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:**

1. With (Z)-3:

   [Diagram of the proposed reaction mechanism with (Z)-3]

2. With (E)-3:

   [Diagram of the proposed reaction mechanism with (E)-3]

**Equations and Structures:**

- **Equation 1:**
  \[
  \text{NR}^2 \quad + \quad \text{R}^2 \quad \text{NH}^2 \quad \xrightarrow{1 (5 \text{ mol}\%)} \quad \text{PhMe, 0 °C} \quad 4 \text{ Å MS} \quad \text{Ph}^+ \quad \text{OMe, 0 °C} \quad \text{H}^+ \quad \text{Bu}^+ \quad \text{Bu}^+
  \]

- **Equation 2:**
  \[
  \text{R}^1 = \text{H, Alk, Cl, Ph, OMe} \quad \text{R}^2 = \text{Boc, Bz, Ac, Cbz}
  \]

- **Equation 3:**
  \[
  \text{R}^1 = \text{Alk, OBn} \quad \text{R}^2 = \text{Boc, Bz, Cbz}
  \]

- **Equation 4:**
  \[
  \text{NR}^2 \quad \text{R}^2 \quad \text{OMe} \quad \text{H}^+ \quad \text{Bu}^+
  \]

**Experimental Details:**

- 17 examples: 53–89% yield, ee from 81.9 to 99.5:0.5, dr from 3:1 to >20:1
- 53–89% yield
- ee from 81.9 to 99.5:0.5
- dr from 3:1 to >20:1

**Key words:**
- enecarbamates
- dicarboxylic acids
- quinone imine ketals