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Visible-Light Mediated Synthesis of 1,2,4-Dithiazolidines from β-Ketothioamides through Hydrogen Atom Transfer Photocatalytic Approach of Eosin Y

Monish A. Ansari, Dhananjay Yadav, Sonam Soni, Abhijeet Srivastava, and Maya Shankar Singh*

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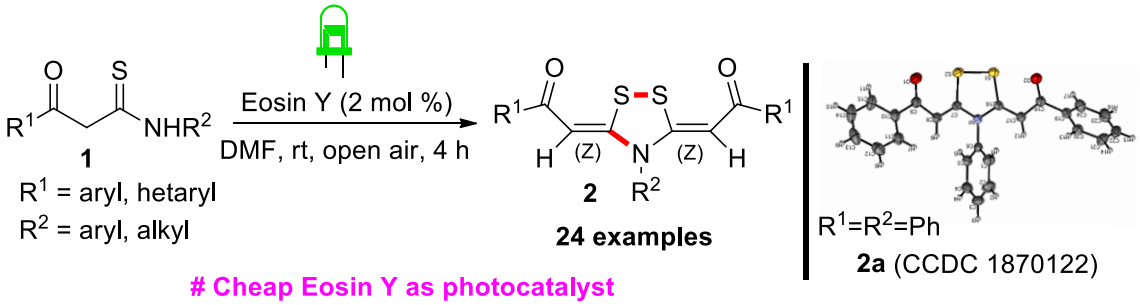


 # Cheap Eosin Y as photocatalyst
 # Hydrogen atom transfer (HAT) catalysis
 # Metal- and additive-free at room temperature
 # Successive S–S & N–C bonds formation

ABSTRACT: An efficient visible-light-mediated construction of a specific class of 1,2,4-dithiazolidines from β-ketothioamides is devised employing Eosin Y as a photoinitiator at ambient temperature in open-pot. The reaction proceeds via *in situ* generated thiyl radical followed by dimerization/deaminative cyclization cascade enabling the creation of dithiazolidine ring through successive formation of S–S and N–C bonds under metal- and additive-free conditions. Remarkably, the benign conditions, sustainability, and quantifying forbearance of wide horizons of functional groups are added characteristics to the strategy. Developed HAT methodology will be helpful in post-synthetic modification via embedded synthetic handles.

INTRODUCTION

Photo-induced organic synthesis occupies an impeccable place in ecological equilibria. Visible-light photoredox catalytic (VLPC) reactions devised by some specific groups and their co-workers are fundamental and path breaking in organic synthesis, and have seen remarkable growths over the recent years.[1] Visible-light promoted reactions revealed several noteworthy applications owing to its intrinsic characteristics of simplicity, safety, cost-effectiveness, and sustainability. In this 21st century, visible-light alone or in combination with an appropriate catalyst has set the remarkable innovations and enabled numerous expedient synthetic manipulations, which were earlier unapproachable by traditional methods.[2] Upon irradiation, photocatalyst after getting excited could activate the substrate either by direct energy-transfer[3a-d] (ET) or via single-electron-transfer[3e-h] (SET) mode resulting numerous efficient synthetic transformations.[3]

Besides above approach, another possibility could be a hydrogen-atom transfer (HAT) pathway, recognized as an important activation mode in photocatalyzed reactions.[4] The key benefit of this mode is that the HAT catalyst activates the substrate even if they are electrochemically unmatchable. Usually, there are three modus operandi of HAT process in photocatalysis.[4a] In the first strategy, a hydrogen atom is abstracted by the excited photocatalyst from the substrate followed by a reverse hydrogen-atom transfer (RHAT) to newly produced intermediate completing the catalytic cycle.[5] Second, the co-catalyst was activated by previously excited photocatalyst. Thus, activated co-catalyst next triggers the reaction via HAT pathway.[6] Third mode is the synchronized transfer of an electron (e^-) and a proton (H^+) from the substrate known as proton-coupled electron-transfer (PCET) process,[7] enabling the generation of a radical, which could be employed in several transformations. Since, the indirect HAT and PCET modes could progress only if some additional reagents are available, the most competent and cost-effective procedure is the direct HAT catalysis amidst these three modes. Nevertheless, the key constraint for the

extensive use of HAT process is restricted by insufficient known photocatalyst,[4] such as aromatic ketones, polyoxometalates (POMs)[8] and the recently reported species uranyl cation.[5e] Furthermore, the above-mentioned catalysts need some additional additives, and suffer from undesired side reactions. Thus, exploring viable and metal-free catalysts, which can promote direct HAT processes, would be of great significance.

Organic dyes are employed as ideal photocatalytic candidates,[9] exhibiting the benefits of non-toxicity, eco-compatibility, and cheapness over the metal-based photocatalysts. Based upon redox potentials of chemical quenchers, Eosin Y dye (Figure 1), one amongst extensively used organophotocatalysts, could follow either reductive or oxidative quenching cycles.[10,11]

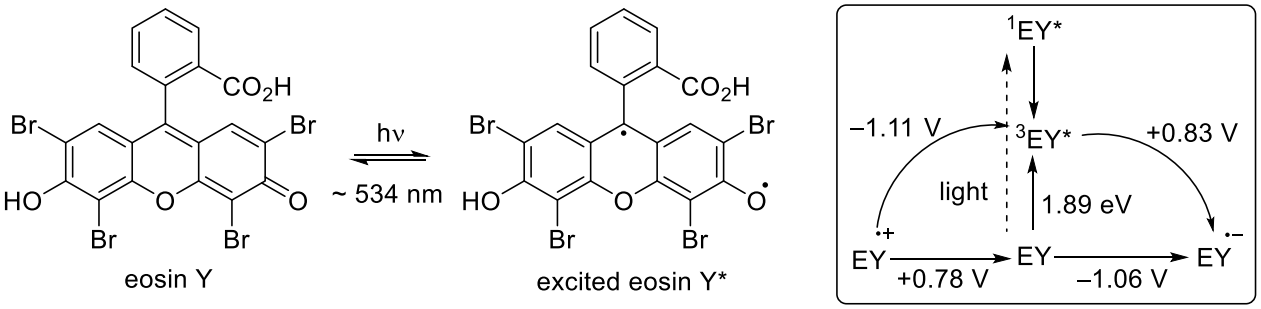


Figure 1. Photo- and Electrochemical properties of Eosin Y.

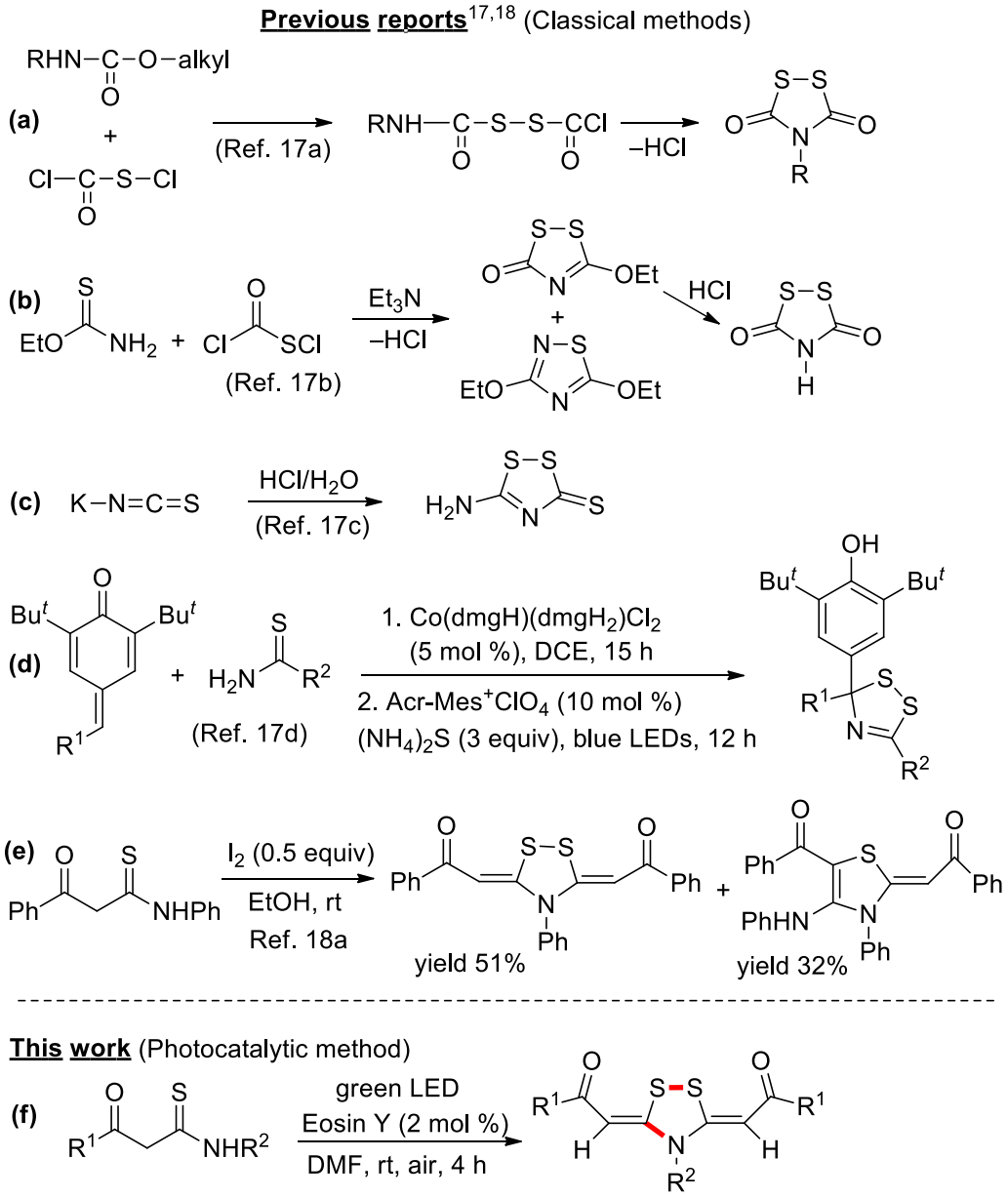
For the success of any protocol, particularly, the selection of substrate is highly crucial and governing factor. One such simple substrate is β-ketothioamide that has been well-documented as an intriguing synthon because of its exceptional reactivity.[12] β-Ketothioamides are comprehensively exploited to access valuable heterocyclic scaffolds.[12] Furthermore; they not only behave as ambiphilic species (having both nucleophilic and electrophilic character), but also could be transformed into radical intermediates for further manipulations. Sulfur-centered radicals (SCRs) are appealing intermediates in organic synthesis. Based on our experience on thermal reactivity/transformation of β-ketothioamides,[13]

we envisaged that the transformation of β-ketothioamides *via* visible-light driven photocatalysis could be a viable alternative for valuable scaffolds. Rare reports are available on the formation of X−X bonds through organo-photocatalysis.[9] Yadav and co-workers have formulated the synthesis of 1,2,4-thiadiazoles via cyclization of thioamides catalyzed by organo-photocatalyst Eosin Y.[14a] Lei and co-workers[14b] developed the synthesis of benzothiazoles from thioamides promoted by $Ru(bpy)_3(PF_6)_2$. Nicewicz *et al.*[14c] observed that sulfur radical cation ($S^{\cdot+}$) could experience Newman-Kwart rearrangement. Recently, the role of Eosin Y dye as a hydrogen-atom transfer photocatalyst toward C–H functionalization has also been disclosed.[15] Based upon literature reports, we envisioned that the Eosin Y could play the role of an ideal HAT photocatalyst and may react with enethiol tautomer of thioamide to generate thiyl radical, which could undergo dimerization enabling the formation of intramolecular disulfide (S-S) bond.

The utility of sulfur heterocycles has become prevalent in medicinal and agricultural industries.[16a] Amongst the diverse heterocyclic frameworks, 1,2,4-dithiazoles and their derivatives are privileged scaffolds having various applications in pharmaceutical sciences.[16b,c] Kühle and Zumach successfully synthesized 1,2,4-dithiazolidine-3,5-diones by the reaction of chlorocarbonylsulfenylchloride with *O*-esters of *N*,*N*-dialkylthiocarbamic acids (Scheme 1a).[17a] Barany *et al*. reported the synthesis of 1,2,4-dithiazolidines via tandem reaction of thioamides with (chlorocarbonyl)sulfenyl chloride (Scheme 1b).[17b] A. P. Guzaev[17c] reported the construction of 1,2,4-dithiazolidine-3-thiones, which were further utilized as sulfurizing agents for oligonucleotide synthesis (Scheme 1c). Recently, Pan and co-workers[17d] devised the synthesis of 1,2,4-dithiazoles via photocatalytic reaction employing thioamides, *para*-quinonemethides, and $(NH_4)_2S$ (Scheme 1d). Li and co-workers[18a] developed the synthesis of thiazolylidenes and 1,4-dithiines from β-ketothioamides (KTAs) catalyzed by molecular iodine (Scheme 1e). For the synthesis of 1,2,4-dithiazolidine derivatives, various other reagents such as CF_3SCl,[18b]

SO_2Cl_2,[18c] and $(NH_4)_2Ce(NO_3)_6$[18d] have been executed. Despite the above examples, the synthetic potential of the visible-light photoredox generation of sulfur radicals from thioamides remains surprisingly underexplored. Hence, the development of efficient and sustainable visible-light induced cyclizations employing thioamides for the synthesis of heterocyclic structures is still highly desirable.

Scheme 1. Previous Attempts and Current Approach for the Synthesis of 1,2,4-Dithiazolidines

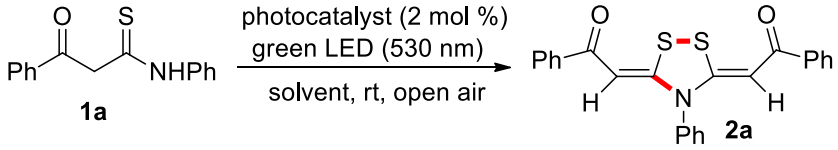


To the extent of our knowledge, synthesis of 1,2,4-dithiazolidines from β-ketothioamides via photocatalysis has not been disclosed till yet. Driven by the need for an efficient and unified synthetic route to 1,2,4-dithiazolidine derivatives, we were fascinated by the probability of visible-light-promoted site-selective dimerization of β-ketothioamides. Herein, we describe the visible-light-enabled transformation of β-ketothioamides into 1,2,4-dithiazolidines catalyzed by Eosin Y dye as a HAT photocatalyst at ambient temperature (Scheme 1f).

RESULTS AND DISCUSSION

To check the credibility of our hypothesis, we commenced our study by using 3-oxo-N,3-diphenylpropanethioamide (**1a**) as a model substrate for optimizing the reaction conditions. The outcomes of the reactions are enlisted in Table 1. The solution of **1a** in 2 mL of dichloromethane (DCM) or in 2 mL of dichloroethane (DCE) separately, was irradiated under green LED with 2 mol % of Eosin Y dye for 12 h in open-pot at room temperature. The anticipated product could not be detected, and the substrate **1a** was recovered completely unreacted (Table 1, entries 1 and 2). Next, we carried out the model reaction in various solvents (Table 1, entries 3-8). To our pleasure, dimethyl formamide (DMF) was found as a solvent of choice providing the expected product **2a** in 76% yield (Table 1, entry 5). Encouraged by this favourable result, to identify the most suitable catalyst, a series of other organic photocatalysts such as Rhodamine B, Rose-Bengal, Acridine Red, Fluorescein and Methylene Blue (Table 1, entries 9-13) were screened. Although the above tested photocatalysts triggered the reaction, but none of them furnished superior result than Eosin Y. Further decrease in the amount of Eosin Y to 1 mol % had a detrimental effect, whereas increasing the amount of Eosin Y (4 mol %) could not improve the efficacy of the reaction (Table 1, entries 14 and 15). In control experiments, we found that visible-light and dye are inevitable components for this novel transformation (Table 1, entries 16 and 17).

Table 1. Optimization of Reaction Conditions for the Synthesis of 2[a]



entry	photocatalyst (mol %)	solvent	time (h)	yield[b] (%)
1	Eosin Y (2 mol %)	DCM	12	NR[c]
2	Eosin Y (2 mol %)	DCE	12	NR[c]
3	Eosin Y (2)	CH_3CN	6	54
4	Eosin Y (2)	THF	6	32
5	Eosin Y (2)	DMF	4	76
6	Eosin Y (2)	DMSO	4	57
7	Eosin Y (2)	Toluene	12	NR[c]
8	Eosin Y (2)	Dioxane	6	24
9	Rhodamine B (2)	DMF	4	52
10	Rose Bengal (2)	DMF	4	58
11	Acridine Red (2)	DMF	4	54
12	Fluorescein (2)	DMF	4	32
13	Methylene blue (2)	DMF	4	28
14	Eosin Y (1)	DMF	4	54
15	Eosin Y (4)	DMF	12	76
16	Eosin Y (2)[d]	DMF	12	NR[c]
17	none	DMF	12	NR[c]
18	Eosin Y (2)[e]	DMF	6	62
19	Eosin Y (2)[f]	DMF	6	56
20	Eosin Y (2)[g]	DMF	6	48

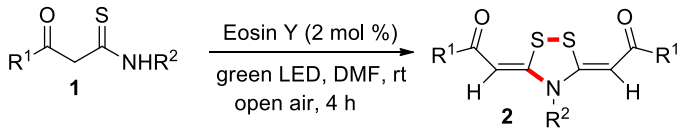
[a]Reaction conditions unless otherwise stated: all the reactions were performed with **1a** (0.25 mmol), Eosin Y (2 mol %) in 2 mL of solvent at rt in open air. [b]Yields. [c]NR = No reaction. [d]Without irradiation. [e]With blue LED. [f]With white LED. [g]With cyan LED.

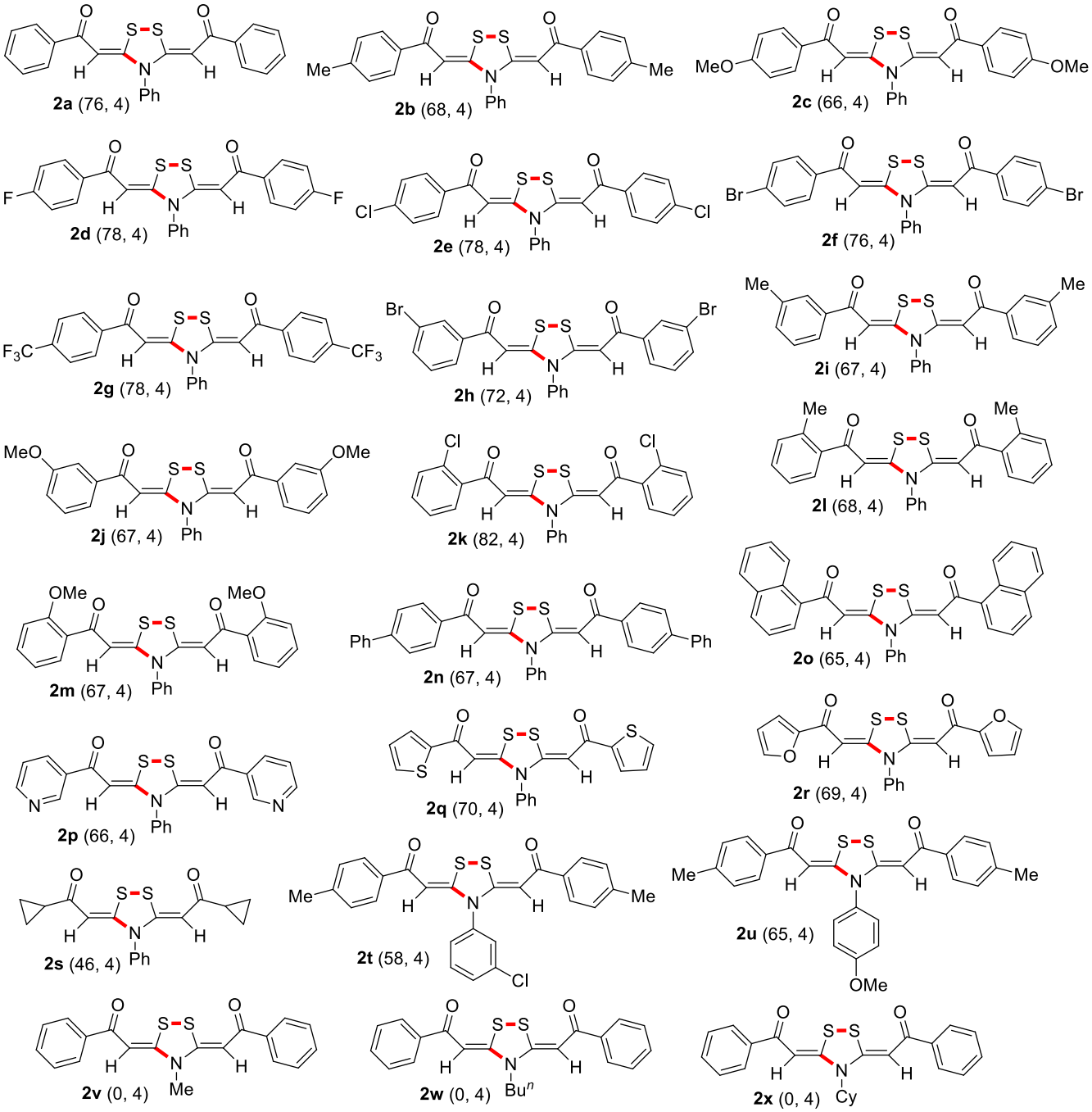
The optimized condition for this reaction was determined as **1a** (0.25 mmol), Eosin Y (2 mol %) in DMF under green LED irradiation for 4 h at room temperature in open air. In place of green LED, when the reaction was performed under the irradiation of different light sources such as blue LED, white LED and cyan LED, the yield of observable product **2a** was diminished by 14-28% (Table 1, entries 18-20), indicating that the green LED is the suitable source for excitation of photocatalyst.

We explored the substrate scope of the protocol employing a range of structurally diverse β-ketothioamides (**1a-1x**) with above mentioned optimized set of reaction conditions. The results of our investigations are enlisted in Scheme 2. Explicitly, R^1 moiety substituted at *o*-, *m*- and *p*-positions with electron-donating and electron-withdrawing groups (such as -Me, -OMe, -F, -Cl, -Br, and -CF_3) were viable participants, and furnished the desired 1,2,4-dithiazolidines (**2b**-**2m**) in 66-82% yields. Notably, thioamides appended with substrates bearing aromatic, heteroaromatic (furyl and thienyl), and extended aromatic moieties as R^1 worked well under the standard conditions. Extended aromatic appendants such as 1-naphthyl and biphenyl groups were also tolerated well furnishing the corresponding dithiazolidines (**2n**, **2o**) in 67% and 65% yields, respectively.

Next, when R^1 moiety was swapped to π-electron-deficient 3-pyridyl substituent and π-electron-rich motifs such as 2-thienyl and 2-furyl, the corresponding desired products **2p**, **2q**, and **2r** were obtained in 66%, 70%, and 69% yield, respectively. R^1 appended with cyclopropyl group (thioamide prepared from cyclopropyl methyl ketone), produced the product **2s** in relatively low (46%) yield. After the effective employment of R^2 as neutral phenyl group, we intended to employ R^2 as phenyl substituted with electron-withdrawing and electron-donating groups to realize the effect of the electronic property of R^2 on the reaction. Consequently, substrate **1** bearing R^2 moiety as 3-chlorophenyl and 4-methoxyphenyl groups gave the corresponding desired products **2t** and **2u** in 58% and 65% yield, respectively.

Scheme 2. Scope and Limitation of β-Ketothioamides

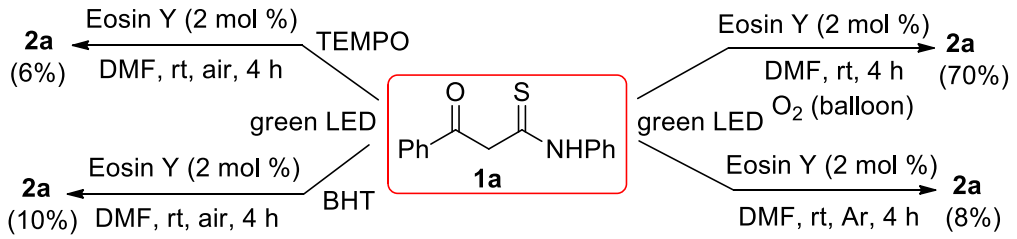




Concurrently, to examine vulnerability of this protocol, moieties as aliphatic groups were employed instead of aromatic groups at R^2. Thus, when R^2 phenyl group was switched to alkyl groups such as methyl, *n*-butyl and cyclohexyl, unfortunately, no expected product was obtained (Scheme 2, **2v**-**2x**). Further, to ascertain the importance of the β-keto group of thioamide, we carried out the reaction with nonketone thioamides such as 2-(3-methoxyphenyl) ethanethioamide and N-(*p*-tolyl) benzothioamide under the previously optimized conditions. The observable product cannot be obtained suggesting that β-keto group is necessary for the progress of the reaction. This could be due the stabilization of enethiol tautomer **1** of β-ketothioamide via intramolecular hydrogen bonding. The structures of all the compounds **2a-2u** were characterized by satisfactory spectral (^{1}H, ^{13}C NMR and HRMS) studies. Additionally, the structure was unambiguously established by the single crystal X-ray diffraction analysis of (2Z,2'Z)-2,2'-(4-phenyl-1,2,4-dithiazolidine-3,5-diylidene)bis(1-phenylethanone) **2a** as a representative compound (see Supporting Information for details).[19]

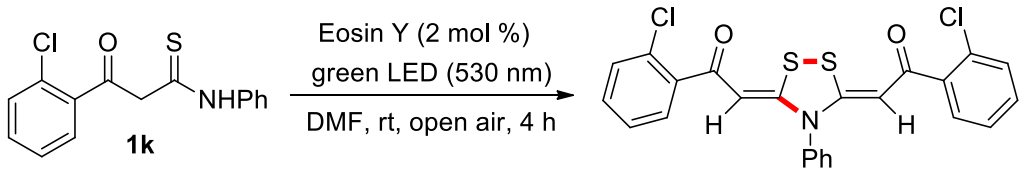
For deeper understanding of mechanistic investigation, some controlled experiments were performed (Scheme 3). In the presence of radical scavengers such as TEMPO or BHT, the yield of the desired product **2a** was drastically reduced to 6-10% indicating the radical pathway. To check whether addition of oxygen improves reaction efficiency, the test reaction was carried out under oxygen purging conditions. No improvement in the outcome of the reaction was observed. The model reaction of **1a** under argon atmosphere dramatically dropped the yield of product **2a** to 8%, indicating that air (O_2) is necessary for the reaction.

Scheme 3. Key Control Experiments



To validate the synthetic utility of the strategy, we performed a large scale experiment with **1k** (3 mmol) in the presence of green LED (530 nm) under the optimal conditions (Scheme 4). The anticipated product **2k** was achieved in 78% yield (566 mg), and found to be comparable with small-scale reaction (Scheme 2, entry **2k**, 82%). The above reaction indicated that this method could be employed for higher-scale synthesis of 1,2,4-dithiazolidine derivatives **2**.

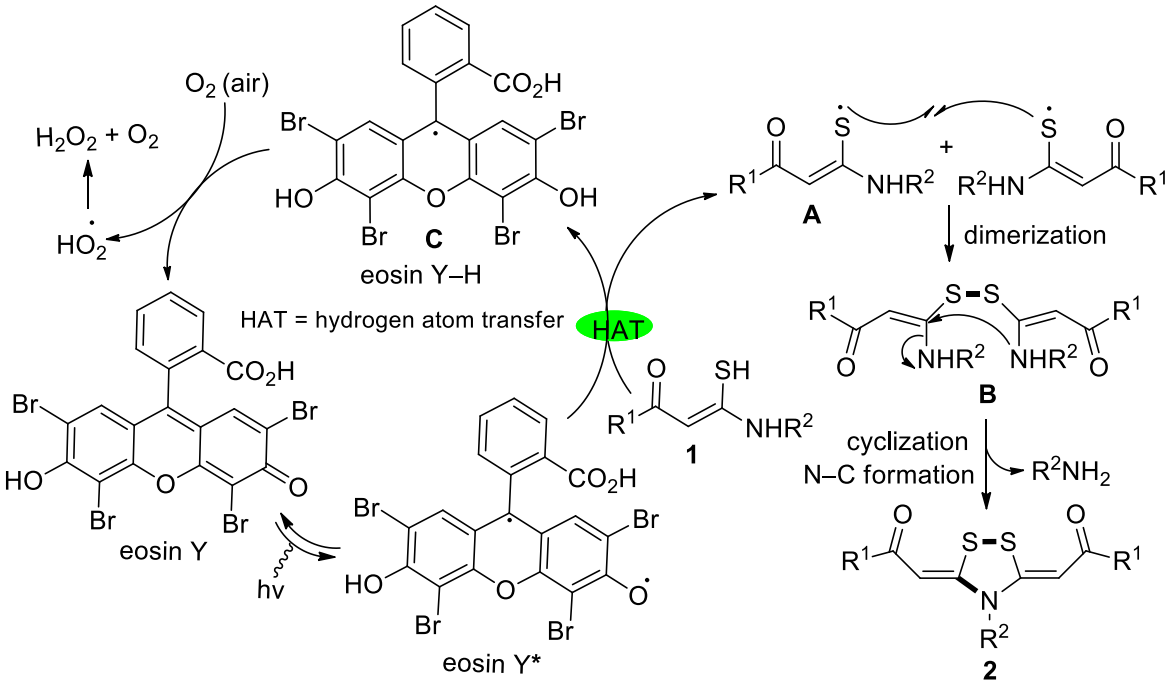
Scheme 4. A 3 mmol Scale Synthesis of 2k



Ensued by control experiments and literature reports,[4,20] the following plausible mechanism has been suggested (Scheme 5). The redox potential of Eosin Y indicated that it was not capable of oxidizing or reducing the substrate, since we obtained the potential of β-ketothioamide in the range of ($E_{1/2}$ = +1.4 V to $E_{1/2}$ = +1.6 V *vs* Ag/AgCl) in 0.1M TBAP/CH_3CN solution. The above values rule out SET mode for this reaction. Eosin Y (EY) is transformed into its excited state (EY*) by irradiation with visible-light, which abstract enethiol hydrogen from substrate **1** producing the radical intermediates **A** and **C**. The thiyl radical **A** undergoes dimerization to give disulfide tethered enamine intermediate **B**, which upon intramolecular deaminative cyclization enabled 1,2,4-dithiazolidine derivative **2**. The intermediate

C undergoes aerial oxidation to regenerate ground state (EY) and produced $HO_2^{\bullet}$ radical, which suffers disproportionation to give oxygen and hydrogen peroxide.[21] Thus, H_2O_2 formed was detected by potassium iodide (KI) and starch as indicator.[4c]

Scheme 5. Proposed Reaction Pathway



CONCLUSION

In conclusion, we have devised an efficient protocol to access highly functionalized 1,2,4-dithiazolidines bearing two exocyclic enone moieties at 3- and 5-positions *via* visible light-mediated oxidative symmetrical dimerizative of β-ketothioamides at room temperature. Remarkably, this strategy employing inexpensive Eosin Y dye as a hydrogen-atom transfer (HAT) photocatalyst and air as an oxidant is not only operationally simple, economic, eco-compatible, metal-/additive-free, but also exhibits excellent functional group compatibility with electron-rich/electron-deficient arenes and heteroarenes. No external redox mediators or prefunctionalization of the substrate is required. This strategy enables a decent alternative to access symmetrical 1,2,4-dithiazolidines to existing ones,

consequently, broadening the chemistry of ketothioamides. Overall, this Eosin Y dye based photocatalytic HAT strategy should be promising towards functionalization of a wide range of C–H, N–H and S–H bonds in a sustainable manner, and can allow to overcome traditional metal-catalyzed reactions, which are environmentally notorious.

EXPERIMENTAL SECTION

General Information. Unless otherwise mentioned, all commercially available solvents and reagents (procured from Merck, Aldrich, and Avra synthesis) were utilized as such without any purification. The β-ketothioamides were synthesized by reported procedure.[13,22] All the reactions were monitored by analytical thin layer chromatography (TLC) using Merck precoated aluminium sheets and visualized by UV lamp. Flash column chromatography was performed on silica gel (230-400 mesh). The ^{1}H and ^{13}C NMR spectra were recorded on JEOL 500 FT-NMR spectrometer operating at 500 and 125 MHz, respectively. Chemical shifts (δ) for ^{1}H and $^{13}C\{^{1}H\}$ NMR are given in parts per million (ppm) using the residual solvent peaks as reference relative to tetramethylsilane (TMS). Coupling constant (*J*) values are reported in Hz. Mass spectra were recorded on Agilent Q-TOF and Waters-Q-TOF Premier-HAB213 instrument. The green light irradiation was done using high-power LUXEON Rebel LEDs (λ = 530 nm, 161 lm @ 700mA). The power of each light is 1W. All the reactions were carried out using a round bottle (25 mL) borosilicate glass without special photochemical equipment. There is 8.0 cm distance between the reactor and LEDs. The melting points are uncorrected. Compound stereochemistry is supported by an X-ray crystallographic structure determination of one of the representative molecule **2a**.

General experimental procedure for compound 2: β-Ketothioamide **1** (0.25 mmol) and Eosin Y (2 mol %) were added to 2 mL of dimethyl formamide (DMF). The resulting mixture was stirred at room temperature in open air for 4 h under the irradiation of green LED (530 nm) placed 8 cm from the flask. After the completion of the reaction (monitored by TLC), the reaction mixture was quenched with water.

The aqueous layer was extracted with ethyl acetate followed by drying over anhydrous $MgSO_4$, and the solvent was evaporated under reduced pressure. The crude residue thus obtained was purified by flash column chromatography over silica gel (230-400 mesh) using ethyl acetate/hexane (20:80) as eluent to afford the desired pure dithiazolidine products **2** in good to excellent yields. Chemical yields refer to pure isolated compounds.

The spectral and analytical data of all the compounds are given as follows:

*(2Z,2'Z)-2,2'-(4-phenyl-1,2,4-dithiazolidine-3,5-diylidene)bis(1-phenylethanone) (**2a**)***:*** The product was obtained as yellow solid (76%, 39 mg); mp 200-201 ^oC; ^1H NMR (500 MHz, $CDCl_3$) δ 7.78-7.72 (m, 3H), 7.69 (d, J = 10.0 Hz, 4H), 7.47-7.42 (m, 4H), 7.37 (t, J = 7.5 Hz, 4H), 6.16 (s, 2H); ^{13}C $\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 185.8, 164.9, 138.2, 137.1, 131.6, 131.2, 130.6, 128.2, 127.67, 127.1, 96.7; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{18}NO_2S_2$ 416.0773; Found 416.0743.

*(2Z,2'Z)-2,2'-(4-phenyl-1,2,4-dithiazolidine-3,5-diylidene)bis(1-(p-tolyl)ethanone) (**2b**)*: The product was obtained as yellow solid (68%, 38 mg); mp 215-216 ^oC; ^1H NMR (500 MHz, $CDCl_3$) δ 7.77-7.70 (m, 3H), 7.58 (d, J = 5.0 Hz, 4H), 7.41 (d, J = 5.0 Hz, 2H), 7.16 (d, J = 10.0 Hz, 4H), 6.13 (s, 2H), 2.35 (s, 6H); ^{13}C $\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 185.6, 164.5, 142.4 134.5, 131.2, 130.5, 128.9, 127.7, 127.2, 96.6, 21.3; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{21}NO_2S_2Na$ 466.0906; Found 466.0906.

*(2Z,2'Z)-2,2'-(4-phenyl-1,2,4-dithiazolidine-3,5-diylidene)bis(1-(4-methoxyphenyl) ethanone) (**2c**)*: The product was obtained as yellow solid (66%, 39 mg); mp 224-225 ^oC; ^1H NMR (500 MHz, $CDCl_3$) δ 7.71-7.61 (m, 7H), 7.37 (d, J = 5.0 Hz, 2H), 6.81 (d, J = 10.0 Hz, 4H), 6.06 (s, 2H), 3.77 (s, 6H); ^{13}C $\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 185.3, 164.9, 163.0, 139.1, 131.8, 131.1, 130.5, 129.8, 128.4, 114.0, 97.0, 55.7; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{22}NO_4S_2$ 476.0985; Found 476.0991.

(2Z,2'Z)-2,2'-(4-phenyl-1,2,4-dithiazolidine-3,5-diylidene)bis(1-(4-fluorophenyl)ethanone) ***(2d)***: The product was obtained as yellow solid (78%, 44 mg); mp 220-221 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80-7.68 (m, 7H), 7.42 (d, J = 5.0 Hz, 2H), 7.04 (t, J = 10 Hz, 4H), 6.10 (s, 2H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 185.3, ,166.1, 165.8 (d, $^{1}J_{CF}$ = 251.25 Hz), 139.2, 134.4, 132.3, 131.7, 130.6 (d, $^{3}J_{CF}$ = 8.75 Hz), 128.6, 116.3 (d, $^{2}J_{CF}$ = 22.5 Hz), 97.4; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{15}F_2NO_2S_2Na$ 474.0404; Found 474.0404.

(2Z,2'Z)-2,2'-(4-phenyl-1,2,4-dithiazolidine-3,5-diylidene)bis(1-(4-chlorophenyl)ethanone) ***(2e)***: The product was obtained as pale yellow solid (78%, 47 mg); mp 275-276 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (t, J = 10.0 Hz, 3H), 7.62 (d, J = 10.0 Hz, 4H), 7.41 (d, J = 5.0 Hz, 2H), 7.33 (d, J = 5.0 Hz, 4H), 6.10 (s, 2H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 184.6, 165.5, 138.1, 135.5, 131.5, 130.9, 128.6, 127.7, 96.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{16}Cl_2NO_2S_2$ 483.9994 (^{35}Cl); Found 483.9995; Calcd for $C_{24}H_{16}Cl_2NO_2S_2$ 485.9970 (^{37}Cl); Found 485.9970.

(2Z,2'Z)-2,2'-(4-phenyl-1,2,4-dithiazolidine-3,5-diylidene)bis(1-(4-bromophenyl)ethanone) ***(2f)***: The product was obtained as yellow solid (76%, 54 mg); mp 238-239 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81-7.77 (m, 3H), 7.67 (s, 2H), 7.53 (d, J = 5.0 Hz, 2H), 7.42 (d, J = 5.0 Hz, 4H), 7.30 (t, J = 7.5 Hz, 2H), 6.10 (s, 2H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 184.5, 165.9, 139.0, 138.2, 134.7, 131.8, 131.7, 131.2, 129.8, 127.7, 127.5, 125.4, 96.7; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{16}Br_2NO_2S_2$ 571.8984 (^{79}Br); Found 571.8992; Calcd for $C_{24}H_{16}Br_2NO_2S_2$ 573.8969 (^{81}Br); Found 573.8973.

(2Z,2'Z)-2,2'-(4-phenyl-1,2,4-dithiazolidine-3,5-diylidene)bis(1-(4-(trifluoromethyl) phenyl)ethanone) ***(2g)***: The product was obtained as yellow solid (78%, 54 mg); mp 219-220 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80-7.76 (m, 7H), 7.63 (d, J = 5.0 Hz, 4H), 7.43 (d, J = 5.0 Hz, 2H), 6.16 (s, 2H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 184.8, 166.3, 140.4, 138.3, 133.5 (q $^{2}J_{CF3}$ = 32.5 Hz), 131.8,

131.3, 127.9, 127.8, 125.7, 125.6, 123.8 (q $^{1}J_{CF3}$ = 273.3 Hz), 97.1; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{16}F_6NO_2S_2$ 552.0521; Found 552.0544.

(2Z,2'Z)-2,2'-(4-phenyl-1,2,4-dithiazolidine-3,5-diylidene)bis(1-(3-bromophenyl)ethanone) ***(2h)***: The product was obtained as yellow solid (72%, 52 mg); mp 205-206 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79-7.71 (m, 5H), 7.53-7.51 (m, 4H), 7.37 (d, J = 10.0 Hz, 2H), 7.20-7.17 (m, 2H), 6.04 (s, 2H); ^{13}C $\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 184.3, 165.8, 139.0, 138.0, 134.6, 131.6, 131.0, 130.4, 129.9, 127.6, 125.7, 122.7, 96.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{16}Br_2NO_2S_2$ 571.8984 (^{79}Br); Found 571.8990; Calcd for $C_{24}H_{16}Br_2NO_2S_2$ 573.8969 (^{81}Br); Found 573.8976.

(2Z,2'Z)-2,2'-(4-phenyl-1,2,4-dithiazolidine-3,5-diylidene)bis(1-(m-tolyl)ethanone) ***(2i)***: The product was obtained as yellow solid (67%, 37 mg); mp 205-206 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78-7.71 (m, 3H), 7.56 (s, 2H), 7.42 (t, J = 7.5 Hz, 4H), 7.27-7.22 (m, 4H), 6.14 (s, 2H), 2.35 (s, 6H); ^{13}C$\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 186.1, 165.0, 138.2, 137.3, 132.6, 131.4, 130.7, 128.1, 127.9, 127.8, 124.3, 97.0, 21.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{22}NO_2S_2$ 444.1086; Found 444.1092.

(2Z,2'Z)-2,2'-(4-phenyl-1,2,4-dithiazolidine-3,5-diylidene)bis(1-(3-methoxyphenyl)ethanone) ***(2j)***: The product was obtained as yellow solid (67%, 40 mg); mp 223-224 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77-7.71 (m, 3H), 7.41 (d, J = 5.0 Hz, 2H), 7.35 (s, 2H), 7.25 (t, J = 7.5 Hz, 2H), 7.15 (d, J = 5.0 Hz, 2H), 6.99 (d, J = 5.0 Hz, 2H), 6.14 (s, 2H), 3.81 (s, 6H); ^{13}C $\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 185.8, 165.2, 159.8, 138.8, 138.4, 131.5, 130.9, 129.3, 127.9, 119.7, 118.3, 112.1, 97.1, 55.4; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{22}NO_4S_2$ 476.0985; Found 476.0985.

(2Z,2'Z)-2,2'-(4-phenyl-1,2,4-dithiazolidine-3,5-diylidene)bis(1-(2-chlorophenyl)ethanone) ***(2k)***: The product was obtained as yellow solid (82%, 50 mg); mp 225-226 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67-7.59 (m, 3H), 7.50 (d, J = 10.0 Hz, 2H), 7.37 (d, J = 10.0 Hz, 2H), 7.31-7.28 (m, 6H), 6.05 (s, 2H); ^{13}C $\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 186.8, 164.7, 138.3, 138.2, 131.5, 131.4, 131.4, 130.9, 130.5,

130.2, 127.9, 127.0, 101.4; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{16}Cl_2NO_2S_2$ 483.9994 (^{35}Cl); Found 483.9993; Calcd for $C_{24}H_{16}Cl_2NO_2S_2$ 485.9970 (^{37}Cl); Found 485.9968.

(2Z,2'Z)-2,2'-(4-phenyl-1,2,4-dithiazolidine-3,5-diylidene)bis(1-(o-tolyl)ethanone) ***(2l)***: The product was obtained as yellow solid (68%, 38 mg); mp 224-225 ^oC; ^1H NMR (500 MHz, $CDCl_3$) δ 7.67-7.58 (m, 3H), 7.35 (d, J = 5.0 Hz, 2H), 7.28-7.25 (m, 4H), 7.17-7.12 (m, 4H), 5.86 (s, 2H), 2.41 (s, 6H); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$) δ 190.2, 164.3, 138.9, 138.5, 137.1, 131.5, 131.4, 130.8, 130.3, 127.9, 127.8, 125.7, 100.7, 20.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{22}NO_2S_2$ 444.1086; Found 444.1080.

(2Z,2'Z)-2,2'-(4-phenyl-1,2,4-dithiazolidine-3,5-diylidene)bis(1-(2-methoxyphenyl)ethanone) ***(2m)***: The product was obtained as yellow solid (67%, 40 mg); mp 224-225 ^oC; ^1H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, J = 10.0 Hz, 2H), 7.71-7.62 (m, 3H), 7.42-7.34 (m, 4H), 6.98 (t, J = 7.5 Hz, 2H), 6.82 (d, J = 10.0 Hz, 2H), 6.46 (s, 2H), 3.58 (s, 6H); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$) δ 185.2, 163.8, 158.0, 139.3, 132.8, 131.0, 130.9, 130.1, 128.3, 127.2, 120.8, 111.6, 102.6, 55.1; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{22}NO_4S_2$ 476.0985; Found 476.0981.

(2Z,2'Z)-2,2'-(4-phenyl-1,2,4-dithiazolidine-3,5-diylidene)bis(1-([1,1'-biphenyl]-4-yl)ethanone) ***(2n)***: The product was obtained as white solid (67%, 47 mg); mp 248-249 ^oC; ^1H NMR (500 MHz, $CDCl_3$) δ 7.75-7.70 (m, 7H), 7.53 (t, J = 7.5 Hz, 8H), 7.41-7.37 (m, 6H), 7.33-7.30 (m, 2H), 6.15 (s, 2H); ^{13}C {^1H} NMR (125 MHz, $CDCl_3$) δ 185.4, 165.0, 144.5, 139.9, 138.4, 136.0, 131.4, 130.8, 128.8, 127.8, 127.0, 96.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{36}H_{26}NO_2S_2$ 568.1399; Found 568.1398.

(2Z,2'Z)-2,2'-(4-phenyl-1,2,4-dithiazolidine-3,5-diylidene)bis(1-(naphthalen-1-yl)ethanone) ***(2o)***: The product was obtained as pale yellow solid (65%, 42 mg); mp 254-255 ^oC; ^1H NMR (500 MHz, $CDCl_3$) δ 8.44 (d, J = 5.0 Hz, 2H), 7.88 (d, J = 10.0 Hz, 2H), 7.83 (d, J = 5.0 Hz, 2H), 7.64 (t, J = 7.5

Hz, 2H), 7.58-7.48 (m, 8H), 7.41-7.39 (m, 3H), 6.03 (s, 2H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 189.5, 164.6, 136.8, 133.6, 131.3, 131.1, 130.7, 130.1, 128.1, 127.6, 127.0, 126.2, 126.2, 125.6, 124.4, 101.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{32}H_{22}NO_2S_2$ 516.1086; Found 516.1115.

(2Z,2'Z)-2,2'-(4-phenyl-1,2,4-dithiazolidine-3,5-diylidene)bis(1-(pyridin-3-yl)ethanone) ***(2p)***: The product was obtained as yellow solid (66%, 34 mg); mp 198-199 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.89 (s, 2H), 8.72 (d, *J* = 5.0 Hz, 2H), 8.11 (d, *J* = 5.0 Hz, 2H), 7.83 (t, *J* = 10.0 Hz, 4H), 7.49 (d, *J* = 5.0 Hz, 3H), 6.22 (s, 2H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 183.0, 151.2, 147.4, 139.1, 134.3, 130.9, 126.7, 122.8, 119.5, 119.1, 96.9; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{22}H_{16}N_3O_2S_2$ 418.0678; Found 418.0677.

(2Z,2'Z)-2,2'-(4-phenyl-1,2,4-dithiazolidine-3,5-diylidene)bis(1-(thiophen-2-yl)ethanone) ***(2q)***: The product was obtained as yellow solid (70%, 37 mg); mp 201-202 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77-7.70 (m, 3H), 7.49 (d, *J* = 5.0 Hz, 2H), 7.41 (d, *J* = 5.0 Hz, 2H), 7.33 (d, *J* = 3.5 Hz, 2H), 7.01 (t, *J* = 5.0 Hz, 2H), 5.98 (s, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 179.0, 164.1, 144.0, 138.1, 131.8, 131.3, 130.8, 129.2, 127.9, 127.8, 96.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{14}NO_2S_4$ 427.9902; Found 427.9869.

(2Z,2'Z)-2,2'-(4-phenyl-1,2,4-dithiazolidine-3,5-diylidene)bis(1-(furan-2-yl)ethanone) ***(2r)***: The product was obtained as brown (69%, 34 mg); mp 204-205 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76-7.70 (m, 3H), 7.40 (d, *J* = 10.0 Hz, 4H), 7.02 (d, *J* = 5.0 Hz, 2H), 6.44 (d, *J* = 5.0 Hz, 2H), 6.05 (s, 2H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 175.6, 164.3, 152.7, 145.1, 138.3, 131.5, 130.9, 129.3, 128.0, 118.6, 115.1, 114.9, 112.4, 96.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{14}NO_4S_2$ 396.0359; Found 396.0357.

(2Z,2'Z)-2,2'-(4-phenyl-1,2,4-dithiazolidine-3,5-diylidene)bis(1-cyclopropylethanone) ***(2s)***: The product was obtained as greenish yellow (46%, 20 mg); mp 236-237 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ

7.71-7.63 (m, 3H), 7.31 (d, *J* = 5.0 Hz, 2H), 5.56 (s, 2H), 1.67-1.63 (m, 2H), 1.04 (s, 4H), 0.80-0.78 (m, 4H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 195.5, 162.0, 138.5, 131.3, 130.6, 128.0, 100.0, 20.2, 10.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{18}H_{18}NO_2S_2$ 344.0773; Found 344.0772.

*(2Z,2'Z)-2,2'-(4-(3-chlorophenyl)-1,2,4-dithiazolidine-3,5-diylidene)bis(1-(p-tolyl)ethanone)(**2t**):*

The product was obtained as yellow (58%, 35 mg); mp 220-221 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 5.0 Hz, 2H), 7.60 (d, *J* = 5.0 Hz, 4H), 7.46 (s, 1H), 7.36 (s, 1H), 7.18 (d, *J* = 5.0 Hz, 4H), 6.12 (s, 2H), 2.36 (s, 6H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 185.9, 164.3, 142.7, 139.5, 136.9, 134.6, 132.4, 131.2, 129.2, 128.5, 127.5, 126.4, 96.8, 21.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{21}ClNO_2S_2$ 478.0697 (^{35}Cl); Found 478.0703; Calcd for $C_{26}H_{21}ClNO_2S_2$ 480.0673 (^{37}Cl); Found 480.0666.

*(2Z,2'Z)-2,2'-(4-(4-methoxyphenyl)-1,2,4-dithiazolidine-3,5-diylidene)bis(1-(p-tolyl)ethanone)(**2u**):*

The product was obtained as yellow (65%, 38 mg); mp 224-225 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 10.0 Hz, 4H), 7.30 (d, *J* = 10.0 Hz, 2H), 7.20 (d, *J* = 10.0 Hz, 3H), 7.16 (d, *J* = 10.0 Hz, 3H), 6.17 (s, 2H), 3.98 (s, 3H), 2.35 (s, 6H); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$) δ 185.9,165.2, 160.8, 142.5, 134.8, 130.9, 129.1, 129.1, 127.5, 116.4, 96.9, 55.7, 21.5; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{24}NO_3S_2$ 474.1192; Found 474.1199.

ASSOCIATED CONTENT

Supporting Information

Copies of ^{1}H, $^{13}C\{^{1}H\}$ NMR spectra (PDF), X-ray crystallographic data (CIF) and cyclic voltamogram of thioamides. The Supporting Information is available free of charge on the ACS Publications website.

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Notes

The authors declare no competing financial interest.

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