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Supporting Information

Water Catalysis in Morita-Baylis-Hillman Reaction: A Mechanistic Perspective

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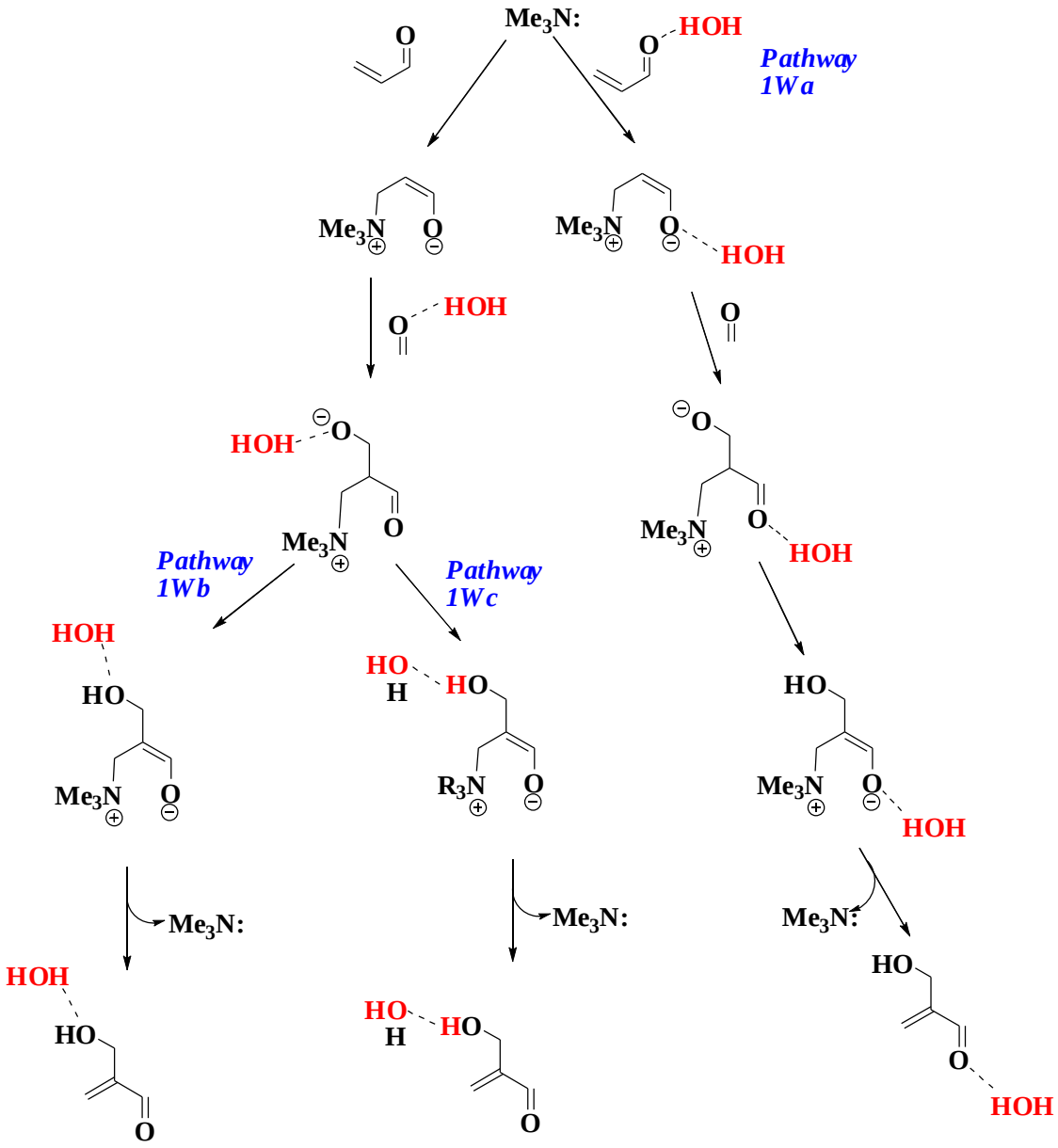

Figure S1. The various modes of one water-assisted pathways in MBH reaction

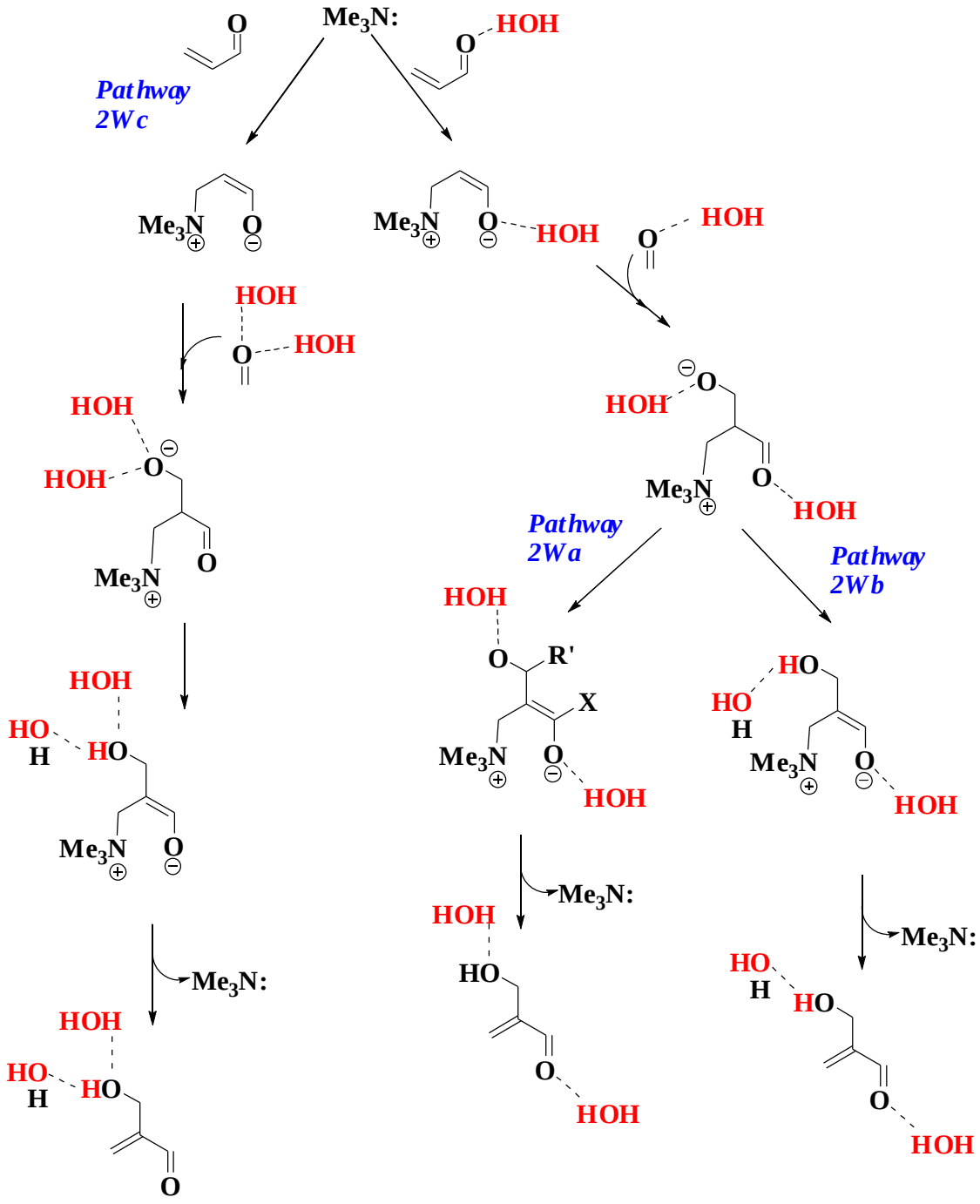

Figure S2. The various modes of two water-assisted pathways MBH reaction.

S1. Computational Methods

All stationary points such as transition states, reactants and products were optimized and characterized first in the gas-phase at the mPW1K/6-31+G** level of theory.[1] The choice of the mPW1K hybrid density functional was on the basis of the earlier reports on the successful applications in describing reaction barriers and other kinetic parameters.[2] The effect of bulk solvation is incorporated using the polarizable continuum model with the integral equation formalism (IEF-PCM). We have employed UAKS radii[3] for the solutes, THF (e = 7.58), DMSO (e = 46.7), and water (e = 78.39) as the continuum solvents. Analysis of the imaginary frequencies as well as intrinsic reaction coordinate (IRC) calculations4 was performed on all the transition states. The geometries of the intermediates and pre-reacting complexes (PRC) were obtained using extended IRC runs, starting from respective transition states. The final geometries obtained from the IRC trajectory on both sides of the first order saddle point were further subjected to full geometry optimization using stringent optimization conditions using the 'OPT=CALCFC' option as implemented in Gaussian03 suite of program. This approach enables a careful *walk down* from the final IRC point on the PES till a minimum is identified. The Gibbs free energies in the gas-phase were obtained by including zero-point vibrational energy as well as thermal corrections to the *bottom-of-the-well* values. All the electronic structure calculations are performed using the Gaussian03 suite of the quantum chemical programs.[5] To develop a qualitative picture on the position-orientation of coordinated solvent molecules in the transition state, ab initio molecular dynamics simulation are performed using the Car-Perinello molecular dynamics protocol.[6] It should be reckoned that ab initio molecular dynamics is desirable when details on solvent

coordination at the transition states are examined. The transition state for the C-C bond formation is placed in a cubic box of dimension 13 Å with eighteen water molecules inside the box. The AIMD run includes a constrained dynamics with the frozen incipient C-C bond while rest of the solute as well as the solvent molecules are subjected to 2 ps of equilibration (300K) and 2 ps production run. The gradient-corrected density functional of Becke with Lee, Yang and Parr correlation functional i.e. BLYP is employed.[7] The electrons are represented using the Vanderbilt's ultra soft pseudopotentials.[8] The Kohn-Sham orbitals are expanded using plane wave basis sets with cutoff radii of 25 Ry. All the simulations are done with fictitious electron mass of 400.0 a.u. and time step of 4 a.u. The trajectory of the molecular dynamics studies are analyzed using MOLDEN and VMD.[9]

S2. AIMD Simulation

In the production run of ab initio MD simulations it is observed that strong hydrogen bonding interaction (O···H distance in the range ~1.4 – 2.5 Å) is maintained dynamically by two water molecules and the oxygen atom of the developing alkoxide. One of these hydrogen bonds are conserved throughout the run. Moreover one water molecule is found to be hydrogen bonded with the carbonyl oxygen of the Michael acceptor (O···H distance in the range 1.7 – 2.0 Å). One interesting observation pertaining to the orientation of the reactant fragments in **TS(1b-1c)** in the constrained MD is that the orientation of the incipient alkoxide remains unaltered with respect to the C- N bond. These findings justify the incorporation two water molecules in near vicinity of the formaldehyde fragment in our electronic structure calculations.

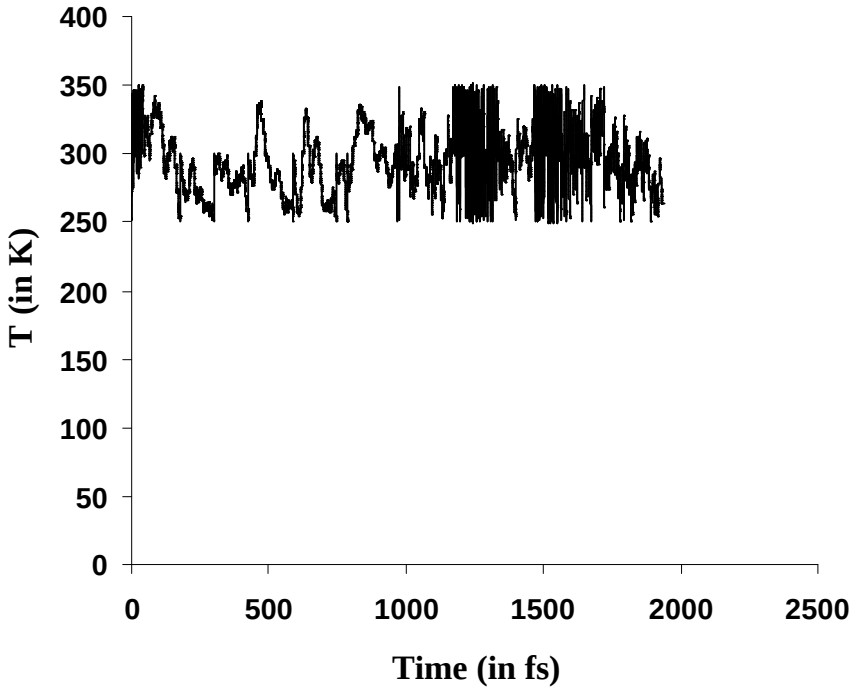

Figure S3. Temperature equilibration run on **TS(b-c)** with eighteen water molecules at 300 ± 50 K.

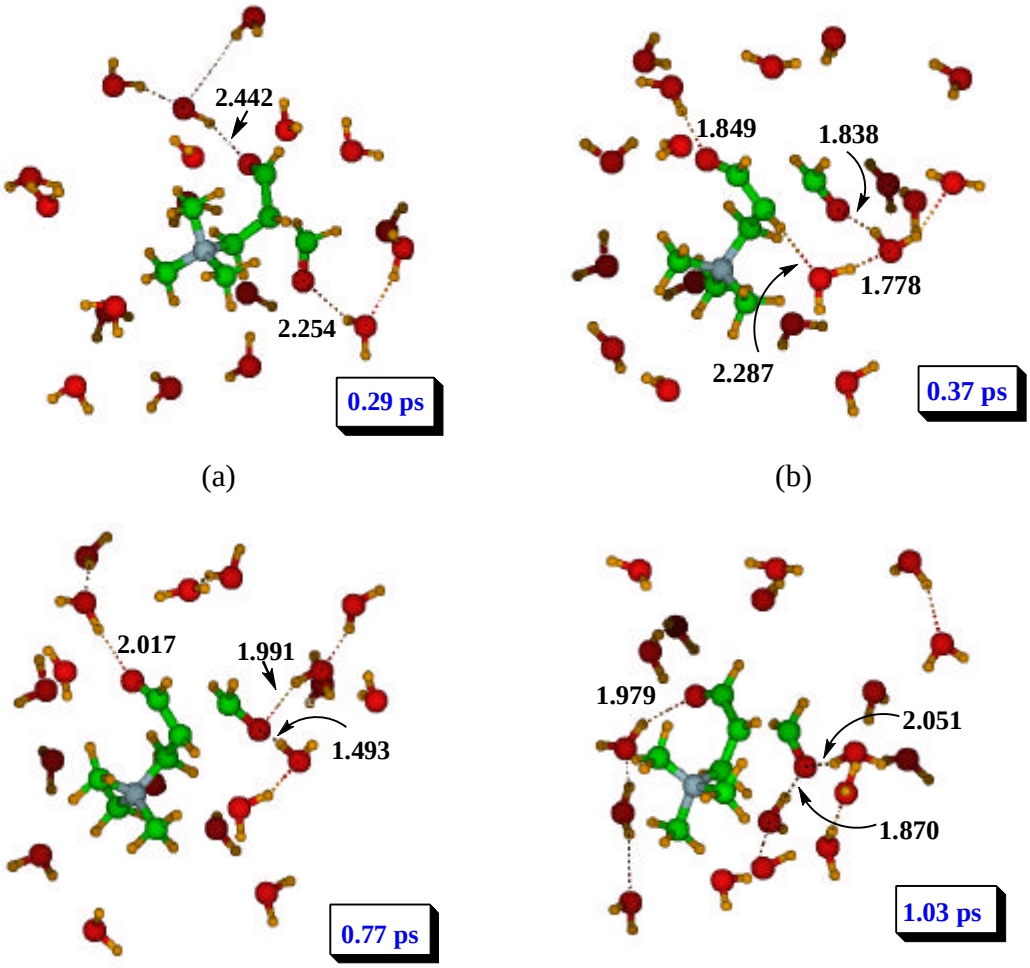

Figure S4. Representative snaps of MD production run.

S3. Calculation of Catalytic Power of Water

The potential energy barrier ($E^{‡}_{1W}$) associated with one water molecule assisted reaction can be expressed as

$$E^{‡}_{1W} = E^{‡} - E^{R}_{1W} + E^{TS}_{1W} \quad \text{(Equation 1)}$$

where $E^{‡}$ is the activation energy of the unassisted mode. E^{R}_{1W} and E^{TS}_{1W} respectively represent the binding energies of the intermediate and transition state with water molecule.

The catalytic contribution of water molecule (E^{Cat}_{1W}) is given as

$$E^{Cat}_{1W} = E^{‡} - E^{‡}_{1W} = E^{R}_{1W} - E^{TS}_{1W} \quad \text{(Equation 2)}$$

Similarly for two water cases

$$E^{Cat}_{2W} = E^{‡} - E^{‡}_{2W} = E^{R}_{2W} - E^{TS}_{2W} \quad \text{(Equation 3)}$$

Thus, we have employed Equations 2 and 3 to estimate the catalytic power of water in various modes of water-assisted MBH reaction. The results are summarized in Table S1.

Table S1. The Catalytic Power of the water molecule(s) in various modes of water-assisted C- C bond formation as well as proton transfer steps in MBH reaction

Species	*Mode of Water Assistance*						
	1Wa	**1Wb**	**1Wc**	**2Wa**	**2Wb**	**2Wc**	**2Wd**
TS(b-c)	-5.01	15.01	15.01	14.49	14.49	16.78	16.78
TS(c-d)	2.44	-11.16	63.56	-4.92	60.18	59.92	129.88

[a] In kcal/mol. Computed at the mPW1K/6-31+G** level of theory.

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(1) (a) B. J. Lynch, P. L. Fast, M. Harris, D. G. Truhlar, *J. Phys. Chem. A* **2000**, *104*, 4811; (b) B. J. Lynch, D. G. Truhlar, *J. Phys. Chem. A* **2001**, *105*, 2936; (c) R. Ditchfield, W. J. Hehre, J. A. Pople, *J. Chem. Phys*. **1971**, *54*, 724; (d) W. J. Hehre, R. Ditchfield, J. A. Pople, *J. Chem. Phys*. **1972**, *56*, 2257; (e) M. S. Gordon, *Chem. Phys. Lett*. **1980**, *76*, 163; (f) P. C. Hariharan, J. A. Pople, *Theo. Chim. Acta*. **1973**, *28*, 213.

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Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

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Table S2. Thermochemical parameters[a] obtained at the CBS-4M level of theory for all the stationary points

Species	E[b]	H[c]	G[d]
NMe_3	-174.152978	-174.152034	-174.186072
Acrolein	-191.624275	-191.623331	-191.654824
CH_2O	-114.357188	-114.356244	-114.381687
Water	-76.347115	-76.346171	-76.367594
a	-365.779862	-365.778918	-365.829012
TS(a-b)	-365.762646	-365.761702	-365.805668
b	-365.762607	-365.761662	-365.805351
TS(b-c)	-480.111747	-480.110803	-480.160005
c	-480.117727	-480.116783	-480.164194
TS(c-d)	-480.070885	-480.069941	-480.118078
d	-480.150491	-480.149547	-480.199252
TS(d-e)	-480.147075	-480.146131	-480.196854
e	-480.161589	-480.160645	-480.217171
a_{1Wa}	-442.129788	-442.128844	-442.186785
$TS(a\text{-}b)_{1Wa}$	-442.117494	-442.11655	-442.168964
b_{1Wa}	-442.128645	-442.1277	-442.176111
$TS(b\text{-}c)_{1Wa}$	-556.471427	-556.470483	-556.525037
c_{1Wa}	-556.470716	-556.469772	-556.524683
$TS(c\text{-}d)_{1Wa}$	-556.446462	-556.445517	-556.498406
d_{1Wa}	-556.516065	-556.515121	-556.56972
$TS(d\text{-}e)_{1Wa}$	-556.506892	-556.505948	-556.562646
e_{1Wa}	-556.525809	-556.524865	-556.585838
$TS(b\text{-}c)_{1Wb}$	-556.478373	-556.477429	-556.532831
c_{1Wb}	-556.486762	-556.485818	-556.538317
$TS(c\text{-}d)_{1Wb}$	-556.451732	-556.450787	-556.503442
d_{1Wb}	-556.509281	-556.508337	-556.563788
$TS(d\text{-}e)_{1Wb}$	-556.504833	-556.503889	-556.560482
e_{1Wb}	-556.524726	-556.523782	-556.583539
$TS(c\text{-}d)_{1Wc}$	-556.470163	-556.469219	-556.520171
d_{1Wc}	-556.502636	-556.501692	-556.558733
$TS(d\text{-}e)_{1Wc}$	-556.497532	-556.496588	-556.496588
e_{1Wc}	-556.514072	-556.513128	-556.57871
$TS(b\text{-}c)_{2Wa}$	-632.840227	-632.839283	-632.899911
c_{2Wa}	-632.841173	-632.840229	-632.900998
$TS(c\text{-}d)_{2Wa}$	-632.810244	-632.8093	-632.867832
d_{2Wa}	-632.872249	-632.871305	-632.931247

[a]In atomic unit. [b]CBS-4M energy. [c]CBS-4M enthalpy. [d]CBS-4M free energy.

Table S2. (Contd…)

Species	E[b]	H[c]	G[d]
TS(d-e)$_{2Wa}$	-632.858176	-632.857232	-632.9213
e$_{2Wa}$	-632.859243	-632.858299	-632.928535
TS(c-d)$_{2Wb}$	-632.829296	-632.828351	-632.885265
d$_{2Wb}$	-632.866842	-632.865897	-632.927753
TS(d-e)$_{2Wb}$	-632.857921	-632.856977	-632.922034
e$_{1Wb}$	-632.878309	-632.877365	-632.945647
TS(b-c)$_{2Wc}$	-632.835993	-632.835048	-632.896252
c$_{2Wc}$	-632.846538	-632.845594	-632.904187
TS(c-d)$_{2Wc}$	-632.847483	-632.846538	-632.902826
d$_{2Wc}$	-632.864232	-632.863288	-632.923547
TS(d-e)$_{2Wc}$	-632.858357	-632.857413	-632.920903
e$_{2Wc}$	-632.878127	-632.877183	-632.944348
c$_{2Wd}$	-632.8463	-632.845355	-632.904644
TS(c-d)$_{2Wd}$	-632.834449	-632.833505	-632.890012
d$_{2Wd}$	-632.85517	-632.854226	-632.915285
TS(d-e)$_{2Wd}$	-632.853981	-632.853037	-632.91576
e$_{2Wd}$	-632.871797	-632.871797	-632.937666
TS(b-c)$_{1Wb(1)}$	-556.468857	-556.467913	-556.523329
TS(b-c)$_{2We}$	-632.828211	-632.827266	-632.88997
TS(b-c)$_{2Wf}$	-632.827652	-632.826707	-632.889623
TS(b-c)$_{2Wg}$	-632.83562	-632.834675	-632.894524
TS(b-c)$_{2Wh}$	-632.834513	-632.833569	-632.893554
TS(c-d)$_{2Wi(1)}$	-632.83715	-632.836206	-632.893784
TS(c-d)$_{2Wi(2)}$	-632.793966	-632.793022	-632.854731
TS(c-d)$_{2Wi(3)}$	-632.833926	-632.832982	-632.88931

[a]In atomic unit. [b]CBS-4M energy. [c]CBS-4M enthalpy. [d]CBS-4M free energy.

Table S3. Thermochemical parameters[a] obtained at the mPW1K/6-31+G** level of theory for all the stationary points

Species	E[b]	H[c]	G[d]
NMe_3	-174.320546	-174.314276	-174.347737
Acrolein	-191.79059	-191.785287	-191.817071
CH_2O	-114.435277	-114.43147	-114.456918
Water	-76.381634	-76.377854	-76.399244
a	-366.114426	-366.101877	-366.153887
TS(a-b)	-366.09514	-366.084861	-366.129222
b	-366.094795	-366.084588	-366.128234
TS(b-c)	-480.522803	-480.510465	-480.560043
c	-480.526816	-480.514591	-480.563486
TS(c-d)	-480.485467	-480.473411	-480.522727
d	-480.564076	-480.5516	-480.600794
TS(d-e)	-480.561915	-480.548943	-480.600638
e	-480.588768	-480.574372	-480.631362
a_{1Wa}	-442.502717	-442.486499	-442.54951
$TS(a\text{-}b)_{1Wa}$	-442.48868	-442.474877	-442.5297
b_{1Wa}	-442.497403	-442.4849	-442.533688
$TS(b\text{-}c)_{1Wa}$	-556.921316	-556.906221	-556.961944
c_{1Wa}	-556.92169	-556.906414	-556.96183
$TS(c\text{-}d)_{1Wa}$	-556.896603	-556.882188	-556.935631
d_{1Wa}	-556.966134	-556.951112	-557.006021
$TS(d\text{-}e)_{1Wa}$	-556.959636	-556.943651	-557.001633
e_{1Wa}	-556.977474	-556.959797	-557.024686

[a]In atomic unit. [b]Sum of electronic and zero-point Energies. [c]Sum of electronic and thermal Enthalpies. [d]Sum of electronic and thermal Free Energies.

Table S3. (Contd…)

Species	E[b]	H[c]	G[d]
TS(b-c)$_{1Wb}$	-556.928431	-556.912924	-556.969866
c$_{1Wb}$	-556.939652	-556.92505	-556.979364
TS(c-d)$_{1Wb}$	-556.902681	-556.888244	-556.942154
d$_{1Wb}$	-556.95979	-556.944244	-557.00086
TS(d-e)$_{1Wb}$	-556.955846	-556.940049	-556.997238
e$_{1Wb}$	-556.980472	-556.963077	-557.026515
TS(c-d)$_{1Wc}$	-556.922144	-556.908624	-556.959423
d$_{1Wc}$	-556.953863	-556.938207	-556.995256
TS(d-e)$_{1Wc}$	-556.950826	-556.934705	-556.993583
e$_{1Wc}$	-556.969288	-556.950679	-557.018417
TS(b-c)$_{2Wa}$	-633.32719	-633.309183	-633.371754
c$_{2Wa}$	-633.329817	-633.311776	-633.375293
TS(c-d)$_{2Wa}$	-633.29881	-633.281391	-633.342624
d$_{2Wa}$	-633.36099	-633.34273	-633.405509
TS(d-e)$_{2Wa}$	-633.351676	-633.331723	-633.400315
e$_{2Wa}$	-633.354476	-633.354476	-633.410513
TS(c-d)$_{2Wb}$	-633.318601	-633.302067	-633.359782
d$_{2Wb}$	-633.355735	-633.355735	-633.400402
TS(d-e)$_{2Wb}$	-633.348489	-633.329096	-633.395072
e$_{1Wb}$	-633.371213	-633.350693	-633.421775
TS(b-c)$_{2Wc}$	-633.30849	-633.289721	-633.354449
c$_{2Wc}$	-633.332721	-633.315562	-633.375957
TS(c-d)$_{2Wc}$	-633.336411	-633.320117	-633.377077
d$_{2Wc}$	-633.353021	-633.334866	-633.397056
TS(d-e)$_{2Wc}$	-633.347251	-633.328295	-633.392836
e$_{2Wc}$	-633.373891	-633.353743	-633.42448
c$_{2Wd}$	-633.334351	-633.317091	-633.378041
TS(c-d)$_{2Wd}$	-633.32339	-633.307444	-633.364688
d$_{2Wd}$	-633.34682	-633.328487	-633.392846
TS(d-e)$_{2Wd}$	-633.344333	-633.344333	-633.390903
e$_{2Wd}$	-633.364886	-633.344315	-633.41586

[a]In atomic unit. [b]Sum of electronic and zero-point Energies. [c]Sum of electronic and thermal Enthalpies. [d]Sum of electronic and thermal Free Energies.

Table S4. The $G_{(solvation)}$ (in au) with all electrostatic and nonelectrostatic terms computed at the IEF-PCM$_{(Solvent)}$/mPW1K/6-31+G**//mPW1K/6-31+G** level [a]

Species	E_{THF}	E_{DMSO}	E_{Water}
NMe_3	-174.447782	-174.44837	-174.449706
Acrolein	-191.85628	-191.856994	-191.859418
CH_2O	-114.464214	-114.464696	-114.466333
Water	-76.408489	-76.409518	-76.414859
TS(a-b)	-366.297326	-366.299795	-366.306539
TS(b-c)	-480.777159	-480.783629	-480.800885
TS(c-d)	-480.734354	-480.739715	-480.754181
TS(d-e)	-480.797029	-480.799432	-480.809973
TS(a-b)$_{1Wa}$	-442.713997	-442.716151	-442.724258
TS(b-c)$_{1Wa}$	-557.193778	-557.199068	-557.215458
TS(c-d)$_{1Wa}$	-557.159435	-557.162698	-557.173586
TS(d-e)$_{1Wa}$	-557.215224	-557.21699	-557.226638
TS(b-c)$_{1Wb}$	-557.188926	-557.191561	-557.202666
TS(c-d)$_{1Wb}$	-557.164701	-557.1676	-557.178424
TS(d-e)$_{1Wb}$	-557.21181	-557.213655	-557.223831
TS(c-d)$_{1Wc}$	-557.195294	-557.200447	-557.222363
TS(d-e)$_{1Wc}$	-557.208972	-557.211188	-557.221934
TS(b-c)$_{2Wa}$	-633.610968	-633.613293	-633.624785
TS(c-d)$_{2Wa}$	-633.583321	-633.585822	-633.597697
TS(d-e)$_{2Wa}$	-633.627898	-633.629485	-633.641438
TS(c-d)$_{2Wb}$	-633.607823	-633.610877	-633.622955
TS(d-e)$_{2Wb}$	-633.627623	-633.629247	-633.639509
TS(b-c)$_{2Wc}$	-633.592352	-633.594832	-633.606543
TS(c-d)$_{2Wc}$	-633.621004	-633.623074	-633.632769
TS(d-e)$_{2Wc}$	-633.627765	-633.629481	-633.63957
TS(c-d)$_{2Wd}$	-633.610783	-633.613437	-633.62435
TS(d-e)$_{2Wd}$	-633.626971	-633.629138	-633.64165

a These energy terms are represented as E since these are single-point energy calculations without the inclusion of entropic contributions of the solute

Table S5. Activation Parameters for Various Steps Involved in MBH Reaction Obtained at the mPW1K/6-31+G** Level of Theory[a]

(a) Gibbs Free Energies of Activation

Species	**W_0**	**1Wa**	**1Wb**	**1Wc**	**2Wa**	**2Wb**	**2Wc**	**2Wd**
a	6.8	9.1	-[b]	-[b]	-[c]	-[c]	-[b]	-[b]
a-b	22.3 (22.1)	21.6	-[b]	-[b]	-[c]	-[c]	-[b]	-[b]
b	22.9	19.0	-[b]	-[b]	-[c]	-[c]	-[b]	-[b]
b-c	38.7 (39.3)	37.0	32.1	32.1	30.4	30.4	41.3	41.3
c	36.5	37.1	26.1	26.1	28.2	28.2	27.8	26.5
c-d	62.1 (62.5)	53.5	49.5	38.6	48.7	37.9	27.1	34.8
d	13.1	9.4	12.6	16.1	9.2	12.4	14.5	17.2
d-e	13.2 (15.9)	12.1	14.9	17.8	12.5	15.8	17.2	18.4
e	-6.0	-2.3	-3.5	1.6	6.1	-1.0	-2.7	2.7

[a]Relative free energy (in kcal/mol) with respect to infinitely separated reactants. Values in parenthesis are calculated at the mPW1K/6-31+G* levels of theory. [b]Similar to the **W_0** mode. [c]Similar to the **1Wa** mode.

Table S5. (Contd…) (b) Enthalpy of Activation

Species	**W_0**	**1Wa**	**1Wb**	**1Wc**	**2Wa**	**2Wb**	**2Wc**	**2wd**
a	-1.4	-5.7	- [b]	- [b]	- [c]	- [c]	- [b]	- [b]
a-b	9.2	1.6	- [b]	- [b]	- [c]	- [c]	- [b]	- [b]
b	9.4	-4.7	- [b]	- [b]	- [c]	- [c]	- [b]	- [b]
b-c	12.9	1.7	-2.5	-2.5	-14.1	-14.1	-1.9	-1.9
c	10.3	1.5	-10.1	-10.1	-15.7	-15.7	-18.1	-19.0
c-d	36.2	16.7	12.9	0.16	3.4	-9.6	-20.9	-13.0
d	-12.9	-26.5	-22.2	-18.4	-35.1	-43.3	-30.2	-26.2
d-e	-11.2	-21.8	-19.5	-16.2	-28.2	-26.6	-26.1	-36.1
e	-27.2	-31.9	-34.0	-26.2	-42.5	-40.1	-42.0	-36.1

Relative enthalpy of activation (in kcal/mol) with respect to infinitely separated reactants.
[b]Similar to the **W_0** mode. [c]Similar to the **1Wa** mode.

Table S5. (Contd…) (c) Activation Energies

Species	**W_0**	**1Wa**	**1Wb**	**1Wc**	**2Wa**	**2Wb**	**2Wc**	**2Wd**
a	-2.1	-6.2	- [b]	- [b]	- [c]	- [c]	- [b]	- [b]
a-b	10.0	2.6	- [b]	- [b]	- [c]	- [c]	- [b]	- [b]
b	10.2	-2.9	- [b]	- [b]	- [c]	- [c]	- [b]	- [b]
b-c	14.8	4.2	-0.2	-0.2	-11.0	-11.0	0.7	0.7
c	12.3	4.0	-7.3	-7.3	-12.6	-12.6	-14.5	-15.5
c-d	38.2	19.7	15.9	3.7	6.8	-5.6	-16.8	-8.6
d	-11.1	-23.9	-19.9	-16.2	-32.2	-28.9	-27.2	-23.3
d-e	-9.7	-19.8	-17.4	-14.3	-26.3	-24.3	-23.6	-21.7
e	-26.6	-31.0	-32.9	-25.9	-28.1	-38.6	-40.3	-34.6

[a] Relative activation energy (in kcal/mol) with respect to infinitely separated reactants (ZPE corrected). [b]Similar to the **W_0** mode. [c]Similar to the **1Wa** mode.

Table S6. The Energies of FMOs (in eV) of formaldehyde in water-bound (through hydrogen bonding) modes obtained at the mPW1K/6-31+G** level of theory

Species	E_{HOMO}	E_{LUMO}
Formaldehyde	-0.33384	-0.01978
Fomaldehyde···One Water	-0.34741	-0.02911
Fomaldehyde···Two Water	-0.35589	-0.03421

Table S7. The CBS-4M Activation Parameters[a] for Alternative Higher Energy Transition States Involved in the C-C Bond Formation and Proton Transfer Steps

Transition States	Activation Parameters (in kcal/mol)	
	$?H^{‡}$	$?G^{‡}$
TS(b-c)		
1Wb(1)	6.2	41.9
2We	-7.1	38.0
2Wf	-2.1	42.5
2Wg	-1.7	42.8
2Wh	-6.7	39.7
2Wh	-6.0	40.3
TS(c-d)		
2Wj(1)	-7.7	40.1
2Wj(2)	19.4	64.7
2Wj(3)	-5.7	43.0

[a]Relative activation parameters (in kcal/mol) with respect to the infinitely separated reactants. (See Figure S12 for more details)

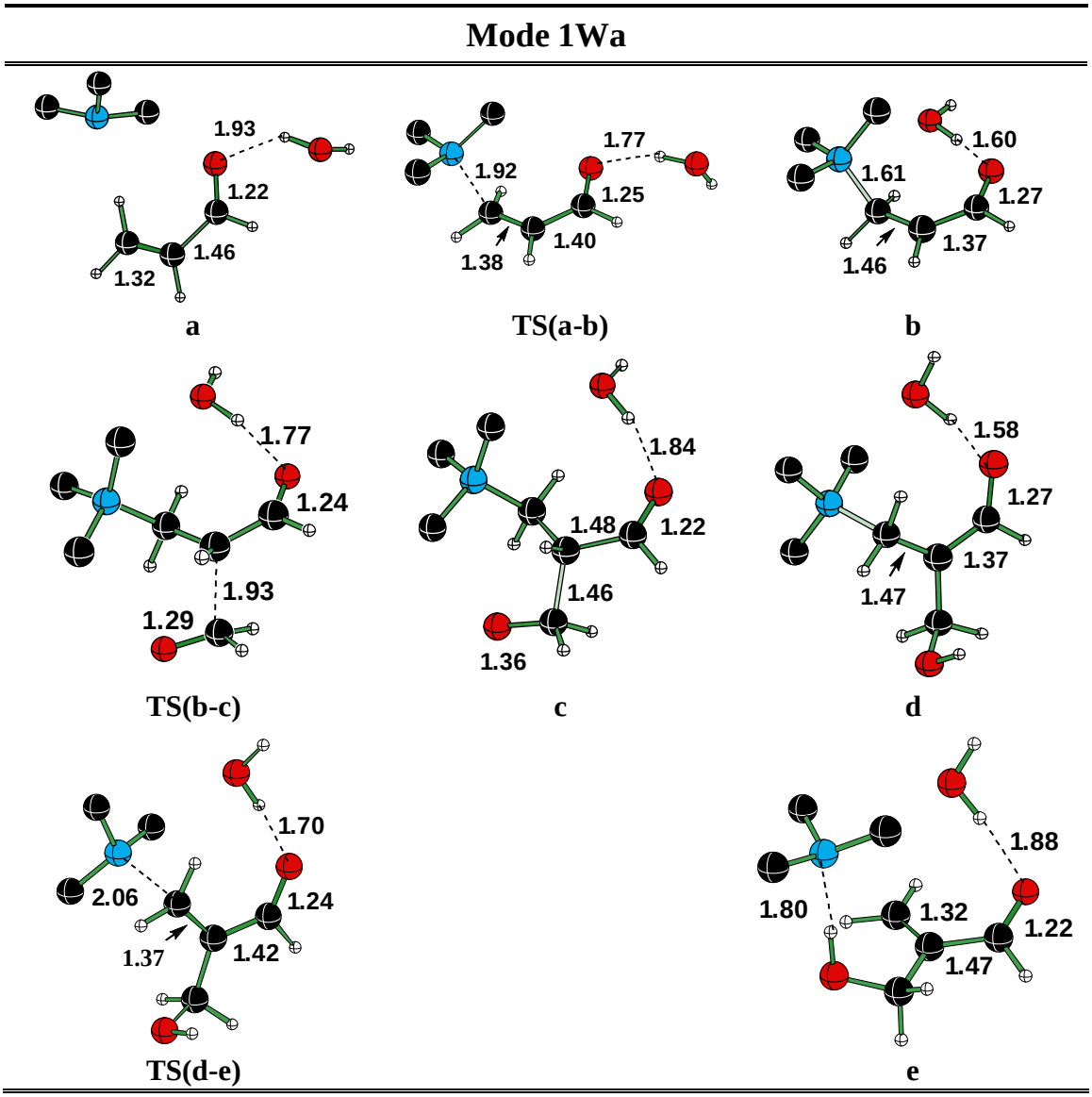


Figure S5. The CBS-4M Optimized Geometries of Transition States and Intermediates in Mode **1Wa**.

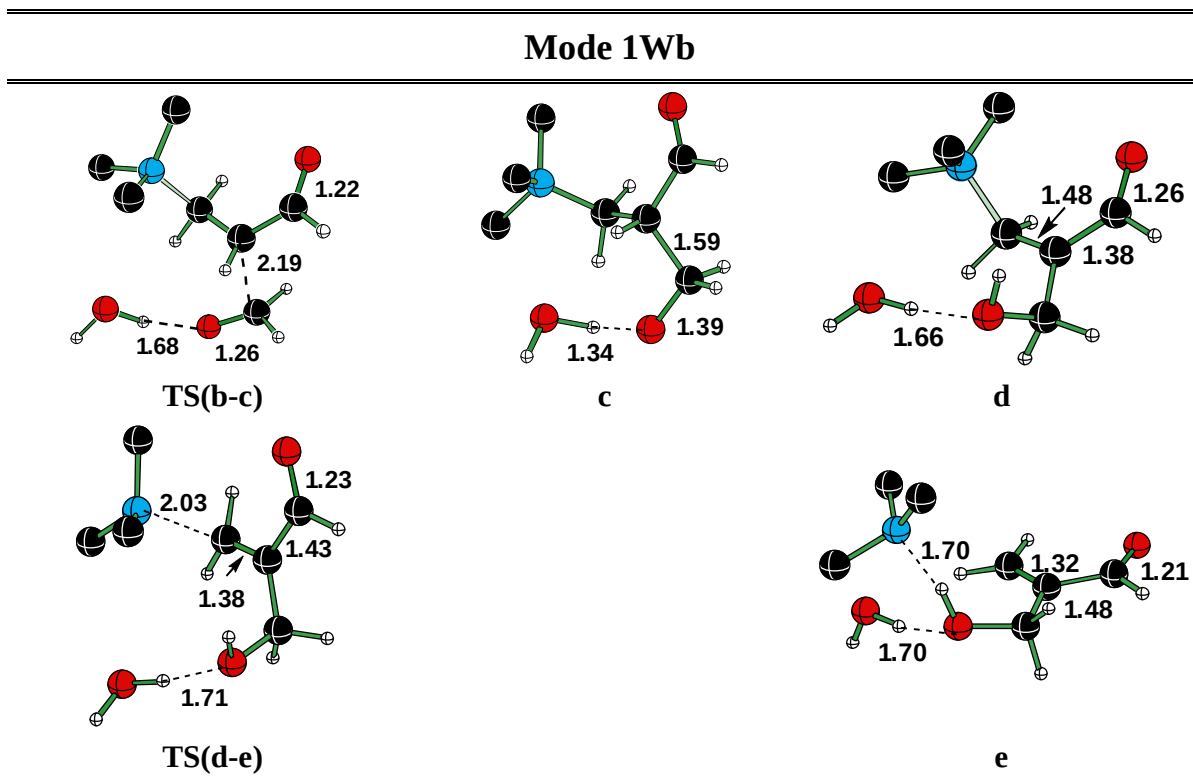


Figure S6. The CBS-4M Optimized Geometries of Transition States and Intermediates in Mode **1Wb**.

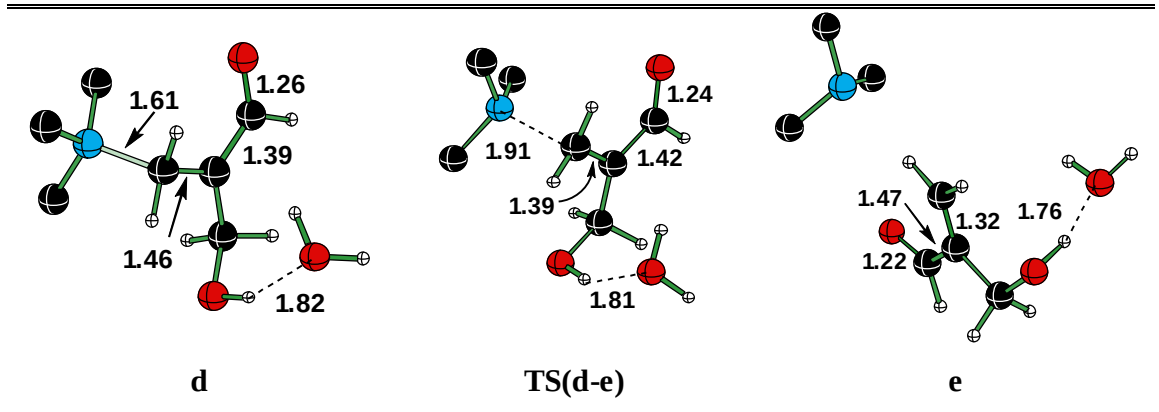


Figure S7. The CBS-4M Optimized Geometries of Transition States and Intermediates in Mode **1Wc**.

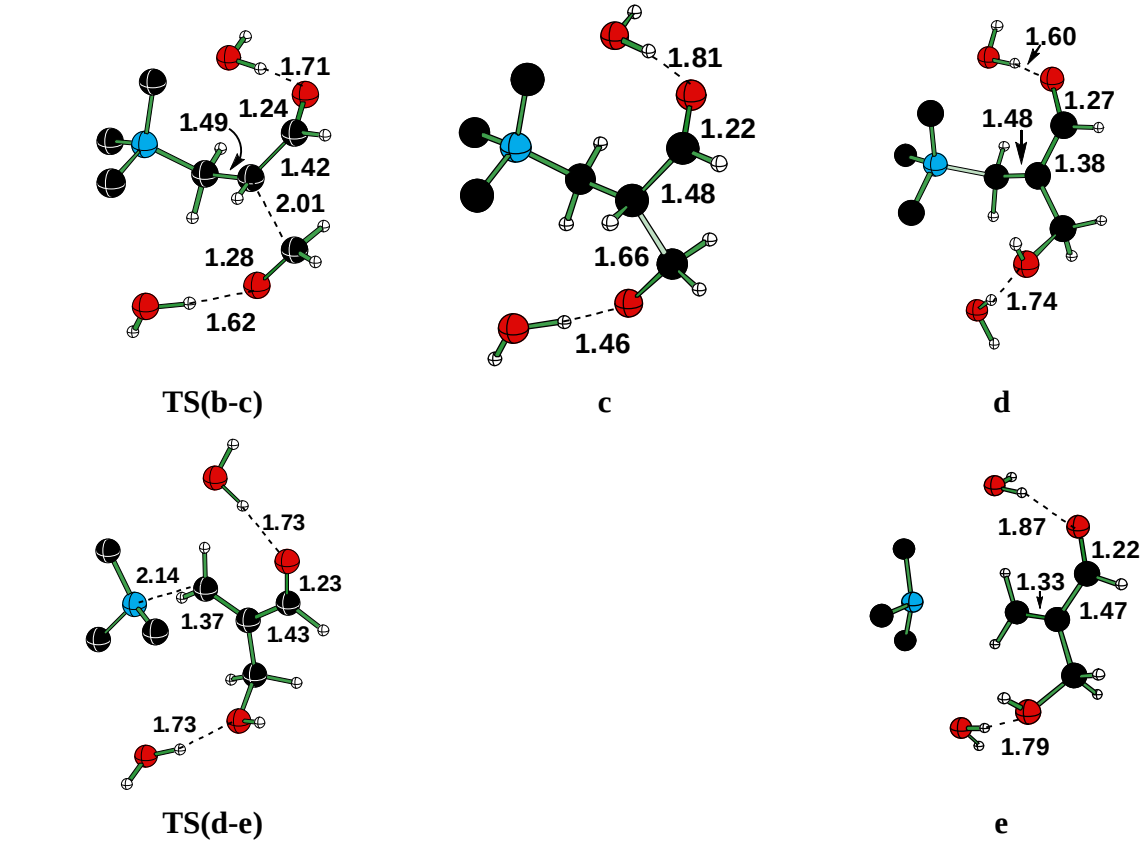


Figure S8. The CBS-4M Optimized Geometries of Transition States and Intermediates in Mode **2Wa**.

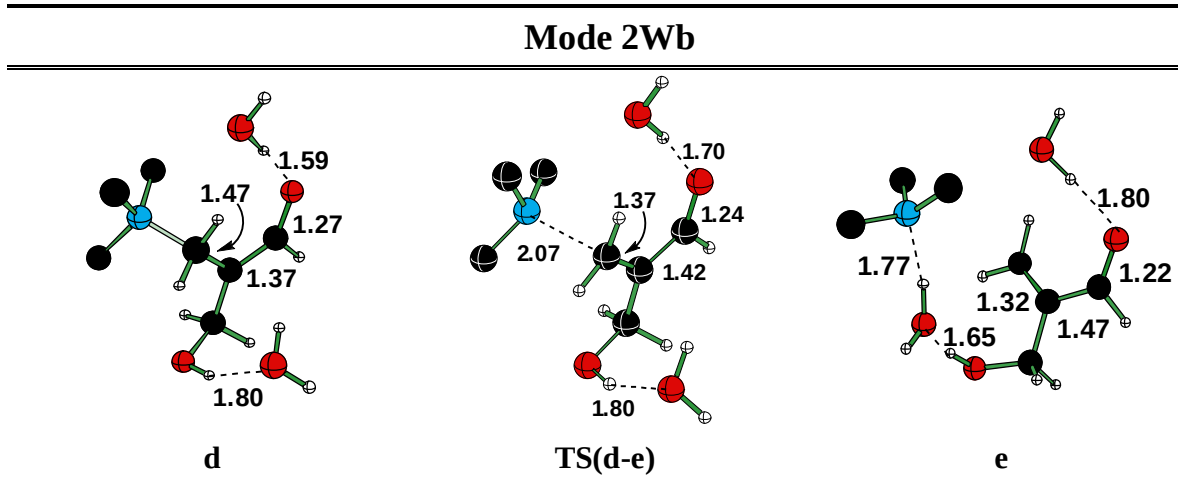


Figure S9. The CBS-4M Optimized Geometries of Transition States and Intermediates in Mode **2Wb**.

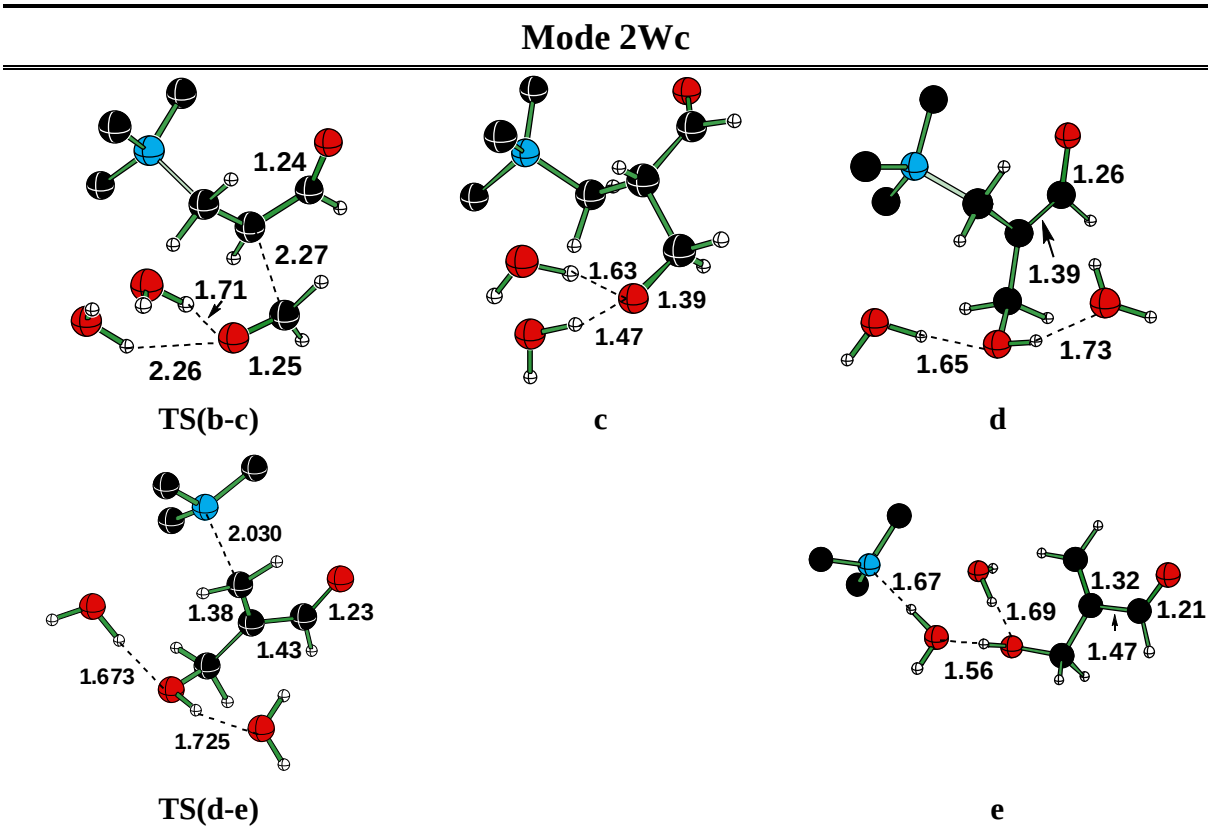


Figure S10. The CBS-4M Optimized Geometries of Transition States and Intermediates in Mode **2Wc**.

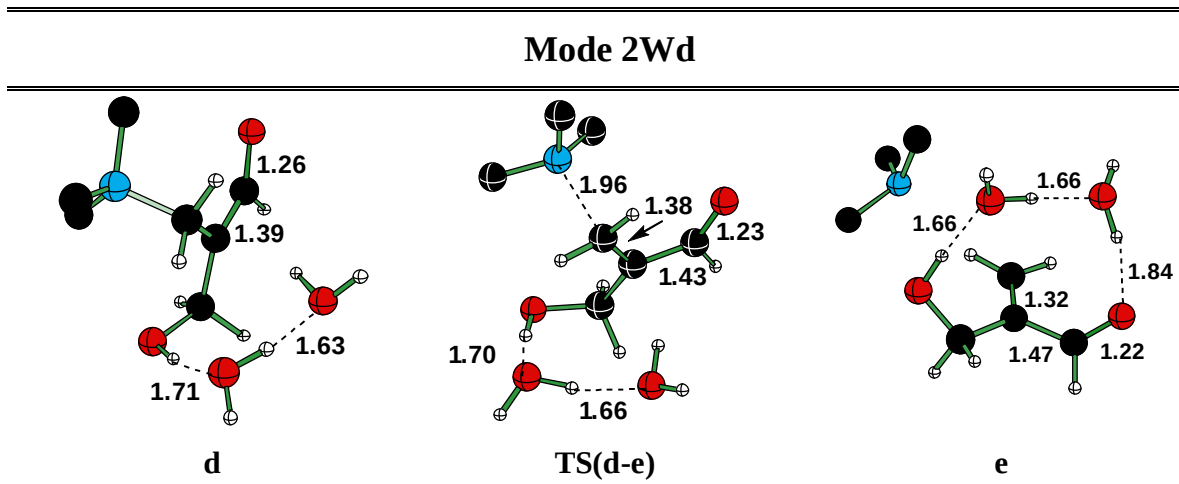
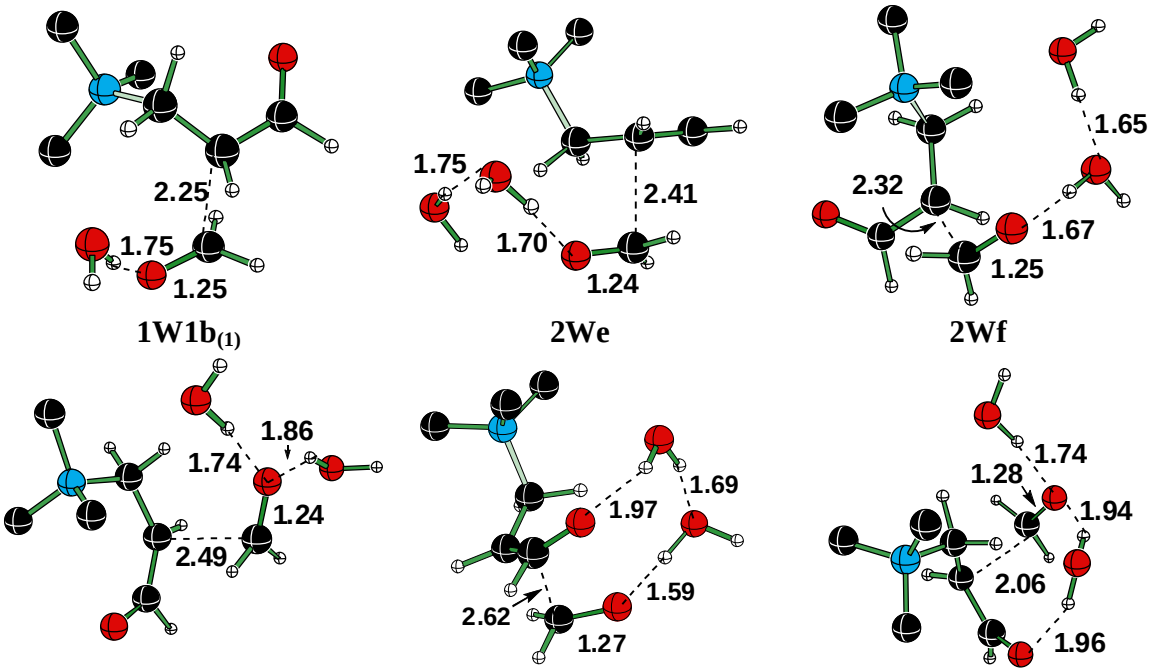


Figure S11. The CBS-4M Optimized Geometries of Transition States and Intermediates in Mode **2Wd**.

Additional Transition States

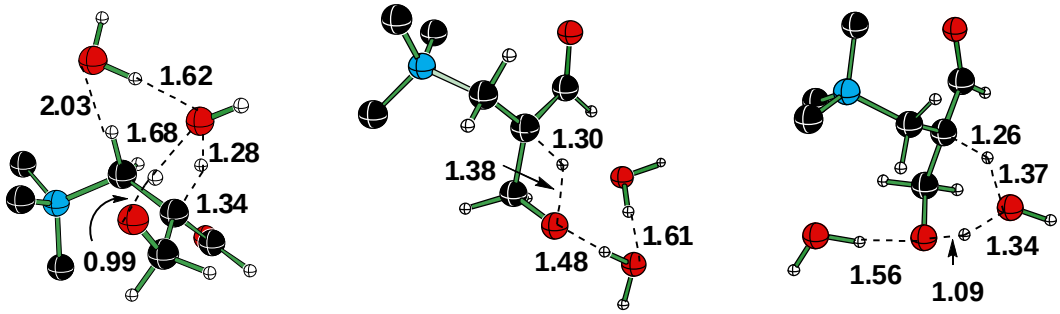
TS(b-c)



1W1b$_{(1)}$ **2We** **2Wf**

2Wg **2Wh** **2Wi**

TS(c-d)



2Wj$_{(1)}$ **2Wj$_{(2)}$** **2Wj$_{(3)}$**

Figure S12. The CBS-4M Optimized Geometries of Alternative Higher Energy Transition States.