

French Polytech network form for PhD Research Grants from the China Scholarship Council

This document describes one of the PhD subjects proposed by the French Polytech network. The network is composed of engineering schools/universities. The document also provides information about the supervisor.

Supervisor information	
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Lab web site	https://icn.univ-cotedazur.fr/
Polytech name	Cliquez ou appuyez ici pour entrer du texte.
University name	UNIVERSITE COTE D'AZUR
Country	France

PhD information	
Title	Sustainable chemistry: novel methodologies towards diversity

Main topics regards to CSC list (3 topics at maximum)	Green chemistry / Sustainable development engineering and lower cost manufacturing
Required skills in science and engineering	Chemistry

Subject description (two pages maximum including biblio)

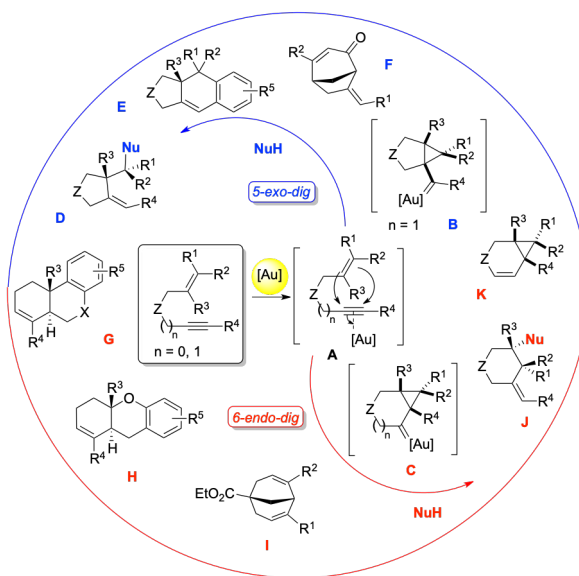
In the last decade, gold catalysis has emerged as an essential tool in modern organic synthesis.¹ Our scientific activity at Côte d'Azur University (Institut de Chimie de Nice) is currently dedicated to molecular chemistry with a special endeavor for novel methodologies towards key building blocks for bioactive molecules, having a long standing experience and interest in catalysis associated to molecular organic synthesis to reach **sustainable development**.

Our group is involved in the development of selective C-C, C-O, C-N and C-F bonds according to homogeneous as well as heterogeneous catalysis. The facets of our research imply **green processes** such as the use of non-toxic species (metals and organic catalyst) and chemistry in environmentally friendly solvents. We also contribute to novel approaches of active molecules with sensorial or bioactive properties.

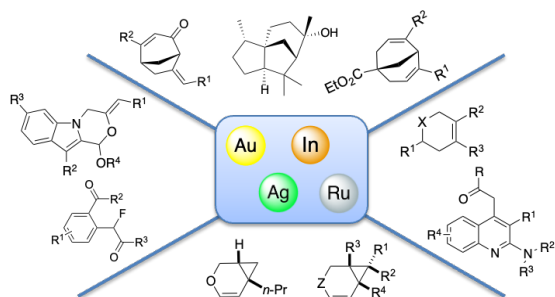
Cycloisomerization reactions catalyzed by gold and iridium complexes, introduced in 2004, have allowed the access to many original structures.² We focused our attention on cycloisomerizations and domino cycloisomerization-nucleophilic addition transformations of 1,5- and 1,6-enyne systems under gold catalysis. It has been proposed that

cycloisomerization of 1,6-enynes occurs via two different pathways in the presence of a gold catalyst: the key step in the first pathway is a 5-exo-dig reaction while a 6-endo-dig reaction can be observed in the second pathway. After the coordination of the gold-based catalyst to the triple bond of A, the species B and/or C were generated by a 5-exo and 6-endo cycloisomerization process. Depending on the different types of 1,6- and 1,5-enyne substrates, reaction conditions, and gold pre-catalysts used, a wide range of cyclic molecules can be obtained by rearrangement (molecules E, F, G, H, I), external addition processes (molecules D, J), and protodemetalation. In some cases, these molecules have been prepared by an enantioselective process in the presence of chiral gold catalysts.

Indeed, as chirality plays a central role in the world around us, and considering that about 80% of the pharmaceutical molecules produced are chiral, asymmetric synthesis is one of the emerging points of my

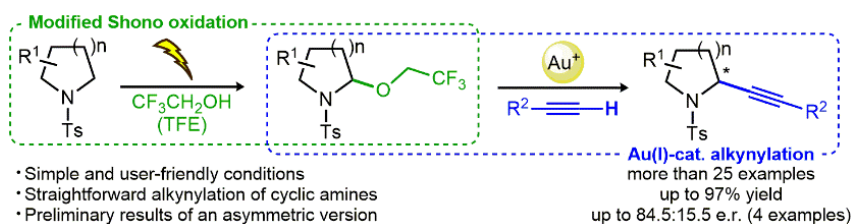


activity in gold chemistry. The emergence of an identified trend in the pharmaceutical industry to "escape from flatness", also underlines the importance of creating three-dimensional architectures, which have a much greater clinical success since the administration of enantiopure drugs brings advantages in terms of efficacy, more predictable pharmaco-kinetics and reduced toxicity. This context strongly influenced our research and led us to establish collaborations with industry, in search of new three-dimensional structures.³



We are developing solvent-free as well as water-friendly novel methodologies, allowing sustainability as well as low-cost processes.

We envisage during this PhD program to address the two main challenges and limitations of catalysis, which are the asymmetric methodologies and the use of non toxic metals. Gold and electrosynthesis could respond to this problematic. We have described recently an unprecedented gold(I)-catalyzed alkylation of N,O-acetal.⁴ Overall, this reaction operated under simple and user-friendly conditions and is amenable to a variety of substrates leading to α -alkynylated saturated *N*-heterocycles. Moreover, this process could be effectively combined to a Shono oxidation in a sequence permitting late-stage functionalization of protected cyclic amines. Preliminary results of an asymmetric version of the studied transformation were obtained leading to enantioenriched heterocycles.



Despite significant progress in its development, it is undeniable that electrosynthesis is experiencing a renaissance today.⁵ Electrochemistry is based on a series of monoelectronic exchanges at the electrode interface, one of the most popular reactions in electrosynthesis being certainly the Shono oxidation for example.⁶ This project will focus on the development of gold catalytic processes under electrochemical conditions⁷ but also will focus on photochemical reactions.⁸ It will involve the synthesis of novel gold complexes, followed by the determination of their electrochemical data. Then the PhD project will

concern the optimization of novel and original processes, under racemic and asymmetric conditions, for the easy access to heterocycles. Applications in bioactive molecules or molecules with olfactory properties will be in the center of our project.⁹

We intend to develop during this PhD program novel methodologies via original reactions. The group of Université Côte d'Azur has gained international notoriety for gold associated with original catalytic reactions and sustainable and green transformations.^{10,11}

Bibliography

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