Diazo Compounds and *N*-Tosylhydrazones: Novel Cross-Coupling Partners in Transition-Metal-Catalyzed Reactions

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Checker： Lei Shi

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Wang, J. et al. *Acc. Chem. Res.* **2012**, DOI: 10.1021/ar300101k

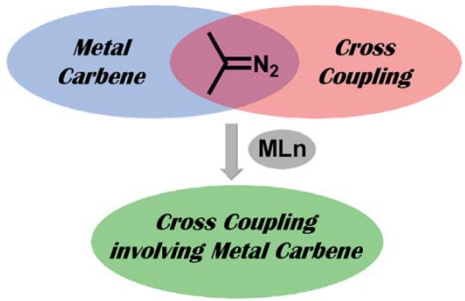
Contents

ACCOUNTS of chemical research

Diazo Compounds and *N*-Tosylhydrazones: Novel Cross-Coupling Partners in Transition-Metal-Catalyzed Reactions

QING XIAO, YAN ZHANG, AND JIANBO WANG*

- **Can cross-coupling and metal carbene transformations bemerged into a single reaction cycle?**



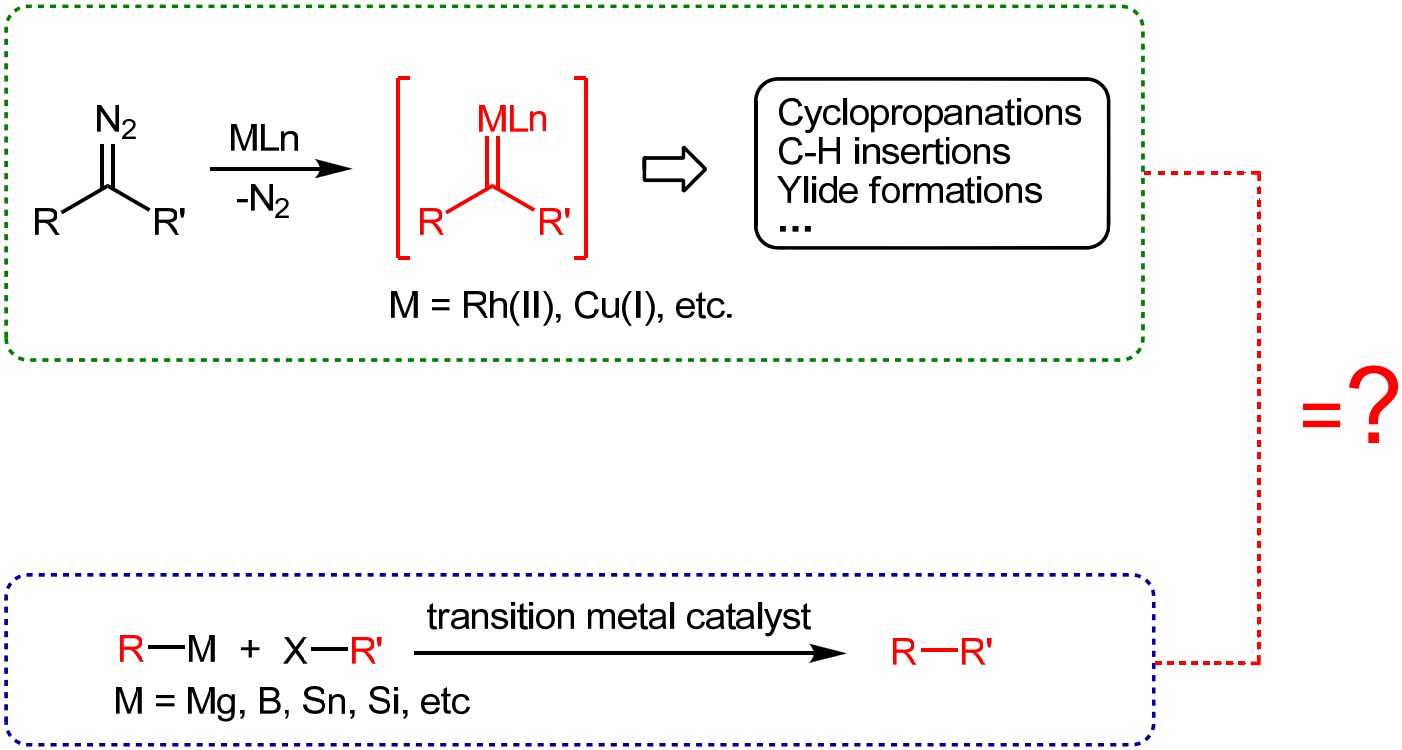
- **How many kinds of transition metals are effective in this cross-coupling reaction?**

  Pd, Cu, Rh, Ni, Co…

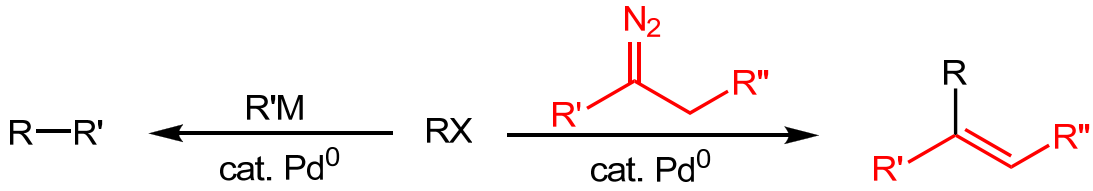
- **The perspective of this novel cross-coupling compared with classic ones.**

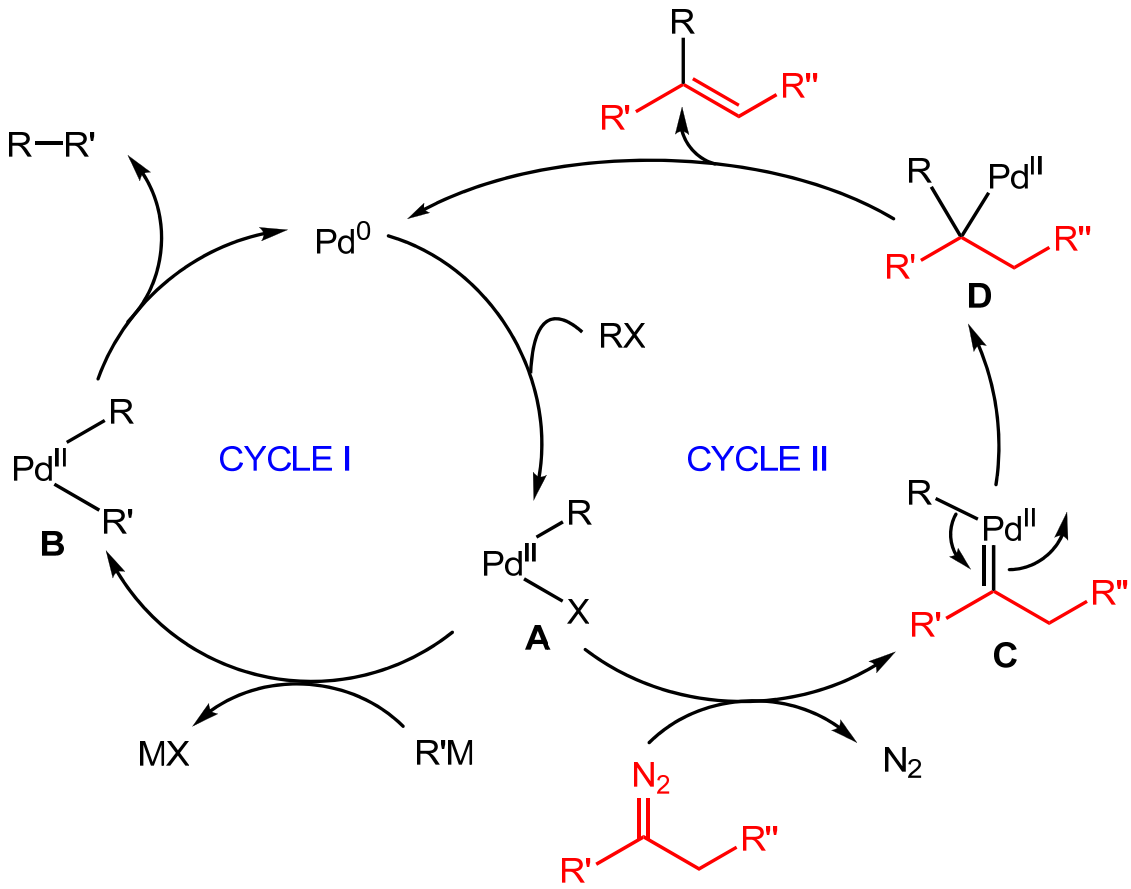
  Heck-Mizoroki reaction, Shapiro reaction…

Conspectus


N2
R
R'
MLn
-N2
MLn
R
R'
Cyclopropanations
C-H insertions
Ylide formations
...
M = Rh(II), Cu(I), etc.
=?
R—M + X—R'
transition metal catalyst
R—R'
M = Mg, B, Sn, Si, etc

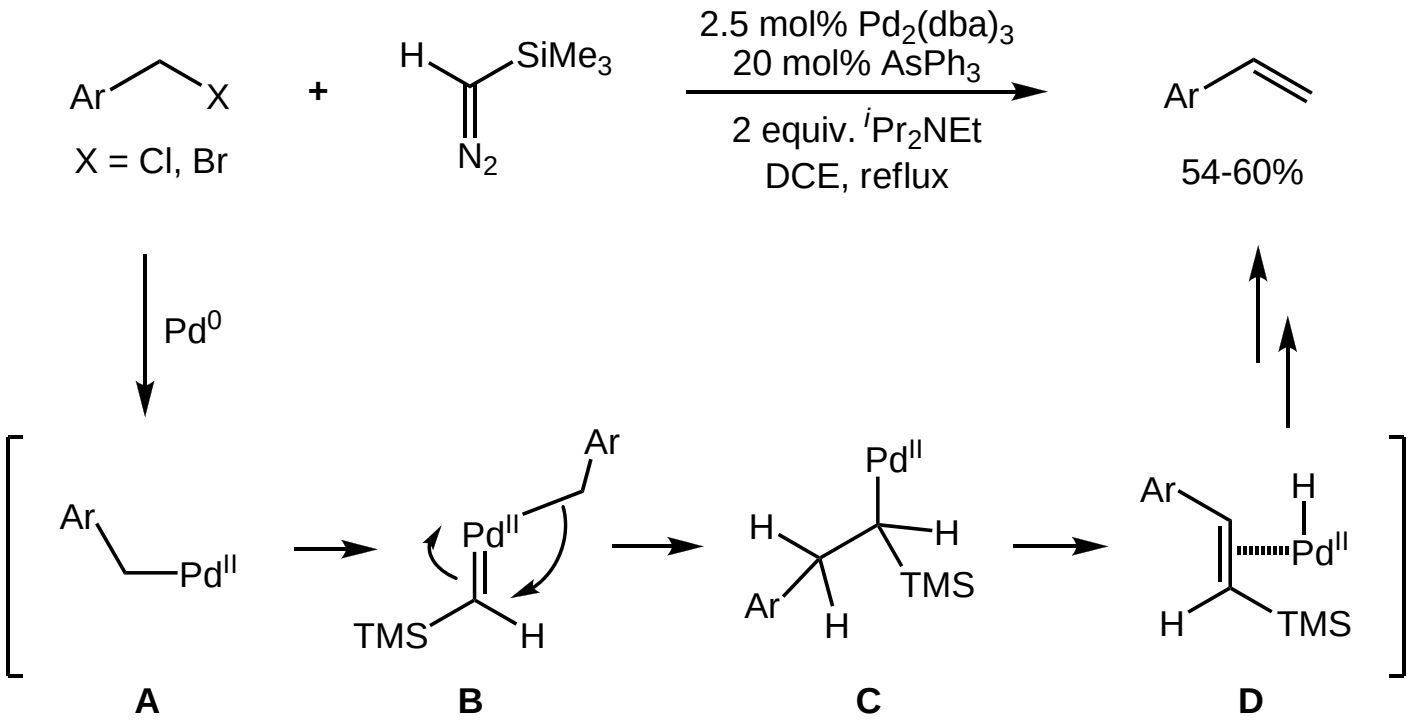
Standard Cross-Coupling *vs* the Coupling Involving a Carbene Process





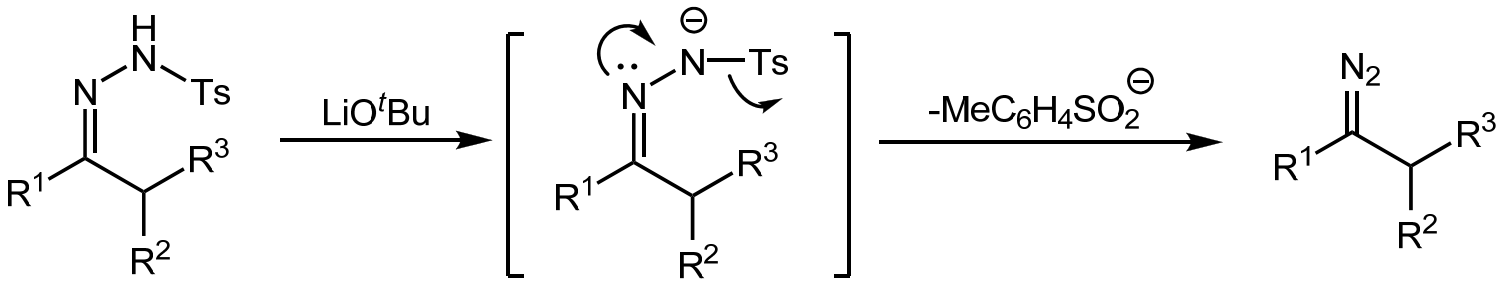
standard coupling *Coupling invoving carbene*

Pd-Catalyzed Cross-Coupling Reaction between Benzyl Halides and $TMSCHN_2$



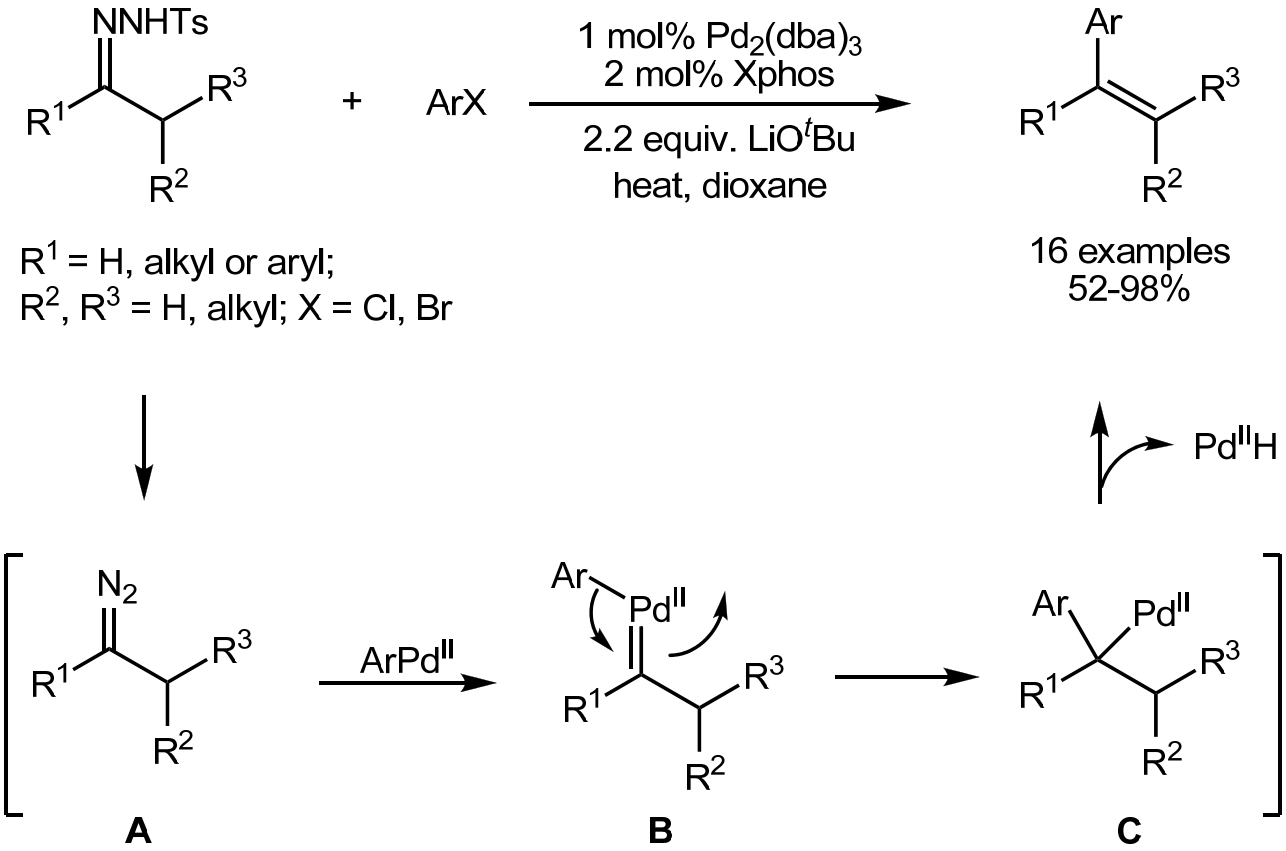
Van Vranken, D. L. et al. *Tetrahedron* **2001**, *57*, 5219–5225

N-tosylhydrazones: generate unstable diazo compounds *in situ*



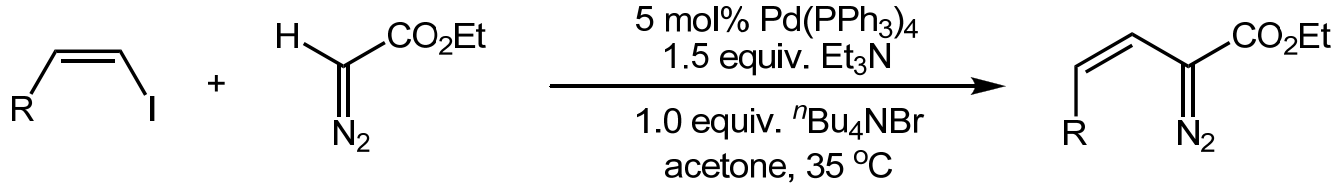
N-tosylhydrazones have been proven to be very useful for the *in situ* generation of nonstabilized diazo compounds through Bamford-Stevens reaction.

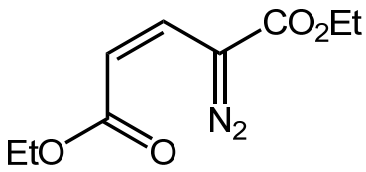
Pd-Catalyzed Cross-Coupling of *N*-Tosylhydrazones



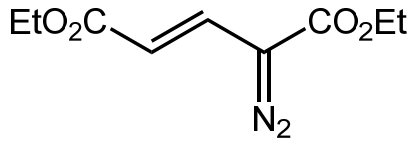
Barluenga, J. et al. *Angew. Chem. Int. Ed.* **2007**, *46*, 5587–5590

Pd-Catalyzed Cross-Coupling of Vinylhalides with EDA

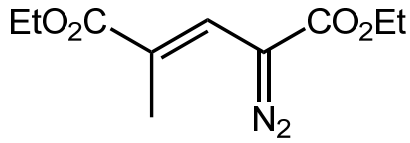




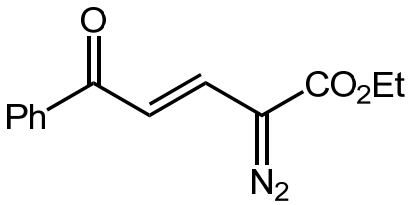
86%



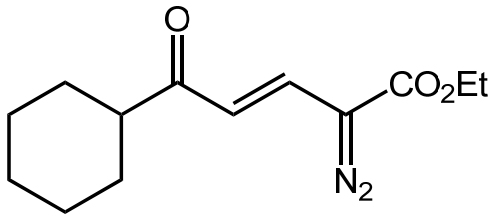
75%



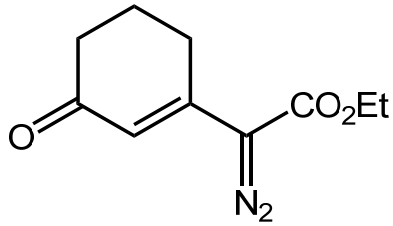
88%



55%



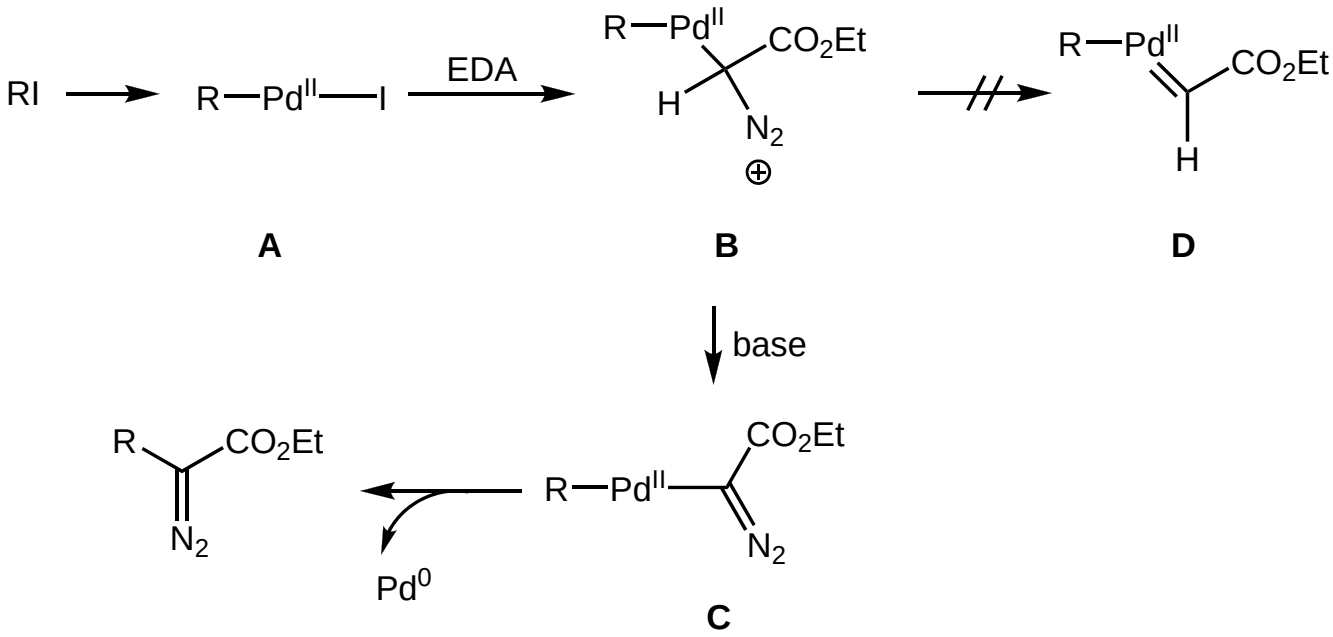
48%



78%

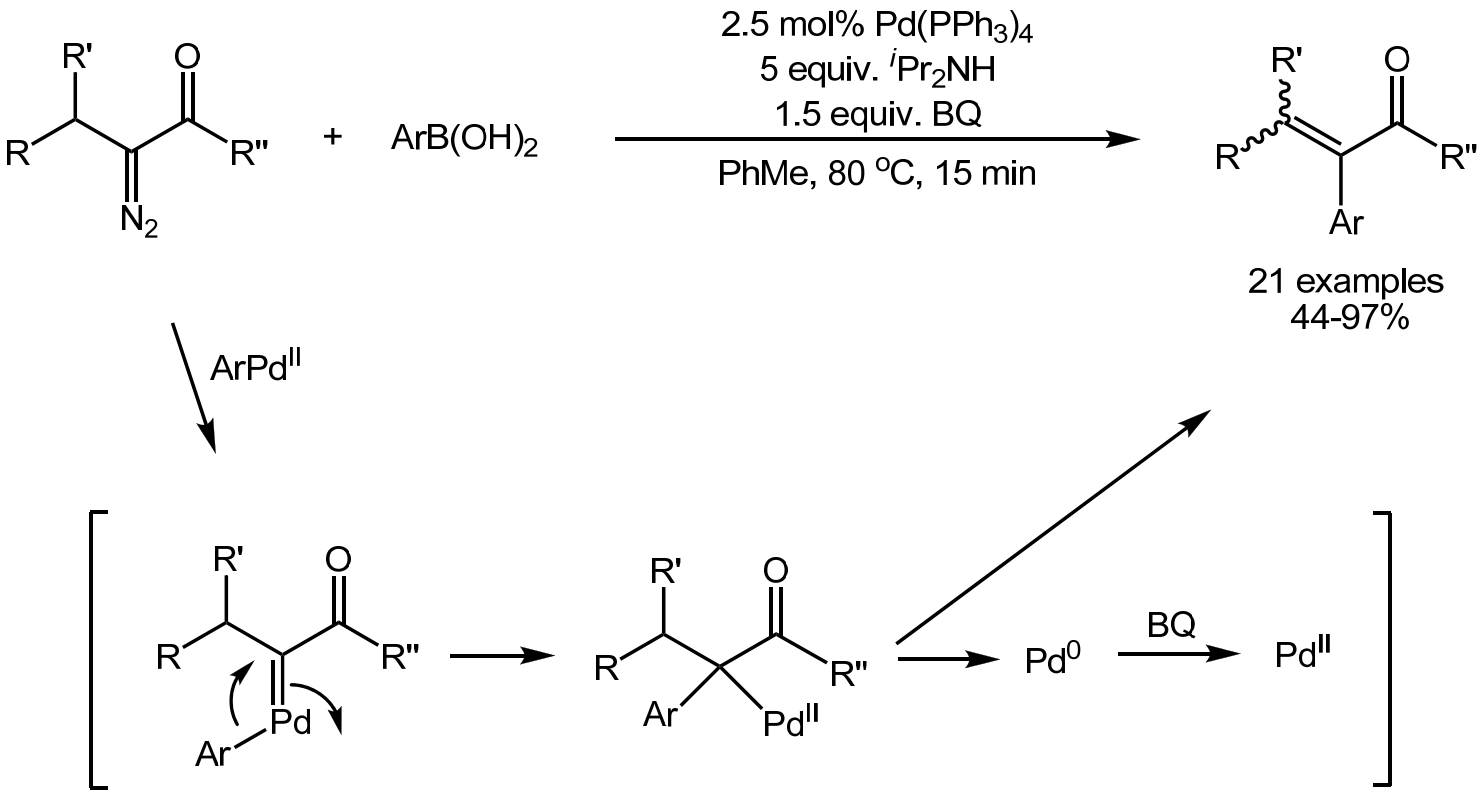
Wang, J. et al. *J. Am. Chem. Soc.* **2007**, *129*, 8708–8709

The Mechanism of Pd-Catalyzed Cross-Coupling of Iodides with EDA



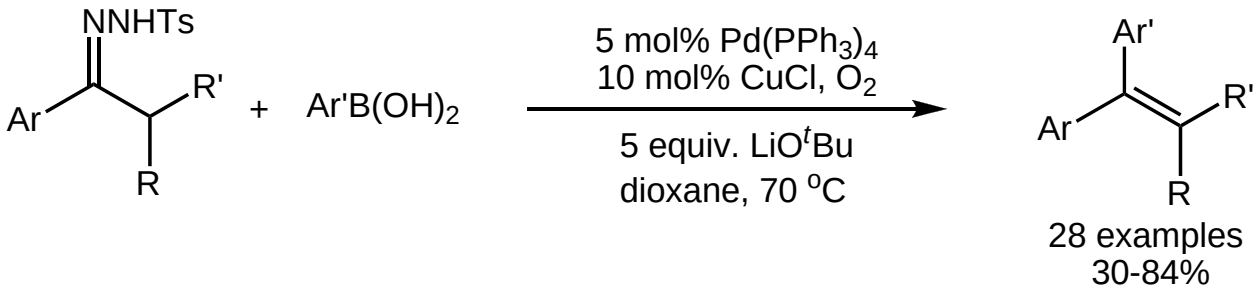
Wang, J. et al. *J. Am. Chem. Soc.* **2007**, *129*, 8708–8709

Pd-Catalyzed Oxidative Cross-Coupling between Boronic Acids and α-Diazocarbonyl Compounds



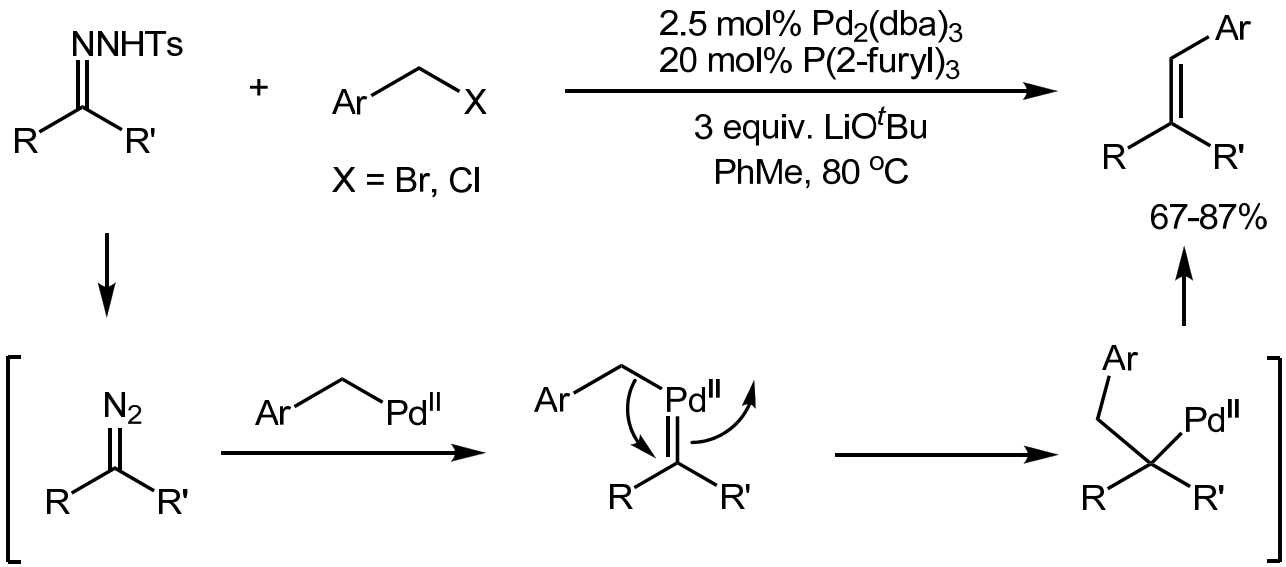
Wang, J. et al. *J. Am. Chem. Soc.* **2008**, *130*, 1566–1567

Pd-Catalyzed Oxidative Cross-Coupling between Boronic Acids and *N*-Tosylhydrazones



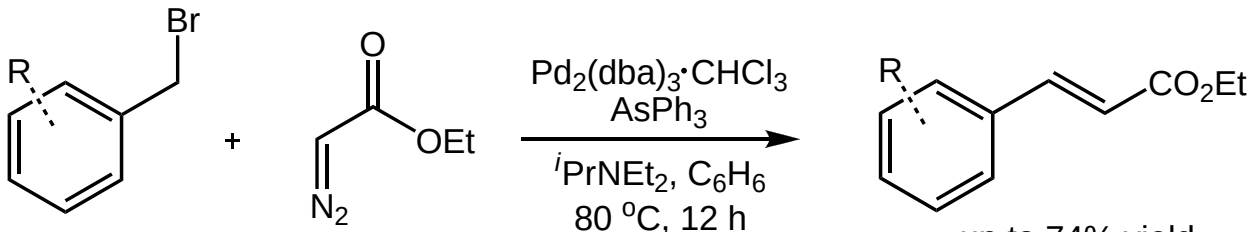
Wang, J. et al. *Chem. Commun.* **2010**, *46*, 1724–1726

Pd-Catalyzed Cross-Coupling between Benzylhalides and *N*-Tosylhydrazones



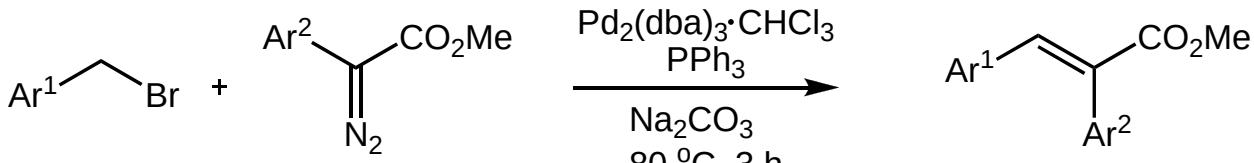
Wang, J. et al. *Org. Lett.* **2009**, *11*, 4732–4735

Pd-Catalyzed Cross-Coupling between Benzylhalides and Diazo Compounds



up to 74% yield

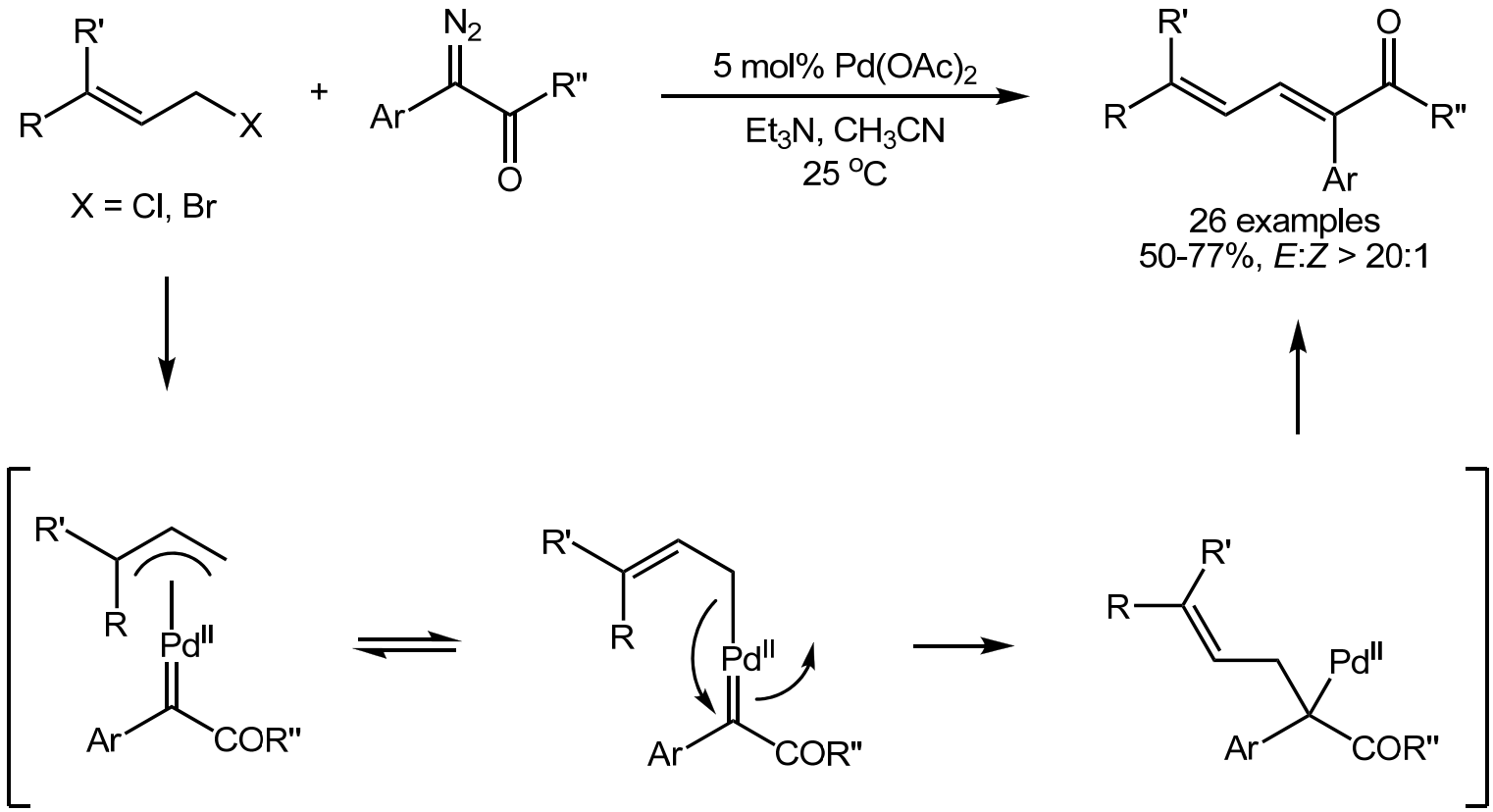
Van Vranken, D. L. et al. *Tetrahedron* **2005**, *61*, 6438–6441



E/*Z* ratio >20:1
up to 88% yield

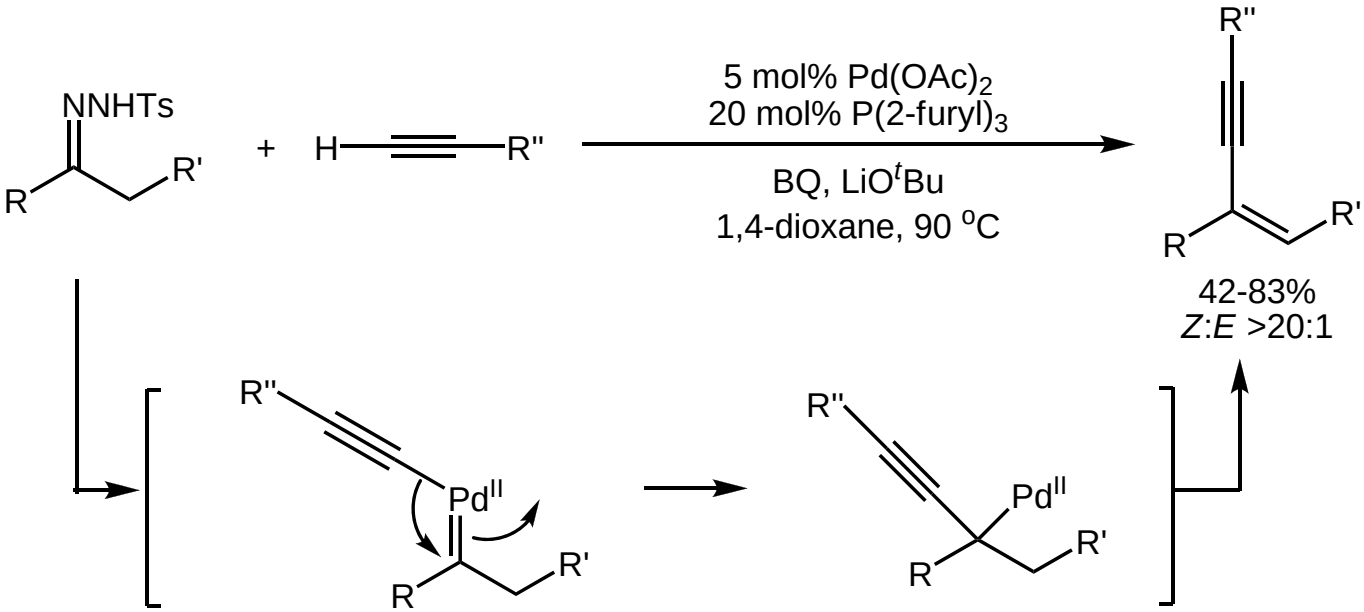
Yu, W.-Y. et al. *Org. Lett.* **2009**, *11*, 469–472

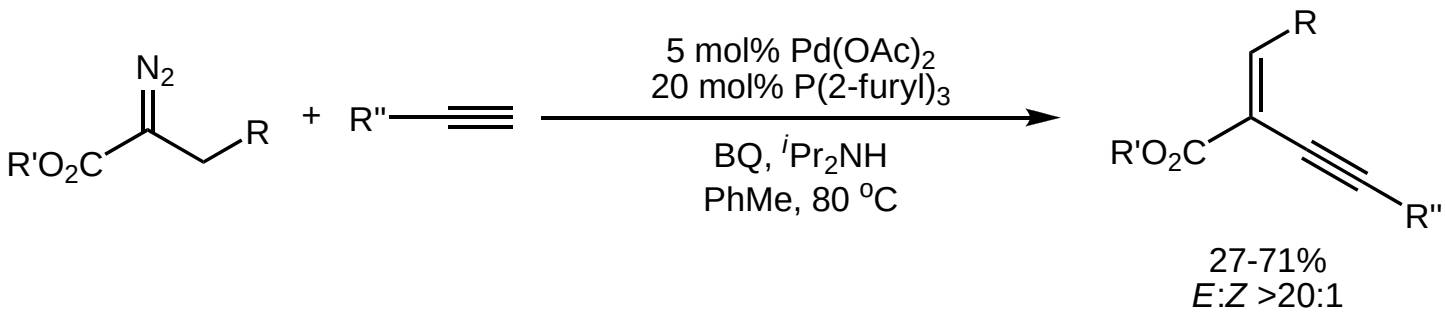
Pd-Catalyzed Cross-Coupling of Diazo Compounds with Allylhalides



Wang, J. et al. *Chem. Commun.* **2008**, 4198–4200

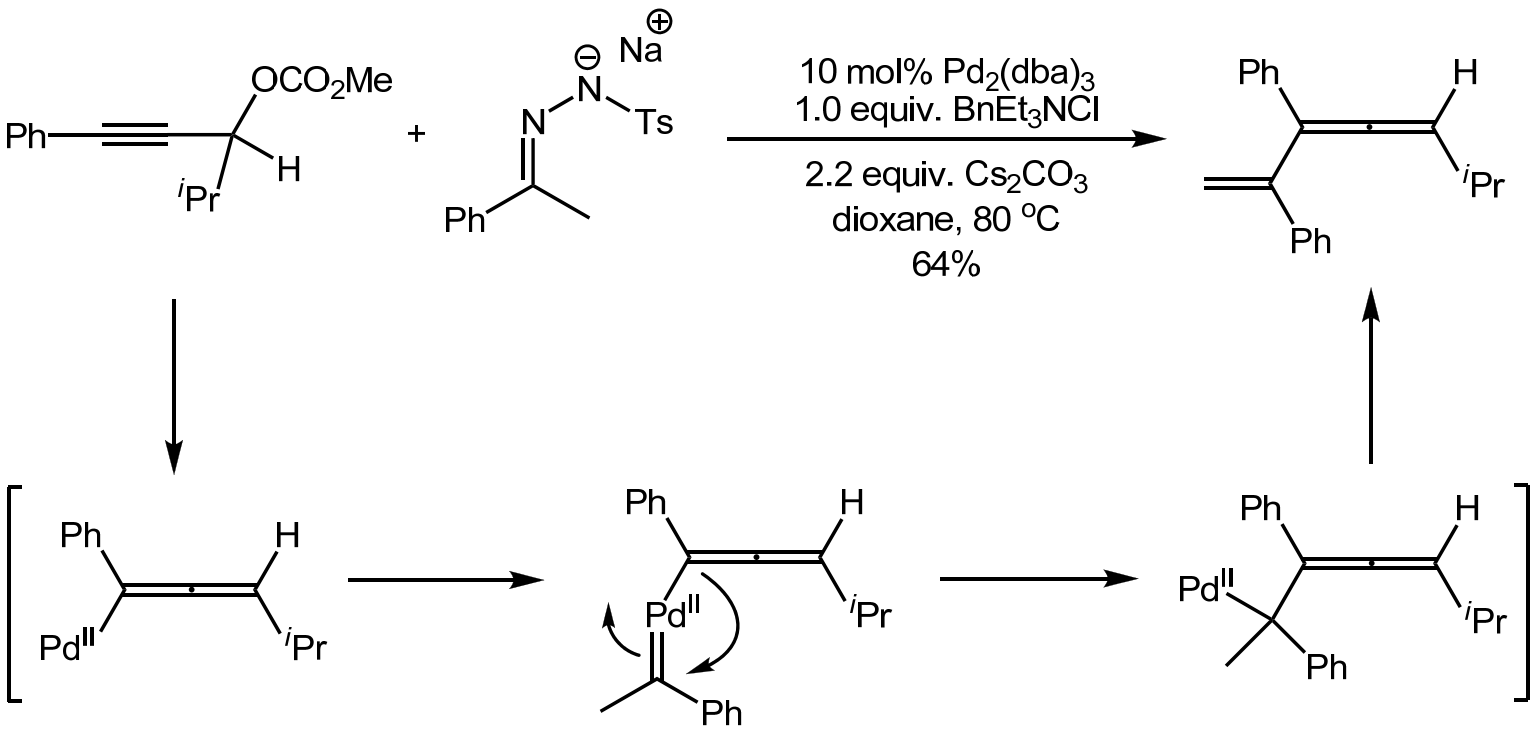
Pd-Catalyzed Oxidative Cross-Coupling of *N*-Tosylhydrazones with Terminal Alkynes





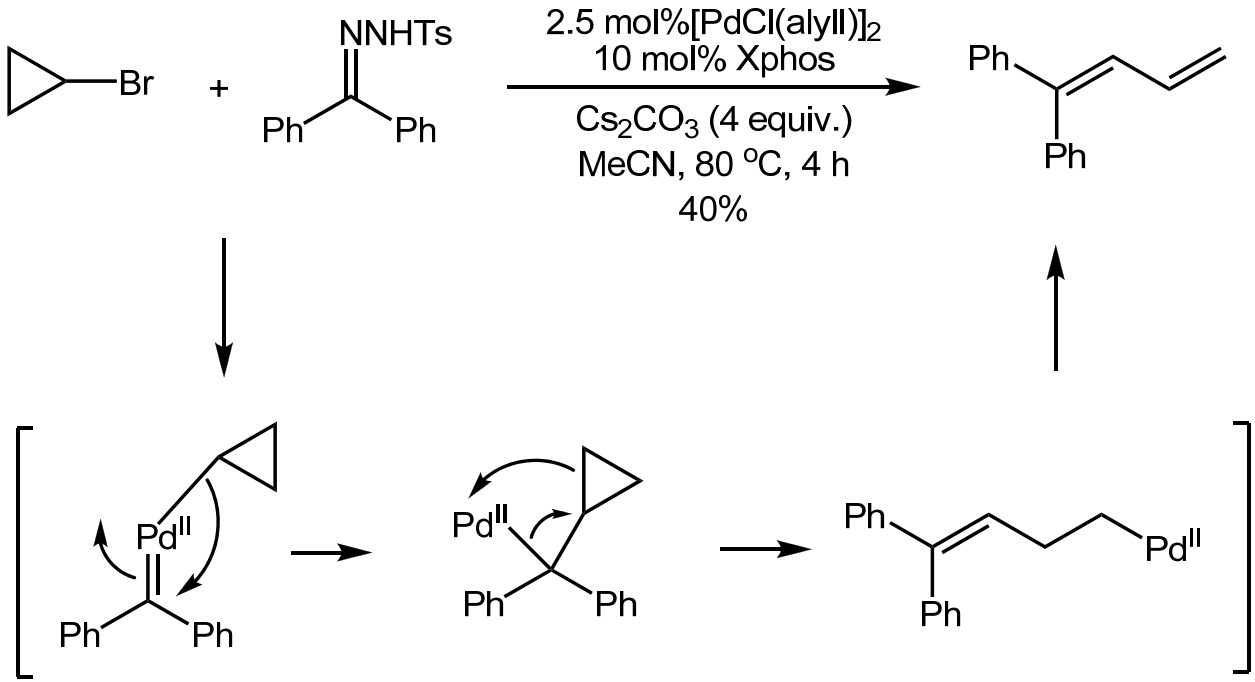
Wang, J. et al. *Angew. Chem. Int. Ed.* **2011**, *50*, 3510–3514

Migratory Insertion Allenyl Group in Pd-Catalyzed Reaction



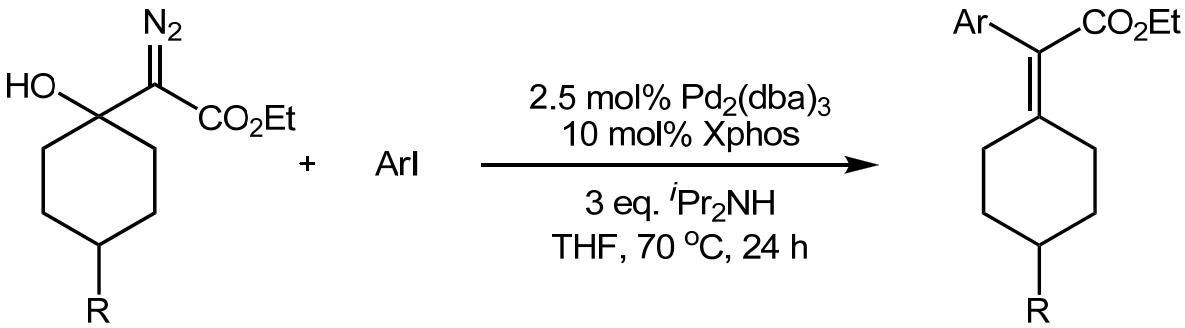
Liang, Y.-M. et al. *Chem. Eur. J.* **2011**, *17*, 6918–6921

Migratory Insertion Cyclopropyl Group in Pd-Catalyzed Reaction



Wang, J. et al. *Org. Lett.* **2012**, *14*, 922–925

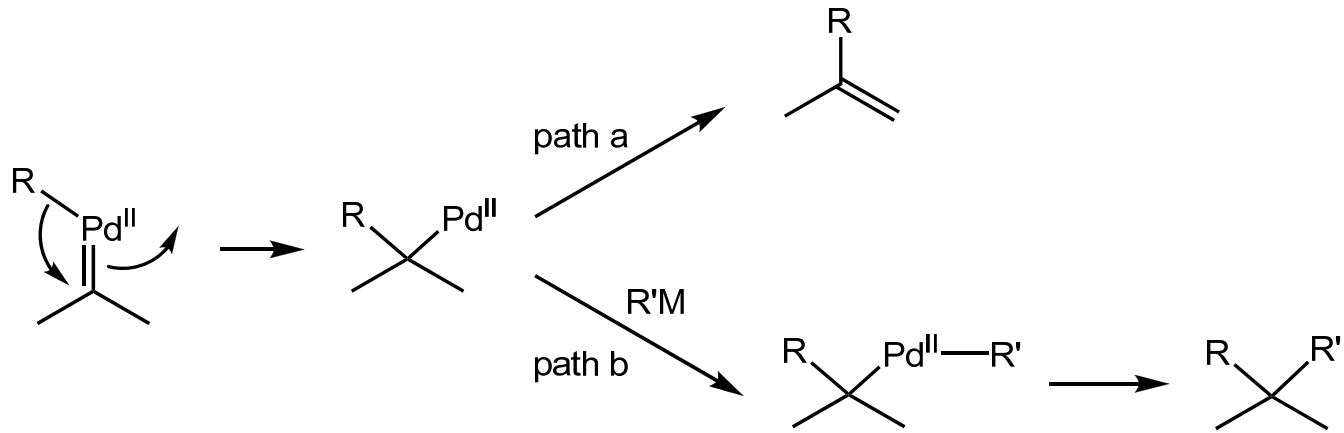
Migratory insertion/β-hydroxy elimination sequence in Pd-Catalyzed Reaction



up to 86% yield

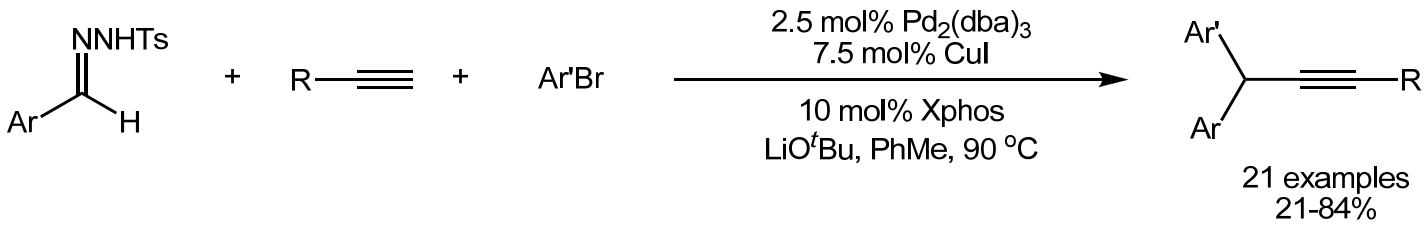
Wang, J. et al. *Chem. Commun.* **2011**, *47*, 3622–3624

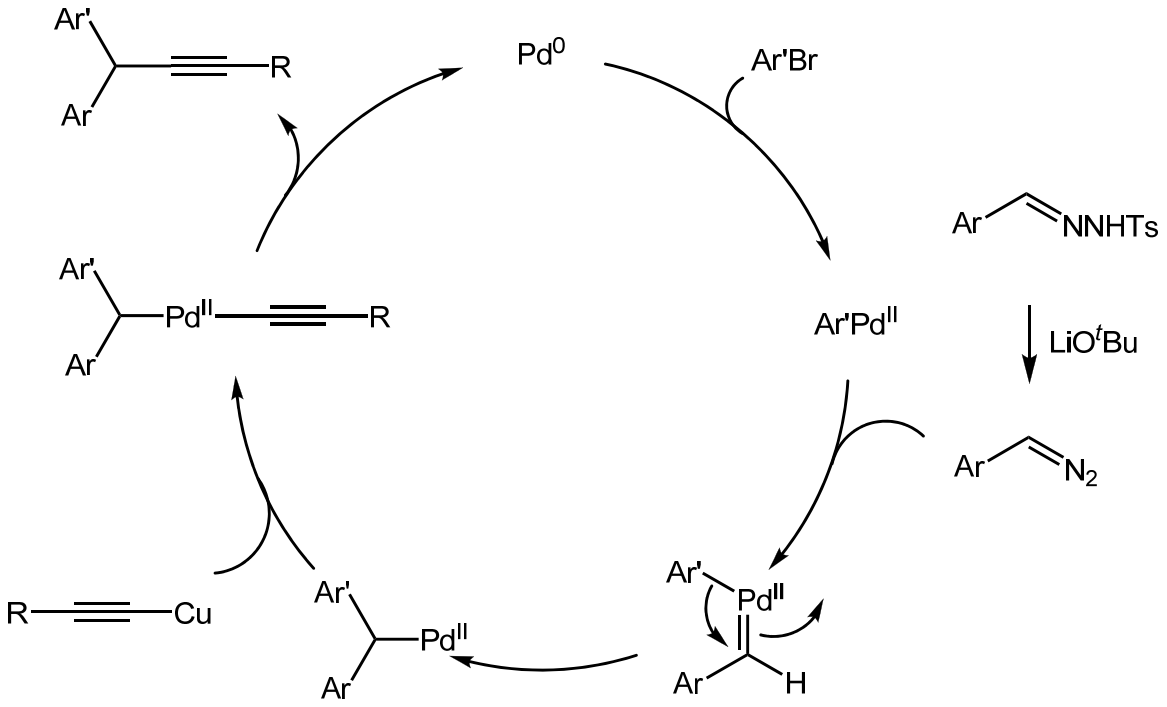
β-Hydrogen Elimination *vs* Transmetalation



In the catalytic cycle of the cross-coupling reactions described above, the alkyl palladium species, which are formed by migratory insertion, typically undergo β-hydrogen elimination to give rise to the final products with the formation of C=C. However, when the β-hydrogens are not available, it may be possible to undergo a cascade process, such as a transmetalation with an organometallic reagent and subsequent reductive elimination to form two separate C-C in a carbenic center.

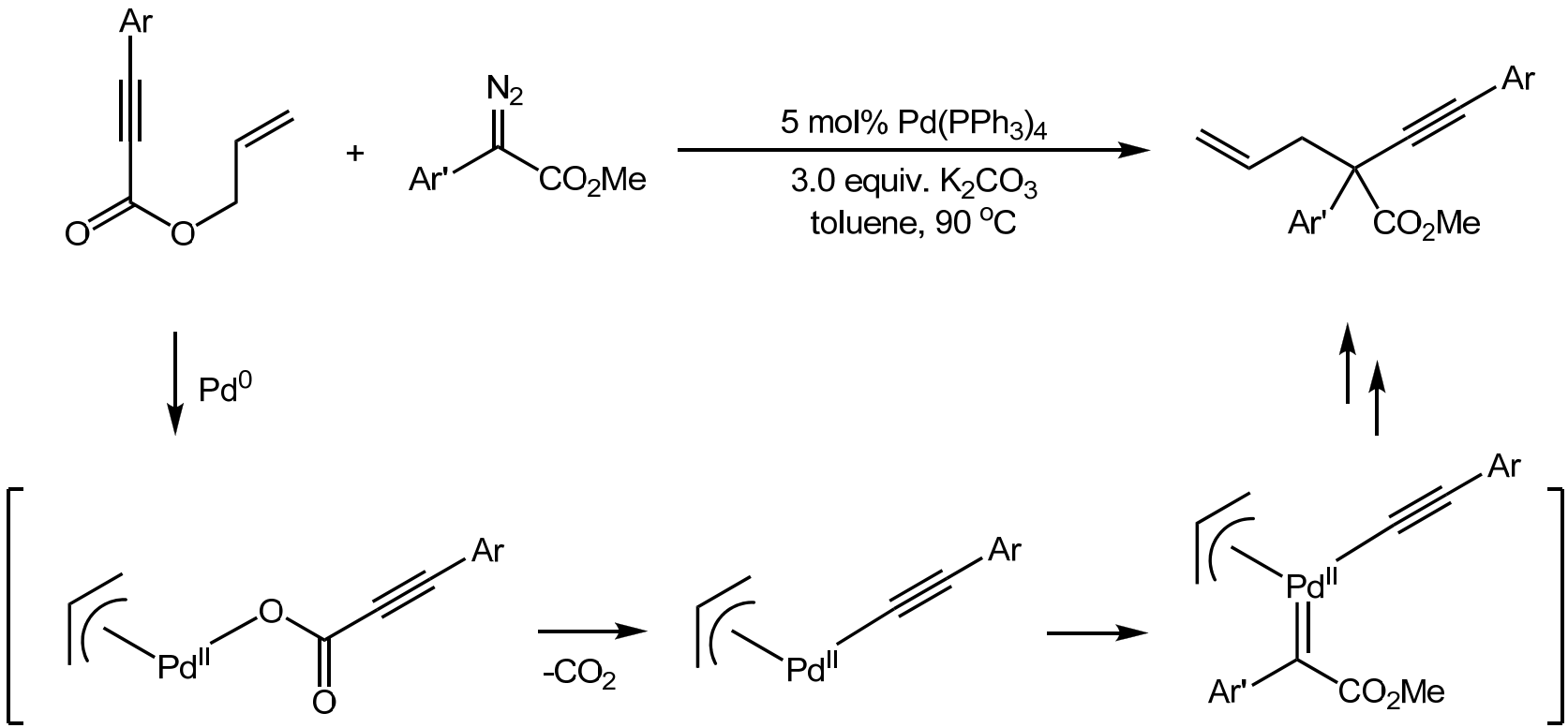
Pd-Catalyzed Three-Component Cross-Coupling Reaction





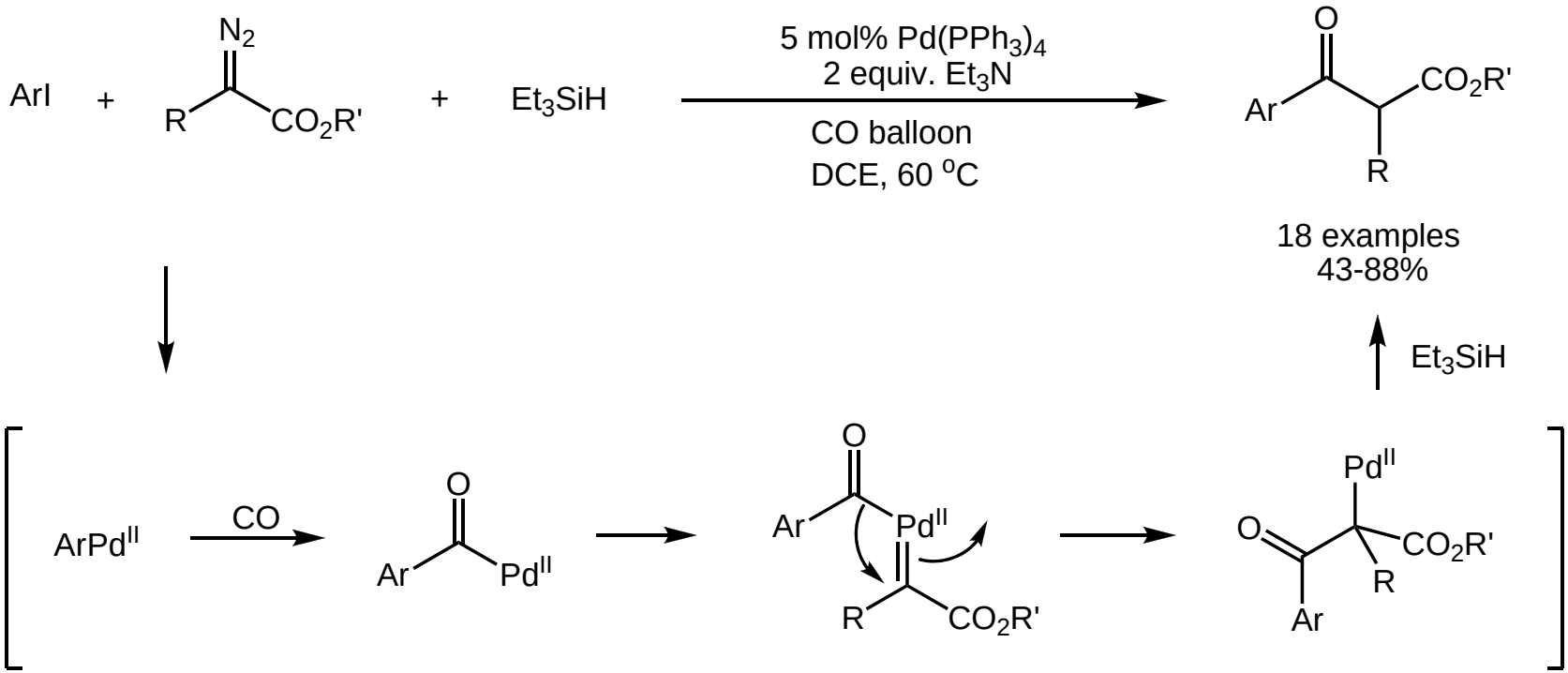
Wang, J. et al. *J. Am. Chem. Soc.* **2010**, *132*, 13590-23591

Pd-Catalyzed Decarboxylation/Migratory Insertion/Reductive Elimination Cascade



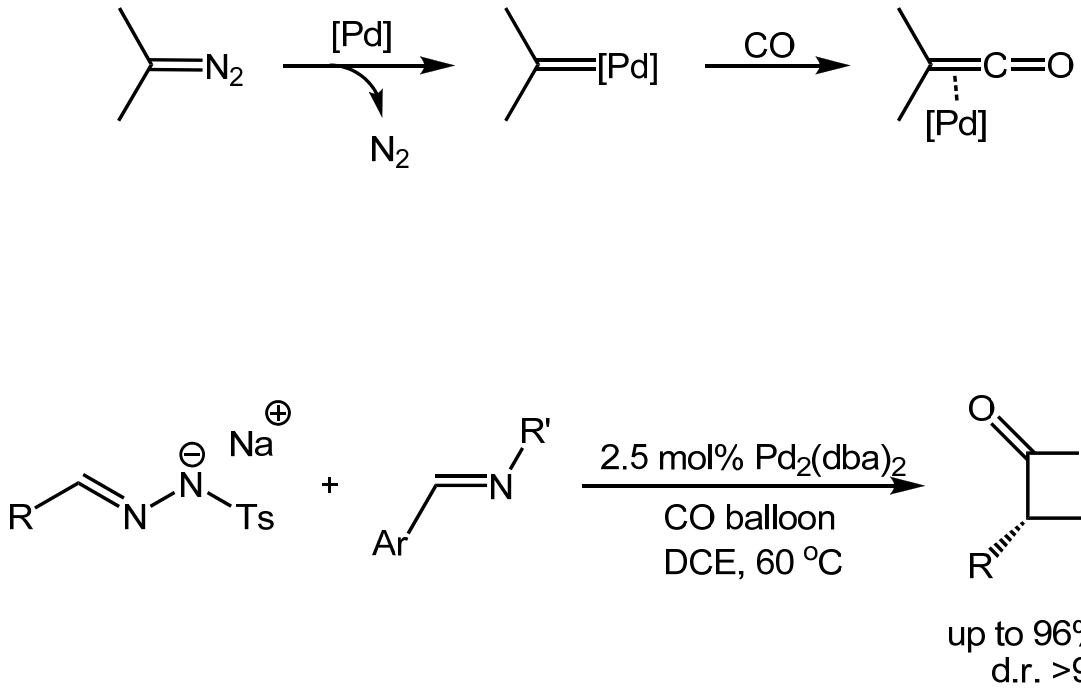
Liang, Y.-M. et al. *Angew. Chem. Int. Ed.* **2012**, *51*, 1370-1374

Pd-Catalyzed Carbonylation/Acyl Migratory Insertion Cascade



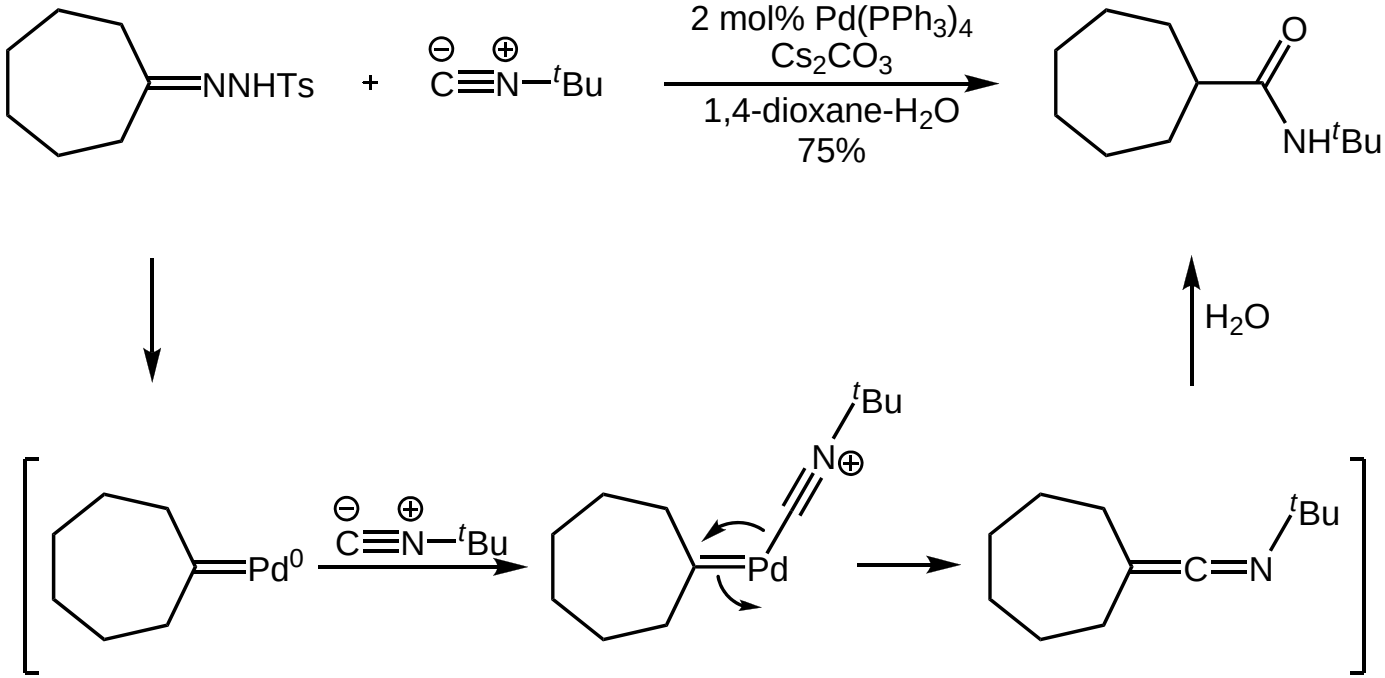
Wang, J. et al. *Angew. Chem. Int. Ed.* **2010**, *49*, 1139-1142

Pd-Catalyzed Carbonylation Staudinger Cycloaddition: β-Lactam Synthesis



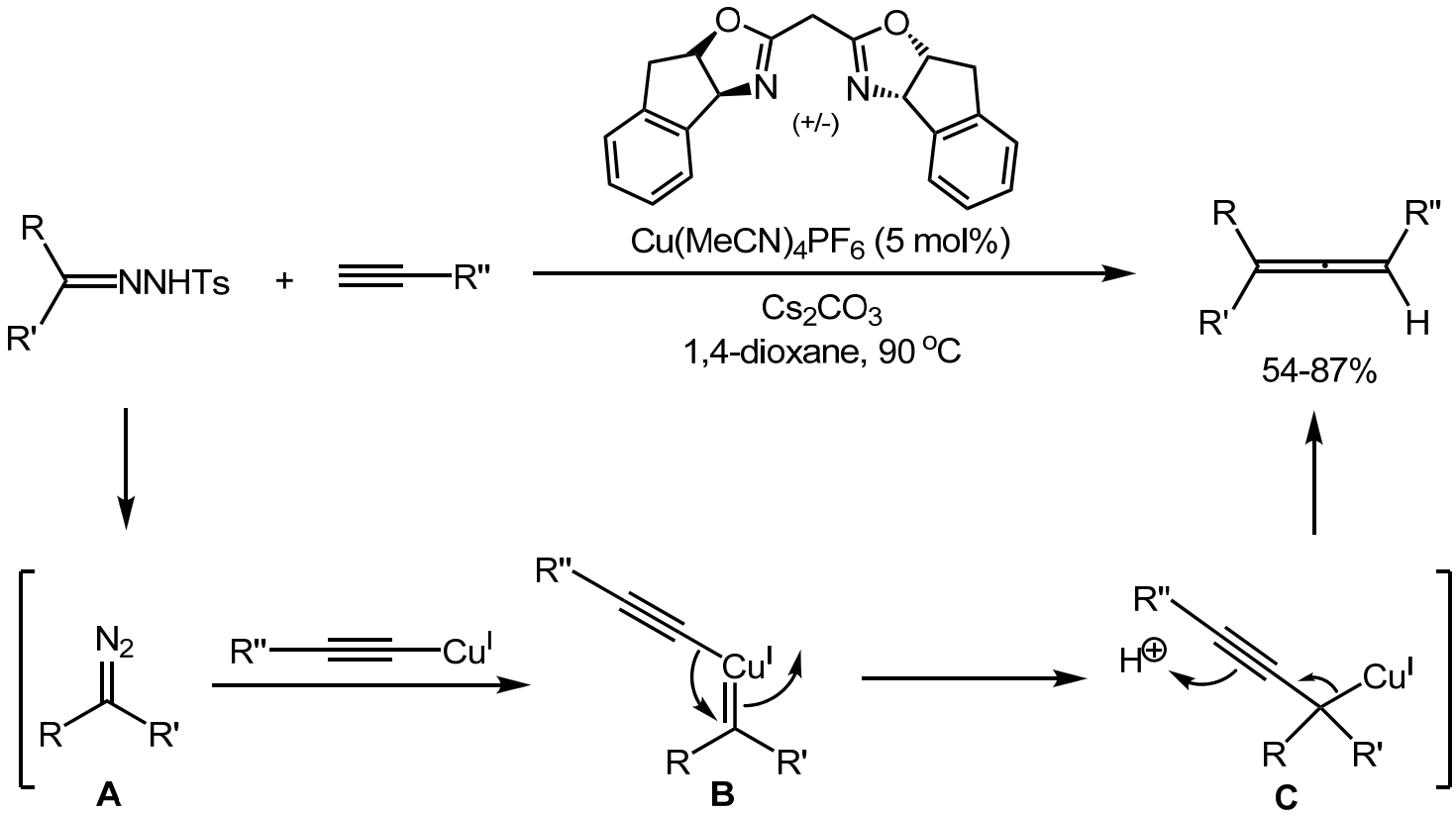
Wang, J. et al. *J. Am. Chem. Soc.* **2011**, *133*, 4330–4341
ACS Catal. **2011**, *1*, 1621–1630

Pd-Catalyzed Amidation of *N*-Tosylhydrazones with Isocyanides



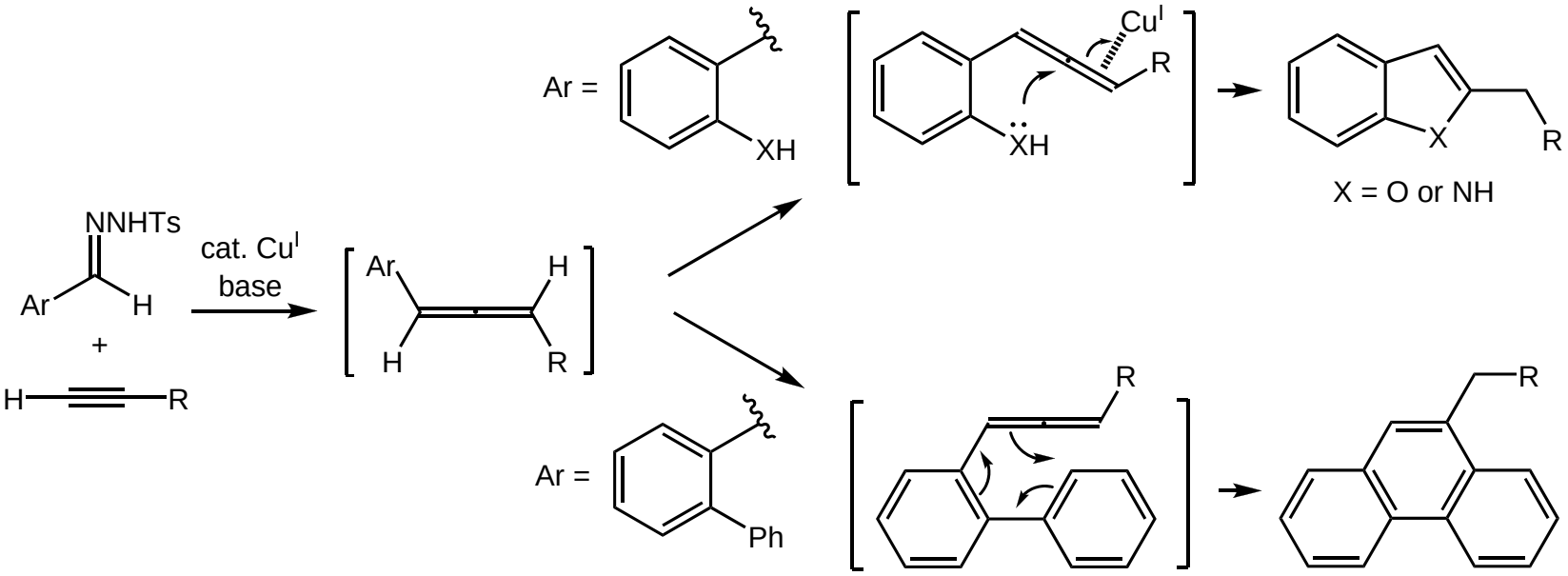
Ding, K. et al. *Chem. Eur. J.* **2011**, *17*, 12268–12271

Cu(I)-Catalyzed Coupling of *N*-Tosylhydrazones with Terminal Alkynes

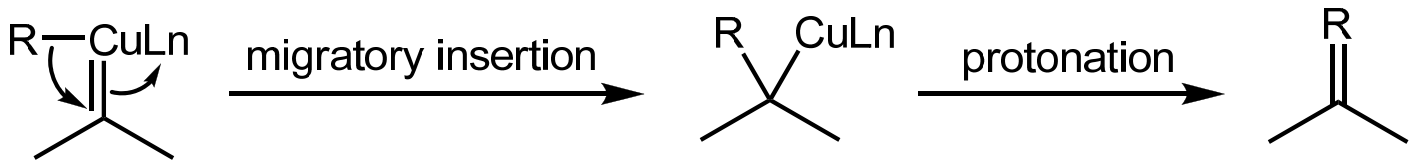


Wang, J. et al. *Angew. Chem. Int. Ed*. **2011**, *50*, 1114–1117

Cu-Catalyzed Synthesis of Benzofurans, Indoles, and Phenanthrenes

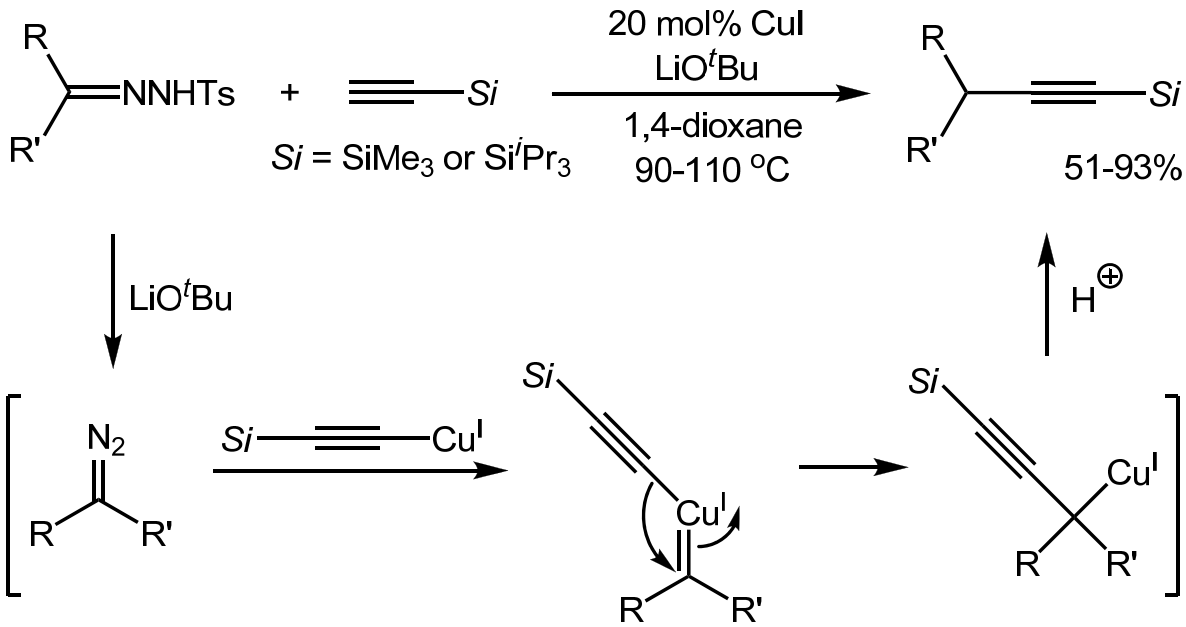


Wang, J. et al. *Org. Lett*. **2011**, *13*, 5020-5023



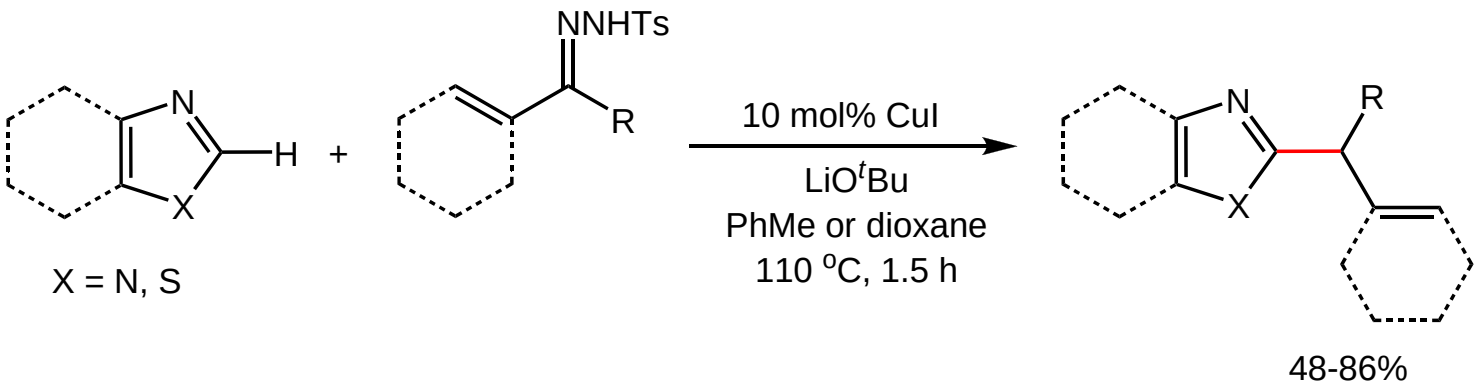
The sequence of migratory insertion/protonation from Cu(I) carbene, provides a new possibility for $C(sp^2)$-$C(sp^3)$ and C(sp)-$C(sp^3)$ single bond formation.

Cu-Catalyzed C(sp)-C(sp^3) Bond Formation



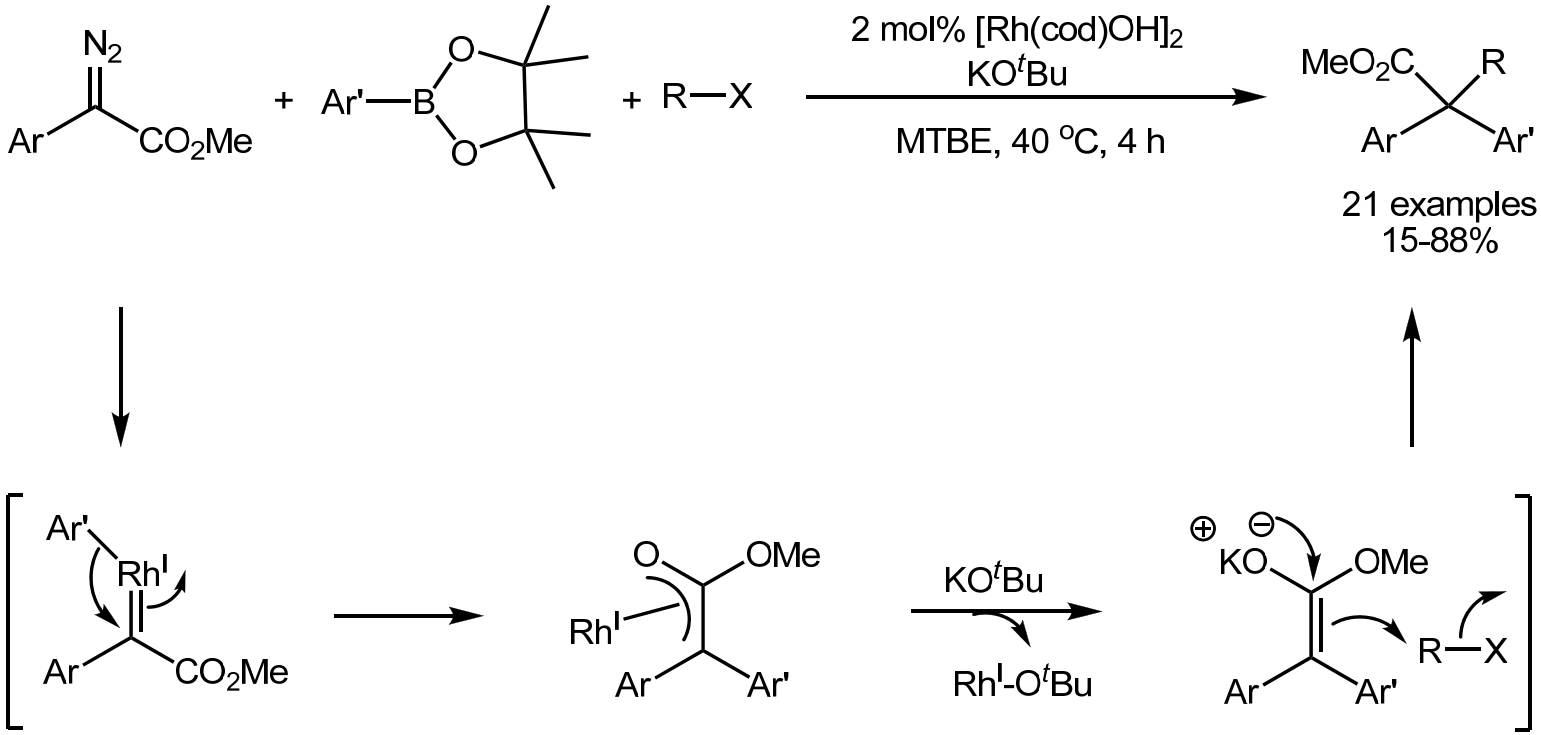
Wang, J. et al. *J. Am. Chem. Soc.* **2012**, *134*, 5742–5745

Cu(I)-Catalyzed Direct Benzylation or Allylation of 1,3-Azoles with *N*-Tosylhydrazones



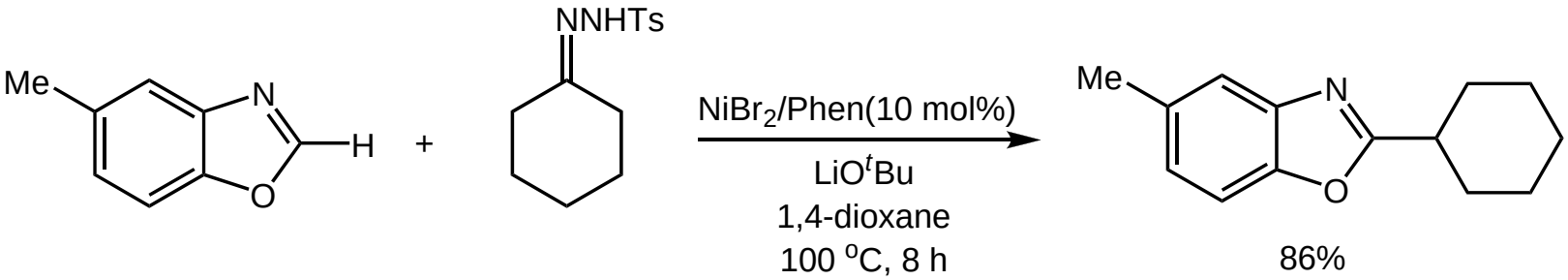
Wang, J. et al. *J. Am. Chem. Soc*. **2011**, *133*, 3296-3299

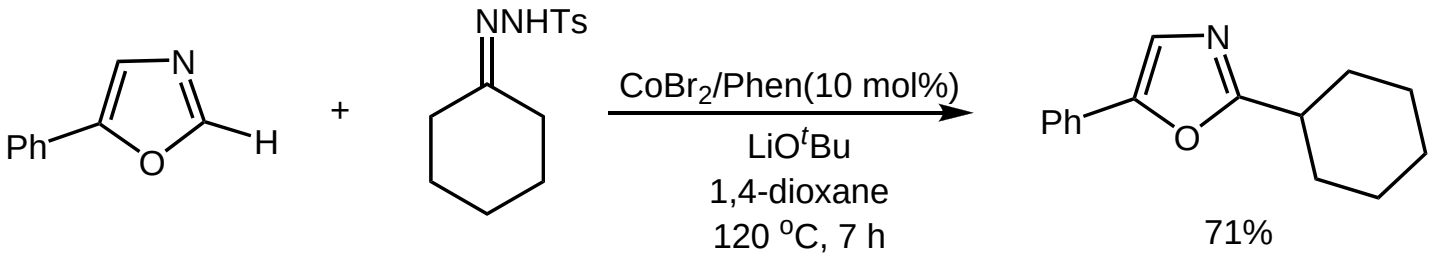
Rh(I)-Catalyzed One-Pot Three-Component Reaction



Yu, W.-Y. et al. *Org. Lett*. **2011**, *13*, 5370-5373

Ni- and Co-Catalyzed Reaction

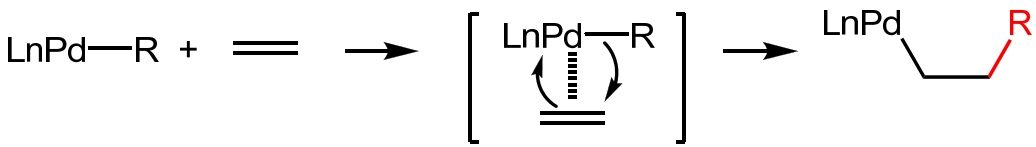




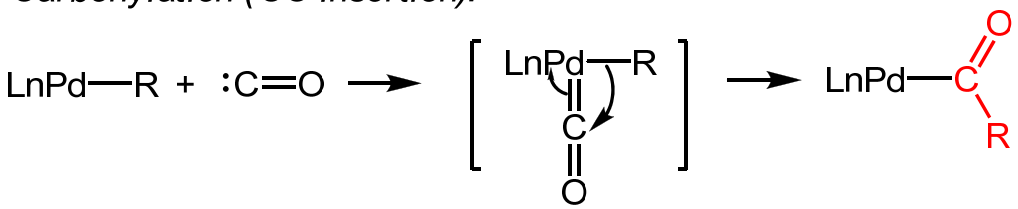
Miura, M. et al. *Angew. Chem. Int. Ed.* **2012**, *51*, 775-779

Summary-Comparison of Migratory Insertions

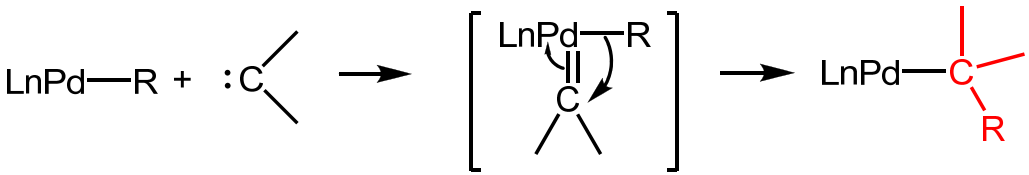
Heck-Mizoroki reaction(Alkene insertion):



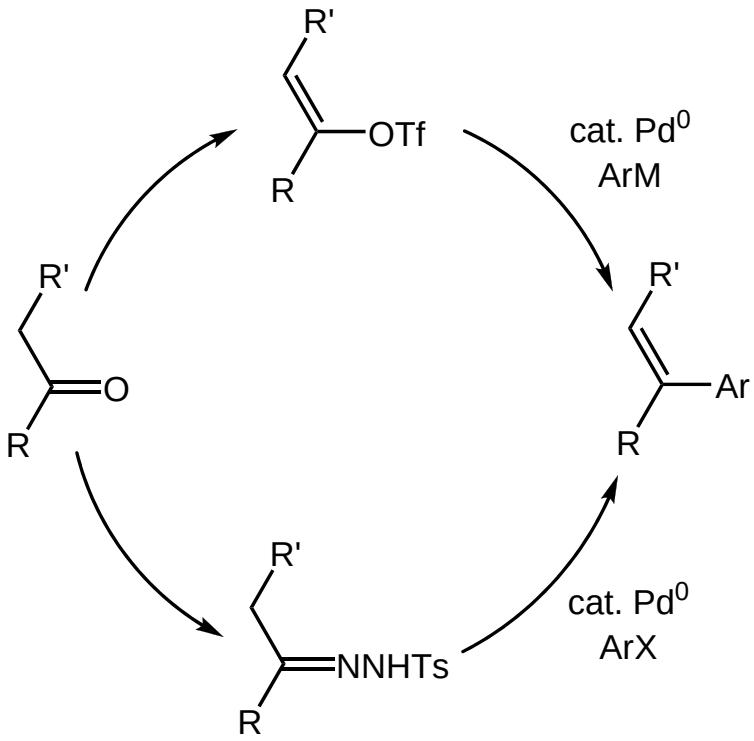
Carbonylation (CO insertion):



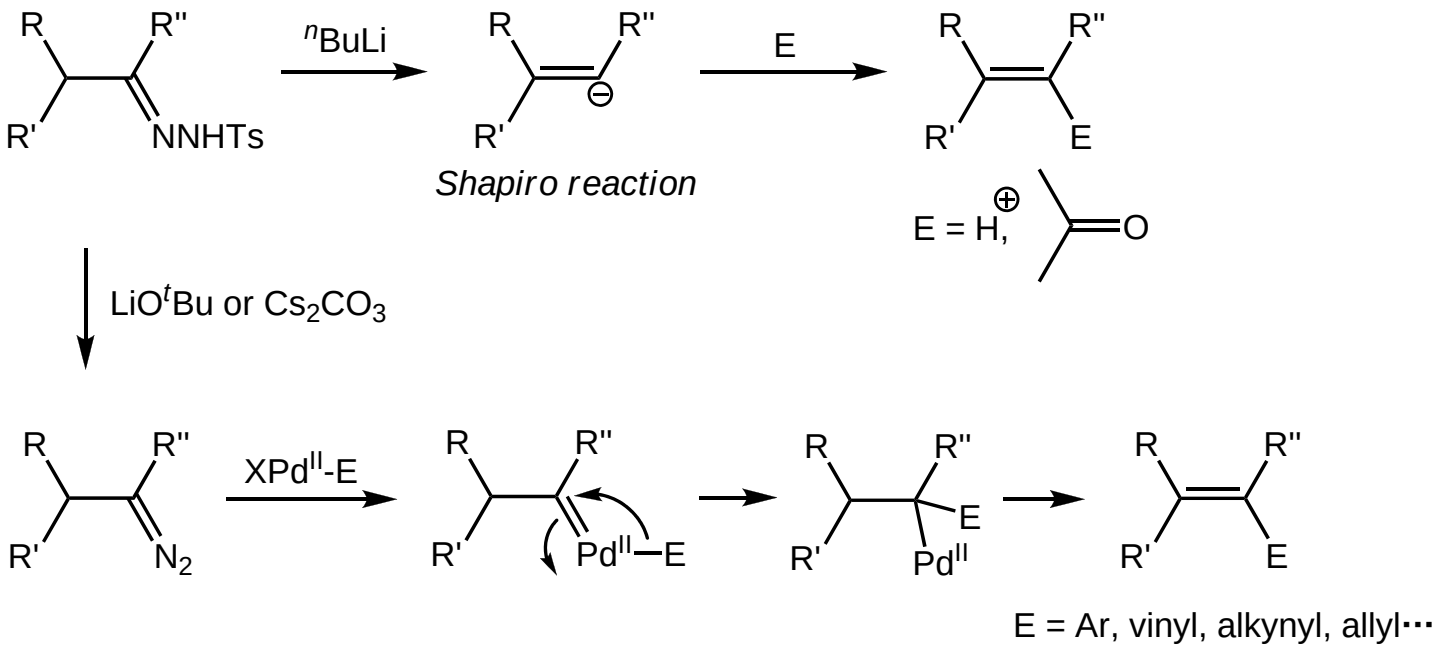
Carbene insertion:



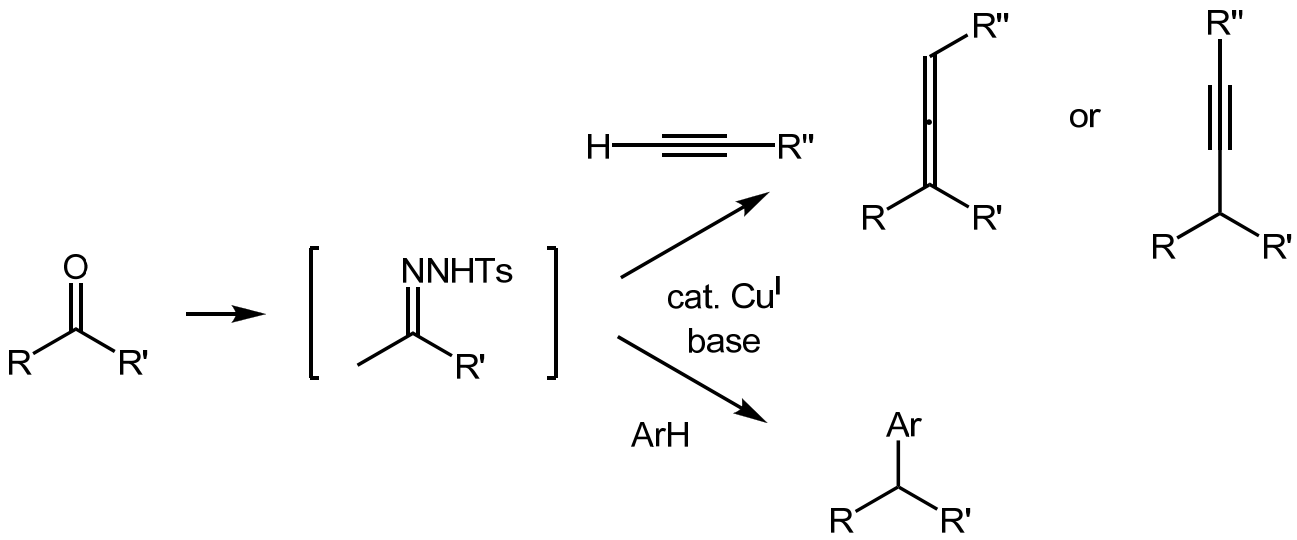
Summary-Cross-Coupling with Carbonyl: Triflate Approach *vs N*-Tosylhydrazone Approach



Summary-Alkene Synthesis : Shapiro Reaction *vs* Pd-Catalyzed Cross-Coupling



Summary-Deoxygenative Transformation of Carbonyl Group into C-C or C=C Bonds



Thanks!