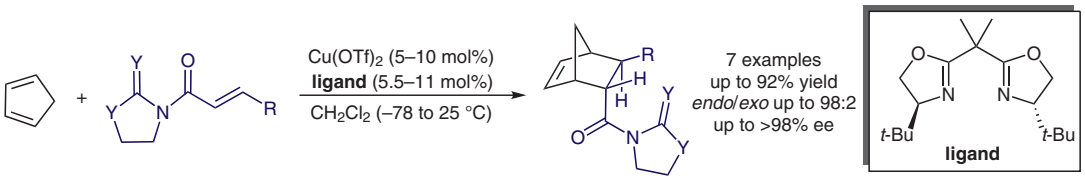
D. A. EVANS*, S. J. MILLER, T. LECTKA (HARVARD UNIVERSITY, CAMBRIDGE, USA)
Bis(oxazoline)copper(II) Complexes as Chiral Catalysts for the Enantioselective Diels–Alder Reaction
J. Am. Chem. Soc. **1993**, *115*, 6460–6461.

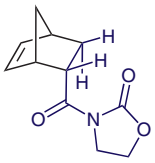
Category
Metals in Synthesis

Key words
copper catalysis
Diels–Alder cycloaddition
Lewis acids

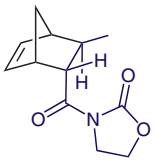
Enantioselective Copper-Catalyzed Diels–Alder Cycloaddition



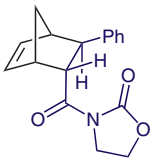
Examples:



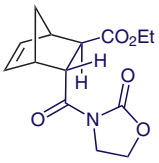
86% yield
endo/*exo* = 98:2
>98% ee (*endo*)



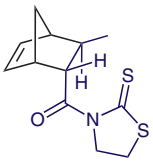
85% yield
endo/*exo* = 96:4
97% ee (*endo*)



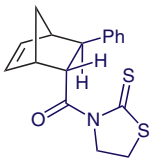
85% yield
endo/*exo* = 90:10
90% ee (*endo*)



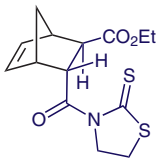
92% yield
endo/*exo* = 94:6
95% ee (*endo*)



82% yield
endo/*exo* = 96:4
94% ee (*endo*)

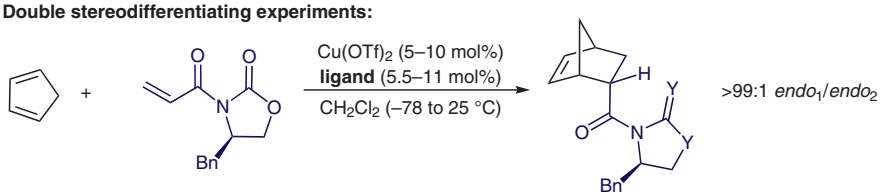


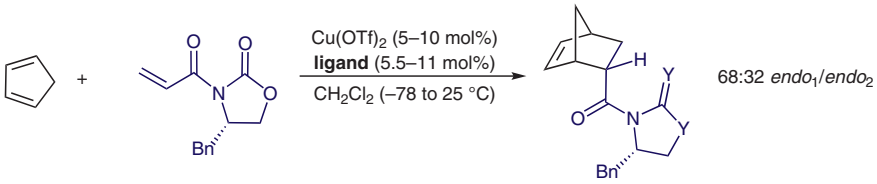
86% yield
endo/*exo* = 92:8
97% ee (*endo*)



88% yield
endo/*exo* = 84:16
96% ee (*endo*)

Double stereodifferentiating experiments:





Significance: Following Narasaka's report on titanium-catalyzed enantioselective Diels–Alder reactions (*J. Am. Chem. Soc.* **1989**, *111*, 5340) and Corey's variants using chiral magnesium(II) and iron(II) catalysts (*J. Am. Chem. Soc.* **1991**, *113*, 728; *Tetrahedron Lett.* **1992**, *33*, 6807), Evans disclosed a highly enantioselective Diels–Alder reaction employing copper(II)-catalysts and BOX ligands.

Comment: Products were obtained in high yields and excellent enantioselectivities. This class of chiral Lewis acid catalysts has since been applied to asymmetric aldol reactions, Michael additions, and carbonyl ene reactions by the same group (J. S. Johnson, D. A. Evans *Acc. Chem. Res.* **2000**, *33*, 325).

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