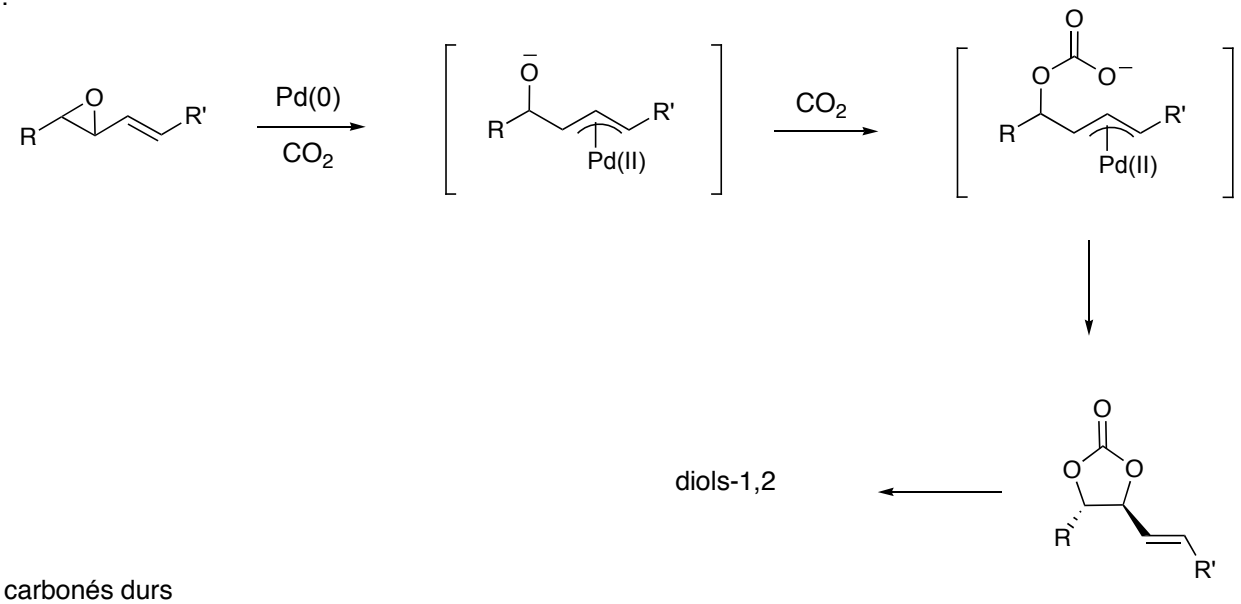
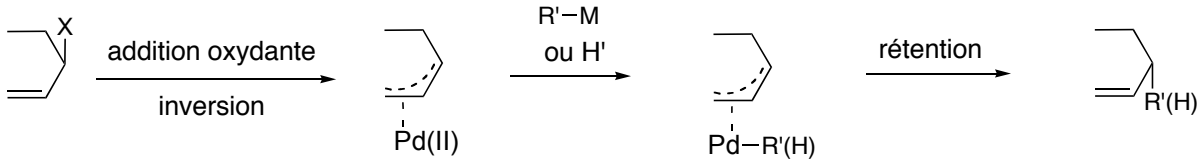
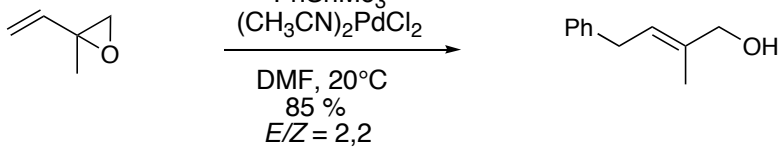
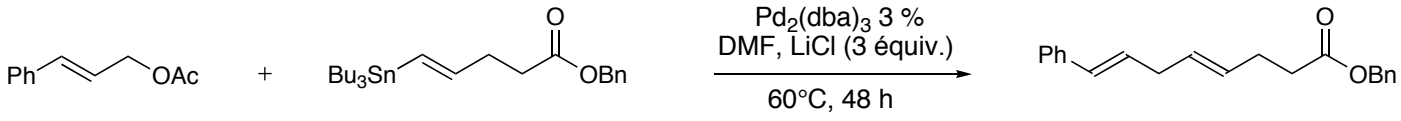
sauf :

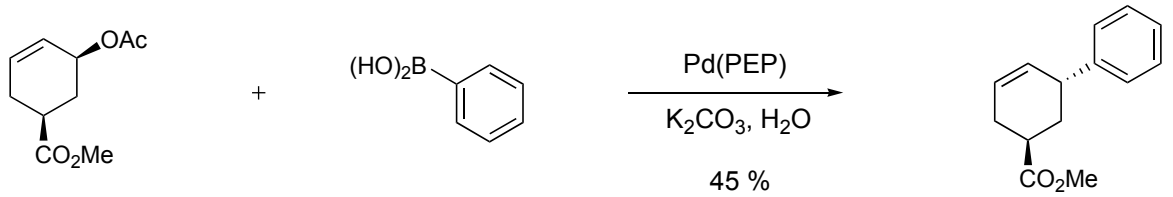


- Nu carbonés durs

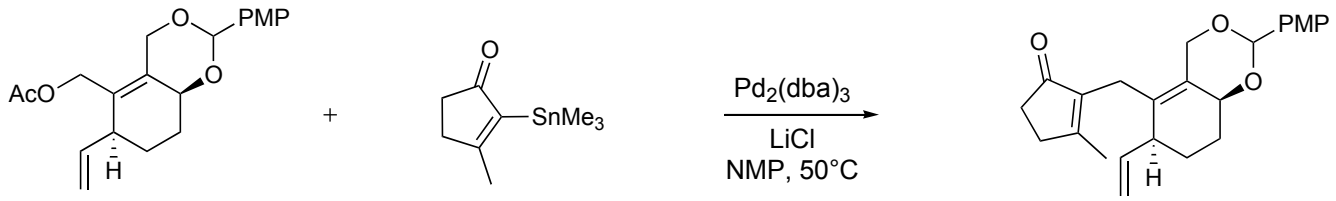


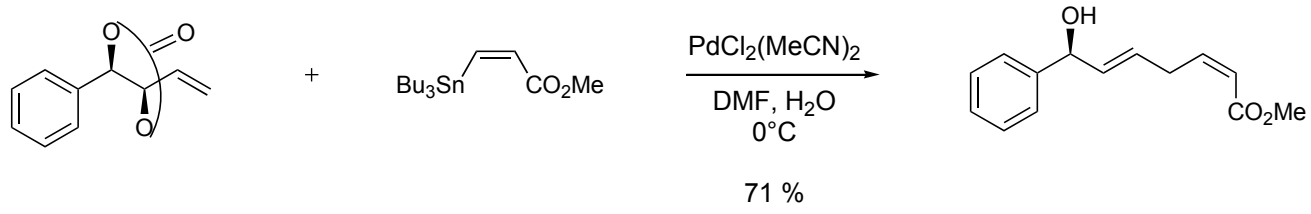


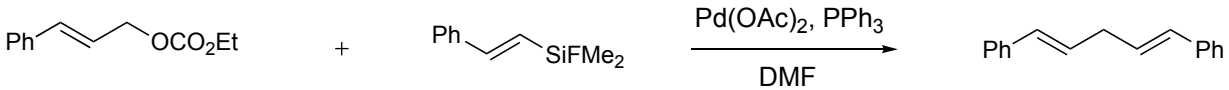


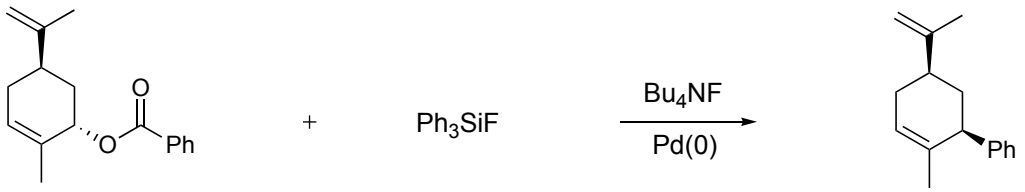

OAc
CO2Me
(HO)2B
Pd(PEP)
K2CO3, H2O
45 %
CO2Me

PEG/PS copo.


O
PMP
AcO
O
H
O
SnMe3
Pd2(dba)3
LiCl
NMP, 50°C
87 %
O
O
PMP
H

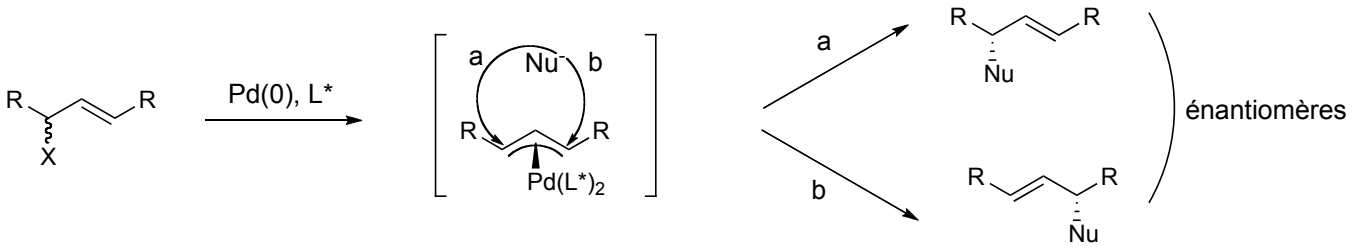

O
O
O
Bu3Sn
CO2Me
PdCl2(MeCN)2
DMF, H2O
0°C
71 %
OH
CO2Me

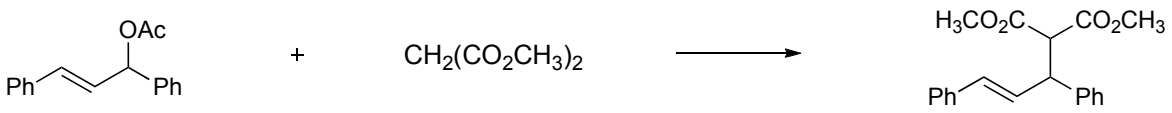

Ph
OCO2Et
Ph
SiFMe2
Pd(OAc)2, PPh3
DMF
91 %
Ph
Ph

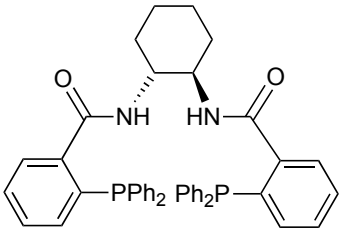

O
O
Ph
Ph3SiF
Bu4NF
Pd(0)
Ph

Catalyse asymétrique

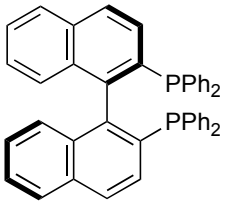
a) Désymétrisation de complexes π-allyl *méso*



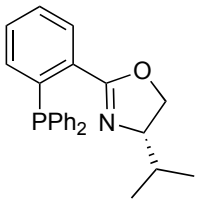




86 % ee
Trost

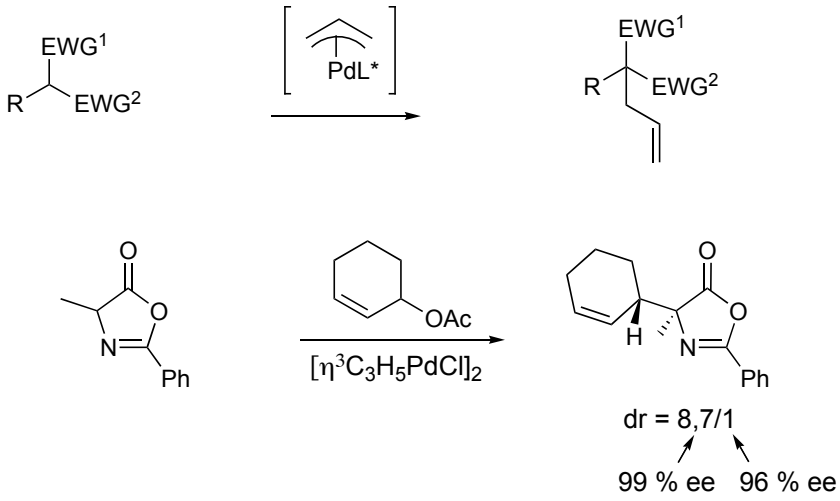


34-90 % ee
Trost
Yamaguchi

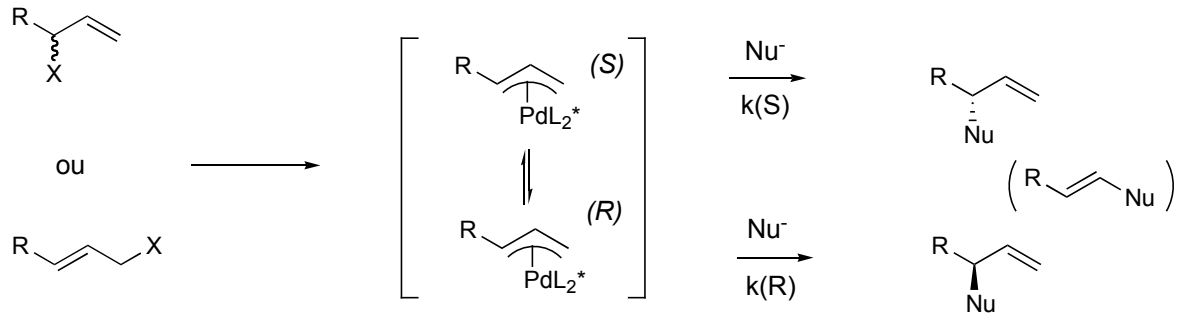


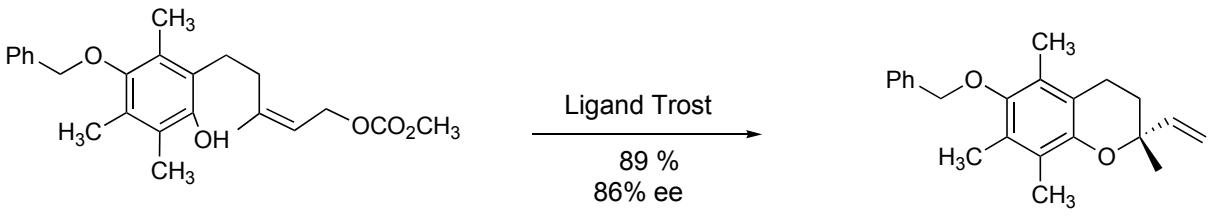
98-99 % ee
Pfaltz

b) Création d'un centre chiral sur le nucléophile



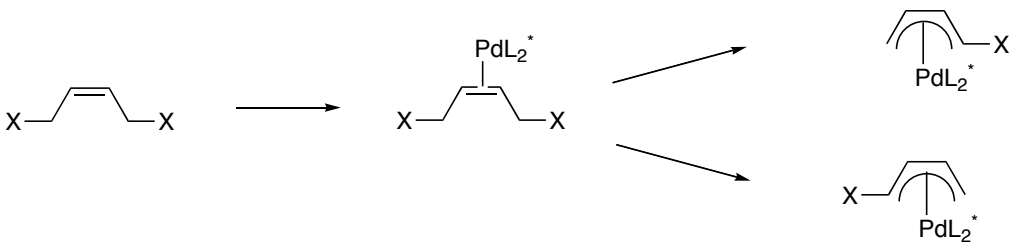
c) Complexe π–allyle disymétrique

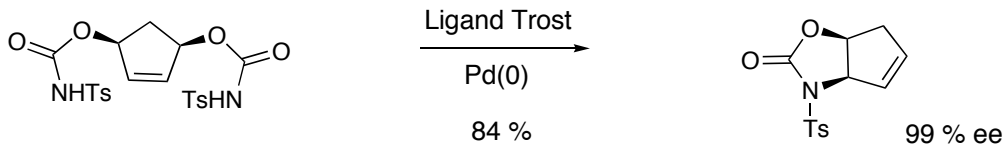




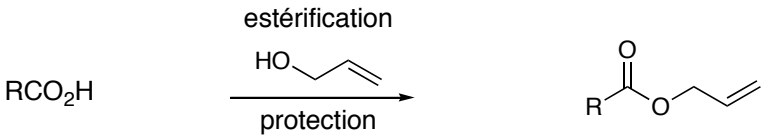
Trost, 99S1491

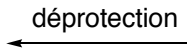
d) Groupements partants énantiotopiques

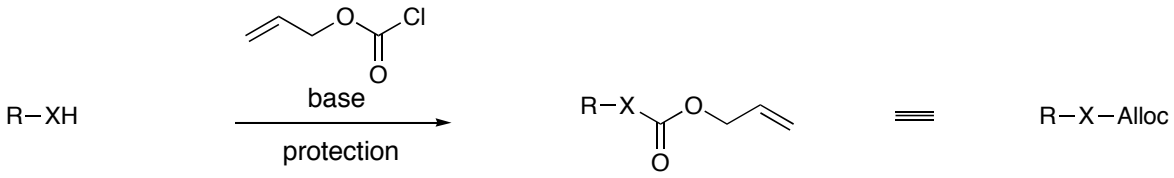




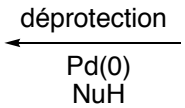
Application dans le développement de nouveaux groupes protecteurs





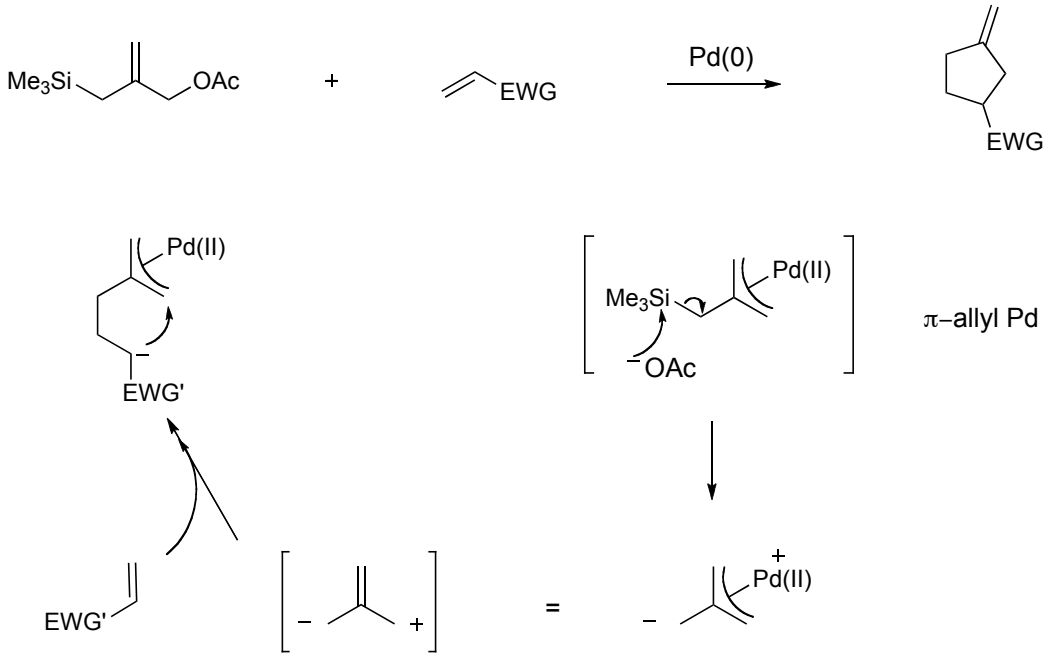


X= O, NH



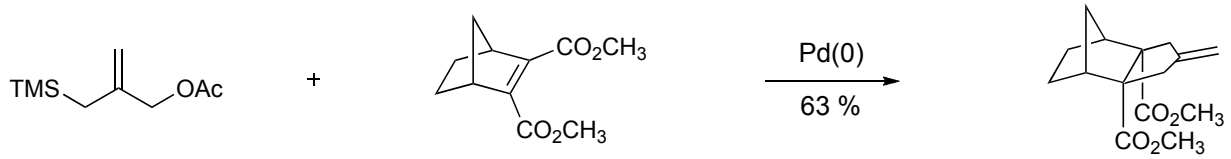
Chimie des TMM

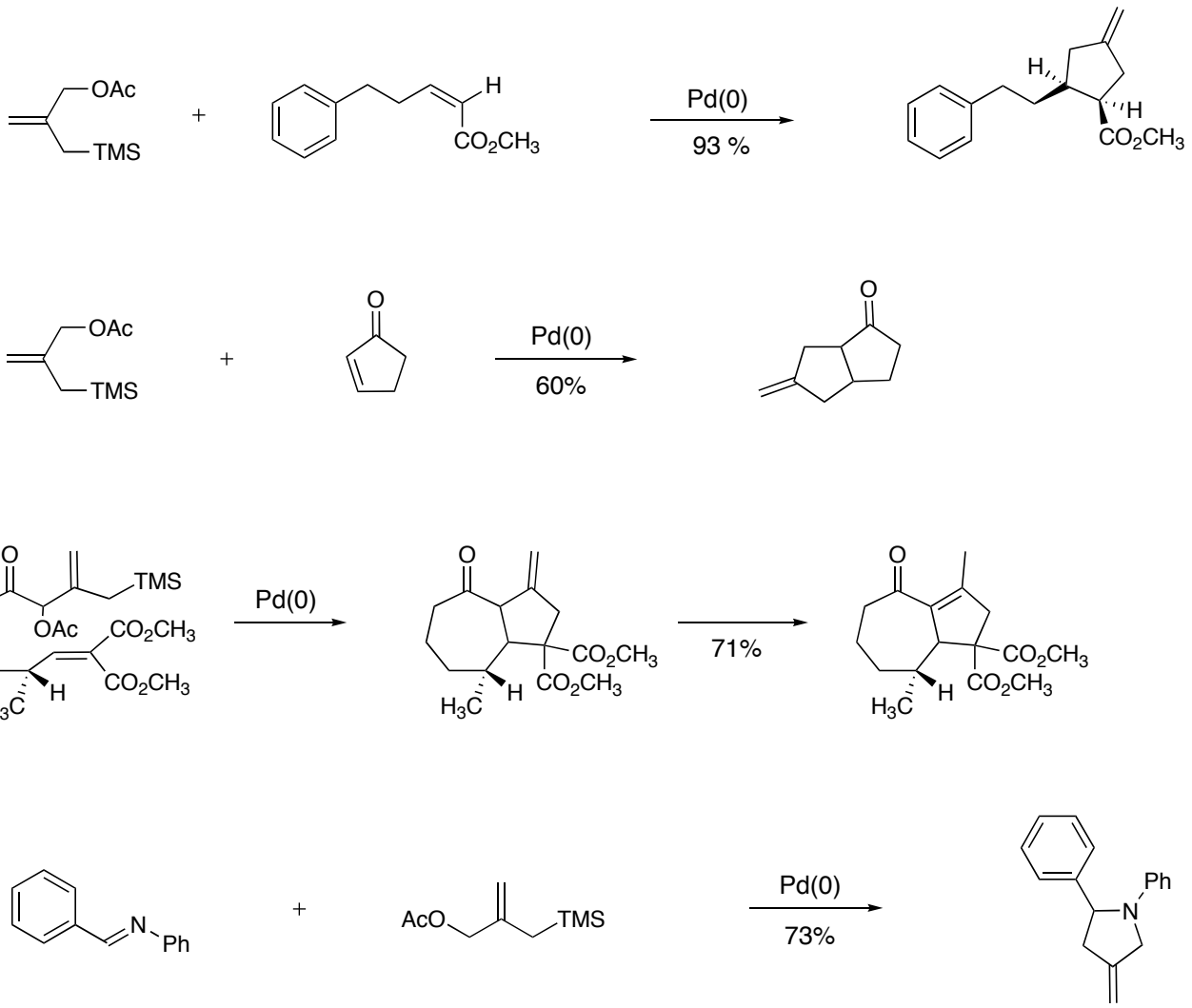
TMM = triméthylèneméthane
Trost, 80's
= cycloaddition [3+2]



forme zwitterionique

2 étapes successives :
- addition de type Michael
- puis l'énolate formé attaque le π–allyl Pd




OAc
TMS
+
H
CO2CH3
Pd(0)
93 %
H
H
CO2CH3
OAc
TMS
+
O
Pd(0)
60%
O
O
TMS
OAc
CO2CH3
CO2CH3
H3C
H
Pd(0)
O
CO2CH3
CO2CH3
H3C
H
71%
O
CO2CH3
CO2CH3
H3C
H
N
Ph
+
AcO
TMS
Pd(0)
73%
Ph
N