Iridium-Catalyzed Enantioselective Alkyne-Imine Reductive Coupling

Significance: This paper demonstrates the first catalytic enantioselective alkyne-imine reductive coupling which the authors use to devise a convenient route for synthesizing optically enriched allylic amines. An advantage of this approach is the absence of stoichiometric byproducts. The scope is very broad with excellent yields and enantioselectivities for a wide variety of alkynes and N-aryl-sulfonyl imines.

Comment: The reaction is both regioselective and enantioselective. The stereochemistry can be explained by the binding of the alkyne and imine to the catalyst (shown above) which results in insertion of the imine at its pro-S face. In the case of unsymmetrical alkynes, the regiochemistry can be explained by the Ir-catalyst binding to the alkyne in a manner where the large substituent points away from the bulky chiral ligand.

Proposed mechanism via:

**Equation:**

\[
\text{Me} \equiv \text{R}^1 + \text{ArO}_2\text{S} + \text{H}^+ \rightarrow \text{PhMe or C}_6\text{H}_6, 60-80 \, ^\circ \text{C} \\
\begin{array}{c}
\text{64-81%} \\
\text{21 examples}
\end{array}
\]

**Formula:**

\[
\text{Me} \equiv \text{R}^1 + \text{ArO}_2\text{S} + \text{H}^+ \rightarrow \text{PhMe or C}_6\text{H}_6, 60-80 \, ^\circ \text{C} \\
\begin{array}{c}
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\text{21 examples}
\end{array}
\]

**Structures:**

- **Diagram:**
  - Proposed mechanism via:
  - Large substituent away from ligand
  - Rᵦ = small substituent
  - Rₛ = large substituent
  - (R)-Cl,MeO-BIPHEP

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