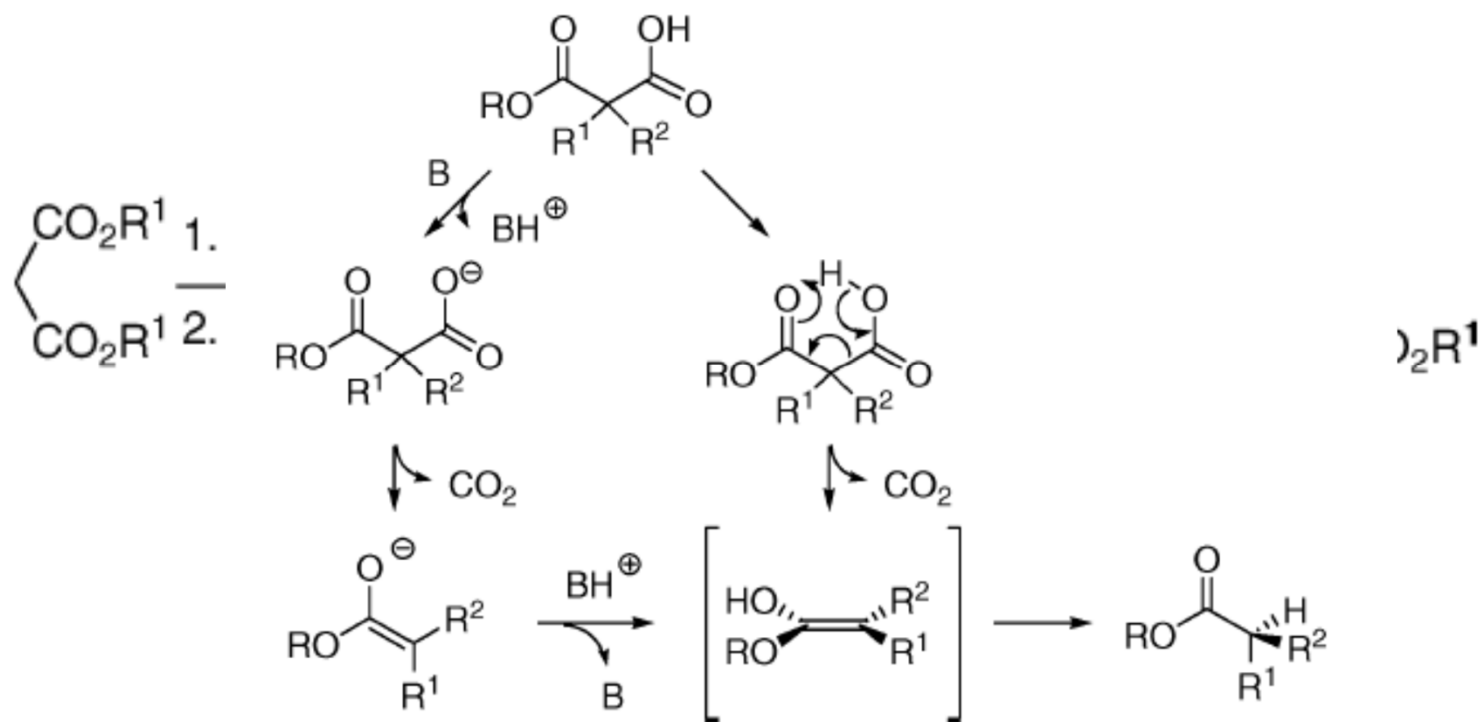


Enols of simple carboxylic acids

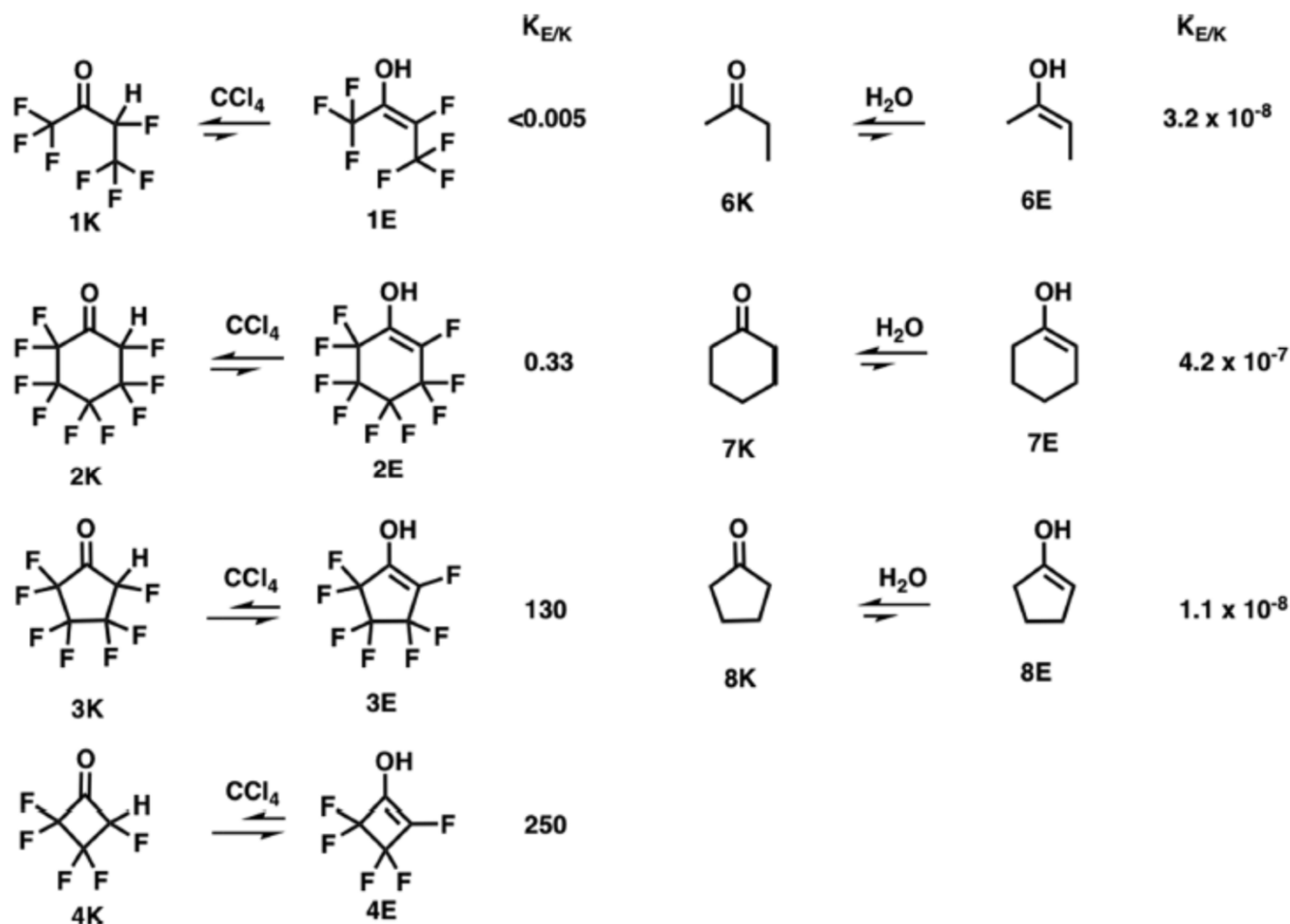
Artur Mardyukov

Gießen, January 17, 2020

The enantioselective decarboxylative protonation (EDP) of malonic acid derivatives is a synthetic methodology by which the chirality of the product is generated during the enol/enolate protonation step.

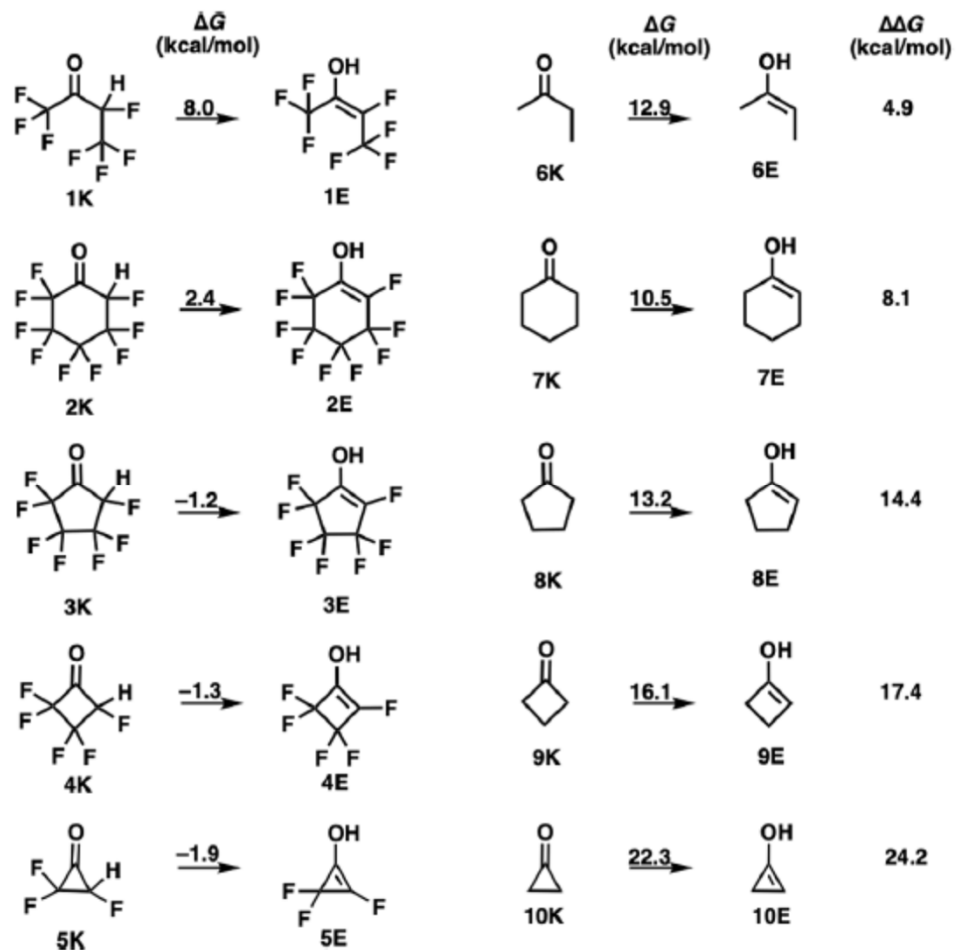


Experimental Equilibria for the Keto–Enol Tautomerization of the Perfluorinated¹⁻³ and Hydrocarbon⁴ Keto–Enol Systems



(1) Lindner, P. E.; Lemal, D. M. J. Org. Chem. 1996, 61, 5109–5115. (2) Lindner, P. E.; Correa, R. A.; Gino, J.; Lemal, D. M. J. Am. Chem. Soc. 1996, 118, 2556–2563. (3) Lindner, P. E.; Lemal, D. M. J. Am. Chem. Soc. 1997, 119, 3259–3266. (4) Keeffe, J. R.; Kresge, A. J.; Schepp, N. P. J. Am. Chem. Soc. 1990, 112, 4862–4868. (5) B. J. Levandowski, R. T. Raines, K. N. Houk. J. Org. Chem. 2019, 84, 6432–6436.

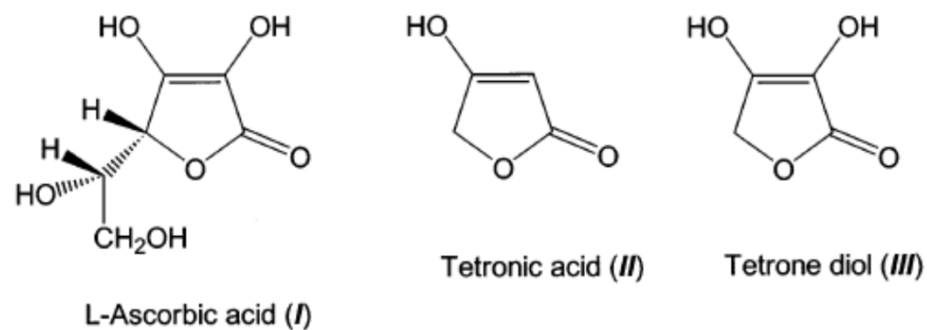
Hyperconjugative $\pi \rightarrow \sigma^*$ CF Interactions Stabilize the Enol Form of Perfluorinated Cyclic Keto–Enol Systems⁵



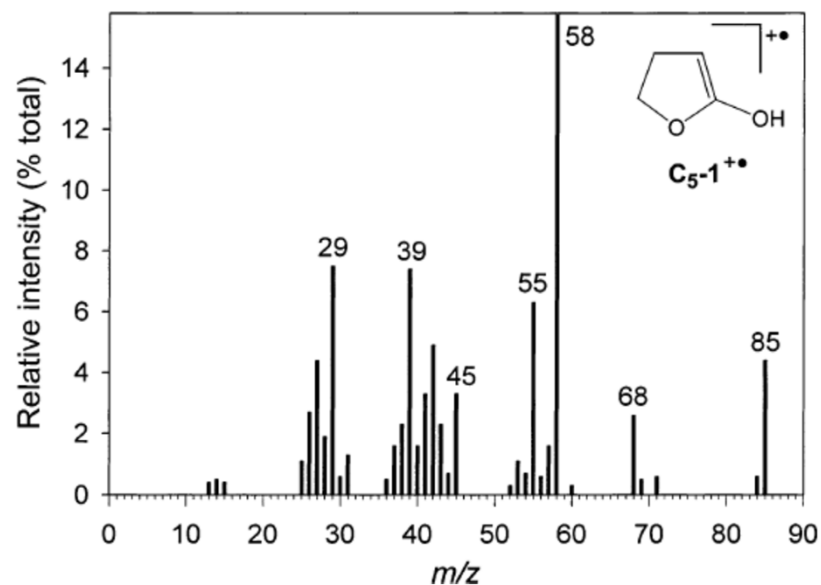
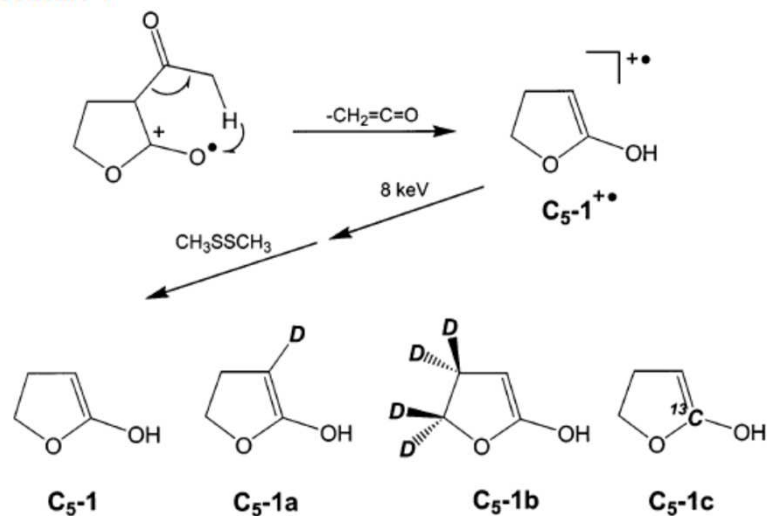
Computed reaction energies (ΔG) for the keto–enol tautomerizations of keto–enol systems.

(1) Lindner, P. E.; Lemal, D. M. J. Org. Chem. 1996, 61, 5109–5115. (2) Lindner, P. E.; Correa, R. A.; Gino, J.; Lemal, D. M. J. Am. Chem. Soc. 1996, 118, 2556–2563. (3) Lindner, P. E.; Lemal, D. M. J. Am. Chem. Soc. 1997, 119, 3259–3266. (4) Keeffe, J. R.; Kresge, A. J.; Schepp, N. P. J. Am. Chem. Soc. 1990, 112, 4862–4868. (5) B. J. Levandowski, R. T. Raines, K. N. Houk. J. Org. Chem. 2019, 84, 6432–6436.

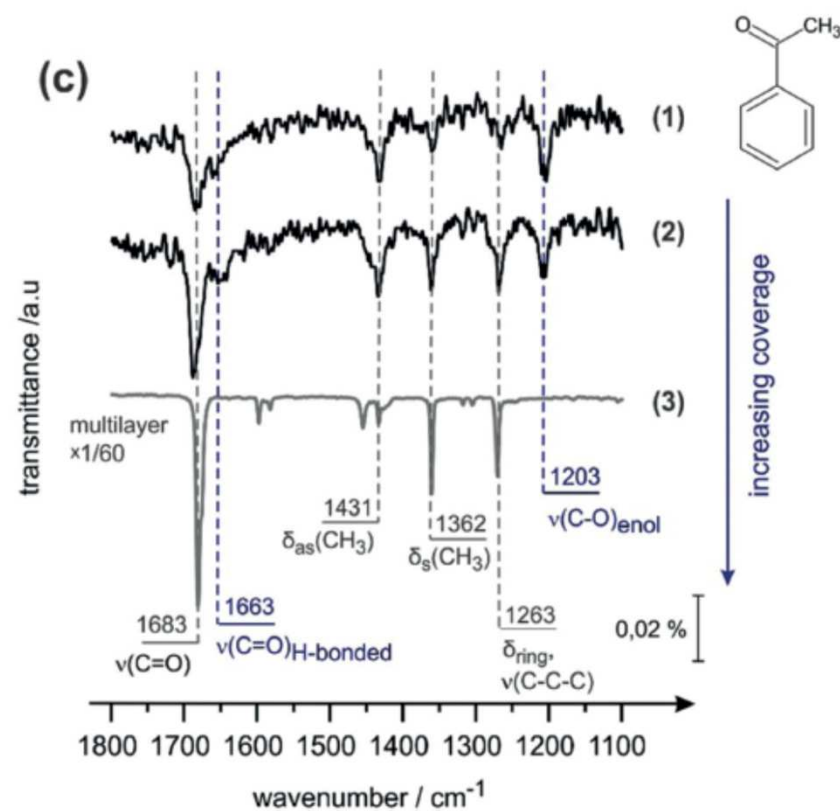
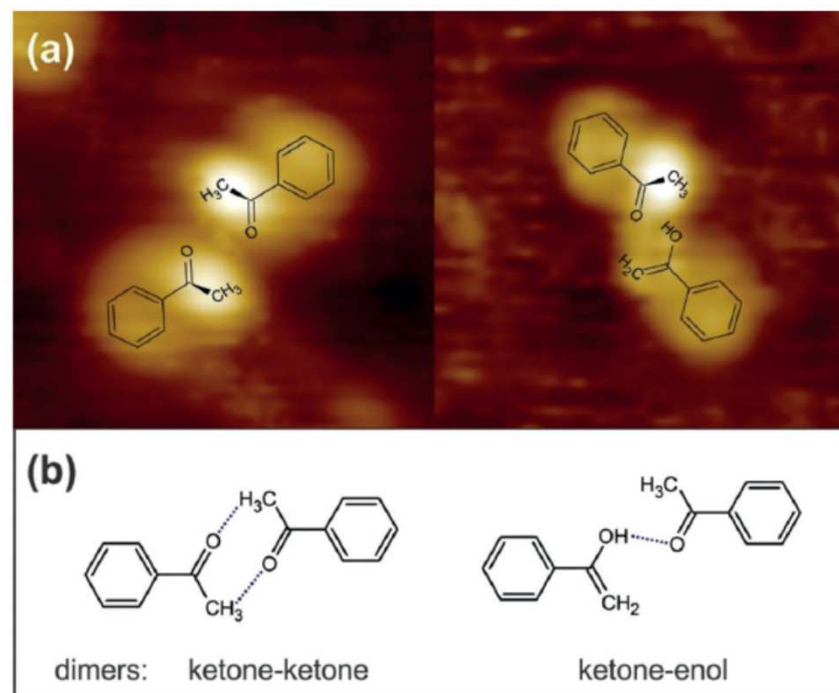
Lactone Enols are Stable in the Gas Phase but Highly Unstable in Solution



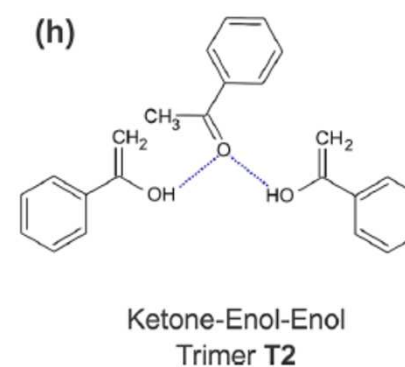
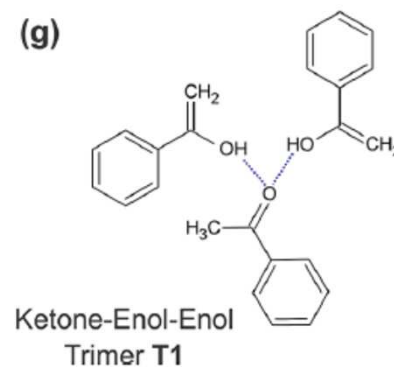
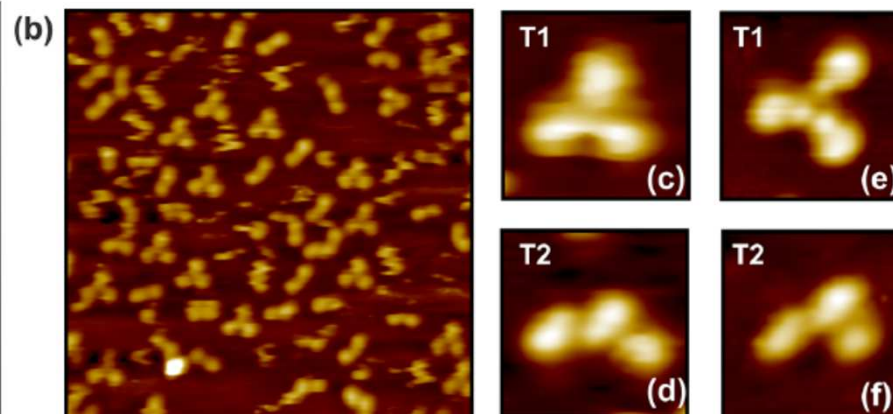
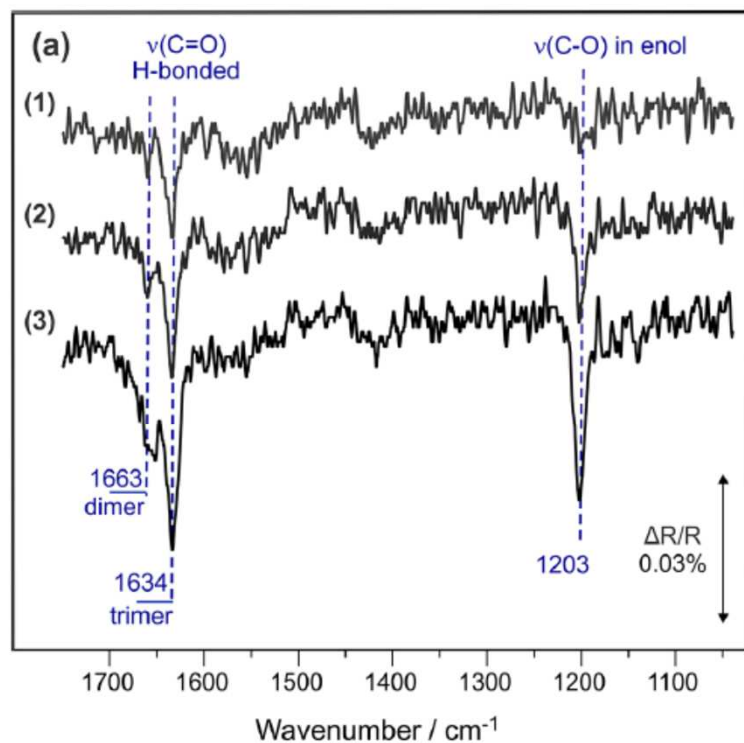
Scheme 1

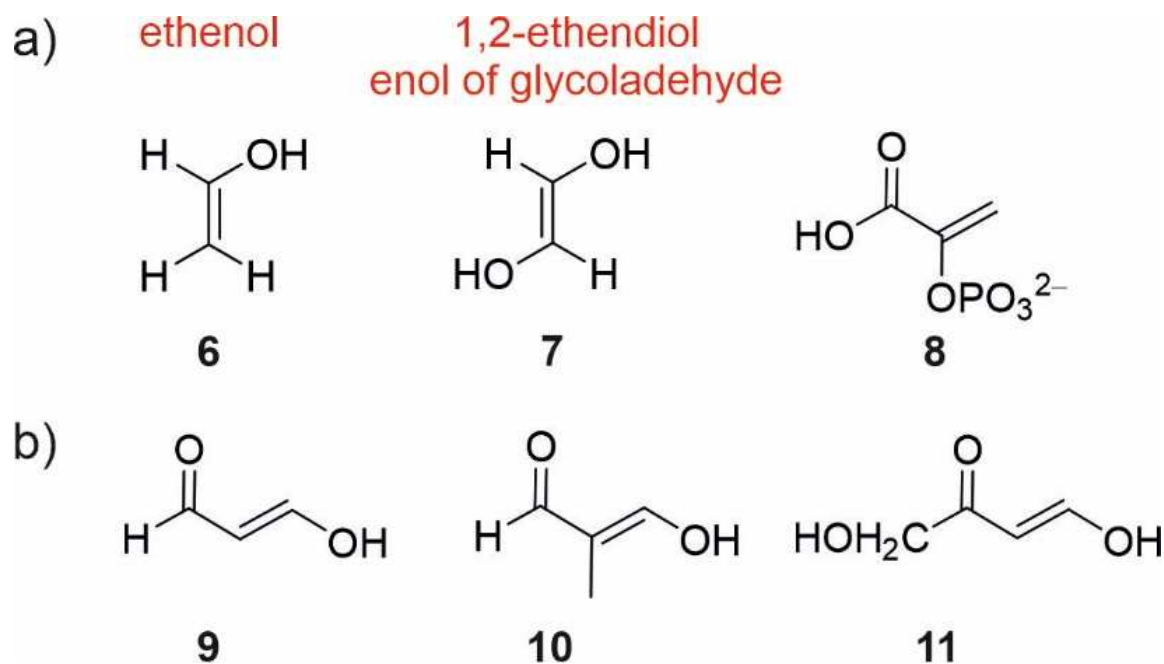


Surface-Driven Keto–Enol Tautomerization



Formation and Stabilization Mechanisms of Enols on Pt through Multiple Hydrogen Bonding

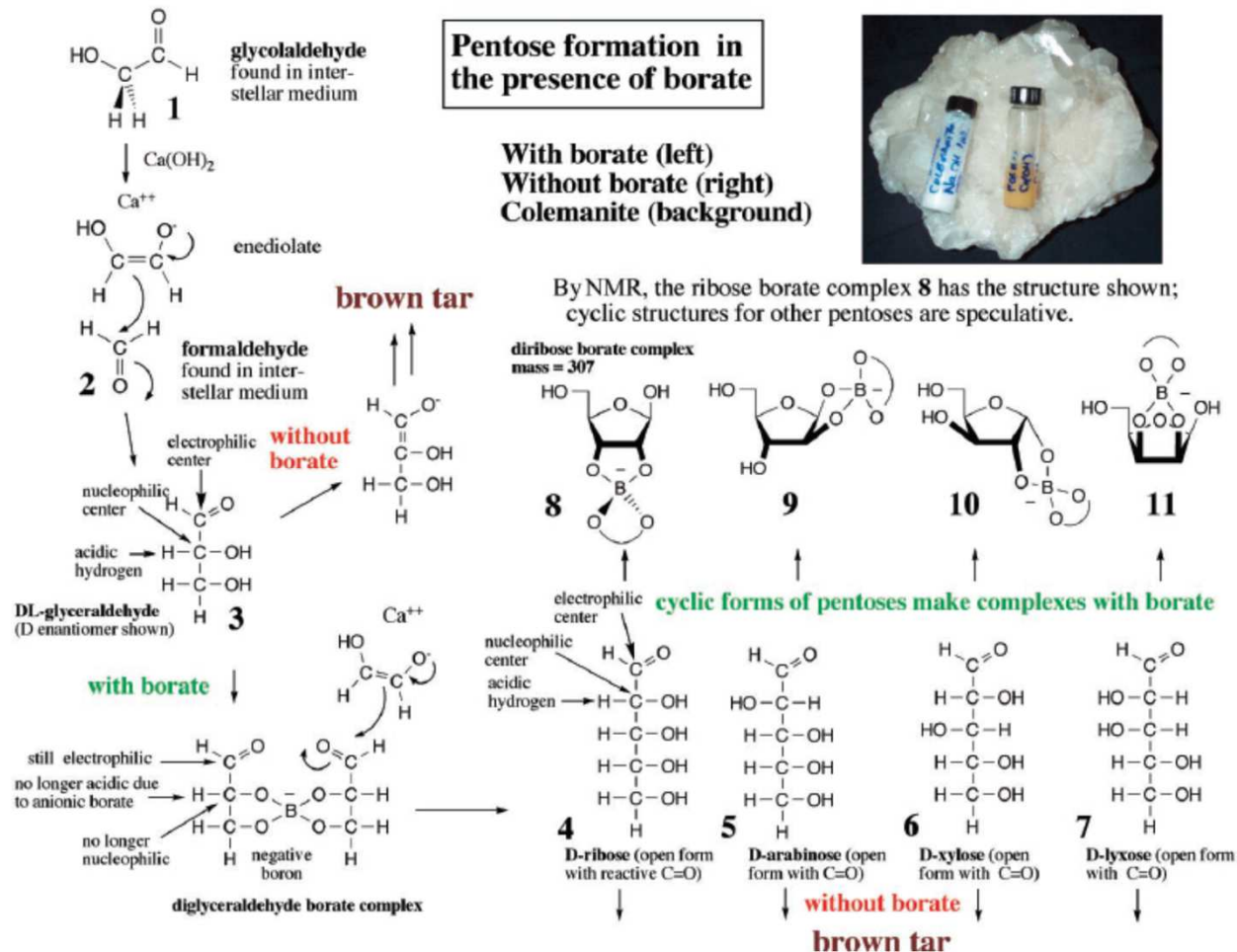




(b) Enols suggested as intermediates in the photooxidation of isoprene.

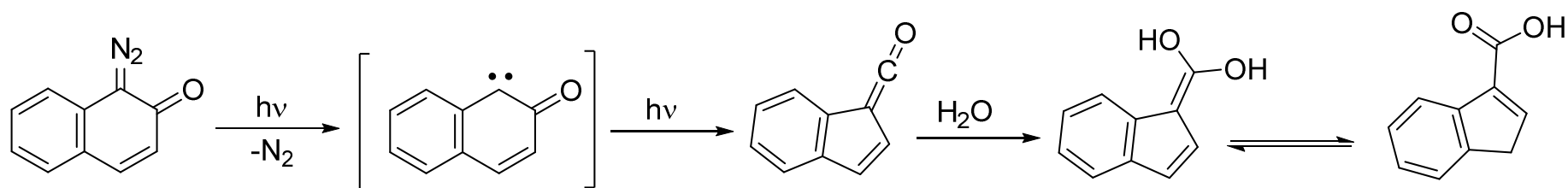
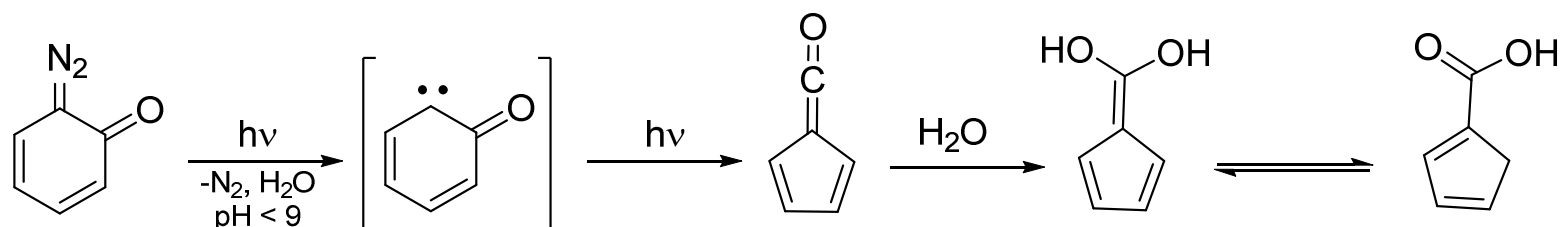
- (1) F. Paulot, J. D. Crounse, H. G. Kjaergaard, J. H. Kroll, J. H. Seinfeld, P. O. Wennberg, *Atmos. Chem. Phys.* **2009**, 9, 1479. (2) A. J. Coggins, M. W. Powner, *Nat. Chem.* **2017**, 9, 310-317. (3) D. U. Andrews, B. R. Heazlewood, A. T. Maccarone, T. Conroy, R. J. Payne, M. J. T. Jordan, S. H. Kable, *Science* **2012**, 337, 1203-1206. (4) A. E. Clubb, M. J. T. Jordan, S. H. Kable, D. L. Osborn, *J. Phys. Chem. Lett.* **2012**, 3, 3522-3526.

Borate Minerals Stabilize Ribose



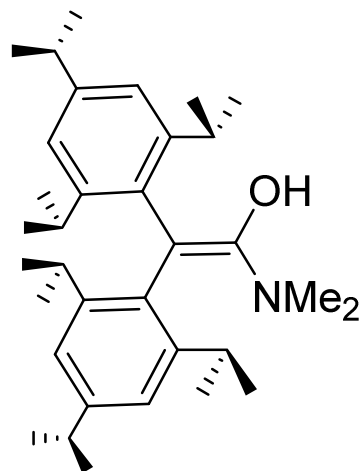
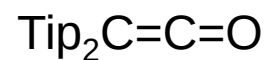
Pentose formation in the presence of borate.

Conjugated Enols – Time Resolved Spectroscopy

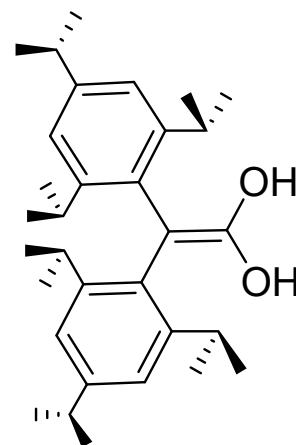


(1) J. I. K. Almstead, B. Urwyler, J. Wirz, *J. Am. Chem. Soc.* **1994**, *116*, 954-960. (2) B. Urwyler, J. Wirz, *Angew. Chem.* **1990**, *102*, 790-792. (3) J. Andraos, Y. Chiang, A. J. Kresge, V. V. Popik, *J. Am. Chem. Soc.* **1997**, *119*, 8417-8424. (4) Y. Chiang, A. J. Kresge, P. Pruszyński, N. P. Schepp, J. Wirz, *Angew. Chem. Int. Ed.* **1990**, *29*, 792-794.

Observation of Kinetically Stabilized Enols

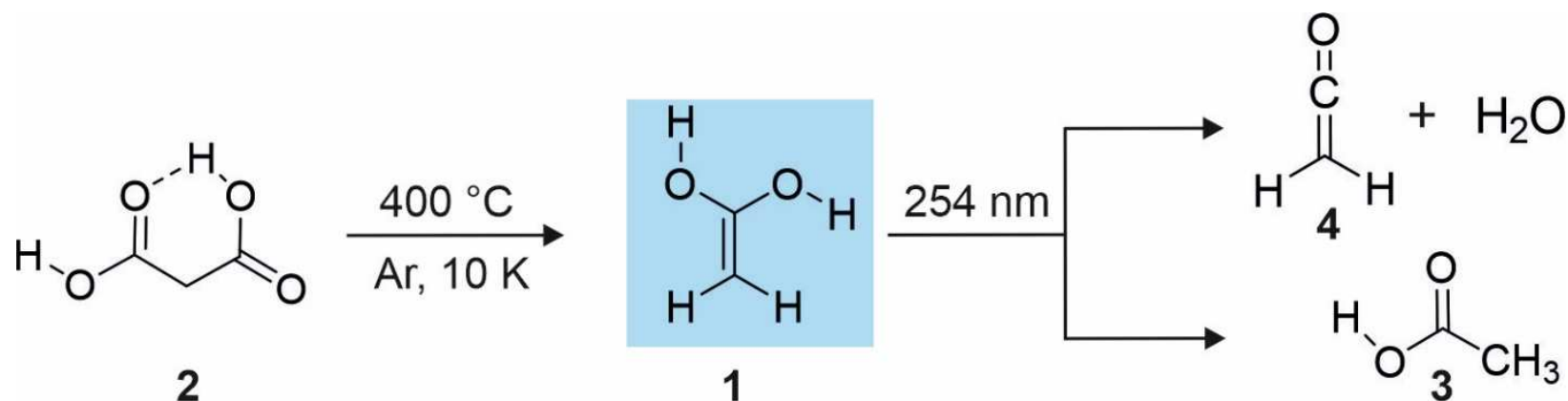


J. Frey, Z. Rappoport,
J. Am. Chem. Soc.
1996, *118*, 5182-
5191.



Frey, J.;
Rappoport, Z.
J. Am. Chem. Soc.
1995, *117*, 1161.

1,1-Ethenediol - The Enol of Acetic Acid



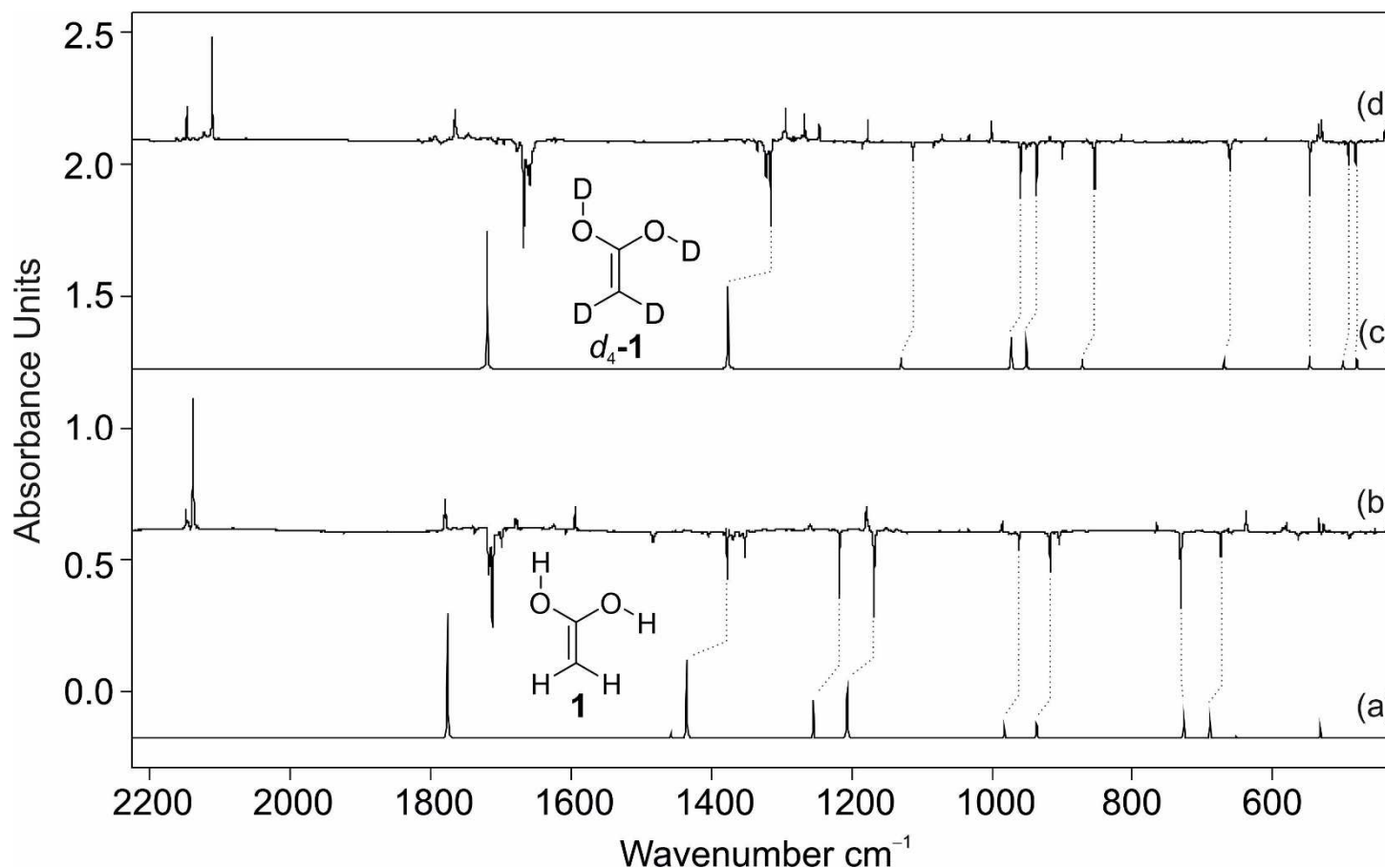
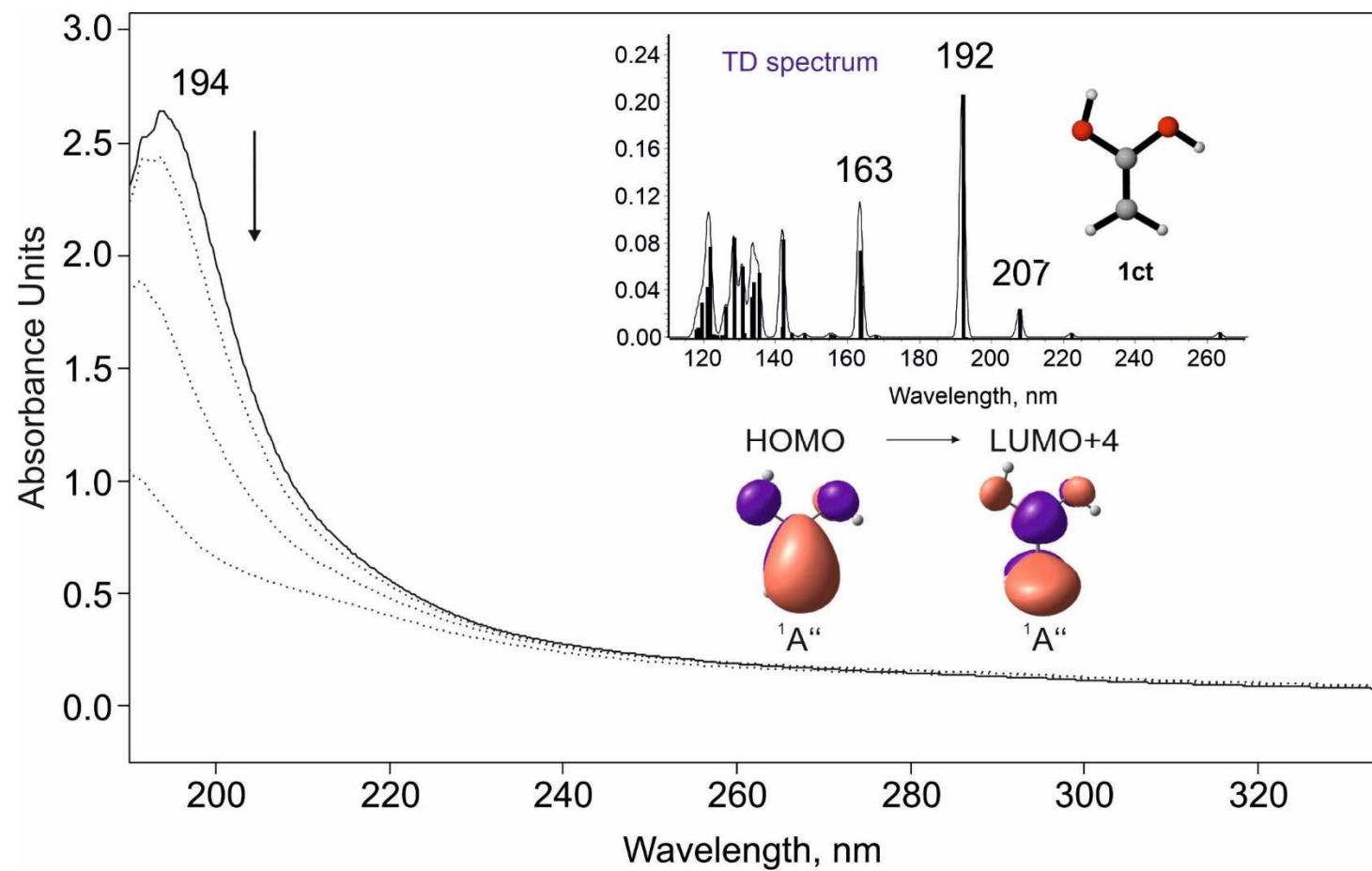
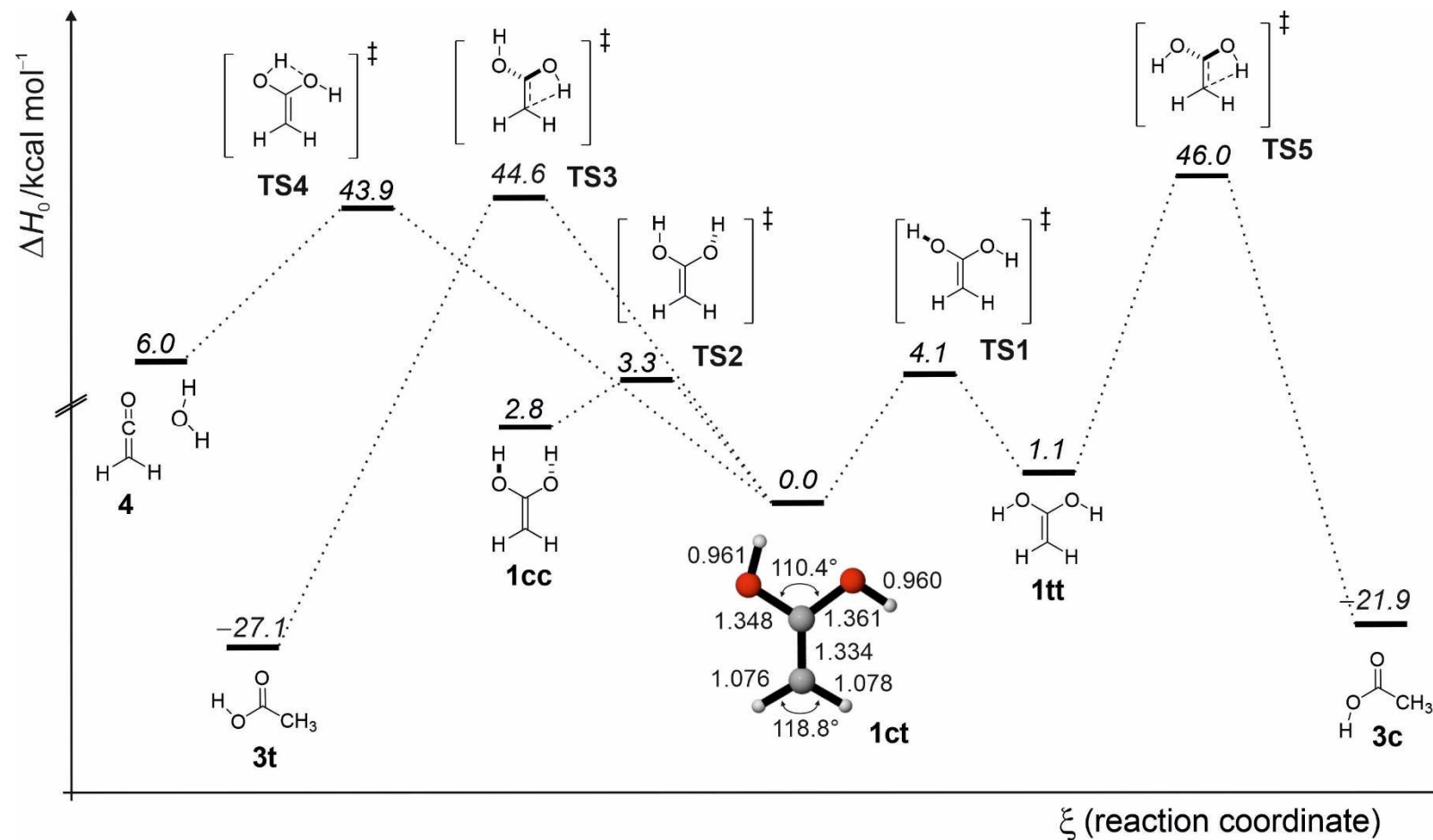


Figure 1. IR spectra showing the pyrolysis product of **2** with subsequent trapping in an argon matrix at 10 K. (a) IR spectrum of **1** computed at AE-CCSD(T)/cc-pCVTZ (unscaled). (b) IR difference spectra showing the photochemistry of **1** after irradiation with $\lambda = 254$ nm in argon at 10 K. Downward bands assigned to **1** disappear while upward bands assigned to **3** and **4** appear after 20 min irradiation time. (c) IR spectrum of d_4 -**1** computed at AE-CCSD(T)/cc-pCVTZ (unscaled). (d) IR difference spectra showing the photochemistry of d_4 -**1** after irradiation with $\lambda = 254$ nm in argon at 10 K. Bands pointing downwards assigned to d_4 -**1** disappear and bands pointing upwards assigned d_4 -**3** and d_4 -**4** appear after 20 min irradiation time.



Potential Energy Profile



Potential energy profile (ΔH_0) in kcal mol^{-1} of the reactions of enol **1** at AE-CCSD(T)/cc-pCVTZ + ZPVE

Organic compounds on comet 67P/Churyumov-Gerasimenko revealed by Cometary Sampling and Composition (COSAC) mass spectrometry (Rosetta's Philae lander)

Table 1. The 16 molecules used to fit the COSAC mass spectrum.

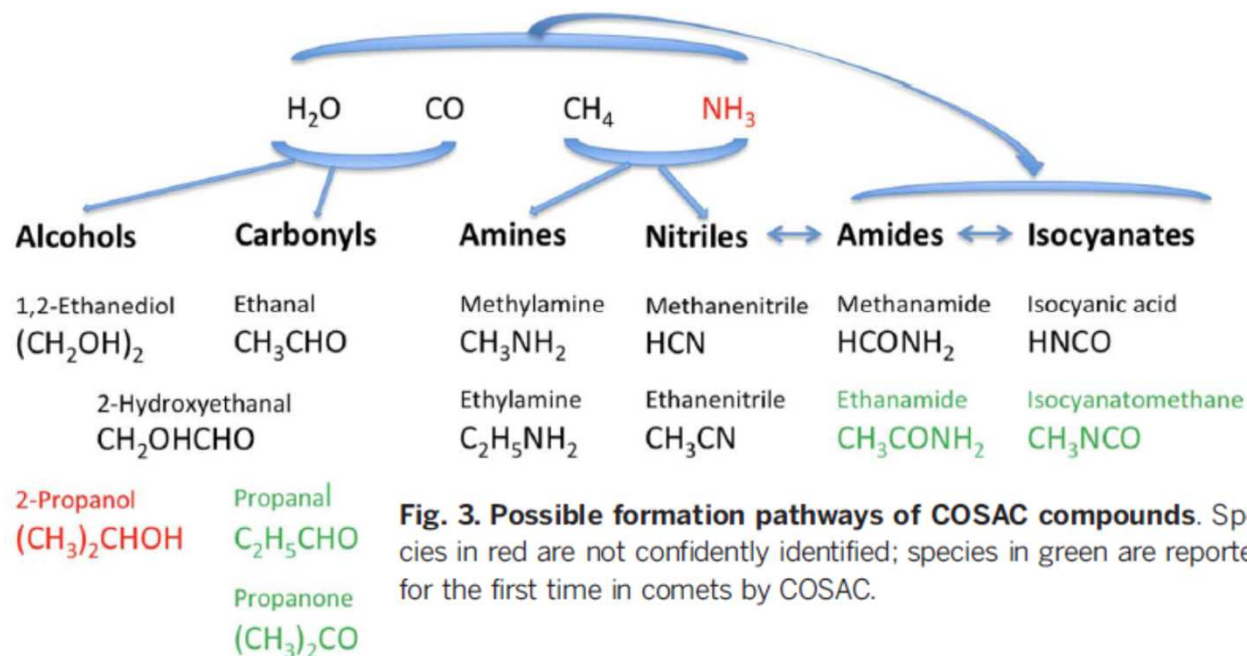
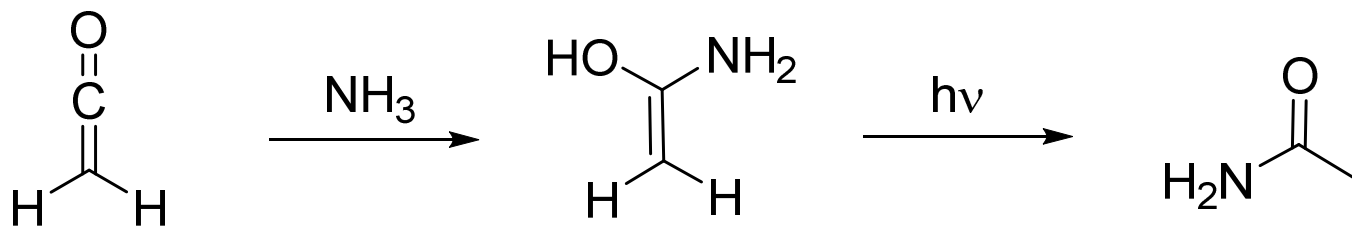
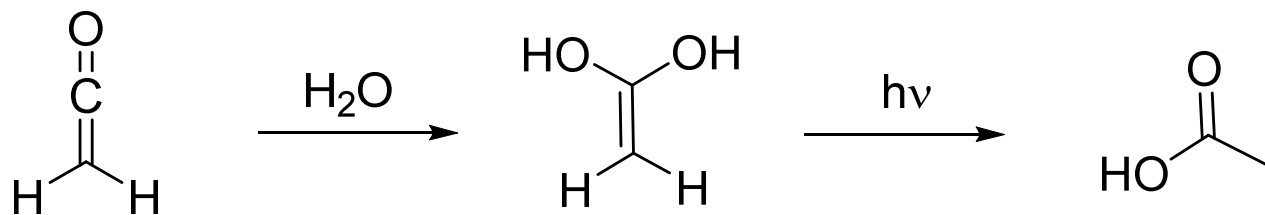


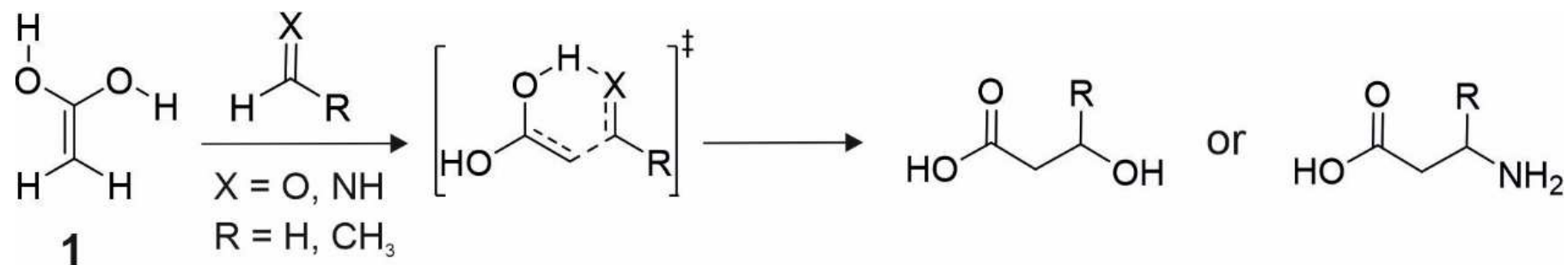
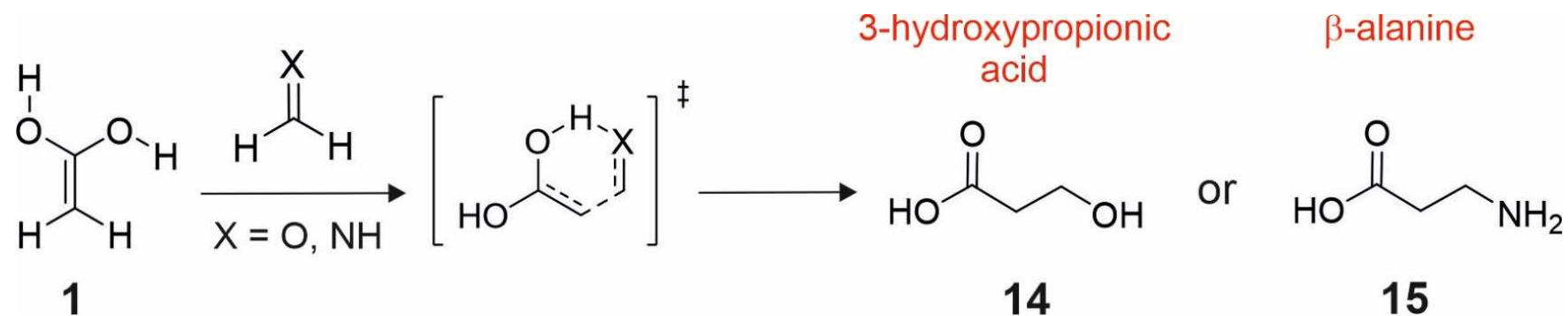
Fig. 3. Possible formation pathways of COSAC compounds. Species in red are not confidently identified; species in green are reported for the first time in comets by COSAC.

1,2-Ethanediol (ethylene glycol)	CH ₂ (OH)CH ₂ (OH)	62	0.79	0.2
----------------------------------	--	----	------	-----

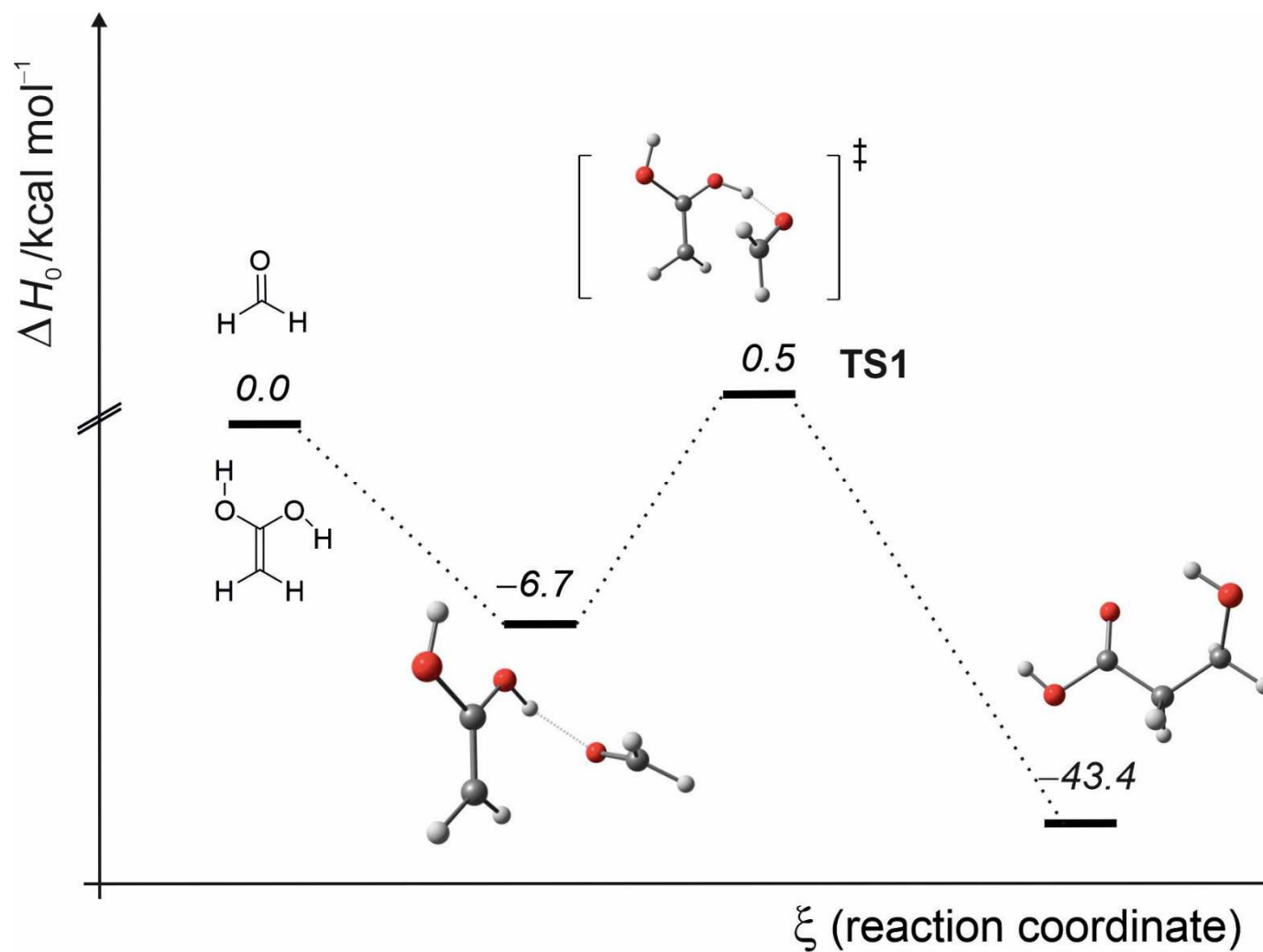
Reaction of Ketene with Water and Ammonia



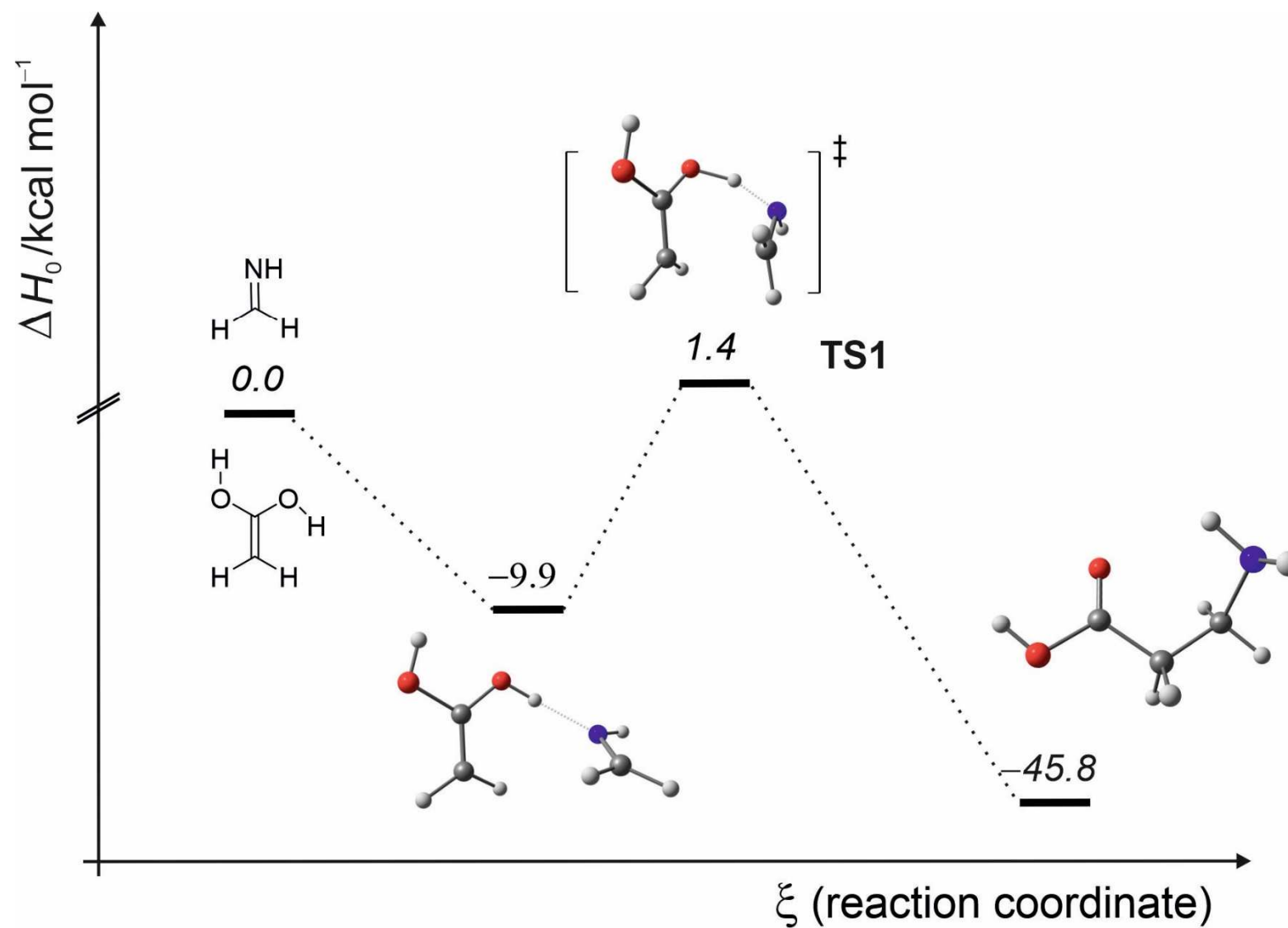
Formation of prebiotic amino acid(s) through enols-molecules reactions



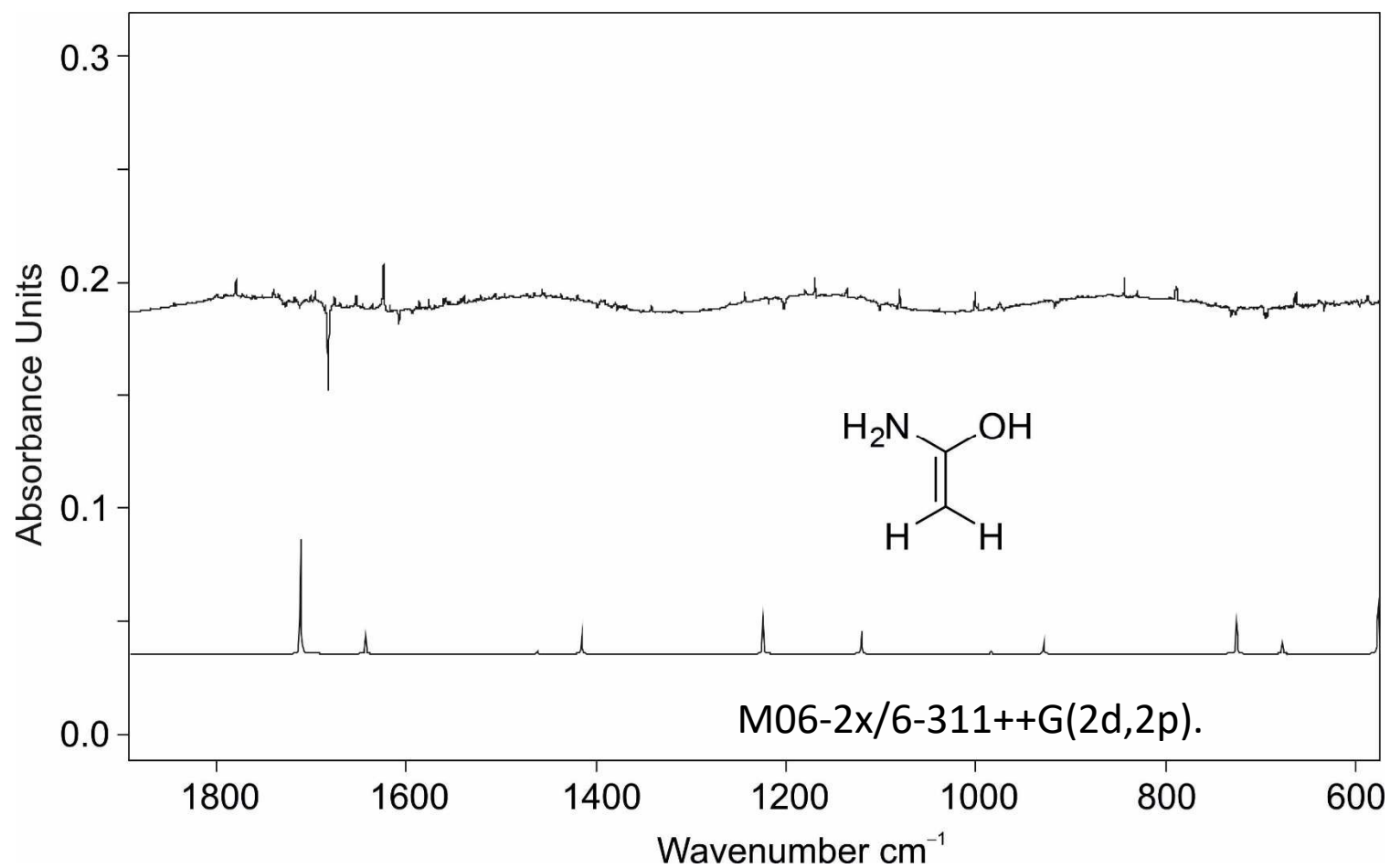
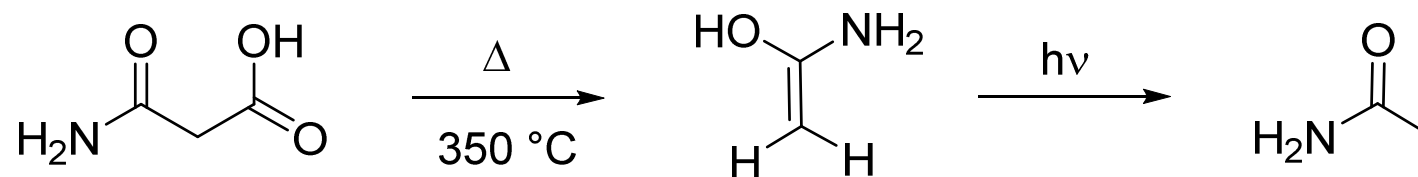
Formation of 3-hydroxypropionic acid through enols-CH₂O reaction



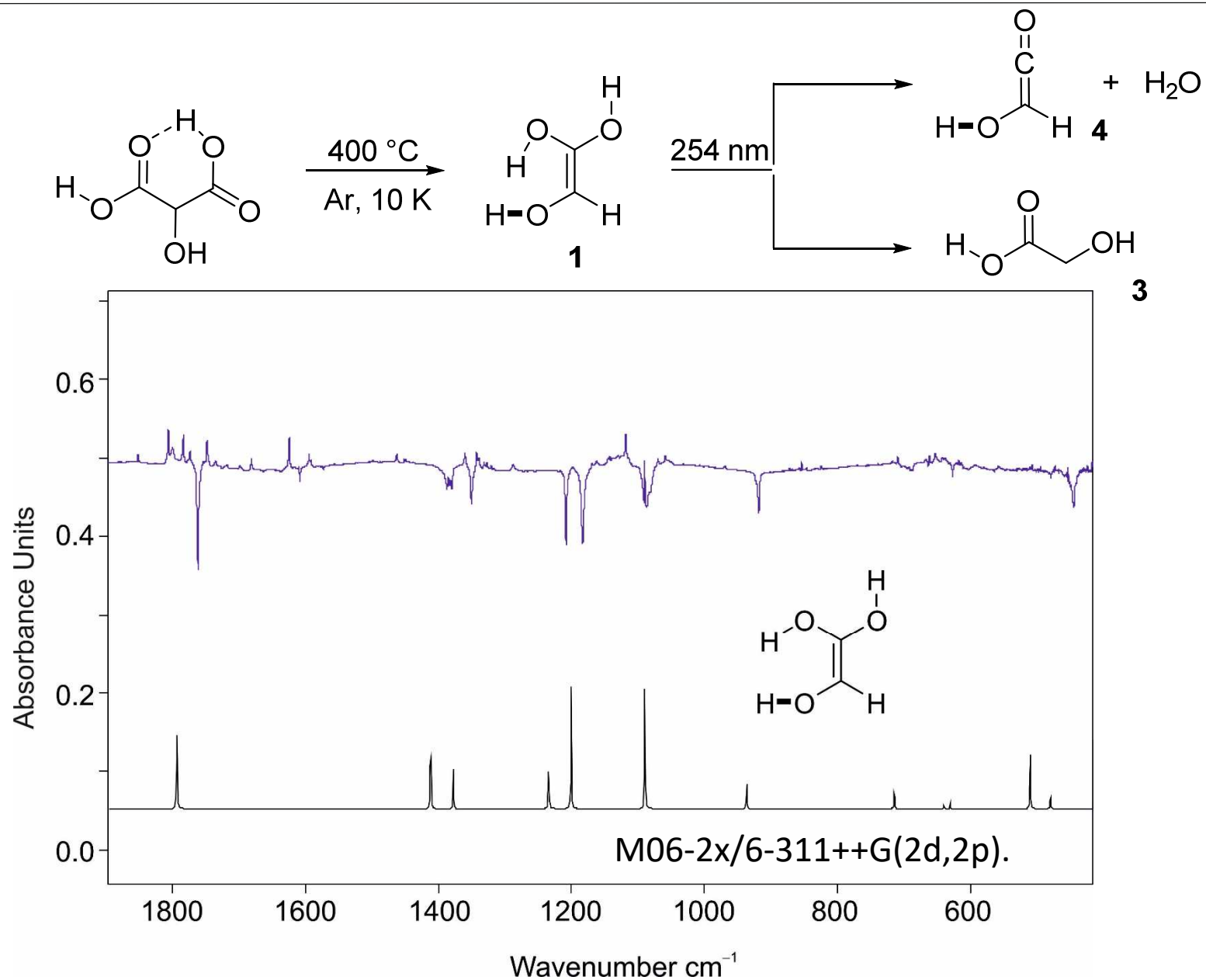
Formation of β -alanine through enols- CH_2NH reaction



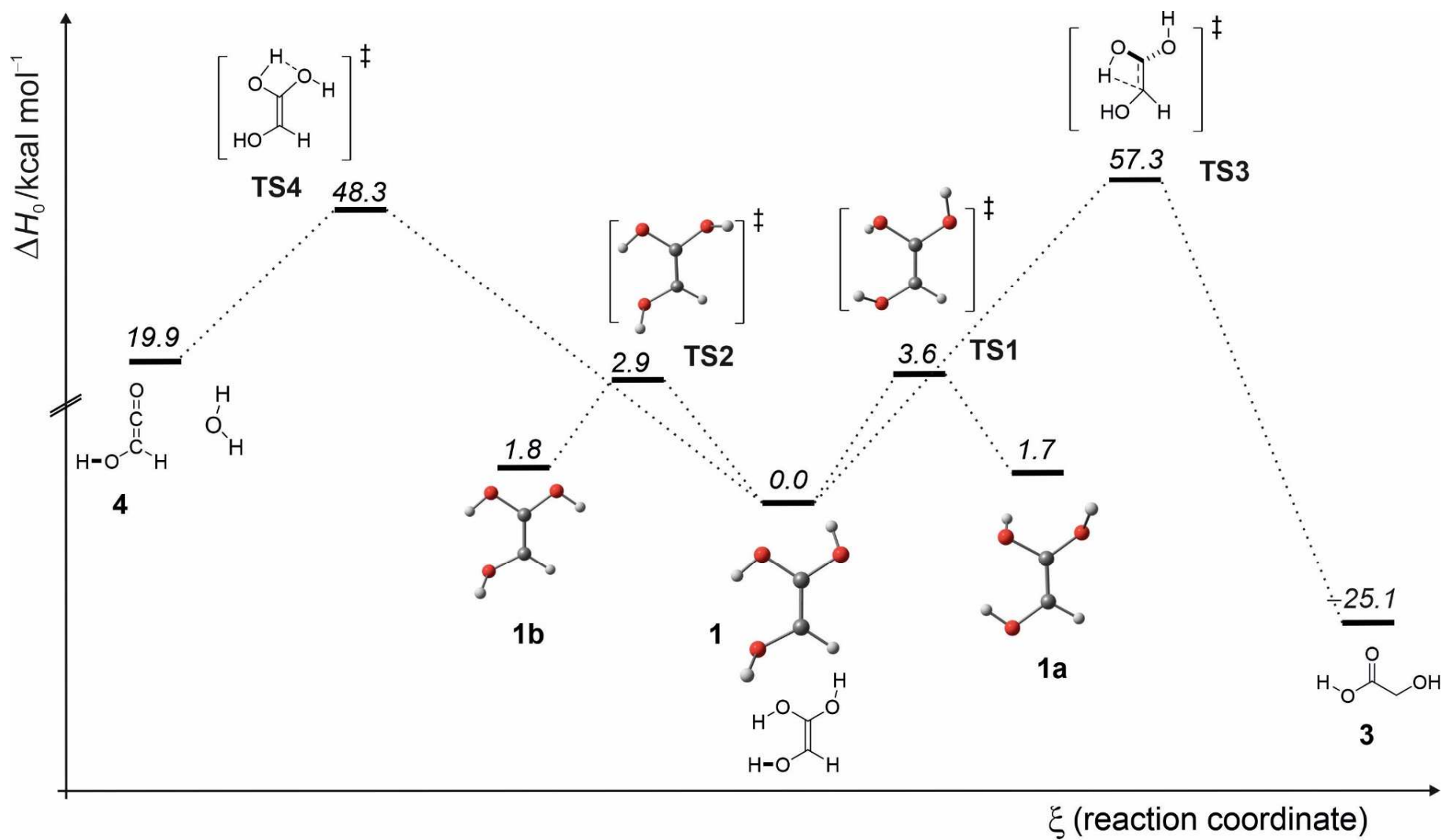
Enol of Acetamide



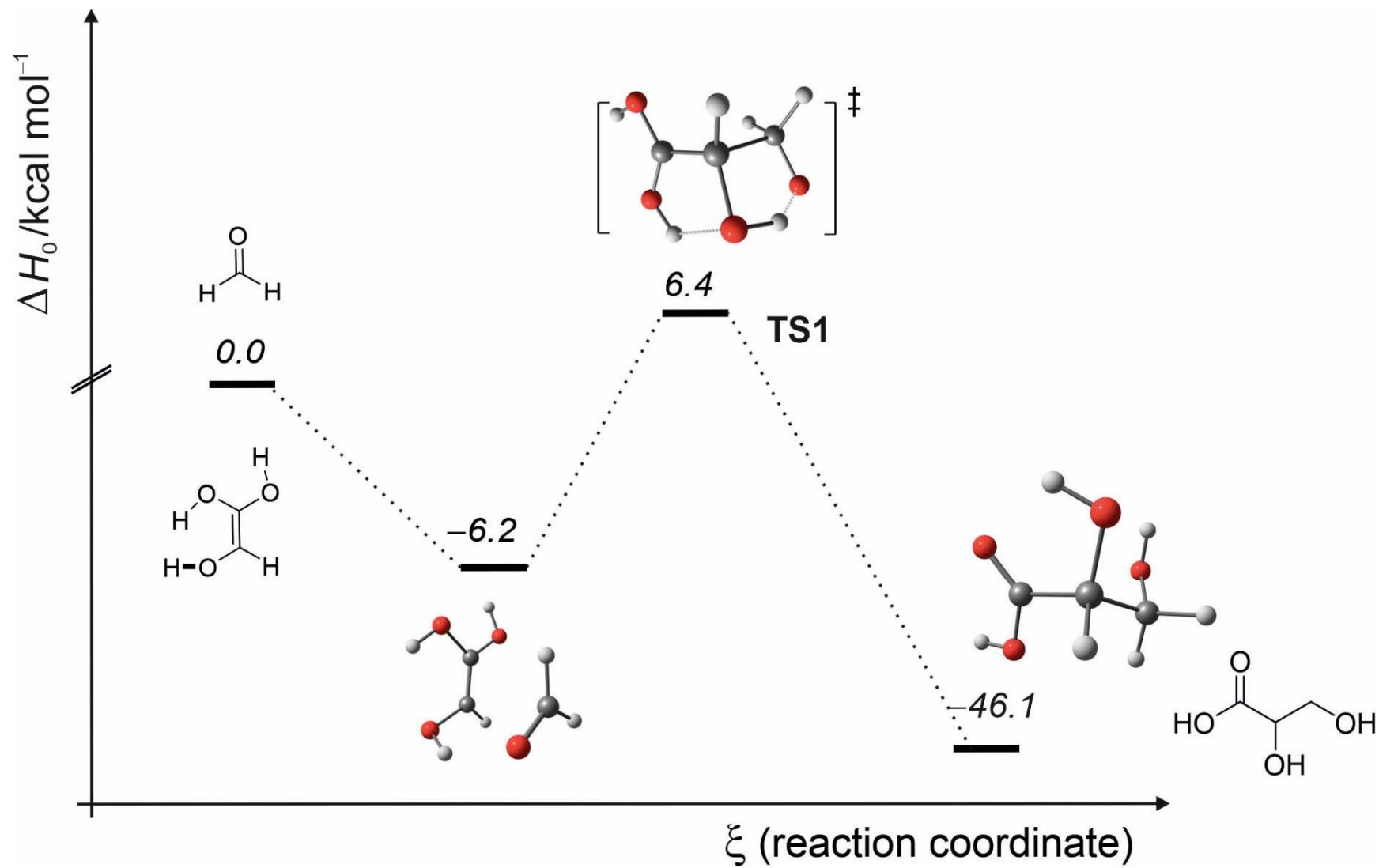
IR Spectra - Matrix Isolation



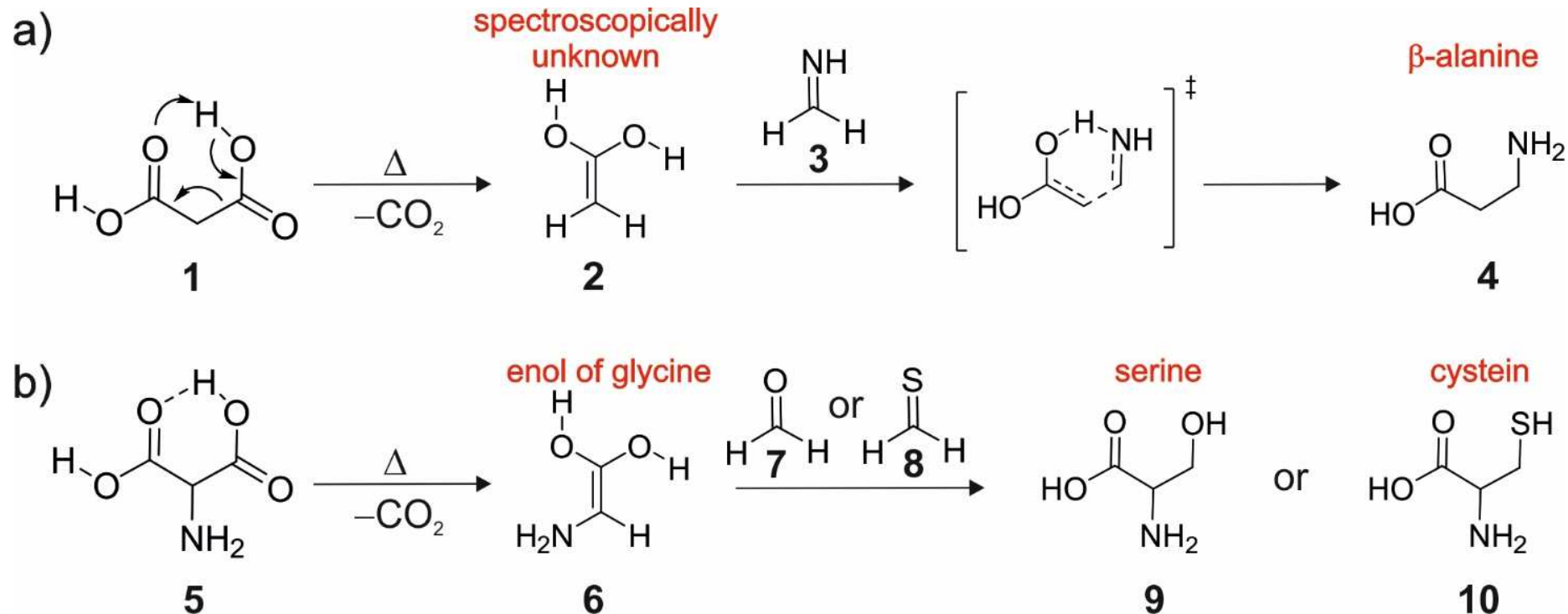
Potential Energy Surface



Reaction of enol with CH₂O



Formation of prebiotic (meteoritic) amino acids through enols-molecules reactions



Acknowledgements

Prof. Dr. Peter R. Schreiner

Felix Keul

Dr. André K. Eckhardt

PRS Group