Curiosity Driven New Reactivity Discovery

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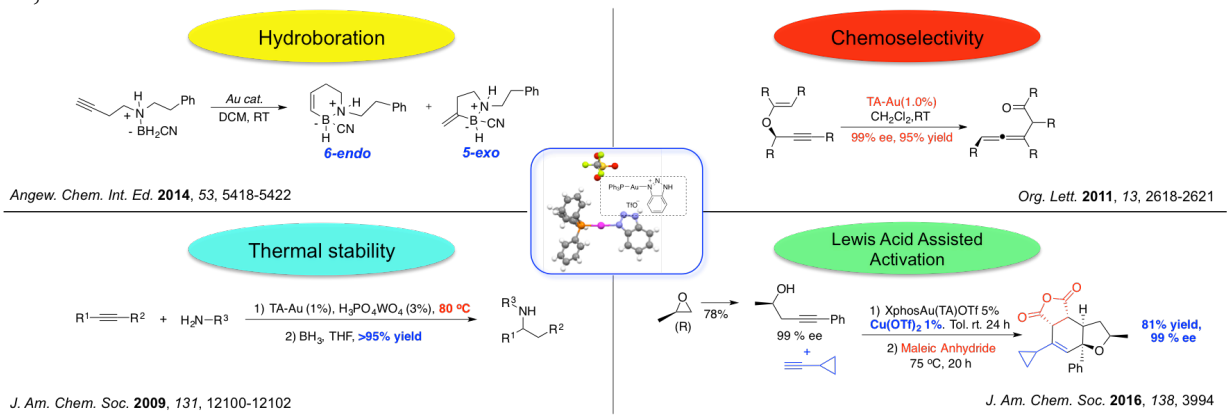
Homogeneous gold catalysis has been developed explosively during the past decades. Despite the remarkable electrophilic activation of alkynes by cationic Au(I) catalysts, such as PPh_3Au^+, one challenge is to overcome their poor stability at high temperature. However, in order to activate some less reactive substrates, such as internal alkynes, harsher reaction conditions are usually required.

As a good σ-donor and π-receptor, triazole has been applied as a ligand to improve the stability of cationic Au(I) catalysts. Taking advantage of the good stability of triazole-Au(I) complexes (TA-Au), we successfully achieved good reactivity of intermolecular hydroamination for both terminal and internal alkynes. Unlike previous reported gold catalysts, the TA-Au catalysts activate alkynes selectively over allenes. With this excellent chemoselectivity, TA-Au catalysts showed interesting reactivity in propargyl ester and vinyl ether rearrangement. This facilitates the development of otherwise challenging transformations, for instance, asymmetric synthesis of substituted allenes, Schmittel cyclization, dienal synthesis, and so on.



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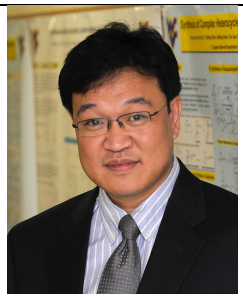

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