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MODULAR APPROACH TO CHIRAL PYRIDINE-CONTAINING MACROCYCLIC LIGANDS (Pc-L*). APPLICATION OF THEIR COPPER(I) COMPLEXES IN ASYMMETRIC CYCLOPROPANATIONS.

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We have recently reported that copper(I) complexes of the new C₁-symmetric pyridine-based 12-membered tetraaza macrocycles, Pyridine Containing Ligands (Pc-L*), are competent catalysts in asymmetric cyclopropanations.¹ Herein we report the synthesis of new C₁- and C₂-symmetric Pc-L* macrocycles and the use of their Cu(I) complexes as catalysts for the title reaction.

The synthetic path is very simple and it takes advantage of commercially available, enantiomerically pure, chiral amino-alcohols and/or primary amines. Compounds **1a-b** have been obtained in a quantitative yield employing naturally occurring L-valinol as starting material.² Differently substituted macrocyclic ligands **4a-d** have been obtained in moderate to good yields (20-70%) and they have been fully characterized including elemental analysis, MS, ¹H-NMR, ¹³C-NMR. The Cu(I) complexes of those ligands have been isolated and characterized, and they showed good catalytic activities in the cyclopropanation of differently substituted olefins employing ethyl diazoacetate (EDA) as carbene precursor.

In all cases a complete conversion of EDA was observed and, depending on the employed ligand, cyclopropanes have been obtained with tunable *cis/trans* stereoselectivities and *e.e.* up to 96%. Moreover, the obtained results allow a direct comparison of the reaction stereoselective outcome between C₁- and C₂-symmetric ligands having the same molecular structure.

1. A. Caselli, F. Cesana, E. Gallo, N. Casati, P. Macchi, M. Sisti, G. Celentano, S. Cenini *Dalton Trans* **2008**, 4202-4205.

2. M. Cernerud, H. Adolfsson and C. Mober, *Tetrahedron: Asymmetry* **1997**, 8, 2655-2662.



