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Catalytic Asymmetric γ-Alkylation of Carbonyl Compounds via Stereoconvergent Suzuki Cross-Couplings


Catalytic Enantioselective γ-Alkylation of Carbonyl Compounds

**Significance:** The authors describe a new method for the catalytic enantioselective γ- (and δ-) alkylation of carbonyl compounds by cross-coupling of γ- (and δ-) haloamides with alkylboranes. The reaction is catalyzed by nickel and uses a commercially available chiral diamine ligand to achieve high enantiomeric excess.

**Comment:** The reaction conditions tolerate alkyl chlorides as well as alkyl bromides as suitable electrophilic cross-coupling partners. Also, an aryl metal, a boronate ester, and a secondary alkyl metal compound are able to undergo the stereoselective cross-coupling with good enantiomeric excess.

**Selected examples:**

\[
\begin{align*}
\text{R}_1\text{N} = \text{NPh}_2, \text{N(OMe)Me} \\
\text{R}_2 = \text{Me, Et, n-Bu, Bn, i-Bu} \\
\text{R}_3 = \text{various substituted alkyl groups} \\
\text{X} = \text{Cl, Br} \\
\text{BBN} = 9\text{-borabicyclo[3.3.1]nonane}
\end{align*}
\]

\[
\begin{align*}
\text{Ph}_2\text{N} & \text{O} \text{O} \\
\text{63% yield} & \text{85% ee} \\
\text{Ph}_2\text{N} & \text{O} \text{Et} \\
\text{80% yield} & \text{89% ee} \\
\text{Ph}_2\text{N} & \text{O} \text{n-Bu} \text{OMe} \\
\text{64% yield} & \text{90% ee} \\
\text{Me} & \text{N} \text{OMe} \text{Et} \\
\text{75% yield (with 25% KI)} & \text{86% ee} \\
\text{Ph}_2\text{N} & \text{O} \text{Et} \text{OTBS} \\
\text{74% yield} & \text{91% ee}
\end{align*}
\]