Y. YANG, T. J. L. MUSTARD, P. H.-Y. CHEONG,* S. L. BUCHWALD* (MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE AND OREGON STATE UNIVERSITY, CORVALLIS, USA)

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

Key words
zinc
palladium
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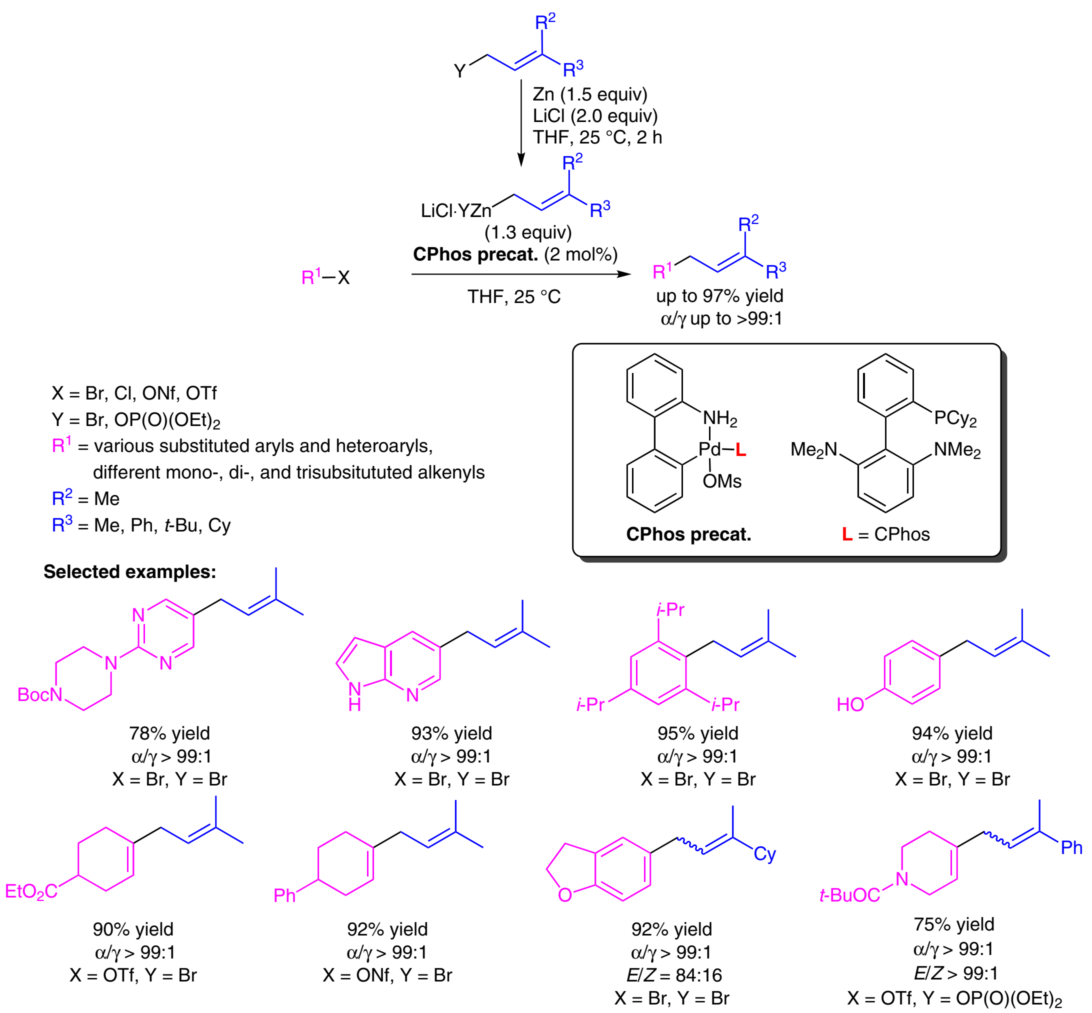
Negishi cross-coupling

SYNFACT of the month

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



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 η^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.

SYNFACTS Contributors: Paul Knochel, Nadja M. Barl
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