Direct Cross-Coupling of Organoaluminum Reagents

\[
\begin{align*}
\text{R}^1 \text{Ar} + \text{AlMe}_2 \cdot \text{LiCl} \quad \text{(2.5 equiv)} \quad \text{R}^2 \text{-X} & \rightarrow \quad \text{R}^1 \text{Ar} \quad \text{R}^2 \\
& \text{THF, 110 °C, 24 h} \quad 63–99\% \text{ yield}
\end{align*}
\]

\( \text{R}^1 = \text{Me, F, NMe}_2, \text{OEt, CH}_2\text{OEt} \)
\( \text{R}^2 = \text{Ar, alkenyl, alkynyl} \)
\( \text{X} = \text{I, Br, Cl} \)

Selected examples:

- \( 91\% \text{ yield} \quad \text{X} = \text{Br} \)
- \( 73\% \text{ yield} \quad \text{X} = \text{Cl} \)  
  \[ \text{THF–TMU (10:1), 130 °C} \]
- \( 95\% \text{ yield} \quad \text{X} = \text{Br} \)
- \( 97\% \text{ yield} \quad \text{X} = \text{Br} \)
- \( 76\% \text{ yield} \quad \text{X} = \text{I} \)
- \( 63\% \text{ yield} \quad \text{X} = \text{I} \)
- \( 68\% \text{ yield} \quad \text{X} = \text{Cl} \)
- \( 76\% \text{ yield} \quad \text{X} = \text{Cl} \)

**Significance:** The authors report a direct cross-coupling of arylaluminum reagents and organic halides without an external catalyst. As the steric and electronic properties of functional groups on the aromatic ring had little influence of the reactivity, a variety of coupling products were obtained in high yields.

**Comment:** Interestingly, the reactions of aromatic iodides or bromides bearing a tosylate, triflate, or carbamate group did show high chemoselectivity, as the coupling only took place at the halide. Additionally, an ICP-MS analysis was performed to exclude traces of transition metals (level of 1 ppb).