Supporting Information

for

Ab initio and Density Functional Theory Evidence on the Rate-Limiting Step in Morita-Baylis-Hillman Reaction

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S1. Computational Methods

All the stationary points such as the transition states, reactants and products were optimized first in the gas-phase at the mPW1K level of theory in conjunction with the 6-31+G* basis set.¹ The choice of mPW1K hybrid density functional is based on the reported successful applications in describing reaction barriers and other kinetic parameters.² The calculations were repeated at the *ab initio* MP2 as well as composite CBS-4M levels of theories.³ Further, effect of solvent is incorporated through single-point calculations at the IEF-PCM_(DMSO)/mPW1K/6-31+G*//mPW1K/6-31+G* level of theory using the integral equation formalism (IEF) within the polarized continuum model (PCM) framework with UAKS radii.⁴ The optimized geometries have been characterized as stationary points on the potential energy surface at respective levels of theory by evaluating the corresponding Hessian indices. All the transition states were characterized by one and only one imaginary frequency pertaining to the desired reaction coordinate. The intrinsic reaction coordinate (IRC) calculations were carried out at all levels of theory (except at the CBS-4M) to further authenticate the transition states.⁵ The geometries of the intermediates and prereacting complex are obtained using extended IRC runs on respective transition states. The final geometries obtained from the IRC path on both sides of the first order saddle points were then subjected to further geometry optimization using stringent optimization conditions using the 'OPT=CALCFC' option. This will enable a careful *walk down* from the final IRC point on the PES. 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 were performed with the Gaussian03 suite of the quantum chemical programs.⁶

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Table S1: Energy of the intermediates and products (in kcal/mol) in the model and real MBH reaction obtained at the mPW1K/6-31+G* level in the gas phase ($\Delta H^\ddagger$ and $\Delta G^\ddagger$ terms) and IEF-PCM/mPW1K/6-31+G*//mPW1K/6-31+G* level theory in DMSO (represented as $\Delta E^\ddagger_{\text{DMSO}}$)

Species	$\Delta H^\ddagger$	$\Delta G^\ddagger$	$\Delta E^\ddagger_{\text{DMSO}}$
1a	-0.54	7.68	2.76
1b	10.20	23.77	-1.17
1c	10.56	36.85	-6.22
1d	-10.36	15.77	-24.17
1e	-18.14	-1.95	-18.76
2a	-1.35	6.37	3.88
2b	9.62	23.64	0.36
2c	15.15	42.81	9.17
2c'	26.61	54.64	13.99
2d	7.43	34.50	2.69
2e	-6.63	15.22	-1.05

Figure S1: The CBS-4M optimized geometries (distances in Å) of the intermediates and product of the MBH reaction between acrolein and formaldehyde catalyzed by NMe₃.

Figure S2: The mPW1K/6-31+G* optimized geometries (distances in Å) of the intermediates and product of the MBH reaction between MVK and benzaldehyde catalyzed by DABCO (only selected hydrogens are shown for clarity).

Table S2: Activation parameters (in kcal/mol) for the water assisted model MBH reaction obtained at the mPW1K/6-31+G* level of theory ($\Delta E^\ddagger$, $\Delta H^\ddagger$, and $\Delta G^\ddagger$ terms) in the gas phase and IEF-PCM/mPW1K/6-31+G*//mPW1K/6-31+G* in the condensed phase ($\Delta E^\ddagger_{\text{Water}}$)

Species	$\Delta E^\ddagger$	$\Delta H^\ddagger$	$\Delta G^\ddagger$	$\Delta E^\ddagger_{\text{Water}}$
TS(1b-1c)_{2w}	-11.37	-14.49	30.10	-12.53
TS(1c-1d)_{2w}	-4.46	-8.50	39.12	-11.93

Figure S3: The mPW1K/6-31+G* optimized geometries (distances in Å) of the transition states of the MBH reaction between acrolein and formaldehyde catalyzed by NMe₃ through water assisted pathway.

S3. The mPW1K/6-31+G* optimized coordinates, electronic energy (E_{tot} in hartree/particle) and number of imaginary frequencies for the real system

2a

NImag = 0

$E_{\text{tot}} = -576.4317344$

6	2.310098	1.479464	-0.004886
7	1.039579	0.770110	-0.012044
6	0.977298	-0.082121	-1.192806
6	2.150037	-1.091776	-1.175121
7	2.964376	-0.893375	0.015494
6	3.480894	0.466087	0.012606
6	2.128835	-1.077736	1.193522
6	0.955636	-0.068395	1.177265
1	2.347596	2.119872	-0.886977
1	2.331470	2.132092	0.868776
1	4.125204	0.583382	-0.859319
1	4.107434	0.593431	0.895993
1	1.768907	-2.106685	1.196529
1	2.756258	-0.952563	2.076733
1	-0.009159	-0.572874	1.164416
1	0.976327	0.582754	2.052337
1	2.793448	-0.978040	-2.048339
1	1.789690	-2.120581	-1.171788
1	1.015027	0.558845	-2.074794
1	0.011849	-0.585319	-1.192205
6	-2.318716	1.875447	-0.006249
1	-2.391890	2.953900	0.002144
1	-1.323590	1.446197	-0.022598
6	-3.413650	1.120868	0.004588
6	-3.350851	-0.360406	-0.005567
1	-4.398147	1.571397	0.022564
6	-4.669393	-1.079920	0.017969
1	-4.510342	-2.153169	0.006422
1	-5.233527	-0.802034	0.909174
1	-5.272222	-0.788877	-0.843189
8	-2.301644	-0.963492	-0.030994

TS(2a-2b)

NImag = 1(-238.1 cm^{-1})

$E_{\text{tot}} = -576.4136095$

6	-1.004619	-0.890326	1.117617
7	-0.559080	-0.480227	-0.212109
6	-1.573672	-0.835885	-1.201240
6	-2.906984	-0.152395	-0.810226
7	-2.721359	0.698466	0.351562
6	-2.292993	-0.116726	1.474822
6	-1.682486	1.674715	0.062250
6	-0.340186	0.970519	-0.229295
1	-1.168731	-1.967446	1.094406
1	-0.182972	-0.692312	1.804630
1	-3.098520	-0.801423	1.736410
1	-2.133426	0.538702	2.329474
1	-2.003209	2.271496	-0.790276
1	-1.596374	2.348604	0.913170
1	0.082105	1.233976	-1.195162
1	0.425280	1.182765	0.512666
1	-3.670712	-0.892261	-0.574634
1	-3.286113	0.456455	-1.629306
1	-1.659585	-1.922124	-1.223890
1	-1.214265	-0.508964	-2.175816
6	1.071526	-1.321772	-0.582456
1	0.665480	-2.324622	-0.505818
1	1.128882	-0.936126	-1.594343

6	2.109051	-0.954812	0.269133
6	2.944718	0.147664	-0.080256
1	2.328387	-1.540656	1.149945
6	4.185083	0.387413	0.750172
1	4.230675	1.435939	1.039330
1	4.232291	-0.237204	1.640092
1	5.062170	0.185609	0.135675
8	2.720637	0.898944	-1.033233

2b

NImag = 0

E_{tot} = -576.4167272

6	-0.962995	-1.039478	1.007463
7	-0.483402	-0.467767	-0.268977
6	-1.518266	-0.665361	-1.305215
6	-2.854576	-0.100155	-0.783503
7	-2.648248	0.661534	0.433002
6	-2.189521	-0.235981	1.477541
6	-1.617767	1.658663	0.190585
6	-0.259979	0.992127	-0.083240
1	-1.197780	-2.086095	0.820232
1	-0.120435	-0.994193	1.694041
1	-3.002245	-0.906097	1.752171
1	-1.949008	0.360313	2.355618
1	-1.929995	2.270745	-0.653885
1	-1.553455	2.314755	1.056503
1	0.256594	1.358590	-0.965105
1	0.444009	1.080551	0.738502
1	-3.558443	-0.902982	-0.570201
1	-3.312922	0.543658	-1.531651
1	-1.570268	-1.730501	-1.522430
1	-1.169773	-0.155088	-2.200211
6	0.870084	-1.165684	-0.698131
1	0.566080	-2.207681	-0.802390
1	1.050456	-0.719555	-1.676534
6	1.986371	-0.949461	0.199125
6	2.840543	0.129024	-0.062419
1	2.254385	-1.712277	0.915073
6	4.123474	0.240252	0.730467
1	4.165066	1.212180	1.221112
1	4.232834	-0.543267	1.478667
1	4.968026	0.193470	0.043515
8	2.605529	1.010428	-0.917154

TS(2b-2c)

NImag = 1(-226.5 cm⁻¹)

E_{tot} = -921.8847243

7	2.028106	-0.240304	-0.488429
6	0.731703	-0.274882	-1.255059
6	-0.446648	0.534899	-0.808182
6	-0.408219	1.878053	-0.320970
6	-1.641560	2.721826	-0.524640
6	-1.248061	-0.709683	0.632444
6	-2.716304	-0.581517	0.368999
6	-3.344848	-1.449598	-0.517543
6	-4.708329	-1.357612	-0.741654
6	-5.465183	-0.406556	-0.068077
6	-4.848610	0.447362	0.834069
6	-3.480946	0.357855	1.049417
6	1.832025	-0.254989	0.999040
6	2.853186	0.946297	-0.864932
6	2.792615	-1.469217	-0.852774
1	1.022596	-0.049607	-2.282922

1	0.404344	-1.316342	-1.196936
1	-2.518672	2.144601	-0.802305
1	-1.846242	3.294834	0.377237
1	-1.432257	3.438036	-1.321154
1	-0.930384	-0.084193	1.481538
1	-1.229704	0.376930	-1.542708
1	-2.747831	-2.205309	-1.007512
1	-5.187750	-2.036036	-1.433759
1	-6.530614	-0.340225	-0.237583
1	-5.433031	1.179219	1.374086
1	-3.001885	1.020523	1.758900
1	1.112786	-1.047212	1.197004
1	1.401670	0.711264	1.241378
1	2.223663	1.820189	-0.732870
1	3.106177	0.821321	-1.916525
1	2.783512	-1.552634	-1.937180
1	2.235922	-2.306005	-0.439142
8	-0.682762	-1.817243	0.446123
8	0.543490	2.384482	0.291532
6	4.096381	0.976850	0.036454
1	4.983460	1.207358	-0.551297
1	3.995818	1.750389	0.794741
6	3.200533	-0.483582	1.659382
1	3.333990	0.210568	2.486537
1	3.277443	-1.490831	2.066042
7	4.282108	-0.296999	0.706675
6	4.214902	-1.356217	-0.279475
1	4.506316	-2.297956	0.181667
1	4.937525	-1.141395	-1.065193

TS(2b-2c')

NImag = 1(-219.1 cm⁻¹)

E_{tot} = -921.8780303

7	-1.815606	0.327050	0.364490
6	-1.072159	1.355424	1.168320
6	0.292491	1.818747	0.746488
6	0.649192	2.204153	-0.594897
6	1.688893	3.292304	-0.725618
6	1.531448	0.549492	1.662579
6	-0.901691	-0.751333	-0.120940
6	-2.541006	0.934238	-0.790285
6	-2.826541	-0.308975	1.258609
1	-1.775151	2.182736	1.276095
1	-0.903024	0.888801	2.144548
1	2.348246	3.355262	0.138092
1	2.268512	3.146756	-1.633438
1	1.171100	4.249362	-0.813730
1	0.533620	2.615934	1.445066
1	-0.323773	-1.059795	0.743686
1	-0.242431	-0.285588	-0.845509
1	-1.814765	1.517360	-1.346143
1	-3.299540	1.588630	-0.364145
1	-3.383796	0.489571	1.743189
1	-2.266014	-0.845267	2.019714
8	0.814949	-0.003741	2.544601
8	0.187953	1.709117	-1.625641
6	-3.149641	-0.200671	-1.628268
1	-4.173732	0.042220	-1.906967
1	-2.583702	-0.338459	-2.546978
6	-1.757521	-1.877921	-0.722501
1	-1.356022	-2.174604	-1.688641
1	-1.750166	-2.759714	-0.083887
7	-3.136740	-1.451889	-0.893510

6	-3.721022	-1.231966	0.413305
1	-3.849123	-2.188707	0.915878
1	-4.711633	-0.800362	0.279334
1	2.204822	1.363442	1.974078
6	2.229019	-0.342725	0.659407
6	2.136031	-1.721442	0.823659
6	2.811974	-2.588583	-0.021523
6	3.607304	-2.087804	-1.041771
6	3.732727	-0.714259	-1.195339
6	3.055593	0.146702	-0.346133
1	1.545005	-2.092260	1.649379
1	2.732220	-3.656967	0.127035
1	4.138094	-2.760040	-1.701092
1	4.362817	-0.312213	-1.976364
1	3.181080	1.212487	-0.468289

2c

NImag = 0

E_{tot} = -921.8884746

7	1.987259	-0.163533	-0.474878
6	0.725614	0.011611	-1.306550
6	-0.524570	0.620406	-0.708423
6	-0.429123	2.055466	-0.327757
6	-1.705004	2.782515	-0.022000
6	-1.128421	-0.385218	0.434799
6	-2.639920	-0.474654	0.270513
6	-3.176365	-1.189366	-0.797219
6	-4.546004	-1.305536	-0.960549
6	-5.411834	-0.719922	-0.043776
6	-4.890607	-0.029469	1.037784
6	-3.514041	0.087412	1.190200
6	1.797322	0.003326	1.005648
6	3.040605	0.790303	-0.930375
6	2.479830	-1.558135	-0.702071
1	1.039560	0.570365	-2.185540
1	0.430537	-0.992754	-1.585095
1	-2.536649	2.438400	-0.631105
1	-1.975284	2.591014	1.016882
1	-1.550475	3.850958	-0.143348
1	-0.964732	0.155222	1.396931
1	-1.241274	0.566515	-1.533277
1	-2.499756	-1.682700	-1.481772
1	-4.943830	-1.865386	-1.796010
1	-6.481554	-0.815292	-0.166358
1	-5.553218	0.412116	1.769530
1	-3.115015	0.610175	2.050554
1	0.963768	-0.656766	1.247806
1	1.542545	1.044717	1.161239
1	2.605263	1.782486	-0.872533
1	3.246017	0.550367	-1.971907
1	2.495862	-1.720746	-1.777334
1	1.717850	-2.197626	-0.261333
8	-0.511622	-1.553402	0.352139
8	0.640330	2.633098	-0.230087
6	4.287986	0.618091	-0.046545
1	5.181102	0.553269	-0.665863
1	4.411384	1.474612	0.613209
6	3.100632	-0.396504	1.715657
1	3.382906	0.365033	2.440229
1	2.968468	-1.329799	2.259911
7	4.187687	-0.573728	0.771164
6	3.876382	-1.707372	-0.076891
1	3.923964	-2.618052	0.516687
1	4.643389	-1.780586	-0.846587

2c'

NImag = 0

E_{tot} = -921.869287

7	1.385452	-0.229899	-0.493116
6	0.203174	0.444818	-1.165522
6	-0.600651	1.545579	-0.486111
6	0.143720	2.780953	-0.119182
6	-0.660450	4.026573	-0.032947
6	-1.694422	1.161157	0.727297
6	1.345099	-0.160476	0.999716
6	2.677518	0.360597	-0.967252
6	1.376570	-1.671964	-0.885176
1	0.606346	0.800841	-2.113264
1	-0.493175	-0.358863	-1.387062
1	-0.978275	4.332310	-1.031103
1	-1.580175	3.766927	0.512279
1	-0.085295	4.822891	0.430528
1	-1.331793	1.811342	-1.252704
1	0.354968	-0.475002	1.301804
1	1.477200	0.885188	1.253216
1	2.598903	1.432252	-0.821641
1	2.739918	0.136677	-2.030284
1	1.254856	-1.713809	-1.964942
1	0.493916	-2.110429	-0.425021
8	-2.600228	2.088206	0.819205
8	1.339797	2.761107	0.151159
6	3.828511	-0.274752	-0.173275
1	4.647410	-0.534095	-0.841865
1	4.217779	0.425308	0.562868
6	2.450591	-1.069116	1.563850
1	2.994694	-0.547063	2.347856
1	2.028321	-1.969693	2.006412
7	3.380159	-1.465739	0.522673
6	2.687356	-2.325848	-0.414482
1	2.476626	-3.281237	0.061718
1	3.349121	-2.521011	-1.256355
6	-2.263071	-0.212176	0.363329
6	-3.083798	-0.345693	-0.755267
6	-3.628721	-1.570772	-1.099326
6	-3.385561	-2.693344	-0.313562
6	-2.610676	-2.566763	0.827231
6	-2.056177	-1.333584	1.157672
1	-3.317208	0.539516	-1.331069
1	-4.262422	-1.652519	-1.971976
1	-3.822485	-3.646977	-0.574423
1	-2.453472	-3.420274	1.473162
1	-1.495327	-1.234644	2.080006
1	-1.070337	1.016188	1.640083

TS(2c-2d)NImag = 1(-1601.7 cm⁻¹)E_{tot} = -921.8341292

7	2.077691	-0.297410	0.372476
6	1.024573	-1.346397	0.805117
6	-0.367541	-1.269983	0.276954
6	-0.556988	-1.593652	-1.129998
6	-1.947012	-1.755158	-1.673698
6	-1.357419	-0.500222	1.196454
6	-2.490129	0.277721	0.548836
6	-3.795462	-0.072458	0.866572
6	-4.868266	0.635094	0.342883
6	-4.652132	1.711507	-0.504698
6	-3.350884	2.078606	-0.819333

6	-2.283167	1.369010	-0.290983
6	1.452607	0.929652	-0.188615
6	2.996102	-0.877550	-0.655527
6	2.899021	0.091105	1.551208
1	1.490479	-2.293899	0.547717
1	0.972677	-1.264251	1.888625
1	-2.651446	-2.080069	-0.913341
1	-2.306285	-0.801787	-2.060822
1	-1.912656	-2.467343	-2.494263
1	-0.775541	0.257543	1.763629
1	-0.963572	-2.129287	1.013696
1	-3.930230	-0.910611	1.534781
1	-5.878176	0.346905	0.600837
1	-5.487036	2.262929	-0.913726
1	-3.168521	2.918358	-1.476139
1	-1.276988	1.670733	-0.551997
1	0.690892	1.254886	0.511963
1	0.966701	0.628981	-1.111198
1	2.359738	-1.316472	-1.419044
1	3.544796	-1.672629	-0.154757
1	3.227211	-0.825622	2.035052
1	2.237433	0.616010	2.236603
8	-1.776237	-1.541098	1.997593
8	0.403112	-1.825736	-1.865087
6	3.926046	0.233669	-1.166684
1	4.951900	-0.126072	-1.218766
1	3.640571	0.545780	-2.169223
6	2.550112	1.987335	-0.403996
1	2.443444	2.442298	-1.386407
1	2.471083	2.784949	0.332657
7	3.868628	1.393194	-0.295091
6	4.074693	0.963679	1.073228
1	4.177078	1.837868	1.713076
1	5.012285	0.413239	1.122993

TS(2c'-2d)

NImag = 1(-1527.5 cm⁻¹)

E_{tot} = -921.8412435

7	1.296831	-0.026833	-0.536381
6	0.209833	0.835595	-1.229894
6	-0.665702	1.702407	-0.398553
6	-0.015938	2.848047	0.220556
6	-0.859448	3.800792	1.020665
6	-2.060280	1.209310	0.092269
6	1.292518	0.107074	0.949162
6	2.644165	0.395817	-1.018189
6	1.096258	-1.462934	-0.888085
1	0.768992	1.449714	-1.928900
1	-0.396158	0.129612	-1.788851
1	-1.881007	3.841785	0.649030
1	-0.893410	3.474791	2.061551
1	-0.400541	4.785214	0.993161
1	-1.532190	2.190870	-1.186873
1	0.274731	-0.048436	1.283809
1	1.585011	1.129557	1.158419
1	2.699028	1.469900	-0.862925
1	2.671425	0.189871	-2.086173
1	0.986380	-1.517354	-1.967947
1	0.156649	-1.770165	-0.435354
8	-2.858768	1.793068	-0.867124
8	1.179706	3.082152	0.047040
6	3.717950	-0.390605	-0.243863
1	4.460325	-0.793839	-0.930018
1	4.240286	0.260063	0.454488

6	2.268388	-0.923972	1.538790
1	2.887229	-0.455922	2.301762
1	1.729580	-1.742879	2.011954
7	3.122110	-1.479826	0.506196
6	2.303166	-2.275556	-0.385411
1	1.961312	-3.164383	0.140584
1	2.922942	-2.607204	-1.216817
6	-2.210558	-0.297606	0.174115
6	-2.635586	-1.004850	-0.947124
6	-2.756229	-2.385996	-0.913978
6	-2.474175	-3.087793	0.252076
6	-2.095249	-2.390365	1.390749
6	-1.972680	-1.007120	1.348738
1	-2.902603	-0.430860	-1.823730
1	-3.092766	-2.918001	-1.793497
1	-2.582770	-4.162905	0.282569
1	-1.919675	-2.920404	2.317174
1	-1.720460	-0.467523	2.254529
1	-2.240995	1.589873	1.111891

2d

NImag = 0

E_{tot} = -921.9007087

7	-2.102174	-0.236009	-0.412121
6	-0.934746	-1.235884	-0.823694
6	0.378699	-1.056914	-0.194753
6	0.480935	-1.524936	1.122271
6	1.808657	-1.726163	1.813356
6	1.497451	-0.647684	-1.101087
6	2.616190	0.188635	-0.500248
6	3.933166	-0.006922	-0.900337
6	4.951769	0.801964	-0.415558
6	4.670228	1.830175	0.469934
6	3.357846	2.039370	0.869117
6	2.344781	1.224837	0.388881
6	-1.576368	0.951807	0.303428
6	-3.071868	-0.936961	0.479847
6	-2.832909	0.219554	-1.618021
1	-1.389041	-2.197019	-0.588265
1	-0.873733	-1.122422	-1.903842
1	2.668219	-1.741073	1.149666
1	1.966512	-0.935245	2.546774
1	1.752568	-2.665662	2.360263
1	1.068199	-0.017602	-1.887604
1	1.910399	-2.526607	-1.286422
1	4.149443	-0.804448	-1.594202
1	5.969849	0.627064	-0.734930
1	5.463041	2.459870	0.848107
1	3.123602	2.832433	1.565899
1	1.330879	1.378077	0.729219
1	-0.772054	1.365115	-0.296914
1	-1.149641	0.577648	1.228912
1	-2.469456	-1.407701	1.255490
1	-3.538999	-1.710644	-0.126640
1	-3.087842	-0.662665	-2.201101
1	-2.141189	0.822428	-2.203018
8	2.047673	-1.749624	-1.830723
8	-0.544135	-1.801227	1.795149
6	-4.094908	0.086610	0.994652
1	-5.104917	-0.312439	0.918464
1	-3.915926	0.317250	2.043002
6	-2.731538	1.946371	0.517301
1	-2.729602	2.307333	1.543770
1	-2.625722	2.815206	-0.130827

7	-4.012725	1.324205	0.237587
6	-4.078403	1.013941	-1.176130
1	-4.155214	1.939920	-1.743099
1	-4.987269	0.443833	-1.360136

TS(2d-2e)

NImag = 1(-217.0 cm⁻¹)

E_{tot} = -921.8975697

7	-2.139329	0.218680	0.413617
6	-0.803096	1.424166	0.876449
6	0.461226	1.253415	0.286928
6	0.611394	1.803191	-1.029717
6	1.981447	2.042436	-1.612675
6	1.583897	0.709336	1.122236
6	2.554246	-0.261717	0.477526
6	3.866807	-0.334634	0.936507
6	4.751734	-1.264839	0.412821
6	4.342049	-2.143295	-0.579125
6	3.038532	-2.076972	-1.045316
6	2.156196	-1.144076	-0.520215
6	-1.562089	-0.918015	-0.303565
6	-3.094830	0.911003	-0.466484
6	-2.840642	-0.262895	1.606233
1	-1.379240	2.272344	0.527940
1	-0.866640	1.261404	1.947703
1	2.769712	2.082298	-0.866734
1	2.220740	1.246511	-2.317993
1	1.949532	2.974958	-2.172192
1	1.116008	0.155746	1.946976
1	1.812624	2.526876	1.735356
1	4.192529	0.354078	1.700181
1	5.767672	-1.300544	0.780747
1	5.032903	-2.866091	-0.989355
1	2.707819	-2.745233	-1.828341
1	1.152200	-1.084564	-0.911543
1	-0.780421	-1.344720	0.320752
1	-1.091718	-0.518426	-1.198008
1	-2.516123	1.364781	-1.268051
1	-3.547601	1.712679	0.115878
1	-3.166483	0.603413	2.180805
1	-2.122904	-0.814135	2.212063
8	2.367831	1.746836	1.714199
8	-0.375470	2.100674	-1.714354
6	-4.147628	-0.106746	-0.953963
1	-5.157544	0.259832	-0.776268
1	-4.050932	-0.282777	-2.023806
6	-2.686424	-1.930026	-0.617206
1	-2.689965	-2.187232	-1.674871
1	-2.548095	-2.855426	-0.059746
7	-3.984366	-1.377647	-0.268272
6	-4.028454	-1.149453	1.163349
1	-4.003729	-2.110667	1.674314
1	-4.979563	-0.677702	1.405320

2e

NImag = 0

E_{tot} = -921.9206799

7	-3.173972	0.186280	-0.675184
6	0.223690	-0.414509	-1.363278
6	1.211891	-0.765200	-0.541064
6	0.882517	-1.015635	0.904431
6	1.992845	-1.151178	1.901532
6	2.617662	-0.936632	-1.065394
6	3.619715	0.051055	-0.512410

6	4.891606	-0.357772	-0.132376
6	5.814496	0.567611	0.334035
6	5.479640	1.909842	0.420782
6	4.212734	2.323814	0.035367
6	3.289790	1.399984	-0.428334
6	-2.986080	1.094424	0.449886
6	-3.575435	-1.117985	-0.161880
6	-4.229543	0.704611	-1.532317
1	-0.797159	-0.289393	-1.024379
1	0.419438	-0.231596	-2.412243
1	2.731409	-1.875895	1.566430
1	2.510867	-0.198935	2.013883
1	1.571271	-1.448161	2.856878
1	2.571692	-0.769915	-2.146534
1	2.506187	-2.862584	-1.255170
1	5.151091	-1.402695	-0.198419
1	6.799373	0.235608	0.630621
1	6.199189	2.628635	0.785658
1	3.940329	3.367741	0.098074
1	2.302084	1.729946	-0.720184
1	-2.644855	2.054025	0.058622
1	-2.190021	0.691869	1.074242
1	-2.757709	-1.506160	0.443018
1	-3.703804	-1.789583	-1.011917
1	-4.332592	0.037113	-2.388704
1	-3.910925	1.674772	-1.915688
8	3.097237	-2.242681	-0.825350
8	-0.273925	-1.095661	1.253861
6	-4.883557	-0.981687	0.654768
1	-5.679771	-1.605986	0.247779
1	-4.737609	-1.280650	1.692819
6	-4.311452	1.241486	1.235834
1	-4.191139	0.947741	2.278683
1	-4.671289	2.270942	1.229702
7	-5.339974	0.400373	0.642436
6	-5.552283	0.814921	-0.734700
1	-5.932714	1.836890	-0.728800
1	-6.331625	0.183529	-1.162522

DABCO

NImag = 0

E_{tot} = -345.2600648

6	-0.774489	-0.912444	-1.018343
7	-1.272897	-0.000152	0.000278
6	-0.773944	-0.426282	1.299414
6	0.774809	-0.425696	1.299117
7	1.272949	0.000211	-0.000451
6	0.774138	-0.912530	-1.018545
6	0.774040	1.338587	-0.281209
6	-0.774619	1.338424	-0.280393
1	-1.175705	-1.904584	-0.809601
1	-1.175969	-0.596342	-1.981538
1	1.175339	-1.904561	-0.809278
1	1.175471	-0.596888	-1.981949
1	1.175629	2.014828	0.473986
1	1.174857	1.653651	-1.245071
1	-1.175486	2.014236	0.475577
1	-1.176523	1.654057	-1.243617
1	1.176492	-1.417792	1.507064
1	1.176030	0.251414	2.053732
1	-1.174732	-1.418815	1.507019
1	-1.175372	0.250030	2.054636

MVK

NImag = 0
E_{tot} = -231.1674247

6	-1.999643	-0.100581	0.000062
1	-2.904095	-0.690530	0.000054
1	-2.094827	0.976109	0.000205
6	-0.796630	-0.662352	-0.000082
6	0.440336	0.162386	-0.000031
1	-0.682312	-1.738697	-0.000208
6	1.740124	-0.589470	0.000060
1	2.573682	0.104974	0.000204
1	1.800468	-1.235782	0.876649
1	1.800658	-1.235623	-0.876636
8	0.400164	1.369957	-0.000040

PhCHO

NImag = 0
E_{tot} = -345.4763897

6	-1.721270	1.056635	0.000044
6	-0.353675	1.281409	-0.000079
6	0.529736	0.208127	-0.000146
6	0.042628	-1.096777	-0.000083
6	-1.321230	-1.320470	0.000040
6	-2.202299	-0.244123	0.000104
1	-2.408677	1.889962	0.000095
1	0.031833	2.292782	-0.000129
1	0.747346	-1.915420	-0.000136
1	-1.704167	-2.330736	0.000084
1	-3.268178	-0.422693	0.000201
6	1.980094	0.463608	-0.000297
8	2.826580	-0.391758	0.000265
1	2.265296	1.529714	0.000263

S4. The mPW1K/6-31+G* optimized coordinates, electronic energy (E_{tot} in hartree/particle) and number of imaginary frequencies of the model system.

1a

NImag = 0
E_{tot} = -366.2846354

6	1.495974	-0.593076	1.237412
7	1.639412	0.104780	-0.016252
6	2.832962	0.909400	-0.036945
6	1.603959	-0.813965	-1.127370
1	1.471776	0.122630	2.057874
1	0.562198	-1.150349	1.239838
1	1.655135	-0.262225	-2.064754
1	0.672020	-1.373796	-1.108900
1	2.810462	1.628562	0.780265
1	2.892157	1.462426	-0.972912
6	-1.514801	1.527515	-0.081431
1	-1.484109	2.607154	-0.112707
1	-0.565332	1.002676	-0.096288
6	-2.678315	0.883575	-0.026139
6	-2.759112	-0.585246	0.018236
1	-3.618459	1.419154	-0.011343
8	-1.811445	-1.330173	0.006875
1	2.322169	-1.296238	1.423782
1	2.440655	-1.528943	-1.106818
1	3.750658	0.309284	0.062803
1	-3.777649	-1.001635	0.065340

TS(1a-1b)

NImag = 1(-268.8 cm⁻¹)

E_{tot} = -366.2692097

6	-1.681677	0.985942	-0.868801
7	-1.140721	-0.075769	-0.036817
6	-2.118066	-0.576931	0.914419
6	-0.586135	-1.144374	-0.860305
1	-2.110649	1.761979	-0.239179
1	-0.865486	1.410152	-1.449635
1	-0.142441	-1.902241	-0.223341
1	0.202933	-0.726173	-1.477439
1	-2.456625	0.238112	1.550297
1	-1.654719	-1.339509	1.535437
6	0.258195	0.647569	0.908278
1	-0.339338	1.393139	1.422816
1	0.451645	-0.242618	1.497838
6	1.325798	1.085061	0.118265
6	2.395464	0.198258	-0.163187
1	1.395126	2.114673	-0.202567
8	2.433687	-1.002196	0.105028
1	-2.450327	0.603450	-1.541353
1	-1.363566	-1.581204	-1.489104
1	-2.979800	-1.010633	0.404806
1	3.267320	0.655676	-0.663107

1b

NImag = 0

E_{tot} = -366.2699215

6	1.629822	1.027931	0.819412
7	1.051921	-0.059254	0.020588
6	2.066973	-0.657226	-0.852794
6	0.481075	-1.082837	0.916880
1	2.092702	1.753229	0.156378
1	0.818403	1.499893	1.365826
1	-0.013087	-1.841545	0.321709
1	-0.271479	-0.603798	1.531901
1	2.444545	0.100142	-1.533626
1	1.610302	-1.459425	-1.424016
6	-0.124886	0.543396	-0.886165
1	0.415677	1.262496	-1.500681
1	-0.411001	-0.327909	-1.474348
6	-1.244954	1.085107	-0.153307
6	-2.328365	0.242855	0.110700
1	-1.328482	2.149160	0.010848
8	-2.363960	-0.984797	-0.078524
1	2.371976	0.629215	1.505922
1	1.277216	-1.504782	1.525673
1	2.886355	-1.054156	-0.259147
1	-3.222883	0.735280	0.529285

TS(1b-1c)

NImag = 1(-184.4 cm⁻¹)

E_{tot} = -480.7289571

6	-1.648064	-1.100142	1.117797
7	-1.452696	-0.148880	0.002105
6	-2.346763	-0.523561	-1.113099
6	-1.767392	1.225721	0.446041
1	-1.356854	-2.091825	0.787532
1	-1.017745	-0.806303	1.947987
1	-1.537275	1.915830	-0.358319
1	-1.143729	1.467163	1.298410
1	-2.076903	-1.516024	-1.459125
1	-2.217499	0.189543	-1.920654
6	-0.018284	-0.236240	-0.503696
1	0.146973	-1.289250	-0.755096
1	0.011816	0.387614	-1.394366

6	1.050490	0.177214	0.432303
6	1.471066	1.557472	0.358989
8	1.146348	2.357199	-0.504534
1	-2.691591	-1.084849	1.419604
1	-2.817705	1.280668	0.719855
1	-3.378511	-0.514509	-0.773387
1	2.204427	1.865390	1.123460
1	0.998661	-0.217037	1.440876
6	2.394461	-0.960150	-0.108243
1	2.708164	-0.458513	-1.043661
1	3.125722	-0.744391	0.689862
8	1.903383	-2.130103	-0.185249

1c

NImag = 0

E_{tot} = -480.7337438

6	-1.585995	0.946428	-0.905609
7	-1.394954	-0.241339	-0.013058
6	-2.369462	-0.154292	1.096103
6	-1.614257	-1.492836	-0.763455
1	-0.940237	1.757102	-0.511398
1	-1.260262	0.685128	-1.906740
1	-1.591323	-2.333735	-0.076847
1	-0.822012	-1.604552	-1.495818
1	-2.265370	0.818835	1.564507
1	-2.157512	-0.936762	1.818418
6	-0.016632	-0.245789	0.608964
1	-0.047949	0.547640	1.351826
1	0.106191	-1.219585	1.078007
6	1.114038	0.067439	-0.337908
6	2.192238	-0.948023	-0.300471
8	2.227646	-1.915300	0.423311
1	-2.644924	1.187628	-0.927639
1	-2.576017	-1.443474	-1.265967
1	-3.374552	-0.273202	0.702326
1	3.040199	-0.741764	-0.973766
1	0.790974	0.180307	-1.373605
6	1.640974	1.544421	0.055045
1	2.267760	1.394203	0.961483
1	2.343478	1.818103	-0.756005
8	0.613706	2.358976	0.225015

TS(1c-1d)

NImag = 1(-1460.3 cm⁻¹)

E_{tot} = -480.6857933

7	1.405387	-0.299766	-0.000596
6	0.091428	-0.346302	-0.821145
6	-1.153394	0.148837	-0.177781
6	-1.291132	1.552087	0.135258
6	-2.008410	-0.892750	0.559566
6	1.146645	-0.323139	1.455192
6	2.155884	0.937092	-0.335877
6	2.222599	-1.475022	-0.366055
1	0.335195	0.201224	-1.728339
1	-0.061359	-1.393906	-1.071244
1	-1.381398	-1.681245	1.023893
1	-2.056997	-0.193120	-0.981326
1	0.544834	-1.190800	1.699001
1	0.612545	0.577648	1.732114
1	1.487684	1.783461	-0.203833
1	2.471648	0.879230	-1.372959
1	2.347040	-1.494976	-1.444322
1	1.713101	-2.377286	-0.043374
8	-2.805664	-1.343644	-0.459193

8	-0.489491	2.436544	-0.129852
1	3.194324	-1.404935	0.114658
1	3.027359	1.006542	0.309253
1	2.100777	-0.365354	1.973082
1	-2.548361	-0.413993	1.398106
1	-2.244579	1.817848	0.616873

1d

NImag = 0

E_{tot} = -480.7684358

7	1.463213	-0.288366	-0.002269
6	0.077546	-0.183993	-0.739523
6	-1.051969	0.199252	0.100095
6	-1.348688	1.566311	0.168430
6	-2.024612	-0.826124	0.554568
6	1.376259	-1.313628	1.049800
6	1.790037	1.017392	0.609499
6	2.495331	-0.654395	-0.984083
1	0.278097	0.567023	-1.503625
1	-0.037157	-1.168315	-1.193547
1	-1.581638	-1.630750	1.145157
1	-2.984803	-0.867146	-1.125890
1	1.134304	-2.270564	0.596843
1	0.585706	-1.022246	1.732952
1	1.005844	1.264946	1.314840
1	1.794719	1.779259	-0.160918
1	2.536441	0.111311	-1.752518
1	2.236606	-1.607298	-1.436320
8	-2.669516	-1.529514	-0.507663
8	-0.650791	2.496366	-0.267967
1	2.325855	-1.378514	1.574701
1	2.755380	0.941112	1.104347
1	3.462305	-0.731975	-0.493985
1	-2.300873	1.814801	0.674255
1	-2.774244	-0.346800	1.191908

TS(1d-1e)

NImag = 1(-252.5 cm⁻¹)

E_{tot} = -480.7632593

7	-1.626351	-0.264512	-0.021922
6	0.096775	-0.124762	0.852628
6	1.157151	0.189684	0.011351
6	1.478137	1.571285	-0.171440
6	2.043885	-0.867084	-0.563124
6	-1.541945	-1.348304	-0.982546
6	-1.857308	1.007205	-0.688389
6	-2.612338	-0.527448	1.007932
1	-0.248282	0.664090	1.509567
1	0.044048	-1.125767	1.264352
1	1.508489	-1.588578	-1.178794
1	3.062546	-1.079751	1.070632
1	-1.319490	-2.280213	-0.468109
1	-0.740536	-1.131036	-1.683141
1	-1.032036	1.201149	-1.367064
1	-1.877755	1.807071	0.044723
1	-2.602944	0.283448	1.732395
1	-2.368618	-1.456901	1.518324
8	2.687042	-1.669648	0.414183
8	0.819201	2.528772	0.214530
1	-2.477922	-1.459772	-1.535246
1	-2.796335	0.986387	-1.246876
1	-3.617245	-0.610469	0.587105
1	2.425230	1.761043	-0.710786
1	2.789213	-0.395567	-1.211808

1e
NImag = 0
E_{tot} = -480.7776431

7	-2.465441	-0.354013	0.004111
6	0.993868	-0.801175	-0.070859
6	1.934863	0.140774	-0.051280
6	1.560539	1.568227	0.028242
6	3.410727	-0.147945	-0.112807
6	-3.377815	-1.467931	-0.011038
6	-2.596871	0.451398	-1.185142
6	-2.629283	0.445984	1.192826
1	-0.061034	-0.556380	-0.021592
1	1.267760	-1.843900	-0.148554
1	3.804703	0.130842	-1.090226
1	3.494050	-1.769267	0.939720
1	-3.222626	-2.087144	0.871327
1	-3.198574	-2.082722	-0.891887
1	-2.416540	-0.161059	-2.067756
1	-1.860850	1.252129	-1.166979
1	-1.893892	1.247429	1.197930
1	-2.472311	-0.170256	2.077317
8	3.735756	-1.496623	0.053045
8	0.434525	1.995478	0.058441
1	-4.432917	-1.152161	-0.024526
1	-3.598008	0.900086	-1.280680
1	-3.633151	0.893333	1.263762
1	2.407701	2.275858	0.060940
1	3.935365	0.474461	0.620894

NMe₃
NImag = 0
E_{tot} = -174.4333783

6	1.228741	-0.614063	0.059876
7	0.000060	-0.000075	-0.369085
6	-1.146206	-0.756973	0.060013
6	-0.082543	1.371060	0.060169
1	1.290061	-1.629392	-0.328473
1	2.077770	-0.053577	-0.328036
1	-0.992406	1.826356	-0.327572
1	0.766042	1.932316	-0.327636
1	-1.084886	-1.772870	-0.326841
1	-2.056313	-0.303271	-0.329059
1	1.322332	-0.661004	1.156783
1	-0.088759	1.475220	1.157125
1	-1.234208	-0.813396	1.156960

Acrylaldehyde
NImag = 0
E_{tot} = -191.8479761

6	1.457968	-0.464952	0.000029
1	2.533688	-0.371547	0.000216
1	1.036360	-1.460216	0.000432
6	0.661781	0.599426	-0.000188
6	-0.807754	0.460314	0.000106
1	1.061037	1.605000	-0.000183
8	-1.390924	-0.593217	-0.000105
1	-1.375670	1.403771	0.000693

Formaldehyde
NImag = 0
E_{tot} = -114.4602254

6	-0.000001	-0.525787	0.000000
8	-0.000001	0.670349	-0.000000

1	0.000005	-1.104033	0.934805
1	0.000005	-1.104033	-0.934805

S5. The CBS-4M optimized coordinates, electronic energy (E_{tot} in hartree/particle) and number of imaginary frequencies of the model system.

1a

NImag = 0

$E_{\text{CBS4M}} = -365.7912379$

6	2.870130	0.858524	-0.000469
7	1.611432	0.105827	-0.000287
6	1.429758	-0.698782	-1.218246
6	1.427355	-0.694043	1.220422
1	2.914213	1.488348	-0.880473
1	2.912299	1.491956	0.877038
1	0.451853	-1.155185	1.185815
1	1.481317	-0.044891	2.086213
1	1.486109	-0.053137	-2.086499
1	0.453941	-1.159317	-1.184112
6	-1.468634	1.547790	-0.002128
1	-1.450653	2.621398	-0.002921
1	-0.514842	1.049185	-0.002666
6	-2.615111	0.891466	-0.000535
6	-2.673505	-0.578634	0.000563
1	-3.559158	1.401378	0.000019
8	-1.714829	-1.326759	0.000152
1	3.746604	0.207236	0.001826
1	2.187668	-1.471119	1.323797
1	2.189907	-1.476658	-1.316747
1	-3.680608	-0.983836	0.001857

TS(1a-1b)

NImag = 1(-295.2 cm^{-1})

$E_{\text{CBS4M}} = -365.7719726$

6	1.832339	1.043819	0.704749
7	1.118258	-0.069357	0.036508
6	1.990812	-0.802221	-0.910891
6	0.506038	-0.986680	1.039666
1	2.292041	1.675664	-0.043028
1	1.106290	1.616614	1.262821
1	-0.177539	-1.651220	0.538281
1	-0.068103	-0.388646	1.728655
1	2.341030	-0.119384	-1.673392
1	1.417032	-1.592484	-1.373347
6	-0.264869	0.653027	-0.915778
1	0.335642	1.372312	-1.446333
1	-0.469888	-0.244035	-1.473859
6	-1.333562	1.110892	-0.134353
6	-2.367427	0.197865	0.154147
1	-1.414883	2.136538	0.161072
8	-2.356013	-1.020227	-0.092384
1	2.596215	0.662534	1.373383
1	1.284137	-1.526220	1.568199
1	2.842465	-1.232384	-0.395489
1	-3.244124	0.637813	0.631310

1b

NImag = 0

$E_{\text{CBS4M}} = -365.772005$

6	1.781427	1.071457	0.673329
7	1.054526	-0.057607	0.024061
6	1.963794	-0.851391	-0.852808

6	0.429003	-0.942295	1.073635
1	2.272481	1.661987	-0.086929
1	1.049586	1.673034	1.189193
1	-0.344762	-1.530710	0.608606
1	-0.044410	-0.303615	1.799117
1	2.334451	-0.214904	-1.643555
1	1.403017	-1.670427	-1.277075
6	-0.156548	0.561843	-0.904370
1	0.392156	1.258994	-1.522606
1	-0.449745	-0.318916	-1.456619
6	-1.270594	1.107955	-0.160410
6	-2.316705	0.237893	0.113207
1	-1.353367	2.159934	0.017797
8	-2.315735	-1.005169	-0.076932
1	2.513606	0.683910	1.369219
1	1.205311	-1.538154	1.534631
1	2.792001	-1.235995	-0.272963
1	-3.208391	0.706700	0.532715

TS(1b-1c)

NImag = 1(-117.2 cm⁻¹)

E_{CBS4M} = -480.1232069

6	-1.671336	-1.135511	1.125917
7	-1.446433	-0.149898	0.011405
6	-2.340406	-0.500488	-1.146725
6	-1.740898	1.251992	0.476098
1	-1.391393	-2.116521	0.775214
1	-1.045805	-0.865295	1.959060
1	-1.386144	1.941423	-0.272058
1	-1.200514	1.426970	1.391328
1	-2.070538	-1.484008	-1.498771
1	-2.185235	0.224513	-1.930513
6	0.016782	-0.263479	-0.488147
1	0.227676	-1.318032	-0.672942
1	0.055242	0.331342	-1.387707
6	1.093167	0.172037	0.452487
6	1.501180	1.566493	0.315342
8	1.065552	2.357399	-0.511334
1	-2.712483	-1.108706	1.414777
1	-2.804041	1.351839	0.643777
1	-3.370365	-0.484563	-0.820512
1	2.295342	1.872932	0.994029
1	0.969781	-0.140741	1.477532
6	2.391756	-0.949752	-0.048241
1	2.821635	-0.409520	-0.902153
1	3.077428	-0.830360	0.797897
8	1.852318	-2.131116	-0.259813

1c

NImag = 0

E_{CBS4M} = -480.1286933

7	1.193913	0.143037	-0.025563
6	0.095499	-0.088542	-1.098450
6	-1.367066	-0.072175	-0.684478
6	-1.898261	1.153569	-0.051254
6	-1.633856	-1.434012	0.210766
6	0.731285	-0.102119	1.407592
6	1.744335	1.538895	-0.140330
6	2.268522	-0.883927	-0.300877
1	0.307732	0.628140	-1.877395
1	0.246416	-1.098160	-1.429640
1	-1.942425	-1.061426	1.198624
1	-1.914360	-0.208453	-1.615607
1	0.306097	-1.103620	1.370976

1	0.020168	0.661179	1.662226
1	0.925177	2.216360	0.024453
1	2.164904	1.670671	-1.126890
1	2.625349	-0.755234	-1.312611
1	1.790723	-1.842160	-0.169463
8	-0.519573	-2.228331	0.211196
8	-1.257674	2.110858	0.352117
1	3.077123	-0.739518	0.400250
1	2.513251	1.669339	0.607002
1	1.604470	-0.024229	2.040520
1	-2.527927	-1.885699	-0.228290
1	-2.978854	1.141202	0.070461

TS(1c-1d)

NImag = (-1712.6 cm⁻¹)

E_{CBS4M} = -480.0820392

7	1.354206	-0.332533	0.013027
6	-0.006056	-0.396235	-0.787072
6	-1.228443	0.241927	-0.196677
6	-1.247501	1.659819	0.052557
6	-2.082137	-0.766066	0.633388
6	1.131669	-0.095249	1.482152
6	2.187099	0.807350	-0.533819
6	2.082029	-1.632159	-0.182722
1	0.253925	0.026871	-1.745805
1	-0.262956	-1.438367	-0.900397
1	-1.510290	-1.321783	1.378578
1	-2.064840	-0.272940	-0.995803
1	0.489985	-0.866055	1.870172
1	0.671000	0.869158	1.597947
1	1.574090	1.691901	-0.482206
1	2.443957	0.579862	-1.557589
1	2.208859	-1.801314	-1.241349
1	1.492095	-2.427704	0.245589
8	-2.537641	-1.540345	-0.482517
8	-0.332636	2.459974	-0.144755
1	3.046410	-1.576468	0.301598
1	3.084755	0.899712	0.061037
1	2.091961	-0.115532	1.978151
1	-2.860817	-0.216805	1.168736
1	-2.195324	2.023842	0.441482

1d

NImag = 0

E_{CBS4M} = -480.1623076

7	-1.443398	-0.310903	-0.010828
6	-0.018642	-0.170419	0.731914
6	1.093491	0.261626	-0.110090
6	1.323361	1.629673	-0.145604
6	2.081477	-0.757768	-0.571805
6	-1.429730	-1.521544	-0.888317
6	-1.671678	0.929600	-0.843100
6	-2.506048	-0.433610	1.034505
1	-0.243813	0.575841	1.480005
1	0.131156	-1.148453	1.166665
1	1.685139	-1.465217	-1.290589
1	2.881742	-1.064053	1.220848
1	-1.283012	-2.399922	-0.277211
1	-0.611975	-1.418794	-1.581135
1	-1.035866	0.864029	-1.709290
1	-1.353703	1.785918	-0.270720
1	-2.513879	0.470414	1.623909
1	-2.279794	-1.280889	1.665431
8	2.547342	-1.628071	0.509132

8	0.559420	2.523732	0.298040
1	-2.368439	-1.590777	-1.421369
1	-2.712738	0.965600	-1.133082
1	-3.467919	-0.572641	0.560694
1	2.266394	1.924623	-0.613959
1	2.923009	-0.259996	-1.046791

TS(1d-1e)

NImag = 1(-320.5 cm⁻¹)

E_{CBS4M} = -480.1590937

7	1.548718	-0.285206	0.035215
6	-0.131006	-0.110943	-0.838789
6	-1.192865	0.262535	-0.023186
6	-1.431932	1.650308	0.133229
6	-2.102401	-0.780798	0.558913
6	1.598786	-1.600990	0.714022
6	1.619896	0.834770	1.009147
6	2.595637	-0.169904	-1.005624
1	0.240010	0.649865	-1.499015
1	-0.130407	-1.111507	-1.229189
1	-1.656132	-1.335417	1.374467
1	-2.836656	-1.393633	-1.181084
1	1.508998	-2.388238	-0.021660
1	0.771710	-1.666515	1.403699
1	0.854281	0.683952	1.754007
1	1.403593	1.757465	0.496450
1	2.520513	0.800697	-1.474774
1	2.444313	-0.940445	-1.750141
8	-2.443996	-1.817256	-0.404952
8	-0.685247	2.565210	-0.237698
1	2.532661	-1.720271	1.254905
1	2.595979	0.860385	1.482901
1	3.585052	-0.280724	-0.573374
1	-2.377242	1.895347	0.622372
1	-3.000439	-0.308021	0.948843

1e

NImag = 0

E_{CBS4M} = -480.1754511

7	-2.409823	-0.367840	-0.004455
6	0.968606	-0.802425	-0.119005
6	1.873088	0.157354	-0.066903
6	1.474813	1.572553	0.037566
6	3.360656	-0.122939	-0.139167
6	-3.374210	-1.471667	-0.049848
6	-2.498137	0.513810	-1.178238
6	-2.465834	0.385857	1.256888
1	-0.088044	-0.609374	-0.075370
1	1.285623	-1.822416	-0.213898
1	3.737254	0.105684	-1.126702
1	3.486360	-1.751755	0.992242
1	-3.208594	-2.131128	0.793201
1	-3.231472	-2.038611	-0.961486
1	-2.362406	-0.073123	-2.078692
1	-1.710765	1.249873	-1.116309
1	-1.678631	1.124713	1.251821
1	-2.308723	-0.292172	2.087324
8	3.664882	-1.511831	0.072471
8	0.336195	1.993872	0.083480
1	-4.409059	-1.124406	-0.017956
1	-3.461674	1.024101	-1.240639
1	-3.426080	0.886647	1.397739
1	2.310218	2.269010	0.074087
1	3.892255	0.506252	0.570466

NMe₃
 NImag = 0
 E_{CBS4M} = -174.1585786

6	-1.023021	-0.970125	0.057149
7	-0.000001	-0.000007	-0.337261
6	-0.328644	1.371025	0.057101
6	1.351666	-0.400897	0.057132
1	-1.980895	-0.668818	-0.348632
1	-0.772914	-1.942643	-0.348584
1	2.068832	0.301949	-0.348633
1	1.569653	-1.381104	-0.348628
1	-1.295918	1.640675	-0.348652
1	0.411239	2.049900	-0.348692
1	-1.122214	-1.064151	1.141477
1	1.482712	-0.439759	1.141458
1	-0.360490	1.503978	1.141425

Acrylaldehyde
 NImag = 0
 E_{CBS4M} = -191.6285365

6	-1.439206	-0.471541	0.000005
1	-2.509591	-0.413043	0.000011
1	-0.998399	-1.450218	-0.000044
6	-0.672020	0.600352	-0.000001
6	0.800311	0.469110	-0.000022
1	-1.075552	1.593709	0.000027
8	1.388514	-0.590907	0.000011
1	1.340920	1.409286	0.000023

Formaldehyde
 NImag = 0
 E_{CBS4M} = -114.3600544

6	-0.000000	-0.530858	0.000000
8	-0.000000	0.676311	-0.000000
1	0.000001	-1.112672	0.913356
1	0.000001	-1.112672	-0.913356

S6. The MP2/6-31+G* optimized coordinates and ground state electronic energy (E_{tot} in hartree/particle) of the model system.

1a
 NImag = 0
 E_{tot} = -365.1705829

6	2.850274	0.891731	-0.042784
7	1.609337	0.128568	-0.017164
6	1.556197	-0.808594	-1.134714
6	1.466668	-0.581402	1.249789
1	2.922468	1.441535	-0.985917
1	2.854756	1.610352	0.782210
1	0.519930	-1.127137	1.250771
1	1.462249	0.140620	2.072418
1	1.624392	-0.255021	-2.076266
1	0.605551	-1.346687	-1.106905
6	-1.524469	1.553659	-0.083945
1	-1.529228	2.640120	-0.112597
1	-0.556625	1.052092	-0.106508
6	-2.683642	0.870572	-0.021620
6	-2.725223	-0.606861	0.019133
1	-3.643329	1.384812	0.001074
8	-1.731376	-1.336736	0.006335
1	3.743945	0.244671	0.053187
1	2.292071	-1.299435	1.420313

1	2.383716	-1.543516	-1.101554
1	-3.733072	-1.063123	0.064094

TS(1a-1b)

NImag = 1(-239.8 cm⁻¹)

E_{tot} = -365.1560673

6	-1.715961	0.998315	-0.853717
7	-1.132943	-0.074668	-0.035385
6	-2.103390	-0.623018	0.922444
6	-0.556678	-1.127396	-0.893492
1	-2.156849	1.752741	-0.196894
1	-0.909657	1.449763	-1.438732
1	-0.085460	-1.883732	-0.264792
1	0.216904	-0.670953	-1.513918
1	-2.446743	0.178669	1.582021
1	-1.611912	-1.396555	1.517607
6	0.253516	0.663391	0.911688
1	-0.346155	1.417172	1.428736
1	0.458747	-0.225690	1.514070
6	1.326309	1.104313	0.118418
6	2.397676	0.204924	-0.160586
1	1.409783	2.141763	-0.195974
8	2.411674	-1.023059	0.104739
1	-2.485572	0.597700	-1.523995
1	-1.340907	-1.568778	-1.520743
1	-2.964222	-1.058498	0.400408
1	3.290415	0.650382	-0.646544

1b

NImag = 0

E_{tot} = -365.1571147

6	1.659110	1.038480	0.814824
7	1.053984	-0.059228	0.020785
6	2.066461	-0.682459	-0.865822
6	0.472671	-1.081203	0.938297
1	2.119100	1.756870	0.132361
1	0.853909	1.519401	1.374049
1	-0.030126	-1.842406	0.342423
1	-0.276132	-0.585042	1.555456
1	2.444476	0.073417	-1.557778
1	1.588134	-1.488533	-1.425501
6	-0.138474	0.561124	-0.894320
1	0.412301	1.285618	-1.506429
1	-0.428902	-0.316834	-1.485107
6	-1.250687	1.102424	-0.145263
6	-2.339860	0.247352	0.113907
1	-1.352901	2.173921	0.005232
8	-2.356397	-1.005608	-0.081730
1	2.411639	0.627664	1.492976
1	1.277593	-1.502308	1.547717
1	2.888757	-1.083171	-0.266933
1	-3.249882	0.726558	0.530145

TS(1b-1c)

NImag = 1(-215.5 cm⁻¹)

E_{tot} = -479.3302347

6	1.617826	1.039493	0.959957
7	1.445990	-0.106334	0.003686
6	2.411593	0.061924	-1.124050
6	1.699618	-1.404901	0.691621
1	1.113713	1.914376	0.537089
1	1.144925	0.783379	1.906714
1	1.634555	-2.207531	-0.045193
1	0.930114	-1.544981	1.450667

1	2.245178	1.042265	-1.573492
1	2.227260	-0.722205	-1.860216
6	0.030678	-0.076473	-0.586813
1	0.007868	0.877435	-1.133232
1	-0.038270	-0.932173	-1.267270
6	-1.065896	-0.123351	0.414772
6	-1.898367	-1.301745	0.384245
8	-1.933666	-2.145262	-0.537618
1	2.686881	1.205058	1.112217
1	2.692132	-1.378625	1.148002
1	3.431454	-0.010873	-0.739815
1	-2.620672	-1.399064	1.221600
1	-0.862415	0.248197	1.417309
6	-2.001588	1.495104	-0.078223
1	-2.513189	1.114476	-0.986011
1	-2.688635	1.538259	0.786569
8	-1.100835	2.404768	-0.208607

1c

NImag = 0

E_{tot} = -479.3373723

7	-1.195831	-0.141555	-0.017329
6	-0.088902	0.008781	-1.083146
6	1.362106	0.098793	-0.653013
6	1.945554	-1.119985	-0.054633
6	1.593705	1.429733	0.259604
6	-0.751392	0.023648	1.412836
6	-1.833529	-1.489167	-0.159636
6	-2.212742	0.933036	-0.282116
1	-0.236095	-0.828070	-1.772567
1	-0.298676	0.955710	-1.579281
1	1.777563	1.057208	1.299750
1	1.906723	0.299344	-1.589291
1	-0.342967	1.036382	1.485976
1	-0.025486	-0.752425	1.642683
1	-1.065654	-2.244193	0.012343
1	-2.244911	-1.579642	-1.166776
1	-2.585846	0.813974	-1.301412
1	-1.688723	1.884740	-0.157763
8	0.540396	2.262394	0.132957
8	1.307869	-2.119870	0.307548
1	-3.031757	0.820906	0.431733
1	-2.635154	-1.575432	0.576426
1	-1.639842	-0.101700	2.036578
1	2.567074	1.845652	-0.075269
1	3.039638	-1.090791	0.114750

TS(1c-1d)

NImag = 1(-1488.8 cm⁻¹)

E_{tot} = -479.2859812

7	1.378553	-0.329778	-0.004253
6	0.057354	-0.318443	-0.855059
6	-1.175785	0.191824	-0.196701
6	-1.234761	1.602700	0.134131
6	-2.015885	-0.838693	0.576667
6	1.131286	-0.090243	1.453091
6	2.301166	0.739964	-0.508403
6	2.031330	-1.664337	-0.168510
1	0.319772	0.262440	-1.743581
1	-0.121983	-1.359220	-1.142217
1	-1.379155	-1.624966	1.044391
1	-2.100453	-0.135999	-0.996432
1	0.406039	-0.816766	1.815440
1	0.750317	0.921482	1.579113

1	1.763549	1.688269	-0.463323
1	2.572506	0.504494	-1.538969
1	2.180059	-1.851341	-1.233341
1	1.373414	-2.426300	0.252885
8	-2.840326	-1.328313	-0.445410
8	-0.350720	2.443326	-0.133746
1	2.992733	-1.661246	0.350240
1	3.195953	0.756588	0.118359
1	2.083233	-0.204196	1.977305
1	-2.555743	-0.343851	1.412857
1	-2.169977	1.942312	0.619002

1d

NImag = 0

E_{tot} = -479.3675938

7	1.469178	-0.289325	-0.005514
6	0.066272	-0.193746	-0.734391
6	-1.044309	0.187896	0.136758
6	-1.356058	1.564381	0.184165
6	-2.027974	-0.838071	0.571433
6	1.397393	-1.335212	1.050442
6	1.792701	1.028672	0.621082
6	2.510046	-0.642798	-1.007565
1	0.253175	0.563505	-1.507159
1	-0.053823	-1.187345	-1.184523
1	-1.590353	-1.681609	1.119429
1	-3.025425	-0.798076	-1.121019
1	1.145363	-2.290014	0.583967
1	0.613861	-1.043000	1.750509
1	1.002198	1.262477	1.333351
1	1.790671	1.794679	-0.153547
1	2.534885	0.137381	-1.770370
1	2.249553	-1.599800	-1.464129
8	-2.699575	-1.510019	-0.538286
8	-0.645540	2.504471	-0.281887
1	2.363173	-1.401984	1.557789
1	2.765629	0.947404	1.113610
1	3.483064	-0.714876	-0.515421
1	-2.308347	1.825439	0.696227
1	-2.775372	-0.371244	1.229726

TS(1d-1e)

NImag = 1(-209.9 cm⁻¹)

E_{tot} = -479.3619588

7	-1.637168	-0.271436	-0.021007
6	0.118565	-0.133554	0.867117
6	1.169108	0.189777	0.013096
6	1.481578	1.585919	-0.173475
6	2.057281	-0.861718	-0.577973
6	-1.637337	-1.498191	-0.824402
6	-1.761722	0.917257	-0.872468
6	-2.656829	-0.310047	1.029943
1	-0.228528	0.659199	1.531054
1	0.071108	-1.143950	1.276584
1	1.516035	-1.600452	-1.177356
1	3.090482	-1.052638	1.080379
1	-1.477304	-2.360731	-0.171890
1	-0.822184	-1.438761	-1.549275
1	-0.898670	0.949656	-1.543010
1	-1.740398	1.811928	-0.248392
1	-2.600650	0.611774	1.614483
1	-2.464077	-1.164699	1.685236
8	2.726338	-1.670783	0.419458
8	0.785949	2.549404	0.209828

1	-2.589915	-1.618292	-1.360100
1	-2.689336	0.876824	-1.460654
1	-3.665605	-0.404167	0.603299
1	2.437153	1.796534	-0.701393
1	2.799906	-0.387806	-1.237230

1e

NImag = 0

E_{tot} = -479.3704583

7	2.037048	-0.326397	-0.042280
6	-0.771227	-0.142121	-1.184726
6	-1.604307	0.231420	-0.193532
6	-1.640911	1.649540	0.235360
6	-2.517152	-0.726408	0.535763
6	3.030047	-1.363767	-0.286357
6	1.568202	-0.375623	1.335006
6	2.575310	0.993388	-0.351976
1	-0.143726	0.593955	-1.675521
1	-0.706760	-1.174285	-1.512728
1	-2.073669	-1.032886	1.489005
1	-3.178766	-1.733501	-1.011370
1	3.339320	-1.332652	-1.335261
1	2.591651	-2.344876	-0.080526
1	1.115837	-1.352528	1.532982
1	0.811610	0.399259	1.486586
1	1.799218	1.747721	-0.196290
1	2.887348	1.021372	-1.400561
8	-2.744891	-1.948429	-0.165432
8	-0.797854	2.496756	-0.068466
1	3.931157	-1.243595	0.346611
1	2.385421	-0.212471	2.064646
1	3.450627	1.247285	0.277238
1	-2.495925	1.943904	0.878029
1	-3.470501	-0.227103	0.767073

NMe₃

NImag = 0

E_{tot} = -173.839502

6	-1.019945	-0.934888	0.064031
7	0.000022	-0.000023	-0.391209
6	-0.299749	1.350700	0.064037
6	1.319646	-0.415765	0.064009
1	-1.995982	-0.624155	-0.319226
1	-0.796182	-1.933827	-0.320853
1	2.072967	0.277375	-0.320895
1	1.538522	-1.416464	-0.319100
1	-1.276739	1.656360	-0.320858
1	0.457411	2.040518	-0.319288
1	-1.079146	-0.990453	1.168736
1	1.397451	-0.439209	1.168745
1	-0.318170	1.429731	1.168738

Acrylaldehyde

NImag = 0

E_{tot} = -191.3228916

6	-1.468664	-0.473982	0.000140
1	-2.549866	-0.381184	-0.000381
1	-1.041136	-1.472593	0.000728
6	-0.667819	0.606330	-0.000085
6	0.808718	0.473995	0.000243
1	-1.076103	1.615190	-0.001018
8	1.406354	-0.602429	-0.000258
1	1.382861	1.419967	0.000946

Formaldehyde

NImag = 0

E_{tot} = -114.1770785

6	-0.000001	-0.539810	0.000000
8	-0.000001	0.684673	0.000000
1	0.000005	-1.119261	0.937927
1	0.000005	-1.119261	-0.937927

S7. The mPW1K/6-31+G* optimized coordinates and ground state electronic energy (E_{tot} in hartree/particle) of the model systems with water molecules.

TS(1b-1c)_{2w}

NImag = 1 (-208.30)

E_{tot} = -633.5616617

6	-0.756818	1.982386	1.035337
7	0.316952	1.465213	0.156477
6	0.424931	2.322744	-1.043015
6	1.608030	1.478453	0.878549
1	-1.721753	1.846284	0.551672
1	-0.742515	1.425144	1.964917
1	2.393629	1.146779	0.206529
1	1.536266	0.801338	1.722065
1	-0.531227	2.324902	-1.556471
1	1.197575	1.916649	-1.688237
6	-0.027662	0.059442	-0.325340
1	-0.942427	0.177478	-0.906400
1	0.780128	-0.216829	-0.996768
6	-0.221221	-0.963864	0.720957
6	0.855233	-1.798060	1.111171
8	1.943092	-1.931525	0.541756
1	-0.561874	3.031979	1.238191
1	1.799710	2.489843	1.227385
1	0.684904	3.332990	-0.740004
1	0.649618	-2.450255	1.974417
1	-0.969226	-0.771469	1.479139
6	-1.450633	-2.225979	-0.316069
1	-0.655136	-2.753834	-0.856148
1	-1.792907	-2.758440	0.579498
8	-2.254786	-1.516866	-0.965241
1	2.765432	-0.961304	-0.676382
8	3.100165	-0.268399	-1.280557
1	3.810348	-0.665008	-1.783822
1	-3.109620	-0.161148	-0.392898
8	-3.421197	0.726234	-0.101753
1	-4.338947	0.782132	-0.365210

TS(1c-1d)_{2w}

NImag = 1 (-209.60)

E_{tot} = -633.5502618

7	0.699536	1.281793	-0.046134
6	0.006725	0.131582	0.665537
6	-0.808285	-0.851715	-0.138471
6	-0.108301	-2.032024	-0.627937
6	-1.909652	-0.328604	-1.075632
6	-0.270987	2.378335	-0.299258
6	1.328906	0.847241	-1.312808
6	1.765174	1.787528	0.853871
1	0.795861	-0.406483	1.181985
1	-0.643838	0.588365	1.407005
1	-1.502641	0.150792	-1.972965
1	-1.512534	-1.206121	0.738413
1	-0.530590	2.825871	0.654714

1	-1.181881	1.976808	-0.731776
1	0.558917	0.516781	-1.998376
1	2.024337	0.043357	-1.102533
1	2.522413	1.016857	0.966187
1	1.319715	2.020742	1.815924
8	-2.727502	0.582644	-0.435252
8	1.048144	-2.350595	-0.409329
1	2.192700	2.686904	0.419099
1	1.860710	1.692756	-1.739959
1	0.199065	3.118929	-0.940087
1	-2.468601	-1.203320	-1.432390
1	-0.732264	-2.723262	-1.214906
8	-2.590364	-0.605540	1.740430
1	-3.286098	-1.158981	2.094273
1	-2.892502	0.181322	0.505362
1	2.540201	-1.655820	0.329024
8	3.248550	-1.054879	0.614377
1	3.988180	-1.605140	0.870320