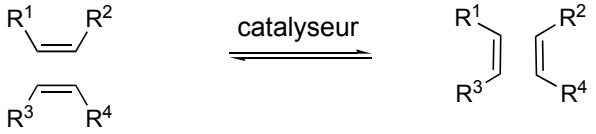
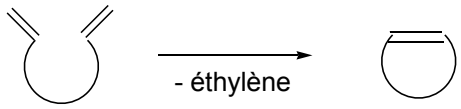
Métathèse

Historiquement

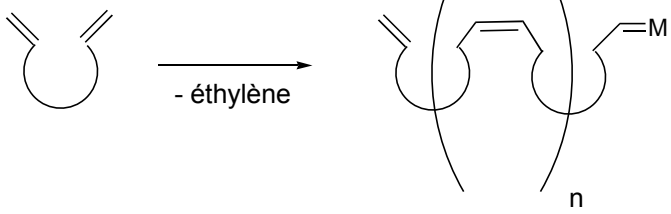


= échange d'alkylidènes, 1957

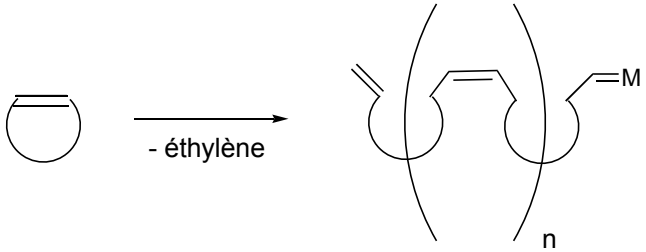
= cross metathesis (CM)



Ring closing metathesis (RCM)

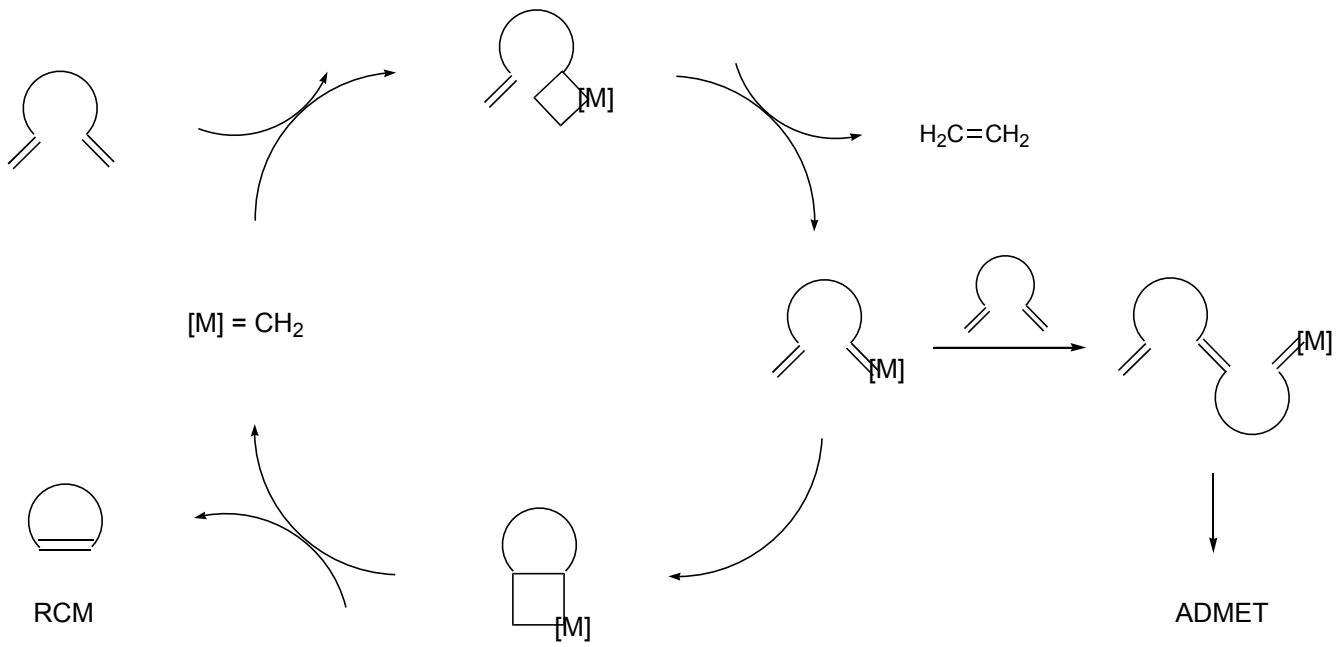


Acyclic Diene Metathesis Polymerization (ADMET)

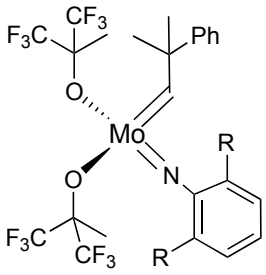


Ring Opening Metathesis Polymerization (ROMP)

RCM : cycle catalytique

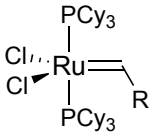


- Catalyseurs



Schrock (1990)

1-Mo

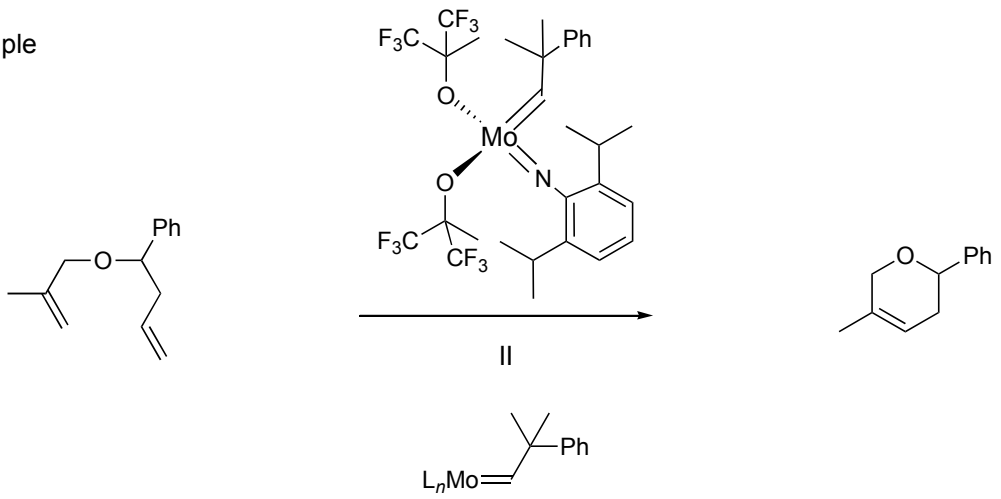


R = $^{-}CH=CPh_2$, Ph

Grubbs (1992, 1995)

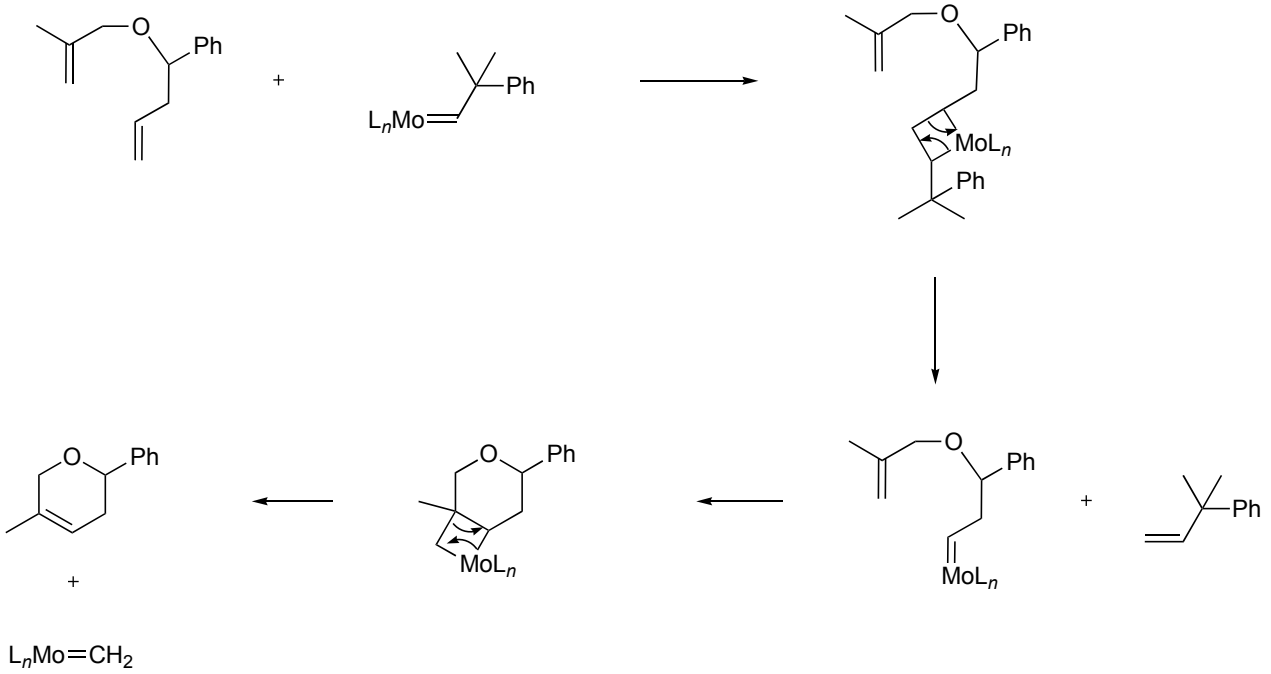
2-Ru , 3-Ru

Exemple

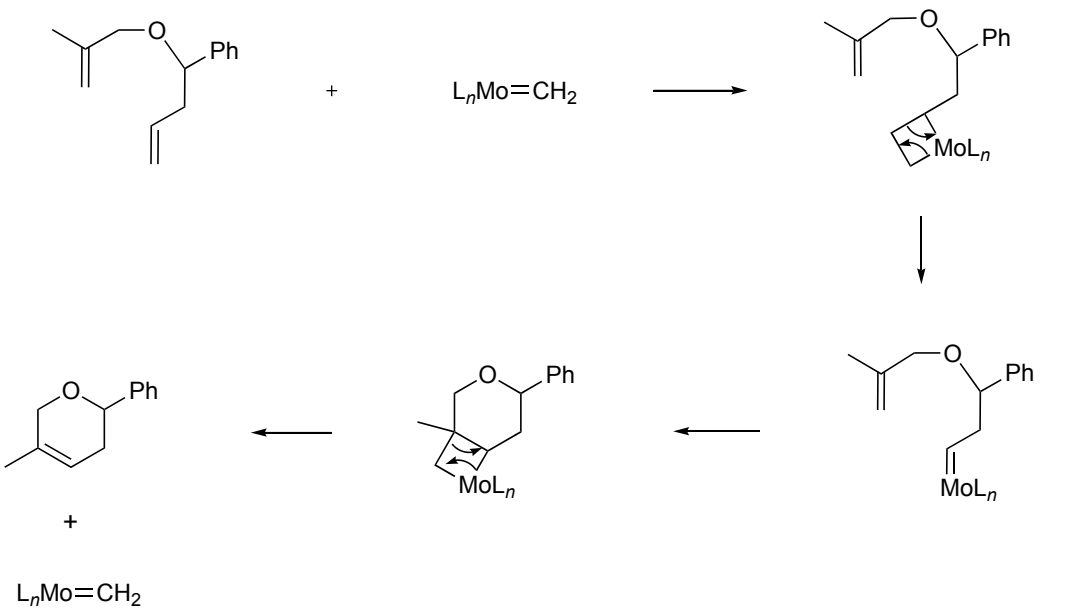


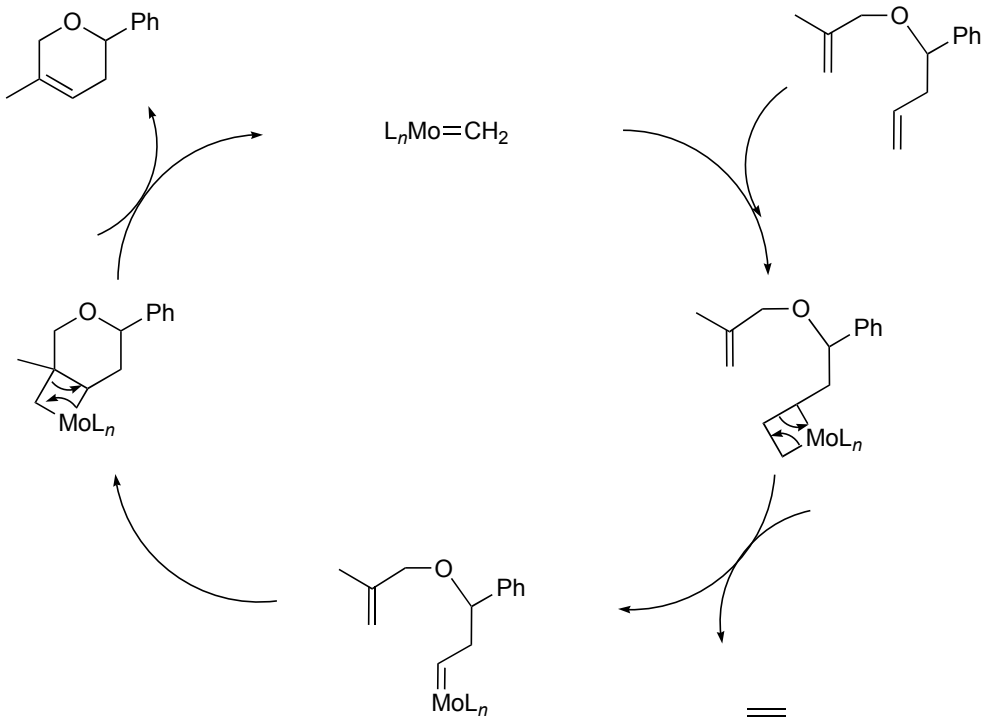
Mo VI (d°), 12 e$^-$

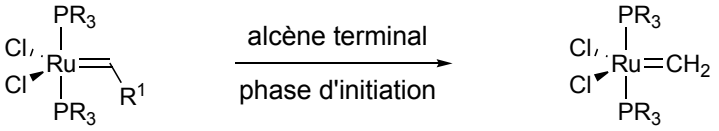
1er cycle catalytique



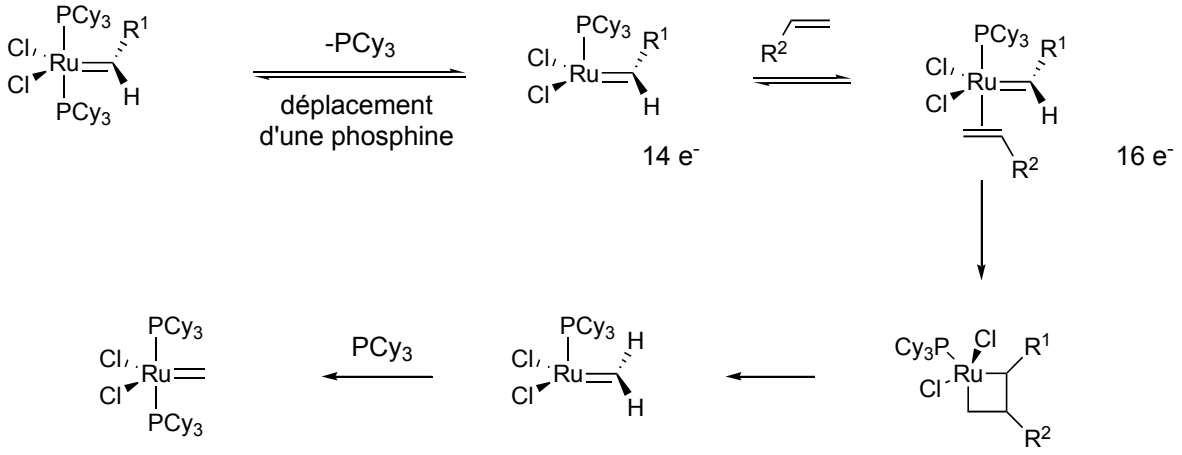
Cycles catalytiques suivants :



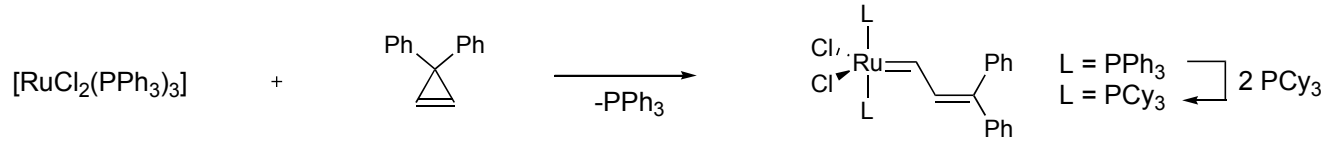


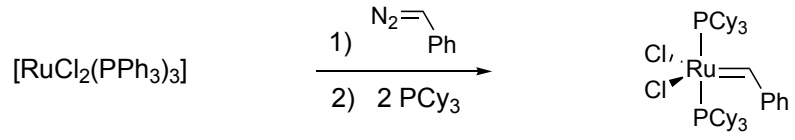


Mécanisme dissociatif

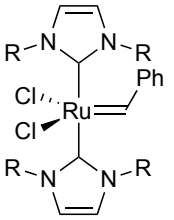


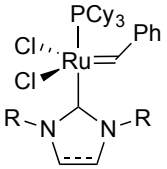
- Synthèse des catalyseurs





Catalyseurs de seconde génération





Hermann, Nolan

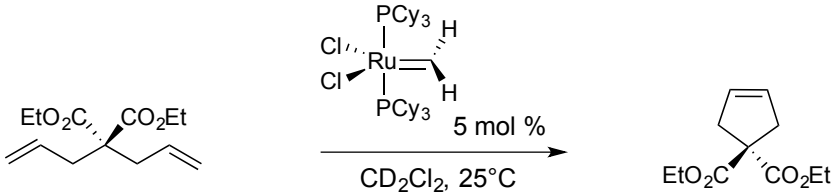
- Mécanisme

Mécanisme de Chauvin via métallocyclobutanes

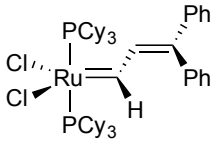
Chauvin et al. Makromol. Chem. 1970, 141, 161-176

Intermédiaires métallocyclobutanes et métaux-carbènes

Grubbs et al. JACS 1975, 3265



- Cycles à 5,6,7 cycloalcanes ou cycles azotés ou oxygénés formés efficacement

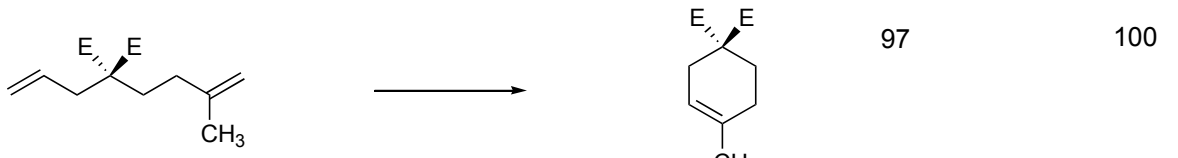
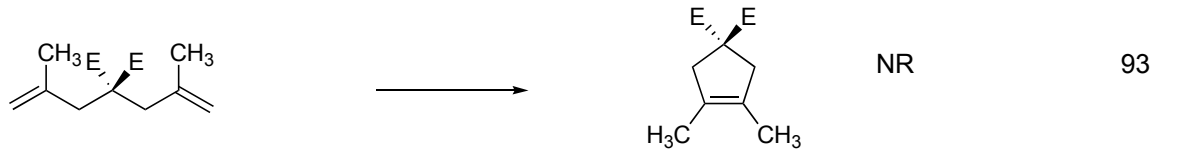
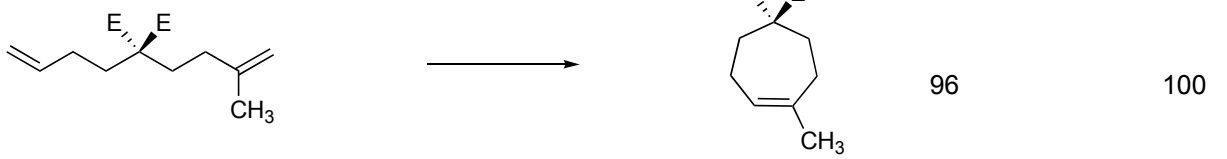
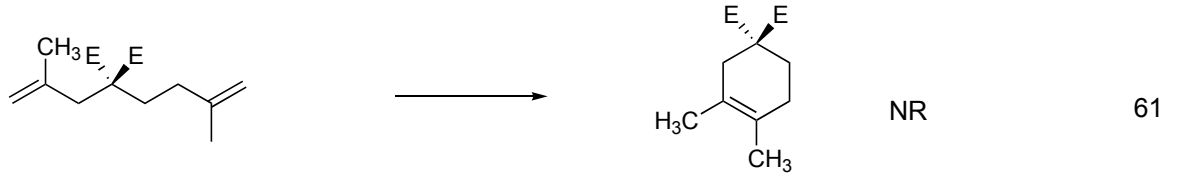


2- Ru utilisable à l'air avec des solvants de pureté normale

catalyseur 1-Mo réagit avec : acides, alcools et aldéhydes

mais catalyseur 2-Ru stables avec ces fonctionnalités.

- Généralités des substrats

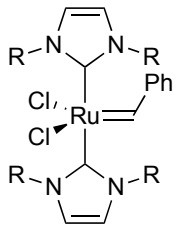
	3-Ru rdt (%)	1-Mo rdt (%)
	97	100
	NR	93
	96	100
	NR	61

→ Si les groupes fonctionnels le permettent, Mo alkylidène est classiquement + efficace pour RCM d'oléfines substituées

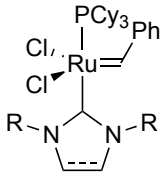
Grubbs 97JOC7310

Métathèse II

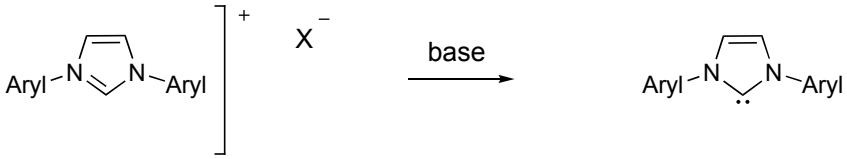
- Catalyseurs de seconde génération

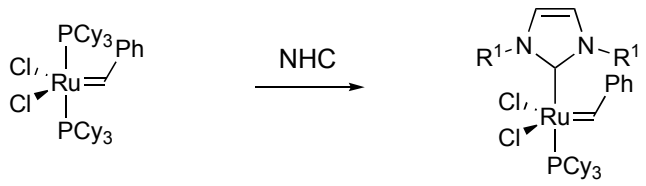


Hermann 98ACIEE2490



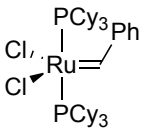
Nolan 99JACS2674
Grubbs 99TL2247, 99OL953
Fürstner, Hermann 99TL4787

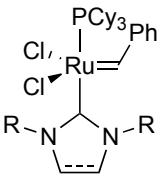


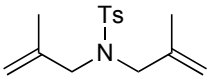


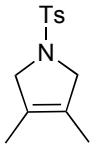
Avec Grubbs I, dissociation de PCy_3 rapide mais la recoordination est compétitive avec l'alcène

Avec Grubbs II, dissociation de PCy_3 peu efficace mais une fois que PCy_3 est partie, il y a coordination facile avec l'oléfine

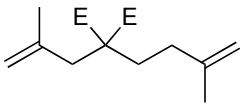


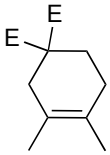




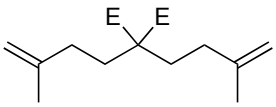


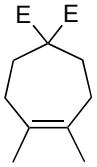
0 % 80 %





0 % 90 %

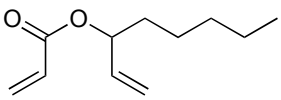


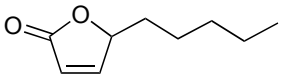


0 % 83 %

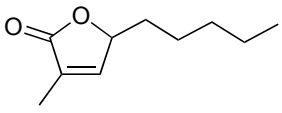
Fürstner, Hermann 99TL4787

- Complexes Ru-carbènes (NHC) : RCM d'acrylates

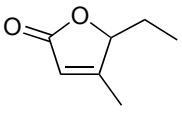




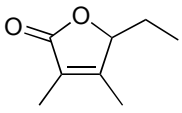
93 %



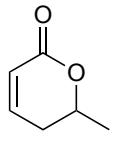
92 %



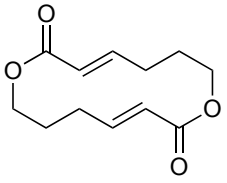
78 %



63 %



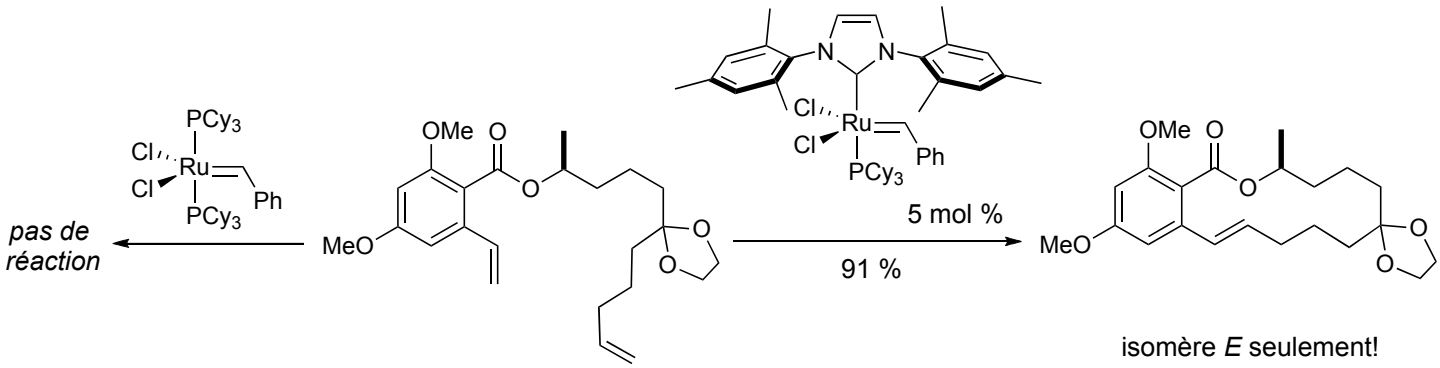
95 %



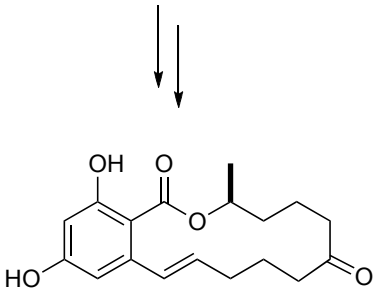
62 %

Fürstner 2000JOC2204

complexe Ruthenium NHC : RCM de styrènes



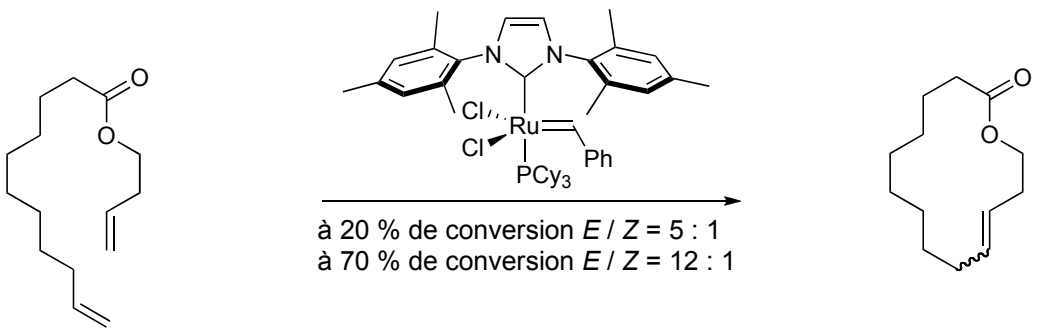
isomère *E* seulement!



Zéaralénone

Fürstner 2000JOC7990

Problèmes de réversibilité



à 20 % de conversion *E* / *Z* = 5 : 1
à 70 % de conversion *E* / *Z* = 12 : 1

Grubbs 2000OL2145