Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supporting Information for the

Barrierless Tautomerization of Criegee Intermediates *via* Acid Catalysis

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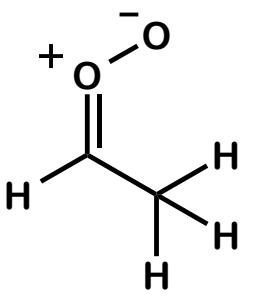
COMPUTATIONAL DETAILS

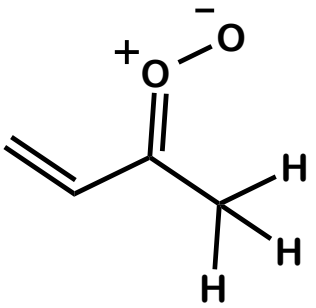
Multiple Criegee intermediates were considered to investigate the uncatalyzed, water-catalyzed, and formic acid-catalyzed gas-phase Criegee tautomerization reaction: (1) *syn*-CH_3CHOO, (2) *syn*-CH_3CH_2CHOO, (3) $(CH_3)_2COO$, (4) $CI_{isoprene1}$ and $CI_{isoprene2}$, and (5) CI_{pinene}. In the first step, the geometries of all stationary points considered in this paper were optimized at the M06-2X/aug-cc-pVTZ level of theory with the exception of the CI_{pinene} case where the aug-cc-pVDZ basis set was used. The stationary points were confirmed to be global minima or transition states by performing frequency calculations on the optimized geometries using the same level of theory. These calculations were also used to estimate the zero-point vibrational energy and the thermal corrections to calculated free energies at 298.15 K. The accuracy of the chosen theoretical method for geometry optimization was verified by calculating the barrier height for the tautomerization of *syn*-CH_3CHOO, using various DFT functionals as well as wavefunction-based methods including coupled cluster with single and double excitations (CCSD), CCSD(T) that also includes perturbative triple contributions, QCISD, and local pair natural orbital coupled electron pair approximation version 1 (LPNO-CEPA/1).[1] In the second step, single point CCSD(T)/aug-cc-pVTZ energy calculations at the M06-2X/aug-cc-pVTZ optimized geometries were performed to obtain more accurate electronic energies. However, in the case of the uncatalyzed and catalyzed isomerization of the larger pinene Criegee intermediate, single point M06-2X/aug-cc-pVTZ calculations were performed at the M06-2X/aug-cc-pVDZ optimized geometries. To account for entropic effects, all the reaction profiles are reported in terms of Gibbs free energies. All of the quantum chemistry calculations were carried out using the NWChem[2] program suite except the LPNO/CEPA-1 calculations, which were performed using the ORCA[3] code.

References.

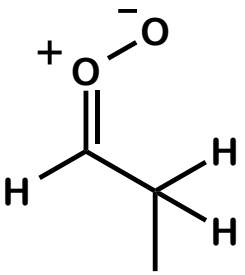
[1]F. Neese, N. Wennmohs and A. Hansen, *J. Chem. Phys.*, 2009, **130**, 114108.
[2]M. Valiev, E. J. Bylaska, N. Govind, K. Kowalski, K. P. Straatsma, H. J. J. van Dam, D. Wang, J. Nieplocha, E. Apra, T. L. Windus, W. A. de Jong, NWChem: *Comput. Phys. Commun.*, 2010, **181**, 1477-1489.
[3]ORCA V2.8.0, an ab initio, DFT, and semiempirical SCF-MO pack- age developed by F. Neese, Bonn University, Germany; available online from http://www.thch.uni-bonn.de/tc/orca/.



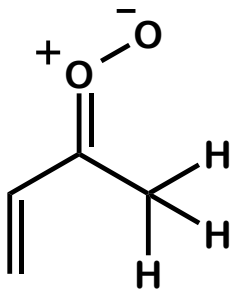
syn-CH_3CHOO



$CI_{isoprene1}$



syn-CH_3CH_2CHOO



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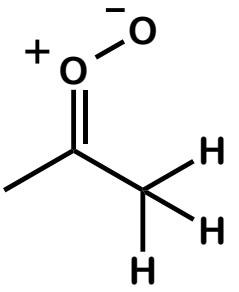
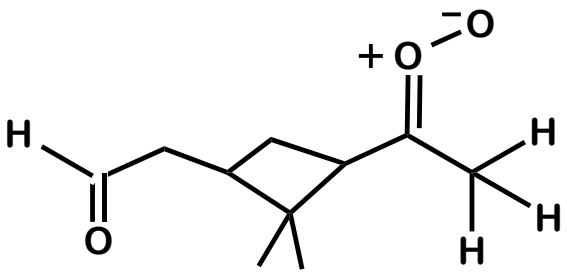


$(CH_3)_2CHOO$



CI_{pinene}

Scheme S1. Structures of the CIs studied in the present study.

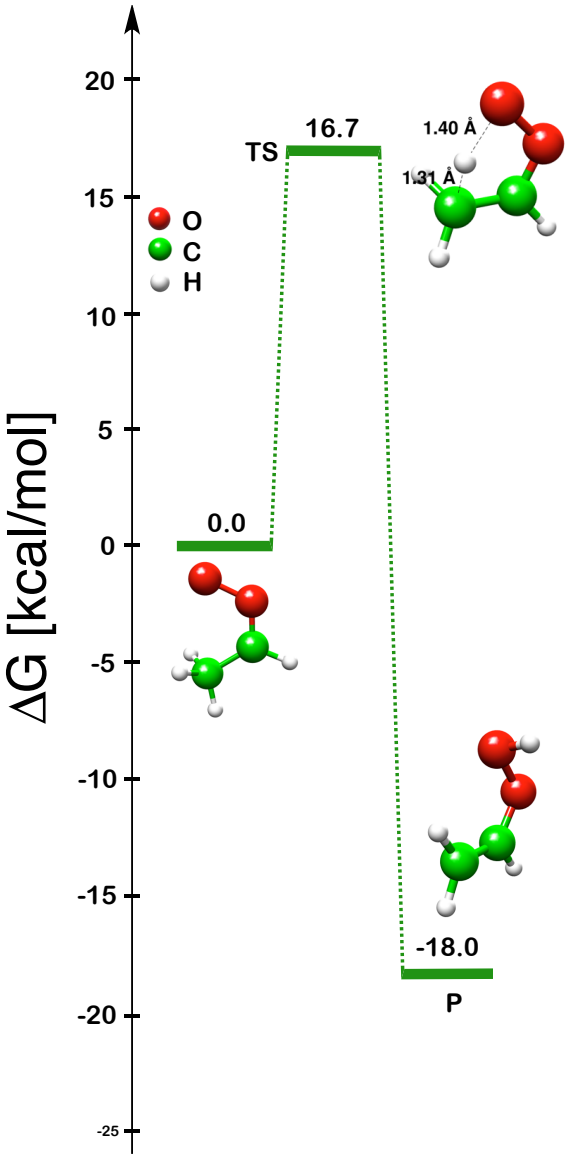


Fig. S1 CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ calculated free-energy profile of the uncatalyzed tautomerization of *syn*-CH_3CHOO (298.15 K, 1 atm, kcal/mol).

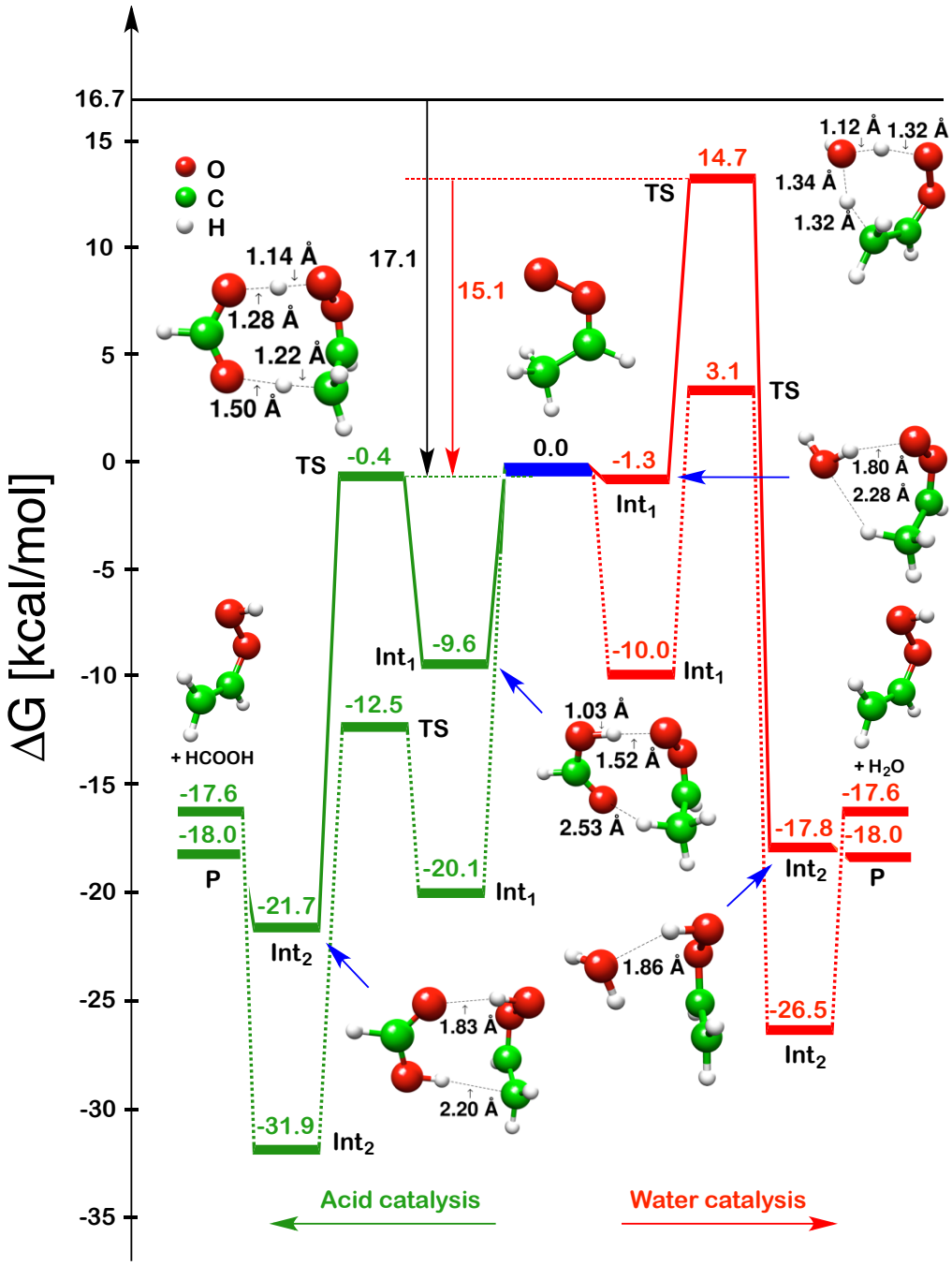


Fig. S2 CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ-calculated free energy (*thick lines*) and enthalpy (*thin lines*) profiles of HCOOH-catalyzed (*left panel*) and water-catalyzed (*right panel*) tautomerization of *syn*-CH_3CHOO (298.15 K, 1 atm, kcal/mol). The free-energy barrier of an uncatalyzed reaction is also shown (horizontal black line).

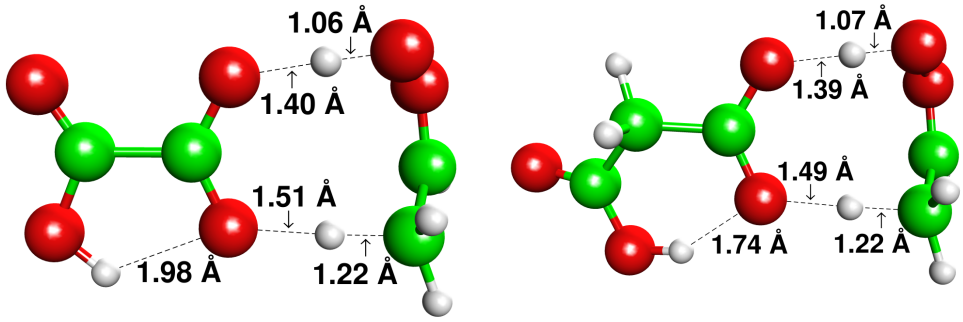


Fig. S3 M06-2X/aug-cc-pVTZ calculated calculated transition state structures for oxalic acid-catalyzed (*left)* and malonic acid-catalyzed (*right*) tautomerization of *syn*-CH_3CHOO.

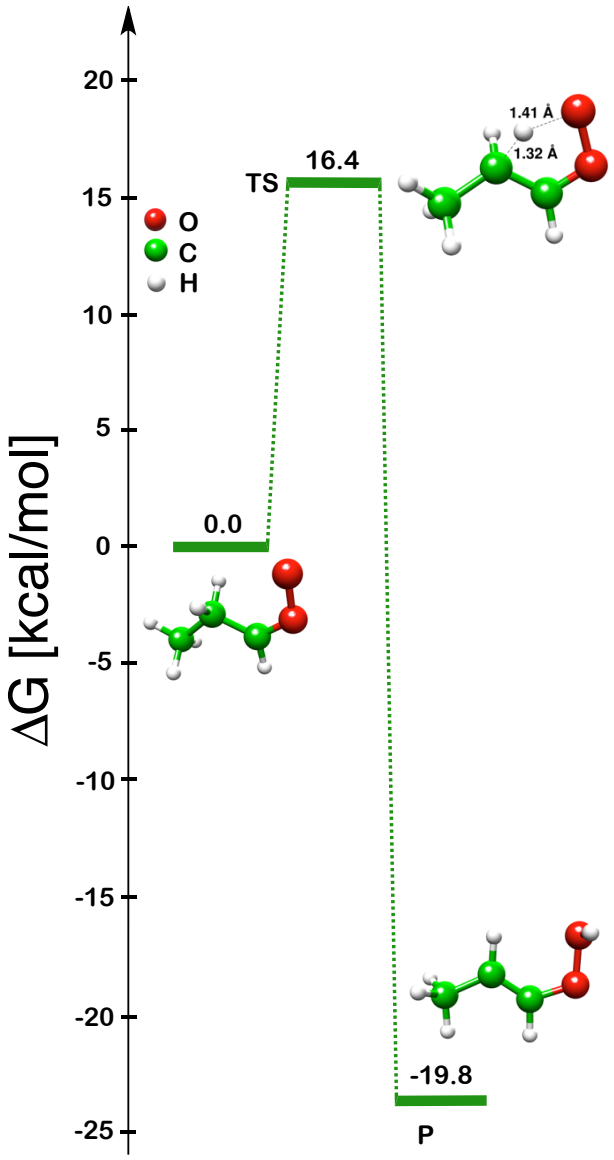


Fig. S4 CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ calculated free-energy profile of the uncatalyzed tautomerization of *syn*-CH_3CH_2CHOO (298.15 K, 1 atm, kcal/mol).

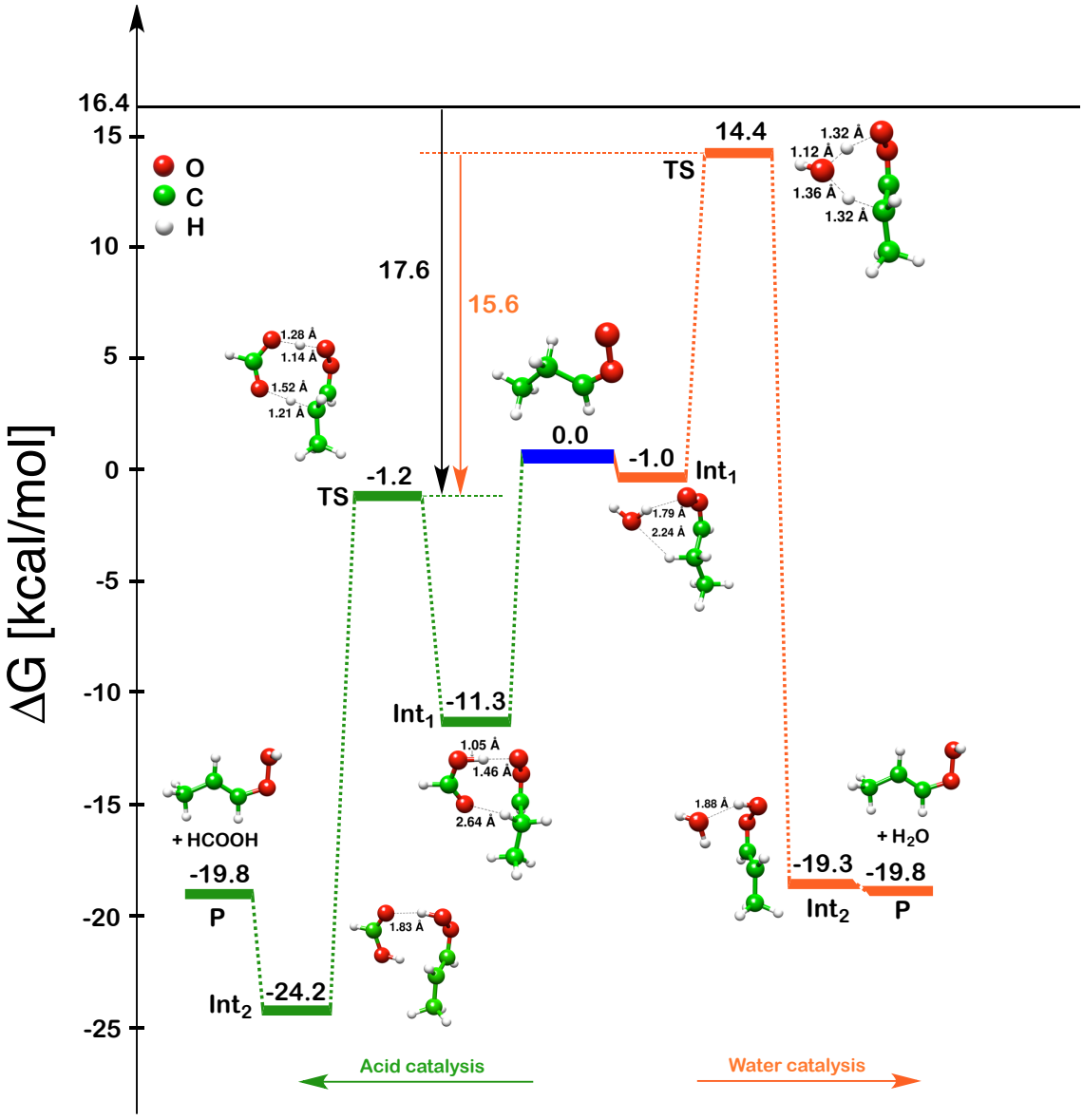


Fig. S5 CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ calculated free-energy profiles of HCOOH-catalyzed (*left panel*) and water-catalyzed (*right panel*) tautomerization of *syn*-CH_3CH_2CHOO (298.15 K, 1 atm, kcal/mol). The horizontal black line corresponds to the free-energy barrier of an unassisted reaction.

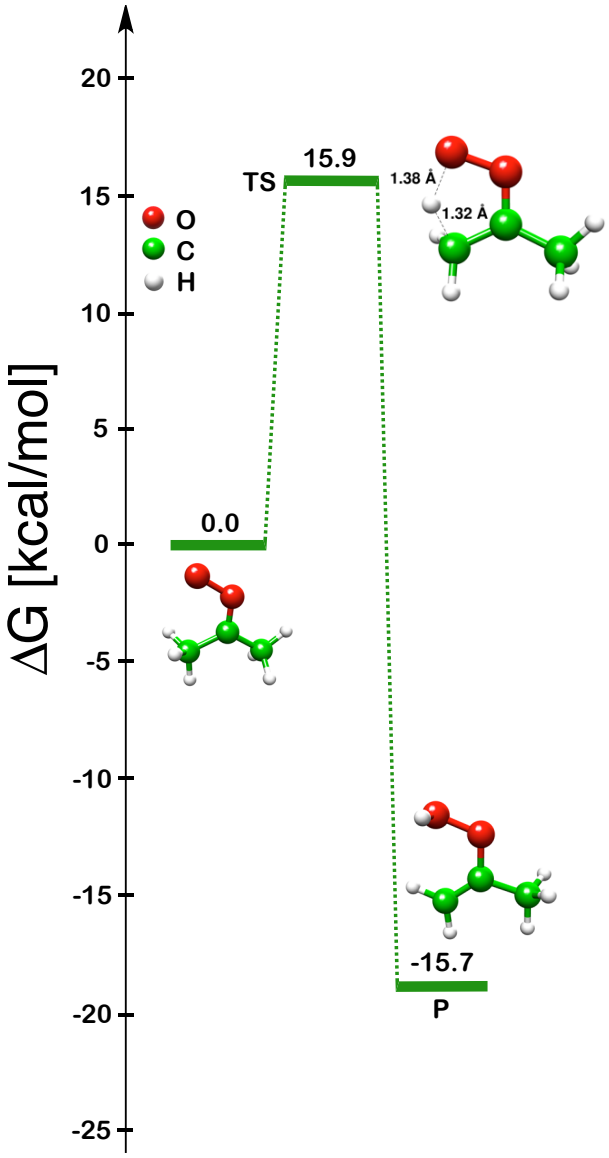


Fig. S6 CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ calculated free-energy profile of the uncatalyzed tautomerization of $(CH_3)_2COO$ (298.15 K, 1 atm, kcal/mol).

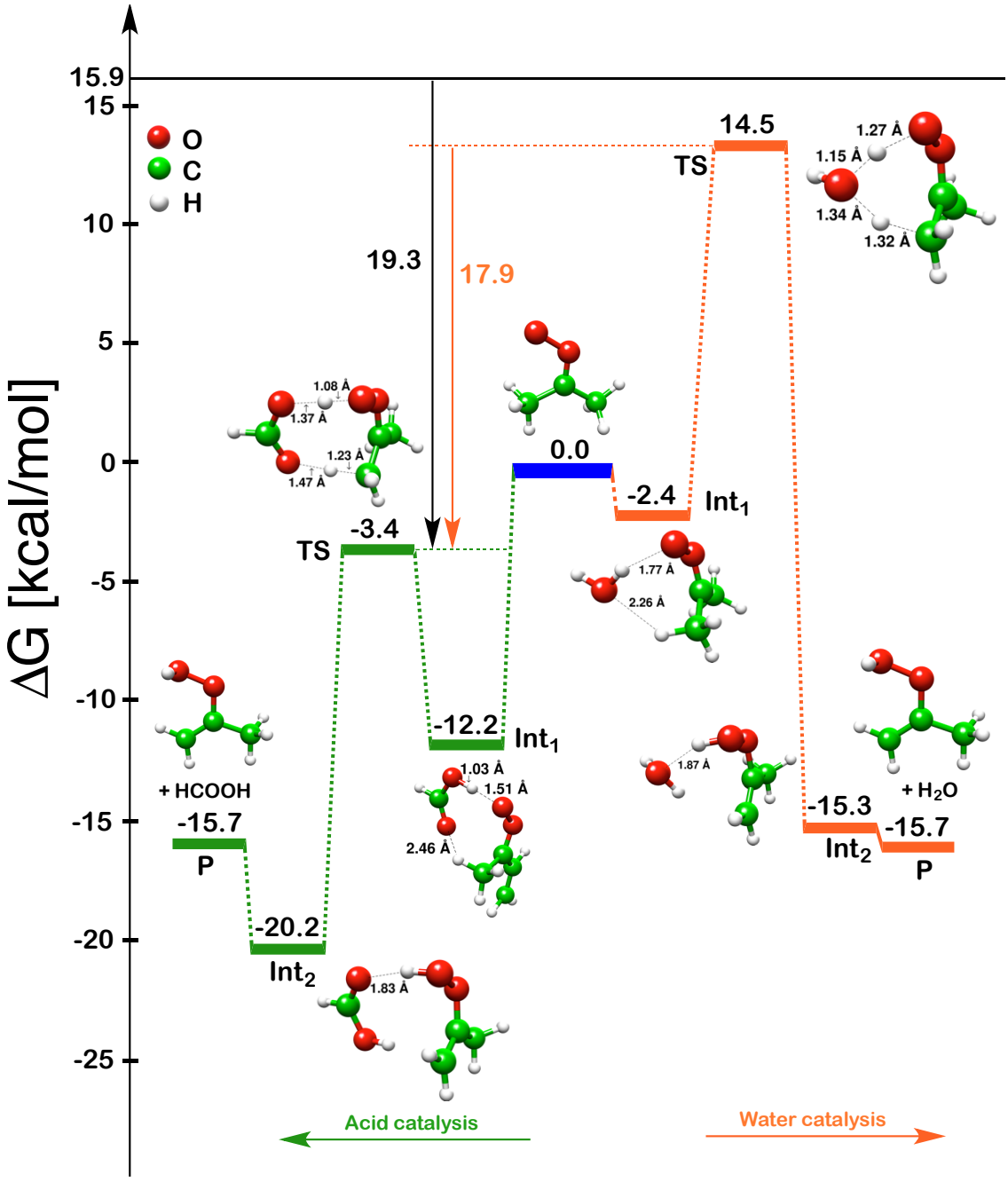


Fig. S7 CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ calculated free-energy profiles of HCOOH-catalyzed (*left panel*) and water-catalyzed (*right panel*) tautomerization of $(CH_3)_2COO$ (298.15 K, 1 atm, kcal/mol). The horizontal black line corresponds to the free-energy barrier of an unassisted reaction.

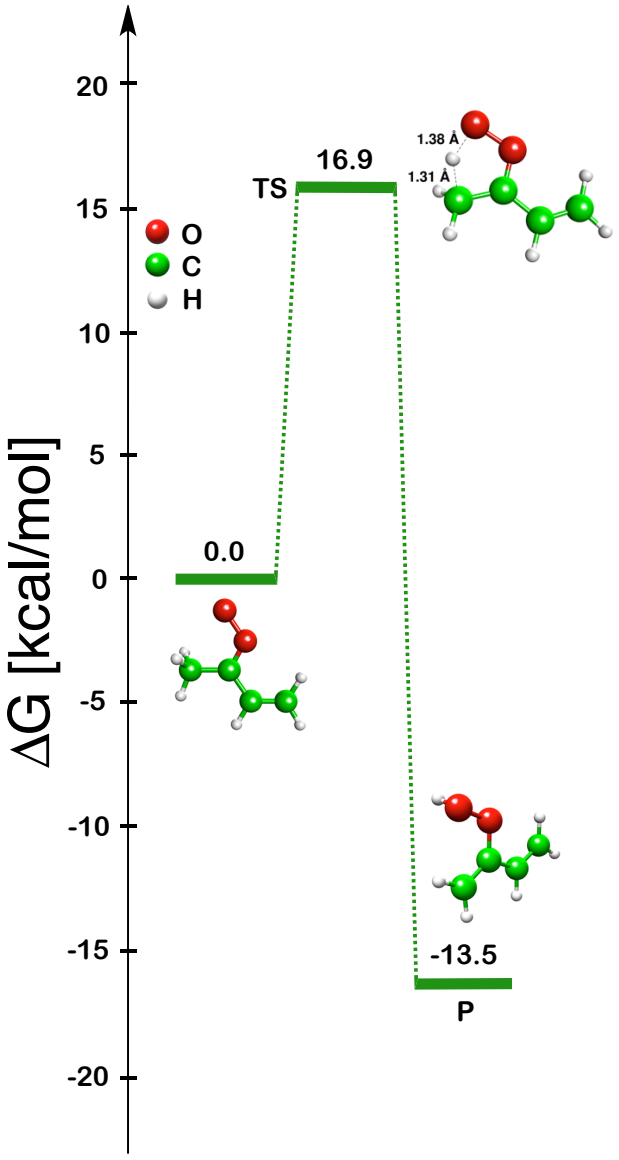


Fig. S8 CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ calculated free-energy profile of the uncatalyzed tautomerization of $CI_{isoprene1}$ (298.15 K, 1 atm, kcal/mol).

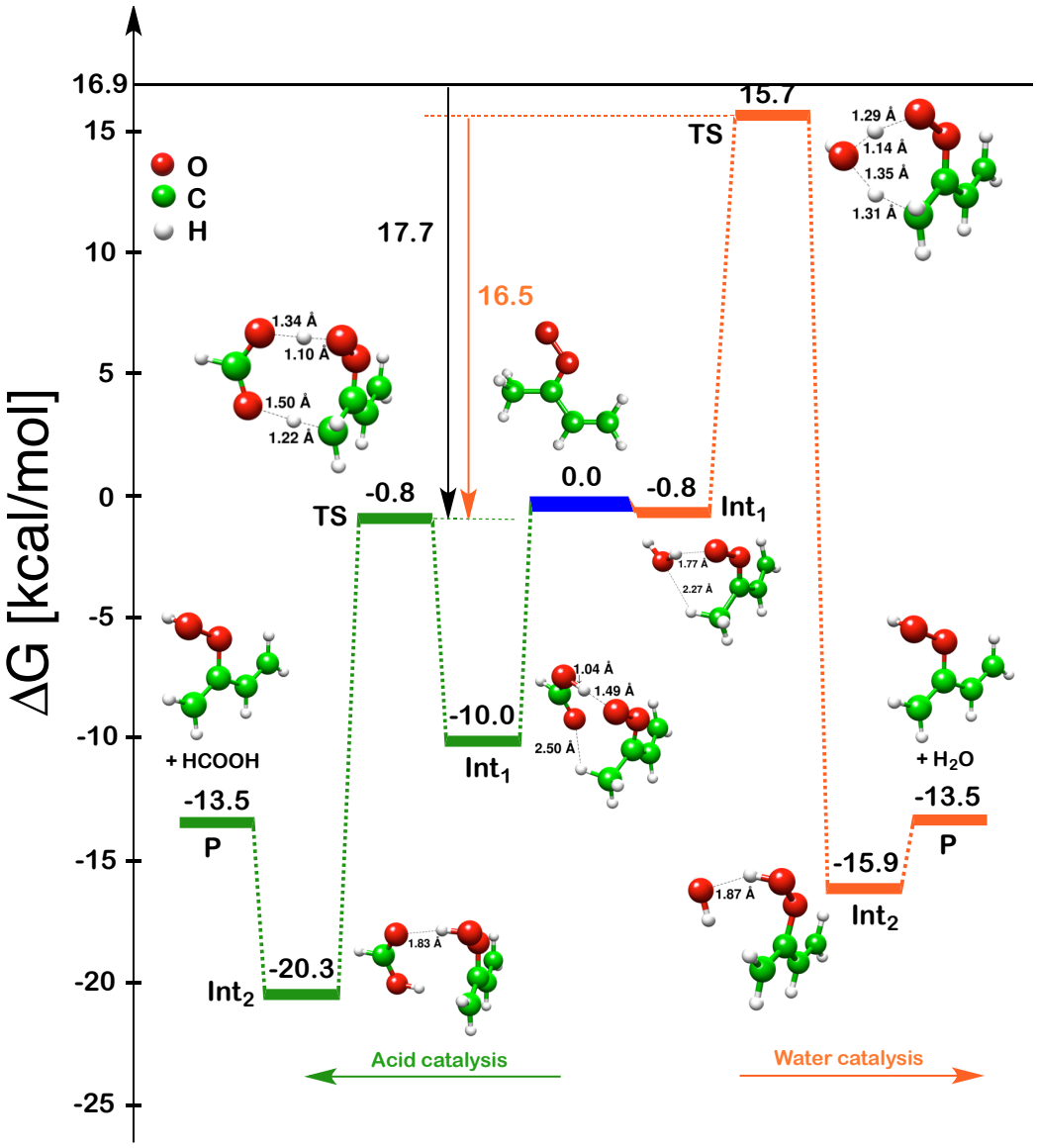


Fig. S9 CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ calculated free-energy profiles of HCOOH-catalyzed (*left panel*) and water-catalyzed (*right panel*) tautomerization of $CI_{isoprene1}$ (298.15 K, 1 atm, kcal/mol). The horizontal black line corresponds to the free-energy barrier of an unassisted reaction.

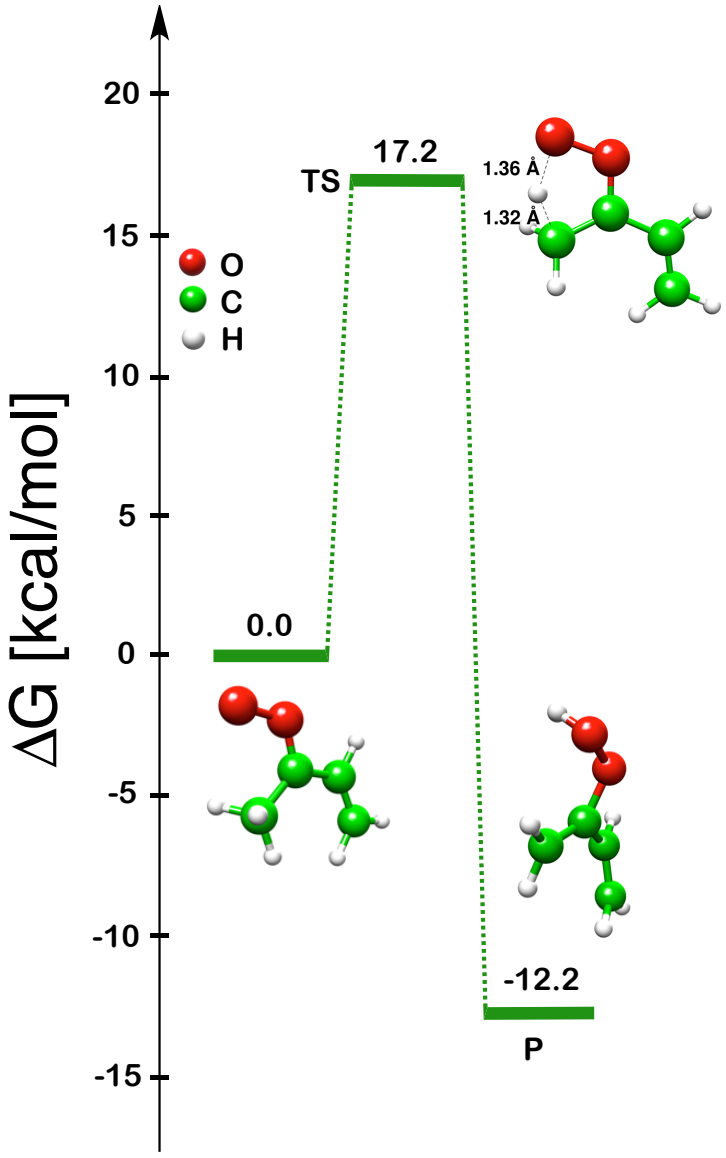


Fig. S10 CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ calculated free-energy profile of the uncatalyzed tautomerization of $CI_{isoprene2}$ (298.15 K, 1 atm, kcal/mol).

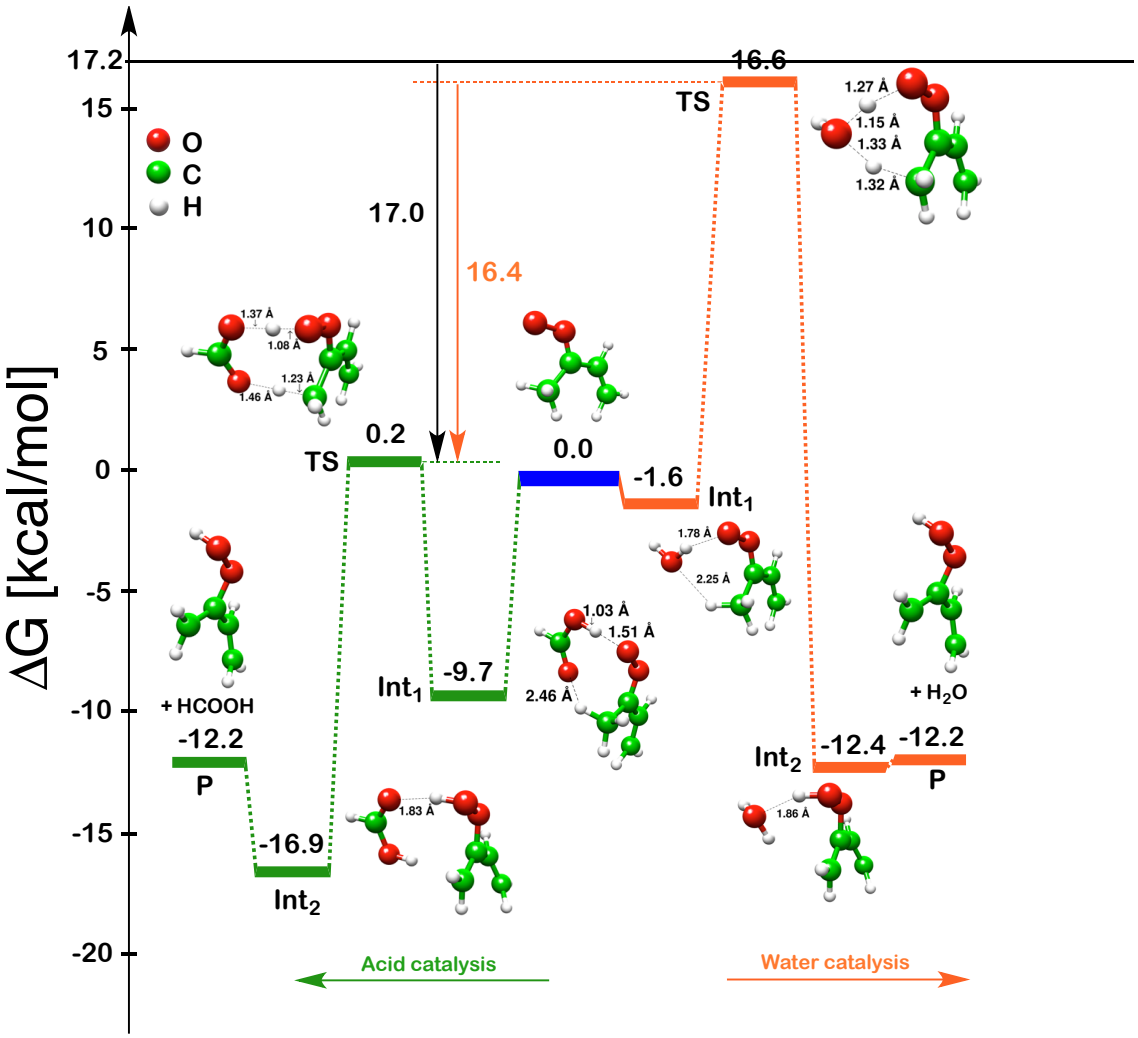


Fig. S11 CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ calculated free-energy profiles of HCOOH-catalyzed (*left panel*) and water-catalyzed (*right panel*) tautomerization of $CI_{isoprene2}$ (298.15 K, 1 atm, kcal/mol). The horizontal black line corresponds to the free-energy barrier of an unassisted reaction.

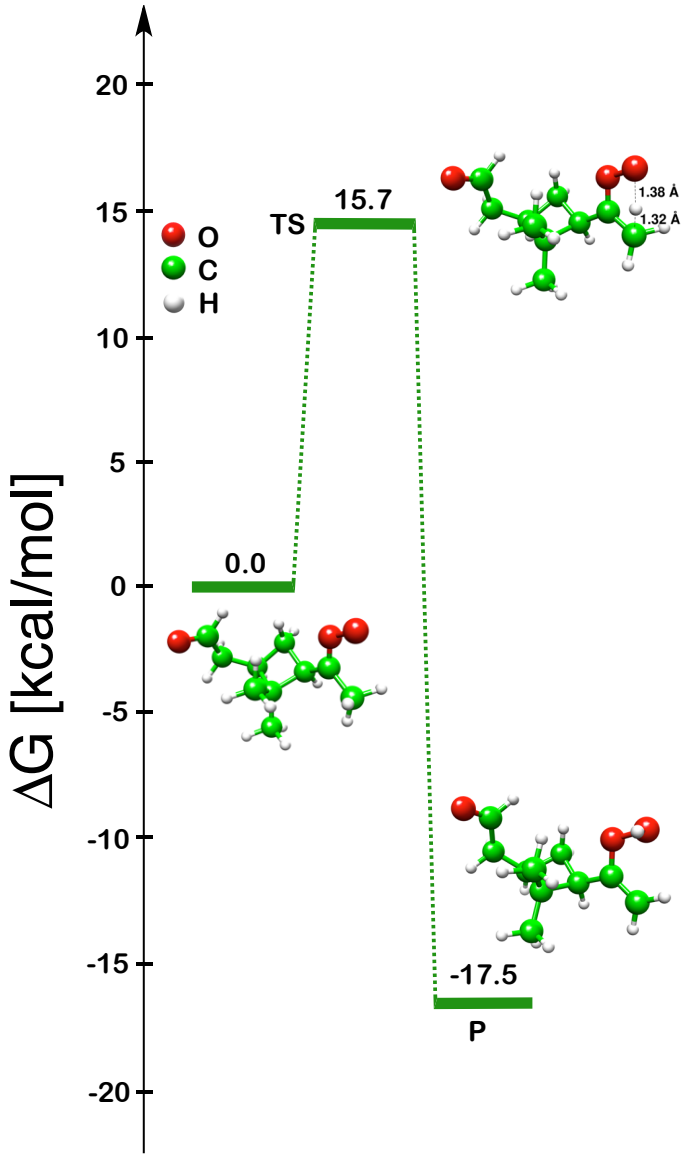


Fig. S12 M06-2X/aug-cc-pVTZ//M06-2X/aug-cc-pVDZ calculated free-energy profile of the uncatalyzed tautomerization of CI_{pinene} (298.15 K, 1 atm, kcal/mol).

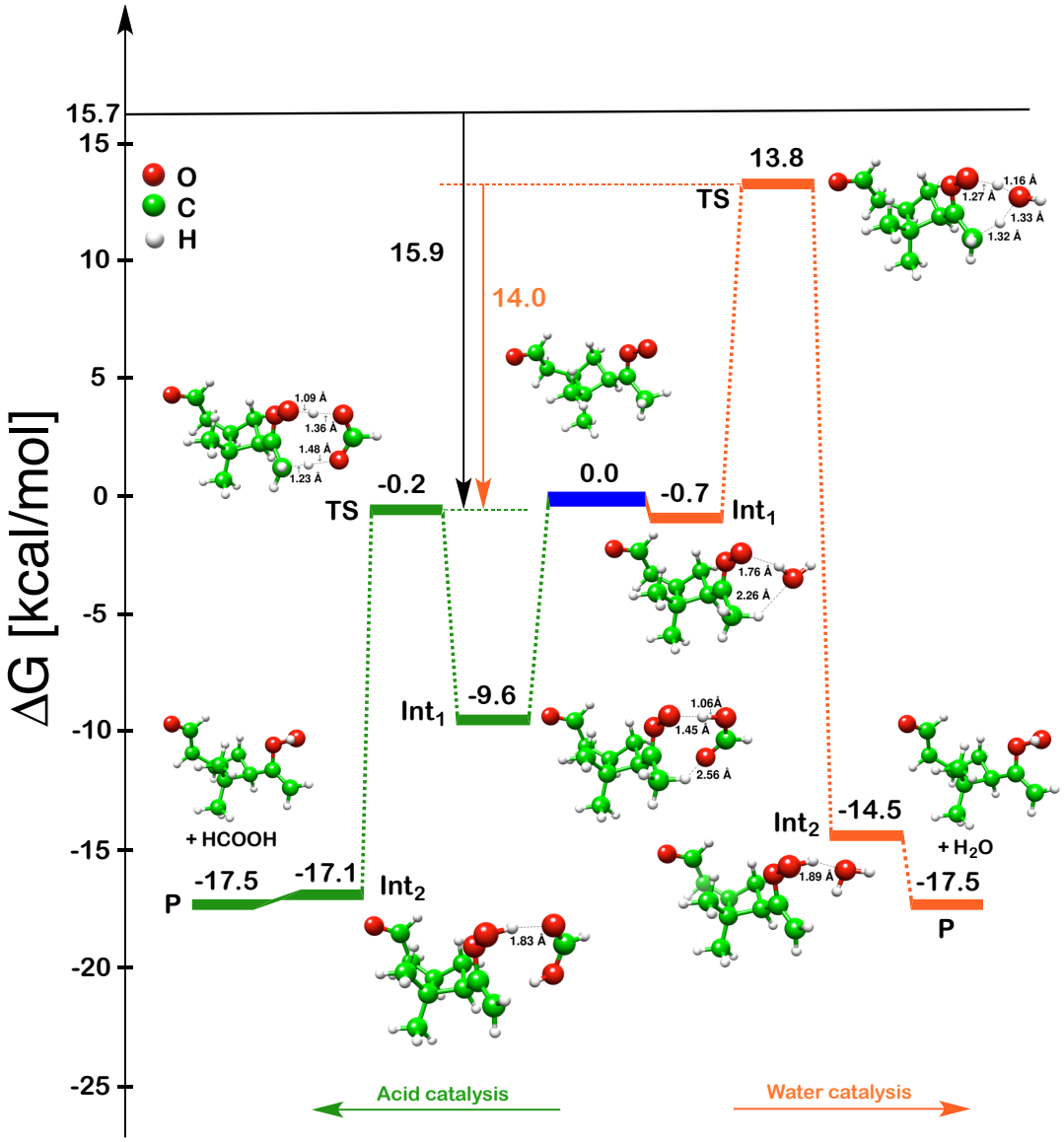


Fig. S13 M06-2X/aug-cc-pVTZ//M06-2X/aug-cc-pVDZ calculated free-energy profiles of HCOOH-catalyzed (*left panel*) and water-catalyzed (*right panel*) tautomerization of CI_{pinene} (298.15 K, 1 atm, kcal/mol). The horizontal black line corresponds to the free-energy barrier of an unassisted reaction.

Table S1. DFT/aug-cc-pVTZ calculated free-energy barrier for the unimolecular gas-phase decomposition of a *syn*-CH_3CHOO molecule (298.15 K, 1 atm, kcal/mol).

DFT Functional	$\Delta G^{\ddagger}$
BP86	13.2
PBE	14.2
MPW1PW91	14.7
TPSSh	15.5
O3LYP	15.8
BLYP	15.8
M05-2X	15.2
M06-2X	15.5
BHandHLYP	19.1

Table S2. Y/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ calculated zero-point uncorrected barrier height (kcal/mol) for the unimolecular gas-phase decomposition of a *syn*-CH_3CHOO molecule (298.15 K, 1 atm, kcal/mol).

Y	$\Delta E^{\ddagger}$
BP86	14.8
PBE	15.9
MPW1PW91	16.3
M05-2X	17.0
TPSSh	17.1
O3LYP	17.2
BLYP	17.6
M06-2X	17.6
BHandHLYP	20.8
LPNO/CEPA-1	25.6
QCISD	21.2
CCSD	20.1
CCSD(T)	18.7

Table S3. CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ calculated energies of various species involved in the uncatalyzed and catalyzed gas-phase tautomerization of a *syn*-CH_3CHOO molecule (298.15 K, 1 atm, kcal/mol). All Energies are reported with respect to the separated reactants. Note that the energies for the oxalic acid and malonic acid catalyzed tautomerization are only calculated at the M06-2X/aug-cc-pVTZ level of theory.

Catalyst	**Int_1**		**TS**		**Int_2**		**P**	
	ΔE	*ΔG*	*ΔE*	*ΔG*	*ΔE*	*ΔG*	*ΔE*	*ΔG*
No	-	-	16.3	16.7			-17.8	-18.0
Water	-9.5	-1.3	4.8	14.7	-26.1	-17.8	-17.8	-18.0
Formic acid	-20.1	-9.6	-11.8	-0.4	-32.0	-21.7	-17.8	-18.0
Oxalic acid	-19.6	-8.7	-13.1	-1.5	-29.1	-18.6	-17.8	-18.0
Malonic acid	-19.1	-7.6	-12.0	0.1	-28.3	-17.8	-17.8	-18.0

Table S4. CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ calculated energies of various species involved in the uncatalyzed and catalyzed gas-phase tautomerization of a *syn*-CH_3CH_2CHOO molecule (298.15 K, 1 atm, kcal/mol). All Energies are reported with respect to the separated reactants.

Catalyst	**Int_1**		**TS**		**Int_2**		**P**	
	ΔE	*ΔG*	*ΔE*	*ΔG*	*ΔE*	*ΔG*	*ΔE*	*ΔG*
No	-	-	16.1	16.4			-19.5	-19.8
Water	-9.5	-1.0	4.6	14.4	-27.7	-19.3	-19.5	-19.8
Formic acid	-21.6	-11.3	-12.7	-1.2	-34.3	-24.2	-19.5	-19.8

Table S5. CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ calculated energies of various species involved in the uncatalyzed and catalyzed gas-phase tautomerization of a $(CH_3)_2COO$ molecule (298.15 K, 1 atm, kcal/mol). All Energies are reported with respect to the separated reactants.

Catalyst	**Int_1**		**TS**		**Int_2**		**P**	
	ΔE	*ΔG*	*ΔE*	*ΔG*	*ΔE*	*ΔG*	*ΔE*	*ΔG*
No	-	-	15.7	15.9			-15.5	-15.7
Water	-10.9	-2.4	4.6	14.5	-23.9	-15.3	-15.5	-15.7
Formic acid	-23.1	-12.2	-14.1	-3.4	-30.6	-20.2	-15.5	-15.7

Table S6. CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ calculated energies of various species involved in the uncatalyzed and catalyzed gas-phase tautomerization of a $CI_{isoprene1}$ molecule (298.15 K, 1 atm, kcal/mol). All Energies are reported with respect to the separated reactants.

Catalyst	**Int_1**		**TS**		**Int_2**		**P**	
	ΔE	*ΔG*	*ΔE*	*ΔG*	*ΔE*	*ΔG*	*ΔE*	*ΔG*
No	-	-	16.9	17.2			-11.8	-12.2
Water	-9.7	-1.6	6.7	16.6	-20.6	-12.4	-11.8	-12.2
Formic acid	-20.5	-9.7	-11.1	0.2	-27.0	-16.9	-11.8	-12.2

Table S7. CCSD(T)/aug-cc-pVTZ//M06-2X/aug-cc-pVTZ calculated energies of various species involved in the uncatalyzed and catalyzed gas-phase tautomerization of a $CI_{isoprene2}$ molecule (298.15 K, 1 atm, kcal/mol). All Energies are reported with respect to the separated reactants.

Catalyst	**Int_1**		**TS**		**Int_2**		**P**	
	ΔE	*ΔG*	*ΔE*	*ΔG*	*ΔE*	*ΔG*	*ΔE*	*ΔG*
No	-	-	16.4	16.9			-13.5	-13.5
Water	-9.4	-0.8	5.5	15.7	-24.5	-15.9	-13.5	-13.5
Formic acid	-20.9	-10.0	-12.3	-0.8	-30.7	-20.3	-13.5	-13.5

Table S8. M06-2X/aug-cc-pVTZ//M06-2X/aug-cc-pVDZ calculated energies of various species involved in the uncatalyzed and catalyzed gas-phase tautomerization of a CI_{pinene} molecule (298.15 K, 1 atm, kcal/mol). All Energies are reported with respect to the separated reactants.

Catalyst	**Int_1**		**TS**		**Int_2**		**P**	
	ΔE	ΔG	ΔE	ΔG	ΔE	ΔG	ΔE	ΔG
No	-	-	15.2	15.7			-17.5	-17.5
Water	-9.3	-0.7	3.6	13.8	-23.5	-14.5	-17.5	-17.5
Formic acid	-20.1	-9.6	-12.2	-0.2	-27.9	-21.2	-17.5	-17.5