Electronic Supplementary Material (ESI) for ChemComm.

The Enol of Propionic acid

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Experimental Procedures

Matrix Apparatus Design. A Sumitomo cryostat system consisting of an RDK 408D2 closed-cycle refrigerator cold head and an F-70 compressor unit was used for matrix isolation experiments. A polished CsI window was mounted in the cold head's sample holder. The sample holder, connected with silicon diodes for temperature measurements, was covered by a vacuum shroud, which was equipped with KBr windows to allow for IR measurements. In some experiments BaF_2 windows were used due to their higher transparency when measuring UV/vis spectra. The sample and the host gas (Ar, purity of 99.999%) were co-deposited at 3.5 K. All spectral data were collected at 3.5 K. The pyrolysis zone was equipped with a heatable 90 mm long quartz tube (inner diameter 7 mm), controlled by a Ni/CrNi thermocouple. The travel distance of the sample from the pyrolysis zone to the matrix was ~45 mm. Ar was stored in a 2 L gas balloon, which was evacuated and filled three times before every experiment. The sample was evaporated from a Schlenk tube at 70 °C (water) and reduced pressure (~3×10^{-6} mbar) and co-deposited with a high excess of argon on both sides of the matrix window in the dark (preventing unwanted photochemistry) at a rate of ~1 mbar min^{-1}, based on the pressure inside the Ar balloon. Pyrolyses were carried out at 500 °C. IR spectra were recorded between 7000 and 350 cm^{-1} with a resolution of 0.7 cm^{-1} with a Bruker Vertex 70 FTIR spectrometer. A spectrum of the cold matrix window before deposition was used as background spectrum for the subsequent IR measurements. UV/vis spectra were recorded between 190 and 800 nm with a resolution of 1 nm with a Jasco V-760 spectrophotometer. A high-pressure-mercury lamp equipped with a monochromator (LOT Quantum Design) or a low-pressure-mercury lamp (Gräntzel) fitted with a Vycor filter were used for irradiation of the matrix during photochemical experiments.

Computations. All DFT computations were performed with the Gaussian 16,[1] Revision C.01 program package (full citations for electronic structure codes are given at the end of this document) at the B3LYP/def2-TZVP[2–4] level of theory. The keywords Opt and Freq=NoRaman were used for the characterization of minima on the PES. For transition structures the keyword Opt=(ts,tight,calcfc,noeigen) was used. UV/Vis absorptions were computed by using the keyword td(50-50,nstates=10).

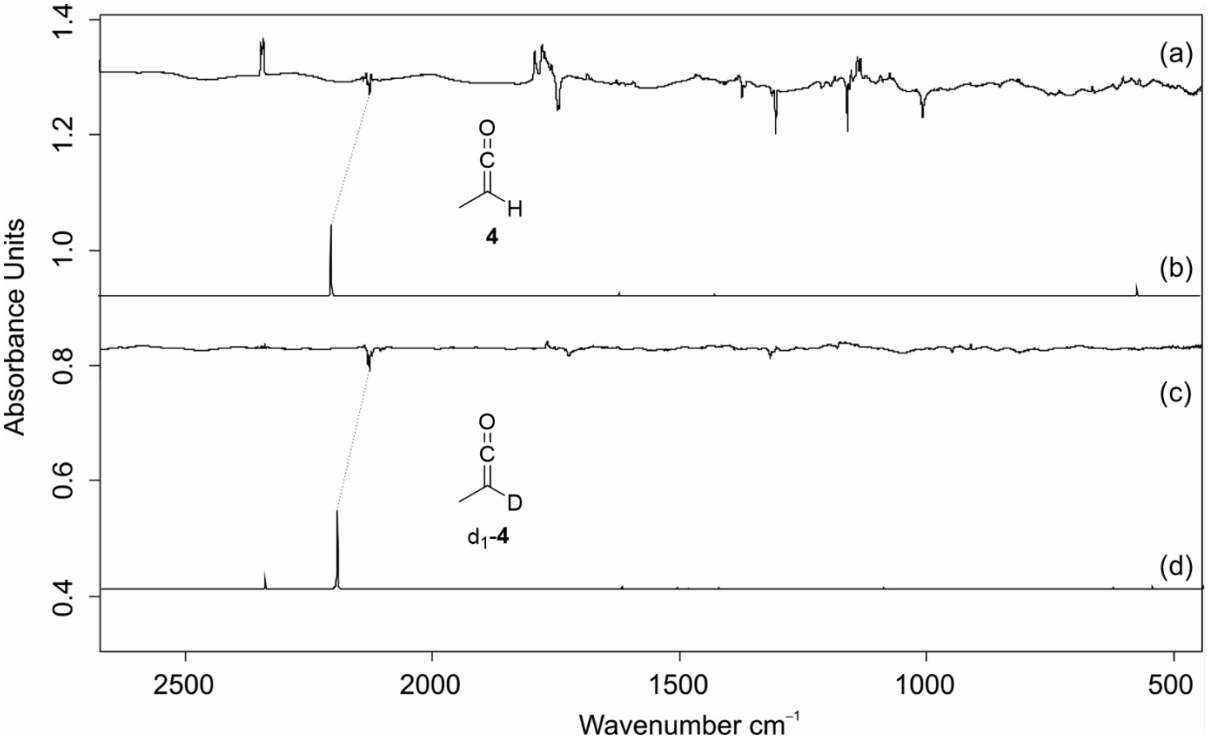


Figure S1: IR spectra showing the pyrolysis product of **1** with subsequent trapping in an argon matrix at 3.5 K (a) IR difference spectra showing the photochemistry of **4** after irradiation with λ = 254 nm in argon at 3.5 K. Downward bands assigned to **4** disappear after 20 min irradiation time. (b) IR spectrum of **4** computed at B3LYP/def2-TZVP. (c) IR difference spectra showing the photochemistry of d_1-**4** after irradiation with λ = 254 nm in argon at 3.5 K. Downward bands assigned to d_1-**4** disappear after 20 min irradiation time. (d) IR spectrum of d_1-**4** computed at B3LYP/def2-TZVP.

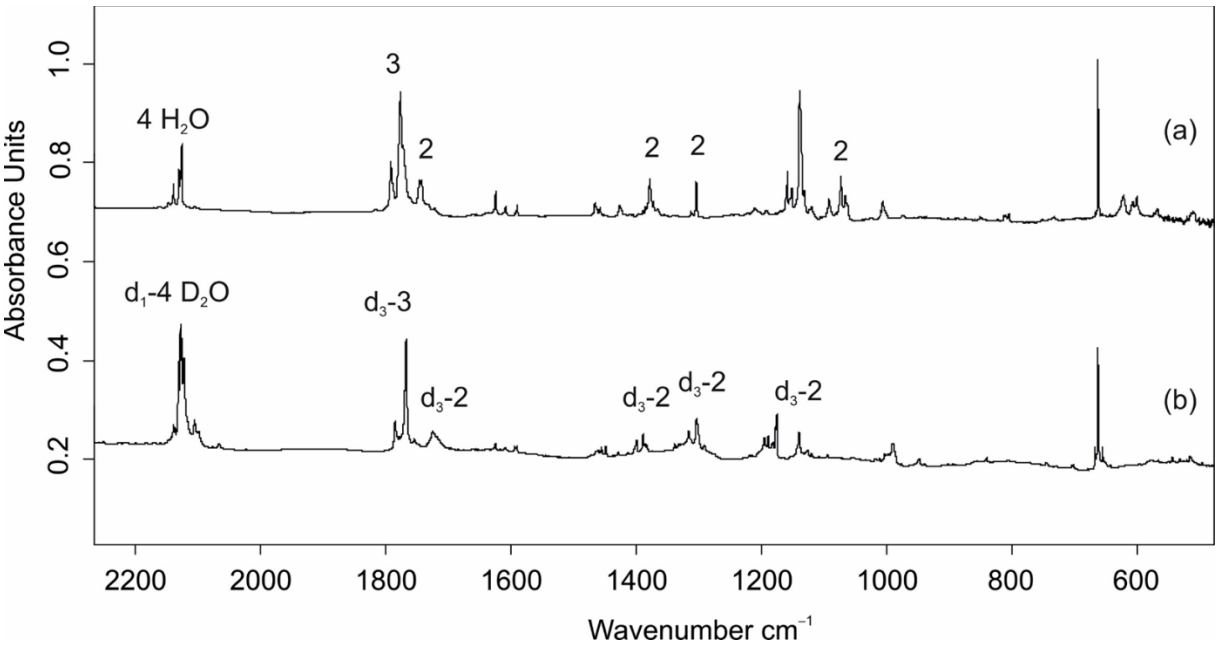


Figure S2: (a) IR spectra showing the product of pyrolysis of **1** in argon matrix with subsequent trapping in an argon matrix at 3.5 K (b) IR spectra showing the product of pyrolysis of d_4-**1** in argon matrix with subsequent trapping in an argon matrix at 10 K.

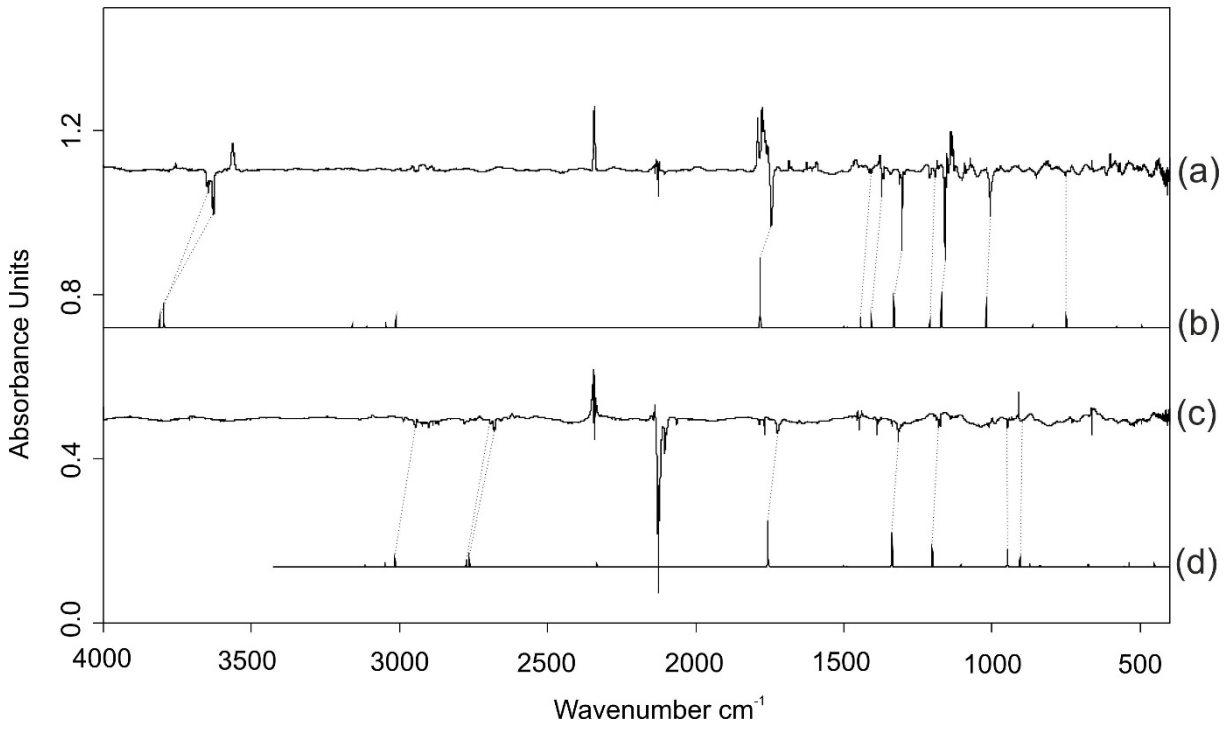
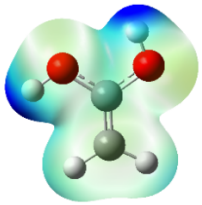
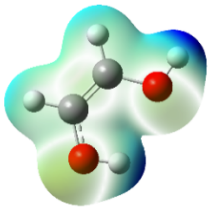
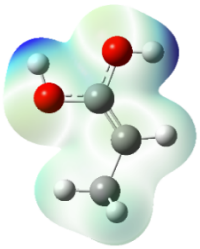


Figure S3: IR spectra showing the pyrolysis product of **1** with subsequent trapping in an argon matrix at 3.5 K. (a) IR difference spectra showing the photochemistry of **2** after irradiation with λ = 254 nm in argon at 3.5 K. Downward bands assigned to **2** disappear while upward bands assigned **3** appear after 20 min irradiation time. (b) IR spectrum of **2** computed at B3LYP/def2TZVP. (c) IR difference spectra showing the photochemistry of d_4-**2** after irradiation with λ = 254 nm in argon at 3.5 K. Downward bands assigned to d_3-**2** disappear while upward bands assigned to d_3-**3** appear after 20 min irradiation time. (d) IR spectrum of d_3-**2** computed at B3LYP/def2-TZVP.

Table S1: Illustration of charge density in comparison to C=C stretching bond in **2**, 1,2- ethenediol, and 1,1-ethenediol computed at the B3LYP/def2-TZVP level of theory.

Illustration of Charge density	C=C stretching bond [a] cm^{-1}	C=C stretching bond cm^{-1}	Charge density in C=C-bond
	1753	1712[5,c]	0.183
	1756	1711[6,c]	0.172
	1784	1744[b]	0.378

[a] B3LYP/def2-TZVP, harmonic approximation, unscaled frequencies. [b] Experiment: argon matrix, 3.5 K [c] Experiment: argon matrix, 10 K;

Table S2: Experimental (Ar matrix, 3.5 K) and computed IR frequencies of **2ct** and d_3-**2ct** - band origins in cm^{-1}, computed intensities (km mol^{-1}) in parentheses.

Mode	**2** Computed[a]	**2** Ar, 3.5 K[b]	d_3-**2** Computed[a]	d_3-**2** Ar, 3.5 K[b]	Assignment
1	3810 (57.0)	3648 (m)	3113 (10.9)	2986 (w)	O–H stretching
2	3795 (104.7)	3630 (s)	3045 (29.7)	2946 (m)	O–H stretching
3	3159 (21.1)	2994 (w)	3013 (51.9)	2901 (m)	C–H stretching
4	3112 (8.6)	2946 (w)	2772 (35.3)	2680 (m)	C–H (CH_3), CH stretching
5	3046 (29.7)	2911 (w)	2762.3 (66.7)	2675 (m)	C–H (CH_3) stretching
6	3013 (53.2)	2876 (w)	2332 (16.0)	2277 (w)	C–H (CH_3) stretching
7	1783 (271.5)	1745 (s)	1755 (272.5)	1722 (s)	C=C stretching
8	1502 (7.1)	1473 (w)	1499 (4.7)	1491 (w)	C–H (CH_3) bending
9	1488 (6.3)	1450 (w)	1488 (6.0)	1473 (w)	C–H (CH_3) twisting
10	1444 (41.9)	1410 (m)	1423 (1.5)	1415 (w)	-
11	1407 (46.3)	1370 (m)	1336 (172.7)	1320 (s)	C–C (CH_3) stretching
12	1331 (158.8)	1305 (s)	1200 (121.5)	1181 (s)	O–H wagging
13	1211 (38.0)	1191 (m)	1104 (9.2)	1093 (w)	O–H and C–H in pl.
14	1172 (171.9)	1161 (s)	1063 (0.2)	-	O–H wagging
15	1112 (3.6)	1106 (w)	947 (85.1)	950 (m)	C–CH_3 twisting
16	1065 (0.6)	1048 (w)	905 (55.3)	-	C–H (CH_3) twisting
17	1020 (121.0)	1005 (s)	870 (19.7)	857 (w)	CCH in pl. def
18	865 (14.5)	850 (m)	837 (6.8)	812 (w)	C–CH_3 twisting
19	750 (68.8)	709 (m)	673 (17.8)	668 (m)	CH wagging
20	641 (4.3)	616 (m)	552 (7.4)	535 (w)	OCO in pl. def.
21	581 (10.7)	565 (w)	536 (26.4)	523 (w)	-
22	495 (12.9)	-	452 (17.5)	-	C–O wagging
23	345 (11.4)	-	269 (9.2)	-	O–H wagging
24	272 (28.7)	-	243 (3.3)	-	CH_3 - def
25	250 (3.5)	-	242 (0.6)	-	C–CH_3 wagging

26	158 (86.2)	-	139 (32.1)	-	CH_3 - twisting
27	77 (68.3)	-	68 (61.4)	-	CH_3 - twisting

[a] B3LYP/def2-TZVP, harmonic approximation, unscaled frequencies, intensities (in parentheses) in km mol^{-1}. [b] Experiment: argon matrix, 3.5 K; approximate relative intensities (w: weak, m: medium, s: strong).

Table S3: Experimental (Ar matrix, 3.5 K) and computed IR frequencies of **4 + H_2O** and d_1-**4** + D_2O - band origins in cm^{-1}, computed intensities (km mol^{-1}) in parentheses.

Mode	**4** + H_2O Computed[a]	**4** + H_2O Ar, 3.5 K[b]	d_1-**4** + D_2O Computed[a]	d_1-**4** + D_2O Ar, 3.5 K[b]	Assignment
1	3860 (100.6)	-	2827 (42.8)	-	assym. O-H (H_2O) strechting
2	3717 (155.1)	-	2687(30.2)	-	sym. O-H (H_2O) strechting
3	2201 (711.3)	2122 (m)	2195 (662.7)	2128 (m)	C=C stretching
4	569 (61.2)	-	542 (14.3)	-	OCO in pl. def.
5	352 (74.6)	-	262 (28.5)	-	O–H wagging
6	240 (95.6)	-	175 (30.0)	-	-
7	43 (72.7)	-	32 (25.0)	-	-

[a] B3LYP/def2-TZVP, harmonic approximation, unscaled frequencies, intensities (in parentheses) in km mol^{-1}. [b] Experiment: argon matrix, 3.5 K; approximate relative intensities (w: weak, m: medium, s: strong).

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B3LYP/def2-TZVP optimized structures (distances in bohr), electronic energies (in hartree) and zero-point vibrational energies (ZPVE)

3T_g: Propionic acid *trans*, *gauche* (C_s)

C	-0.590199000	-0.815614000	0.000000000
C	0.000000000	0.572668000	0.000000000
O	-0.967528000	1.523068000	0.000000000
O	1.171190000	0.847672000	0.000000000
H	-1.249341000	-0.888781000	0.869832000
H	-0.518598000	2.383032000	0.000000000
C	0.458718000	-1.918842000	0.000000000
H	-0.022858000	-2.897490000	0.000000000
H	1.099864000	-1.851585000	-0.878863000
H	1.099864000	-1.851585000	0.878863000
H	-1.249341000	-0.888781000	-0.869832000

E = –268.421915
ZPVE = 16.8437 kcal mol^{-1}

3T_t: Propionic acid *trans*, *trans* (C_1)

C	0.691794000	-0.731425000	0.000006000
C	-0.562702000	0.106370000	0.000005000
O	-1.676277000	-0.667789000	-0.000005000
O	-0.615378000	1.308260000	0.000002000
H	0.641255000	-1.392684000	0.869840000
H	-2.437889000	-0.066937000	-0.000010000
C	1.970655000	0.094320000	-0.000004000
H	2.842822000	-0.560655000	-0.000006000
H	2.023655000	0.736795000	-0.878873000
H	2.023661000	0.736807000	0.878853000
H	0.641256000	-1.392689000	-0.869823000

E = –268.427817
ZPVE = 16.8441 kcal mol^{-1}

3C_t: Propionic acid *cis*, *trans* (C_s)

C	-0.543447000	-0.820609000	0.000000000
C	0.000000000	0.597980000	0.000000000
O	-0.944578000	1.578756000	0.000000000
O	1.159881000	0.890383000	0.000000000
H	-1.193349000	-0.931388000	0.875133000
H	-1.831910000	1.197439000	0.000000000
C	0.547136000	-1.883103000	0.000000000
H	1.184029000	-1.786348000	0.878719000
H	0.105993000	-2.880684000	0.000000000
H	1.184029000	-1.786348000	-0.878719000

H	-1.193349000	-0.931388000	-0.875133000

E = –268.419824
ZPVE = 16.8436 kcal mol^{-1}

3C_g: Propionic acid *cis*, *gauche* (C_1)

C	-1.880934000	0.074665000	-0.273415000
C	-0.696804000	-0.640215000	0.383619000
C	0.677605000	-0.095711000	0.031225000
O	0.816432000	1.257156000	0.069841000
O	1.619862000	-0.780085000	-0.245281000
H	-2.811106000	-0.437715000	-0.025874000
H	-1.784729000	0.089263000	-1.359995000
H	-1.994264000	1.107620000	0.068115000
H	-0.684113000	-1.694351000	0.111895000
H	-0.791859000	-0.595087000	1.473973000
H	-0.023488000	1.681265000	0.286830000

E = –268.417695
ZPVE = 16.8434 kcal mol^{-1}

2ct: Enol *cis*, *anti* (C_s)

O	0.484943000	1.747677000	0.000000000
C	0.000000000	0.469226000	0.000000000
O	-1.352502000	0.485390000	0.000000000
C	0.727765000	-0.646519000	0.000000000
C	0.156695000	-2.031989000	0.000000000
H	1.448583000	1.725370000	0.000000000
H	-1.642187000	1.405966000	0.000000000
H	1.805957000	-0.534433000	0.000000000
H	-0.932419000	-2.007130000	0.000000000
H	0.476887000	-2.599307000	0.879344000
H	0.476887000	-2.599307000	-0.879344000

E = –268.385474
ZPVE = 16.8414 kcal mol^{-1}

2cc: Enol *cis*, *cis* (C_1)

O	1.639201000	-0.766582000	-0.093169000
C	0.463858000	-0.068535000	0.008326000
O	0.624479000	1.289656000	0.078456000
C	-0.720546000	-0.667065000	0.028801000
C	-2.040058000	0.036441000	-0.019368000
H	2.254766000	-0.442876000	0.578833000
H	1.302932000	1.554187000	-0.557479000

H	-0.706918000	-1.747980000	0.081513000
H	-1.912984000	1.111141000	-0.142112000
H	-2.613991000	-0.130585000	0.897215000
H	-2.652766000	-0.333534000	-0.846817000

E = –268.381738
ZPVE = 16.8412 kcal mol^{-1}

2tc: Enol *anti*, *syn* (C_1)

O	1.726225000	-0.618777000	0.001764000
C	0.494251000	-0.035096000	-0.001152000
O	0.628291000	1.318297000	-0.101561000
C	-0.672158000	-0.680021000	0.034426000
C	-2.017218000	-0.023127000	-0.017692000
H	1.621891000	-1.576563000	-0.048514000
H	0.490686000	1.732229000	0.757738000
H	-0.645281000	-1.762902000	0.101016000
H	-1.926159000	1.047099000	-0.201439000
H	-2.575301000	-0.160883000	0.914215000
H	-2.631212000	-0.445686000	-0.818130000

E = –268.378994
ZPVE = 16.8410 kcal mol^{-1}

2tt: Enol *anti*, *anti* (C_1)

O	-1.735635000	-0.596030000	0.000258000
C	-0.507716000	-0.026427000	0.002626000
O	-0.683108000	1.313252000	-0.004498000
C	0.658425000	-0.682775000	0.007339000
C	2.017274000	-0.046606000	-0.004071000
H	-1.633277000	-1.553412000	-0.036431000
H	0.178218000	1.742137000	0.047633000
H	0.616976000	-1.765270000	0.034401000
H	2.523429000	-0.118590000	0.964346000
H	1.987774000	1.014695000	-0.270040000
H	2.668924000	-0.522487000	-0.741353000

E = –268.382319
ZPVE = 16.8412 kcal mol^{-1}

4: Keten (C_1)

O	1.944225000	-1.189009000	-0.248953000
C	1.222140000	-0.362573000	0.133609000
C	0.391536000	0.560678000	0.554895000
C	-0.067965000	1.726361000	-0.294011000

H	0.109405000	0.499383000	1.599392000
H	0.299813000	1.640095000	-1.315977000
H	0.295398000	2.671341000	0.115342000
H	-1.157603000	1.767276000	-0.333003000

E = –268.380126
ZPVE = 16.8411kcal mol^{-1}

TS1: Enol rotation **2ct** – **2tt** (C_1)

O	1.726224000	-0.618778000	0.001764000
C	0.494250000	-0.035096000	-0.001152000
O	0.628296000	1.318296000	-0.101561000
C	-0.672160000	-0.680020000	0.034427000
C	-2.017219000	-0.023125000	-0.017693000
H	1.621889000	-1.576565000	-0.048516000
H	0.490682000	1.732228000	0.757737000
H	-0.645284000	-1.762901000	0.101018000
H	-1.926160000	1.047103000	-0.201429000
H	-2.575307000	-0.160891000	0.914210000
H	-2.631209000	-0.445675000	-0.818139000

E = –268.378994
ZPVE = 16.8410 kcal mol^{-1}

TS2: Enol rotation **2ct** – **2cc** (C_1)

O	1.672160000	-0.707542000	-0.097082000
C	0.462857000	-0.050422000	-0.010000000
O	0.597790000	1.306203000	0.040661000
C	-0.712924000	-0.667587000	-0.014503000
C	-2.041286000	0.022190000	0.006811000
H	1.962992000	-0.976726000	0.782466000
H	1.501945000	1.516367000	-0.223386000
H	-0.686602000	-1.749139000	-0.037500000
H	-1.927685000	1.104056000	-0.046028000
H	-2.600202000	-0.213047000	0.917885000
H	-2.661933000	-0.295888000	-0.835912000

E = –268.381272
ZPVE = 16.8411 kcal mol^{-1}

TS3: Enol rotation **2ct** – **2tc** (C_1)

O	-1.647916000	-0.775027000	0.041859000
C	-0.475054000	-0.079363000	-0.005159000
O	-0.664272000	1.282813000	-0.100129000
C	0.709450000	-0.679991000	0.003148000

C	2.030252000	0.022999000	-0.006337000
H	-2.350607000	-0.179216000	-0.245715000
H	-0.597366000	1.688389000	0.772839000
H	0.699231000	-1.762599000	0.025794000
H	1.909820000	1.100084000	-0.120368000
H	2.655700000	-0.330116000	-0.831178000
H	2.592840000	-0.160701000	0.914873000

E = –268.380695
ZPVE = 16.8411 kcal mol^{-1}

TS4: Enol **2tt** – propionic acid **3*C*$_t$** (C_1)

O	1.531416000	-0.839845000	0.141325000
C	0.594783000	0.005200000	-0.061371000
O	0.887352000	1.294645000	-0.015945000
C	-0.671238000	-0.635238000	-0.188222000
C	-1.969033000	0.063637000	0.143753000
H	0.473329000	-1.515155000	0.314000000
H	0.120262000	1.810434000	-0.301129000
H	-0.691383000	-1.249889000	-1.087941000
H	-1.942866000	0.517798000	1.137196000
H	-2.791877000	-0.652009000	0.145456000
H	-2.244695000	0.848834000	-0.575574000

E = –268.313397
ZPVE = 16.8369 kcal mol^{-1}

TS5: Enol **2tt** – propionic acid **3*C*$_g$** (C_1)

O	1.622288000	-0.738064000	0.210771000
C	0.576958000	0.028739000	-0.056685000
O	0.728890000	1.297209000	0.035863000
C	-0.704729000	-0.315896000	-0.581770000
C	-1.931527000	-0.131793000	0.314480000
H	1.345498000	-1.663286000	0.226766000
H	-0.280792000	1.162279000	-0.684720000
H	-0.744297000	-1.218754000	-1.190398000
H	-2.824862000	-0.004769000	-0.298662000
H	-1.841689000	0.754945000	0.944089000
H	-2.107493000	-0.989872000	0.973699000

E = –268.306292
ZPVE = 16.8364 kcal mol^{-1}

TS6: Enol **2ct** – propionic acid **3*T*$_t$** (C_1)

O	1.568027000	-0.821793000	0.210759000

C	0.554043000	-0.016638000	-0.049788000
O	0.716680000	1.265595000	-0.004762000
C	-0.720071000	-0.385104000	-0.539609000
C	-1.958535000	-0.091513000	0.307361000
H	2.377983000	-0.293154000	0.289816000
H	-0.285367000	1.083153000	-0.738190000
H	-0.765403000	-1.333061000	-1.068910000
H	-2.834885000	0.018101000	-0.333074000
H	-1.853504000	0.832906000	0.877347000
H	-2.169091000	-0.898825000	1.017252000

E = –268.309356
ZPVE = 16.8366 kcal mol^{-1}

TS7: Enol **2ct** – propionic acid **3*T*$_g$** (C_1)

O	1.481120000	-0.888282000	0.135655000
C	0.559755000	-0.010897000	-0.078221000
O	0.846845000	1.278832000	-0.080029000
C	-0.722474000	-0.594859000	-0.163913000
C	-2.000901000	0.149621000	0.130116000
H	0.390277000	-1.499736000	0.374638000
H	1.766393000	1.395281000	0.205575000
H	-0.765550000	-1.298141000	-0.995084000
H	-2.313038000	0.804580000	-0.690976000
H	-1.906441000	0.766832000	1.025264000
H	-2.813642000	-0.556408000	0.307680000

E = –268.316276
ZPVE = 16.8371 kcal mol^{-1}

TS8: Enol **2ct** – ketene (**4**) – H_2O elimination (C_1)

O	-1.719768000	-0.687179000	-0.081255000
C	-0.322677000	0.084728000	-0.024175000
O	-0.809816000	1.258709000	0.010515000
C	0.803069000	-0.614957000	-0.033278000
C	2.147444000	0.053352000	0.025145000
H	-1.874654000	-1.166025000	0.748072000
H	-1.904262000	0.461034000	0.008900000
H	0.741834000	-1.690074000	-0.116656000
H	2.041830000	1.135165000	0.106667000
H	2.736493000	-0.158184000	-0.871863000
H	2.728417000	-0.292896000	0.884648000

E = –268.318666
ZPVE = 16.8372 kcal mol^{-1}