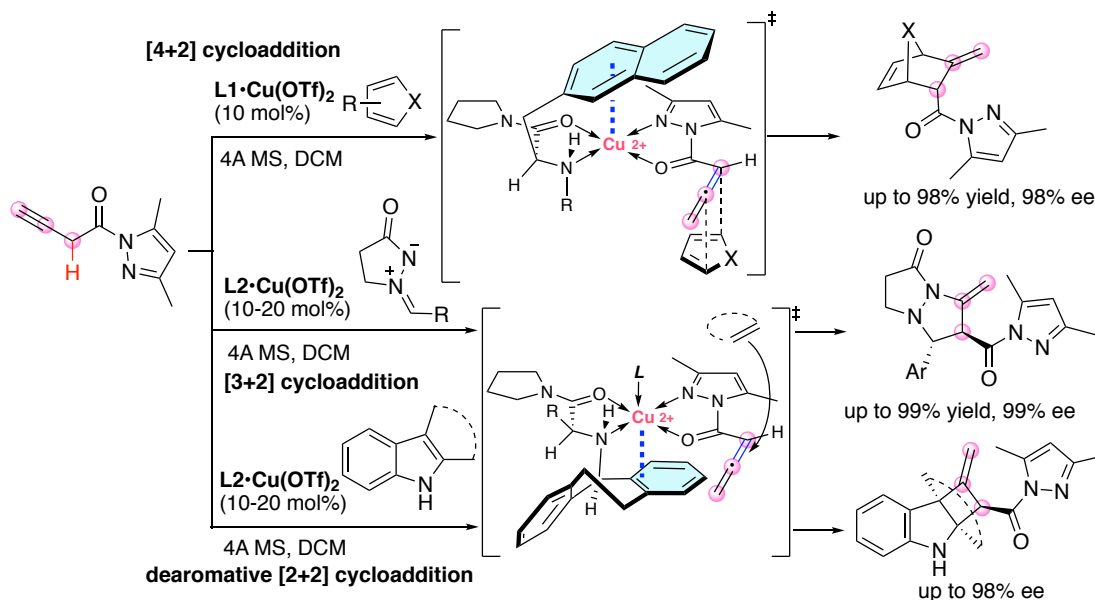


Tandem Enantioselective [4+2], [3+2] and [2+2] Cycloaddition Reactions of *In Situ*-generated *N*-Allenoylpyrazoles Induced by Chiral π -Cu(II) Catalyst

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Allenes are important building blocks, and derivatation of products *via* their cycloadditions could be a powerful strategy for constructing carbocyclic and heterocyclic rings. The synthesis of allenes and developing their enantioselective cycloaddition reactions, however, still present challenge. Here, we report chiral π -copper(II) complex¹-catalyzed isomerization of *N*-(but-3-ynoyl)-3,5-dimethyl-1*H*-pyrazoles to *in situ* generate *N*-allenoylpyrazoles and successive enantioselective [4+2], [3+2] and [2+2] cycloaddition reactions. The asymmetric environment created by intramolecular π -Cu(II) interaction gives the corresponding adducts in high yields with excellent enantioselectivity. To the best of our knowledge, it is the first successful method for Lewis acid-catalyzed one-pot enantioselective cycloaddition of *N*-allenoylpyrazoles.



References

- For recent examples of π -Cu(II) catalysis, see: (a) K. Ishihara, K. Nishimura, K. Yamakawa, *Angew. Chem. Int. Ed.*, **59**, 17641 (2020); (b) K. Nishimura, Y. Wang, Y. Ogura, J. Kumagai, K. Ishihara, *ACS Catal.*, **12**, 1012 (2022); (c) K. Nishimura, K. Ishihara, *Synlett*, **33**, 585 (2022).