Enantioselective Arylation of Enecarbamates with Quinone Imine Ketals

**Significance:** The asymmetric enantioselective arylation of enecarbamates catalyzed by a chiral Brønsted acid is reported. An axially chiral dicarboxylic acid (1) catalyzes the reaction of quinone imine ketals 2 with enecarbamates 3 to give α-amino-β-aryl ethers 4 in good yields and enantioselectivities. The products could be transformed into various useful chiral building blocks.

**Comment:** It is notable that opposite enantiomers of the products are obtained by changing from Z- to E-enecarbamates. The authors propose that the isomeric enecarbamates approach the quinone imine ketals 2 from the same prochiral face, and that diastereomeric intermediates are generated that lead to the opposite enantiomers after aromatization.

**Proposed reaction mechanism:**

with (Z)-3

\[
\begin{align*}
&\text{R}^1 = \text{H, Alk, Cl, Ph, OMe} \\
&\text{R}^2 = \text{Boc, Bz, Ac, Cbz}
\end{align*}
\]

with (E)-3

\[
\begin{align*}
&\text{R}^1 = \text{H, Alk, Cl, Ph, OMe} \\
&\text{R}^2 = \text{Boc, Bz, Ac, Cbz}
\end{align*}
\]

17 examples 53–89% yield ef from 81:9 to 99.5:0.5 dr from 3:1 to >20:1