Regioselective ortho-Arylation and Alkenylation of N-Alkyl Benzamides with Boronic Acids via Ruthenium-Catalyzed C–H Bond Activation: An Easy Route to Fluorenones Synthesis

Ruthenium-Catalyzed ortho-Arylation and Alkenylation of N-Alkyl Benzamides

Significance: The authors report a highly regioselective ruthenium-catalyzed ortho-arylation and alkenylation of various N-alkyl benzamides with different (hetero)aromatic and alkenyl boronic acids in the presence of silver salts. The corresponding benzamides are obtained in good to very good yield.

Comment: Noteworthy, this methodology may be applied to the synthesis of fluorenones by treatment of the biarylic coupling products with trifluoroacetic anhydride and hydrogen chloride.

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\begin{align*}
\text{R}^1 \text{O} \text{N} \text{H} \text{R}^2 & \rightarrow \text{R}^3 \\
\text{[(RuCl}_2(\text{p-cymene})_2]} (3.0 \text{ mol%}) \\
\text{AgSbF}_6 (12 \text{ mol%}) \\
\text{Ag}_2\text{O} (1.0 \text{ equiv}) \\
\text{THF}, 110 \degree \text{C}, 16 \text{ h} \\
\text{up to 87% yield}
\end{align*}
\]

\[
\begin{align*}
\text{R}^1 &= \text{OMe, Me, I, Br, NO}_2, \text{CN, 1,3-dioxolane, Naph, thiendl}
\text{R}^2 &= \text{Me, Et, t-Bu}
\text{R}^3 &= \text{4-BrC}_6\text{H}_4, 4-\text{FC}_6\text{H}_4, \text{Tol, PMP,}
\text{4-HOC}_6\text{H}_4, 1-\text{Naph, 3-thienyl, various alkenyls}
\end{align*}
\]

Selected examples:

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\begin{align*}
\text{O} \text{N} \text{H} \text{Me} & \quad \text{64% yield}
\end{align*}
\]

- \[
\begin{align*}
\text{O} \text{N} \text{H} \text{t-Bu} & \quad \text{74% yield}
\end{align*}
\]

- \[
\begin{align*}
\text{O} \text{N} \text{H} \text{Me} & \quad \text{87% yield}
\end{align*}
\]

- \[
\begin{align*}
\text{O} \text{N} \text{H} & \quad \text{65% yield}
\end{align*}
\]

- \[
\begin{align*}
\text{O} \text{N} \text{H} & \quad \text{75% yield}
\end{align*}
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- \[
\begin{align*}
\text{O} \text{N} \text{H} & \quad \text{81% yield}
\end{align*}
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