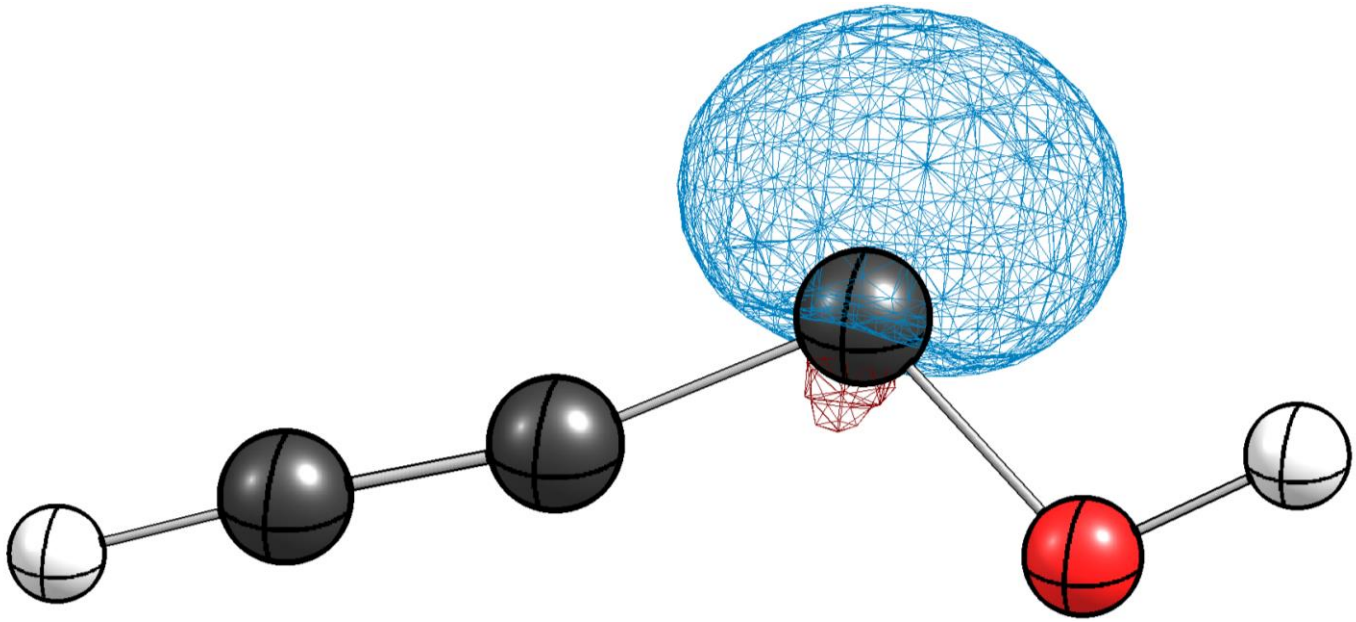
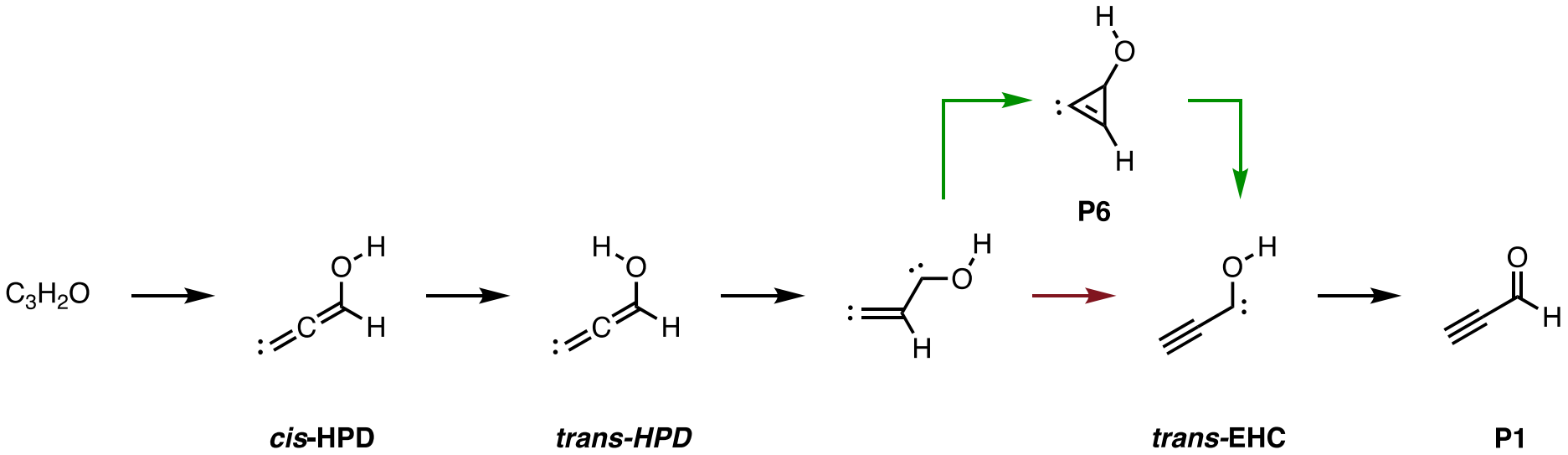
Generation, Characterization, and Computations of Elusive Ethynylhydroxycarbene



11.27.2020

Marcel Ruth

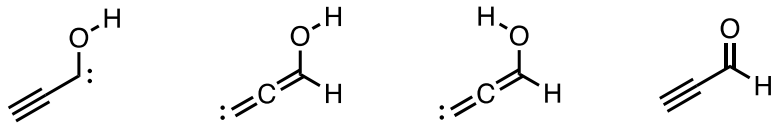
Institute of Organic Chemistry
Justus Liebig University
35392 Giessen, Germany



B. J. Ortman, R. H. Hauge, J. L. Margrave, Z. H. Kafafi, *J. Phys. Chem.* **1990**, 94, 7973-7977;R. Liu, X. Zhou, P. Pulay, *J. Phys. Chem*. **1992**, 96, 5748-5752;J. Szczepanski, S. Ekern, M. Vala, *J. Phys. Chem*. **1995**, 99, 8002-8012

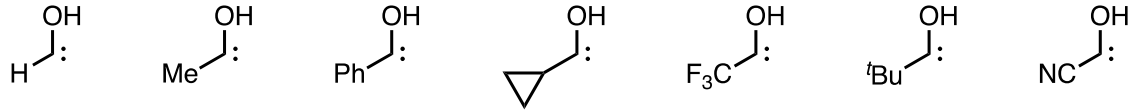


- Hauge, Kafafi, Margrave, and Ortman stated to have made ethynylhydroxycarbene (**EHC**)
- Theorist computed the PES of C_3H_2O and showed that hydroxypropadienylidene **(HPD)** was made instead
- Can we generated and characterized **EHC**?
- Does ***trans*-EHC** undergo quantum mechanical tunneling (**QMT**) to propynal **(P1)?**



trans*-EHC** ***cis*-HPD** ***trans-HPD **P1**

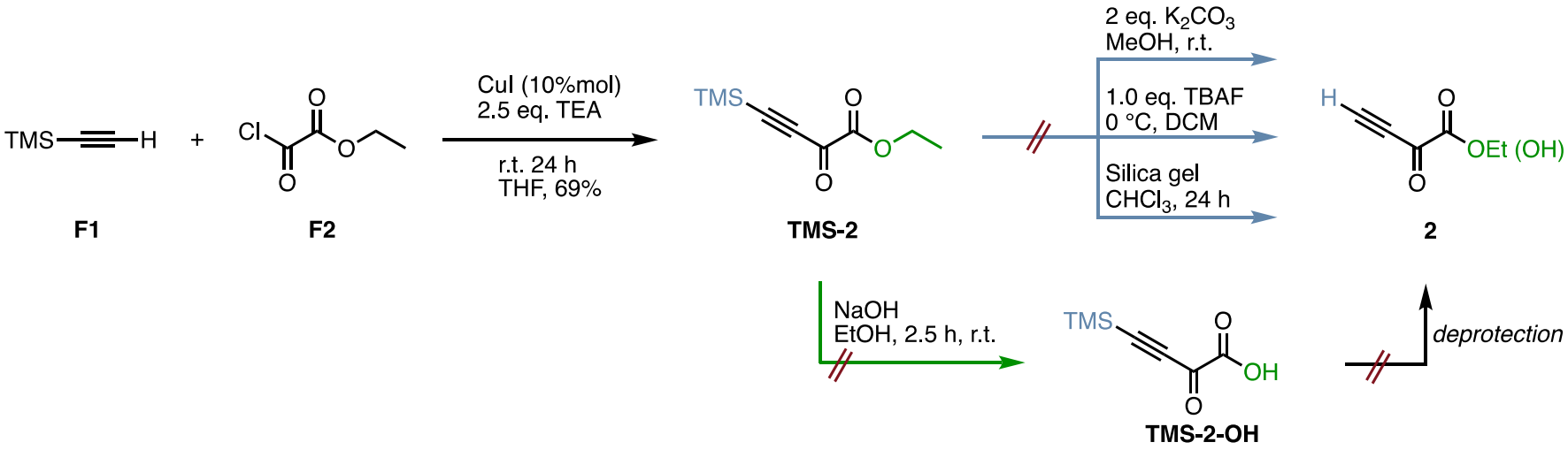
- Elongate the list of hydroxycarbenes



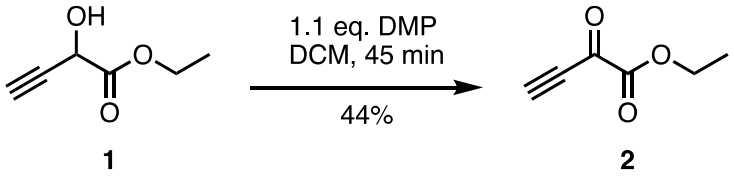
B. J. Ortman, R. H. Hauge, J. L. Margrave, Z. H. Kafafi, *J. Phys. Chem.* **1990**, 94, 7973-7977;R. Liu, X. Zhou, P. Pulay, *J. Phys. Chem*. **1992**, 96, 5748-5752;J. Szczepanski, S. Ekern, M. Vala, *J. Phys. Chem*. **1995**, 99, 8002-8012; A. Mardyukov, H. Quanz, P. R. Schreiner, *Nat. Chem.* **2017**, 9, 71-76;D. Ley, D. Gerbig, P. R. Schreiner, *Chem. Sci.* **2013**, 4, 677-684;P. R. Schreiner, H. P. Reisenauer, D. Ley, D. Gerbig, C.-H. Wu, W. D. Allen, *Science* **2011**, 332, 1300-1303;D. Ley, D. Gerbig, J. P. Wagner, H. P. Reisenauer, P. R. Schreiner, *J. Am. Chem. Soc.* **2011**, 133, 13614-13621;D. Gerbig, H. P. Reisenauer, C.-H. Wu, D. Ley, W. D. Allen, P. R. Schreiner, *J. Am. Chem. Soc.* **2010**, 132, 7273-7275;P. R. Schreiner, H. P. Reisenauer, F. C. t. Pickard, A. C. Simmonett, W. D. Allen, E. Mátyus, A. G. Császár, *Nature* **2008**, 453, 906-909. A. K. Eckhardt, F. R. Erb, P. R. Schreiner, *Chem. Sci.* **2019**, 10, 802-808.

Synthesis of the precursor ethyl ethynylglyoxylate **2** for high vacuum flash pyrolysis (HVFP)

Method A



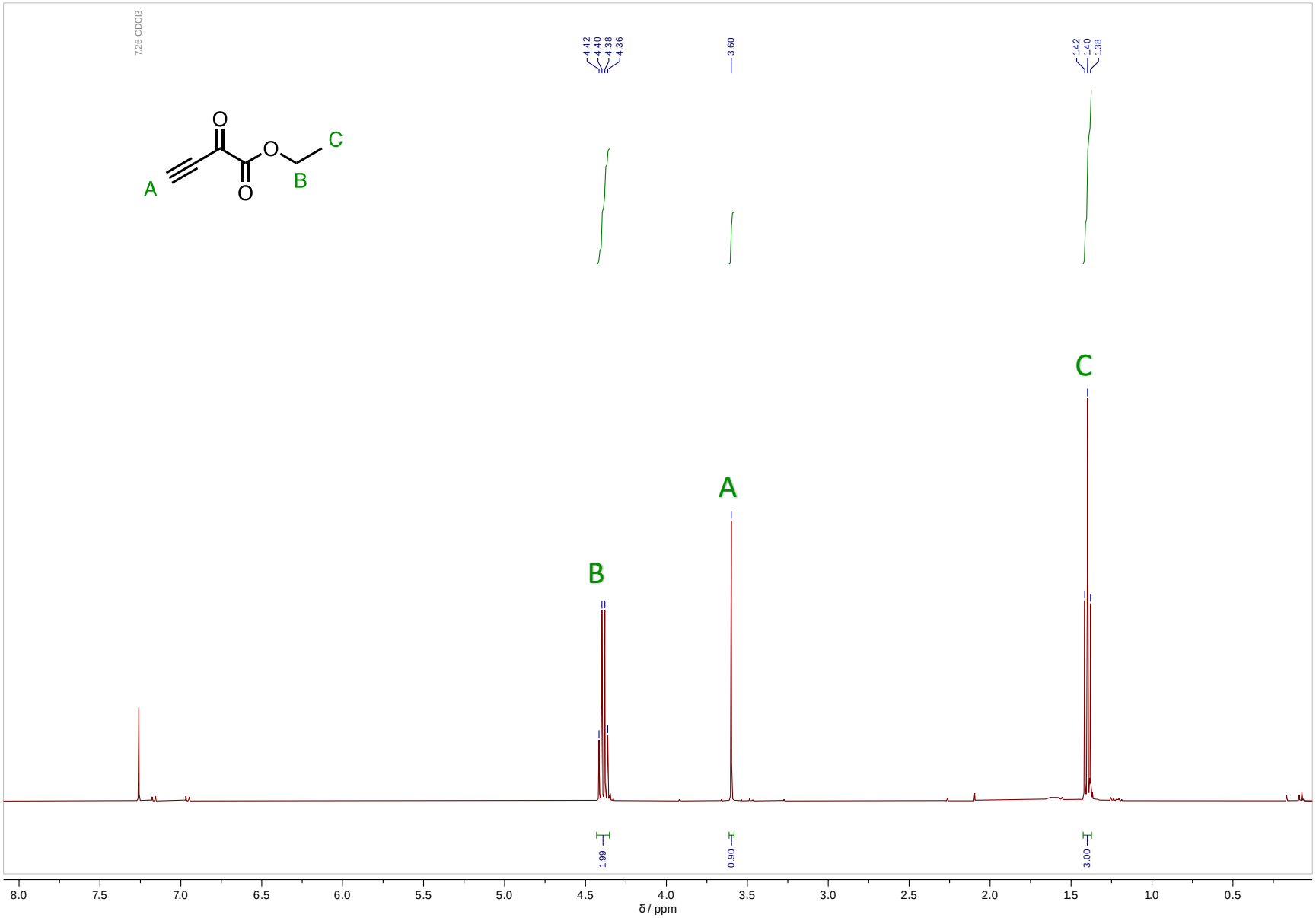
Method B



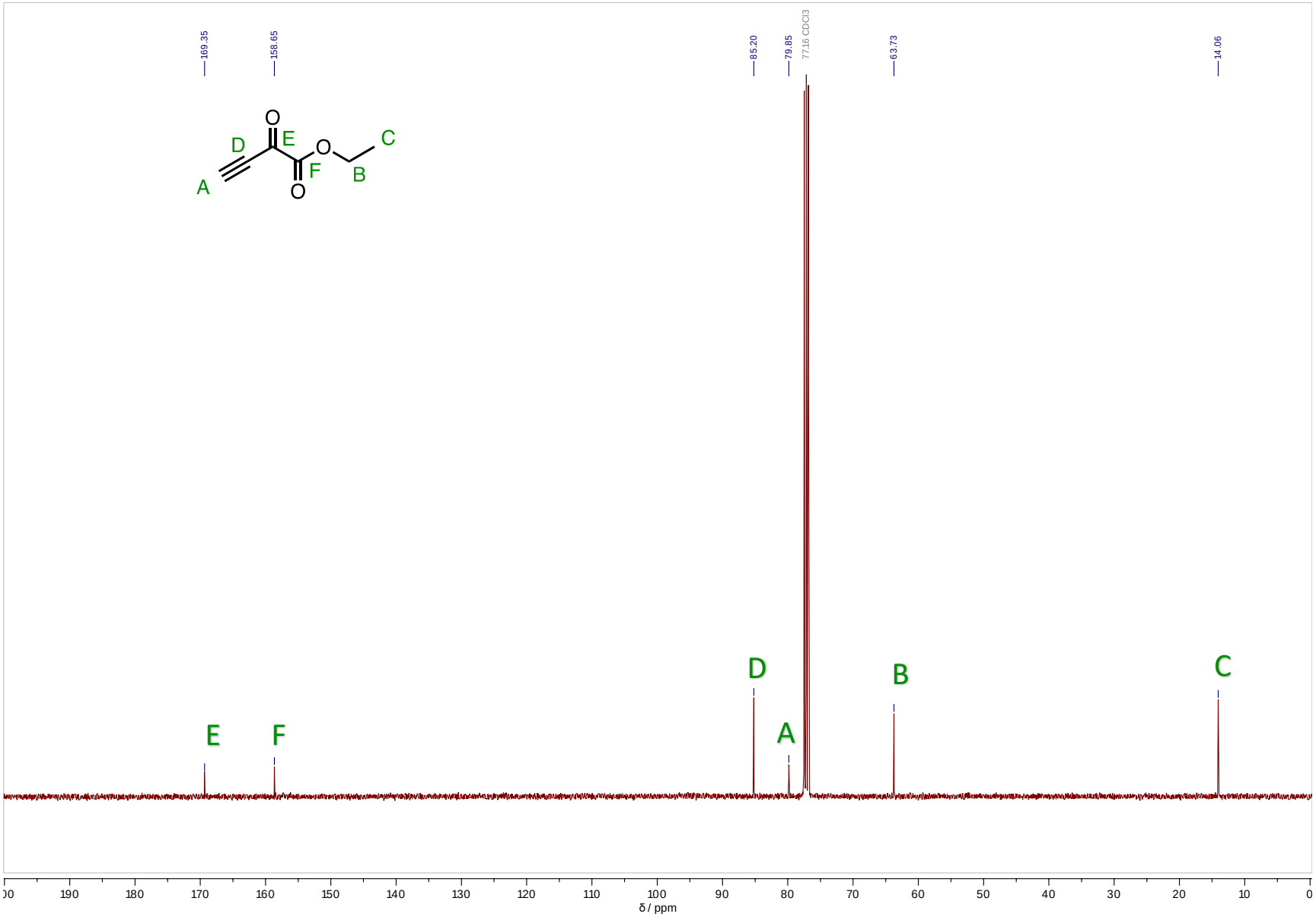
MS (M + MeOH + Na^+): 181.046 u

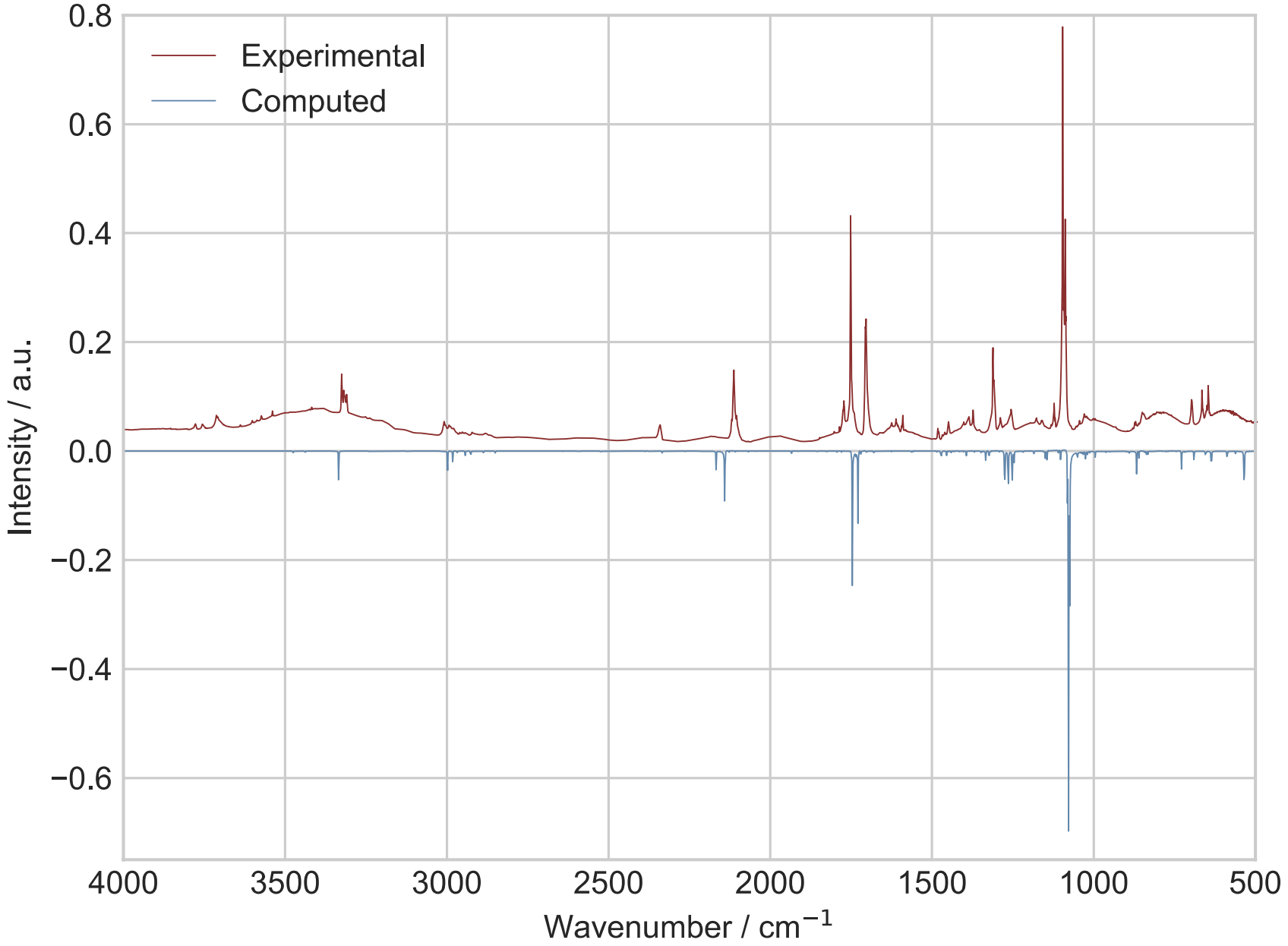
Exact mass (M + MeOH + Na^+): 181.0471 u

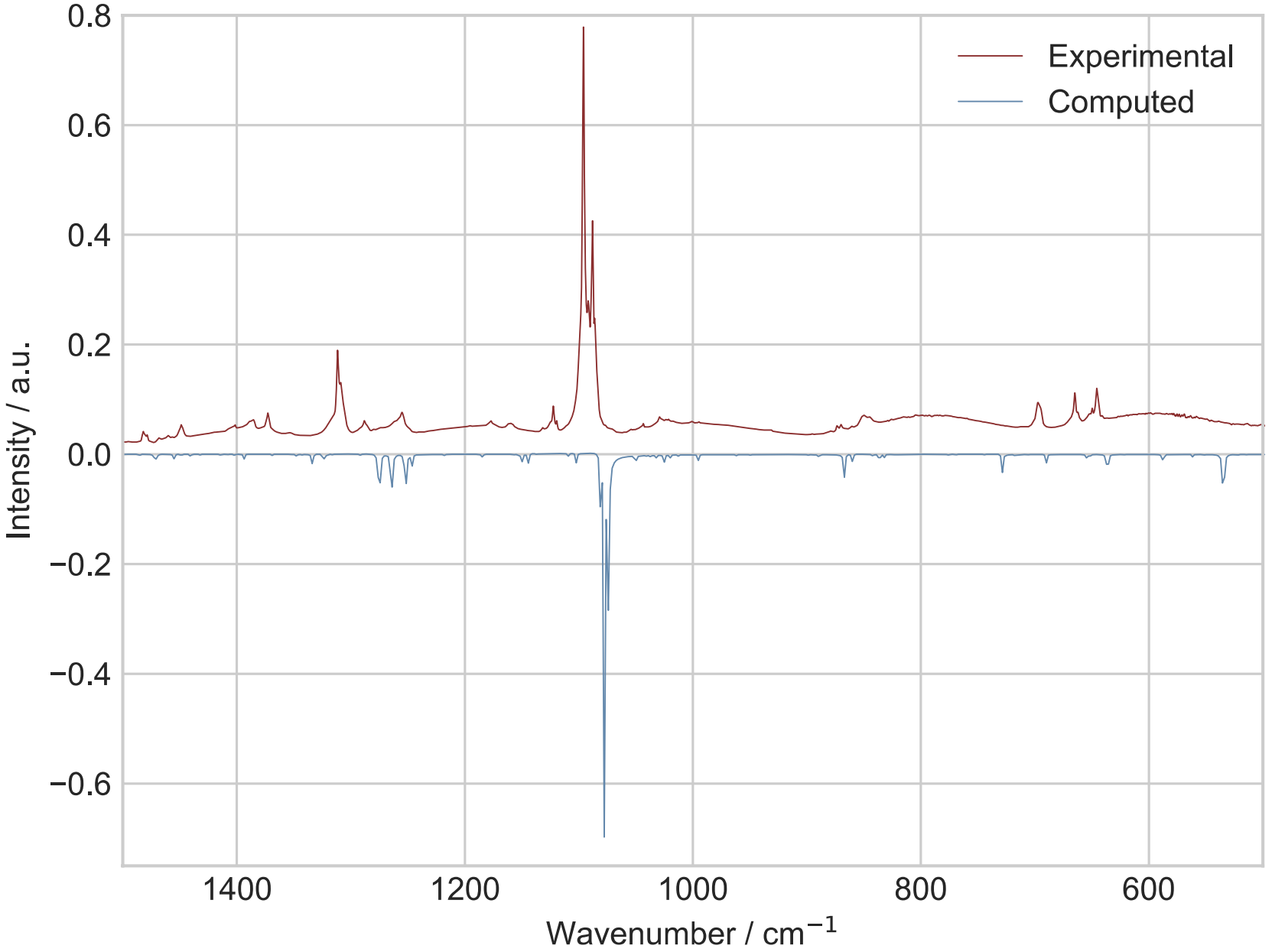
^{1}H-NMR spectrum of ethyl ethynylglyoxylate **2**

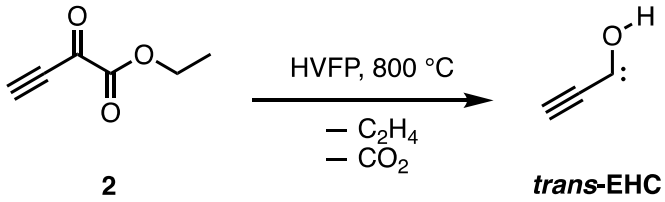


^{13}C-NMR spectrum of ethyl ethynylglyoxylate **2**



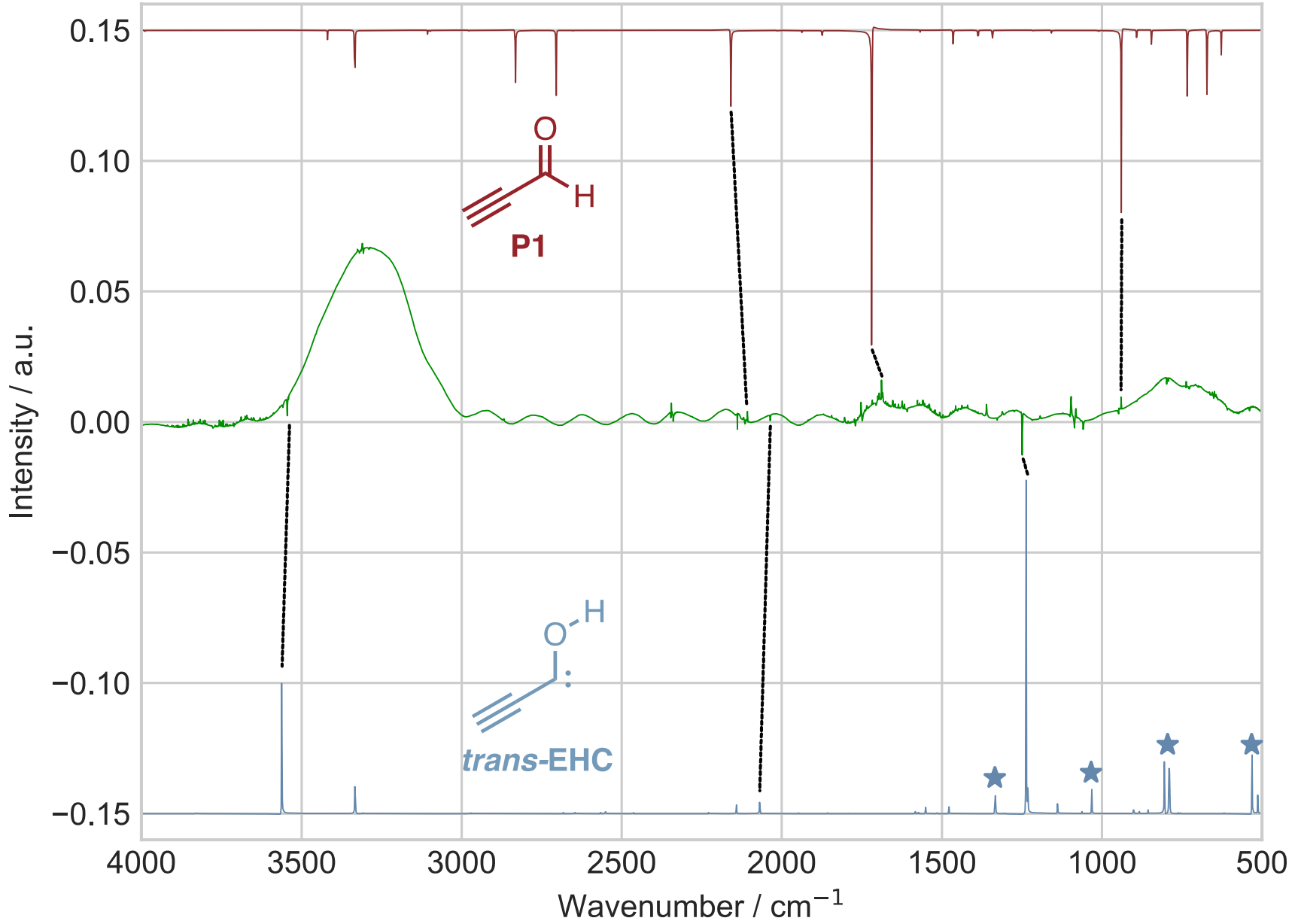

Experimental
Computed
0.8
0.6
0.4
0.2
0.0
−0.2
−0.4
−0.6
Intensity / a.u.
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber / cm^{-1}

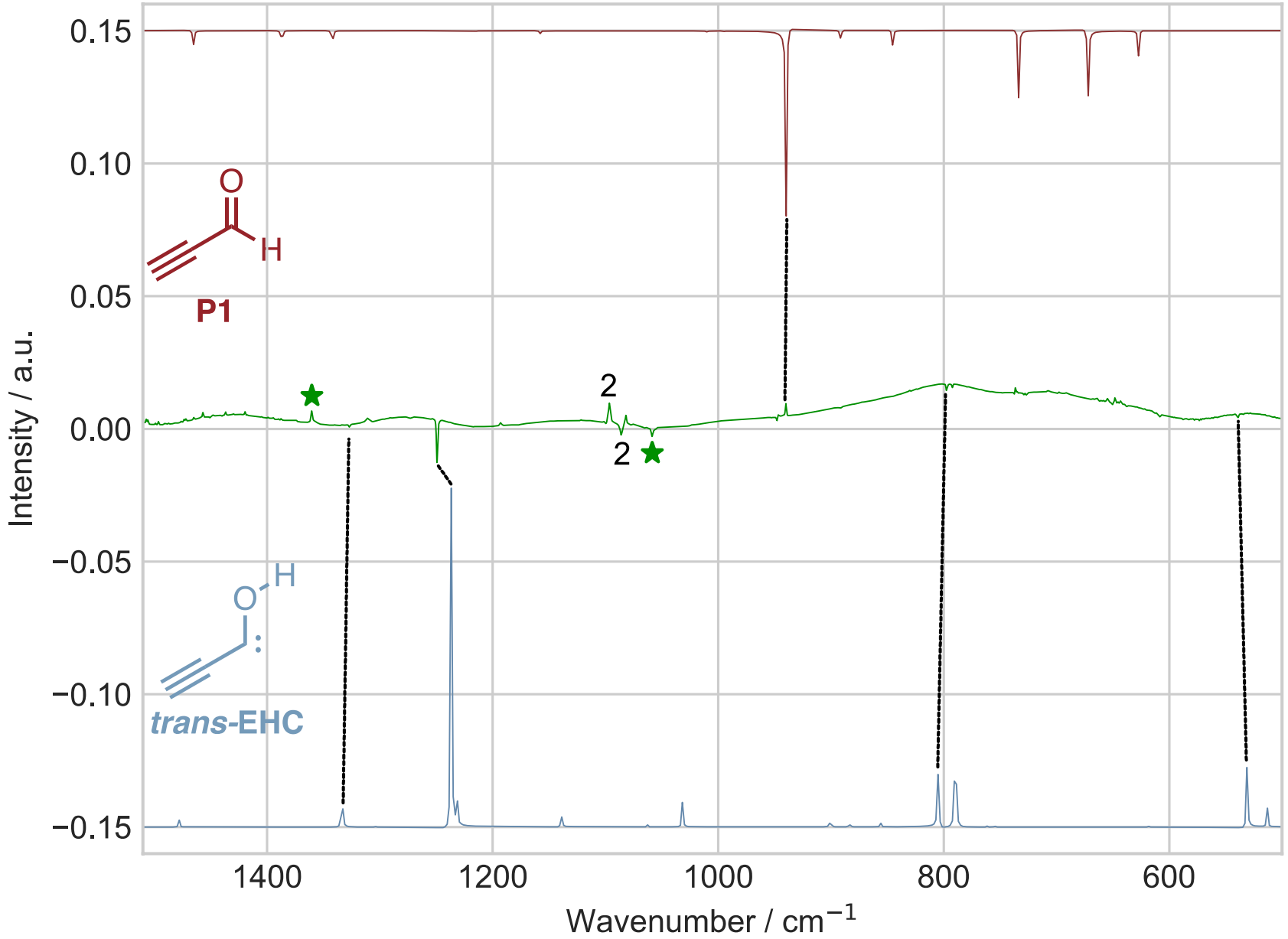

Experimental
Computed
Intensity / a.u.
0.8
0.6
0.4
0.2
0.0
−0.2
−0.4
−0.6
1400
1200
1000
800
600
Wavenumber / cm^{-1}



- Several temperatures were tested → best results were obtained at 800 ° C
- Deposition was carried out at 15 K
- Spectra were measured at 3 K
- Generated from an ester precursor and not the typical acid precursor (like cyanohydroxycarbene)

A. K. Eckhardt, F. R. Erb, P. R. Schreiner, *Chem. Sci.* **2019**, 10, 802-808.

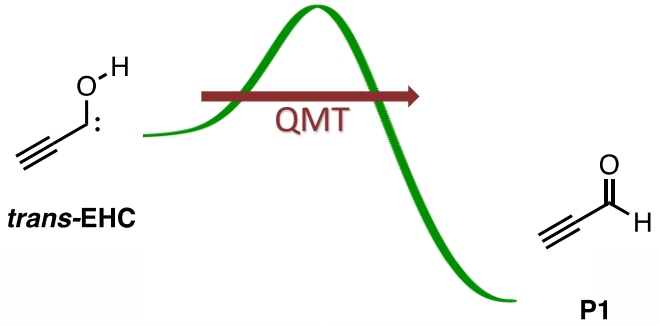

0.15
0.10
0.05
0.00
−0.05
−0.10
−0.15
Intensity / a.u.
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber / cm−1
O
H
P1
O
H
trans-EHC


0.15
0.10
0.05
0.00
−0.05
−0.10
−0.15
Intensity / a.u.
1400
1200
1000
800
600
Wavenumber / cm^{-1}
O
H
P1
2
2
O
H
trans-EHC

Assignment of the computed (B3LYP/Def2-QZVPP) and experimental data

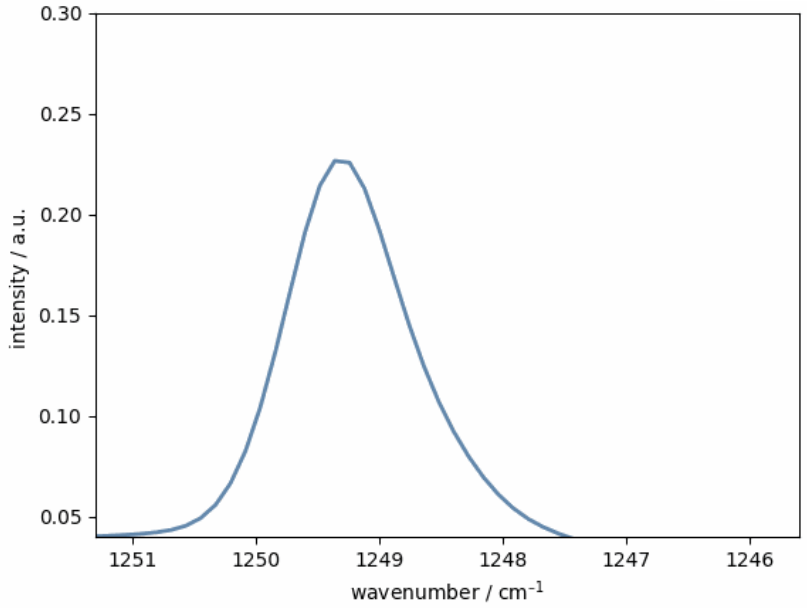
symmetry	mode	$\nu_{exp.}$ / cm^{-1}	$\nu_{comp.}$ / cm^{-1}	IR intensity / km mol^{-1}	approximate description
a'	ν_1	--------	239.5	12.8	δ (CCC)
a"	ν_2	--------	267.0	10.6	π (CCC)
a'	ν_3	539.0	514.8	17.2	δ (CH)
a'	ν_4	--------	619.5	0.8	δ (CCO)
a"	ν_5	797.7	763.8	1.3	δ (CH)
a"	ν_6	--------	806.3	62.3	δ (OH)
a'	ν_7	--------	902.0	7.8	ν_s (CCC)
a'	ν_8	1249.7	1238.4	321.2	ν (CO)
a'	ν_9	1327.2	1335.2	38.8	δ (COH)
a'	ν_{10}	2036.2	2069.9	19.6	ν (C≡C)
a'	ν_{11}	--------	3333.6	57.1	ν (CH)
a'	ν_{12}	3545.0	3563.1	130.3	ν (OH)

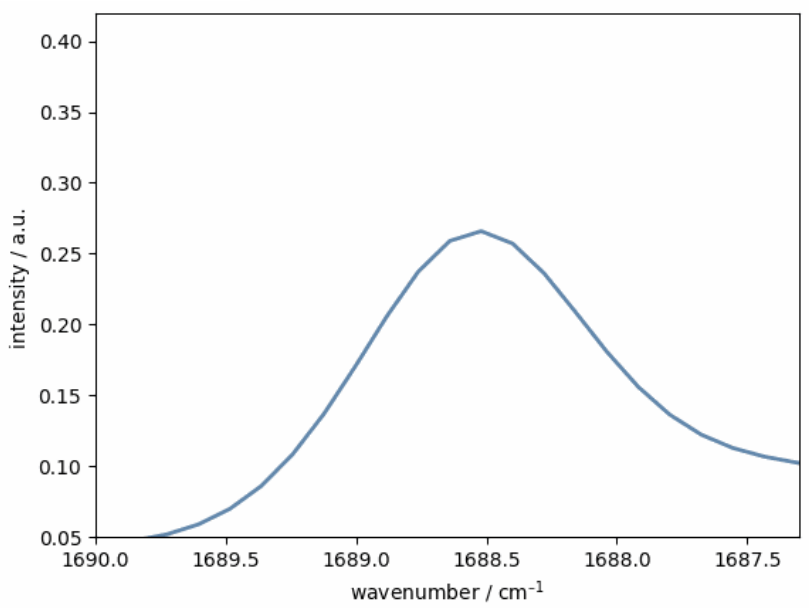
- Covered under a black blanket
- Time interval was 60 min
- Evaluated with python



trans-EHC

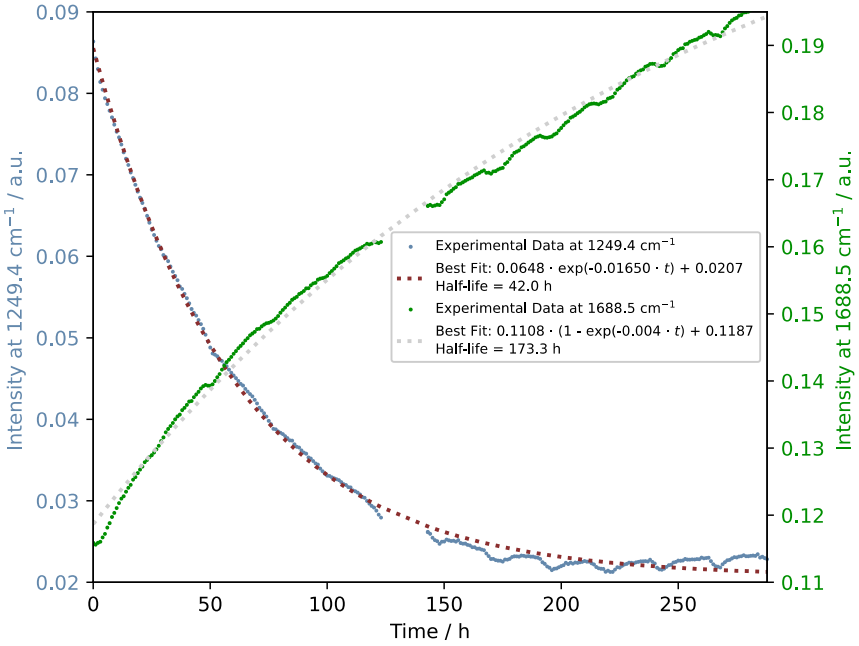
P1



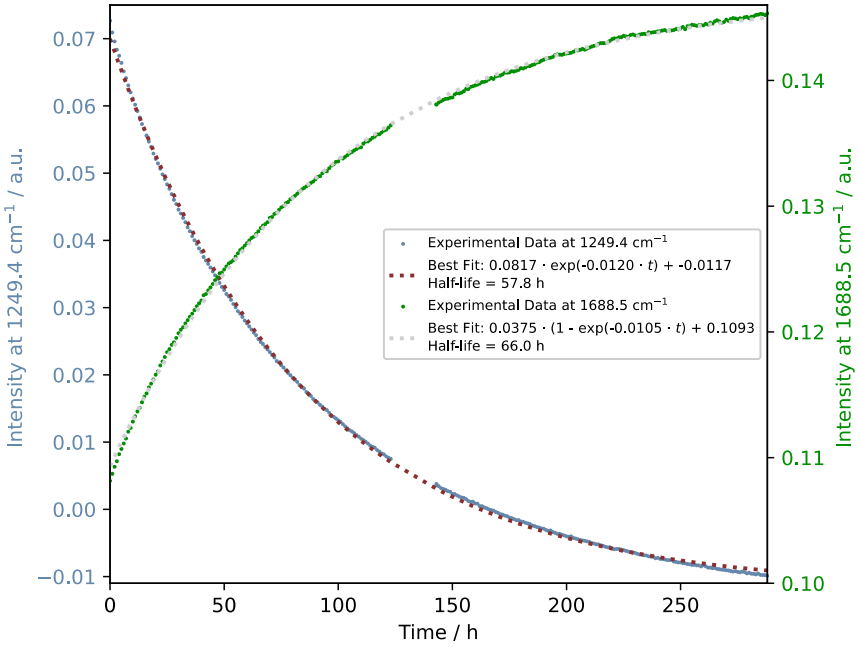


Evaluation of the kinetic measurements

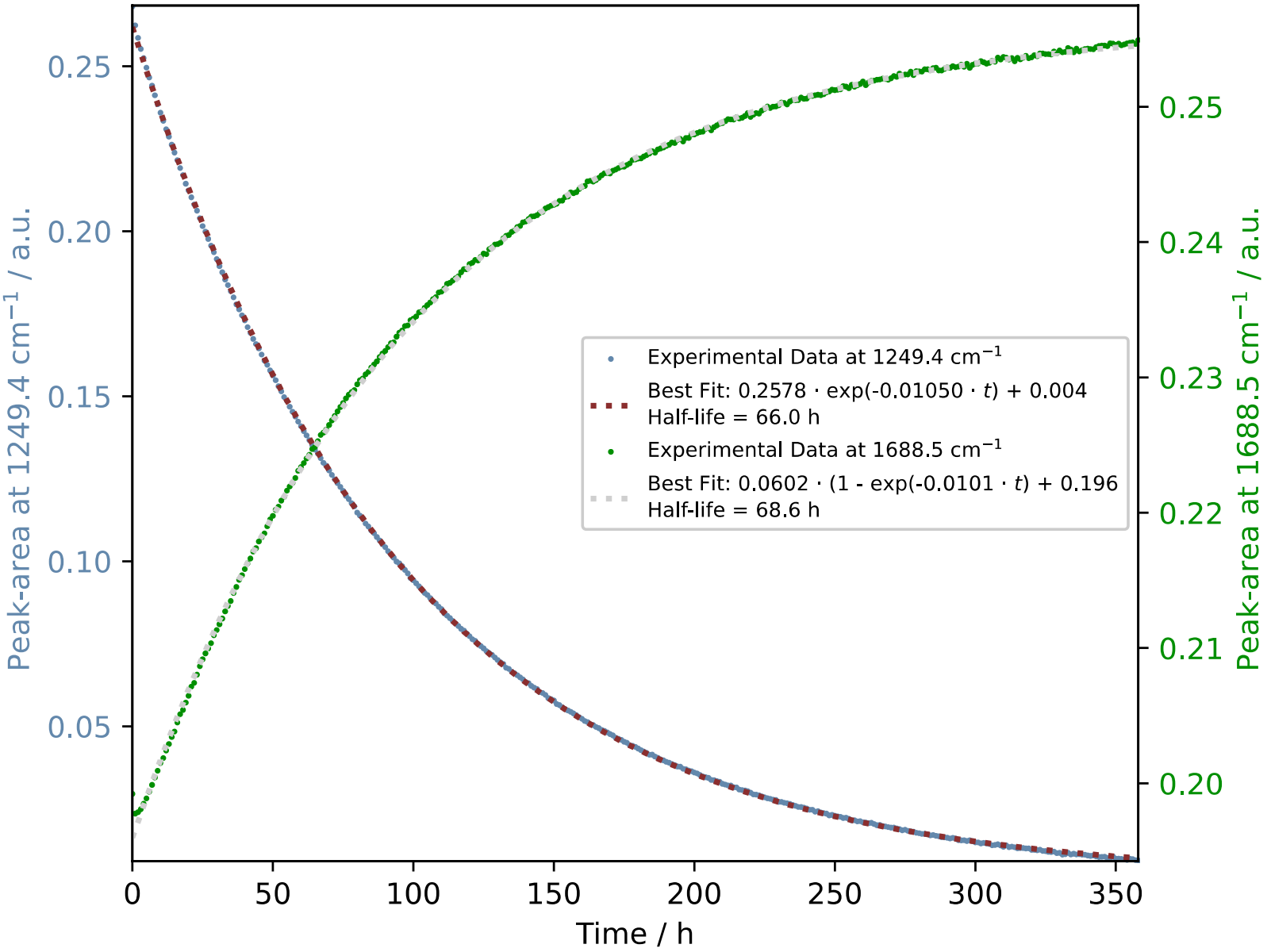
unnormalized



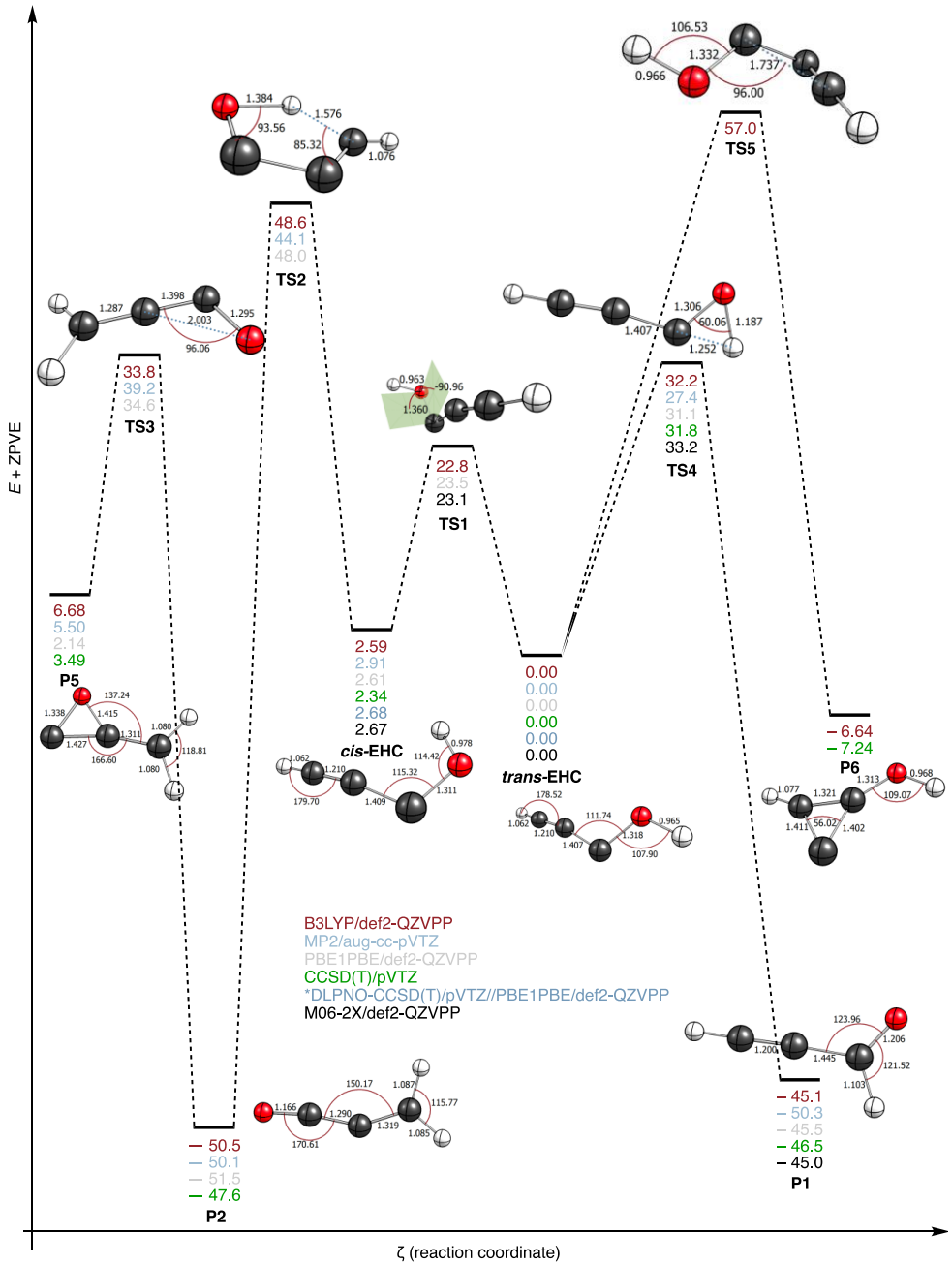
normalized

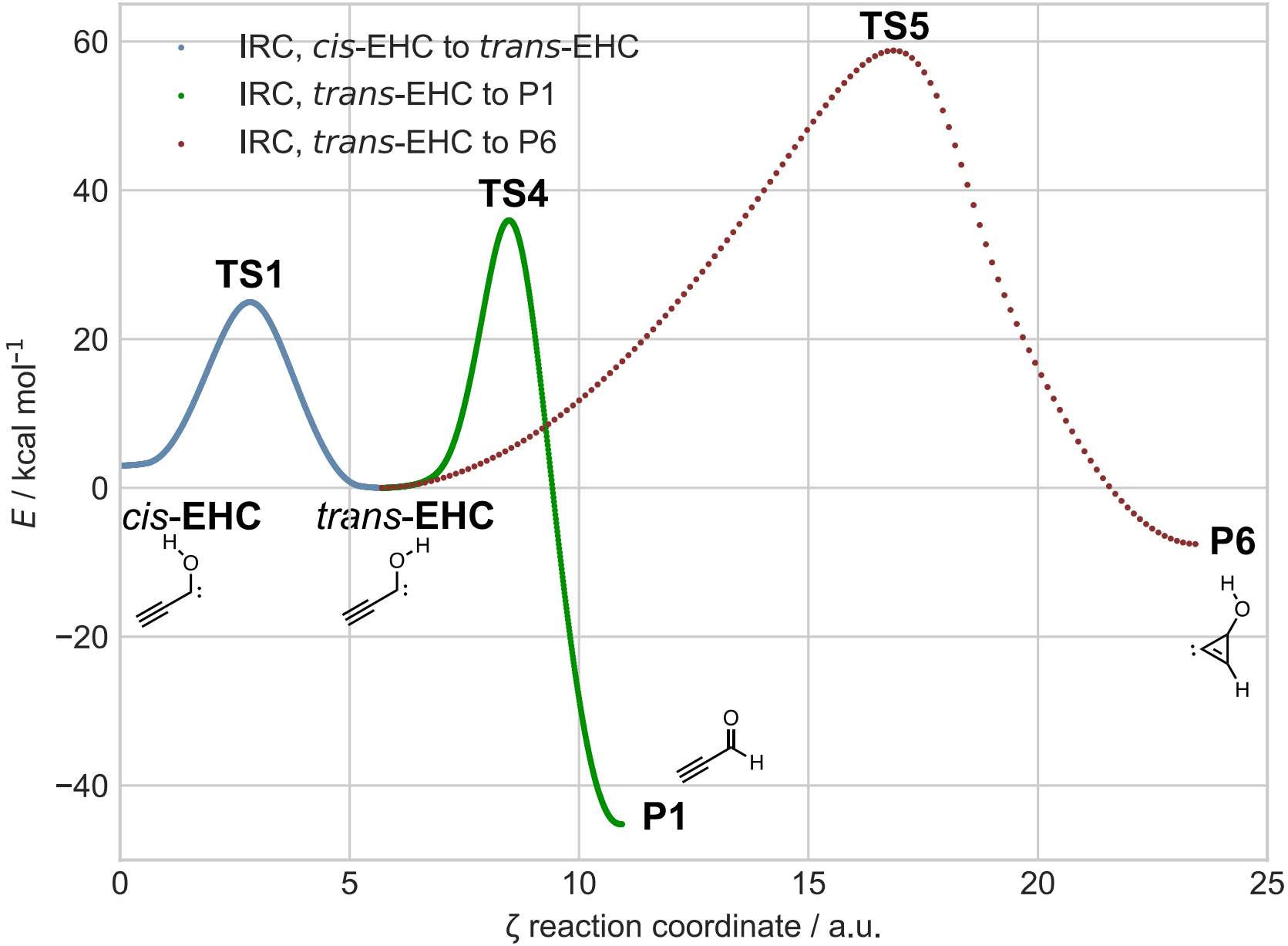


$$\tau = \frac{\ln(2)}{k}$$



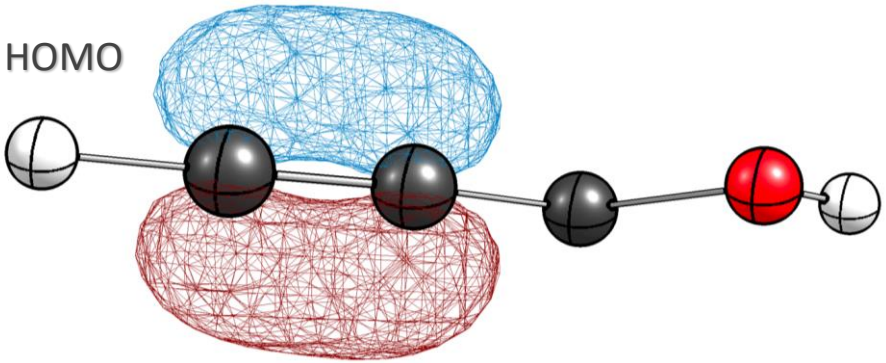
Selected section of the potential energy surface



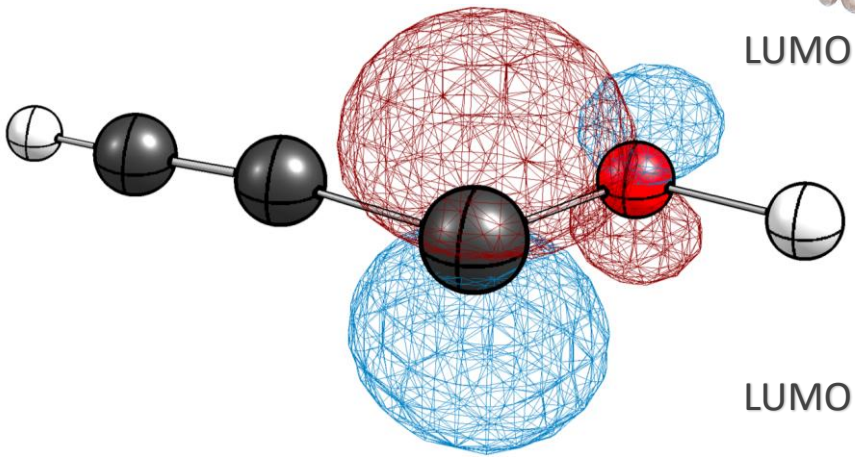

IRC, *cis*-EHC to *trans*-EHC
IRC, *trans*-EHC to P1
IRC, *trans*-EHC to P6
TS1
TS4
TS5
cis-EHC
trans-EHC
P1
P6
E / kcal mol^{-1}
ζ reaction coordinate / a.u.
60
40
20
0
−20
−40
0
5
10
15
20
25

NBO computations at the HF/6-311++G(2d,2p)//CCSD(T)/def2-QZVPP level of theory

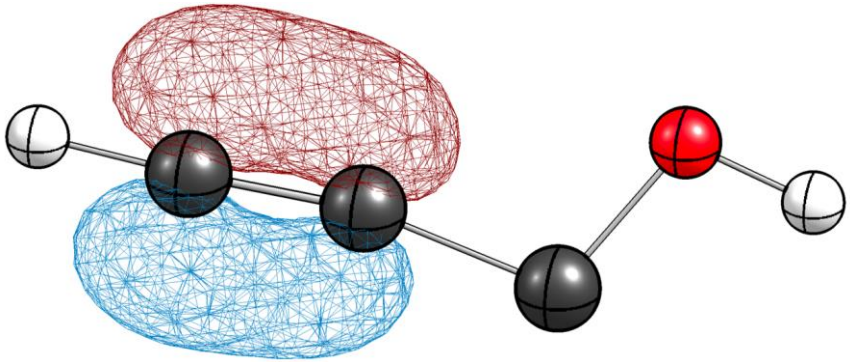
HOMO



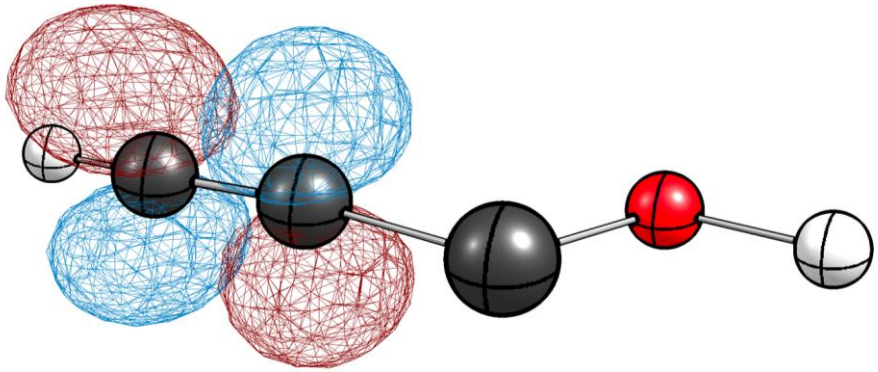
LUMO



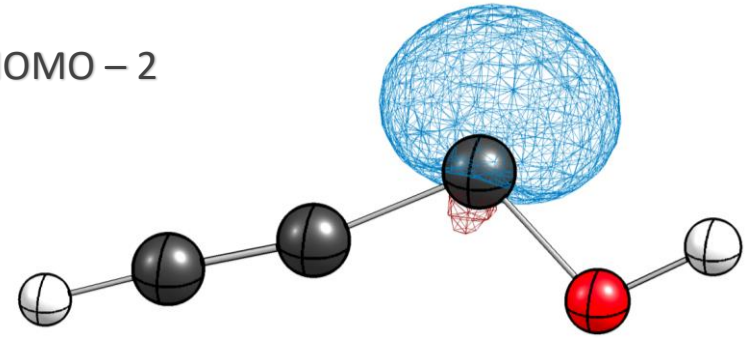
HOMO – 1



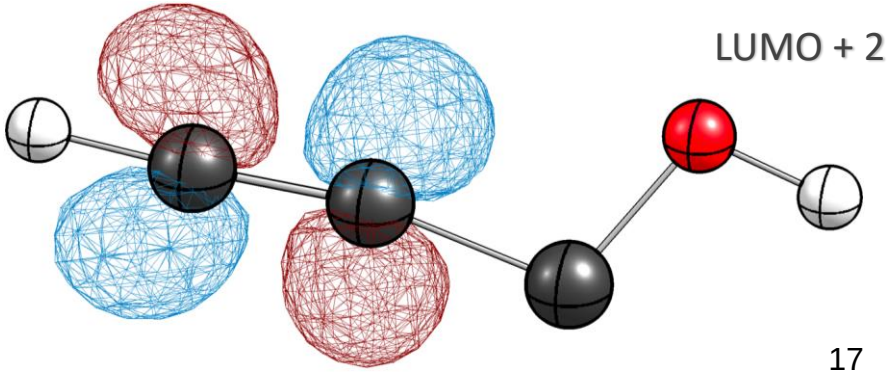
LUMO + 1



HOMO – 2

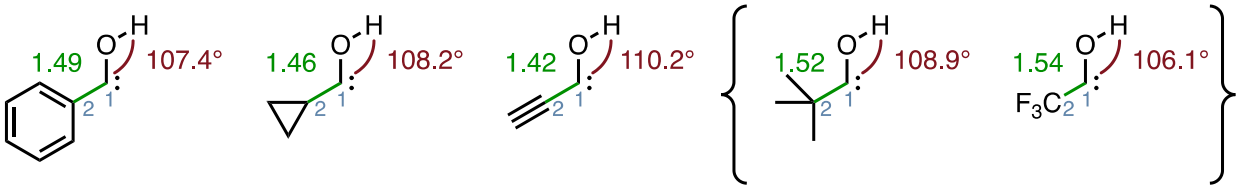


LUMO + 2



Attempt to explain the trend in half-lives

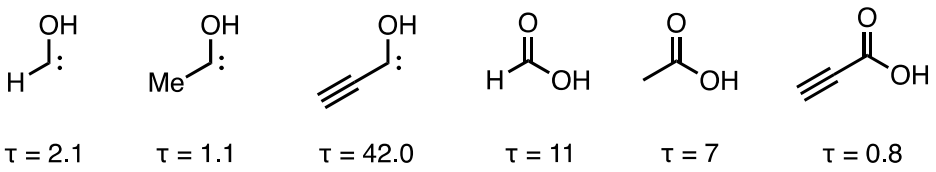
Hyperconjugation should increase C2-C1 bond length



A. Mardyukov, H. Quanz, P. R. Schreiner, *Nat. Chem.* **2017**, 9, 71-76;D. Ley, D. Gerbig, P. R. Schreiner, *Chem. Sci.* **2013**, 4, 677-684;D. Ley, D. Gerbig, J. P. Wagner, H. P. Reisenauer, P. R. Schreiner, *J. Am. Chem. Soc.* **2011**, 133, 13614-13621;D. Gerbig, H. P. Reisenauer, C.-H. Wu, D. Ley, W. D. Allen, P. R. Schreiner, *J. Am. Chem. Soc.* **2010**, 132, 7273-7275

Trend in hydroxycarbenes vs carboxylic acids

Trend in acids is different than in hydroxycarbenes



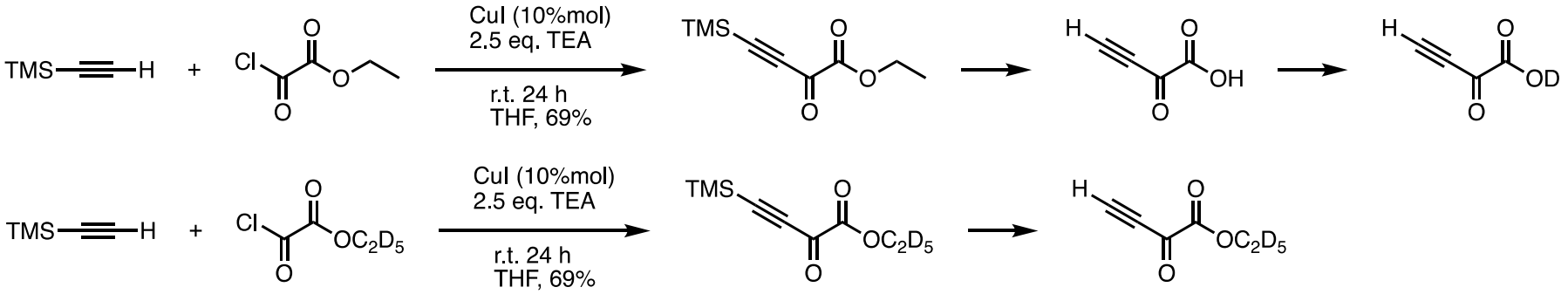
τ = 2.1 τ = 1.1 τ = 42.0 τ = 11 τ = 7 τ = 0.8

A. Mardyukov, H. Quanz, P. R. Schreiner, *Nat. Chem.* **2017**, 9, 71-76;D. Ley, D. Gerbig, P. R. Schreiner, *Chem. Sci.* **2013**, 4, 677-684;D. Ley, D. Gerbig, J. P. Wagner, H. P. Reisenauer, P. R. Schreiner, *J. Am. Chem. Soc*. **2011**, 133, 13614-13621;D. Gerbig, H. P. Reisenauer, C.-H. Wu, D. Ley, W. D. Allen, P. R. Schreiner, *J. Am. Chem. Soc.* **2010**, 132, 7273-7275



- Successful synthesized **2**
- Elusive **trans-EHC** was generated and isolated *via* HVFP
- QMT to propynal is apparent
- Photochemical reactions could be triggered
- Computations of possible products were presented

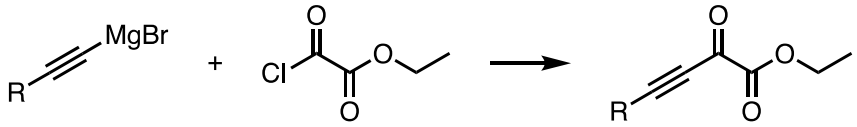
- Synthesis of the deuterated precursor



- Investigating the tunneling half-life at different temperatures to further support the prediction of QMT (done by M. Sc. Bastian Bernhardt)

- Measure with a cut-off filter to exclude the influence of the spectrometer (in progress)

- Attaching different substituents on the alkyne moiety



- Second-order perturbation energy analysis in NBO

Acknowledgment

Prof. Dr. Peter R. Schreiner

M. Sc. Bastian Bernhardt

Dr. Fumito Saito
Dr. Dennis Gerbig
M. Sc. Henrik Quanz
M. Sc. Felix Keul
M. Sc. Friedemann Dreßler
M. Sc. Jan M. Schümann

AG Schreiner



Picture: Katrina Friese

Thank you for your kind attention



Chemie-Neubau. Foto: HGEsch, Hennef. (https://www.uni-giessen.de/ueber-uns/pressestelle/pm/PM15616ChemieNeubau_Einweihungsfeier.jpg/@@images/image/large) [23.09.2019 22:47 Uhr]