Silica "SHB"chiral Pc-L* Cu(I) complexes for continuous flow cyclopropanation reactions with carbon dioxide as a carrier.

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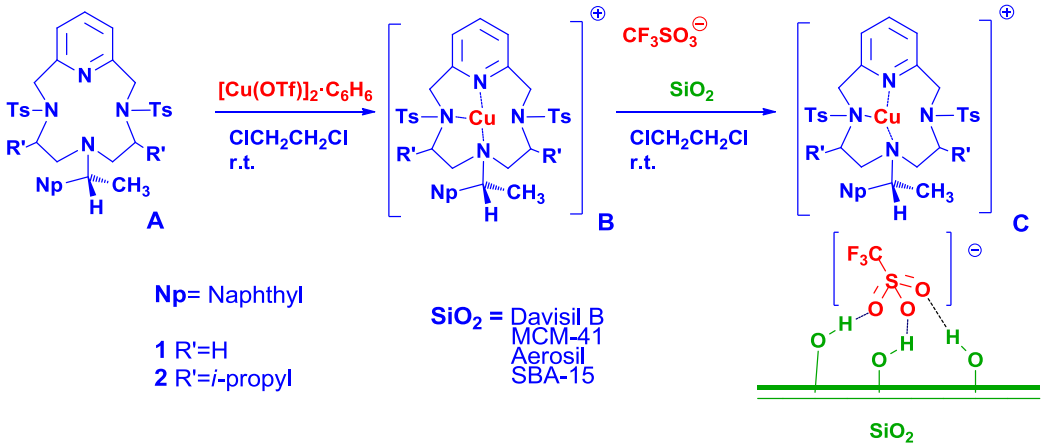
We have recently reported that copper(I) complexes of the new C_1-symmetric pyridine-based 12-membered tetraaza macrocycles, *Pyridine Containing Ligands* (**Pc-L***), are competent catalysts in the asymmetric cyclopropanation [1,2]. In order to improve our catalytic system Cu(I) complexes based on **Pc-L*** ligands were heterogeneised on mesoporous ordered and non-ordered silicas (Davisil B, MCM-41, etc.) by the Supported by HydrogenBond (SHB) method [3].



Supported catalysts **C** were tested in enantioselective cyclopropanation in batch conditions showing good catalytic activities employing ethyl diazoacetate (EDA) as carbene precursor in *n*-hexane. The silica support has a strong influence on the diastereoselective outcome of the reaction, favoring the formation of the more challenging *cis*-isomer. Then, **C** were tested as catalyst for the cyclopropanation reaction under flow conditions focusing our attention on the use of supercritical CO_2. Under optimised conditions, the catalyst was stable over at least 10 h of continuous flow, without drop in activity or selectivity.

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[2] B. Castano, S. Guidone, E. Gallo, F. Ragaini, N. Casati, P. Macchi, M. Sisti, A. Caselli *Dalton Trans.* **2013**, *42*, 2451
[3] B. Castano, P. Zardi, Y. Hönneman, E. Gallo, A. Caselli, V. Dal Santo, A. Galarneau,, submitted manuscript