【Grant-in-Aid for Scientific Research (S)】

Science and Engineering (Chemistry)

Title of Project : Development of Molecular Transformations by Means of Light and Metals Directing towards Straightforward Synthesis

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Research Area : Organic Synthesis
Keyword : Molecular Transformation, Light, Metal Catalyst

【Purpose and Background of the Research】

It is highly demanded in the field of synthetic chemistry to offer better synthetic ways to chemical products like medicines and functional materials. One of the challenging issues the current chemistry faces is to innovate the conventional synthetic pathways requiring multi-step functional group manipulations, in order to make the synthesis environmentally benign. This research project aims at the development of innovative molecular transformations directing towards straightforward synthesis, in which readily available substances are converted into the desired products with minimum reaction steps, isolation procedures as well as wastes.

【Research Methods】

Transformations of readily available substances will be explored by exploiting light and metals. Particular emphases are placed on (1) direct transformations of non-polar σ-bonds like C–C and C–H bonds, and (2) one-pot multiple functionalization of alkynes.

(1) Direct transformations of non-polar σ-bonds

Nonpolar σ-bonds like C–C and C–H bonds are omnipresent in organic molecules. They are thermodynamically stable and kinetically inert in general. Nonetheless, it would provide efficient synthetic ways starting from readily available substances if such non-polar σ-bonds are site-selectively cleaved and directly utilized for construction and/or functionalization of organic skeletons. This project explores the new reactivities of C–C and C–H bonds induced by light and metals. Endergonic photoreactions producing energetic compounds and transition metal-catalyzed reactions of the energetic compounds will be studied. Reactions involving both in a cooperative manner will be also pursued.

(2) One-pot multiple functionalization of alkynes

A wide variety of alkyne derivatives are available from commercial sources and are prepared by the well-established methods. This project focuses on the development of one-pot methods to introduce multiple functional groups and/or C–C bonds onto alkynes. For example, the new reactivities of 1,2,3-triazoles prepared from alkynes will be investigated by means of transition metal catalysts and sequential procedures starting from alkynes will be developed on this basis.

【Expected Research Achievements and Scientific Significance】

Conventional organic synthesis has mainly exploited the reactivities of reactive polar bonds like carbon–metal and carbon–halogen bonds. Consequently, pre-installation of such reactive functional groups are often required for the formation of the desired bond, making the synthetic pathway multi-step and wasteful. On the other hand, this project will develop straightforward synthesis starting from readily available substances. It will streamline the synthetic pathway to contribute to speed-up of development of new chemical products and reduction of environmental load.

【Publications Relevant to the Project】

・ Naoki Ishida, Shota Sawano, Masahiro Murakami, Stereospecific ring expansion from orthocyclophanes with central chirality to metacyclophanes with planar chirality, *Nature Commun.* **2014**, *5*, 3111.
・ Tomoya Miura, Takayuki Nakamuro, Chia-Jung Liang, Masahiro Murakami, Synthesis of *trans*-Cycloalkenes via Enantioselective Cyclopropanation and Skeletal Rearrangement, *J. Am. Chem. Soc.* **2014**, *136*, 15905.

【Term of Project】 FY2015-2019

【Budget Allocation】 154,600 Thousand Yen

【Homepage Address and Other Contact Information】

http://www.sbchem.kyoto-u.ac.jp/murakami-lab/index.html