

Carbon Unit Transfer Reactions Along With Forming Three New Bonds via α -Diazo Onium Salts

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Supervisor: Prof. Shengming Ma

March 31, 2023

Content

1 Background

2 Carbon unit transfer reactions

2.1 via diazomethyl radical

2.2 via carbyne carbocation

2.3 via carbene

3 Summary and outlook

Content

1 Background

2 Carbon unit transfer reactions

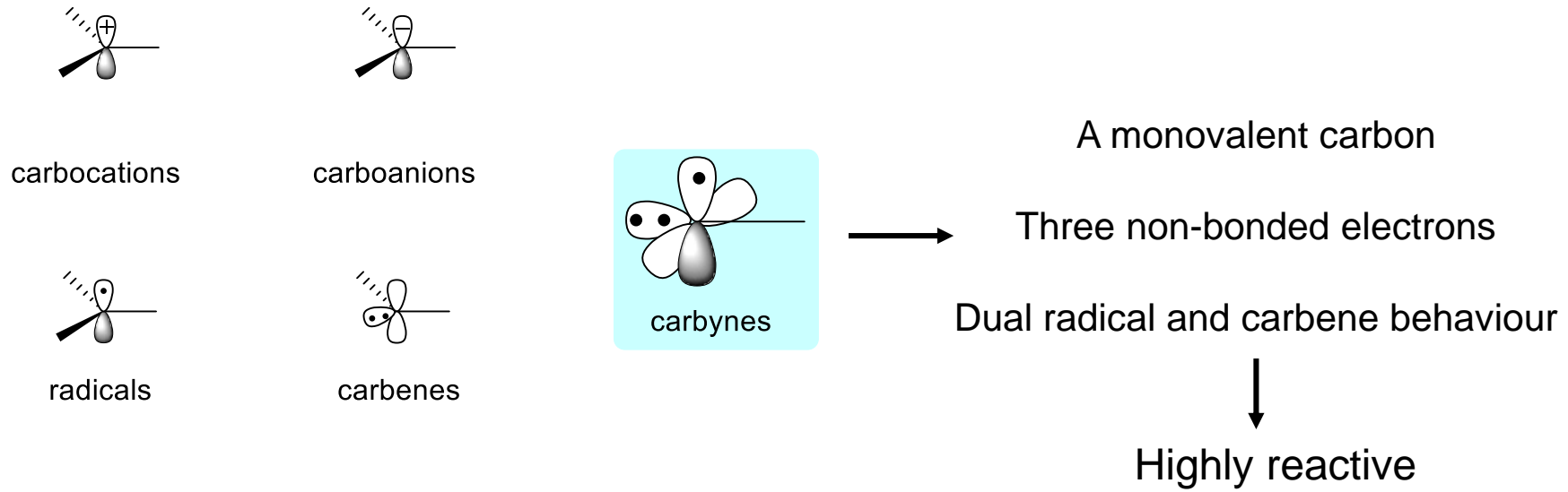
2.1 via diazomethyl radical

2.2 via carbyne carbocation

2.3 via carbene

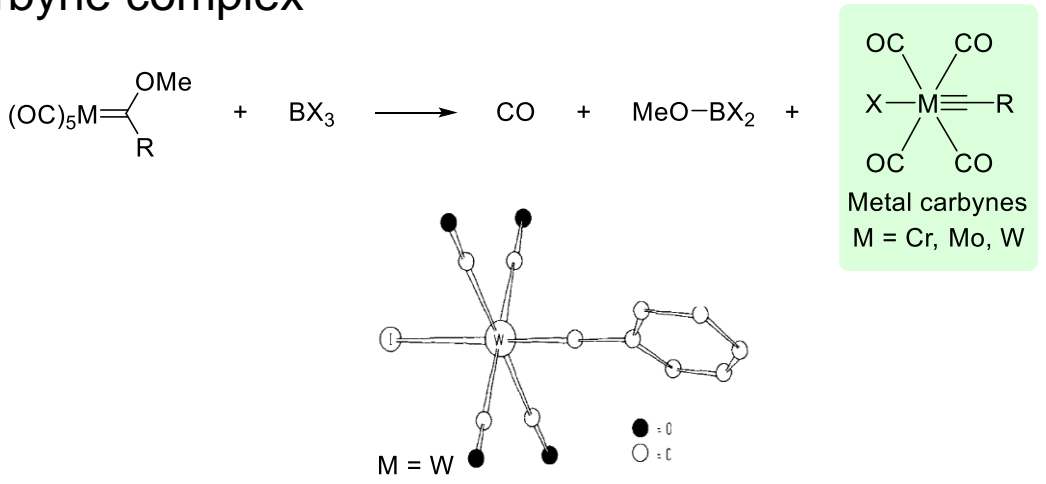
3 Summary and outlook

Background



Suero, M. G. *et al.*, *Nature* **2018**, 554, 86-91.

The first metal carbyne complex

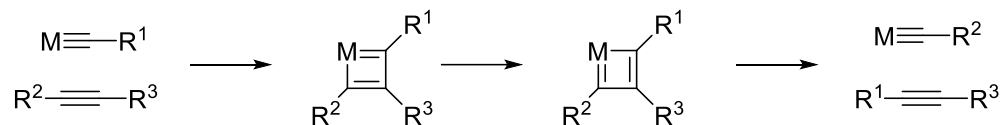


Fischer, E. O. *et al.*, *Angew. Chem. Int. Ed.* **1973**, 12, 564-565.

Wang, C. *et al.*, *Chin. J. Chem.* **2021**, 39, 3481-3484.

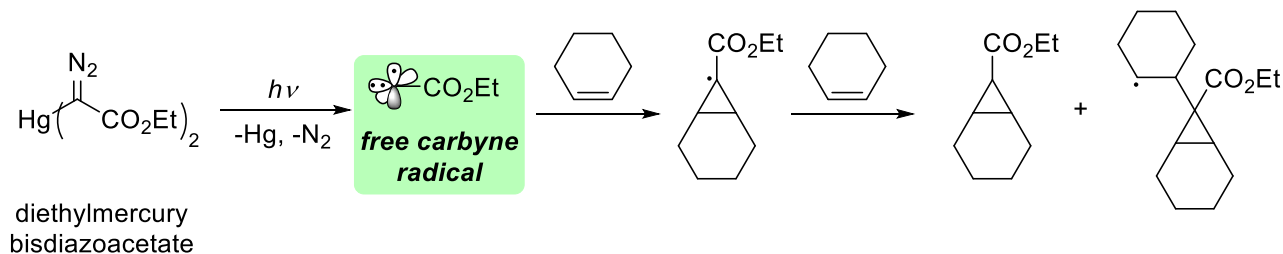
Background

Metal carbyne complex catalyzed alkyne metathesis (well-established)



Fürstner, A. *Angew. Chem. Int. Ed.* **2013**, 52, 2794-2819.

Reaction through free carbyne radical



Mixture

Strausz, O. P. *et al.*, *J. Am. Chem. Soc.* **1967**, 89, 6785-6787.

Strausz, O. P. *et al.*, *J. Am. Chem. Soc.* **1968**, 90, 1930-1931.

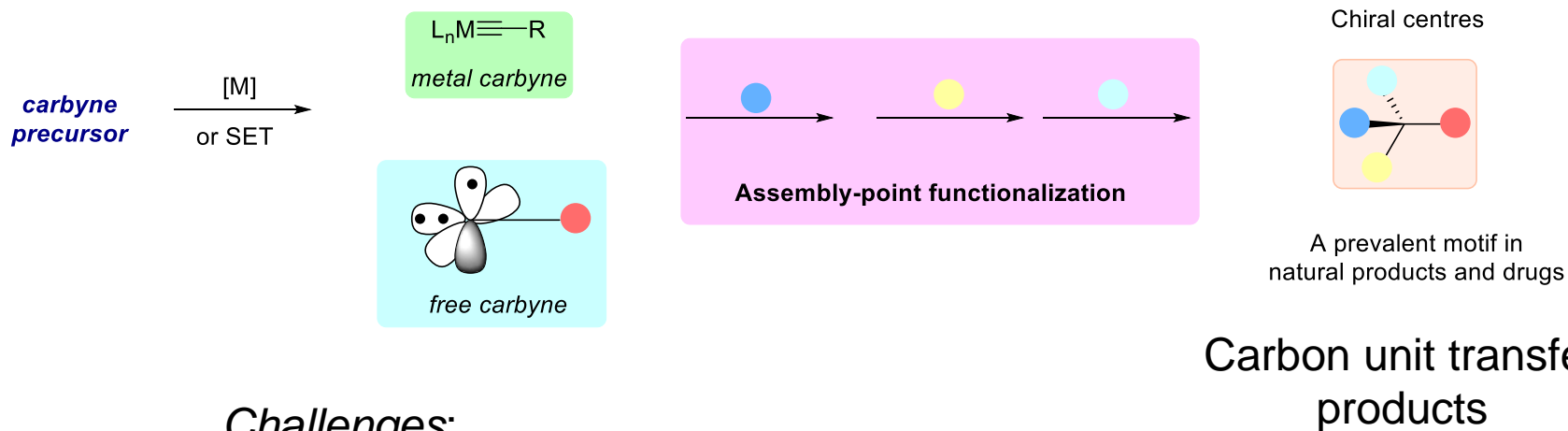
Strausz, O. P. *et al.*, *J. Am. Chem. Soc.* **1974**, 96, 5723-5732.

Patrick, T. B. *et al.*, *J. Org. Chem.* **1975**, 40, 1527-1528.

Patrick, T. B. *et al.*, *J. Org. Chem.* **1978**, 43, 1506-1509.

Warnhoff, E. W. *et al.*, *Org. React.* **2011**, 18, 217-401.

Background



Challenges:

- Lack of efficient carbyne precursor
- Lack of practicability
- Controlling reactivity
- Stoichiometric toxic metal

Content

1 Background

2 Carbon unit transfer reactions

2.1 via diazomethyl radical

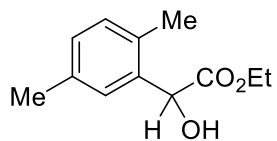
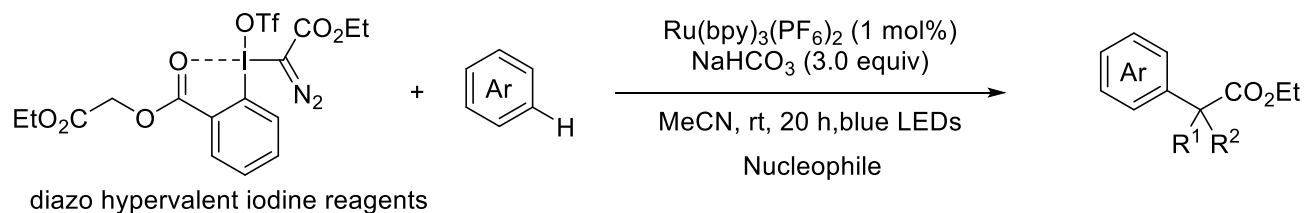
2.2 via carbyne carbocation

2.3 via carbene

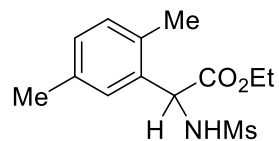
3 Summary and outlook

Carbon unit transfer reactions — Via diazomethyl radical

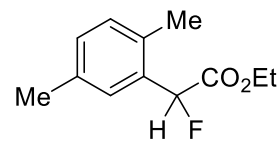
Suero (2018)



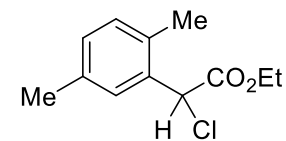
with H₂O
53%



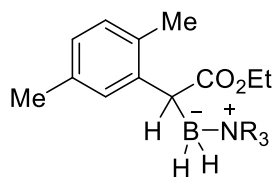
with MsNH₂
66%



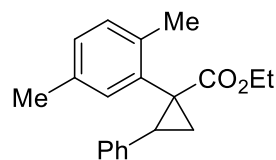
with NaF
25%



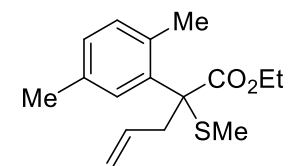
with KCl
72%



with BH₃-NR₃
35%

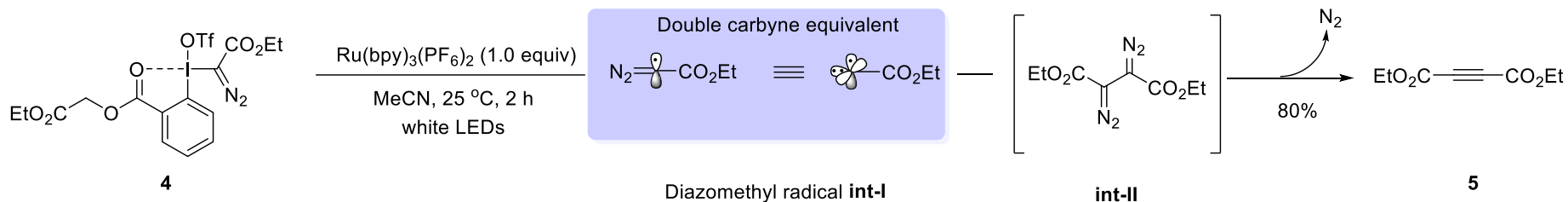


with silylene
47%



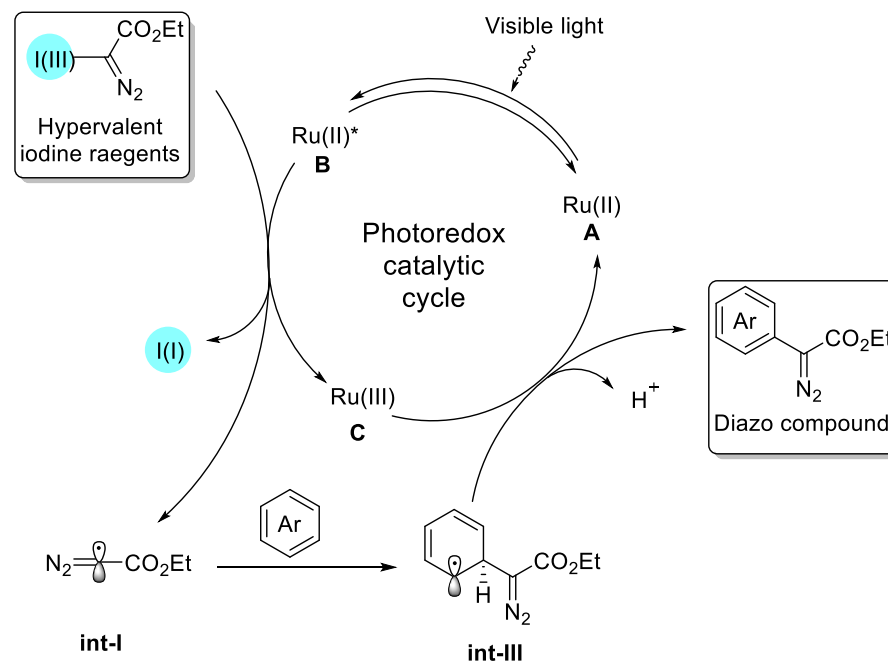
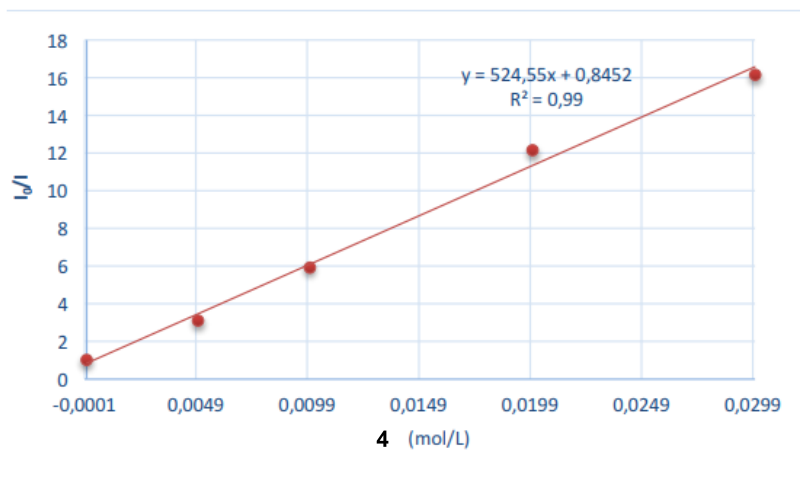
with allyl(methyl)sulfane
51%

Carbon unit transfer reactions



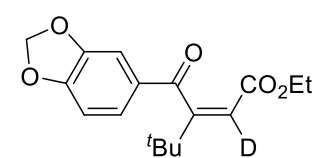
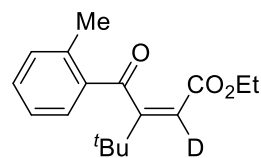
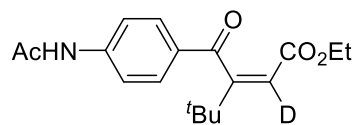
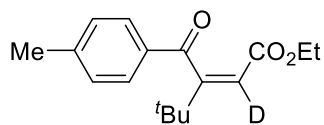
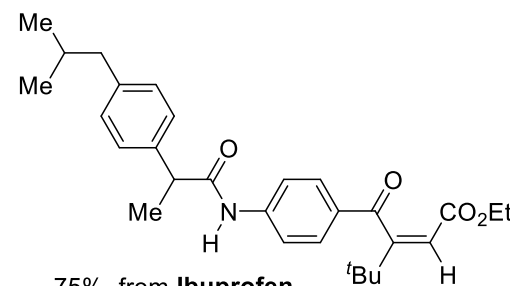
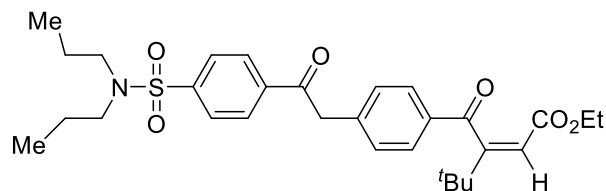
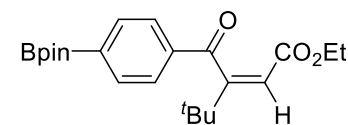
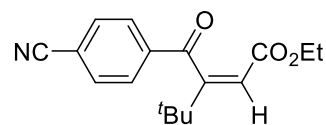
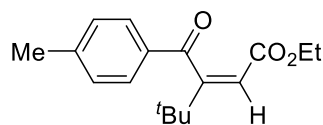
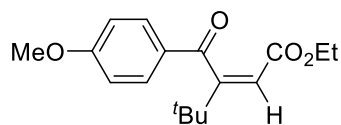
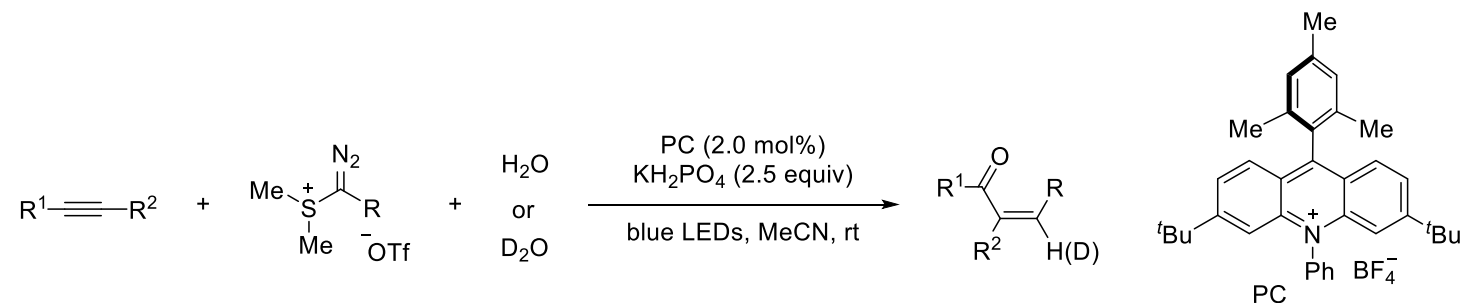
Mechanism

Stern-Volmer fluorescence quenching



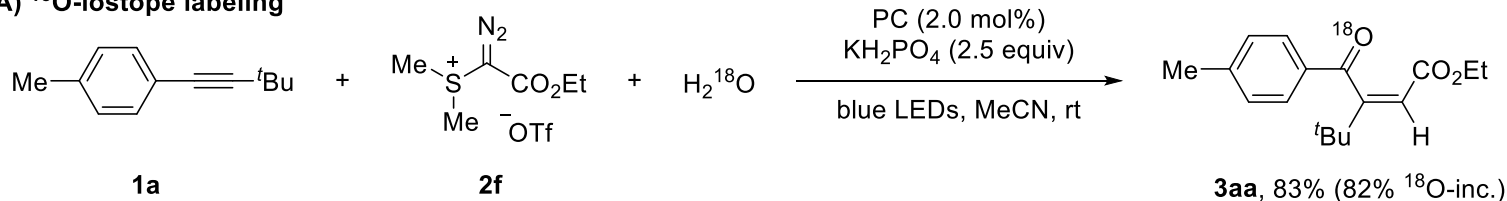
Carbon unit transfer reactions — Via diazomethyl radical

Wang (2022)

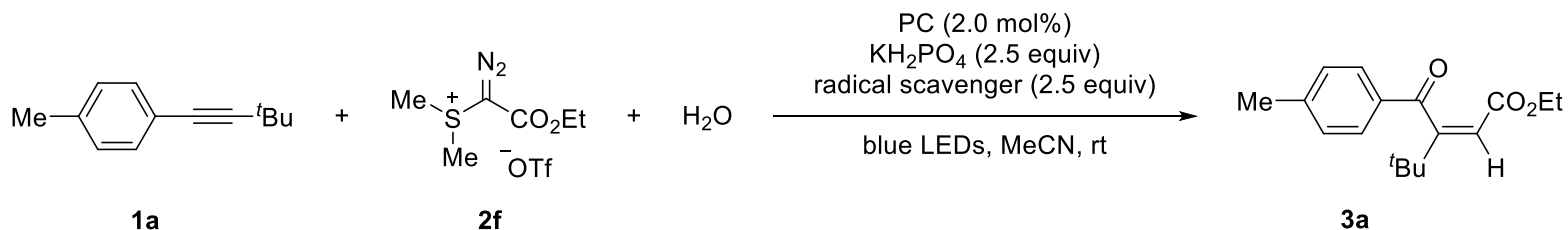


Carbon unit transfer reactions

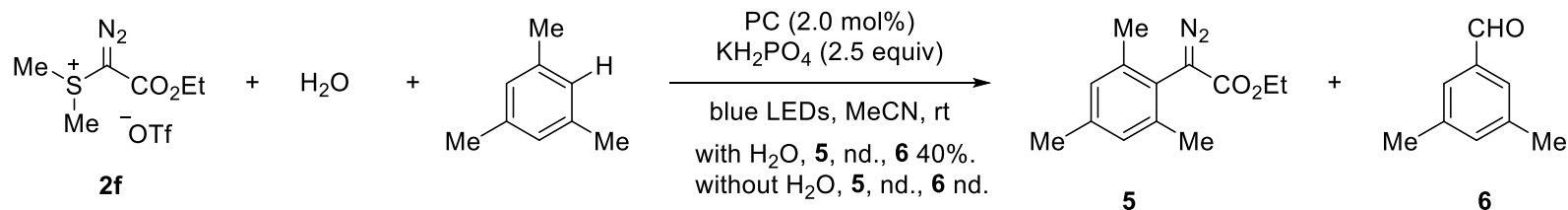
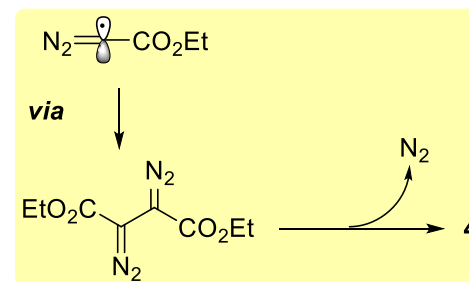
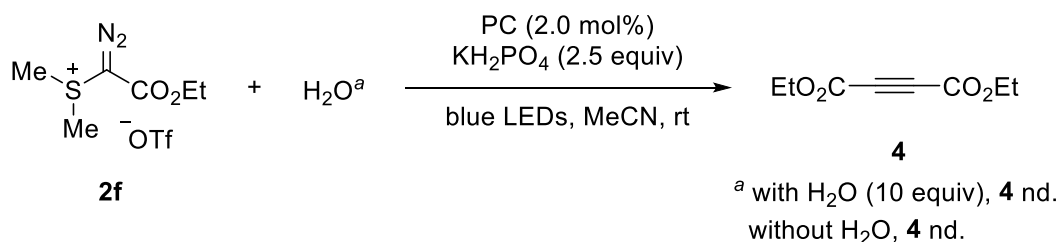
A) ¹⁸O-isotope labeling



B) Radical capture

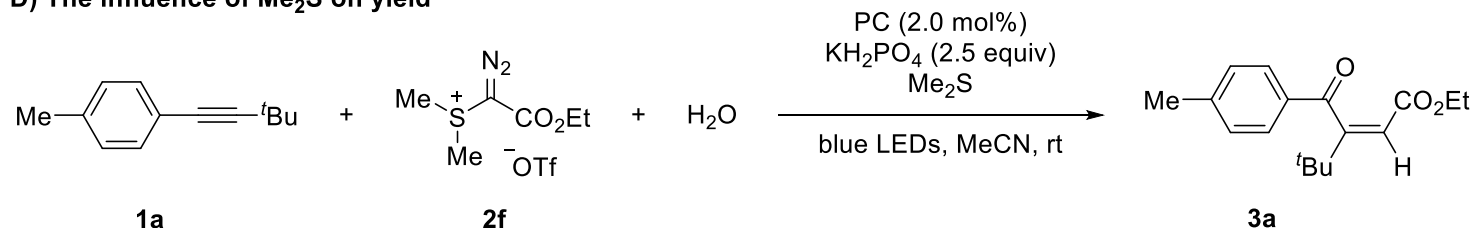


C) Diazomethyl radical probe

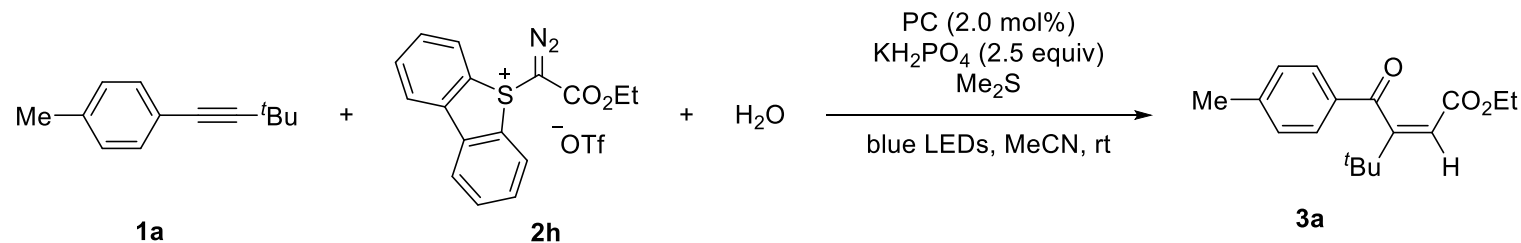
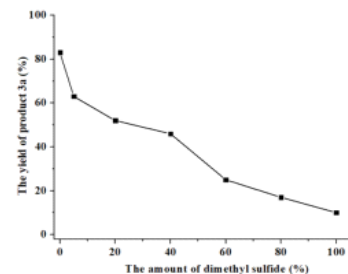


Carbon unit transfer reactions

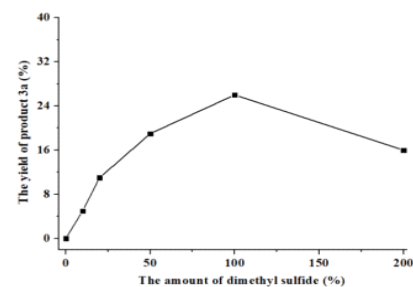
D) The influence of Me₂S on yield



entry	1	2	3	4	5	6	7
Me ₂ S	0%	5%	20%	40%	60%	80%	100%
yield	83%	63%	52%	46%	25%	17%	10%

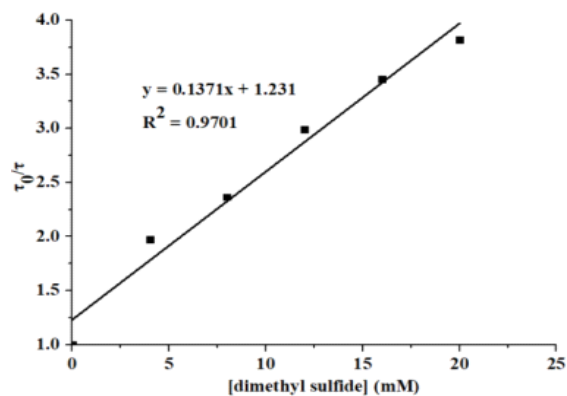


entry	1	2	3	4	5	6
Me ₂ S	0%	10%	20%	50%	100%	200%
yield	0%	5%	11%	19%	26%	16%

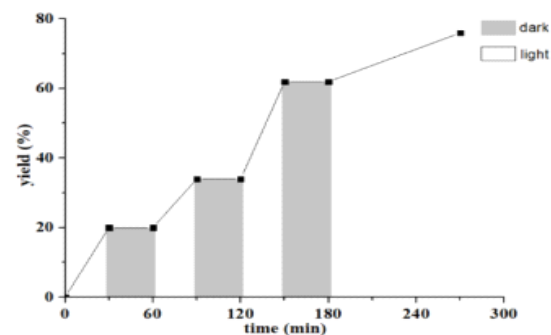


Carbon unit transfer reactions

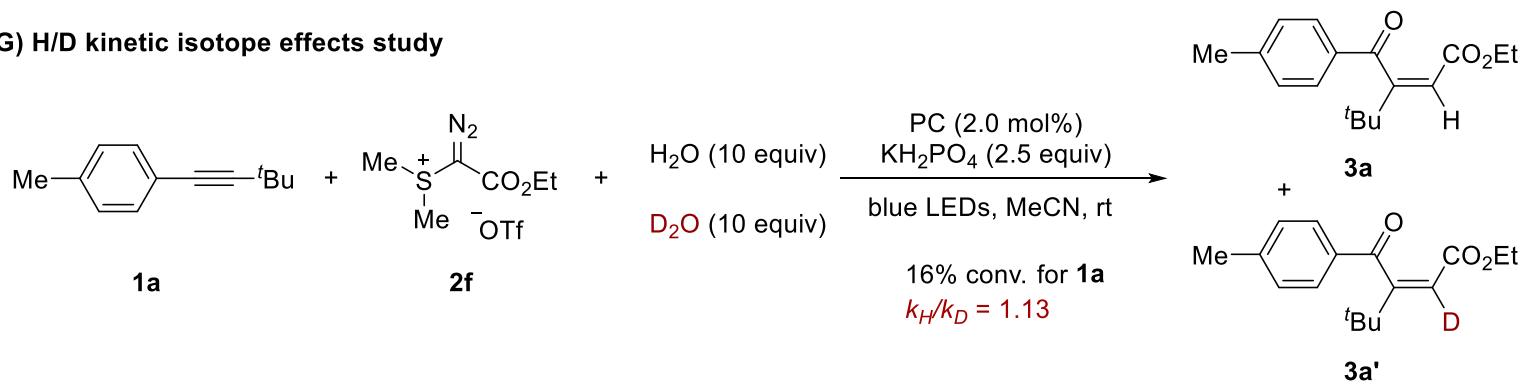
E) Stern-volmer fluorescent quenching



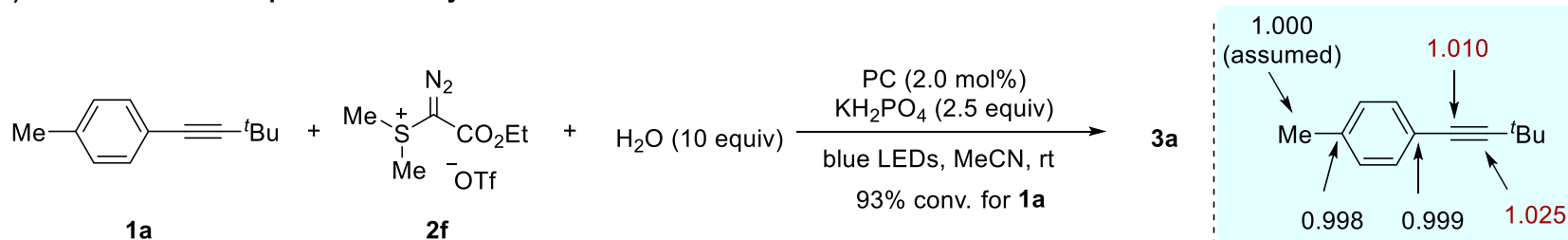
F) Light on-off experiments and quantum yield



G) H/D kinetic isotope effects study

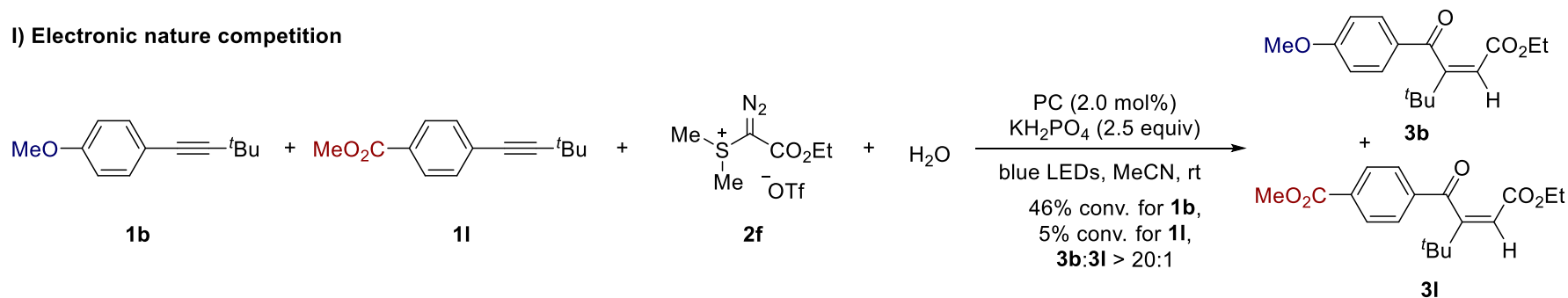


H) ¹²C/¹³C kinetic isotope effects study

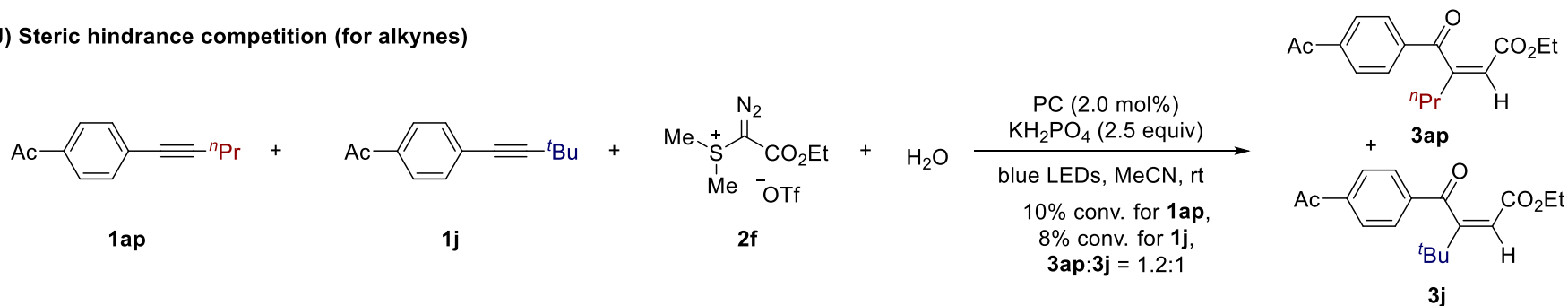


Carbon unit transfer reactions

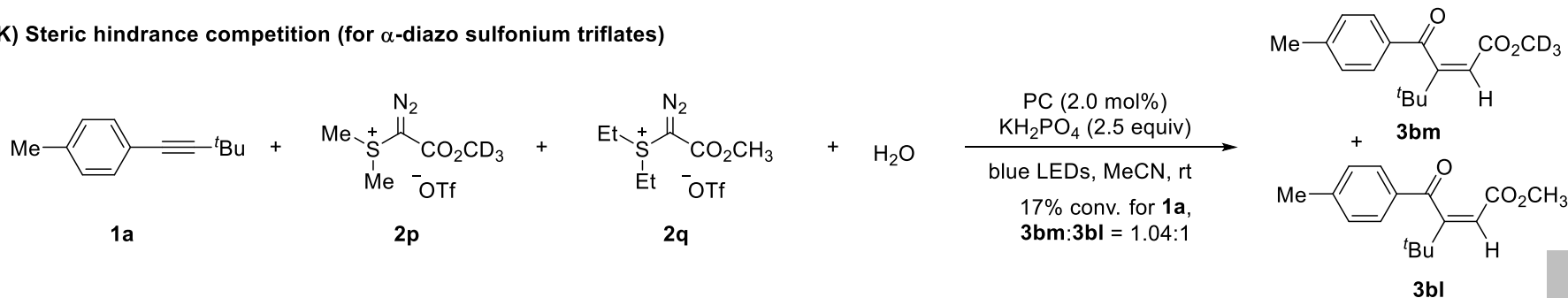
I) Electronic nature competition



J) Steric hindrance competition (for alkynes)

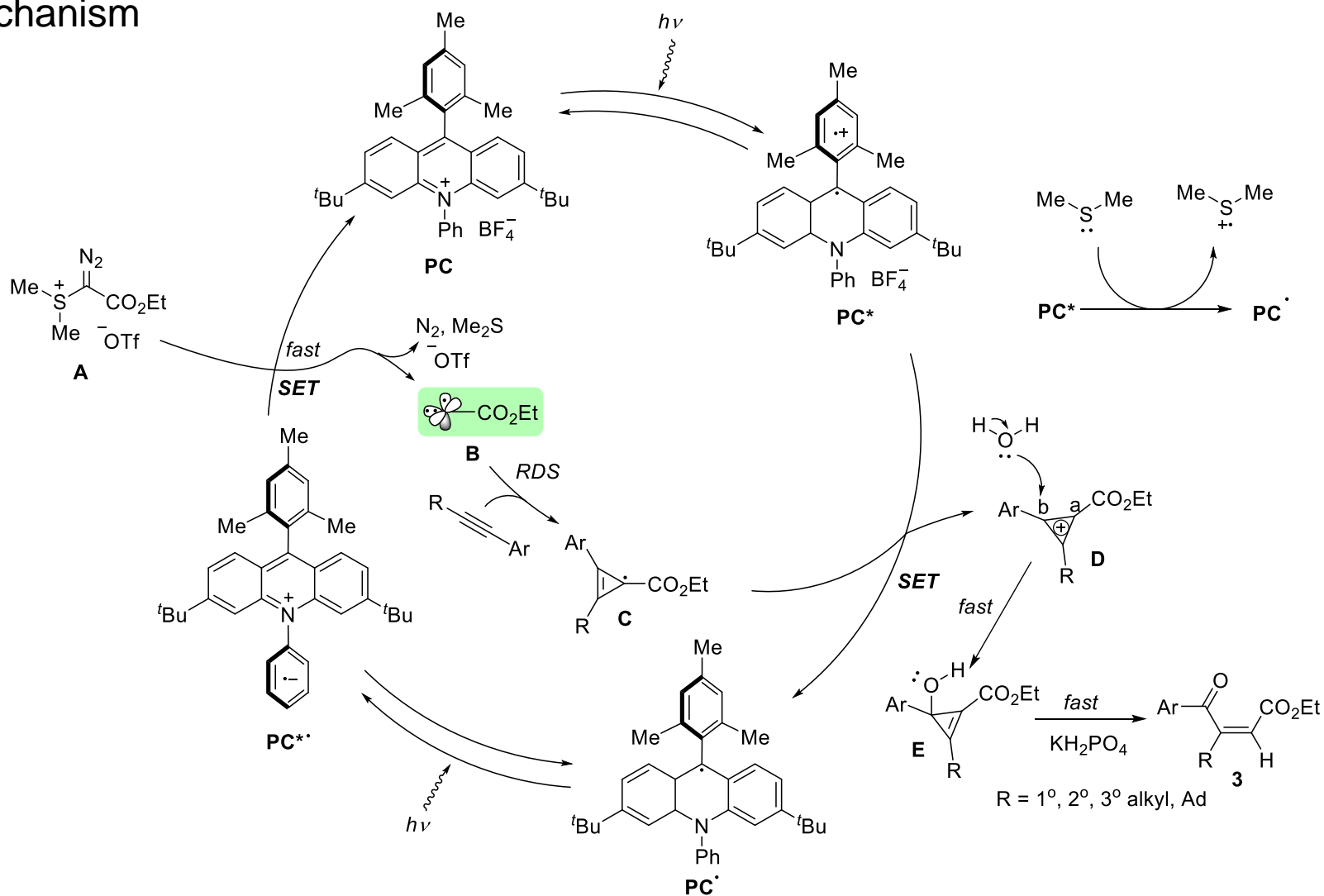


K) Steric hindrance competition (for α -diazo sulfonium triflates)



Carbon unit transfer reactions

Mechanism



Content

1 Background

2 Carbon unit transfer reactions

2.1 via diazomethyl radical

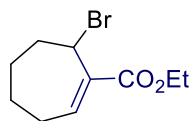
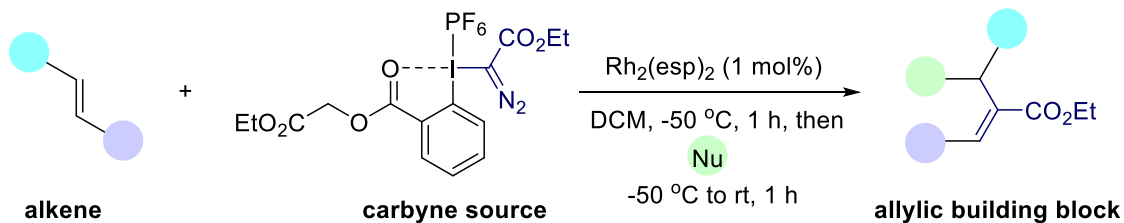
2.2 via carbyne carbocation

2.3 via carbene

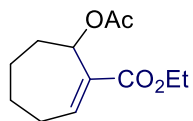
3 Summary and outlook

Carbon unit transfer reactions — Via carbyne carbocation

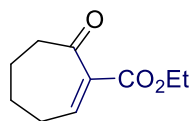
Suero (2019)



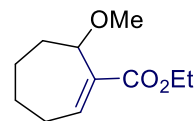
with Bu_4NBr
76% (13%)^a



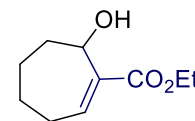
with Bu_4NOAc
45% (22%)^a



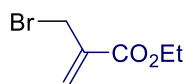
with TEMPO
31% (17%)^a



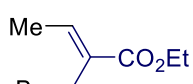
with MeOH
72% (5%)^a



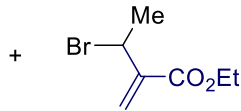
with H_2O
64% (15%)^a



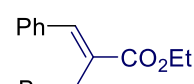
with Bu_4NBr
from ethylene
75%



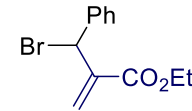
linear
with Bu_4NBr , from propylene
89%, (*l*:*b* = 14:1), *l* = 3:1 (Z:E)



branched



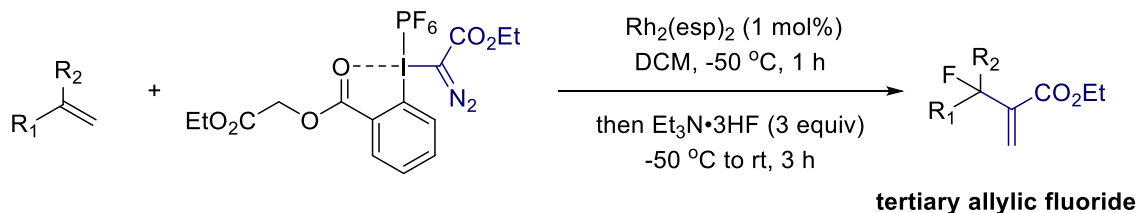
linear



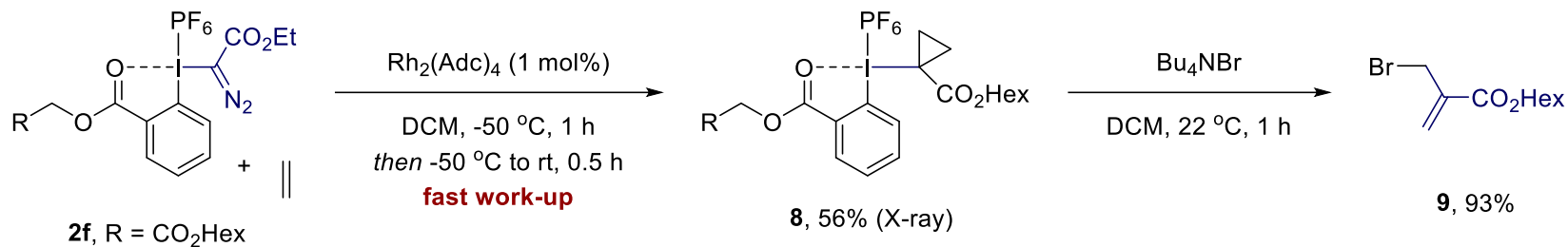
branched

with Bu_4NBr , from styrene
98%, (*l*:*b* = >20:1), *l* = 10:1 (Z:E)

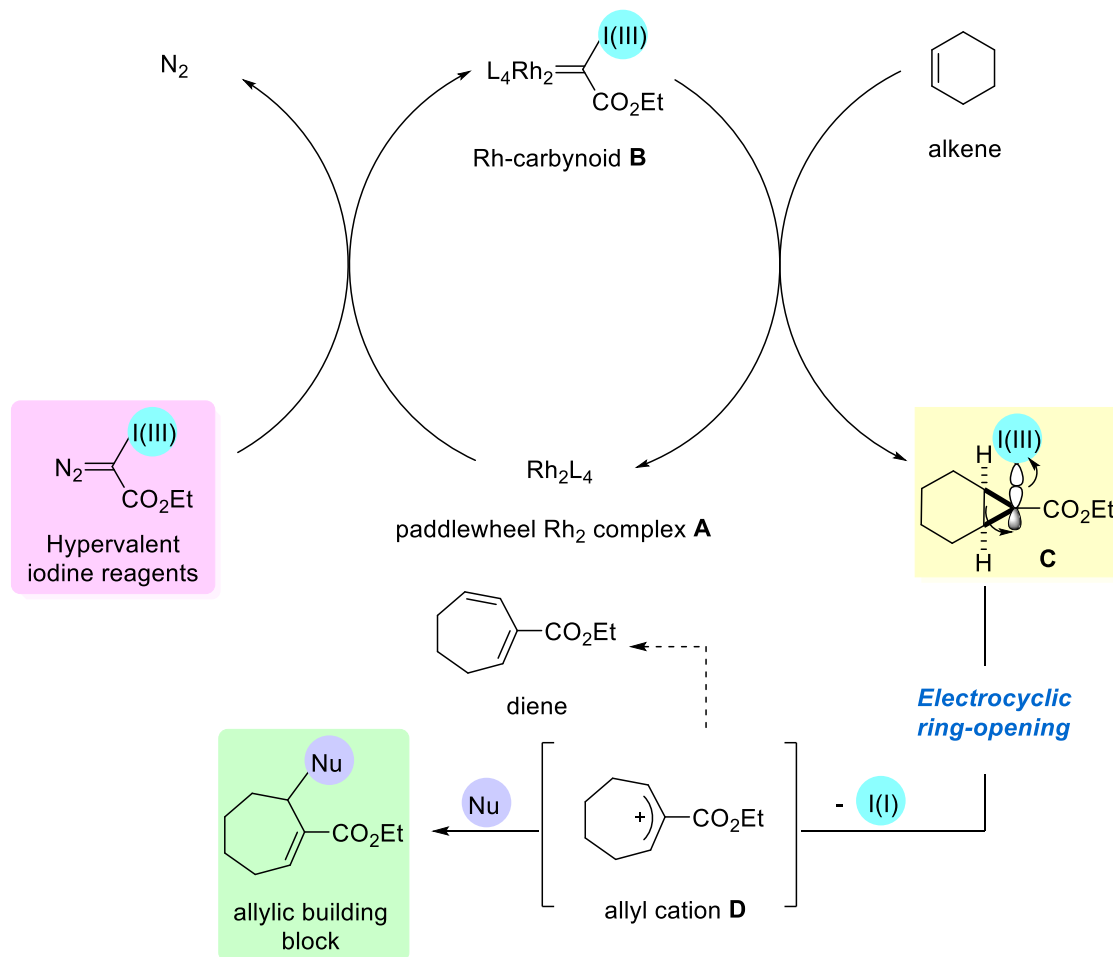
^a Yield of parentheses are of dienes.



Carbon unit transfer reactions

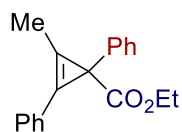
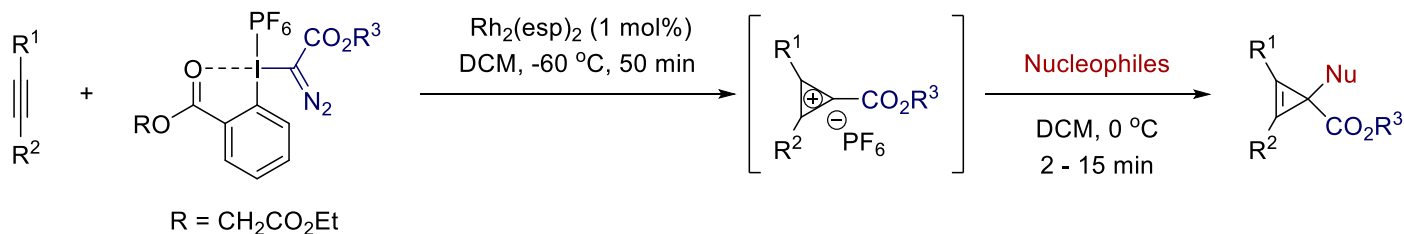


Mechanism

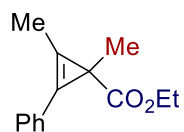


Carbon unit transfer reactions — Via carbyne carbocation

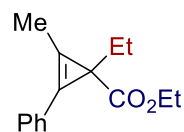
Suero (2022)



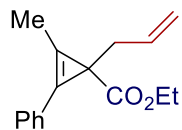
with PhMgBr , 95%



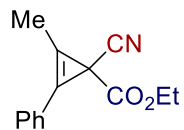
with MeMgBr , 77%



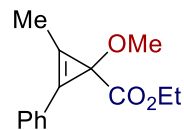
with Et_2Zn , 73%



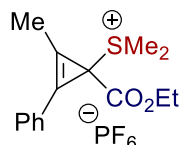
with TMS-allyl, 91%



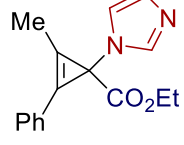
with TMS-CN, 88%



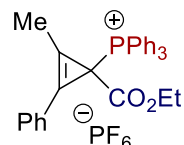
with MeOH, 92%



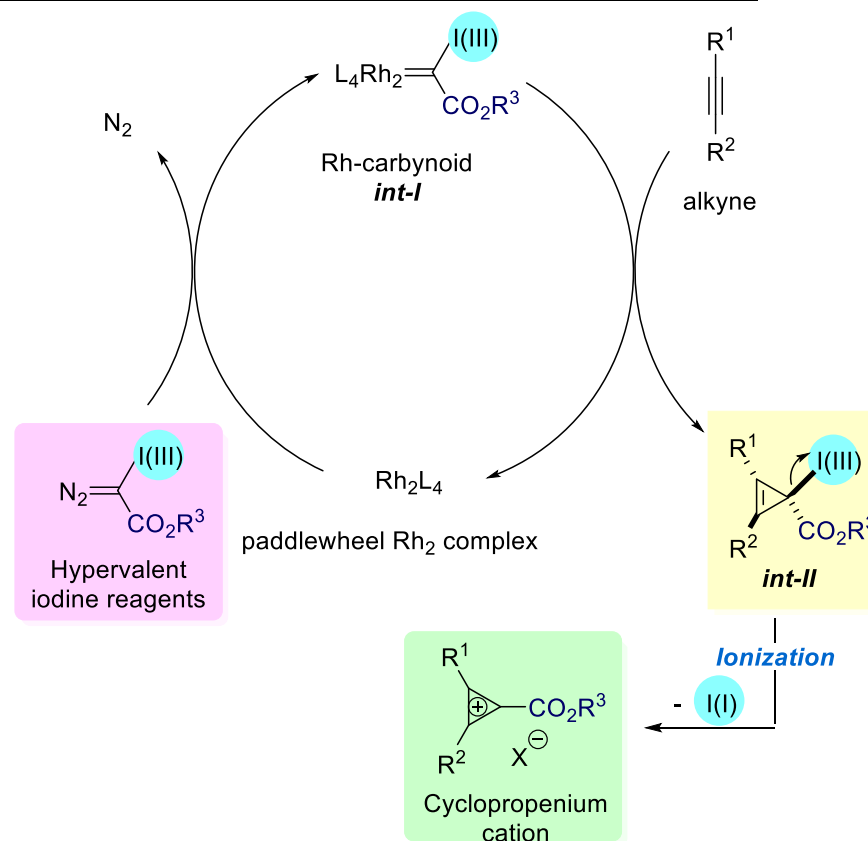
with dimethyl sulfide, 94%



with imidazole, 51%



with PPh_3 , 92%



Content

1 Background

2 Carbon unit transfer reactions

2.1 via diazomethyl radical

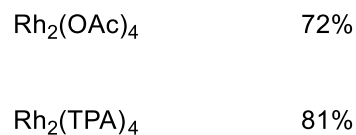
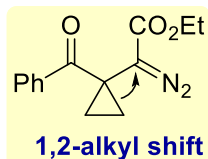
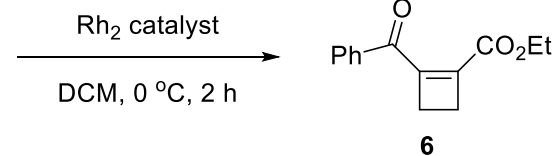
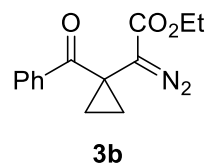
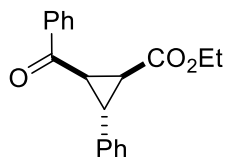
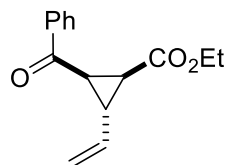
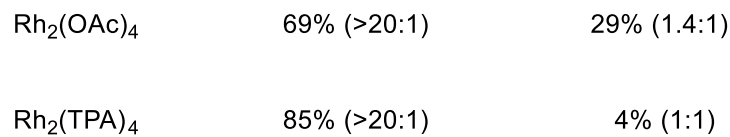
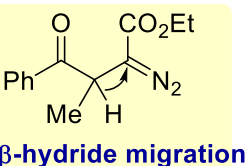
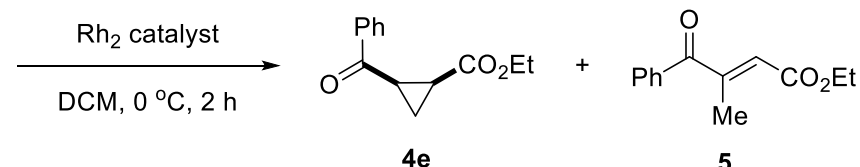
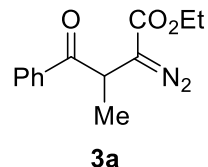
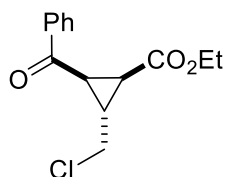
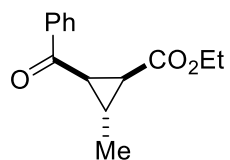
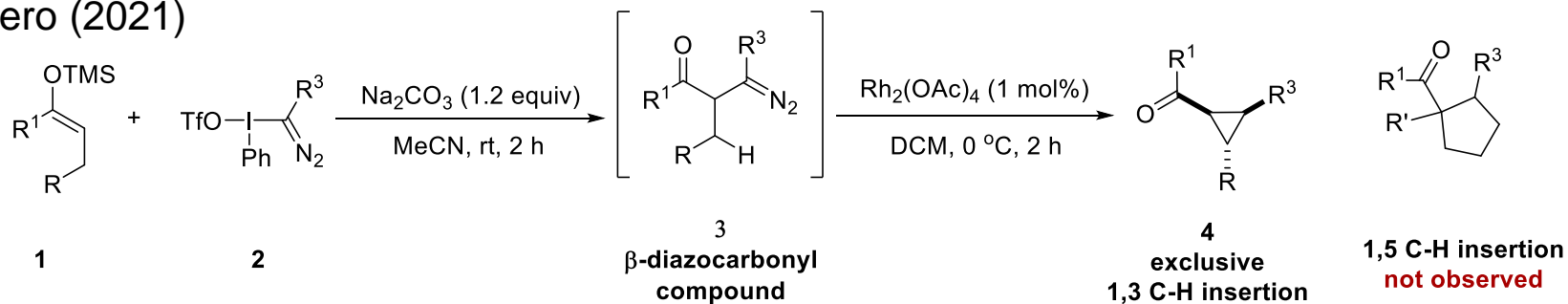
2.2 via carbyne carbocation

2.3 via carbene

3 Summary and outlook

Carbon unit transfer reactions — Via carbene

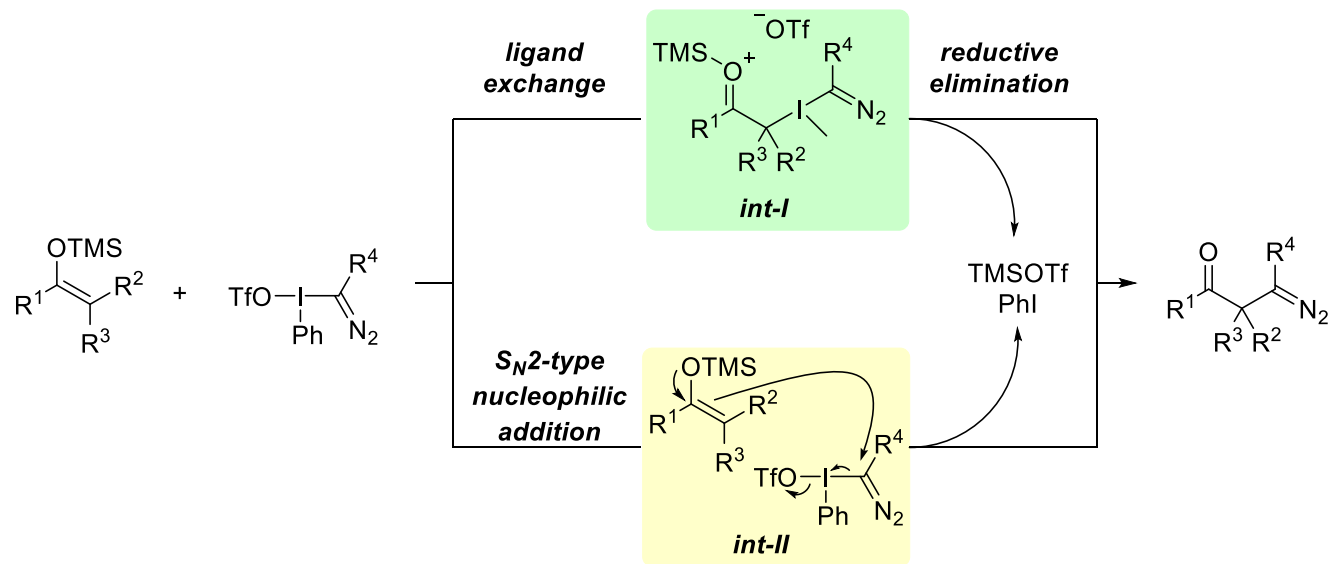
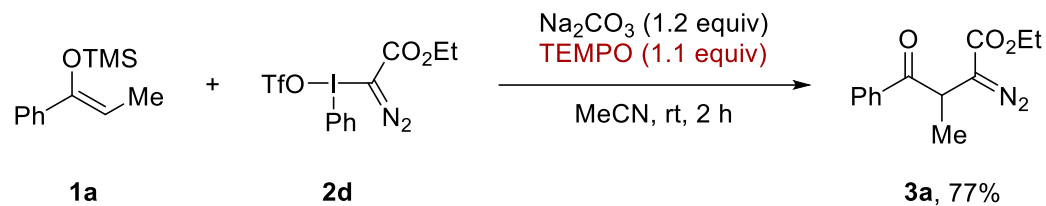
Suero (2021)



^a $\text{Rh}_2(\text{TPA})_4$ was used.

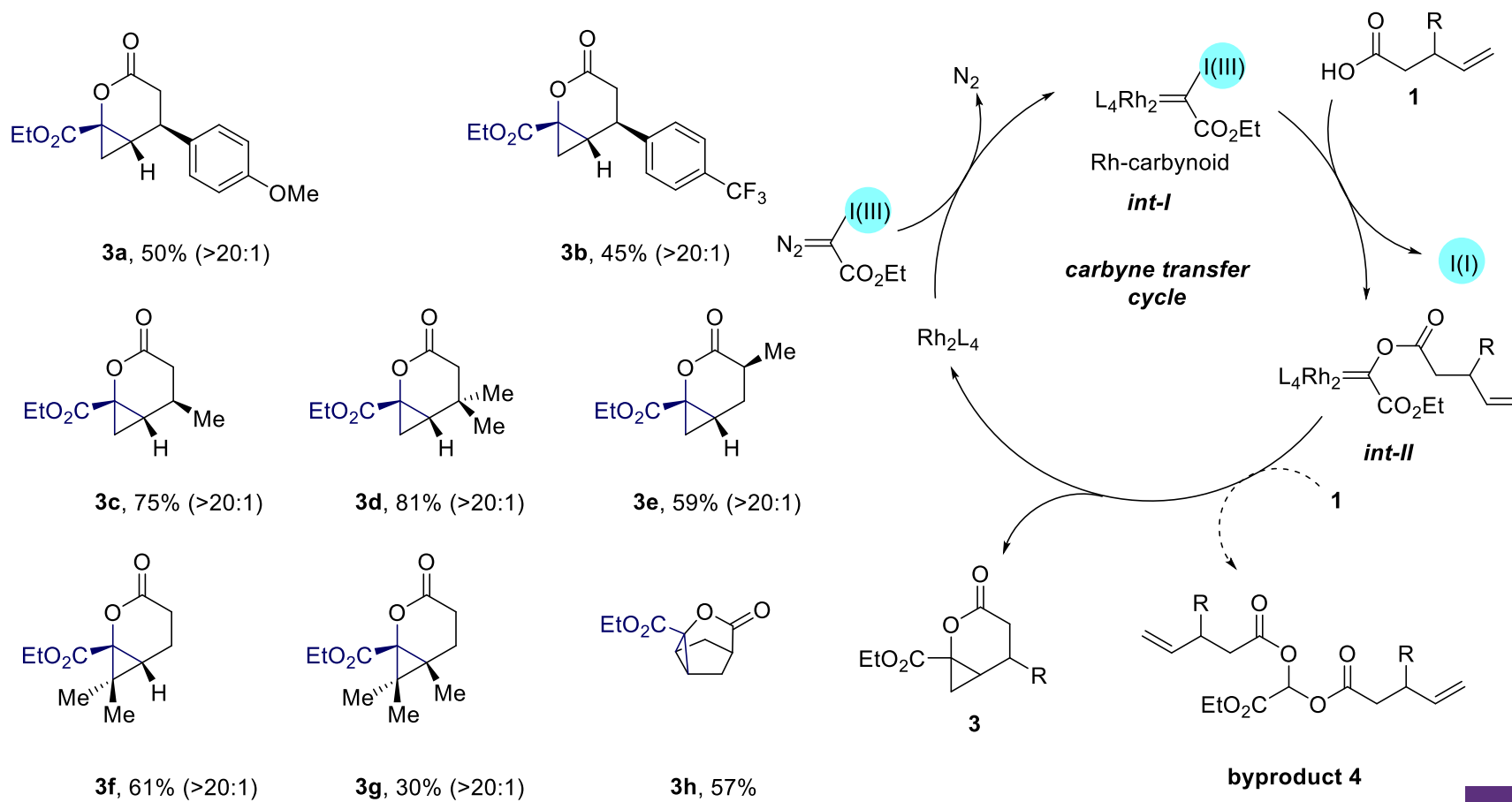
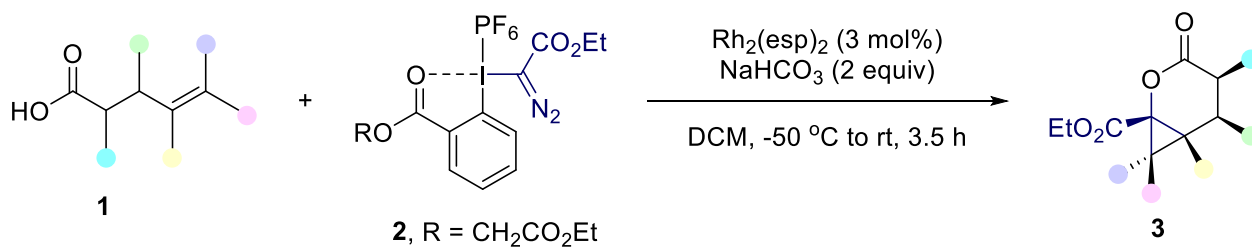
Carbon unit transfer reactions

Mechanism



Carbon unit transfer reactions — Via carbene

Suero (2023)



Content

1 Background

2 Carbon unit transfer reactions

2.1 via carbyne radical

2.2 via carbyne carbocation

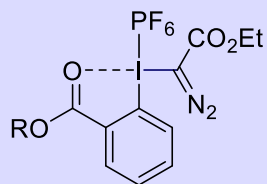
2.3 via carbene

3 Summary and outlook

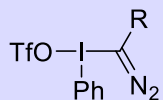


Summary

α -dialzo onium salts



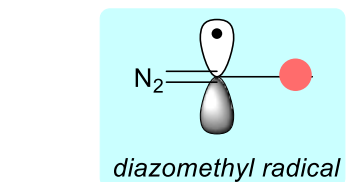
pseudocyclic α -diazo
hypervalent reagent



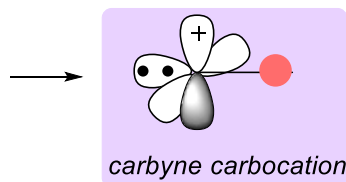
linear α -diazo
hypervalent reagent



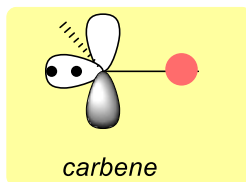
α -diazo
sulfonium triflates



diazomethyl radical

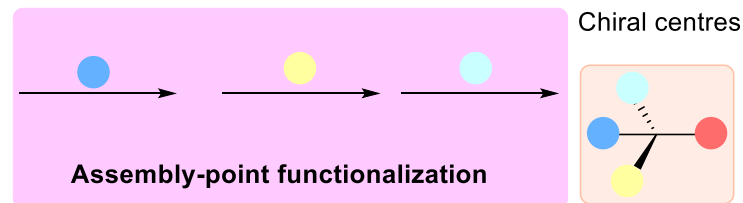


carbyne carbocation



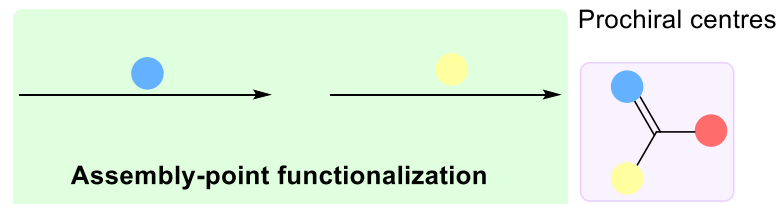
carbene

Carbon unit transfer products



Chiral centres

Assembly-point functionalization



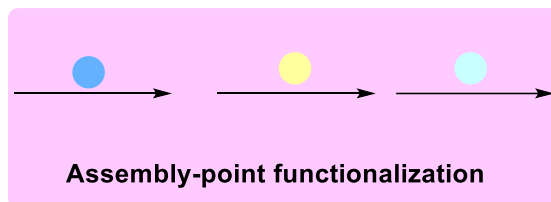
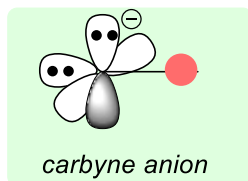
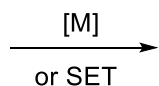
Prochiral centres

Assembly-point functionalization

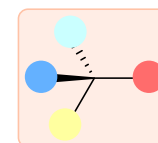
Three new bonds
were formed

Outlook

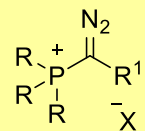
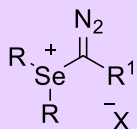
carbyne precursor



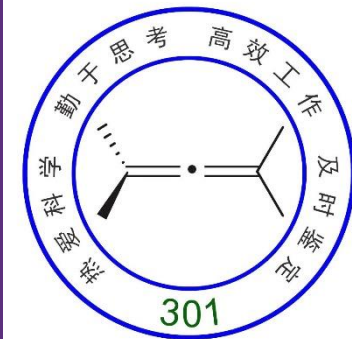
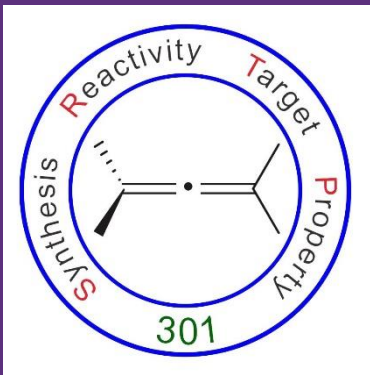
Chiral centres



A prevalent motif in natural products and drugs



- Development of various carbyne precursors
- Different intermediates
- Asymmetric reactions
- Heteroatom carbynes (Si, Ge, Sn...)



Thanks for your attention!