Electronic Supplementary Material (ESI) for Organdic and Biomolecular Chemistry

Supporting Information for:

Effects of Geminal Methyl Groups on the Tunneling Rates in the Ring Opening of Cyclopropylcarbinyl Radical at Cryogenic Temperature

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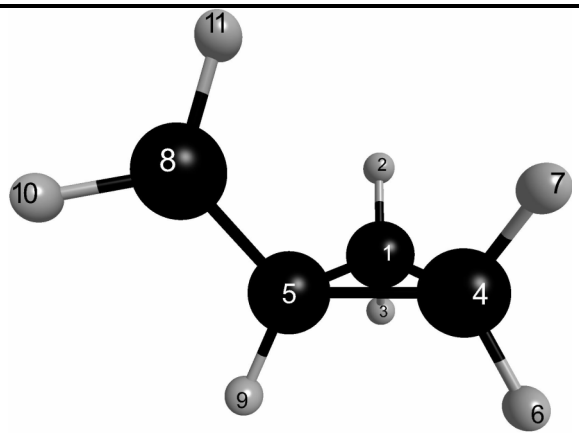
The optimized B3LYP/6-31+G(d,p) geometries, energies, thermal corrections, and harmonic frequencies for **1a**, **1b** and **2a**, **2b**, **2c** and transition structure connecting them, the CVT and CVT + SCT rate constants for these reactions.

Cyclopropylcarbinyl Radical (**1a**)
$^2A''$ UB3LYP/6-31+G(d,p) C_s Geometry

Nuclear repulsion energy	116.294912 Hartree
RB3LYP/6-31+G(d,p) energy ($<S^2>$ = 0.7500)	-156.563032 Hartree
Zero-point correction	0.094585 Hartree
Thermal correction to Energy @ 298K	0.099512 Hartree
Thermal correction to Enthalpy @ 298K	0.100456 Hartree
Thermal correction to Gibbs Free Energy @ 298K	0.067278 Hartree



	X	Y	Z
C1	0.302967	-0.872141	0.748314
H2	-0.613479	-1.144539	1.263823
H3	1.213501	-1.150352	1.271801
C4	0.302967	-0.872141	-0.748314
C5	0.302967	0.468684	0.000000
H6	1.213501	-1.150352	-1.271801
H7	-0.613479	-1.144539	-1.263823
C8	-0.875680	1.325263	0.000000
H9	1.256797	0.990672	0.000000
H10	-0.782939	2.404991	0.000000
H11	-1.873233	0.896125	0.000000

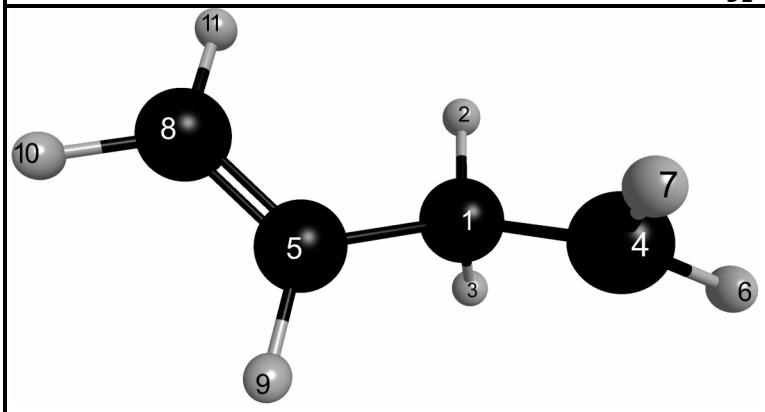
(1-2)	1.086	(1-3)	1.087	(1-4)	1.497	(1-5)	1.536	(5-8)	1.457
(5-9)	1.087	(8-10)	1.084	(8-11)	1.086				
(2-1-3)	114.5	(2-1-4)	118.3	(2-1-5)	116.8	(3-1-4)	118.8		
(3-1-5)	117.3	(4-1-5)	60.8	(1-5-4)	58.3	(1-5-8)	120.9		
(1-5-9)	114.8	(8-5-9)	115.3	(5-8-10)	121.1	(5-8-11)	120.7		
(10-8-11)	118.2								
(2-1-4-5)	106.6	(2-1-4-6)	-146.5	(2-1-4-7)	0.0				
(3-1-4-5)	-107.0	(3-1-4-6)	0.0	(2-1-5-4)	-109.1				
(2-1-5-8)	0.4	(2-1-5-9)	146.0	(3-1-5-4)	109.4				
(3-1-5-8)	-141.0	(3-1-5-9)	4.5	(4-1-5-8)	109.5				
(4-1-5-9)	-104.9	(1-5-8-10)	145.4	(1-5-8-11)	-34.6				
(9-5-8-10)	0.0	(9-5-8-11)	180.0						

Frequencies(cm^{-1}): 176.1 334.4 370.4 502.0 761.9 779.2 804.9 850.1
928.2 1021.3 1043.1 1065.1 1113.8 1200.8 1208.9 1216.3 1386.3 1471.6
1481.2 1505.1 3132.2 3136.2 3159.4 3160.6 3213.6 3229.5 3265.8

3-Butenyl Radical (**2a**)

^{2}A UB3LYP/6-31+G(d,p) C_1 Geometry

Nuclear repulsion energy	109.416723 Hartree
RB3LYP/6-31+G(d,p) energy (<S^2> = 0.7538)	-156.567773 Hartree
Zero-point correction	0.093220 Hartree
Thermal correction to Energy @ 298K	0.098861 Hartree
Thermal correction to Enthalpy @ 298K	0.099805 Hartree
Thermal correction to Gibbs Free Energy @ 298K	0.064656 Hartree



	X	Y	Z
C1	-0.620073	0.550311	0.131665
H2	-0.434088	1.274002	-0.682159
H3	-0.895816	1.154785	1.007973
C4	-1.761180	-0.351003	-0.223811
C5	0.663067	-0.193153	0.416933
H6	-2.782725	-0.088855	0.031825
H7	-1.596862	-1.223308	-0.848742
C8	1.802997	-0.046990	-0.264822
H9	0.622546	-0.905061	1.241862
H10	2.694124	-0.614285	-0.012183
H11	1.883953	0.647732	-1.098369

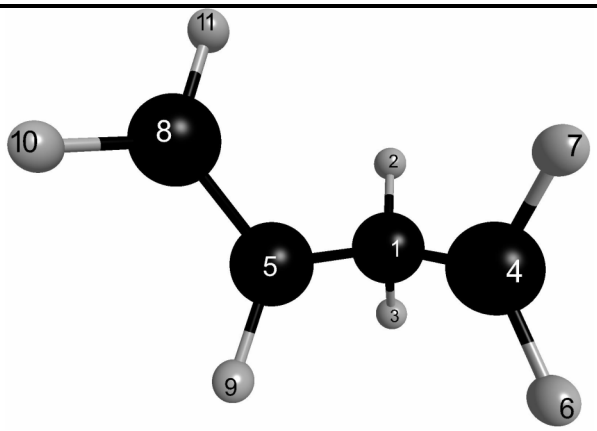
(1-2)	1.105	(1-3)	1.100	(1-4)	1.497	(1-5)	1.510	(4-6)	1.085
(4-7)	1.086	(5-8)	1.336	(5-9)	1.090	(8-10)	1.086	(8-11)	1.088
(2-1-3)	105.6	(2-1-4)	110.4	(2-1-5)	108.6	(3-1-4)	109.2		
(3-1-5)	109.5	(4-1-5)	113.3	(1-4-6)	121.1	(1-4-7)	120.3		
(6-4-7)	118.2	(1-5-8)	125.1	(1-5-9)	115.6	(8-5-9)	119.3		
(5-8-10)	121.6	(5-8-11)	121.6	(10-8-11)	116.8				
(2-1-4-6)	-89.6	(2-1-4-7)	83.0	(3-1-4-6)	26.1				
(3-1-4-7)	-161.3	(5-1-4-6)	148.4	(5-1-4-7)	-39.0				
(2-1-5-8)	-3.7	(2-1-5-9)	176.9	(3-1-5-8)	-118.6				
(3-1-5-9)	62.1	(4-1-5-8)	119.3	(4-1-5-9)	-60.1				
(1-5-8-10)	-179.8	(1-5-8-11)	0.3	(9-5-8-10)	-0.5				
(9-5-8-11)	179.6								

Frequencies(cm^{-1}): 97.6 128.2 324.3 419.4 499.4 655.1 798.2 897.9
942.0 1021.8 1047.7 1074.4 1116.1 1238.0 1317.5 1336.8 1448.4 1463.8
1469.8 1705.6 2952.8 3026.5 3141.1 3149.2 3155.0 3230.7 3261.7

Transition Structure for **1a** → **2a**

^{2}A UB3LYP/6-31+G(d,p) C_1 Geometry

Nuclear repulsion energy	114.012157 Hartree
RB3LYP/6-31+G(d,p) energy (<S^2> = 0.7501)	-156.550836 Hartree
Zero-point correction	0.093444 Hartree
Thermal correction to Energy @ 298K	0.093634 Hartree
Thermal correction to Enthalpy @ 298K	0.093698 Hartree
Thermal correction to Gibbs Free Energy @ 298K	0.092368 Hartree



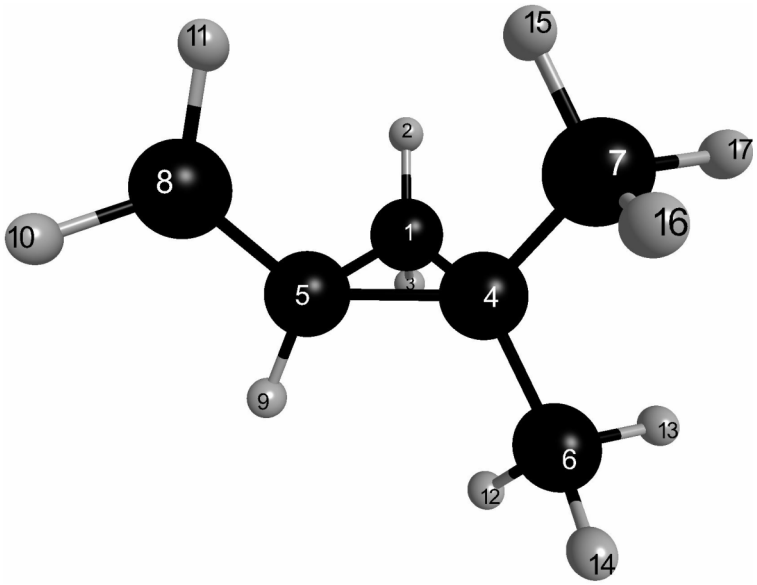
	X	Y	Z
C1	-0.804879	0.731736	-0.146767
H2	-0.644862	1.155876	-1.139138
H3	-1.387356	1.404000	0.484457
C4	-1.186118	-0.701364	-0.112000
C5	0.419884	0.147863	0.483927
H6	-1.743608	-1.112174	0.721471
H7	-0.992543	-1.339541	-0.964457
C8	1.607624	-0.116545	-0.182948
H9	0.391877	0.028692	1.563568
H10	2.444128	-0.580346	0.328370
H11	1.713298	0.073351	-1.247544

(1-2)	1.091	(1-3)	1.091	(1-4)	1.483	(1-5)	1.496	(4-6)	1.084
(4-7)	1.082	(5-8)	1.388	(5-9)	1.087	(8-10)	1.085	(8-11)	1.087
(2-1-3)	111.4	(2-1-4)	115.8	(2-1-5)	114.5	(3-1-4)	116.4		
(3-1-5)	115.7	(4-1-5)	79.8	(1-4-6)	121.1	(1-4-7)	120.3		
(6-4-7)	118.3	(1-5-8)	124.9	(1-5-9)	116.1	(8-5-9)	118.6		
(5-8-10)	121.0	(5-8-11)	121.4	(10-8-11)	117.5				
(2-1-4-6)	-154.8	(2-1-4-7)	19.4	(3-1-4-6)	-21.0				
(3-1-4-7)	153.2	(5-1-4-6)	92.7	(5-1-4-7)	-93.0				
(2-1-5-8)	-13.2	(2-1-5-9)	160.0	(3-1-5-8)	-144.9				
(3-1-5-9)	28.3	(4-1-5-8)	100.6	(4-1-5-9)	-86.2				
(1-5-8-10)	-177.4	(1-5-8-11)	-1.4	(9-5-8-10)	9.6				
(9-5-8-11)	-174.4								

Frequencies(cm^{-1}): -579.2 279.6 393.5 491.5 606.5 699.9 740.1 827.2
895.4 910.8 990.7 1095.0 1189.7 1203.2 1224.5 1270.2 1413.9 1463.6
1498.4 1521.8 3089.5 3153.7 3155.7 3176.2 3185.9 3250.4 3290.3

2,2-Dimethylcyclopropylcarbinyl Radical (**1b**)
$^2A''$ UB3LYP/6-31+G(d,p) C_1 Geometry

Nuclear repulsion energy	239.883701 Hartree
RB3LYP/6-31+G(d,p) energy (< S^2> = 0.7500)	-235.202245 Hartree
Zero-point correction	0.150339 Hartree
Thermal correction to Energy @298K	0.158036 Hartree
Thermal correction to Enthalpy @ 298K	0.158581 Hartree
Thermal correction to Gibbs Free Energy @ 298K	0.119231 Hartree



	X	Y	Z
C1	0.212886	-0.664628	1.159233
H2	0.688068	-0.065815	1.932605
H3	-0.157365	-1.627740	1.503194
C4	-0.516999	0.046320	0.061177
C5	0.859572	-0.613789	-0.234678
C6	-1.729517	-0.637299	-0.547979
C7	-0.620163	1.560282	0.106088
C8	2.079985	0.134848	-0.489486
H9	0.771683	-1.535336	-0.806950
H10	2.751317	-0.164025	-1.286490
H11	2.345526	1.011831	0.090799
H12	-1.609220	-1.725594	-0.572832
H13	-2.633143	-0.415786	0.035174
H14	-1.901351	-0.293630	-1.575352
H15	0.257602	2.022754	0.564939
H16	-0.729254	1.977562	-0.902218
H17	-1.498452	1.861382	0.691004

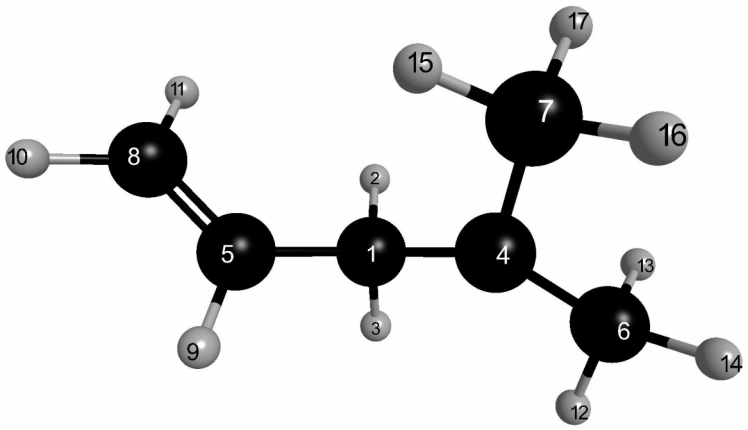
(1-2)	1.087	(1-3)	1.088	(1-4)	1.498	(1-5)	1.537	(4-5)	1.555
(4-6)	1.519	(4-7)	1.518	(5-8)	1.454	(5-9)	1.088	(6-12)	1.095
(6-13)	1.098	(6-14)	1.097	(7-15)	1.093	(7-16)	1.097	(7-17)	1.097
(8-10)	1.084	(8-11)	1.085						
(2-1-3)	114.3	(2-1-4)	118.2	(2-1-5)	116.3	(3-1-4)	119.1		
(3-1-5)	117.3	(4-1-5)	61.6	(1-4-5)	60.4	(1-4-6)	118.0		
(1-4-7)	119.0	(5-4-6)	116.1	(5-4-7)	119.3	(6-4-7)	114.0		
(1-5-4)	57.9	(1-5-8)	121.9	(1-5-9)	114.5	(4-5-8)	123.9		
(4-5-9)	112.8	(8-5-9)	114.3	(4-6-12)	111.6	(4-6-13)	110.7		
(4-6-14)	111.1	(12-6-13)	107.6	(12-6-14)	107.9	(13-6-14)	107.8		
(4-7-15)	112.3	(4-7-16)	111.0	(4-7-17)	110.1	(15-7-16)	107.7		
(15-7-17)	107.6	(16-7-17)	107.8	(5-8-10)	120.4	(5-8-11)	121.9		
(10-8-11)	117.7								
(2-1-4-5)	106.3	(2-1-4-6)	-148.0	(2-1-4-7)	-2.8				
(3-1-4-5)	-107.3	(3-1-4-6)	-1.6	(3-1-4-7)	143.6				
(5-1-4-6)	105.7	(5-1-4-7)	-109.2	(2-1-5-4)	-109.4				
(2-1-5-8)	3.2	(2-1-5-9)	148.0	(3-1-5-4)	110.0				
(3-1-5-8)	-137.3	(3-1-5-9)	7.5	(4-1-5-8)	112.6				
(4-1-5-9)	-102.6	(1-4-5-8)	-109.3	(1-4-5-9)	105.5				
(6-4-5-1)	-108.9	(6-4-5-8)	141.8	(6-4-5-9)	-3.3				
(7-4-5-1)	108.7	(7-4-5-8)	-0.6	(7-4-5-9)	-145.8				
(1-4-6-12)	-33.9	(1-4-6-13)	86.0	(1-4-6-14)	-154.4				
(5-4-6-12)	34.9	(5-4-6-13)	154.7	(5-4-6-14)	-85.6				
(7-4-6-12)	179.3	(7-4-6-13)	-60.9	(7-4-6-14)	58.8				
(1-4-7-15)	32.5	(1-4-7-16)	153.3	(1-4-7-17)	-87.4				
(5-4-7-15)	-37.9	(5-4-7-16)	82.9	(5-4-7-17)	-157.8				
(6-4-7-15)	179.0	(6-4-7-16)	-60.3	(6-4-7-17)	59.1				

(1-5-8-10)	152.7	(1-5-8-11)	-28.3	(4-5-8-10)	-136.9		
(4-5-8-11)	42.1	(9-5-8-10)	7.8	(9-5-8-11)	-173.2		

Frequencies(cm^{-1}): 167.0 188.2 204.2 236.2 264.4 354.9 375.0 430.8
449.4 525.9 646.5 764.6 844.3 886.3 923.6 968.9 1000.3 1021.2
1053.2 1067.6 1114.9 1140.8 1202.3 1282.8 1333.9 1398.0 1415.6 1426.6
1478.9 1484.9 1489.6 1497.1 1504.2 1512.5 3019.4 3029.0 3079.6 3085.5
3101.4 3118.3 3121.4 3143.8 3166.7 3205.9 3265.5

1,1-Dimethyl-3-butenyl Radical (**2b**)
^{2}A UB3LYP/6-31+G(d,p) C_1 Geometry

Nuclear repulsion energy	225.627098 Hartree
RB3LYP/6-31+G(d,p) energy (<S^2> = 0.7500)	-235.213754 Hartree
Zero-point correction	0.150028 Hartree
Thermal correction to Energy @ 298K	0.158410 Hartree
Thermal correction to Enthalpy @ 298K	0.159354 Hartree
Thermal correction to Gibbs Free Energy @ 298K	0.116389 Hartree



	X	Y	Z
C1	0.299934	-0.750242	0.307649
H2	0.489359	-0.645178	1.392941
H3	0.123057	-1.821519	0.135381
C4	-0.941124	0.015299	-0.083104
C5	1.548086	-0.339540	-0.437503
C6	-2.260946	-0.692595	-0.061892
C7	-0.934918	1.509779	0.018684
C8	2.669020	0.120509	0.126069
H9	1.500544	-0.437294	-1.522821
H10	3.536908	0.390252	-0.468988
H11	2.757587	0.238846	1.204156
H12	-2.183634	-1.717053	-0.444689
H13	-2.669914	-0.768820	0.963787
H14	-3.014466	-0.161233	-0.655528
H15	0.038761	1.935955	-0.243346
H16	-1.696012	1.961580	-0.628952
H17	-1.162502	1.845206	1.048643

(1-2)	1.107	(1-3)	1.099	(1-4)	1.510	(1-5)	1.511
(4-6)	1.498	(4-7)	1.498	(5-8)	1.336	(5-9)	1.091
(6-12)	1.096	(6-13)	1.107	(6-14)	1.097	(7-15)	1.095
(7-16)	1.097	(7-17)	1.107	(8-10)	1.086	(8-11)	1.088

(2-1-3)	105.9	(2-1-4)	110.3	(2-1-5)	108.5	(3-1-4)	108.7
(3-1-5)	108.7	(4-1-5)	114.4	(1-4-6)	118.8	(1-4-7)	119.0
(6-4-7)	118.3	(1-5-8)	125.4	(1-5-9)	115.5	(8-5-9)	119.1
(4-6-12)	112.0	(4-6-13)	111.8	(4-6-14)	111.6	(12-6-13)	106.6
(12-6-14)	108.2	(13-6-14)	106.3	(4-7-15)	112.1	(4-7-16)	111.6
(4-7-17)	111.4	(15-7-16)	108.4	(15-7-17)	106.7	(16-7-17)	106.4
(5-8-10)	121.6	(5-8-11)	121.6	(10-8-11)	116.8		

(2-1-4-6)	-91.1	(2-1-4-7)	66.3	(3-1-4-6)	24.6
(3-1-4-7)	-178.0	(5-1-4-6)	146.4	(5-1-4-7)	-56.3
(2-1-5-8)	-2.3	(2-1-5-9)	177.7	(3-1-5-8)	-117.0
(3-1-5-9)	63.0	(4-1-5-8)	121.2	(4-1-5-9)	-58.8
(1-4-6-12)	-40.1	(1-4-6-13)	79.4	(1-4-6-14)	-161.6
(7-4-6-12)	162.4	(7-4-6-13)	-78.1	(7-4-6-14)	40.9
(1-4-7-15)	36.2	(1-4-7-16)	158.0	(1-4-7-17)	-83.3
(6-4-7-15)	-166.4	(6-4-7-16)	-44.6	(6-4-7-17)	74.1
(1-5-8-10)	179.4	(1-5-8-11)	-0.3	(9-5-8-10)	-0.6

(9-5-8-11)	179.7

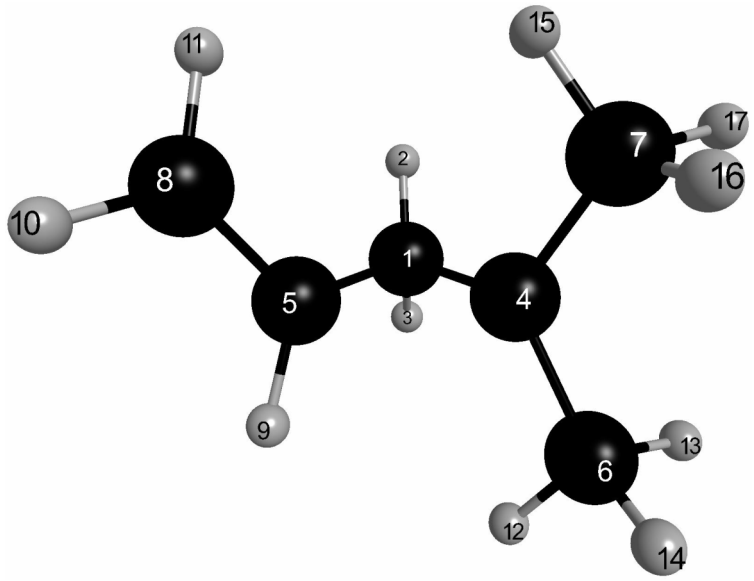
Frequencies(cm^{-1}):

43.1	89.9	127.3	133.2	208.9	312.8	347.7	411.2	432.0	624.7
795.9	887.9	927.7	939.3	942.7	990.6	994.3	1025.4	1044.2	1119.5
1209.4	1258.5	1291.8	1320.7	1352.0	1403.2	1419.2	1450.5	1466.0	1475.2
1480.7	1489.7	1495.2	1704.7	2930.0	2931.0	2938.6	3028.5	3045.7	3051.8
3093.3	3107.3	3137.9	3146.4	3228.6					

Transition Structure for **1b** → **2b**

^{2}A UB3LYP/6-31+G(d,p) C_1 Geometry

Nuclear repulsion energy	236.077466 Hartree
RB3LYP/6-31+G(d,p) energy (<S^2> = 0.7729)	-235.194029 Hartree
Zero-point correction	0.149396 Hartree
Thermal correction to Energy @298K	0.156821 Hartree
Thermal correction to Enthalpy @ 298K	0.157765 Hartree
Thermal correction to Gibbs Free Energy @ 298K	0.118193 Hartree



	X	Y	Z
C1	0.268230	-0.568915	1.094960
H2	0.680834	0.094207	1.857781
H3	-0.045313	-1.523410	1.522869
C4	-0.651068	0.059933	0.108517
C5	1.077030	-0.641644	-0.167323
C6	-1.749977	-0.761968	-0.506288
C7	-0.777251	1.554472	0.037160
C8	2.156064	0.182092	-0.472706
H9	0.893752	-1.503395	-0.803693
H10	2.673369	0.091766	-1.422011
H11	2.477510	0.974662	0.196575
H12	-1.495900	-1.826743	-0.542786
H13	-2.676817	-0.672363	0.084860
H14	-1.985907	-0.432489	-1.525383
H15	0.144314	2.056391	0.345253
H16	-1.018559	1.891885	-0.977992
H17	-1.585457	1.905677	0.698603

(1-2)	1.092	(1-3)	1.092	(1-4)	1.488	(1-5)	1.501
(4-6)	1.504	(4-7)	1.502	(5-8)	1.391	(5-9)	1.087
(6-12)	1.095	(6-13)	1.103	(6-14)	1.097	(7-15)	1.094
(7-16)	1.097	(7-17)	1.102	(8-10)	1.085	(8-11)	1.086

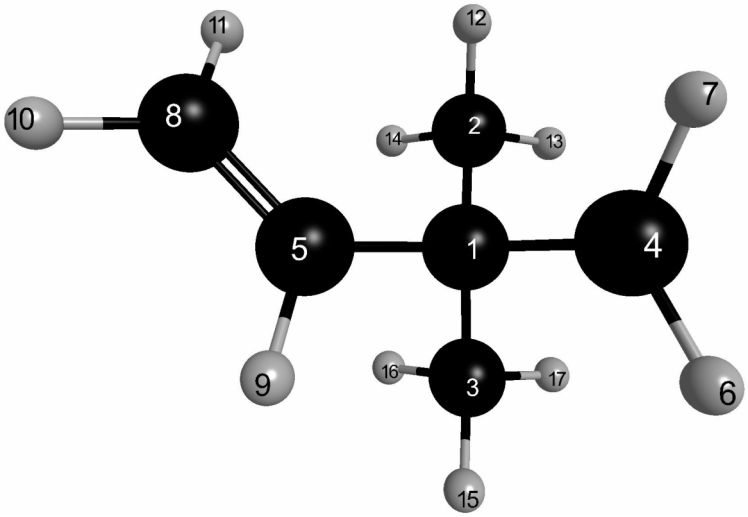
(2-1-3)	111.4	(2-1-4)	116.1	(2-1-5)	114.4	(3-1-4)	116.9
(3-1-5)	116.2	(4-1-5)	78.2	(1-4-6)	119.4	(1-4-7)	120.3
(6-4-7)	117.6	(1-5-8)	125.0	(1-5-9)	116.1	(8-5-9)	118.1
(4-6-12)	112.1	(4-6-13)	110.5	(4-6-14)	111.9	(12-6-13)	107.0
(12-6-14)	108.1	(13-6-14)	107.0	(4-7-15)	111.9	(4-7-16)	111.6
(4-7-17)	110.5	(15-7-16)	107.8	(15-7-17)	107.6	(16-7-17)	107.2
(5-8-10)	120.8	(5-8-11)	121.8	(10-8-11)	117.3		

(2-1-4-6)	-150.1	(2-1-4-7)	10.9	(3-1-4-6)	-15.3
(3-1-4-7)	145.7	(5-1-4-6)	98.4	(5-1-4-7)	-100.7
(2-1-5-8)	-9.0	(2-1-5-9)	160.9	(3-1-5-8)	-141.2
(3-1-5-9)	28.7	(4-1-5-8)	104.5	(4-1-5-9)	-85.6
(1-4-6-12)	-27.4	(1-4-6-13)	91.8	(1-4-6-14)	-149.0
(7-4-6-12)	171.1	(7-4-6-13)	-69.7	(7-4-6-14)	49.5
(1-4-7-15)	29.0	(1-4-7-16)	149.8	(1-4-7-17)	-90.9
(6-4-7-15)	-169.7	(6-4-7-16)	-48.9	(6-4-7-17)	70.4
(1-5-8-10)	-178.0	(1-5-8-11)	-1.6	(9-5-8-10)	12.3
(9-5-8-11)	-171.3				

Frequencies(cm^{-1}): -522.2 148.7 156.9 184.9 227.8 307.4 369.6 401.3
445.1 503.9 695.5 747.3 878.5 891.8 952.6 961.4 981.3 1024.5
1037.0 1082.4 1173.1 1184.1 1265.3 1311.2 1329.4 1410.1 1412.8 1422.5
1476.3 1483.3 1486.6 1498.9 1503.9 1520.3 2978.0 2992.0 3055.1 3062.5
3075.6 3100.2 3115.9 3143.3 3155.6 3175.3 3248.0

2,2-Dimethyl-3-butenyl Radical (**2c**)
^{2}A UB3LYP/6-31+G(d,p) C_1 Geometry

Nuclear repulsion energy	235.960576 Hartree
RB3LYP/6-31+G(d,p) energy (<S^2> = 0.7500)	-235.202142 Hartree
Zero-point correction	0.149723 Hartree
Thermal correction to Energy @ 298K	0.157712 Hartree
Thermal correction to Enthalpy @ 298K	0.158656 Hartree
Thermal correction to Gibbs Free Energy @ 298K	0.118219 Hartree



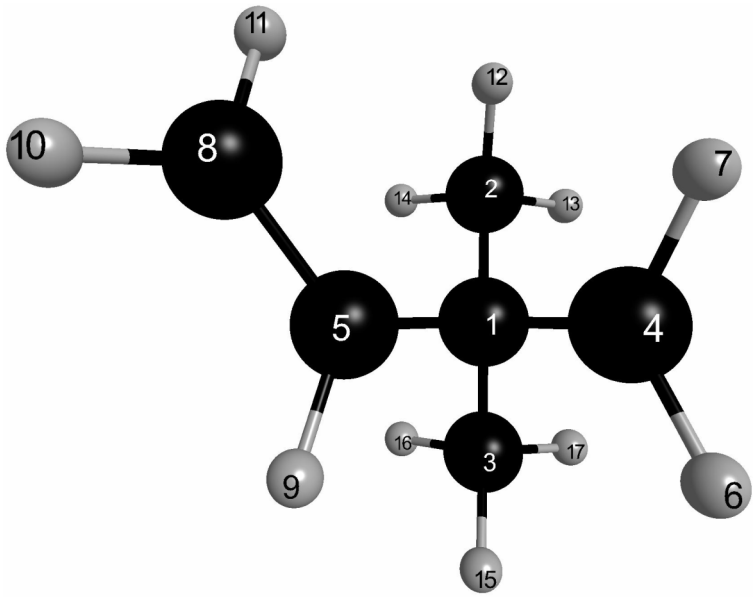
	X	Y	Z
C1	0.393989	0.005845	0.046900
C2	0.296391	1.524245	-0.189504
C3	1.313503	-0.632466	-1.019965
C4	0.932117	-0.270538	1.427168
C5	-0.968554	-0.683210	-0.010973
H6	1.449321	-1.201114	1.643878
H7	0.611200	0.340233	2.265983
C8	-2.173132	-0.106845	-0.099736
H9	-0.916155	-1.770949	0.052391
H10	-3.077718	-0.708038	-0.115006
H11	-2.305374	0.969071	-0.162634
H12	-0.316633	2.011789	0.575760
H13	1.294110	1.973110	-0.152949
H14	-0.141585	1.743151	-1.169387
H15	1.398465	-1.714907	-0.870679
H16	0.918205	-0.460335	-2.026824
H17	2.320283	-0.204197	-0.963878

(1-2)	1.540	(1-3)	1.546	(1-4)	1.507	(1-5)	1.528	(2-12)	1.095
(2-13)	1.095	(2-14)	1.095	(3-15)	1.096	(3-16)	1.095	(3-17)	1.096
(4-6)	1.086	(4-7)	1.086	(5-8)	1.338	(5-9)	1.091	(8-10)	1.086
(8-11)	1.086								
(2-1-3)	109.8	(2-1-4)	110.1	(2-1-5)	112.5	(3-1-4)	110.1		
(3-1-5)	108.5	(4-1-5)	105.7	(1-2-12)	111.5	(1-2-13)	110.0		
(1-2-14)	111.1	(12-2-13)	107.7	(12-2-14)	108.2	(13-2-14)	108.2		
(1-3-15)	111.1	(1-3-16)	110.8	(1-3-17)	110.5	(15-3-16)	108.0		
(15-3-17)	107.9	(16-3-17)	108.5	(1-4-6)	120.6	(1-4-7)	119.9		
(6-4-7)	117.9	(1-5-8)	127.7	(1-5-9)	113.9	(8-5-9)	118.5		
(5-8-10)	120.8	(5-8-11)	122.7	(10-8-11)	116.5				
(3-1-2-12)	-177.7	(3-1-2-13)	-58.2	(3-1-2-14)	61.5				
(4-1-2-12)	-56.3	(4-1-2-13)	63.2	(4-1-2-14)	-177.1				
(5-1-2-12)	61.3	(5-1-2-13)	-179.2	(5-1-2-14)	-59.5				
(2-1-3-15)	180.0	(2-1-3-16)	-60.0	(2-1-3-17)	60.2				
(4-1-3-15)	58.5	(4-1-3-16)	178.5	(4-1-3-17)	-61.2				
(5-1-3-15)	-56.7	(5-1-3-16)	63.3	(5-1-3-17)	-176.5				
(2-1-4-6)	-154.6	(2-1-4-7)	39.7	(3-1-4-6)	-33.4				
(3-1-4-7)	160.9	(5-1-4-6)	83.6	(5-1-4-7)	-82.0				
(2-1-5-8)	-7.4	(2-1-5-9)	174.1	(3-1-5-8)	-129.1				
(3-1-5-9)	52.4	(4-1-5-8)	112.8	(4-1-5-9)	-65.7				
(1-5-8-10)	-178.9	(1-5-8-11)	1.3	(9-5-8-10)	-0.4				

(9-5-8-11)	179.8								
Frequencies(cm^{-1}):	105.8	171.4	256.9	277.1	295.0	297.1	352.7	380.3	
	393.8	521.8	562.9	688.3	721.9	889.9	916.1	931.0	955.9	978.6
	1020.6	1030.8	1080.9	1195.9	1235.5	1261.9	1337.0	1400.7	1413.9	1445.3
	1467.4	1493.7	1495.1	1507.6	1518.7	1682.5	3031.7	3039.6	3103.0	3109.0
	3111.1	3114.4	3135.4	3144.4	3158.6	3237.9	3251.7			

Transition Structure for **1b** → **2c**
^{2}A UB3LYP/6-31+G(d,p) C_1 Geometry

Nuclear repulsion energy	238.640072 Hartree
RB3LYP/6-31+G(d,p) energy (<S_2> = 0.7729)	-235.190943 Hartree
Zero-point correction	0.149238 Hartree
Thermal correction to Energy @298K	0.156402 Hartree
Thermal correction to Enthalpy @ 298K	0.157346 Hartree
Thermal correction to Gibbs Free Energy @ 298K	0.118745 Hartree

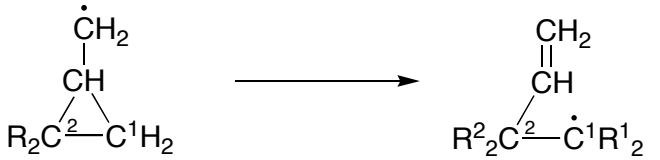


	X	Y	Z
C1	0.456980	0.027069	0.049833
C2	0.523439	1.551633	0.109573
C3	1.660866	-0.574916	-0.675301
C4	0.075909	-0.648274	1.321119
C5	-0.866905	-0.573492	-0.347363
H6	0.390440	-1.664160	1.533244
H7	-0.462505	-0.105474	2.088672
C8	-2.093879	0.067912	-0.429986
H9	-0.812016	-1.599320	-0.705063
H10	-2.983877	-0.487932	-0.704618
H11	-2.222675	1.115820	-0.181072
H12	-0.302696	1.975875	0.687343
H13	1.457392	1.865517	0.588537
H14	0.490002	1.982030	-0.897607
H15	1.595046	-1.667607	-0.717186
H16	1.722142	-0.200513	-1.703455
H17	2.590287	-0.313826	-0.156040

(1-2)	1.527	(1-3)	1.529	(1-4)	1.489	(1-5)	1.507	(2-12)	1.094
(2-13)	1.096	(2-14)	1.096	(3-15)	1.095	(3-16)	1.096	(3-17)	1.096
(4-6)	1.084	(4-7)	1.083	(5-8)	1.387	(5-9)	1.088	(8-10)	1.085
(8-11)	1.085								
(2-1-3)	112.2	(2-1-4)	115.5	(2-1-5)	116.5	(3-1-4)	115.3		
(3-1-5)	114.2	(4-1-5)	79.6	(1-2-12)	112.0	(1-2-13)	109.9		
(1-2-14)	110.8	(12-2-13)	107.6	(12-2-14)	108.1	(13-2-14)	108.4		
(1-3-15)	111.3	(1-3-16)	110.8	(1-3-17)	110.4	(15-3-16)	108.0		
(15-3-17)	107.9	(16-3-17)	108.4	(1-4-6)	121.2	(1-4-7)	120.3		
(6-4-7)	118.4	(1-5-8)	127.5	(1-5-9)	114.7	(8-5-9)	117.5		
(5-8-10)	120.3	(5-8-11)	122.6	(10-8-11)	117.1				
(3-1-2-12)	-176.1	(3-1-2-13)	-56.6	(3-1-2-14)	63.1				
(4-1-2-12)	-41.2	(4-1-2-13)	78.3	(4-1-2-14)	-161.9				
(5-1-2-12)	49.6	(5-1-2-13)	169.2	(5-1-2-14)	-71.1				
(2-1-3-15)	-179.5	(2-1-3-16)	-59.4	(2-1-3-17)	60.7				
(4-1-3-15)	45.5	(4-1-3-16)	165.6	(4-1-3-17)	-74.3				
(5-1-3-15)	-44.2	(5-1-3-16)	75.9	(5-1-3-17)	-164.0				
(2-1-4-6)	-153.7	(2-1-4-7)	21.8	(3-1-4-6)	-20.2				
(3-1-4-7)	155.3	(5-1-4-6)	91.8	(5-1-4-7)	-92.8				
(2-1-5-8)	-12.8	(2-1-5-9)	160.3	(3-1-5-8)	-146.1				
(3-1-5-9)	27.0	(4-1-5-8)	100.6	(4-1-5-9)	-86.2				

(1-5-8-10)	-178.3	(1-5-8-11)	-1.4	(9-5-8-10)	8.7				
(9-5-8-11)	-174.4								
Frequencies(cm^{-1}):	-526.7	197.3	220.6	256.2	275.2	362.9	371.2	395.7	
	476.4	514.5	628.2	693.2	731.9	747.4	867.1	924.9	949.6	966.5
	1014.1	1028.2	1085.2	1178.4	1249.3	1265.8	1331.4	1405.3	1416.3	1424.4
	1474.0	1490.5	1491.2	1506.1	1513.4	1527.4	3029.6	3039.4	3100.4	3103.8
	3107.1	3117.6	3161.8	3165.0	3170.2	3255.0	3278.4			

Tabel S1. UB3LYP/6-31+G(d,p) CVT and CVT+SCT Rate Constants(s^{-1}) for ring opening of **1a-c** to **2a-e** at 20K.



1a, R = H
b, R = CH_3
c, R = D

2a, $R^1 = R^2 = H$
b, $R^1 = CH_3$, $R^2 = H$
c, $R^1 = H$, $R^2 = CH_3$
d, $R^1 = D$, $R^2 = H$
e, $R^1 = H$, $R^2 = D$

	k_{CVT}	$k_{CVT+SCT}$
1a → 2a	8.5656E-65	4.4586E-01
1b → 2b	6.3163E-39	4.4235E+03
1b → 2c	3.6561E-59	5.7136E-03
1c → 2d	1.8547E-67	4.2494E-02[a]
1c → 2e	1.7220E-64	2.5828E-01[a]

[a] The UB3LYP/6-31+G(d,p) CVT + SCT rate ratios for *k* (**1a**)/2*k*(**1c**) are 5.25 for forming **2d** and 0.86 for forming **2d**. These ratios are similar to the previously published values (ref. 13) of, respectively, 6.47 and 0.85, obtained with the 6-31G(d) basis set and given in Table 1 of this manuscript.