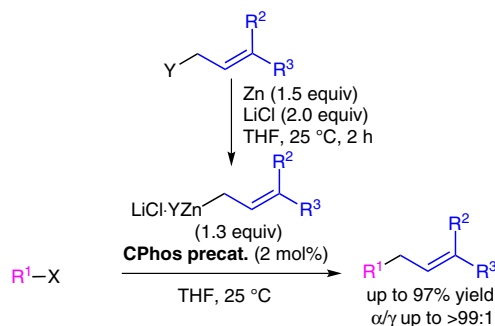


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Palladium-Catalyzed Completely Linear-Selective Negishi Cross-Coupling of Allylzinc Halides with Aryl and Vinyl Electrophiles

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# Palladium-Catalyzed Linear-Selective Negishi Cross-Coupling of Allylzinc Halides



X = Br, Cl, ONf, OTf

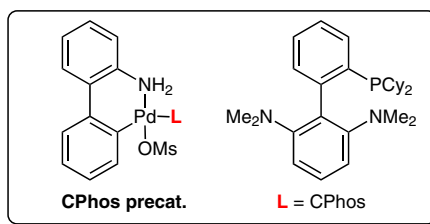
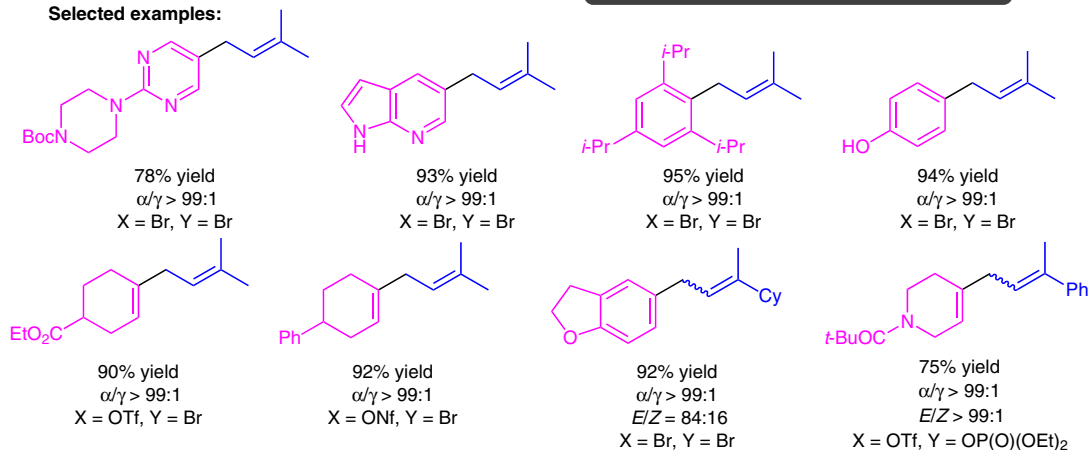
Y = Br, OP(O)(OEt)<sub>2</sub>

$R^1$  = various substituted aryls and heteroaryl,  
different mono-, di-, and trisubstituted alkenyls

$R^2$  = Me

$R^3$  = Me, Ph, *t*-Bu, Cy

## Selected examples:



**Significance:** Cheong, Buchwald, and co-workers report the first completely linear-selective palladium-catalyzed Negishi cross-coupling of various 3,3-disubstituted allylzinc reagents with (hetero)aryl and vinyl (pseudo)halides, leading to prenylated (hetero)aryl and alkenyl compounds in high yield and with excellent regioselectivity.

**Comment:** Apart from (hetero)aryl and vinyl bromides and chlorides, nonaflates and triflates were successfully used in this protocol. Computational studies reveal that an  $\eta^1$ - $\alpha$  reductive elimination is preferred due to energetic reasons, leading exclusively to the prenylated products. Thus, the choice of catalyst and transmetalation reagent is crucial.

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