"Development of Visible-Light Mediated Photoredox Catalysis and other Sustainable Methods for the Synthesis of Medicinally-Relevant Scaffolds"

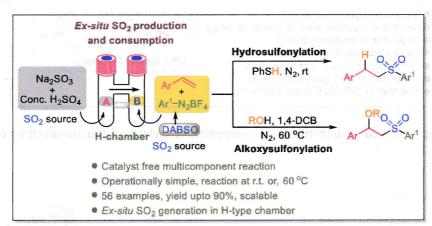
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In recent years, photoredox catalysis has emerged as a powerful tool in organic synthesis for the activation of small molecules. For drug discovery and development, selective and direct functionalization of drug-like moieties is essential where photoredox chemistry has found various applications to install crucial functionalities. The major objectives of this research work is the study of visible light mediated photoredox catalyzed reactions as well as other sustainable methods to construct challenging carbon-carbon or carbon-heteroatom bonds to result into biologically and medicinally important molecules.

A biomimetic approach for highly selective monodemethylation of N,N-dimethyl anilines to generate secondary amines followed by coupling with α -ketocarboxylic acids or alkynyl carboxylic acids to form medicinally important α -ketoamides or alkynamides respectively under visible light photoredox catalyst in a single operation is described (Scheme 1).

Scheme 1. Photoredox-Catalyzed Tandem Demethylation of N,N-Dimethyl Anilines Followed by Amidation with α -Keto or Alkynyl Carboxylic Acids.

We have achieved the synthesis of medicinally relevant sulfone bearing compounds in mild and environment friendly sustainable method. A unified strategy for the hydroarylsulfonylation of vinyl arenes has been developed under catalyst, additive-free conditions at room temperature from the corresponding aryldiazonium salts, DABSO (DABCO.2SO₂), and thiophenol as hydrogen atom transfer



Scheme 2. Metal-Free, Multicomponent Anti-Markovnikov Hydroarylsulfonylation and Alkoxyarylsulfonylation of Vinyl Arenes.

(HAT) reagent. A four-component difunctionalization with alkoxy group has been achieved under oxidative condition (Scheme 2).

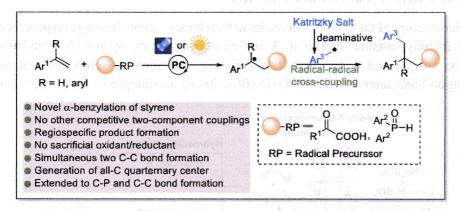
A combination of aryldiazonium salts and DABSO provides a unique opportunity for sulfonylative multicomponent cross-coupling reactions. A copper-catalyzed three-component cross-coupling of aryldiazonium salts, DABSO with arylboronic acids to obtain medicinally relevant unsymmetrical diarylsulfones is disclosed. Interestingly, a metal-free approach for the synthesis of arylvinylsulfones from the corresponding vinyl boronic acid or vinyl halides is also explored under basic condition. Tethered diazonium salts provided the corresponding annulated alkylvinylsulfones *via* alkene difunctionalisation under the same metal-free condition (**Scheme 3**).

$$(HO)_2B \xrightarrow{DTBP/KHCO_3} Cu(II)/Bphen \xrightarrow{DTBP/KHCO_3} Ar^3 \xrightarrow{Ar^1} diarylsulfones$$

$$X \xrightarrow{Ar^1} X = B(OH)_2, I, Br \xrightarrow{MCA_1} Iransition \xrightarrow{MCA_1} Irans$$

Scheme 3. Aryldiazonium Salts and DABSO: a Versatile Combination for Three-Component Sulfonylative Cross-Coupling Reactions.

We have also been able to prepare medicinally significant all-carbon quaternary center from commodity chemicals like styrene, ketocarboxylic acids and benzyl amines *via* alkene dicarbofunctionalisation. Simultaneous C–C bond formation across the styrenyl double bond occurs at exceptionally mild photocatalytic condition to access acylative benzylation of styrenes. Phosphonobenzylation can also be obtained using organic photocatalyst (**Scheme 4**).



Scheme 4. Photocatalysed deaminative three-component benzylative difunctionalization of styrenes.

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