

## FT2 Ruthenium Phthalocyanines with Orthogonal Substituents Bearing (1R,2S,5R)-Menthoxo Groups as Prototype of Chiral Catalysts

A.P.Kroitor,<sup>1,2</sup> A. A. Dmitrienko,<sup>1,3</sup> A. G. Martynov,<sup>\*1</sup> Yu. G. Gorbunova,<sup>\*1,4</sup>  
A. Yu. Tsivadze,<sup>1,4</sup> A. B. Sorokin<sup>\*2</sup>

<sup>1</sup> A.N.Frumkin IPCE RAS, Bldg. 4, 31, Leninskiy Prospekt, Moscow, Russia.

<sup>2</sup> IRCELYON, 2 Av. Albert Einstein, Villeurbanne, France.

<sup>3</sup> Lomonosov Moscow State University, Chemistry Department, Moscow, Russia.

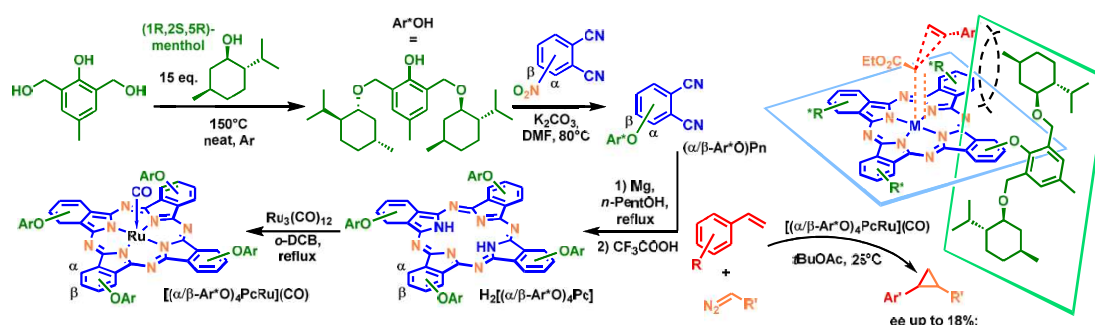
<sup>4</sup> N.C. Kurnakov IGIC RAS, Leninskiy Prospekt, 31, Moscow, Russia.

E-mail: andreykroitor96@gmail.com

Metal complexes of phthalocyanines (MPc) show significant catalytic activity in a wide range of catalytic reactions.<sup>1</sup> Although phthalocyanines with chiral substituents have been described,<sup>2</sup> MPc have not been unexplored in enantioselective catalysis since chiral groups are typically situated far from the metal site in the macrocyclic plane that prevents a chiral induction.

We present here a novel approach to the synthesis of phthalocyanines with picket-fence architecture with bulky chiral substituents arranged orthogonally to the plane of the macrocycle that creates a chiral environment around the metal site. Natural (1R,2S,5R)-menthol was chosen as the chiral inductor, which interacted with 2,6-bis-(hydroxymethyl)-p-cresol to give the phenol **Ar\*OH**. X-ray analysis of the phthalonitrile precursors confirmed the orthogonality of the phthalonitrile rings to the aryloxy-group.

The  $[(\alpha/\beta\text{-Ar}^*\text{O})_4\text{PcRu}](\text{CO})$  complexes were prepared by the reaction of the metal free phthalocyanines  $\text{H}_2[(\alpha/\beta\text{-Ar}^*\text{O})_4\text{Pc}]$  with  $\text{Ru}_3(\text{CO})_{12}$ .<sup>3</sup> Using the reaction of styrene with ethyl diazoacetate (EDA) as a benchmark reaction, it was found that peripherally substituted ruthenium phthalocyaninate  $[(\beta\text{-Ar}^*\text{O})_4\text{PcRu}](\text{CO})$  showed virtually no asymmetric induction, whereas the complex  $[(\alpha\text{-Ar}^*\text{O})_4\text{PcRu}](\text{CO})$  allowed the cis-isomer of the cyclopropanation product to be obtained with ee = 18%, highlighting the importance of introducing substituents in non-peripheral positions.<sup>4</sup>



The development of a second generation of chiral phthalocyanine complexes with improved catalytic properties is in great progress in our laboratories.

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