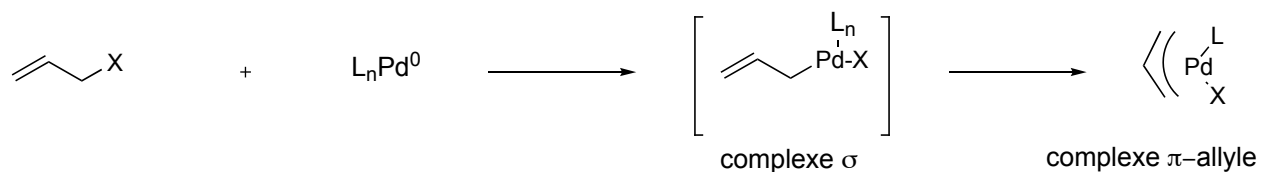
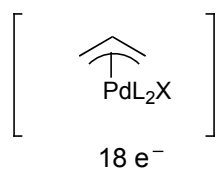
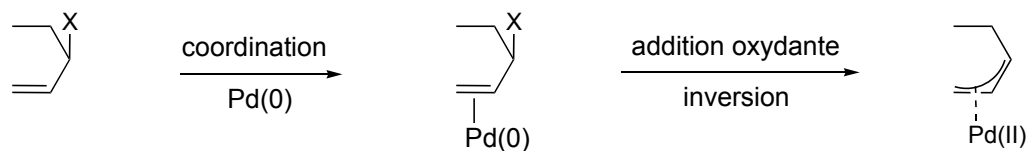
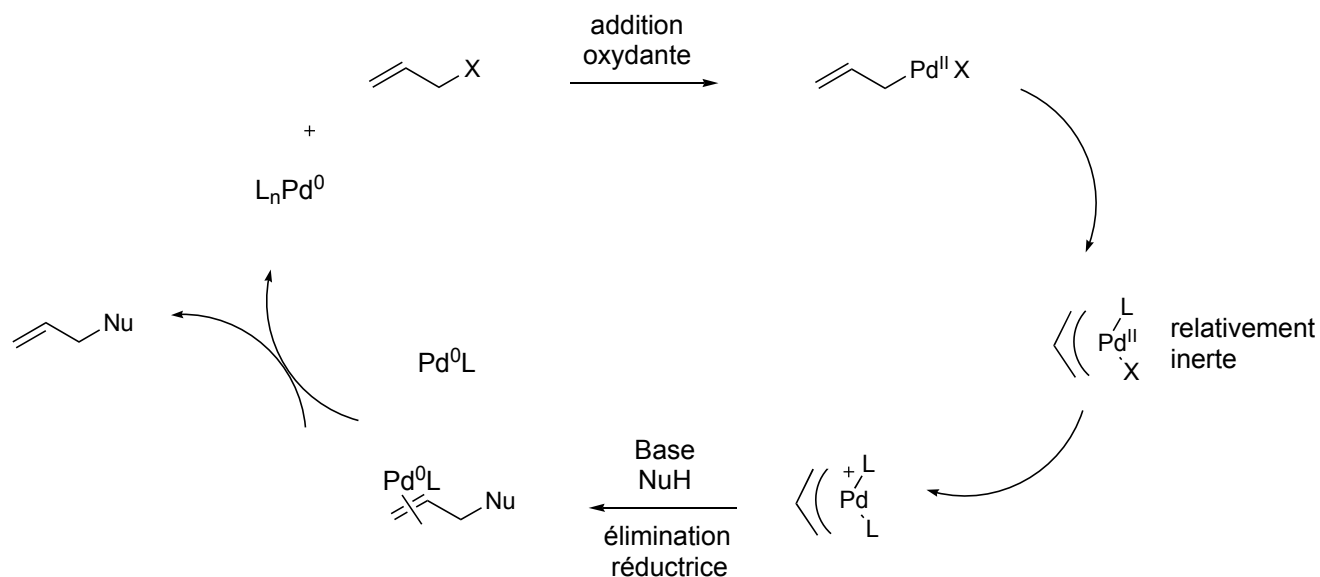


Réaction de Tsuji-Trost

Formation du complexe π -allyle

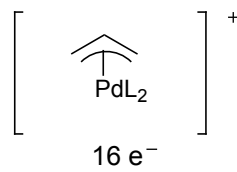


Réaction des substrats allyliques :



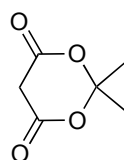
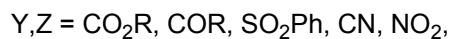
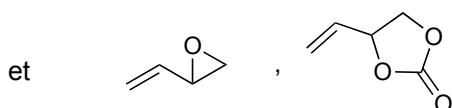
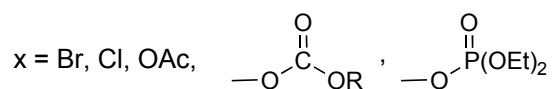
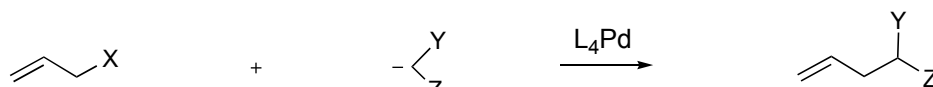
Le groupe X^- reste lié

et/ou



Cationique avec $\text{X} = \text{OAc}$

Nucléophiles mous :



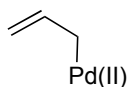
Nécessité d'une base externe : car

NuH

base

Nu⁻

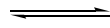
Equilibre des complexes



forme σ

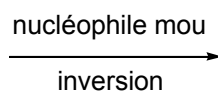
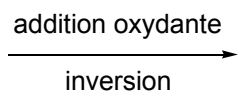


forme π

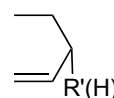
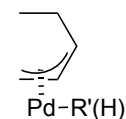
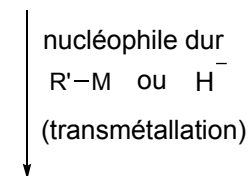


forme σ

Réaction avec des nucléophiles



double inversion
=
rétention

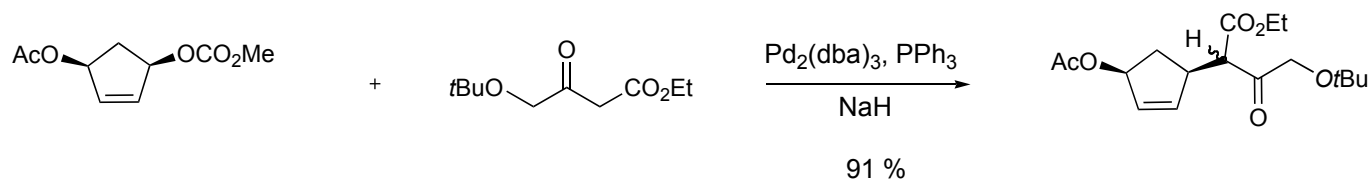
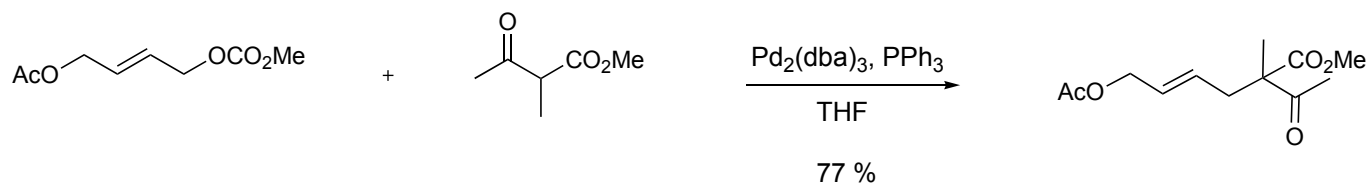
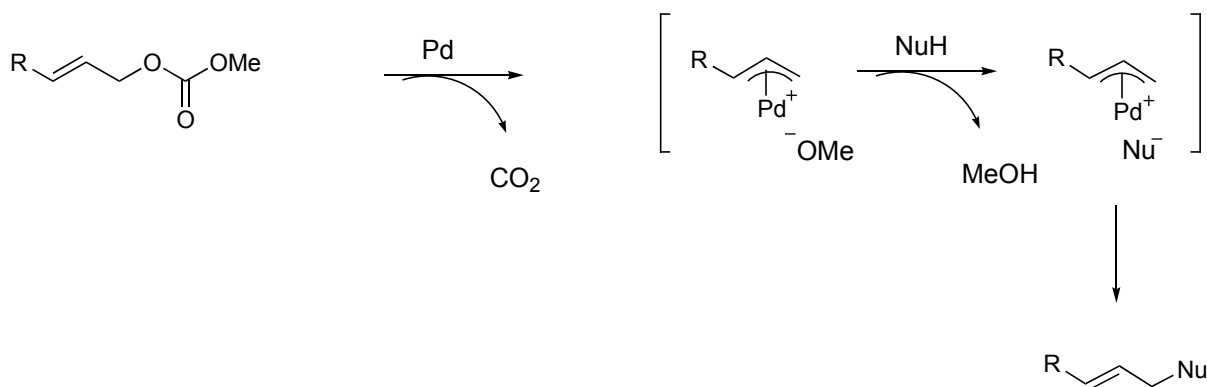
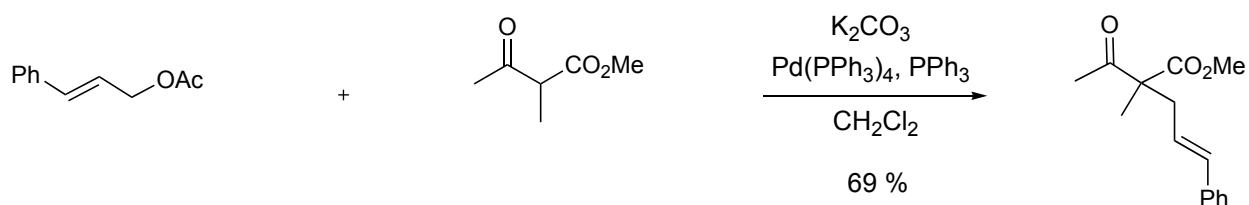


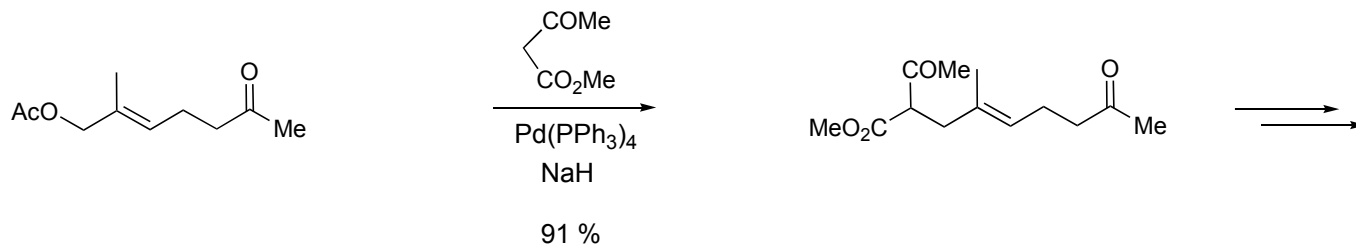
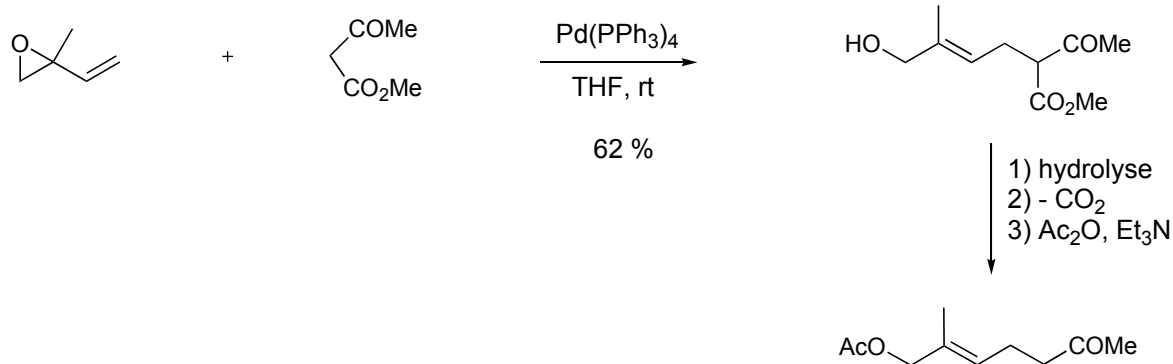
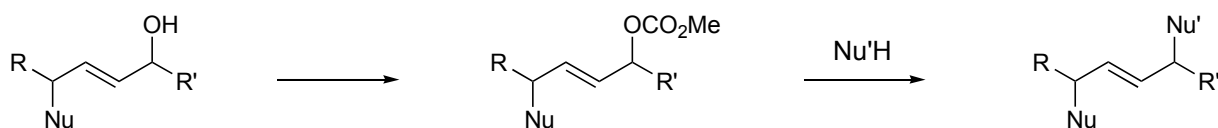
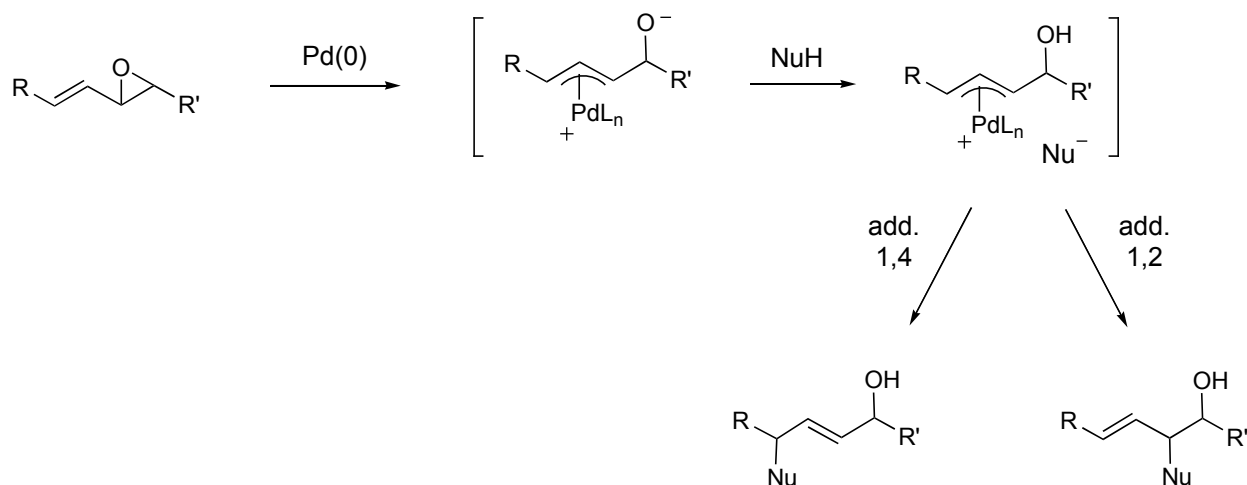
inversion + rétention
=
inversion

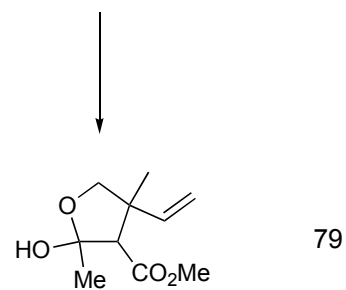
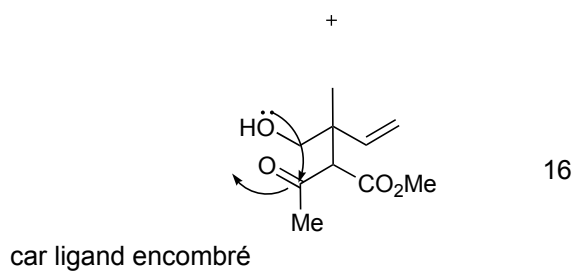
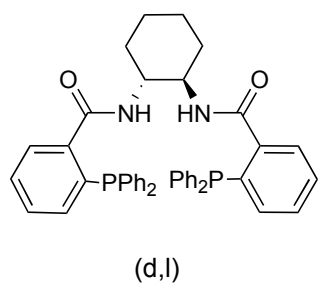
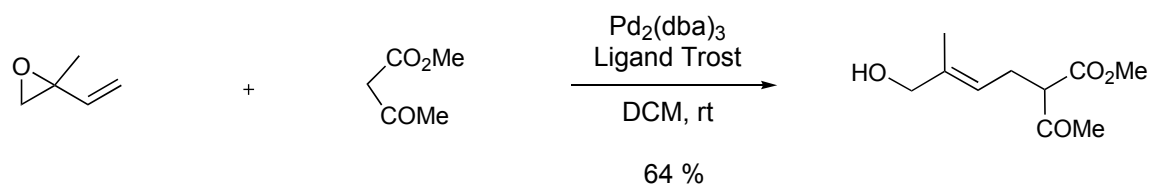
→ attaque différente selon le caractère dur ou mou

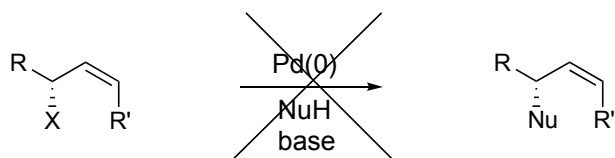
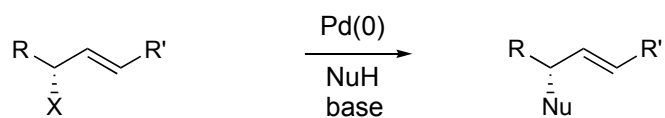
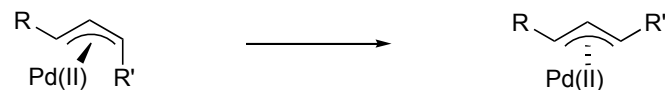
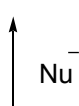
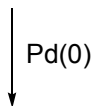
- Nu mous ($pK < 20$)
- Nu durs ($pK > 20$) (organométalliques ou hydrures)

Exemples

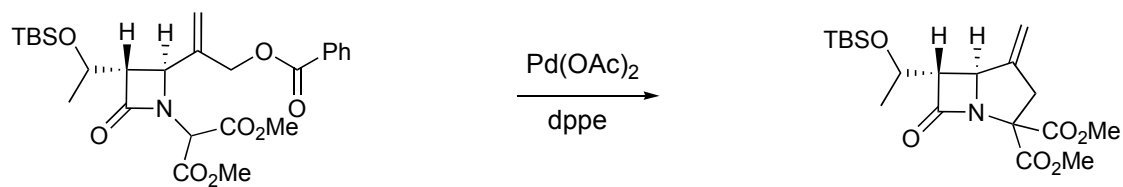
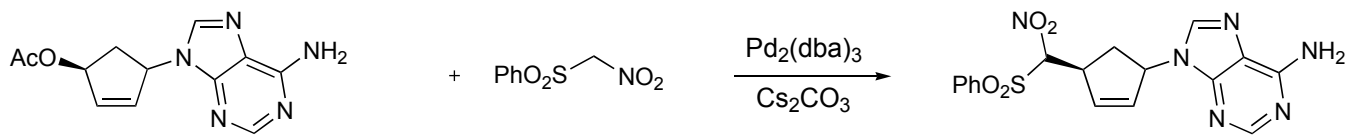




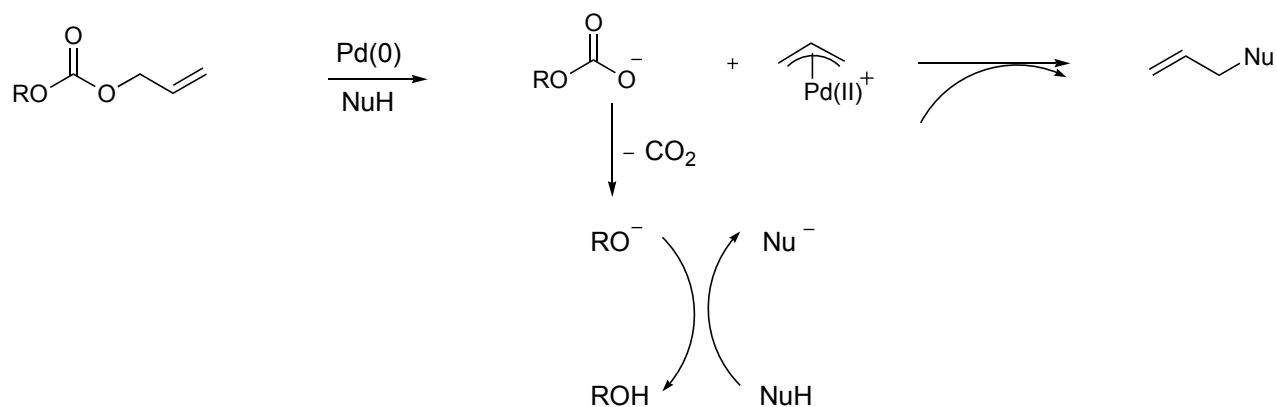


Produit de *cis*-réarrangement π - σ - π *cis*

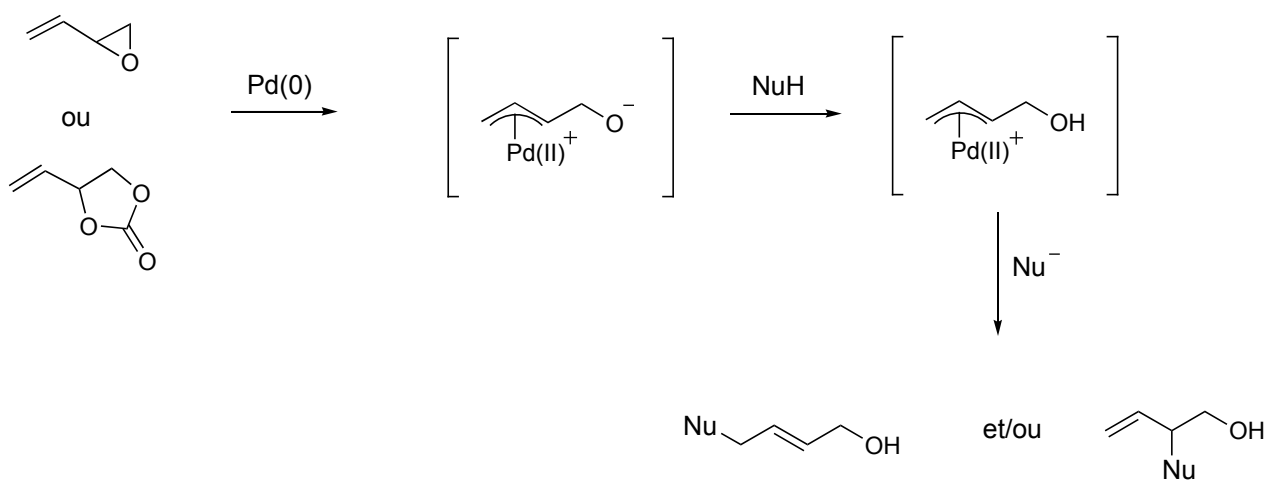
Exemples

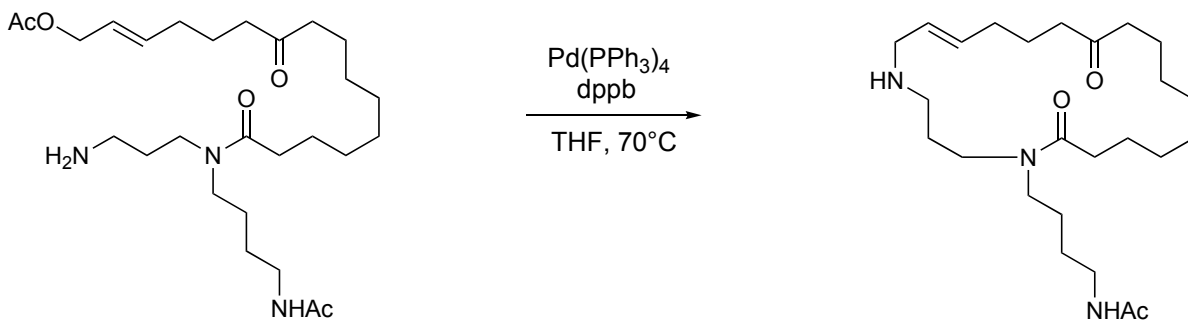


- Avec des carbonates développés par Tsuji, il y a réaction en milieu neutre sans base externe



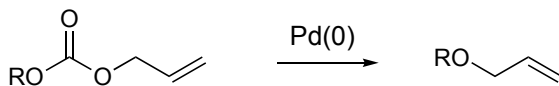
idem avec





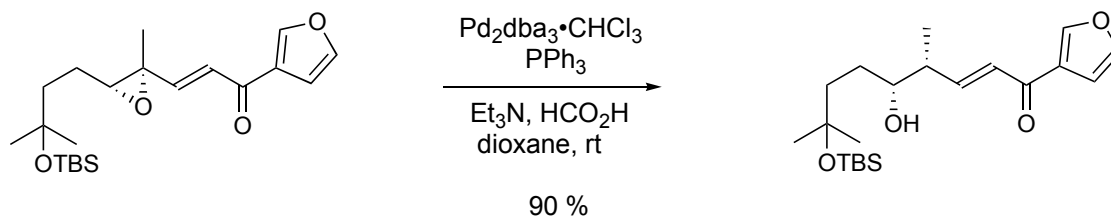
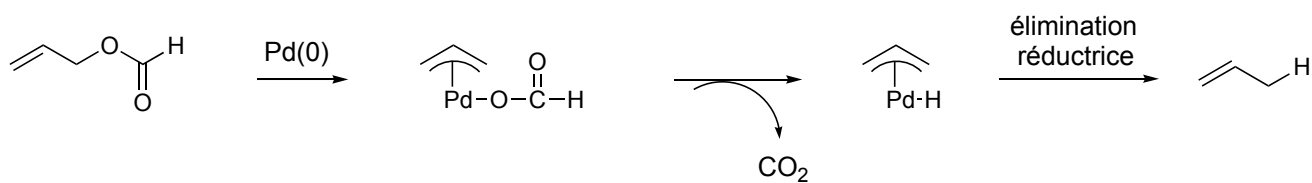
82JACS6881

- Avec des carbonates, en l'absence de nucléophile, l'alcolate formé est capable de réagir avec les complexes π -allyles

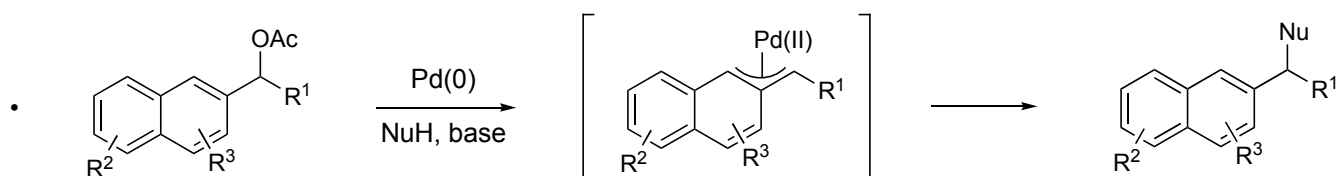
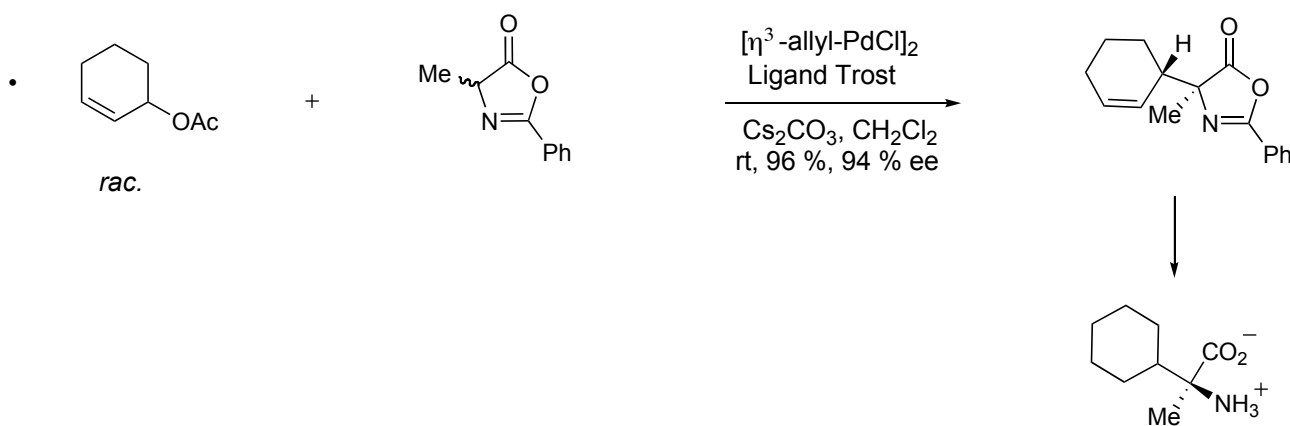
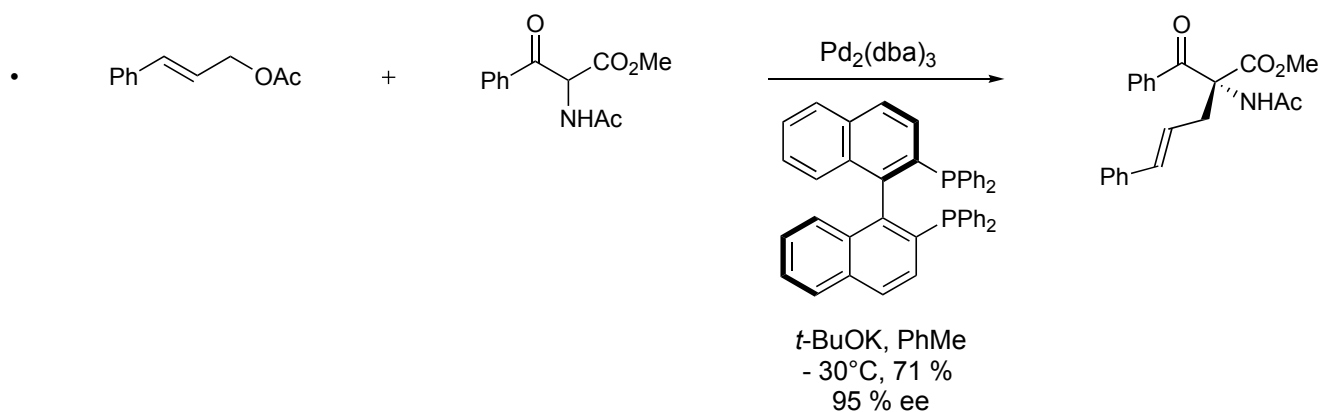
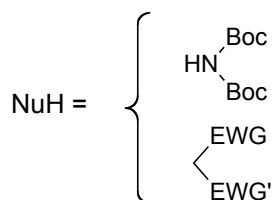
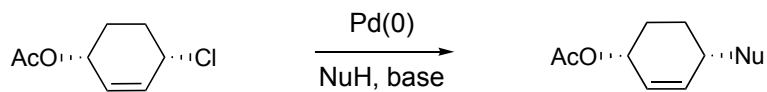


81TL3591

- Formates d'allyle

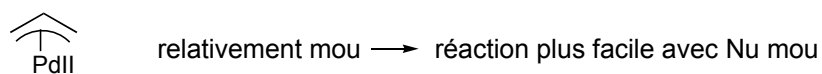


réactivité : $\text{Cl} > \text{OCO}_2\text{R} > \text{OAc} \gg \text{OH}$

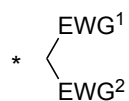


attention, pas pour des dérivés du benzène !

Nature du nucléophile



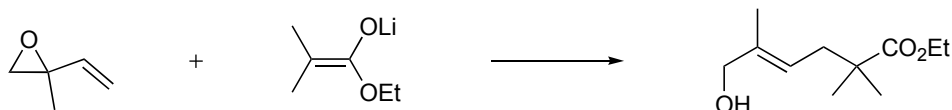
- Nu carbonés mous



* imino esters

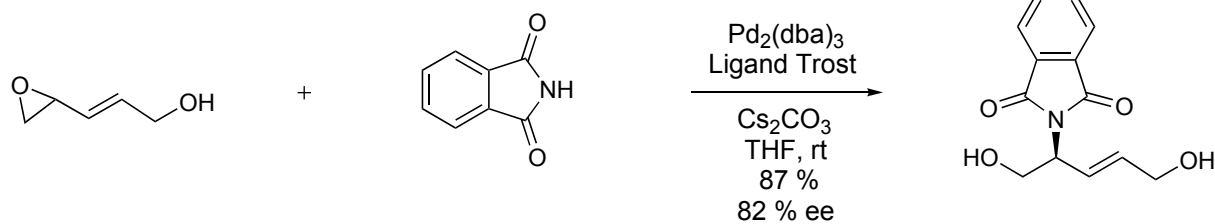
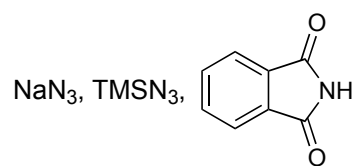
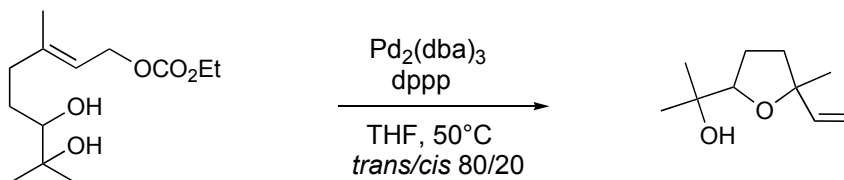
* éthers d'énols silylés

* énolates de métaux



E/Z : 8/2

- Nu azotés

- Nu oxygénés
trop durs sauf en intramoléculaire

- Nu de types acides carboxyliques

