Enantioselective Palladium(II)-Catalyzed Borylation

Selected examples:

\[
\begin{align*}
\text{NHArF} & \quad \text{Bpin} \\
\text{ArF} = 4-\text{F}_3\text{CC}_6\text{H}_4
\end{align*}
\]

78% yield, 95.6% ee (with L2)

75% yield, 98.4% ee (with L1)

75% yield, 99.8% ee (with L1)

77% yield, 97.4% ee (with L1)

52% yield, 88.3% ee (with L1)

Solvent = MeCN–DCE (4:1)

Synthetic application:

\[
\begin{align*}
\text{NHArF} & \quad \text{PhthN} \\
\text{ArF} = 4-\text{F}_3\text{CC}_6\text{H}_4
\end{align*}
\]

88% yield, 95.8% ee

88% yield, 99.2% ee

99.2% ee

99.2% ee

99.3% ee

99.2% ee

99.2% ee

Proposed asymmetric induction model:

Significance: The authors developed a palladium(II)-catalyzed borylation of cyclic amides by using chiral bidentate ligands. A wide variety of borylated cyclobutanes bearing an amide group were obtained with high selectivities.

Comment: A transformation of the product, including the removal of the amide auxiliary, was accomplished to demonstrate the synthetic utility of the reaction. An asymmetric induction model is also proposed.