Cu-Catalyzed Asymmetric 1,6-Conjugate Addition of Dialkylzinc

**Selected examples:**

- n-C7H15OEt + n-C7H15Zn (3.0 equiv) → 70% yield, 1,6/1,4 = 72:28, 84% ee
- n-C7H15OEt + n-C7H15Zn (3.0 equiv) → 41% yield, 1,6/1,4 = 98:2, 96% ee
- n-C7H15OEt + n-C7H15Zn (3.0 equiv) → 84% yield, 1,6/1,4 = 97:3, 98% ee

**Isomerization and 1,4-conjugate addition of 1,6-adducts:**

- R1 = n-C7H15, R2 = Ph: 55% yield, >97% de
- R1 = Me, R2 = 4-ClC6H4: 81% yield, 93% de

**Plausible reaction mechanism:**

The authors reported the asymmetric 1,6-conjugate addition of dialkylzinc to acyclic dienones catalyzed by copper/phosphinoazomethine salt (DIPPAM). After the isomerization of the conjugate adducts, stereoselective sequential 1,4-conjugate addition of diethylzinc was also demonstrated.

**Comment:** The control of regioselectivity of the 1,6-conjugate addition is difficult due to many parameters. Using copper and the DIPPAM ligand, a highly enantio- and regioselective 1,6-conjugate addition was achieved. With the BINAP ligand, unprecedented highly stereoselective induction is noteworthy.