Mechanistic Investigation of Copper-Catalyzed Asymmetric Esterification: Revealing A New NLEs Analysis Model

Xiaotao Zhu[+],[1] Meirong Huang[+],[2] Hongli Bao*,[1] and Xinhao Zhang *,[2]

Fujian Institute of Research on the Structure of Matter, Chinese Academy of Science, Fuzhou, China

hlbao@fjirsm.ac.cn

Non-linear effects (NLEs), dealing with the relationship between ee values of ligand and product, classically serve as a widespread tool for investigating asymmetric reaction mechanisms. However, the NLEs analysis model only often provides intuitive information in simple systems, leaving the application in complex systems indirect and vague. Here, we report a new NLEs analysis model that directly connects the relationship between ee values of metal complexes and products, with the purpose of solving the challenges that occur in complex systems. Through an in-depth analysis of the mechanism of our previous copper-catalyzed asymmetric esterification reactions, we found an intrinsic linear relationship between the ee values of the key active metal complex (LLCuI) and product within this traditionally non-linear system. This new NLEs model holds promise as a powerful tool for the exploration of asymmetric catalysis mechanisms, heralding new avenues in the understanding and application of catalytic processes.

References:

[1] (a) Puchot, C.; Samuel, O.; Dunach, E.; Zhao, S.; Agami, C.; Kagan, H. B. *J. Am. Chem. Soc.* **1986**, *108*, 2353-2357; (b) Guillaneux, D.; Zhao, S.-H.; Samuel, O.; Rainford, D.; Kagan, H. B. *J. Am. Chem. Soc.* **1994**, *116*, 9430-9439; (c) Zhang, S. Y.; Girard, C.; Kagan, H. B. *Tetrahedron: Asymmetry* **1995**, *6*, 2637-2640; (d) Girard, C.; Kagan, H. B. *Angew. Chem. Int. Ed.* **1998**, *37*, 2922-2959; (e) Kagan, H. B. *Adv. Synth. Catal.* **2001**, 343, 227-233

[2] (a) Satyanarayana, T.; Abraham, S.; Kagan, H. B. *Angew. Chem. Int. Ed.* **2009**, *48*, 456-494. (b) Ahn, J. M.; Ratani, T. S.; Hannoun, K. I.; Fu, G. C.; Peters, J. C. *J. Am. Chem. Soc.* **2017**, *139*, 12716-12723. (c) Geiger, Y.; Achard, T.; Maisse‐François, A.; Bellemin‐Laponnaz, S. *Eur. J. Org. Chem.* **2021**, *2021*, 2916-2922. (d) Zhu, X.; Li, Y.; Bao, H. *Chin. J. Chem.* **2023**, *41*, 3097-3114.