

Literature Report 5

Rhodium-Catalyzed Intramolecular Nitrogen Atom Insertion into Arene Rings

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Checker: Jian Chen

2023-8-21

Li, H.; Wei, H.* *J. Am. Chem. Soc.* **2023**, *145*, 17570-17576

CV of Prof. Hao Wei



Research:

- Skeletal editing
 - Energetic materials
 - The active composition of marine organisms
-

Background:

- **2007-2011** Ph.D., Lanzhou University (Prof. Peng-Fei Xu)
 - **2011-2013** Postdoc., Peking University (Prof. Zhen Yang)
 - **2013-2015** Postdoc., University of Idaho (Prof. J. M. Shreeve)
 - **2015-Now** Professor, Northwest University
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Contents

1 Introduction: Single-Atom Skeletal Edit

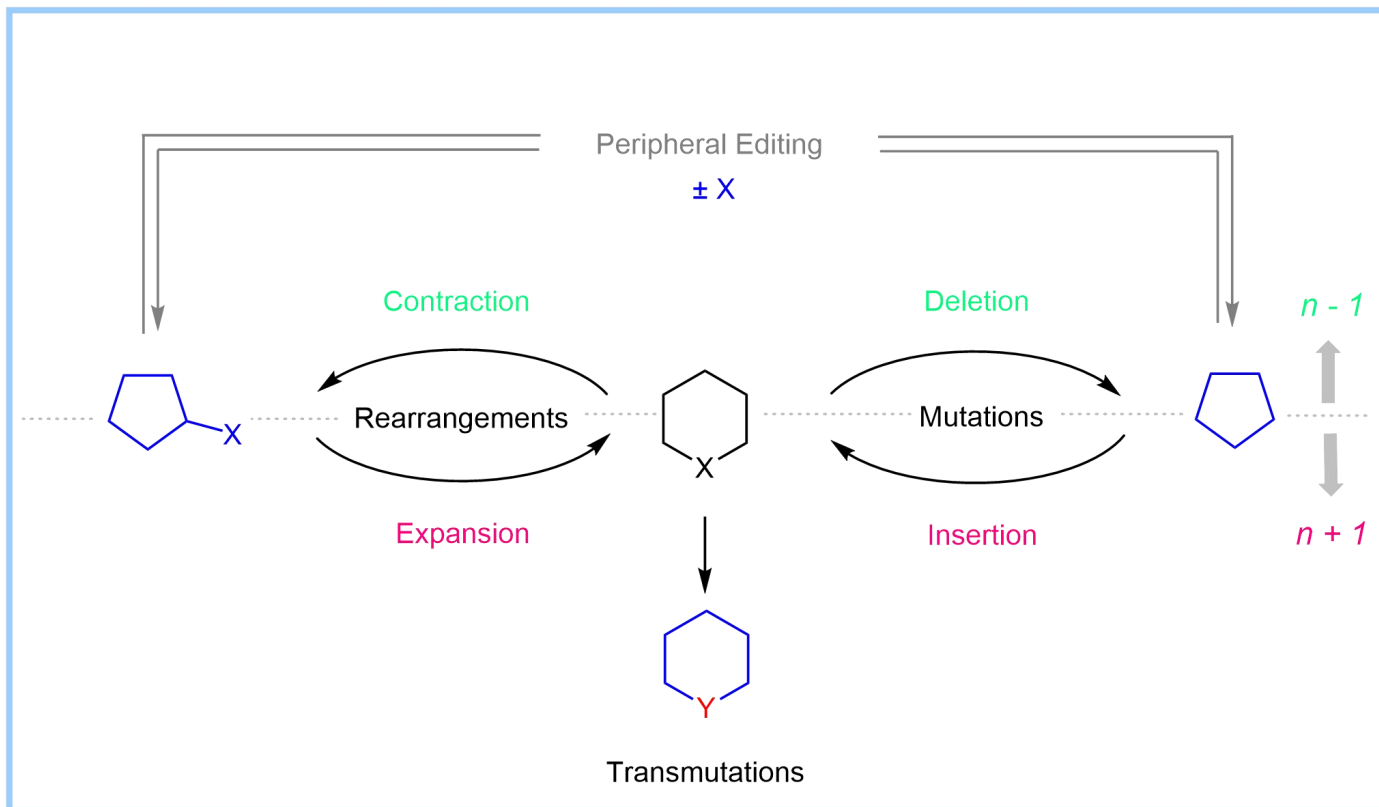
2 Nitrogen Atom Insertion into Carbocyclic Frameworks

3 Rhodium-Catalyzed Nitrogen Atom Insertion

4 Summary

Introduction

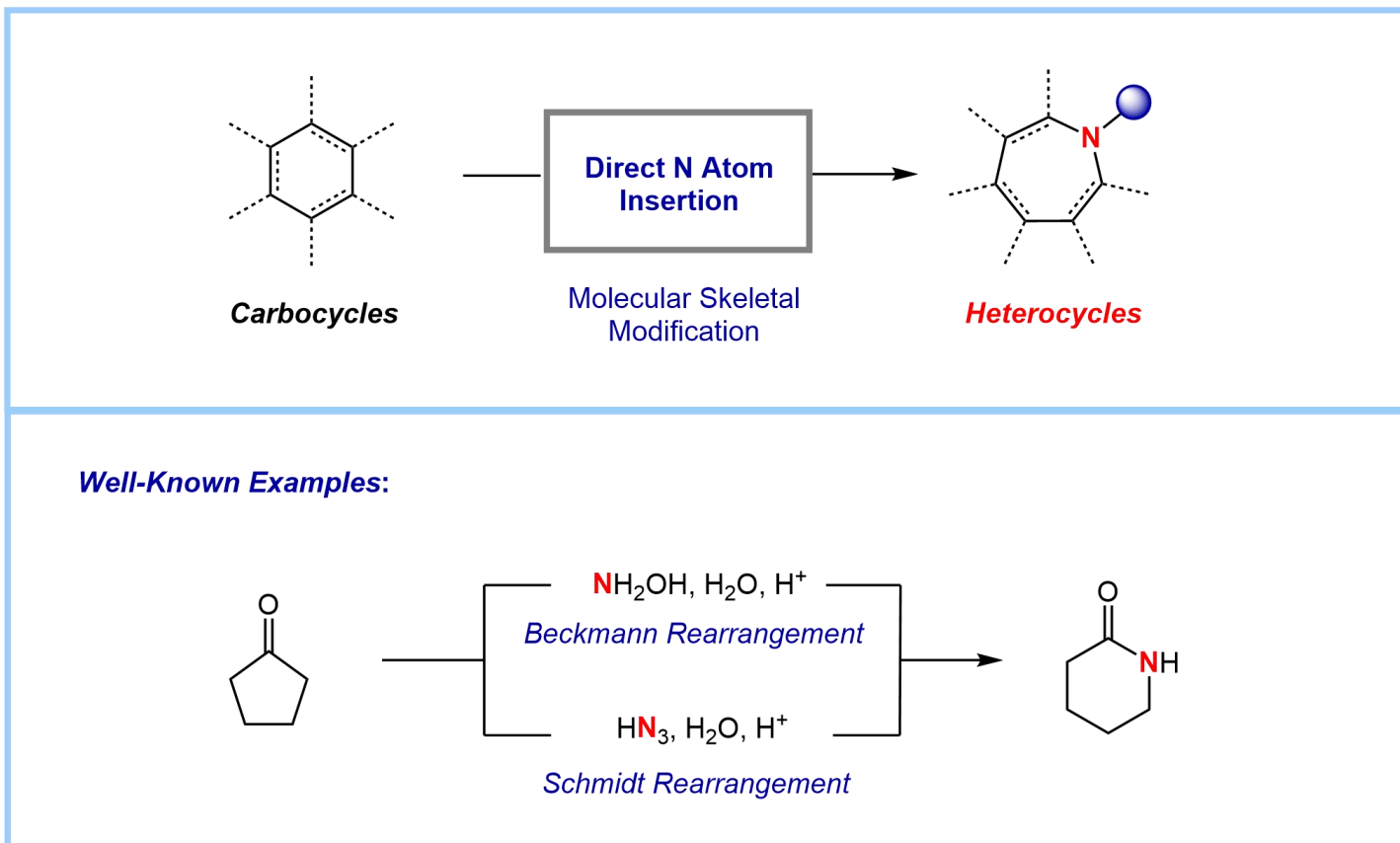
Single-Atom Skeletal Edit



Jurczyk, J.; Sarpong, R.* *Nat. Syn.* **2022**, *1*, 352-364

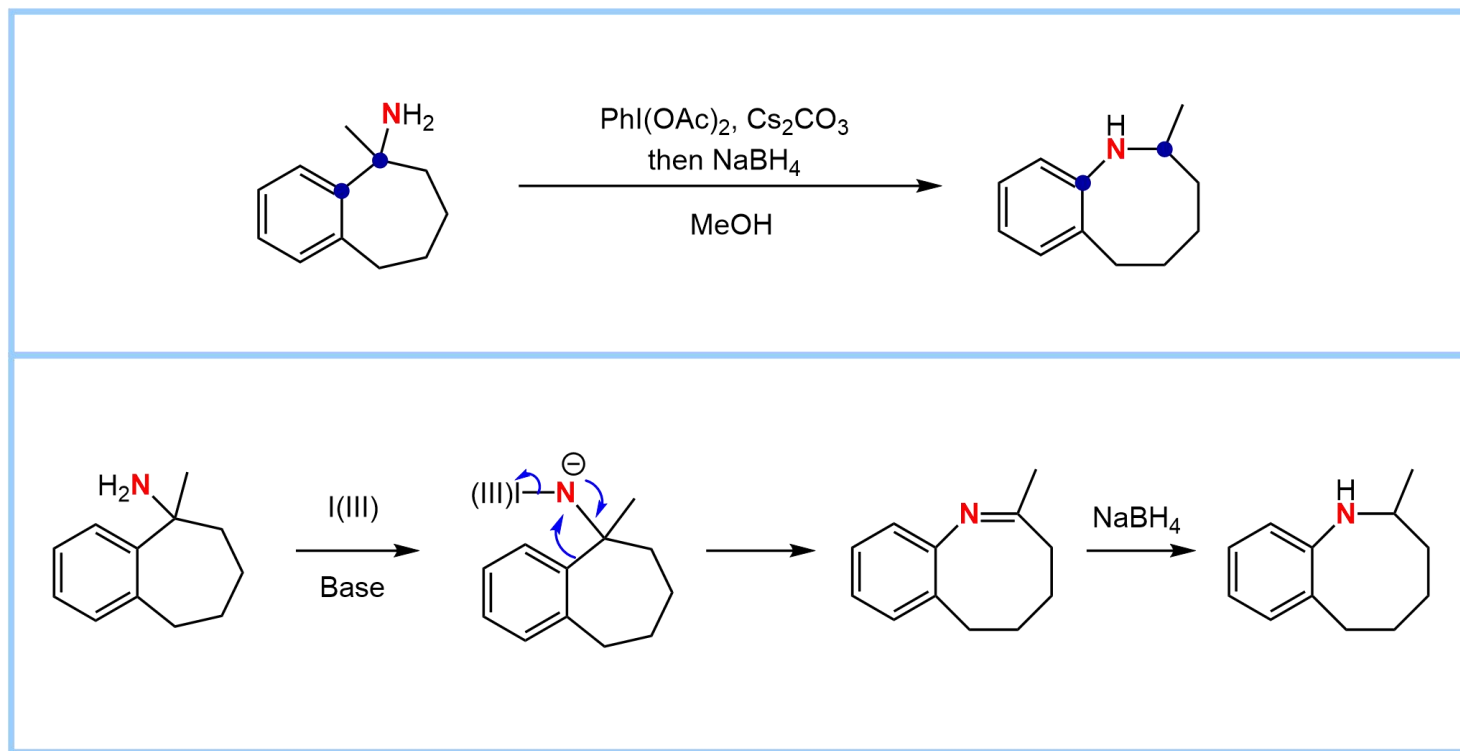
Introduction

Nitrogen Atom Insertion into Carbocyclic Frameworks



Nitrogen Atom Insertion into Cycloalkanes

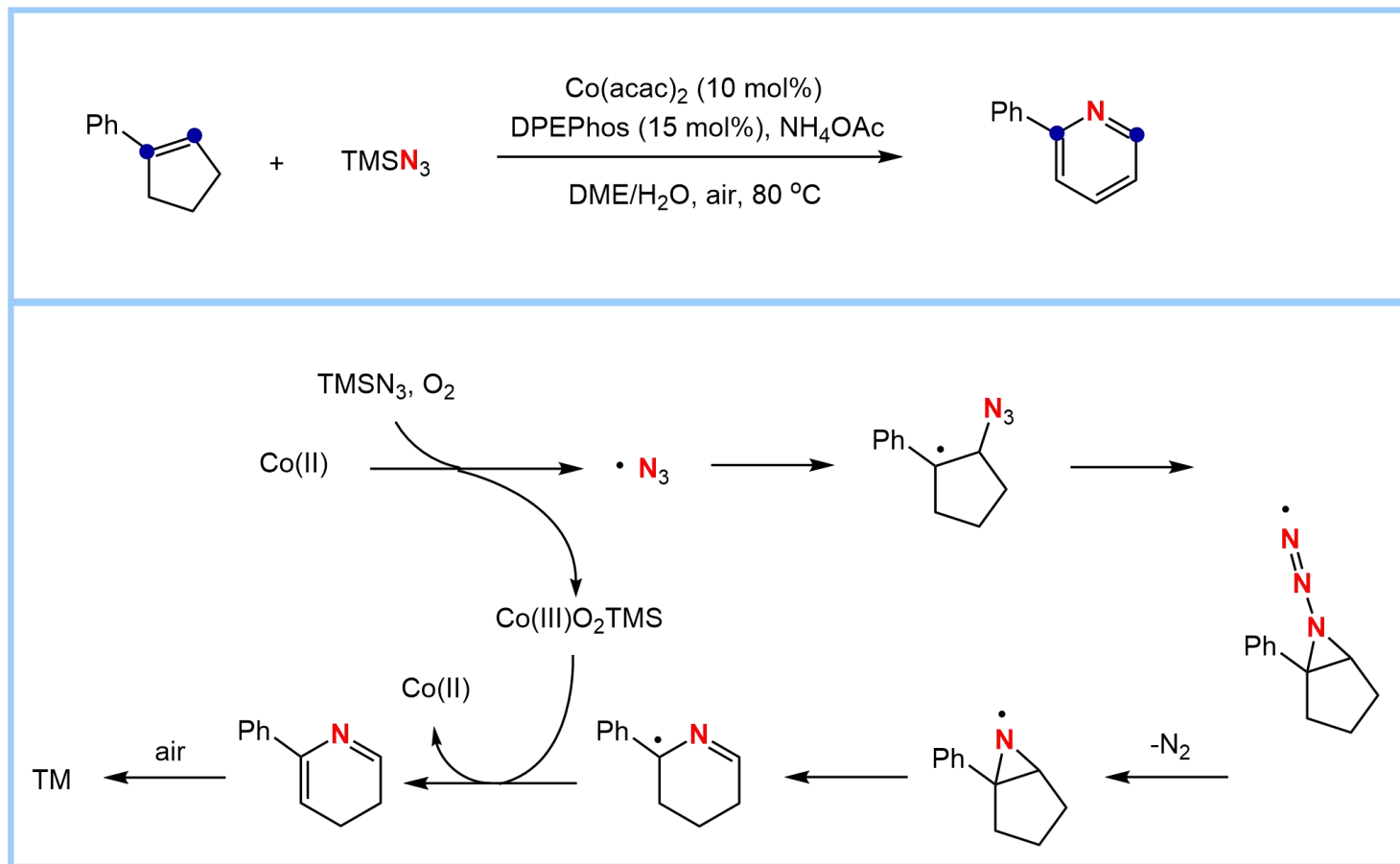
Oxidative Rearrangement of Primary Amines



Yamakoshi, W.; Murai, K.* *Org. Lett.* **2019**, 21, 3023-3027

Nitrogen Atom Insertion into Cycloalkenes

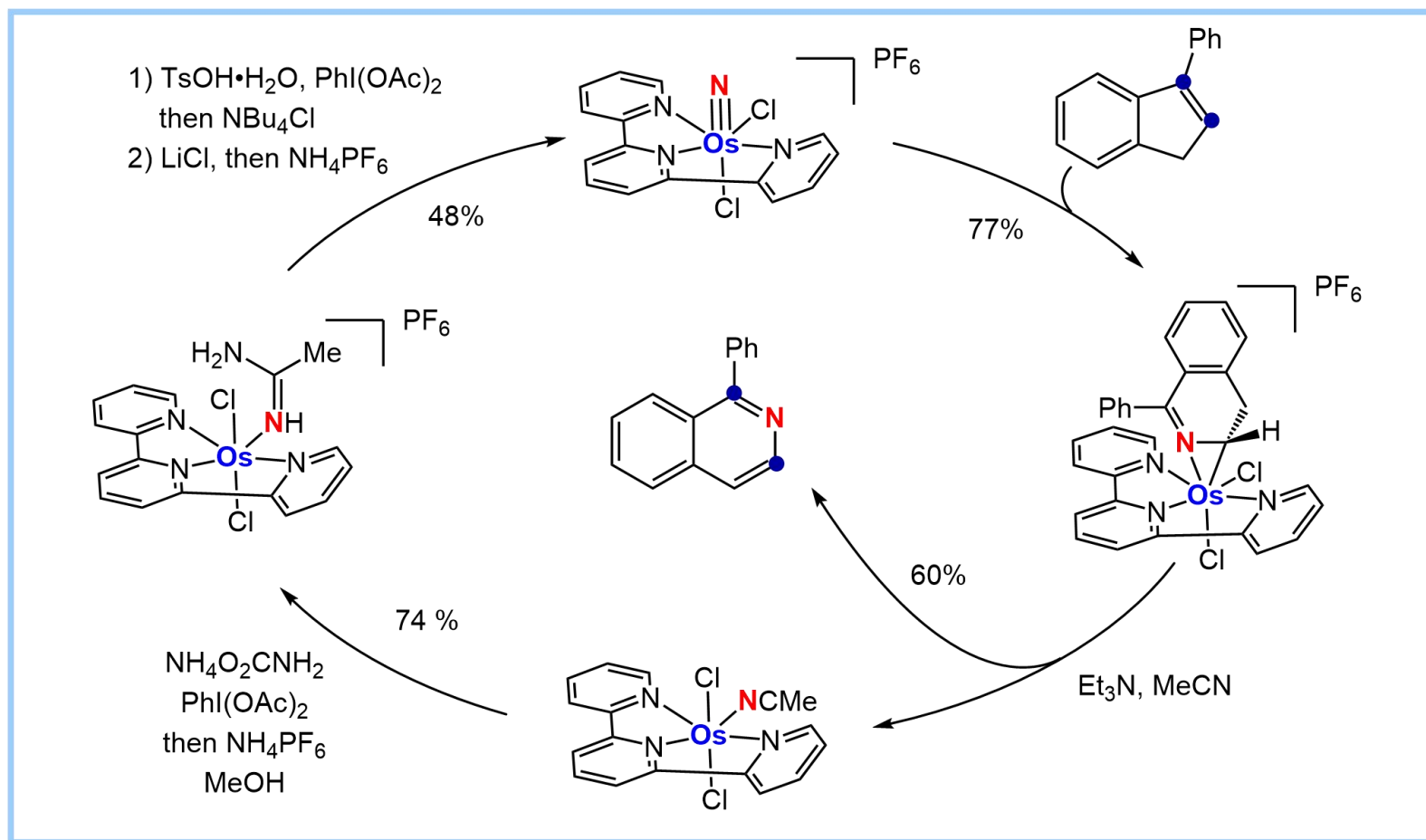
Cobalt-Catalyzed Nitrogen Atom Insertion into Arylcycloalkenes



Wang, J.; Wei, H.* *J. Am. Chem. Soc.* **2022**, *144*, 22433-22439

Nitrogen Atom Insertion into Cycloalkenes

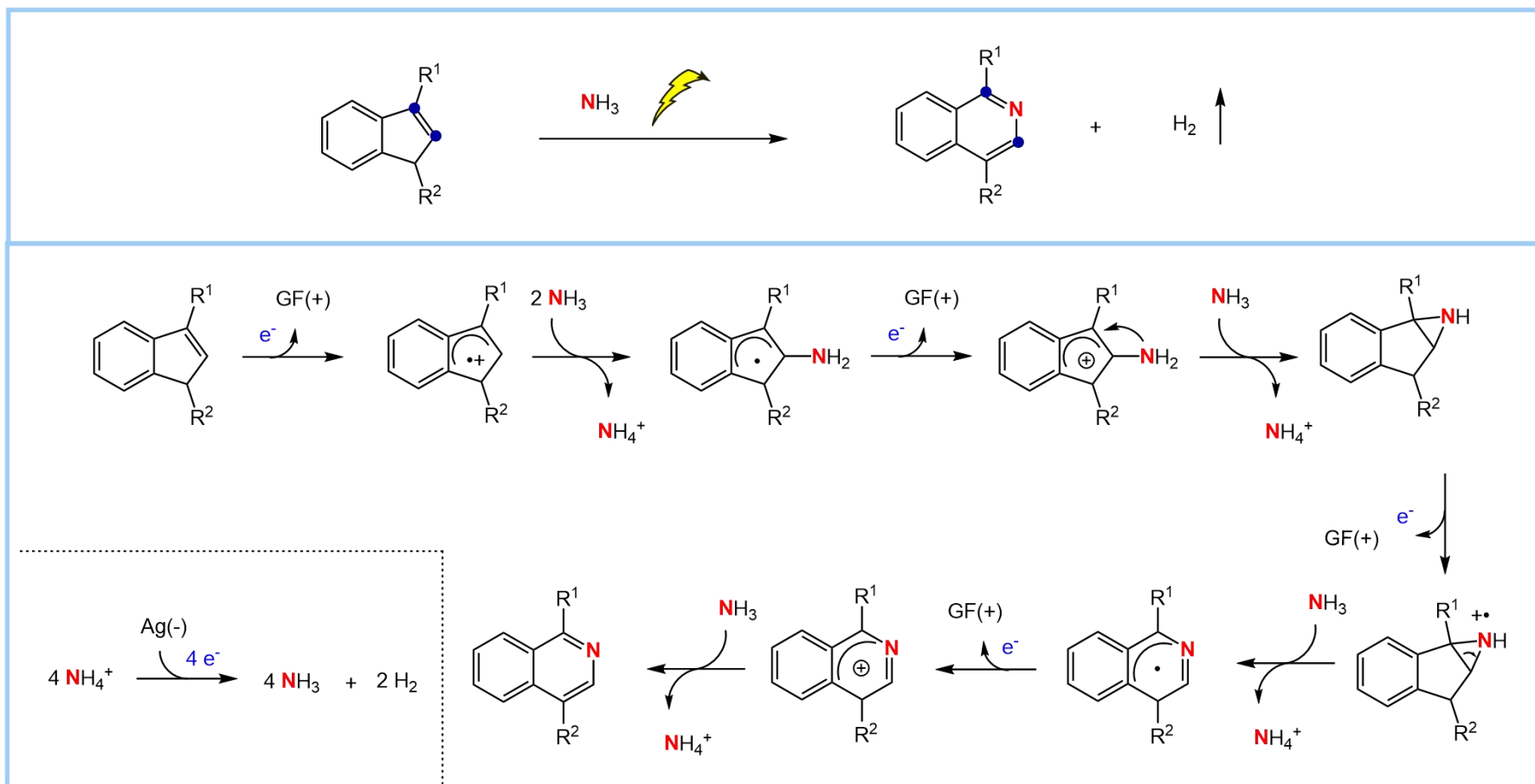
Osmium(VI) Nitrides-Promoted Nitrogen Atom Insertion into Phenylindene



Kelly, P. Q.; Levin, M. D.* *Angew. Chem. Int. Ed.* **2022**, *61*, e202213041

Nitrogen Atom Insertion into Cycloalkenes

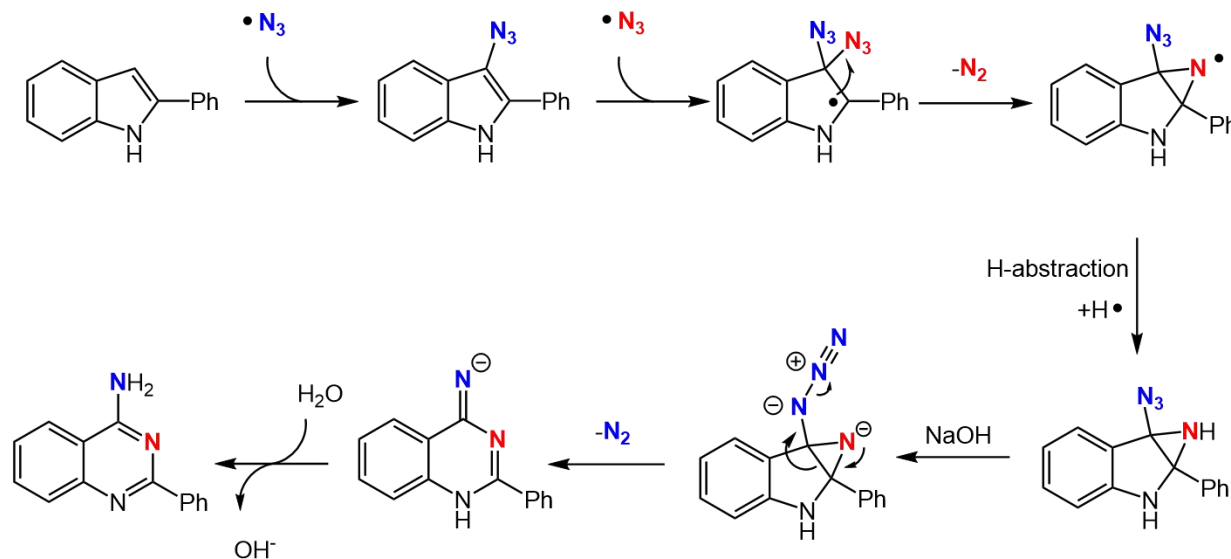
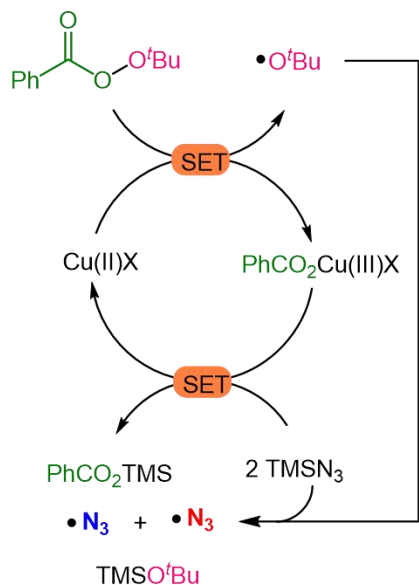
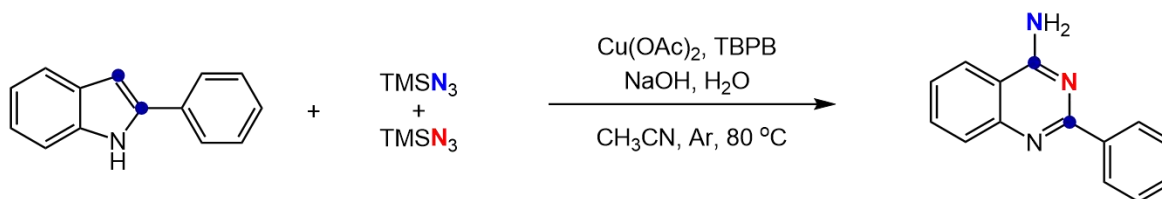
Insertion of Ammonia into Phenylindene via Electrochemical Method



Liu, S.; Cheng, X.* *Nat. Commun.* **2022**, *13*, 425

Nitrogen Atom Insertion into Aromatic Compounds

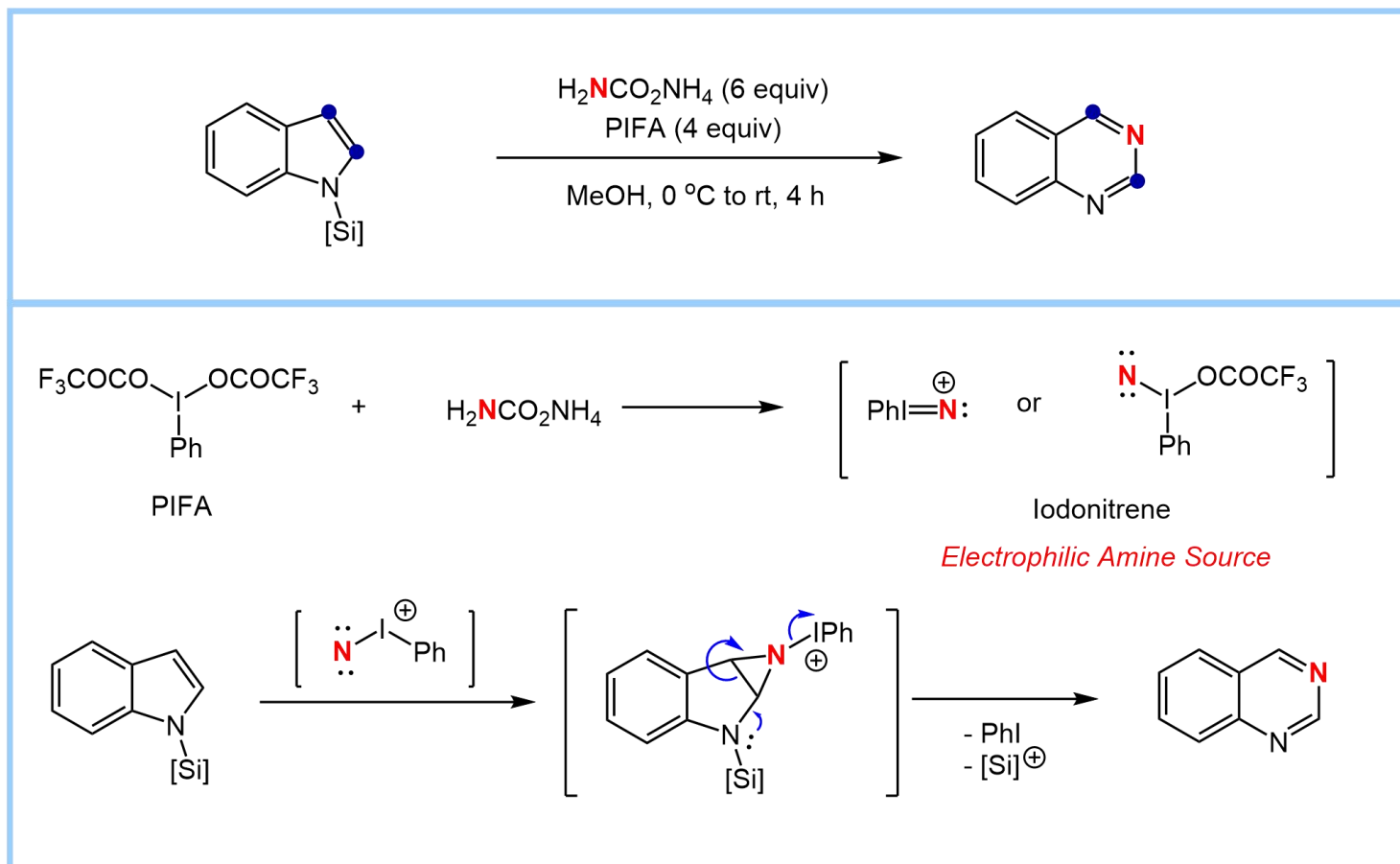
Copper-Catalyzed Nitrogen Atom Insertion into 2-Arylindoles



Xu, M.-M.; Ji, S.-J.* *Chem. Commun.* **2018**, 54, 12602-12605

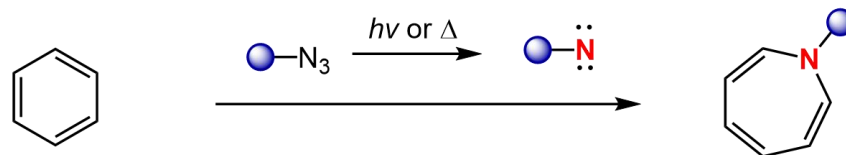
Nitrogen Atom Insertion into Aromatic Compounds

Insertion of Nitrogen Atom into Indole via Electrophilic Nitrene



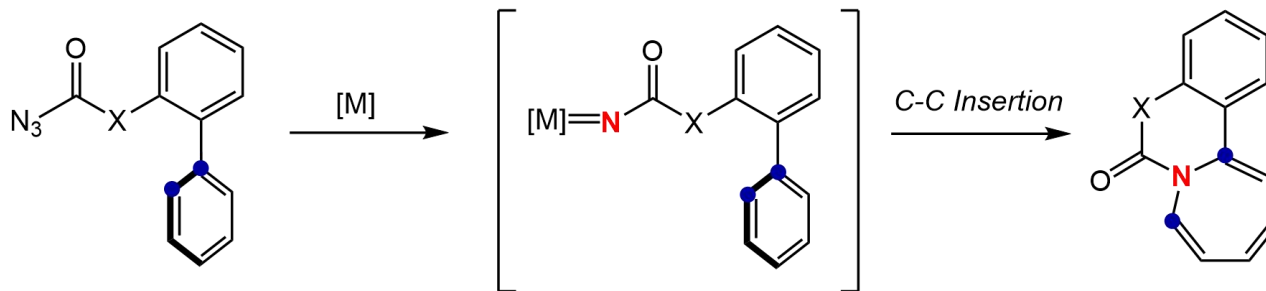
Reisenbauer, J. C.; Morandi, B.* *Science* **2022**, 377, 1104-1109

Project Synopsis



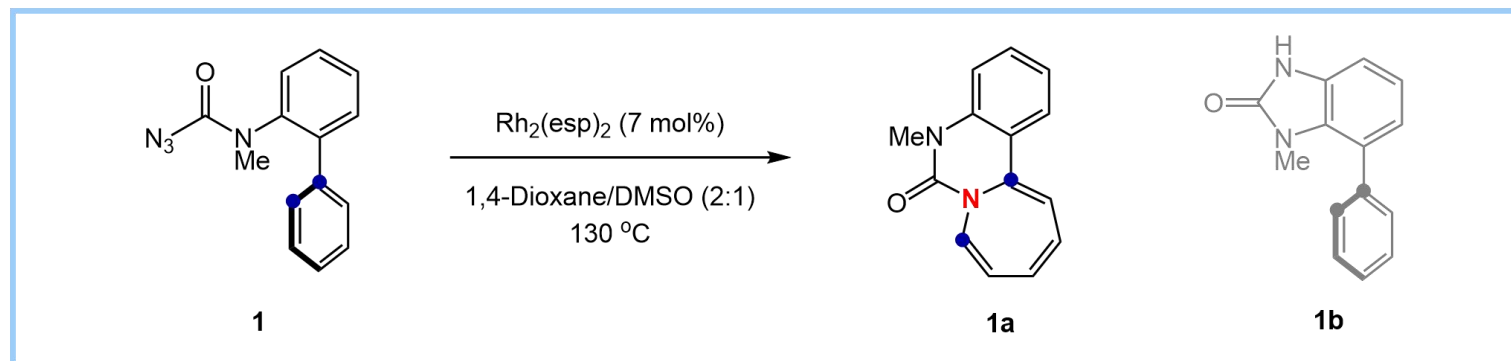
- ♥ *direct skeletal modification*
- ♣ *low yielding*
- ♣ *benzene solvent*
- ♣ *lacking regioselectivities*
- ♣ *limited investigation of group*
- ♣ *many side products*

Cotter, R. J.; Beach, W. F. *J. Org. Chem.* **1964**, 29, 751-754



Li, H.; Wei, H.* *J. Am. Chem. Soc.* **2023**, 145, 17570-17576

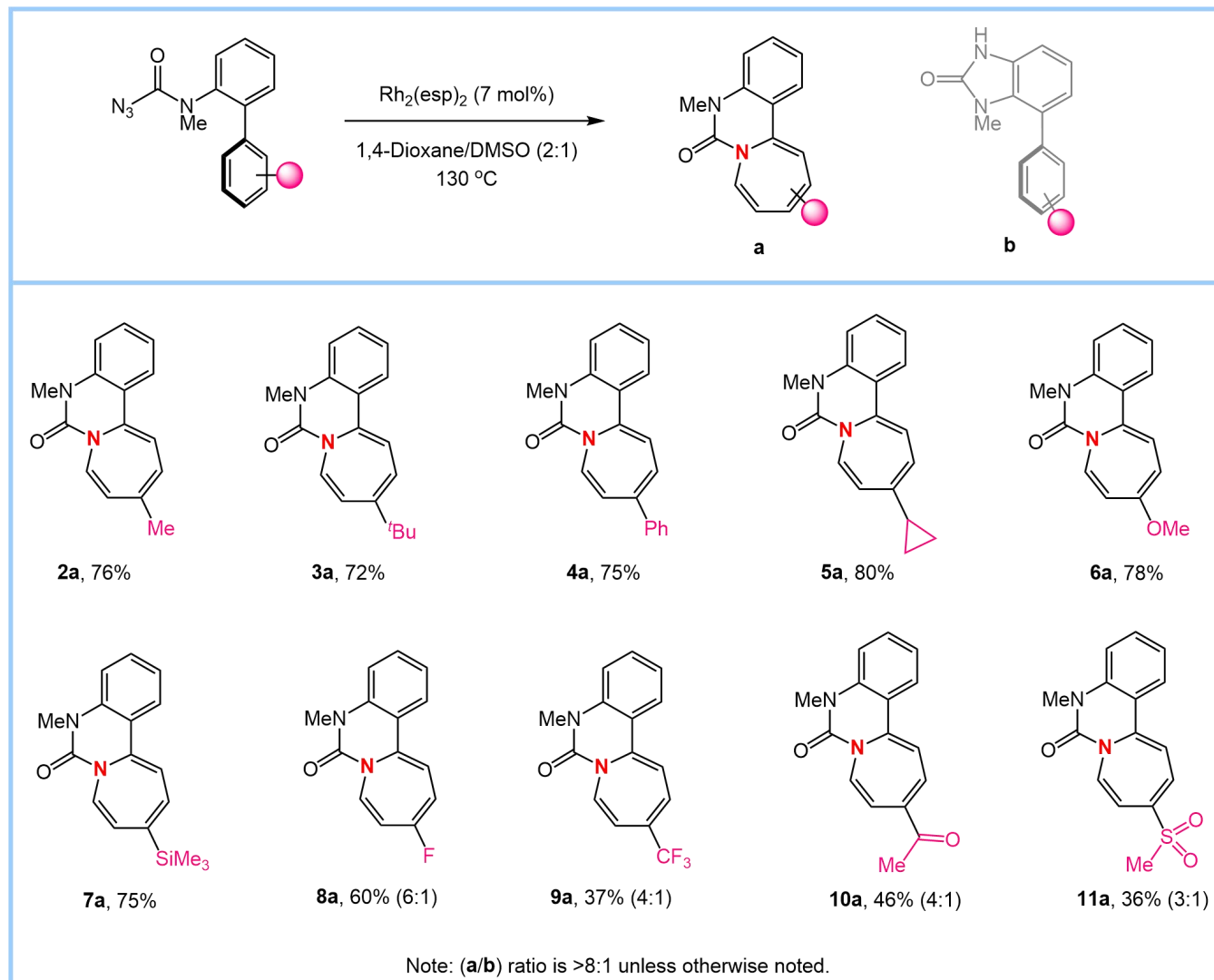
Optimization of Reaction Conditions



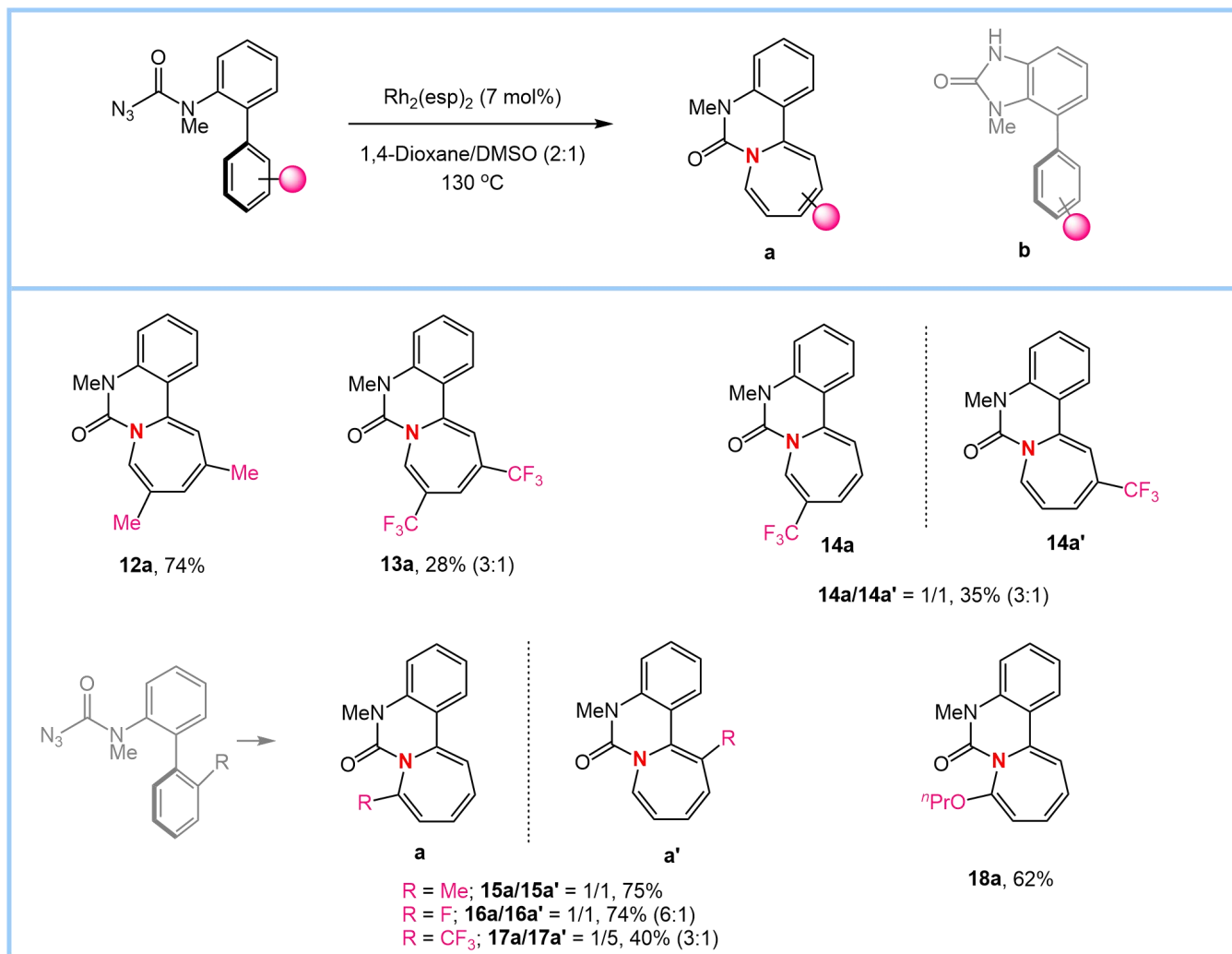
Entry ^a	Variation	Yield ^b (%)	
		1a	1b
1	None	80	9
2 ^c	w/o $\text{Rh}_2(\text{esp})_2$	39	37
3	$\text{Rh}_2(\text{OAc})_4$ instead of $\text{Rh}_2(\text{esp})_2$	62	7
4	$\text{Rh}(\text{PPh}_3)\text{Cl}$ instead of $\text{Rh}_2(\text{esp})_2$	50	11
5	$[\text{Cp}^*\text{Rh}(\text{CH}_3\text{CN})](\text{SbF}_6)_2$ instead of $\text{Rh}_2(\text{esp})_2$	17	56
6	CoTPP instead of $\text{Rh}_2(\text{esp})_2$	46	15
7	Fe(TPP)Cl instead of $\text{Rh}_2(\text{esp})_2$	35	37

[a] All reactions were carried out using **1** (0.1 mmol) with 7 mol% $\text{Rh}_2(\text{esp})_2$ in Dioxane/DMSO (2/1) at 130 °C for 24 h. [b] Isolated yields. [c] The reaction time was 48 h.

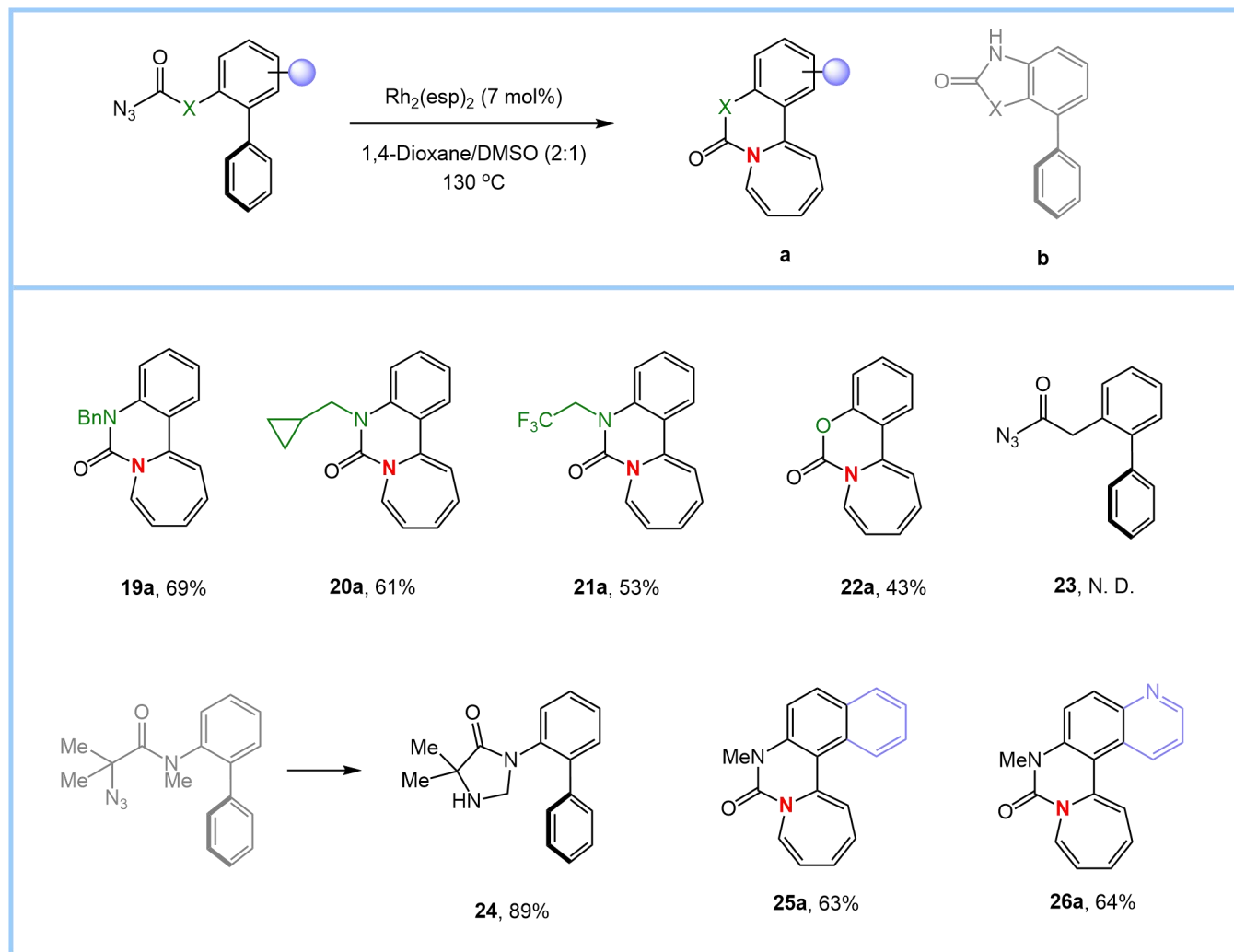
Substrate Scope



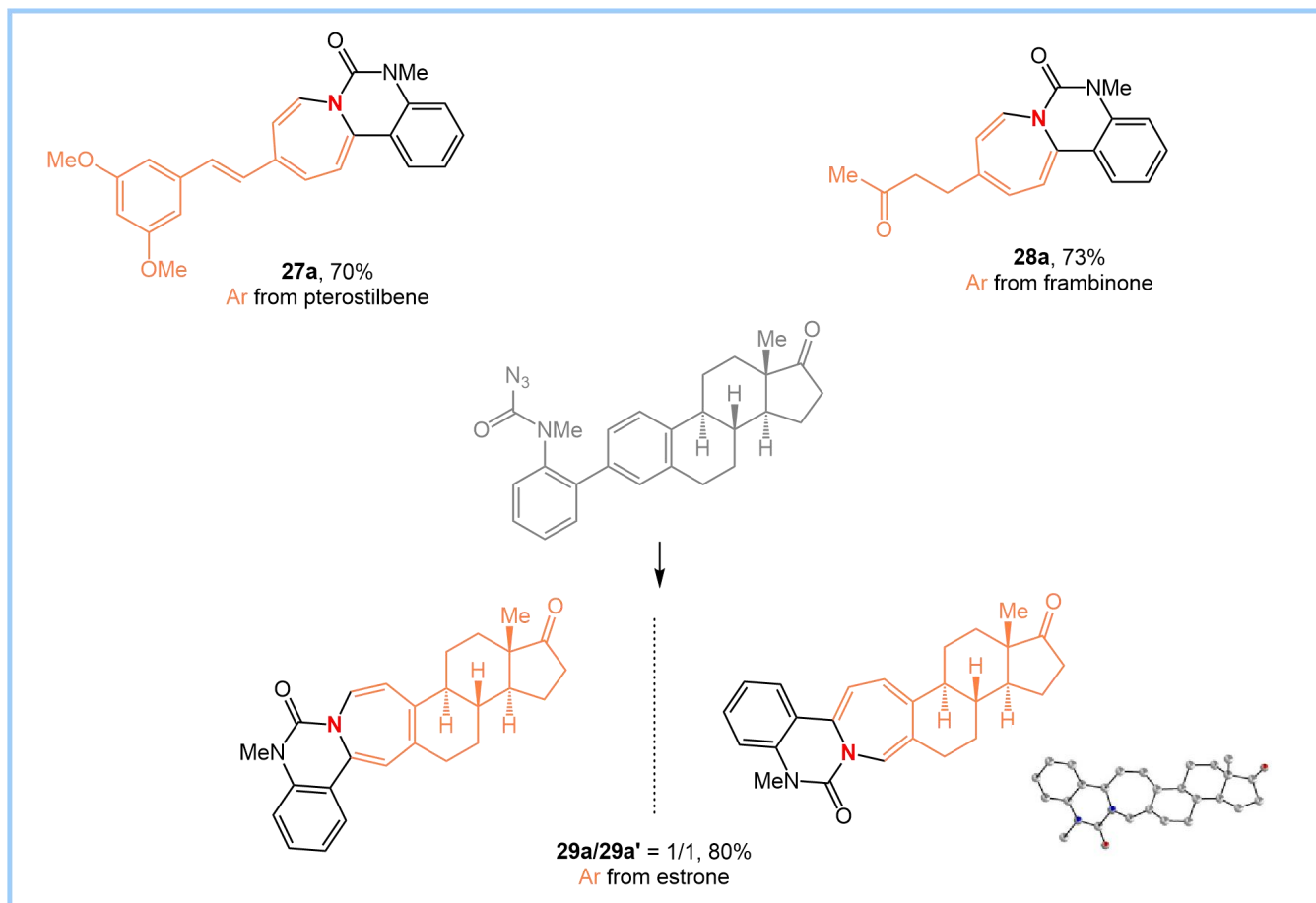
Substrate Scope



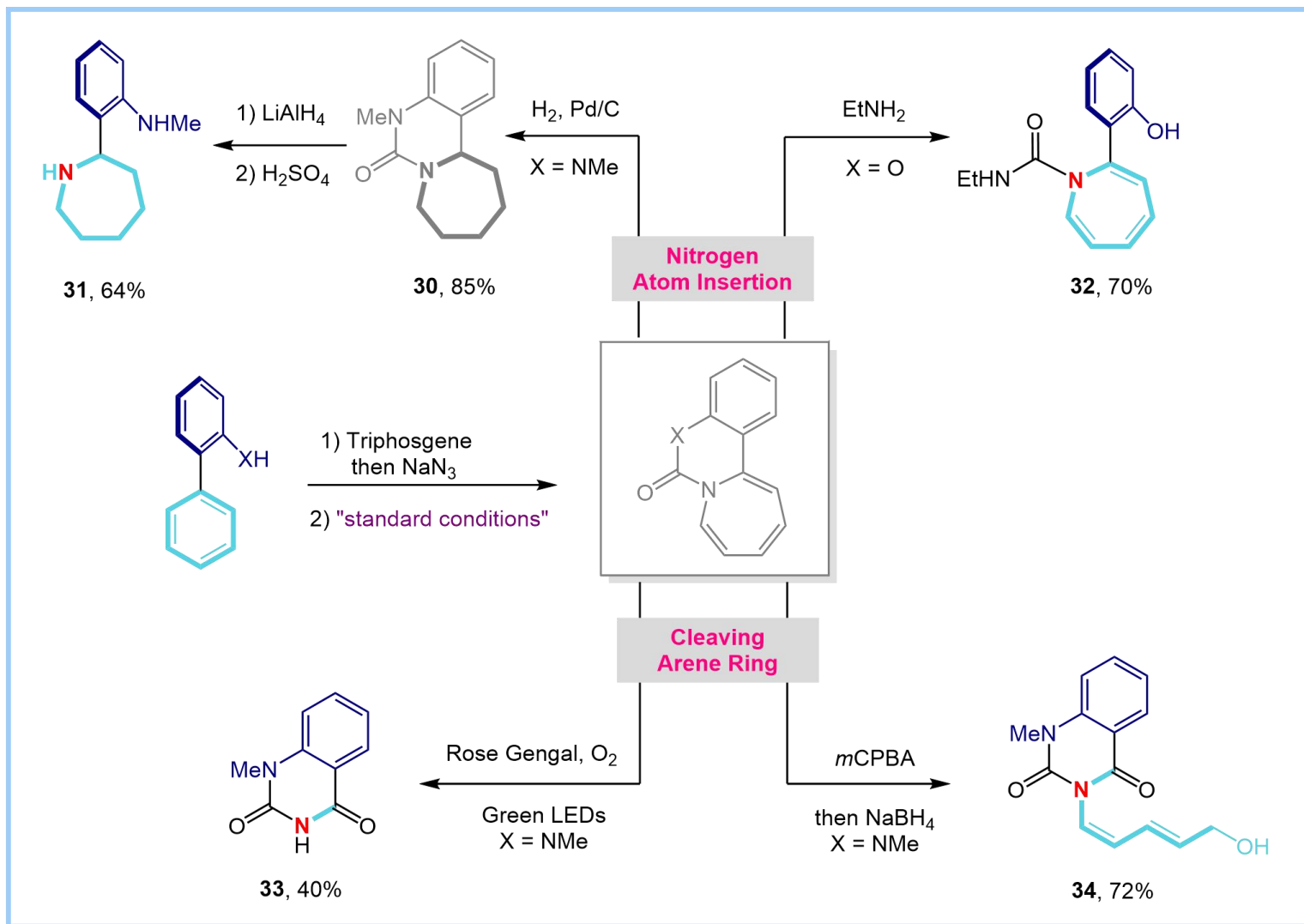
Substrate Scope



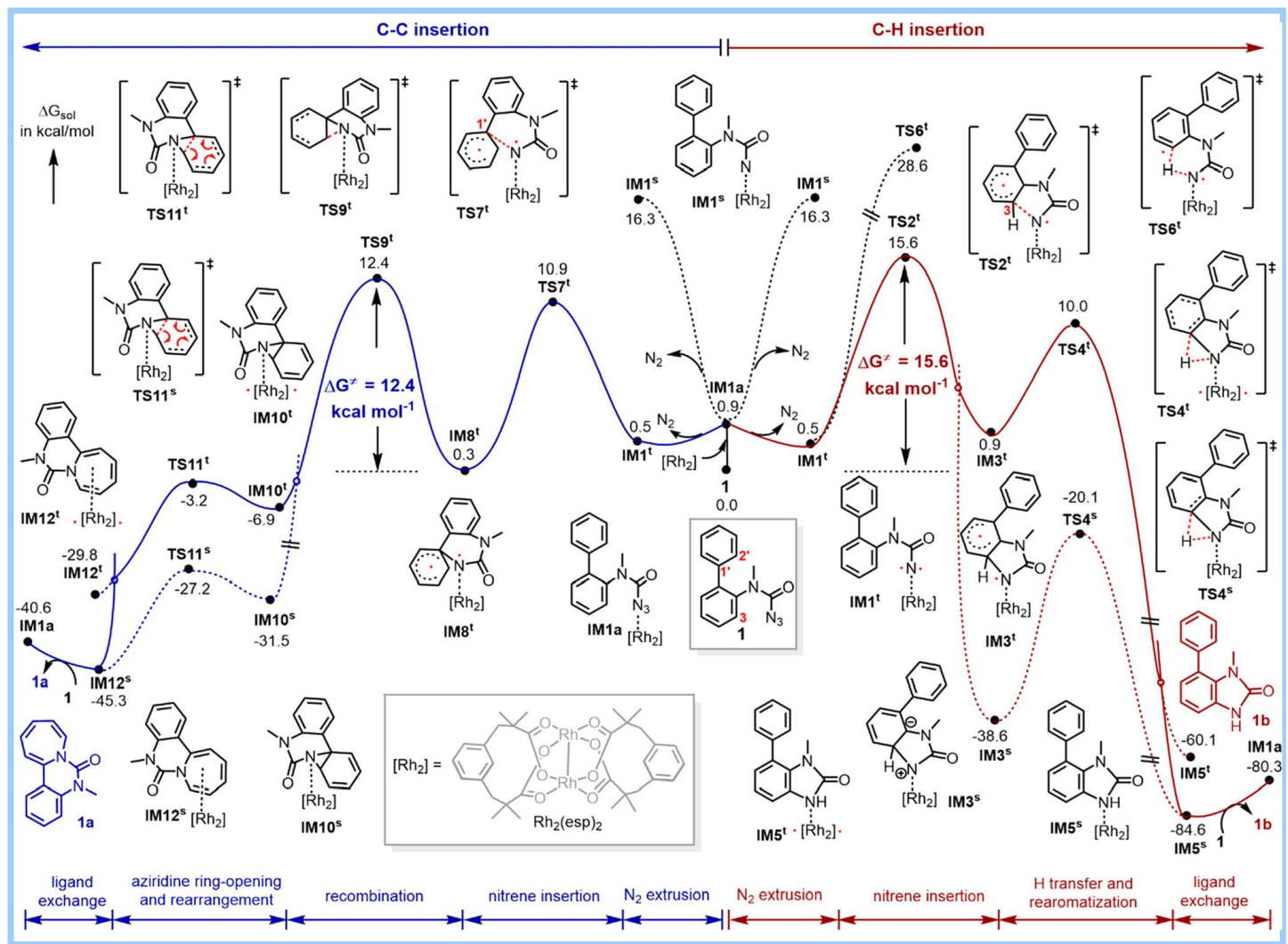
Substrate Scope



Transformations of Products

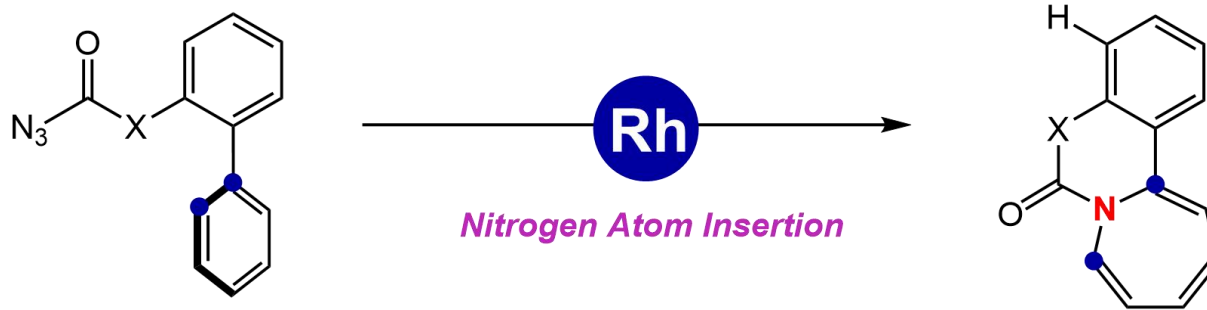


Proposed Mechanism



Summary

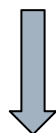
Rhodium-Catalyzed Intramolecular Nitrogen Atom Insertion into Arene Rings



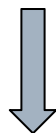
Challenge: C-H Insertion **VS** C-C Insertion

写作思路

芳烃作为有机分子普遍存在结构具有重要意义



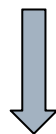
芳烃的C-H键官能团化得到快速发展



芳烃的C-C键活化仍存在挑战

写作思路

总结工作：铑催化氮原子插入芳环C-C键新策略



提出展望：铑催化剂改变反应选择性值得进一步研究

Representative Examples

- Recently, **considerable effort has been dedicated to** the development of versatile C-H functionalization strategies to modify target arenes. (投入很大努力)
- **Given the widespread abundance of** arene rings... (鉴于...的普遍性)
- To **elucidate** the reaction mechanism and the origin of the chemoselectivity, DFT calculations were performed. (elucidate: 解释, 阐释, 可代替explain、expound、interpret)

Acknowledgement

Thanks for Your Attention