December, 13th 2012

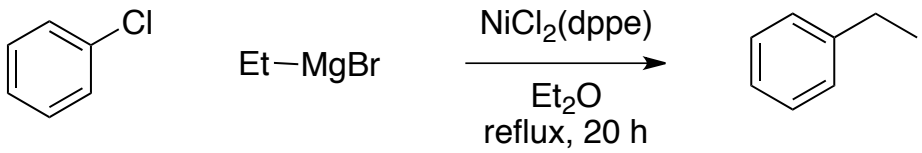
UNIVERSITÄT BERN

Nickel Catalyzed Cross-Coupling Reactions

Topic Review

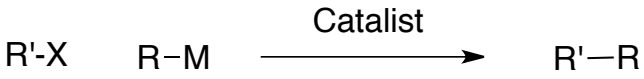
Julien

Introduction



Tamao, K.; Sumitani, K.; Kumada, M. *J. Am. Chem. Soc.* **1972**, 94, 4374

Introduction



- Kumada reaction (1972)[1]:

  M = MgX and Pd or Ni catalysis
- Sonogashira reaction (1973):

  M = [Cu] and R = alkynyl, Pd catalysis, base
- Negeshi reaction (1977):

  M = ZnX, Pd catalysis
- Stille reaction(1977):

  M = SnX_3, Pd catalysis
- Suzuki reaction (1979):

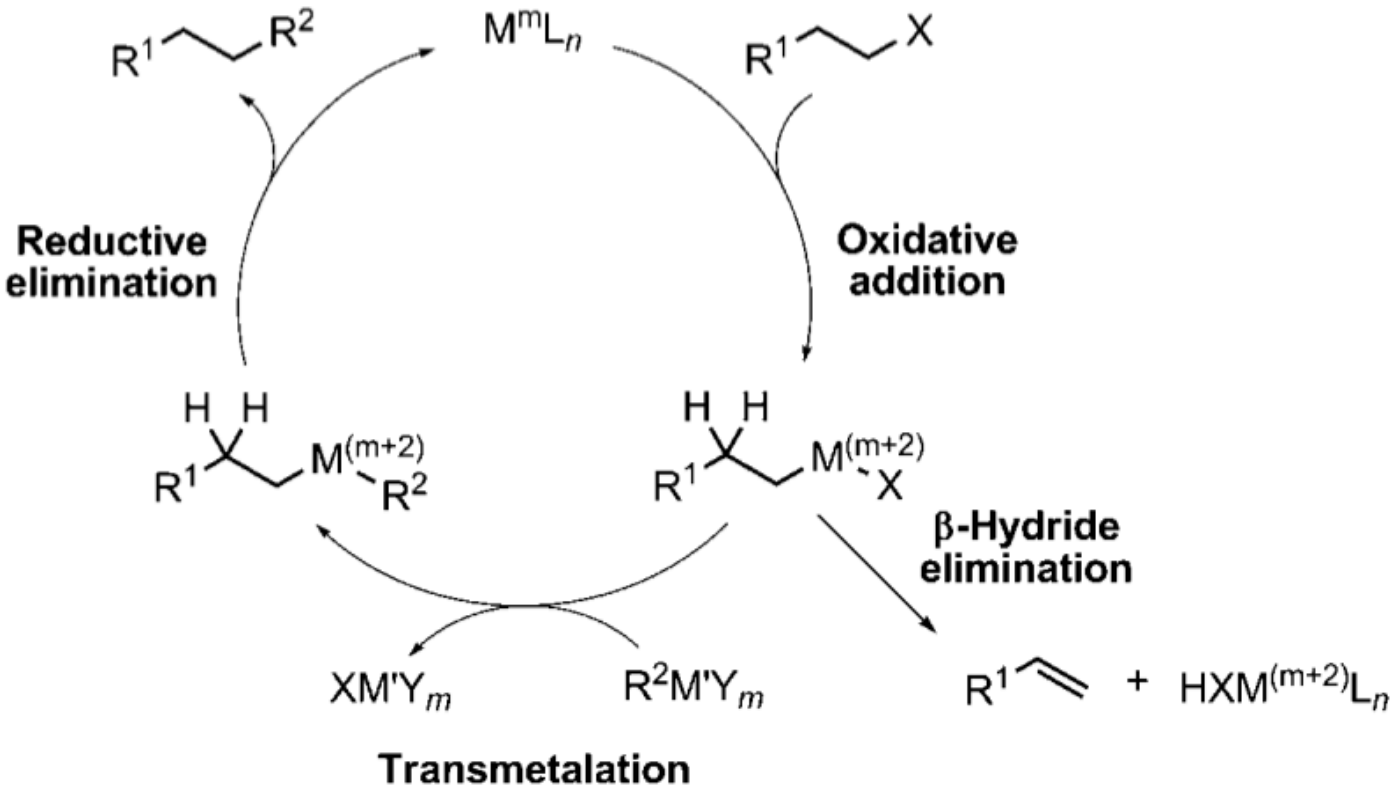
  M = BY_2, Pd catalysis, base

Introduction

UNIVERSITÄT BERN

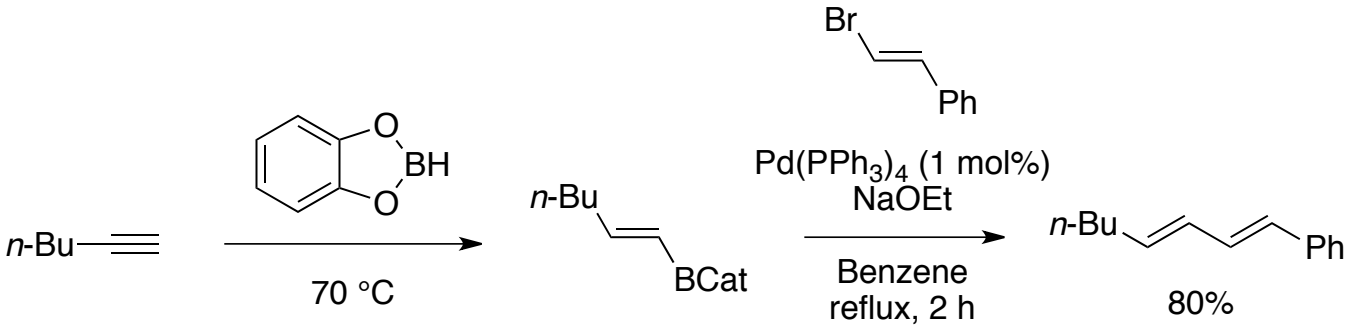
- Cross-coupling : Nobel Price 2010

Introduction

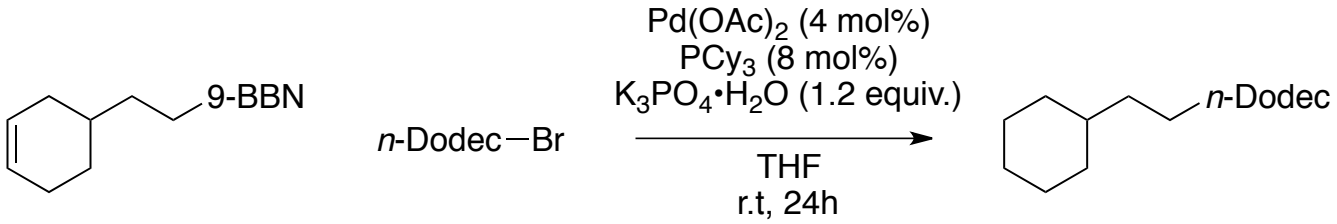


Rudolph, A.; Lautens, M. *Angew. Chem. Int. Ed.* **2009**, 48, 2656

Suzuki Cross-Coupling

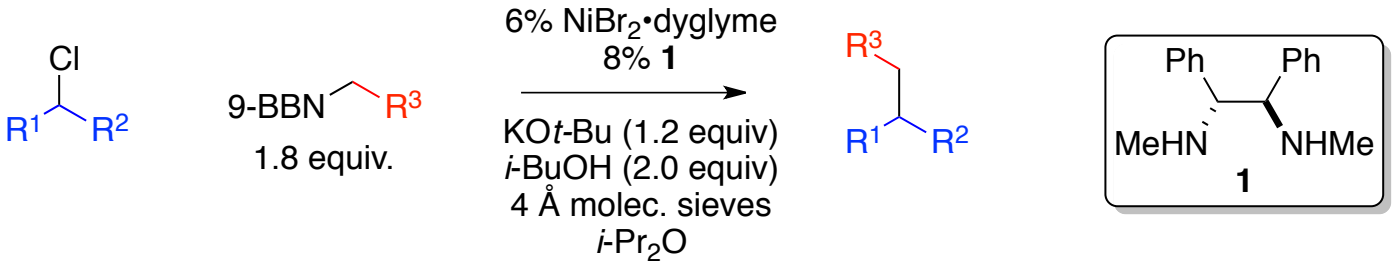


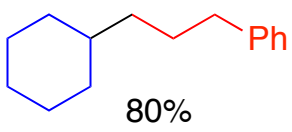
Miyaura, N.; Yamada, K.; Suzuki, A. *Tetrahedron Lett.* **1972**, 36, 3437

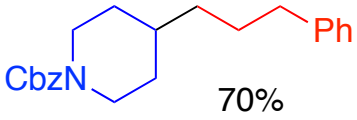


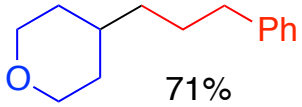
Lou, S.; Fu, G. C. *Org. Syn.* **2010**, 87, 299

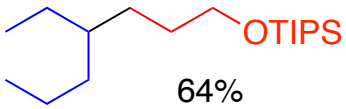
Suzuki Cross-Coupling

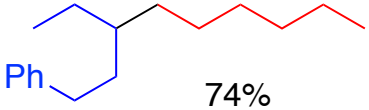


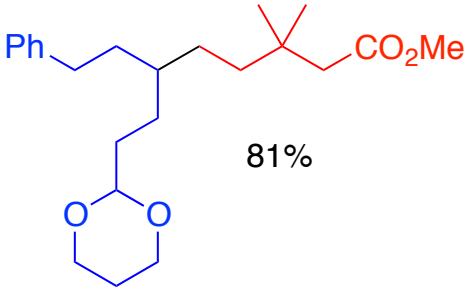






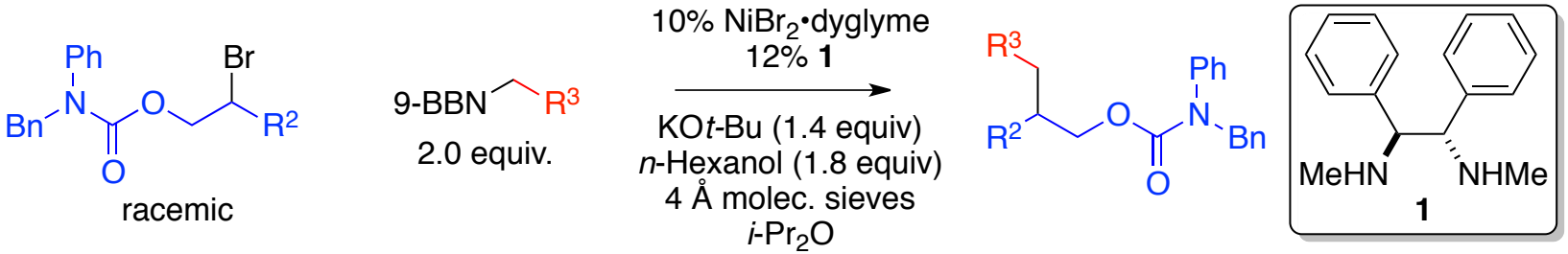


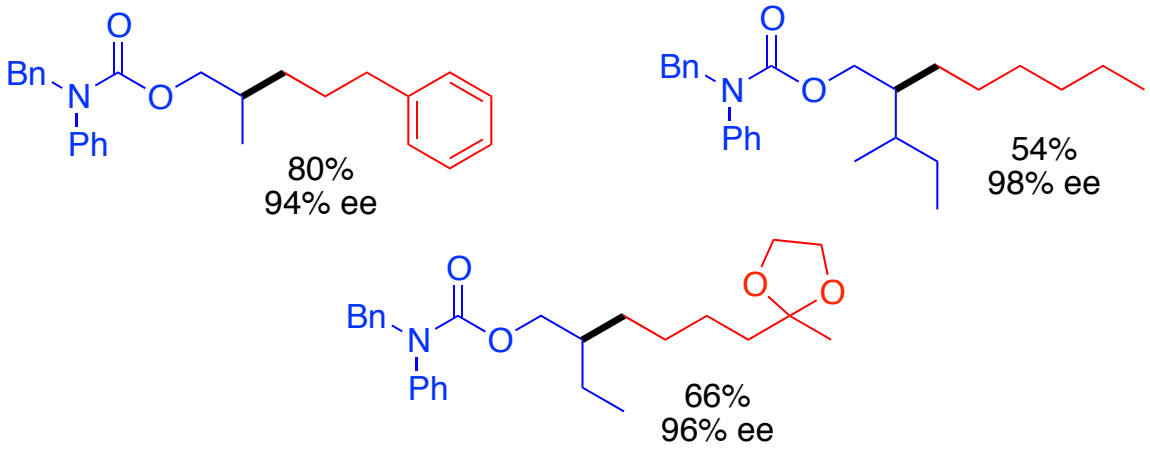




Lu, Z.; Fu, G. C. *Angew. Chem. Int. Ed.* **2010**, 49, 6676

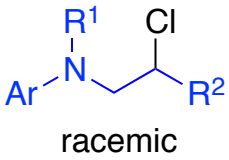
Suzuki Cross-Coupling



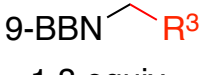


Owston, N. A.; Fu, G. C. *J. Am. Chem. Soc.* **2010**, 132, 11908.

Suzuki Cross-Coupling



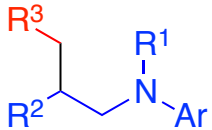
racemic

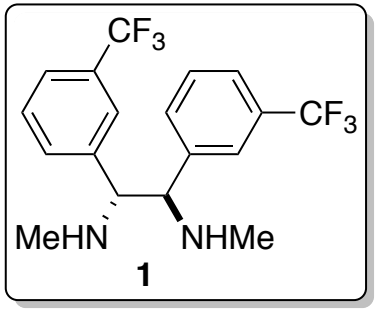


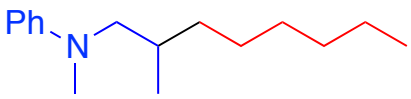
1.8 equiv.

10% $NiBr_2$•dyglyme
12% **2**

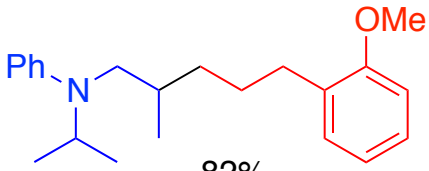
KO*t*-Bu (1.2 equiv)
i-BuOH (2.0 equiv)
4 Å molec. sieves
i-Pr_2O



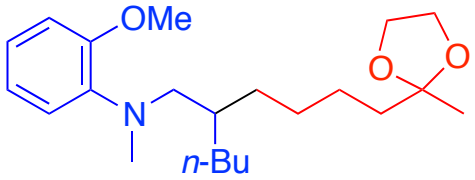




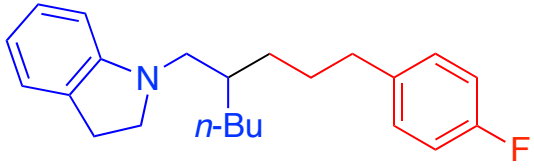
84%
88% ee



82%
72% ee



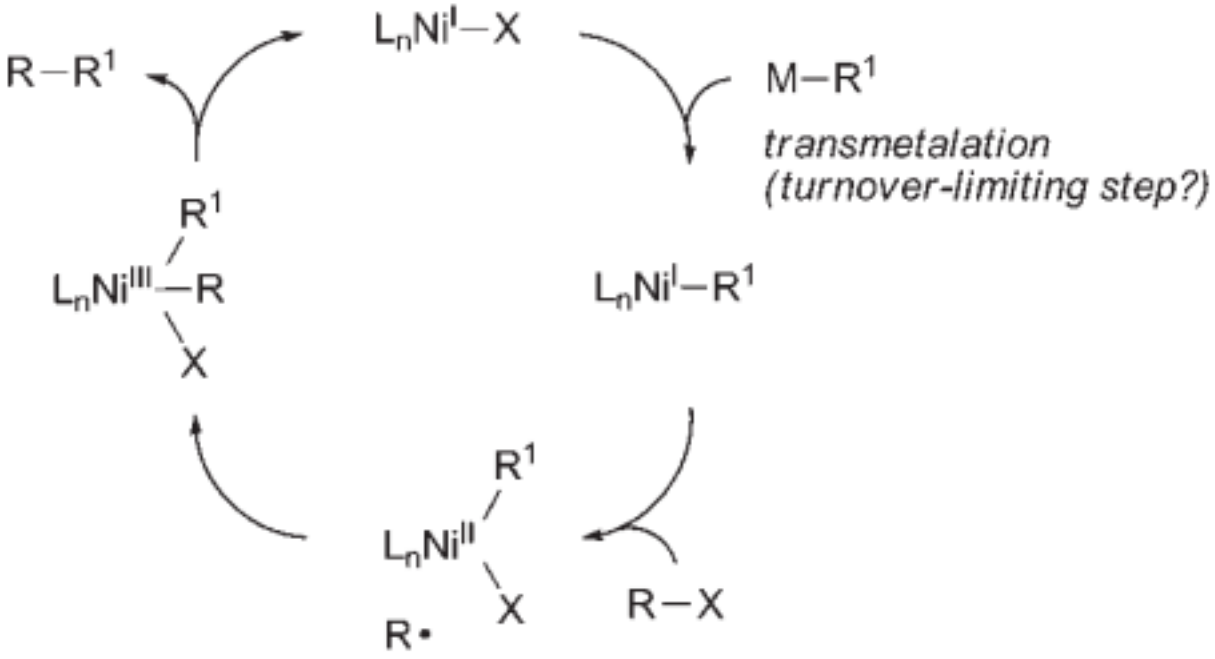
94%
86% ee



92%
57% ee

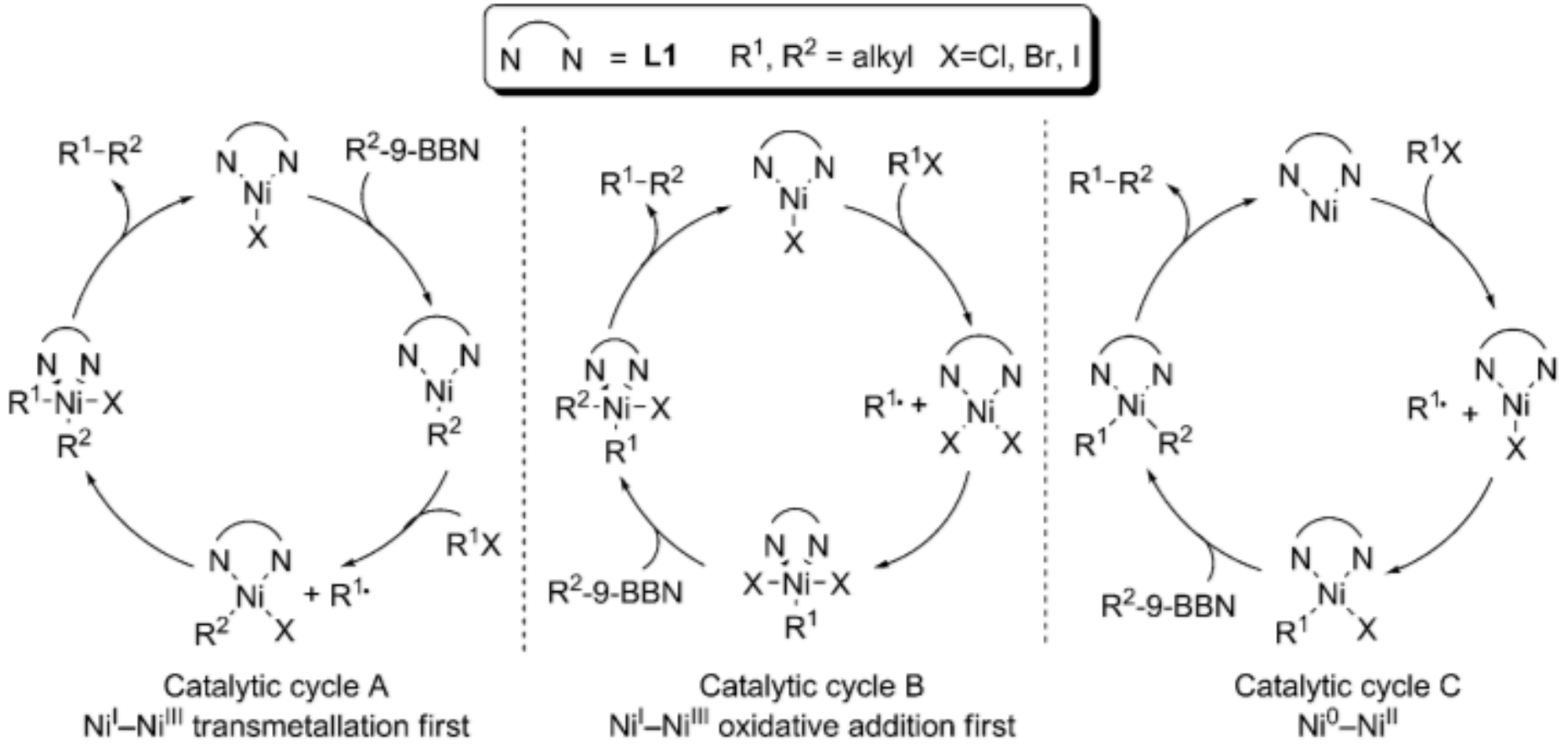
Lu, Z.; Wilsily, A.; Fu, G. C. *J. Am. Chem. Soc.* **2011**, 133, 8154.

Suzuki Cross-Coupling



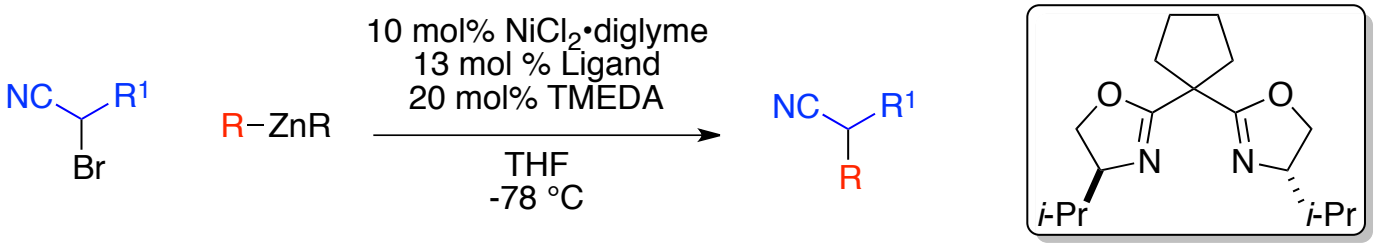
Lu, Z.; Wilsily, A.; Fu, G. C. *J. Am. Chem. Soc.* **2011**, 133, 8154.

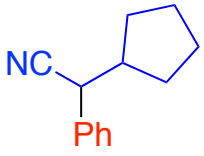
Suzuki Cross-Coupling



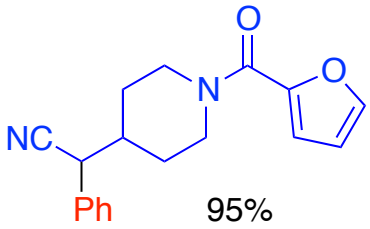
Li, Z.; Jiang, Y.-Y.; Fu, Y. *Chem. Eur. J.* **2012**, 18, 4345

Negeshi Cross-Coupling





77%
92% ee



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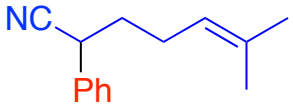
85% ee



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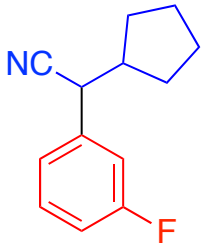
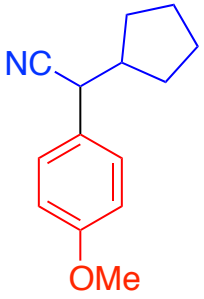
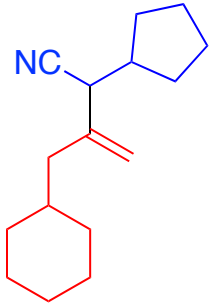
78% ee



99%
93% ee



81%
94% ee



59%
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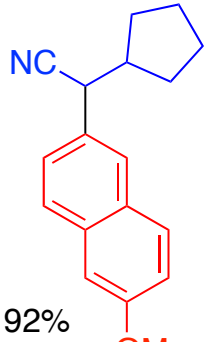
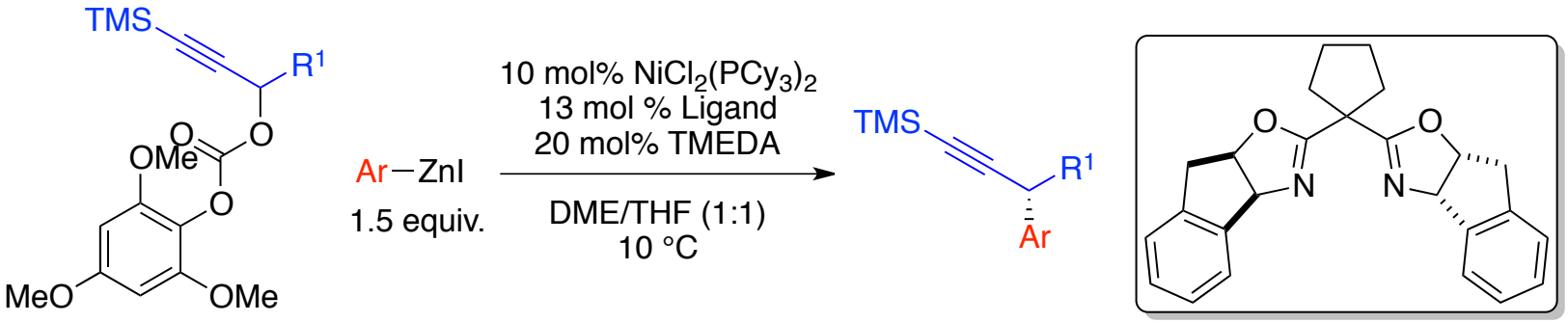
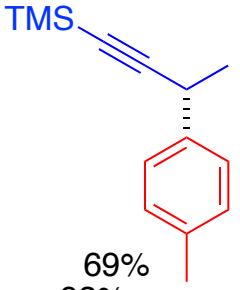


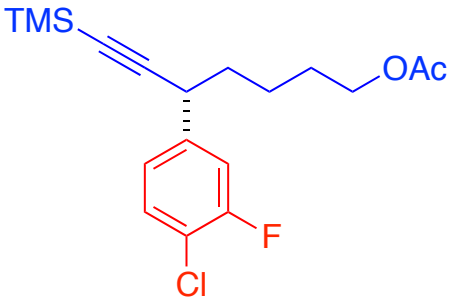
92%
92% ee

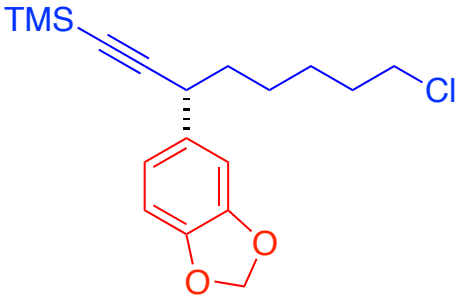
Choi, J.; Fu, G. C. *J. Am. Chem. Soc.* **2012**, 134, 9102.

Negeshi Cross-Coupling



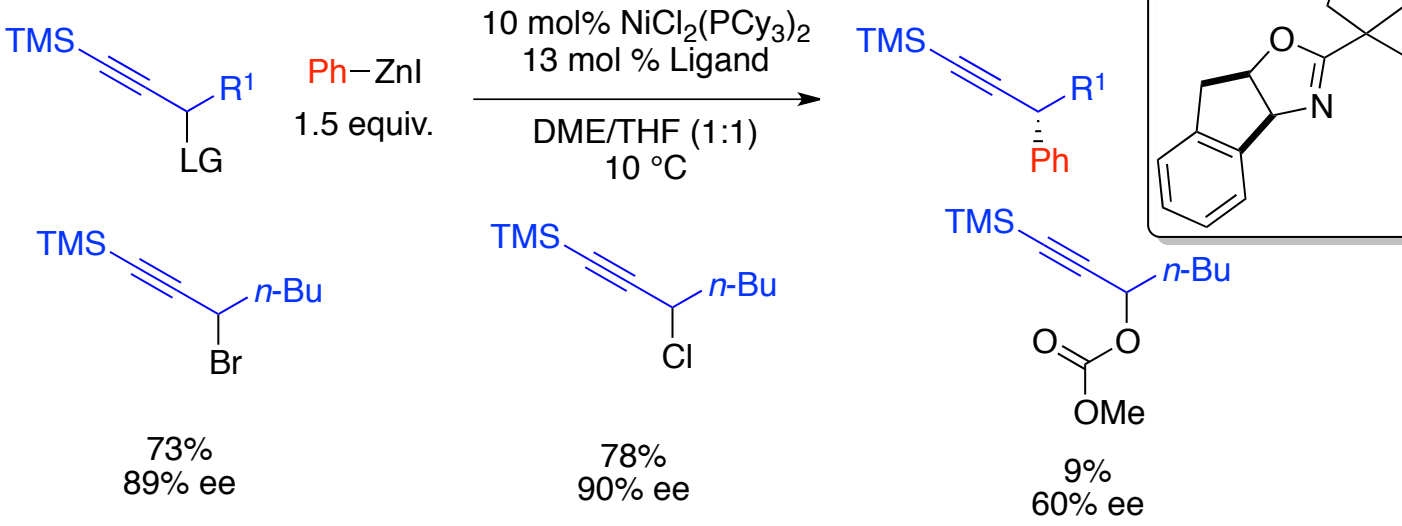






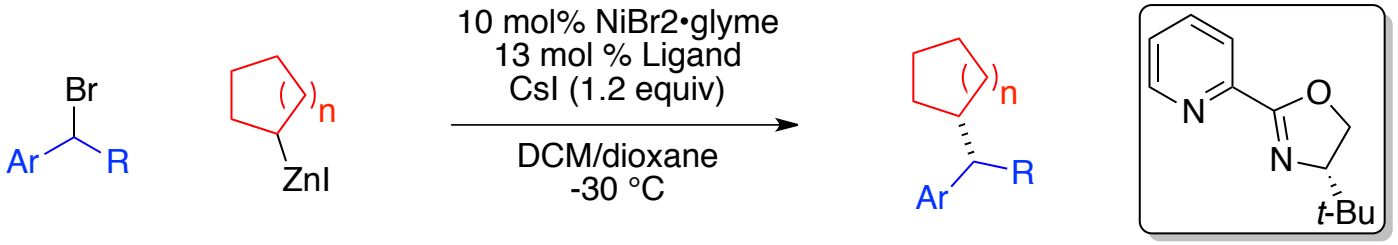
Oelke, A. J.; Sun, J.; Fu, G. C. *J. Am. Chem. Soc.* **2012**, 134, 2966.

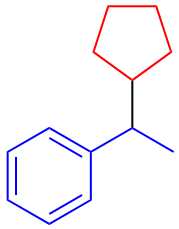
Negeshi Cross-Coupling



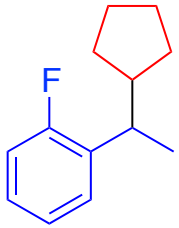
Oelke, A. J.; Sun, J.; Fu, G. C. *J. Am. Chem. Soc.* **2012**, 134, 2966.

Negeshi Cross-Coupling





91%
96% ee



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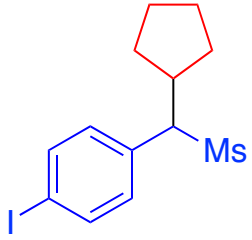

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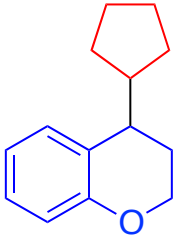

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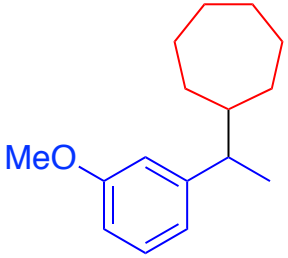
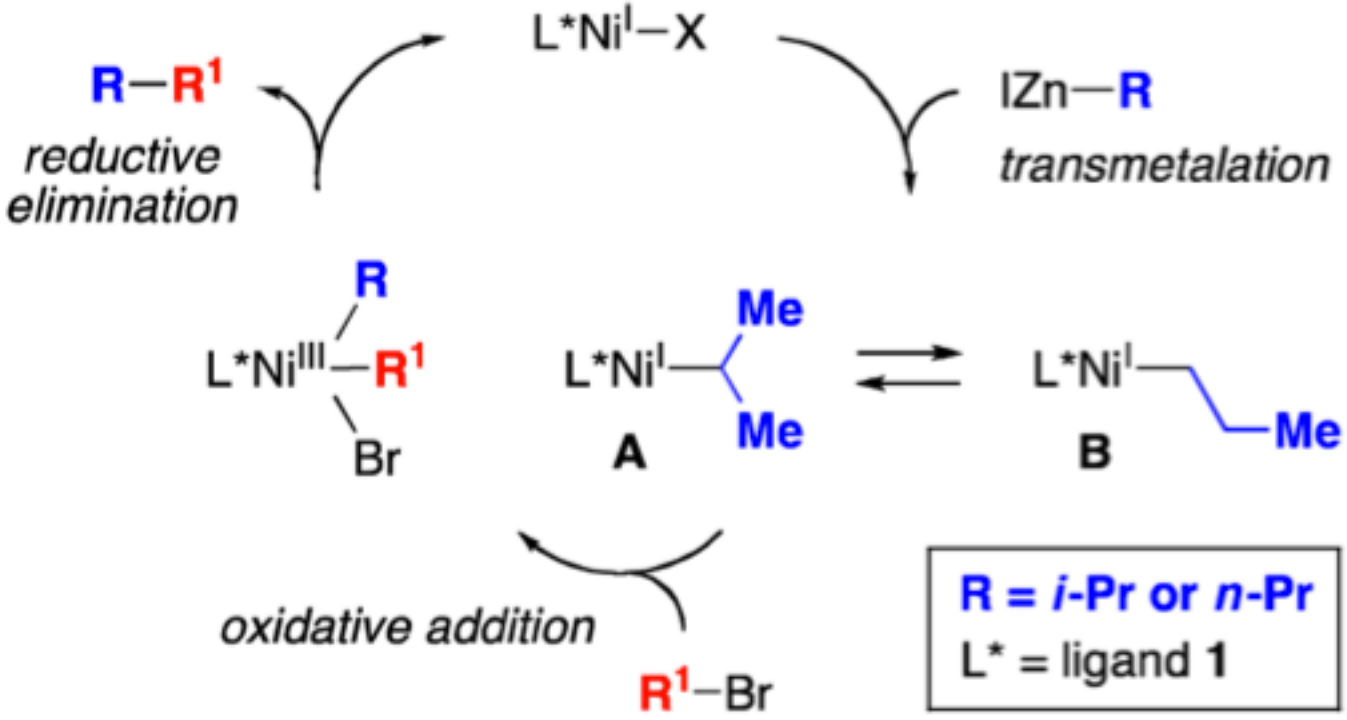


52%
84% ee

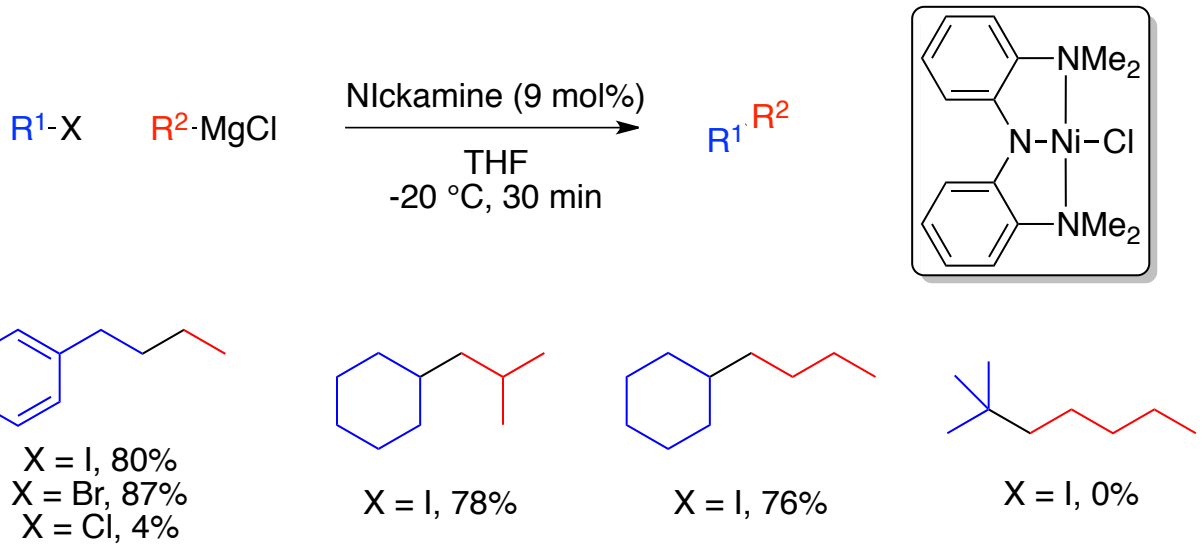
Binder, J. T.; Cordier, C. J.; Fu, G. C. *J. Am. Chem. Soc.* **2012**, 134, 17003.

Negeshi Cross-Coupling



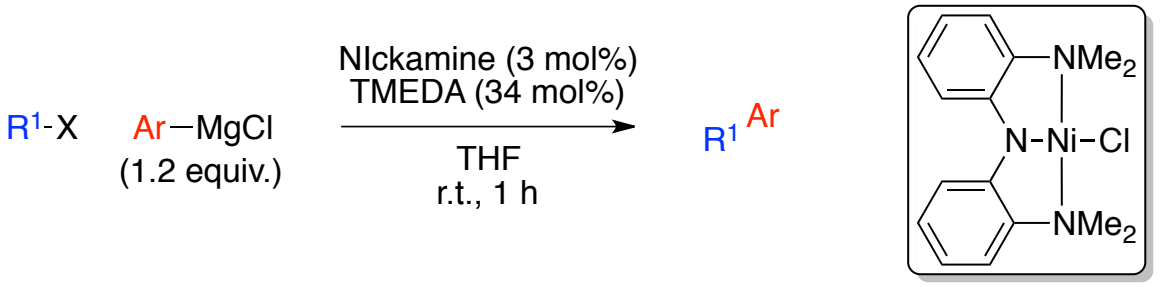
Binder, J. T.; Cordier, C. J.; Fu, G. C. *J. Am. Chem. Soc.* **2012**, 134, 17003.

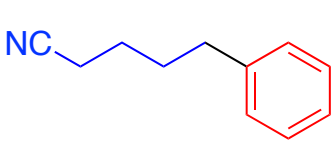
Kumada-Corriu-Tamao Cross-Coupling



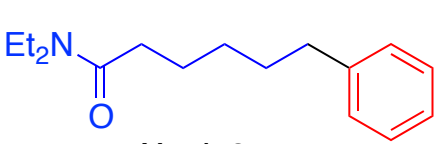
Vechorkin, O.; Csok, Z.; Scopelliti, R.; Hu, X. *Chem. Eur. J.* **2009**, 15, 3889.

Kumada-Corriu-Tamao Cross-Coupling

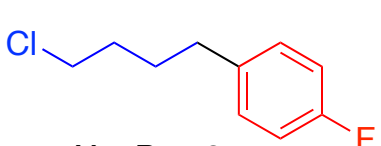




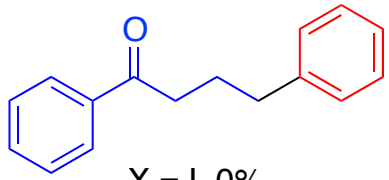
X = I, 80%



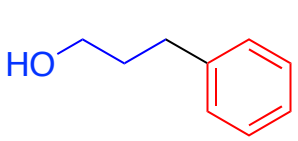
X = I, 84%



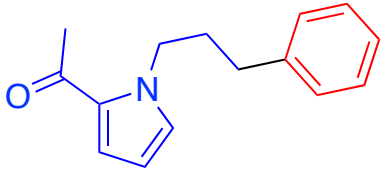
X = Br, 76%



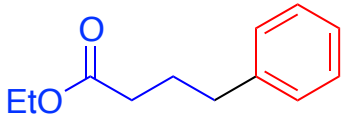
X = I, 0%



X = Br, 76%
(2.4 equiv of PhMgCl)



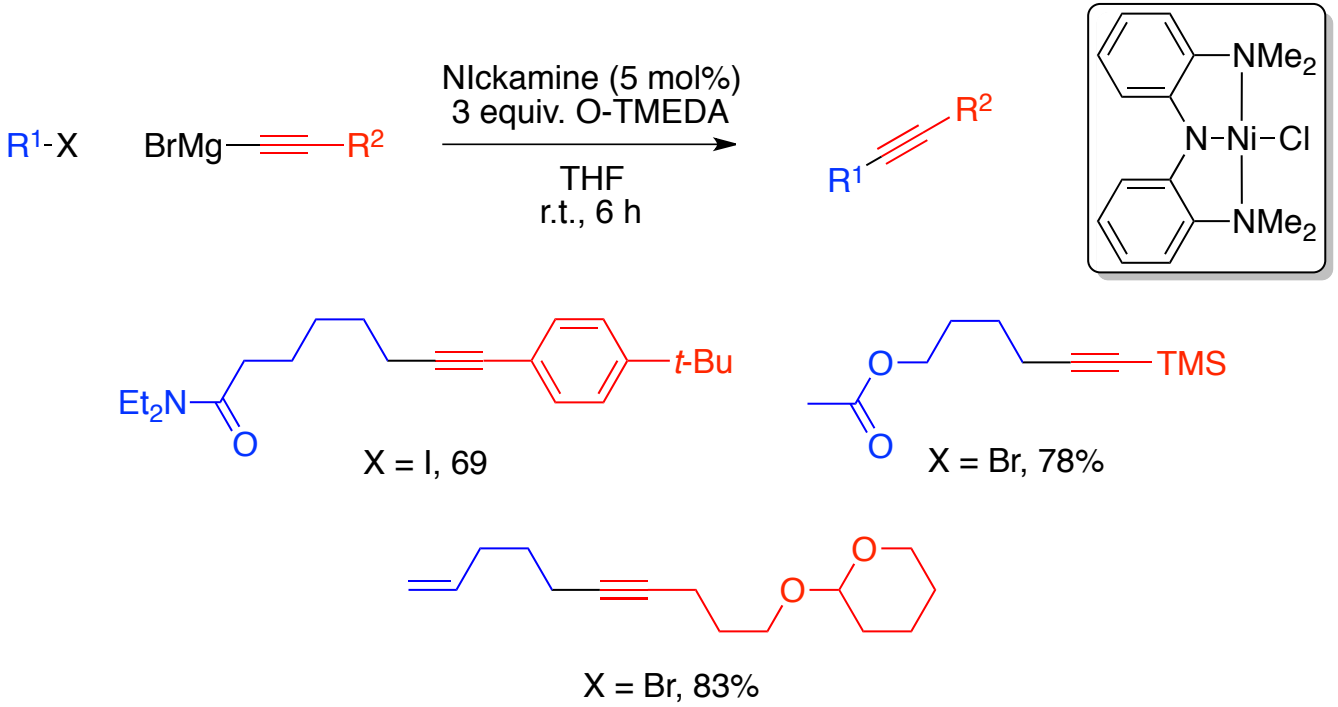
X = I, 62%
(60 mol% of O-TMEDA)



X = I, 75%
(60 mol% of O-TMEDA)

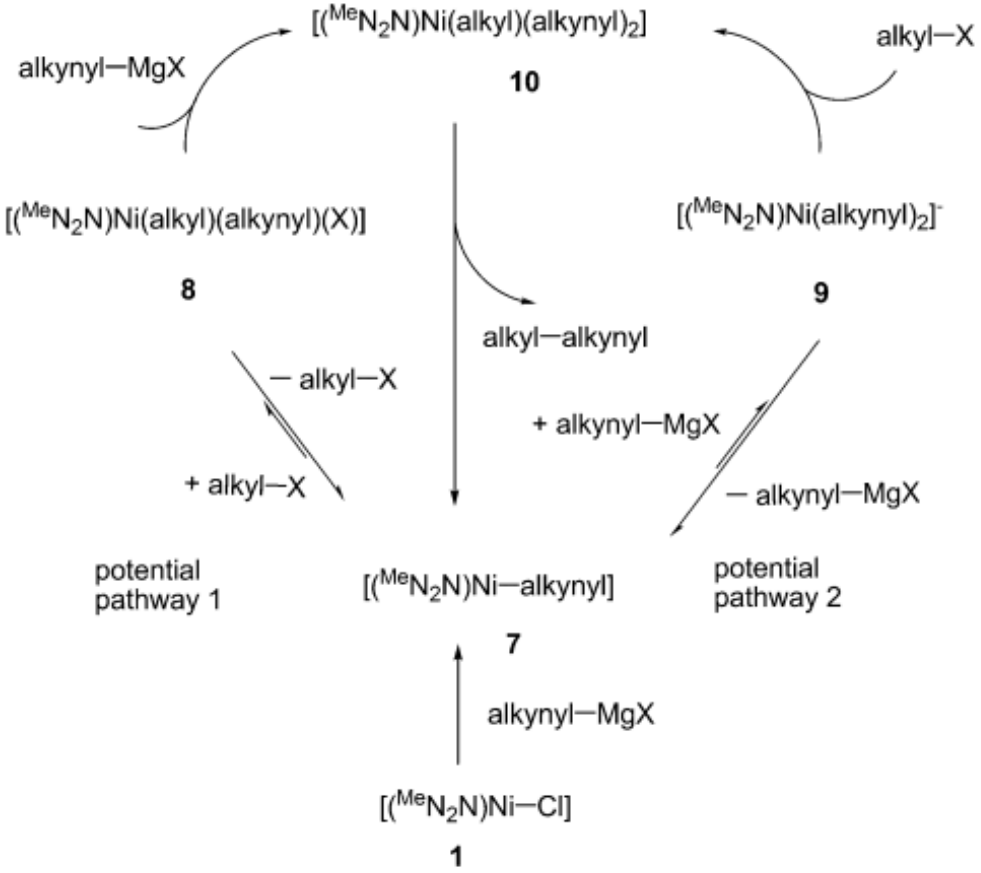
Vechorkin, O.; Proust, V.; Hu, X. *J. Am. Chem. Soc.* **2009**, 131, 9756.

Kumada-Corriu-Tamao Cross-Coupling



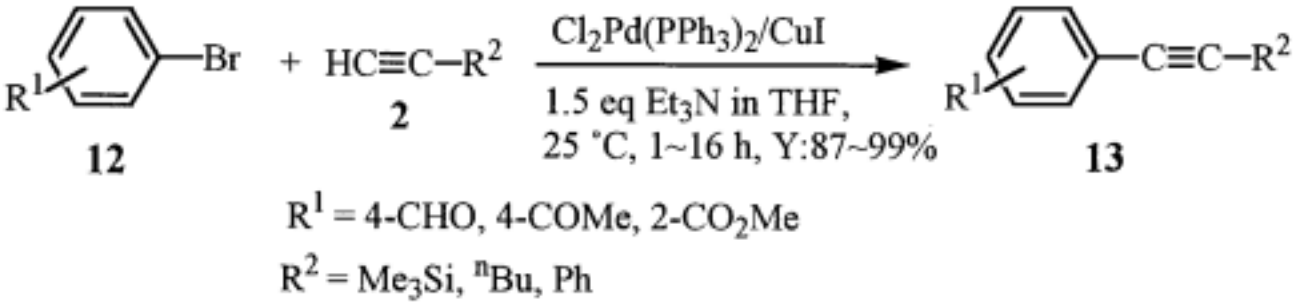
Vechorkin, O.;Godinat, A..; Scopelliti, R., Hu, X. *Angew. Chem. Int. Ed.* **2011**, 50, 11777.

Kumada-Corriu-Tamao Cross-Coupling



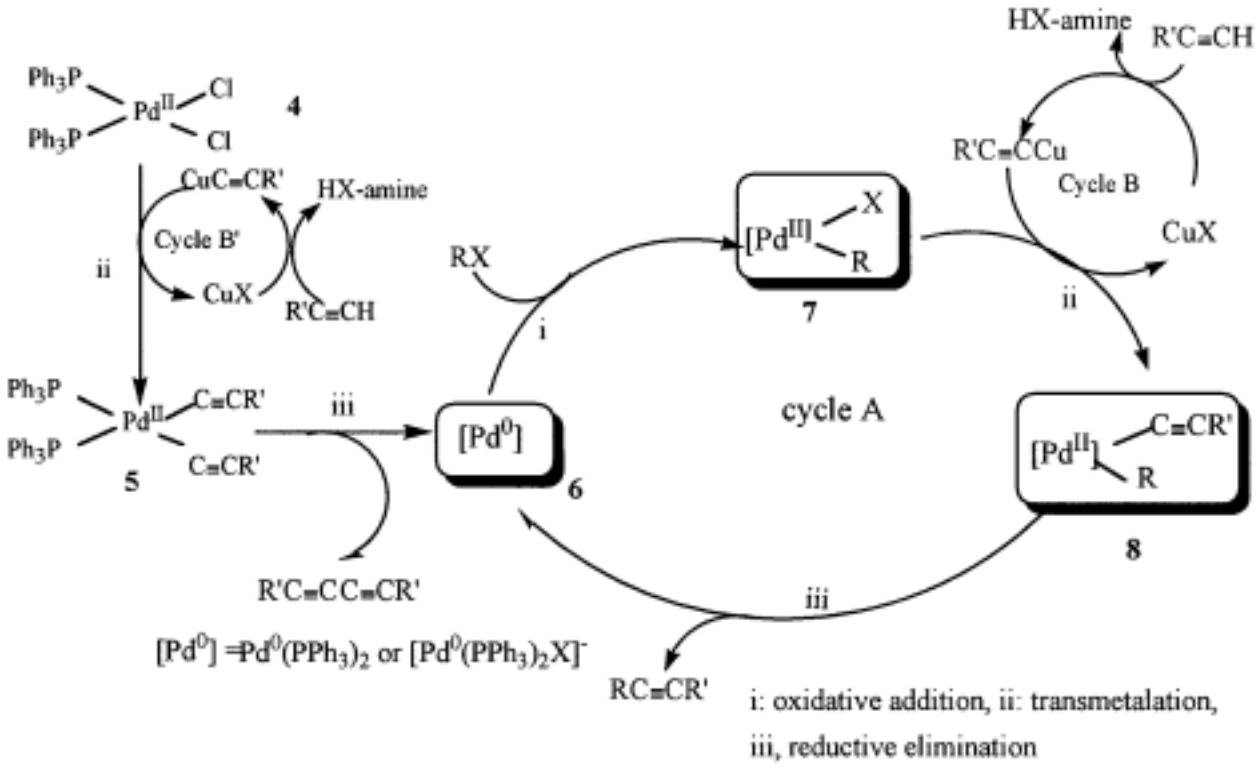
Vechorkin, O.;Godinat, A..; Scopelliti, R., Hu, X. *Angew. Chem. Int. Ed.* **2011**, 50, 11777.

Sonogashira Cross-Coupling



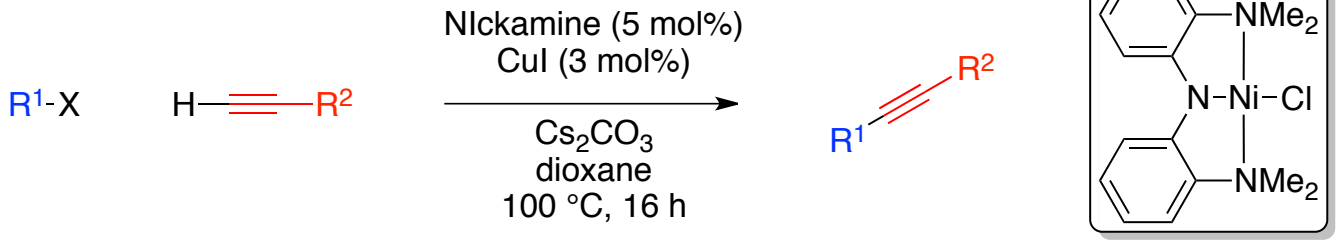
Sonogashira, K. *J. Organomet. Chem.* **2002**, 653, 46

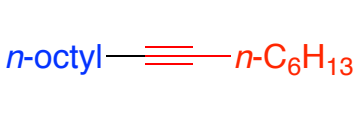
Sonogashira Cross-Coupling



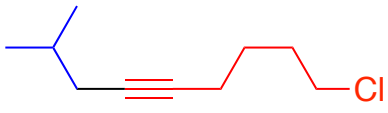
Sonogashira, K. *J. Organomet. Chem.* **2002**, 653, 46

Sonogashira Cross-Coupling

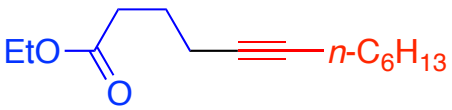




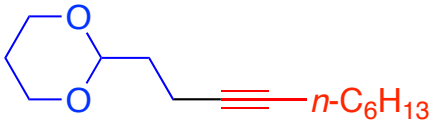
X = I, 83%



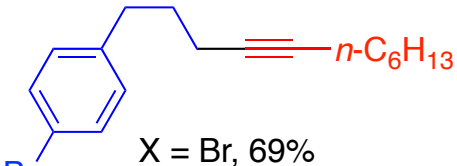
X = I, 84%



X = Br, 73%
with NaI (20 mol%)



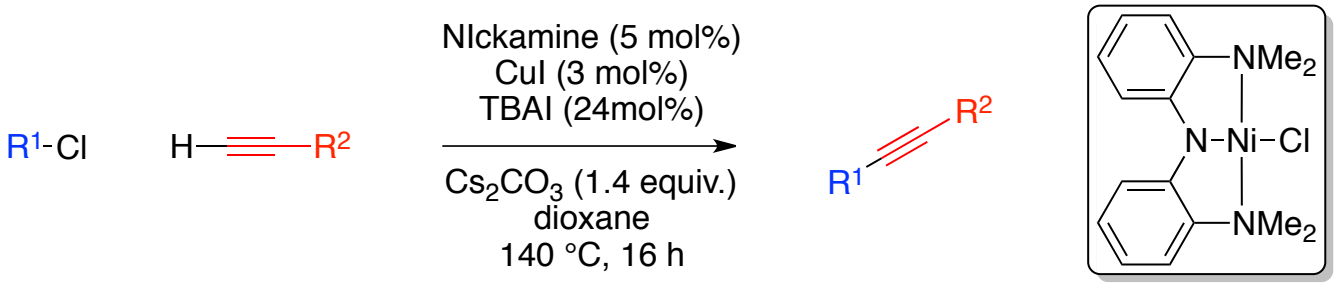
X = Br, 76%
with NaI (20 mol%)

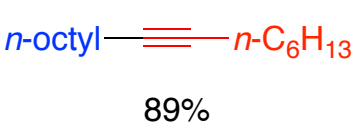


X = Br, 69%
with NaI (20 mol%)

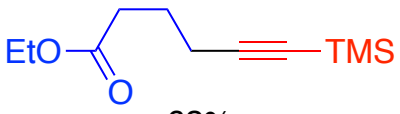
Vechorkin, O.; Barmaz, D.; Proust, V.; Hu, X. *J. Am. Chem. Soc.* **2009**, 131, 12078

Sonogashira Cross-Coupling

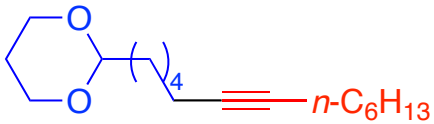




89%



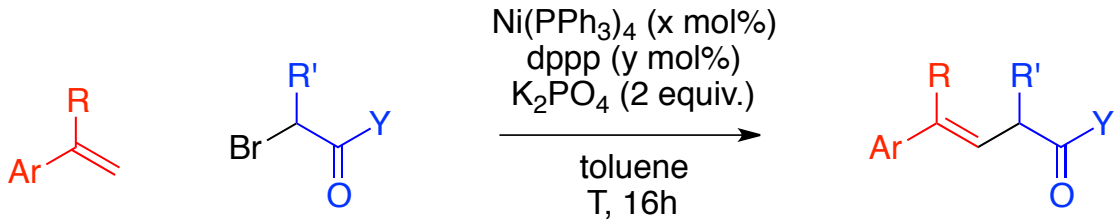
62%

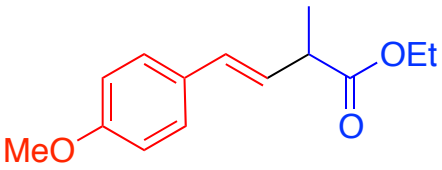


73%

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

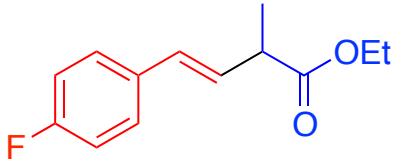
Heck-Type Cross-Coupling





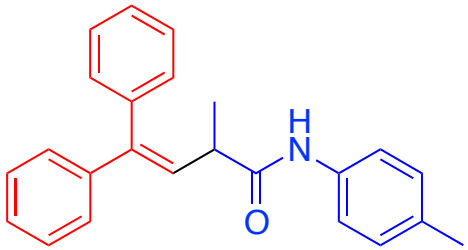
77%

with: $Ni(PPh_3)_4$ (5 mol%)
dppb (6 mol%)
60 °C



49%

with: $Ni(PPh_3)_4$ (5 mol%)
dppb (6 mol%)
60 °C

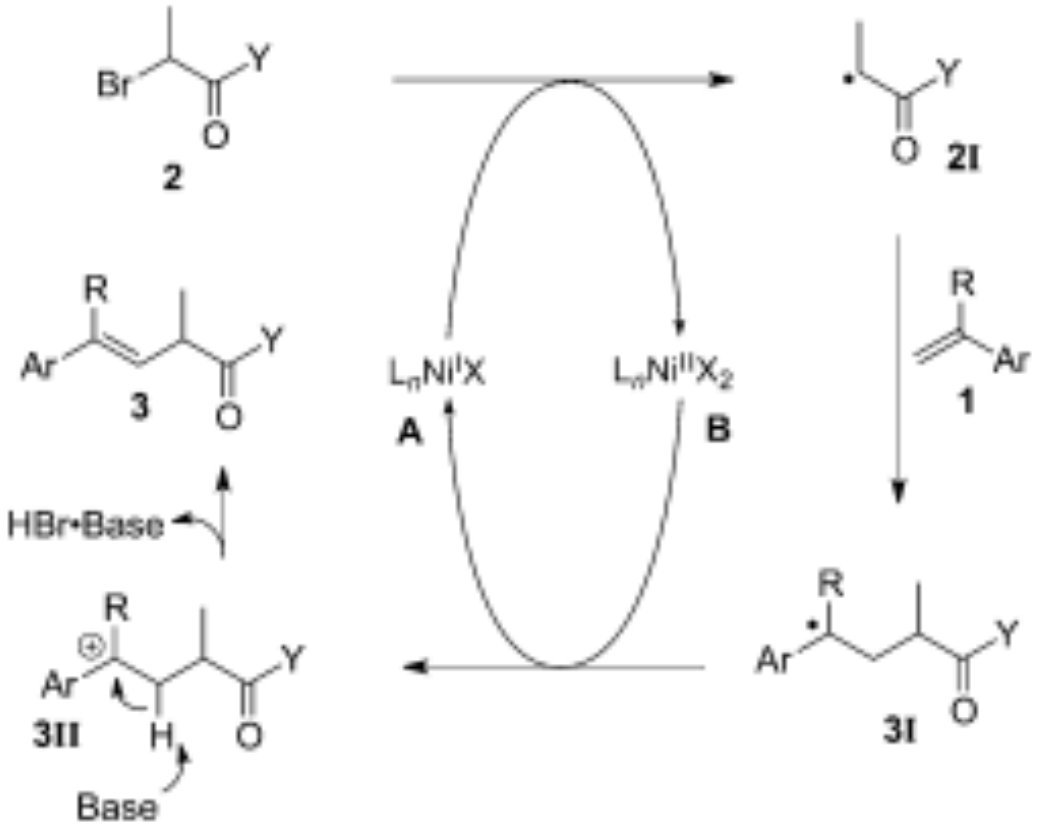


89%

with: $Ni(PPh_3)_4$ (10 mol%)
dppb (12 mol%)
100 °C

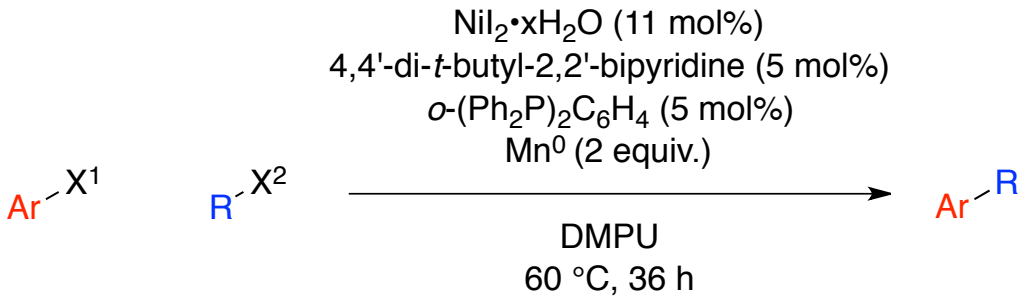
Liu, C.; Tang,S.; Yuan, J.; Zheng, L.; Meng. L.; Lei,A. *Angew. Chem. Int. Ed.* **2012**, 51, 3638.

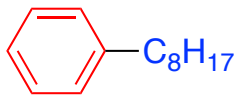
Heck-Type Cross-Coupling



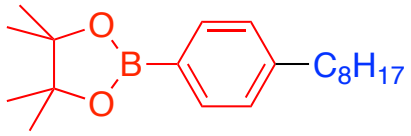
Liu, C.; Tang,S.; Yuan, J.; Zheng, L.; Meng. L.; Lei,A. *Angew. Chem. Int. Ed.* **2012**, 51, 3638.

Cross-Coupling of Aryl-Halide with Alkyl-Halide

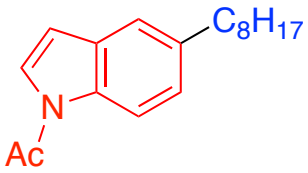




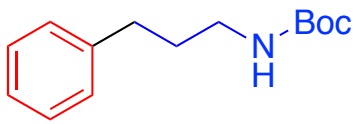
X^1= Br, X^2 = I
82%



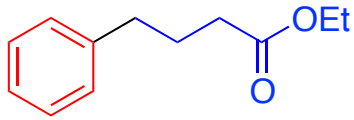
X^1= Br, X^2 = I
82%



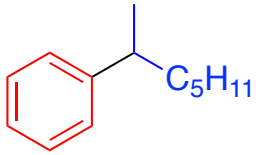
X^1= Br, X^2 = I
77%



X^1= I, X^2 = Br
85%



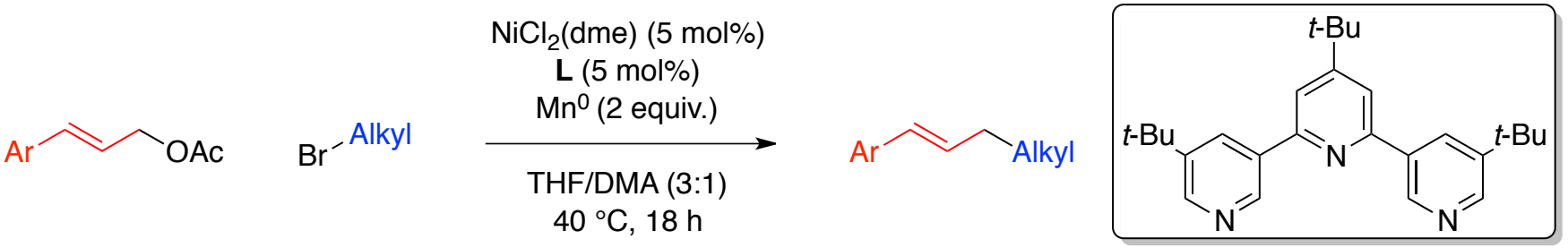
X^1= I, X^2 = Br
77% (T = 80 °C)

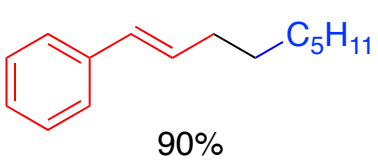


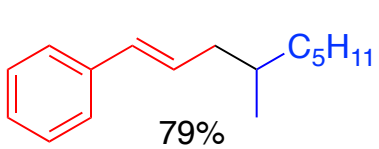
X^1= I, X^2 = Br
77%
(T = 80 °C, t = 36 h)

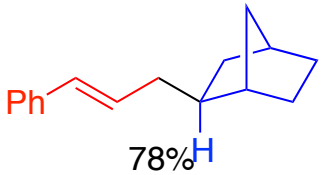
Everson, D. A.; Shrestha, R.; Weix, D. J. *J. Am. Chem. Soc.* **2010**, 132, 920

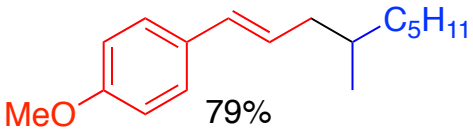
Cross-Coupling of Alkyl-Halides with Allylic Acetates

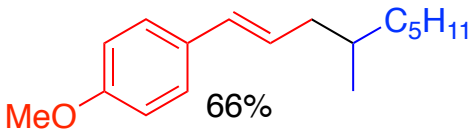






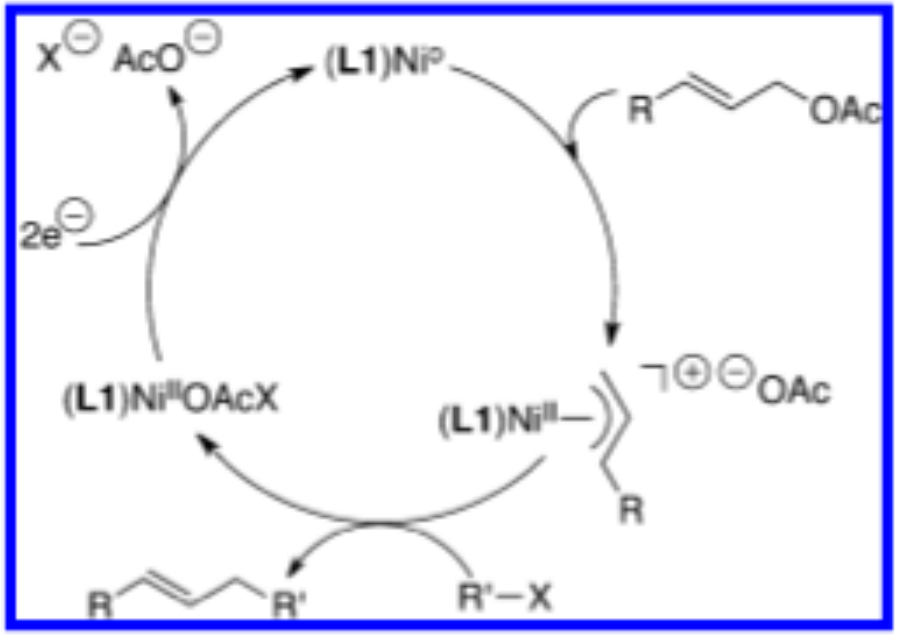






Anka-Lufford, L. L..; Prinsell, M. R.; Weix, D. J. *J. Org. Chem.*. **2012**, 77, 9989

Cross-Coupling of Alkyl-Halides with Allylic Acetates



Anka-Lufford, L. L..; Prinsell, M. R.; Weix, D. J. *J. Org. Chem.*. **2012**, 77, 9989

Conclusion

- Cross-Coupling C_{Sp3}-C_{Sp3}:
  - Pd : β-H elimination
  - Ni : more or less easy

- 2 distinctives methods :
  - Pd : retention of configuration
  - Ni : non retention