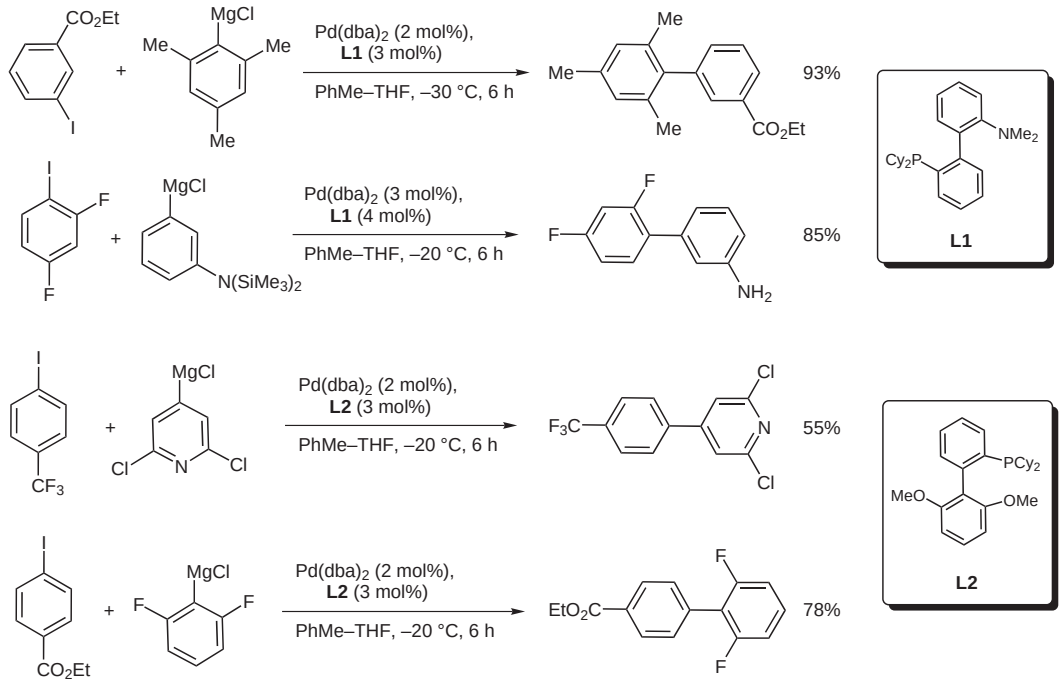
R. MARTIN, S. L. BUCHWALD* (MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CABRIDGE, USA)

Pd-Catalyzed Kumada–Corriu Cross-Coupling Reactions at Low Temperatures Allow the Use of Knochel-type Grignard Reagents

J. Am. Chem. Soc. **2007**, *129*, 3844-3845.

Low-Temperature Cross-Coupling of Functionalized Grignard Reagents



Significance: The Kumada–Corriu cross-coupling process is very attractive since the required (het)arylmagnesium species, including polyfunctionalized ones, can be readily prepared directly by the halogen–magnesium exchange or a metallation reaction. The group of Buchwald report herein a robust protocol, allowing a very efficient coupling of polyfunctionalized arylmagnesium species at the temperatures, which tolerate a vast majority of functional groups. This method is therefore extremely attractive for the direct synthesis of functionalized biaryls starting from (het)aryl halides.

Comment: While the preparation of polyfunctionalized (het)aryl Grignard reagents has become recently a great progress, the low temperatures (around –40 °C in some cases) required for their stability limited their direct use in cross-coupling processes. The use of the new generation of biaryl phosphine catalysts, developed in the group of Buchwald, overcomes this problem. Several reactions can be performed even at –65 °C, which has never been found for a Pd-catalyzed cross-coupling reaction.

Review: For a recent review on the preparation of polyfunctionalized Grignard reagents, see: H. Ila, O. Baron, A. J. Wagner, P. Knochel *Chem. Commun.* **2006**, 583-593.

SYNFACTS Contributors: Paul Knochel, Andrei Gavryushin
Synfacts 2007, 6, 0633-0633 Published online: 22.05.2007
DOI: 10.1055/s-2007-968538; **Reg-No.:** P04807SF