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.

Concept:

- six-membered aromatic (QUINAP)
- five-membered heteroaromatic configurationally unstable

Synthesis of L1:

1. K2CO3, MeOH
2. PhN(SO2CF3)2, Et3N
3. Ni(PPh3)2Cl2, ClPPh2
   Zn, DMF, 110 °C, 60%

Selected example:

CyCHO + L1 (5.5 mol%) CuBr (5 mol%) HNBn2 (1 equiv) 95% yield 97% ee

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