



Challenging Unsurmountable Activation Barriers – From “Tunneling Control” to “Controlling Tunneling”

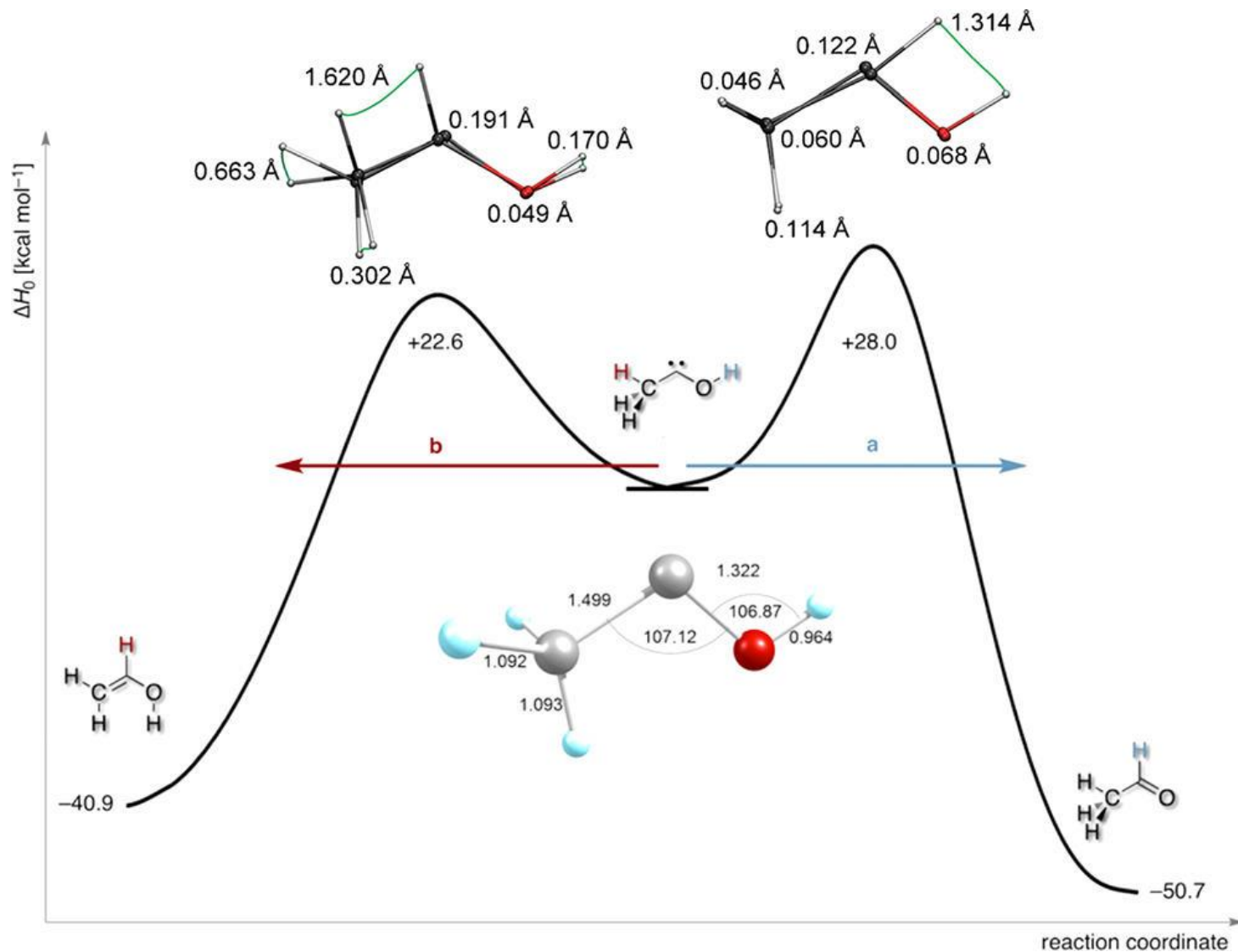
Group Seminar by

Bastian Bernhardt

23rd October 2020



Tunneling Control

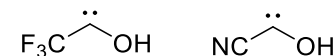


P. R. Schreiner, H. P. Reisenauer, D. Ley, D. Gerbig, C.-H. Wu, W. D. Allen, *Science* **2011**, 332, 1300–1304; P. R. Schreiner, *J. Am. Chem. Soc.* **2017**, 139, 15276–15283.

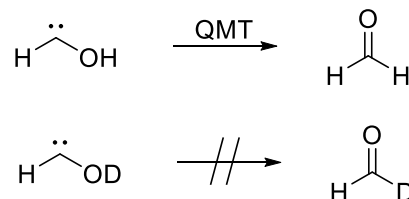


How to influence/control tunneling?

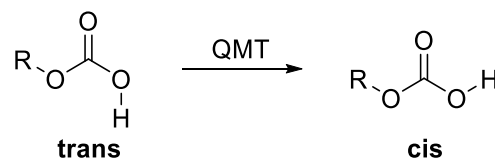
- Selecting only specific conformers (e.g. by NIR excitation)



- Isotopologues



- (Remote) molecular structure



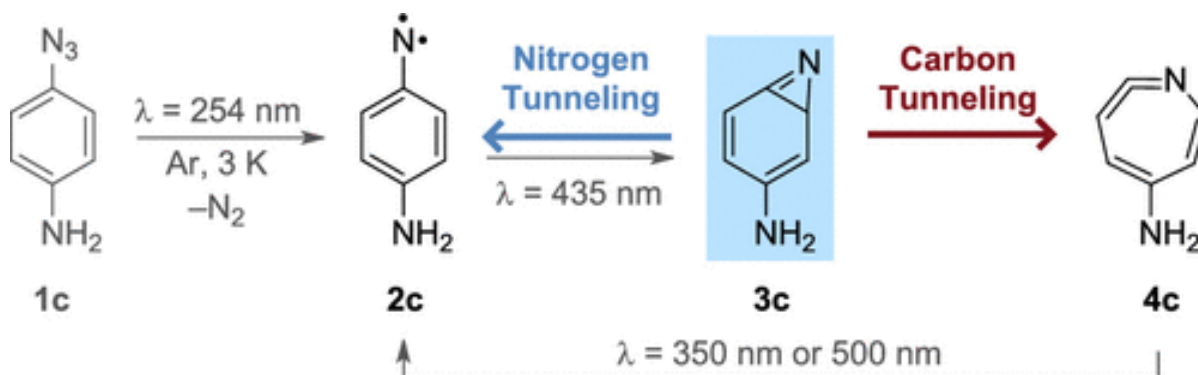
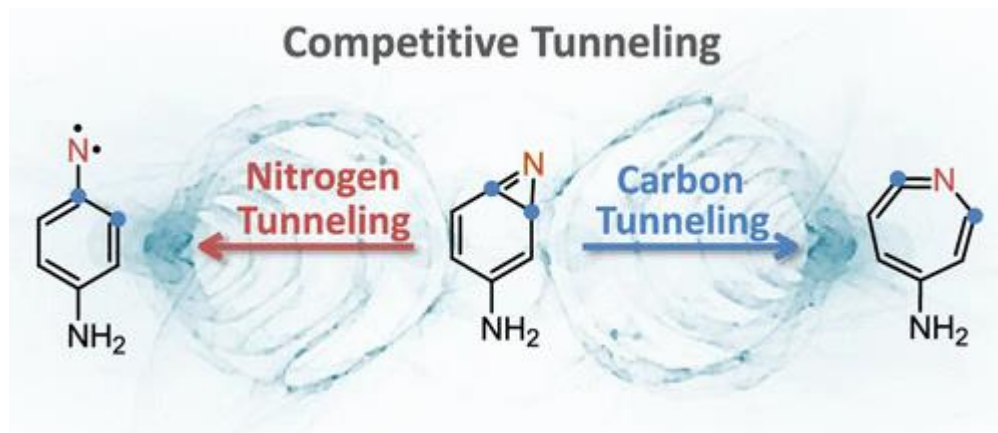
$$t_{1/2}: \text{R} = \text{H} < \text{CH}_3 < \text{CD}_3$$

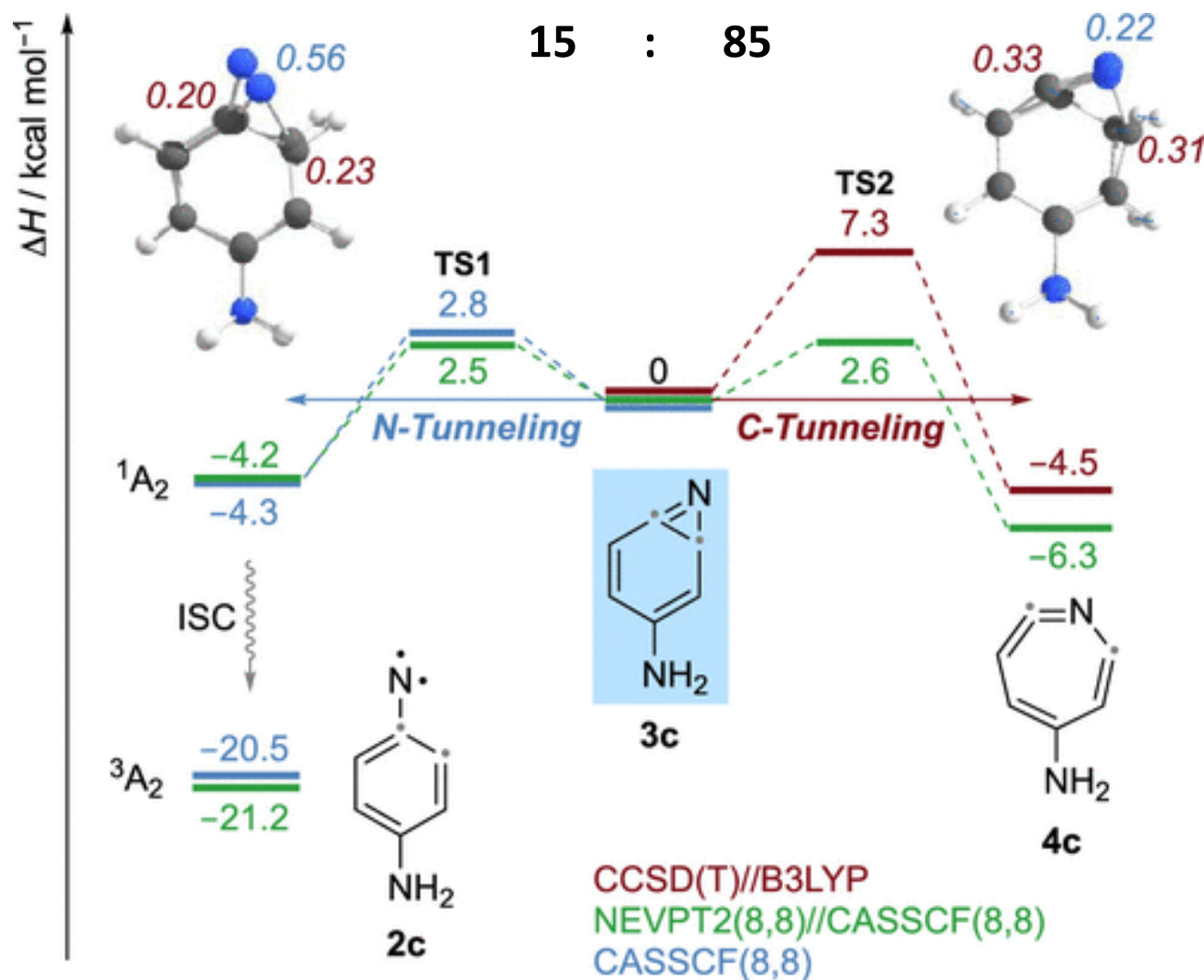
in contrast to

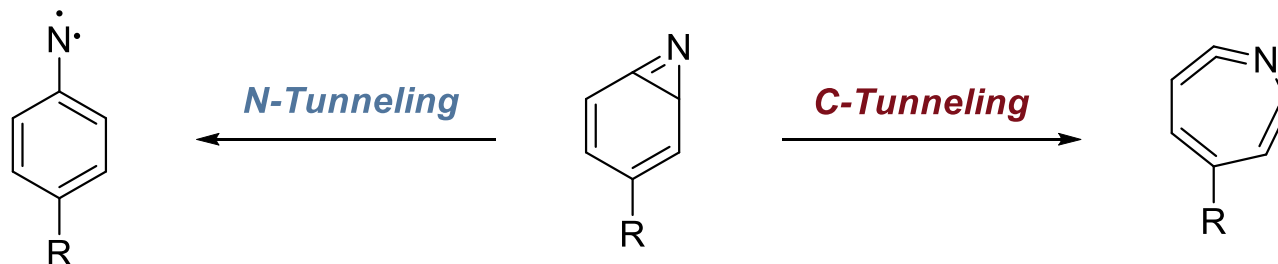
$$t_{1/2}: \text{formic acid} > \text{acetic acid}$$

- Matrix material

- Temperature, light

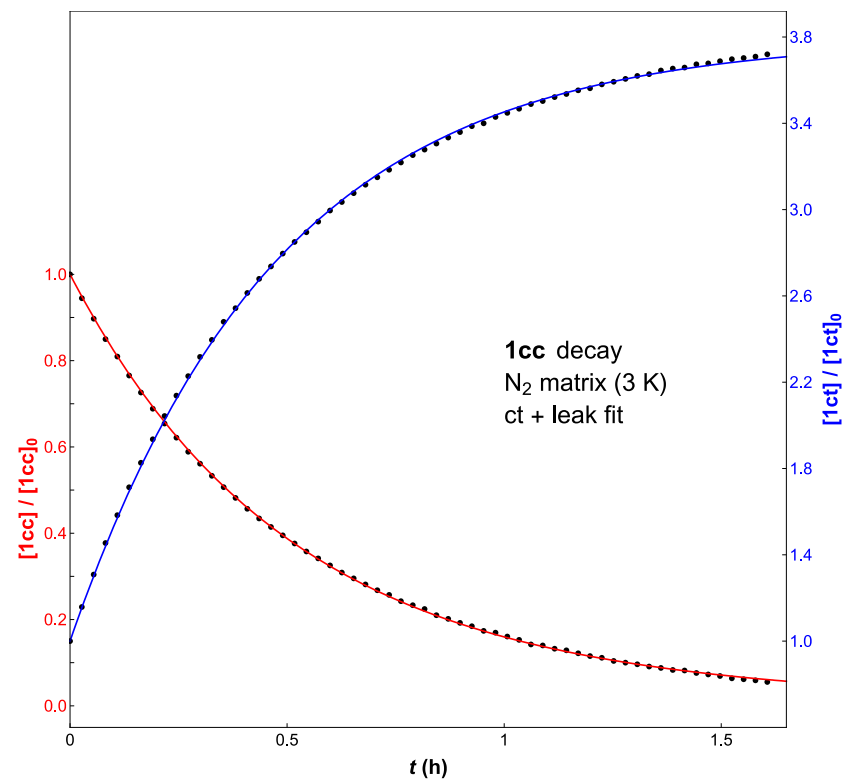
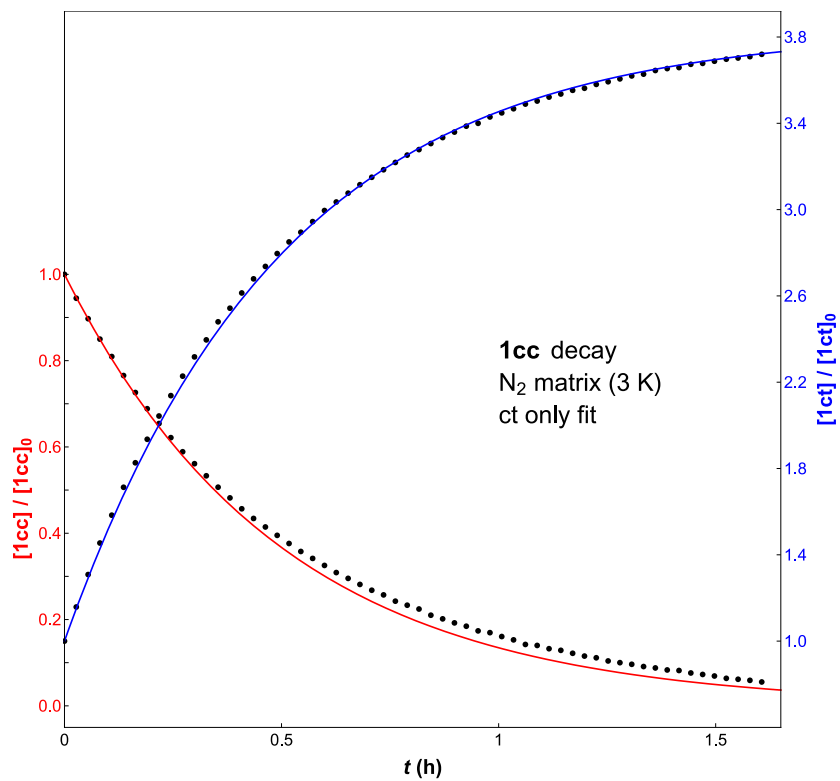
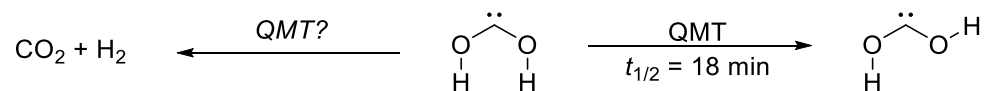






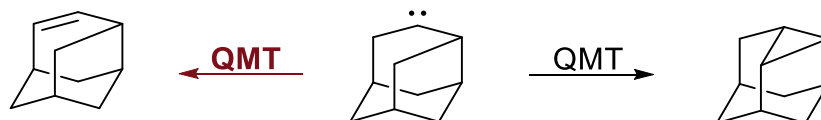
R =	N-QMT	C-QMT
NH ₂	15%	85%
NMe ₂	> 15%	< 85%
OH	~ 0%	~ 100%
OH (without filter)	> 50%	< 50%

Dihydroxycarbene

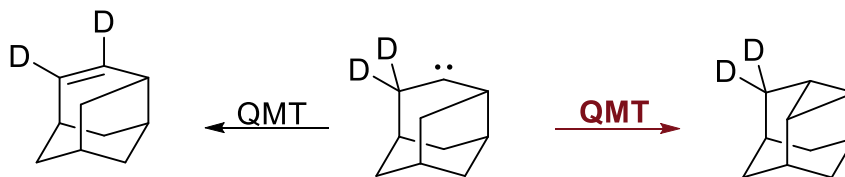




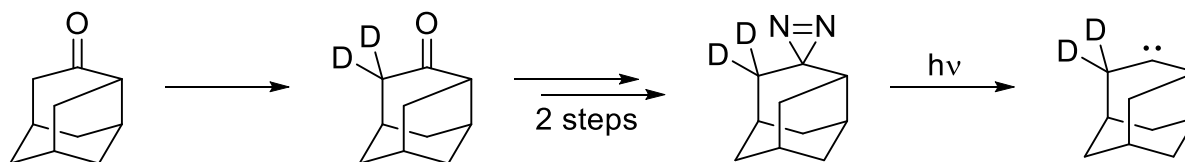
- Competing tunneling paths:

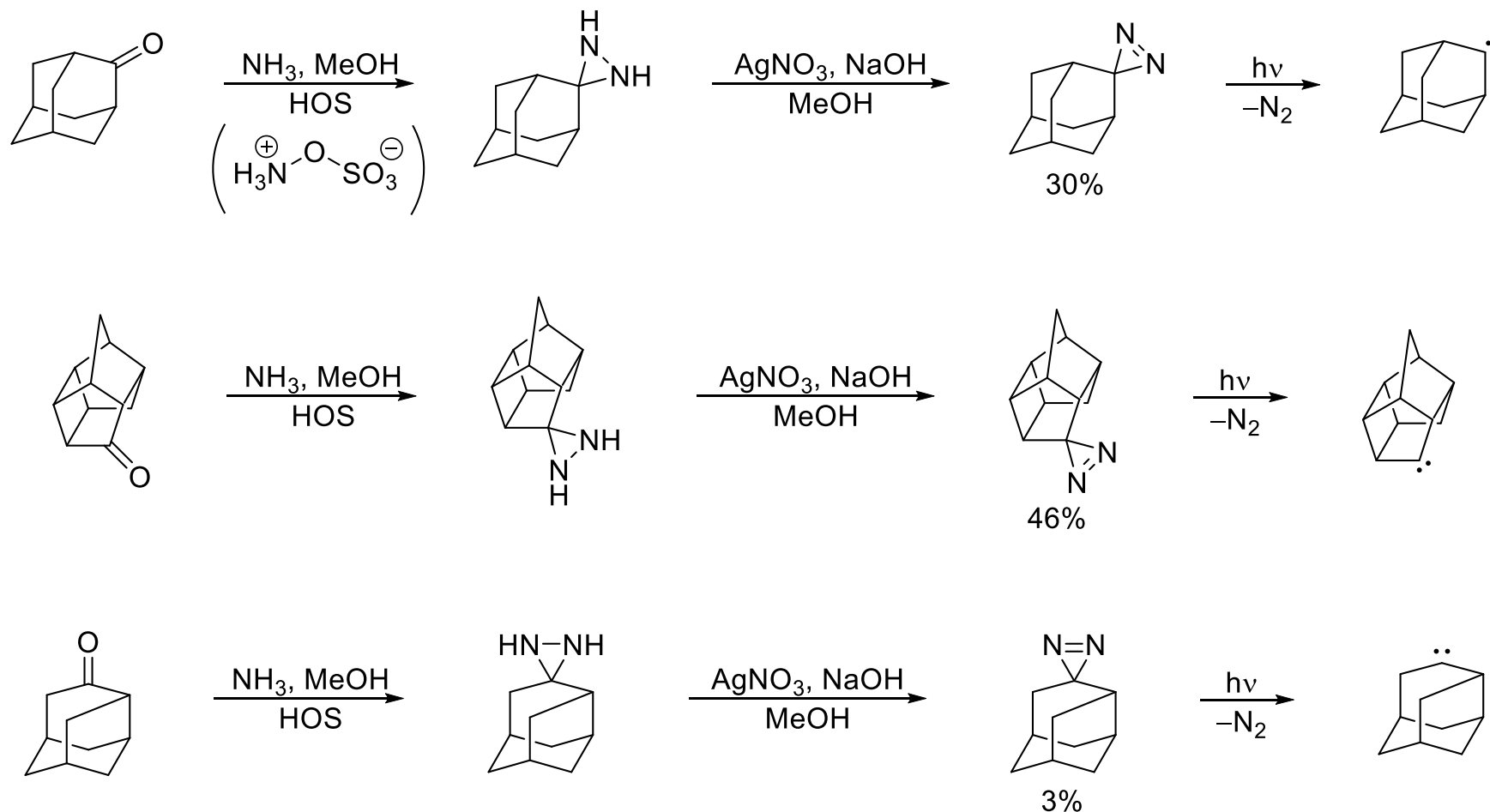


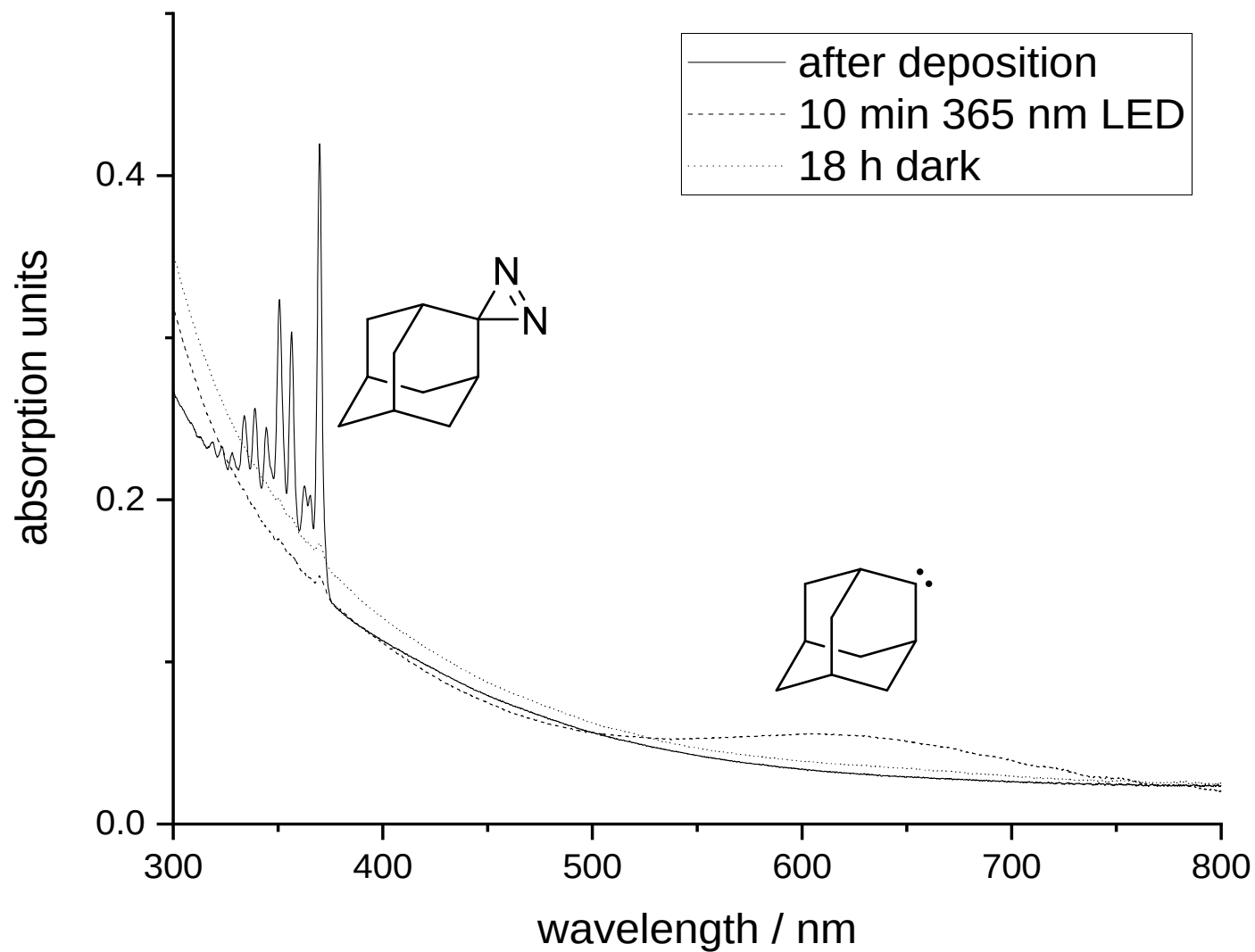
- Use the α -dideuterated carbene:



- Synthesis:

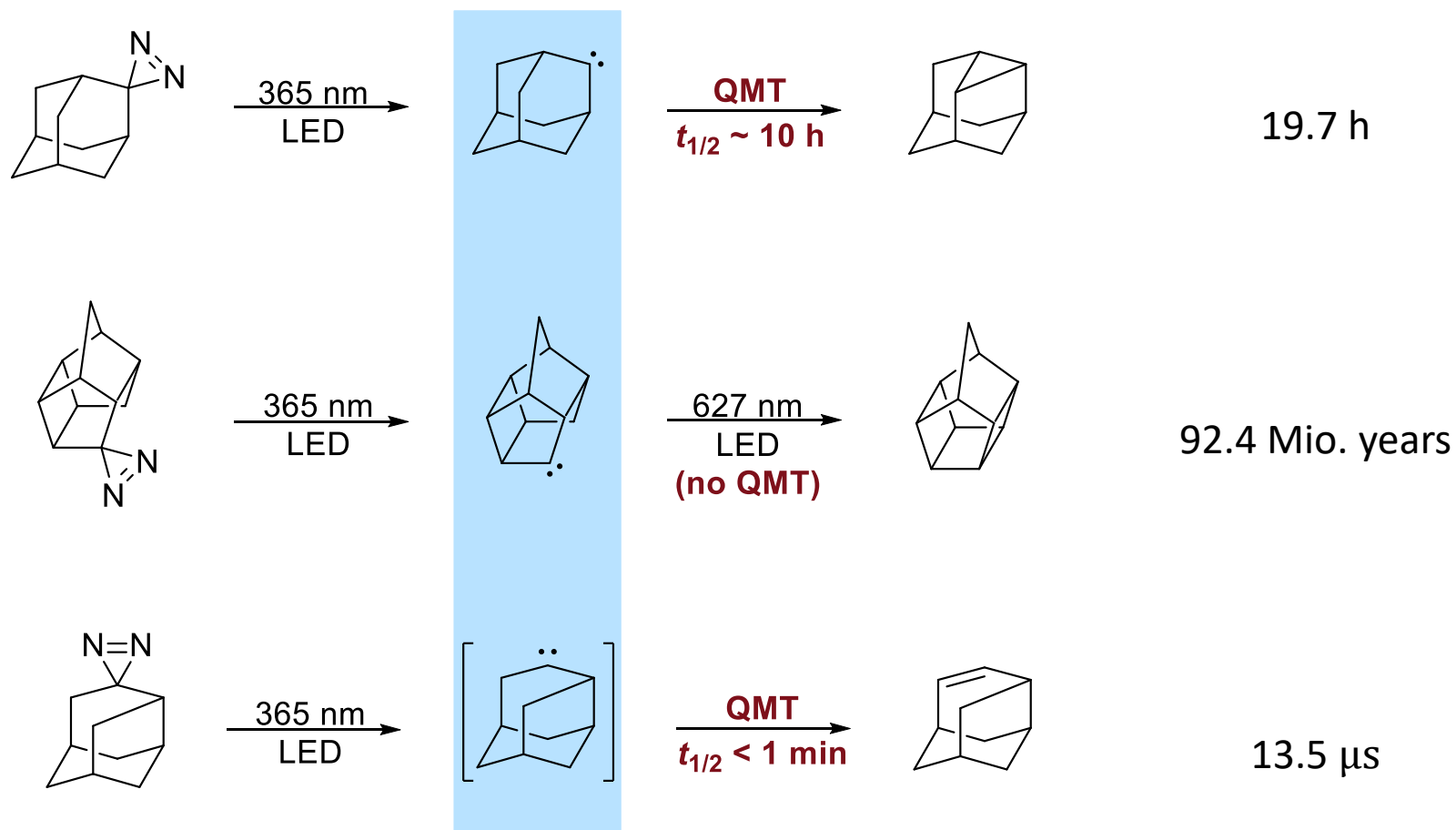


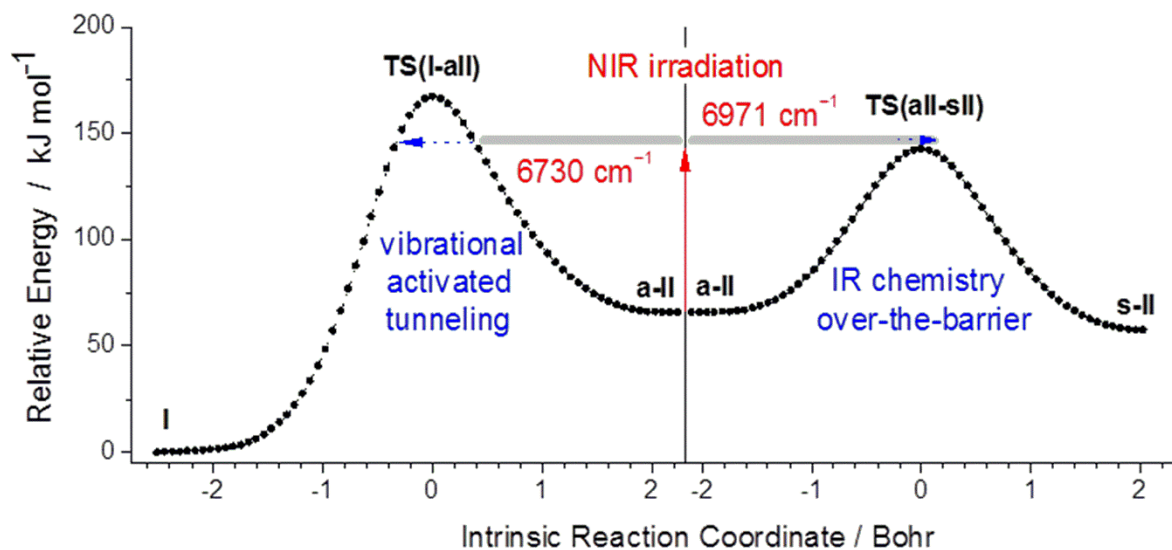
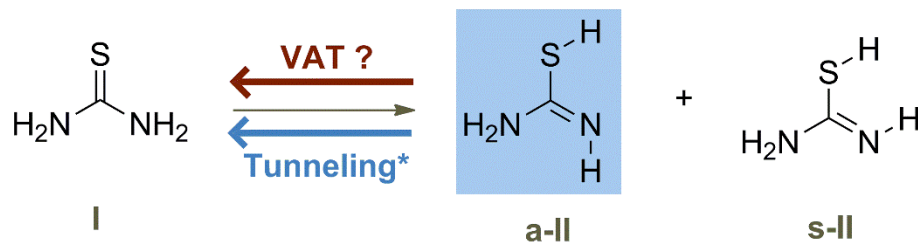






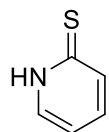
CVT/SCT//B3LYP/6-31G*



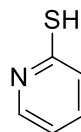




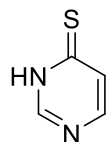
Thioamide $\rightarrow$ Thiylimine:



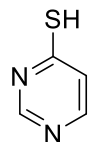
$> 330 \text{ nm}$



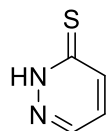
Nowak *et al.* 1990



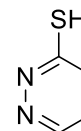
$> 330 \text{ nm}$



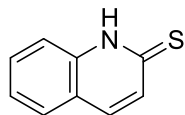
Nowak *et al.* 1991



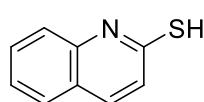
$> 330 \text{ nm}$



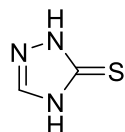
Nowak *et al.* 1991



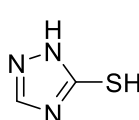
$> 355 \text{ nm}$



Prusinowska *et al.* 1995



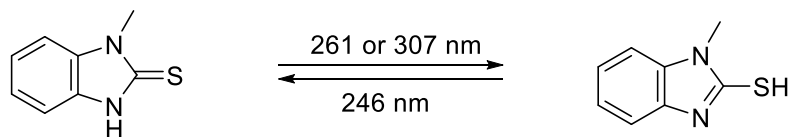
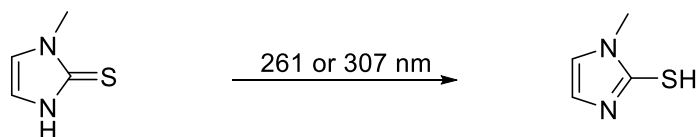
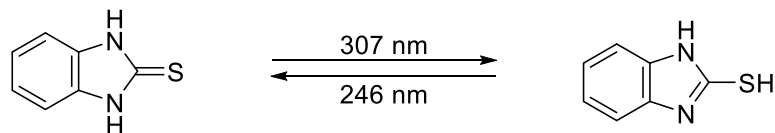
$> 275 \text{ nm}$



Rostkowska *et al.* 2017

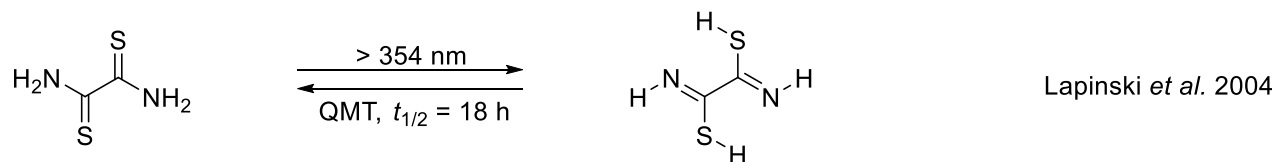
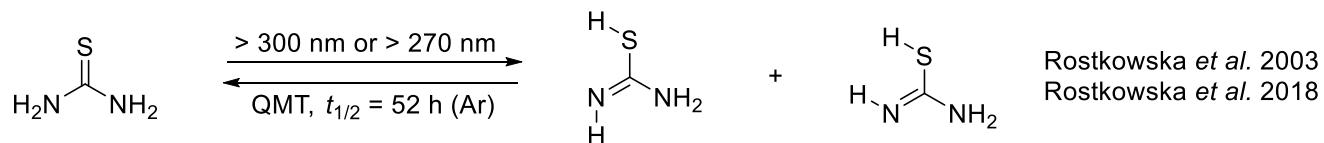


Thioamide $\rightleftharpoons$ Thiolimine:



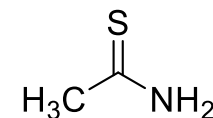
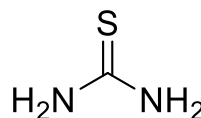
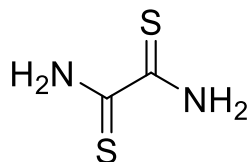
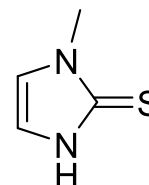
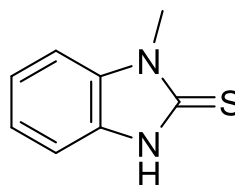
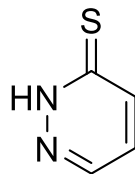
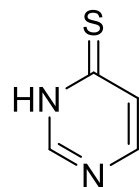
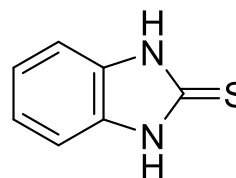
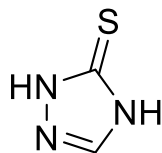
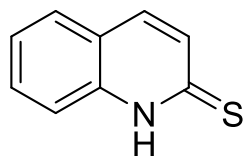


Thiolimine $\rightarrow$ Thiolimine *via* QMT:





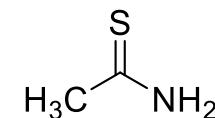
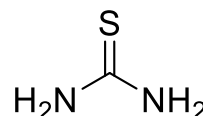
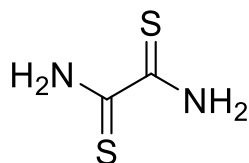
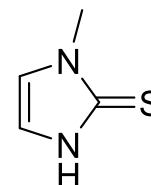
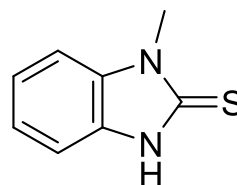
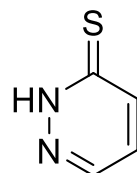
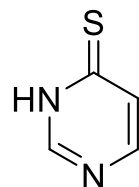
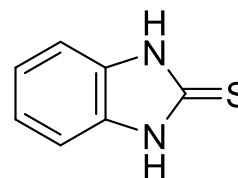
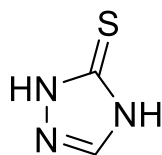
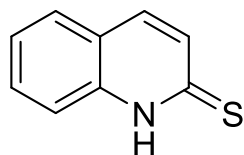
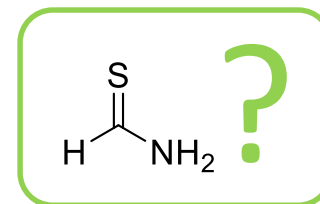
Matrix-isolated thioamides:



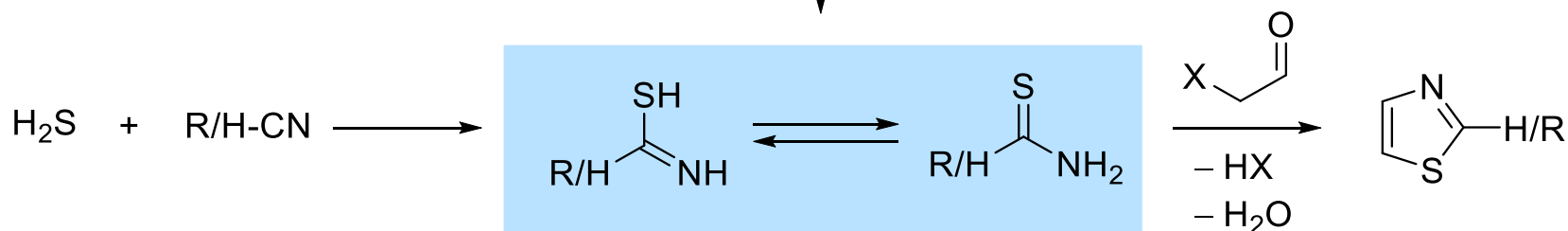
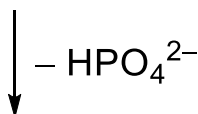
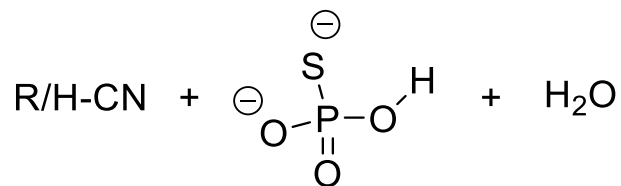
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Matrix-isolated thioamides:



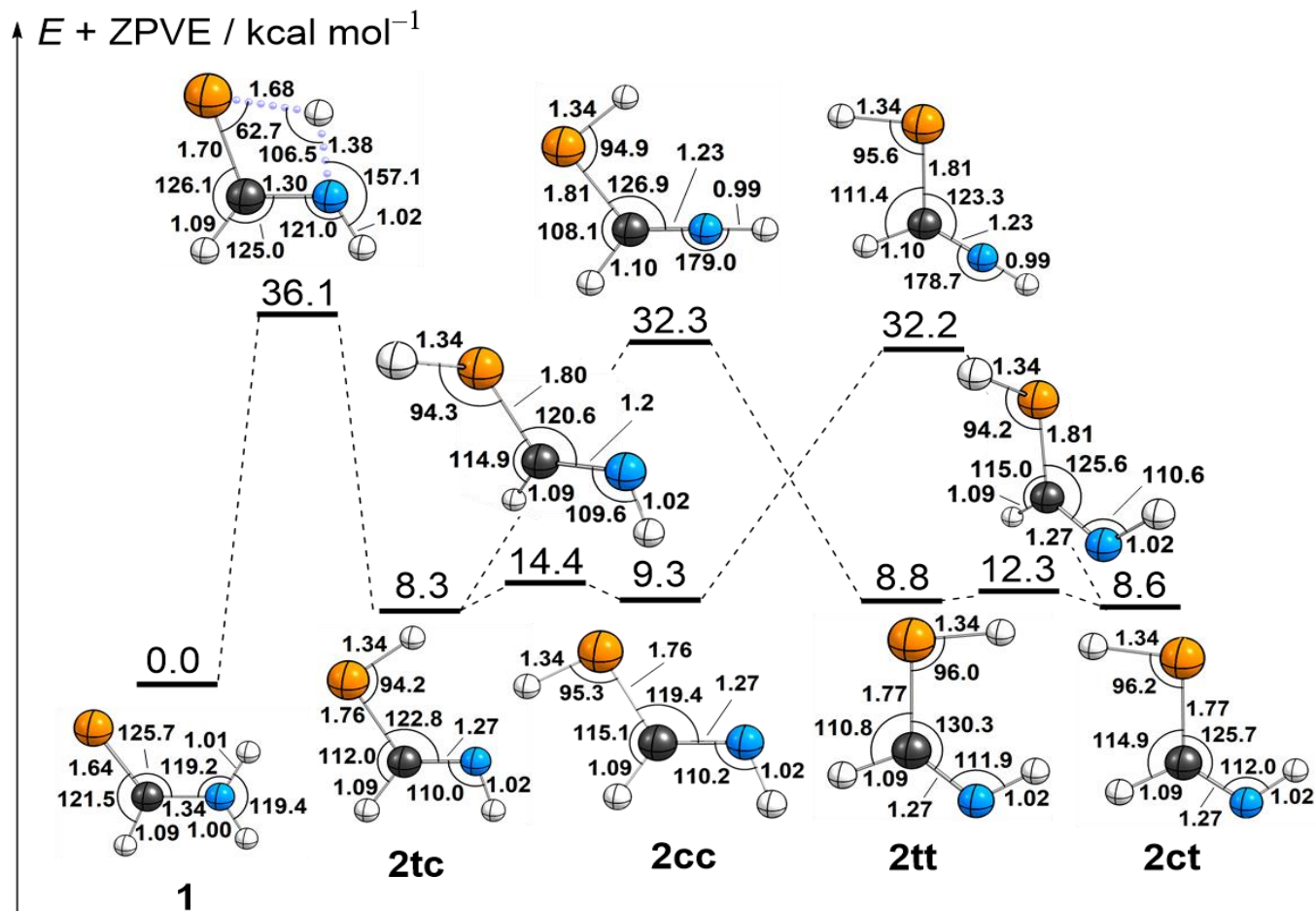
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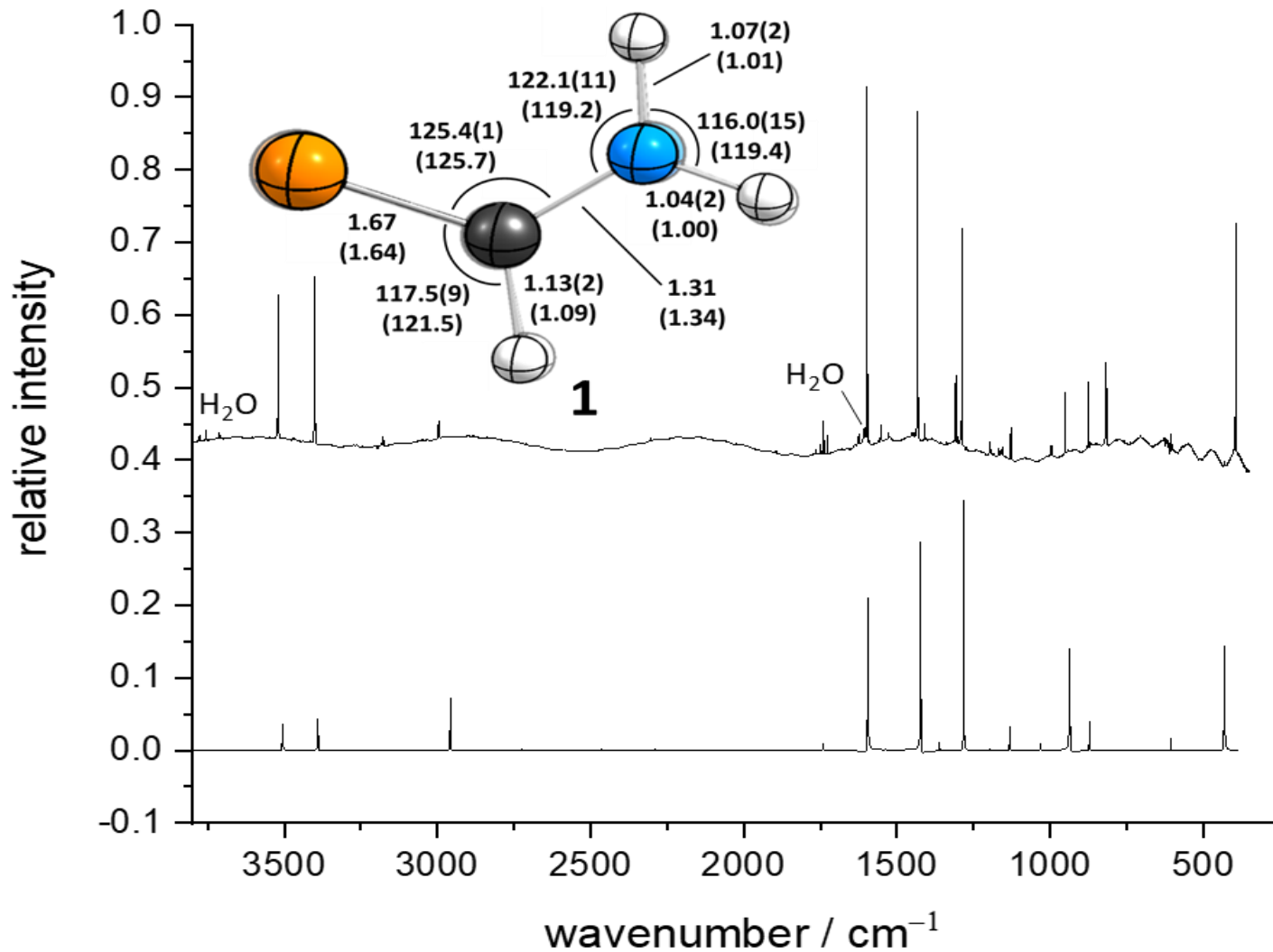
Sutherland
et al. 2015

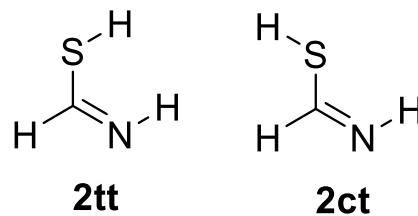
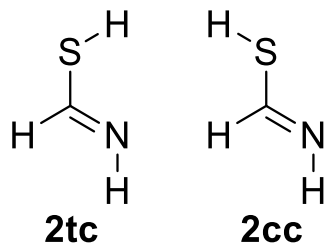
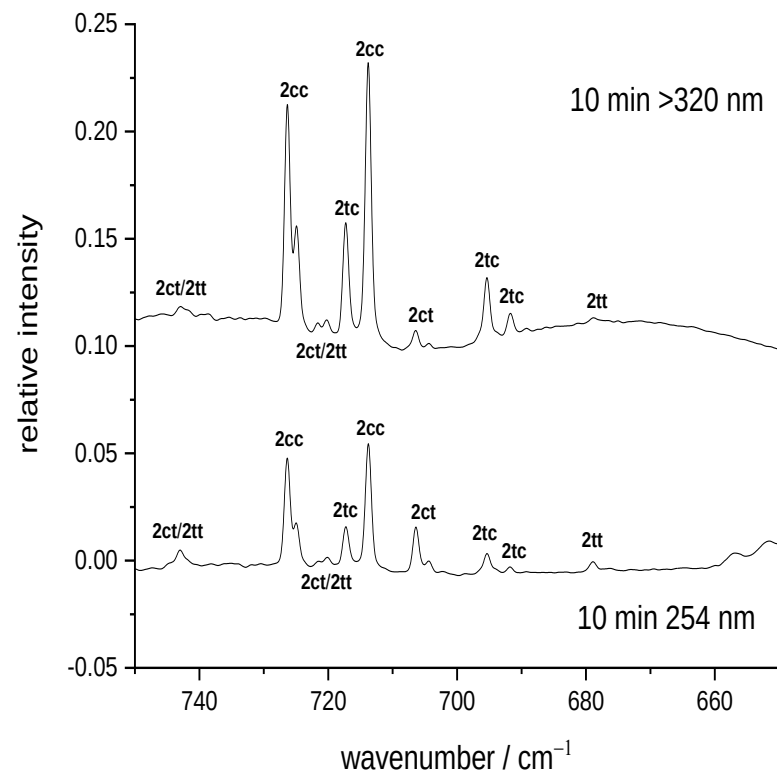
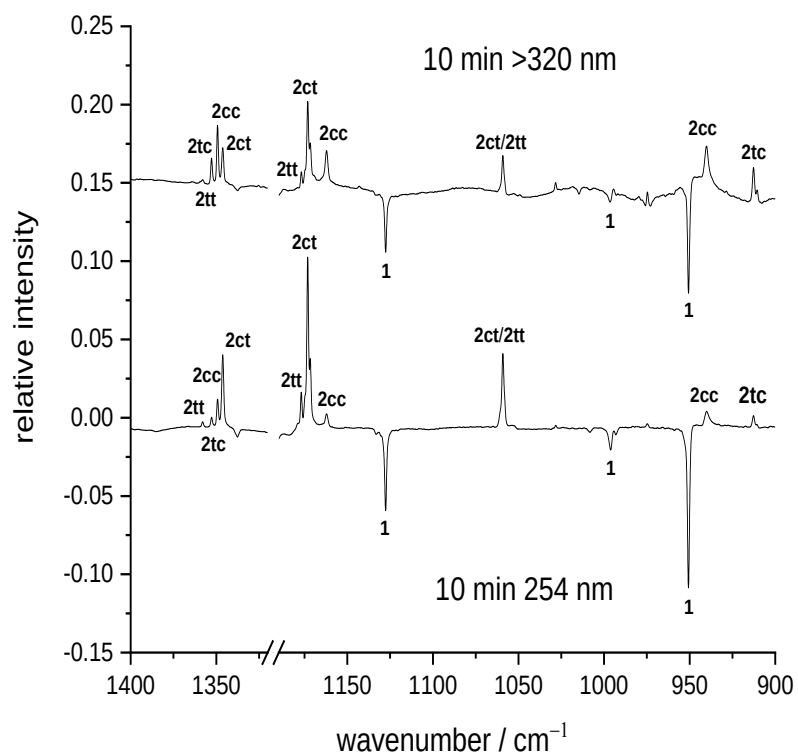


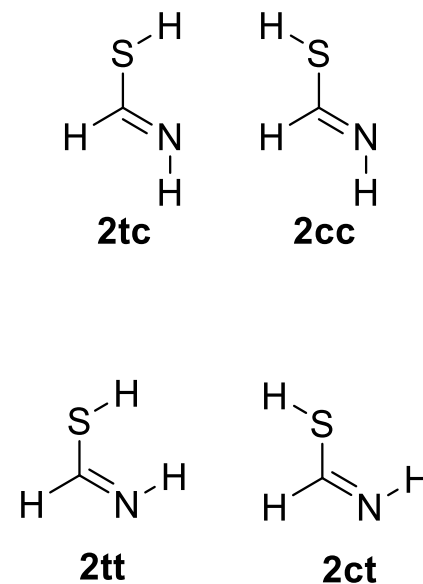
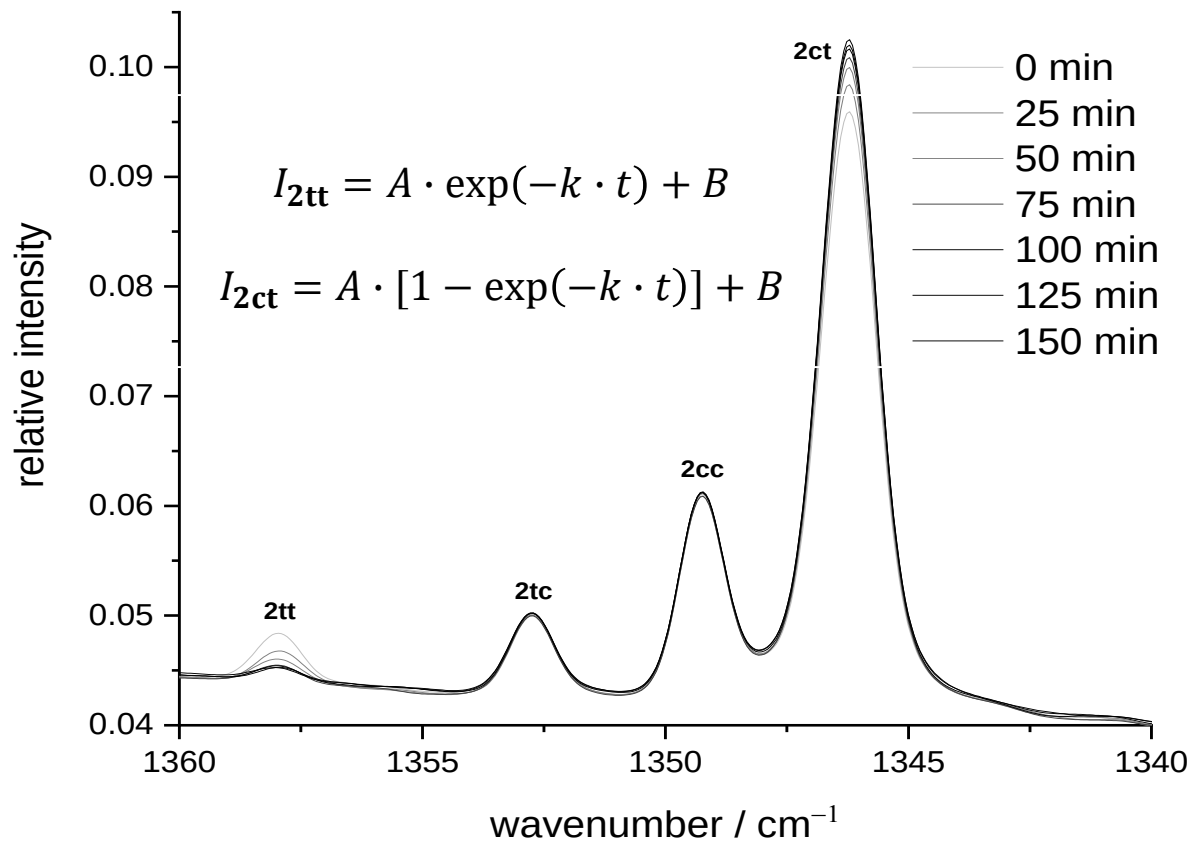
amino acids (Val, Leu, Pro, Arg)



AE-CCSD(T)/aug-cc-pCVTZ









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Cite this: DOI: 10.1039/c9cp03417j

S–H rotamerization *via* tunneling in a thiol form of thioacetamide†Sándor Góbi,^a Cláudio M. Nunes,^a Igor Reva,^a György Tarczay^{b,c} and Rui Fausto^a

Rotamerization of a hydroxyl (O–H) group by tunneling is well-known and has been extensively studied. On the other hand, similar tunneling processes for the thiol (S–H) group have not been reported yet. In this work, the imino-thiol forms of thioacetamide were studied in cryogenic matrices (Ar, Xe) after UV-irradiation of the common amino-thione form of the compound, corresponding to the *cis* or *trans* thiol (**C/T**) (*syn* and *anti*; **S/a**). Noteworthy, the *syn-cis* (**SC**) imino-thiol form was *syn-trans* (**ST**) form (with a half-life of 80 min), in a process which was temperature independent (*i.e.*, at 11 or 20 K). Such conformational transformation was observed by an S–H rotamerization occurring by tunneling. Kramers–Brillouin formalism predicts a tunneling half-life for the S–H

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rsc.li/pccp

1. Introduction

acid,²⁵ tribromoacetic acid,²⁶ propionic acid,²⁸ propiolic acid,²⁹ and

PCCP

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DOI: 10.1039/c9cp05370k

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1. Introduction

The infrared (IR) spectroscopy of compounds containing thio-

Selective conformational control by excitation of NH imino vibrational antennas†

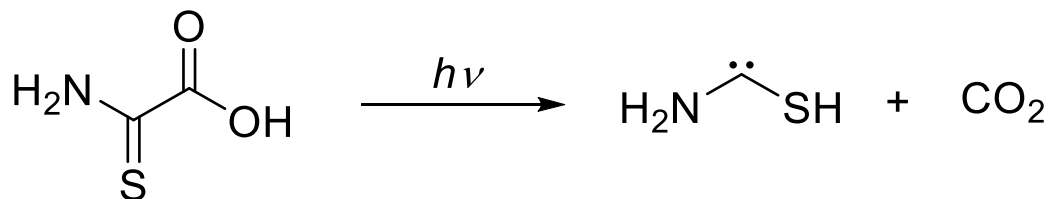
Sándor Góbi,^a Igor Reva,^a István Pál Csonka,^b Cláudio M. Nunes,^a György Tarczay^{b,c} and Rui Fausto^{a,d}

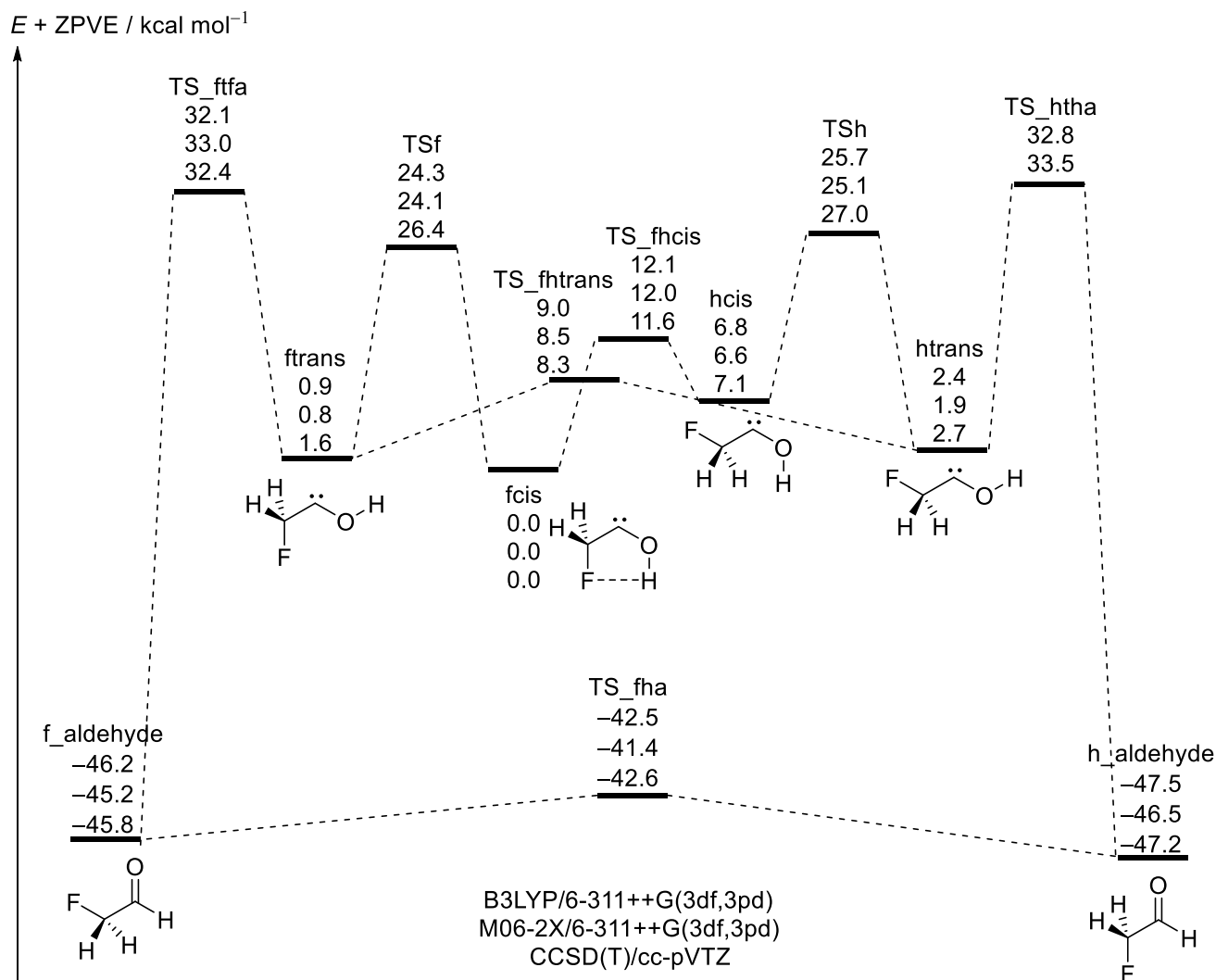
An imino group was used for the first time as a vibrational antenna to manipulate molecular conformations. Imino-thiol isomers of thioacetamide were generated upon UV-irradiation of its amino-thione tautomer isolated in argon matrices at 11 K. Selective and reversible conformational isomerizations were induced by narrowband near-IR irradiation tuned at the frequencies of the 2ν(NH) first stretching overtone of each imino-thiol isomer. The conformational isomerization concerns the change in the orientation of a remote –SH group, while the orientation of the imino (C=NH) group remains the same. Supported by quantum chemical anharmonic computations, this allowed for a reliable, isomer-selective vibrational assignment of the four imino-thiol isomers extending now over the full mid-IR and near-IR ranges. It was found that the experimental IR intensities of the 2ν(NH) first stretching overtones (computed 4–5 km mol^{−1}) of the imino-thiol forms are comparable to those of the ν(NH) stretching fundamentals (computed 2–4 km mol^{−1}). This is the first time such a phenomenon is reported for an imine molecule. The kinetics of conformational isomerization was monitored *in situ*, indicating that the irradiation-induced processes are significantly faster than the tunneling-driven spontaneous *cis*–*trans* rotamerization of the –SH group. Quantum yields for the rotamerizations of the –SH group resulting from the vibrational excitation of a remote –NH group were estimated and found to be comparable to those observed for matrix-isolated carboxylic acids and amino acids, where conformational changes of the –OH group were induced by the direct vibrational excitation of 2ν(OH) first stretching overtones.

Compared to the commonly found thione tautomer, the elusive thiol isomeric forms might be considered to represent more attractive systems for investigation, in part because they



Cooperation with Markus:

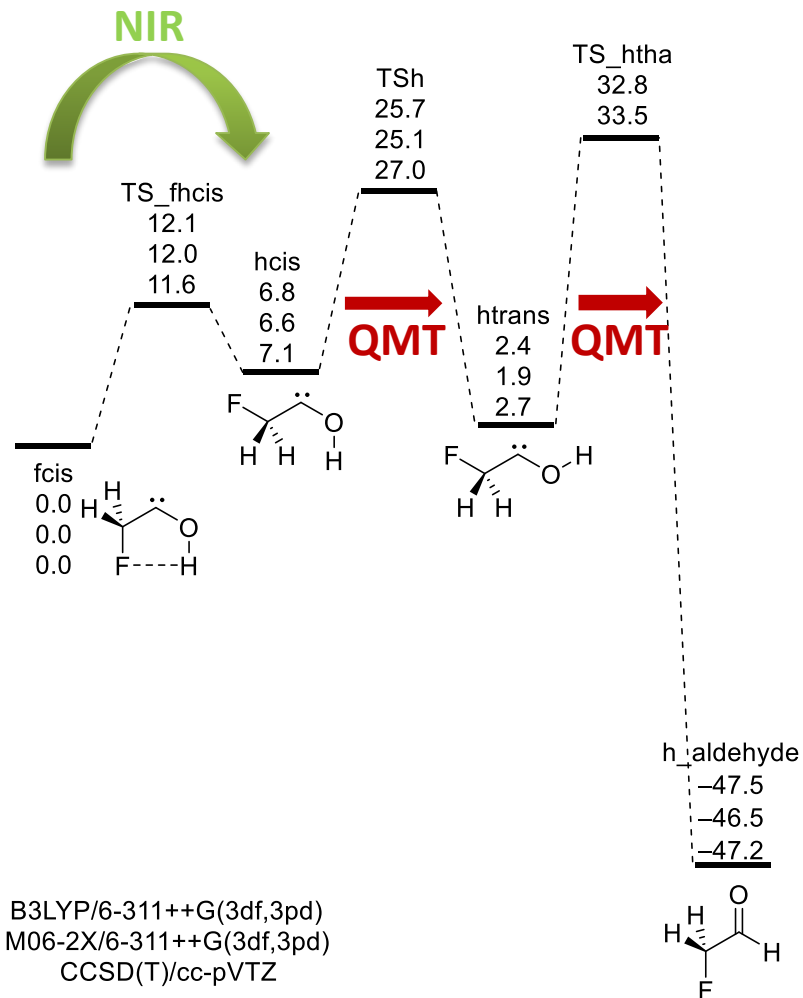




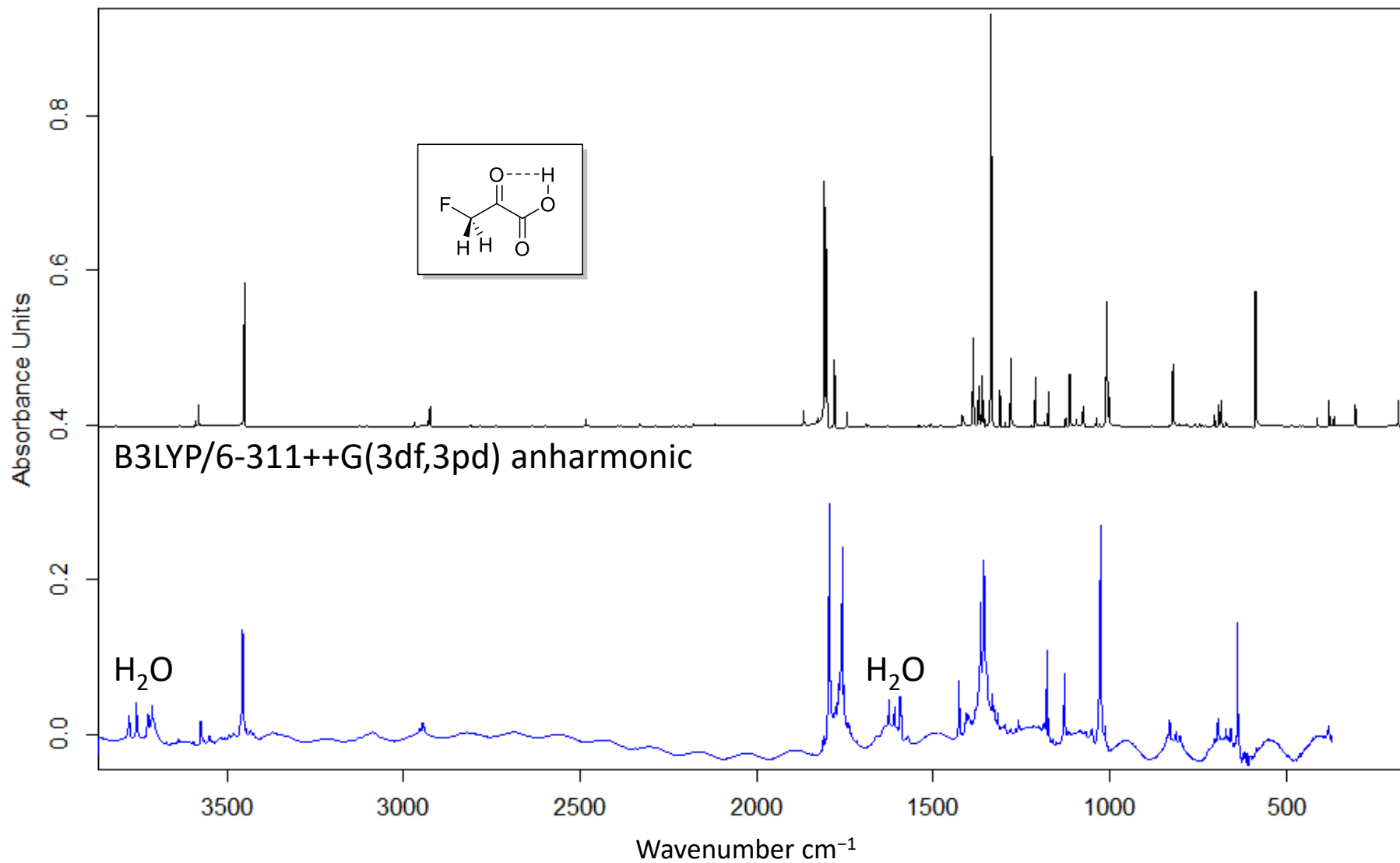
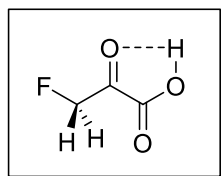
Monofluoromethylhydroxycarbene

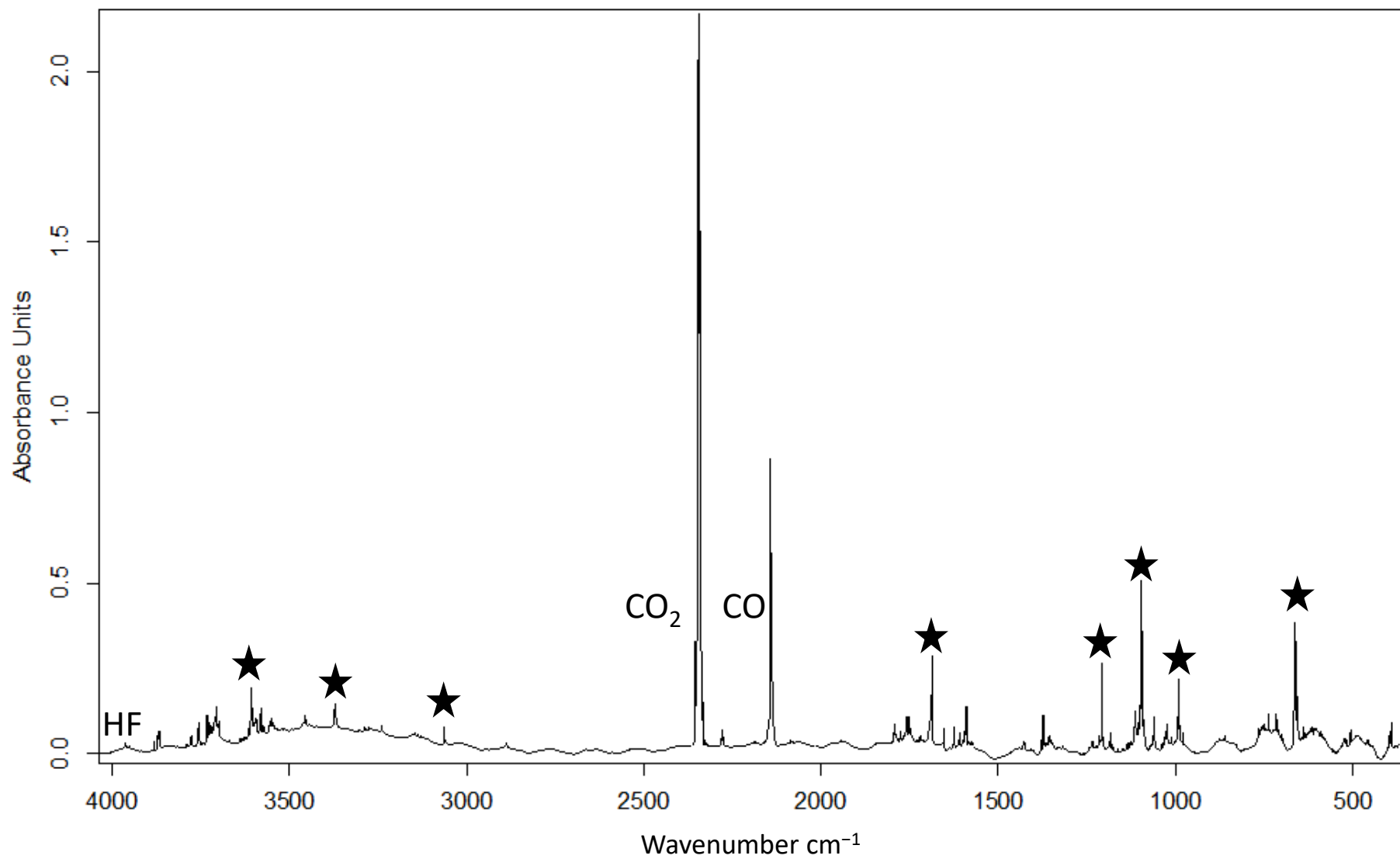


$E + \text{ZPVE} / \text{kcal mol}^{-1}$

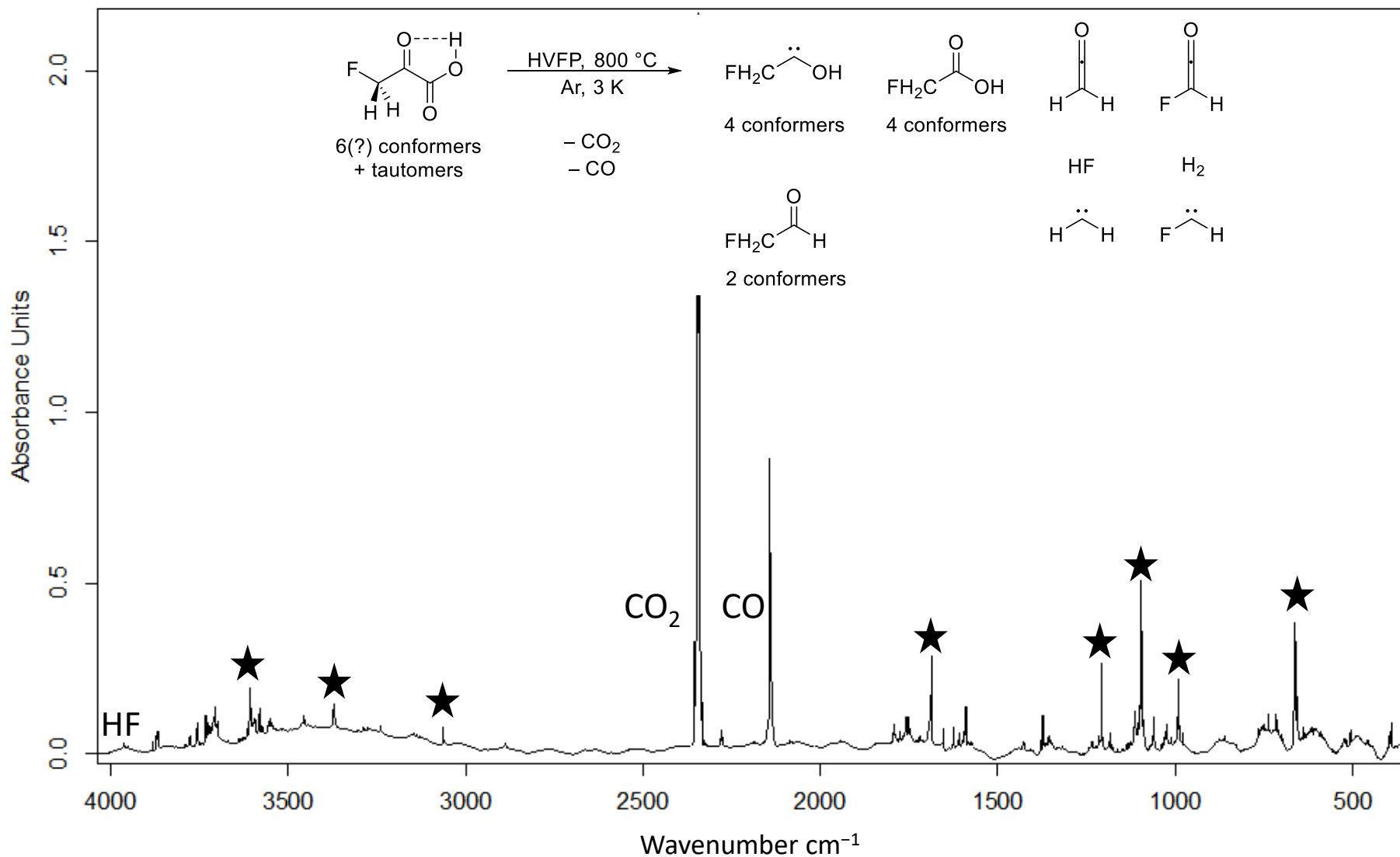


Fluoropyruvic Acid

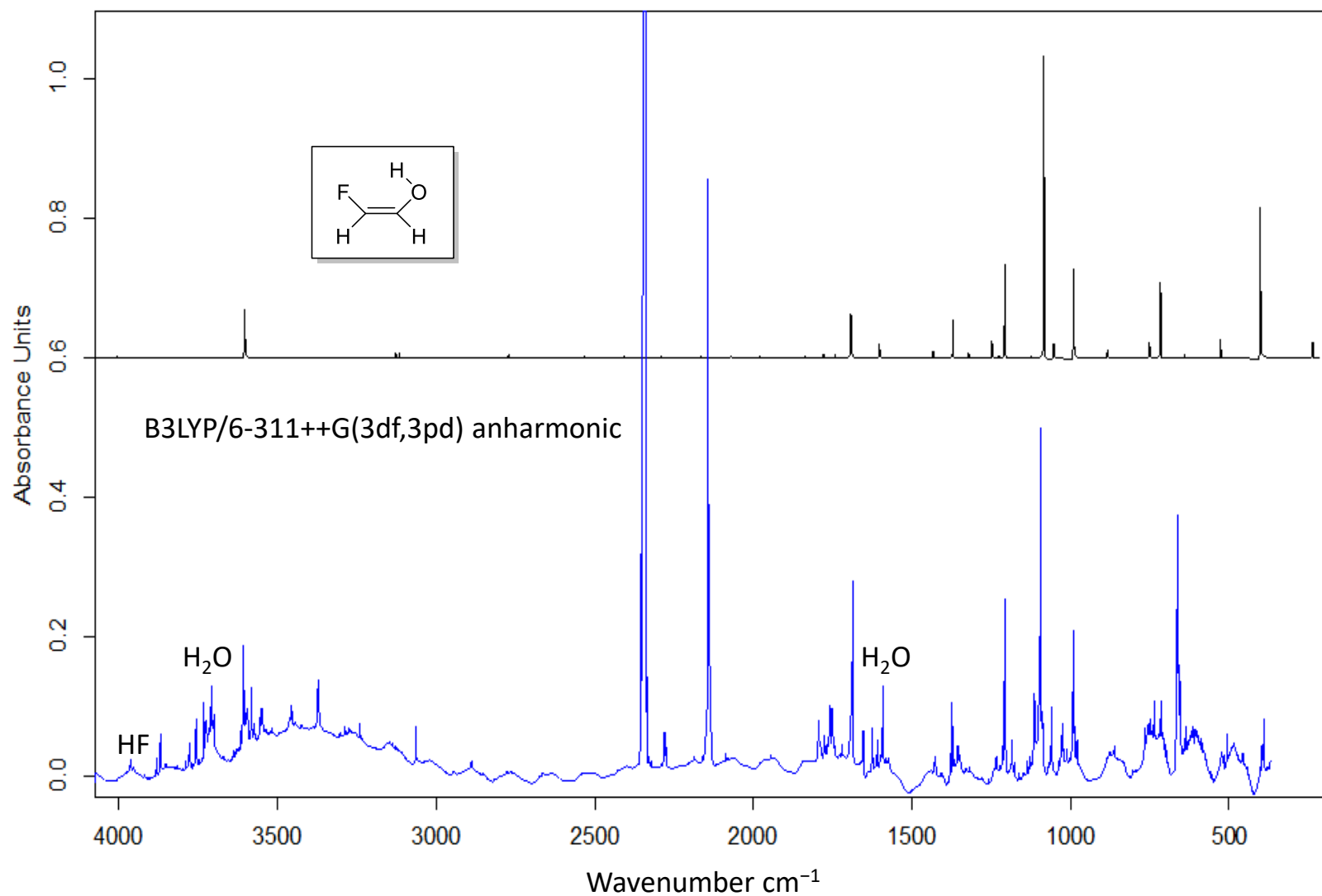




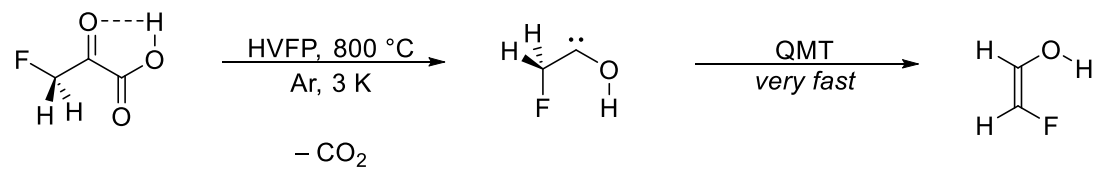
Pyrolysis of Fluoropyruvic Acid

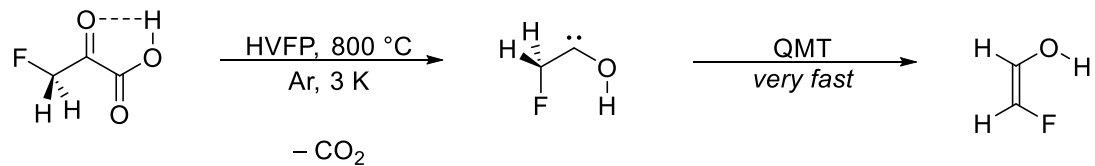


2-Fluorovinyl Alcohol



2-Fluorovinyl Alcohol

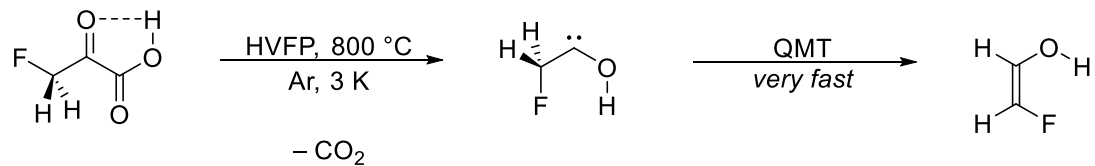




Polyrate

B3LYP/6-311++G(3df,3pd): 32.6 h

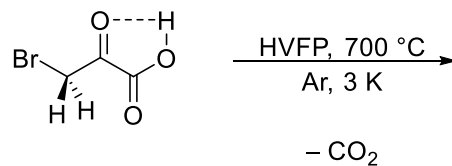
M06-2X/6-311++G(3df,3pd): 32.1 h



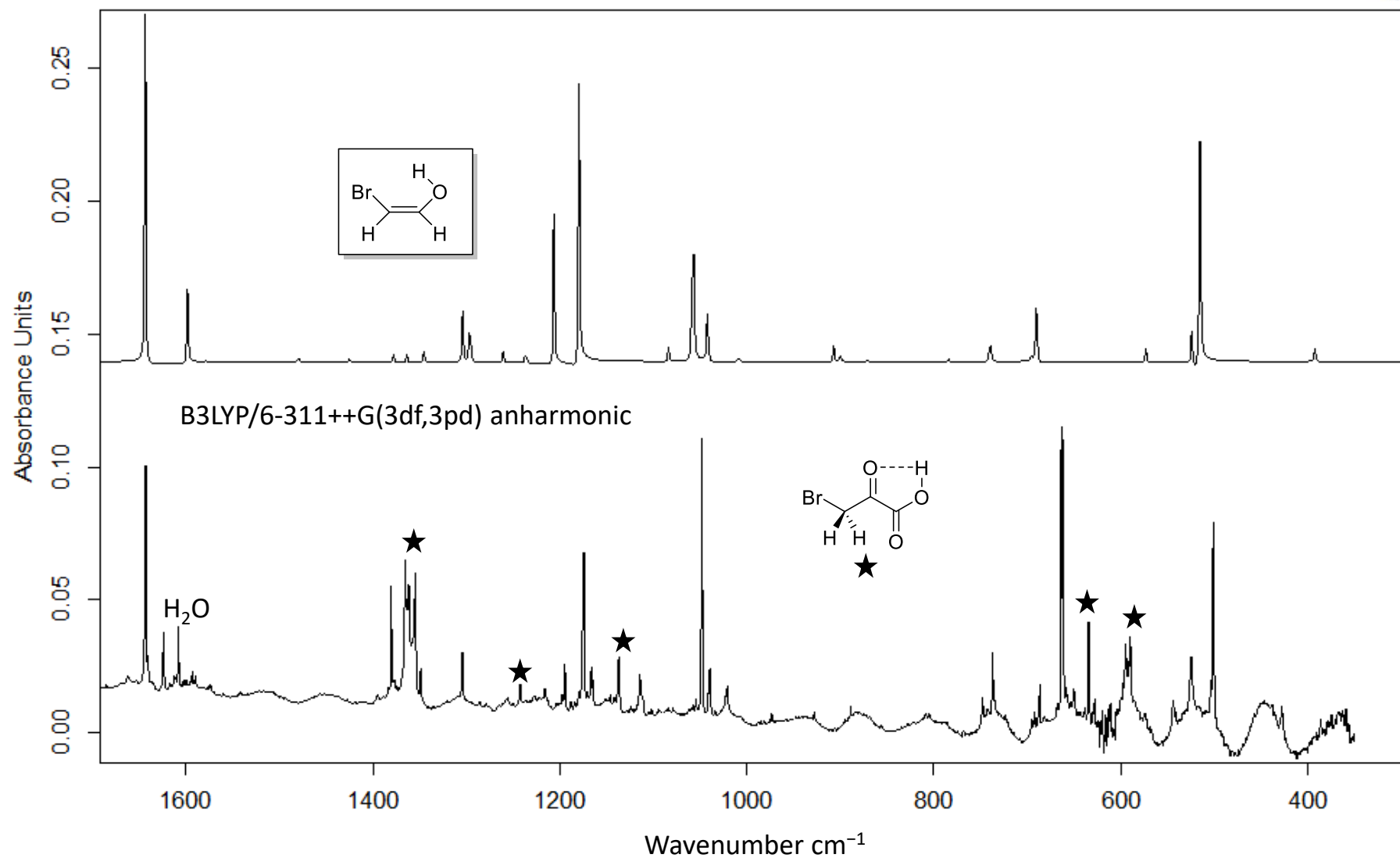
Polyrate

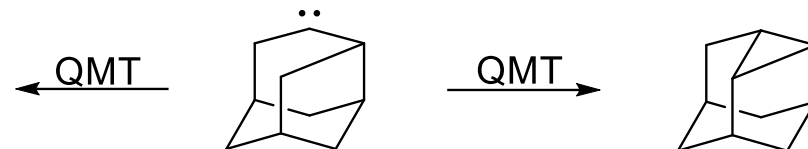
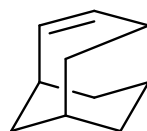
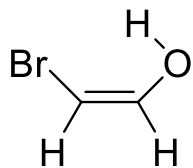
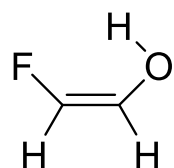
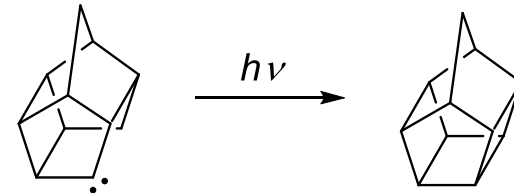
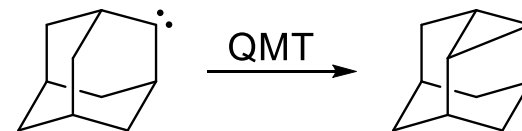
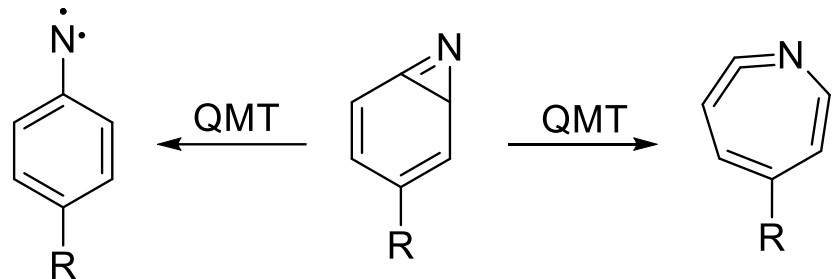
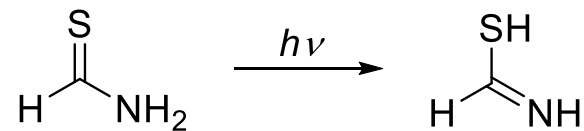
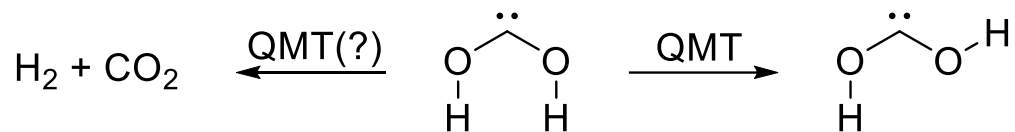
B3LYP/6-311++G(3df,3pd): 32.6 h

M06-2X/6-311++G(3df,3pd): 32.1 h



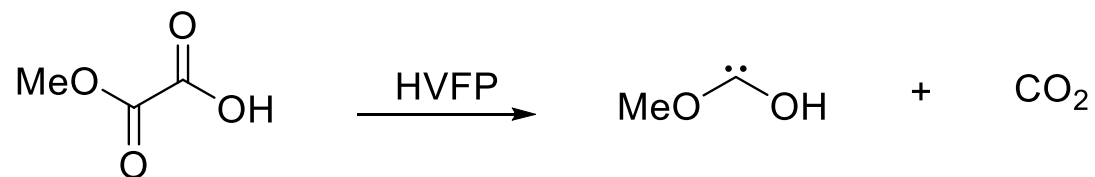
2-Bromovinyl Alcohol



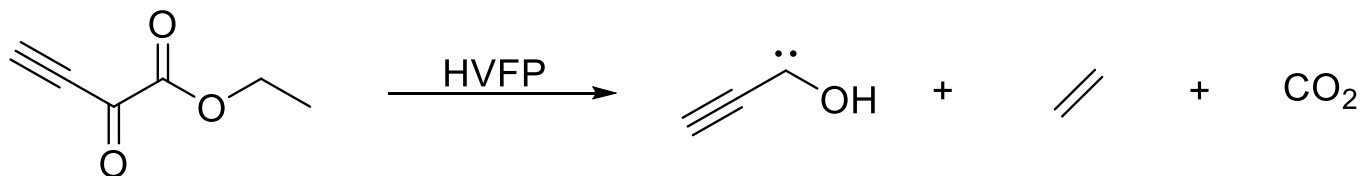




- Methoxyhydroxycarbene:



- Hydroxyethynylcarbene:





- Prof. Dr. Peter R. Schreiner
- Markus Schauermann, Henrik Quanz, Dr. Artur Mardyukov, Dr. Dennis Gerbig, Felix Keul, Dr. André K. Eckhardt
- Friedemann Dreßler, Frederik R. Erb, Gina M. Würl
- Dr. Cláudio M. Nunes
- Dr. Marina Šekutor, Dr. Marija Alešković, Dr. Nicola Basarić
- Prof. Dr. Wesley D. Allen, Dr. Marcus A. Bartlett
- Marcel Ruth
- B201
- PRS Group

