Electronic Supplementary Information (ESI)

Rate Coefficients and Product Branching Ratios for (E)-2-Butenal + H Reactions

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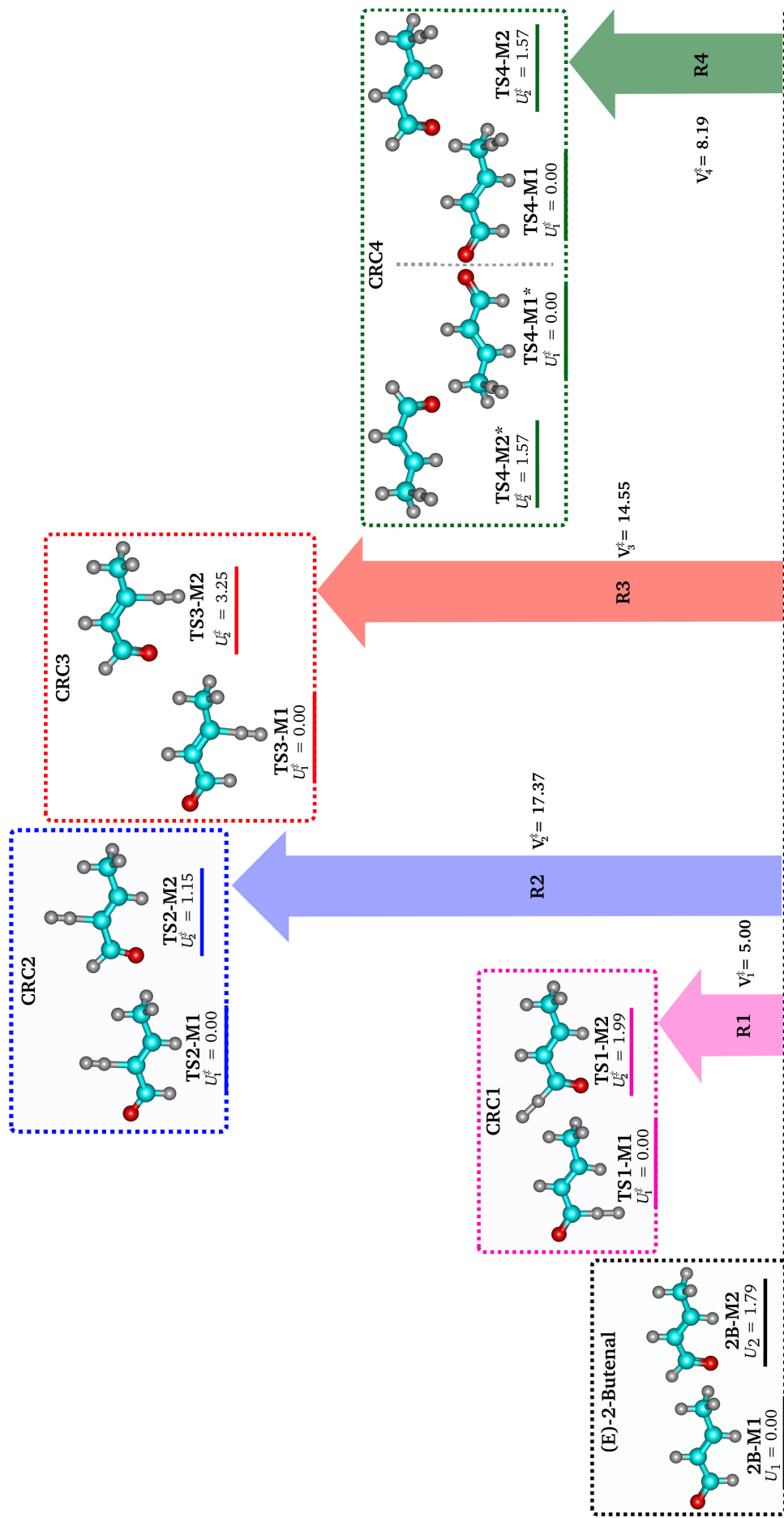
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Figure S1: Energetic profile showing the difference in energy between all conformations of (E)-2-butenal and transition states structure of each CRC, and the forward classical barriers for (R1)–(R4). The relative energies (in kcal/mol) are calculated at the MPWB1K/6-31+G(d,p) level of theory.

Table S1: Cartesian coordinates (in Å) and non-scaled vibrational frequencies (in cm^{-1}) for the 2B-M1

Cartesian Coordinates			
Element	X	Y	Z
C	-0.127307	0.000014	-0.073142
C	-0.105061	0.000010	1.385164
C	1.052924	0.000003	2.042501
C	1.211701	-0.000002	3.515637
H	0.866260	-0.000017	-0.554827
H	-1.058919	0.000016	1.893797
H	1.966650	-0.000002	1.456936
H	0.252440	0.000021	4.023646
H	1.776262	-0.873335	3.839046
H	1.776307	0.873301	3.839049
O	-1.130203	-0.000008	-0.740095
Vibrational Frequencies			
3272.3928	3229.1692	3211.8864	3181.3963
3114.2932	2998.7855	1875.3468	1780.9350
1513.7213	1506.6561	1445.8117	1437.6289
1350.1399	1301.0687	1203.0475	1139.1440
1096.6137	1057.0042	1030.1160	960.6809
814.0989	553.7997	465.3252	301.7063
203.6354	201.6211	130.1352	

Energy MPWB1K/6-31+G(d,p) (a.u.): -231.1225483

Table S2: Cartesian coordinates (in Å) and non-scaled vibrational frequencies (in cm^{-1}) for the 2B-M2

Cartesian Coordinates			
Element	X	Y	Z
C	-0.149836	0.010822	-0.077243
C	-0.113003	0.008037	1.389621
C	1.044731	0.007666	2.047573
C	1.196674	0.004958	3.520239
H	-1.154090	0.010908	-0.528921
H	-1.059219	0.006303	1.913577
H	1.948084	0.009509	1.448969
H	0.237345	0.003242	4.029013
H	1.763405	-0.867672	3.842441
H	1.762059	0.877217	3.84579
O	0.826587	0.012924	-0.784996
Vibrational Frequencies			
3255.3823	3247.1338	3215.0219	3179.4551
3112.1202	3033.2019	1873.5144	1765.8484
1513.5736	1506.2959	1466.4420	1440.9949
1350.6235	1343.6312	1176.2937	1104.6826
1066.2487	1061.2413	1027.7935	922.1058
793.5765	758.8636	401.2674	245.5252
208.2092	204.7759	144.5907	

Energy MPWB1K/6-31+G(d,p) (a.u.): -231.1196897

Table S3: Cartesian coordinates (in Å) and non-scaled vibrational frequencies (in cm^{-1}) for the TS1-M1

Cartesian Coordinates			
Element	X	Y	Z
C	-0.075887	-0.000763	-0.06802
C	-0.080182	-0.000669	1.387196
C	1.069771	0.000282	2.059839
C	1.197284	0.000479	3.534526
H	1.096259	0.000137	-0.553033
H	-1.043984	-0.001397	1.879513
H	1.990516	0.00097	1.488032
H	0.229427	-0.000248	4.025717
H	1.758478	-0.871936	3.865838
H	1.757109	0.873816	3.865724
O	-1.013906	-0.001558	-0.799228
H	2.072014	0.000887	-0.945486
Vibrational Frequencies			
1408.4163i	3252.0206	3241.3230	3221.6288
3184.4586	3116.1776	1943.7559	1772.1914
1511.6805	1505.9437	1442.7926	1431.0303
1367.3666	1325.3162	1299.5668	1166.1616
1161.8096	1101.6217	1099.7816	1019.7629
958.8218	824.1526	539.9781	484.6194
423.9928	363.4318	222.1255	220.9368
195.856	118.7017		

Energy MPWB1K/6-31+G(d,p) (a.u.): -231.6105357

Table S4: Cartesian coordinates (in Å) and non-scaled vibrational frequencies (in cm^{-1}) for the TS1-M2

Cartesian Coordinates			
Element	X	Y	Z
C	-0.066151	0.029979	-0.093126
C	-0.076274	0.012646	1.369030
C	1.063733	0.011107	2.058841
C	1.170128	-0.005715	3.534811
H	-1.232116	0.029042	-0.586235
H	-1.042230	0.001331	1.852502
H	1.986981	0.023164	1.491641
H	0.196076	-0.017023	4.013800
H	1.731963	-0.879067	3.863258
H	1.721843	0.866090	3.883877
O	0.878442	0.044023	-0.817929
H	-2.215944	0.027514	-0.939889
Vibrational Frequencies			
1415.6485i	3275.1824	3245.7417	3220.4282
3182.2192	3114.3301	1938.4793	1755.9533
1510.3169	1504.4048	1441.8901	1438.5795
1366.9429	1341.9460	1280.9430	1168.0481
1166.9265	1103.3459	1055.8758	1026.0923
925.1171	805.4245	719.6160	398.0810
373.1760	304.4104	208.5277	195.3660
190.5107	110.7882		

Energy MPWB1K/6-31+G(d,p) (a.u.): -231.6073621

Table S5: Cartesian coordinates (in Å) and non-scaled vibrational frequencies (in cm^{-1}) for the TS2-M1

Cartesian Coordinates			
Element	X	Y	Z
C	-0.132250	-0.000010	-0.102464
C	0.011187	0.000001	1.342326
C	1.138461	-0.000013	2.031509
C	1.262781	-0.000001	3.510653
H	0.833614	-0.000032	-0.644141
H	-1.272123	0.000032	2.074404
H	2.070890	-0.000035	1.467059
H	0.291339	0.000023	3.992960
H	1.819908	-0.874272	3.843024
H	1.819944	0.874252	3.843007
O	-1.171379	0.000004	-0.705900
H	-1.996091	0.000051	2.509298
Vibrational Frequencies			
999.5811i	3236.1371	3186.6298	3150.4093
3118.4941	2955.9249	2341.1694	1866.7649
1770.6437	1513.1751	1507.6724	1441.7546
1431.1312	1307.4704	1178.3468	1129.6055
1085.3450	1034.6272	1030.0951	952.1331
943.5093	822.2652	575.1250	462.6525
256.0735	250.6831	238.7411	185.3293
175.0983	108.5051		

Energy MPWB1K/6-31+G(d,p) (a.u.): -231.5908257

Table S6: Cartesian coordinates (in Å) and non-scaled vibrational frequencies (in cm^{-1}) for the TS2-M2

Cartesian Coordinates			
Element	X	Y	Z
C	-0.146858	-0.001681	-0.109539
C	0.020010	0.002846	1.341034
C	1.140586	0.012158	2.040646
C	1.251114	0.016365	3.519895
H	-1.181380	-0.009629	-0.478941
H	-1.254519	-0.004178	2.073712
H	2.067062	0.017178	1.469876
H	0.277259	0.010804	3.997953
H	1.813588	-0.852564	3.857655
H	1.801613	0.894487	3.853582
O	0.781327	0.002882	-0.879286
H	-1.998576	-0.008309	2.487902
Vibrational Frequencies			
1040.4416i	3231.4908	3185.5113	3178.5978
3117.4173	3063.8890	2271.1577	1843.3768
1759.9580	1512.3196	1507.8598	1455.1858
1439.0856	1302.1071	1165.8194	1138.6074
1088.2012	1056.4554	1054.0192	971.2754
887.3339	829.9777	728.4333	401.2153
253.4849	249.1521	221.4634	179.6356
173.2951	43.6608		

Energy MPWB1K/6-31+G(d,p) (a.u.): -231.5889931

Table S7: Cartesian coordinates (in Å) and non-scaled vibrational frequencies (in cm^{-1}) for the TS3-M1

Cartesian Coordinates			
Element	X	Y	Z
C	-0.077713	0.003816	-0.120344
C	-0.099513	0.003002	1.343047
C	1.008335	0.003595	2.062920
C	1.275560	0.003049	3.505511
H	0.922689	0.004953	-0.579154
H	-1.079694	0.001879	1.810025
H	2.209755	0.005072	1.307284
H	0.348356	0.001916	4.076763
H	1.858004	-0.872423	3.786476
H	1.856449	0.879249	3.787426
O	-1.070562	0.003304	-0.801259
H	2.964571	0.005985	0.859002
Vibrational Frequencies			
1243.1706i	3205.2554	3193.6451	3192.7109
3106.0483	3043.2866	1971.9493	1870.0373
1770.6926	1500.6529	1490.5139	1445.2884
1428.1519	1261.8063	1178.7011	1150.1971
1089.6762	1078.9297	1051.7414	1019.4902
969.1424	836.2949	535.1024	450.1237
329.9868	318.6896	243.9720	196.8483
161.8824	123.9598		

Energy MPWB1K/6-31+G(d,p) (a.u.): -231.5953211

Table S8: Cartesian coordinates (in Å) and non-scaled vibrational frequencies (in cm^{-1}) for the TS3-M2

Cartesian Coordinates			
Element	X	Y	Z
C	-0.130505	0.031070	-0.136344
C	-0.095442	0.015568	1.334724
C	1.015830	0.009969	2.050220
C	1.262095	-0.004892	3.496076
H	-1.143056	0.033864	-0.570235
H	-1.059467	0.008550	1.836329
H	2.251849	0.019877	1.321088
H	0.330617	-0.012520	4.060780
H	1.845325	-0.881470	3.773008
H	1.842221	0.867695	3.791515
O	0.833969	0.040391	-0.855477
H	3.032270	0.025180	0.950820
Vibrational Frequencies			
1198.9300i	3189.8738	3189.2313	3185.4807
3102.8006	3027.4305	2087.7272	1879.2032
1754.5133	1500.2966	1490.0064	1465.0629
1430.0891	1319.0238	1132.5232	1110.6015
1073.1057	1059.2017	1046.5445	1005.1681
911.7945	798.3973	754.9574	366.4809
323.1910	299.8967	222.0230	210.5074
159.6228	76.7134		

Energy MPWB1K/6-31+G(d,p) (a.u.): -231.5901445

Table S9: Cartesian coordinates (in Å) and non-scaled vibrational frequencies (in cm^{-1}) for the TS4-M1

Cartesian Coordinates			
Element	X	Y	Z
C	-0.133212	-0.907330	-0.233300
C	-0.127682	-0.731520	1.211692
C	0.987116	-0.346462	1.847051
C	1.114732	-0.174863	3.284142
H	0.829997	-0.706625	-0.733450
H	-1.054652	-0.917303	1.735741
H	1.877776	-0.180534	1.251150
H	0.176684	-0.138548	3.825772
H	1.666861	-1.192368	3.750437
H	1.800753	0.604324	3.595842
O	-1.097103	-1.245141	-0.873646
H	2.094275	-2.001756	4.218950
Vibrational Frequencies			
1650.0671i	3272.7284	3270.6372	3224.1969
3182.5136	3005.0700	1859.9523	1733.9959
1505.0414	1442.8994	1374.9327	1361.8458
1344.8271	1336.4210	1295.3645	1200.0429
1160.2422	1074.2802	1049.8262	1017.5643
984.4824	845.1954	599.8914	551.7619
458.5635	404.3299	254.7436	204.7340
175.3615	119.4956		

Energy MPWB1K/6-31+G(d,p) (a.u.): -231.6054565

Table S10: Cartesian coordinates (in Å) and non-scaled vibrational frequencies (in cm^{-1}) for the TS4-M2

Cartesian Coordinates			
Element	X	Y	Z
C	-0.166717	-0.906950	-0.241465
C	-0.153030	-0.751963	1.214139
C	0.962663	-0.380976	1.856985
C	1.083177	-0.233233	3.296257
H	-1.130429	-1.205290	-0.681412
H	-1.074334	-0.938957	1.748576
H	1.843670	-0.212290	1.250225
H	0.143898	-0.207142	3.837166
H	1.635700	-1.250219	3.746422
H	1.766423	0.543093	3.621683
O	0.791336	-0.728418	-0.953761
H	2.065026	-2.070434	4.216605
Vibrational Frequencies			
1644.2511i	3268.6884	3259.9063	3248.8107
3179.0243	3035.8280	1858.4971	1715.7764
1505.8143	1464.2169	1388.4525	1366.3305
1357.0346	1331.4759	1319.9084	1189.8889
1083.1866	1067.5485	1059.3730	1012.5255
943.1908	824.3824	762.7700	591.4961
393.5958	382.4876	236.1212	200.6561
183.1629	120.5420		

Energy MPWB1K/6-31+G(d,p) (a.u.): -231.6029627

Table S11: Cartesian coordinates (in Å) and non-scaled vibrational frequencies (in cm^{-1}) for the CH$_3$CH=CHĊO

Cartesian Coordinates			
Element	X	Y	Z
C	-0.147656	-0.000137	-0.052455
C	-0.119286	-0.000050	1.404569
C	1.047566	-0.000073	2.047039
C	1.212427	0.000008	3.517891
H	-1.068854	0.000032	1.928406
H	1.948555	-0.000158	1.446226
H	0.257400	0.000088	4.033760
H	1.780828	-0.872999	3.835217
H	1.780916	0.872998	3.835111
O	-1.078673	-0.000132	-0.778094
Vibrational Frequencies			
3250.1673	3222.2346	3221.0318	3183.4994
3115.4605	1990.7840	1767.7626	1509.8354
1505.4697	1441.2283	1347.7694	1297.3102
1167.5767	1101.8484	1099.9901	1011.7375
946.3818	820.2462	519.1490	466.8835
337.3411	207.3927	204.0627	116.2663

Energy MPWB1K/6-31+G(d,p) (a.u.): -230.4731246

Table S12: Cartesian coordinates (in Å) and non-scaled vibrational frequencies (in cm^{-1}) for the CH$_3$CH=ĊCOH

Cartesian Coordinates			
Element	X	Y	Z
C	-0.168679	-0.000058	-0.107691
C	0.031386	-0.000089	1.326073
C	1.127625	0.000042	2.052850
C	1.198497	-0.000003	3.537422
H	0.784271	0.000112	-0.673644
H	2.080426	0.000212	1.520834
H	0.209250	-0.000163	3.980902
H	1.742402	-0.875029	3.888877
H	1.742148	0.875153	3.888944
O	-1.221411	-0.000194	-0.685389
Vibrational Frequencies			
3239.5673	3188.3177	3133.4832	3118.7252
2945.0128	1864.7484	1787.5628	1509.3068
1509.0659	1437.0800	1425.2739	1294.2918
1160.6509	1124.5397	1080.4320	1017.3690
935.8914	789.4991	545.6963	437.3385
212.3120	197.2083	160.9111	101.5023

Energy MPWB1K/6-31+G(d,p) (a.u.): -230.4350400

Table S13: Cartesian coordinates (in Å) and non-scaled vibrational frequencies (in cm^{-1}) for the CH$_3$Ċ=CHCOH

Cartesian Coordinates			
Element	X	Y	Z
C	-0.106643	-0.000001	-0.092004
C	-0.205522	0.000012	1.368974
C	0.860048	-0.000009	2.137932
C	1.245628	-0.000007	3.540404
H	0.917091	-0.000031	-0.495014
H	-1.210692	0.000043	1.785365
H	0.365749	0.000022	4.188500
H	1.843988	-0.877634	3.775944
H	1.844035	0.877591	3.775929
O	-1.062525	0.000018	-0.824375
Vibrational Frequencies			
3198.2262	3173.4394	3172.1601	3081.3989
3043.8249	1866.6121	1797.2179	1491.9016
1480.2582	1444.2031	1421.9092	1255.4545
1168.0129	1087.7513	1059.5312	1045.6205
958.3914	803.7351	527.2394	420.6062
312.2002	169.8338	151.2648	120.5677

Energy MPWB1K/6-31+G(d,p) (a.u.): -230.4437113

Table S14: Cartesian coordinates (in Å) and non-scaled vibrational frequencies (in cm^{-1}) for the $\dot{C}H_2CH=CHCOH$

Cartesian Coordinates			
Element	X	Y	Z
C	-0.089297	0.028145	-0.121104
C	-0.099299	-0.025836	1.313039
C	1.074486	-0.131992	2.053695
C	1.115841	-0.186647	3.415456
H	0.902257	-0.019469	-0.598991
H	-1.061525	0.019367	1.803306
H	2.008081	-0.173073	1.505670
H	0.209388	-0.148772	4.000339
H	2.049375	-0.268899	3.947440
O	-1.092730	0.120652	-0.800712
Vibrational Frequencies			
3347.9246	3274.4875	3243.3597	3235.6700
3025.1160	1751.6448	1571.7451	1527.3422
1448.6623	1327.2789	1311.9309	1259.7071
1186.7315	1041.7083	1013.3548	989.0932
912.4174	832.0997	586.8066	552.4691
471.8208	273.5588	211.0873	148.9446

Energy MPWB1K/6-31+G(d,p) (a.u.): -230.4811000

Table S15: Cartesian coordinates (in Å) and non-scaled vibrational frequencies (in cm^{-1}) for the H_2

Cartesian Coordinates			
Element	X	Y	Z
H	0.000000	0.000000	0.131093
H	0.000000	0.000000	0.868907
Vibrational Frequencies			
4535.8789			

Energy MPWB1K/6-31+G(d,p) (a.u.): -1.16489677538

Table S16: Cartesian coordinates (in Å) for the H

Cartesian Coordinates			
Element	X	Y	Z
H	0.000000	0.000000	0.000000

Energy MPWB1K/6-31+G(d,p) (a.u.): -0.4959576

Torsional Potential Energy Surface

The potential $V_{\text{tor}}(\phi_1, \phi_2)$ are obtained from a fit to Fourier series of the type

$$
\begin{aligned}
V_{\text{tor}}(\phi_1, \phi_2) =& V_1(\phi_1) + V_2(\phi_1) + \\
& \sum_{L_1=1}^{L_{1,max}} \sum_{L_2=1}^{L_{2,max}} c_{L_1 L_2} \cos(L_1 \phi_1) \cos(L_2 \phi_2) + \\
& \sum_{P_1=1}^{P_{1,max}} \sum_{P_2=1}^{P_{2,max}} d_{P_1 P_2} \sin(P_1 \phi_1) \sin(P_2 \phi_2) +
\end{aligned}
\tag{1}
$$

where $c_{L_1 L_2}(L_1 = 1, ..., L_{1,max}, L_2 = 1, ..., L_{2,max})$ and $d_{P_1 P_2}(P_1 = 1, ..., P_{1,max}, P_2 = 1, ..., P_{2,max})$ are fitting parameters. $L_{1,max}, L_{2,max}, P_{1,max}$, and $P_{2,max}$, indicate the largest number of each series.

The one-dimensional potentials are:

$$
V_1(\phi_1) = a_0 + \sum_{M=1}^{M_{max}} a_M \cos(M\phi_1)
\tag{2}
$$

and

$$
V_2(\phi_2) = b_0 + \sum_{N=1}^{N_{max}} b_N \cos(N\phi_2)
\tag{3}
$$

where, $a_0, b_0, a_M(M = 1, ..., M_{max})$ and $b_N(N = 1, ..., N_{max})$ are fitting parameters. M_{max} and N_{max}, are the largest number of each series.

Table S17: Parameters (in cm^{-1}) used to fit by Fourier series the two-dimensional torsional potential for (E)-2-butenal (including coupling parameters).

Parameters	
a_0	+1942.79565
a_1	-200.91937
a_2	-1483.33282
a_3	-139.36742
a_4	+199.24267
a_5	+15.45355
a_6	-41.77088
a_7	-4.19294
a_8	+13.05390
b_3	-331.05911
b_6	+10.27008
b_9	-0.52212
c_{13},d_{13}	+14.63306,-11.37822
c_{23},d_{23}	+11.48102,-18.57446
c_{33},d_{33}	+1.51861,+1.58047
c_{43},d_{43}	-3.47200,+4.67024
c_{53},d_{53}	-0.23764,+0.15817
c_{63},d_{63}	+1.06962,-1.12613
c_{73},d_{73}	+0.00529,+0.47261
c_{83},d_{83}	-0.45726,+0.81341
c_{16},d_{16}	+0.33524,-0.56582
c_{26},d_{26}	-1.45002,+0.31744
c_{36},d_{36}	+0.07322,-1.04773
c_{46},d_{46}	+0.76266,-1.24961
c_{56},d_{56}	+0.00951,-0.27703
c_{66},d_{66}	-0.20890,-0.22114
c_{76},d_{76}	+0.06147,-0.28468
c_{86},d_{86}	-0.12291,-0.44229
c_{19},d_{19}	-0.98930,+0.54466
c_{29},d_{29}	+0.24635,-0.27197
c_{39},d_{39}	-0.09631,+0.01662
c_{49},d_{49}	-0.00832,+0.04164
c_{59},d_{59}	+0.24369,-0.35419
c_{69},d_{69}	+0.06994,+0.05118

Table S17 – continued from previous page

Parameters	
c_{79},d_{79}	-0.16163,-0.14998
c_{89},d_{89}	-0.03874,-0.11608

Table S18: Parameters (in cm^{-1}) used to fit by Fourier series the two-dimensional torsional potential for CRC1 (including coupling parameters).

Parameters	
a_0	+1810.74692
a_1	-241.54122
a_2	-1316.76435
a_3	-151.23686
a_4	+198.57729
a_5	+41.99889
a_6	-42.19300
a_7	-9.94637
a_8	+15.01788
b_3	-328.05396
b_6	+9.96448
b_9	-0.41057
c_{13},d_{13}	+9.76888,-6.23399
c_{23},d_{23}	+8.96263,-24.15753
c_{33},d_{33}	+1.11079,+2.08280
c_{43},d_{43}	-3.76320,+6.20379
c_{53},d_{53}	-0.67976,+0.07852
c_{63},d_{63}	+1.07334,-2.21970
c_{73},d_{73}	+0.25338,+0.16473
c_{83},d_{83}	-0.69587,+1.45063
c_{16},d_{16}	+0.58630,-1.21343
c_{26},d_{26}	-1.41153,+0.51423
c_{36},d_{36}	+0.02751,-1.09816
c_{46},d_{46}	+0.87628,-1.47339
c_{56},d_{56}	+0.03776,-0.32818
c_{66},d_{66}	-0.22830,-0.19813
c_{76},d_{76}	+0.04828,-0.30884
c_{86},d_{86}	-0.12981,-0.55199
c_{19},d_{19}	-1.18798,+0.60903
c_{29},d_{29}	+0.33300,-0.27555
c_{39},d_{39}	-0.05676,-0.02853
c_{49},d_{49}	-0.04551,+0.07305
c_{59},d_{59}	+0.27366,-0.39924
c_{69},d_{69}	+0.08947,+0.04995

Table S18 – continued from previous page	
Parameters	
c_{79}, d_{79}	-0.19287,-0.18026
c_{89}, d_{89}	-0.07108,-0.12635

Table S19: Parameters (in cm^{-1}) used to fit by Fourier series the two-dimensional torsional potential for CRC2 (including coupling parameters).

Parameters	
a_0	+1034.93889
a_1	-117.78218
a_2	-617.35798
a_3	-82.75887
a_4	+89.36228
a_5	-13.68510
a_6	-18.82553
a_7	+0.36820
a_8	+6.47374
b_3	-304.33212
b_6	+10.82540
b_9	-0.15193
c_{13},d_{13}	+11.42417,-7.82978
c_{23},d_{23}	+5.60927,+6.68146
c_{33},d_{33}	+1.62426,-0.24179
c_{43},d_{43}	-2.66180,-2.44468
c_{53},d_{53}	+0.34429,+0.14377
c_{63},d_{63}	+1.11106,+1.24637
c_{73},d_{73}	-0.23541,+0.53692
c_{83},d_{83}	-0.47548,+0.00707
c_{16},d_{16}	+0.38476,-0.92753
c_{26},d_{26}	-2.09969,-2.70681
c_{36},d_{36}	+0.06064,-0.80257
c_{46},d_{46}	+0.42839,-0.18171
c_{56},d_{56}	-0.07447,-0.27524
c_{66},d_{66}	-0.10893,-0.55274
c_{76},d_{76}	+0.11668,-0.30741
c_{86},d_{86}	-0.01875,-0.28605
c_{19},d_{19}	-0.92377,+0.44077
c_{29},d_{29}	+0.46168,-0.44649
c_{39},d_{39}	-0.01941,+0.01282
c_{49},d_{49}	-0.17515,+0.02987
c_{59},d_{59}	+0.14631,-0.25368
c_{69},d_{69}	+0.05869,+0.15875

Table S19 – continued from previous page

Parameters	
c_{79},d_{79}	-0.13712,-0.14125
c_{89},d_{89}	-0.06615,-0.15854

Table S20: Parameters (in cm^{-1}) used to fit by Fourier series the two-dimensional torsional potential for CRC3 (including coupling parameters).

Parameters	
a_0	+1914.57806
a_1	-466.87671
a_2	-1285.63630
a_3	-112.65084
a_4	+189.06161
a_5	-1.87906
a_6	-34.02690
a_7	-0.12796
a_8	+10.71416
b_3	-233.16223
b_6	+7.30751
b_9	-0.49738
c_{13},d_{13}	+12.76976, -5.13297
c_{23},d_{23}	+5.79362,-13.96958
c_{33},d_{33}	+1.07186, +5.45895
c_{43},d_{43}	-2.70946, -0.35225
c_{53},d_{53}	+0.75521, +0.00524
c_{63},d_{63}	+0.27981, -0.44664
c_{73},d_{73}	+0.20382, +0.57974
c_{83},d_{83}	-0.57476, +0.00221
c_{16},d_{16}	-0.35521, +0.62917
c_{26},d_{26}	-0.71617, +0.20336
c_{36},d_{36}	+0.14812, -0.90745
c_{46},d_{46}	+0.31372, -0.26262
c_{56},d_{56}	-0.07696, -0.00148
c_{66},d_{66}	-0.00435, -0.14965
c_{76},d_{76}	-0.02445, -0.16783
c_{86},d_{86}	-0.06700, -0.04960
c_{19},d_{19}	-0.31538, -0.09045
c_{29},d_{29}	-0.03931, -0.04254
c_{39},d_{39}	-0.06590, +0.10818
c_{49},d_{49}	+0.11358, -0.10552
c_{59},d_{59}	+0.07052, -0.17595
c_{69},d_{69}	-0.01143, +0.03237

Parameters	
c_{79},d_{79}	-0.00677, -0.02755
c_{89},d_{89}	-0.06261, -0.07667

Table S21: Parameters (in cm^{-1}) used to fit by Fourier series the two-dimensional torsional potential for CRC4 (including coupling parameters).

Parameters	
a_0	+2587.19187
a_1	-163.26767
a_2	-1519.30034
a_3	-131.23943
a_4	+196.78200
a_5	+14.93042
a_6	-41.82678
a_7	-3.90435
a_8	+13.22472
b_1	+34.39882
b_2	+938.21384
b_3	-207.12122
b_4	+90.14449
b_5	-20.35260
b_6	+24.38168
b_7	-7.10353
b_8	+5.13389
c_{11},d_{11}	+22.41554,-23.81130
c_{21},d_{21}	+5.65890,-21.09229
c_{31},d_{31}	-5.12162, +1.48183
c_{41},d_{41}	-1.81764, +3.84514
c_{51},d_{51}	+1.07385, -0.70877
c_{61},d_{61}	+0.91667, -0.85601
c_{71},d_{71}	-0.36383, +0.24064
c_{81},d_{81}	-0.37222, +0.41444
c_{12},d_{12}	-4.15169, -9.38520
c_{22},d_{22}	+61.71244,+15.27658
c_{32},d_{32}	-6.43865,-10.06612
c_{42},d_{42}	-10.75712, +4.56080
c_{52},d_{52}	-0.76670, +2.06663
c_{62},d_{62}	+4.52472, -1.39973
c_{72},d_{72}	+0.45581, -0.96705
c_{82},d_{82}	-1.77525, +0.64042
c_{13},d_{13}	+14.92587,-14.09373

Table S21 – continued from previous page

Parameters	
c_{23}, d_{23}	+7.29995, -15.18460
c_{33}, d_{33}	+0.25957, -1.32437
c_{43}, d_{43}	-2.21401, +3.18678
c_{53}, d_{53}	-0.10353, +0.09918
c_{63}, d_{63}	+0.63376, -0.81238
c_{73}, d_{73}	+0.08341, +0.13523
c_{83}, d_{83}	-0.27704, +0.30006
c_{14}, d_{14}	-3.49896, -2.19127
c_{24}, d_{24}	+19.22350, +1.44701
c_{34}, d_{34}	-2.23652, -3.43943
c_{44}, d_{44}	-2.90725, +1.46655
c_{54}, d_{54}	-0.34750, +0.21176
c_{64}, d_{64}	+1.20712, -0.23816
c_{74}, d_{74}	-0.01222, -0.10070
c_{84}, d_{84}	+0.22805, +0.10093
c_{15}, d_{15}	+1.70103, -1.82547
c_{25}, d_{25}	-1.30399, -1.76236
c_{35}, d_{35}	+0.04997, -0.11988
c_{45}, d_{45}	+0.39323, -0.01652
c_{55}, d_{55}	+0.01957, -0.13492
c_{65}, d_{65}	-0.10640, +0.01612
c_{75}, d_{75}	-0.00331, +0.02556
c_{85}, d_{85}	+0.04862, -0.02675
c_{16}, d_{16}	-2.50912, +0.31264
c_{26}, d_{26}	+4.05092, +1.43338
c_{36}, d_{36}	-0.58921, -1.02129
c_{46}, d_{46}	-0.29350, +0.09298
c_{56}, d_{56}	-0.17809, -0.02617
c_{66}, d_{66}	+0.08944, +0.08402
c_{76}, d_{76}	-0.03517, -0.01340
c_{86}, d_{86}	-0.06428, -0.04661
c_{17}, d_{17}	+0.73290, -0.01591
c_{27}, d_{27}	-1.14947, -0.58711
c_{37}, d_{37}	+0.11491, +0.23698
c_{47}, d_{47}	+0.37258, -0.08950
c_{57}, d_{57}	+0.10026, -0.02441

Parameters	
c_{67},d_{67}	-0.03387, +0.07483
c_{77},d_{77}	+0.06771, +0.02807
c_{87},d_{87}	+0.11926, -0.00924
c_{18},d_{18}	-0.82678, -0.02635
c_{28},d_{28}	+1.17362, +0.16916
c_{38},d_{38}	-0.20086, -0.30440
c_{48},d_{48}	-0.14421, +0.13343
c_{58},d_{58}	-0.08185, -0.02927
c_{68},d_{68}	-0.02206, -0.01281
c_{78},d_{78}	-0.03806, +0.01218
c_{88},d_{88}	-0.02566, +0.01039

Table S22: Translational, electronic, and rovibrational (MS-HO[a] and E2DT[b]) partition functions for the (E)-2-butenal. $Q_{\mathrm{T}}^{\mathrm{MS\text{-}HO}}$ and $Q_{\mathrm{T}}^{\mathrm{E2DT}}$ stands for the total partition functions[c]. Power of 10 in parentheses.

T(K)	Q_{trans}	Q_{elec}	$Q^{\mathrm{MS\text{-}HO}}$	Q^{E2DT}	$Q_{\mathrm{T}}^{\mathrm{MS\text{-}HO}}$	$Q_{\mathrm{T}}^{\mathrm{E2DT}}$
200	4.617(+01)	1.000(+00)	1.396(+05)	1.370(+05)	6.446(+06)	6.326(+06)
300	8.482(+01)	1.000(+00)	7.764(+05)	7.913(+05)	6.586(+07)	6.712(+07)
400	1.306(+02)	1.000(+00)	3.790(+06)	3.990(+06)	4.949(+08)	5.211(+08)
500	1.825(+02)	1.000(+00)	1.718(+07)	1.852(+07)	3.135(+09)	3.380(+09)
600	2.399(+02)	1.000(+00)	7.365(+07)	8.066(+07)	1.767(+10)	1.935(+10)
700	3.023(+02)	1.000(+00)	3.001(+08)	3.323(+08)	9.074(+10)	1.005(+11)
800	3.694(+02)	1.000(+00)	1.165(+09)	1.299(+09)	4.303(+11)	4.798(+11)
900	4.408(+02)	1.000(+00)	4.315(+09)	4.835(+09)	1.902(+12)	2.131(+12)
1000	5.162(+02)	1.000(+00)	1.527(+10)	1.716(+10)	7.883(+12)	8.859(+12)
1500	9.484(+02)	1.000(+00)	4.604(+12)	5.139(+12)	4.365(+15)	4.872(+15)
2000	1.460(+03)	1.000(+00)	5.931(+14)	6.405(+14)	8.661(+17)	9.353(+17)
2500	2.041(+03)	1.000(+00)	3.962(+16)	4.083(+16)	8.085(+19)	8.332(+19)

[a] MS-OH (ZPE): 55.643 kcal/mol

[b] E2DT (ZPE): 55.636 kcal/mol

[c] $Q_{\mathrm{T}}^{\mathrm{X}} = Q_{\mathrm{trans}}Q_{\mathrm{elec}}Q_{\mathrm{rovib}}^{\mathrm{X}}$, where X = MS-HO or E2DT

Table S23: Components of the E2DT partition function for the (E)-2-butenal. $Q_{\mathrm{tor,cl}}^{\mathrm{(C)}}$ is the classical torsional partition function, $Q_{\mathrm{tor}}^{\mathrm{2D\text{-}NS}}$ a quantum version of the classical function, and Q^{EHR} the extended hindered-rotor (EHR) rovibrational partition function. Power of 10 in parentheses.

T(K)	$Q_{\mathrm{tor}}^{\mathrm{2D\text{-}NS}}$	$Q_{\mathrm{tor,cl}}^{\mathrm{(C)}}$	Q^{EHR}
200	2.156(+00)	6.908(–01)	4.391(+04)
300	3.712(+00)	1.687(+00)	3.596(+05)
400	5.935(+00)	3.249(+00)	2.184(+06)
500	8.837(+00)	5.431(+00)	1.138(+07)
600	1.241(+01)	8.250(+00)	5.362(+07)
700	1.663(+01)	1.170(+01)	2.338(+08)
800	2.148(+01)	1.578(+01)	9.545(+08)
900	2.693(+01)	2.046(+01)	3.674(+09)
1000	3.294(+01)	2.572(+01)	1.340(+10)
1500	7.063(+01)	5.978(+01)	4.349(+12)
2000	1.183(+02)	1.043(+02)	5.651(+14)
2500	1.731(+02)	1.566(+02)	3.694(+16)

Table S24: Translational, electronic, and rovibrational (MS-HO[a] and E2DT[b]) partition functions for the transition state of CRC1. $Q_T^{\text{MS-HO}}$ and Q_T^{E2DT} stands for the total partition functions[c]. Power of 10 in parentheses.

T(K)	Q_{trans}	Q_{elec}	$Q^{\text{MS-HO}}$	Q^{E2DT}	$Q_T^{\text{MS-HO}}$	Q_T^{E2DT}
200	4.717(+01)	2.000(+00)	2.287(+05)	2.418(+05)	2.158(+07)	2.281(+07)
300	8.666(+01)	2.000(+00)	1.692(+06)	1.870(+06)	2.932(+08)	3.241(+08)
400	1.334(+02)	2.000(+00)	1.110(+07)	1.269(+07)	2.962(+09)	3.387(+09)
500	1.865(+02)	2.000(+00)	6.698(+07)	7.835(+07)	2.498(+10)	2.922(+10)
600	2.451(+02)	2.000(+00)	3.756(+08)	4.464(+08)	1.841(+11)	2.188(+11)
700	3.089(+02)	2.000(+00)	1.965(+09)	2.362(+09)	1.214(+12)	1.460(+12)
800	3.774(+02)	2.000(+00)	9.622(+09)	1.165(+10)	7.263(+12)	8.793(+12)
900	4.503(+02)	2.000(+00)	4.420(+10)	5.379(+10)	3.981(+13)	4.844(+13)
1000	5.274(+02)	2.000(+00)	1.911(+11)	2.332(+11)	2.016(+14)	2.460(+14)
1500	9.689(+02)	2.000(+00)	1.305(+14)	1.570(+14)	2.529(+17)	3.042(+17)
2000	1.492(+03)	2.000(+00)	3.088(+16)	3.569(+16)	9.214(+19)	1.065(+20)
2500	2.085(+03)	2.000(+00)	3.325(+18)	3.628(+18)	1.386(+22)	1.513(+22)

[a] MS-OH (ZPE): 54.459 kcal/mol

[b] E2DT (ZPE): 54.444 kcal/mol

[c] $Q_T^X = Q_{\text{trans}} Q_{\text{elec}} Q_{\text{rovib}}^X$, where X = MS-HO or E2DT

Table S25: Components of the E2DT partition function for the transition state of CRC1. $Q_{\text{tor,cl}}^{(C)}$ is the classical torsional partition function, $Q_{\text{tor}}^{\text{2D-NS}}$ a quantum version of the classical function, and Q^{EHR} the extended hindered-rotor (EHR) rovibrational partition function. Power of 10 in parentheses.

T(K)	$Q_{\text{tor}}^{\text{2D-NS}}$	$Q_{\text{tor,cl}}^{(C)}$	Q^{EHR}
200	2.450(+00)	8.570(-01)	8.461(+04)
300	4.289(+00)	2.076(+00)	9.051(+05)
400	6.909(+00)	3.973(+00)	7.297(+06)
500	1.035(+01)	6.624(+00)	5.013(+07)
600	1.462(+01)	1.006(+01)	3.072(+08)
700	1.970(+01)	1.429(+01)	1.713(+09)
800	2.557(+01)	1.930(+01)	8.794(+09)
900	3.219(+01)	2.506(+01)	4.188(+10)
1000	3.952(+01)	3.154(+01)	1.861(+11)
1500	8.541(+01)	7.353(+01)	1.352(+14)
2000	1.437(+02)	1.281(+02)	3.182(+16)
2500	2.100(+02)	1.917(+02)	3.311(+18)

Table S26: Translational, electronic, and rovibrational (MS-HO[a] and E2DT[b]) partition functions for the transition state of CRC2. $Q_{\text{T}}^{\text{MS-HO}}$ and $Q_{\text{T}}^{\text{E2DT}}$ stands for the total partition functions[c]. Power of 10 in parentheses.

T(K)	Q_{trans}	Q_{elec}	$Q^{\text{MS-HO}}$	Q^{E2DT}	$Q_{\text{T}}^{\text{MS-HO}}$	$Q_{\text{T}}^{\text{E2DT}}$
200	4.717(+01)	2.000(+00)	3.846(+05)	4.188(+05)	3.628(+07)	3.951(+07)
300	8.666(+01)	2.000(+00)	3.899(+06)	4.301(+06)	6.757(+08)	7.454(+08)
400	1.334(+02)	2.000(+00)	3.177(+07)	3.470(+07)	8.479(+09)	9.261(+09)
500	1.865(+02)	2.000(+00)	2.204(+08)	2.356(+08)	8.220(+10)	8.787(+10)
600	2.451(+02)	2.000(+00)	1.353(+09)	1.407(+09)	6.632(+11)	6.896(+11)
700	3.089(+02)	2.000(+00)	7.513(+09)	7.568(+09)	4.642(+12)	4.676(+12)
800	3.774(+02)	2.000(+00)	3.829(+10)	3.728(+10)	2.890(+13)	2.814(+13)
900	4.503(+02)	2.000(+00)	1.808(+11)	1.699(+11)	1.628(+14)	1.530(+14)
1000	5.274(+02)	2.000(+00)	7.974(+11)	7.228(+11)	8.411(+14)	7.624(+14)
1500	9.689(+02)	2.000(+00)	5.687(+14)	4.326(+14)	1.102(+18)	8.382(+17)
2000	1.492(+03)	2.000(+00)	1.361(+17)	8.838(+16)	4.061(+20)	2.637(+20)
2500	2.085(+03)	2.000(+00)	1.472(+19)	8.301(+18)	6.138(+22)	3.461(+22)

[a] MS-OH (ZPE): 54.098 kcal/mol

[b] E2DT (ZPE): 54.088 kcal/mol

[c] $Q_{\text{T}}^{\text{X}} = Q_{\text{trans}} Q_{\text{elec}} Q_{\text{rovib}}^{\text{X}}$, where X = MS-HO or E2DT

Table S27: Components of the E2DT partition function for the transition state of CRC2. $Q_{\text{tor,cl}}^{\text{(C)}}$ is the classical torsional partition function, $Q_{\text{tor}}^{\text{2D-NS}}$ a quantum version of the classical function, and Q^{EHR} the extended hindered-rotor (EHR) rovibrational partition function. Power of 10 in parentheses.

T(K)	$Q_{\text{tor}}^{\text{2D-NS}}$	$Q_{\text{tor,cl}}^{\text{(C)}}$	Q^{EHR}
200	3.063(+00)	1.203(+00)	1.646(+05)
300	6.087(+00)	3.201(+00)	2.261(+06)
400	1.058(+01)	6.486(+00)	2.127(+07)
500	1.649(+01)	1.112(+01)	1.588(+08)
600	2.371(+01)	1.704(+01)	1.011(+09)
700	3.209(+01)	2.415(+01)	5.696(+09)
800	4.149(+01)	3.234(+01)	2.905(+10)
900	5.178(+01)	4.148(+01)	1.361(+11)
1000	6.283(+01)	5.145(+01)	5.919(+11)
1500	1.266(+02)	1.107(+02)	3.784(+14)
2000	1.992(+02)	1.802(+02)	7.994(+16)
2500	2.768(+02)	2.554(+02)	7.660(+18)

Table S28: Translational, electronic, and rovibrational (MS-HO^a and E2DT^b) partition functions for the transition state of CRC3. $Q_T^{\text{MS-HO}}$ and Q_T^{E2DT} stands for the total partition functions^c. Power of 10 in parentheses.

T(K)	Q_{trans}	Q_{elec}	$Q^{\text{MS-HO}}$	Q^{E2DT}	$Q_T^{\text{MS-HO}}$	Q_T^{E2DT}
200	4.717(+01)	2.000(+00)	2.727(+05)	2.806(+05)	2.573(+07)	2.647(+07)
300	8.666(+01)	2.000(+00)	2.130(+06)	2.245(+06)	3.691(+08)	3.891(+08)
400	1.334(+02)	2.000(+00)	1.420(+07)	1.504(+07)	3.790(+09)	4.014(+09)
500	1.865(+02)	2.000(+00)	8.623(+07)	9.071(+07)	3.216(+10)	3.383(+10)
600	2.451(+02)	2.000(+00)	4.877(+08)	5.072(+08)	2.390(+11)	2.486(+11)
700	3.089(+02)	2.000(+00)	2.583(+09)	2.653(+09)	1.596(+12)	1.639(+12)
800	3.774(+02)	2.000(+00)	1.283(+10)	1.302(+10)	9.684(+12)	9.827(+12)
900	4.503(+02)	2.000(+00)	5.987(+10)	6.005(+10)	5.392(+13)	5.408(+13)
1000	5.274(+02)	2.000(+00)	2.630(+11)	2.610(+11)	2.774(+14)	2.753(+14)
1500	9.689(+02)	2.000(+00)	1.933(+14)	1.814(+14)	3.745(+17)	3.515(+17)
2000	1.492(+03)	2.000(+00)	4.823(+16)	4.252(+16)	1.439(+20)	1.269(+20)
2500	2.085(+03)	2.000(+00)	5.396(+18)	4.433(+18)	2.250(+22)	1.848(+22)

^{a} MS-OH (ZPE): 54.042 kcal/mol

^{b} E2DT   (ZPE): 54.038 kcal/mol

^{c} $Q_T^X = Q_{\text{trans}} Q_{\text{elec}} Q_{\text{rovib}}^X$, where X = MS-HO or E2DT

Table S29: Components of the E2DT partition function for the transition state of CRC3. $Q_{\text{tor,cl}}^{(C)}$ is the classical torsional partition function, $Q_{\text{tor}}^{\text{2D-NS}}$ a quantum version of the classical function, and Q^{EHR} the extended hindered-rotor (EHR) rovibrational partition function. Power of 10 in parentheses.

T(K)	$Q_{\text{tor}}^{\text{2D-NS}}$	$Q_{\text{tor,cl}}^{(C)}$	Q^{EHR}
200	2.597(+00)	9.633(-01)	1.041(+05)
300	4.477(+00)	2.265(+00)	1.136(+06)
400	6.941(+00)	4.136(+00)	8.958(+06)
500	1.002(+01)	6.604(+00)	5.976(+07)
600	1.376(+01)	9.707(+00)	3.577(+08)
700	1.819(+01)	1.347(+01)	1.965(+09)
800	2.330(+01)	1.791(+01)	1.001(+10)
900	2.910(+01)	2.303(+01)	4.752(+10)
1000	3.557(+01)	2.882(+01)	2.114(+11)
1500	7.695(+01)	6.688(+01)	1.576(+14)
2000	1.306(+02)	1.174(+02)	3.822(+16)
2500	1.928(+02)	1.770(+02)	4.071(+18)

Table S30: Translational, electronic, and rovibrational (MS-HO^a and E2DT^b) partition functions for the transition state of CRC4. $Q_\text{T}^\text{MS-HO}$ and Q_T^E2DT stands for the total partition functions^c. Power of 10 in parentheses.

T(K)	Q_trans	Q_elec	$Q^\text{MS-HO}$	Q^E2DT	$Q_\text{T}^\text{MS-HO}$	Q_T^E2DT
200	4.717(+01)	2.000(+00)	4.353(+05)	4.154(+05)	4.107(+07)	3.919(+07)
300	8.666(+01)	2.000(+00)	3.040(+06)	2.966(+06)	5.268(+08)	5.140(+08)
400	1.334(+02)	2.000(+00)	1.884(+07)	1.900(+07)	5.028(+09)	5.071(+09)
500	1.865(+02)	2.000(+00)	1.082(+08)	1.133(+08)	4.035(+10)	4.226(+10)
600	2.451(+02)	2.000(+00)	5.826(+08)	6.347(+08)	2.856(+11)	3.111(+11)
700	3.089(+02)	2.000(+00)	2.952(+09)	3.346(+09)	1.824(+12)	2.068(+12)
800	3.774(+02)	2.000(+00)	1.409(+10)	1.659(+10)	1.064(+13)	1.252(+13)
900	4.503(+02)	2.000(+00)	6.338(+10)	7.743(+10)	5.708(+13)	6.973(+13)
1000	5.274(+02)	2.000(+00)	2.695(+11)	3.405(+11)	2.843(+14)	3.592(+14)
1500	9.689(+02)	2.000(+00)	1.750(+14)	2.506(+14)	3.391(+17)	4.856(+17)
2000	1.492(+03)	2.000(+00)	4.041(+16)	6.163(+16)	1.206(+20)	1.839(+20)
2500	2.085(+03)	2.000(+00)	4.290(+18)	6.684(+18)	1.789(+22)	2.787(+22)

^{a} MS-OH (ZPE): 54.175 kcal/mol

^{b} E2DT (ZPE): 54.167 kcal/mol

^{c} $Q_\text{T}^\text{X} = Q_\text{trans} Q_\text{elec} Q_\text{rovib}^\text{X}$, where X = MS-HO or E2DT

Table S31: Components of the E2DT partition function for the transition state of CRC4. $Q_\text{tor,cl}^\text{(C)}$ is the classical torsional partition function, $Q_\text{tor}^\text{2D-NS}$ a quantum version of the classical function, and Q^EHR the extended hindered-rotor (EHR) rovibrational partition function. Power of 10 in parentheses.

T(K)	$Q_\text{tor}^\text{2D-NS}$	$Q_\text{tor,cl}^\text{(C)}$	Q^EHR
200	4.552(+00)	1.577(+00)	1.438(+05)
300	7.945(+00)	3.816(+00)	1.425(+06)
400	1.291(+01)	7.377(+00)	1.085(+07)
500	1.964(+01)	1.249(+01)	7.201(+07)
600	2.825(+01)	1.931(+01)	4.339(+08)
700	3.885(+01)	2.800(+01)	2.411(+09)
800	5.151(+01)	3.863(+01)	1.244(+10)
900	6.627(+01)	5.127(+01)	5.991(+10)
1000	8.314(+01)	6.596(+01)	2.702(+11)
1500	1.980(+02)	1.696(+02)	2.146(+14)
2000	3.584(+02)	3.187(+02)	5.481(+16)
2500	5.545(+02)	5.048(+02)	6.085(+18)

Table S32: The ratio between anharmonic and harmonic total partition function, $F^{\text{E2DT,X}}$, calculated by the Eq. (21).

T(K)	(2)-2-butenal	CRC1	CRC2	CRC2	CRC4
200	0.999	1.098	1.117	1.039	0.974
300	1.031	1.133	1.122	1.061	0.989
400	1.062	1.165	1.106	1.064	1.019
500	1.086	1.188	1.080	1.056	1.056
600	1.102	1.204	1.049	1.043	1.097
700	1.113	1.215	1.015	1.030	1.140
800	1.120	1.222	0.980	1.017	1.183
900	1.125	1.227	0.945	1.005	1.227
1000	1.128	1.230	0.911	0.994	1.269
1500	1.119	1.209	0.763	0.940	1.436
2000	1.082	1.160	0.651	0.882	1.528
2500	1.032	1.094	0.565	0.822	1.561

Table S33: Recrossing (Γ_j^{CVT}) and quantum tunneling ($\kappa_j^{\text{CVT/SCT}}$) coefficients for the individual paths of CRC1.

T(K)	Path 1			Path 2	
	Γ_1^{CVT}	$\kappa_1^{\text{CVT/SCT}}$		Γ_2^{CVT}	$\kappa_2^{\text{CVT/SCT}}$
200	0.9991	11.7470		0.9986	10.6270
300	0.9992	3.0452		0.9988	2.9041
400	0.9993	1.8798		0.9988	1.8291
500	0.9993	1.5002		0.9988	1.4739
600	0.9993	1.3262		0.9988	1.3099
700	0.9993	1.2309		0.9987	1.2197
800	0.9993	1.1726		0.9986	1.1644
900	0.9993	1.1341		0.9985	1.1279
1000	0.9993	1.1074		0.9985	1.1024
1500	0.9993	1.0464		0.9982	1.0444
2000	0.9812	1.0259		0.9639	1.0247
2500	0.9512	1.0165		0.9349	1.0158

Table S34: Recrossing (Γ_j^{CVT}) and quantum tunneling ($\kappa_j^{\text{CVT/SCT}}$) coefficients for the individual paths of CRC2.

T(K)	Path 1			Path 2	
	Γ_1^{CVT}	$\kappa_1^{\text{CVT/SCT}}$		Γ_2^{CVT}	$\kappa_2^{\text{CVT/SCT}}$
200	0.6374	9.3735		0.6324	9.5113
300	0.8289	2.4135		0.5076	2.4041
400	0.9448	1.6072		0.4478	1.6008
500	0.9886	1.3468		0.4130	1.3427
600	0.9956	1.2270		0.3905	1.2242
700	0.9986	1.1610		0.3751	1.1590
800	0.9997	1.1206		0.3641	1.1190
900	1.0000	1.0938		0.3559	1.0926
1000	0.9999	1.0752		0.3497	1.0742
1500	0.9978	1.0326		0.3332	1.0322
2000	0.9962	1.0182		0.3265	1.0179
2500	0.9952	1.0116		0.3231	1.0114

Table S35: Recrossing (Γ_j^{CVT}) and quantum tunneling ($\kappa_j^{\text{CVT/SCT}}$) coefficients for the individual paths of CRC3.

| T(K) | Path 1 | | | Path 2 | |
	Γ_1^{CVT}	$\kappa_1^{\text{CVT/SCT}}$		Γ_2^{CVT}	$\kappa_2^{\text{CVT/SCT}}$
200	0.4558	49.6950		0.8426	34.2550
300	0.6318	4.5794		0.9905	3.8875
400	0.7433	2.2620		0.9998	2.0674
500	0.8155	1.6680		0.9962	1.5755
600	0.8602	1.4211		0.9829	1.3661
700	0.8894	1.2924		0.9664	1.2556
800	0.9093	1.2160		0.9505	1.1894
900	0.9233	1.1666		0.9368	1.1464
1000	0.9334	1.1327		0.9253	1.1168
1500	0.9306	1.0567		0.8913	1.0501
2000	0.9188	1.0314		0.8764	1.0278
2500	0.9121	1.0200		0.8684	1.0177

Table S36: Recrossing (Γ_j^{CVT}) and quantum tunneling ($\kappa_j^{\text{CVT/SCT}}$) coefficients for the individual paths of CRC4.

| T(K) | Path 1 | | | Path 2 | |
	Γ_1^{CVT}	$\kappa_1^{\text{CVT/SCT}}$		Γ_2^{CVT}	$\kappa_2^{\text{CVT/SCT}}$
200	0.7450	229.8700		0.9311	388.5400
300	0.7931	12.0780		0.9115	18.3720
400	0.8139	4.2518		0.8924	5.6642
500	0.8241	2.5830		0.8766	3.1622
600	0.8295	1.9546		0.8639	2.2682
700	0.8323	1.6458		0.8538	1.8434
800	0.8338	1.4692		0.8456	1.6059
900	0.8345	1.3578		0.8388	1.4585
1000	0.8348	1.2826		0.8331	1.3602
1500	0.7643	1.1184		0.8141	1.1490
2000	0.7569	1.0653		0.8034	1.0817
2500	0.7518	1.0414		0.7965	1.0517

Table S37: Harmonic 1W-CVT/SCT thermal rate constants for (R1)–(R4) in a wide range of temperatures[a]. All rate constants are in cm^3 molecule^{-1} s^{-1}.

T(K)	(R1)	(R2)	(R3)	(R4)
200	1.04(-14)	6.01(-28)	2.47(-24)	1.50(-16)
300	7.14(-14)	1.49(-22)	1.94(-20)	2.65(-15)
400	2.47(-13)	1.09(-19)	3.11(-18)	1.83(-14)
500	5.95(-13)	5.54(-18)	7.85(-17)	7.09(-14)
600	1.16(-12)	9.23(-17)	7.38(-16)	1.95(-13)
700	1.97(-12)	7.28(-16)	3.91(-15)	4.30(-13)
800	3.06(-12)	3.56(-15)	1.43(-14)	8.17(-13)
900	4.44(-12)	1.26(-14)	4.03(-14)	1.39(-12)
1000	6.13(-12)	3.55(-14)	9.47(-14)	2.19(-12)
1500	1.94(-11)	9.47(-13)	1.49(-12)	1.05(-11)
2000	4.06(-11)	5.73(-12)	6.27(-12)	2.69(-11)
2500	6.91(-11)	1.85(-11)	1.74(-11)	4.98(-11)

[a] Power of 10 in parentheses.

Table S38: Harmonic MP-CVT/SCT thermal rate constants for (R1)–(R4) in a wide range of temperatures[a]. All rate constants are in cm^3 molecule^{-1} s^{-1}.

T(K)	(R1)	(R2)	(R3)	(R4)
200	1.03(-14)	6.16(-28)	2.47(-24)	1.96(-16)
300	7.08(-14)	1.55(-22)	1.87(-20)	3.24(-15)
400	2.52(-13)	1.14(-19)	2.89(-18)	2.16(-14)
500	6.25(-13)	5.88(-18)	7.12(-17)	8.13(-14)
600	1.25(-12)	9.70(-17)	6.61(-16)	2.17(-13)
700	2.19(-12)	7.56(-16)	3.48(-15)	4.69(-13)
800	3.46(-12)	3.66(-15)	1.27(-14)	8.74(-13)
900	5.11(-12)	1.28(-14)	3.60(-14)	1.47(-12)
1000	7.16(-12)	3.57(-14)	8.54(-14)	2.29(-12)
1500	2.38(-11)	9.19(-13)	1.27(-12)	9.96(-12)
2000	4.83(-11)	5.45(-12)	6.32(-12)	2.56(-11)
2500	8.15(-11)	1.73(-11)	1.82(-11)	4.97(-11)

[a] Power of 10 in parentheses.