

Development of Novel Catalytic Organic Transformations

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Education

1984 B.S. Hokkaido University
1990 Ph.D. Hokkaido University

Professional Employment

1988 JSPS Research Fellow
1988 Research Associate, Hokkaido University
1990 Assistant Professor, Hokkaido University
1994 Research Associate, Columbia University
1995 Lecturer, Kyoto University
1997 Professor, Nagoya City University
2000 Professor, Institute for Molecular Science
Professor, The Graduate University for Advanced Studies
2007 Research team leader, RIKEN
2014 Distinguished Professor, Three George University
2003 Research Project Leader, JST CREST Project (–2008)
2008 Research Project Leader, NEDO Project (–2012)
2011 Deputy Research Project Leader, JST CREST (–2016)
2014 Research Project Leader, JST ACCEL Project (–2019)

Awards

1991 Eisai Award, Synthetic Organic Chemistry
1998 The Pharmaceutical Society of Japan Award for Young Scientist
2007 The Chemical Society of Japan (CSJ) Award for Creative Work
2007 MEXT Ministerial Award for Green Sustainable Chemistry
2010 Inoue Prize for Science
2014 The Commendation for Science and Technology by the Minister of MEXT (Research Category)

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Keywords

Transition Metal Catalysis, Green Chemistry, Photocatalysis

Our research interests lie in the development of catalytic reaction systems toward ideal (highly efficient, selective, green, safe, simple, etc.) organic transformations. In particular, development of a wide variety of the heterogeneous aquacatalytic systems, continuous flow catalytic systems, and super active catalysts working at ppm-ppb loading levels, have been achieved. Furthermore, we have recently been developing a novel photocatalysis where, for example, the carbonyl groups underwent two successive one-electron reduction to generate carbinol anion species achieving electrophilic carbonyl substitution.

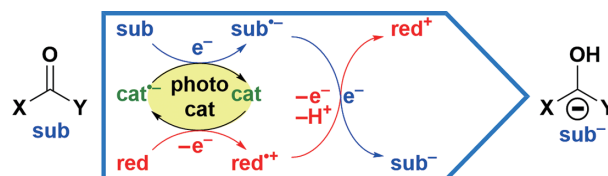


Figure 1. The outlined concept of photocatalytic reductive activation of substrate through two successive one-electron transfer process (e.g. carbonyl reduction to carbinol anion).

Selected Publications

- S. Okumura and Y. Uozumi, "Photocatalytic Carbinol Cation/Anion Umpolung: Direct Addition of Aromatic Aldehydes and Ketones to Carbon Dioxide," *Org. Lett.* **23**, 7194–7198 (2021).
- G. Hamasaka, D. Roy, A. Tazawa and Y. Uozumi, "Arylation of Terminal Alkynes by Aryl Iodides Catalyzed by a Parts-per-Million Loading of Palladium Acetate," *ACS Catal.* **9**, 11640–11646 (2019).
- R. David and Y. Uozumi, "Recent Advances in Palladium-Catalyzed Cross-Coupling Reactions at ppm-ppb Molecular Catalyst Loadings (review)," *Adv. Synth. Catal.* **360**, 602–625 (2018).
- T. Osako, K. Torii, S. Hirata and Y. Uozumi, "Chemoselective Continuous-Flow Hydrogenation of Aldehydes Catalyzed by Platinum Nanoparticles Dispersed in an Amphiphilic Resin," *ACS Catal.* **7**, 7371–7377 (2017).
- Y. M. A. Yamada, S. M. Sarkar and Y. Uozumi, "Self-Assembled Poly(imidazole-palladium): Highly Active, Reusable Catalyst at Parts per Million to Parts per Billion Levels," *J. Am. Chem. Soc.* **134**, 3190–3198 (2012).
- G. Hamasaka, T. Muto and Y. Uozumi, "Molecular-Architecture-Based Administration of Catalysis in Water: Self-Assembly of an Amphiphilic Palladium Pincer Complex," *Angew. Chem., Int. Ed.* **50**, 4876–4878 (2011).
- Y. Uozumi, Y. Matsuura, T. Arakawa and Y. M. A. Yamada, "Asymmetric Suzuki-Miyaura Coupling in Water with a Chiral Palladium Catalyst Supported on Amphiphilic Resin," *Angew. Chem., Int. Ed.* **48**, 2708–2710 (2009).
- Y. M. A. Yamada, T. Arakawa, H. Hocke and Y. Uozumi, "A Nanoplatinum Catalyst for Aerobic Oxidation of Alcohols in Water," *Angew. Chem., Int. Ed.* **46**, 704–706 (2007).

1. Umposed Carbonyl Chemistry

Carbonyl chemistry is dominated by nucleophilic additions in which a carbonyl compound (an aldehyde or ketone) serves as an electrophilic carbinol cation to form a secondary or tertiary alcohol product [Figure 2(a)]. In contrast to the well-investigated conventional chemistry of carbonyl compounds, their umposed nucleophilic reactivity has been less-well explored [Figure 2(b)]. Symmetrization of the carbonyl reactivity, which would permit carbonyl compounds to react as nucleophilic carbinol anions (i.e., carbinol cation/anion umpolung), could open a new avenue in synthetic organic chemistry.

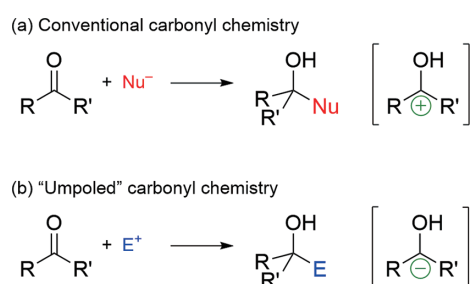


Figure 2. Carbonyl Reactivity: Conventional vs. Umposed.

In previous report, we have developed a novel photocatalytic carboxylation of aromatic aldehydes and ketones to give mandelic acid derivatives [Figure 3(a)]. In this reaction, nucleophilic carbinol anion species were generated under visible light that subsequently reacted with carbon dioxide. Here, in 2023, we developed photocatalytic cross-pinacol coupling between two different carbonyl compounds to afford the unsymmetric 1,2-diols, where the resulting carbinol anions reacted with second carbonyl compounds [Figure 3(b)]. We also achieved the photocatalytic 1,4-addition of carbonyl compounds with electron-deficient olefins to give the corresponding γ -substituted alcohols [Figure 3(c)].

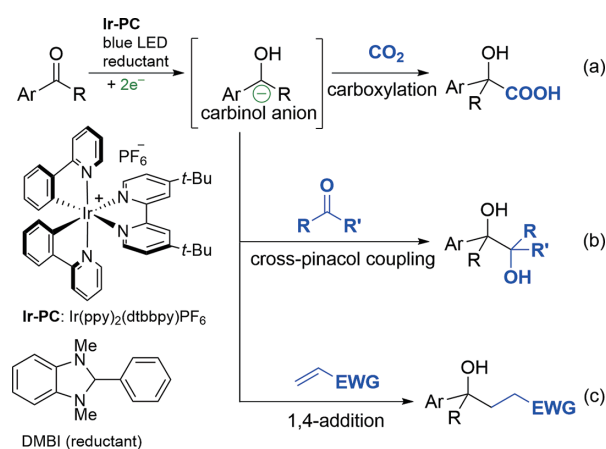


Figure 3. Photocatalytic Electrophilic Substitution of Carbonyls: (a) carboxylation, (b) cross-pinacol coupling, (c) 1,4-addition.

1-1. Cross-Pinacol Coupling¹⁾

We have developed the first photocatalytic cross-pinacol coupling between two different carbonyl compounds, promoted by a CO₂ additive. The cross-pinacol coupling took place with a various combination of two aldehydes, two ketones, or an aldehyde and a ketone in the presence of an iridium photocatalyst and 1,3-dimethyl-2-phenyl-2,3-dihydro-1*H*-benzimidazole (DMBI) as a reductant under visible-light irradiation to afford the corresponding unsymmetric vicinal 1,2-diols in up to 91% yield [Figure 3(b)]. In the coupling reaction, an umposed carbinol anions are generated in situ through successive one-electron reduction and the resulting anions attack the more-electron-rich carbonyl compounds serving as electrophiles. CV and DFT calculations revealed that the CO₂ additive plays a key role in the second reduction to suppress undesired dimerization.

1-2. Conjugate Addition of Carbonyls to Electron-Deficient Olefins²⁾

A 1,4-addition reaction of aromatic aldehydes and ketones to electron-deficient olefins was achieved under photocatalytic conditions [Figure 3(c)]. In the reaction, an umposed carbinol anion generated in situ through two successive one-electron reductions of the carbonyl compound reacted nucleophilically with the electron-deficient olefin. Various electron-deficient aromatic aldehydes and ketones successfully underwent the reaction to afford the corresponding γ -functionalized alcohols.

2. Transition Metal Catalysis Forming C–H, C–C, C–N, C–S Bonds^{3,4)}

We have developed transition metal-catalyzed C–H, C–C, C–N, C–S bond forming reactions. A phenylboronic ester-activated aryl iodide-selective Buchwald–Hartwig-type C–N bond forming reaction using Ni(acac)₂ catalyst was developed. This reaction does not proceed in the absence of phenylboronic ester.³⁾ C–S bond formation was achieved in the reaction of 2,2'-dithiobis(benzenamine)s with various aldehydes in the presence of CuOAc catalyst under air without any additives to afford the corresponding benzothiazoles.⁴⁾ We recently developed in-water C–H bond forming catalysis with PS-PEG supported palladium nanoparticles using tetrahydroxydiboron (B₂(OH)₄) as a water-compatible reducing agent.

References

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- 3) R. H. Dhital, A. Sen, H. Hu, R. Ishii, T. Sato, Y. Yashiroda, H. Kimura, C. Boone, M. Yoshida, Y. Futamura, H. Hirano, H. Osada, D. Hashizume, Y. Uozumi and Y. M. A. Yamada, *ACS Omega* **7**, 24184–24189 (2022). DOI: 10.1021/acsomega.2c01092
- 4) K. Minami, M. Minakawa and Y. Uozumi, *Asian J. Org. Chem.* **11**, e202200211 (2022). DOI: 10.1002/ajoc.202200211