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

**Concept:**

- Six-membered aromatic (QUINAP)
- Five-membered heteroaromatic configurally unstable

**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:**

- CyCHO + L1 (5.6 mol%) CuBr (5 mol%) HNBn2 (1 equiv)  
- 95% yield 97% ee

**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.