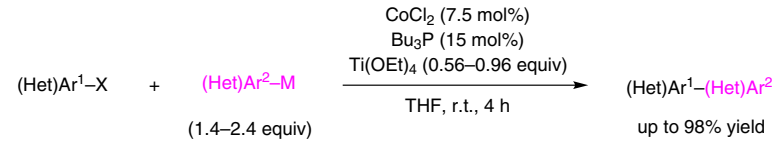
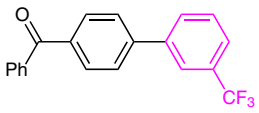
J. ZENG, K. M. LIU, X. F. DUAN* (BEIJING NORMAL UNIVERSITY, P. R. OF CHINA)
Selective Co/Ti Cooperatively Catalyzed Biaryl Couplings of Aryl Halides with Aryl Metal Reagents
Org. Lett. **2013**, *15*, 5342–5345.

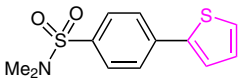
Co/Ti Cooperative C(sp^2)–C(sp^2) Cross-Coupling Reactions

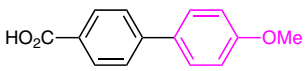


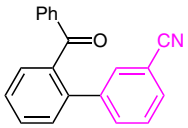
(Het)$Ar^{1/2}$ = various substituted (hetero)aromatics
X = F, Cl, Br
M = MgBr, MgCl, Li

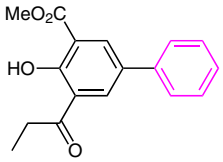
Selected examples:

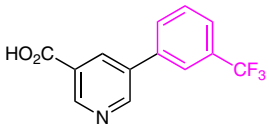

82% yield

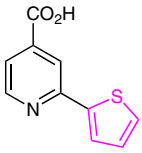

81% yield

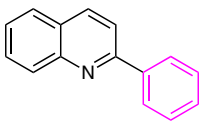

72% yield

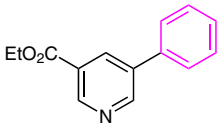

72% yield


80% yield


87% yield


81% yield


91% yield


73% yield

Significance: A novel method for cobalt-catalyzed cross-coupling reactions between aryl chlorides or bromides and aromatic magnesium or lithium reagents is reported by Duan and co-workers. The presence of 40 mol% of $Ti(OEt)_4$ suppresses undesired homocoupling side-products resulting from the organometallic reagent.

Comment: Interestingly, the reaction can also take place in the presence of a free carboxylic acid, a hydroxyl, or an amide residue. Therefore, this protocol allows an efficient arylation of highly functionalized aryl halides without protection–deprotection sequences.

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Synfacts 2014, 10(1), 0071 Published online: 13.12.2013
DOI: 10.1055/s-0033-1340366; **Reg-No.:** P15613SF

Category
Metal-Mediated Synthesis

Key words
cobalt
titanium
cooperative catalysis