

Matrix Isolation and Photorearrangement of *Cis*- and *Trans*-1,2-Ethenediol to Glycolaldehyde

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Experimental Procedures

Matrix Apparatus Design. For the matrix isolation studies, we used an APD Cryogenics HC-2 cryostat with a closed-cycle refrigerator system, equipped with an inner CsI window for IR measurements. Spectra were recorded with a Bruker IFS 55 FT-IR spectrometer with a spectral range of 4500–400 cm^{-1} and a resolution of 0.7 cm^{-1} and UV/Vis spectra were recorded with a JASCO V-670 spectrophotometer equipped with an inner sapphire window. A high-pressure mercury lamp (HBO 200, Osram) with a monochromator (Bausch & Lomb) was used for irradiation.

For the combination of high-vacuum flash pyrolysis with matrix isolation, we employed a small, home-built, water-cooled oven, which was directly connected to the vacuum shroud of the cryostat. The pyrolysis zone consisted of an empty quartz tube with an inner diameter of 8 mm, which was resistively heated over a length of 50 mm by a coaxial wire. The temperature was monitored with a NiCr–Ni thermocouple. Compounds **3** (at 10 °C), d_2 -**3** (at 5 °C) and **5** (at 170 °C), d_2 -**5** (at 150 °C) were evaporated from a storage bulb into the quartz pyrolysis tube. At a distance of approximately 50 mm, all pyrolysis products were co-condensed with a large excess of argon (typically 60–120 mbar from a 2000 mL storage bulb) on the surface of the matrix window at 10 K. Several experiments with pyrolysis temperatures ranging from 400 to 800 °C were performed in order to determine the optimal pyrolysis conditions.

Computations. All coupled cluster computations were carried out with the CFOUR^[1] program package. In general, the all electron coupled cluster level of theory^[2] including single, double, and perturbatively included triple excitations [AE-CCSD(T)] utilizing the Dunning correlation consistent split valence basis set cc-pVTZ^[3] was employed for geometry optimizations and frequency computations. For all B3LYP^[4] computations we used the Gaussian16^[5] program package.

Synthesis of *endo,cis*-Bicyclo[2.2.1]hept-5-ene-2,3-diol (3**).** *N*-Methylmorpholine *N*-oxide (1.9 g, 16.2 mmol) and $\text{K}_2\text{OsO}_4 \cdot 2\text{H}_2\text{O}$ (29.4 mg, 0.081 mmol) were added to a solution of norbornadiene (1.5 g, 16.2 mmol) in acetone and H_2O (20 + 5 mL) and the reaction mixture was stirred at 40 °C for 14 h. After cooling to rt, $\text{Na}_2\text{S}_2\text{O}_5$ (0.10 g) was added and the reaction mixture was stirred at rt for another 30 min. All volatiles were removed under reduced pressure and the black residue was purified by flash chromatography (hexane/EtOAc = 2:1) to afford **3** as a colorless crystalline solid (1.10 g, 8.7 mmol 55%). ^1H NMR (400 MHz, CDCl_3): δ = 6.04 (m, 2H), 3.71 (m, 2H), 2.95 (m, 2H), 2.70 (m, 2H), 1.89 (d, J = 9.2 Hz, 1H), 1.63 (d, J = 9.2 Hz, 1H) ppm. ^{13}C NMR (126 MHz, CDCl_3): δ = 136.6, 69.2, 48.2, 42.4 ppm. The spectral data were consistent with the literature.^[6]

Synthesis of d_2 -3**.** A solution of **3** (126 mg, 1 mmol) in dry THF (5 mL) was added dropwise to a suspension of NaH (48 mg, 2 mmol) in dry THF (1 mL). The reaction mixture was stirred at rt for 30 min then quenched by dropwise addition of D_2O (5 mL) and the mixture was extracted with dry ethylacetate. The combined organic extracts dried over Na_2SO_4 , filtered, and the solvent was removed under reduced pressure.

Synthesis of *trans*-9,10-dihydro-9,10-ethanoanthracene-11,12-diol (5**).** A solution of *trans*-11,12-diacetyl-9,10-dihydro-9,10-ethanoanthracene^[7] (2.46 g, 8.47 mmol) and *m*CPBA (16.66 g, 74.34 mmol) in DCM was stirred at rt for 28 d. The resulting suspension was diluted with Et_2O (200 mL) and subsequently washed with 10% aq. Na_2SO_3 (3 × 120 mL), sat. aq. NaHCO_3

(3 × 120 mL), and brine (120 mL). The organic phase was dried over MgSO₄, filtered, and the solvent was removed under reduced pressure. To the crude product (2.22 g, 6.89 mmol) were added MeOH/H₂O (5:2, 170 mL) and K₂CO₃ (1.91 g, 13.82 mmol) and the mixture was stirred at rt for 2 h. The pH was adjusted to ~ 4 with 1 N HCl and all volatiles were removed under reduced pressure. Purification by flash chromatography (DCM/MeOH = 20:1) afforded **5** as a colorless solid (1.18 g, 4.95 mmol, 59% over two steps). ¹H NMR (400 MHz, MeOH-*d*₄): δ = 7.33 – 7.27 (m, 4H), 7.14 – 7.09 (m, 4H), 4.19 (m, 2H), 3.70 (dd, *J* = 2.5, 1.3 Hz, 2H) ppm. ¹³C NMR (101 MHz, MeOH-*d*₄): δ = 141.9, 141.4, 127.2, 127.2, 127.1, 125.2, 79.6, 53.6 ppm. HRMS (ESI): *m/z* = 261.0886 [M+Na]⁺ (calcd *m/z* = 261.0886).

Synthesis of *d*₂-5**.** A solution of **5** (238 mg, 1 mmol) in dry THF (5 mL) was added dropwise to a suspension of NaH (48 mg, 2 mmol) in dry THF (1 mL). The reaction mixture was stirred at rt for 30 min then quenched by dropwise addition of D₂O (5 mL) and the mixture was extracted with dry ethylacetate. The combined organic extracts dried over Na₂SO₄, filtered, and the solvent was removed under reduced pressure.

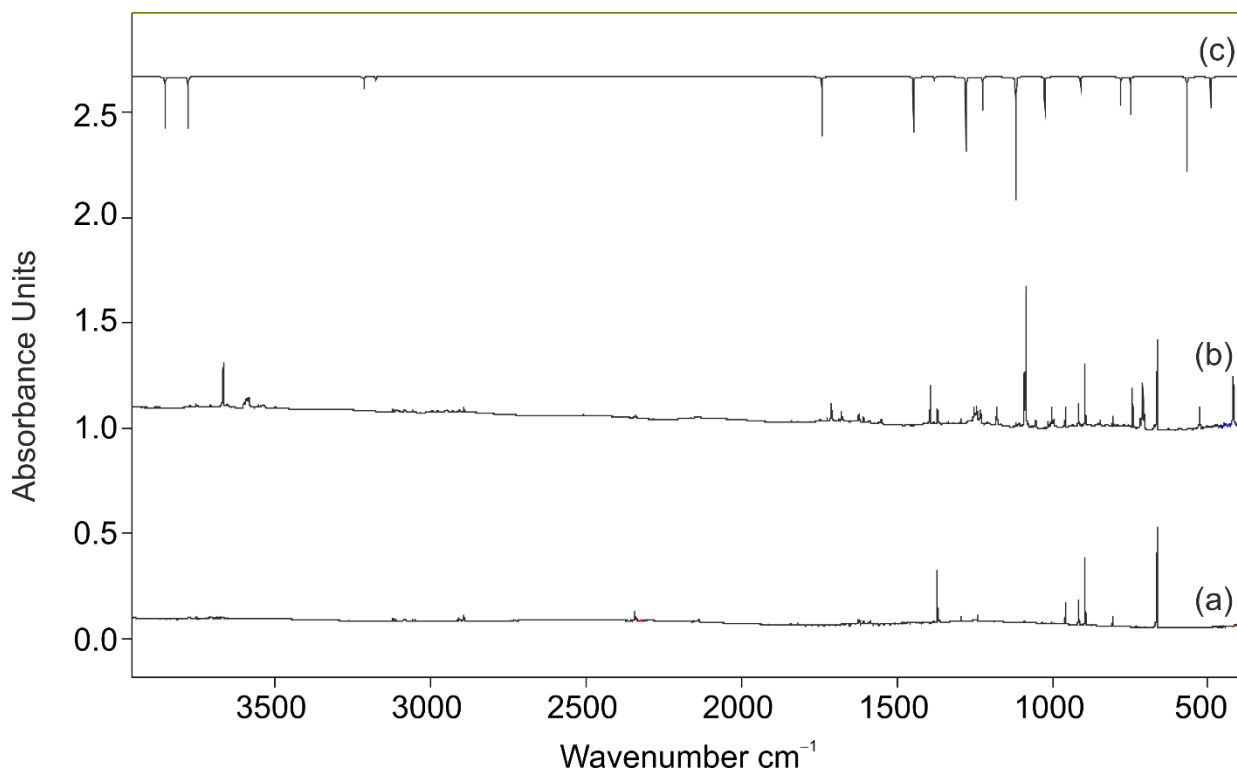


Figure S1. (a) IR spectra of **4** in argon matrix. (b) IR spectra showing the product of pyrolysis of **3** with subsequent trapping in an argon matrix at 10 K. (c) IR spectra showing the product of pyrolysis of **4** with subsequent trapping in an argon matrix at 10 K. (c) IR spectrum of *cis*-**2** computed at CCSD(T)/cc-pVTZ (unscaled).

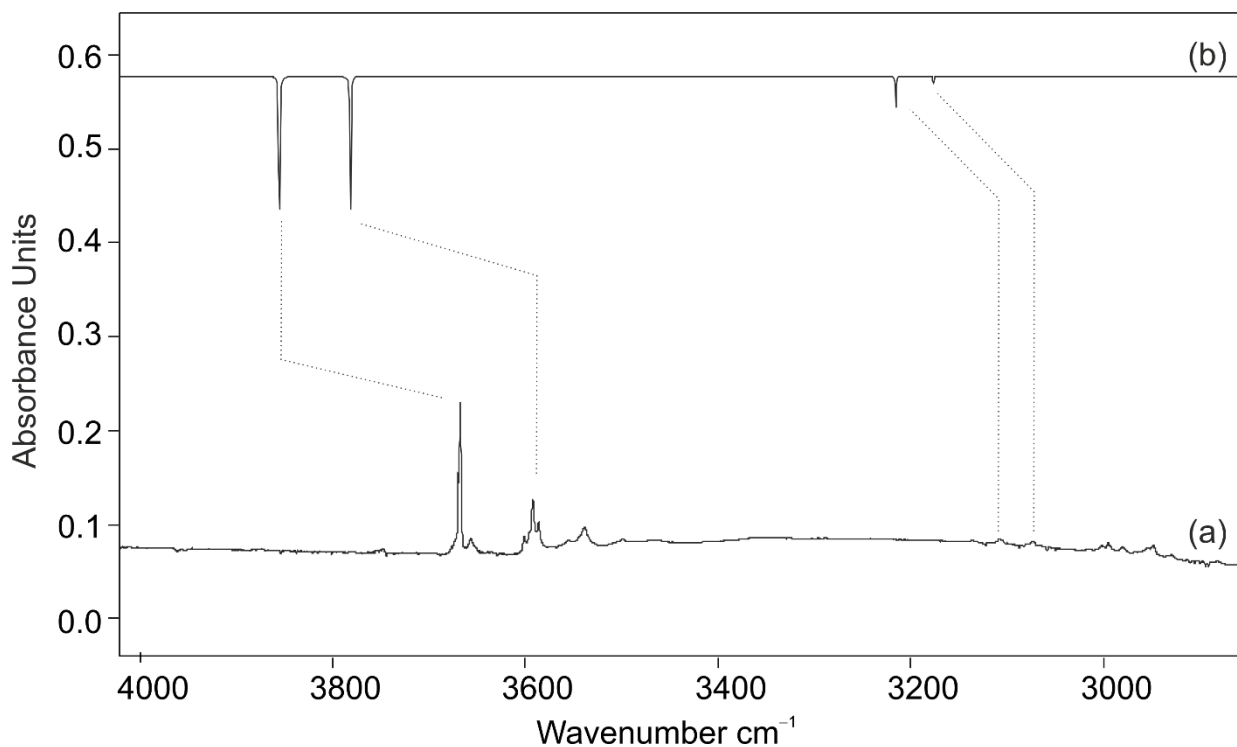


Figure S2. (a) IR spectrum showing the pyrolysis product of **3** with subsequent trapping in an argon matrix at 10 K. The matrix isolation spectrum of **4** was subtracted (downward bands). (b) IR spectrum of *cis*-**2** computed at AE-CCSD(T)/cc-pVTZ (unscaled).

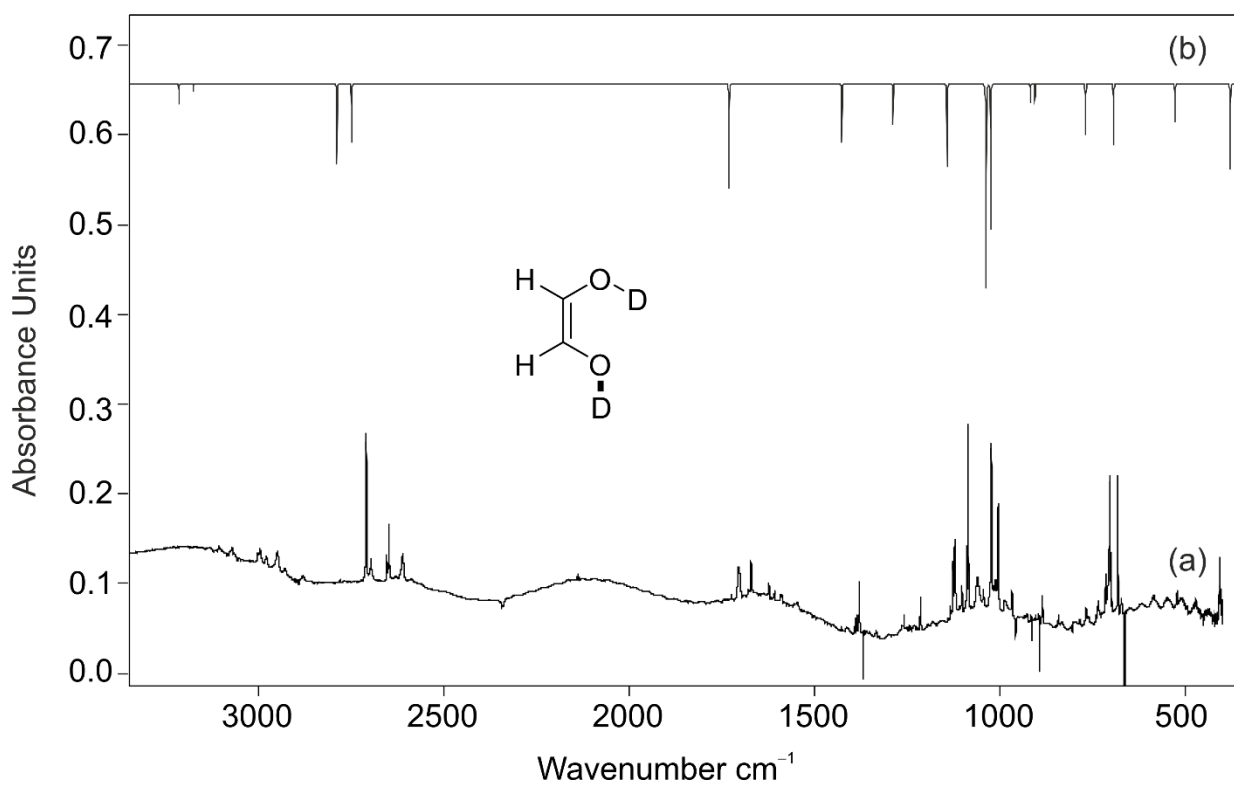


Figure S3. (a) IR spectra showing the product of pyrolysis of d_2 -3 in argon matrix with subsequent trapping in an argon matrix at 10 K. The matrix isolation spectrum of **4** was subtracted (downward bands). (b) IR spectrum of d_2 -cis-2 computed at AE-CCSD(T)/cc-pVTZ (unscaled).

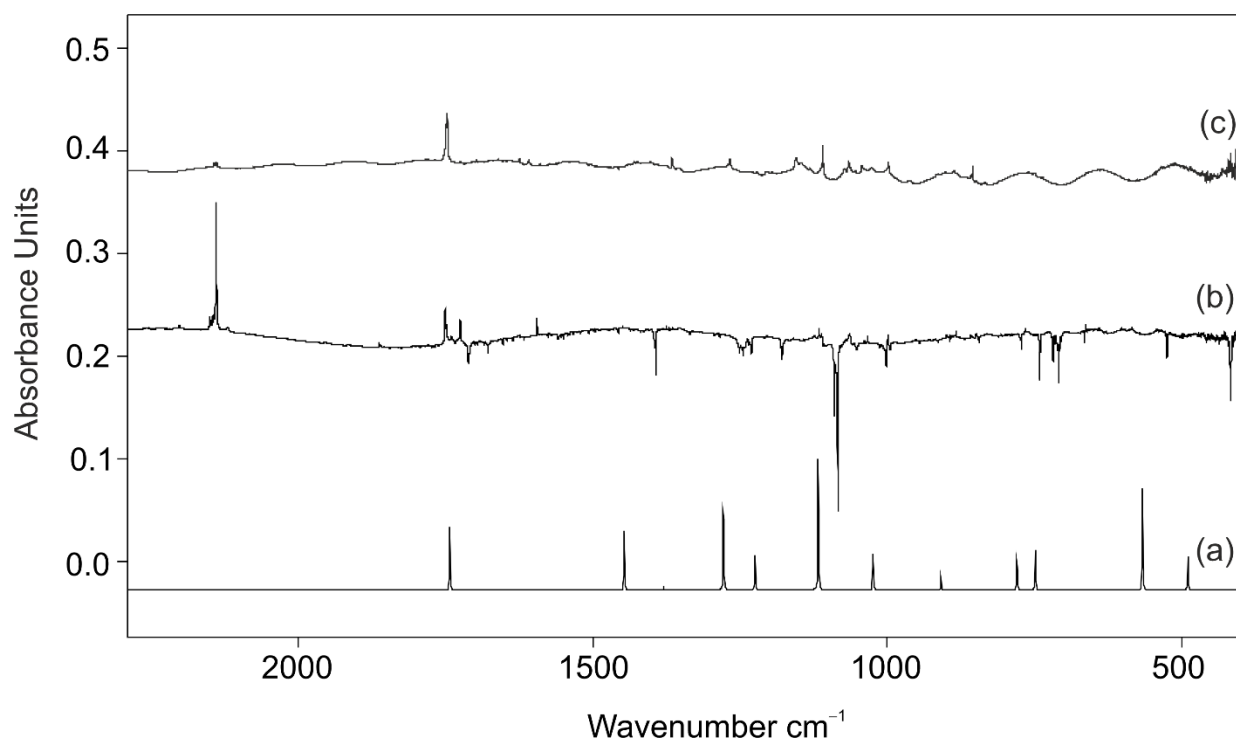


Figure S4. IR spectra showing the product of pyrolysis of **3** in argon matrix with subsequent trapping in an argon matrix at 10 K. (a) IR spectrum of *cis*-**2** computed at AE-CCSD(T)/cc-pVTZ (unscaled). (b) IR difference spectra showing the photochemistry of *cis*-**2** after irradiation first with $\lambda > 200$ nm in argon at 10 K for 1 h then with $\lambda = 180$ -254 nm in argon at 10 K for 1 h then. Downward bands assigned to *cis*-**2** disappear while upward bands assigned to **1** and CO. (c) IR spectrum of **1** isolated in argon matrix.

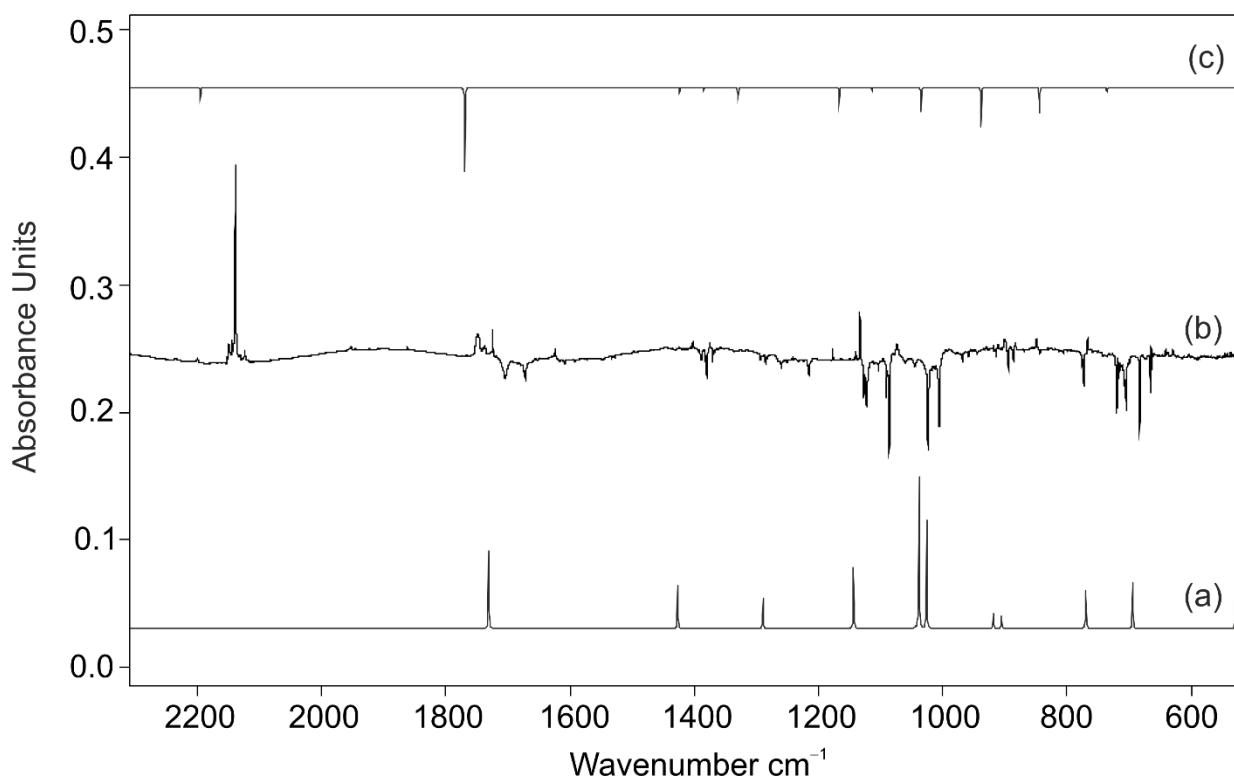


Figure S5. IR spectra showing the product of pyrolysis of d_2 -**3** in argon matrix with subsequent trapping in an argon matrix at 10 K. (a) IR spectrum of d_2 -*cis*-**2** computed at AE-CCSD(T)/cc-pVTZ (unscaled) (b) IR difference spectra showing the photochemistry of d_2 -*cis*-**2** after irradiation first with $\lambda > 200$ nm in argon at 10 K for 1 h then with $\lambda = 180$ -254 nm in argon at 10 K for 1 h. Downward bands assigned to d_2 -*cis*-**2** disappear while upward bands assigned to d_2 -**1** and CO. (c) IR spectrum of d_2 -**1** computed at AE-CCSD(T)/cc-pVTZ (unscaled).

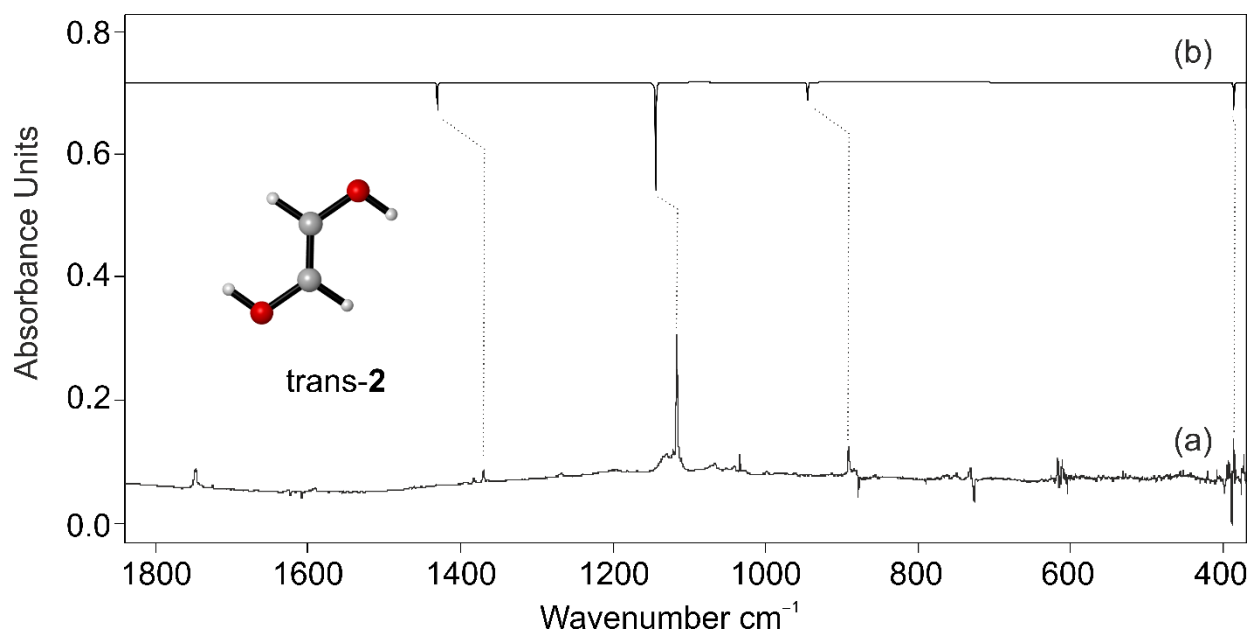


Figure S6. (a) IR spectrum showing the pyrolysis product of **5** with subsequent trapping in an argon matrix at 10 K. The matrix isolation spectrum of **6** was subtracted (downward bands). (b) IR spectrum of *trans*-**2** computed at AE-CCSD(T)/cc-pVTZ (unscaled).

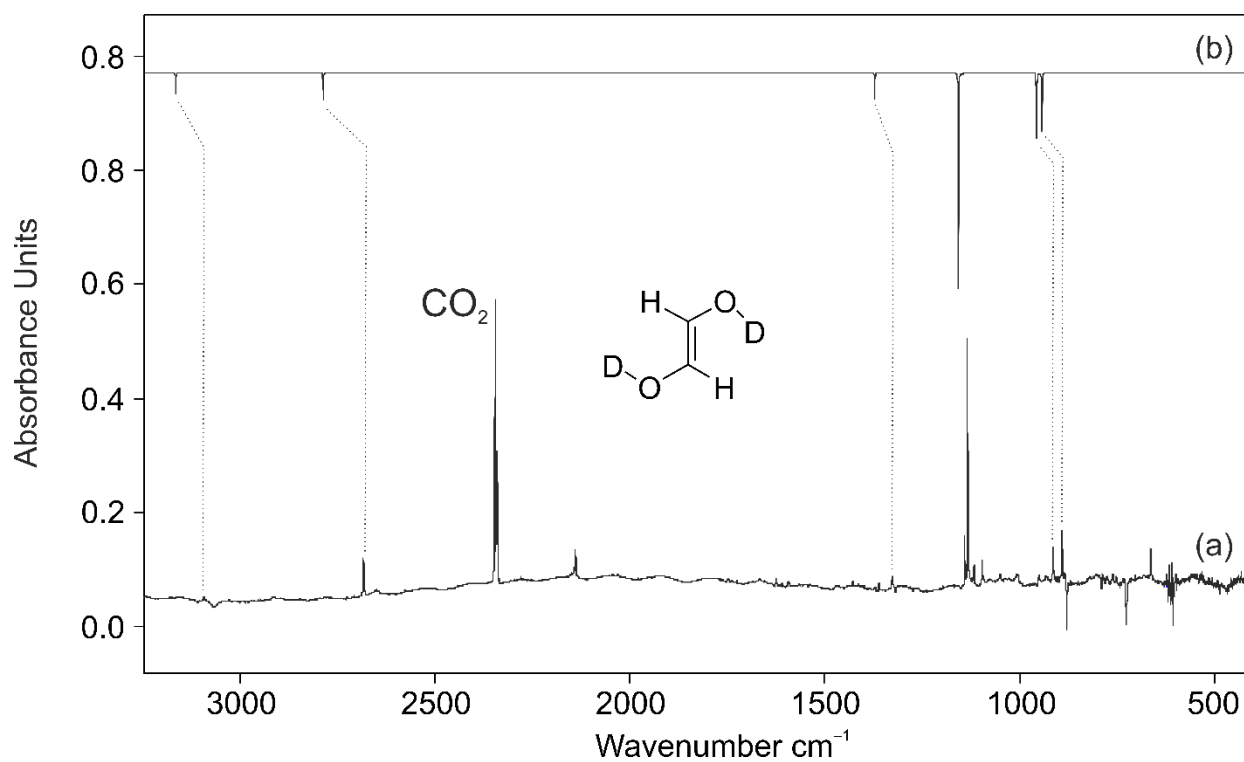


Figure S7. (a) IR spectra showing the product of pyrolysis of d_2 -**5** in argon matrix with subsequent trapping in an argon matrix at 10 K. The matrix isolation spectrum of **6** was subtracted (downward bands). (b) IR spectrum of d_2 -trans-**2** computed at AE-CCSD(T)/cc-pVTZ (unscaled).

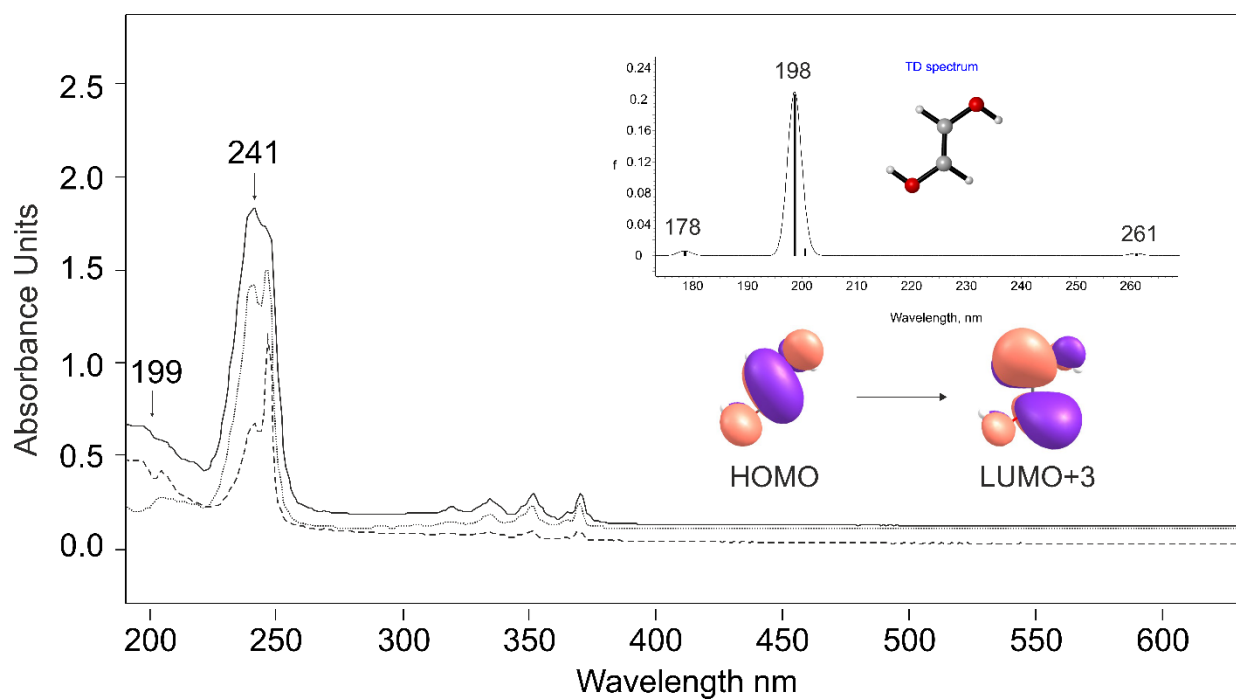


Figure S8. Solid line: UV/Vis spectrum showing the pyrolysis product of **5** with subsequent trapping in an argon matrix at 10 K. Dashed line: after irradiation at $\lambda = 180\text{-}254$ nm for 30 min in argon at 10 K. Dotted line: UV/Vis spectrum of matrix-isolated **6** in argon at 10 K. Inset: computed [TD-B3LYP/6-311++G(2d,p)] electronic transitions for *trans*-**2**.

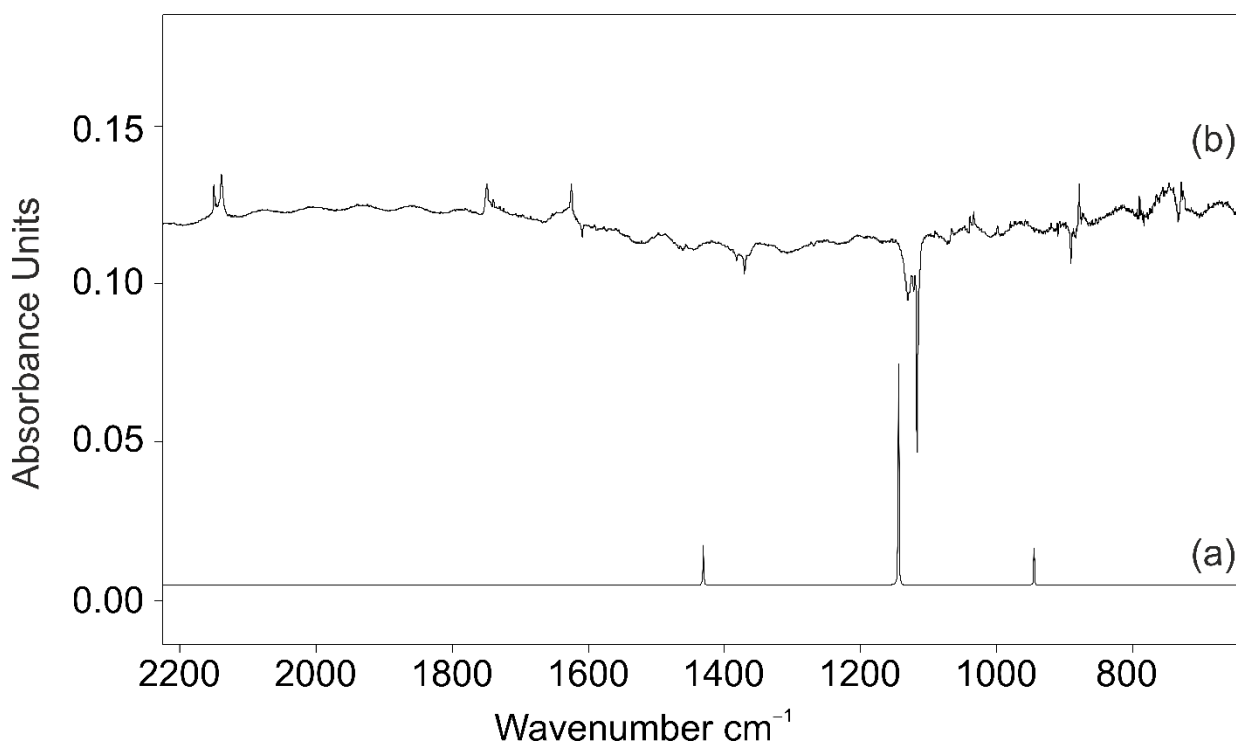


Figure S9. IR spectra showing the product of pyrolysis of **5** in argon matrix with subsequent trapping in an argon matrix at 10 K. (a) IR spectrum of *trans*-**2** computed at AE-CCSD(T)/cc-pVTZ (unscaled). (b) IR difference spectra showing the photochemistry of *trans*-**2** after irradiation $\lambda = 180\text{-}254$ nm in argon at 10 K for 1 h. Downward bands assigned to *trans*-**2** disappear while upward bands assigned to **1** and CO.

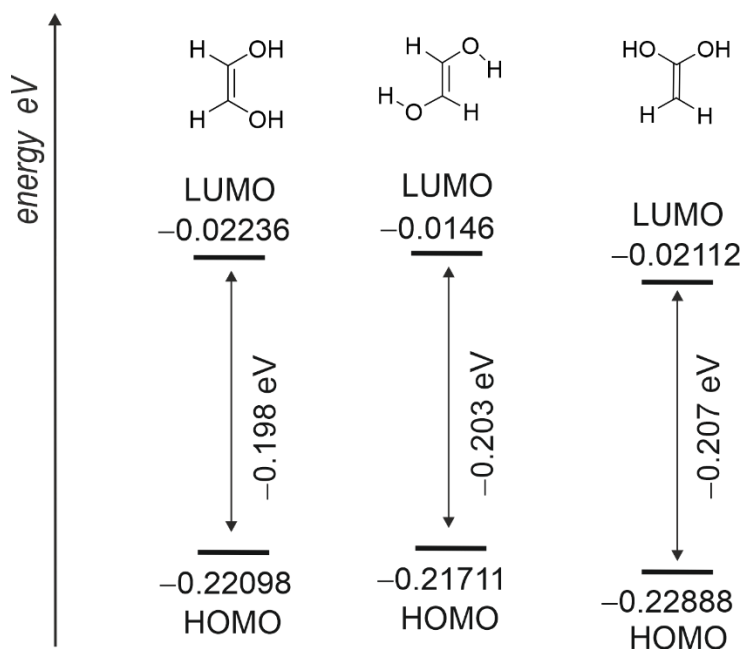


Figure S10. HOMO – LUMO energies of enols computed at the B3LYP/6-311++G(2d,2p) level of theory.

Table S1. Experimental (Ar matrix, 10 K) and computed IR frequencies of *cis-2as* and *d₂-cis-2as*, band origins in cm⁻¹, computed intensities (km mol⁻¹) in parentheses.

Mode	2	2	<i>d₂-2</i>	<i>d₂-2</i>	Assignment
	Computed ^a	Ar, 10 K ^b	Computed ^a	Ar, 10 K ^b	
18	3855 (66)	3667 (s)	2789 (38)	2710 (s)	OH str.
17	3781 (48)	3592 (m)	2750 (29)	2650 (m)	OH str.
16	3215 (11)	3108 (w)	3215 (10)	3108 (w)	CH str.
15	3177 (3)	3074 (w)	3177 (4)	3074 (w)	CH str.
14	1742 (50)	1711 (m)	1731 (49)	1704 (m)	C=C str.
13	1447 (49)	1393 (s)	1427 (28)	1379 (m)	CH def./COH def.
12	1380 (3)	1333 (w)	1143 (42)	1085 (s)	CO str.
11	1278 (108)	1245 (m)	1289 (22)	1259 (m)	CO str.
10	1224 (31)	1178 (m)	919 (13)	894 (w)	OH def./ CH def.
9	1117 (150)	1084 (s)	1038 (114)	1024 (s)	2CO str. asym
8	1025 (42)	1001 (m)	1026 (69)	1006 (s)	2CO str. sym
7	909 (9)	-	906 (11)	886 (w)	CH out-of-pl. def
6	780 (35)	742 (s)	770 (37)	704 (s)	CH out-of-pl. def.
5	749 (33)	709 (s)	694 (30)	682 (s)	CCO def.
4	568 (82)	525 (m)	529 (20)	523 (w)	CC twisting
3	491 (43)	418 (s)	380 (86)	407 (s)	CO twisting
2	275 (115)	-	242 (27)	-	OH wagging
1	242 (25)	-	186 (50)	-	CCO def.

^a AE-CCSD(T)/cc-pVTZ, harmonic approximation, unscaled frequencies, intensities (in parentheses) in km mol⁻¹. ^b Experiment: argon matrix, 10 K.; approximate relative intensities (w: weak, m: medium, s: strong).

Table S2. Experimental (Ar matrix, 10 K) and computed IR frequencies of *trans-2ss* and d_2 *trans-2ss*, band origins in cm^{-1} , computed intensities (km mol^{-1}) in parentheses.

Mode	2t		d_2 - 2t		Assignment
	Computed ^a	Ar, 10 K ^b	Computed ^a	Ar, 10 K ^b	
18	3831 (0)	-	2787 (0)	-	2OH str.sym
17	3827 (69.1)	3637(s)	2785 (47.1)	2683 (m)	2OH str. asym
16	3167 (0)	-	3167 (0)	-	2CH str. sym
15	3163 (27)	3099 (w)	3163 (25.7)	3092 (w)	2CH str. asym
14	1736 (0)	-	1732 (0)	-	C=C str.
13	1431 (94)	1369 (m)	1372 (35.2)	1328 (w)	CH def./COH def.
12	1363 (0)	-	1338 (0)	-	2COH def. sym
11	1338 (0)	-	1212 (0)	-	2CCH def. sym
10	1232 (1.8)	-	927 (0)	-	2CH/OH def. sym.
9	1144 (380)	1117 (s)	1157 (279)	1134 (s)	2CO str. asym
8	1076 (0)	-	957 (80.1)	915 (m)	2CO str. sym
7	945 (84)	891 (s)	943 (72.2)	890 (m)	CH out-of-pl. def
6	827 (0)	-	825 (0)	-	CH out-of-pl. def. sym
5	564 (0)	-	524 (0)	-	2CCO def. sym
4	386 (94.4)	386 (s)	365 (31.1)	-	2CO twisting asym
3	323 (0)	-	258 (0)	-	2CO twisting sym
2	323 (33.7)	-	305 (32)	-	COH wagging
1	263 (95.7)	-	200 (72)	-	CCO def.

^a AE-CCSD(T)/cc-pVTZ, harmonic approximation, unscaled frequencies, intensities (in parentheses) in km mol^{-1} . ^b Experiment: argon matrix, 10 K.; approximate relative intensities (w: weak, m: medium, s: strong).

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AE-CCSD(T)/cc-pVTZ optimized structures (distances in bohr), electronic energies (in hartree) and zero-point vibrational energies (ZPVE).

1a: Glycolaldehyde (C_2)

6	0.802158360	-0.543389553	0.000000000
1	1.392113537	-1.475585358	0.000000000
8	1.336908925	0.546306002	0.000000000
6	-0.699349889	-0.688910090	0.000000000
1	-0.976461313	-1.284282518	0.880277416
1	-0.976461313	-1.284282518	-0.880277416
8	-1.339496406	0.556989562	0.000000000
1	-0.622248568	1.206829833	0.000000000

E = -228.7084908
ZPVE = 38.7632 kcal mol⁻¹

1b: Glycolaldehyde (C_1)

6	-0.553264387	-0.539391661	0.076823387
1	-0.621942899	-1.086893265	1.020206888
6	0.681780458	0.342766165	0.147969611
8	-1.746143944	0.216143029	-0.040030751
1	-0.423029320	-1.271234552	-0.725501029
8	1.797949698	-0.042607828	-0.118440341
1	0.482005923	1.381011091	0.478288924
1	-1.789447481	0.564173317	-0.934515285

E = -228.7027185
ZPVE = 34.4118 kcal mol⁻¹

cis-2as: 1,2-ethendiol (C_1)

1	-0.768177142	1.240265109	0.028959860
8	-1.410719070	0.519232611	0.008673062
6	-0.679800838	-0.633211311	0.000086034
1	-1.277032011	-1.531547927	-0.029678192
6	0.656614497	-0.664301141	0.006867186
1	1.219349363	-1.586623986	-0.020645263
8	1.349242613	0.540961714	-0.048816861
1	2.077611566	0.501111968	0.575683992

E = -228.6952486
ZPVE = 38.9769 kcal mol⁻¹

cis-2aa: 1,2-ethendiol (C_{2v})

1	0.000000000	1.200690319	1.561544641
6	0.000000000	0.668112609	0.620229010
8	0.000000000	1.399121288	-0.544235855
1	0.000000000	2.328472057	-0.309087229
6	0.000000000	-0.668112609	0.620229010
8	0.000000000	-1.399121288	-0.544235855
1	0.000000000	-1.200690319	1.561544641
1	0.000000000	-2.328472057	-0.309087229

E = -228.6877326
ZPVE = 38.472 kcal mol⁻¹

trans-2ss: 1,2-ethendiol (C_{2h})

1	0.479593494	1.472394261	0.000000000
6	0.542303411	0.391461283	0.000000000
8	1.847534527	-0.046919554	0.000000000
1	1.841290913	-1.009128414	0.000000000
6	-0.542303411	-0.391461283	0.000000000
1	-0.479593494	-1.472394261	0.000000000
8	-1.847534527	0.046919554	0.000000000
1	-1.841290913	1.009128414	0.000000000

E = -228.6885105
ZPVE = 38.5228 kcal mol⁻¹

trans -2as: 1,2-ethendiol (C_1)

6	-0.537855105	-0.382763212	0.031903938
1	-0.447516606	-1.459169021	0.063713089
6	0.538763057	0.409046626	0.012121810
8	-1.841207922	0.039169943	-0.010183101
1	0.459875297	1.492971382	-0.027872126
8	1.808527983	-0.140047135	-0.060742547
1	-1.845981212	0.999967700	-0.069129858
1	2.341466042	0.254272134	0.634723408

E = -228.6878023
ZPVE = 38.523 kcal mol⁻¹

trans -2aa: 1,2-ethendiol (C_2)

1	-0.443337666	1.472055730	0.099700724
6	-0.537538361	0.394802778	0.024046931
6	0.537538361	-0.394802778	-0.024046931
1	0.443337666	-1.472055730	-0.099700724
8	-1.805975941	-0.149888916	0.027757538
1	-2.392953929	0.466634150	-0.415261316
8	1.805975941	0.149888916	-0.027757538
1	2.392953929	-0.466634150	0.415261316

E = -228.6867281
ZPVE = 38.2884 kcal mol⁻¹

TS1: (C_1)

6	-0.669679466	-0.614099630	-0.002991899
1	-1.218300465	-1.548275659	0.001806209
6	0.666739754	-0.633558975	-0.010657831
8	-1.390941462	0.549984096	-0.006248869
1	1.187207518	-1.584266014	-0.010931871
8	1.433220603	0.515957946	0.065311199
1	-2.320601726	0.323286240	0.057941633
1	1.715696741	0.747638969	-0.823652953

E = -228.686267
ZPVE = 37.2615 kcal mol⁻¹

TS2: (C_1)

6	-0.670118974	-0.682250939	0.001347343
1	-1.212698541	-1.577713202	0.291827272
6	0.728344066	-0.646569745	0.021650821
8	-1.301223466	0.573580745	0.034496176
1	-0.954827647	-0.271801125	-1.057246724
8	1.276111862	0.561882435	-0.006164121
1	1.397877817	-1.492976123	-0.016557887
1	0.474911561	1.143906028	0.058491856

E = -228.5944022
ZPVE = 35.755 kcal mol⁻¹

TS2': (C_1)

6	-0.548541120	0.560585385	-0.352179794
1	-1.015359968	1.526893649	-0.535202805
6	0.746111256	0.532574869	0.279415933
8	-1.460665518	-0.441241537	0.110298705
8	1.386674971	-0.514843885	-0.082858113
1	1.253034537	1.255541769	0.921375549
1	-1.841828086	-0.121267428	0.934399591
1	0.426003444	-0.503470337	-0.889687595

E = -228.5728224
ZPVE = 34.869 kcal mol⁻¹

TS3: (C_1)

6	-0.539312988	-0.384353692	-0.023982181
1	-0.454710029	-1.461286619	-0.077413763
6	0.536990752	0.409001683	0.009474247
8	-1.842643680	0.035294191	0.011306121
1	0.454789226	1.492167837	0.028301209
8	1.833975815	-0.084150015	-0.048588616
1	-1.848287996	0.997728052	0.040345204
1	2.013424477	-0.546711299	0.773211079

E = -228.58853
ZPVE = 38.16225 kcal mol⁻¹

TS4: (C_1)

6	-0.536160283	-0.410376443	0.018253260
1	-0.442925919	-1.490012577	0.031305830
6	0.535404385	0.386475634	0.028240909
1	-1.830137433	0.093343020	0.038926204
1	0.433099717	1.466557187	0.051291796
8	1.805988921	-0.136222035	-0.048258975
1	-2.011401019	0.485651679	-0.818092448

1 2.413481953 0.502907652 0.330014586
E = -228.6848065
ZPVE = 37.972 kcal mol⁻¹

TS5: (C₁)

6 -0.472661002 -0.361070078 0.154279288
6 0.649599634 0.518968536 0.123670962
1 -0.404715845 -1.002757797 1.035093009
8 -1.783545472 0.071486576 -0.071707227
8 1.702321638 -0.168610297 -0.131897429
1 0.716847489 1.597374745 0.258191417
1 -1.908864154 0.108303067 -1.022237907
1 0.779035733 -1.041565895 -0.349198860
E = -228.5922204
ZPVE = 34.7951 kcal mol⁻¹

7: 1,1-ethenediol (C_s)

1 -0.018795953 1.876089259 0.000000000
8 -0.625977817 1.130191040 0.000000000
6 0.113833334 -0.016309539 0.000000000
8 -0.694721943 -1.098785301 0.000000000
1 -1.600631789 -0.772277128 0.000000000
6 1.448596922 -0.096228935 0.000000000
1 1.926045777 -1.062233251 0.000000000
1 2.050256108 0.799965571 0.000000000
E = -228.7083741
ZPVE = 38.5604 kcal mol⁻¹