

CHIRAL C₂-SYMMETRIC BI(OXAZOLINES): SYNTHESIS AND USES FOR ASYMMETRIC CATALYSIS

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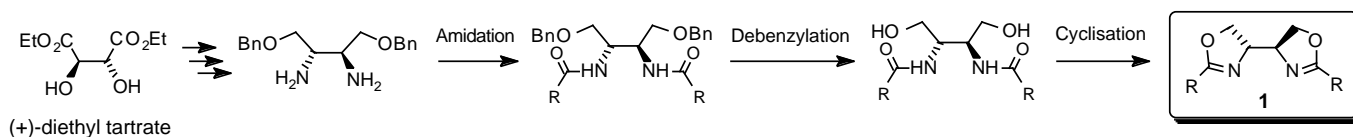
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Purpose:

Preparation of new chiral ligands for asymmetric catalysis.

Synthesis of ligands:



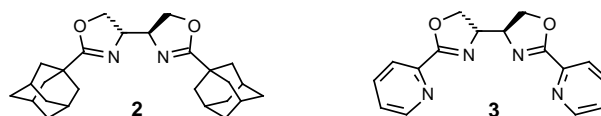
Amidation: $\text{RCOCl}/\text{Et}_3\text{N}$ or RCO_2H , DCC, cat. DMAP \Rightarrow easy modulation of R

Debenzylation: $\text{BCl}_3 \cdot \text{Me}_2\text{S}$ or cat. $\text{Pd}(\text{OH})_2/\text{C}$, cyclohexene

Cyclisation: MsCl , Et_3N then aq. NaOH or DAST then NaHCO_3 .

Among a series of C₂-symmetric bi(oxazolines) **1** tested for asymmetric catalysis, two emerged as the best ligands:

- **2** for asymmetric cyclopropanation,
- **3** for asymmetric hydrocyanation.



Asymmetric cyclopropanation:1

Catalytic system: 2 mol% CuOTf + 3 mol% bi(oxazoline) **2**,

Operating conditions: excess alkene (ca. 8 equiv.), CH_2Cl_2 , slow addition of diazoacetate, molecular sieves, 0 to ca. 20 °C.

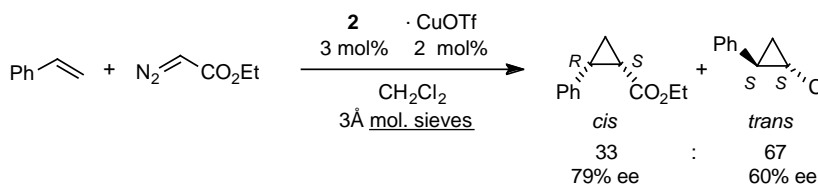
With 1,1-diphenylethylene:



The presence of a desiccant is essential.
Without molecular sieves: 10% yield.

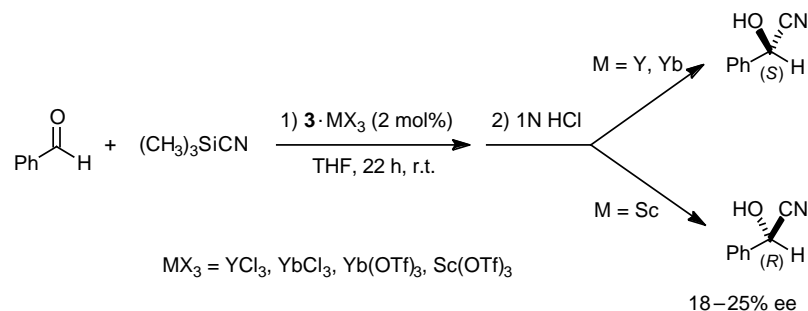
In contrast to most literature catalysts, works with commercial CuOTf , $\text{Cu}(\text{OTf})_2$ yields the same ee !

With styrene:



More *cis*-isomer than most literature catalysts.

Asymmetric hydrocyanation:2



Reversal of enantioselectivity depends on the metallic salt.

Although enantioselectivities were low (ee 25%), **3** was the most enantioselective ligand which was found.

Substitution of the pyridine ring of **3** with *tert*-butyl groups led to an excellent catalysis but with little or no enantioselectivity.

¹ R. Boulch, A. Scheurer, P. Mosset, R. W. Saalfrank, *Tetrahedron Lett.* **2000**, *41*, 1023-1026.

² R. Boulch, PhD thesis, University of Rennes, **2000**.