

XU GROUP  
*Department of Chemistry, Peking University*

# *Selected Weekly Literature Presentations*

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# Single Carbon Atom Doping

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**Reporter: Yiming Liu**

**Date: 2025.09.06**

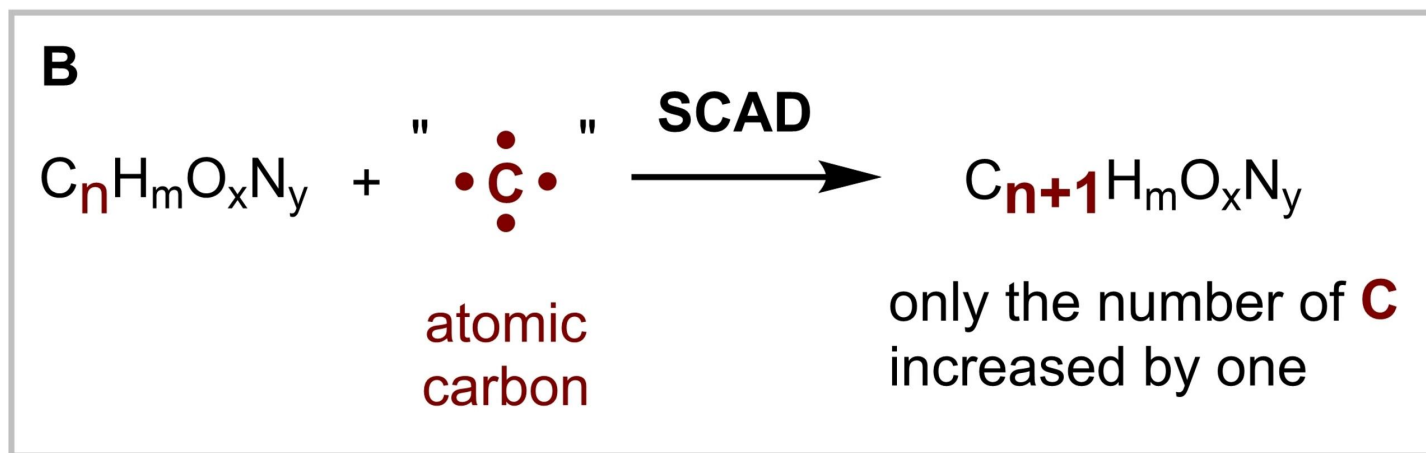
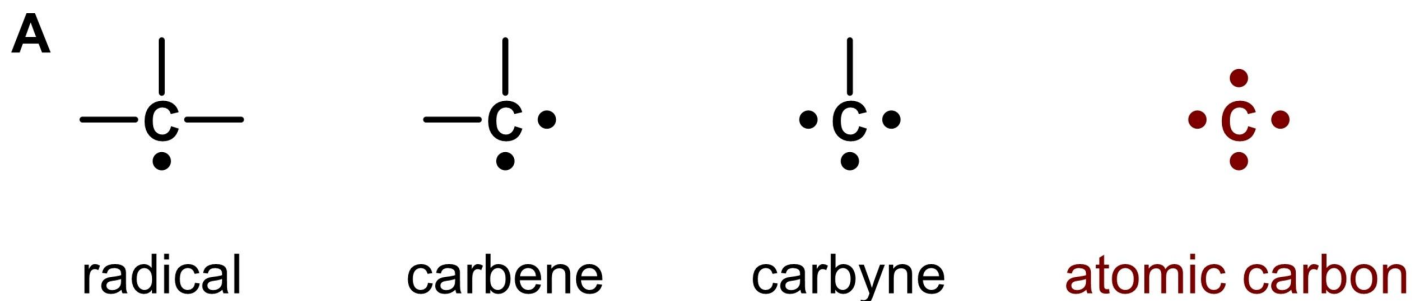
# Outline

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- **Introduction**
- Atomic Carbon Generated by Physical Methods
- Chemical Methods Using Atomic Carbon Equivalents
- Summary and Outlook

# Introduction

- different form of carbon



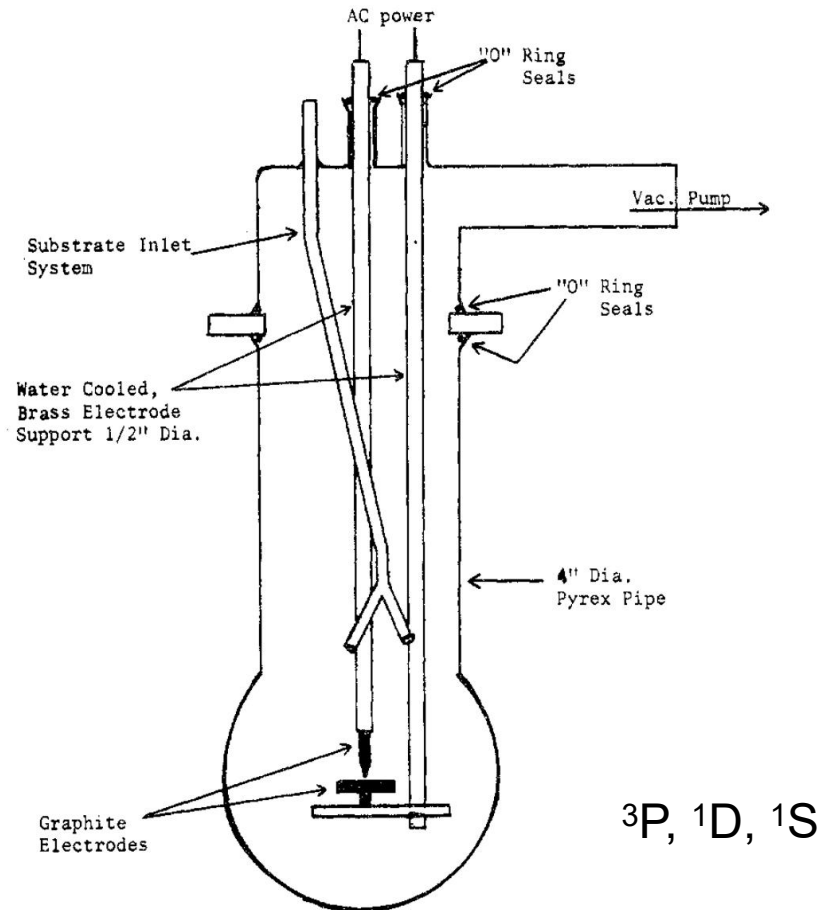
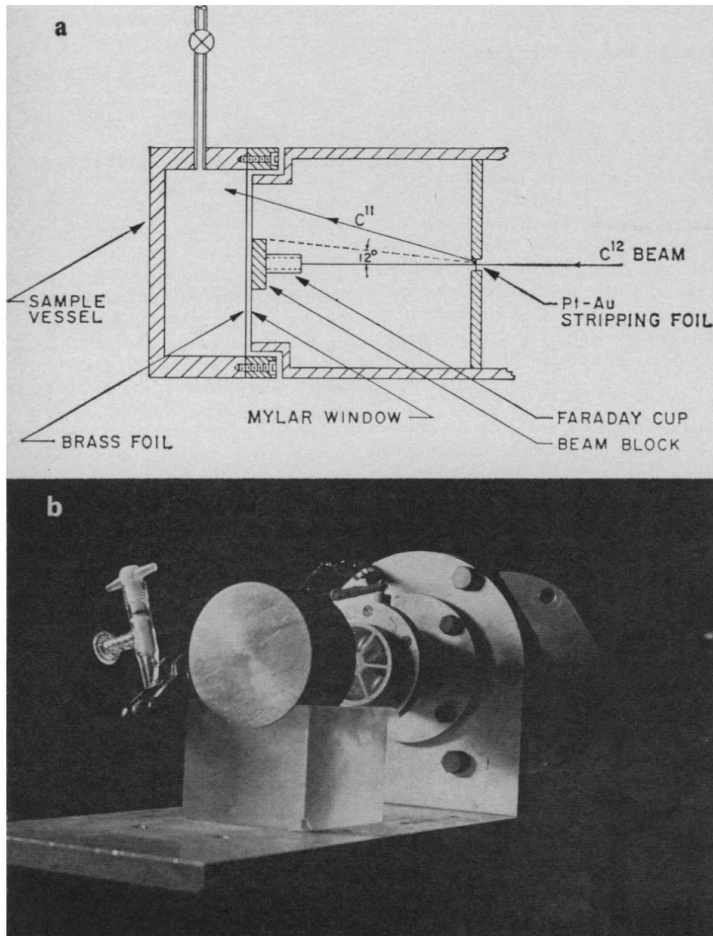
# Outline

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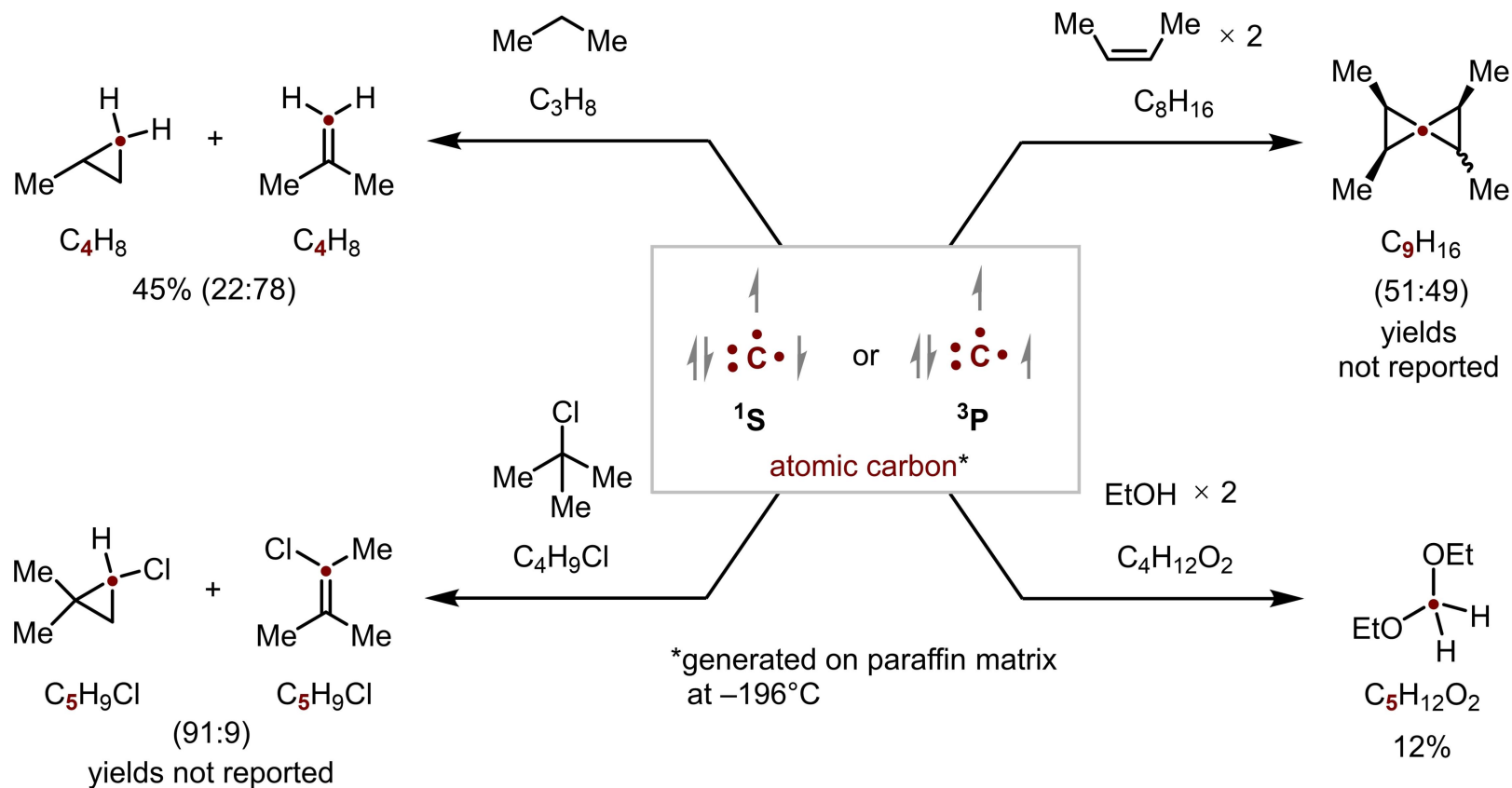
- Introduction
- **Atomic Carbon Generated by Physical Methods**
- Chemical Methods Using Atomic Carbon Equivalents
- Summary and Outlook

# Physical Methods

- nuclear transformation and arc discharge



# Atomic Carbon Doping



P. S. Skell, R. R. Engel, *J. Am. Chem. Soc.* **1965**, *87*, 1135–1136.

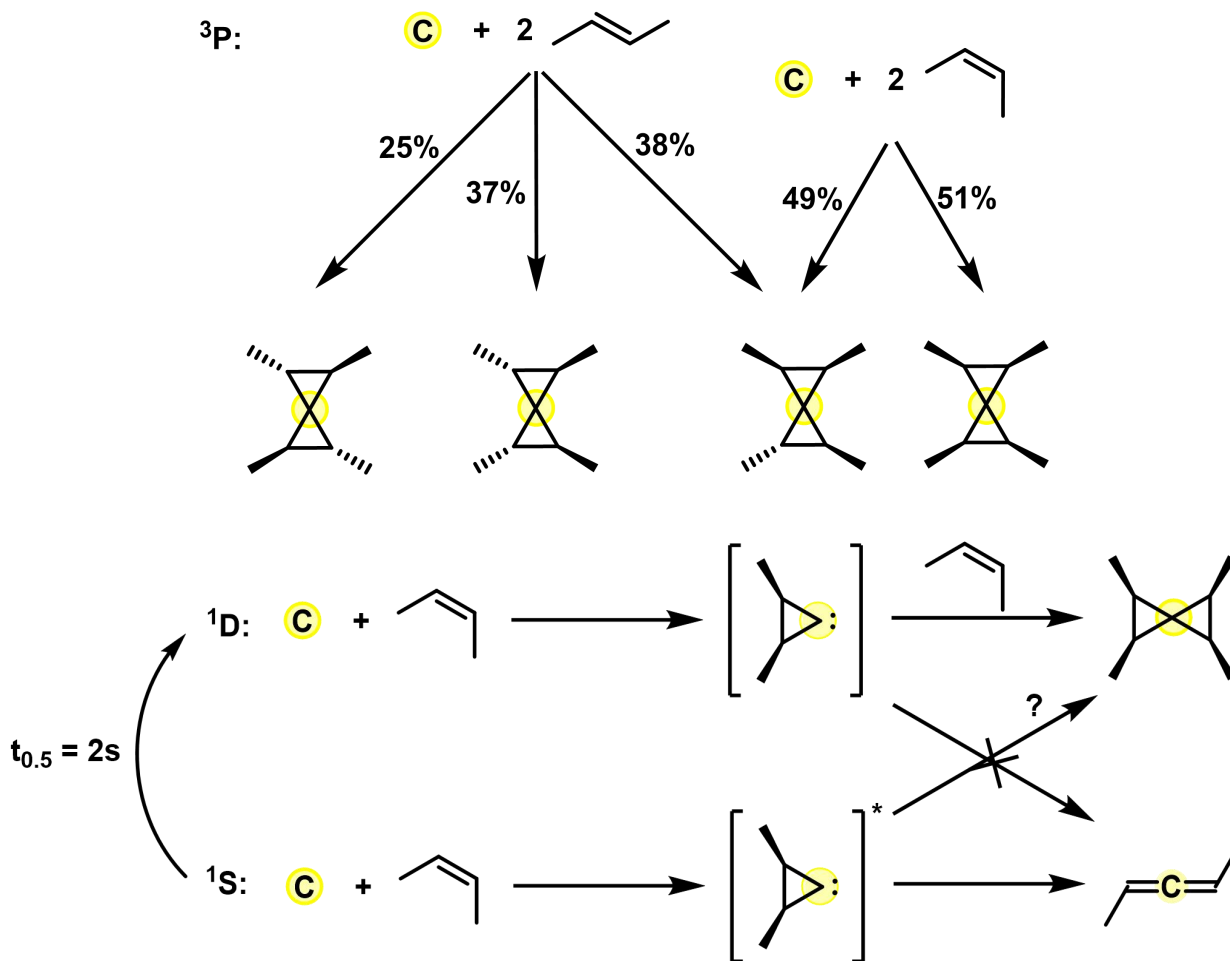
P. S. Skell, R. R. Engel, *J. Am. Chem. Soc.* **1966**, *88*, 4883–4890.

P. S. Skell, R. F. Harris, *J. Am. Chem. Soc.* **1965**, *87*, 5807–5808.

P. S. Skell, R. R. Engel, *J. Am. Chem. Soc.* **1966**, *88*, 3749–3758.

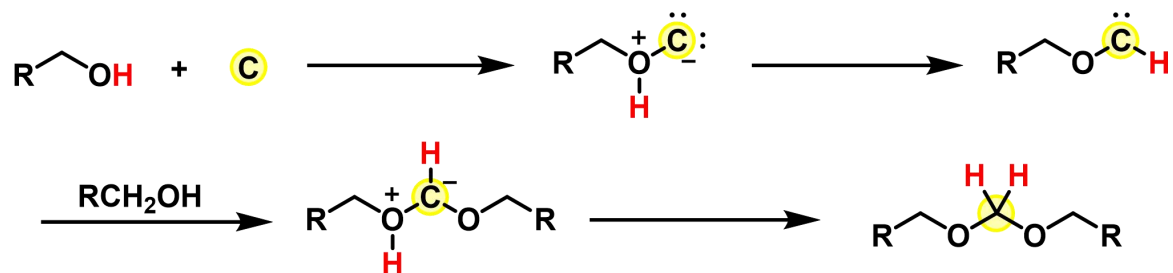
P. S. Skell, R. F. Harris, *J. Am. Chem. Soc.* **1969**, *91*, 4440–4445.

# Doping of Alkenes



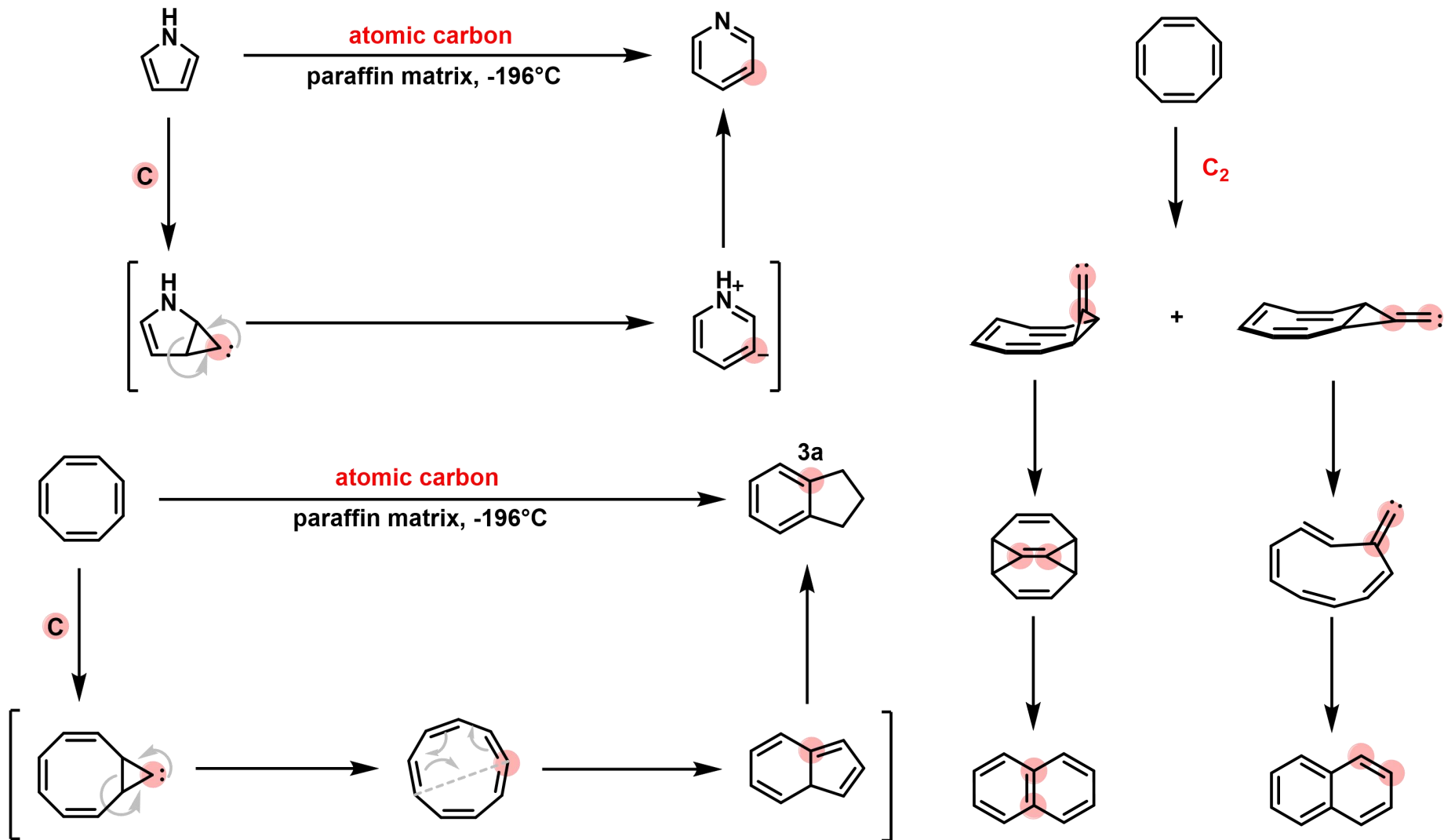
P. S. Skell, R. R. Engel, *J. Am. Chem. Soc.* **1965**, 87, 1135–1136.

# Doping of Alcohols



	Methanol	Ethanol	1-Propanol	2-Propanol	Methanol (:CH <sub>2</sub> )
OH insertion	17.8	12.8	11.5	10.6	-
CH insertion	6.3	12.5	11.3	11.1	-
Total insertion	24.1	25.3	22.8	21.7	-
OH:CH ration per bond	8.5	5.1	7.1	6.7	21.8

# Skeletal Editing



C. J. Emanuel, P. B. Shevlin, *J. Am. Chem. Soc.* **1994**, *116*, 5991–5992.

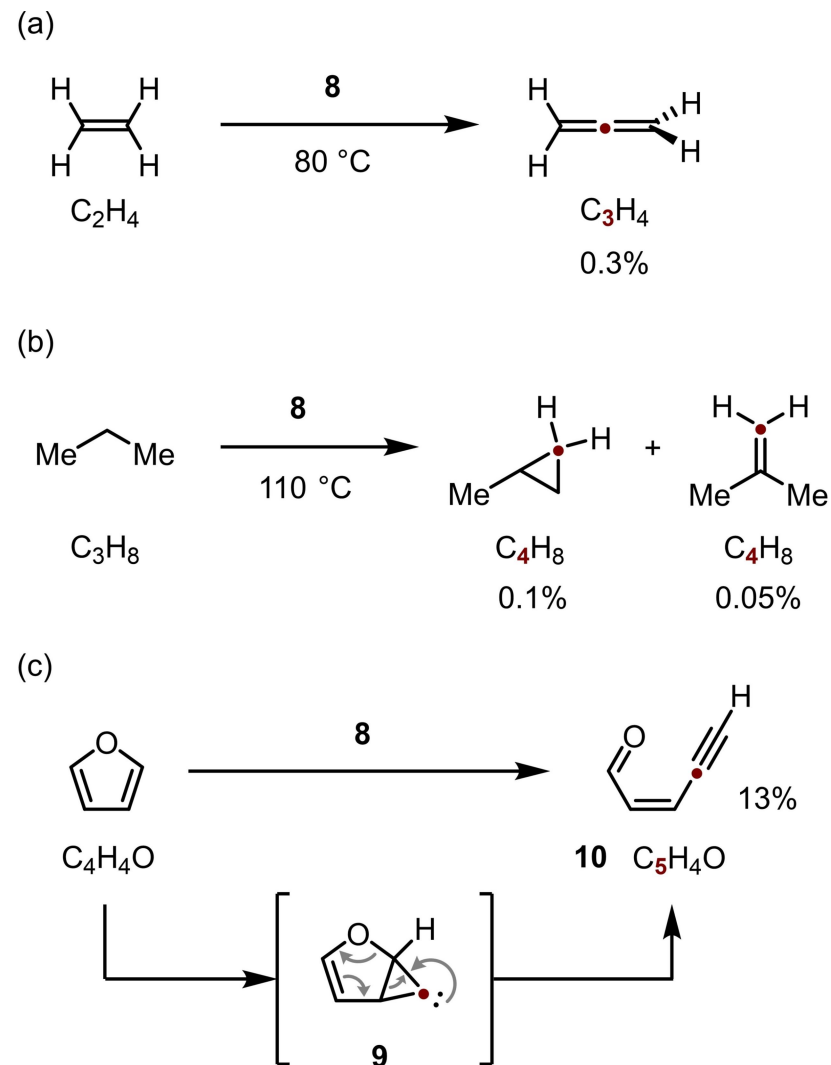
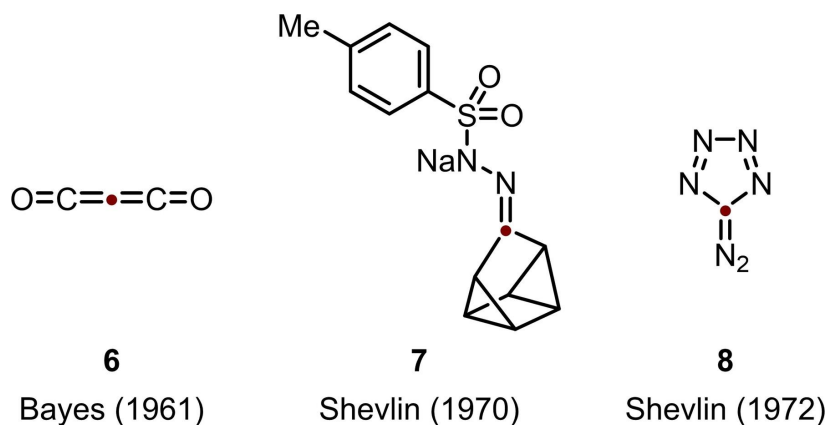
W. Pan, P. B. Shevlin, *J. Am. Chem. Soc.* **1996**, *118*, 10004–10005.

# Outline

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- Introduction
- Atomic Carbon Generated by Physical Methods
- **Chemical Methods Using Atomic Carbon Equivalents**
- Summary and Outlook

# Precursors of Atomic Carbon



K. Bayes, *J. Am. Chem. Soc.* **1961**, *83*, 3712–3713.

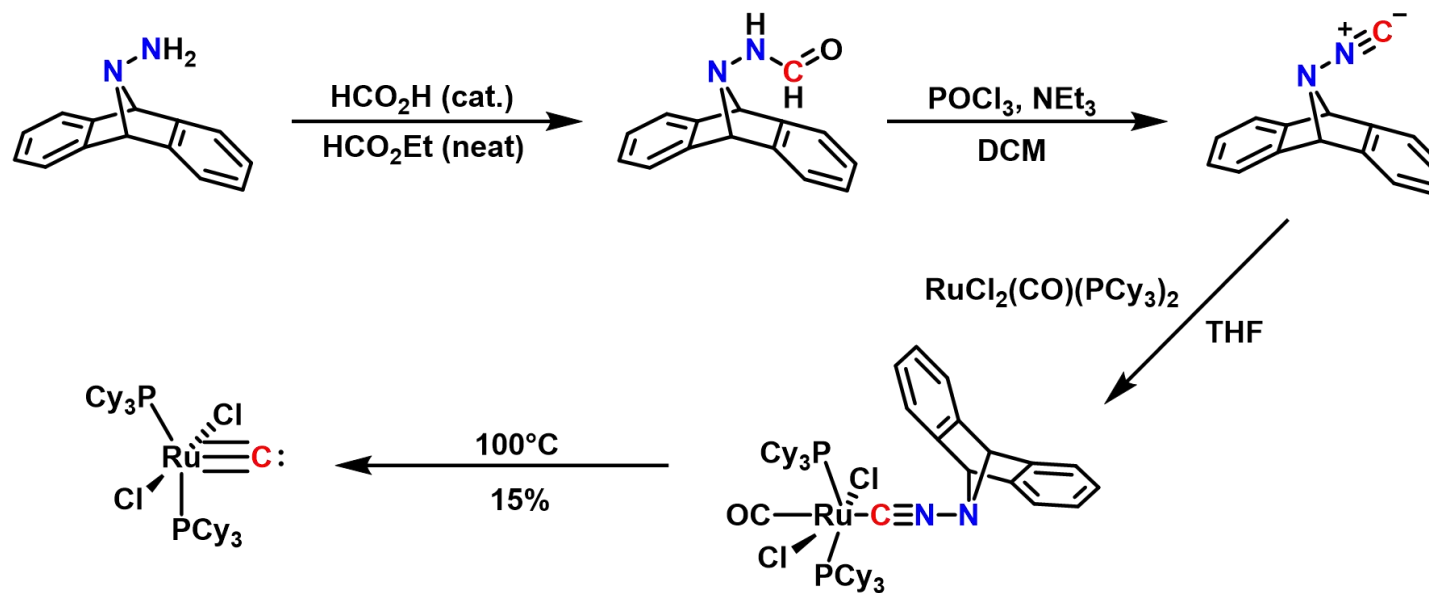
P. B. Shevlin, A. P. Wolf, *Tetrahedron Lett.* **1970**, *11*, 3987–3990.

P. B. Shevlin, *J. Am. Chem. Soc.* **1972**, *94*, 1379–1380.

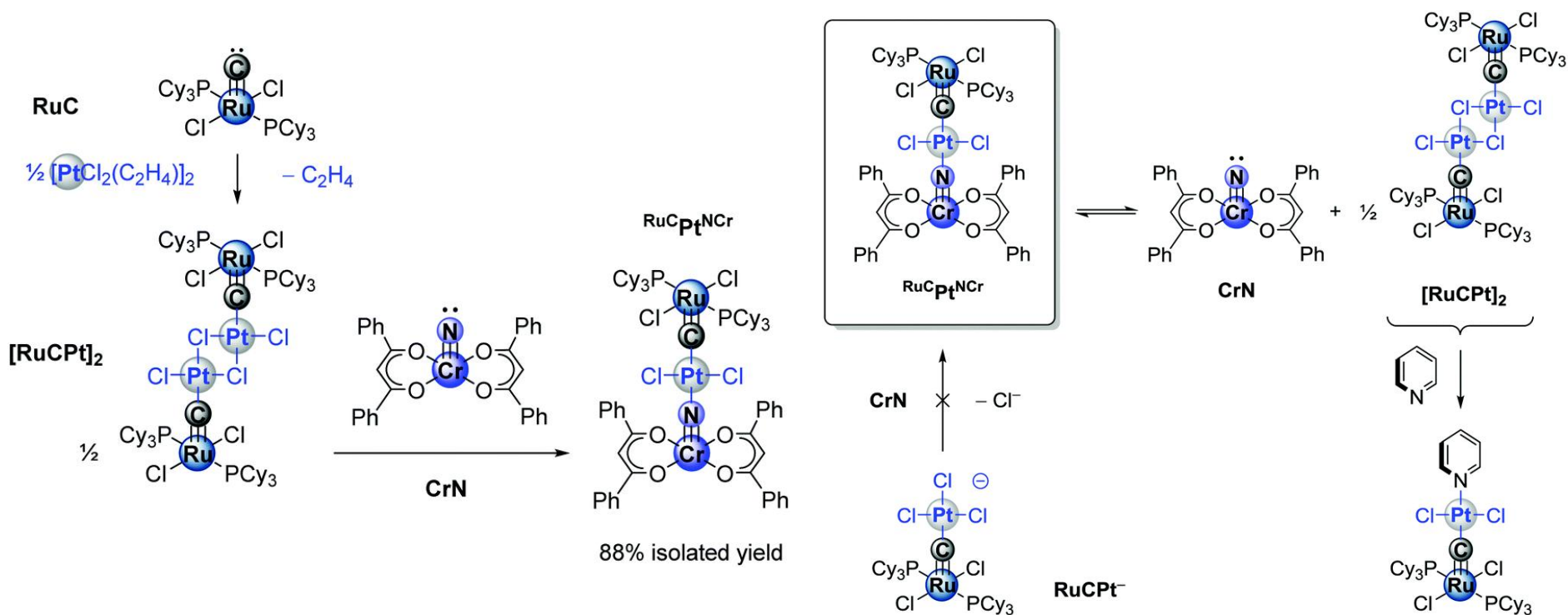
P. B. Shevlin, S. Kammula, *J. Am. Chem. Soc.* **1977**, *99*, 2627–2631.

S. F. Dyer, P. B. Shevlin, *J. Am. Chem. Soc.* **1979**, *101*, 1303–1304.

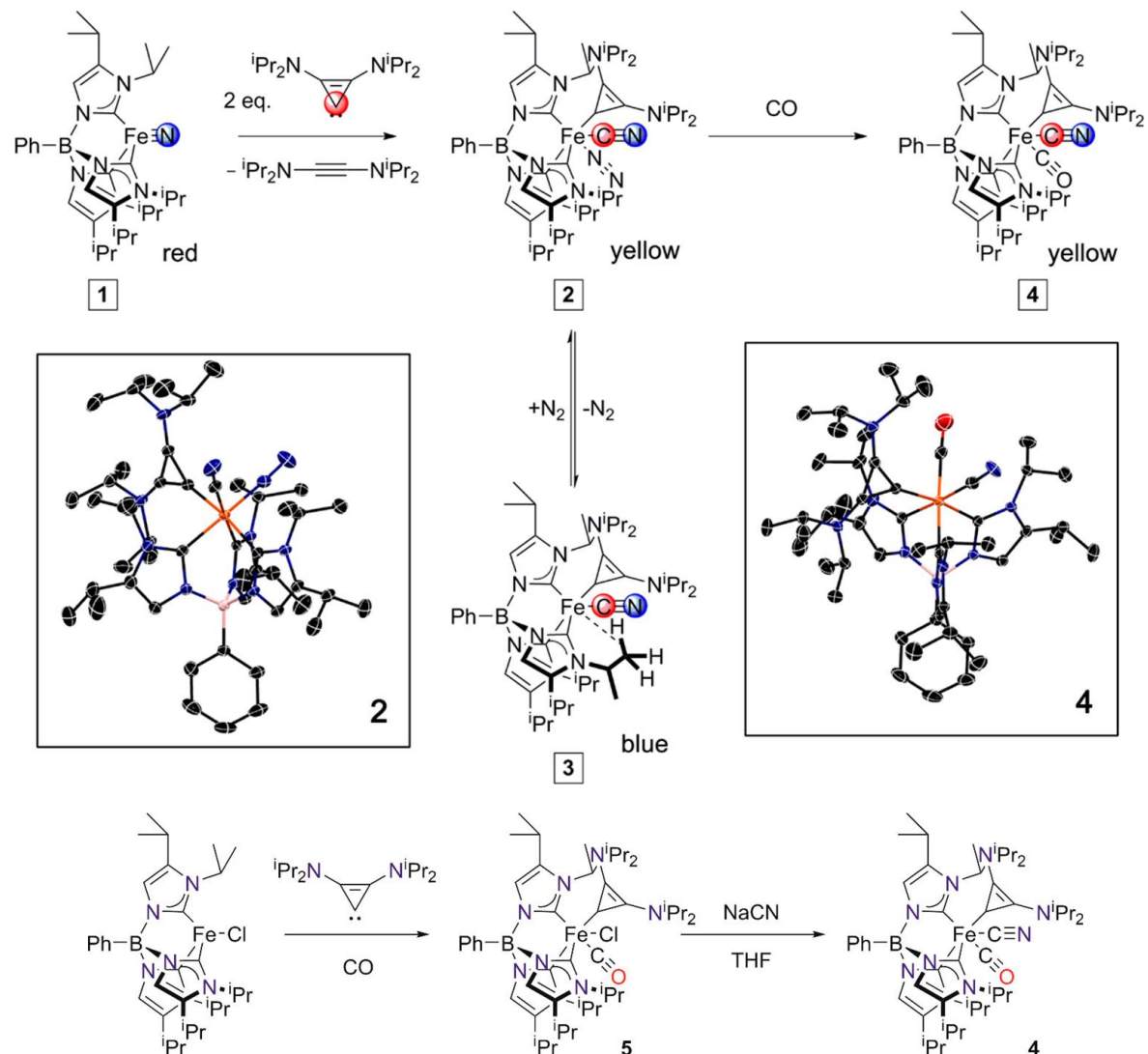
# Organometallic Compounds



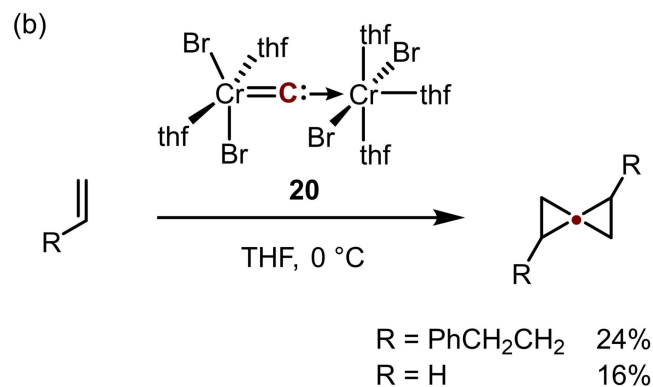
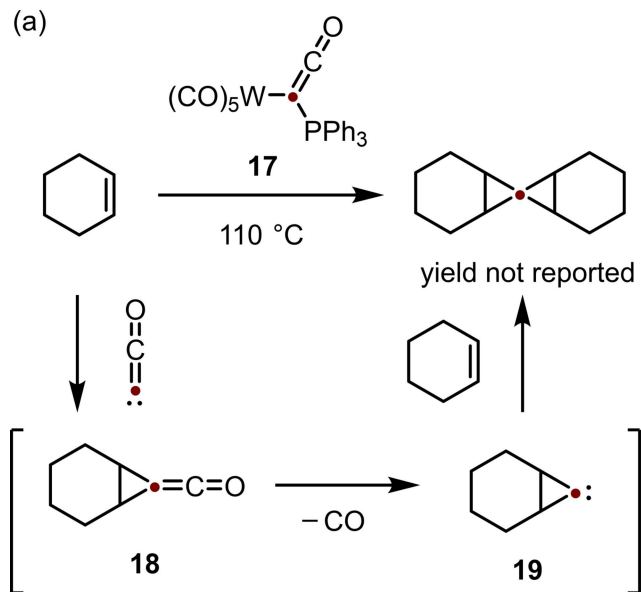
# Organometallic Compounds



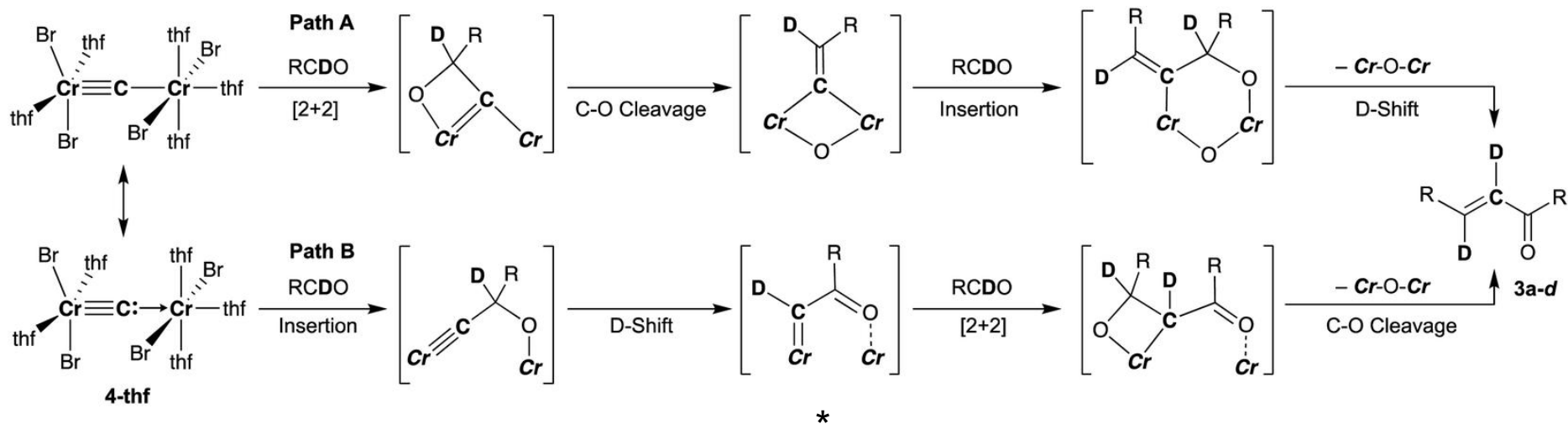
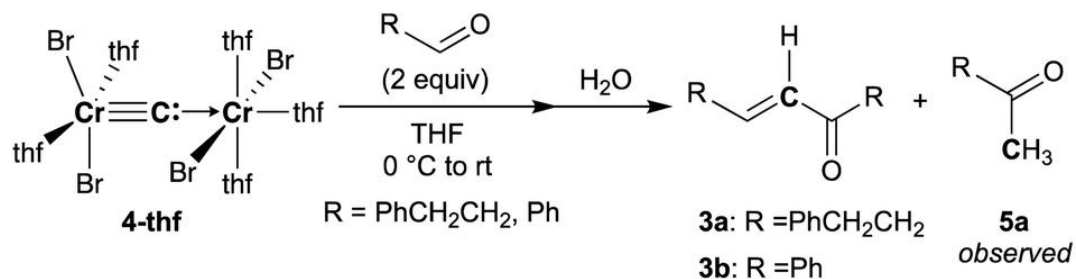
# Organometallic Compounds



# Organometallic Compounds



# Organometallic Compounds



# Chemical Equivalents

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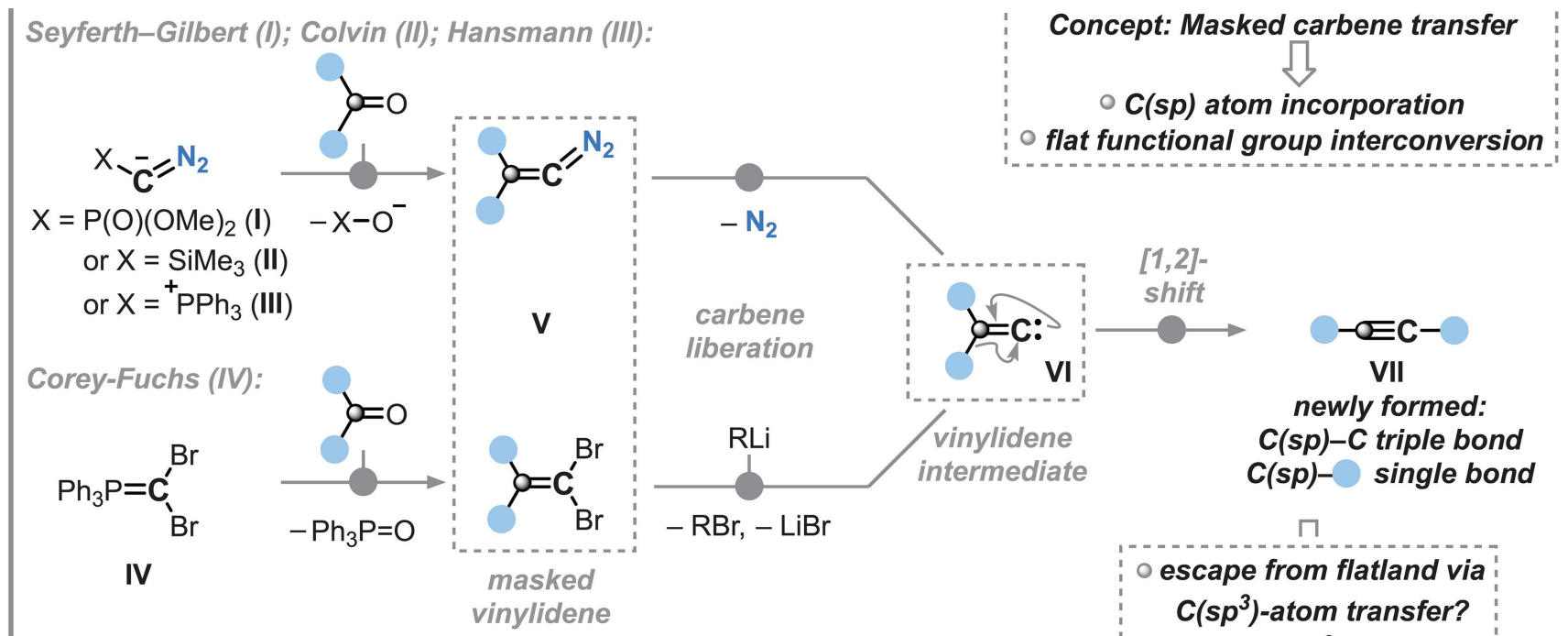
Max Martin Hansmann



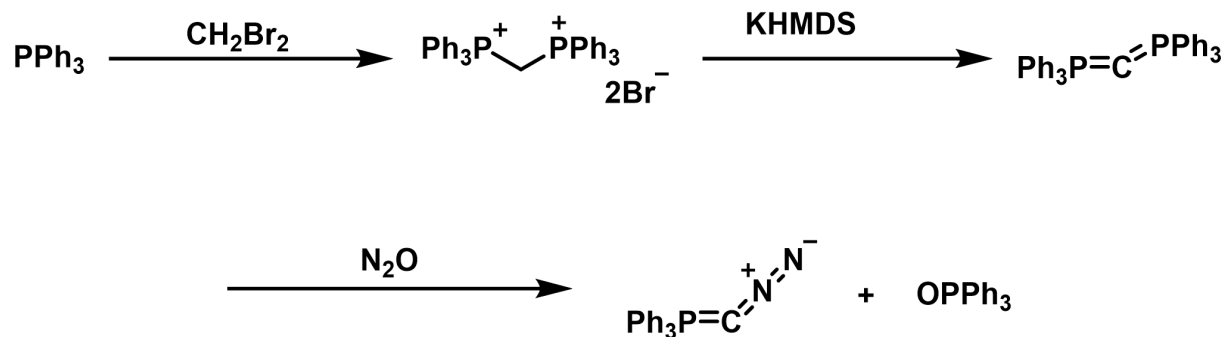
Mamoru Tobisu

# Chemical Equivalents

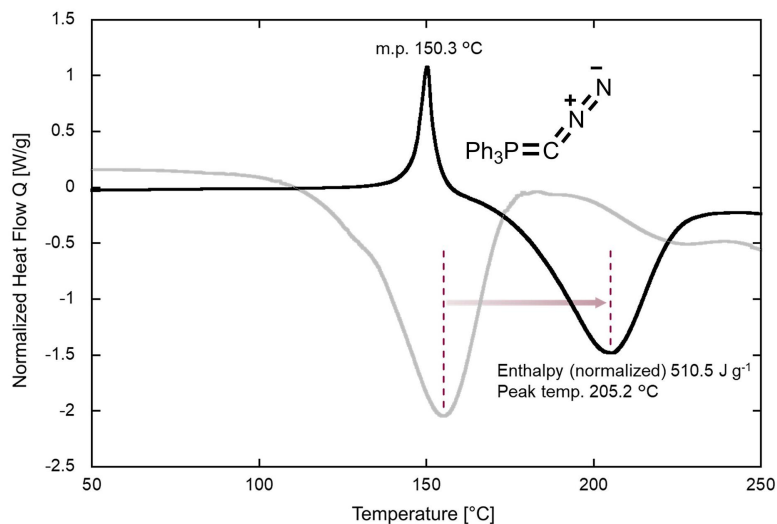
- conventional C-atom transfer



# Chemical Equivalents

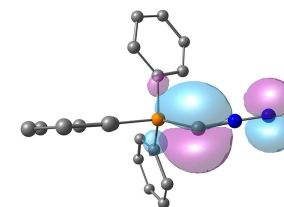


## D High thermal stability

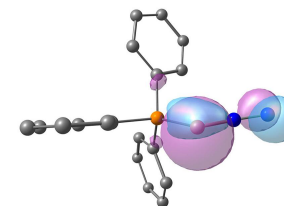


T. Koike *et al. Science*, 2024, 385, 305-311.

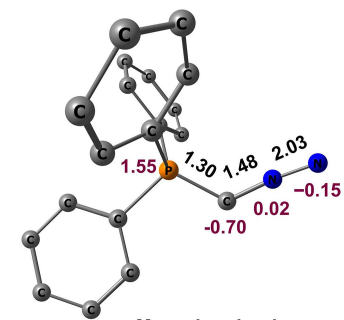
## E Evidence of C(0) nature



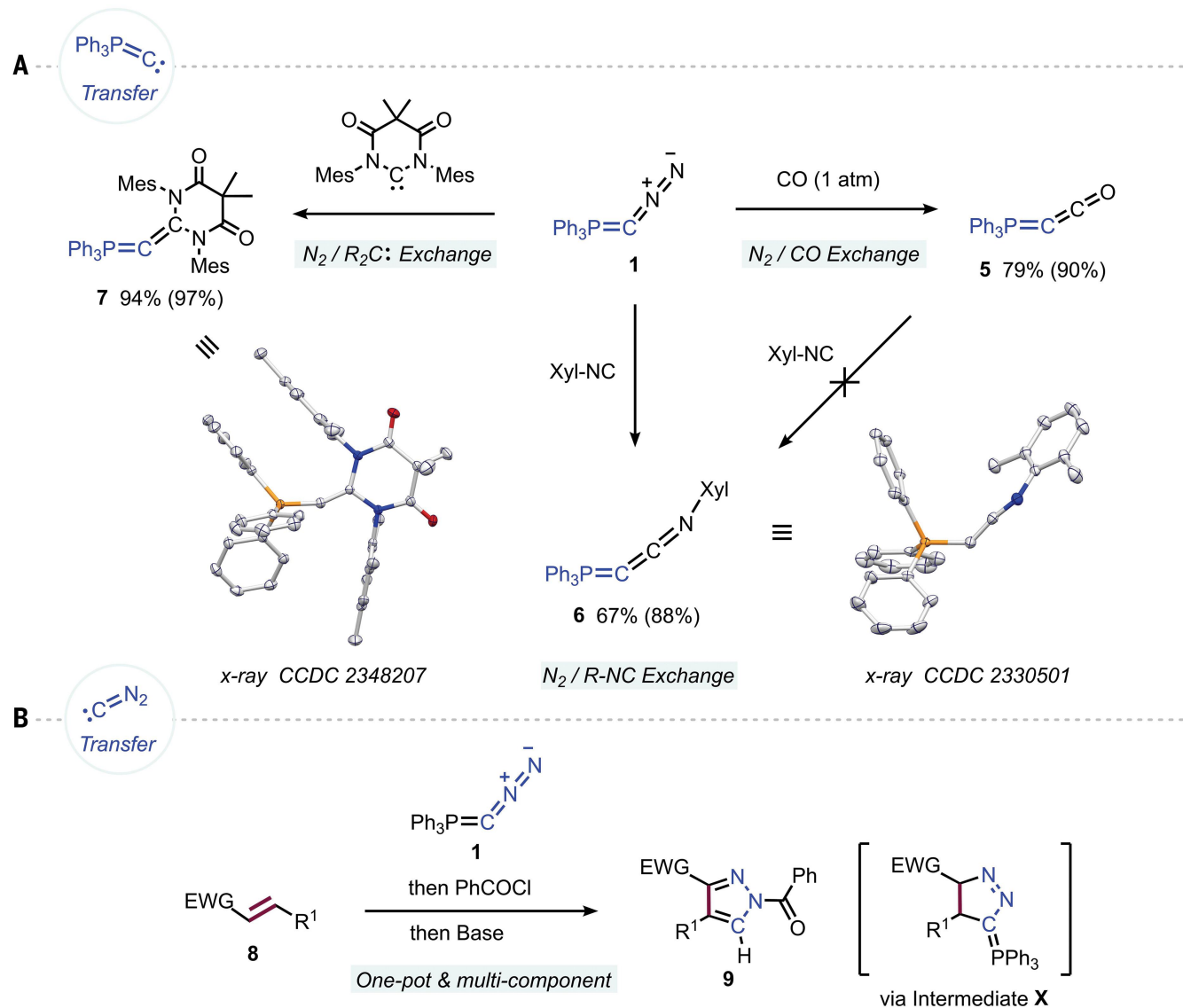
HOMO (-6.53 eV)



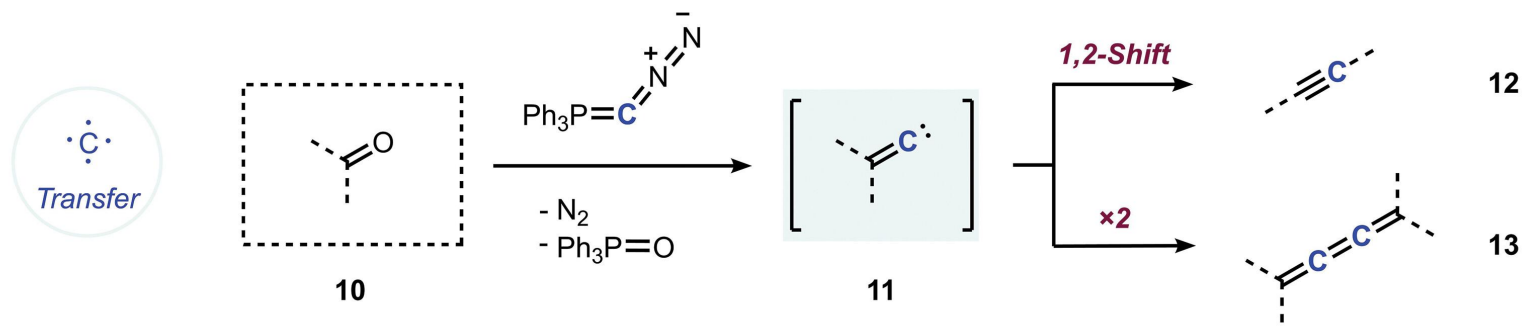
HOMO-1 (-7.06 eV)



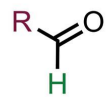
# Chemical Equivalents



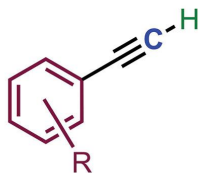
# Chemical Equivalents



## Aldehydes



10a-10g



12aa R = H 76% (94%)

12ab R = 2-Br 84% (92%)

12ac R = 2-NO<sub>2</sub> 90% (95%)

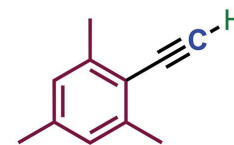
12ad R = 2-OMe 86% (93%)

12ae R = 4-<sup>t</sup>Bu 86% (94%)

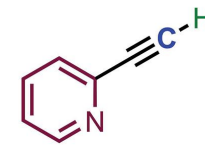
12af R = 4-CN 94% (98%)

12ag R = 4-CF<sub>3</sub> 78% (86%)

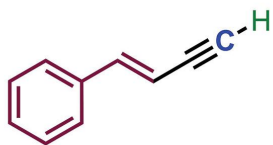
12ah R = 4-NO<sub>2</sub> 87% (94%)



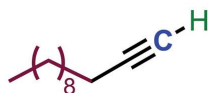
12ai 92% (96%)



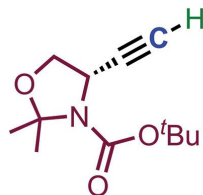
12b 80% (96%)



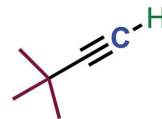
12c 63% (81%)\*  
from Cinnamaldehyde



12d 84% (96%)

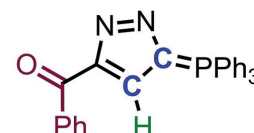


12e 77% (95%)  
from Garner's alkyne

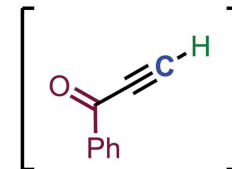


12f (97%)

## One-pot "C-atom" transfer + click reaction

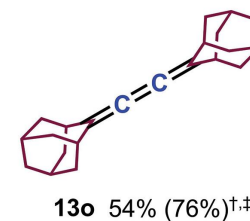
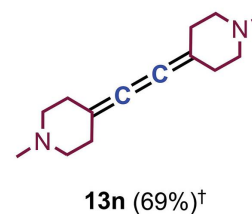
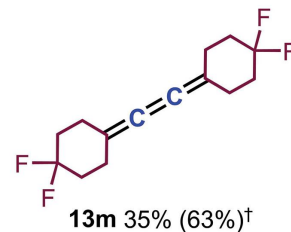
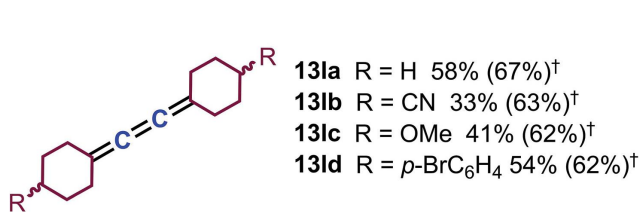
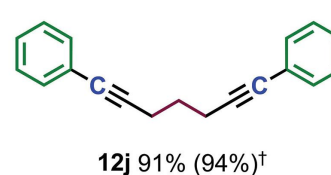
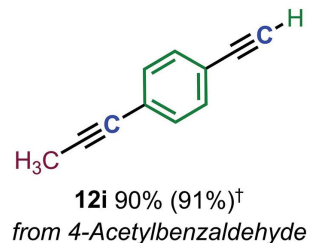
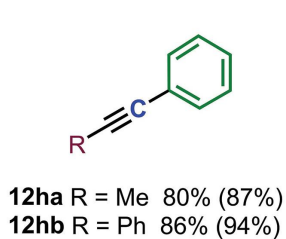
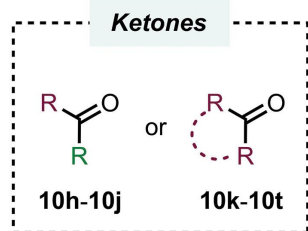


12g 24% (67%)<sup>†</sup>  
from Phenyl glyoxal

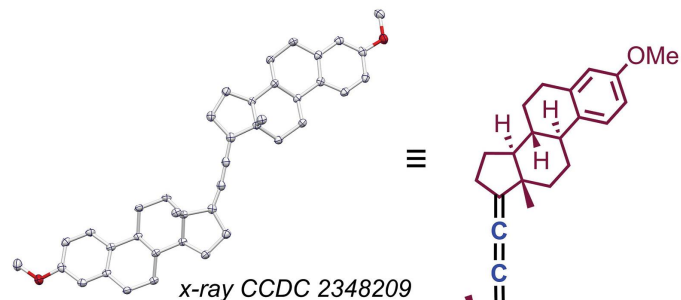
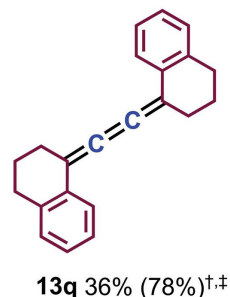
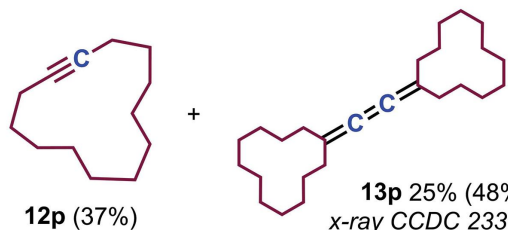


via Ynone 12g

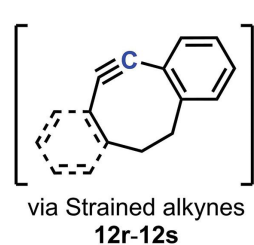
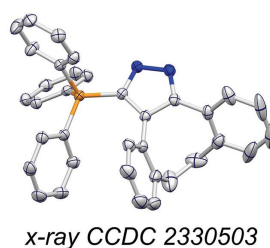
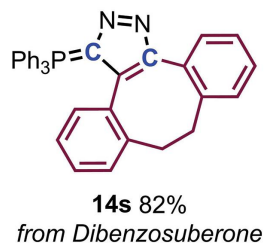
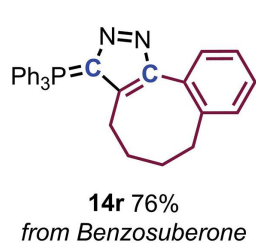
# Chemical Equivalents



Cyclic alkyne vs butatriene formation <sup>†,‡</sup>

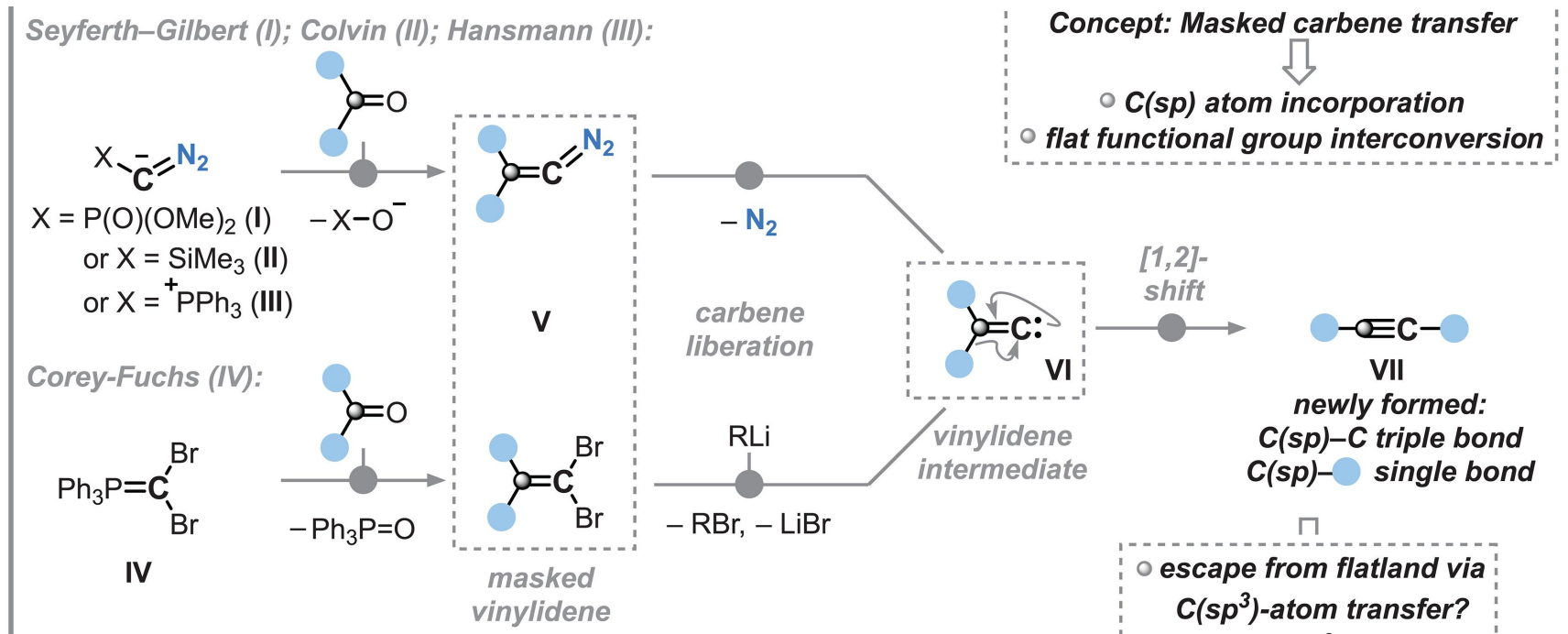


One-pot "C-atom" transfer + click reaction <sup>†,‡</sup>

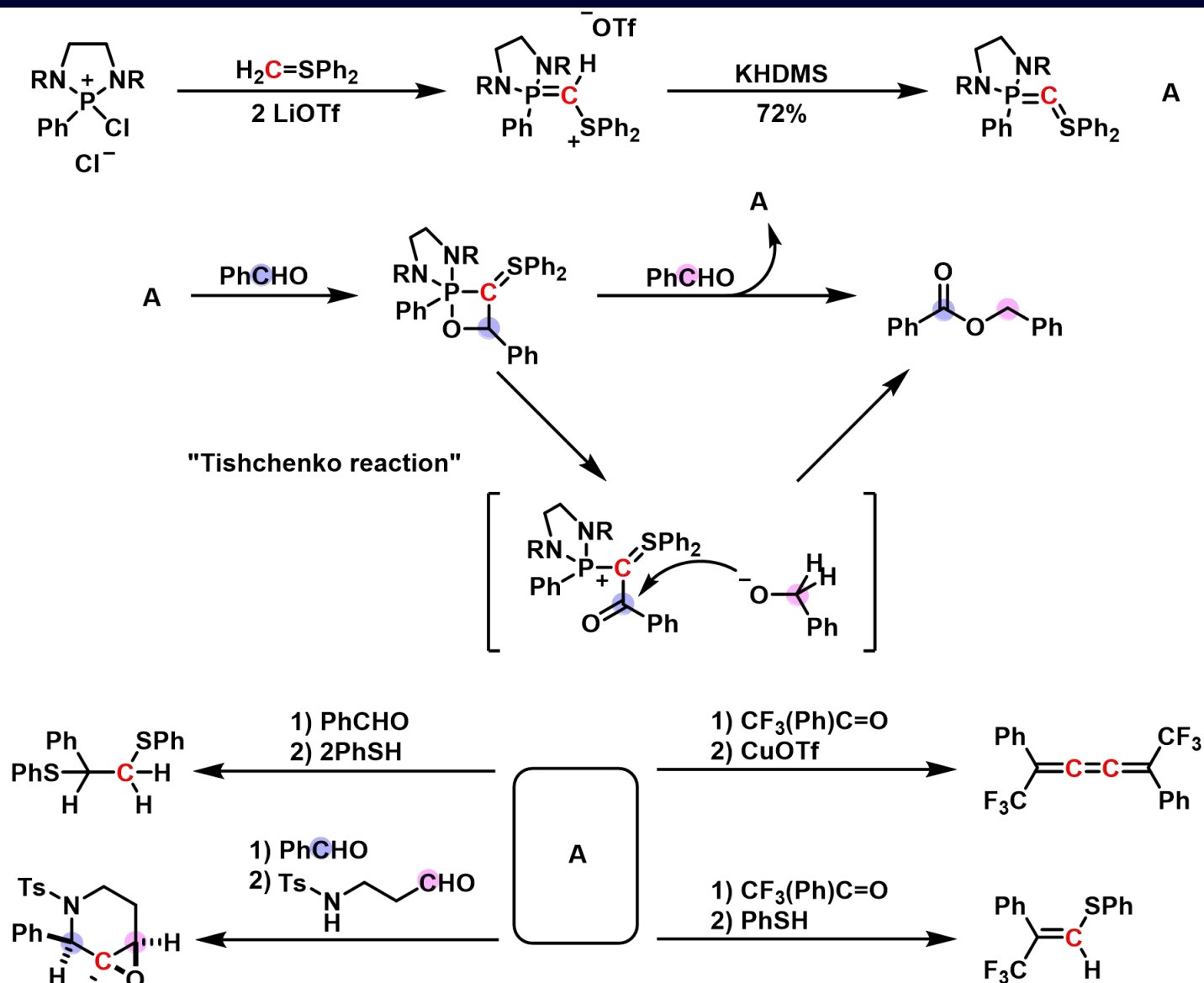


# Chemical Equivalents

- conventional C-atom transfer

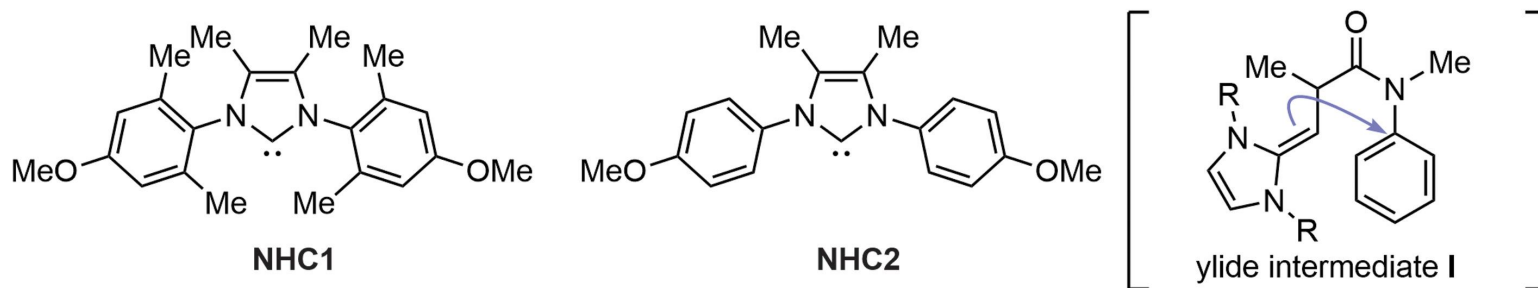
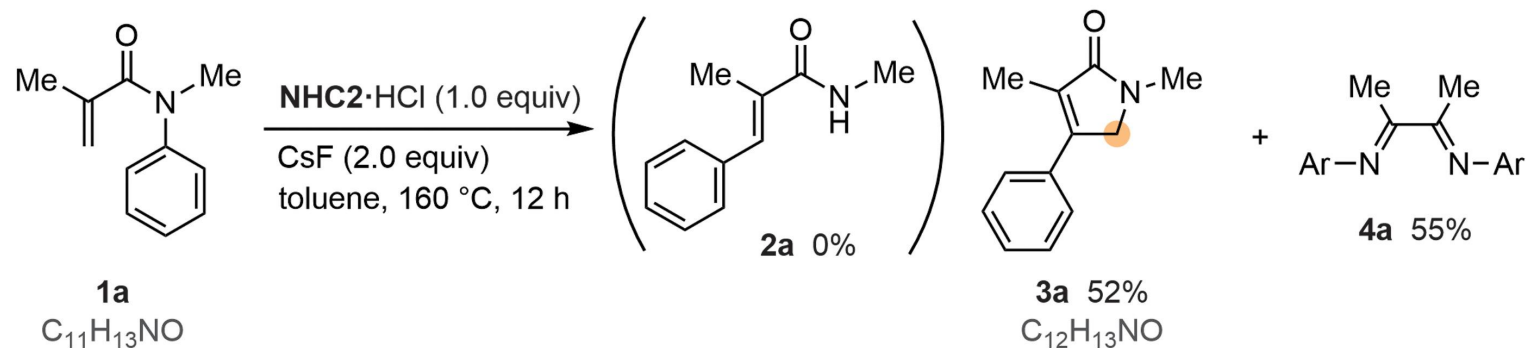


# Chemical Equivalents

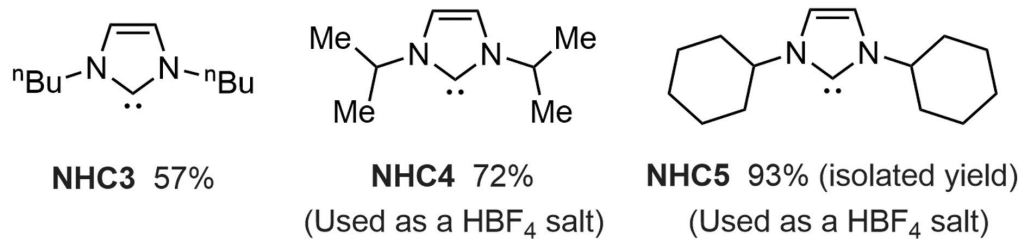


# Chemical Equivalents

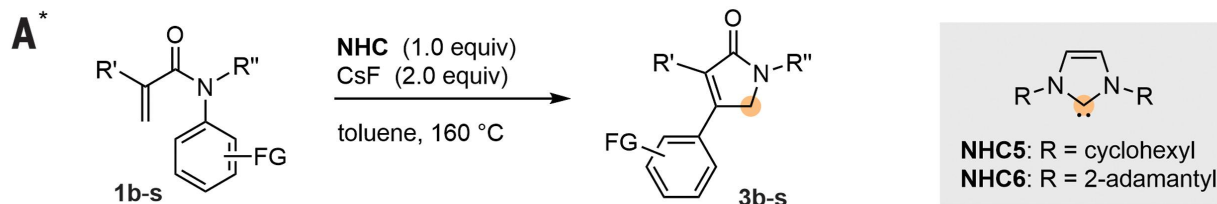
**A**



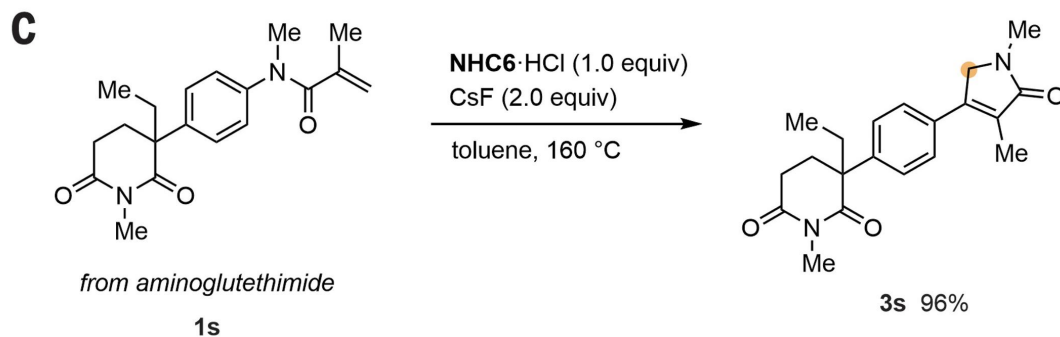
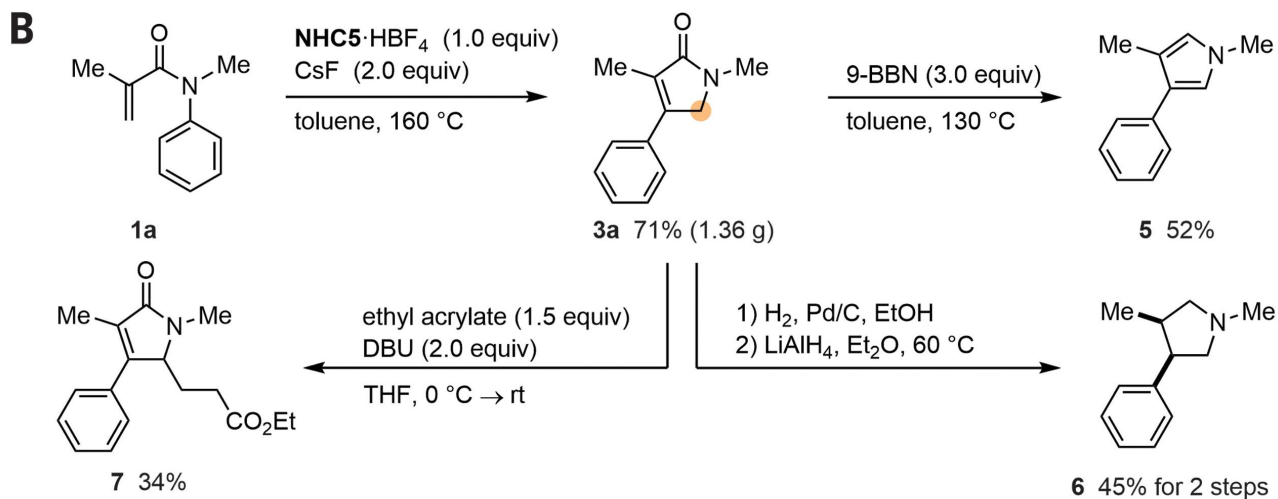
**B**



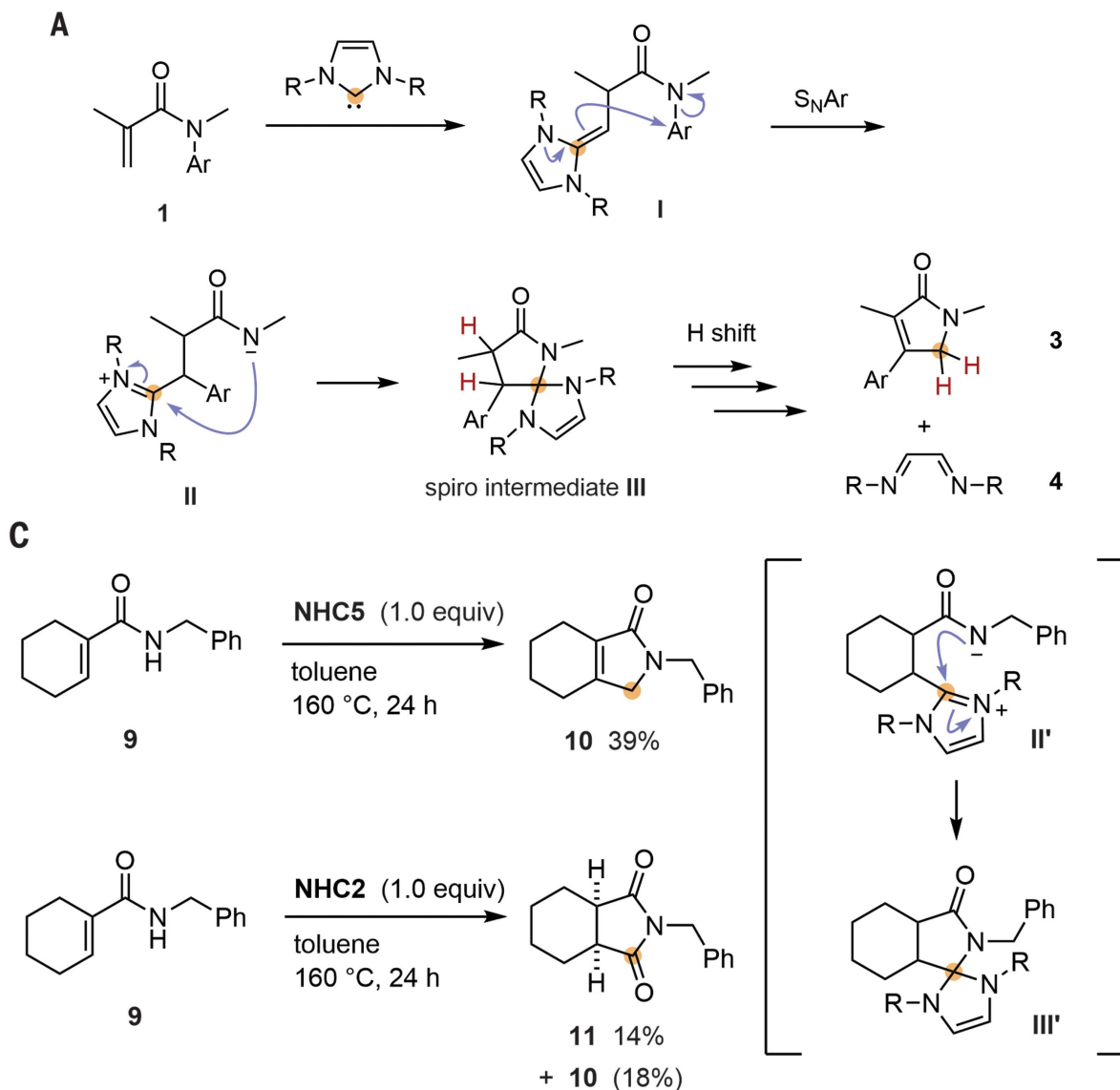
# Chemical Equivalents



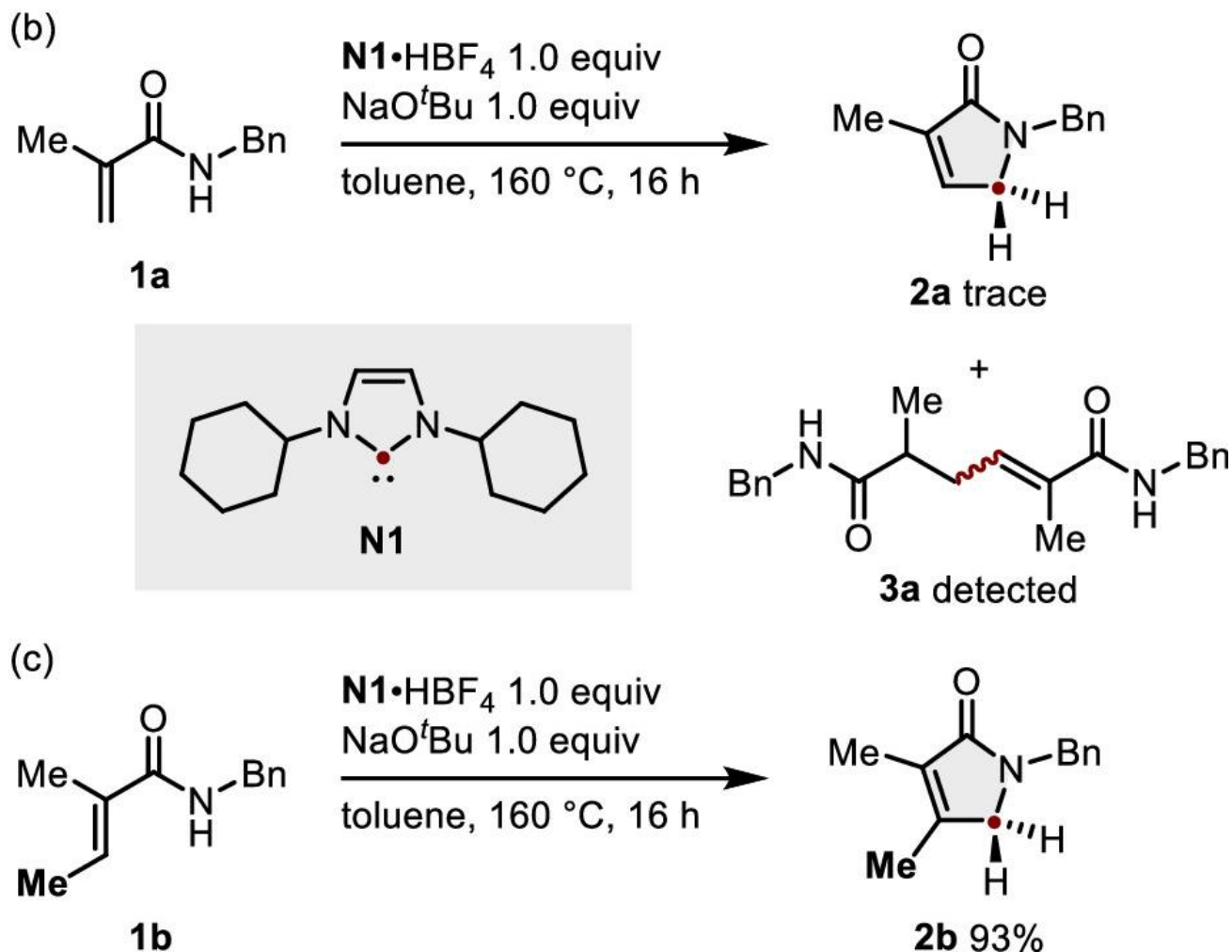
$R'' = \text{Me, } i\text{-Pr, Bn, PMP}$ ;  $\text{FG} = \text{R, EWG, EDG, } -\text{CH}=\text{CH}-\text{CH}=\text{CH}-$



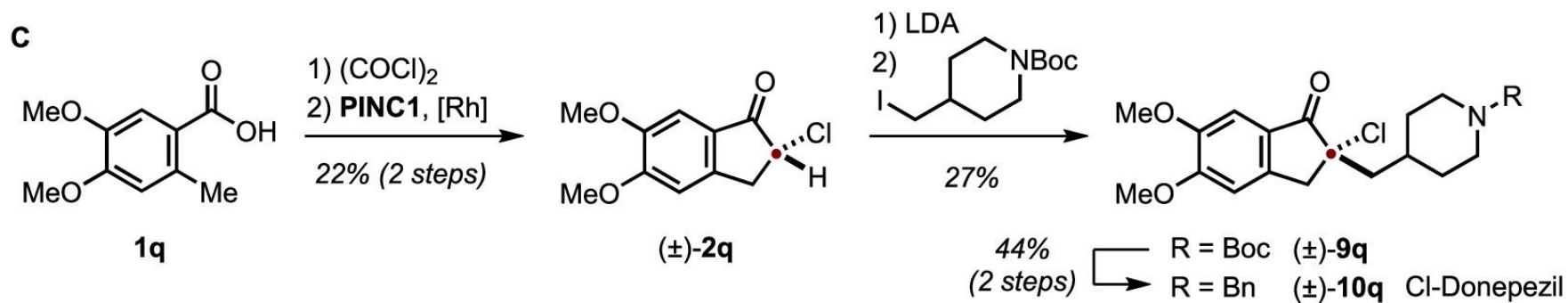
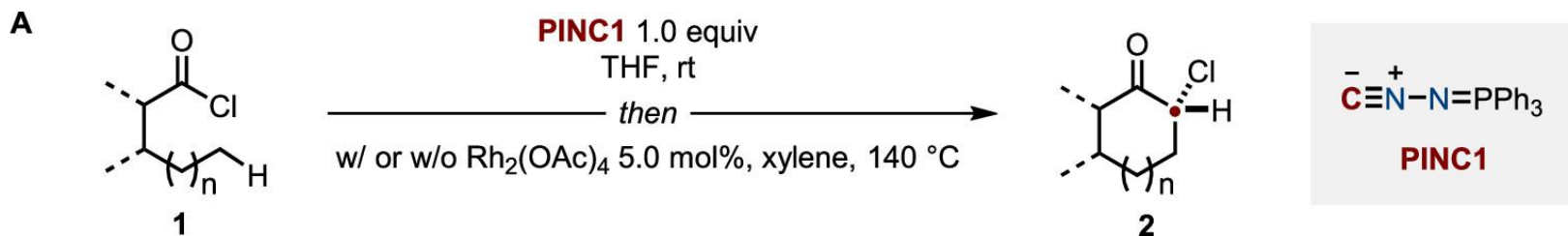
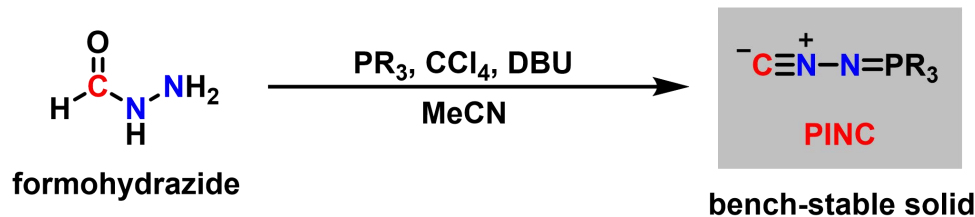
# Chemical Equivalents



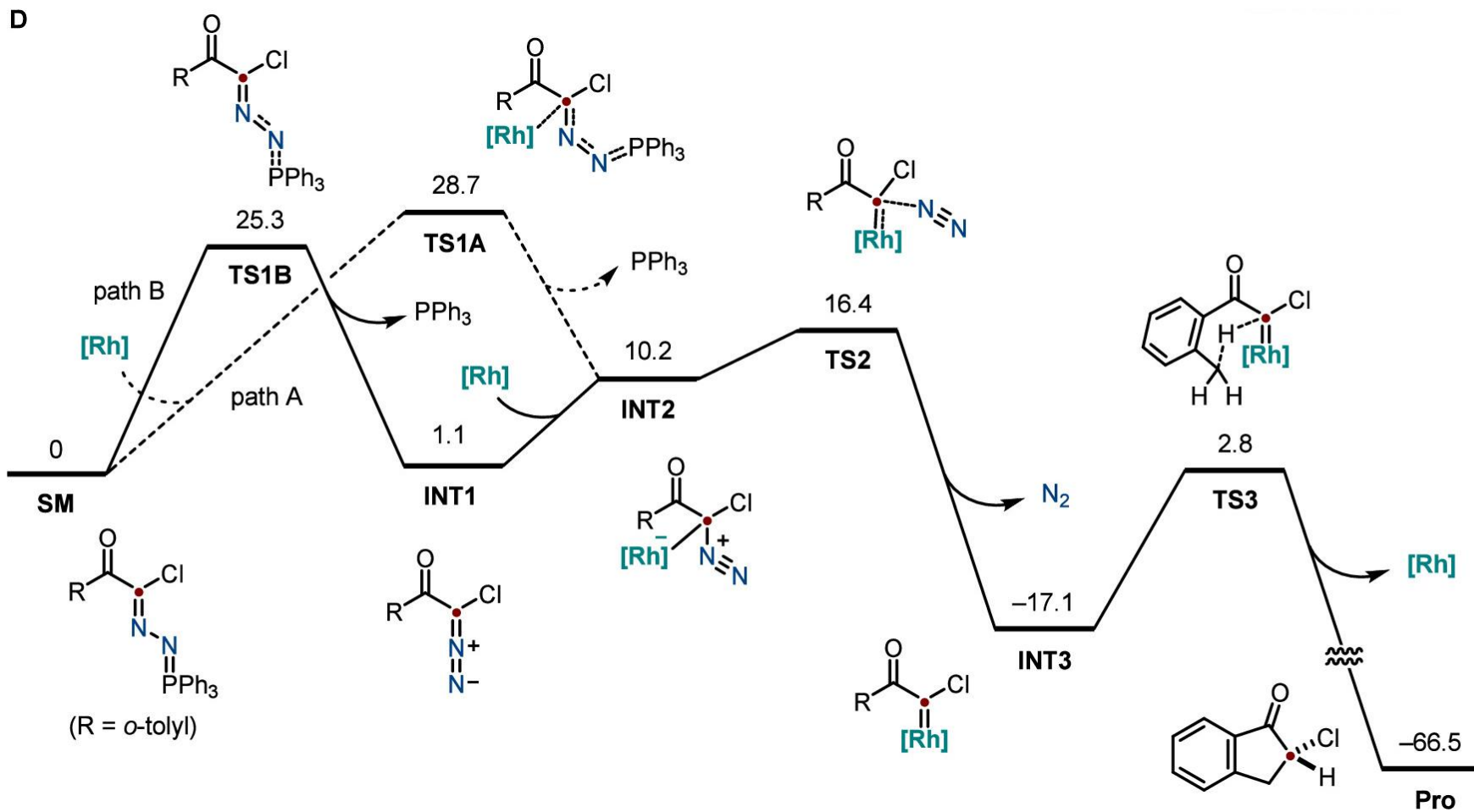
# Chemical Equivalents



# Chemical Equivalents

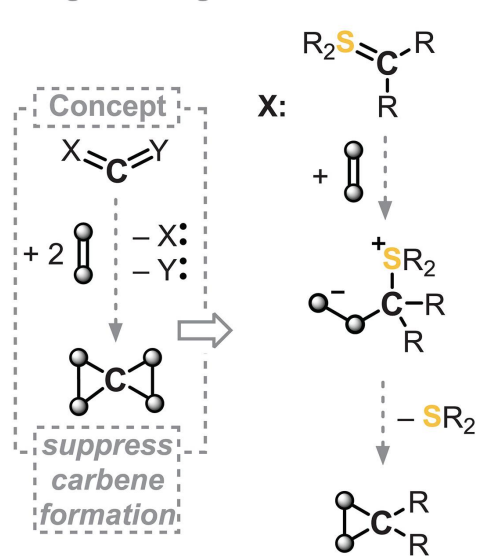


# Chemical Equivalents

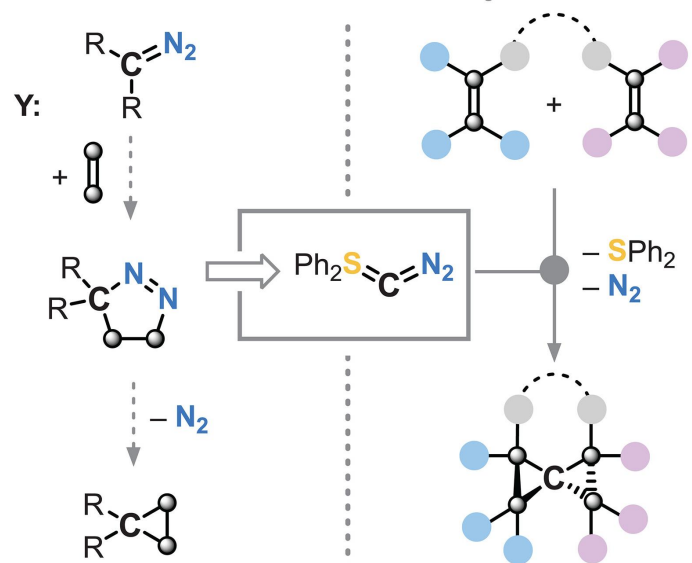


# Chemical Equivalents

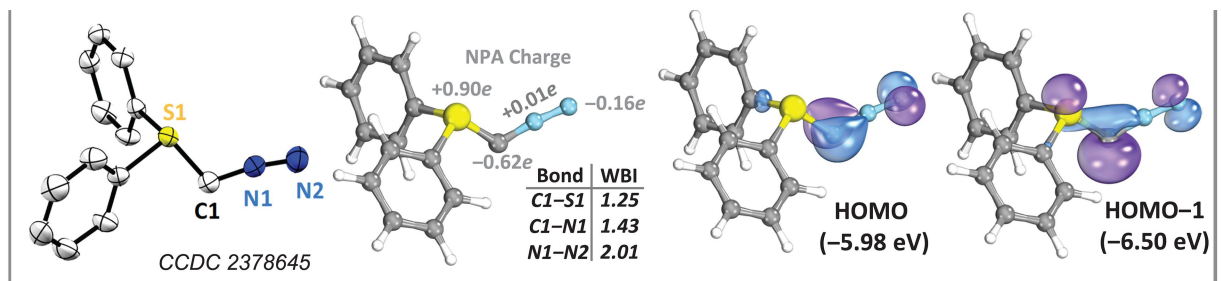
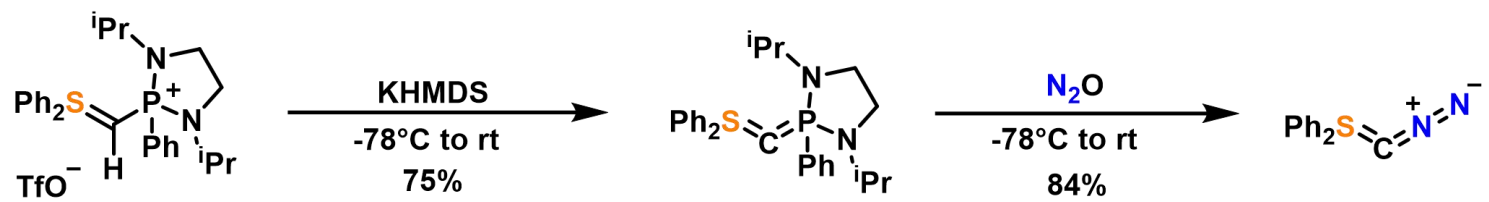
Reagent design:



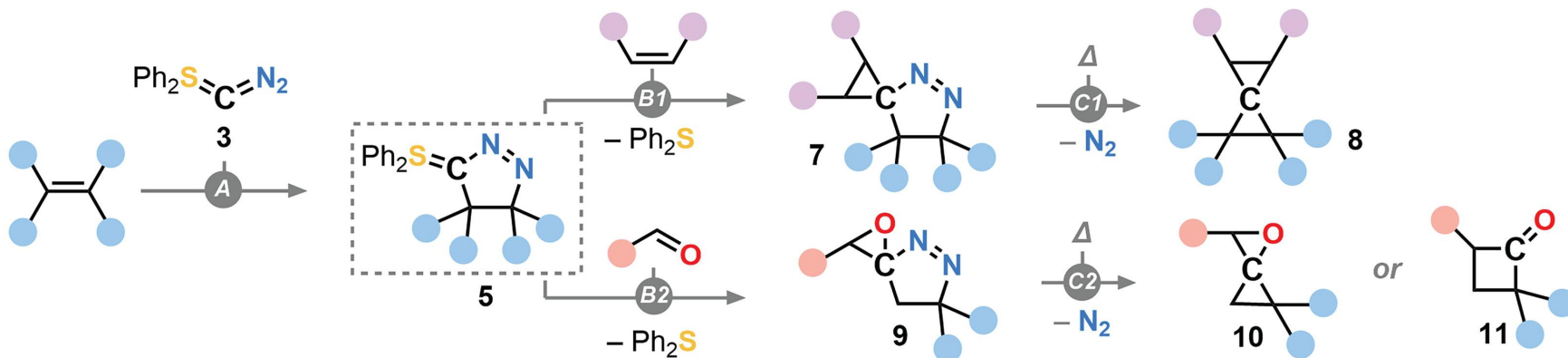
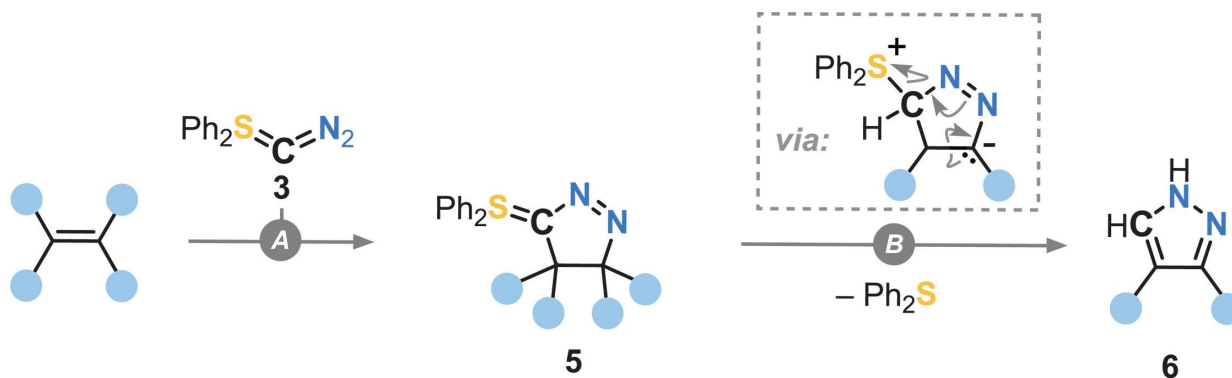
Reactivity:



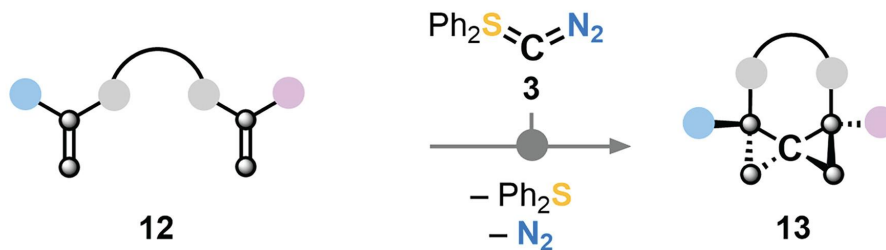
- $\text{C}(\text{sp}^3)$ -atom transfer
- single step or stepwise
- 4 new  $\text{C}(\text{sp}^3)$ -C bonds formed
- construction of 3D spirocyclic scaffolds



# Chemical Equivalents



# Chemical Equivalents



## Single step $\text{C}(\text{sp}^3)$ -atom transfer

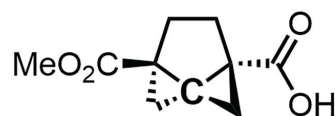
### 2-Atom linkers



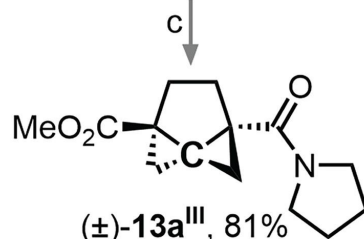
(±)-**13a**: R = Me, 72%  
 (±)-**13b**: R = Et, 69%



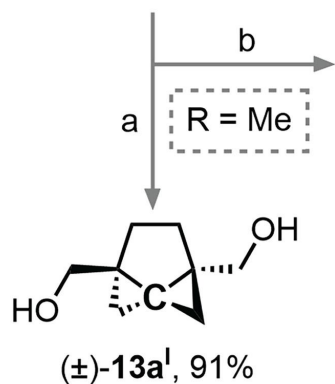
(±)-**13a**- $^{13}\text{C}$ , 72%



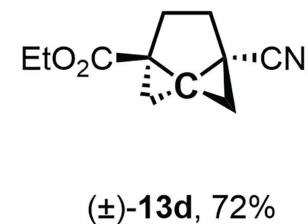
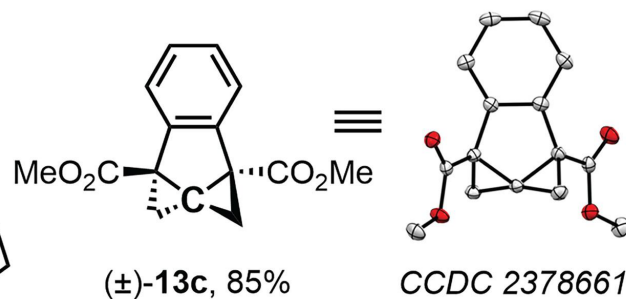
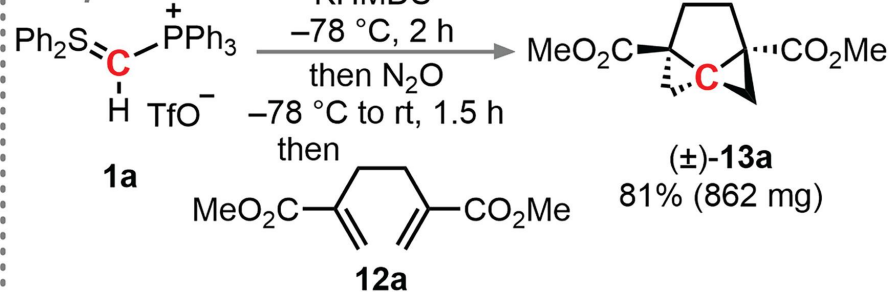
(±)-**13a**<sup>II</sup>, 98%



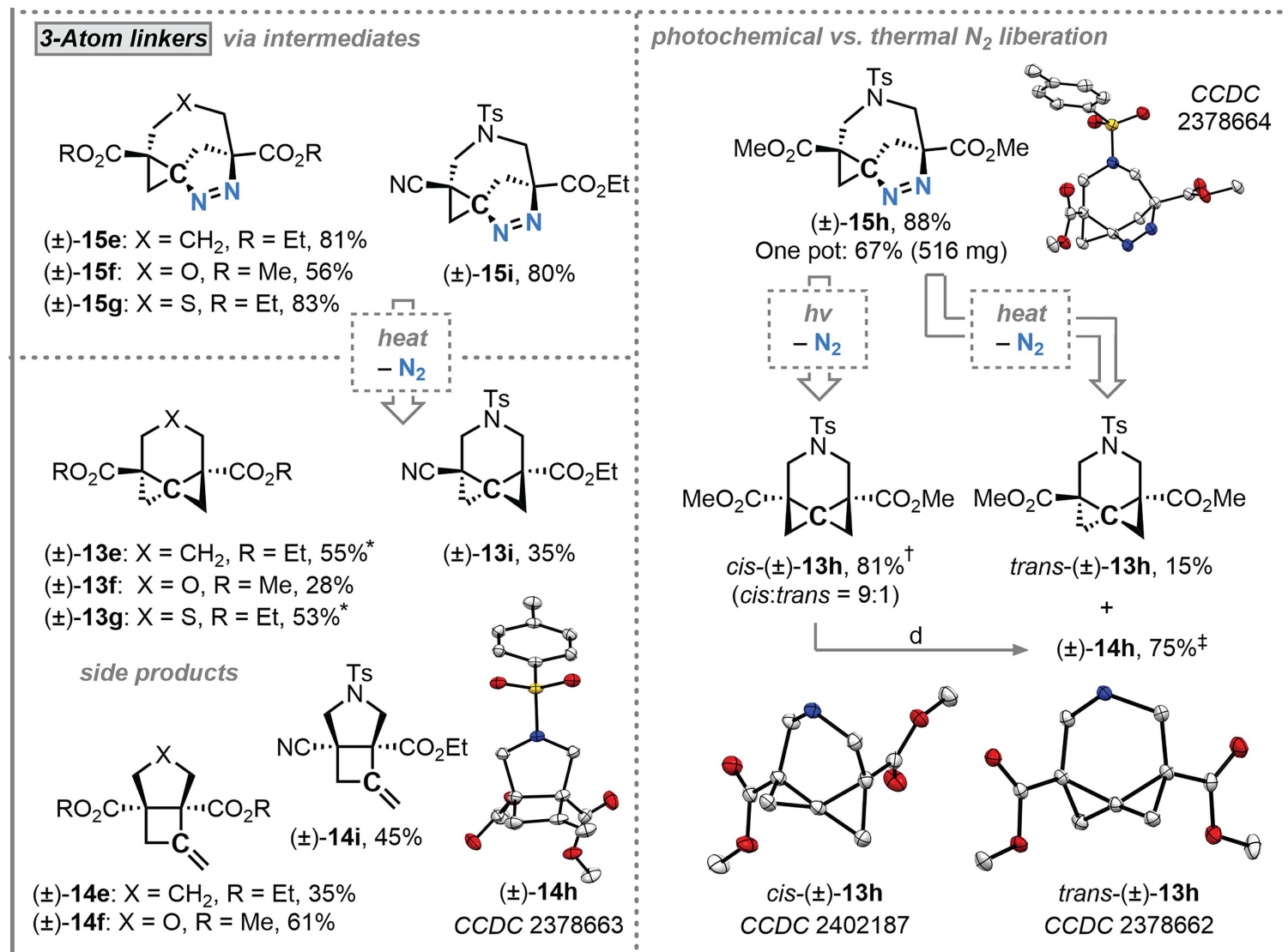
(±)-**13a**<sup>III</sup>, 81%



### One pot



# Chemical Equivalents



# Outline

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- Introduction
- Atomic Carbon Generated by Physical Methods
- Chemical Methods Using Atomic Carbon Equivalents
- **Summary and Outlook**

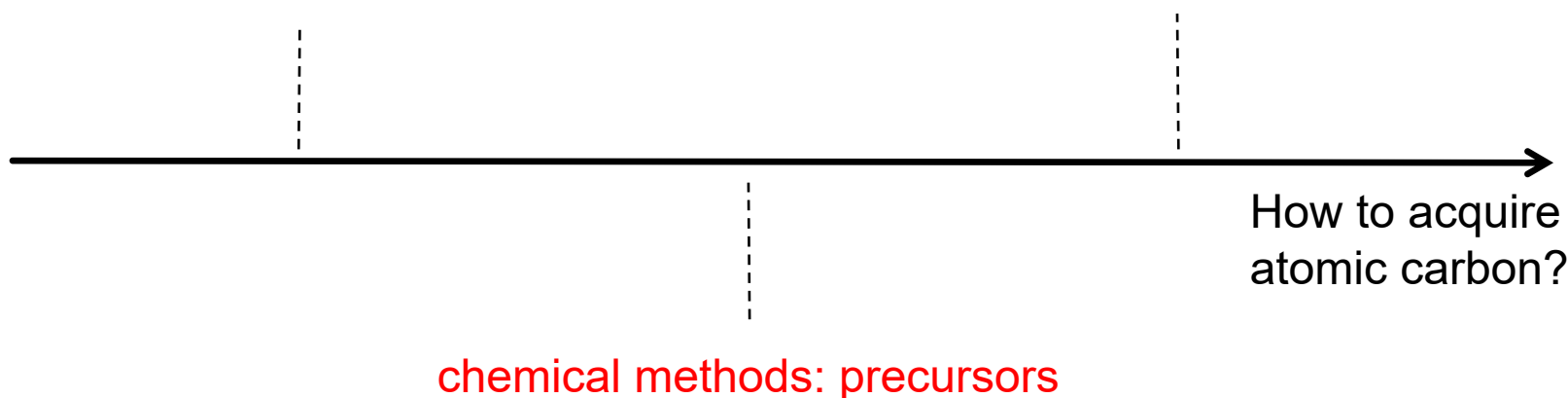
# Summary and Outlook

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physical methods: arc discharge

-196 °C on a paraffin matrix

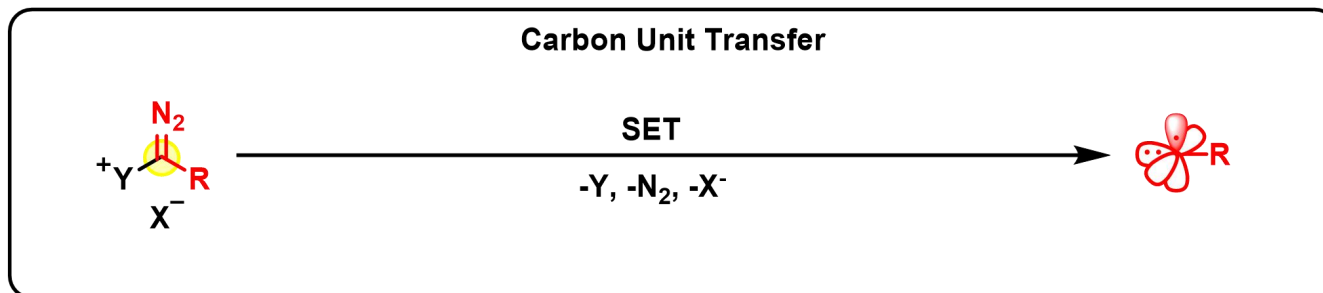
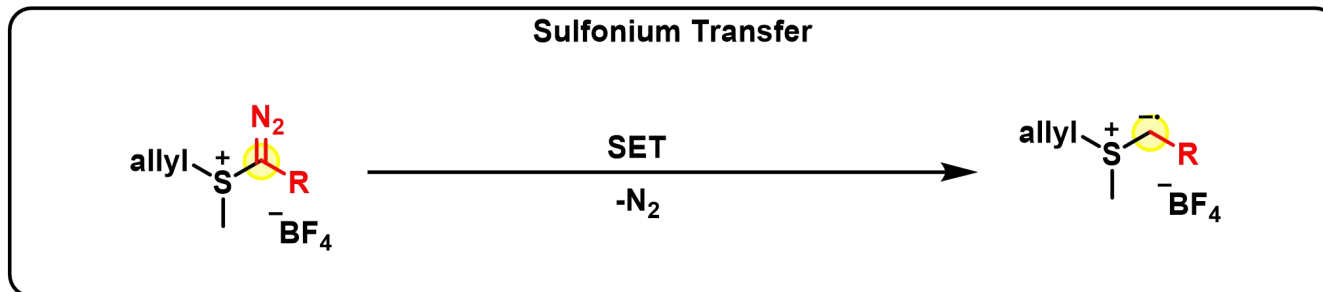
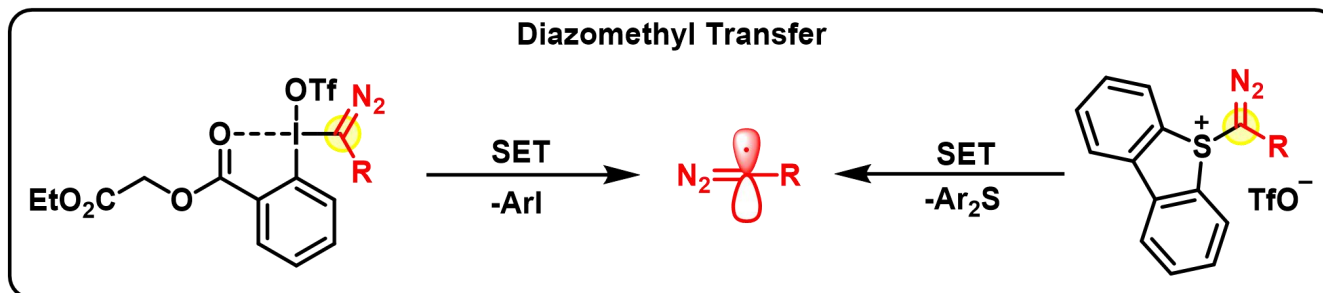
chemical methods: equivalents



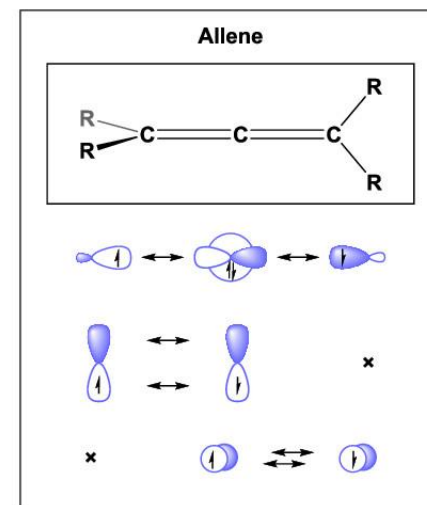
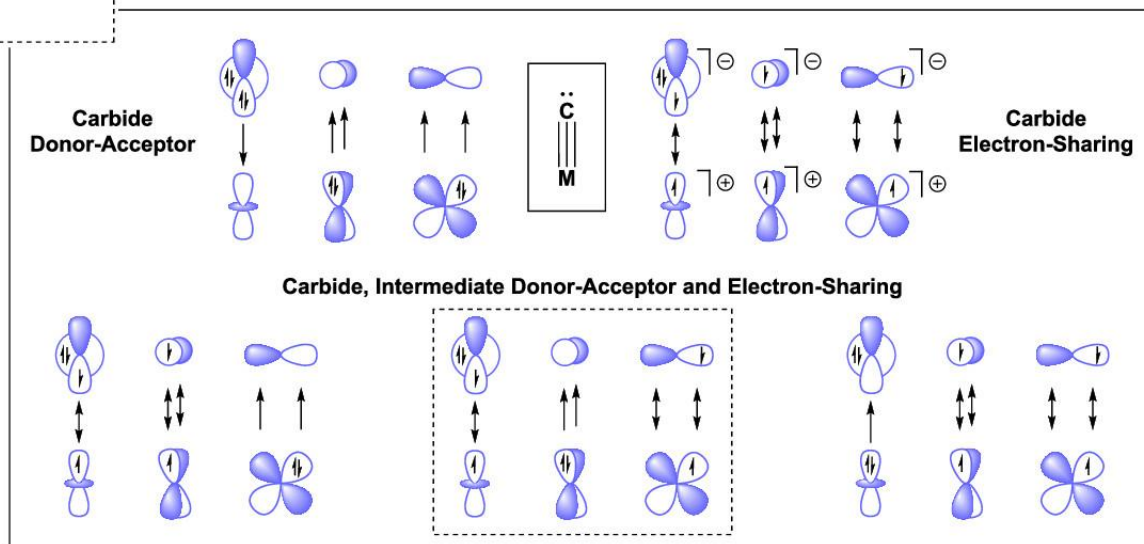
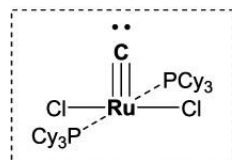
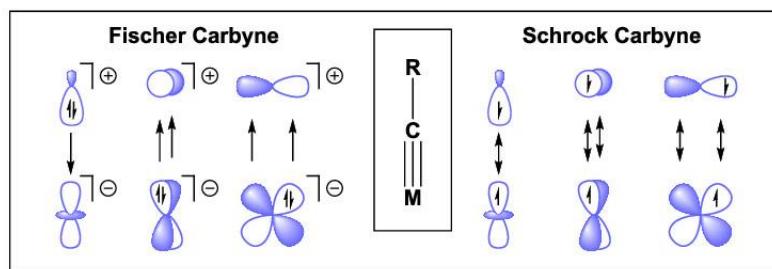
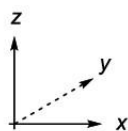
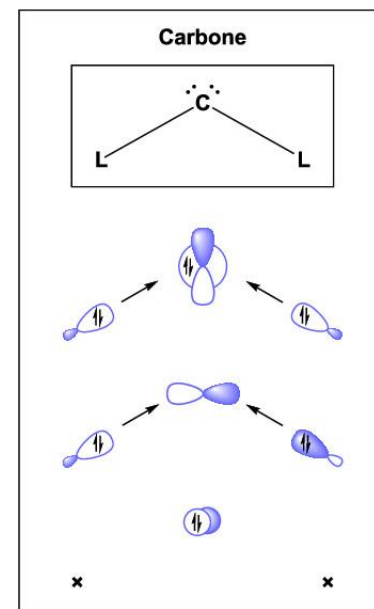
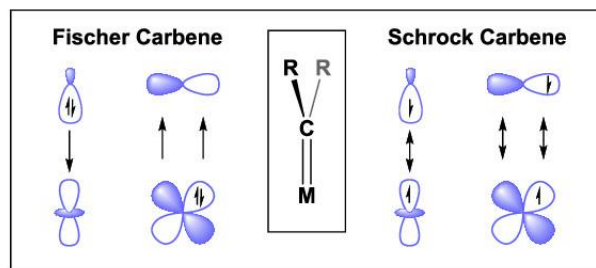
- development of practical atomic carbon equivalents
  - balanced reactivity and stability
- application to catalytic systems

# Back-up Slides

- carbyne precursor

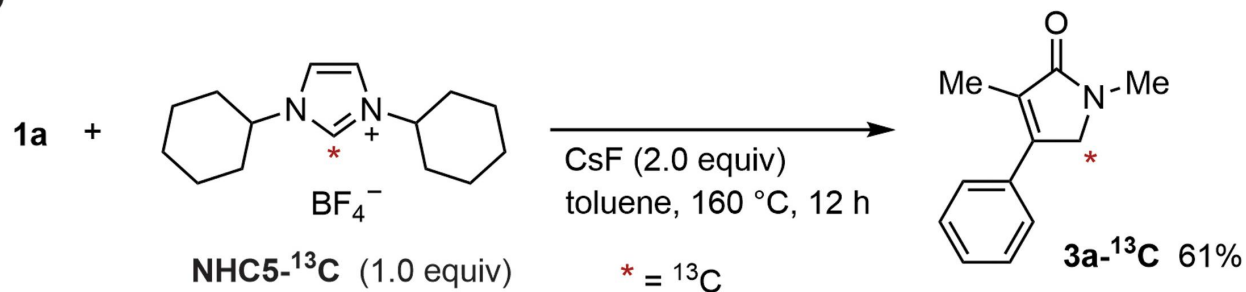


# Back-up Slides

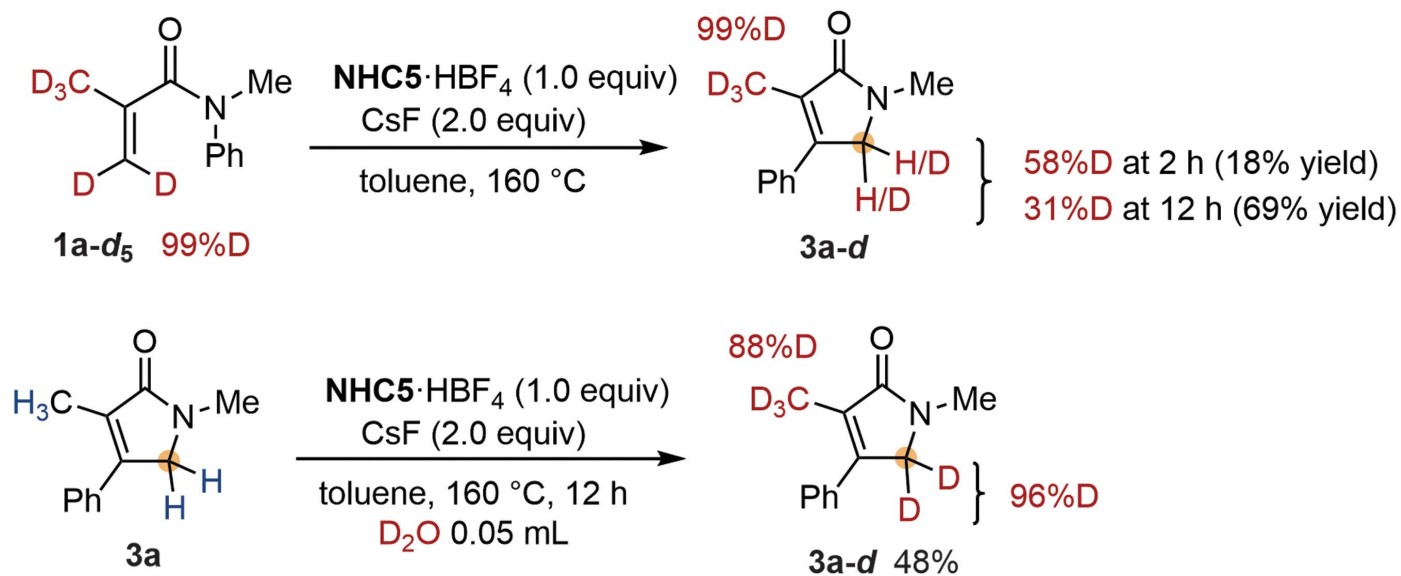


# Back-up Slides

C



D



# Back-up Slides

