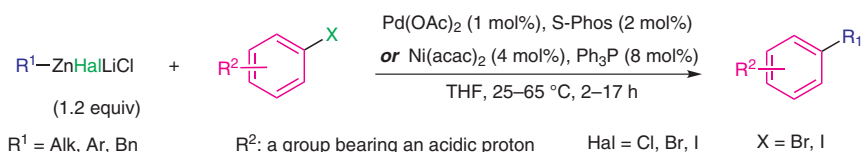


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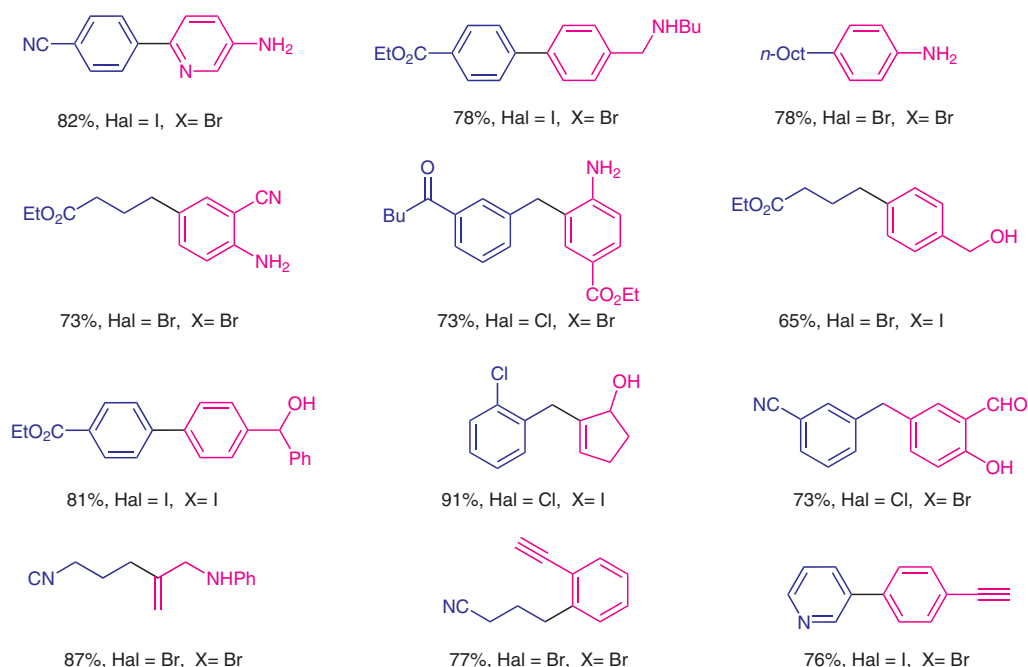
Palladium- and Nickel-Catalyzed Cross-Couplings of Unsaturated Halides Bearing Relatively Acidic Protons with Organozinc Reagents

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Negishi Cross-Coupling of Substrates Bearing Relatively Acidic Protons



Examples (overall 85 examples):



Significance: Alkyl- or arylzinc halides are believed to be incompatible with the presence of acidic protons like free OH or NH₂ groups. However, in many cases the rate of their protonation allows performing the Negishi cross-coupling even in the presence of such acidic groups. The organozinc compounds are readily available directly from the corresponding halides. This method allows a simple one-pot reaction leading to a new C–C bond formation.

Comment: The rate of the protonation of organozinc species decreases in the row aryl > alkyl > benzyl. Benzylzinc is quenched by aniline at 25 °C only within several hours. In most of the reactions, Pd(OAc)₂/S-Phos catalytic system was used. However, cheaper Ni(II)/Ph₃P is almost equally useful, at least for the coupling of aryl- and benzylzinc halides. Slow addition of the zinc reagent with a syringe pump is always advantageous in this reaction.

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