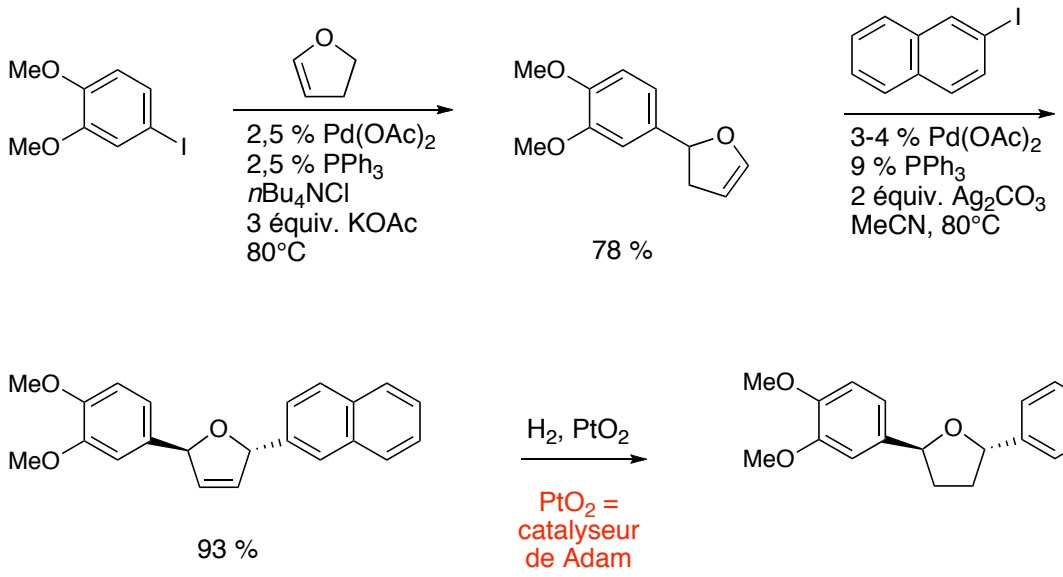
Réaction de Heck intermoléculaire (suite)

1.



Larock 90JOC407

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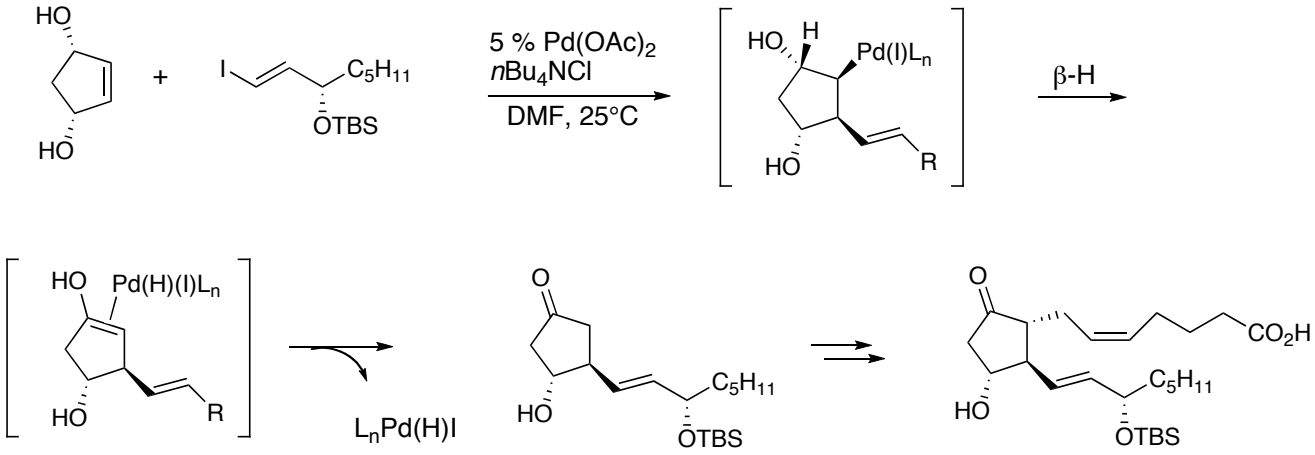
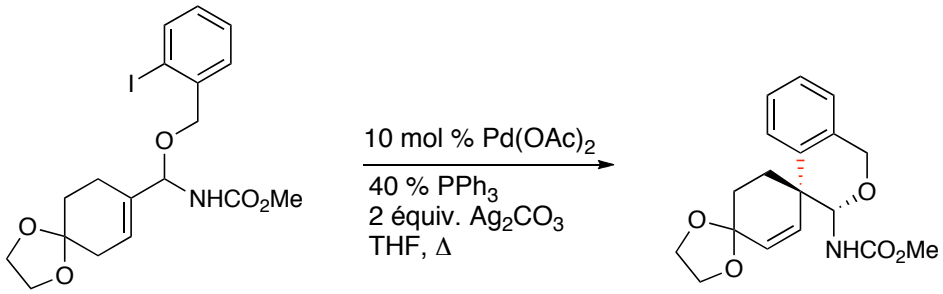
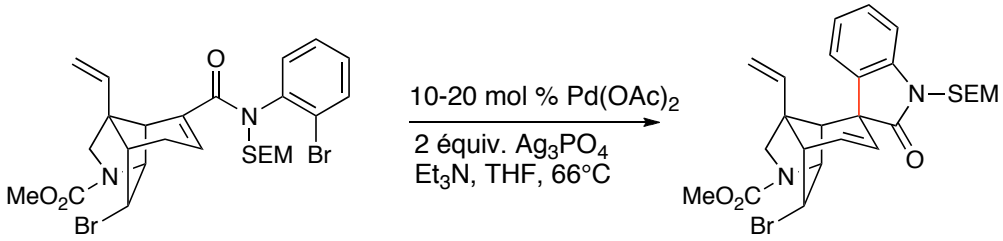


Larock 90PAC653407

Réaction de Heck intramoléculaire

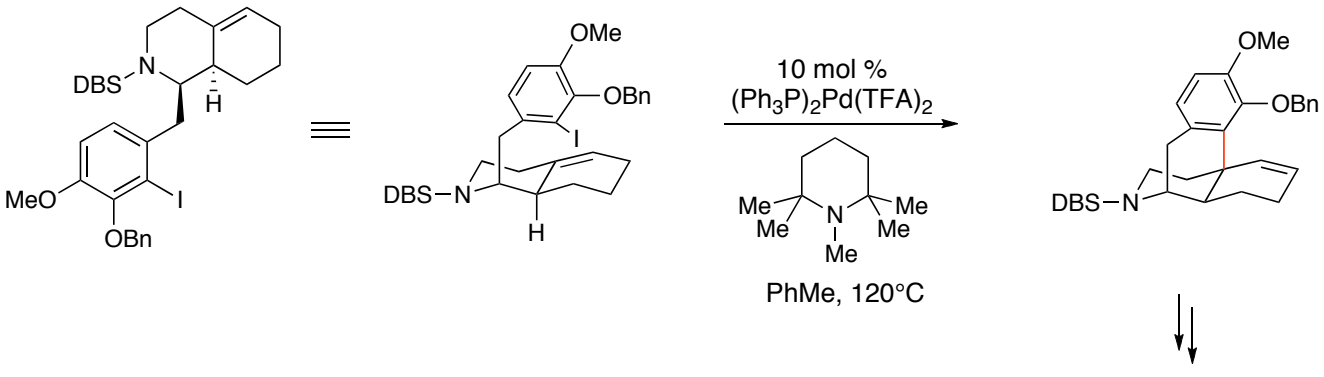


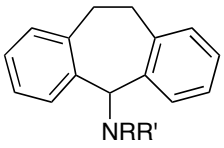
Overman 90JACS6959
Overman 87JOC4130



Overman 92TL4859

N-SEM = $NCH_2OCH_2CH_2Si(CH_3)_3$





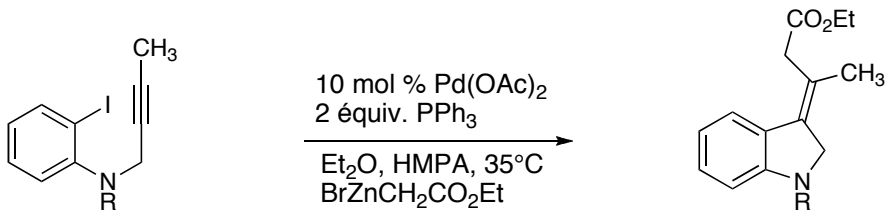
5-dibenzosubéryl

= RR'N-DBS

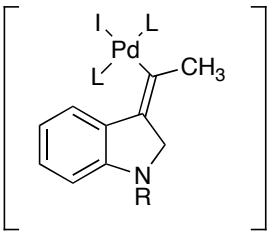
(-)-Morphine

Overman 93JACS11028

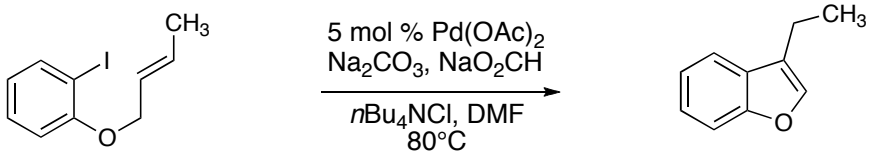
Réaction de Heck intramoléculaire



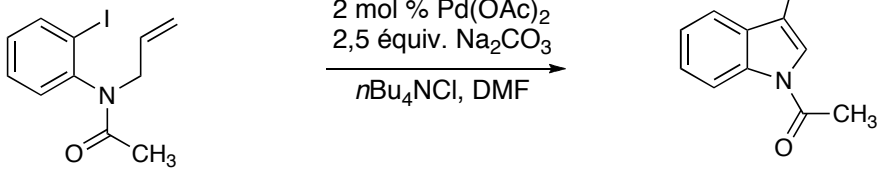
via :



Grigg 89TL1135



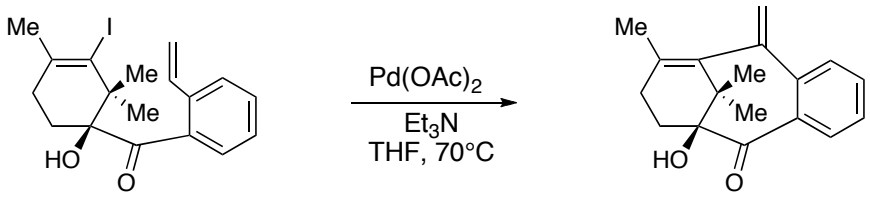
83 %



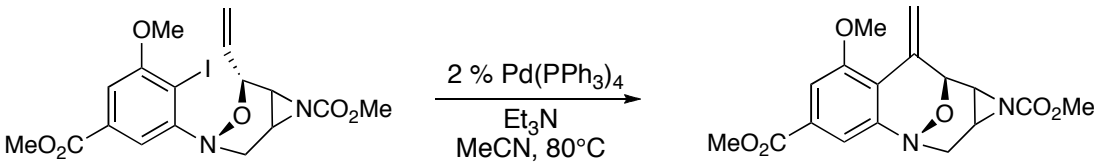
90 %

Larock 90PAC653

Réaction de Heck - Applications

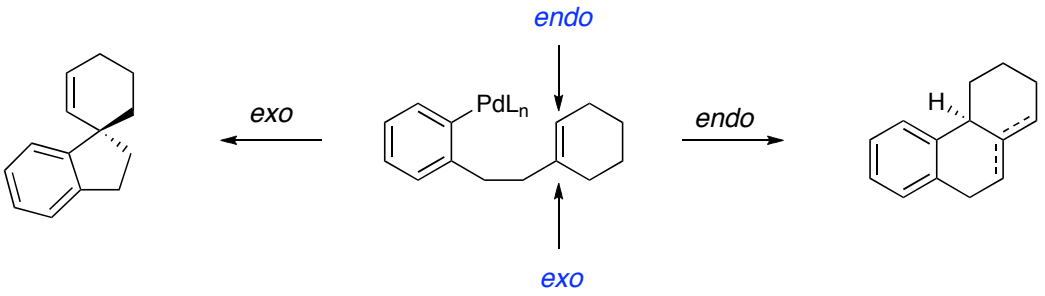


Danishefsky 93TL7253

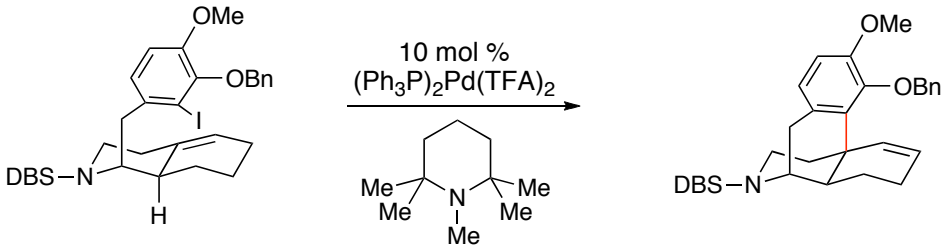


Danishefsky 92JACS6094

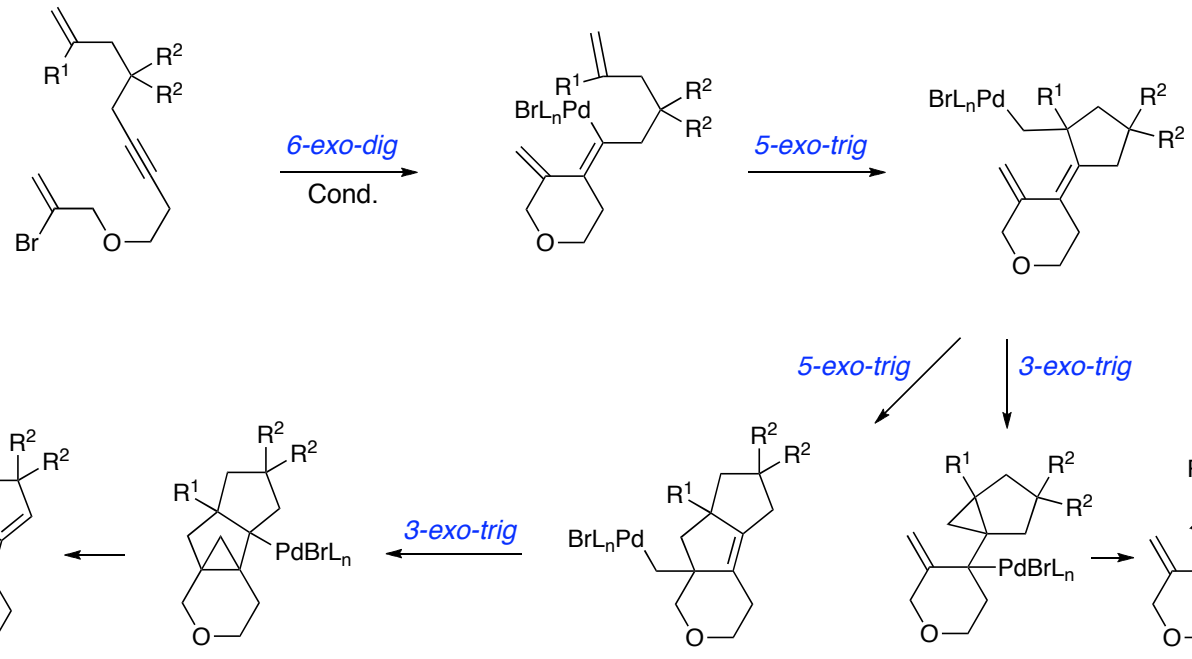
Réaction de Heck - Mode de fermeture de cycle



Les fermetures de cycles à 5, 6 et 7 (les cyclisations par réaction de Heck les plus efficaces) conduisent généralement majoritairement aux produits *exo*.



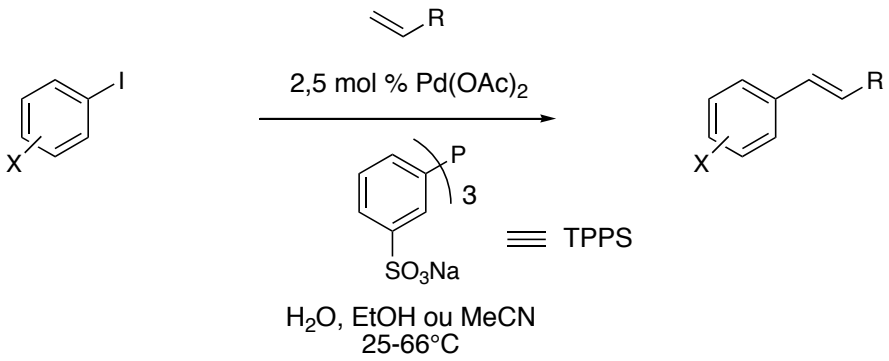
6-exo-trig

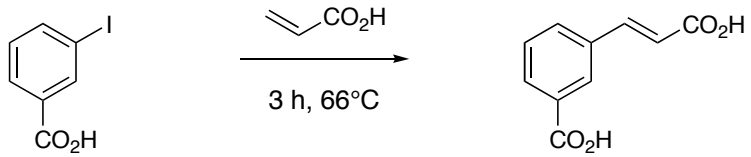


de Meijere 91JOC6487

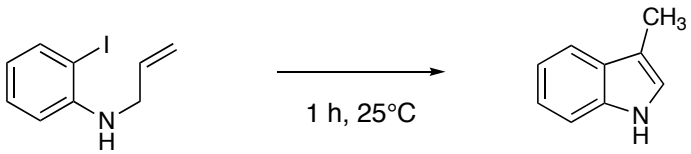
Cond. : $Pd(OAc)_2$ (3-5 mol %), PPh_3 (12-20 mol %), Ag_2CO_3, MeCN, 80-130°C

Réaction de Heck dans l'eau

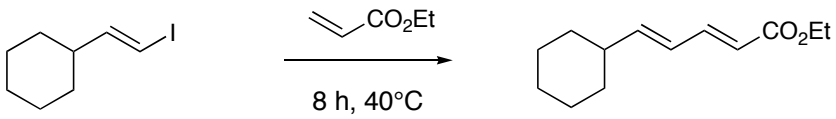




94 %



97 %

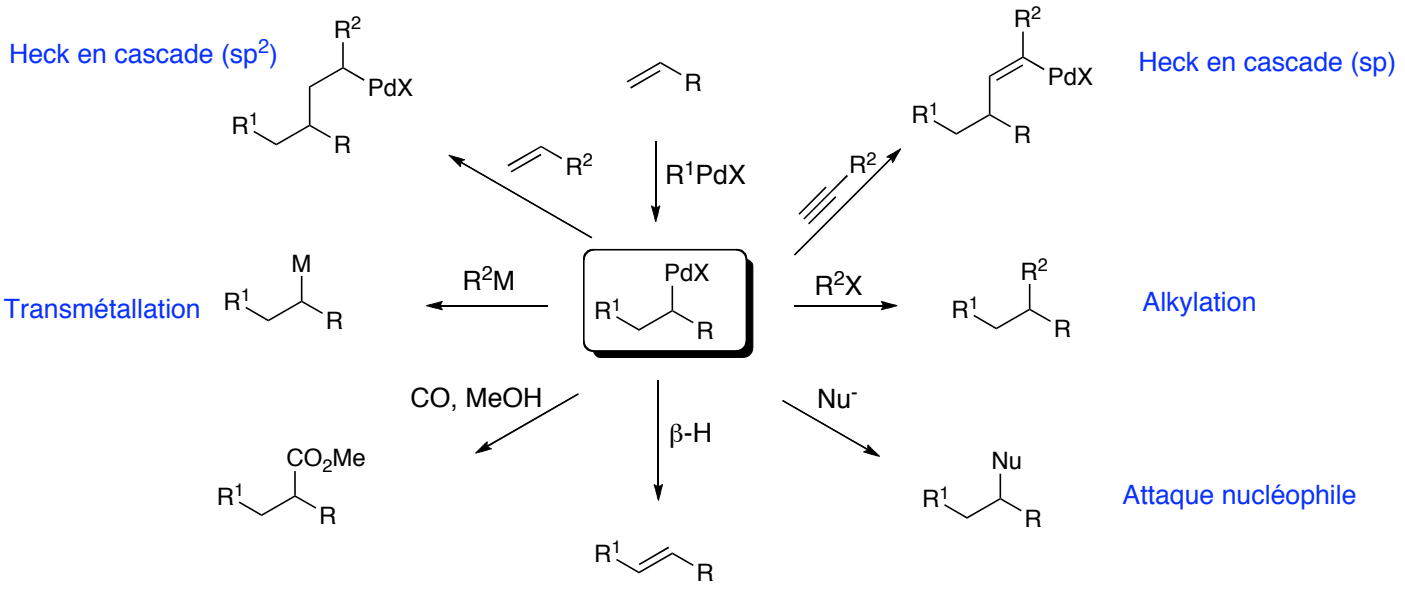


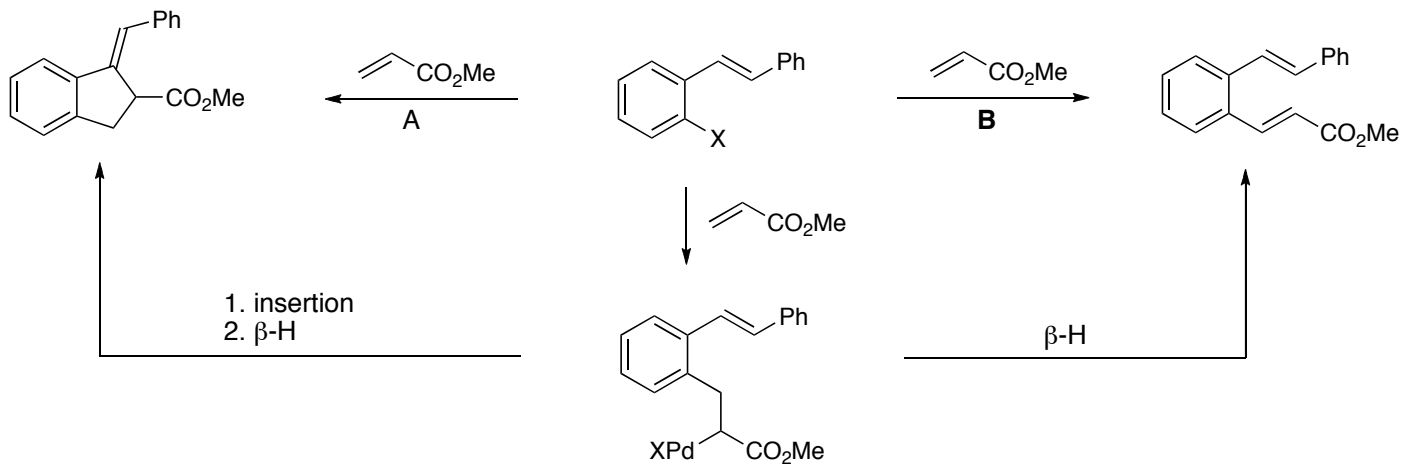
87 %

93 : 7

Genêt 92SL715

• Réaction en cascade et couplages multiples



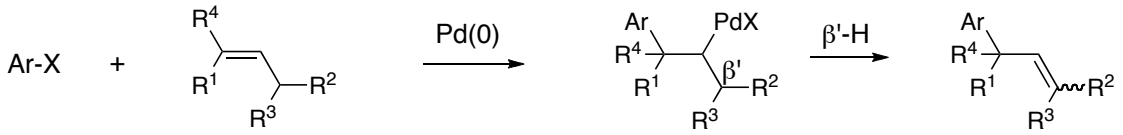


A = $Pd(OAc)_2$, NMP, $KHCO_3$, Bu_4NCl
B = $Pd(OAc)_2$, NEt_3, PAr_3, NMP

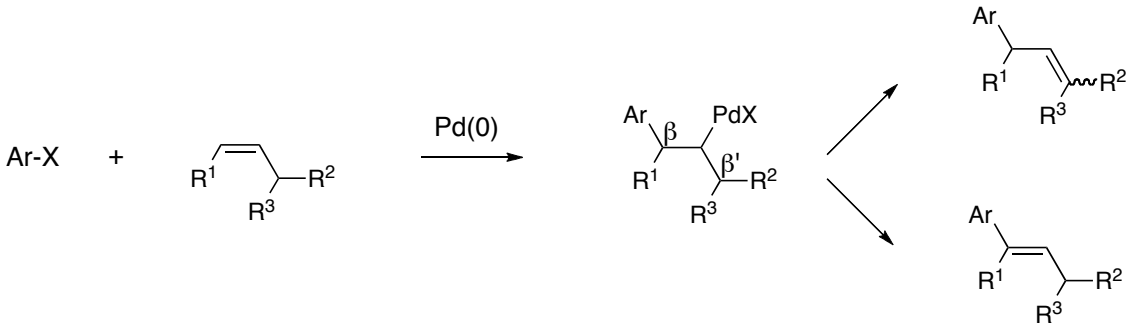
• Réaction de Heck asymétrique

- encore assez limité
- ligands bidentates

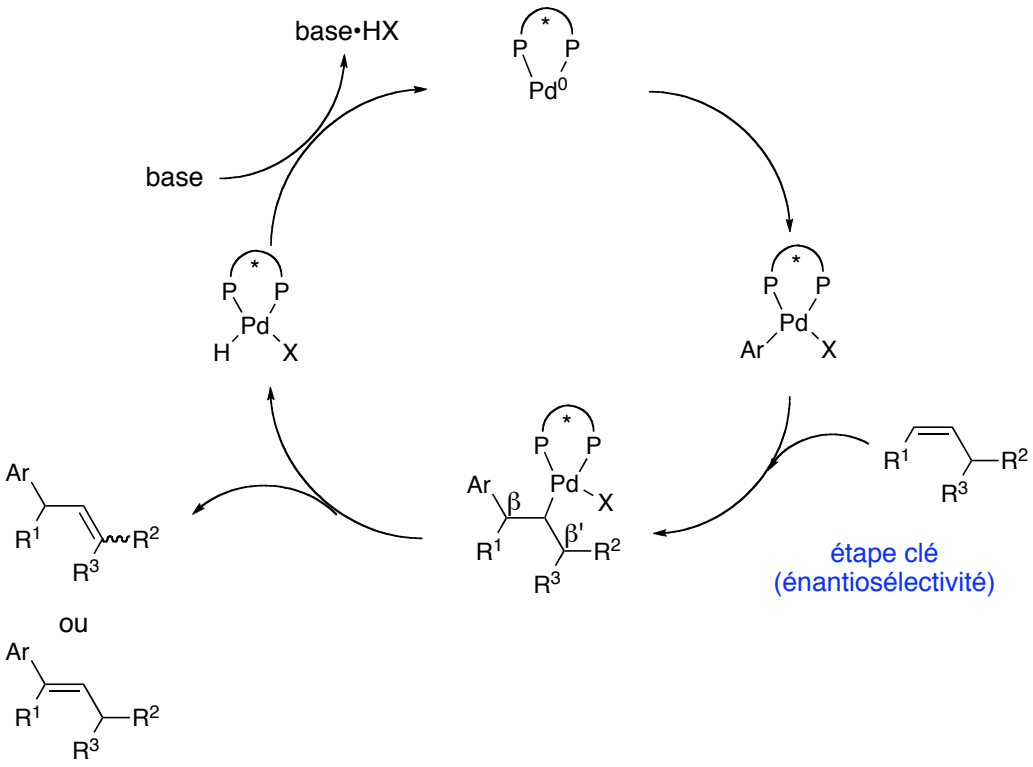
construction de C quaternaires

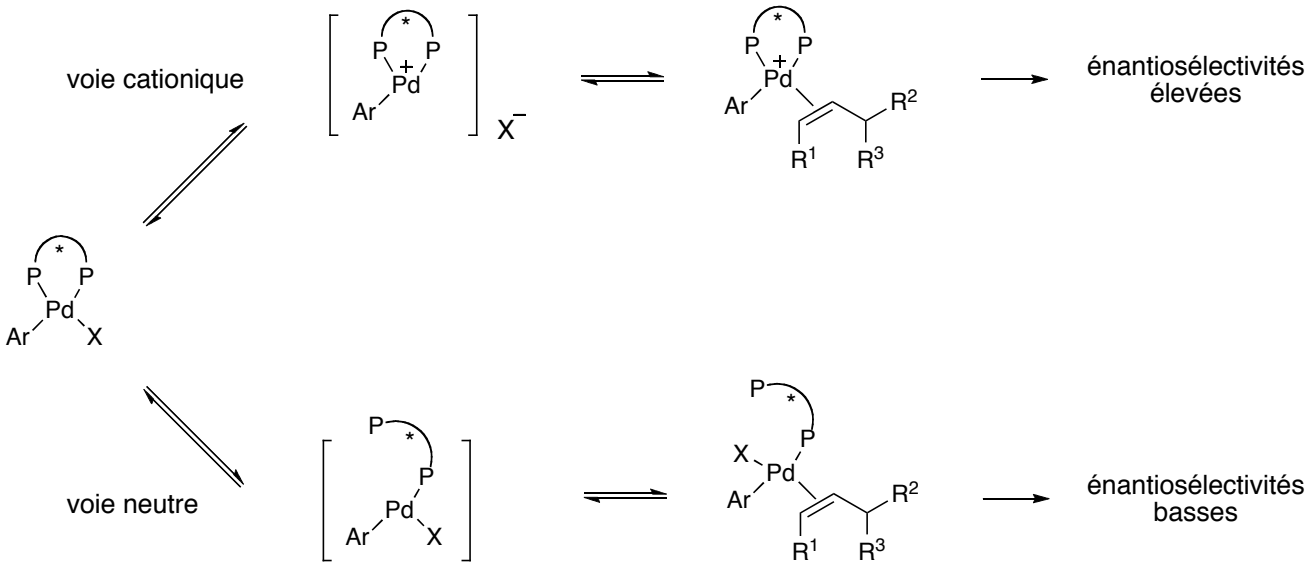


construction de C tertiaires

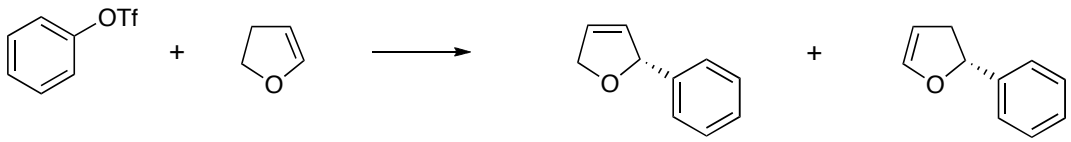


-> favoriser β'-H par rapport à β-H





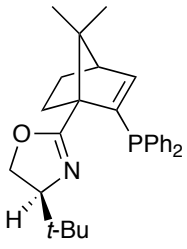
Exemples



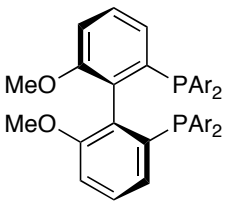
$Pd_2(dba)_3$, **A**, *i*-Pr_2NEt, PhH, 70°C — 100 %, 96 % ee

$Pd(OAc)_2$, **B**, 40°C — 65 %, 98 % ee

A



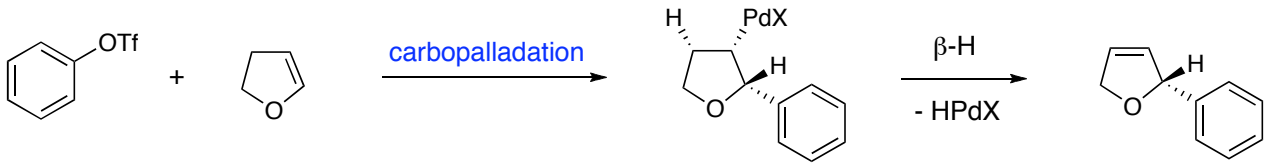
B

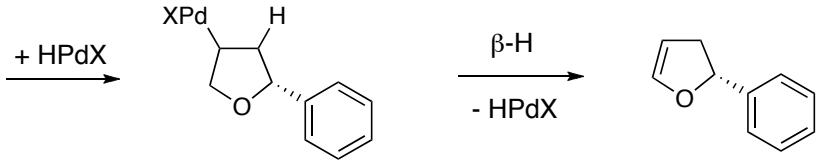


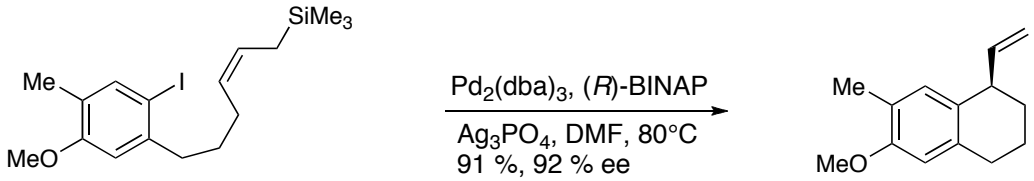
Ar = 3,5-(*t*-Bu)$_2C_6H_3$

Hayashi

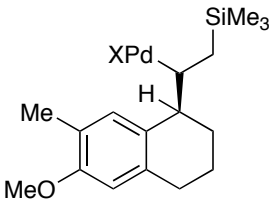
Exemples



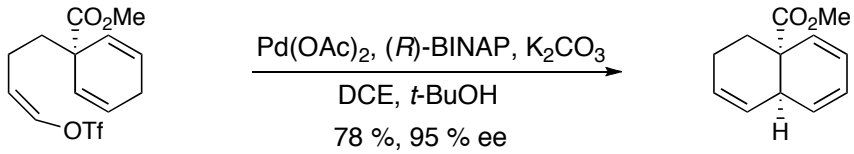


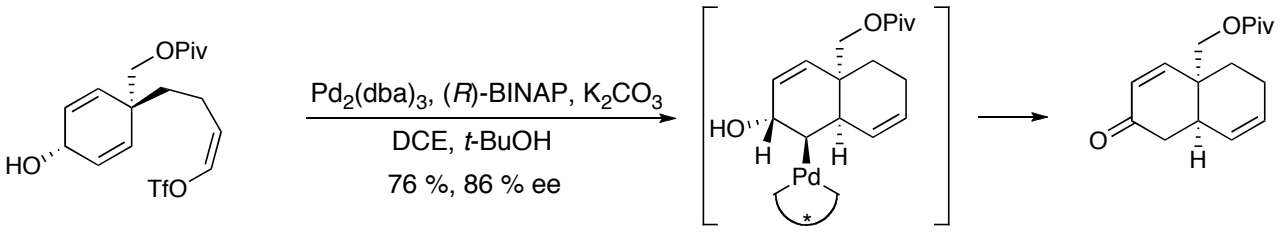


via



Tietze





Shibasaki