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Nickel-Catalyzed Reductive Cross-Coupling of Aryl Halides with Alkyl Halides

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Significance: The authors report herein a new, general method for performing direct reductive cross-coupling using a dual ligand–nickel catalytic system. The reaction tolerates a broad number of functional groups and generally offers high yields of products.

Comment: The reaction takes place with slightly lower yield if the phosphine ligand is omitted. Organic iodides in all cases are better than the bromides. The reaction probably does not involve the RMnX intermediate, as the insertion of manganese(0) does not occur under the same conditions at a comparable rate.

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\begin{align*}
R^1 \text{X} + R^2 \text{Y} &\xrightarrow{\text{NiI}_2 \cdot x\text{H}_2\text{O} (10.7 \text{ mol\%})} \\
&\quad \text{DTBBPy (5 mol\%)} \\
&\quad 2-(\text{Ph}_2\text{P})_2\text{C}_6\text{H}_4 (5 \text{ mol\%}) \\
&\quad \text{py (10 mol\%), Mn (2 equiv)} \\
&\quad \text{DMPU, 60–80 °C, 24–36 h} \\
\end{align*}
\]

\[
\begin{align*}
R^1 &\text{= 4-OMe, 2-Me, 4-CN, etc.} \\
R^2 &\text{= Alk, (CH}_2)_3\text{NHCbz, etc.} \\
\text{DTBBPy} &\text{= 4,4'-di-t-butyl-2,2'-bipyridine} \\
X, Y &\text{= Br, I}
\end{align*}
\]

Examples:

- 64% yield
- 78% yield
- 77% yield
- 77% yield
- 69% yield
- 38% yield
- 88% yield
- 82% yield