

Supplementary Information

Efficient and region-selective conversion of octanes to epoxides under ambient conditions: Performance of tri-copper catalyst, $[\text{Cu}_3^{\text{I}}(\text{L})]^{+1}$ (L=7-N-Etppz)

Penumaka Nagababu^{*a}, Perala Sudheer Paul^b, Thatiparthi Byragi Reddy^b & Reddithota J Krupadam^a

^aEnvironmental Materials Division, CSIR-National Environmental Engineering Research Institute, Nehru Marg, Nagpur 440 020, India

^bDepartment of Environmental Science, College of Science and Technology, Andhra University, Visakhapatnam 530 003, India

E-mail: babupenumaka@gmail.com; p.nagababu@neeri.res.in

Received 8 October 2020; accepted (revised) 4 March 2021

Preparation of Ligand

A solution of epichlorohydrin (1.85 g, 20 mmol) in methanol (15.0 ml) was added drop-wise to a solution of homopiperazine (1.02 g, 10 mmol) in methanol (30.0 ml) with stirring at around -5°C. After stirring for 72 h at around -5°C, the resulting mixture was purified by column chromatography on silica gel using 8% CH₃OH in dichloromethane as the solvent ^[1-3] and compound **A1** was obtained (78 % yield). Detailed spectral characterization of **A1** and **L2** has been reported in our previous reports (copied from).^[3] Ligand was prepared by mixing **A1** (6 mmol), ethylpiperazine **B1** (12 mmol) and K₂CO₃ (12 mmol) in acetonitrile, heated to 70-80°C for 48 h (nitrogen atmosphere). After cooling to room temperature, the solution was filtered, and upon evaporation of the filtrate to dryness, the ligand was obtained in 85% yield.

Preparation of the Cu^{II}₃ tricopper complex

A anhydrous CH₃CN solution (25 ml) containing **L** (2.205 g, 5.0 mmol) and three equivalents of Cu^{II}(ClO₄)₂·6H₂O (5.49 g, 15.1 mmol) were mixed and stirred for 1 h to give a deep green solution, which was filtered, washed with CH₂Cl₂, and dried in vacuum to give a green powder^[3].

Catalytic Oxidation of Substrates

The efficacy of the $[\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}(\text{L})]^{1+}$ complexes as acatalyst for oxidation 500 equiv. of selected substrates *n*-octane (C₈H₁₈), cyclooctene (C₈H₁₄), and 1, 5 cyclooctadine (C₈H₁₂) by H₂O₂, with 200 and

one equiv of $[\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}(\text{L})]^{1+}$ in CH_3CN (total volume 3 mL) at room temperature for 1 h. According to GC-MS analysis, the products consisted with epoxides, alcohol and ketones ^[3].

Time-course studies

The time course of product formation during the oxidation of selected substrates mediated by catalytic turnover of the $[\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}\text{Cu}^{\text{I}}(\text{L})]^{1+}$ complex in the presence of 200 equiv. of starting H_2O_2 . The reaction was essentially completed within 30 min, when the H_2O_2 in the solution was exhausted ^[3]

Figure S1 *n*- octane oxidation reaction

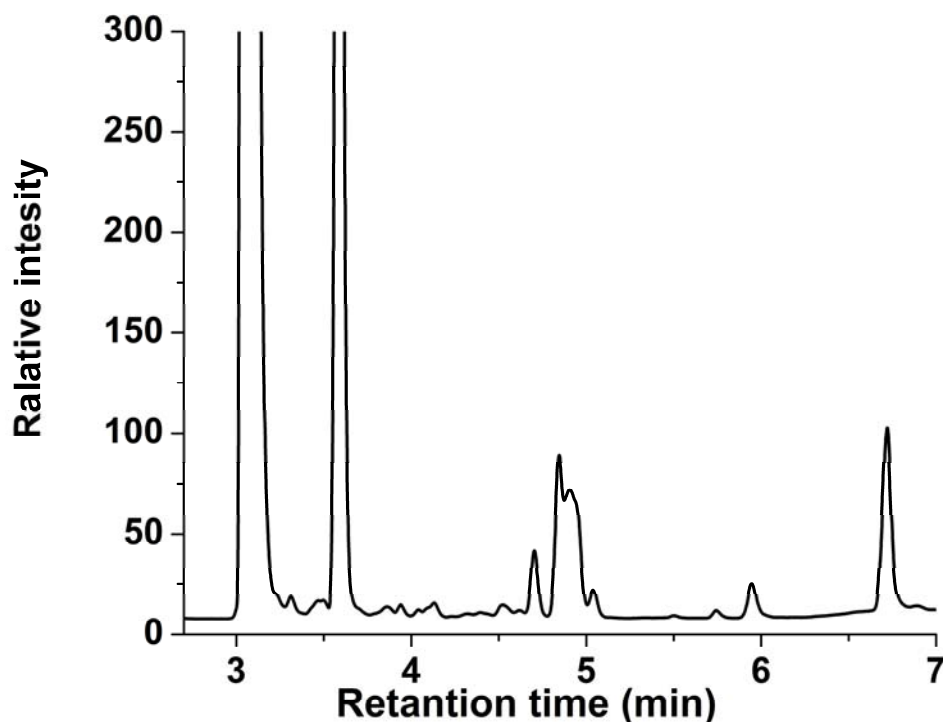


Figure S1. GC chromatograms obtained for the products 2-octanol retention time (tR) at 5.0, 4-octanol retention time (tR) at 5.9, 2-octanone retention time (tR) at 4.7 and 4-octanone retention time (tR) at 4.9. The oxidation of 500 equiv. of *n*-octanol is mediated by 1 equiv. of catalyst in the presence of 200 equiv. of starting H_2O_2 . Quantification of the products is determined by co-injection of a nitrobenzene external standard retention time (tR) at 6.9.

Figure S2 cyclooctene oxidation reaction

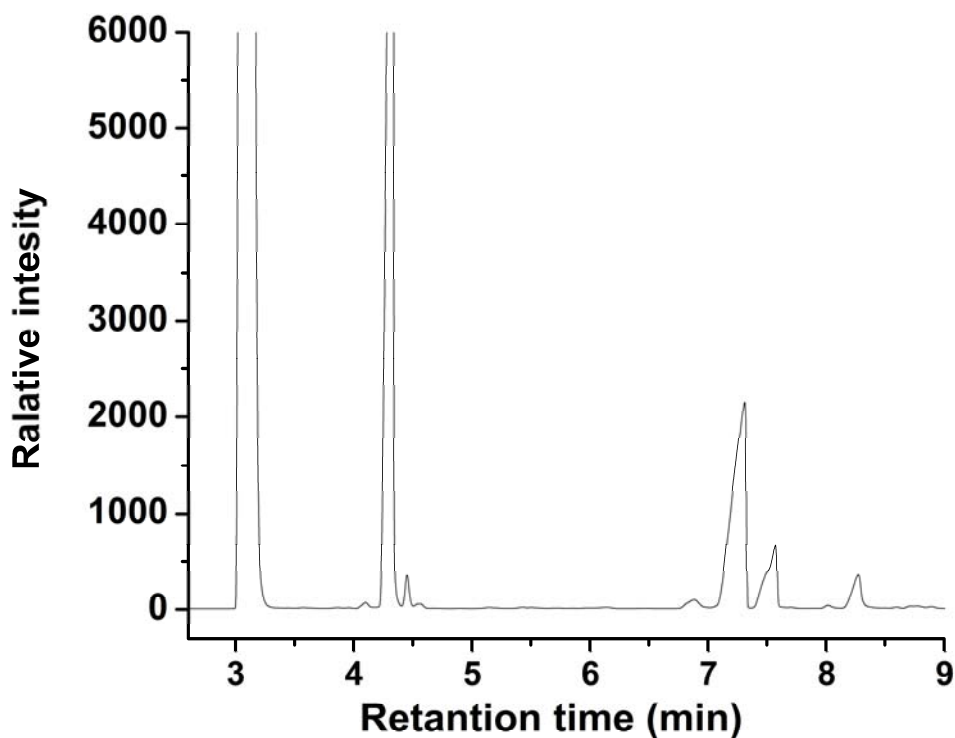


Figure S2. GC chromatograms obtained for the products 9-oxabicyclo[6.1.0]nonane retention time (tR) at 7.3, (Z)-cyclooct-4-en-1-ol retention time (tR) at 7.5, and (Z)-cyclooct-4-en-1-one retention time (tR) at 8.6 The oxidation of 500 equiv. of cyclooctene is mediated by 1 equiv. of catalyst in the presence of 200 equiv. of starting H₂O₂. Quantification of the products is determined by co-injection of a nitrobenzene external standard retention time (tR) at 6.9.

Figure S3 cyclooctadiene oxidation reaction

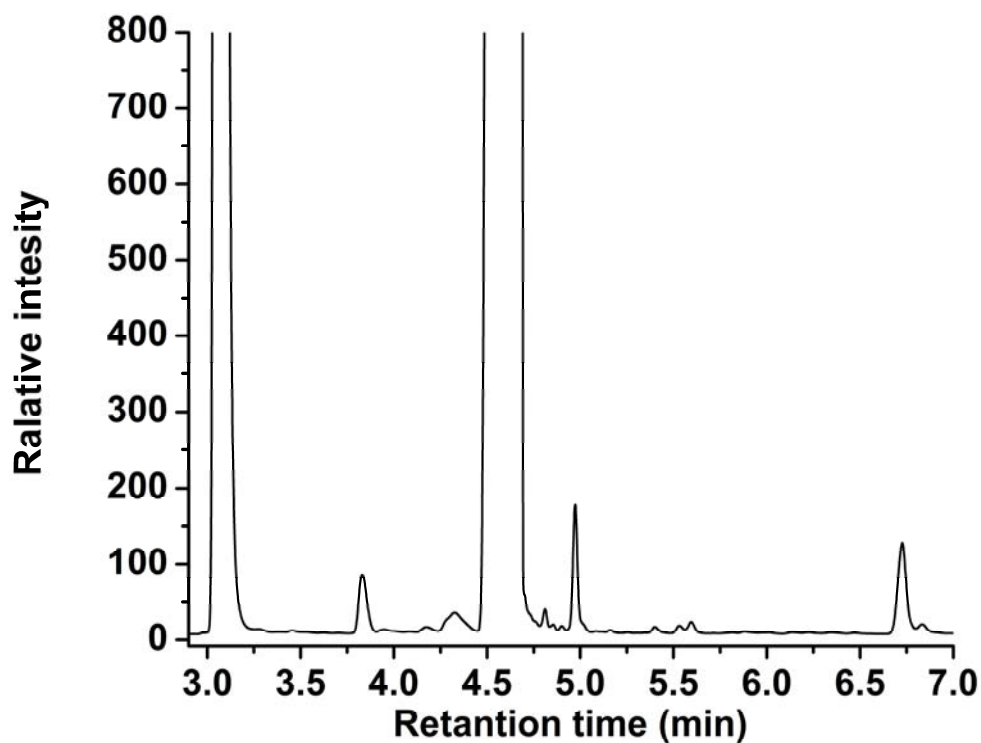


Figure S3. GC chromatograms obtained for the products 5,10-Dioxatricyclo[7.1.0.0(4,6)]decane retention time (tR) at 4.9 and 4-vinylcyclohex-1-ene retention time (tR) at 3.8, The oxidation of 500 equiv. of cyclooctadiene is mediated by 1 equiv. of catalyst in the presence of 200 equiv. of starting H_2O_2 . Quantification of the products is determined by co-injection of a nitrobenzene external standard retention time (tR) at 6.9.

References

- [1]. D. M. Burness, H. O. Bayer, *J. Org. Chem.* 1963, 28, 2283.
- [2]. S. Hayashi, M. Furukawa, Y. Fujino, M. Sugita, T. Nakao, *Chem & Pharm. Bull.* 1971, 19, 2003.
- [3]. P. Nagababu, S. Maji, M. P. Kumar, S. S. F. Yu, S. I. Chan, *Adv. Synth. Catal.* 2012, 354, 3275.