Electronic Supplementary Information (ESI)

Differences in the torsional anharmonicity between reactant and transition state: the case of 3-butenal + H abstraction reactions

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Torsional Potential Energy Surface

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

$$\begin{aligned}V_{\rm tor}(\phi_1,\phi_2) =& V_1(\phi_1)+V_2(\phi_1)+\\ &\sum_{L_1=1}^{L_{1,max}}\sum_{L_2=1}^{L_{2,max}} c_{L_1L_2}\cos(L_1\phi_1)\cos(L_2\phi_2)+\\ &\sum_{P_1=1}^{P_{1,max}}\sum_{P_2=1}^{P_{2,max}} d_{P_1P_2}\sin(P_1\phi_1)\sin(P_2\phi_2)+ \sum_{L'_1=1}^{L'_{1,max}}\sum_{L'_2=1}^{L'_{2,max}} c'_{L'_1L'_2}\cos(L'_1\phi_1)\sin(L'_2\phi_2)+\\ &\sum_{P'_1=1}^{P'_{1,max}}\sum_{P'_2=1}^{P'_{2,max}} d'_{P'_1P'_2}\sin(P'_1\phi_1)\cos(P'_2\phi_2) \qquad (1)\end{aligned}$$

where $c_{L_1L_2}(L_1=1,...,L_{1,max},L_2=1,...,L_{2,max})$, $d_{P_1P_2}(P_1=1,...,P_{1,max},P_2=1,...,P_{2,max})$, $c'_{L'_1L'_2}(L'_1=1,...,L'_{1,max},L'_2=1,...,L'_{2,max})$, and $d'_{P'_1P'_2}(P'_1=1,...,P'_{1,max},P'_2=1,...,P'_{2,max})$ are fitting parameters. $L_{1,max}$,$L_{2,max}$,$L'_{1,max}$,$L'_{2,max}$, $P_{1,max}$, $P_{2,max}$, $P'_{1,max}$, and $P'_{2,max}$, indicate the largest number of each series.

The one-dimensional potentials are:

$$V_1(\phi_1) = a_0+\sum_{M=1}^{M_{max}} a_M\cos(M\phi_1)+\sum_{M=1}^{M_{max}} a'_M\sin(M\phi_1) \qquad (2)$$

and

$$V_2(\phi_2) = b_0+\sum_{N=1}^{N_{max}} b_N\cos(N\phi_2)+\sum_{N=1}^{N_{max}} b'_N\sin(N\phi_2) \qquad (3)$$

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

Table S1: Parameters (in cm^{-1}) used to fit by Fourier series the two-dimensional torsional potential for 3-butenal (including coupling parameters).

Parameters	
a_0	+694.6103
a_1	-141.8636
a_2	-147.5198
a_3	+215.6993
a_4	-15.5629
a_5	+5.4467
a_6	+1.8822
a_7	+1.1580
a_8	+0.0799
a_9	-0.0744
a_{10}	+0.1226
b_1	+143.2052
b_2	+130.3129
b_3	-236.9447
b_4	+25.0537
b_5	-5.4749
b_6	+10.4460
b_7	-2.2289
b_8	+0.5164
b_9	-0.4289
b_{10}	-0.1409
c_{11},d_{11}	-130.6986 , +7.3143
c_{21},d_{21}	+119.7630 , +1.6295
c_{31},d_{31}	-5.5331 , -15.3181
c_{41},d_{41}	-6.7536 , +4.6546
c_{51},d_{51}	+1.7502 , +0.4648
c_{61},d_{61}	-0.2652 , +0.9868
c_{71},d_{71}	+0.2579 , +0.0317
c_{81},d_{81}	+0.1167 , -0.1181
c_{91},d_{91}	-0.1393 , -0.0700
c_{101},d_{101}	+0.1656 , +0.1273
c_{12},d_{12}	+139.2229 , -239.8053
c_{22},d_{22}	-64.6275 , +92.5732
c_{32},d_{32}	-16.6150 , +20.8889

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Table S1 – continued from previous page

Parameters	
c_{42},d_{42}	+18.9465 , -16.9536
c_{52},d_{52}	+1.2943 , +0.7800
c_{62},d_{62}	-0.6790 , +1.6510
c_{72},d_{72}	-0.1670 , +0.3775
c_{82},d_{82}	-0.0905 , +0.0130
c_{92},d_{92}	-0.0219 , -0.0434
c_{102},d_{102}	+0.0046 , +0.1205
c_{13},d_{13}	+53.8969 , -84.7810
c_{23},d_{23}	+69.9925 , -76.5627
c_{33},d_{33}	-6.2132 , +0.7293
c_{43},d_{43}	+0.8661 , -2.0325
c_{53},d_{53}	+6.2695 , -8.0044
c_{63},d_{63}	-2.4561 , +2.3742
c_{73},d_{73}	-0.1604 , +0.5842
c_{83},d_{83}	+0.0737 , -0.1860
c_{93},d_{93}	+0.0770 , -0.0758
c_{103},d_{103}	-0.0534 , +0.0353
c_{14},d_{14}	+19.8210 , -29.1254
c_{24},d_{24}	+24.8769 , -33.9313
c_{34},d_{34}	+5.0801 , -0.7241
c_{44},d_{44}	+9.3616 , -7.6849
c_{54},d_{54}	+1.0784 , -1.6631
c_{64},d_{64}	-1.1246 , +0.6648
c_{74},d_{74}	+0.2991 , -0.1419
c_{84},d_{84}	-0.0648 , -0.1403
c_{94},d_{94}	+0.0881 , -0.0170
c_{104},d_{104}	-0.0940 , +0.0048
c_{15},d_{15}	-0.2262 , +6.9837
c_{25},d_{25}	+17.8936 , -23.9126
c_{35},d_{35}	+3.5013 , -5.0361
c_{45},d_{45}	+5.8253 , -4.7867
c_{55},d_{55}	-0.5286 , +0.6486
c_{65},d_{65}	-0.5474 , +0.1106
c_{75},d_{75}	+0.2308 , -0.3436
c_{85},d_{85}	+0.1286 , -0.0706
c_{95},d_{95}	-0.0438 , -0.1128

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Parameters	
c_{105},d_{105}	+0.0026 , +0.0491
c_{16},d_{16}	-0.5205 , +3.0572
c_{26},d_{26}	-0.2176 , +1.8142
c_{36},d_{36}	+2.6233 , -2.8892
c_{46},d_{46}	+2.1820 , -2.1509
c_{56},d_{56}	+0.1531 , +0.2181
c_{66},d_{66}	-0.6988 , +0.4585
c_{76},d_{76}	+0.3140 , -0.4552
c_{86},d_{86}	+0.1411 , -0.0219
c_{96},d_{96}	-0.1183 , +0.0837
c_{106},d_{106}	+0.0701 , -0.0637
c_{17},d_{17}	-1.1565 , +1.5560
c_{27},d_{27}	-1.0600 , +2.2239
c_{37},d_{37}	+0.2484 , -0.5455
c_{47},d_{47}	-1.1343 , +0.4800
c_{57},d_{57}	+0.5101 , -0.5025
c_{67},d_{67}	-0.3057 , +0.4877
c_{77},d_{77}	-0.1277 , -0.2668
c_{87},d_{87}	+0.2452 , -0.0279
c_{97},d_{97}	+0.0228 , +0.1710
c_{107},d_{107}	-0.0315 , -0.1710
c_{18},d_{18}	-0.4633 , -0.7449
c_{28},d_{28}	-1.7875 , +2.4587
c_{38},d_{38}	-0.3650 , +0.8257
c_{48},d_{48}	-1.2907 , +0.9226
c_{58},d_{58}	+0.4285 , -0.6002
c_{68},d_{68}	-0.2184 , +0.3529
c_{78},d_{78}	-0.2392 , +0.0087
c_{88},d_{88}	+0.1955 , -0.1052
c_{98},d_{98}	+0.0532 , +0.2466
c_{108},d_{108}	-0.1118 , -0.1581
c_{19},d_{19}	-0.1742 , -0.3086
c_{29},d_{29}	-0.6271 , -0.1534
c_{39},d_{39}	-0.3123 , +0.6025
c_{49},d_{49}	-0.8753 , +1.1892
c_{59},d_{59}	+0.1227 , -0.5343

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Table S1 – continued from previous page

Parameters	
c_{69},d_{69}	+0.0512 , +0.2118
c_{79},d_{79}	-0.2507 , +0.1073
c_{89},d_{89}	+0.0381 , -0.0308
c_{99},d_{99}	+0.1269 , -0.0874
c_{109},d_{109}	-0.0564 , +0.2127
c_{110},d_{110}	+0.2272 , +0.0364
c_{210},d_{210}	-0.4348 , -0.4999
c_{310},d_{310}	+0.1891 , +0.3651
c_{410},d_{410}	-0.4932 , +0.3763
c_{510},d_{510}	+0.2019 , -0.1480
c_{610},d_{610}	-0.1102 , +0.0715
c_{710},d_{710}	-0.1283 , +0.1533
c_{810},d_{810}	+0.1155 , -0.0104
c_{910},d_{910}	-0.1306 , -0.1294
c_{1010},d_{1010}	+0.0256 , +0.1520

Table S2: Parameters (in cm^{-1}) used to fit by Fourier series the two-dimensional torsional potential for CRC1 (including coupling parameters).

Parameters	
a_0	+717.4953
a_1	+2.4101
a_2	-103.8992
a_3	+191.8351
a_4	-12.7525
a_5	+0.7351
a_6	+0.8981
a_7	+0.6797
a_8	+0.0073
a_9	-0.0971
a_{10}	-0.0276
b_1	+134.8187
b_2	+153.8959
b_3	-238.7042
b_4	+24.7767
b_5	-7.5153
b_6	+10.5966
b_7	-2.1790
b_8	+0.7372
b_9	-0.3915
b_{10}	+0.1203
c_{11},d_{11}	-27.6147 , -16.8639
c_{21},d_{21}	+148.9874 , -32.6210
c_{31},d_{31}	+22.1186 , -32.7313
c_{41},d_{41}	-6.6001 , -2.2626
c_{51},d_{51}	-2.7652 , +3.4027
c_{61},d_{61}	-1.8957 , +3.3823
c_{71},d_{71}	+0.6746 , +0.8855
c_{81},d_{81}	+0.6689 , -1.1073
c_{91},d_{91}	-0.1442 , -0.3261
c_{101},d_{101}	-0.2312 , +0.1898
c_{12},d_{12}	+93.7319 , -184.1258
c_{22},d_{22}	-64.4824 , +102.1510
c_{32},d_{32}	+3.5303 , -3.4981

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Table S2 – continued from previous page

Parameters	
c_{42},d_{42}	+25.8748 , -28.3723
c_{52},d_{52}	+4.0631 , -0.9857
c_{62},d_{62}	-2.0206 , +3.7798
c_{72},d_{72}	-1.1903 , +1.1418
c_{82},d_{82}	-0.5046 , -0.0415
c_{92},d_{92}	+0.3377 , -0.1915
c_{102},d_{102}	+0.0937 , +0.2207
c_{13},d_{13}	+45.2690 , -79.9750
c_{23},d_{23}	+51.3502 , -62.1129
c_{33},d_{33}	-1.1373 , -6.0456
c_{43},d_{43}	+8.8662 , -9.6632
c_{53},d_{53}	+6.7909 , -6.2278
c_{63},d_{63}	-3.7776 , +3.7194
c_{73},d_{73}	-2.2163 , +1.5045
c_{83},d_{83}	+0.2542 , -0.3790
c_{93},d_{93}	+0.5194 , -0.4274
c_{103},d_{103}	+0.1458 , -0.2768
c_{14},d_{14}	+19.9658 , -31.7138
c_{24},d_{24}	+19.2432 , -29.3673
c_{34},d_{34}	+10.3343 , -5.9933
c_{44},d_{44}	+16.3851 , -14.0622
c_{54},d_{54}	+5.3093 , -5.9776
c_{64},d_{64}	-1.3257 , +0.4786
c_{74},d_{74}	-0.8917 , +0.7787
c_{84},d_{84}	-0.3491 , +0.6365
c_{94},d_{94}	+0.0346 , -0.0517
c_{104},d_{104}	+0.0760 , -0.2901
c_{15},d_{15}	-0.2802 , +3.3870
c_{25},d_{25}	+16.5609 , -22.9662
c_{35},d_{35}	+5.7691 , -5.3038
c_{45},d_{45}	+6.9822 , -6.2661
c_{55},d_{55}	+2.3099 , -3.0224
c_{65},d_{65}	-0.0565 , -0.4039
c_{75},d_{75}	-0.3929 , +0.6325
c_{85},d_{85}	-0.4595 , +0.4075
c_{95},d_{95}	-0.1785 , -0.3041

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Parameters	
c_{105},d_{105}	+0.1950 , -0.2559
c_{16},d_{16}	-0.5301 , +3.8837
c_{26},d_{26}	+0.0145 , +1.8950
c_{36},d_{36}	+2.1417 , -2.1623
c_{46},d_{46}	+0.9277 , -0.8527
c_{56},d_{56}	-0.4120 , +0.4024
c_{66},d_{66}	-1.3125 , +1.5731
c_{76},d_{76}	-0.5324 , +0.4419
c_{86},d_{86}	-0.3817 , +0.3130
c_{96},d_{96}	-0.2805 , +0.0884
c_{106},d_{106}	+0.0746 , -0.0828
c_{17},d_{17}	-0.6812 , +2.2251
c_{27},d_{27}	-1.0944 , +2.2414
c_{37},d_{37}	-0.9237 , +0.5502
c_{47},d_{47}	-2.9260 , +2.4408
c_{57},d_{57}	-1.1165 , +1.4203
c_{67},d_{67}	-1.5937 , +1.6342
c_{77},d_{77}	-0.9852 , +0.4038
c_{87},d_{87}	-0.0652 , +0.1230
c_{97},d_{97}	+0.1024 , +0.1829
c_{107},d_{107}	+0.0235 , -0.2609
c_{18},d_{18}	+0.1230 , -0.5690
c_{28},d_{28}	-1.9158 , +2.6315
c_{38},d_{38}	-0.6818 , +1.1658
c_{48},d_{48}	-2.2363 , +2.1457
c_{58},d_{58}	-1.0315 , +1.2432
c_{68},d_{68}	-1.5580 , +1.6167
c_{78},d_{78}	-0.9097 , +0.8465
c_{88},d_{88}	+0.0183 , +0.1455
c_{98},d_{98}	-0.1563 , +0.1954
c_{108},d_{108}	+0.0397 , -0.1612
c_{19},d_{19}	-0.0153 , -0.4678
c_{29},d_{29}	-0.1388 , -0.3429
c_{39},d_{39}	-0.0774 , +0.7856
c_{49},d_{49}	-1.1711 , +0.7466
c_{59},d_{59}	-0.5893 , +0.3654

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Table S2 – continued from previous page

Parameters	
c_{69},d_{69}	-0.6287 , +0.6608
c_{79},d_{79}	-0.4155 , +0.5244
c_{89},d_{89}	-0.0574 , +0.0911
c_{99},d_{99}	+0.0768 , +0.2424
c_{109},d_{109}	-0.0189 , -0.2975
c_{110},d_{110}	-0.1974 , +0.0841
c_{210},d_{210}	+0.0411 , -0.0292
c_{310},d_{310}	+0.1450 , +0.1151
c_{410},d_{410}	-0.0852 , +0.3715
c_{510},d_{510}	+0.1086 , +0.0398
c_{610},d_{610}	-0.1962 , +0.2349
c_{710},d_{710}	-0.0550 , +0.0850
c_{810},d_{810}	-0.1627 , +0.0285
c_{910},d_{910}	+0.0248 , -0.0423
c_{1010},d_{1010}	-0.0495 , +0.0963

Table S3: Parameters (in cm^{-1}) used to fit by Fourier series the two-dimensional torsional potential for CRC2 (including coupling parameters).

Parameters	
a_0	+1617.9965
a_1	-58.0898
a_2	-557.3912
a_3	+118.8347
a_4	-20.4812
a_5	+11.0135
a_6	+6.4386
a_7	+0.5664
a_8	-0.6256
a_9	-0.0998
a_{10}	-0.1262
b_1	+105.4562
b_2	-306.9214
b_3	-136.6444
b_4	+28.2825
b_5	+9.7861
b_6	+6.3942
b_7	-2.9992
b_8	-1.1916
b_9	+0.2917
b_{10}	+0.2193
a'_1	+69.8061
a'_2	+474.3082
a'_3	+38.0493
a'_4	-53.0671
a'_5	-5.5665
a'_6	+2.1179
a'_7	+1.4477
a'_8	+0.7076
a'_9	-0.0819
a'_{10}	-0.1771
b'_1	+10.1995
b'_2	-514.3444
b'_3	+85.3679

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Table S3 – continued from previous page

Parameters	
b'_4	+32.7501
b'_5	-0.3031
b'_6	-7.2736
b'_7	+1.3281
b'_8	-0.0540
b'_9	+0.3731
b'_{10}	-0.0075
c_{11},d_{11}	-96.7885 , -26.2489
c_{21},d_{21}	+110.3342 , -5.6055
c_{31},d_{31}	-7.0654 , -10.4786
c_{41},d_{41}	-2.4678 , +0.4573
c_{51},d_{51}	+3.0421 , -1.0036
c_{61},d_{61}	-0.9650 , +1.8910
c_{71},d_{71}	-0.2744 , +0.4301
c_{81},d_{81}	+0.2412 , -0.4816
c_{91},d_{91}	+0.0966 , -0.1173
c_{101},d_{101}	-0.0137 , +0.1011
c_{12},d_{12}	+132.0684 , -208.1351
c_{22},d_{22}	-13.5489 , +9.0599
c_{32},d_{32}	-7.8923 , +16.6189
c_{42},d_{42}	+20.9921 , -5.3960
c_{52},d_{52}	+0.6228 , -2.6006
c_{62},d_{62}	-1.2977 , -0.8933
c_{72},d_{72}	-0.0170 , +0.2581
c_{82},d_{82}	-0.2283 , +0.1041
c_{92},d_{92}	+0.0792 , -0.0399
c_{102},d_{102}	+0.0850 , +0.1424
c_{13},d_{13}	+53.7537 , -78.7624
c_{23},d_{23}	+66.9632 , -67.7519
c_{33},d_{33}	+1.8885 , -8.6361
c_{43},d_{43}	-2.7112 , +1.2670
c_{53},d_{53}	+2.9892 , -4.0100
c_{63},d_{63}	-1.4856 , +2.1349
c_{73},d_{73}	+0.1704 , +0.2554
c_{83},d_{83}	+0.4759 , -0.5183
c_{93},d_{93}	-0.1594 , +0.0315

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Table S3 – continued from previous page

Parameters	
c_{103},d_{103}	+0.0111 , +0.1106
c_{14},d_{14}	+12.7021 , -17.9038
c_{24},d_{24}	+27.2463 , -25.1241
c_{34},d_{34}	+7.9232 , -5.6487
c_{44},d_{44}	+4.7092 , -6.3377
c_{54},d_{54}	-0.3505 , -0.2609
c_{64},d_{64}	-0.4476 , +0.2976
c_{74},d_{74}	+0.6668 , -0.6017
c_{84},d_{84}	+0.1435 , +0.1011
c_{94},d_{94}	-0.1121 , +0.0888
c_{104},d_{104}	+0.0003 , -0.0028
c_{15},d_{15}	-1.8036 , +2.7684
c_{25},d_{25}	+12.0761 , -17.4132
c_{35},d_{35}	+1.7283 , -2.0786
c_{45},d_{45}	+6.6627 , -5.1407
c_{55},d_{55}	-0.1910 , +0.6297
c_{65},d_{65}	-0.7939 , +0.6434
c_{75},d_{75}	+0.5074 , -0.5641
c_{85},d_{85}	-0.0127 , -0.0522
c_{95},d_{95}	-0.2165 , +0.0399
c_{105},d_{105}	+0.1158 , +0.0361
c_{16},d_{16}	-0.1837 , +3.1059
c_{26},d_{26}	+1.9883 , -2.1579
c_{36},d_{36}	+1.2643 , -1.8779
c_{46},d_{46}	+2.1736 , -2.1107
c_{56},d_{56}	+0.4464 , +0.0262
c_{66},d_{66}	-0.6438 , +0.6233
c_{76},d_{76}	+0.3045 , -0.3266
c_{86},d_{86}	-0.0038 , -0.1174
c_{96},d_{96}	-0.1682 , +0.0420
c_{106},d_{106}	+0.1057 , -0.0090
c_{17},d_{17}	+0.2828 , +0.6296
c_{27},d_{27}	-0.6717 , +1.9227
c_{37},d_{37}	+0.3286 , -0.3144
c_{47},d_{47}	-0.7958 , +0.5396
c_{57},d_{57}	+0.6531 , -0.4571

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Table S3 – continued from previous page

Parameters	
c_{67},d_{67}	-0.6297 , +0.3527
c_{77},d_{77}	-0.0178 , -0.0989
c_{87},d_{87}	+0.1611 , -0.0709
c_{97},d_{97}	-0.0892 , +0.1182
c_{107},d_{107}	+0.0184 , -0.1256
c_{18},d_{18}	+0.1753 , -0.4518
c_{28},d_{28}	-1.5121 , +1.9807
c_{38},d_{38}	+0.1783 , +0.3114
c_{48},d_{48}	-1.3799 , +0.8516
c_{58},d_{58}	+0.5460 , -0.3764
c_{68},d_{68}	-0.3898 , +0.2800
c_{78},d_{78}	-0.0177 , -0.0154
c_{88},d_{88}	+0.2077 , -0.1127
c_{98},d_{98}	-0.0340 , +0.1401
c_{108},d_{108}	-0.0490 , -0.0502
c_{19},d_{19}	-0.2314 , -0.1313
c_{29},d_{29}	-0.5189 , +0.3013
c_{39},d_{39}	-0.0495 , +0.4265
c_{49},d_{49}	-0.8036 , +0.4220
c_{59},d_{59}	+0.0359 , -0.2622
c_{69},d_{69}	-0.1265 , +0.1280
c_{79},d_{79}	+0.0149 , +0.0520
c_{89},d_{89}	+0.1820 , -0.1788
c_{99},d_{99}	+0.0421 , +0.1649
c_{109},d_{109}	-0.0845 , -0.0868
c_{110},d_{110}	-0.2922 , +0.1018
c_{210},d_{210}	+0.0383 , +0.1191
c_{310},d_{310}	-0.1022 , +0.3268
c_{410},d_{410}	-0.1827 , -0.0440
c_{510},d_{510}	-0.1387 , -0.0171
c_{610},d_{610}	+0.0733 , -0.1157
c_{710},d_{710}	-0.0560 , +0.1543
c_{810},d_{810}	+0.2141 , -0.1747
c_{910},d_{910}	-0.0415 , +0.0741
c_{1010},d_{1010}	-0.0622 +0.0102
c'_{11},d'_{11}	-8.7497 , +2.6477

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Table S3 – continued from previous page

Parameters	
c'_{21},d'_{21}	-9.5548 , -8.7925
c'_{31},d'_{31}	-2.2938 , -5.9322
c'_{41},d'_{41}	+2.2634 , +2.0010
c'_{51},d'_{51}	+1.5851 , +0.6256
c'_{61},d'_{61}	-0.4251 , -0.0887
c'_{71},d'_{71}	-0.1807 , -0.0776
c'_{81},d'_{81}	-0.0818 , +0.0777
c'_{91},d'_{91}	-0.0067 , -0.0264
c'_{101},d'_{101}	+0.0760 , -0.0460
c'_{12},d'_{12}	-0.8022 , -25.4287
c'_{22},d'_{22}	+110.3040 , -67.8798
c'_{32},d'_{32}	+3.1431 , +3.1181
c'_{42},d'_{42}	-13.4768 , +5.0009
c'_{52},d'_{52}	-1.1279 , -0.6724
c'_{62},d'_{62}	+0.5911 , +1.5567
c'_{72},d'_{72}	+1.0146 , +0.3168
c'_{82},d'_{82}	+0.1292 , -0.5636
c'_{92},d'_{92}	-0.1655 , -0.1649
c'_{102},d'_{102}	+0.1060 , +0.0622
c'_{13},d'_{13}	+1.4192 , +11.2411
c'_{23},d'_{23}	+7.4479 , +16.9094
c'_{33},d'_{33}	-0.3135 , -3.7194
c'_{43},d'_{43}	+0.2338 , -0.5262
c'_{53},d'_{53}	+0.6016 , +0.4629
c'_{63},d'_{63}	-0.9278 , -1.3436
c'_{73},d'_{73}	+0.0503 , -0.0458
c'_{83},d'_{83}	-0.0241 , +0.0734
c'_{93},d'_{93}	-0.0643 , +0.0732
c'_{103},d'_{103}	+0.1823 , +0.0679
c'_{14},d'_{14}	-3.7443 , -4.1941
c'_{24},d'_{24}	-4.3592 , +8.7777
c'_{34},d'_{34}	-0.2663 , +0.7048
c'_{44},d'_{44}	+0.0599 , +0.3569
c'_{54},d'_{54}	-0.3440 , +0.1233
c'_{64},d'_{64}	-0.0277 , -0.8121
c'_{74},d'_{74}	+0.0370 , -0.1189

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Table S3 – continued from previous page

Parameters	
c'_{84},d'_{84}	+0.0093 , -0.0391
c'_{94},d'_{94}	+0.0002 , +0.1319
c'_{104},d'_{104}	+0.0536 , +0.0900
c'_{15},d'_{15}	-0.8451 , -0.9492
c'_{25},d'_{25}	-3.7579 , -2.7596
c'_{35},d'_{35}	-0.2966 , -0.6721
c'_{45},d'_{45}	+1.7160 , +0.8166
c'_{55},d'_{55}	-0.2819 , -0.1968
c'_{65},d'_{65}	-0.0716 , +0.3160
c'_{75},d'_{75}	-0.1259 , -0.0113
c'_{85},d'_{85}	-0.0392 , -0.1733
c'_{95},d'_{95}	+0.1147 , +0.1281
c'_{105},d'_{105}	+0.0279 , +0.0214
c'_{16},d'_{16}	+0.9958 , +0.8467
c'_{26},d'_{26}	+1.0404 , +0.0654
c'_{36},d'_{36}	-0.4479 , -0.1885
c'_{46},d'_{46}	+0.5556 , +0.6645
c'_{56},d'_{56}	+0.3034 , -0.1926
c'_{66},d'_{66}	+0.0462 , -0.0198
c'_{76},d'_{76}	-0.1376 , -0.0367
c'_{86},d'_{86}	-0.1440 , -0.0648
c'_{96},d'_{96}	+0.0994 , +0.0542
c'_{106},d'_{106}	+0.0048 , +0.0426
c'_{17},d'_{17}	+0.6416 , +0.7240
c'_{27},d'_{27}	+1.1282 , +0.6132
c'_{37},d'_{37}	+0.3071 , +0.1096
c'_{47},d'_{47}	-0.1572 , +0.1831
c'_{57},d'_{57}	+0.0780 , +0.0979
c'_{67},d'_{67}	+0.0602 , -0.0013
c'_{77},d'_{77}	-0.0329 , -0.0727
c'_{87},d'_{87}	-0.0313 , -0.0194
c'_{97},d'_{97}	+0.0116 , -0.0225
c'_{107},d'_{107}	+0.0166 , +0.0543
c'_{18},d'_{18}	-0.0994 , -0.1135
c'_{28},d'_{28}	+0.0300 , +0.1814
c'_{38},d'_{38}	+0.3045 , -0.1671

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Table S3 – continued from previous page

Parameters	
c'_{48},d'_{48}	-0.1005 , -0.2131
c'_{58},d'_{58}	-0.0726 , +0.0795
c'_{68},d'_{68}	-0.0419 , +0.0723
c'_{78},d'_{78}	-0.0137 , -0.0854
c'_{88},d'_{88}	-0.0561 , +0.0020
c'_{98},d'_{98}	+0.0763 , +0.0120
c'_{108},d'_{108}	+0.0333 , -0.0160
c'_{19},d'_{19}	-0.3343 , -0.2236
c'_{29},d'_{29}	-0.1727 , +0.1928
c'_{39},d'_{39}	-0.0075 , -0.0489
c'_{49},d'_{49}	+0.0396 , -0.0375
c'_{59},d'_{59}	-0.0757 , -0.0096
c'_{69},d'_{69}	-0.0263 , +0.0437
c'_{79},d'_{79}	-0.0381 , -0.0669
c'_{89},d'_{89}	-0.0111 , +0.0126
c'_{99},d'_{99}	+0.0392 , +0.0179
c'_{109},d'_{109}	-0.0033 , -0.0655
c'_{110},d'_{110}	-0.2140 , -0.1697
c'_{210},d'_{210}	+0.0114 , +0.2076
c'_{310},d'_{310}	-0.0053 , -0.0468
c'_{410},d'_{410}	+0.0294 , -0.0078
c'_{510},d'_{510}	-0.0245 , -0.0285
c'_{610},d'_{610}	-0.0678 , +0.0791
c'_{710},d'_{710}	-0.0169 , -0.1104
c'_{810},d'_{810}	+0.0537 , +0.0636
c'_{910},d'_{910}	+0.0370 , -0.0468
c'_{1010},d'_{1010}	-0.0226 , -0.0056

Table S4: Parameters (in cm^{-1}) used to fit by Fourier series the two-dimensional torsional potential for CRC3 (including coupling parameters).

Parameters	
a_0	+525.9577
a_1	-216.4556
a_2	-140.1909
a_3	+209.8433
a_4	-15.7680
a_5	+5.6794
a_6	+1.3821
a_7	+0.7912
a_8	+0.1833
a_9	-0.0617
a_{10}	-0.0069
b_1	-129.1291
b_2	+81.2365
b_3	-197.1739
b_4	+26.2454
b_5	-5.1609
b_6	+9.3416
b_7	-2.6084
b_8	+0.5818
b_9	-1.0836
b_{10}	+0.2272
c_{11},d_{11}	+80.9784 , -104.5749
c_{21},d_{21}	+82.0394 , +57.9061
c_{31},d_{31}	+1.7838 , -25.9564
c_{41},d_{41}	-11.5362 , +7.8094
c_{51},d_{51}	+0.1847 , -0.2503
c_{61},d_{61}	+0.4798 , -0.1966
c_{71},d_{71}	-0.1505 , +0.3154
c_{81},d_{81}	+0.0371 , -0.0501
c_{91},d_{91}	+0.0789 , -0.0295
c_{101},d_{101}	-0.0463 , -0.0254
c_{12},d_{12}	+95.3199 , -166.6894
c_{22},d_{22}	-21.5595 , +52.2536
c_{32},d_{32}	-12.3422 , +10.1463

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Table S4 – continued from previous page

Parameters	
c_{42},d_{42}	+8.7399 , -11.9282
c_{52},d_{52}	+1.7162 , -0.4338
c_{62},d_{62}	-0.5763 , +1.0800
c_{72},d_{72}	-0.6300 , +0.0985
c_{82},d_{82}	+0.1416 , +0.0989
c_{92},d_{92}	-0.0167 , +0.1042
c_{102},d_{102}	-0.0104 , -0.0869
c_{13},d_{13}	+60.1527 , -80.0550
c_{23},d_{23}	+14.6980 , -12.6883
c_{33},d_{33}	+0.1510 , -4.0827
c_{43},d_{43}	-6.9385 , +4.9751
c_{53},d_{53}	+5.9567 , -7.6951
c_{63},d_{63}	-1.6595 , +1.7562
c_{73},d_{73}	-0.5024 , +0.7207
c_{83},d_{83}	+0.2174 , -0.0209
c_{93},d_{93}	+0.0120 , +0.0290
c_{103},d_{103}	-0.0072 , -0.1817
c_{14},d_{14}	+9.0860 , -27.0984
c_{24},d_{24}	+13.6538 , -20.9596
c_{34},d_{34}	+3.7953 , +2.0840
c_{44},d_{44}	+9.1703 , -10.1018
c_{54},d_{54}	-0.1758 , -0.9239
c_{64},d_{64}	-0.4513 , +0.5014
c_{74},d_{74}	+0.0048 , -0.2417
c_{84},d_{84}	+0.0990 , +0.1990
c_{94},d_{94}	+0.0178 , +0.3025
c_{104},d_{104}	-0.0465 , -0.2703
c_{15},d_{15}	-0.9655 , +3.3446
c_{25},d_{25}	+3.6184 , -5.7508
c_{35},d_{35}	+0.1480 , -0.4386
c_{45},d_{45}	+1.9274 , -1.4398
c_{55},d_{55}	+1.2136 , -1.2028
c_{65},d_{65}	-0.7482 , +0.5515
c_{75},d_{75}	+0.0894 , +0.0703
c_{85},d_{85}	+0.1122 , -0.0238
c_{95},d_{95}	-0.0972 , +0.0504

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Table S4 – continued from previous page

Parameters	
c_{105},d_{105}	+0.0544 , -0.1247
c_{16},d_{16}	-1.2120 , +2.8900
c_{26},d_{26}	+2.3225 , -3.8564
c_{36},d_{36}	+1.6827 , -1.9103
c_{46},d_{46}	+4.0459 , -3.6351
c_{56},d_{56}	-0.7616 , +0.8648
c_{66},d_{66}	-0.1810 , +0.4903
c_{76},d_{76}	+0.3833 , -0.3872
c_{86},d_{86}	-0.2528 , +0.2071
c_{96},d_{96}	-0.1037 , +0.2141
c_{106},d_{106}	+0.0162 , -0.0917
c_{17},d_{17}	+0.0945 , +2.1452
c_{27},d_{27}	-0.7903 , +1.0363
c_{37},d_{37}	-0.6912 , -0.2023
c_{47},d_{47}	-0.4160 , +0.5015
c_{57},d_{57}	+0.7815 , -0.4901
c_{67},d_{67}	-0.2781 , +0.4262
c_{77},d_{77}	+0.1427 , -0.2385
c_{87},d_{87}	-0.1895 , +0.0984
c_{97},d_{97}	-0.1120 , -0.0709
c_{107},d_{107}	+0.2154 , +0.0309
c_{18},d_{18}	+0.1827 , -0.5053
c_{28},d_{28}	-0.1557 , +0.3978
c_{38},d_{38}	+0.3920 , -0.6553
c_{48},d_{48}	-0.1256 , +0.2796
c_{58},d_{58}	+0.2199 , -0.1623
c_{68},d_{68}	-0.5689 , +0.5499
c_{78},d_{78}	+0.3598 , -0.0358
c_{88},d_{88}	-0.2829 , +0.0617
c_{98},d_{98}	-0.3647 , +0.2162
c_{108},d_{108}	+0.2566 , +0.1441
c_{19},d_{19}	+0.3810 , -0.1616
c_{29},d_{29}	-0.5270 , +0.7200
c_{39},d_{39}	-0.0788 , +0.2280
c_{49},d_{49}	-0.6862 , +0.5153
c_{59},d_{59}	+0.3955 , -0.1887

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Table S4 – continued from previous page

Parameters	
c_{69},d_{69}	-0.1073 , +0.2228
c_{79},d_{79}	-0.1456 , +0.0457
c_{89},d_{89}	-0.0463 , -0.0201
c_{99},d_{99}	-0.0530 , +0.1083
c_{109},d_{109}	+0.0512 , +0.0138
c_{110},d_{110}	+0.0190 , -0.4244
c_{210},d_{210}	+0.1009 , +0.0094
c_{310},d_{310}	+0.1167 , +0.0617
c_{410},d_{410}	-0.3073 , -0.0295
c_{510},d_{510}	+0.2334 , +0.0340
c_{610},d_{610}	-0.2634 , +0.1521
c_{710},d_{710}	-0.0140 , +0.0035
c_{810},d_{810}	-0.0004 , -0.1032
c_{910},d_{910}	-0.1351 , +0.2768
c_{1010},d_{1010}	+0.0455 , -0.0172

Table S5: Parameters (in cm^{-1}) used to fit by Fourier series the two-dimensional torsional potential for CRC4 (including coupling parameters).

Parameters	
a_0	+638.4483
a_1	-107.0919
a_2	-169.7664
a_3	+213.8027
a_4	-14.8229
a_5	+5.4566
a_6	+1.1463
a_7	+0.9746
a_8	+0.0665
a_9	-0.1036
a_{10}	+0.0561
b_1	+88.5672
b_2	+76.5103
b_3	-225.1711
b_4	+19.2116
b_5	-4.3115
b_6	+8.7894
b_7	-1.6147
b_8	+0.6977
b_9	-1.0443
b_{10}	-0.0247
c_{11},d_{11}	-94.7676 , -15.5823
c_{21},d_{21}	+74.0644 , +26.3690
c_{31},d_{31}	-0.0446 , -22.5598
c_{41},d_{41}	-6.0767 , +6.9698
c_{51},d_{51}	+1.6379 , +0.5029
c_{61},d_{61}	-0.8911 , +1.1102
c_{71},d_{71}	-0.0546 , -0.2225
c_{81},d_{81}	+0.1566 , -0.0524
c_{91},d_{91}	-0.0900 , +0.1018
c_{101},d_{101}	-0.0598 , -0.0141
c_{12},d_{12}	+162.1790 , -250.5826
c_{22},d_{22}	-103.7707 , +135.9888
c_{32},d_{32}	-9.0966 , +10.1289

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Table S5 – continued from previous page

Parameters	
c_{42},d_{42}	+14.6685 , -13.5559
c_{52},d_{52}	+0.3779 , +1.7521
c_{62},d_{62}	-0.5709 , +1.3760
c_{72},d_{72}	-0.3653 , +0.1583
c_{82},d_{82}	-0.0093 , +0.2807
c_{92},d_{92}	+0.0196 , +0.0553
c_{102},d_{102}	-0.0855 , -0.0724
c_{13},d_{13}	+50.4019 , -79.1064
c_{23},d_{23}	+55.8316 , -55.5163
c_{33},d_{33}	-0.7502 , -4.2287
c_{43},d_{43}	-4.2918 , +2.9138
c_{53},d_{53}	+5.3310 , -6.9805
c_{63},d_{63}	-2.0159 , +2.1747
c_{73},d_{73}	-0.1983 , +0.4599
c_{83},d_{83}	+0.2048 , -0.0600
c_{93},d_{93}	-0.1272 , +0.1566
c_{103},d_{103}	-0.0287 , -0.2096
c_{14},d_{14}	+15.4899 , -27.0314
c_{24},d_{24}	+18.1384 , -23.2867
c_{34},d_{34}	+6.6639 , -2.1002
c_{44},d_{44}	+4.8463 , -4.0463
c_{54},d_{54}	+0.1002 , -0.9752
c_{64},d_{64}	-0.4991 , +0.4809
c_{74},d_{74}	+0.1830 , -0.0538
c_{84},d_{84}	-0.0091 , +0.0003
c_{94},d_{94}	-0.0970 , +0.1372
c_{104},d_{104}	-0.0089 , -0.0903
c_{15},d_{15}	-2.4055 , +7.1633
c_{25},d_{25}	+16.2691 , -20.7769
c_{35},d_{35}	+2.9743 , -3.6922
c_{45},d_{45}	+3.7028 , -3.2313
c_{55},d_{55}	-1.2904 , +1.5958
c_{65},d_{65}	-0.0304 , -0.1798
c_{75},d_{75}	+0.1740 , -0.1576
c_{85},d_{85}	+0.0698 , -0.0527
c_{95},d_{95}	-0.1519 , +0.1116

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Table S5 – continued from previous page

Parameters	
c_{105},d_{105}	+0.0602 , -0.0963
c_{16},d_{16}	-0.0324 , +2.3329
c_{26},d_{26}	-0.8330 , +1.5108
c_{36},d_{36}	+1.8103 , -2.0809
c_{46},d_{46}	+2.2642 , -2.0505
c_{56},d_{56}	-0.6481 , +1.1681
c_{66},d_{66}	-0.1945 , +0.3160
c_{76},d_{76}	+0.1605 , -0.3523
c_{86},d_{86}	+0.0448 , -0.0095
c_{96},d_{96}	-0.1889 , +0.1407
c_{106},d_{106}	+0.0918 , -0.0315
c_{17},d_{17}	-0.4378 , +1.5103
c_{27},d_{27}	-0.9312 , +1.0898
c_{37},d_{37}	+0.3526 , -0.6055
c_{47},d_{47}	-0.4300 , +0.1502
c_{57},d_{57}	+0.1715 , -0.1332
c_{67},d_{67}	-0.2655 , +0.5583
c_{77},d_{77}	+0.1211 , -0.3007
c_{87},d_{87}	-0.0690 , +0.0106
c_{97},d_{97}	+0.0306 , -0.0482
c_{107},d_{107}	+0.0119 , +0.0338
c_{18},d_{18}	-0.0371 , -0.8312
c_{28},d_{28}	-1.3876 , +2.0274
c_{38},d_{38}	-0.1390 , +0.2981
c_{48},d_{48}	-0.7224 , +0.5411
c_{58},d_{58}	+0.2746 , -0.3134
c_{68},d_{68}	-0.2851 , +0.3329
c_{78},d_{78}	+0.0312 , -0.0139
c_{88},d_{88}	-0.0787 , +0.0006
c_{98},d_{98}	-0.0645 , +0.0848
c_{108},d_{108}	+0.0177 , -0.0655
c_{19},d_{19}	+0.3666 , -0.1965
c_{29},d_{29}	-0.4858 , +0.4568
c_{39},d_{39}	+0.0300 , -0.0158
c_{49},d_{49}	-0.7607 , +0.8032
c_{59},d_{59}	+0.2445 , -0.2105

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Table S5 – continued from previous page

Parameters	
c_{69},d_{69}	-0.2378 , +0.0682
c_{79},d_{79}	+0.1332 , +0.1946
c_{89},d_{89}	-0.1997 , -0.0939
c_{99},d_{99}	+0.1066 , -0.0114
c_{109},d_{109}	+0.0128 , +0.0272
c_{110},d_{110}	+0.1683 , -0.2022
c_{210},d_{210}	-0.0200 , +0.0071
c_{310},d_{310}	-0.2707 , +0.4605
c_{410},d_{410}	-0.1151 , -0.1154
c_{510},d_{510}	-0.2074 , +0.0348
c_{610},d_{610}	+0.2529 , -0.0033
c_{710},d_{710}	-0.3012 , +0.1312
c_{810},d_{810}	+0.2406 , -0.1277
c_{910},d_{910}	-0.2161 , +0.2246
c_{1010},d_{1010}	+0.1499 , -0.1509

Table S6: Parameters (in cm^{-1}) used to fit by Fourier series the two-dimensional torsional potential for CRC5 (including coupling parameters).

Parameters	
a_0	+861.0770
a_1	-201.0337
a_2	-179.3936
a_3	+218.1258
a_4	-13.7300
a_5	+4.6728
a_6	+1.4225
a_7	+1.2853
a_8	-0.0020
a_9	+0.0321
a_{10}	+0.0695
b_1	+312.6199
b_2	+233.5583
b_3	-143.7110
b_4	+40.6440
b_5	-12.8162
b_6	+0.6016
b_7	-5.0871
b_8	+2.0162
b_9	+1.0893
b_{10}	-0.1145
c_{11},d_{11}	-340.0809 , +195.0669
c_{21},d_{21}	+143.8937 , -42.7099
c_{31},d_{31}	+0.9619 , -33.1350
c_{41},d_{41}	-7.8941 , +13.6312
c_{51},d_{51}	+1.8537 , -1.2754
c_{61},d_{61}	-0.2010 , -0.0003
c_{71},d_{71}	+0.3385 , +0.0985
c_{81},d_{81}	-0.0152 , +0.0092
c_{91},d_{91}	+0.0944 , -0.0025
c_{101},d_{101}	+0.0871 , +0.1723
c_{12},d_{12}	+20.1320 , -91.5249
c_{22},d_{22}	-27.1694 , +23.6238
c_{32},d_{32}	-10.6070 , +5.6669

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Table S6 – continued from previous page

Parameters	
c_{42},d_{42}	+14.2559 , -7.6214
c_{52},d_{52}	+2.6884 , -0.9968
c_{62},d_{62}	-0.1919 , +0.6067
c_{72},d_{72}	-0.6674 , +0.4281
c_{82},d_{82}	-0.1831 , +0.1790
c_{92},d_{92}	+0.1793 , -0.0393
c_{102},d_{102}	-0.0558 , +0.1479
c_{13},d_{13}	-3.0589 , -6.4185
c_{23},d_{23}	+119.8740 , -137.9558
c_{33},d_{33}	-5.2989 , -5.6293
c_{43},d_{43}	-2.5503 , +3.7570
c_{53},d_{53}	+7.6660 , -8.5054
c_{63},d_{63}	-2.2382 , +2.2444
c_{73},d_{73}	-0.7955 , +0.8202
c_{83},d_{83}	+0.1447 , -0.1330
c_{93},d_{93}	+0.0279 , +0.0403
c_{103},d_{103}	-0.0579 , +0.1251
c_{14},d_{14}	+8.2406 , -12.0184
c_{24},d_{24}	+64.8583 , -72.7239
c_{34},d_{34}	+4.7681 , -1.7684
c_{44},d_{44}	+8.4133 , -8.1271
c_{54},d_{54}	-0.3341 , +0.0755
c_{64},d_{64}	-1.1344 , +1.4129
c_{74},d_{74}	+0.0566 , -0.0835
c_{84},d_{84}	-0.1588 , +0.0975
c_{94},d_{94}	-0.0453 , -0.0332
c_{104},d_{104}	+0.0174 , -0.0383
c_{15},d_{15}	+3.0673 , -0.5915
c_{25},d_{25}	+39.2317 , -36.3591
c_{35},d_{35}	+4.5882 , -3.4998
c_{45},d_{45}	+7.9795 , -9.7722
c_{55},d_{55}	-4.9334 , +4.8910
c_{65},d_{65}	-0.9244 , +1.1396
c_{75},d_{75}	+0.6124 , -0.6027
c_{85},d_{85}	-0.2238 , +0.4430
c_{95},d_{95}	-0.0282 , -0.0974

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Table S6 – continued from previous page

Parameters	
c_{105},d_{105}	+0.0604 , -0.0491
c_{16},d_{16}	+2.9096 , -5.8997
c_{26},d_{26}	+3.3039 , +2.4060
c_{36},d_{36}	+4.7610 , -2.5672
c_{46},d_{46}	+5.7836 , -6.4343
c_{56},d_{56}	-5.5300 , +5.4871
c_{66},d_{66}	-1.1434 , +0.8375
c_{76},d_{76}	+0.7441 , -0.9992
c_{86},d_{86}	-0.1428 , +0.5755
c_{96},d_{96}	-0.0027 , -0.0574
c_{106},d_{106}	+0.0760 , -0.1491
c_{17},d_{17}	-0.9141 , +0.8517
c_{27},d_{27}	-5.0719 , +4.9792
c_{37},d_{37}	+1.0867 , -1.3103
c_{47},d_{47}	+2.0197 , -1.3464
c_{57},d_{57}	-4.0103 , +3.9324
c_{67},d_{67}	-0.6871 , +0.4304
c_{77},d_{77}	+0.4269 , -0.7503
c_{87},d_{87}	-0.1080 , +0.1681
c_{97},d_{97}	+0.1907 , +0.0749
c_{107},d_{107}	-0.0943 , -0.1014
c_{18},d_{18}	-1.5497 , +2.1188
c_{28},d_{28}	-4.8167 , +2.5343
c_{38},d_{38}	-0.9653 , +0.4067
c_{48},d_{48}	+0.9107 , -0.0323
c_{58},d_{58}	-2.0617 , +2.1738
c_{68},d_{68}	-0.1383 , +0.1485
c_{78},d_{78}	+0.2645 , -0.4627
c_{88},d_{88}	-0.0643 , -0.1069
c_{98},d_{98}	+0.1880 , +0.1428
c_{108},d_{108}	-0.0266 , -0.1551
c_{19},d_{19}	-0.0419 , +2.0701
c_{29},d_{29}	-0.1975 , -0.7732
c_{39},d_{39}	-1.2875 , +0.7481
c_{49},d_{49}	+0.3061 , -0.1178
c_{59},d_{59}	-0.7518 , +0.8358

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Table S6 – continued from previous page

Parameters	
c_{69},d_{69}	+0.2566 , -0.0364
c_{79},d_{79}	+0.2995 , -0.0946
c_{89},d_{89}	-0.2759 , -0.2151
c_{99},d_{99}	+0.2701 , -0.1165
c_{109},d_{109}	-0.0756 , +0.2570
c_{110},d_{110}	+0.5583 , -0.4201
c_{210},d_{210}	+0.7728 , -0.7385
c_{310},d_{310}	+0.0334 , +0.8740
c_{410},d_{410}	+0.4958 , -0.7593
c_{510},d_{510}	-0.3394 , +0.0709
c_{610},d_{610}	+0.4100 , -0.0832
c_{710},d_{710}	+0.1245 , +0.1577
c_{810},d_{810}	+0.0626 , -0.1298
c_{910},d_{910}	-0.1324 , -0.2286
c_{1010},d_{1010}	+0.1448 , +0.0818

Table S7: Cartesian coordinates (em Å) and non-scaled vibrational frequencies (in cm^{-1}) for the 3B-T−A+

Cartesian Coordinates			
Element	X	Y	Z
C	-0.971808	-0.067590	-1.033474
C	-0.756347	-0.115184	0.448793
C	0.672632	-0.198405	0.853125
C	1.227257	0.567807	1.778477
H	-2.020241	0.067986	-1.348889
H	-1.253633	0.746603	0.896043
H	-1.316235	-0.987693	0.802588
H	1.269602	-0.936971	0.336446
H	2.267820	0.464552	2.043343
H	0.661709	1.326682	2.300982
O	-0.104207	-0.182934	-1.852647
Vibrational Frequencies			
3206.33	3148.63	3113.64	3035.77
2971.72	2902.73	1839.51	1722.52
1446.87	1407.82	1395.91	1330.08
1297.62	1222.84	1143.93	1034.51
1005.18	968.07	952.11	868.15
746.77	704.32	551.19	394.74
227.47	147.24	81.98	
Energy MPWB1K/6-31+G(d,p) (a.u.): -231.1103623			

Table S8: Cartesian coordinates (em Å) and non-scaled vibrational frequencies (in cm^{-1}) for the 3B-G+A−

Cartesian Coordinates			
Element	X	Y	Z
C	-0.619104	0.050937	-1.016229
C	-0.512219	0.033218	0.483027
C	0.919240	-0.009140	0.909682
C	1.510125	-1.060302	1.457031
H	-0.155232	-0.809417	-1.527387
H	-1.023180	0.912076	0.868752
H	-1.026374	-0.859841	0.840936
H	1.495400	0.889172	0.728064
H	2.553221	-1.038956	1.731389
H	0.968121	-1.973747	1.657705
O	-1.151021	0.920712	-1.646476
Vibrational Frequencies			
3207.13	3130.57	3113.70	3083.05
3008.87	2907.09	1837.96	1710.22
1441.68	1423.64	1391.67	1305.50
1270.79	1223.61	1131.43	1067.12
1021.89	959.39	951.59	944.04
804.77	644.62	494.10	385.99
304.92	84.60	59.29	
Energy MPWB1K/6-31+G(d,p) (a.u.): -231.1101883			

Table S9: Cartesian coordinates (em Å) and non-scaled vibrational frequencies (in cm^{-1}) for the 3B-G+A+

Cartesian Coordinates			
Element	X	Y	Z
C	-0.580138	-0.311846	-1.062196
C	-0.441067	-0.336481	0.431896
C	0.987233	-0.359759	0.863667
C	1.557916	0.577370	1.604102
H	0.082489	-1.000893	-1.614054
H	-0.980964	0.509761	0.846928
H	-0.938725	-1.250558	0.770423
H	1.578145	-1.205371	0.532918
H	2.596492	0.513508	1.888645
H	1.003401	1.436617	1.953044
O	-1.353825	0.385956	-1.654388
Vibrational Frequencies			
3209.44	3123.13	3113.25	3087.21
2980.51	2897.92	1840.57	1717.14
1441.40	1418.05	1403.77	1309.43
1265.23	1209.87	1148.21	1052.32
1020.91	996.53	956.62	928.11
750.32	621.24	504.26	409.69
264.63	107.23	60.69	
Energy MPWB1K/6-31+G(d,p) (a.u.): -231.1096713			

Table S10: Cartesian coordinates (em Å) and non-scaled vibrational frequencies (in cm^{-1}) for the 3B-G+C+

Cartesian Coordinates			
Element	X	Y	Z
C	-0.718304	-0.229452	-0.754833
C	-0.538122	-0.223987	0.731130
C	0.896707	-0.272310	1.152386
C	1.920216	0.115778	0.405875
H	-0.187689	-1.036552	-1.287577
H	-1.048271	0.644049	1.145246
H	-1.053366	-1.108538	1.113865
H	1.086455	-0.645833	2.149589
H	2.931704	0.061546	0.776431
H	1.790855	0.510084	-0.592469
O	-1.392518	0.556879	-1.359535
Vibrational Frequencies			
3205.61	3134.15	3113.89	3061.56
2994.01	2910.22	1838.39	1838.39
1429.74	1423.57	1397.39	1319.68
1305.97	1195.49	1100.26	1100.26
1017.45	989.09	955.41	937.49
767.03	579.79	519.54	452.86
230.43	115.84	61.46	
Energy MPWB1K/6-31+G(d,p) (a.u.): -231.1087717			

Table S11: Cartesian coordinates (em Å) and non-scaled vibrational frequencies (in cm^{-1}) for the 3B-TC

Cartesian Coordinates			
Element	X	Y	Z
C	-1.123916	0.054056	-0.685193
C	-0.790779	0.010004	0.770919
C	0.630163	-0.049037	1.220830
C	1.726878	-0.070141	0.477066
H	-2.209232	0.095960	-0.885759
H	-1.288826	0.876366	1.218076
H	-1.347956	-0.839132	1.179702
H	0.738341	-0.076920	2.298354
H	2.693854	-0.114159	0.954808
H	1.694345	-0.044910	-0.598780
O	-0.349541	0.047829	-1.600663
Vibrational Frequencies			
3233.63	3131.89	3109.42	2996.57
2972.39	2886.31	1843.17	1714.37
1434.17	1407.96	1395.97	1389.30
1317.86	1224.87	1069.88	1044.40
1026.50	992.93	980.96	824.29
758.19	746.30	513.14	391.36
238.05	125.54	75.88	
Energy MPWB1K/6-31+G(d,p) (a.u.): -231.1074061			

Table S12: Cartesian coordinates (em Å) and non-scaled vibrational frequencies (in cm^{-1}) for the TS1-T−A+

Cartesian Coordinates			
Element	X	Y	Z
C	-0.728374	0.230536	-1.112923
C	-0.393404	-0.767770	-0.045615
C	0.769337	-0.382259	0.798921
C	0.741040	-0.347760	2.121249
H	-1.785230	-0.066037	-1.724153
H	-1.293369	-0.937938	0.544953
H	-0.210737	-1.704896	-0.580178
H	1.672979	-0.111799	0.270415
H	1.611067	-0.066138	2.693287
H	-0.151436	-0.598764	2.676904
O	-0.112795	1.192493	-1.425830
H	-2.680132	-0.351181	-2.227732
Vibrational Frequencies			
-1340.85	3208.13	3146.82	3114.87
3050.96	2986.23	1902.33	1718.66
1440.91	1402.01	1369.58	1327.41
1295.70	1226.53	1222.51	1152.99
1057.77	1009.00	960.14	957.28
864.37	801.07	704.48	546.90
392.38	314.60	286.00	187.90
100.57	70.03		
Energy MPWB1K/6-31+G(d,p) (a.u.): -231.5985738			

Table S13: Cartesian coordinates (em Å) and non-scaled vibrational frequencies (in cm^{-1}) for the TS1-G+A+

Cartesian Coordinates			
Element	X	Y	Z
C	-0.363376	0.271444	-1.132147
C	-0.119090	-0.725955	-0.036350
C	1.018746	-0.314713	0.838218
C	0.906071	-0.095461	2.138314
H	0.694895	0.599778	-1.734023
H	-1.040333	-0.864327	0.524234
H	0.122254	-1.665688	-0.540273
H	1.978696	-0.192932	0.353585
H	1.757700	0.196243	2.732434
H	-0.038708	-0.204324	2.651216
O	-1.401857	0.729913	-1.467056
H	1.600156	0.842659	-2.231916
Vibrational Frequencies			
-1359.70	3212.49	3137.73	3118.56
3078.62	2990.01	1902.85	1717.74
1438.95	1414.57	1367.62	1367.62
1271.15	1259.27	1206.97	1135.56
1079.06	1015.53	973.62	960.48
920.22	824.20	624.26	495.27
420.50	361.59	283.48	198.54
91.43	52.27		
Energy MPWB1K/6-31+G(d,p) (a.u.): -231.5977537			

Table S14: Cartesian coordinates (em Å) and non-scaled vibrational frequencies (in cm^{-1}) for the TS1-G+A−

Cartesian Coordinates			
Element	X	Y	Z
C	-0.635274	0.393826	-0.906304
C	-0.406224	-0.635775	0.166731
C	0.739036	-0.216782	1.032081
C	1.920599	-0.813300	1.043919
H	0.300531	0.415581	-1.759967
H	-1.326111	-0.737937	0.739265
H	-0.176255	-1.580087	-0.323885
H	0.564736	0.642801	1.665553
H	2.717348	-0.463966	1.681537
H	2.128607	-1.671303	0.420985
O	-1.547049	1.143088	-1.000043
H	1.077044	0.399141	-2.464707
Vibrational Frequencies			
-1397.89	3212.65	3138.36	3118.73
3083.65	3017.61	1901.18	1710.46
1440.83	1422.09	1356.40	1305.60
1279.97	1262.80	1202.95	1138.75
1063.44	1019.15	964.38	955.83
939.87	857.36	644.68	488.14
401.92	385.36	275.13	206.50
76.39	48.09		
Energy MPWB1K/6-31+G(d,p) (a.u.): -231.5976140			

Table S15: Cartesian coordinates (em Å) and non-scaled vibrational frequencies (in cm^{-1}) for the TS1-G+C+

Cartesian Coordinates			
Element	X	Y	Z
C	-0.494709	0.050165	-0.910703
C	-0.224812	-0.923426	0.194201
C	0.905785	-0.505914	1.079520
C	1.402308	0.718864	1.156125
H	0.525571	0.279720	-1.618738
H	-1.143278	-1.077900	0.759856
H	0.023886	-1.871639	-0.287485
H	1.322776	-1.287241	1.700022
H	2.216887	0.946843	1.824953
H	1.021321	1.535604	0.559306
O	-1.528004	0.561020	-1.184204
H	1.368517	0.433031	-2.231917
Vibrational Frequencies			
-1395.04	3209.20	3138.28	3116.57
3053.65	2996.85	1901.22	1711.89
1427.02	1419.33	1358.52	1310.14
1302.12	1278.83	1184.78	1112.94
1040.62	1016.29	986.14	957.34
937.68	819.00	577.20	534.70
459.92	332.81	276.70	177.08
113.76	50.08		
Energy MPWB1K/6-31+G(d,p) (a.u.): -231.5963996			

Table S16: Cartesian coordinates (em Å) and non-scaled vibrational frequencies (in cm^{-1}) for the TS1-TC

Cartesian Coordinates			
Element	X	Y	Z
C	-0.866491	-0.024835	-0.896295
C	-0.483457	-0.940110	0.217828
C	0.643244	-0.575846	1.125978
C	1.404122	0.507264	1.090441
H	-1.827448	-0.499126	-1.544047
H	-1.400977	-1.102728	0.790482
H	-0.299656	-1.910602	-0.251835
H	0.828951	-1.315360	1.895373
H	2.188488	0.634688	1.820444
H	1.275809	1.282349	0.354119
O	-0.404322	1.018322	-1.216479
H	-2.652305	-0.944690	-2.070260
Vibrational Frequencies			
-1301.59	3250.86	3143.64	3113.35
3012.54	2984.64	1904.00	1720.90
1437.69	1400.55	1390.85	1365.79
1315.52	1234.83	1229.75	1099.95
1066.13	1021.80	977.24	973.94
828.14	821.54	732.20	528.69
400.67	303.22	293.45	233.29
98.98	62.15		
Energy MPWB1K/6-31+G(d,p) (a.u.): -231.5962652			

Table S17: Cartesian coordinates (em Å) and non-scaled vibrational frequencies (in cm^{-1}) for the TS2-T+A−

Cartesian Coordinates			
Element	X	Y	Z
C	-0.865151	0.742642	-0.858384
C	-0.680918	-0.358828	0.120844
C	0.664501	-0.509176	0.689518
C	1.183382	-1.673264	1.061072
H	-1.821101	0.733657	-1.405331
H	-1.448560	-0.034375	1.006935
H	-1.134669	-1.287131	-0.218447
H	1.233111	0.403152	0.800703
H	2.173995	-1.735484	1.482959
H	0.637909	-2.599799	0.950664
O	-0.067410	1.622539	-1.039745
H	-2.164486	0.185047	1.821814
Vibrational Frequencies			
-1391.00	3211.00	3156.69	3116.39
3070.60	2925.00	1815.87	1697.51
1447.72	1401.61	1374.71	1338.42
1298.57	1274.46	1197.47	1141.80
1041.69	1013.62	987.78	951.03
880.83	791.12	723.41	612.83
405.05	314.76	286.34	223.32
138.52	100.20		
Energy MPWB1K/6-31+G(d,p) (a.u.): -231.5972301			

Table S18: Cartesian coordinates (em Å) and non-scaled vibrational frequencies (in cm^{-1}) for the TS2-C−A−

Cartesian Coordinates			
Element	X	Y	Z
C	-0.563781	0.933543	-0.660063
C	-0.354570	-0.181507	0.297916
C	1.004388	-0.313696	0.843890
C	1.613927	-1.473159	1.060299
H	0.069189	1.823058	-0.501958
H	-1.089850	0.116903	1.215072
H	-0.789405	-1.105785	-0.069424
H	1.517920	0.607820	1.090542
H	2.609169	-1.515022	1.473557
H	1.136603	-2.413823	0.827237
O	-1.379778	0.914952	-1.540490
H	-1.796729	0.287320	2.052831
Vibrational Frequencies			
-1380.62	3213.92	3124.55	3115.84
3095.53	2903.42	1821.11	1696.31
1443.02	1443.02	1388.26	1312.92
1285.21	1259.06	1190.54	1157.08
1058.08	1033.63	1003.76	950.50
935.69	795.95	634.70	521.00
451.11	296.43	289.92	230.94
133.30	83.37		
Energy MPWB1K/6-31+G(d,p) (a.u.): -231.5964320			

Table S19: Cartesian coordinates (em Å) and non-scaled vibrational frequencies (in cm^{-1}) for the TS2-C−G+

Cartesian Coordinates			
Element	X	Y	Z
C	-0.573286	0.506376	-0.751195
C	-0.354592	-0.598250	0.224052
C	1.015876	-0.748360	0.753940
C	1.711486	0.231958	1.319722
H	0.143950	1.340794	-0.695967
H	-1.088553	-0.297539	1.145580
H	-0.806592	-1.514853	-0.139285
H	1.464593	-1.728278	0.666487
H	2.716970	0.071388	1.674714
H	1.298556	1.221376	1.458187
O	-1.474459	0.519124	-1.543823
H	-1.754337	-0.089120	1.977733
Vibrational Frequencies			
-1402.56	3211.50	3140.58	3117.40
3103.40	2927.26	1815.91	1684.52
1427.99	1391.49	1370.14	1323.98
1302.66	1281.46	1166.90	1117.61
1044.56	1006.87	983.17	970.08
948.61	789.27	639.00	564.10
436.19	318.44	297.22	207.13
102.10	69.35		
Energy MPWB1K/6-31+G(d,p) (a.u.): -231.5943244			

Table S20: Cartesian coordinates (em Å) and non-scaled vibrational frequencies (in cm^{-1}) for the TS2-T+C+

Cartesian Coordinates			
Element	X	Y	Z
C	-0.987870	0.319331	-0.801289
C	-0.706756	-0.752927	0.187327
C	0.632999	-0.931605	0.772989
C	1.599259	-0.022613	0.858722
H	-1.961766	0.214603	-1.307853
H	-1.484311	-0.478537	1.079890
H	-1.145505	-1.688452	-0.153987
H	0.809794	-1.913584	1.192086
H	2.537808	-0.280460	1.324774
H	1.489421	0.972689	0.464238
O	-0.279839	1.257729	-1.046841
H	-2.205678	-0.262864	1.896802
Vibrational Frequencies			
-1390.14	3244.11	3140.04	3122.04
3059.10	2904.99	1822.08	1690.50
1437.29	1404.48	1399.86	1372.74
1323.57	1276.11	1182.61	1087.90
1041.52	1022.43	1005.30	974.49
846.54	808.94	745.90	608.01
397.22	324.28	286.46	237.85
128.21	72.28		
Energy MPWB1K/6-31+G(d,p) (a.u.): -231.5942176			

Table S21: Cartesian coordinates (em Å) and non-scaled vibrational frequencies (in cm^{-1}) for the TS2-G−C−

Cartesian Coordinates			
Element	X	Y	Z
C	-0.696531	0.586860	-0.533167
C	-0.443519	-0.515631	0.421667
C	0.911459	-0.648583	0.990254
C	1.993042	0.006035	0.583948
H	-0.192878	1.540581	-0.310773
H	-1.185413	-0.246850	1.366790
H	-0.876547	-1.449112	0.072319
H	1.005202	-1.354717	1.804785
H	2.947092	-0.156386	1.059790
H	1.974440	0.706646	-0.237331
O	-1.440318	0.494929	-1.473425
H	-1.822026	-0.092446	2.212590
Vibrational Frequencies			
-1469.84	3214.52	3133.27	3122.80
3079.87	2928.23	1812.45	1693.57
1425.82	1410.94	1343.50	1322.38
1307.95	1274.36	1181.44	1101.33
1047.14	1019.58	996.41	964.09
949.06	823.34	609.90	553.17
461.92	307.88	292.64	213.98
105.67	84.25		
Energy MPWB1K/6-31+G(d,p) (a.u.): -231.5939114			

Table S22: Cartesian coordinates (em Å) and non-scaled vibrational frequencies (in cm^{-1}) for the TS3-TC

Cartesian Coordinates			
Element	X	Y	Z
C	-1.291854	0.252873	-0.380811
C	-0.405608	-0.957985	-0.324532
C	0.970868	-0.784340	0.168771
C	1.693708	0.218849	0.608016
H	-2.306616	0.041786	-0.760890
H	-0.934451	-1.703111	0.277065
H	-0.398033	-1.385265	-1.331597
H	1.659328	-2.005828	0.156996
H	2.717242	0.062080	0.918344
H	1.289692	1.219837	0.671069
O	-0.986431	1.364901	-0.059254
H	2.112950	-2.762603	0.158731
Vibrational Frequencies			
-1182.44	3195.66	3105.41	3010.20
2980.53	2893.72	1895.03	1840.64
1720.28	1418.65	1401.13	1388.44
1333.02	1216.46	1142.50	1035.32
1027.12	990.00	976.77	943.64
836.27	729.71	727.52	727.52
374.69	309.22	278.28	226.80
120.50	71.16		
Energy MPWB1K/6-31+G(d,p) (a.u.): -231.5831966			

Table S23: Cartesian coordinates (em Å) and non-scaled vibrational frequencies (in cm^{-1}) for the TS3-G+A−

Cartesian Coordinates			
Element	X	Y	Z
C	-1.075062	-0.467843	0.330753
C	-0.156285	0.254870	-0.620143
C	1.213456	0.386423	-0.086811
C	1.897089	1.407460	0.375462
H	-1.008479	-0.148284	1.383482
H	-0.177315	-0.263099	-1.576038
H	-0.578194	1.254905	-0.768863
H	1.921780	-0.843427	-0.046574
H	2.905247	1.291573	0.745577
H	1.477351	2.407551	0.393675
O	-1.845906	-1.319296	-0.006866
H	2.380175	-1.584673	-0.013490
Vibrational Frequencies			
-1151.69	3175.66	3076.39	3073.85
2965.38	2920.13	1965.02	1841.73
1709.78	1415.80	1400.32	1392.13
1263.65	1195.43	1116.62	1079.53
1056.37	983.10	954.36	934.15
928.97	749.68	629.89	480.52
394.64	334.02	266.21	197.27
67.76	56.51		
Energy MPWB1K/6-31+G(d,p) (a.u.): -231.5830959			

Table S24: Cartesian coordinates (em Å) and non-scaled vibrational frequencies (in cm^{-1}) for the TS3-G+A+

Cartesian Coordinates			
Element	X	Y	Z
C	-0.575110	-0.596105	-0.945370
C	-0.513668	-0.117115	0.480015
C	0.871946	0.026495	0.966934
C	1.578596	1.060568	1.358558
H	0.149836	-1.379657	-1.218173
H	-1.068270	0.817776	0.559250
H	-1.038511	-0.863423	1.083316
H	1.569726	-1.205999	1.028485
H	2.602505	0.954393	1.685607
H	1.156665	2.059367	1.370803
O	-1.360821	-0.181124	-1.748294
H	2.010957	-1.959170	1.089059
Vibrational Frequencies			
-1159.91	3177.58	3079.68	3049.96
2981.91	2922.37	1944.79	1842.06
1713.70	1415.25	1401.37	1395.60
1262.46	1182.26	1124.03	1092.54
1045.77	996.56	981.15	925.59
910.33	736.63	613.40	494.91
400.16	327.36	264.13	196.10
85.11	55.10		
Energy MPWB1K/6-31+G(d,p) (a.u.): -231.5830725			

Table S25: Cartesian coordinates (em Å) and non-scaled vibrational frequencies (in cm^{-1}) for the TS3-G+C+

Cartesian Coordinates			
Element	X	Y	Z
C	-0.812947	0.442779	-0.666863
C	-0.286527	-0.874222	-0.169596
C	1.101987	-0.738192	0.323154
C	1.801563	0.284283	0.759524
H	-0.229346	0.902376	-1.480836
H	-0.947308	-1.254648	0.606414
H	-0.306821	-1.581140	-1.002369
H	1.817182	-1.951513	0.306704
H	2.826785	0.164907	1.078153
H	1.380497	1.281363	0.829305
O	-1.783686	0.987397	-0.224139
H	2.286565	-2.690309	0.288192
Vibrational Frequencies			
-1156.36	3173.79	3077.80	3072.06
2996.16	2920.38	1943.42	1837.05
1705.01	1422.76	1403.73	1393.65
1279.08	1184.49	1125.04	1064.41
1041.75	988.20	976.15	925.86
917.15	786.41	593.26	479.66
451.30	311.39	267.03	209.81
74.68	46.26		
Energy MPWB1K/6-31+G(d,p) (a.u.): -231.5830223			

Table S26: Cartesian coordinates (em Å) and non-scaled vibrational frequencies (in cm^{-1}) for the TS3-T+A+

Cartesian Coordinates			
Element	X	Y	Z
C	-0.977981	-0.487921	-0.937657
C	-0.838549	0.033212	0.464887
C	0.551846	0.191054	0.920083
C	1.238928	1.228358	1.334079
H	-2.019498	-0.630959	-1.271106
H	-1.378755	0.984593	0.517473
H	-1.391057	-0.650702	1.114829
H	1.286322	-1.033603	0.919075
H	2.271550	1.137837	1.637517
H	0.796750	2.217780	1.381541
O	-0.063568	-0.740203	-1.667039
H	1.750231	-1.763945	0.947055
Vibrational Frequencies			
-1122.00	3174.73	3074.10	3013.28
2966.73	2904.57	2025.27	1846.14
1724.16	1419.94	1394.67	1391.14
1313.31	1202.06	1101.43	1076.22
1010.08	947.83	944.43	920.89
852.91	742.81	691.85	572.38
347.74	320.44	258.18	155.34
141.18	61.70		
Energy MPWB1K/6-31+G(d,p) (a.u.): -231.5823019			

Table S27: Cartesian coordinates (em Å) and non-scaled vibrational frequencies (in cm^{-1}) for the TS4-T−A+

Cartesian Coordinates			
Element	X	Y	Z
C	-0.993113	-0.670373	-0.877480
C	-0.834752	0.213104	0.323090
C	0.577930	0.338863	0.793120
C	1.142244	1.470909	1.139997
H	-2.013366	-0.712117	-1.294457
H	-1.280243	1.182823	0.101198
H	-1.463582	-0.224425	1.105449
H	1.147692	-0.581245	0.834040
H	2.535940	1.369040	1.575872
H	0.765510	2.482342	1.154708
O	-0.110378	-1.315464	-1.367883
H	3.342103	1.256921	1.816225
Vibrational Frequencies			
-1012.42	3175.52	3125.28	3045.31
2977.62	2904.31	2218.84	1839.55
1672.16	1412.08	1392.87	1334.57
1266.19	1203.37	1101.77	1090.27
1017.14	939.25	932.23	920.24
865.68	748.54	701.18	162.46
406.55	266.33	223.93	
137.07	73.31		
Energy MPWB1K/6-31+G(d,p) (a.u.): -231.5793902			

Table S28: Cartesian coordinates (em Å) and non-scaled vibrational frequencies (in cm^{-1}) for the TS4-G+A−

Cartesian Coordinates			
Element	X	Y	Z
C	-1.081887	-0.519726	0.342427
C	-0.246320	0.235044	-0.653589
C	1.162668	0.378319	-0.154038
C	1.697372	1.504820	0.256111
H	-1.141580	-0.063390	1.344490
H	-0.277593	-0.297550	-1.600907
H	-0.692439	1.220613	-0.786468
H	1.751905	-0.530986	-0.122096
H	3.080954	1.411326	0.720414
H	1.298009	2.506510	0.303360
O	-1.647136	-1.549008	0.104081
H	3.882699	1.304807	0.978943
Vibrational Frequencies			
-1020.83	3176.42	3112.04	3086.48
3015.44	2911.26	2208.93	1838.55
1658.82	1434.52	1391.80	1286.81
1258.55	1199.32	1097.91	1088.12
1062.58	953.62	929.90	923.61
919.07	809.18	699.24	496.25
396.90	336.93	225.07	179.17
80.96	55.40		
Energy MPWB1K/6-31+G(d,p) (a.u.): -231.5790817			

Table S29: Cartesian coordinates (em Å) and non-scaled vibrational frequencies (in cm^{-1}) for the TS4-G+A+

Cartesian Coordinates			
Element	X	Y	Z
C	-0.581261	-0.692841	-0.941534
C	-0.543590	-0.164313	0.462647
C	0.861170	-0.029908	0.969756
C	1.405055	1.101173	1.351937
H	0.085741	-1.547291	-1.148004
H	-1.086718	0.774846	0.498363
H	-1.077816	-0.888078	1.085165
H	1.451029	-0.939455	1.012193
H	2.790493	1.004100	1.809872
H	1.009011	2.104083	1.392225
O	-1.282546	-0.248843	-1.805520
H	3.593064	0.891730	2.063109
Vibrational Frequencies			
-1016.93	3181.58	3102.44	3091.78
2986.10	2901.30	2212.55	1840.45
1668.42	1425.01	1402.40	1296.49
1249.16	1189.05	1109.23	1089.73
1043.91	995.99	933.47	920.82
902.60	752.25	681.15	511.59
408.12	315.60	222.49	171.05
103.10	57.58		
Energy MPWB1K/6-31+G(d,p) (a.u.): -231.5786816			

Table S30: Cartesian coordinates (em Å) and non-scaled vibrational frequencies (in cm^{-1}) for the TS4-TC

Cartesian Coordinates			
Element	X	Y	Z
C	-1.297857	0.194263	-0.412812
C	-0.413948	-1.006908	-0.340678
C	0.982487	-0.851577	0.174738
C	1.576785	0.240862	0.594783
H	-2.307435	-0.018361	-0.805057
H	-0.950339	-1.752353	0.254174
H	-0.394694	-1.439535	-1.345525
H	1.548891	-1.777296	0.190455
H	2.943774	0.027980	1.027969
H	1.246890	1.261036	0.679686
O	-1.003147	1.311175	-0.092042
H	3.742930	-0.163061	1.268193
Vibrational Frequencies			
-1052.97	3237.12	3087.21	3005.77
2977.52	2893.85	2142.48	1842.51
1671.14	1410.65	1396.88	1377.05
1275.92	1216.60	1118.07	1036.77
1009.31	969.01	951.06	932.86
832.99	773.99	757.73	587.41
421.66	257.77	219.73	214.35
122.59	88.34		
Energy MPWB1K/6-31+G(d,p) (a.u.): -231.5782805			

Table S31: Cartesian coordinates (em Å) and non-scaled vibrational frequencies (in cm^{-1}) for the TS4-G+C+

Cartesian Coordinates			
Element	X	Y	Z
C	-0.834697	0.390366	-0.641406
C	-0.244156	-0.903804	-0.174575
C	1.166931	-0.762306	0.320843
C	1.716350	0.359829	0.724795
H	-0.217280	0.956036	-1.359246
H	-0.889439	-1.334083	0.588788
H	-0.251318	-1.587203	-1.027337
H	1.755687	-1.671606	0.348611
H	3.100247	0.237793	1.179781
H	1.335064	1.366765	0.799733
O	-1.903942	0.808472	-0.296058
H	3.898959	0.106907	1.433831
Vibrational Frequencies			
-1009.83	3178.11	3110.85	3067.84
2994.64	2909.55	2222.40	1840.98
1659.77	1421.32	1396.12	1310.84
1262.31	1192.70	1092.77	1073.14
1036.98	972.84	931.12	917.38
910.13	767.37	643.12	537.01
457.58	277.26	215.74	189.61
107.22	59.89		
Energy MPWB1K/6-31+G(d,p) (a.u.): -231.5779270			

Table S32: Cartesian coordinates (em Å) and non-scaled vibrational frequencies (in cm^{-1}) for the TS5-T−A+

Cartesian Coordinates			
Element	X	Y	Z
C	-0.851757	-0.687369	-0.957943
C	-0.803033	0.199236	0.248469
C	0.550468	0.291476	0.865819
C	1.111962	1.400238	1.285622
H	-1.821981	-0.711474	-1.481323
H	-1.193254	1.180230	-0.021008
H	-1.525765	-0.217150	0.957842
H	1.093900	-0.644726	0.955441
H	2.071507	1.568673	1.746902
H	0.359937	2.639468	1.100053
O	0.064664	-1.354311	-1.348446
H	-0.101584	3.348047	0.973660
Vibrational Frequencies			
-1048.36	3192.49	3082.84	3051.58
2979.19	2907.99	2146.47	1839.25
1680.34	1412.95	1394.02	1337.74
1241.47	1199.90	1130.31	1093.75
1016.45	947.41	938.08	892.38
856.25	737.40	705.76	577.84
447.48	264.71	246.26	176.95
144.49	47.62		
Energy MPWB1K/6-31+G(d,p) (a.u.): -231.5800902			

Table S33: Cartesian coordinates (em Å) and non-scaled vibrational frequencies (in cm^{-1}) for the TS5-G+A−

Cartesian Coordinates			
Element	X	Y	Z
C	-1.068713	-0.529475	0.200538
C	-0.078057	0.186735	-0.674602
C	1.237027	0.325225	0.027925
C	1.713592	1.436997	0.538708
H	-1.271371	-0.044464	1.169806
H	0.022619	-0.369483	-1.602703
H	-0.480192	1.175789	-0.892839
H	1.817343	-0.588062	0.135470
H	2.633631	1.627158	1.067311
H	0.923956	2.650442	0.340496
O	-1.611212	-1.556147	-0.095619
H	0.446998	3.344266	0.197792
Vibrational Frequencies			
-1047.84	3193.87	3094.99	3061.98
3020.72	2911.79	2151.92	1837.74
1664.00	1433.07	1391.10	1282.14
1250.97	1200.25	1122.23	1083.36
1063.75	945.15	944.00	912.24
908.08	804.61	664.42	495.78
437.75	347.99	234.95	202.96
65.01	56.68		
Energy MPWB1K/6-31+G(d,p) (a.u.): -231.5794746			

Table S34: Cartesian coordinates (em Å) and non-scaled vibrational frequencies (in cm^{-1}) for the TS5-G+A+

Cartesian Coordinates			
Element	X	Y	Z
C	-0.386833	-0.733214	-0.985371
C	-0.524644	-0.173907	0.400926
C	0.796798	-0.034052	1.085372
C	1.295504	1.087030	1.551128
H	0.349711	-1.547300	-1.101359
H	-1.063512	0.766767	0.350711
H	-1.142723	-0.884937	0.957370
H	1.381652	-0.945593	1.194275
H	2.227898	1.280142	2.056353
H	0.490722	2.297975	1.388369
O	-1.027546	-0.358755	-1.925652
H	0.004268	2.989951	1.282310
Vibrational Frequencies			
-1042.67	3193.11	3102.86	3050.04
2984.40	2894.77	2165.64	1842.87
1674.79	1422.52	1405.34	1293.71
1240.62	1188.58	1133.38	1087.72
1048.31	1000.90	940.35	901.66
887.97	740.36	641.85	517.71
446.50	85.11	252.75	202.82
85.11	57.59		
Energy MPWB1K/6-31+G(d,p) (a.u.): -231.5785707			

Table S35: Cartesian coordinates (em Å) and non-scaled vibrational frequencies (in cm^{-1}) for the TS5-G+C+

Cartesian Coordinates			
Element	X	Y	Z
C	-0.614564	0.315179	-0.812315
C	-0.188461	-0.892176	-0.029262
C	1.114759	-0.745831	0.691611
C	1.637245	0.374873	1.136123
H	0.197892	0.864475	-1.315174
H	-0.993930	-1.170271	0.648231
H	-0.102908	-1.705723	-0.753566
H	1.668888	-1.664896	0.862922
H	2.560971	0.539924	1.666877
H	0.892834	1.622370	1.013595
O	-1.756341	0.658543	-0.934410
H	0.444503	2.349708	0.964873
Vibrational Frequencies			
-1065.60	3191.23	3066.59	3062.29
2998.01	2922.83	2128.35	1839.27
1665.95	1415.99	1399.85	1313.98
1258.79	1199.71	1152.10	1073.73
1046.06	986.64	954.12	954.12
894.50	729.46	611.28	578.24
457.68	331.93	288.03	232.62
108.87	69.04		
Energy MPWB1K/6-31+G(d,p) (a.u.): -231.5777716			

Table S36: Cartesian coordinates (em Å) and non-scaled vibrational frequencies (in cm^{-1}) for the $H_2C{=}CHCH_2\dot{C}O$

Cartesian Coordinates			
Element	X	Y	Z
C	-1.058330	1.152752	1.094796
C	-0.698353	0.108616	2.126455
C	0.471777	0.485915	2.968529
C	0.441268	0.528961	4.290910
H	-1.581041	-0.107030	2.722405
H	-0.498817	-0.788887	1.536113
H	1.375228	0.751191	2.436819
H	1.311316	0.810307	4.863179
H	-0.453324	0.283074	4.845419
O	-0.390151	2.023172	0.676416
Vibrational Frequencies			
3328.42	3263.34	3231.53	3196.10
3115.22	2023.23	1775.89	1492.53
1458.01	1349.34	1311.07	1240.86
1137.12	1047.28	991.12	980.32
877.08	851.77	720.21	548.50
407.77	204.21	142.76	73.52
Energy MPWB1K/6-31+G(d,p) (a.u.): -230.4624898			

Table S37: Cartesian coordinates (em Å) and non-scaled vibrational frequencies (in cm^{-1}) for the $H_2C{=}CH\dot{C}HCOH$

Cartesian Coordinates			
Element	X	Y	Z
C	-0.489077	0.743249	0.518634
C	-0.078528	-0.479258	1.157526
C	1.131096	-0.572915	1.848287
C	1.557979	-1.706316	2.465820
H	-1.456718	0.720642	-0.000832
H	-0.733038	-1.337320	1.092430
H	1.739994	0.320362	1.876574
H	2.499045	-1.740866	2.990226
H	0.965095	-2.608842	2.449403
O	0.171631	1.765739	0.531291
Vibrational Frequencies			
3344.16	3270.04	3262.06	3238.44
3061.73	1747.77	1583.04	1516.69
1453.00	1388.02	1317.01	1238.48
1085.65	1055.50	1027.70	951.67
927.81	782.23	763.17	606.16
399.37	264.54	209.41	179.41
Energy MPWB1K/6-31+G(d,p) (a.u.): -230.4804561			

Table S38: Cartesian coordinates (em Å) and non-scaled vibrational frequencies (in cm^{-1}) for the $H_2C{=}\dot{C}CH_2COH + H_2$

Cartesian Coordinates			
Element	X	Y	Z
C	-0.961866	1.139431	1.425525
C	-0.054584	-0.063838	1.490318
C	1.300182	0.161871	1.986666
C	2.073881	1.112354	2.432457
H	-1.973050	0.914142	1.043826
H	-0.571542	-0.811804	2.097693
H	-0.033749	-0.493145	0.484900
H	3.094042	0.916686	2.733975
H	1.712142	2.133017	2.513497
O	-0.666296	2.253728	1.744249
Vibrational Frequencies			
3271.10	3171.56	3127.58	3093.88
2997.68	1910.74	1821.04	1462.07
1445.08	1428.99	1354.54	1255.59
1065.18	1034.30	1004.74	943.11
865.66	741.28	733.15	459.60
353.44	190.51	155.38	123.22
Energy MPWB1K/6-31+G(d,p) (a.u.): -230.4308316			

Table S39: Cartesian coordinates (em Å) and non-scaled vibrational frequencies (in cm^{-1}) for the trans-H$\dot{C}$=CHCH$_2$COH

Cartesian Coordinates			
Element	X	Y	Z
C	-0.250583	-0.915876	0.342167
C	-0.099655	-0.014519	1.529818
C	1.318534	0.124880	1.995226
C	1.867012	1.249785	2.363636
H	-1.268007	-0.963532	-0.081118
H	-0.551511	0.948936	1.295804
H	-0.723250	-0.446670	2.319182
H	1.899133	-0.790221	2.006714
H	1.585748	2.285786	2.445088
O	0.634269	-1.570951	-0.130784
Vibrational Frequencies			
3327.86	3229.42	3162.69	3090.82
3013.26	1909.46	1742.40	1464.82
1444.57	1380.22	1292.73	1238.93
1116.29	1052.02	951.17	902.34
849.39	763.28	723.68	619.51
375.19	232.84	148.27	77.90
Energy MPWB1K/6-31+G(d,p) (a.u.): -230.4242626			

Table S40: Cartesian coordinates (em Å) and non-scaled vibrational frequencies (in cm^{-1}) for the cis-H$\dot{C}$=CHCH$_2$COH

Cartesian Coordinates			
Element	X	Y	Z
C	-0.092208	-0.920267	0.395308
C	0.100096	-0.034123	1.586984
C	1.517717	0.038862	2.048527
C	2.114761	1.125946	2.452942
H	-1.110737	-0.922679	-0.027146
H	-0.301729	0.953068	1.362857
H	-0.544426	-0.440988	2.373099
H	2.070531	-0.898428	2.023034
H	3.088215	1.399487	2.819189
O	0.763536	-1.610620	-0.082656
Vibrational Frequencies			
3342.23	3172.09	3165.32	3090.29
3018.34	1907.35	1753.14	1465.42
1446.69	1387.01	1284.10	1237.07
1136.45	1055.08	952.04	866.10
814.20	750.68	732.38	594.49
399.51	229.90	152.43	78.34
Energy MPWB1K/6-31+G(d,p) (a.u.): -230.4255248			

Table S41: 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 S42: 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			

Table S43: Forward classical barriers ($V^{\ddagger}$), vibrationally adiabatic ground-state barriers ($V_{\mathrm{a}}^{G,\ddagger}$), electronic energy ($\Delta E$), and enthalpy of reaction at 0 K (ΔH_0^0). All values are in kcal/mol.

Reaction	$V^{\ddagger}$	$V_{\mathrm{a}}^{G,\ddagger}$	ΔE	ΔH_0^0
(R1)	4.86	3.36	-13.22	-14.62
(R2)	5.70	4.38	-24.49	-26.02
(R3)	14.51	12.91	6.65	4.20
(R4)	16.90	15.32	10.77	8.46
(R5)	16.46	14.77	9.98	7.56

Table S44: Harmonic ($Q_{\mathrm{T}}^{\mathrm{MS\text{-}HO}}$) and anharmonic ($Q_{\mathrm{T}}^{\mathrm{MS\text{-}T(C)}}$ and $Q_{\mathrm{T}}^{\mathrm{E2DT}}$) total partition functions for the 3-butenal.

T(K)	$Q_{\mathrm{T}}^{\mathrm{MS\text{-}HO}}$	$Q_{\mathrm{T}}^{\mathrm{MS\text{-}T(C)}}$	$Q_{\mathrm{T}}^{\mathrm{E2DT}}$
200.00	5.356E+07	4.629E+07	6.224E+07
300.00	6.315E+08	5.859E+08	7.467E+08
400.00	4.969E+09	4.754E+09	5.848E+09
500.00	3.188E+10	3.054E+10	3.679E+10
600.00	1.799E+11	1.693E+11	2.014E+11
700.00	9.204E+11	8.421E+11	9.948E+11
800.00	4.340E+12	3.838E+12	4.513E+12
900.00	1.908E+13	1.624E+13	1.904E+13
1000.00	7.868E+13	6.434E+13	7.532E+13
1100.00	3.059E+14	2.404E+14	2.812E+14
1200.00	1.128E+15	8.513E+14	9.955E+14
1300.00	3.957E+15	2.870E+15	3.355E+15
1400.00	1.325E+16	9.245E+15	1.080E+16
1500.00	4.254E+16	2.855E+16	3.336E+16
2000.00	8.310E+18	4.665E+18	5.458E+18
2500.00	7.675E+20	3.687E+20	4.320E+20

[a] MS-OH (ZPE): 55.564 kcal/mol

[b] E2DT (ZPE): 55.563 kcal/mol

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

Table S45: Harmonic ($Q_{\mathrm{T}}^{\mathrm{MS\text{-}HO}}$) and anharmonic ($Q_{\mathrm{T}}^{\mathrm{MS\text{-}T(C)}}$ and $Q_{\mathrm{T}}^{\mathrm{E2DT}}$) total partition functions for the transition state of CRC1.

T(K)	$Q_{\mathrm{T}}^{\mathrm{MS\text{-}HO}}$	$Q_{\mathrm{T}}^{\mathrm{MS\text{-}T(C)}}$	$Q_{\mathrm{T}}^{\mathrm{E2DT}}$
200.00	1.435E+08	1.372E+08	1.550E+08
300.00	2.622E+09	2.625E+09	2.915E+09
400.00	3.050E+10	3.080E+10	3.368E+10
500.00	2.758E+11	2.741E+11	2.966E+11
600.00	2.109E+12	2.034E+12	2.187E+12
700.00	1.421E+13	1.317E+13	1.412E+13
800.00	8.597E+13	7.643E+13	8.167E+13
900.00	4.747E+14	4.036E+14	4.307E+14
1000.00	2.415E+15	1.962E+15	2.092E+15
1100.00	1.140E+16	8.857E+15	9.435E+15
1200.00	5.032E+16	3.740E+16	3.985E+16
1300.00	2.089E+17	1.486E+17	1.582E+17
1400.00	8.187E+17	5.584E+17	5.948E+17
1500.00	3.042E+18	1.993E+18	2.122E+18
2000.00	1.105E+21	5.998E+20	6.385E+20
2500.00	1.656E+23	7.650E+22	8.143E+22

[a] MS-OH (ZPE): 54.064 kcal/mol

[b] E2DT (ZPE): 54.065 kcal/mol

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

Table S46: Harmonic ($Q_{\mathrm{T}}^{\mathrm{MS\text{-}HO}}$) and anharmonic ($Q_{\mathrm{T}}^{\mathrm{MS\text{-}T(C)}}$ and $Q_{\mathrm{T}}^{\mathrm{E2DT}}$) total partition functions for the transition state of CRC2.

T(K)	$Q_{\mathrm{T}}^{\mathrm{MS\text{-}HO}}$	$Q_{\mathrm{T}}^{\mathrm{MS\text{-}T(C)}}$	$Q_{\mathrm{T}}^{\mathrm{E2DT}}$
200.00	3.926E+07	3.614E+07	1.848E+07
300.00	6.024E+08	5.748E+08	3.809E+08
400.00	6.549E+09	6.494E+09	4.953E+09
500.00	5.796E+10	5.952E+10	4.945E+10
600.00	4.423E+11	4.665E+11	4.106E+11
700.00	2.996E+12	3.215E+12	2.953E+12
800.00	1.829E+13	1.982E+13	1.881E+13
900.00	1.019E+14	1.108E+14	1.080E+14
1000.00	5.231E+14	5.678E+14	5.658E+14
1100.00	2.493E+15	2.689E+15	2.732E+15
1200.00	1.110E+16	1.185E+16	1.225E+16
1300.00	4.642E+16	4.898E+16	5.138E+16
1400.00	1.834E+17	1.907E+17	2.028E+17
1500.00	6.859E+17	7.027E+17	7.559E+17
2000.00	2.559E+20	2.394E+20	2.696E+20
2500.00	3.907E+22	3.320E+22	3.852E+22

[a] MS-OH (ZPE): 54.236 kcal/mol

[b] E2DT (ZPE): 53.901 kcal/mol

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

Table S47: Harmonic ($Q_{\mathrm{T}}^{\mathrm{MS\text{-}HO}}$) and anharmonic ($Q_{\mathrm{T}}^{\mathrm{MS\text{-}T(C)}}$ and $Q_{\mathrm{T}}^{\mathrm{E2DT}}$) total partition functions for the transition state of CRC3.

T(K)	$Q_{\mathrm{T}}^{\mathrm{MS\text{-}HO}}$	$Q_{\mathrm{T}}^{\mathrm{MS\text{-}T(C)}}$	$Q_{\mathrm{T}}^{\mathrm{E2DT}}$
200.00	4.410E+08	4.002E+08	5.595E+08
300.00	6.880E+09	6.549E+09	8.168E+09
400.00	7.203E+10	6.837E+10	8.073E+10
500.00	6.064E+11	5.598E+11	6.422E+11
600.00	4.403E+12	3.905E+12	4.405E+12
700.00	2.849E+13	2.412E+13	2.695E+13
800.00	1.670E+14	1.347E+14	1.495E+14
900.00	8.980E+14	6.895E+14	7.624E+14
1000.00	4.468E+15	3.267E+15	3.602E+15
1100.00	2.071E+16	1.444E+16	1.589E+16
1200.00	9.003E+16	5.987E+16	6.579E+16
1300.00	3.687E+17	2.342E+17	2.572E+17
1400.00	1.429E+18	8.684E+17	9.532E+17
1500.00	5.255E+18	3.063E+18	3.358E+18
2000.00	1.842E+21	8.854E+20	9.700E+20
2500.00	2.704E+23	1.103E+23	1.208E+23

[a] MS-OH (ZPE): 53.851 kcal/mol

[b] E2DT (ZPE): 53.896 kcal/mol

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

Table S48: Harmonic ($Q_{\mathrm{T}}^{\mathrm{MS\text{-}HO}}$) and anharmonic ($Q_{\mathrm{T}}^{\mathrm{MS\text{-}T(C)}}$ and $Q_{\mathrm{T}}^{\mathrm{E2DT}}$) total partition functions for the transition state of CRC4.

T(K)	$Q_{\mathrm{T}}^{\mathrm{MS\text{-}HO}}$	$Q_{\mathrm{T}}^{\mathrm{MS\text{-}T(C)}}$	$Q_{\mathrm{T}}^{\mathrm{E2DT}}$
200.00	2.082E+08	1.881E+08	2.299E+08
300.00	3.858E+09	3.699E+09	4.378E+09
400.00	4.481E+10	4.373E+10	5.079E+10
500.00	4.039E+11	3.906E+11	4.494E+11
600.00	3.080E+12	2.903E+12	3.323E+12
700.00	2.066E+13	1.880E+13	2.149E+13
800.00	1.245E+14	1.089E+14	1.244E+14
900.00	6.840E+14	5.735E+14	6.556E+14
1000.00	3.462E+15	2.780E+15	3.181E+15
1100.00	1.628E+16	1.251E+16	1.434E+16
1200.00	7.153E+16	5.268E+16	6.044E+16
1300.00	2.957E+17	2.087E+17	2.398E+17
1400.00	1.155E+18	7.821E+17	9.000E+17
1500.00	4.278E+18	2.784E+18	3.207E+18
2000.00	1.533E+21	8.294E+20	9.605E+20
2500.00	2.278E+23	1.051E+23	1.221E+23

[a] MS-OH (ZPE): 53.985 kcal/mol

[b] E2DT (ZPE): 53.983 kcal/mol

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

Table S49: Harmonic ($Q_{\mathrm{T}}^{\mathrm{MS\text{-}HO}}$) and anharmonic ($Q_{\mathrm{T}}^{\mathrm{MS\text{-}T(C)}}$ and $Q_{\mathrm{T}}^{\mathrm{E2DT}}$) total partition functions for the transition state of CRC5.

T(K)	$Q_{\mathrm{T}}^{\mathrm{MS\text{-}HO}}$	$Q_{\mathrm{T}}^{\mathrm{MS\text{-}T(C)}}$	$Q_{\mathrm{T}}^{\mathrm{E2DT}}$
200.00	1.585E+08	1.459E+08	1.530E+08
300.00	2.825E+09	2.720E+09	2.832E+09
400.00	3.272E+10	3.192E+10	3.304E+10
500.00	2.969E+11	2.867E+11	2.966E+11
600.00	2.282E+12	2.150E+12	2.231E+12
700.00	1.544E+13	1.406E+13	1.468E+13
800.00	9.375E+13	8.219E+13	8.627E+13
900.00	5.185E+14	4.368E+14	4.614E+14
1000.00	2.640E+15	2.135E+15	2.268E+15
1100.00	1.249E+16	9.685E+15	1.034E+16
1200.00	5.513E+16	4.108E+16	4.404E+16
1300.00	2.289E+17	1.638E+17	1.764E+17
1400.00	8.976E+17	6.178E+17	6.677E+17
1500.00	3.337E+18	2.212E+18	2.397E+18
2000.00	1.213E+21	6.751E+20	7.406E+20
2500.00	1.818E+23	8.703E+22	9.615E+22

[a] MS-OH (ZPE): 53.880 kcal/mol

[b] E2DT (ZPE): 53.897 kcal/mol

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

Table S50: Anharmonic factor ($F^{\text{MS-T(C),Y}}$) for 3-Butenal and transition states of each CRC, and the multiplicative coefficient ($F^{\text{X}}_{\text{anh}}$) to account the torsional anharmonicity in the reactions (R1)–(R5)

T(K)	$F^{\text{MS-T(C),Y}}$						$F^{\text{MS-T(C)}}_{\text{anh}}$				
	3-butenal	CRC1	CRC2,6	CRC3	CRC4	CRC5	(R1)	(R2)	(R3)	(R4)	(R5)
200	0.856	0.957	0.921	0.906	0.902	0.939	1.118	1.076	1.059	1.054	1.097
300	0.920	1.002	0.955	0.949	0.957	0.979	1.090	1.038	1.032	1.041	1.064
400	0.949	1.010	0.993	0.947	0.976	0.991	1.064	1.046	0.997	1.028	1.044
500	0.950	0.994	1.028	0.920	0.967	0.980	1.046	1.082	0.968	1.017	1.032
600	0.934	0.964	1.056	0.884	0.942	0.956	1.032	1.130	0.946	1.009	1.023
700	0.908	0.928	1.075	0.844	0.910	0.924	1.021	1.183	0.929	1.002	1.018
800	0.878	0.889	1.086	0.804	0.875	0.890	1.013	1.237	0.916	0.996	1.014
900	0.845	0.850	1.090	0.765	0.839	0.855	1.006	1.289	0.905	0.992	1.011
1000	0.813	0.813	1.088	0.729	0.803	0.821	1.000	1.339	0.897	0.988	1.010
1100	0.781	0.777	1.081	0.694	0.769	0.788	0.995	1.385	0.889	0.985	1.009
1200	0.750	0.743	1.071	0.662	0.737	0.756	0.991	1.428	0.883	0.983	1.009
1300	0.721	0.712	1.058	0.633	0.706	0.727	0.988	1.468	0.878	0.980	1.009
1400	0.693	0.682	1.043	0.606	0.678	0.699	0.985	1.505	0.874	0.978	1.009
1500	0.667	0.655	1.027	0.581	0.651	0.673	0.982	1.540	0.871	0.976	1.010
2000	0.558	0.543	0.938	0.479	0.541	0.566	0.973	1.682	0.858	0.970	1.014
2500	0.478	0.462	0.852	0.406	0.462	0.486	0.967	1.784	0.851	0.967	1.018

Table S51: Recrossing ($\Gamma_j^{\mathrm{CVT}}(T)$) coefficient for the individual paths of CRC1.

T(K)	Path 1	Path 2	Path 3	Path 4	Path 5
200.00	9.9069E-01	9.8834E-01	8.1264E-01	9.9192E-01	5.3518E-01
300.00	9.9507E-01	9.9365E-01	9.5580E-01	9.9455E-01	7.1427E-01
400.00	9.9683E-01	9.9590E-01	9.8182E-01	9.9588E-01	8.0111E-01
500.00	9.9770E-01	9.9703E-01	9.8515E-01	9.9665E-01	8.2903E-01
600.00	9.9819E-01	9.9768E-01	9.8709E-01	9.9713E-01	8.3854E-01
700.00	9.9849E-01	9.9808E-01	9.8831E-01	9.9745E-01	3.5419E-01
800.00	9.9869E-01	9.9835E-01	9.8911E-01	9.9767E-01	3.3512E-01
900.00	9.9882E-01	9.9853E-01	9.8966E-01	9.9783E-01	3.2110E-01
1000.00	9.9893E-01	9.9867E-01	9.9006E-01	9.9796E-01	3.1041E-01
1100.00	9.9900E-01	9.9877E-01	9.9035E-01	9.9805E-01	3.0203E-01
1200.00	9.9906E-01	9.9885E-01	9.9057E-01	9.9813E-01	2.9531E-01
1300.00	9.9911E-01	9.9891E-01	9.9074E-01	9.9819E-01	2.8982E-01
1400.00	9.9915E-01	9.9897E-01	9.9087E-01	9.9824E-01	2.8528E-01
1500.00	9.9918E-01	9.9901E-01	9.9098E-01	9.9829E-01	2.8148E-01
1600.00	9.9921E-01	9.9904E-01	9.9106E-01	9.9832E-01	2.7825E-01
1700.00	9.9923E-01	9.9907E-01	9.9112E-01	9.9835E-01	2.7549E-01
1800.00	9.9925E-01	9.9910E-01	9.9118E-01	9.9838E-01	2.7311E-01
1900.00	9.9927E-01	9.9912E-01	9.9122E-01	9.9841E-01	2.7105E-01
2000.00	9.9929E-01	9.9914E-01	9.9126E-01	9.9843E-01	2.6925E-01
2500.00	9.9934E-01	9.9921E-01	9.7546E-01	9.9851E-01	2.6300E-01

Table S52: Tunneling ($\kappa_j^{\mathrm{CVT/SCT}}(T)$) coefficient for the individual paths of CRC1.

T(K)	Path 1	Path 2	Path 3	Path 4	Path 5
200	8.258	9.100	27.530	11.240	7.359
300	2.522	2.650	5.148	2.905	2.409
400	1.678	1.730	2.663	1.820	1.640
500	1.392	1.421	1.915	1.467	1.373
600	1.258	1.276	1.586	1.305	1.246
700	1.183	1.196	1.411	1.216	1.176
800	1.137	1.147	1.305	1.161	1.132
900	1.107	1.115	1.236	1.126	1.103
1000	1.086	1.092	1.188	1.101	1.083
1100	1.070	1.075	1.154	1.082	1.068
1200	1.059	1.063	1.128	1.069	1.057
1300	1.050	1.053	1.108	1.058	1.048
1400	1.043	1.046	1.093	1.050	1.041
1500	1.037	1.040	1.081	1.043	1.036
2000	1.021	1.022	1.045	1.024	1.020
2500	1.013	1.014	1.029	1.015	1.013

Table S53: Recrossing ($\Gamma_j^{\mathrm{CVT}}(T)$) coefficient for the individual paths of CRC2 and CRC6..

T(K)	Path 1	Path 2	Path 3	Path 4	Path 5
200.00	8.7170E-01	7.3261E-01	9.9479E-01	6.8977E-01	9.6615E-01
300.00	9.5194E-01	9.6965E-01	9.9951E-01	8.8379E-01	9.8562E-01
400.00	9.7536E-01	9.9298E-01	9.9445E-01	9.6373E-01	9.9332E-01
500.00	9.8743E-01	9.9932E-01	9.8853E-01	9.9816E-01	9.9671E-01
600.00	9.9386E-01	9.9961E-01	9.8342E-01	9.2303E-01	9.9831E-01
700.00	9.9731E-01	9.9622E-01	9.7931E-01	8.8937E-01	9.9911E-01
800.00	9.9910E-01	9.9155E-01	9.7605E-01	8.6246E-01	9.9953E-01
900.00	9.9987E-01	9.8669E-01	9.7345E-01	8.4070E-01	9.9976E-01
1000.00	9.9994E-01	9.8200E-01	9.7136E-01	8.2282E-01	9.9988E-01
1100.00	9.9912E-01	9.7758E-01	9.6965E-01	8.0789E-01	9.9995E-01
1200.00	9.9743E-01	9.7343E-01	9.6824E-01	7.9502E-01	9.9998E-01
1300.00	9.9502E-01	9.6949E-01	9.6707E-01	7.8369E-01	1.0000E+00
1400.00	9.9203E-01	9.6572E-01	9.6607E-01	7.7360E-01	1.0000E+00
1500.00	9.8859E-01	9.6204E-01	9.6522E-01	7.6451E-01	1.0000E+00
1600.00	9.8485E-01	9.5836E-01	9.6449E-01	7.5624E-01	9.9999E-01
1700.00	9.8090E-01	9.5452E-01	9.4333E-01	7.4864E-01	9.9998E-01
1800.00	9.7683E-01	9.4766E-01	8.9761E-01	7.4161E-01	9.9997E-01
1900.00	9.7271E-01	9.3859E-01	8.5763E-01	7.3505E-01	9.9996E-01
2000.00	9.6859E-01	9.2950E-01	8.2246E-01	7.2888E-01	9.9994E-01
2500.00	9.4742E-01	8.8896E-01	6.9616E-01	6.9149E-01	9.9989E-01

Table S54: Tunneling ($\kappa_j^{\mathrm{CVT/SCT}}(T)$) coefficient for the individual paths of CRC2 and CRC6.

T(K)	Path 1	Path 2	Path 3	Path 4	Path 5
200	20.910	17.530	26.390	23.200	31.690
300	3.826	3.529	4.175	3.961	4.437
400	2.125	2.031	2.228	2.165	2.288
500	1.620	1.574	1.669	1.639	1.693
600	1.398	1.370	1.427	1.410	1.440
700	1.279	1.260	1.298	1.287	1.306
800	1.208	1.194	1.221	1.213	1.227
900	1.161	1.150	1.171	1.165	1.175
1000	1.128	1.120	1.137	1.132	1.139
1100	1.105	1.098	1.112	1.108	1.114
1200	1.088	1.082	1.093	1.090	1.095
1300	1.074	1.069	1.079	1.076	1.080
1400	1.064	1.060	1.067	1.065	1.069
1500	1.055	1.052	1.059	1.057	1.060
2000	1.031	1.029	1.033	1.031	1.033
2500	1.020	1.018	1.021	1.020	1.021

Table S55: Recrossing ($\Gamma_j^{\mathrm{CVT}}(T)$) coefficient for the individual paths of CRC3.

T(K)	Path 1	Path 2	Path 3	Path 4	Path 5
200.00	2.5226E-01	7.7510E-01	1.4873E-01	3.4956E-01	4.2580E-01
300.00	2.9354E-01	9.5021E-01	2.5220E-01	9.9704E-01	6.0397E-01
400.00	9.9907E-01	9.8553E-01	3.2735E-01	9.8566E-01	7.2707E-01
500.00	9.9422E-01	9.9715E-01	3.8152E-01	9.7309E-01	8.1551E-01
600.00	9.8839E-01	9.9994E-01	4.2100E-01	9.6180E-01	8.7981E-01
700.00	9.8292E-01	9.9908E-01	4.5010E-01	9.5232E-01	9.2619E-01
800.00	9.7818E-01	9.9637E-01	4.7181E-01	9.4455E-01	9.4796E-01
900.00	9.7420E-01	9.9301E-01	4.8817E-01	9.3823E-01	9.6021E-01
1000.00	9.7089E-01	9.8958E-01	5.0066E-01	9.3307E-01	9.6829E-01
1100.00	9.6814E-01	9.8630E-01	5.1028E-01	9.2884E-01	9.7386E-01
1200.00	9.6585E-01	9.8327E-01	5.1778E-01	9.2533E-01	9.7785E-01
1300.00	9.6392E-01	9.8052E-01	5.2368E-01	9.2241E-01	9.8080E-01
1400.00	9.6230E-01	9.7803E-01	5.2836E-01	9.1995E-01	9.8304E-01
1500.00	9.6091E-01	9.7577E-01	5.3211E-01	9.1786E-01	9.8477E-01
1600.00	9.5973E-01	9.7373E-01	5.3514E-01	9.1607E-01	9.8614E-01
1700.00	9.5870E-01	9.6544E-01	5.3760E-01	9.1453E-01	9.8724E-01
1800.00	9.5782E-01	9.5421E-01	5.3960E-01	9.1319E-01	9.8813E-01
1900.00	9.5704E-01	9.4415E-01	5.4125E-01	9.1202E-01	9.8887E-01
2000.00	9.5636E-01	9.3509E-01	5.4260E-01	9.1099E-01	9.8949E-01
2500.00	9.5392E-01	9.0078E-01	5.4659E-01	9.0730E-01	9.9146E-01

Table S56: Tunneling ($\kappa_j^{\mathrm{CVT/SCT}}(T)$) coefficient for the individual paths of CRC3.

T(K)	Path 1	Path 2	Path 3	Path 4	Path 5
200	55,280	41,000	43,740	41,610	31,360
300	4,850	4,202	4,322	4,264	3,773
400	2,332	2,155	2,190	2,176	2,035
500	1,699	1,617	1,634	1,627	1,560
600	1,439	1,391	1,401	1,397	1,357
700	1,304	1,272	1,279	1,276	1,249
800	1,224	1,201	1,206	1,204	1,185
900	1,173	1,155	1,159	1,158	1,143
1000	1,138	1,124	1,127	1,126	1,114
1100	1,112	1,101	1,104	1,103	1,093
1200	1,093	1,084	1,086	1,085	1,078
1300	1,079	1,071	1,073	1,072	1,066
1400	1,068	1,061	1,063	1,062	1,056
1500	1,059	1,053	1,054	1,054	1,049
2000	1,033	1,029	1,030	1,030	1,027
2500	1,021	1,019	1,019	1,019	1,017

Table S57: Recrossing ($\Gamma_j^{\mathrm{CVT}}(T)$) coefficient for the individual paths of CRC4.

T(K)	Path 1	Path 2	Path 3	Path 4	Path 5
400.00	9.7636E-01	6.6995E-01	3.0280E-01	5.8786E-01	2.3251E-01
500.00	9.9327E-01	7.6799E-01	2.9788E-01	6.5676E-01	2.2701E-01
600.00	9.9894E-01	8.3841E-01	2.9525E-01	7.0774E-01	2.2381E-01
700.00	9.9999E-01	8.8892E-01	2.9392E-01	7.4609E-01	2.2194E-01
800.00	9.9902E-01	9.2196E-01	2.9338E-01	7.7528E-01	2.2088E-01
900.00	9.9717E-01	9.4280E-01	2.9333E-01	7.9774E-01	2.2036E-01
1000.00	9.9503E-01	9.5637E-01	2.9360E-01	8.1521E-01	2.2019E-01
1100.00	9.9289E-01	9.6555E-01	2.9408E-01	8.2895E-01	2.2025E-01
1200.00	9.9088E-01	9.7198E-01	2.9469E-01	8.3987E-01	2.2048E-01
1300.00	9.8903E-01	9.7663E-01	2.9539E-01	8.4867E-01	2.2082E-01
1400.00	9.8737E-01	9.8008E-01	2.9614E-01	8.5582E-01	2.2123E-01
1500.00	9.8589E-01	9.8270E-01	2.9692E-01	8.6168E-01	2.2169E-01
1600.00	9.8457E-01	9.8474E-01	2.9772E-01	8.6654E-01	2.2219E-01
1700.00	9.8340E-01	9.8635E-01	2.9853E-01	8.7058E-01	2.2271E-01
1800.00	9.8235E-01	9.8764E-01	2.9934E-01	8.7397E-01	2.2325E-01
1900.00	9.8142E-01	9.8870E-01	3.0014E-01	8.7406E-01	2.2378E-01
2000.00	9.8058E-01	9.8957E-01	3.0093E-01	8.6964E-01	2.2433E-01
2500.00	9.7750E-01	9.9226E-01	3.0467E-01	8.5349E-01	2.2697E-01

Table S58: Tunneling ($\kappa_j^{\mathrm{CVT/SCT}}(T)$) coefficient for the individual paths of CRC4.

T(K)	Path 1	Path 2	Path 3	Path 4	Path 5
200	11.680	12.610	12.530	19.920	12.460
300	2.586	2.666	2.662	3.193	2.657
400	1.664	1.692	1.691	1.864	1.690
500	1.376	1.391	1.390	1.477	1.389
600	1.245	1.254	1.253	1.307	1.253
700	1.173	1.180	1.179	1.216	1.179
800	1.129	1.134	1.134	1.161	1.134
900	1.101	1.104	1.104	1.125	1.104
1000	1.081	1.083	1.083	1.100	1.083
1100	1.066	1.068	1.068	1.081	1.068
1200	1.055	1.057	1.057	1.068	1.057
1300	1.047	1.048	1.048	1.058	1.048
1400	1.040	1.042	1.041	1.049	1.041
1500	1.035	1.036	1.036	1.043	1.036
2000	1.019	1.020	1.020	1.024	1.020
2500	1.012	1.013	1.013	1.015	1.013

Table S59: Recrossing ($\Gamma_j^{\mathrm{CVT}}(T)$) coefficient for the individual paths of CRC5.

T(K)	Path 1	Path 2	Path 3	Path 4
200.00	2.6417E-01	6.2600E-01	2.8102E-01	7.5604E-01
300.00	4.2266E-01	8.1962E-01	4.2217E-01	9.1457E-01
400.00	5.3609E-01	9.2399E-01	5.2057E-01	9.6877E-01
500.00	6.1799E-01	9.6852E-01	5.9157E-01	9.8955E-01
600.00	6.7810E-01	9.8871E-01	6.4400E-01	9.9737E-01
700.00	7.2282E-01	9.9713E-01	6.8326E-01	9.9977E-01
800.00	7.5647E-01	9.9980E-01	7.1296E-01	9.9986E-01
900.00	7.8211E-01	9.9961E-01	7.3567E-01	9.9893E-01
1000.00	8.0188E-01	9.9754E-01	7.5320E-01	9.9758E-01
1100.00	8.1730E-01	9.9445E-01	7.6689E-01	9.9612E-01
1200.00	8.2947E-01	9.9089E-01	7.7768E-01	9.9469E-01
1300.00	8.3918E-01	9.8718E-01	7.8627E-01	9.9334E-01
1400.00	8.4701E-01	9.8349E-01	7.9318E-01	9.9211E-01
1500.00	8.5338E-01	9.7992E-01	7.9878E-01	9.9101E-01
1600.00	8.5861E-01	9.7651E-01	8.0336E-01	9.9001E-01
1700.00	8.6294E-01	9.7328E-01	8.0713E-01	9.8912E-01
1800.00	8.6655E-01	9.7022E-01	8.1025E-01	9.8833E-01
1900.00	8.6249E-01	9.6733E-01	8.1285E-01	9.8761E-01
2000.00	8.5850E-01	9.6459E-01	8.1503E-01	9.8698E-01
2500.00	8.4396E-01	9.5239E-01	8.2180E-01	9.8461E-01

Table S60: Tunneling ($\kappa_j^{\mathrm{CVT/SCT}}(T)$) coefficient for the individual paths of CRC5.

T(K)	Path 1	Path 2	Path 3	Path 4
200	16.540	15.520	15.880	21.370
300	2.941	2.883	2.878	3.291
400	1.782	1.765	1.760	1.894
500	1.436	1.427	1.425	1.491
600	1.282	1.277	1.275	1.315
700	1.199	1.195	1.194	1.221
800	1.148	1.146	1.145	1.165
900	1.115	1.113	1.112	1.127
1000	1.092	1.090	1.090	1.102
1100	1.075	1.074	1.073	1.083
1200	1.063	1.062	1.061	1.069
1300	1.053	1.052	1.052	1.059
1400	1.046	1.045	1.045	1.050
1500	1.040	1.039	1.039	1.044
2000	1.022	1.022	1.022	1.024
2500	1.014	1.014	1.014	1.016

Table S61: Representative tunneling energy (RTE) at 200 K and the maxima of the vibrationally adiabatic ground-state potential curves for reaction paths 1–5 of CRC1. All values are in kcal/mol.

Path	RTE	V_a^G
Path 1	57.684	59.035
Path 2	58.162	59.501
Path 3	57.790	59.675
Path 4	58.693	60.267
Path 5	59.484	60.667

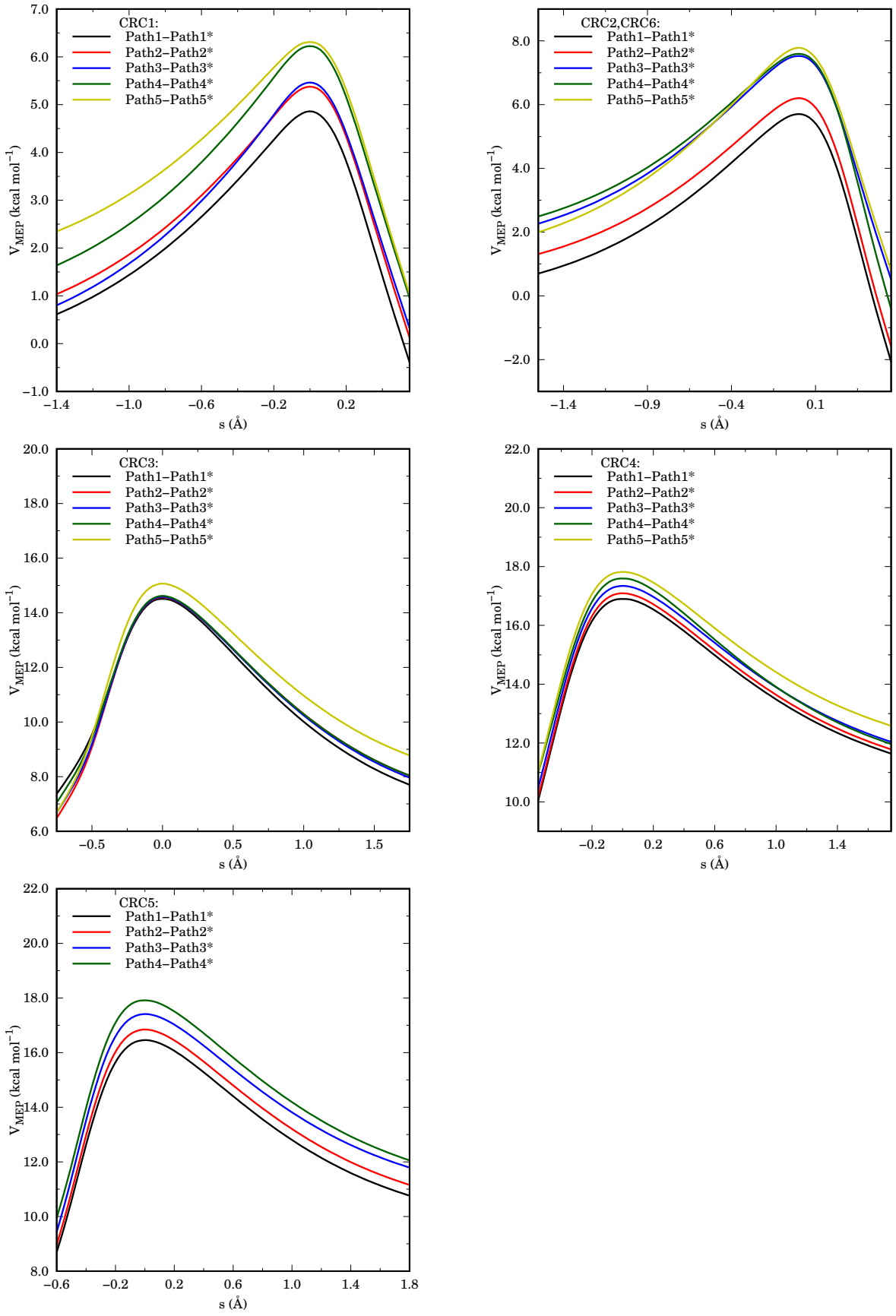

Figure S1: Minimum energy potentials (V_{MEP}) for the individual paths of CRC1–CRC6.

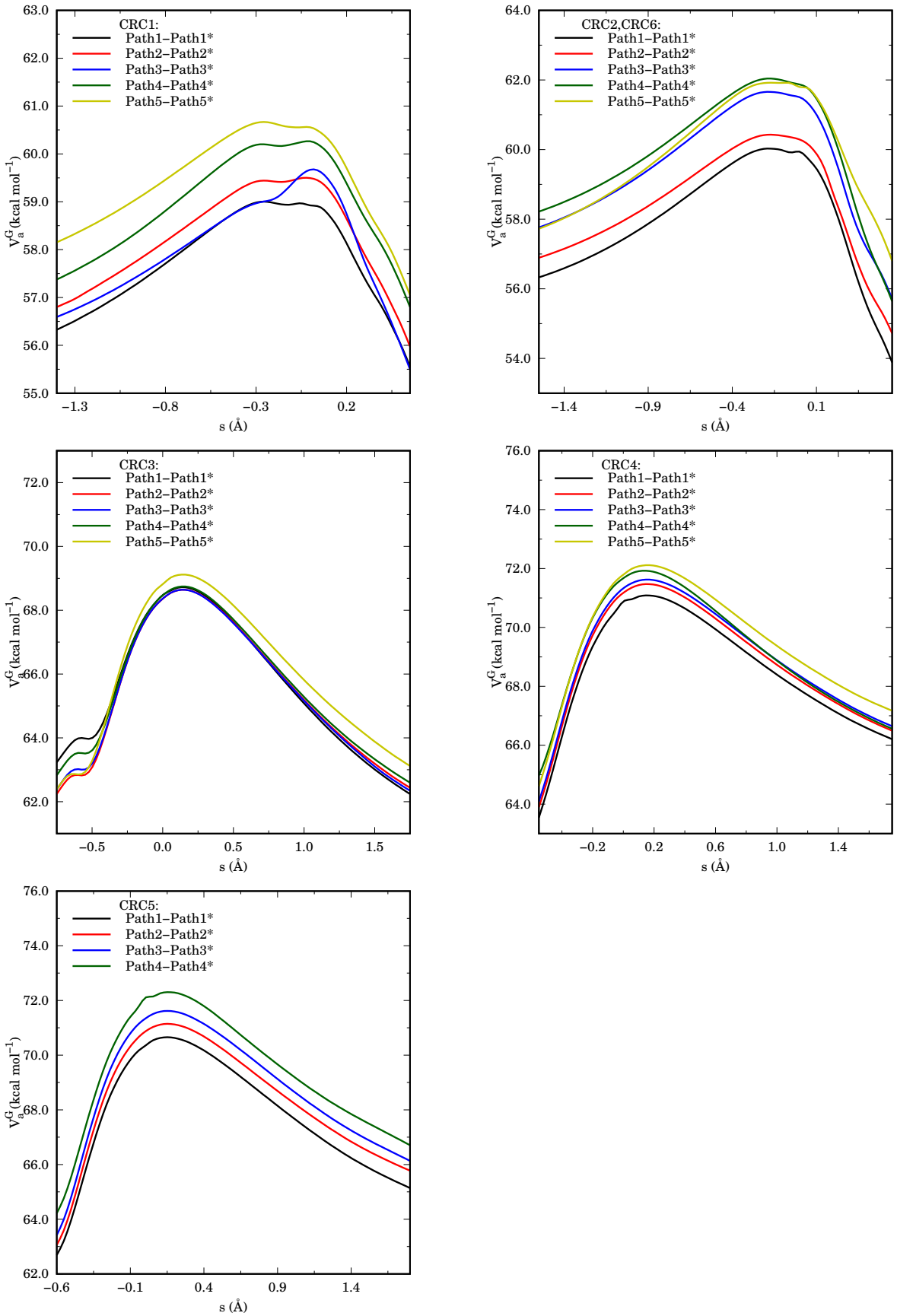

Figure S2: Vibrationally adiabatic potentials (V_a^G) for the individual paths of CRC1–CRC6.

Table S62: Harmonic MS-TST thermal rate constants for (R1)–(R5) in a wide range of temperatures. All rate constants are in cm^3 $molecule^1$ s^1.

T(K)	(R1)	(R2)	(R3)	(R4)	(R5)
200.00	2.209E-15	4.699E-17	3.316E-25	2.741E-28	8.206E-28
300.00	4.683E-14	1.960E-15	1.642E-20	1.338E-22	2.441E-22
400.00	2.453E-13	1.469E-14	4.050E-18	1.054E-19	1.526E-19
500.00	7.199E-13	5.448E-14	1.189E-16	6.251E-18	7.944E-18
600.00	1.566E-12	1.402E-13	1.195E-15	1.008E-16	1.179E-16
700.00	2.854E-12	2.901E-13	6.481E-15	7.664E-16	8.468E-16
800.00	4.634E-12	5.204E-13	2.379E-14	3.628E-15	3.846E-15
900.00	6.942E-12	8.448E-13	6.715E-14	1.248E-14	1.282E-14
1000.00	9.804E-12	1.275E-12	1.573E-13	3.424E-14	3.433E-14
1100.00	1.324E-11	1.819E-12	3.210E-13	7.951E-14	7.821E-14
1200.00	1.725E-11	2.485E-12	5.900E-13	1.628E-13	1.576E-13
1300.00	2.184E-11	3.278E-12	9.994E-13	3.019E-13	2.885E-13
1400.00	2.702E-11	4.200E-12	1.586E-12	5.179E-13	4.894E-13
1500.00	3.277E-11	5.256E-12	2.388E-12	8.338E-13	7.805E-13
2000.00	6.995E-11	1.255E-11	1.086E-11	4.789E-12	4.343E-12
2500.00	1.203E-10	2.313E-11	2.938E-11	1.490E-11	1.327E-11

Table S63: MP-CVT/SCT thermal rate constants for (R1)–(R5), including the torsional anharmonicity estimated with MS-T(C) method All rate constants are in cm^3 $molecule^{-1}$ s^{-1}.

T(K)	(R1)	(R2)	(R3)	(R4)	(R5)
200.00	2.486E-14	8.173E-16	8.166E-24	2.327E-27	6.789E-27
300.00	1.433E-13	5.823E-15	5.121E-20	2.619E-22	4.765E-22
400.00	4.602E-13	2.329E-14	7.024E-18	1.455E-19	2.037E-19
500.00	1.061E-12	6.537E-14	1.592E-16	7.507E-18	8.996E-18
600.00	2.012E-12	1.490E-13	1.390E-15	1.126E-16	1.235E-16
700.00	3.363E-12	2.922E-13	6.632E-15	8.103E-16	8.501E-16
800.00	5.152E-12	5.136E-13	2.293E-14	3.612E-15	3.763E-15
900.00	7.407E-12	8.308E-13	5.957E-14	1.198E-14	1.182E-14
1000.00	1.015E-11	1.261E-12	1.355E-13	3.165E-14	2.936E-14
1100.00	1.328E-11	1.811E-12	2.638E-13	7.184E-14	6.643E-14
1200.00	1.696E-11	2.502E-12	4.770E-13	1.457E-13	1.334E-13
1300.00	2.110E-11	3.343E-12	7.979E-13	2.628E-13	2.438E-13
1400.00	2.571E-11	4.344E-12	1.254E-12	4.490E-13	3.930E-13
1500.00	3.080E-11	5.512E-12	1.873E-12	7.212E-13	6.279E-13
2000.00	6.296E-11	1.401E-11	8.202E-12	4.133E-12	3.539E-12
2500.00	1.056E-10	2.712E-11	2.204E-11	1.290E-11	1.096E-11

Table S64: Fitting parameters to the MP-CVT/SCT thermal rate constants for (R1)–(R5), including the torsional anharmonicity estimated with MS-T(C) method. The parameters for the the overall thermal rate constants were also listed.

	A/cm^3 $molecule^{-1}$ s^{-1}	n	E/K	T_0/K	RMSR
(R1)	1.62 x 10^{-12}	2.10	620	171	6.72 x 10^{-5}
(R2)	1.23 x 10^{-13}	2.73	833	227	3.07 x 10^{-4}
(R3)	4.62 x 10^{-13}	2.62	3990	112	9.88 x 10^{-5}
(R4)	3.94 x 10^{-13}	2.69	5285	102	1.11 x 10^{-4}
(R5)	2.69 x 10^{-13}	2.75	5042	103	2.63 x 10^{-4}
Overall	6.93 x 10^{-13}	2.69	379	127	3.34 x 10^{-5}

Table S65: Activation energies (in kcal/mol) for the overall thermal rate constants of (E)-2-Butenal and 3-Butenal with H-atom.

T(K)	(E)-2-Butenal + H	3-Butenal + H
200.0	1.86	1.86
300.0	2.81	2.54
400.0	3.53	3.12
500.0	4.13	3.66
600.0	4.69	4.20
800.0	5.76	4.74
1000.0	6.82	6.36
1500.0	9.47	9.09
2000.0	12.14	11.83
2500.0	14.82	14.58