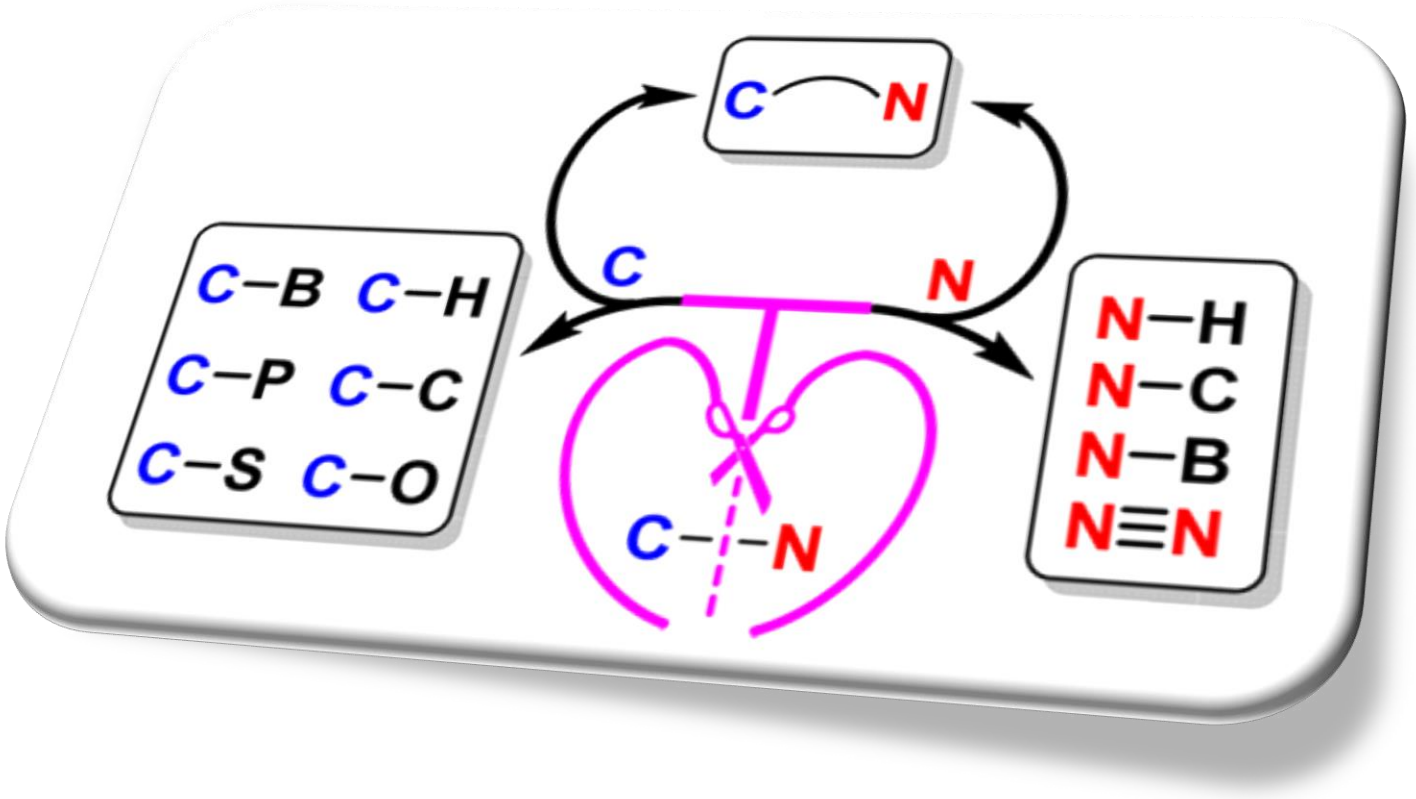
Transition-Metal-Catalyzed Cleavage of C–N Single Bonds



Yan Xu

Jan. 20, 2016

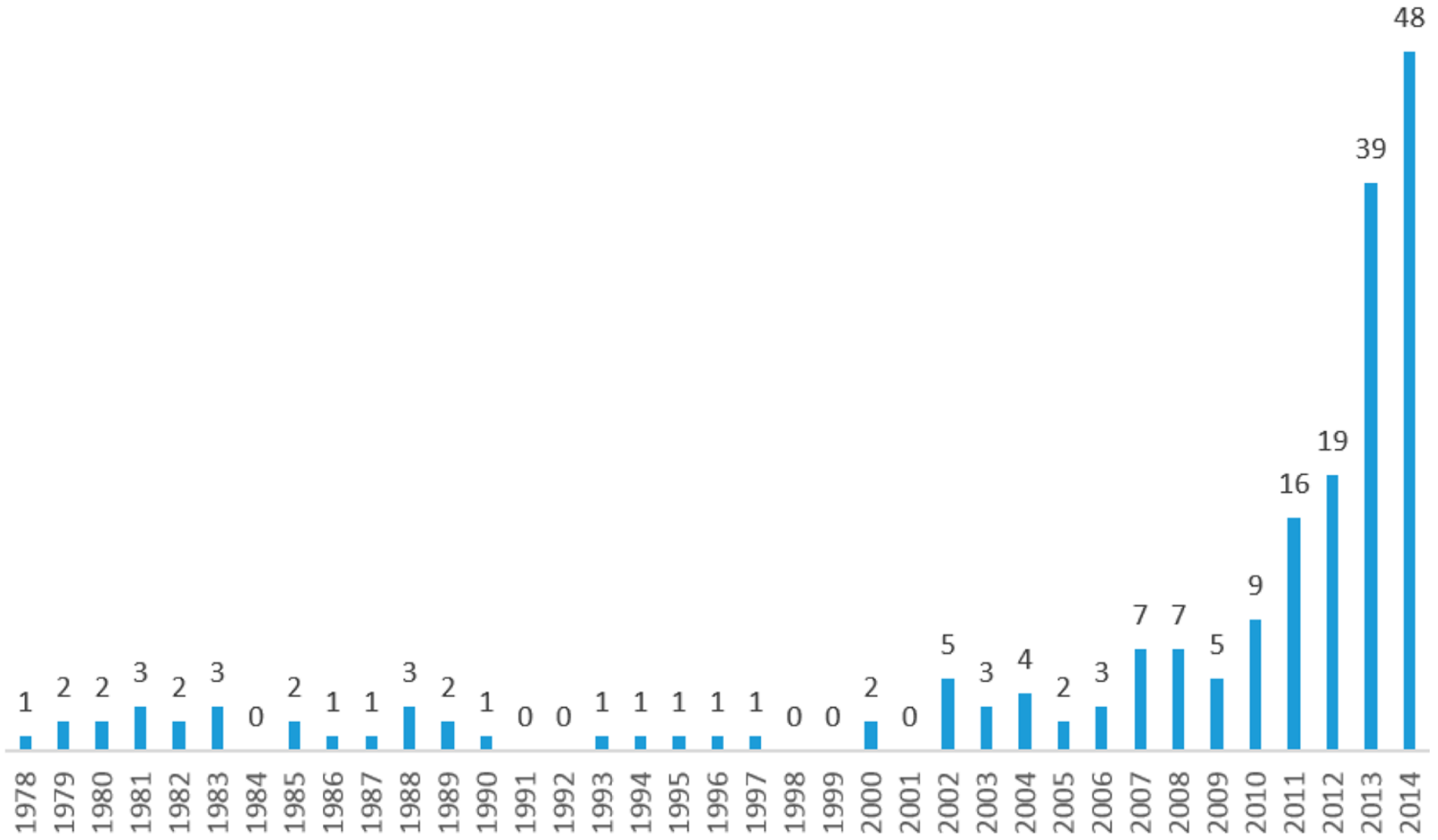
Reference

✓ ***Transition-Metal-Catalyzed Cleavage of C–N Single Bonds***

K. Ouyang, W. Hao, W.-X. Zhang, Z. Xi, *Chem. Rev.* **2015**, *115*, 12045−12090

✓ ***Transition-metal catalysed C–N bond activation***

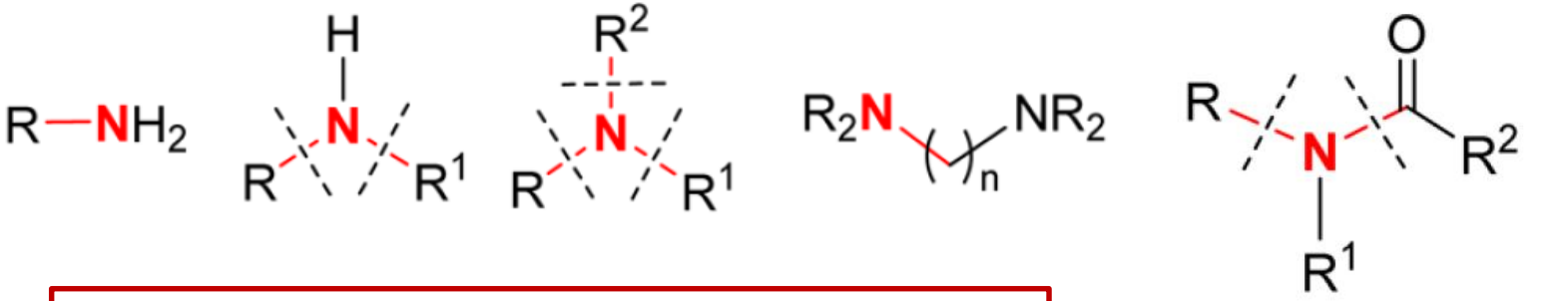
Q. Wang, Y. Su, L. Li, H. Huang, *Chem. Soc. Rev.* **2016**, DOI: 10.1039/c5cs00534e



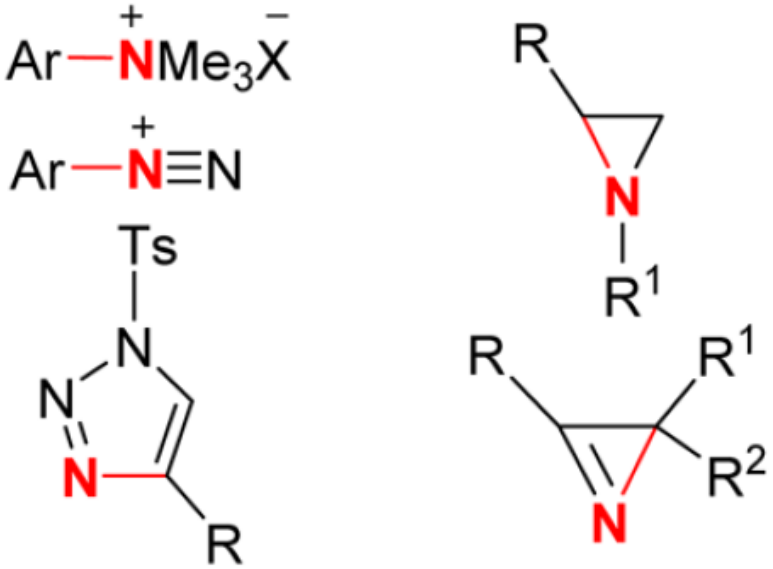
■ Annual Published Items on the Topic of Transition-Metal-Catalyzed Cleavage of C–N Single Bonds

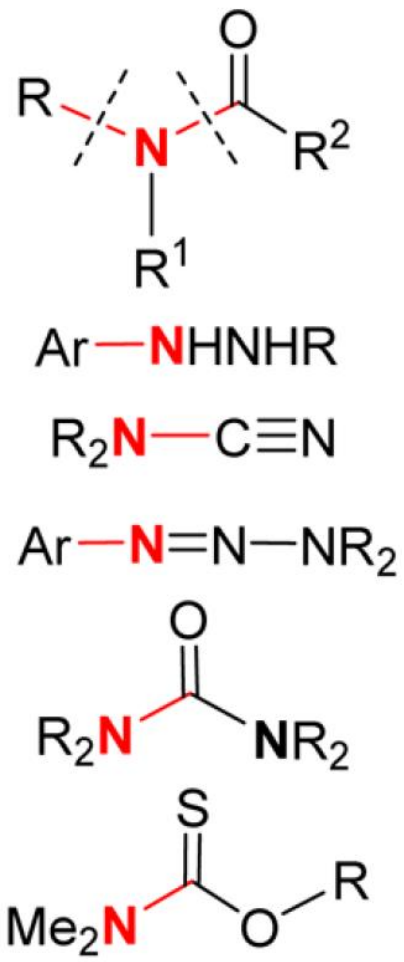
Simple *N*-containing compounds

1) Unactivated C–N bonds



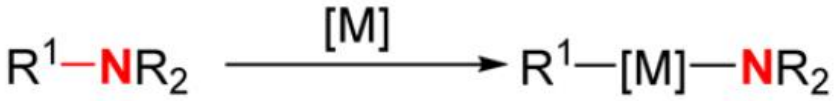
2) Activated C–N bonds



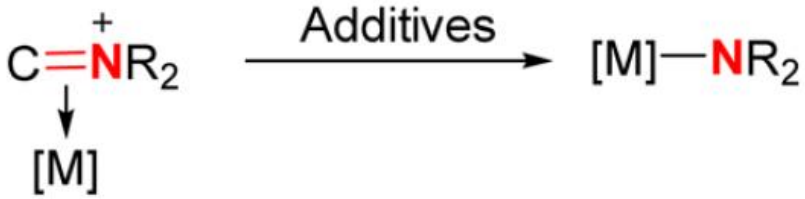


Main pathways

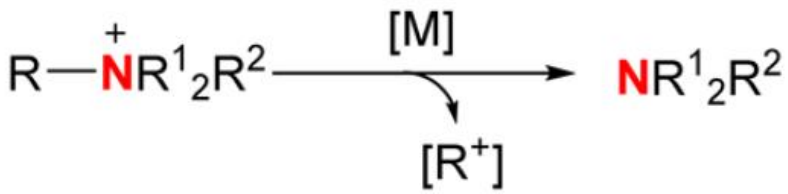
1) Oxidative addition



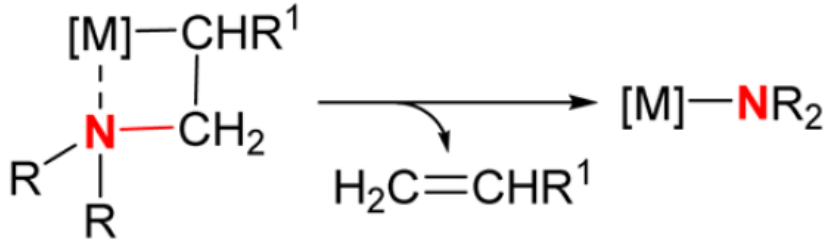
2) Iminium species



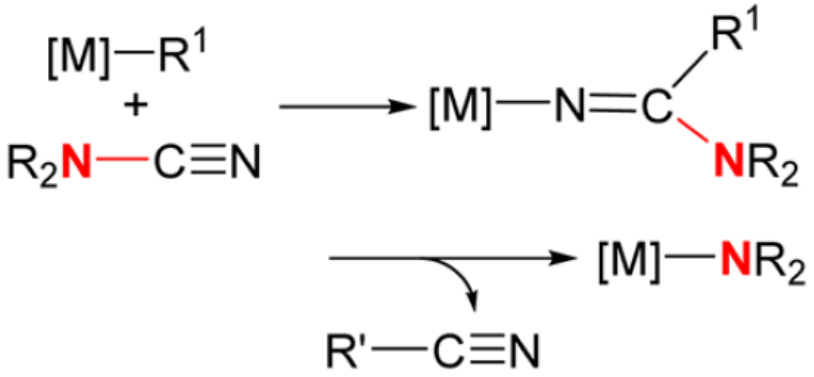
3) Dealkylation of ammonium species

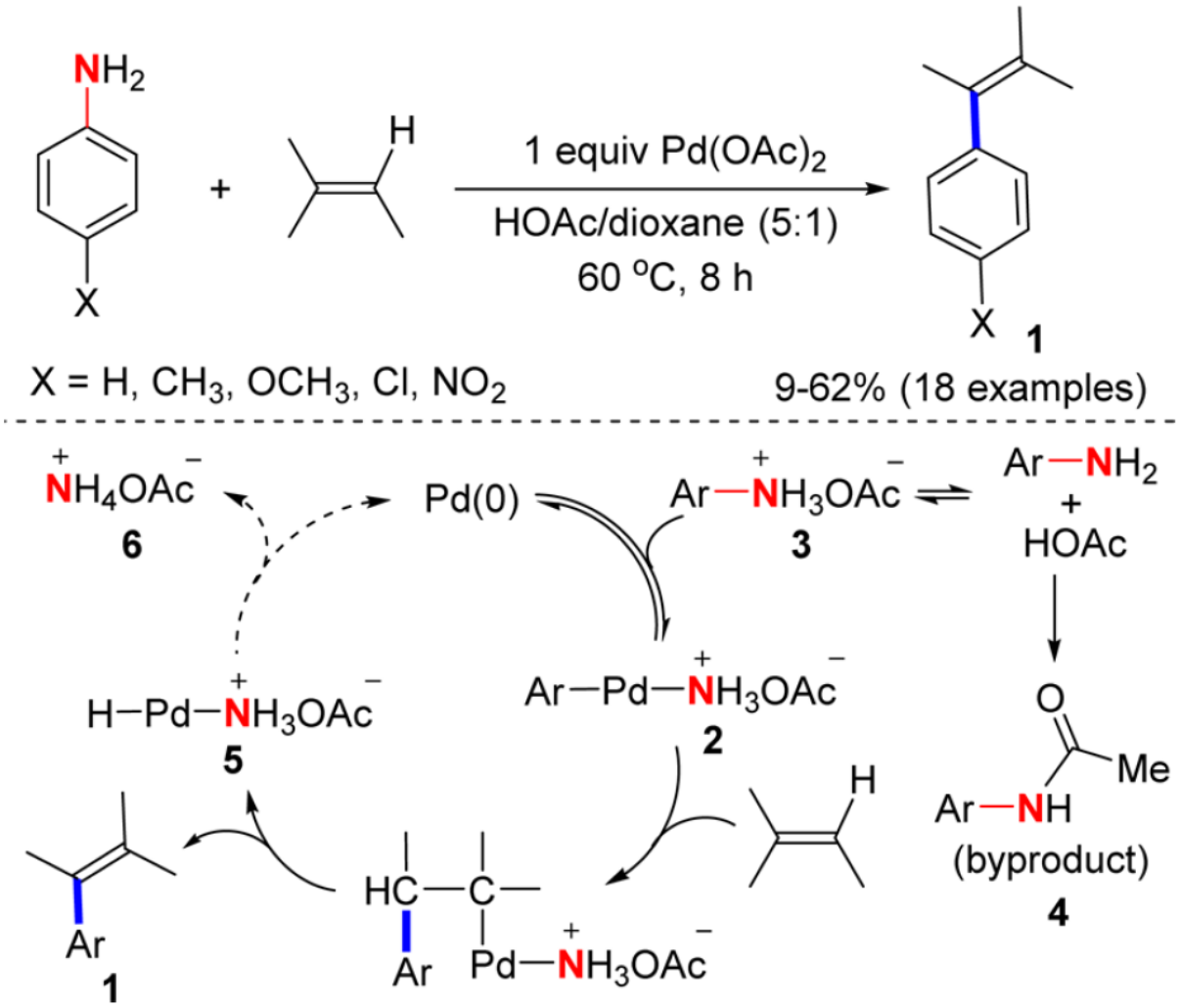


4) β-Amino elimination



5) Insertion/de-insertion





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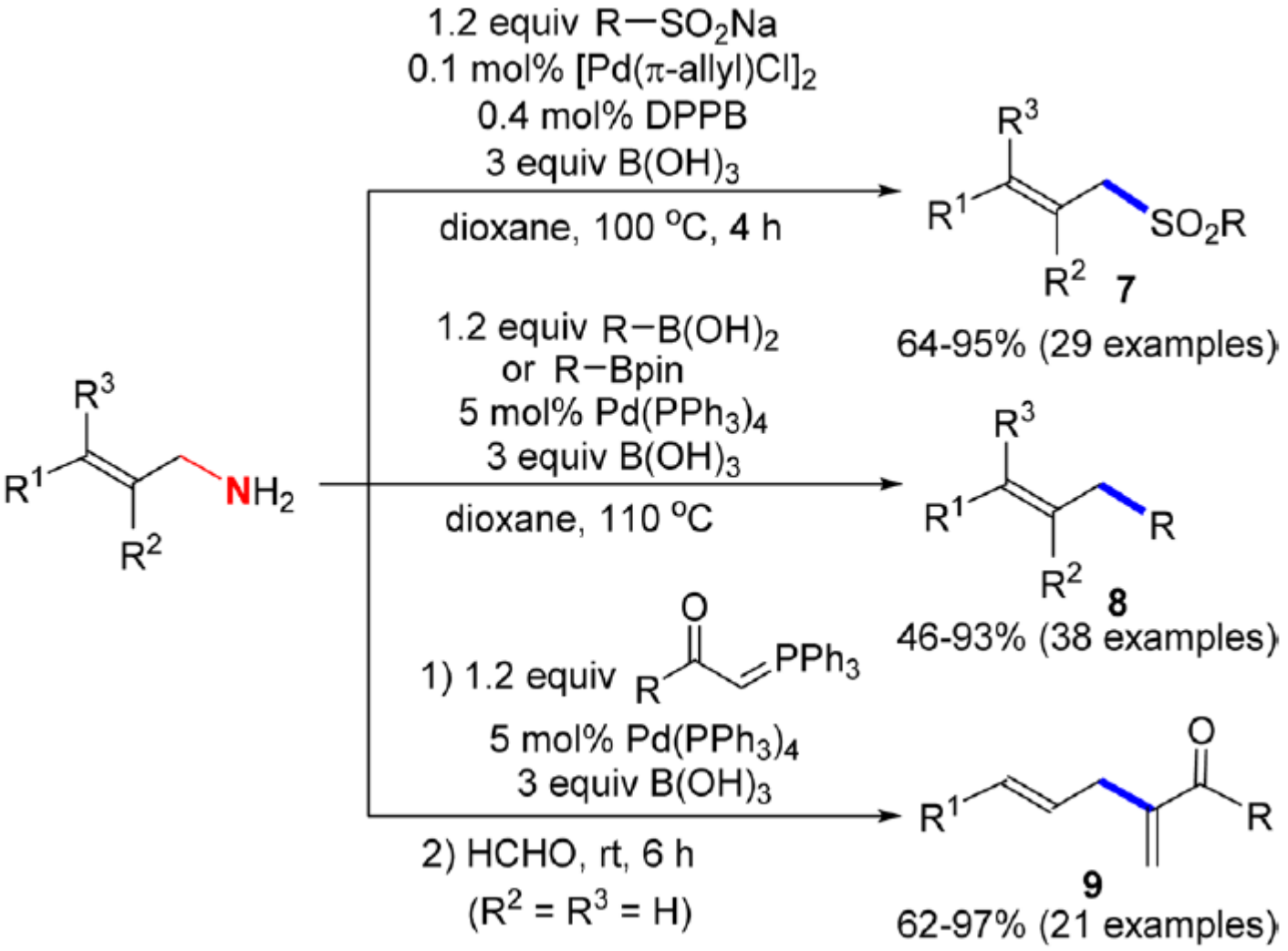
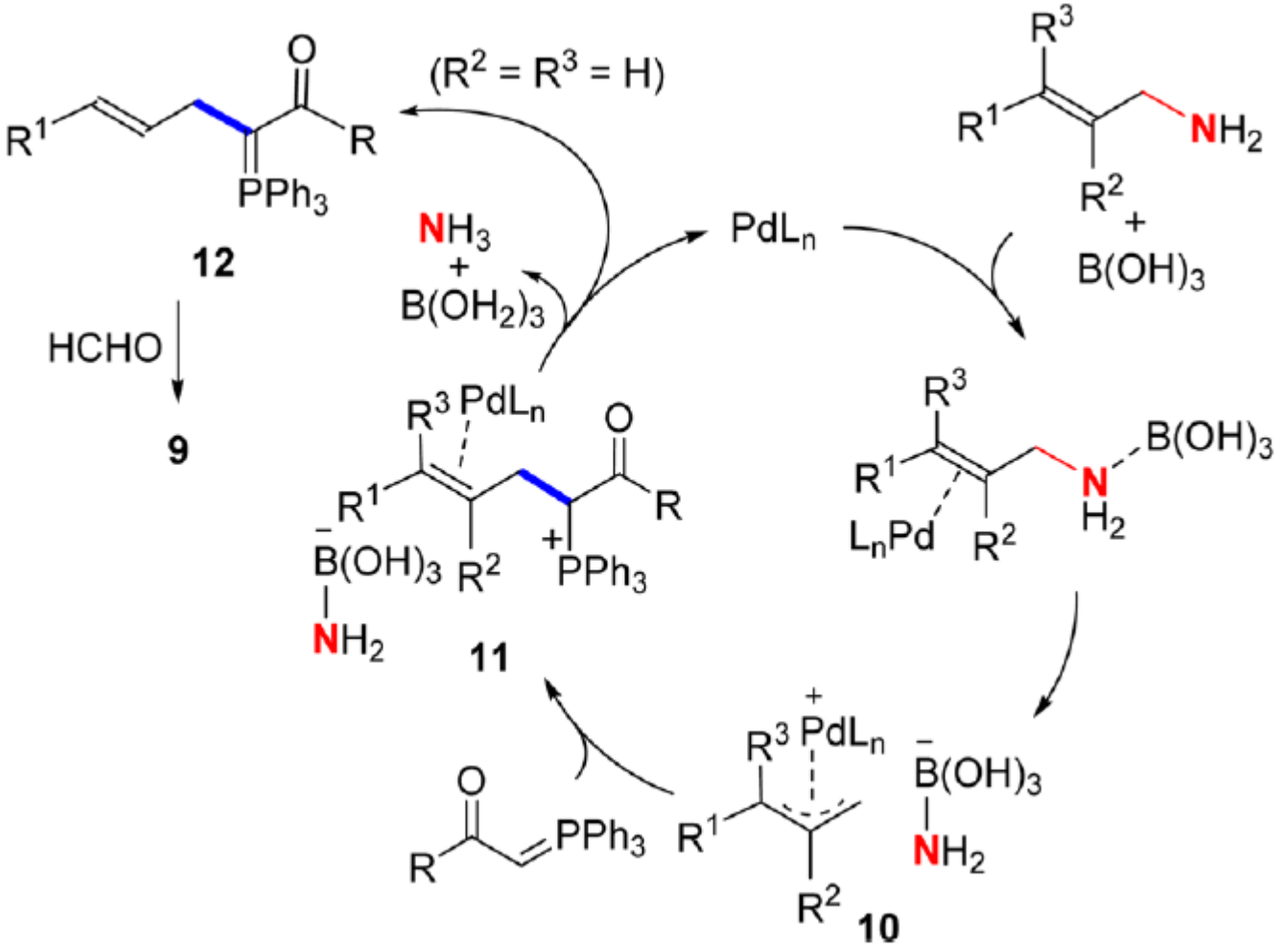
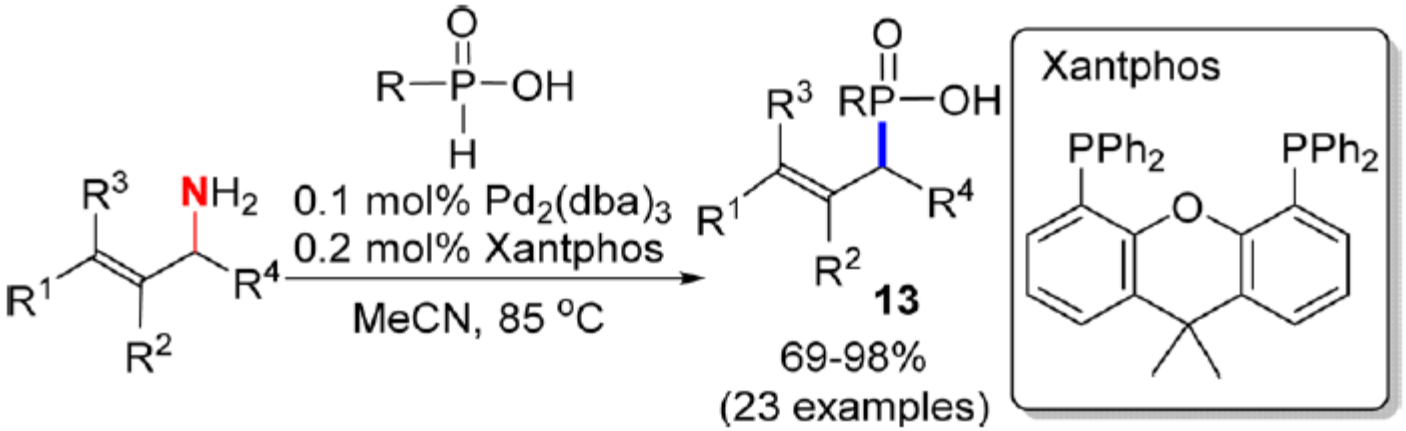
- Akiyama, F.; Miyazaki, H.; Kaneda, K.; Teranishi, S.; Fujiwara, Y.; Abe, M.; Taniguchi, H. Arylation and Alkylation of Olefins by Arylamines or Hydrazines via Carbon–Nitrogen Bond Cleavage in the Presence of Palladium(II) Salts. J. *Org. Chem*. 1980, *45*, 2359–2361.



- Wu, X.-S.; Chen, Y.; Li, M.-B.; Zhou, M.-G.; Tian, S.-K. Direct Substitution of Primary Allylic Amines with Sulfinate Salts. *J. Am. Chem. Soc*. 2012, *134*, 14694–14697.
- Li, M. B.; Wang, Y.; Tian, S.-K. Regioselective and Stereospecific Cross-Coupling of Primary Allylic Amines with Boronic Acids and Boronates through Palladium-Catalyzed C–N Bond Cleavage. *Angew. Chem., Int. Ed.* 2012, *51*, 2968–2971.



- Wu, X.-S.; Chen, Y.; Li, M.-B.; Zhou, M.-G.; Tian, S.-K. Direct Substitution of Primary Allylic Amines with Sulfinate Salts. *J. Am. Chem. Soc*. 2012, *134*, 14694−14697.
- Li, M. B.; Wang, Y.; Tian, S.-K. Regioselective and Stereospecific Cross-Coupling of Primary Allylic Amines with Boronic Acids and Boronates through Palladium-Catalyzed C−N Bond Cleavage. *Angew. Chem., Int. Ed.* 2012, *51*, 2968−2971.



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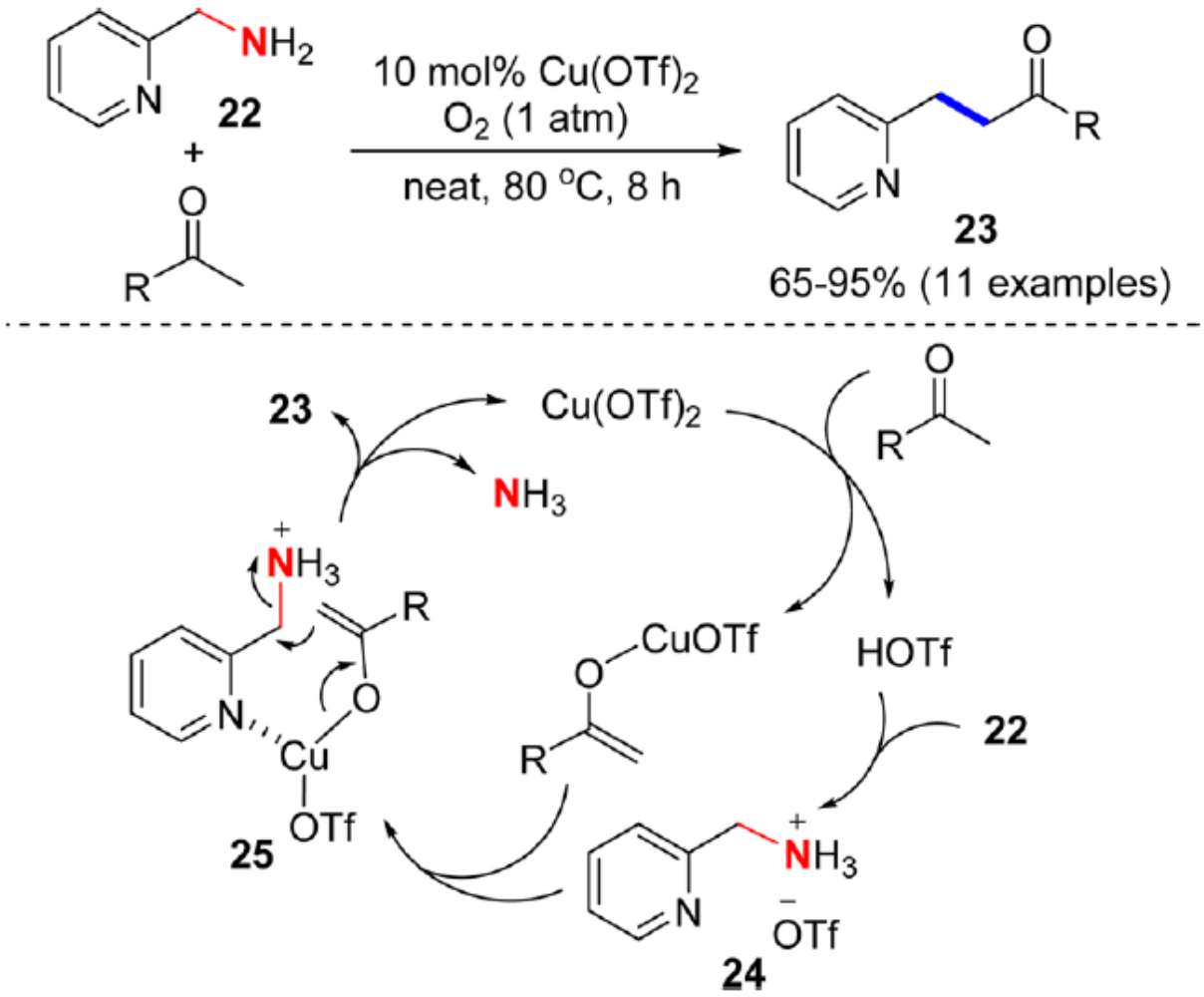
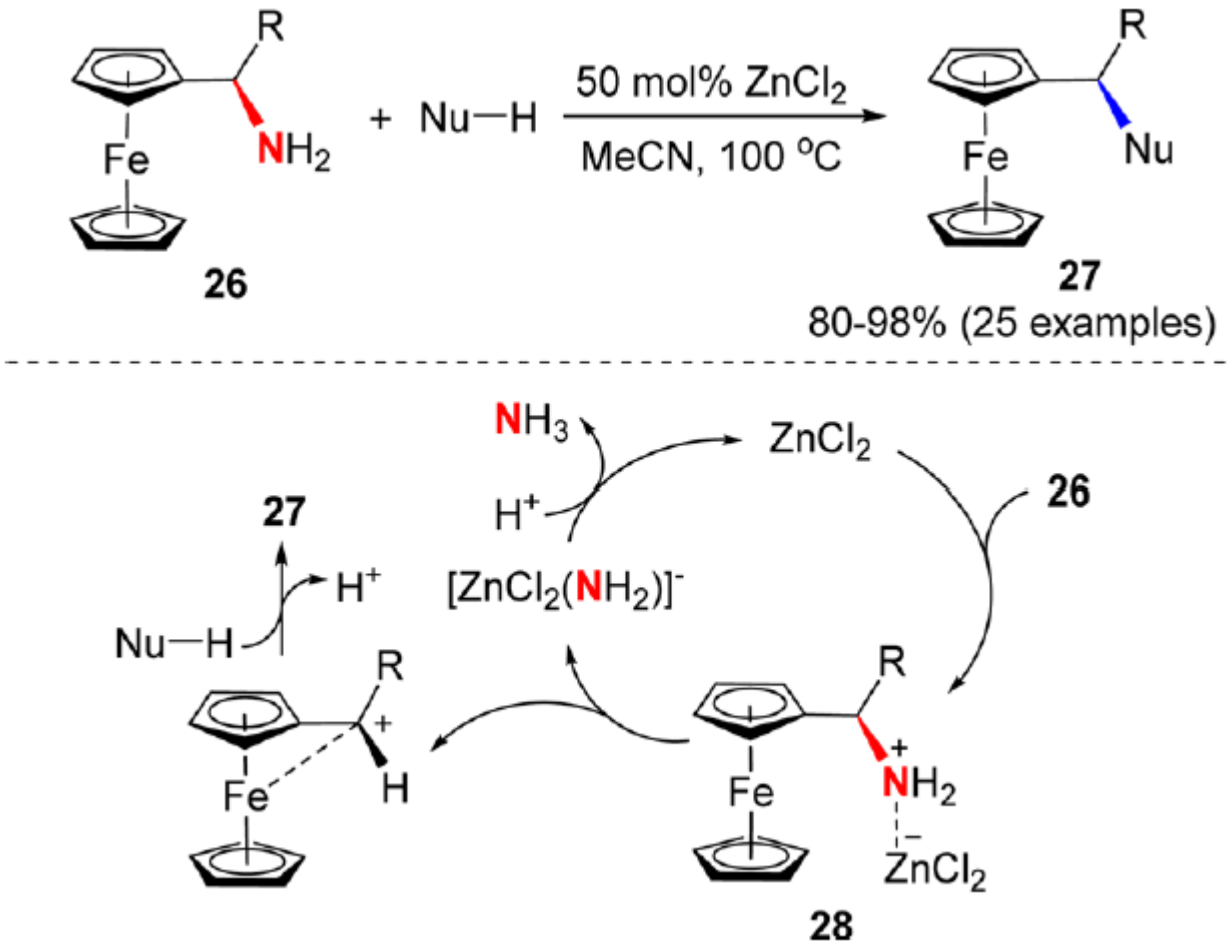


■ Huang, H.; Ji, X.; Wu, W.; Huang, L.; Jiang, H. Copper-Catalyzed Formal C–N Bond Cleavage of Aromatic Methylamines: Assembly of Pyridine Derivatives. *J. Org. Chem.* 2013, *78*, 3774–3782



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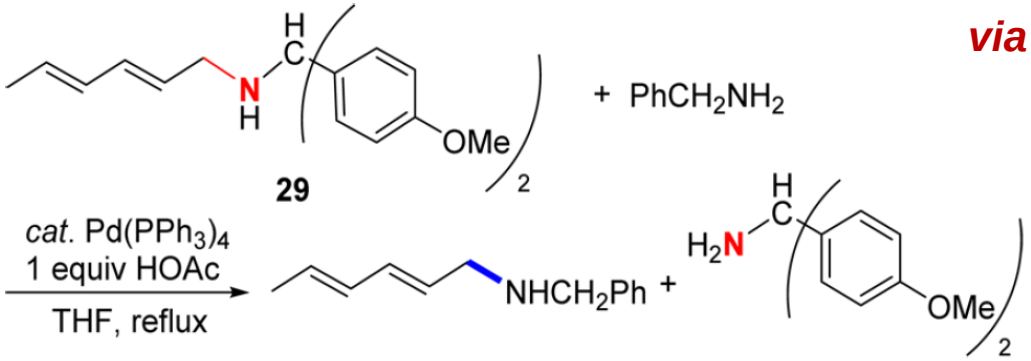
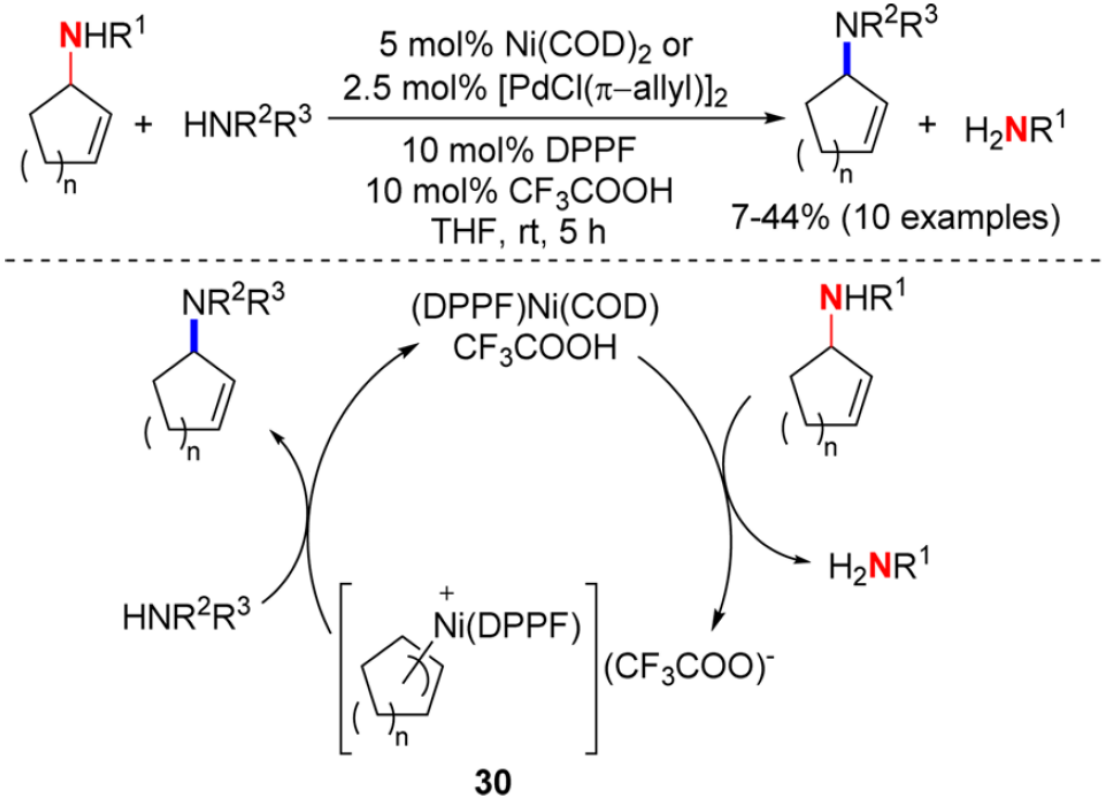
Secondary Amines

via Oxidative Addition





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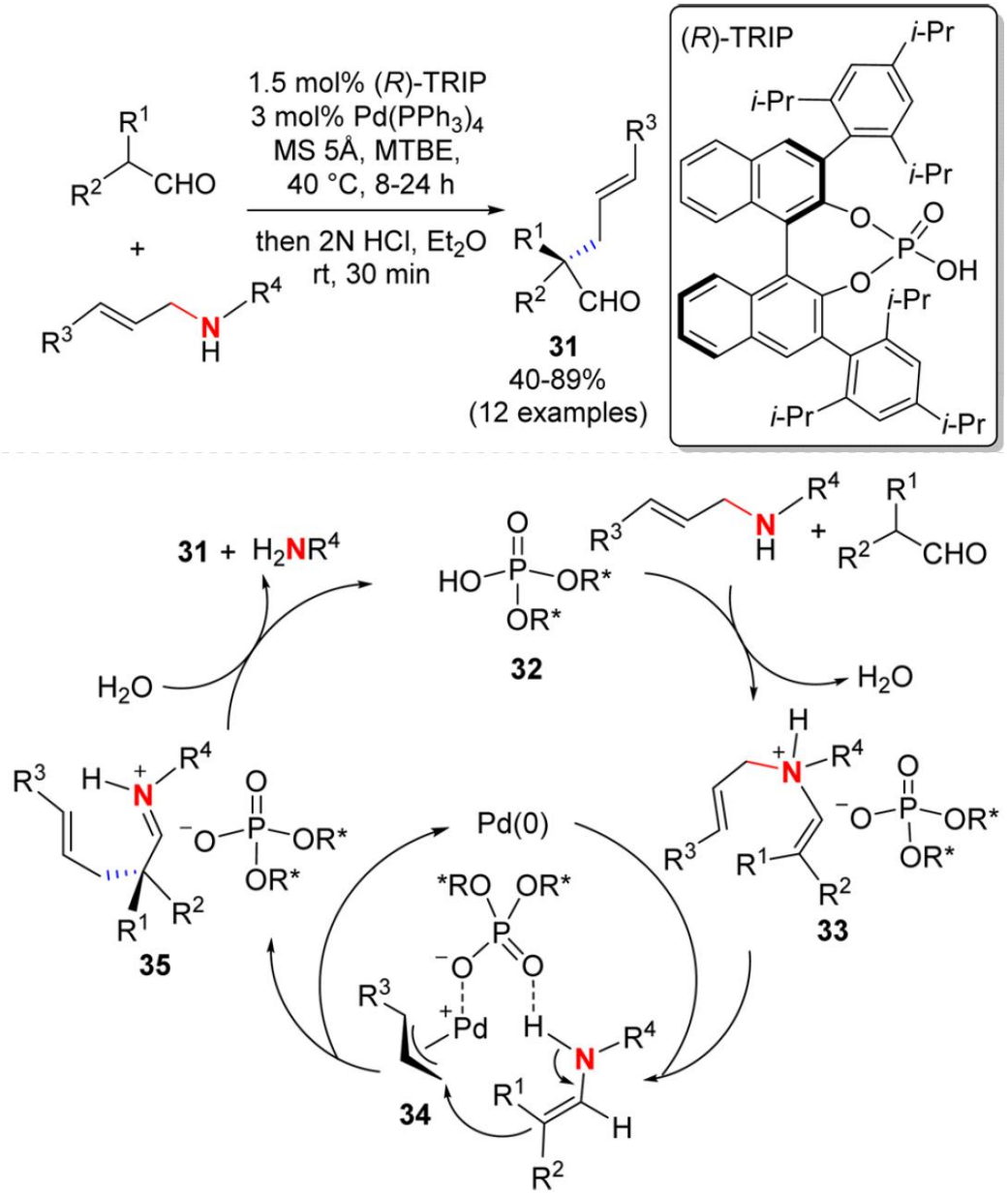
- Pawlas, J.; Nakao, Y.; Kawatsura, M.; Hartwig, J. F. A General Nickel-Catalyzed Hydroamination of 1,3-Dienes by Alkylamines: Catalyst Selection, Scope, and Mechanism. *J. Am. Chem. Soc*. 2002, *124*, 3669–3679.



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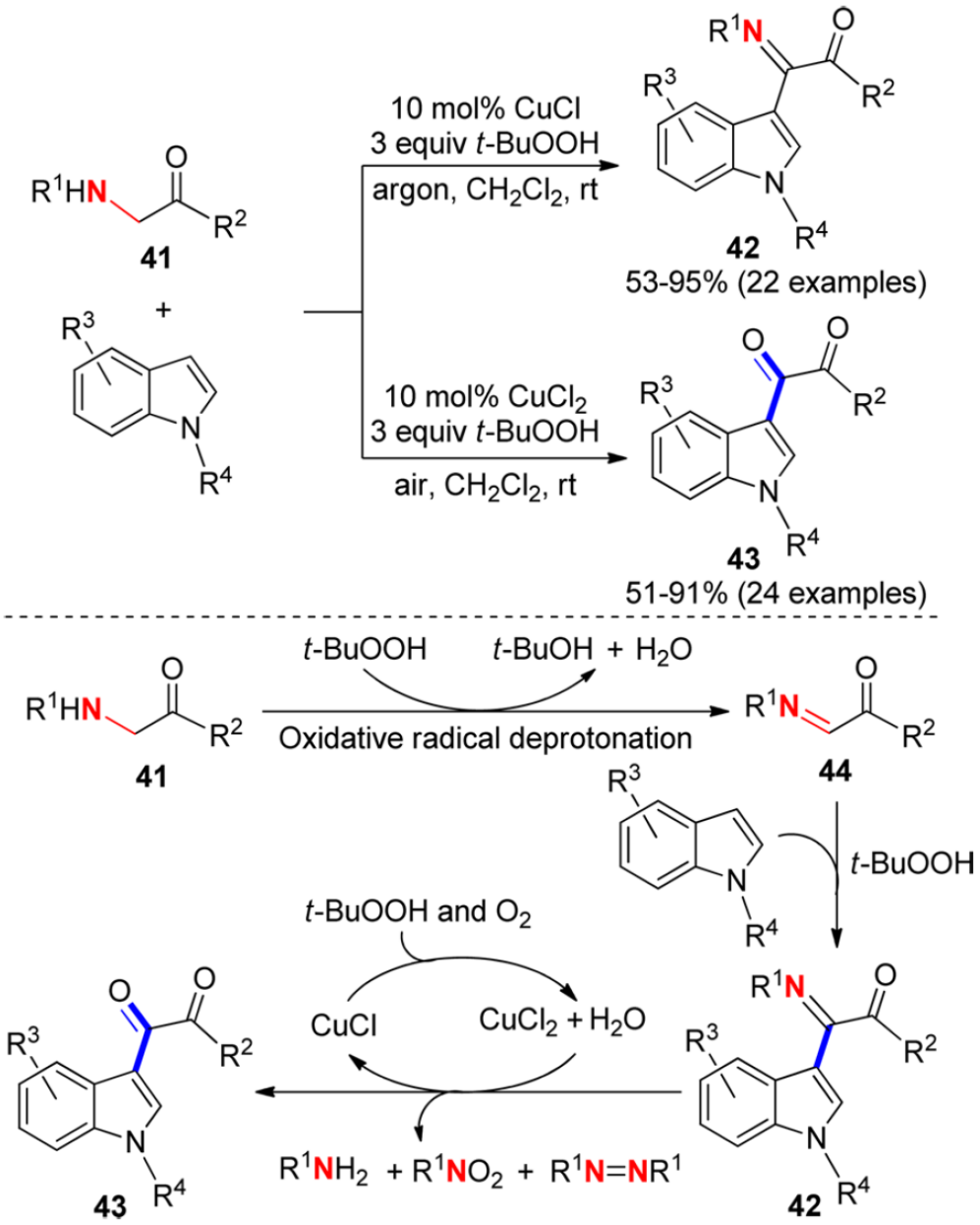
Secondary Amines

via Iminium or Imine



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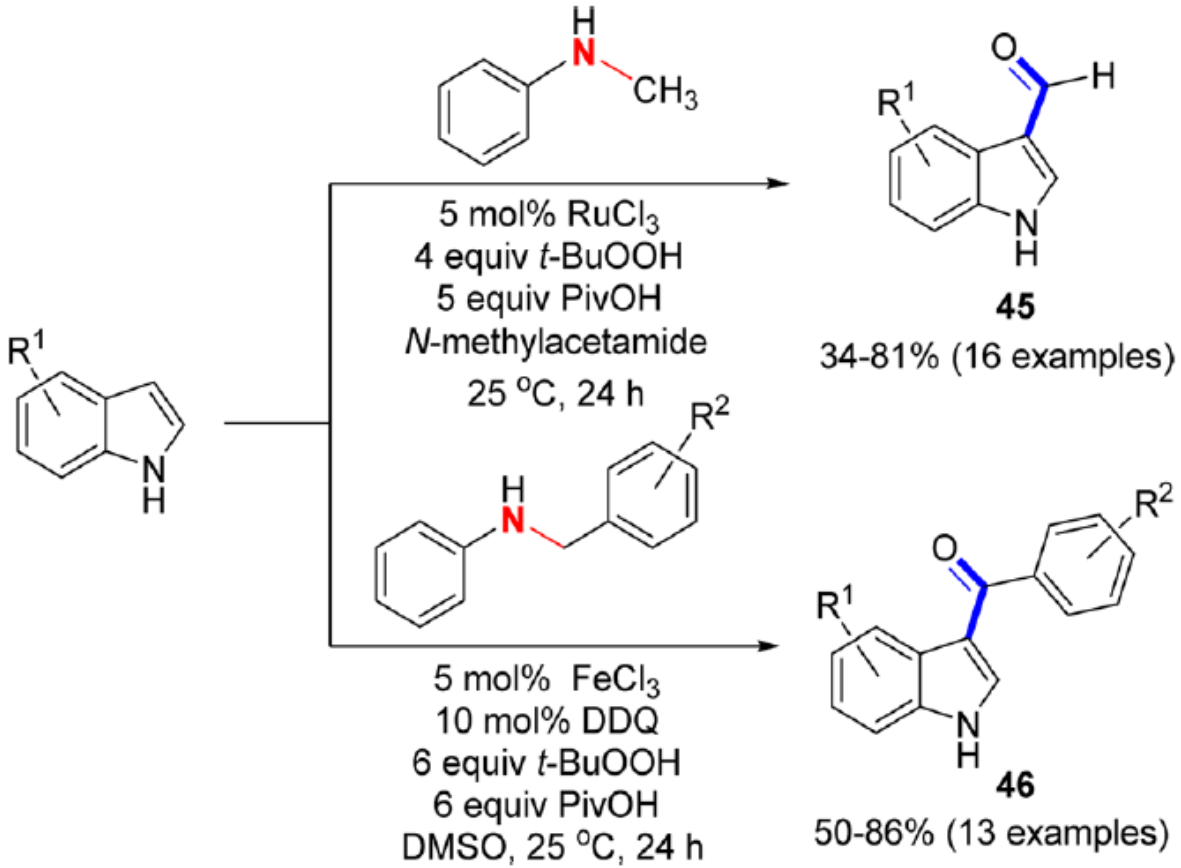

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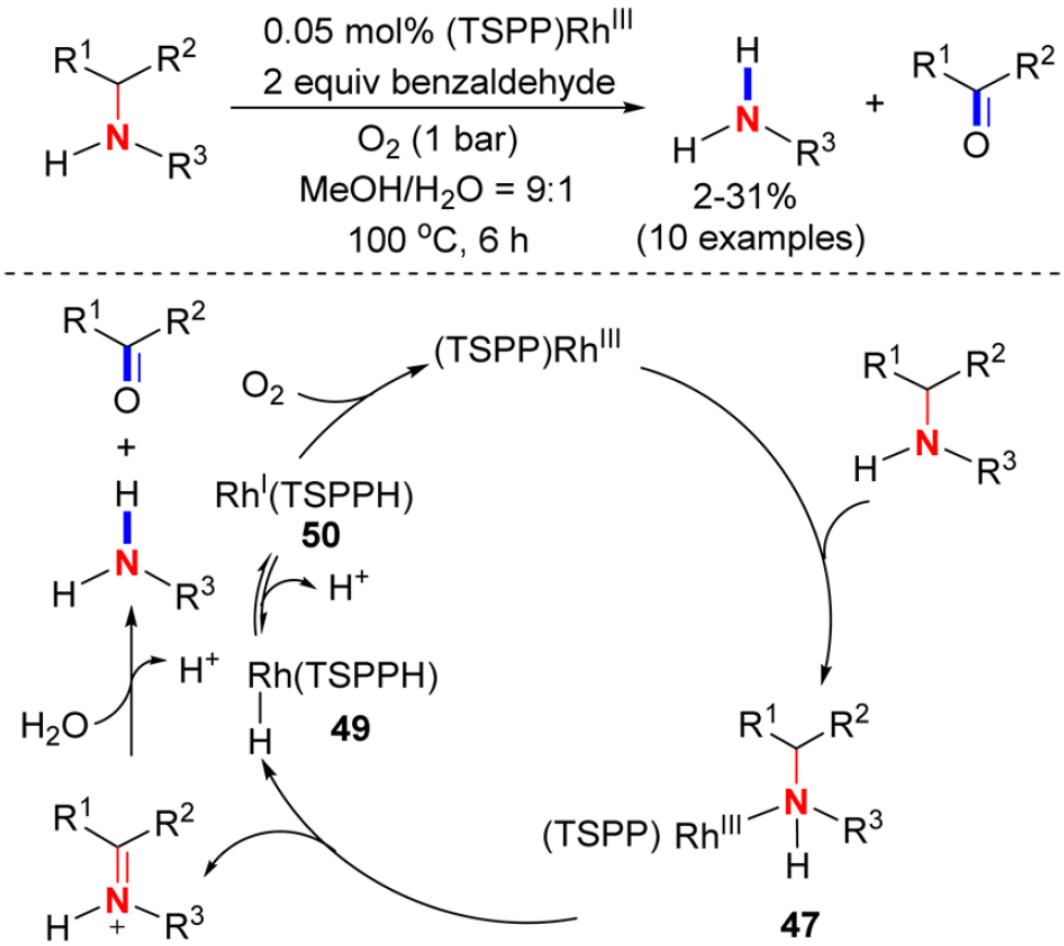

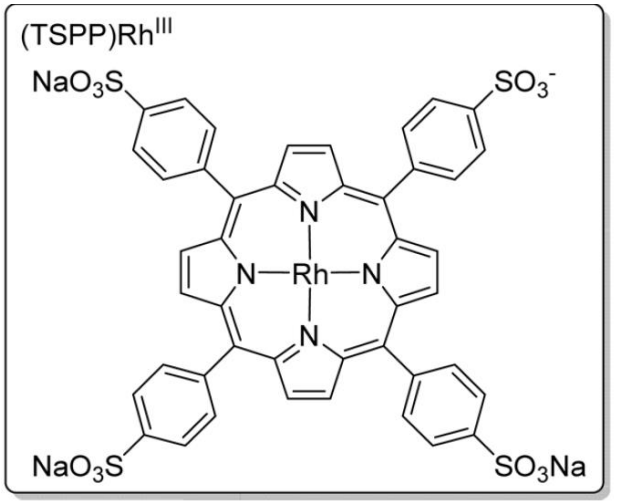

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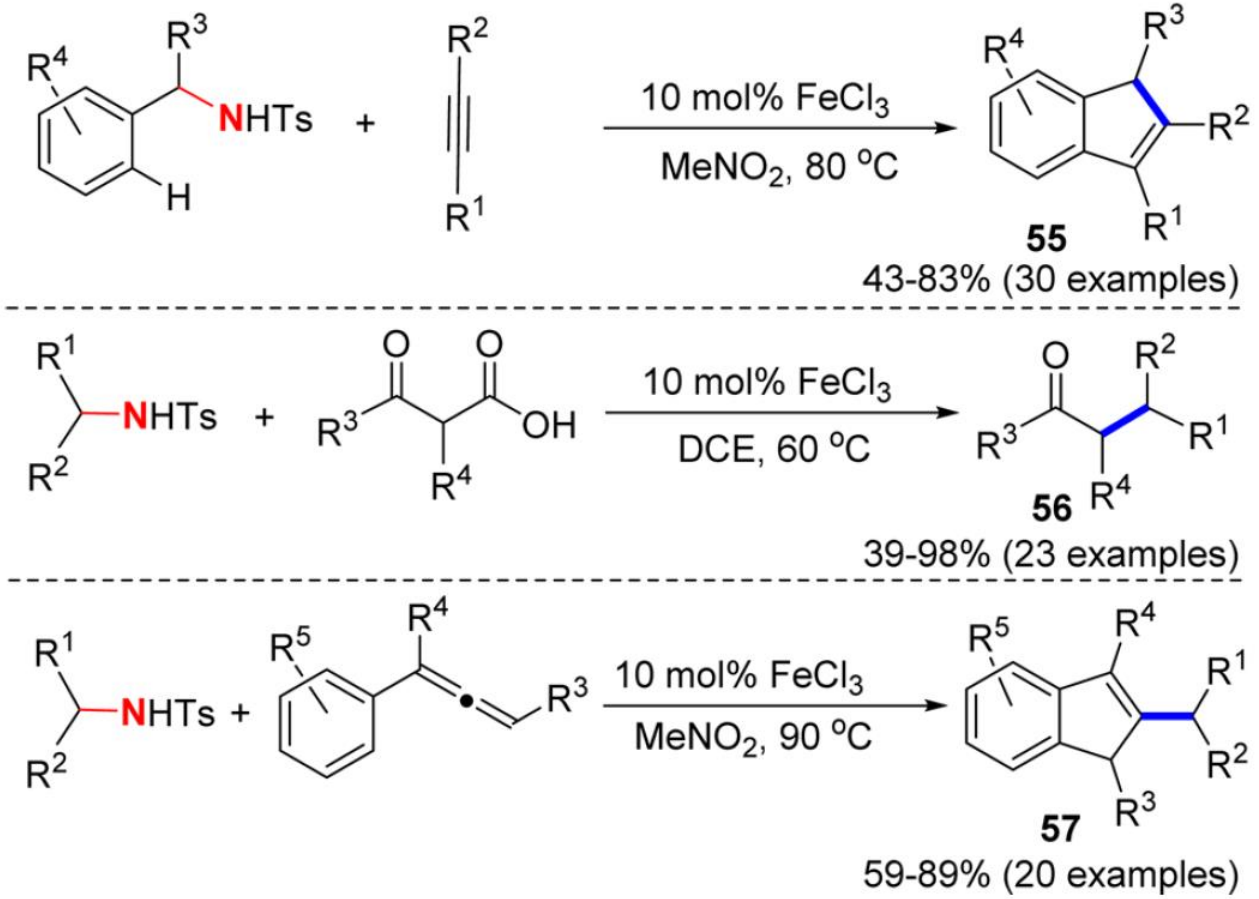

- Liu, C.-R.; Li, M.-B.; Yang, C.-F.; Tian, S.-K. Selective Benzylic and Allylic Alkylation of Protic Nucleophiles with Sulfonamide through Double Lewis Acid Catalyzed Cleavage of sp^3 Carbon−Nitrogen Bonds. *Chem. - Eur. J.* 2009, *15*, 793−797.
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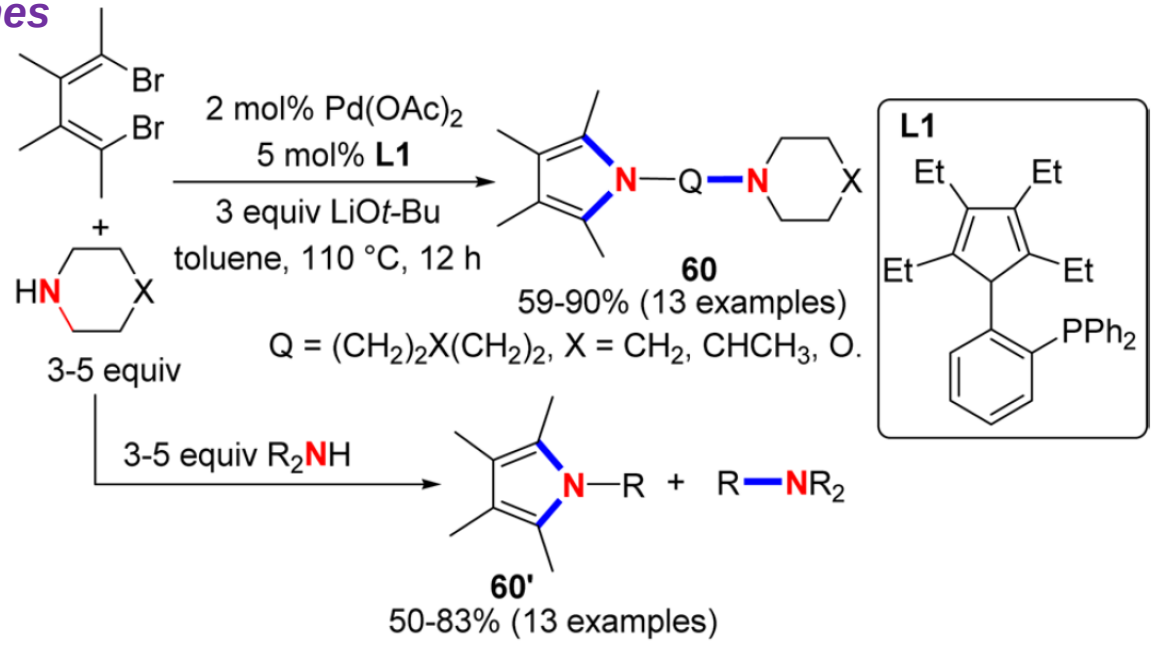
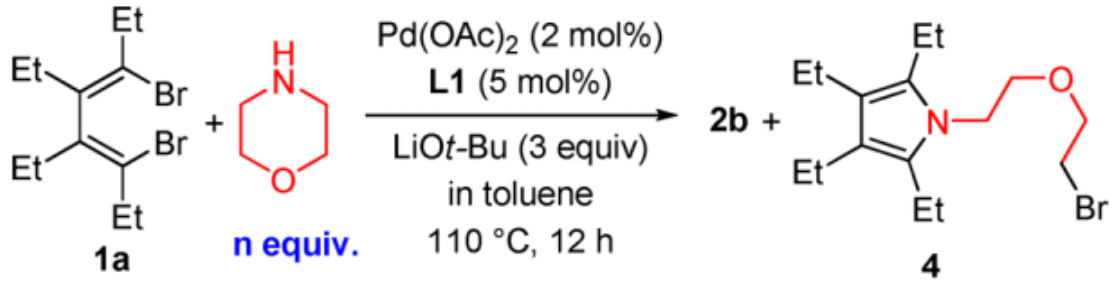
Secondary Amines

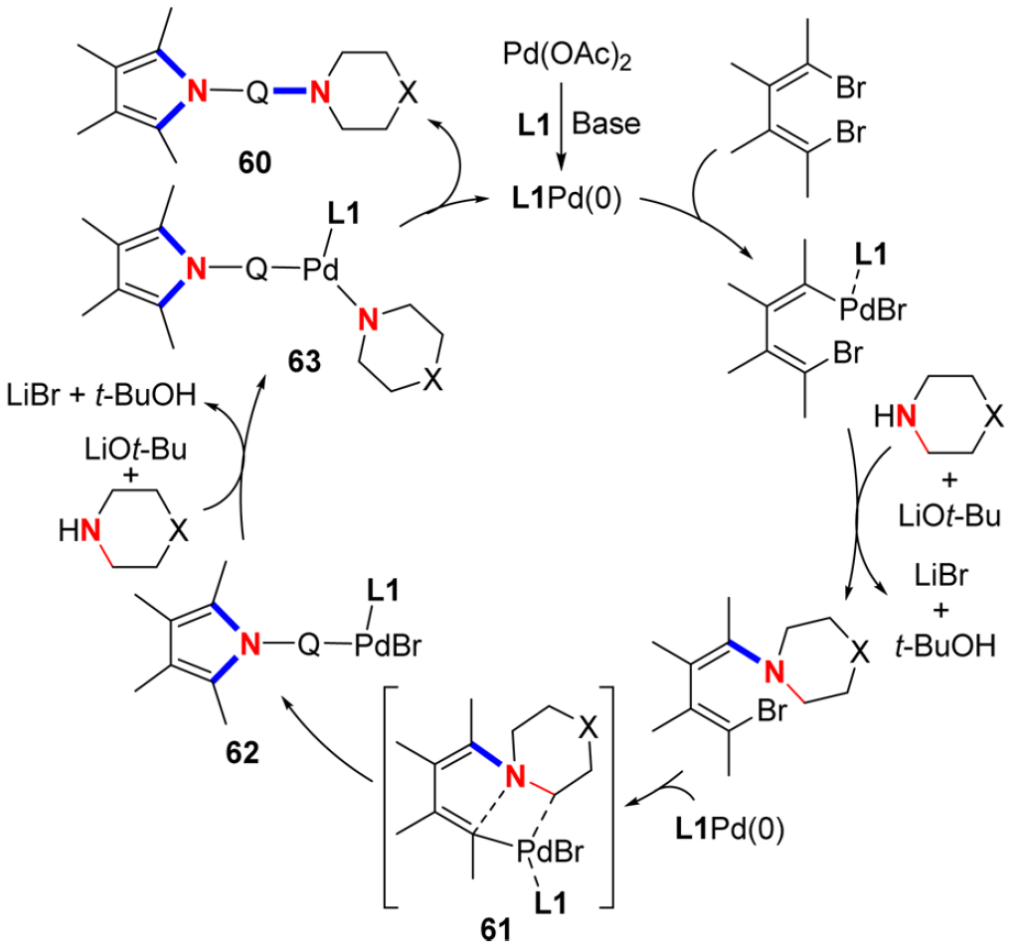
via σ-metathesis



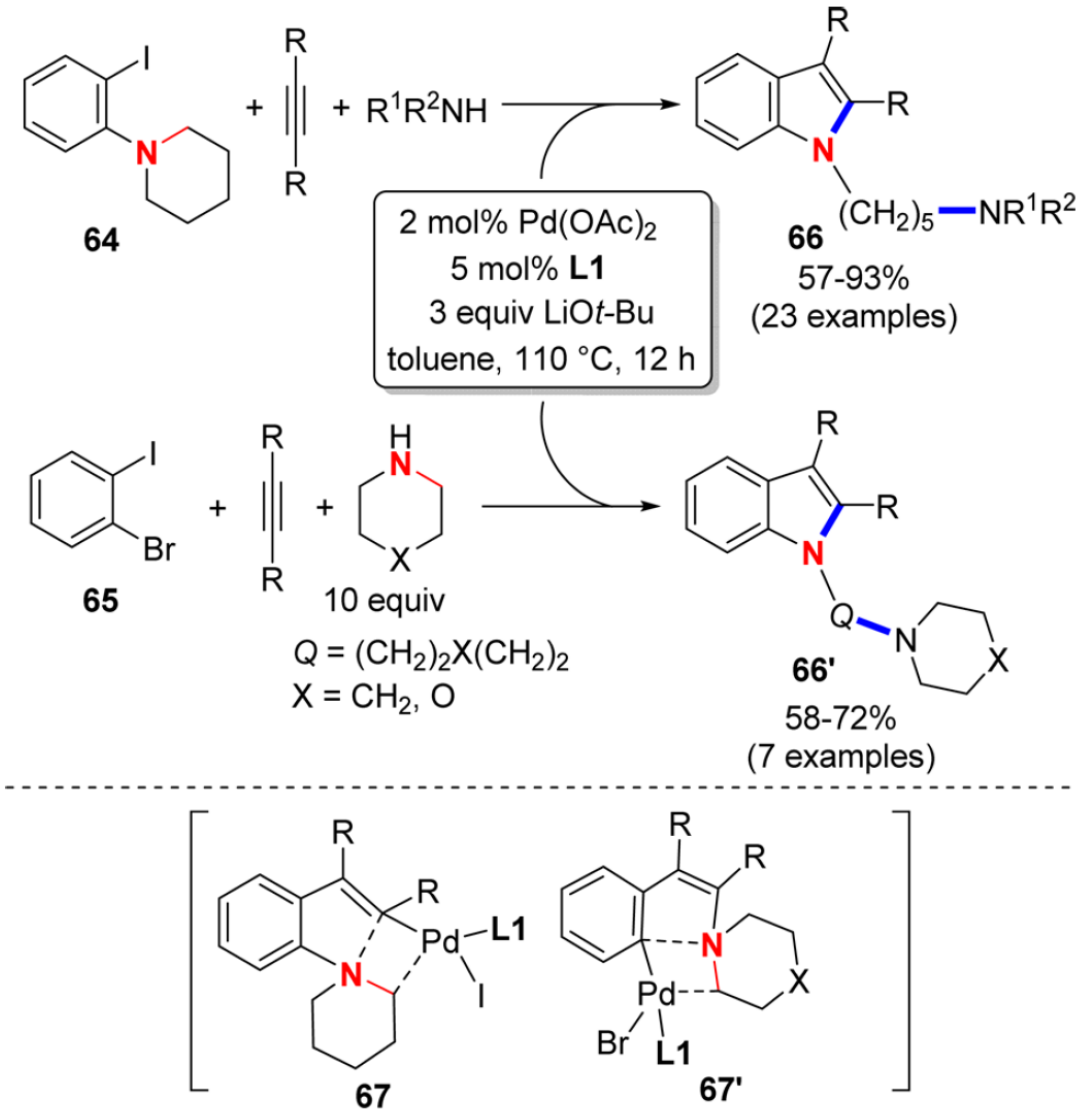


morpholine **n** equivalents	yield of **2b**	yield of **4**
n = 5	76%	trace
n = 2	52%	11%
n = 1	27%	19%

- Geng, W.; Zhang, W.-X.; Hao, W.; Xi, Z. Cyclopentadiene–Phosphine/Palladium-Catalyzed Cleavage of C–N Bonds in Secondary Amines: Synthesis of Pyrrole and Indole Derivatives from Secondary Amines and Alkenyl or Aryl Dibromides. *J. Am. Chem. Soc.* 2012, *134*, 20230–20233.



■ Geng, W.; Zhang, W.-X.; Hao, W.; Xi, Z. Cyclopentadiene–Phosphine/Palladium-Catalyzed Cleavage of C–N Bonds in Secondary Amines: Synthesis of Pyrrole and Indole Derivatives from Secondary Amines and Alkenyl or Aryl Dibromides. *J. Am. Chem. Soc.* 2012, *134*, 20230–20233.



- Hao, W.; Geng, W.; Zhang, W.-X.; Xi, Z. Palladium-Catalyzed One-Pot Three- or Four-Component Coupling of Aryl Iodides, Alkynes, and Amines through C–N Bond Cleavage: Efficient Synthesis of Indole Derivatives. *Chem. - Eur. J.* 2014, *20*, 2605–2612.
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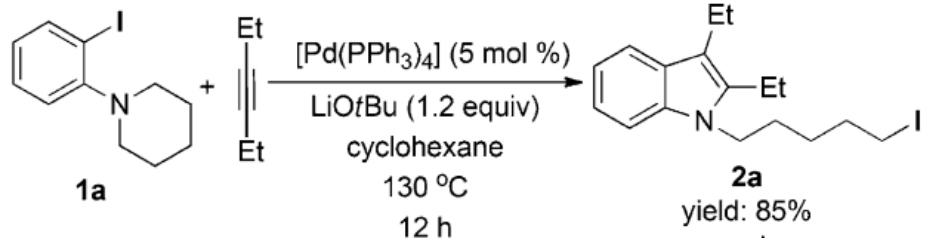
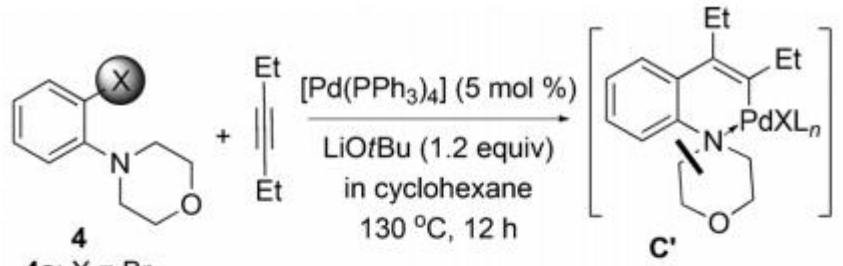
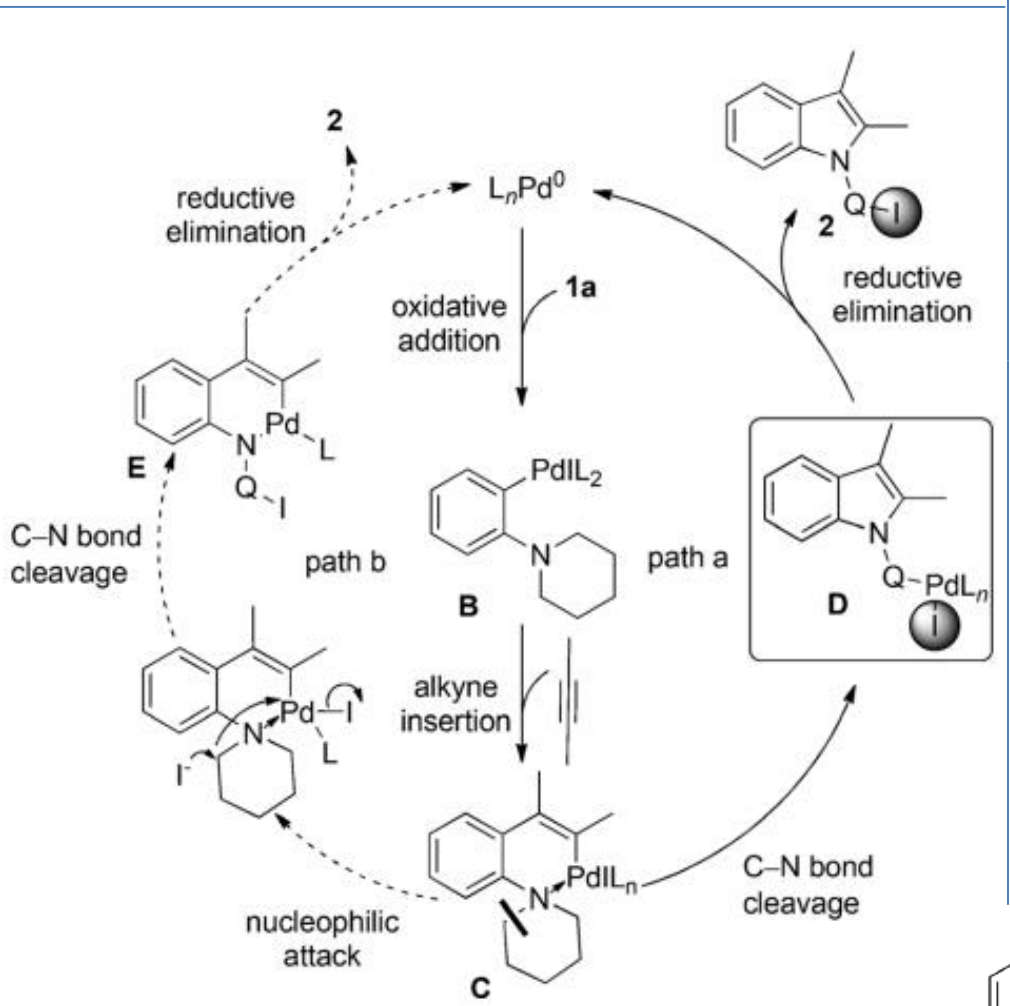
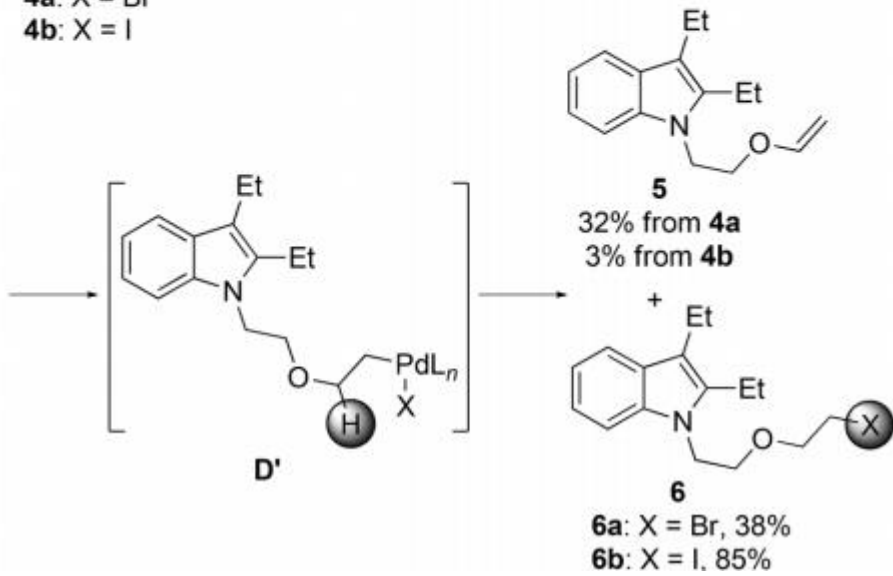
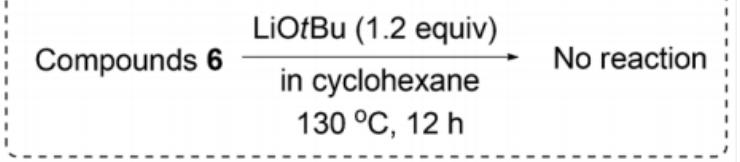
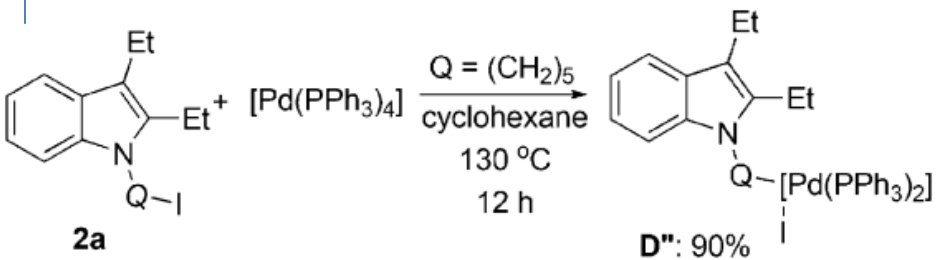

[Pd(PPh3)4] (5 mol %)
LiOtBu (1.2 equiv)
cyclohexane
130 °C
12 h
1a
2a
yield: 85%

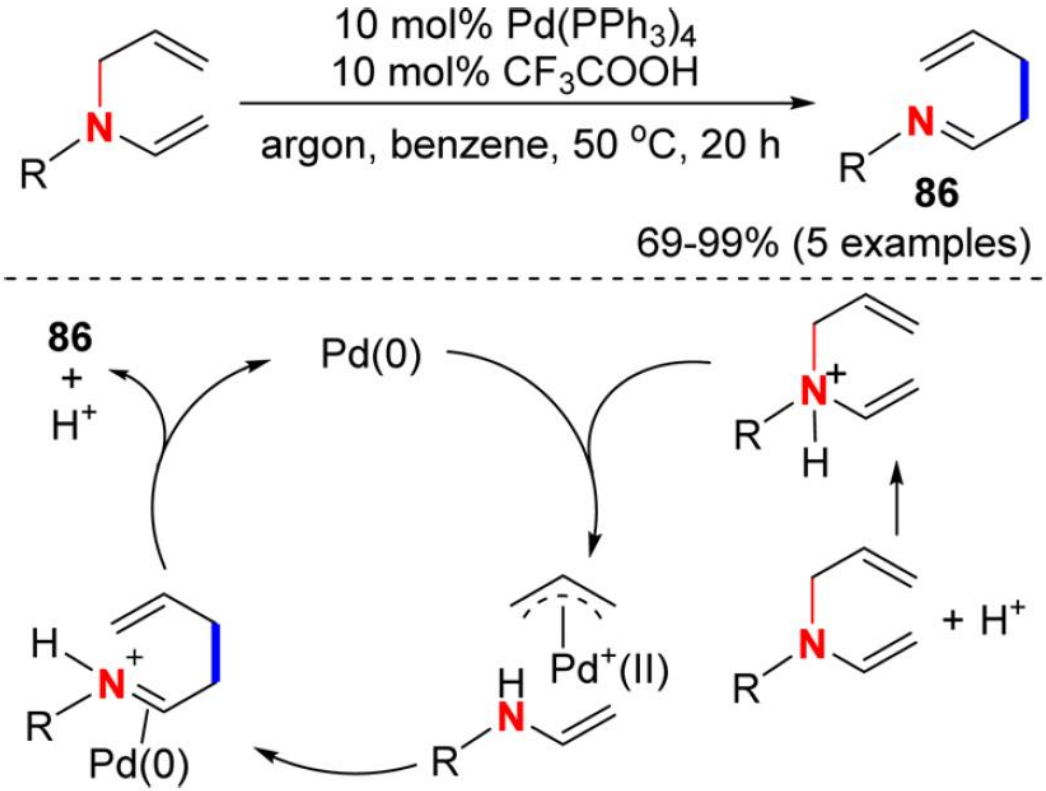

[Pd(PPh3)4] (5 mol %)
LiOtBu (1.2 equiv)
in cyclohexane
130 °C, 12 h
4
4a: X = Br
4b: X = I
C'


reductive elimination
LnPd0
oxidative addition
1a
2
reductive elimination
C–N bond cleavage
path b
path a
E
B
D
alkyne insertion
nucleophilic attack
C
C–N bond cleavage


D'
5
32% from 4a
3% from 4b
6
6a: X = Br, 38%
6b: X = I, 85%

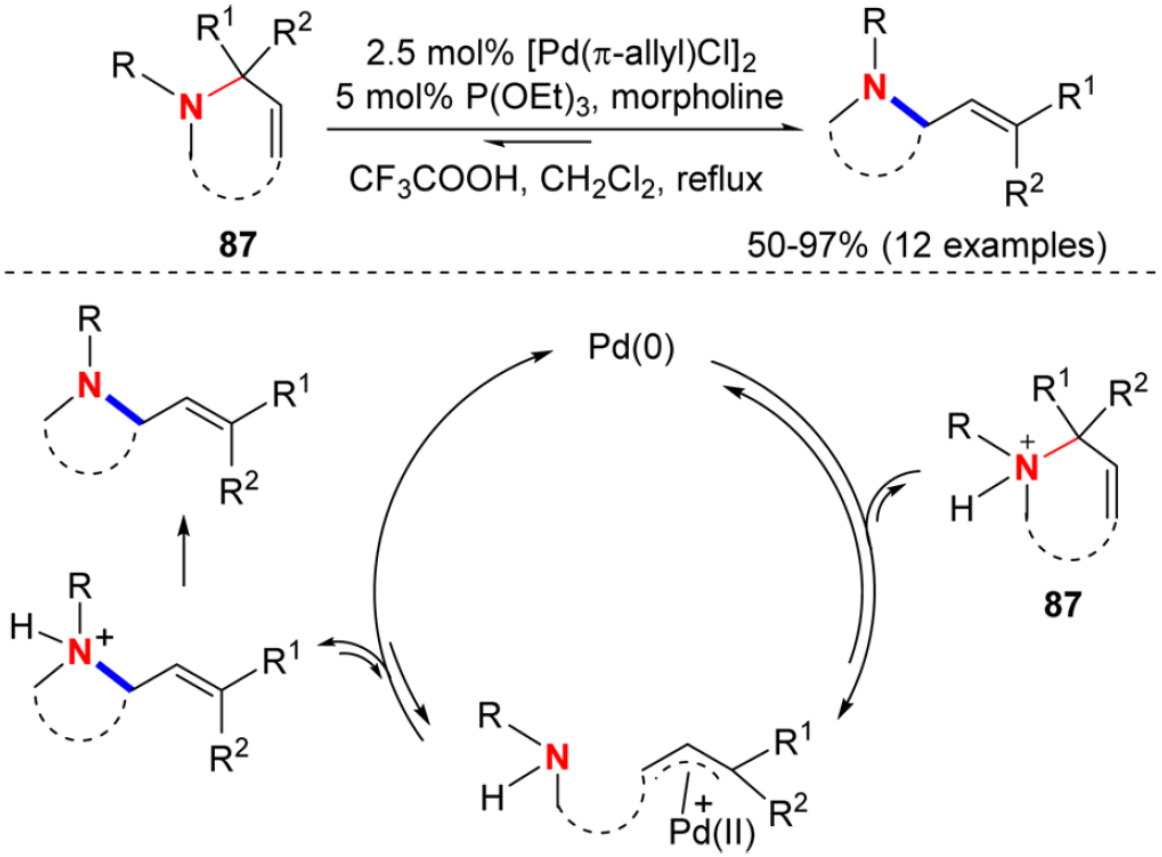

Compounds 6
LiOtBu (1.2 equiv)
in cyclohexane
130 °C, 12 h
No reaction


2a
[Pd(PPh3)4]
Q = (CH2)5
cyclohexane
130 °C
12 h
D": 90%



- *Pd(II) salt: no reaction*
- *Pd(0) catalyst such as $Pd(PPh_3)_4$, $Pd(OAc)_2$-PPh_3, $Pd_2(dba)_3$: low yield*
- *Pd(0) catalyst + TFA: good yield*

- Murahashi, S.-I.; Makabe, Y.; Kunita, K. Palladium(0)-Catalyzed Rearrangement of N-Allylenamines. Synthesis of δ,ε-Unsaturated Imines and γ,δ-Unsaturated Carbonyl Compounds. *J. Org. Chem.* 1988, *53*, 4489−4495



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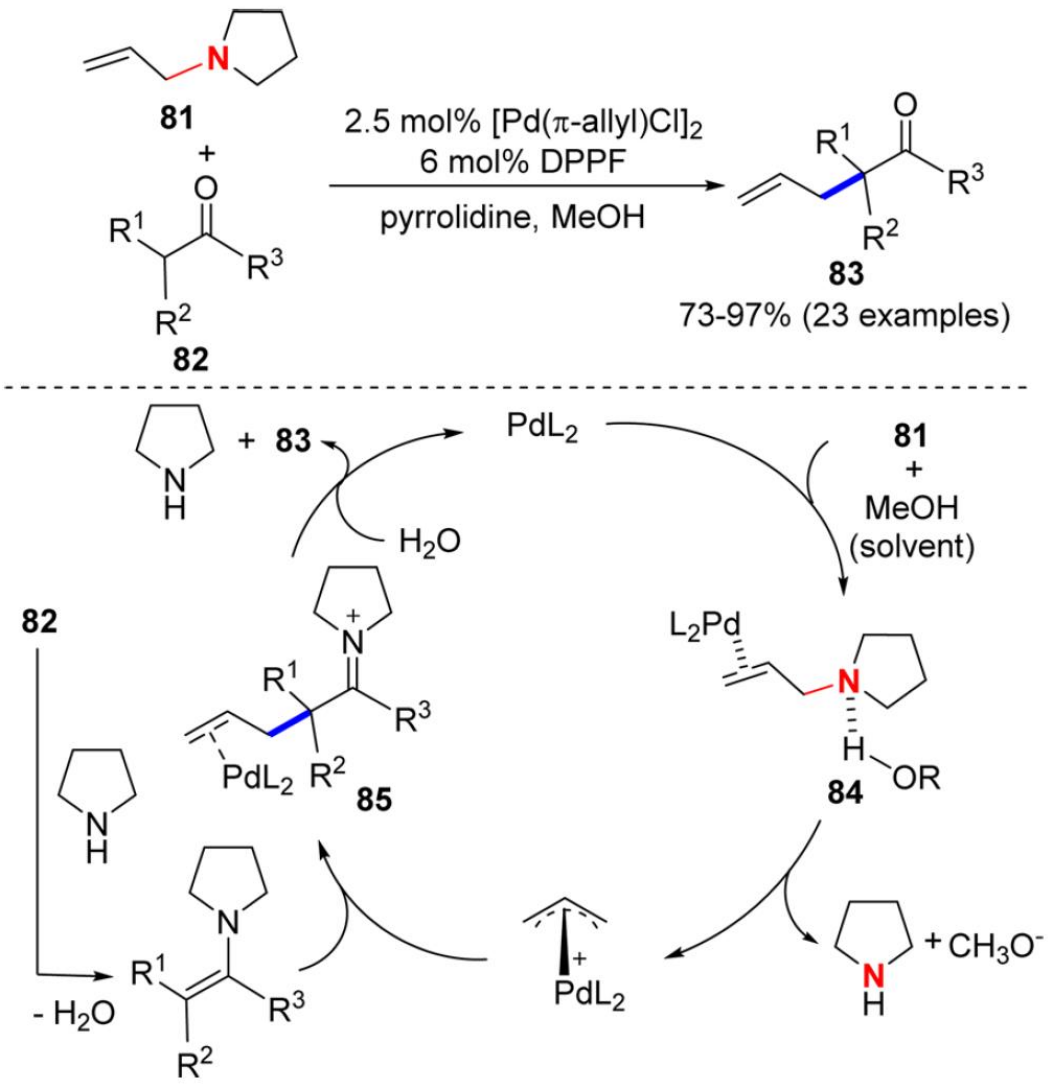

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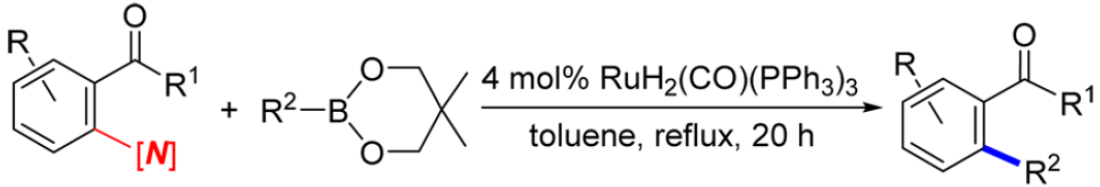
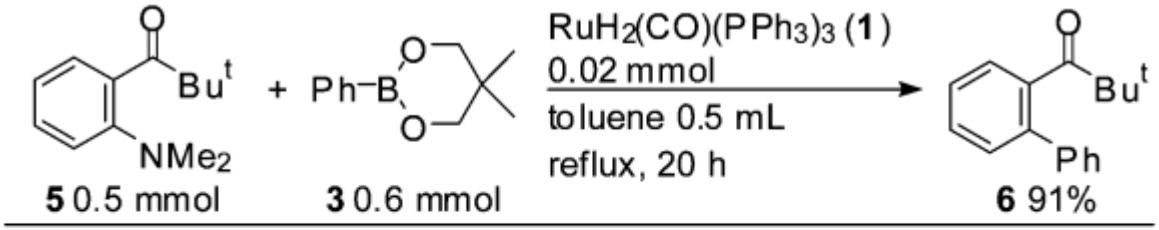


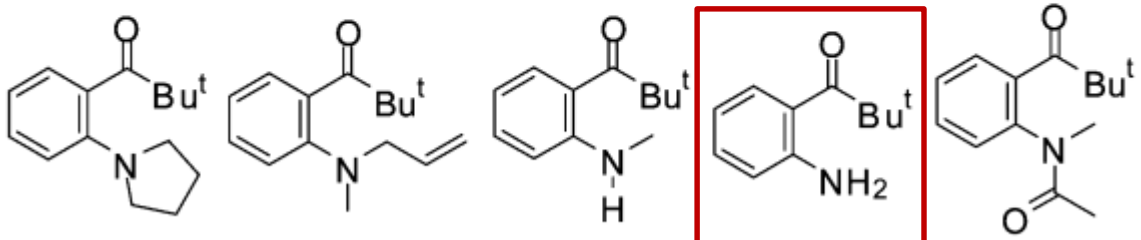
95
45-99%
(37 examples)

Kakiuchi's work:
[*N*] = NH_2, NHMe, NMe_2, etc.
R^1 = *t*-Bu, Me
R^2 = Ar, Bn, CH_2TMS

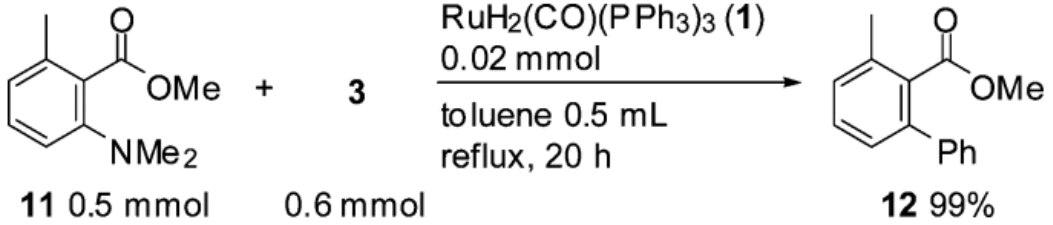
Snieckus's work:
[*N*] = NMe_2, NMePh
R^1 = NEt_2, $N(i\text{-}Pr)_2$
R^2 = Ar, Alk, etc.



5 0.5 mmol **3** 0.6 mmol **6** 91%



83% 82% 87% 82%[b] 51%[c]



11 0.5 mmol 0.6 mmol **12** 99%

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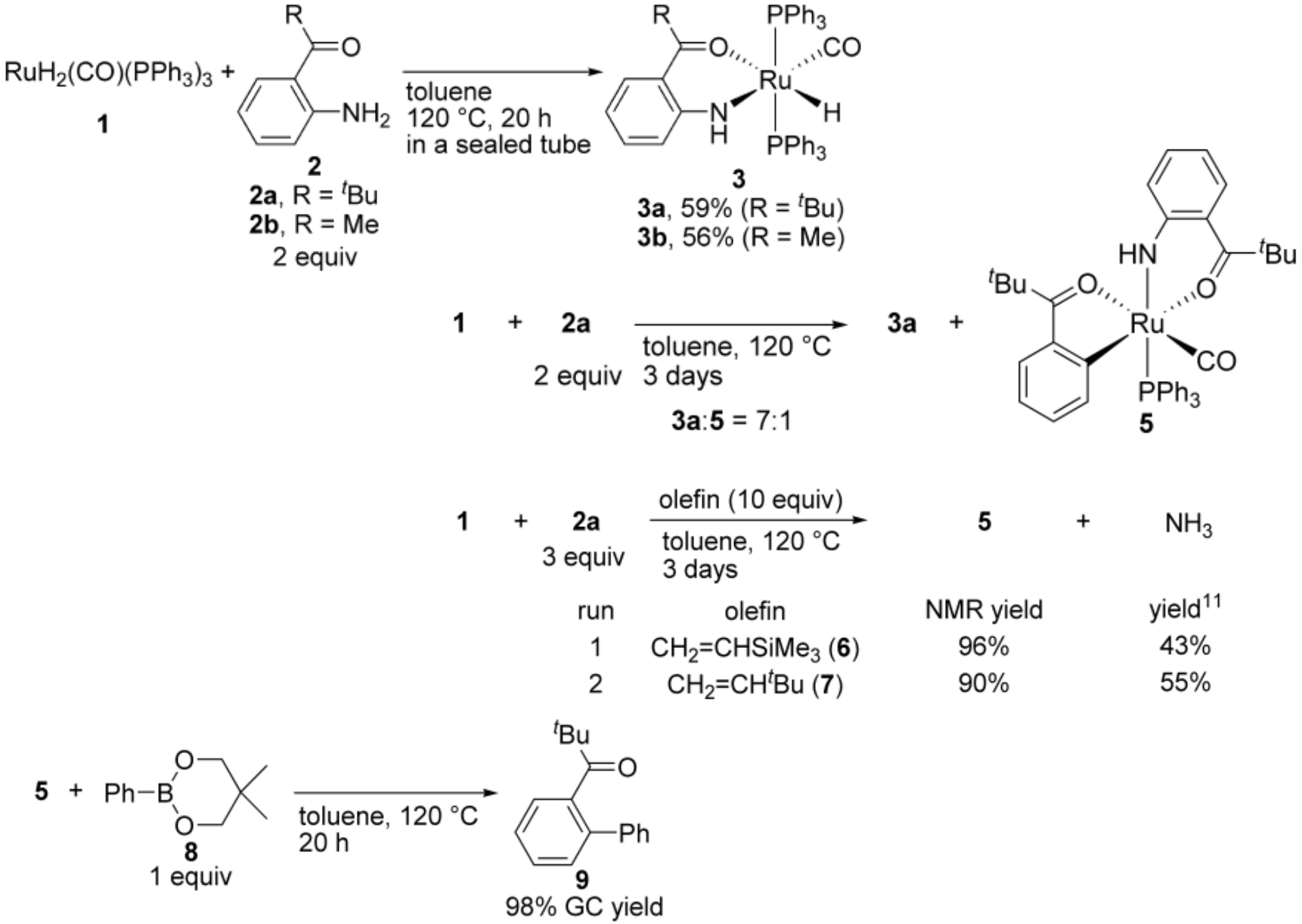
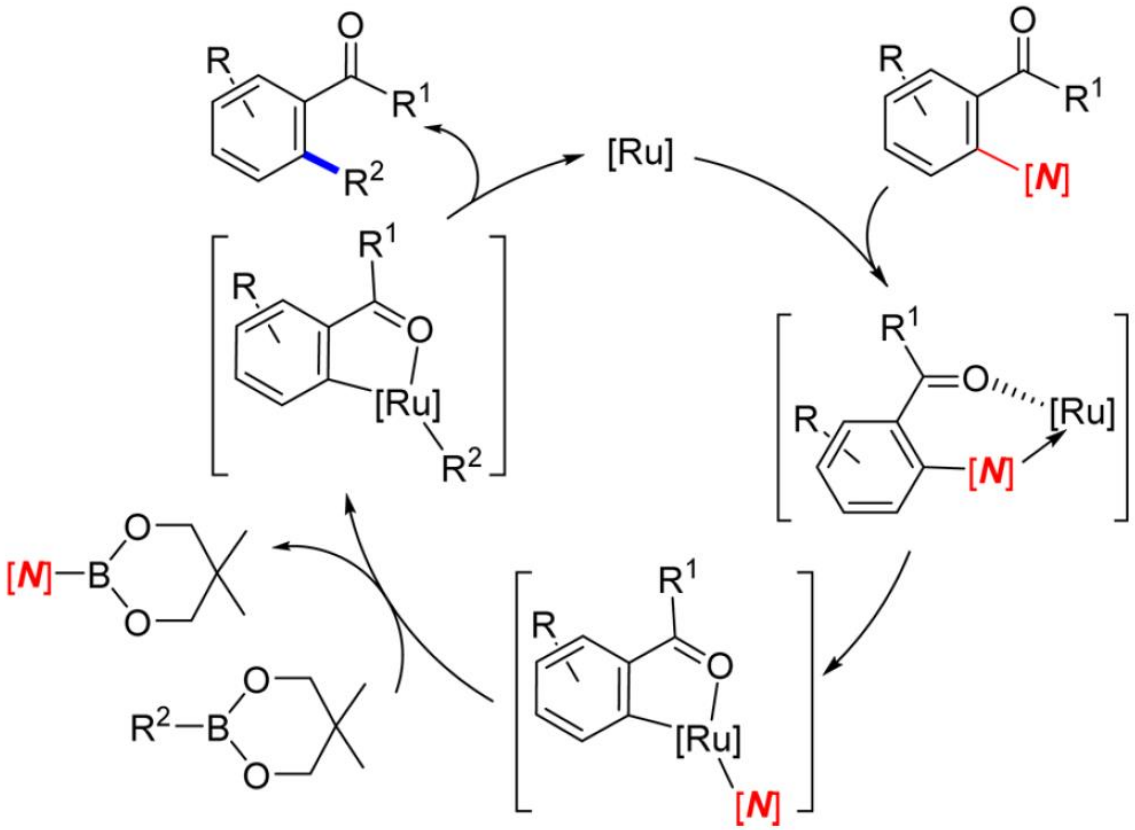


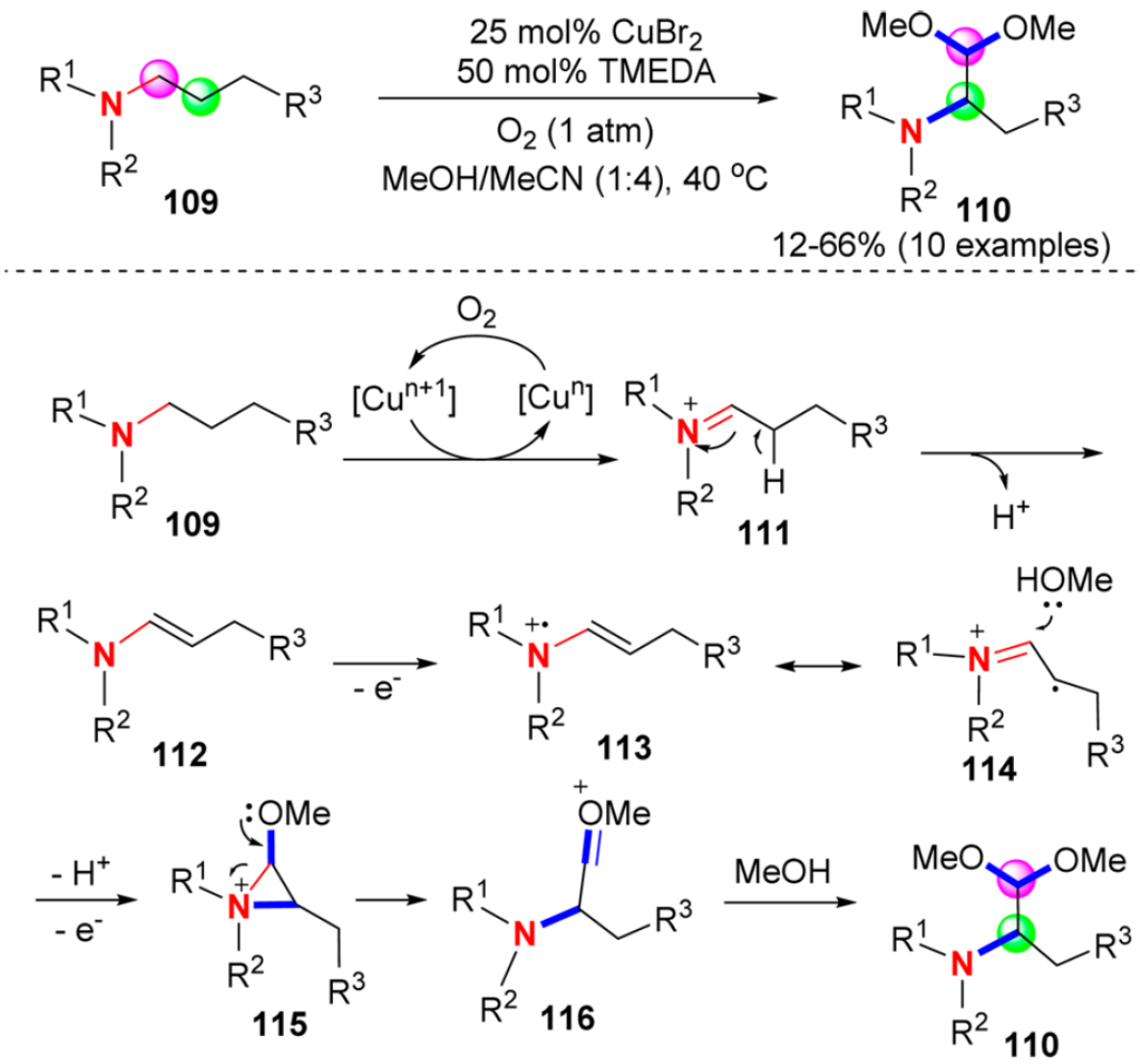
- Koreeda, T.; Kochi, T.; Kakiuchi, F. Cleavage of C–N Bonds in Aniline Derivatives on a Ruthenium. *J. Am. Chem. Soc.* 2009, *131*, 7238–7239.



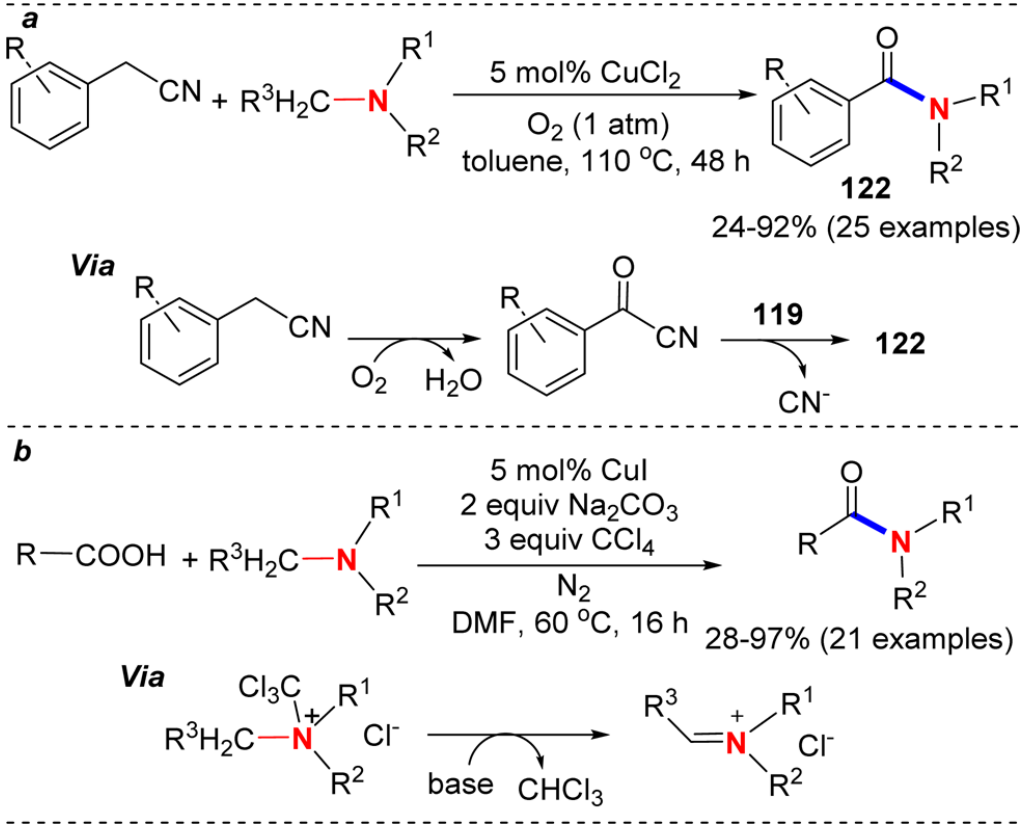
■ Koreeda, T.; Kochi, T.; Kakiuchi, F. Cleavage of C–N Bonds in Aniline Derivatives on a Ruthenium. *J. Am. Chem. Soc.* 2009, *131*, 7238–7239.

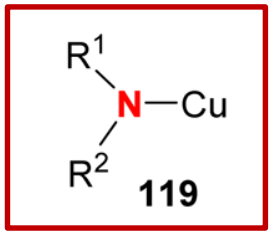
Tertiary Amines

via Imine or Iminium

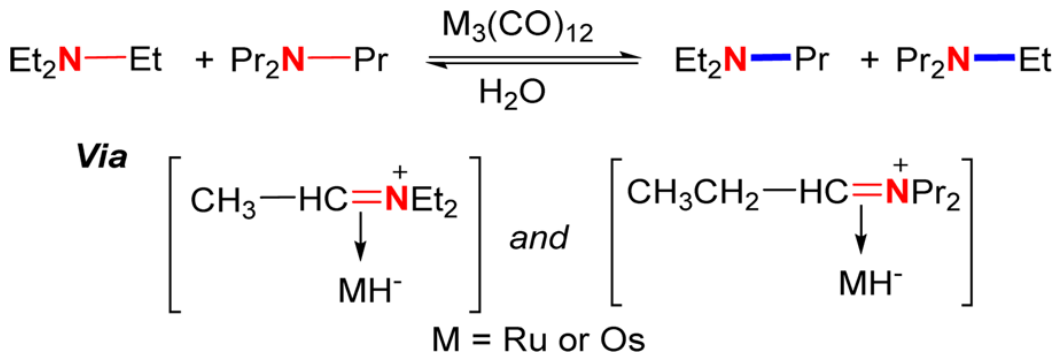


- Tian, J.-S.; Loh, T.-P. Copper-Catalyzed Rearrangement of Tertiary Amines through Oxidation of Aliphatic C–H Bonds in Air or Oxygen: Direct Synthesis of α-Amino Acetals. *Angew. Chem., Int. Ed.* 2010, *49*, 8417–8420.





- For similar reaction catalyzed by **Ag**, see: Zhang, X.; Yang, W.; Wang, L. Silver-Catalyzed Amidation of Benzoylformic Acids with Tertiary Amines via Selective Carbon−Nitrogen Bond Cleavage. *Org. Biomol. Chem*. **2013**, *11*, 3649−3654.
- For silimar reaction catlayzed by **Pd**, see: Bao, Y.-S.; Zhaorigetu, B.; Agula, B.; Baiyin, M.; Jia, M. Aminolysis of Aryl Ester Using Tertiary Amine as Amino Donor via C−O and C−N Bond Activations. *J. Org. Chem*. **2014**, *79*, 803−808.



- Chen, X.; Chen, T.; Li, Q.; Zhou, Y.; Han, L.-B.; Yin, S.-F. Copper-Catalyzed Aerobic Oxidative Inert C−C and C−N Bond Cleavage: A New Strategy for the Synthesis of Tertiary Amides. *Chem.- Eur. J.* 2014, *20*, 12234−12238.
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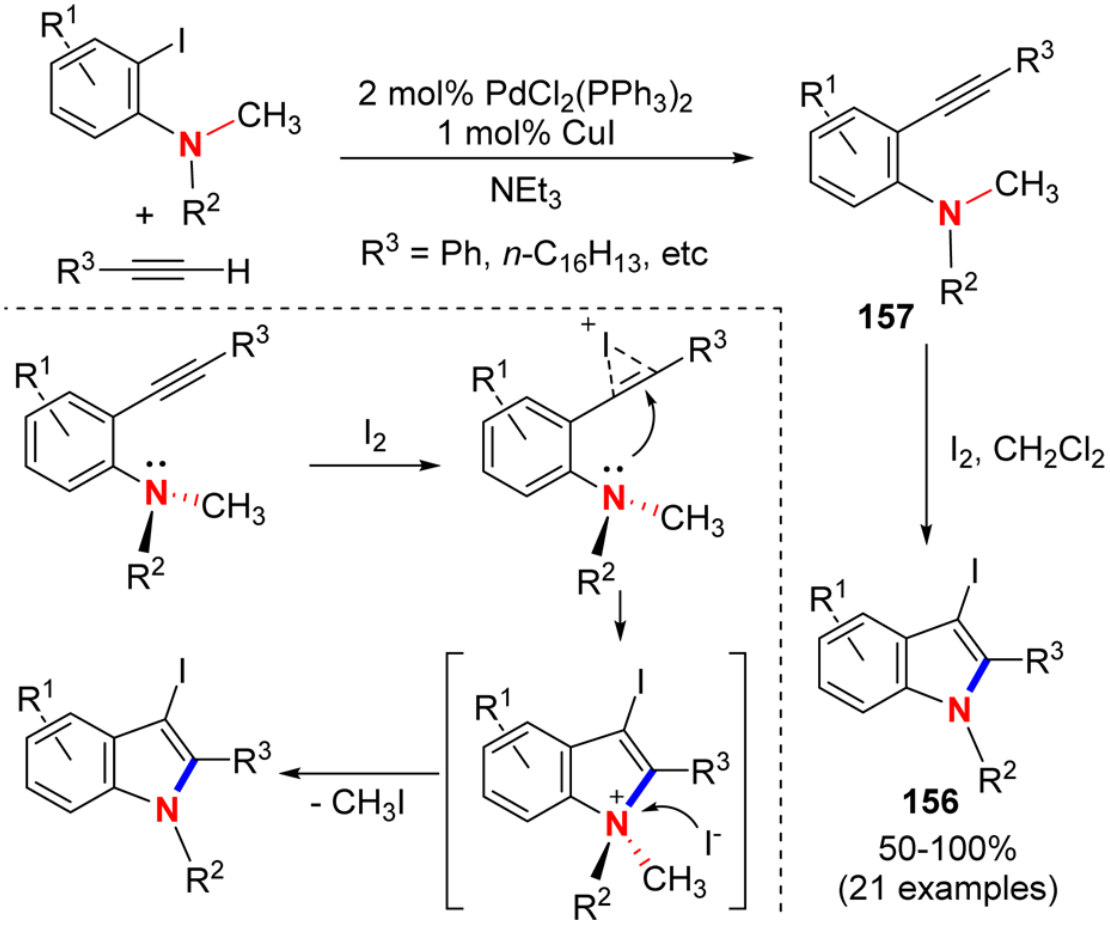

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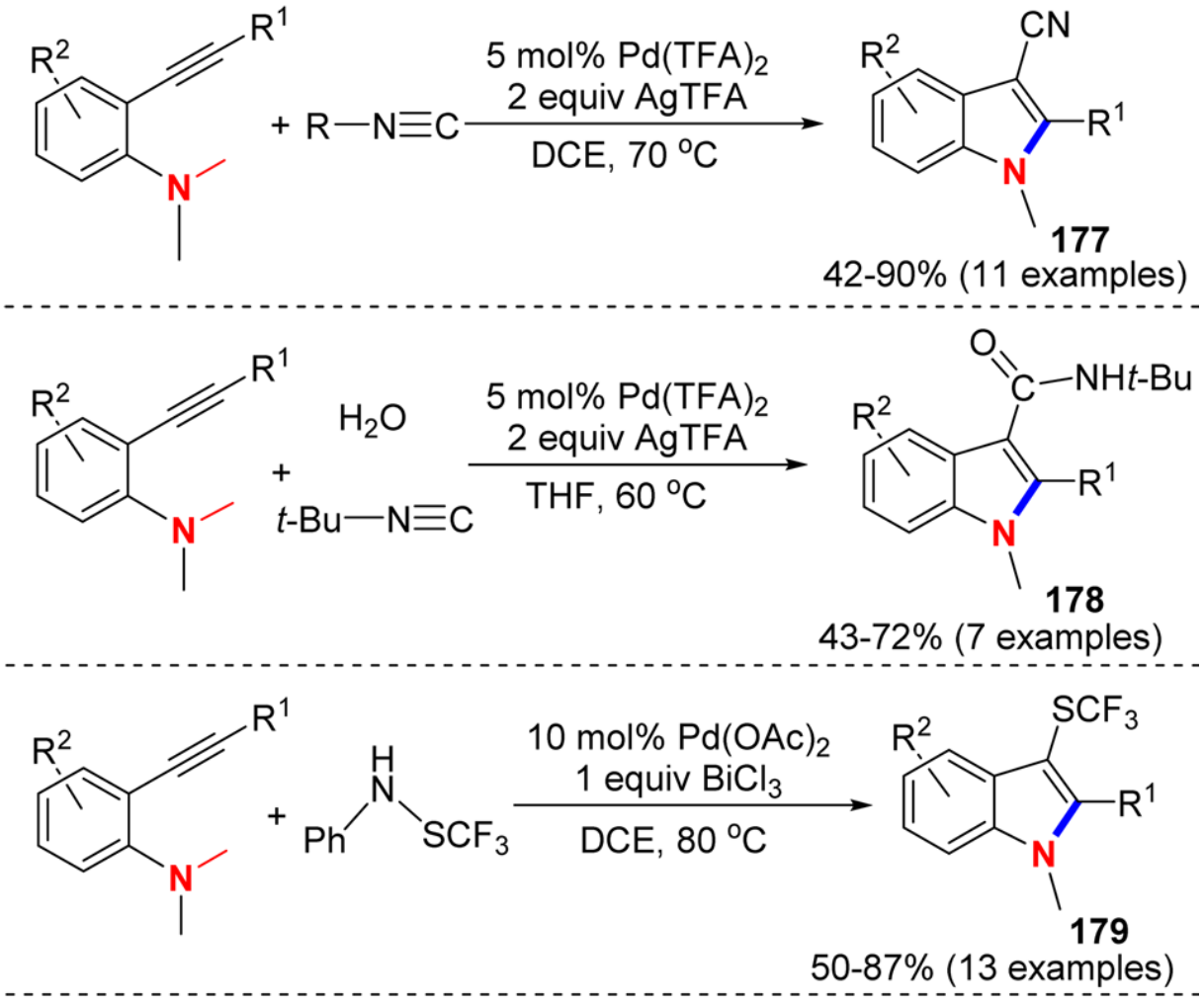

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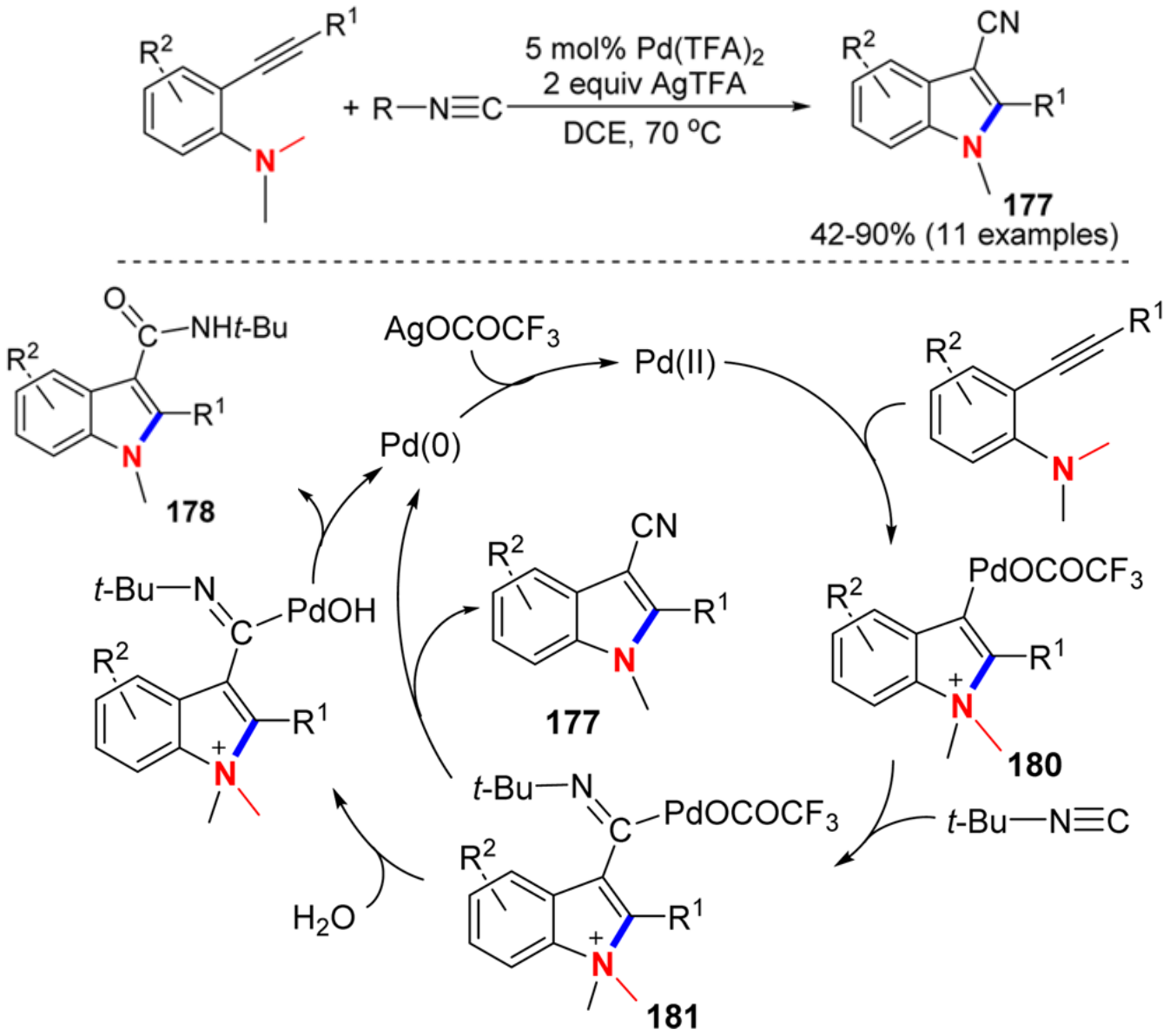
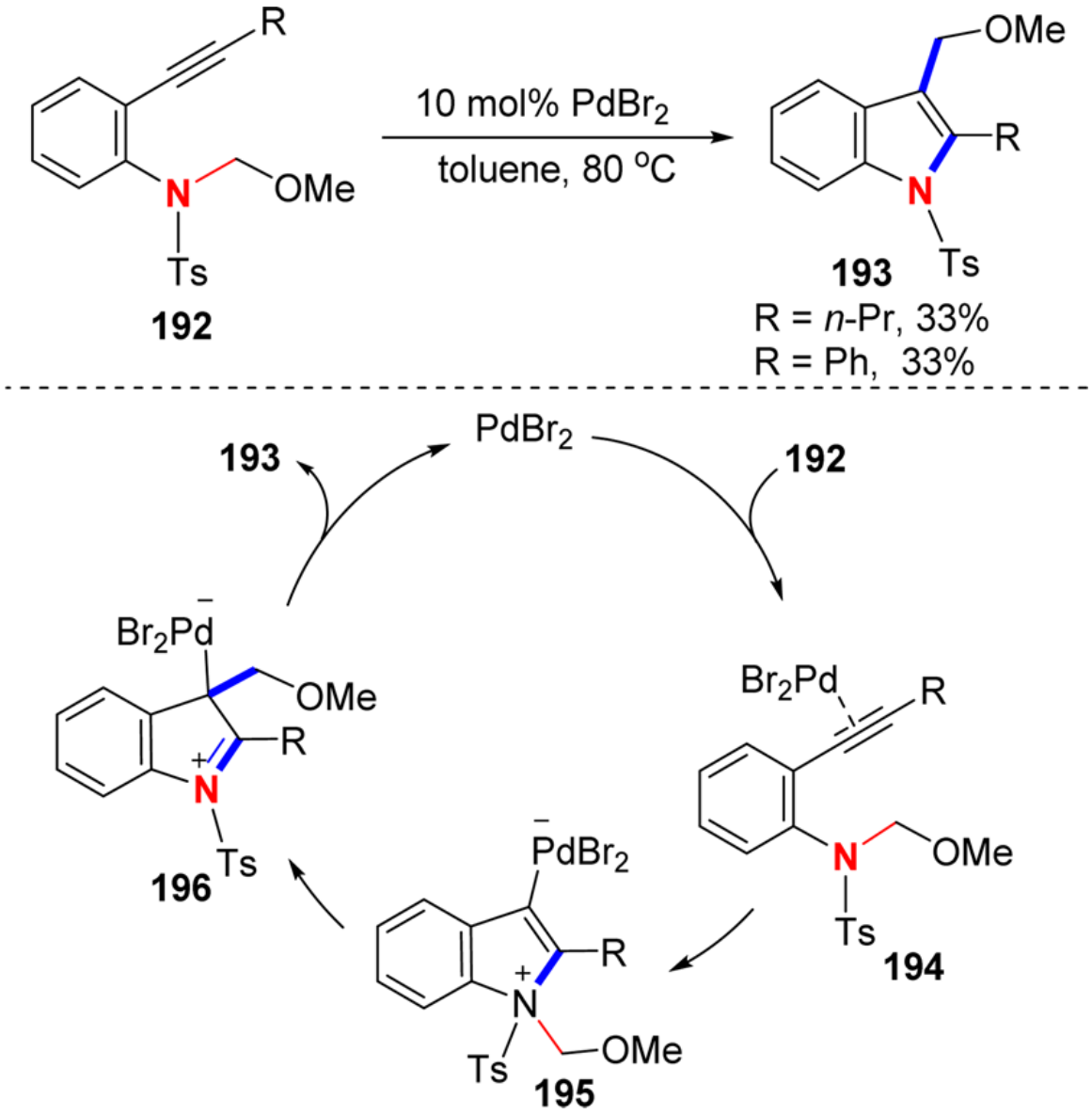


- Qiu, G.; Qiu, X.; Liu, J.; Wu, J. Switchable Synthesis of 3-Cyanoindoles and 3-Amidylindoles via a Palladium-Catalyzed Reaction of *N,N*-Dimethyl-2-alkynylaniline with Isocyanide. *Adv. Synth. Catal*. 2013, *355*, 2441–2446.
- Qiu, G.; Chen, C.; Yao, L.; Wu, J. An Efficient Route to 3-Amidylindoles via a Palladium-Catalyzed Tandem Reaction of 2- Alkynylanilines with Isocyanides. *Adv. Synth. Catal.* 2013, *355*, 1579–1584.

Tertiary Amines

via Alkyl Migration



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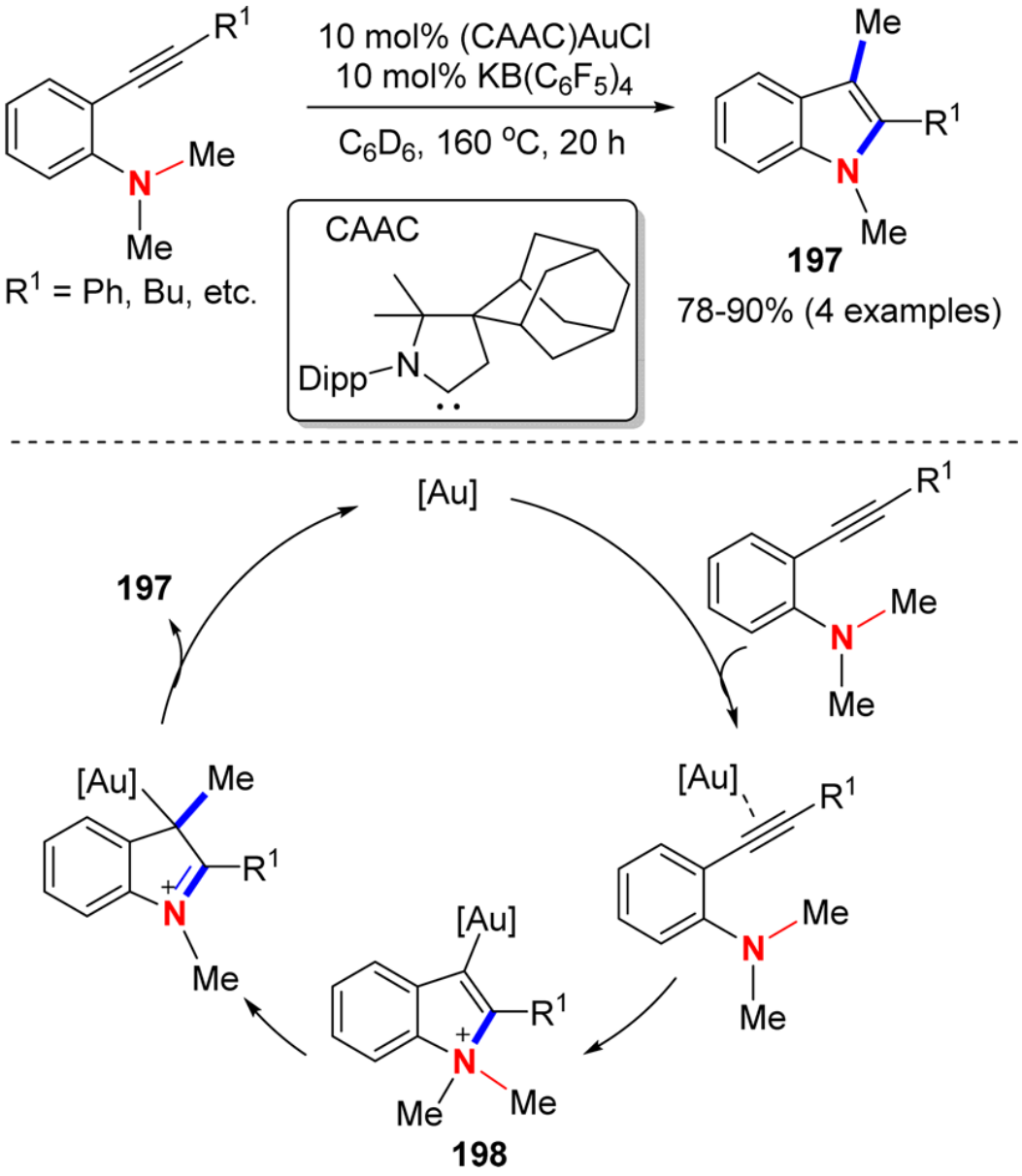

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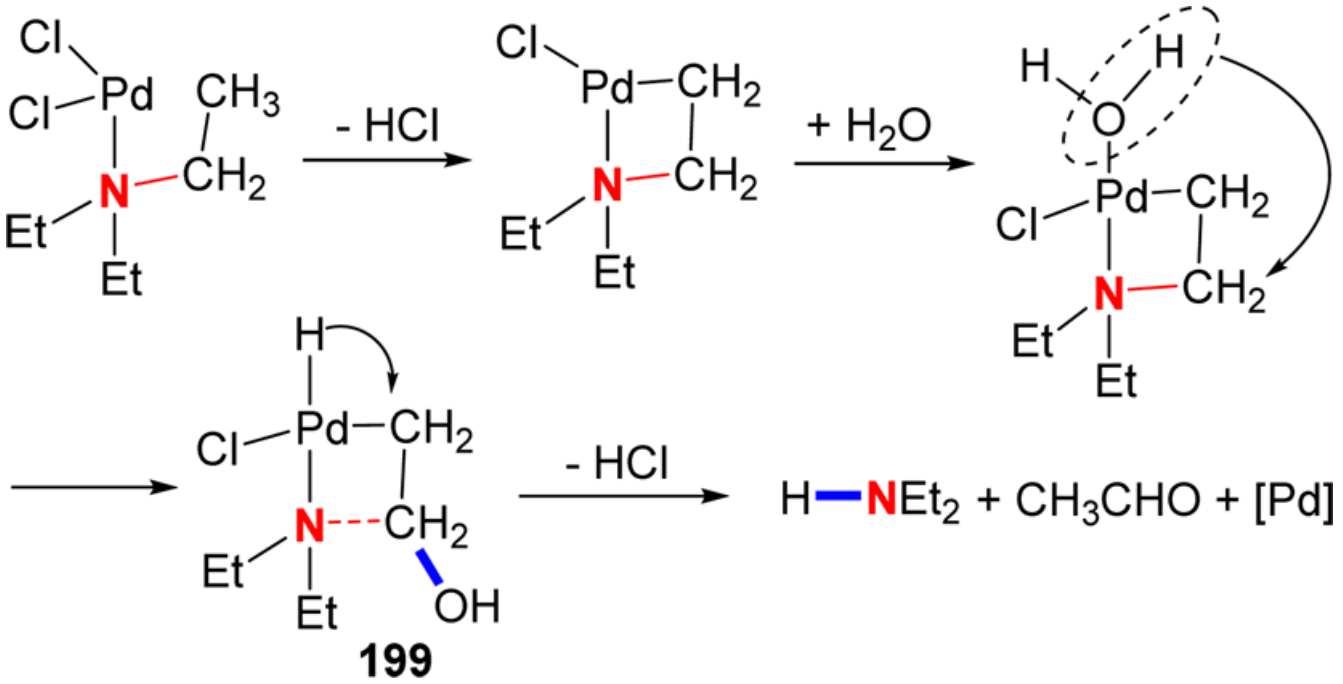
via β-Amino Elimination



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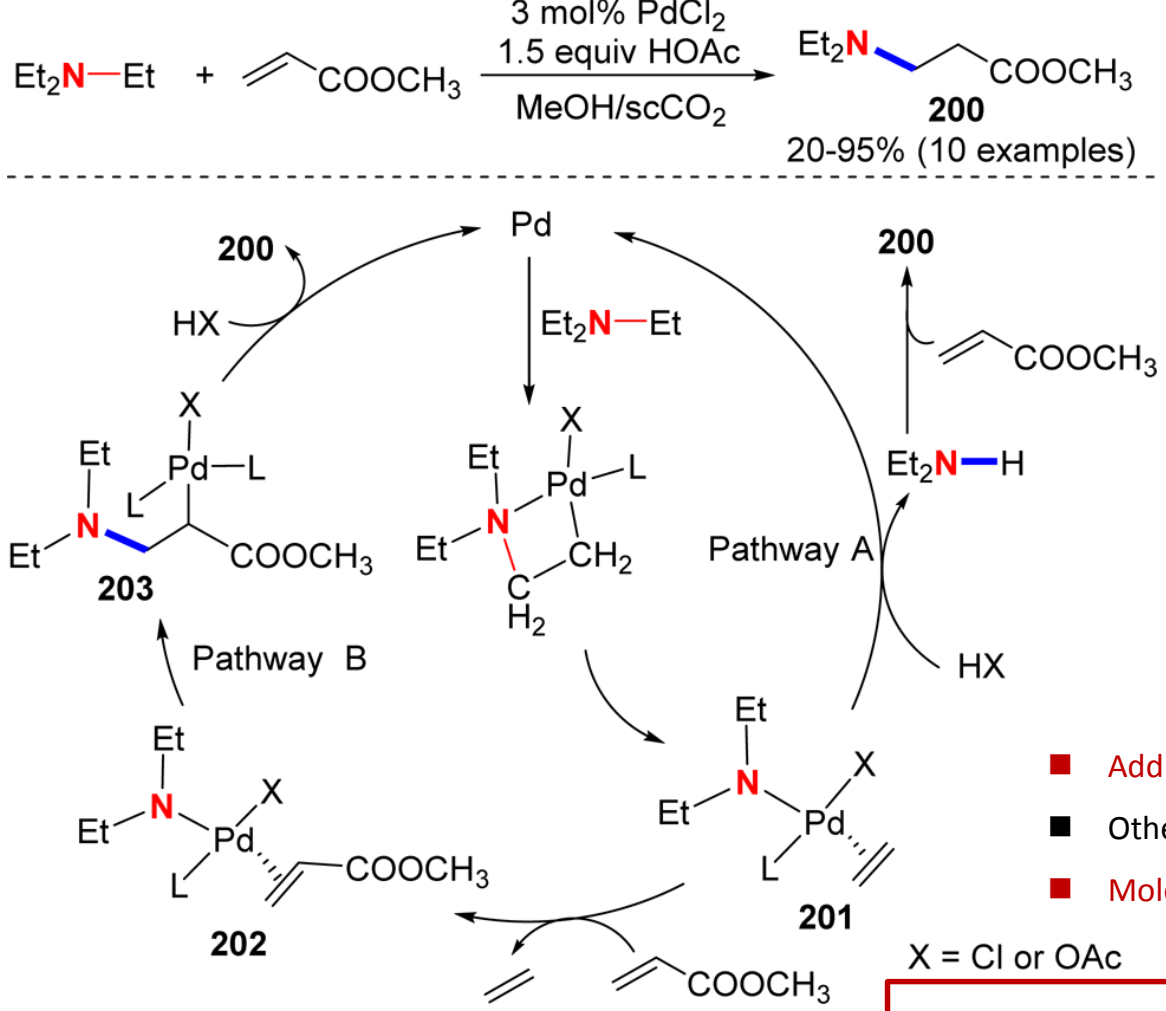
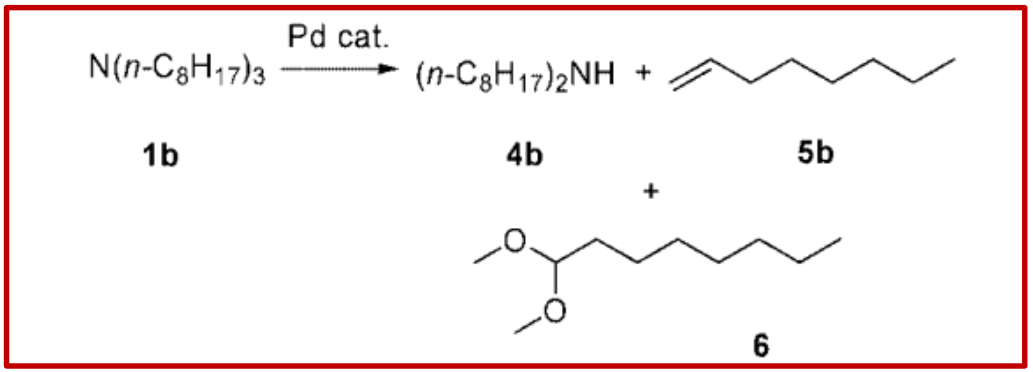


- Addition of HOAc: necessary for this transformation
- Otherwise, stoichiometric $PdCl_2$ must be used.
- Molecular O_2 was found to be negative for this process

X = Cl or OAc



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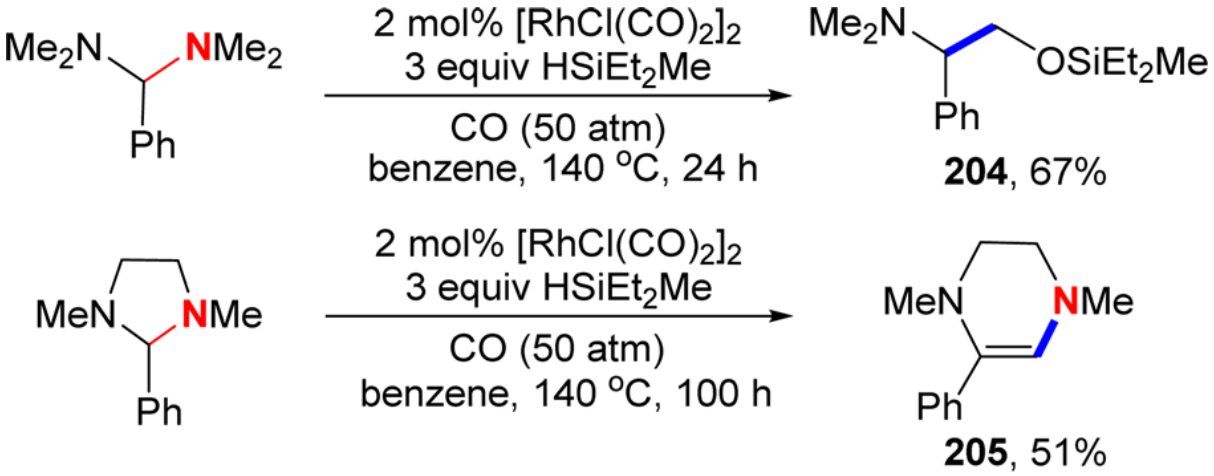
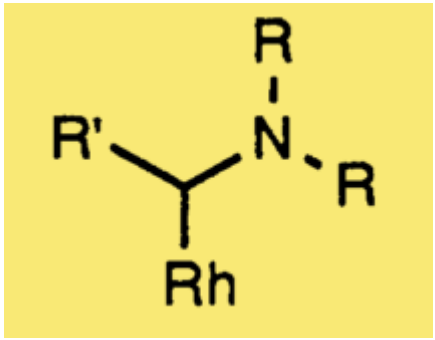
Diamines

via Oxidative Addition





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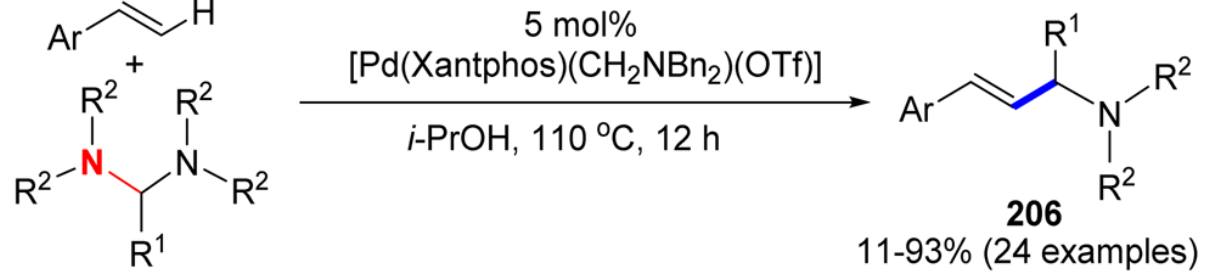

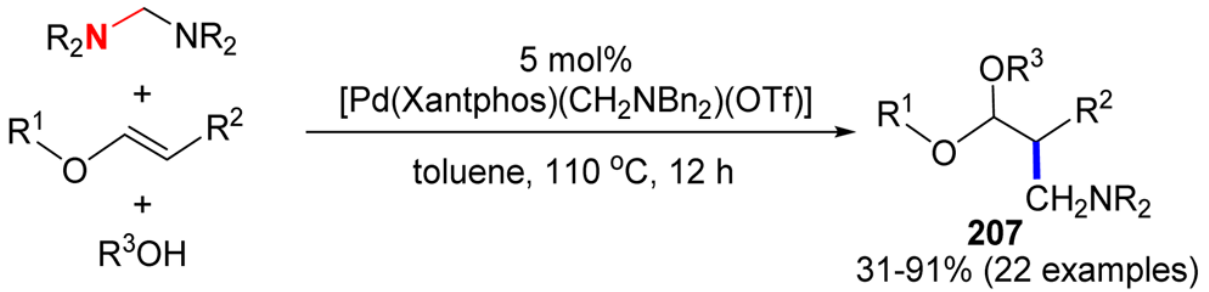

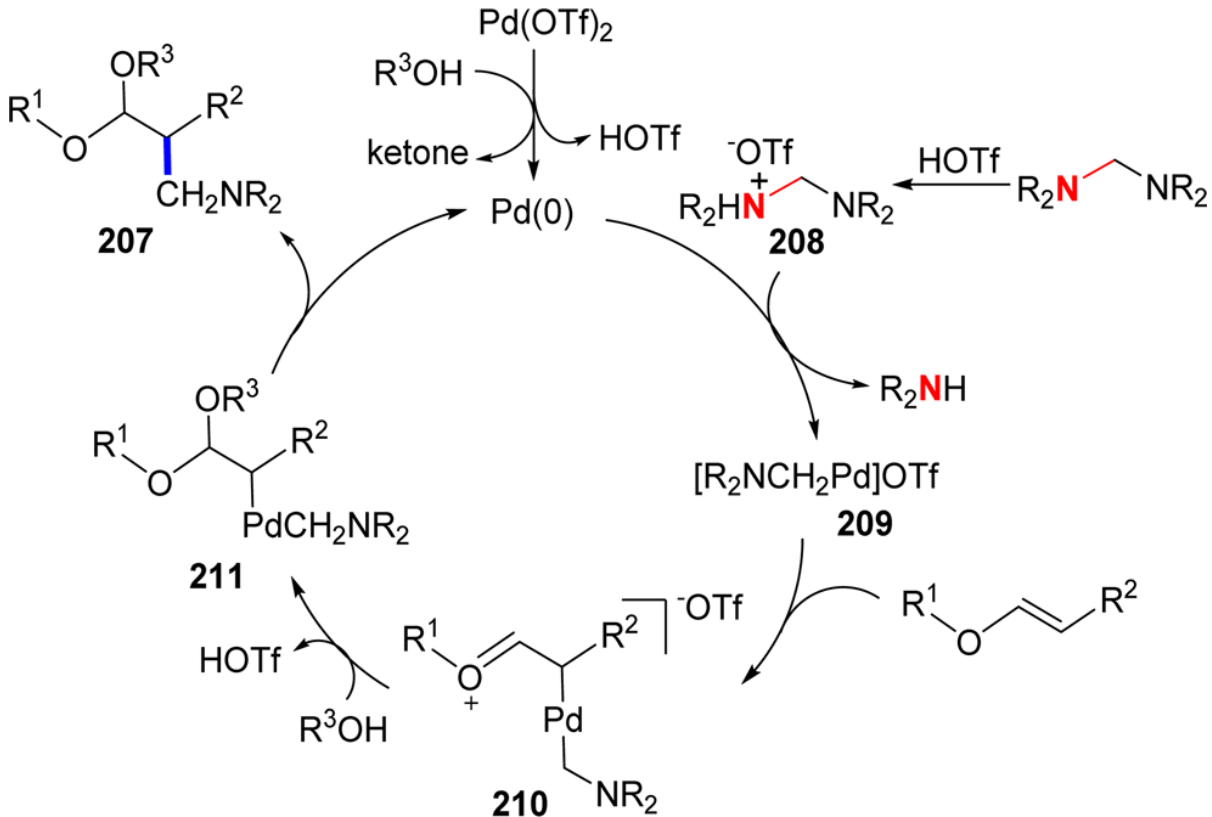

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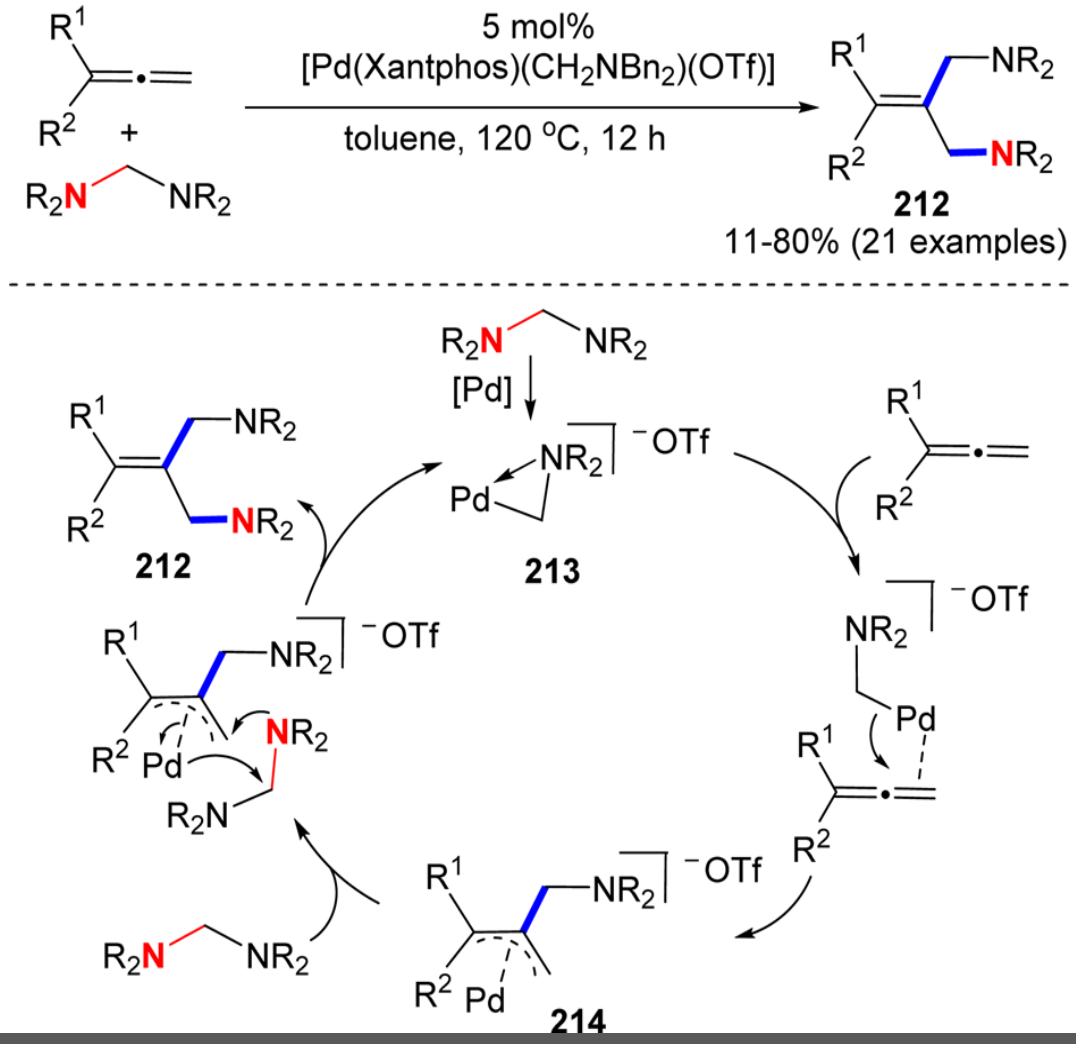
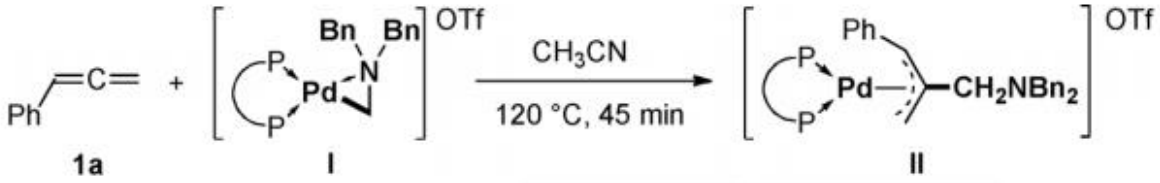
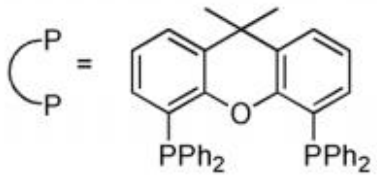


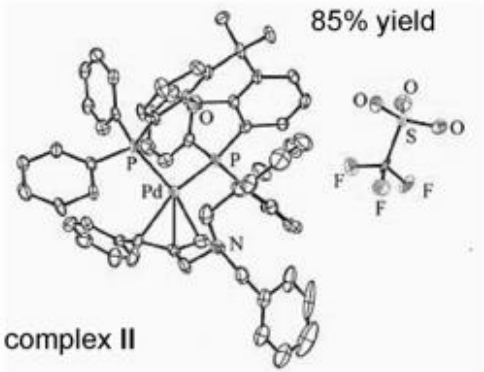
■ Hu, J.; Xie, Y.; Huang, H. Palladium-Catalyzed Insertion of an Allene into an Aminal: Aminomethylamination of Allenes by C–N Bond Activation. *Angew. Chem., Int. Ed.* 2014, *53*, 7272–7276.



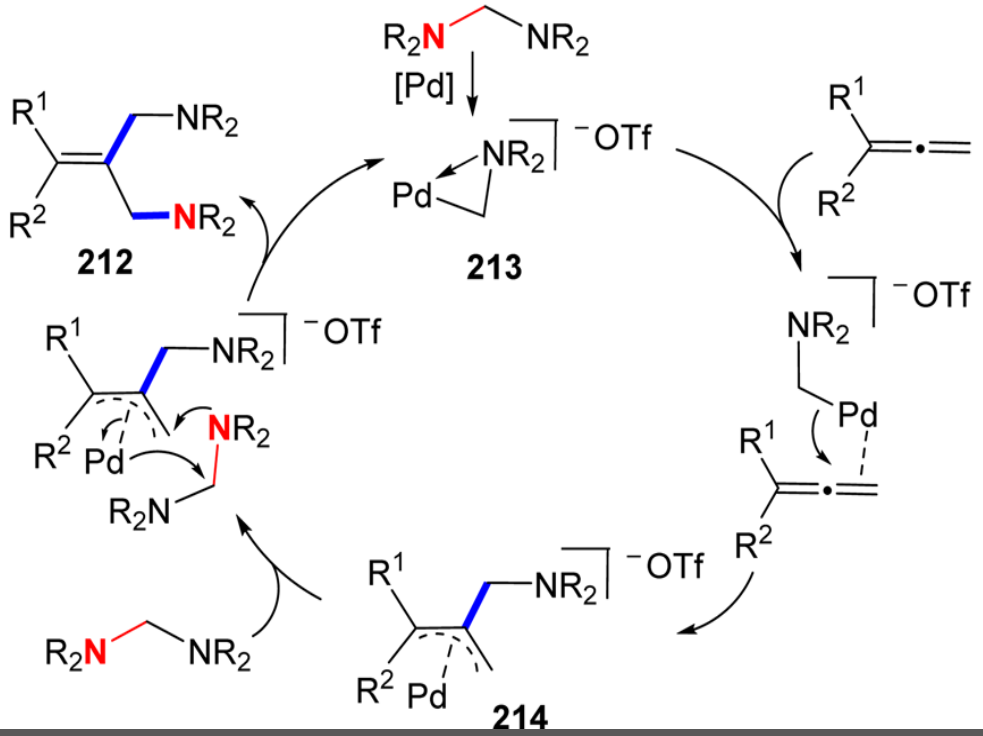


Xantphos

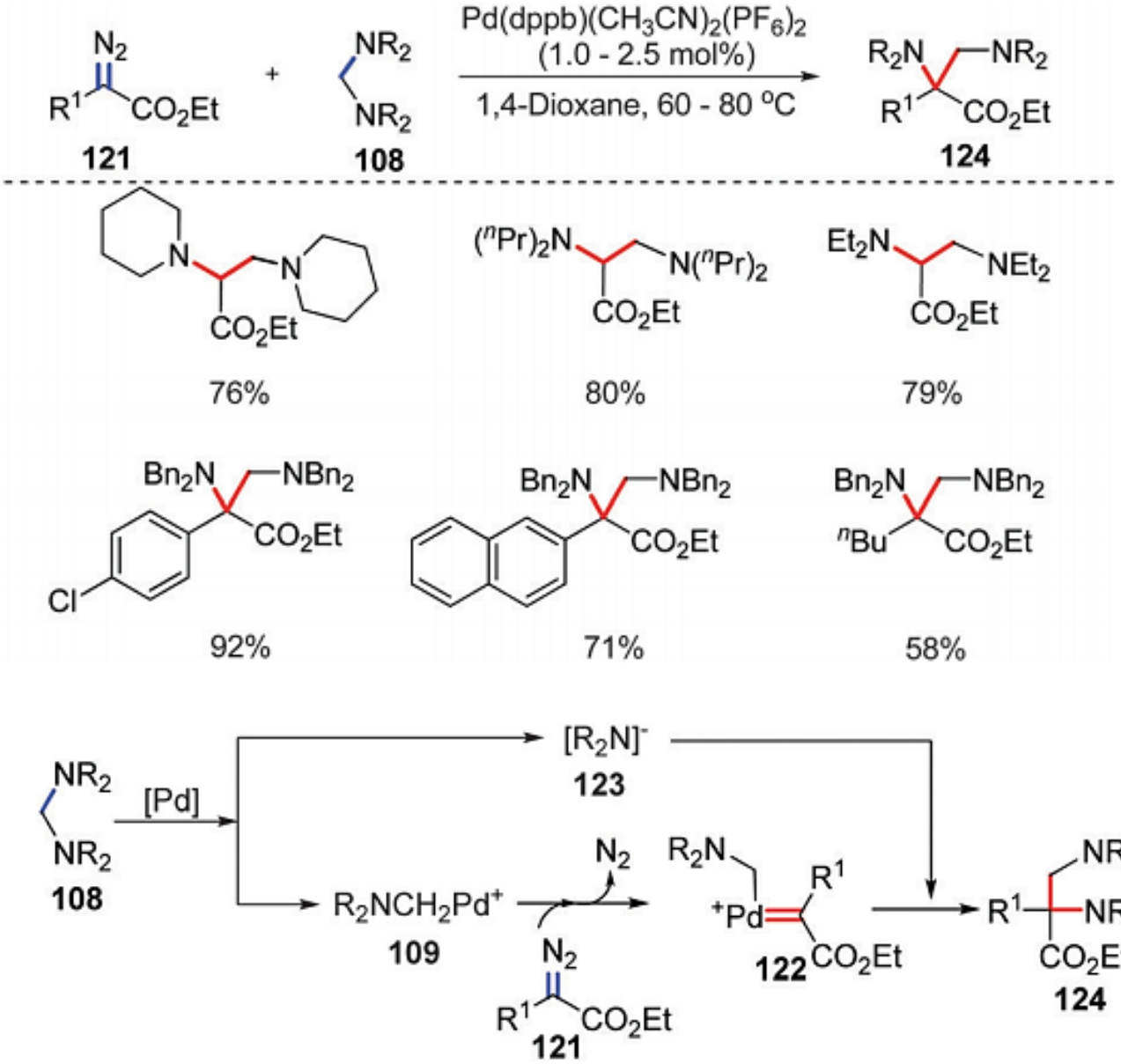
85% yield



X-ray structure of complex **II**



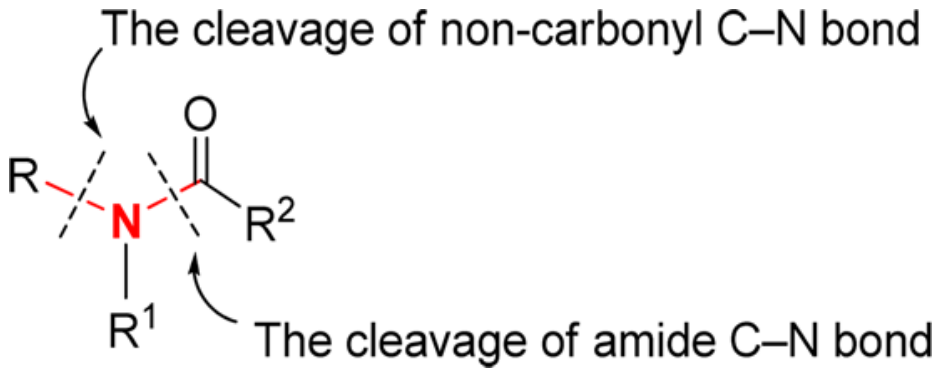
■ Hu, J.; Xie, Y.; Huang, H. Palladium-Catalyzed Insertion of an Allene into an Aminal: Aminomethylamination of Allenes by C–N Bond Activation. *Angew. Chem., Int. Ed.* 2014, *53*, 7272–7276.



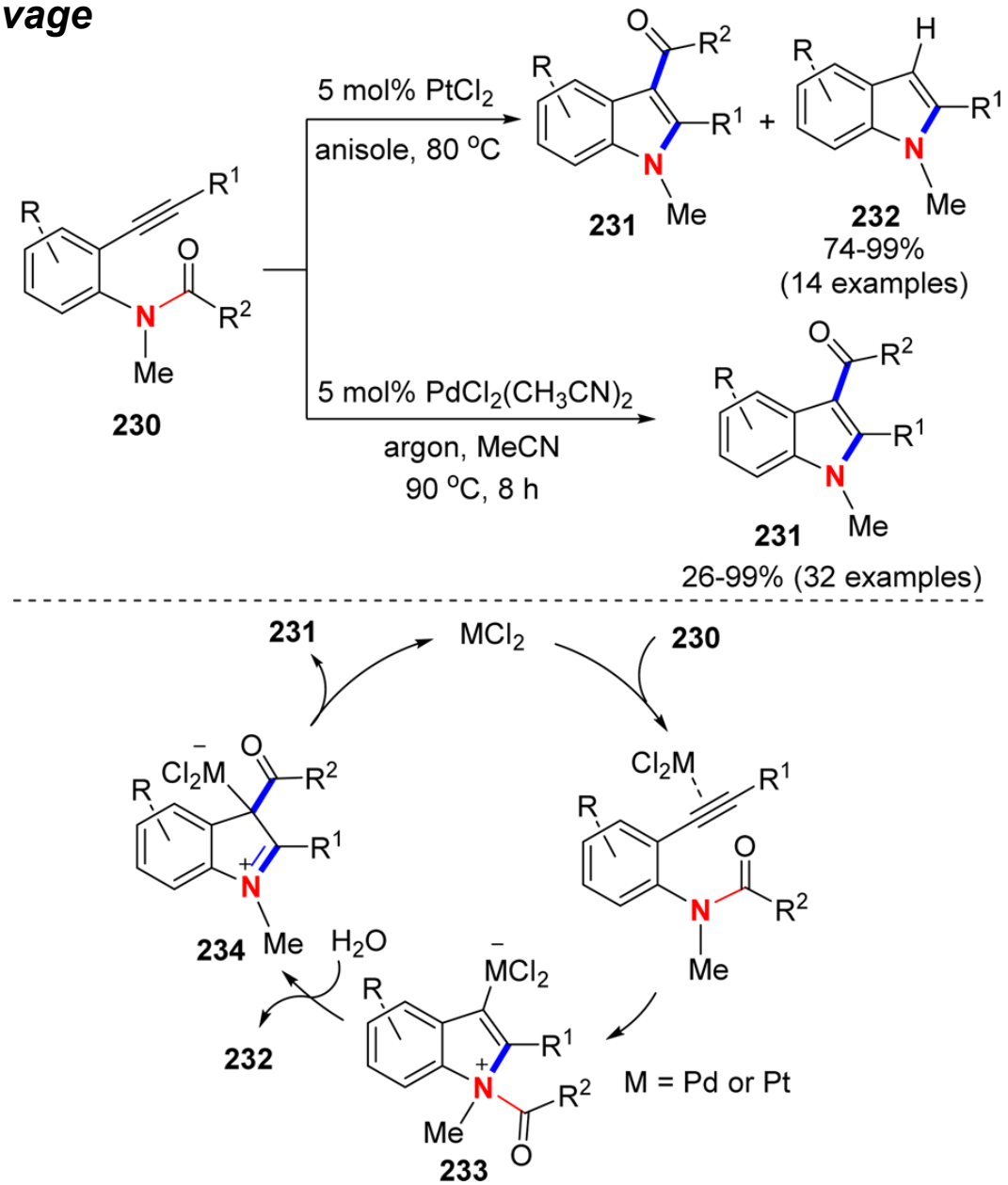
- Hu, J.; Xie, Y.; Huang, H. Palladium-Catalyzed Insertion of an Allene into an Aminal: Aminomethylamination of Allenes by C–N Bond Activation. *Angew. Chem., Int. Ed.* 2014, *53*, 7272–7276.

Amides

- *Two Types of C–N Bonds in Amides*



Amide C–N Bond Cleavage



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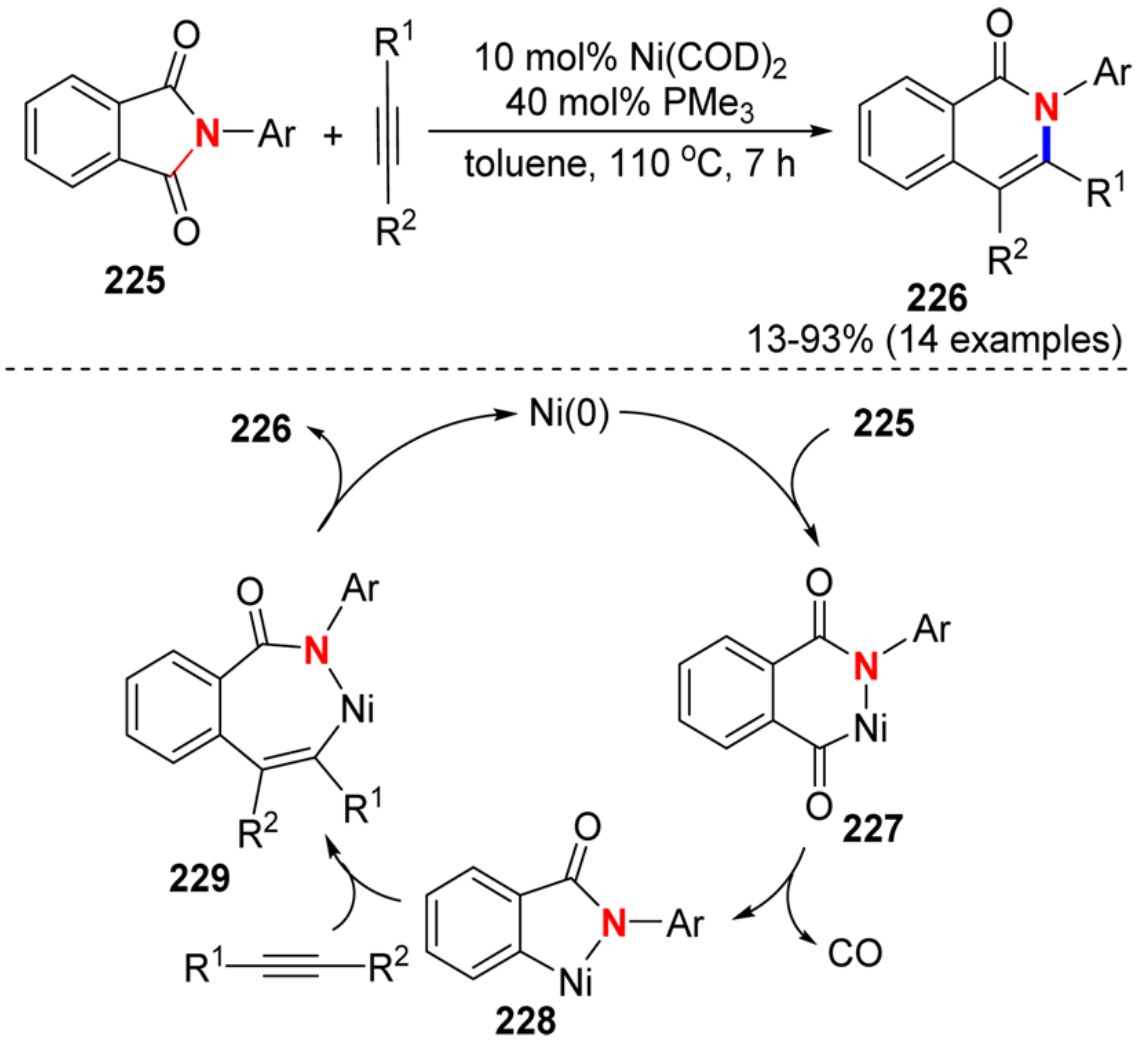
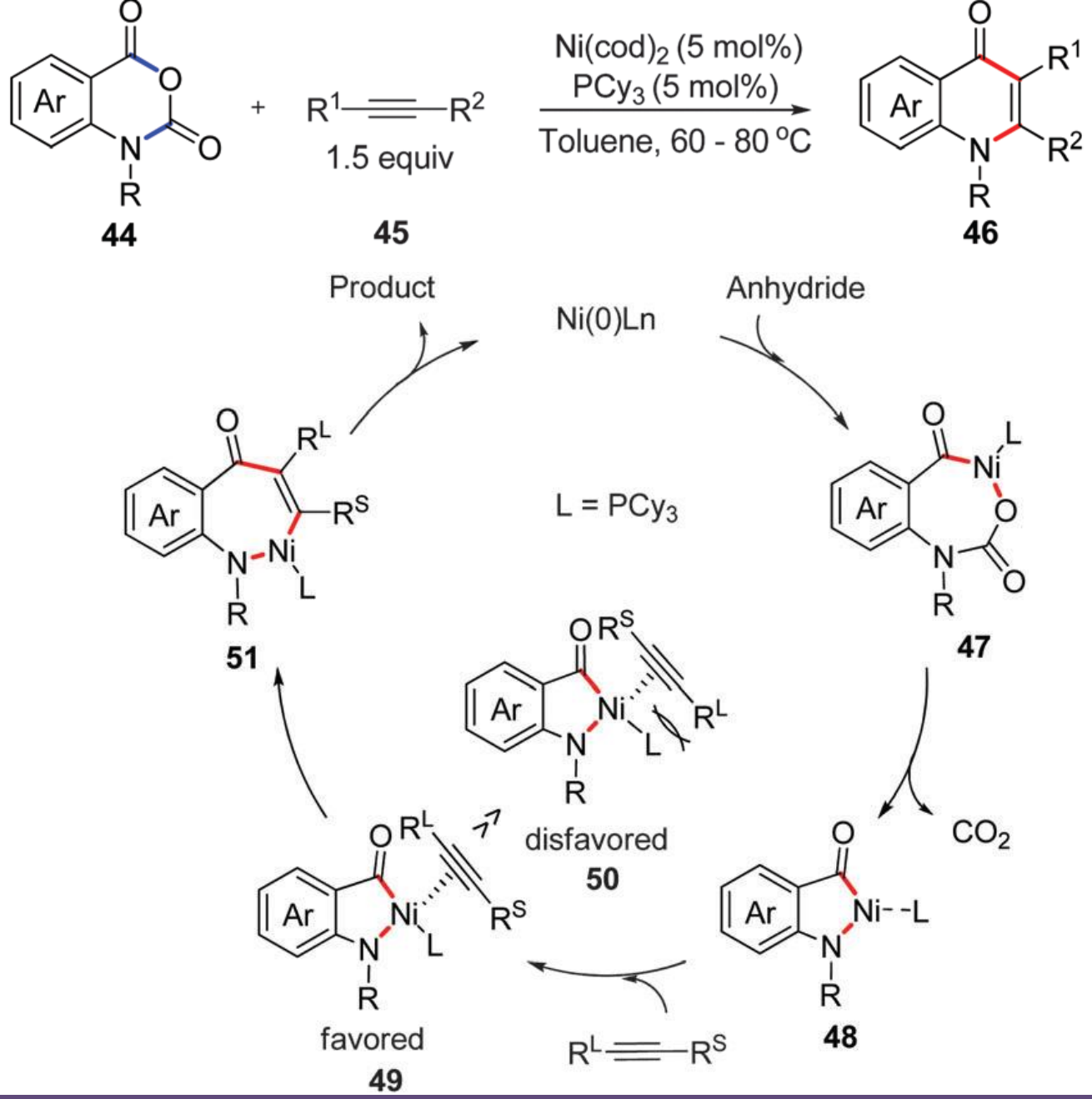
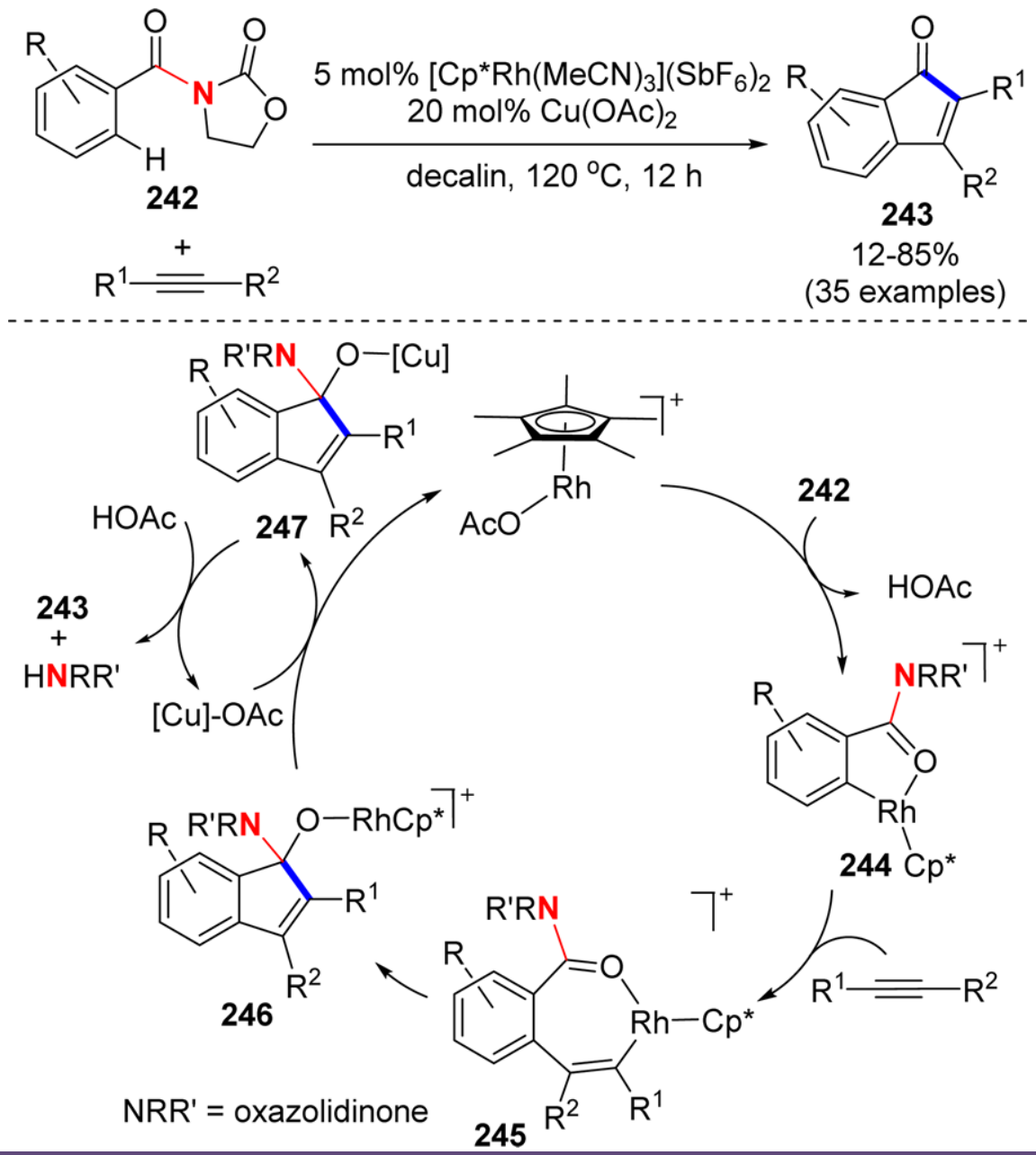


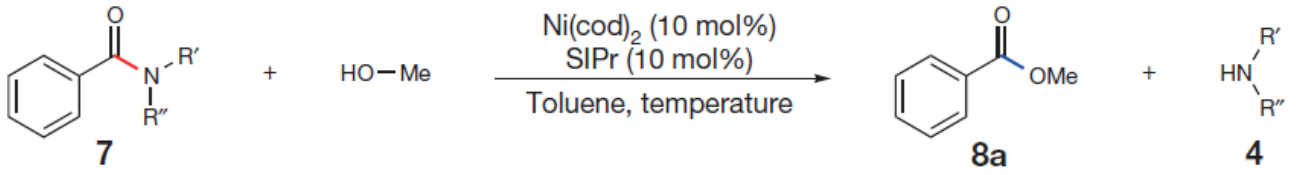
■ Kajita, Y.; Matsubara, S.; Kurahashi, T. Nickel-Catalyzed Decarbonylative Addition of Phthalimides to Alkynes. *J. Am. Chem. Soc*. 2008, *130*, 6058−6059.

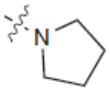
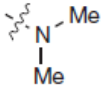
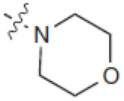
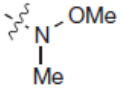
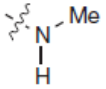
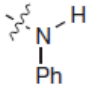
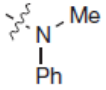


■ Y. Yoshino, T. Kurahashi and S. Matsubara, *J. Am. Chem. Soc.*, 2009, *131*, 7494



■ Li, B.-J.; Wang, H.-Y.; Zhu, Q.-L.; Shi, Z.-J. Rhodium/Copper-Catalyzed Annulation of Benzimides with Internal Alkynes: Indenone Synthesis through Sequential C–H and C–N Cleavage. *Angew. Chem., Int. Ed*. 2012, *51*, 3948–3952



Entry		Calculated ΔG (kcal mol^{-1})	Calculated oxidative addition barrier with Ni/SIPr (kcal mol^{-1})	Temperature (°C)	Equivalents of MeOH	Yield of ester
1	 **7a**	+2.4	36.8	110	2.0	0%
2	 **7b**	0.0	36.2	110	2.0	0%
3	 **7c**	–1.1	34.0	110	2.0	23%
4	 **7d**	–6.1	31.9	110	2.0	22%
5	 **7e**	+3.1	39.0	110	2.0	0%
6	 **7f**	–4.3	30.6	110	2.0	55%
7	 **7g**	–6.8	26.0	110	2.0	>99%
8				80	1.2	>99%

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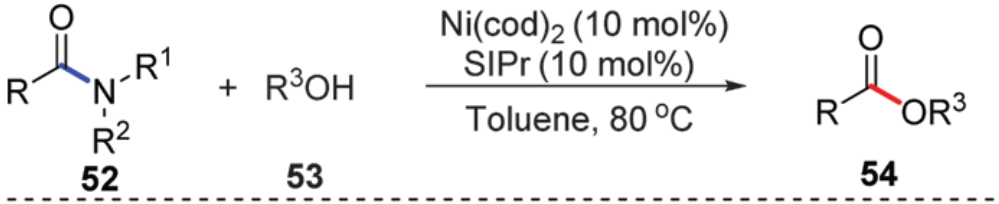

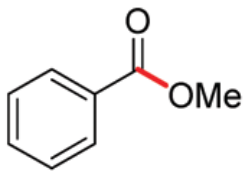
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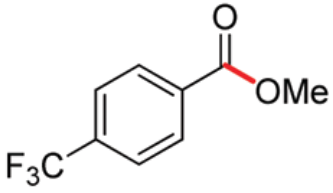
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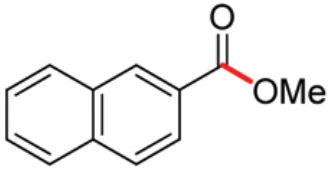
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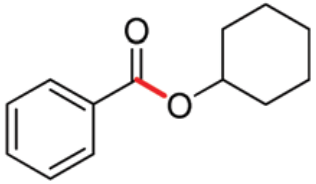
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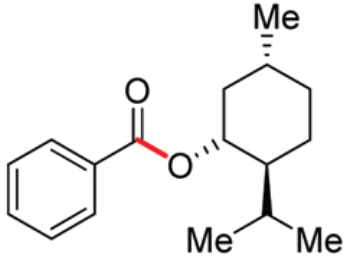
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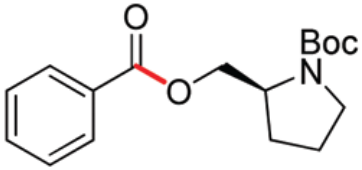
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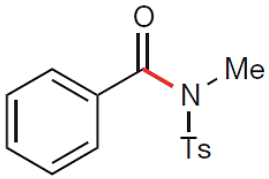
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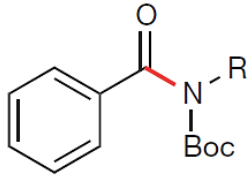
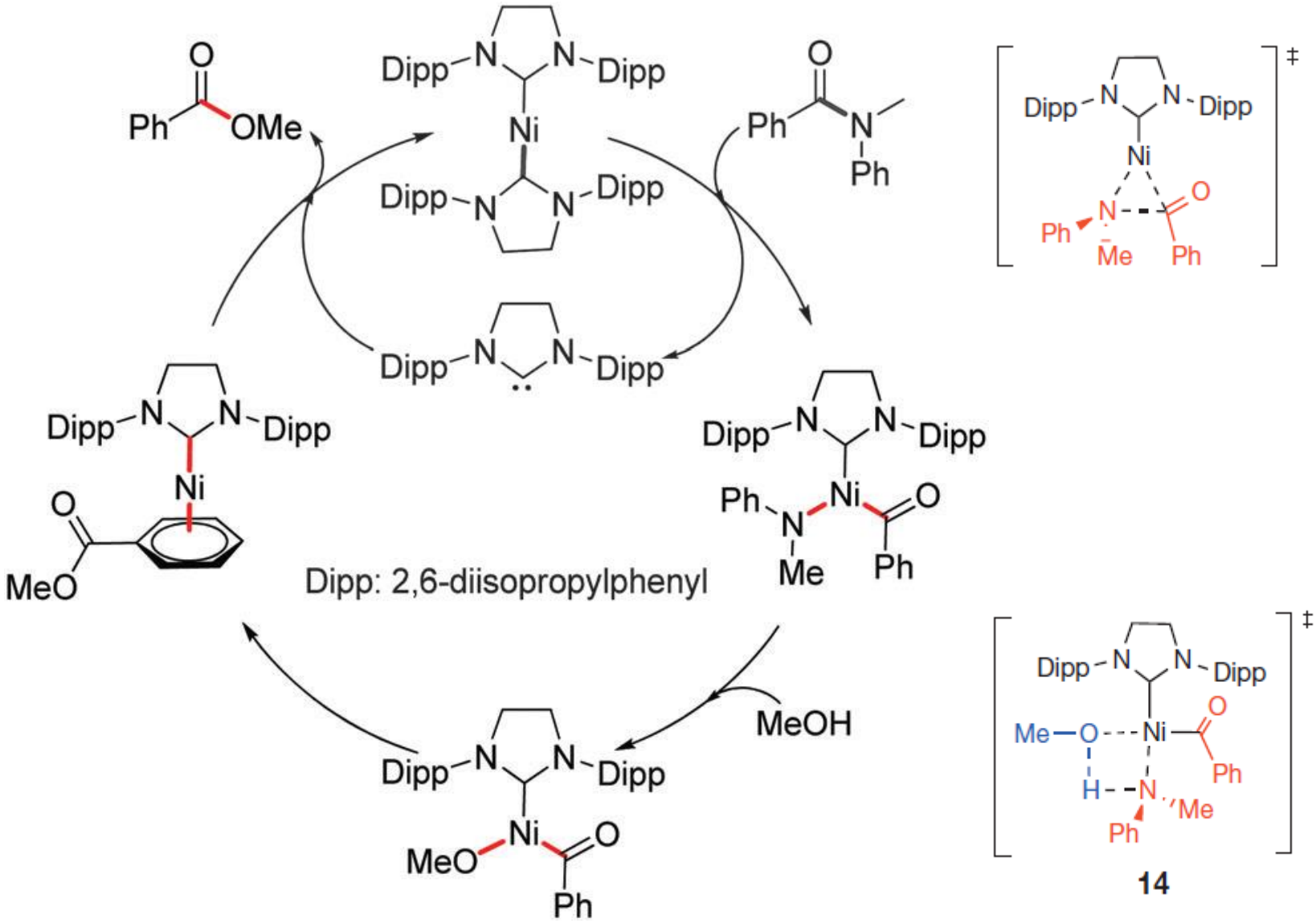
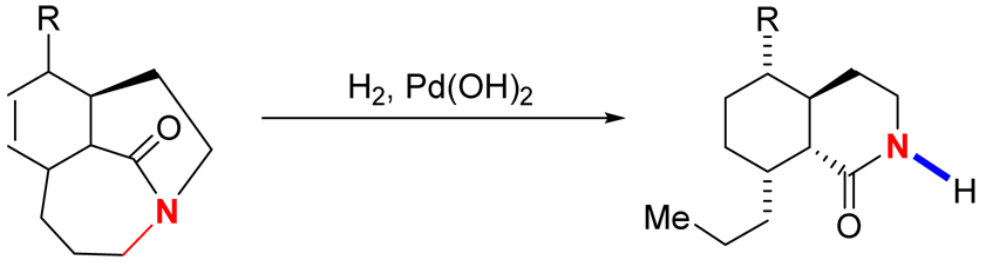

84% (R = Me)
89% (R = Bn)

L. Hie, N. F. F. Nathel, T. K. Shah, E. L. Baker, X. Hong, Y.-F. Yang, P. Liu, K. N. Houk and N. K. Garg, *Nature*, 2015, *524*, 79.

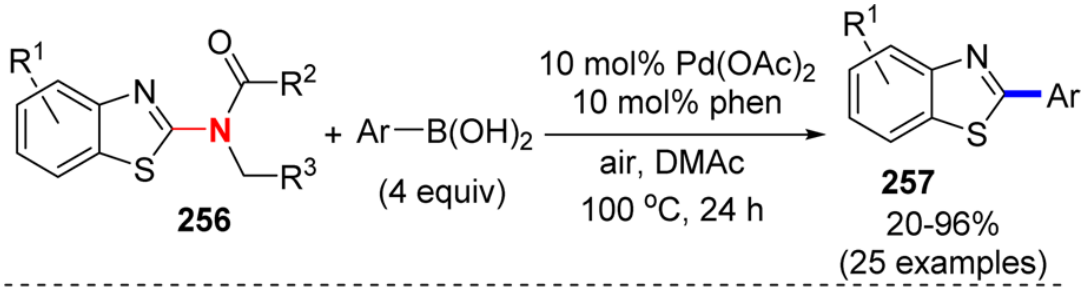


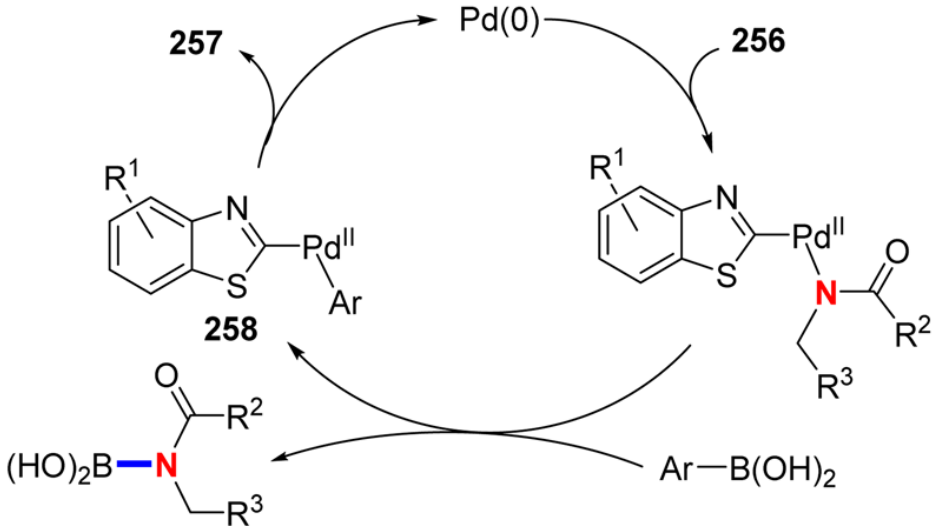
L. Hie, N. F. F. Nathel, T. K. Shah, E. L. Baker, X. Hong, Y.-F. Yang, P. Liu, K. N. Houk and N. K. Garg, *Nature*, 2015, *524*, 79.

Non-Carbonyl C–N Bond Cleavage *via Oxidative Addition*



80-92% (3 examples)





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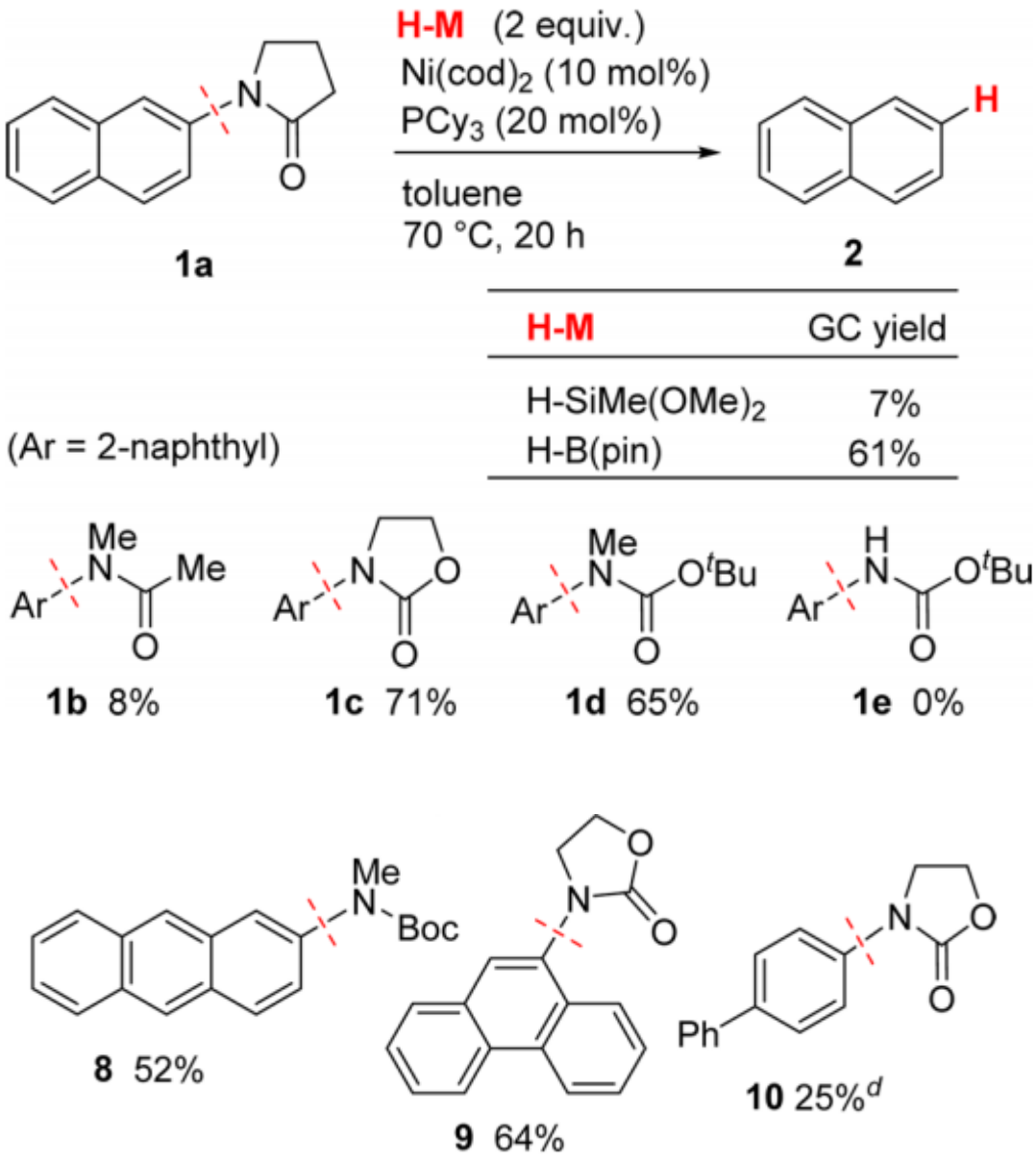
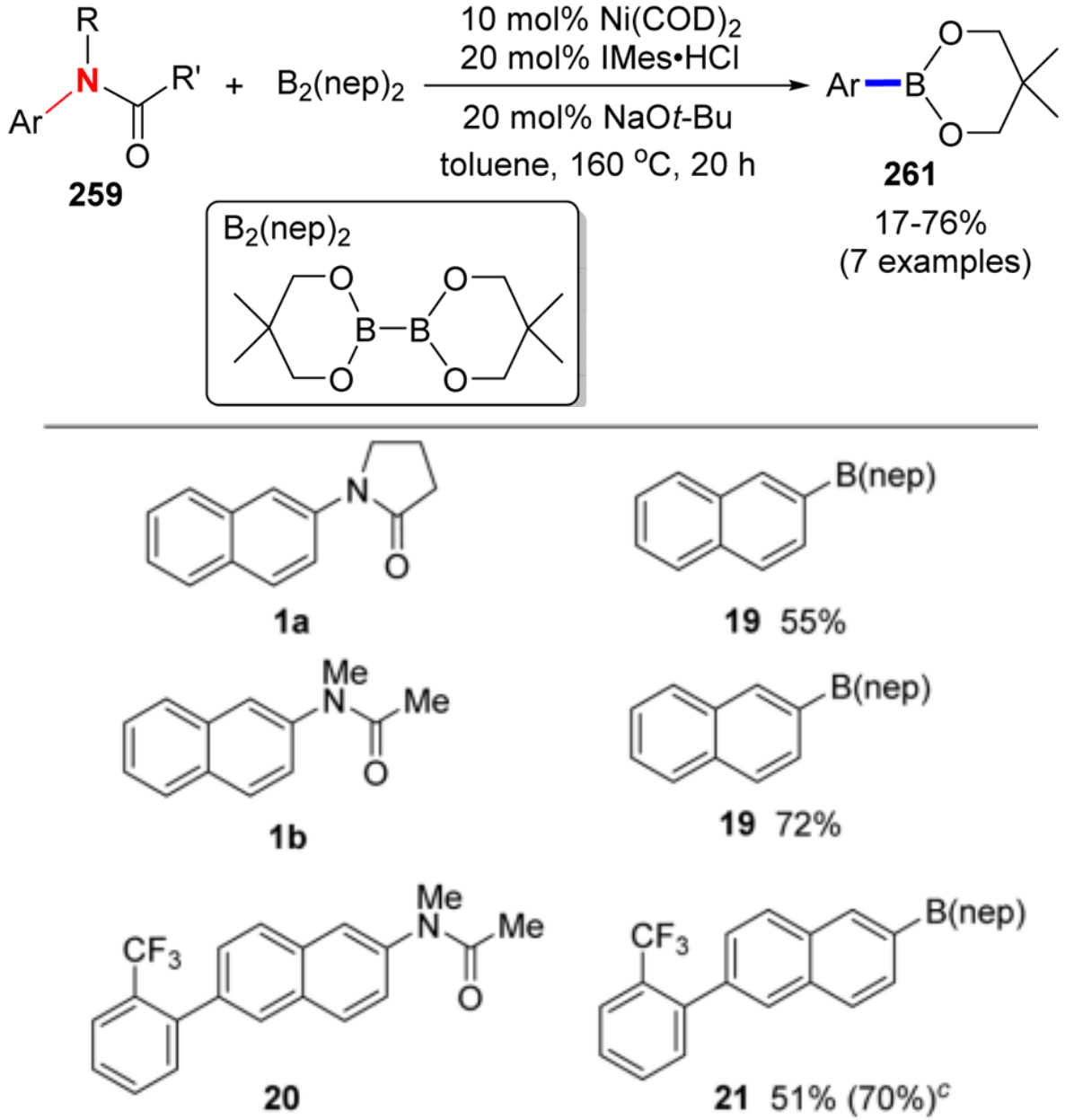


other reducing agents, including $BH_3 \cdot Me_2S$, KBH_4, and DIBALH, led exclusively to the reduction of the carbonyl group

- Tobisu, M.; Nakamura, K.; Chatani, N. Nickel-Catalyzed Reductive and Borylative Cleavage of Aromatic Carbon−Nitrogen Bonds in N-Aryl Amides and Carbamates. *J. Am. Chem. Soc.* 2014, *136*, 5587−5590.



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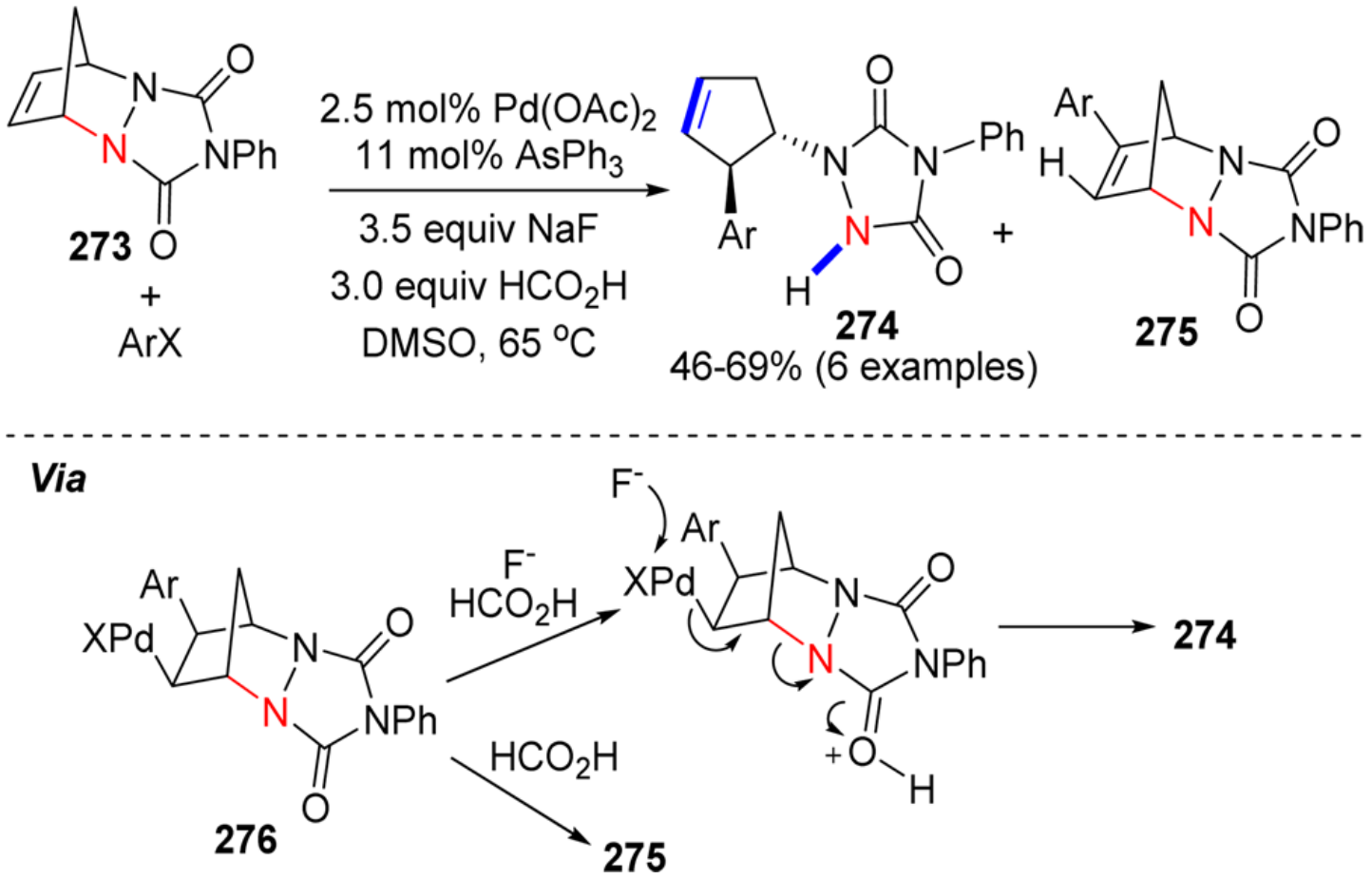
Non-Carbonyl C–N Bond Cleavage *via β-Amino Elimination*



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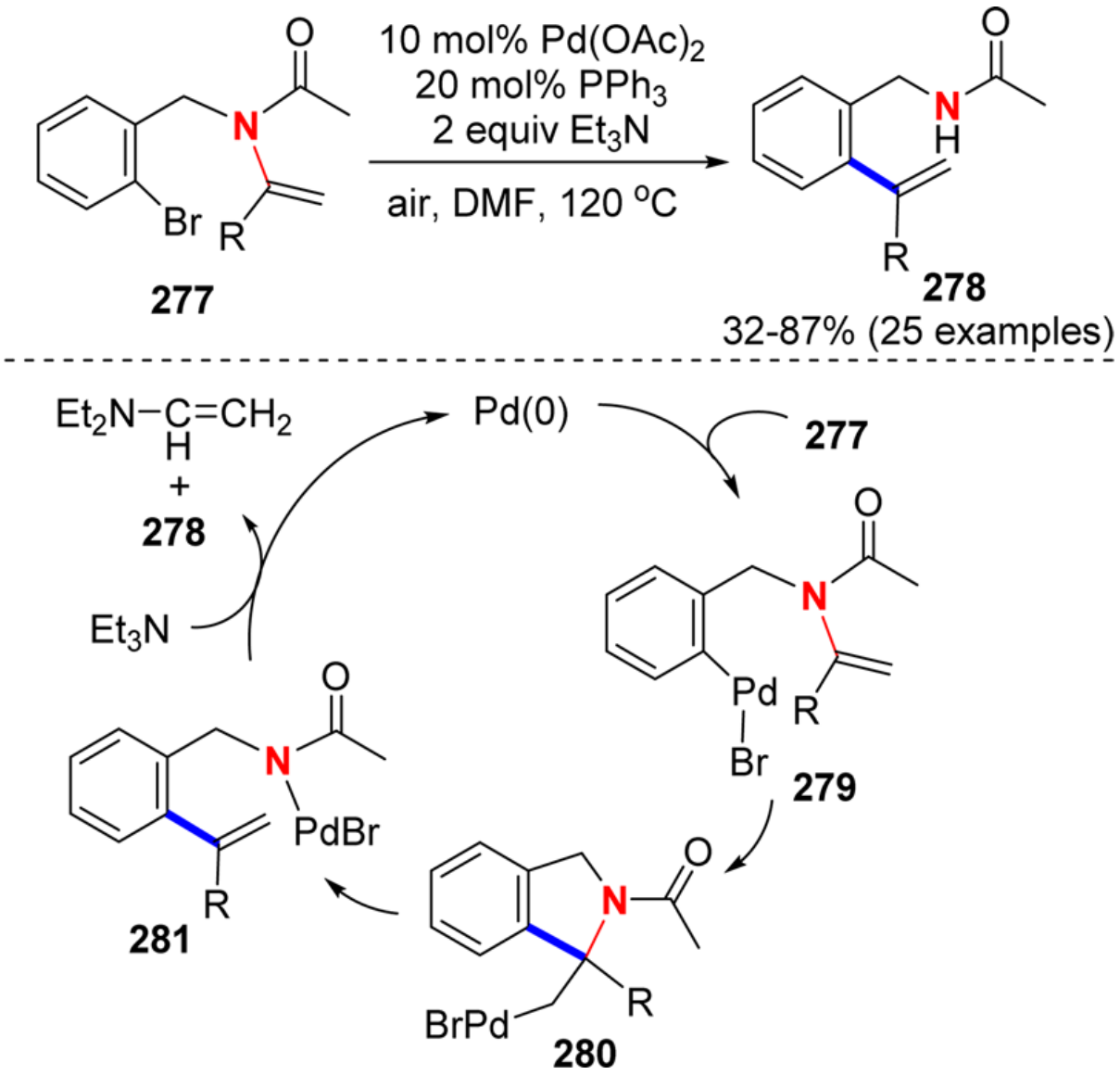
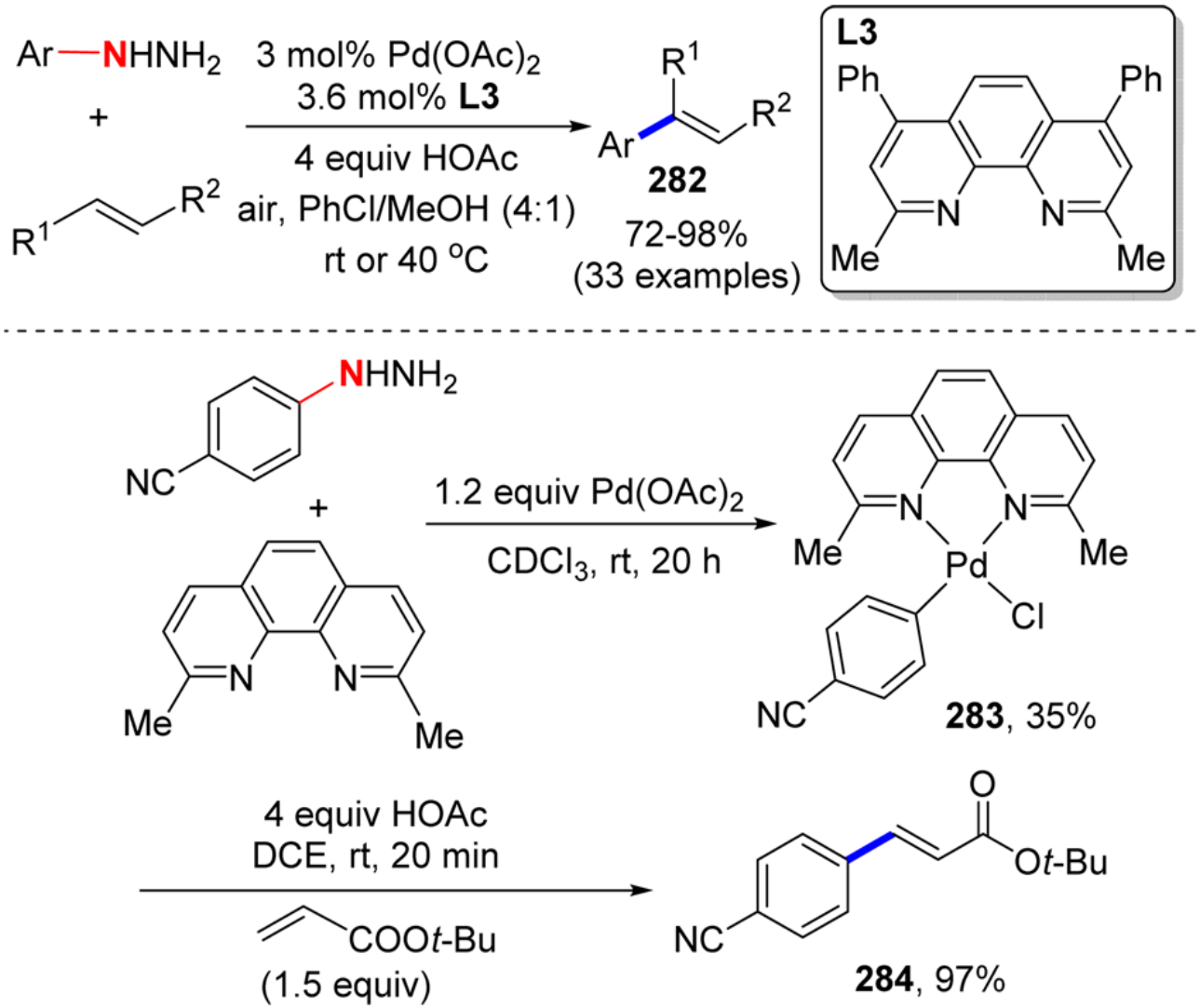


Wang, M.; Zhang, X.; Zhuang, Y.-X.; Xu, Y.-H.; Loh, T.-P. Pd-Catalyzed Intramolecular C−N Bond Cleavage, 1,4-Migration, sp^3 C−H Activation, and Heck Reaction: Four Controllable Diverse Pathways Depending on the Judicious Choice of the Base and Ligand. *J. Am. Chem. Soc*. 2015, *137*, 1341−1347.

Hydrazines



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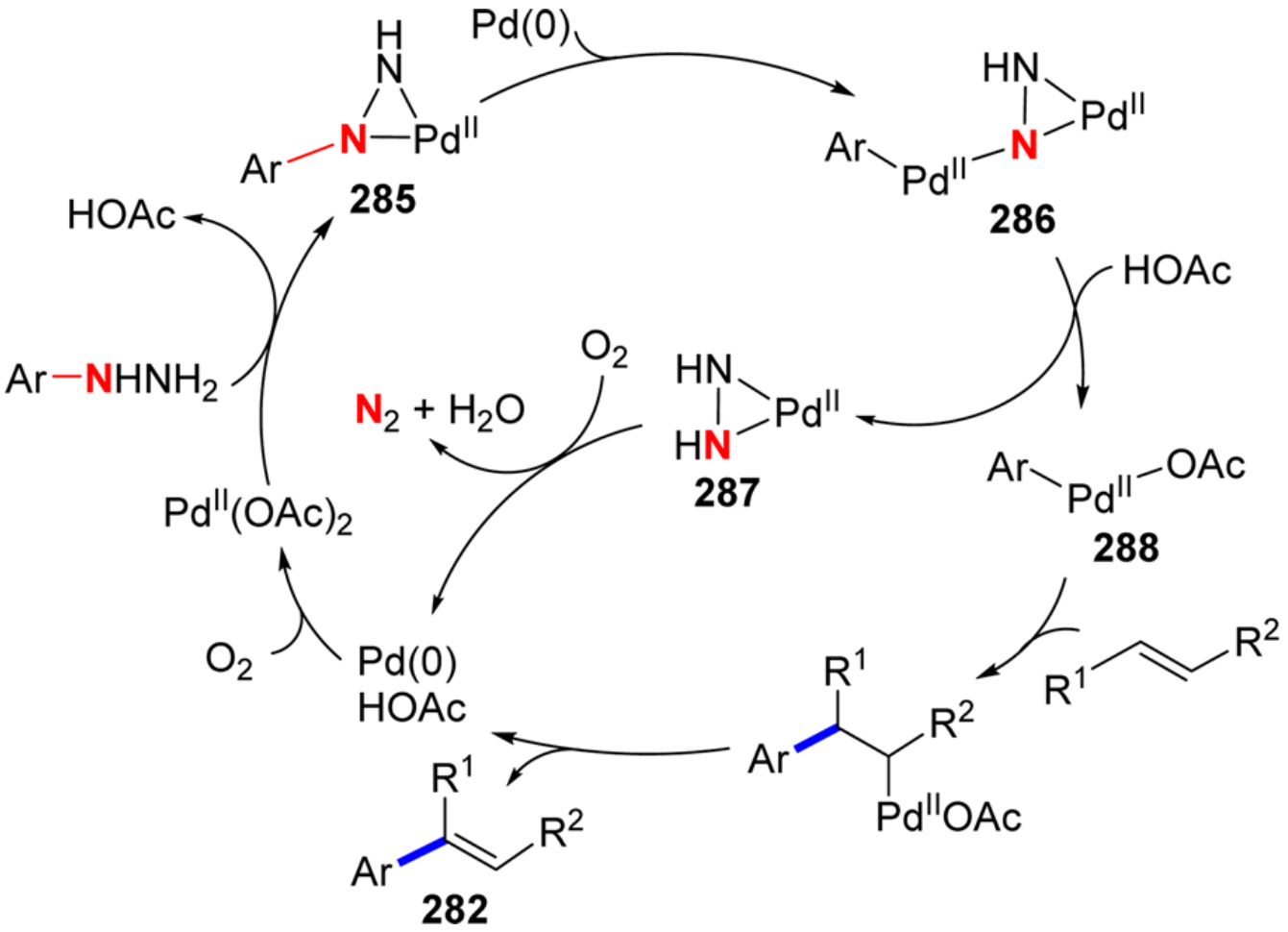

- Zhu, M.-K.; Zhao, J.-F.; Loh, T.-P. Palladium-Catalyzed C−C Bond Formation of Arylhydrazines with Olefins via Carbon−Nitrogen Bond Cleavage. *Org. Lett*. 2011, *13*, 6308−6311.
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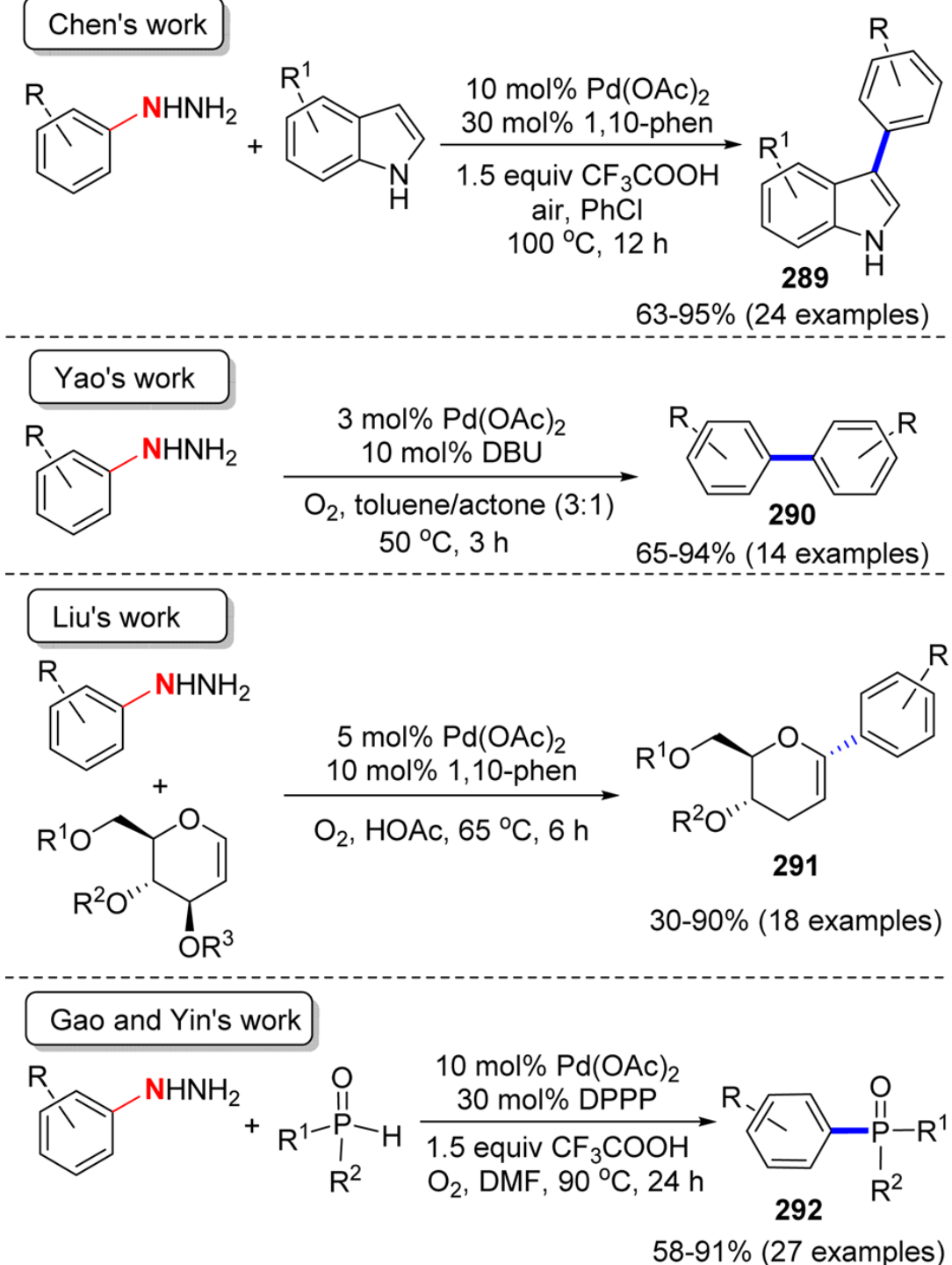

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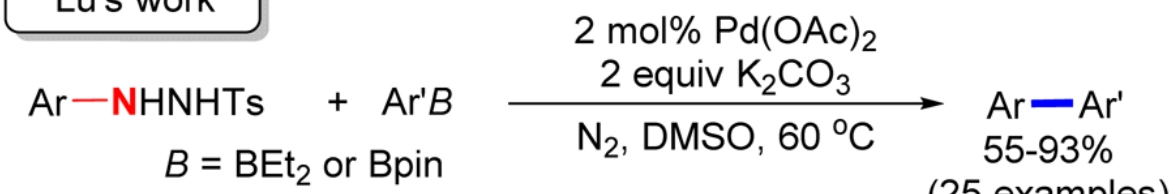
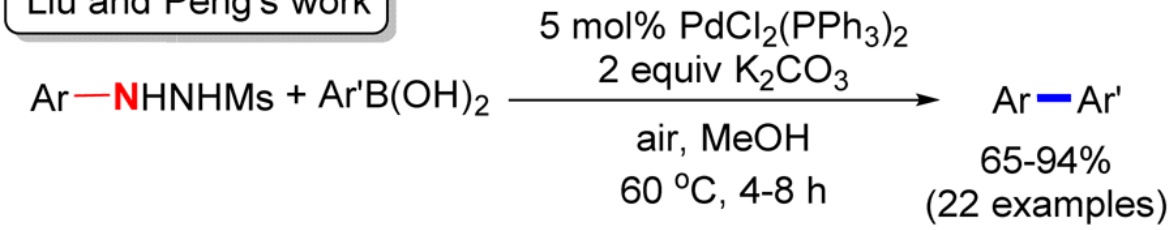
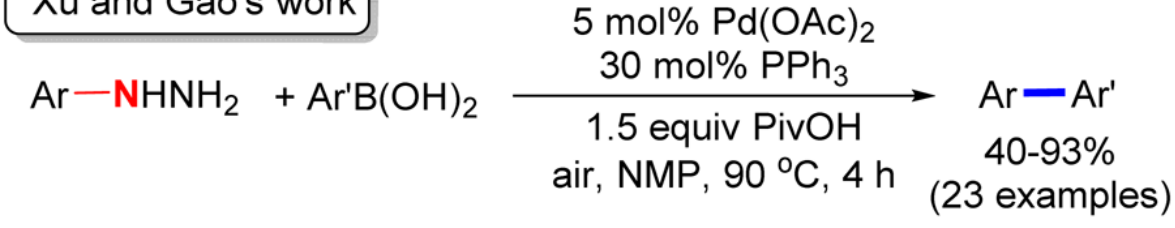
Lu's work

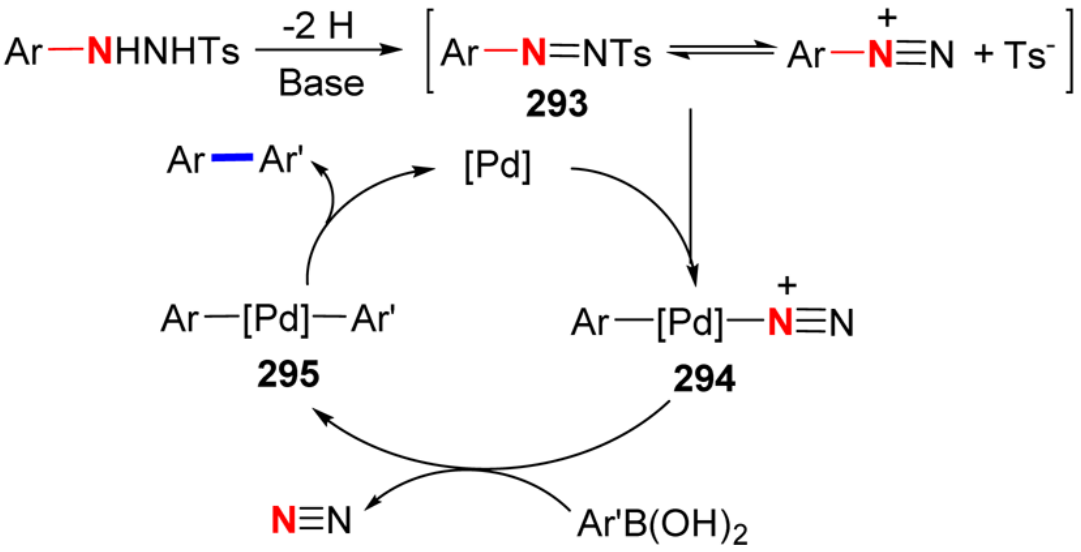


Liu and Peng's work



Xu and Gao's work





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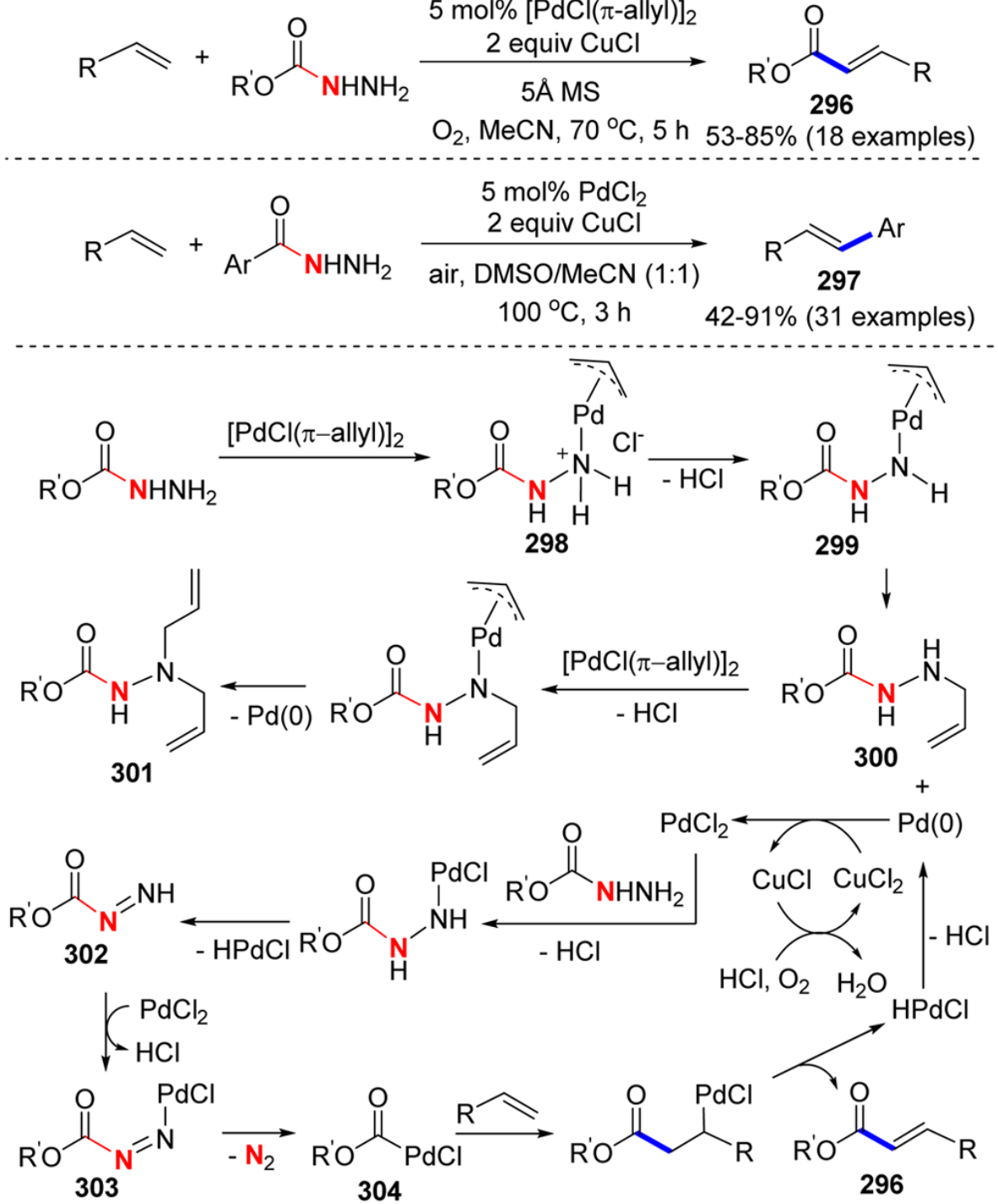

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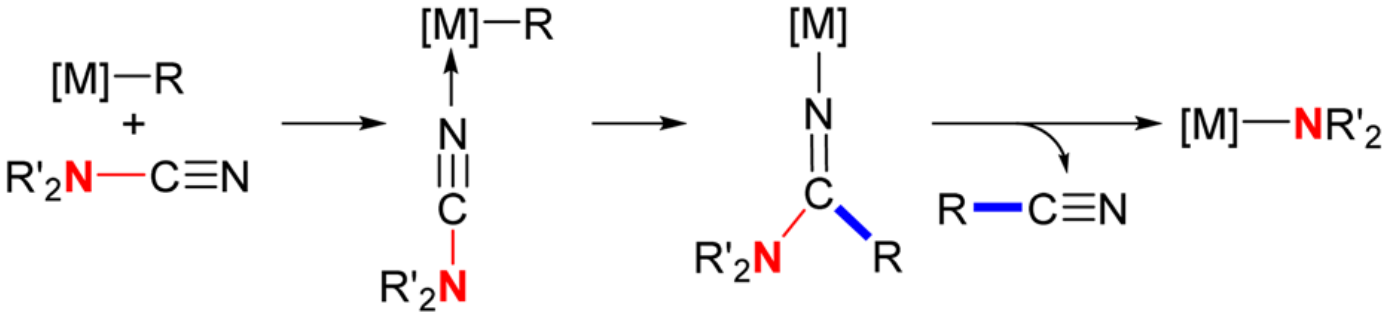
Cyanamides

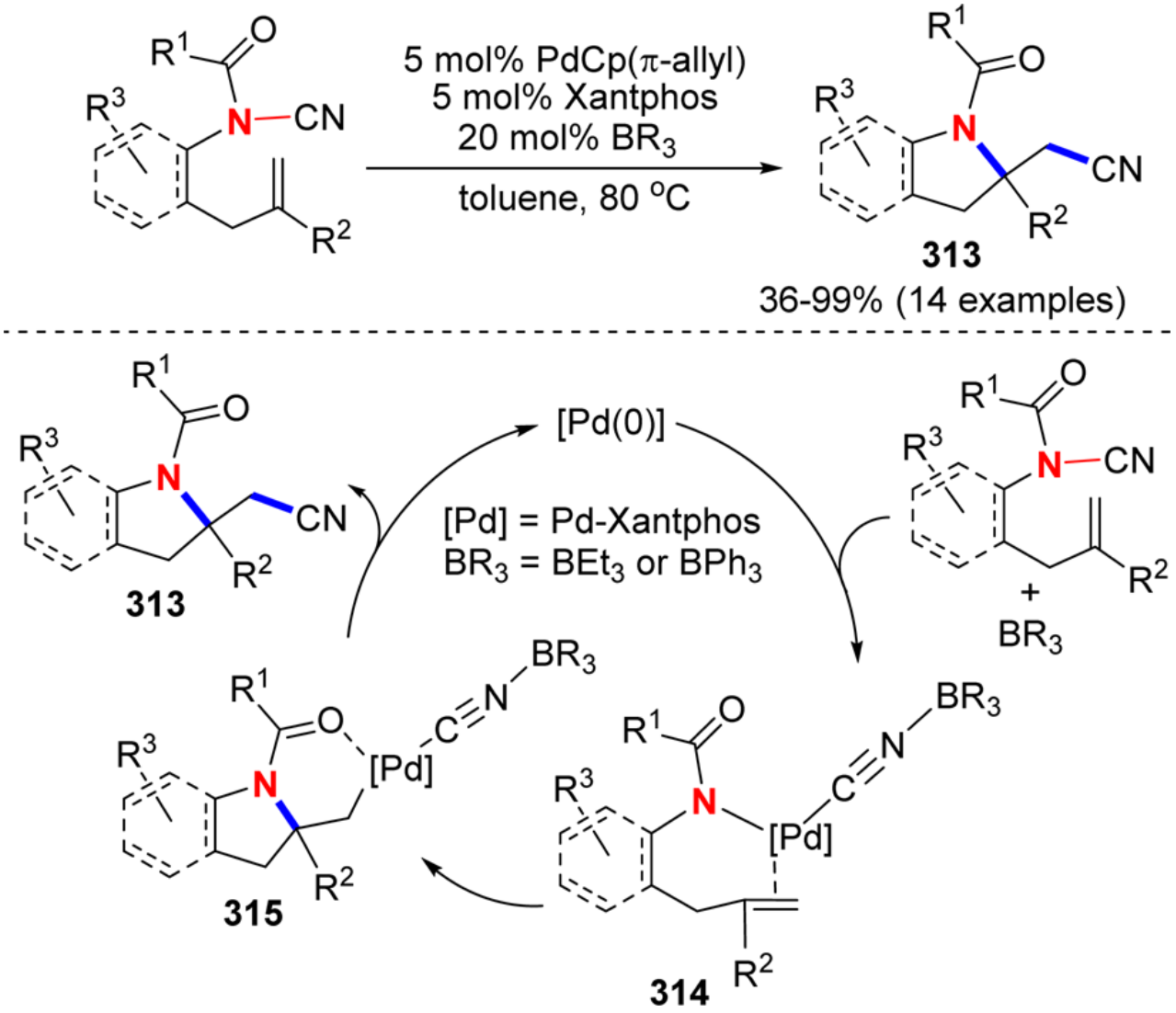
$R_2N–CN$

- *Two Major Pathways for the C–N Bond Cleavage of Cyanamides*

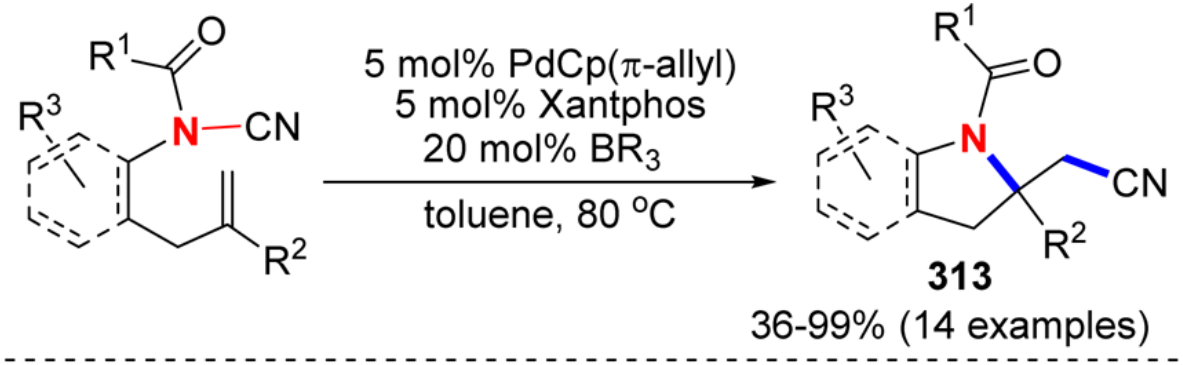
i) Lewis acid (**LA**) activated oxidative addition

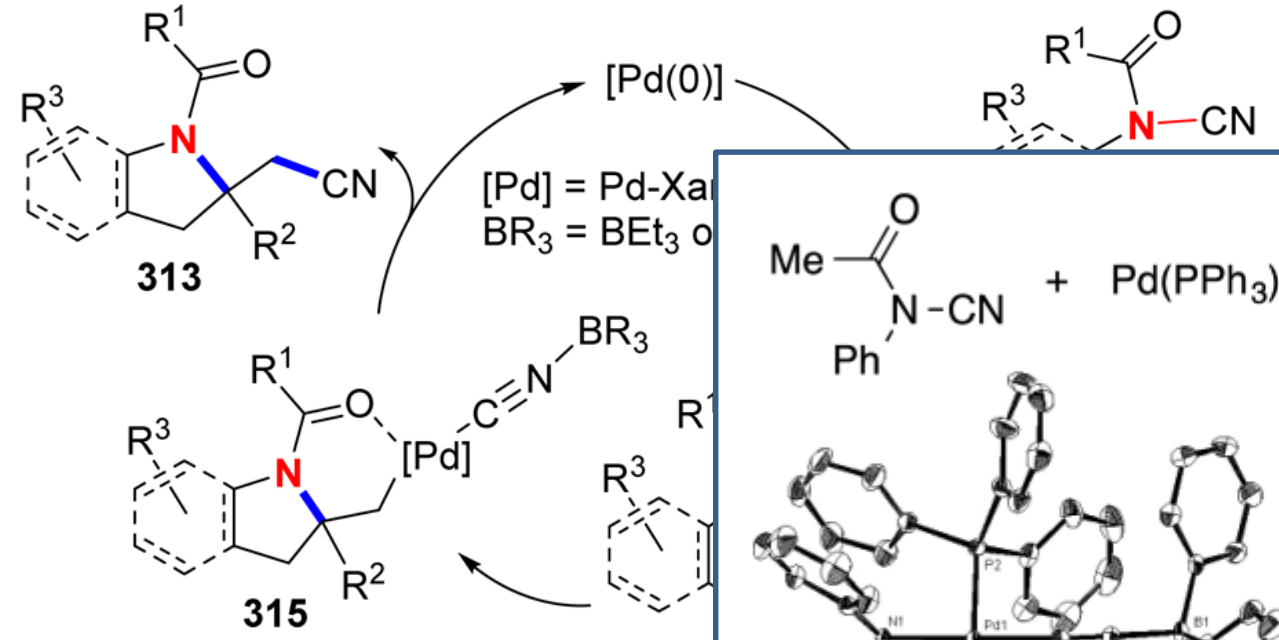
ii) Insertion/de-insertion

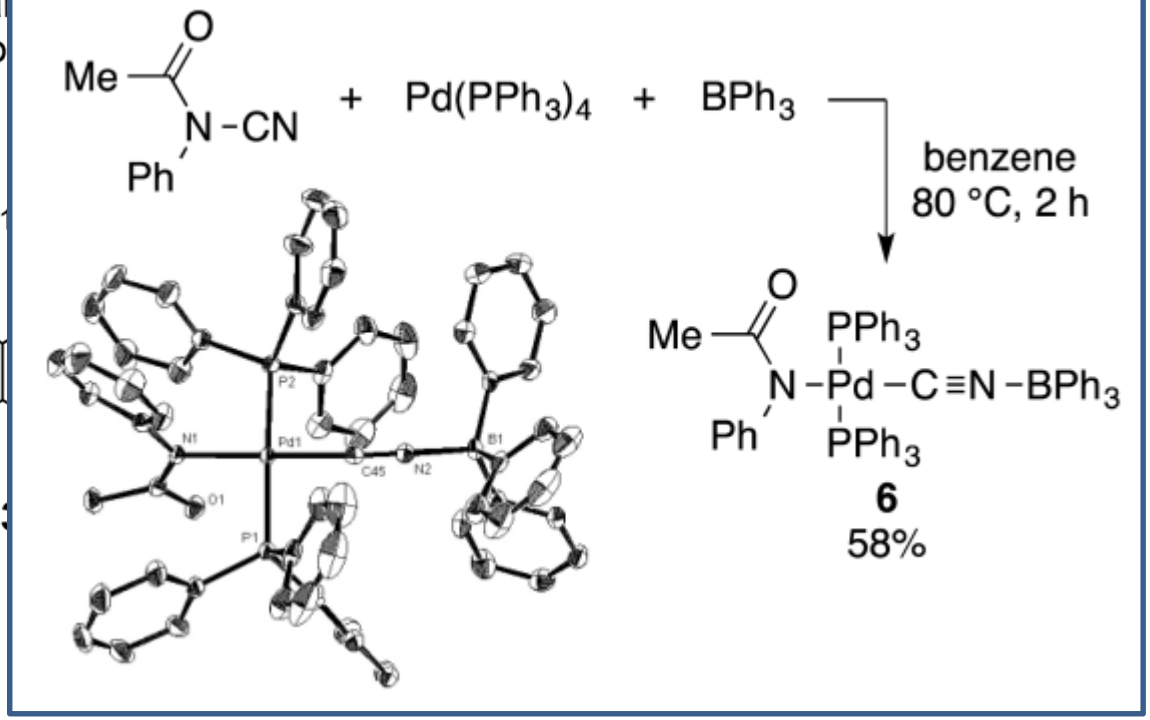




■ Miyazaki, Y.; Ohta, N.; Semba, K.; Nakao, Y. Intramolecular Aminocyanation of Alkenes by Cooperative Palladium/Boron Catalysis. *J. Am. Chem. Soc.* 2014, *136*, 3732−3735.







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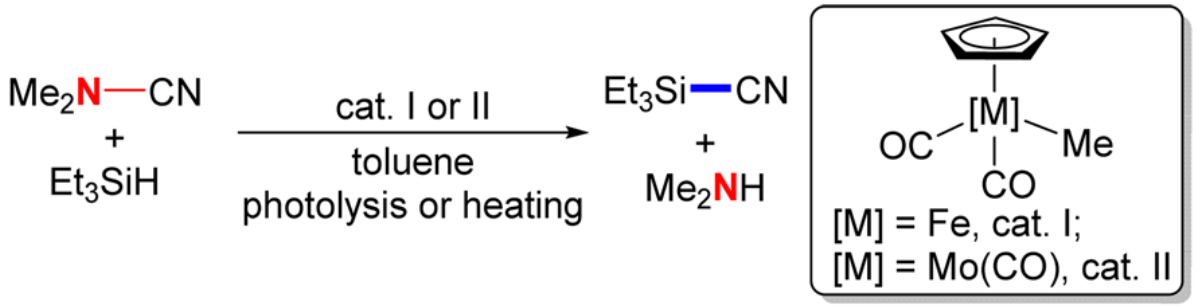

Mechanism?

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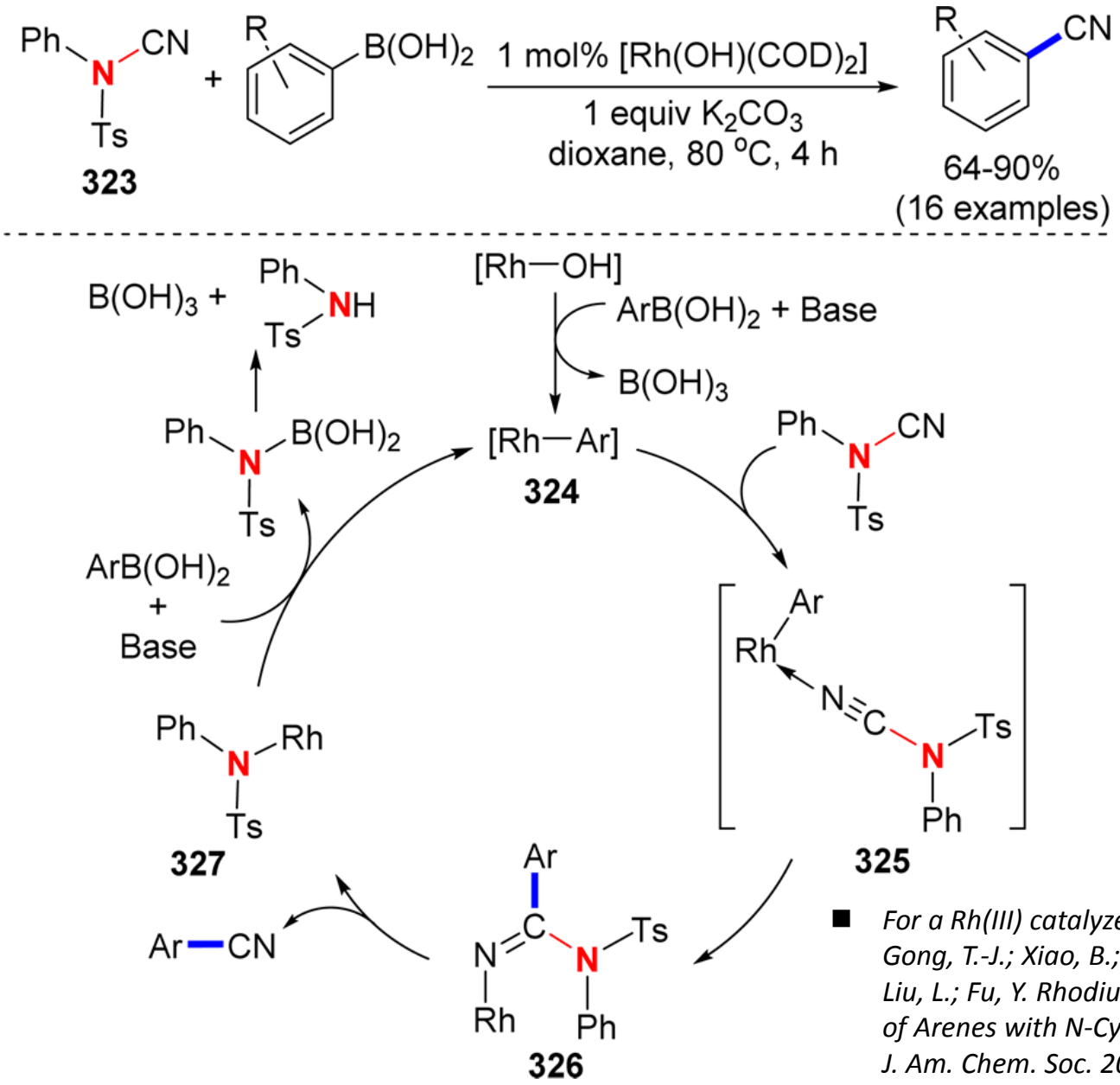

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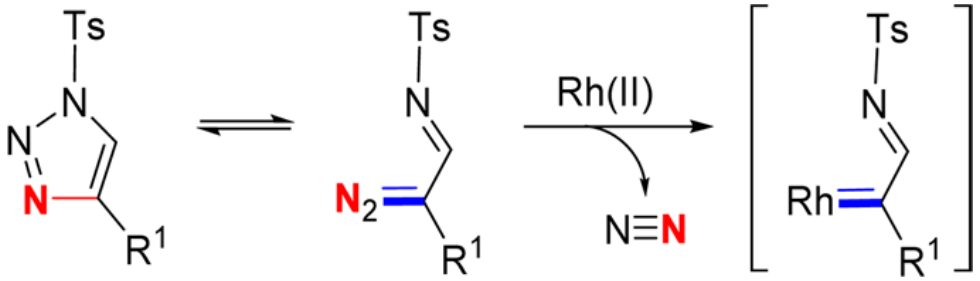
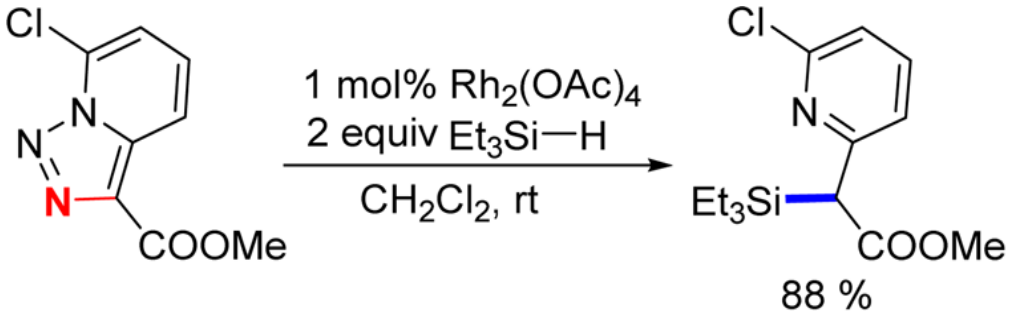
CLEAVAGE OF ACTIVATED C–N SINGLE BONDS (selected work)

Triazoles

as Metal Carbene Precursors





Via

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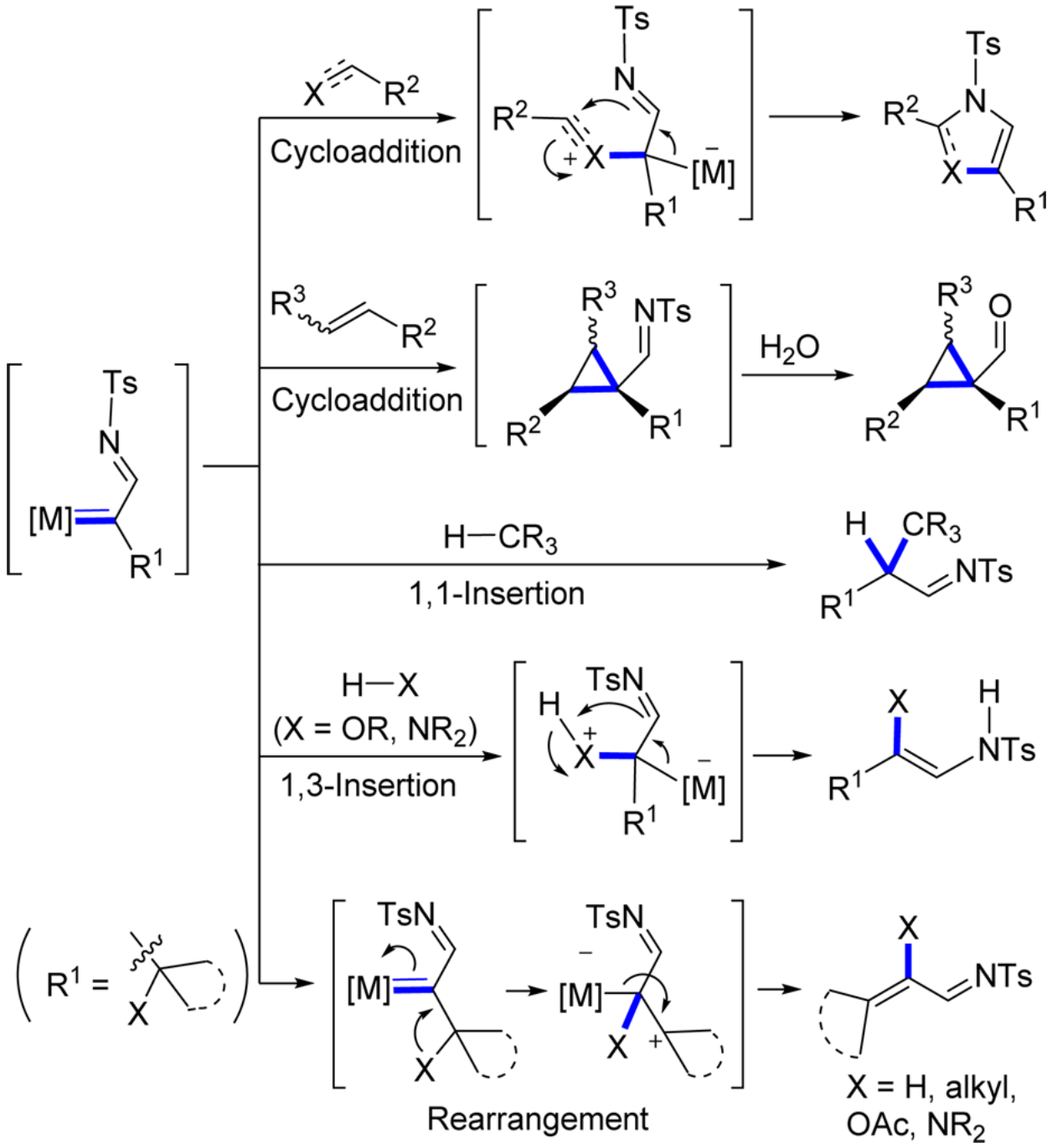

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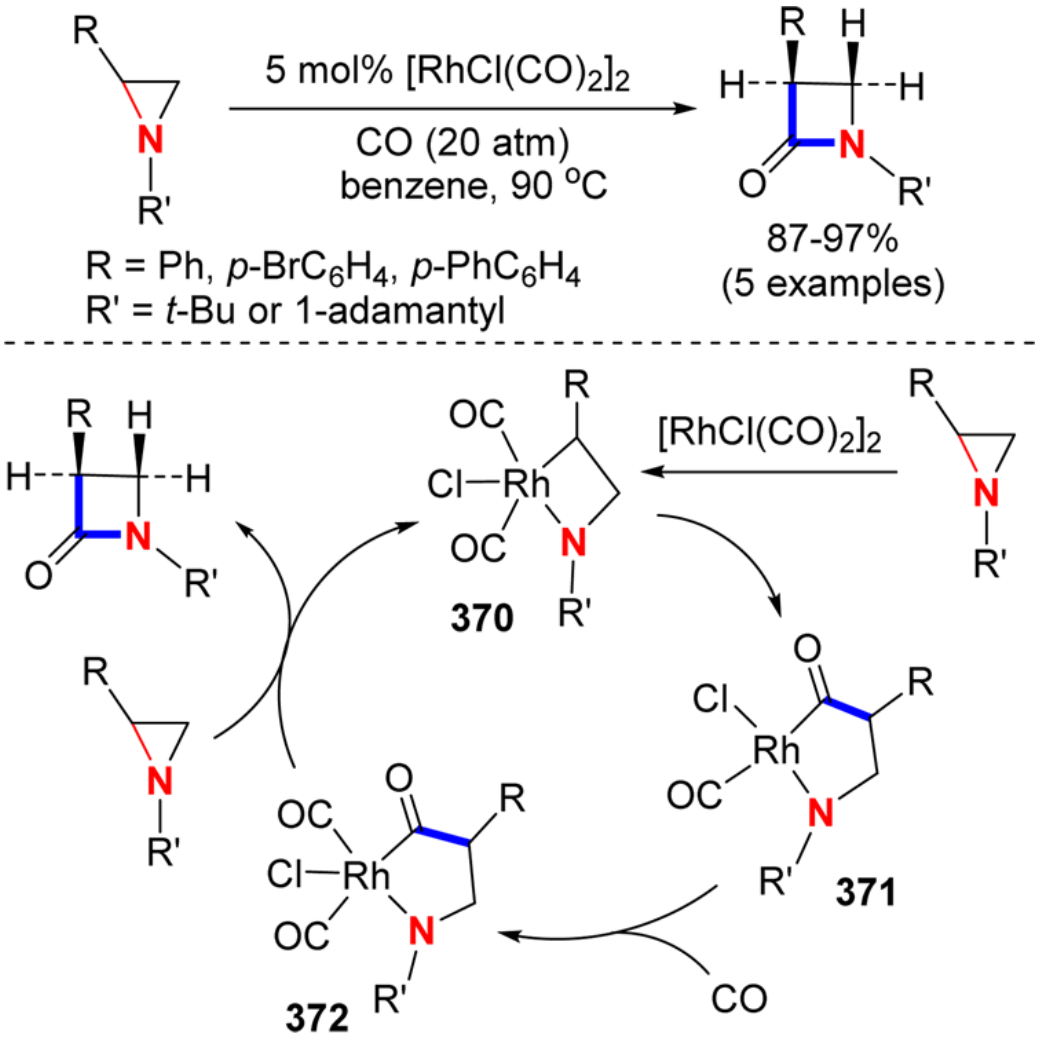
Aziridines (Selected work)



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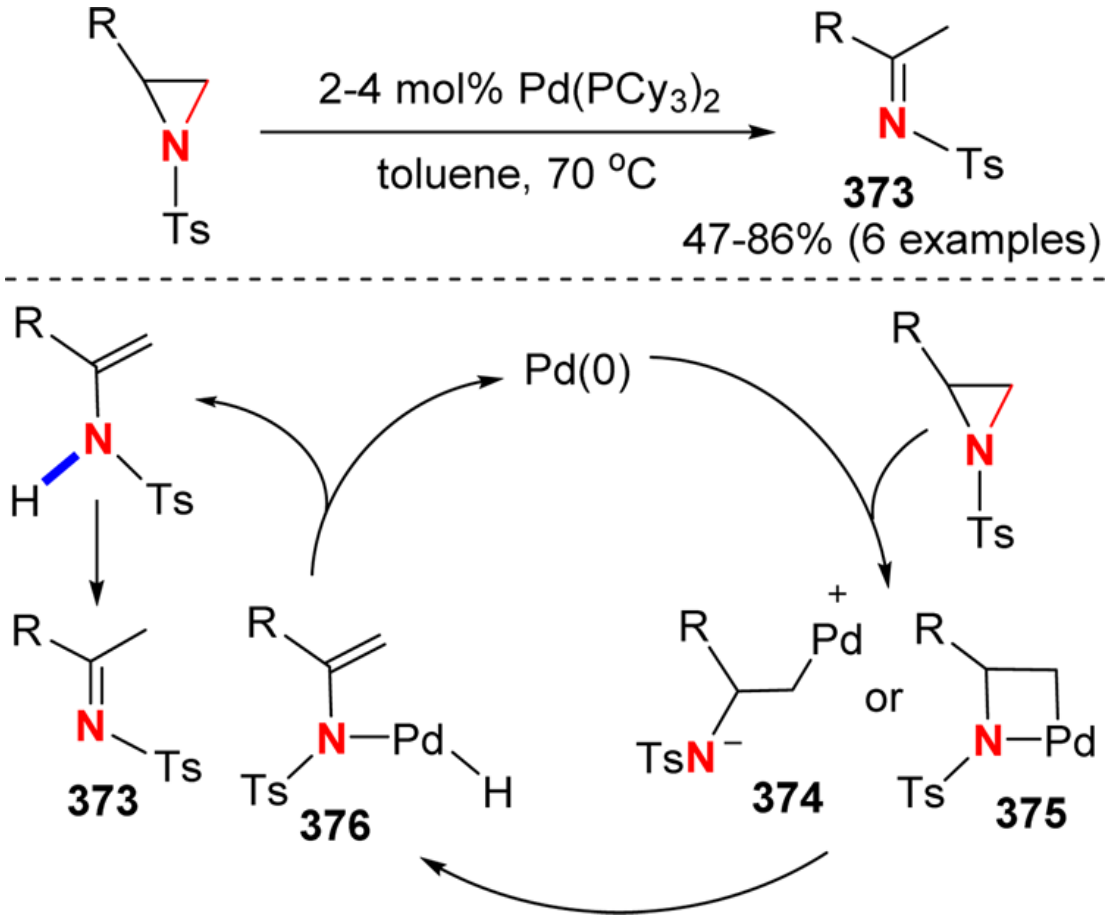

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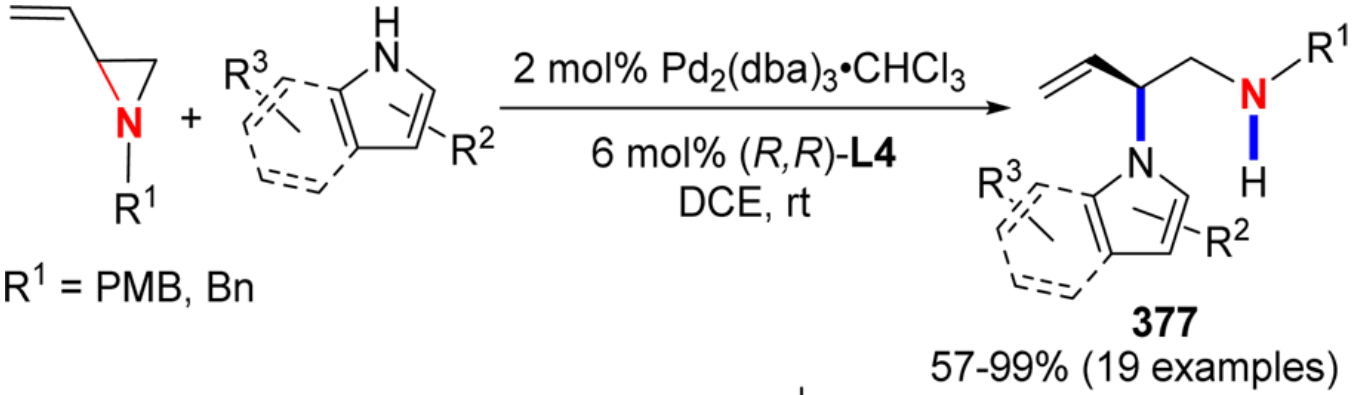

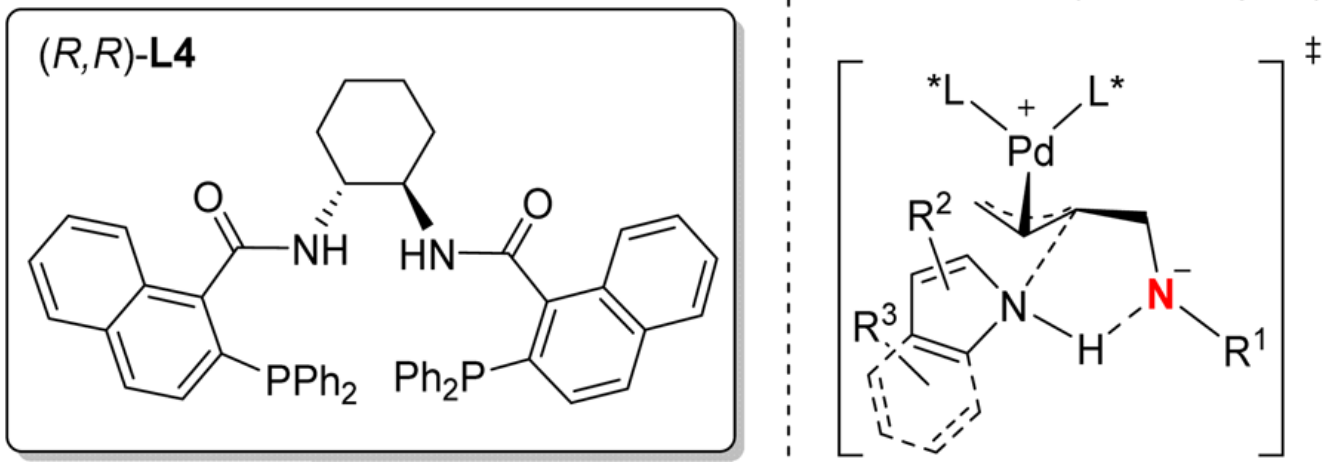

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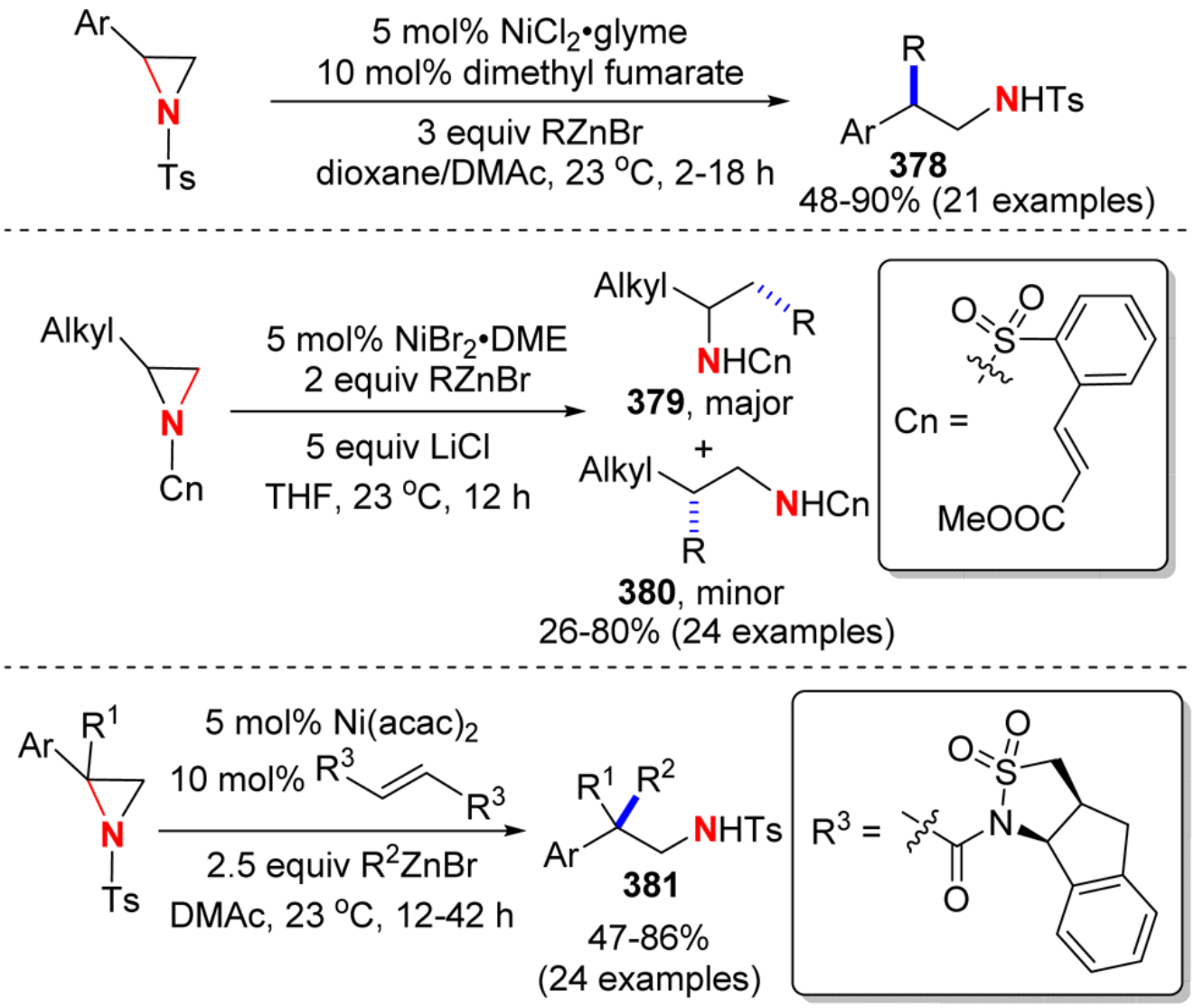

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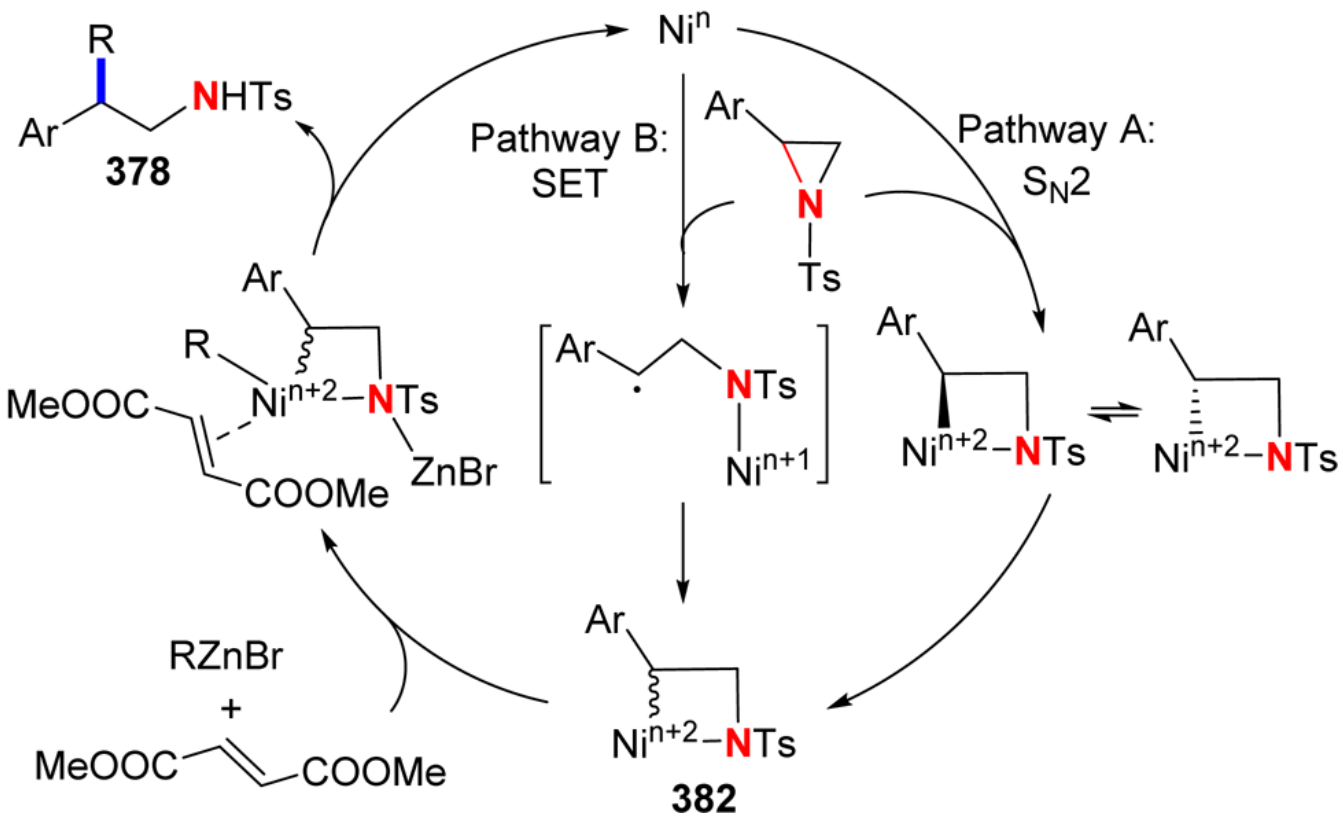

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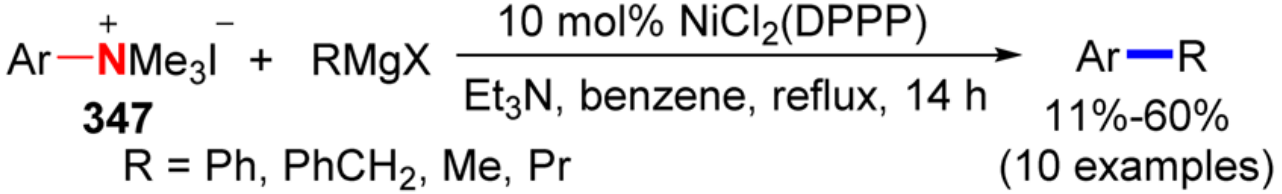
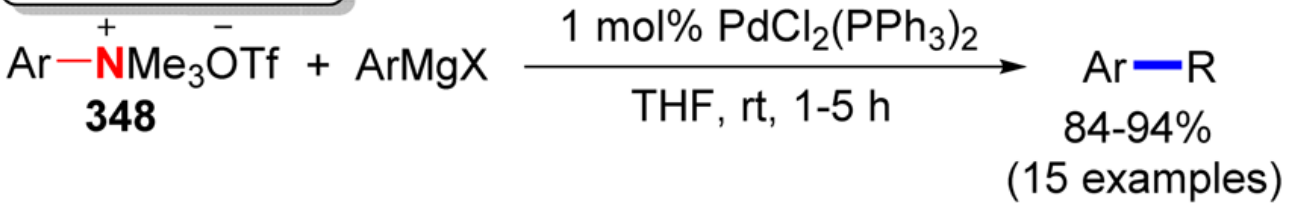
Quaternary Ammonium Salts

Wenkert's work



Reeves's work



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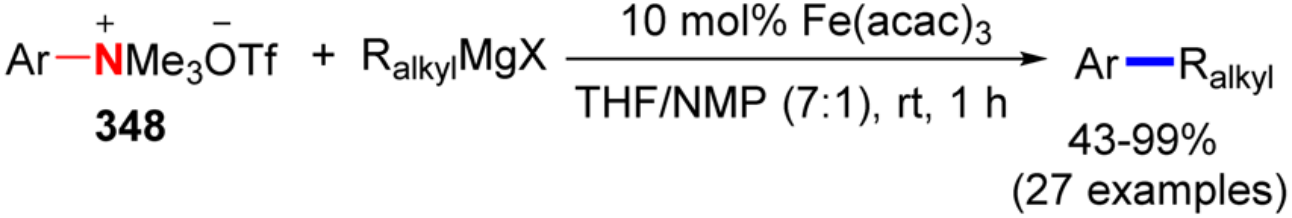

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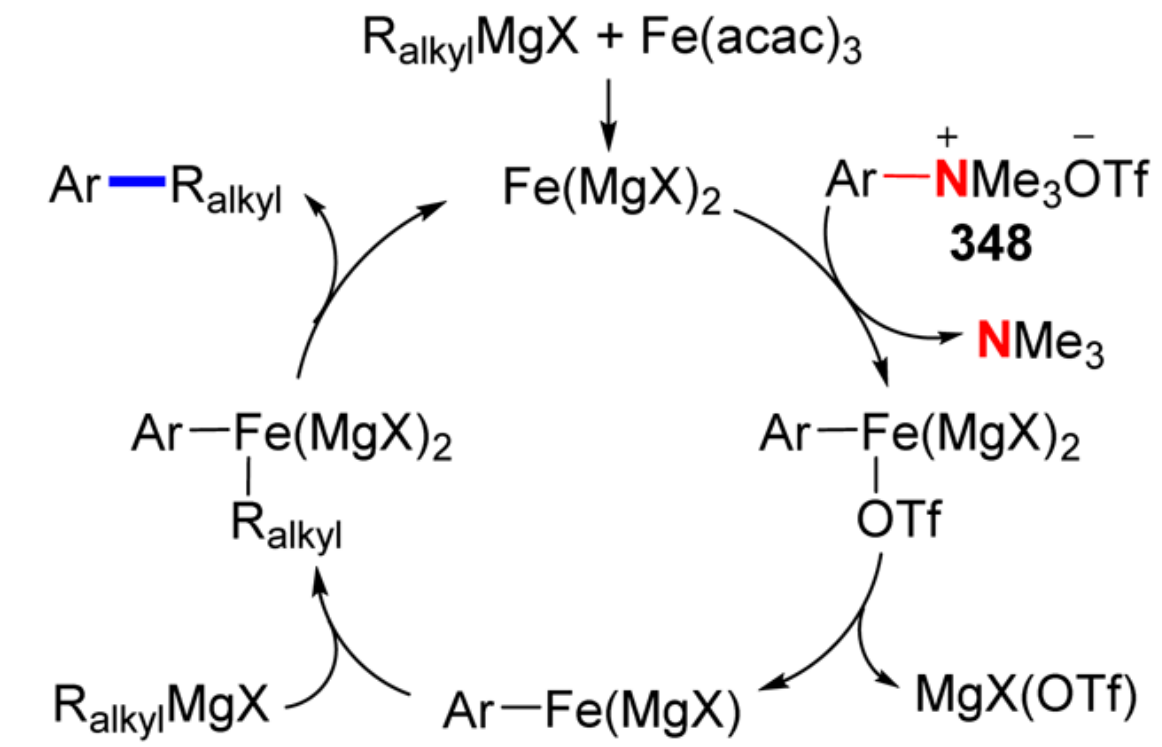
CLEAVAGE OF ACTIVATED C–N SINGLE BONDS

Quaternary Ammonium Salts



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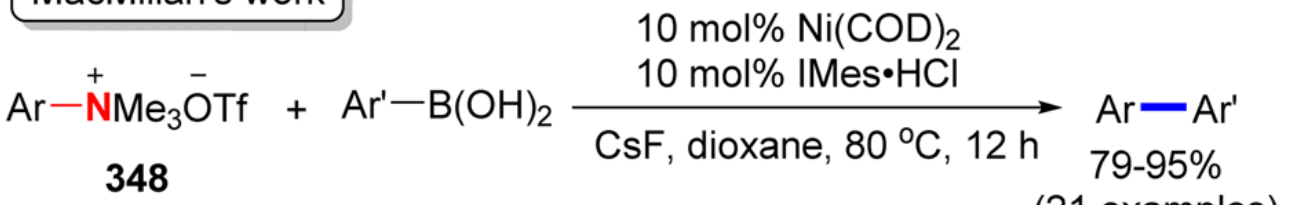
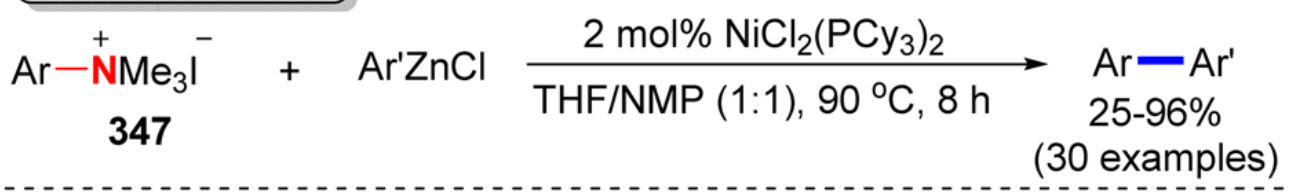
MacMillan's work



Wang's work



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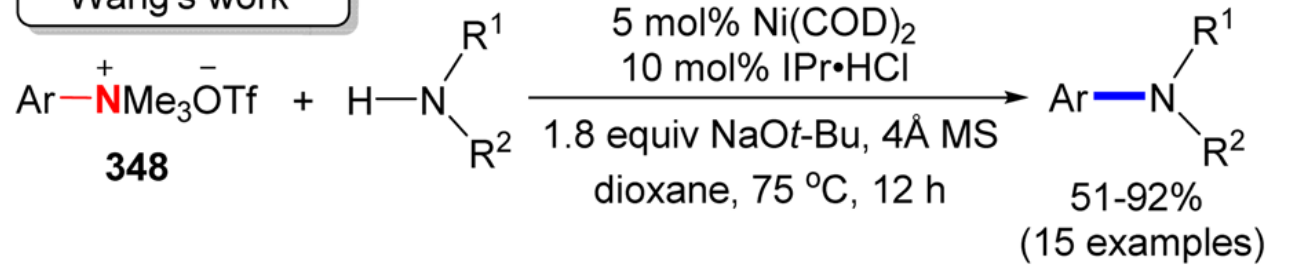

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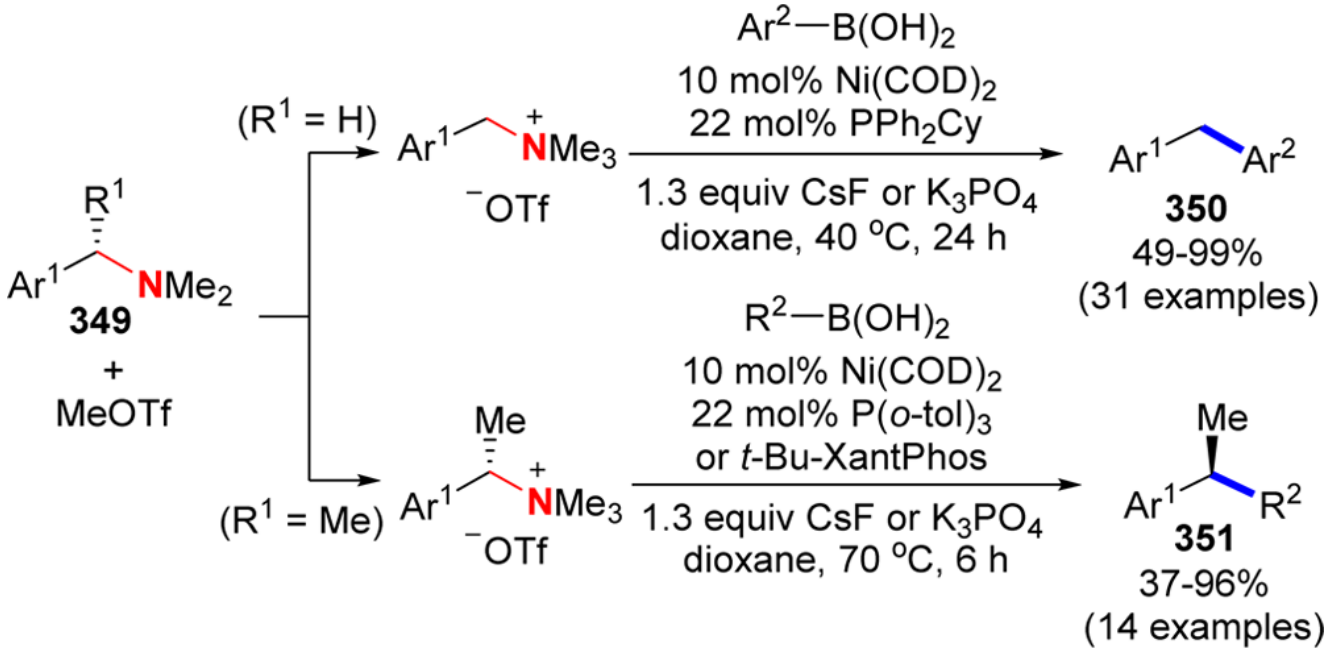

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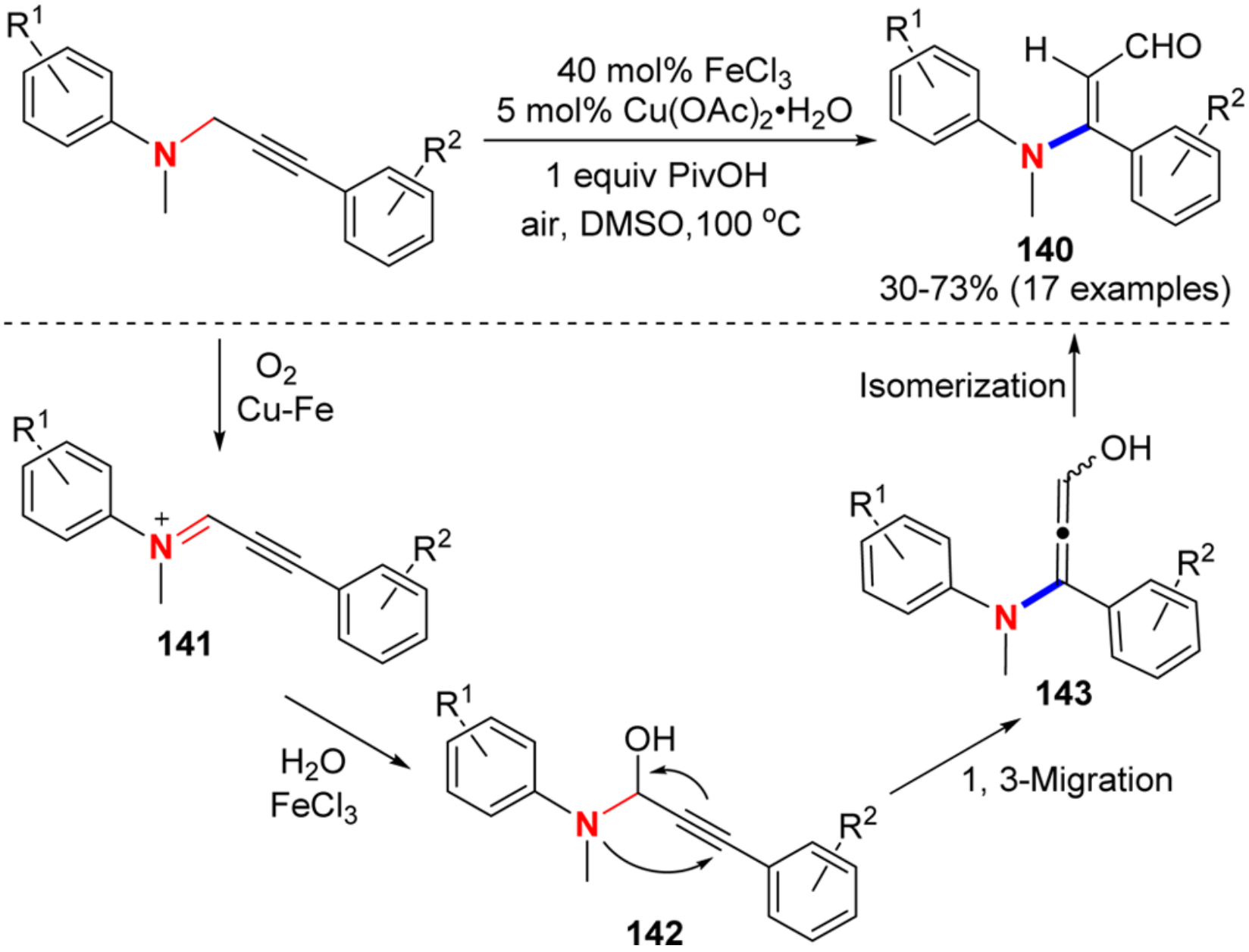
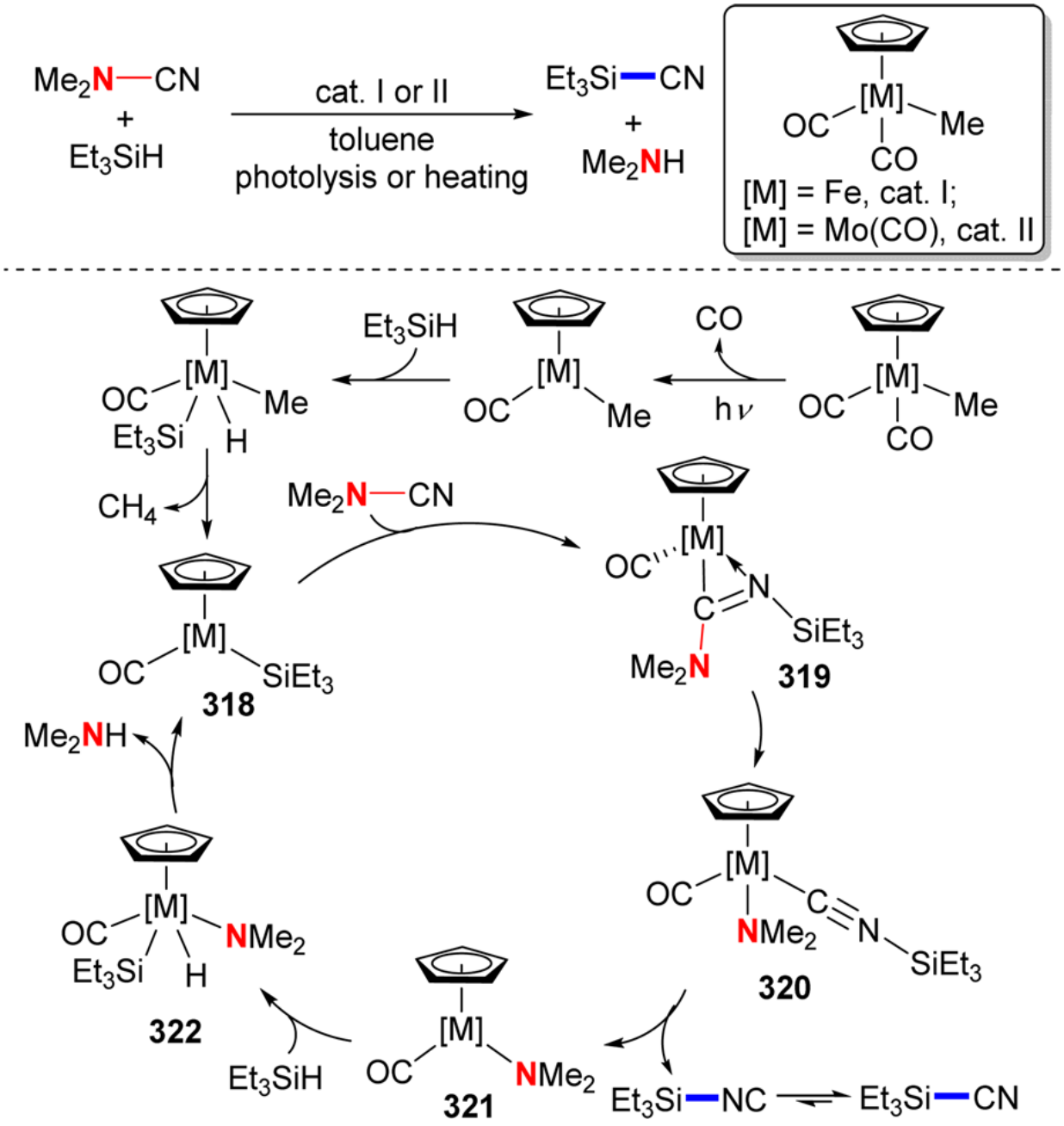
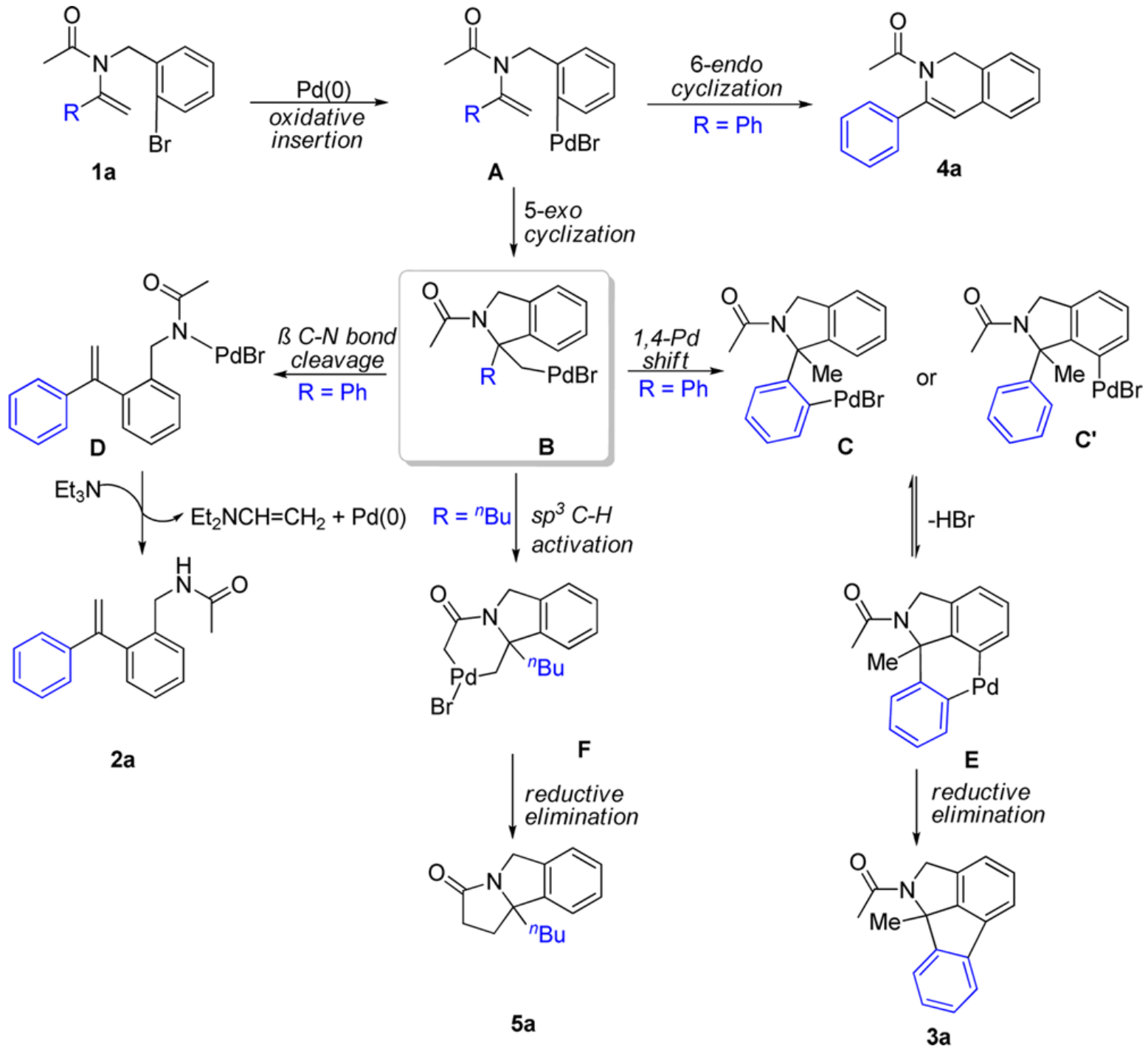
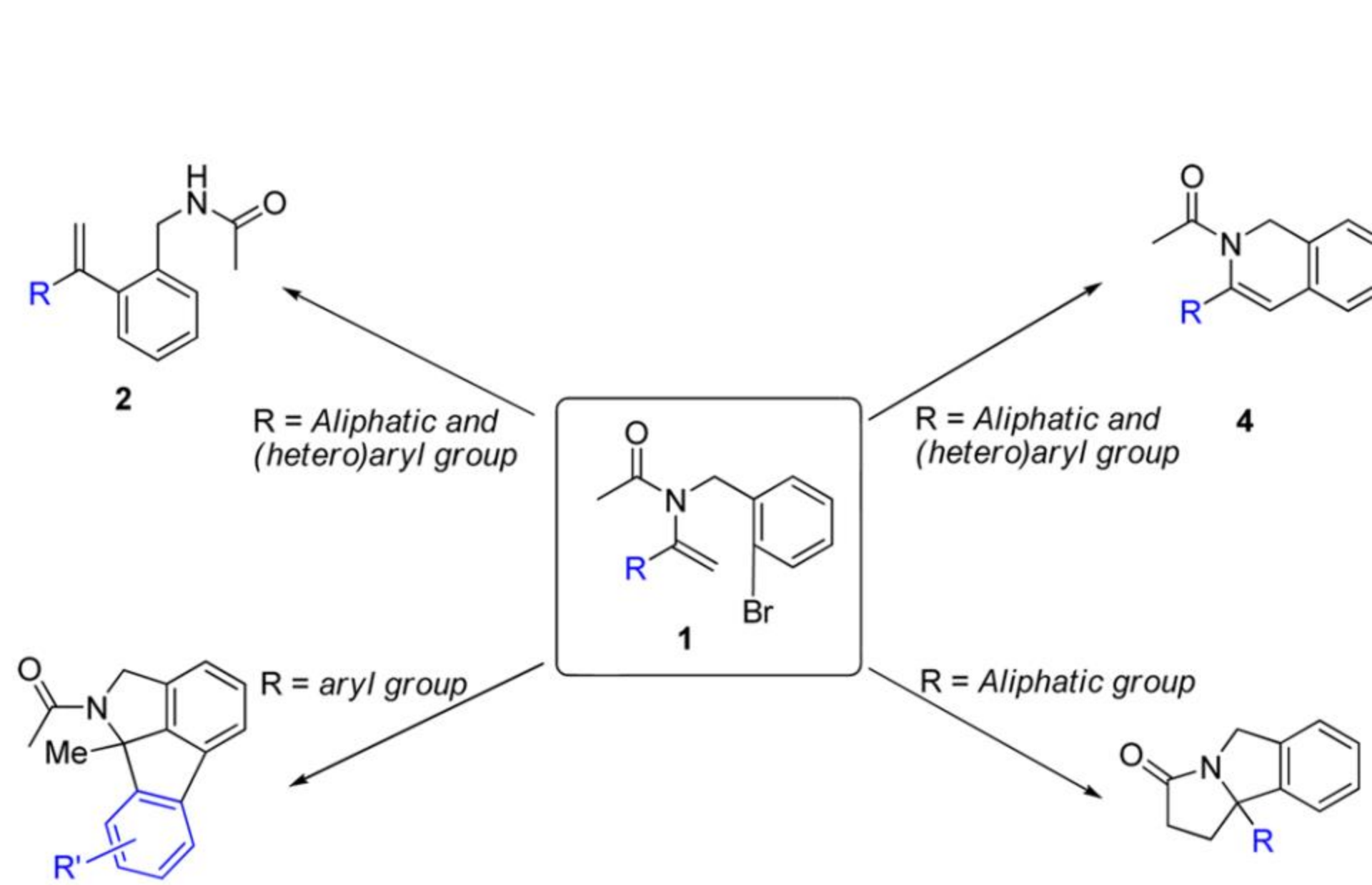
WAKE UP AND

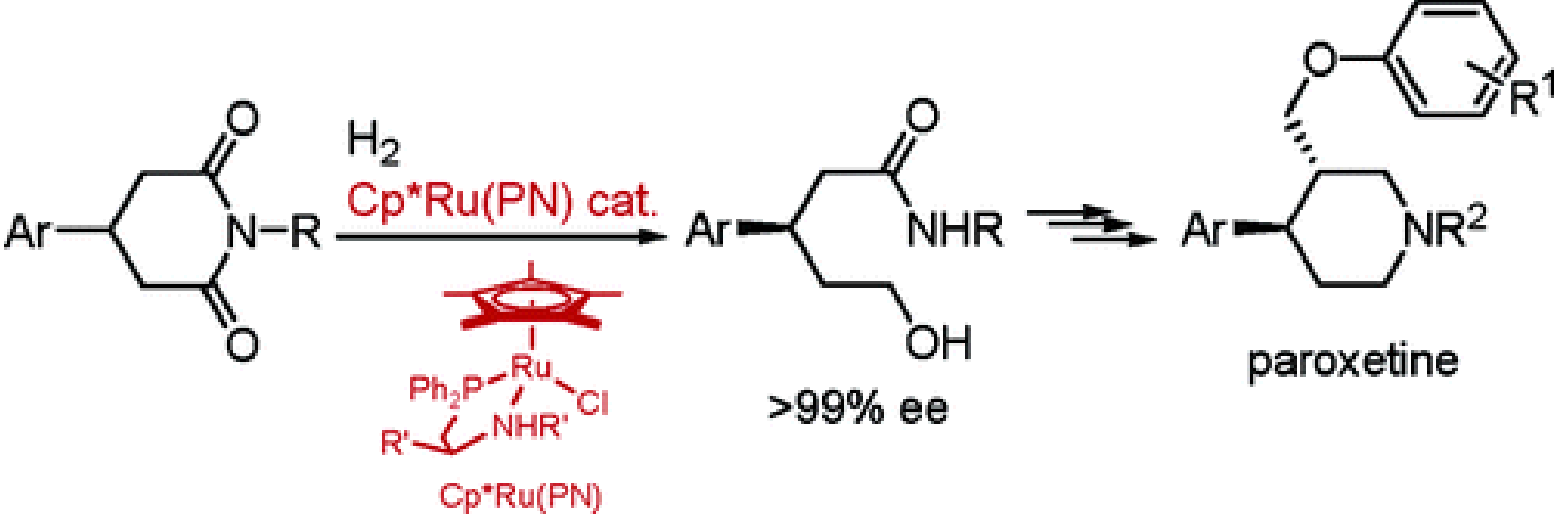
THANK YOU FOR YOUR ATTENTION

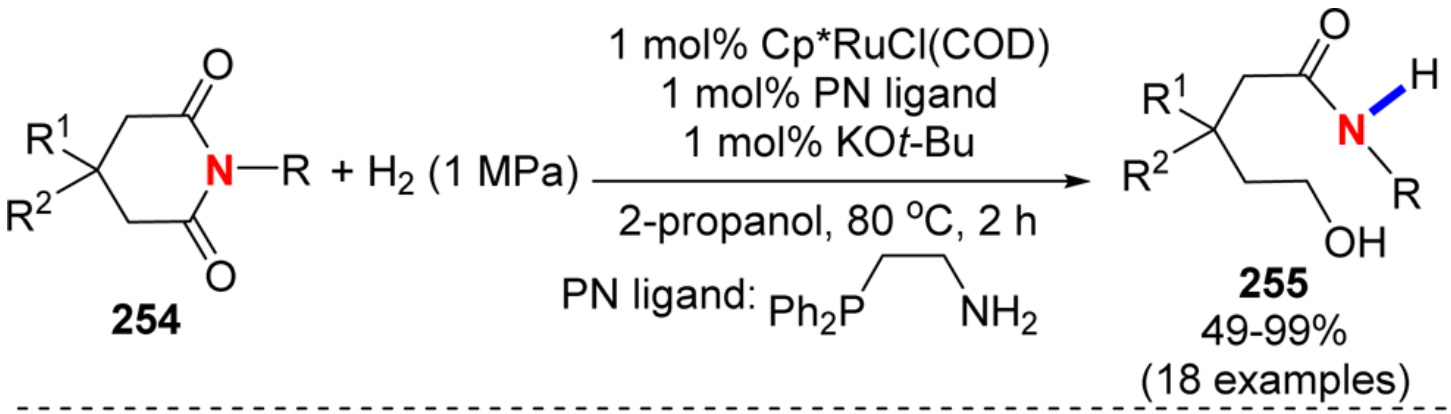

R1
N
R2
40 mol% FeCl3
5 mol% Cu(OAc)2•H2O
1 equiv PivOH
air, DMSO,100 °C
H
CHO
140
30-73% (17 examples)
O2
Cu-Fe
Isomerization
141
143
H2O
FeCl3
OH
142
1, 3-Migration

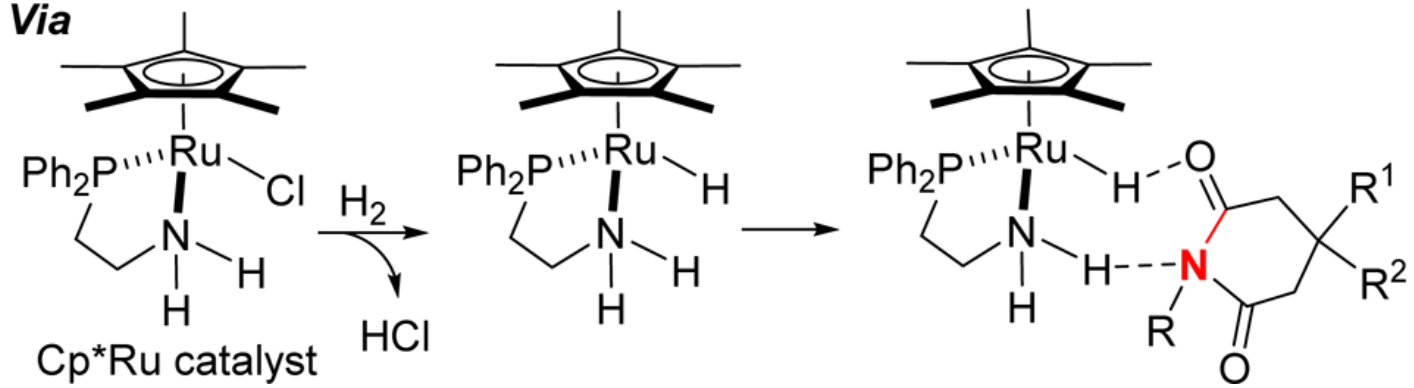

Me2N—CN
+
Et3SiH
cat. I or II
toluene
photolysis or heating
Et3Si—CN
+
Me2NH
[M]
OC
Me
CO
[M] = Fe, cat. I;
[M] = Mo(CO), cat. II
Et3SiH
CO
hν
CH4
Me2N—CN
Et3Si
H
SiEt3
N
C
318
319
320
321
322
NMe2
Me2NH
Et3Si—NC
Et3Si—CN


Pd(0)
oxidative
insertion
6-endo
cyclization
R = Ph
5-exo
cyclization
ß C-N bond
cleavage
R = Ph
1,4-Pd
shift
R = Ph
or
Et3N
Et2NCH=CH2 + Pd(0)
R = nBu
sp3 C-H
activation
-HBr
reductive
elimination
reductive
elimination
1a
A
4a
D
B
C
C'
2a
F
E
5a
3a


H
N
O
R
2
R = Aliphatic and
(hetero)aryl group
O
N
R
Br
1
R = Aliphatic and
(hetero)aryl group
O
N
R
4
O
N
Me
R'
R = aryl group
R = Aliphatic group
O
N
R







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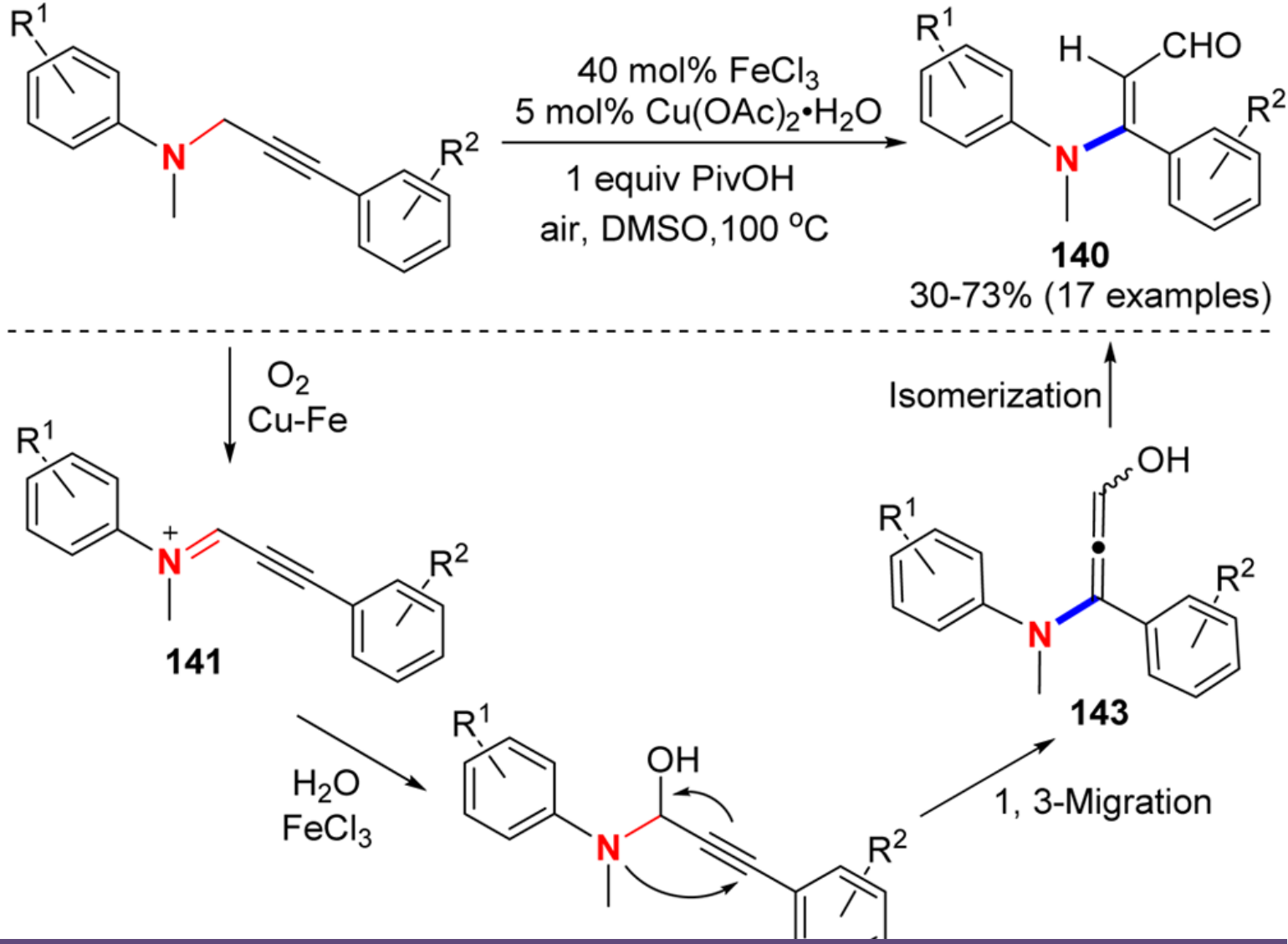

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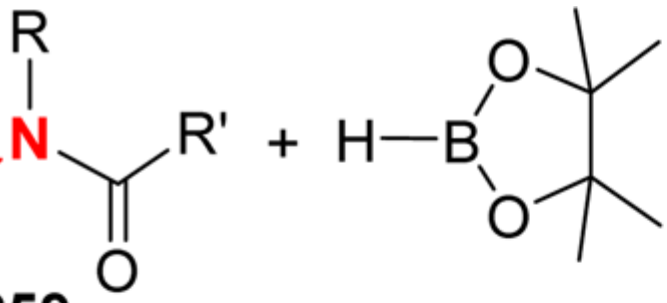


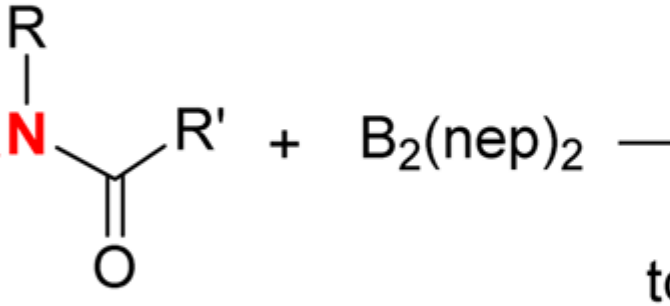
259

10 mol% $Ni(COD)_2$
20 mol% PCy_3

toluene, 80 °C, 20 h

260

25-78%
(8 examples)



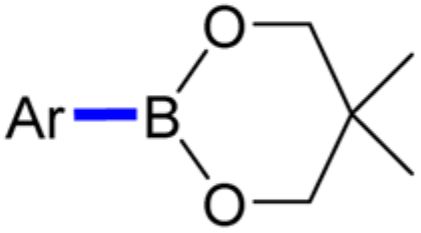
259

10 mol% $Ni(COD)_2$
20 mol% IMes•HCl

$B_2(nep)_2$

20 mol% NaO*t*-Bu

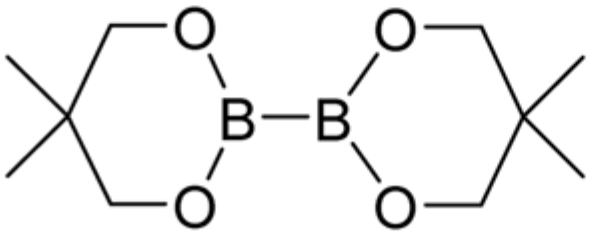
toluene, 160 °C, 20 h

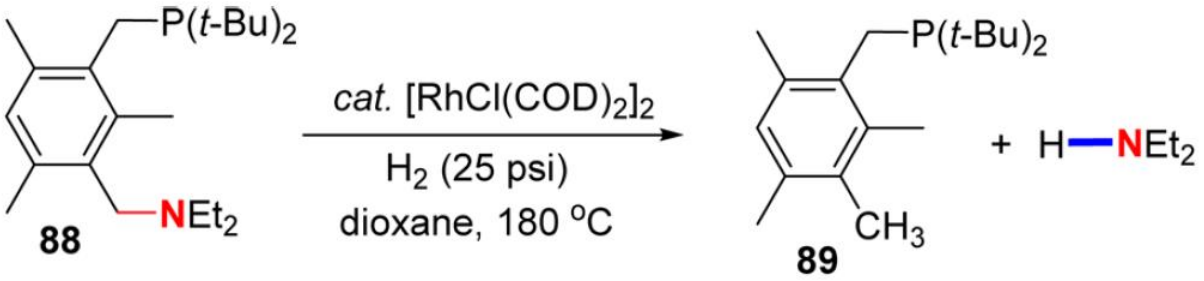


261

17-76%
(7 examples)

$B_2(nep)_2$





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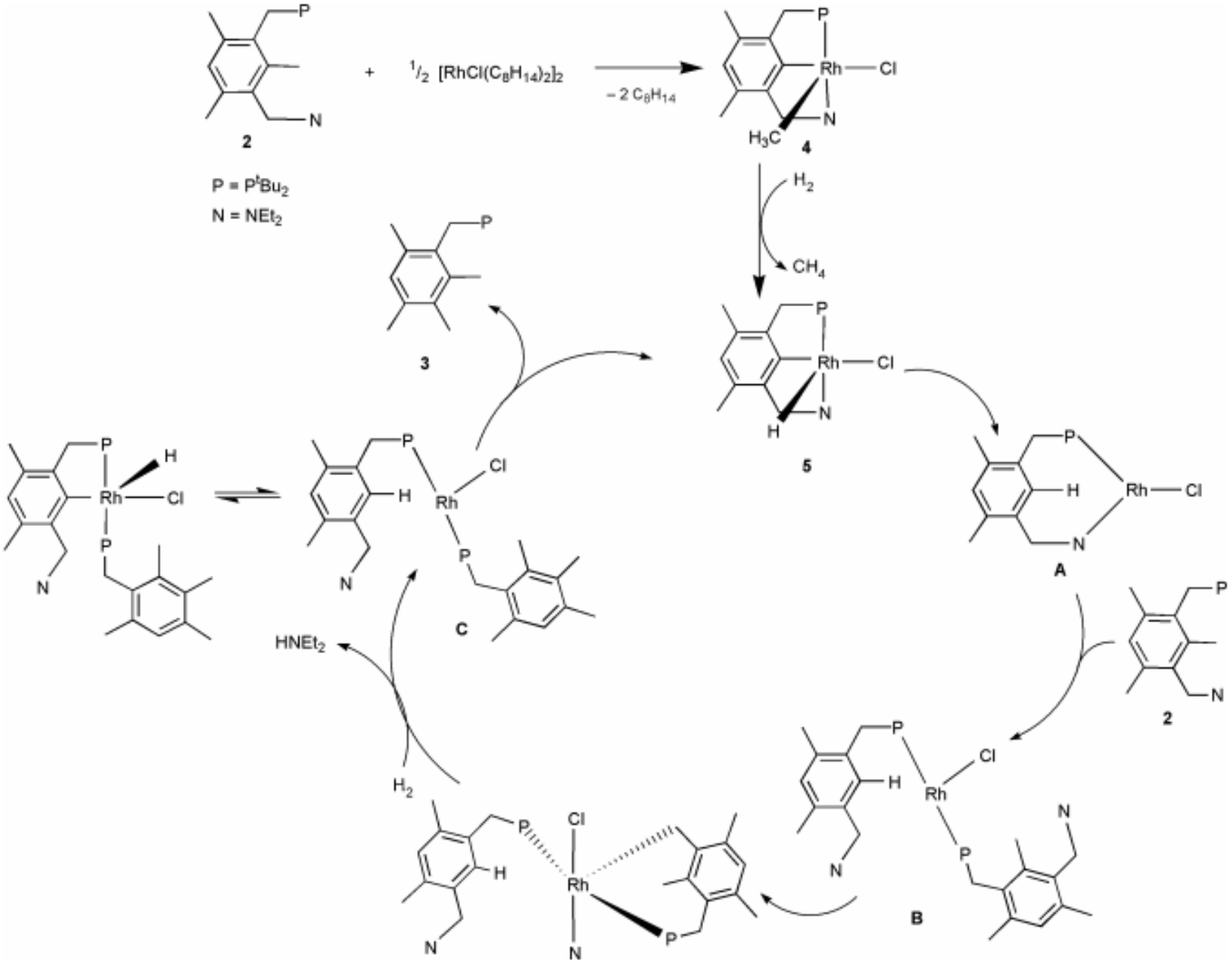

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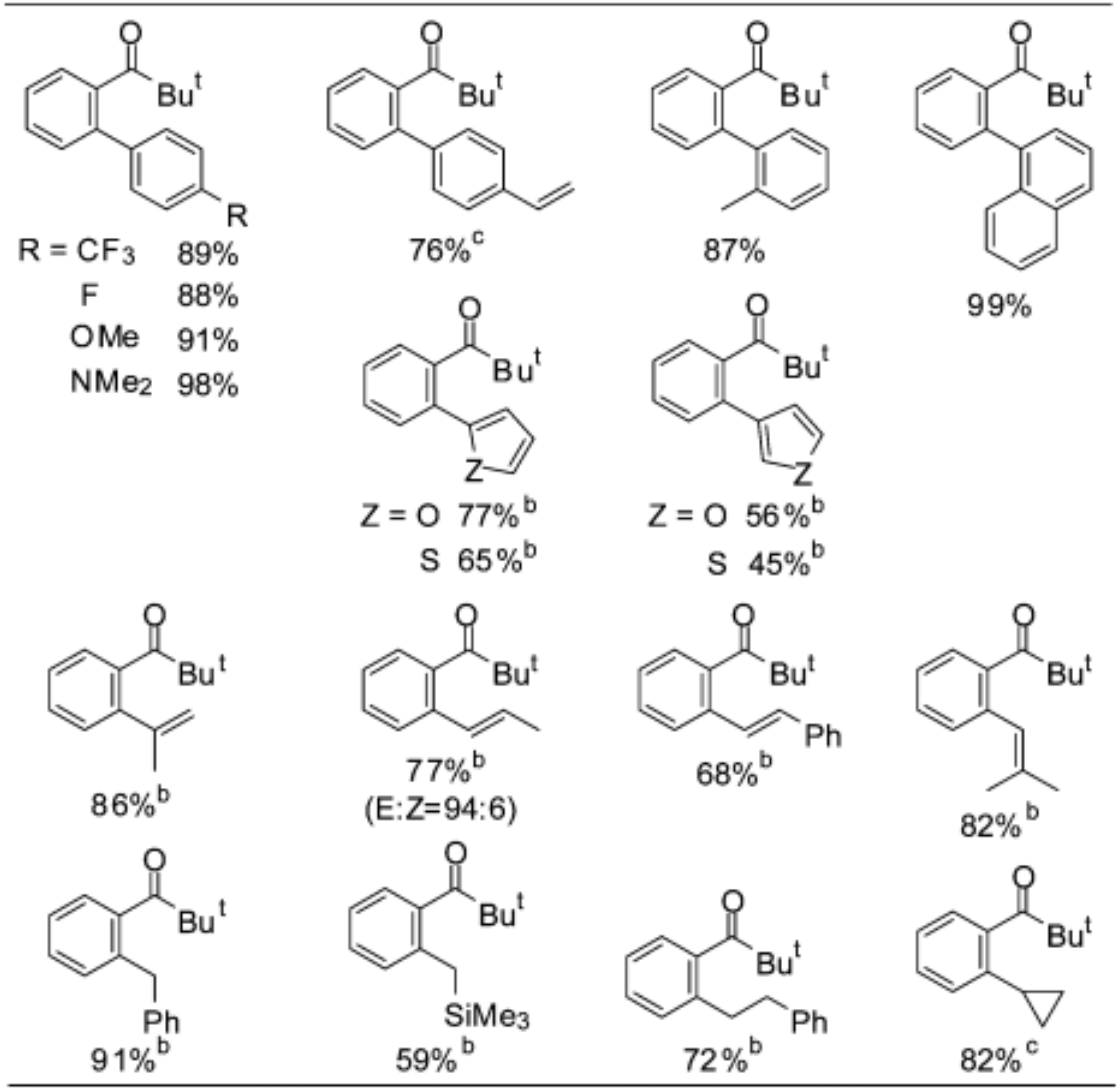

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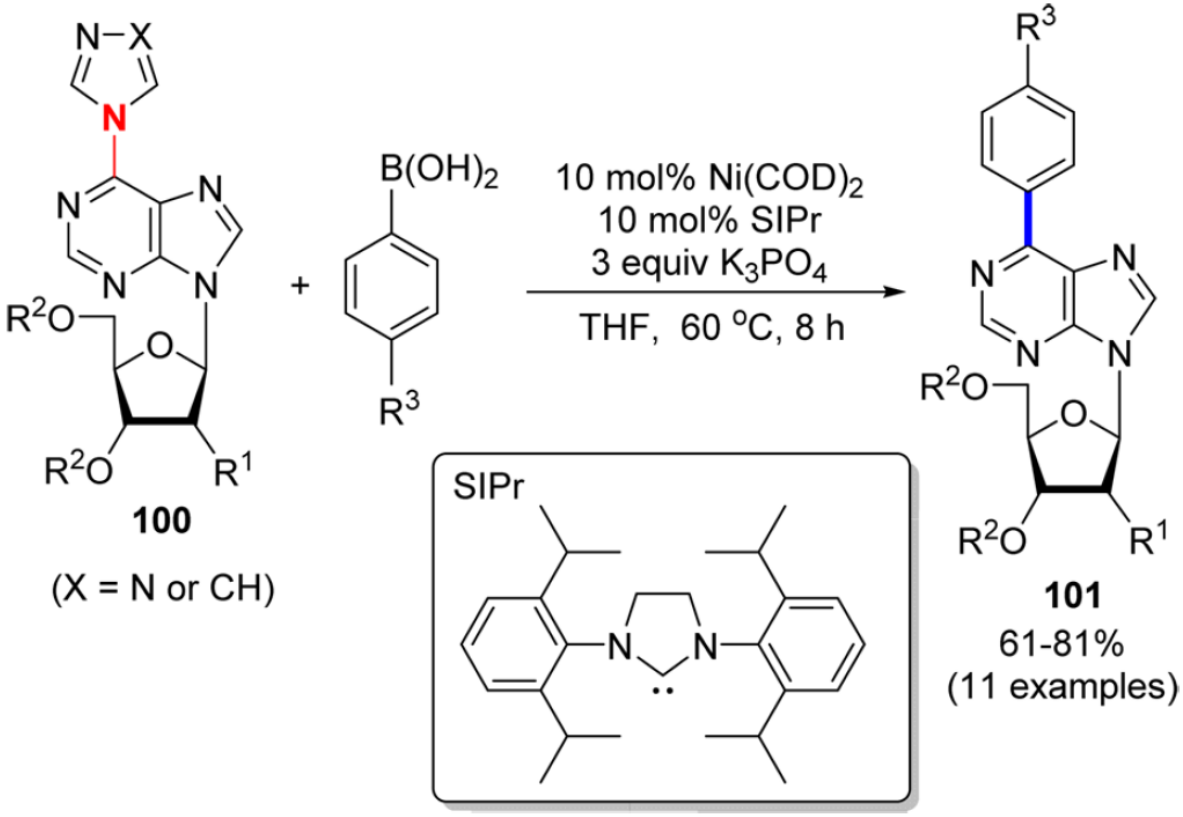

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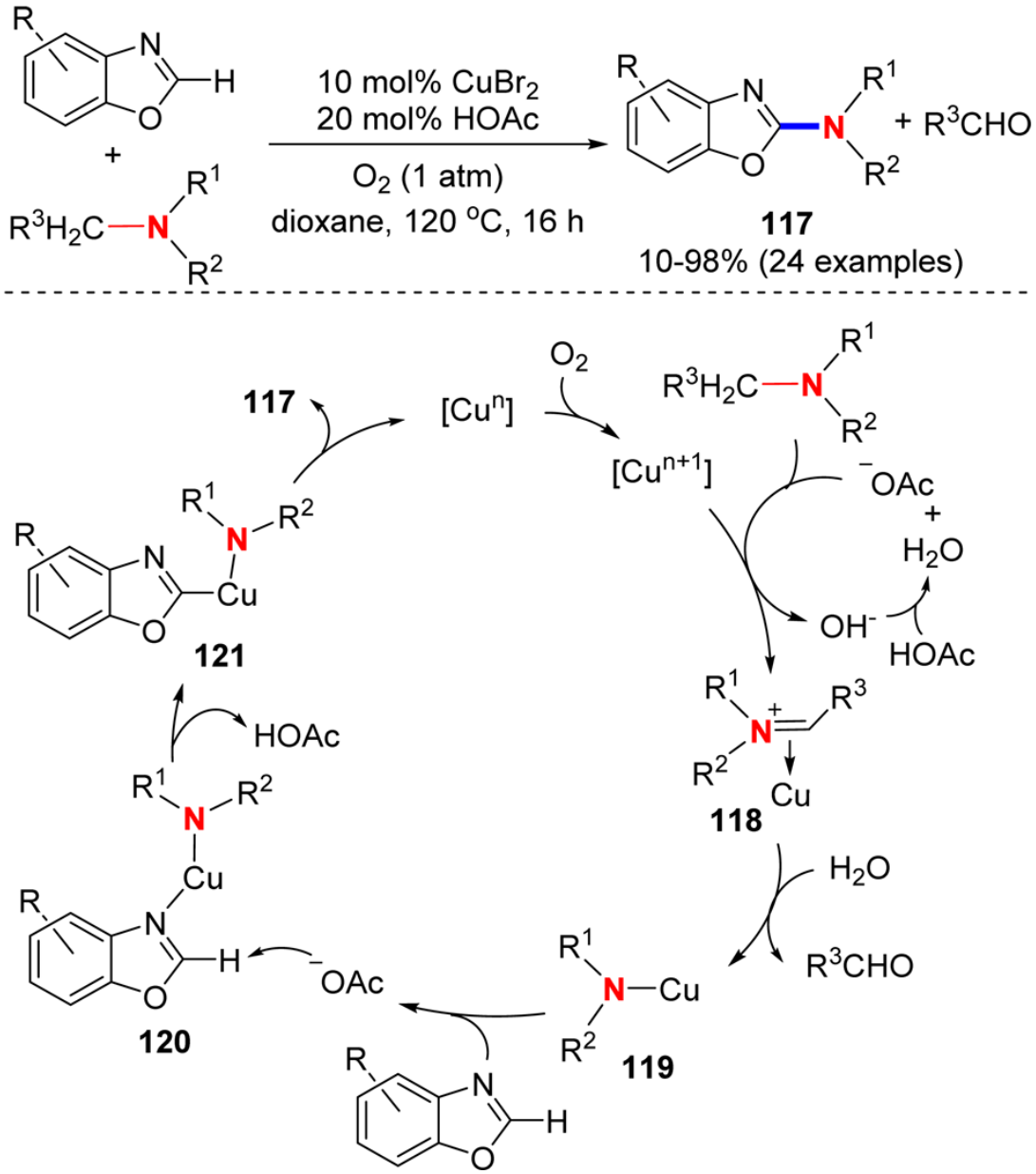

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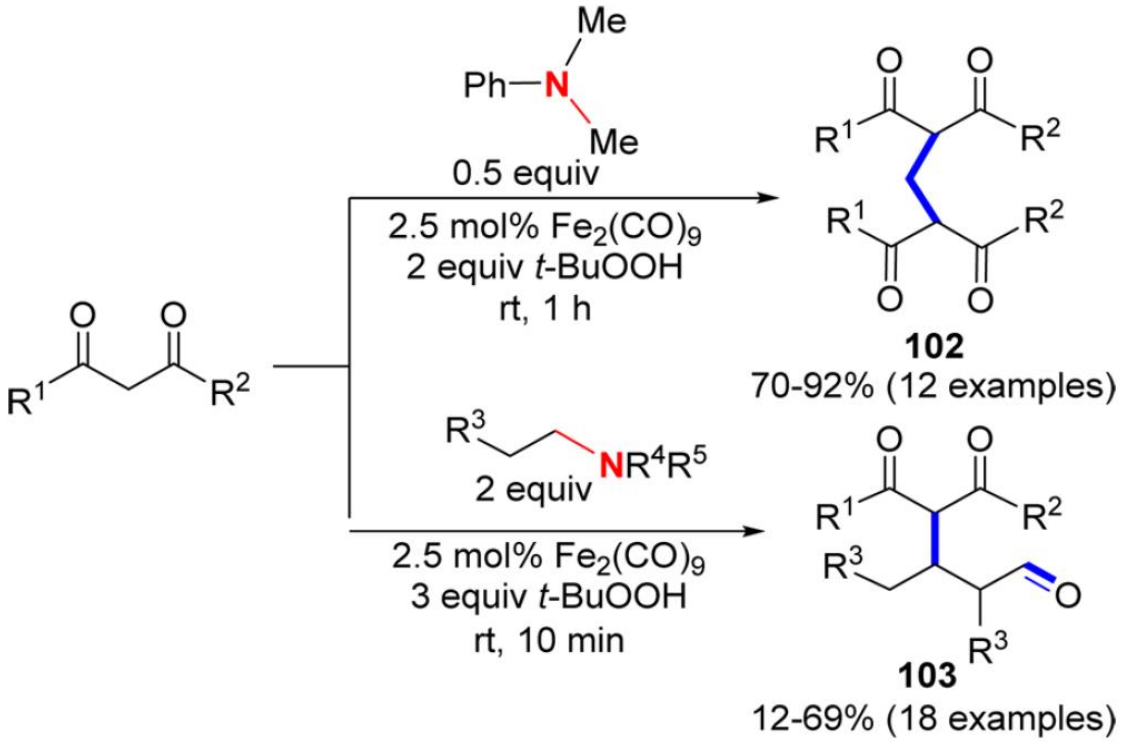

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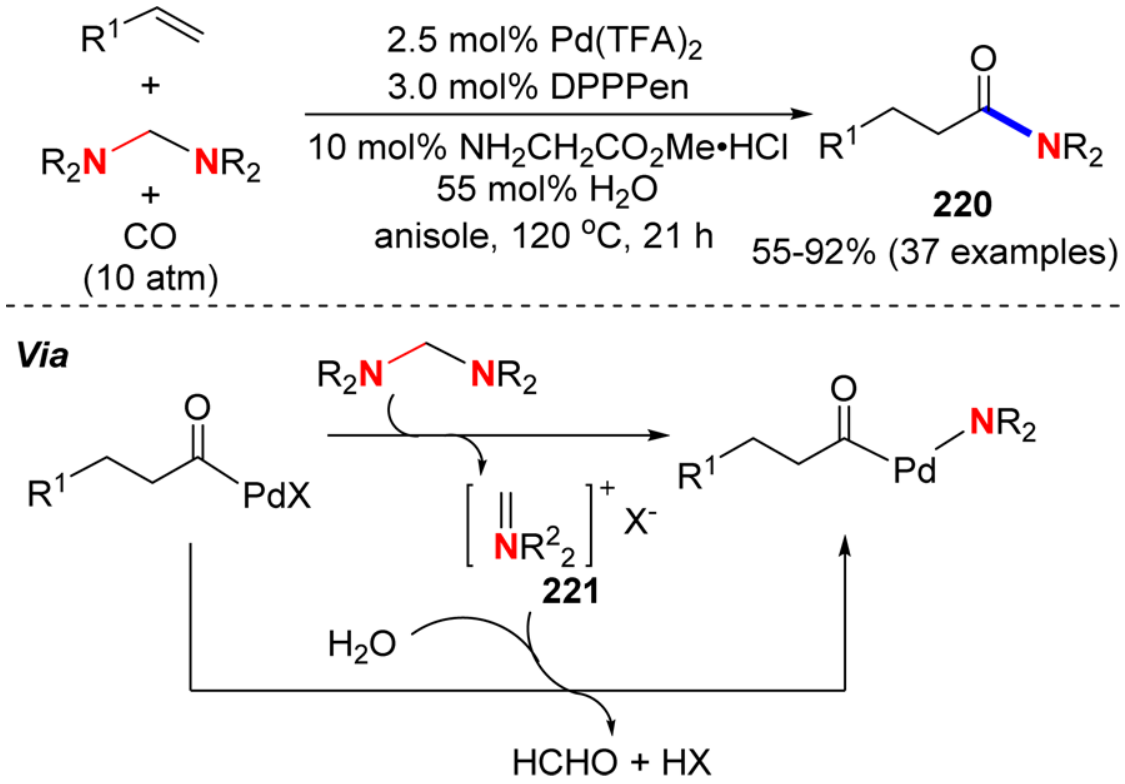

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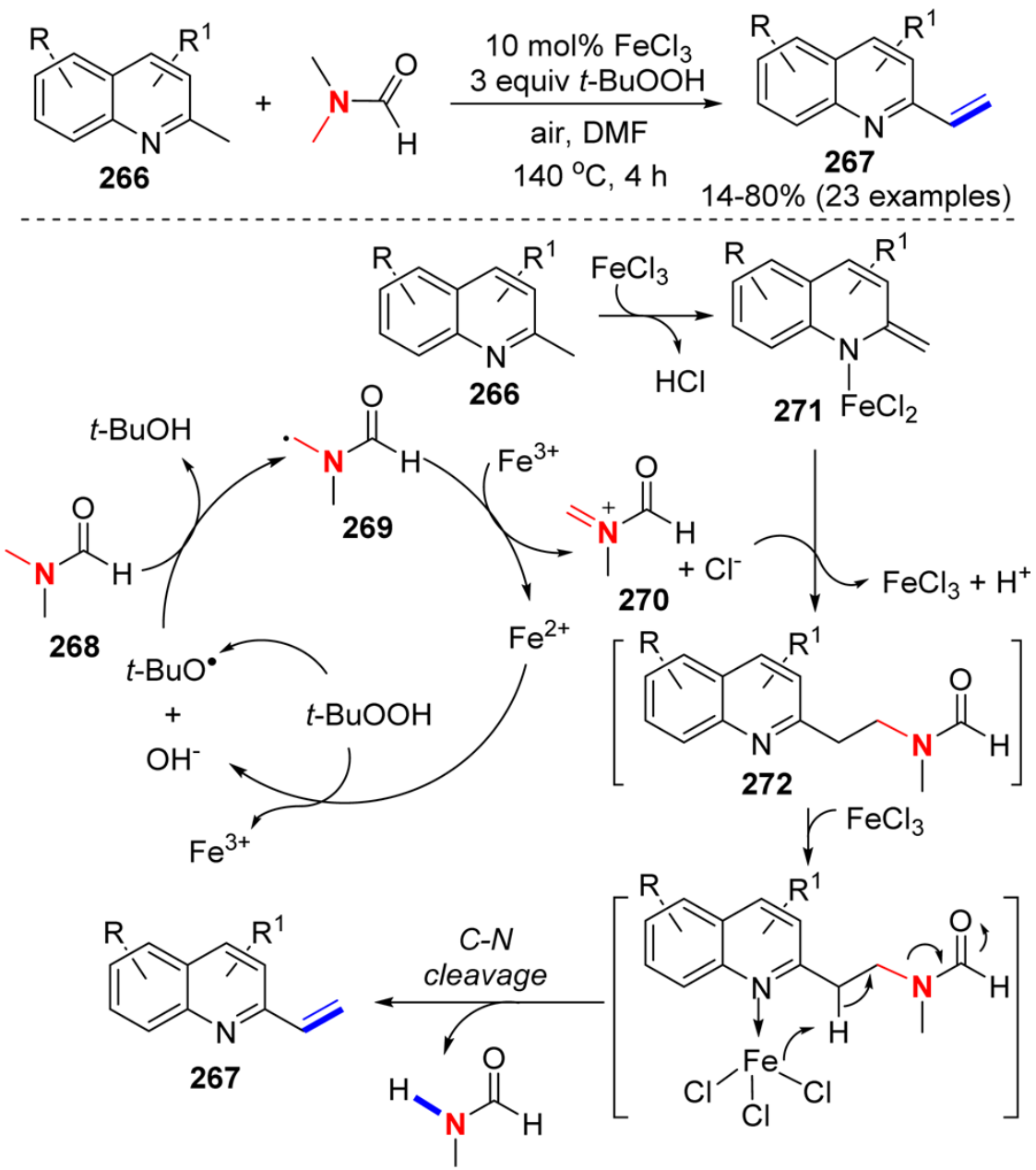

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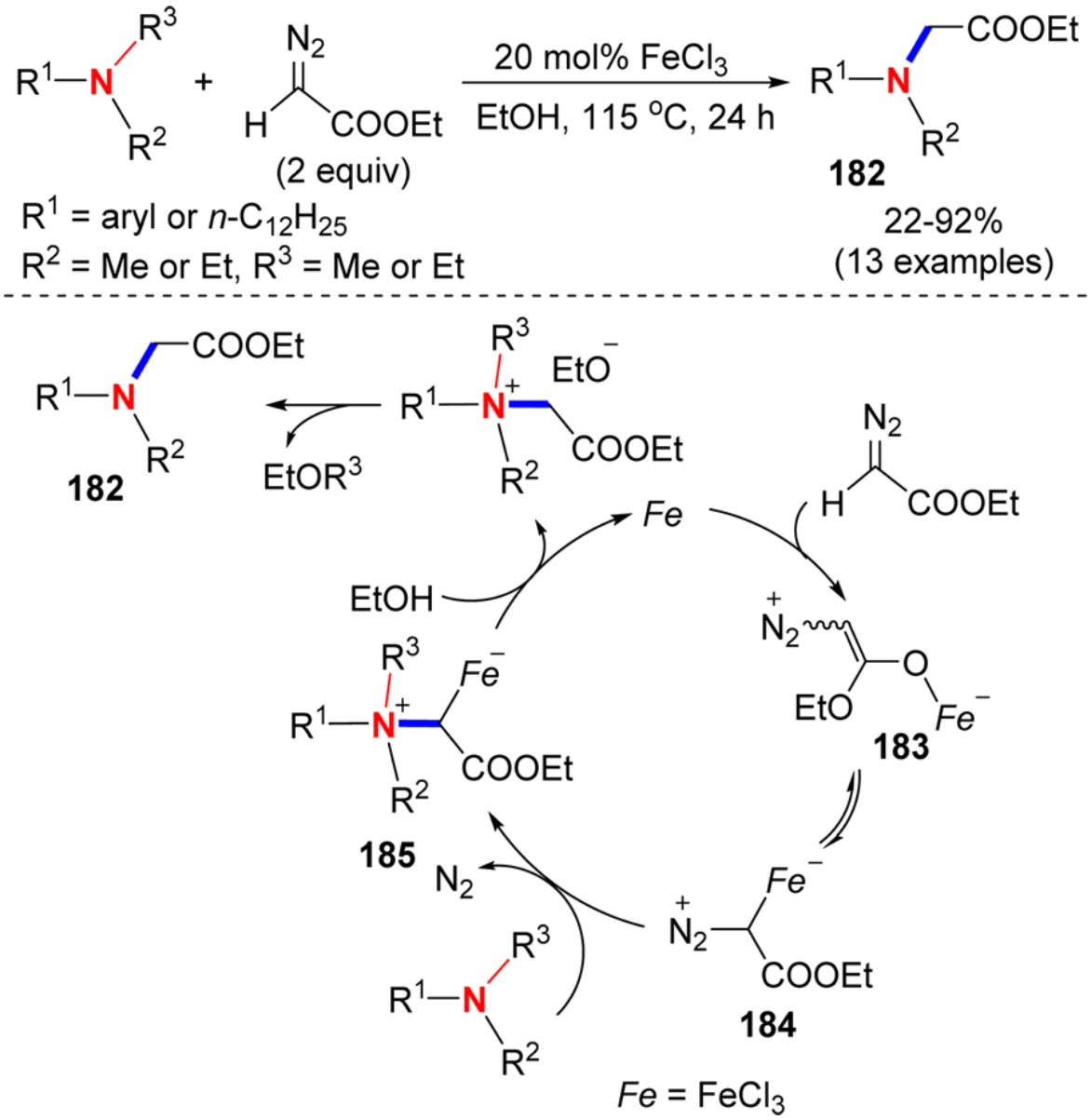

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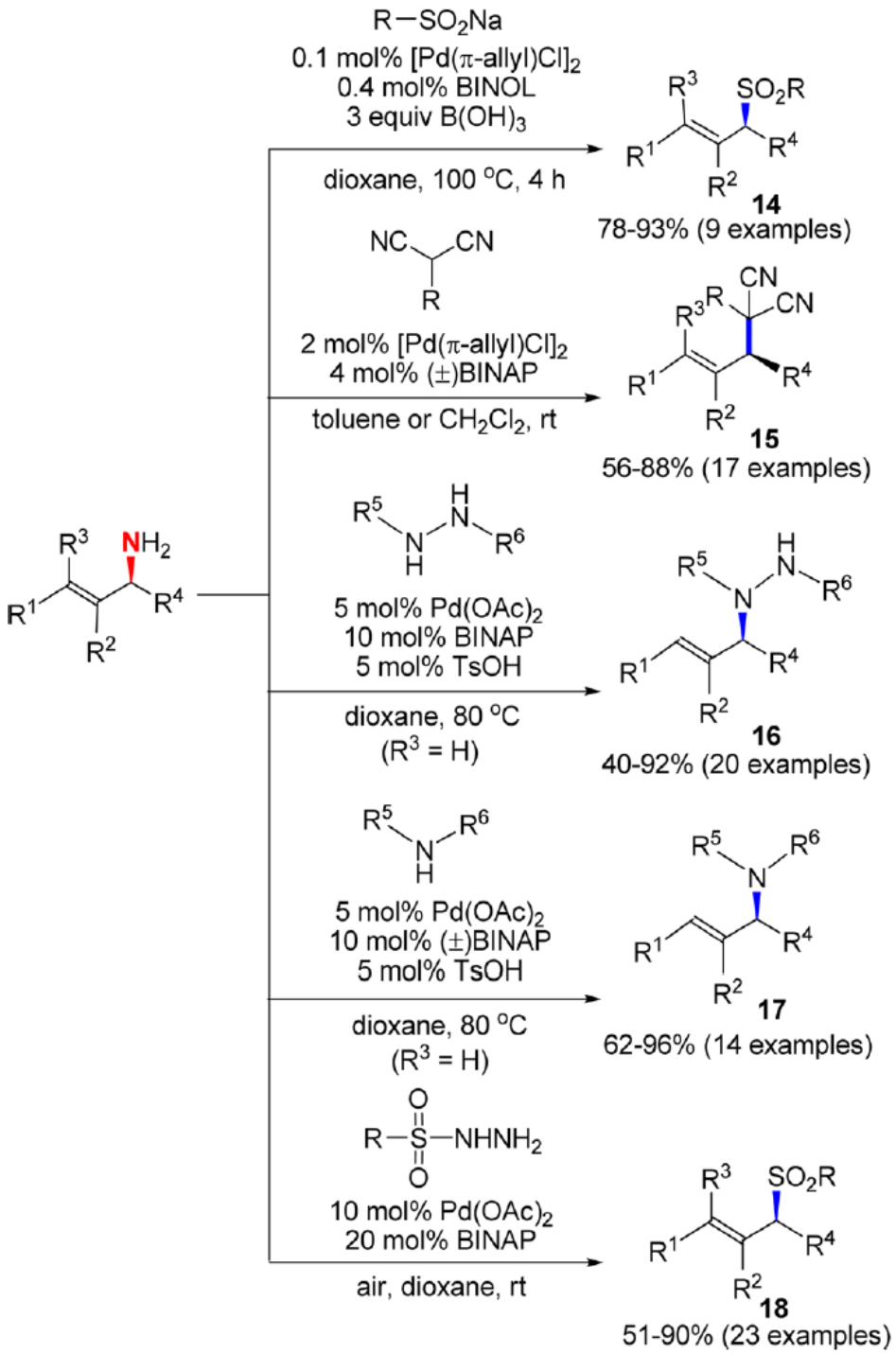

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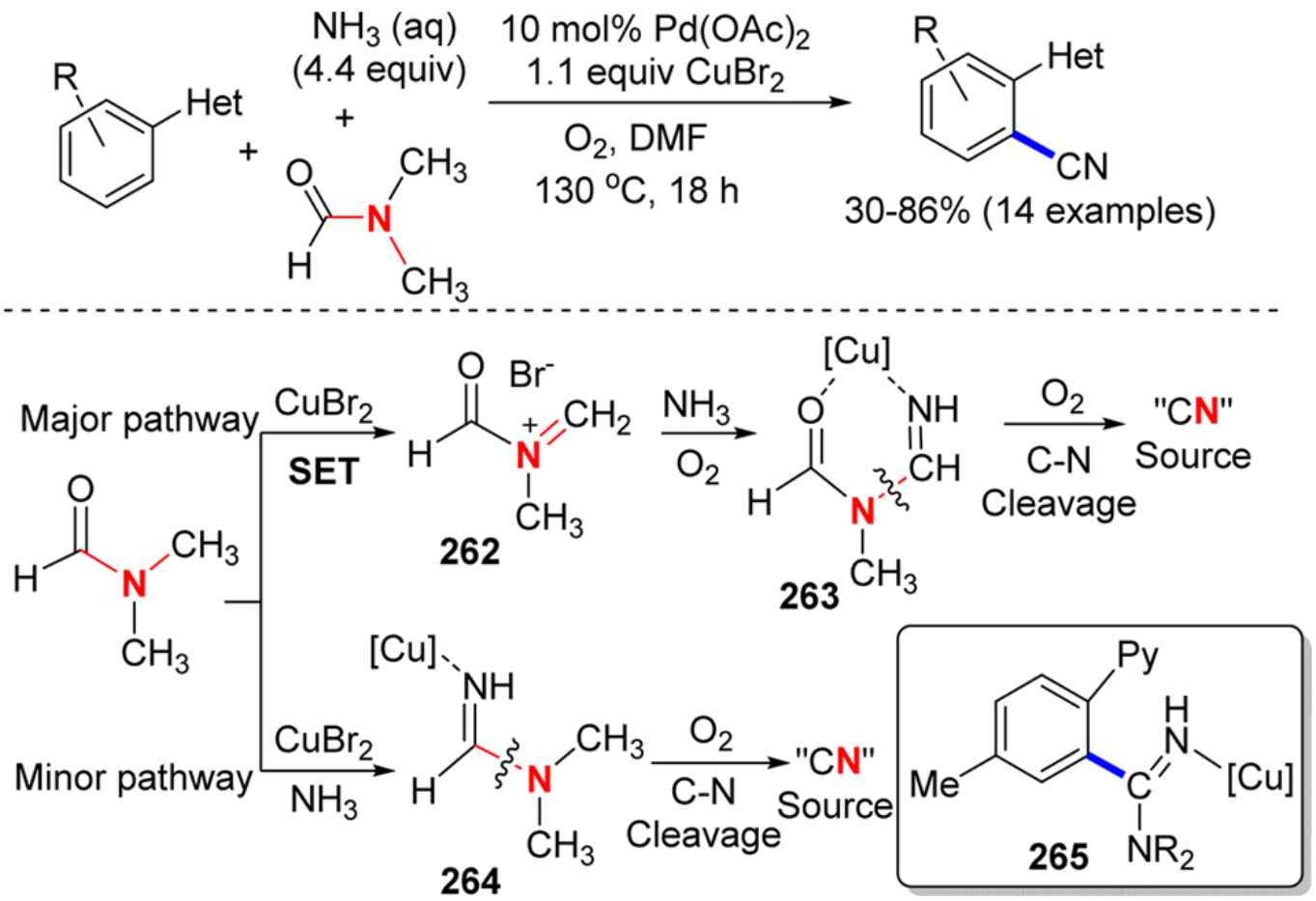
Non-Carbonyl C–N Bond Cleavage *via Imine or Iminiums*



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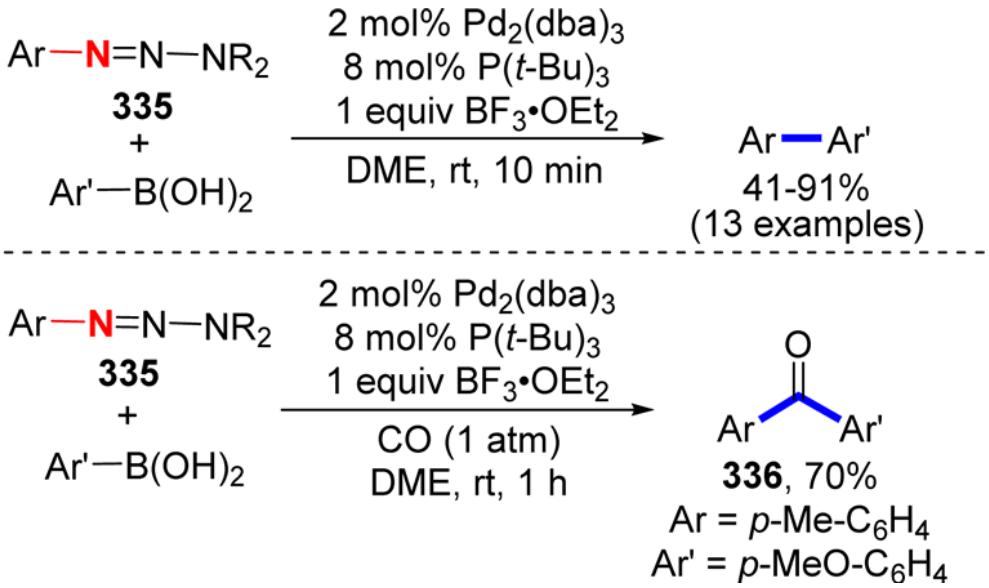
Triazenes



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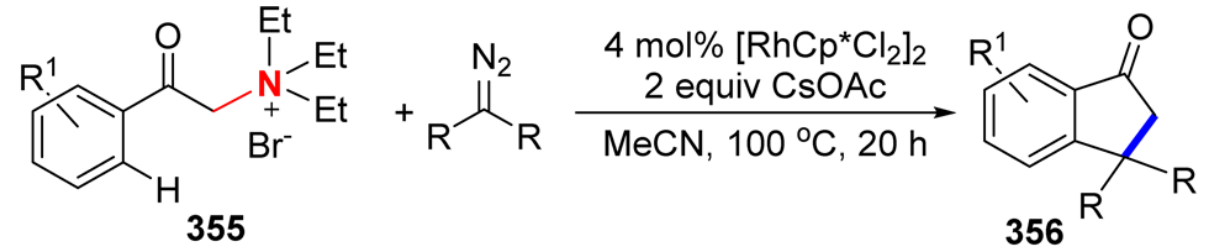

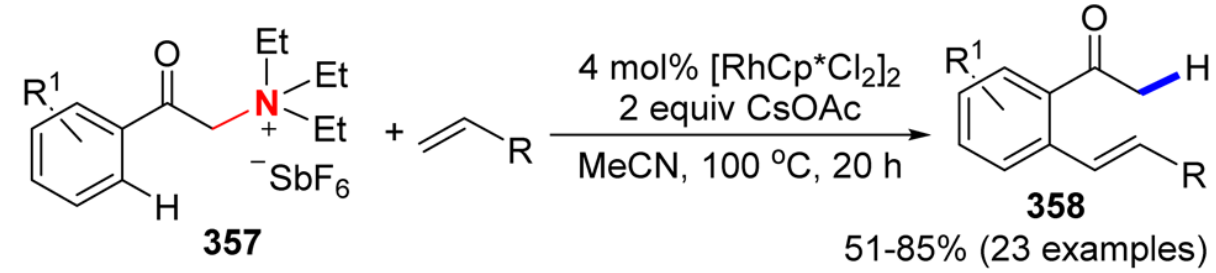

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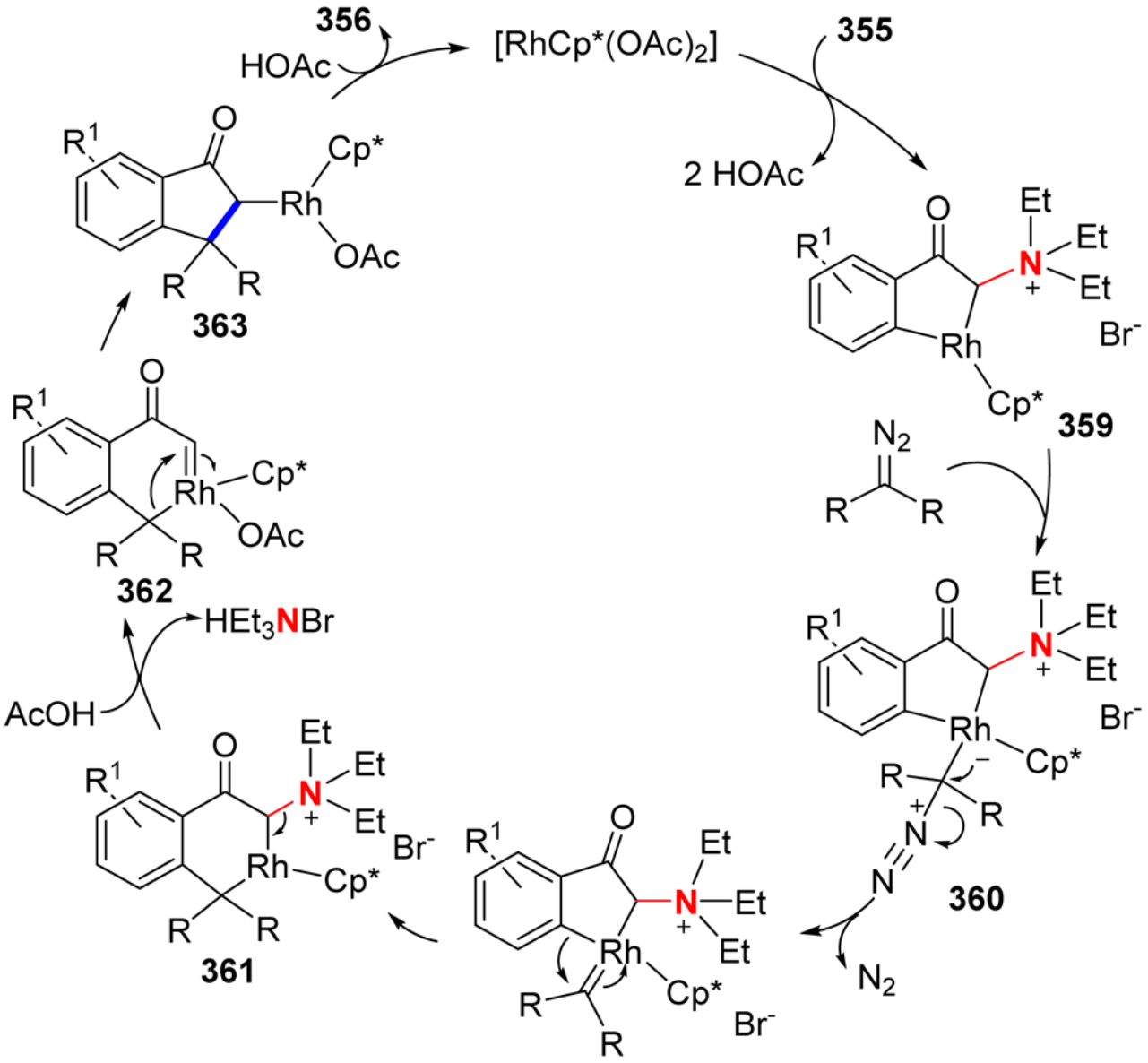

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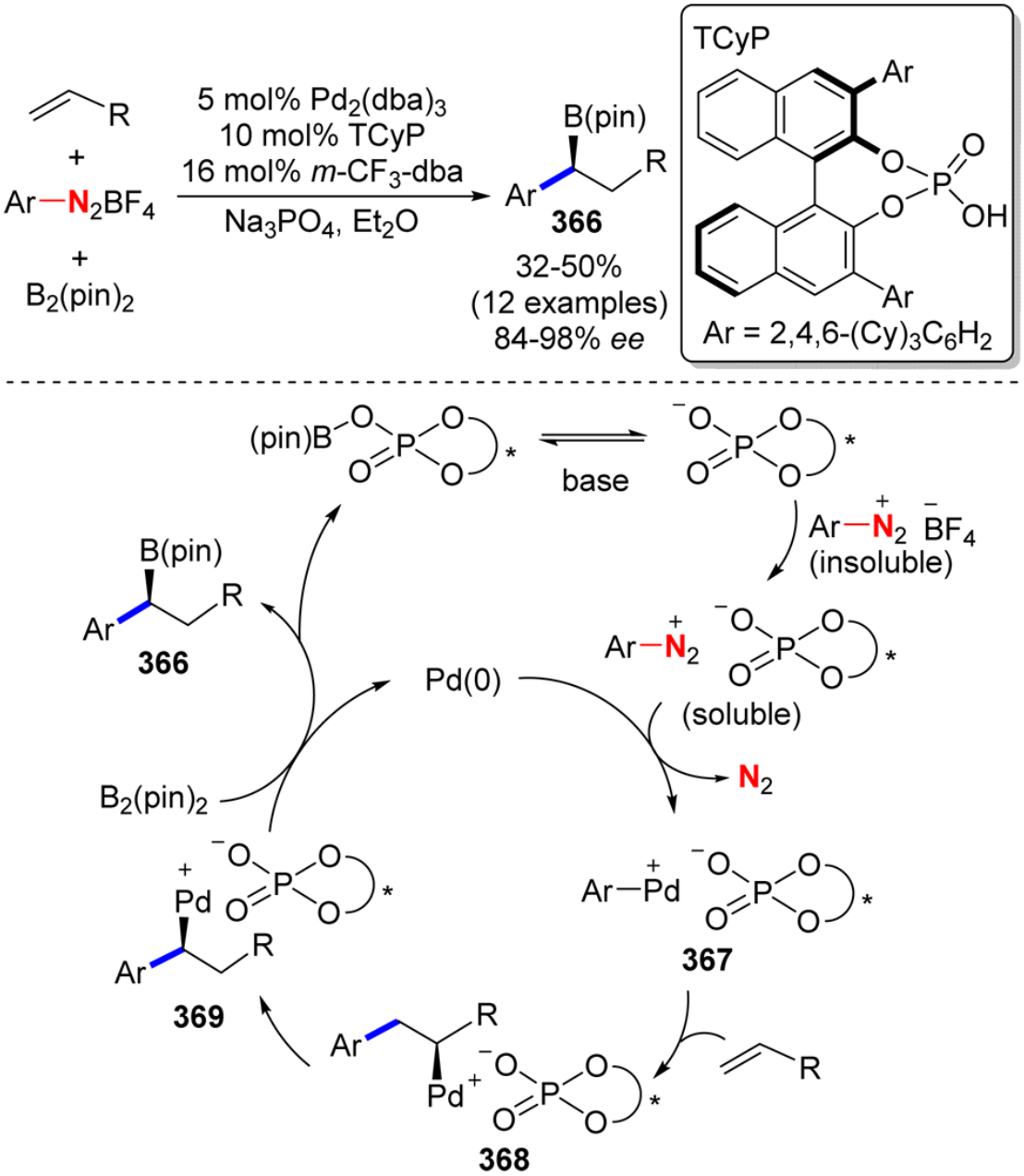

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