G. DILAURO, A. F. QUIVELLI, P. VITALE, V. CAPRIATI*, F. M. Perna (Università di Bari, Italy)

Water and Sodium Chloride: Essential Ingredients for Robust and Fast Pd-Catalysed Cross-Coupling Reactions between Organolithium Reagents and (Hetero)aryl Halides


Water-Stable Cross-Couplings between Organolithiums and Aryl Halides

Significance: Capriati and co-workers report a water- and air-stable palladium-catalyzed cross-coupling between alkyl- and phenyllithium reagents and (hetero)aryl chlorides and bromides. This reaction provides the desired coupling products in excellent yields and in short reaction times.

Comment: Interestingly, the cross-coupling proceeds without the formation of undesired side products such as the dehalogenated reagent or homocoupling of the metal species. Furthermore, it was shown that the presence of both sodium chloride and air in the reaction mixture was crucial for the reaction to proceed. The chloride ion presumably led to a lower barrier of the oxidative addition step and air induced the formation of an activated catalyst.

Selected examples:

- \( \text{Het} \) + \( R-Li \) (Pd[PF(t-Bu)₃]₂ (2.5 mol%), NaCl (1.0 equiv), \( H_2O, r.t., \text{air, 20 s} \))

- \( X = \text{Cl, Br} \)

- \( (1.0 \text{ equiv}) \)

- \( (1.1–2.2 \text{ equiv}) \)

- \( 98\% \) yield

- 98% yield

- 75% yield

- 91% yield

- 81% yield

- 84% yield

- 78% yield

- 74% yield

- 72% yield

- 75% yield

- 75% yield

- 68% yield

SYNFACTS Contributors: Paul Knochel, Moritz Balkenhohl

Synfacts 2019, 15(03), 0257 Published online: 15.02.2019
DOI: 10.1055/s-0037-1612148; Reg-No.: P00919SF