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Current Organic Synthesis, XXXX, XX, 1-32

Transition Metals Catalyzed Direct C-H Chalcogentaion of Arenes and Heteroarenes

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DOI: 10.2174/1570179420666230428122124 **Abstract:** Transition metals catalyzed C-H bond activation reactions have appeared as an emerging field to introduce different functional groups in the inactivated saturated and unsaturated C-H bonds. C-S and C-Se bond constructions in aromatic scaffolds are very interesting due to the important applications of organochalcogen reagents in pharmaceutical chemistry and the material world. The introduction of sulphur or selenium moiety to an inert C-H functionality of an arene under transition metal catalysis has become one of the prime challenges and targets in recent years. In this perspective, various transition metals such as Cu, Ni, Co, Pd, Rh, Ru *etc.* have been extensively studied. Aromatic arenes owning bearing suitable directing groups appeared as the most promising coupling partners to selectively synthesize differently substituted aryl sulfones and aryl sulfides/selenides. The synthetic strategies were highly convenient owing to the regioselectivity of products, broad substrate scope, mild reaction conditions and excellent functional group tolerance. The current review article comprehensively summarizes the extent of C-S/Se bond formation *via* transition metal-catalyzed C-H bond activation with the assistance of directing groups to govern the site selectivity.

Keywords: Transition metal catalysis, sulfenylation, selenylation, C-H activation, diaryl diselenides, directing groups.

1. INTRODUCTION

Transition metals promoted catalytic reactions have reached a paramount level of sophistication and have been enriched by the incorporation of chalcogen atoms into activated C-H bond functionalities, emerging as outstanding strategies in modern organic synthesis.[1-8] In addition to the significant advancements in organometallic chemistry, notable innovations have been achieved in the area of C-Z (Z = S. Se) bond constructions as these structural motifs demand massive applications in pharmaceutical chemistry, [9, 10] material science[11, 12] and fluorescence spectroscopy [13, 14]. Due to prevalent structural fragments, acceptable stability and excellent functionality, the C-H bond in the aromatic ring has been extensively analysed in organic chemistry [15-17]. In the past few years, researchers have successfully employed transition metal catalysis to achieve C(sp2)-H bond functionalization reactions such as C-H halogenation[18, 19] oxygenation [20, 21] acylation [22] and alkylation [23, 24]. Synthesis of aryl-substituted chalcogenides via traditional methods involves harsh reaction conditions, poor functional group tolerance, elevated reaction temperature and affording minimum yields. However, transi-

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tion metal-catalyzed direct transformation of an unreactive C(sp2)-H functionality to a C-chalcogen framework has emerged as a powerful tool to realize enormous promising conversions as these methodologies require mild reaction conditions, step and atom economy, sustainable and environmentally benign green protocols.[25-27] The ease of selective cleavage of a particular C-H bond of arenes is overwhelmed by the presence of directing groups and assistance of coordinating ligands which directs a transition metal atom into the close proximity of a specific C-H centre.[28-30] Besides, the strong coordinating nature of the chalcogen atoms (S and Se) has enabled them to get incorporated into an inert C-H motif. The excellent regioselectivity, siteselectivity, wider substrate scope and outstanding functional group compatibility of the arenes undergoing C-H bond functionalization reactions under standard protocols have been at the forefront of our current investigations.

In the past few years, activated C-H bond functionalization reactions of arenes under metal- and solvent-free protocols have extensively been employed to highlight the significant contribution to the sustainable development of green chemistry [31-34]. It is worth mentioning that the advancement of novel and practical catalytic methods involving C-S/Se bond constructions through transition metal-promoted direct C-H activation is still less explored in comparison to C-C, C-N and C-O bond functionalization reactions. In con-

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Progress in the Research of Naturally Occurring Biflavonoids: A Look Through

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Abstract: Biflavonoids are dimers of monomeric flavonoids and have reported to exhibit several pharmacological activities, like anti-microbial, anti-inflammatory, antienzymatic, antioxidant, anticancer, anti-Perkinson, anti-ulcer, anti-hypertensive, antidiabetic, anti-depressant and anti-protozoan. Extensive research work on this important segment of natural compounds is in progress. In this chapter, we report the progress of research on natural biflavonoids from the period of 2005 to early 2020; it includes enlisting newly isolated bioflavonoids from plant sources, biological activities exhibited by the known as well as new compounds and synthetic strategies developed for synthesizing such compounds. In this time period, a total of 247 biflavonoids have been reported either in terms of their first-time appearance or evaluation of their biological activities or both. Out of the reported 247 biflavonoids, 176 have been reported as new compounds from natural plant sources. They have been reported to exhibit a wide range of biological and pharmacological properties, including antimicrobial and antiviral, cytotoxic and anti-cancer, anti-diabetic, anti-anoxic, antioxidant, NO-inhibitory activity, anti-enzymatic, anti-HIV, anti thrombin, antiallergic, cytoprotective, neuroprotective and anti-inflammatory, which have been discussed in a comprehensive manner. Different synthetic strategies that have been reported for the synthesis of structurally different biflavonoids are also included. This chapter cites 177 references.

Anti-cancer, Anti-diabetic, Anti-enzymatic, Keywords: Anti-microbial, Antioxidant, Antiviral, Biflavonoids, Biological activities, Cytotoxic, Natural distribution, Nomenclature, Occurrence, Structural aspects, Synthesis.

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