

04.6

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

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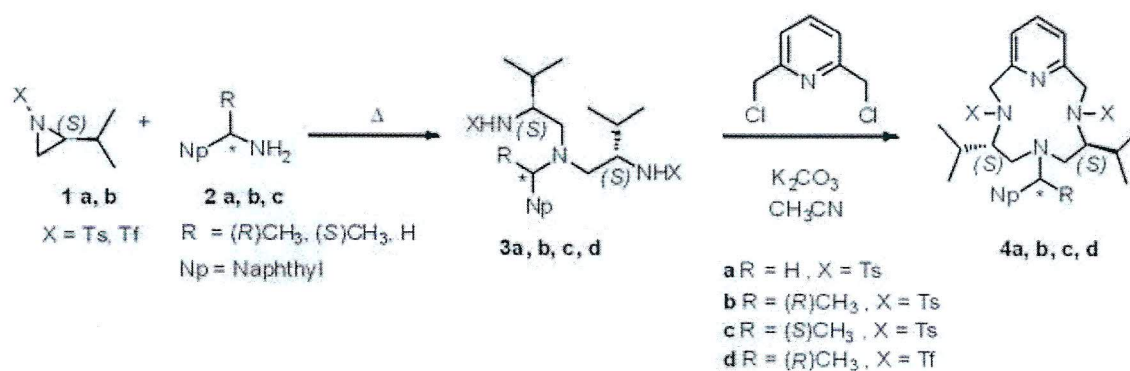
We have recently reported that copper(I) complexes of the new C<sub>1</sub>-symmetric pyridine-based 12-membered tetraaza macrocycles, Pyridine Containing Ligands (Pc-L\*), are competent catalysts in asymmetric cyclopropanations.<sup>1</sup> Herein we report the synthesis of new C<sub>1</sub>- and C<sub>2</sub>-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.<sup>2</sup> 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, <sup>1</sup>H-NMR, <sup>13</sup>C-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 C<sub>1</sub>- and C<sub>2</sub>-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.





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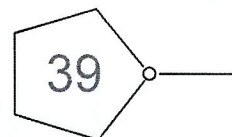
# PROGRAM

Conference Website:

<http://cqe.ist.utl.pt/events/icomc25/>

## Scientific Program

15.00 – 15.15	O4.3 Dinickel(I) Catalysts Bearing Bulky NHC Ligand; Synthesis and Catalytic Behavior Toward Cross-Coupling Reactions of Aryl Halides <b>Matsubara, K.</b>	O5.3 Carbon-Hydrogen Bond Activation with Cationic Pincer Platinum Complexes <b>Ozerov, O. V.</b>	O6.3 Highly Regio- and Stereoselective Synthesis of Multi-Substituted Olefins from Alkynylboronates Through Sequential Cross-Couplings <b>Nishihara, Y.</b>	J2.2 Chemistry of Low Valent Silicon <b>Roesky, H. W.</b>
15.15 – 15.30	O4.4 Well-Defined Copper(I) Catalysts for True Click Cycloaddition Reactions <b>Díez-González, S.</b>	O5.4 Metallaioxetane Complexes and Their Applications <b>Del Río, M. P.</b>	O6.4 Chain-Walking Strategy for Catalytic Cycloisomerization of 1,n-Dienes <b>Kochi, T.</b>	
15.30 – 15.45	O4.5 Predicting Ligand Effects on Organometallic Catalytic Cycles <b>Fey, N.</b>	O5.5 Selective CO <sub>2</sub> Activation Using Electrocatalysts Based on Non-Noble Naturally-Abundant Metal Carbonyl Complexes: [Mn(bipyridyl)(CO) <sub>3</sub> Br] <b>Chardon-Noblat, S.</b>	O6.5 Stereoselective Synthesis of Complex Heterocycles by Transition Metal Catalyzed Skeletal Rearrangement of Enzymatically Desymmetrized Building Blocks <b>Deska, J.</b>	J2.3 Late Transition Metal NHC-Complexes: Catalysis And Pholeds <b>Strassner, T.</b>
15.45 – 16.00	O4.6 Modular Approach to Chiral Pyridine-Containing Macrocyclic Ligands (Pc-L*). Application of Their Copper(I) Complexes in Asymmetric Cyclopropanations <b>Caselli, A.</b>	O5.6 Steric Effects in the Reductive Coupling of CO with U(III) Mixed Sandwich Complexes <b>Tsoureas, N.</b>	O6.6 Fascin(Ates): Synthetic and Structural Consequences of Bimetallic Co-operation in Metallation Chemistry <b>Mulvey, R. E.</b>	


 16.00 – 16.30 **Coffee break**