Direct Cross-Coupling of Organoaluminum Reagents

**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 on 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).

Selected examples:

- **(2.5 equiv) AlMe₂·LiCl**
  - THF, 110 °C, 24 h
  - 63–99% yield

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\begin{align*}
R^1 &= \text{Me, F, NMe}_2, \text{OEt, CH}_2\text{OEt} \\
R^2 &= \text{Ar, alkenyl, alkynyl} \\
X &= \text{I, Br, Cl}
\end{align*}
\]

91% yield
X = Br

73% yield
X = Cl
[THF–TMU (10:1), 130 °C]

95% yield
X = Br

97% yield
X = Br

76% yield
X = I

63% yield
X = I

68% yield
X = Cl

76% yield
X = Cl