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Author(s)	MEJRI, EMNA
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学位論文内容の要旨

博士の専攻分野の名称 博士 (理学) 氏名 Emna Mejri

学位論文題名

Functionalization of Carbon-Carbon Multiple Bonds by High Oxidation State Chemical Species

(高酸化度化学種を利用した炭素-炭素不飽和結合の修飾)

Alkenes and alkynes are readily available feedstock materials, and it is highly desirable to functionalize these materials to value added molecules. However, the non-polar C-C multiple bonds are less reactive than other polar C-X multiple bonds, such as C=O carbonyl groups. I envisioned that a molecule with high oxidation state will have enough reactivity to realize functionalization of C-C multiple bonds. To this end, I planned two approaches: Au(III)-catalyzed functionalization of alkynes, and visible light-induced amino-difunctionalization of alkenes.

Chapter 1 describes a general introduction of this functionalization of C-C multiple bonds by high oxidation state chemical species. I classified the reactions into two categories, “functionalization of C-C multiple bonds using high oxidation state transition metal catalysts” and “Functionalization of C-C multiple bonds using high oxidation state non-metallic chemical species”, and discussed representative examples of these reactions.

Chapter 2 describes a novel approach to synthesize neutral C,N,N Au(III) complexes with *N*-(8-quinoliny)benzamide derivatives and chiral *N*-(2-(oxazolin-2-yl)phenyl)benzamide derivatives. The convenient synthetic method for amide ligands as well as an operationally simple complexation by direct C-H auration permitted changes to both the steric and electronic properties of the Au(III) complexes. The catalytic activities of the

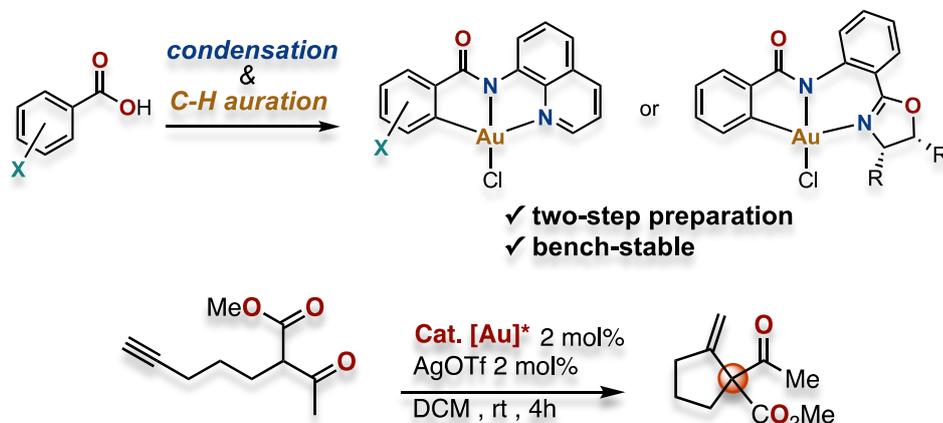


Figure 1. Direct C-H auration using *N*-(8-quinoliny)benzamide derivatives as ligands for Au(III) pincer complexes and application in Conia-ene reaction.

synthesized Au(III) complexes were tested to promote the catalytic three-component coupling of an aldehyde, an amine, and an alkyne. Conia-ene reaction, one of the functionalization of C-C multiple bonds, were also assessed with the Au(III) complexes.

Chapter 3 describes the development of an *N*-internal vicinal aminochlorination of terminal alkenes using *N*-chloro-(fluorenone imine) as both aminating and chlorinating agents. Photolysis of N-Cl bond simultaneously generates iminyl radical and chlorine radical, and subsequent reaction between an electron rich alkene and the electrophilic chlorine radical generates a carbon radical intermediate. Then, radical-radical coupling between the iminyl radical and the carbon radical produce the aminochlorination product. The reaction does not require any catalyst, and only visible- light irradiation is necessary for the reaction. The fluorene carbon skeleton of the *N*-chloroketimine was critically important to promote the reaction, and other *N*-chloroketimines were far less reactive under the same reaction conditions. This simple protocol introduces an imine moiety exclusively at the internal position and affords the corresponding free primary amines after imine hydrolysis under mild conditions. Functionalization of the amino group and transformation of the alkyl chloride moiety were possible, demonstrating the potential utility of the products.

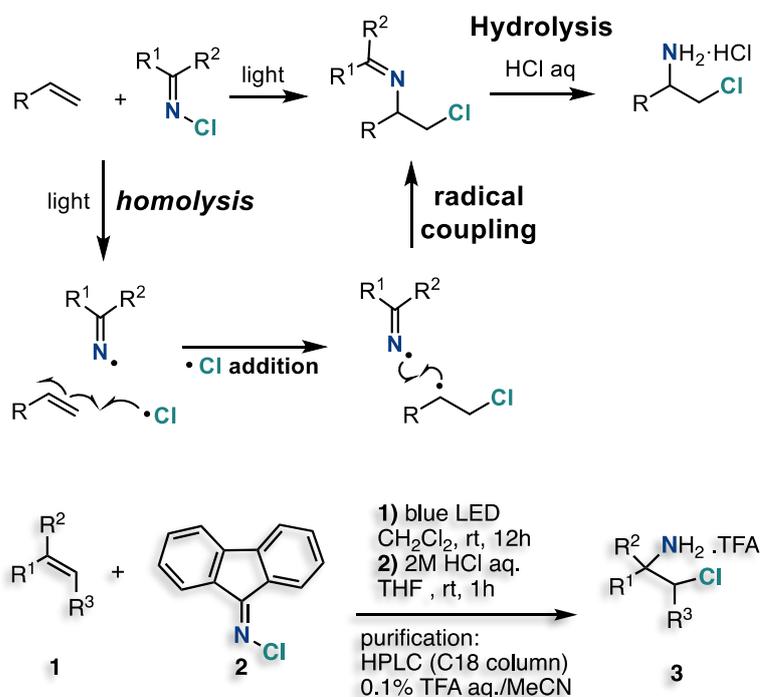


Figure 2. Photoinduced *N*-internal vicinal Aminochlorination of Alkenes and Radical pathway for accessing *N*-internal vicinal amine.