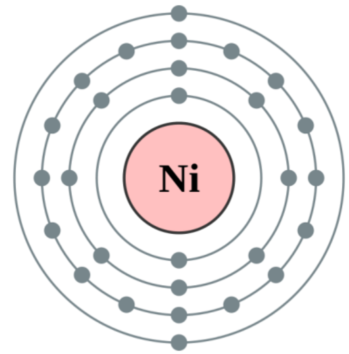
Recent Advances in Homogeneous Nickel Catalysis



Wenjun Miao

Oct. 27th 2014

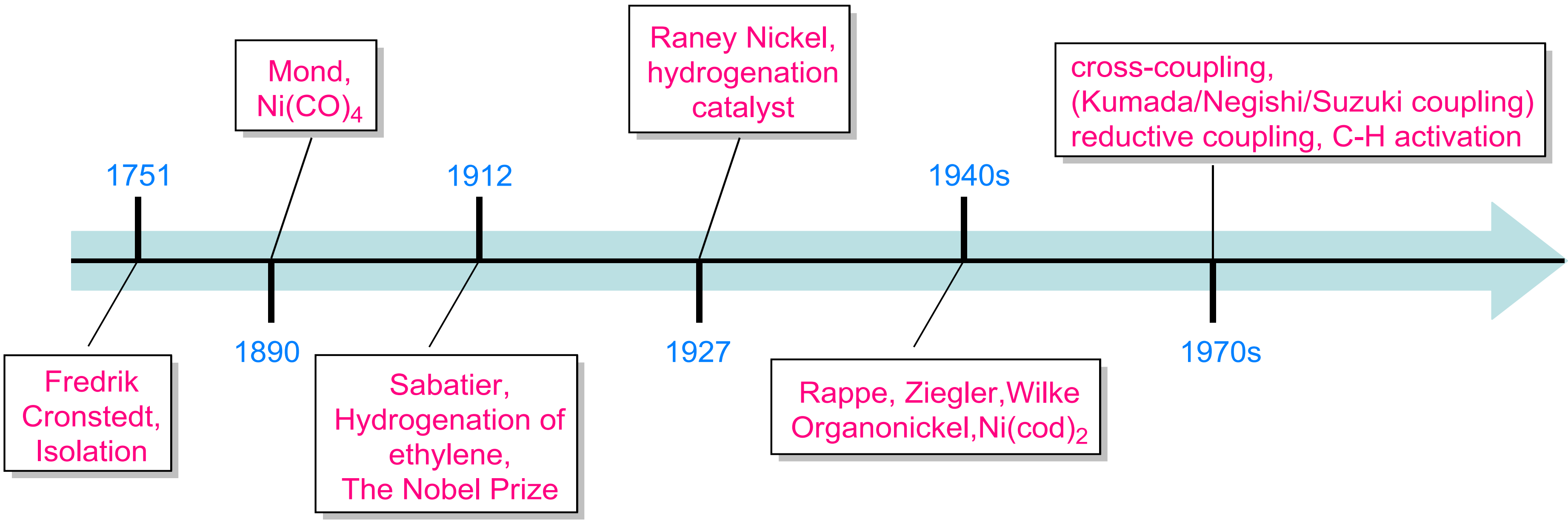
Basic Characteristics of Nickel

Nickel	Palladium
[Ar]$3d^8 4s^2$	[Kr]$4d^{10}$
-1 **0** **+1** **+2** **+3** +4	**0** +1 **+2** +3 **+4**
Electronegativity 1.8	Electronegativity 2.2
Small atomic radius	Larger atomic radius
Less electronegative	More electronegative
Harder	Softer
Facile Oxidation addition	Facile reduction elimination
Facile β-migratory insertion	Facile β -hydride elimination
Radical pathways more accessible	

Price: The cost of Ni in its elemental form is roughly **2,000** times lower than **Pd** and **10,000** times lower than **Pt** on a mole-for-mole basis.
Disadvantage: Toxicity

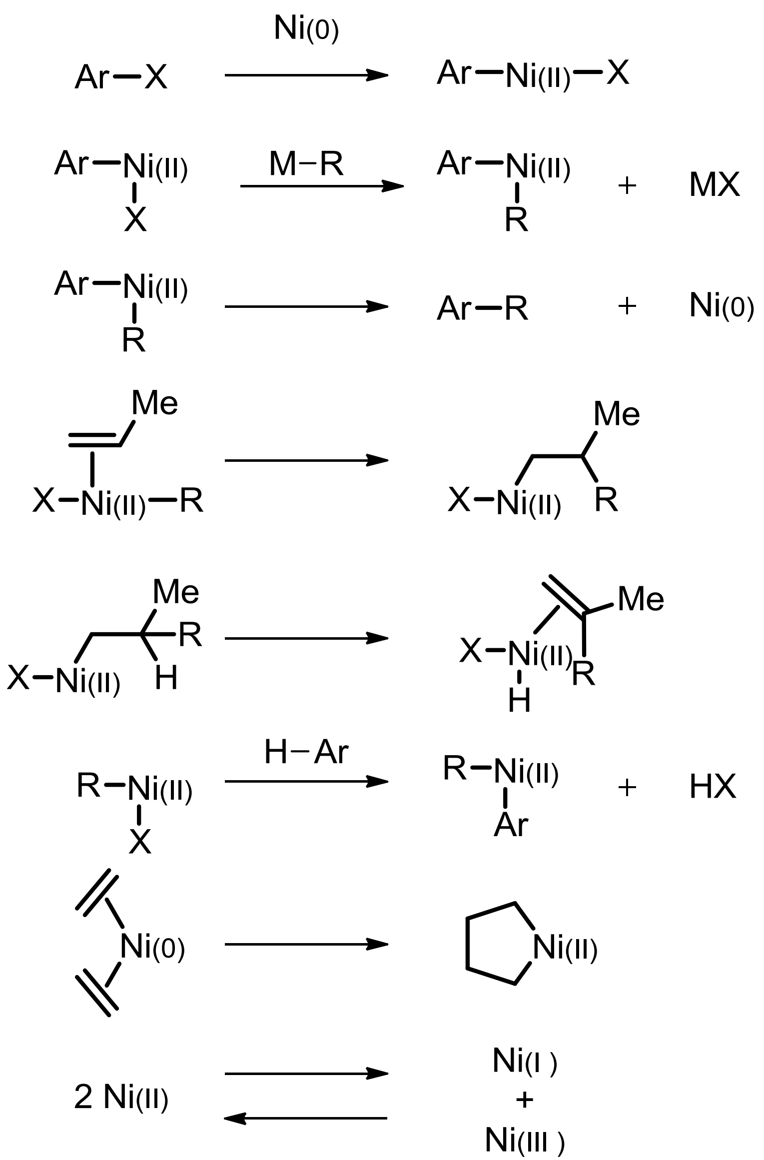
Tasker, S. Z.; Standley, E. A.; Jamison, T. F. *Nature* **2014**, *509*, 299.

Timeline of Achievements in Nickel Chemistry



Wilke, G. *Angew. Chem., Int. Ed.* **1988**, *27*, 185.
Modern Organonickel Chemistry; Tamaru Y., Ed.; Wiley-VCH: Weinheim, 2005.

The Elementary Organometallic Reactions of Ni



Oxidative addition

Transmetallation

Reductive elimination

β-migratory insertion

β-hydride elimination

C-H activation

Oxidative cyclization

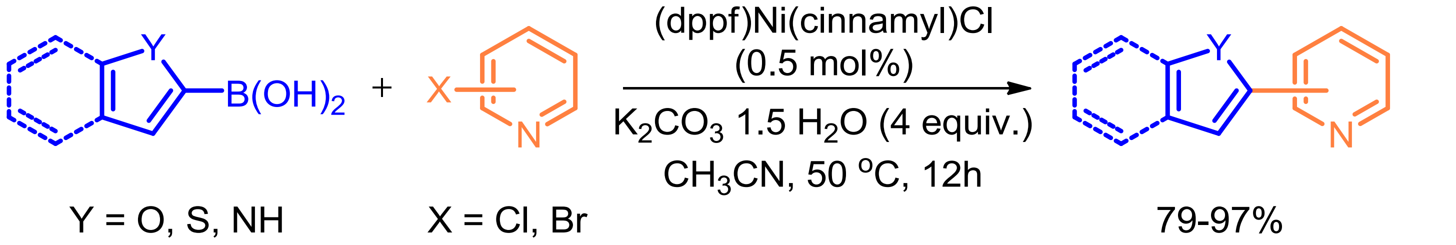
Disproportionation

Comproportionation

Cross-coupling of Aryl Halides

Challenges of catalytic synthesis of the hetero-biaryl compounds:

- The ligation of the heteroaryl coupling partner can poison the catalyst.
- The scope is limited .
- Heteroaromatic boronic acid: undergo protodeboronation under the basic reaction conditions.



Ge, S.; Hartwig, J. F. *Angew. Chem. Int. Ed.* **2012**, *51*, 12837.

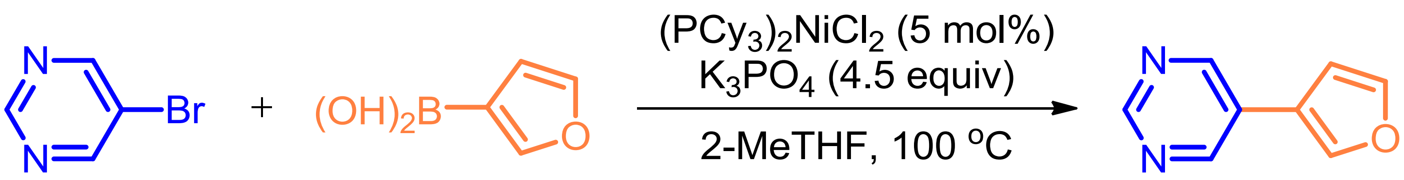
Cross-coupling of Aryl Halides

(Het)Ar-X + $(HO)_2B$-(Het)Ar → (Het)Ar-(Het)Ar

$(PCy_3)_2NiCl_2$ (5 mol%)
K_3PO_4 (4.5 equiv)
t-amyl alcohol or 2-MeTHF
100 or 120 ^oC, 12h

X = Cl, Br, $OCONEt_2$, OMs
OSO_2NMe_2, OPiv

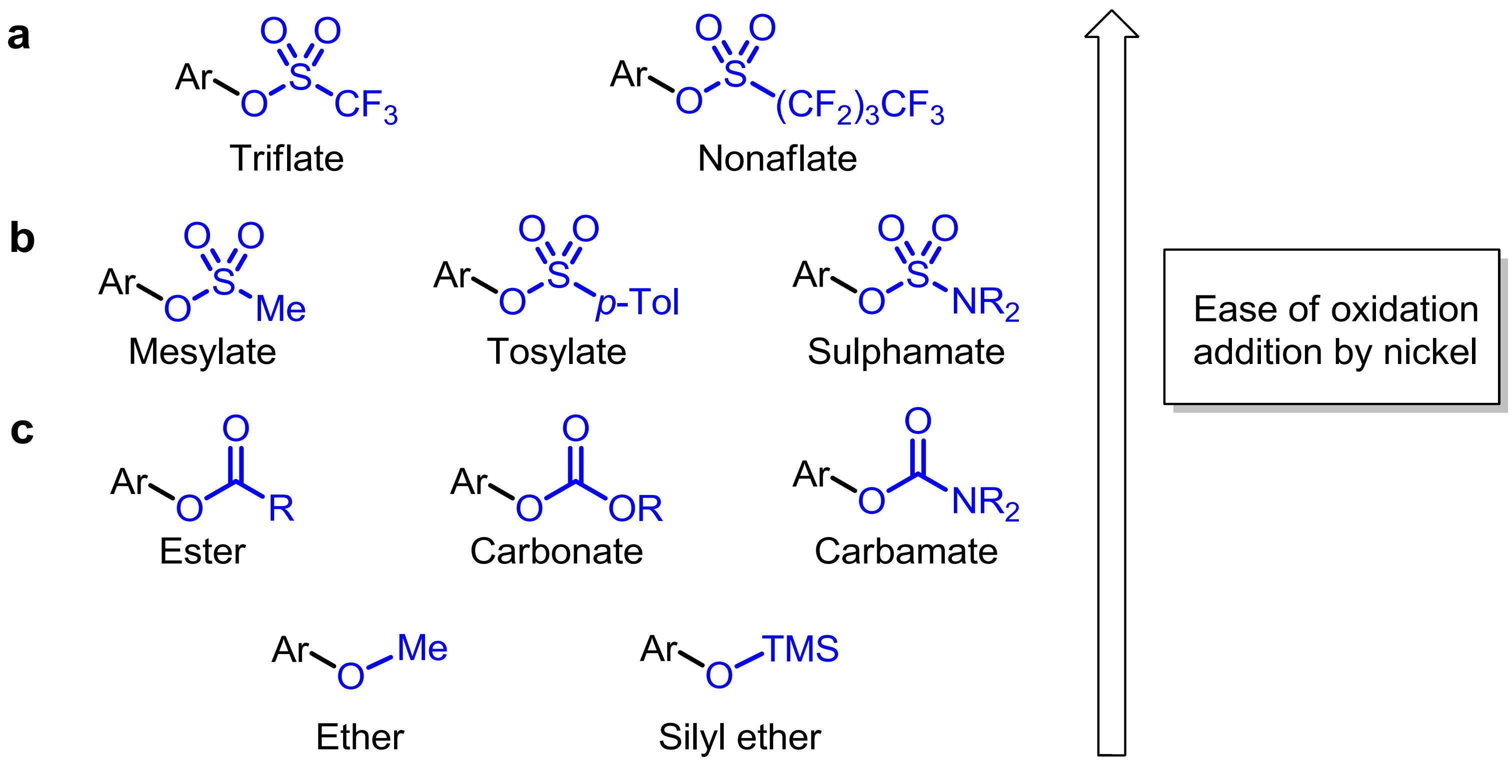
47-100%



97%
gram scale

Ramgren, S. D.; Hie, L.; Ye, Y.; Garg, N. K. *Org Lett*. **2013**, *15*, 3950.

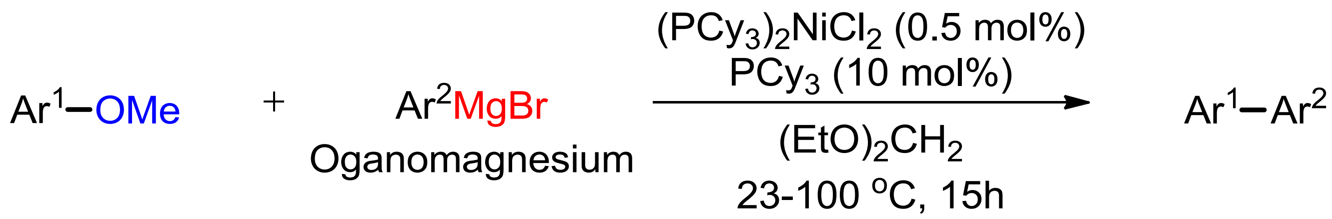
Cross-coupling of Phenol Derivatives



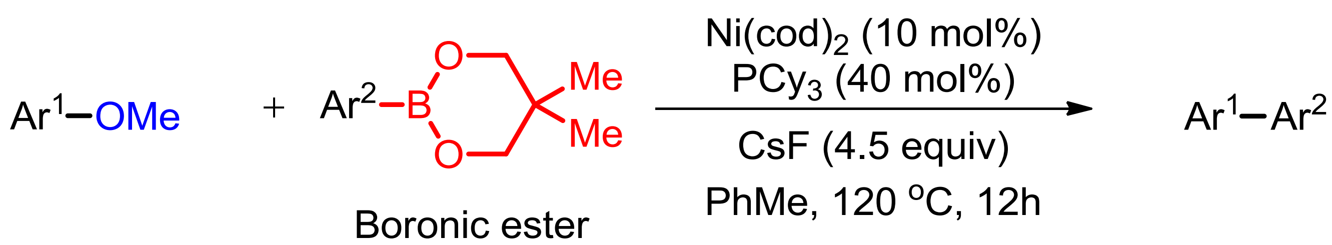
Triflate: Prone to hydrolysis, especially under basic conditions.

Tosylate, mesylate: Stable

Cross-coupling of Phenol Derivatives

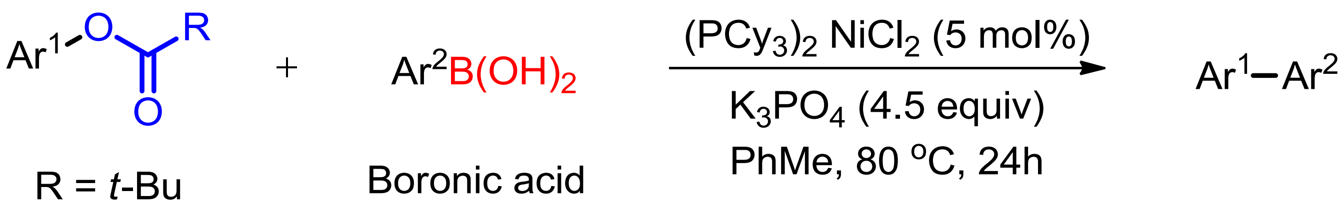


Dankwardt, J. W. *Angew. Chem. Int. Ed.* **2004**, *43*, 2428.

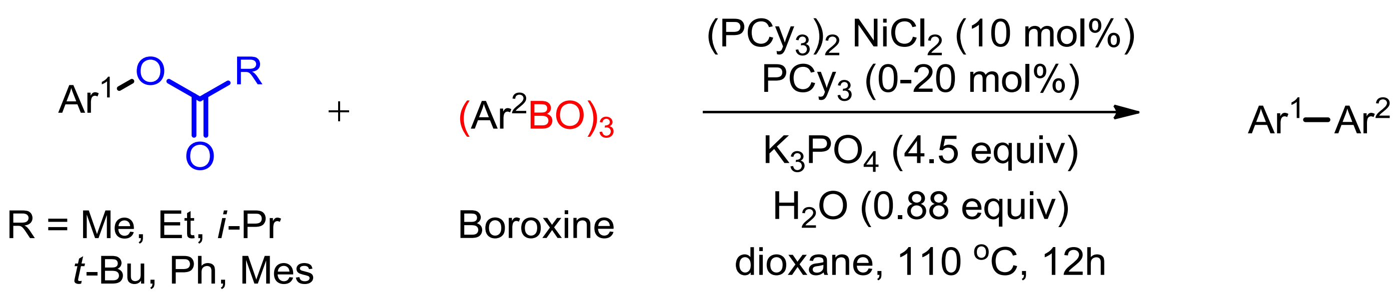


Tobisu, M.; Shimasaki, T.; Chatani, N. *Angel. Chem. Int. Ed.* **2008**, *47*, 4866.

Cross-coupling of Phenol Derivatives

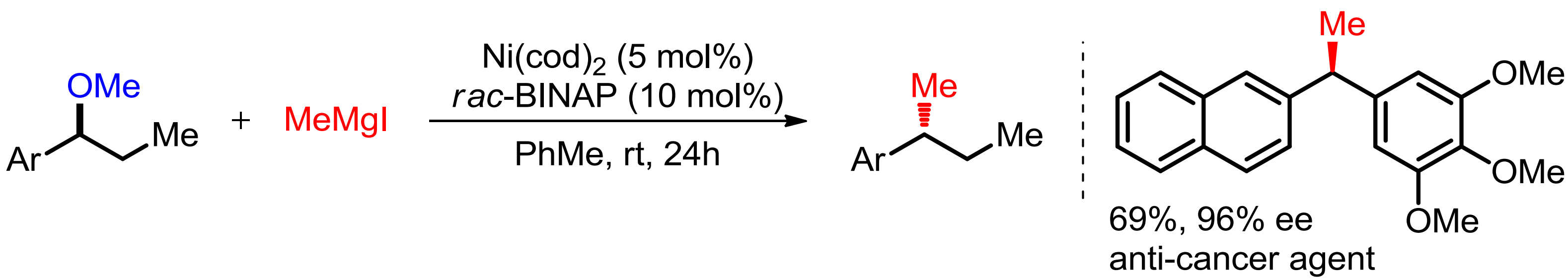


Quasdorf, K. W.; Tian, X.; Garg, N. K. *J. Am. Chem. Soc.* **2008**, *130*, 14422.



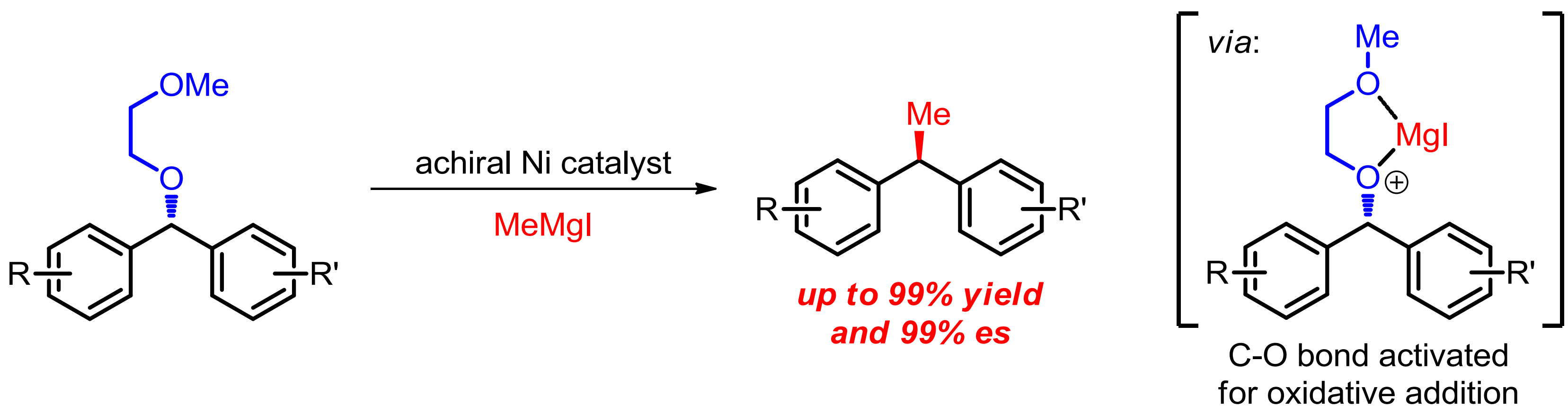
Guan, B.-T.; Wang, Y.; Li, B.-J.; Yu, D.-G.; Shi, Z.-J. *J. Am. Chem. Soc.* **2008**, *130*, 14468.

Benzylic Cross-coupling



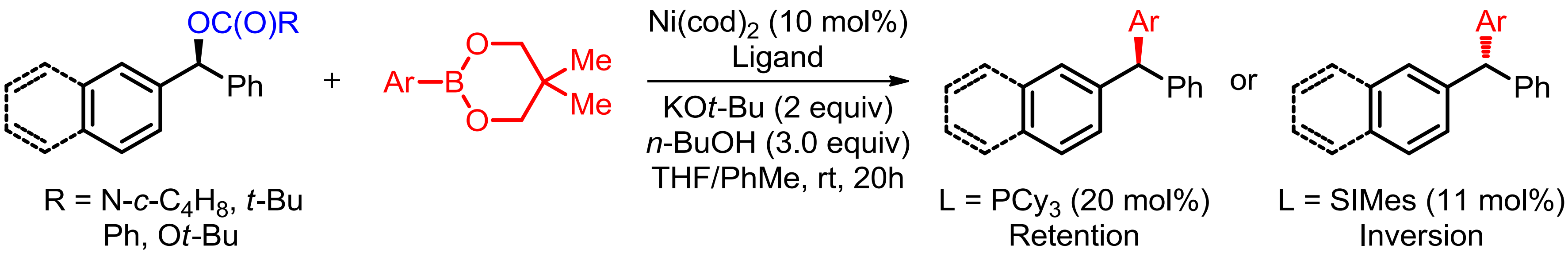
First stereospecific nickel-catalysed alkyl–alkyl cross-coupling reaction

Taylor, B. L. H.; Swift, E. C.; Waetzig, J. D.; Jarvo, E. R. *J. Am. Chem. Soc.* **2010**, *133*, 389.

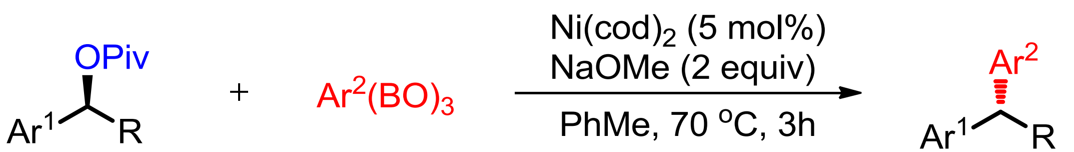


Greene, M. A.; Yonova, I. M.; Williams, F. J.; Jarvo, E. R. *Org Lett.* **2012**, *14*, 4293.

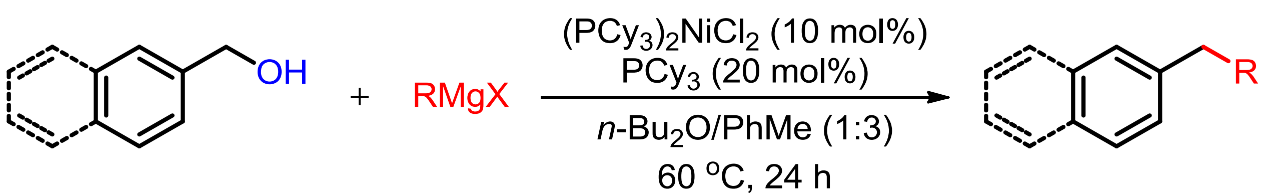
Benzylic Cross-coupling



Harris, M. R.; Hanna, L. E.; Greene, M. A.; Moore, C. E.; Jarvo, E. R. **2013**, *135*, 3303.

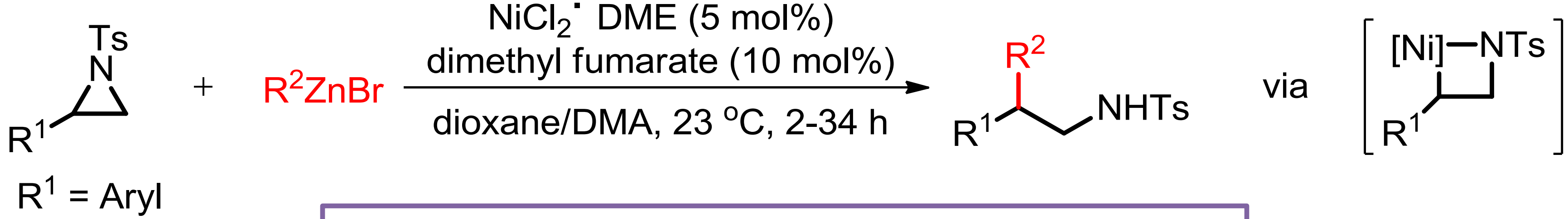


Zhou, Q.; Srinivas, H. D.; Dasgupta, S.; Watson, M. P. *J. Am. Chem. Soc.* **2013**, *135*, 3307.



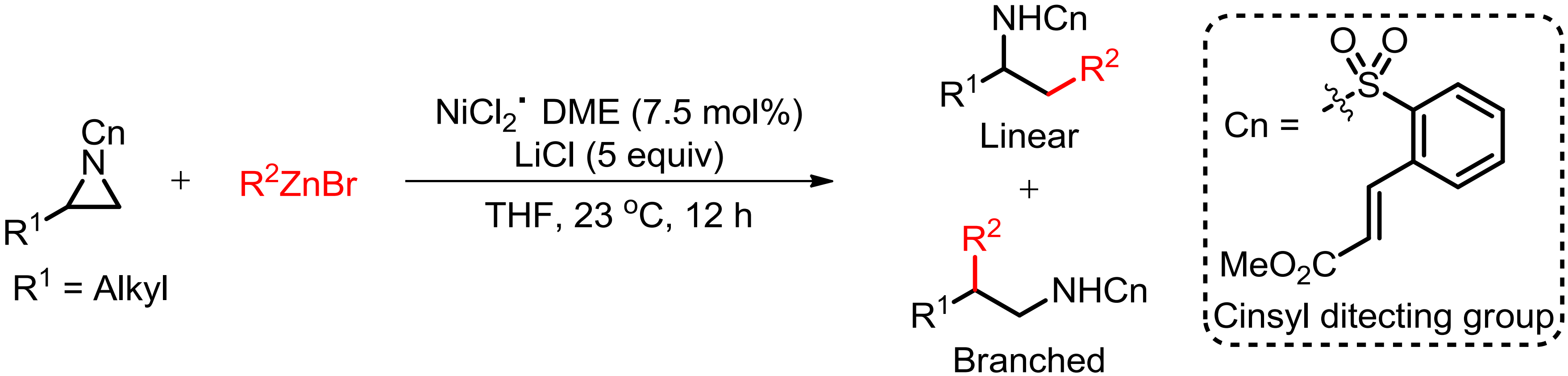
Yu, D.-G.; Wang, X.; Zhu, R.-Y.; Luo, S.; Zhang, X.-B.; Wang, B.-Q.; Wang, L.; Shi, Z.-J. *J. Am. Chem. Soc.* **2012**, *134*, 14638.

Cross-coupling of Aziridines



Dimethyl fumarate: accelerate reductive elimination through π-coordination to nickel

Huang, C.-Y.; Doyle, A. G. *J. Am. Chem. Soc.* **2012**, *134*, 9541.



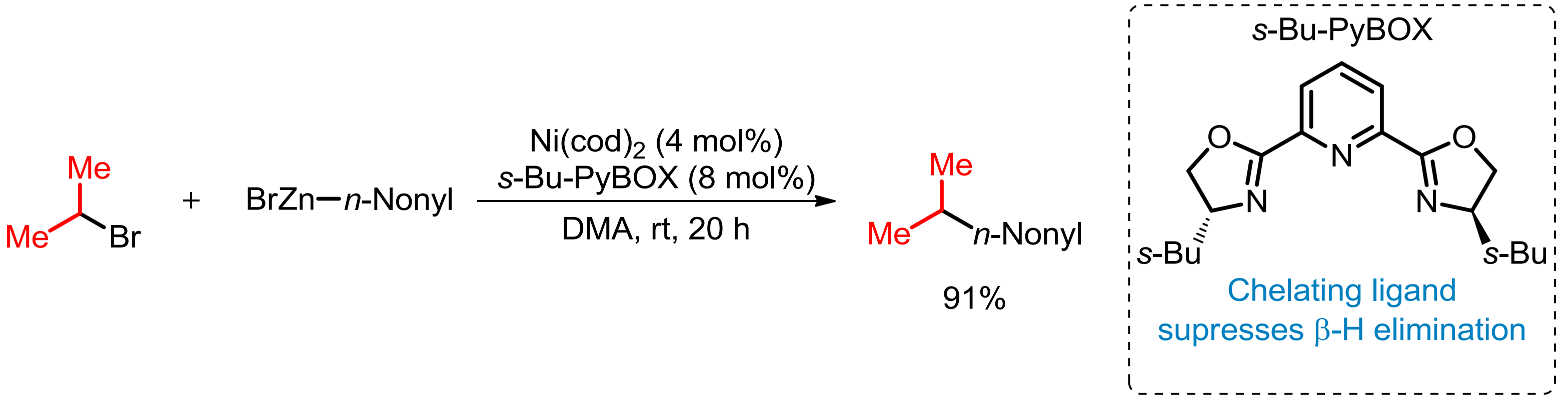
Nielsen, D. K.; Huang, C.-Y.; Doyle, A. G. *J. Am. Chem. Soc.* **2013**, *135*, 13605.

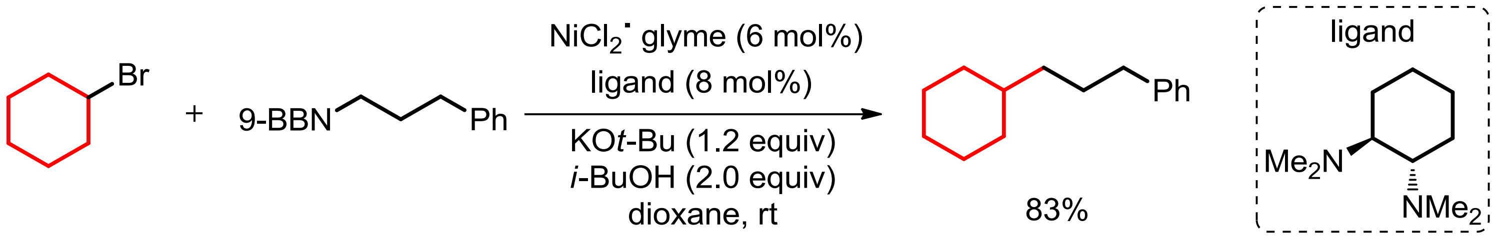
Cross-coupling of *sp*^{3} Halides

Challenges:

◆The electrophile is sp^3 hybridized, the activation energy for oxidative addition can be large, C(sp^3)-X are more electron-rich than C(sp^2)-X, which can be reluctant to oxidatively add to the metal catalyst.

◆Intramolecular β-H elimination

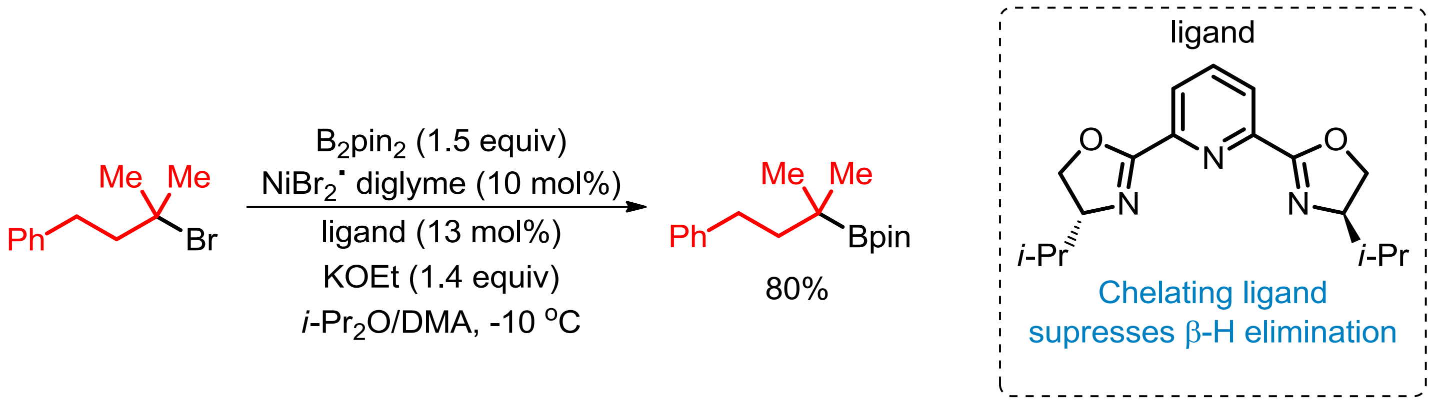




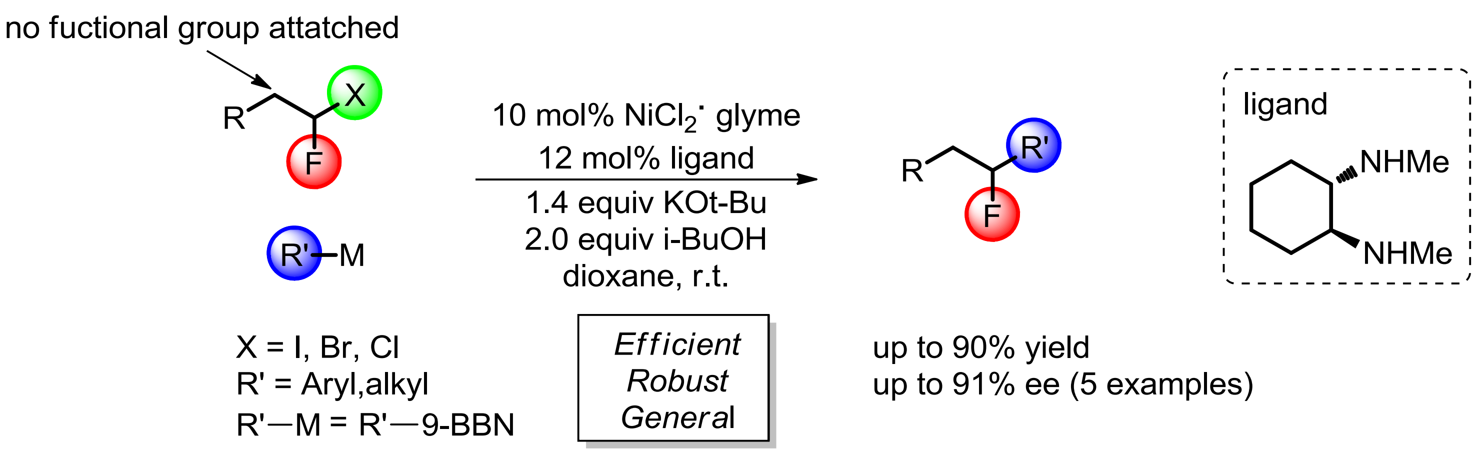
Zhou, J.; Fu, G. C. *J. Am. Chem. Soc.* **2003**, *125*, 14726.

Zhou, J.; Fu, G. C. *J. Am. Chem. Soc.* **2004**, *126*, 1340.

Cross-coupling of *sp*^{3} Halides

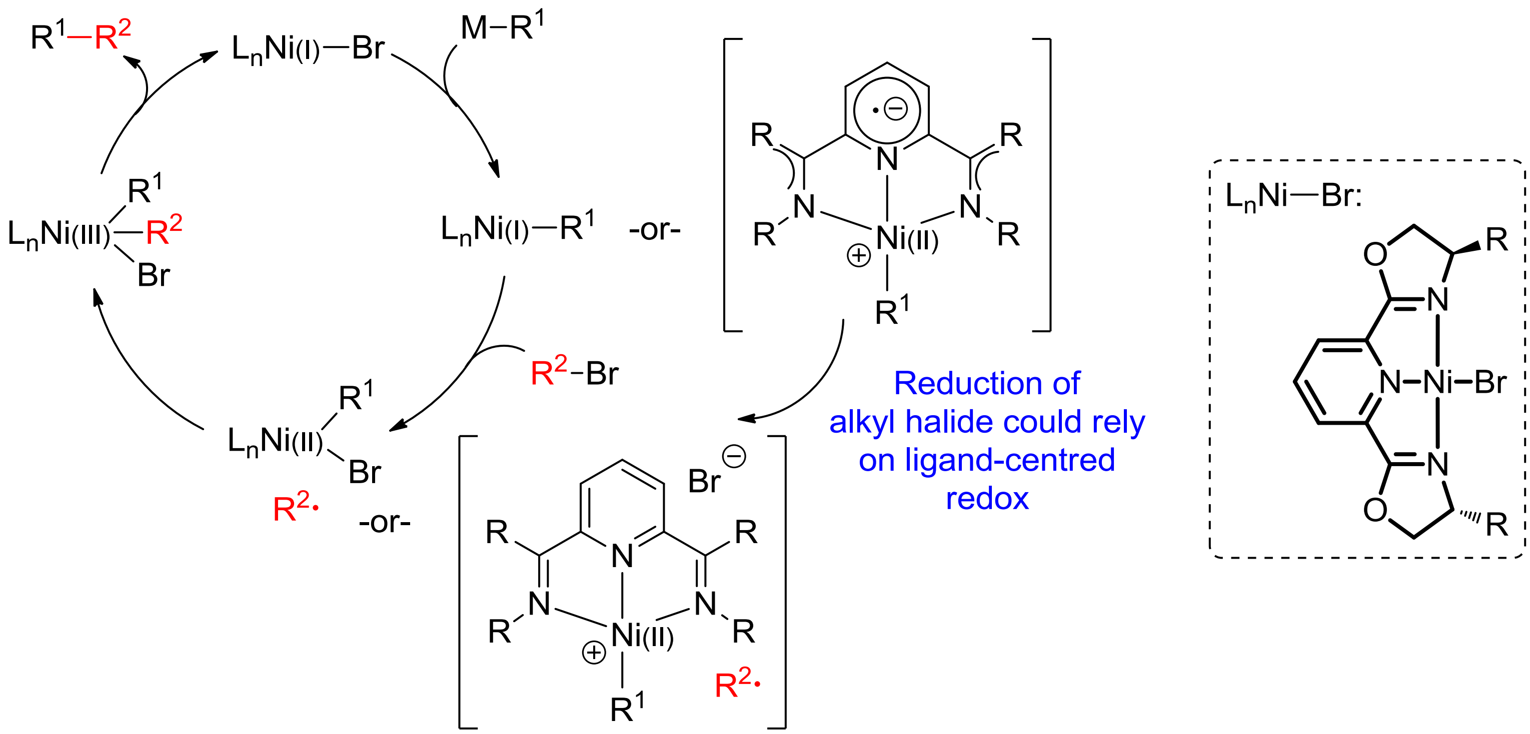


Dudnik, A. S.; Fu, G. C *J. Am. Chem. Soc.* **2012**, *134*, 10693.



Jiang, X.; Sakthivel, S.; Kulbitski, K.; Nisnevich, G.; Gandelman, M. *J. Am. Chem. Soc.* **2014**, *136*, 9548

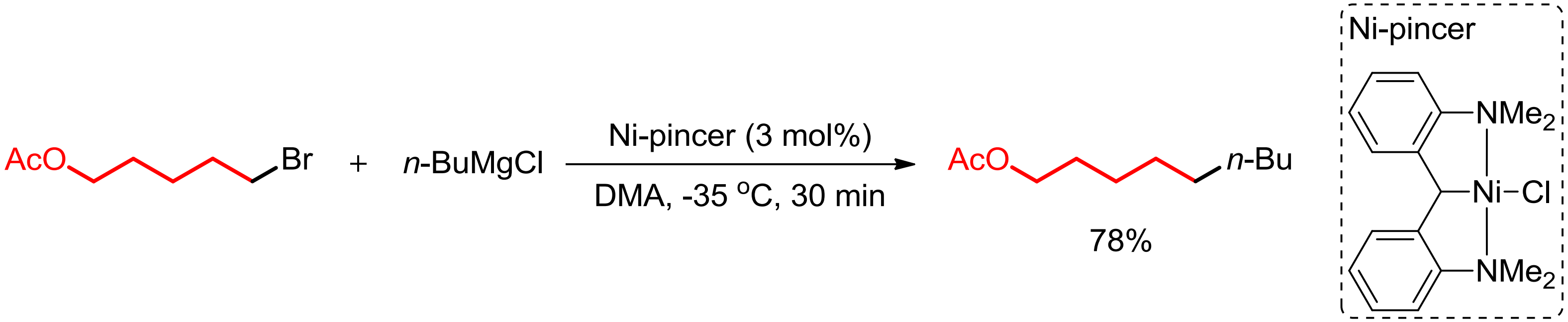
Cross-coupling of *sp*^{3} Halides



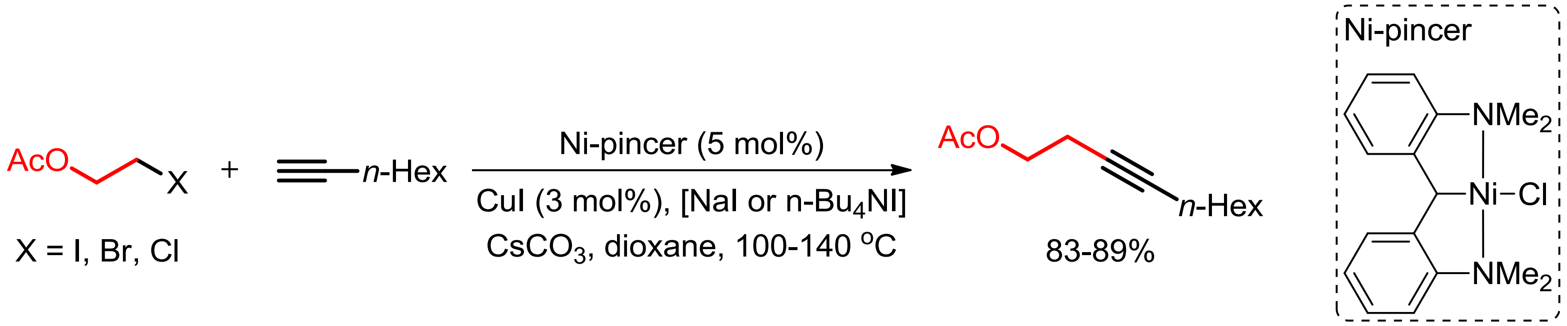
Proposed mechanisms for C(sp^3)–C(sp^3) cross-coupling

Vicic, D. A. *J. Am. Chem. Soc.* **2006**, *128*, 13175.
Dudnik, A. S.; Fu, G. C. *J. Am. Chem. Soc.* **2012**, *134*, 10693.
Zultanski, S. L.; Fu, G. C. *J. Am. Chem. Soc.* **2013**, *135*, 624.

Cross-coupling of sp^3 Halides

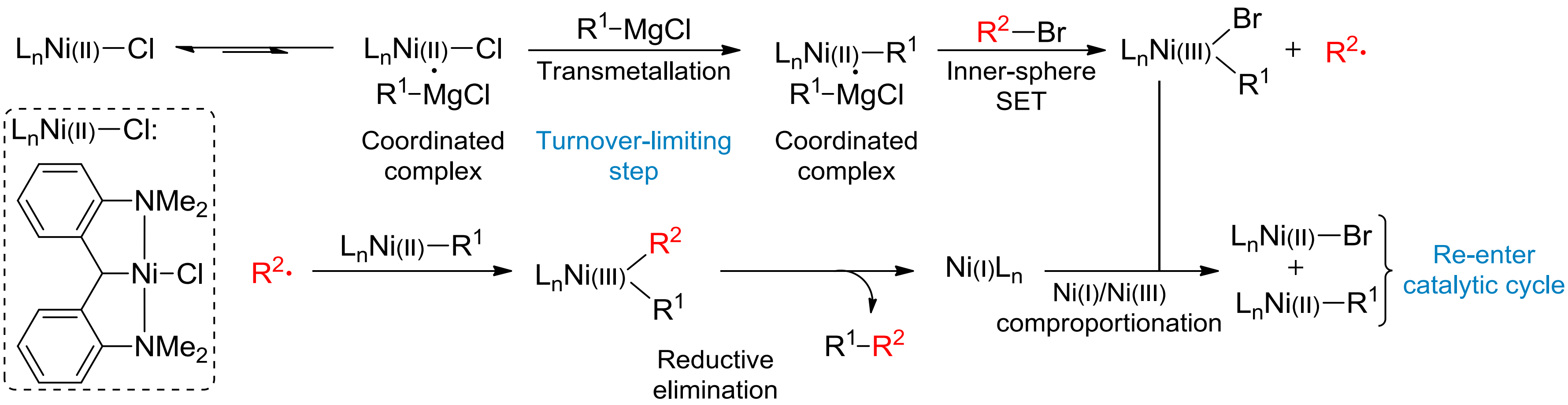


Csok, Z.; Vechorkin, O.; Scopelliti, R.; Hu, X. *J. Am. Chem. Soc.* **2008**, *130*, 8156.
Vechorkin, O.; Hu, X. *Angew. Chem. Int. Ed.* **2009**, *48*, 2937.



Vechorkin, O.; Barmaz, D.; Proust, V.; Hu, X. *J. Am. Chem. Soc.* **2009**, *131*, 12078.

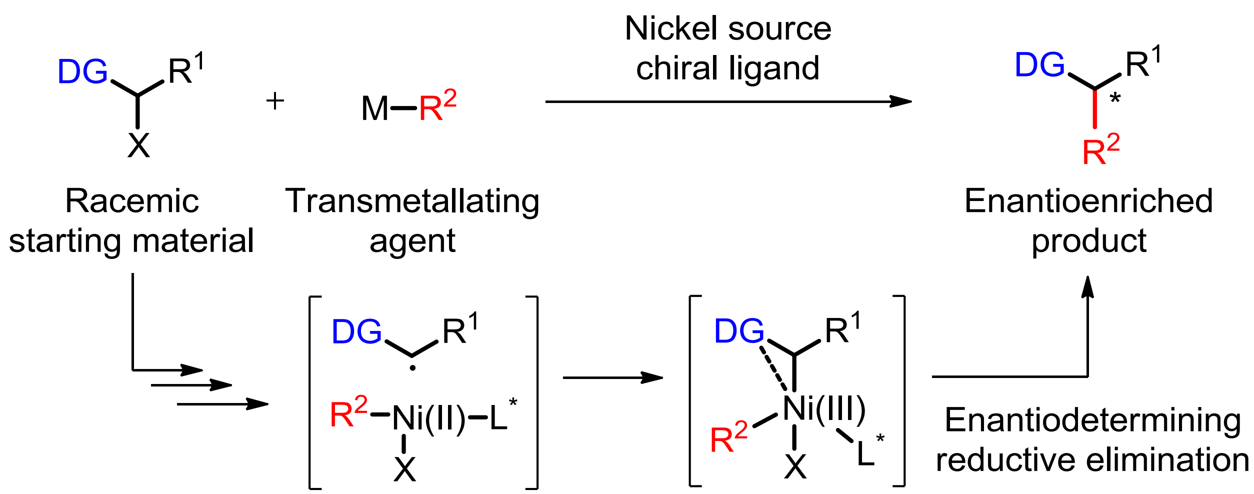
Cross-coupling of *sp*^{3} Halides

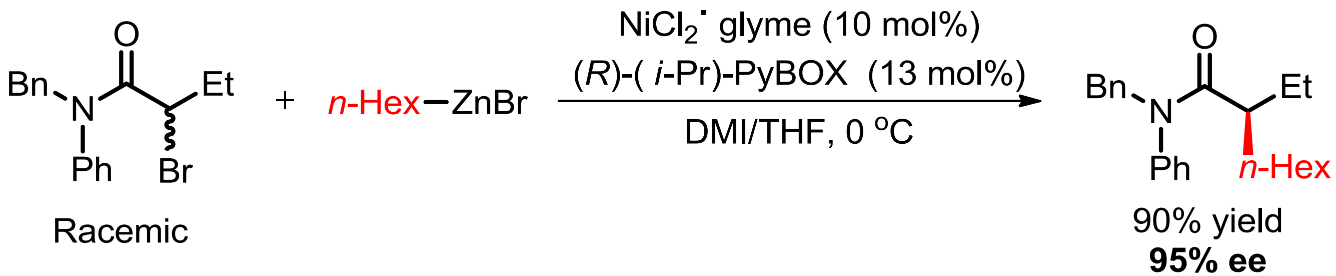


Proposed mechanisms for C(sp^3)–C(sp^3) cross-coupling

Breitenfeld, J.; Ruiz, J.; Wodrich, M. D.; Hu, X. *J. Am. Chem. Soc.* **2013**, *135*, 12004.

Cross-coupling of *sp*^{3} Halides

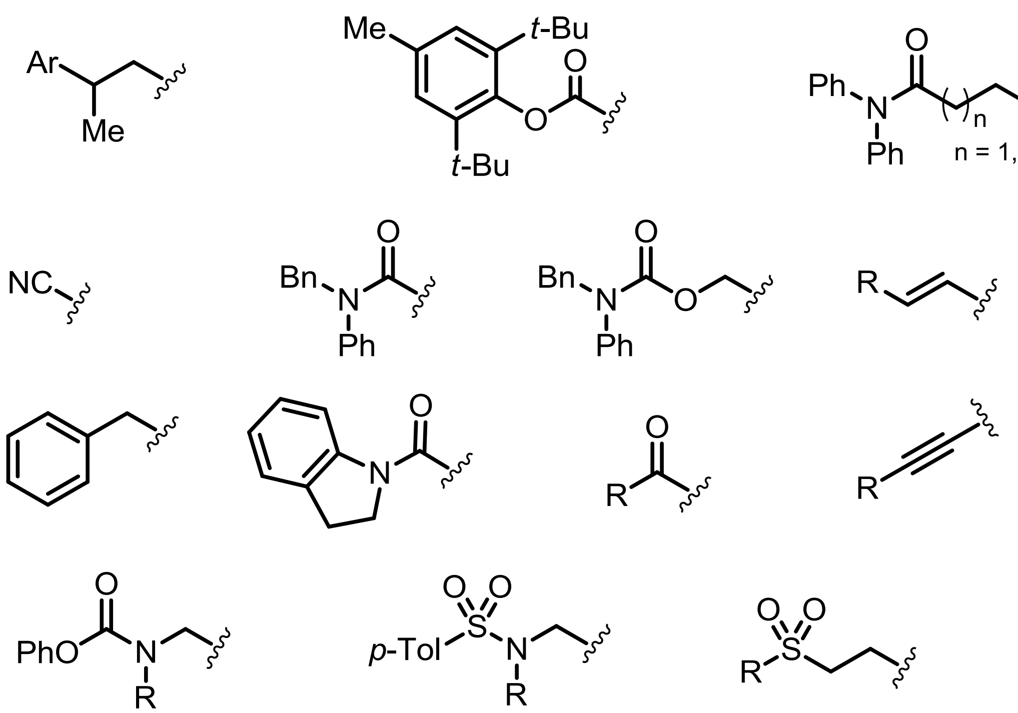




Fischer, C.; Fu, G. C. *J. Am. Chem. Soc.* **2005**, *127*, 4594.

Cross-coupling of *sp*^{3} Halides

Directing groups



Transmetallating agents

alkyl, aryl, alkenyl

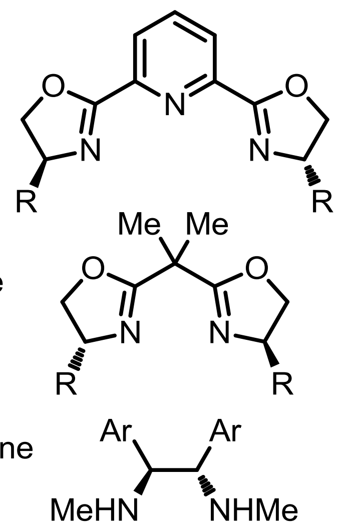
zinc (Negishi), boron (Suzuki)
silicon (Hiyama), magnesium (Kumada),
and zirconium reagents

Ligand classes

PyBOX

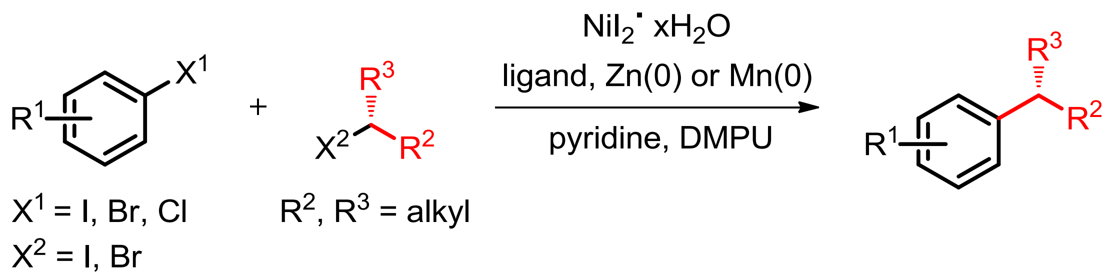
Oxazoline

1,2-Diamine

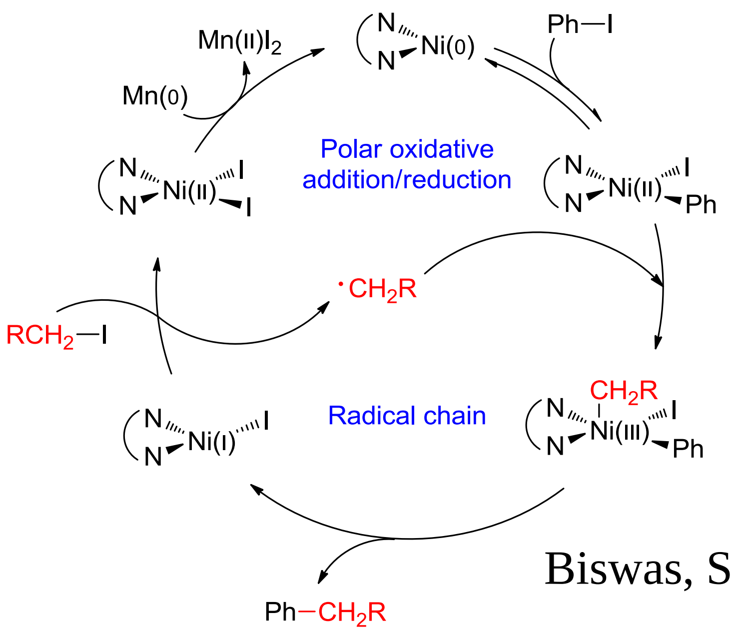


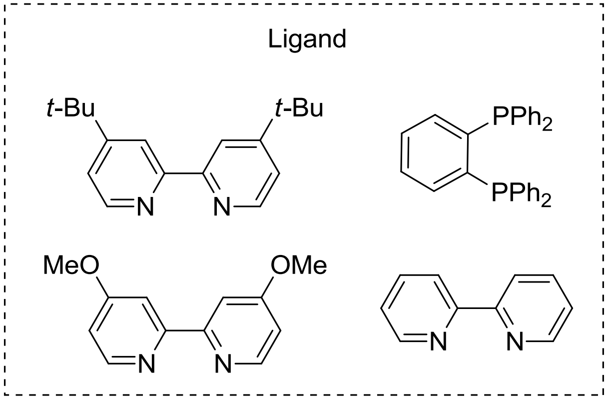
Reductive Cross-coupling

Challenge: the differentiation between the two electrophiles, suppress homodimerization of either component.



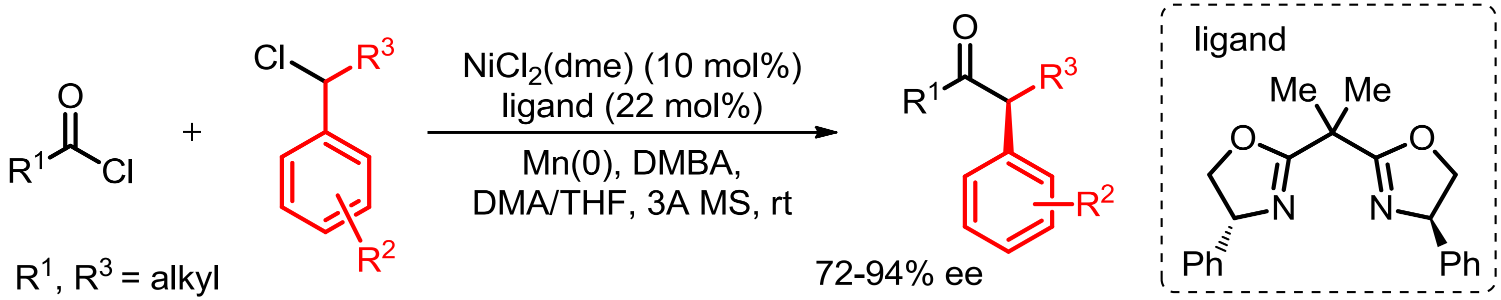
Everson, D. A.; Shrestha, R.; Weix, D. J. *J. Am. Chem. Soc.* **2010**, *132*, 920.





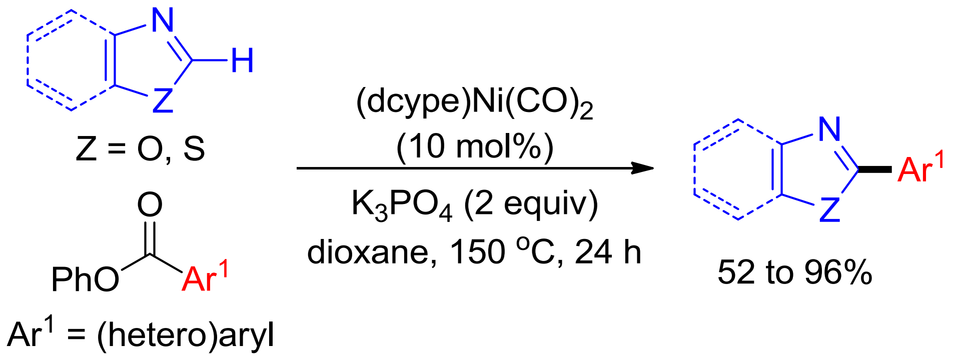
Biswas, S.; Weix, D. J. *J. Am. Chem. Soc.* **2013**, *135*, 16192.

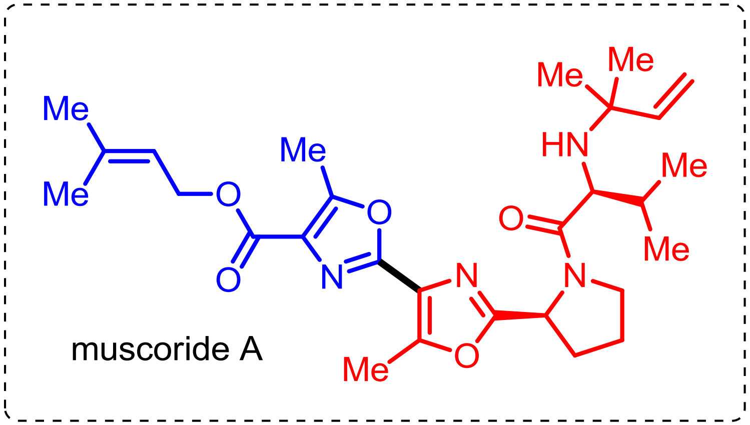
Reductive Cross-coupling



Cherney, A. H.; Kadunce, N. T.; Reisman, S. E. *J. Am. Chem. Soc.* **2013**, *135*, 7442.

C–H Activation

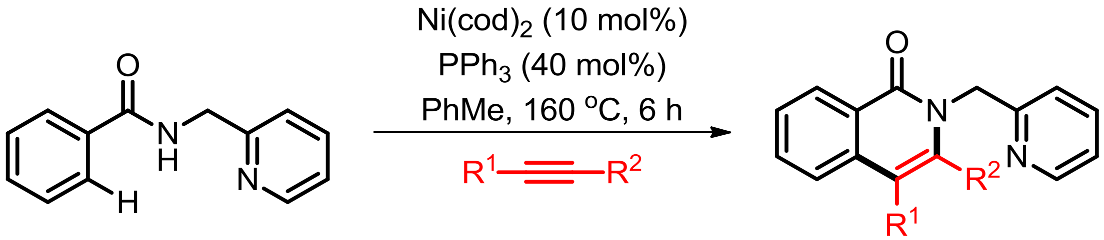




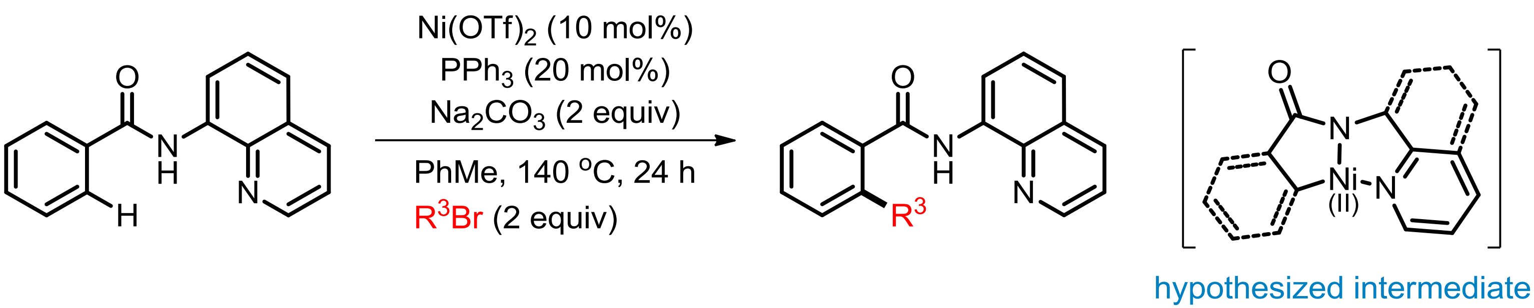
Muto, K.; Yamaguchi, J.; Itami, K. *J. Am. Chem. Soc.* **2011**, *134*, 169.

Amaike, K.; Muto, K.; Yamaguchi, J.; Itami, K. *J. Am. Chem. Soc.* **2012**, *134*, 13573.

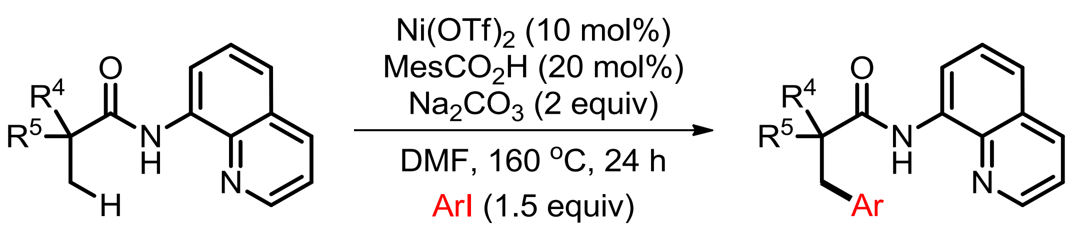
C–H Activation



Shiota, H.; Ano, Y.; Aihara, Y.; Fukumoto, Y.; Chatani, N. *J. Am. Chem. Soc.* **2011**, *133*, 14952.

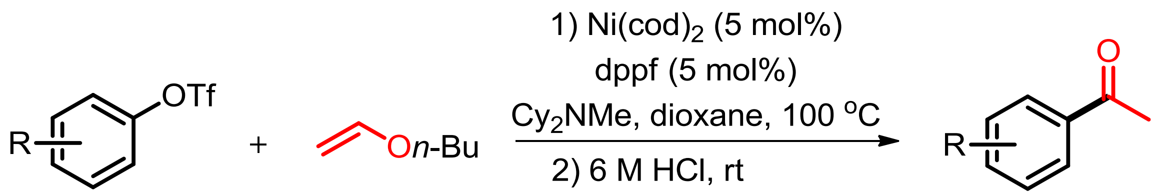


Aihara, Y.; Chatani, N. *J. Am. Chem. Soc.* **2013**, *135*, 5308.

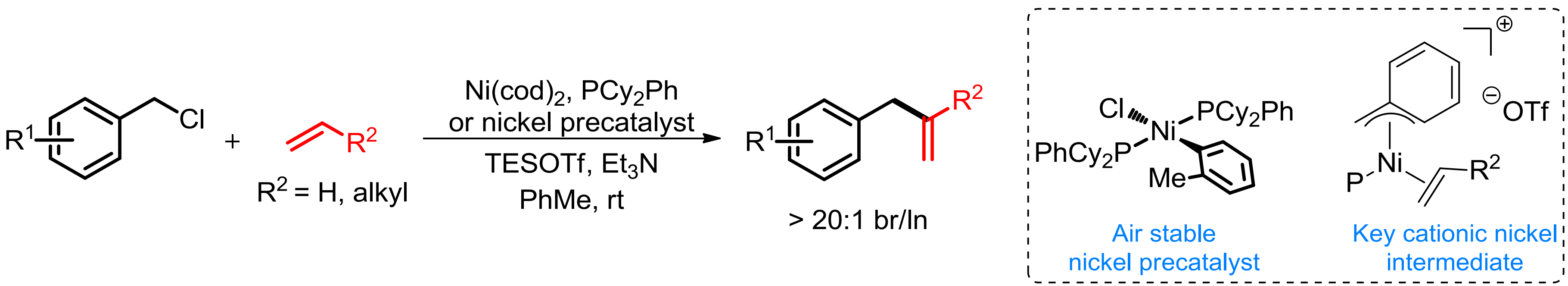


Aihara, Y.; Chatani, N. *J. Am. Chem. Soc.* **2013**, *136*, 898.

Heck Reaction

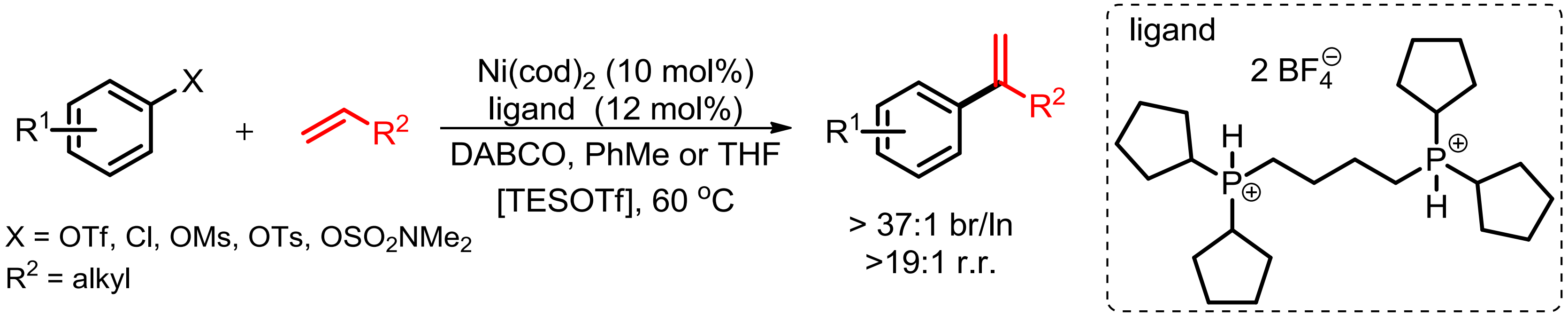


Gøgsig, T. M.; Kleimark, J.; Nilsson Lill, S. O.; Korsager, S.; Lindhardt, A. T.; Norrby, P.-O.; Skrydstrup, T. *J. Am. Chem. Soc.* **2011**, *134*, 443.



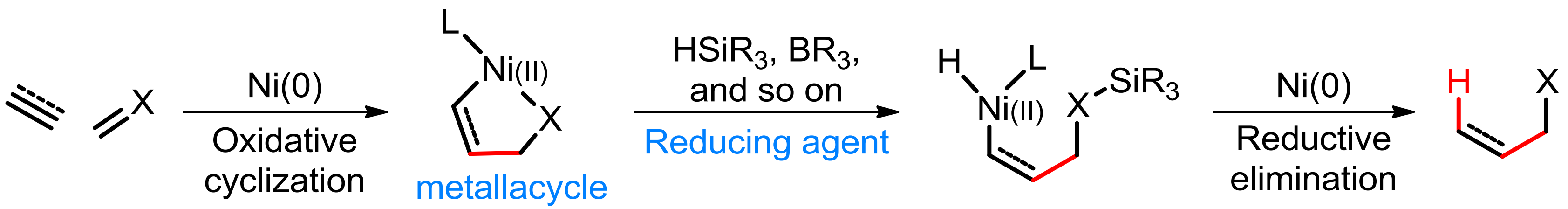
Matsubara, R.; Gutierrez, A. C.; Jamison, T. F. *J. Am. Chem. Soc.* **2011**, *133*, 19020.
Standley, E. A.; Jamison, T. F. *J. Am. Chem. Soc.* **2013**, *135*, 1585.

Heck Reaction



Tasker, S. Z.; Gutierrez, A. C.; Jamison, T. F. *Angew. Chem. Int. Ed.* **2014**, *53*, 1858.

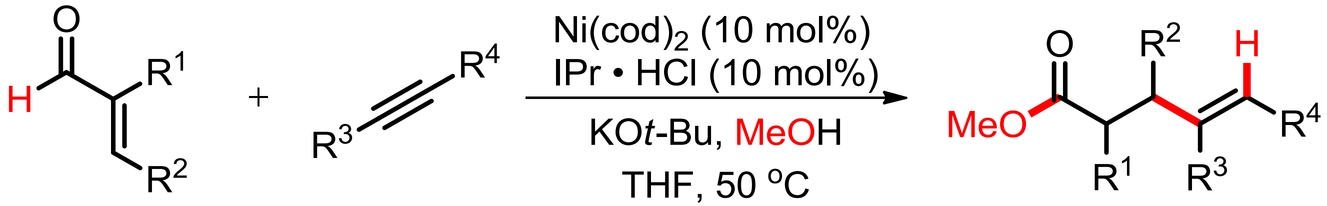
Reductive Coupling



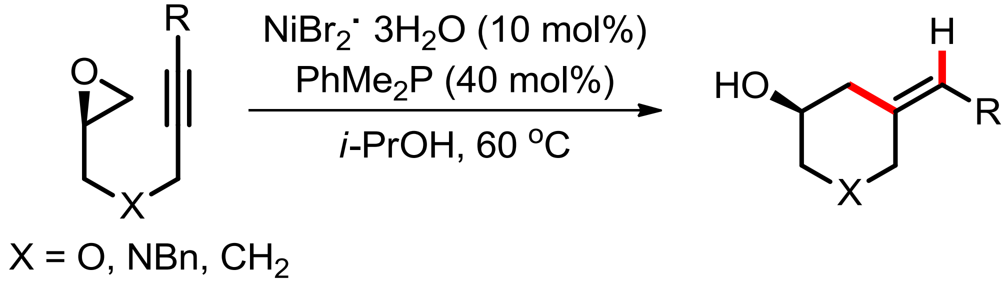
Moslin, R. M.; Miller-Moslin, K.; Jamison, T. F. *Chem. Commun.* **2007**, 4441.

Ng, S.-S.; Ho, C.-Y.; Jamison, T. F. *Pure Appl. Chem.* **2008,** *80*, 929.

Reductive Coupling



Herath, A.; Li, W.; Montgomery, J. *J. Am. Chem. Soc.* **2007**, *130*, 469.



Beaver, M. G.; Jamison, T. F. *Org Lett.* **2011**, *13*, 4140.

Summary and Outlook

Outlook:

- Design new catalysts, develop new transformations. Such as C-F formation.
- Further in the area of $C(sp^3)–C(sp^3)$ bond formation, particularly in expansion of substrate scope and application to the synthesis of complex molecules.
- in the development of low-cost, air-stable, and easier-to-handle sources of nickel for catalysis.
- Gain more recognition, not as an inexpensive substitute for palladium, but rather as possessing a number of inherent properties that provide a complement to catalysis by other metals

Thank you for your attention!