

International Research Center for Elements Science – Synthetic Organotransformation –

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*Project for Iron-Catalyzed
Selective Organotransformation

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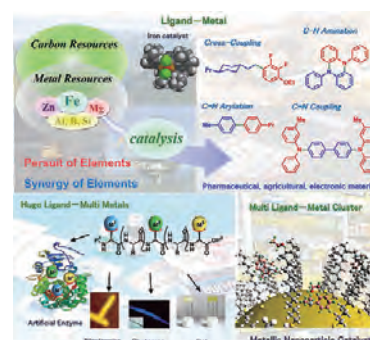
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Scope of Research

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

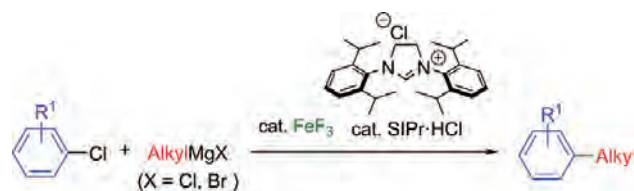
Selective Organic Reaction Iron Catalyst Metalated Peptide Metallic Nanoparticle Catalyst Solution-Phase XAS Analysis

Selected Publications

- Iwamoto, T.; Hosokawa, A.; Nakamura, M., Endergonic Addition of N-methylamines to Aromatic Ketones Driven by Photochemical Offset of the Entropic Cost, *Chem. Commun.*, **55**, 11683-11686 (2019).
- Aoki, Y.; O'Brien, H. M.; Kawasaki, H.; Takaya, H.; Nakamura, M., Ligand-Free Iron-Catalyzed C–F Amination of Diarylamines: A One-Pot Regioselective Synthesis of Diaryl Dihydrophenazines, *Org. Lett.*, **21**, 461-464 (2019).
- Agata, R.; Kawamura, S.; Isozaki, K.; Nakamura, M., Iron-catalyzed Alkyl–Alkyl Negishi Coupling of Organoaluminum Reagents, *Chem. Lett.*, **48**, 238-241 (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 Fe^{II}/Fe^{IV} Mechanism Supported by X-ray Absorption Spectroscopy and Density Functional Theory Calculations, *Bull. Chem. Soc. Jpn.*, **92**, 381-390 (2019).
- Iwamoto, T.; Okuzono, C.; Adak, L.; Jin, M.; Nakamura, M., Iron-Catalyzed Enantioselective Suzuki–Miyaura Coupling of Racemic Alkyl Bromides, *Chem. Commun.*, **55**, 1128-1131 (2019).

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 recent representative examples, we developed the iron-catalyzed cross coupling of aryl chlorides with alkyl Grignard reagents (Figure 1a). By using X-ray absorption spectrometry and DFT calculations, we revealed that the reaction proceeds via the formation of Fe-Mg dinuclear intermediate (Figure 1b).



ArCl: including deactivated aryl chlorides
 AlkylMgX: with or without β -hydrogens

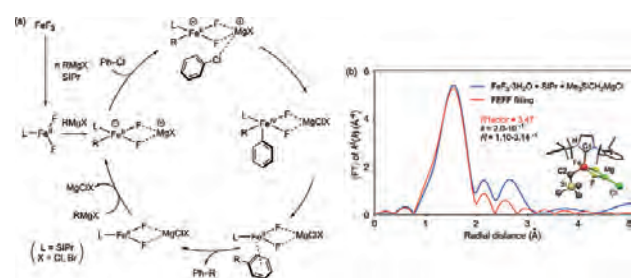


Figure 1. Iron-catalyzed cross coupling of aryl chlorides with alkyl Grignard reagents. (a) Proposed mechanism and (b) EXAFS fitting of Fe-Mg dinuclear intermediate.

Moreover, we developed iron-catalyzed C-F amination reaction of various diarylamines for the one-pot diastereoselective synthesis of diaryl dihydrophenazines, which are of significant research interest due to the potent applicability as organic luminescent materials and photoredox catalysts (Figure 2).

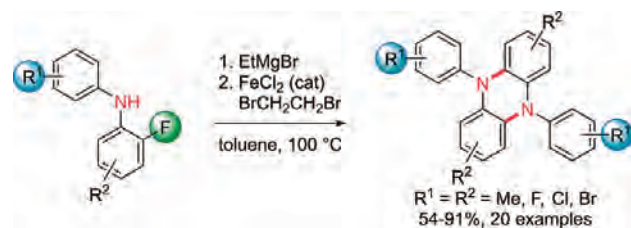


Figure 2. One-pot regioselective synthesis of diaryl dihydrophenazines by iron-catalyzed C-F amination of diarylamines.

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.

