Rhodium-Catalyzed Xanthone Formation from 2-Aryloxybenzaldehydes via Cross-Dehydrogenative Coupling

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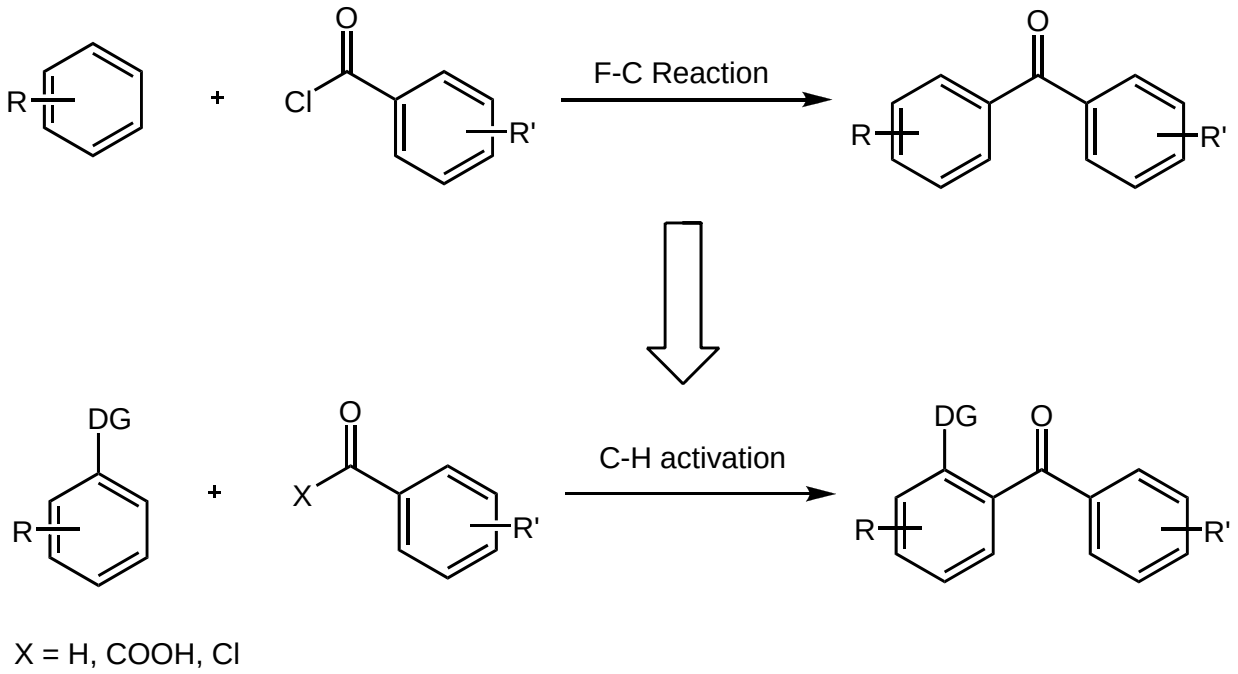
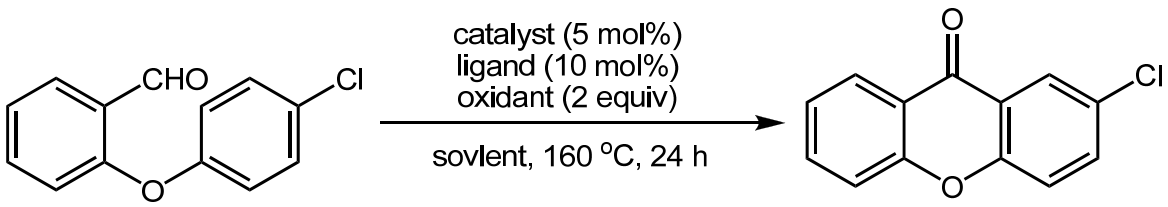
Li, C.-J. et al. *Org. Lett.* **2012**, *14*, 902

引言

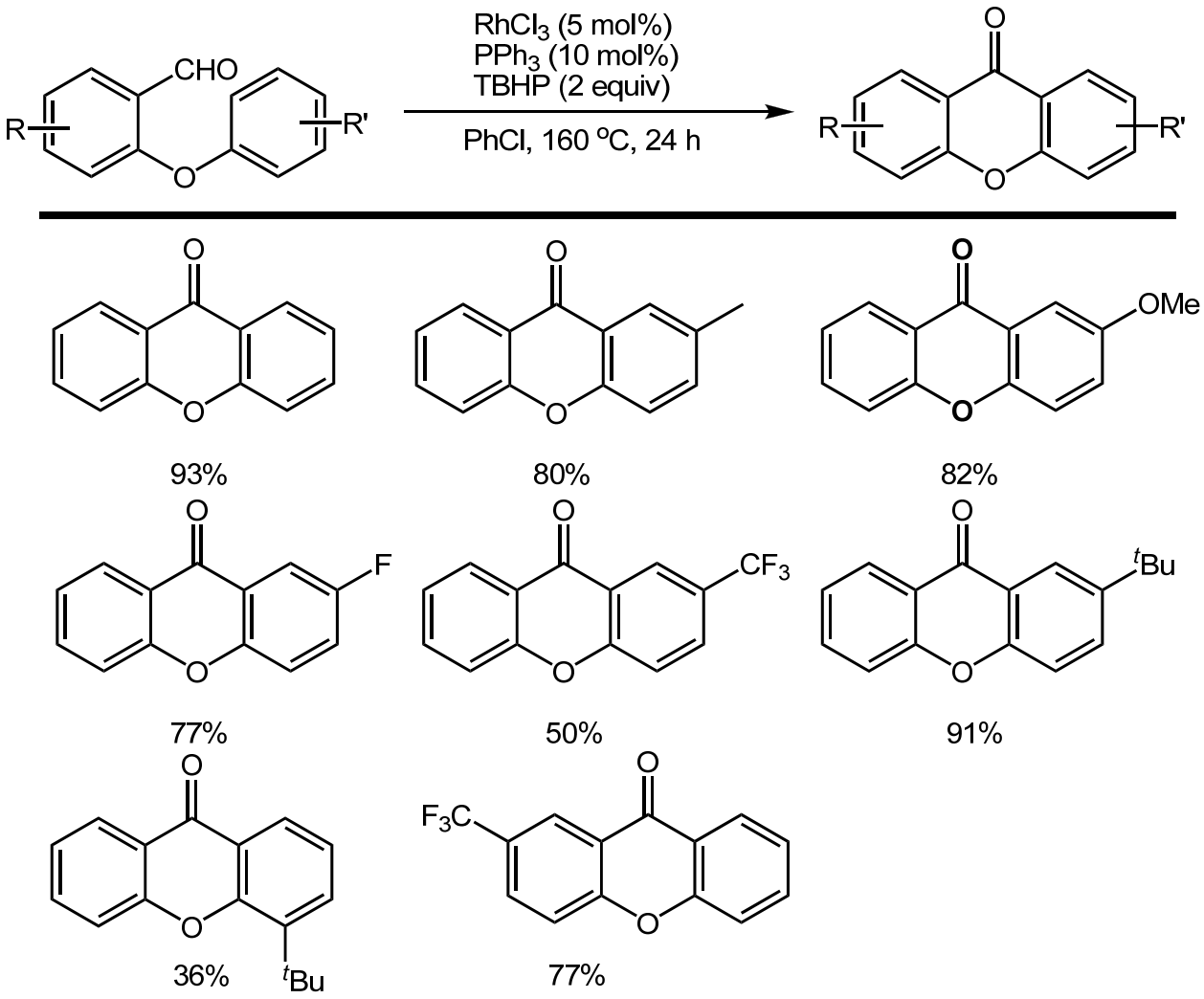


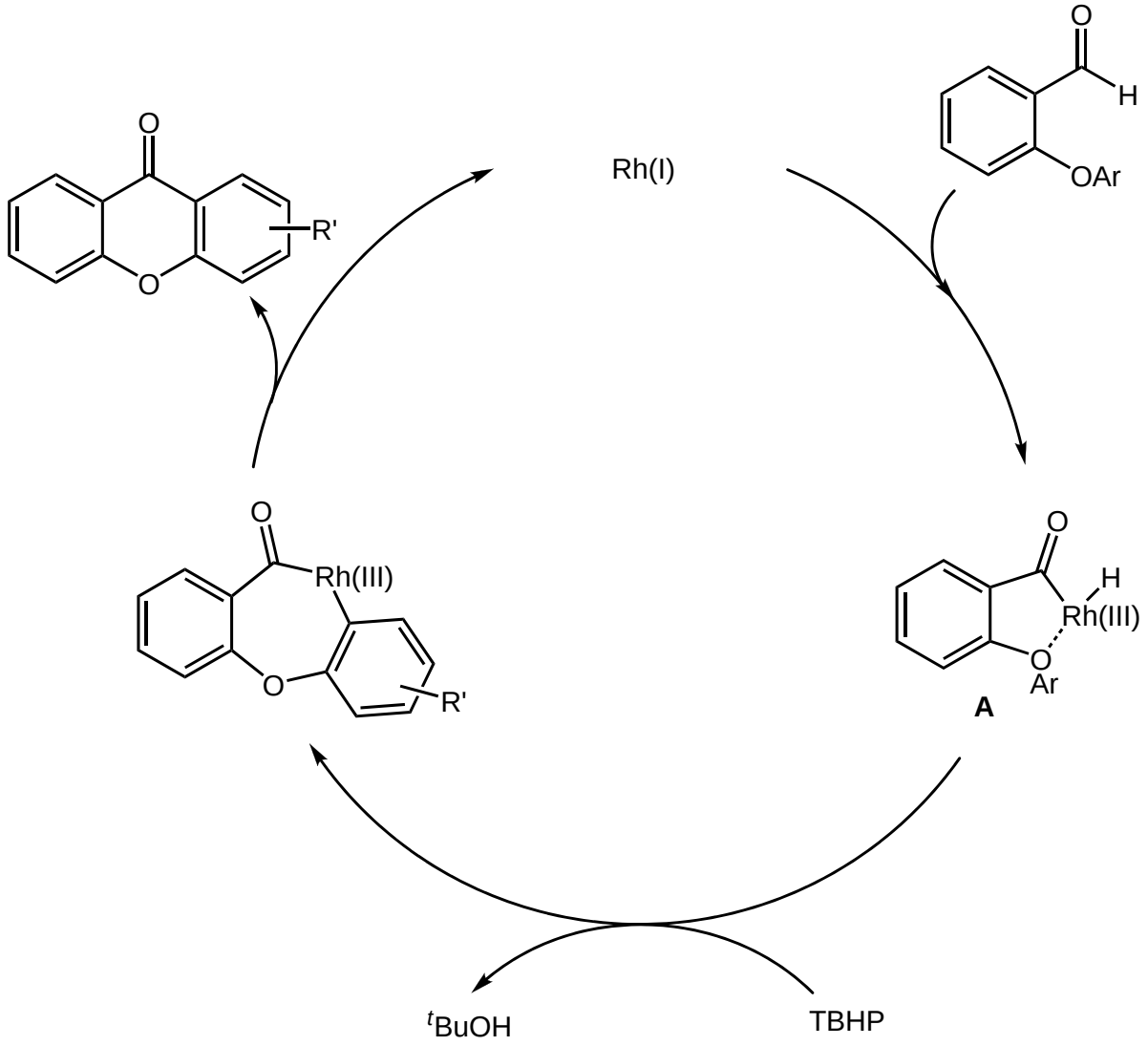
X = H, COOH, Cl

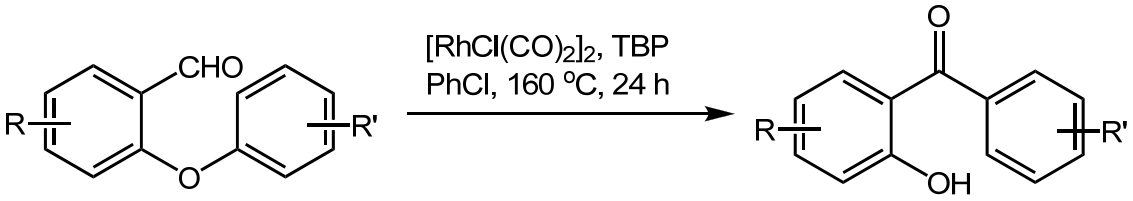
Rh



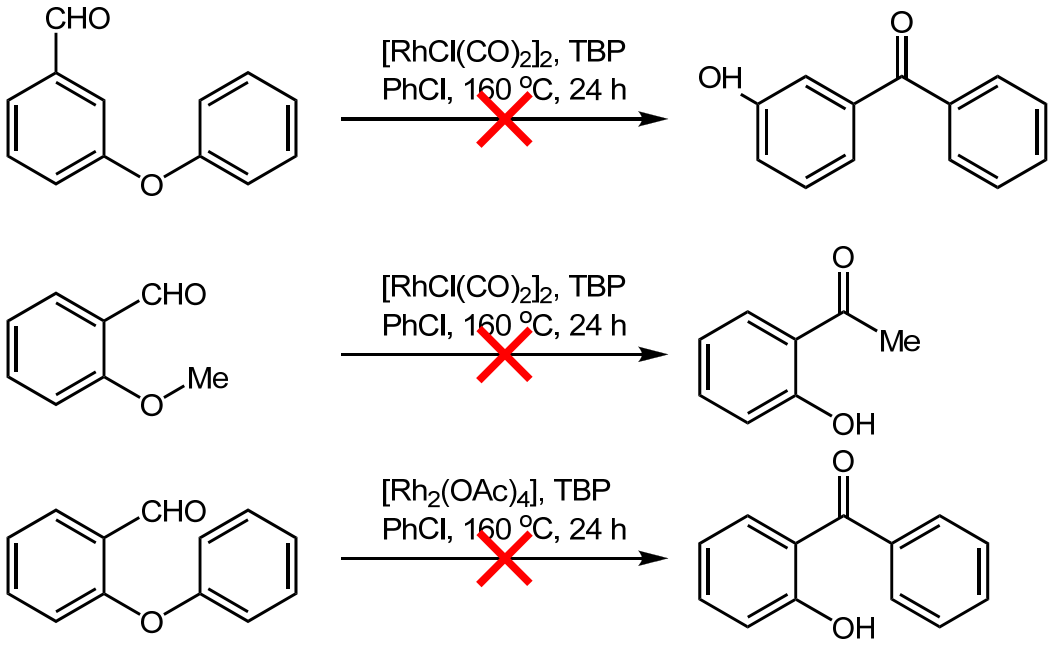
Entry	Cat.	Ligand	Solvent	Oxidant	Yield (%)
1	$[RhCl(COD)]_2$	-	PhCl	TBHP	16
2	$RhCl_3$	-	PhCl	TBHP	49
3	$RhCl_3$	PPh_3	PhCl	TBHP	54
4	$RhCl_3$	dppe	PhCl	TBHP	50
5	$RhCl_3$	PPh_3	Toluene	TBHP	50
6	$RhCl_3$	PPh_3	DCE	TBHP	45
7	$RhCl_3$	PPh_3	PhCl	TBP	20


RhCl3 (5 mol%)
PPh3 (10 mol%)
TBHP (2 equiv)
PhCl, 160 °C, 24 h
CHO
R
R'
O
OMe
F
CF3
tBu
F3C
93%
80%
82%
77%
50%
91%
36%
77%

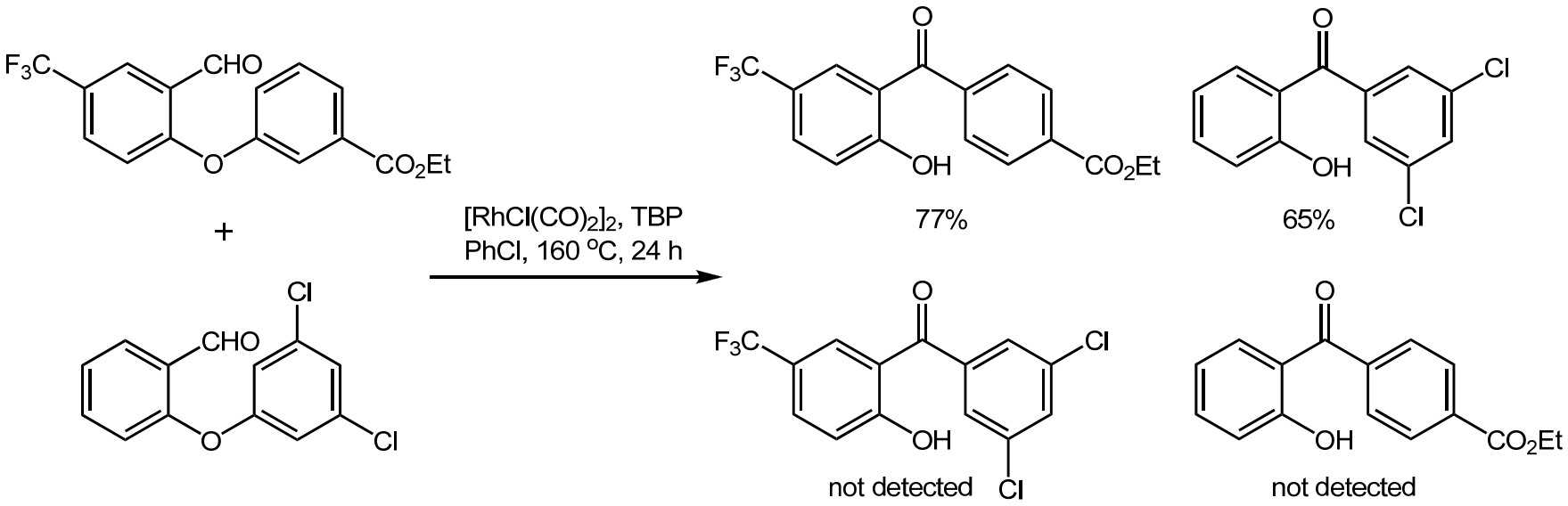

Rh(I)
O
H
OAr
O
Rh(III)
H
O
Ar
A
O
Rh(III)
O
R'
O
R'
^{t}BuOH
TBHP

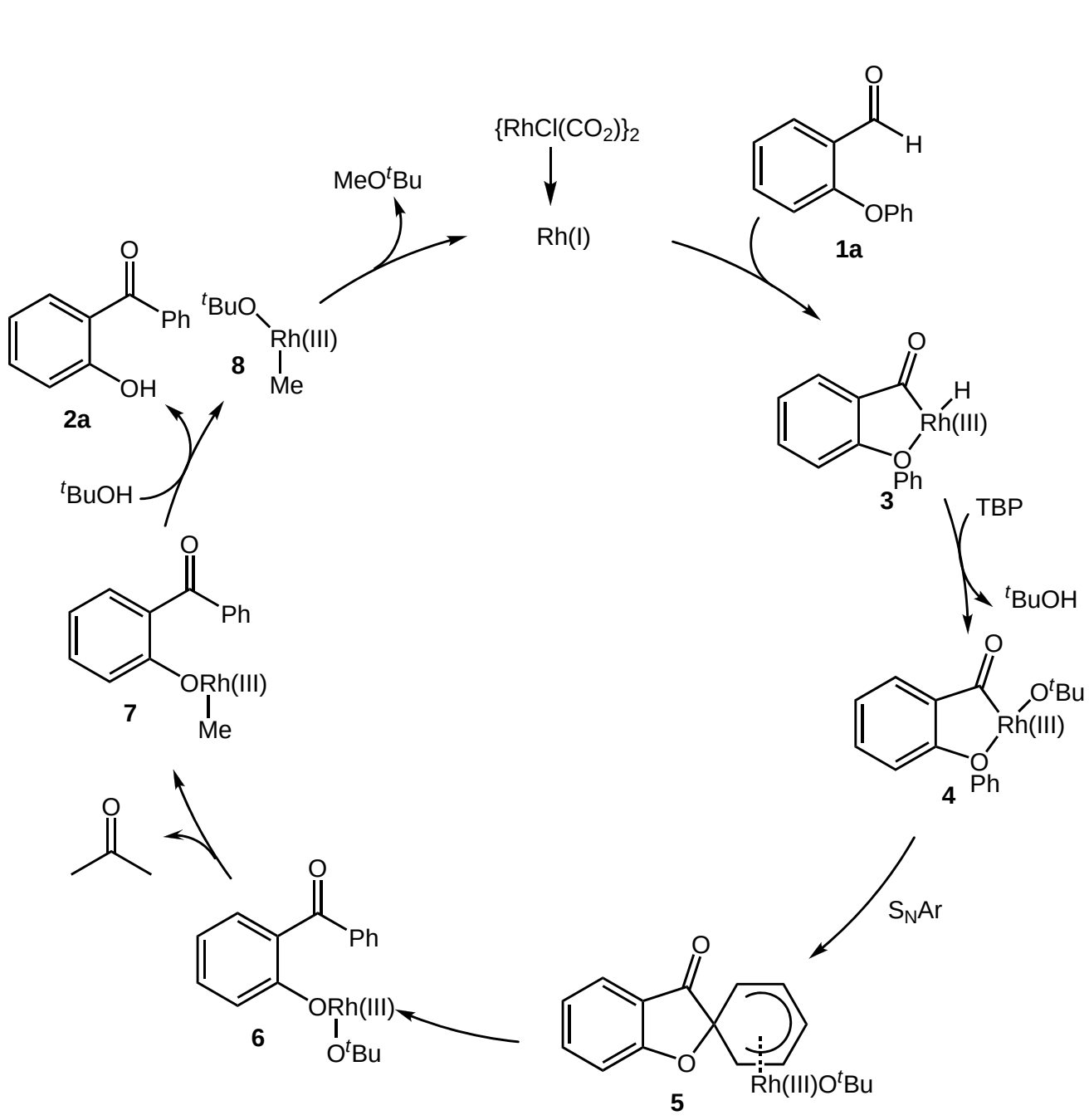


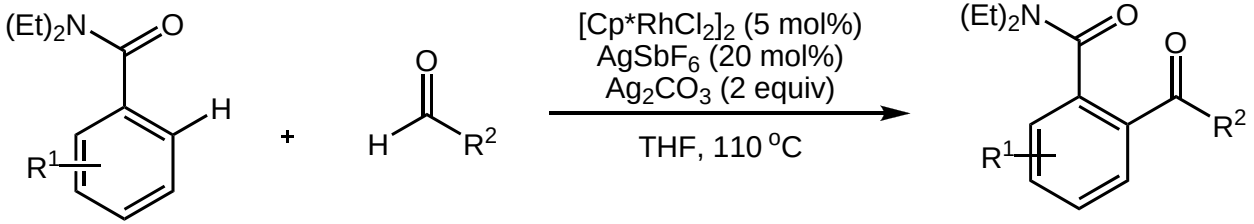
Investigation of the mechanistic pathway for the rearrangement



Li, C.-J. et al. *Angew. Chem., Int. Ed.* **2011**, *50*, 8936

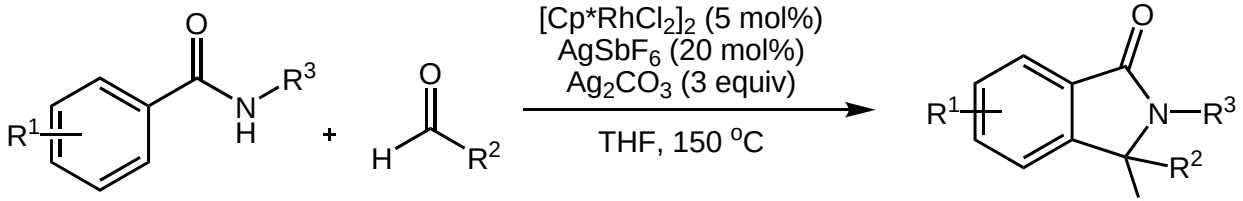

F3C
CHO
O
CO2Et
+
Cl
CHO
O
Cl
[RhCl(CO)2]2, TBP
PhCl, 160 °C, 24 h
O
F3C
OH
CO2Et
77%
O
Cl
OH
Cl
65%
O
F3C
Cl
OH
Cl
not detected
O
OH
CO2Et
not detected


{RhCl(CO2)}2
Rh(I)
MeOtBu
1a
2a
8
3
TBP
tBuOH
4
SNAr
5
6
7
tBuOH



up to 72% yield

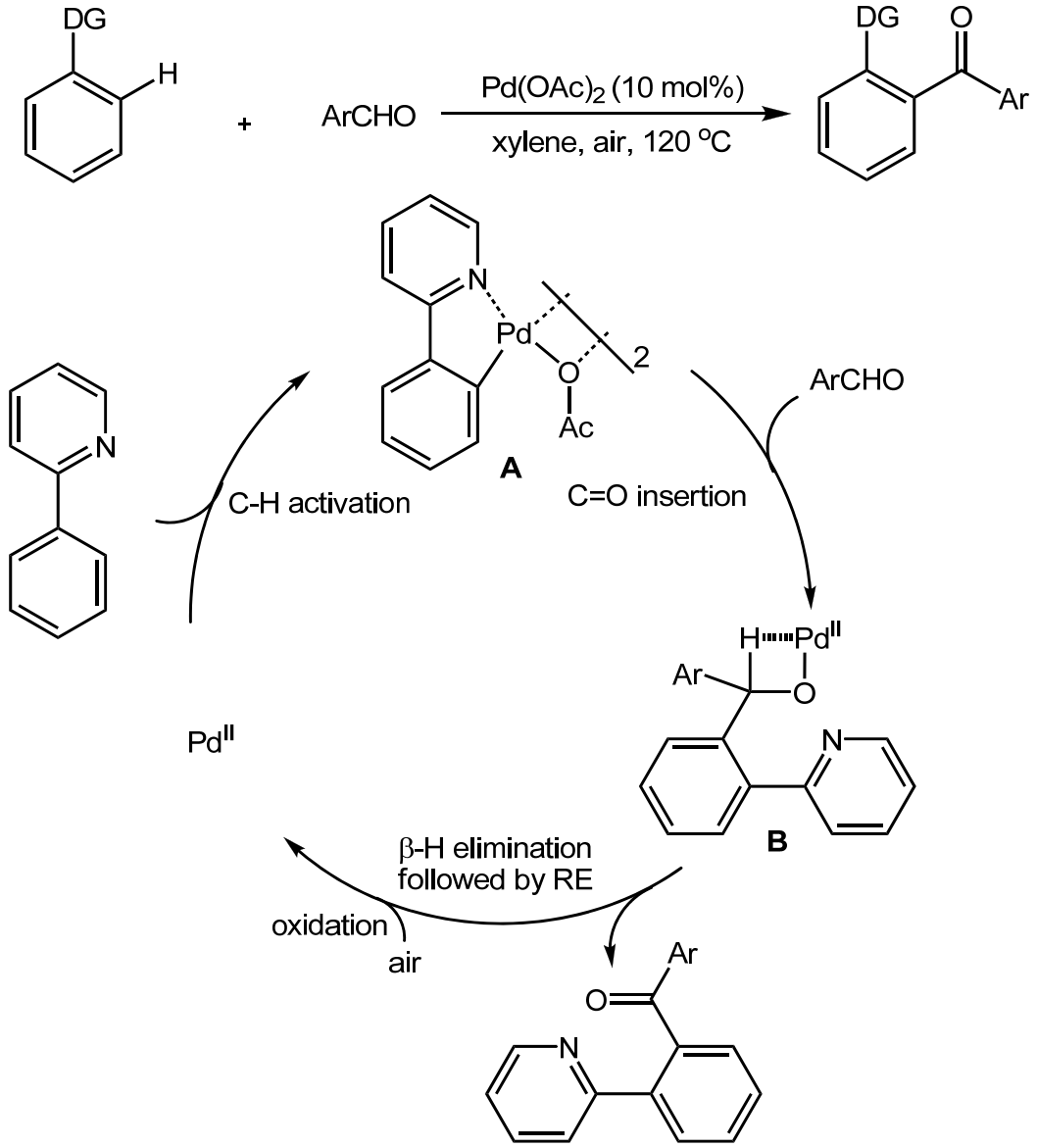
Kim, I. et al. *Org. Lett.* **2011**, *13*, 4390



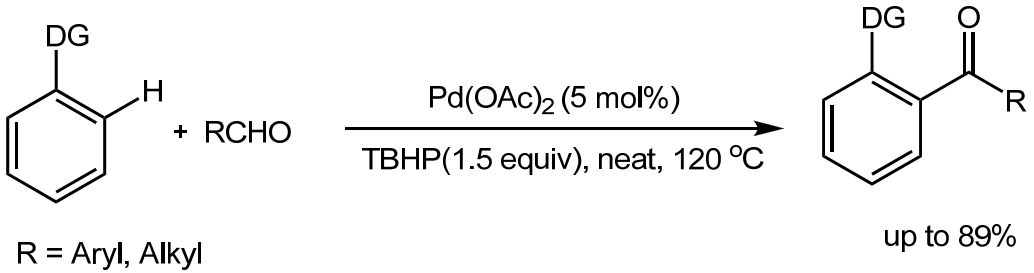
up to 83% yield

Kim, I. et al. *Org. Lett.* **2012**, *14*, 906

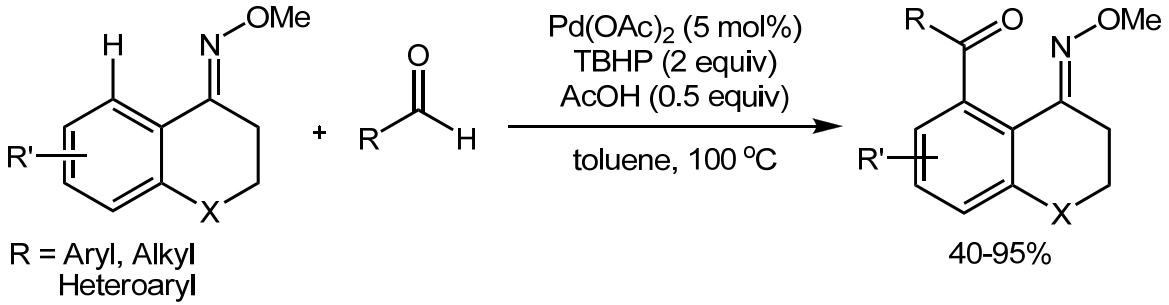
Pd



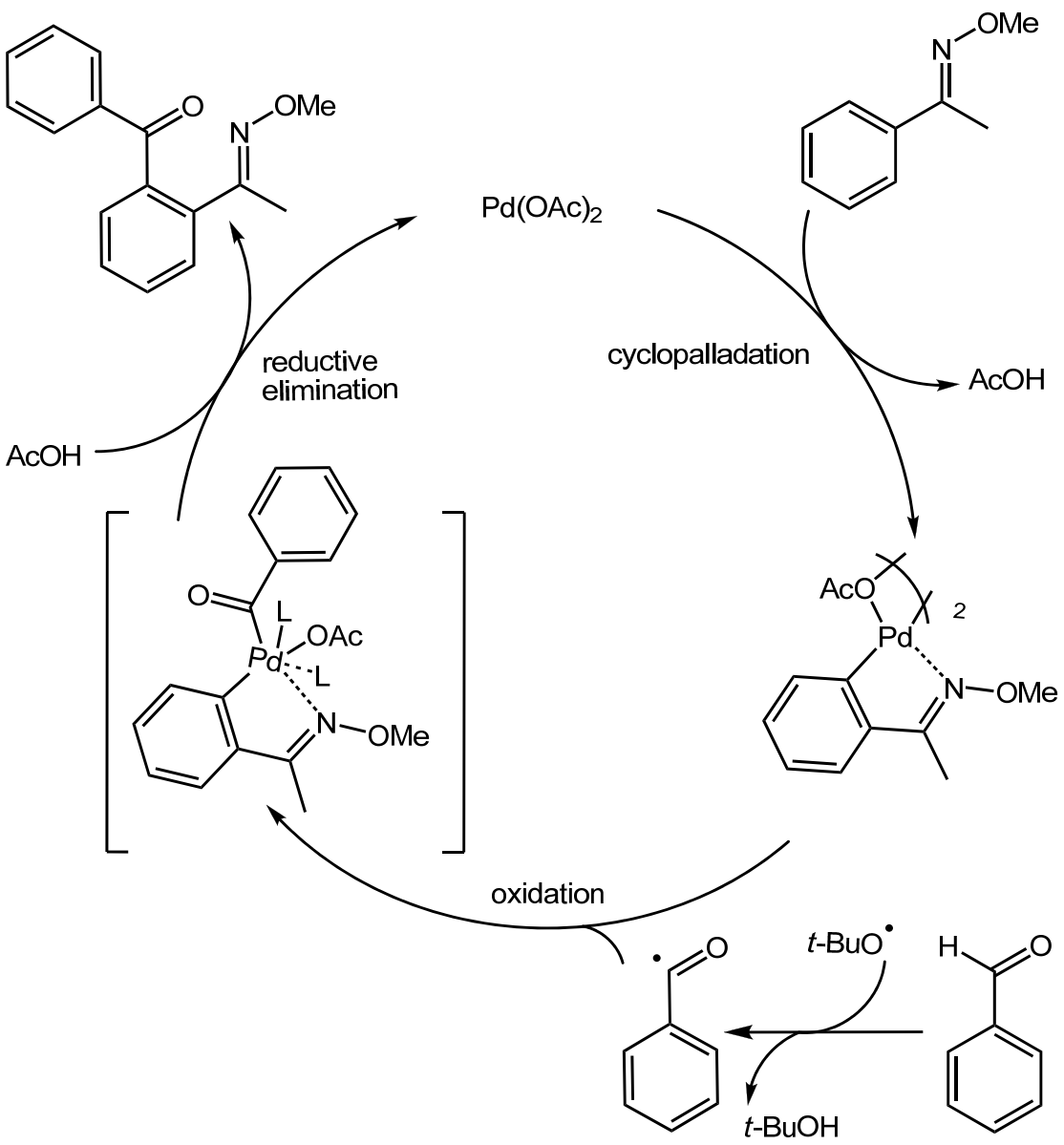
Cheng, J. et al. *Org. Lett.* **2009**, *11*, 3120

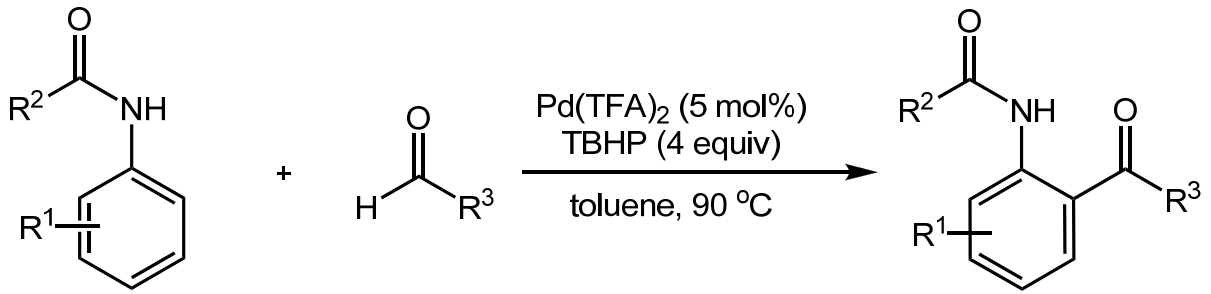


Li, C.-J. et al. *Adv. Synth. Catal.* **2010**, *352*, 1145

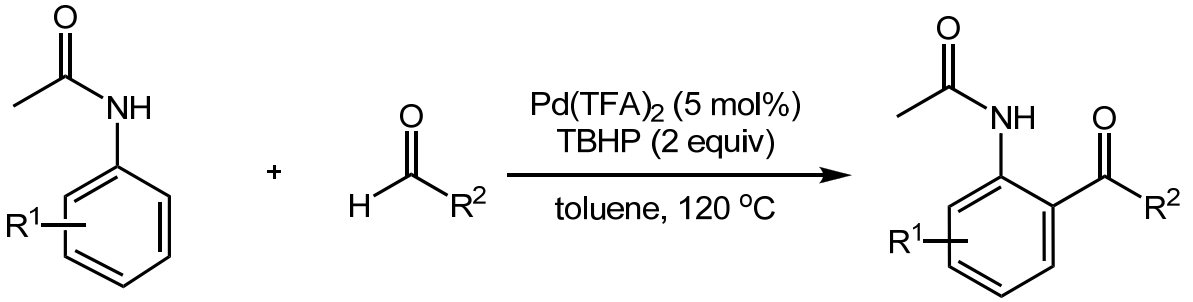


Yu, W.-Y. et al. *Org. Lett.* **2010**, *12*, 3926

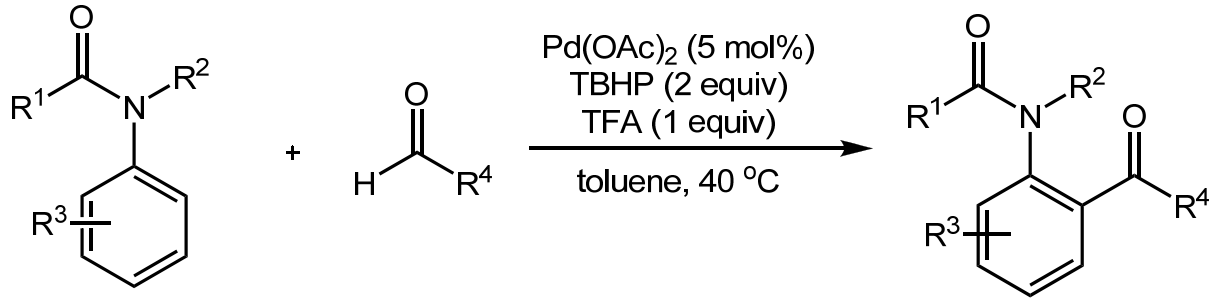

Pd(OAc)2
cyclopalladation
AcOH
reductive
elimination
AcOH
oxidation
t-BuO
t-BuOH



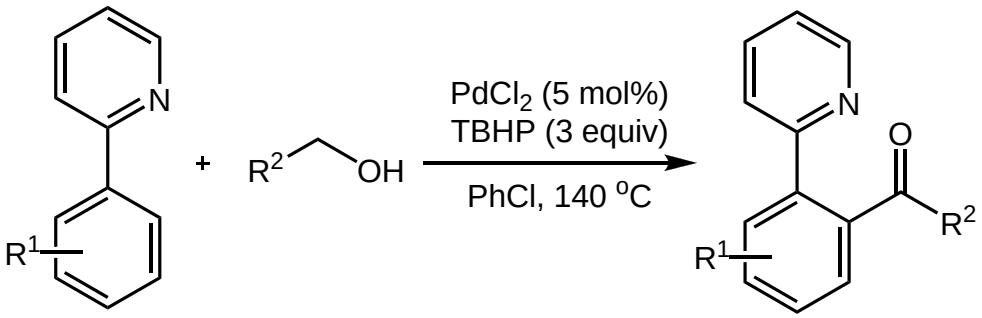
Wang, L. et al. *Chem. Eur. J.* **2011**, *17*, 10208



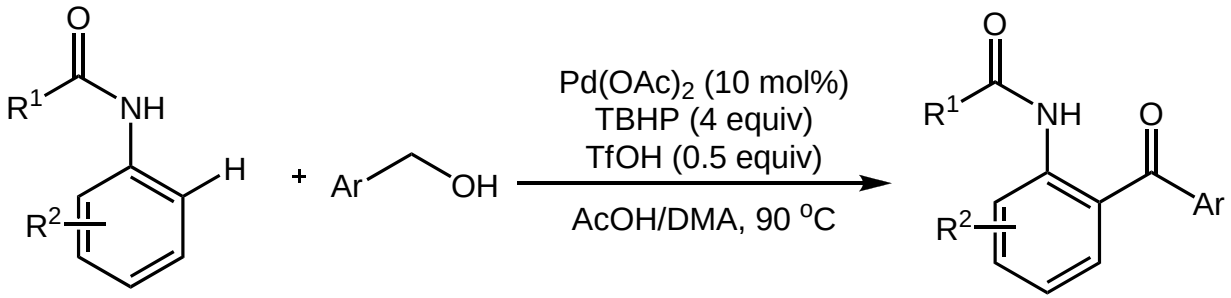
Kwong, F. et al. *Org. Lett.* **2011**, *13*, 3528



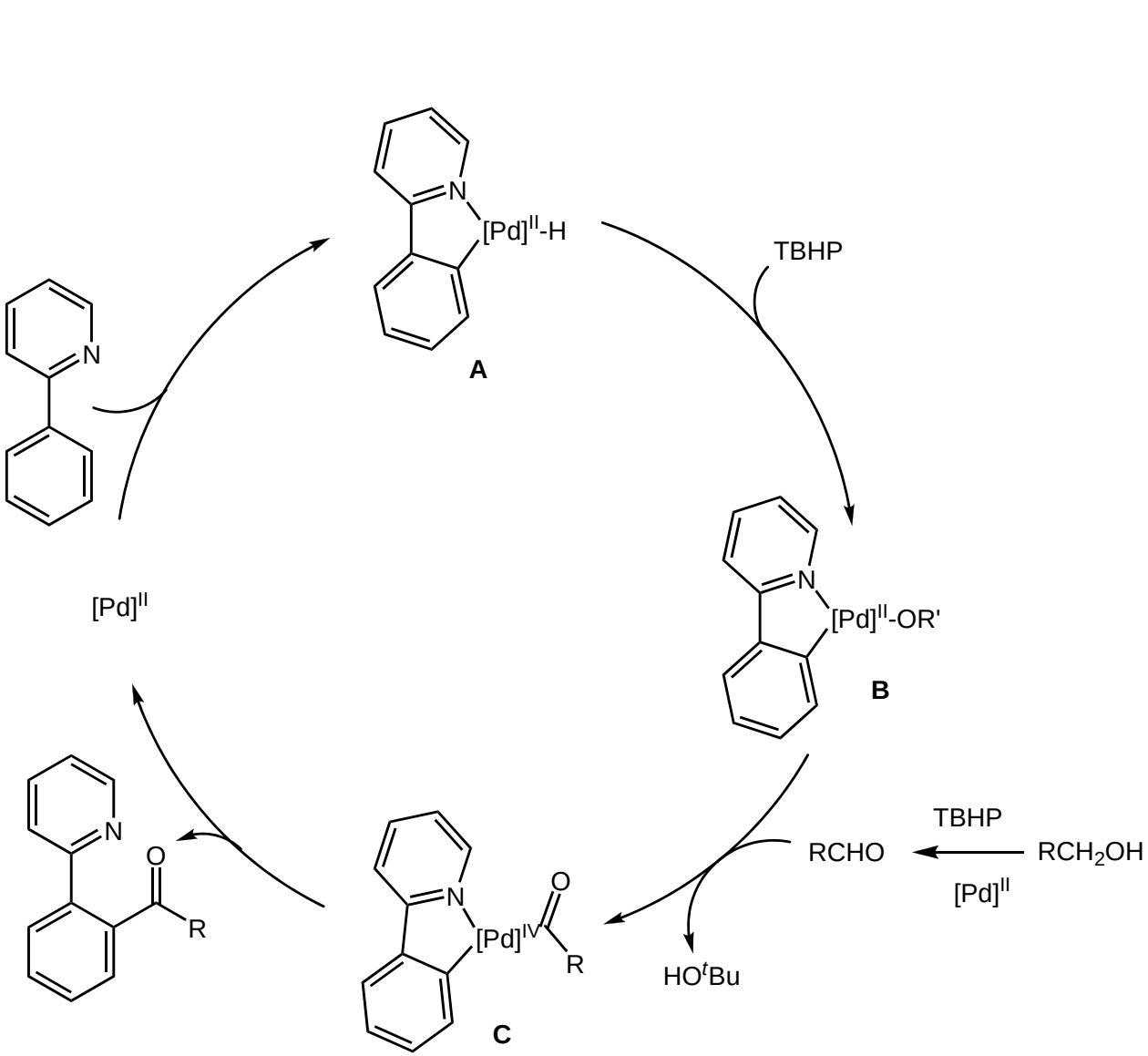
Yu, W.-Y. et al. *Adv. Synth. Catal.* **2011**, *353*, 2999

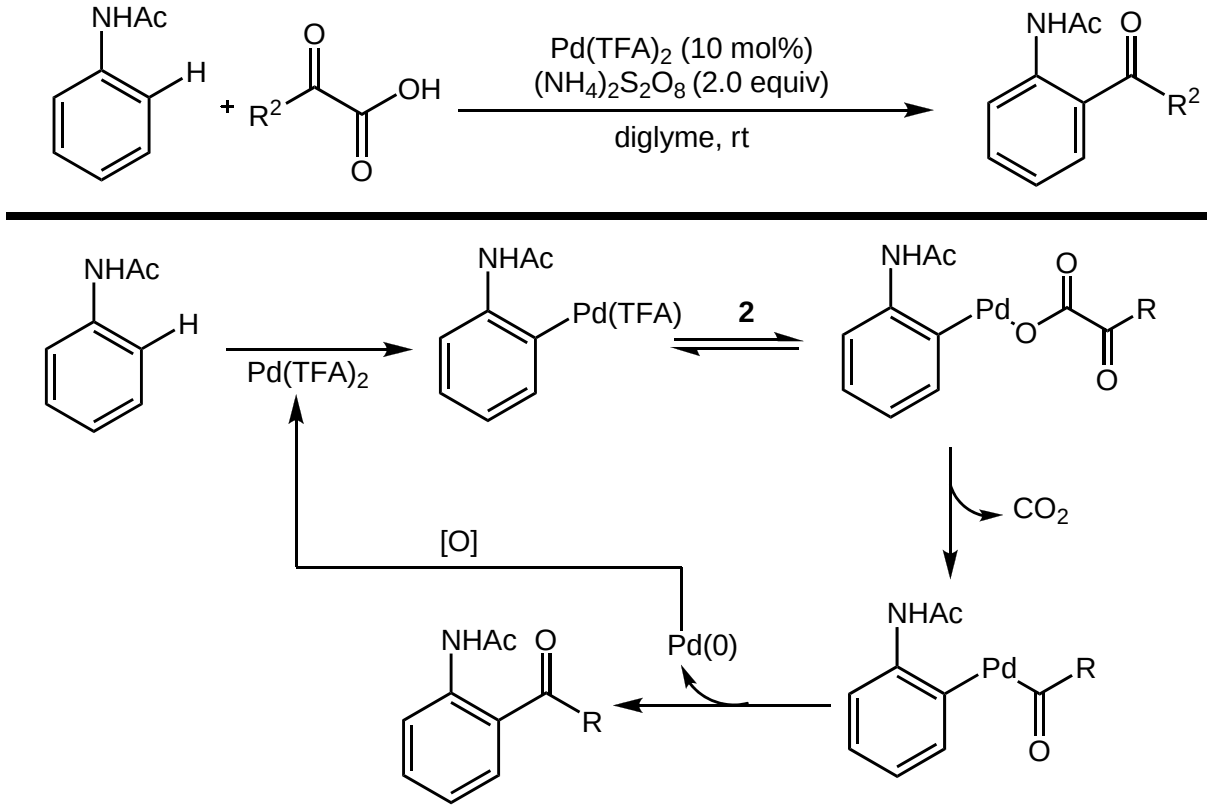


Li, C.-J. et al. *Org. Lett.* **2011**, *13*, 1614

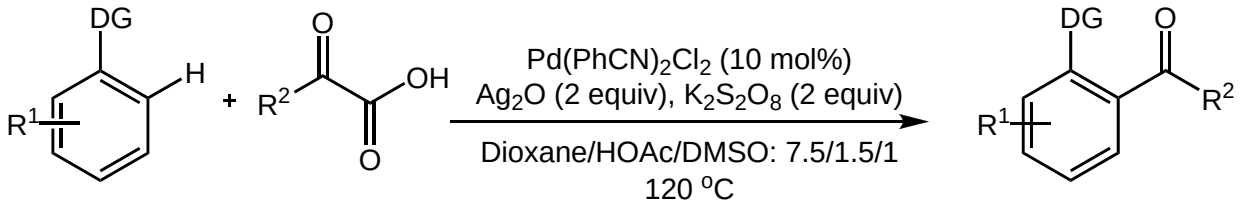


Yuan, Y. et al. *Adv. Synth. Catal.* **2011**, *353*, 3373


N
[Pd]II-H
A
TBHP
N
[Pd]II-OR'
B
TBHP
RCHO
RCH2OH
[Pd]II
HOtBu
N
O
[Pd]IV
R
C
N
O
R
[Pd]II



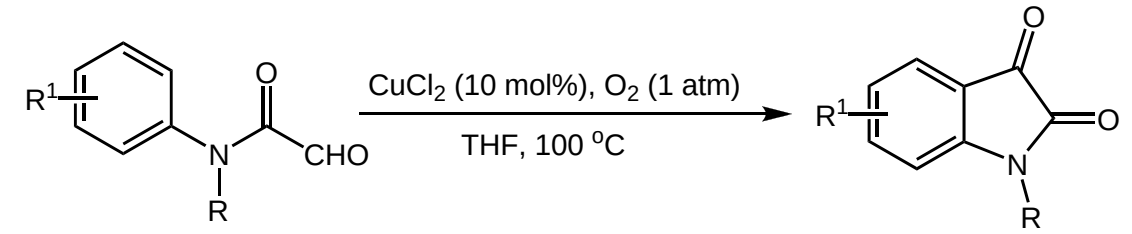
Ge, H. et al. *J. Am. Chem. Soc.* **2010**, *132*, 11898

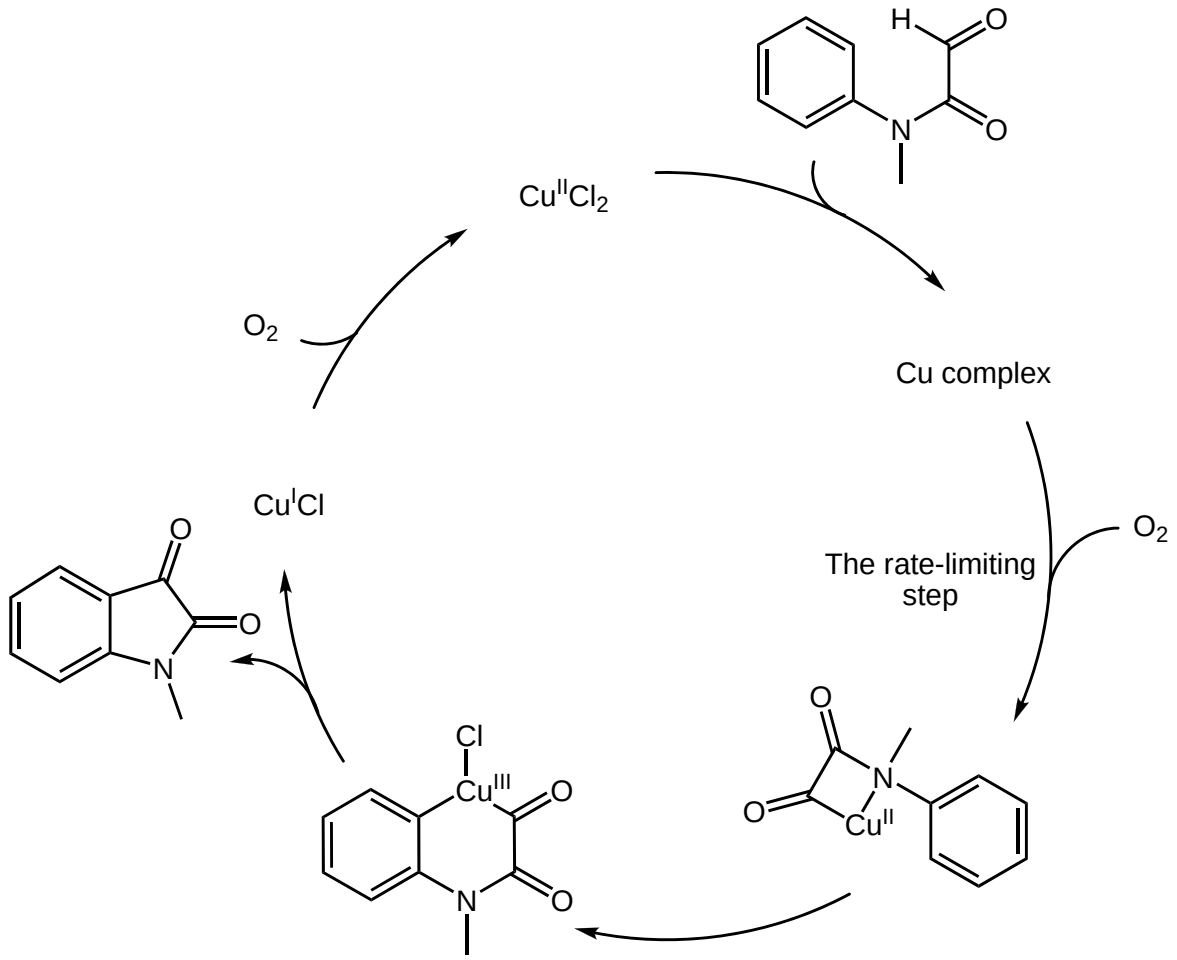


DG = 2-Py

Ge, H. et al. *Org. Lett.* **2010**, *12*, 3464

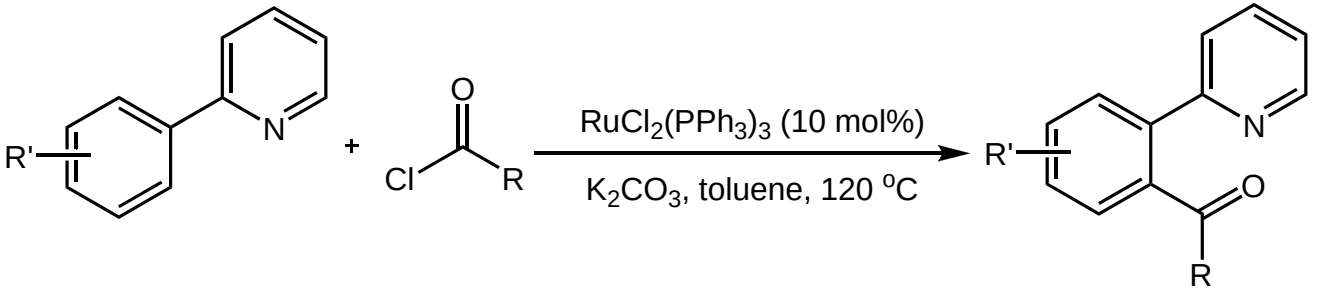
Cu

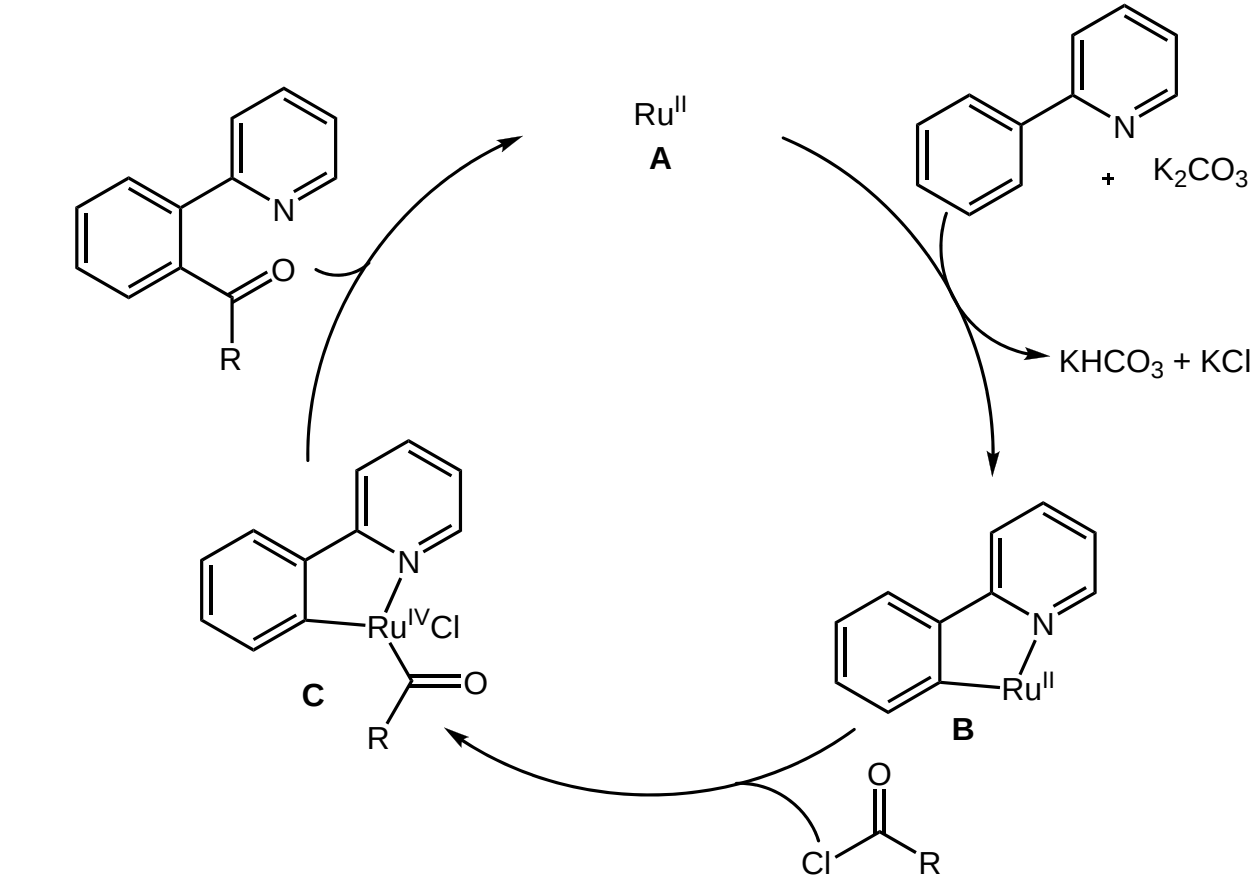




Li, J.-H. et al. *J. Am. Chem. Soc.* **2010**, *132*, 8900

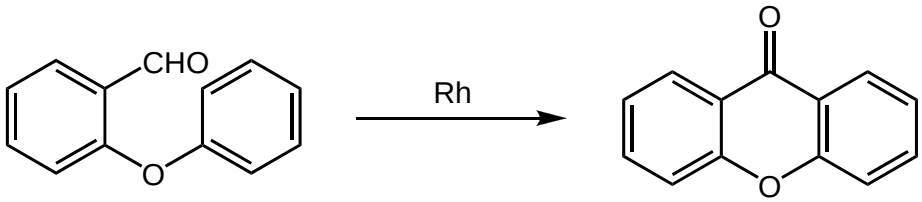
Ru



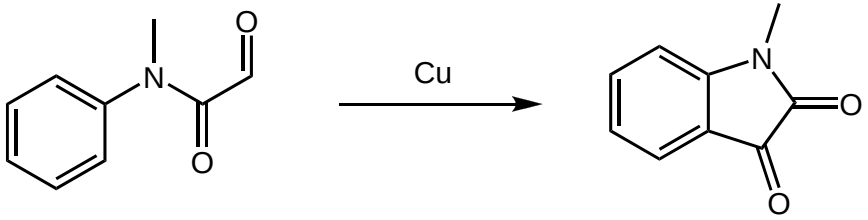


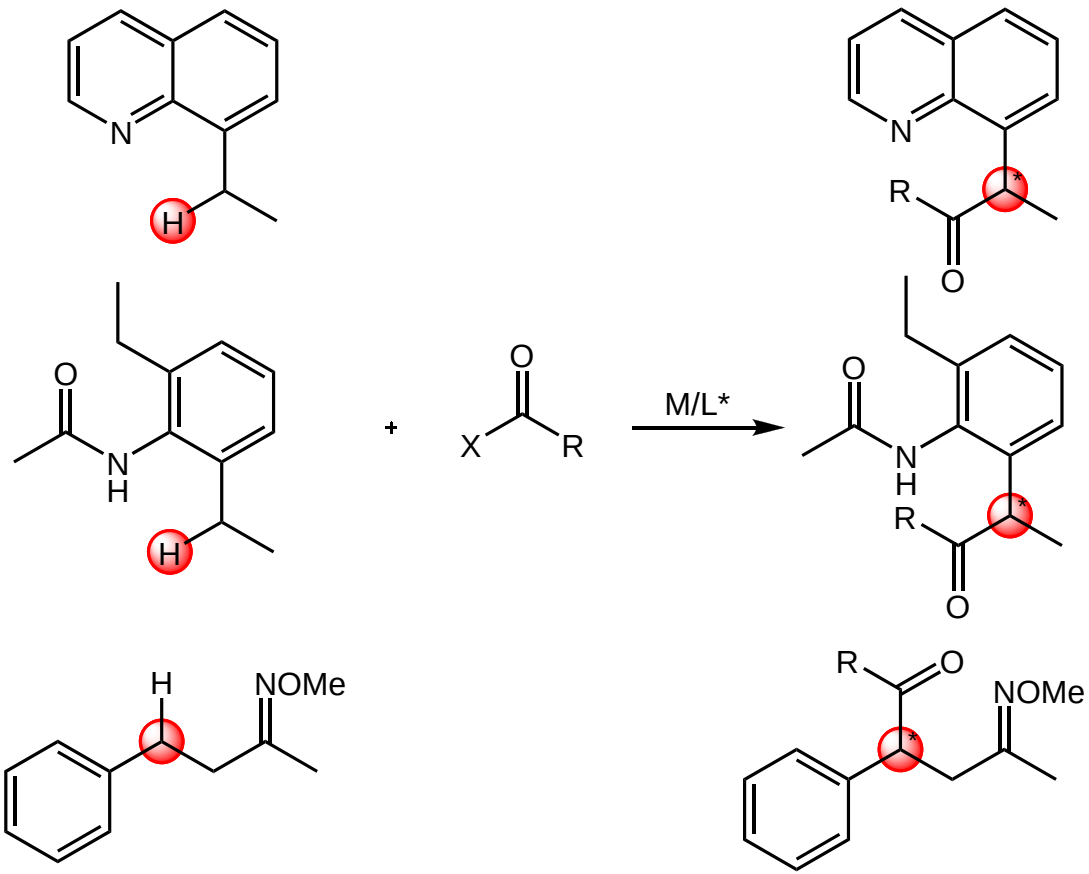
Kakiuchi, F. et al. *Chem. Lett.* **2011**, *40*, 1018

总结与展望



DG = 2-Py, C(O)NR^{1}R^2, NHAc, CH=NOMe
X = H, COOH, Cl
M = Pd, Ru




N
H
O
N
H
H
+
O
X
R
M/L*
N
R
*
O
O
N
H
R
*
O
H
NOMe
R
O
NOMe
*

The xanthone substructure is of great significance in natural products such as mangiferin and psorospermin due to its excellent biological and pharmacological activities. Thus, construction of such substructures has always been synthetically attractive. Various approaches to the xanthone skeleton from a range of functionalized diaryl ethers via varied mechanisms have been developed, most frequently, via the Friedel-Crafts reactions. In the early days, Jackson used aluminumchloride and oxalyl chloride to obtain xanthones from diaryl ethers in methylene chloride at room temperature. Subsequently, Frahm presented a series of substituted xanthones synthesized from 2-aryloxybenzoic acids in the presence of PPA. Recently, Lu resorted to copper(II)-catalyzed aza-Friedel-Crafts reaction of *o*-phenoxyl-*N*-tosylbenzaldimine to construct nonsubstituted xanthone. In addition, Liebeskind achieved the xanthone skeleton by a cascade of electrocyclization reactions of cyclobutenedione derivatives via the benzannulation intermediate.

In summary, we have developed a new way to construct xanthone skeletons from aldehydes directly. It does not require any preactivation of the aldehyde group. In addition, the reaction can tolerate diverse functional groups and can be applied to obtain a rather wide range of xanthone derivatives. In this sense, it is a useful complementary method for synthesizing xanthones.

Thank You