

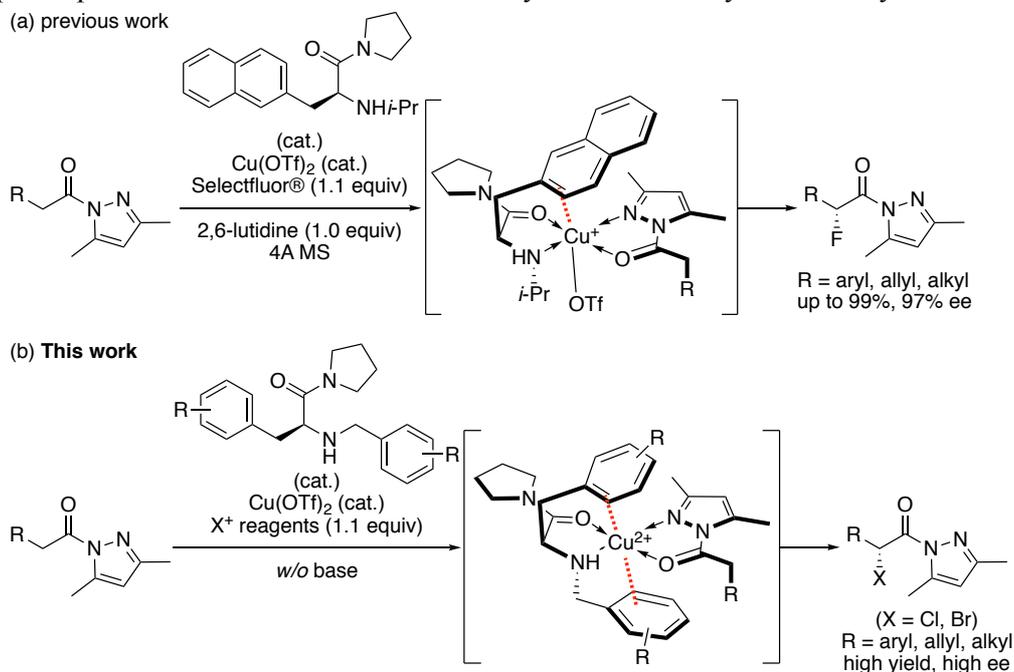
π -Cu(II)- π Complexes as Extremely Active Catalysts for Enantioselective α -Halogenation of *N*-Acyl-3,5-dimethylpyrazoles

(Graduate School of Engineering, Nagoya University) ○Kazuki Nishimura, Yanzhao Wang, Yoshihiro Ogura, Jun Kumagai, Kazuaki Ishihara

Keywords: π -Cu(II) Complex; Halogenation Reaction; Lewis Acid Catalyst; *N*-Acylpyrazole; π -Cu(II) Interaction

We have already developed the enantioselective α -fluorination reaction of *N*-acylpyrazoles catalyzed by chiral π -Cu(II) catalysts.¹⁾ Here, we developed the enantioselective α -halogenation reaction of *N*-acylpyrazoles catalyzed by chiral π -Cu(II)- π complexes, which were prepared *in situ* from copper(II) triflate and (*S*)-arylalanine amides.²⁾ Although there are vast reports of α -halogenation reaction, the carbonyl substrates for these are limited to aldehydes, ketones, and 1,3-dicarbonyl compounds that have relatively low pK_a values associated with the α -hydrogen atoms. Against this background, here the development of highly efficient enantioselective α -halogenation of *N*-acylpyrazoles is described.

The double π -Cu(II) interaction between the two unsaturated bonds on the chiral ligand and Cu(II) center might play a critical role in the construction of chiral cavity as well as high catalytic activity. The corresponding *N*-(α -haloacyl)pyrazoles were obtained in high yield with high enantioselectivity without the addition of an external base. We would like to propose a possible transition state based on X-ray diffraction analysis of the key intermediates.



1) Ishihara, K.; Nishimura, K.; Yamakawa, K. *Angew. Chem. Int. Ed.* **2010**, *59*, 17641. 2) Nishimura, K.; Wang, Y.; Ogura, Y.; Kumagai, J.; Ishihara, K. *ACS Catal.* **2022**, in press.