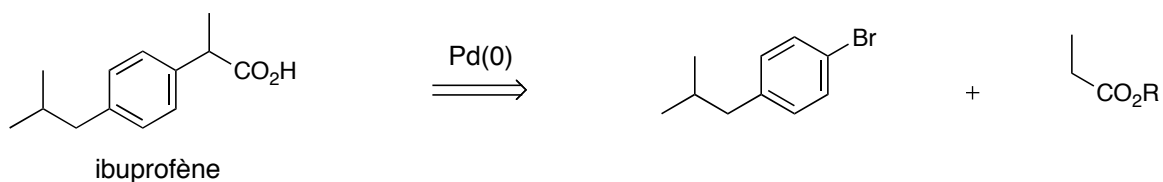


Arylation et alcénylation

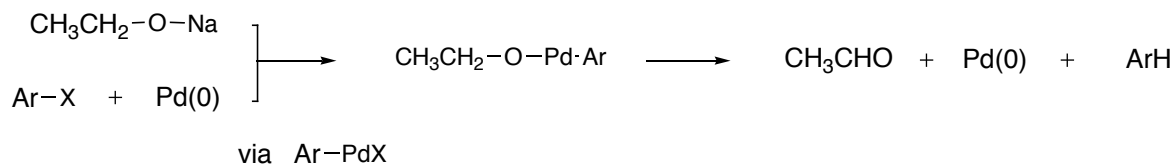
α -arylation et α -alcénylation des carbonyles ont toujours été considérées comme des réactions difficiles

Percée récente grâce à de nouveaux ligands $\begin{cases} \text{ligands encombrés} \\ \text{ligands riches en électrons} \end{cases}$

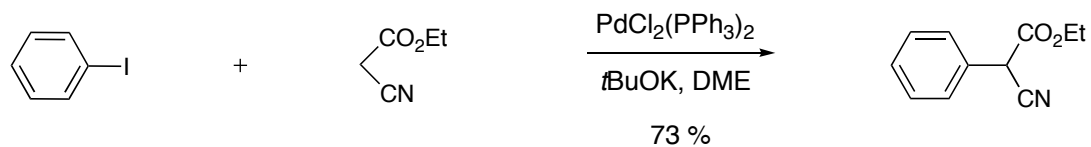


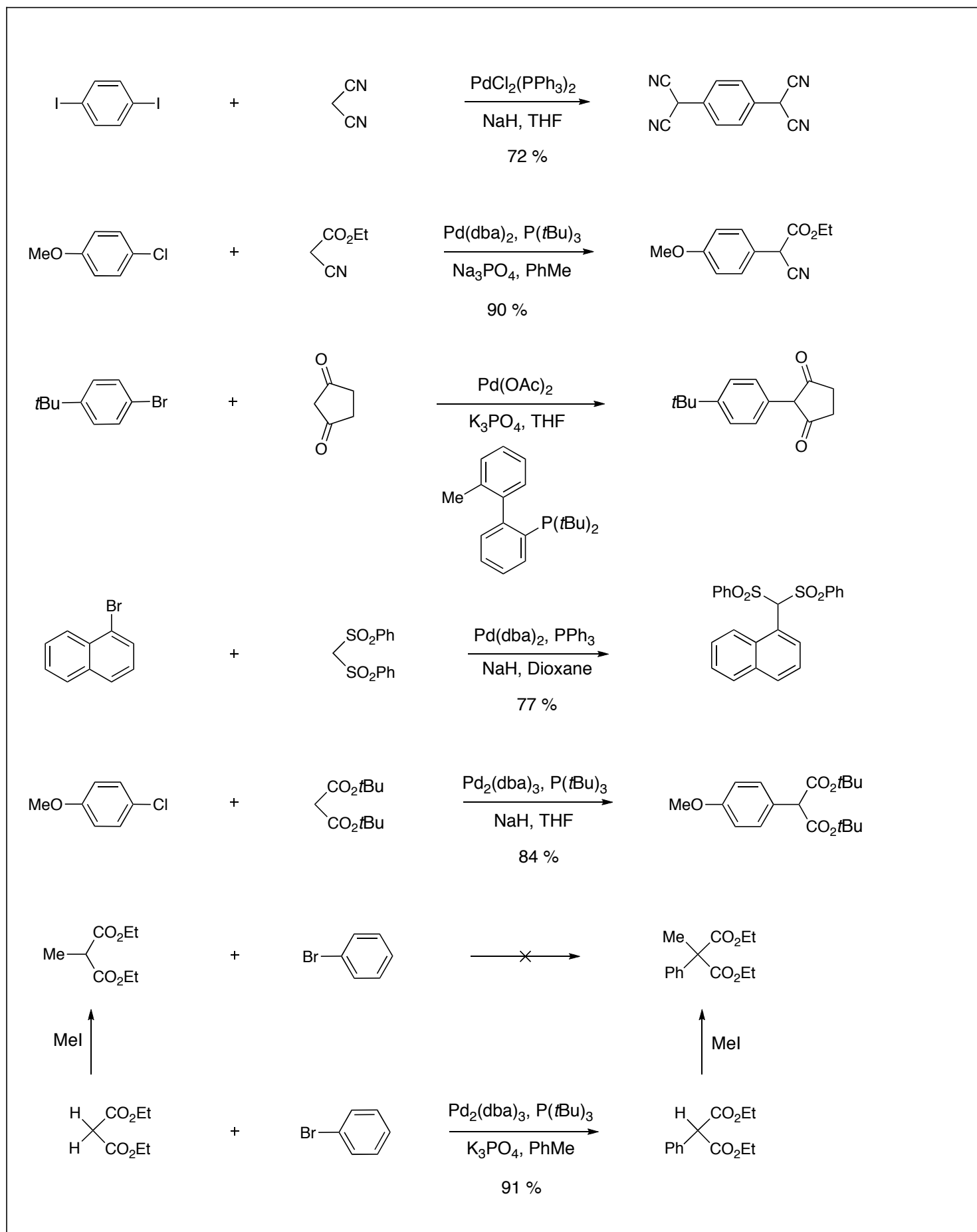
Sélection de bases aussi importantes : MHMDS, NaH, $\text{C(CH}_3)_3\text{ONa}$

MeONa, EtONa généralement pas utilisables comme bases car elles sont facilement oxydables en aldéhyde avec les halogénures d'aryle



1) Arylation de composés à méthylène actif



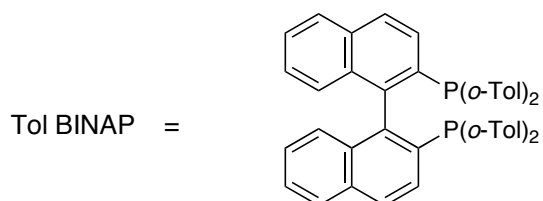
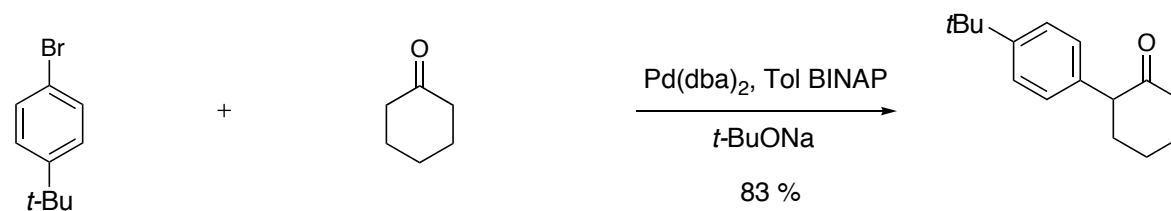
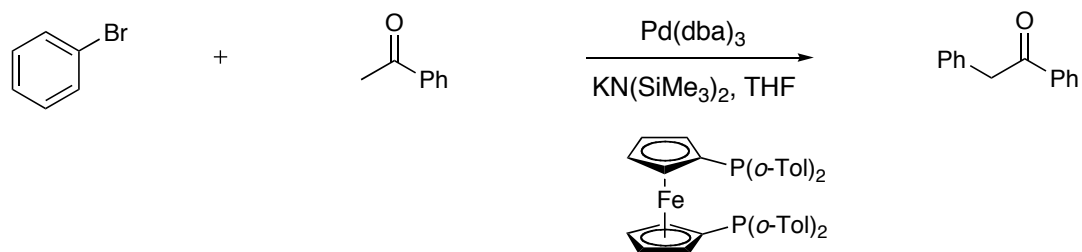
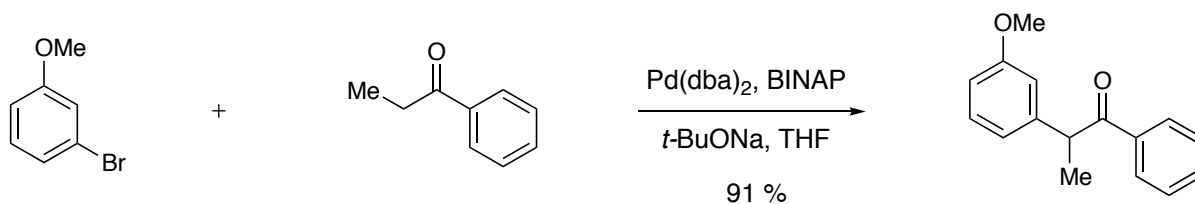
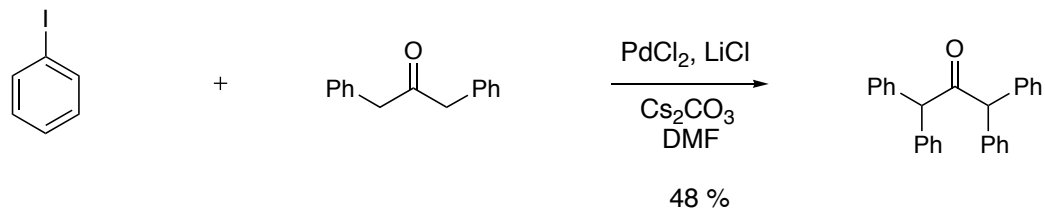


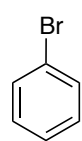
2) Arylation de cétones

Toujours considérée comme une réaction difficile

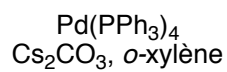
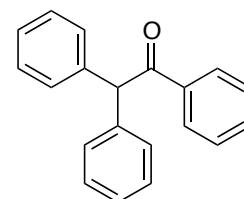
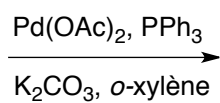
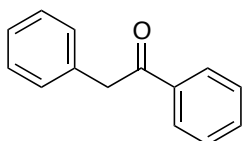
Découverte par Miura, Buchwald et Hartwig presque simultanément (1997)

└─ maintenant les α -ary cétones sont facilement accessibles

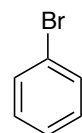
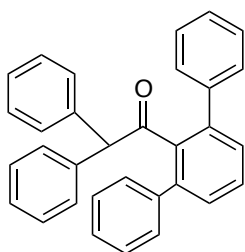




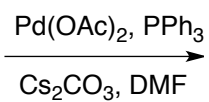
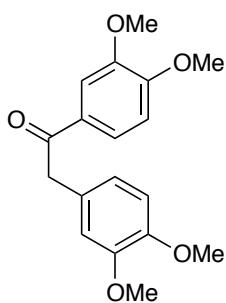
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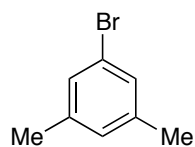
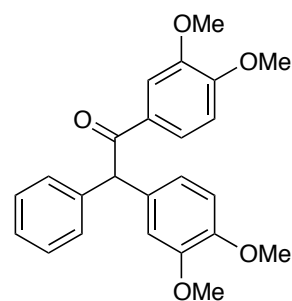
61 %



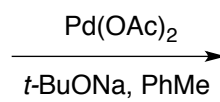
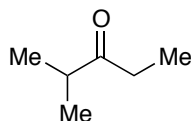
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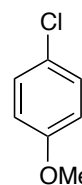
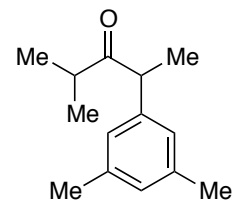
85 %



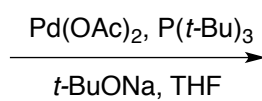
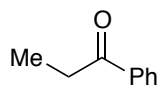
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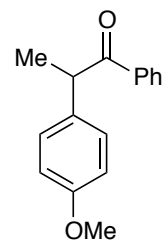
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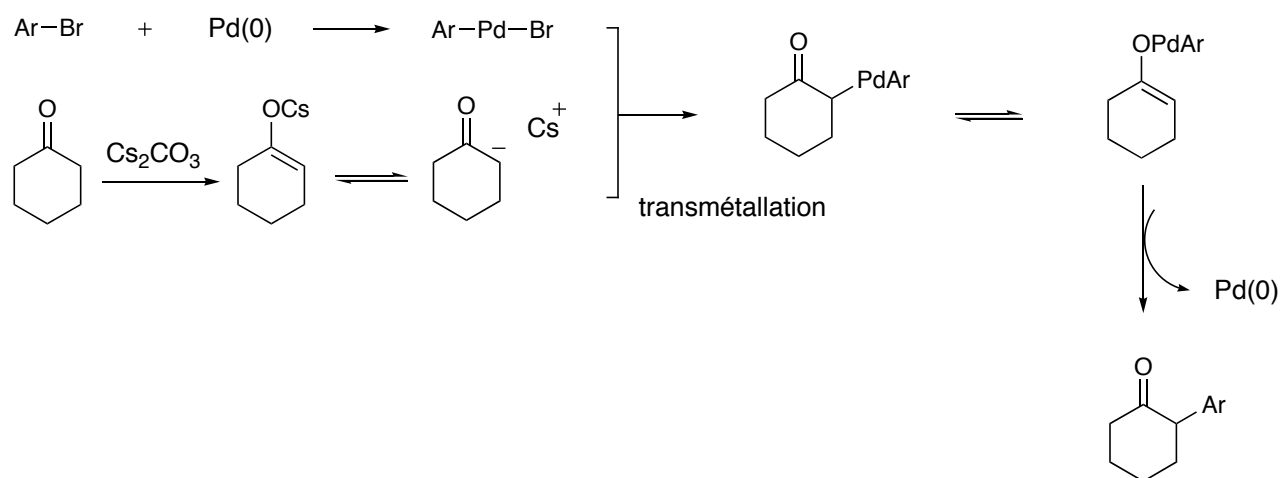
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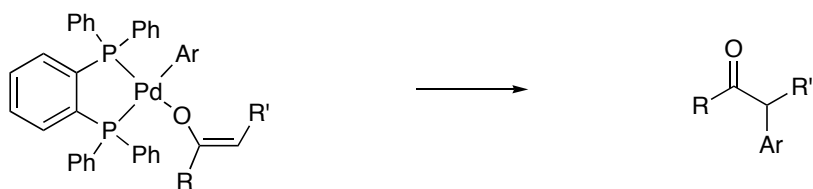
91 %



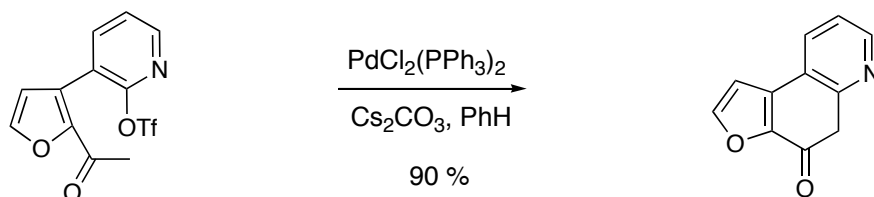
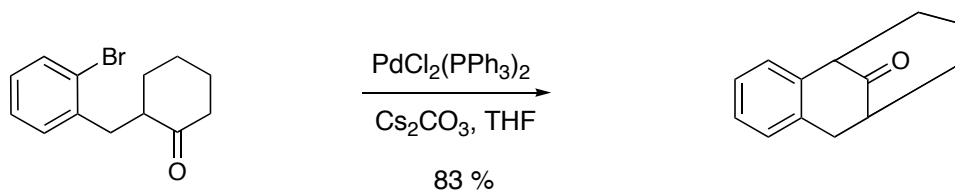
• Mécanisme

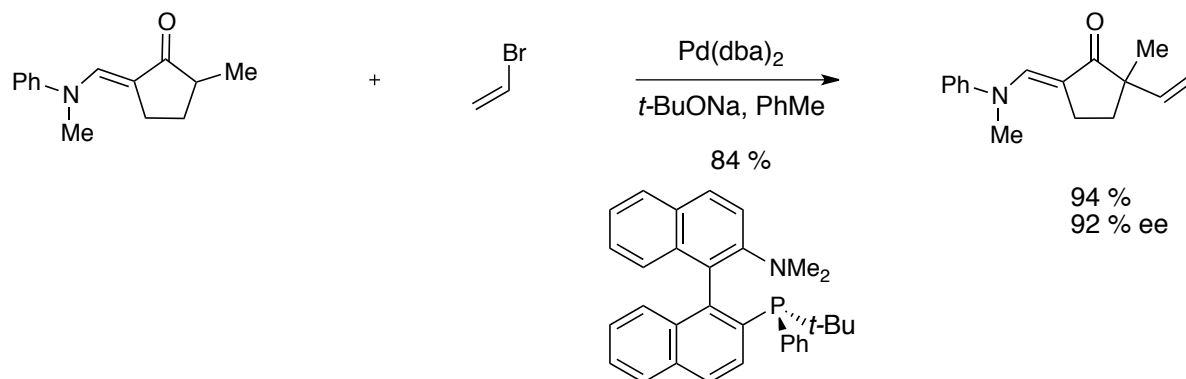
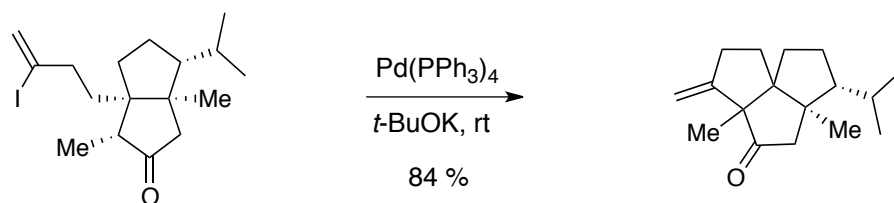


Complexe isolé par Hartwig

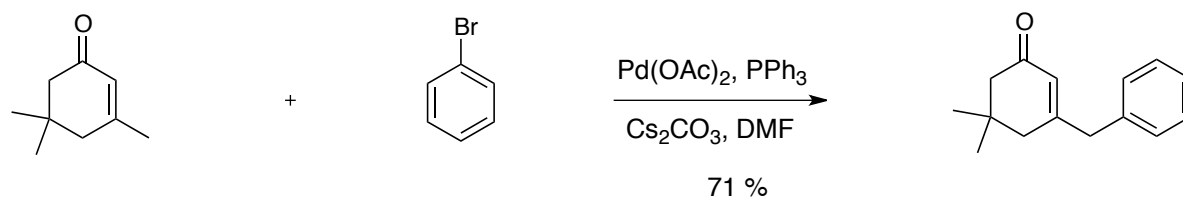
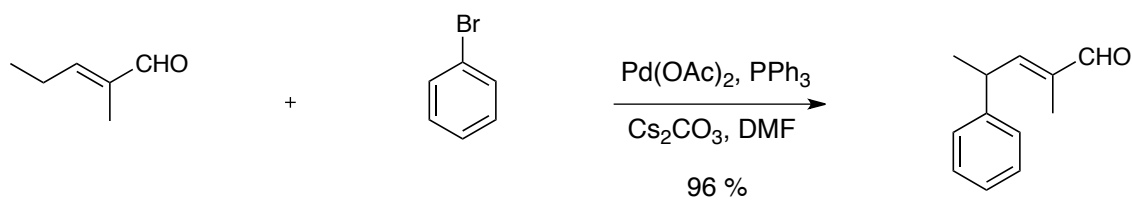
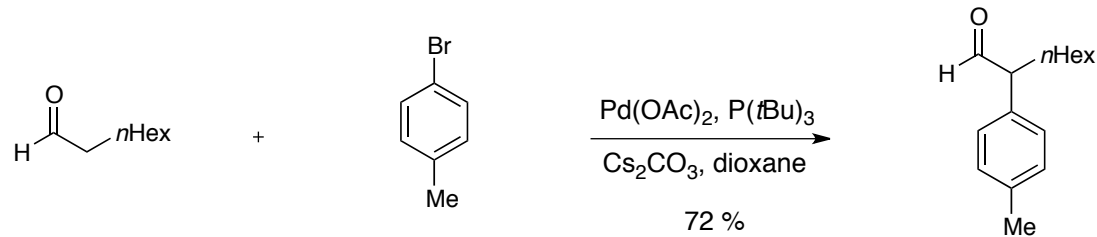


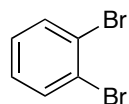
• Intramoléculaire



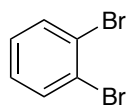


• Aldéhydes

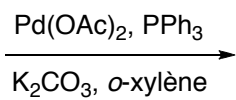
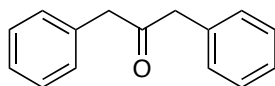




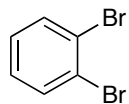
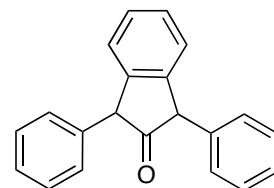
: intérêt



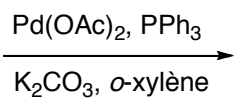
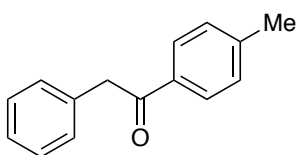
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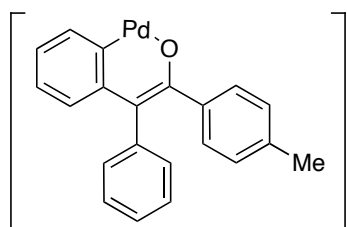
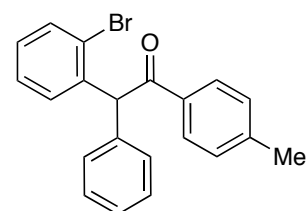
64 %



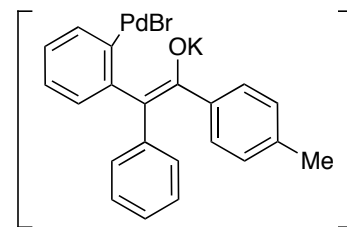
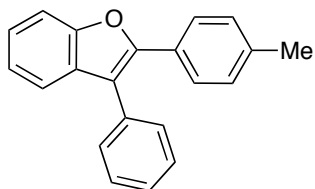
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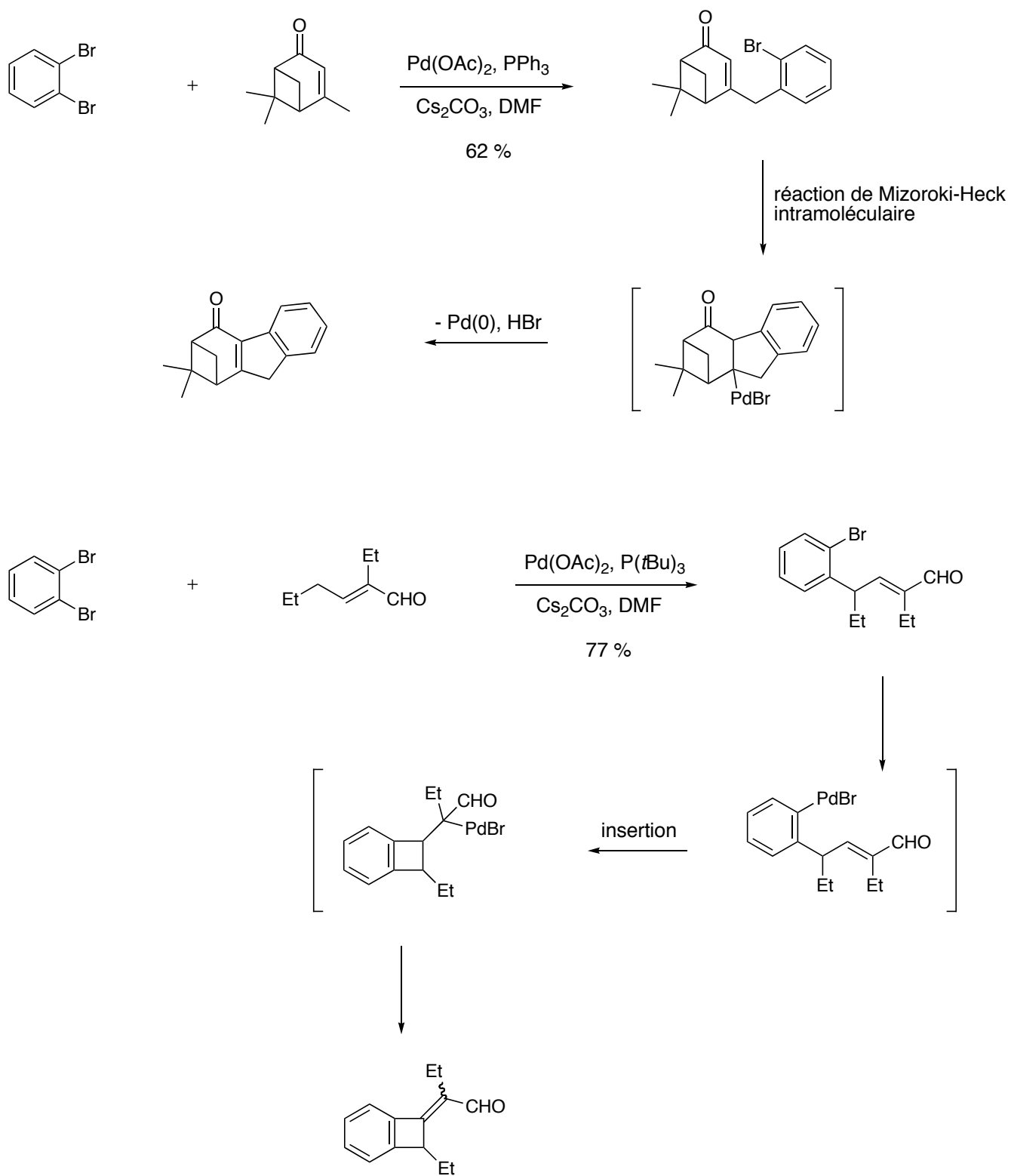


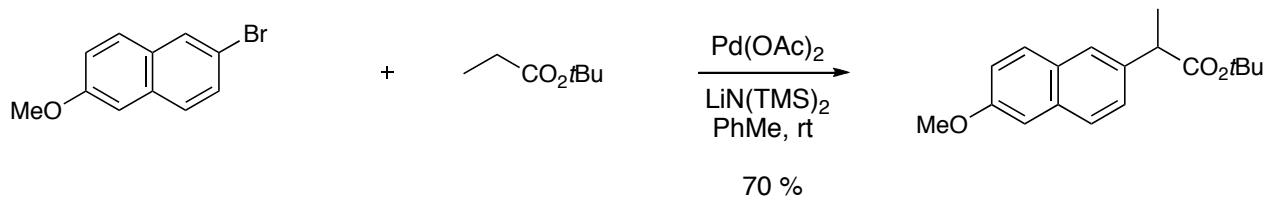
74 %



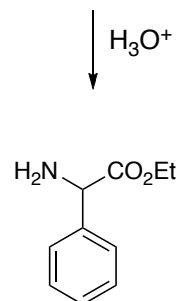
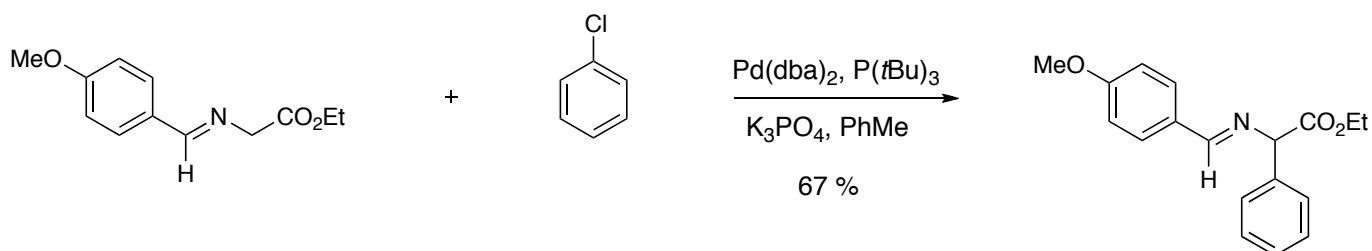
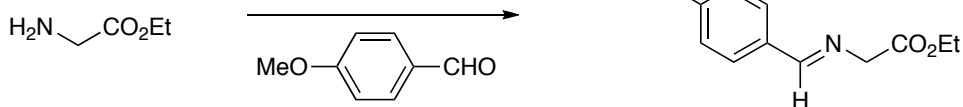
transmétallation

élimination
réductrice

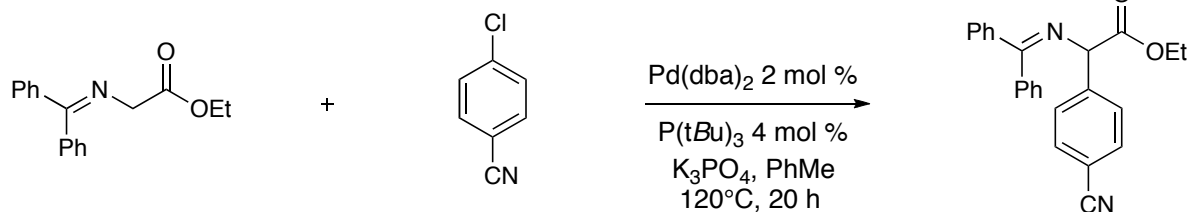


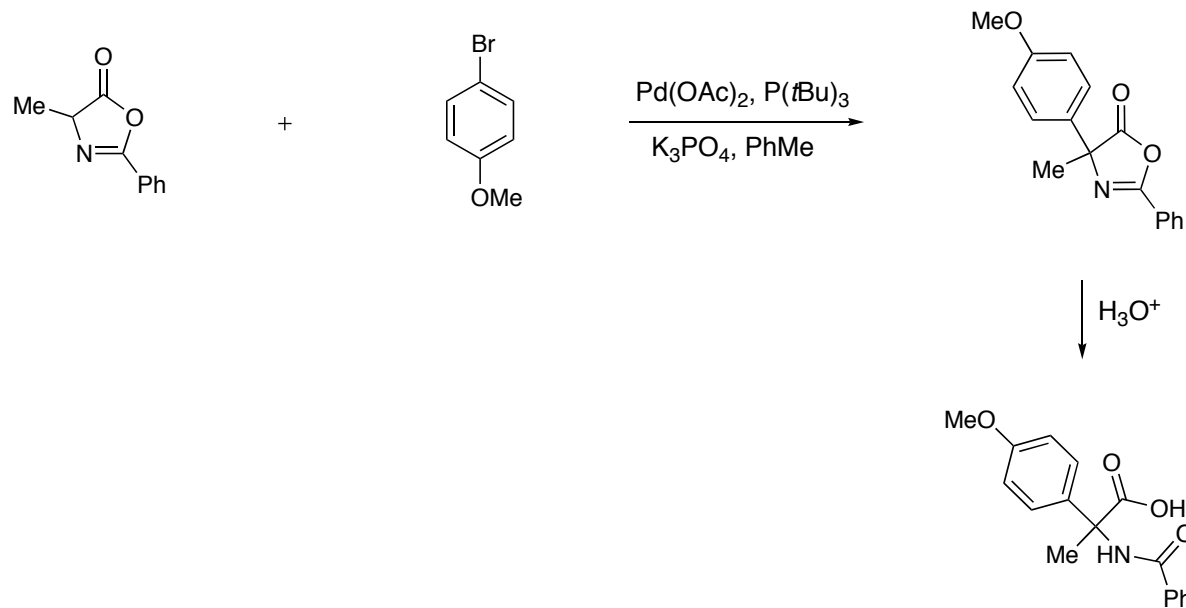
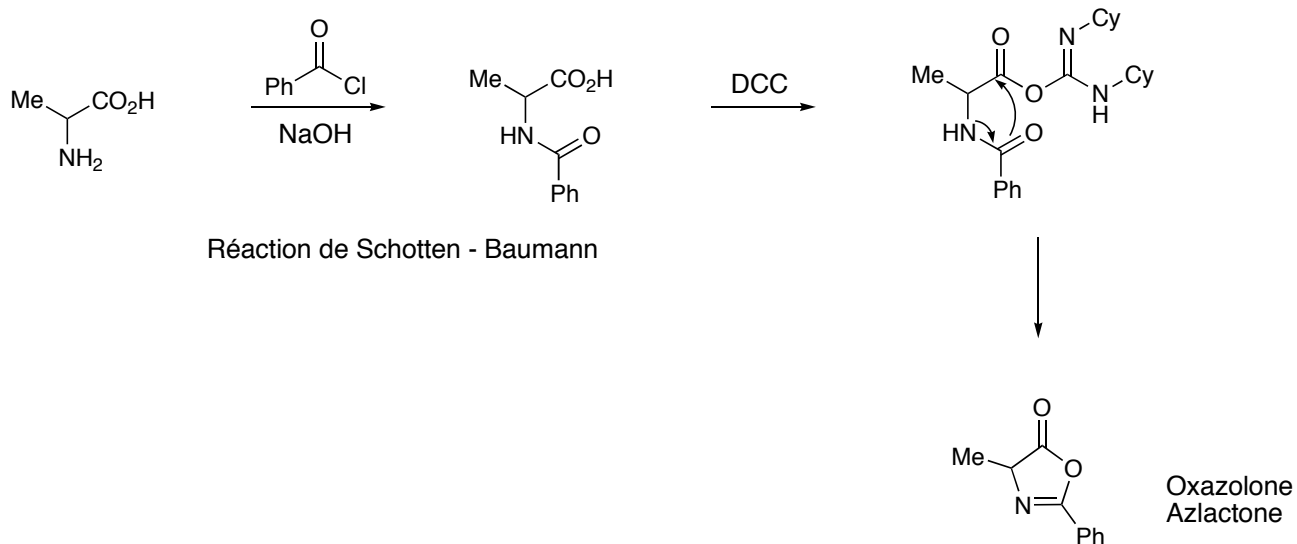


• Dérivés d'acide aminés



Hartwig





Hartwig 2003OL1915

→ futur : asymétrique

