SUPPORTING INFORMATION

Thermal Rearrangement of Optically Active Tetradeuterated 2-methoxymethyl-methylenecyclopropane and the Bent Bond / Antiperiplanar Hypothesis

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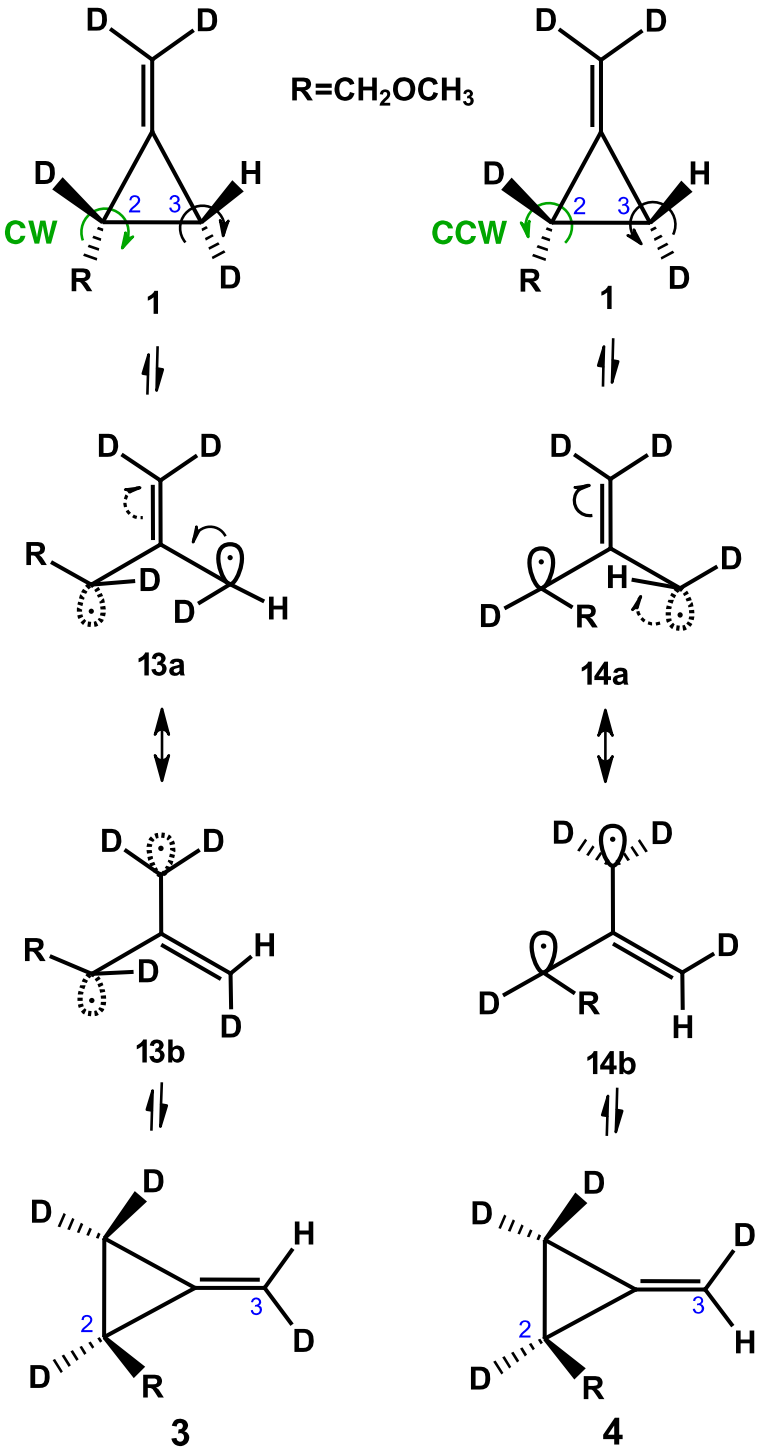


Fig. SI-1. Conrotatory cleavage of **1** with no inversion. Radical inversions shown in red. Rotational direction at C_2 (CW/CCW) shown in green.

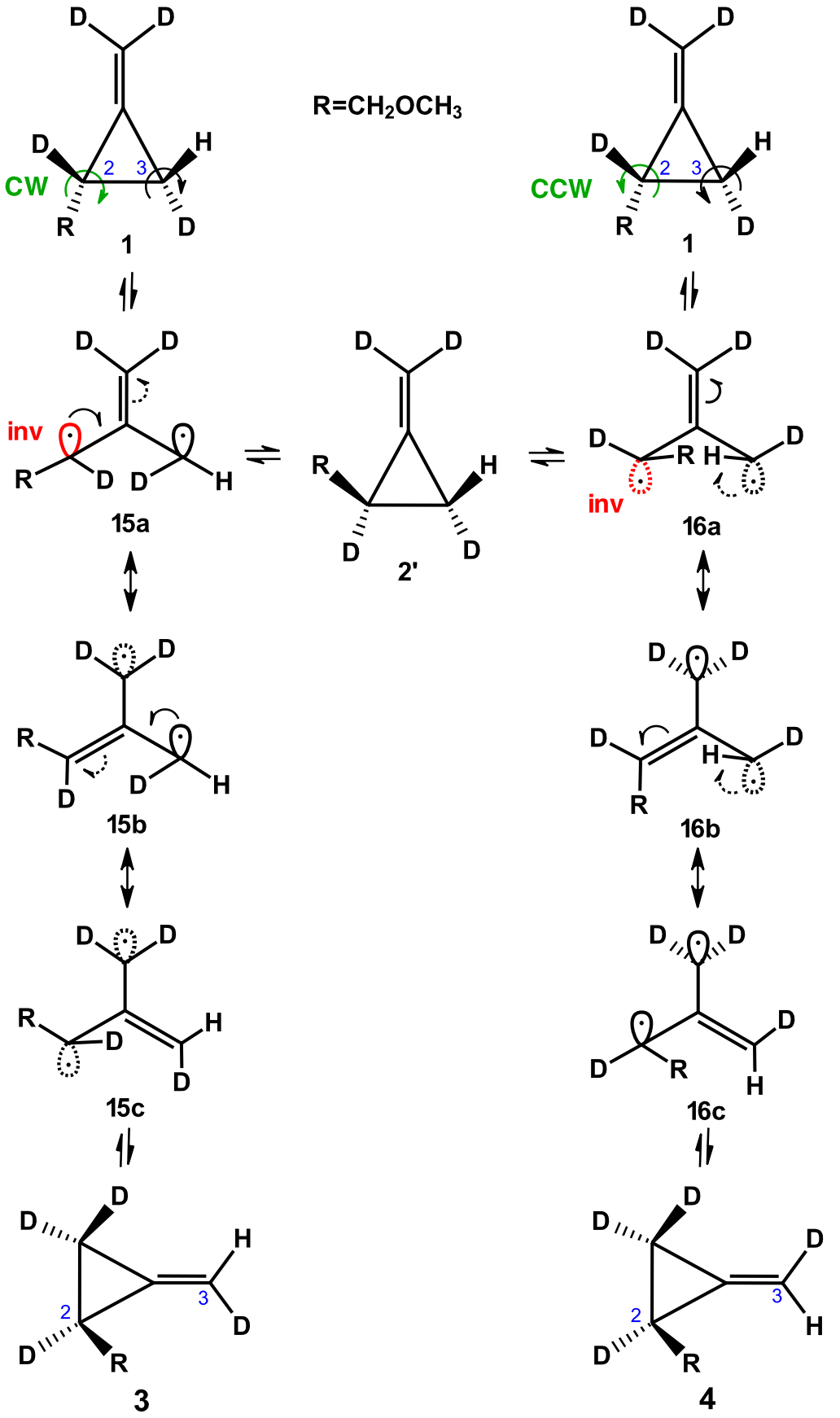


Fig. SI-2. Conrotatory cleavage of **1** with single inversion at C_2. Radical inversions shown in red. Rotational direction at C_2 (CW/CCW) shown in green.

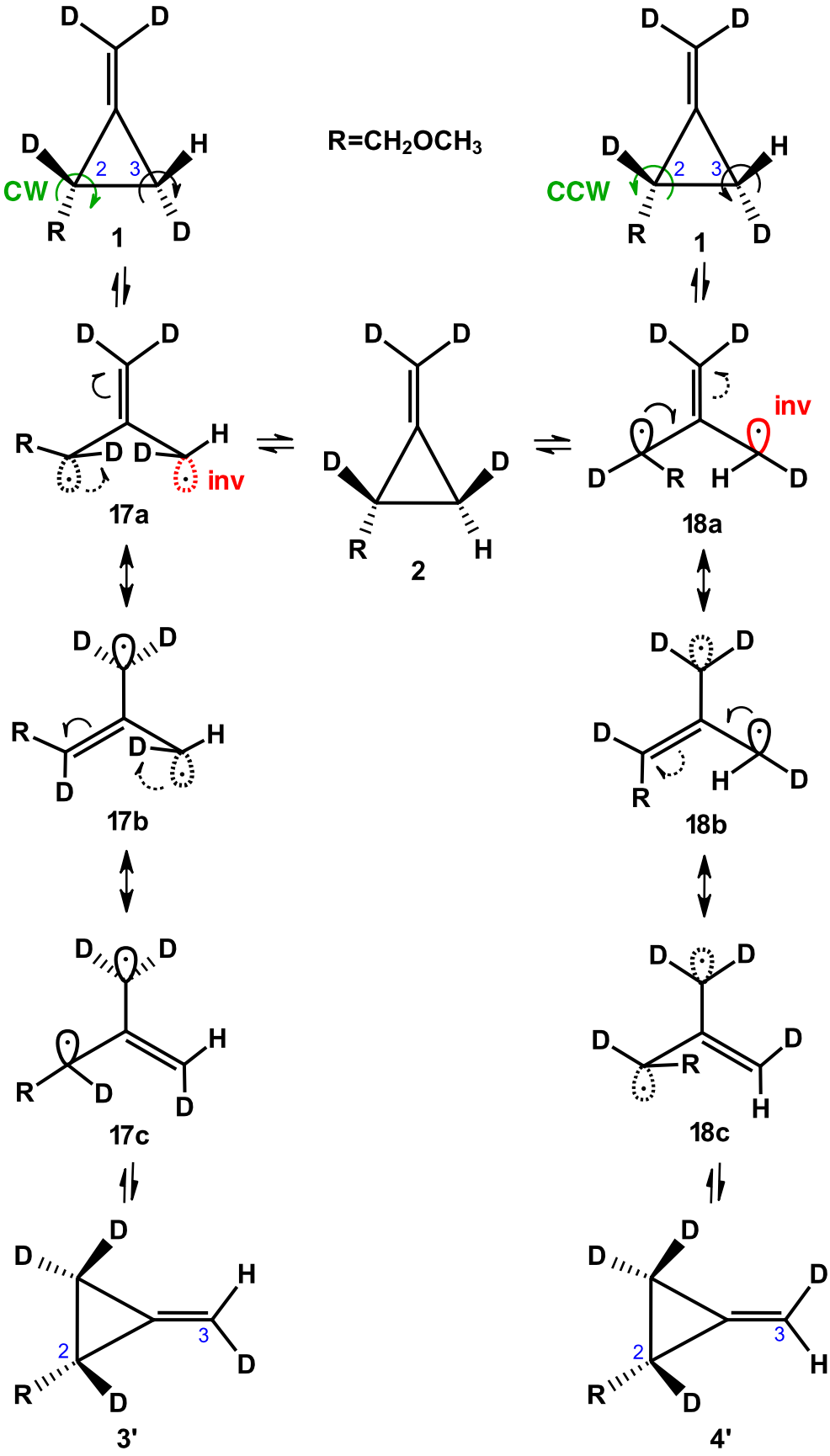


Fig. SI-3. Conrotatory cleavage of **1** with single inversion at C_3. Radical inversions shown in red. Rotational direction at C_2 (CW/CCW) shown in green.

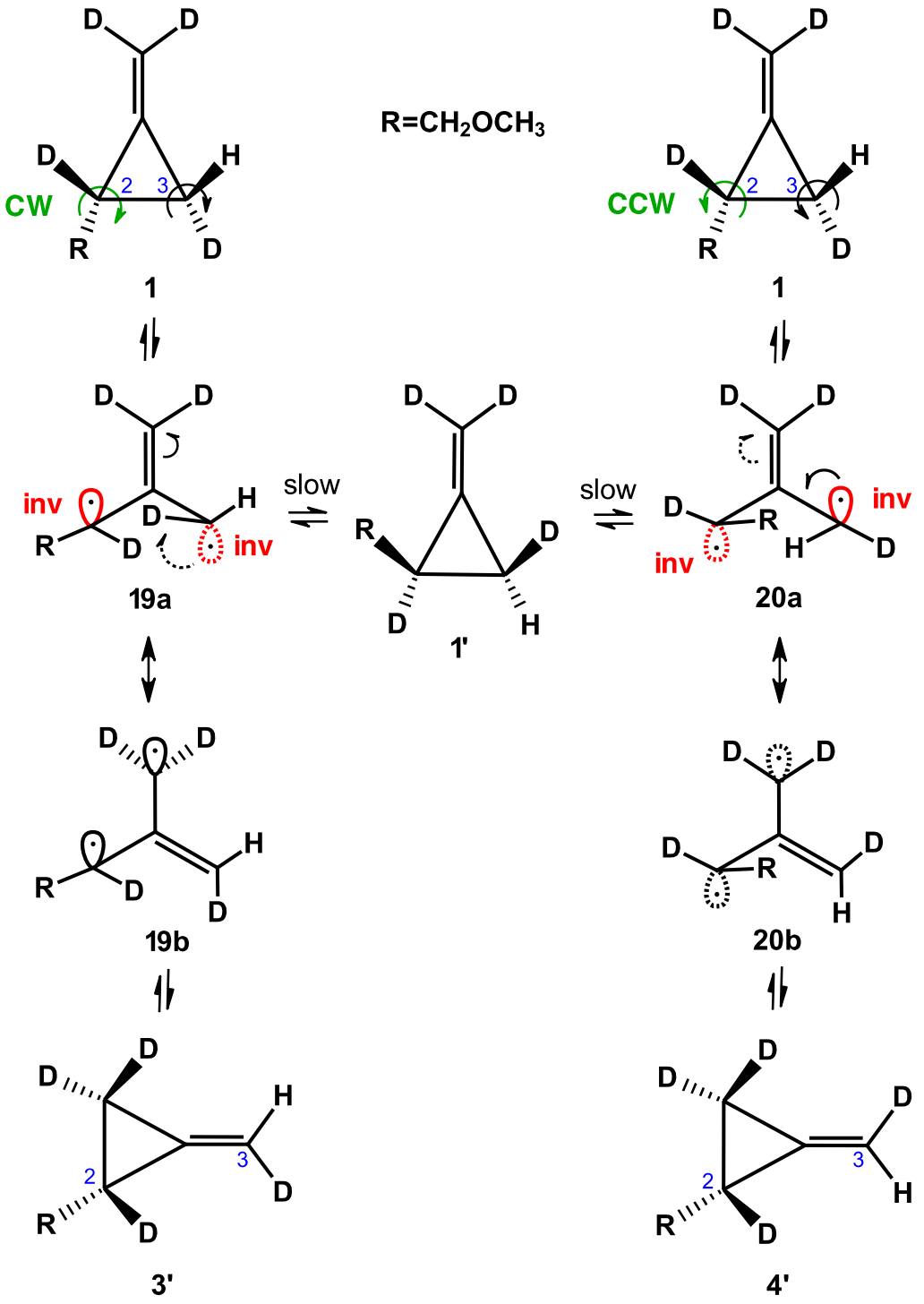


Fig. SI-4. Conrotatory cleavage of **1** with double inversion at C_2 and C_3. Radical inversions shown in red. Rotational direction at C_2 (CW/CCW) shown in green.

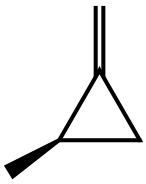
Table SI-1. BBAH analysis summary for disrotatory mode of cleavage of **1-4** and **1′-4′**

Stereoisomer	Inversion	Products
1	none	**3′, 4′, 1**
″	C_2	**3′, 4′, 2′**
″	C_3	**3, 4, 2**
″	C_2 and C_3	**3, 4, 1′**
1′	none	**3, 4, 1′**
″	C_2	**3, 4, 2**
″	C_3	**3′, 4′, 2′**
″	C_2 and C_3	**3′, 4′, 1**
2	none	**3′, 4′, 2**
″	C_2	**3′, 4′, 1′**
″	C_3	**3, 4, 1**
″	C_2 and C_3	**3, 4, 2′**
2′	none	**3, 4, 2′**
″	C_2	**3, 4, 1**
″	C_3	**3′, 4′, 1′**
″	C_2 and C_3	**3′, 4′, 2**
3	none	**1′, 2′, 3**
″	C_2	**1′, 2′, 3′**
″	C_3	**1, 2, 3′**
″	C_2 and C_3	**1, 2, 3′**
3′	none	**1, 2, 3′**
″	C_2	**1, 2, 3**
″	C_3	**1′, 2′, 3′**
″	C_2 and C_3	**1′, 2′, 3**
4	none	**1′, 2′, 4**
″	C_2	**1′, 2′, 4′**
″	C_3	**1, 2, 4**
″	C_2 and C_3	**1, 2, 4′**
4′	none	**1, 2, 4′**
″	C_2	**1, 2, 4**
″	C_3	**1′, 2′, 4′**
″	C_2 and C_3	**1′, 2′, 4**

Table SI-2. BBAH analysis summary for conrotatory mode of cleavage of **1-4** and **1′-4′**

Stereoisomer	Inversion	Products
1	none	**3, 4, 1**
″	C_2	**3, 4, 2′**
″	C_3	**3′, 4′, 2**
″	C_2 and C_3	**3′, 4′, 1′**
1′	none	**3′, 4′, 1′**
″	C_2	**3′, 4′, 2**
″	C_3	**3, 4, 2′**
″	C_2 and C_3	**3, 4, 1**
2	none	**3, 4, 2**
″	C_2	**3, 4, 1′**
″	C_3	**3′, 4′, 1**
″	C_2 and C_3	**3′, 4′, 2′**
2′	none	**3′, 4′, 2′**
″	C_2	**3′, 4′, 1**
″	C_3	**3, 4, 1′**
″	C_2 and C_3	**3, 4, 2**
3	none	**1, 2, 3**
″	C_2	**1, 2, 3′**
″	C_3	**1′, 2′, 3**
″	C_2 and C_3	**1′, 2′, 3′**
3′	none	**1′, 2′, 3′**
″	C_2	**1′, 2′, 3**
″	C_3	**1, 2, 3′**
″	C_2 and C_3	**1, 2, 3**
4	none	**1, 2, 4**
″	C_2	**1, 2, 4′**
″	C_3	**1′, 2′, 4**
″	C_2 and C_3	**1′, 2′, 4′**
4′	none	**1′, 2′, 4′**
″	C_2	**1′, 2′, 4**
″	C_3	**1, 2, 4′**
″	C_2 and C_3	**1, 2, 4**

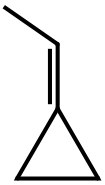
Table SI-3. XYZ coordinates for geometry optimized 2-methyl-1-methylenecyclopropane



-122544.86 kcal/mol (G16,[1] wB97XD/Def2TZVPP)

Atom	**X**	**Y**	**Z**
C	0.761585	0.032436	0.066817
C	-0.630466	0.107508	0.505245
H	-0.788616	0.2178	1.57319
C	-1.711221	-0.652474	-0.223188
H	-2.679916	-0.164212	-0.106528
H	-1.796328	-1.671076	0.15758
H	-1.485809	-0.713912	-1.288726
C	0.063183	1.297357	-0.168803
H	0.314266	2.155372	0.442263
H	-0.234466	1.536472	-1.183359
C	1.854725	-0.682199	-0.069985
H	2.74057	-0.271275	-0.538252
H	1.90346	-1.704941	0.283313

Table SI-4. XYZ coordinates for geometry optimized 1-ethylidenecyclopropane



-122545.84 kcal/mol (G16,[1] wB97XD/Def2TZVPP)

Atom	X	Y	Z
C	-0.312249	-0.209715	0.000901
C	-1.238725	0.92189	-0.000149
H	-1.363156	1.494071	-0.911347
H	-1.365203	1.494036	0.910794
C	-1.736623	-0.529319	-0.000299
H	-2.186606	-0.903569	-0.911592
H	-2.188414	-0.902711	0.910455
C	0.934082	-0.626633	0.0
C	2.127813	0.276282	-0.000109
H	2.753229	0.097948	-0.877789
H	2.753729	0.097582	0.87716
H	1.827793	1.323543	0.000257
H	1.122838	-1.695926	-0.000262

[1] Gaussian 16, Revision B.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2016.