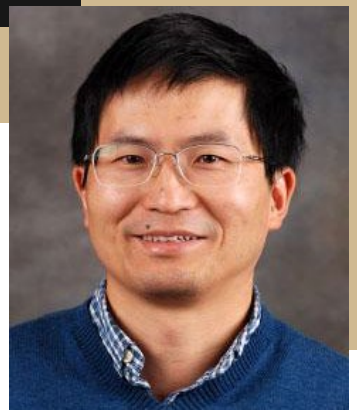
ORGANIC SEMINAR



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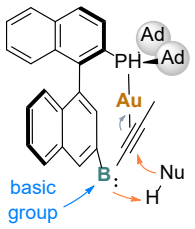
Recent Developments in Gold(I) Catalysis: from Ligand-Enabled Asymmetric Catalysis to Stereoselective Synthesis of Glycosides and Unnatural Amino Acids

Although homogeneous gold(I) catalysis has been extensively studied for the past twenty years, there remain exciting opportunities for developing versatileand highly valuable synthetic methodologies with this approach. In this talk, three aspects of gold(I) catalysis will be discussed:

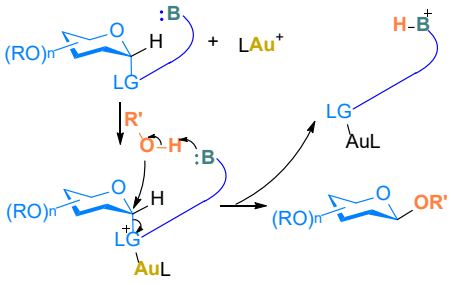
a) Metal-ligand cooperation is a versatile strategy for achieving efficient and/or stereoselective catalysis. Since 2014, we have developed various remotely basic group-functionalized biaryl-2-ylphosphine ligands (see Scheme A) to enable cooperative gold catalysis. With chiral elements built into these ligands, asymmetric transformations[1] have recently been developed in mechanistically rational manners, leading to synthetically valuable structures.

b) A long-standing challenge in carbohydrate synthesis is the absence of a general method applicable to stereoselective construction of every type of glycosidic bond. As shown in Scheme B, we have recently advanced a Directing-Group-on-Leaving-Group strategy, in which a basic group is installed onto the anomeric leaving group of a carbohydrate donor and serves to direct the backend attack by a carbohydrate acceptor upon the leaving group activation. Homogeneous gold catalysis is employed as the activation strategy in two implementations of this strategy.[2,3]

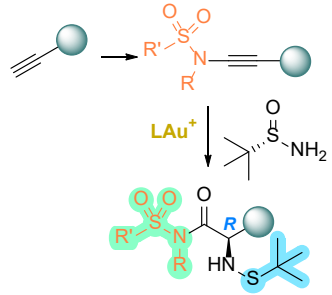
A. *Designed bifunctional ligands for asymmetric gold catalysis*



B. *The Directing-Group-on-Leaving-Group strategy toward S_N2 glycosylation*



C. *Two-step Access to UAAs*



c) Unnatural amino acids (UAA) are highly valuable chemicals. By employing gold catalysis as a key step, a two-step synthesis of UAAs is realized with good overall yields and excellent enantioselectivities. Moreover, the UAAs are properly *N*-protected and *C*-activated and can undergo amide/peptide formation directly without further manipulation (Scheme C).

References: [1], Cheng, X. P.; Zhang, L. M. *CCS Chem.* **2021**, *3*, 1989. [2], Ma, X.; Zheng, Z.; Fu, Y.; Zhu, X.; Liu, P.; Zhang, L. *J. Am. Chem. Soc.* **2021**, *143*, 11908. [3], Ma, X.; Zhang, Y.; Zhu, X.; Wei, Y.; Zhang, L. *J. Am. Chem. Soc.* **2023**, DOI: 10.1021/jacs.3c02792.

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