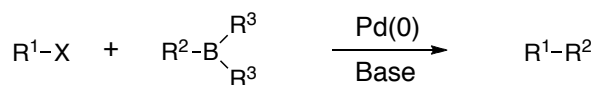


Réaction de Suzuki-Miyaura

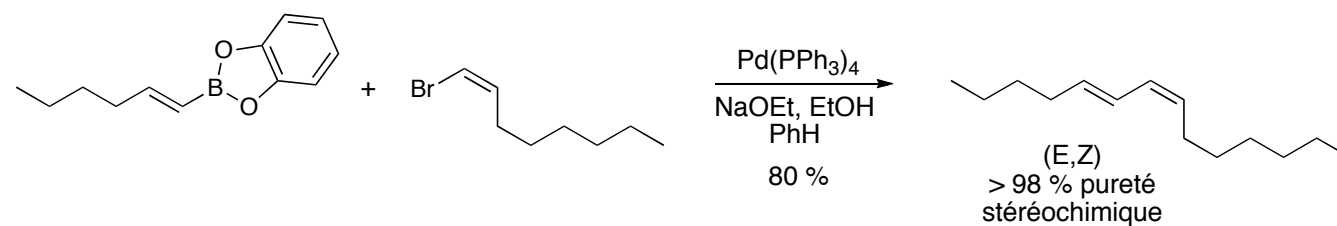
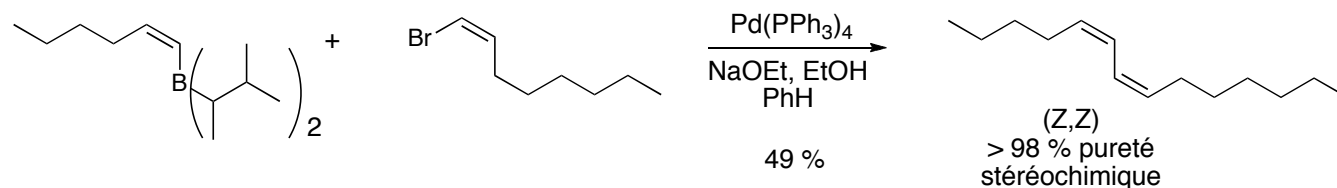
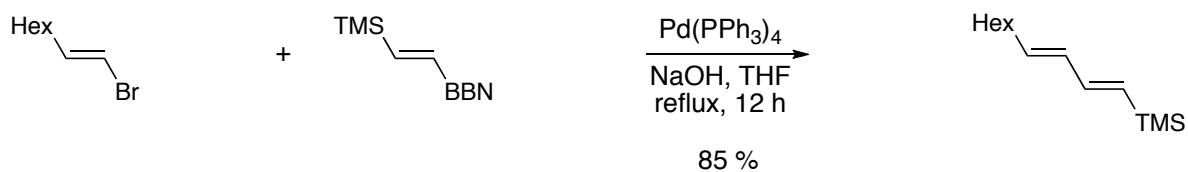
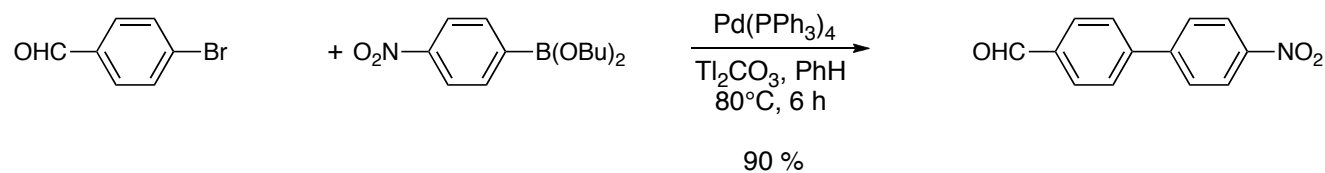
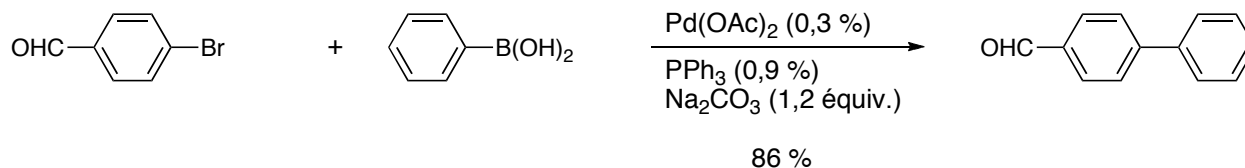


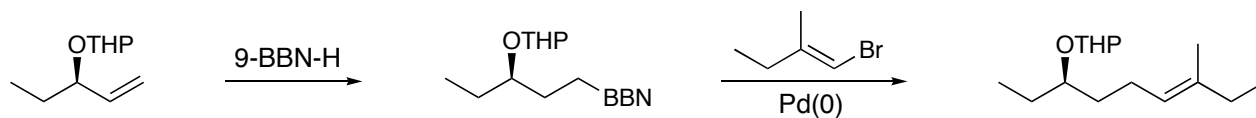
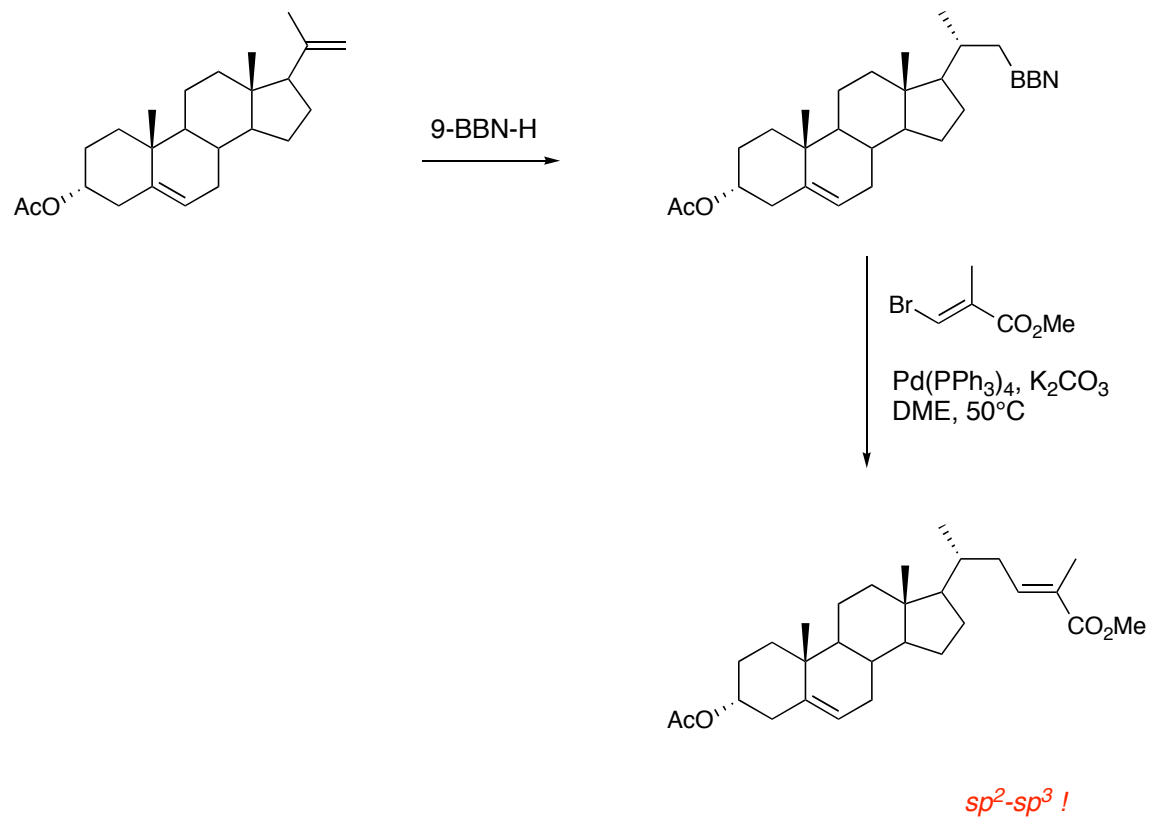
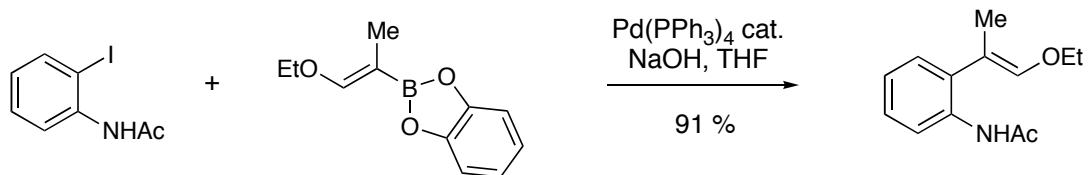
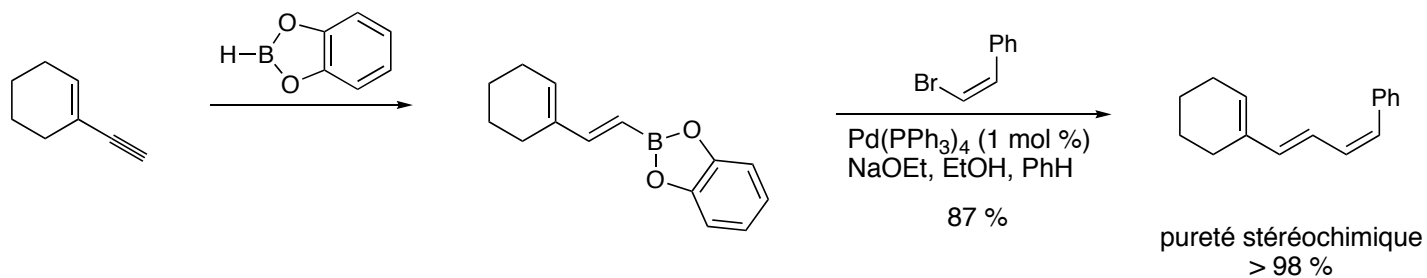
R^1 : vinyl, aryl
 R^2 : vinyl, aryl, alkyl
 R^3 : OH, OR, alkyl
 X : I, OTf, Br, Cl

Miyaura, Suzuki 95CR2457
 Suzuki 99JOM147

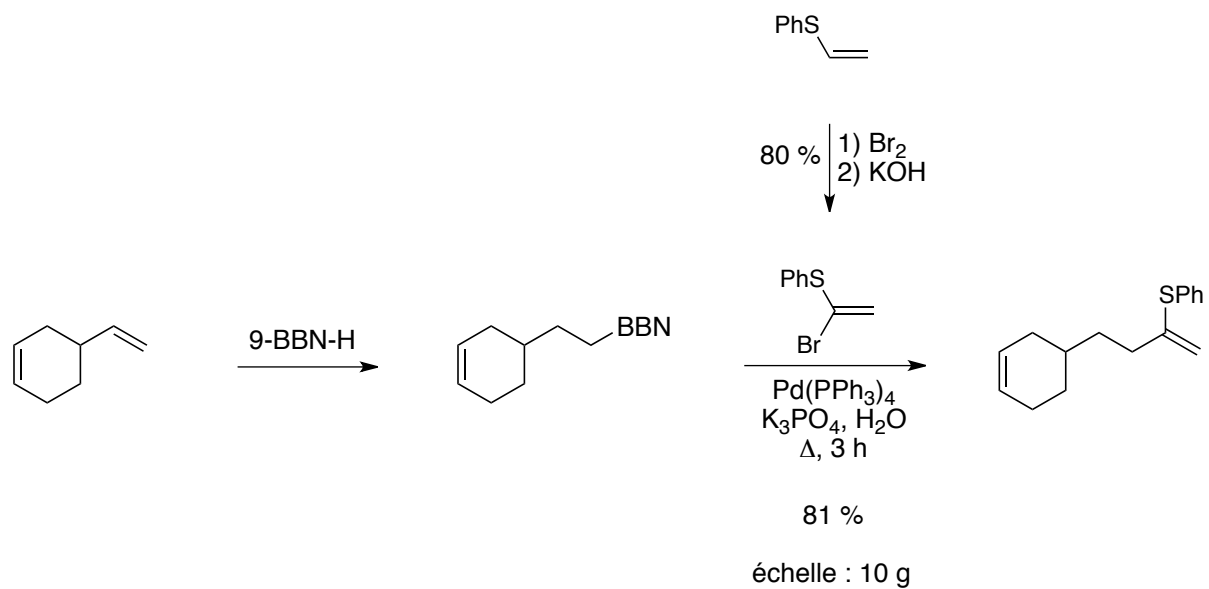
Heck, 1968 : sp^2 - sp^2
 Stille, 1985 : sp^2 - sp^2 (Sn)
 Suzuki, 1981 : sp^2 - sp^2 (B)
 sp^2 - sp^3 (B)

• Exemples



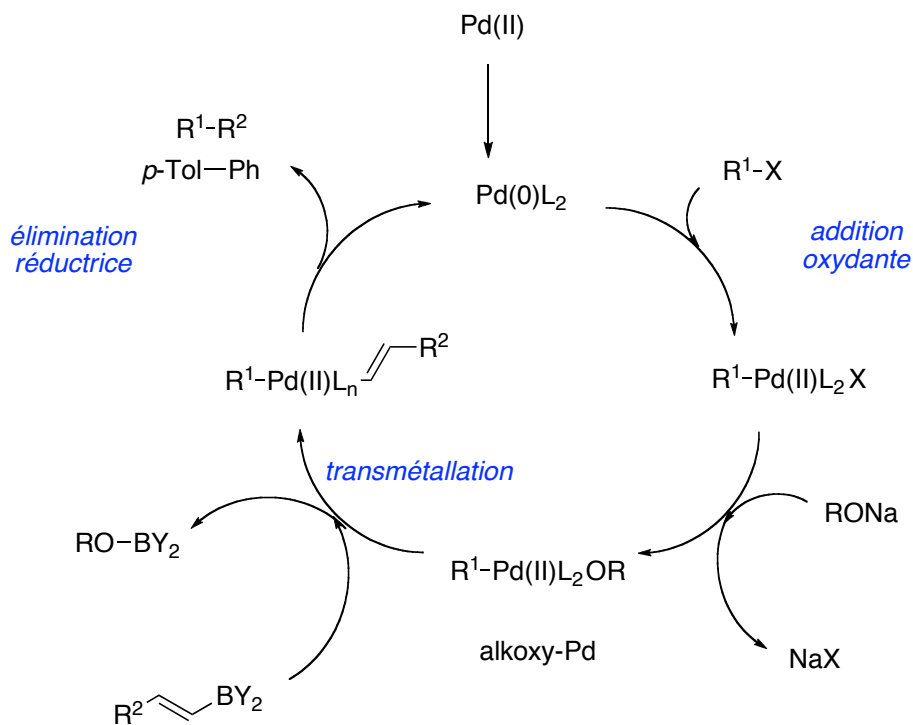


Mori 90L159

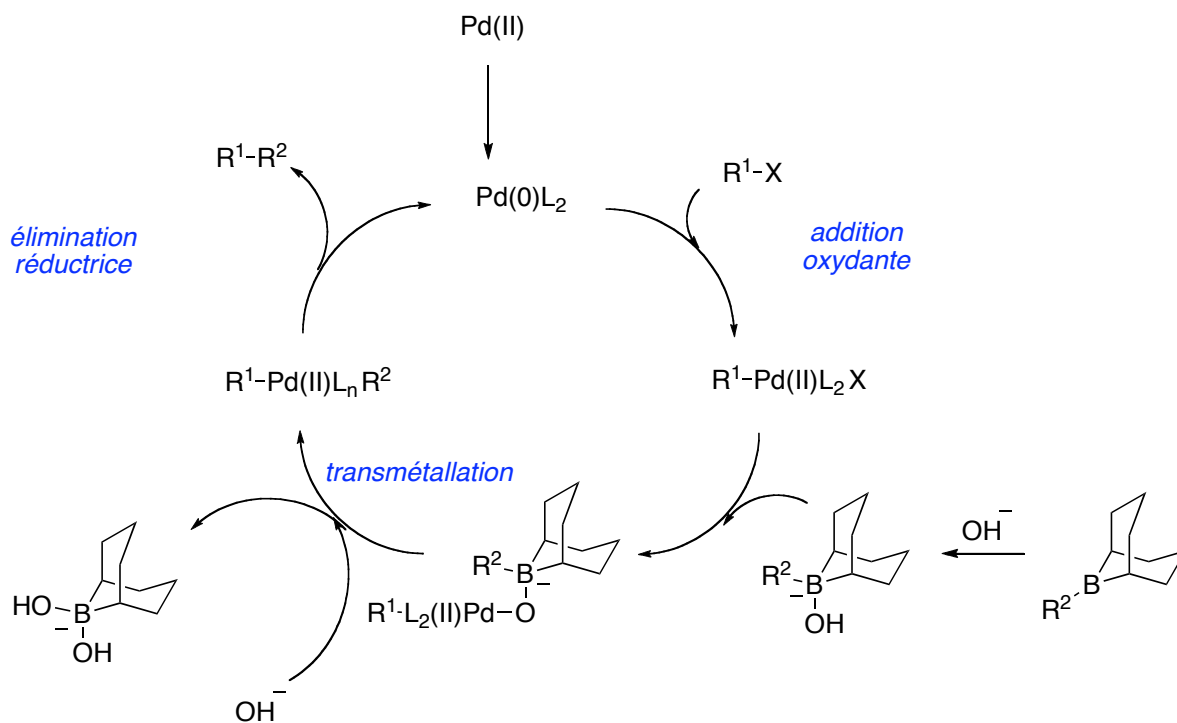


93OS89

• Cycle catalytique



Mécanisme via un complexe "ate"



Danishefsky 2001ACIEE4544

OH⁻ : 1^{er} équivalent pour activer borane
 2^{ème} équivalent pour capturer l'espèce de bore

Caractéristiques générales

• Nature de la base

KOH, NaOH, Ba(OH)₂, Na₂CO₃, Cs₂CO₃, NaOEt, Et₃N

Récemment : TlOH, Tl₂CO₃ (nombreuses réactions à 20°C, formation de sels insolubles de thallium, toxicité donc pas recommandé sur grande échelle)

• Systèmes de solvants : organiques, biphasiques, aqueux

• Avantages de la réaction de Suzuki :

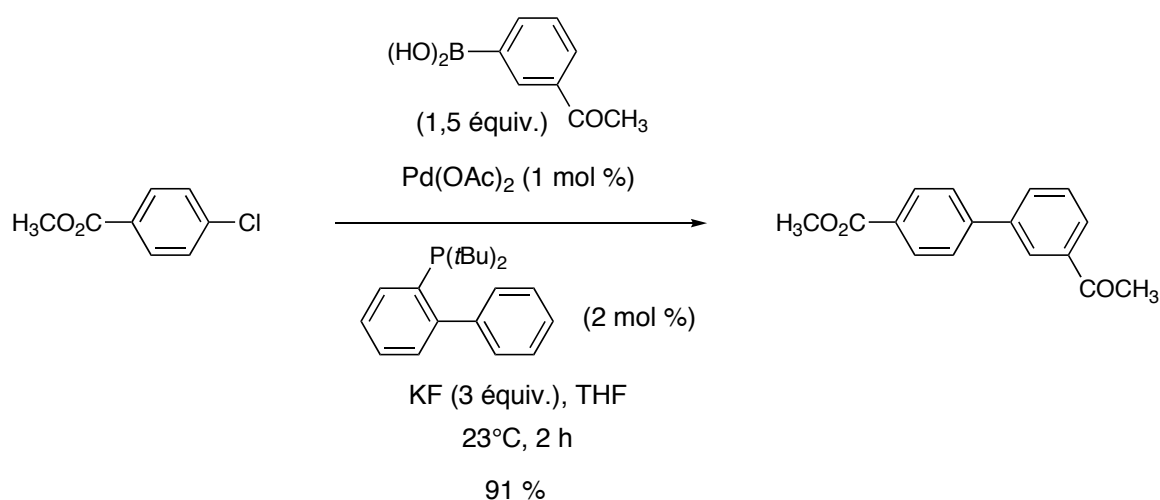
- Nombreux organoboranes disponibles commercialement (en particulier acides boroniques et esters boroniques)
- Stabilité des acides boroniques à : chaleur, air et humidité
- Grande tolérance de groupes fonctionnels : CO₂R, CN, CHO, NH₂, NO₂
- Conditions réactionnelles douces : conditions anhydres pas nécessaires
- Toxicité peu élevée
- Séparation facile des sous-produits inorganiques du bore

• Réactivités relatives des groupes partants :

I⁻ > OTf⁻ > Br⁻ > Cl⁻

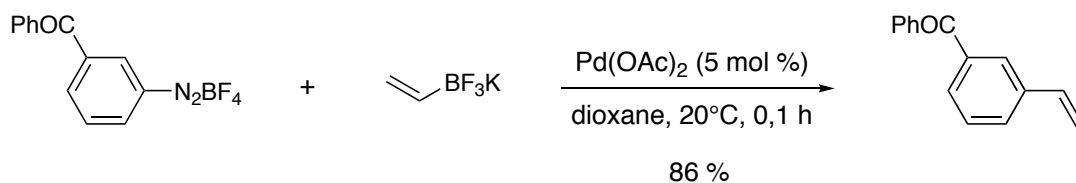
I⁻, OTf⁻ et Br⁻ les plus utilisés

- Intérêt des chlorés sur le plan industriel



Buchwald 99ACIEE2413
 99JOC6797
 99JACS9550

- Utilisation des diazoniums

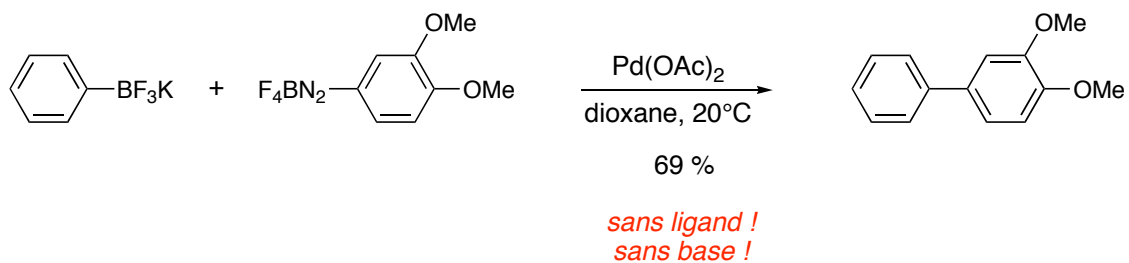
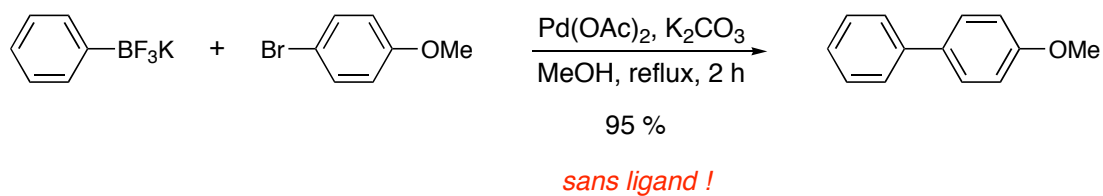


98TL5045

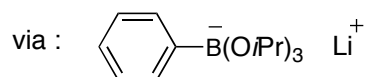
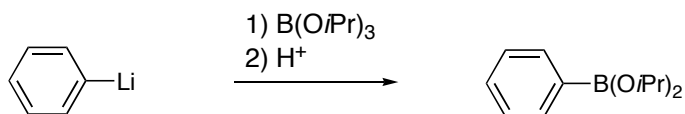
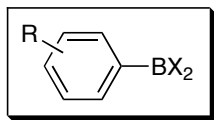
souvent à 20°C, sans base et sans ligands !

96BCSF1095
97JOC3405

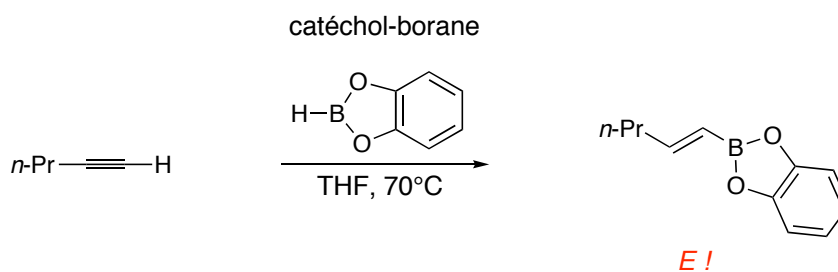
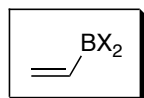
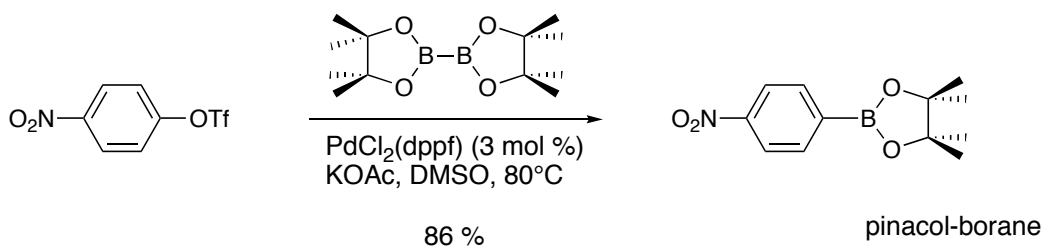
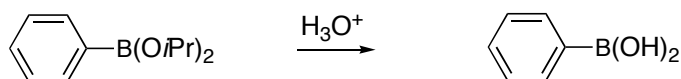
• Organotrifluoroborates : bons partenaires pour la réaction de Suzuki



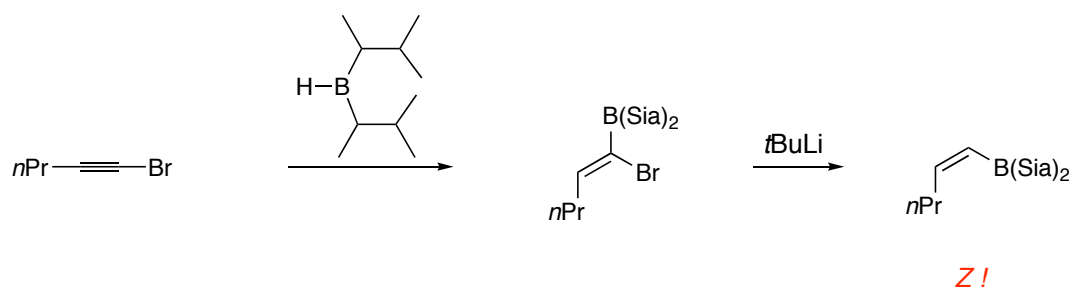
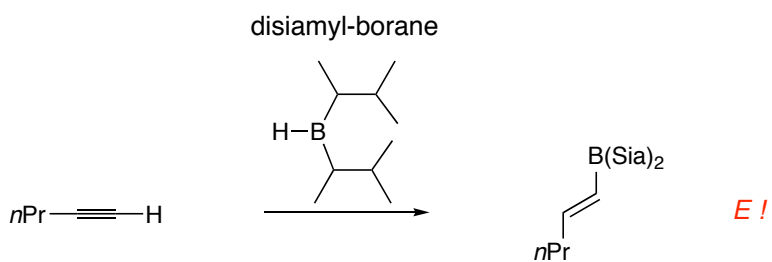
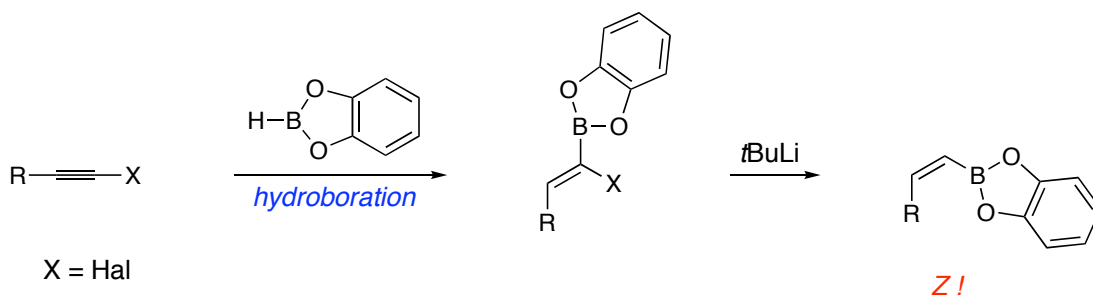
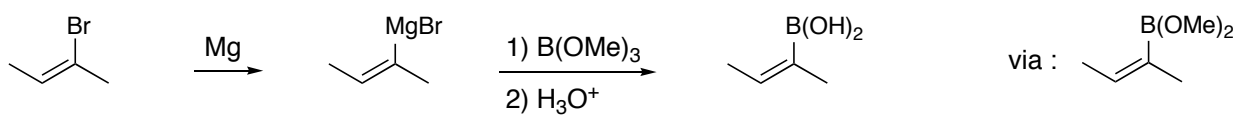
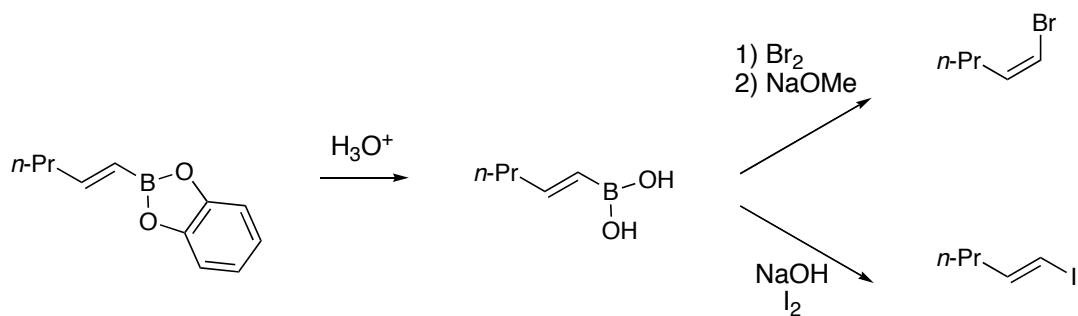
• Préparation des réactifs

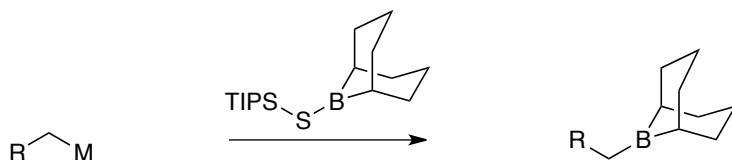
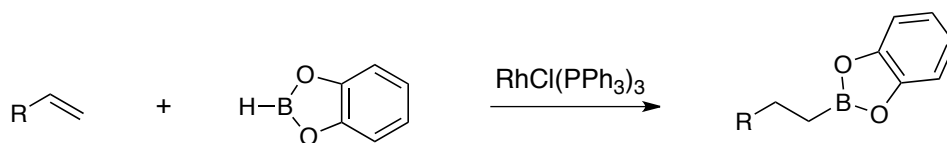
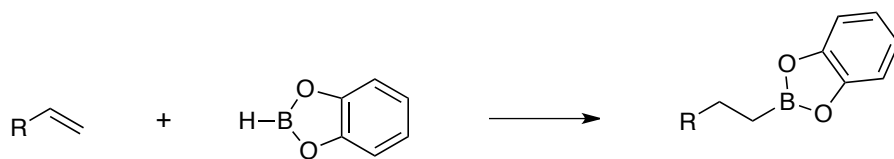
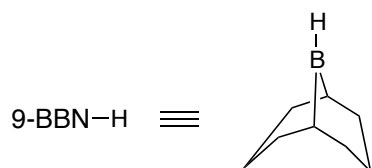


Brown 83OM1316



Brown 72JACS4370



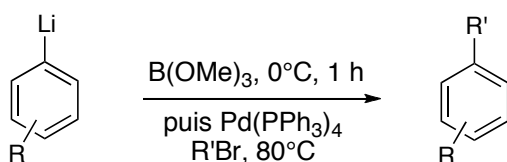
Alk-BR₂

M = MgBr, Li

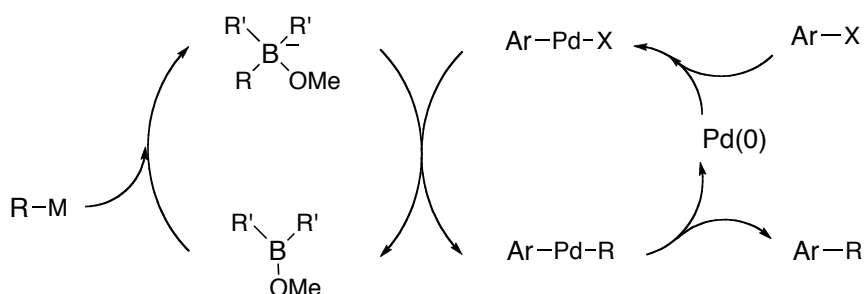
-> Transfert de groupes alkyl I beaucoup plus rapide que alkyl II
 -> Transfert de groupe sélectivement à l'étape de transmétallation

- Espèce organométallique

- Beaucoup d'acides arylboroniques disponibles commercialement
- Certaines réactions sont possibles en "un seul pot" : espèce organométallique formée in situ



- Version catalytique



Füstner 95T11165

