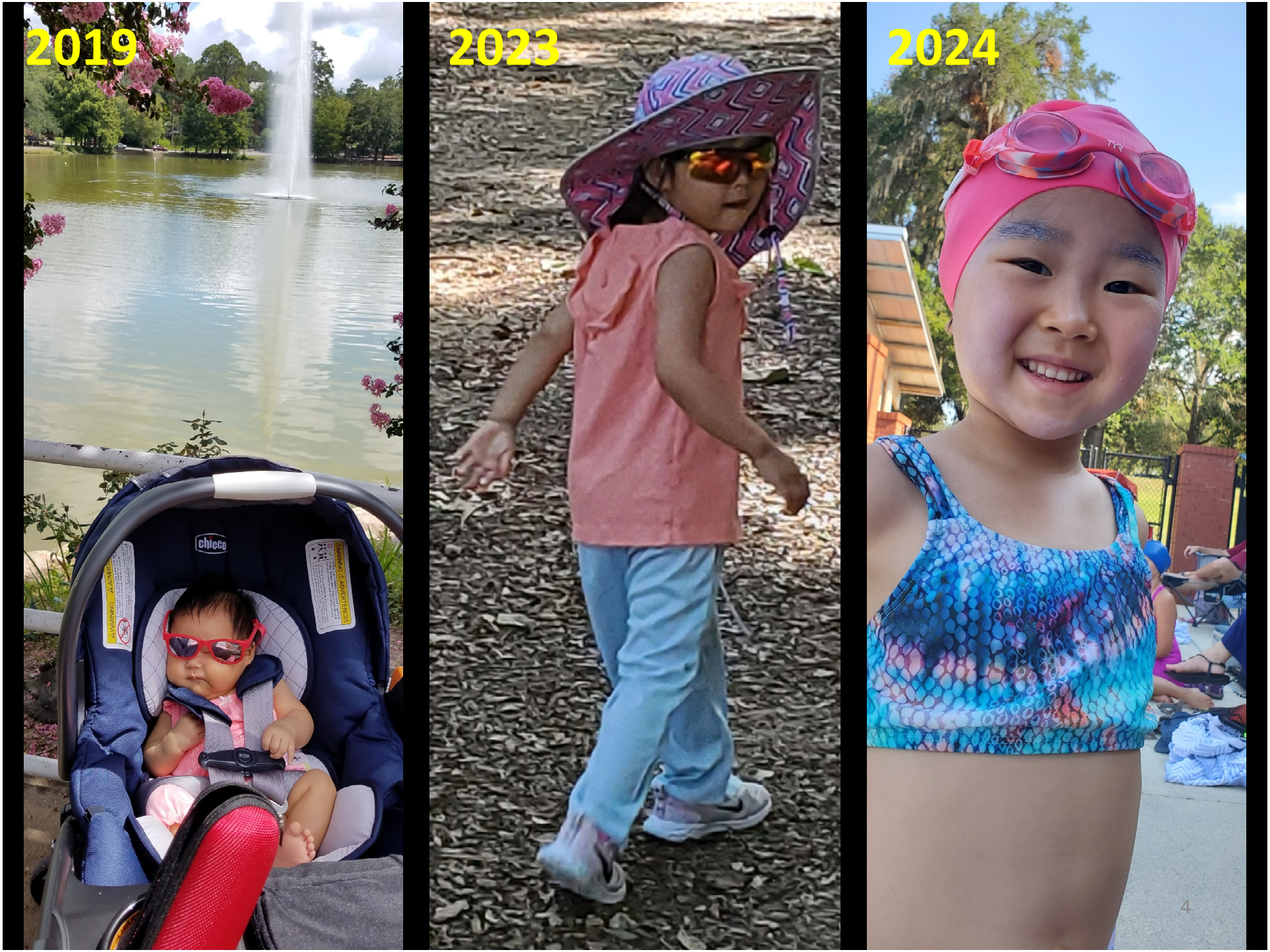
Fluorescent organic molecules

Lei Zhu, Florida State University

July 9, 2024

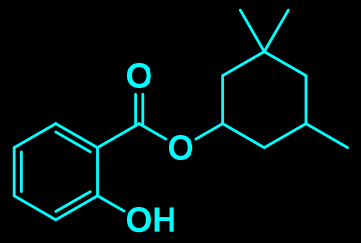

NASA
I NEED MY SPACE!
Kennedy Space Center
Frankly
my Dear,
I DON'T GIVE
A DAMN!
GONE WITH THE WIND


2019
2023
2024

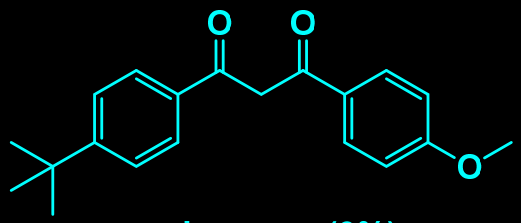
Sunscreen

- Ultraviolet (UV): 10 – 400 nm
- UVA: 315 – 400 nm (soft UV)
- UVB: 280 – 315 nm (intermediate UV)
- UVC: 100 – 280 nm (hard UV)
- SPF – "sun protection factor"

oxybenzone (6%)

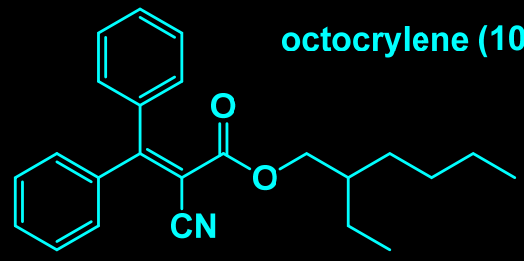


homosalate (15%)



avobenzone (3%)

octisalate (5%)



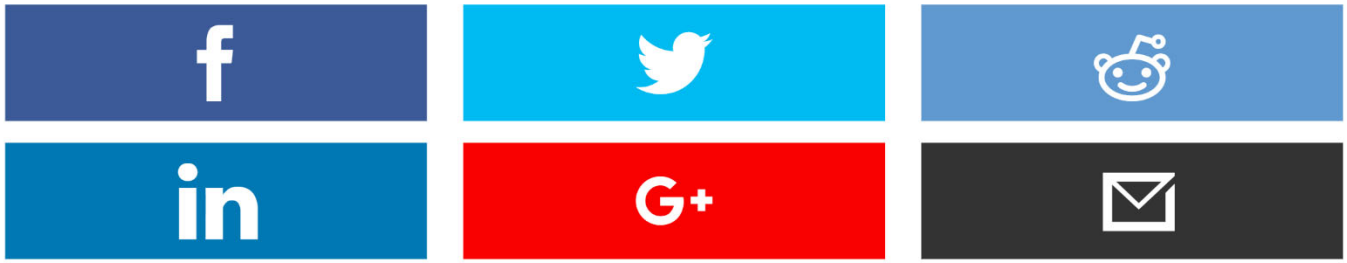
octocrylene (10%)

“the benefits way outweigh the risks”

Health | Sun

Sunscreen: What science says about ingredient safety

Sunscreen is essential for staying protected in the Sun - but recent research suggests some of the ingredients could be improved. BBC Future analyses the evidence.



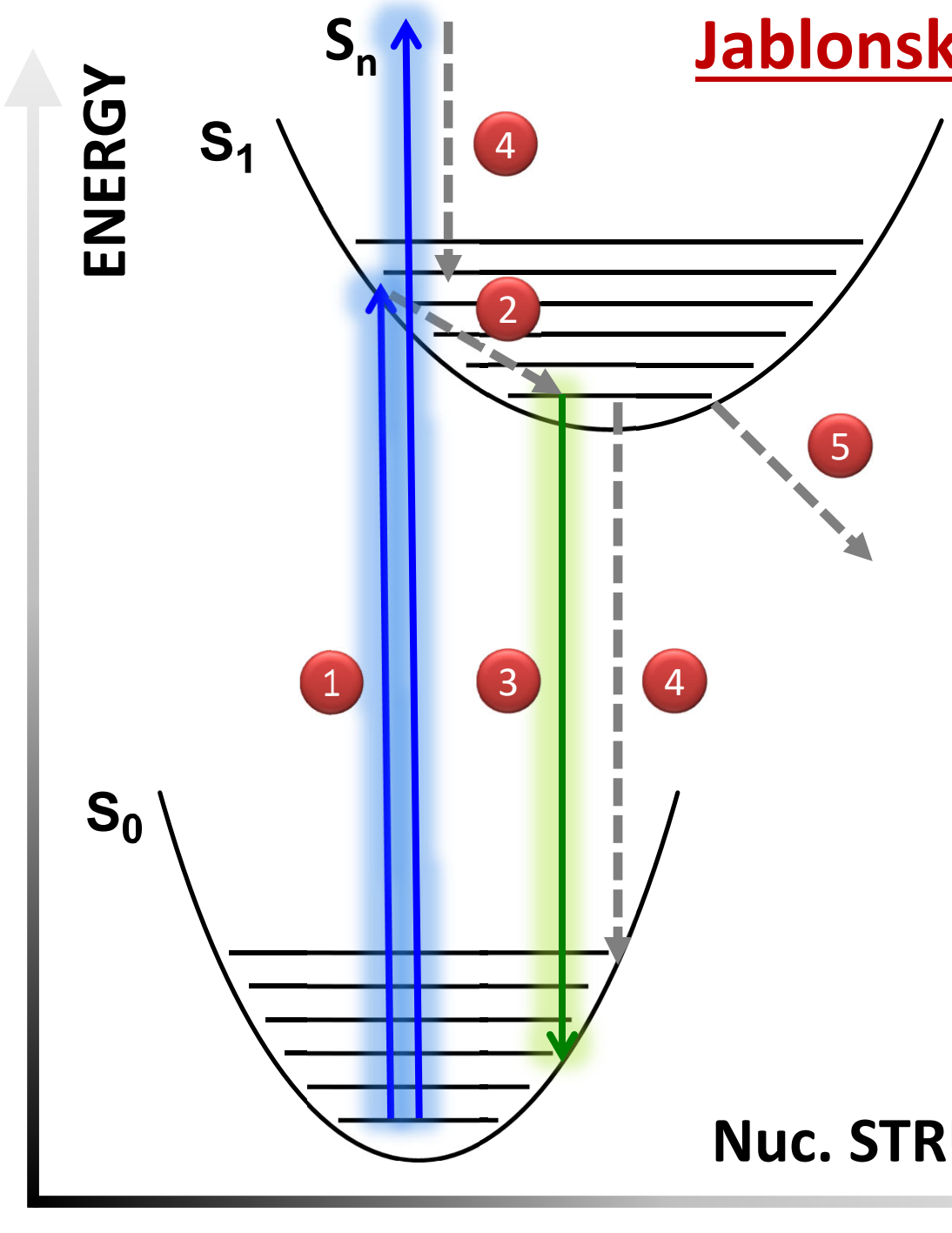
By Jessica Brown

23 July 2019

An exercise of critical thinking

What happens when an organic compound absorbs a photon and how would we quantitatively describe it?

Jablonski Diagram

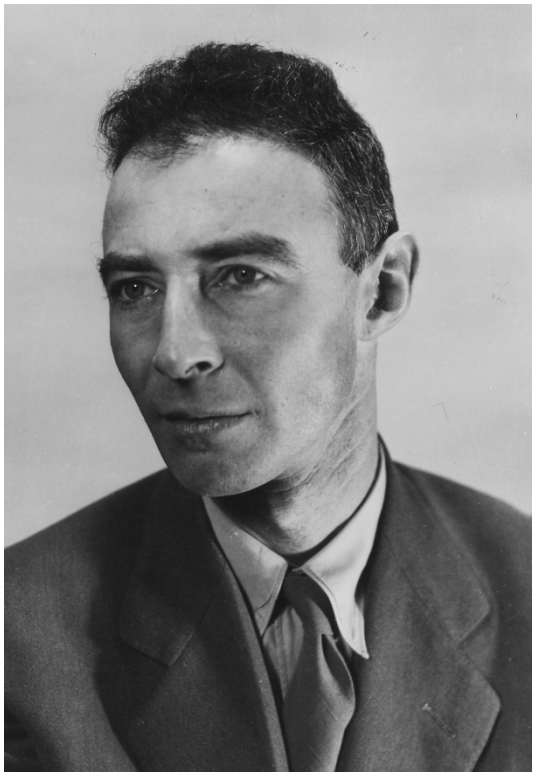


1. Absorption
2. Vibrational relaxation
3. Fluorescence
4. Internal conversion (IC)
5. Other non-radiatives

Born-Oppenheimer Approximation

Max Born

Olivia Newton-John's grandfather



Robert Oppenheimer

The guy in the movie

Pictures taken from Wikipedia

“Physics, as we know it, will be over in six months.”

- Max Born in 1928 after Paul Dirac published his equation

Quark?

Neutrino?

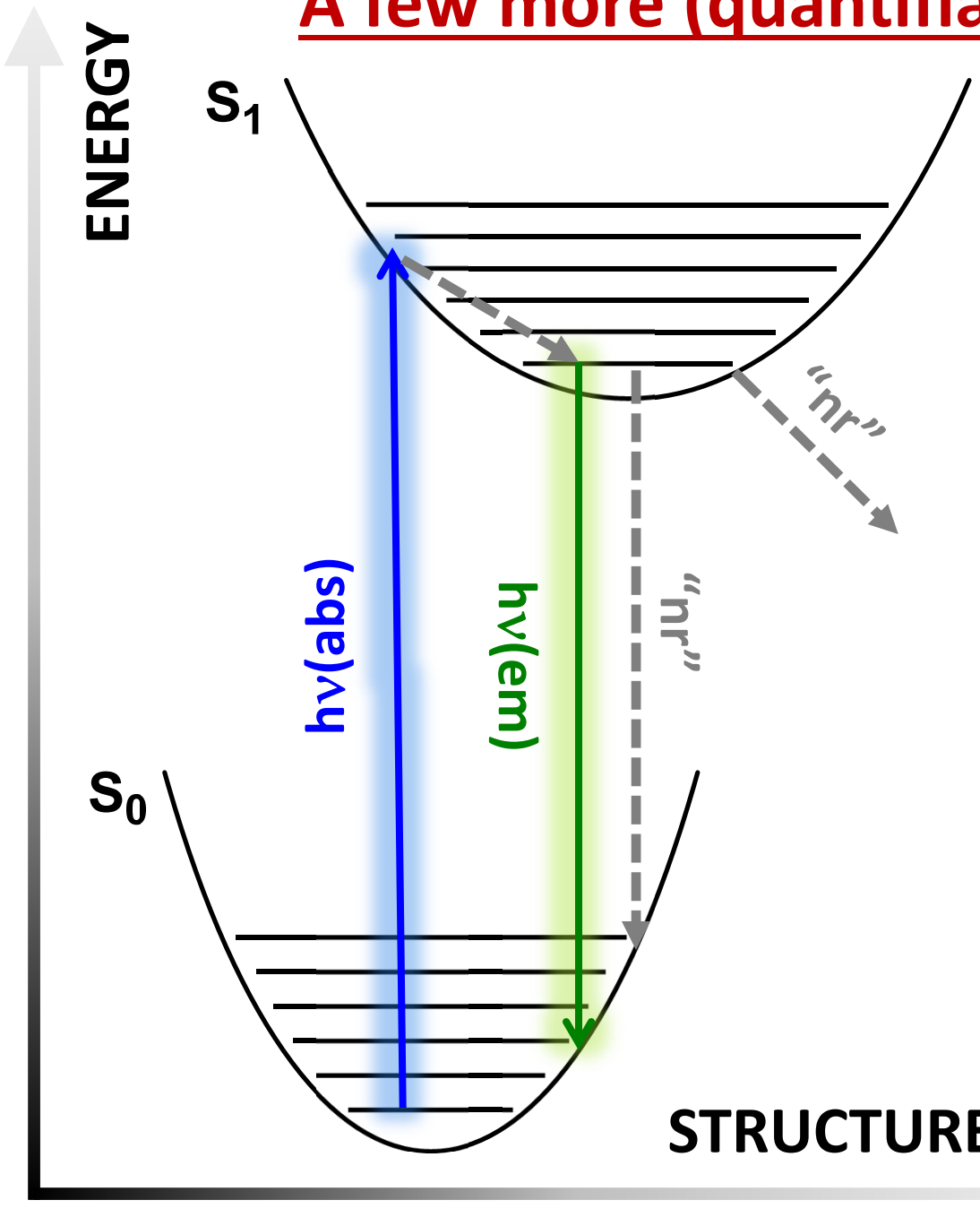
Black hole?

…

…

…

A few more (quantifiable) concepts



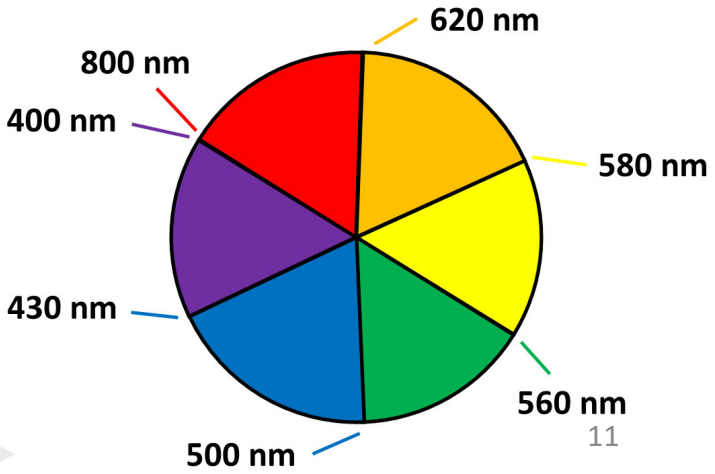
$$E = h\nu = h\frac{c}{\lambda}$$

Vertical radiative transitions

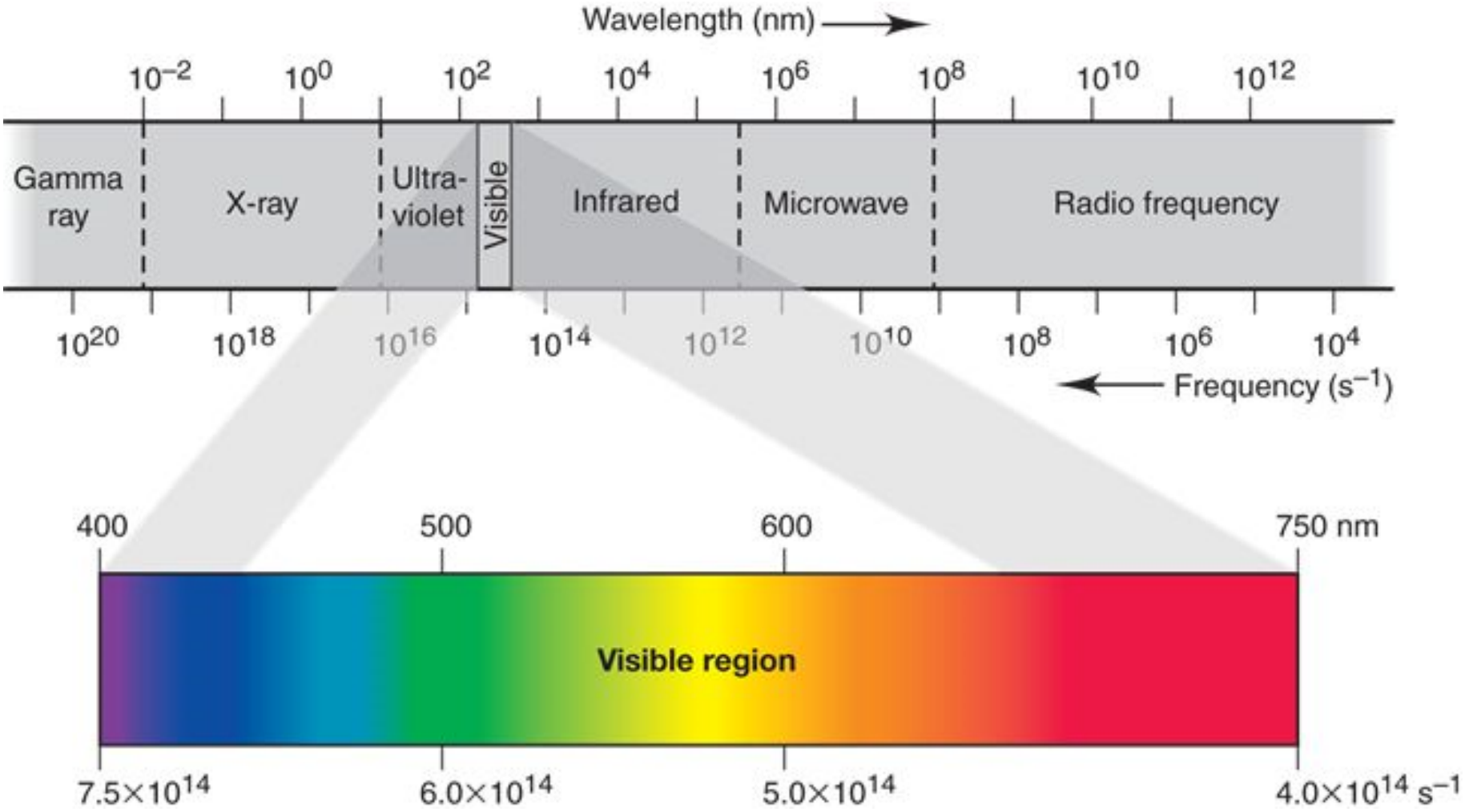
$$h\nu(abs) > h\nu(em)$$

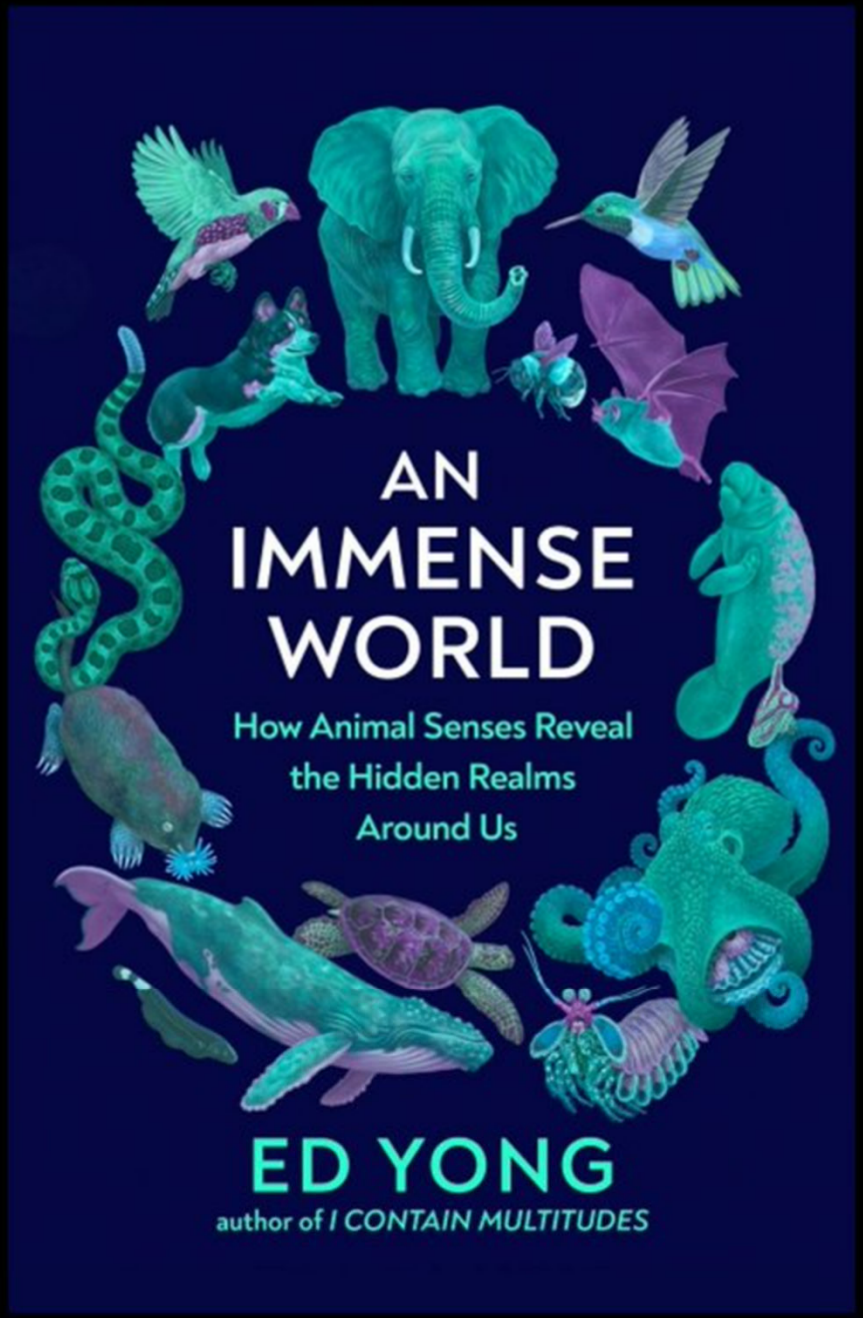
$$\phi_f = \frac{k_r}{k_r + \sum k_{nr}}$$

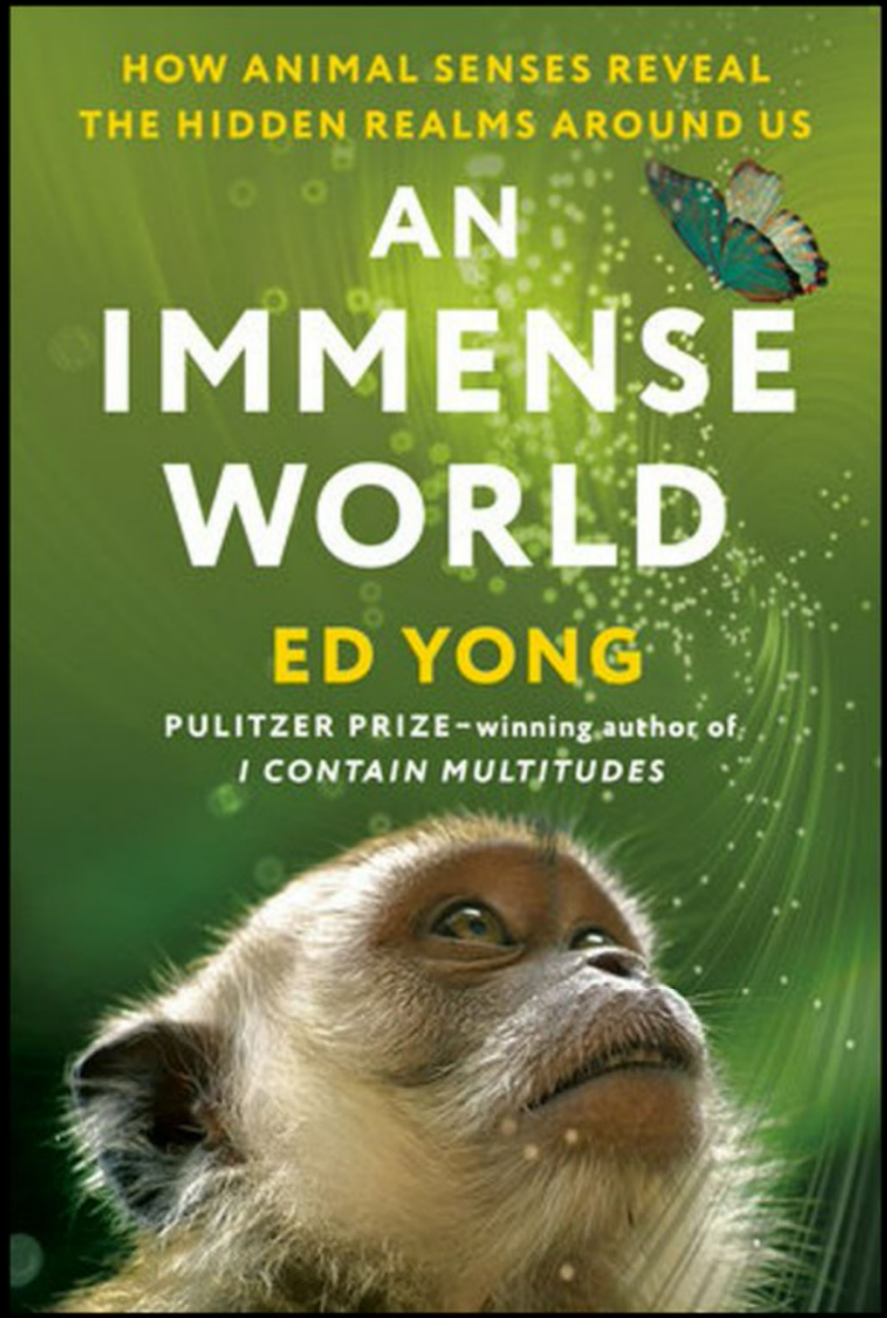
$$\tau = \frac{1}{k_r + \sum k_{nr}}$$



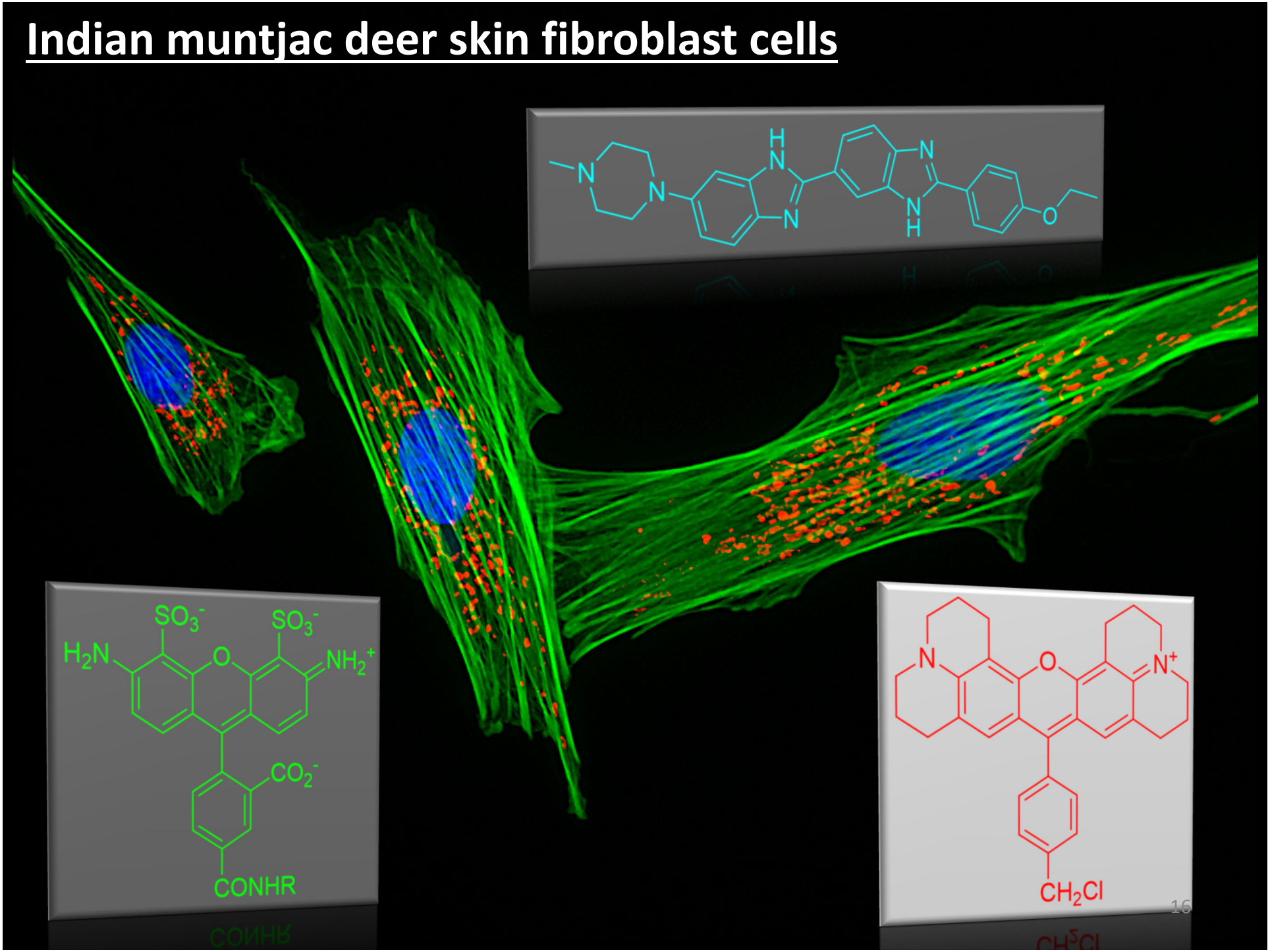
We (visually) perceive a tiny sliver of the physical world




AN
IMMENSE
WORLD
How Animal Senses Reveal
the Hidden Realms
Around Us
ED YONG
author of I CONTAIN MULTITUDES

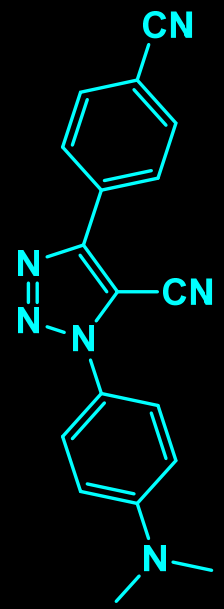

HOW ANIMAL SENSES REVEAL
THE HIDDEN REALMS AROUND US
AN
IMMENSE
WORLD
ED YONG
PULITZER PRIZE–winning author of
I CONTAIN MULTITUDES

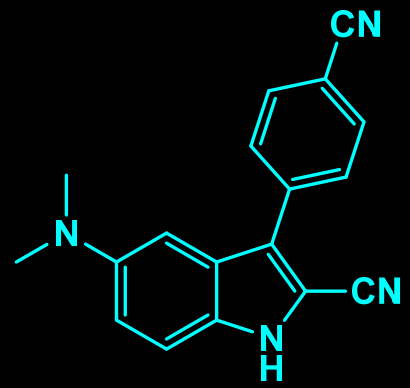
Indian muntjac deer skin fibroblast cells



Cosmic Baseball

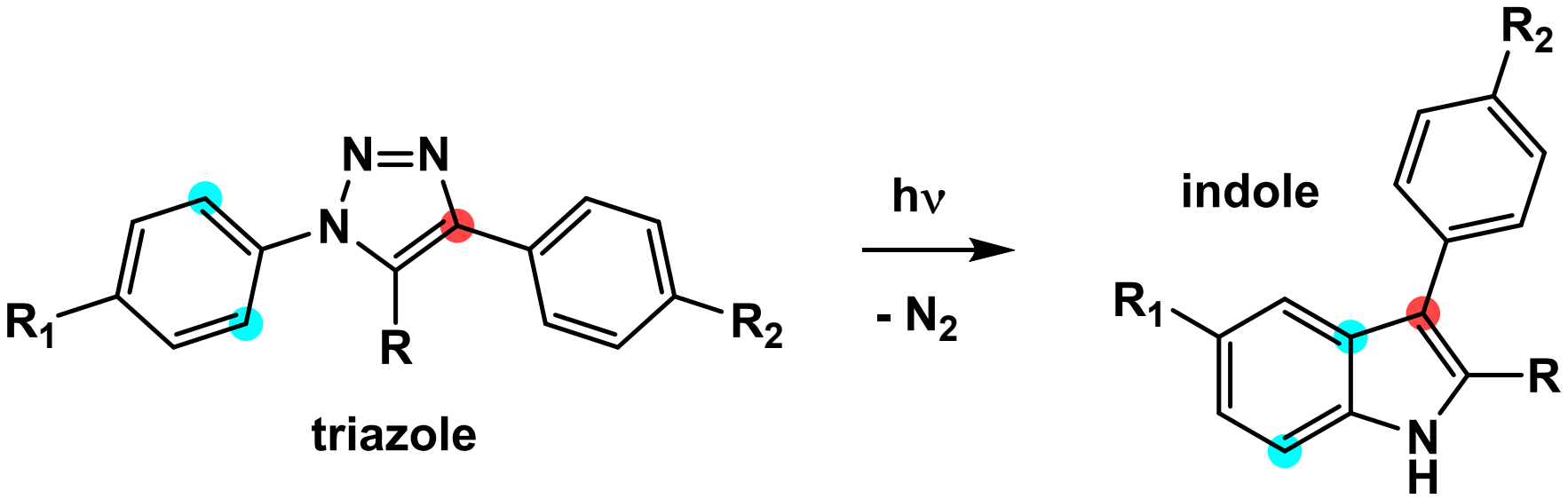
Fluorescent Triazoles and Indoles





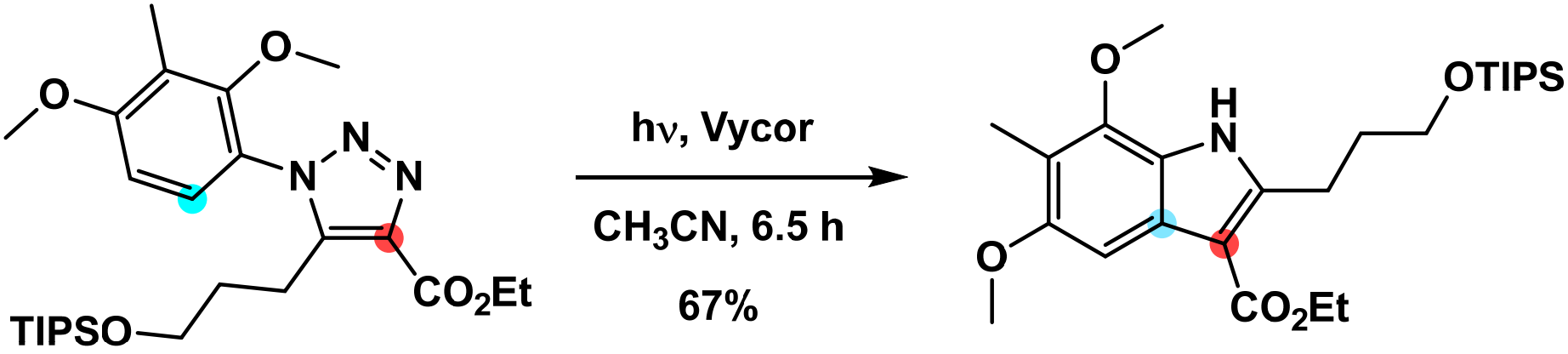
Joe Accardo, Brandon Nusser

Photochemical conversion to indole



The earliest reference that I can find:
"Photochemical Decomposition of 1H-1,2,3-Triazole Derivatives"
Burgess and coworkers, *J. Am. Chem. Soc.* **1968**, *90*, 1923-1924.

An early example of triazole photoconversion to indole



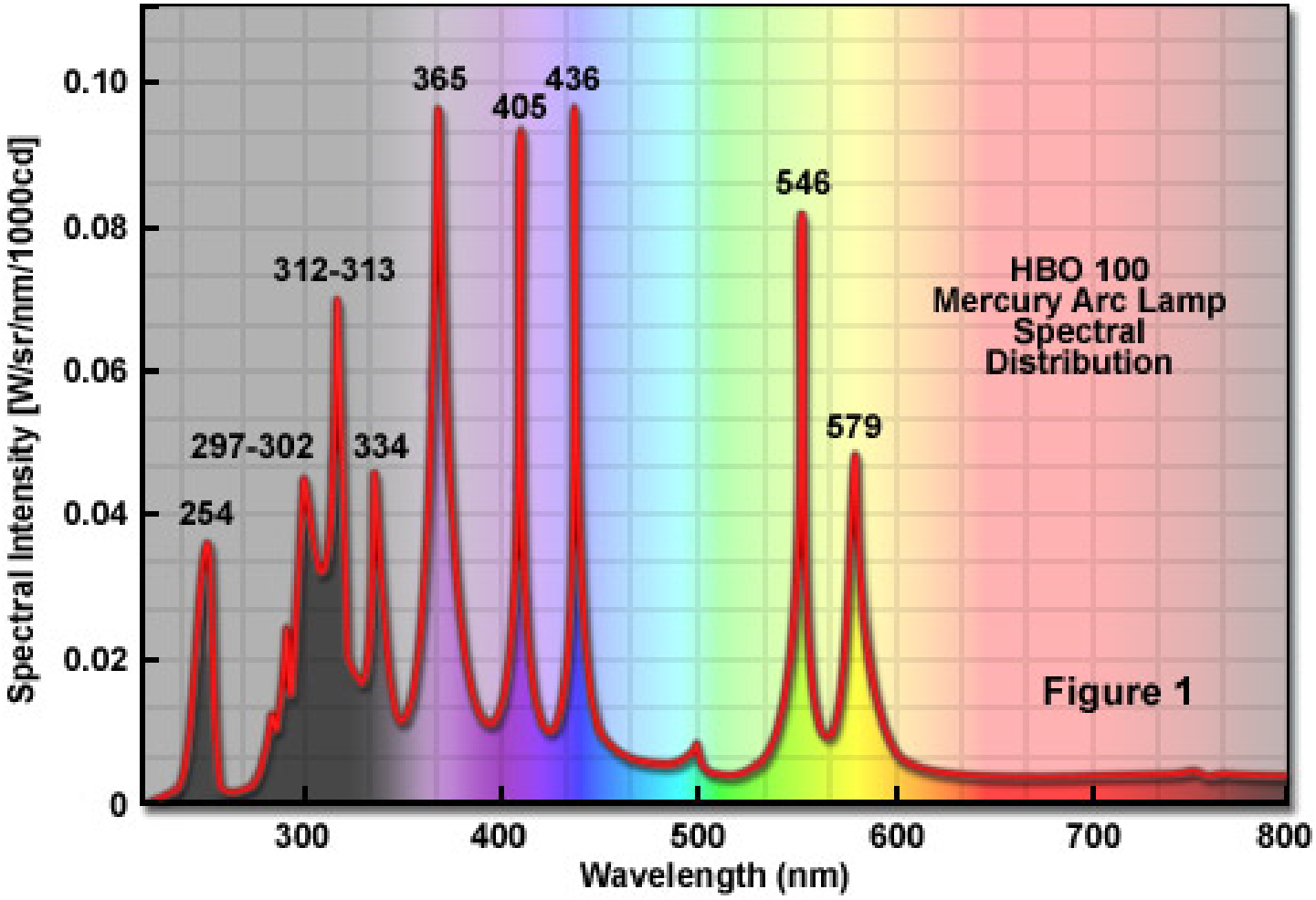
Light source?

Reaction vessel?

Concentration?

Wender and Cooper, *Tetrahedron Lett.* **1987**, *28*, 6125-6128.

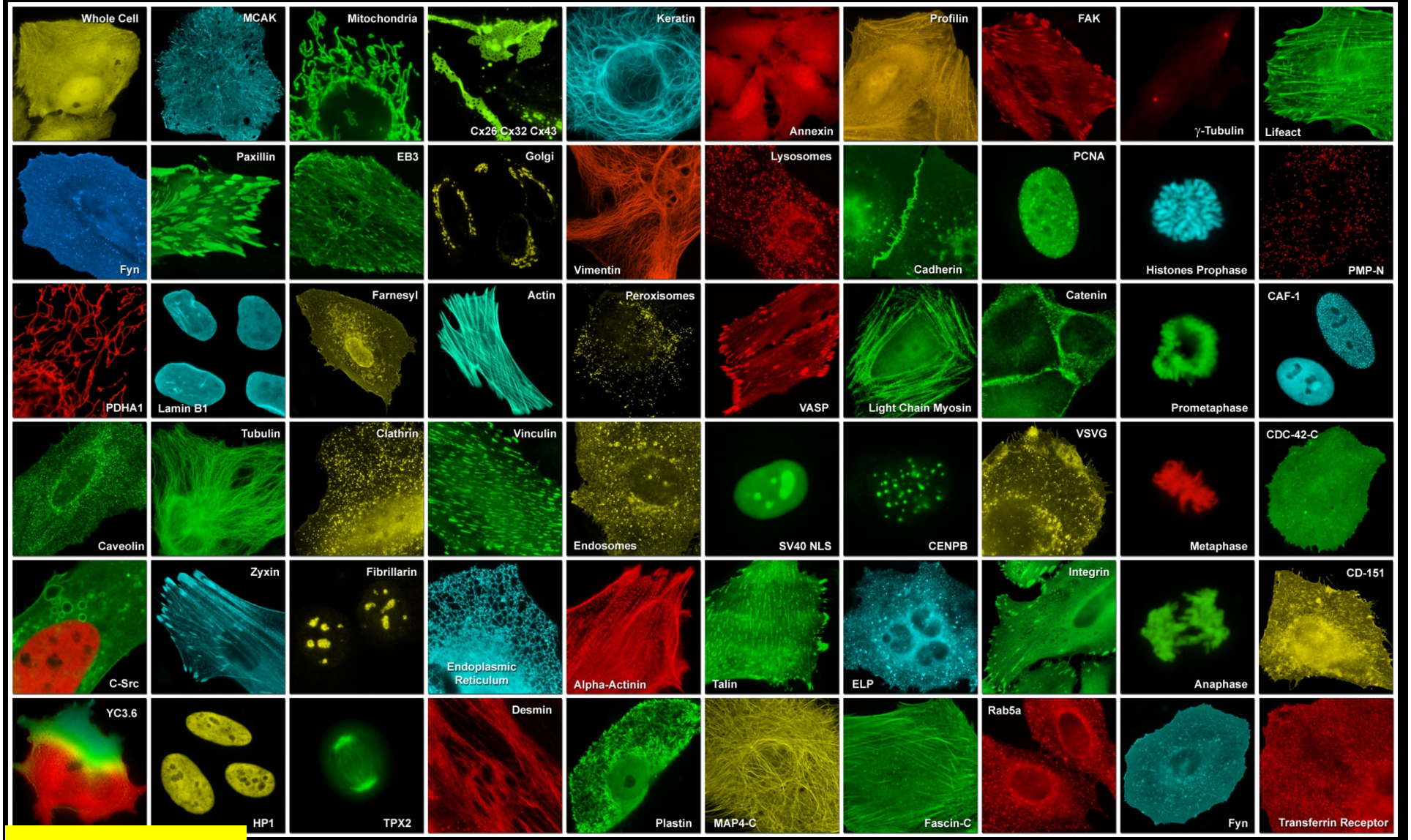
Light Source



Michael W. Davidson, https://zeiss-campus.magnet.fsu.edu/articles/lightsources/mercuryarc.html

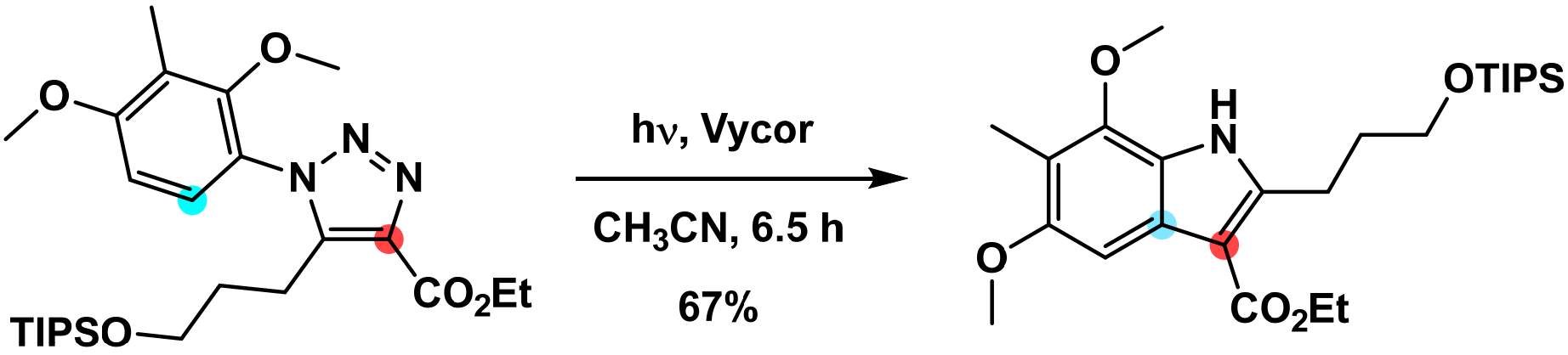
ART

Fluorescent Protein Fusions for Live Cell Imaging



SCIENCE

An early example of triazole photoconversion to indole



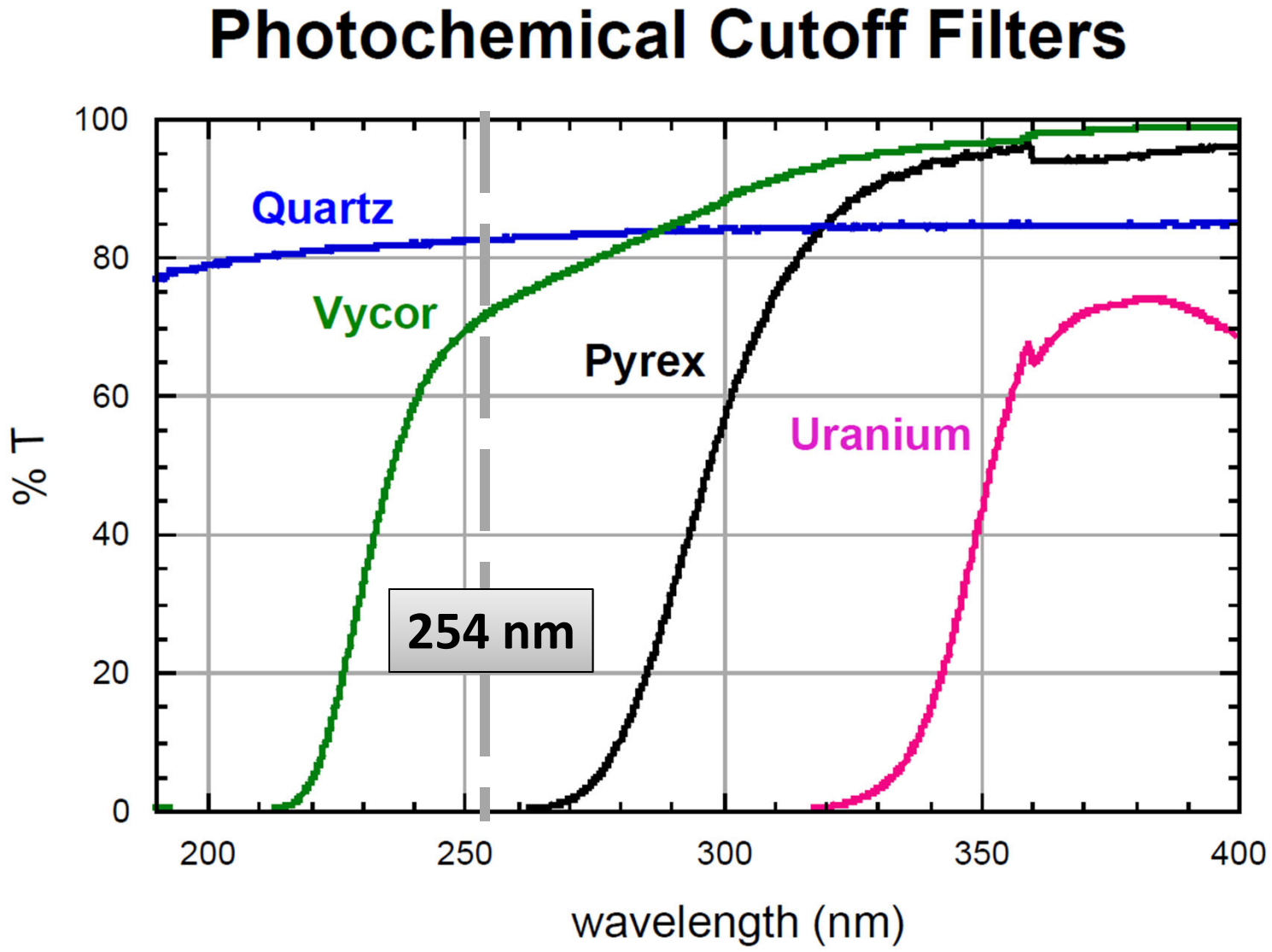
Light source?

Reaction vessel?

Concentration?

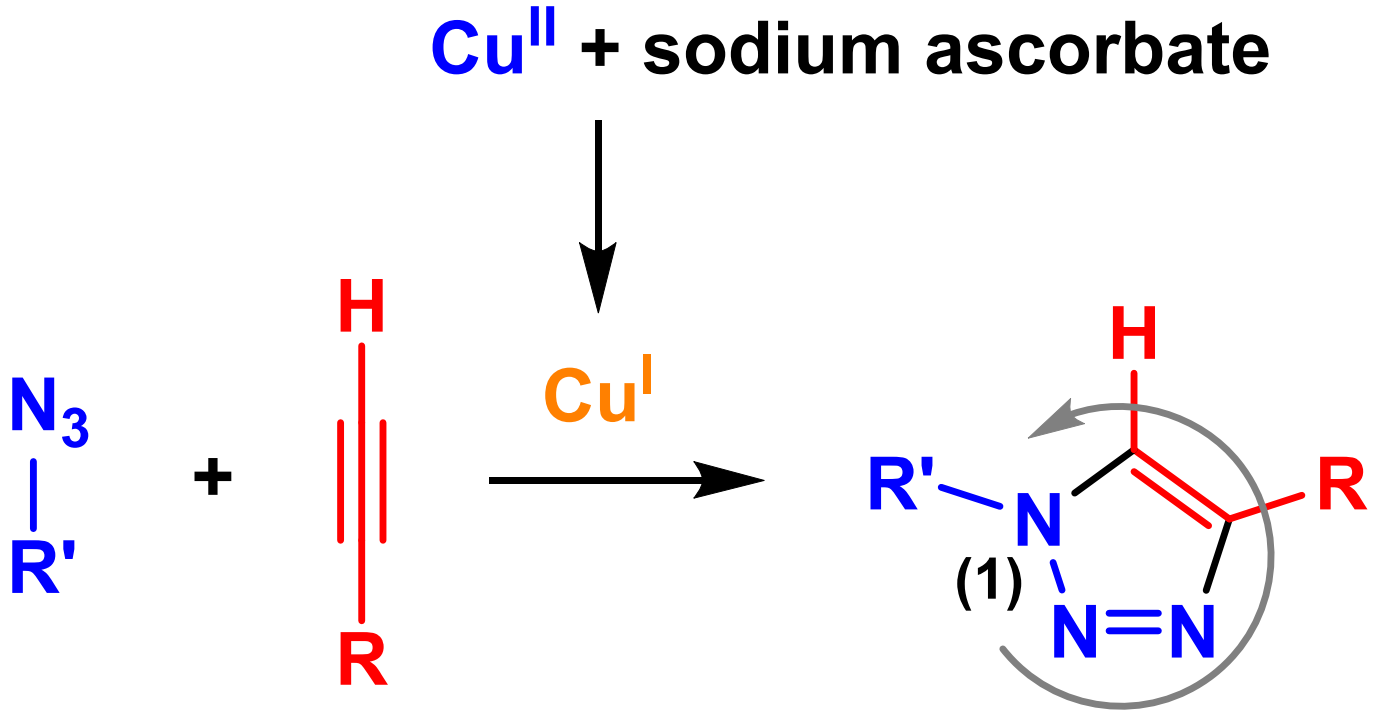
Wender and Cooper, *Tetrahedron Lett.* **1987**, *28*, 6125-6128.

Reaction vessel



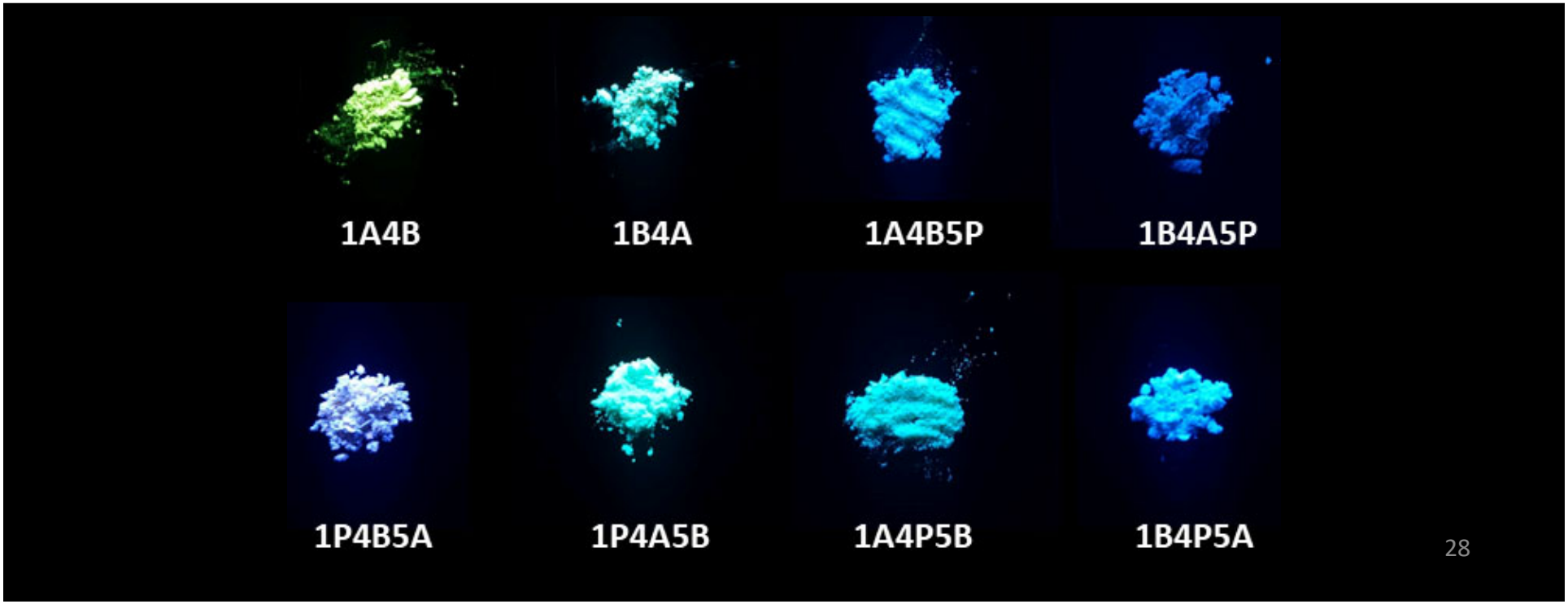
Google found this

Cu(I)-catalyzed azide-alkyne cycloaddition – triazole formation

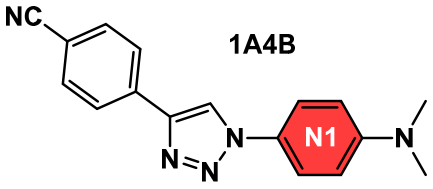


M. Meldal and coworkers, *J. Org. Chem.* **2002**, *67*, 3057.

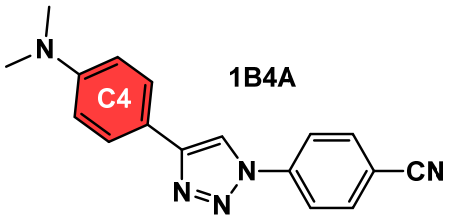
V. V. Fokin, K. B. Sharpless, and coworkers, *Angew. Chem. Int. Ed.* **2002**, *41*, 2596.


1A4B
1B4A
1A4B5P
1B4A5P
1P4B5A
1P4A5B
1A4P5B
1B4P5A

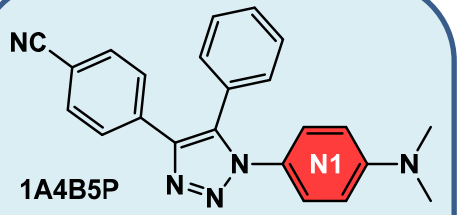
Outcomes of photoconversion



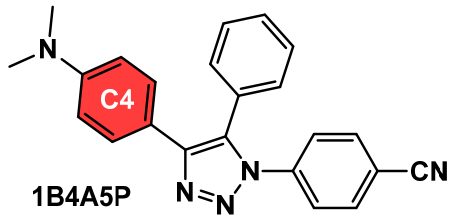
40%



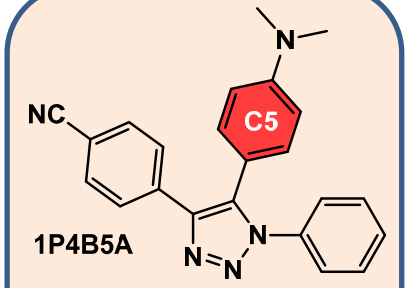
33%



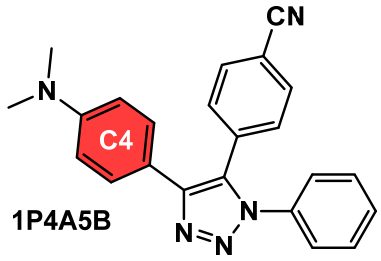
69% (57/12)



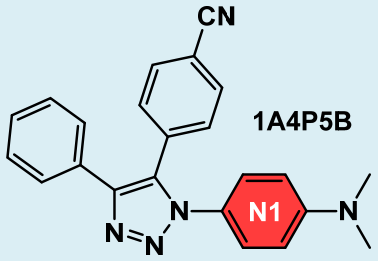
33%



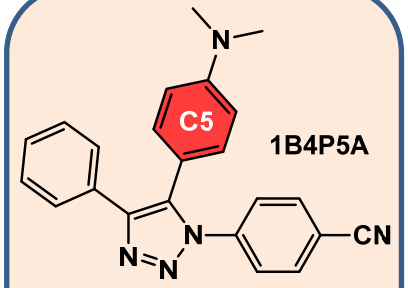
trace



17%



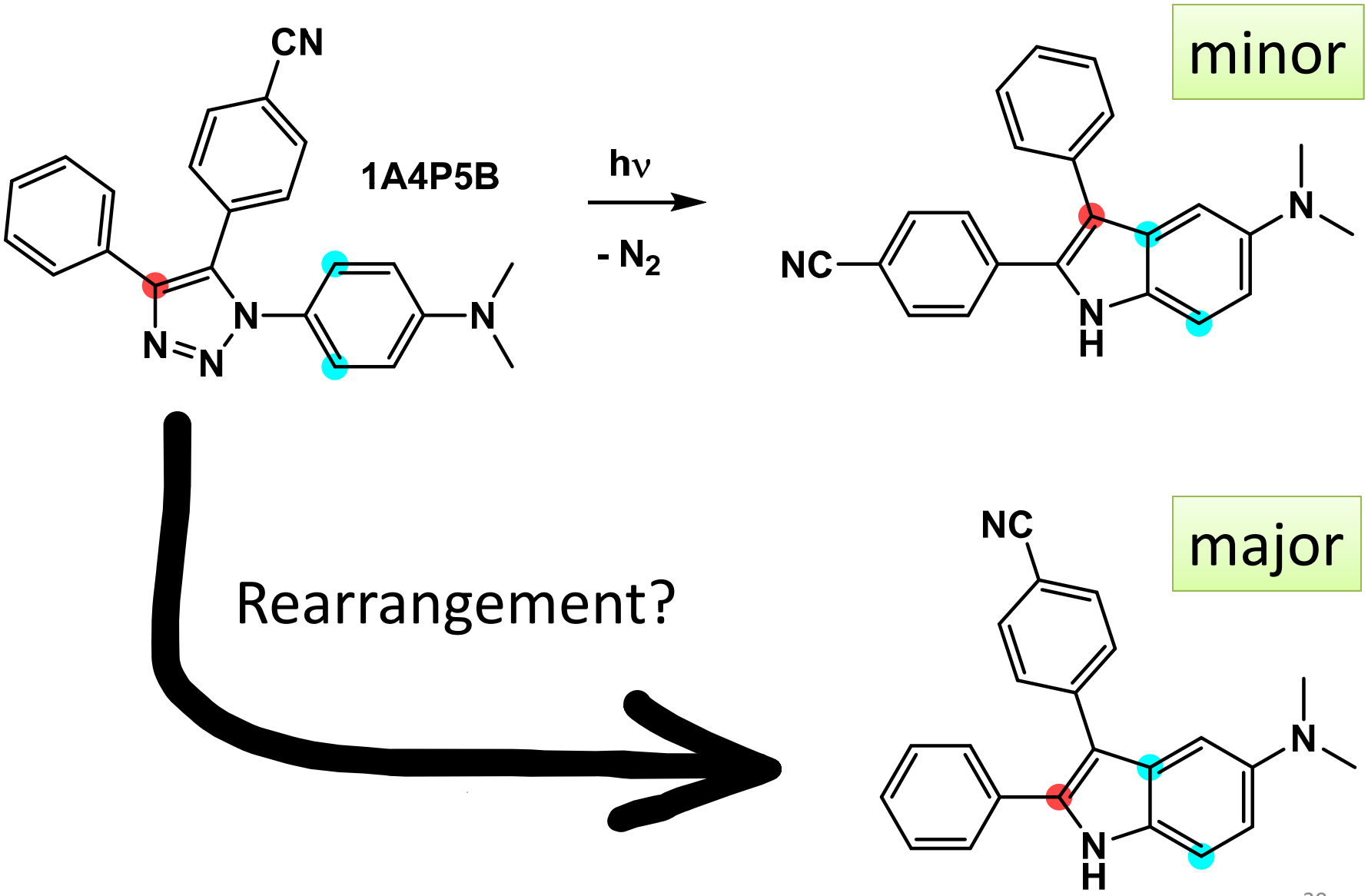
76% (51/25)



5%

Conditions: irradiation using 390-nm LED for 6 hours. [] = 1.5 mM in acetonitrile.

Two indole isomers

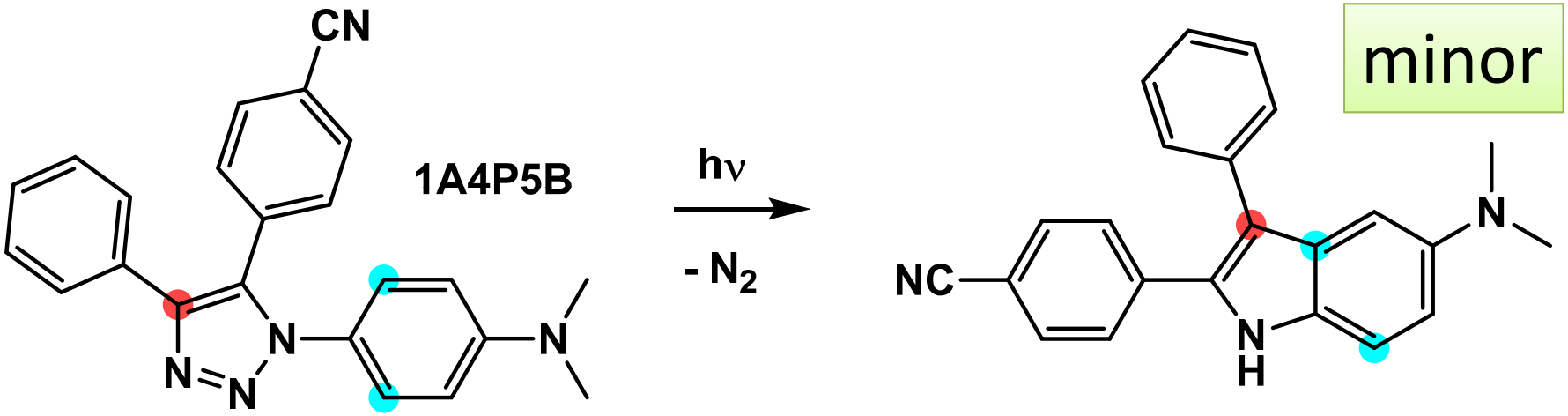


Factors on conversion

Original conditions: irradiation using 390-nm LED for 6 hours. [] = 1.5 mM in acetonitrile.

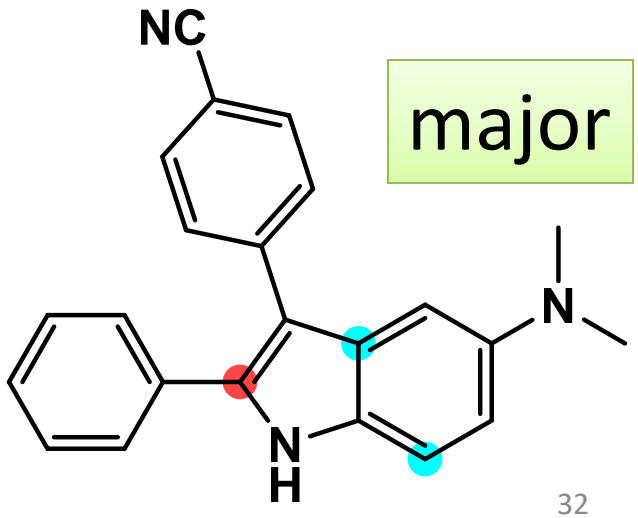
- Solvent
- Irradiation power and wavelength
- Light penetration (pathlength, conc., turbidity)
- Distance from the light source
- Temperature; Additives

Changing solvent from acetonitrile to dichloromethane

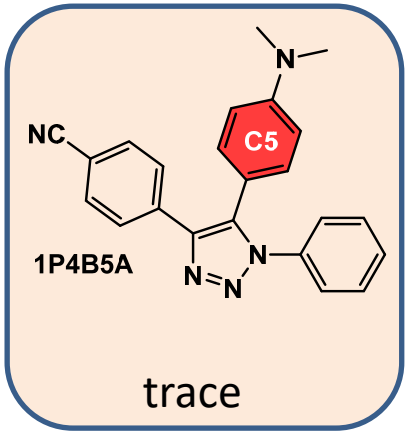


Acetonitrile: 76% in 6 hours

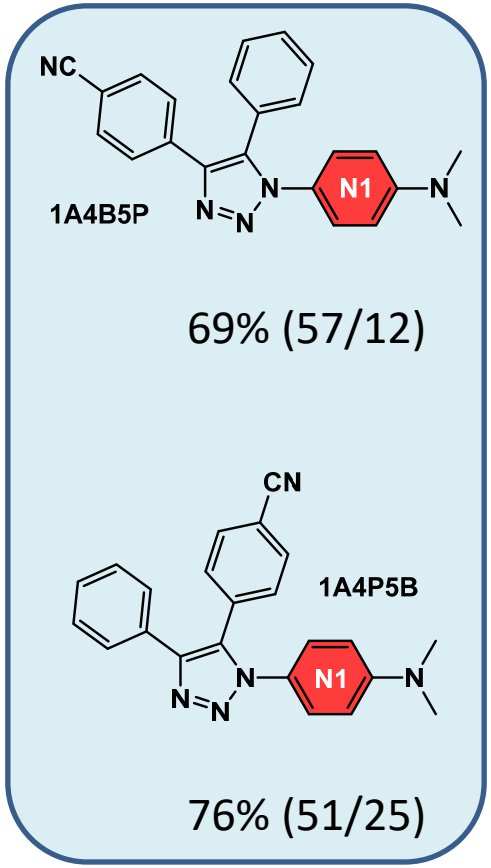
DCM: 100% in 30 minutes

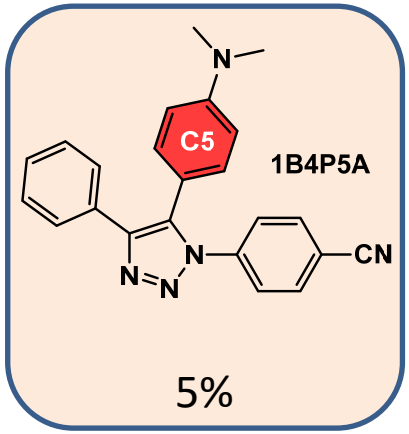


Explain the outcomes of photoconversion



trace

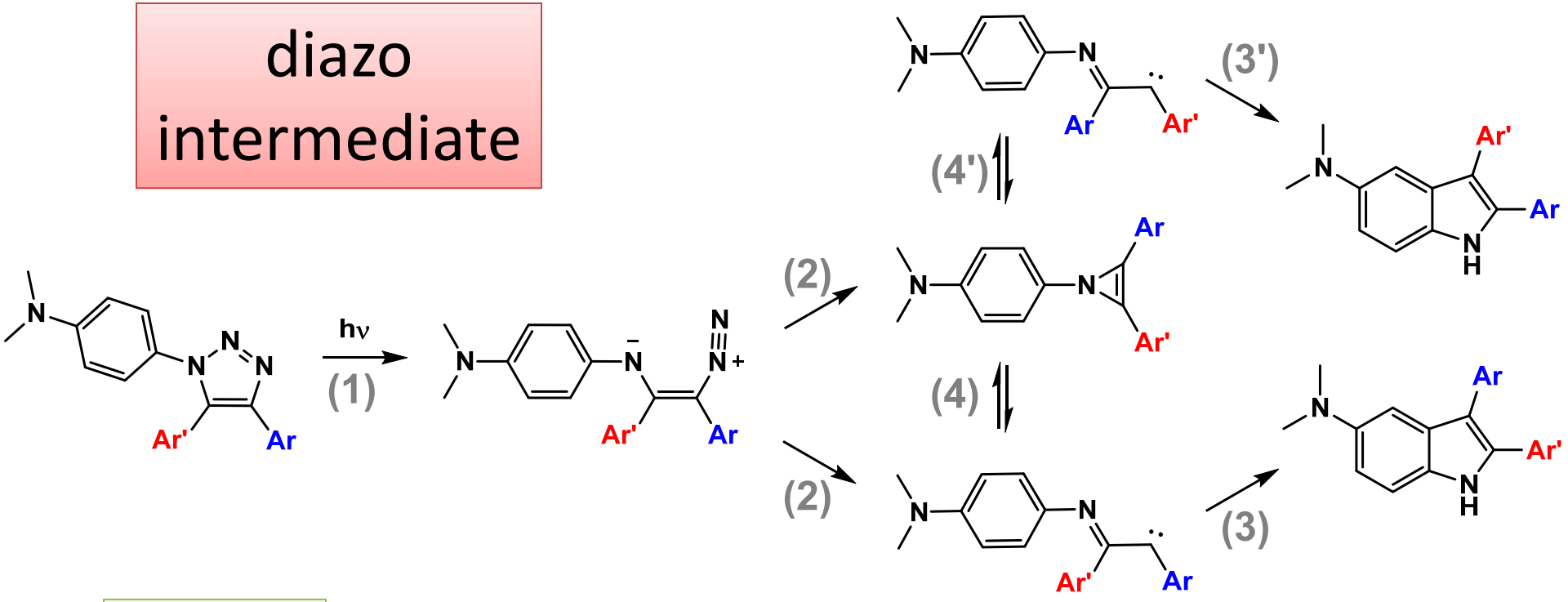




Brandon Nusser, et al. *ChemPhysChem* **2023**, *24*, e202300209.

Key (proposed) mechanistic steps

diazo intermediate



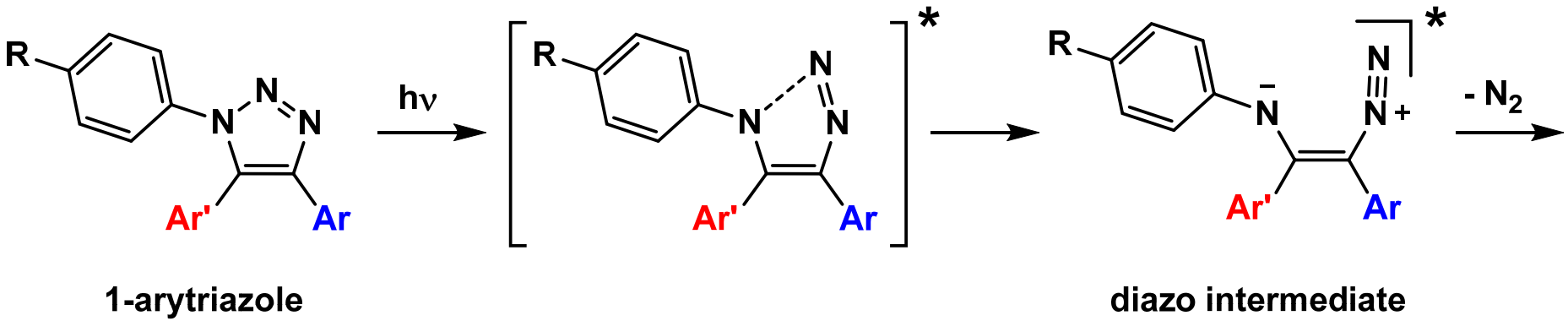
azirine

carbene

indole

triazole

Reactivity



1-arytriazole

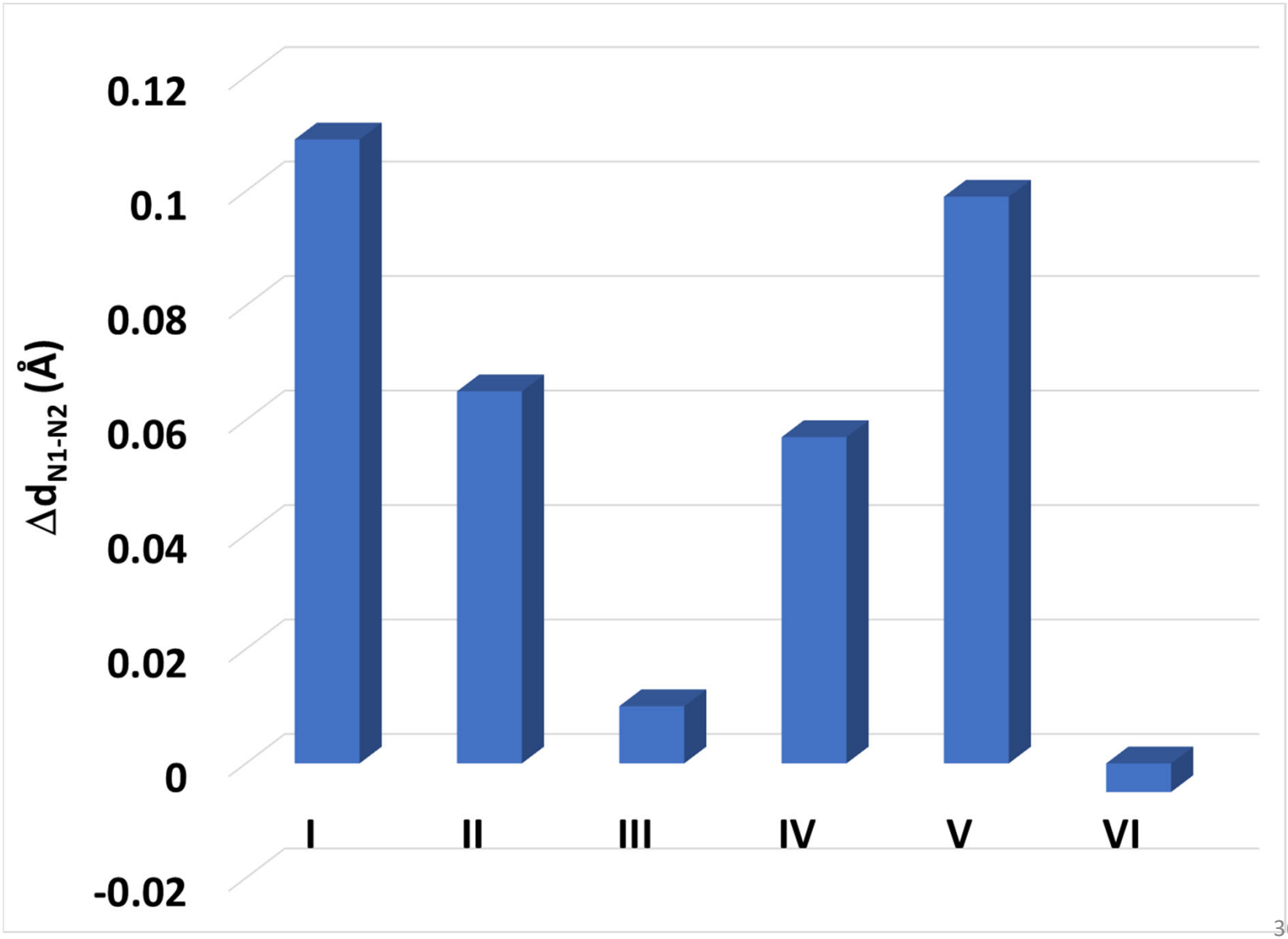
diazo intermediate

Telltale signs of geometric changes?

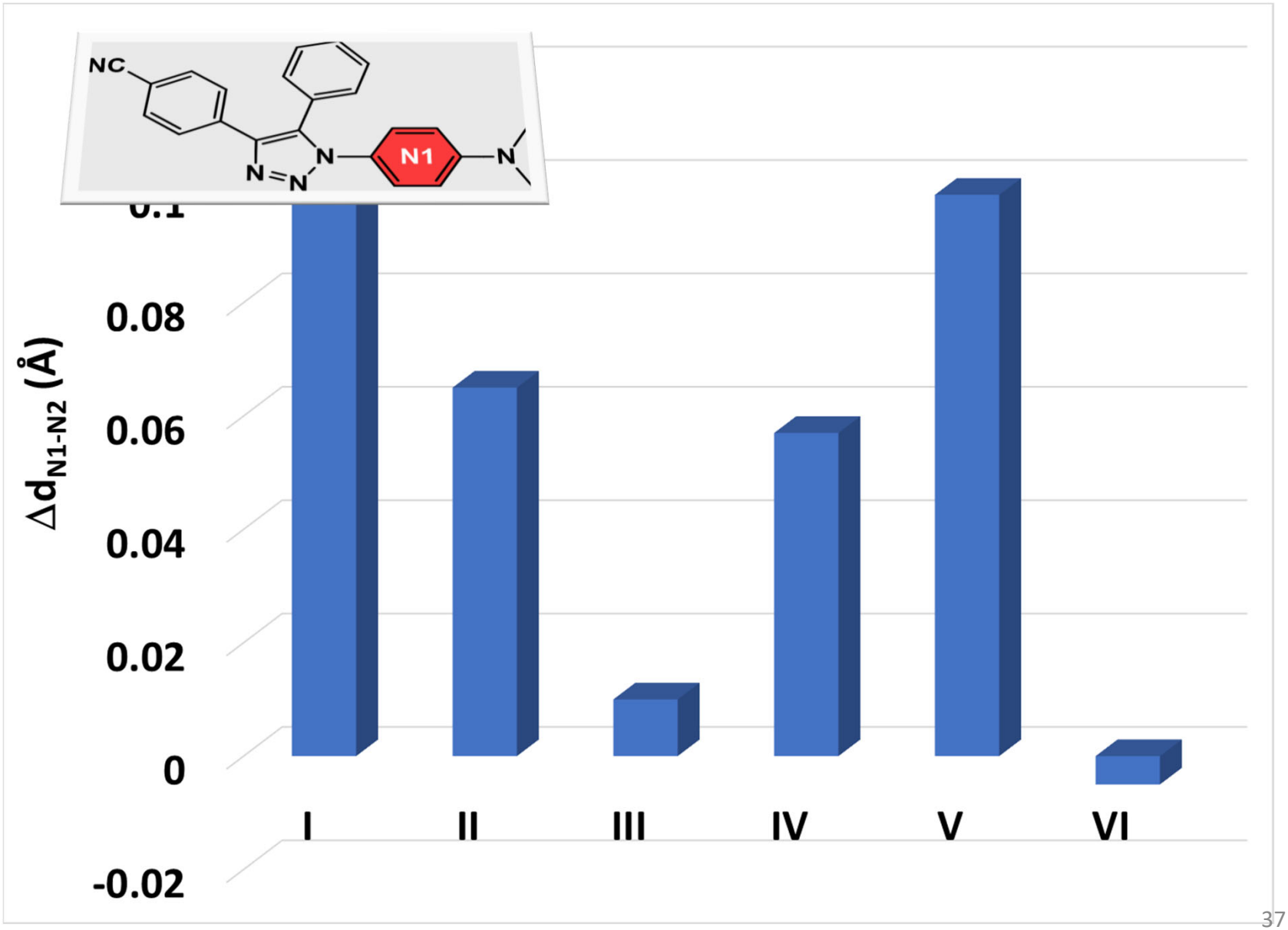
Energy barrier of each step?

A way to return to the ground state?

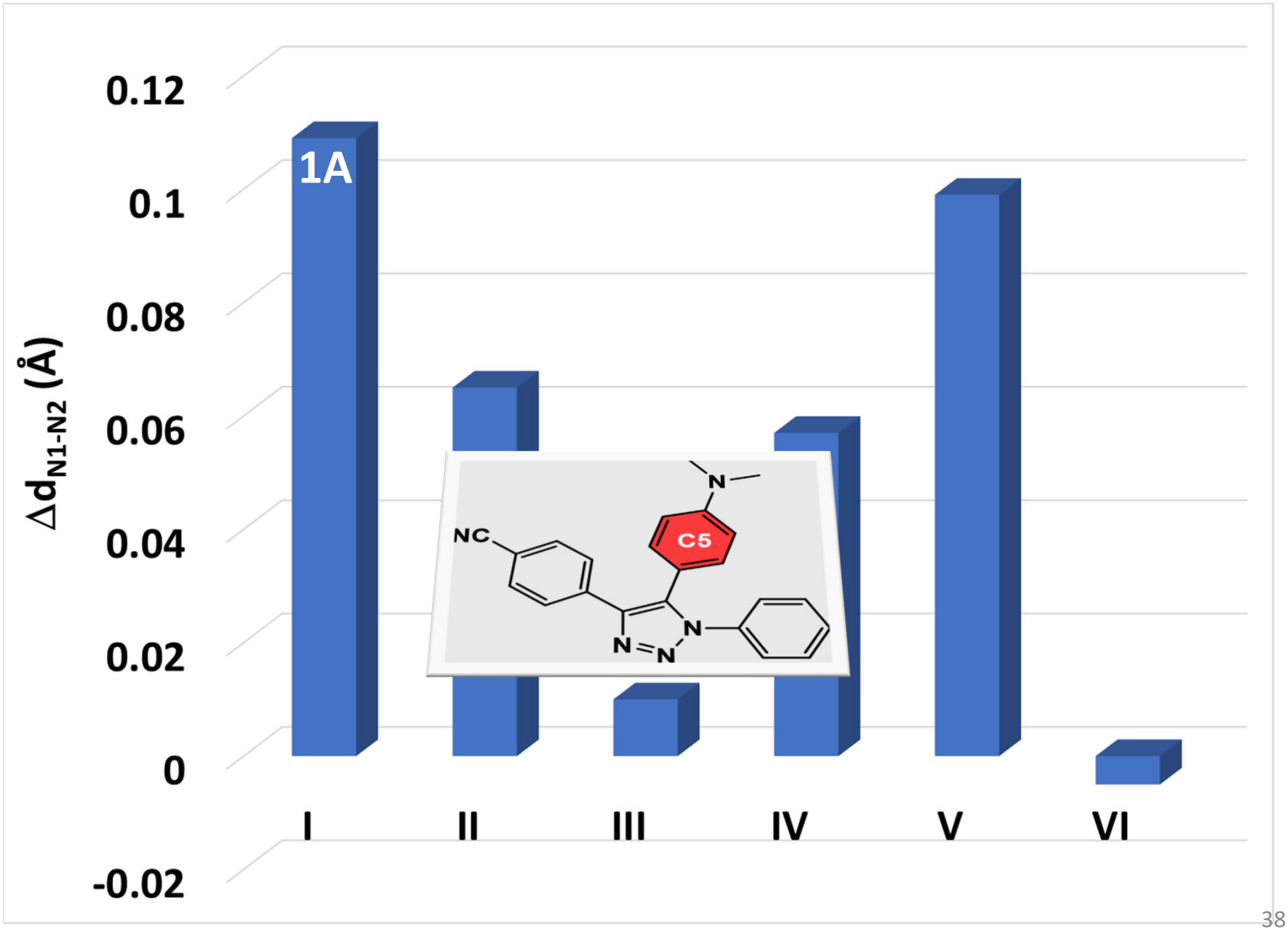
N1-N2 distance change upon excitation



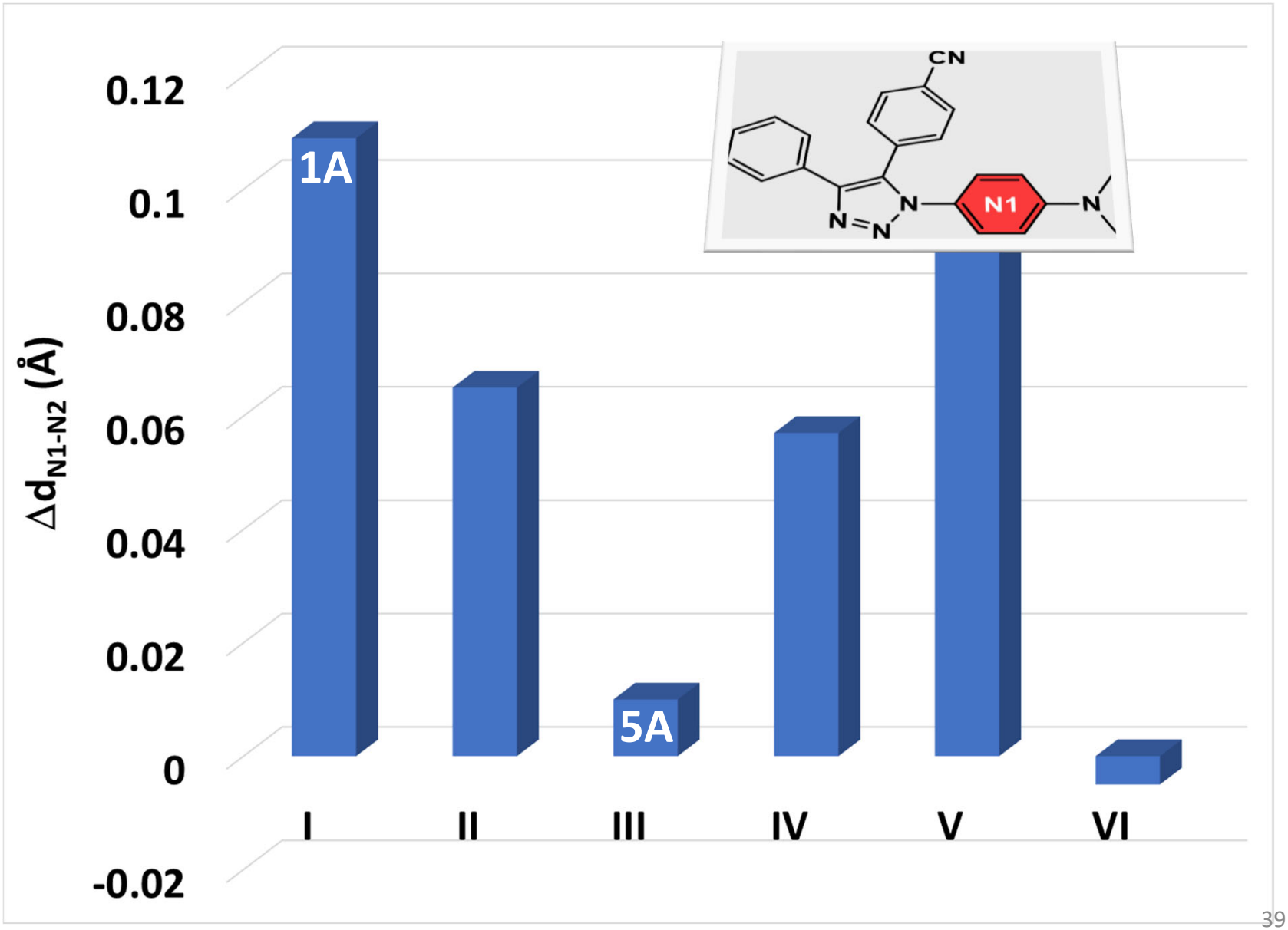
N1-N2 distance change upon excitation



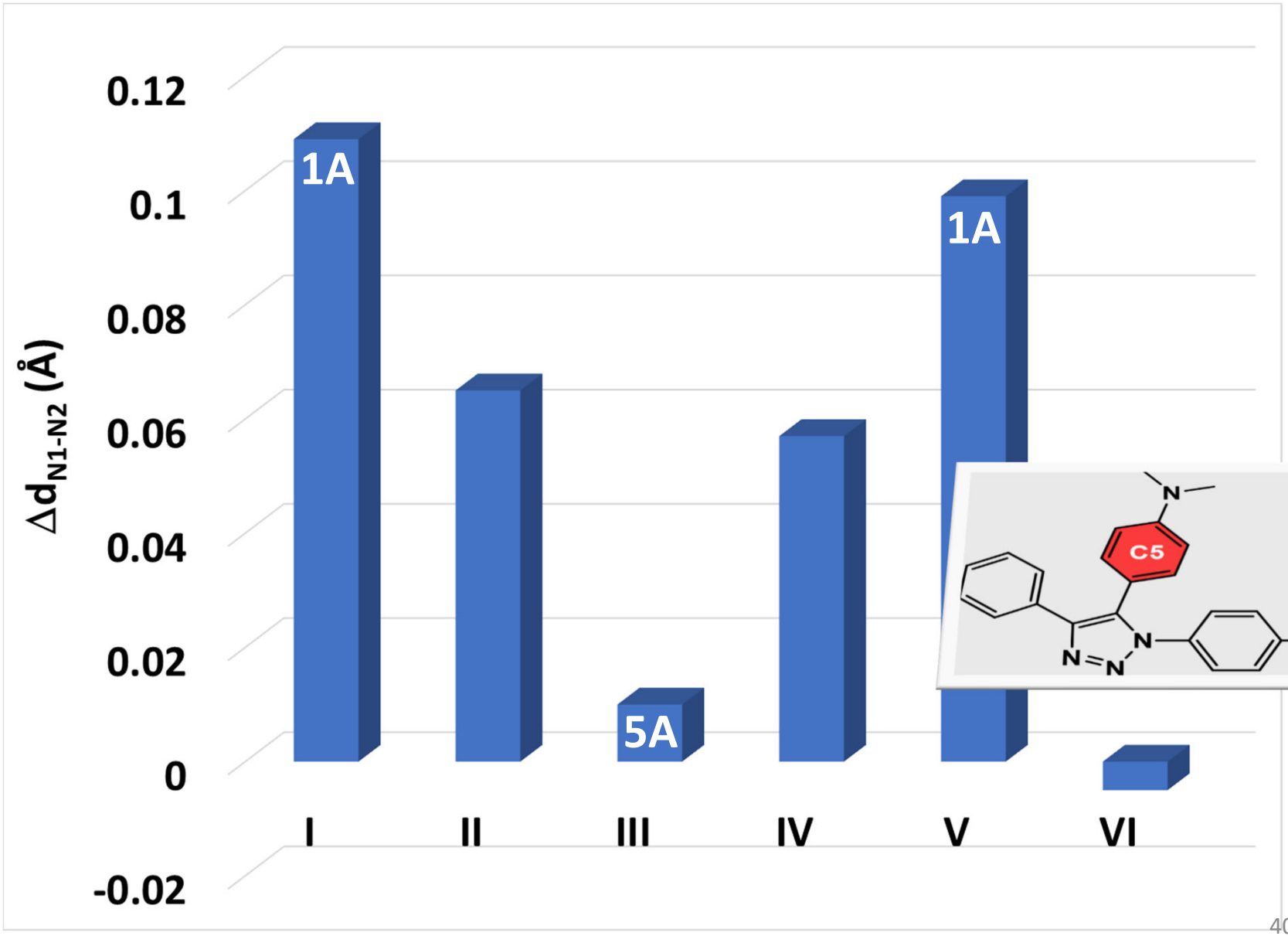
N1-N2 distance change upon excitation



N1-N2 distance change upon excitation

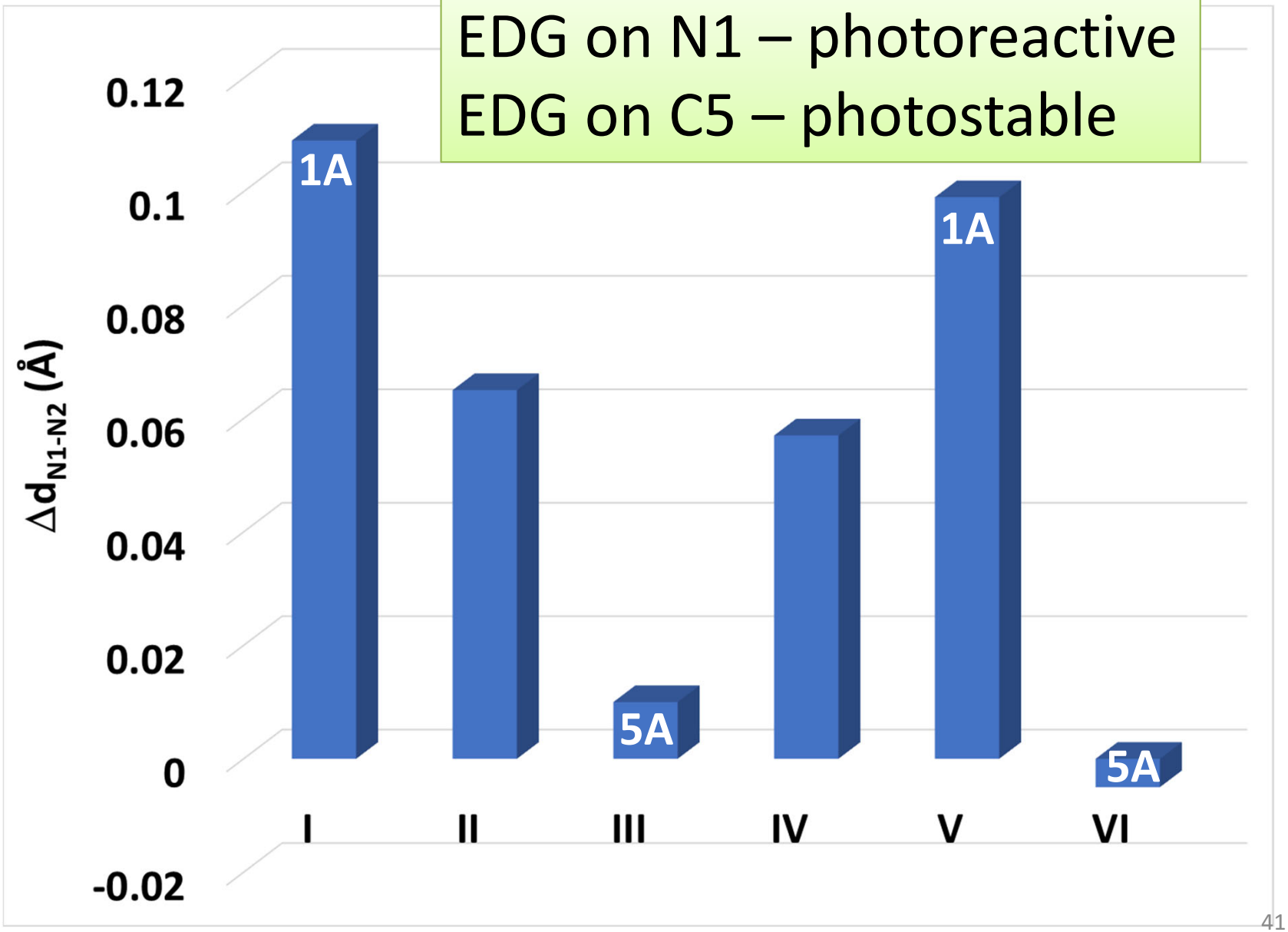


N1-N2 distance change upon excitation

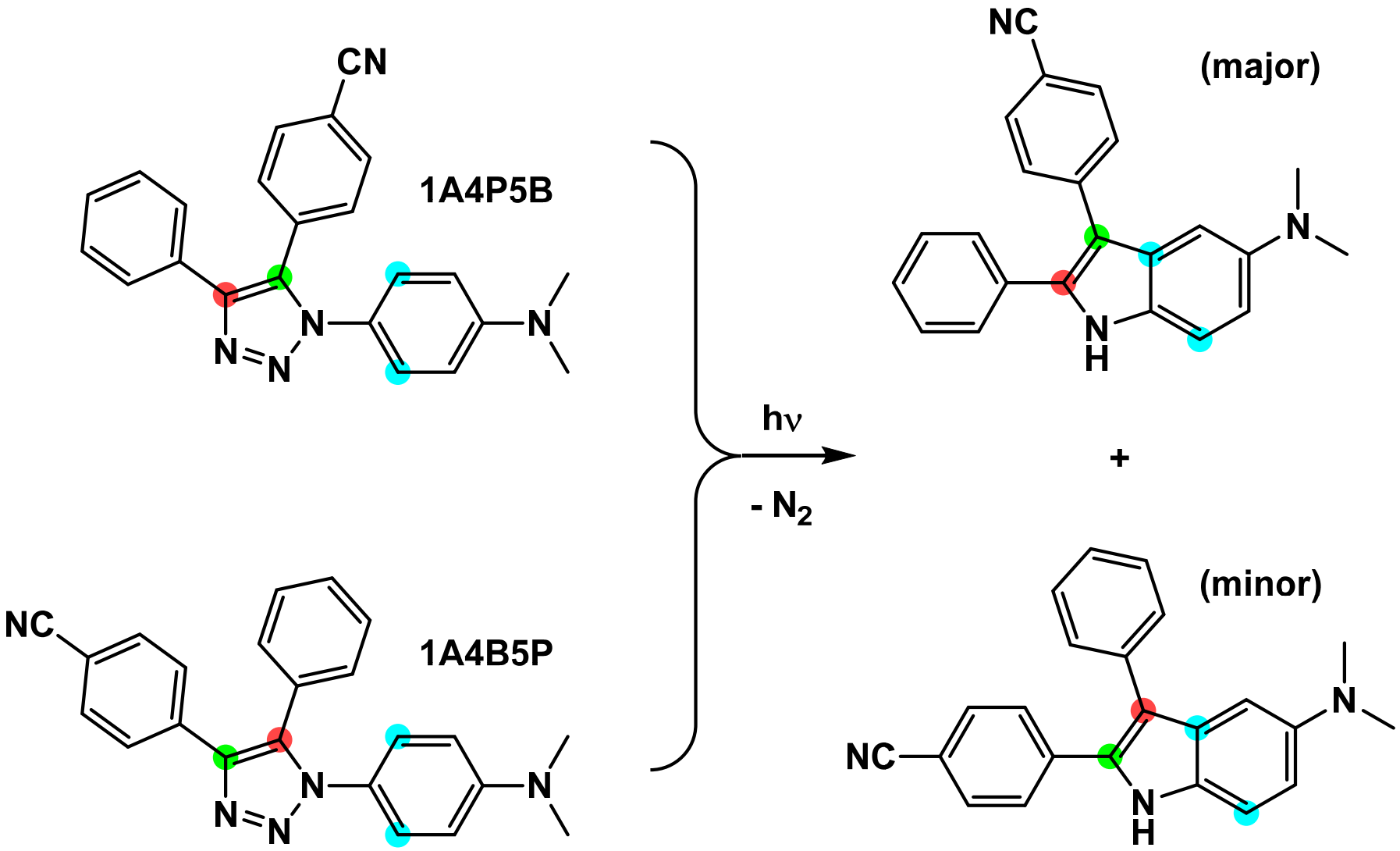


N1-N2 distance change upon excitation

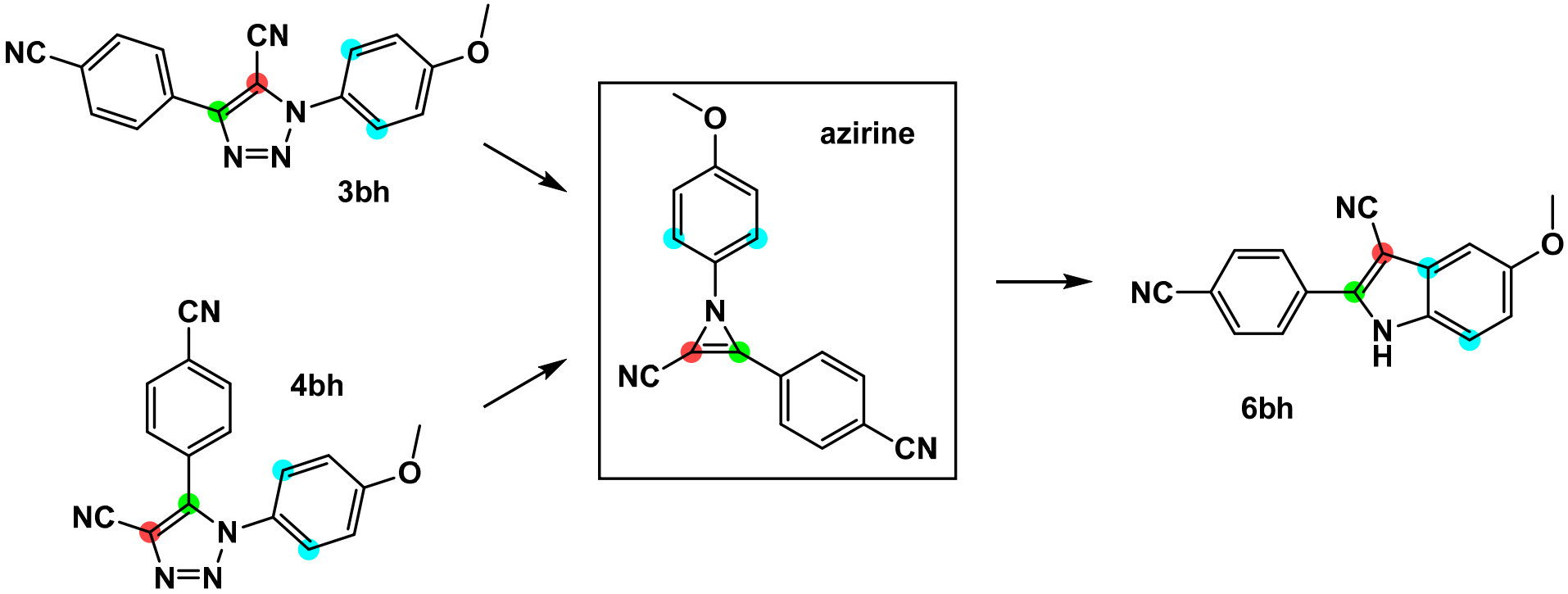
EDG on N1 – photoreactive
EDG on C5 – photostable



Selectivity – Case #1

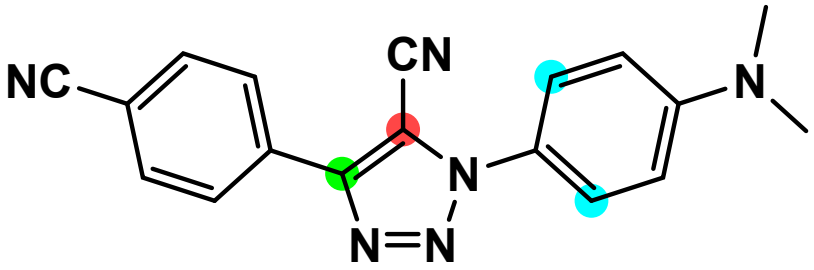


Selectivity – Case #2

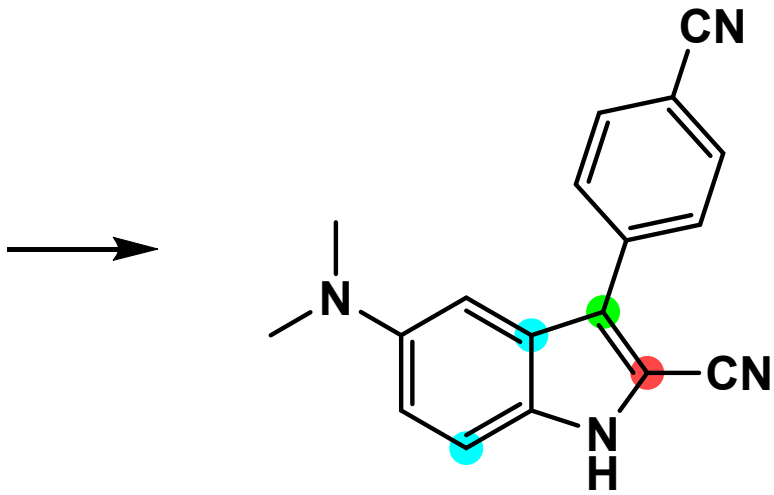


Brandon Nusser and others, *Submitted*.

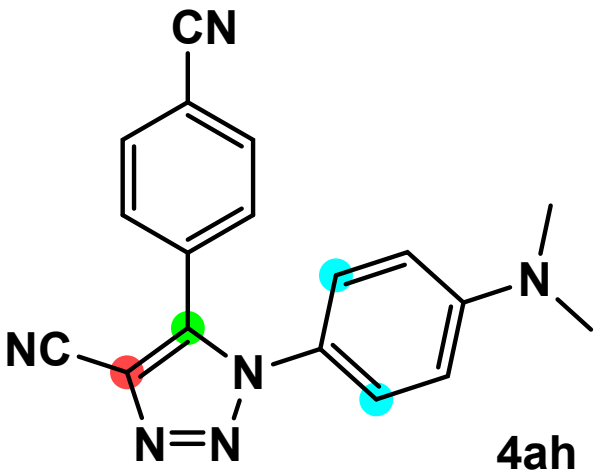
Selectivity – Case #3



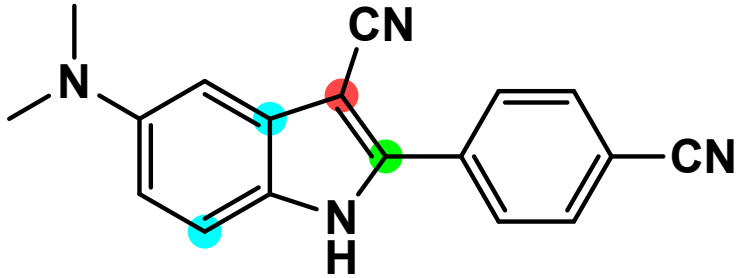
3ah



5ah



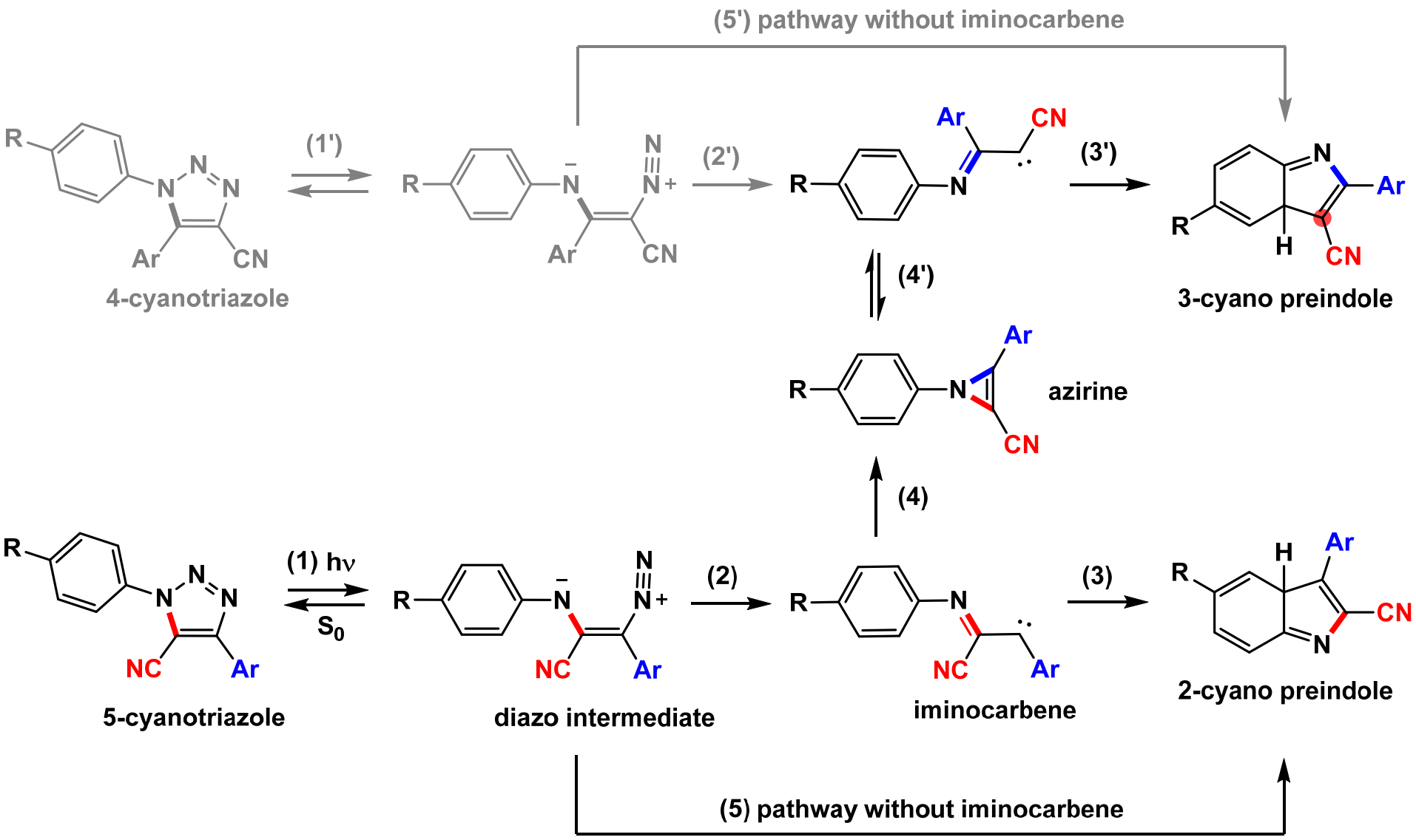
4ah



6ah

Brandon Nusser and others, *Submitted*.

Selectivity of cyanotriazole photoconversion



ACKNOWLEDGEMENT

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