



# $P^{III}/P^V=O$ Catalysis

Reporter: Chu Haoke (储豪科)

Supervisor: Prof. Zhang Junliang

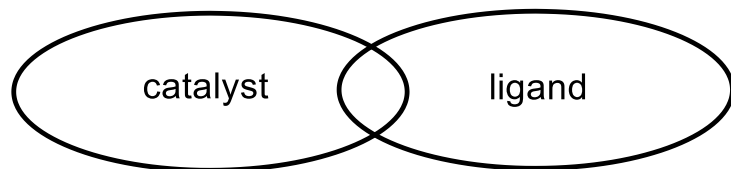
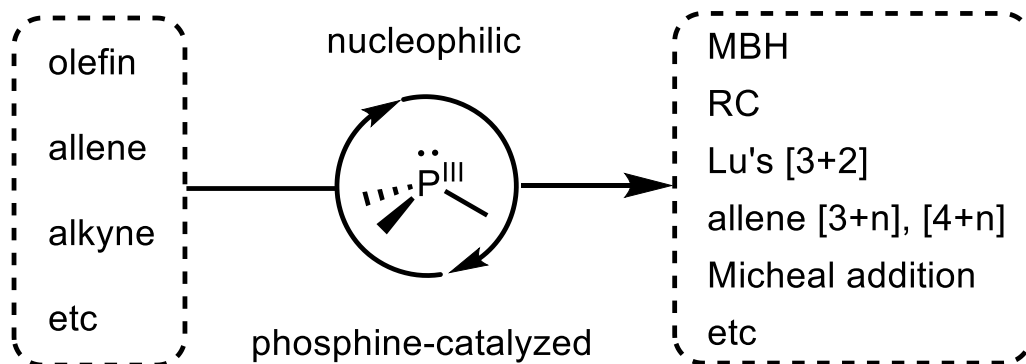
2019.12.27

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  - 2.2 Staudinger Reaction
  - 2.3 Aza-Wittig Reaction
  - 2.4 Recent Reports
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# 1. Introduction

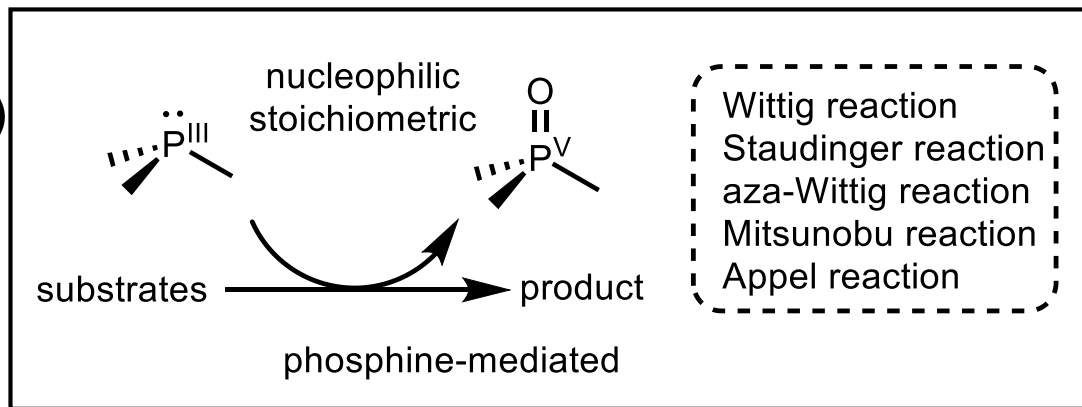
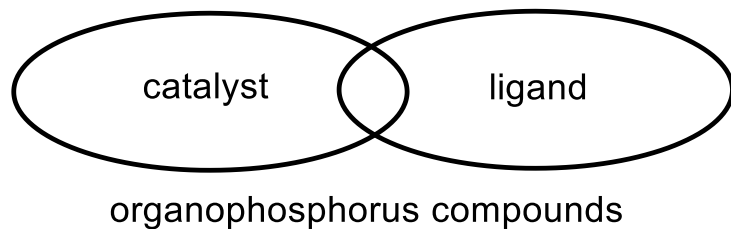
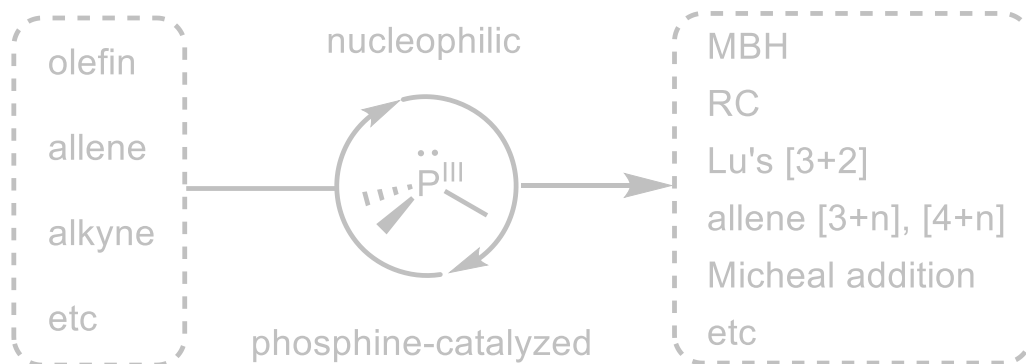
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密度 / g·cm <sup>-3</sup>	1.828(白)
熔点 / °C	44.1(白)
沸点 / °C	280.5(白)
原子序数	15
英文名称	Phosphorus
原子半径/pm	110.5
发现年代	1669年
发现者	布兰德
电子排布	[Ne]3s <sup>2</sup> 3p <sup>3</sup>
相对原子质量	30.97
电负性	2.1
元素符号	P
第一电离能/kJ·mol <sup>-1</sup>	1060
氧化态	5, ±3, 4
生命必需元素	是
复杂立方	面心立方
复杂立方	复杂立方



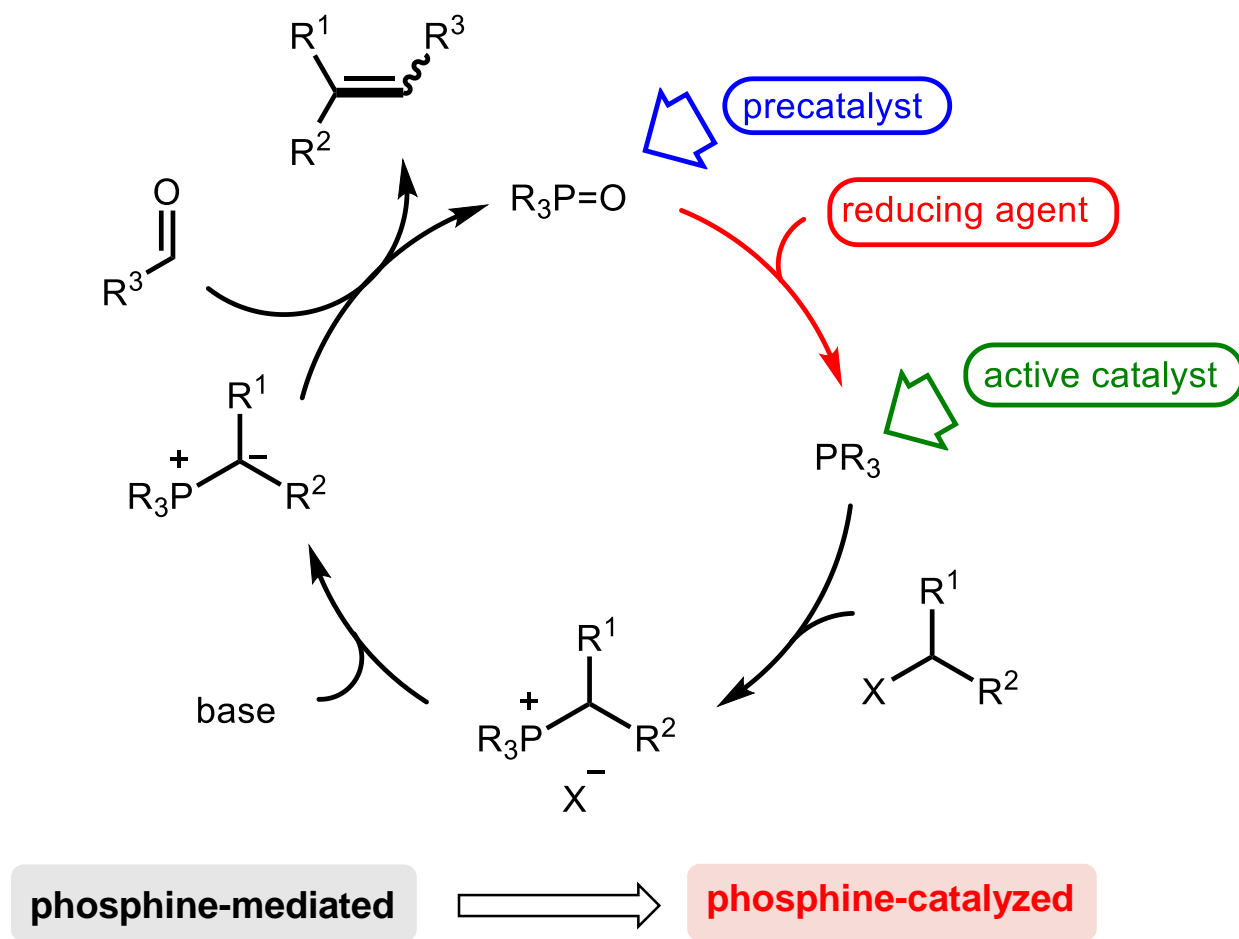
organophosphorus compounds

# 1. Introduction

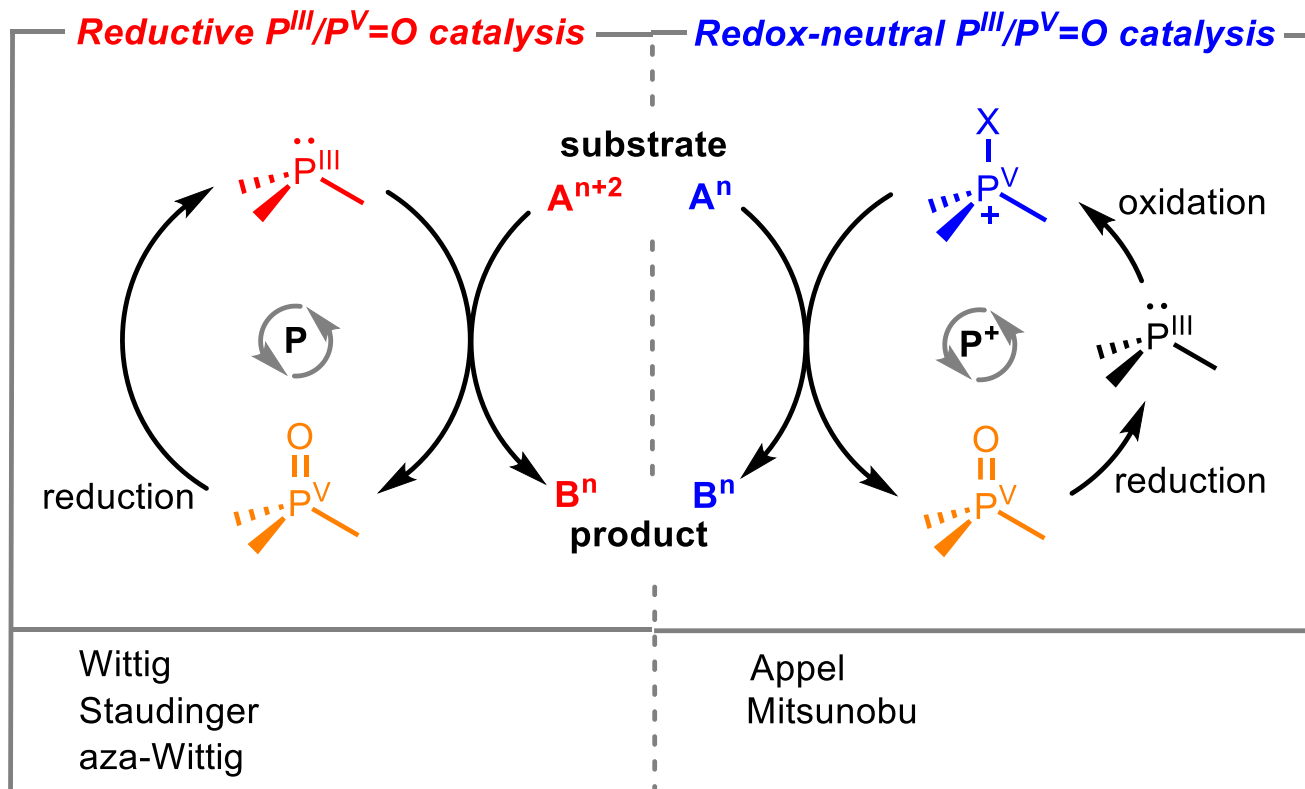
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生命必需元素	是
晶体结构	复杂立方 面心立方 复杂立方



# 1. Introduction



# 1. Introduction



- **Radosevich Group:** *JACS* **2015**; *JACS* **2017**; *JACS* **2018**; *JACS* **2018**; *ACIE* **2019**; *JACS* **2019**
- **Mecinović Group:** *CC* **2014**

- T. Mukaiyama, *Angew. Chem. Int. Ed.* **2004**, *43*, 5590
- H. Guo, O. Kwon, et al. *Chem. Rev.* **2018**, *118*, 10049

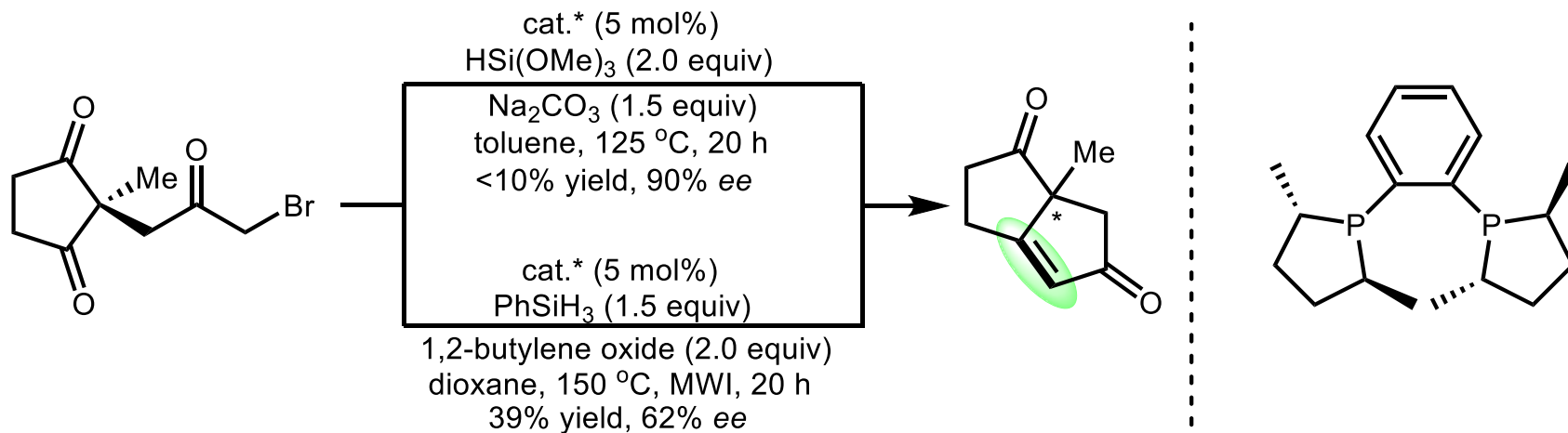
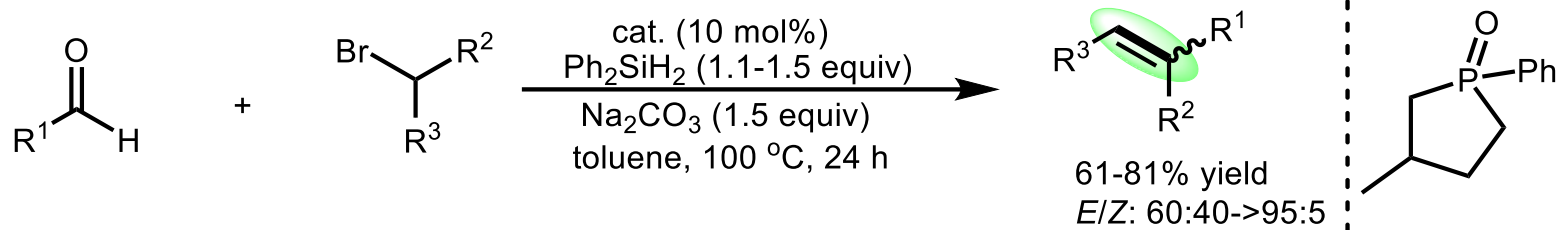
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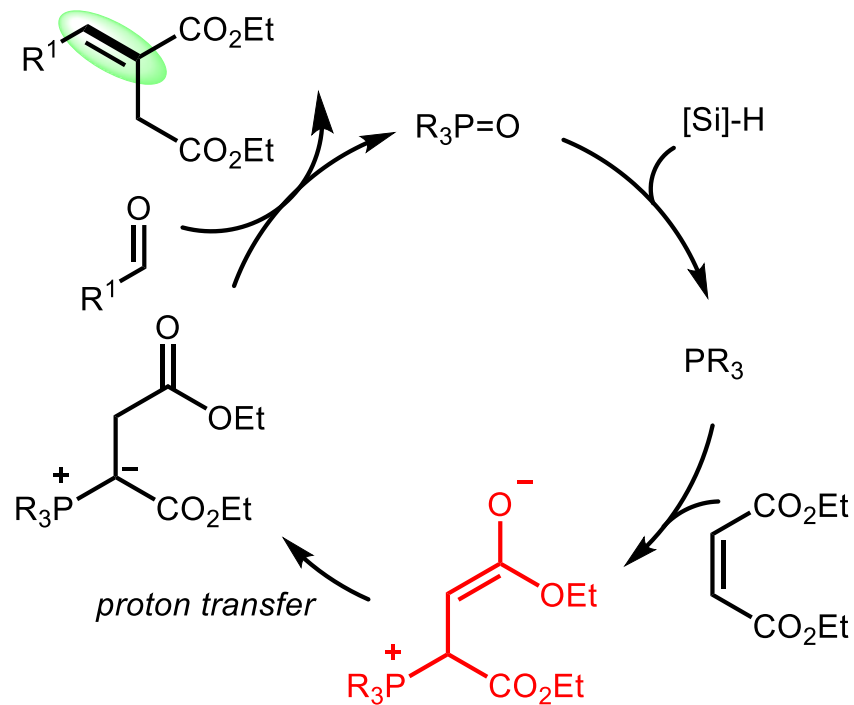
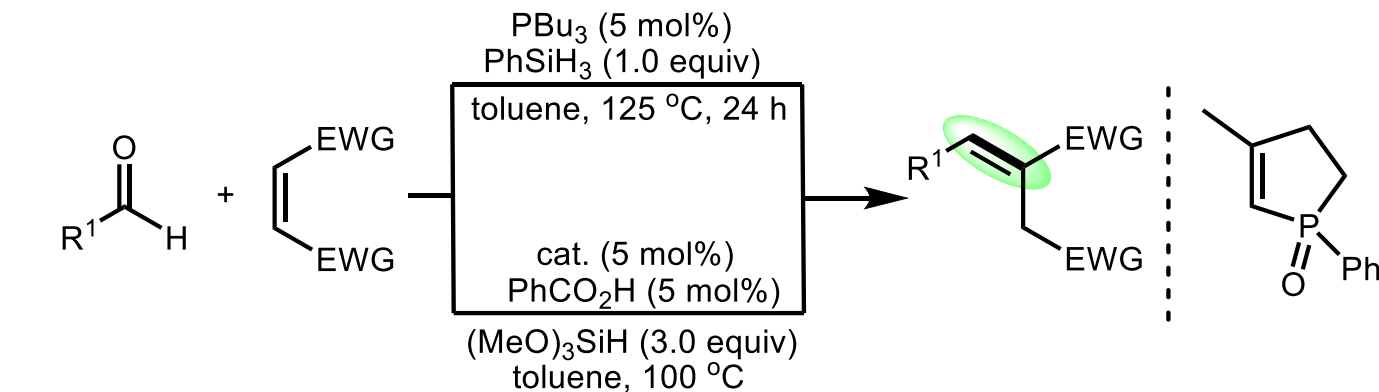


# 2.1 Wittig Reaction



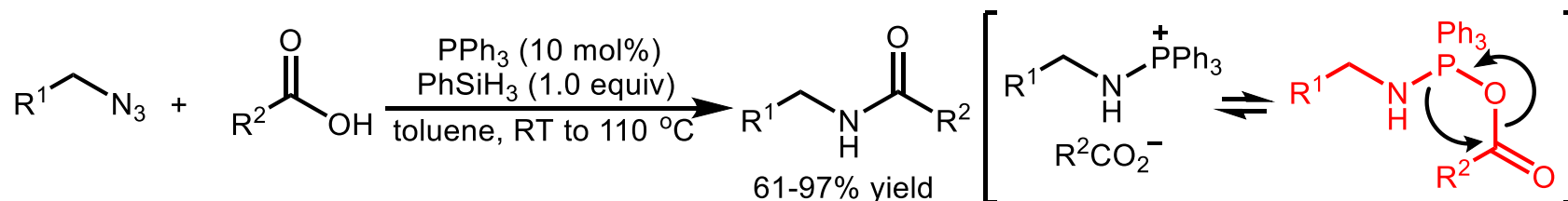
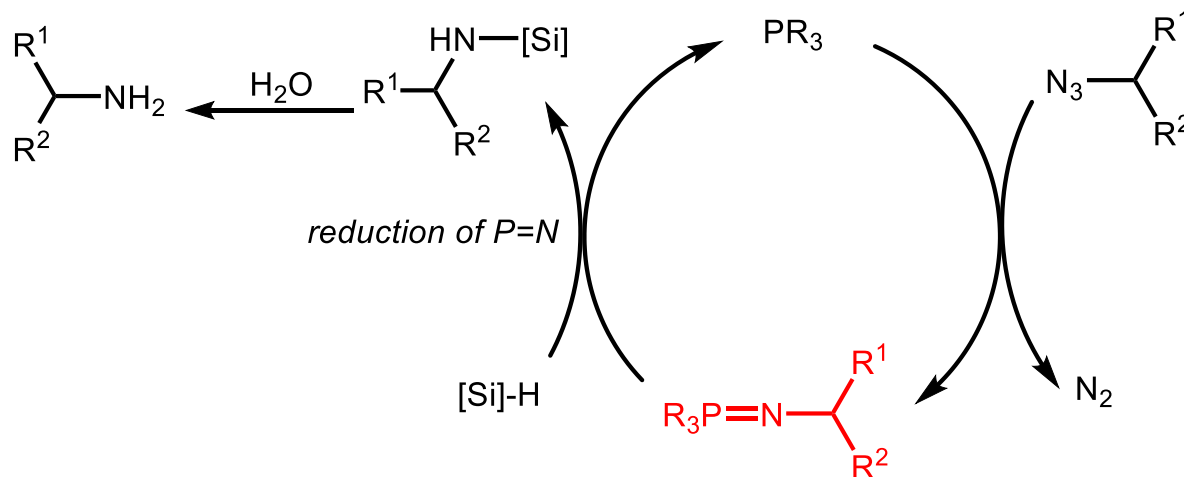
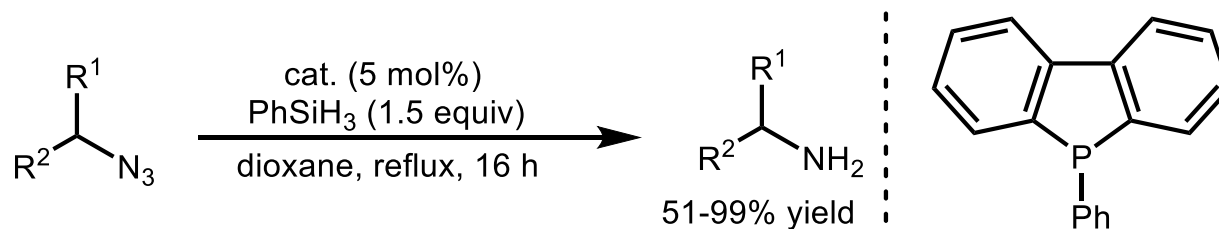
- C. J. O'Brien, G. A. Chass, et al. *Angew. Chem. Int. Ed.* **2009**, 48, 6836; for his further research, see: *Chem. Eur. J.* **2013**, 19, 5854; *Chem. Eur. J.* **2013**, 19, 15281; *ACIE* **2014**, 53, 12907
- T. Werner, et al. *Eur. J. Org. Chem.* **2014**, 6630

## 2.1 Wittig Reaction



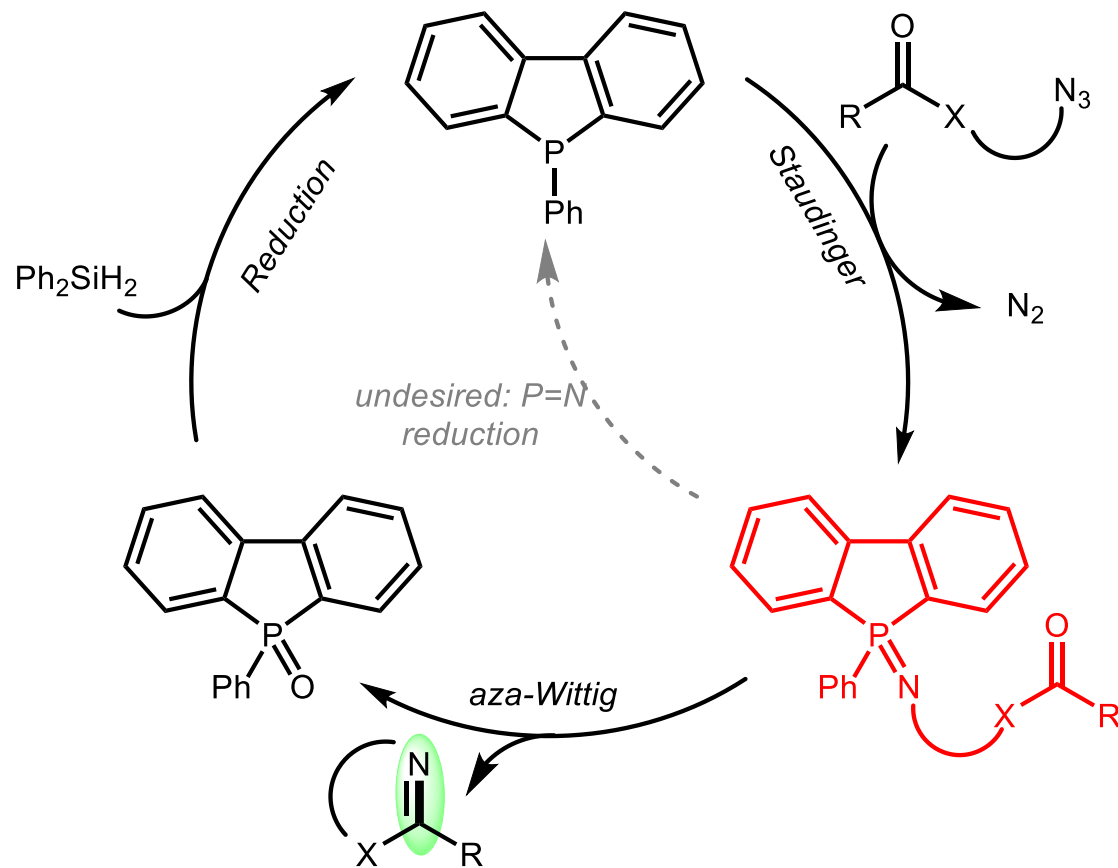
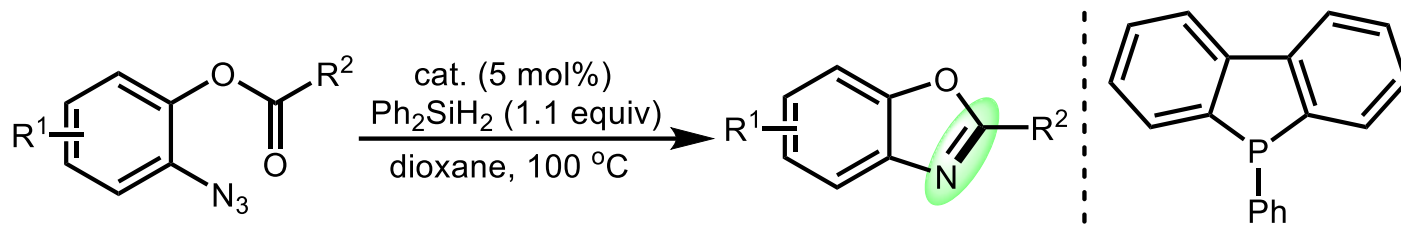
- T. Werner, et al. *Org. Lett.* **2015**, *17*, 3078
- Y.-L. Tsai, W. Lin, et al. *Asian J. Org. Chem.* **2015**, *4*, 1040

## 2.2 Staudinger Reaction

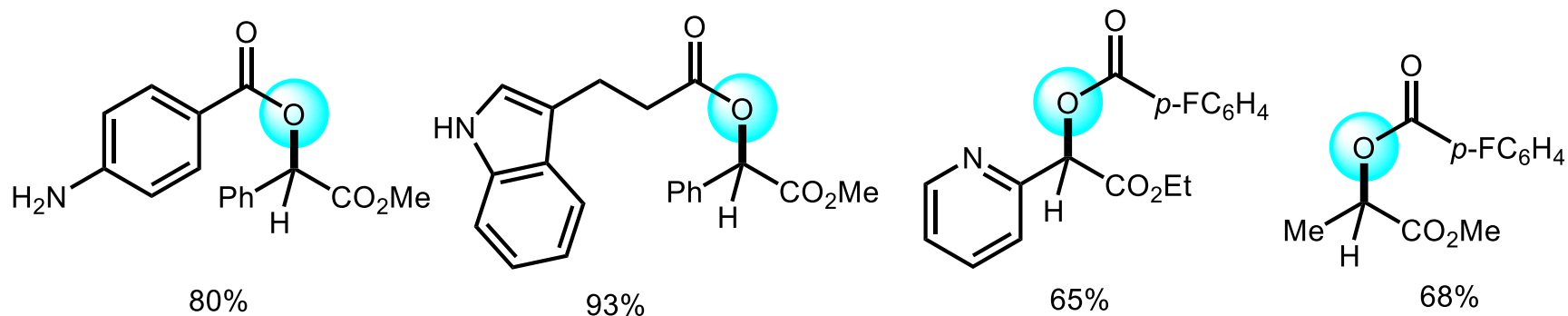
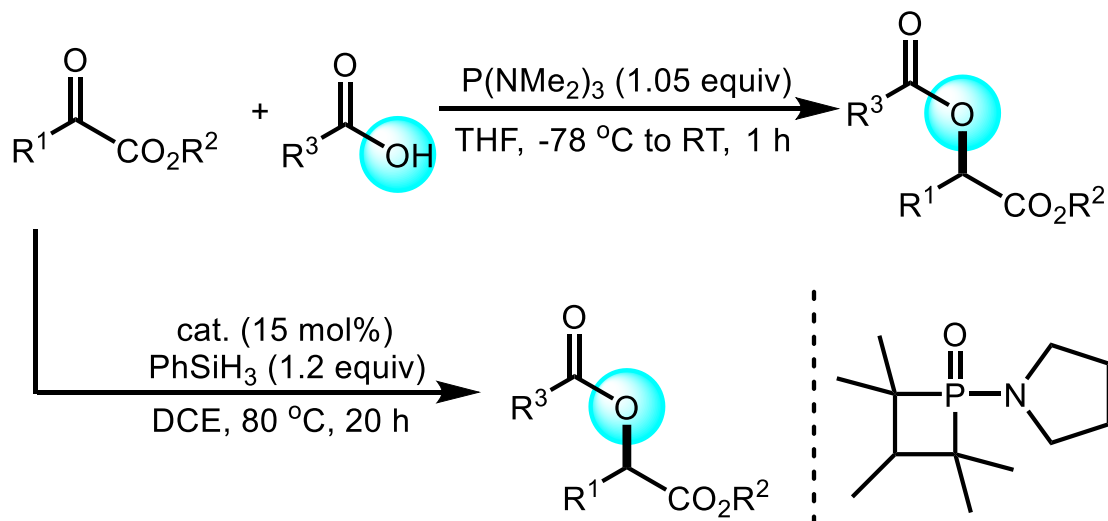


- F. L. van Delft, et al. *Adv. Synth. Catal.* **2012**, 354, 1417
- B. L. Ashfeld, et al. *Angew. Chem. Int. Ed.* **2012**, 51, 12036

## 2.3 Aza-Wittig Reaction

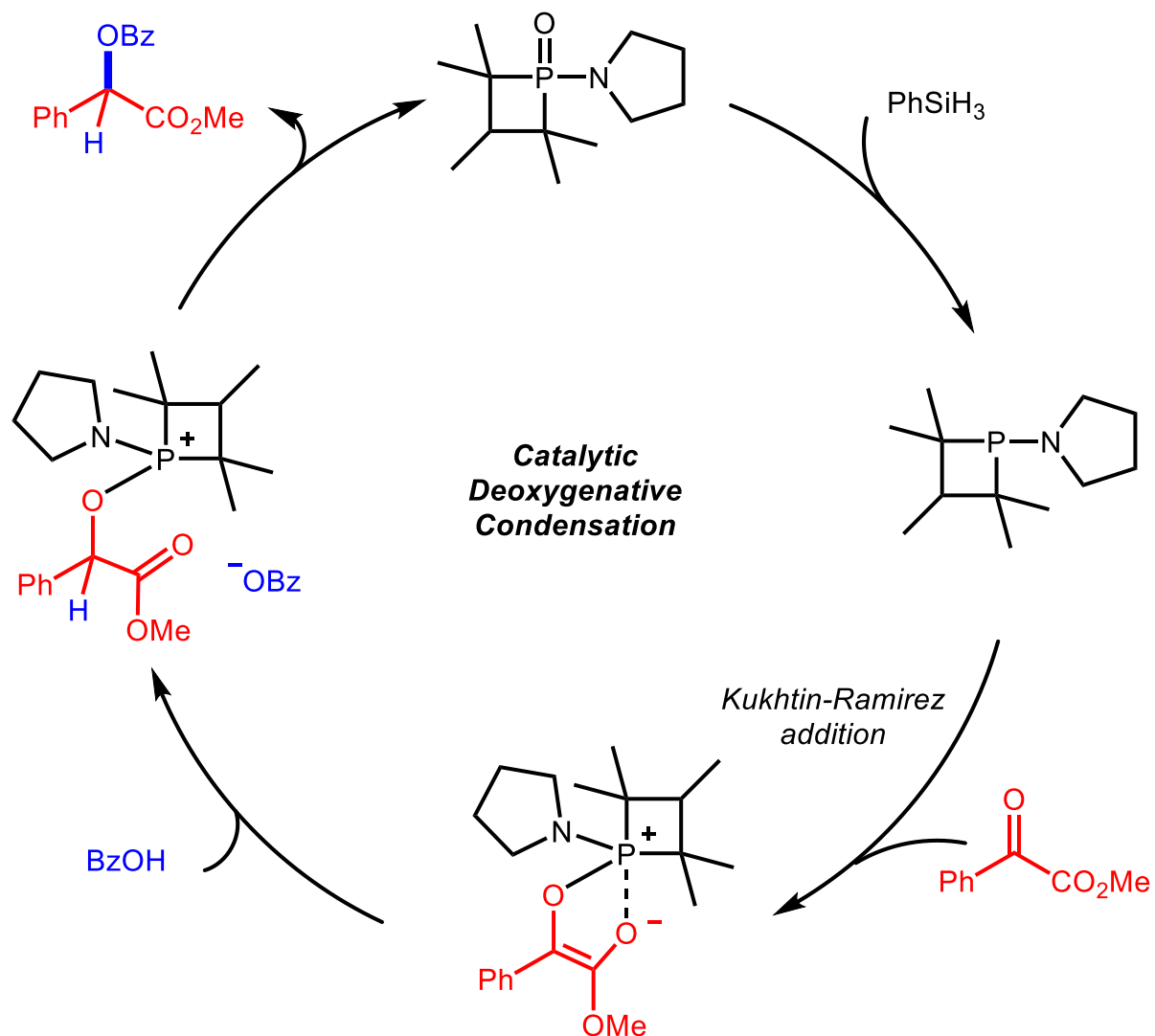


## 2.4 Recent Reports—Catalytic Deoxygenative Condensation



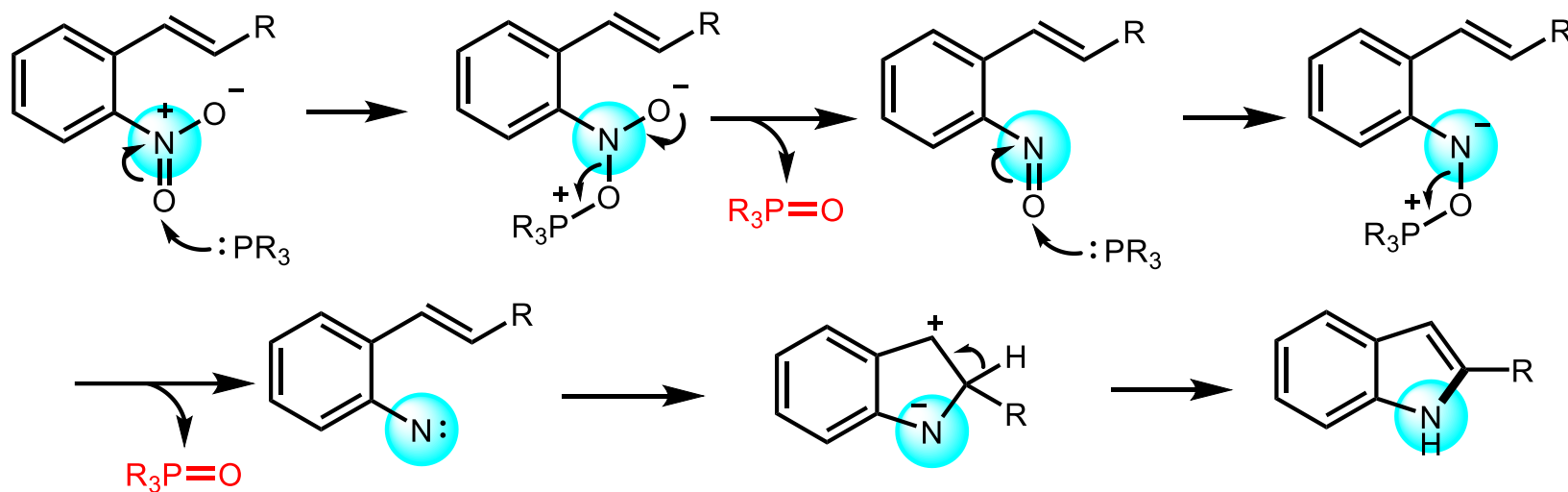
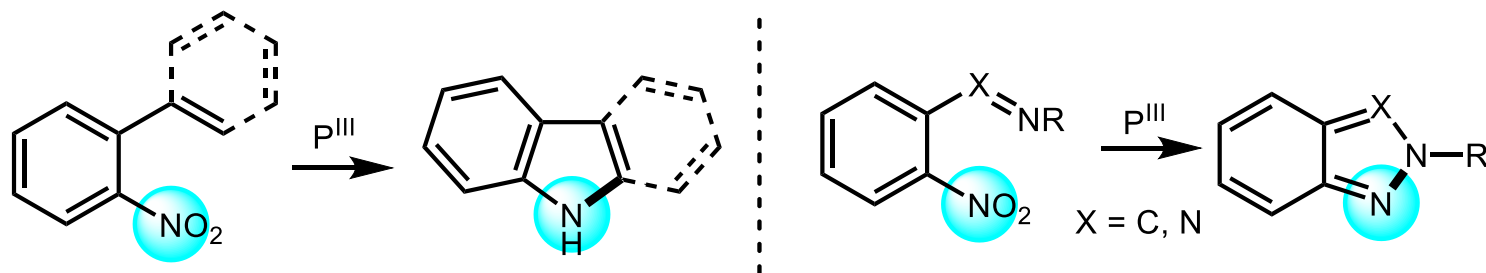
- A. T. Radosevich, et al. *Angew. Chem. Int. Ed.* **2012**, *51*, 10605
- A. T. Radosevich, et al. *J. Am. Chem. Soc.* **2015**, *137*, 616

## 2.4 Recent Reports—Catalytic Deoxygenative Condensation



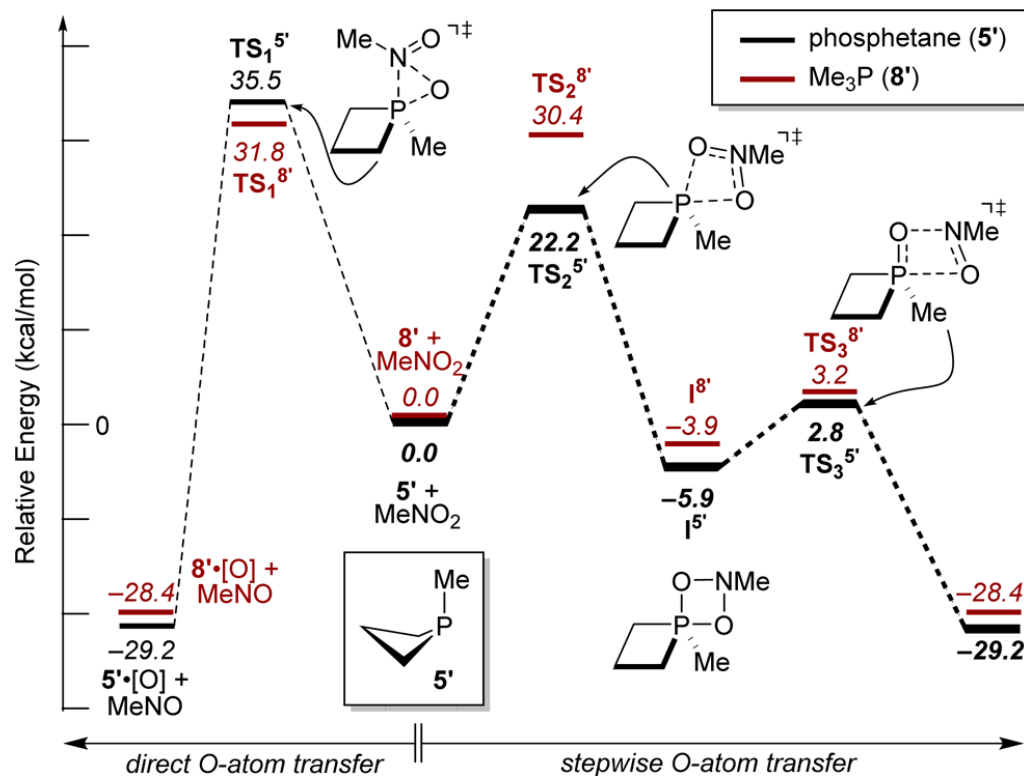
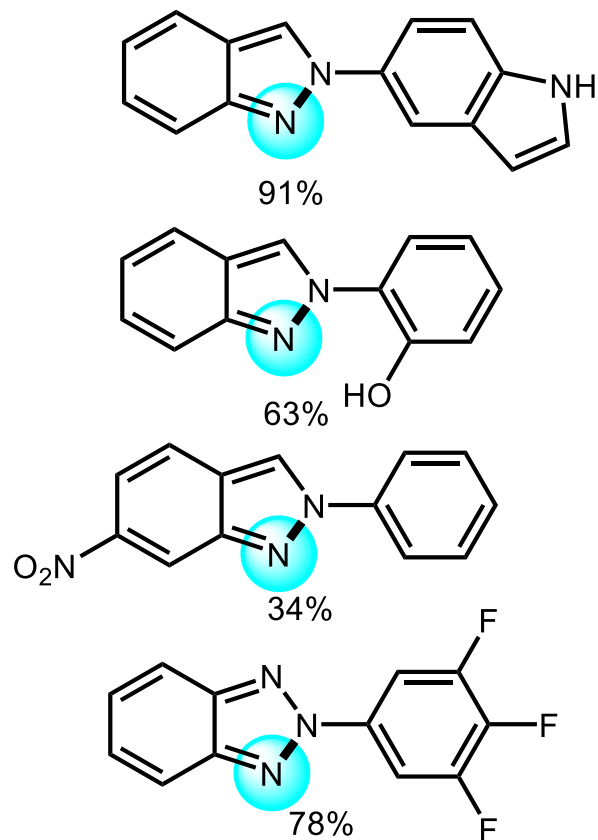
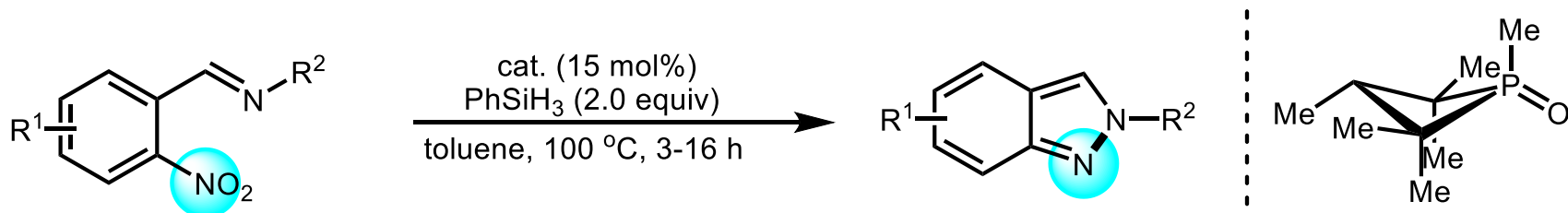
• A. T. Radosevich, et al. *J. Am. Chem. Soc.* **2015**, 137, 616

## 2.4 Recent Reports—Catalytic Cadogan Reaction



- For  $\text{P}^{\text{III}}$ -mediated Cadogan reaction, see: *J. Chem. Soc.* **1965**, 4831; *Synthesis* **1969**, 11; *J. Chem. Soc. C* **1969**, 2808; *Q. Rev. Chem. Soc.* **1968**, 22, 222

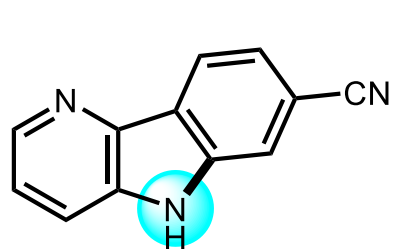
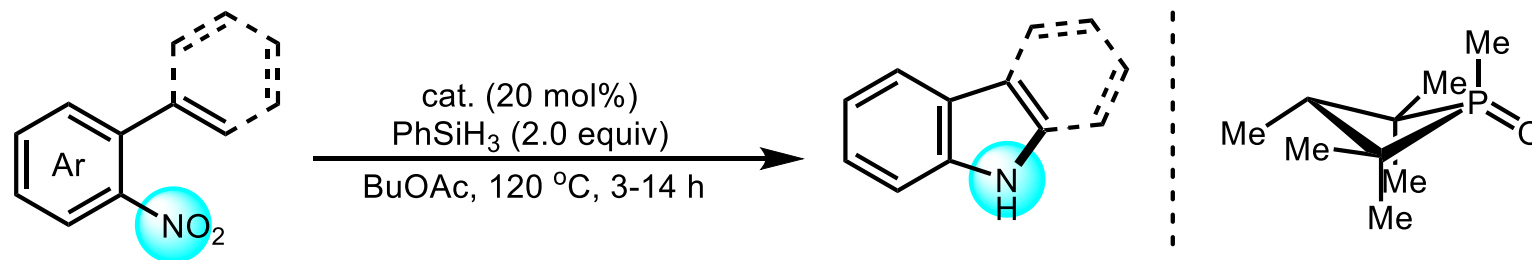
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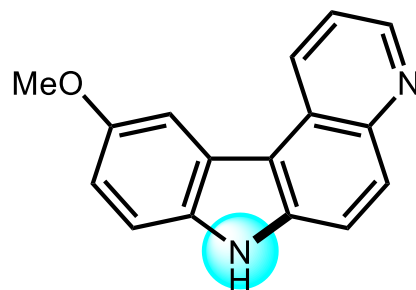
- A. T. Radosevich, et al. *J. Am. Chem. Soc.* **2017**, 139, 6839



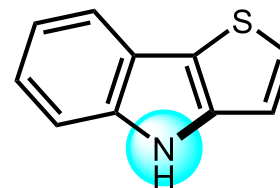
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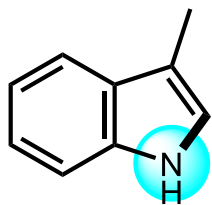
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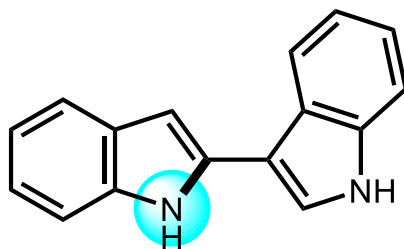
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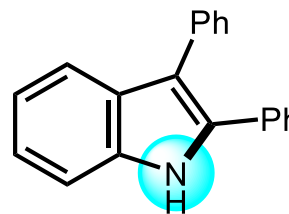
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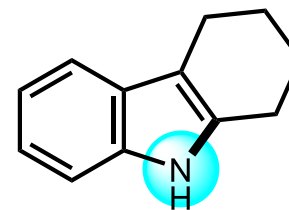
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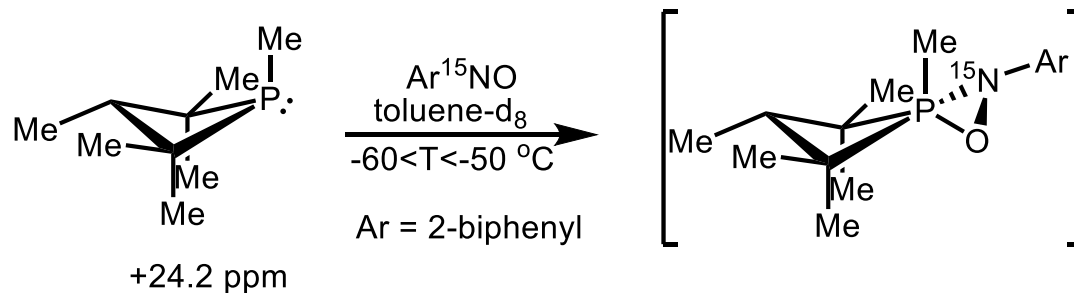
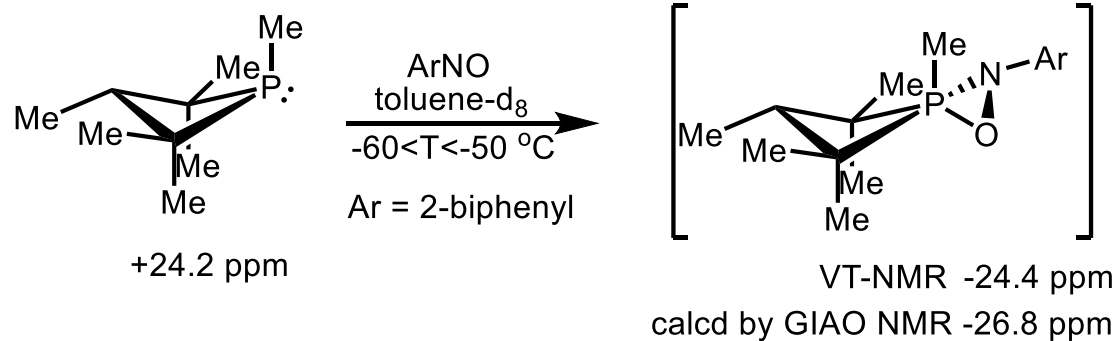
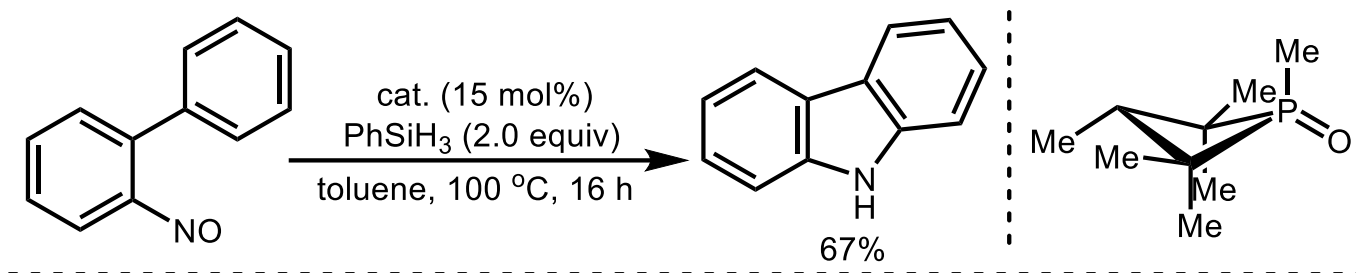
82%



86%

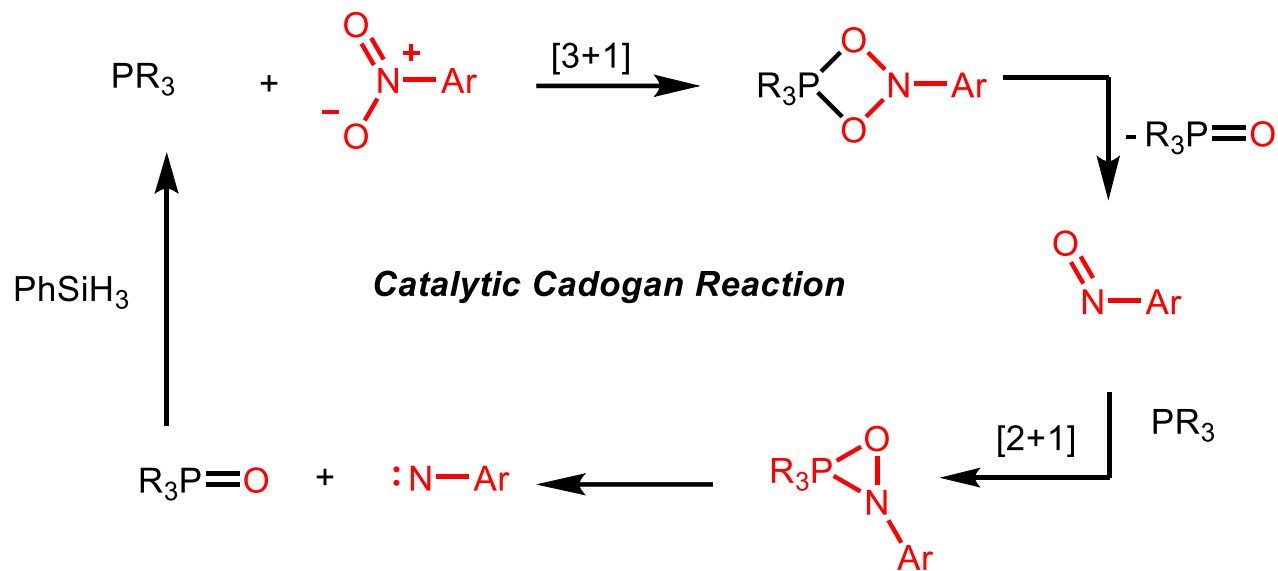
- A. T. Radosevich, et al. *J. Am. Chem. Soc.* **2018**, *140*, 3103

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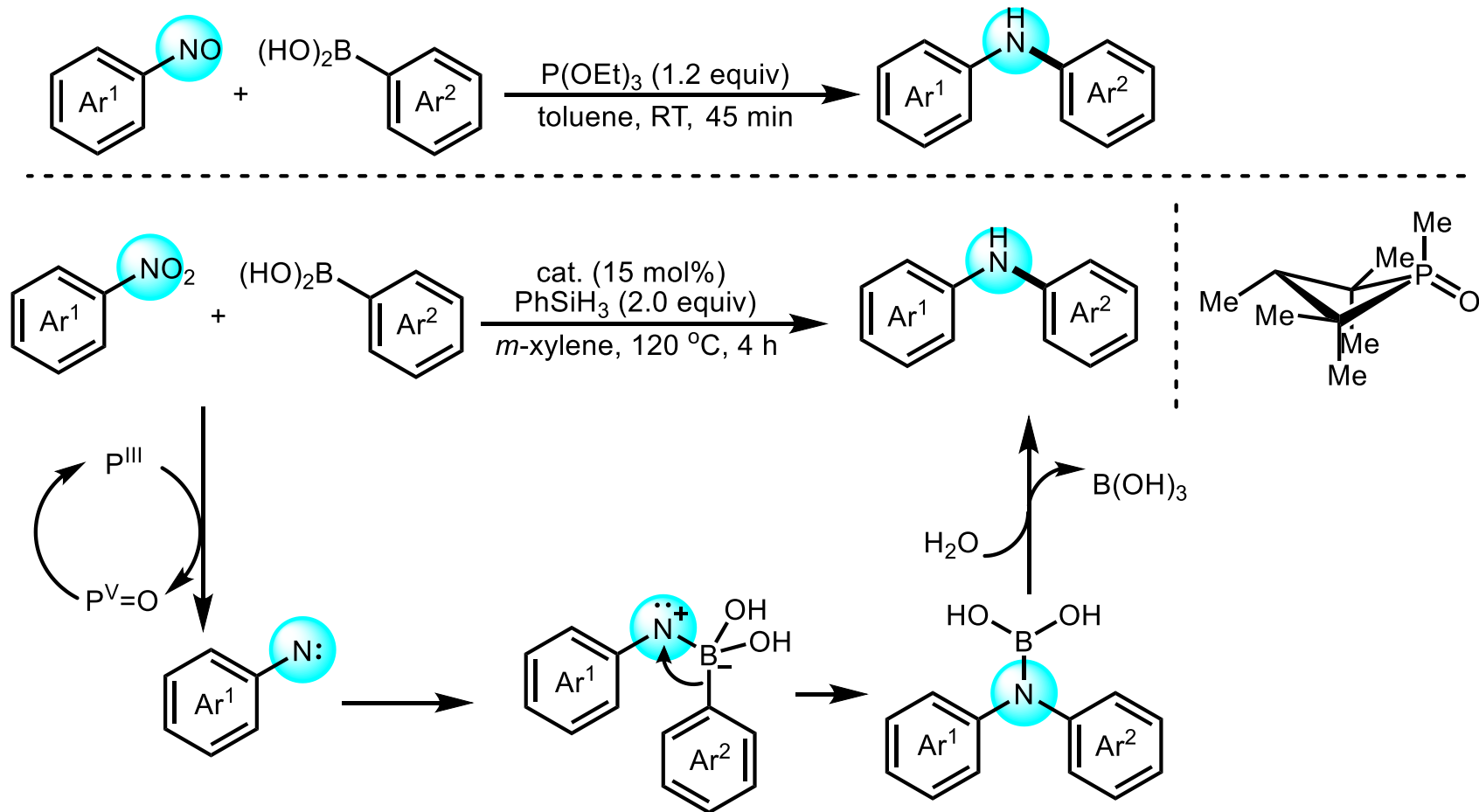
- A. T. Radosevich, et al. *J. Am. Chem. Soc.* **2018**, *140*, 3103

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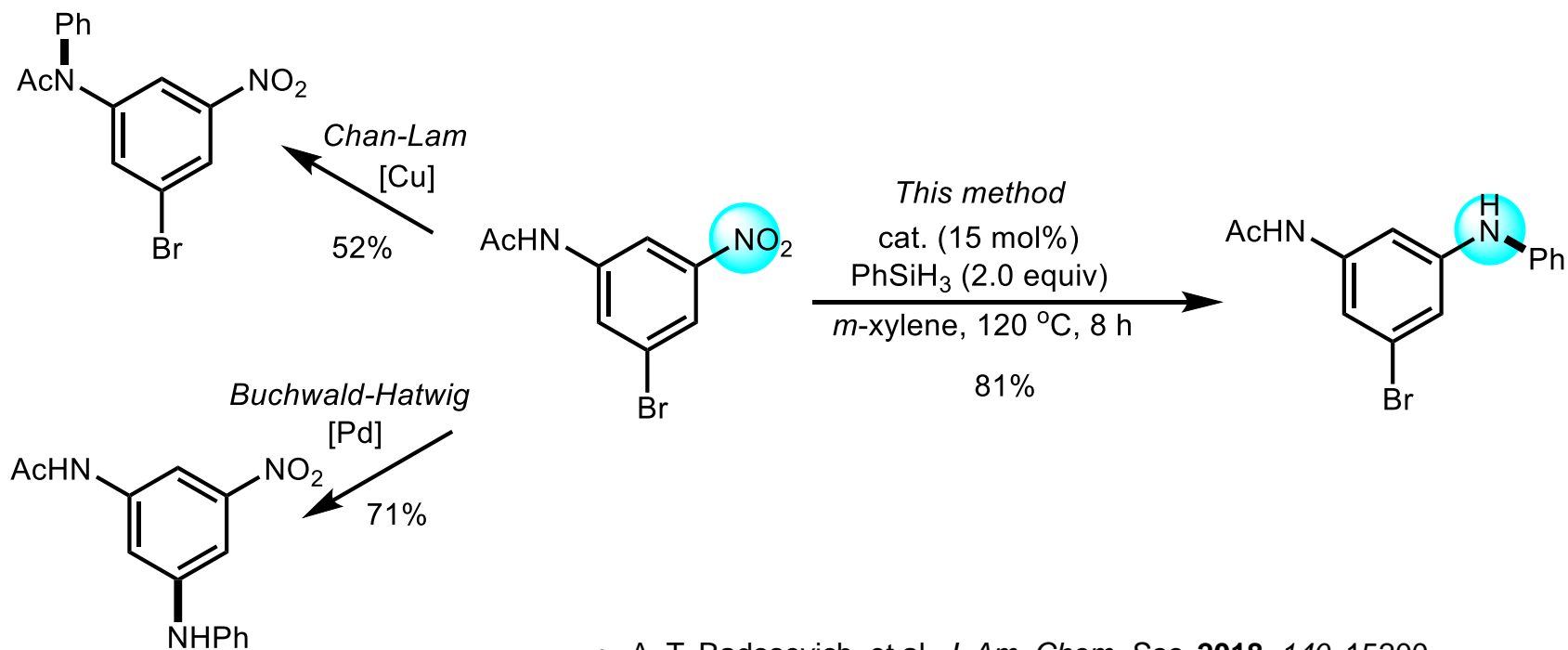
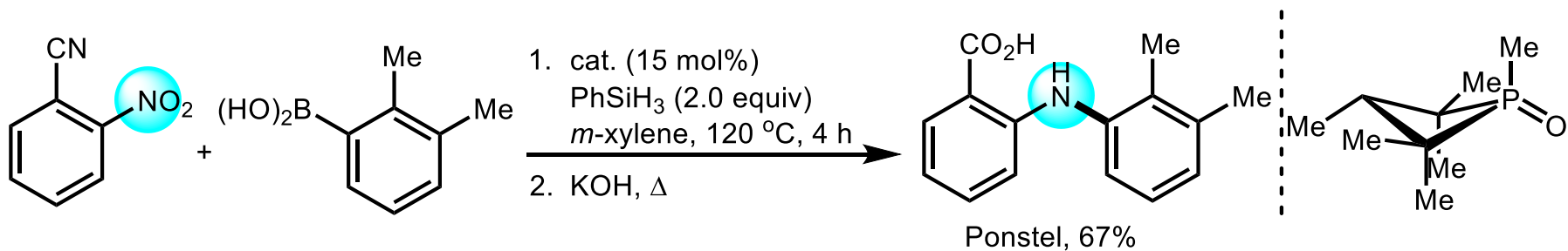
- A. T. Radosevich, et al. *J. Am. Chem. Soc.* **2017**, *139*, 6839
- A. T. Radosevich, et al. *J. Am. Chem. Soc.* **2018**, *140*, 3103

## 2.4 Recent Reports—Catalytic *N*-Arylation



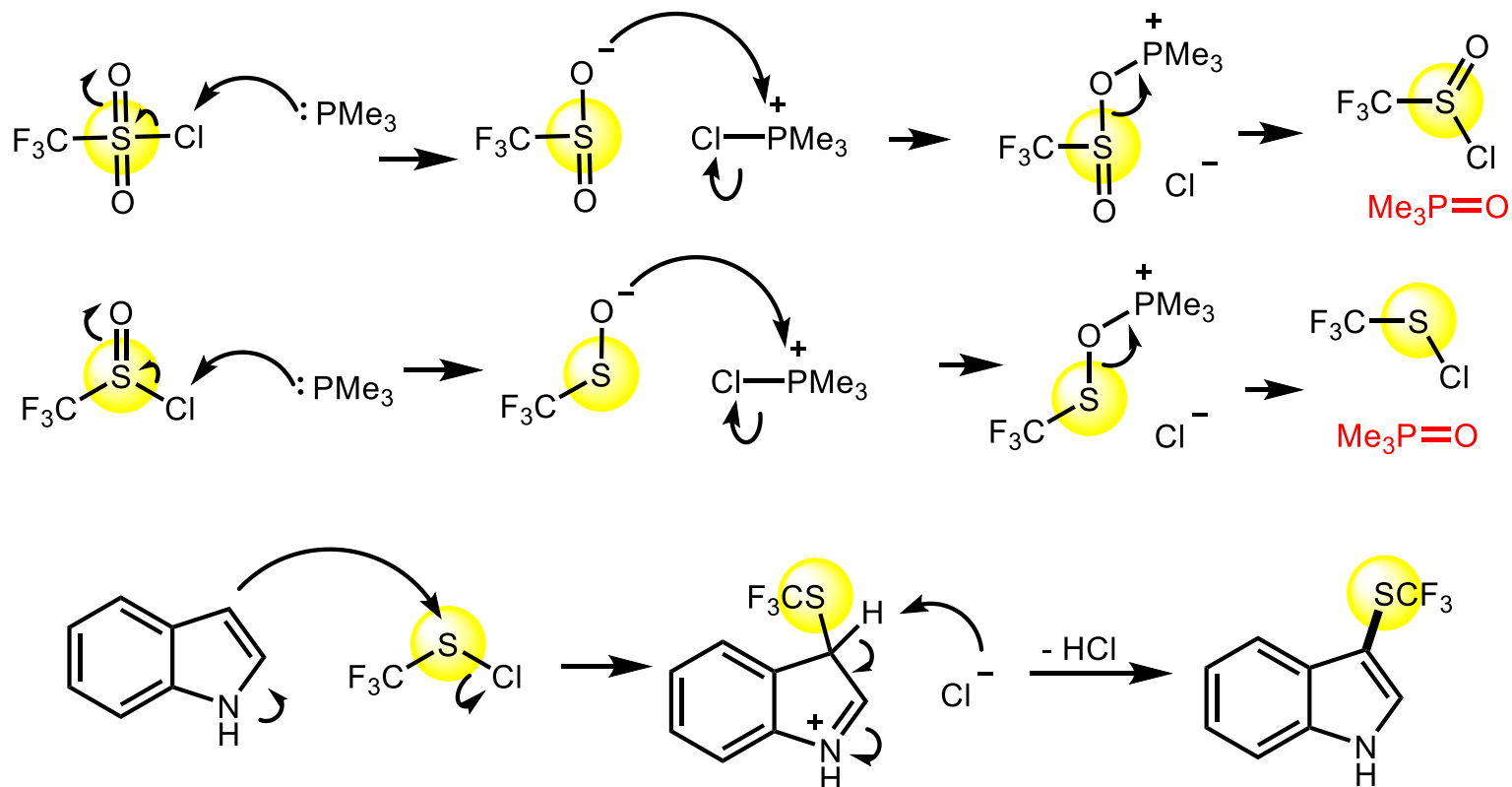
- A. G. Csáký, et al. *Org. Lett.* **2018**, *20*, 1667
- A. T. Radosevich, et al. *J. Am. Chem. Soc.* **2018**, *140*, 15200

## 2.4 Recent Reports—Catalytic *N*-Arylation



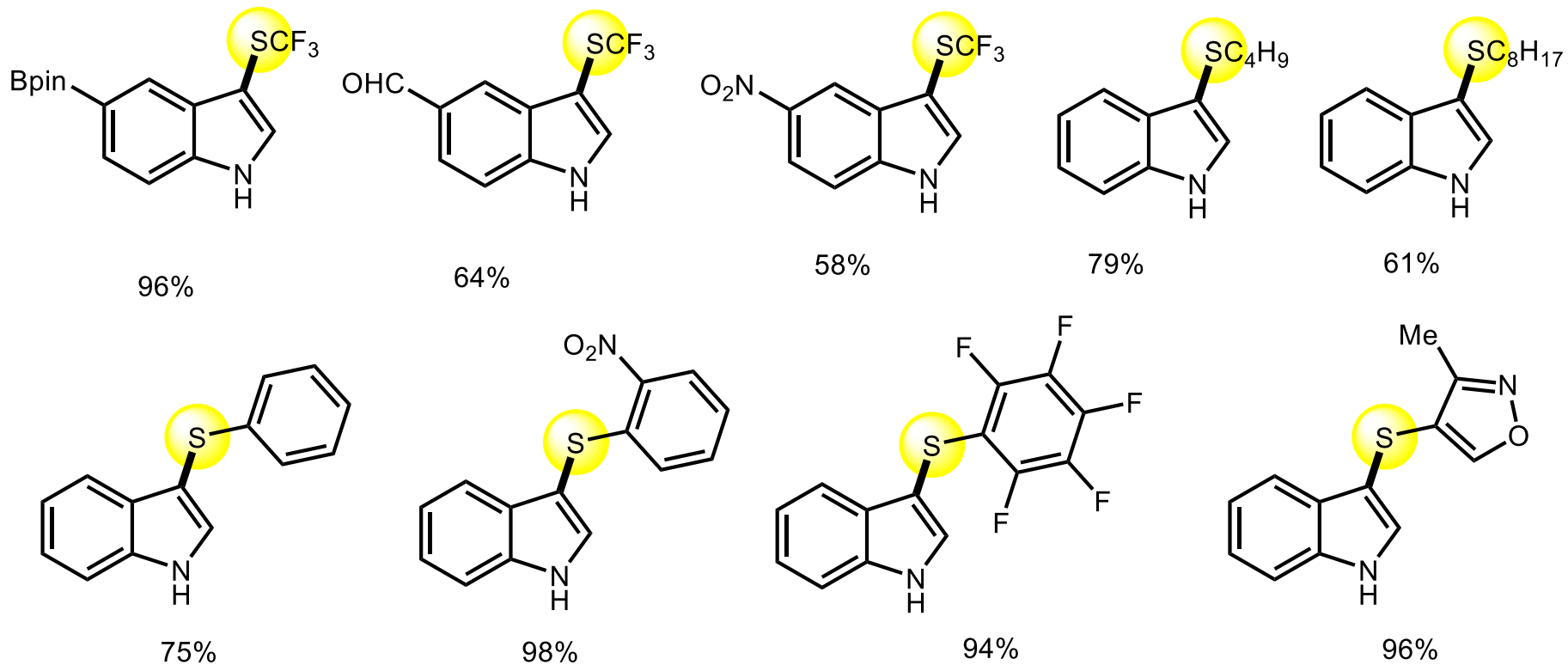
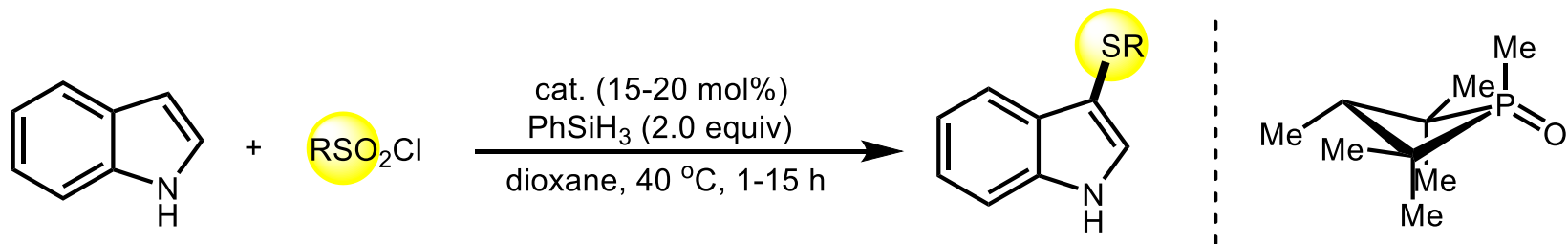
• A. T. Radosevich, et al. *J. Am. Chem. Soc.* **2018**, *140*, 15200

## 2.4 Recent Reports—Catalytic Thiolation



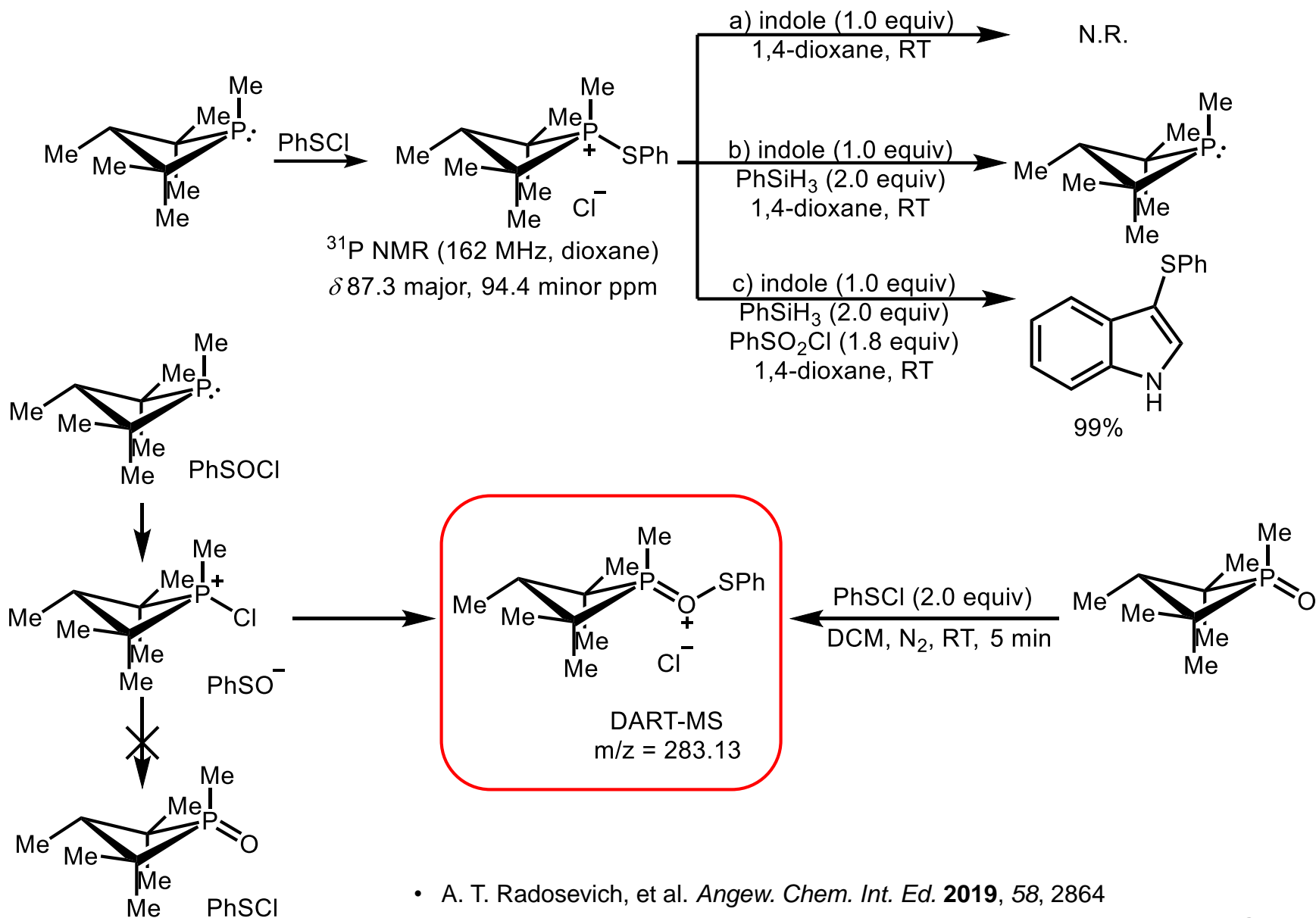
- N. Shibata, D. Cahard, et al. *Org. Lett.* **2016**, *18*, 2467

## 2.4 Recent Reports—Catalytic Thiolation



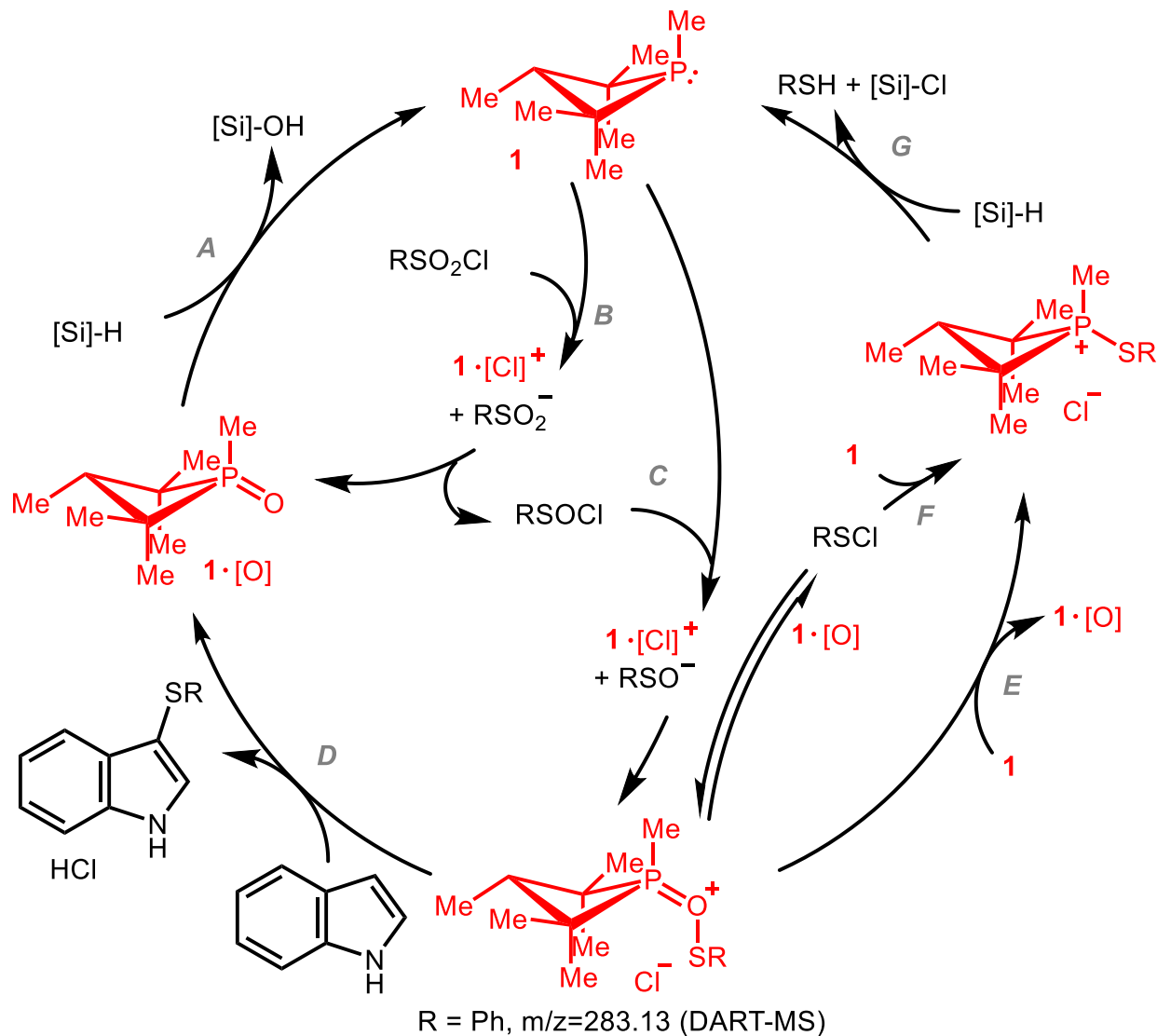
• A. T. Radosevich, et al. *Angew. Chem. Int. Ed.* **2019**, *58*, 2864

## 2.4 Recent Reports—Catalytic Thiolation





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- A. T. Radosevich, et al. *Angew. Chem. Int. Ed.* **2019**, *58*, 2864

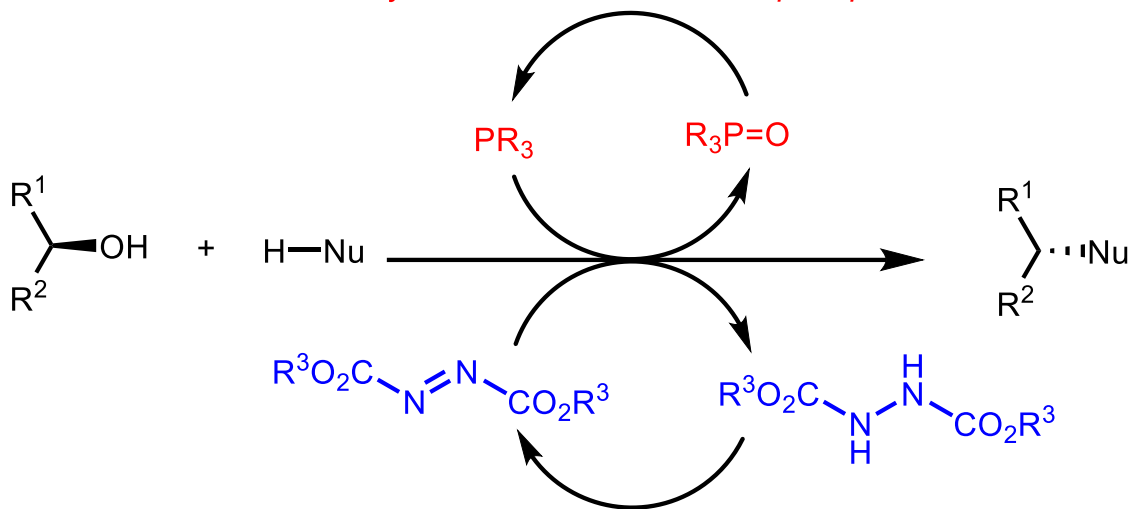
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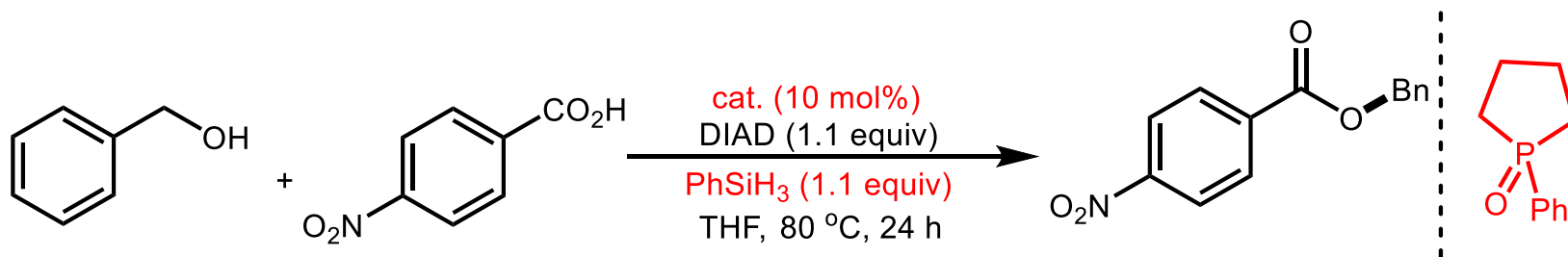
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# 3.1 Catalytic Mitsunobu Reaction

*catalytic Mitsunobu reaction in phosphine*

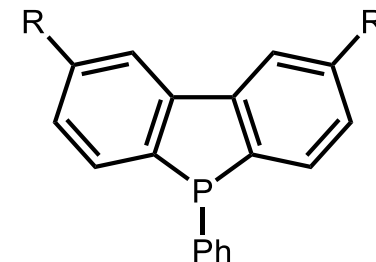
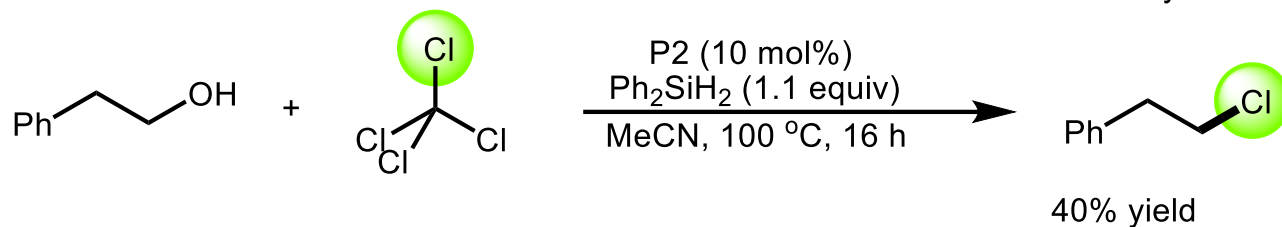
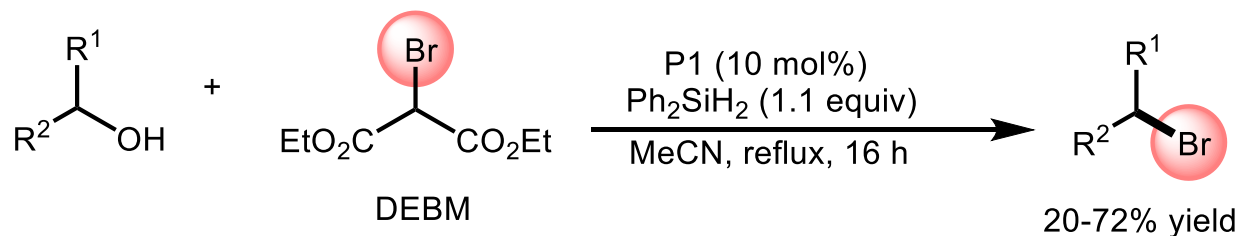


*catalytic Mitsunobu reaction in azodicarboxylate*

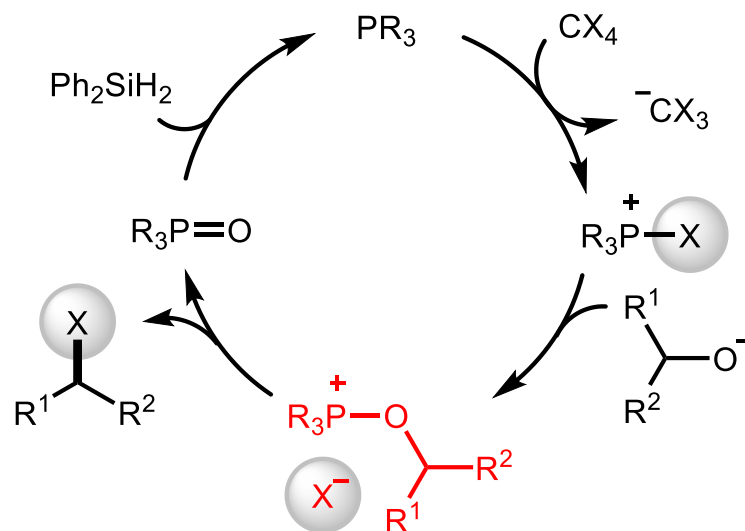


- C. C. Aldrich, et al. *Angew. Chem. Int. Ed.* **2015**, 54, 13041
- Azo-catalyzed: *JACS.* **2006**, 128, 9636; *Synlett* **2010**, 1115; *ACIE.* **2013**, 52, 4613; *Chem. Sci.* **2016**, 7, 5148

## 3.2 Catalytic Appel Reaction

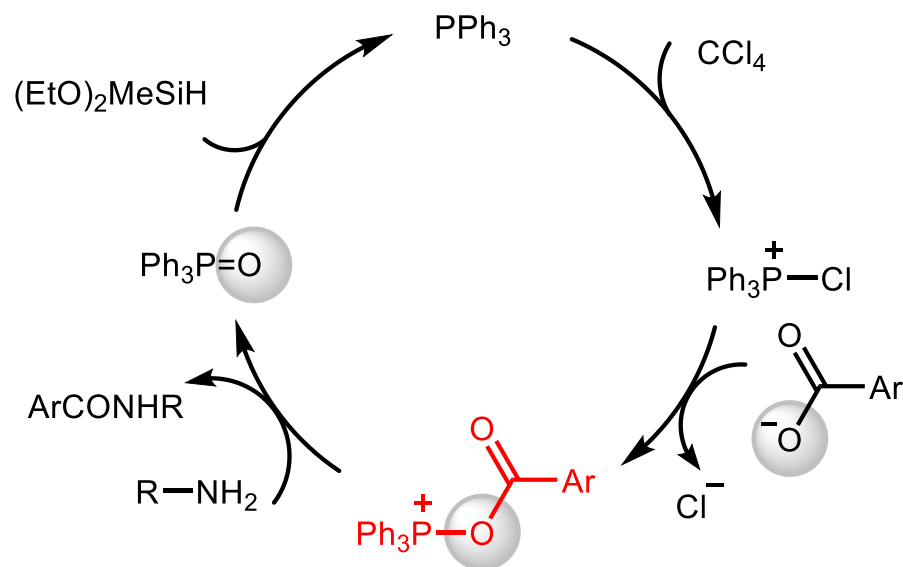
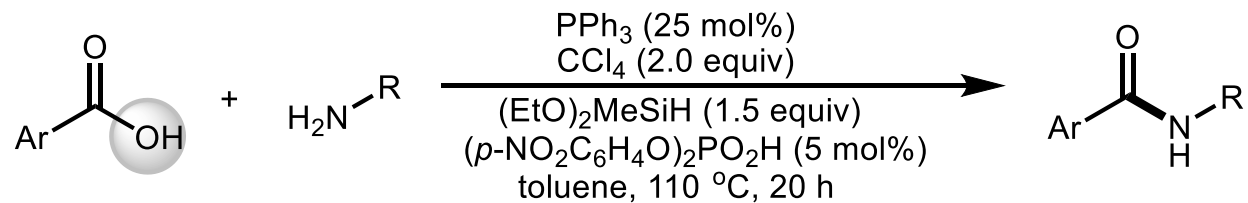


P1: R = H  
P2: R = OMe

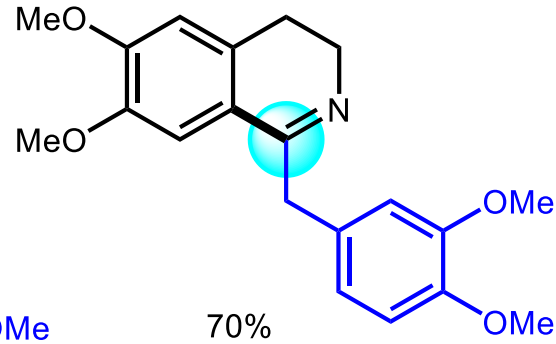
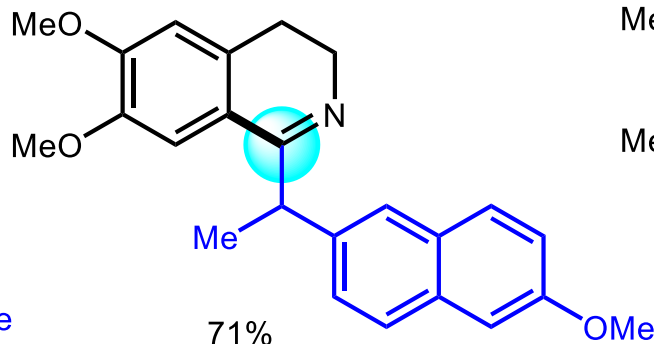
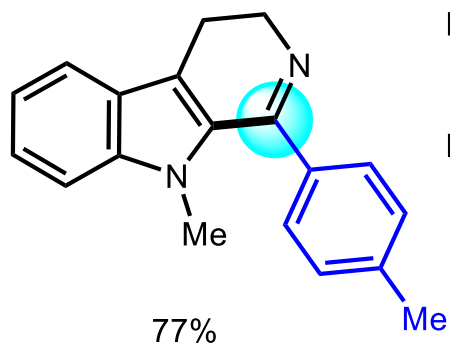
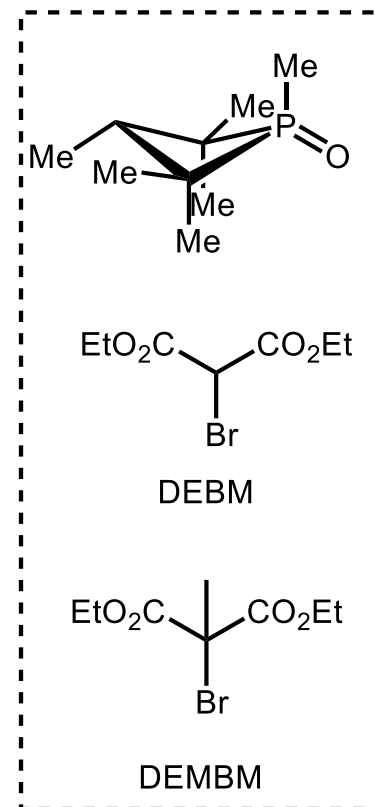
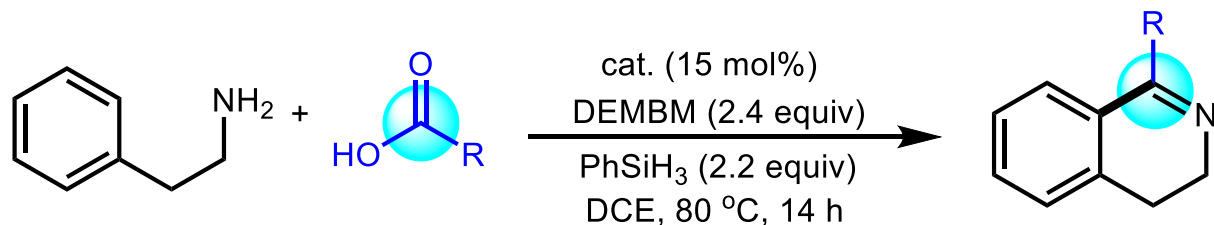
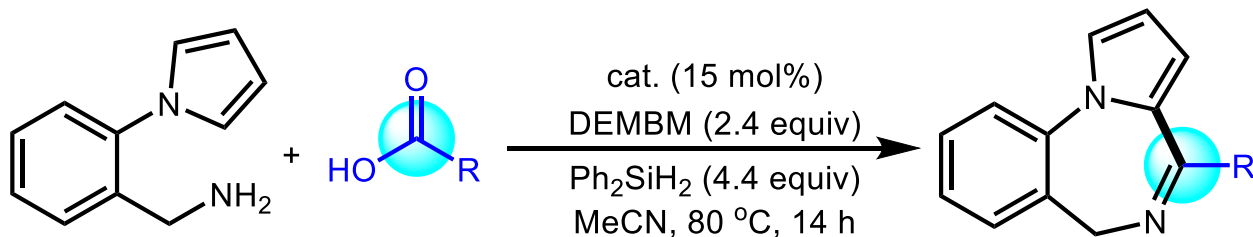
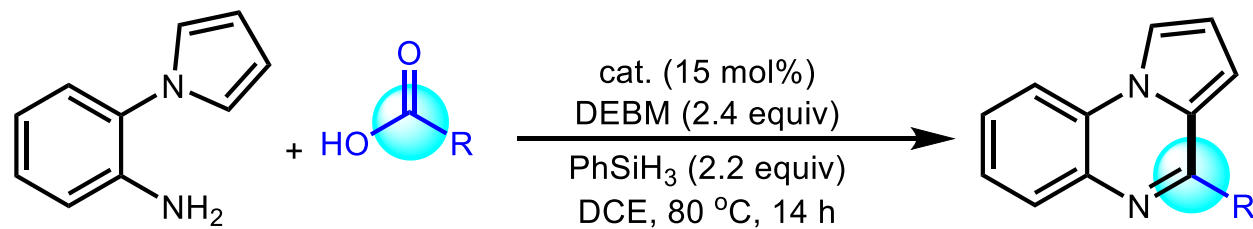


- F. L. van Delft, et al. *Chem. - Eur. J.* **2011**, 17, 11290
- F. L. van Delft; F. P. J. T. Rutjes, et al. *Pure Appl. Chem.* **2013**, 85, 817

### 3.3 Recent Reports—Amidation

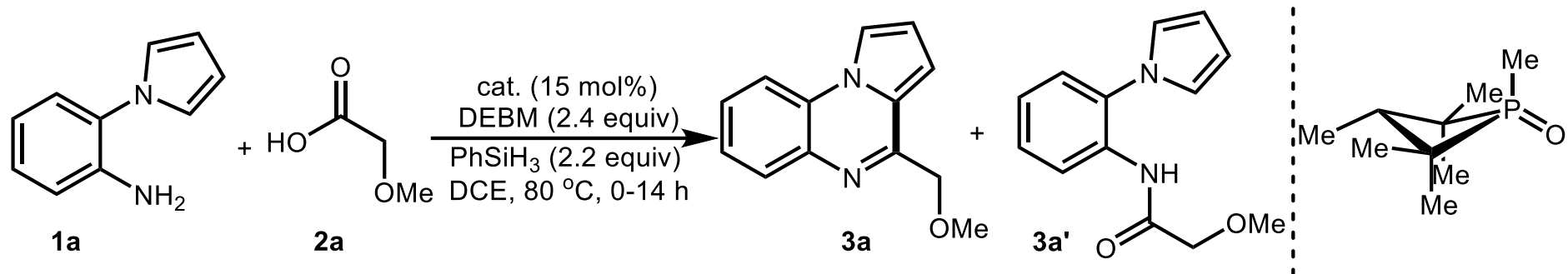


### 3.3 Recent Reports—Amidation

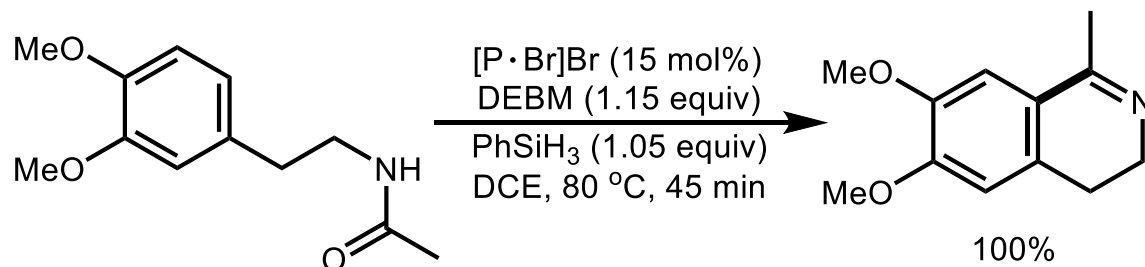
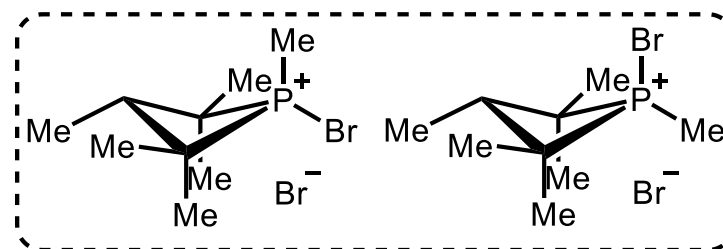
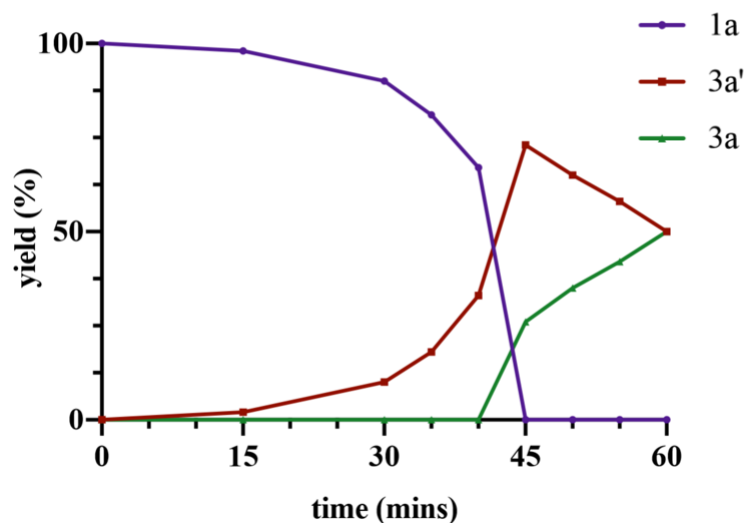


• A. T. Radosevich, et al. *J. Am. Chem. Soc.* **2019**, *141*, 12507

### 3.3 Recent Reports—Amidation

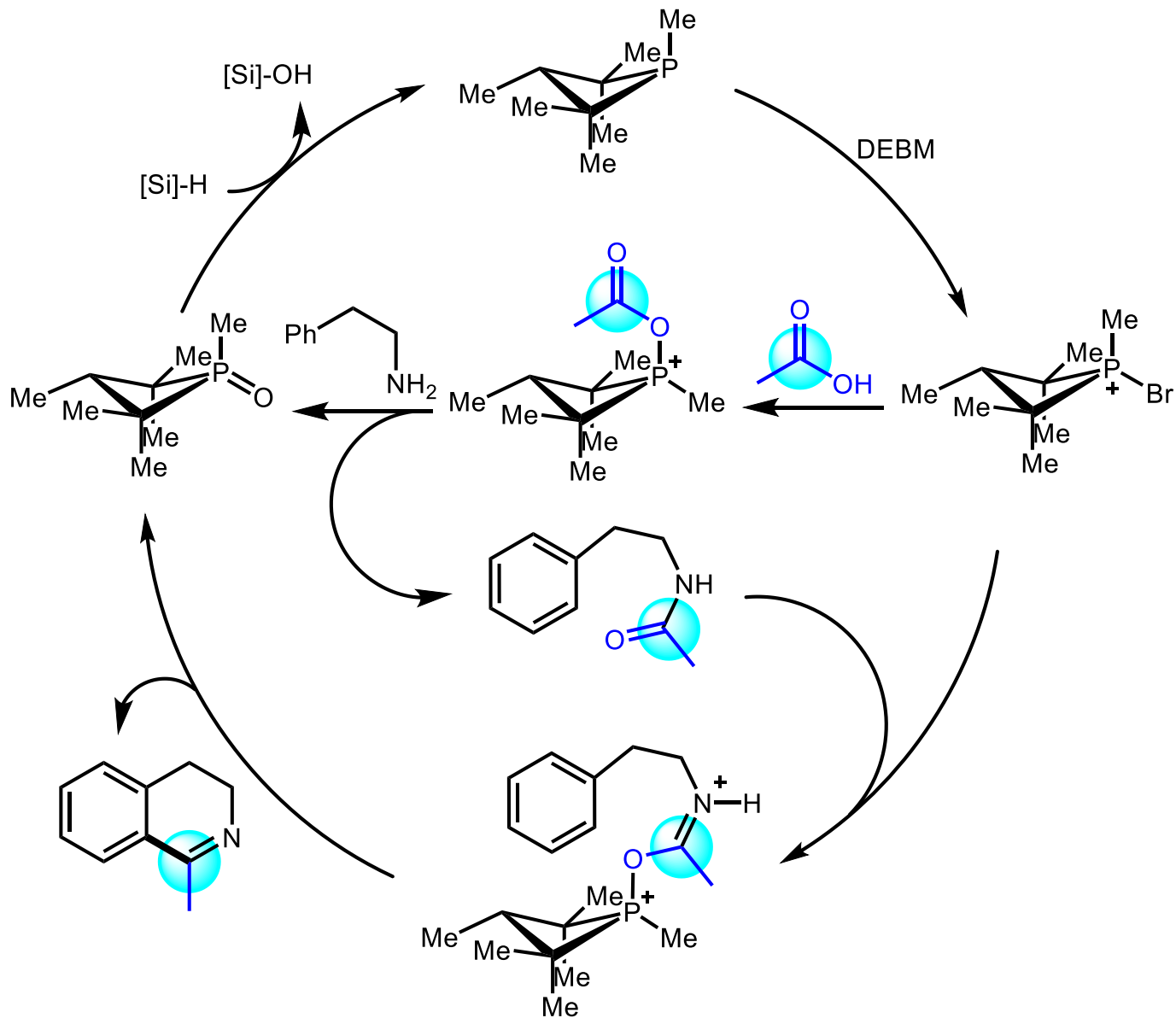


Reaction of **1a** and **2a** (0-60 min)



- A. T. Radosevich, et al. *J. Am. Chem. Soc.* **2019**, *141*, 12507

### 3.3 Recent Reports—Amidation



- A. T. Radosevich, et al. *J. Am. Chem. Soc.* **2019**, *141*, 12507

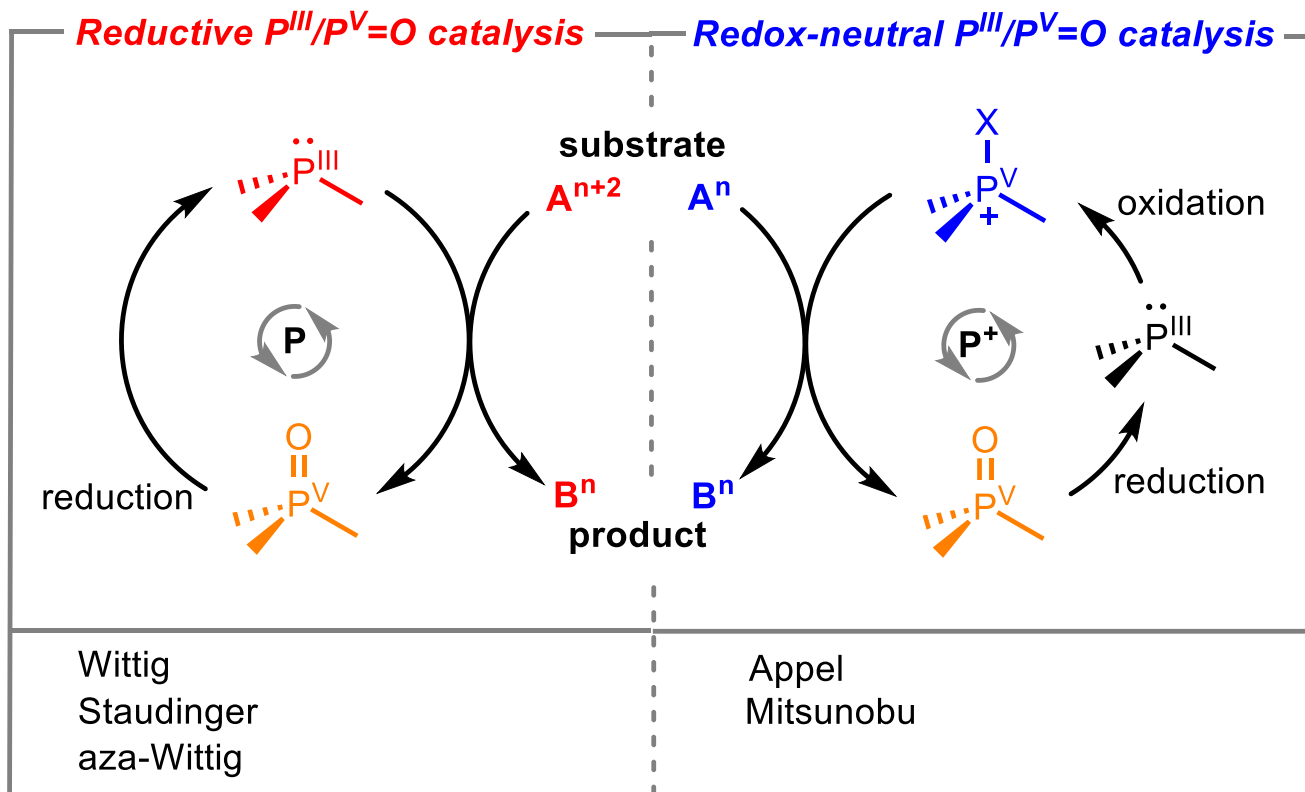


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# 4. Summary and Prospection



## Radosevich Group

**JACS 2015:** Deoxygenative Condensation

**JACS 2017:** Cadogan Reaction

**JACS 2018:** Cadogan Reaction

**JACS 2018:** N-Arylation

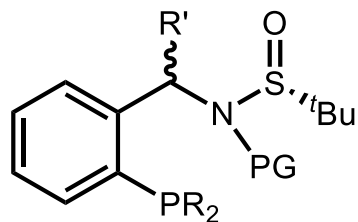
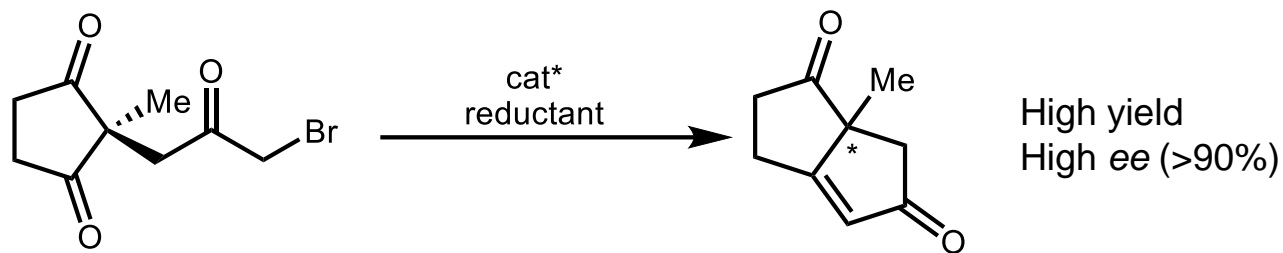
**ACIE 2019:** Thiolation

**JACS 2019:** Amidation/Annulation

## Mecinović Group

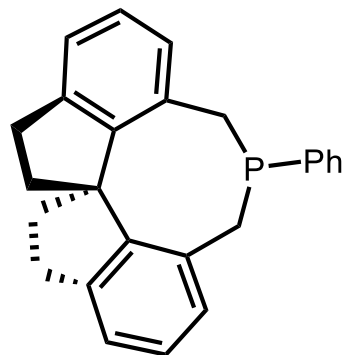
**CC 2014:** Amidation

## 4. Summary and Prospection

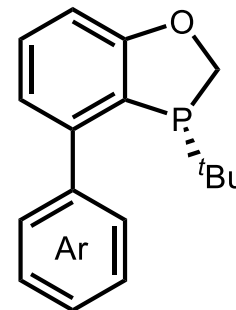


R = Ph, Ming-Phos  
R = Cy, Xu-Phos  
R = Ad, Xiang-Phos

**Zhang's Sadphos**



**Zhou's**



**Tang's**

***THANKS FOR YOUR ATTENTION***