

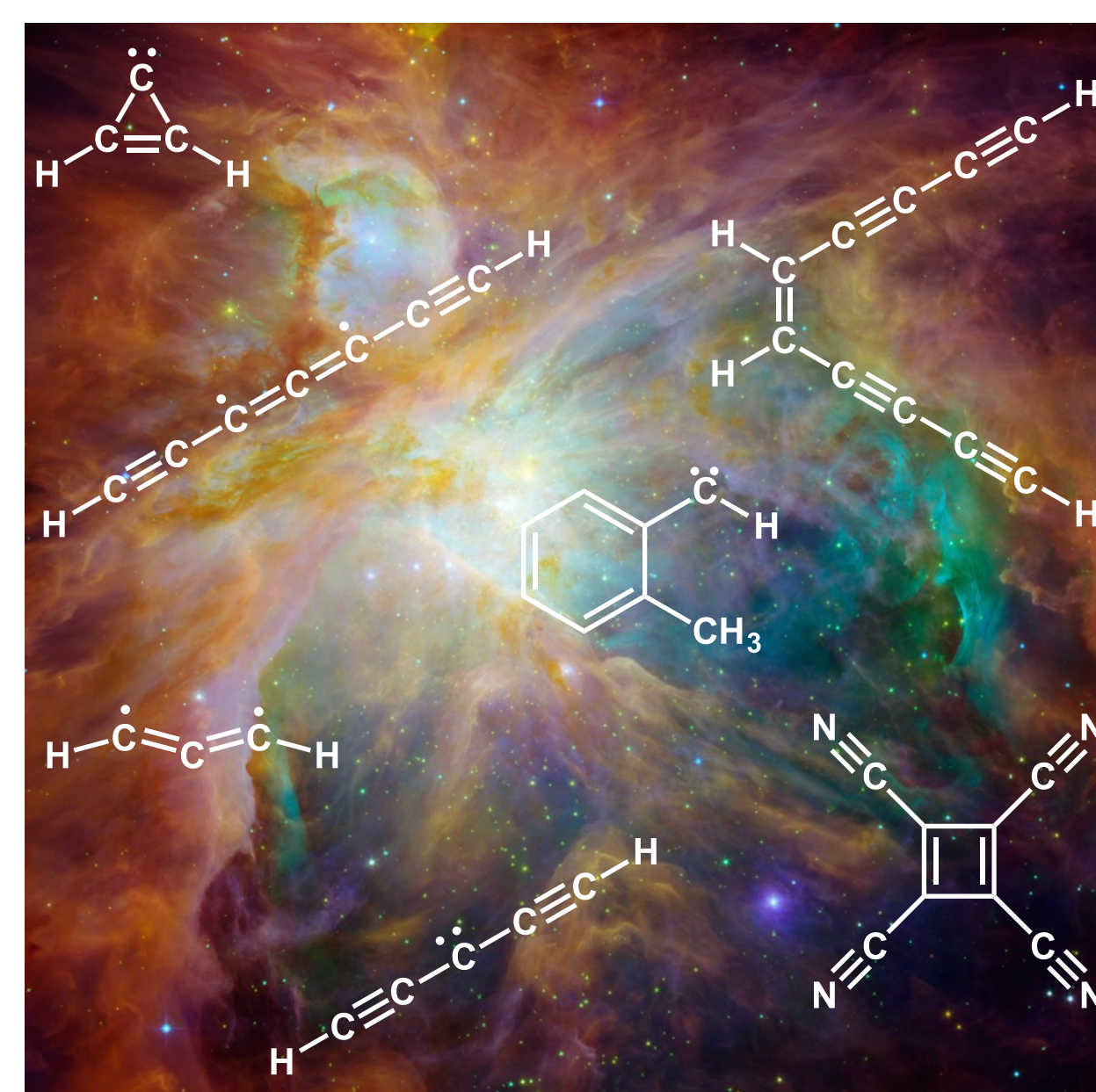


McMahon Research Group

Synthesis, Matrix Isolation, Spectroscopy, Mechanistic Studies, and Computational Chemistry

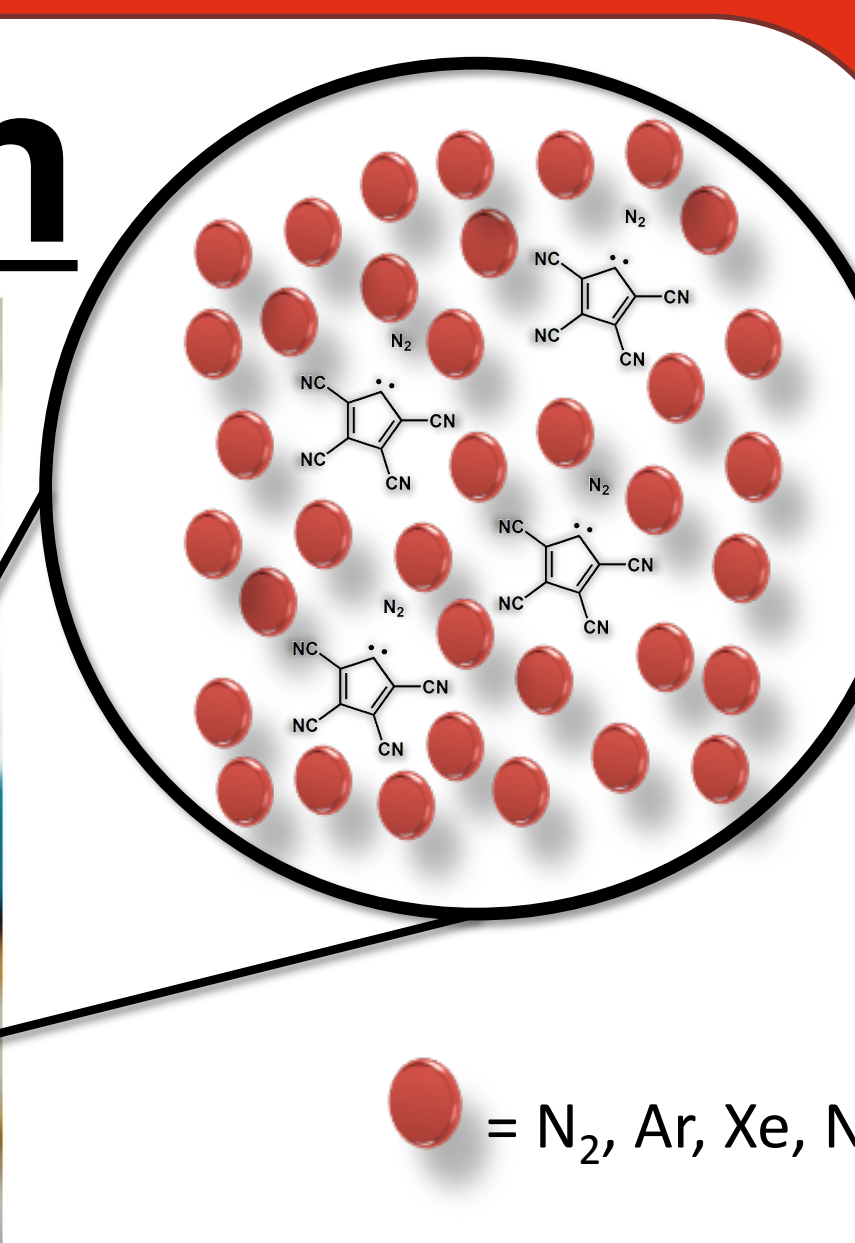
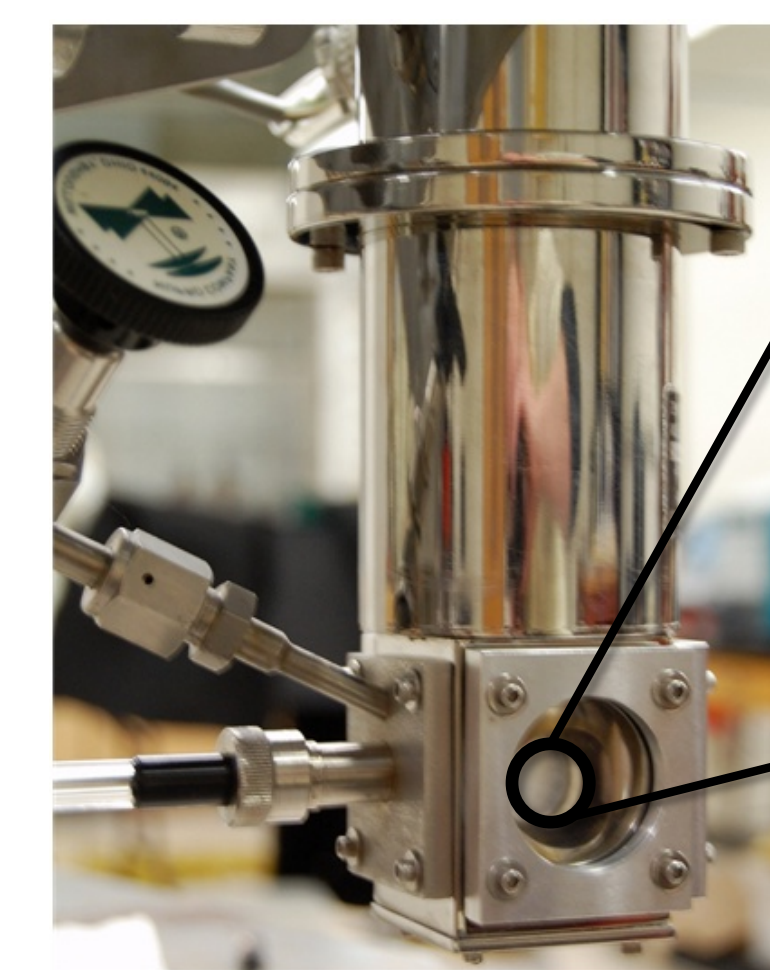
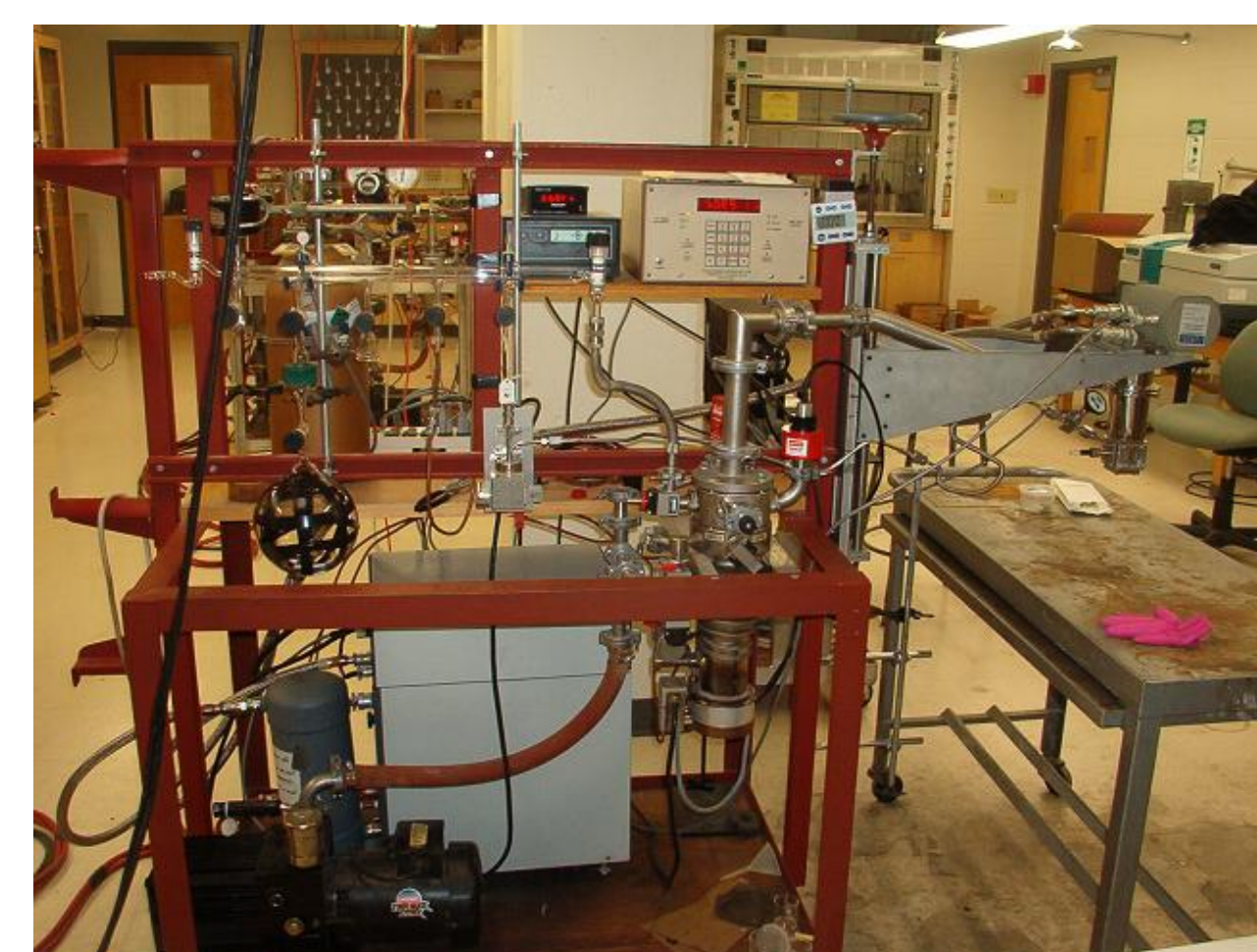
Introduction

The McMahon group has an interest in the areas of astrochemistry, reactive intermediates, and combustion chemistry. The inherent complexity of these chemical environments demands an integrated study involving organic synthesis, matrix isolation spectroscopy, mechanistic studies, rotational spectroscopy, and computational chemistry. Through these combined efforts, it is possible to generate and characterize the prototypical reactive intermediates in organic chemistry and to probe their structure in unprecedented detail. These fundamental structural, spectroscopic, and mechanistic data provide a foundation for understanding the chemistry of organic matter in harsh environments.



Orion Nebula viewed from the Hubble Telescope

Matrix Isolation



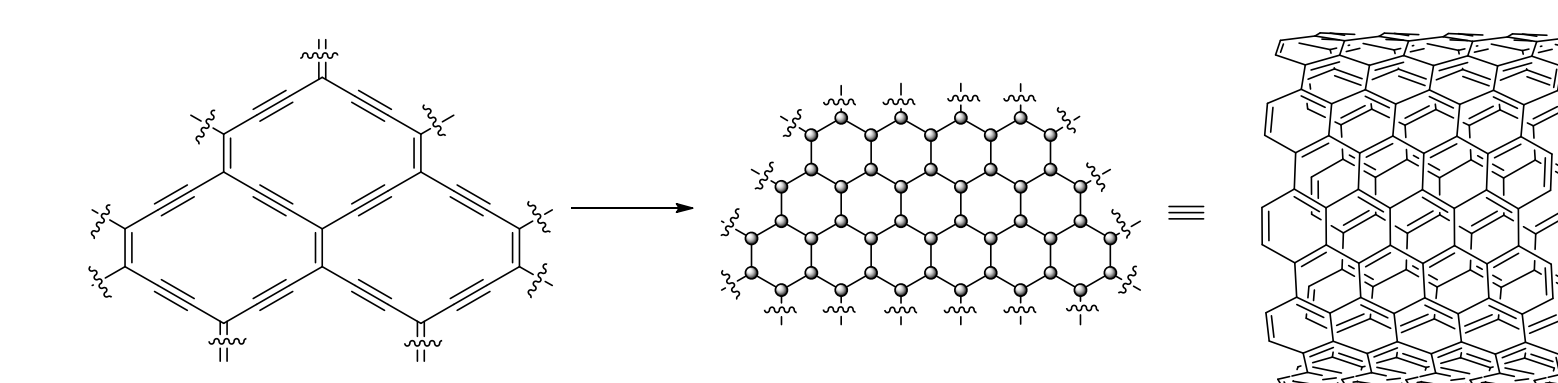
● = N₂, Ar, Xe, Ne

A precursor, or the reactive intermediate, is generated in the gas phase and then frozen in an inert gas (N₂, Ar, Ne, Xe) at 10 to 25 K on a spectroscopic window. The matrix-isolated compounds can then be studied using IR, UV-vis, or EPR spectroscopy. Often, irradiation of the precursor using either a Hg or Xe lamp yields the reactive species, whose identity is confirmed by comparison to calculated spectra. The matrix can then be further irradiated with different wavelengths of light to study the photochemical properties and reactivity of these species.

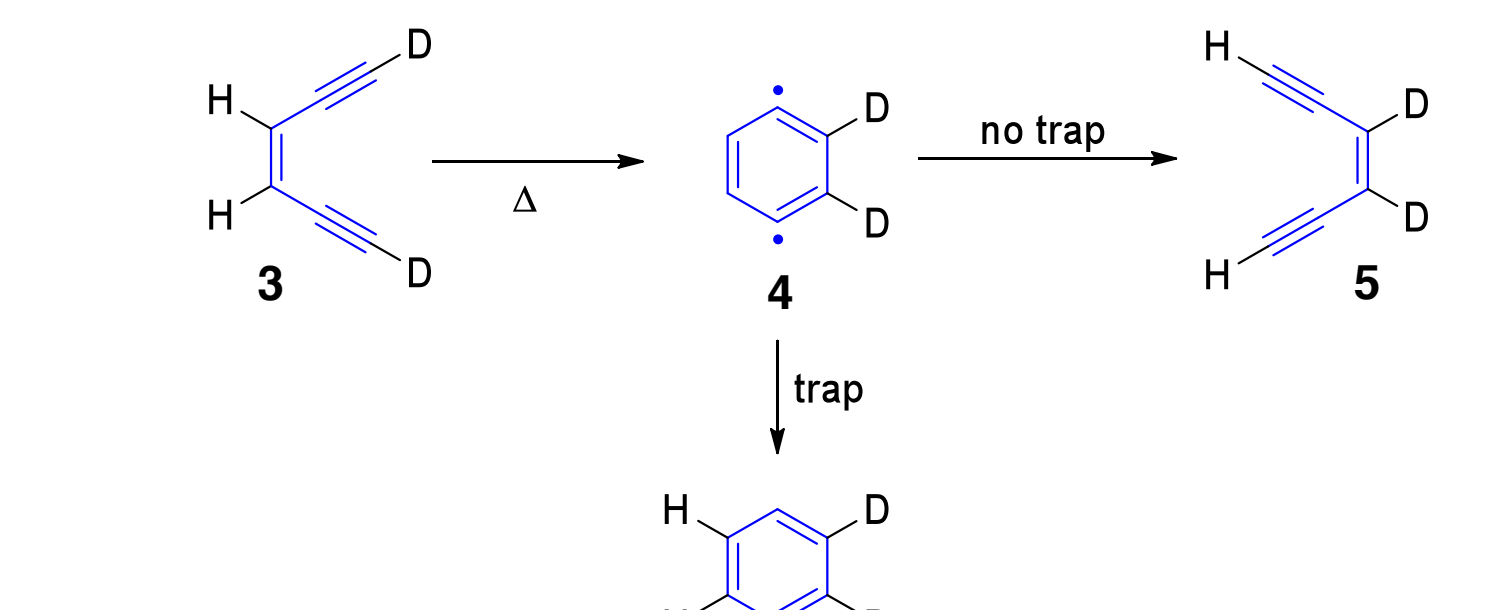
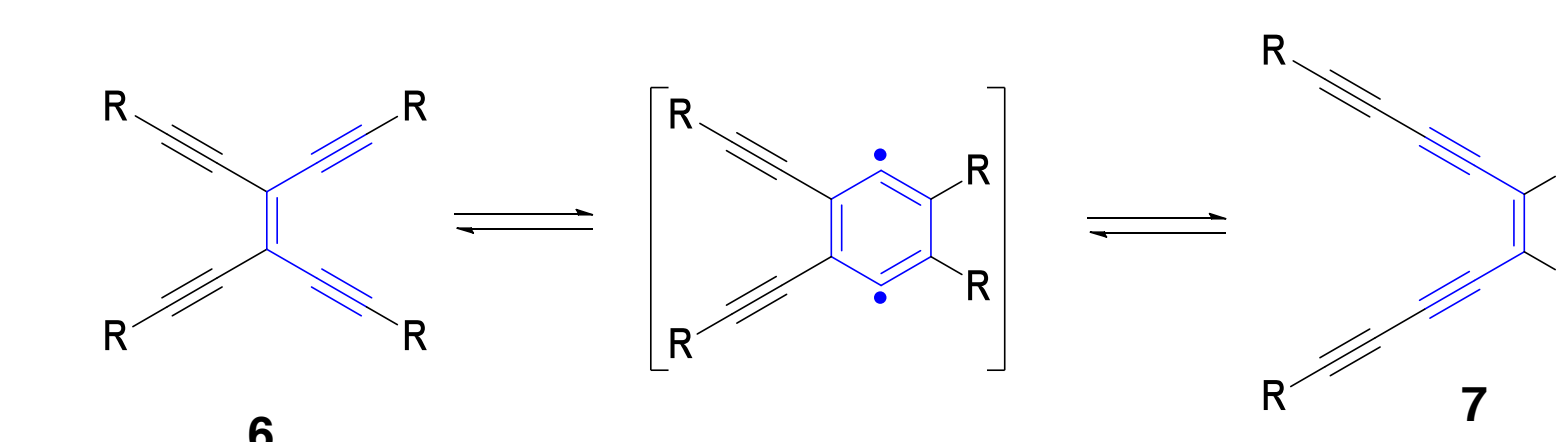
Bergman Cyclization of TEE (6)

Eneidyne can undergo a process known as the Bergman cyclization either photochemically or thermally. Demonstrating this type of reactivity, deuterium labeled *cis*-hex-3-ene-1,5-diyne (**3**), the simplest eneidyne, has been shown to isomerize via a Bergman cyclization to yield *para*-benzynes (**4**). The *p*-benzyne diradical can either be trapped to produce labelled benzene, or, if a sufficient hydrogen donor is not present, rearrange to afford isomer (**5**).

This type of reactivity could have implications of the mechanism of formation and rearrangement of fullerenes.

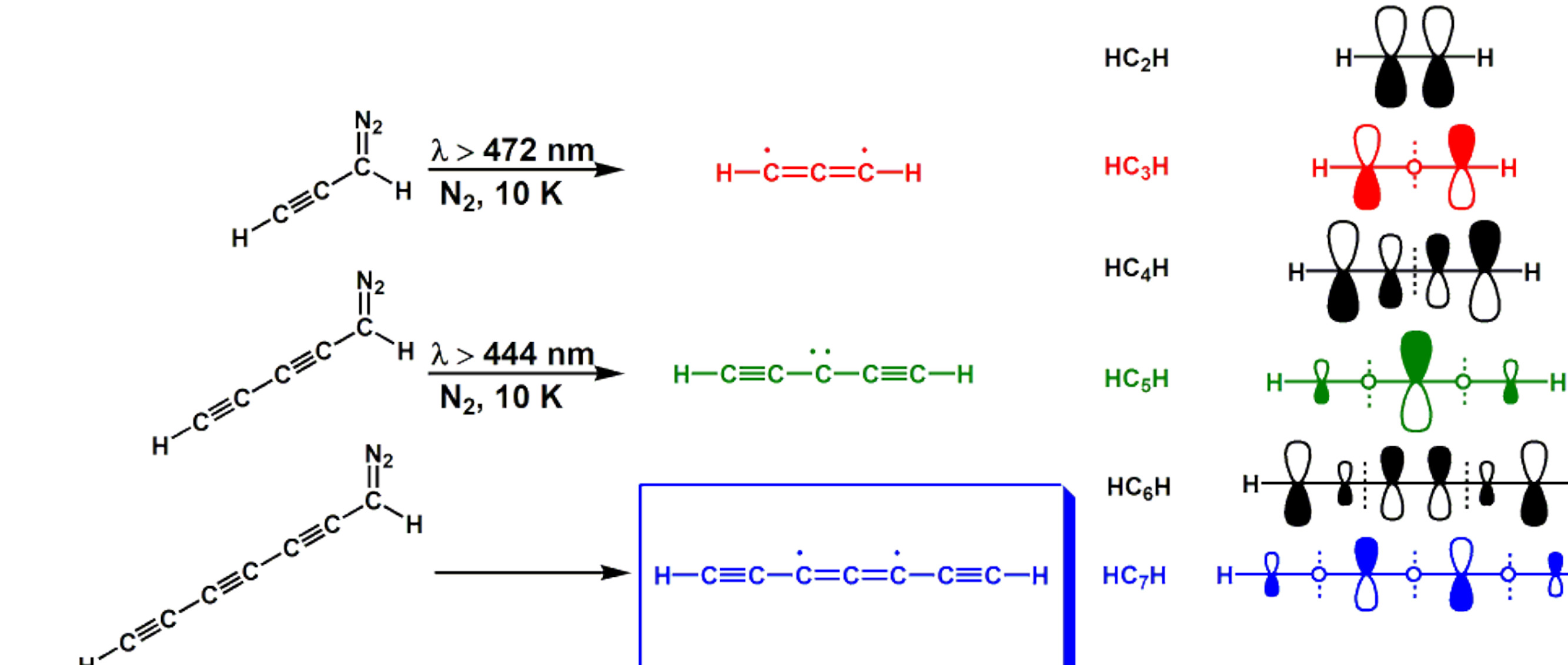


To the best of our knowledge, there have been no documented Bergman cyclizations of a tetraethynylethene, such as **6**.

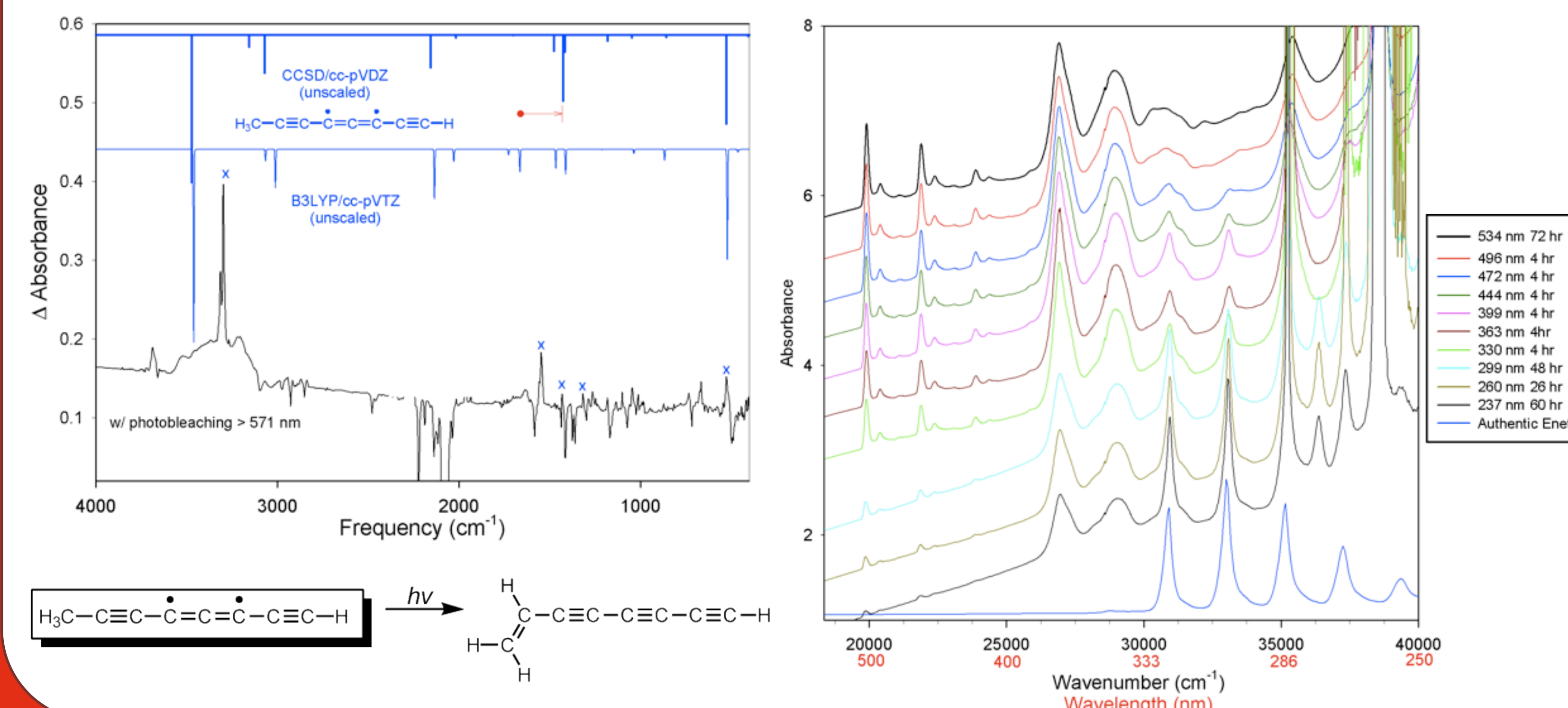
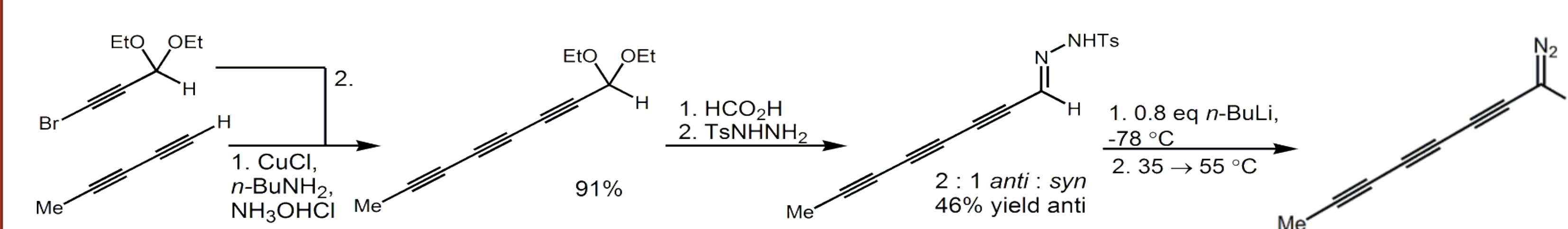


Linear Carbon Chains

The exploration of varying lengths of unsaturated carbon chains has been a primary focus of the group. The HC₃H and HC₅H systems have been synthesized and characterized. Both are believed to be important molecules in the Interstellar Medium (ISM). Further studies of the substituted HC₃H and the HC₇H systems are currently underway.



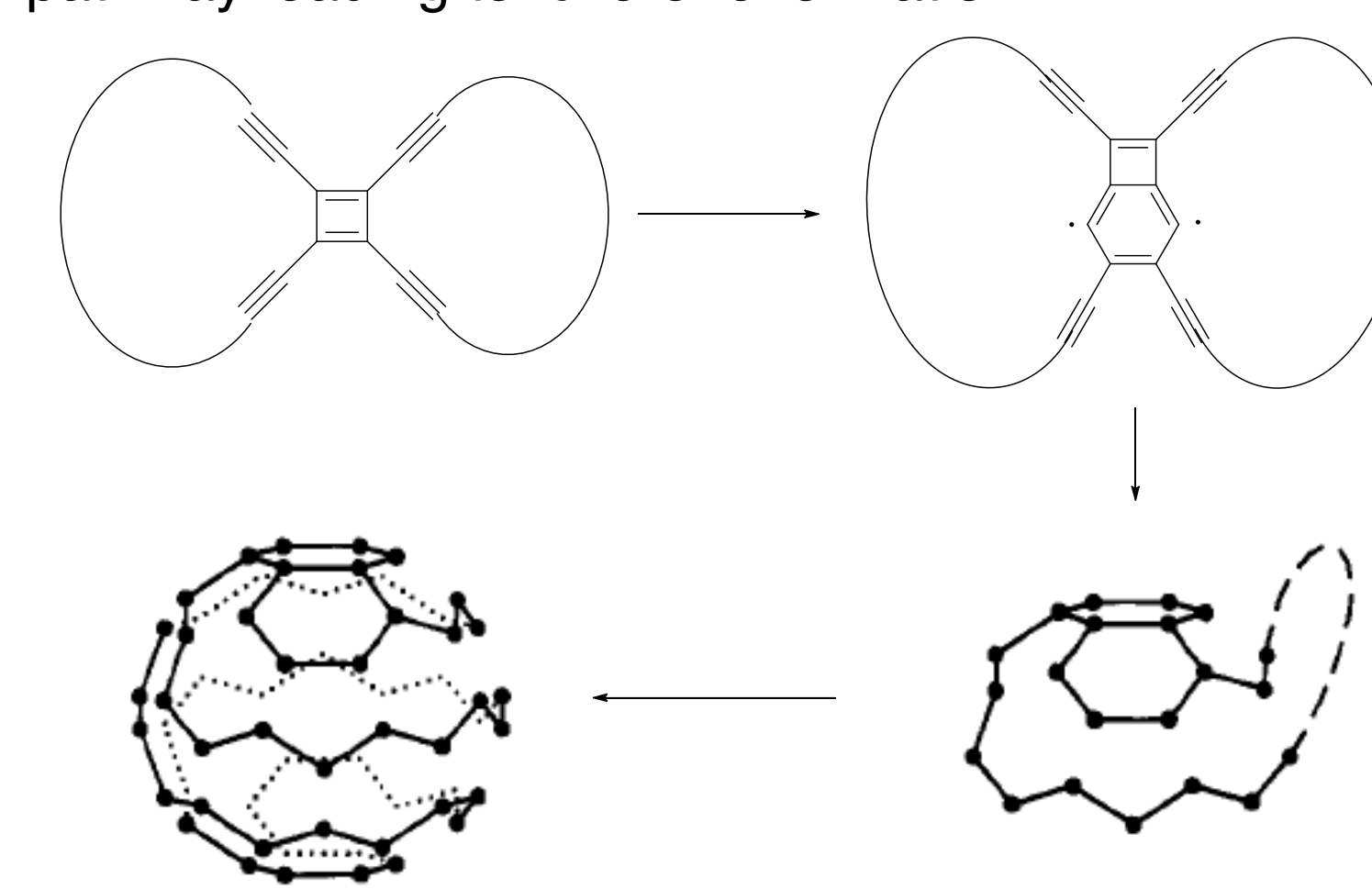
The precursor to HC₇H polymerizes in the final step. MeC₇H was synthesized as a more stable alternative. Photoisomerization of MeC₇H leads to the eneidyne product. An authentic eneidyne sample was synthesized to confirm the pathway.



Cyclobutadienes

The Bergman cyclization of a tetraethynylcyclobutadiene derivative has been proposed as the first step in a pathway leading to fullerene formation.

A general pathway between the low energy isomers has been computed at the B3LYP/6-31G* level. Energies are in kcal/mol. A search for transition states between these isomers to confirm these pathways has begun.

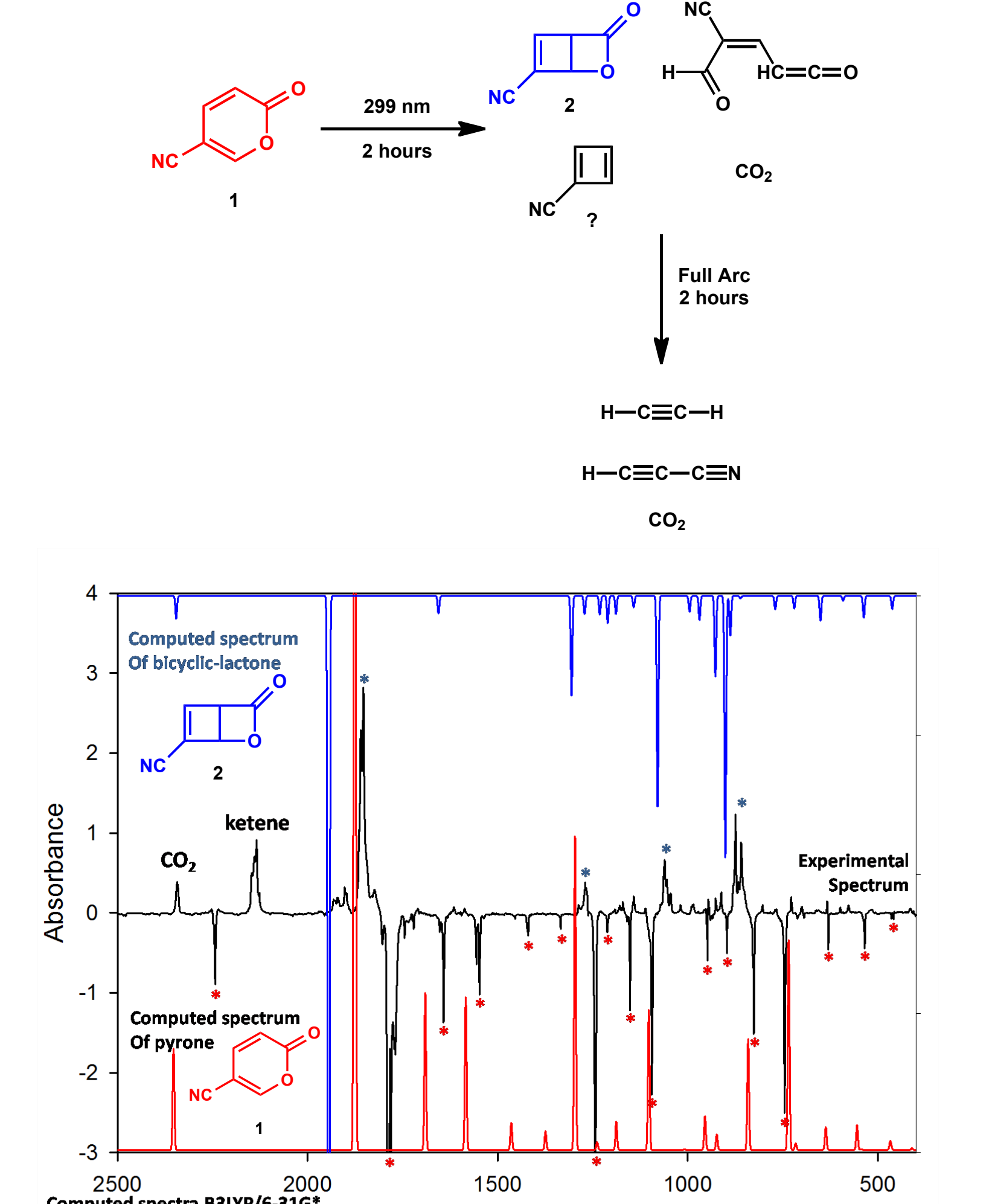


Goroff, N. S. *Acc. Chem. Res.* 1996, 29, 77.

Computational studies have been completed to determine the effect varying numbers of cyano substituents has on the stability of cyclobutadiene rings (ΔH°_{rxn} (kcal/mol) B3LYP/6-31G*) as well as the singlet triplet gaps (CASPT2/ANO-L-VTZP). A negative number means a ground state singlet.

ΔH°_{rxn}		Singlet-Triplet Gap	
0.00	0.00	-12.07	
-4.65	-7.05	-8.66	
-9.44	-11.05	-10.39	
-5.98		-8.29	
-11.04		-9.04	
-8.33		-12.04	-9.52
-9.29		-12.10	-8.46

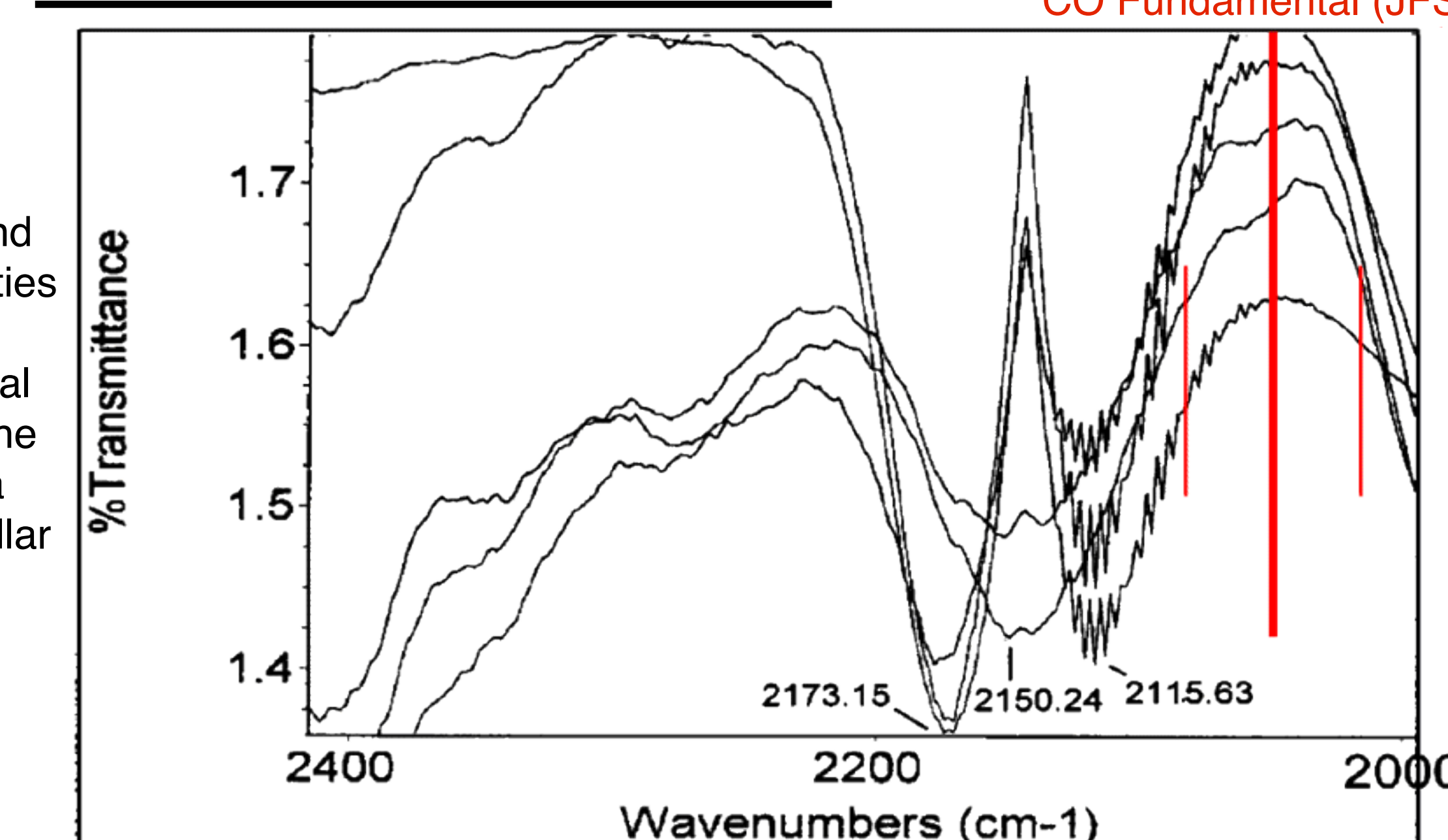
Irradiation at 299 nm with a Hg lamp converts pyrene **1** to bicycle **2**. Further irradiation produces CO₂, acetylene, and cyano acetylene, all of which are decomposition products of monocyanocyclobutadiene, but it has not yet been identified in the matrix.



Diazirinone

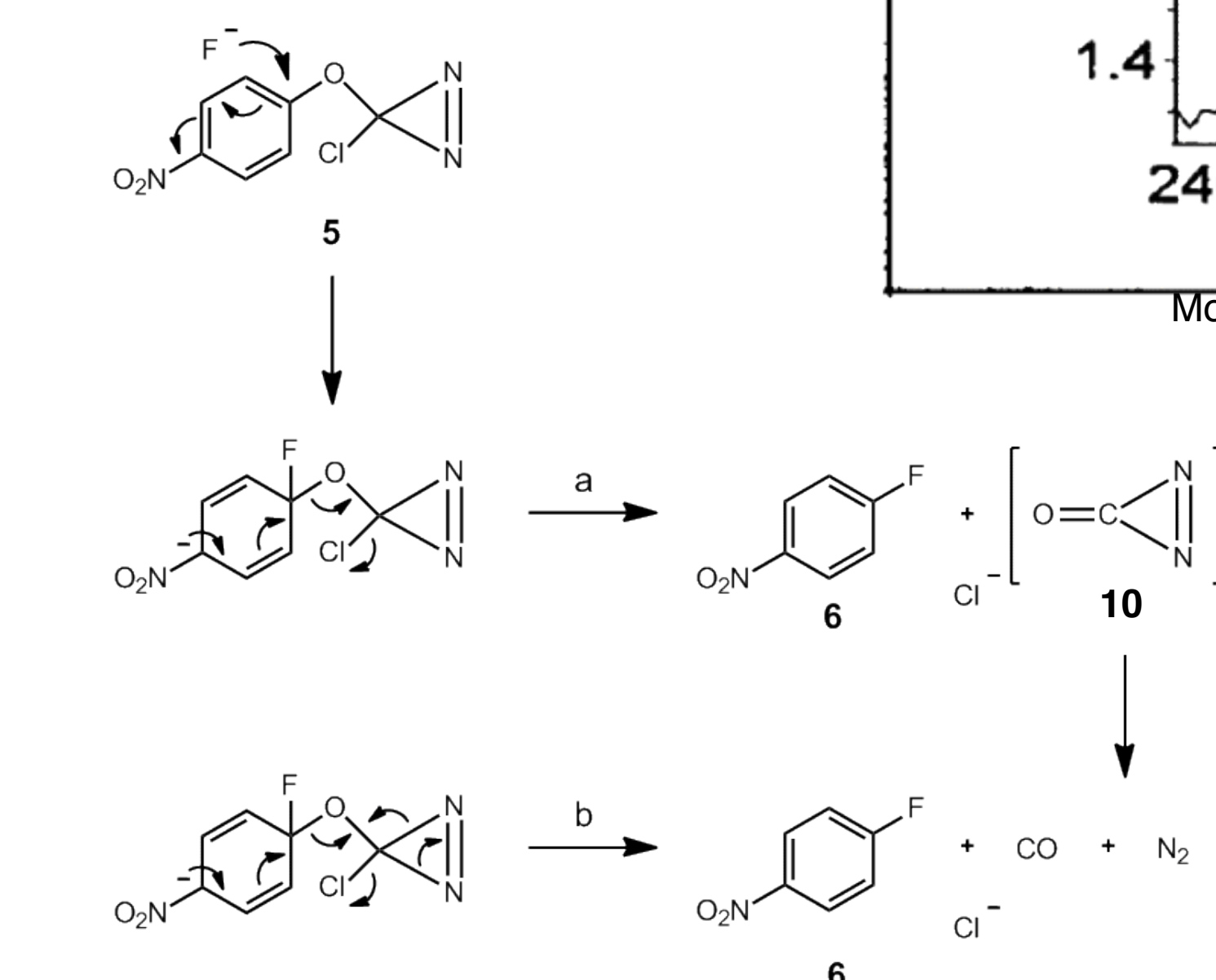
CO Fundamental (JFS)

Diazirinone (**10**) is an intriguing species, inasmuch as it is a mixed dimer of the two most strongly bonded diatomic molecules, CO and N₂. Diazirinone provides opportunities to probe the limits of chemical (in)stability. The laboratory rotational spectrum of it would also provide the basis to search for diazirinone as a possible component of the interstellar medium via radioastronomy.



Moss, R.; Chu, G.; Sauters, R. *J. Am. Chem. Soc.* 2005, 127, 2409.

The reaction of 3-chloro-3-(*p*-nitrophenoxy)diazirine with Bu₄N⁺F⁻ affords *p*-fluoronitrobenzene, nitrogen, and carbon monoxide. Although we cannot exclude the mechanism proposed for the formation of diazirinone (pathway a), our observations require a much shorter lifetime for diazirinone than originally suggested (pathway b). Two plausible explanations are that diazirinone is formed, but is unstable to the reaction conditions, or that N₂ and CO are produced without diazirinone as an intermediate.



Recent Publications

- Shaffer, C. J.; Esselman, B. J.; McMahon, R. J.; Stanton, J. F.; Woods, R. C., Attempted Isolation and Characterization of Diazirinone (N₂CO). *J. Org. Chem.* 2010, ACS ASAP.
- Thomas, P. S.; Bowling, N. P.; McMahon, R. J., Spectroscopy and Photochemistry of Triplet Methylpentadiynylidene (Me-C=C-C=C-C-H). *J. Am. Chem. Soc.* 2009, 131 (24), 8649-8659.
- Seburg, R. A.; Patterson, E. V.; McMahon, R. J., Structure of Triplet Propynylidene (HCCCH) as Probed by IR, UV/vis, and EPR Spectroscopy of Isotopomers. *J. Am. Chem. Soc.* 2009, 131 (26), 9442-9455.
- Seburg, R. A.; Hodges, J. A.; McMahon, R. J., Propynal Equivalents and Diazopropyne: Synthesis of All Mono-¹³C Isotopomers. *Helv. Chim. Acta* 2009, 92 (8), 1626-1643.

Group Memebers

- Brent Amberger
- Nikki Burmann
- Thomas Draxler
- Brian Esselman
- Laura Kopff
- Terese Kreifels
- Jessica Menke
- Alex Nolan
- Chris Shaffer
- Colleen Sylvester
- Andrew Wiederhold
- Katherine Windsor



Funding

