

ASYMMETRIC CYCLOPROPANATION CATALYZED BY C₂-SYMMETRIC BI(OXAZOLINES)

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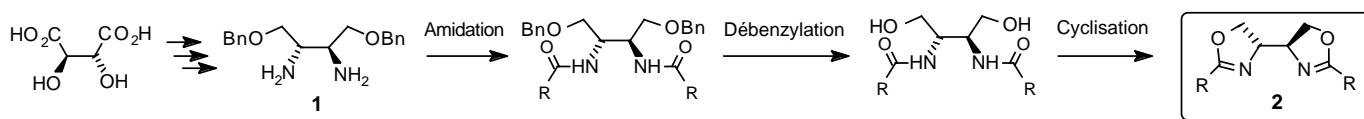
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Purpose:

Synthesis of new chiral ligands for asymmetric catalysis.

Preparation of ligands:

Starting from (+)-diethyl tartrate, a series of new C₂-symmetric bi(oxazolines) **2** was prepared via the intermediate diamine **1**.



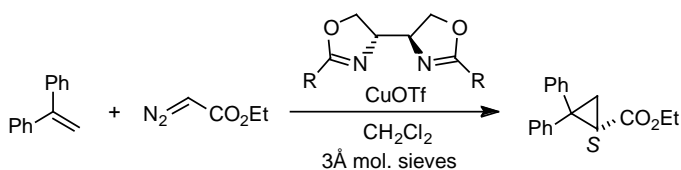
R can easily be modulated by simple use of RCO₂H or RCOCl in the amidation step.

Asymmetric cyclopropanation:

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

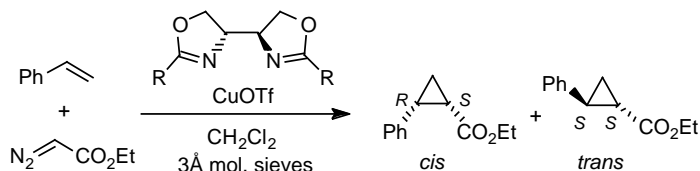
Operating conditions: excess alkene (ca. 8 equiv.), CH₂Cl₂, slow addition of diazoacetate, molecular sieves, 0 to ca. 20 °C.

With 1,1-diphenylethylene:



R	% ee	Yield (%)	
		with 3Å MS	without 3Å MS
	30	70	13
	35	36	10
	78	86	10

With styrene:



R	Diastereoselectivity cis : trans	Enantioselectivity		Yield (%)
		cis % ee	trans % ee	
	68 : 32	9	26	85
	49 : 51	18	28	13
	33 : 67	79	60	41

Conclusions:

Markedly different reactivities compared with literature catalysts:

- commercial grade reagents,
- requirement of a dessiccant,
- more *cis* isomer.

Best ligand:

