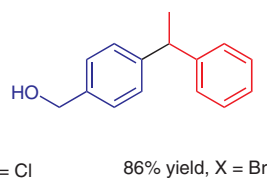
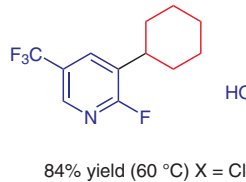
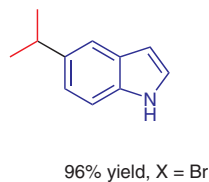
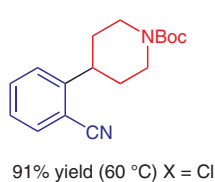
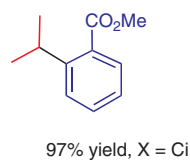
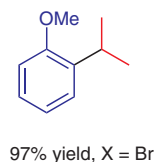
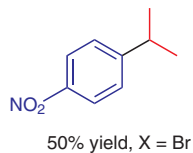
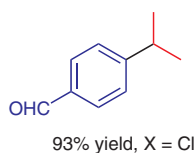
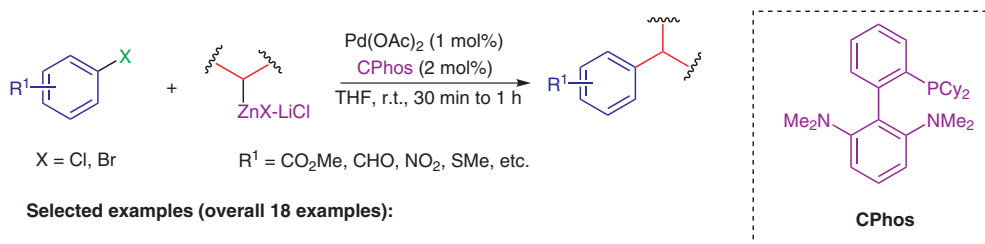


C. HAN, S. L. BUCHWALD\* (MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, USA)

Negishi Coupling of Secondary Alkylzinc Halides with Aryl Bromides and Chlorides

*J. Am. Chem. Soc.* **2009**, *131*, 7532-7533.

## Coupling of Secondary Alkylzinc Halides with Aryl Bromides and Chlorides



**Significance:** Direct cross-coupling of secondary acyclic organometallic species is a rather challenging task. This reaction is often plagued by  $\beta$ -hydride elimination or metal migration. The fine tuning of the ligand for the Negishi coupling allowed the development of a high-yielding, simple procedure for this coupling reaction, suitable for a broad substrate range with excellent functional group tolerance.

**Comment:** One of the main side products of the  $sp^2$ - $sp^3$  coupling of *i*-PrZnHal and similar species is the *n*-propyl adduct. Mechanistic studies of the authors showed that the ratio of *i*-Pr to *n*-Pr products depends on the rate of reductive elimination from the ligated ArPd(*i*-Pr) species, which competes with the  $\beta$ -hydride elimination-reinsertion process. Interestingly, free alcohols are tolerated in this coupling.

**SYNFACTS Contributors:** Paul Knochel, Andrei Gavryushin  
Synfacts 2009, 9, 1015-1015    Published online: 21.08.2009  
DOI: 10.1055/s-0029-1217689; Reg-No.: P09209SF

2009 © THIEME STUTTGART • NEW YORK

Category

Metal-Mediated  
Synthesis

Key words

Negishi coupling  
alkylzinc halides  
aryl halides  
palladium

**SYNFACTS**  
*of the month*