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Letter

Photo-oxidative Ruthenium(II)-Catalyzed Formal [3 + 2] Heterocyclization of Thioamides to Thiadiazoles

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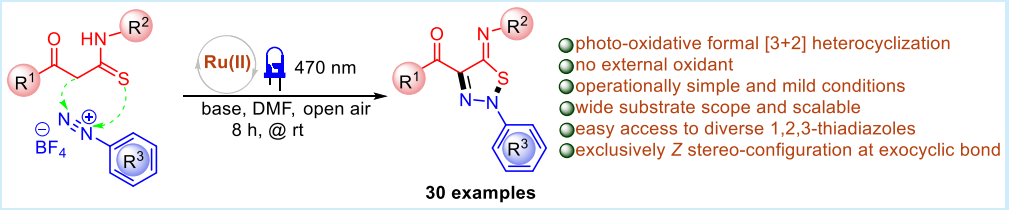


ABSTRACT: An operationally simple and sustainable one-pot photo-oxidative formal [3 + 2] heterocyclization of β-ketothioamides with aryldiazonium salts catalyzed by $Ru(bpy)_3Cl_2$ has been realized to provide 2,4-disubstituted 5-imino-1,2,3-thiadiazoles in good to high yields under mild reaction conditions for the first time. The reaction proceeded via an α-phenylhydrazone adduct of thioamides leading to 1,2,3-thiadiazoles via N−S bond formation at room temperature. Notably, the products possess *Z*-stereochemistry with regard to the exocyclic C═N double bond at the 5-position of the ring.

Among five-membered heterocyclic compounds, thiadiazoles have exciting potential as chemical therapeutics. The distinctive 1,2,3-thiadiazoles have appeared as substructures in some bioactive molecules.[1] Their widespread applications have been applied to materials,[2] antimicrobials, biological activities,[3−6] and herbicidal growth regulators[7] (Figure 1). A valuable synthetic impression is associated with

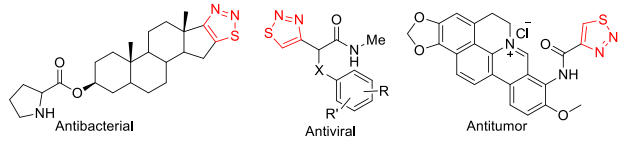
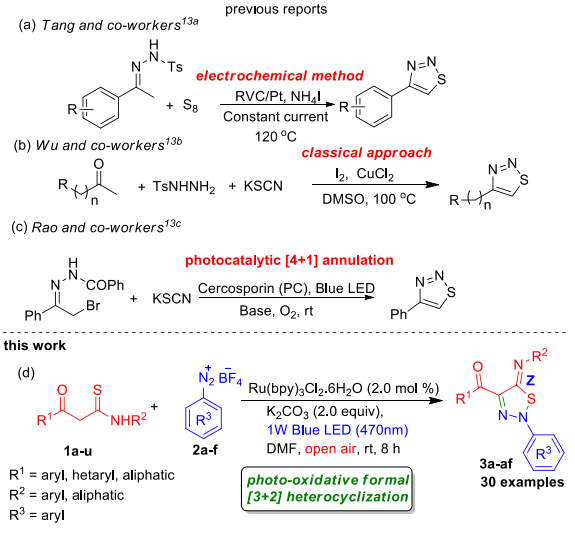


Figure 1. Biologically active 1,2,3-thiadiazoles.

its role of reactive intermediates in various transformations.[8] Its bioisosteric abilities to replace carboxylic acids, esters, carboxamides, and other broadly similar functionalities owe to its vivacious synthetic utility.

Owing to their great synthetic and practical significance and wide applications, over the years, numerous protocols have been developed to construct the 1,2,3-thiadiazole skeletons. The classical synthetic approaches including Hurd−Mori synthesis,[9] Wolff synthesis,[10] and Pechmann synthesis[11] among others[12] have been reported. Recently, Tang and co-workers[13a] reported an external oxidant-free, high-temperature electrochemical approach to access 1,2,3-thiadiazoles via introducing elemental sulfur into *N*-tosylhydrazones. (Scheme 1a). A $I_2/CuCl_2$-promoted strategy for the construction of 1,2,3-thiadiazoles has been developed by Wu and co-workers (Scheme 1b).[13b] Moreover, a photocatalytic [4 + 1] annulation

Scheme 1. Synthesis of 1,2,3-Thiadiazoles



of azoalkanes with thiocyanates toward the synthesis of 1,2,3-thiadiazoles is also reported[13c] (Scheme 1c). Although the recently reported approaches[13a−c] are practical implements

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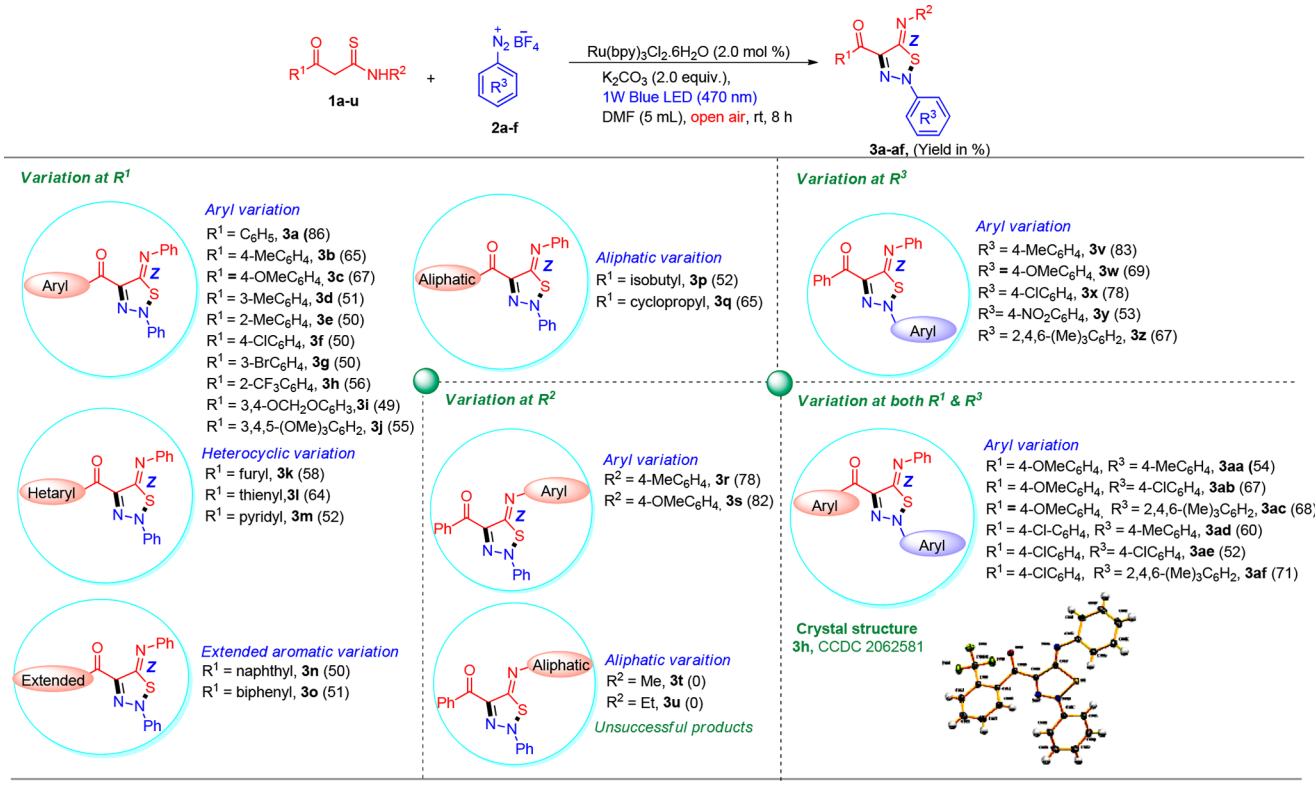
Scheme 2. Scope of 1 and 2 for the Synthesis of Compounds 3a−3af[a]



toward the edifice of 1,2,3-thiadiazoles, most of them are tedious[14] to modern synthetic chemistry practitioners.

In recent years, visible-light-mediated photocatalytic approaches have emerged as powerful synthetic tools for the several chemical transformations. Their intrinsic characteristics such as operational simplicity, safety, sustainability, and easy-to-enable conditions make these protocols more popular than traditional approaches.[15,16] Visible-light-driven reactions have opened a greener and economical pathway to construct challenging C−C and C−heteroatom bonds.[17] Recently, metallo-photoredox catalysis has experienced noteworthy advances in heterocyclization reactions via a reductive or oxidative quenching process.[18] Photocatalysis also provides an opportunity to generate highly reactive intermediates with unconventional reactivities.

For the successful synthesis of any targeted scaffold, a judicious choice of substrates is a preliminary requirement. Hence, for the synthesis of 1,2,3-thiadiazoles we prefer *β*-ketothioamide (KTA), one such substrate that has been well-documented for the synthesis of various sulfur-containing frameworks.[19] Our laboratory has a long-standing interest in thermal reactivity/transformation of KTAs to diverse heterocyclic scaffolds.[20] Very recently, we have devised a domino protocol to access thiazoline derivatives employing KTAs.[21] Based on our experience, we became intrigued by studying the photochemical reaction of diazonium salts with KTAs that could be a viable alternative for valuable scaffolds. As part of our ongoing project to investigate efficient synthetic methods for thiadiazoles,[22] herein we report the first visible-light-sensitized photoredox catalytic aerobic oxidative heterocyclization of KTAs with aryldiazonium salts for the efficient synthesis of 2,4-disubstituted 5-imino-1,2,3-thiadiazole frameworks (Scheme 1d). On the basis of a literature survey, this visible-light-mediated metallo-photoredox strategy enabled N−S bond formation via a formal [3 + 2] heterocyclization route to provide fully substituted 1,2,3-thiadiazole scaffolds has not been documented so far.

To optimize the reaction conditions for the photooxidative cyclization of *β*-ketothioamides (KTAs) with diazonium salts, our initial investigation began by using 3-oxo-*N*,3-diphenylpropanethioamide (**1a**, 0.5 mmol), tetrafluoroborate phenyldiazonium salt (**2a**, 0.5 mmol), $Ru(bpy)_3Cl_2{\cdot}6H_2O$ (1.0 mol %), and K_2CO_3 (1.0 equiv) in acetonitrile at room temperature in an open atmosphere under 1 W blue light (λ_{max} = 470 nm). Gratifyingly, the reaction undergoes with the formation of a new product, which was characterized as (*Z*)-(2-phenyl-5-(phenylimino)-2,5-dihydro-1,2,3-thiadiazol-4-yl)(*p*-tolyl)-methanone (**3a**) by spectroscopic (^1H, and ^{13}C) and HRMS analysis (Table S1, entry 1). In contrast to other preparations of thiadiazoles,[9−13] here the formation of product **3a** is accompanied by the initial formation of intermediate (*Z*)-3-oxo-*N*-phenyl-2-(2-phenylhydrazono)-3-(*p*-tolyl)propanethioamide (**I**) at room temperature followed by its chemoselective intramolecular cyclization to desired thiadiazole product **3a** under photocatalysis. According to a thorough literature survey, there is no previous report for the one-pot synthesis of thiadiazole involving photo-oxidative heterocyclization of *β*-ketothioamide (KTA) with diazonium salt. Encouraged by the synthesis of (*Z*)-(2-phenyl-5-(phenylimino)-2,5-dihydro-1,2,3-thiadiazol-4-yl)(*p*-tolyl)methanone **3a** via photocatalysis, further optimization of reaction parameters was carried out by varying the photocatalyst, solvent, base, and light source to enhance the efficacy of the reaction, as summarized in Table S1. Use of other metal photocatalysts such as ($[Ir\{dFCF_3ppy\}_2(bpy)]PF_6$) (P2) and organic photocatalysts such as eosin Y (P3), alizarine red S (P4), and rose bengal (P5) could not illustrate better photocatalytic activity than $Ru(bpy)_3Cl_2.6H_2O$ (P1) (Table

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S1, entries 2−5). Hence, P1 is established as a suitable catalyst for the formation of **3a**. Next, to optimize the catalytic loading, 2.0 mol % of $Ru(bpy)_3Cl_2·6H_2O$ is found to be superlative for the model reaction, providing product **3a** in 60% yield within 12 h (Table S1, entry 6). Moreover, increments in the catalytic loading (3.0 mol %) could not demonstrate any notable improvement in the result (Table S1, entry 7). Subsequently, the impact of diverse solvents was tested for this domino process. Use of solvent DCM instead of ACN yielded product **3a** in 57% and was found almost equally effective (Table S1, entry 8). Solvents DMSO and DMF were found to be advanced to that of ACN in terms of both time and yield (Table S1, entries 9 and 10). Moreover, the model reaction in EtOH and MeOH could not provide better result than ACN (Table S1, entries 11 and 12). Therefore, a brief investigation of various solvents indicated that solvent DMF was the best choice for the further optimization (Table S1, entry 10). Next, we optimized the loading of base. When the loading of K_2CO_3 was increased from 1.0 to 2.0 equiv in DMF, the yield of **3a** increased from 70% to 86% within 8 h (Table S1, entry 13). Further increments of base loading (3.0 equiv) as well as using a strong inorganic base such as Cs_2CO_3 did not exhibit any noteworthy change in the yield and reaction time. The above observation suggested that the higher loading and basic strength did not show any significant impact on the outcome of the reaction (Table S1, entries 14 and 15).

The reaction without blue LED light (in dark box) under otherwise identical reaction conditions yielded **3a** in a trace amount (5%) (Table S1, entry 16). The reaction in inert atmosphere under otherwise optimized conditions yielded the desired product in 8% after 24 h (Table S1, entry 17). The temperature of the surrounding reaction mixture remained close to 30 °C throughout the reaction period due to the use of 1 W blue LED, signifying the photochemical nature of the reaction. To demonstrate the effect of wavelength of different light sources, the model reaction was performed with a white (40 W, LED bulb) and a green (1 W, λ_{max} = 530 nm) LED. The yield of the desired product **3a** decreased noticeably (65 and 75% respectively, Table S1, entries 18 and 19). Consequently, the proficient wavelength for this transformation was found to be 470 nm (1 W blue LED). After the complete screening of the model reaction under various conditions, the optimized conditions for this reaction were determined as **1a** (0.5 mmol), **2a** (0.5 mmol), P1 (2.0 mol %), and K_2CO_3 (2.0 equiv) in DMF (5 mL) at room temperature under 1 W blue LED irradiation for 8 h in open air (Table S1, entry 13, see the SI for details).

With the optimized reaction conditions in hand, next we investigated the substrate scope and limitations of the protocol employing a wide range of variously substituted *β*-ketothioamides (**1a−1u**, Scheme 1) and aryldiazonium tetrafluoroborate salts (**2a−2f**, Scheme 1). As shown in Scheme 2, a range of thioamides have been introduced, providing the corresponding desired product **3** in good to excellent yield. To demonstrate the electronic and steric effects of various substituents R^1 and R^2 in thioamides, a range of thioamides bearing both electron-donating (Me, OMe) and electron-withdrawing (Cl, Br, CF_3) groups at their particular positions are studied. All of these thioamides are well tolerated under optimized reaction conditions and provide the desired products in 50−86% yields (Scheme 2, **3a−3h**). Notably, the products derived from thioamides containing halogen (e.g., chloro and bromo) substituents are attractive because of their further synthetic applications. Remarkably, KTAs with a multisubstituted aryl as the R^1 moiety, such as 3,4-$OCH_2OC_6H_3$ and 3,4,5-$(OCH_3)_3C_6H_2$, afforded the corresponding desired products in 49% and 55% yields, respectively (Scheme 2, **3i**, **3j**). Importantly, when the R^1 moiety was changed to a *π*-electron-rich motif such as 2-furyl or 2-thienyl and an electron-deficient 3-pyridyl substituent, the corresponding desired products were obtained in 58%, 64%, and 52% yield, respectively (Scheme 2, **3k**, **3l**, and **3m**). To further elaborate the substrate scope, we also introduced thioamides bearing R^1 as an extended aromatic system, such as 2-naphthyl and biphenyl groups, to provide the corresponding thiadiazoles in 50% and 51% yields, respectively (Scheme 2, **3n**, **3o**).

Further, the R^1 moiety appended with aliphatic moieties such as isobutyl and cyclopropyl groups afforded the corresponding products in 52% and 65% yields, respectively (Scheme 2, **3p**, **3q**). To further illustrate the broad synthetic utility and generality of our one-pot photo-oxidative heterocyclization, we intended to employ R^2 as a substituted-phenyl group. Accordingly, thioamides bearing 4-methylphenyl and 4-methoxyphenyl groups as R^2 gave their corresponding desired products **3r** and **3s** in 78% and 82% yields, respectively (Scheme 2). The yield obtained was comparable with one isolated from unsubstituted R^2, i.e., phenyl moiety **3a** (Scheme 2, 86%); hence, the substituted phenyl group as R^2 did not demonstrate any obvious electronic effects. On the other hand when the R^2 phenyl group was switched to an alkyl group such as methyl or ethyl, unfortunately, the photocatalytic cyclization of their respective adducts lead a very unclear TLC pattern (formation of several inseparable undesired products and no expected product could be formed). The resulting complexity may be due to the strong basic nature of the nitrogen atom attached with alkyl fragments (which make nitrogen more basic due to the +I effect). Hence, the possibility of other side reactions is very high under light, thus limiting the scope of photocyclization up to some extent (Scheme 2, **3t**, **3u**). Moreover, we also investigated the effect of R^3 on the efficacy of this protocol. We explored the scope of the reaction with different substituted aryl diazonium salts. When the R^3 moiety was swapped with various electron-donating and electron-withdrawing motifs such as *p*-methyl, *p*-methoxy, *p*-chloro, *p*-nitro, and 2,4,6-trimethyl, the corresponding desired products were obtained in good yields (Scheme 2, **3v**, **3w**, **3x**, **3y**, and **3z**). Further, when R^1 moiety was swapped to either an electron-donating or electron-withdrawing group along with a *para*-substituted electron-donating or electron-withdrawing group at R^3, the resultant desired products were obtained in moderate to good yields (Scheme 2, **3aa−3af**). Consequently, the reported Ru(II)-catalyzed photo-oxidative cyclization of thioamides with aryldiazonium salts allows a novel entry of various fully substituted 1,2,3-thiadiazole scaffolds **3a−af**, which were difficult to prepare via previously reported methods.

To validate the synthetic utility of synthesized 1,2,3-thiadiazoles **3**, we performed the oxidation and reduction of two representative compounds **3a** and **3s**, respectively. The oxidation of compound (*Z*)-phenyl(2-phenyl-5-(phenylimino)-2,5-dihydro-1,2,3-thiadiazol-4-yl)methanone (**3a**) with *m*-CPBA in DCM yielded an open-chain product 3-oxo-*N*,3-diphenyl-2-(2-phenylhydrazineylidene) propanamide (**4**, 90%),in excellent yield. On the other hand, reduction of compound (*Z*)-(5-((4-methoxyphenyl)imino)-2-phenyl-2,5-dihydro-1,2,3-thiadiazol-4-yl)(phenyl)methanone (**3s**) with

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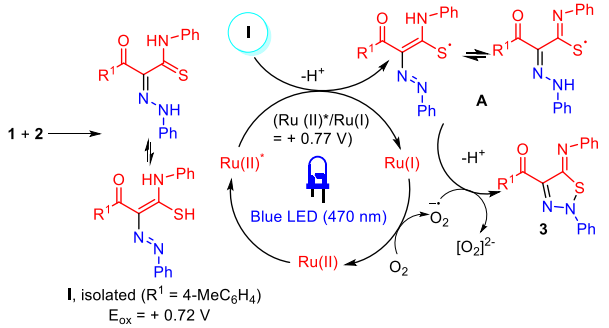
$NaBH_4$ in methanol successfully reduced exocyclic imine bond and provided (5-((4-methoxyphenyl)amino)-2-phenyl-2,3-dihydro-1,2,3-thiadiazol-4-yl)(phenyl)methanone (**5**, 72%), an amino derivative of **3s**, in good yield (see the SI for details).

The structures of all newly synthesized compounds **3a-af**, **I**, **4**, and **5** were fully characterized by spectral (^{1}H and ^{13}C NMR) and HRMS analysis. Moreover, the structure of (*Z*)-(2-phenyl-5-(phenylimino)-2,5-dihydro-1,2,3-thiadiazol-4-yl)(2-(trifluoromethyl)phenyl)methanone (**3h**) was also established by single-crystal X-ray diffraction analysis (see the SI for details).

On the basis of control experiments (see the SI for details) and previous literature reports,[23] the following tentative mechanism has been postulated (Scheme 3). The first step

Scheme 3. Proposed Reaction Pathway



of the reaction involved the formation of intermediates **I** (isolated for the synthesis of **3b** and fully characterized via spectral studies and HRMS analysis) at room temperature, which undergo the oxidation (E_{ox} = +0.72 V) via excited photocatalyst (Ru(II)*/Ru(I) = +0.77 V)[23c] through a reductive quenching process to generate thiyl radical **A** (see the SI for details). Concurrently, molecular oxygen completes the catalytic cycle via oxidation of Ru(I) to Ru(II) and generates a reduced superoxide ion $O_2^{\bullet-}$. Thiyl radical **A** undergoes subsequent oxidation via superoxide ion $O_2^{\bullet-}$ to generate product **3** and eliminate O_2^{2-} as a byproduct.

In conclusion, we described a mild photocatalytic route for 1,2,3-thiadiazoles by reacting *β*-ketothioamides with aryl diazonium salts under visible-light irradiation. The reaction proceeds smoothly at room temperature using air as oxidant, thus making this strategy operationally simple and eco-compatible while exhibiting excellent functional group tolerance. Thus, it provides an environmentally benign synthesis of thiadiazoles employing a photo-oxidative hetero-cyclization pathway as an alternative to conventional routes. The reported protocol allows a straight alternative to access thiadiazoles symmetrical to the existing ones, thus elaborating the chemistry of *β*-ketothioamides.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c00766.

HRMS analyses reports (ZIP)
FAIR data, including the primary NMR FID files, for compounds **3a-af**, **I**, **4 and 5** (ZIP)
Experimental details, spectra and spectral data for all compounds; X-ray crystallographic data for **3h**(PDF)

Accession Codes

CCDC 2062581 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

†P.P. and G.S. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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