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Design, Preparation, and Implementation of an Imidazole-Based Chiral Biaryl P,N-Ligand for Asymmetric Catalysis


**A Chiral Biaryl P,N-Ligand for Asymmetric Catalysis**

**Significance:** The authors reported the preparation of a new chiral biaryl P,N-ligand incorporating a five-membered electron-rich heteroaromatic. This ligand is easy to prepare and an effective catalyst for the enantioselective alkynylation of imines.

**Comment:** In contrast to the six-membered P,N-ligands, five-membered P,N-ligands are configurationally unstable. The authors have succeeded in preparing a configurationally stable five-membered P,N-ligand involving π-stacking interaction, which would offer a new, unexplored chemical diversity.

**Synthesis of L1:**

1. TBSCI, Et3N, CH2Cl2, 78%  
2. NaH, THF, C6F5CH2Br, –78 °C, 94%  
3. Ni(PPh3)2Cl2, ClPPh2, Zn, DMF, 110 °C, 60%

**Importance of π-stacking:**

L1 (X = F) half-life: 8.7 h at 75 °C in DCE  
L1-H5 (X = H) half-life: 22 min

**Selected example:**

\[
\text{CyCHO} + \text{TMS} \rightarrow \text{Cy \( \equiv \) TMS}
\]

95% yield 97% ee

**Concept:**

![Image of ligand structures](image)

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