Co/Ti Cooperative C(sp²)–C(sp²) Cross-Coupling Reactions

\[
\text{(Het)Ar}^1\cdots X + \text{(Het)Ar}^2\cdots M \rightarrow \text{(Het)Ar}^1\cdots	ext{(Het)Ar}^2
\]

\begin{align*}
\text{CoCl}_2 (7.5 \text{ mol}\%) \\
\text{Bu}_3\text{P} (15 \text{ mol}\%) \\
\text{Ti(OEt)}_4 (0.56-0.96 \text{ equiv}) \\
\text{THF, r.t., 4 h}
\end{align*}

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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\begin{align*}
\text{Ph} & \text{O} \text{CF}_3 & \text{82\% yield} \\
\text{Ph} & \text{O} \text{CN} & \text{72\% yield} \\
\text{MeO} & \text{2C} & \text{87\% yield} \\
\text{CO}_2\text{H} & \text{81\% yield} \\
\text{N} & \text{CO}_2\text{H} & \text{81\% yield} \\
\text{N} & \text{EtO}_2\text{C} & \text{73\% yield}
\end{align*}
\]