

# International Research Center for Elements Science – Synthetic Organotransformation –

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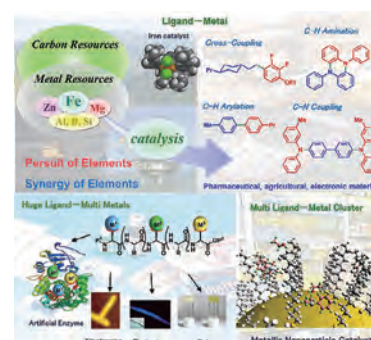
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## Scope of Research

Our research activity focuses on the development of new molecular transformations, which can contribute to better or ideal synthesis of functional molecules as well as to exploitation of new chemical (metal and carbon) resources. The present research subjects are (1) metal-catalyzed carbon–carbon and carbon–heteroatom bond forming reactions by using universal metals such as iron (2) development of smart materials based on synergistic effect of various metals on artificial peptides (3) development of smart metallic nanoparticle catalysts based on supramolecular approaches (4) understanding of reaction mechanism of these catalytic reactions with the help of quantum chemical methods and synchrotron X-ray absorption spectroscopy.



## KEYWORDS

Synthetic Organic Chemistry    Iron Catalysis    Supramolecular Catalysis    Metal Nanocluster    Woody Biomass

## Recent Selected Publications

Isozaki, K.; Ueno, R.; Ishibashi, K.; Nakano, G.; Yin, H.; Iseri, K.; Sakamoto, M.; Takaya, H.; Teranishi, T.; Nakamura, M., Gold Nanocluster Functionalized with Peptide Dendron Thiolates: Acceleration of the Photocatalytic Oxidation of an Amino Alcohol in a Supramolecular Reaction Field, *ACS Catal.*, **11**, 13180-13187 (2021).

Adak, L.; Jin, M.; Saito, S.; Kawabata, T.; Itoh, T.; Ito, S.; Sharma, A. K.; Gower, N. J.; Cogswell, P.; Geldsetzer, J.; Takaya, H.; Isozaki, K.; Nakamura, M., Iron-Catalysed Enantioselective Carbometalation of azabicycloalkenes, *Chem. Commun.*, **57**, 6975-6978 (2021).

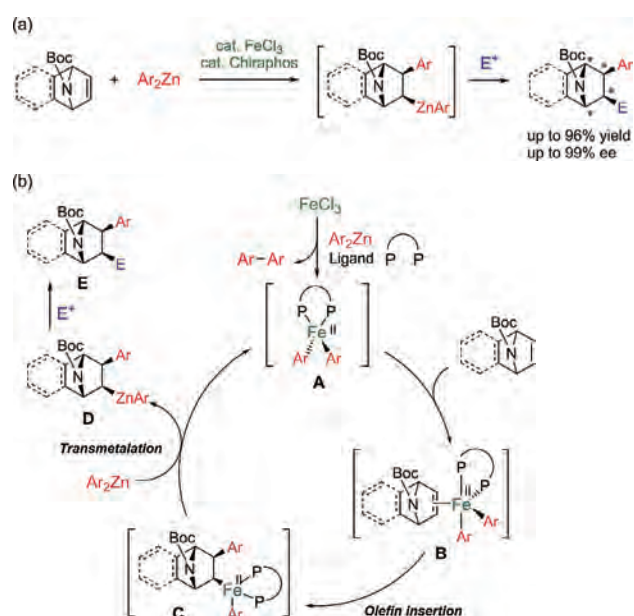
Iwamoto, T.; Okuzono, C.; Adak, L.; Jin, M.; Nakamura, M., Iron-Catalysed Enantioselective Suzuki-Miyaura Coupling of Racemic Alkyl Bromides, *Chem. Commun.*, **55**, 1128-1131 (2019).

Agata, R.; Takaya, H.; Matsuda, H.; Nakatani, N.; Takeuchi, K.; Iwamoto, T.; Hatakeyama, T.; Nakamura, M., Iron-Catalyzed Cross Coupling of Aryl Chlorides with Alkyl Grignard Reagents: Synthetic Scope and FeII/FeIV Mechanism Supported by X-Ray Absorption Spectroscopy and Density Functional Theory Calculations, *Bull. Chem. Soc. Jpn.*, **92**, 381-390 (2019).

Adak, L.; Kawamura, S.; Toma, G.; Takenaka, T.; Isozaki, K.; Takaya, H.; Orita, A.; Li, H. C.; Shing, T. K. M.; Nakamura, M., Synthesis of Aryl C-Glycosides via Iron-Catalyzed Cross Coupling of Halosugars: Stereoselective Anomeric Arylation of Glycosyl Radicals, *J. Am. Chem. Soc.*, **139**, 10693-10701 (2017).

## Iron-catalyzed Cross-Coupling Reactions

Transition-metal-catalyzed carbon-carbon and carbon-heteroatom bond forming reactions are powerful tools for the synthesis of functional molecules. Our group focuses on use of iron as a catalyst, and so far developed a variety of iron-catalyzed cross-coupling reactions, some of which can't be achieved by conventional transition-metal catalysts such as palladium. As a recent representative example, we developed the iron-catalyzed enantioselective carbometalation of azabicycloalkenes (Figure 1a), which is of significant interest due to the facile installation of four stereocenters retaining the azabicyclic skeleton. By the combination of X-ray absorption spectroscopy and DFT calculation, we proposed a catalytic cycle of diaryliron complex involving coordination of azabicyclic alkene, olefin insertion, and transmetalation steps (Figure 1b).



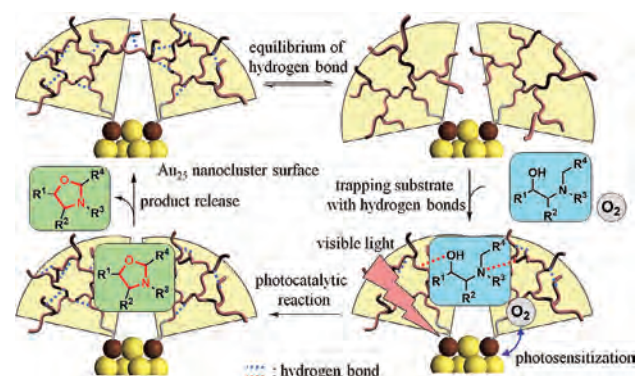
**Figure 1.** Iron-catalyzed enantioselective carbometalation of azabicycloalkenes. (a) General reaction scheme and (b) proposed catalytic cycle.

## Novel Transition-Metal Catalyst Bound with Functional Amino Acid or Peptide

This project focuses on development of smart materials based on synergistic effect of various metals on artificial peptides. Based on this concept, we have developed novel ruthenium complex bound with norvaline, which catalyze efficient and selective oxidation of several methoxybenzene analogues to quinones. Now we are trying further modification of the catalysts toward investigation of future chemical resources.

## Supramolecular Approach for Creating Enhanced Catalysis of Metallic Nanoparticles

This project focuses on the development of highly active and selective metallic nanoparticle and cluster catalysts. To achieve this purpose, four key methodologies have been developed: 1) creation of reaction field with advanced self-assembly, 2) design of selective molecular transformation with multi-points intermolecular interaction, 3) size selective synthesis of metallic nanoparticles and clusters, and 4) utilization of plasmonic resonance with light. As a recent representative example, we reported the supramolecular reaction field effect of peptide dendron thiolate ligands on  $Au_{25}$  nanocluster accelerating the photocatalytic oxidation of amino alcohols through the intermolecular interaction between peptide dendrons and substrates. The supramolecular reaction field effect was demonstrated by the 21 times faster conversion of amino alcohols to oxazolidine derivatives with peptide dendron thiolate ligands than that with conventional alkyl thiolate ligands.



**Figure 2.** Schematic illustration of photocatalytic oxidation of amino alcohol accelerated by supramolecular reaction field constructed of peptide dendron thiolates on  $Au_{25}$  nanocluster.