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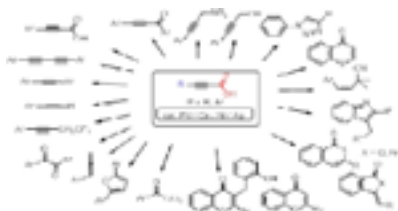
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Decarboxylative coupling reactions of propiolic acid derivatives

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Transition-metal-catalyzed decarboxylative coupling of alkynoic acids have been studied by our lab for a decade. Since our first report that palladium-catalyzed reactions of aryl halides and propiolic acids afforded the symmetrical and unsymmetrical diaryl alkynes in good yields, a variety of related methodology have been reported by many research groups including us. The development of simple and convenient method for the preparation of aryl alkynoic acids made it easy accessible tool for the introduction of alkynyl group in organic synthesis. Although the decarboxylative coupling of alkynoic acids and Sonogashira type coupling of terminal alkyne showed similar reactivity in most cases, the unique reactivity of alkynoic acid has been found in the multicomponent reactions including metal-free reactions. Especially, arylpropiolic acids readily prepared from the coupling reaction of aryl halides and propiolic acid without column chromatography procedure. In this presentation, we would like to discuss some of our recent research progress towards the decarboxylative coupling reactions of alkynoic acids. Homoisoflavonoid and flavone were selectively obtained from the reaction with salicylaldehydes and arylpropiolic acid in the presence of ruthenium catalyst and base. When the reaction was conducted in DMSO, a variety of homoisoflavonoids were exclusively obtained in good yields, while, several flavones were dominantly formed under t-AmOH solvent. 2,2,2-Trichloro-acetophenone derivatives were synthesized via decarboxylative trichlorination from arylpropiolic acids and trichloroisocyanuric acid (TCCA). The reaction was conducted in the presence of H₂O at room temperature, and afforded the desired products in good yields. The reaction showed good functional group tolerance towards halides, cyano, nitro, ketone, ester and aldehyde groups. In addition, 2,2,2-trichloroacetophenone derivatives were readily transformed into esters, amides, and hydrazides.



Recent publications

1. Jayaraman A, Cho E, Irudayanathan F M and Lee S (2018) Metal-free decarboxylative trichlorination of alkynyl carboxylic acids: synthesis of trichloromethylketones *Adv. Synth. & Catal.* 360:130-141.
2. Irudayanathan F M and Lee S (2017) Selective synthesis of (E)- and (Z)-allyl nitriles via decarboxylative reactions of alkynyl carboxylic acids with azobis(alkylcarbonitriles). *Org. Lett.* 19:2318-2321.
3. Park K and Lee S (2013) Transition metal-catalyzed decarboxylative coupling reactions of alkynyl carboxylic acids. *RSC Adv.* 3:14165-14182.
4. Moon J, Jeon M, Nam H, Ju J and Moon (2008) One-pot synthesis of diarylalkynes using palladium-catalyzed sonogashira reaction and decarboxylative coupling of sp and sp² carbon. *Org. Lett.* 10:945-9449.

Biography

Sunwoo Lee completed his BS in Chemistry Education at Pusan National University (1987-94, including military service), he obtained his MS (1996) and PhD (1999) in Department of Chemistry at POSTECH under the supervision of Professor Jaiwook Park. He did his Post-doctoral studies in the Department of Chemistry at Yale University (1999-2001) with Professor John F Hartwig. He worked at LG Chem as a Senior Researcher (2001-2004). In 2004, he began his current position as a Professor in the Department of Chemistry at Chonnam National University. He had been in the Hartwig group at University of California, Berkeley as a Visiting Scholar (2014-2015). The main focus of his work is the development of catalytic transformations and high-throughput screening methods and their applications.

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