

# International Research Center for Elements Science – Synthetic Organotransformation –

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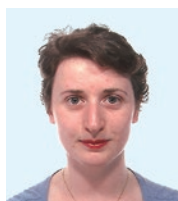
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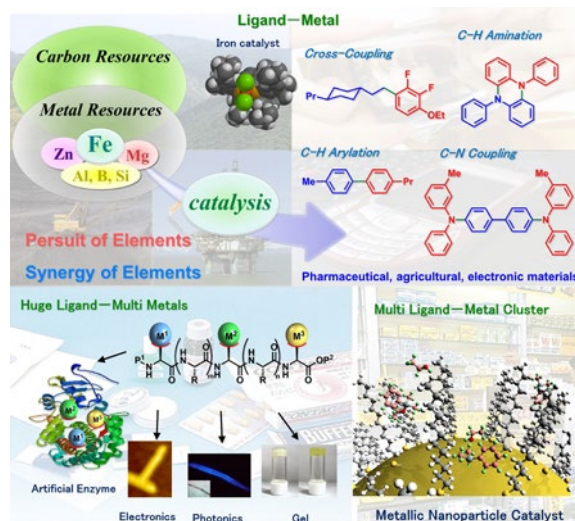
O'BRIEN, Harry University of Bristol, UK, 21 June–29 August

## 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 Catalyst	Metallic Nanoparticle Catalyst
Solution-Phase XAS Analysis	

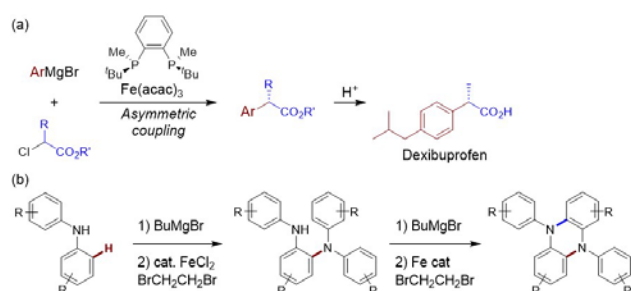


## Selected Publications

Yoshida, R.; Isozaki, K.; Yokoi, T.; Yasuda, N.; Sadakane, K.; Iwamoto, T.; Takaya, H.; Nakamura, M., ONO-pincer Ruthenium Complex-bound Norvaline for Efficient Catalytic Oxidation of Methoxybenzenes with Hydrogen Peroxide, *Org. Biomol. Chem.*, **14**, 7468-7479 (2016).  
Yamaguchi, A.; Isozaki, K.; Nakamura, M.; Takaya, H.; Watanabe, T., Discovery of 12-mer Peptides that Bind to Wood Lignin, *Scientific Reports*, **6**, 21833 (2016).  
Isozaki, K.; Yokoi, T.; Yoshida, R.; Ogata, K.; Hashizume, D.; Yasuda, N.; Sadakane, K.; Takaya, H.; Nakamura, M., Synthesis and Functions of ONO-Pincer Ruthenium-Complex-Bound Norvalines, *Chemistry an Asian Journal*, **11**, 1076-1091 (2016).

## Iron-Catalyzed Cross-Coupling Reactions

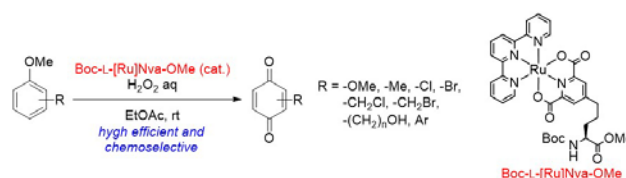
Transition-metal-catalyzed carbon-carbon and carbon-heteroatom bond forming reactions are powerful tools for the synthesis of functional molecules. Our group focuses on use of iron as a catalyst, and so far developed a variety of iron-catalyzed cross-coupling reactions, some of which can't be achieved by conventional transition-metal catalysts such as palladium. For example, we recently developed iron-catalyzed enantioselective cross-coupling reaction of  $\alpha$ -chloroesters with aryl Grignard reagents, which is the first iron-catalyzed enantioselective coupling reaction. In addition, we found a novel intermolecular and intramolecular C-H amination of diarylamines to provide dihydrophenazine derivatives. Importantly, these reactions enable facile access to several important pharmaceutical and functional molecules. Furthermore we clarified the mechanisms of these reactions by using synchrotron X-ray absorption spectroscopy combined with theoretical calculations.



**Figure 1.** (a) Iron-catalyzed enantioselective cross-coupling reaction of  $\alpha$ -chloroesters with aryl Grignard reagents, and (b) intermolecular and intramolecular C-H 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, novel ruthenium catalysts bound with norvaline have been developed, achieving efficient and selective oxidation of several methoxy-benzene analogues to quinones. In this reaction, norvaline acts as a mediator inducing micelle-like aggregates, which is the origin of high efficiency and selectivity. Now we are trying further modification of the catalysts to oxidize much challenging aromatic substrate toward investigation of future chemical resources.



**Figure 2.** Efficient catalytic oxidation of methoxybenzenes with ruthenium catalyst bound with norvaline.

## 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.

