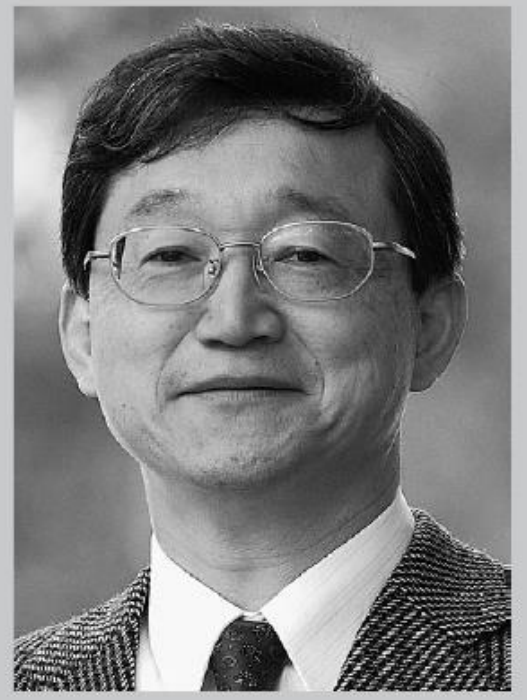
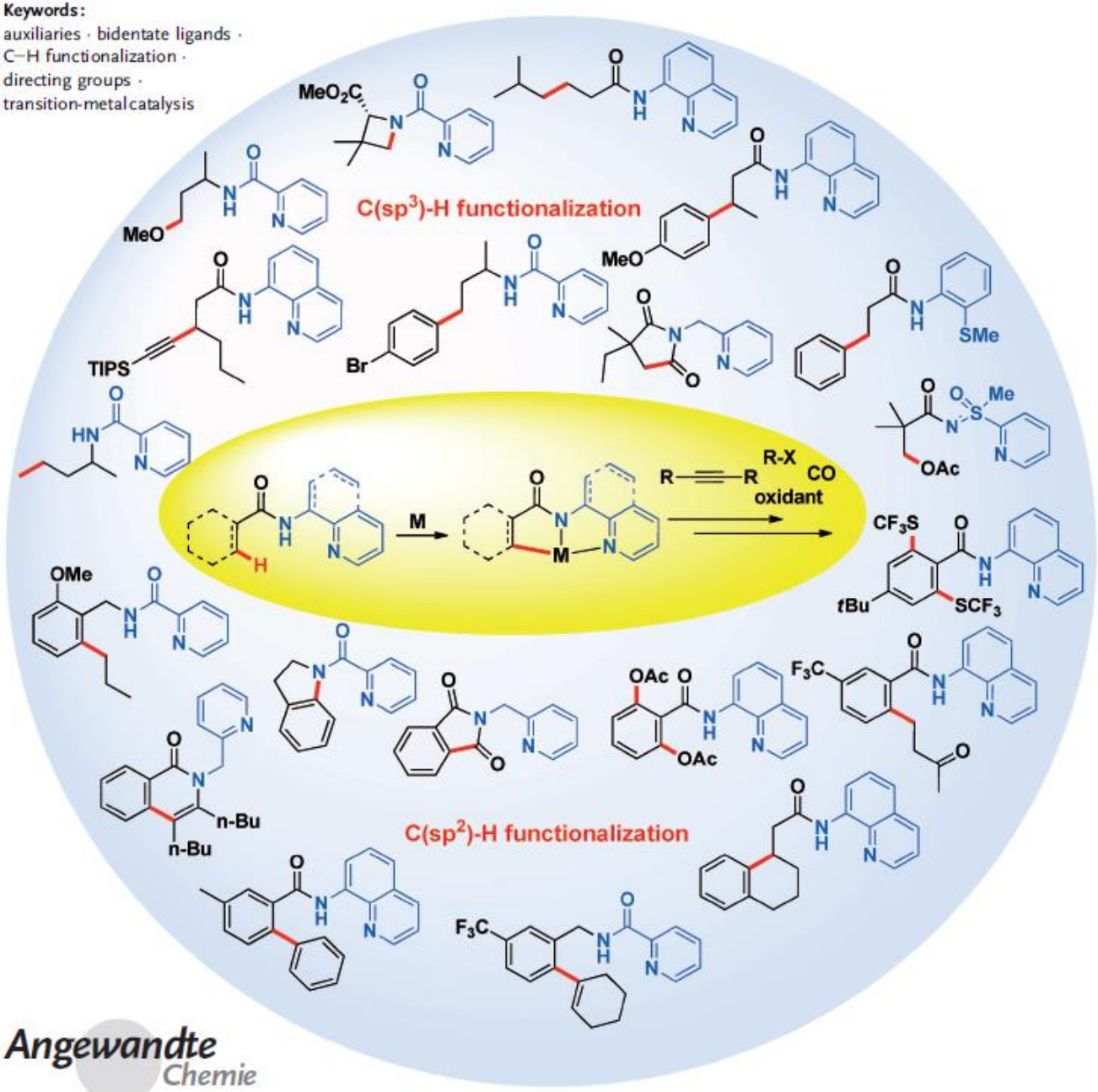
Catalytic Functionalization of C(sp^2)H and C(sp^3)H Bonds by Using Bidentate Directing Groups

Guy Rouquet and Naoto Chatani，*Angew. Chem. Int. Ed.* **2013**, 52, 2–20



Naoto Chatani studied chemistry at Osaka University and received his PhD in 1984 under the guidance of Profs. Noboru Sonoda and Shinji Murai. He then joined the Institute of Scientific and Industrial Research at Osaka University as an Assistant Professor in the group of Prof. Terukiyo Hanafusa. After postdoctoral studies with Prof. Scott E. Denmark at the University of Illinois, Urbana-Champaign, he returned to Osaka University (Prof. Shinji Murai's group), and became Associate Professor in 1992 and Professor in 2003. His research interests center on the area of catalysis.

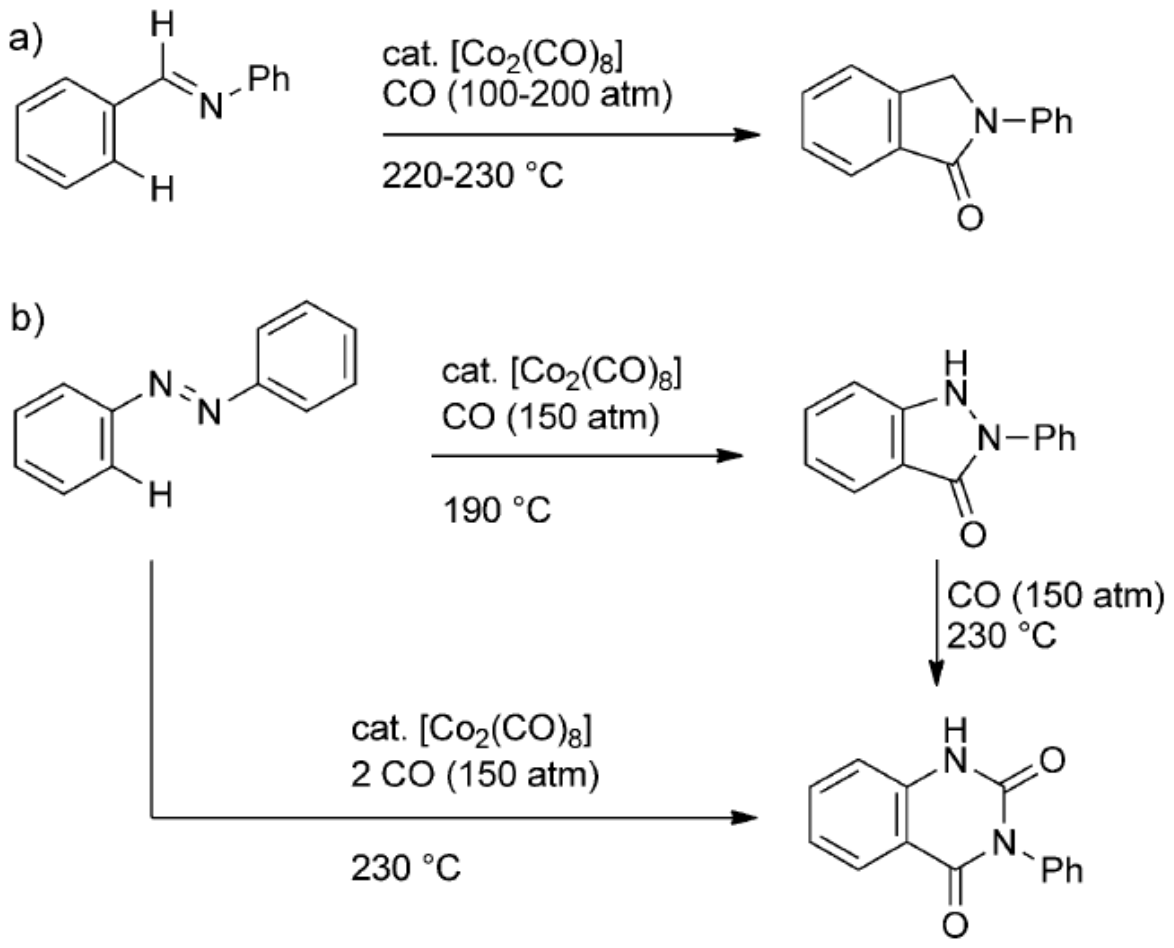
Keywords:
auxiliaries · bidentate ligands · C–H functionalization · directing groups · transition-metal catalysis



Angewandte Chemie

Contents

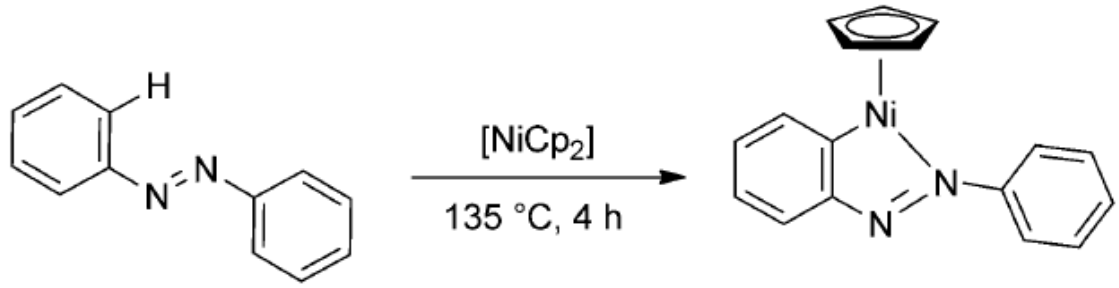
1 Introduction



Notes：

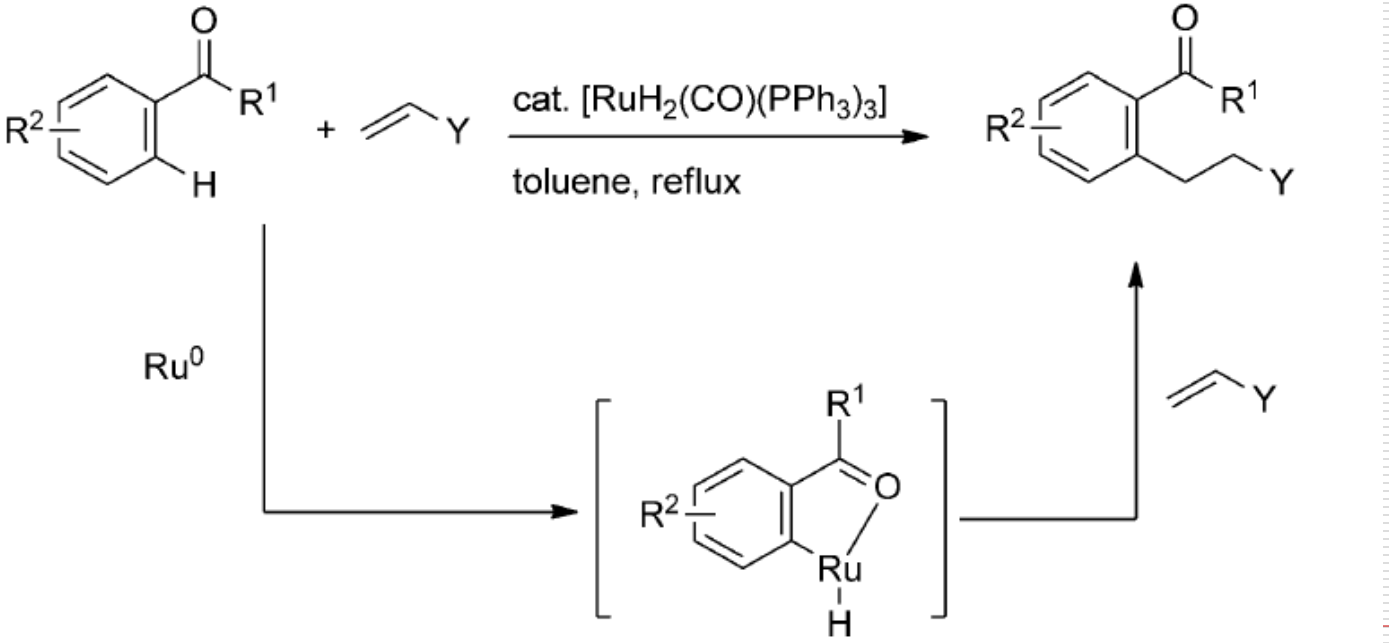
1. **The oldest examples**
2. **The mechanism was not well understood**

S. Murahashi, *J. Am. Chem. Soc*. **1955**, 77, 6403;
S.Murahashi, S. Horiie, *J. Am. Chem. Soc*. **1956**, 78, 4816.



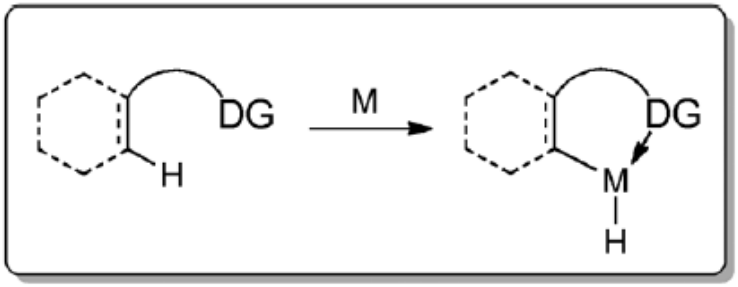
J. P. Kleiman, M. Dubeck, *J. Am. Chem. Soc.* **1963**, 85, 1544.

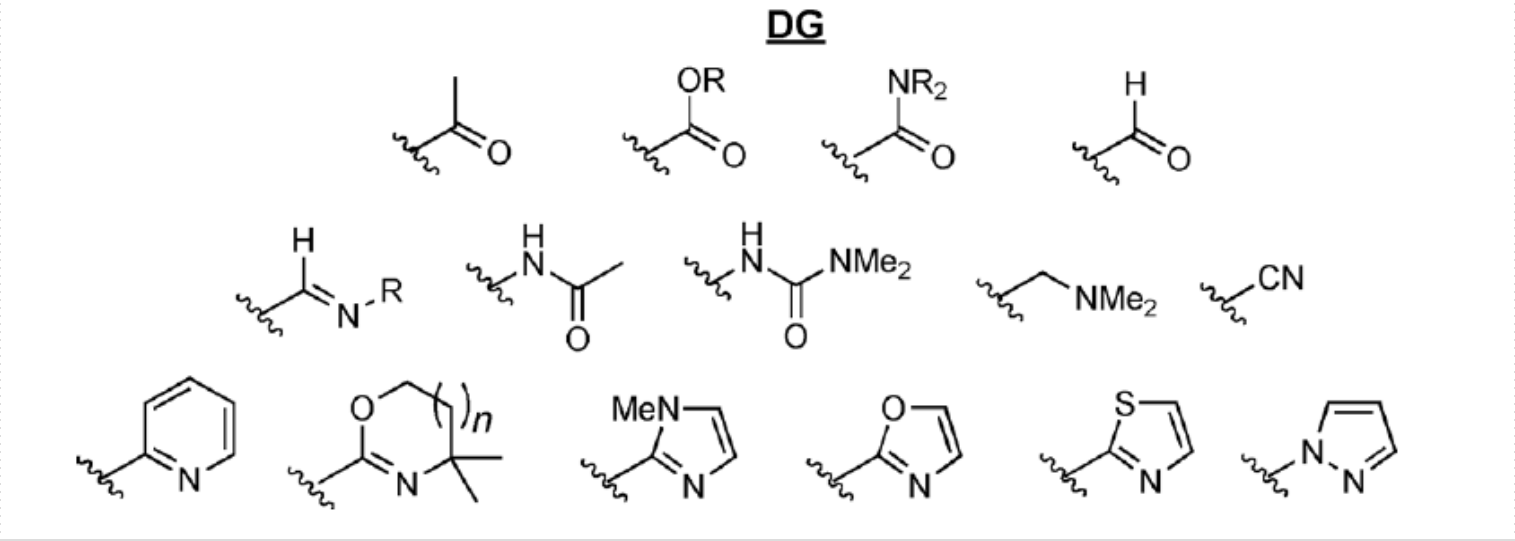
Notes: (1) Some functional groups can promote the insertion of metal into an ortho-C(sp2)H bond.
(2) Much progress was made in the field in the following 30 years, but need the stoichiometric amount of metal, and a few examples were catalytic reactions.



S. Murai, F. Kakiuchi, S. Sekine, Y. Tanaka, A. Kamatani, M. Sonoda, N. Chatani, *Nature* **1993**, 366, 529.

Notes: (1) this was a real breakthrough.

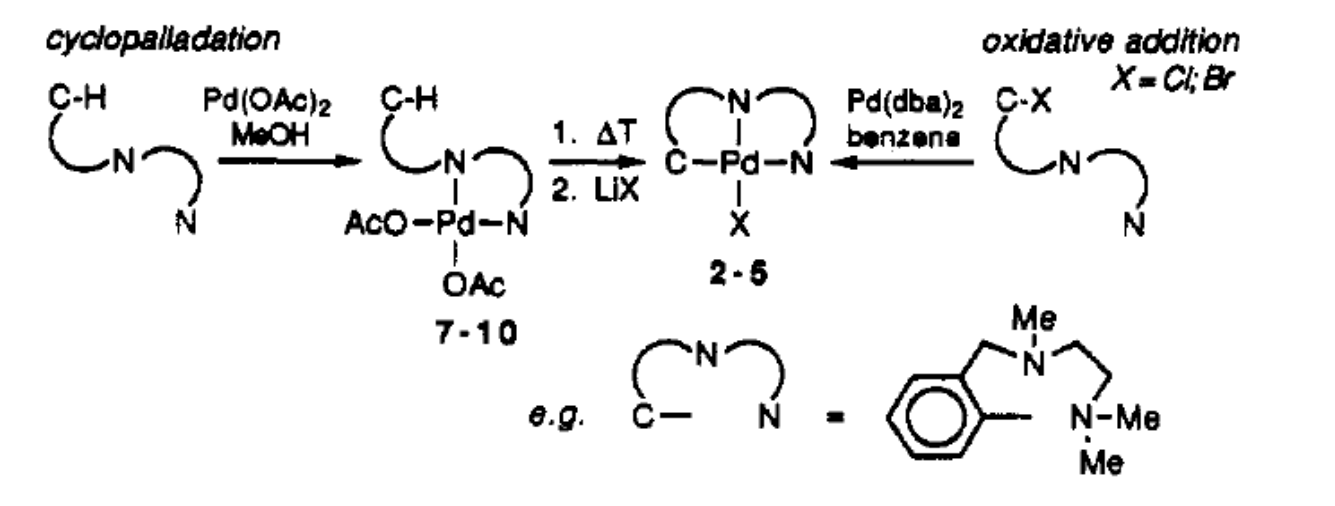


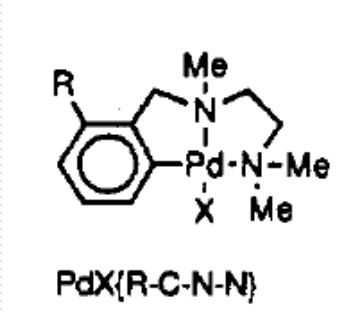


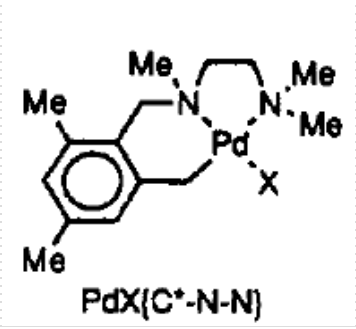
Notes: (1) Metals: Pd, Rh, Ru, Cu, Ni, etc.

(2) C-X(X= C, O, N, F, Cl, Br, I, Si, P, etc.) bond formations

(3) Some inherent limitations in monodentate directing groups

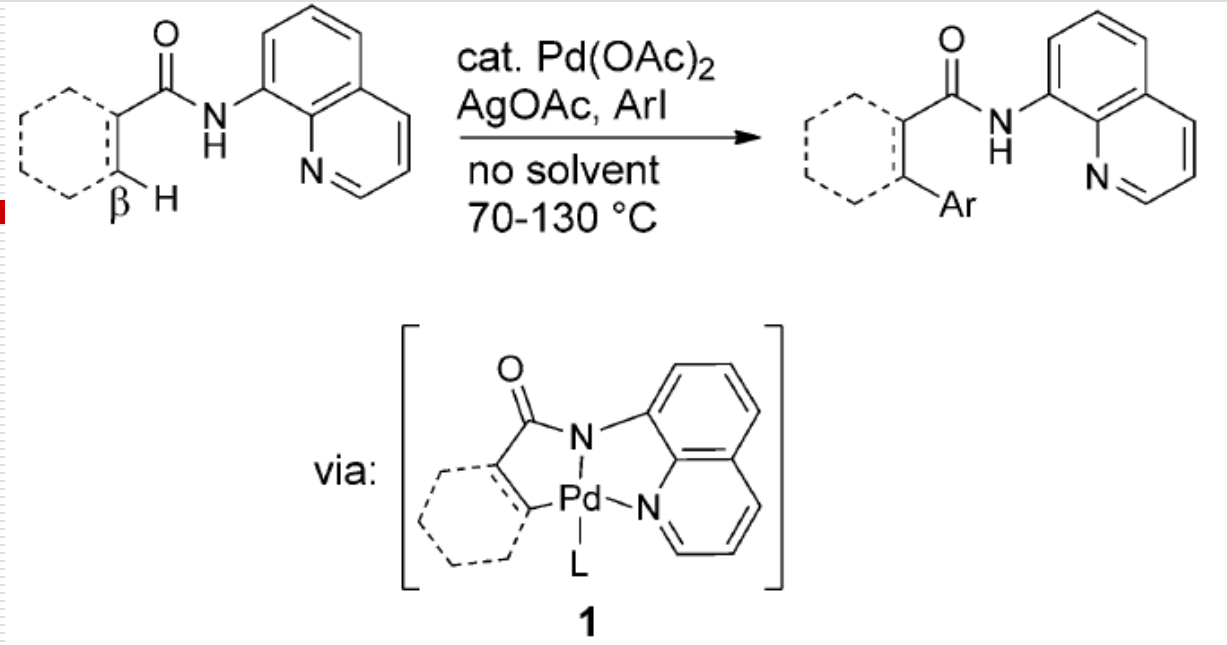






L. Spek, G. van Koten, *Organometallics* **1993**, 12, 1831.

Notes: a stoichiometric amount of a stable metallacycle

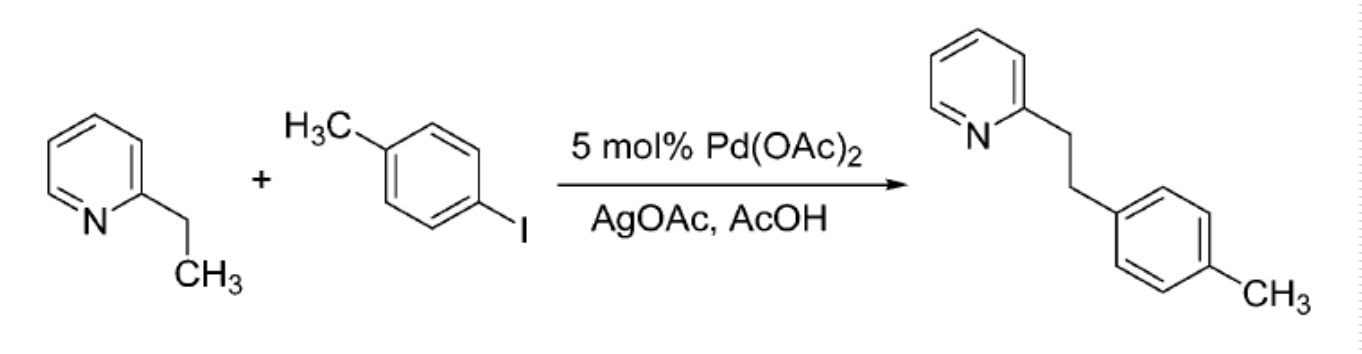


V. G. Zaitsev, D. Shabashov, O. Daugulis, *J. Am. Chem. Soc.* 2005, 127, 13154

Notes: (1) Catalytic reaction
(2) B C-H activation of amides
(3) This bidentate directing grouping is interesting and easily removable
(4) New catalytic strategies have been developed in the following years.

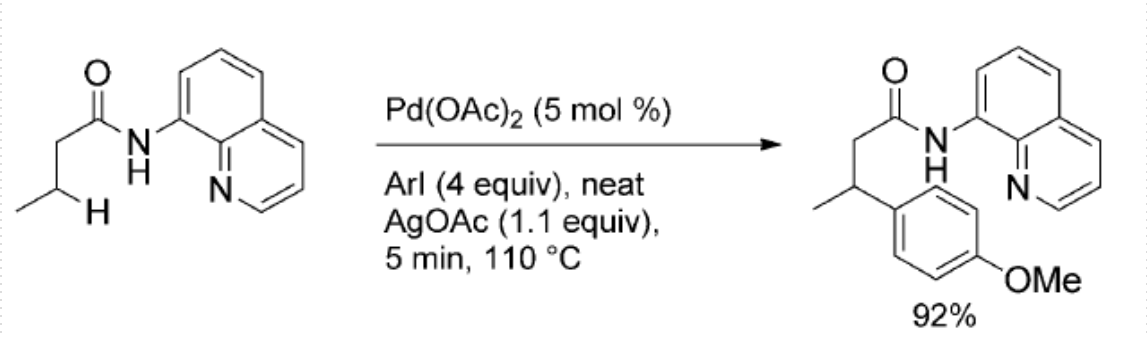
2 Palladium Catalyst

Arylation and Alkenylation of C-H Bonds

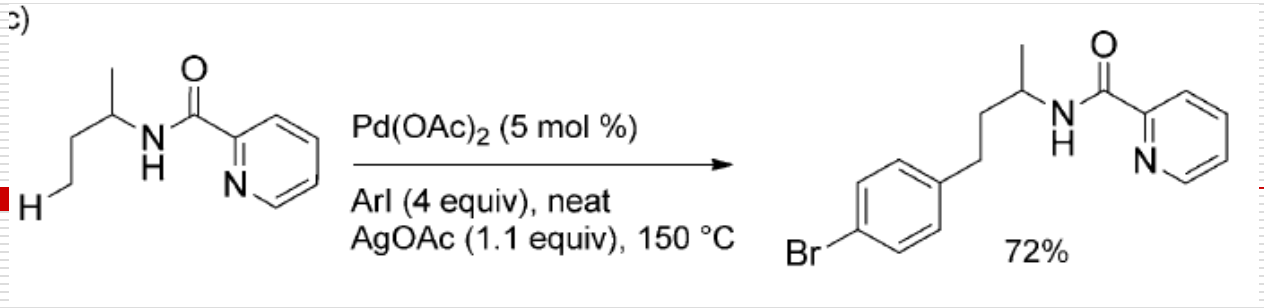


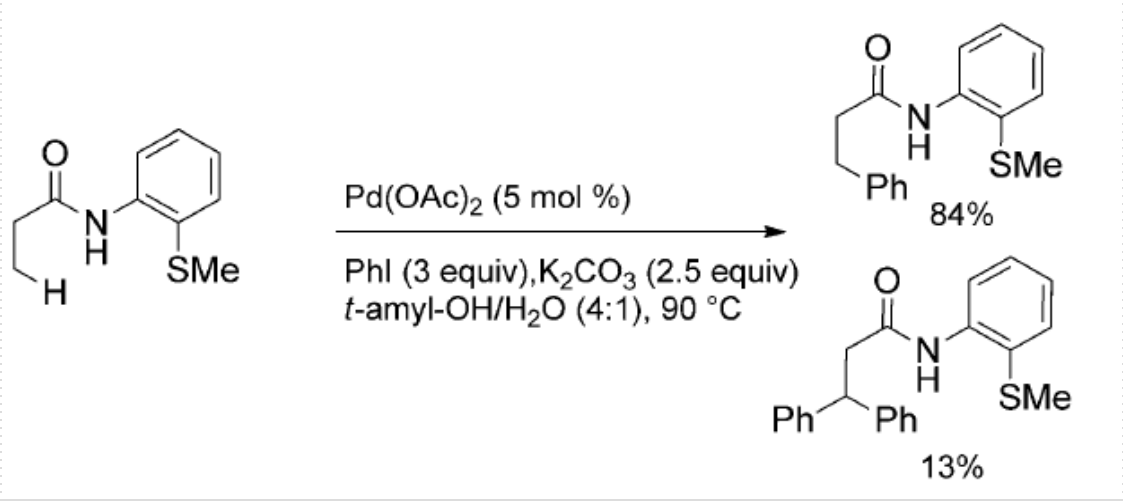
D. Shabashov, O. Daugulis, *Org. Lett.* 2005, 7, 3657.

Notes: the scope of this reaction was very limited.



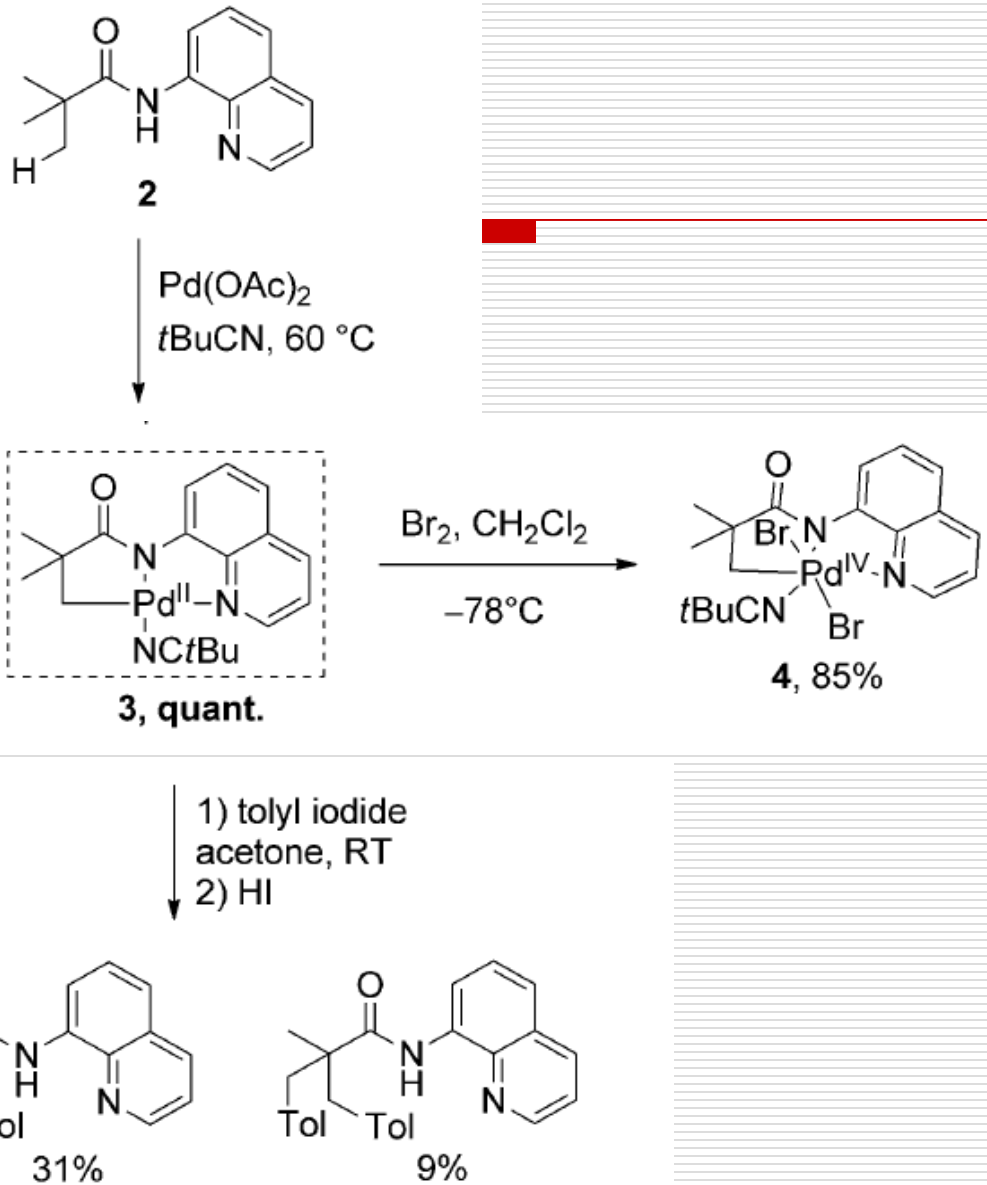
V. G. Zaitsev, D. Shabashov, O. Daugulis, *J. Am. Chem. Soc.* 2005, 127, 13154



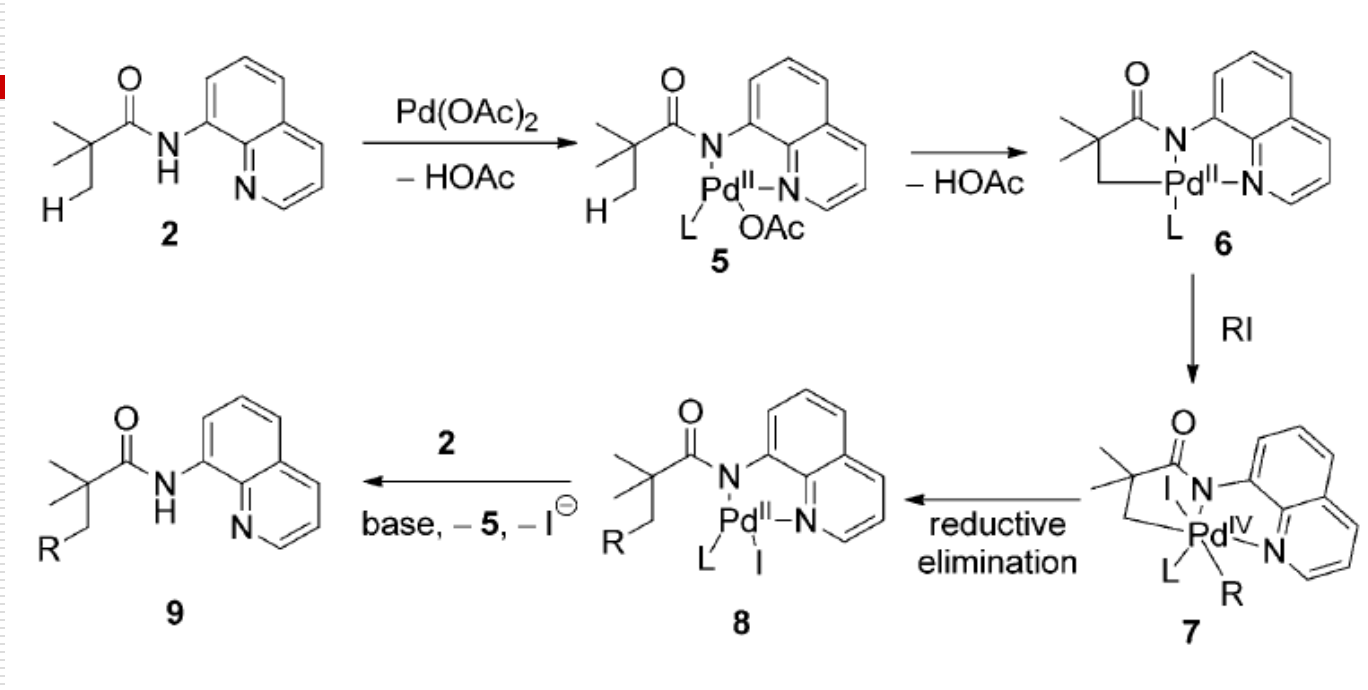


D. Shabashov, O. Daugulis, *J. Am. Chem. Soc.* **2010**, 132, 3965.

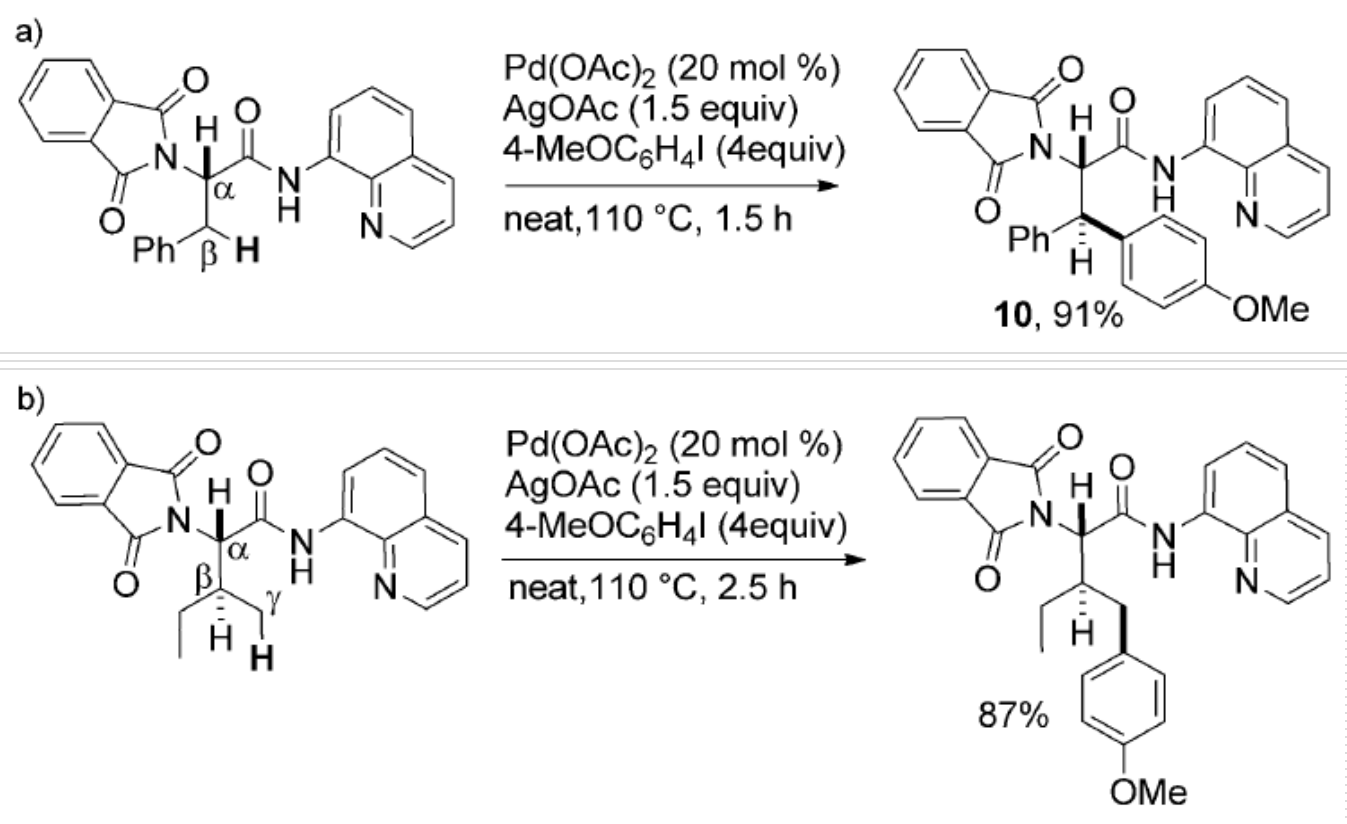
Notes: (1) 8-aminoquinoline or picolinic acid as directing groups are easily removable.
(2) the double coordination of the metal can stabilize Pd(IV) species and retard b-hydride elimination step by saturating the coordination sites of the metal.
(3) methylene C(sp3)H bond activation of amides was achieved.



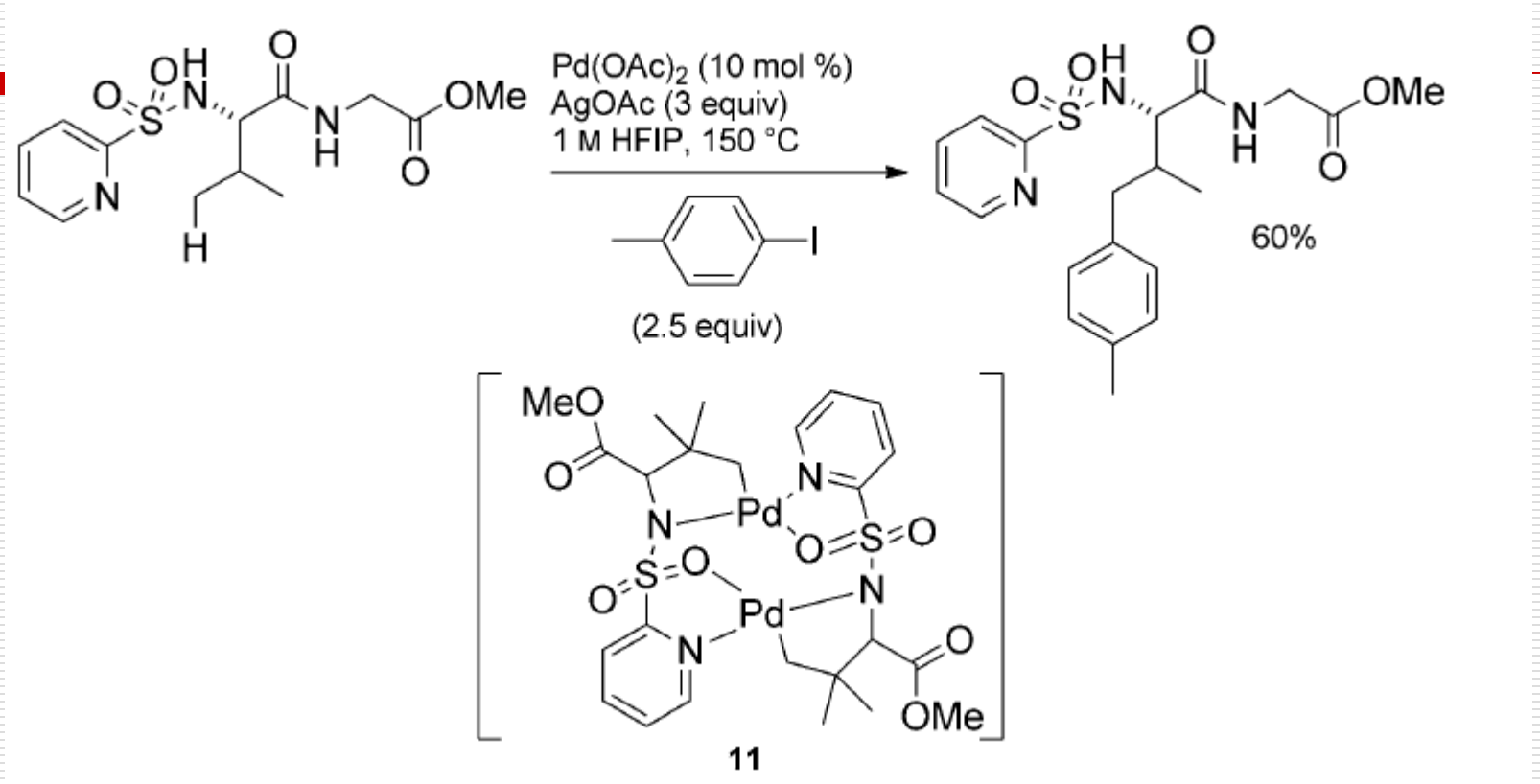
Notes: a palladium(IV) complex by direct reaction of **3** with an aryl iodide was not obtained



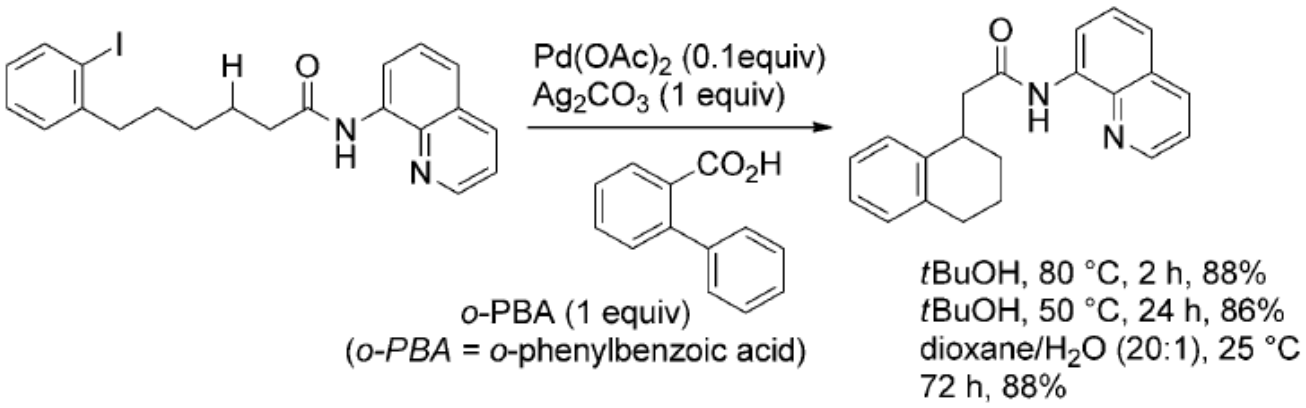
Notes: a Pd(II)/Pd(IV) process



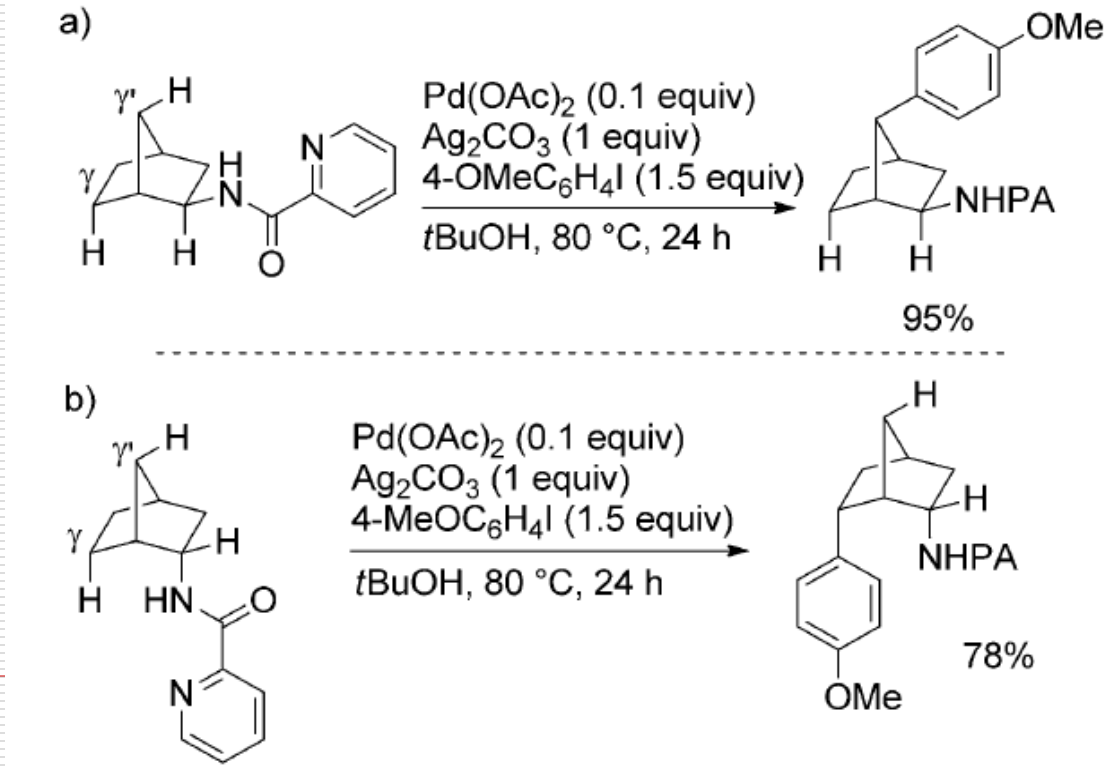
B. V. S. Reddy, L. R. Reddy, E. J. Corey, *Org. Lett*. **2006**, 8, 3391.



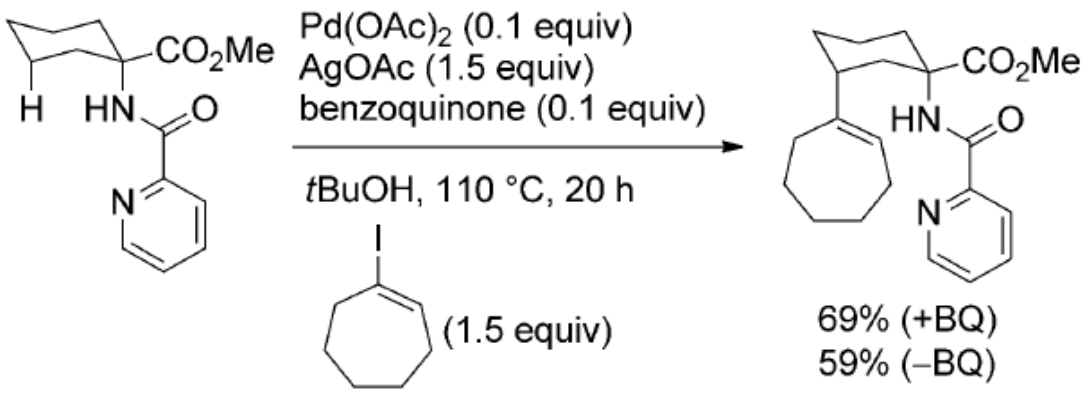
J. C. Carretero, *Angew. Chem. Int. Ed.* **2009**, 48, 6511.

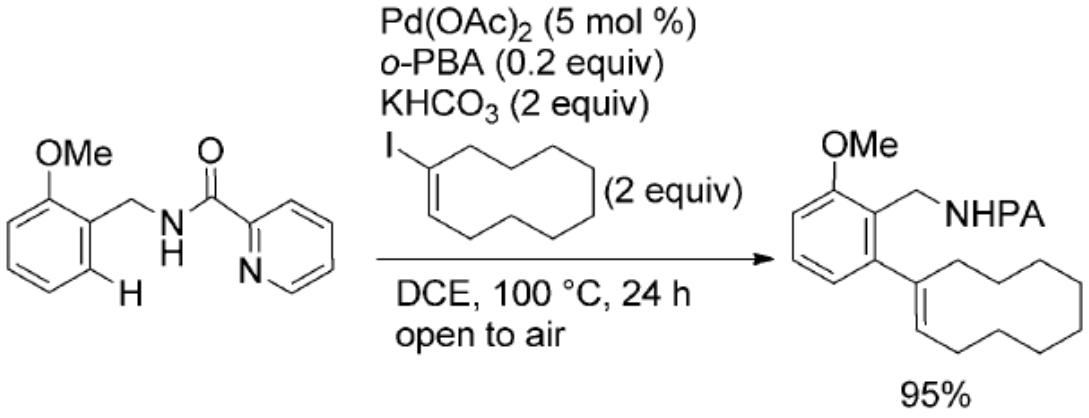


Y. Feng, Y. Wang, B. Landgraf, S. Liu, G. Chen, *Org. Lett*. **2010**, 12, 3414.

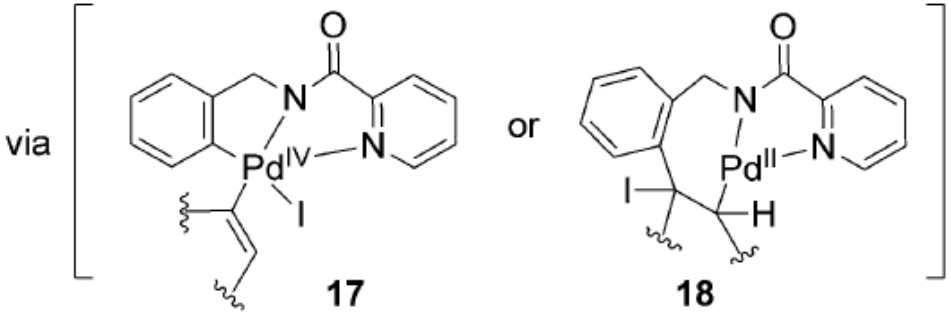


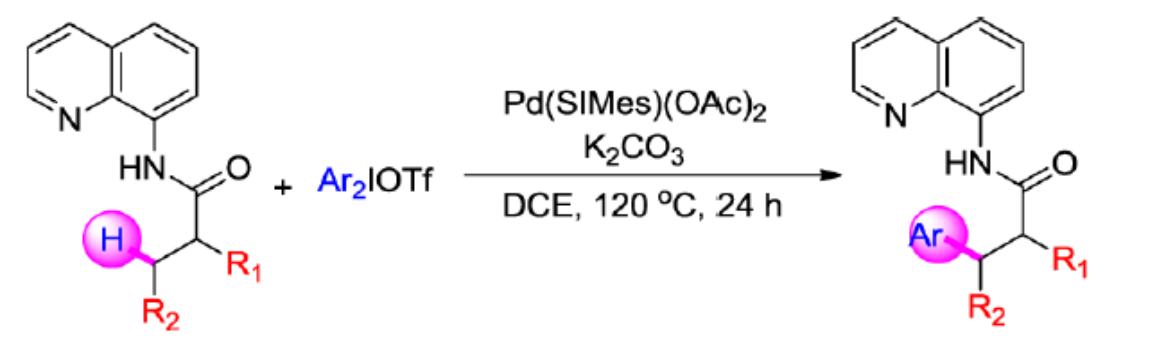
G. He, G. Chen, *Angew. Chem. Int. Ed.* **2011**, 50, 5192.



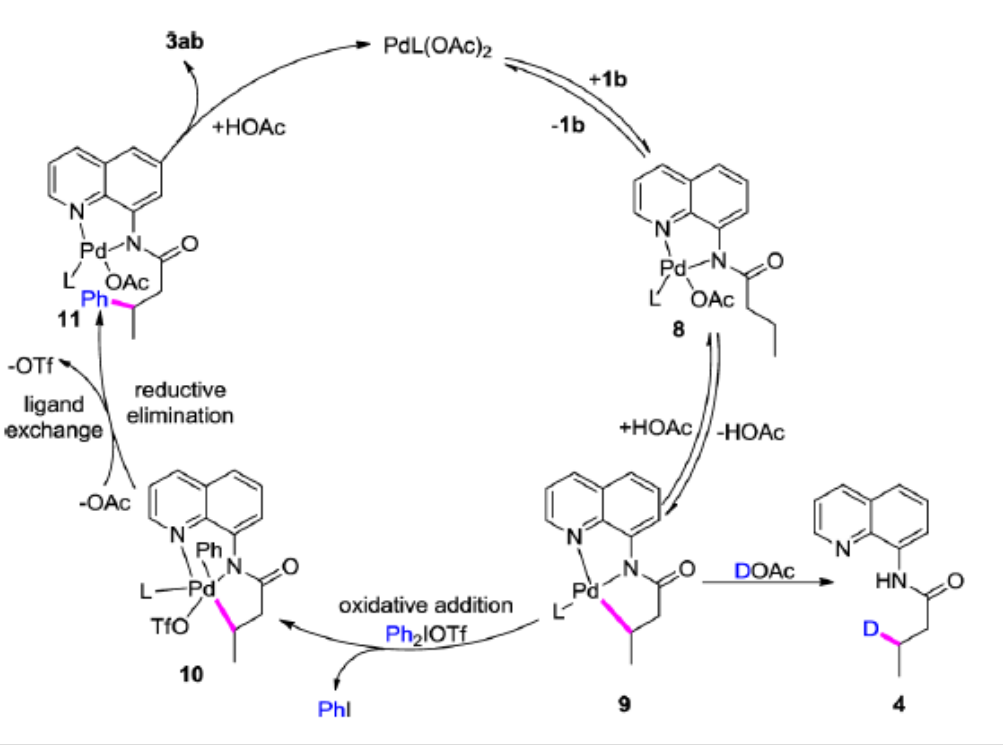


speculated intermediates

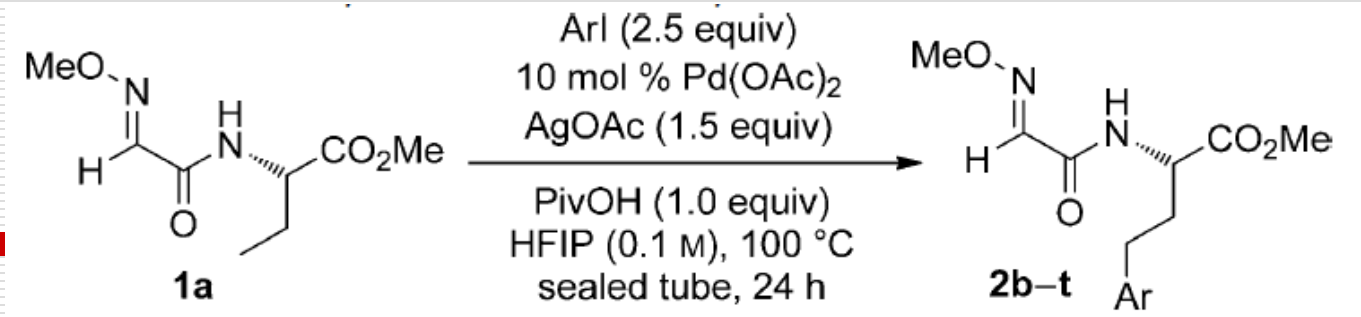




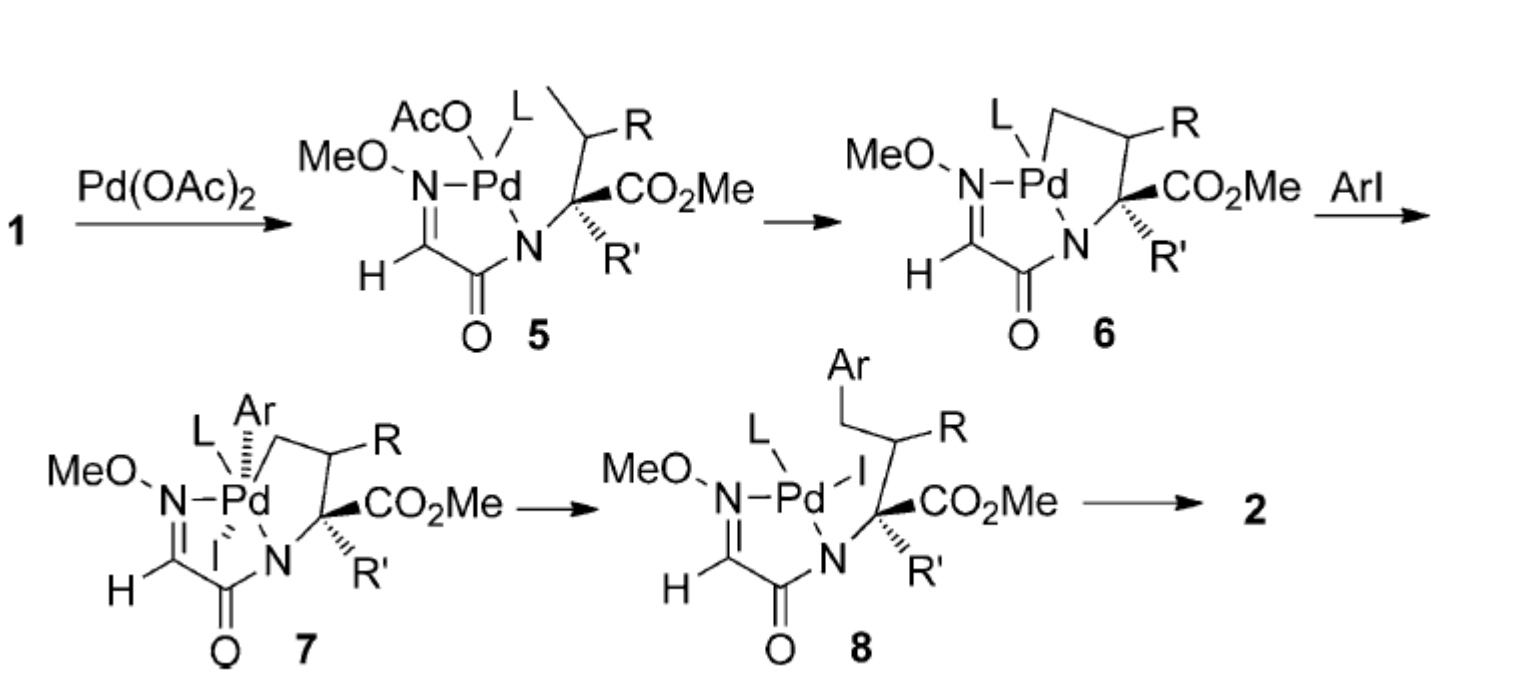
Z. Shi，*Org. Lett*. **2013**, 15, 4758.



Notes: Pd(II)/Pd(IV) catalytic cycle

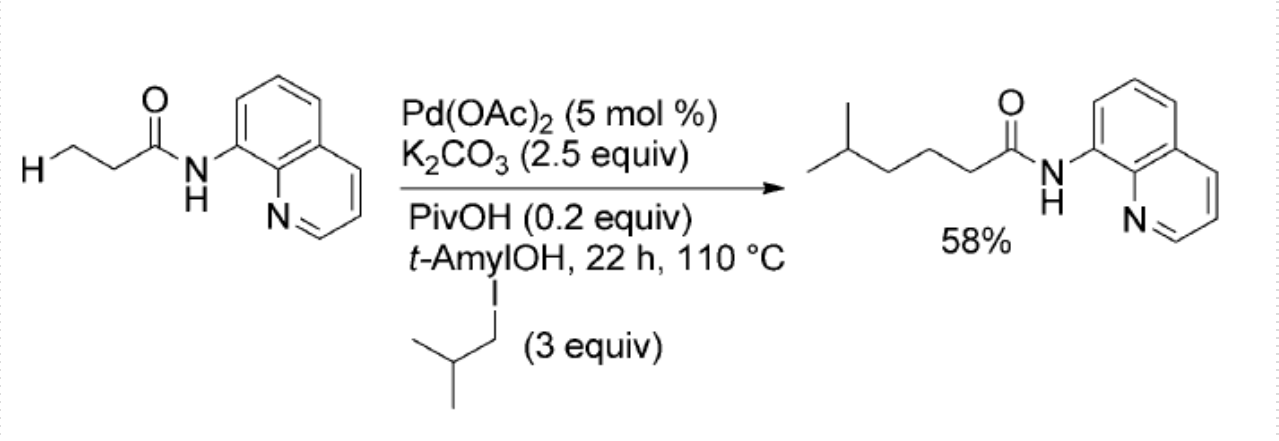


2-methoxyiminoacetyl



D. Ma, *Angew. Chem. Int. Ed.* **2013**, 52, 1-5

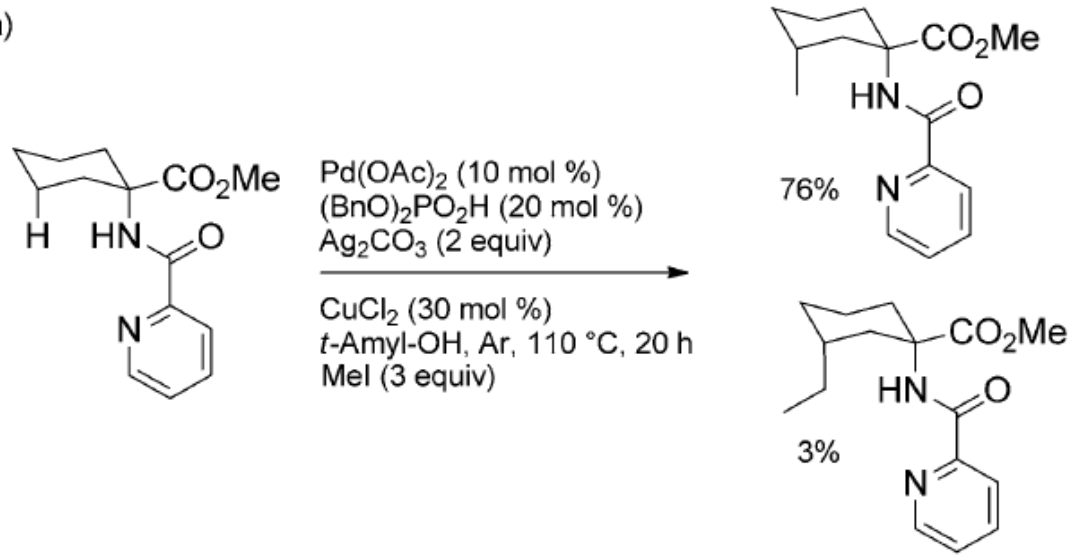
Alkylation of C-H Bonds



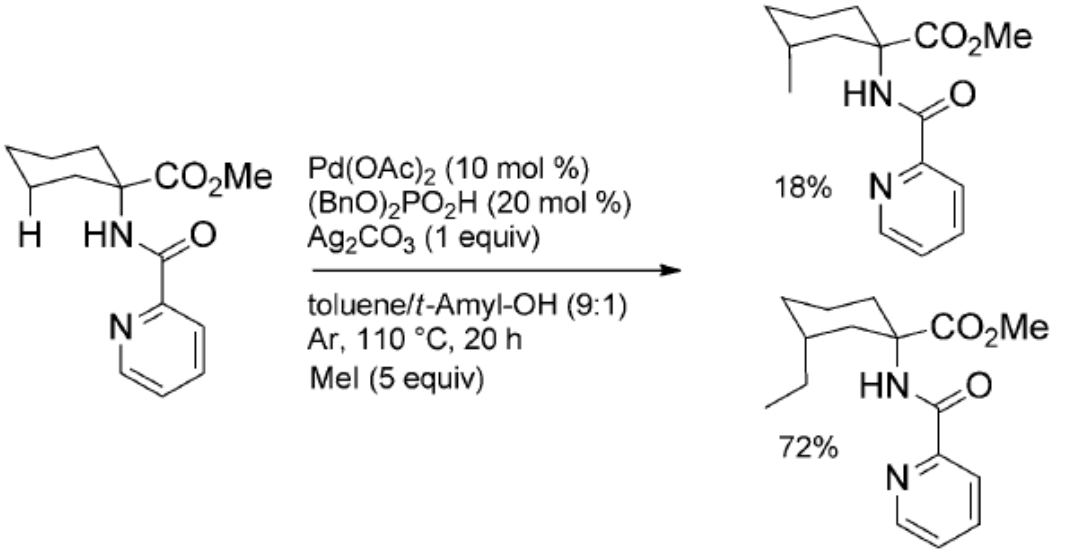
D. Shabashov, O. Daugulis, *J. Am. Chem. Soc.* **2010**, 132, 3965.

Notes: This reaction represents notable progress.

a)

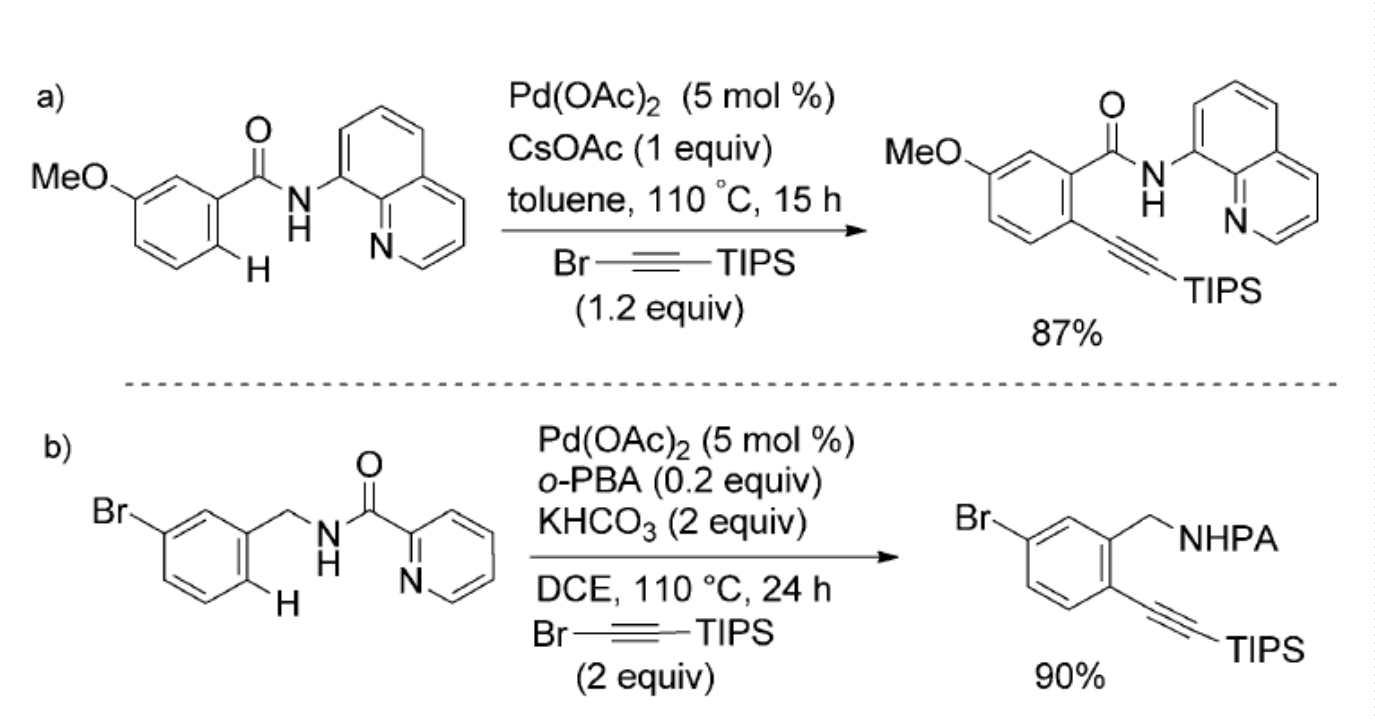


b)



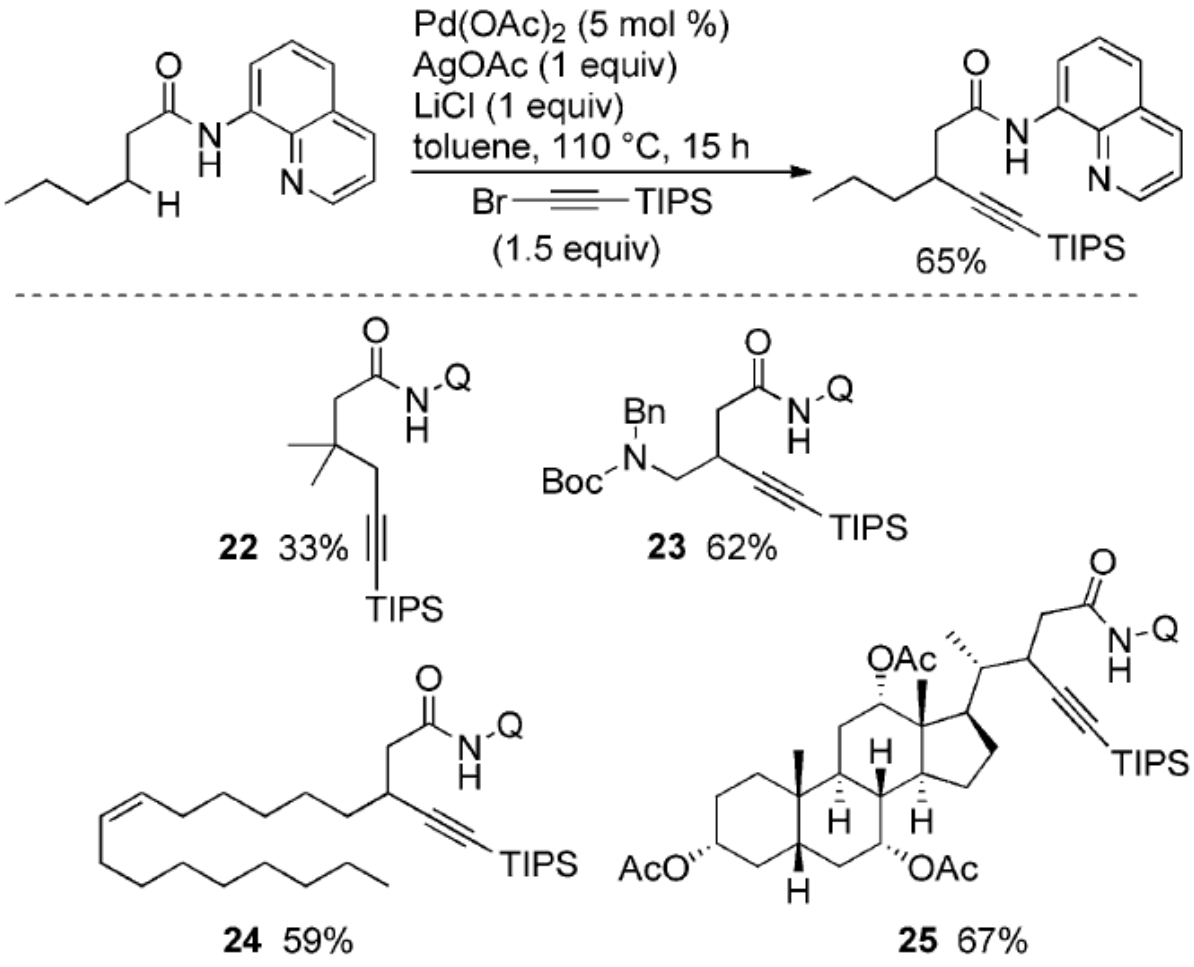
S.-Y. Zhang, G. He,W. A. Nack, Y. Zhao, Q. Li, G. Chen, *J. Am. Chem. Soc.* **2013**, 135, 2124

Alkynylation of C-H Bonds



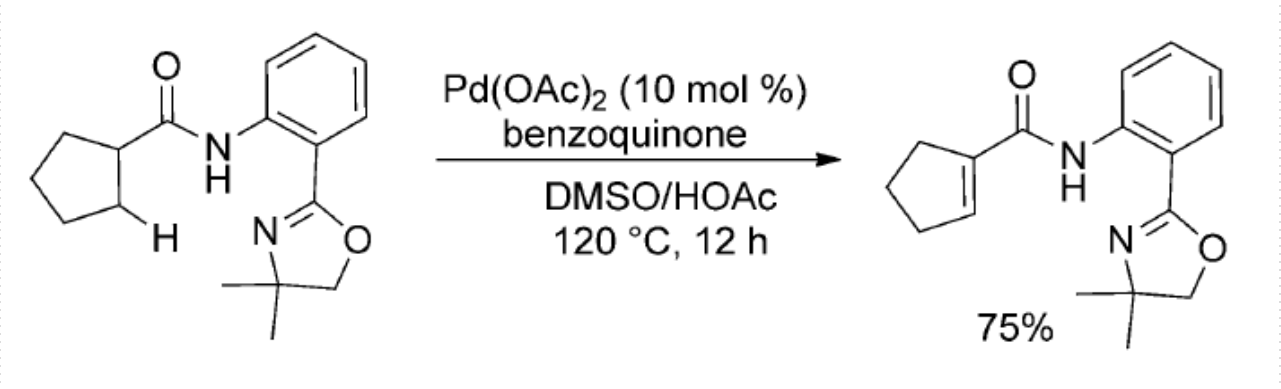
Y. Ano, M. Tobisu, N. Chatani, *Org. Lett.* **2012**, 14, 354.

Y. Zhao, G. He, W. A. Nack, G. Chen, *Org. Lett.* **2012**, 14, 2948.



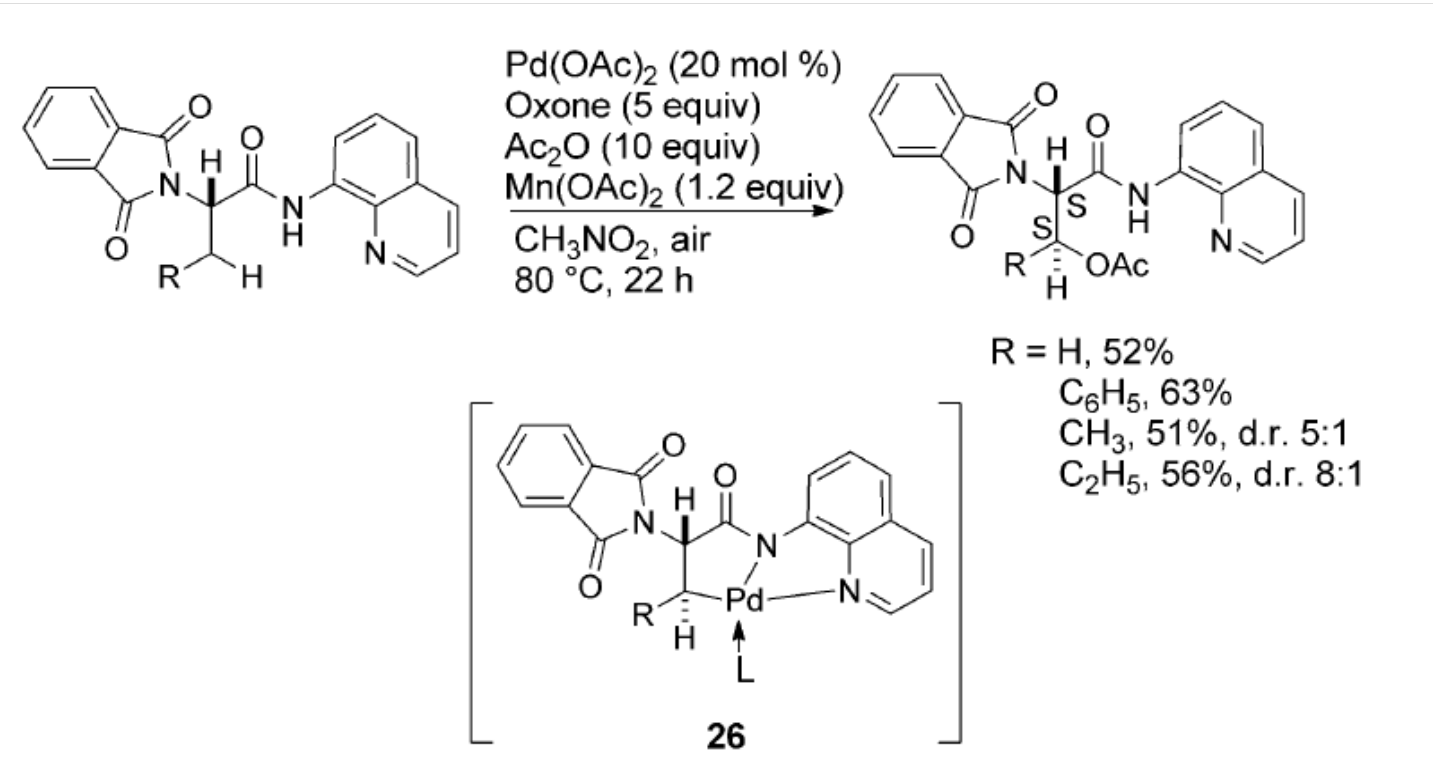
Y. Ano, M. Tobisu, N. Chatani, *J. Am. Chem. Soc.* **2011**, 133, 12984.

Dehydrogenation through C-H Bond Activation

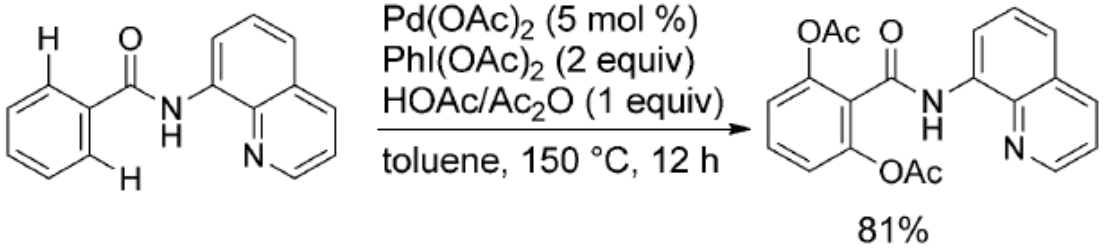


R. Giri, N. Maugel, B. M. Foxman, J.-Q. Yu, *Organometallics* **2008**, 27, 1667.

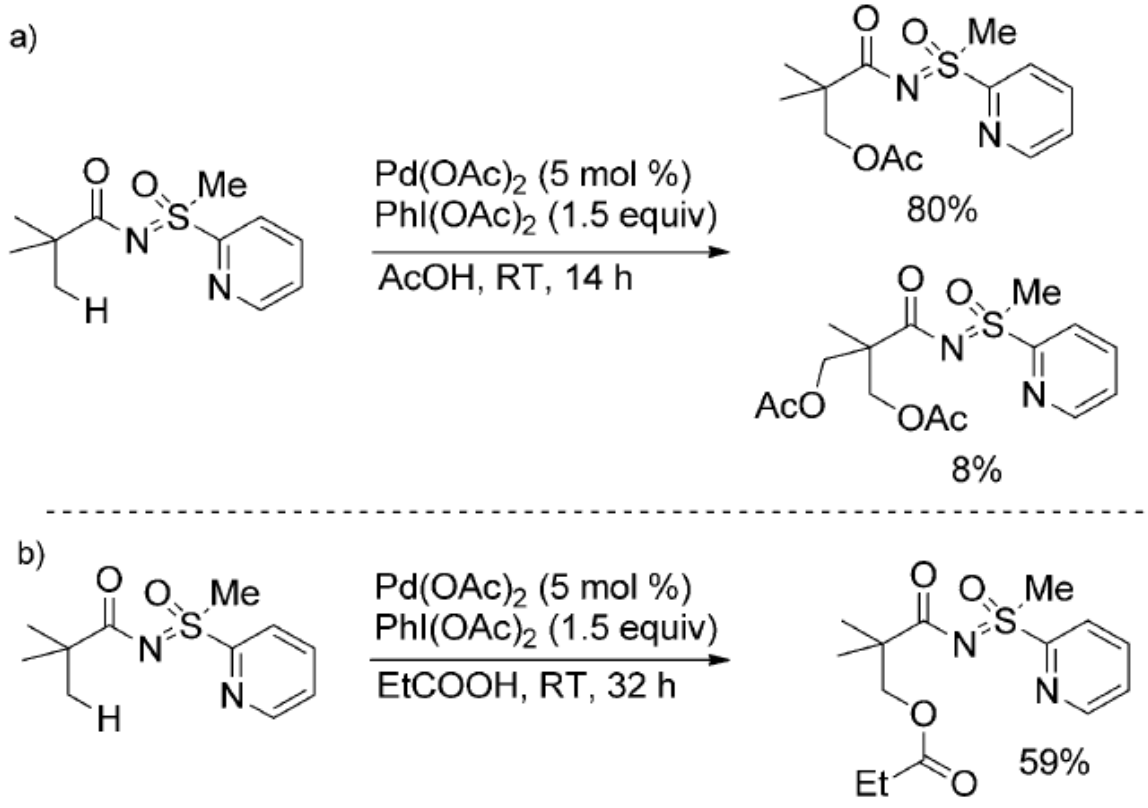
Oxidation of C-H Bonds



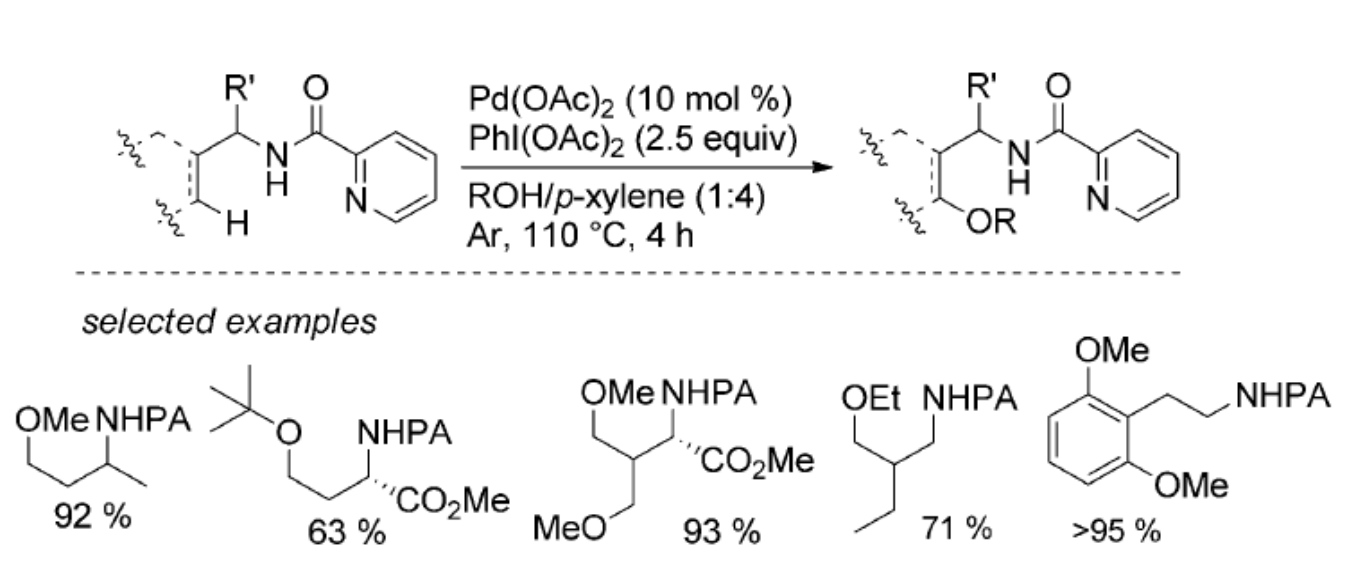
B. V. S. Reddy, L. R. Reddy, E. J. Corey, *Org. Lett*. **2006**, 8, 3391.



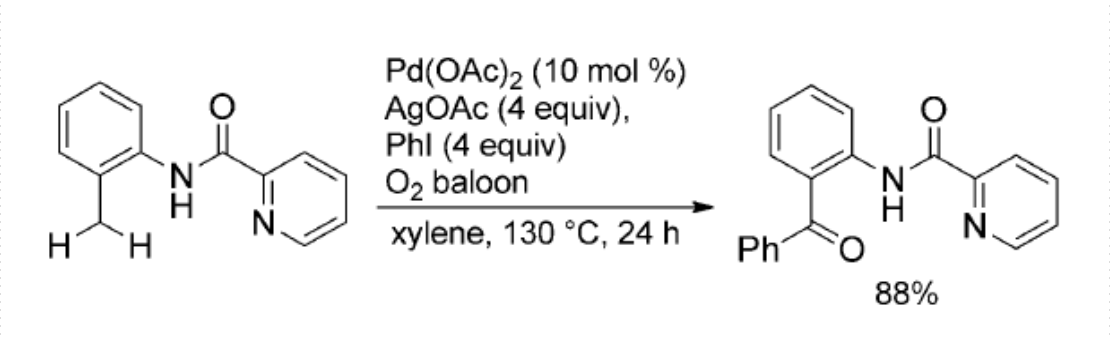
Y.-M. Liang, *Org. Lett.* **2009**, 11, 5726



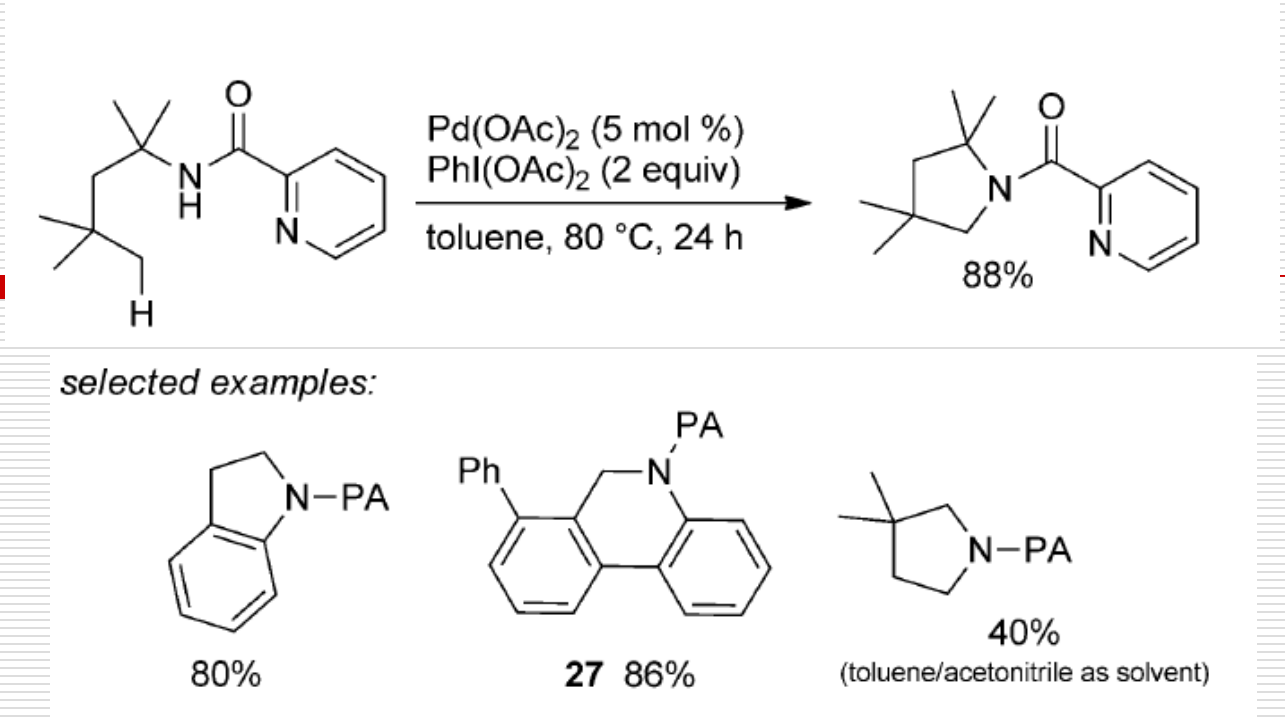
A. K. Sahoo, *Org. Lett.* **2012**, 14, 3724.



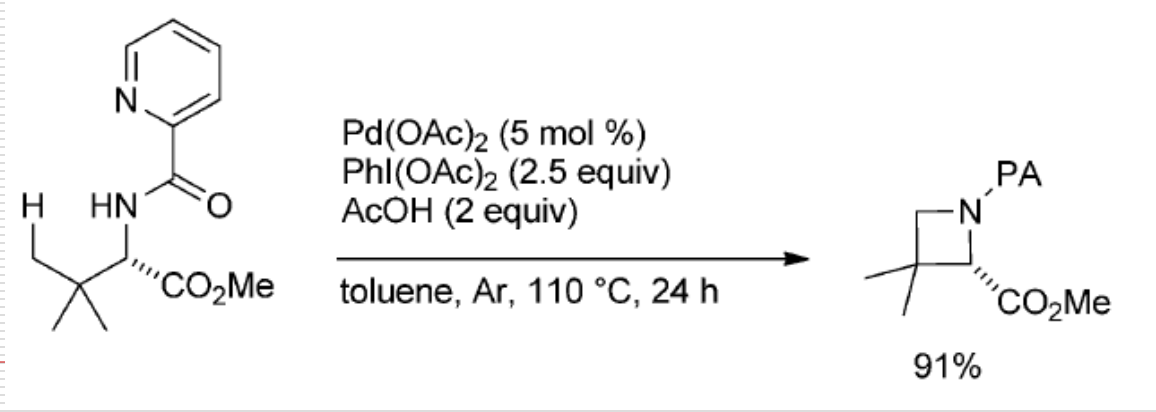
G. Chen, *J. Am. Chem. Soc.* **2012**, 134, 7313.

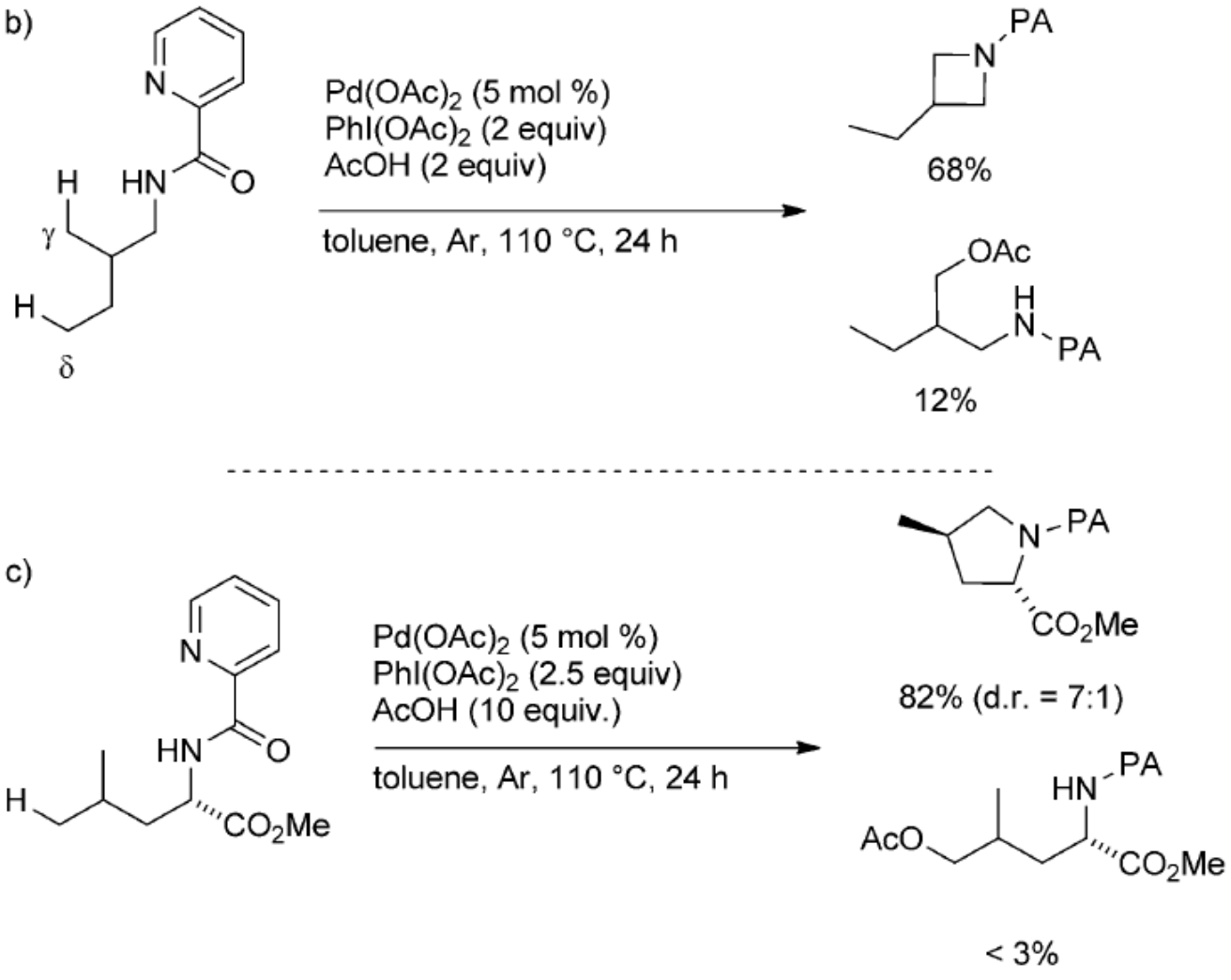


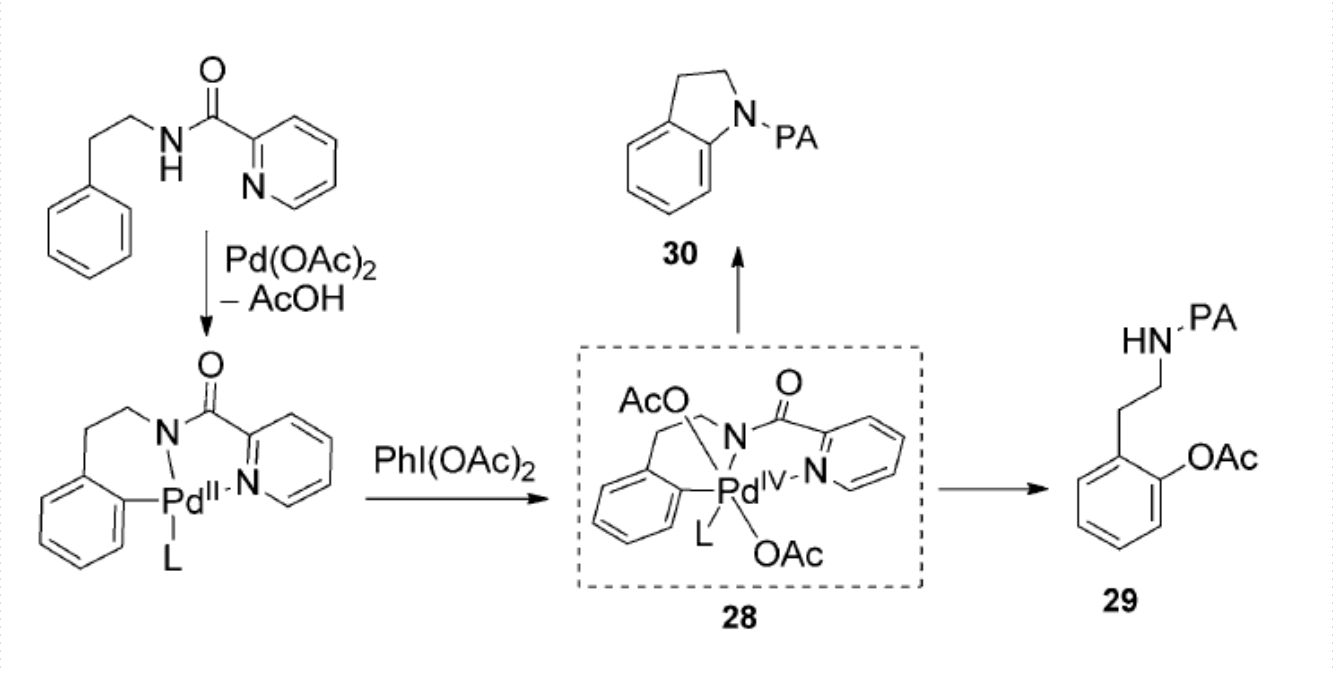
Y. Xie, Y. Yang, L. Huang, X. Zhang, Y. Zhang, *Org. Lett*. **2012**, 14, 1238.

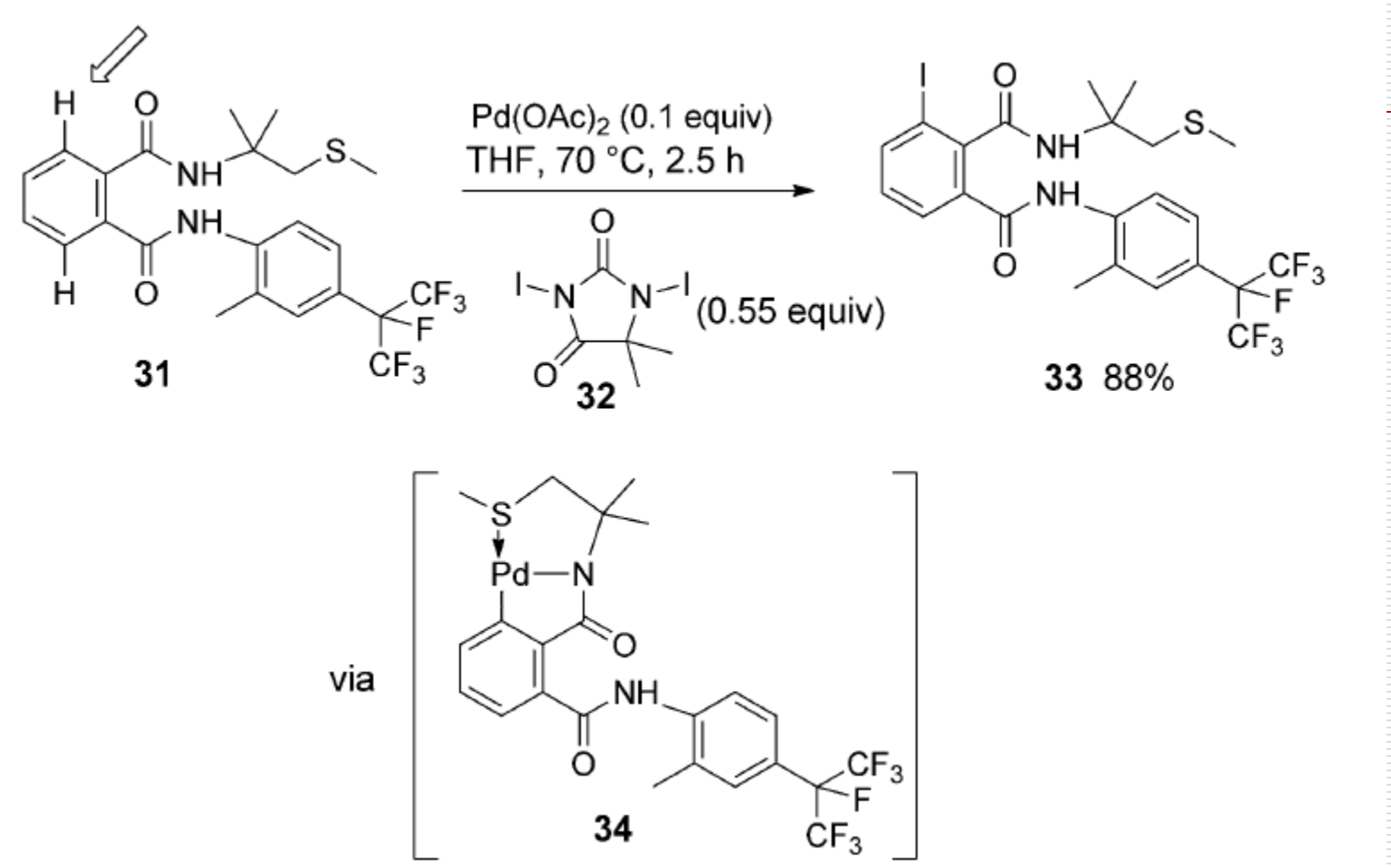


E. T. Nadres, O. Daugulis, *J. Am. Chem. Soc.* 2012, 134, 7.



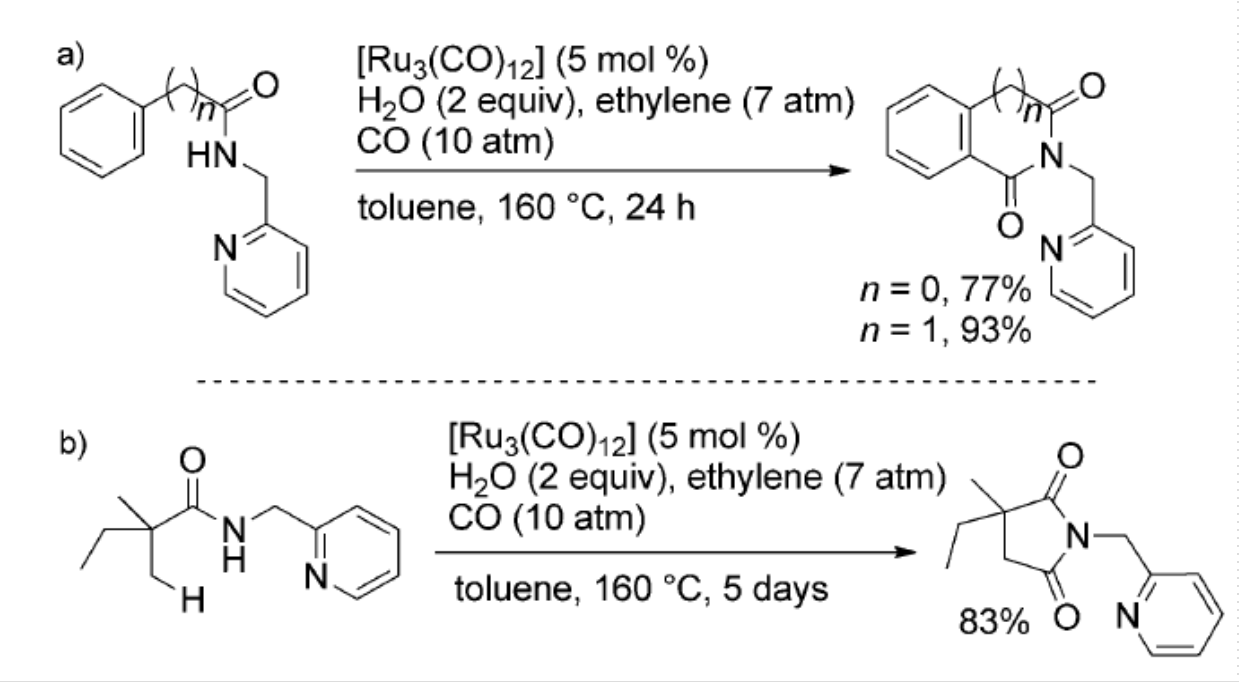

b)
N
H
HN
O
γ
H
δ
Pd(OAc)2 (5 mol %)
PhI(OAc)2 (2 equiv)
AcOH (2 equiv)
toluene, Ar, 110 °C, 24 h
PA
N
68%
OAc
H
N
PA
12%
c)
N
HN
O
H
CO2Me
Pd(OAc)2 (5 mol %)
PhI(OAc)2 (2.5 equiv)
AcOH (10 equiv.)
toluene, Ar, 110 °C, 24 h
N
PA
CO2Me
82% (d.r. = 7:1)
HN
PA
AcO
CO2Me
< 3%


O
N
H
N
Pd(OAc)2
– AcOH
O
N
PdII
N
L
PhI(OAc)2
N
PA
30
AcO
O
N
PdIV
N
L
OAc
28
HN
PA
OAc
29

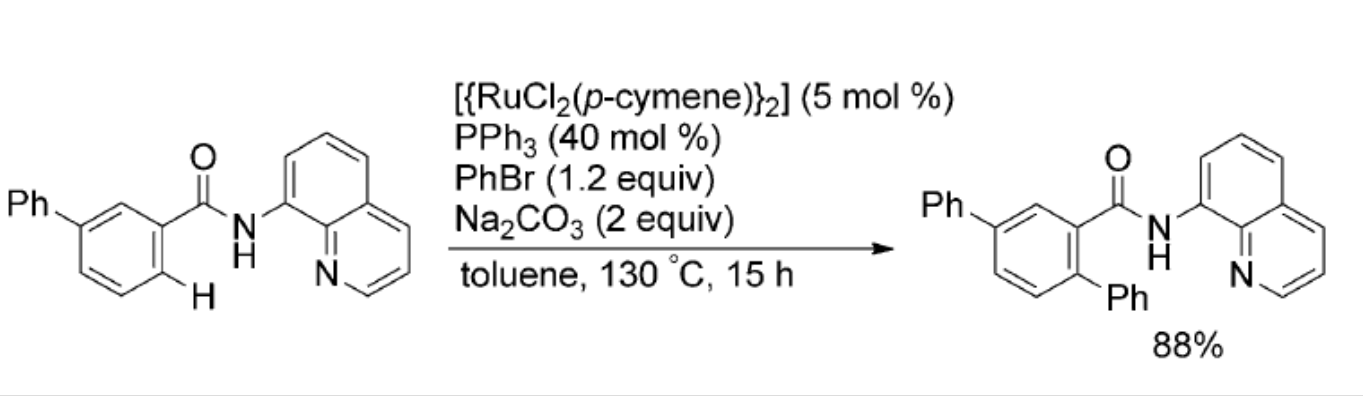


H. Kodama, T. Katuhira, T. Nishida, T. Hino, K. Tsubata, 2001, Patent WO2001083421A.

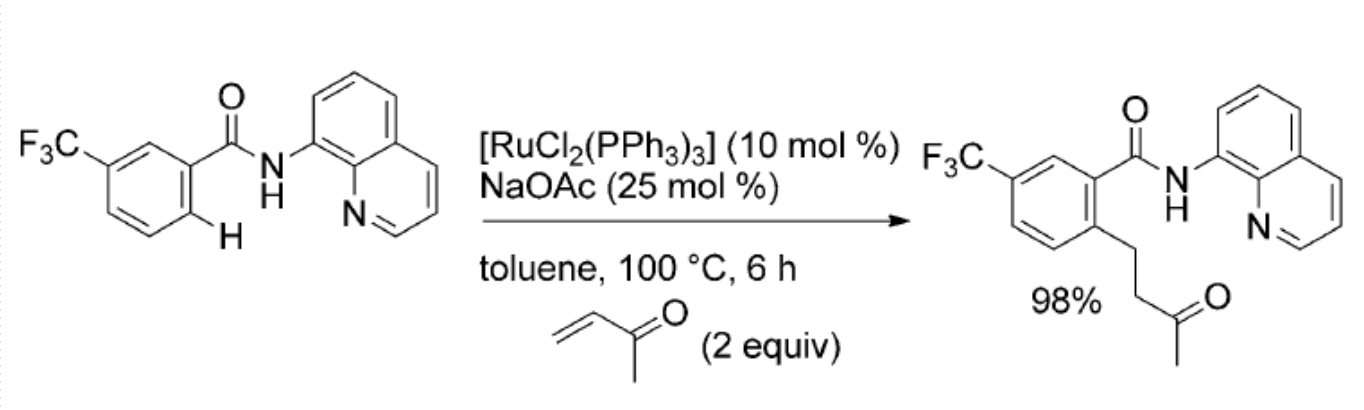
3 Ruthenium Catalyst



S. Inoue, H. Shiota, Y. Fukumoto, N. Chatani, *J. Am. Chem. Soc.* **2009**, 131, 6898.

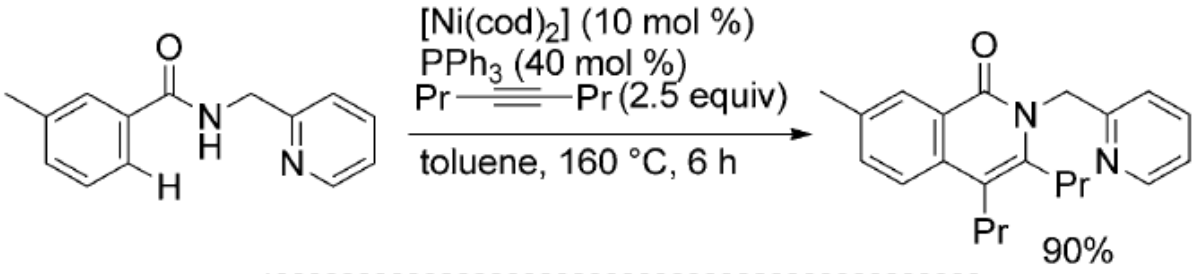


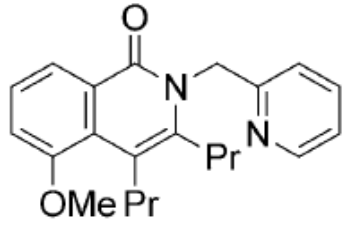
Y. Aihara, N. Chatani, *Chem. Sci.* **2013**, 4, 664.



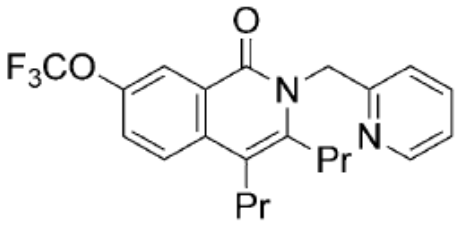
G. Rouquet, N. Chatani, *Chem. Sci.* **2013**, 4, 2201.

4 Nickle Catalyst

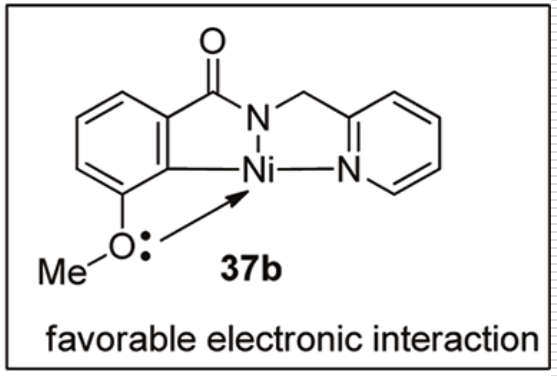




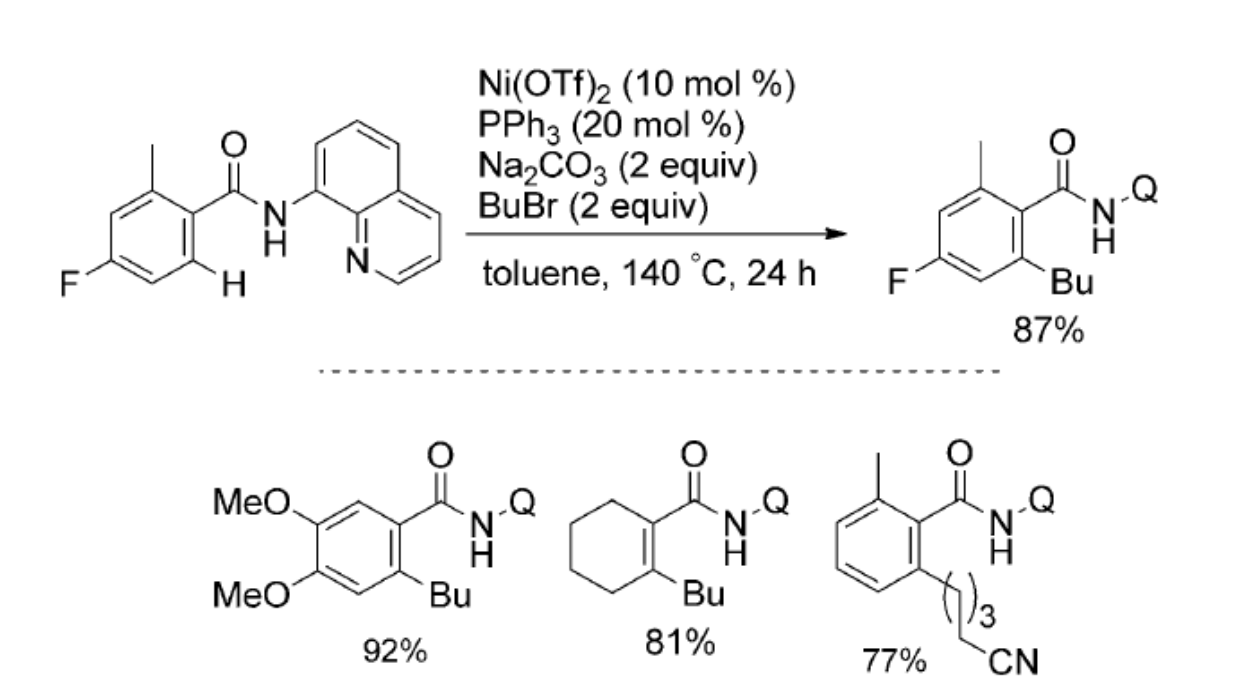
38 87%



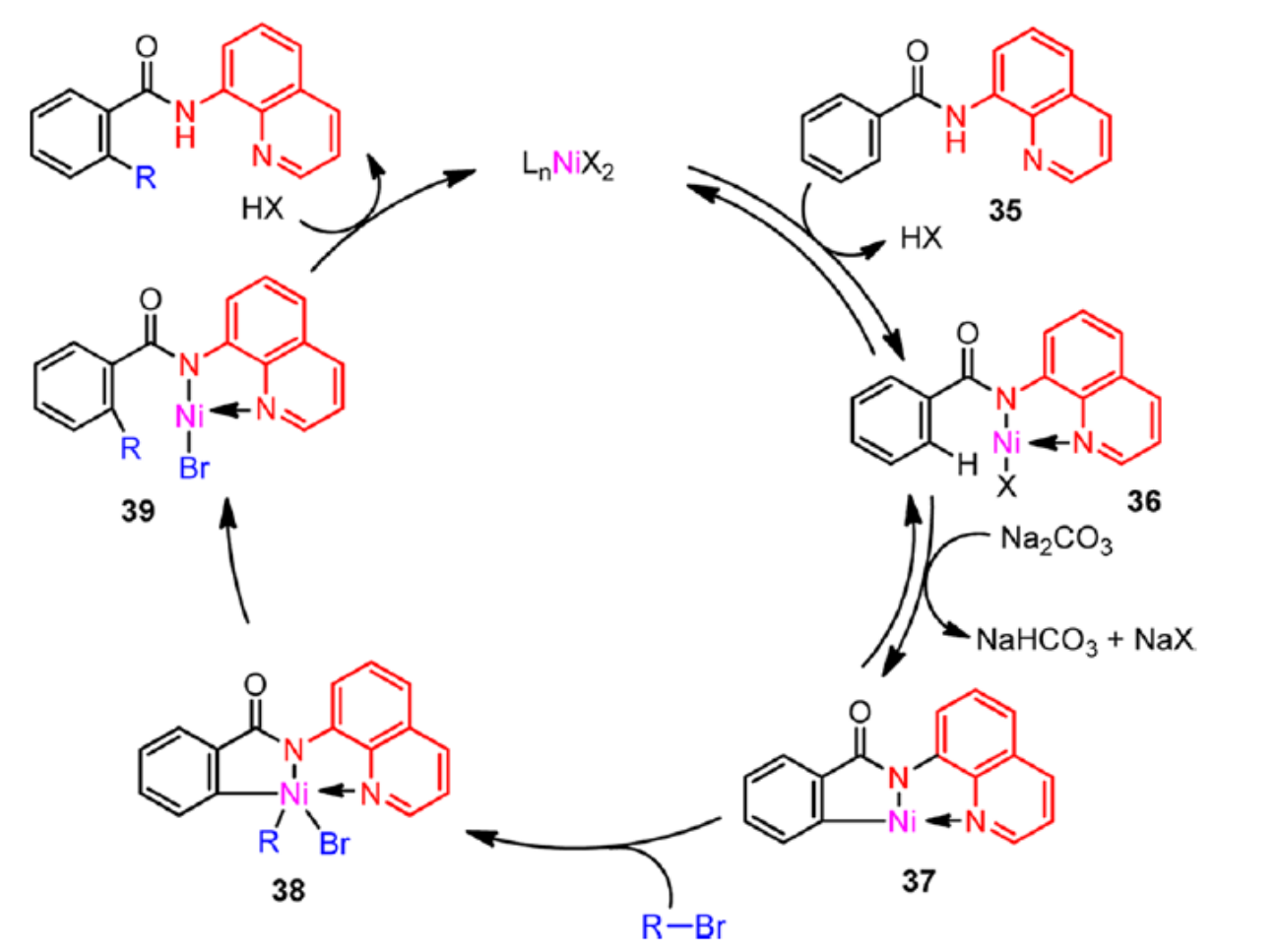
39 84% (20:1)



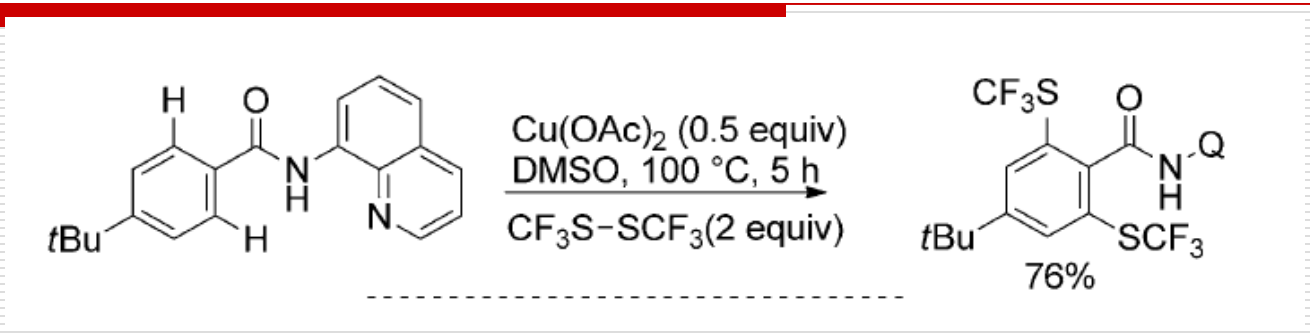
H. Shiota, Y. Ano, Y. Aihara, Y. Fukumoto, N. Chatani, *J. Am. Chem. Soc.* **2011**, 133, 14952.

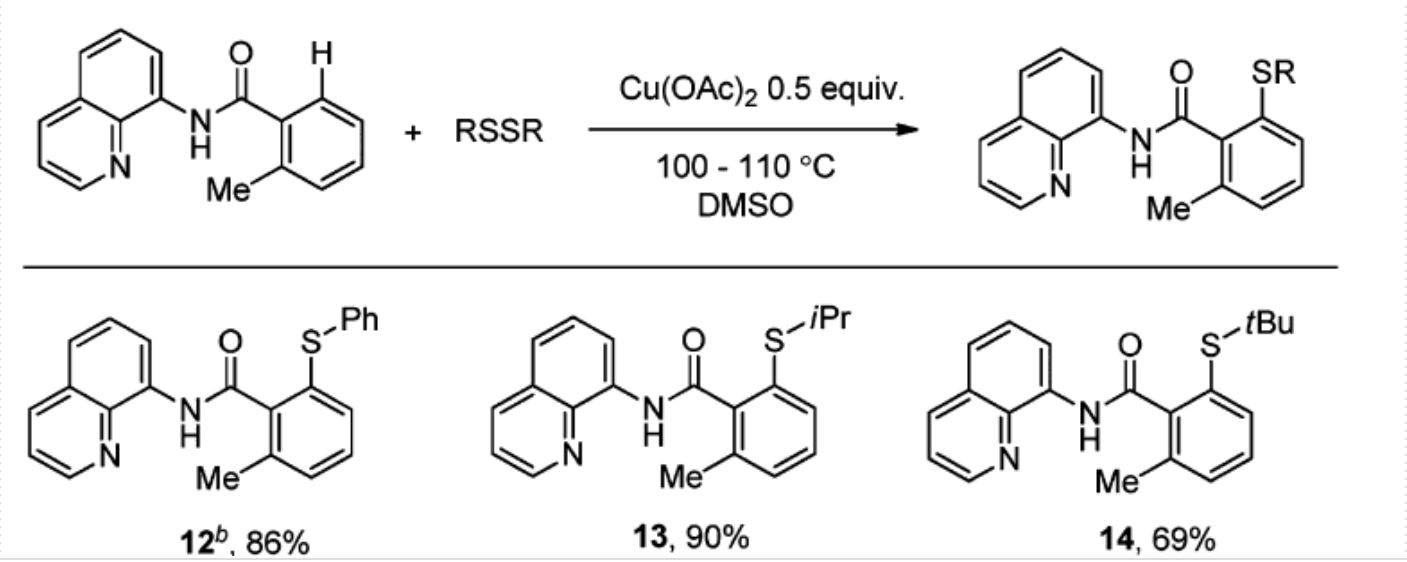


Y. Aihara, N. Chatani, *J. Am. Chem. Soc.* **2013**, 135, 5308.


LnNiX2
HX
35
HX
36
Na2CO3
NaHCO3 + NaX
37
R—Br
38
39

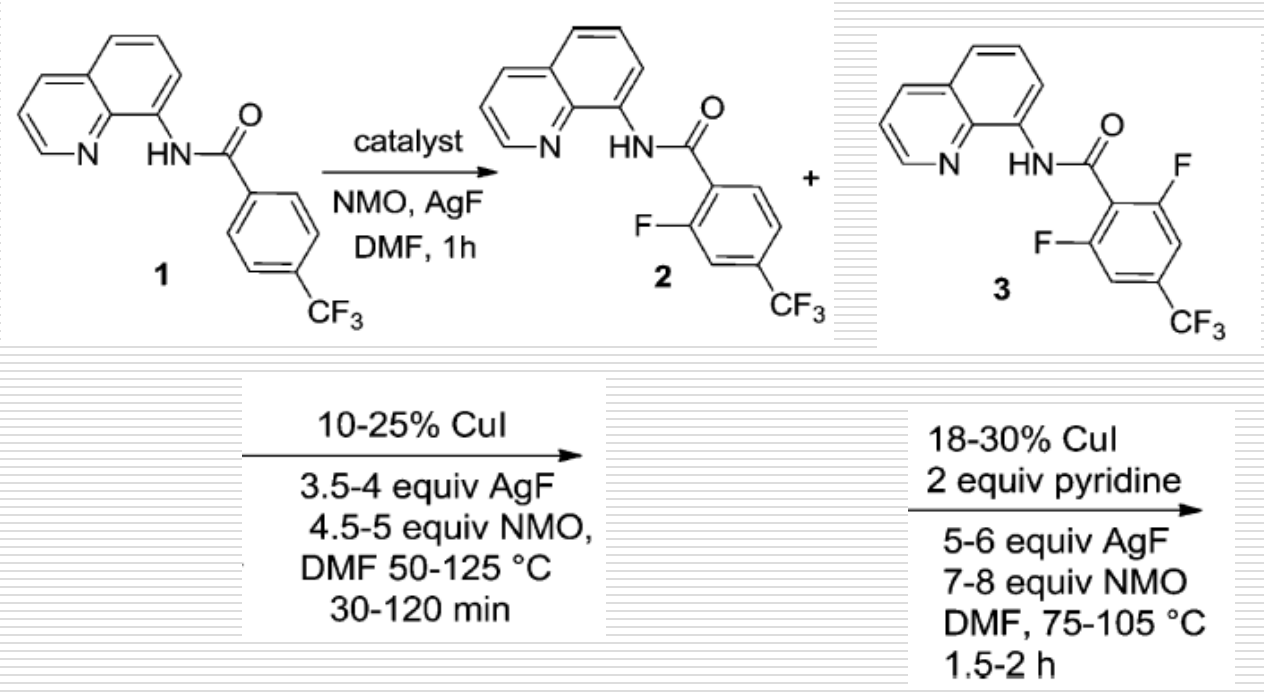
4 Copper Catalyst



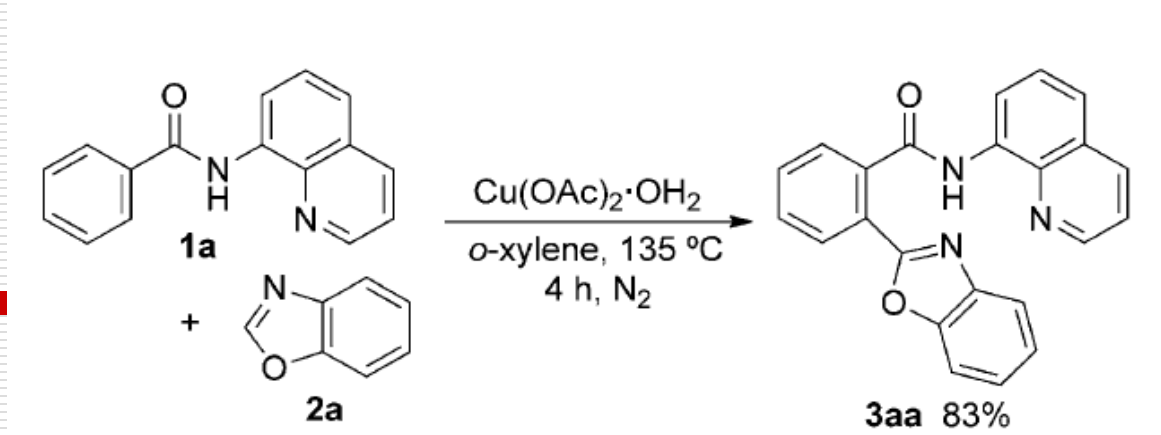


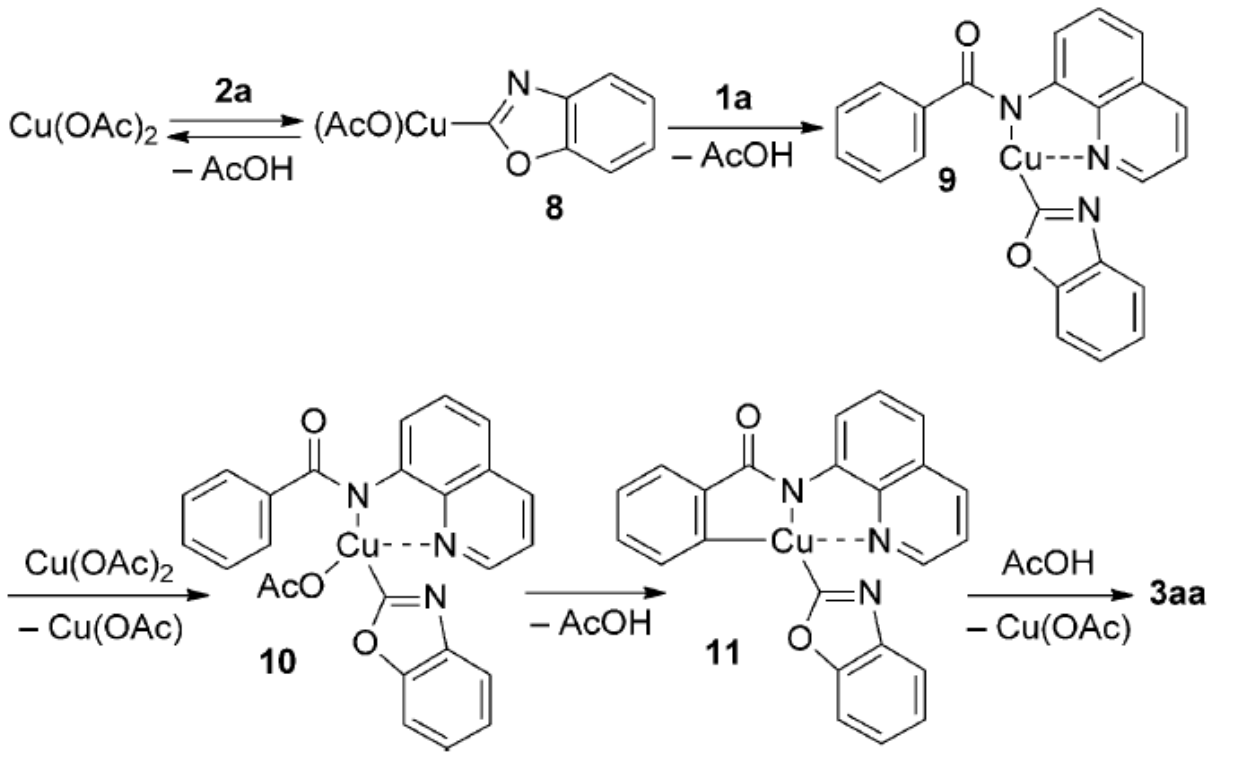
L. D. Tran, I. Popov, O. Daugulis, *J. Am. Chem. Soc.* **2012**, 134,18237.

Fluorination of Arene



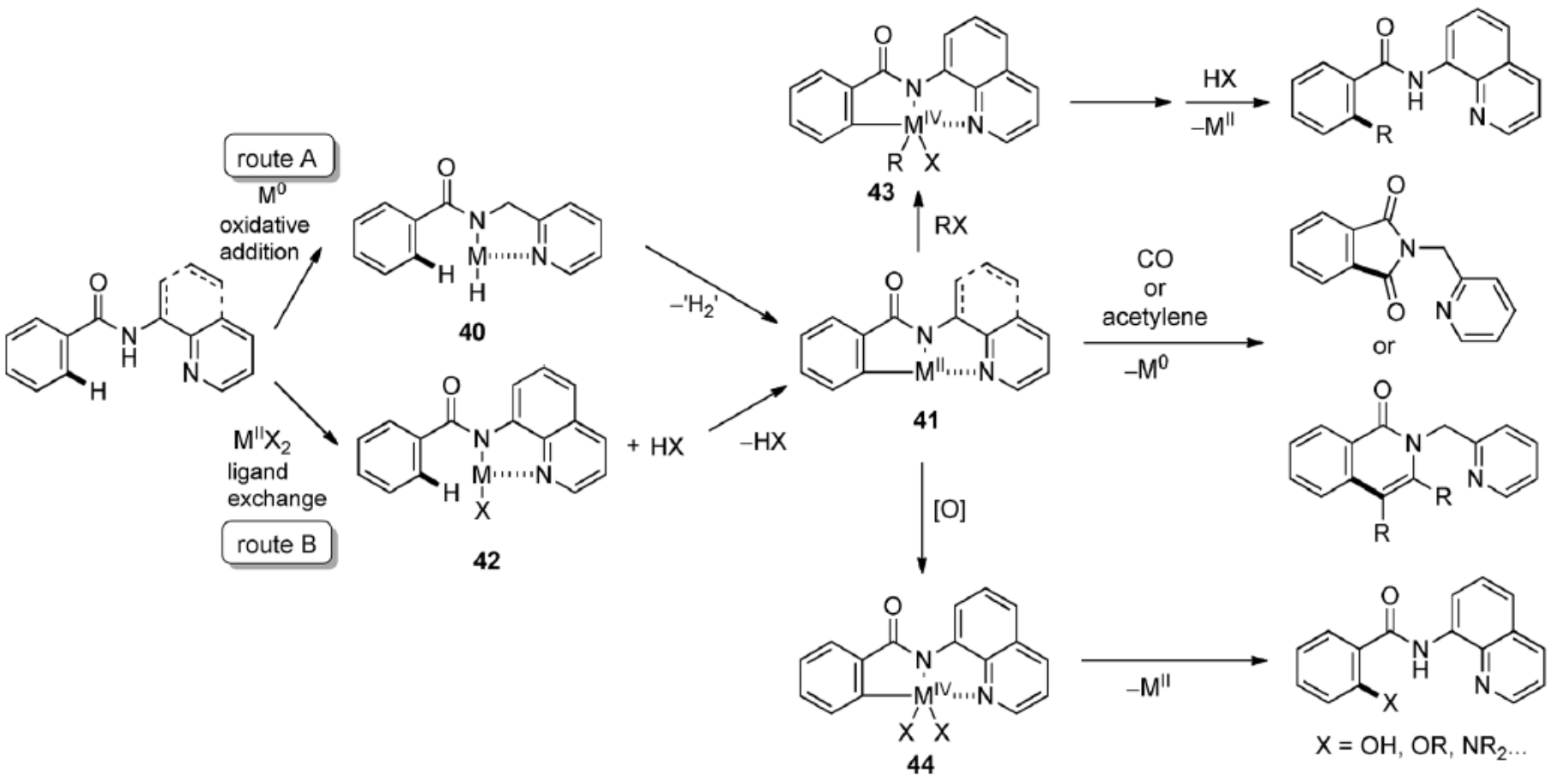
O. Daugulis, *J. Am. Chem. Soc.* **2013**, 135, 9342.





M. Miura, *Angew. Chem. Int. Ed.* **2013**, 52, 4457.

6 Mechansim


route A
M0
oxidative addition
MIIX2
ligand exchange
route B
40
42
–'H2'
+ HX
–HX
41
RX
43
HX
–MII
CO
or
acetylene
–M0
or
[O]
44
–MII
X = OH, OR, NR2...

7 Conclusions

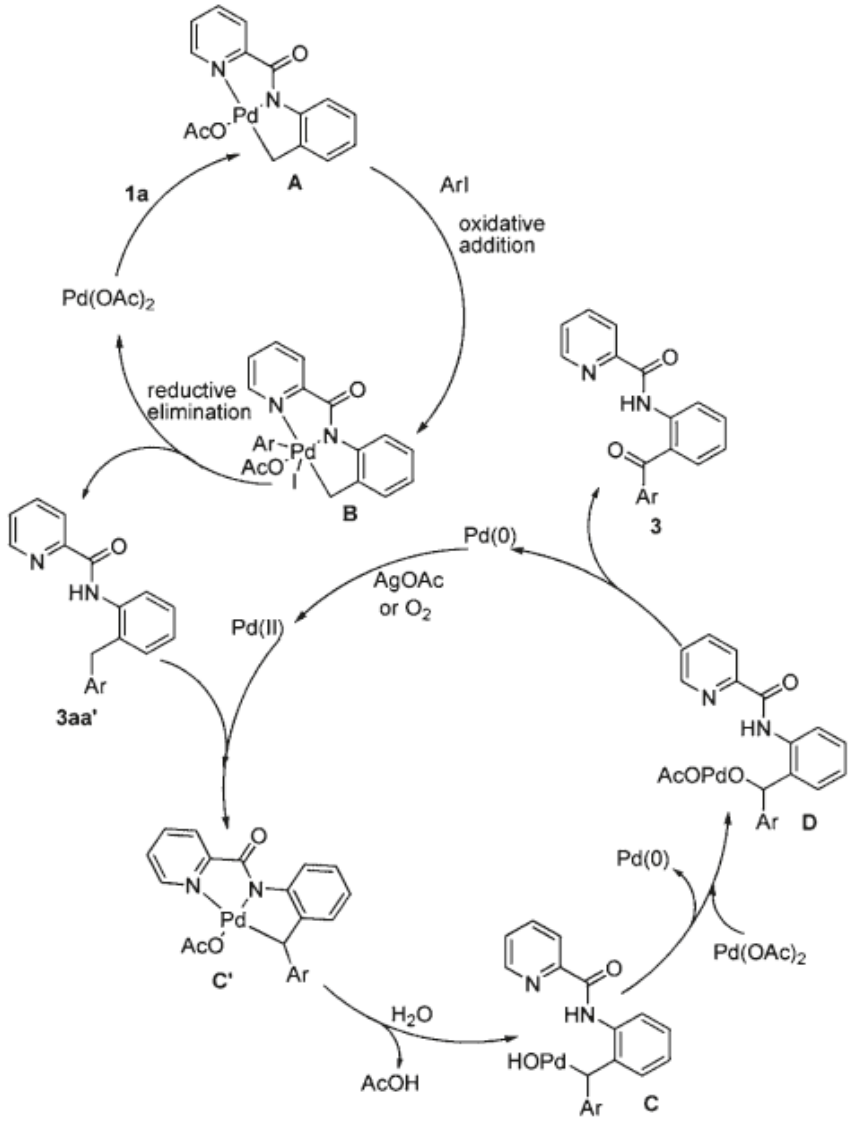
(1) Much progress has been made in the catalytic transformation of C-H bonds into C-C bonds (arylation, vinylation, alkylation, alkynylation, carbonylation), as well as C-X bonds (oxygenation, amination,sulfuration, halogenation) with bidentate directing groups.

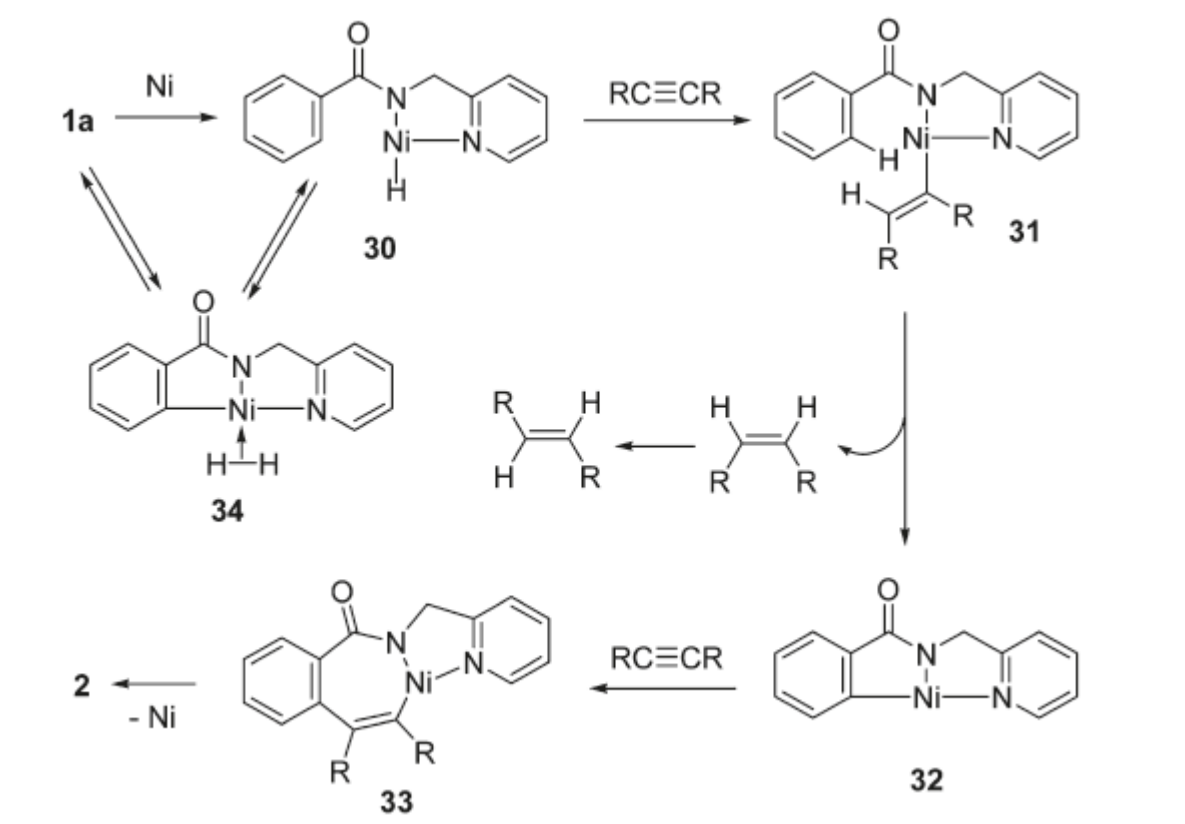
(2) Compared with the problematic or difficult procedures involving conventionally used monodentate systems, the ability of didentate directing groups has been clearly highlighted.

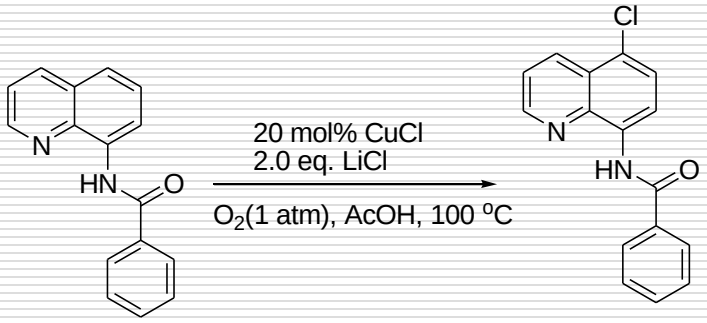
(3) Bidendate-chelation-assisted metal-catalyzed C-H functionalization is still in its infancy.

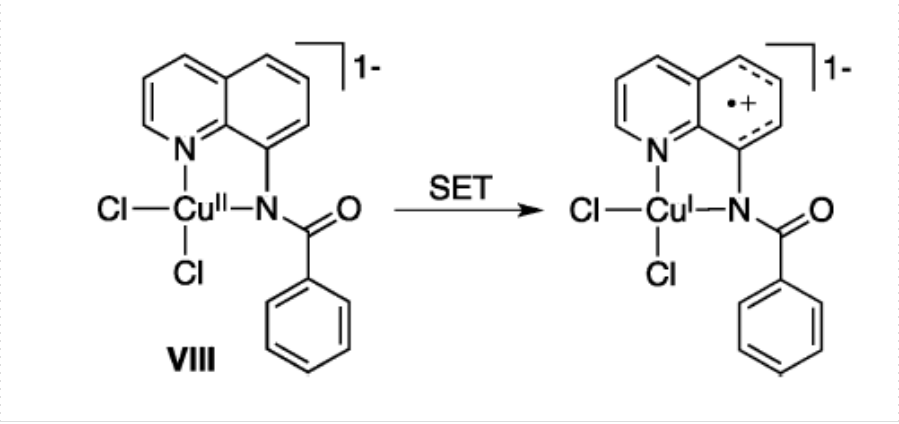
Thank you for your attention

Answers of questions




1a
Ni
30
RC≡CR
31
34
32
RC≡CR
33
2
- Ni


Cl
N
HN
O
20 mol% CuCl
2.0 eq. LiCl
O2(1 atm), AcOH, 100 oC
N
HN
O


1-
N
Cl—Cu^II—N
O
Cl
SET
1-
•+
N
Cl—Cu^I—N
O
Cl

VIII