(1.1 equiv)

• desulfitative cross-coupling

Cu^I carboxylate as promoter

neutral conditions

Metals in Synthesis

Category

Pd₂dba₃ (1.0 mol%) P(2-furyl)₃ (3.0 mol%) CuTC (1.6 equiv) $(HO)_2B-R^3$ THF 50 °C, 18 h R^1 , $R^2 = Alk$, Ar $R^3 = Ar$, styryl

13 examples 52-93% yield

Proposed mechanism

Selected examples:

Significance: In 2000, Liebeskind and Sroql disclosed a copper(I)-promoted palladium-catalyzed cross-coupling of thioesters and boronic acids for the synthesis of ketones under neutral conditions. This base-free desulfitative process is mediated by a palladium(0) catalyst and stoichiometric amounts of a copper(I) carboxylate salt.

Comment: The copper(I) carboxylate CuTC is a key feature of this transformation as it facilitates both the C(sp²)–S bond cleavage via coordination of the copper center by the sulfur atom and the activation of the boronic acid through coordination of the carboxylate unit to the boron atom. Since its discovery, the Liebeskind-Srogl coupling has been thoroughly studied, and the scope of this transformation has been considerably extended.

Review: H. Prokopcová, C. O. Kappe Angew. Chem. Int. Ed. 2009, 48, 2276-2286.

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