4th GSC Encouragement Award

Development of New Hypervalent Iodine Catalytic Method in Oxidative Coupling Reactions

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2015.7.7

Oxidative coupling that directly uses carbon-hydrogen group for a new bond-forming event is, in theory, an ideal strategy in organic synthesis to reduce the number of synthetic steps and byproduct generation. Despite their ideal aspect in green chemistry, the early oxidative coupling studies employing heavy metal oxidants usually suffered from undesired formation of homodimers and uncontrolled over-oxidations.

Recently, our research group reported for the first time a series of the metal-free oxidative cross-coupling successes using hypevalent iodine reagent for reacting various electron-rich aromatic compounds (Ar-H). The methods can suppress the problems of homocoupling and over-oxidization, providing desired cross-coupling products in high selectivities.

Notably, we have now achieved further extension of the reaction system to the catalytic and recyclable versions by utilizing designer organo-iodine catalysts that can in situ generate highly reactive hypervalent iodine species under oxidative conditions. This is the first report of the oxidative cross-coupling between two aromatic compounds in the intermolecular manner under the organocatalysis.

Due to their low toxicities and ready availabilities, hypervalent iodine reagents are promising alternative to many metal oxidants for developing greener synthesis, especially for manufacturing valuable biaryl compounds in fine chemicals. As iodine is one of the few elements in which Japan is self-sufficient and most iodine derivatives show lower long-term toxicities compared with metal elements, the new use of iodine-based chemicals has a significant benefit for Japan with its poor endowment of natural resources.