Supporting Information for

Formation of Methylglyoxal ($CH_3C(O)CHO$) in Interstellar Analog Ices – A Key Intermediate in Cellular Metabolism

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This file includes:

Figures S1 to S10

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Supplementary Source code

Supplementary References

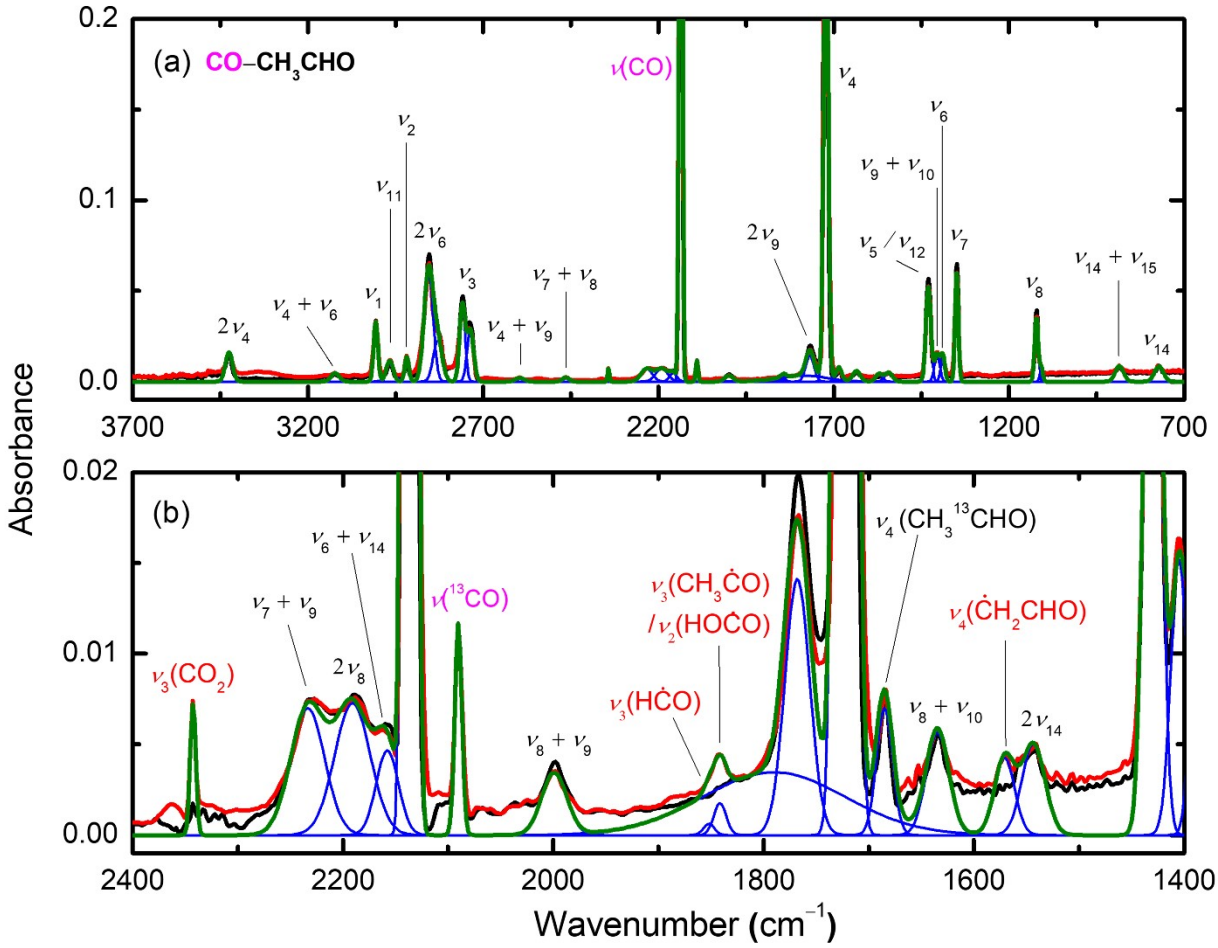


Figure S1. Infrared spectra of (a) CO–CH_3CHO ice before (black) and after (red) low dose irradiation (24 nA, 5 minutes) at 5 K with (b) a magnified view and deconvolution of the region 2400–1400 cm^{-1}. The Gaussian fits (blue) and sum of fits (green) are presented. The assignments of the absorptions of CO, CH_3CHO, and new absorptions after irradiation are labeled in magenta, black, and red, respectively. Detailed assignments are compiled in Table S9.

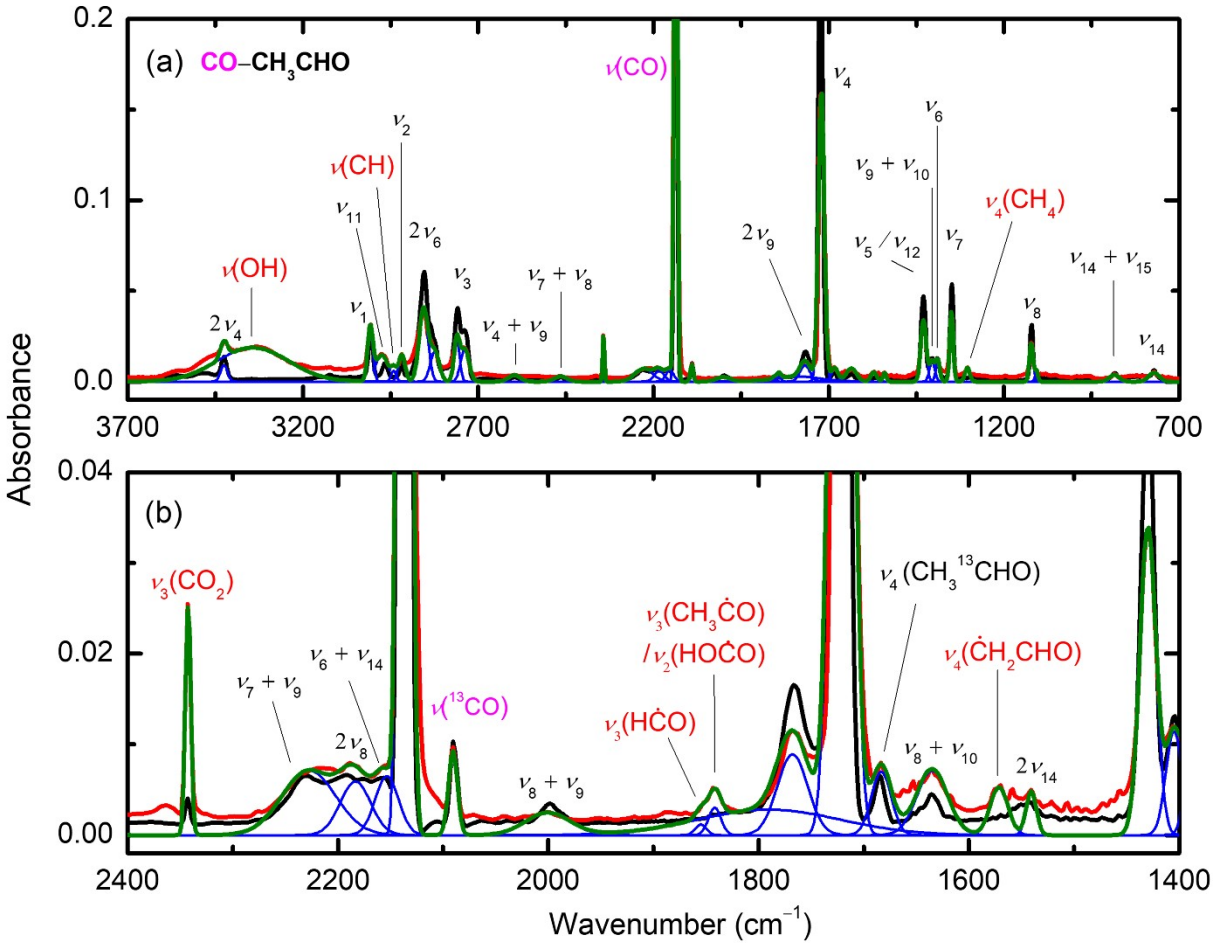


Figure S2. Infrared spectra of (a) CO–CH_3CHO ice before (black) and after (red) high dose irradiation (37 nA, 30 minutes) at 5 K with (b) a magnified view and deconvolution of the region 2400–1400 cm^{-1}. The Gaussian fits (blue) and sum of fits (green) are presented. The assignments of the absorptions of CO, CH_3CHO, and new absorptions after irradiation are labeled in magenta, black, and red, respectively. Detailed assignments are compiled in Table S10.

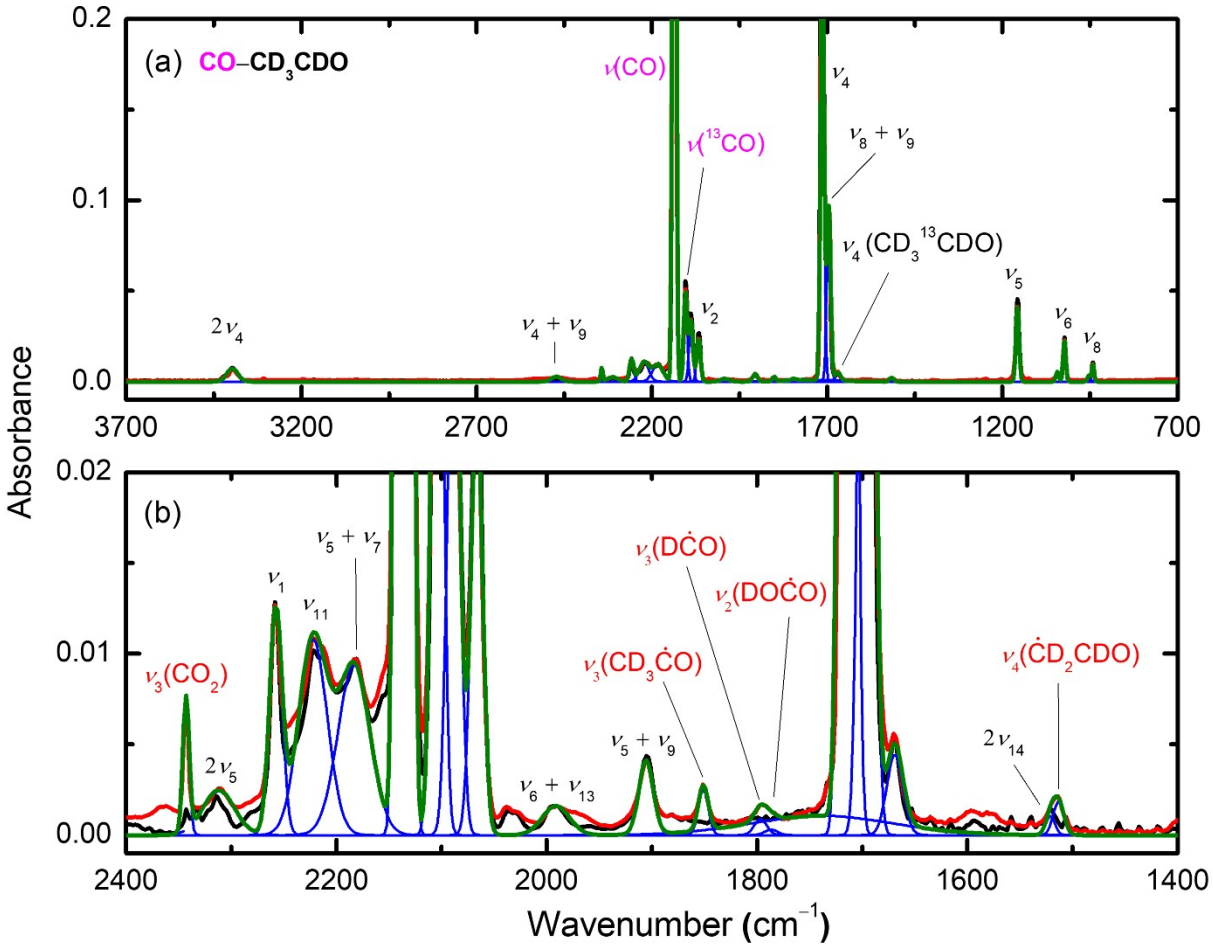


Figure S3. Infrared spectra of (a) CO–CD_3CDO ice before (black) and after (red) low dose irradiation (23 nA, 5 minutes) at 5 K with (b) a magnified view and deconvolution of the region 2400–1400 cm^{-1}. The Gaussian fits (blue) and sum of fits (green) are presented. The assignments of the absorptions of CO, CD_3CDO, and new absorptions after irradiation are labeled in magenta, black, and red, respectively. Detailed assignments are compiled in Table S11.

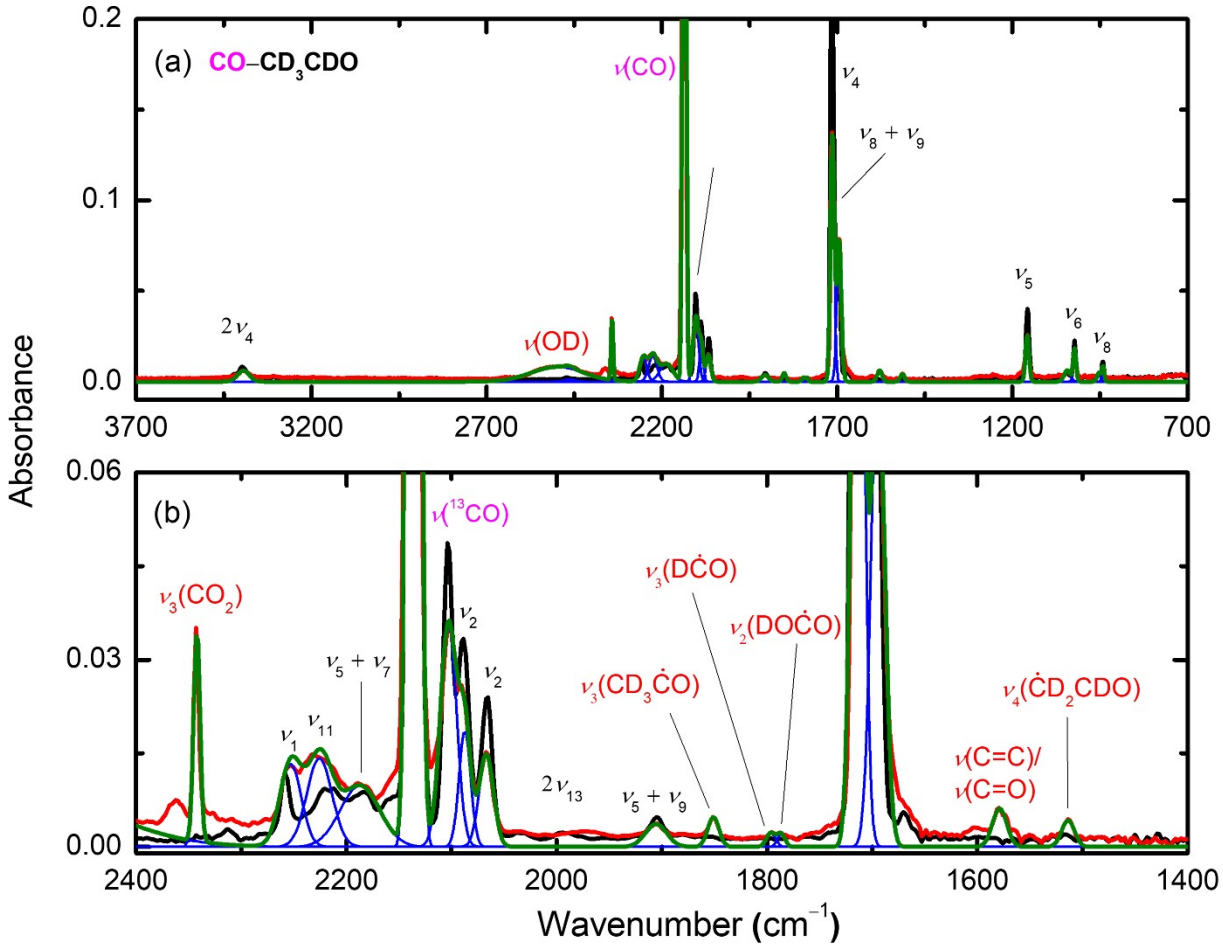


Figure S4. Infrared spectra of (a) CO–CD_3CDO ice before (black) and after (red) high dose irradiation (37 nA, 30 minutes) at 5 K with (b) a magnified view and deconvolution of the region 2400–1400 cm^{-1}. The Gaussian fits (blue) and sum of fits (green) are presented. The assignments of the absorptions of CO, CD_3CDO, and new absorptions after irradiation are labeled in magenta, black, and red, respectively. Detailed assignments are compiled in Table S12.

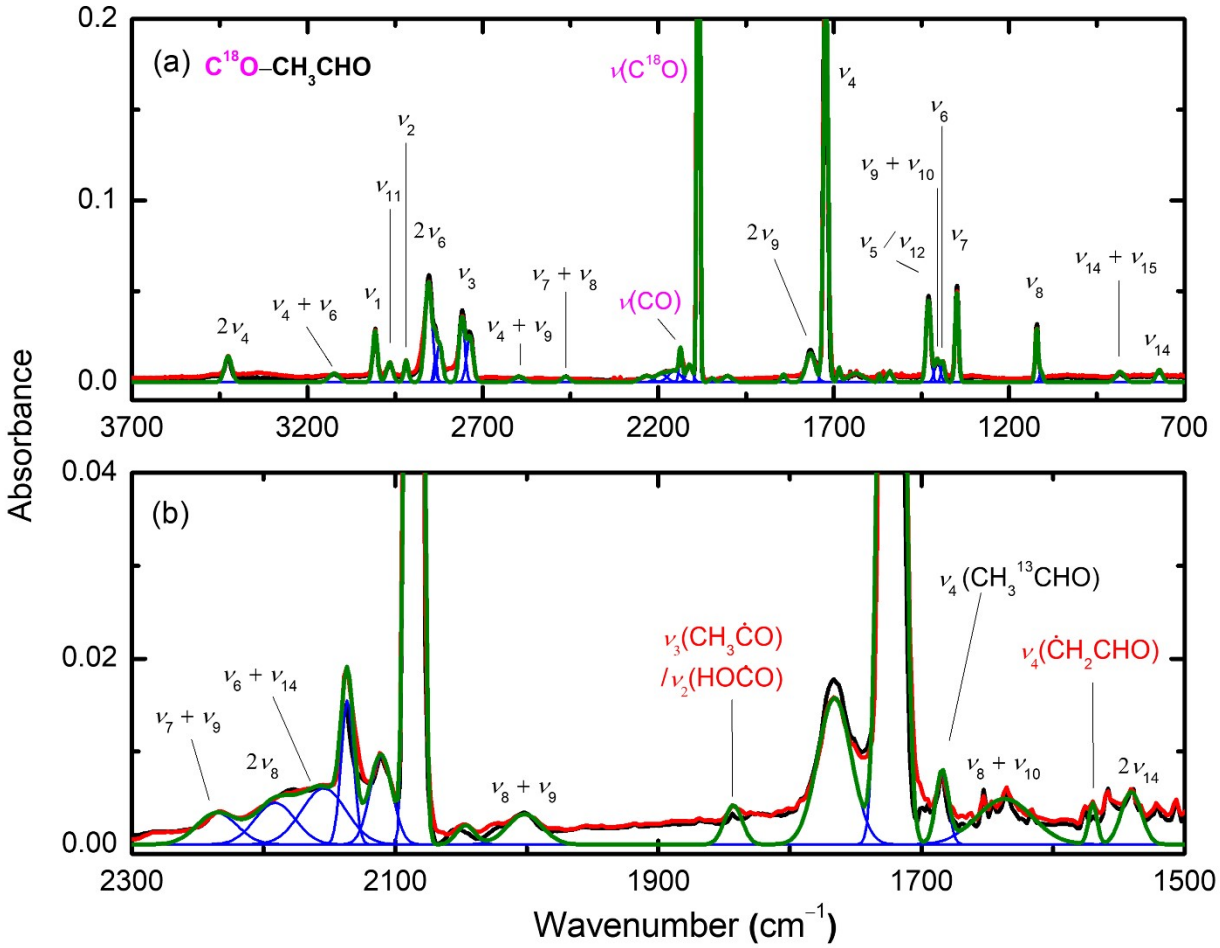


Figure S5. Infrared spectra of (a) $C^{18}O$–CH_3CHO ice before (black) and after (red) low dose irradiation (22 nA, 5 minutes) at 5 K with (b) a magnified view and deconvolution of the region 2300–1500 cm^{-1}. The Gaussian fits (blue) and sum of fits (green) are presented. The assignments of the absorptions of $C^{18}O$, CH_3CHO, and new absorptions after irradiation are labeled in magenta, black, and red, respectively. Detailed assignments are compiled in Table S13.

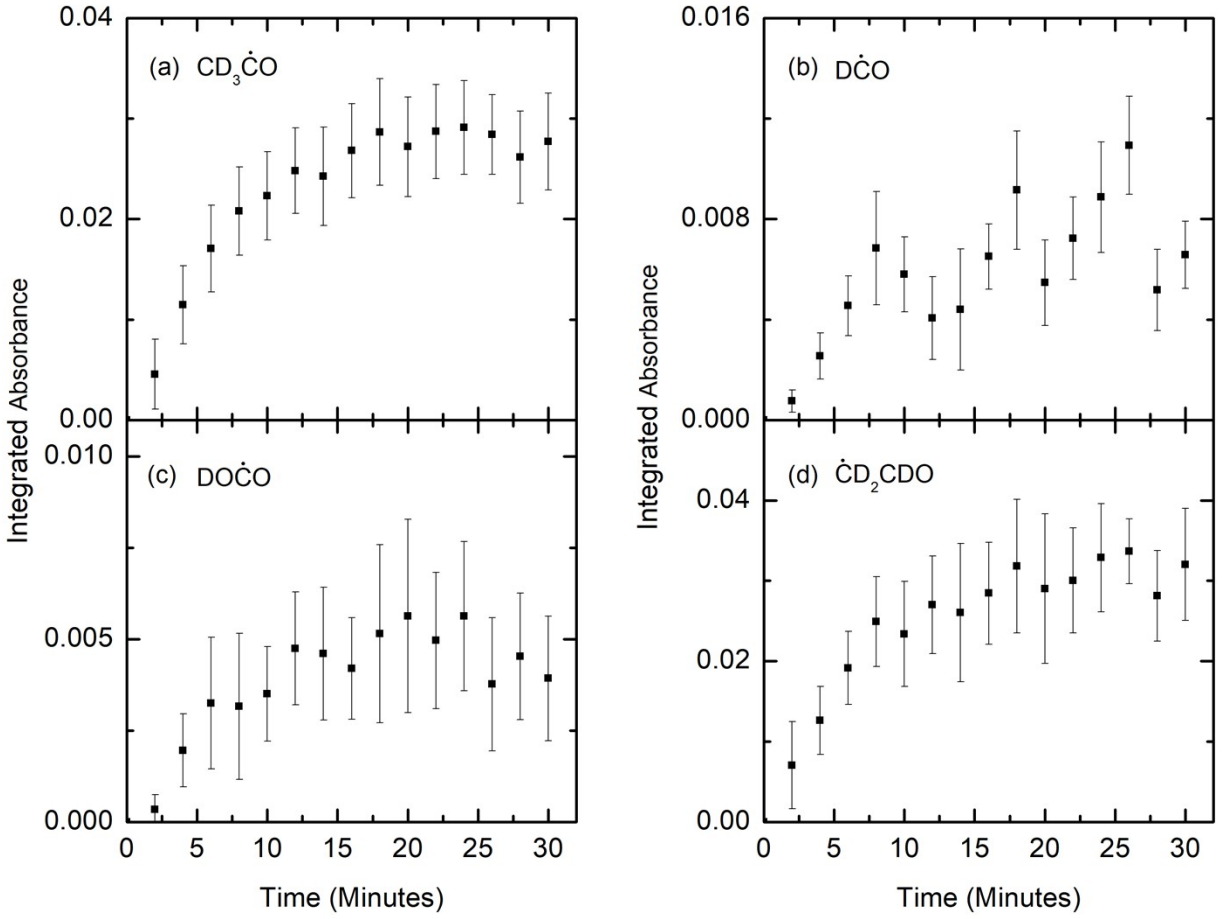


Figure S6. Temporal evolution of three radicals formed during irradiation of CO–CD_3CDO ice at 5 K: (a) **14**-d_3 ($CD_3\dot{C}O$, 1851 cm^{-1}), (b) **13**-d_1 ($D\dot{C}O$, 1794 cm^{-1}), (c) hydroxycarbonyl-d_1 ($DO\dot{C}O$, 1786 cm^{-1}), and **17**-d_3 ($\dot{C}D_2CDO$, 1513 cm^{-1}).

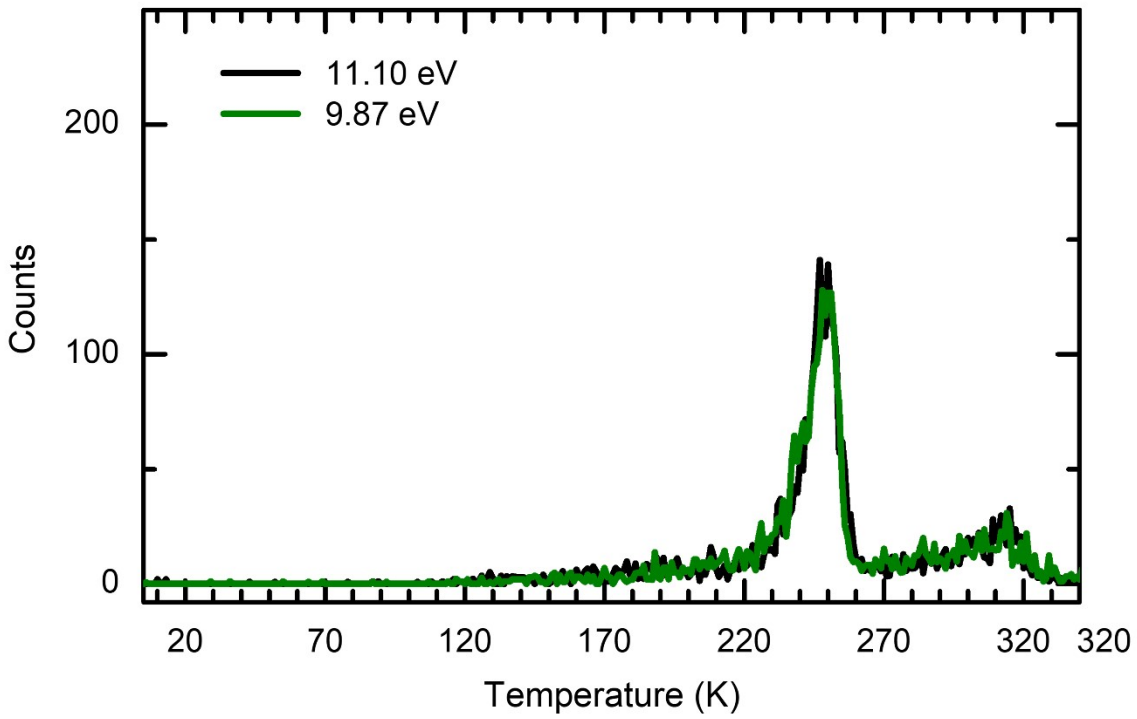


Figure S7. TPD profiles of *m/z* = 72 in low dose irradiated CO–CH_3CHO ice recorded at 11.10 eV and 9.87 eV match well, ruling out the formation of **18**.

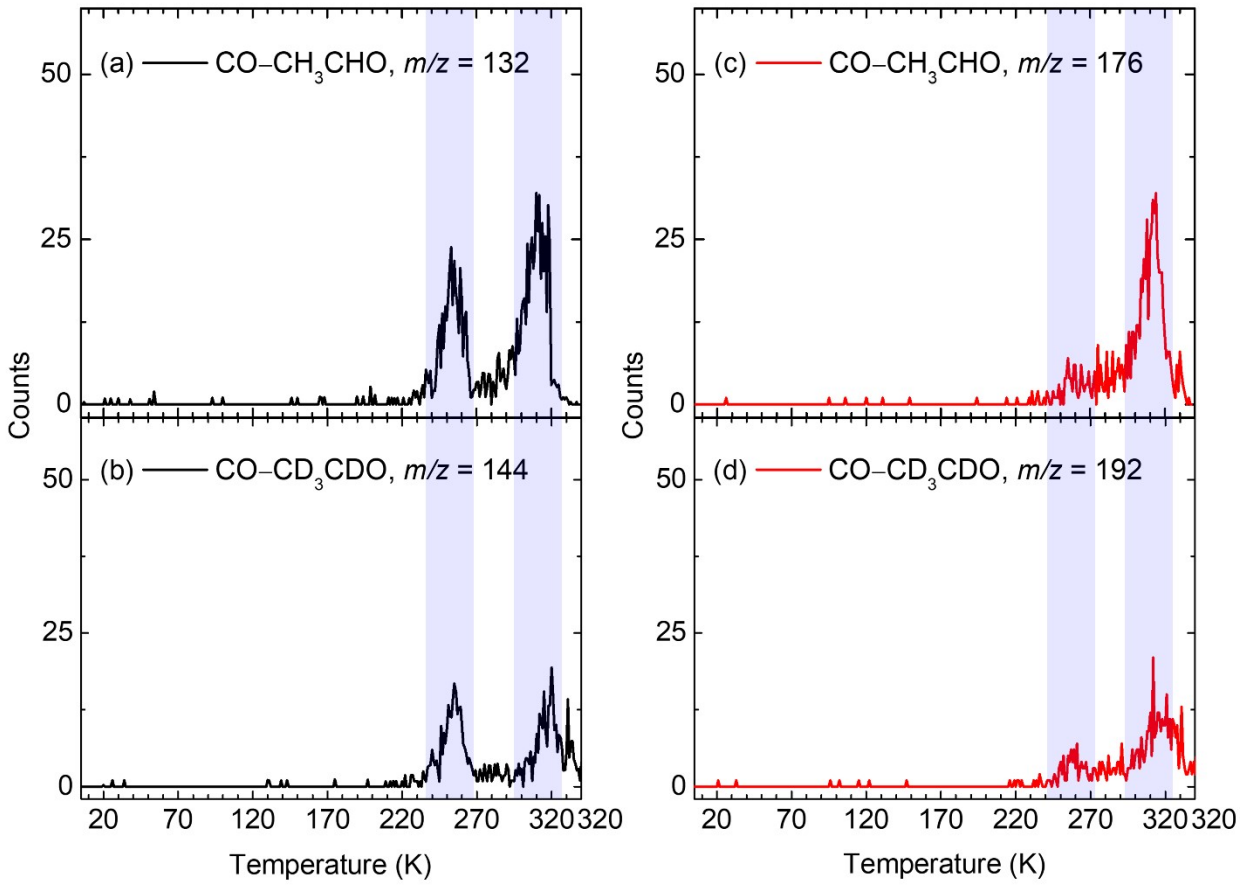


Figure S8. TPD profiles recorded at 11.10 eV with irradiated CO–CH_3CHO ice (*m/z* = 132 and 176) and CO–CD_3CDO ice (*m/z* = 144 and 192), confirming the formulae $C_6H_{12}O_3$ ((a) and (b)) and $C_8H_{16}O_4$ ((c) and (d)). The blue shaded regions indicate the sublimation temperatures of Peaks I and II.

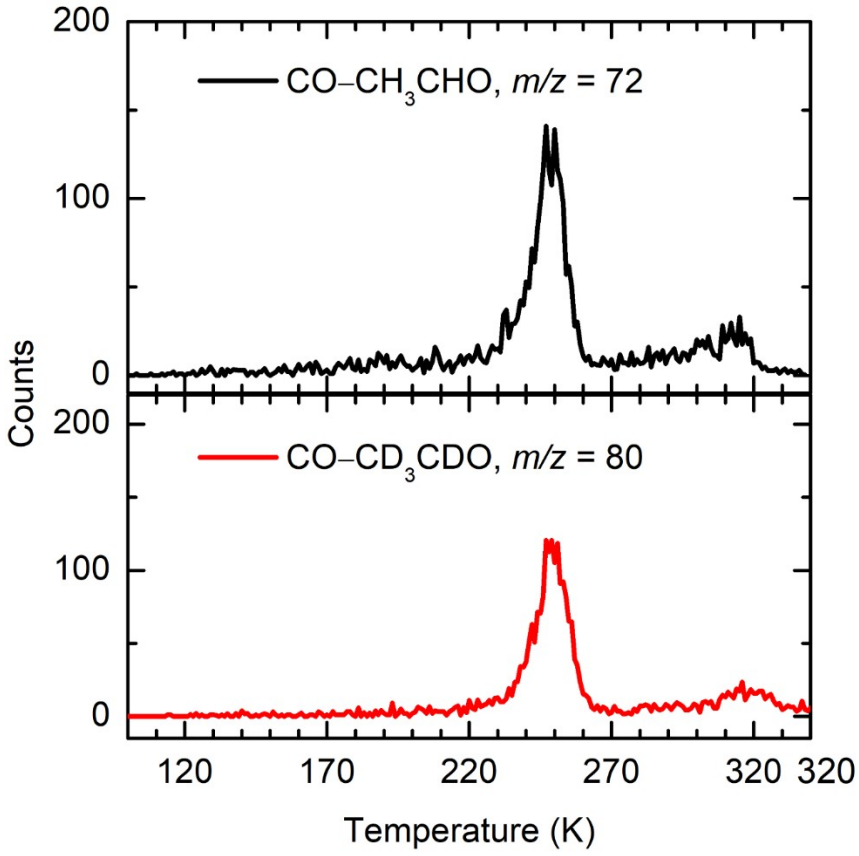


Figure S9. TPD profiles recorded at 11.10 eV with irradiated CO–CH_3CHO ice (*m/z* = 72) and CO–CD_3CDO ice (*m/z* = 80), indicating that C_4H_8O isomers contribute to Peaks I and II.

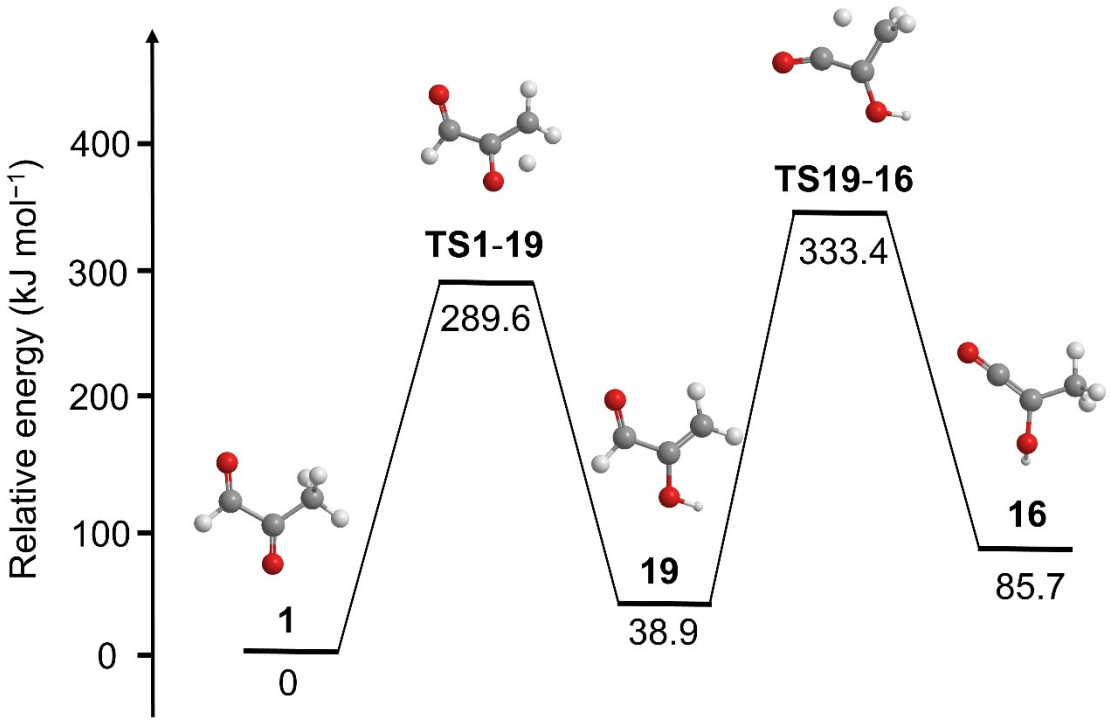


Figure S10. Potential energy surfaces of isomerization of methylglyoxal (**1**) leading to the formation of 2-hydroxypropenal (**19**) and 2-hydroxypropenone (**16**). Energies (kJ mol^{-1}) were computed using the CBS–QB3 composite approach and are relative to methylglyoxal (**1**).

Table S1. Experimental conditions of carbon monoxide–acetaldehyde ices including ice composition and thickness, irradiation parameters, and VUV photon energies.

Exp.	Ice	Composition of carbon monoxide to acetaldehyde	Thickness (nm)	Current (nA)	Irradiation time (s)	Dose (eV/ carbon monoxide)	Dose (eV/ acetaldehyde)	Photon energy (eV)
1	CO–CH_3CHO	1.3 ± 0.4 : 1	750 ± 30	–	–	–	–	11.10
2	CO–CH_3CHO	1.2 ± 0.4 : 1	750 ± 30	25 ± 2	300 ± 10	0.15 ± 0.03	0.30 ± 0.05	11.10
3	CO–CD_3CDO	1.9 ± 0.5 : 1	750 ± 30	23 ± 6	300 ± 10	0.14 ± 0.04	0.27 ± 0.08	11.10
4	$C^{18}O$–CH_3CHO	1.6 ± 0.5 : 1	750 ± 30	22 ± 1	300 ± 10	0.13 ± 0.02	0.26 ± 0.04	11.10
5	CO–CH_3CHO	1.2 ± 0.5 : 1	750 ± 30	24 ± 1	300 ± 10	0.15 ± 0.03	0.29 ± 0.04	9.87
6	CO–CH_3CHO	1.3 ± 0.6 : 1	770 ± 30	23 ± 1	300 ± 10	0.14 ± 0.03	0.27 ± 0.04	9.39
7	CO–CH_3CHO	1.3 ± 0.6 : 1	750 ± 30	22 ± 1	300 ± 10	0.13 ± 0.02	0.26 ± 0.04	8.77
8	CO–CH_3CHO	1.3 ± 0.5 : 1	750 ± 30	37 ± 1	1800 ± 10	1.35 ± 0.19	2.65 ± 0.37	8.77
9	CO–CD_3CDO	2.0 ± 0.4 : 1	750 ± 30	37 ± 1	1800 ± 10	1.35 ± 0.19	2.65 ± 0.37	8.77
10	CO–CH_3CHO	1.2 ± 0.5 : 1	750 ± 30	40 ± 5	1800 ± 10	1.46 ± 0.27	2.86 ± 0.52	7.60

Table S2. Vacuum ultraviolet (VUV) light generation parameters with an uncertainty of photon energies of less than 0.001 eV.

VUV photon energy (eV)	Nonlinear medium in four-wave mixing	ω_1 laser wavelength (nm)	ω_1 Dye	ω_2 laser wavelength (nm)	ω_2 Dye
11.10 ($2\omega_1 + \omega_2$)	Xenon	249.628	Coumarin 503	1064	–
9.87 ($2\omega_1 - \omega_2$)	Krypton	212.556	Stilbene 420	690.323	LDS 698
9.39 ($2\omega_1 - \omega_2$)	Xenon	222.566	Coumarin 450	707.956	LDS 698
8.77 ($2\omega_1 - \omega_2$)	Xenon	249.628	Coumarin 503	1064	–
7.60 ($2\omega_1 - \omega_2$)	Xenon	249.628	Coumarin 503	532	–

Table S3. Cartesian coordinates (Å), harmonic frequencies (cm^{-1}), infrared (IR) intensities (km mol^{-1}), and dipole moment (Debye) for methylglyoxal (**1**).

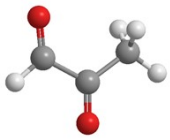
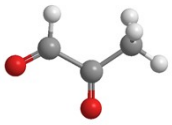
Structure	Geometry			Frequency	IR intensity
 **1a** Dipole moment (Debye) X: -0.3194 Y: 0.9648 Z: 0.0034 Total: 1.0163	C	-1.3485666413	-0.0865833859 -0.1387568206	73.6844	5.9247
	C	-0.2020053727	-0.8117634665 0.5875264819	134.3589	15.1708
	C	1.1128971011	-0.0884710095 0.6895557506	247.5145	15.9045
	O	-1.2407178033	1.011307249 -0.6167669781	470.1703	0.2564
	H	-2.2831390077	-0.6831702047 -0.1741067494	482.9286	25.0205
	O	-0.4261236507	-1.9144390498 1.0298508391	570.7444	13.8849
	H	0.9744606318	0.8703282326 1.1973571327	775.7253	14.4266
	H	1.4879337211	0.1474148351 -0.3106112943	906.4094	0.5899
	H	1.8316910217	-0.7034132001 1.2282616381	1007.7517	2.73
				1077.8641	2.8809
				1237.8913	23.1416
				1353.6507	1.9827
				1390.9208	39.7178
				1457.9117	16.1981
				1461.0255	11.5253
				1796.0035	105.8722
				1808.8035	117.1068
				2921.4344	96.88
				3039.8422	0.1128
				3094.5589	3.8097
				3151.0982	6.2718
 **1b** Dipole moment (Debye) X: 2.9920 Y: -4.0393 Z: 0.0019 Total: 5.0267	C	-1.3563457277	-0.0904932032 -0.1275090571	77.5352	6.3843
	C	-0.1958976206	-0.8078549864 0.6186189426	126.9107	0.3912
	C	0.7001626138	-1.6691801622 -0.2388519645	261.5062	2.0017
	O	-2.1367423593	0.6219939773 0.4368904658	401.0387	3.202
	H	-1.4172783994	-0.2804699189 -1.2225179526	464.9074	0.8182
	O	-0.0636425059	-0.6539831553 1.8048256573	636.2775	18.786
	H	1.1557836551	-1.0703302086 -1.0351117859	799.5861	27.5862
	H	0.115109424	-2.4536573181 -0.731498522	877.0806	0.5883
	H	1.4786409199	-2.1209250246 0.3732742164	966.7175	32.0158
				1074.342	2.4631
				1175.1998	56.8531
				1385.0301	39.4458
				1402.4241	4.1224
				1459.5821	16.3435
				1468.2848	11.9457
				1803.406	182.6718
				1835.6309	34.4782
				2866.4125	117.4244
				3023.0739	1.5264
				3074.7805	7.3408
				3147.2186	5.9417

Table S4. Cartesian coordinates (Å), harmonic frequencies (cm^{-1}), infrared (IR) intensities (km mol^{-1}), and dipole moment (Debye) for propanedial (**18**).

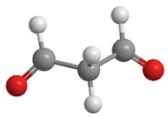
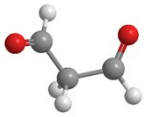
Structure	Geometry	Frequency	IR intensity
 **18a** Dipole moment (Debye) X: 0.0000 Y: 3.3573 Z: 1.2152 Total: 3.5705	C -1.2984418333 -0.167478195 -0.153283553 C -0.163143146 -0.9833710855 0.4399534217 C 0.369554994 -2.0366277642 -0.5157632531 O -2.35028177 0.0174428789 0.3964644604 O 0.5148074447 -3.1932814206 -0.2262110041 H -1.0919624814 0.2693379669 -1.1551770321 H -0.4713055483 -1.4405984487 1.3796373185 H 0.6640515491 -0.2812212163 0.6257154305 H 0.6327107913 -1.6633527156 -1.5299857887	63.4257 117.5762 282.748 452.1445 549.3128 733.1112 870.0173 954.7325 1089.4891 1112.3929 1190.3469 1254.2659 1421.3375 1431.4666 1435.0912 1807.0583 1837.5543 2859.2571 2879.5205 2997.1427 3129.0232	9.7117 1.6301 9.5357 3.1478 29.1182 2.3155 19.3537 75.9626 1.4543 31.1248 35.0134 7.3357 6.9328 6.117 16.6722 321.117 102.0926 11.8485 208.9849 1.623 2.8236
 **18b** Dipole moment (Debye) X: 1.6835 Y: 3.1146 Z: 1.2840 Total: 3.7661	C -1.3144382211 -1.4789376217 -0.4252812173 C -0.1510509949 -0.912653016 0.3668664151 C 1.14065341 -0.7965624217 -0.4189443227 O -2.4198761764 -1.0048603916 -0.4010096601 O 1.2936728784 -1.2003182329 -1.5421523379 H -1.0830204255 -2.3776031996 -1.0285546152 H 0.0499145192 -1.5772000643 1.2212837932 H -0.4275469502 0.0580571768 0.7904949859 H 1.9704419605 -0.2990622289 0.1278369591	40.2195 108.3346 229.7122 462.8054 639.3883 697.4472 857.7984 914.6311 1061.3582 1091.9962 1214.9935 1307.3679 1411.2453 1415.9712 1432.0593 1809.8922 1823.9981 2882.52 2934.1665 2998.8611 3072.2047	12.0726 0.7678 11.6198 12.5021 5.0189 5.9348 6.2403 9.5936 58.7593 12.8524 7.5318 36.9695 19.4173 14.5308 11.1684 203.9804 128.5002 131.9529 70.4563 2.0832 4.6324

Table S5. Cartesian coordinates (Å), harmonic frequencies (cm^{-1}), infrared (IR) intensities (km mol^{-1}), and dipole moment (Debye) for 2-hydroxypropenone (**16**).

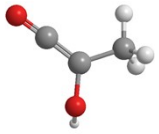
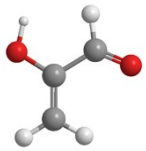
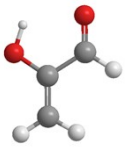
Structure	Geometry			Frequency	IR intensity
				181.9091	1.3263
				187.7001	0.0515
				277.0078	96.0453
				295.3076	17.8531
				363.3187	8.689
				512.4422	21.8917
	O 0.3103291869	-0.5432242651	-1.9553186994	691.5249	1.907
	C 0.1630202061	-0.2218488461	-0.8428299774	765.2709	8.4858
	C 0.0049482677	0.1252435796	0.4207175729	996.5632	6.8124
	O 0.4359744058	1.4023976391	0.7972909485	1043.0043	4.7179
	C -0.5061980935	-0.8163602942	1.4699341621	1198.1139	110.6414
	H -0.3434507905	1.960871279	0.9046852914	1275.0583	27.1237
	H -0.7195412064	-1.803851527	1.0537501402	1410.4861	29.9699
	H -1.4310334153	-0.439634701	1.9236293903	1416.5385	4.7732
	H 0.2364814392	-0.9328428644	2.2661011714	1468.0557	9.0596
				1507.3983	12.4262
				2210.7729	525.24
				3002.0864	38.2593
				3052.9164	26.237
				3097.4575	16.5393
				3765.7384	29.4633
Dipole moment (Debye) X: 2.2821 Y: -0.8236 Z: 1.4500 Total: 2.8265					

Table S6. Cartesian coordinates (Å), harmonic frequencies (cm^{-1}), infrared (IR) intensities (km mol^{-1}), and dipole moment (Debye) for 2-hydroxypropenal (**19**).

Structure	Geometry	Frequency	IR intensity
 **19a** Dipole moment (Debye) X: 1.4612 Y: -1.6479 Z: -0.0035 Total: 2.2024	C -1.3257324546 -0.0474302748 -0.0077925995 C -0.2032685759 -0.7507325909 0.6746357479 C 0.9493497327 -0.1293781276 0.9377294296 O -1.3134598894 1.0985641682 -0.377542114 H -2.2292266143 -0.6893182681 -0.1620261533 O -0.4163902717 -2.0560311392 1.0155415045 H 1.0581026227 0.905105663 0.6445526415 H 1.76571659 -0.6370542142 1.4334215493 H -1.3016411395 -2.3220952164 0.741299994	158.5643 247.004 286.0181 432.5565 469.3063 603.492 737.4448 899.008 903.1035 979.099 1011.7238 1215.4258 1335.6847 1413.3089 1426.9986 1692.6066 1808.1063 2803.1146 3168.3921 3269.5002 3799.3483	6.7495 109.5079 9.4267 9.2891 6.4079 10.3984 3.4833 60.4998 53.9914 50.7624 0.5729 40.6783 231.7812 33.3666 6.723 82.3906 99.9871 172.461 2.3965 0.0953 51.8364
 **19b** Dipole moment (Debye) X: -1.5354 Y: -1.9639 Z: 0.0003 Total: 2.4928	C -1.2965728332 -0.063922938 -0.0152919337 C -0.2106035558 -0.772380307 0.6959297224 C -0.132113346 -0.7560125419 2.032672035 O -1.360403123 -0.083709883 -1.2271672313 H -2.032663418 0.4742544171 0.6075976557 O 0.6618404112 -1.4139362843 -0.108849827 H -0.8748061217 -0.2158747421 2.604339911 H 0.6572996782 -1.2702680967 2.5642364058 H 0.3542723085 -1.250509624 -1.0174467379	205.3749 291.1645 409.284 532.2568 581.9783 683.8242 738.1645 881.0345 898.6639 984.7133 1007.395 1266.4532 1371.14 1409.7075 1448.7836 1717.1801 1756.0365 2967.5354 3164.0893 3257.4972 3664.436	4.0187 23.546 2.0394 0.0128 98.0849 2.1752 13.9714 63.3021 52.5974 37.8731 0.0521 63.4805 18.0169 232.6025 36.5058 14.9187 259.674 64.0139 0.0142 1.7513 102.821

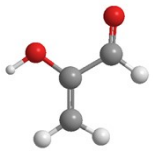
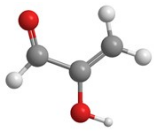
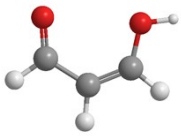
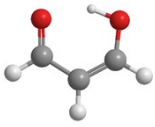
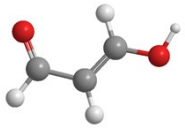
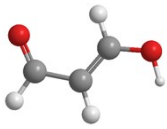
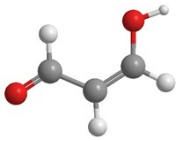
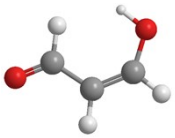
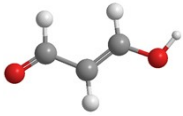
 **19c** Dipole moment (Debye) X: -4.2780 Y: -1.6331 Z: 0.0000 Total: 4.5791	C -1.3971024091 -1.4950276051 1.1076985536 C -0.1926135668 -0.7339602269 0.6739764024 C -0.0565504781 0.5492209881 1.0347318379 O -1.6090532983 -2.6481774907 0.835177467 H -2.1010147145 -0.8931275502 1.7193905887 O 0.6685886086 -1.4639424989 -0.0722120627 H -0.8204921932 1.0222584618 1.6369264638 H 0.7974287956 1.1528006649 0.749123518 H 1.4215392557 -0.915084743 -0.3183027686	164.6382 273.5106 423.0266 430.6895 522.9738 659.1123 726.6233 865.6826 877.7793 981.6836 1016.7923 1199.8171 1388.923 1419.8639 1458.807 1686.4367 1802.1916 2899.6575 3150.5067 3239.2684 3819.7464	1.2857 4.1576 125.0331 8.2425 0.4342 27.6319 1.3647 64.2762 63.491 20.7059 0.006 147.8404 3.2494 24.7226 13.2616 101.5033 235.4222 92.8123 2.7786 4.1331 43.9889
 **19d** Dipole moment (Debye) X: 3.4795 Y: 0.2231 Z: 0.0000 Total: 3.4867	C -1.4064892456 -1.4833003505 1.1215849359 C -0.2158253259 -0.7321982596 0.6201598443 C -0.2315872261 -0.0768327732 -0.5431574961 O -2.4570193316 -1.5609908655 0.5351702226 H -1.2381153251 -1.9744399986 2.1012570808 O 0.8232459675 -0.8258604485 1.4999460067 H -1.1372942407 -0.0957722076 -1.1331628642 H 0.6235986188 0.4721581067 -0.9200297471 H 1.5804861087 -0.3365532033 1.1605820172	159.9836 284.1328 392.4444 441.6726 486.3537 603.5144 727.7701 876.9063 901.0149 973.1587 1031.1843 1167.3377 1346.7241 1425.8323 1431.9774 1684.1637 1808.0803 2921.0295 3151.3636 3250.7445 3826.9428	7.721 4.4523 122.019 12.0009 3.0718 13.7543 2.8393 55.298 46.8113 43.2255 0.2679 191.9868 0.5759 24.3833 24.7373 147.173 89.6747 104.6566 7.9936 0.5513 44.539

Table S7. Cartesian coordinates (Å), harmonic frequencies (cm^{-1}), infrared (IR) intensities (km mol^{-1}), and dipole moment (Debye) for 3-hydroxypropenal (**20**).

Structure	Geometry	Frequency	IR intensity
 **20a** Dipole moment (Debye) X: -4.0262 Y: 2.9393 Z: 0.0000 Total: 4.9849	C 0. -0.3105118433 1.334912086 C 0. -1.0239181309 0.0544823451 C 0. -0.460769553 -1.1683382615 O 0. 0.8920051039 1.4882918356 H 0. -0.9888237734 2.2176717607 O 0. 0.8639794144 -1.3871868197 H 0. -1.0928662305 -2.0545569012 H 0. -2.1072553423 0.0937434622 H 0. 1.0345003552 -2.3338595072	159.8987 190.0585 325.6807 458.7611 495.9448 787.1323 878.3505 922.6683 974.9 1031.5775 1116.5034 1274.4851 1315.9093 1432.1376 1470.4759 1682.1779 1785.2423 2854.7557 3126.2387 3182.113 3844.652	2.5035 3.89 115.5542 18.0309 23.582 30.2507 19.6953 71.7678 0.6691 5.4472 16.3774 81.7729 205.0192 3.7016 22.0192 303.6493 146.3769 196.4424 15.6588 9.9996 124.2114
 **20b** Dipole moment (Debye) X: -0.6282 Y: 3.1283 Z: 0.0000 Total: 3.1907	C 0. 0.329485714 -1.2357997769 C 0. 1.0986072054 -0.0200895247 C 0. 0.4513111528 1.1804756372 O 0. -0.9072844693 -1.262426978 H 0. 0.8860694873 -2.1891226658 O 0. -0.8600193448 1.3174995882 H 0. 0.9826999082 2.1283995412 H 0. 2.1790679656 -0.0550585652 H 0. -1.2343076192 0.3925027441	278.4153 293.9169 395.8439 521.2067 788.2107 896.9044 929.6361 1001.0524 1012.4617 1043.0019 1115.9373 1291.9089 1400.7859 1407.0405 1475.5736 1634.1752 1704.2931 2963.143 3140.8929 3189.8537 3215.0294	7.9795 4.3255 6.142 18.26 35.1881 6.9645 71.1421 44.5141 20.4751 18.3627 11.2576 155.7593 51.4475 63.0864 52.846 267.6262 204.5528 121.7864 154.2756 76.3697 2.4332

 **20c** Dipole moment (Debye) X: 2.9616 Y: 0.1992 Z: 0.0000 Total: 2.9683	C 0. -0.4396051577 -1.4475765735 C 0. -0.7240237335 -0.0104454632 C 0. 0.2892149324 0.8695179335 O 0. 0.6700914628 -1.9448801872 H 0. -1.3412805521 -2.0954291609 O 0. 0.0958511506 2.201299217 H 0. 1.3151911021 0.5097884279 H 0. -1.7536889618 0.328446852 H 0. 0.9442197571 2.6551489545	210.5211 215.7994 263.6568 444.5599 447.8478 753.6584 847.5965 992.5887 998.5713 1033.8961 1175.6222 1260.0647 1345.6419 1369.4857 1430.9827 1679.3859 1775.9985 2890.1746 3156.5837 3184.7179 3842.9363	12.4721 49.7608 3.3245 105.682 5.3998 92.1523 17.2491 26.1592 27.0044 0.5903 7.5389 198.3248 6.5224 179.9842 10.9735 437.1256 111.0015 168.2566 2.7136 5.2775 123.7711
 **20d** Dipole moment (Debye) X: 2.6471 Y: 3.2182 Z: 0.0000 Total: 4.1670	C 0. -0.4338862553 -1.4399627031 C 0. -0.6968234103 0.0023408984 C 0. 0.3233521095 0.8789415734 O 0. 0.6664149204 -1.9535058859 H 0. -1.347624289 -2.0719337583 O 0. 0.2433697116 2.2172587632 H 0. 1.3506077511 0.5331725783 H 0. -1.731049304 0.336548967 H 0. -0.682841234 2.491219567	209.7618 210.8385 263.6413 449.261 572.4657 751.1318 827.5731 999.767 1018.8366 1035.9132 1162.265 1299.5918 1323.9714 1400.8063 1433.7671 1653.4555 1776.3593 2882.3347 3148.6409 3202.6158 3787.2677	3.0483 0.3837 5.8202 7.5241 93.0732 71.8291 39.0187 99.596 38.1564 6.8044 146.155 8.5605 52.691 0.223 4.0478 596.5689 118.5084 167.5456 14.636 0.176 61.2518
 **20e** Dipole moment (Debye) X: -6.0057	C 0. 0.3648054847 -1.0779509272 C 0. -0.729387609 -0.1071163015 C 0. -0.5596408953 1.2247831825 O 0. 0.1944460305 -2.280117577 H 0. 1.3857972295 -0.6483647262 O 0. 0.6607594807 1.8110990691 H 0. -1.4131216637 1.8984201939	162.3813 204.6846 279.8592 451.6196 476.0536 692.6553 810.1836 980.6541 1020.994	3.1374 0.847 127.9658 11.1902 16.2279 13.9568 45.4142 0.6803 116.2571

Y: 0.1586 Z: 0.0000 Total: 6.0078	H 0. -1.7376768203 -0.5030183139 H 0. 0.564998763 2.7671554004	1033.9043 1148.3736 1249.3361 1298.2161 1393.2811 1465.2152 1708.8881 1761.0895 2920.2493 3142.7136 3195.4977 3863.1498	1.877 33.6588 18.3138 267.2602 6.7297 16.286 143.7531 281.2062 79.5013 13.4044 3.6016 138.4099
 **20f** Dipole moment (Debye) X: -3.1854 Y: -0.6304 Z: 0.0000 Total: 3.2472	C 0. 0.3152303772 -1.0850709784 C 0. -0.7443680147 -0.089408155 C 0. -0.5516707225 1.245641156 O 0. 0.1408221884 -2.2847829634 H 0. 1.3611816459 -0.6877048591 O 0. 0.6097372469 1.9231768388 H 0. -1.3890186171 1.934922206 H 0. -1.7618356436 -0.4607042559 H 0. 1.3594615394 1.315471011	167.742 216.4288 314.5744 476.8064 573.0876 698.5511 821.8712 991.9663 1013.6442 1025.7649 1151.0359 1237.7738 1363.8141 1404.3481 1473.2109 1673.5908 1767.5016 2779.7369 3181.2251 3200.1243 3795.4202	7.599 13.5399 8.3495 8.5071 107.5598 7.7633 42.7736 0.0323 85.4221 7.5172 103.7279 168.6832 6.2237 14.4096 19.768 238.5524 300.9672 161.7348 3.485 4.5389 35.6446
 **20g** Dipole moment (Debye) X: 4.4373 Y: -3.6445 Z: 0.0000 Total: 5.7421	C 0. -0.3407154593 -1.3339997538 C 0. 0.3595304365 -0.055302885 C 0. -0.3413919876 1.0877190567 O 0. 0.1946269039 -2.4213919364 H 0. -1.453070294 -1.2509024753 O 0. 0.244765388 2.3014571791 H 0. -1.4302380185 1.0731879495 H 0. 1.4434159538 -0.0538370509 H 0. -0.4242629228 2.9925199162	151.853 222.1789 322.4901 423.1217 493.6045 565.956 858.4186 970.6923 1024.4799 1141.5686 1166.1719 1217.5643 1335.9267 1356.6834 1440.4173 1720.1445 1772.5058 2830.7036	0.1462 4.0125 27.3819 99.569 9.7135 35.7823 10.5887 41.7144 1.3294 79.5854 17.3571 184.5488 211.0437 8.2269 4.797 221.9424 313.3378 133.7324

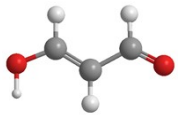
		3129.2715	14.7561
		3191.007	1.4896
		3846.2099	129.2742
 **20h** Dipole moment (Debye) X: 3.6208 Y: -0.6969 Z: 0.0000 Total: 3.6873	C 0. -0.3613032576 1.3360939883 C 0. 0.3328034219 0.0533123401 C 0. -0.3635160757 -1.095717293 O 0. 0.1846416543 2.4183017769 H 0. -1.4726820394 1.2595426034 O 0. 0.1262700704 -2.3458074551 H 0. -1.4491267859 -1.1045896671 H 0. 1.419174958 0.0722678344 H 0. 1.0917780539 -2.3189141279	153.7181 219.0258 328.4563 491.6946 556.5436 571.7957 849.6213 988.8478 1029.6191 1137.2908 1161.6961 1241.3101 1337.2375 1381.9607 1441.0921 1689.4385 1771.3154 2848.2047 3157.4805 3177.2999 3790.1275	4.838 18.8104 21.3251 0.4915 84.5556 3.8835 26.9024 47.6585 10.6349 334.3373 17.528 61.8383 17.4665 7.8929 5.9683 349.5535 284.9879 126.252 6.8307 6.1571 62.9968

Table S8. Cartesian coordinates (Å) for transitions states of **TS1-19**, and **TS19-16**.

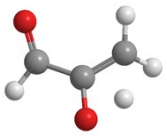
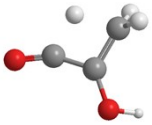
Structure		Geometry		
 **TS1-19**	C	-1.533221	0.022278	-0.169685
	C	-0.208303	-0.430615	0.370671
	C	1.003961	0.273540	0.532689
	O	-1.873335	1.176864	-0.185197
	H	-2.176248	-0.807219	-0.525399
	O	-0.107566	-1.626863	0.826121
	H	1.035441	1.351880	0.641986
	H	1.816421	-0.142767	-0.064321
	H	0.985050	-1.041247	1.244874
 **TS19-16**	O	0.262221	-0.802240	-1.590891
	C	-0.131275	-0.444574	-0.525166
	C	0.041305	0.368513	0.594446
	O	0.469841	1.646756	0.639275
	C	-0.397899	-0.487221	1.661613
	H	-0.027320	2.138382	1.303435
	H	-0.643765	-1.340061	0.453599
	H	-1.449747	-0.691391	1.853394
	H	0.205988	-0.523166	2.576735

Table S9. Absorption peaks observed in CO–CH_3CHO ice before and after low dose irradiation (24 nA, 5 minutes) at 5 K. Vibration mode: stretching (ν), bending in plane (δ), and out of plane (γ). Indication: asymmetric (a) and symmetric (s).

Absorptions of pristine ice (cm^{-1})		
CO	Assignment[1]	
4249	$2\nu(^{13}CO)$	overtone
2136	$\nu(CO)$	$\nu(CO)$
2090	$\nu(^{13}CO)$	$\nu(^{13}CO)$
CH_3CHO	Assignment[2]	
3425	$2\nu_4$	overtone
3123	$\nu_4 + \nu_6$	combination
3007	ν_1	$\nu_a(CH_3)$
2967	ν_{11}	$\nu(CH_3)$
2918	ν_2	$\nu_s(CH_3)$
2856, 2830	$2\nu_6$	overtone
2759, 2737	ν_3	$\nu(CH)$
2596	$\nu_4 + \nu_9$	combination
2465	$\nu_7 + \nu_8$	combination
2234	$\nu_7 + \nu_9$	combination
2191	$2\nu_8$	overtone
2158	$\nu_6 + \nu_{14}$	combination
1999	$\nu_8 + \nu_9$	combination
1768	$2\nu_9$	overtone
1722	ν_4	$\nu(CO)$
1685	ν_4 ($CH_3{}^{13}CHO$)	$\nu(^{13}CO)$
1635	$\nu_8 + \nu_{10}$	combination
1543	$2\nu_{14}$	overtone
1430	ν_5 / ν_{12}	$\delta(CH_3)$ / $\delta_a(CH_3)$
1405	$\nu_9 + \nu_{10}$	combination
1389	ν_6	$\delta(CH)$
1349	ν_7	$\delta_s(CH_3)$
1122	ν_8	$\gamma(CH_3)$
1107	ν_8 ($^{13}CH_3CHO$)	$\gamma(^{13}CH_3)$
885	$\nu_{14} + \nu_{15}$	combination
772	ν_{14}	$\gamma(CH)$
New absorptions after irradiation (cm^{-1})	Assignment[1, 3-5]	
2343	$\nu_3(CO_2)$	
1852	$\nu_3(H\dot{C}O)$	
1841	$\nu_3(CH_3\dot{C}O)$ / $\nu_2(HO\dot{C}O)$	
1571	$\nu_4(\dot{C}H_2CHO)$	

Table S10. Absorption peaks observed in CO–CH_3CHO ice before and after high dose irradiation (37 nA, 30 minutes) at 5 K. Vibration mode: stretching (ν), bending in plane (δ), and out of plane (γ). Indication: asymmetric (a) and symmetric (s).

Absorptions of pristine ice (cm^{-1})		
CO	Assignment[1]	
4249	$2\nu(^{13}CO)$	overtone
2137	$\nu(CO)$	$\nu(CO)$
2091	$\nu(^{13}CO)$	$\nu(^{13}CO)$
CH_3CHO	Assignment[2]	
3425	$2\nu_4$	overtone
3008	ν_1	$\nu_a(CH_3)$
2975	ν_{11}	$\nu(CH_3)$
2918	ν_2	$\nu_s(CH_3)$
2856, 2824	$2\nu_6$	overtone
2761, 2738	ν_3	$\nu(CH)$
2597	$\nu_4 + \nu_9$	combination
2465	$\nu_7 + \nu_8$	combination
2228	$\nu_7 + \nu_9$	combination
2184	$2\nu_8$	overtone
2154	$\nu_6 + \nu_{14}$	combination
2001	$\nu_8 + \nu_9$	combination
1768	$2\nu_9$	overtone
1721	ν_4	$\nu(CO)$
1683	ν_4 ($CH_3{}^{13}CHO$)	$\nu(^{13}CO)$
1635	$\nu_8 + \nu_{10}$	combination
1541	$2\nu_{14}$	overtone
1430	ν_5 / ν_{12}	$\delta(CH_3)$ / $\delta_a(CH_3)$
1405	$\nu_9 + \nu_{10}$	combination
1389	ν_6	$\delta(CH)$
1350	ν_7	$\delta_s(CH_3)$
1122	ν_8	$\gamma(CH_3)$
1107	ν_8 ($^{13}CH_3CHO$)	$\gamma(^{13}CH_3)$
885	$\nu_{14} + \nu_{15}$	combination
772	ν_{14}	$\gamma(CH)$
New absorptions after irradiation (cm^{-1})	Assignment[1, 3-5]	
3343	$\nu(OH)$	
2941	$\nu(CH)$	
2343	$\nu_3(CO_2)$	
1304	$\nu_4(CH_4)$	
1852	$\nu_3(H\dot{C}O)$	
1841	$\nu_3(CH_3\dot{C}O)$ / $\nu_2(HO\dot{C}O)$	
1571	$\nu_4(\dot{C}H_2CHO)$	

Table S11. Absorption peaks observed in CO–CD_3CDO ice before and after low dose irradiation (23 nA, 5 minutes) at 5 K. Vibration mode: stretching (ν), bending in plane (δ), and out of plane (γ). Indication: asymmetric (*a*) and symmetric (*s*).

Absorptions of pristine ice (cm^{-1})		
CO	Assignment[1]	
4250	$2\nu(^{13}CO)$	overtone
2136	$\nu(CO)$	$\nu(CO)$
2088	$\nu(^{13}CO)$	$\nu(^{13}CO)$
CD_3CDO	Assignment[2]	
3397	$2\nu_4$	overtone
2472	$\nu_4 + \nu_9$	combination
2312	$2\nu_5$	overtone
2258	ν_1	$\nu_a(CD_3)$
2222	ν_{11}	$\nu(CD_3)$
2183	$\nu_5 + \nu_7$	combination
2104, 2066	ν_2	$\nu_s(CD_3)$
1991	$\nu_6 + \nu_{13}$	combination
1906	$\nu_5 + \nu_9$	combination
1714	ν_4	$\nu(CO)$
1696	$\nu_{8+}\nu_9$	overtone
1669	ν_4 ($CD_3{}^{13}CDO$)	$\nu(^{13}CO)$
1521	$2\nu_{14}$	overtone
1157	ν_5	$\nu(CC)$
1043	ν_{12}	$\delta(CD_3)$
1023	ν_6	$\delta_a(CD_3)$
953	ν_{13}	$\gamma(CD)$
941	ν_8	$\delta_s(CD_3)$
New absorptions after irradiation (cm^{-1})	Assignment[1, 3, 4]	
2343	$\nu_3(CO_2)$	
1851	$\nu_3(CD_3\dot{C}O)$	
1797	$\nu_3(D\dot{C}O)$	
1787	$\nu_2(DO\dot{C}O)$	
1513	$\nu_4(\dot{C}D_2CDO)$	

Table S12. Absorption peaks observed in CO–CD_3CDO ice before and after high dose irradiation (37 nA, 30 minutes) at 5 K. Vibration mode: stretching (ν), bending in plane (δ), and out of plane (γ). Indication: asymmetric (a) and symmetric (s).

Absorptions of pristine ice (cm^{-1})		
CO	Assignment[1]	
4250	2ν(CO)	overtone
2136	ν(CO)	ν(CO)
2087	$\nu(^{13}CO)$	$\nu(^{13}CO)$
CD_3CDO	Assignment[2]	
3394	$2\nu_4$	overtone
2462	$\nu_4 + \nu_9$	combination
2253	ν_1	$\nu_a(CD_3)$
2226	ν_{11}	$\nu(CD_3)$
2187	$\nu_5 + \nu_7$	combination
2103, 2067	ν_2	$\nu_s(CD_3)$
1906	$\nu_5 + \nu_9$	combination
1714	ν_4	ν(CO)
1695	$\nu_8 + \nu_9$	overtone
1521	$2\nu_{14}$	overtone
1158	ν_5	ν(CC)
1043	ν_{12}	$\delta(CD_3)$
1022	ν_6	$\delta_a(CD_3)$
953	ν_{13}	γ(CD)
941	ν_8	$\delta_s(CD_3)$
New absorptions after irradiation (cm^{-1})	Assignment[1, 3, 4, 6]	
2498	ν(OD)	
2342	$\nu_3(CO_2)$	
1851	$\nu_3(CD_3\dot{C}O)$	
1794	$\nu_3(D\dot{C}O)$	
1786	$\nu_2(DO\dot{C}O)$	
1578	ν(C=C) / ν(C=O)	
1513	$\nu_4(\dot{C}D_2CDO)$	

Table S13. Absorption peaks observed in $C^{18}O$–CH_3CHO ice before and after low dose irradiation (22 nA, 5 minutes) at 5 K. Vibration mode: stretching (ν), bending in plane (δ), and out of plane (γ). Indication: asymmetric (a) and symmetric (s).

Absorptions of pristine ice (cm^{-1})		
$C^{18}O$	Assignment[7]	
4148	$2\nu(C^{18}O)$	overtone
2136	ν(CO)	ν(CO)
2086	$\nu(C^{18}O)$	$\nu(C^{18}O)$
CH_3CHO	Assignment[2]	
3426	$2\nu_4$	overtone
3124	$\nu_4 + \nu_6$	combination
3007	ν_1	$\nu_a(CH_3)$
2966	ν_{11}	$\nu(CH_3)$
2918	ν_2	$\nu_s(CH_3)$
2855, 2836	$2\nu_6$	overtone
2760, 2737	ν_3	ν(CH)
2597	$\nu_4 + \nu_9$	combination
2464	$\nu_7 + \nu_8$	combination
2235	$\nu_7 + \nu_9$	combination
2191	$2\nu_8$	overtone
2154	$\nu_6 + \nu_{14}$	combination
2002	$\nu_8 + \nu_9$	combination
1766	$2\nu_9$	overtone
1723	ν_4	ν(CO)
1684	ν_4 ($CH_3{}^{13}CHO$)	$\nu(^{13}CO)$
1637	$\nu_8 + \nu_{10}$	combination
1541	$2\nu_{14}$	overtone
1430	ν_5 / ν_{12}	$\delta(CH_3)$ / $\delta_a(CH_3)$
1405	$\nu_9 + \nu_{10}$	combination
1389	ν_6	δ(CH)
1349	ν_7	$\delta_s(CH_3)$
1121	ν_8	$\gamma(CH_3)$
1109	ν_8 ($^{13}CH_3CHO$)	$\gamma(^{13}CH_3)$
884	$\nu_{14} + \nu_{15}$	combination
772	ν_{14}	γ(CH)
New absorptions after irradiation (cm^{-1})	Assignment[4, 5]	
1843	$\nu_3(CH_3\dot{C}O)$ / $\nu_2(HO\dot{C}O)$	
1570	$\nu_4(\dot{C}H_2CHO)$	

Table S14. Error analysis of adiabatic ionization energies (IEs) and relative energies (ΔE) of methylglyoxal (**1**) and its enol tautomers (**16** and **19**); IEs and ΔE were computed at CBS–QB3 level of theory including the zero-point vibrational energy (ZPVE) corrections. The IE ranges are corrected for the thermal and Stark effect by –0.03 eV and the combined error limits of –0.05/+0.03 eV.[8]

Name	Isomer	ΔE (kJ mol^{-1})	Computed IE (eV)	Corrected IE ranges (eV)
Methylglyoxal	**1a**	0.0	9.60	9.52 – 9.60
	1b	21.9	9.37	9.29 – 9.37
2-Hydroxypropenone	**16**	85.7	8.17	8.09 – 8.17
2-Hydroxypropenal	**19a**	45.4	9.53	9.45 – 9.53
	19b	15.2	9.64	9.56 – 9.64
	19c	39.4	9.78	9.70 – 9.78
	19d	38.9	9.60	9.52 – 9.60

Table S15. Error analysis of IEs and relative energies (ΔE) of propanedial (**18**) and its enol tautomer 3-hydroxypropenal (**20**); IEs and ΔE were computed at CBS–QB3 level of theory including the ZPVE corrections. The IE ranges are corrected for the thermal and Stark effect by –0.03 eV and the combined error limits of –0.05/+0.03 eV.[8]

Name	Isomer	ΔE (kJ mol^{-1})	Computed IE (eV)	Corrected IE ranges (eV)
Propanedial	**18a**	23.8	10.21	10.13 – 10.21
	18b	18.9	10.08	10.00 – 10.08
3-Hydroxypropenal	**20a**	50.7	9.48	9.40 – 9.48
	20b	1.7	9.55	9.47 – 9.55
	20c	35.9	9.49	9.41 – 9.49
	20d	34.3	9.60	9.52 – 9.60
	20e	37.8	9.63	9.57 – 9.63
	20f	38.1	9.79	9.71 – 9.79
	20g	30.9	9.67	9.59 – 9.67
	20h	26.5	9.78	9.70 – 9.78

Supplementary Source code. The source code of the program for conformer sorting.

```
def generate_input(filename):

  with open(filename + '.gjf','r') as file:
    data = file.read()

  data = data.split('\n\n')[:-1]

  del(file)

  from re import search, MULTILINE

  variables = ['']
  old_variables = []

  for line in data[4].split('\n'):
    match = search(r'^\s*(?P<variable_name>\w\d+)\s+(?P<variable_value>-
?\d+\.\d+)\s*(?P<number_of_scan_steps>(?:\d+)?)\s*(?P<scan_step_size>(?:-?\d+\.\d+)?)$', line,
flags = MULTILINE)
    if match['number_of_scan_steps'] == '' and match['scan_step_size'] == '':
      for index, item in enumerate(variables):
        variables[index] = item + line + '\n'
    else:
      old_variables = variables[:]
      variables = []
      pattern = (' ' * 3) + '{var_name}' + (' ' * 13) + '{var_value}'
      name = match['variable_name']
      initial_value = float(match['variable_value'])
      number_of_scan_steps = int(match['number_of_scan_steps'])
      scan_step_size = float(match['scan_step_size'])
      for scan_step in range(number_of_scan_steps):
        value = (initial_value + scan_step_size * scan_step)
        if value > 180:
          value = value - 360
        if value <= -180:
          value = value + 360
        tmp = pattern.format(var_name = name, var_value = value)
        for item in old_variables:
          variables.append(item + tmp + '\n')

  del(old_variables, line, match, index, item, pattern, name, initial_value, number_of_scan_steps,
scan_step_size, scan_step, value, tmp)

  pattern_neutral_cbs = '''%nprocshared={nproc}
  %Chk={chk_name}_neutral_{conformer}.chk
```

```
  # cbs-qb3 int(grid=ultrafine)

  {title}\t|\tneutral {conformer}

  {molecule_specification}

  {variables_data}'''

  pattern_ion_cbs = '''%nprocshared={nproc}
  %Chk={chk_name}_ion_{conformer}.chk
  %OldChk={chk_name}_neutral_{conformer}.chk

  # cbs-qb3 int(grid=ultrafine) Geom=Check

  {title}\t|\tion {conformer}

  1 2
  '''

  number_of_processors_per_node = 16

  initial_chk_name = search(r'^%[Cc]hk=(?P<initial_chk_name>.+?)\.chk$', data[0], flags =
MULTILINE)['initial_chk_name']

  neutral_conformers_preopt = variables[:]
  ion_conformers_preopt = []
  cbs = []

  for index, item in enumerate(neutral_conformers_preopt):
    neutral_conformers_preopt[index] = pattern_neutral_cbs.format(nproc =
number_of_processors_per_node,
                                chk_name = initial_chk_name,
                                conformer = index + 1,
                                title = data[2],
                                molecule_specification = data[3],
                                variables_data = item)
    ion_conformers_preopt.append(pattern_ion_cbs.format(nproc =
number_of_processors_per_node,
                                        chk_name = initial_chk_name,
                                        conformer = index + 1,
                                        title = data[2]))

  neutral_conformers_preopt = '\n--Link1--\n'.join(neutral_conformers_preopt)
  ion_conformers_preopt = '\n--Link1--\n'.join(ion_conformers_preopt)
```

```
  gjf_content = '\n--Link1--\n'.join((neutral_conformers_preopt, ion_conformers_preopt))
  gjf_content = gjf_content + '\n' * 5

  del(pattern_neutral_cbs, pattern_ion_cbs, number_of_processors_per_node, initial_chk_name,
neutral_conformers_preopt, ion_conformers_preopt, cbs, index, item)

  with open(filename + '.txt','w') as file:
    file.write(gjf_content)

  del(file)

  #%% Generating inputs

  generate_input('C:\IP
calculation\IP\H_CO_CHOH_CH3_enol_tautomer\H_CO_CHOH_CH3_enol_conformers_initia
l')
```

Supplementary References

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