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CRITICAL REVIEW

Recent advances in transition-metal catalyzed reactions using molecular oxygen as the oxidant

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The author

Ning Jiao

Ning Jiao received his PhD degree (2004) (with Prof. Shengming Ma) at Shanghai Institute of Organic Chemistry (SIOC), CAS. He spent 2004–2006 as an Alexander von Humboldt postdoctoral fellow with Prof. Manfred T. Reetz at Max Planck Institute für Kohlenforschung. In 2007, he joined the faculty at Peking University as an Associate Professor, and was promoted to Full Professor in 2010. His current research efforts are focused on: (1) To develop green and efficient synthetic methodologies through Single Electron Transfer (SET) processes, aerobic oxidation, and the activation of inert chemical bonds; (2) Directed evolution of enzymes and protein hybrid catalysts.

Contents

1,Introduction

- (1) Oxidation is a fundamentally important component of organic synthesis.
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- (2) 3 fundamental chanllenges:
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- the cocatalyst
- the chemselectivity

- (3) Great development in 5 years
- C-H functionalization,
- oxidative Heck reactions,
- oxidative dehydrogenative coulpling,
- Free radical reactions

2,Dehydrogenative oxidation
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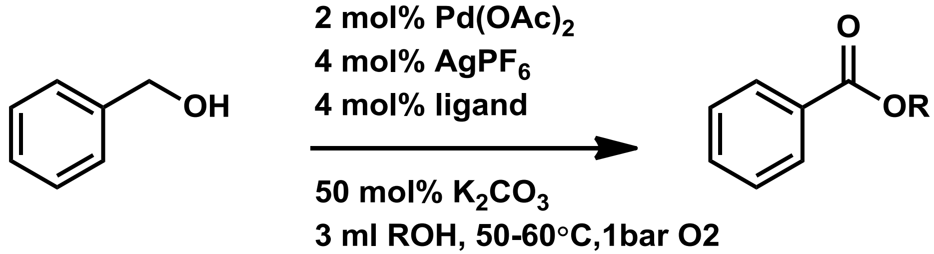

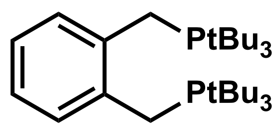

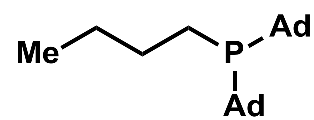

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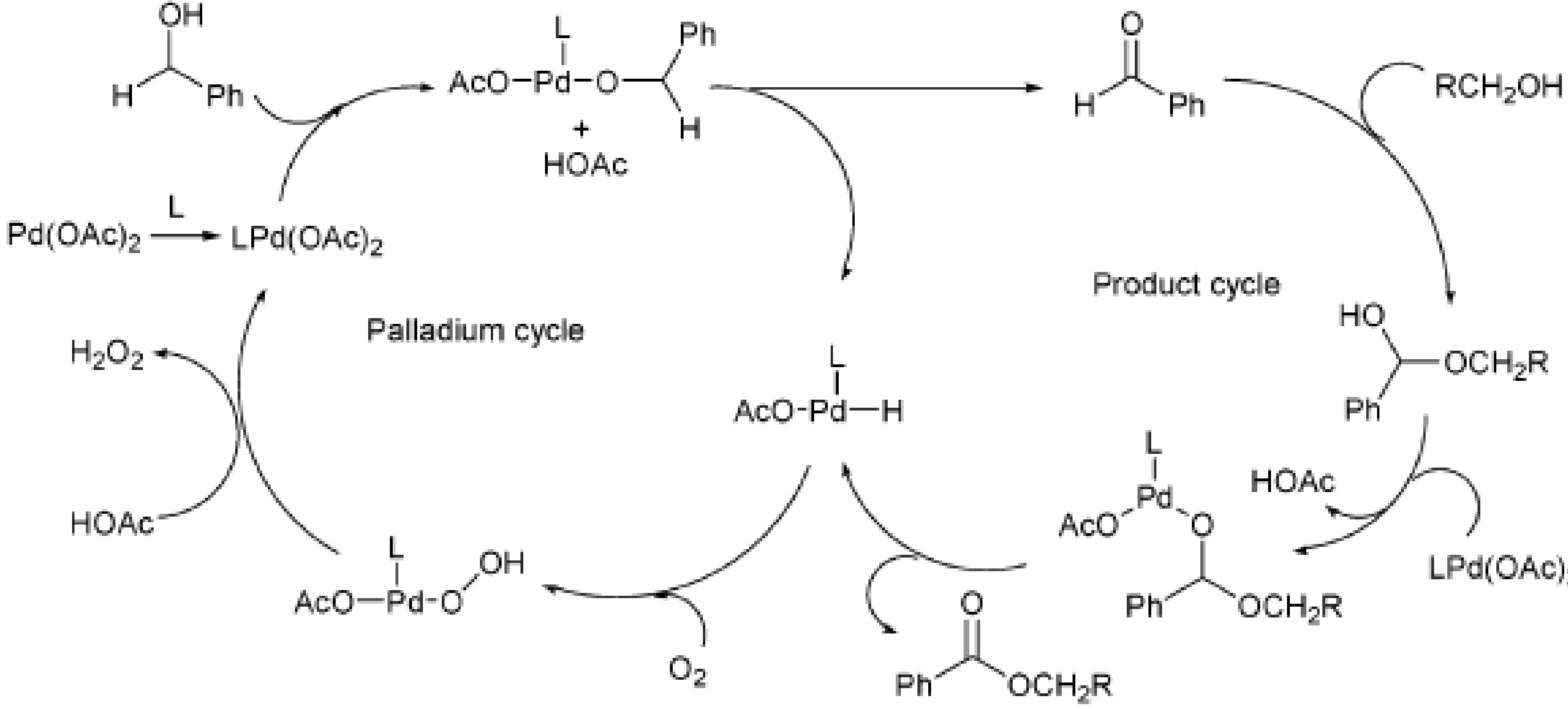
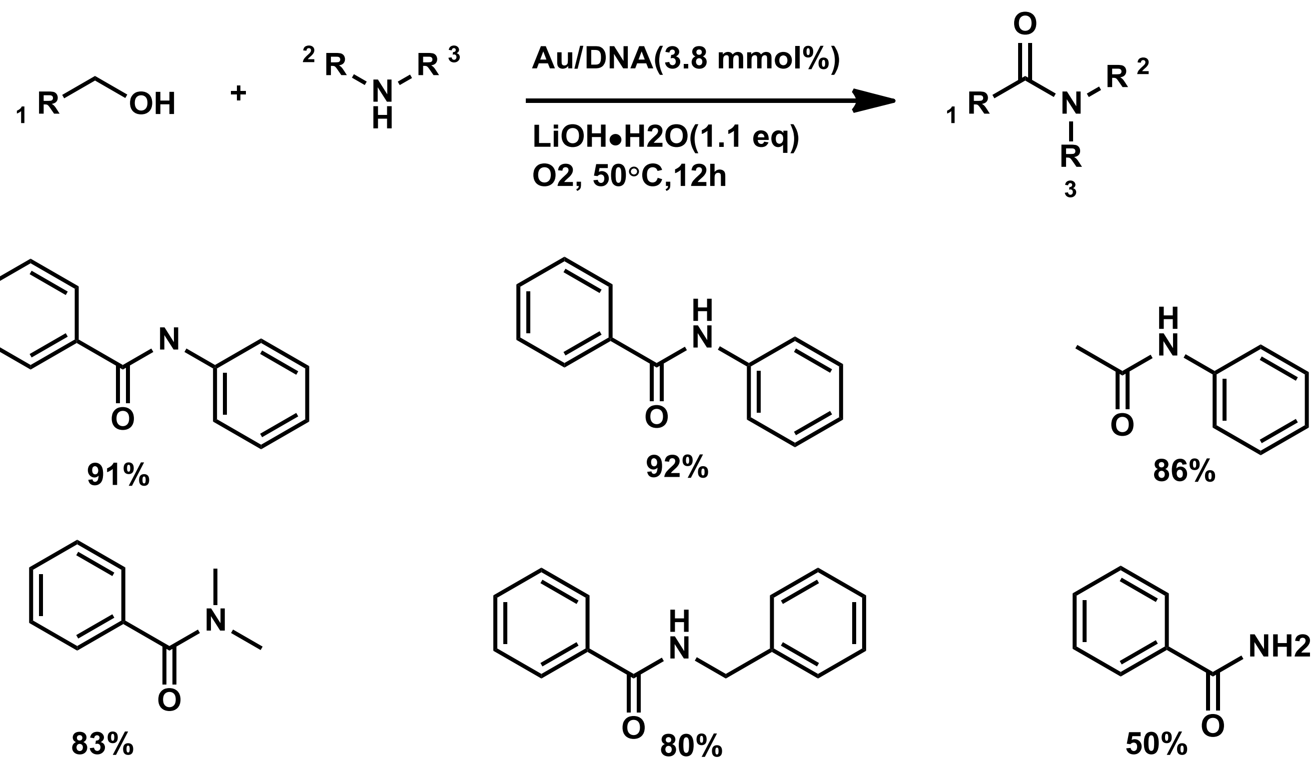
M.Zhang*, et, al. Thetrahedron. Lett***.** **2011**, *52*, 80

The mechanism proposed of oxidative esterification



Oxidative amidation of different alcohols with amines



Y. Wang, *et. al. Angew. Chem. Int* **. 2011**, *50*, 8917

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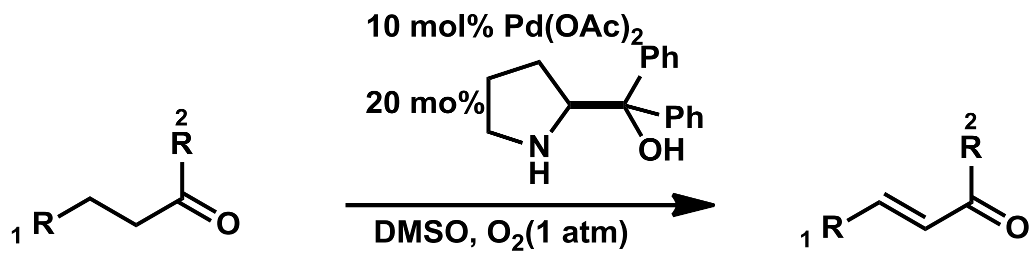
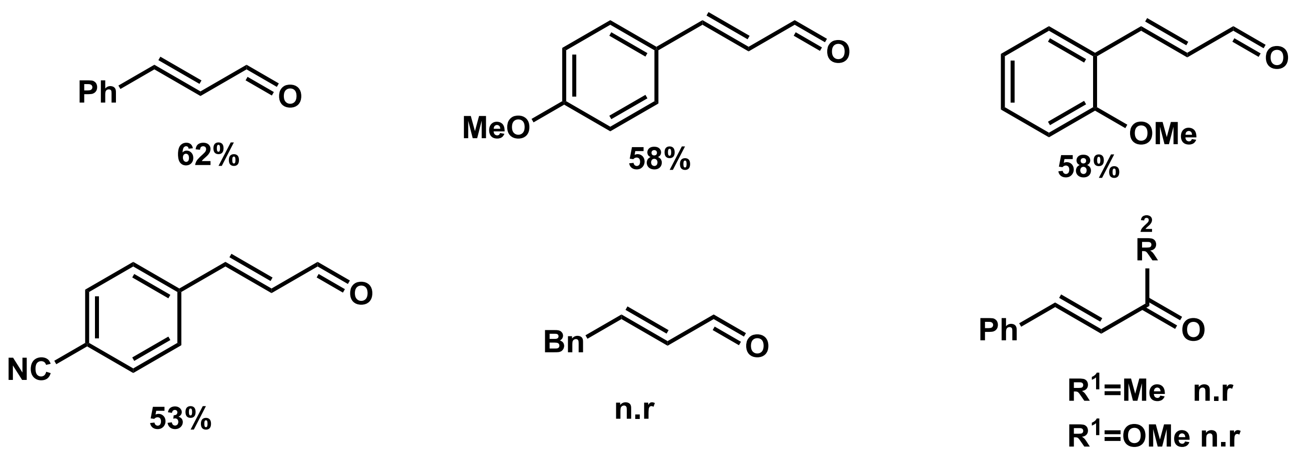
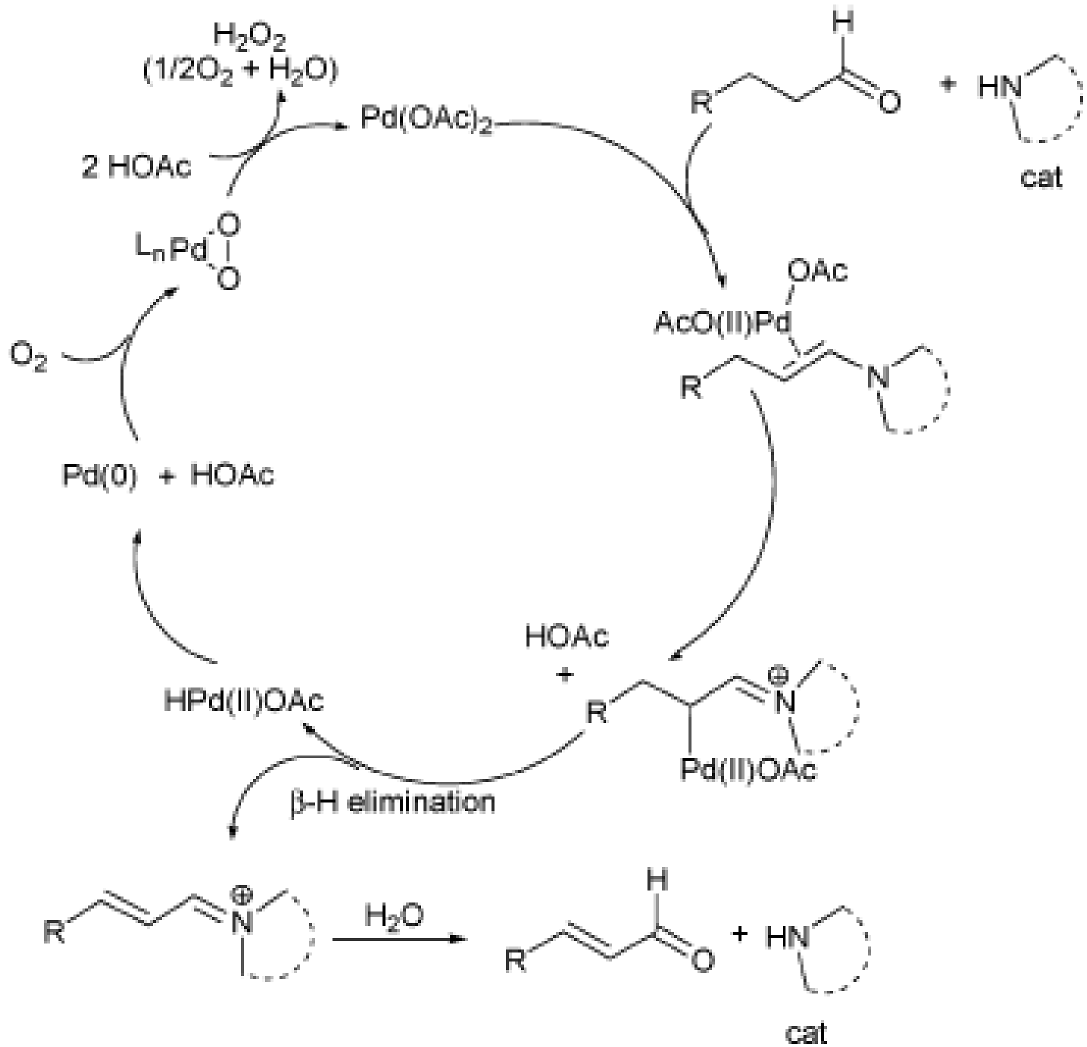
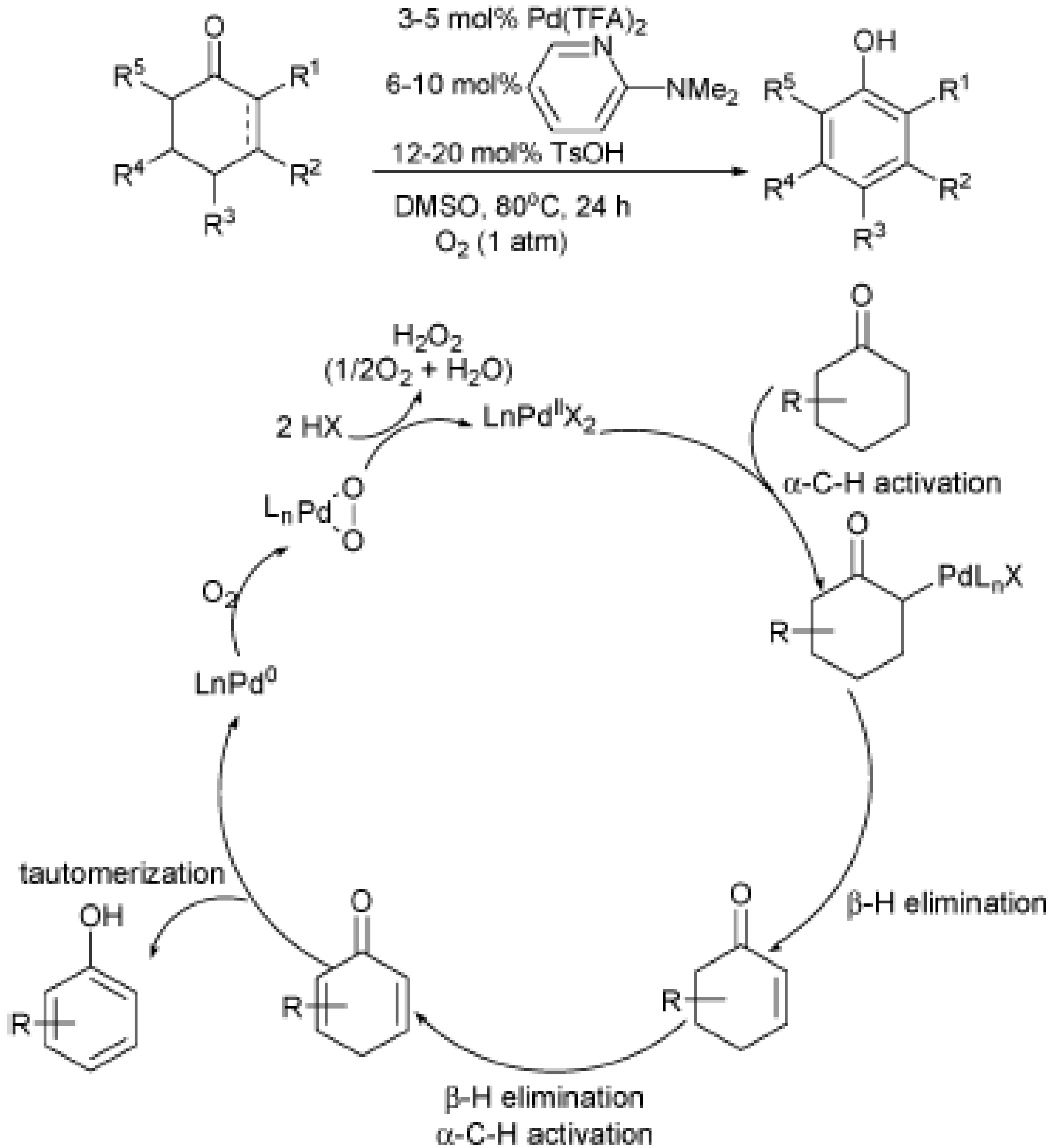




J. Liu, *et,al. Chem Commu*., **2010**, *46*, 415

A plausible mechanism





S. S. Stahl. *et, al. Science.* **2011**, *333,* 209

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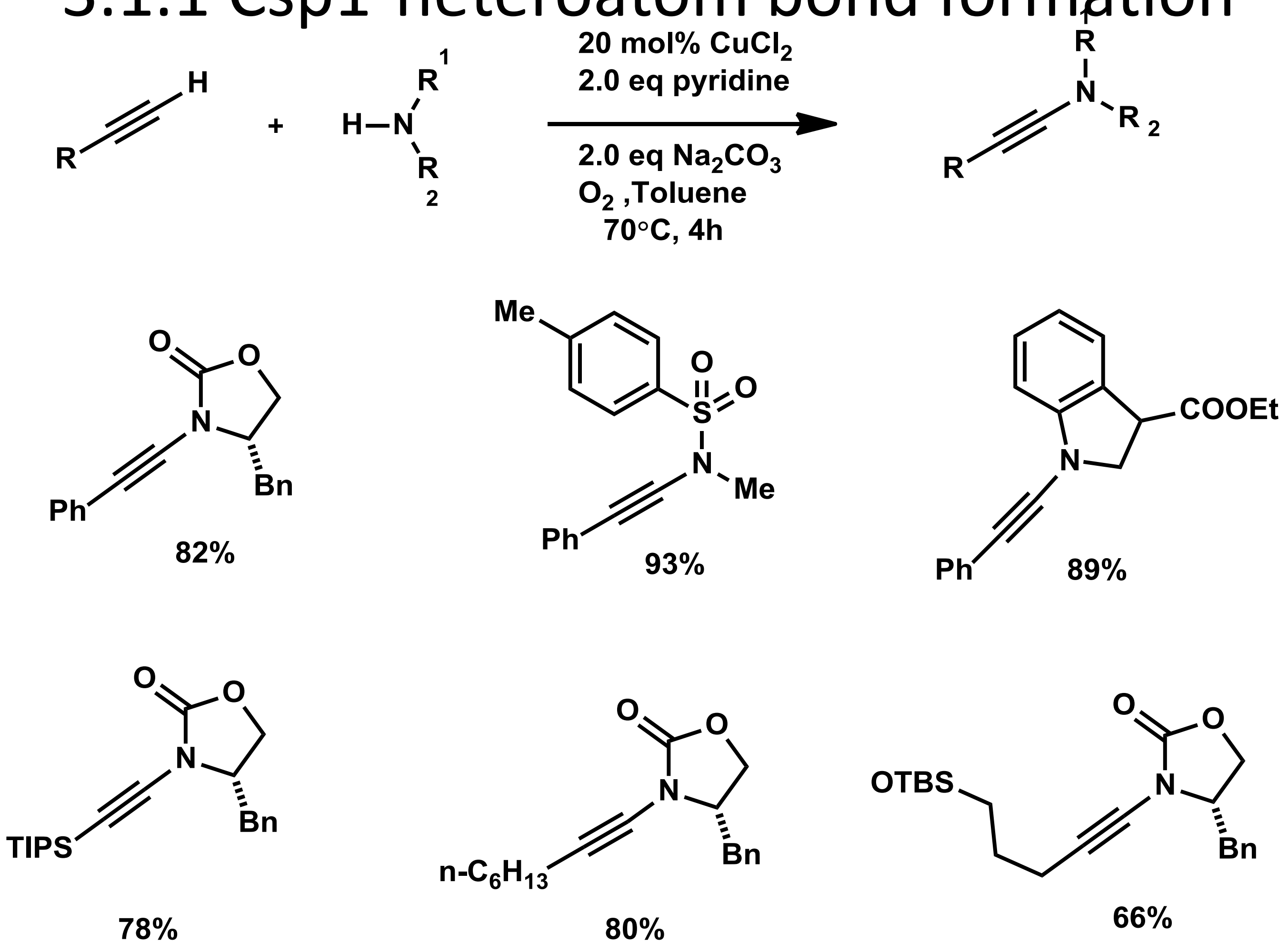
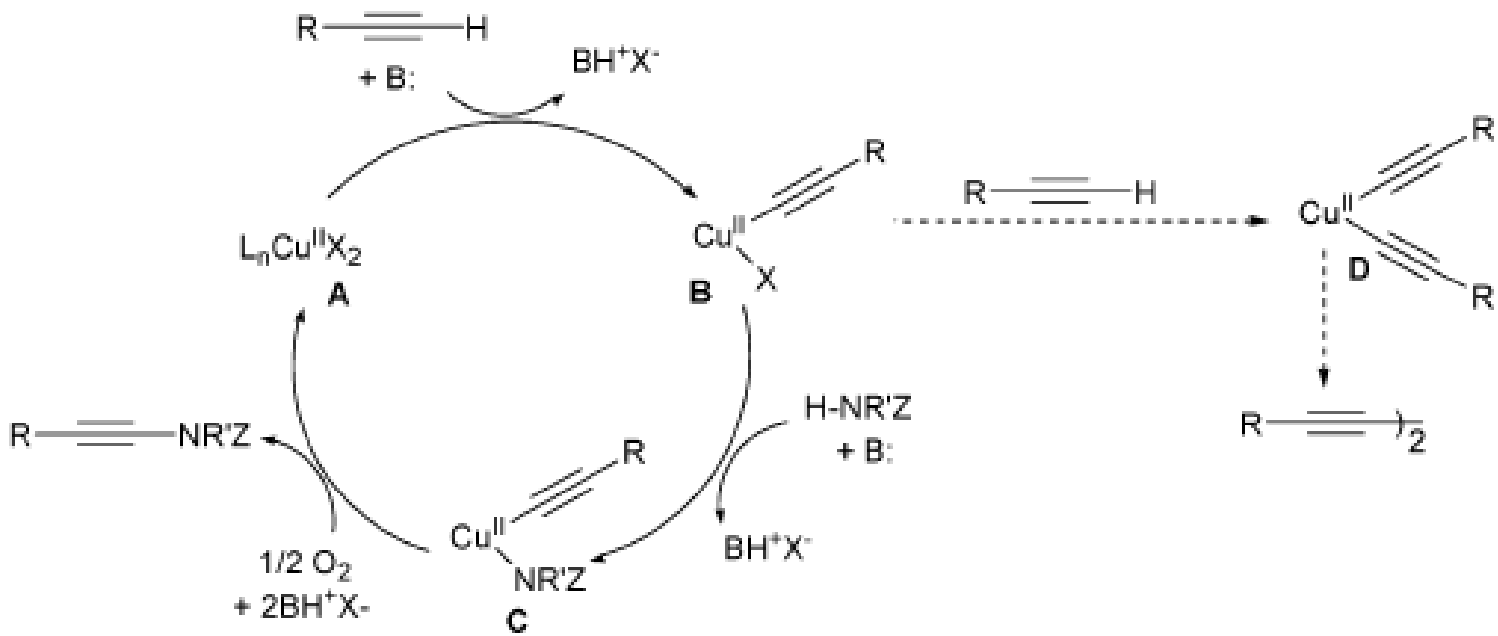
3.1 C-Heteroatom bond formation
3.1.1 Csp1-heteroatom bond formation

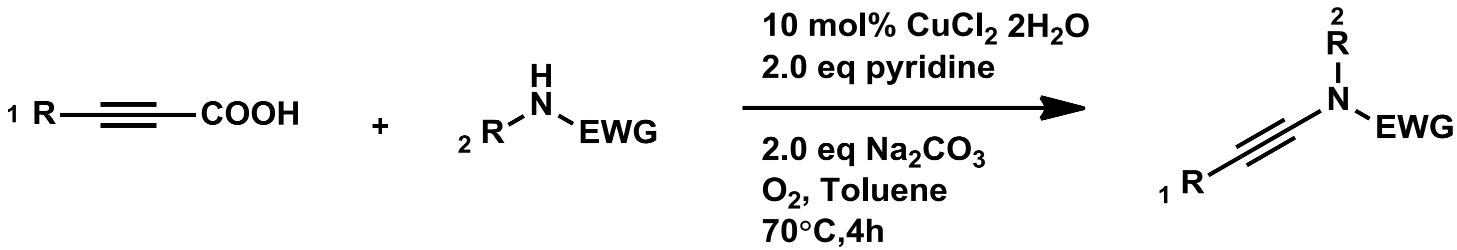


T. Hamada, *et al. J. Am. Chem. Soc*. **2008**, *130*, 833

Mechanism proposal for Cu-catalyzed oxiditive amidation of alkynes



other Cu catalyzed oxidative



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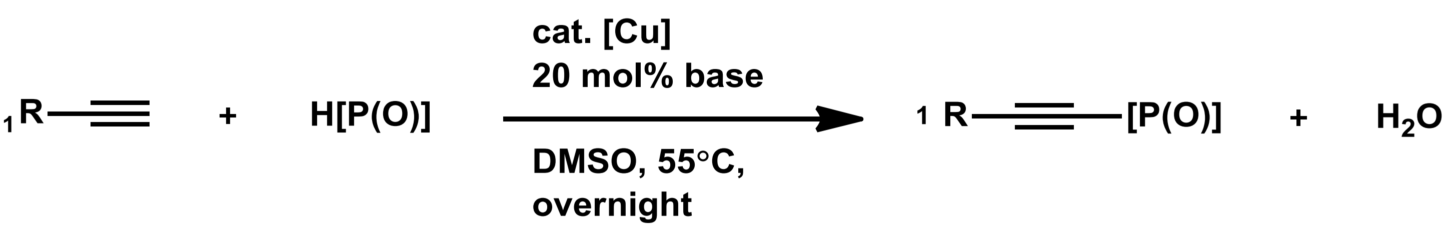
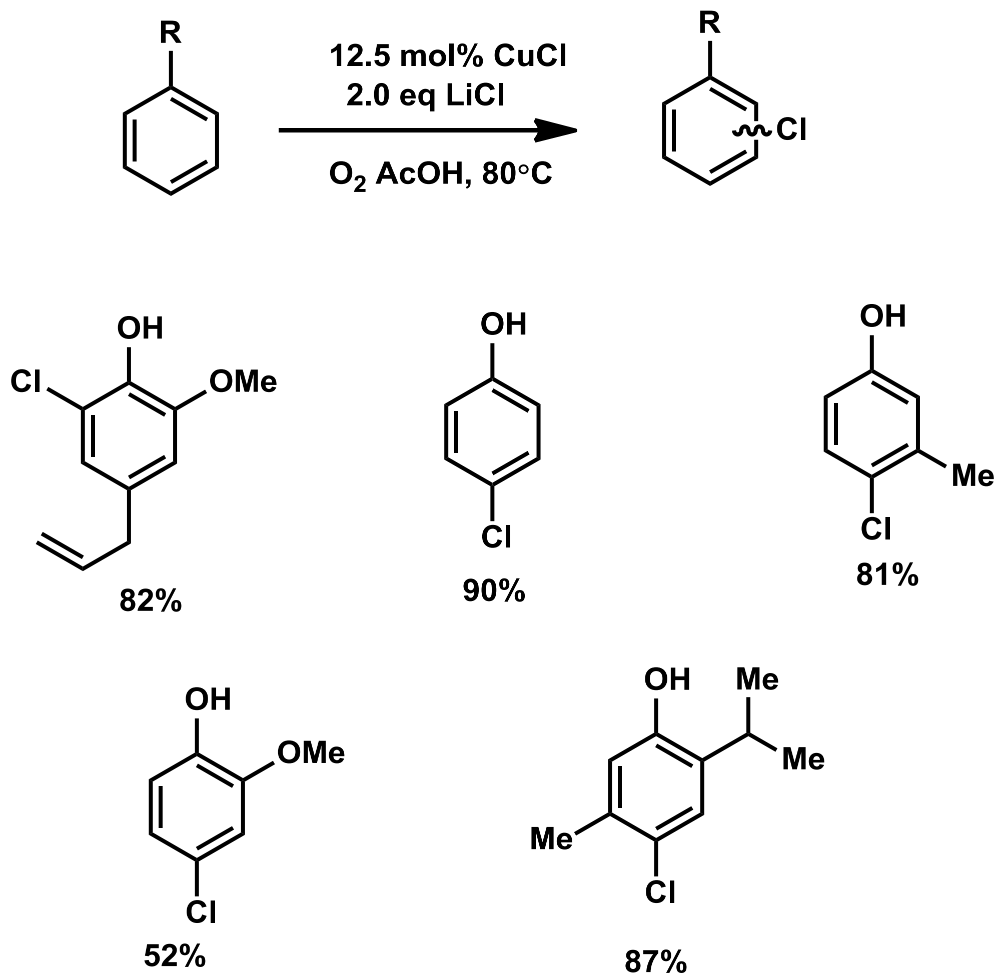


(2)

(1) W. Jia. and N. Jiao, *Org.Lett.* **2010**, *12*, 2000
(2) Y. Zhao*, et,al. J. Am. Chem. Soc*. **2009***, 351*,1229

3.1.2 Csp2-heteroatom bond formation



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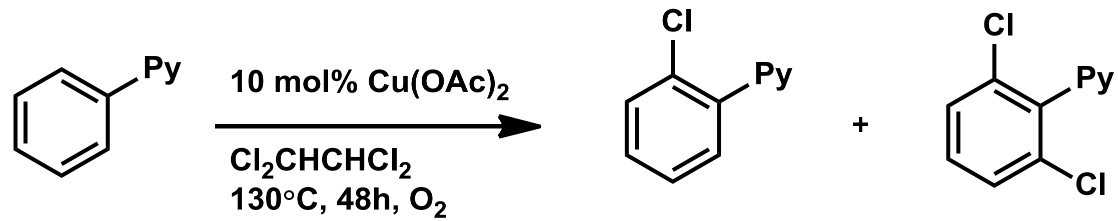
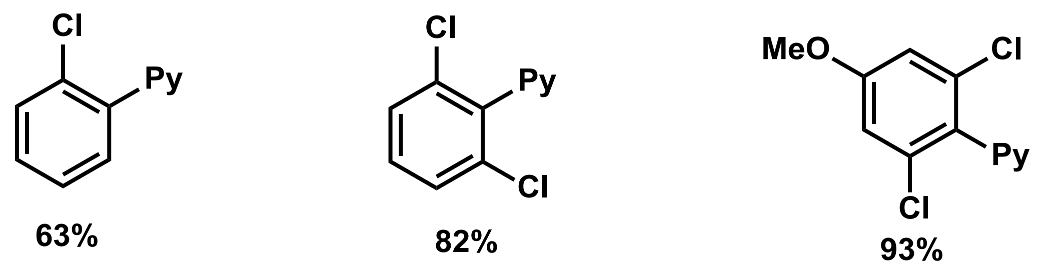
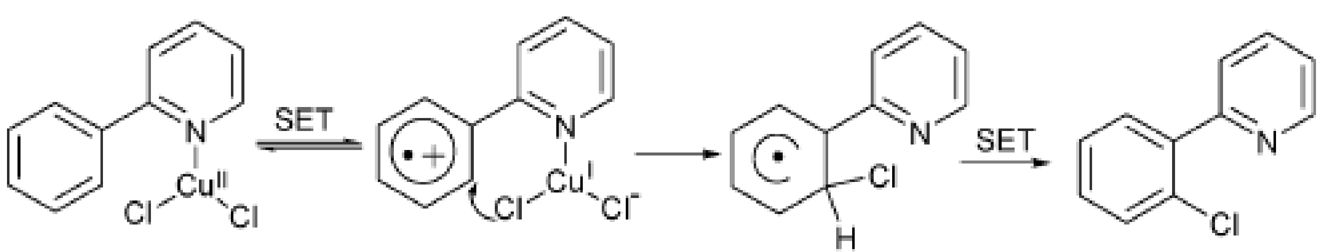
Cu catalyzed chlorination of 2-arylpyridine substrates

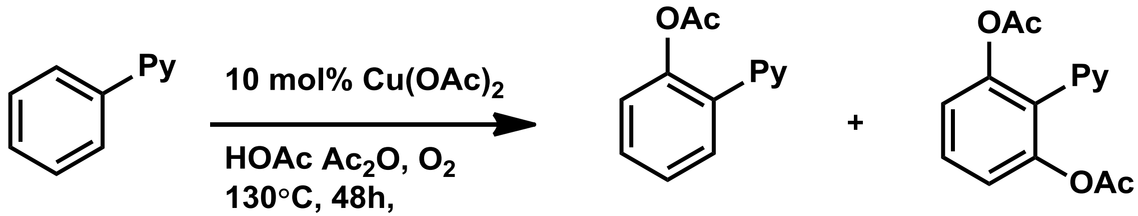




The proposed mechanism:



X. Chen, *et. al. J. Am. Chem. Soc*. **2006**, *128*, 6790



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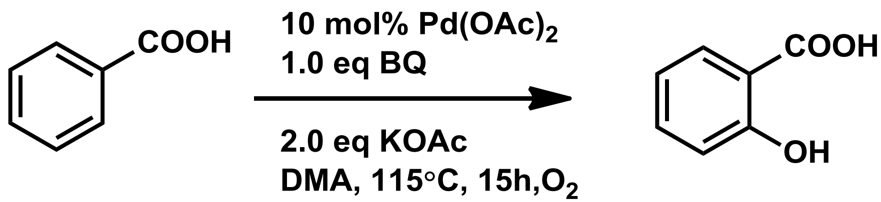

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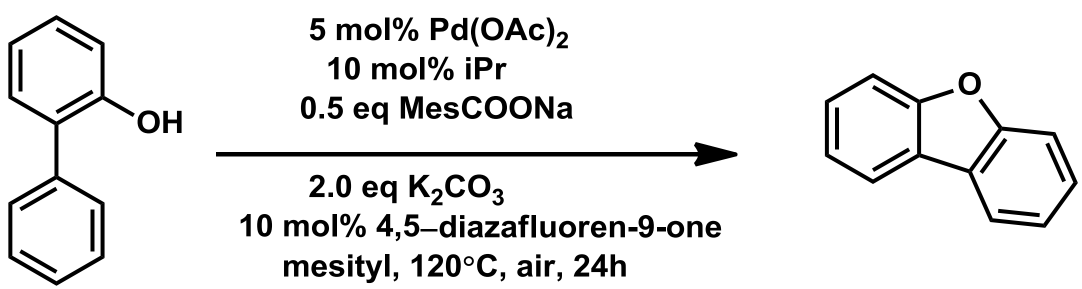

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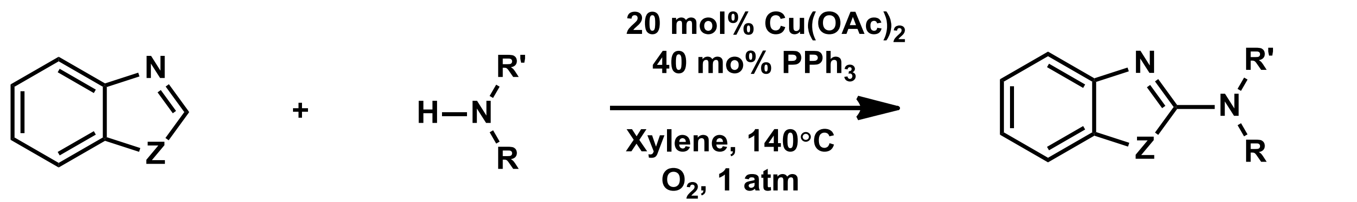
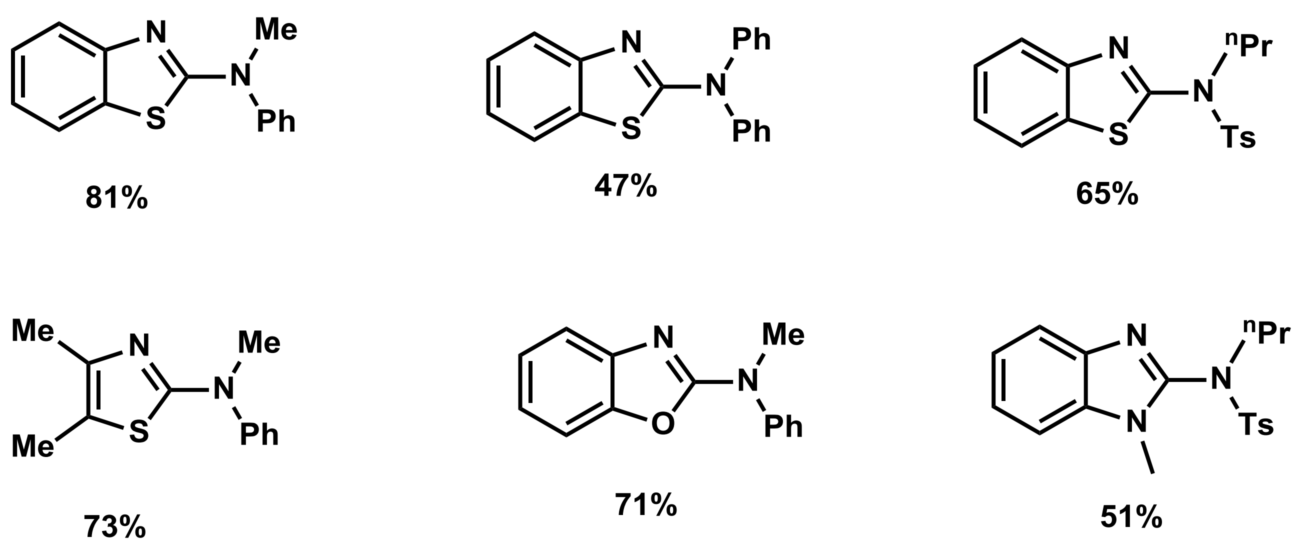
(1) J. Yu, *et, al. J. Am. Chem. Soc*. **200**9*, 131*, 14654
(2) W. Wang*, et, al. J. Org. Chem*. **2010***, 75*, 2415
(3)B. Xiao, *et.al. J. Am. Chem. Soc*. **2011**, *133*, 9250

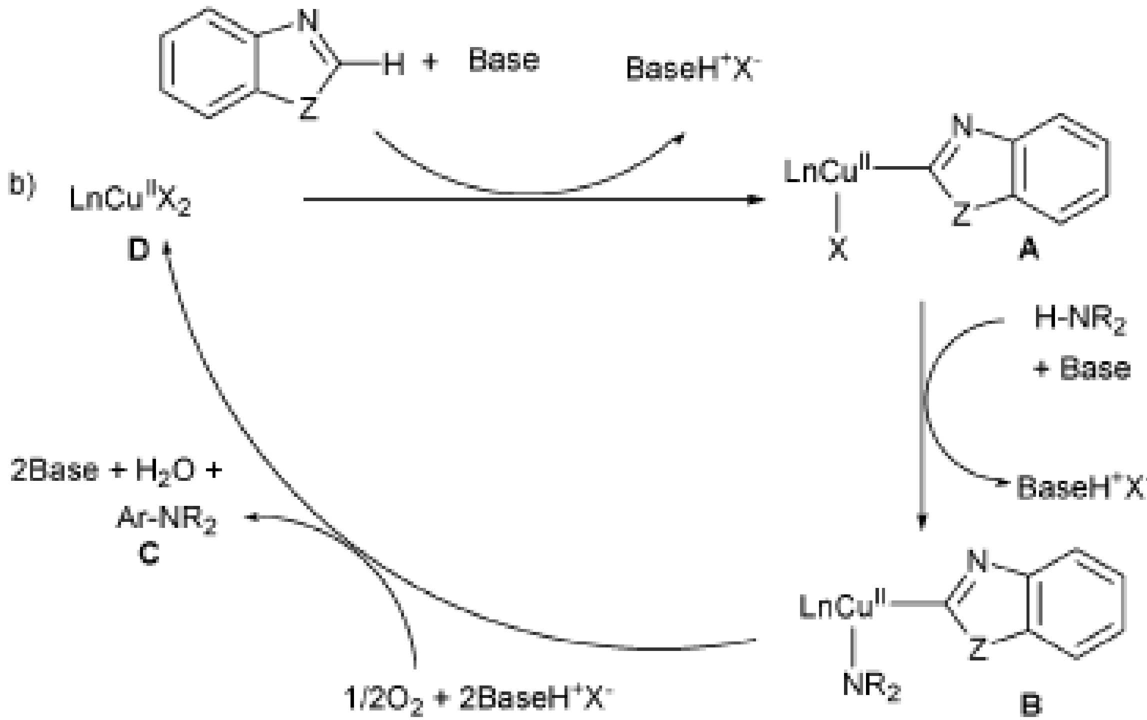
Cu catalyzed oxidative coupling of azoles with a variety of nitrogen nucleophies



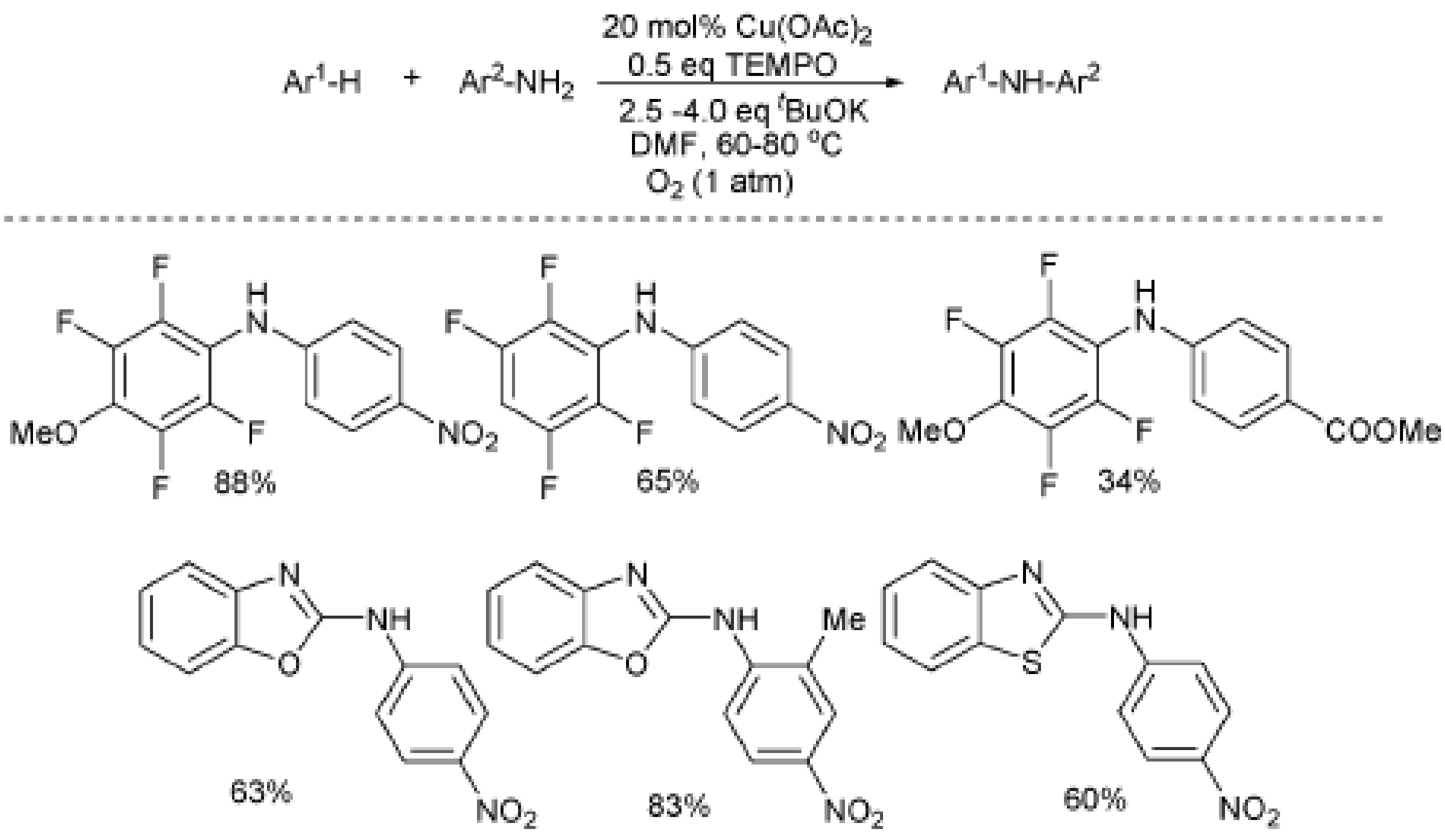


D. Monguchi, *et.al. Org. Lett*. **2009**, *11*, 1607

The proposed mechanism

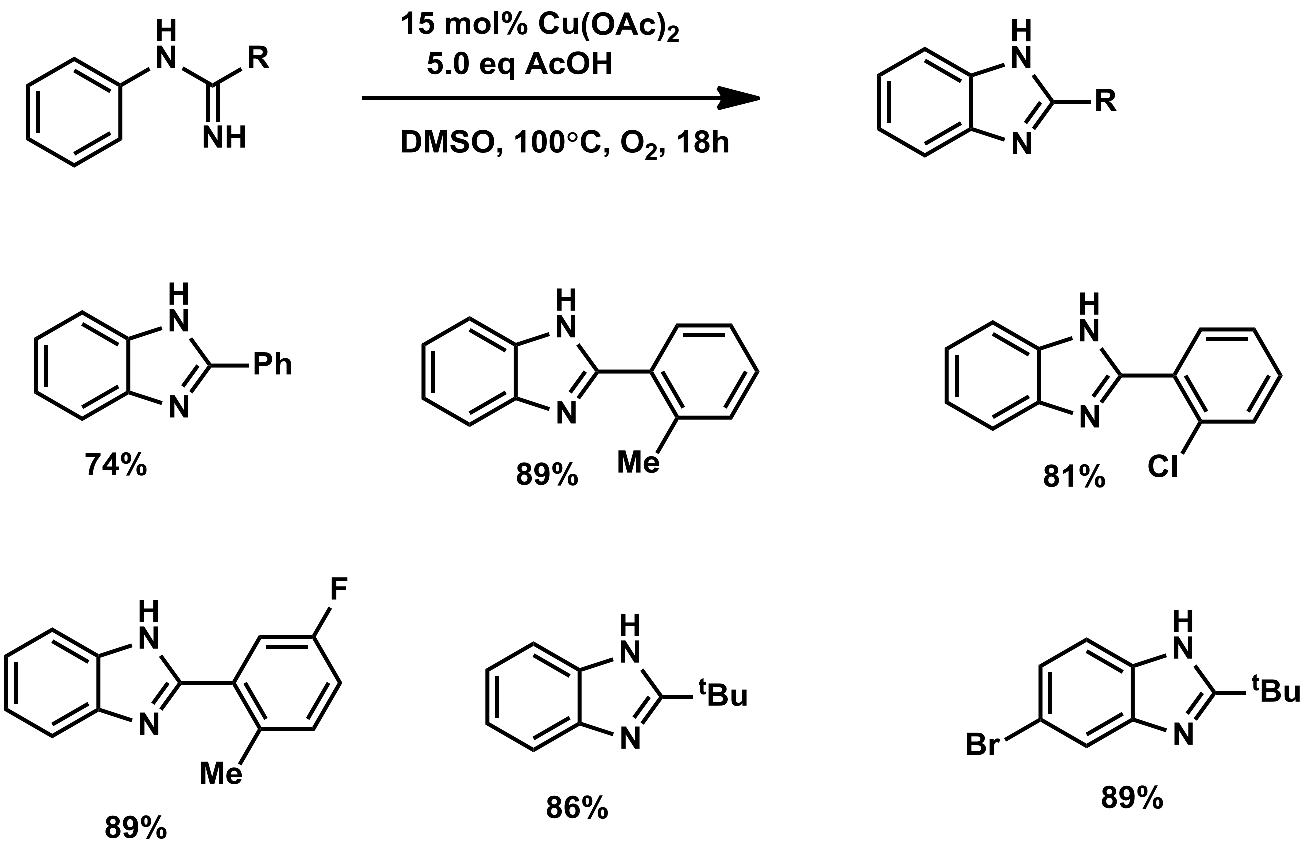


Cu-catalyzed amination of polyfluorobenzenes and azoles with amines



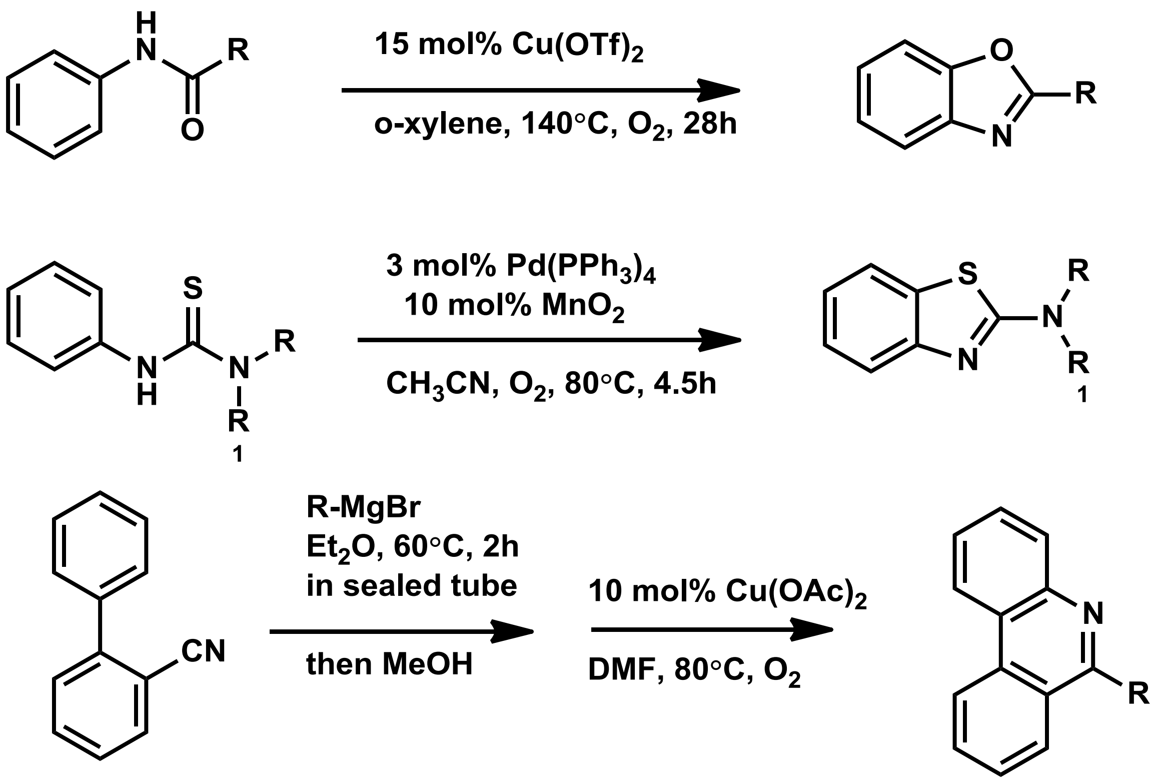
M. Wang, *et. al, Adv. Synth. Catal*. **2010**, *352*, 1301

Copper catalyzed synthesis of benzimidazoles from amidines



S. L. Buchwald, *et,al*. *Angew. Chem. Int. Ed* . **2008**, *47*, 1932

the series of Copper-catalyzed sythesis



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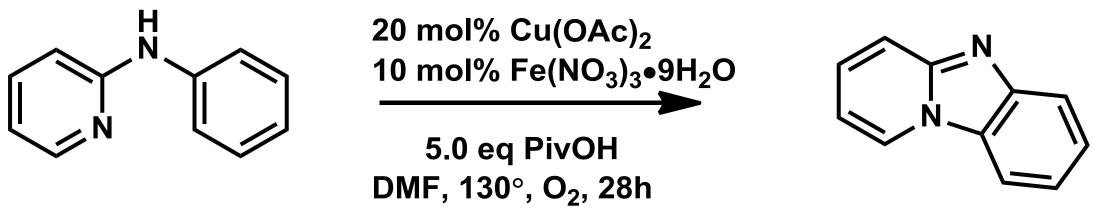
(1) S. Ueda and H. Nagasawa, *Angew. Chem. Int. Ed*. **2008**, *47*, 6411
(2) R.A.Batey, *et, al. Org. Lett*. **2009**, *11*, 2792
(3) T. Doi, *et,al. Adv. Synth. Cata*. **2010**, *11,* 2792

Cu and Fe co-catalyzed aerobic oxidative intromolecular alkene C-H amination leading to N-heterocycles



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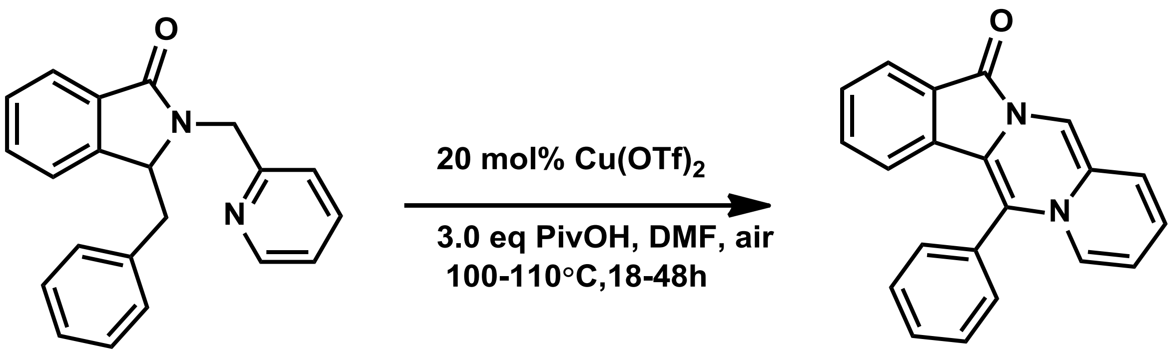

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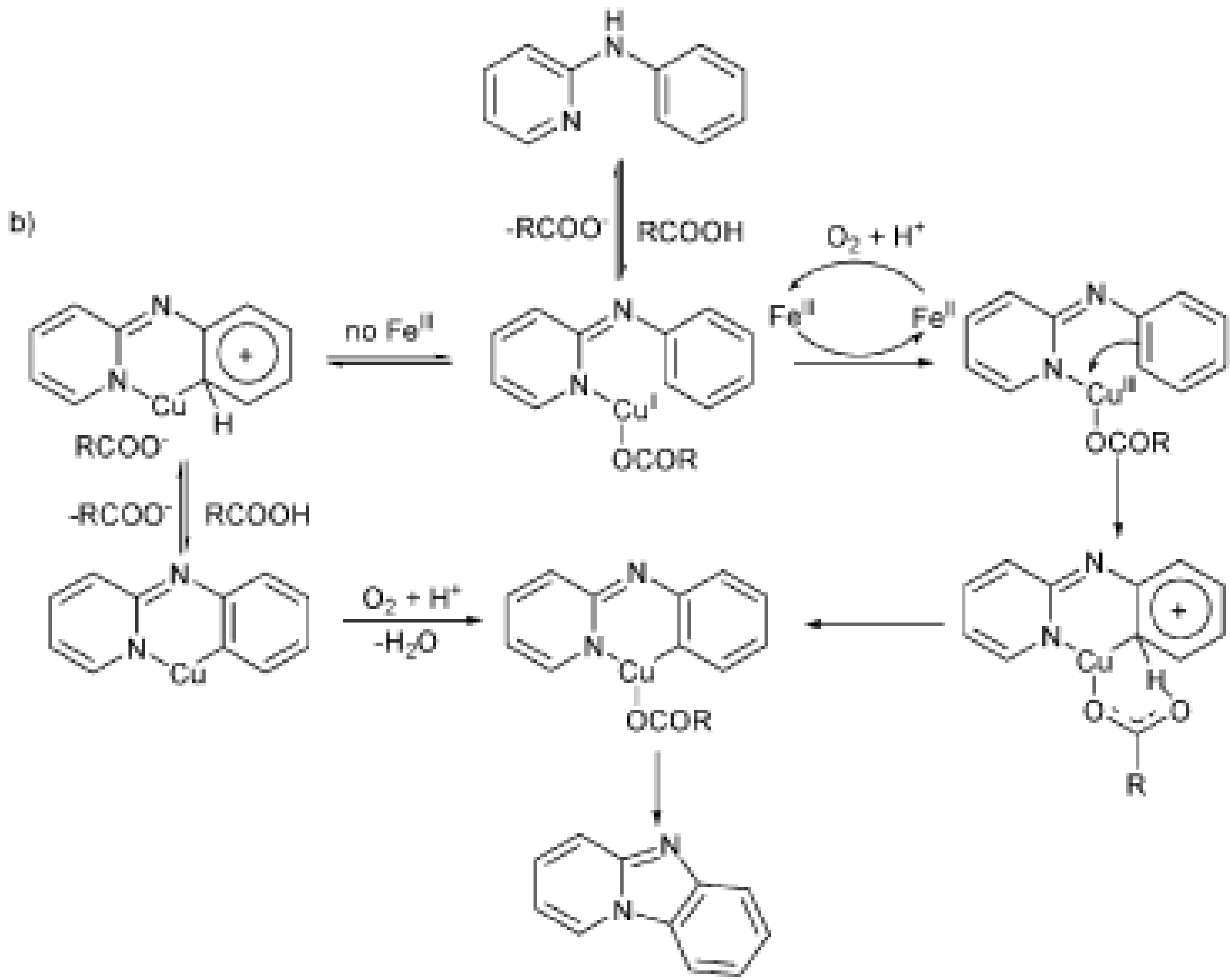
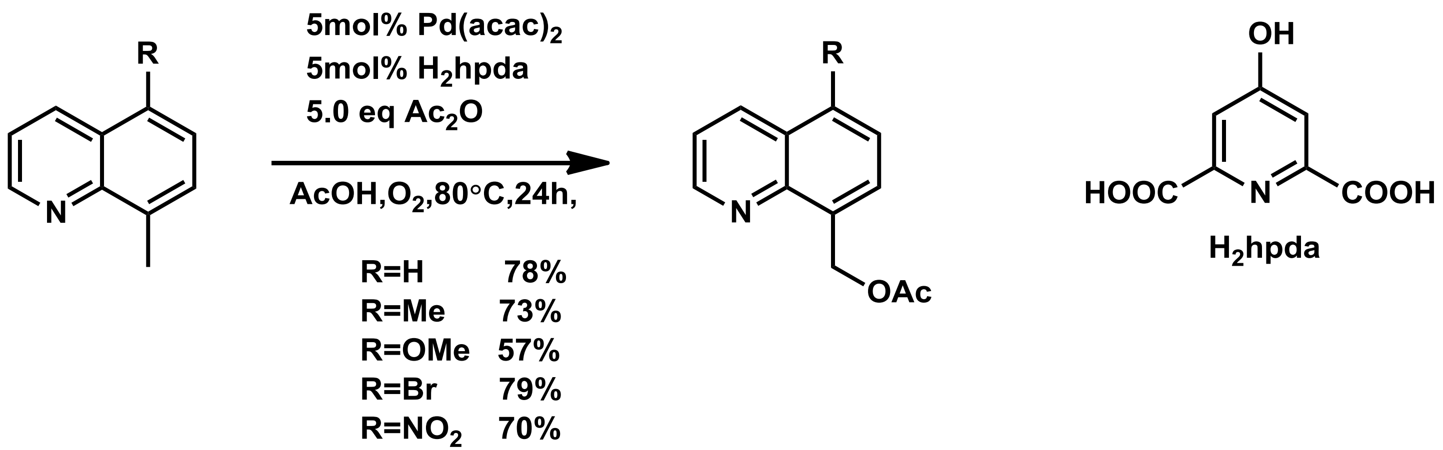
(1) Q. Zhu, *et.al. J. Am. Chem. Soc*. **2010**, *132*, 13217
(2) H. Fu, *et,al. Org. Lett*. **2011**, *13*, 3694

Proposed mechanism with and without iron salt



3.1.3 Csp3-heteroatom bond formation -----Palladium-catalyzed



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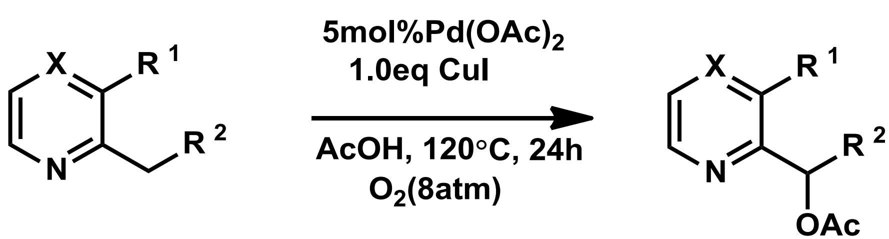

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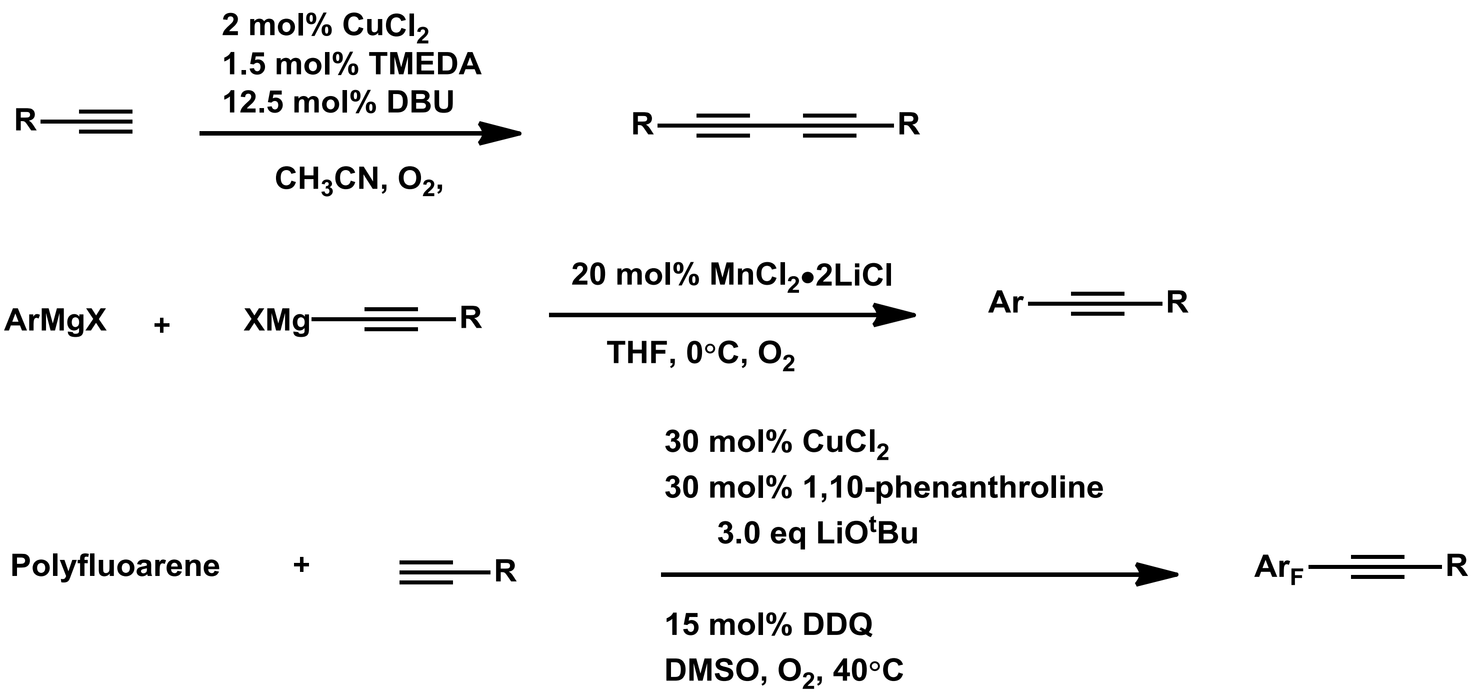
(1) J. Zhang, *et.al. Chem. Commun*. **2008**, 3625

(2) H. Jiang, *et.al. Chem. Commun*. **2010**, *46*, 7259

3.2 direct C-C bond formation
3.2.1 Csp1-Csp1 bond formation
3.2.2 Csp1-Csp2 bond formation



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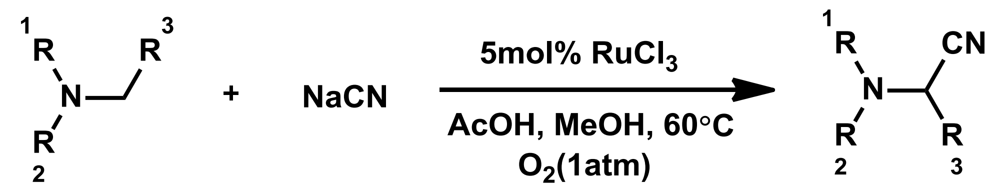
(1) S. Adimurthy, *et. al, J. Org. Chem*. **2009**, *74*, 5648
(2) C. Duplais, *et. al, Angew. Chem. Int. Ed*. **2009**, *48*, 6731
(3) Y. Wei, *et. al, J. Am. Chem. Soc*. **2010**, *132*, 522

3.2.3 Csp1-Csp3 bond formation



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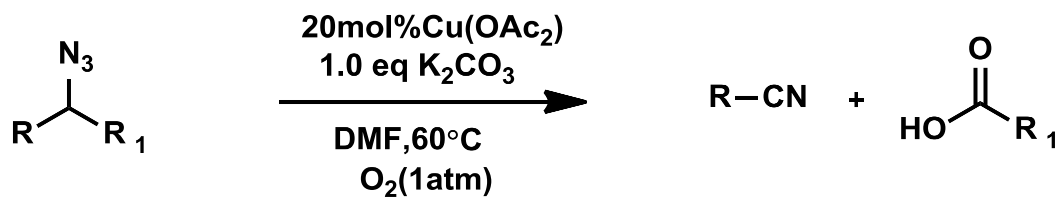

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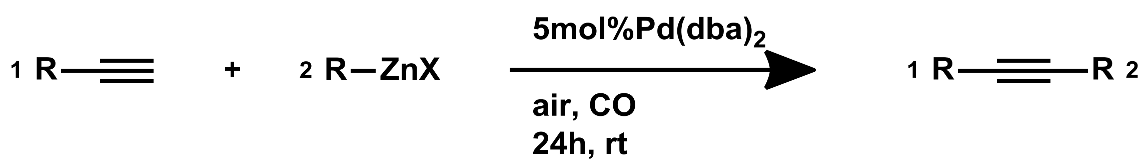

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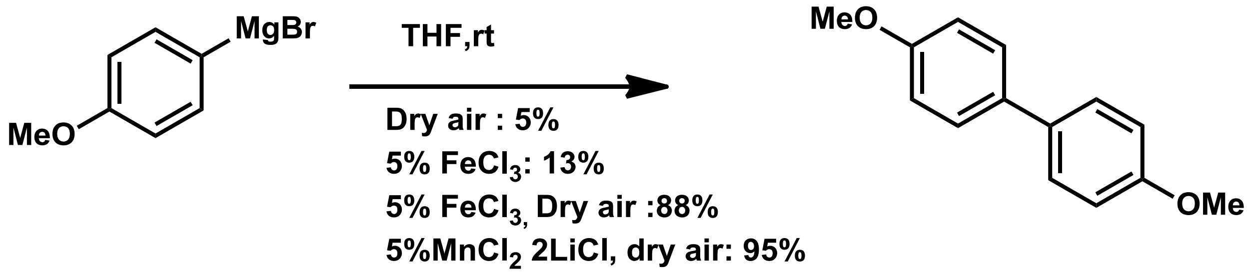
(2) S. Chiba, *et. al. Org. Lett*. **2010**, *12*, 2052
(3) M. Chen, *et,al. J. Org. Chem. Soc*. **2010**, *132*, 2052

3.2.4 Csp2-Csp2 bond formation



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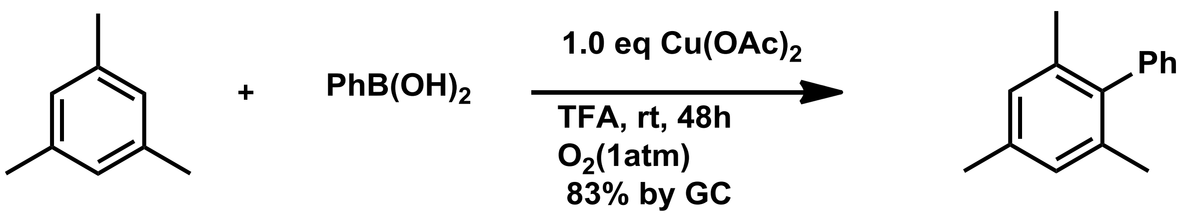

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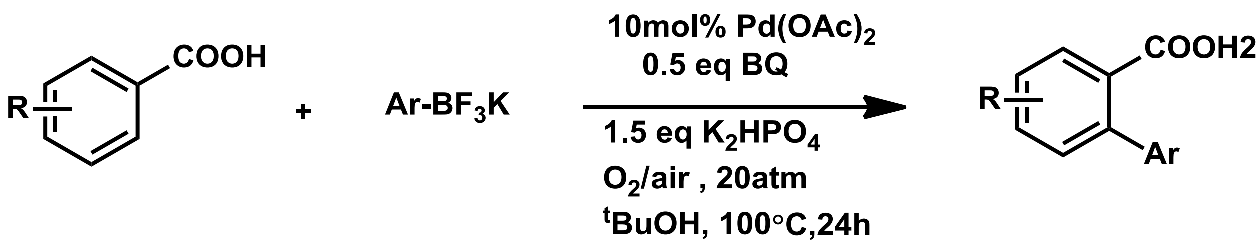

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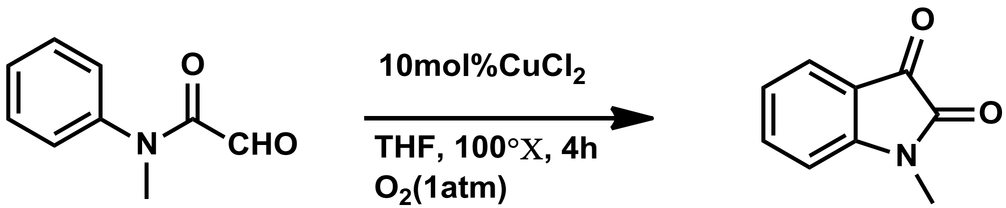
(1) A. Moyeux. *et. al . J. Am. Chem. Soc* **. 2007***, 129*, 13788
(2) I. Ban, *et.al. Org. Lett.* **2008***, 10*, 3607
(3) D. H. Wang*, et. al . J. Am. Chem. Soc .* **2008**, *130*, 17676



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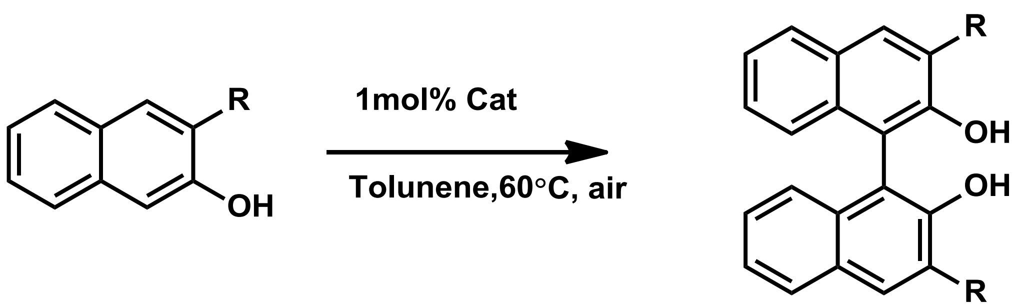

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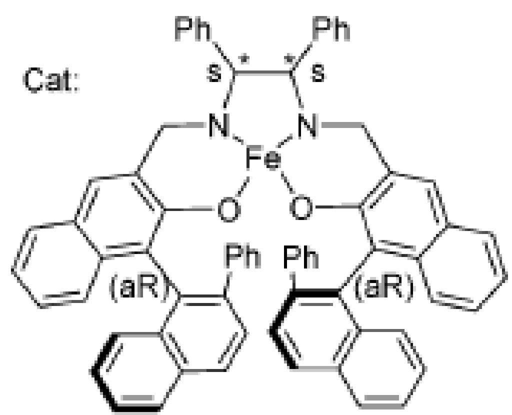


R = Me, 89%, 77% ee

R = Ph, 94%, 93% ee

R = PhC≡C, 91%, 96% ee

R =Cl, 82%, 94% ee

R = Br, 86%, 94% ee

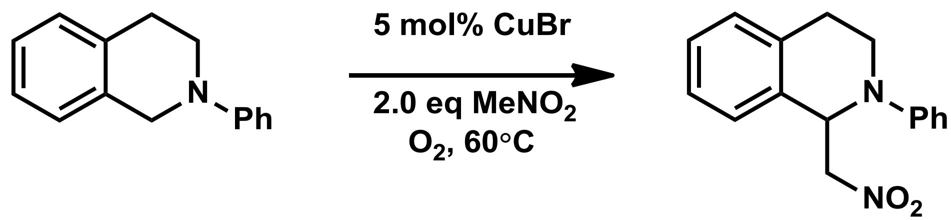
R = I, 77%, 96% ee

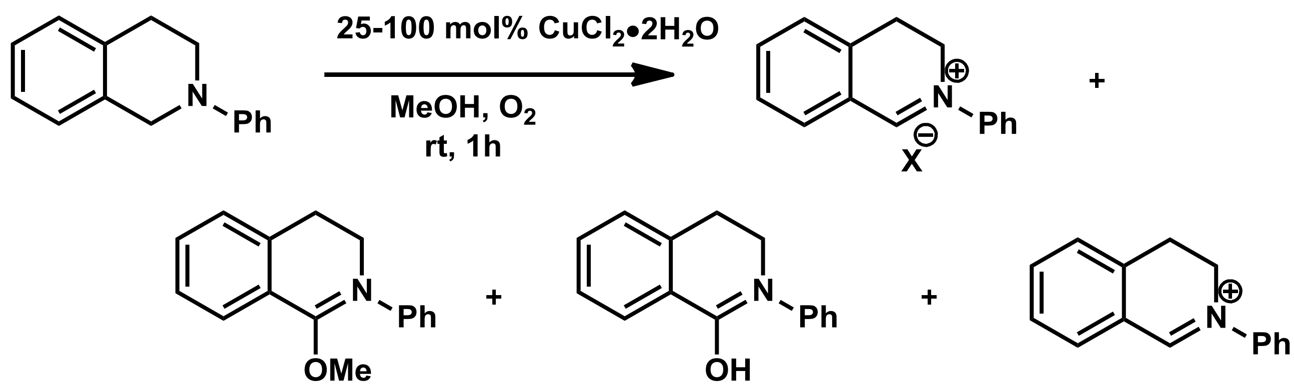
R = COOMe, n.r.

(1) J. Li*, et. al, J. Am. Chem. Soc*. **2010**, *132*, 8900

(2) T. Katsuki. *et. al, J. Am. Chem. Soc*. **2009**, *131*, 6082

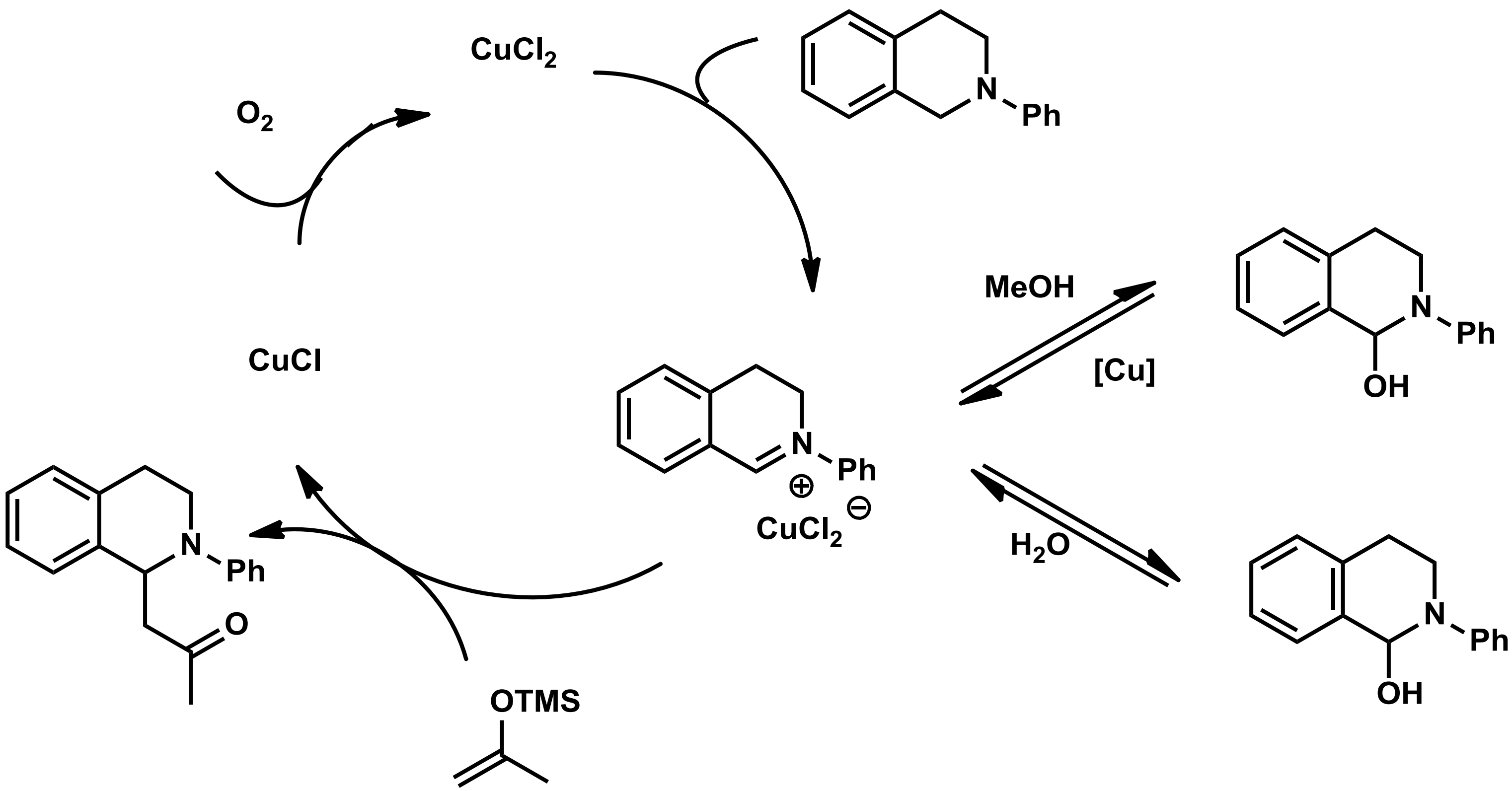
3.2.5 Csp3-Csp3 bond formation



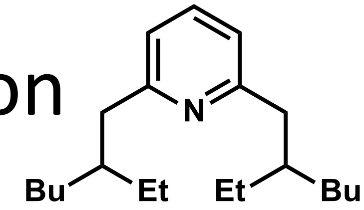


E. Boess, *et. al . J. Am. Chem. Soc*. **2011**, *133*, 8106

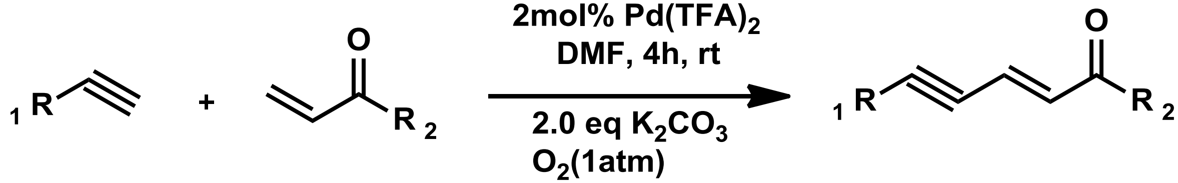
The role of methaol as a solvent in the Cu-catalyzed aerobic oxidative coupling reaction



3.3 Oxodative Heck reaction



1 catalyst



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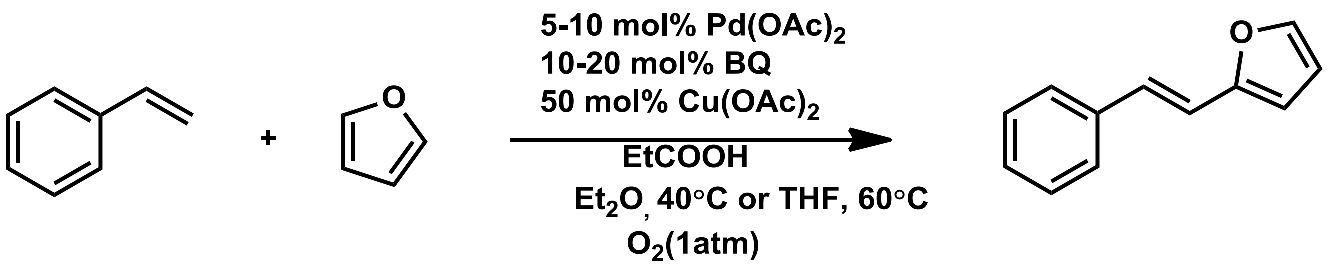

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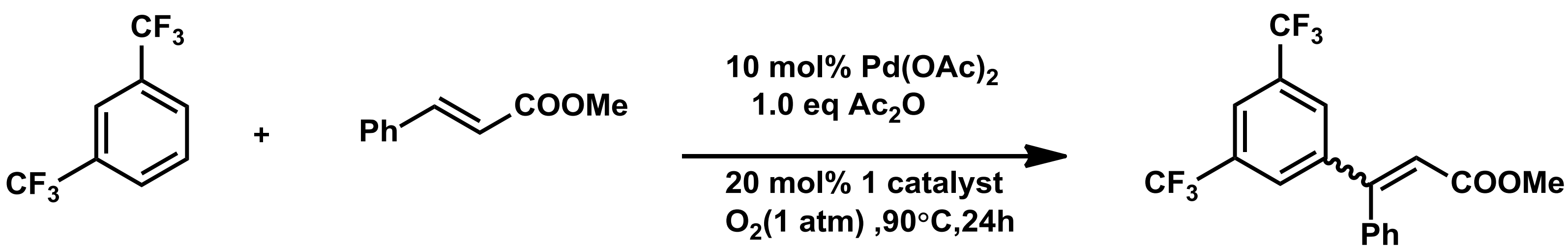
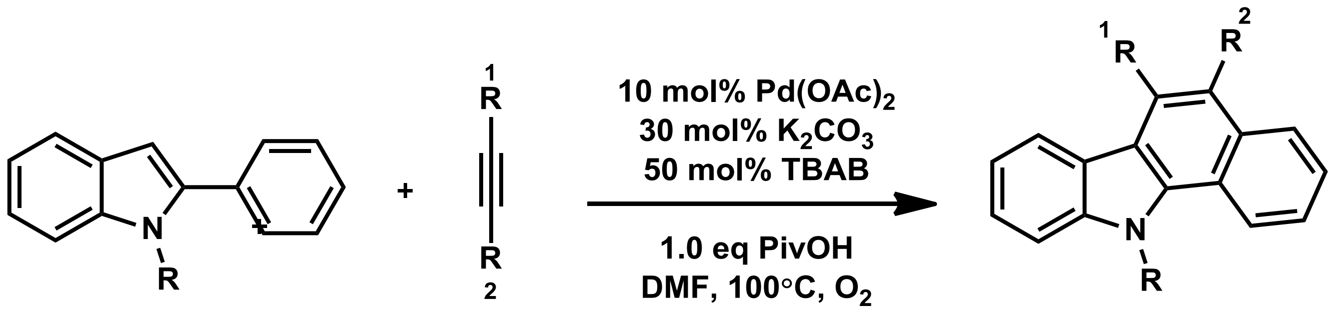


(3)

(1) V. Hadi, *et. al, Thetrahedron Lett*. **2009**, *50*,2370
(2) C. Aouf, *et, al. Org. Lett*. **2009**, *11*, 4096
(3) Y. Zhang, *et,al. J. Am. Chem.Soc*, **2009**, *131*, 5072

3.4 insertion of alkynes/CO/carbene



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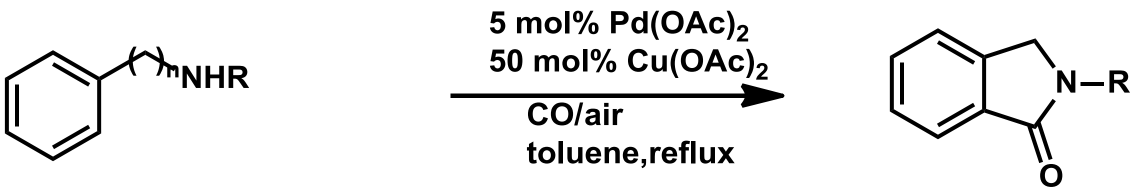

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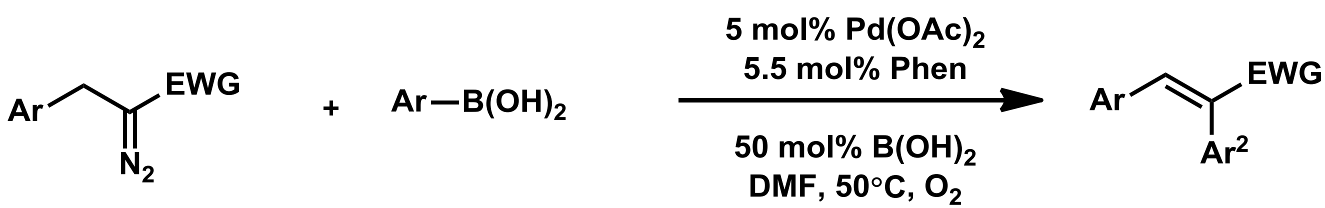

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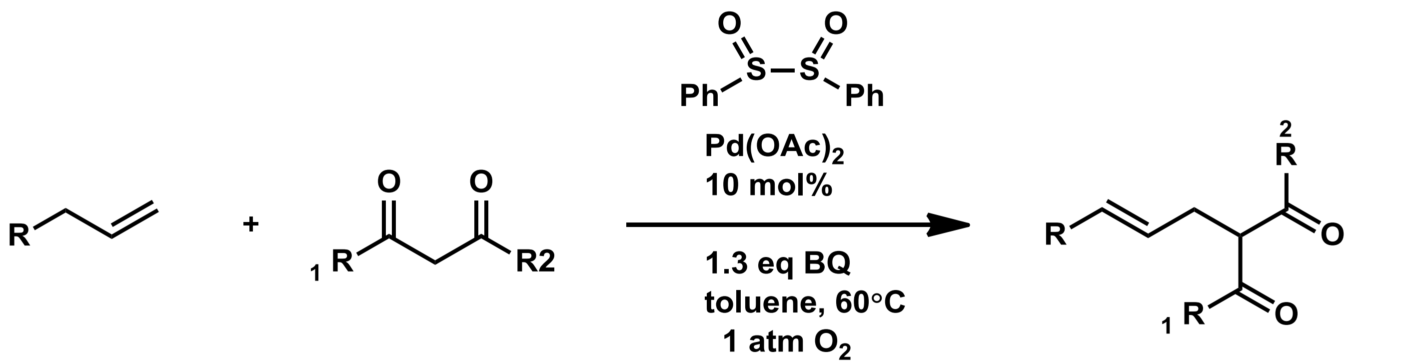
(1) Z. Shi, *et,al. Angew. Chem. Int. Ed.* **2009**, *48*, 7895

(2) K. Orito, *et,al. J.Am. Chem.Soc*. **2004**, *126*, 4342

(3) W. Yu, *et,al. Org. Lett*. **2010**, *12*, 4506

3.5 Allylic and benzylic C-H bond functionalization
3.6 Heteroatom-heteroatom coupling



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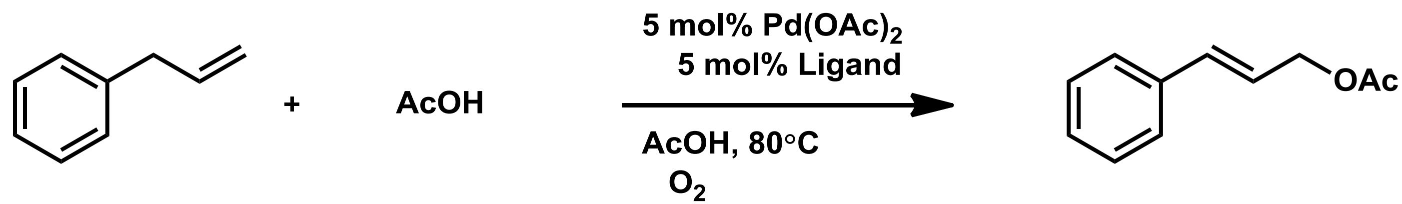

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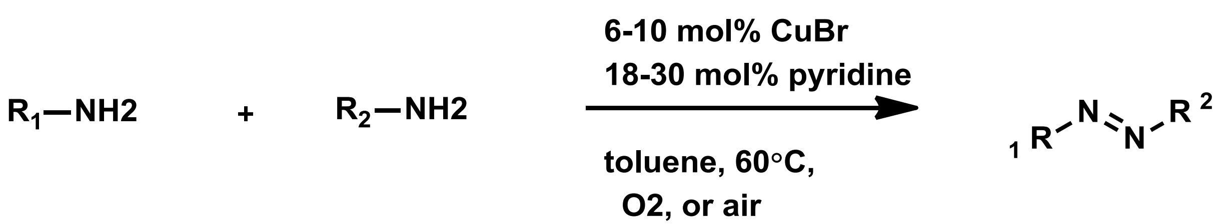

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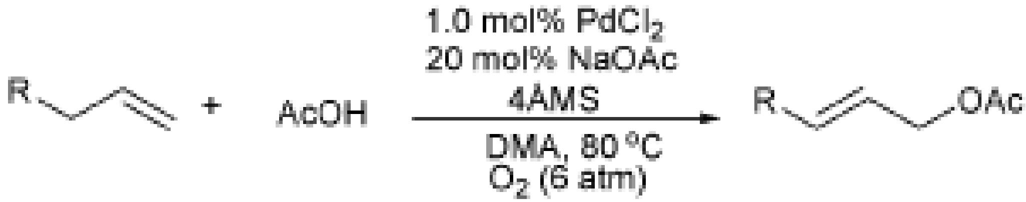
(1) Z. Shi, *et. al. J. Am. Chem. Soc*. **2008**, *130*, 12901
(2) S. S. Stahl*, et,al. J. Am. Chem. Soc*. **2010**, *132*, 15116
(3) C. Zhang and N. Jiao *et, al. Angew. Chem. Int. Ed*. **2010**, *49*, 6174

3.7 Wacker and Wacker-type reaction



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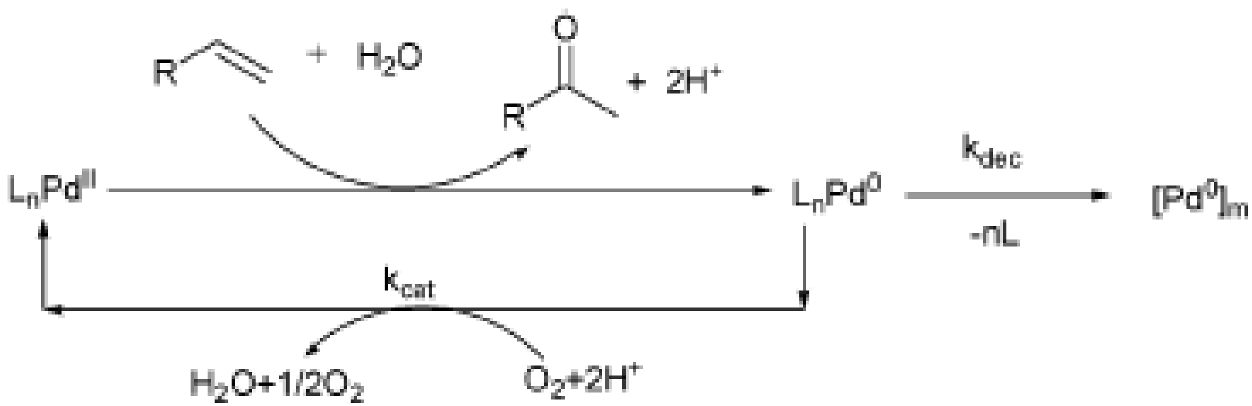

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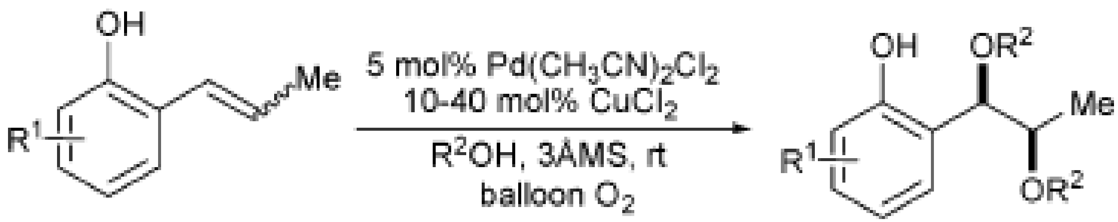
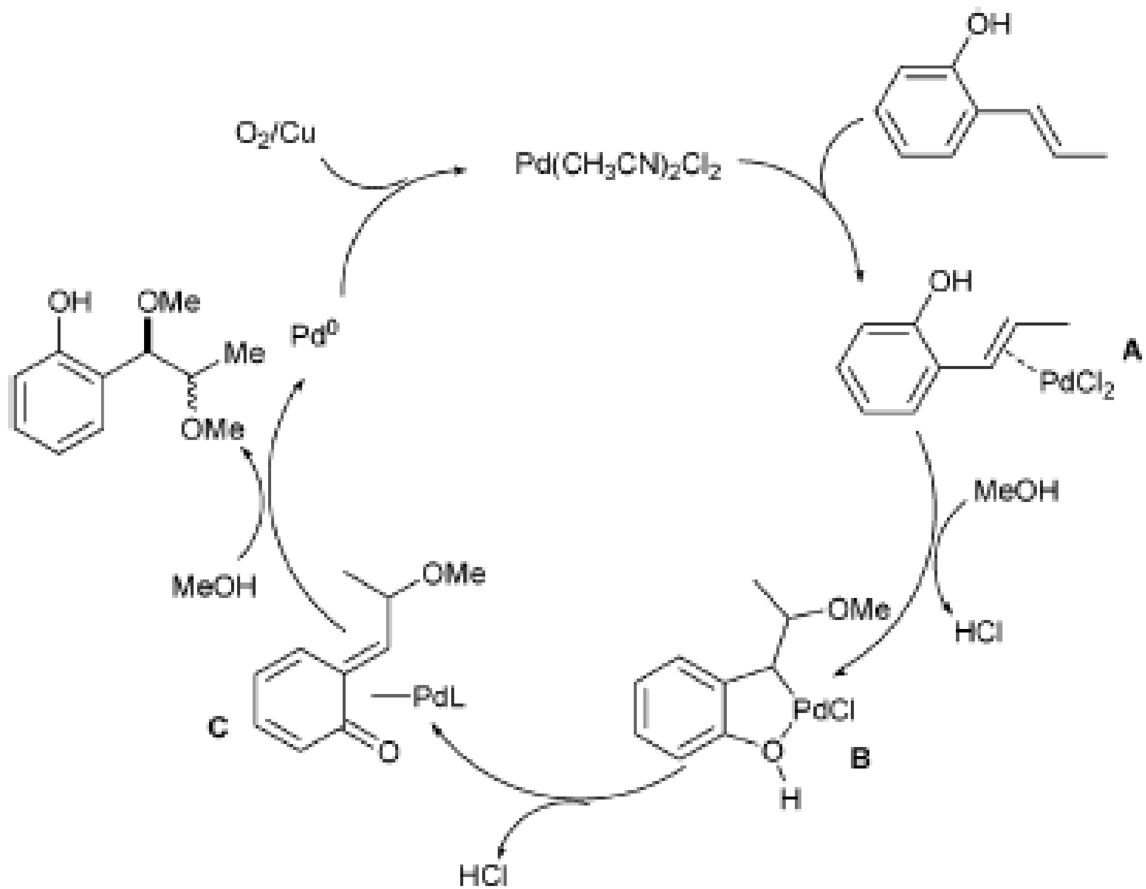


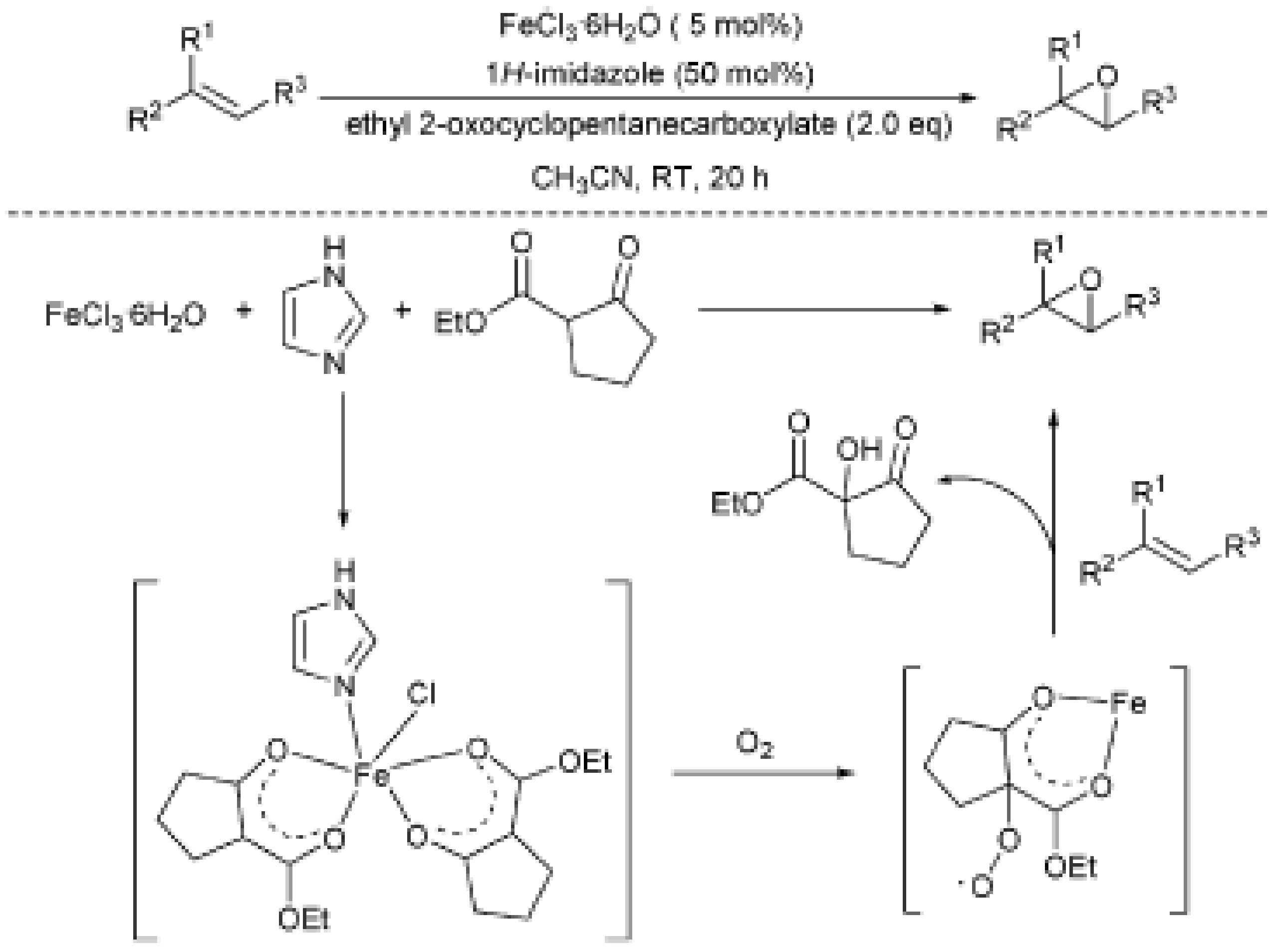
(3)

(1) E. V. Gusevskaya. et,*al, Adv. Synth. Catal***. 2009**, *352*, 1533
(2) E. V. Gusevskaya*, et,al, Adv. Synth. Catal*. **2009**, *351*, 2491
(3) M. S. Sigman*. et, al. J. Am. Chem. Soc.* **2006**, *128*. 2794

Proposed mechanism for the Pd-catalyzed dialkoxylation of olefins

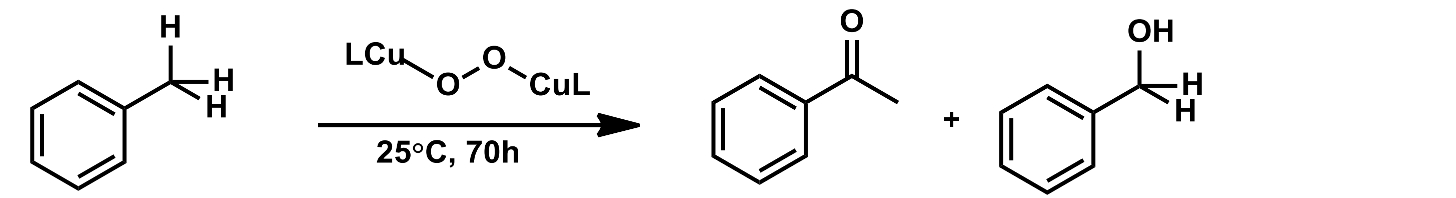


Iron-Catalyzed epoxidation of olefins



(1) M. Beller, *et.al, Angew. Chem. Int. Ed.* **2011,** *50*, 1425

4 , Areobic oxidation with oxygen-atom incorporation



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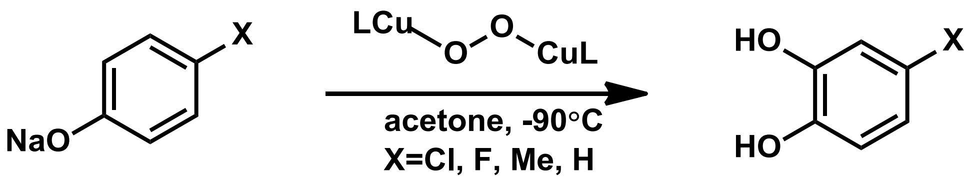

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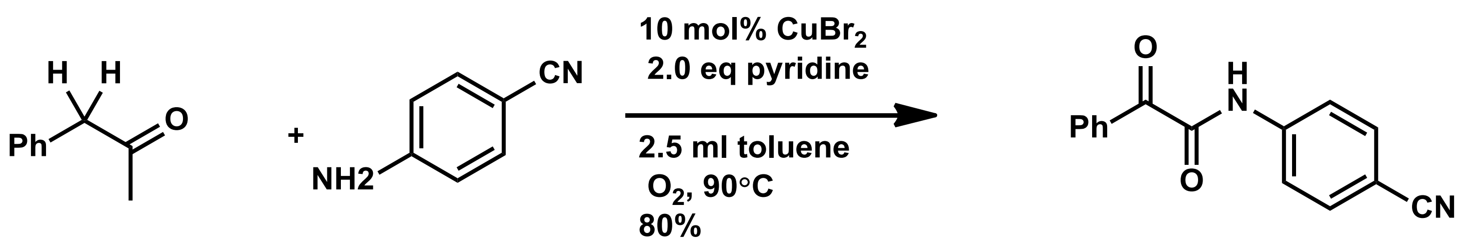
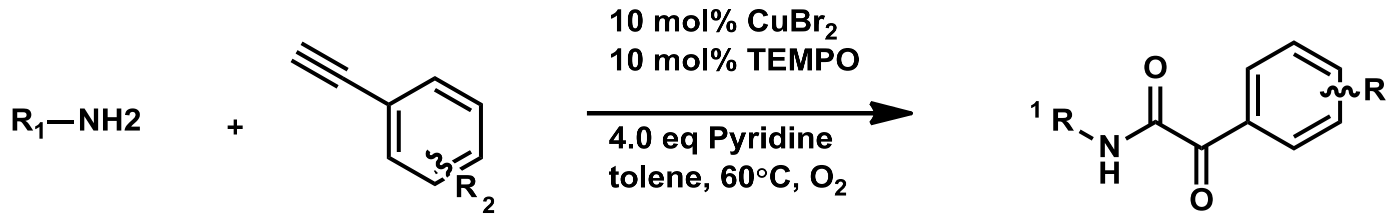
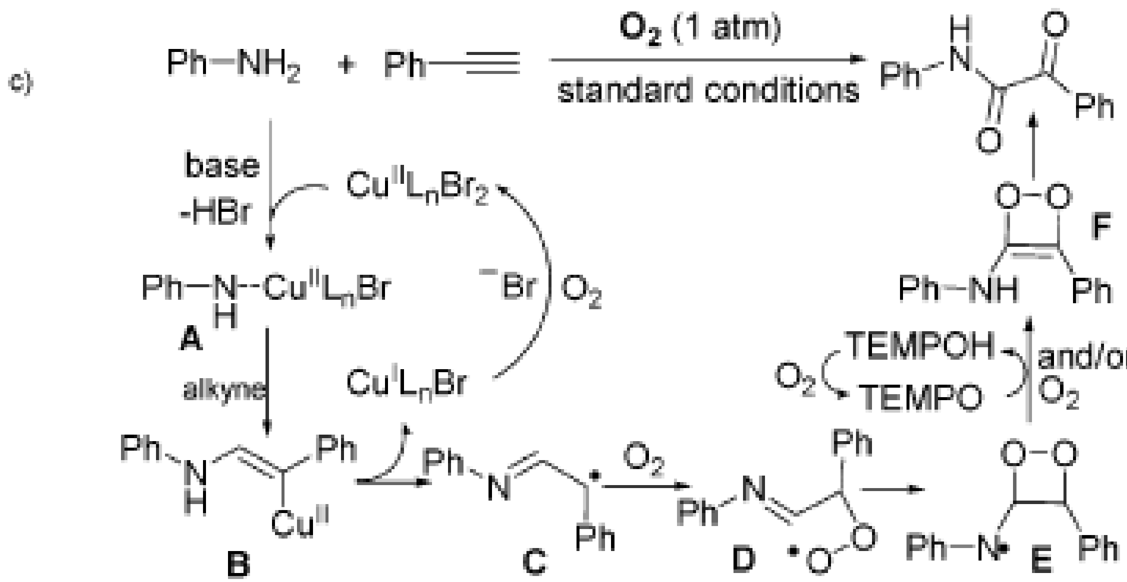


(3)

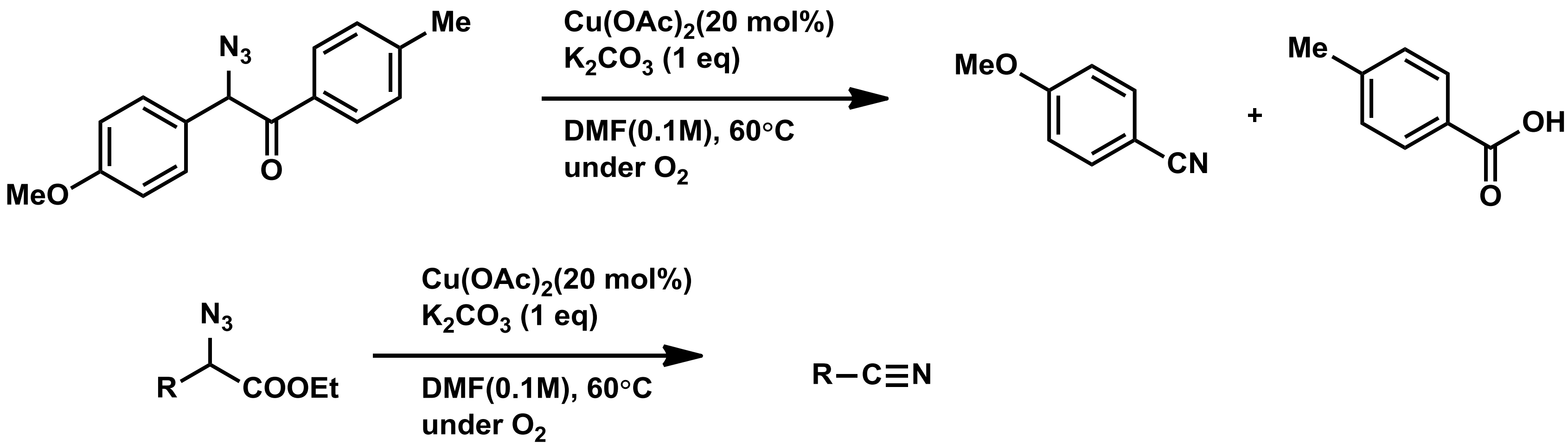
(1) M. *Costas.et, al. Anew. Chem. Int. Ed*. **2010**, *49*, 2406
(2) E. Roduner, *et, al. Chem. Commun*. **2011**, *47*, 6954
(3) N. Jiao. *et, al. Angew. Chem. Int. Ed*. **2011,** *50*, 11088





C. Zhang and N. Jiao, *et. al, J. Am. Chem. Soc*. **2010**, *132*, 7266

Cu catalyzed reaction



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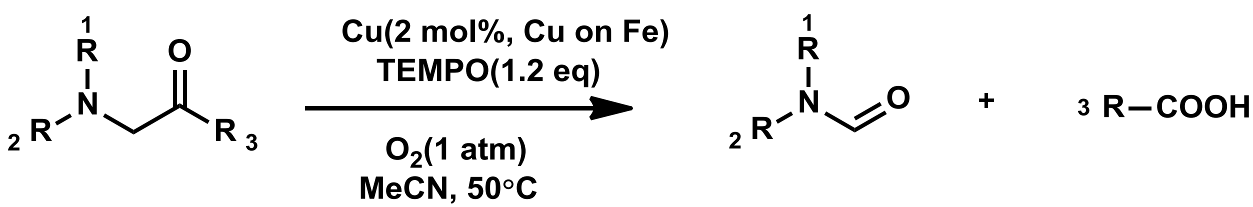
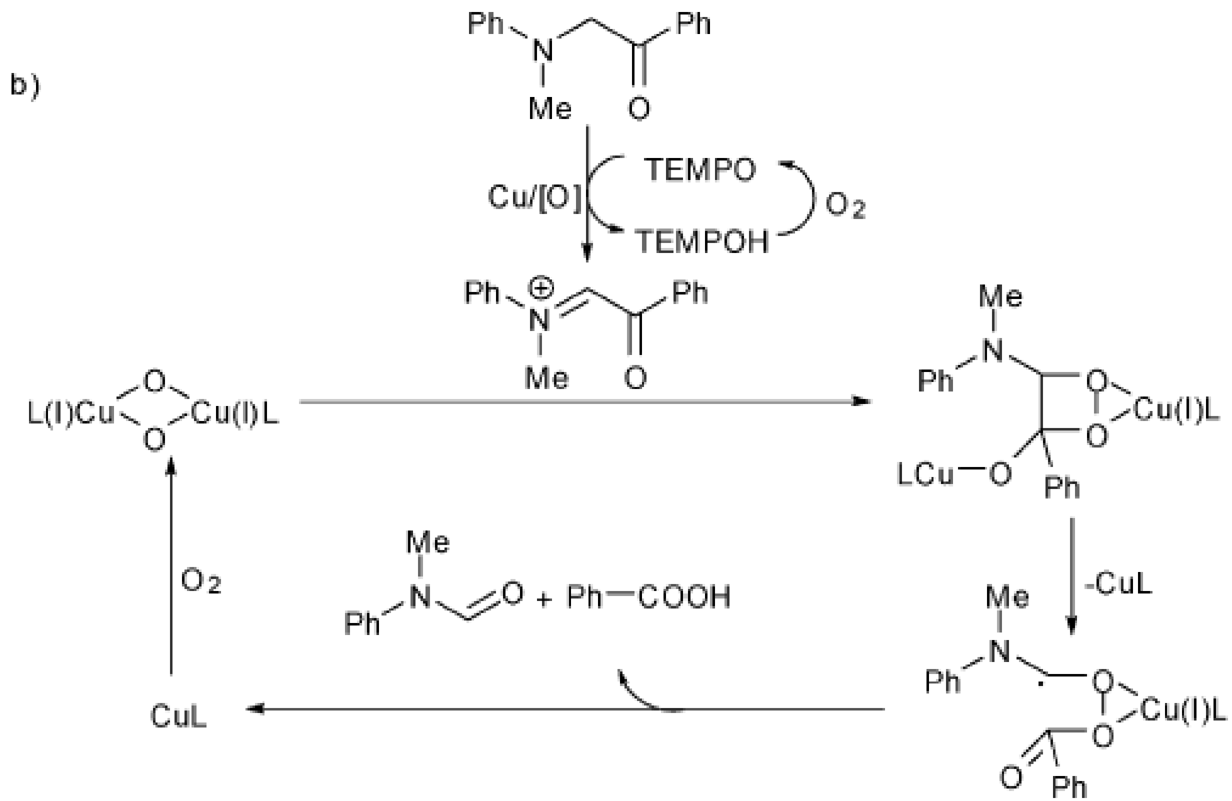


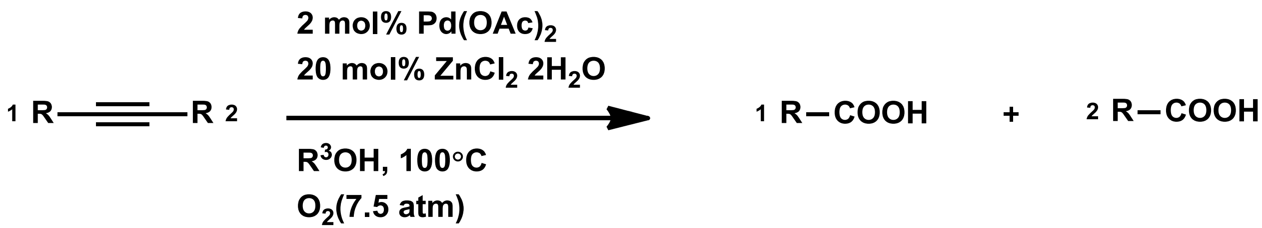
(2)

(1) S. Chiba, *et. al, Org. Lett*. **2010**, *12,* 2052

(2) Y. Wang , *et, al. Chem. Commun*. **2011**, *47*, 3275

The plausible mechanism





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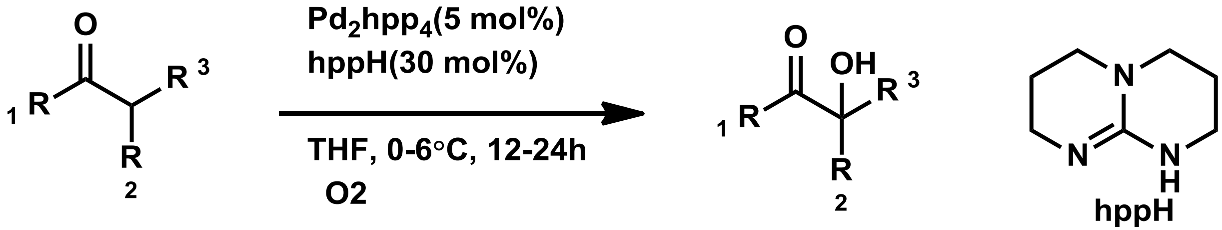

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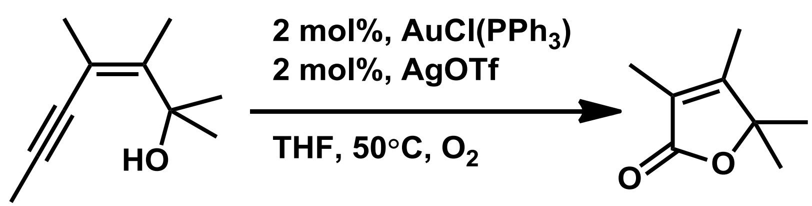
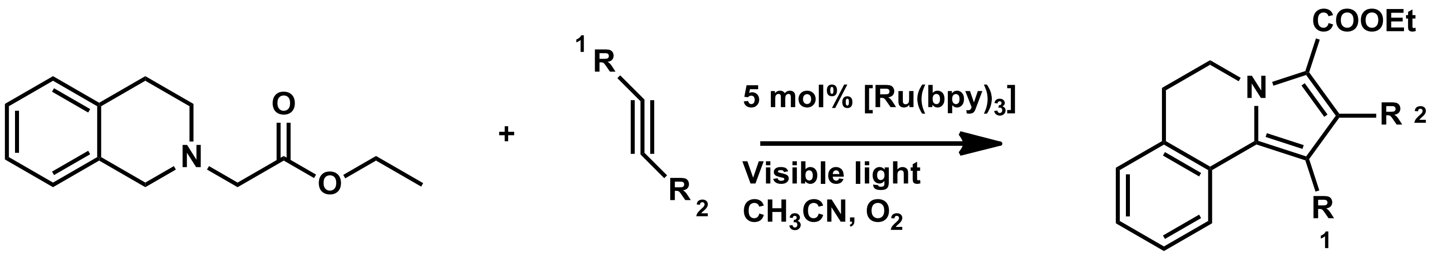


(3)

(1) H. Jiang. *et, al. J. Am. Chem. Soc*. **2008**, *130*, 5030
(2) T. Ritter. *et, al. J. Am. Chem. Soc*. **2011**, *133*, 1760
(3) S. Guo, *et,al. J. Am. Chem. Soc*. **2006***, 128*, 11332

5, Miscellaneous



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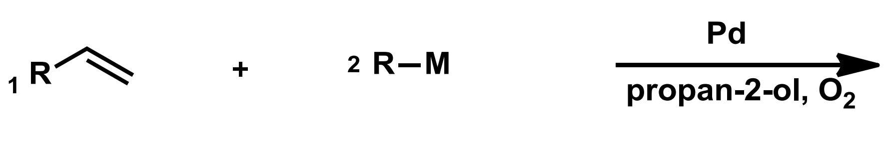

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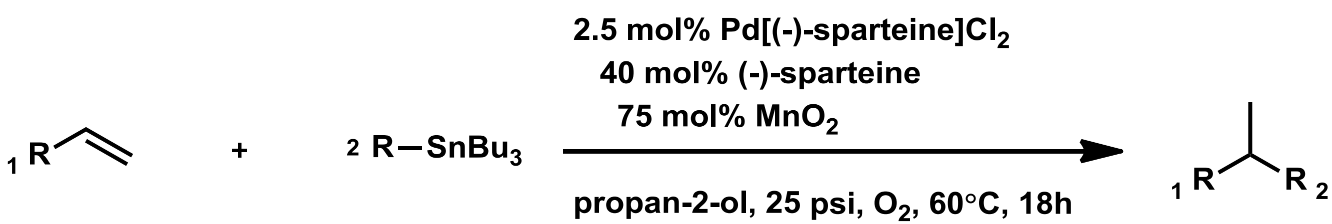
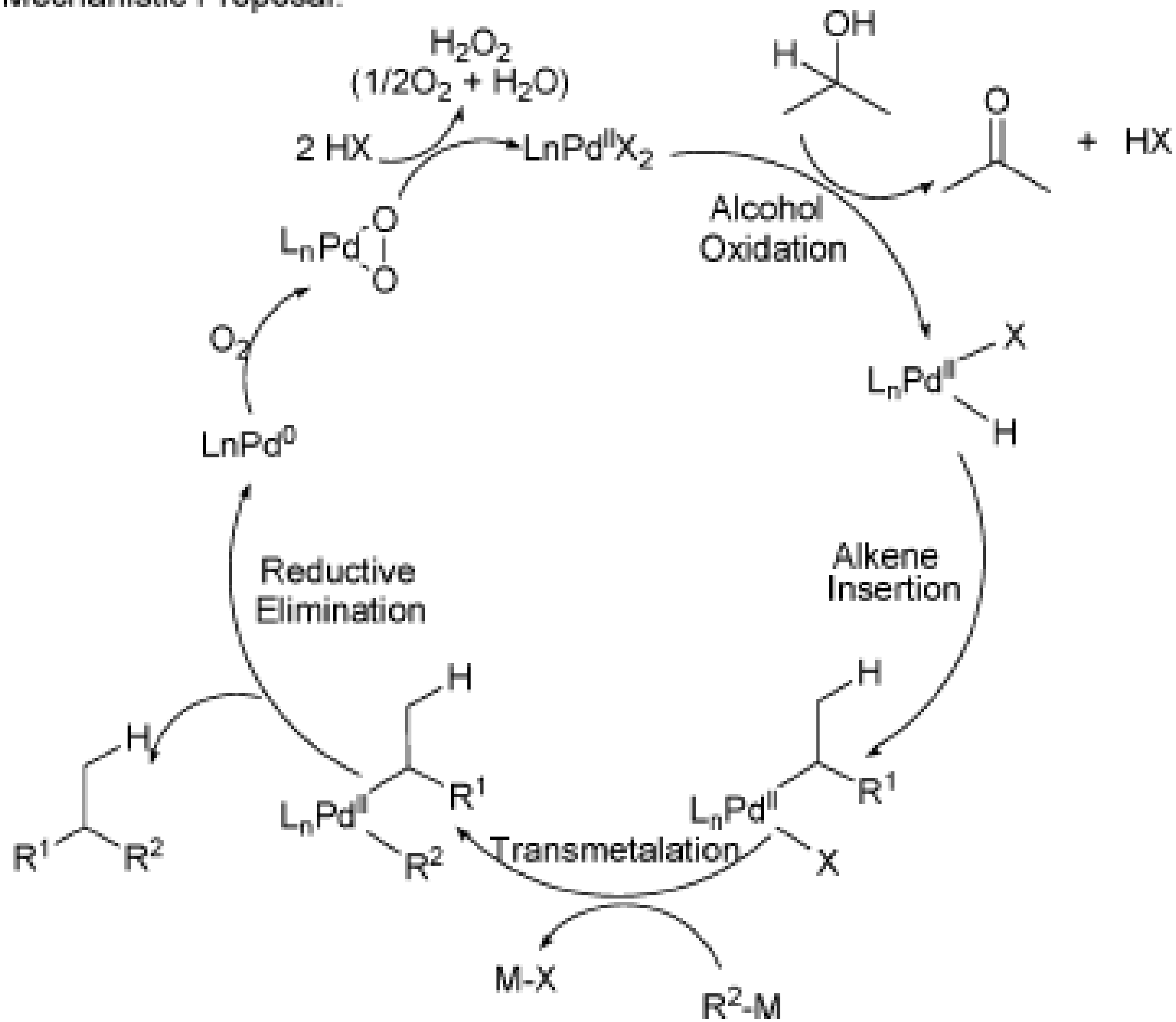


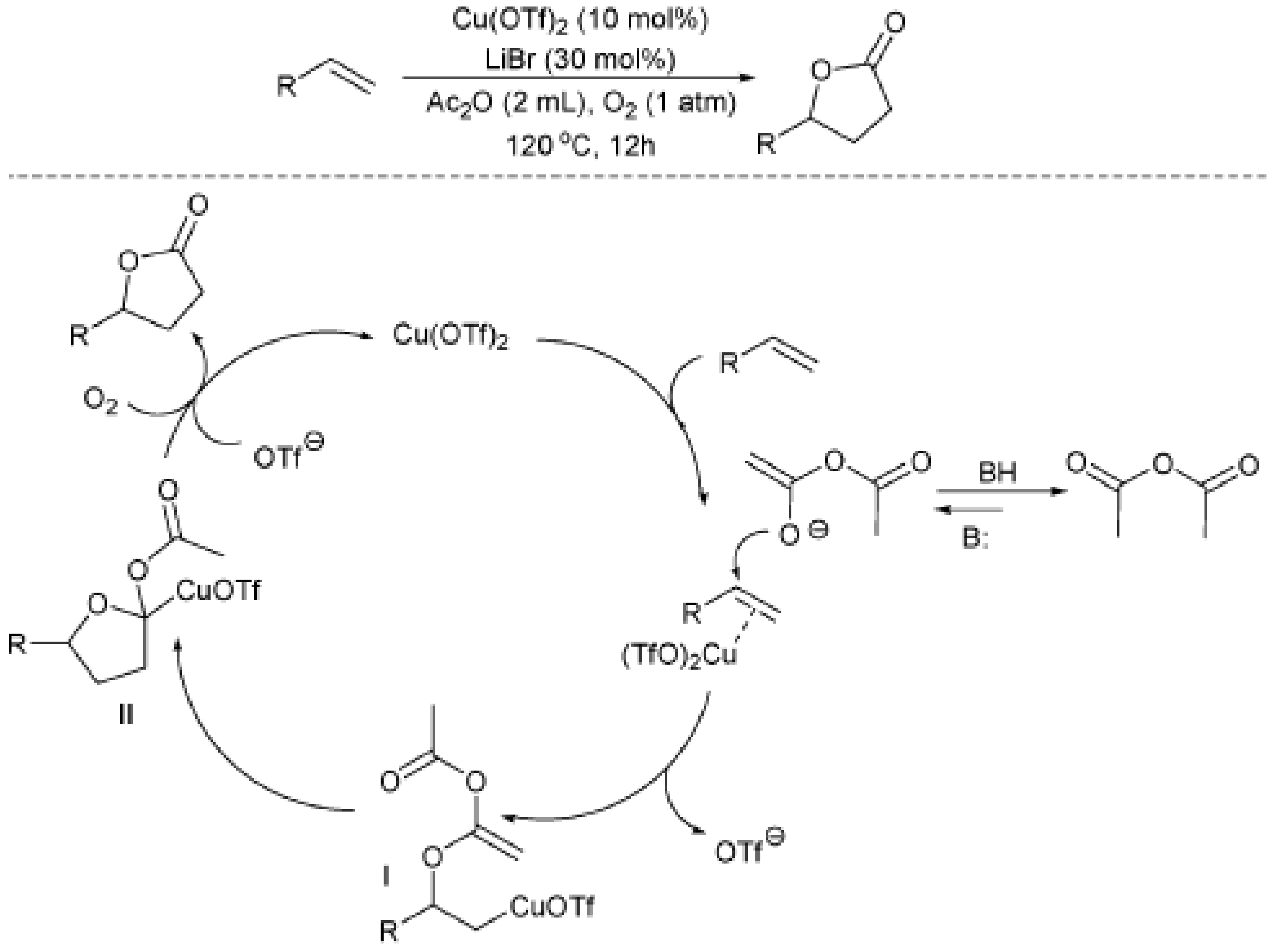
(3)

(1) W. Xiao*, et, al. Angew. Chem. Int. Ed.* **2011***, 50*, 7171
(2) M.S. Sigman. *et, al. J. An. Chem. Soc*. **2007**, *129*, 14193
(3) M.S. Sigman. *et, al. Org. Chem*. **2010**, *12*, 2848

Mechanistic Proposal:



Copper catalyzed intermolecular oxidation [3+2] cycloaddition between alkenes and anhydrides



X. Liu, *et,al. J. Am. Chem. Soc*. **2010**, *132*, 17652

6,Conclusion

- In recent years numerous important advances that have been made in the development of transition-metal catalyzed reactions using molecular oxygen as the oxidant.
- The future seems bright as there are many challenges that remain to be addressed.
- Another clear frontier in this field is asymmetric catalysis.
- Finally, the future development of novel reactions in this field will be closely tied to mechanism investigations.

Thank you for your attention!