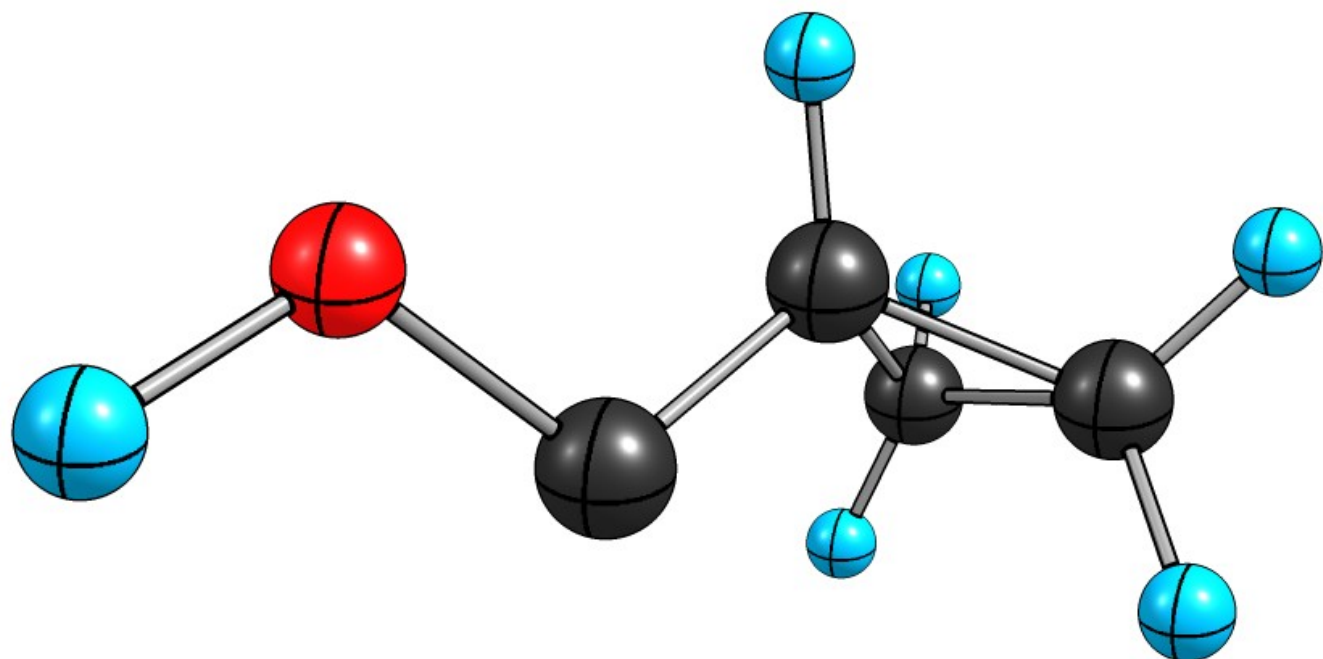
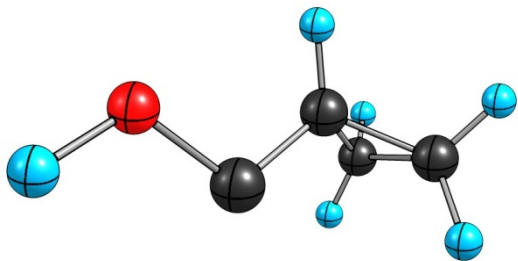


CYCLOPROPYLHYDROXYCARBENE



DAVID LEY

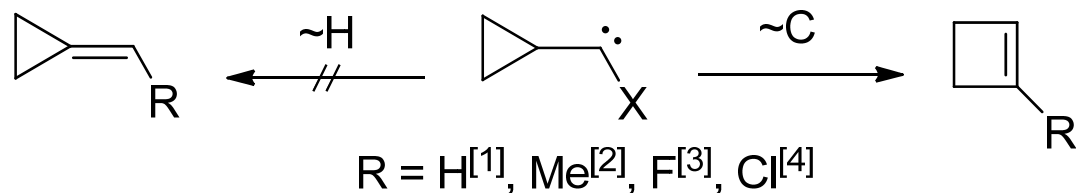
11.02.2011



MOTIVATION

- Hitherto unknown hydroxycarbene
- Purely hydrocarbon electron-donor
- Substituent with unique electronic properties
- Comparison to other cyclopropyl carbenes
- Easily accessible, volatile precursor

KNOWN CYCLOPROPYL CARBENES



- Cyclopropyl moiety promotes the C-shift reaction
- Carbenes always undergo ring expansion
- Halogen substituents increase the carbene's lifetime
- (**Cl**: factor 70, **F**: factor 291)

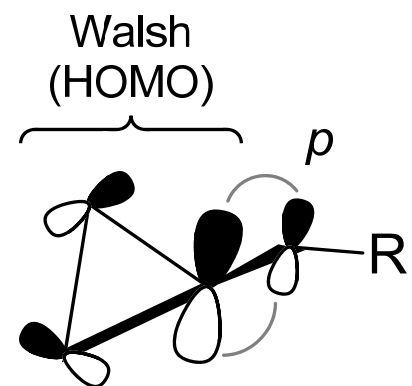
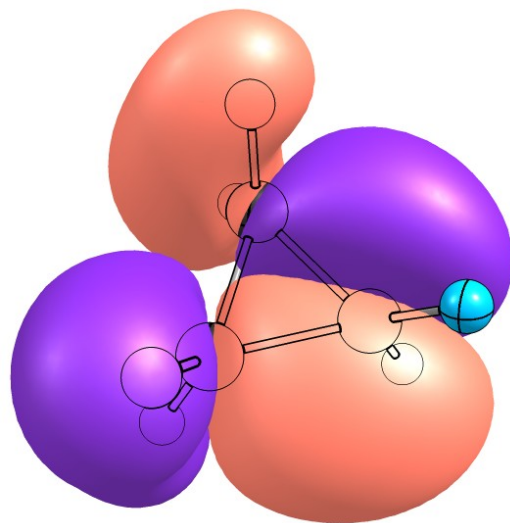
[1] Friedman, L.; Shechter, H. *J. Am. Chem. Soc.* **1960**, 82, 1002.

[2] Modarelli, D. A.; Platz, M. S.; *J. Am. Chem. Soc.* **1993**, 115, 10440–10441.

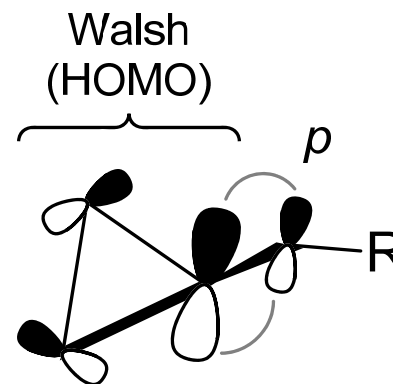
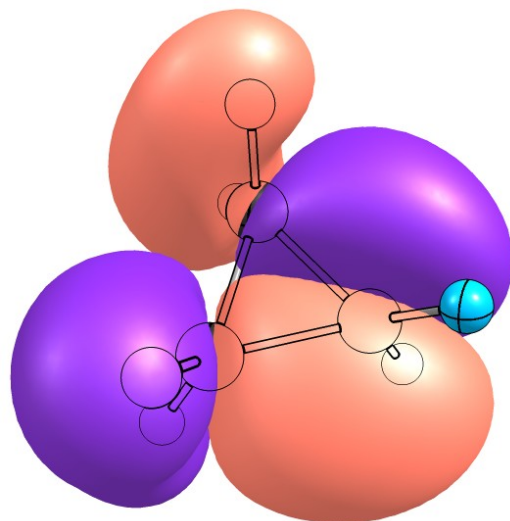
[3] Moss, R. A.; Ho, G. J.; Liu, W. *J. Am. Chem. Soc.* **1992**, 114, 959–963.

[4] Liu, M. T. H.; Bonneau, R. *J. Phys. Chem.* **1989**, 93, 7298–7300.

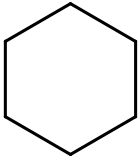
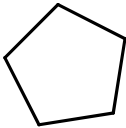
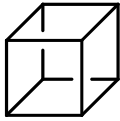
ELECTRONIC EFFECTS



ELECTRONIC EFFECTS

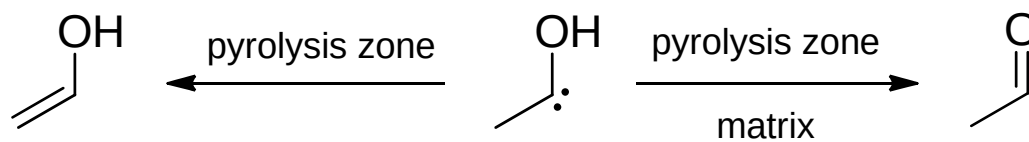


RING STRAIN

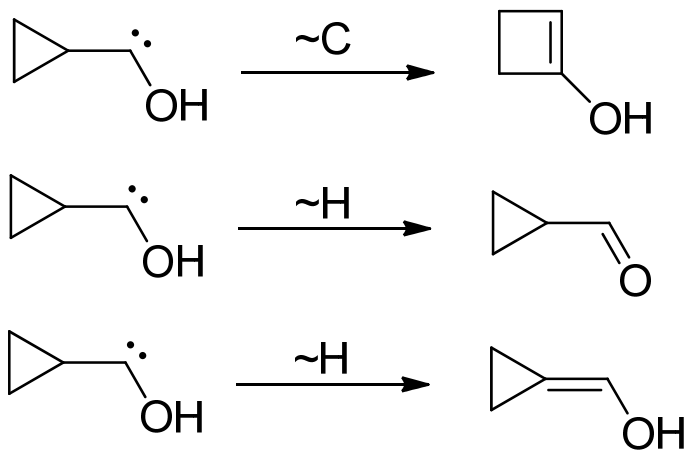
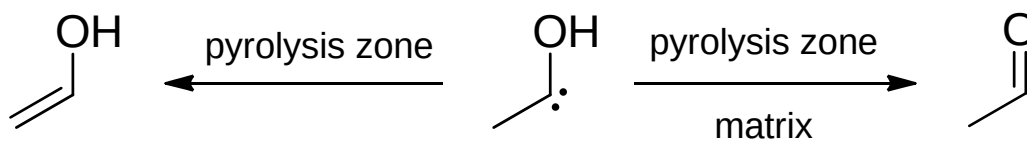
						
SE ^[1] [kcal / mol]	0	6.2	26.5	27.5	28.4	154.7

[1] Wiberg, K. B. Angew. Chemie. Intl. Ed. **1986**, 25, 312–322.

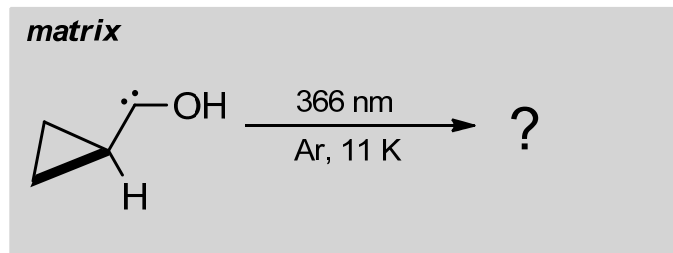
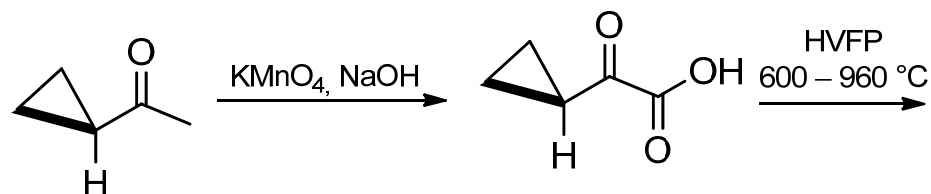
HOW DOES THE REACTIVITY TRANSLATE INTO A HYDROXYCARBENE?



HOW DOES THE REACTIVITY TRANSLATE INTO A HYDROXYCARBENE?



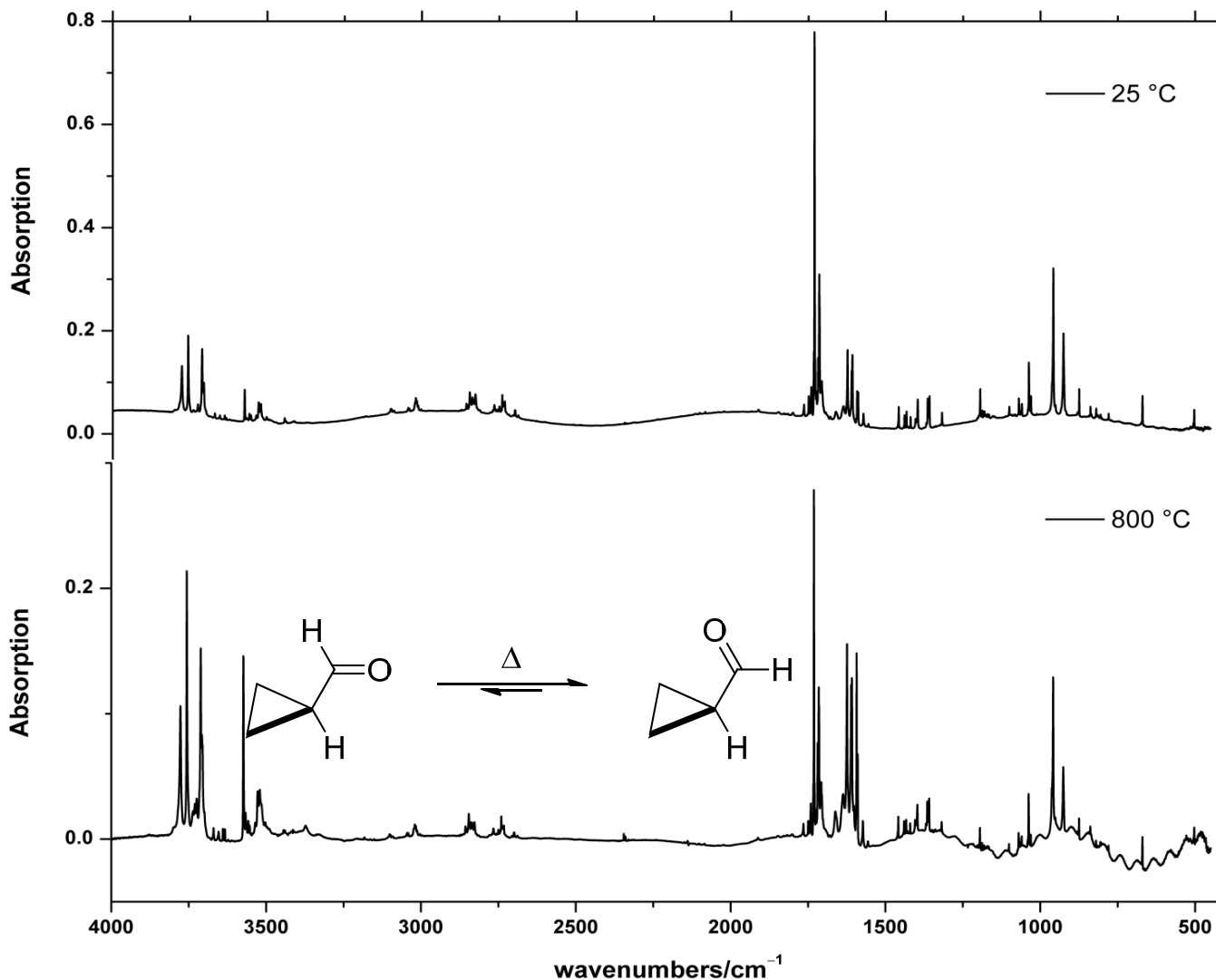
GENERATION OF THE CARBENE



Questions:

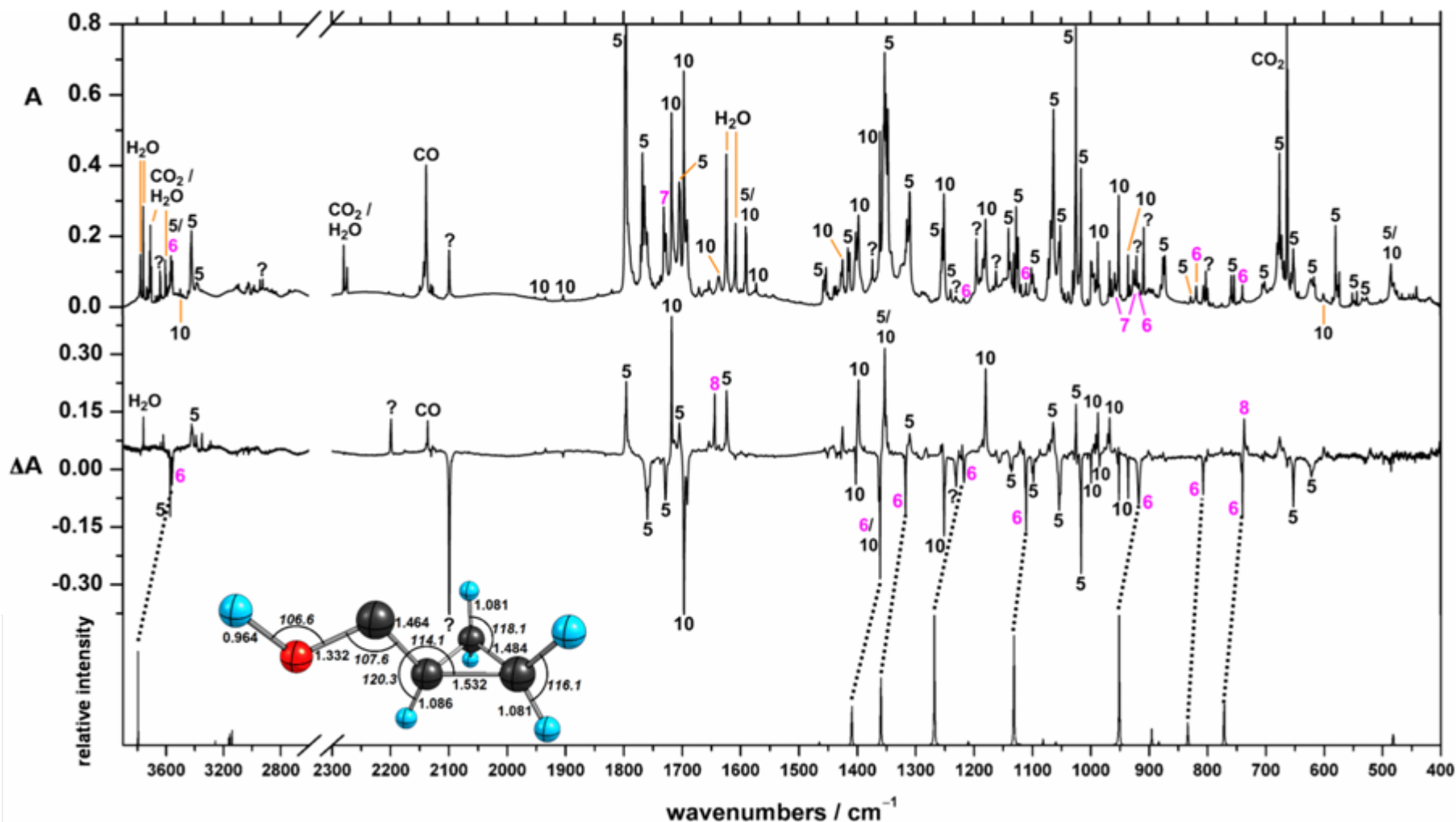
- Does the carbene undergo [1,2]H-tunneling?
- What happens upon irradiation?
- Does the cyclopropyl moiety survive pyrolysis conditions?
- Is the the cyclopropyl moiety involved in consecutive reactions?

STABILITY OF THE CYCLOPROPYL MOIETY

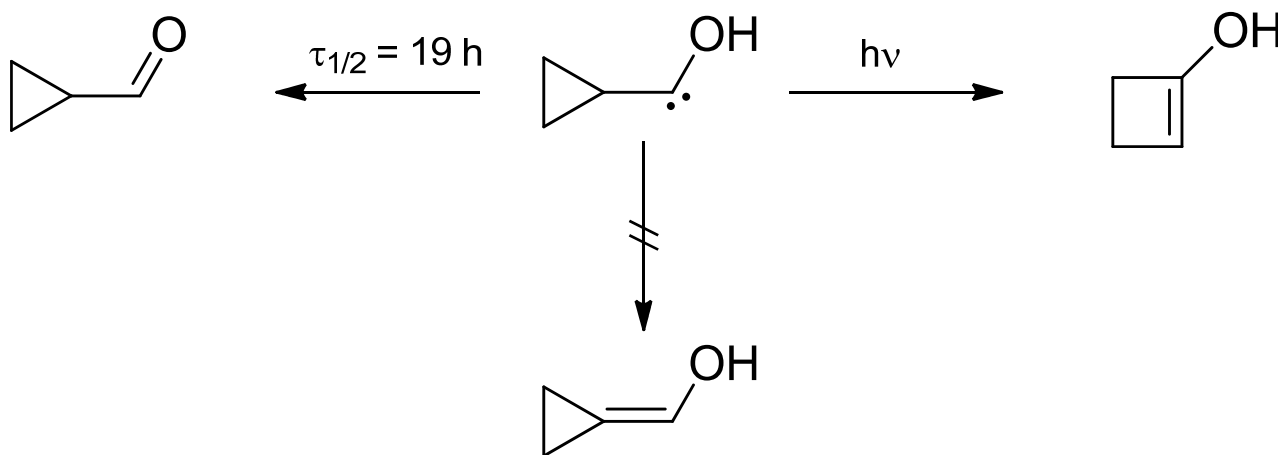


✓ Cyclopropyl moiety is stable towards pyrolysis conditions

PYROLYSIS OF THE PRECURSOR AT 800 °C

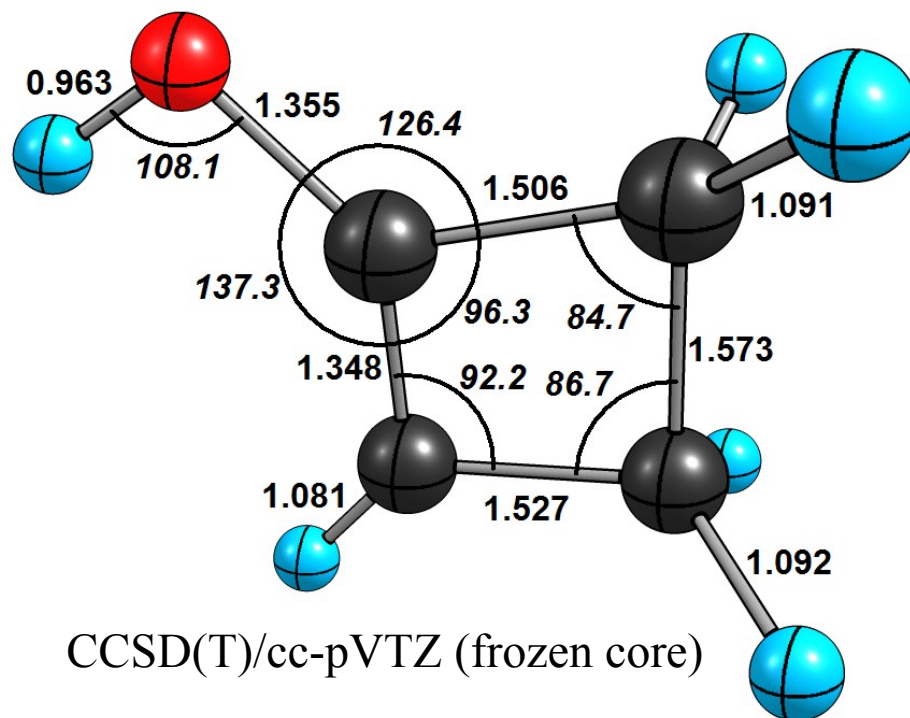


EXPERIMENTAL RESULTS



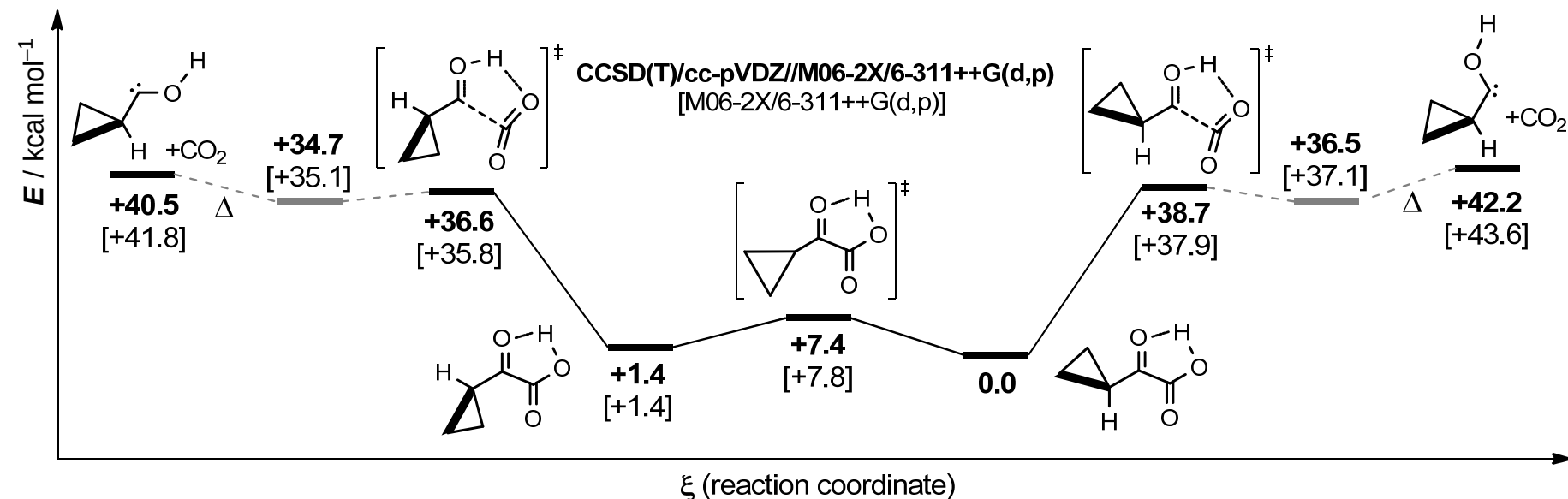
- Carbene vanishes upon irradiation ($\lambda = 366 \text{ nm}$)
- Newly arising signals match the computed cyclobutenol signals
- [1,2]H-tunneling yields cyclopropylcarboxaldehyde
- Tunneling half-life: $\tau_{1/2} = 19 \text{ h}$

CYCLOBUTENOL



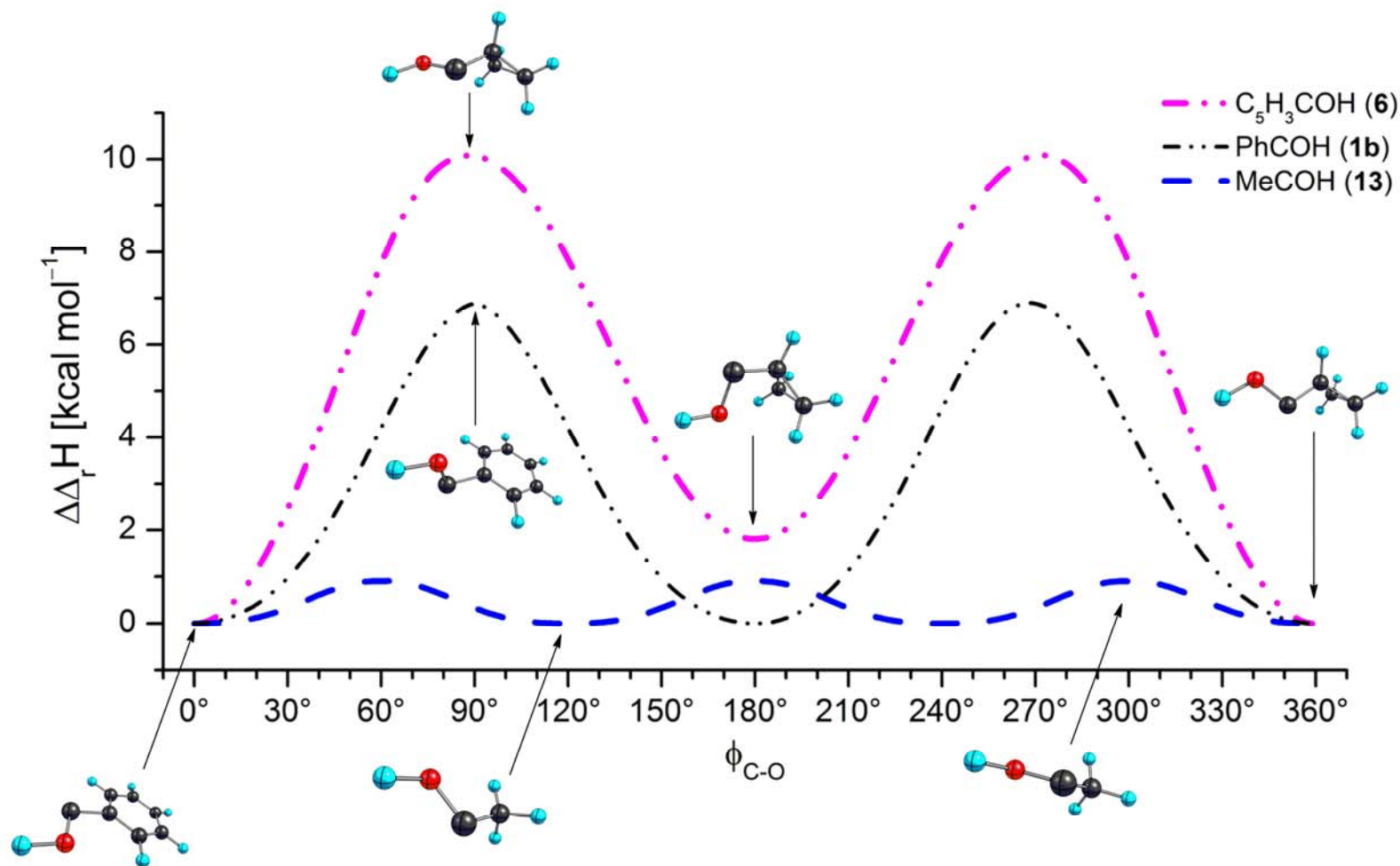
- Cyclic vinyl alcohol
- Not even derivatives have been characterized
- Highly strained system
- **Ring opening reactions possible?**

COMPUTATIONAL STUDY



- Experiment:
 - Only the more stable carbene conformer is present
 - Carbene · CO₂ complex could not be detected
- Computational:
 - Disfavored precursor conformer yields preferred carbene conformer
 - Lower decarboxylation barrier towards the preferred carbene

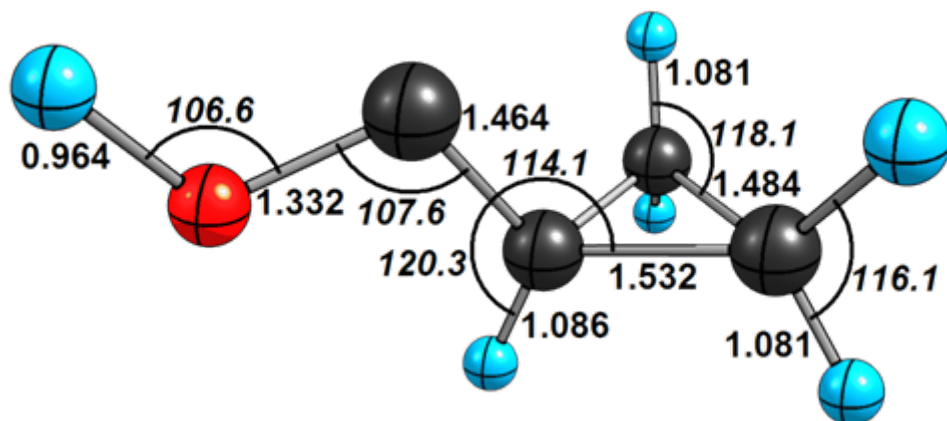
CONFORMATIONAL ANALYSIS



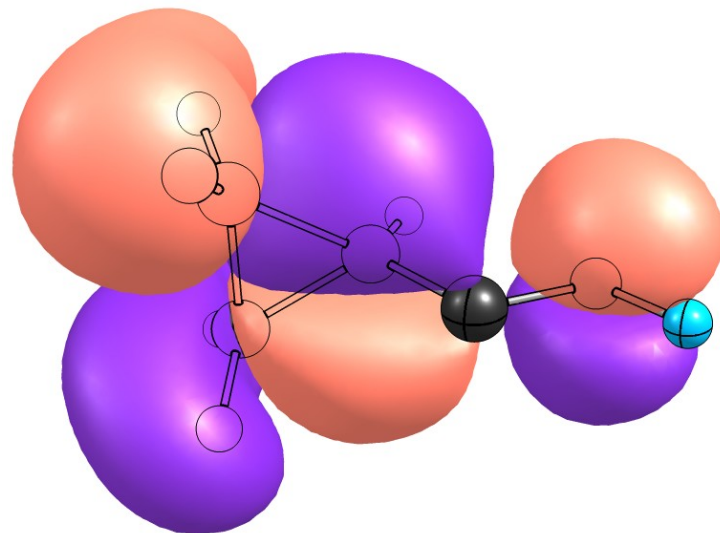
Relaxed scan [M06-2X/6-311++G(d,p)] around the C–C bond:

- Large rotational barrier (10 kcal mol^{-1} without ZPVE corrections)
- Electronic effects stronger than those in PhCOH

CONFORMATIONAL ANALYSIS

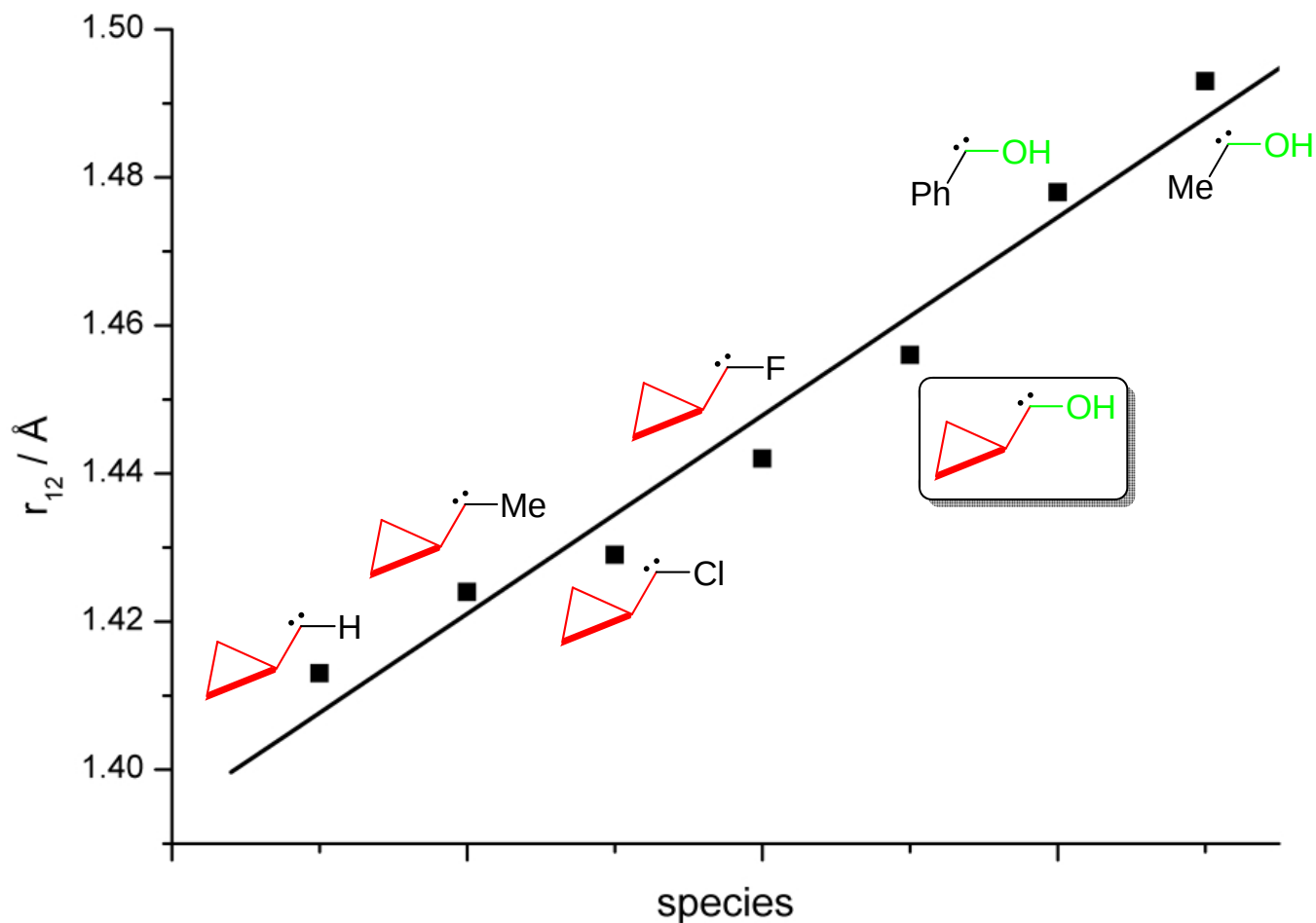


CCSD(T)/cc-pVTZ (frozen core)



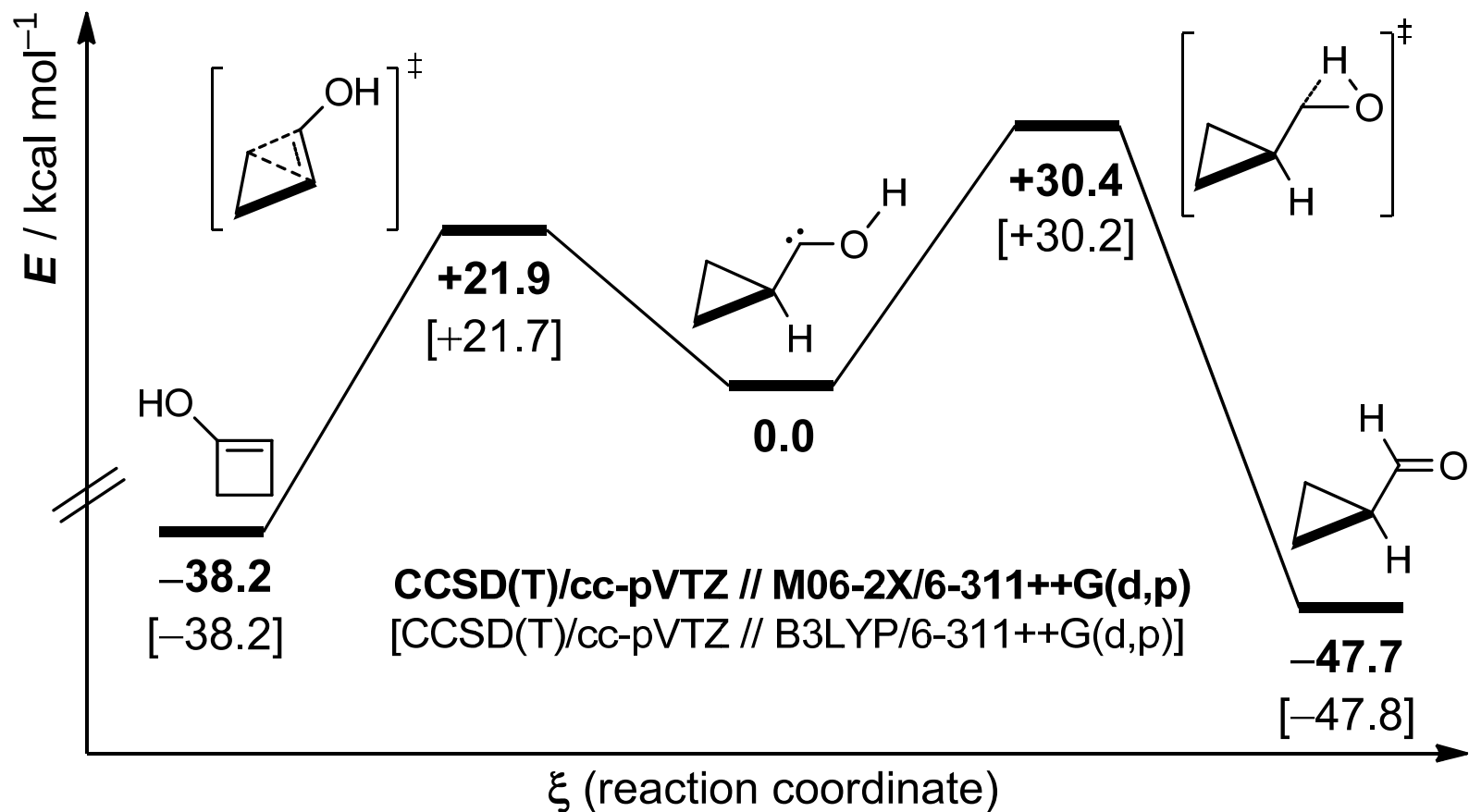
- Carbene vanishes upon irradiation ($\lambda = 366 \text{ nm}$)
- Newly arising signals match cyclobuten-1-ol
- [1,2]H-tunneling yields cyclopropylcarboxaldehyde
- Tunneling half-life: $\tau_{1/2} = 19 \text{ h}$

COMPARISON TO BOTH PARENT SPECIES

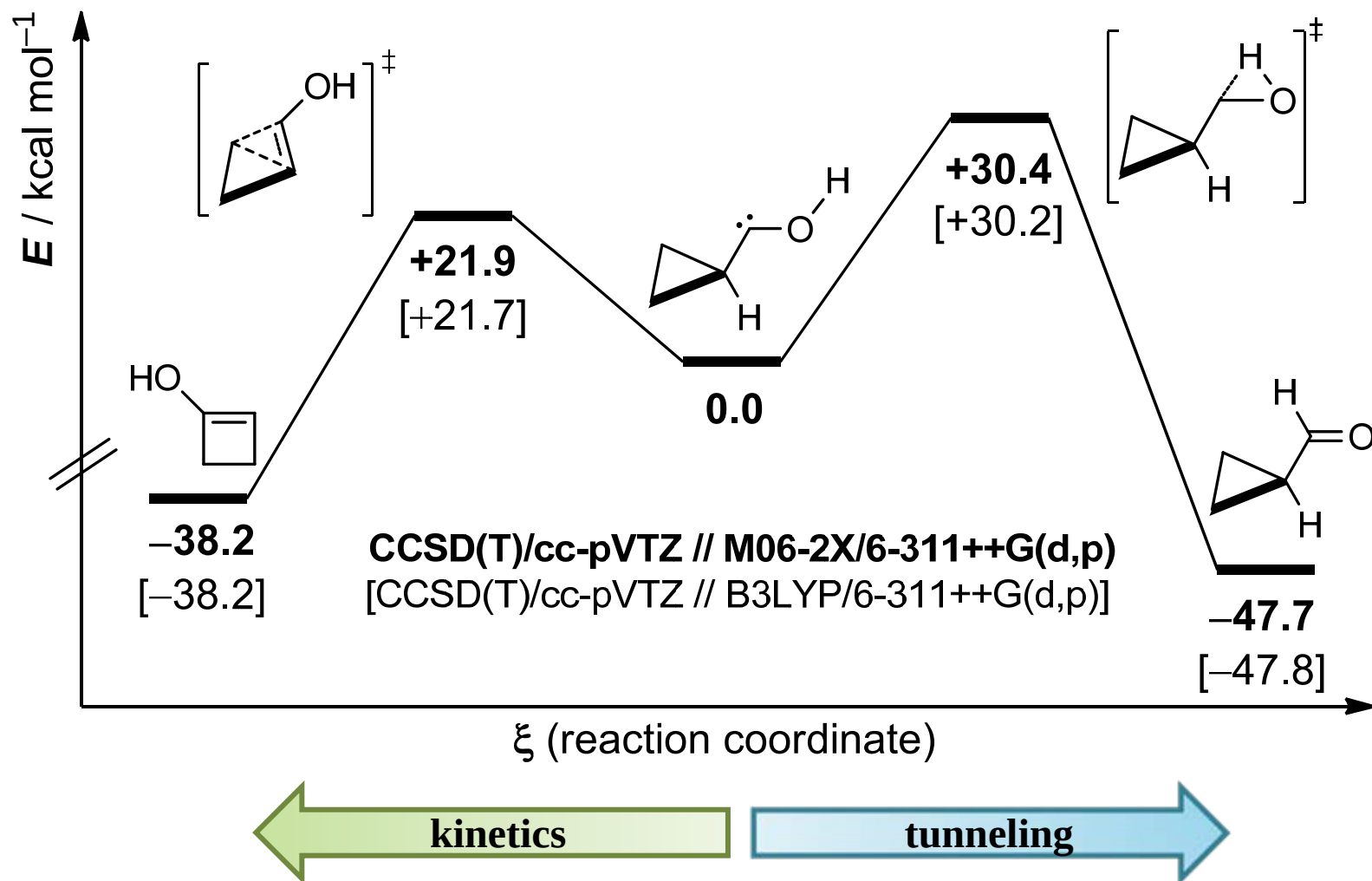


- Short central C–C bond compared to other hydroxycarbenes
- Long central C–C bond compared to other cyclopropylcarbenes

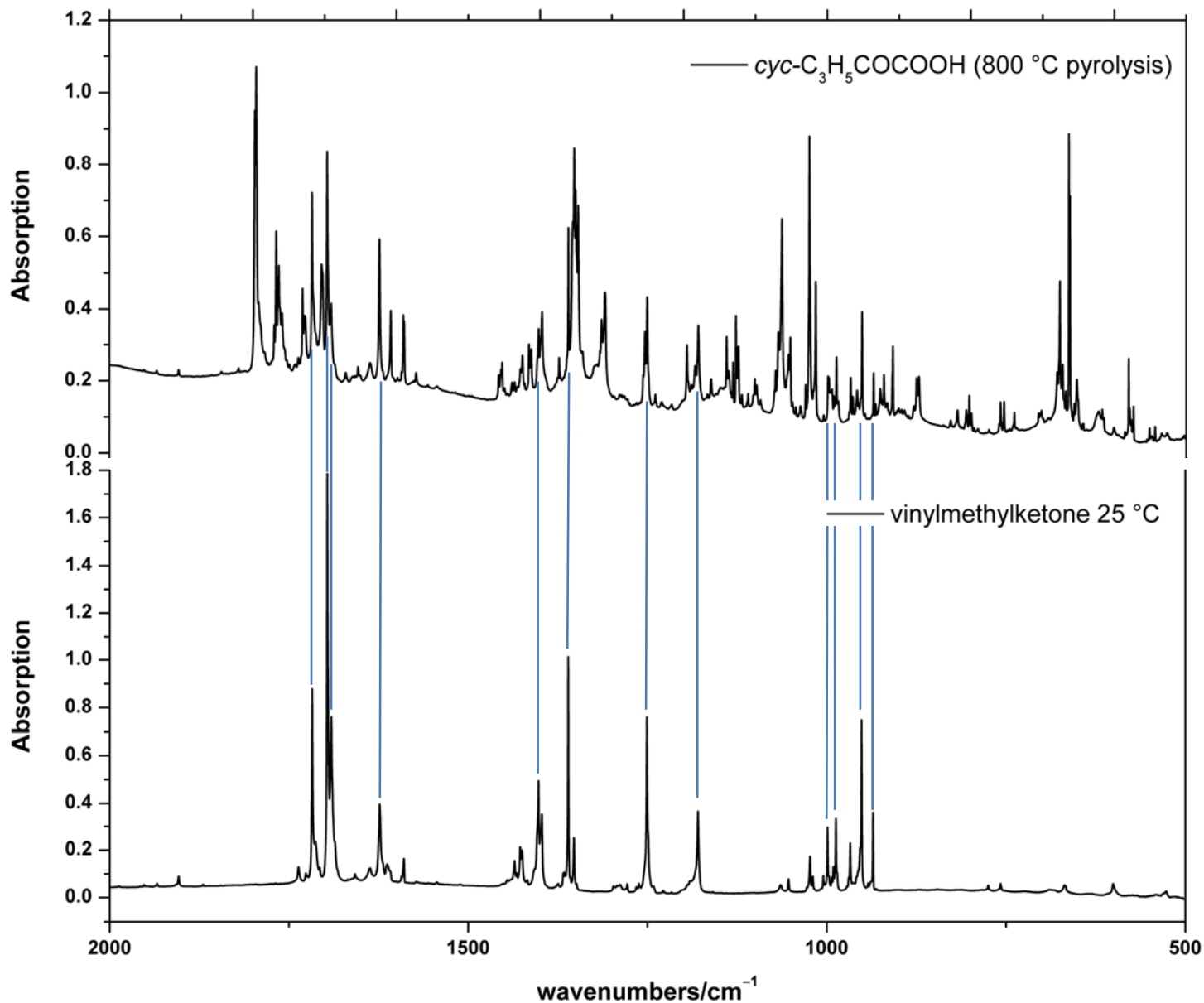
OCCURRING REACTIONS



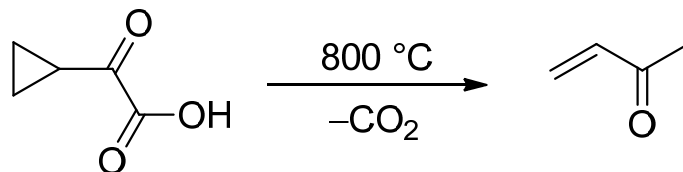
OCCURRING REACTIONS



MAJOR PYROLYSIS PRODUCT



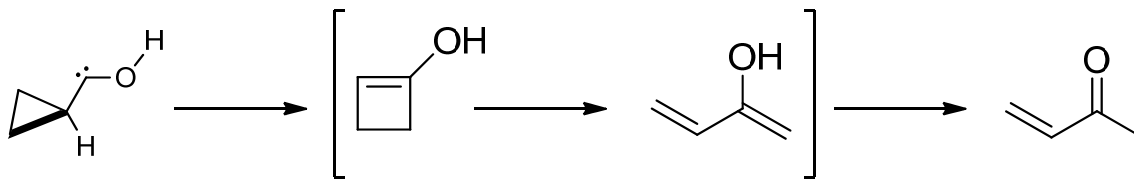
SURPRISING PYROLYSIS PRODUCT



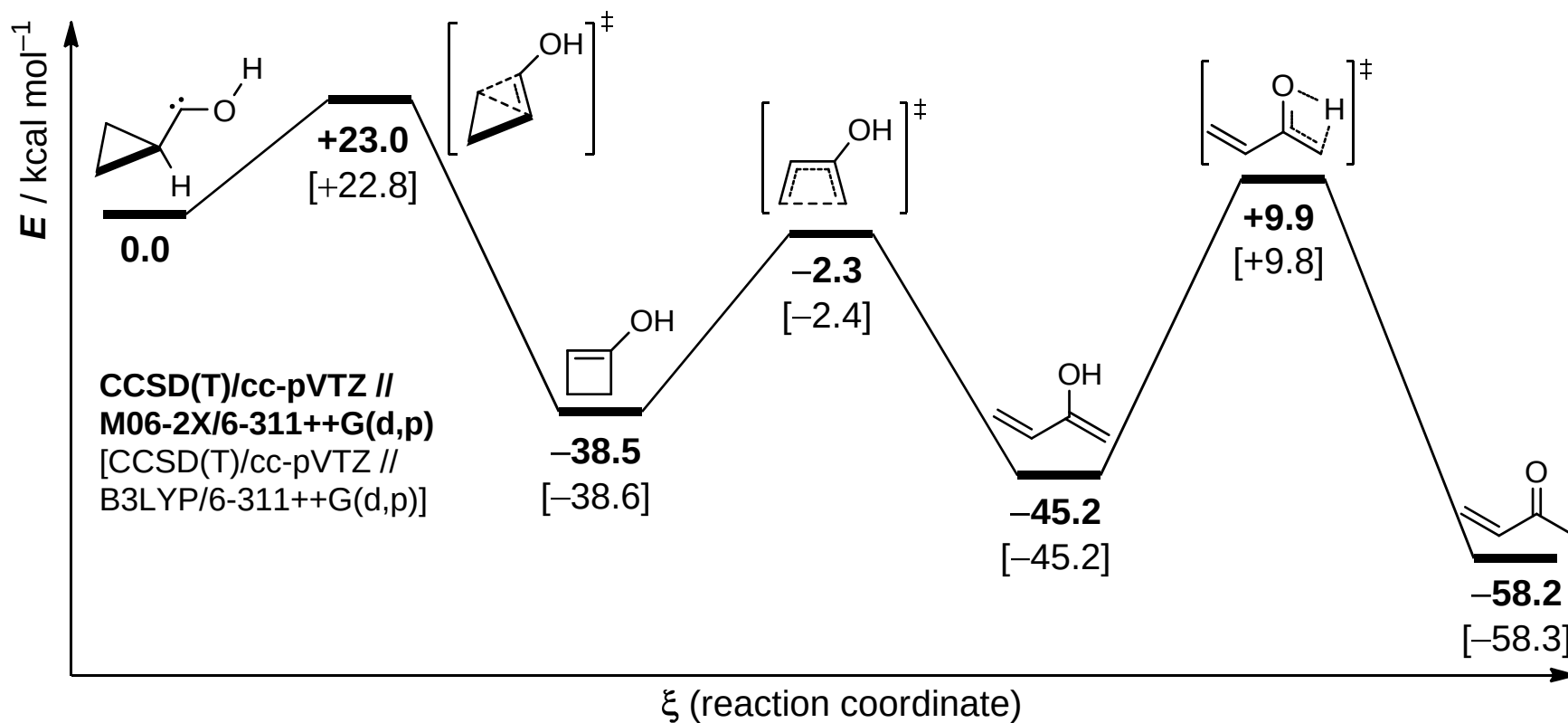
Carbene reactions:

- Ring insertion
- Ring opening
- Keto-enol tautomerism

Cyclopropyl moiety most likely does not undergo ring-opening

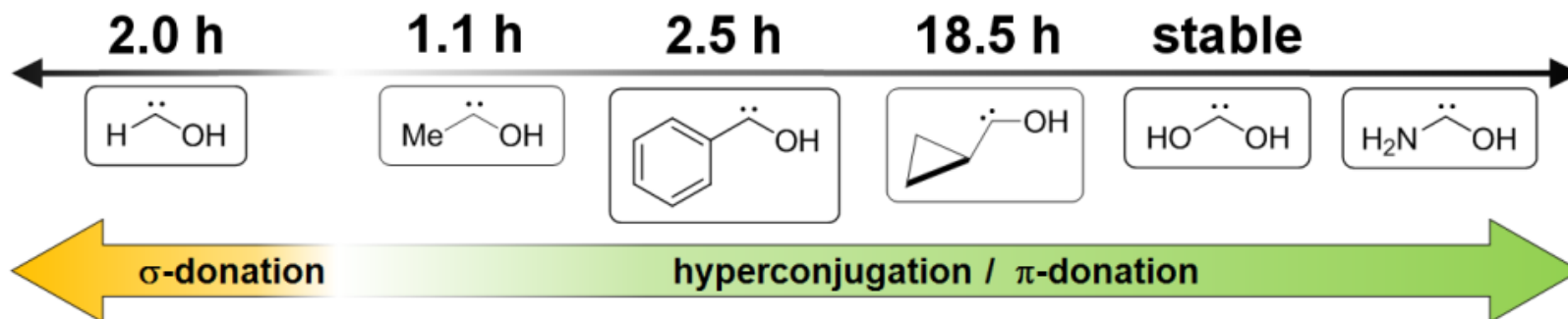


C-SHIFT REACTION SEQUENCE



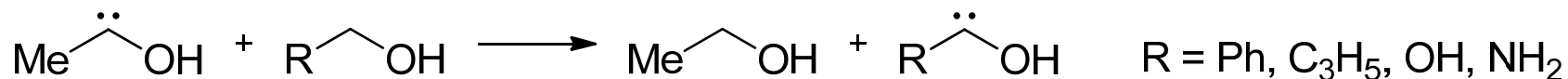
HALF-LIFE ORDER

half-life τ of H-tunneling in solid Ar at 11 K



- Only hydroxycarbenes without a second hetero substituent undergo tunneling
- Carbene's half-life corresponds to the substituent's electron donor strength
- $-\text{OH}, -\text{NH}_2 \gg \text{cyc-C}_3\text{H}_5 > \text{C}_6\text{H}_5 > \text{CH}_3$
- HCOH steps out of the line (only σ -donation)

CONCEPT FOR STABILIZATION



carbene	$\Delta_r H_{0K}^\circ$ ^a	$\Delta_r H_{0K}^\circ$ ^b
PhCOH	-2.3	-2.6
cyc-H ₅ C ₃ COH	-4.1	-4.0
HOCOH	-23.8	-24.0
H ₂ NCOH	-28.7	-28.8
^a CCSD(T)/cc-pVDZ//M06-2X/6-311++G(d,p)		
^b CCSD(T)/cc-pVDZ//B3LYP/6-311++G(d,p)		

How to evaluate the carbene's stability:

- Standard system: methylhydroxycarbene
- Hypothetic H₂ transfer to the respective alcohol
- Stabilization energy correlates with carbene tunneling half-life

CONCEPT FOR STABILIZATION

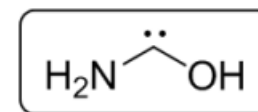
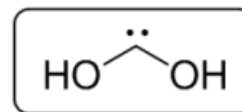
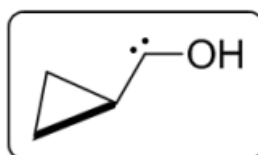
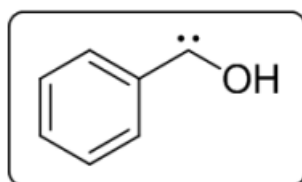
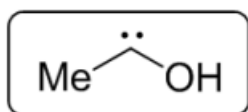
half-life τ of H-tunneling in solid Ar at 11 K

1.1 h

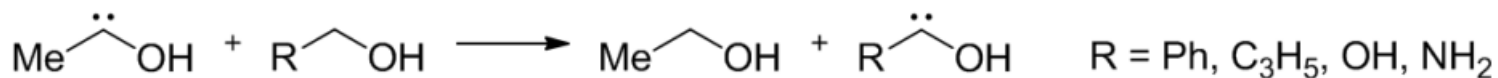
2.5 h

18.5 h

stable



isodesmic stabilization



$$\Delta_r H_{0K}^\circ = \sum_i \nu_i \Delta_f H_{0K}^\circ$$

SUMMARY

- Cyclopropylhydroxycarbene is an easily accessible hydroxycarbene
- Stabilization occurs through the cyclopropyl moiety
- Longest half-life of all tunneling hydroxycarbenes (exp: 19 h, comp: 16 h)
- The major decomposition product is vinylmethylketone
- Photochemical product: Cyclobutenol
- Tunneling product: Cyclopropylcarboxaldehyde
- Tunneling product is the same as thermodynamic product – tunneling control

THANK YOU FOR YOUR ATTENTION