

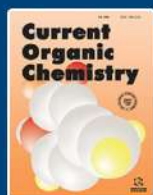


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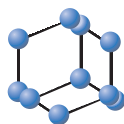


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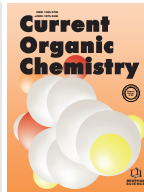


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Synthesis of Aryl/Heteroaryl Selenides Using Transition Metals Catalyzed Cross Coupling and C–H Activation



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Abstract: Aryl and heteroaryl selenides are an important class of organic compounds and their synthesis has been widely studied all over the world in the last two decades. Transition metals catalyzed cross-coupling and directed C–H activation in unactivated arenes in the presence of diselenides/aryl selenols are found to be the most important tools for their synthesis. In recent years different transition metal catalysts were found to be effective to perform C–Se cross-coupling in both aryl and heteroaryl rings. The present review article covers all the recent advances made in the last ten years in the field of the synthesis of aryl and heteroaryl selenides through homogeneous and heterogeneous transition metals catalyzed cross-coupling reactions and directed selenylation *via* C–H bond activations.



Debasish Kundu

Keywords: Cross-coupling, C-H activation, transition metal, selenides, homogeneous and heterogeneous catalysis, organic compounds.

1. INTRODUCTION

In the last two decades, researchers have witnessed the different transition metals catalyzed cross-coupling reactions as powerful organic synthetic methods for the generation of several biologically important molecules and natural products based on Carbon-heteroatom bonds. The diaryl diselenide compounds are attracting considerable attention from organic chemists due to their potential biological activities (*e.g.*, anticancer, antitumor, antiviral, antimicrobial, antioxidant and antithyroid) [1-9]. They also exhibit tremendous catalytic activity in modern organic synthesis [10]. Diselenides, which mostly serve as a valuable source of organoselenium reagents, allows the inclusion of selenium moieties into the aromatic rings of organic molecules for the successful implementation in the generation of C–Se bonds [11]. A number of sustainable, new, and greener methodologies have been reported in the literature to prepare unsymmetrical diaryl selenides. Although C–Se cross-coupling reactions under conventional pathways suffer from several drawbacks such as the use of expensive and toxic solvents, longer reaction times, stoichiometric or greater quantity of metallic reagents, and high reaction temperature [12-19]. Selenation *via* C–H activation has been introduced as a sustainable alternative for this purpose.

Due to the much lower toxicity, availability, and acceptable stability of selenium, diselenides have received significant attention because they have been postulated as one of the most attractive sources of selenium as well as important selenylating agents in the cross-coupling reactions with pre-functionalized reactants like haloarenes, aryl boronic acids, diazonium salts and aryl amines to

synthesize unsymmetrical selenides [20-26]. The preparation of diaryl selenides from organoboron compounds is traditionally less explored compared to aryl halides. Based on the earlier reports of an ever-increasing number of groups, the researchers were intrigued by the chemistry of Se–Se bond in diselenides because it can generate nucleophiles (RS^-), electrophiles (RS^+) or radicals (RS^\cdot) which underwent various nucleophilic, electrophilic as well as photochemical transformations.

Cross-coupling reactions *via* transition metals catalysis have emerged as an interesting and appropriate technique for the synthesis of organoselenides [27-34]. Synthesis of highly potent diaryl selenides through such a concise and convenient catalytic route has motivated the area of research at its vital stage of development. Over the past few years, significant developments in C–Se cross-coupling chemistry have been successfully achieved by employing transition metals like copper, silver, iron, nickel, palladium, indium, *etc.*, but catalytic systems consisting of some transition metals are not highly desirable and anticipated due to their tremendous cost, toxicity, and low turnover number. Although, the metal-assisted transformations are highly efficient, regio- and stereoselective leading to a decrease in the production of waste, the costly and toxic heavy metal complexes go through difficulties in the separation of soluble metal catalysts from the reaction centre. A number of specialized works toward the metal-free synthesis of diaryl selenides are available in the literature [35-39], but our current research focuses on the applicability of transition metals to catalyze their synthesis.

In recent times, selenylation reactions of activated $C(sp^2)-H$ bonds by transition metals catalysis have gained growing importance regarding photochemical transformations in modern organic chemistry. Transition metals-assisted aromatic C–H oxygenation [40-42], amination [43-45], and halogenation [46-48] reactions have been successfully achieved by researchers in synthetic

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