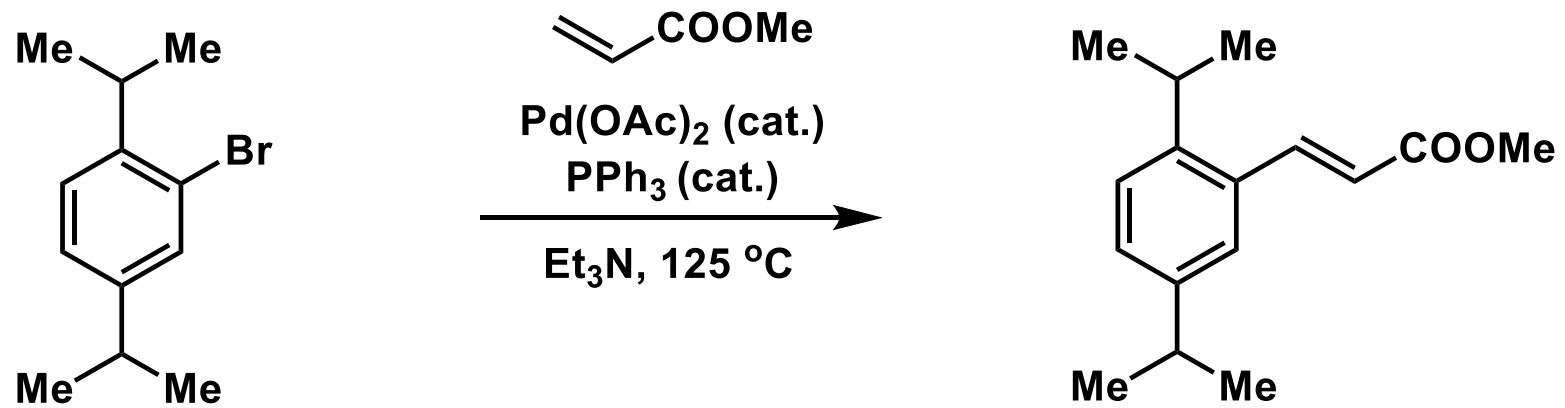
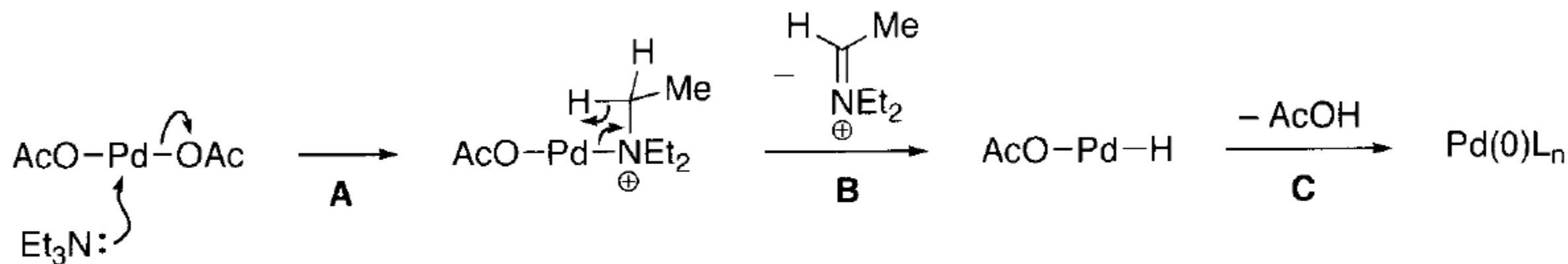
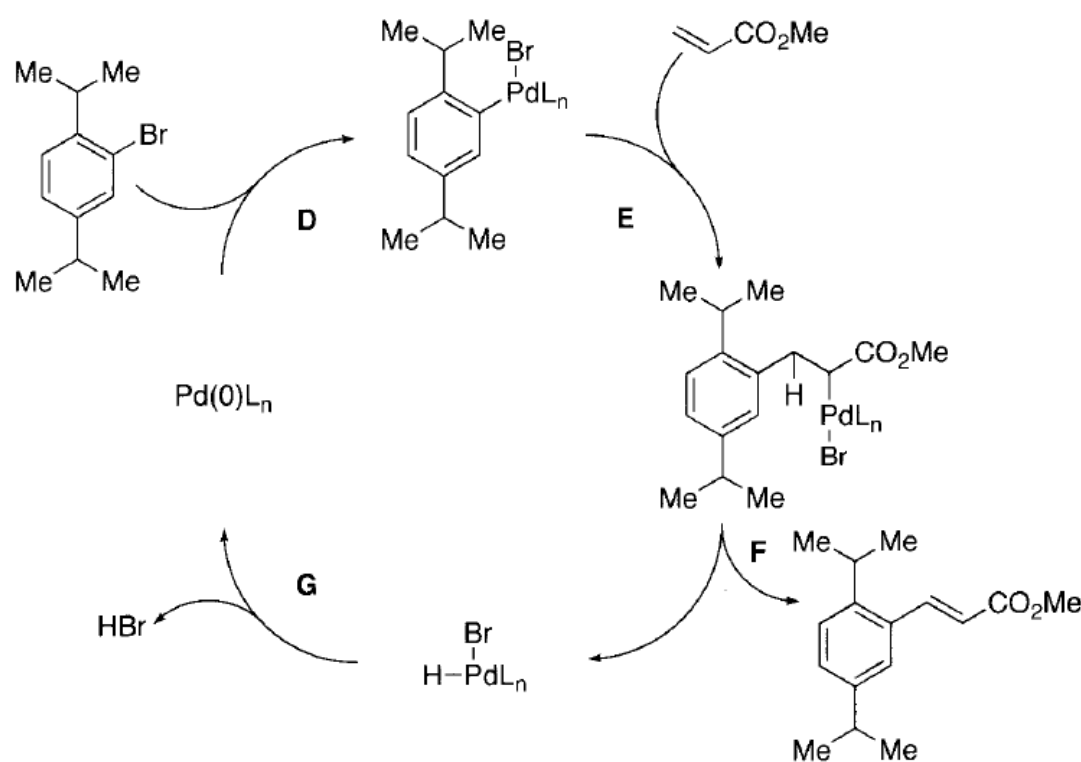


1.

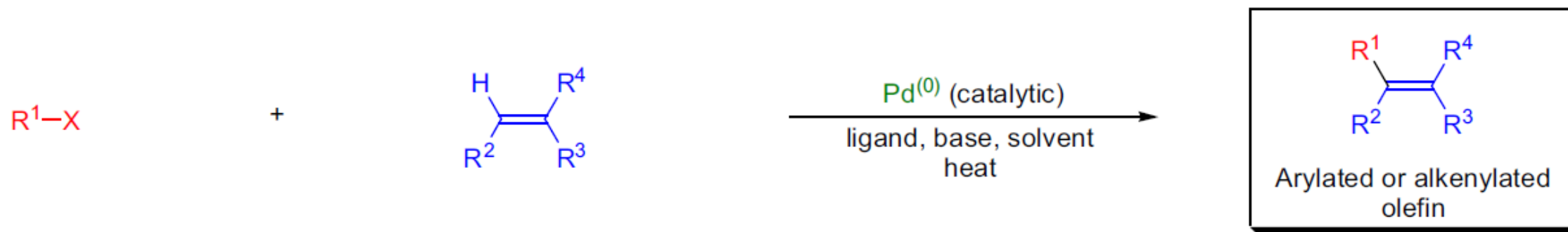




Reduction of $\text{Pd}(\text{OAc})_2$ to $\text{Pd}(0)$ using Et_3N . **A:** Ligand exchange. **B:** β -Elimination. **C:** Reductive elimination of AcOH .

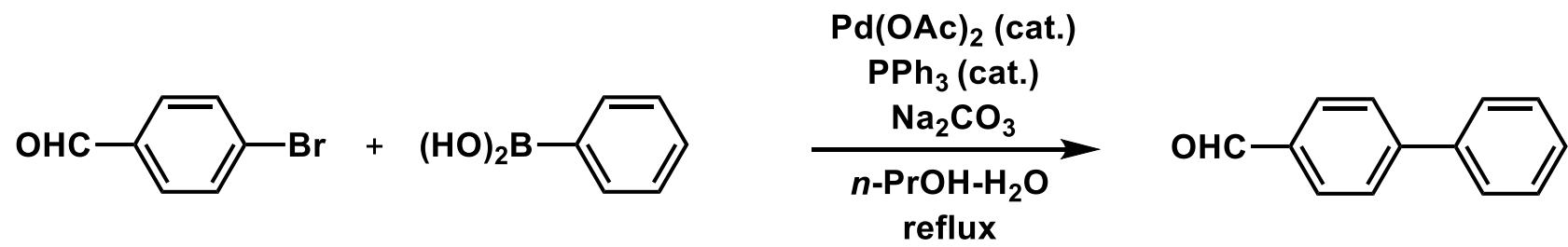


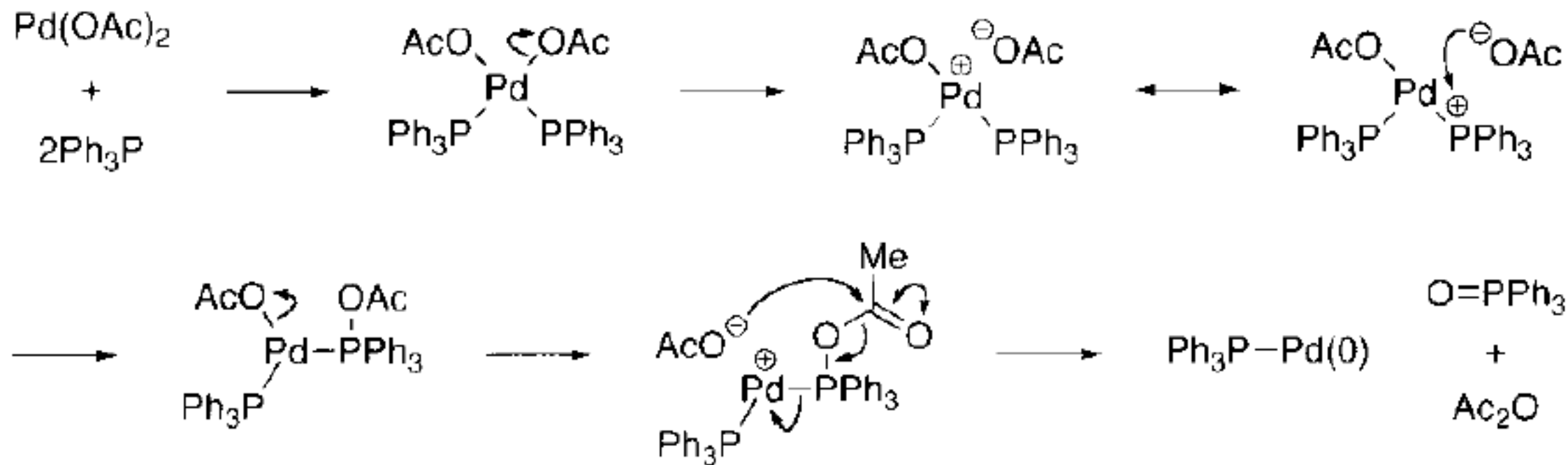
Heck reaction. **D**: Oxidative addition. **E**: Carbopalladation. **F**: β-Elimination to form the product. **G**: Reductive elimination of HBr.



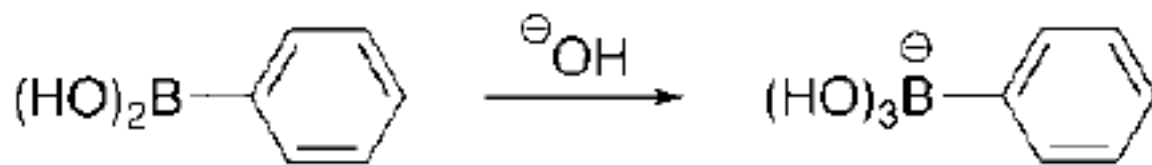
R¹ = aryl, benzyl, vinyl (alkenyl), alkyl (no β hydrogen); R², R³, R⁴ = alkyl, aryl, alkenyl; X = Cl, Br, I, OTf, OTs, N₂⁺; ligand = trialkylphosphines, triarylphosphines, chiral phosphines; base = 2° or 3° amine, KOAc, NaOAc, NaHCO₃

2.

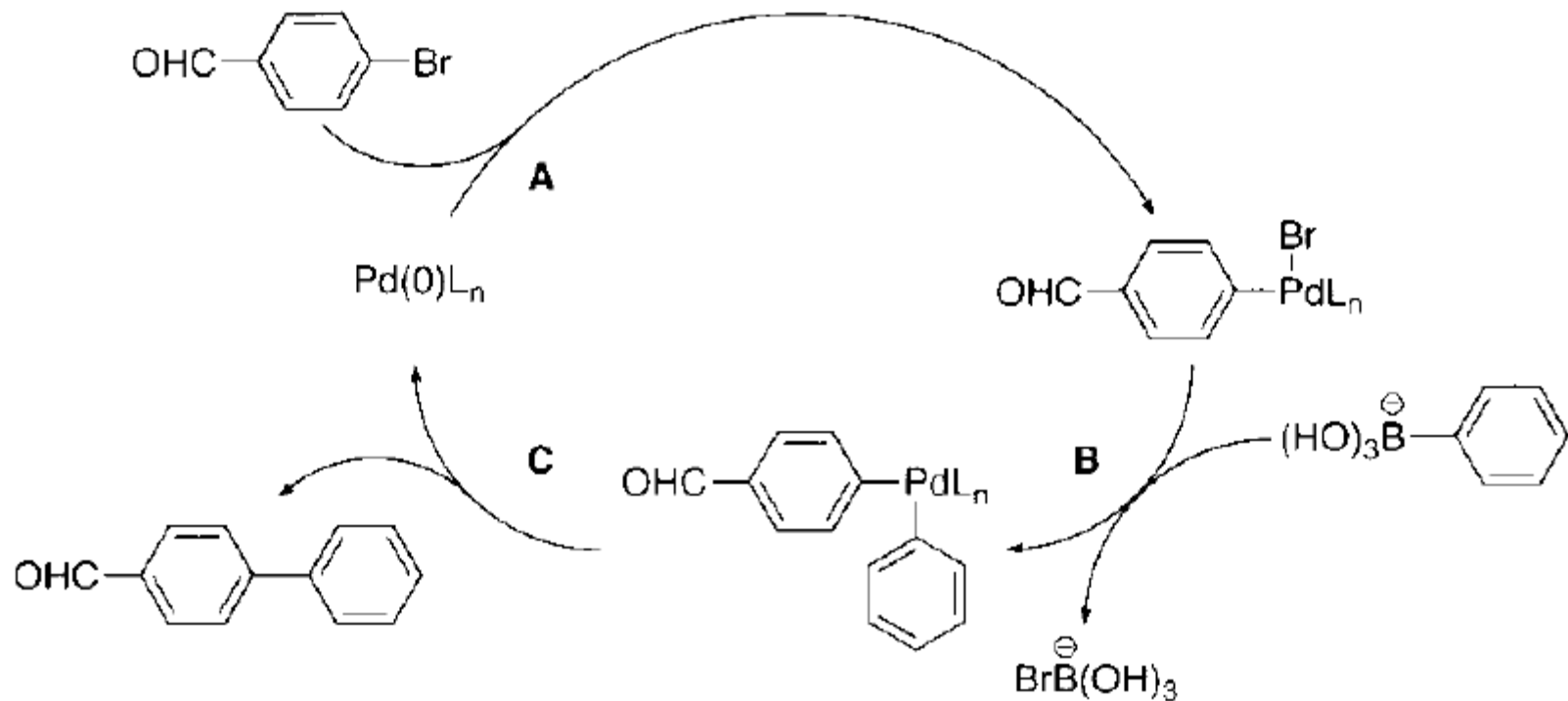




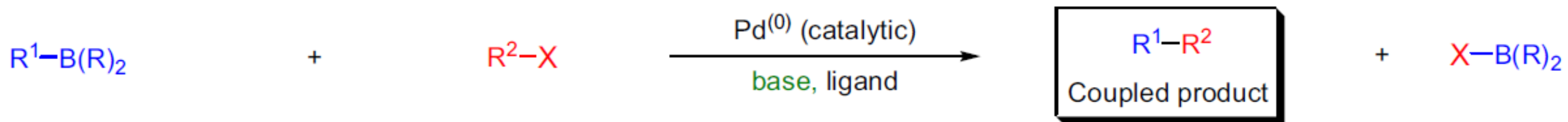
Reduction of Pd(OAc)_2 to Pd(0) using Ph_3P .



Activation of boronic acid.



Suzuki-Miyaura coupling. **A**: Oxidative addition. **B**: Transmetalation. **C**: Reductive elimination.



R^1 = alkyl, allyl, alkenyl, alkynyl, aryl; R = alkyl, OH, O-alkyl; R^2 = alkenyl, aryl, alkyl; X = Cl, Br, I, OTf, OPO(OR)₂ (enol phosphate);
base = Na₂CO₃, Ba(OH)₂, K₃PO₄, Cs₂CO₃, K₂CO₃, TIOH, KF, CsF, Bu₄F, NaOH, M⁺(⁻O-alkyl)

常用的催化剂:

- 二价钯类催化剂: $\text{PdCl}_2/\text{配体}$, $\text{Pd(OAc)}_2/\text{配体}$, Pd(dppf)Cl_2 , 各种Pre-catalyst等
- 零价钯类催化剂: $\text{Pd(PPh}_3)_4$, $\text{Pd}_2(\text{dba})_3/\text{配体}$ 等

偶联中二价钯如何还原为零价钯

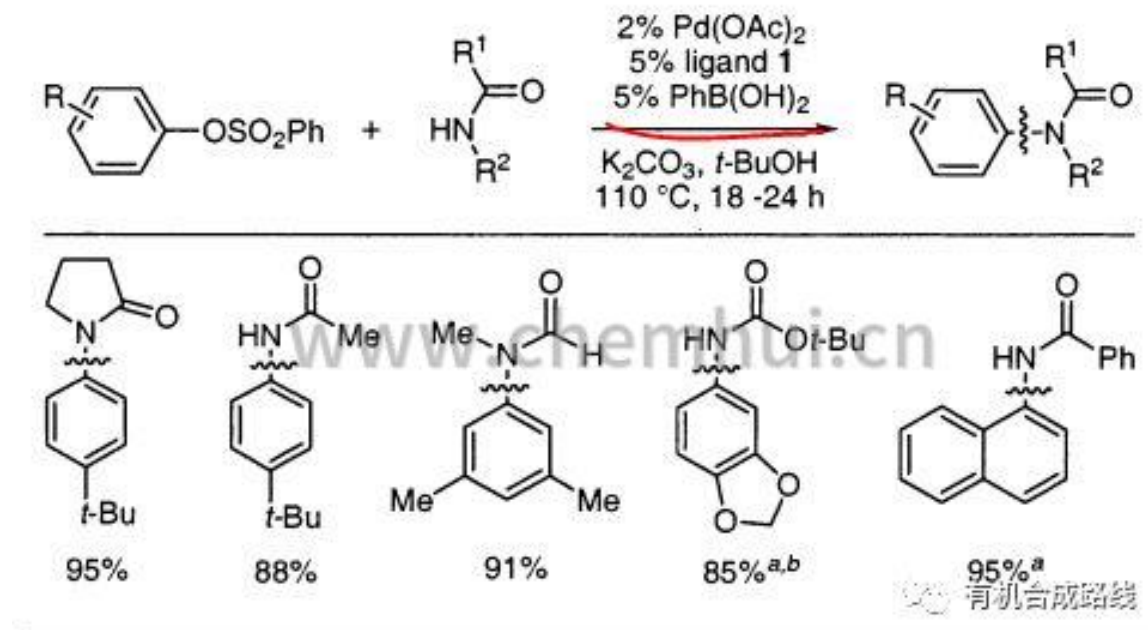
1. 膦配体还原二价钯

以 $\text{Pd(OAc)}_2/\text{XPhos}$ 为例, 水作为媒介, 整个二价钯的预活化可以做到可视化, 具体见下图, 反应条件是 Pd(OAc)_2 (0.01 mmol), **1** (0.03 mmol), H_2O (0.04 mmol), 1 mL 1,4-dioxane, 80 °C。

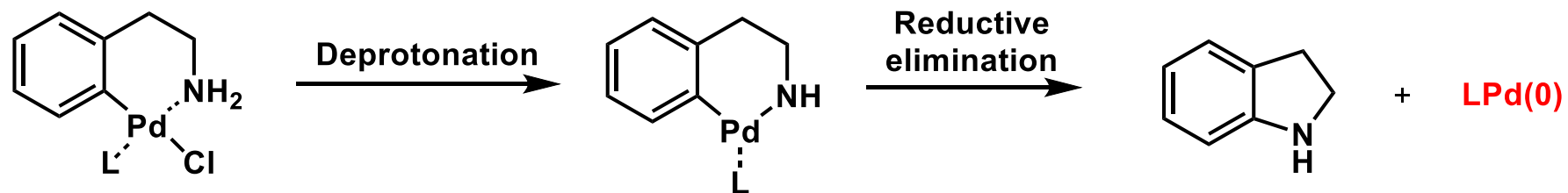


2. 三级胺还原二价钯；胺类底物还原二价钯（Buchwald偶联中）

3. 芳基硼酸还原二价钯

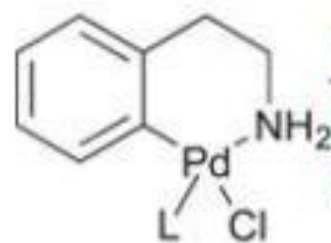


4. Pre-Catalyst的使用



Efficient formation of
 L_1Pd under
basic reaction conditions

No additives necessary
for
catalyst activation



Not possible for
all ligands



Catalytically
active
species

No additives

necessary,

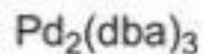
reduction of

Pd not required

dba can bind

Pd and retard

reaction

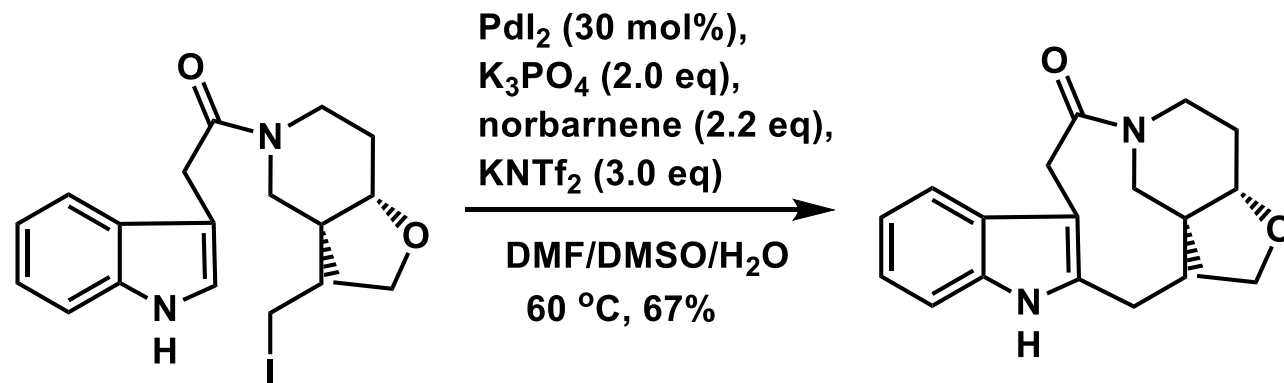


Economically
attractive

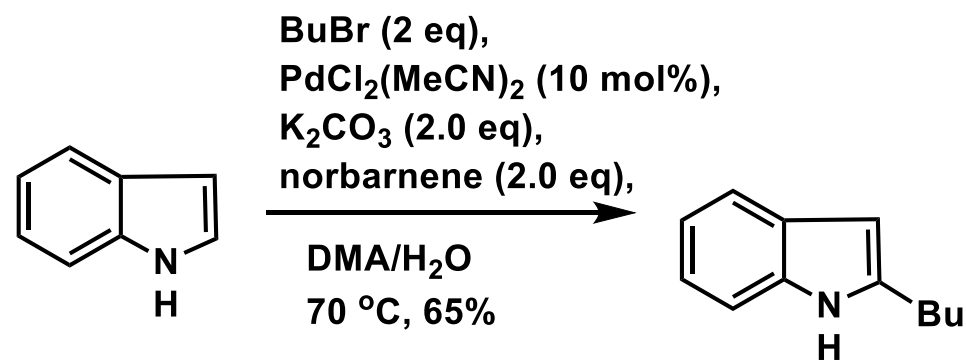
Coupling of anilines and
amides requires addition of
exogenous reductant
(added NR_3 or $PhB(OH)_2$)
or consumption of 1 equiv.
of phosphine ligand for
efficient reduction of Pd(II)



3.



10.1002/anie.202010759



J. Am. Chem. Soc. **2012**, *134*, 14563-14572

