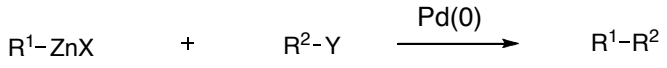
Réaction de Negishi

• Développée après la réaction de Kumada : Zn vs Mg : meilleure tolérance des groupes fonctionnels



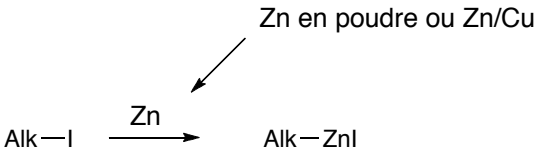
Revues 82ACR340
92T9577

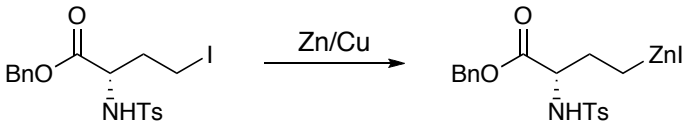
• Désavantage vs B, Sn : nécessité de préparation in situ R'ZnX ni isolables, ni purifiables

⟶ Réaction moins utilisée que Suzuki et Stille

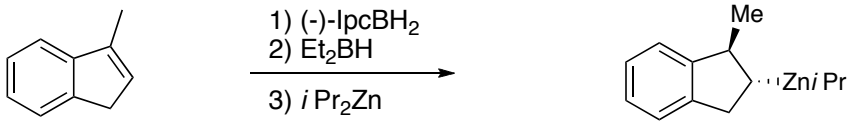
• Cycle catalytique classique

• Préparations des R' ZnX

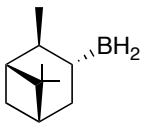




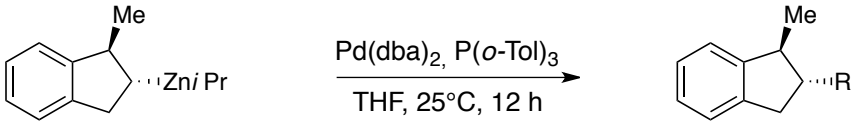
Transmétallation

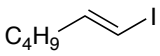


Knochel 99TL687

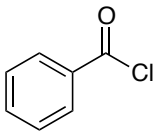
(-) $IpcBH_2$ 

Met	LG		
MgX	Br, I	Corriu Kumada	1972 1972
ZnX	Br, I	Negishi	1977
SnR_3	Br, I, OTf	Stille, Migita	1977-78
$B(OH)_2$	Br, I	Suzuki	1981
$SiRF_2$	I	Hiyama	1989



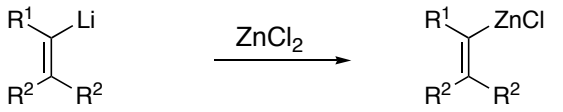


rdt : 35 %

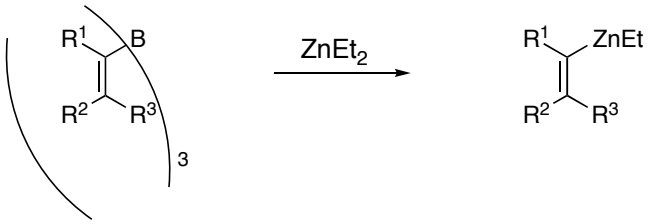


41 %

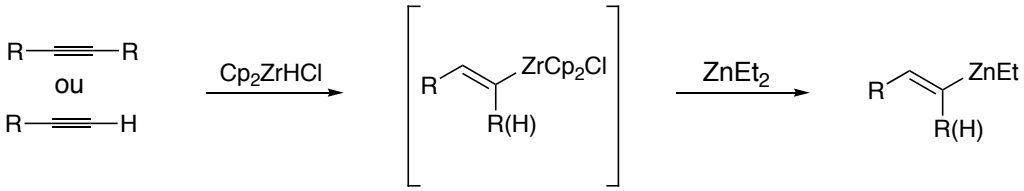
• Vinyl Zn



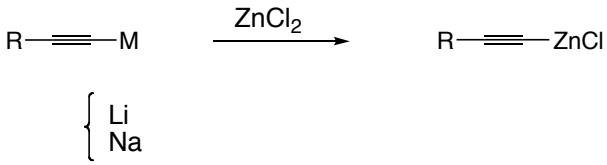
83JACS943

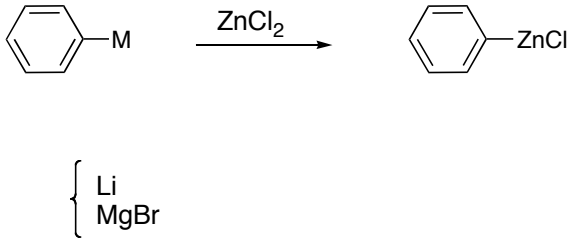


93JOC6908

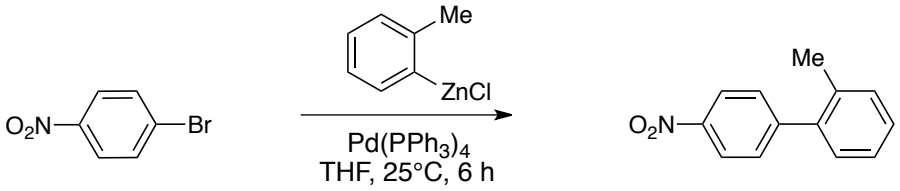


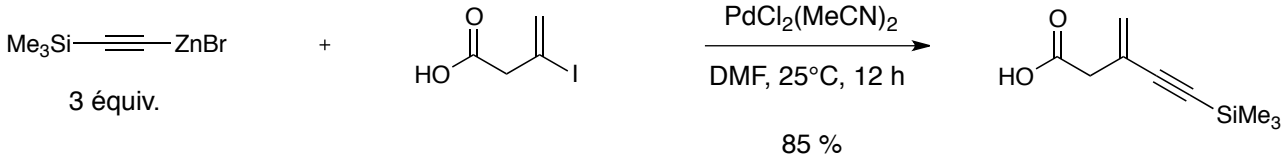
• Acétylénures et aryles



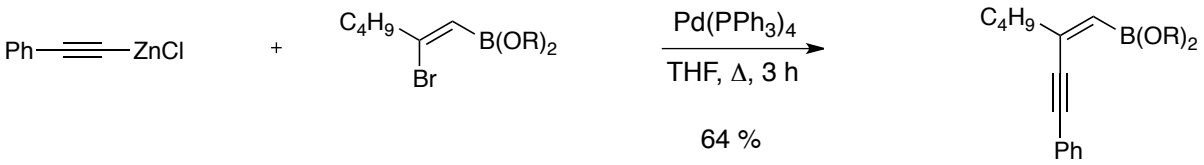


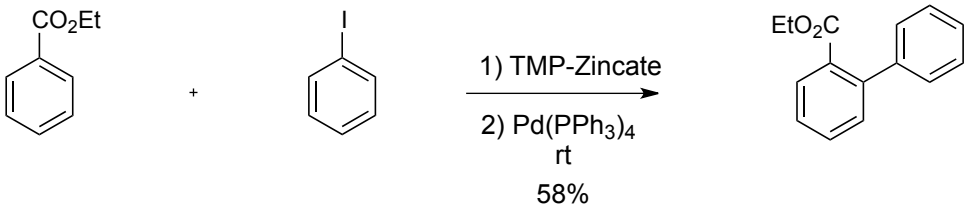
Exemples



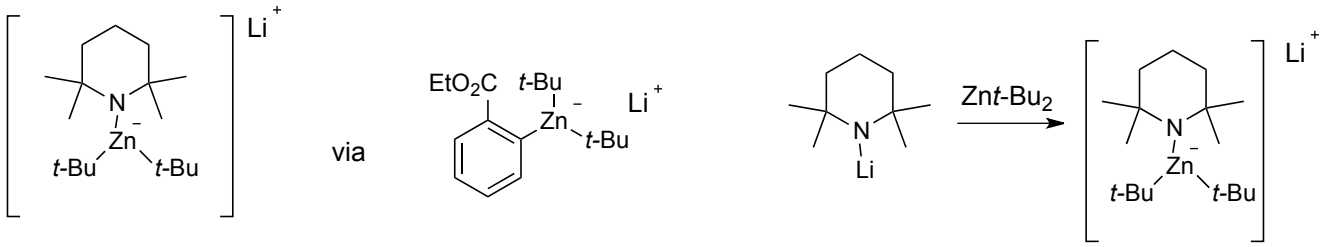


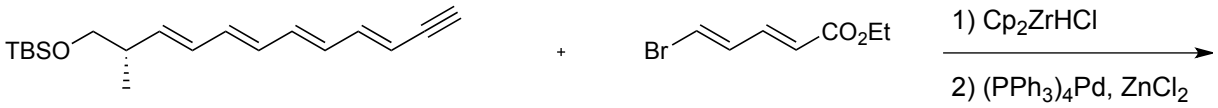
2000JOC7475

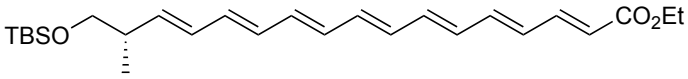


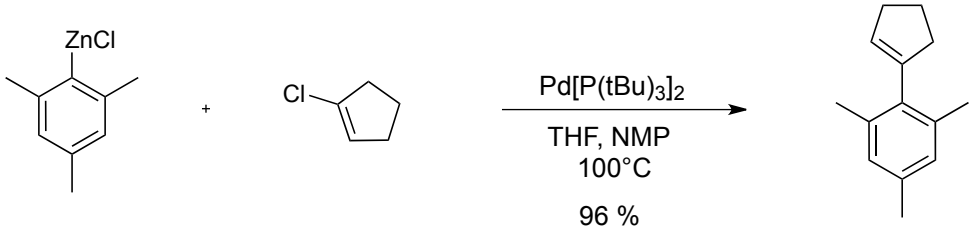


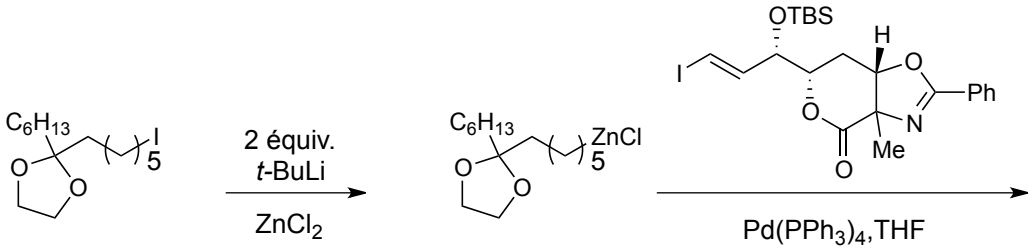
99JACS3539



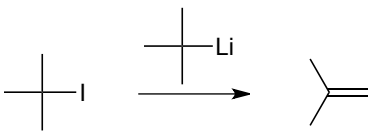


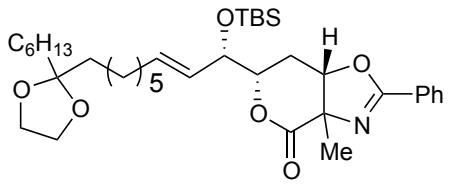






2 équiv. *t*-BuLi car :





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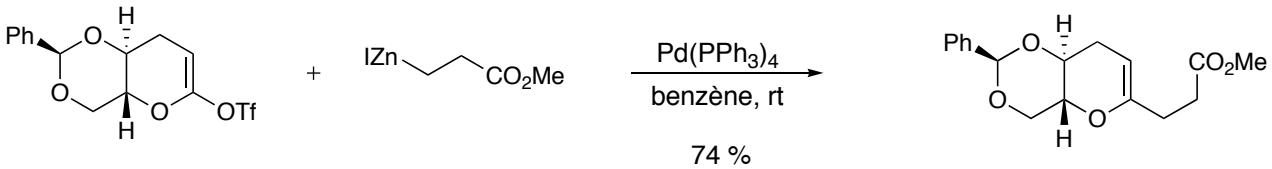

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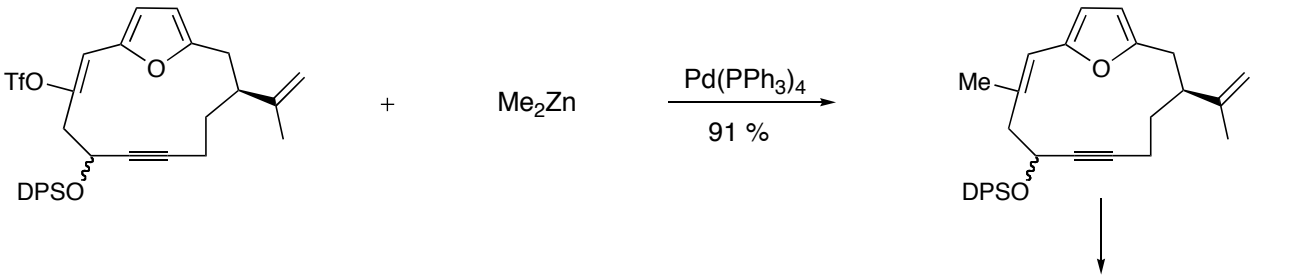
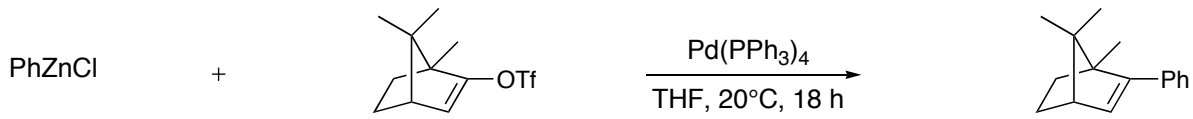


DPS = *t*-Butyl diphényl silyl

Synthèse totale du gambiérol

•



90 JACS7399

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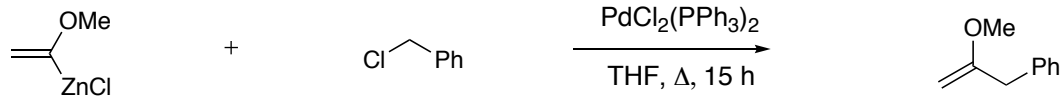
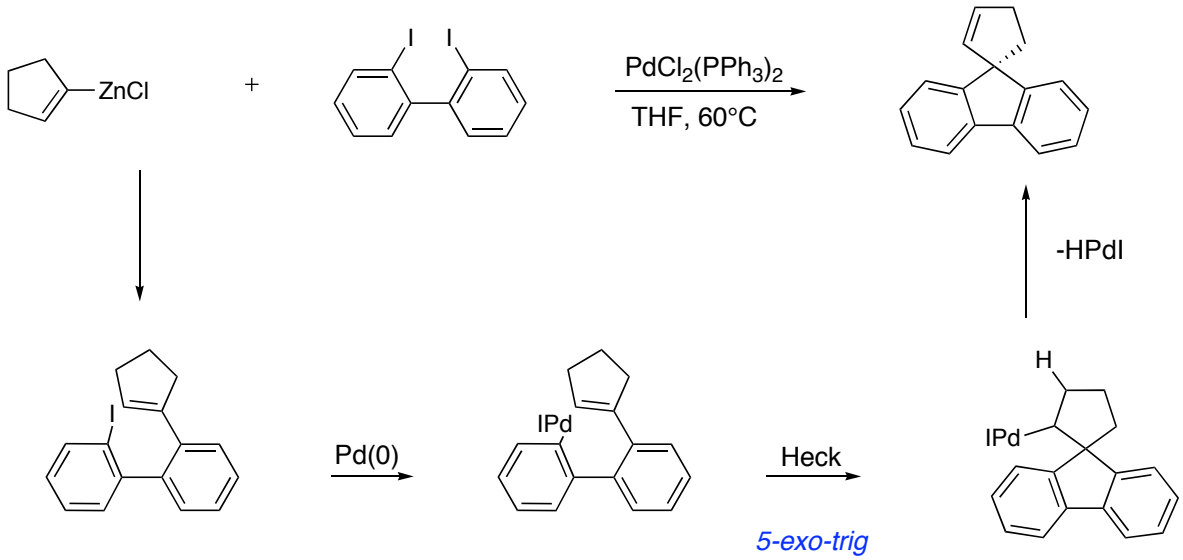
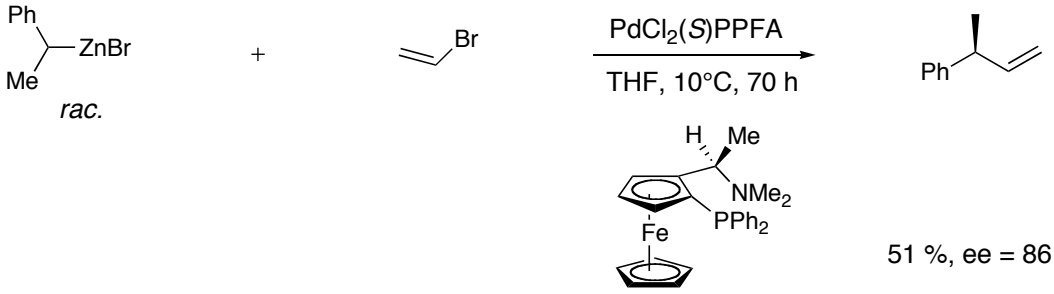


89CL1959

• Tandem Negishi-Heck



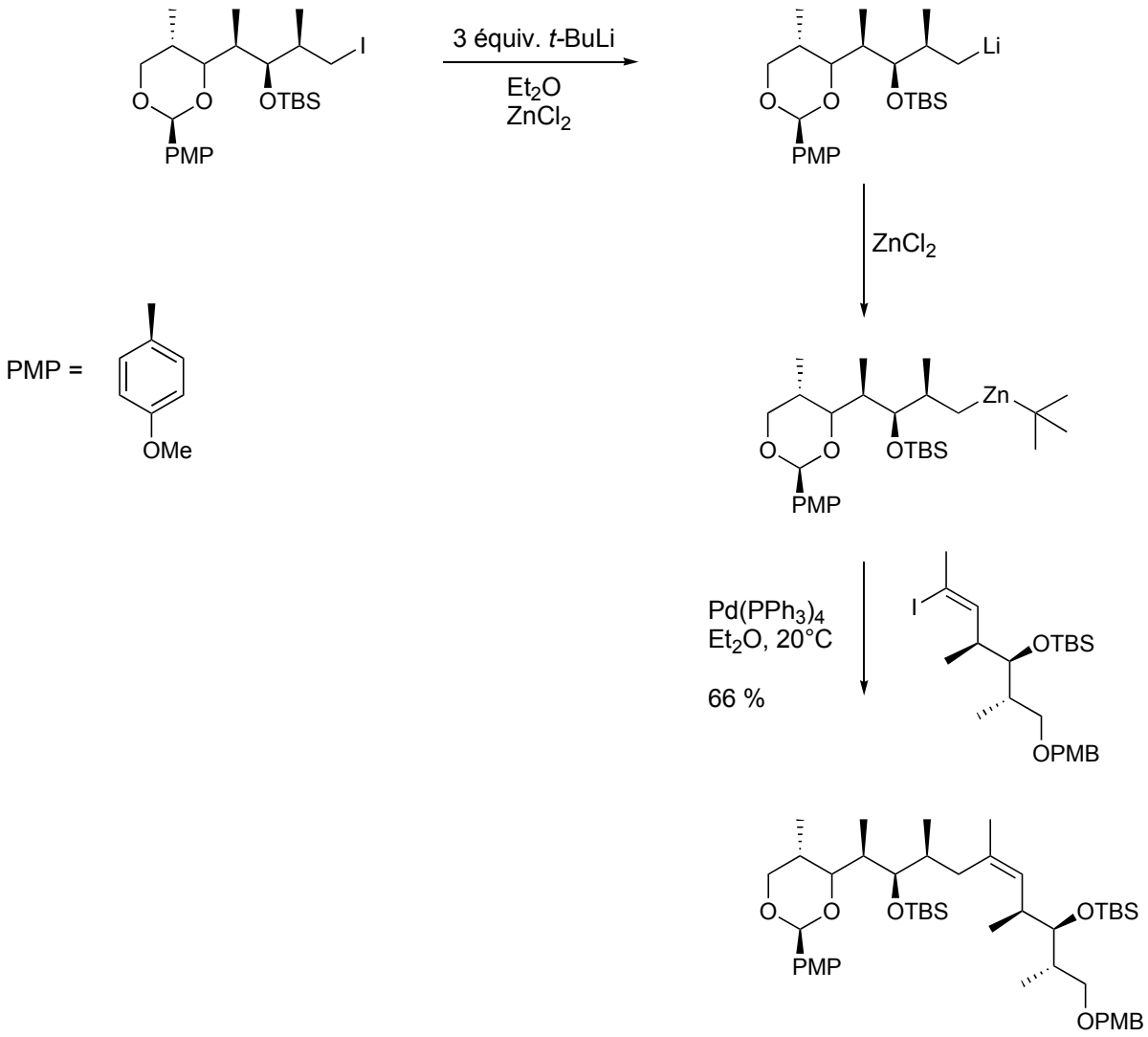
• Version catalytique asymétrique



ligand bidentate N,P

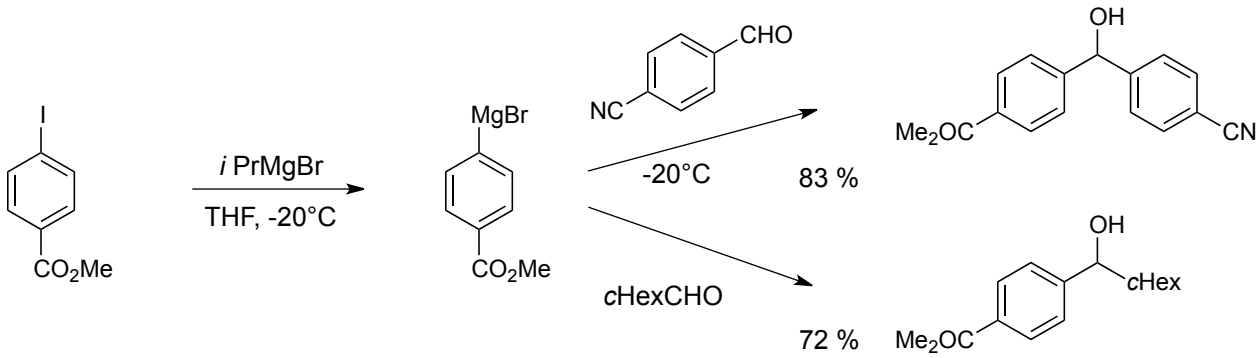
Hayashi 92TA213

• En synthèse totale (10 g)

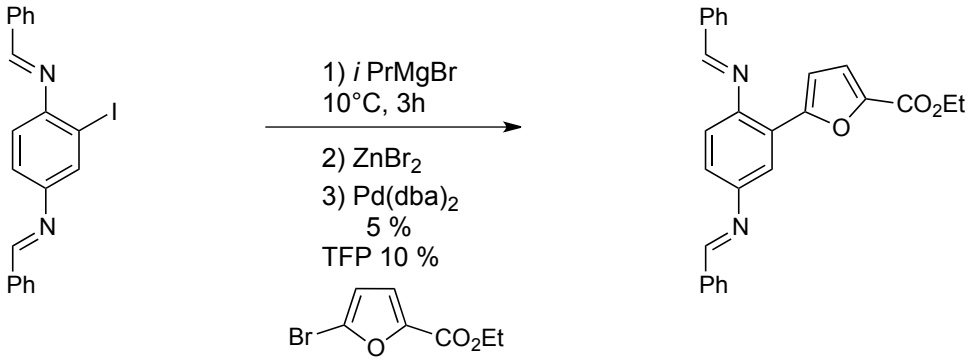


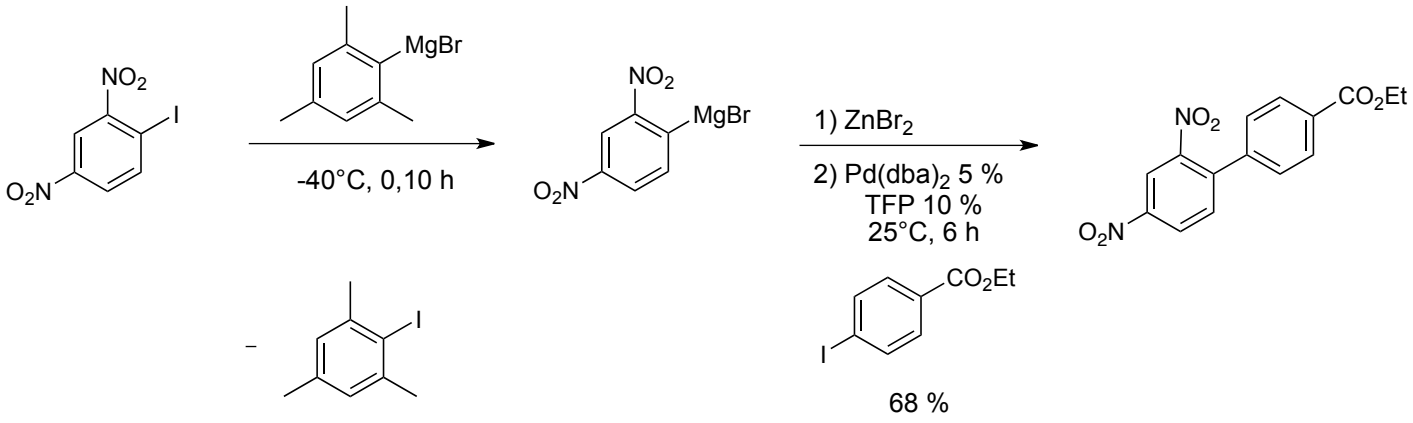
Smith III 2000JACS8654

Préparation d'arylmagnésiens fonctionnalisés



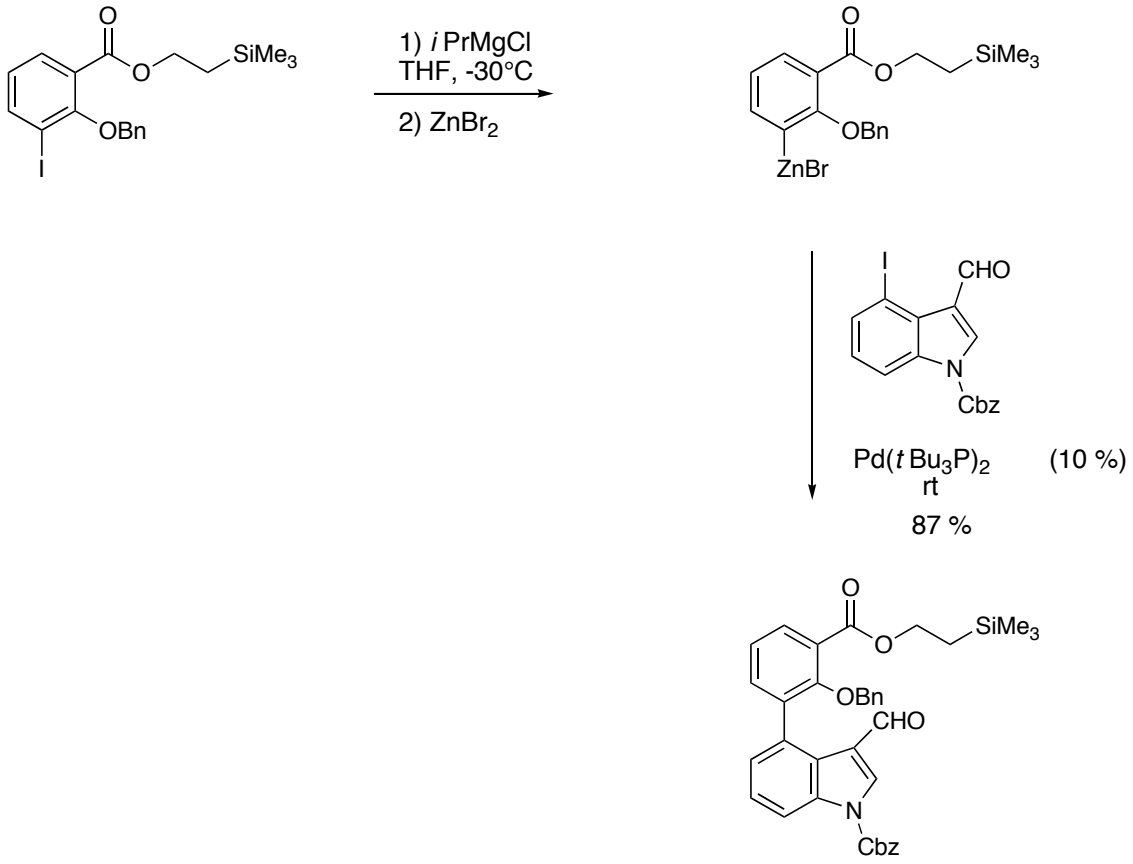
disponibilité grignard fonctionnalisés ⟶ important pour cross-coupling



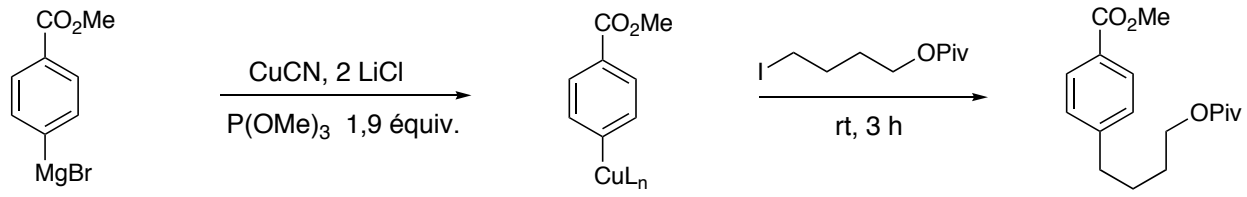


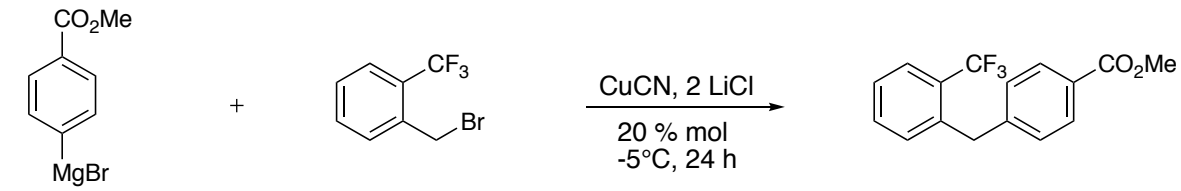
Knochel 2005JOC2445

hautement fonctionnalisés :

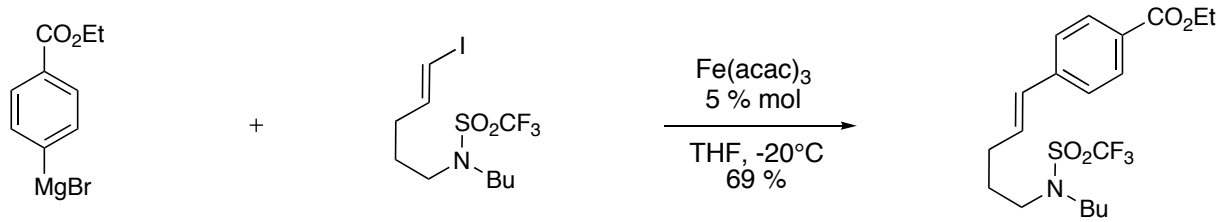


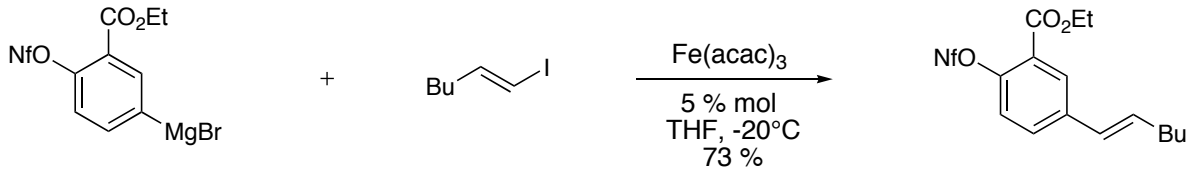
Transmétallation Mg ⟶ Cu





Catalyse au Fe(III)





Nf = C_4F_9