

XU GROUP  
*Department of Chemistry, Peking University*

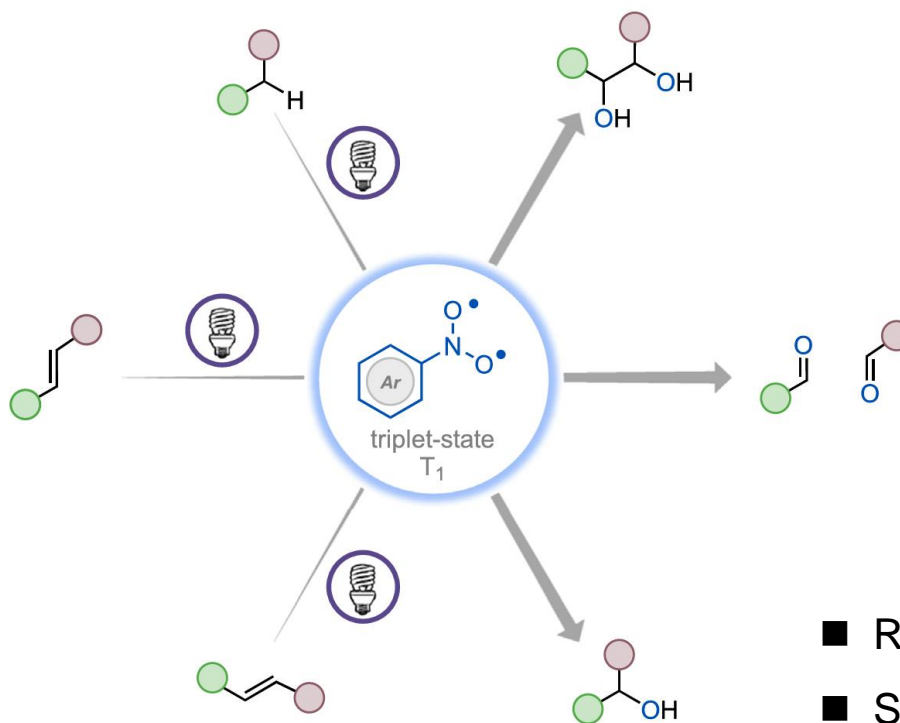
# *Selected Weekly Literature Presentations*

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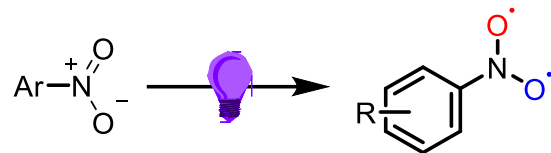
# Excited Nitroarenes in Organic Synthesis, Principle and Application



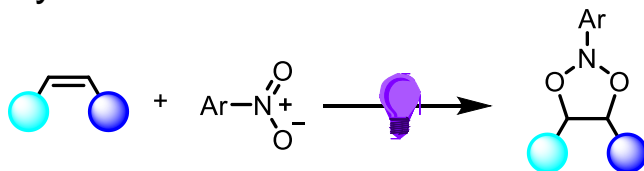
- Reporter: Peimiao He
- Supervisor: Yan Xu
- Date: 2024. 3. 23

# Outline

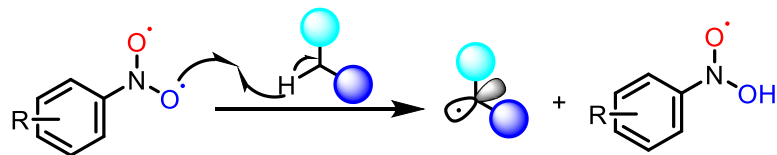
## ■ Introduction: Photochemistry of Nitroarenes



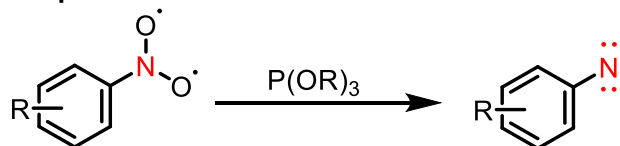
## ■ Reaction with $\pi$ -Systems



## ■ Photoinduced HAT reactions



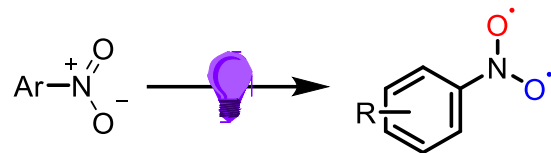
## ■ Reduction to Nitrene Species



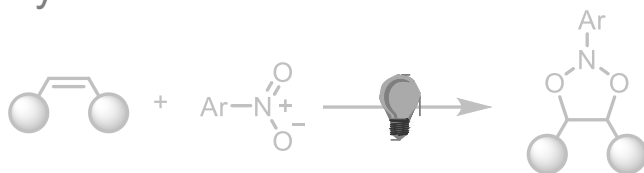
## ■ Summary and Perspective

# Outline

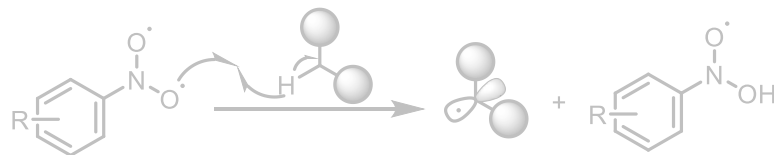
## ■ Introduction: Photochemistry of Nitroarenes



## ■ Reaction with $\pi$ -Systems



## ■ Photoinduced HAT reactions



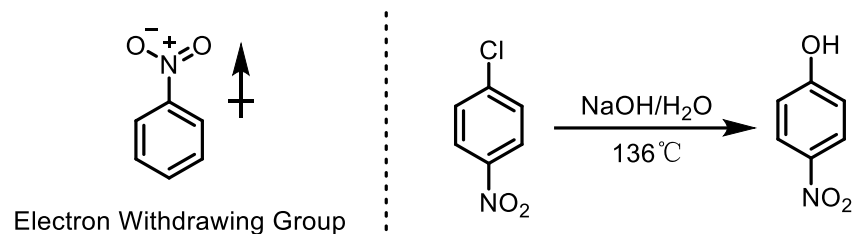
## ■ Reduction to Nitrene Species



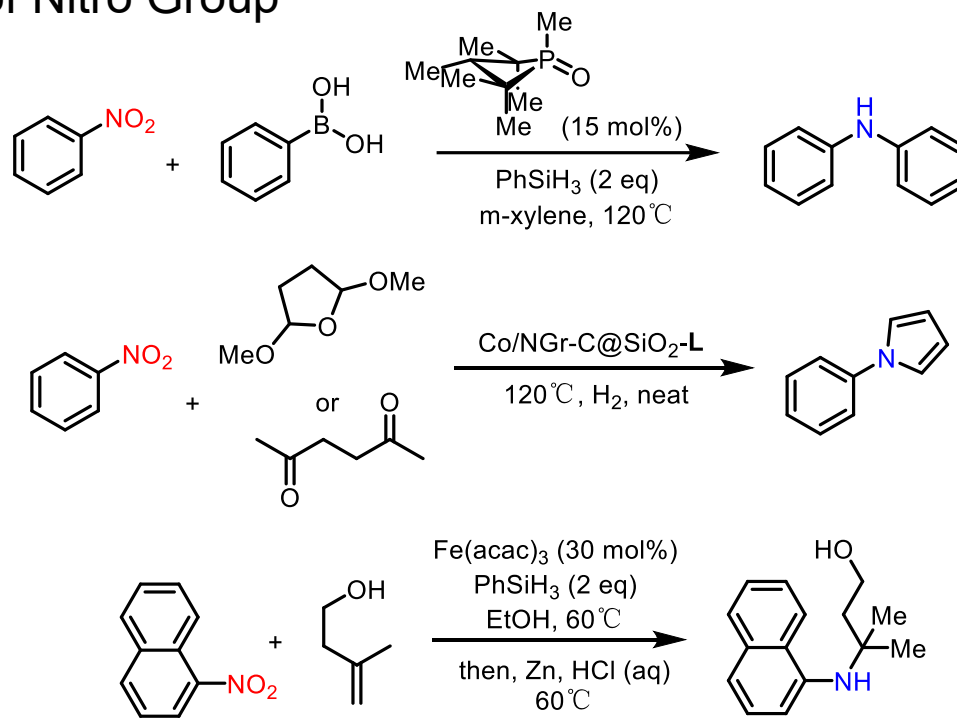
## ■ Summary and Perspective

# Conventional Transformation of Nitroarene

## ■ Aromatic Nucleophilic Substitution



## ■ Transformation of Nitro Group



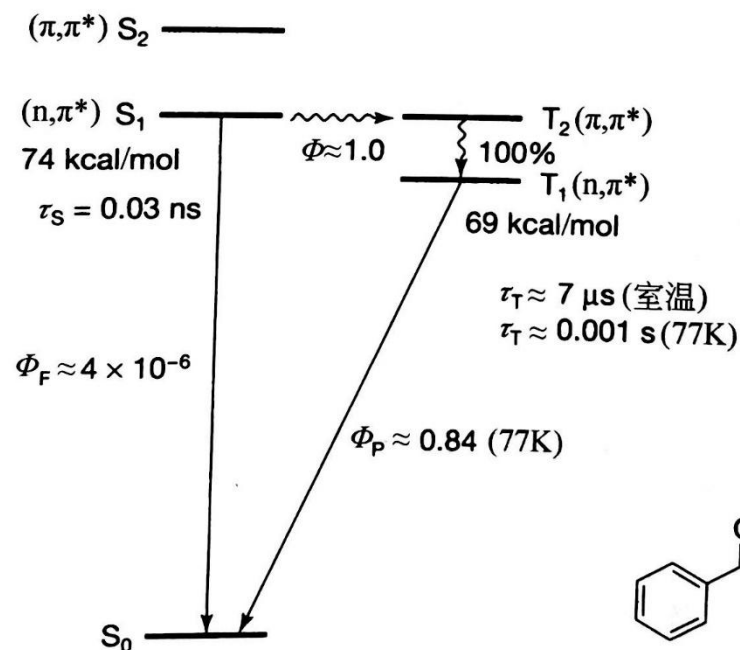
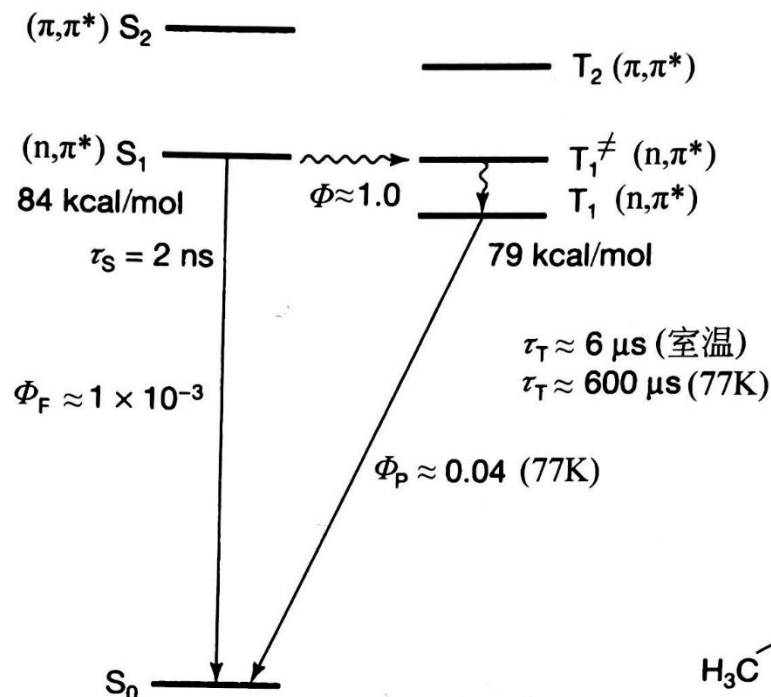
Radosevich, A. T. *et. al. J. Am. Chem. Soc.* **2018**, 140, 15200–15205

Beller, M. *et. al. Angew. Chem. Int. Ed.* **2020**, 59, 18679–18685

Baran, P. S. *et. al. Science* **2015**, 348, 886–891.

# Introduction: Aryl Ketone And Alkyl Ketone

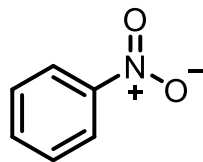
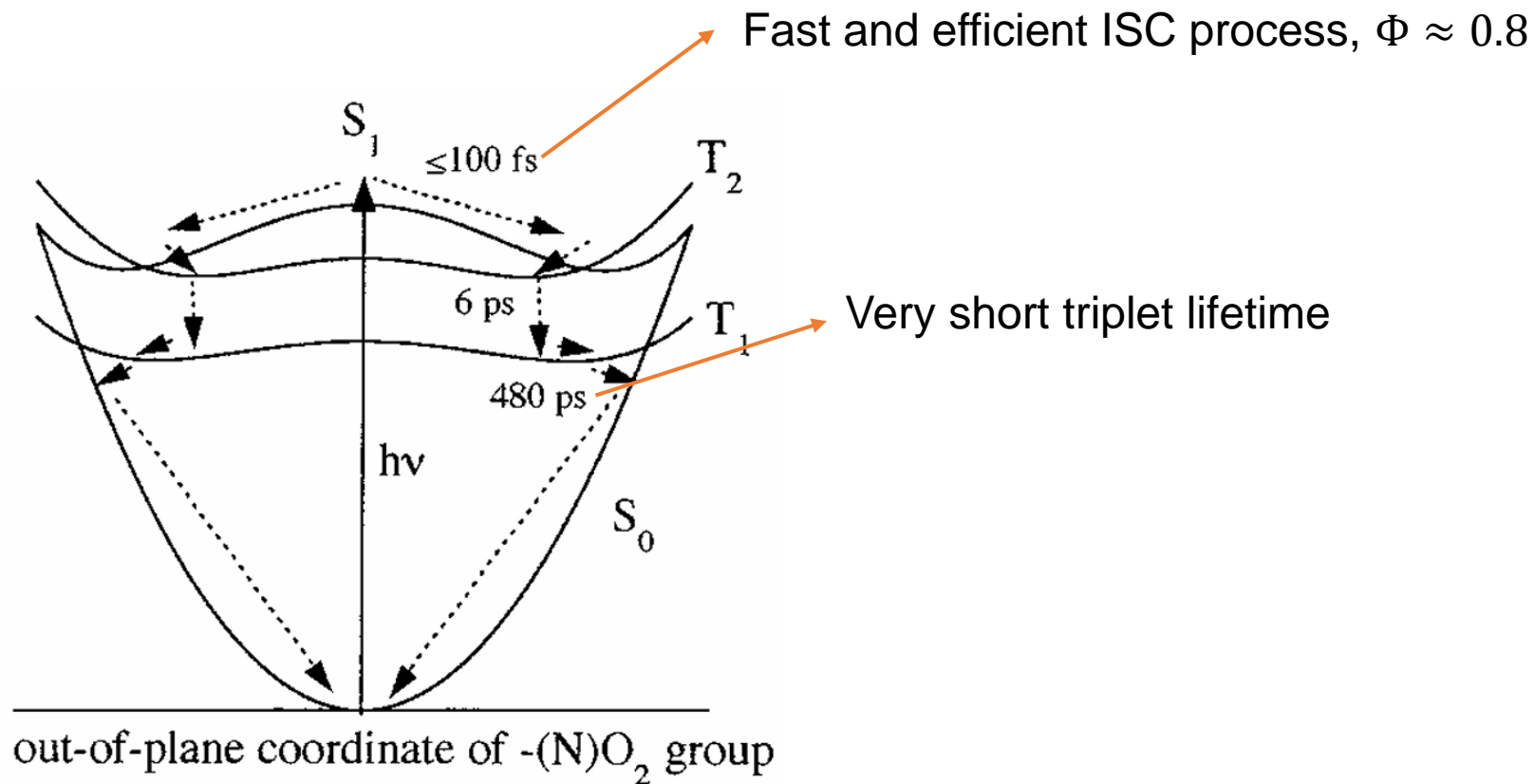
- Low energy gap between  $S_1$  and  $T_1$
- $S_1$  - $T_1$  Symmetry forbidden (El-Sayed Rule)
- Moderate ISC ( $10^7 \sim 10^8 \text{ s}^{-1}$ )
- Low energy gap between  $S_1$  and  $T_2$
- $S_1$  - $T_2$  Spin-orbit coupling
- **Very fast ISC** ( $10^{11} \sim 10^{12} \text{ s}^{-1}$ )



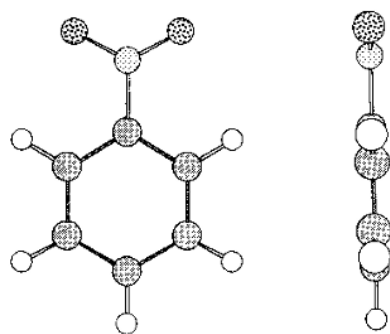
- Photochemical behaviors of nitroarenes are similar to those of aryl ketones.

# Introduction: Nitroarenes

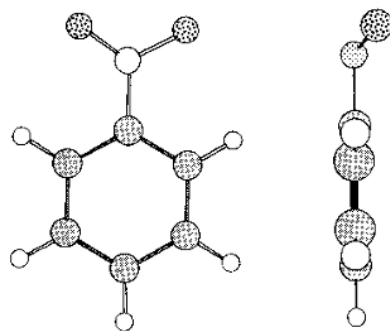
## ■ Photochemical behaviors of nitroarenes



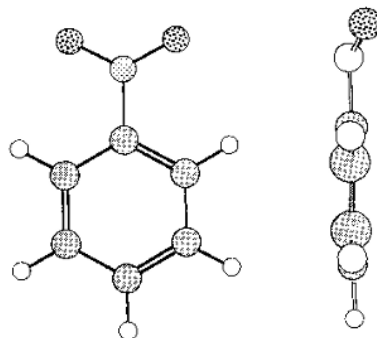
# Structure Deformation of Triplet Nitroarenes



(a)  $S_0$  state

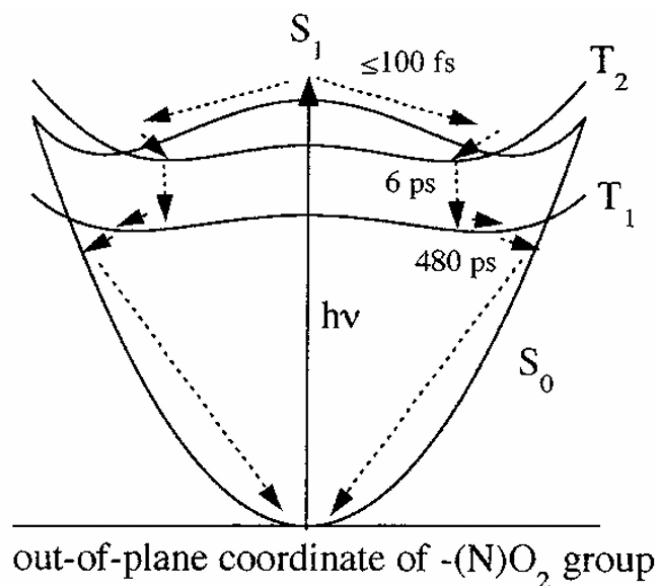
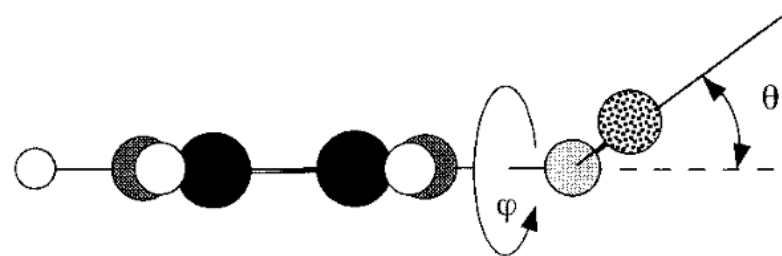


(b)  $S_1$  state



(c)  $T_1$  state

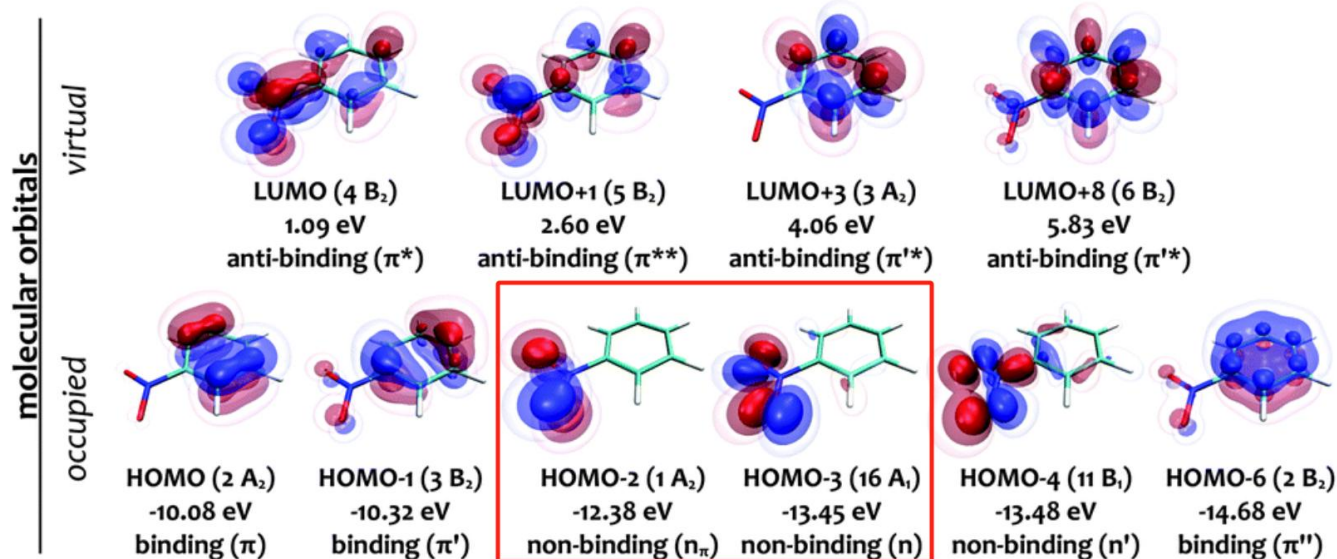
$$\theta = 38.8^\circ$$



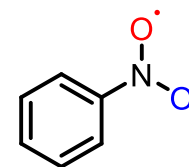
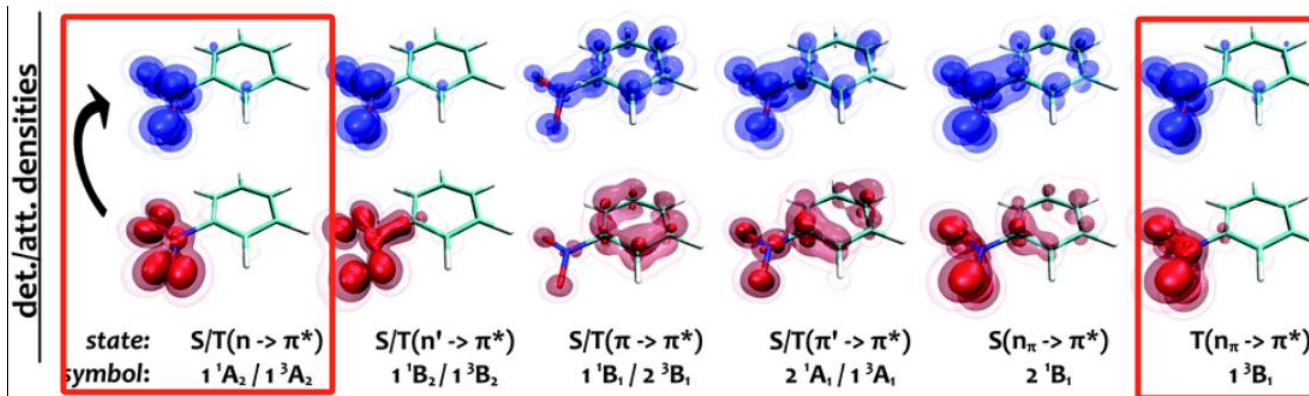
The dramatic difference in the curvature of the potential curve between the  $T_1$  and  $S_0$  states makes the Franck-Condon (FC) factor large for the  $T_1$  to  $S_0$  ISC.

# $\pi - \pi^*$ Character And Localized Excitation

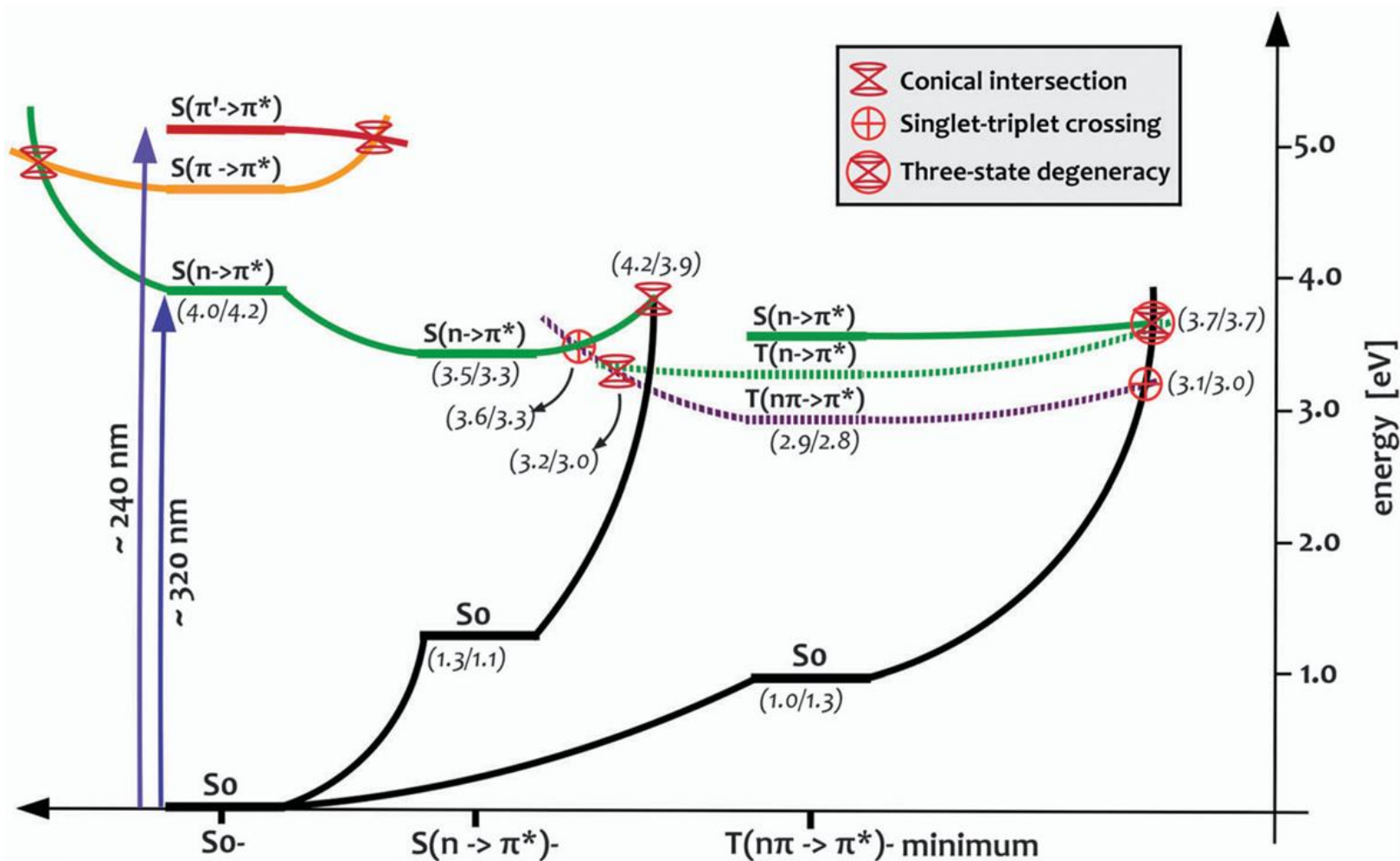
- The energy gap between  $T(\pi - \pi^*)$  and  $T(n - \pi^*)$  is very close



- The excitation is localized on nitro group



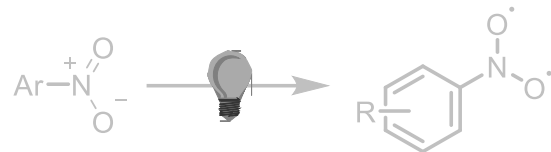
# Overall Diagram



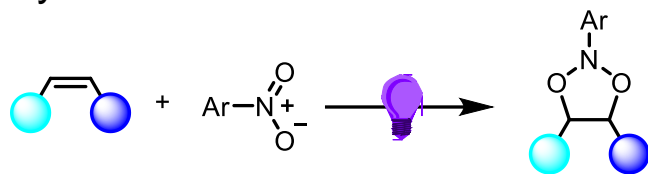
# Outline

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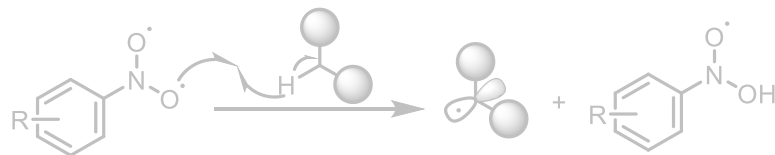
## ■ Introduction: Photochemistry of Nitroarenes



## ■ Reaction with $\pi$ -Systems



## ■ Photoinduced HAT reactions



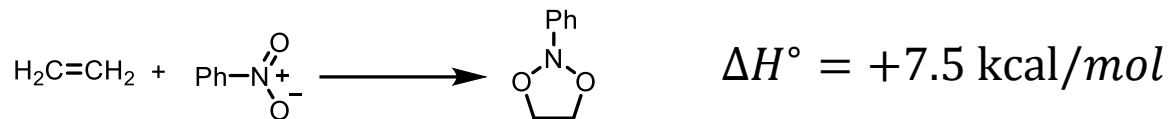
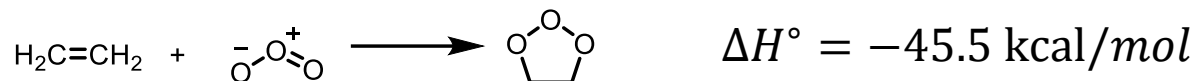
## ■ Reduction to Nitrene Species



## ■ Summary and Perspective

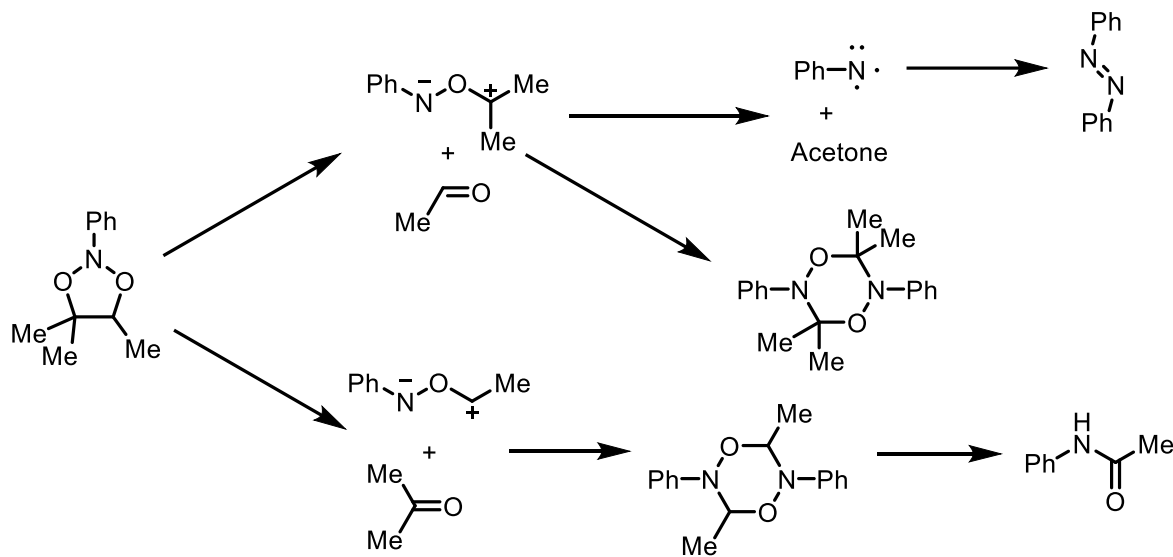
# Earlier Development

## ■ Kinetically And Thermodynamically Disfavored



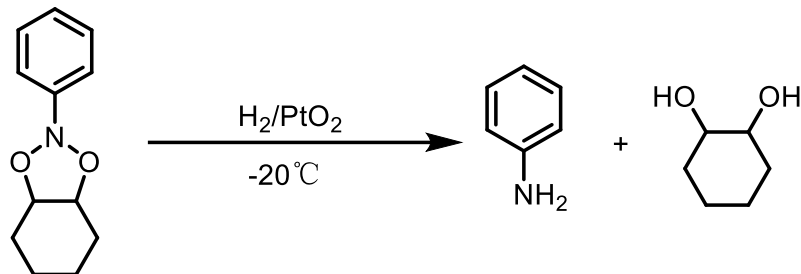
Ranganathan, S.; Ranganathan, D. *et. al. Tetrahedron*, **1981**, 37, 4171–4184

## ■ Decomposition of Primary Product

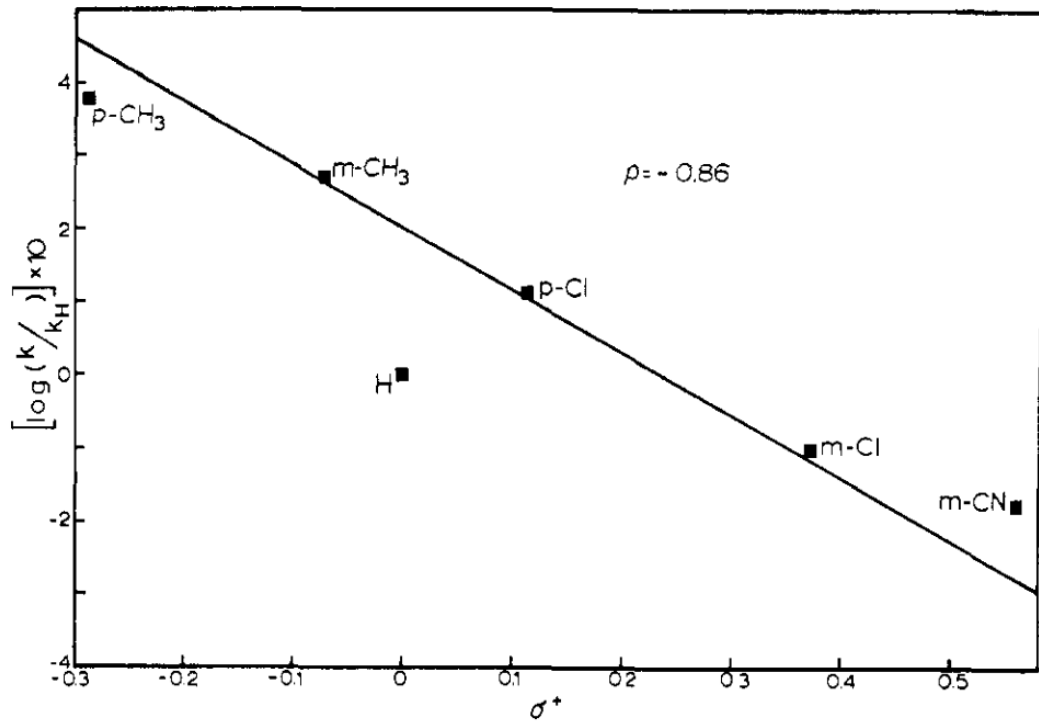


Buchi, G.; Ayer, D. E. *J. Am. Chem. Soc.* **1956**, 78, 689–690

# Earlier Development



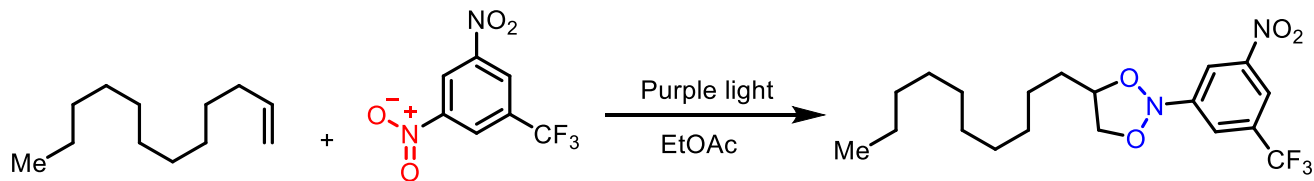
- Electrophilic attack of a short-lived,  $n, \pi^*$  triplet on the olefin proceeding through a discrete (biradical) intermediate.



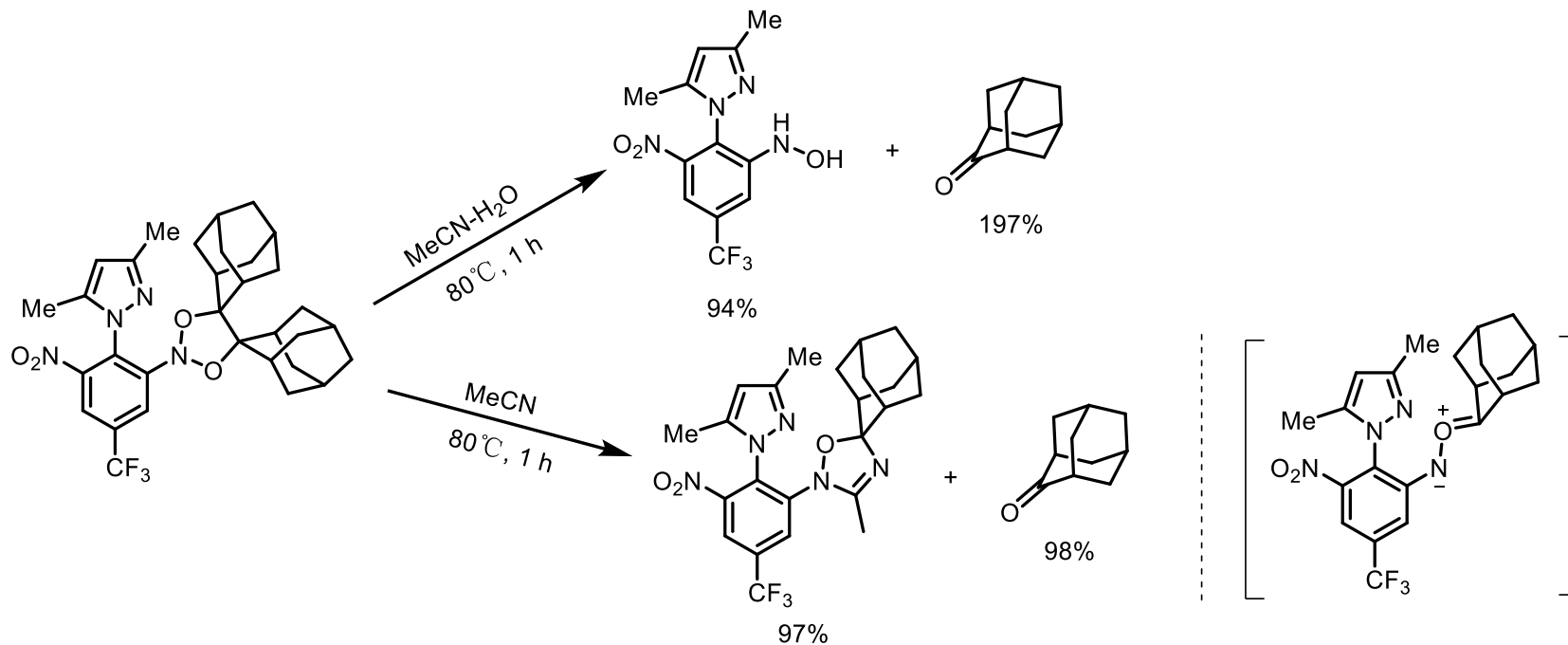
- Electron-withdrawing groups stabilized the adducts, but in no case was a product stable at room temperature obtained.

# Oxidative Cleavage of Alkenes

## ■ Stable Additive



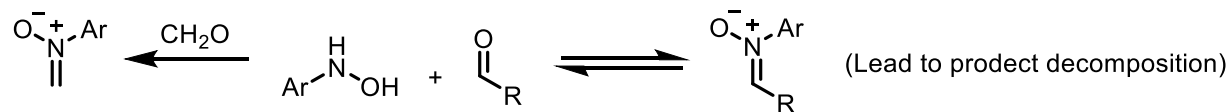
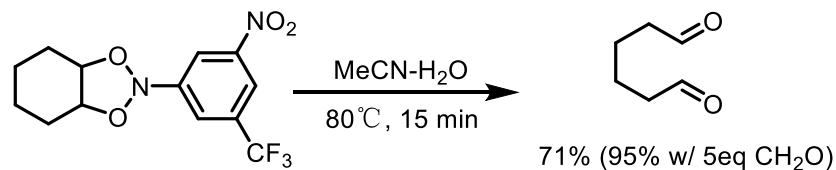
## ■ Decompose Pathway



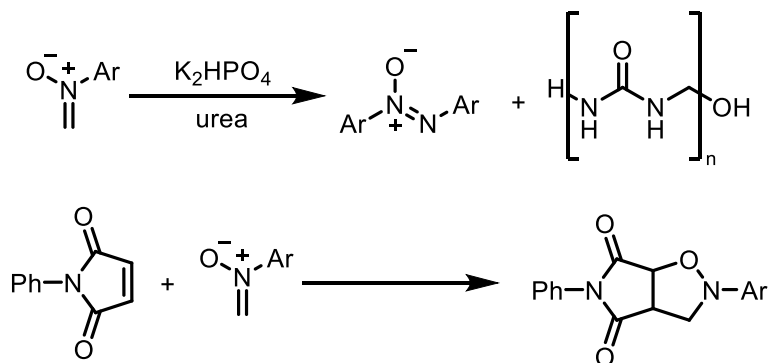
## ■ No nitrene formation

# Oxidative Cleavage of Alkenes

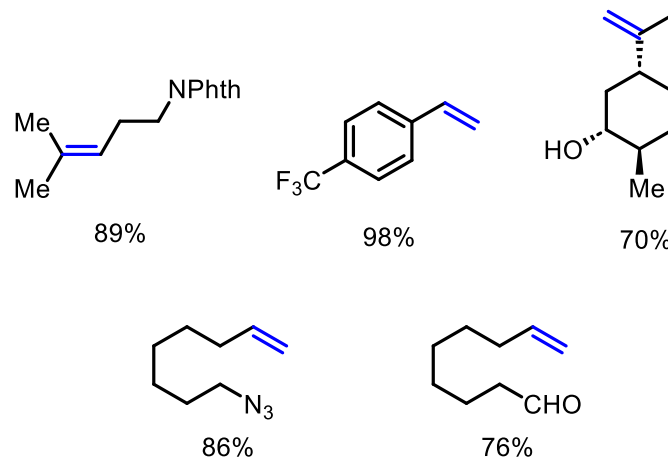
## Decompose Pathway



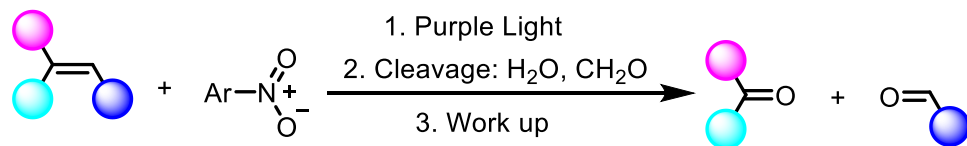
## Work Up Procedure



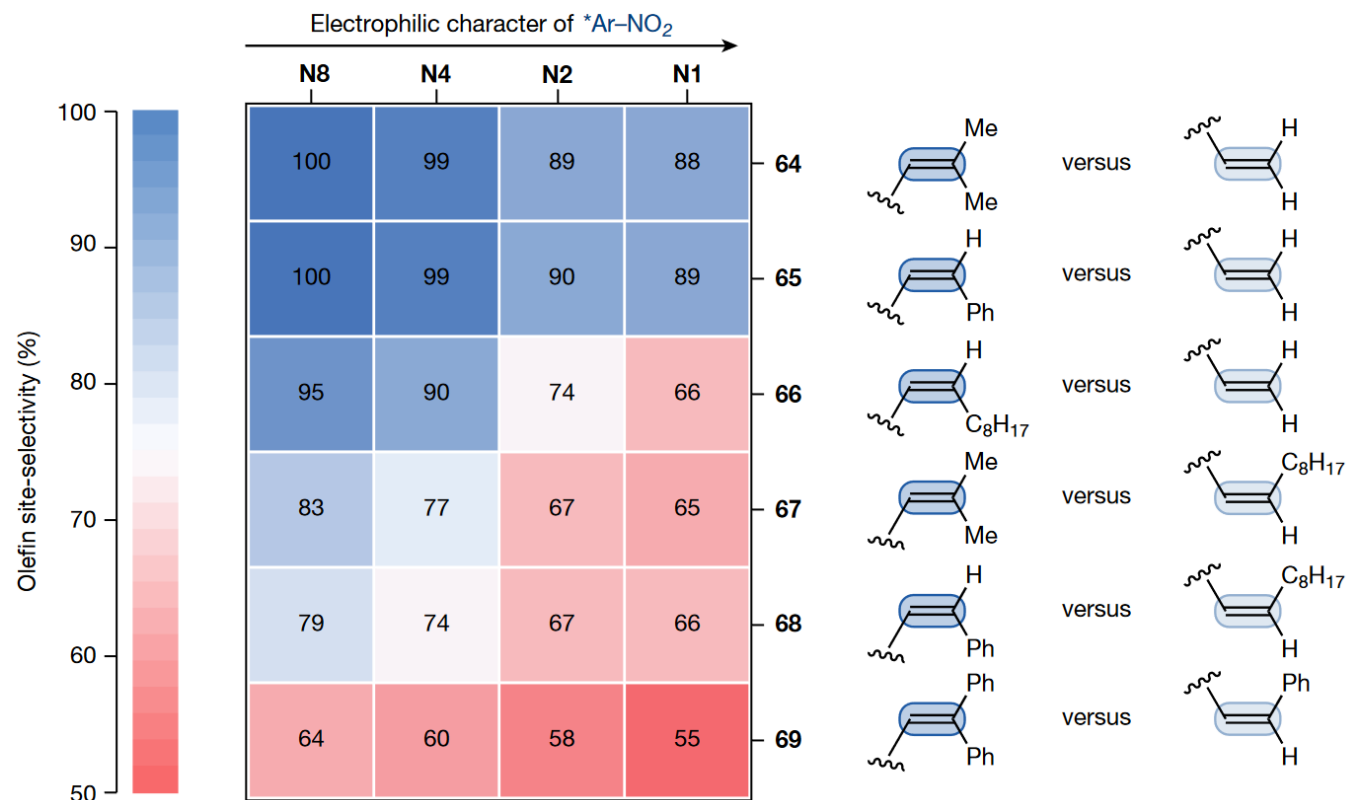
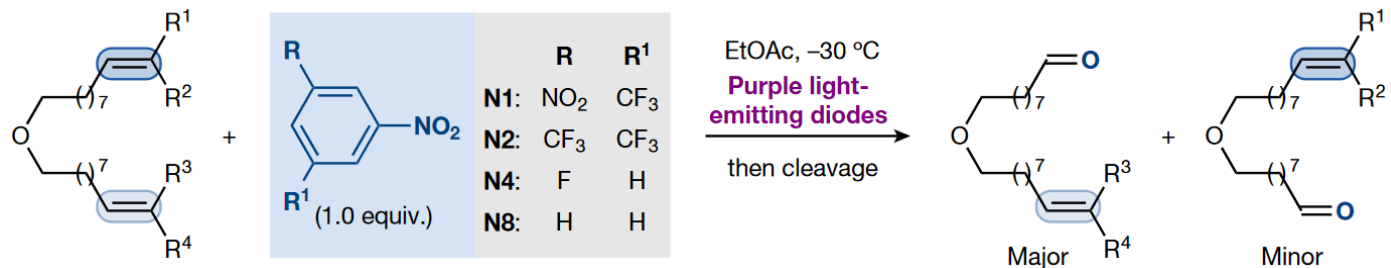
## Substrates Scope



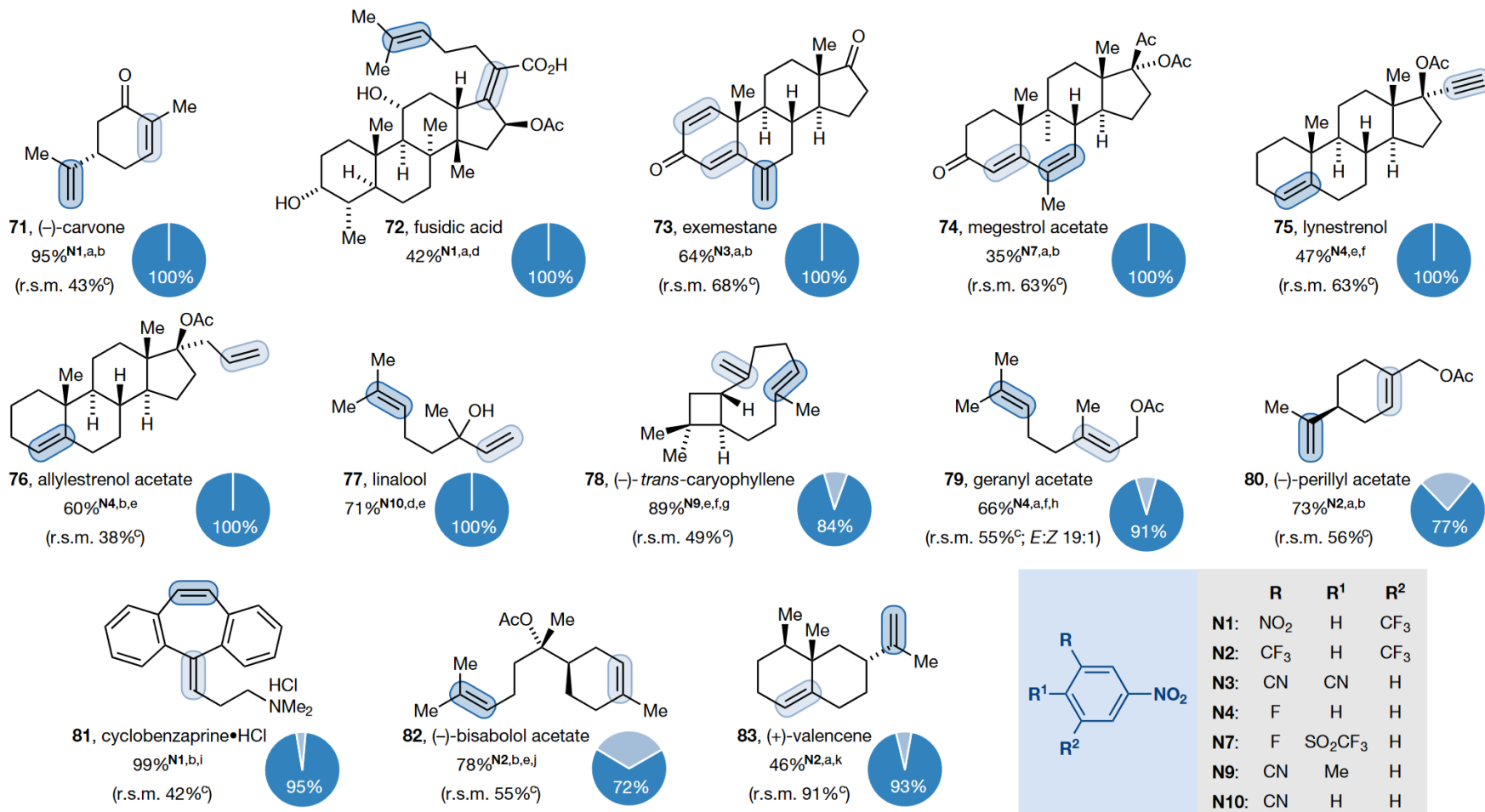
## Overall Reaction



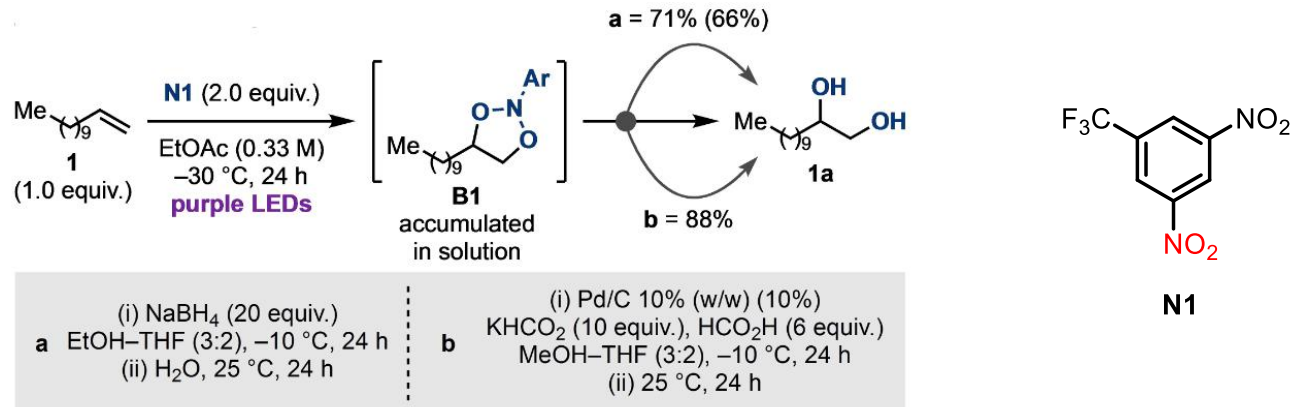
# Achieving Regiocontrol



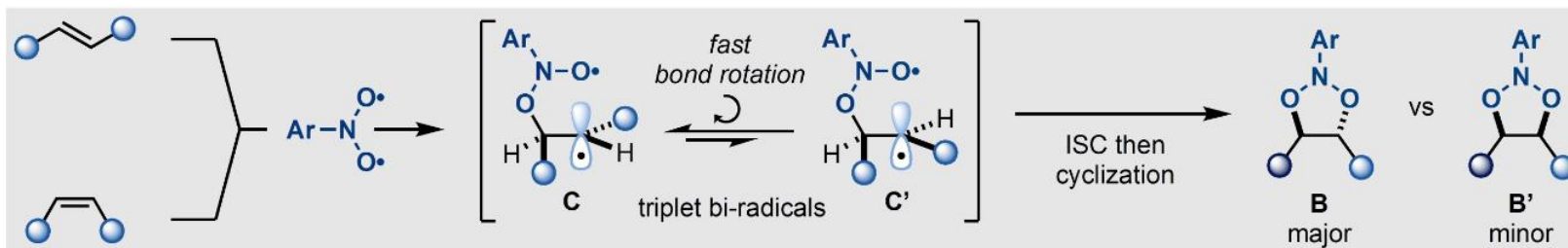
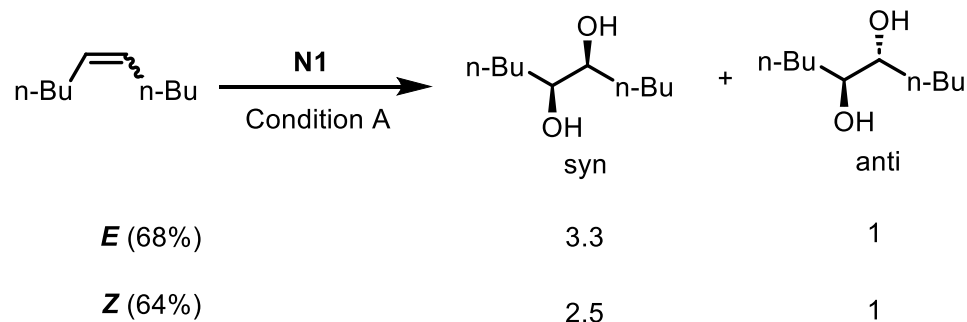
# Achieving Regiocontrol



# Olefin Dihydroxylation

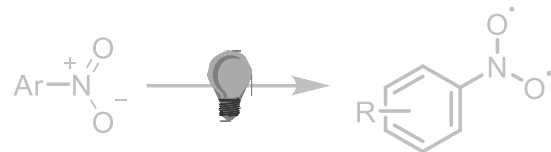


## ■ Diastereoconvergence

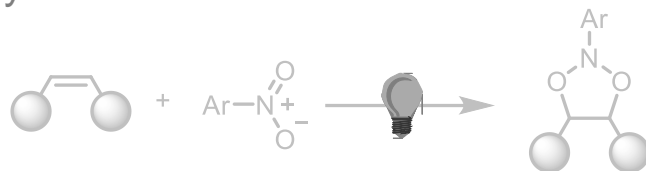


# Outline

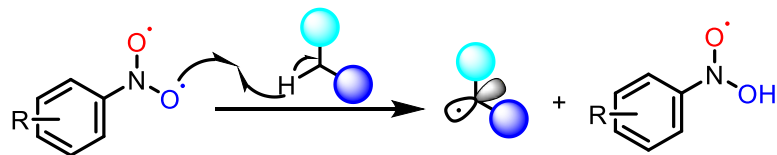
## ■ Introduction: Photochemistry of Nitroarenes



## ■ Reaction with $\pi$ -Systems



## ■ Photoinduced HAT reactions



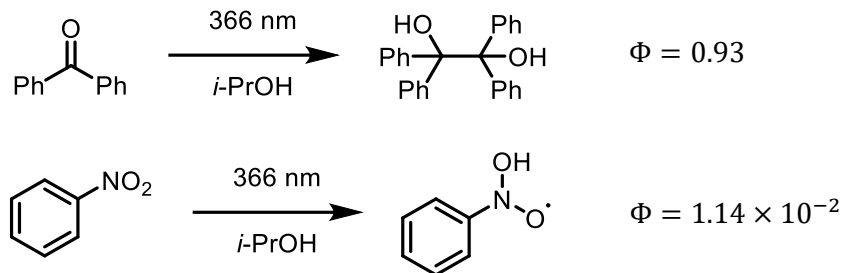
## ■ Reduction to Nitrene Species



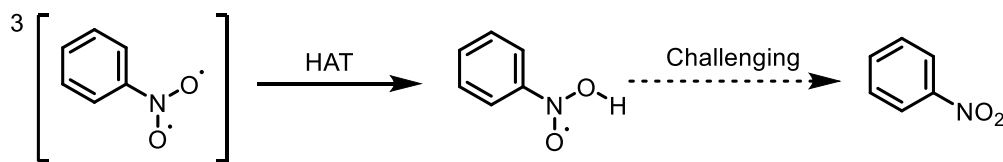
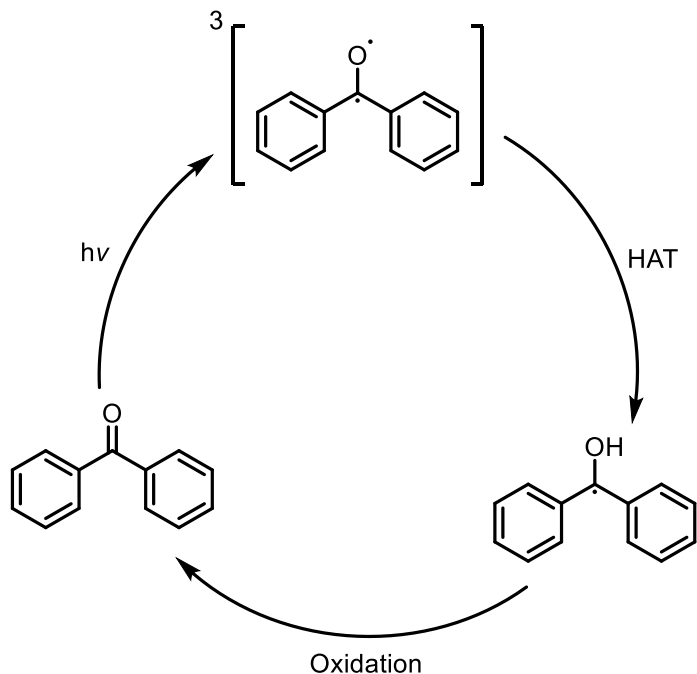
## ■ Summary and Perspective

# Nitroarenes vs. Benzophenone

## ■ Quantum Yield



## ■ Hard to Recycle



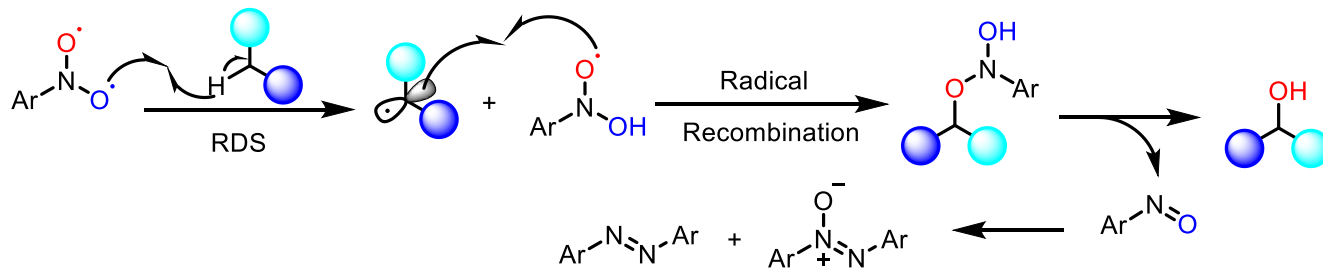
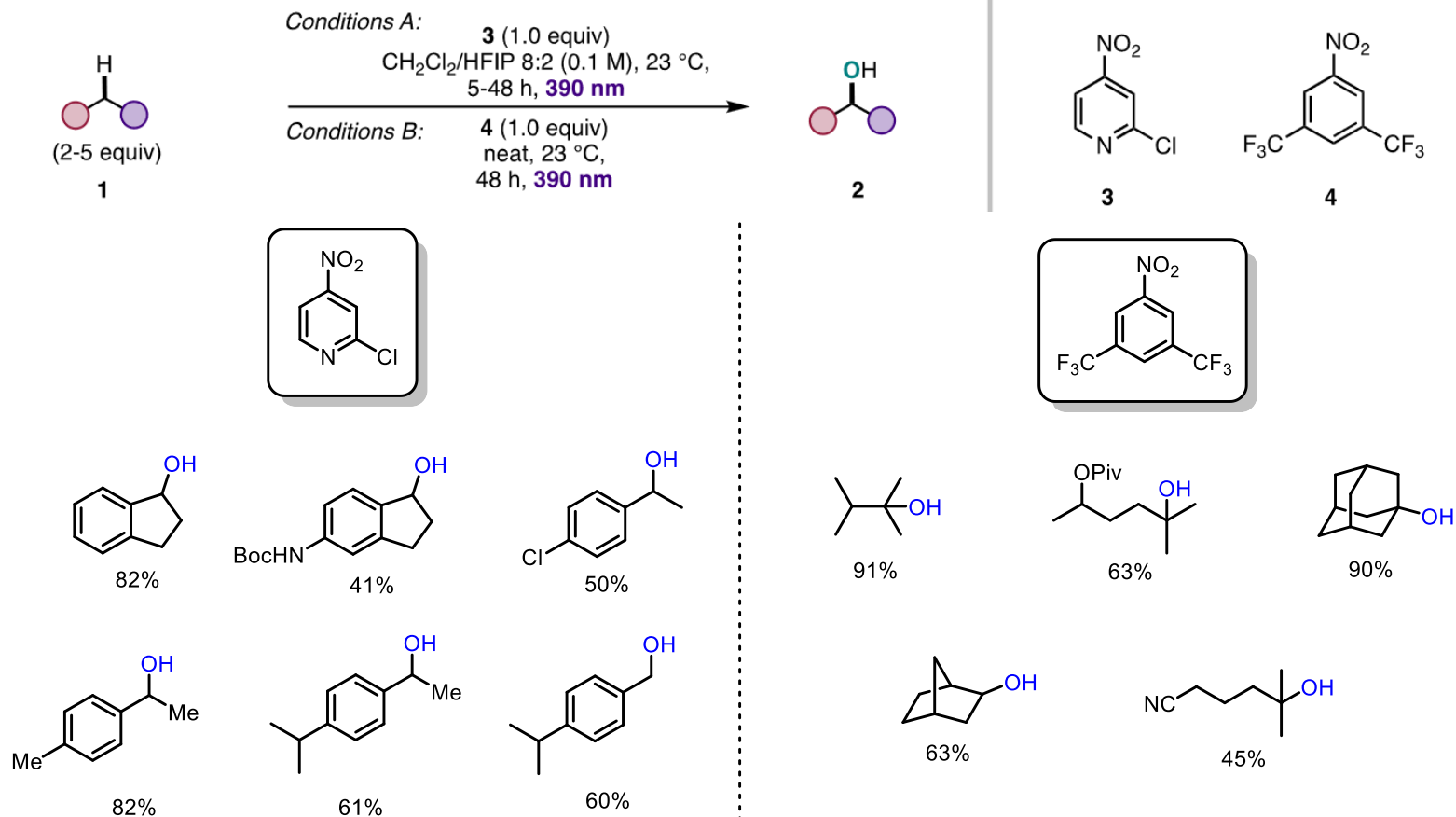
■ Bonding Ability of Oxygen

■ Oxidant

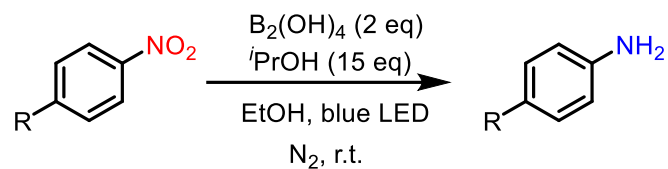
Pitts, J. N. *et. al. J. Am. Chem. Soc.* **1959**, 81, 1068-1077

Testa, A.C. *et. al. J. Am. Chem. Soc.* **1966**, 88, 4330-4332.

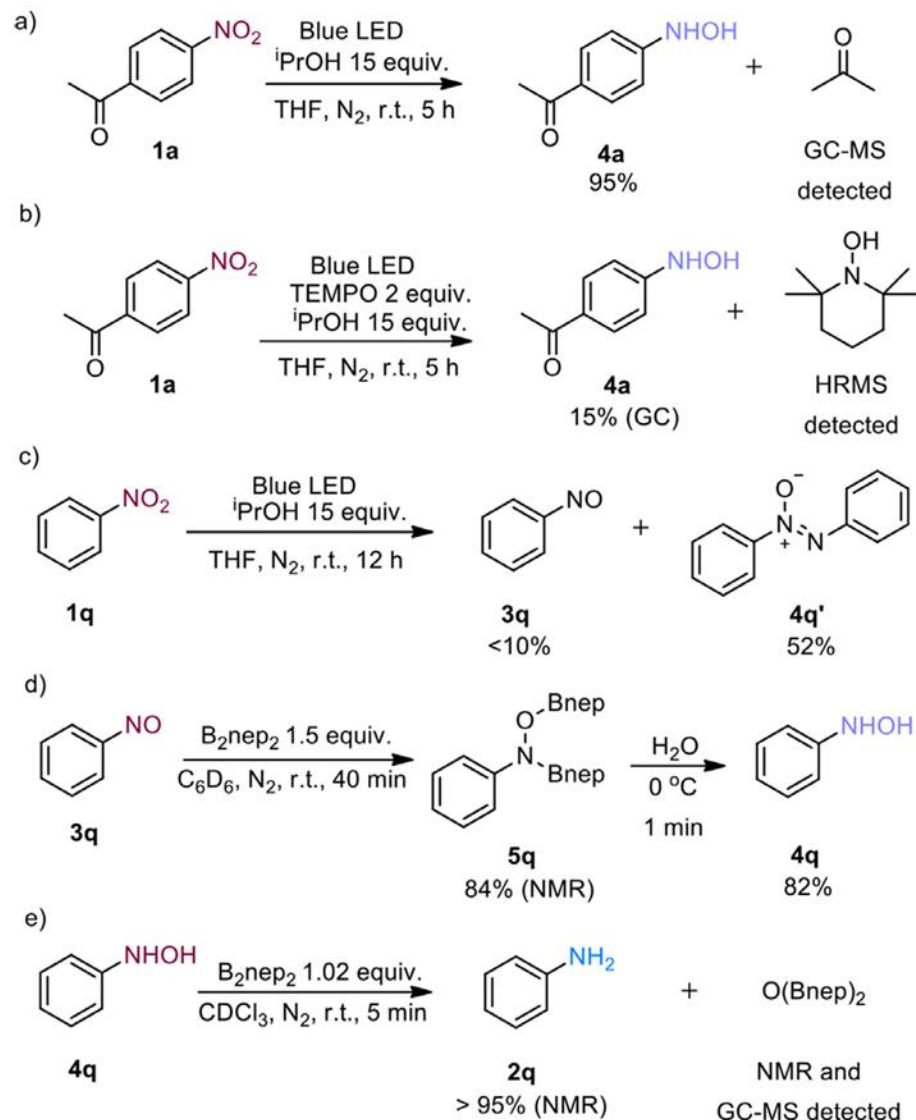
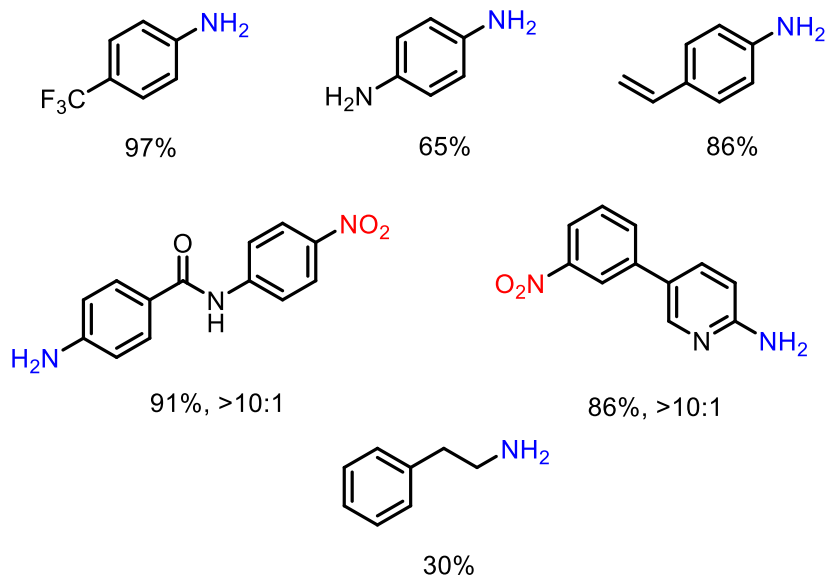
# Anaerobic Hydroxylation



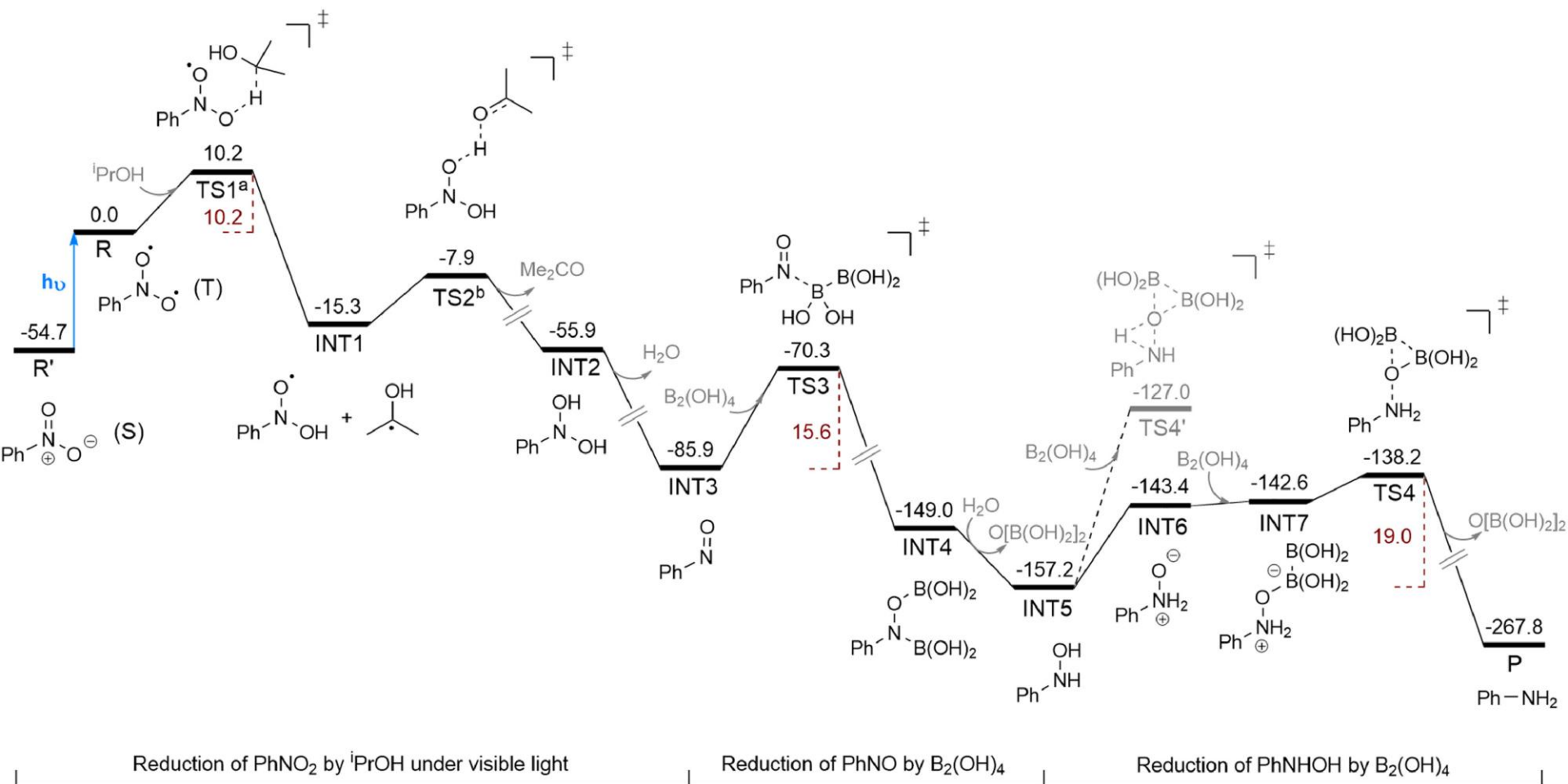
# Reduction of Nitro Group



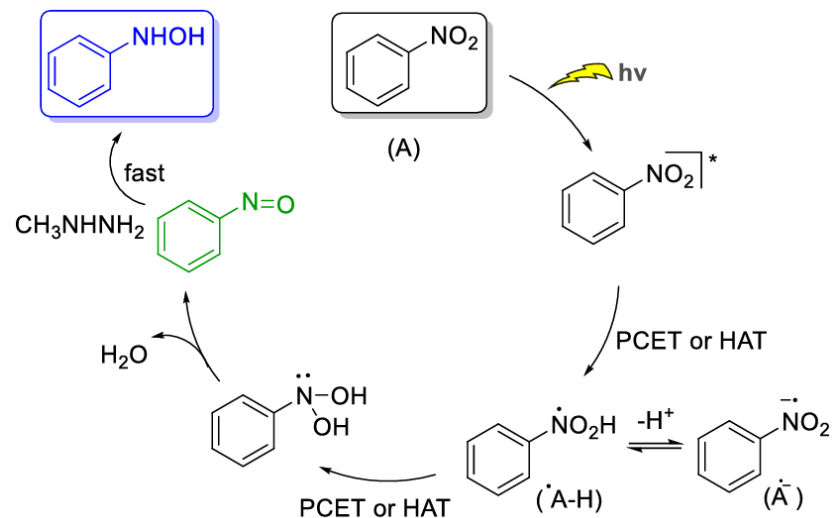
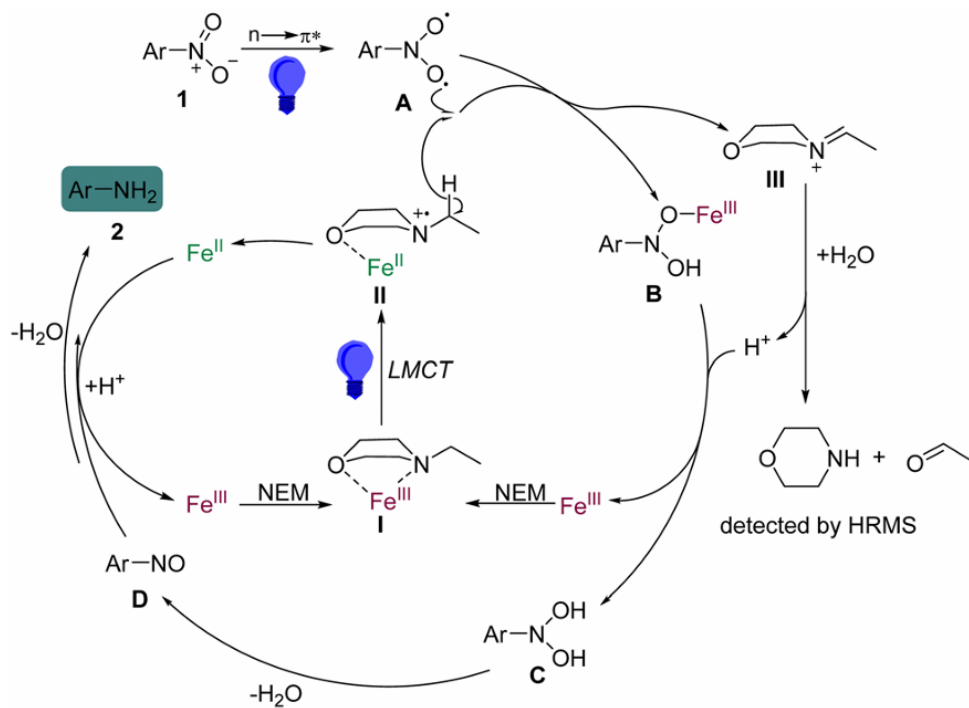
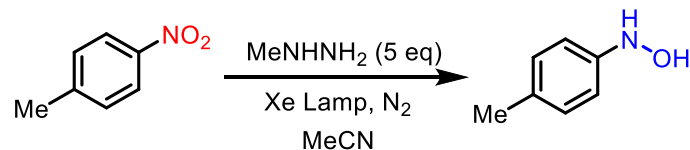
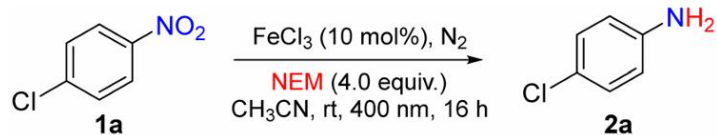
## Substrates Scope



# Reaction Mechanism



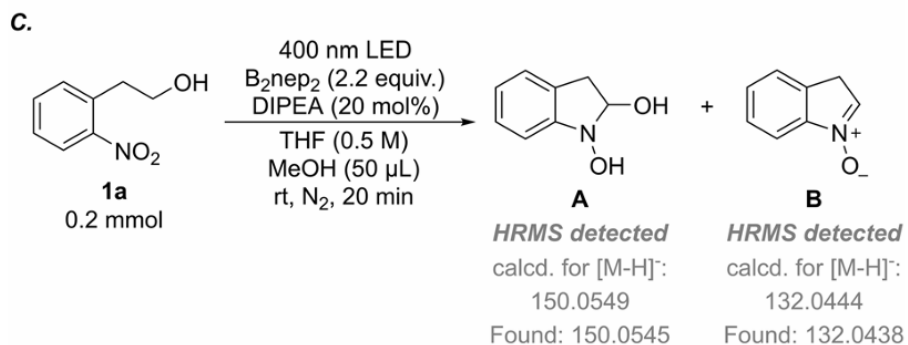
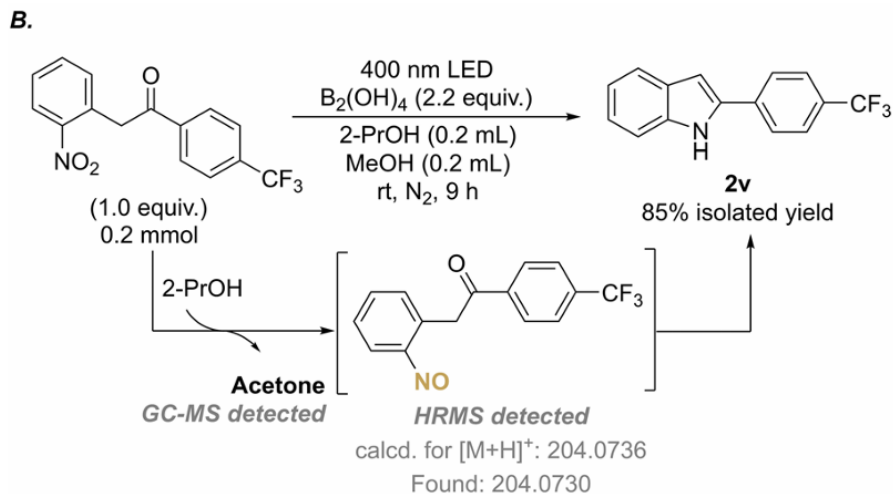
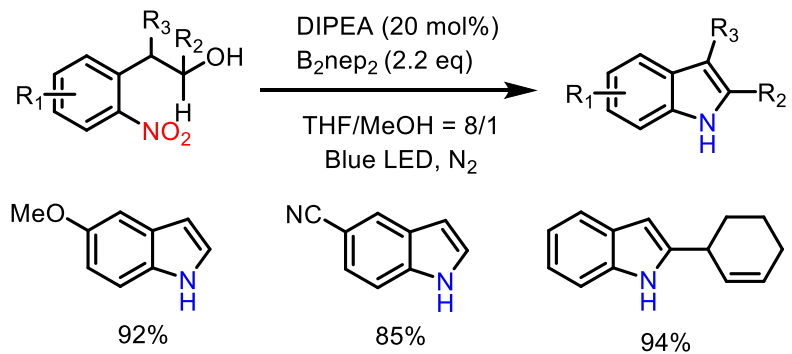
# Reduction of Nitro Group



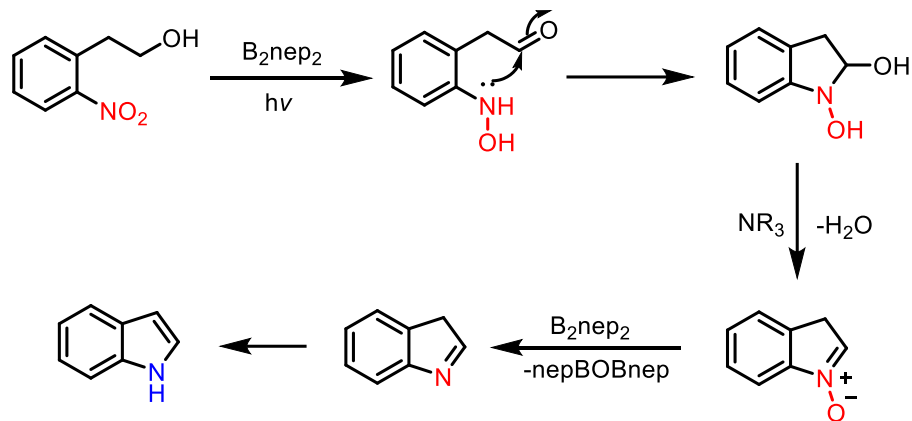
Yu, X. *et al. Chem. Commun.* **2023**, 59, 14177-14180

Lykakis, I. N. *et al. Org. Lett.* **2020**, 22, 4339-4343

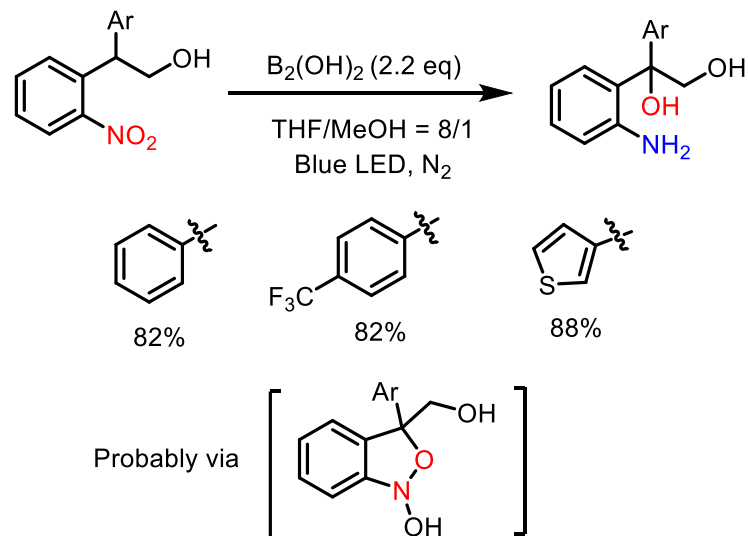
# Function Group Interconversion of Nitro Group



## Mechanism

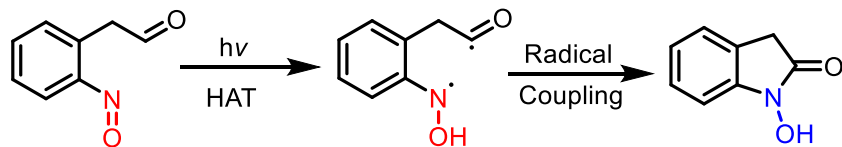
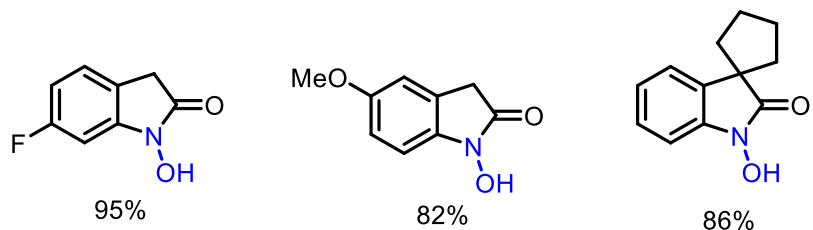
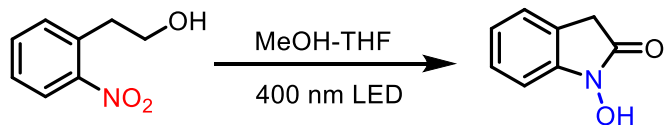


## Oxidation of Benzylic Position

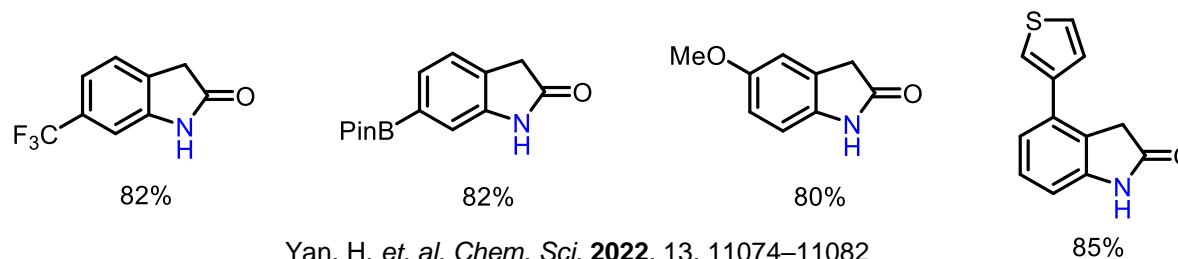
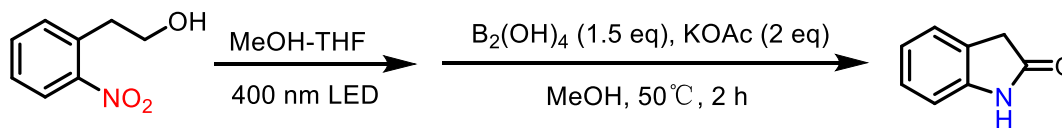


# Function Group Interconversion of Nitro Group

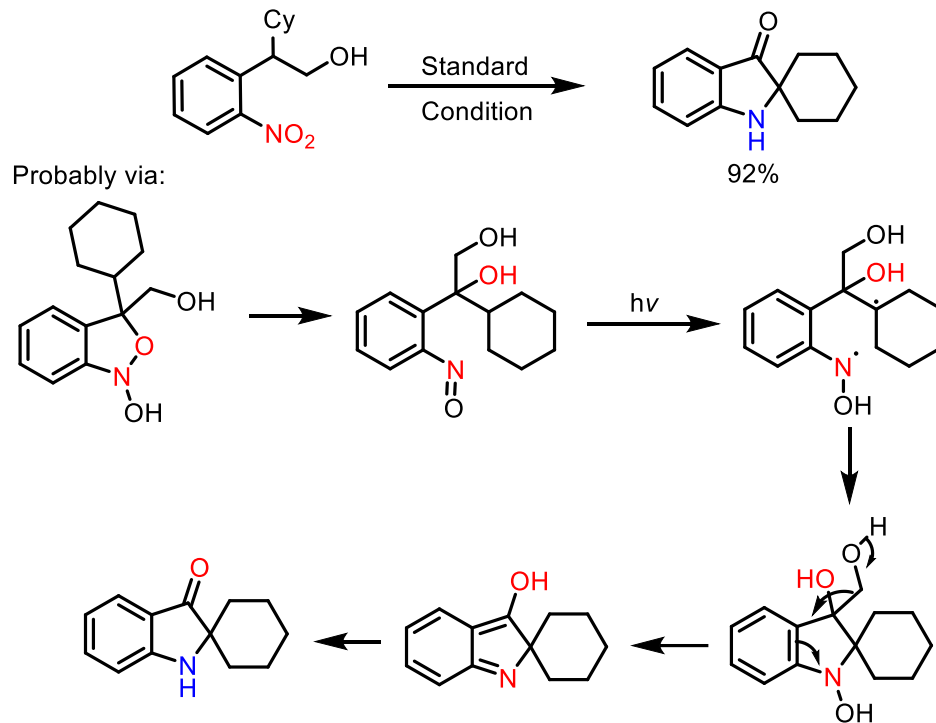
## ■ N-Hydroxyl Oxindole



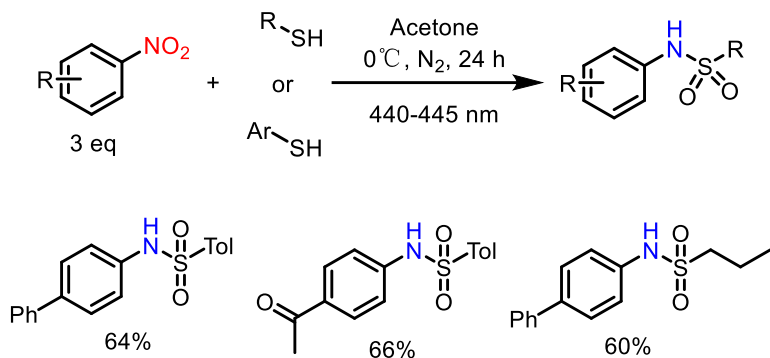
## ■ N-H Oxindole



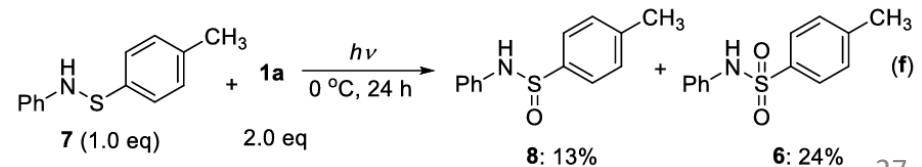
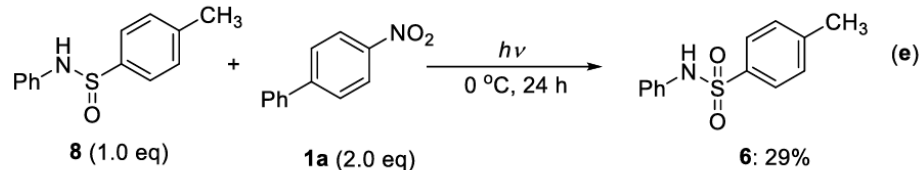
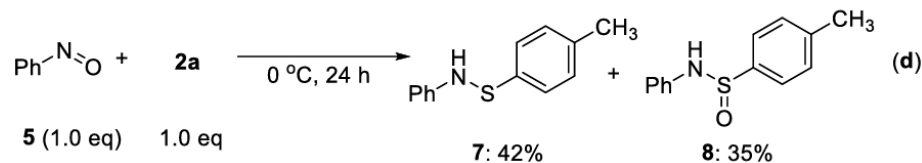
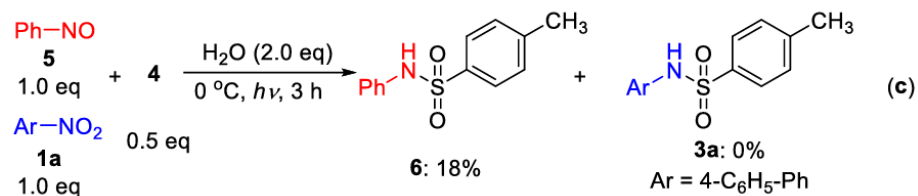
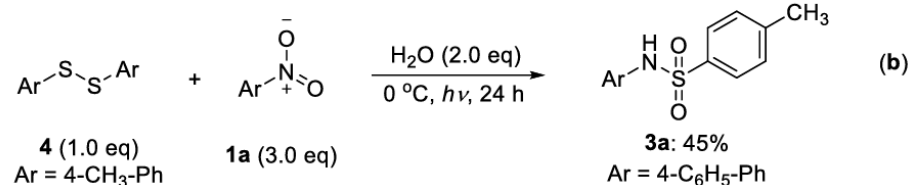
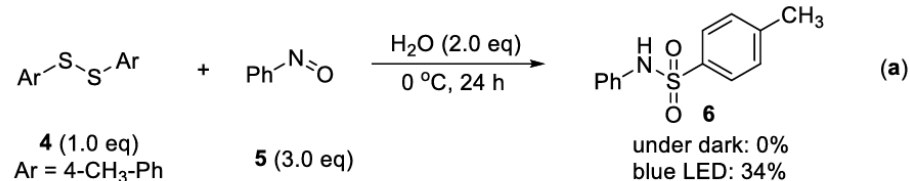
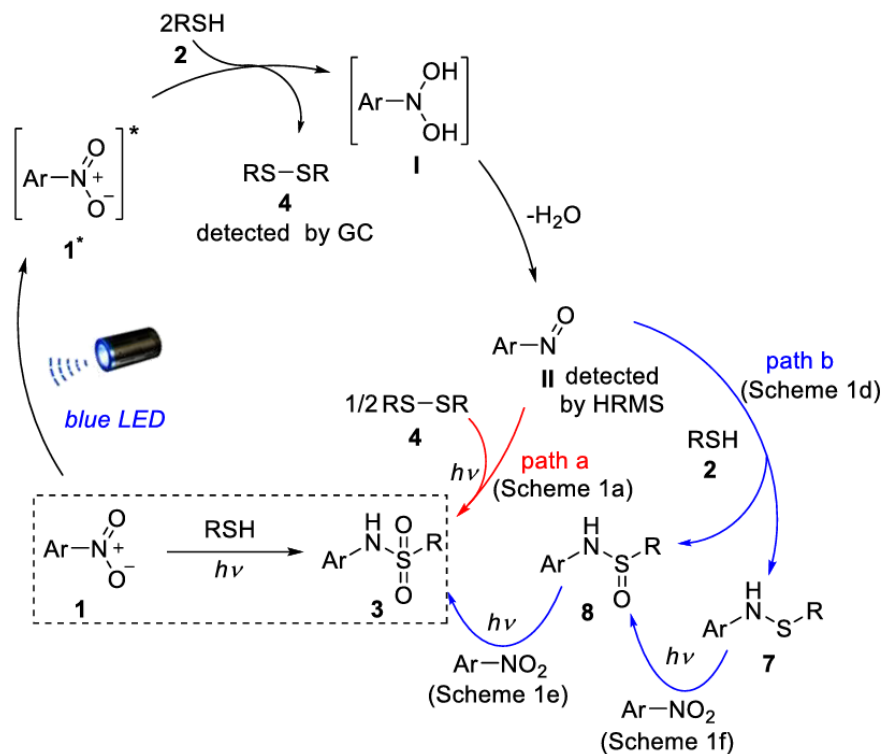
## ■ Exception



# Function Group Interconversion of Nitro Group



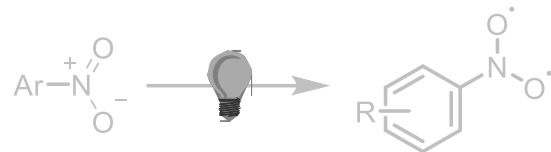
## Mechanism



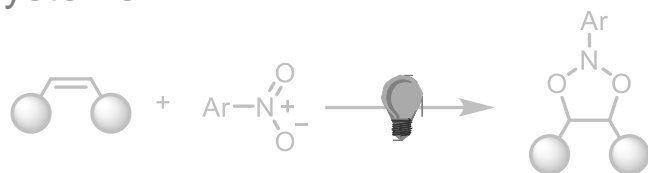
# Outline

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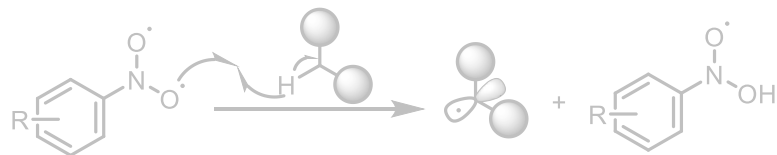
## ■ Introduction: Photochemistry of Nitroarenes



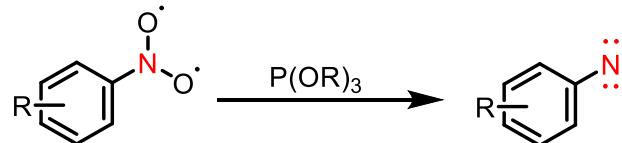
## ■ Reaction with $\pi$ -Systems



## ■ Photoinduced HAT reactions



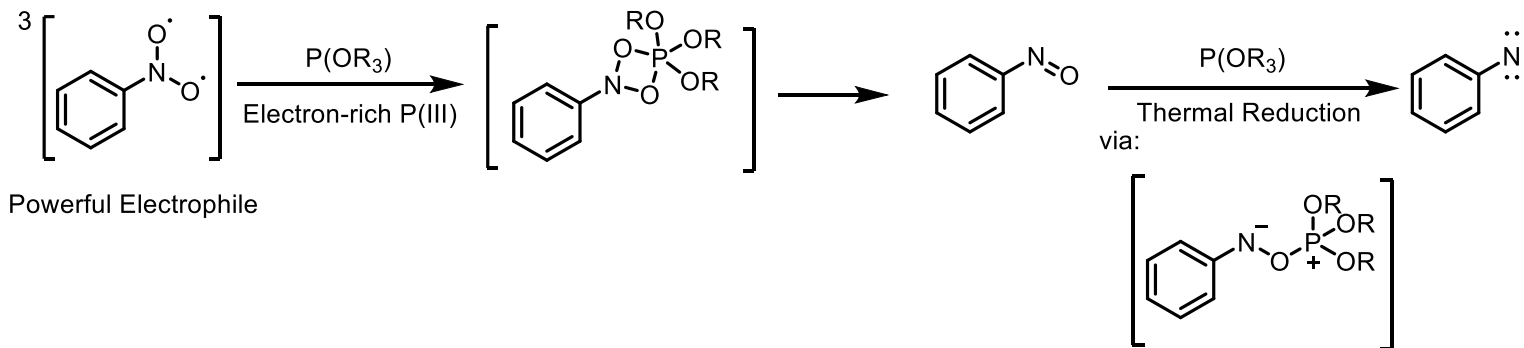
## ■ Reduction to Nitrene Species



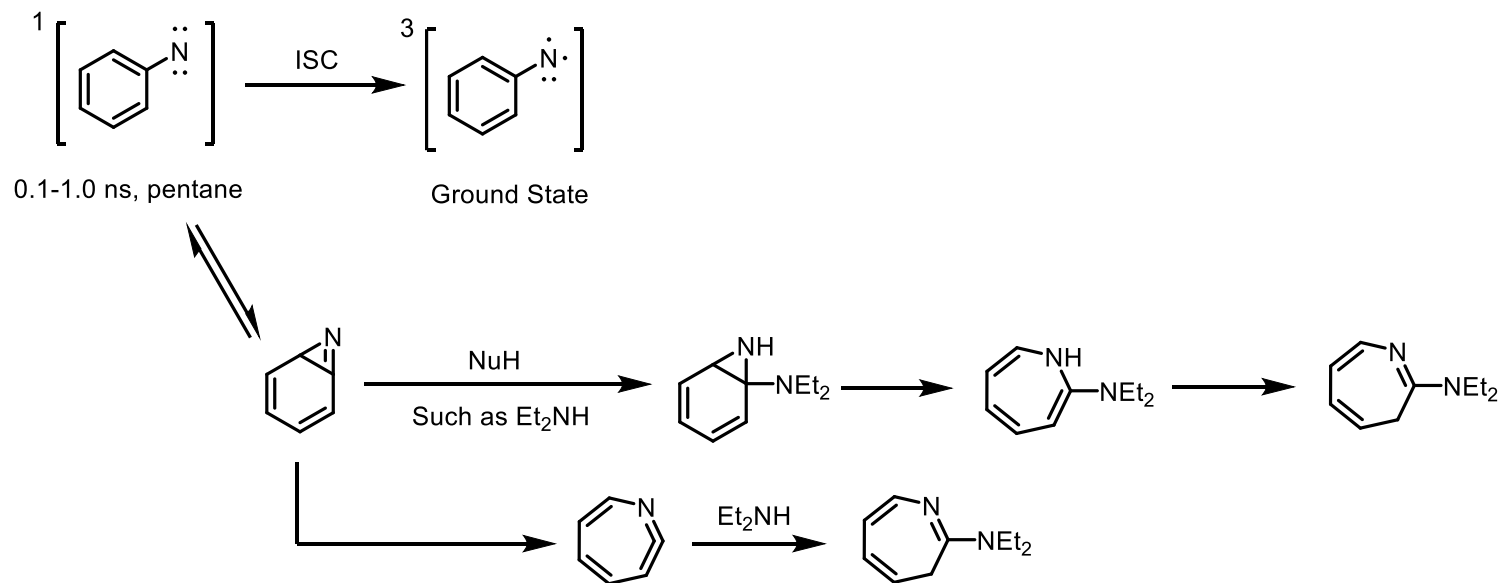
## ■ Summary and Perspective

# Basic Model

## ■ Photoreduction of Nitro Group



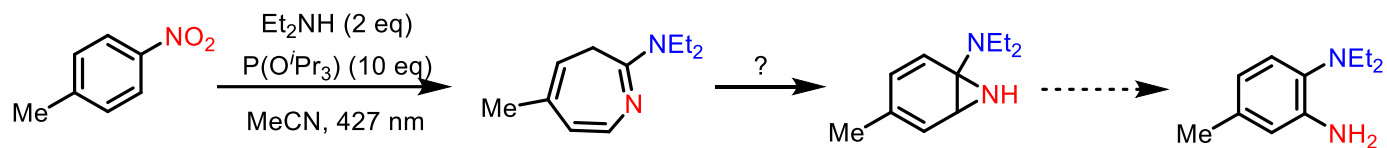
## ■ Singlet vs. Triplet



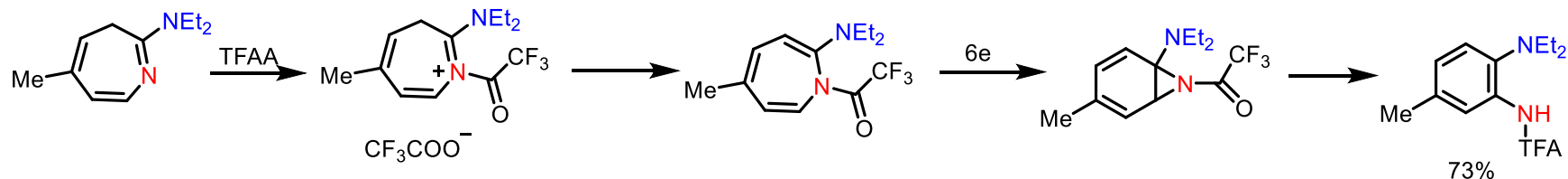
Platz, M. S. *et. al. J. Am. Chem. Soc.* **1997**, 119, 5059-5060

Gallagher, P. T. *et. al. Angew. Chem. Int. Ed. Engl.* **1979**, 18, 900-917

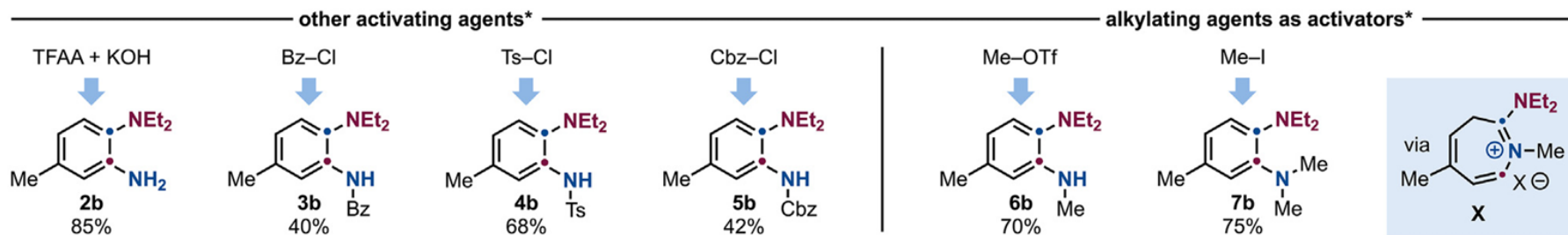
# Dearomative-Rearomative Coupling



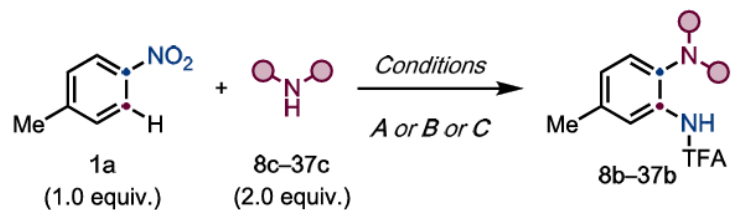
## ■ Thermodynamic Perturbation



## ■ Other Electrophiles



# Dearomative-Rearomative Coupling



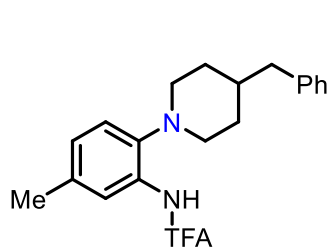
*one-pot conditions*

*stepwise conditions*

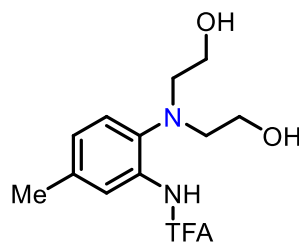
A: P(O*i*Pr)<sub>3</sub> (10 equiv.), CH<sub>3</sub>CN (0.1 M)  
r.t., 16 h, hν = 427nm light  
then TFAA (25 equiv.), CH<sub>3</sub>CN (0.1M), r.t. 4h

B: P(O*i*Pr)<sub>3</sub> (20 equiv.), *i*-PrOH (0.1M)  
r.t., 16 h, hν = 427nm light  
then TFAA (25 equiv.), CH<sub>3</sub>CN (0.1 M), r.t. 4h

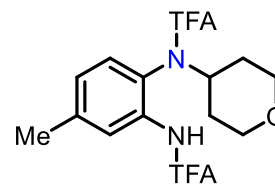
C: (i) P(O*i*Pr)<sub>3</sub> (20 equiv.), *i*-PrOH (0.1M)  
r.t., 16 h, hν = 427nm light  
(ii) TFAA (4 equiv.), CH<sub>3</sub>CN (0.1M), r.t. 4h



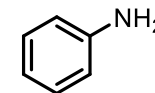
A: 54%



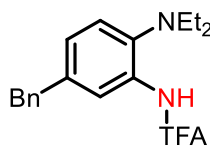
A: 62%



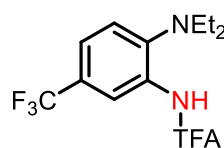
A: 61%



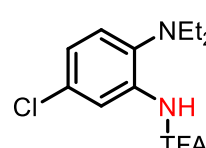
Limitation



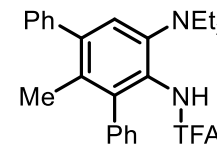
C: 72%



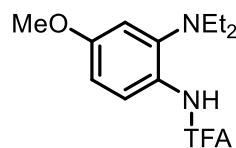
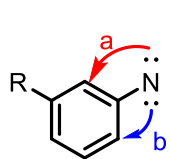
C: 99%



A: 43%

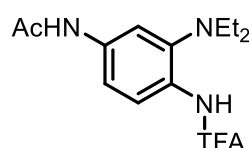


C: 69%



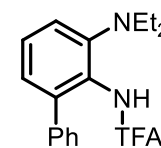
C: 24%

path b



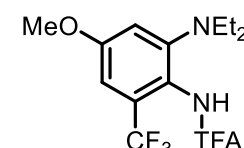
C: 37%

path b



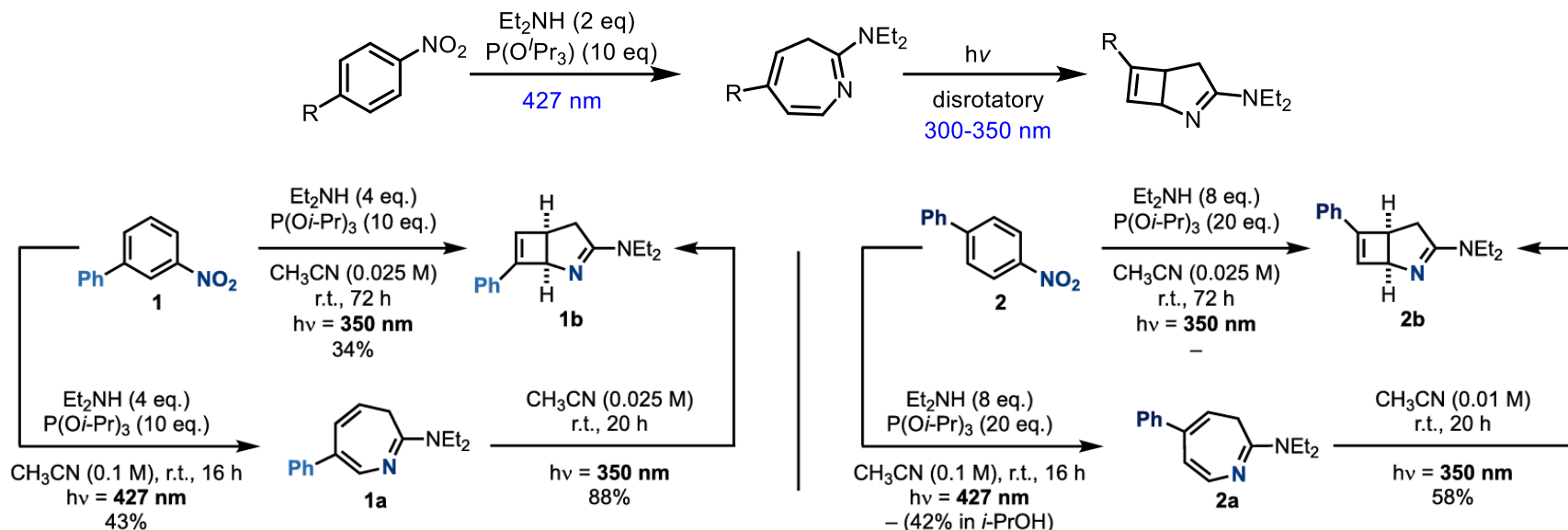
A: 30%

path a

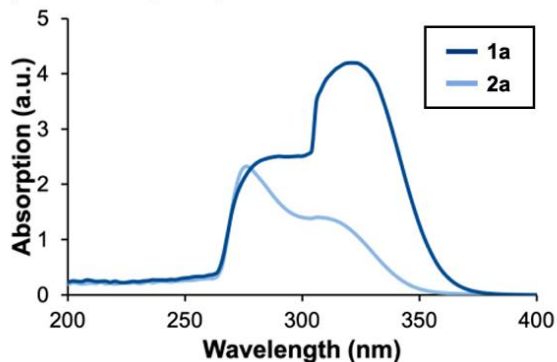


B: 81%

# Conversion into Pyrrolidine Analogues



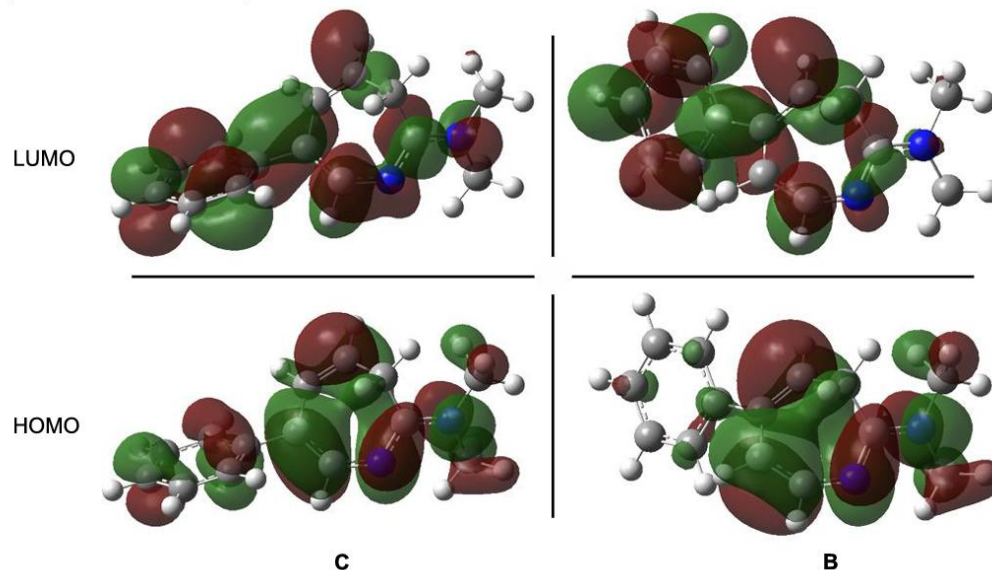
C) UV/Vis absorption spectra



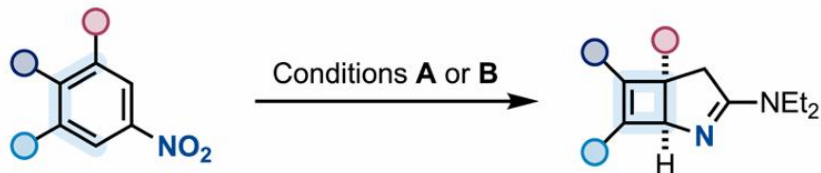
D) S<sub>1</sub> excitation energies and oscillator strengths

Substrate	E <sub>ex</sub> (eV)	f
A	3.80	0.3641
B	4.32	0.1350
C	4.15	0.4753
D	4.00	0.2846

E) HOMO and LUMO analysis for C and B

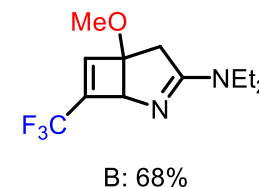
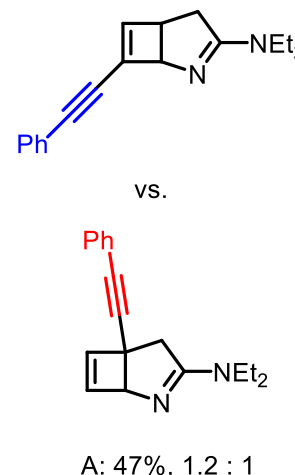
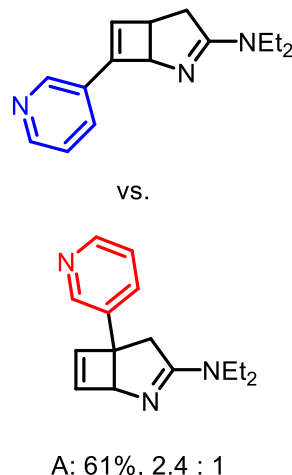
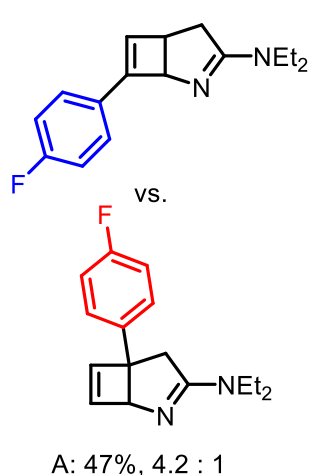
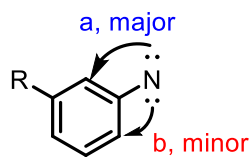
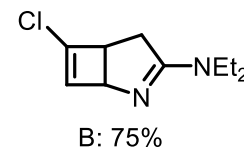
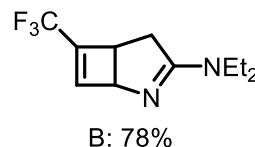
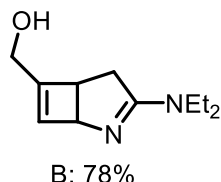
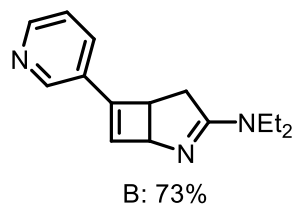


# Conversion into Pyrrolidine Analogues

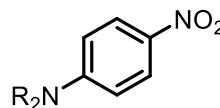
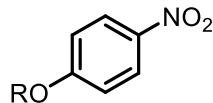
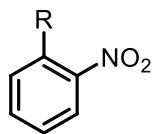


**Conditions A**  
 Et<sub>2</sub>NH (4 eq), P(O*i*-Pr)<sub>3</sub> (10 eq)  
 r.t., 16 h, hv = 350–427 nm

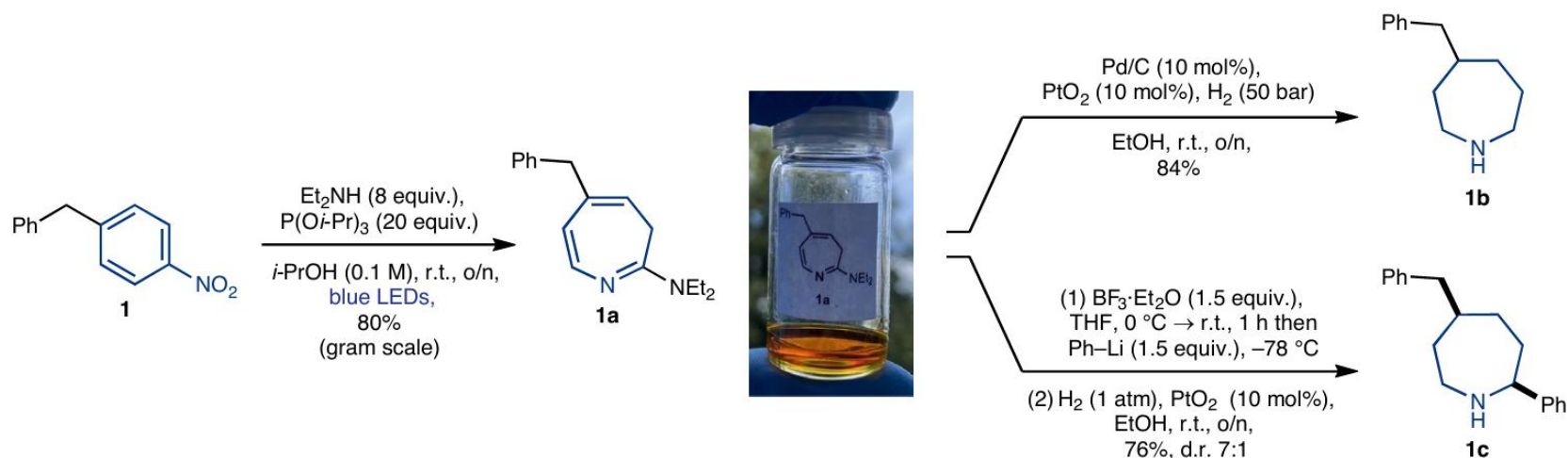
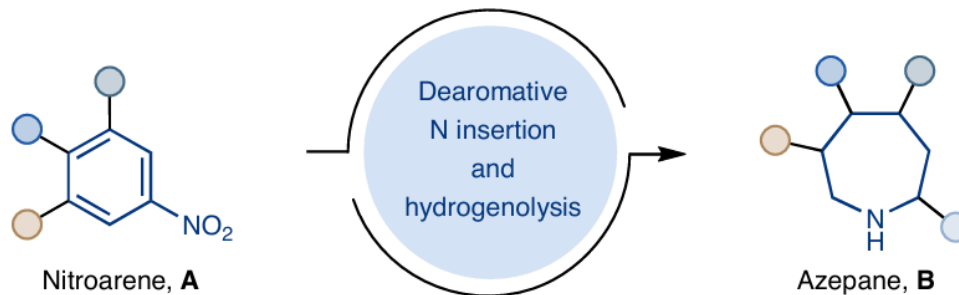
**Conditions B**  
 Et<sub>2</sub>NH (8 eq), P(O*i*-Pr)<sub>3</sub> (20 eq)  
 r.t., 16 h, hv = 427 nm  
 then r.t., 16 h, hv = 300–350 nm



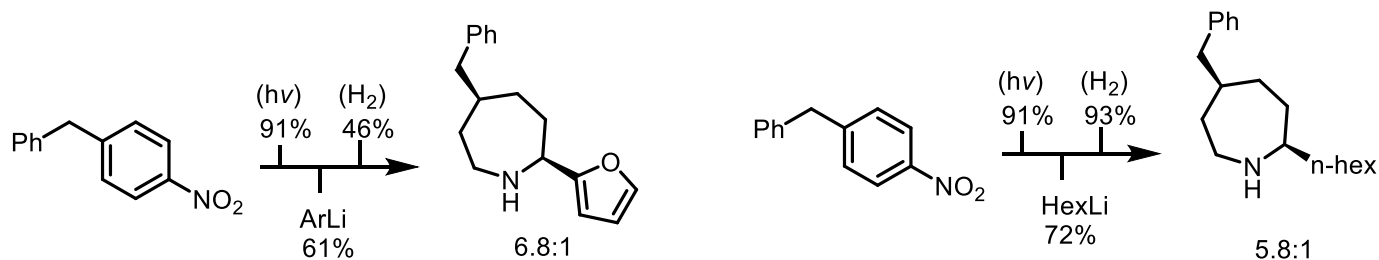
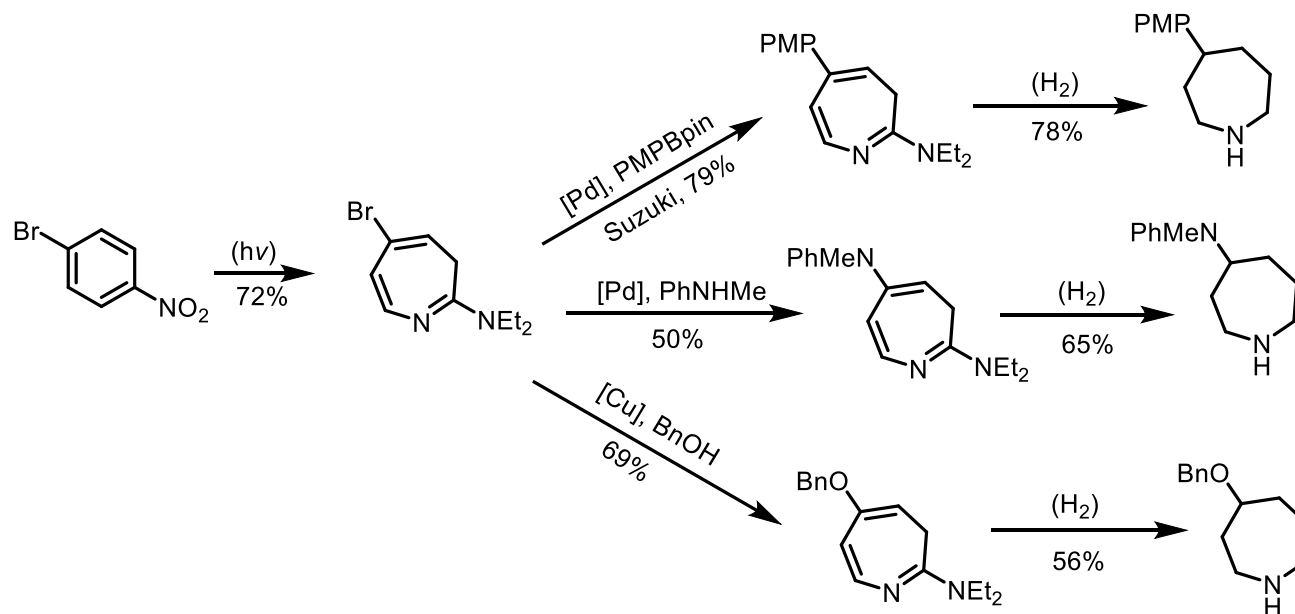
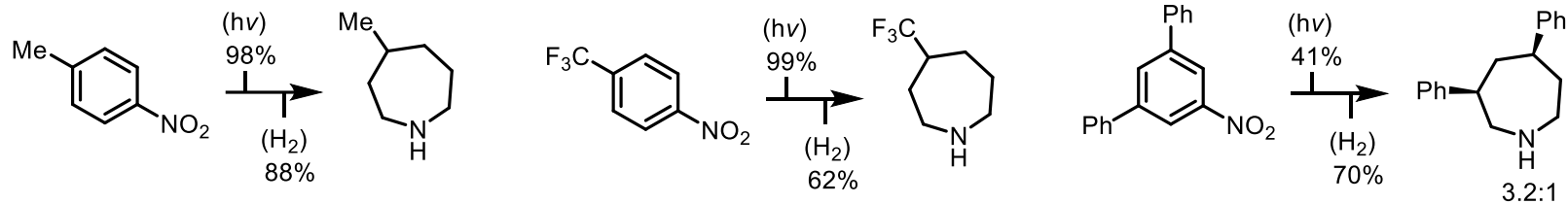
Limitations:



# Polysubstituted Azepanes



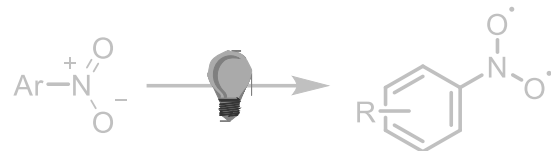
# Polysubstituted Azepanes



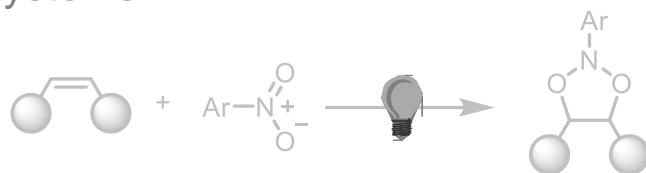
# Outline

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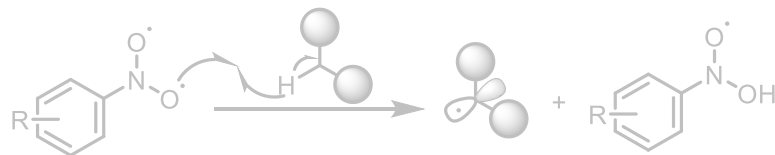
## ■ Introduction: Photochemistry of Nitroarenes



## ■ Reaction with $\pi$ -Systems



## ■ Photoinduced HAT reactions



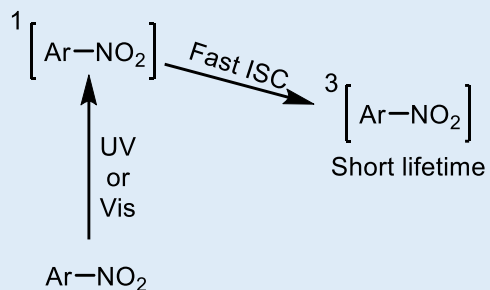
## ■ Reduction to Nitrene Species



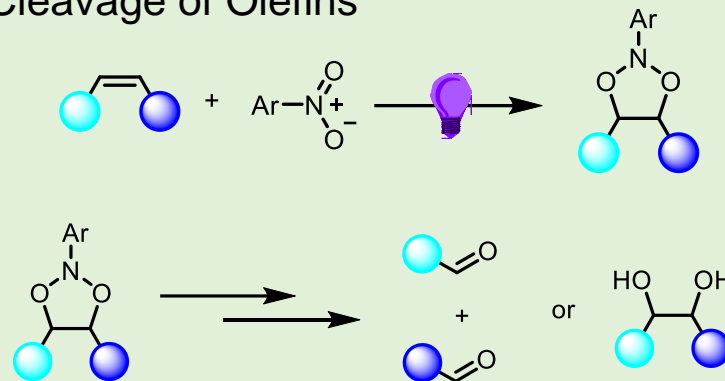
## ■ Summary and Perspective

# Summary

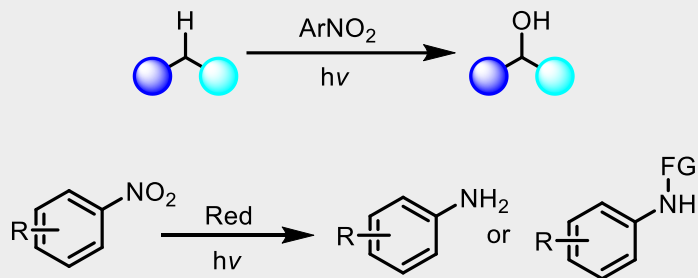
## ■ Photochemistry of Nitroarene



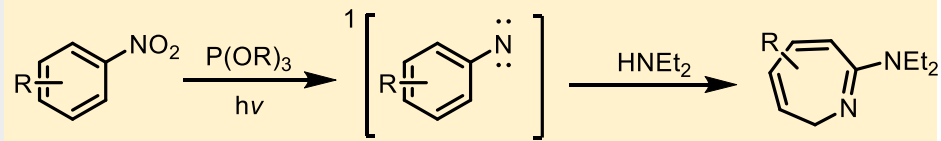
## ■ Cleavage of Olefins



## ■ HAT Reaction



## ■ Reduction to Nitrene



■ Favoring Electron-Deficient Nitroarene

■ Only Nitrobenzene Derivatives

# **Back-up Slides**

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# Franck-Condon Factor

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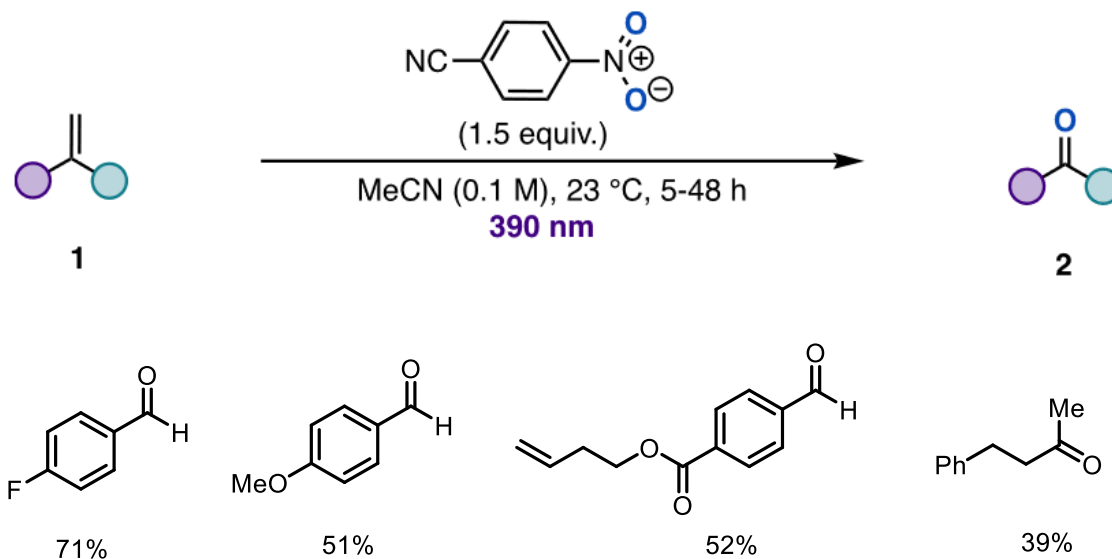
The radiationless decay rate constant  $k$  is given by

$$k^{nr} = A |\langle n | H_{s_0} | \pi \rangle|^2 \rho(E_T) F,$$

Where  $A$  is a constant.  $\rho(E_T)$  is the density of the ground vibronic states in the energy region of  $E$ , and  $F$  is the Franck-Condon (FC) factor between the  $S_0$  and  $T_1$  states.

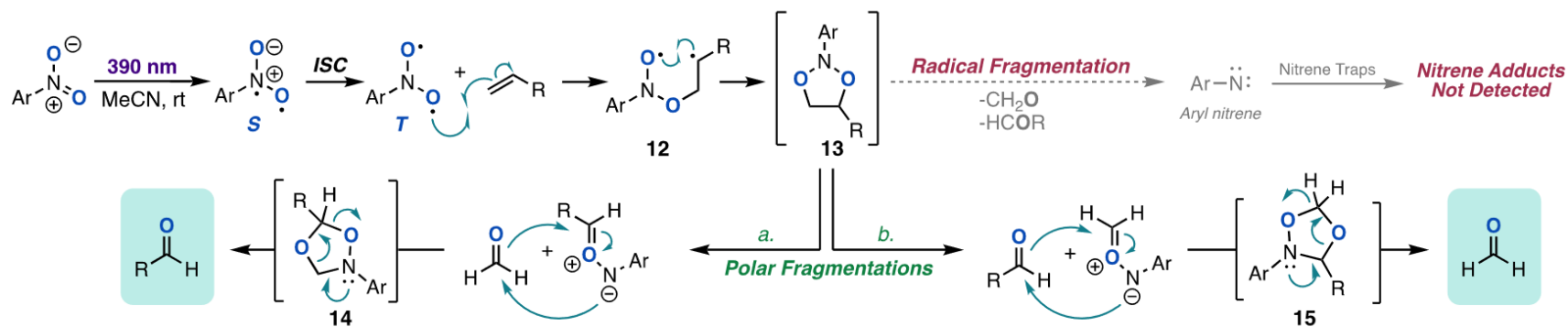
Theoretically, when the positions of the minima or the curvatures of the potential surfaces of the two states are very different (displaced or distorted oscillators, respectively), the FC factor can be large.

# Oxidative Cleavage of Alkenes

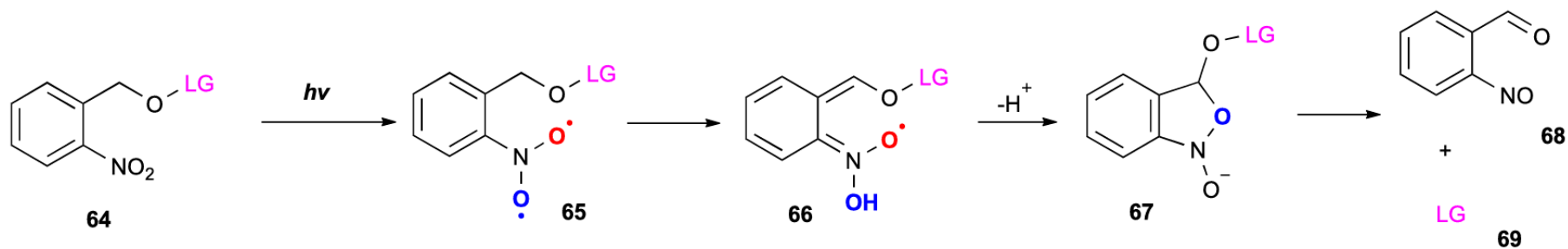


## ■ Mechanism

### Proposed Mechanism



# Photocleavage of Nitroarene Protecting Group



# Carbonyl and Imine Derivatives

