800	0.06085000	H	-0.69678000	-5.50823000	-0.73454700
Mn	1.52765500	0.32435000	1.69701800	O	3.01017600	-2.24171500	-2.32506500
Mn	-0.17890500	-1.58423800	0.54741900	C	2.76798600	-3.45552000	-2.35054600
Mn	-0.12753700	-3.26882200	-1.67452000	O	1.61716000	-4.00244500	-2.07593800
O	1.77987000	1.55274200	0.39298300	C	3.84828200	-4.46859800	-2.72023700
O	-0.26352600	0.40079500	1.01319800	H	3.95001700	-5.15651600	-1.86760500
O	1.58017200	-1.17724300	0.67815800	H	3.45784600	-5.07827400	-3.54837500
O	0.08355600	-1.47716300	-1.69836500	C	5.19309100	-3.83867300	-3.08032900
O	0.02963600	-3.29931700	0.11366100	H	5.58629300	-3.24664500	-2.24618000
O	3.32988800	1.55722400	-2.98484700	H	5.09716000	-3.16951600	-3.94331300
H	2.89447000	2.43024200	-2.85055400	H	5.92483800	-4.61804800	-3.32813900
H	2.90514400	1.20818400	-3.79458600	O	0.45690200	3.81827800	-0.54171800
O	1.28918500	-0.07661300	-3.88052500	C	1.12712000	4.24045800	-1.55847300
H	0.50917400	0.40326500	-3.53578200	O	1.42776000	3.53836000	-2.55678700
H	0.94890000	-1.00680000	-3.89612800	C	1.55093100	5.70232600	-1.48019900
O	-0.19364300	-2.19986000	-3.17732300	H	0.69897700	6.27603600	-1.08874000
O	-0.46276600	-5.39706200	-1.67735400	H	2.32822500	5.76276100	-0.70109000

C	2.06431900	6.29160300	-2.79716300	O	-2.15888200	-1.64778700	0.11579200
H	1.27812600	6.21019400	-3.56130800	O	-2.06696200	-3.20014000	-1.53158000
H	2.90259300	5.68325700	-3.16132800	O	-0.24814500	2.95977200	1.79107000
C	2.50015400	7.75359800	-2.65040800	C	0.46225200	2.78273900	2.83652600
H	1.66797600	8.38843400	-2.31458200	O	1.27860300	1.83758000	3.02063800
H	3.31121600	7.85653100	-1.91573200	C	0.31126100	3.83020600	3.93295900
H	2.86273100	8.15700500	-3.60480400	H	-0.75277000	4.09597900	3.99093000
N	-1.98985900	2.24500300	-0.26028000	H	0.82247100	4.73251700	3.56264900
C	-2.67451700	1.98632800	-1.42811400	C	0.86659000	3.41472500	5.29565200
H	-2.13693400	1.73365600	-2.33072800	H	0.74635600	4.23030400	6.02005100
C	-4.02579700	2.07545500	-1.19362400	H	0.34407300	2.53184400	5.68427600
N	-4.13968200	2.40724200	0.15184200	H	1.93025800	3.16342900	5.22575900
H	-5.00777700	2.31553800	0.68654300	O	4.21689800	-0.06142700	0.04154100
C	-2.89627800	2.48038100	0.67777200	C	4.34423300	0.06174500	1.27203100
H	-2.67442000	2.68318800	1.71488100	O	3.37683100	0.23610600	2.12646800
C	-5.19357300	1.90408300	-2.13018500	C	5.71768300	0.00603200	1.91840000
H	-5.26267900	2.76895800	-2.80709200	H	6.49533400	-0.03413700	1.15107500
H	-4.98968900	1.03775600	-2.77509900	H	5.78252300	-0.88431500	2.55731600
C	-6.58171600	1.73421300	-1.46154500	H	5.86452700	0.88086200	2.56282400
H	-6.89521300	2.67386400	-0.99250400	O	1.06703700	-0.74484700	3.32534300
H	-7.31591800	1.50079600	-2.24478800	C	0.09873900	-1.55705400	3.39918600
C	-6.59099500	0.67261500	-0.36437500	O	-0.62152400	-1.93166300	2.41767200
O	-6.44359300	0.97778200	0.82620900	C	-0.24226200	-2.12397900	4.76762900
N	-6.70804800	-0.61806500	-0.77416700	H	-0.71240200	-1.31199200	5.34473000
H	-6.79240300	-0.80199300	-1.76623300	H	-0.99219700	-2.91312400	4.63813400
C	-6.46345300	-1.74641100	0.12926000	C	0.99045200	-2.64262400	5.52746100
H	-6.95531400	-1.51531800	1.07980400	H	1.72645700	-1.83208400	5.59950000
H	-6.95730000	-2.62623600	-0.30270400	H	1.46413500	-3.44334000	4.94034900
C	-4.96724700	-2.00727600	0.37362900	C	0.63383700	-3.16491700	6.92285400
H	-4.51823800	-1.11320700	0.81950500	H	0.18764900	-2.37373800	7.54186900
H	-4.87346800	-2.81080700	1.11840200	H	1.52596900	-3.53356100	7.44543400
C	-4.20074400	-2.38538100	-0.89842000	H	-0.08787200	-3.99216400	6.87019600
H	-4.39256800	-1.64244700	-1.68940100	O	0.21210700	1.33464500	-1.65851000
H	-4.51893100	-3.35610100	-1.29945200	H	0.57673100	2.13291400	-2.14097400
C	-2.68577500	-2.41059500	-0.73497700				

Pro:

Ca	2.27949900	0.49787000	-1.46138400	O	0.54887100	-1.40059600	-2.05981800
Mn	-0.44502300	1.90988800	0.18625500	O	0.79914700	-3.12700500	-0.07229600
Mn	1.40507100	0.62226100	1.73705800	O	2.86888800	2.50600200	-2.81113700
Mn	0.13871800	-1.53451100	0.55812600	H	2.10904900	3.13268900	-2.75528700
Mn	0.66963800	-3.14678100	-1.81240300	H	2.78167200	2.10555600	-3.69747300
O	1.33366000	1.92508900	0.47780600	O	1.57572800	0.35787400	-4.00010700
O	-0.38242800	0.32097600	1.15522100	H	0.68731400	0.75622300	-4.02698500
O	1.76789000	-0.73641200	0.60172200	H	1.35671300	-0.61474100	-4.01434100

O	0.35179700	-1.93332600	-3.38701300	H	-6.47612300	-2.24069600	-1.77187600
O	0.80258400	-5.28589900	-1.89306600	C	-5.85801100	-3.23593400	0.02182500
H	1.78004300	-5.29895100	-1.98254800	H	-6.36723100	-3.22737700	0.99129100
H	0.62202400	-5.48505600	-0.95335600	H	-6.12582100	-4.16749400	-0.49294800
O	3.49434400	-1.39750900	-2.30670700	C	-4.33869000	-3.13392200	0.23855800
C	3.53982500	-2.63063100	-2.41254300	H	-4.11757100	-2.20819700	0.78046700
O	2.53725700	-3.44522600	-2.23264500	H	-4.02824300	-3.96321000	0.89081700
C	4.84016800	-3.34098000	-2.78080600	C	-3.53168600	-3.16735400	-1.06483000
H	5.08846500	-4.00860200	-1.94183500	H	-3.91000000	-2.39870300	-1.75788700
H	4.62633800	-4.00253900	-3.63285100	H	-3.62104900	-4.13087200	-1.58195300
C	6.00021300	-2.39508900	-3.08806200	C	-2.05038900	-2.85563300	-0.88610600
H	6.21949500	-1.75029900	-2.22965200	O	-1.72585000	-2.02811900	0.01220600
H	5.76377200	-1.74383100	-3.93786300	O	-1.26248300	-3.43883700	-1.70363800
H	6.90445600	-2.96643800	-3.33371300	O	-0.89495100	2.82176200	1.92378200
O	-0.51290500	3.76694200	-0.48403300	C	-0.16026400	2.75530300	2.96744500
C	-0.03904200	4.29670400	-1.55704100	O	0.82873100	1.98804300	3.12977700
O	0.35868000	3.64806300	-2.56080600	C	-0.51959200	3.71756200	4.09395700
C	0.02028400	5.81943000	-1.54411600	H	-1.61504000	3.73856900	4.17253400
H	-0.90465700	6.18528800	-1.07690200	H	-0.22928500	4.71978800	3.74222700
H	0.82947400	6.09533300	-0.84829400	C	0.13807400	3.40382900	5.43805600
C	0.24917500	6.46502300	-2.91397200	H	-0.14737900	4.15461000	6.18598400
H	-0.56072600	6.16683800	-3.59525900	H	-0.16769100	2.41754700	5.80848000
H	1.17371400	6.06548300	-3.35108600	H	1.22962100	3.39735900	5.34854000
C	0.32497400	7.99354700	-2.83168100	O	4.10742800	0.96560500	0.06130400
H	-0.60248800	8.41955700	-2.42364600	C	4.20554400	1.06566800	1.29668200
H	1.15067100	8.31757000	-2.18266500	O	3.22956500	0.96963500	2.15249400
H	0.48732400	8.43654800	-3.82285400	C	5.55599400	1.31486200	1.94723200
N	-2.50548300	1.71022700	-0.07973200	H	6.31877500	1.48525700	1.18282500
C	-3.15474600	1.38082900	-1.24978700	H	5.83183900	0.44509200	2.55757700
H	-2.60745100	1.30829300	-2.17887200	H	5.49368700	2.17828900	2.62022500
C	-4.48353100	1.15072500	-0.98557500	O	1.26209400	-0.62468100	3.30393100
N	-4.62292200	1.35883200	0.38230600	C	0.59479900	-1.69817500	3.34744200
H	-5.42487300	1.02848000	0.92508600	O	0.01289900	-2.25107900	2.35487600
C	-3.40858800	1.67380600	0.88876400	C	0.46063300	-2.39060700	4.69403000
H	-3.20258800	1.85228600	1.93376100	H	-0.27071900	-1.81035200	5.27941700
C	-5.61637600	0.79498400	-1.91227700	H	0.03089600	-3.38577400	4.52953700
H	-5.92024000	1.67928200	-2.49279200	C	1.78565100	-2.47260900	5.46938700
H	-5.23887100	0.07154100	-2.64840700	H	2.19487300	-1.46028600	5.57626600
C	-6.89233600	0.22937800	-1.23770000	H	2.51537700	-3.04245200	4.87526100
H	-7.40764800	1.01824400	-0.67796000	C	1.61346800	-3.12649800	6.84413400
H	-7.57829700	-0.11160700	-2.02521900	H	0.91278500	-2.55681500	7.47091100
C	-6.59408300	-0.88916700	-0.24252600	H	2.57099900	-3.17912200	7.37824400
O	-6.48089000	-0.65791000	0.96797800	H	1.22343100	-4.15034900	6.75660700
N	-6.40234700	-2.12783500	-0.76844200	O	-0.17727500	1.24292100	-1.50417100

H -0.09464300 2.06981300 -2.05692200

Table S24 Reaction parameters for the open-cubane W2 (hydroxyl/oxyl)-O5 (oxo) nucleophilic attack with deprotonated Wx:

Spin state	Spin topology (Mn1~Mn4-O10)	Gibbs Free energy (a.u.)		
		Rea	TS	Pro
doublet	αααββα	\	\	\
	αβαβα	-3366.2138	-3366.1366	-3366.1573
	αββαα	-3366.2151	-3366.1356	-3366.2313
	βααβα	-3366.2244	-3366.1530	-3366.1724
	βαβαα	-3366.2270	-3366.1480	-3366.1664
	ββαaα	-3366.2261	-3366.1466	-3366.2298
sextet	αααββ	-3366.2276	-3366.1471	-3366.1659
	αααβαβ	-3366.2277	-3366.1532	-3366.1684
	αβααβ	-3366.2273	-3366.1166	-3366.1522
	βαααβ	-3366.2158	-3366.1043	-3366.2002
octet	αααβα	-3366.2143	-3366.1358	-3366.1549
	αααβαα	-3366.2154	-3366.1378	-3366.1564
	αβαaα	-3366.2145	-3366.1532	-3366.1662
	βαaaα	-3366.2274	-3366.1409	-3366.2428
12-et	αaaaβ	\	\	\
14-et	αaaaα	-3366.2153	-3366.1519	-3366.1679

Spin state	Spin topology (Mn1~Mn4-O4/O10)	Relative Gibbs Free energy (kcal/mol)			
		$\Delta G^{\neq}$(Rea-TS)	ΔG(Rea-Pro)	ΔG(Rea)	ΔG(Pro)
doublet	αααββα	\	\	\	\
	αβαβα	48.4	35.5	8.7	53.7
	αββαα	49.9	-10.2	7.9	7.2
	βααβα	44.8	32.6	2.1	44.2
	βαβαα	49.6	38.0	0.4	47.9
	ββαaα	49.9	-2.3	1.0	8.2
sextet	αααββ	50.5	38.7	0.1	48.3
	αααβαβ	46.7	37.2	0.0	46.7
	αβααβ	69.5	47.1	0.3	56.9
	βαααβ	70.0	9.8	7.5	26.7
octet	αααβα	49.3	37.3	8.4	55.2
	αααβαα	48.7	37.0	7.7	54.2
	αβαaα	38.5	30.3	8.3	48.1
	βαaaα	54.3	-9.7	0.2	0.0
12-et	αaaaβ	\	\	\	\
14-et	αaaaα	39.8	29.7	7.8	47.0

Spin state	Spin topology (Mn1~Mn4-O10)		Mulliken spin density		
			Rea	TS	Pro
doublet	α	Mn1	\	\	\
	α	Mn2	\	\	\
	β	Mn3	\	\	\
	β	Mn4	\	\	\
	α	O10	\	\	\
		O7	\	\	\
	α	Mn1	2.80	2.80	2.80
	β	Mn2	-2.91	-2.91	-2.89
	α	Mn3	2.87	3.49	3.80
	β	Mn4	-2.83	-3.81	-3.80
	α	O10	0.90	0.90	0.89
		O7	-0.03	0.31	0.01
	α	Mn1	2.80	2.78	2.96
	β	Mn2	-2.93	-2.95	-2.93
	β	Mn3	-2.89	-3.52	-2.84
	α	Mn4	2.87	3.83	3.86
	α	O10	0.89	0.91	0.02
		O7	0.04	-0.31	0.01
	β	Mn1	-2.80	-2.77	-2.76
	α	Mn2	2.93	2.96	2.97
	α	Mn3	2.90	3.51	3.82
	β	Mn4	-2.84	-3.82	-3.81
	α	O10	0.67	0.64	0.66
		O7	-0.04	0.33	0.01
	β	Mn1	-2.79	-2.81	-2.81
	α	Mn2	2.91	2.91	2.89
	β	Mn3	-2.87	-3.51	-3.80
	α	Mn4	2.86	3.83	3.81
	α	O10	0.69	0.70	0.72
		O7	0.04	-0.30	0.00
	β	Mn1	-2.80	-2.79	-2.91
	β	Mn2	-2.94	-2.90	-2.95
	α	Mn3	2.87	3.77	3.80
	α	Mn4	2.91	2.16	3.93
	α	O10	0.70	0.73	0.04
		O7	0.04	-0.17	-0.50
		O5	0.10	-0.01	-0.52
sextet	α	Mn1	2.81	2.82	2.82
	α	Mn2	2.95	2.97	2.97
	α	Mn3	2.91	3.56	3.83
	β	Mn4	-2.86	-3.84	-3.81

	β	O10	-0.68	-0.68	-0.71
		O7	-0.04	0.30	0.01
	α	Mn1	2.80	2.78	2.81
	α	Mn2	2.93	2.93	2.91
	β	Mn3	-2.87	-3.56	-3.79
	α	Mn4	2.84	3.59	3.80
	β	O10	-0.69	-0.43	-0.71
		O7	0.03	-0.26	-0.01
	α	Mn1	2.81	2.78	2.85
	β	Mn2	-2.91	-2.81	-2.88
	α	Mn3	2.89	3.64	3.86
	α	Mn4	2.88	1.96	1.94
	β	O10	0.68	-0.63	-0.65
		O7	0.04	0.24	-0.03
	β	Mn1	-2.80	-2.79	-2.92
	α	Mn2	2.93	2.96	2.93
	α	Mn3	2.91	3.67	2.94
	α	Mn4	2.87	1.95	1.98
	β	O10	-0.89	-0.90	-0.01
		O7	0.04	0.23	-0.01
	α	Mn1	2.82	2.81	2.81
	α	Mn2	2.94	2.96	2.96
	α	Mn3	2.91	3.53	3.83
	β	Mn4	-2.83	-3.82	-3.80
	α	O10	0.90	0.90	0.90
		O7	-0.04	0.31	0.01
	α	Mn1	2.81	2.80	2.79
octet	α	Mn2	2.92	2.92	2.91
	β	Mn3	-2.86	-3.48	-3.78
	α	Mn4	2.87	3.84	3.81
	α	O10	0.90	0.91	0.90
		O7	0.01	-0.31	0.00
	α	Mn1	2.80	2.80	2.81
	β	Mn2	-2.91	-2.90	-2.89
	α	Mn3	2.88	3.62	3.88
	α	Mn4	2.91	3.69	3.86
	α	O10	0.90	-0.39	-0.71
		O7	0.04	0.29	0.01
	β	Mn1	-2.78	-2.74	-2.80
	α	Mn2	2.93	2.94	2.90
	α	Mn3	2.90	3.80	3.80
	α	Mn4	2.91	2.15	3.91
	α	O10	0.70	0.74	0.04
		O7	0.04	-0.17	-0.58

		O5	0.10	0.04	-0.49
12-et	α	Mn1	\	\	\
	α	Mn2	\	\	\
	α	Mn3	\	\	\
	α	Mn4	\	\	\
	β	O10	\	\	\
		O7	\	\	\
14-et	α	Mn1	2.82	2.90	2.81
	α	Mn2	2.94	2.96	2.89
	α	Mn3	2.92	3.91	3.88
	α	Mn4	2.91	2.78	3.86
	α	O10	0.91	-0.31	0.71
		O7	0.04	0.32	0.01
		O5	0.09	0.20	0.10

'\' denotes TSs for some spin states do not exist due to the failure of IRC verification on reactants concerning W2 returning back to Mn4.

Rea:

Ca	2.20008300	0.13855800	-1.51294800	C	5.57783700	-3.63638700	-1.77828500
Mn	-0.20160400	1.92644800	-0.00055500	H	5.74053900	-2.91696500	-0.96810500
Mn	1.32244600	0.49022600	1.78539800	H	5.71263600	-3.09991600	-2.72516500
Mn	-0.15079500	-1.54451000	0.52042600	H	6.34634100	-4.41728700	-1.71245500
Mn	0.06911300	-3.06749600	-1.70416200	O	0.20050800	3.36329500	-1.24198000
O	1.53633900	1.62423800	0.39068800	C	1.31500900	3.53023700	-1.90397000
O	-0.44279300	0.42621200	1.04971000	O	2.12913600	2.63820200	-2.18560800
O	1.53812200	-1.06278100	0.91141300	C	1.53304700	4.97696800	-2.34024200
O	0.24608000	-1.36939300	-1.27906800	H	0.65899000	5.26767000	-2.94284200
O	0.00424600	-3.26555200	0.12559500	H	1.48496000	5.60352200	-1.43694200
O	4.36949700	1.05206100	-2.45212900	C	2.83257700	5.22069900	-3.11122100
H	4.79809000	0.99740200	-1.57183900	H	2.86120400	4.55898100	-3.98767500
H	4.03993500	1.96941900	-2.52864300	H	3.68596000	4.93180400	-2.48131800
O	1.72102700	-0.61960700	-3.85285200	C	2.98355900	6.68140700	-3.55042800
H	2.54133000	-0.99938500	-4.21044600	H	2.15856100	6.98779400	-4.20881700
H	1.09327900	-1.39568700	-3.80434300	H	2.98732000	7.36110900	-2.68671700
O	0.13533400	-2.86355300	-3.55065000	H	3.92179600	6.83464600	-4.09911100
H	-0.77454900	-2.67113600	-3.84417100	N	-2.25047700	2.22389300	-0.23739500
O	-0.26528900	-5.21203400	-1.68856900	C	-2.95508100	2.10311800	-1.41543300
H	0.68423800	-5.41774000	-1.82477400	H	-2.43356300	1.97824100	-2.35408400
H	-0.39076600	-5.26196500	-0.71752700	C	-4.30227700	2.14240400	-1.14734600
O	3.29031200	-2.01294800	-1.75001300	N	-4.39421800	2.30282500	0.23163800
C	3.05176300	-3.22558100	-1.74287000	H	-5.24650800	2.12128000	0.76761200
O	1.86806200	-3.76836600	-1.78192300	C	-3.14011900	2.32764600	0.73831500
C	4.18217600	-4.25207800	-1.68734500	H	-2.90586300	2.39604100	1.79045100
H	4.05934900	-4.80945200	-0.74640400	C	-5.48588700	2.07128800	-2.07562600
H	4.01171700	-4.98272700	-2.49108400	H	-5.62287600	3.03417200	-2.59088700

H	-5.25196900	1.34309200	-2.86465200	C	0.71034000	3.98064500	5.00970000
C	-6.84152500	1.70618000	-1.41736100	H	0.62082200	4.87846000	5.63448600
H	-7.21433200	2.54883000	-0.82416200	H	0.16618400	3.16480800	5.50088600
H	-7.57518100	1.51989100	-2.21366700	H	1.76567600	3.69047700	4.96532100
C	-6.74708900	0.51676600	-0.46419800	O	4.08754900	0.44284500	0.20144300
O	-6.62444500	0.68246300	0.75629700	C	4.16684100	0.54744800	1.44073900
N	-6.74544600	-0.71676900	-1.03371900	O	3.16745300	0.55340700	2.26952800
H	-6.82140400	-0.78397600	-2.04102300	C	5.51818200	0.69289100	2.12125900
C	-6.44101700	-1.93041300	-0.26925800	H	5.57827100	1.67409800	2.60963900
H	-6.99602700	-1.87239500	0.67325500	H	6.32728600	0.59327800	1.39232500
H	-6.83308400	-2.78159300	-0.84044200	H	5.62312900	-0.06674500	2.90495800
C	-4.94279200	-2.10450400	0.03029100	O	0.78515300	-0.51516400	3.42531800
H	-4.59767500	-1.25802500	0.63328200	C	-0.04719500	-1.47399800	3.42503300
H	-4.82107300	-3.00326300	0.65190200	O	-0.61777600	-1.96602500	2.39989300
C	-4.07747900	-2.22426900	-1.22931500	C	-0.40644500	-2.07356100	4.77588100
H	-4.23760800	-1.34793200	-1.87767900	H	-1.03040000	-1.33389800	5.30231400
H	-4.33556800	-3.11092400	-1.82251300	H	-1.02328600	-2.96335200	4.60398300
C	-2.57913000	-2.26156400	-0.94903000	C	0.82544000	-2.40473500	5.63509400
O	-2.14564400	-1.64751000	0.05888000	H	1.42893200	-1.49577000	5.75170100
O	-1.87963100	-2.91052600	-1.80802700	H	1.45416000	-3.13014600	5.09765200
O	-0.39464500	3.19388300	1.55024500	C	0.44158900	-2.96919000	7.00667700
C	0.25424200	3.07727200	2.64389200	H	-0.16087900	-2.24940800	7.57875100
O	0.96354600	2.08681300	2.97860800	H	1.33435900	-3.20331700	7.60096000
C	0.15619700	4.25123100	3.61079600	H	-0.14696800	-3.89237800	6.91059800
H	-0.89775200	4.55974000	3.64433100	O	-0.19779300	1.04843700	-1.57135800
H	0.69121000	5.08641800	3.13269300				

TS:

Ca	2.43728300	-0.06486200	-1.16624300	H	-0.82514300	-1.76699500	-3.05246300
Mn	-0.12122200	1.95179000	-0.18677100	O	-0.01944700	-5.52522000	-1.06084400
Mn	1.09242800	0.59002600	1.85847800	H	0.93817600	-5.69734900	-1.21727500
Mn	-0.39564400	-1.44753200	0.62612400	H	-0.16722400	-5.60253800	-0.09773000
Mn	0.17923800	-3.42103100	-1.26515300	O	3.28954500	-2.33453000	-1.73761400
O	1.53710100	1.63650200	0.45204000	C	3.16042900	-3.57342700	-1.83823500
O	-0.59161500	0.56022800	0.94646300	O	2.02613200	-4.19541800	-1.85816300
O	1.32815700	-0.97500400	1.01696100	C	4.39344900	-4.46818400	-1.96114900
O	0.33668900	-1.58343300	-1.37668400	H	4.36081800	-5.17632600	-1.11896900
O	-0.04117400	-3.22980200	0.48005900	H	4.26230600	-5.08362300	-2.86360100
O	4.73614700	0.75679600	-1.86532900	C	5.72375900	-3.71688300	-1.99030300
H	5.04174600	0.80489700	-0.93634200	H	5.86392700	-3.12975200	-1.07551400
H	4.42354800	1.65498900	-2.09316200	H	5.76603200	-3.01839100	-2.83442900
O	2.35938100	-0.46675600	-3.65633100	H	6.56182200	-4.41978900	-2.08287800
H	2.99765400	-1.20416200	-3.63585900	O	0.49156000	3.23794200	-1.49007400
H	1.48619200	-0.91709200	-3.70878500	C	1.70496200	3.32832400	-1.97622500
O	0.13032800	-1.98099600	-3.03347100	O	2.52924100	2.40698200	-2.03067900

C	2.02129600	4.72235800	-2.51207700	H	-4.48883800	-3.39151500	-1.61020800
H	1.25702800	4.95940100	-3.26783400	C	-2.69267700	-2.43275000	-0.96051500
H	1.85140000	5.43644400	-1.69217700	O	-2.26322000	-1.63970100	-0.05711500
C	3.42926400	4.87413700	-3.09278300	O	-1.99208100	-3.19640100	-1.68505400
H	3.57430500	4.12728200	-3.88523100	O	-0.44399100	3.34730800	1.21837000
H	4.16845500	4.64104300	-2.31327200	C	0.04417000	3.28090800	2.39930000
C	3.68287500	6.28172800	-3.64382900	O	0.64500400	2.28877500	2.89597000
H	2.97636200	6.52894500	-4.44863400	C	-0.12210500	4.52863000	3.25903200
H	3.57212800	7.04476300	-2.86051300	H	-1.15277600	4.88463400	3.12406300
H	4.69756300	6.36928300	-4.05320700	H	0.51689000	5.30126500	2.80395700
N	-2.11600000	2.28369200	-0.69925900	C	0.22120500	4.34082400	4.73685700
C	-2.71474600	1.98830300	-1.90474000	H	0.09665200	5.28654400	5.27962800
H	-2.11358800	1.72731500	-2.76445500	H	-0.42830200	3.58957400	5.20240500
C	-4.08047100	2.06617400	-1.76796100	H	1.25534300	4.00135400	4.86013100
N	-4.29189100	2.43343700	-0.44374900	O	4.06724700	0.24386900	0.72025900
H	-5.19448800	2.34448800	0.03249200	C	3.96552800	0.47261700	1.94398500
C	-3.08904200	2.53447900	0.16460100	O	2.85853400	0.62165100	2.59647900
H	-2.94830300	2.76048500	1.21107800	C	5.20829300	0.60856400	2.80810700
C	-5.18074800	1.84073100	-2.77247400	H	5.26117200	1.62634900	3.21561000
H	-5.22302600	2.68122200	-3.48164700	H	6.10791600	0.39691000	2.22354900
H	-4.91795200	0.95837800	-3.37301000	H	5.14400400	-0.07893200	3.65989300
C	-6.60670000	1.66061300	-2.19066400	O	0.40768800	-0.27829200	3.50490800
H	-6.97492100	2.61170300	-1.78941900	C	-0.50049600	-1.17217100	3.55574900
H	-7.27908500	1.37163300	-3.01010600	O	-1.06997700	-1.69891000	2.55679300
C	-6.67130000	0.65218900	-1.04469300	C	-0.93561000	-1.61551300	4.94583100
O	-6.62220800	1.02210400	0.13610300	H	-1.53124400	-0.79398200	5.37500100
N	-6.72867000	-0.65912900	-1.39326200	H	-1.60008600	-2.48073800	4.83607400
H	-6.73303300	-0.89554300	-2.37769500	C	0.24351900	-1.93137700	5.88058300
C	-6.54008000	-1.73629000	-0.41481500	H	0.89618800	-1.05100300	5.93429100
H	-7.10552200	-1.46178000	0.48171500	H	0.84588400	-2.73958700	5.43946600
H	-6.99244800	-2.64327800	-0.83619900	C	-0.21886700	-2.33822800	7.28352600
C	-5.06438400	-1.96570600	-0.04648000	H	-0.79672400	-1.53393800	7.76065200
H	-4.65721300	-1.04529300	0.38548400	H	0.63761000	-2.56320900	7.93246600
H	-5.02141400	-2.72716300	0.74555600	H	-0.85790400	-3.23198300	7.25254700
C	-4.19878600	-2.40225200	-1.23278000	O	0.05419500	0.89931700	-1.63682500
H	-4.33395300	-1.69787900	-2.07048200				

Pro:

Ca	2.40616000	-0.17425600	-1.12231900	O	1.31973700	-0.72429800	1.13855200
Mn	-0.21626300	1.90048400	-0.41645800	O	0.56642900	-1.93529300	-1.38466400
Mn	1.08043700	0.92090700	1.77869800	O	0.01582600	-3.02891300	0.99733900
Mn	-0.45231400	-1.27267600	0.98397300	O	4.67182800	0.57174500	-1.99249800
Mn	0.40389400	-3.62038000	-0.62277000	H	4.98333900	0.79427600	-1.09110400
O	1.46329600	1.75263200	0.21254500	H	4.32393600	1.40256700	-2.37308800
O	-0.64913000	0.74262200	0.96620000	O	2.44642400	-0.90518600	-3.55512600

H	3.08152200	-1.62774500	-3.39018000	C	-6.70181400	0.20122700	-1.12907500
H	1.58385900	-1.36121300	-3.63924700	O	-6.67640100	0.65696000	0.02185200
O	0.22039400	-2.37015300	-2.72965600	N	-6.68828400	-1.13333700	-1.38126100
H	-0.76138600	-2.42476900	-2.63872600	H	-6.68138000	-1.44223500	-2.34528500
O	0.16055700	-5.53696000	0.18320000	C	-6.46945700	-2.12588200	-0.32288800
H	1.06583800	-5.89964200	0.10151100	H	-7.08650700	-1.83138900	0.53267200
H	0.03687400	-5.25593800	1.11492100	H	-6.84527400	-3.08730900	-0.69589800
O	3.36135800	-2.57217900	-1.44263600	C	-4.99912400	-2.23105900	0.11538500
C	3.21545600	-3.80862600	-1.50634300	H	-4.67044600	-1.25794500	0.49484600
O	2.09663700	-4.44482200	-1.30670800	H	-4.94262300	-2.93145200	0.96126000
C	4.39993600	-4.71318400	-1.84443500	C	-4.05510400	-2.68954900	-1.00128700
H	4.51281500	-5.42084600	-1.00899200	H	-4.20322500	-2.05758600	-1.89288300
H	4.10563400	-5.32925100	-2.70708200	H	-4.25775800	-3.72223200	-1.31333600
C	5.70848800	-3.97024000	-2.11076400	C	-2.56547300	-2.58409500	-0.66450400
H	6.00433700	-3.36954900	-1.24320200	O	-2.23533500	-1.67169000	0.15939000
H	5.61211000	-3.28521400	-2.96163500	O	-1.78021100	-3.37507100	-1.27516800
H	6.51539100	-4.68021000	-2.33316500	O	-0.53856300	3.51390300	0.72216900
O	0.31791700	2.92601800	-1.96472700	C	-0.02680100	3.65653800	1.88848700
C	1.51628100	2.96945500	-2.48926700	O	0.60559500	2.77750700	2.53354900
O	2.37618100	2.08317400	-2.39828400	C	-0.21139200	5.03003200	2.52504000
C	1.76934600	4.25313100	-3.27631700	H	-1.25782700	5.32599000	2.36755300
H	0.97842100	4.32766600	-4.03814100	H	0.38552300	5.73125200	1.92153700
H	1.59470000	5.09706700	-2.59197600	C	0.18144700	5.11125700	4.00013500
C	3.15597300	4.34174600	-3.91813100	H	0.03987600	6.13248400	4.37671200
H	3.30914700	3.46862300	-4.56703600	H	-0.42706100	4.43263400	4.61015100
H	3.92206400	4.27723900	-3.13245600	H	1.23000400	4.82855800	4.14376700
C	3.34433200	5.63363500	-4.72117500	O	4.05467400	0.45814800	0.64193200
H	2.60979300	5.70864100	-5.53536500	C	3.96392100	0.89148100	1.81173000
H	3.22461400	6.52192000	-4.08503800	O	2.86610700	1.12239200	2.45033600
H	4.34486500	5.67796100	-5.17049100	C	5.21819100	1.21134100	2.60883200
N	-2.22966200	2.08916500	-0.94026500	H	5.28428000	2.29691200	2.75994500
C	-2.81885000	1.67944900	-2.11573900	H	6.10925300	0.86073900	2.08046700
H	-2.21234400	1.39205700	-2.96331600	H	5.15963400	0.74821500	3.60049400
C	-4.18585700	1.69070700	-1.97065100	O	0.49380000	0.31988900	3.56872300
N	-4.40869300	2.13553100	-0.67211900	C	-0.41545200	-0.53518800	3.85427900
H	-5.30215200	2.03449000	-0.18204100	O	-1.06481000	-1.21882700	3.01784900
C	-3.20845300	2.34387800	-0.08494400	C	-0.72613100	-0.70182500	5.33688000
H	-3.07346000	2.64154500	0.94452500	H	-1.29691600	0.18754200	5.64920600
C	-5.27651700	1.33585100	-2.94778600	H	-1.38647300	-1.57008600	5.45011500
H	-5.36464000	2.11843900	-3.71655900	C	0.52690200	-0.83453500	6.21696900
H	-4.97049400	0.42628800	-3.48399400	H	1.16984900	0.03823500	6.04759800
C	-6.68924200	1.12631100	-2.34501300	H	1.10385900	-1.71349200	5.89197500
H	-7.10381600	2.08397200	-2.01017900	C	0.18468200	-0.96341700	7.70495100
H	-7.34885700	0.74589300	-3.13710500	H	-0.36412600	-0.08124700	8.06435400

H	1.09314400	-1.06119400	8.31380800	O	-0.04571700	0.56851000	-1.62024100
H	-0.44298000	-1.84492400	7.89824100				

W2 (hydroxyl/oxo)-Wx (oxo/hydroxyl)

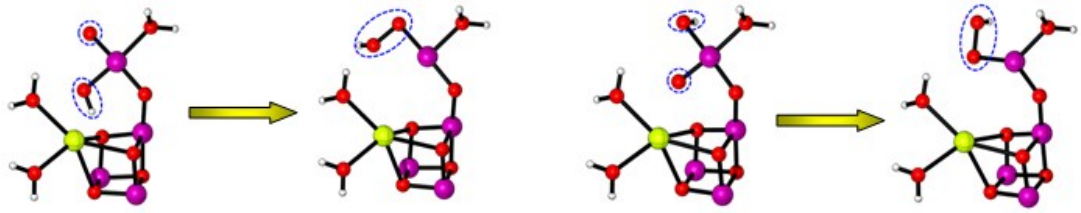

Fig. S11 Pictorial exhibitions for the closed-cubane Wx (hydroxyl)-W2 (oxo) (left) and W2 (hydroxyl)-Wx (oxo) (right) nucleophilic attack.

W2 (hydroxyl)-Wx (hydroxyl) coupling was inspected to be impracticable because of no observation of the corresponding eigenvector with negative eigenvalue and imaginary vibration of O7-O10 after many attempts.

Table S25 Reaction parameters for the closed-cubane Wx (hydroxyl)-W2 (oxyl) nucleophilic attack:

Spin state	Spin topology (Mn1~Mn4-O7)	Gibbs Free energy (a.u.)		
		Rea	TS	Pro
doublet	ααββα	-3366.2173	-3366.1596	-3366.1733
	αβαβα	-3366.2193	-3366.1612	-3366.1754
	αββαα	-3366.2029	-3366.1847	-3366.2253
	βααβα	-3366.2175	-3366.1628	-3366.1761
	βαβαα	-3366.2017	-3366.1838	-3366.2240
	ββααα	-3366.2009	-3366.1835	-3366.2236
sextet	αααββ	-3366.2049	-3366.1866	-3366.2270
	ααβαβ	-3366.2194	-3366.1626	-3366.1774
	αβααβ	-3366.2171	-3366.1597	-3366.1736
	βαααβ	-3366.2185	-3366.1608	-3366.1746
octet	αααβα	-3366.2198	-3366.1650	-3366.1788
	ααβαα	-3366.2042	-3366.1860	-3366.2265
	αβααα	-3366.2018	-3366.1836	-3366.2239
	βαααα	-3366.2030	-3366.1851	-3366.2250
12-et	aaaaβ	-3366.2197	-3366.1633	-3366.1762
14-et	aaaaa	-3366.2047	-3366.1864	-3366.2265
Spin state	Spin topology	Relative Gibbs Free energy (kcal/mol)		

	(Mn1~Mn4-O7)	$\Delta G^{\neq}$(Rea-TS)	ΔG(Rea-Pro)	ΔG(Rea)	ΔG(Pro)
doublet	ααββα	36.2	27.6	1.6	33.7
	αβαβα	36.5	27.5	0.3	32.4
	αββαα	11.4	-14.1	10.6	1.1
	βααβα	34.3	26.0	1.4	31.9
	βαβαα	11.2	-14.0	11.4	1.9
	ββααα	10.9	-14.2	11.9	2.1
sextet	αααββ	11.5	-13.9	9.3	0.0
	ααβαβ	35.6	26.4	0.3	31.1
	αβααβ	36.0	27.3	1.7	33.5
	βαααβ	36.2	27.5	0.8	32.9
octet	αααβα	34.4	25.7	0.0	30.2
	ααβαα	11.4	-14.0	9.8	0.3
	αβααα	11.4	-13.9	11.3	1.9
	βαααα	11.2	-13.8	10.5	1.3
12-et	ααααβ	35.4	27.3	0.1	31.9
14-et	ααααα	11.5	-13.7	9.5	0.3

Spin state	Spin topology (Mn1~Mn4-O7)		Mulliken spin density		
			Rea	TS	Pro
doublet	α	Mn1	2.93	2.94	2.93
	α	Mn2	2.94	2.95	2.95
	β	Mn3	-2.83	-2.83	-2.87
	β	Mn4	-2.57	-2.69	-1.96
	α	O7	0.59	0.27	-0.02
		O10	-0.07	0.40	0.01
	α	Mn1	2.93	2.94	2.93
	β	Mn2	-2.94	-2.94	-2.94
	α	Mn3	2.80	2.81	2.78
	β	Mn4	-2.62	-2.65	-1.89
	α	O7	0.72	0.32	-0.01
		O10	-0.05	0.39	0.01
	α	Mn1	2.92	2.92	2.93
	β	Mn2	-2.93	-2.93	-2.93
	β	Mn3	-2.84	-2.82	-2.82
	α	Mn4	2.74	3.12	3.87
	α	O7	1.04	0.64	-0.02
		O10	0.13	0.17	0.01
	β	Mn1	-2.92	-2.92	-2.92
	α	Mn2	2.93	2.93	2.93
	α	Mn3	2.83	2.83	2.80
	β	Mn4	-2.61	-2.65	-1.88

	α	O7	0.71	0.32	-0.01
		O10	-0.05	0.40	0.01
	β	Mn1	-2.93	-2.93	-2.93
	α	Mn2	2.94	2.94	2.95
	β	Mn3	-2.82	-2.80	-2.80
	α	Mn4	2.75	3.12	3.87
	α	O7	1.03	0.64	-0.02
		O10	0.14	0.17	0.01
	β	Mn1	-2.93	-2.93	-2.93
	β	Mn2	-2.95	-2.95	-2.95
	α	Mn3	2.84	2.85	2.85
	α	Mn4	2.79	3.22	3.92
	α	O7	1.06	0.64	-0.01
		O10	0.13	0.15	0.01
sextet	α	Mn1	2.93	2.93	2.93
	α	Mn2	2.93	2.93	2.93
	α	Mn3	2.85	2.83	2.83
	β	Mn4	-2.75	-3.12	-3.86
	β	O7	-1.03	-0.64	0.02
		O10	-0.13	-0.17	-0.01
	α	Mn1	2.93	2.93	2.93
	α	Mn2	2.94	2.95	2.95
	β	Mn3	-2.80	-2.79	-2.76
	α	Mn4	2.61	2.66	1.88
	β	O7	-0.71	-0.33	0.01
		O10	0.05	-0.40	-0.01
	α	Mn1	2.93	2.93	2.93
	β	Mn2	-2.93	-2.94	-2.94
	α	Mn3	2.85	2.85	2.88
	α	Mn4	2.57	2.68	1.96
	β	O7	-0.59	-0.27	0.02
		O10	0.06	-0.40	-0.01
	β	Mn1	-2.92	-2.93	-2.92
	α	Mn2	2.93	2.93	2.93
	α	Mn3	2.87	2.87	2.91
	α	Mn4	2.57	2.69	1.96
	β	O7	-0.59	-0.27	0.02
		O10	0.07	-0.40	-0.01
octet	α	Mn1	2.93	2.94	2.93
	α	Mn2	2.93	2.93	2.93
	α	Mn3	2.84	2.84	2.81
	β	Mn4	-2.60	-2.65	-1.89
	α	O7	0.71	0.32	-0.01
		O10	-0.06	0.39	0.01

	α	Mn1	2.93	2.93	2.93
	α	Mn2	2.94	2.95	2.95
	β	Mn3	-2.80	-2.78	-2.78
	α	Mn4	2.74	3.12	3.86
	α	O7	1.03	0.64	-0.02
		O10	0.13	0.16	0.01
	α	Mn1	2.93	2.93	2.93
	β	Mn2	-2.94	-2.94	-2.94
	α	Mn3	2.85	2.86	2.86
	α	Mn4	2.79	3.22	3.92
	α	O7	1.06	0.65	-0.01
		O10	0.13	0.15	0.01
	β	Mn1	-2.92	-2.92	-2.92
	α	Mn2	2.93	2.93	2.94
	α	Mn3	2.88	2.89	2.89
	α	Mn4	2.79	3.22	3.92
	α	O7	1.06	0.64	-0.01
		O10	0.13	0.15	0.01
12-et	α	Mn1	2.93	2.93	2.93
	α	Mn2	2.93	2.93	2.93
	α	Mn3	2.88	2.88	2.91
	α	Mn4	2.58	2.69	1.96
	β	O7	-0.59	-0.27	0.02
		O10	0.06	-0.40	-0.01
14-et	α	Mn1	2.93	2.93	2.93
	α	Mn2	2.93	2.93	2.93
	α	Mn3	2.88	2.89	2.90
	α	Mn4	2.79	3.22	3.92
	α	O7	1.06	0.65	-0.01
		O10	0.13	0.15	0.01

Rea:

Ca	-2.55146500	0.07793100	-1.23872300	O	-2.12097400	0.75001400	-3.65621000
Mn	0.06050700	-1.76297900	-0.23131400	H	-2.81534900	1.41209500	-3.81589400
Mn	-1.50991400	-0.97591500	1.82974100	H	-1.29635500	1.28850800	-3.54545900
Mn	0.07472700	0.96371100	0.69107900	O	0.98092500	4.23707100	-2.97835300
Mn	0.32452100	3.26873200	-1.58259200	O	0.52603100	5.02709800	-0.35926300
O	-1.68169300	-1.78013600	0.21183900	H	-0.29591200	5.46362800	-0.66653000
O	0.31962200	-0.85777400	1.36987600	H	0.25423500	4.52303100	0.44124000
O	-1.68430600	0.63312500	1.04868800	O	-2.93561900	2.42597500	-1.50482400
O	-0.02179200	-0.04281100	-0.91209700	C	-2.62476600	3.62471600	-1.60949600
O	-0.23312000	2.55161600	0.01083100	O	-1.43538600	4.09109600	-1.82549000
O	-4.68824100	-0.65290900	-2.36226600	C	-3.73258300	4.67961500	-1.54749200
H	-5.11475100	-0.91651100	-1.52222600	H	-4.29385100	4.59203800	-2.49074100
H	-4.27811700	-1.46416100	-2.72485300	H	-4.42554300	4.35753500	-0.75938600

C	-3.27719700	6.12397500	-1.33574200	H	4.60913000	2.06707500	2.01488800
H	-2.60436500	6.45005100	-2.13701400	C	4.19221800	2.18284900	-0.11060200
H	-2.75013300	6.23896600	-0.37814400	H	4.56743300	1.74078400	-1.04633500
H	-4.14106100	6.80047900	-1.31651100	H	4.44062800	3.25125400	-0.16601300
O	-0.21487600	-2.71028400	-1.87936300	C	2.67104000	2.06934800	-0.20980100
C	-1.30863700	-2.82318700	-2.57722000	O	2.07512400	1.24062600	0.53168000
O	-2.29207800	-2.06732400	-2.49173300	O	2.17228200	2.82918800	-1.10444800
C	-1.28764500	-3.98682200	-3.56180300	O	0.24594900	-3.46820400	0.85301800
H	-0.38845900	-3.86926500	-4.18559300	C	-0.35982800	-3.64925500	1.96734800
H	-1.11732200	-4.90413500	-2.97734400	O	-1.07686900	-2.80912500	2.58881900
C	-2.54041300	-4.11300400	-4.43189100	C	-0.20241800	-5.03660300	2.58098100
H	-2.69653100	-3.17184500	-4.97670200	H	0.83649300	-5.35366000	2.41938900
H	-3.41894200	-4.24051600	-3.78350500	H	-0.81685200	-5.71279300	1.96593100
C	-2.45010700	-5.28218300	-5.41892800	H	-5.74317400	-2.35840300	2.45826200
H	-1.59730500	-5.16293800	-6.10197900	C	-0.60212000	-5.13522200	4.05370000
H	-3.35843100	-5.35573300	-6.03089700	H	-0.47940800	-6.16509100	4.41234500
H	-2.32242700	-6.24001500	-4.89496200	H	0.01720500	-4.47910700	4.67768600
N	2.09466900	-1.94036700	-0.58900600	H	-1.64610600	-4.83743800	4.19830300
C	2.82680600	-1.45177400	-1.64951300	O	-4.35248900	-0.58709900	0.36244900
H	2.34400300	-0.95515600	-2.48015400	C	-4.37804400	-0.97086200	1.54964900
C	4.16181900	-1.70948400	-1.43853800	O	-3.34224200	-1.15101900	2.30891200
N	4.21173100	-2.38516200	-0.22471100	C	-5.69745400	-1.28501400	2.23255500
H	5.06951700	-2.51347700	0.31984400	H	-6.53790900	-1.00786500	1.59037800
C	2.95454500	-2.48364500	0.25966400	H	-5.75977600	-0.74999300	3.18735800
H	2.69383100	-2.93223700	1.20640400	O	-1.03077400	-0.05745600	3.53075500
C	5.37252800	-1.39182200	-2.27861800	C	-0.29362200	0.98124200	3.57583000
H	5.43390300	-2.08441000	-3.13144100	O	0.25635200	1.56942600	2.58778800
H	5.22671700	-0.39485300	-2.71671200	C	-0.03387300	1.56856900	4.95512300
C	6.74147500	-1.44294900	-1.54543500	H	0.65687100	0.88238500	5.47066500
H	7.03391200	-2.48193800	-1.35695800	H	0.48701700	2.52516300	4.82982700
H	7.50277900	-1.00420200	-2.20475500	C	-1.31124800	1.73331900	5.79531400
C	6.71370800	-0.74544300	-0.18706700	H	-1.81276800	0.76029400	5.86941300
O	6.55722800	-1.39009800	0.85865800	H	-2.00609400	2.40314000	5.26686900
N	6.78655300	0.61139700	-0.19787100	C	-1.01901000	2.28946000	7.19269400
H	6.86820400	1.07699600	-1.09373300	H	-0.35110600	1.62160300	7.75482700
C	6.37777800	1.41208500	0.96219800	H	-1.94356400	2.40233100	7.77353800
H	6.80234600	0.93687900	1.85179400	H	-0.53555700	3.27506700	7.14012800
H	6.83382200	2.40447600	0.85609700	O	0.13742100	1.89502800	-2.69063600
C	4.84615100	1.50968600	1.09777500	H	0.34697600	1.06740000	-2.16387500
H	4.43632800	0.50240200	1.23211000				

TS:

Ca	-2.47349500	-0.09366700	-1.28525400	Mn	0.01326400	0.94654500	0.67196900
Mn	0.19659000	-1.76174600	-0.20772900	Mn	0.01099600	3.32474900	-1.57562600
Mn	-1.45717400	-1.07680100	1.81921900	O	-1.55172000	-1.89723900	0.20271800

O	0.37352500	-0.83907900	1.39352900	H	2.78526400	-2.30501800	1.56668400
O	-1.72105200	0.51255000	1.02169200	C	5.60872800	-1.38998800	-2.02365700
O	0.01568800	-0.07724700	-0.89951300	H	5.76171700	-2.22155100	-2.72771600
O	-0.42952800	2.48715700	-0.03265300	H	5.44324700	-0.50073800	-2.64823000
O	-4.53491600	-0.97049300	-2.45268900	C	6.92727000	-1.21864700	-1.22166300
H	-4.95734700	-1.24856300	-1.61475700	H	7.25769700	-2.18366000	-0.82189300
H	-4.05997400	-1.75638800	-2.79173200	H	7.70696100	-0.86677400	-1.91106400
O	-2.15636400	0.59103400	-3.71803500	C	6.78756300	-0.28168400	-0.02252100
H	-2.94393000	1.15127900	-3.83504400	O	6.63721800	-0.72874600	1.12266000
H	-1.41081900	1.23430900	-3.72853900	N	6.75821000	1.05008400	-0.28616600
O	0.48716100	4.07718700	-3.17747300	H	6.84430000	1.35224700	-1.24898800
O	0.25096300	5.10831300	-0.19293000	C	6.28882900	2.02082100	0.70995000
H	-0.61518500	5.49712800	-0.42911700	H	6.76970400	1.77307300	1.66157200
H	0.04762800	4.52067800	0.56669800	H	6.64574900	3.00984700	0.39640800
O	-3.05351900	2.22402000	-1.59348800	C	4.75805400	2.00837700	0.87931800
C	-2.90982900	3.45899500	-1.52548600	H	4.44466100	1.02175400	1.23730800
O	-1.78778500	4.08954900	-1.66236100	H	4.49090900	2.72670100	1.66735400
C	-4.14266900	4.33737900	-1.31514500	C	4.01868200	2.35314700	-0.41527700
H	-4.76245100	4.21969100	-2.21708400	H	4.36566600	1.70038700	-1.23198500
H	-4.71715300	3.87345100	-0.50180100	H	4.22233500	3.38253100	-0.73779900
C	-3.87721700	5.81695100	-1.03596000	C	2.50009500	2.17930100	-0.38466800
H	-3.31299500	6.28057000	-1.85328900	O	1.99605000	1.41825500	0.48064700
H	-3.30251000	5.94994800	-0.10954500	O	1.89963800	2.82447500	-1.31551700
H	-4.82318700	6.36092900	-0.91935500	O	0.45124900	-3.46914100	0.90923700
O	0.04441000	-2.73938900	-1.85874900	C	-0.16730900	-3.67260200	2.00711400
C	-1.01950000	-2.91775000	-2.58601800	O	-0.93778300	-2.86095500	2.61005700
O	-2.04816300	-2.22009800	-2.53241300	C	0.03459800	-5.04658000	2.63905400
C	-0.90643000	-4.08318600	-3.56307800	H	1.08106300	-5.33497600	2.47432400
H	0.00422000	-3.92205300	-4.16015800	H	-0.56524200	-5.74823600	2.03799900
H	-0.70607600	-4.98723500	-2.96762400	H	-5.62201400	-2.71460500	2.31743100
C	-2.12322300	-4.28107600	-4.47001900	C	-0.35368700	-5.13819800	4.11553200
H	-2.31432500	-3.35215100	-5.02472800	H	-0.20096600	-6.15966900	4.48682800
H	-3.01265100	-4.45313300	-3.84742600	H	0.25135400	-4.45796300	4.72793000
C	-1.94055000	-5.44796700	-5.44696500	H	-1.40434600	-4.86644400	4.26275500
H	-1.07505500	-5.28624000	-6.10501200	O	-4.28037400	-0.86124300	0.27605500
H	-2.82469200	-5.57324700	-6.08542300	C	-4.31271800	-1.24093000	1.46489600
H	-1.77738100	-6.39517500	-4.91364200	O	-3.29012500	-1.35359300	2.25363000
N	2.25753900	-1.83046900	-0.44890700	C	-5.62867700	-1.63592000	2.11273200
C	3.03183900	-1.54256800	-1.55017200	H	-6.46844200	-1.39274200	1.45591500
H	2.57663200	-1.30821500	-2.50286000	H	-5.74066100	-1.12372900	3.07533000
C	4.36272400	-1.62324100	-1.20663100	O	-1.06396100	-0.10431300	3.51690400
N	4.36585400	-1.98952900	0.13413500	C	-0.38805300	0.97608600	3.55928300
H	5.19045900	-1.94787700	0.74000700	O	0.14364300	1.58441500	2.57403700
C	3.08533200	-2.08230900	0.55361900	C	-0.18709700	1.59160300	4.93691800

H	0.52347200	0.94590100	5.47712500	H	-0.57115500	1.66187500	7.72837200
H	0.28959500	2.57095000	4.81101500	H	-2.19935200	2.36488900	7.70150700
C	-1.48969900	1.70436800	5.74641200	H	-0.82052900	3.29720700	7.08881800
H	-1.94532500	0.70908000	5.82132300	O	-0.03430100	2.30408300	-3.24391400
H	-2.20371900	2.33360600	5.19405000	H	0.88346100	2.00960000	-3.40058700
C	-1.25730000	2.29008500	7.14293200				

Pro:

Ca	-2.37669900	0.16384400	-1.35051800	H	-1.51778600	-1.59525700	-5.91327900
Mn	0.34707100	-1.63716500	-0.57300800	H	-2.27414700	-3.04268300	-5.26600600
Mn	-1.50857000	-1.65772400	1.38904400	C	-0.98068700	-3.41683800	-6.96338100
Mn	-0.14158000	0.70481700	0.98674300	H	-0.06051300	-3.02591100	-7.42016900
Mn	-0.32920700	3.36193500	-0.81398000	H	-1.78274000	-3.33437100	-7.70818400
O	-1.41429200	-1.97562200	-0.39941600	H	-0.82119100	-4.48541700	-6.76166100
O	0.32385800	-1.19836000	1.22698800	N	2.42406600	-1.53562800	-0.57420300
O	-1.84890700	0.07391000	1.05707400	C	3.31150900	-1.14152200	-1.54996800
O	0.07835900	0.15114900	-0.78457300	H	2.96487800	-0.86910200	-2.53760400
O	-0.70406100	2.32743400	0.62780600	C	4.59265500	-1.18379000	-1.04622700
O	-4.16271300	-0.47630800	-3.00108900	N	4.44990100	-1.64048500	0.25881900
H	-4.66425800	-1.00681800	-2.34952600	H	5.19184100	-1.61825600	0.96370800
H	-3.58873200	-1.10442100	-3.48402600	C	3.13425300	-1.81832400	0.50754000
O	-1.20460400	1.91076000	-2.74735700	H	2.71988000	-2.11090700	1.46139200
H	-1.76545900	2.65644500	-3.02898100	C	5.91324600	-0.82800200	-1.68162400
H	-0.32083500	2.10951800	-3.14638100	H	6.20376400	-1.59812100	-2.41174700
O	0.12188000	4.31962000	-2.36037200	H	5.76975400	0.09232200	-2.26535100
O	-0.11585000	4.99258000	0.87750800	C	7.10930800	-0.64191800	-0.70910500
H	-0.99435000	5.37259200	0.67952800	H	7.46090400	-1.61463000	-0.34825700
H	-0.31216600	4.25964800	1.49928500	H	7.93773300	-0.18154100	-1.26483600
O	-3.42426600	2.32983900	-1.09580600	C	6.76265500	0.17266300	0.53717900
C	-3.27161300	3.53245900	-0.80174900	O	6.54068100	-0.38444400	1.62083700
O	-2.14090800	4.16451200	-0.82578600	N	6.63497100	1.51466900	0.37886400
C	-4.50156100	4.35735400	-0.42839700	H	6.79469800	1.91186100	-0.53884400
H	-5.12051700	4.41857000	-1.33651900	C	6.02268800	2.35884000	1.41255300
H	-5.08121300	3.74884600	0.27885300	H	6.49113000	2.10467900	2.36923000
C	-4.22910700	5.75377000	0.13139900	H	6.28037000	3.39857500	1.17541500
H	-3.66255900	6.36433300	-0.58116400	C	4.49759600	2.17556400	1.51882200
H	-3.65329500	5.70250300	1.06525500	H	4.27983300	1.14571300	1.82013500
H	-5.17210800	6.27025300	0.35194500	H	4.13043900	2.82311900	2.32756800
O	0.43287600	-2.09001300	-2.44881100	C	3.76588500	2.50316200	0.21505900
C	-0.51092500	-1.98472000	-3.33231300	H	4.18115700	1.90028100	-0.60825200
O	-1.55623900	-1.31882600	-3.19456200	H	3.90028800	3.55541100	-0.06921900
C	-0.23522100	-2.75410000	-4.62112100	C	2.26587800	2.21834600	0.20832000
H	0.72432900	-2.38875600	-5.01911800	O	1.80121800	1.38285400	1.02626600
H	-0.05135700	-3.80233500	-4.34096800	O	1.61197800	2.86218300	-0.68945100
C	-1.33375400	-2.65344800	-5.68195800	O	0.63566600	-3.58332100	0.02226100

C	-0.03964000	-4.12376400	0.95899700	O	-1.31530300	-1.16857200	3.31859800
O	-0.90823200	-3.55749500	1.69653700	C	-0.74007000	-0.10105400	3.71309100
C	0.21969300	-5.60839700	1.19629100	O	-0.18650500	0.78718000	2.98379000
H	1.29895200	-5.77532200	1.08233900	C	-0.70975700	0.12851200	5.21688700
H	-0.25306500	-6.13822100	0.35428600	H	-0.07033300	-0.65406200	5.65406600
H	-5.52593500	-3.62737800	1.04169300	H	-0.23320900	1.09666200	5.41005500
C	-0.29929700	-6.14774000	2.52988400	C	-2.10729700	0.05955300	5.85770500
H	-0.09173600	-7.22232700	2.61266400	H	-2.55843200	-0.91083600	5.61473100
H	0.17999400	-5.64067400	3.37651600	H	-2.75036700	0.82728700	5.40188300
H	-1.37952100	-5.99277900	2.62304600	C	-2.06041900	0.25924400	7.37593900
O	-4.20830500	-1.19730100	-0.32256200	H	-1.44835300	-0.51485800	7.85994300
C	-4.30110400	-1.89291000	0.70929700	H	-3.06676700	0.20963800	7.81170300
O	-3.33922100	-2.15279400	1.54054300	H	-1.63028900	1.23570400	7.63931700
C	-5.62359300	-2.53511700	1.09105300	O	0.95841000	3.44830300	-3.17885400
H	-6.41920000	-2.20468900	0.41770600	H	1.70323700	3.28602100	-2.55437700
H	-5.87626200	-2.27876100	2.12664200				

Table S26 Reaction parameters for the closed-cubane W2 (hydroxyl)-Wx (oxyl) nucleophilic attack:

Spin state	Spin topology (Mn1~Mn4-O7/O10)	Gibbs Free energy (a.u.)		
		Rea	TS	Pro
doublet	ααββα	-3366.2506	-3366.1785	-3366.1807
	αβαβα	-3366.2510	-3366.1802	-3366.1831
	αββαα	-3366.2116	-3366.1906	-3366.2130
	βααβα	-3366.2493	-3366.1796	-3366.1826
	βαβαα	-3366.2113	-3366.1892	-3366.2115
	ββααα	-3366.2088	-3366.1885	-3366.2129
sextet	αααββ	-3366.2140	-3366.1927	-3366.2155
	ααβαβ	-3366.2522	-3366.1811	-3366.1837
	αβααβ	-3366.2503	-3366.1785	-3366.1825
	βαααβ	-3366.2481	-3366.1787	-3366.1815
octet	αααβα	-3366.2535	-3366.1822	-3366.1849
	ααβαα	-3366.2131	-3366.1919	-3366.2146
	αβααα	-3366.2095	-3366.1887	-3366.2122
	βαααα	-3366.2101	-3366.1900	-3366.2142
12-et	ααααβ	-3366.2517	-3366.1819	-3366.1854
14-et	ααααα	-3366.2121	-3366.1917	-3366.2159

Spin state	Spin topology (Mn1~Mn4-O7/O10)	Relative Gibbs Free energy (kcal/mol)			
		$\Delta G^{\neq}$(Rea-TS)	ΔG(Rea-Pro)	ΔG(Rea)	ΔG(Pro)
doublet	ααββα	45.2	43.9	1.8	22.1
	αβαβα	44.4	42.6	1.6	20.6

	αββαα	13.2	-0.9	26.3	1.8
	βααβα	43.7	41.9	2.6	20.9
	βαβαα	13.9	-0.1	26.5	2.8
	ββααα	12.7	-2.6	28.0	1.9
sextet	αααββ	13.4	-0.9	24.8	0.3
	ααβαβ	44.6	43.0	0.8	20.2
	αβααβ	45.1	42.5	2.0	21.0
	βαααβ	43.5	41.8	3.4	21.6
octet	αααβα	44.7	43.0	0.0	19.5
	ααβαα	13.3	-0.9	25.4	0.8
	αβααα	13.1	-1.7	27.6	2.3
	βαααα	12.6	-2.6	27.2	1.1
12-et	ααααβ	43.8	41.6	1.1	19.1
14-et	ααααα	12.8	-2.4	26.0	0.0

Spin state	Spin topology (Mn1~Mn4-O7/O10)		Mulliken spin density		
			Rea	TS	Pro
doublet	α	Mn1	2.92	2.93	2.93
	α	Mn2	2.94	2.95	2.95
	β	Mn3	-2.91	-2.84	-2.84
	β	Mn4	-1.87	-2.43	-2.01
	α	O7	0.04	0.33	0.01
		O10	-0.16	0.09	0.00
	α	Mn1	2.93	2.96	2.93
	β	Mn2	-2.93	-2.93	-2.94
	α	Mn3	2.88	2.91	2.93
	β	Mn4	-1.81	-2.40	-1.99
	α	O7	0.06	0.35	0.03
		O10	-0.13	0.10	-0.01
	α	Mn1	2.92	2.92	2.91
	β	Mn2	-2.93	-2.93	-2.93
	β	Mn3	-2.83	-2.83	-2.82
	α	Mn4	2.63	3.34	3.78
	α	O7	0.33	0.21	-0.02
		O10	0.86	0.33	0.09
	β	Mn1	-2.91	-2.90	-2.91
	α	Mn2	2.93	2.93	2.93
	α	Mn3	2.90	2.91	2.95
	β	Mn4	-1.80	-2.39	-1.98
	α	O7	0.06	0.35	0.03
		O10	-0.13	0.10	-0.01
	β	Mn1	-2.92	-2.92	-2.92
	α	Mn2	2.93	2.93	2.94
	β	Mn3	-2.82	-2.82	-2.81

	α	Mn4	2.64	3.34	3.78
	α	O7	0.33	0.21	-0.02
		O10	0.86	0.33	0.09
	β	Mn1	-2.92	-2.92	-2.92
	β	Mn2	-2.94	-2.94	-2.94
	α	Mn3	2.87	2.89	2.90
	α	Mn4	-2.71	3.40	3.86
	α	O7	0.38	0.24	-0.02
		O10	0.84	0.33	0.08
sextet	α	Mn1	2.92	2.92	2.92
	α	Mn2	2.93	2.93	2.93
	α	Mn3	2.84	2.84	2.84
	β	Mn4	-2.64	-3.34	-3.78
	β	O7	-0.33	-0.21	0.02
		O10	-0.86	-0.33	-0.09
	α	Mn1	2.92	2.91	2.92
	α	Mn2	2.94	2.95	2.95
	β	Mn3	-2.87	-2.87	-2.90
	α	Mn4	1.80	2.39	1.98
	β	O7	-0.06	-0.36	-0.03
		O10	0.13	-0.10	0.01
	α	Mn1	2.92	2.92	2.93
	β	Mn2	-2.92	-2.94	-2.94
	α	Mn3	2.92	2.86	2.86
	α	Mn4	1.87	2.43	2.01
	β	O7	-0.04	-0.33	-0.01
		O10	0.16	-0.10	0.00
	β	Mn1	-2.91	-2.92	-2.92
	α	Mn2	2.92	2.93	2.93
	α	Mn3	2.93	2.88	2.88
	α	Mn4	1.87	2.43	2.01
	β	O7	-0.04	-0.33	-0.01
		O10	0.16	-0.09	0.00
octet	α	Mn1	2.93	2.95	2.93
	α	Mn2	2.92	2.93	2.93
	α	Mn3	2.89	2.93	2.96
	β	Mn4	-1.80	-2.39	-1.98
	α	O7	0.06	0.35	0.03
		O10	-0.13	0.10	-0.01
	α	Mn1	2.93	2.93	2.92
	α	Mn2	2.94	2.94	2.94
	β	Mn3	-2.79	-2.79	-2.79
	α	Mn4	2.63	3.34	3.78
	α	O7	0.33	0.21	-0.02

		O10	0.86	0.33	0.09
	α	Mn1	2.93	2.94	2.92
	β	Mn2	-2.93	-2.93	-2.93
	α	Mn3	2.89	2.91	2.92
	α	Mn4	2.71	3.40	3.86
	α	O7	0.38	0.24	-0.02
		O10	0.84	0.33	0.08
	β	Mn1	-2.91	-2.91	-2.91
	α	Mn2	2.93	2.93	2.93
	α	Mn3	2.90	2.92	2.93
	α	Mn4	2.71	3.40	3.86
	α	O7	0.38	0.24	-0.02
		O10	0.84	0.33	0.08
12-et	α	Mn1	2.92	2.92	2.93
	α	Mn2	2.92	2.93	2.93
	α	Mn3	2.94	2.89	2.90
	α	Mn4	1.87	2.43	2.01
	β	O7	-0.04	-0.33	-0.01
		O10	0.16	-0.09	0.00
14-et	α	Mn1	2.93	2.93	2.93
	α	Mn2	2.93	2.93	2.93
	α	Mn3	2.92	2.93	2.94
	α	Mn4	2.71	3.40	3.86
	α	O7	0.38	0.24	-0.02
		O10	0.84	0.33	0.08

Rea:

Ca	-2.27540500	-0.33457600	-1.68948100	O	-0.94957900	4.97405400	0.41246100
Mn	0.43329100	-1.74092300	-0.33309500	H	-1.78917800	5.20973500	-0.03281000
Mn	-1.58283500	-1.53758600	1.45891900	H	-1.19824000	4.28924100	1.06859600
Mn	-0.32307200	0.79006000	0.73258700	O	-3.12740000	1.91213100	-1.95049000
Mn	-0.33498700	3.50187700	-1.08607600	C	-3.14454400	3.15415600	-1.92268000
O	-1.30820200	-2.18708400	-0.20190200	O	-2.12614600	3.92968800	-1.70896000
O	0.22695100	-0.96261900	1.34633600	C	-4.45829200	3.88339500	-2.21363800
O	-1.99003500	0.07379300	0.76400500	H	-4.60326400	3.82846100	-3.30412400
O	0.07191200	-0.03871700	-0.88911800	H	-5.26023000	3.27592700	-1.77534600
O	-0.92473700	2.31816500	0.09053400	C	-4.53620200	5.33815700	-1.74738700
O	-3.99260800	-1.34622500	-3.23949700	H	-3.74634500	5.94368600	-2.20564200
H	-4.49425200	-1.75820400	-2.50717800	H	-4.43365600	5.41257800	-0.65568500
H	-3.36067000	-2.02882300	-3.54674400	H	-5.50588400	5.77605000	-2.01620800
O	-1.33321000	0.69967100	-3.79621700	O	0.61149800	-2.59406900	-2.05015900
H	-2.05590800	1.26035800	-4.12681800	C	-0.30311900	-2.83597500	-2.94142700
H	-0.68851100	1.35287800	-3.42270000	O	-1.41445300	-2.27703300	-2.99740300
O	0.33268000	4.71631300	-2.33429800	C	0.08587100	-3.89163000	-3.96899600
H	1.29729200	4.74667300	-2.17725100	H	0.12716400	-4.86001400	-3.44558400

H	-0.71626100	-3.94947500	-4.71471800	C	1.99477700	2.70621400	0.52802000
C	1.44264400	-3.62476700	-4.64294400	O	1.54273500	1.60227700	0.92721300
H	2.21369500	-3.55394700	-3.86497300	O	1.41969900	3.57760400	-0.21299000
H	1.40925900	-2.64554900	-5.14363200	O	0.85540000	-3.46456600	0.69071500
C	1.81338500	-4.71053000	-5.65857300	C	0.13955600	-3.87286800	1.66820200
H	1.88353100	-5.69683800	-5.17832300	O	-0.85905700	-3.27971300	2.18164300
H	2.78241800	-4.49898000	-6.12953600	C	0.52757800	-5.22744100	2.25285000
H	1.06336000	-4.78382000	-6.45841900	H	1.62433000	-5.26144600	2.30382500
N	2.46893900	-1.40925100	-0.41727100	H	0.24367600	-5.97825100	1.49889900
C	3.11272500	-0.50736300	-1.23809400	H	-5.44725100	-3.80542400	1.09479600
H	2.54942000	0.10310500	-1.93155100	C	-0.10919000	-5.55157700	3.60463100
C	4.46220900	-0.54471000	-0.97795600	H	0.20721600	-6.54573400	3.94530700
N	4.61638900	-1.50662600	0.01622500	H	0.18338700	-4.81860100	4.36639500
H	5.44478500	-1.57191800	0.61113600	H	-1.20232400	-5.53764900	3.53763400
C	3.39255300	-1.98449100	0.33708800	O	-4.13993400	-1.52859000	-0.49154500
H	3.19733900	-2.72481600	1.09893700	C	-4.28459400	-2.06141500	0.62705000
C	5.60747300	0.20943200	-1.60028200	O	-3.38385000	-2.13014000	1.55962900
H	5.91183700	-0.26984900	-2.54320100	C	-5.59931500	-2.72184000	1.00430100
H	5.23904100	1.20595300	-1.87905000	H	-6.36121400	-2.52050700	0.24622400
C	6.88165900	0.34883200	-0.72111100	H	-5.93390200	-2.35815800	1.98274200
H	7.42537700	-0.60186200	-0.68519900	O	-1.60792000	-0.70270100	3.27553300
H	7.54808500	1.08744200	-1.18722800	C	-1.13888900	0.45747800	3.51421000
C	6.55309200	0.72128500	0.72200400	O	-0.58771600	1.24557400	2.67706500
O	6.46450700	-0.14419800	1.60103200	C	-1.22917600	0.94321000	4.95432500
N	6.28856100	2.03529900	0.95894000	H	-0.44591300	0.41156400	5.51855400
H	6.33697100	2.67483200	0.17508500	H	-0.97499500	2.00982200	4.97442500
C	5.57418200	2.47583500	2.16129300	C	-2.59575500	0.68081900	5.60677900
H	5.96609900	1.89230900	2.99977300	H	-2.81986700	-0.39092000	5.53799800
H	5.82709400	3.53005800	2.33321300	H	-3.37634700	1.19920800	5.02989700
C	4.05146600	2.27378700	2.04688800	C	-2.64027600	1.14162900	7.06735000
H	3.84436800	1.20818100	1.89775900	H	-1.89083600	0.61372500	7.67390700
H	3.58581400	2.55148400	3.00305300	H	-3.62501100	0.94867400	7.51240900
C	3.42749400	3.08407200	0.90771800	H	-2.43949400	2.21865700	7.15571200
H	4.00739700	2.94899000	-0.01930900	O	0.21018500	2.42100900	-2.32543800
H	3.44192200	4.16190400	1.11801200				

TS:

Ca	-2.28049000	-0.07617100	-1.72524300	O	0.06461700	0.09671200	-0.83061900
Mn	0.35851300	-1.66401700	-0.44407400	O	-0.84151500	2.38890500	0.35457800
Mn	-1.70145300	-1.57860600	1.31133900	O	-3.98592100	-0.88534000	-3.40419000
Mn	-0.34509100	0.76181900	0.87236300	H	-4.51415700	-1.35787500	-2.72976200
Mn	-0.11571000	3.37408200	-0.89964500	H	-3.36334800	-1.54719200	-3.76943900
O	-1.39818200	-2.06635700	-0.40062700	O	-1.37290700	1.13234500	-3.75564500
O	0.12780300	-1.05771500	1.30324300	H	-2.08355100	1.75377800	-3.98859400
O	-2.03441200	0.11091400	0.77423100	H	-0.64094200	1.71833800	-3.42515600

O	0.72509000	4.25132400	-2.45405000	N	6.35873300	1.67814400	1.31884000
H	1.68433800	4.22750300	-2.26398100	H	6.44461100	2.39467200	0.60815200
O	-0.51381900	5.27426800	0.46156200	C	5.62288300	2.01320300	2.54278000
H	-1.35721100	5.39976100	-0.02005700	H	5.97523700	1.33562600	3.32625100
H	-0.75746400	4.73691300	1.23940100	H	5.89875700	3.03629000	2.82906900
O	-3.11277400	2.18450200	-1.73873100	C	4.09935000	1.86716400	2.36681100
C	-2.99292200	3.41978500	-1.65169900	H	3.87228700	0.82836700	2.10180700
O	-1.87456000	4.05816900	-1.50545500	H	3.61042300	2.05394200	3.33292100
C	-4.24610400	4.28822700	-1.77718900	C	3.53109100	2.80784200	1.30095000
H	-4.56512100	4.21814600	-2.82869700	H	4.15625700	2.79040100	0.39513900
H	-5.03314700	3.78752700	-1.19817300	H	3.53124300	3.85340000	1.64060600
C	-4.09556800	5.75303400	-1.36520300	C	2.11756300	2.49098300	0.81105000
H	-3.31957600	6.25448600	-1.95485900	O	1.55775600	1.44213900	1.22255000
H	-3.82778900	5.84351900	-0.30333300	O	1.65477200	3.34889700	-0.01774100
H	-5.03983000	6.29279000	-1.51172300	O	0.69996600	-3.49493800	0.40981400
O	0.56375500	-2.35112200	-2.23100000	C	-0.05460900	-3.97704000	1.32251800
C	-0.33144000	-2.48756900	-3.16369200	O	-1.04939700	-3.40765400	1.86885100
O	-1.42731900	-1.89773100	-3.19548000	C	0.27668100	-5.39578400	1.77491000
C	0.06246800	-3.45261600	-4.27495900	H	1.37038600	-5.47301800	1.84104600
H	0.07691200	-4.46525500	-3.84175100	H	-0.01671400	-6.05732900	0.94476600
H	-0.72370600	-3.42718000	-5.03920700	H	-5.61547400	-3.68620100	0.67913400
C	1.43792000	-3.14928700	-4.89357600	C	-0.39829000	-5.83057600	3.07621100
H	2.19276000	-3.16404900	-4.09679100	H	-0.12271600	-6.86448000	3.32036600
H	1.43108000	-2.12781300	-5.30249200	H	-0.09662700	-5.18843400	3.91278400
C	1.81359800	-4.14365100	-5.99719100	H	-1.48870000	-5.77087700	2.99236600
H	1.85690900	-5.17105900	-5.60865800	O	-4.20472800	-1.32290200	-0.69139600
H	2.79622400	-3.90739400	-6.42643600	C	-4.39365800	-1.94631800	0.37182200
H	1.08050100	-4.12933800	-6.81573700	O	-3.51857900	-2.12312600	1.31485800
N	2.40671300	-1.39937400	-0.45268800	C	-5.73598000	-2.59515700	0.66106200
C	3.10395700	-0.44750700	-1.16708800	H	-6.46812300	-2.31849000	-0.10249400
H	2.58029000	0.25941900	-1.79793600	H	-6.09153800	-2.29142400	1.65255800
C	4.44678200	-0.57920600	-0.90110000	O	-1.75666600	-0.93523400	3.20110100
N	4.54105100	-1.64880900	-0.01543800	C	-1.26319300	0.18027900	3.57019800
H	5.35754000	-1.81967300	0.57498000	O	-0.65646400	1.02611100	2.83476400
C	3.29149700	-2.09734300	0.24215200	C	-1.40035200	0.52747600	5.04559200
H	3.05087700	-2.90607200	0.91641300	H	-0.68935300	-0.11237100	5.59246800
C	5.63656200	0.17868300	-1.42861000	H	-1.07987200	1.56664000	5.18598000
H	5.92960900	-0.21108700	-2.41531400	C	-2.81815700	0.30045300	5.59522300
H	5.32177000	1.21682500	-1.60087000	H	-3.10697900	-0.74110000	5.40683000
C	6.90419200	0.15849400	-0.52876800	H	-3.52693500	0.92698900	5.03325700
H	7.40140400	-0.81585000	-0.59266600	C	-2.91939700	0.61893700	7.09045700
H	7.61134200	0.91026200	-0.90522300	H	-2.24346300	-0.01721000	7.67923300
C	6.57192300	0.38707000	0.94319800	H	-3.93943200	0.45393300	7.46102000
O	6.43243300	-0.56362700	1.72177300	H	-2.65444100	1.66534900	7.29739900

O	0.55761800	2.47773100	-2.40107100				

Pro:

Ca	-2.27934100	0.03140700	-1.72862200	H	2.80435300	-3.52295700	-6.62118000
Mn	0.35165300	-1.64017200	-0.51652700	H	1.08966400	-3.73883200	-7.01856800
Mn	-1.71768200	-1.64458100	1.22948000	N	2.39968100	-1.37195300	-0.50768800
Mn	-0.35938800	0.71552200	0.91797700	C	3.09551200	-0.36442200	-1.14373700
Mn	-0.11874800	3.39354800	-0.72999300	H	2.57116300	0.39622200	-1.70911400
O	-1.40591500	-2.04422800	-0.50187200	C	4.43933000	-0.52273800	-0.89807800
O	0.11167600	-1.12159800	1.25923100	N	4.53586900	-1.66417000	-0.10714600
O	-2.04759900	0.07035700	0.77814700	H	5.35395500	-1.88552800	0.46333500
O	0.06125500	0.13283700	-0.81423200	C	3.28625800	-2.12907000	0.11963300
O	-0.87810700	2.35579300	0.44405000	H	3.04635700	-2.99187300	0.72353300
O	-3.97278500	-0.69931400	-3.45486100	C	5.62887800	0.27313500	-1.36625300
H	-4.50110200	-1.20801200	-2.80738100	H	5.92411400	-0.04135500	-2.37889300
H	-3.34607300	-1.33882400	-3.85131400	H	5.31284800	1.32083000	-1.46089600
O	-1.27315700	1.35285900	-3.63018300	C	6.89490900	0.18678700	-0.46770100
H	-1.92796300	2.06296400	-3.74337300	H	7.39628900	-0.77743900	-0.60742600
H	-0.45599500	1.82967800	-3.31727300	H	7.60009500	0.96882200	-0.78102200
O	0.90552700	4.01544900	-2.41170100	C	6.55751100	0.29600600	1.01679000
H	1.82215500	4.16068500	-2.09435900	O	6.42368100	-0.71398500	1.71739000
O	-0.29343800	5.57059600	0.14779500	N	6.33421800	1.55269400	1.49147000
H	-1.20478100	5.58860000	-0.21861100	H	6.41421700	2.32161300	0.83707600
H	-0.39464900	5.42487000	1.10522400	C	5.58646200	1.78738400	2.73136600
O	-3.14847700	2.28990300	-1.66795400	H	5.92247400	1.03849500	3.45468100
C	-3.02549400	3.51593900	-1.48093300	H	5.86966500	2.77766200	3.11121000
O	-1.89617800	4.13913900	-1.36585300	C	4.06387200	1.67565800	2.52500900
C	-4.29293600	4.36992100	-1.42527100	H	3.82896300	0.66863100	2.16207200
H	-4.76796900	4.28634100	-2.41427400	H	3.56456300	1.77727200	3.49853800
H	-4.97760800	3.86338800	-0.73124300	C	3.51649200	2.71656300	1.54467700
C	-4.10442200	5.83758500	-1.04179300	H	4.15417600	2.77937600	0.64940100
H	-3.43234500	6.35004400	-1.74050600	H	3.52175700	3.72567100	1.98139000
H	-3.68385200	5.93490300	-0.03152800	C	2.10656100	2.46139900	1.00699800
H	-5.06724700	6.36443800	-1.04829800	O	1.53530500	1.38249400	1.32111500
O	0.56371700	-2.24041900	-2.33308900	O	1.65538200	3.38575000	0.25051800
C	-0.32552500	-2.31554800	-3.27819400	O	0.69008700	-3.51379000	0.24954600
O	-1.41687700	-1.71682700	-3.28405800	C	-0.06851900	-4.03911000	1.13400500
C	0.07197400	-3.21582200	-4.44145200	O	-1.06744400	-3.49719800	1.70105100
H	0.09698400	-4.25065700	-4.06526500	C	0.26162300	-5.47730000	1.52153500
H	-0.71605000	-3.15427100	-5.20172600	H	1.35483200	-5.55505500	1.59563600
C	1.44308800	-2.86536000	-5.04508100	H	-0.02110900	-6.09915900	0.65772400
H	2.20011000	-2.91788900	-4.25191700	H	-5.62724600	-3.71191300	0.45502700
H	1.42568500	-1.82257300	-5.39567200	C	-0.42526400	-5.97547900	2.79352200
C	1.82513200	-3.79235800	-6.20377800	H	-0.14904200	-7.01915400	2.99106500
H	1.87907100	-4.83959600	-5.87392400	H	-0.13425400	-5.37305100	3.66275200

H	-1.51494800	-5.91467600	2.70133800	H	-0.73821900	-0.37585500	5.58591300
O	-4.20732400	-1.27663300	-0.76985900	H	-1.13530000	1.31777300	5.25244200
C	-4.40326400	-1.95779100	0.25576900	C	-2.86922200	0.02543000	5.59132700
O	-3.53487300	-2.18701000	1.19391700	H	-3.15118700	-1.00795000	5.35391800
C	-5.74750300	-2.62157600	0.49936000	H	-3.57718600	0.67321700	5.05298200
H	-6.47501900	-2.30097300	-0.25133900	C	-2.98285400	0.27545000	7.09865200
H	-6.10889000	-2.37543200	1.50461400	H	-2.30790300	-0.38342600	7.66310400
O	-1.78585200	-1.09317300	3.15022400	H	-4.00465600	0.08908300	7.45398200
C	-1.29878700	0.00502900	3.57451200	H	-2.72459500	1.31270300	7.35455900
O	-0.68707900	0.88552000	2.88499900	O	0.80404200	2.53811600	-2.34532300
C	-1.44885700	0.28428500	5.06314100				

W3 (water)-O5 (oxo)

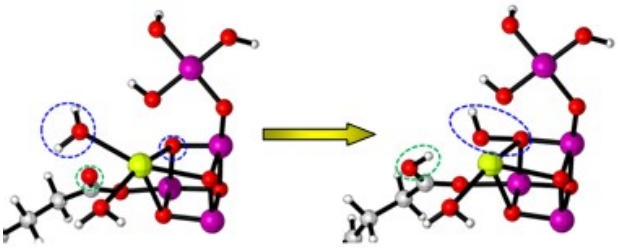

Fig. S12 Pictorial exhibitions for the closed-cubane W3 (hydroxyl)-O5 (oxo) nucleophilic attack with COO^- of Glu189 as the proton acceptor.

Table S27 Reaction parameters for the closed-cubane W3 (hydroxyl)-O5 (oxo) nucleophilic attack with COO^- of Glu189 as the proton acceptor.

Spin state	Spin topology (Mn1~Mn4-OX)	Gibbs Free energy (a.u.)		
		Rea	TS	Pro
doublet	ααββα	-3366.1992	-3366.1590	-3366.1867
	αβαβα	-3366.1894	-3366.1593	-3366.2186
	αββαα	-3366.1952	-3366.1602	-3366.1893
	βααβα	-3366.1924	-3366.1655	-3366.2185
	βαβαα	-3366.1870	-3366.1515	-3366.1578
	ββααα	-3366.1899	-3366.1611	-3366.2124
sextet	αααββ	-3366.1892	-3366.1549	-3366.1609
	ααβαβ	-3366.1871	-3366.1577	-3366.2226
	αβααβ	-3366.1858	-3366.1538	-3366.1577
	βαααβ	-3366.1934	-3366.1585	-3366.1873
octet	αααβα	-3366.1909	-3366.1612	-3366.2211
	ααβαα	-3366.1980	-3366.1612	-3366.1887
	αβααα	-3366.1832	-3366.1596	-3366.2172
	βαααα	-3366.1973	-3366.1624	-3366.2147
12-et	ααααβ	-3366.1871	-3366.1558	-3366.1665

14-et	αααααα	-3366.1909	-3366.1605	-3366.2187	

Spin state	Spin topology (Mn1~Mn4-OX)	Relative Gibbs Free energy (kcal/mol)			
		$\Delta G^{\neq}$(Rea-TS)	ΔG(Rea-Pro)	ΔG(Rea)	ΔG(Pro)
doublet	ααββα	25.2	7.8	0.0	22.5
	αβαβα	18.9	-18.3	6.1	2.5
	αββαα	22.0	3.7	2.5	20.9
	βααβα	17.9	-16.4	4.3	2.6
	βαβαα	22.3	18.3	7.7	40.7
	ββααα	18.1	-14.1	5.8	6.4
sextet	αααββ	21.5	17.8	6.3	38.7
	ααβαβ	18.4	-22.3	7.6	0.0
	αβααβ	20.1	17.6	8.4	40.7
	βααβ	21.9	3.8	3.6	22.2
octet	αααβα	18.6	-19.0	5.2	0.9
	ααβαα	23.1	5.8	0.8	21.3
	αβααα	14.8	-21.3	10.0	3.4
	βαααα	21.9	-10.9	1.2	5.0
12-et	αααβ	19.6	12.9	7.6	35.2
14-et	αααααα	19.1	-17.4	5.2	2.4

Spin state	Spin topology (Mn1~Mn4-OX)		Mulliken spin density		
			Rea	TS	Pro
doublet	α	Mn1	2.89	3.41	3.86
	α	Mn2	2.93	2.92	2.94
	β	Mn3	-2.81	-2.74	-2.88
	β	Mn4	-2.53	-2.91	-2.91
		O4	0.43	-0.15	-0.14
	α	O8	0.00	0.35	0.00
		O5	-0.01	0.13	0.08
	α	Mn1	2.81	3.01	2.97
	β	Mn2	-2.88	-2.90	-2.92
	α	Mn3	2.70	3.27	3.83
	β	Mn4	-2.88	-2.86	-2.82
		O4	0.20	0.07	-0.05
	α	O8	0.00	0.45	0.00
		O5	0.52	0.00	-0.04
	α	Mn1	2.80	3.39	3.87
	β	Mn2	-2.92	-2.89	-2.86
	β	Mn3	-2.79	-2.75	-2.86
	α	Mn4	2.88	2.87	2.87
	α	O4	-0.18	-0.10	-0.07
		O8	0.00	0.37	0.00

		O5	0.56	0.14	0.07
	β	Mn1	-2.78	-2.80	-2.93
	α	Mn2	2.81	2.91	2.94
	α	Mn3	2.75	3.39	3.83
	β	Mn4	-2.88	-2.86	-2.83
		O4	0.15	0.04	-0.04
	α	O8	0.00	0.34	0.00
		O5	0.01	0.09	0.04
		O1	0.54	-0.08	-0.07
	β	Mn1	-2.85	-2.32	-1.96
	α	Mn2	2.92	2.89	2.89
	β	Mn3	-2.73	-2.77	-2.82
	α	Mn4	2.88	2.87	2.87
		O4	-0.17	-0.11	-0.08
	α	O8	0.19	0.24	0.00
		O5	0.78	0.10	0.06
	β	Mn1	-2.87	-2.83	-2.95
	β	Mn2	-2.92	-2.90	-2.93
	α	Mn3	2.69	3.37	3.86
	α	Mn4	2.91	2.92	2.89
		O4	0.21	0.12	0.00
		O8	0.00	0.37	0.00
	α	O5	0.57	0.09	0.04
		O2	0.46	-0.06	-0.05
		O1	-0.11	-0.12	-0.07
	α	Mn1	2.87	2.33	1.98
	α	Mn2	2.91	2.87	2.91
	α	Mn3	2.78	2.81	2.86
	β	Mn4	-2.88	-2.87	-2.87
		O4	0.15	0.09	0.07
	β	O8	-0.21	-0.24	0.00
		O5	-0.75	-0.09	-0.05
		O1	0.14	0.14	0.14
	α	Mn1	2.78	2.47	2.95
sextet	α	Mn2	2.91	2.93	2.93
	β	Mn3	-2.76	-3.13	-3.81
	α	Mn4	2.88	2.87	2.82
		O4	-0.11	0.01	0.04
	β	O8	0.00	-0.26	0.00
		O5	-0.61	-0.05	-0.04
	α	Mn1	2.76	2.26	2.02
	β	Mn2	-2.89	-2.91	-3.01
	α	Mn3	2.89	2.98	2.94
	α	Mn4	2.91	2.93	2.93

		O4	0.04	-0.04	-0.02
	β	O8	0.00	-0.24	0.01
		O5	-0.58	-0.02	0.04
	β	Mn1	-2.79	-3.38	-3.87
	α	Mn2	2.91	2.89	2.87
	α	Mn3	2.84	2.79	2.90
	α	Mn4	2.92	2.92	2.92
		O4	0.17	0.15	0.13
	β	O8	0.00	-0.36	0.00
		O5	-0.57	-0.14	-0.07
	α	Mn1	2.85	3.02	2.98
	α	Mn2	2.80	2.91	2.95
	α	Mn3	2.80	3.34	3.86
	β	Mn4	-2.87	-2.86	-2.82
		O4	0.18	0.06	-0.05
		O8	0.00	0.44	0.00
	α	O5	0.09	0.00	-0.03
		O1	0.63	0.12	0.07
		O2	0.40	0.07	0.05
	α	Mn1	2.80	3.42	3.86
octet	α	Mn2	2.84	2.92	2.94
	β	Mn3	-2.66	-2.70	-2.82
	α	Mn4	2.87	2.87	2.87
		O4	-0.20	-0.11	-0.07
		O8	0.00	0.35	0.00
	α	O5	0.22	0.13	0.08
		O1	0.56	0.08	0.05
		O2	0.35	0.00	-0.03
	α	Mn1	2.81	3.00	2.97
	β	Mn2	-2.88	-2.90	-2.92
	α	Mn3	2.75	3.33	3.88
	α	Mn4	2.91	2.92	2.89
		O4	0.22	0.12	0.12
	α	O8	0.00	0.45	0.00
		O5	0.52	0.01	-0.04
		O1	0.52	0.09	0.07
	β	Mn1	-2.80	-2.81	-2.94
	α	Mn2	2.81	2.91	2.94
	α	Mn3	2.79	3.43	3.89
	α	Mn4	2.91	2.92	2.90
		O4	0.17	0.10	0.11
	α	O8	0.00	0.36	0.00
		O5	0.01	0.09	0.04
		O1	0.54	-0.08	-0.07

		O2	0.42	0.05	0.04
12-et	α	Mn1	2.78	2.26	2.01
	α	Mn2	2.91	2.93	2.91
	α	Mn3	2.94	3.00	2.90
	α	Mn4	2.91	2.93	2.92
		O4	0.05	-0.04	0.17
	β	O8	0.00	-0.23	0.00
		O5	-0.57	-0.01	-0.04
14-et	α	Mn1	2.86	3.01	2.98
	α	Mn2	2.80	2.91	2.95
	α	Mn3	2.85	3.40	3.91
	α	Mn4	2.91	2.92	2.89
		O4	0.17	0.11	0.11
		O8	0.00	0.44	0.00
	α	O5	0.09	0.00	-0.03
		O1	0.63	0.12	0.07
		O2	0.41	0.07	0.05

‘X’ denotes atypism for the ascription of spin center.

Rea:

Ca	-2.66268800	-0.65825900	-1.61564400	H	-6.33270400	3.32458300	-1.74641100
Mn	1.38161500	-1.46403800	-0.27283200	C	-7.29490400	1.53549000	-0.94725900
Mn	-0.75398300	-2.11320200	1.34283100	H	-7.12879900	0.78413700	-0.16618000
Mn	-0.59923400	0.52044900	0.54964600	H	-7.37257700	1.01059500	-1.90788700
Mn	-1.93116600	2.75066700	-1.56877100	H	-8.25777100	2.02510100	-0.75325200
O	-0.09419000	-2.49514900	-0.37770700	O	2.27231400	-1.98961200	-1.84716400
O	0.66393500	-0.87247500	1.33172500	C	1.97894300	-2.85202700	-2.80119400
O	-1.78733300	-0.88966500	0.64020500	O	0.86733000	-3.01444100	-3.30282500
O	0.19258300	-0.24570900	-0.98416800	C	3.17730500	-3.67208200	-3.27057900
O	-1.84872800	1.39501900	-0.23649300	H	3.42634100	-4.37436900	-2.45901200
O	-4.78515100	-1.67484400	-2.49465800	H	2.85544600	-4.26379600	-4.13572600
H	-4.78351700	-2.42662500	-1.86815700	C	4.42305700	-2.83666200	-3.60901300
H	-5.35137500	-0.98514300	-2.09331900	H	4.71704400	-2.26390800	-2.71963200
O	-1.28212700	-1.36098000	-3.44611300	H	4.16718400	-2.10359500	-4.38961200
H	-0.90484400	-0.47474700	-3.60902400	C	5.59425000	-3.70289800	-4.08522200
H	-0.50729300	-1.97261500	-3.34022800	H	5.89205000	-4.42603000	-3.31287900
O	-1.97609700	3.83839000	-3.02147100	H	6.47243300	-3.08857900	-4.32430200
H	-1.98070800	4.73314900	-2.63152200	H	5.32951500	-4.27143400	-4.98730400
O	-1.83527100	4.19089500	-0.42897300	N	2.97783100	-0.23408500	0.08397900
H	-2.70844500	4.23090800	0.00220900	C	3.89381500	0.30245100	-0.79550800
O	-4.61494600	0.73652700	-1.24209700	H	3.84852000	0.07103100	-1.85033600
C	-4.77317400	1.97590400	-1.19640800	C	4.77506100	1.09749000	-0.09908600
O	-3.86124200	2.87910700	-1.31745700	N	4.37786900	1.00012900	1.22988300
C	-6.16698100	2.56604100	-0.96931800	H	4.71650500	1.61229100	1.97947400
H	-6.12648200	3.12141800	-0.02046400	C	3.28541200	0.21292700	1.29528800

H	2.71811200	0.00741300	2.19126600	H	2.85878400	-5.39473900	1.54053200
C	5.92450400	1.94530900	-0.58257300	H	-4.85823100	-4.79929000	0.16722400
H	6.77270100	1.30643200	-0.87006700	C	2.01322000	-5.33319400	3.54942900
H	5.60462700	2.44601500	-1.50704900	H	2.70526200	-6.08355100	3.95185300
C	6.45962900	3.00187000	0.42085200	H	1.79910100	-4.60386200	4.33966900
H	7.05492300	2.51745800	1.20254300	H	1.07083800	-5.83090900	3.29575900
H	7.12809100	3.68414800	-0.12179300	O	-3.33001700	-2.87832800	-0.51083500
C	5.35596500	3.77363600	1.14649700	C	-3.09292000	-3.59094100	0.48232100
O	5.03721700	3.48189000	2.30854200	O	-2.09981300	-3.44547500	1.31240600
N	4.70318400	4.72507500	0.43649100	C	-3.98287400	-4.77379500	0.82192600
H	4.98397700	4.89077400	-0.52235300	H	-4.29487100	-4.71928000	1.87142900
C	3.45900600	5.34363000	0.91551800	H	-3.40955300	-5.70183400	0.70029000
H	3.63601000	5.71199300	1.93218400	O	-1.19947700	-1.37046500	3.10088300
H	3.26824000	6.21051400	0.27126900	C	-1.27881200	-0.10642100	3.31105200
C	2.25399300	4.38584200	0.91659900	O	-1.07465300	0.82737100	2.47286400
H	2.41900200	3.59774800	1.65841500	C	-1.66025100	0.31674400	4.72008700
H	1.37209100	4.95344400	1.24468000	H	-1.82764700	-0.58488400	5.32028600
C	1.98398700	3.75986100	-0.45774800	H	-0.79679800	0.85066700	5.14595100
H	2.85902900	3.17425900	-0.77781300	C	-2.89265000	1.23971800	4.74449300
H	1.80288300	4.52698500	-1.21969000	H	-3.74654900	0.71126300	4.29516500
C	0.79281500	2.80750300	-0.49077200	H	-2.69294600	2.11102500	4.10802600
O	0.66527800	2.01449600	0.50932900	C	-3.25034200	1.68788400	6.16505500
O	0.07505500	2.85285100	-1.52596700	H	-3.47450100	0.82898900	6.81278700
O	2.30090400	-2.92532500	0.73241600	H	-4.13207900	2.34145100	6.16028100
C	1.74624200	-3.60071700	1.66776200	H	-2.42335000	2.24595600	6.62608300
O	0.55316300	-3.47846600	2.07494700	O	-2.01939900	1.31931100	-2.82812200
C	2.62702500	-4.65703900	2.32364300	H	-2.20362800	1.77509100	-3.66785800
H	3.58409300	-4.17369900	2.56384100				

TS:

Ca	2.72772100	0.36343500	-1.62585700	H	-0.56921600	0.83090800	-3.29839900
Mn	-1.52829800	1.47506800	-0.34380400	O	2.20867000	-4.38494900	-2.22788900
Mn	0.64008400	2.27318900	1.01723600	H	2.44175200	-5.14008400	-1.65446400
Mn	0.58147700	-0.47555300	0.56903500	O	2.04482900	-4.06780500	0.35381100
Mn	2.08226900	-2.97337200	-1.09983300	H	2.27789200	-3.50224700	1.11364700
O	-0.15759800	2.59430700	-0.55964500	O	4.76765700	-0.79676300	-1.30616000
O	-0.69487600	0.92238500	1.20448800	C	4.94701000	-2.01893200	-1.06761100
O	1.66298600	0.96292900	0.38535300	O	4.04825400	-2.92134900	-0.92929000
O	-0.44309200	-0.05769200	-1.03894100	C	6.37110800	-2.55478200	-0.89670000
O	1.89417100	-1.39800800	-0.12228400	H	6.44182100	-2.94623200	0.12871100
O	4.50420700	1.42384100	-3.00211000	H	6.47060500	-3.43170800	-1.55087000
H	4.51797700	2.24593900	-2.46677000	C	7.47326400	-1.53111000	-1.16597300
H	5.21888500	0.85753200	-2.64675900	H	7.37531600	-0.66108800	-0.50593100
O	0.46763500	0.12444700	-2.55615700	H	7.43693100	-1.17067700	-2.20199900
H	0.67521300	-0.84547000	-2.73003500	H	8.46174500	-1.97853900	-0.99999000

O	-2.43930400	1.95693600	-2.10663900	H	-2.79654900	-3.21938200	-0.45405500
C	-2.16559400	2.03591000	-3.32561300	H	-1.80461600	-4.62686000	-0.89265700
O	-1.20328100	1.40402400	-3.92117500	C	-0.70514000	-2.94379600	-0.18704400
C	-2.98488500	2.92984800	-4.23209100	O	-0.59043700	-2.07944300	0.74579400
H	-2.37289500	3.83121300	-4.40236000	O	0.07800600	-3.13146300	-1.16334100
H	-3.06584000	2.43790300	-5.21072900	O	-2.47179100	3.00082100	0.74234600
C	-4.35749400	3.32183800	-3.67522100	C	-1.82148100	3.73043300	1.55461000
H	-4.22523100	3.78932000	-2.69132600	O	-0.59400600	3.59675000	1.87652200
H	-4.95268400	2.41265600	-3.50391400	C	-2.58478700	4.88729700	2.19257800
C	-5.11322100	4.26676700	-4.61545700	H	-3.59081300	4.51972000	2.43452600
H	-4.55512600	5.19983800	-4.77521800	H	-2.72506900	5.63522700	1.39618400
H	-6.09374800	4.53263900	-4.20086800	H	4.74423300	4.76684800	-0.59102000
H	-5.27995000	3.80745700	-5.59983400	C	-1.90605600	5.51910700	3.40859300
N	-3.14424900	0.24914300	0.08419800	H	-2.50924900	6.35234000	3.79163100
C	-4.05541500	-0.39199100	-0.72792400	H	-1.78054100	4.78801300	4.21683800
H	-4.05906900	-0.23594000	-1.79778600	H	-0.91133800	5.89817900	3.15076100
C	-4.87204700	-1.18999600	0.03964400	O	3.22196700	2.76737500	-0.99329500
N	-4.44087900	-0.99294700	1.34605700	C	2.97935600	3.61079700	-0.10057200
H	-4.72389900	-1.57394100	2.14170500	O	2.02258400	3.56696500	0.77098000
C	-3.39364500	-0.14276800	1.32777000	C	3.84307000	4.85638300	0.02238800
H	-2.81343200	0.14483500	2.19271800	H	4.11147100	5.02888800	1.07055200
C	-5.98808800	-2.12201600	-0.35852300	H	3.26305200	5.72618400	-0.31360800
H	-6.86815600	-1.54464100	-0.67875800	O	1.26055100	1.65693500	2.85434300
H	-5.65982000	-2.67966700	-1.24709500	C	1.36778900	0.43482200	3.17695500
C	-6.45978200	-3.11867700	0.73169100	O	1.12781500	-0.58879800	2.44092900
H	-7.04193100	-2.59635400	1.49879900	C	1.83112200	0.13787300	4.59544000
H	-7.12679700	-3.85381700	0.26087300	H	1.05432900	0.51420900	5.27855600
C	-5.31288300	-3.81273800	1.46933900	H	1.89417200	-0.94889800	4.72252700
O	-4.96760500	-3.43978000	2.59979400	C	3.17346000	0.81364300	4.92915900
N	-4.66097500	-4.79416000	0.80089300	H	3.07511900	1.89370500	4.76067100
H	-4.96805400	-5.02877500	-0.13506300	H	3.94125900	0.45367300	4.22804200
C	-3.40857000	-5.38473000	1.29280700	C	3.61879200	0.53845200	6.36895700
H	-3.57425200	-5.71629600	2.32440900	H	2.88182200	0.91550600	7.09191100
H	-3.21894000	-6.27439200	0.67996900	H	4.57805100	1.02654500	6.58481600
C	-2.20551900	-4.42695600	1.25005300	H	3.74322200	-0.53800100	6.55133200
H	-2.36017200	-3.61594100	1.96896200	O	2.10890000	-1.82195400	-2.68108100
H	-1.32257900	-4.98843700	1.58703100	H	2.31961900	-2.43669800	-3.40479700
C	-1.94110400	-3.83786300	-0.14366100				

Pro:

Ca	-2.97442300	-0.37513300	-1.37953900	O	0.20051300	-2.57243300	-0.57909100
Mn	1.62393100	-1.49740400	-0.43689500	O	0.74567900	-0.84383100	1.11976900
Mn	-0.51416900	-2.21258500	1.02298200	O	-1.62502900	-0.93768400	0.42009800
Mn	-0.62191400	0.53381300	0.59757400	O	0.27808000	0.31163900	-1.14092700
Mn	-2.25890600	2.97310700	-0.99844400	O	-2.01816000	1.44158400	0.02088800

O	-3.90449200	-1.80102700	-3.16325500	C	6.41032500	3.30401400	0.34319800
H	-3.91378400	-2.57815700	-2.55378300	H	7.03660900	2.80166600	1.08861300
H	-4.80436400	-1.70284800	-3.51436600	H	7.03904800	4.05078000	-0.16096900
O	-0.58953300	-0.03021300	-2.25378900	C	5.28071700	3.97958600	1.12381600
H	-1.00974800	0.88186300	-2.53883400	O	4.99554600	3.61390800	2.27319400
H	0.26552800	-1.00148100	-3.18392300	N	4.57673200	4.93768100	0.47468000
O	-2.45364900	4.31107400	-2.20885400	H	4.83665400	5.17011700	-0.47592800
H	-2.71174300	5.09417600	-1.68665500	C	3.34392600	5.51854300	1.02412400
O	-2.21035000	4.12637300	0.39671100	H	3.56174900	5.87664100	2.03716900
H	-2.38030600	3.57847400	1.18638800	H	3.10464000	6.39076400	0.40358400
O	-4.97166900	0.77260300	-1.05170500	C	2.15592100	4.54282400	1.07264500
C	-5.12774100	1.99924700	-0.83166900	H	2.36537000	3.74942100	1.79719200
O	-4.21770400	2.90152200	-0.77604500	H	1.28741500	5.10034800	1.45154400
C	-6.53627600	2.55112200	-0.59518300	C	1.81472000	3.92015400	-0.28975500
H	-6.51546500	3.08838700	0.36341300	H	2.65411500	3.29817500	-0.63511300
H	-6.71110400	3.32392300	-1.35767200	H	1.62948900	4.69120500	-1.04695000
C	-7.64155100	1.49622500	-0.61370000	C	0.58330400	3.02018900	-0.23388100
H	-7.47117400	0.73129900	0.15320100	O	0.54358300	2.15923900	0.70662300
H	-7.68610000	0.98570000	-1.58327300	O	-0.27450500	3.20660700	-1.14617600
H	-8.61848500	1.96061600	-0.42592900	O	2.59433800	-3.01931200	0.75997300
O	2.34006900	-1.94086800	-2.31921800	C	1.92496700	-3.70076800	1.58815100
C	1.82097400	-2.16961100	-3.42956500	O	0.69634500	-3.51902800	1.89892200
O	0.71120800	-1.62946200	-3.85637400	C	2.63886500	-4.86204300	2.27666100
C	2.45412400	-3.12891200	-4.40998100	H	3.64411300	-4.50967100	2.54440000
H	1.82147400	-4.03192200	-4.40124400	H	2.79102100	-5.62910100	1.50093800
H	2.34770700	-2.70511200	-5.41806200	H	-4.67393100	-4.85599200	-0.19927300
C	3.90806600	-3.49444200	-4.09494300	C	1.91103200	-5.45645400	3.48295200
H	3.96458300	-3.89483300	-3.07469200	H	2.48465700	-6.29379400	3.90157800
H	4.52069400	-2.58116200	-4.09977800	H	1.77472900	-4.70673800	4.27207700
C	4.47646400	-4.50723500	-5.09450300	H	0.91687300	-5.82052300	3.20189600
H	3.90156900	-5.44365000	-5.08356800	O	-3.23545300	-2.80877300	-0.83864300
H	5.51805200	-4.75373900	-4.85363100	C	-2.87608600	-3.67068200	0.00896400
H	4.45449400	-4.11590800	-6.12119400	O	-1.91350600	-3.56783900	0.84979700
N	3.21232400	-0.20902300	-0.11921200	C	-3.61863900	-4.99822800	0.05695400
C	4.06665600	0.45194900	-0.97690100	H	-3.52262200	-5.46595400	1.04085700
H	4.04606300	0.26382200	-2.04184600	H	-3.17395700	-5.67355900	-0.68776100
C	4.86377700	1.31288700	-0.25847000	O	-1.13768700	-1.63739900	2.88573900
N	4.48028400	1.13527600	1.06555800	C	-1.25146000	-0.42686200	3.23034100
H	4.76753900	1.74381000	1.83882100	O	-1.04984000	0.60938900	2.49735200
C	3.47823700	0.23324300	1.10463600	C	-1.70260200	-0.12753300	4.65455100
H	2.93639800	-0.05547600	1.99417700	H	-1.26411000	0.83453300	4.95001400
C	5.91699400	2.28879200	-0.71860800	H	-2.79187000	0.03709200	4.60492200
H	6.79902200	1.74554100	-1.08895800	C	-1.38318000	-1.22838000	5.67227100
H	5.51818700	2.83330500	-1.58650000	H	-0.29531000	-1.38772900	5.70214500

H	-1.81931300	-2.17377700	5.32637000	H	-2.98847100	-0.75587000	7.07917800
C	-1.89704700	-0.88693300	7.07515100	O	-2.28835600	1.72724000	-2.56254800
H	-1.45110800	0.04461600	7.45139300	H	-2.46050300	2.32647400	-3.30943100
H	-1.65511600	-1.68448900	7.78961300				

W3 (hydroxyl) as the reagent

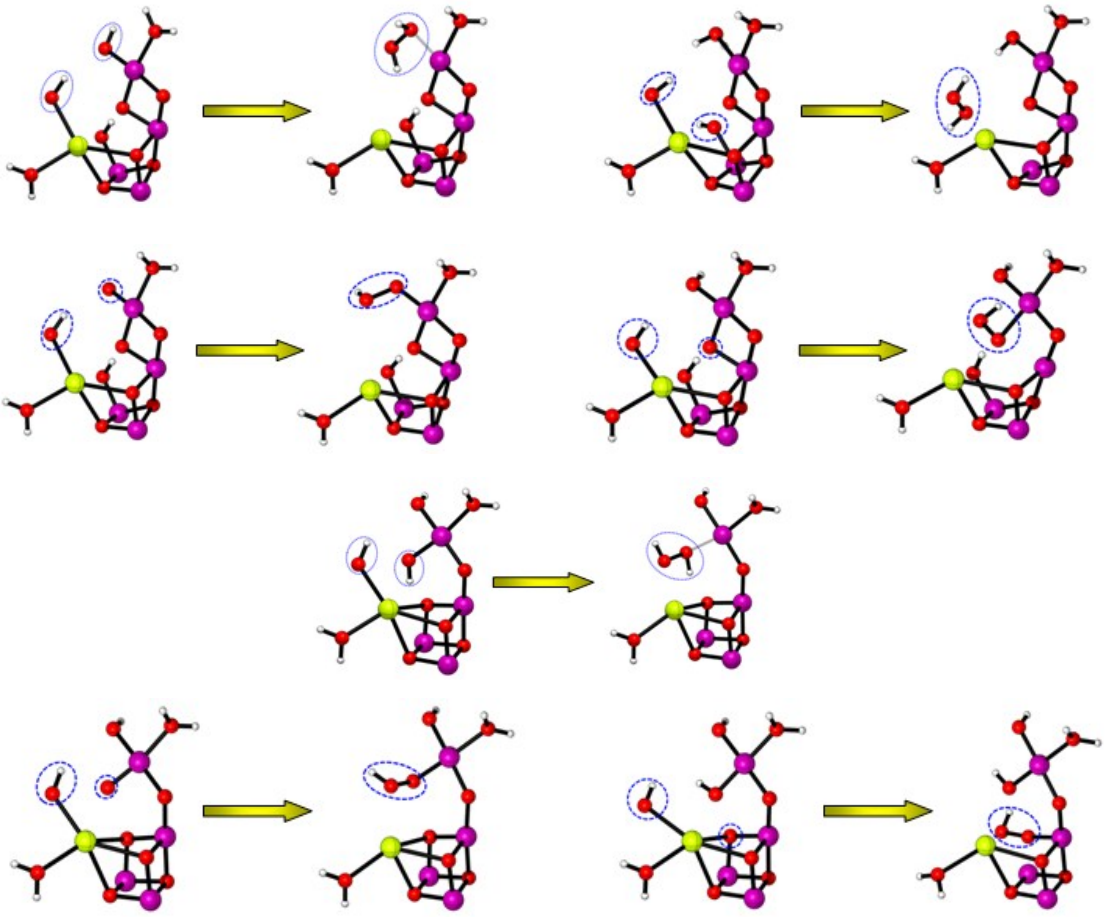

Fig. S13 Pictorial exhibitions for couplings of W3 (hydroxyl)-W2 (hydroxyl)/Wx (hydroxyl), nucleophilic attack of W3 (hydroxyl) on W2 (oxo)/O5 (oxo) in the open-cubane structure, and coupling of W3 (hydroxyl)-Wx (hydroxyl), nucleophilic attack of W3 (hydroxyl) on Wx (oxo)/O5 (oxo) in the closed-cubane structure.

Table S28 Reaction parameters for the open-cubane W3 (hydroxyl)-W2 (hydroxyl) coupling:

Spin state	Spin topology (Mn1~Mn4-O8)	Gibbs Free energy (a.u.)		
		Rea	TS	Pro
doublet	ααββα	-3366.2003	-3366.1707	-3366.1721
	αβαβα	-3366.2004	-3366.1722	-3366.1735
	αββαα	-3366.2033	-3366.1712	-3366.2117
	βααβα	-3366.2001	-3366.1723	-3366.1932

	βαβαα	-3366.2032	-3366.1716	-3366.2115
	ββααα	-3366.2024	-3366.1676	-3366.2063
sextet	αααββ	-3366.2045	-3366.1724	-3366.2127
	ααβαβ	-3366.2023	-3366.1733	-3366.1949
	αβααβ	-3366.2022	-3366.1715	-3366.1737
	βαααβ	-3366.2017	-3366.1716	-3366.1737
octet	αααβα	-3366.2026	-3366.1737	-3366.1938
	ααβαα	-3366.2045	-3366.1723	-3366.2130
	αβααα	-3366.2039	-3366.1692	-3366.2077
	βαααα	-3366.2039	-3366.1690	-3366.2084
12-et	ααααβ	-3366.2029	-3366.1728	-3366.1748
14-et	ααααα	-3366.2048	-3366.1702	-3366.2088

Spin state	Spin topology (Mn1~Mn4-O8)	Relative Gibbs Free energy (kcal/mol)			
		$\Delta G^{\neq}$(Rea-TS)	ΔG(Rea-Pro)	ΔG(Rea)	ΔG(Pro)
doublet	ααββα	18.6	17.7	2.8	25.7
	αβαβα	17.7	16.9	2.8	24.8
	αββαα	20.1	-5.3	0.9	0.8
	βααβα	17.4	4.3	2.9	12.4
	βαβαα	19.8	-5.2	1.0	0.9
	ββααα	21.8	-2.4	1.5	4.2
sextet	αααββ	20.1	-5.1	0.2	0.2
	ααβαβ	18.2	4.6	1.6	11.4
	αβααβ	19.3	17.9	1.6	24.7
	βαααβ	18.9	17.6	1.9	24.7
octet	αααβα	18.1	5.5	1.4	12.0
	ααβαα	20.2	-5.3	0.2	0.0
	αβααα	21.8	-2.4	0.6	3.3
	βαααα	21.9	-2.8	0.6	2.9
12-et	ααααβ	18.9	17.6	1.2	24.0
14-et	ααααα	21.7	-2.5	0.0	2.6

Spin state	Spin topology (Mn1~Mn4-O8)		Mulliken spin density		
			Rea	TS	Pro
doublet	α	Mn1	2.96	2.96	2.96
	α	Mn2	2.94	2.94	2.94
	β	Mn3	-2.86	-2.88	-2.83
	β	Mn4	-2.88	-2.59	-2.00
	α	O8	0.93	0.50	0.00
	α	Mn1	2.95	2.96	2.96
	β	Mn2	-2.92	-2.92	-2.91
	α	Mn3	2.85	2.91	3.05
	β	Mn4	-2.84	-2.52	-2.05

	α	O8	0.94	0.48	0.00
	α	Mn1	2.95	2.96	2.95
	β	Mn2	-2.94	-2.93	-2.93
	β	Mn3	-2.91	-2.88	-2.84
	α	Mn4	2.83	3.27	3.85
	α	O8	0.98	0.51	0.00
	β	Mn1	-2.95	-2.95	-2.91
	α	Mn2	2.94	2.94	2.94
	α	Mn3	2.88	2.94	3.85
	β	Mn4	-2.84	-2.53	-2.69
	α	O8	0.95	0.48	0.00
	β	Mn1	-2.96	-2.97	-2.96
	α	Mn2	2.91	2.91	2.92
	β	Mn3	-2.88	-2.86	-2.81
	α	Mn4	2.83	3.27	3.85
	α	O8	0.98	0.51	0.01
	β	Mn1	-2.96	-2.97	-2.96
	β	Mn2	-2.94	-2.94	-2.94
	α	Mn3	2.90	2.91	2.94
	α	Mn4	2.88	3.36	3.86
	α	O8	0.98	0.48	0.00
	α	Mn1	2.97	2.98	2.97
	α	Mn2	2.96	2.95	2.95
	α	Mn3	2.92	2.89	2.84
	β	Mn4	-2.83	-3.27	-3.85
	β	O8	-0.98	-0.51	0.00
	α	Mn1	2.96	2.96	2.91
	α	Mn2	2.94	2.94	2.91
	β	Mn3	-2.85	-2.91	-3.82
	α	Mn4	2.84	2.53	2.69
sextet	β	O8	-0.94	-0.48	0.00
	α	Mn1	2.96	2.95	2.95
	β	Mn2	-2.92	-2.92	-2.92
	α	Mn3	2.86	2.88	2.83
	α	Mn4	2.88	2.59	2.01
	β	O8	-0.93	-0.50	0.00
	β	Mn1	-2.95	-2.95	-2.95
	α	Mn2	2.94	2.94	2.93
	α	Mn3	2.90	2.92	2.87
	α	Mn4	2.88	2.59	2.01
	β	O8	-0.94	-0.50	0.00
	α	Mn1	2.97	2.97	2.96
octet	α	Mn2	2.96	2.96	2.96
	α	Mn3	2.89	2.94	3.86

	β	Mn4	-2.84	-2.52	-2.69
	α	O8	0.95	0.48	0.00
	α	Mn1	2.96	2.97	2.96
	α	Mn2	2.94	2.94	2.94
	β	Mn3	-2.88	-2.85	-2.81
	α	Mn4	2.83	3.27	3.85
	α	O8	0.98	0.51	0.00
	α	Mn1	2.96	2.97	2.96
	β	Mn2	-2.91	-2.91	-2.92
	α	Mn3	2.90	2.92	2.93
	α	Mn4	2.88	3.36	3.86
	α	O8	0.98	0.48	0.00
	β	Mn1	-2.95	-2.96	-2.95
	α	Mn2	2.94	2.93	2.93
	α	Mn3	2.93	2.95	2.97
	α	Mn4	2.88	3.36	3.86
	α	O8	0.98	0.48	0.00
12-et	α	Mn1	2.97	2.96	2.97
	α	Mn2	2.96	2.96	2.95
	α	Mn3	2.90	2.92	2.87
	α	Mn4	2.88	2.59	2.01
	α	O8	-0.93	-0.50	0.00
14-et	α	Mn1	2.97	2.99	2.97
	α	Mn2	2.96	2.95	2.95
	α	Mn3	2.93	2.95	2.97
	α	Mn4	2.88	3.36	3.86
	α	O8	0.98	0.48	0.00

Rea:

Ca	1.90707100	1.04576200	-1.68759400	O	1.55789100	-2.75134100	-3.36844300
Mn	-1.08966900	1.62813400	-0.14056900	O	2.71978800	-4.69709500	-1.29548900
Mn	1.10395400	1.38243600	1.52227800	H	3.62977100	-4.32940500	-1.29956500
Mn	0.90363600	-1.26082300	0.57570600	H	2.50422300	-4.81691100	-0.34852700
Mn	1.76964000	-2.75275700	-1.50839300	O	3.86446300	-0.18692300	-2.26770700
O	0.54102700	2.35984600	0.10147700	C	4.35925800	-1.30929400	-2.06355900
O	-0.35271500	0.29141700	0.95752500	O	3.69256200	-2.38416000	-1.78856800
O	2.08385700	0.11457200	0.66696200	C	5.87689200	-1.46501700	-2.14655700
O	0.97828200	-1.20236700	-1.27151800	H	6.16882000	-1.10657600	-3.14410200
O	1.98060400	-2.65722900	0.30366900	H	6.29405500	-0.73351500	-1.44002300
O	1.77231800	3.23181200	-2.78887300	C	6.43625800	-2.86203500	-1.87862300
H	2.08209100	3.80592300	-2.06491600	H	6.04785200	-3.59458300	-2.59772500
H	0.82904900	3.47271600	-2.94777400	H	6.18025300	-3.20575000	-0.86851800
O	1.70133600	-0.11379100	-3.94842900	H	7.53034300	-2.85769300	-1.96374800
H	1.55245700	-1.10586900	-3.77377500	O	-1.90799100	3.23420600	-0.90320900
H	2.35658200	-3.11182400	-3.79458300	C	-1.70474400	3.84556600	-2.02296500

O	-0.99816300	3.40861800	-2.96231200	H	-1.72940900	-5.30995700	-0.80973000
C	-2.41387700	5.19097600	-2.13806500	C	-0.77180200	-3.44408600	-0.41172900
H	-3.45223800	5.04702000	-1.80593700	O	-0.71445200	-2.51444600	0.43312200
H	-1.95894800	5.85725000	-1.38742500	O	0.11820000	-3.74059400	-1.28665600
C	-2.35752800	5.82507300	-3.53066000	O	-1.89725300	2.40680100	1.54630900
H	-2.80758300	5.13688600	-4.25966700	C	-1.21057800	2.80497600	2.54336700
H	-1.30830300	5.93819400	-3.83419000	O	0.01822100	2.57460900	2.73031700
C	-3.06944900	7.18136700	-3.58165500	C	-1.94924500	3.64694900	3.57674800
H	-4.13091500	7.08745500	-3.31189600	H	-2.93533100	3.18723300	3.72868700
H	-2.61417000	7.89890100	-2.88436500	H	-2.14683000	4.61714400	3.09502800
H	-3.01894000	7.61749300	-4.58770100	C	-1.20614000	3.83795600	4.89915600
N	-2.89004500	0.59222600	-0.31891600	H	-1.79475800	4.46784800	5.57826500
C	-3.29902100	-0.14379400	-1.41090600	H	-1.02412400	2.87613500	5.39391100
H	-2.70379800	-0.15662300	-2.31336300	H	-0.23274300	4.31359900	4.73803800
C	-4.47007600	-0.79605600	-1.10645400	O	3.31920800	2.62685200	-0.37976500
N	-4.76328800	-0.42600300	0.20179100	C	3.42074000	2.90853600	0.83011400
H	-5.42894900	-0.92722200	0.79576500	O	2.63610500	2.49467500	1.77989300
C	-3.78035200	0.39172600	0.64207400	C	4.54680800	3.80316400	1.32175700
H	-3.72265600	0.81026000	1.63577800	H	5.23606000	3.20873500	1.93575000
C	-5.33932800	-1.69186700	-1.95009000	H	4.14665800	4.59926100	1.96048300
H	-5.90413000	-1.09098000	-2.67882200	H	5.09111600	4.23004900	0.47490100
H	-4.68208200	-2.33995500	-2.54638600	O	1.41225700	0.43760700	3.25214300
C	-6.36565400	-2.56174500	-1.17876500	C	1.24128700	-0.80625100	3.42075600
H	-7.16852900	-1.93479000	-0.77456300	O	0.91320500	-1.63445400	2.51206000
H	-6.82627800	-3.26409300	-1.88691100	C	1.46629700	-1.37820300	4.81212000
C	-5.74562100	-3.29775100	0.00607700	H	0.78217500	-2.22828000	4.93531600
O	-5.81079800	-2.83779900	1.15332200	H	2.48256700	-1.80600700	4.80666900
N	-5.06793200	-4.44017500	-0.28261100	C	1.32458400	-0.36945600	5.95717000
H	-5.01966600	-4.73704800	-1.24954200	H	0.30983900	0.05472500	5.94125600
C	-4.17714400	-5.08288000	0.68821700	H	2.00789600	0.47084400	5.78176400
H	-4.69648100	-5.09223400	1.65201300	C	1.60133800	-1.00327000	7.32478900
H	-4.03871200	-6.12339500	0.36776000	H	0.90905500	-1.83157000	7.53207200
C	-2.82713300	-4.35937600	0.83541100	H	1.49084400	-0.26690000	8.13127600
H	-3.00531900	-3.34084800	1.19706000	H	2.62310700	-1.40501200	7.37847400
H	-2.24332700	-4.87066400	1.61418600	O	-0.60858600	1.00817000	-1.78859900
C	-2.02553100	-4.30922400	-0.46889100	H	-0.81958600	1.75650200	-2.41210600
H	-2.63896600	-3.87655700	-1.27500100				

TS:

Ca	2.24728800	0.27635700	-1.52995400	O	-0.29854600	0.39508000	0.97134600
Mn	-0.50676700	1.84197800	-0.21521100	O	1.98053900	-0.55361600	0.83232100
Mn	1.40340000	0.97876400	1.59077800	O	0.52686000	-1.39718100	-1.11973700
Mn	0.42449300	-1.50098100	0.68877200	O	1.08864300	-3.12744100	0.37954500
Mn	0.86402500	-3.11311300	-1.42973300	O	2.91112900	2.25868100	-2.80012700
O	1.25149800	2.02192300	0.10441300	H	3.43804800	2.70478900	-2.11092000

H	2.12815100	2.83583500	-2.96743800	H	-7.45174800	-1.02698900	-2.10206100
O	0.91080400	-0.84547100	-3.72612900	C	-6.51151300	-1.31983000	-0.15759200
H	0.12898400	-0.63402900	-3.16569800	O	-6.47365600	-0.81057400	0.97041100
H	1.58686200	-2.82186100	-3.80787600	N	-6.22387400	-2.63002700	-0.37321100
O	0.72608500	-2.61152300	-3.39535500	H	-6.22967400	-2.97052700	-1.32693200
O	1.15029400	-5.26805600	-1.45212400	C	-5.61472800	-3.47197800	0.66199300
H	2.13029100	-5.19379400	-1.49745300	H	-6.13858200	-3.26391600	1.60044200
H	0.93895900	-5.47803400	-0.52221000	H	-5.80830400	-4.51757100	0.39015500
O	3.81142500	-1.42586000	-2.05186400	C	-4.10849200	-3.20943700	0.83763600
C	3.88627700	-2.66917300	-1.99143600	H	-3.96105700	-2.16880700	1.14670900
O	2.87114600	-3.46368500	-1.90797000	H	-3.74102500	-3.83434300	1.66389300
C	5.27009400	-3.31619700	-2.03803400	C	-3.29859500	-3.49142600	-0.43039700
H	5.74698100	-2.96568100	-2.96476000	H	-3.72389500	-2.94211600	-1.28513100
H	5.84760600	-2.85742300	-1.22288700	H	-3.32933100	-4.55411200	-0.70701500
C	5.30905700	-4.84128700	-1.94433200	C	-1.83066900	-3.07192600	-0.37481800
H	4.75080600	-5.30769100	-2.76583600	O	-1.47718800	-2.24783200	0.51452700
H	4.87780800	-5.19213500	-0.99809000	O	-1.09143600	-3.59017500	-1.27853400
H	6.34433100	-5.20227700	-1.99372200	O	-1.10666500	2.90711500	1.38836900
O	-0.71914600	3.60547400	-1.05854100	C	-0.386		
C	-0.19917200	4.09691000	-2.13286100	H	-0.74310800	5.14620700	2.86289900
O	0.40634200	3.43080700	-3.00738900	C	-0.19220800	4.19614100	4.74503400
C	-0.37472500	5.60402500	-2.28462200	H	-0.59188300	5.00707500	5.36717300
H	-1.39284100	5.85725100	-1.95760700	H	-0.34626800	3.24836500	5.27499200
H	0.29573200	6.07563000	-1.54728000	H	0.88822800	4.33977400	4.63665400
C	-0.08768400	6.14042600	-3.69017400	O	3.98867900	1.45408000	-0.21340300
H	-0.76283800	5.65307900	-4.40791400	C	4.10560500	1.73477900	0.99684000
H	0.92778900	5.84759800	-3.98722200	O	3.19274800	1.58621800	1.90762200
C	-0.24497600	7.66247000	-3.77630600	C	5.41304200	2.29423300	1.53318700
H	-1.26472600	7.97604800	-3.51176400	H	5.87272000	1.55491500	2.20201100
H	0.44581600	8.17514400	-3.09195600	H	5.22319700	3.19615400	2.12687100
H	-0.03783900	8.02520700	-4.79141300	H	6.09910100	2.51564600	0.71099200
N	-2.53755600	1.43036300	-0.47362300	O	1.30768800	0.06032700	3.35187900
C	-3.12985300	0.83929900	-1.56930300	C	0.78991900	-1.08314400	3.53720400
H	-2.55048200	0.63107400	-2.45756800	O	0.27712400	-1.81571300	2.63366600
C	-4.45309300	0.58806600	-1.29247800	C	0.79860700	-1.64650400	4.95009200
N	-4.64774900	1.05670600	0.00183100	H	-0.09211900	-2.27912000	5.05974900
H	-5.45728800	0.81122900	0.57901300	H	1.66334900	-2.32878500	5.00175900
C	-3.47076400	1.53599600	0.46196400	C	0.88740900	-0.59887500	6.06529100
H	-3.31089300	1.93456200	1.45249200	H	0.02450400	0.07951500	5.99309300
C	-5.53502400	-0.02284100	-2.14540100	H	1.77716800	0.02240600	5.90376400
H	-5.84954300	0.69008800	-2.92238200	C	0.93054500	-1.23743400	7.45781100
H	-5.10246700	-0.87714000	-2.68481600	H	0.03421400	-1.84389700	7.65041400
C	-6.81401900	-0.47835500	-1.39548400	H	0.98971800	-0.47181100	8.24220000
H	-7.38401300	0.39223400	-1.05173400	H	1.80452100	-1.89498100	7.56773700

O	-0.16417600	1.06561900	-1.85569300	H	-0.04610500	1.84693700	-2.46413100

Pro:

Ca	2.47193000	0.48809500	-1.08390200	H	0.18385100	7.78604000	-5.16160000
Mn	-0.51637500	1.81946400	-0.29256700	N	-2.46705000	1.29616800	-0.82272000
Mn	1.16020200	1.10978800	1.79415200	C	-2.85295500	0.51382800	-1.89180900
Mn	0.46812600	-1.44158000	0.78245100	H	-2.13027600	0.18936800	-2.62721500
Mn	1.24207900	-3.16016600	-1.12950900	C	-4.19861800	0.24829000	-1.79905200
O	1.16613900	2.12453400	0.27508400	N	-4.62028600	0.90411700	-0.64819300
O	-0.39900700	0.42175800	0.94742900	H	-5.50427300	0.69874300	-0.17337100
O	1.92854300	-0.38448000	1.14028700	C	-3.54822700	1.50223700	-0.08299800
O	0.83334400	-1.39243000	-1.00897800	H	-3.56516400	2.05524100	0.84408500
O	1.32322900	-3.01104600	0.67012600	C	-5.10817000	-0.53800500	-2.70718900
O	2.83242100	2.05251600	-2.90381700	H	-5.32337800	0.04073400	-3.61813200
H	3.60496100	2.62536200	-3.02886100	H	-4.56190200	-1.42974800	-3.04427000
H	2.03039800	2.59522400	-3.11574100	C	-6.47126700	-0.96206700	-2.09905600
O	0.24981100	-1.56958700	-3.54733600	H	-7.12356900	-0.08932000	-1.98083700
H	0.21419500	-1.20932300	-2.61165700	H	-6.96579000	-1.64554000	-2.80279100
H	1.85068900	-2.64383500	-3.55120800	C	-6.33039000	-1.59663000	-0.71726800
O	0.92275900	-2.84424400	-3.30063600	O	-6.47825700	-0.92534500	0.31282500
O	1.93586400	-5.17494300	-1.00640300	N	-5.97137400	-2.90679200	-0.69050200
H	2.85943200	-4.95347700	-1.27374900	H	-5.81394200	-3.37225100	-1.57621600
H	1.94661900	-5.32980600	-0.04231400	C	-5.44813800	-3.54486300	0.52268700
O	3.93610100	-1.10104800	-2.02666500	H	-6.05114900	-3.18213300	1.36074700
C	4.19984100	-2.32934100	-2.03530900	H	-5.61497500	-4.62562500	0.42641700
O	3.30995400	-3.25642300	-2.02476300	C	-3.96178500	-3.22614000	0.76470200
C	5.67034900	-2.74152700	-2.09384200	H	-3.84424500	-2.14282100	0.88157600
H	6.07150700	-2.33384900	-3.03381700	H	-3.65892600	-3.67525900	1.72114300
H	6.18453600	-2.18694100	-1.29630400	C	-3.04951900	-3.72676400	-0.35806300
C	5.94939900	-4.24080200	-1.99081700	H	-3.42698600	-3.39349000	-1.33783800
H	5.44917600	-4.79589200	-2.79353200	H	-3.02744800	-4.82444500	-0.40373400
H	5.59995600	-4.64536600	-1.03172300	C	-1.59736400	-3.24798300	-0.30966600
H	7.02671800	-4.43824700	-2.06124000	O	-1.33309900	-2.27377200	0.47186300
O	-0.68228000	3.53469300	-1.25757600	O	-0.78851300	-3.83704400	-1.07807300
C	-0.20069300	3.95980700	-2.37308700	O	-1.37659500	2.91563200	1.15785600
O	0.41157400	3.25438800	-3.21553900	C	-0.83419200	3.16886700	2.28599900
C	-0.44831700	5.44149600	-2.63960300	O	0.20361100	2.61771600	2.74514400
H	-1.53251300	5.60987600	-2.55443600	C	-1.51347000	4.24585800	3.12364000
H	-0.00221200	5.99929200	-1.80181900	H	-2.59135600	4.03082100	3.11874900
C	0.08207900	5.95032900	-3.98249800	H	-1.39868000	5.18749900	2.56542300
H	-0.36490900	5.36105800	-4.79459800	C	-0.97665200	4.38407300	4.54816100
H	1.16394300	5.76565100	-4.03803000	H	-1.50593900	5.18711000	5.07683000
C	-0.20441500	7.44103100	-4.19451800	H	-1.10880000	3.45379800	5.11330100
H	-1.28393600	7.64704100	-4.17639900	H	0.09389300	4.61651400	4.54432700
H	0.26150100	8.05416000	-3.41019600	O	4.02984900	1.56205400	0.42985900

C	3.91800700	1.91810900	1.62042400	H	1.24363200	-1.96881100	5.32908300
O	2.85021500	1.82346900	2.35259100	C	-0.10113600	-0.46162400	6.12505700
C	5.09923000	2.53600700	2.35035900	H	-1.06570100	-0.00704700	5.85360700
H	5.31135900	1.96459500	3.26219100	H	0.63875900	0.34796200	6.09880200
H	4.84510400	3.55784000	2.65959100	C	-0.18849600	-1.05743100	7.53416900
H	5.98099700	2.55196100	1.70413100	H	-0.94227300	-1.85561900	7.58751300
O	0.87379800	0.21291600	3.53323100	H	-0.46170900	-0.29115900	8.27121100
C	0.42058100	-0.96706800	3.66013200	H	0.77364400	-1.48951000	7.84373200
O	0.09674400	-1.73969800	2.70715200	O	0.09615400	0.97844300	-1.81157700
C	0.27301700	-1.51301200	5.07213300	H	0.10252800	1.68663400	-2.50982900
H	-0.45681500	-2.33152800	5.04099100				

Table S29 Reaction parameters for the open-cubane W3 (hydroxyl)-Wx (hydroxyl) coupling:

Spin state	Spin topology (Mn1~Mn4-O8)	Gibbs Free energy (a.u.)		
		Rea	TS	Pro
doublet	ααββα	-3366.1931	-3366.1803	-3366.2072
	αβαβα	-3366.1940	-3366.1819	-3366.2095
	αββαα	-3366.1935	-3366.1815	-3366.2096
	βααβα	-3366.1941	-3366.1646	-3366.1702
	βαβαα	-3366.1944	-3366.1683	-3366.1707
	ββααα	-3366.1923	-3366.1662	-3366.1706
sextet	αααββ	-3366.1949	-3366.1668	-3366.1716
	ααβαβ	-3366.1935	-3366.1666	-3366.1708
	αβααβ	-3366.1929	-3366.1652	-3366.1693
	βαααβ	-3366.2092	-3366.1879	-3366.2101
octet	αααβα	-3366.1938	-3366.1800	-3366.2087
	ααβαα	-3366.1945	-3366.1818	-3366.2084
	αβααα	-3366.1945	-3366.1825	-3366.2099
	βαααα	-3366.1940	-3366.1675	-3366.1722
12-et	ααααβ	-3366.2015	-3366.1744	-3366.1780
14-et	ααααα	-3366.1957	-3366.1826	-3366.2094

Spin state	Spin topology (Mn1~Mn4-O8)	Relative Gibbs Free energy (kcal/mol)			
		$\Delta G^{\neq}$(Rea-TS)	ΔG(Rea-Pro)	ΔG(Rea)	ΔG(Pro)
doublet	ααββα	18.8	-7.2	1.1	2.5
	αβαβα	17.9	-8.3	0.9	1.2
	αββαα	16.8	-9.4	1.4	0.6
	βααβα	36.8	22.6	1.4	32.6
	βαβαα	35.9	21.5	1.5	31.6
	ββααα	36.5	22.0	1.6	32.2
sextet	αααββ	31.4	19.0	0.4	28.0
	ααβαβ	32.0	19.5	0.3	28.4

	αβααβ	32.1	17.6	4.1	30.3
	βαααβ	18.0	-8.5	0.6	0.7
octet	αααβα	18.6	-7.6	0.2	1.2
	ααβαα	17.3	-3.8	0.8	5.5
	αβααα	16.7	-9.4	0.8	0.0
	βαααα	37.3	22.6	0.6	31.8
12-et	αααaβ	31.9	19.3	0.2	28.1
14-et	ααααα	17.8	-8.2	0.0	0.4

Spin state	Spin topology (Mn1~Mn4-O8)		Mulliken spin density		
			Rea	TS	Pro
doublet	α	Mn1	2.99	3.46	3.90
	α	Mn2	2.94	2.96	2.98
	β	Mn3	-2.93	-2.93	-2.92
	β	Mn4	-2.89	-2.89	-2.89
	α	O8	0.92	0.57	0.01
	α	Mn1	2.99	3.45	3.91
	β	Mn2	-2.92	-2.91	-2.90
	α	Mn3	2.88	2.89	2.91
	β	Mn4	-2.84	-2.84	-2.84
	α	O8	0.92	0.57	0.01
	α	Mn1	2.98	3.43	3.90
	β	Mn2	-2.94	-2.93	-2.92
	β	Mn3	-2.91	-2.91	-2.91
	α	Mn4	2.84	2.84	2.85
	α	O8	0.92	0.58	0.01
	β	Mn1	-2.92	-2.38	-1.99
	α	Mn2	2.94	2.94	2.94
	α	Mn3	2.90	2.92	2.95
	β	Mn4	-2.83	-2.83	-2.82
	α	O8	0.89	0.33	0.00
	β	Mn1	-2.93	-2.38	-1.99
	α	Mn2	2.92	2.93	2.93
	β	Mn3	-2.89	-2.89	-2.91
	α	Mn4	2.84	2.84	2.84
	α	O8	0.90	0.33	0.00
	β	Mn1	-2.93	-2.40	-2.01
	β	Mn2	-2.94	-2.95	-2.97
	α	Mn3	2.92	2.94	2.96
	α	Mn4	2.89	2.89	2.88
	α	O8	0.90	0.34	0.01
sextet	α	Mn1	2.95	2.40	2.02
	α	Mn2	2.96	2.96	2.98
	α	Mn3	2.91	2.91	2.93

	β	Mn4	-2.85	-2.84	-2.84
	β	O8	-0.90	-0.33	-0.01
	α	Mn1	2.93	2.40	2.01
	α	Mn2	2.94	2.95	2.97
	β	Mn3	-2.87	-2.90	-2.93
	α	Mn4	2.83	2.83	2.82
	β	O8	-0.90	-0.34	-0.01
	α	Mn1	2.93	2.38	1.99
	β	Mn2	-2.92	-2.93	-2.93
	α	Mn3	2.92	2.93	2.93
	α	Mn4	2.88	2.88	2.87
	β	O8	-0.90	-0.33	0.00
	β	Mn1	-2.95	-3.43	-3.85
	α	Mn2	2.94	2.93	2.92
	α	Mn3	2.94	2.94	2.93
	α	Mn4	2.91	2.91	2.92
	β	O8	-0.80	-0.53	0.00
octet	α	Mn1	3.01	3.45	3.92
	α	Mn2	2.96	2.97	2.99
	α	Mn3	2.91	2.91	2.93
	β	Mn4	-2.84	-2.84	-2.83
	α	O8	0.92	0.56	0.01
	α	Mn1	2.99	3.46	3.90
	α	Mn2	2.94	2.96	2.98
	β	Mn3	-2.88	-2.89	-2.89
	α	Mn4	2.84	2.84	2.84
	α	O8	0.92	0.56	0.01
	α	Mn1	2.99	3.44	3.91
	β	Mn2	-2.91	-2.91	-2.90
	α	Mn3	2.92	2.93	2.94
	α	Mn4	2.89	2.89	2.89
	α	O8	0.92	0.58	0.01
	β	Mn1	-2.92	-2.38	-1.99
	α	Mn2	2.94	2.94	2.94
	α	Mn3	2.94	2.96	2.98
	α	Mn4	2.89	2.89	2.88
	α	O8	0.89	0.34	0.00
12-et	α	Mn1	2.95	2.38	2.02
	α	Mn2	2.95	2.96	2.97
	α	Mn3	2.95	2.95	2.96
	α	Mn4	2.88	2.88	2.87
	α	O8	-0.88	-0.32	-0.01
14-et	α	Mn1	3.01	3.48	3.92
	α	Mn2	2.96	2.98	2.99

	α	Mn3	2.95	2.96	2.96
	α	Mn4	2.89	2.89	2.89
	α	O8	0.92	0.56	0.01

Rea:

Ca	-0.59203300	-2.13043300	-1.70632500	H	7.49827800	-3.62240200	-2.56501000
Mn	1.99449200	-0.34216400	-0.30931800	H	8.03122900	-2.06843700	-1.89786200
Mn	0.40127800	-1.80557400	1.41395800	H	7.86708400	-3.48024700	-0.83631800
Mn	-1.43221300	0.16661600	0.57681400	N	2.47592700	1.68380800	-0.46194500
Mn	-3.45701100	0.60761800	-1.16593700	C	2.18916600	2.52210900	-1.51868100
O	1.42201800	-2.03309500	-0.08058000	H	1.76018100	2.12622300	-2.42881800
O	0.57477300	0.01895000	0.85995900	C	2.51248400	3.81381800	-1.17518300
O	-1.22867200	-1.64185100	0.64584000	N	3.01521800	3.73066900	0.11832700
O	-1.65993700	0.11788600	-1.22527800	H	3.12212000	4.53868800	0.73839700
O	-3.23931000	0.30498000	0.54302400	C	2.95793100	2.43971300	0.51434600
O	0.93844200	-3.51060600	-3.02759800	H	3.24909100	2.07956800	1.48966400
H	1.19369200	-4.18785100	-2.37533700	C	2.41534200	5.09325300	-1.96552700
H	1.75738000	-2.99735500	-3.22624200	H	3.20562900	5.12447100	-2.73061800
O	-0.46927000	-0.37328700	-3.59931000	H	1.46647600	5.08047600	-2.51999100
H	-0.90946000	0.21229200	-2.92774800	C	2.51743800	6.40606000	-1.14585700
H	-3.14512800	2.03854800	-3.25122800	H	3.54145700	6.54857800	-0.78247800
O	-3.57410000	1.16169900	-3.29535300	H	2.28875000	7.24866300	-1.81268600
H	-4.51815000	1.35587200	-3.05798600	C	1.61228500	6.41326400	0.08396200
O	-5.16321100	1.31557900	-1.26962300	O	2.04641000	6.10478500	1.20160400
H	-5.77791400	0.57362400	-1.11997600	N	0.30357100	6.70838700	-0.13027100
O	-2.80825800	-2.55789500	-2.34362600	H	0.00761700	6.92261200	-1.07459600
C	-3.96440600	-2.21315400	-2.04123600	C	-0.72515200	6.47066200	0.88771300
O	-4.32777100	-1.05907100	-1.58280100	H	-0.32677700	6.82468500	1.84406000
C	-5.09770600	-3.22328800	-2.22316300	H	-1.59129800	7.09336100	0.63016500
H	-5.04928700	-3.55200100	-3.27125100	C	-1.12023800	4.98861800	1.00915200
H	-4.81487500	-4.10324900	-1.62725600	H	-0.24220700	4.40694900	1.31028000
C	-6.50253400	-2.74494300	-1.85857900	H	-1.85510500	4.89185600	1.82075200
H	-6.80467800	-1.88899900	-2.47472100	C	-1.70045500	4.41271900	-0.28672400
H	-6.55666900	-2.43819600	-0.80730700	H	-0.99229600	4.57144300	-1.11616500
H	-7.23183200	-3.54980500	-2.01724900	H	-2.63701300	4.90977400	-0.57060900
O	3.66081700	-0.83089400	-1.21267000	C	-1.96528000	2.91127600	-0.25050600
C	3.86477300	-1.42939000	-2.33955800	O	-1.27472300	2.19731400	0.52355600
O	2.98314400	-1.63969500	-3.20643000	O	-2.87010800	2.49980200	-1.05579100
C	5.30719600	-1.84991600	-2.59313200	O	3.20930800	-0.33473800	1.29360800
H	5.32013300	-2.46811200	-3.49918800	C	3.08874000	-1.12788200	2.28706000
H	5.87668100	-0.93359300	-2.81694500	O	2.08748300	-1.85790600	2.52449300
C	5.96355500	-2.57722300	-1.40839100	C	4.27528300	-1.19370800	3.24021100
H	5.38352400	-3.48241700	-1.17286200	H	4.62717100	-0.16485000	3.39691400
H	5.90419500	-1.93191700	-0.52278500	H	5.08201600	-1.70078400	2.68848200
C	7.42003800	-2.95871400	-1.69263900	C	3.99310200	-1.90176300	4.56551100

H	4.89949800	-1.92479900	5.18367400	C	-1.64161300	-0.25096100	4.84742600
H	3.20538800	-1.38780700	5.12950900	H	-1.16234100	-1.00328500	5.48430700
H	3.65897200	-2.93128400	4.39792600	H	-1.30185600	0.74279500	5.17622900
O	-0.32590800	-4.25705100	-0.48169100	C	-3.17640800	-0.32720800	4.95762800
C	-0.10882800	-4.53519600	0.71435000	H	-3.51272000	-1.31511800	4.60998000
O	0.19108000	-3.68790200	1.65225600	H	-3.61590000	0.41075400	4.27443700
C	-0.19998700	-5.97154000	1.20062500	C	-3.66684400	-0.08768200	6.38899500
H	-1.08890000	-6.07713400	1.83654300	H	-3.25374200	-0.83142300	7.08464100
H	0.67220400	-6.22169200	1.81531700	H	-4.76131300	-0.14982900	6.44512700
H	-0.28057600	-6.65608400	0.35174200	H	-3.36949200	0.90698300	6.75024600
O	-0.38555100	-1.42844200	3.18960400	O	1.10502400	-0.21622200	-1.92013000
C	-1.16189600	-0.44888600	3.42033500	H	1.73551100	-0.61053800	-2.58739200
O	-1.57376400	0.37978200	2.55183800				

TS:

Ca	0.13238700	-2.20665600	-1.70654400	O	3.67967300	0.50929700	-1.32059400
Mn	1.98712300	0.40528900	-0.33018500	C	4.08413400	-0.08054500	-2.39266800
Mn	1.03873500	-1.54172700	1.38052300	O	3.31979800	-0.60410500	-3.24303900
Mn	-1.38667100	-0.34394400	0.62483600	C	5.58943900	-0.07496300	-2.61732800
Mn	-3.45827200	-0.60011900	-1.10881400	H	5.80389100	-0.72137000	-3.47717300
O	2.01457000	-1.39185400	-0.14992800	H	5.86925900	0.95114500	-2.90499100
O	0.52840100	0.22223500	0.86810800	C	6.40245200	-0.49441300	-1.38147800
O	-0.57109400	-1.96680800	0.65390900	H	6.11101900	-1.51348200	-1.08545400
O	-1.59904800	-0.43873100	-1.18494200	H	6.13145700	0.16066700	-0.54380500
O	-3.13552200	-0.83751600	0.59084000	C	7.91298700	-0.44244900	-1.63246600
O	1.97321800	-3.03431200	-3.09451000	H	8.20660600	-1.10845400	-2.45582000
H	2.40215800	-3.62331700	-2.44623100	H	8.23736900	0.57401500	-1.89668500
H	2.61620100	-2.31109300	-3.28136300	H	8.47292800	-0.74993900	-0.73976000
O	-0.15522700	-0.18983200	-3.38691100	N	1.69697600	2.45367900	-0.53687700
H	-0.87397000	0.06558200	-2.75035900	C	1.10108200	3.12976500	-1.58214000
H	-3.68797500	0.87100500	-3.18202600	H	0.81342500	2.60527400	-2.48335800
O	-3.79306000	-0.09904100	-3.23119200	C	0.96226900	4.45579300	-1.24415900
H	-4.74166800	-0.24077100	-2.97409800	N	1.50533300	4.56465900	0.03076500
O	-5.30569000	-0.52468500	-1.18992100	H	1.35110200	5.36770600	0.64766000
H	-5.62354500	-1.43497400	-1.04459500	C	1.91652000	3.33987200	0.42510500
O	-1.79574500	-3.31683000	-2.41709300	H	2.35069900	3.11044000	1.38713200
C	-2.99190200	-3.40094000	-2.07992400	C	0.39249800	5.61351600	-2.02320300
O	-3.70757700	-2.46309000	-1.55346700	H	1.08898300	5.90850800	-2.82233600
C	-3.71779500	-4.72831500	-2.29897800	H	-0.51580700	5.26618000	-2.53533600
H	-3.58722900	-4.97678100	-3.36202500	C	0.06717200	6.88941400	-1.20293600
H	-3.13778100	-5.48369300	-1.74890000	H	0.99245600	7.38418100	-0.88678300
C	-5.19165700	-4.77229900	-1.89776800	H	-0.47060000	7.59119400	-1.85502500
H	-5.78204500	-4.04499900	-2.46882100	C	-0.72763200	6.59638200	0.06780900
H	-5.31956100	-4.54669200	-0.83247900	O	-0.16311400	6.47514100	1.16309500
H	-5.60841800	-5.76974800	-2.08801700	N	-2.06465400	6.40982300	-0.08344100

H	-2.45949900	6.49338100	-1.01210000	O	1.16623200	-4.10336700	-0.53051800
C	-2.89417300	5.83169800	0.97935400	C	1.50570000	-4.28418100	0.65833400
H	-2.59941000	6.30860200	1.91960800	O	1.50668800	-3.38924300	1.59546500
H	-3.93523600	6.10884700	0.77043000	C	1.95253400	-5.65891300	1.12660000
C	-2.73673000	4.30571500	1.10047200	H	1.17359000	-6.08543900	1.77247600
H	-1.69648400	4.07115700	1.35146500	H	2.86609200	-5.57902800	1.72654700
H	-3.34882800	3.95986700	1.94522000	H	2.11142200	-6.32060700	0.27056400
C	-3.14232800	3.55913400	-0.17383600	O	0.20430300	-1.49447000	3.18092700
H	-2.58572100	3.95955500	-1.03668800	C	-0.86624100	-0.86435200	3.44299700
H	-4.20847700	3.68993200	-0.40070500	O	-1.57306500	-0.23286400	2.59665100
C	-2.85562900	2.06108700	-0.15766600	C	-1.34747100	-0.85821000	4.88357500
O	-1.95627600	1.62359600	0.60564500	H	-0.63213800	-1.42448100	5.49102700
O	-3.55993400	1.37077900	-0.97418700	H	-1.33559500	0.18657700	5.23007200
O	3.17471500	0.85040100	1.31206700	C	-2.77160200	-1.42654200	5.02691800
C	3.33904900	0.02788500	2.26796200	H	-2.78253500	-2.46453900	4.66296800
O	2.65284400	-1.01939300	2.46093700	H	-3.44535600	-0.85931000	4.37221800
C	4.47170800	0.32695200	3.24387700	C	-3.27045700	-1.38053400	6.47462600
H	4.42221600	1.39935200	3.47843700	H	-2.61954800	-1.96214600	7.14232200
H	5.40696400	0.19190500	2.67887500	H	-4.28454900	-1.79301300	6.55459100
C	4.47363300	-0.52606900	4.51255900	H	-3.29837900	-0.34892400	6.85325900
H	5.32603800	-0.25790300	5.14983500	O	1.07020900	0.14347300	-2.10049100
H	3.55285500	-0.37918300	5.08977100	H	1.84999600	-0.06175400	-2.71141500
H	4.54170900	-1.59210700	4.26999100				

Pro:

Ca	-1.42885800	-1.90414100	-1.55402800	O	-3.49958800	-1.41726800	-2.49907700
Mn	1.75975300	-0.95647700	-0.28650800	C	-4.46040700	-0.67760600	-2.20341000
Mn	-0.19554100	-1.84184700	1.43791200	O	-4.38717600	0.47728500	-1.63409300
Mn	-1.28955200	0.60561700	0.65340600	C	-5.87375400	-1.15880100	-2.52965000
Mn	-2.97139100	1.72043400	-1.18497400	H	-5.87474300	-1.39647700	-3.60323000
O	0.57008400	-2.32812300	-0.14188800	H	-5.99224600	-2.12445400	-2.01672000
O	0.51739900	-0.16248500	0.94954600	C	-7.01434200	-0.20633000	-2.17330900
O	-1.73594900	-1.14026500	0.73677500	H	-6.92013300	0.74606800	-2.70958800
O	-1.47087300	0.59624200	-1.19486600	H	-7.02721500	0.01278700	-1.09912800
O	-2.93341100	1.38584200	0.52411400	H	-7.98057300	-0.65192000	-2.44257800
O	-0.48632200	-3.50998600	-3.15058800	O	3.03629400	-1.95043200	-1.47201400
H	-0.48328300	-4.38661000	-2.72842600	C	2.98003500	-2.59075400	-2.57350700
H	0.45559600	-3.31176600	-3.37550300	O	2.07026400	-2.44932000	-3.44960600
O	0.35000800	0.62106800	-3.04617500	C	4.12422500	-3.55290600	-2.86648800
H	-0.36609400	0.89204300	-2.39114700	H	3.80161200	-4.22927300	-3.66818800
H	-2.15728900	2.89321400	-3.33974800	H	4.94649600	-2.94701800	-3.28207000
O	-2.88998800	2.24800200	-3.32876000	C	4.62987100	-4.32808600	-1.64144400
H	-3.68027800	2.79408500	-3.07248900	H	3.80549700	-4.92856700	-1.22809700
O	-4.30170700	3.00194200	-1.32286100	H	4.90716400	-3.61013800	-0.85960600
H	-5.14581400	2.53951900	-1.16664100	C	5.81550400	-5.23937800	-1.97556800

H	5.55007500	-5.98123800	-2.74192000	O	3.04507800	-1.50142400	1.37538000
H	6.66771000	-4.65965500	-2.35788100	C	2.58641300	-2.22278700	2.30545200
H	6.15672200	-5.78641900	-1.08712700	O	1.35530300	-2.50724300	2.48219000
N	2.86250000	0.78728800	-0.48367900	C	3.58142800	-2.83159100	3.28942700
C	2.90362800	1.71047800	-1.51141800	H	4.33501800	-2.06173600	3.50413900
H	2.34183300	1.54961000	-2.42292400	H	4.11398900	-3.62042500	2.73523900
C	3.68292000	2.77731200	-1.13115100	C	2.96968700	-3.39464600	4.57281900
N	4.12495400	2.46810700	0.15026700	H	3.75121700	-3.82692200	5.21113400
H	4.52097700	3.15735800	0.79468700	H	2.45567400	-2.61117300	5.14312800
C	3.59566900	1.27807100	0.50830300	H	2.23237100	-4.17279000	4.34801700
H	3.74244700	0.79292600	1.46257200	O	-1.89654500	-3.94282400	-0.36246300
C	4.06583200	4.02615600	-1.88172300	C	-1.68820700	-4.25739000	0.83036400
H	4.84158800	3.79535600	-2.62738200	O	-1.04408900	-3.55478100	1.70410200
H	3.19025900	4.35670100	-2.45763800	C	-2.22399000	-5.57095300	1.37634100
C	4.59336700	5.20150900	-1.01759200	H	-2.99956100	-5.35986500	2.12403400
H	5.59939500	4.97773000	-0.64515700	H	-1.42410300	-6.12145700	1.88522500
H	4.67368000	6.09227500	-1.65556800	H	-2.64992800	-6.17544800	0.57081800
C	3.72533800	5.47336100	0.20875000	O	-0.79637200	-1.22475900	3.24185800
O	4.01581200	5.00217800	1.31567800	C	-1.24240500	-0.06132700	3.47108500
N	2.59328400	6.19526100	-0.00089200	O	-1.41671700	0.85289400	2.59989800
H	2.40080200	6.52532700	-0.93851300	C	-1.60947600	0.28950200	4.90268100
C	1.53039000	6.28980400	1.00523700	H	-1.36735400	-0.56727800	5.54193600
H	2.01032400	6.47051100	1.97263200	H	-0.97536100	1.13507400	5.20949400
H	0.92379700	7.17047900	0.75866500	C	-3.09121300	0.68583900	5.04404600
C	0.66415300	5.02118600	1.08873800	H	-3.72072000	-0.15470700	4.71642100
H	1.29520500	4.17548300	1.38268000	H	-3.30059300	1.51848500	4.36038100
H	-0.07182200	5.15710700	1.89357800	C	-3.45253200	1.07300000	6.48156700
C	-0.05745600	4.69465200	-0.22275700	H	-3.26998500	0.24321300	7.17860800
H	0.67148300	4.62848600	-1.04656300	H	-4.51221200	1.34835300	6.56048900
H	-0.77583000	5.47707800	-0.50043100	H	-2.85762400	1.93168000	6.82370600
C	-0.80277600	3.36401900	-0.21758700	O	0.61276200	-0.66960800	-2.40424100
O	-0.43775000	2.47062700	0.58828600	H	1.21824800	-1.20058800	-3.03791200
O	-1.74121700	3.26319300	-1.08442900				

Table S30 Reaction parameters for the open-cubane W3 (hydroxyl)-W2 (oxo) nucleophilic attack:

Spin state	Spin topology (Mn1~Mn4-O8)	Gibbs Free energy (a.u.)		
		Rea	TS	Pro
doublet	ααββα	-3365.7150	-3365.6989	-3365.7064
	αβαβα	-3365.7151	-3365.6999	-3365.7055
	αββαα	-3365.7090	-3365.6974	-3365.7464
	βααβα	-3365.7158	-3365.6999	-3365.7087
	βαβαα	-3365.7085	-3365.6961	-3365.7454
	ββααα	-3365.7083	-3365.6950	-3365.7482

sextet	ααααββ	-3365.7097	-3365.6975	-3365.7462
	ααβαβ	-3365.7170	-3365.7002	-3365.7061
	αβααβ	-3365.7154	-3365.6987	-3365.7054
	βαααβ	-3365.7165	-3365.6992	-3365.7069
octet	αααβα	-3365.7176	-3365.7007	-3365.7102
	ααβαα	-3365.7103	-3365.6982	-3365.7525
	αβααα	-3365.7096	-3365.6962	-3365.7492
	βαααα	-3365.7092	-3365.6958	-3365.7429
12-et	αααααβ	-3365.7173	-3365.7001	-3365.7053
14-et	ααααα	-3365.7098	-3365.6964	-3365.7473

Spin state	Spin topology (Mn1~Mn4-O8)	Relative Gibbs Free energy (kcal/mol)			
		$\Delta G^{\neq}$(Rea-TS)	ΔG(Rea-Pro)	ΔG(Rea)	ΔG(Pro)
doublet	ααββα	10.1	5.4	1.6	28.9
	αβαβα	9.5	6.0	1.6	29.5
	αββαα	7.3	-23.5	5.4	3.8
	βααβα	10.0	4.5	1.1	27.5
	βαβαα	7.8	-23.2	5.7	4.5
	ββααα	8.3	-25.0	5.8	2.7
sextet	ααααββ	7.7	-22.9	5.0	4.0
	ααβαβ	10.5	6.8	0.4	29.1
	αβααβ	10.5	6.3	1.4	29.6
	βαααβ	10.9	6.0	0.7	28.6
octet	αααβα	10.6	4.6	0.0	26.5
	ααβαα	7.6	-26.5	4.6	0.0
	αβααα	8.4	-24.8	5.0	2.1
	βαααα	8.4	-21.1	5.3	6.0
12-et	αααααβ	10.8	7.5	0.2	29.6
14-et	ααααα	8.4	-23.5	4.9	3.3

Spin state	Spin topology (Mn1~Mn4-O8)		Mulliken spin density		
			Rea	TS	Pro
doublet	α	Mn1	2.95	2.94	2.94
	α	Mn2	2.93	2.93	2.95
	β	Mn3	-2.79	-2.80	-2.79
	β	Mn4	-2.71	-2.28	-1.96
	α	O8	0.54	0.29	0.01
	α	Mn1	2.93	2.93	2.92
	β	Mn2	-2.90	-2.90	-2.92
	α	Mn3	2.78	2.81	2.78
	β	Mn4	-2.67	-2.26	-1.93
	α	O8	0.54	0.28	0.01
	α	Mn1	2.92	2.93	2.92

	β	Mn2	-2.92	-2.92	-2.92
	β	Mn3	-2.82	-2.84	-2.83
	α	Mn4	2.69	3.03	3.88
	α	O8	0.95	0.64	0.01
	β	Mn1	-2.93	-2.94	-2.94
	α	Mn2	2.92	2.92	2.93
	α	Mn3	2.83	2.85	2.82
	β	Mn4	-2.68	-2.26	-1.94
	α	O8	0.54	0.28	0.01
	β	Mn1	-2.93	-2.93	-2.92
	α	Mn2	2.91	2.90	2.92
	β	Mn3	-2.78	-2.79	-2.80
	α	Mn4	2.69	3.02	3.87
	α	O8	0.95	0.64	0.01
	β	Mn1	-2.94	-2.95	-2.95
	β	Mn2	-2.93	-2.93	-2.94
	α	Mn3	2.79	2.82	2.86
	α	Mn4	2.71	3.07	3.89
	α	O8	0.96	0.63	0.01
	α	Mn1	2.95	2.95	2.95
	α	Mn2	2.94	2.94	2.94
	α	Mn3	2.83	2.84	2.83
	β	Mn4	-2.69	-3.02	-3.88
	β	O8	-0.95	-0.64	-0.01
	α	Mn1	2.95	2.95	2.92
	α	Mn2	2.93	2.93	2.91
	β	Mn3	-2.78	-2.81	-2.81
	α	Mn4	2.68	2.27	1.95
sextet	β	O8	-0.54	-0.29	0.02
	α	Mn1	2.93	2.93	2.92
	β	Mn2	-2.90	-2.90	-2.93
	α	Mn3	2.79	2.80	2.79
	α	Mn4	2.71	2.28	1.97
	β	O8	-0.54	-0.28	-0.01
	β	Mn1	-2.92	-2.92	-2.92
	α	Mn2	2.92	2.92	2.92
	α	Mn3	2.83	2.84	2.83
	α	Mn4	2.71	2.28	1.96
	β	O8	-0.54	-0.28	0.01
	α	Mn1	2.95	2.95	2.96
	α	Mn2	2.95	2.94	2.95
octet	α	Mn3	2.85	2.86	2.82
	β	Mn4	-2.68	-2.27	-1.94
	α	O8	0.46	0.29	0.01

	α	Mn1	2.94	2.95	2.96
	α	Mn2	2.93	2.93	2.95
	β	Mn3	-2.78	-2.79	-2.80
	α	Mn4	2.69	3.03	3.87
	α	O8	0.95	0.64	0.02
	α	Mn1	2.93	2.93	2.94
	β	Mn2	-2.91	-2.91	-2.92
	α	Mn3	2.79	2.82	2.86
	α	Mn4	2.72	3.08	3.89
	α	O8	0.96	0.62	0.01
	β	Mn1	-2.92	-2.93	-2.91
	α	Mn2	2.92	2.92	2.92
	α	Mn3	2.84	2.87	2.91
	α	Mn4	2.71	3.07	3.89
	α	O8	0.96	0.63	0.01
12-et	α	Mn1	2.96	2.95	2.95
	α	Mn2	2.95	2.94	2.94
	α	Mn3	2.84	2.85	2.83
	α	Mn4	2.71	2.29	1.96
	β	O8	-0.54	-0.29	0.01
14-et	α	Mn1	2.95	2.95	2.96
	α	Mn2	2.94	2.94	2.95
	α	Mn3	2.84	2.87	2.90
	α	Mn4	2.72	3.08	3.89
	α	O8	0.96	0.63	0.01

Rea:

Ca	-2.41000800	0.15637900	-1.35647300	H	0.41125100	5.09158700	0.06276400
Mn	-0.00651800	-1.91052300	-0.32153500	O	-3.37985300	2.34771000	-1.54884500
Mn	-1.23638500	-0.62224000	1.78093900	C	-3.10533300	3.52540300	-1.23588400
Mn	0.21113300	1.56379200	0.72185300	O	-1.93078900	4.01710800	-1.08776700
Mn	-0.11966400	3.27126900	-1.41526200	C	-4.27544400	4.48443900	-0.99333200
O	-1.65970000	-1.54978800	0.27176500	H	-4.90353600	4.43901200	-1.89440900
O	0.43173200	-0.59972000	0.92299700	H	-4.87849500	4.03833500	-0.18933500
O	-1.48361800	1.03134000	1.18677600	C	-3.90215700	5.92810100	-0.65670300
O	-0.29784200	1.53275200	-1.04429400	H	-3.31989100	6.38504100	-1.46706000
O	0.07521900	3.26941200	0.64574700	H	-3.29941600	5.97664200	0.25859800
O	-4.69041900	-0.76233800	-2.10653100	H	-4.80441600	6.53637900	-0.50237800
H	-4.95939600	-0.77518700	-1.16301100	O	-0.64785500	-3.36286000	-1.47719700
H	-4.28433400	-1.63741500	-2.27970400	C	-1.71571500	-3.30275900	-2.20188600
O	-2.03187900	1.34093000	-3.56847800	O	-2.49628800	-2.33491200	-2.30324100
H	-1.37357200	2.11227700	-3.44767600	C	-1.97305700	-4.58502600	-3.00350300
O	-0.30975800	3.34671000	-3.06729600	H	-1.14894200	-4.67951200	-3.72883200
O	0.24938400	5.48220600	-0.82753800	H	-1.86127500	-5.43824200	-2.31853300
H	-0.72266500	5.60138500	-0.83954500	C	-3.32247100	-4.62838700	-3.72360100

H	-3.41138500	-3.74634600	-4.37137000	O	2.17220500	1.63303000	0.15335500
H	-4.13099900	-4.54175800	-2.98310400	O	1.87426500	3.14334100	-1.51922400
C	-3.51152100	-5.90787400	-4.54663500	O	0.31286000	-3.36210400	1.05755600
H	-2.73474500	-6.00298200	-5.31929500	C	-0.24273300	-3.37606800	2.20712200
H	-3.45515600	-6.80474500	-3.91258400	O	-0.90553500	-2.44208500	2.72811900
H	-4.48668900	-5.91811700	-5.05252300	C	-0.07948900	-4.67472900	2.99801500
N	2.02966700	-2.24910400	-0.79059700	H	0.97340400	-4.97948200	2.91688000
C	2.64390300	-1.94314000	-1.98369700	H	-0.65115200	-5.44212900	2.45374800
H	2.04866500	-1.66594200	-2.84306000	C	-0.52933200	-4.59459200	4.45684500
C	4.00788000	-2.01878900	-1.83098700	H	-0.40419300	-5.56659900	4.95356900
N	4.20430200	-2.39753800	-0.50598200	H	0.05316600	-3.84715300	5.00927400
H	5.09973800	-2.33845700	-0.01773700	H	-1.58208500	-4.29915600	4.52486800
C	2.98835900	-2.50493900	0.08351900	O	-4.15238200	-0.26210500	0.50814400
H	2.82917200	-2.73668200	1.12636000	C	-4.12136800	-0.56075400	1.72168800
C	5.11365500	-1.77192700	-2.82351500	O	-3.06844100	-0.72679700	2.44578600
H	5.14354800	-2.58118900	-3.56942500	C	-5.42817300	-0.78101300	2.47765500
H	4.86803200	-0.86065200	-3.38777400	H	-6.28258800	-0.47356800	1.86708700
C	6.53899300	-1.64279800	-2.23216200	H	-5.41547700	-0.21961600	3.41929200
H	6.88522100	-2.61342000	-1.85901700	H	-5.52474300	-1.84512200	2.73244000
H	7.22231600	-1.33897300	-3.03779800	O	-0.55064000	0.07197100	3.52377300
C	6.62917400	-0.67320700	-1.05327400	C	0.33090900	0.98493300	3.60421800
O	6.66654900	-1.08723800	0.11280800	O	0.85900100	1.60327800	2.63652100
N	6.62935300	0.65020900	-1.36219000	C	0.77485500	1.39497200	5.00615700
H	6.49192000	0.90871400	-2.33205500	H	1.78762900	1.81130000	4.92836600
C	6.43220600	1.68889400	-0.34355700	H	0.11947500	2.22905900	5.30752100
H	7.01382200	1.38510300	0.53288700	C	0.70574700	0.27641000	6.05176800
H	6.86864000	2.61726600	-0.73610300	H	1.36076900	-0.55082300	5.73947300
C	4.95932000	1.88777500	0.04789800	H	-0.31216400	-0.13227200	6.06733200
H	4.56494400	0.94981100	0.45399200	C	1.10958800	0.75516000	7.45075000
H	4.91730100	2.62004700	0.86730300	H	2.13714400	1.14692300	7.46081800
C	4.07067400	2.35621100	-1.10765600	H	1.05720400	-0.06184900	8.18345600
H	4.17114500	1.67432800	-1.96772700	H	0.44767600	1.56018400	7.80169700
H	4.35642700	3.35359700	-1.46740800	O	-0.06740700	-0.86848500	-1.80660200
C	2.57435800	2.38638900	-0.78043500	H	0.27400900	0.04342900	-1.61283400

TS:

Ca	-2.43048700	0.15506800	-1.28519900	O	-0.11758700	3.22689800	0.59874600
Mn	0.10650700	-1.92400600	-0.37637200	O	-4.62855800	-0.83541700	-2.12105600
Mn	-1.14130500	-0.73983800	1.78447400	H	-4.91704000	-0.90361700	-1.18544500
Mn	0.18112000	1.52879600	0.75569700	H	-4.18835500	-1.68843800	-2.32242100
Mn	-0.43119300	3.16538700	-1.37311700	O	-1.68183800	1.44691800	-3.46598600
O	-1.54732900	-1.61002200	0.23620300	H	-0.78533600	1.15327500	-3.72082500
O	0.51447400	-0.62517400	0.90771500	O	-0.74880300	3.15841100	-3.04888100
O	-1.47271300	0.92134100	1.27195200	O	-0.09301600	5.52812100	-0.80772900
O	-0.36076500	1.40803900	-0.96482900	H	-1.07265700	5.52287200	-0.76068700

H	0.16482200	5.10735700	0.04184200	H	6.93581400	1.86067800	0.43325000
O	-3.62251500	2.22247000	-1.10355600	H	6.69520200	3.02717600	-0.88211900
C	-3.40840300	3.44435500	-0.98100300	C	4.84786300	2.20968300	-0.03845900
O	-2.25877500	4.01570900	-0.99484700	H	4.52058900	1.26460200	0.40814000
C	-4.62162400	4.36371900	-0.79153200	H	4.77285300	2.96734400	0.75519300
H	-5.28607700	4.17670000	-1.64755800	C	3.91082900	2.57862700	-1.19219200
H	-5.16226500	3.98922900	0.08969200	H	4.04116000	1.87257600	-2.02869400
C	-4.31932600	5.85599000	-0.65362600	H	4.12593700	3.57848600	-1.59214200
H	-3.79065800	6.23411700	-1.53738300	C	2.41875200	2.52670800	-0.83561000
H	-3.68673000	6.05222100	0.22116800	O	2.09946600	1.77109600	0.13585400
H	-5.24784400	6.43305400	-0.53725800	O	1.65163100	3.21004500	-1.57194300
O	-0.52688600	-3.35840200	-1.55799800	O	0.47043700	-3.40644400	0.96022700
C	-1.59774300	-3.28658900	-2.27725200	C	-0.06552900	-3.46956100	2.11632600
O	-2.38343900	-2.32029700	-2.35970400	O	-0.74105000	-2.56677500	2.67546800
C	-1.85268800	-4.55584500	-3.10118400	C	0.13865500	-4.78743500	2.86448800
H	-1.02787700	-4.63752800	-3.82732600	H	1.19299600	-5.07376400	2.74565300
H	-1.73979700	-5.41985700	-2.43016600	H	-0.43721900	-5.54719200	2.31383100
C	-3.20162400	-4.59112500	-3.82255900	C	-0.27281300	-4.75616400	4.33651200
H	-3.29330900	-3.69908000	-4.45628400	H	-0.12263000	-5.74064500	4.80065700
H	-4.01076500	-4.51907900	-3.08120300	H	0.31542500	-4.01809700	4.89557700
C	-3.38686100	-5.85756600	-4.66641300	H	-1.32675700	-4.47620500	4.44099100
H	-2.60948600	-5.93817200	-5.44014400	O	-4.10103500	-0.53525200	0.54718900
H	-3.32825100	-6.76426400	-4.04682000	C	-4.03245600	-0.83312200	1.75824500
H	-4.36183400	-5.86232400	-5.17271000	O	-2.95882200	-0.94600500	2.46449000
N	2.16861500	-2.18773200	-0.82533700	C	-5.31178300	-1.10495000	2.54387400
C	2.78227400	-1.88090600	-2.01809700	H	-6.19078400	-0.97870000	1.90471500
H	2.18628600	-1.67849100	-2.89723000	H	-5.37141500	-0.41638500	3.39602700
C	4.14463400	-1.84436900	-1.84000400	H	-5.28755700	-2.12453700	2.94968100
N	4.34311600	-2.15554600	-0.49784900	O	-0.42567000	-0.05323700	3.53016500
H	5.22134200	-2.00681000	0.00296100	C	0.37148900	0.93176500	3.61661300
C	3.12687300	-2.33440100	0.07407000	O	0.83127300	1.61650300	2.65465600
H	2.96598500	-2.53028100	1.12405600	C	0.80267200	1.35583200	5.01839400
C	5.24640100	-1.54545900	-2.82260400	H	1.80087500	1.80633300	4.93889000
H	5.34692800	-2.37057100	-3.54467400	H	0.12180000	2.17001600	5.31762200
H	4.94629800	-0.66962300	-3.41618600	C	0.77264300	0.23863900	6.06660100
C	6.64838300	-1.29722300	-2.21499500	H	1.45319900	-0.56775400	5.75488000
H	7.05353100	-2.22809800	-1.80199600	H	-0.23107100	-0.20367000	6.08623700
H	7.32317000	-0.97569600	-3.02099900	C	1.16385900	0.73461500	7.46323800
C	6.65463700	-0.28283400	-1.07038900	H	2.17810100	1.15977300	7.46971700
O	6.69892200	-0.65291100	0.11019200	H	1.13993700	-0.08153700	8.19835300
N	6.57812900	1.02606000	-1.42624100	H	0.47690500	1.51860500	7.81362000
H	6.44351000	1.24351500	-2.40635000	O	0.04736700	-0.88019200	-1.85655800
C	6.32460500	2.08966100	-0.44607300	H	0.29510000	0.04752000	-1.59957300

Pro:

Ca	2.50264200	-0.03167200	-1.02126400	H	-2.22222300	1.31132500	-3.01788600
Mn	-0.26238800	1.91594400	-0.46596900	C	-4.22857900	1.45329400	-2.04975300
Mn	0.96396200	0.88641000	1.78678100	N	-4.49838000	1.87680900	-0.75157500
Mn	-0.09798000	-1.51906900	0.72410300	H	-5.38486400	1.71888000	-0.26829700
Mn	0.82547800	-3.19993500	-1.23389100	C	-3.31869800	2.18375900	-0.15838000
O	1.37807200	1.76714700	0.24629700	H	-3.21149600	2.49163600	0.87116400
O	-0.62352400	0.60974100	0.83765500	C	-5.27195000	0.99503700	-3.03452600
O	1.48669000	-0.72778500	1.28056000	H	-5.39835900	1.74330400	-3.83237200
O	0.45088300	-1.38888800	-0.97282000	H	-4.89485000	0.09134100	-3.53502400
O	0.44842000	-3.18135200	0.62647700	C	-6.67652000	0.70953500	-2.44903800
O	4.58674200	1.10662300	-1.93016200	H	-7.15654200	1.64505900	-2.13979900
H	4.86482300	1.27350700	-1.00464300	H	-7.29875000	0.26824700	-3.24053900
H	4.07928200	1.90310400	-2.20011000	C	-6.65739300	-0.19143400	-1.21305900
O	1.69107000	-1.58797300	-3.32891200	O	-6.77203800	0.28434800	-0.07571900
H	0.84897800	-1.11204500	-3.47287600	N	-6.47850500	-1.51861900	-1.44101400
O	1.18956600	-2.93699500	-3.05617300	H	-6.28316700	-1.81092700	-2.39117100
O	0.65209900	-5.46833200	-0.96059500	C	-6.16751200	-2.46433600	-0.36154600
H	1.61647400	-5.46572600	-0.76360100	H	-6.78012800	-2.17071800	0.49705800
H	0.22594500	-5.29341800	-0.09689600	H	-6.50046000	-3.45742800	-0.69319600
O	3.81365600	-2.01827700	-0.94995700	C	-4.68142500	-2.47840700	0.03061200
C	3.82629900	-3.26736100	-0.84364400	H	-4.39129000	-1.48214800	0.38203900
O	2.79546800	-4.02048500	-0.88381000	H	-4.56177700	-3.15364200	0.89054200
C	5.18946500	-3.94307500	-0.65279600	C	-3.74287800	-2.91226800	-1.09909200
H	5.82041100	-3.62046800	-1.49380300	H	-3.90103500	-2.27848500	-1.98739500
H	5.64179000	-3.49326400	0.24313200	H	-3.93849900	-3.94561800	-1.41698200
C	5.16286000	-5.46783500	-0.54392900	C	-2.24208200	-2.80108600	-0.77511000
H	4.72454500	-5.91872400	-1.44283100	O	-1.95158000	-1.96558500	0.15512700
H	4.55989400	-5.79091800	0.31381900	O	-1.45598200	-3.49182900	-1.45960700
H	6.17847600	-5.86979900	-0.41827600	O	-0.80929900	3.39788300	0.81811700
O	0.32510800	3.36212500	-1.65117100	C	-0.35376300	3.51844200	2.00339900
C	1.43538600	3.34164000	-2.31285500	O	0.34922400	2.67764200	2.62259700
O	2.28438100	2.42757300	-2.32734300	C	-0.70012200	4.82928500	2.71121300
C	1.64950500	4.60463700	-3.15853600	H	-1.76105600	5.03944500	2.51624900
H	0.85383800	4.61970700	-3.92060400	H	-0.14159200	5.61982000	2.18653400
H	1.45624600	5.47544600	-2.51510800	C	-0.38943000	4.84845100	4.20799100
C	3.02451300	4.70555400	-3.82208800	H	-0.63846100	5.82668200	4.64194900
H	3.19707500	3.80716100	-4.42957300	H	-0.96257200	4.07933600	4.74030900
H	3.80292100	4.69835400	-3.04526300	H	0.67159100	4.64427400	4.38855200
C	3.17162300	5.96214400	-4.68791100	O	4.03043900	0.90521200	0.75465100
H	2.42568200	5.97910500	-5.49583700	C	3.84546200	1.25260400	1.94272400
H	3.03212500	6.87684900	-4.09355200	O	2.72129800	1.28317300	2.56842700
H	4.16602100	6.01473500	-5.15204900	C	5.03300100	1.71425900	2.78205400
N	-2.31786900	2.01257000	-1.00595500	H	5.97424700	1.50562400	2.26447600
C	-2.86474500	1.55729600	-2.18390200	H	5.01948100	1.21489100	3.75788800

H	4.94865700	2.79408600	2.96539200	H	-1.83692500	0.41592100	5.62907300
O	0.26773100	0.15308800	3.51055300	H	-0.12753000	0.38881900	6.02903700
C	-0.40548000	-0.92275900	3.59436600	C	-1.37577000	-0.74460300	7.40021100
O	-0.75731400	-1.66638100	2.63413700	H	-2.29158500	-1.35347200	7.39238200
C	-0.80731200	-1.37494300	4.99643000	H	-1.53479000	0.08749800	8.09986700
H	-1.69972800	-2.00713300	4.90238500	H	-0.56818700	-1.37117300	7.80591800
H	0.00285900	-2.03207300	5.35407900	O	-0.06108200	0.84304700	-1.90528000
C	-1.02934400	-0.23493100	5.99673700	H	-0.21276200	-0.09976400	-1.60649700

Table S31 Reaction parameters for the open-cubane W3 (hydroxyl)-O5 (oxo) nucleophilic attack:

Spin state	Spin topology (Mn1~Mn4-O8)	Gibbs Free energy (a.u.)		
		Rea	TS	Pro
doublet	ααββα	-3365.7323	-3365.7008	-3365.7070
	αβαβα	-3365.7250	-3365.7130	-3365.7313
	αββαα	-3365.7303	-3365.7005	-3365.7077
	βααβα	-3365.7253	-3365.7120	-3365.7292
	βαβαα	-3365.7325	-3365.7004	-3365.7076
	ββααα	-3365.7220	-3365.7120	-3365.7310
sextet	αααββ	-3365.7340	-3365.7015	-3365.7079
	ααβαβ	-3365.7326	-3365.7176	-3365.7399
	αβααβ	-3365.7335	-3365.7025	-3365.7216
	βαααβ	-3365.7337	-3365.7019	-3365.7071
octet	αααβα	-3365.7406	-3365.7246	-3365.7451
	ααβαα	-3365.7338	-3365.7015	-3365.7095
	αβααα	-3365.7399	-3365.7252	-3365.7474
	βαααα	-3365.7402	-3365.7240	-3365.7456
12-et	aaaaβ	-3365.7344	-3365.7030	-3365.7082
14-et	aaaaa	-3365.7412	-3365.7251	-3365.7463

Spin state	Spin topology (Mn1~Mn4-O8)	Relative Gibbs Free energy (kcal/mol)			
		$\Delta G^{\neq}$(Rea-TS)	ΔG(Rea-Pro)	ΔG(Rea)	ΔG(Pro)
doublet	ααββα	19.8	15.9	5.6	25.4
	αβαβα	7.5	-4.0	10.2	10.1
	αββαα	18.7	14.2	6.8	24.9
	βααβα	8.3	-2.4	10.0	11.4
	βαβαα	20.1	15.6	5.5	25.0
	ββααα	6.3	-5.6	12.0	10.3
sextet	αααββ	20.4	16.4	4.5	24.8
	ααβαβ	9.4	-4.6	5.4	4.7
	αβααβ	19.5	7.5	4.8	16.2
	βαααβ	20.0	16.7	4.7	25.3
octet	αααβα	10.0	-2.8	0.4	1.4

	ααβαα	20.3	15.2	4.6	23.8
	αβααα	9.2	-4.7	0.8	0.0
	βαααα	10.2	-3.4	0.6	1.1
12-et	αααaβ	19.7	16.4	4.3	24.6
14-et	ααααα	10.1	-3.2	0.0	0.7

Spin state	Spin topology (Mn1~Mn4-O8)		Mulliken spin density		
			Rea	TS	Pro
doublet	α	Mn1	2.94	2.95	2.97
	α	Mn2	2.94	2.95	2.94
	β	Mn3	-2.85	-2.50	-1.98
	β	Mn4	-2.92	-2.85	-2.85
	α	O8	0.96	0.45	0.00
	α	Mn1	2.93	2.94	2.94
	β	Mn2	-2.91	-2.90	-2.88
	α	Mn3	2.85	3.39	3.80
	β	Mn4	-2.82	-2.79	-2.78
	α	O8	0.78	0.47	0.01
	α	Mn1	2.93	2.94	2.97
	β	Mn2	-2.93	-2.92	-2.93
	β	Mn3	-2.87	-2.47	-2.01
	α	Mn4	2.85	2.88	2.86
	α	O8	0.95	0.46	0.01
	β	Mn1	-2.93	-2.93	-2.93
	α	Mn2	2.93	2.94	2.94
	α	Mn3	2.89	3.44	3.83
	β	Mn4	-2.82	-2.78	-2.78
	α	O8	0.79	0.45	0.02
	β	Mn1	-2.94	-2.94	-2.94
	α	Mn2	2.91	2.93	2.94
	β	Mn3	-2.84	-2.45	-1.97
	α	Mn4	2.85	2.88	2.85
	α	O8	0.95	0.46	0.01
	β	Mn1	-2.94	-2.94	-2.94
	β	Mn2	-2.94	-2.92	-2.90
	α	Mn3	2.85	3.37	3.82
	α	Mn4	2.88	2.88	2.88
	α	O8	0.79	0.49	0.02
sextet	α	Mn1	2.96	2.96	2.96
	α	Mn2	2.95	2.94	2.92
	α	Mn3	2.87	2.47	1.99
	β	Mn4	-2.85	-2.88	-2.83
	β	O8	-0.95	-0.45	-0.02
	α	Mn1	2.95	2.94	2.94

	α	Mn2	2.94	2.93	2.90
	β	Mn3	-2.84	-3.33	-3.81
	α	Mn4	2.85	2.81	2.78
	β	O8	-0.94	-0.58	-0.01
	α	Mn1	2.94	2.94	2.86
	β	Mn2	-2.91	-2.94	-3.82
	α	Mn3	2.85	2.51	2.79
	α	Mn4	2.92	2.85	2.86
	β	O8	-0.96	-0.46	0.00
	β	Mn1	2.93	-2.94	-2.94
	α	Mn2	2.93	2.92	2.91
	α	Mn3	2.88	2.52	2.00
	α	Mn4	2.92	2.85	2.87
	β	O8	-0.96	-0.45	0.00
octet	α	Mn1	2.96	2.96	2.95
	α	Mn2	2.95	2.96	2.96
	α	Mn3	2.89	3.42	3.85
	β	Mn4	-2.87	-2.82	-2.79
	α	O8	0.94	0.54	0.01
	α	Mn1	2.95	2.95	2.97
	α	Mn2	2.94	2.95	2.94
	β	Mn3	-2.84	-2.45	-1.98
	α	Mn4	2.85	2.88	2.87
	α	O8	0.95	0.46	0.01
	α	Mn1	2.94	2.94	2.93
	β	Mn2	-2.92	-2.90	-2.88
	α	Mn3	2.86	3.37	3.86
	α	Mn4	2.92	2.92	2.89
	α	O8	0.95	0.57	0.02
	β	Mn1	-2.93	-2.93	-2.92
	α	Mn2	2.93	2.94	2.95
	α	Mn3	2.89	3.43	3.88
	α	Mn4	2.92	2.92	2.88
	α	O8	0.95	0.56	0.02
12-et	α	Mn1	2.96	2.96	2.96
	α	Mn2	2.95	2.94	2.91
	α	Mn3	2.88	2.52	2.01
	α	Mn4	2.92	2.85	2.88
	β	O8	-0.96	-0.45	0.00
14-et	α	Mn1	2.96	2.96	2.94
	α	Mn2	2.95	2.96	2.96
	α	Mn3	2.90	3.44	3.89
	α	Mn4	2.92	2.92	2.88
	β	O8	0.95	0.56	0.02

Rea:

Ca	2.22385400	0.45241200	-1.43623400	C	-3.03758500	1.29715700	-1.45237200
Mn	-0.42968000	1.93480100	0.14828900	H	-2.40361400	1.22076100	-2.32532900
Mn	1.38223900	0.65995500	1.77603600	C	-4.38157000	1.05307200	-1.29740500
Mn	0.37543100	-1.62211000	0.37198500	N	-4.63950100	1.28187700	0.05140700
Mn	0.98196900	-3.19911600	-1.78655600	H	-5.48314500	0.96698800	0.53301600
O	1.31513600	2.00412800	0.51945000	C	-3.47065800	1.62126600	0.64967400
O	-0.31442200	0.31781800	1.01412500	H	-3.35082300	1.82233600	1.70423300
O	1.94446800	-0.70995100	0.79151800	C	-5.42709000	0.66775600	-2.31058200
O	0.66741700	-1.35805500	-1.34057100	H	-5.67451400	1.53008100	-2.94904900
O	0.94279200	-3.25756500	0.06351200	H	-4.98885500	-0.08180300	-2.98496800
O	2.98906100	2.72041800	-2.08041000	C	-6.75932100	0.12835000	-1.73276600
H	3.36047700	2.89298900	-1.19350100	H	-7.31906800	0.93577700	-1.24706700
H	2.19765700	3.30189400	-2.16982500	H	-7.37520200	-0.24319100	-2.56393900
O	1.95754800	-0.29697800	-3.84271200	C	-6.55732400	-0.95734700	-0.67656600
H	1.58567600	-1.24819700	-3.78113600	O	-6.64306300	-0.70039600	0.53073700
O	0.97977400	-2.79505600	-3.62247700	N	-6.23599200	-2.19195700	-1.14728500
O	1.00260400	-5.01332200	-1.89680900	H	-6.08447500	-2.28619500	-2.14466200
H	0.03360900	-2.76579100	-3.85554700	C	-5.68433700	-3.24007500	-0.28087400
H	1.09831200	-5.29743000	-0.96707600	H	-6.24295900	-3.19994100	0.65971300
O	3.76051400	-1.17763500	-2.24584000	H	-5.89526400	-4.20529900	-0.76074100
C	3.86314000	-2.41126100	-2.05411900	C	-4.18058600	-3.07294500	-0.00826000
O	2.92470600	-3.25036300	-1.82482500	H	-4.01105500	-2.13172700	0.52636600
C	5.25236000	-3.06018000	-2.08840400	H	-3.86353800	-3.87676200	0.67165200
H	5.35158900	-3.66381300	-1.17578900	C	-3.31924500	-3.10057300	-1.27491100
H	5.24424100	-3.77952100	-2.92076700	H	-3.64489200	-2.31133800	-1.97165300
C	6.40429700	-2.06582800	-2.22908300	H	-3.41120300	-4.05475900	-1.81055200
H	6.41740200	-1.35814200	-1.39139600	C	-1.82925900	-2.84798400	-1.02438100
H	6.30510900	-1.47799900	-3.14888800	O	-1.52678600	-2.18578900	0.01057900
H	7.36903800	-2.59207400	-2.25358500	O	-1.04481900	-3.31873800	-1.90242900
O	-0.60605100	3.85981800	-0.39187400	O	-1.06333600	2.73879800	1.90477600
C	-0.09755900	4.50617700	-1.37710300	C	-0.35689900	2.72116200	2.96774800
O	0.52039600	3.99837700	-2.34626800	O	0.69032200	2.04926600	3.15426900
C	-0.28520800	6.02378400	-1.30516600	C	-0.84347400	3.62975600	4.09704300
H	-1.29404300	6.22214000	-0.91706000	H	-1.93401200	3.51301600	4.16696600
H	0.40777700	6.39134200	-0.53015800	H	-0.67729600	4.66356700	3.75669700
C	-0.03862100	6.75664200	-2.62662700	C	-0.16623200	3.38642500	5.44588200
H	-0.74390600	6.38411400	-3.38376600	H	-0.54704100	4.08750900	6.20121500
H	0.96098500	6.49618900	-2.99722100	H	-0.34880800	2.36451900	5.80014700
C	-0.17592600	8.27734000	-2.49204800	H	0.91898000	3.51233500	5.36582400
H	-1.18119100	8.56103800	-2.14795000	O	4.02852400	1.33033300	0.14380000
H	0.54498500	8.67992700	-1.76577100	C	4.13261700	1.37529000	1.38780200
H	0.00220100	8.78159500	-3.45167100	O	3.19791300	1.15150200	2.25171700
N	-2.49307100	1.65474500	-0.23982700	C	5.48538600	1.69339600	2.01580400

H	5.36246500	2.29653500	2.92198600	C	-0.24448800	-3.67745700	4.65988600
H	6.12801000	2.20597700	1.29318000	H	0.25155400	-4.33112000	3.93025300
H	5.96758300	0.74932900	2.30510900	H	-1.26651000	-3.53279300	4.28394600
O	1.19448600	-0.50329200	3.35894000	C	-0.28109000	-4.35279000	6.03573300
C	0.56155300	-1.61285800	3.34502900	H	0.73342700	-4.53781200	6.41766600
O	0.01549800	-2.14049700	2.34329100	H	-0.80099400	-5.31959300	5.99201000
C	0.47567200	-2.32734600	4.69231200	H	-0.80156000	-3.72779300	6.77637400
H	1.50690900	-2.44125000	5.05948000	O	-0.09746900	1.43264000	-1.58741200
H	-0.01268300	-1.63669200	5.39722400	H	0.04955400	2.29269400	-2.06140800

TS:

Ca	1.41410600	-1.70568700	-1.46906900	H	5.90856600	2.61524600	-0.59785200
Mn	1.57256100	1.39281700	0.07508400	C	6.09233900	3.08524500	-2.71285100
Mn	1.35851900	-0.78367300	1.72202100	H	5.46732600	3.52260600	-3.50506700
Mn	-1.17319000	-1.02177800	0.40339800	H	6.30272500	2.05672700	-3.03296400
Mn	-2.51380300	-2.68147200	-1.48022200	C	7.39755500	3.87844100	-2.58335100
O	2.49211800	-0.08384300	0.46789600	H	7.20624900	4.92089500	-2.28996300
O	0.20895400	0.51479000	0.95272000	H	8.05694100	3.43907700	-1.82082800
O	0.41514800	-1.93513900	0.76105500	H	7.95151800	3.89582600	-3.53194900
O	-0.94269500	-1.47507300	-1.35242400	N	0.29479000	3.01508100	-0.38170000
O	-2.30858000	-2.42012300	0.28997600	C	-0.37787600	3.15517500	-1.57552600
O	3.69929600	-1.38976200	-2.34571900	H	-0.19003600	2.45732800	-2.38111100
H	4.08479000	-1.73247300	-1.51316600	C	-1.26143100	4.20302900	-1.47997700
H	3.90058200	-0.42286800	-2.36339400	N	-1.10165400	4.70149000	-0.18929300
O	-0.58620600	-0.71590900	-2.85629700	H	-1.77683700	5.31347500	0.27085500
H	-1.22825700	-1.35804400	-3.29648200	C	-0.17101300	3.94061800	0.43986200
O	-2.46516300	-2.52906000	-3.37505700	H	0.13459200	4.06098600	1.46927800
O	-4.01855500	-3.65330500	-1.29014300	C	-2.18929700	4.78842800	-2.51098300
H	-3.26743000	-2.01921100	-3.58974400	H	-1.61498700	5.35672500	-3.25926300
H	-4.11243700	-3.72476600	-0.31987100	H	-2.65237200	3.95826300	-3.06304900
O	0.63910100	-3.78396700	-2.30620900	C	-3.29227800	5.73109200	-1.96993100
C	-0.28751100	-4.57582600	-2.02636500	H	-2.84935100	6.66228200	-1.59812400
O	-1.46309700	-4.30090400	-1.58702600	H	-3.96289100	5.99602400	-2.79964000
C	-0.06960100	-6.08306600	-2.21373700	C	-4.07709500	5.12478900	-0.80824200
H	-0.47654900	-6.58951800	-1.32850300	O	-3.82181400	5.42405900	0.36452400
H	-0.71253900	-6.38926500	-3.05310100	N	-5.03154000	4.21681900	-1.14985900
C	1.38494300	-6.47836500	-2.46700000	H	-5.09607100	3.95613100	-2.12681400
H	2.02491000	-6.18594200	-1.62510500	C	-5.63161800	3.30489300	-0.17028700
H	1.77667200	-5.98008700	-3.36115300	H	-5.77471600	3.88164800	0.74901300
H	1.47394900	-7.56513800	-2.60596400	H	-6.62198300	3.01837600	-0.54982500
O	3.18170800	2.44291600	-0.51791200	C	-4.76416200	2.06823000	0.11393700
C	4.01074000	2.21498800	-1.47006600	H	-3.80010100	2.39010600	0.52310200
O	3.84724600	1.39252100	-2.40700000	H	-5.25468900	1.47672500	0.90082600
C	5.29488200	3.04589200	-1.40650900	C	-4.51935700	1.18473200	-1.11470400
H	5.02754500	4.05672100	-1.06828000	H	-4.09380200	1.78580300	-1.93486600

H	-5.44957200	0.74158300	-1.49315900	H	5.07126500	-4.09713700	1.09346700
C	-3.51757300	0.05156100	-0.87069700	H	3.78254800	-4.73187000	2.14363000
O	-2.61644900	0.27569400	-0.00775000	O	0.28893900	-1.19557900	3.33214900
O	-3.67461000	-0.98624600	-1.57731000	C	-0.98676600	-1.17063700	3.34380700
O	1.96312000	2.38188100	1.80319700	O	-1.73439000	-0.96228700	2.35395400
C	2.29266300	1.77571200	2.87808200	C	-1.63322300	-1.41564200	4.70534600
O	2.22676700	0.53646400	3.08429000	H	-1.28295800	-2.40173300	5.04744200
C	2.83160300	2.66844800	3.99654900	H	-1.20067800	-0.68861500	5.40946500
H	2.15846000	3.53369200	4.07805500	C	-3.16233000	-1.35075500	4.71541400
H	3.79091000	3.07257700	3.63841200	H	-3.55561600	-2.06798200	3.98327500
C	3.00434800	1.96723100	5.34385500	H	-3.48447300	-0.35993400	4.36617400
H	3.41024500	2.66219300	6.09186900	C	-3.74943200	-1.63384400	6.10310700
H	2.04619900	1.58223800	5.71330100	H	-3.46724000	-2.63515500	6.45962000
H	3.68374800	1.11238900	5.25491700	H	-4.84681800	-1.58299800	6.09021100
O	3.16330900	-2.78929100	0.01872000	H	-3.39094300	-0.90740100	6.84730100
C	3.32284900	-2.83231000	1.26074700	O	1.29050100	0.79362700	-1.63061100
O	2.69985900	-2.13471800	2.14797100	H	2.11444400	1.05646100	-2.11674000
C	4.32399300	-3.82338600	1.84514800				
H	4.80549300	-3.41133200	2.73838800				

Pro:

Ca	1.61991900	-1.69046900	-1.27583800	H	-0.37680900	-6.07272400	-3.56893900
Mn	1.50976700	1.42906200	0.04719200	C	1.70135600	-6.27045300	-2.94669700
Mn	1.38190100	-0.68669600	1.78853300	H	2.31517200	-6.14645300	-2.04528500
Mn	-1.12978400	-1.05999300	0.47495700	H	2.11836600	-5.61229000	-3.71728200
Mn	-2.34242600	-2.77156200	-1.46639700	H	1.79830700	-7.31140300	-3.28608900
O	2.50132900	0.01948700	0.51713100	O	3.06984000	2.54950300	-0.57969200
O	0.18127200	0.53574300	0.96407600	C	3.92951400	2.33302600	-1.50527800
O	0.52213900	-1.90044600	0.83353000	O	3.83899800	1.45722400	-2.40410300
O	-0.82211200	-1.39201700	-1.43979300	C	5.15529500	3.24972800	-1.46327200
O	-2.10469600	-2.57844300	0.27783500	H	4.81634100	4.25511700	-1.17714400
O	3.87922600	-1.31004000	-2.19119500	H	5.78240700	2.89893900	-0.62677300
H	4.29706000	-1.59348100	-1.35320000	C	5.97053700	3.28159700	-2.75881200
H	4.02368100	-0.33423500	-2.25636600	H	5.33174500	3.63977000	-3.57929000
O	-1.06263800	-0.42620000	-2.52100000	H	6.25298600	2.25556400	-3.02732000
H	-1.58846600	-1.07436400	-3.10832000	C	7.21884200	4.16434900	-2.64896400
O	-2.38515800	-2.47889600	-3.36739700	H	6.95499700	5.20431200	-2.40762800
O	-3.74707200	-3.88806300	-1.33522400	H	7.89264300	3.80511500	-1.85760400
H	-3.31285500	-2.23969500	-3.54222200	H	7.78635100	4.17458100	-3.58965000
H	-3.84282200	-4.00440100	-0.36977200	N	0.15464600	2.94823500	-0.50371100
O	0.91794700	-3.63412400	-2.38627600	C	-0.56737400	2.94965600	-1.67691100
C	0.00426800	-4.47736100	-2.22264900	H	-0.38418000	2.18465800	-2.41993400
O	-1.15557800	-4.29151100	-1.71325000	C	-1.49201500	3.96524300	-1.63877800
C	0.23850000	-5.92583400	-2.66767300	N	-1.30584800	4.58712300	-0.40629000
H	-0.19390200	-6.58394100	-1.90286500	H	-1.99058900	5.21005600	0.02425800

C	-0.32038000	3.92566600	0.25027200	H	1.88580200	3.76732000	3.95943200
H	0.01756000	4.15109500	1.25153700	H	3.55329200	3.41596400	3.55105100
C	-2.48709900	4.41219900	-2.67655800	C	2.83436000	2.32399600	5.29542000
H	-1.96906300	4.91999800	-3.50507200	H	3.17628300	3.07857000	6.01724900
H	-2.94402800	3.51565000	-3.11914500	H	1.90448100	1.88087600	5.67152700
C	-3.59924600	5.36860100	-2.17969200	H	3.57908900	1.52170900	5.24872000
H	-3.17357000	6.34284900	-1.91261800	O	3.35600400	-2.68181500	0.22990500
H	-4.30860100	5.53569800	-3.00267200	C	3.47344300	-2.65310800	1.47833500
C	-4.32011000	4.84750500	-0.93812900	O	2.78732900	-1.94372900	2.30517900
O	-4.02603400	5.25253100	0.19308500	C	4.50041600	-3.56343000	2.14343400
N	-5.26312700	3.89127200	-1.16101400	H	4.90715900	-3.09945300	3.04808400
H	-5.35612000	3.54669000	-2.10934600	H	5.30220000	-3.80984800	1.43979500
C	-5.77973000	3.03685400	-0.08622600	H	4.00028000	-4.49665500	2.43788900
H	-5.88137000	3.67379600	0.79806600	O	0.32522600	-1.10340100	3.40033100
H	-6.78368800	2.70268100	-0.38219600	C	-0.94904100	-1.18886400	3.39521800
C	-4.86060500	1.84432200	0.22458400	O	-1.69609600	-1.05344200	2.39432800
H	-3.87900200	2.21906000	0.53528000	C	-1.59051400	-1.47593500	4.75024700
H	-5.27324200	1.30366900	1.08879000	H	-1.18692100	-2.44215600	5.09090400
C	-4.67955200	0.87537100	-0.94870400	H	-1.20658000	-0.72888300	5.46127300
H	-4.39032500	1.42510900	-1.85953900	C	-3.12084800	-1.50088500	4.74805700
H	-5.60916200	0.34245700	-1.18856700	H	-3.46542500	-2.23705600	4.01024700
C	-3.57475000	-0.16512700	-0.73694800	H	-3.49780600	-0.52910800	4.39987500
O	-2.67016900	0.12462400	0.09577700	C	-3.70162000	-1.82330400	6.12983500
O	-3.66381600	-1.20838000	-1.45162500	H	-3.36432000	-2.80789600	6.48508700
O	1.83587100	2.51317200	1.72222100	H	-4.79999900	-1.83651200	6.10821800
C	2.16488100	1.97689800	2.83518400	H	-3.39204400	-1.08022900	6.87953400
O	2.15533800	0.74891900	3.10304600	O	1.30481300	0.72657000	-1.64740400
C	2.62437700	2.95388000	3.91858500	H	2.11701600	1.03649200	-2.12437600

Table S32 Reaction parameters for the closed-cubane W3 (hydroxyl)-Wx (hydroxyl) coupling:

Spin state	Spin topology (Mn1~Mn4-O8)	Gibbs Free energy (a.u.)		
		Rea	TS	Pro
doublet	ααββα	-3366.1963	-3366.1726	-3366.1782
	αβαβα	-3366.1976	-3366.1751	-3366.1796
	αββαα	-3366.1980	-3366.1919	-3366.2223
	βααβα	-3366.1988	-3366.1760	-3366.1804
	βαβαα	-3366.1970	-3366.1909	-3366.2212
	ββααα	-3366.1968	-3366.1909	-3366.2203
sextet	αααββ	-3366.2000	-3366.1938	-3366.2239
	ααβαβ	-3366.1994	-3366.1765	-3366.1809
	αβααβ	-3366.1967	-3366.1742	-3366.1785
	βαααβ	-3366.1984	-3366.1756	-3366.1796
octet	αααβα	-3366.2009	-3366.1780	-3366.1824

	ααβαα	-3366.1995	-3366.1934	-3366.2236
	αβααα	-3366.1973	-3366.1911	-3366.2207
	βαααα	-3366.1980	-3366.1923	-3366.2218
12-et	αααaβ	-3366.1996	-3366.1767	-3366.1811
14-et	ααααα	-3366.1998	-3366.1938	-3366.2231

Spin state	Spin topology (Mn1~Mn4-O8)	Relative Gibbs Free energy (kcal/mol)			
		$\Delta G^{\neq}$(Rea-TS)	ΔG(Rea-Pro)	ΔG(Rea)	ΔG(Pro)
doublet	ααββα	14.9	11.4	2.9	28.5
	αβαβα	14.1	11.3	2.1	27.6
	αββαα	3.8	-15.2	1.8	0.8
	βααβα	14.3	11.5	1.3	27.1
	βαβαα	3.8	-15.2	2.4	1.5
	ββααα	3.7	-14.7	2.6	2.1
sextet	αααββ	3.9	-15.0	0.6	-0.2
	ααβαβ	14.4	11.6	0.9	26.8
	αβααβ	14.1	11.4	2.6	28.3
	βαααβ	14.3	11.8	1.6	27.6
octet	αααβα	14.4	11.6	0.0	25.9
	ααβαα	3.8	-15.1	0.9	0.0
	αβααα	3.9	-14.7	2.3	1.8
	βαααα	3.6	-14.9	1.8	1.1
12-et	αααaβ	14.4	11.6	0.8	26.7
14-et	ααααα	3.8	-14.6	0.7	0.3

Spin state	Spin topology (Mn1~Mn4-O8)		Mulliken spin density		
			Rea	TS	Pro
doublet	α	Mn1	2.93	2.93	2.94
	α	Mn2	2.94	2.95	2.95
	β	Mn3	-2.83	-2.81	-2.79
	β	Mn4	-2.86	-2.25	-1.94
	α	O8	0.75	0.27	0.01
	α	Mn1	2.92	2.92	2.92
	β	Mn2	-2.94	-2.95	-2.95
	α	Mn3	2.79	2.76	2.74
	β	Mn4	-2.81	-2.22	-1.90
	α	O8	0.75	0.28	0.01
	α	Mn1	2.92	2.92	2.93
	β	Mn2	-2.93	-2.93	-2.93
	β	Mn3	-2.81	-2.80	-2.77
	α	Mn4	2.83	3.29	3.84
	α	O8	0.93	0.53	0.00
	β	Mn1	-2.92	-2.93	-2.93

	α	Mn2	2.93	2.93	2.93
	α	Mn3	2.82	2.80	2.77
	β	Mn4	-2.80	-2.21	-1.90
	α	O8	0.75	0.27	0.01
	β	Mn1	-2.92	-2.92	-2.92
	α	Mn2	2.94	2.94	2.95
	β	Mn3	-2.79	-2.78	-2.75
	α	Mn4	2.83	3.29	3.85
	α	O8	0.93	0.53	0.00
	β	Mn1	-2.93	-2.93	-2.94
	β	Mn2	-2.94	-2.95	-2.95
	α	Mn3	2.83	2.82	2.80
	α	Mn4	2.88	3.35	3.89
	α	O8	0.92	0.53	0.00
	α	Mn1	2.93	2.92	2.93
	α	Mn2	2.93	2.93	2.93
	α	Mn3	2.82	2.81	2.78
	β	Mn4	-2.83	-3.29	-3.85
	β	O8	-0.93	-0.53	0.00
	α	Mn1	2.93	2.93	2.94
	α	Mn2	2.94	2.95	2.95
	β	Mn3	-2.77	-2.75	-2.72
	α	Mn4	2.81	2.21	1.90
sextet	β	O8	-0.75	-0.27	-0.01
	α	Mn1	2.92	2.92	2.92
	β	Mn2	-2.94	-2.94	-2.95
	α	Mn3	2.84	2.82	2.80
	α	Mn4	2.86	2.25	1.95
	β	O8	-0.76	-0.27	-0.01
	β	Mn1	-2.92	-2.92	-2.93
	α	Mn2	2.93	2.93	2.93
	α	Mn3	2.87	2.86	2.84
	α	Mn4	2.86	2.25	1.94
	β	O8	-0.75	-0.27	-0.01
	α	Mn1	2.93	2.93	2.93
	α	Mn2	2.93	2.93	2.93
	α	Mn3	2.82	2.80	2.78
	β	Mn4	-2.80	-2.21	-1.90
	α	O8	0.75	0.27	0.01
octet	α	Mn1	2.93	2.93	2.94
	α	Mn2	2.95	2.95	2.95
	β	Mn3	-2.78	-2.76	-2.73
	α	Mn4	2.83	3.29	3.84
	α	O8	0.93	0.53	0.00

	α	Mn1	2.93	2.93	2.93
	β	Mn2	-2.94	-2.94	-2.94
	α	Mn3	2.84	2.83	2.82
	α	Mn4	2.88	3.35	3.89
	α	O8	0.92	0.53	0.00
	β	Mn1	-2.92	-2.92	-2.93
	α	Mn2	2.93	2.93	2.93
	α	Mn3	2.87	2.86	2.85
	α	Mn4	2.88	3.35	3.89
	α	O8	0.92	0.53	0.00
12-et	α	Mn1	2.93	2.93	2.93
	α	Mn2	2.93	2.93	2.93
	α	Mn3	2.87	2.86	2.85
	α	Mn4	2.86	2.24	1.94
	α	O8	-0.75	-0.27	-0.01
14-et	α	Mn1	2.93	2.93	2.93
	α	Mn2	2.93	2.93	2.93
	α	Mn3	2.87	2.88	2.86
	α	Mn4	2.88	3.35	3.89
	α	O8	0.92	0.53	0.00

Rea:

Ca	-2.72623800	0.06289200	-1.22659000	O	-2.08534600	4.26684800	-0.72404400
Mn	0.14828500	-1.61322900	-0.74088600	C	-4.46362200	4.44140900	-0.74228900
Mn	-1.47154400	-1.69613400	1.42279100	H	-4.82027900	4.51366900	-1.78159100
Mn	-0.21950200	0.69877900	0.92264500	H	-5.21443200	3.84290900	-0.21053300
Mn	-0.24613900	3.68795500	-0.45425100	C	-4.31512800	5.83580900	-0.13243600
O	-1.56644600	-2.01278400	-0.36217000	H	-3.57635500	6.43011500	-0.68115200
O	0.31076600	-1.18265000	1.05757400	H	-3.99561400	5.78018500	0.91778200
O	-1.89679700	0.03057100	1.13791500	H	-5.27449700	6.36802700	-0.15581500
O	-0.20165900	0.18645400	-0.89549700	O	-0.02456400	-2.09687200	-2.59742000
O	-0.76370100	2.33926000	0.67446100	C	-1.08047000	-2.06896200	-3.35268200
O	-4.73677300	-0.66537900	-2.54321900	O	-2.12626300	-1.43908700	-3.10080800
H	-5.09374800	-1.24377700	-1.84059500	C	-0.96014300	-2.88703300	-4.63243700
H	-4.22821700	-1.24302200	-3.14636500	H	-0.95116600	-3.94957600	-4.34182900
O	-2.29888500	1.75186300	-3.06744400	H	-1.86217300	-2.71301000	-5.23142900
H	-1.47841000	2.26948300	-2.80494200	C	0.30774900	-2.57763200	-5.44690200
H	0.04242100	1.71440600	-1.59397000	H	1.18511200	-2.74247500	-4.80831400
O	0.24382100	5.22852900	-1.25578000	H	0.31060400	-1.51100200	-5.71785400
H	1.21893100	5.25607500	-1.25547300	C	0.40825200	-3.43040900	-6.71592800
O	-0.53266900	4.79395100	1.41806900	H	0.43808300	-4.50203300	-6.47306900
H	-1.31336500	5.31207500	1.14032400	H	1.31731200	-3.19119100	-7.28315000
H	-0.88724800	3.99032400	1.85964400	H	-0.45180300	-3.26421300	-7.37937100
O	-3.29849600	2.36770800	-0.95695600	N	2.17090900	-1.36074500	-1.11607400
C	-3.18884200	3.60156100	-0.80352900	C	2.77355600	-0.38530200	-1.88205500

H	2.18361800	0.34583000	-2.41807400	O	-0.75845300	-3.58241700	1.63112800
C	4.13945900	-0.52694300	-1.80527000	C	0.44381000	-5.55732500	1.01378100
N	4.34429500	-1.62871900	-0.98187300	H	1.52243700	-5.64720100	0.82646400
H	5.23691600	-1.83445100	-0.52590300	H	-0.04419500	-6.11271700	0.19760000
C	3.13910100	-2.08463300	-0.57445000	H	-5.67816700	-2.44226800	2.72476100
H	2.98933500	-2.91538800	0.09873800	C	0.05664400	-6.14189300	2.37251100
C	5.25080400	0.26003900	-2.45009700	H	0.34544900	-7.19921800	2.42693400
H	5.37704000	-0.04963300	-3.49852500	H	0.55503400	-5.60773600	3.19068200
H	4.93878700	1.31264600	-2.48700100	H	-1.02314900	-6.06647400	2.53973600
C	6.64282300	0.15178300	-1.76713400	O	-4.37236300	-1.27906600	0.09989500
H	7.09620300	-0.82294500	-1.97929500	C	-4.31629900	-1.99955900	1.11683200
H	7.30117900	0.91806900	-2.19860600	O	-3.24519000	-2.26077600	1.80079000
C	6.56158200	0.27550500	-0.24772000	C	-5.56470600	-2.67272500	1.65891900
O	6.52489600	-0.72930200	0.47385400	H	-5.45836400	-3.76184000	1.57217800
N	6.45019400	1.53545600	0.25228700	H	-6.44910900	-2.34283900	1.10712500
H	6.44571700	2.30696600	-0.40390600	O	-1.09437800	-1.23863600	3.32628400
C	5.95856700	1.78383700	1.61194000	C	-0.51951500	-0.15848600	3.68265600
H	6.43007200	1.04404800	2.26575600	O	-0.08264000	0.76226800	2.91644200
H	6.30780600	2.77867700	1.91656300	C	-0.34642500	0.05292700	5.17907000
C	4.42517700	1.67104900	1.70924100	H	0.24421800	0.96346000	5.33404900
H	4.12376100	0.66051500	1.41132700	H	-1.34981800	0.23194900	5.59654700
H	4.12811400	1.78784300	2.76089800	C	0.29256500	-1.15318400	5.88849800
C	3.70112200	2.70456200	0.84316800	H	1.28538800	-1.34251500	5.45301600
H	4.13904500	2.73320200	-0.16712300	H	-0.31359100	-2.04452300	5.68330400
H	3.80996900	3.72068700	1.24552100	C	0.42390500	-0.93546800	7.39931100
C	2.20910600	2.46238200	0.61229900	H	1.04539200	-0.05789700	7.62622400
O	1.72837000	1.33429700	0.89455100	H	0.88503200	-1.80536300	7.88472600
O	1.61428800	3.46879200	0.09124200	H	-0.55887200	-0.77553100	7.86457500
O	0.61129700	-3.51465500	-0.18961400	O	-0.03064300	2.65704700	-1.91181800
C	0.06488100	-4.09365400	0.81369100				

TS:

Ca	-2.66674300	0.00101500	-1.22221400	O	-1.95784600	1.61182300	-3.03275100
Mn	0.30154800	-1.56836200	-0.74364400	H	-1.33958300	1.48940900	-3.77768400
Mn	-1.35057600	-1.80437100	1.37689800	H	-0.29127600	1.60833000	-1.69736700
Mn	-0.24136400	0.68588000	0.96224600	O	-0.28565800	5.14198700	-1.39017700
Mn	-0.65594800	3.63061000	-0.47114800	H	0.68552700	5.22226700	-1.43279200
O	-1.39417400	-2.06683900	-0.42394200	O	-0.80563600	4.77231500	1.47575000
O	0.40824100	-1.18066300	1.06113200	H	-1.65428200	5.20330500	1.25492700
O	-1.87299600	-0.10720400	1.13803900	H	-1.05098100	3.93131500	1.92089500
O	-0.14248700	0.21394000	-0.86267200	O	-3.61801800	2.11224600	-0.70942000
O	-0.92781700	2.26816800	0.74060600	C	-3.59129100	3.35061300	-0.64503800
O	-4.55253000	-0.84575800	-2.65749200	O	-2.53120000	4.09680400	-0.55841000
H	-4.90672900	-1.43303200	-1.95966900	C	-4.90808900	4.12619000	-0.70698100
H	-3.97228100	-1.40201800	-3.21492300	H	-5.17517100	4.17188500	-1.77461700

H	-5.67170300	3.49926900	-0.22994900	H	4.11946800	1.21411200	1.54506600
C	-4.88154700	5.53606300	-0.11326700	H	3.93786000	2.60857000	2.60040500
H	-4.13047700	6.15807300	-0.61223800	C	3.46045100	3.00447400	0.52364000
H	-4.64478500	5.51227300	0.95954300	H	3.89602100	2.81598300	-0.47031900
H	-5.86123900	6.01837900	-0.22481700	H	3.47055600	4.09455700	0.65736600
O	0.21801100	-1.98787700	-2.62845000	C	1.99795300	2.57631300	0.40390000
C	-0.82928700	-2.01335500	-3.39375700	O	1.63949900	1.49486000	0.93762600
O	-1.90509400	-1.42768700	-3.15776800	O	1.28997500	3.38311700	-0.29677600
C	-0.67082900	-2.84481200	-4.66236800	O	0.84425500	-3.46327900	-0.25342800
H	-0.76358400	-3.90136000	-4.36210700	C	0.31120900	-4.10456000	0.71806100
H	-1.51810300	-2.62015200	-5.32210900	O	-0.54208400	-3.66046100	1.54401500
C	0.66719900	-2.64612500	-5.39151600	C	0.75094100	-5.55757200	0.86521300
H	1.48473300	-2.85884900	-4.69120200	H	1.82957600	-5.59768300	0.66285800
H	0.76875100	-1.58845000	-5.68053900	H	0.27431400	-6.10513400	0.03692700
C	0.79111700	-3.53082300	-6.63656600	H	-5.56254500	-2.78792100	2.53679100
H	0.72704600	-4.59612500	-6.37378400	C	0.40189200	-6.20112200	2.20770500
H	1.75133000	-3.36980100	-7.14386400	H	0.73081700	-7.24798500	2.22420900
H	-0.00810200	-3.31935400	-7.36053300	H	0.88951000	-5.67600700	3.03831700
N	2.33549900	-1.22585300	-1.00017700	H	-0.67787200	-6.17178500	2.38871000
C	2.98274500	-0.41283800	-1.90413100	O	-4.23777200	-1.54767900	-0.02233900
H	2.43670600	0.09782100	-2.68557500	C	-4.16253200	-2.28000000	0.98448800
C	4.33025500	-0.39947200	-1.62345800	O	-3.09564600	-2.48357000	1.69496100
N	4.47852300	-1.24576600	-0.53103400	C	-5.37970600	-3.03770300	1.48472800
H	5.32201600	-1.28906700	0.04857100	H	-5.18579100	-4.11681200	1.43676700
C	3.25743200	-1.70210400	-0.17700300	H	-6.25946200	-2.79051700	0.88445900
H	3.06376500	-2.34426100	0.66919900	O	-1.02637800	-1.37388700	3.29721600
C	5.47004800	0.32477500	-2.29441300	C	-0.52431600	-0.26976500	3.68865100
H	5.70661000	-0.15168100	-3.25759500	O	-0.12807200	0.69403800	2.95311200
H	5.12725200	1.33911100	-2.54233000	C	-0.39699200	-0.07890100	5.19262900
C	6.79381200	0.40918100	-1.48670700	H	0.17993400	0.83516600	5.37615800
H	7.29302400	-0.56599900	-1.47140700	H	-1.41472400	0.09067600	5.57903200
H	7.46573200	1.11160800	-1.99859400	C	0.22663900	-1.28716800	5.91032400
C	6.58154300	0.80971000	-0.02787900	H	1.23556300	-1.46382700	5.50768800
O	6.54628100	-0.04296300	0.86964400	H	-0.36392400	-2.18134500	5.67466800
N	6.35691300	2.12652500	0.21774700	C	0.30404000	-1.08498900	7.42706500
H	6.35927500	2.76801000	-0.56596300	H	0.90957000	-0.20475100	7.68474300
C	5.78889000	2.58470400	1.49148900	H	0.75570200	-1.95622800	7.91896600
H	6.32667700	2.06996900	2.29384900	H	-0.69554400	-0.93832000	7.85981700
H	5.99791900	3.65843400	1.57721800	O	-0.68682000	2.46868400	-2.04223100
C	4.28033200	2.29602900	1.60395700				

Pro:

Ca	-2.66133700	-0.05485400	-1.17086500	Mn	-0.27117600	0.70026500	0.94266100
Mn	0.34716100	-1.58828800	-0.71164100	Mn	-0.76899500	3.64228200	-0.53571000
Mn	-1.32122100	-1.82466700	1.39062900	O	-1.34530900	-2.11080400	-0.41507100

O	0.42466200	-1.17043000	1.07890700	C	3.30258800	-1.65162000	-0.13081700
O	-1.88526000	-0.15100200	1.13295900	H	3.12023000	-2.30384700	0.71018700
O	-0.13800700	0.17932300	-0.87243700	C	5.47453500	0.44955300	-2.21738600
O	-1.03817000	2.21479100	0.62200500	H	5.73480700	-0.01747700	-3.17906500
O	-4.42503600	-0.94824600	-2.71231200	H	5.10356700	1.45357000	-2.46645700
H	-4.79897300	-1.56572700	-2.05211700	C	6.78677000	0.57150600	-1.39571100
H	-3.81088600	-1.46881000	-3.26723600	H	7.31438300	-0.38856900	-1.37654500
O	-1.65593600	1.59941900	-2.97438200	H	7.44282400	1.29432000	-1.89967200
H	-1.36755400	1.05347100	-3.73345900	C	6.54563000	0.96353200	0.06098900
H	-0.09312200	1.35276100	-1.88620400	O	6.51858200	0.10734400	0.95576000
O	-0.43144300	5.09959200	-1.54787500	N	6.28636700	2.27381200	0.30533000
H	0.53608800	5.19727200	-1.61716300	H	6.28131700	2.91479900	-0.47882900
O	-1.01947500	4.76534900	1.54849100	C	5.67931200	2.71573800	1.56721600
H	-1.88706300	5.12140700	1.27638600	H	6.21054500	2.21081300	2.38005300
H	-1.22105900	3.87746100	1.91243300	H	5.86255100	3.79358800	1.65991500
O	-3.71330200	2.03044800	-0.89794200	C	4.17536200	2.39320100	1.64269500
C	-3.72818100	3.26703000	-0.73275800	H	4.04105600	1.30784900	1.57877300
O	-2.69411100	4.03340900	-0.64344000	H	3.80194700	2.69503100	2.63123100
C	-5.08120200	3.97722700	-0.67094500	C	3.36478300	3.08461400	0.54451700
H	-5.43601400	4.04206900	-1.71169300	H	3.83192800	2.91734300	-0.43877200
H	-5.77825300	3.30132400	-0.15921300	H	3.34116400	4.17396600	0.68494700
C	-5.07065500	5.36707200	-0.03222700	C	1.91609500	2.62463400	0.38031000
H	-4.38042900	6.03522100	-0.55870000	O	1.56322300	1.55080700	0.94750900
H	-4.75743000	5.31893800	1.01994300	O	1.21206600	3.37643800	-0.36980800
H	-6.07389100	5.81194300	-0.05859600	O	0.92224100	-3.46033600	-0.20352100
O	0.29026300	-2.03217100	-2.60889500	C	0.39417500	-4.10212600	0.77173700
C	-0.70752800	-1.93813800	-3.42064400	O	-0.47471200	-3.66592200	1.58410000
O	-1.74027400	-1.25374700	-3.22115500	C	0.86538800	-5.54281500	0.93891400
C	-0.57687300	-2.74908300	-4.70613500	H	1.94995600	-5.55668800	0.76625800
H	-0.86420300	-3.78317400	-4.45310000	H	0.42628600	-6.10639300	0.10077300
H	-1.32372200	-2.37682800	-5.41886000	H	-5.53304800	-2.90788100	2.49671300
C	0.82882800	-2.75484900	-5.32507100	C	0.49676500	-6.18781700	2.27534100
H	1.54376300	-3.11108500	-4.57303300	H	0.85225300	-7.22558300	2.30705300
H	1.12142900	-1.72184300	-5.56942200	H	0.94759800	-5.64548900	3.11551200
C	0.90773400	-3.62148300	-6.58641800	H	-0.58794700	-6.18604100	2.42704600
H	0.65371300	-4.66772400	-6.36538300	O	-4.20274000	-1.66014100	-0.05049800
H	1.91864600	-3.60746300	-7.01403500	C	-4.11826700	-2.38190900	0.96481400
H	0.21301800	-3.26825900	-7.36120100	O	-3.05681300	-2.54564200	1.69198700
N	2.37400700	-1.19692000	-0.95911600	C	-5.31943100	-3.17165400	1.45383000
C	3.00613900	-0.35955700	-1.85225000	H	-5.08820800	-4.24416200	1.43195700
H	2.45416700	0.14460600	-2.63389600	H	-6.19424800	-2.96582400	0.83118200
C	4.35015200	-0.31018800	-1.55996900	O	-1.02043600	-1.35511400	3.30105500
N	4.51306300	-1.15874800	-0.47162800	C	-0.56638500	-0.22435600	3.67844500
H	5.35113800	-1.17604600	0.11780800	O	-0.19627200	0.74186200	2.93288900

C	-0.46425800	-0.00647300	5.18040700	C	0.29579300	-0.93584300	7.42886100
H	0.04678400	0.94727500	5.35637800	H	0.83752800	-0.01268000	7.67797600
H	-1.49365500	0.09389500	5.55943800	H	0.80488100	-1.76781200	7.93253000
C	0.23928500	-1.16045100	5.91438000	H	-0.71344400	-0.85410400	7.85624400
H	1.25985700	-1.27052300	5.51741100	O	-0.38427700	2.12641500	-2.48443400
H	-0.28682600	-2.09622700	5.68735400				

Table S33 Reaction parameters for the closed-cubane W3 (hydroxyl)-Wx (oxo) nucleophilic attack:

Spin state	Spin topology (Mn1~Mn4-O8)	Gibbs Free energy (a.u.)		
		Rea	TS	Pro
doublet	ααββα	-3365.7204	-3365.7041	-3365.7083
	αβαβα	-3365.7211	-3365.7027	-3365.7072
	αββαα	-3365.7183	-3365.7176	-3365.7580
	βααβα	-3365.7182	-3365.7061	-3365.7076
	βαβαα	-3365.7187	-3365.7179	-3365.7575
	ββααα	-3365.7156	-3365.7140	-3365.7480
sextet	αααββ	-3365.7202	-3365.7192	-3365.7492
	ααβαβ	-3365.7231	-3365.7120	-3365.7127
	αβααβ	-3365.7212	-3365.7064	-3365.7069
	βαααβ	-3365.7233	-3365.7061	-3365.7089
octet	αααβα	-3365.7238	-3365.7059	-3365.7071
	ααβαα	-3365.7211	-3365.7198	-3365.7612
	αβααα	-3365.7164	-3365.7149	-3365.7594
	βαααα	-3365.7185	-3365.7168	-3365.7594
12-et	ααααβ	-3365.7225	-3365.7080	-3365.7101
14-et	ααααα	-3365.7206	-3365.7190	-3365.7626

Spin state	Spin topology (Mn1~Mn4-O8)	Relative Gibbs Free energy (kcal/mol)			
		$\Delta G^{\neq}$(Rea-TS)	ΔG(Rea-Pro)	ΔG(Rea)	ΔG(Pro)
doublet	ααββα	10.2	7.6	2.1	34.1
	αβαβα	11.5	8.7	1.7	34.8
	αββαα	0.4	-24.9	3.5	2.9
	βααβα	7.6	6.7	3.5	34.5
	βαβαα	0.5	-24.3	3.2	3.2
	ββααα	1.0	-20.3	5.1	9.2
sextet	αααββ	0.6	-18.2	2.3	8.4
	ααβαβ	7.0	6.5	0.4	31.3
	αβααβ	9.3	9.0	1.6	35.0
	βαααβ	10.8	9.0	0.3	33.7
octet	αααβα	11.2	10.5	0.0	34.8
	ααβαα	0.8	-25.2	1.7	0.9

	αβααα	0.9	-27.0	4.6	2.0
	βαααα	1.1	-25.7	3.3	2.0
12-et	αααaβ	9.1	7.8	0.8	32.9
14-et	ααααα	1.0	-26.4	2.0	0.0

Spin state	Spin topology (Mn1~Mn4-O8)		Mulliken spin density		
			Rea	TS	Pro
doublet	α	Mn1	2.91	2.91	2.91
	α	Mn2	2.94	2.94	2.95
	β	Mn3	-2.82	-2.81	-2.81
	β	Mn4	-2.69	-2.36	-1.97
	α	O8	0.56	0.36	0.01
	α	Mn1	2.93	0.93	2.93
	β	Mn2	-2.94	-2.95	-2.95
	α	Mn3	2.79	2.79	2.77
	β	Mn4	-2.65	-2.31	-1.94
	α	O8	0.57	0.35	0.01
	α	Mn1	2.91	2.91	2.99
	β	Mn2	-2.92	-2.92	-2.93
	β	Mn3	-2.82	-2.81	-2.77
	α	Mn4	2.74	3.07	3.90
	α	O8	0.79	0.62	0.00
	β	Mn1	-2.93	-2.93	2.93
	α	Mn2	2.94	2.95	-2.95
	α	Mn3	2.79	2.78	2.77
	β	Mn4	-2.65	-2.29	-1.92
	α	O8	0.57	0.34	0.01
	β	Mn1	-2.93	-2.92	-2.89
	α	Mn2	2.94	2.94	2.95
	β	Mn3	-2.80	-2.79	-2.76
	α	Mn4	2.74	3.07	3.91
	α	O8	0.79	0.61	0.01
	β	Mn1	-2.91	-2.91	-2.94
	β	Mn2	-2.94	-2.94	-2.94
	α	Mn3	2.84	2.83	2.81
	α	Mn4	2.81	3.12	3.92
	α	O8	0.77	0.60	0.01
sextet	α	Mn1	2.93	2.92	2.93
	α	Mn2	2.92	2.92	2.91
	α	Mn3	2.83	2.83	2.83
	β	Mn4	-2.74	-3.07	-3.88
	β	O8	-0.79	-0.61	-0.01
	α	Mn1	2.91	2.92	2.92
	α	Mn2	2.94	2.95	2.95

	β	Mn3	-2.74	-2.72	-2.70
	α	Mn4	2.65	2.28	1.91
	β	O8	-0.56	-0.34	-0.02
	α	Mn1	2.93	2.93	2.92
	β	Mn2	-2.94	-2.94	-2.94
	α	Mn3	2.84	2.84	2.85
	α	Mn4	2.69	2.36	1.97
	β	O8	-0.57	-0.36	-0.01
	β	Mn1	-2.90	-2.90	-2.91
	α	Mn2	2.92	2.92	2.93
	α	Mn3	2.87	2.86	2.87
	α	Mn4	2.69	2.35	1.97
	β	O8	-0.56	-0.36	-0.01
	α	Mn1	2.93	2.93	2.93
	α	Mn2	2.91	2.92	2.92
	α	Mn3	2.83	2.83	2.79
	β	Mn4	-2.67	-2.30	-1.94
	α	O8	0.55	0.34	0.01
	α	Mn1	2.92	2.92	2.99
octet	α	Mn2	2.95	2.95	2.95
	β	Mn3	-2.77	-2.76	-2.73
	α	Mn4	2.74	3.07	3.90
	α	O8	0.78	0.61	0.00
	α	Mn1	2.93	2.92	2.99
	β	Mn2	-2.93	-2.93	-2.94
	α	Mn3	2.88	2.87	2.80
	α	Mn4	2.82	3.11	3.92
	α	O8	0.76	0.61	0.01
	β	Mn1	-2.90	-2.90	-2.90
	α	Mn2	2.92	2.92	2.93
	α	Mn3	2.89	2.88	2.81
	α	Mn4	2.82	3.11	3.95
	α	O8	0.76	0.61	0.01
	α	Mn1	2.93	2.92	2.92
12-et	α	Mn2	2.92	2.92	2.93
	α	Mn3	2.89	2.89	2.89
	α	Mn4	2.59	2.36	1.97
	β	O8	-0.57	-0.36	-0.01
	α	Mn1	2.93	2.93	2.99
14-et	α	Mn2	2.92	2.92	2.93
	α	Mn3	2.91	2.91	2.83
	α	Mn4	2.82	3.11	3.93
	α	O8	0.76	0.61	0.01

Rea:

Ca	2.45113800	-0.00512400	-1.31504800	C	-3.19794400	1.29603800	-1.62832300
Mn	-0.37241200	1.71062600	-0.26902100	H	-2.72697600	1.26851100	-2.60171000
Mn	1.29383900	1.31623300	1.79552100	C	-4.51478500	1.09979300	-1.27872100
Mn	0.05434300	-0.93784900	0.75312600	N	-4.54652600	1.25683900	0.10369700
Mn	0.69205000	-3.15204500	-1.49539700	H	-5.34220400	1.02451100	0.69976200
O	1.34436200	2.03279400	0.12443800	C	-3.28397600	1.49947900	0.52982200
O	-0.49969900	0.90593500	1.38670800	H	-2.98734500	1.59608600	1.56449900
O	1.71813200	-0.27747000	1.12662500	C	-5.71435800	0.76480500	-2.12799600
O	-0.04994000	0.03848000	-0.83022600	H	-5.97780900	1.61894200	-2.77040100
O	0.74057700	-2.44191800	0.21771600	H	-5.42971900	-0.04329000	-2.81802400
O	4.40843300	1.37459300	-2.36571300	C	-6.99608200	0.35562800	-1.35965200
H	4.61830300	1.71419000	-1.47044000	H	-7.43545700	1.22542800	-0.85874300
H	3.73233800	1.97597500	-2.73676700	H	-7.73382500	-0.01183100	-2.08709900
O	2.81544100	-1.33343500	-3.40737300	C	-6.75344800	-0.68642800	-0.26546600
H	3.23689900	-2.13397500	-3.03943000	O	-6.76321400	-0.36776400	0.93074500
O	0.53063800	-4.27761300	-2.96176400	N	-6.48110500	-1.95051900	-0.68215200
H	0.71488900	-3.72216500	-3.73913900	H	-6.37550500	-2.10461300	-1.67808100
O	0.30218600	-5.35973700	-0.64333800	C	-5.90324800	-2.95388000	0.22311400
H	0.23980800	-5.52697400	-1.61080600	H	-6.46716600	-2.90218600	1.16020100
H	1.26881100	-5.34370000	-0.48866500	H	-6.08429400	-3.93811100	-0.22865300
O	3.72364000	-2.01831300	-0.67016600	C	-4.40505700	-2.73585200	0.49529900
C	3.49027100	-3.23331200	-0.59225100	H	-4.26540100	-1.77495800	1.00197700
O	2.48897000	-3.86001500	-1.13603300	H	-4.06841000	-3.51042800	1.19950300
C	4.43599100	-4.15294200	0.18298100	C	-3.54653600	-2.77802700	-0.77112400
H	3.89333400	-4.45305100	1.09329600	H	-3.91770500	-2.04267500	-1.50267000
H	4.57629600	-5.07294500	-0.40157900	H	-3.59076100	-3.76051500	-1.25835900
C	5.77200400	-3.50458500	0.54407000	C	-2.06599400	-2.43150600	-0.56515700
H	5.61126200	-2.59177800	1.12775700	O	-1.79258400	-1.66055500	0.40593200
H	6.32956600	-3.22103600	-0.35759100	O	-1.29592700	-2.93367000	-1.43389300
H	6.39420200	-4.19455600	1.13093400	O	-0.79927800	3.50594500	0.71551200
O	-0.34046500	2.56618000	-2.02449100	C	-0.22392000	3.82361100	1.80320100
C	0.66299800	2.60435600	-2.83857400	O	0.60527400	3.12773400	2.47080200
O	1.72145100	1.95551900	-2.72890500	C	-0.53796400	5.20452700	2.38614900
C	0.45258200	3.53981200	-4.03201600	H	0.38418400	5.79800900	2.28790800
H	-0.43013700	3.17005900	-4.57762700	H	-0.69256200	5.07518500	3.46604900
H	0.16141900	4.52440100	-3.63587300	H	5.25401500	3.36812200	2.29383900
C	1.65277900	3.65563300	-4.97405300	C	-1.71539200	5.92988900	1.73424800
H	1.94326300	2.65152800	-5.30978700	H	-1.86071300	6.91948900	2.18928500
H	2.51460800	4.04814200	-4.41528900	H	-1.54827300	6.06025700	0.65926800
C	1.36807500	4.55547500	-6.18202800	H	-2.64582300	5.35993600	1.85215200
H	0.53164600	4.16624600	-6.78060400	O	4.11819200	1.29605000	0.29849300
H	2.24346500	4.62697000	-6.84172500	C	4.11098900	1.74077800	1.46128400
H	1.10164200	5.57574400	-5.86918100	O	3.09086400	1.79349900	2.25612900
N	-2.45518100	1.54274600	-0.49892600	C	5.38842300	2.30019400	2.07718100

H	6.23430300	2.16335500	1.39712300	C	-0.07960500	-0.23559300	6.15395300
H	5.58992800	1.79767000	3.03112000	H	-1.04727500	0.23129900	5.91462200
O	0.95233400	0.42487100	3.57480800	H	0.66707900	0.56677000	6.10803800
C	0.37120500	-0.70641800	3.66990300	C	-0.13226100	-0.83542300	7.56335000
O	-0.10349600	-1.41934600	2.73305700	H	-0.89106700	-1.62812500	7.63467900
C	0.25376300	-1.28086700	5.08130100	H	-0.37657000	-0.07137900	8.31424800
H	-0.49105300	-2.08599700	5.06053300	H	0.83441600	-1.27951800	7.84197100
H	1.22494400	-1.74871000	5.31252100	O	1.01108500	-1.77682900	-2.38520300

TS:

Ca	-2.42896100	0.10867500	-1.25220000	H	-0.06742200	-4.06204900	-4.12446900
Mn	0.42098900	-1.67362200	-0.42967900	C	-1.56463400	-3.05065300	-5.35032500
Mn	-1.25846200	-1.55012400	1.65587500	H	-1.86490800	-2.01591700	-5.56152800
Mn	-0.08802400	0.84771700	0.85382500	H	-2.42393700	-3.51835400	-4.84837100
Mn	-0.77066400	3.27709000	-1.18610200	C	-1.26593000	-3.79142000	-6.65883800
O	-1.28500900	-2.08168700	-0.08504500	H	-0.43165000	-3.32255700	-7.20062200
O	0.52315300	-1.05064700	1.30249300	H	-2.13808500	-3.79017200	-7.32668300
O	-1.72854400	0.08935200	1.16260000	H	-0.98943900	-4.83962100	-6.47293200
O	0.05643700	0.03997500	-0.81389600	N	2.50309200	-1.43582000	-0.62121600
O	-0.86233600	2.33741500	0.42102100	C	3.26304800	-1.09543200	-1.71418900
O	-4.33859000	-1.08196600	-2.53790800	H	2.81131100	-1.00898600	-2.69327000
H	-4.58019200	-1.54248300	-1.70620500	C	4.56854900	-0.89899500	-1.32372600
H	-3.66287400	-1.64139400	-2.97138500	N	4.57588300	-1.15393600	0.04436200
O	-2.51235600	1.80151600	-3.12047300	H	5.35494800	-0.95361200	0.67279300
H	-2.90579800	2.63086200	-2.78579000	C	3.31047900	-1.45058200	0.42530700
O	-0.63171900	4.59214400	-2.50286800	H	2.99397200	-1.62590700	1.44372700
H	-0.35296500	4.13605500	-3.31500200	C	5.77696300	-0.47641900	-2.11964600
O	-0.42460800	5.25612000	-0.06274600	H	6.07480200	-1.27517900	-2.81604900
H	-0.27926800	5.55565600	-0.99290600	H	5.48713600	0.37300200	-2.75589400
H	-1.39911800	5.29006100	0.03214500	C	7.03154800	-0.09490800	-1.29447800
O	-3.80832200	1.96970900	-0.45646300	H	7.48462500	-0.98922400	-0.85248000
C	-3.61966600	3.19091100	-0.33095800	H	7.77335900	0.34656000	-1.97516700
O	-2.63762600	3.87228200	-0.83662400	C	6.74113100	0.85237700	-0.12768400
C	-4.61146600	4.03952100	0.46910400	O	6.75044900	0.44376200	1.04079600
H	-4.09188500	4.33032800	1.39593900	N	6.42942600	2.13446500	-0.45061000
H	-4.78527500	4.97349000	-0.08358900	H	6.32635000	2.36025800	-1.43302300
C	-5.92254000	3.32432100	0.79357800	C	5.81640300	3.04985000	0.52231400
H	-5.72889600	2.39797100	1.34518100	H	6.37691900	2.94570500	1.45712400
H	-6.45984400	3.05079200	-0.12337500	H	5.97061600	4.06965300	0.14559300
H	-6.57866900	3.96551500	1.39888500	C	4.32354200	2.77115400	0.76732900
O	0.40357300	-2.32180200	-2.27584900	H	4.20767600	1.77718300	1.21243200
C	-0.59425700	-2.26297700	-3.09454300	H	3.96042000	3.49076200	1.51537100
O	-1.65984300	-1.64106600	-2.91284400	C	3.47258500	2.86773800	-0.50150700
C	-0.36920700	-3.03907000	-4.39538400	H	3.85612300	2.17064100	-1.26354200
H	0.51044800	-2.59353100	-4.88664900	H	3.51417300	3.87366600	-0.93915300

C	1.99292500	2.50323000	-0.32141300	C	-5.32971700	-2.67653400	1.75275600
O	1.72429300	1.66699400	0.59933000	H	-6.16763900	-2.50042600	1.07183200
O	1.21762800	3.05604700	-1.14973100	H	-5.56696400	-2.27942700	2.74736700
O	0.88871700	-3.55687800	0.34977700	O	-0.95039100	-0.83619400	3.51828200
C	0.32197800	-4.00551300	1.39516500	C	-0.41766400	0.30347100	3.73217200
O	-0.52391100	-3.40781600	2.13304700	O	0.03875000	1.12431800	2.87860200
C	0.67272400	-5.43293000	1.82564400	C	-0.34284600	0.74176600	5.19475900
H	-0.23898300	-6.03265100	1.68013200	H	0.39393700	1.55123400	5.26946900
H	0.84291400	-5.41311400	2.91087700	H	-1.32393600	1.18095300	5.44046100
H	-5.16085800	-3.75554900	1.86466100	C	-0.02919600	-0.39493300	6.17587700
C	1.85367700	-6.06098500	1.08525100	H	0.94860200	-0.83192100	5.92183600
H	2.02717700	-7.08866200	1.43363100	H	-0.76673900	-1.19490600	6.03642000
H	1.67115100	-6.08409600	0.00507400	C	-0.02006800	0.07379300	7.63512600
H	2.77372600	-5.48517300	1.24725000	H	0.72924000	0.86171800	7.79953100
O	-4.06945500	-1.44276300	0.11790600	H	0.21079200	-0.75401100	8.31981600
C	-4.06207200	-2.01398000	1.22494900	H	-0.99787700	0.48428100	7.92622800
O	-3.05259100	-2.12358900	2.02704000	O	-0.97900600	1.97387000	-2.28110100

Pro:

Ca	-2.48308000	0.35397500	-0.88694900	C	-6.40079000	2.67265200	1.35426600
Mn	0.48999400	-1.33753700	-1.02427900	H	-6.22175400	1.73470100	1.89327100
Mn	-1.05410900	-2.22211500	0.98049400	H	-6.63809100	2.40883600	0.31704700
Mn	-0.07670700	0.38951600	1.21042700	H	-7.27610300	3.16796300	1.79845900
Mn	-1.03562300	3.34570900	0.31621800	O	0.39520600	-1.14755400	-2.97174700
O	-1.16841700	-1.97601400	-0.82263900	C	-0.64815500	-0.81092900	-3.65444500
O	0.66974900	-1.49148800	0.79945700	O	-1.73750300	-0.41968600	-3.18934300
O	-1.64616600	-0.57238400	1.24455700	C	-0.45074300	-0.91015000	-5.16985000
O	0.00511600	0.34972100	-0.64583500	H	0.35312200	-0.20466400	-5.43441000
O	-0.99184300	1.84453600	1.41719100	H	-0.04843600	-1.91051800	-5.38907500
O	-4.37773000	-0.19685800	-2.53188700	C	-1.70353600	-0.62426100	-6.00043500
H	-4.60144100	-0.97576800	-1.97970600	H	-2.09740100	0.36325800	-5.72648700
H	-3.71681100	-0.50736400	-3.18384700	H	-2.48731200	-1.34798200	-5.73345700
O	-2.43522800	3.35723900	-1.98666200	C	-1.43699200	-0.68604000	-7.50881700
H	-2.08742100	4.25394900	-1.72769100	H	-0.68076600	0.05327600	-7.81022900
O	-0.97459600	5.08799900	-0.55301600	H	-2.34975000	-0.48103000	-8.08457000
H	-0.12240700	5.07863200	-1.02502500	H	-1.06715200	-1.67678200	-7.81105700
O	-0.67600900	4.81329900	1.98490700	N	2.54368300	-0.90226300	-1.16729600
H	-0.71329200	5.38601000	1.16539500	C	3.23812000	-0.14541000	-2.08001500
H	-1.61882400	4.73601900	2.23610300	H	2.73765500	0.26905100	-2.94479800
O	-3.96482800	1.83629000	0.28310700	C	4.55257700	-0.03911400	-1.68443500
C	-3.90796900	2.96441900	0.80437500	N	4.63391600	-0.77930600	-0.50863900
O	-2.86997700	3.72731700	0.89278500	H	5.43386400	-0.78675200	0.12499000
C	-5.17246400	3.57946700	1.41619800	C	3.39975600	-1.26028900	-0.22575900
H	-4.93642700	3.85561400	2.45467200	H	3.13707800	-1.81569100	0.66358800
H	-5.35637700	4.52911800	0.89169900	C	5.70489000	0.71085800	-2.30228800

H	6.00969100	0.23521600	-3.24708000	H	1.30722800	-6.09309700	0.39892800
H	5.34809200	1.71328000	-2.58187100	H	-4.82056200	-4.59084000	0.39449200
C	6.97422100	0.84325700	-1.42367400	C	2.23309900	-5.83731500	-1.56363000
H	7.49458200	-0.11855900	-1.35678800	H	2.47933000	-6.90072500	-1.69058100
H	7.65935800	1.55367300	-1.90783700	H	1.98475200	-5.41641700	-2.54433800
C	6.68934700	1.26854000	0.01924000	H	3.13142700	-5.31879400	-1.20517400
O	6.79112600	0.46062500	0.95144700	O	-3.97015200	-1.67960200	-0.27984400
N	6.27724800	2.54948600	0.20427000	C	-3.86068200	-2.66128400	0.48200400
H	6.10205500	3.11129100	-0.62059300	O	-2.79890200	-3.02352900	1.12505700
C	5.66896400	2.99247300	1.46704500	C	-5.05836400	-3.57215500	0.72716100
H	6.29585500	2.60642700	2.27761900	H	-5.93903300	-3.20196500	0.19413500
H	5.72918300	4.08874400	1.48425600	H	-5.26808600	-3.62180400	1.80283000
C	4.21730900	2.51759800	1.65022200	O	-0.66216300	-2.31995200	2.95615200
H	4.19736000	1.42463200	1.71665700	C	-0.18954300	-1.32896000	3.60810100
H	3.85651800	2.89392600	2.61837900	O	0.16523700	-0.19593200	3.16012700
C	3.28071400	2.98174100	0.53157800	C	-0.05829000	-1.52574700	5.11846000
H	3.64522700	2.61074000	-0.43951500	H	0.64801300	-0.77659000	5.49758900
H	3.24978200	4.07746000	0.46442000	H	-1.04238600	-1.28043600	5.55123400
C	1.83303500	2.48691800	0.64622100	C	0.34869700	-2.94374600	5.53789700
O	1.66061200	1.37506100	1.24702800	H	1.32872400	-3.18362700	5.09796600
O	0.97174200	3.22601000	0.09964300	H	-0.36278400	-3.65798800	5.10545500
O	1.09437500	-3.33427700	-1.13716900	C	0.41298800	-3.11044100	7.06020600
C	0.62273200	-4.21961800	-0.35669300	H	1.13815600	-2.41693900	7.51023000
O	-0.19870100	-4.04952400	0.59920800	H	0.71032700	-4.13090100	7.33881100
C	1.07075500	-5.66617900	-0.58535500	H	-0.56420100	-2.90990900	7.52305000
H	0.18293900	-6.21257300	-0.93942200	O	-1.39504400	2.55169700	-1.31428100

Table S34 Reaction parameters for the closed-cubane W3 (hydroxyl)-O5 (oxo) nucleophilic attack:

Spin state	Spin topology (Mn1~Mn4-O8)	Gibbs Free energy (a.u.)		
		Rea	TS	Pro
doublet	αααββα	-3365.7244	-3365.7102	-3365.7361
	αβαβα	-3365.7263	-3365.7147	-3365.7423
	αββαα	-3365.7275	-3365.7142	-3365.7419
	βααβα	-3365.7274	-3365.7132	-3365.7120
	βαβαα	-3365.7267	-3365.7046	-3365.7124
	ββααα	-3365.7241	-3365.7109	-3365.7374
sextet	αααββ	-3365.7289	-3365.7073	-3365.7146
	ααβαβ	-3365.7228	-3365.7084	-3365.7332
	αβααβ	-3365.7265	-3365.7035	-3365.7099
	βαααβ	-3365.7211	-3365.7072	-3365.7370
octet	αααβα	-3365.7291	-3365.7176	-3365.7411
	ααβαα	-3365.7284	-3365.7151	-3365.7414

	αβααα	-3365.7254	-3365.7135	-3365.7404
	βαααα	-3365.7260	-3365.7123	-3365.7371
12-et	αααaβ	-3365.7264	-3365.7047	-3365.7110
14-et	ααααα	-3365.7275	-3365.7155	-3365.7398

Spin state	Spin topology (Mn1~Mn4-O4/O10)	Relative Gibbs Free energy (kcal/mol)			
		$\Delta G^{\neq}$(Rea-TS)	ΔG(Rea-Pro)	ΔG(Rea)	ΔG(Pro)
doublet	ααββα	8.9	-7.3	2.5	3.9
	αβαβα	7.3	-10.0	1.3	0.0
	αββαα	8.3	-9.0	0.6	0.3
	βααβα	8.9	9.7	0.6	19.0
	βαβαα	13.9	9.0	1.1	18.8
	ββαaα	8.3	-8.3	2.7	3.1
sextet	αααββ	13.6	9.0	-0.3	17.4
	ααβαβ	9.0	-6.5	3.5	5.7
	αβααβ	14.4	10.4	1.2	20.3
	βαααβ	8.7	-10.0	4.6	3.3
octet	αααβα	7.2	-7.5	-0.4	0.8
	ααβαα	8.3	-8.2	0.0	0.6
	αβααα	7.5	-9.4	1.9	1.2
	βαααα	8.6	-7.0	1.5	3.3
12-et	αααaβ	13.6	9.7	1.3	19.6
14-et	ααααα	7.5	-7.7	0.6	1.6

Spin state	Spin topology (Mn1~Mn4-O8)		Mulliken spin density		
			Rea	TS	Pro
doublet	α	Mn1	2.92	3.32	3.87
	α	Mn2	2.94	2.95	2.96
	β	Mn3	-2.77	-2.69	-2.82
	β	Mn4	-2.92	-2.91	-2.91
	α	O8	0.95	0.60	0.01
	α	Mn1	2.92	3.21	3.87
	β	Mn2	-2.94	-2.93	-2.90
	α	Mn3	2.75	2.90	2.82
	β	Mn4	-2.84	-2.84	-2.84
	α	O8	0.96	0.65	0.00
	α	Mn1	2.91	3.29	3.88
	β	Mn2	-2.92	-2.92	-2.89
	β	Mn3	-2.75	-2.68	-2.78
	α	Mn4	2.83	2.84	2.84
	α	O8	0.96	0.63	0.01
	β	Mn1	-2.91	-2.82	-1.98
	α	Mn2	2.92	2.93	2.91

	α	Mn3	2.75	3.27	2.79
	β	Mn4	-2.84	-2.83	-2.84
	α	O8	0.96	0.54	0.00
	β	Mn1	-2.91	-2.56	-1.97
	α	Mn2	2.94	2.95	2.93
	β	Mn3	-2.74	-2.67	-2.74
	α	Mn4	2.84	2.84	2.84
	α	O8	0.96	0.49	0.01
	β	Mn1	-2.92	-2.85	-2.88
	β	Mn2	-2.94	-2.93	-2.89
	α	Mn3	2.77	3.27	3.83
	α	Mn4	2.91	2.92	2.92
	α	O8	0.95	0.56	0.00
	α	Mn1	2.92	2.56	1.98
	α	Mn2	2.92	2.93	2.94
	α	Mn3	2.78	2.72	2.79
	β	Mn4	-2.84	-2.84	-2.84
	β	O8	-0.96	-0.49	0.00
	α	Mn1	2.92	2.84	2.94
	α	Mn2	2.94	2.93	2.90
	β	Mn3	-2.73	-3.20	-3.78
	α	Mn4	2.85	2.85	2.78
sextet	β	O8	-0.88	-0.56	0.00
	α	Mn1	2.92	2.55	1.97
	β	Mn2	-2.94	-2.95	-2.93
	α	Mn3	2.81	2.73	2.81
	α	Mn4	2.92	2.91	2.91
	β	O8	-0.96	-0.48	0.00
	β	Mn1	-2.91	-3.28	-3.88
	α	Mn2	2.92	2.92	2.89
	α	Mn3	2.83	2.74	2.86
	α	Mn4	2.92	2.92	2.93
	β	O8	-0.88	-0.62	-0.01
	α	Mn1	2.92	3.24	3.87
	α	Mn2	2.92	2.93	2.95
	α	Mn3	2.80	2.96	2.86
	β	Mn4	-2.91	-2.83	-2.84
	α	O8	0.89	0.62	0.01
octet	α	Mn1	2.92	3.32	3.87
	α	Mn2	2.95	2.95	2.97
	β	Mn3	-2.71	-2.63	-2.75
	α	Mn4	2.83	2.84	2.84
	α	O8	0.96	0.61	0.02
	α	Mn1	2.92	3.20	3.87

	β	Mn2	-2.94	-2.93	-2.90
	α	Mn3	2.81	2.98	2.88
	α	Mn4	2.91	2.91	2.92
	α	O8	0.95	0.64	0.01
	β	Mn1	-2.91	-2.83	-2.87
	α	Mn2	2.92	2.92	2.93
	α	Mn3	2.82	3.33	3.86
	α	Mn4	2.91	2.92	2.92
	α	O8	0.95	0.55	0.00
12-et	α	Mn1	2.92	2.56	1.98
	α	Mn2	2.92	2.93	2.94
	α	Mn3	2.85	2.78	2.85
	α	Mn4	2.92	2.91	2.91
	β	O8	-0.95	-0.48	0.00
14-et	α	Mn1	2.92	3.23	3.87
	α	Mn2	2.92	2.93	2.95
	α	Mn3	2.85	3.06	2.92
	α	Mn4	2.91	2.91	2.91
	β	O8	0.95	0.62	0.01

Rea:

Ca	-2.62363600	0.52349800	-0.85126000	H	-4.05948400	4.83323700	-2.27479500
Mn	-0.28675600	-1.82750800	-0.24778500	H	-4.09918800	5.05694100	-0.53781000
Mn	-1.46328400	-1.00094200	2.01589600	C	-2.92415100	6.56510400	-1.58731000
Mn	0.19508700	0.81393800	0.74208000	H	-2.28606000	6.64706500	-2.47483600
Mn	0.58438700	3.62759900	-1.04640500	H	-2.31807700	6.86838800	-0.72554100
O	-1.95331000	-1.68635800	0.41060700	H	-3.76074100	7.27113300	-1.69205200
O	0.28868800	-1.09439300	1.34539400	O	-0.93171800	-2.67542200	-1.89360500
O	-1.54115100	0.64795000	1.36008700	C	-2.05890900	-2.48380800	-2.49155800
O	-0.22112000	-0.12187400	-0.82536800	O	-2.84288500	-1.53362500	-2.29232900
O	-0.10134100	2.38863000	0.13035200	C	-2.38630600	-3.54725700	-3.54276800
O	-5.00711900	0.03563600	-1.69565900	H	-1.55742700	-3.55112000	-4.26754500
H	-5.25651400	-0.22832500	-0.78515400	H	-2.34295300	-4.52717200	-3.04335700
H	-4.66334900	-0.77478100	-2.12523400	C	-3.72528500	-3.35359200	-4.25743500
O	-1.92480100	1.45304800	-3.04811000	H	-3.74995800	-2.35303000	-4.70963900
H	-0.99220400	1.87923700	-2.87814900	H	-4.53685700	-3.37054900	-3.51589300
O	1.34579400	4.83797600	-2.19050900	C	-3.98108800	-4.42088800	-5.32781800
H	1.51458600	5.60064700	-1.60548700	H	-3.20079600	-4.40354000	-6.10240300
O	0.90939900	4.81072800	0.33056800	H	-4.94756400	-4.26409500	-5.82585500
H	0.56225100	4.35118800	1.11704400	H	-3.98984000	-5.43092800	-4.89278900
H	0.64045800	3.10890300	-3.29152400	N	1.61678500	-2.17887500	-1.00754200
O	-2.76901500	2.87857500	-1.07279800	C	2.22343100	-1.42395600	-1.98828200
C	-2.36817100	4.05128700	-1.25370200	H	1.71802100	-0.55818100	-2.39875900
O	-1.16387700	4.47475500	-1.33148100	C	3.46733100	-1.94550600	-2.25251900
C	-3.44220300	5.13736300	-1.41642500	N	3.59104200	-3.04933700	-1.40997600

H	4.48533200	-3.47312900	-1.16418500	C	-0.47060600	-5.23527200	2.47166800
C	2.46148400	-3.13513300	-0.66425700	H	0.58599600	-5.52390900	2.37038700
H	2.27482800	-3.87725500	0.09882100	H	-1.02423300	-5.90054600	1.79216300
C	4.51879300	-1.52293900	-3.24253200	H	-5.79200700	-1.91219600	2.95992700
H	4.30368900	-1.94332200	-4.23746700	C	-0.95099700	-5.40204100	3.91311200
H	4.44435200	-0.43342700	-3.35916200	H	-0.82527500	-6.44233300	4.24385100
C	5.97798500	-1.91595700	-2.88085800	H	-0.38869800	-4.75132600	4.59316900
H	6.14341200	-2.98389000	-3.06320900	H	-2.00894400	-5.13197400	4.00735100
H	6.66443700	-1.36168900	-3.53633000	O	-4.36111500	-0.12044900	0.93079100
C	6.29585200	-1.67009800	-1.40739000	C	-4.31914700	-0.61485000	2.07707800
O	6.28502800	-2.59756900	-0.58941600	O	-3.25988100	-0.99282300	2.71186600
N	6.52028800	-0.37262200	-1.05886800	C	-5.60973700	-0.83404600	2.85709300
H	6.40355000	0.32083300	-1.78899200	H	-6.45472200	-0.36753800	2.34213200
C	6.35558400	0.09945000	0.32145100	H	-5.50973000	-0.42258400	3.86835100
H	6.70492500	-0.70895600	0.97063800	O	-0.68188600	-0.25387900	3.70026900
H	7.01960700	0.96313900	0.46357200	C	0.15113600	0.71456500	3.69149000
C	4.89364900	0.45754400	0.64530200	O	0.65449800	1.29205100	2.68218800
H	4.26854100	-0.43323300	0.51446700	C	0.55539800	1.24653000	5.06551400
H	4.82427700	0.72844800	1.70843900	H	-0.17283400	2.03421700	5.32117600
C	4.34567900	1.59779900	-0.21729500	H	0.41061700	0.44001700	5.79576800
H	4.57330300	1.42947100	-1.28161100	C	1.97741500	1.81531400	5.13334600
H	4.81124600	2.55931400	0.03841100	H	2.08470800	2.59552100	4.36978000
C	2.82287400	1.80395400	-0.17248300	H	2.69495000	1.02488100	4.86621900
O	2.14542800	0.89220300	0.40101400	C	2.31822300	2.37698100	6.51813900
O	2.43436200	2.85076400	-0.74853400	H	1.63541500	3.19330600	6.79468900
O	-0.13999600	-3.65724200	0.72779100	H	3.34142700	2.77585700	6.54600700
C	-0.60642500	-3.81870400	1.90612300	H	2.23979800	1.60390200	7.29638200
O	-1.16463000	-2.95152500	2.64133700	O	0.38776300	2.49797000	-2.57467900

TS:

Ca	-2.57679600	1.00496400	-0.58165200	O	2.12369100	4.93360700	-1.50681500
Mn	-0.69133600	-1.85959300	-0.40260900	H	2.21963900	5.62885400	-0.82811500
Mn	-1.46874400	-0.95579900	2.01123200	O	1.27119000	4.69828200	0.89392000
Mn	0.35356200	0.70443000	0.73321100	H	0.82257000	4.16658700	1.57671900
Mn	1.14178900	3.66942800	-0.62788400	H	1.24802300	3.33533700	-2.92904300
O	-2.22149200	-1.42491500	0.44346400	O	-2.35216300	3.34153200	-0.78135000
O	0.16631700	-1.25392700	1.14126700	C	-1.75707800	4.39024000	-1.11323500
O	-1.32435100	0.74133600	1.48406600	O	-0.49846800	4.62166200	-1.15888100
O	-0.32832400	-0.02566200	-0.89934200	C	-2.63327900	5.58014900	-1.54365700
O	0.22826700	2.35163800	0.29109200	H	-3.21465900	5.23792000	-2.41341600
O	-5.04644000	1.04242500	-1.27939300	H	-3.36891600	5.72869300	-0.73977400
H	-5.28288900	0.77965300	-0.36433900	C	-1.89104500	6.87891500	-1.85703900
H	-4.90029600	0.20262800	-1.76441100	H	-1.16651500	6.73255400	-2.66634500
O	-0.86790700	1.00526200	-2.36674900	H	-1.32990100	7.22980500	-0.98290100
H	-0.08449100	1.65753400	-2.30780100	H	-2.59688800	7.66703000	-2.15746900

O	-1.65584700	-2.38915200	-2.03197000	C	4.53612700	1.05954900	-0.27070300
C	-2.74187200	-1.89491700	-2.51822100	H	4.62398400	0.96993800	-1.36643400
O	-3.30825700	-0.84548000	-2.14550100	H	5.18246200	1.89670800	0.02074600
C	-3.32744600	-2.71440600	-3.67173900	C	3.07998200	1.48878800	-0.04666400
H	-2.56462700	-2.73885200	-4.46561400	O	2.24834300	0.54856600	0.16800200
H	-3.42240400	-3.75413500	-3.32415200	O	2.87522200	2.72566600	-0.15143900
C	-4.65709300	-2.19525700	-4.22256000	O	-0.76289000	-3.77039000	0.54240900
H	-4.53396200	-1.14781000	-4.52922600	C	-1.13668600	-3.87467700	1.75405300
H	-5.40550400	-2.18912900	-3.41688900	O	-1.45421600	-2.93441700	2.54754300
C	-5.17343500	-3.02990600	-5.40031300	C	-1.22109100	-5.30208800	2.30398600
H	-4.45820900	-3.02546400	-6.23550300	H	-0.27406100	-5.80174600	2.05365100
H	-6.12884500	-2.64110200	-5.77836500	H	-1.99215300	-5.81944500	1.71293100
H	-5.33175400	-4.07848900	-5.10911800	H	-5.82926000	-1.15291200	3.26676000
N	1.06060300	-2.43785500	-1.34636000	C	-1.52207800	-5.40382900	3.79928400
C	1.69398500	-1.71244000	-2.33230400	H	-1.57467000	-6.45590800	4.11245300
H	1.24509200	-0.80383800	-2.71389600	H	-0.74618100	-4.90470300	4.39212800
C	2.88879300	-2.31815900	-2.63770600	H	-2.47505500	-4.91972800	4.04056700
N	2.95335500	-3.44321200	-1.81728700	O	-4.24859300	0.51917500	1.27413600
H	3.81601200	-3.95136500	-1.61887100	C	-4.19804800	-0.06915100	2.37709200
C	1.84201400	-3.46029100	-1.04170600	O	-3.17726200	-0.67613600	2.88011200
H	1.62674700	-4.19475600	-0.27848700	C	-5.44050300	-0.12556900	3.25816400
C	3.94892100	-1.93567200	-3.63544200	H	-6.21210600	0.55172600	2.88007500
H	3.64813800	-2.23537400	-4.65155100	H	-5.18102000	0.13407200	4.29096200
H	4.00591900	-0.83877700	-3.65512600	O	-0.41500600	-0.46522000	3.65968500
C	5.36016700	-2.52917900	-3.38174800	C	0.56016700	0.35047400	3.62204800
H	5.37594600	-3.59655800	-3.63028900	O	1.05772900	0.91755400	2.59788700
H	6.07518000	-2.02727200	-4.04885000	C	1.18649700	0.71180900	4.96710100
C	5.79928500	-2.41812200	-1.92260700	H	0.65632000	1.60938400	5.32649200
O	5.71832200	-3.38747200	-1.15736000	H	0.95310200	-0.09439400	5.67412300
N	6.22702300	-1.19035400	-1.52103300	C	2.69339300	0.99134000	4.91229500
H	6.15751100	-0.43552600	-2.19398300	H	2.88102400	1.78349800	4.17716100
C	6.28643100	-0.81171300	-0.10460600	H	3.21279900	0.09543500	4.53961800
H	6.55695700	-1.71799400	0.44536600	C	3.26423500	1.38886200	6.27806200
H	7.09945700	-0.08250900	0.01639600	H	2.78463900	2.30247000	6.65780100
C	4.95037000	-0.24848200	0.41037200	H	4.34412200	1.58104100	6.21793600
H	4.16380700	-0.99780800	0.26458800	H	3.10659600	0.59801000	7.02582200
H	5.03391000	-0.09005400	1.49574000	O	1.14181100	2.65958600	-2.23656300

Pro:

Ca	-2.70680500	0.93064200	-0.47594500	O	0.20971200	-1.22765800	1.00366900
Mn	-0.73978100	-2.00014800	-0.50397100	O	-1.25852700	0.74381100	1.41106700
Mn	-1.35482400	-0.97615900	1.93068900	O	-0.11442700	0.12948600	-1.04325500
Mn	0.41591800	0.76917600	0.68322000	O	0.30518600	2.44575900	0.33939000
Mn	1.09526400	3.73809700	-0.69945300	O	-5.17906900	0.94025900	-1.12531100
O	-2.19925700	-1.43430700	0.40068600	H	-5.37816300	0.65009600	-0.20866600

H	-5.03175600	0.12022900	-1.64202700	H	6.10465200	-2.16076300	-4.05898700
O	-0.81101200	0.95247600	-2.00812100	C	5.84201100	-2.36168500	-1.90705000
H	-0.10909000	1.73944800	-2.18469300	O	5.76010500	-3.25152100	-1.05027700
O	1.92698300	5.00272600	-1.72467600	N	6.28343500	-1.10579100	-1.62873600
H	2.08384100	5.72341600	-1.08533700	H	6.21595300	-0.41609800	-2.36825600
O	1.39298800	4.79186200	0.76953900	C	6.38740500	-0.60276700	-0.25388200
H	1.02404300	4.26804100	1.50486500	H	6.70531400	-1.44939000	0.36213500
H	0.78250200	3.38182500	-3.00623400	H	7.18455700	0.15305900	-0.23377300
O	-2.40059100	3.23929600	-0.80733600	C	5.05940400	-0.03011400	0.26936400
C	-1.87080000	4.36165900	-0.97044700	H	4.29021700	-0.80955500	0.22530500
O	-0.62837200	4.66215700	-1.03040200	H	5.18488700	0.22385200	1.33222500
C	-2.82181900	5.56042000	-1.13680000	C	4.57455000	1.20209500	-0.50089100
H	-3.49414700	5.31395300	-1.97218600	H	4.61190800	1.01730400	-1.58749600
H	-3.46062500	5.57081000	-0.24091500	H	5.20778100	2.07864300	-0.31574600
C	-2.15430200	6.91908400	-1.34710900	C	3.11684000	1.60336000	-0.23002000
H	-1.52881400	6.91554200	-2.24759800	O	2.33767600	0.66466000	0.11838700
H	-1.50099300	7.16827000	-0.50301400	O	2.86767000	2.82345000	-0.43571600
H	-2.90998700	7.71131300	-1.45090300	O	-0.70009800	-3.90192800	0.62282500
O	-1.78043900	-2.42546900	-2.12603900	C	-1.04333900	-3.91192700	1.84138200
C	-2.87475100	-1.89919300	-2.55186800	O	-1.34190100	-2.90535500	2.56221300
O	-3.37779600	-0.82102000	-2.16211400	C	-1.12689300	-5.28456600	2.51925900
C	-3.56252500	-2.70694900	-3.65639000	H	-0.21886800	-5.83857300	2.24142700
H	-2.85053100	-2.77523500	-4.49389800	H	-1.95864700	-5.82006800	2.03555700
H	-3.67755800	-3.73703200	-3.28696700	H	-5.80046300	-1.25584100	3.24052500
C	-4.90130900	-2.14320800	-4.13670900	C	-1.31555600	-5.25195200	4.03618100
H	-4.75824000	-1.10407500	-4.46262800	H	-1.37950500	-6.27159400	4.44177800
H	-5.60180600	-2.10131500	-3.28991600	H	-0.47965200	-4.73747600	4.52583500
C	-5.51597900	-2.96965200	-5.27233400	H	-2.22928600	-4.71022000	4.30445800
H	-4.85085700	-3.00069400	-6.14742100	O	-4.26924500	0.45190300	1.38407400
H	-6.47665800	-2.54889300	-5.59910700	C	-4.12439000	-0.15005700	2.47912700
H	-5.69572200	-4.00839800	-4.95947400	O	-3.05561000	-0.70755400	2.91005900
N	1.01841200	-2.58450600	-1.45934900	C	-5.32672000	-0.27823400	3.40895300
C	1.64642900	-1.91667300	-2.48840700	H	-6.06034900	0.50693600	3.19969800
H	1.16131700	-1.08775700	-2.98601900	H	-5.00943800	-0.23849100	4.45620100
C	2.90291100	-2.44124500	-2.67197200	O	-0.31829000	-0.48341800	3.58976500
N	3.01458600	-3.46113900	-1.73041500	C	0.65352400	0.33344400	3.56784200
H	3.90246600	-3.88310600	-1.45178500	O	1.14441900	0.92077500	2.55303500
C	1.86763100	-3.49538100	-1.01023900	C	1.28651400	0.66737200	4.91759700
H	1.67360300	-4.15548200	-0.17638000	H	0.79152900	1.58427600	5.27814500
C	3.98090100	-2.06473900	-3.65394600	H	1.02271800	-0.13193500	5.62150900
H	3.71220800	-2.40789300	-4.66509800	C	2.80326700	0.88963600	4.86505100
H	4.01561100	-0.96779100	-3.71284600	H	3.02051100	1.67441300	4.12999000
C	5.39820800	-2.61188500	-3.34792200	H	3.28891700	-0.02496600	4.49224300
H	5.42923300	-3.69693500	-3.50044000	C	3.38839800	1.26484100	6.23107700

H	2.94307600	2.19548100	6.61140300	H	3.20061500	0.48003200	6.97821300
H	4.47495800	1.41620900	6.17206200	O	0.90460700	2.70577800	-2.31753300

Table S35 Reaction parameters for W3 (water) deprotonation in the open-cubane structure:

Spin state	Spin topology (Mn1~Mn4-O8)	Gibbs Free energy (a.u.)		
		Rea	TS	Pro
doublet	ααββα	-3595.4884	-3595.4578	-3595.4585
	αβαβα	-3595.4880	-3595.4542	-3595.4591
	αββαα	-3595.4800	-3595.4519	-3595.4589
	βααβα	-3595.4881	-3595.4544	-3595.4604
	βαβαα	-3595.4800	-3595.4513	-3595.4606
	ββααα	-3595.4792	-3595.4506	-3595.4600
sextet	αααββ	-3595.4813	-3595.4529	-3595.4616
	ααβαβ	-3595.4894	-3595.4555	-3595.4615
	αβααβ	-3595.4895	-3595.4596	-3595.4613
	βαααβ	-3595.4892	-3595.4590	-3595.4596
octet	αααβα	-3595.4898	-3595.4560	-3595.4604
	ααβαα	-3595.4815	-3595.4531	-3595.4603
	αβααα	-3595.4806	-3595.4520	-3595.4601
	βαααα	-3595.4803	-3595.4518	-3595.4613
12-et	ααααβ	-3595.4865	-3595.4523	-3595.4606
14-et	ααααα	-3595.4815	-3595.4529	-3595.4608

Spin state	Spin topology (Mn1~Mn4-O8)	Relative Gibbs Free energy (kcal/mol)			
		$\Delta G^{\neq}$(Rea-TS)	ΔG(Rea-Pro)	ΔG(Rea)	ΔG(Pro)
doublet	ααββα	19.2	18.8	0.9	1.9
	αβαβα	21.2	18.1	1.1	1.6
	αββαα	17.6	13.2	6.1	1.7
	βααβα	21.1	17.4	1.1	0.8
	βαβαα	18.0	12.2	6.1	0.6
	ββααα	17.9	12.0	6.7	1.0
sextet	αααββ	17.8	12.4	5.3	0.0
	ααβαβ	21.3	17.5	0.3	0.1
	αβααβ	18.8	17.7	0.2	0.2
	βαααβ	19.0	18.6	0.4	1.3
octet	αααβα	21.2	18.4	0.0	0.8
	ααβαα	17.8	13.3	5.2	0.8
	αβααα	17.9	12.9	5.8	0.9
	βαααα	17.9	11.9	6.0	0.2
12-et	ααααβ	21.5	16.3	2.1	0.6
14-et	ααααα	17.9	13.0	5.2	0.5

Rea:

Ca	-1.73182100	-1.75721700	-1.27594400	C	3.94785500	-4.30737100	-1.28704300
Mn	1.28316000	-1.38282800	0.36864300	H	4.67075300	-3.48149100	-1.34057800
Mn	-0.96847400	-1.26021100	1.97005900	H	4.21638400	-4.87683800	-0.38268400
Mn	-1.21330000	1.12182400	0.50411800	C	4.03297200	-5.20440200	-2.52558000
Mn	-2.27280900	2.14814600	-1.75486800	H	3.74047500	-4.62073700	-3.41185800
O	-0.17486400	-2.35620700	0.75579100	H	3.29433900	-6.01150800	-2.43447800
O	-2.11872300	-0.39768800	0.85276200	C	5.43413600	-5.78988300	-2.73093800
O	0.27738900	-0.03626100	1.25383600	H	6.18565800	-4.99743600	-2.85407900
O	-2.52508000	2.23693400	0.01081400	H	5.73855200	-6.40287200	-1.87103100
O	-1.24996100	0.77075900	-1.32694800	H	5.47245500	-6.42754200	-3.62385500
O	-1.16099900	-4.15863700	-1.46818400	N	2.81557000	0.03406900	0.12941600
H	-0.18062100	-4.21026100	-1.34759400	C	3.43781300	0.54970000	-0.99083600
H	-1.55160400	-4.40792400	-0.61009000	H	3.21651900	0.18212400	-1.98615700
O	-1.37969600	-1.96159900	-3.69860600	C	4.29187500	1.55922500	-0.60998200
H	-0.61231900	-2.54455500	-3.90043800	N	4.18091400	1.62859500	0.77325300
O	-2.05381500	2.23914800	-3.66243900	H	4.56096600	2.38580400	1.34816800
H	-1.03193800	1.12152500	-4.28091100	C	3.27374100	0.71260900	1.17260300
O	-3.48058800	3.93599400	-2.13940800	H	2.95637300	0.56936300	2.19378200
H	-4.34746100	3.48210900	-2.11881300	C	5.18467300	2.44823800	-1.43879900
H	-3.22515600	3.91928500	-3.08759500	H	5.99263000	1.85306100	-1.88933100
O	-0.44703100	0.42768100	-4.72818000	H	4.59764500	2.83467500	-2.28449300
H	-1.15088600	-1.10874700	-4.14302600	C	5.84800100	3.63248900	-0.69077400
H	-0.54134300	0.58876900	-5.68164200	H	6.60084400	3.26428700	0.01516100
O	1.91834100	-0.53661200	-3.60660900	H	6.36998400	4.25706400	-1.42889000
H	1.16209300	-0.04803100	-4.01446300	C	4.86120200	4.46627500	0.12540100
H	1.79723400	-1.46191200	-3.92086700	O	4.74376600	4.30916900	1.34828400
O	1.11817900	-3.18815900	-4.10010800	N	4.07994500	5.33529800	-0.56645700
H	1.27246400	-3.88612200	-4.75778500	H	4.19363100	5.39354700	-1.57095000
H	1.28084700	-3.61217900	-3.21427400	C	2.92213100	5.99333300	0.04905400
O	0.64746300	-1.16570300	-1.29646700	H	2.64606000	6.83577200	-0.59755100
H	1.23641000	-0.80758800	-2.01717000	H	3.24608000	6.39972600	1.01314200
O	-3.82829800	-0.86634300	-1.98152300	C	1.72932300	5.04597300	0.26575600
C	-4.47405900	0.16968700	-2.17505000	H	2.02475400	4.24812000	0.95517200
O	-3.98475000	1.37662900	-2.20298800	H	0.92790100	5.61249700	0.76126500
C	-5.97839000	0.07061100	-2.42820800	C	1.20373500	4.43287300	-1.03709400
H	-6.09686900	-0.55389800	-3.32568200	H	0.82405700	5.19935400	-1.72392600
H	-6.38496400	-0.52631100	-1.60006000	H	2.02008400	3.90695400	-1.55708500
C	-6.73632200	1.38971300	-2.57658700	C	0.10829100	3.39315700	-0.83873700
H	-6.36221300	1.97210700	-3.42806000	O	0.17375200	2.62006500	0.14866700
H	-7.80430400	1.19982900	-2.74372700	O	-0.79445200	3.38514800	-1.75220400
H	-6.64331900	2.00529300	-1.67277000	O	0.25510200	-1.99955200	3.38156400
O	2.56527500	-2.74531600	-0.18447700	C	1.50691300	-2.08295900	3.21986600
C	2.56275200	-3.70553800	-1.03540900	O	2.14429600	-1.75808500	2.16591500
O	1.56420700	-4.17806400	-1.62987200	C	2.34252400	-2.63488800	4.36857500

H	3.26422200	-2.03965900	4.41838800	O	-1.52230000	-0.07744400	3.47341600
H	2.65817500	-3.64292500	4.05728300	C	-1.57898700	1.18622300	3.38725900
C	1.62573900	-2.68524000	5.71824400	O	-1.36549100	1.86198000	2.33193000
H	2.28515500	-3.11501800	6.48305100	C	-1.95962600	1.97092500	4.63334100
H	1.32781700	-1.68203300	6.04706500	H	-1.47751800	2.95496700	4.56655400
H	0.71745600	-3.29433900	5.65814100	H	-3.04354600	2.15801600	4.55676700
O	-2.96971600	-3.17210900	0.40671400	C	-1.63838800	1.27210700	5.95929800
C	-3.04632000	-3.20756500	1.65110000	H	-0.55567000	1.08588400	6.01692000
O	-2.29731800	-2.54356900	2.47603900	H	-2.11785300	0.28533200	5.96973700
C	-4.09773200	-4.06822200	2.33168400	C	-2.08819400	2.09504800	7.17137800
H	-4.49011500	-4.81213100	1.63244300	H	-1.59882600	3.07906400	7.19377100
H	-3.68412400	-4.55334300	3.22237400	H	-1.84587000	1.58071500	8.11038800
H	-4.92210900	-3.42059800	2.66023600	H	-3.17387500	2.26612400	7.15579000

TS:

Ca	1.76430900	1.71992800	-1.24085800	H	-1.28497300	1.01302100	-1.96802500
Mn	-1.22864400	1.41179400	0.44682000	O	3.84823000	0.81612500	-1.96118300
Mn	1.04026800	1.12452500	2.00694900	C	4.46437900	-0.23585000	-2.17542100
Mn	1.15628600	-1.20165000	0.44393900	O	3.94718700	-1.42738400	-2.19572900
Mn	2.16412800	-2.14524200	-1.87840200	C	5.96763200	-0.17014000	-2.44902200
O	0.28450100	2.29770000	0.84581100	H	6.09606100	0.53537100	-3.28206400
O	2.13673300	0.25489100	0.84033900	H	6.41083600	0.32498100	-1.57320600
O	-0.26517400	-0.01779400	1.26093300	C	6.67007300	-1.49633300	-2.73854800
O	2.40595100	-2.36100000	-0.12734300	H	6.25757400	-1.97940500	-3.63374600
O	1.19803800	-0.76493400	-1.37324100	H	7.74120300	-1.33120500	-2.91187600
O	1.35663700	4.15888900	-1.33686500	H	6.56944900	-2.19207700	-1.89618000
H	0.38309300	4.25301700	-1.19229500	O	-2.43881000	2.85302900	-0.04094800
H	1.77892800	4.34579800	-0.47744000	C	-2.38966200	3.83326900	-0.87015500
O	1.30868500	1.87837200	-3.63587400	O	-1.36848800	4.27532600	-1.44616600
H	0.69336800	2.61158500	-3.86667400	C	-3.74807900	4.49602600	-1.11334800
O	1.95294100	-2.02374500	-3.79794100	H	-4.49560000	3.69869300	-1.22927800
H	1.31935000	-1.28428100	-4.08561800	H	-4.01836200	5.01982300	-0.18251900
O	3.28186200	-3.90983800	-2.46215000	C	-3.77880300	5.46403700	-2.29964800
H	4.15228900	-3.45934100	-2.48227300	H	-3.48475800	4.92210700	-3.21128000
H	2.98510700	-3.91126900	-3.39553900	H	-3.01847700	6.24159500	-2.14806600
O	0.29222900	-0.13532100	-4.57973500	C	-5.15688300	6.10389000	-2.49889200
H	0.80701900	0.76866500	-4.21622500	H	-5.92889000	5.34351600	-2.68253400
H	0.33065700	-0.07783600	-5.55134900	H	-5.46143200	6.67611100	-1.61140000
O	-2.03522500	0.88216900	-3.51777300	H	-5.15658100	6.79226200	-3.35417700
H	-1.30027500	0.36230900	-3.93786000	N	-2.82630600	0.07819100	0.18916100
H	-1.86379300	1.80395400	-3.81972900	C	-3.49369100	-0.35590200	-0.93946500
O	-1.03672700	3.46343300	-4.00982600	H	-3.28610100	0.05994400	-1.91871700
H	-1.19319200	4.20044400	-4.62269100	C	-4.37237500	-1.35498900	-0.58867500
H	-1.13906100	3.84683100	-3.09878500	N	-4.22966400	-1.50103600	0.78580100
O	-0.63866000	1.21488100	-1.23205700	H	-4.62285400	-2.27338900	1.33098900

C	-3.28171800	-0.63815700	1.20793000	C	-2.16340100	2.55650300	4.51110300
H	-2.93314200	-0.56087500	2.22608200	H	-3.11022800	2.00176500	4.55726700
C	-5.31327200	-2.17079300	-1.43920800	H	-2.43839300	3.58817400	4.24153000
H	-6.10782600	-1.52632900	-1.84332000	C	-1.42186900	2.52582300	5.84790900
H	-4.75764500	-2.53652600	-2.31482500	H	-2.04775400	2.95691800	6.63966500
C	-6.00398600	-3.36564600	-0.73438500	H	-1.16433800	1.49905800	6.13550700
H	-6.72631300	-3.00578700	0.00687400	H	-0.48795400	3.09532400	5.79229700
H	-6.56573800	-3.93280200	-1.48947300	O	3.09374600	3.01325800	0.49305000
C	-5.03224700	-4.27578700	0.01570400	C	3.19255100	2.99293400	1.73582500
O	-4.88186100	-4.18508400	1.24177200	O	2.43248500	2.32217500	2.54568600
N	-4.30117300	-5.13840500	-0.73633800	C	4.28644000	3.78382700	2.43390900
H	-4.43922600	-5.14297400	-1.73943900	H	4.70569000	4.53233900	1.75553200
C	-3.16179800	-5.87602800	-0.17953000	H	3.90109700	4.25758000	3.34330800
H	-2.93359800	-6.69365100	-0.87482700	H	5.08368300	3.09052800	2.73488500
H	-3.48561400	-6.31933500	0.76825500	O	1.55946100	-0.15066900	3.45202000
C	-1.92572200	-4.99256800	0.06314300	C	1.56260500	-1.40929200	3.30914800
H	-2.17638700	-4.21819600	0.79568700	O	1.30901800	-2.02884100	2.22674000
H	-1.14262900	-5.61696700	0.51673500	C	1.92318100	-2.26749400	4.51188000
C	-1.39333000	-4.33825800	-1.21669300	H	1.37797400	-3.21593300	4.41836100
H	-1.05189800	-5.08445400	-1.94459200	H	2.99042000	-2.51969300	4.39754900
H	-2.19497000	-3.75698500	-1.69915700	C	1.67964300	-1.60685600	5.87325300
C	-0.25646200	-3.35025800	-0.98504100	H	0.61308300	-1.35449200	5.96724300
O	-0.29369100	-2.61301800	0.03305700	H	2.22202900	-0.65390800	5.91172700
O	0.63946000	-3.33987800	-1.90175800	C	2.10429500	-2.50796200	7.03792000
O	-0.12559800	1.85783700	3.46498400	H	1.55269400	-3.45874000	7.03301000
C	-1.37445200	2.00951800	3.32772800	H	1.91857300	-2.01976000	8.00338200
O	-2.04211400	1.75756900	2.27328300	H	3.17587100	-2.74723000	6.98626300

Pro:

Ca	-1.70270600	-1.77546800	-1.20112100	H	-1.38748800	1.85261100	-3.86925500
Mn	1.35561400	-1.29269800	0.31861100	O	-3.80464300	3.58498100	-2.31634800
Mn	-0.89377800	-1.28843100	1.93698300	H	-4.63743400	3.07308800	-2.26200800
Mn	-1.31628000	1.11961000	0.49972600	H	-3.50056200	3.45892900	-3.24645100
Mn	-2.48578700	1.94425400	-1.79097400	O	0.23243100	0.81883300	-4.49791000
O	-0.06917600	-2.32322600	0.64992800	H	-0.19818700	0.05486500	-4.02715000
O	-2.11665200	-0.47820300	0.89345600	H	-0.02811000	0.70475100	-5.42845400
O	0.29978800	-0.03061000	1.22505500	O	2.46001400	-0.55087600	-3.54748500
O	-2.68017200	2.11815300	0.03607900	H	1.82907700	0.04944900	-4.01635500
O	-1.34609400	0.68634200	-1.29924700	H	2.32806200	-1.43274300	-3.95527800
O	-1.04320000	-4.12527700	-1.62086700	O	1.49930900	-3.17211700	-4.15471700
H	-0.06482100	-4.14931300	-1.47476500	H	1.34038200	-3.85197700	-4.83052000
H	-1.44486500	-4.46171600	-0.79697300	H	1.62524500	-3.65715200	-3.28927100
O	-0.52392400	-1.54078900	-3.32682000	O	0.75824900	-1.02208800	-1.41104000
H	0.14201900	-2.21679200	-3.64756500	H	1.46061700	-0.76301200	-2.06698100
O	-2.33713300	1.87427400	-3.62401300	O	-3.74484100	-1.17124700	-2.22067500

C	-4.52245100	-0.19768200	-2.19876200	H	2.13306200	7.00084600	-0.81972600
O	-4.19910000	1.02541500	-1.94296000	H	2.64872600	6.74316000	0.85718900
C	-6.00649100	-0.44538200	-2.46942100	C	1.27725500	5.23055600	0.13858900
H	-6.05608100	-1.05891800	-3.37952500	H	1.58063900	4.50908600	0.90410700
H	-6.35891800	-1.09632200	-1.65551000	H	0.41623400	5.78098300	0.54443800
C	-6.89101900	0.79538400	-2.59011600	C	0.86349400	4.48617000	-1.13644600
H	-6.56639700	1.43550600	-3.42105300	H	0.46874100	5.17095000	-1.89674200
H	-7.93311900	0.50673300	-2.77867500	H	1.74004400	3.98135000	-1.57222100
H	-6.86596400	1.39143200	-1.66994400	C	-0.17101700	3.39149800	-0.90350600
O	2.70265500	-2.57567200	-0.30603600	O	-0.03290800	2.64638300	0.10607600
C	2.71000900	-3.58088900	-1.09870800	O	-1.08152000	3.30515000	-1.79457400
O	1.71280700	-4.08933000	-1.67280400	O	0.38959100	-2.04618400	3.30879000
C	4.09957600	-4.18667700	-1.31276300	C	1.63564200	-2.08609000	3.12044300
H	4.81449800	-3.35977100	-1.42490800	O	2.23996200	-1.71363100	2.05887600
H	4.37249700	-4.68545100	-0.36881600	C	2.52375700	-2.63492200	4.23018900
C	4.19798400	-5.17101400	-2.48200600	H	3.41096500	-1.99005000	4.28819000
H	3.91175500	-4.65617800	-3.41154800	H	2.89020600	-3.61006400	3.87357600
H	3.46315800	-5.97406400	-2.33772700	C	1.83507800	-2.77668100	5.58785400
C	5.60388000	-5.76232000	-2.63181800	H	2.53124500	-3.19819900	6.32409000
H	6.35239400	-4.97671100	-2.80599500	H	1.48855100	-1.80504100	5.96043900
H	5.90358900	-6.30938700	-1.72699400	H	0.96069900	-3.43272600	5.51874600
H	5.65309700	-6.46288500	-3.47563900	O	-2.80768800	-3.33962000	0.39945300
N	2.79971600	0.22832200	0.16388100	C	-2.84594400	-3.38824600	1.64828400
C	3.54791100	0.73487300	-0.88024900	O	-2.13258900	-2.67164300	2.45458700
H	3.53373200	0.27655700	-1.86140100	C	-3.80821800	-4.33576600	2.34497400
C	4.21437500	1.86126100	-0.45519700	H	-4.13842900	-5.11810000	1.65541900
N	3.86734700	2.00650000	0.88240700	H	-3.34523700	-4.77349800	3.23568700
H	4.09507900	2.82102100	1.46032900	H	-4.68589200	-3.76294400	2.67463100
C	3.00602200	1.02165500	1.20759600	O	-1.43381200	-0.16782700	3.47036900
H	2.52501500	0.92132600	2.16822100	C	-1.57226600	1.09492000	3.40738800
C	5.10012600	2.81647200	-1.21565800	O	-1.42260400	1.80070000	2.36455100
H	6.00005700	2.29187100	-1.56817900	C	-1.97617700	1.82337700	4.67999600
H	4.56814800	3.13163000	-2.12548000	H	-1.57318400	2.84274900	4.62083900
C	5.57100400	4.07292400	-0.44155000	H	-3.07302900	1.92682700	4.63520500
H	6.26576800	3.79106100	0.35749200	C	-1.56715800	1.12746500	5.98327400
H	6.12029700	4.71959900	-1.13986100	H	-0.47209900	1.02415000	6.01028500
C	4.43689300	4.84812100	0.23079400	H	-1.96986100	0.10690400	5.98621000
O	4.21122900	4.73200200	1.44371200	C	-2.04579700	1.89164500	7.22251000
N	3.65853300	5.61675000	-0.57201900	H	-1.63278400	2.90986700	7.25179400
H	3.86678700	5.65318800	-1.56221200	H	-1.73974700	1.38095100	8.14477000
C	2.41921200	6.23628300	-0.08665400	H	-3.14138100	1.97880500	7.23767800

Table S36 Reaction parameters for W3 (water) deprotonation in the closed-cubane structure:

Spin state	Spin	Gibbs Free energy (a.u.)

	topology (Mn1~Mn4-O8)	Rea	TS	Pro
doublet	ααββα	-3595.4931	-3595.4469	-3595.4595
	αβαβα	-3595.4752	-3595.4407	-3595.4588
	αββαα	-3595.4669	-3595.4384	-3595.4567
	βααβα	-3595.4759	-3595.4417	-3595.4597
	βαβαα	-3595.4664	-3595.4387	-3595.4558
	ββααα	-3595.4653	-3595.4350	-3595.4551
sextet	αααββ	-3595.4691	-3595.4422	-3595.4584
	ααβαβ	-3595.4765	-3595.4426	-3595.4604
	αβααβ	-3595.4931	-3595.4503	-3595.4597
	βαααβ	-3595.4928	-3595.4474	-3595.4621
octet	αααβα	-3595.4783	-3595.4440	-3595.4616
	ααβαα	-3595.4681	-3595.4395	-3595.4578
	αβααα	-3595.4663	-3595.4357	-3595.4558
	βαααα	-3595.4672	-3595.4369	-3595.4568
12-et	ααααβ	-3595.4676	-3595.4365	-3595.4578
14-et	ααααα	-3595.4689	-3595.4385	-3595.4581

Spin state	Spin topology (Mn1~Mn4-O8)	Relative Gibbs Free energy (kcal/mol)			
		$\Delta G^{\neq}$(Rea-TS)	ΔG(Rea-Pro)	ΔG(Rea)	ΔG(Pro)
doublet	ααββα	29.0	21.1	0.0	1.6
	αβαβα	21.6	10.3	11.2	2.1
	αββαα	17.9	6.4	16.4	3.4
	βααβα	21.5	10.2	10.8	1.5
	βαβαα	17.4	6.7	16.8	4.0
	ββααα	19.0	6.4	17.4	4.4
sextet	αααββ	16.9	6.7	15.1	2.3
	ααβαβ	21.3	10.1	10.4	1.1
	αβααβ	26.9	21.0	0.0	1.5
	βαααβ	28.5	19.3	0.2	0.0
octet	αααβα	21.5	10.5	9.3	0.3
	ααβαα	17.9	6.5	15.7	2.7
	αβααα	19.2	6.6	16.8	4.0
	βαααα	19.0	6.5	16.3	3.3
12-et	ααααβ	19.5	6.1	16.0	2.7
14-et	ααααα	19.1	6.8	15.2	2.5

Rea:

Ca	-2.51689900	-0.10138400	0.89848300	O	-0.83620000	1.85179800	1.39215300
Mn	0.76408600	0.98678600	1.33055400	O	-1.42780100	1.20419800	-1.00933600
Mn	-0.65338900	2.62743200	-0.26604900	O	0.96702200	1.64492200	-0.37199800
Mn	0.03675500	0.15595200	-1.29486800	O	-0.95218300	-1.05930800	-2.10062000
Mn	-1.31313300	-2.73051300	-1.49746300	O	0.04436200	-0.42544400	0.46271100

O	-3.11176700	1.41696600	2.96871400	N	2.71926500	0.28366600	1.24380000
H	-3.70906000	1.97143800	2.42902700	C	3.30743600	-0.78108300	1.88806800
H	-2.23675900	1.83756300	2.82031000	H	2.75958700	-1.36199700	2.61655100
O	-4.16729400	-1.74254900	1.79560200	C	4.60389300	-0.92139800	1.44886900
H	-3.94572900	-2.11868600	2.67780300	N	4.78710500	0.10886300	0.53368600
O	-1.73823100	-4.46345200	-1.07018800	H	5.58016100	0.17467300	-0.10978900
H	-3.28828900	-4.40843500	-0.23211100	C	3.62707900	0.79338900	0.42451200
O	-1.01967600	-3.19907600	-3.57833500	H	3.45200600	1.61021100	-0.26074300
H	-1.97715900	-3.21581300	-3.79298000	C	5.65877900	-1.93260300	1.81841000
H	-0.75660600	-2.26690700	-3.75709600	H	6.05045000	-1.72286400	2.82507900
O	-2.85965500	-2.68955700	4.04254300	H	5.17219400	-2.91563900	1.88948400
H	-3.14694200	-2.60392900	4.96598100	C	6.87534200	-2.02432300	0.86044400
H	-2.27603100	-1.90024000	3.84080400	H	7.53473200	-1.16041300	0.99834800
O	-1.56564600	-4.29330800	2.10172400	H	7.45421400	-2.92110900	1.12076600
H	-2.39944600	-4.59996800	1.67585100	C	6.48820600	-2.03078800	-0.61835300
H	-1.88611900	-3.85656300	2.92158600	O	6.59357100	-1.00825000	-1.30926700
O	-3.91188800	-4.37554400	0.54480700	N	5.96299100	-3.18220500	-1.10769900
H	-4.19258700	-2.52740000	1.20426500	H	5.86186700	-3.97264600	-0.48286100
H	-4.54798100	-5.09648800	0.40558400	C	5.32260400	-3.24591700	-2.42683400
O	-1.69334500	-2.45593800	0.20786800	H	6.00894300	-2.79684600	-3.15334500
H	-1.36234000	-3.12857800	0.89424600	H	5.21231400	-4.30801700	-2.67841400
O	-3.88198300	-0.81181200	-0.98009900	C	3.96647800	-2.52111200	-2.48702600
C	-3.98010100	-1.60464400	-1.92280000	H	4.12190100	-1.45210000	-2.30971200
O	-3.12703000	-2.54542600	-2.21811100	H	3.57949100	-2.61945700	-3.51185100
C	-5.21930300	-1.55086300	-2.81867200	C	2.94110800	-3.06858000	-1.48733600
H	-6.05260700	-1.93817700	-2.21239800	H	3.33975700	-2.98822100	-0.46407200
H	-5.43766000	-0.48698600	-2.97714500	H	2.72109400	-4.12756400	-1.66813500
C	-5.13127000	-2.30402900	-4.14701100	C	1.61431900	-2.31106300	-1.47071900
H	-4.94662000	-3.37318500	-3.98830700	O	1.65271000	-1.05706700	-1.62060900
H	-6.06764600	-2.20052400	-4.71042100	O	0.59474200	-3.05993800	-1.27175300
H	-4.32142000	-1.90943500	-4.77536800	O	0.41475500	4.10184700	0.62094300
O	0.70516500	0.24160700	3.12585800	C	1.24153600	3.87432200	1.55939500
C	-0.21796700	-0.48542100	3.64851400	O	1.58624300	2.73211400	2.01109600
O	-1.29351200	-0.79775600	3.08299100	C	1.89459400	5.07748600	2.23343900
C	0.04244500	-0.91910200	5.08507200	H	2.97368900	4.87478200	2.28115100
H	-0.52200400	-1.83937800	5.28568100	H	1.54892600	5.07109100	3.27843100
H	1.11131700	-1.13632700	5.20734000	C	1.60607600	6.42493000	1.57165600
C	-0.37335100	0.18791500	6.07755900	H	2.10020000	7.23388500	2.12509400
H	-1.43346500	0.43369100	5.91784900	H	1.96894100	6.44457000	0.53698500
H	0.19747900	1.09791600	5.84634300	H	0.52992500	6.62893100	1.54515600
C	-0.14324700	-0.21800700	7.53665300	O	-2.23125600	3.66974900	-0.24101000
H	-0.72047400	-1.11586600	7.79897900	C	-3.44429800	3.25798800	-0.00928200
H	0.91661200	-0.43790500	7.72572000	O	-3.75720700	2.14297300	0.44632400
H	-0.44567900	0.58476400	8.22134100	C	-4.50995200	4.28295700	-0.35629000

H	-4.20678400	5.28286600	-0.02688600	H	1.07254300	2.42311200	-4.98866100
H	-4.62115800	4.31611500	-1.44860300	C	1.13583600	4.50698500	-4.31973900
H	-5.46780000	4.00199000	0.09027100	H	0.52012300	5.16189800	-3.69091000
O	-0.18685000	3.26103900	-2.10725200	H	2.10840700	4.41621000	-3.81283100
C	0.21717700	2.48441500	-3.03365700	C	1.33230700	5.12996200	-5.70582500
O	0.40824700	1.22644600	-2.95124200	H	1.96622600	4.49870000	-6.34438500
C	0.47474000	3.12294900	-4.39205900	H	1.81001400	6.11556600	-5.63209000
H	-0.50633500	3.20844900	-4.88765700	H	0.37091700	5.26320600	-6.22178500

TS:

Ca	-2.55039900	-0.08474100	0.89963600	H	-5.99534800	-2.40205300	-1.84984000
Mn	0.75875700	1.08819500	1.30766500	H	-5.71871200	-0.89482500	-2.70877500
Mn	-0.65063700	2.61713300	-0.40579600	C	-5.27078000	-2.68727800	-3.87650900
Mn	0.06706800	0.09788000	-1.27130200	H	-4.91568800	-3.71199000	-3.71647000
Mn	-1.28260600	-2.77722800	-1.41753000	H	-6.27013600	-2.74032500	-4.32720700
O	-0.84716500	1.94530300	1.28983300	H	-4.60454500	-2.20415500	-4.60423100
O	-1.40299500	1.13970300	-1.07135100	O	0.67898700	0.46073200	3.13563500
O	0.97798400	1.63086700	-0.43932400	C	-0.25791100	-0.23299700	3.68637300
O	-0.90777100	-1.16490700	-2.05669700	O	-1.32294800	-0.57402600	3.12393500
O	0.06373700	-0.37925200	0.50836100	C	-0.02361600	-0.58381100	5.14945500
O	-3.17803700	1.57871500	2.83266000	H	-0.50888200	-1.54680000	5.35800500
H	-3.75636300	2.10562700	2.24701000	H	1.05308600	-0.69026200	5.33062800
H	-2.29711100	1.98754900	2.68943600	C	-0.59994600	0.50965800	6.07460500
O	-4.06064200	-1.81637700	1.73075900	H	-1.66855100	0.64135500	5.85131500
H	-4.01629400	-2.01427500	2.68842500	H	-0.11085100	1.46498700	5.83714700
O	-1.78865900	-4.54775500	-0.92480600	C	-0.40856700	0.18102200	7.55855400
H	-2.68551200	-4.44439800	-0.46460300	H	-0.90680600	-0.76102400	7.82797300
O	-1.02679200	-3.34729600	-3.48657700	H	0.65620200	0.07640600	7.80876100
H	-1.98531100	-3.40668100	-3.68453600	H	-0.82560700	0.97250400	8.19439400
H	-0.78223300	-2.43230000	-3.74799000	N	2.71100800	0.37706100	1.28258100
O	-2.79635800	-2.53458100	4.18838000	C	3.27634100	-0.66613100	1.98042700
H	-2.95164700	-2.47733800	5.14478500	H	2.71380500	-1.20315400	2.73102900
H	-2.30160300	-1.70995100	3.92913900	C	4.57283800	-0.84867900	1.55750100
O	-1.50333800	-4.07762700	2.19857500	N	4.77979000	0.13382900	0.59620500
H	-2.38073800	-4.33632900	1.79657300	H	5.57856300	0.15480400	-0.04379200
H	-1.77721300	-3.61695500	3.02409500	C	3.63281900	0.83202800	0.44647800
O	-3.76928500	-4.06167400	0.80268300	H	3.47718300	1.61798600	-0.27837100
H	-3.96552000	-2.98377800	1.17713400	C	5.60804000	-1.85845700	1.98286800
H	-4.57268700	-4.57968800	0.97877900	H	5.98486400	-1.61488600	2.98752300
O	-1.55293500	-2.35424000	0.26960000	H	5.10832500	-2.83239900	2.08254600
H	-1.31981000	-3.02939200	1.01573300	C	6.83963200	-2.00141900	1.05119200
O	-3.82759200	-0.80786700	-1.04319000	H	7.50096300	-1.13459000	1.15845800
C	-3.98774300	-1.74535500	-1.82748900	H	7.40933600	-2.88690300	1.36486900
O	-3.10876300	-2.68013900	-2.08289700	C	6.47711500	-2.07921000	-0.43164500
C	-5.31814600	-1.90505500	-2.56187000	O	6.58672000	-1.08912800	-1.16799300

N	5.96876200	-3.25612900	-0.87579800	H	2.01008300	6.46417300	0.15844500
H	5.86738400	-4.01974600	-0.21853000	H	0.53385000	6.73096600	1.09226900
C	5.35675500	-3.38739400	-2.20323500	O	-2.23069300	3.64405500	-0.47216600
H	6.05496500	-2.96830700	-2.93635800	C	-3.44867100	3.23474600	-0.25129300
H	5.25811500	-4.46091900	-2.40623500	O	-3.76445300	2.14720100	0.26154900
C	3.99807400	-2.67545500	-2.32530500	C	-4.50959500	4.22776600	-0.69153600
H	4.14342800	-1.59883500	-2.19037600	H	-4.22241000	5.24863000	-0.41667200
H	3.63444600	-2.82109400	-3.35304800	H	-4.58935600	4.19165600	-1.78650300
C	2.95366000	-3.18601000	-1.32534800	H	-5.47804800	3.96713400	-0.25573200
H	3.33273900	-3.06519500	-0.29863100	O	-0.16319200	3.13765100	-2.28121600
H	2.73689900	-4.25095200	-1.47054500	C	0.26318400	2.30954200	-3.14983200
C	1.62947400	-2.42579600	-1.36482000	O	0.46199600	1.05986000	-2.98435100
O	1.67483900	-1.17351800	-1.51696700	C	0.54093800	2.86142400	-4.54148700
O	0.60000300	-3.17438600	-1.20715100	H	-0.43123800	2.90364100	-5.05969100
O	0.40245800	4.14576700	0.38960700	H	1.15689800	2.13106500	-5.08022800
C	1.22248900	3.98416700	1.34786100	C	1.18694400	4.25448400	-4.54657000
O	1.56884300	2.87473200	1.87368100	H	0.55296600	4.94179600	-3.97289400
C	1.85999600	5.23187300	1.95074500	H	2.15052900	4.20720500	-4.01713500
H	2.93441200	5.02780700	2.05662500	C	1.40341200	4.78864900	-5.96631900
H	1.47308800	5.30834000	2.97854700	H	2.05541100	4.12449800	-6.55099000
C	1.60662900	6.52545200	1.17642300	H	1.87000200	5.78207800	-5.94771700
H	2.08476300	7.37237200	1.68512100	H	0.45067100	4.87783400	-6.50714100

Pro:

Ca	-2.50261300	0.17029000	0.59763900	H	-3.80549200	-2.27646900	4.32243700
Mn	0.76796700	1.04444700	1.35500400	H	-2.60892100	-1.52728600	3.60821800
Mn	-0.34778700	2.73951900	-0.39691000	O	-1.73500900	-4.26420400	2.01918900
Mn	0.14361400	0.16342400	-1.28235100	H	-2.48284500	-4.71958900	1.57260300
Mn	-1.44019900	-2.68981800	-1.50644900	H	-2.14407900	-3.82241700	2.79276000
O	-0.72518700	2.05338000	1.25225900	O	-3.98643400	-4.59706900	0.38373700
O	-1.21403500	1.37835600	-1.15320700	H	-4.12915800	-3.61656100	0.49009300
O	1.16760000	1.59672600	-0.34683200	H	-4.86081900	-4.99489600	0.24636500
O	-0.96282500	-0.98830000	-2.00479800	O	-1.91524200	-2.26715200	0.22575900
O	-0.01262500	-0.33704200	0.49887200	H	-1.66463200	-3.01797100	0.85169700
O	-4.15317200	1.02101400	2.37907900	O	-3.83479700	-0.43244800	-1.34132300
H	-4.23686800	1.87468900	1.89964000	C	-3.96871400	-1.36445300	-2.13923000
H	-3.47576600	1.16840000	3.06435800	O	-3.20548100	-2.42261400	-2.23524800
O	-3.96647300	-1.95950400	1.08603800	C	-5.15931000	-1.36686800	-3.10166700
H	-3.67301600	-2.23370600	1.99850000	H	-6.01643000	-1.76111700	-2.53314600
O	-1.77610000	-4.44346200	-1.35409200	H	-5.39232800	-0.31612200	-3.31217100
H	-2.64837200	-4.58912100	-0.91535500	C	-4.97363600	-2.16806100	-4.39256000
O	-0.96616100	-2.98236600	-3.59889900	H	-4.78389400	-3.22642900	-4.17936100
H	-1.86981700	-3.18505600	-3.91140200	H	-5.87152400	-2.10112500	-5.02031600
H	-0.85635800	-2.01042400	-3.71674800	H	-4.13007200	-1.78202600	-4.98132300
O	-3.07300600	-2.40921600	3.69821500	O	0.44417100	0.40248300	3.18837400

C	-0.63144300	-0.05433600	3.69746600	C	2.77086000	-3.28023500	-1.24990900
O	-1.73592100	-0.17999200	3.08798400	H	3.07535700	-3.28636400	-0.19159600
C	-0.55643300	-0.46568600	5.16410800	H	2.48237000	-4.30724400	-1.50509000
H	-0.81900600	-1.53311100	5.22651800	C	1.50823200	-2.42139600	-1.30363300
H	0.47467400	-0.34720700	5.51497600	O	1.64805900	-1.17929600	-1.49537800
C	-1.52310100	0.34399600	6.04945100	O	0.43191100	-3.08077800	-1.10721500
H	-2.54838200	0.21243500	5.67455600	O	0.80578200	4.14062600	0.50923300
H	-1.29035000	1.41481400	5.95196600	C	1.53216400	3.87373600	1.51744600
C	-1.45096800	-0.06731500	7.52338600	O	1.72315800	2.72393000	2.03606500
H	-1.70253900	-1.12920400	7.65383600	C	2.24996500	5.03556000	2.19853100
H	-0.44188600	0.08678600	7.92902700	H	3.28499200	4.71542300	2.38156100
H	-2.14928100	0.52043100	8.13302000	H	1.79345000	5.13711700	3.19522500
N	2.63155800	0.12477100	1.49081200	C	2.19794500	6.36161000	1.43957000
C	3.01392900	-1.01559200	2.16033400	H	2.72235100	7.14404400	2.00329700
H	2.32110200	-1.54491300	2.79972100	H	2.67079200	6.27318800	0.45392700
C	4.32755300	-1.30059000	1.86516500	H	1.16307600	6.68301100	1.27840900
N	4.73334000	-0.28186800	1.01073000	O	-1.82463700	3.93119600	-0.45841400
H	5.59619200	-0.30092800	0.46042500	C	-3.04128000	3.67106600	-0.09469800
C	3.68054400	0.53788600	0.79544500	O	-3.45223500	2.57669200	0.34099000
H	3.68292000	1.38255700	0.12161100	C	-3.98831700	4.84878800	-0.25091600
C	5.20915500	-2.43706800	2.31635700	H	-3.58379600	5.72742000	0.26571700
H	5.50183600	-2.29673400	3.36778100	H	-4.06956500	5.10642100	-1.31465400
H	4.60824800	-3.35723600	2.29721100	H	-4.97867900	4.60068800	0.14067200
C	6.51124200	-2.65141900	1.50062400	O	0.29624000	3.23832200	-2.23067400
H	7.24345500	-1.87252000	1.74024800	C	0.65640100	2.37970900	-3.10057800
H	6.95029500	-3.61412000	1.79652600	O	0.70789200	1.11287800	-2.95686900
C	6.29979300	-2.58583900	-0.01190400	C	1.04859500	2.92267200	-4.46851800
O	6.59260100	-1.56689200	-0.65253800	H	0.10815200	3.12484500	-5.00698100
N	5.71595100	-3.66323000	-0.59442500	H	1.56692300	2.12623500	-5.01609900
H	5.45281400	-4.44589200	-0.00802500	C	1.89212100	4.20490700	-4.41149400
C	5.20627400	-3.62039200	-1.97052800	H	1.34905500	4.96049300	-3.83039600
H	5.99681000	-3.20406400	-2.60426200	H	2.82270200	3.99998200	-3.86088700
H	5.03441100	-4.65822600	-2.28199400	C	2.22594400	4.74395500	-5.80639900
C	3.92659000	-2.77895600	-2.12165200	H	2.79014800	4.00864600	-6.39725200
H	4.15125200	-1.73555000	-1.87749800	H	2.83255500	5.65674800	-5.74293100
H	3.63248500	-2.79862100	-3.18101900	H	1.31267800	4.98882500	-6.36698700

Data Summary

Table S37 The summary table of the upper and lower limits of barriers and driving forces in the form of Gibbs free energy (in kcal mol^{-1}) in optimal spin states of O-O bond formation :

Substrates	Deprotonation site	Reactive forms	Open-cubane structure		Closed-cubane structure	
			$\Delta G^{\neq}$	ΔG	$\Delta G^{\neq}$	ΔG
O5-Wx	Wx	oxo-oxyl	5.3~5.9[a]	-15.0~-14.9	25.7~30.2[b]	11.1~16.4

	W1	oxo-hydroxyl	11.0~16.0[a']	-5.9~-3.0	6.5~15.2[b']	-2.3~5.0
	W2		\	\	\	\
W3-W2	W2	water-oxyl	34.0~36.6[c]	8.8~11.1	\	\
			29.0~30.2[d]	-8.6~-7.9	\	\
	W3	hydroxyl-hydroxyl	19.8~21.9[e]	-5.3~-2.4	\	\
	W3, W2	hydroxyl-oxo	7.3~8.4[f]	-26.5~-22.9	\	\
W3-Wx	Wx	water-oxo/oxyl	\	\	51.5~52.7[c']	51.3~52.8
			\	\	47.1~47.9[d']	45.9~48.9
			\	\	38.6~41.8[e']	37.8~40.8
	W3	hydroxyl-hydroxyl	16.7~18.8[g]	-9.4~-3.8	3.6~3.9[f']	-15.2~-14.6
	W3, Wx	hydroxyl-oxo	\	\	0.4~1.1[g']	-27.0~-18.2
W1-W2	W1	hydroxyl-hydroxyl	28.4~29.2[h]	2.8~4.6	23.5~23.8[h']	-6.7~-6.5
	W2	water-oxo	\	\	\	\
	W1, W2	hydroxyl-oxyl	18.6~18.7[i]	-7.4~-6.7	21.6~23.2[i']	7.6~16.2
O2-O4	W1	oxo-oxo/oxyl	20.3~38.8[j]	-3.6~5.8	25.3[j']	5.7
	W2		33.6~36.6[k]	10.6~14.5	51.3~66.6[k']	53.4~61.9
	Wx		38.6~56.1[l]	20.0~30.1	46.2~52.2[l']	27.4~36.6
W1-O4	W1	hydroxyl-oxo	14.1~18.4[m]	-2.9~0.1	15.5~21.6[m']	5.4~21.3
	W2	water-oxo	\	\	\	\
	Wx		\	\	\	\
W2-O5	W1	hydroxyl-oxo	19.6~25.6[n]	4.5~8.6	\	\
	Wx		49.9~54.3[o]	-10.2~-2.3	\	\
	W2	oxyl-oxo	19.4~24.9[p]	-1.6~4.0	\	\
W2-Wx	W1	hydroxyl-hydroxyl	\	\	\	\
	W2	hydroxyl-oxyl	\	\	34.3~36.5[n']	25.7~27.6
	Wx		\	\	43.5~45.2[o']	41.6~43.9
W3-O5	W1	water-oxo	\	\	17.9~21.9[p']	-22.3~-14.1
	W2		\	\	\	\
	Wx		\	\	\	\
	W3	hydroxyl-oxo	9.2~10.2[q]	-4.6~-2.8	7.2~9.0[q']	-10.0~-6.5

'\' denotes the infeasibility of reactions that have been testified for deliberation and trials (see detailed interpretations in related sections). Here are specific meanings for each letter: (a) open-cubane Wx (oxyl)-O5 (oxo) coupling; (b) open-cubane Wx (hydroxyl)-O5 (oxo) nucleophilic attack; (c) open-cubane W3 (water)-W2 (oxyl) nucleophilic attack with Ca-bound O of Asp170 as the proton acceptor; (d) open-cubane crystal or solvent water-W2 (oxyl) nucleophilic attack with O5 as the proton acceptor; (e) open-cubane W3 (hydroxyl)-W2 (hydroxyl) coupling; (f) open-cubane W3 (hydroxyl)-W2 (oxo) nucleophilic attack; (g) open-cubane W3 (hydroxyl)-Wx (hydroxyl) coupling; (h) open-cubane W1 (hydroxyl)-W2 (hydroxyl) coupling; (i) open-cubane

W1(hydroxyl)-W2 (oxyl) nucleophilic attack; (j) open-cubane O2 (oxo)-O4 (oxo/oxyl) coupling with deprotonated W1; (k) open-cubane O2 (oxo)-O4 (oxo/oxyl) coupling with deprotonated W2; (l) open-cubane O2 (oxo)-O4 (oxo/oxyl) coupling with deprotonated Wx; (m) open-cubane W1 (hydroxyl)-O4 (oxo) nucleophilic attack; (n) open-cubane W2 (hydroxyl)-O5 (oxo) nucleophilic attack with deprotonated W1; (o) open-cubane W2 (hydroxyl)-O5 (oxo) nucleophilic attack with deprotonated Wx; (p) open-cubane W2 (oxyl)-O5 (oxo) nucleophilic attack with deprotonated W2; (q) open-cubane W3 (hydroxyl)-O5 (oxo) nucleophilic attack; (a') closed-cubane Wx (oxyl)-O5(oxo) coupling; (b') closed-cubane Wx (hydroxyl)-O5 (oxo) nucleophilic attack; (c') closed-cubane W3 (water)-Wx (oxo/oxyl) nucleophilic attack with Ca-bound O of Asp170 as the proton acceptor; (d') closed-cubane W3 (water)-Wx (oxo/oxyl) nucleophilic attack with Mn4-bound O of Asp170 as the proton acceptor; (e') closed-cubane crystal or solvent water-Wx (oxo/oxyl) nucleophilic attack with W2 as the proton acceptor; (f') closed-cubane W3 (hydroxyl)-Wx (hydroxyl) coupling; (g') closed-cubane W3 (hydroxyl)-Wx (oxo) nucleophilic attack; (h') closed-cubane W1 (hydroxyl)-W2 (hydroxyl) coupling; (i') closed-cubane W1(hydroxyl)-W2 (oxyl) nucleophilic attack; (j') closed-cubane O2 (oxo)-O4 (oxo/oxyl) coupling with deprotonated W1; (k') closed-cubane O2 (oxo)-O4 (oxo/oxyl) coupling with deprotonated W2; (l') closed-cubane O2 (oxo)-O4 (oxo/oxyl) coupling with deprotonated Wx; (m') closed-cubane W1 (hydroxyl)-O4 (oxo) nucleophilic attack; (n') closed-cubane Wx (hydroxyl)-W2 (oxo) nucleophilic attack; (o') closed-cubane W2 (hydroxyl)-Wx (oxo) nucleophilic attack; (p') closed-cubane W3 (water)-O5 (oxo) nucleophilic attack with COO^- of Glu189 as the proton acceptor. (q') closed-cubane W3 (hydroxyl)-O5 (oxo) nucleophilic attack. All the videos with corresponding letters are uploaded as 'video_open/closed-cubane.zip'.

Table S38 Comparisons of upper and lower limits of barriers and driving forces (in kcal mol^{-1})* in different energy representations in stable spin states for all the mechanisms of O-O bond formation in the open-cubane structures:

Open-cubane	Free energies in solution phases with thermal corrections				Electronic energies in solution phases without thermal corrections		Electronic energies in gas phases without thermal corrections	
Mecha-nisms	[a]Method 1		[b]Method 2		[a]Method 1		$\Delta E^{\neq}$(Rea-TS)	ΔE(Rea-Pro)
	$\Delta G^{\neq}$(Rea-TS)	ΔG(Rea-Pro)	$\Delta G^{\neq}$(Rea-TS)	ΔG(Rea-Pro)	$\Delta E^{\neq}$(Rea-TS)	ΔE(Rea-Pro)		

a	5.3~ 5.9	-15.0~ -14.9	5.3~ 5.8	-15.0~ -14.9	6.3~ 6.9	-13.0~ -12.9	7.7~ 7.8	-8.1~ -8.0
b	25.7~ 30.2	11.1~ 16.4	25.7~ 30.4	11.1~ 16.5	27.1~ 33.7	14.5~ 18.5	25.1~ 32.7	14.8~ 23.5
c	34.0~ 36.6	8.8~ 11.1	34.1~ 36.5	8.7~ 11.1	34.7~ 37.0	9.6~ 12.5	35.3~ 38.2	15.8~ 17.6
d	29.0~ 30.2	-8.6~ -7.9	29.0~ 30.3	-8.5~ -7.7	30.3~ 32.1	-7.8~ -5.9	31.6~ 34.2	-5.5~ 2.7
e	19.8~ 21.9	-5.3~ -2.4	19.7~ 21.9	-5.3~ -2.5	21.9~ 23.5	-3.2~ -0.1	22.3~ 24.4	-2.8~ 3.9
f	7.3 ~8.4	-26.5~ -22.9	7.5 ~8.4	-26.5~ -23.0	8.8 ~10.1	-23.3~ -19.8	9.1 ~12.7	-20.5~ -17.6
g	16.7~ 18.8	-9.4~ -3.8	16.7~ 18.9	-9.4~ -3.6	18.2~ 20.4	-7.3~ -1.5	19.2~ 22.9	-8.3~ -5.5
h	28.4~ 29.2	2.8~ 4.6	28.4~ 29.3	2.8~ 4.7	30.1~ 33.7	3.2~ 7.3	32.5~ 38.2	3.9~ 9.6
i	18.6~ 18.7	-7.4~ -6.7	18.5~ 18.7	-7.2~ -6.7	20.6~ 22.8	-5.1 ~ -3.7	21.9~ 26.0	-7.1 ~ -1.1
j	20.3~ 38.8	-3.6~ 5.8	20.3~ 39.0	-3.6~ 5.9	22.8~ 40.5	-1.2~ 7.7	22.8~ 44.2	-4.6~ 12.6
k	33.6~ 36.6	10.6~ 14.5	33.6~ 36.7	10.6~ 14.7	36.8~ 39.2	13.7~ 17.0	35.8~ 40.6	15.4~ 21.6
l	38.6~ 56.1	20.0~ 30.1	38.6~ 55.9	20.1~ 30.2	41.9~ 59.2	23.1~ 34.0	43.3~ 59.1	20.1~ 38.3
m	14.1~ 18.4	-2.9~ 0.1	14.1~ 18.3	-2.9~ 0.3	16.3~ 21.3	0.8~ 2.9	17.3~ 21.1	-0.5~ 4.3
n	19.6~ 25.6	4.5~ 8.6	19.6~ 25.6	4.5~ 8.5	22.1~ 28.7	7.5~ 10.8	19.4~ 29.2	4.0~ 9.1
o	49.9~ 54.3	-10.2~ -2.3	49.8~ 54.3	-10.2~ -2.2	53.2~ 58.3	-7.2~ 1.2	49.8~ 61.3	-8.2~ 5.2
p	19.4~ 24.9	-1.6~ 4.0	19.4~ 24.7	-1.6~ 4.1	21.6~ 27.3	2.8~ 6.4	22.6~ 26.3	-2.5~ 6.9
q	9.2~ 10.2	-4.6~ -2.8	9.2~ 10.2	-4.5~ -2.9	12.5~ 14.2	-1.9~ 1.5	13.5~ 17.2	-5.8~ 3.3
W3 deproton -ation	17.8~ 21.5	11.9~ 18.8	17.8~ 21.6	11.9~ 19.2	21.0~ 23.8	13.9~ 22.2	19.3~ 24.5	15.9~ 22.6

Table S39 Comparisons of upper and lower limits of barriers and driving forces (in kcal mol^{-1})* in different energy representations in stable spin states for all the mechanisms of O-O bond formation in the closed-cubane structures:

Closed-cubane	Free energies in solution phases with thermal corrections	Electronic energies in solution phases	Electronic energies in gas phases

Mecha-nisms					without thermal corrections		without thermal corrections	
	[a]Method 1		[b]Method 2		[a]Method 1		$\Delta E^{\neq}$(Rea-TS)	ΔE(Rea-Pro)
	$\Delta G^{\neq}$(Rea-TS)	ΔG(Rea-Pro)	$\Delta G^{\neq}$(Rea-TS)	ΔG(Rea-Pro)	$\Delta E^{\neq}$(Rea-TS)	ΔE(Rea-Pro)		
a'	11.0~16.0	-5.9~-3.0	11.2~16.1	-5.8~-3.0	12.1~15.8	-5.5~-2.9	12.5~16.7	-4.4~-1.6
b'	6.5~15.2	-2.3~5.0	6.5~15.2	-2.3~5.0	8.5~17.3	0.8~8.5	7.2~16.1	-2.0~4.8
c'	51.5~52.7	51.3~52.8	51.5~52.5	51.3~52.6	55.5~57.7	56.3~57.8	50.5~53.7	51.7~60.8
d'	47.1~47.9	45.9~48.9	47.1~47.9	46.0~48.9	52.3~54.5	49.9~52.0	57.3~58.6	53.4~55.5
e'	38.6~41.8	37.8~40.8	38.6~41.8	37.8~40.9	40.6~44.4	38.5~43.0	39.8~45.2	36.6~45.0
f'	3.6~3.9	-15.2~-14.6	3.6~3.8	-15.2~-14.6	5.9~6.1	-12.3~-11.6	4.0~7.8	-9.3~-7.2
g'	0.4~1.1	-27.0~-18.2	0.6~1.1	-27.2~-18.1	3.8~5.1	-24.8~-15.3	3.7~4.5	-19.1~-11.9
h'	23.5~23.8	-6.7~-6.5	23.6~23.8	-6.7~-6.5	26.5~27.8	-3.7~-2.5	24.5~29.0	-2.6~2.8
i'	21.6~23.2	7.6~16.2	21.6~23.4	7.6~16.9	25.4~27.2	9.9~18.7	22.4~26.2	7.5~16.7
j'	25.3	5.7	25.2	5.6	28.8	9.0	27.5	8.6
k'	51.3~66.6	53.4~61.9	51.3~66.9	53.4~62.0	55.3~68.6	59.4~66.9	52.9~70.1	63.4~68.5
l'	46.2~52.2	27.4~36.6	46.2~52.1	27.4~36.7	49.1~58.5	30.7~36.0	47.1~56.5	25.7~36.6
m'	15.5~21.6	5.4~21.3	15.5~21.7	5.3~21.3	18.5~25.6	7.9~27.4	18.5~25.6	8.9~30.4
n'	34.3~36.5	25.7~27.6	34.3~36.4	25.7~27.5	37.1~39.8	29.7~32.6	37.1~39.8	33.3~35.2
o'	43.5~45.2	41.6~43.9	43.5~45.2	41.5~43.9	48.4~48.5	44.6~48.9	41.4~46.5	49.6~52.9
p'	17.9~21.9	-22.3~-14.1	17.9~21.9	-22.2~-13.9	21.1~25.8	-19.3~-10.1	24.1~27.8	-16.3~-8.5
q'	7.2~9.0	-10.0~-6.5	7.2~9.0	-10.0~-6.6	10.2~13.0	-8.4~-3.5	11.2~16.0	-12.0~-1.5
W3 deproton-ation	26.9~29.0	19.3~21.1	27.0~29.0	19.5~21.0	28.6~31.7	24.3~25.2	29.6~35.5	24.0~29.3

* $\Delta G(E)^{\neq}$(Rea-TS) = G(E)(TS) – G(E)(Rea); $\Delta G(E)$(Rea-Pro) = G(E)(Pro) – G(E)(Rea)

Level 1: small basis sets; Level 2: larger basis sets.

[a]**Method 1:**

G(free energy of solute in solvent phase, 298.15K, 1M) = E(single point energy of solute at level 2 in SMD solvent model for the structure optimized at level 1) + ΔG(thermal correction to Gibbs free energy at level 1, 298.15K, 1atm)

[b]**Method 2:**

G(free energy of solute in solvent phase, 298.15K, 1M) = G(free energy of solute in gas phase, 298.15K, 1atm) + ΔG(solvation free energy in SMD solvent model, 1M) + 1.89 kcal/mol (free energy change of gas at 1atm to 1M in solvent due to concentration change, 298.15K)

G(free energy of solute in gas phase, 298.15K, 1atm) = E(single point energy of solute at level 2 in gas phase for the structure optimized at level 1) + ΔG(thermal correction to Gibbs free energy at level 1, 298.15K, 1atm)

ΔG(solvation free energy in SMD solvent model, 1M) = E(single point energy in SMD solvent model at level 1) - E(single point energy in gas phase at level 1)