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


**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 $\eta^1$-α 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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