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Authors: Umesh A. Kshirsagar, Shrikant D. Tambe, and Rajendra S. Rohokale

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Visible Light Mediated Eosin Y Photo-redox Catalyzed Vicinal Thioamination of Alkynes: Radical Cascade Annulation Strategy for 2-Substituted-3-sulfenylindoles

Shrikant D. Tambe[a] Rajendra S. Rohokale[a,b] and Umesh A. Kshirsagar*[a]

Dedication ((optional))

Abstract: Organic dye photo-redox catalyzed regio-specific radical cascade annulation strategy of 2-alkynyl-azidoarenes to generate important scaffold; 3-sulfenylindoles via vicinal thioamination of alkynes at room temperature, mediated by visible light was developed. The method requires mild condition such as visible light as a traceless green energy source, room temperature, eosin Y organic dye as a photo-redox catalyst, ambient air as oxidant and easily available starting materials thus provide green, efficient, metal and strong oxidant-free synthesis of 3-sulfenylindoles with broad substrate scope through vicinal thioamination of alkynes.

Introduction

Over the past decade, visible light mediated photo-redox catalysis for single electron transfer (SET) has been emerged as an alternative, green, economical, practical and versatile tool for important organic transformations such as oxidation/reduction, C-C bond formation and importantly carbon-heteroatom bond formation.[1] Visible light photoredox catalysis becomes great alternative not only for classical synthetic methods but also for photochemical and electro-chemical reaction since these methods suffer from cost-effectiveness and some limitations such as by-products formation, a requirement of a specially designed set-up. Hence photoredox catalysis has become the most attractive and powerful approach in contemporary organic synthesis. In this context, metal-based photo-redox catalyst such as Ir, Ru and organic dyes photo-redox catalysts such as eosin-Y, rose-bengal, rhodamine have been applied.[2,3] Recently, organic dyes have received increased attention due to cost effectiveness and non-toxicity in comparison to metal based photo-catalysts.

Substituted indoles are important and versatile motif due to its increased importance in medicinal and pharmaceutical chemistry as well as its dominance in several natural products.[4] Of particularly, 2-Substituted-3-sulfenylindoles have attracted significant attention due to their potent biological activities and their therapeutic interest such as in the treatment of cancer, HIV, heart disease, obesity, bacterial infection, and allergies.[5] For example, 5-lipoxygenase inhibitor and anticancer agent MK-886 (**I**), human breast cancer cell growth inhibitor and tubulin

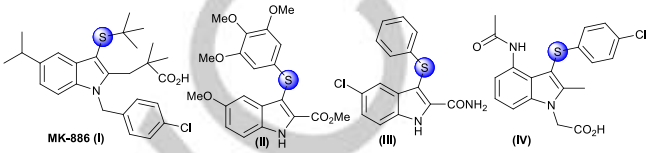
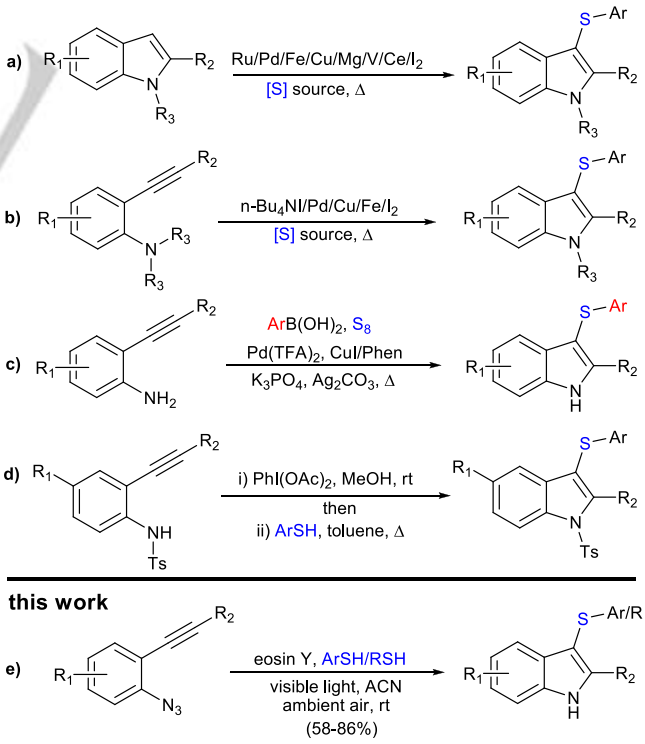


Figure 1. Some biologically active 3-sulfenylindoles.

polymerization inhibitor 3- sulfenylindoal (**II**), selective CRTh2 antagonist (**IV**) (Figure 1). Consequently, considerable synthetic efforts have been reported for the synthesis of this scaffold. Due to the electron- rich nature of indole ring at third position, majority approaches are focused on direct C_3−H sulfenylation of indole ring catalyzed by metal such as ruthenium, iron, copper, magnesium, vanadium, cerium with suitable sulfur source and under transition metal free conditions such as iodine with activated sulfur reagents (Scheme 1, a).[6] Another strategy for these compounds is electrophilic annulations of 2-alkynyl-aniline derivatives (Scheme 1, b).[7] Such as Larock et al. reported a



Scheme 1. Synthesis of 2-substituted-3-sulfenylindoles.

[a] Department of Chemistry, Savitribai Phule Pune University (Formerly: University of Pune), Pune 411007, India.
E-mail: uakshirsagar@gmail.com, uakshirsagar@chem.unipune.ac.in
[b] CSIR-National Chemical Laboratory, Division of Organic Chemistry, Dr. Homi Bhabha Road, Pune - 411008, India.

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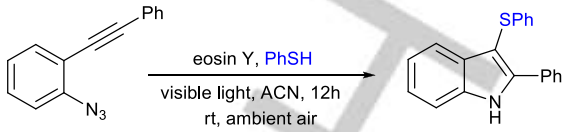
novel approach to the synthesis of 3-sulfenylindoles from N,N-dialkyl-2-alkynyl-anilines via TBAI mediated electrophilic cyclization with arylsulfenyl chloride.[7a,b] Li et al developed palladium and iron/I_2 catalyzed electrophilic annulation of 2-alkynyl-anilines and N,N-dialkyl-2-alkynyl-anilines respectively with disulfide for the synthesis of 3-sulfenylindoles.[7c,d] Zhou et al developed copper catalyzed strategy from 2-alkynyl-anilines.[7e] Tao et al.[7f] and Kuhkarn et al.[7g] disclosed iodine promoted electrophilic cyclization of 2-alkynyl-aniline and N,N-dialkyl-2-alkynyl-anilines respectively to construct 3-sulfenylindoles. Recently, Jiang and co-workers developed palladium catalyzed arylthiolation of 2-alkynyl-anilines in presence of CuI/Phenathroline with arylboronic acid and S_8 (Scheme 1, c).[8] Fan and co-workers reported $PhI(OAc)_2$ mediated one pot two-step approach involving an oxidative nucleophilic cyclization of 2-alkynyl-aniline with thiophenols (Scheme 1, d).[9] In the report by Montevecchi and co-workers on the study of vinyl radical cyclization onto the azido group, preparation of one compound (**3a**) was found which was prepared by refluxing corresponding azido compound in benzene in the presence of AIBN.[10] In spite of these, development of alternative, practical and environmentally friendly approach for 2-substituted-3-sulfenylindoles is still desirable. In continuation of our efforts to develop simple, cheap, sustainable and green methods for the construction of bioactive compounds,[11] herein we would like to report mild and convenient, visible light mediated, organic dye photoredox catalyzed vicinal thioamination of alkyne and cascade annulation strategy for 2-substituted-3-sulfenylindoles from 2-alkynyl-azidoarenes.

Results and Discussion

Optimization of the reaction conditions was commenced with the reaction between 1-azido-2-(phenylethynyl)benzene **1a** (1.0 equiv.) and thiophenol **2a** (1.5 equiv.) which was performed at room temperature in the presence of 5 mol% eosin Y as photocatalysts in an ambient air atmosphere. When dichloromethane (DCM) was used as a solvent (entry 1, Table 1) after 12h irradiation at room temperature, formation of **3a** was observed in 42% yield. With this encouragement, the reaction was studied by varying the solvents systems (entries 1-7). When THF was used as a solvent, it afforded **3a** in 61% yield (entry 2). Formation of **3a** was observed in 75% yield when the reaction was performed in acetonitrile (entry 3). When methanol was used as a solvent, yield was dropped to 20% (entry 4). Product formation was not observed in the solvent DMF and DMSO (entry 5 and 6). Various photo-redox catalysts were screened (entries 7-11). Na_2-Eosin Y afforded slightly lower yield (68%, entry 7) whereas rose-bengal gave 46% yield of **3a** (entry 8). Similarly, no improvement in the yield of **3a** was observed when other photo-catalysts were used such as Acr-Mes^+ (49%, entry 9), $Ru(bpy)_3Cl_2$ (27%, entry 10) and $Ir(ppy)_3$ (55%, entry 11). Effect of equivalents of thiophenol on reaction yield was studied and observed that when 1.0 equivalent of thiophenol (entery 12) was used, **3a** was isolated in 32% along with unreacted starting material **1a**. Use of 2.0 equivalent of thiophenol (entry 13) gave 37% of **3a** along with some unidentified side products. When a

Table 1. Optimization Studies of the reaction[a,b].

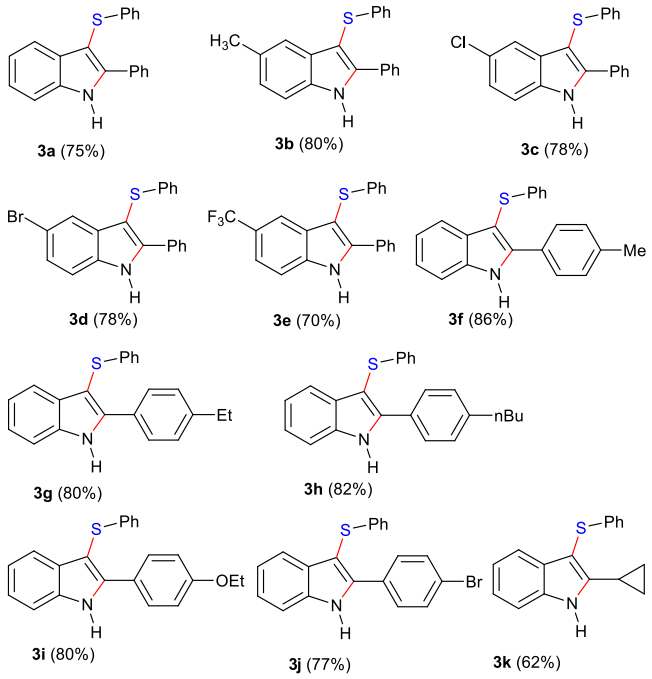


1a **3a**

entry	photo-catalyst	solvents	yield (%)[b]
1	Eosin Y	DCM	42
2	Eosin Y	THF	61
3	Eosin Y	CH_3CN	75
4	Eosin Y	CH_3OH	20
5	Eosin Y	DMF	trace
6	Eosin Y	DMSO	trace
7	Na_2-Eosin Y	CH_3CN	68
8	Rose Bengal	CH_3CN	46
9	Acr-Mes^+	CH_3CN	49
10	$Ru(bpy)_3Cl_2$	CH_3CN	27
11	$Ir(ppy)_3$	CH_3CN	55
12[c]	Eosin Y	CH_3CN	32
13[d]	Eosin Y	CH_3CN	37
14[e]	Eosin Y	CH_3CN	10
15[f]	Eosin Y	CH_3CN	56

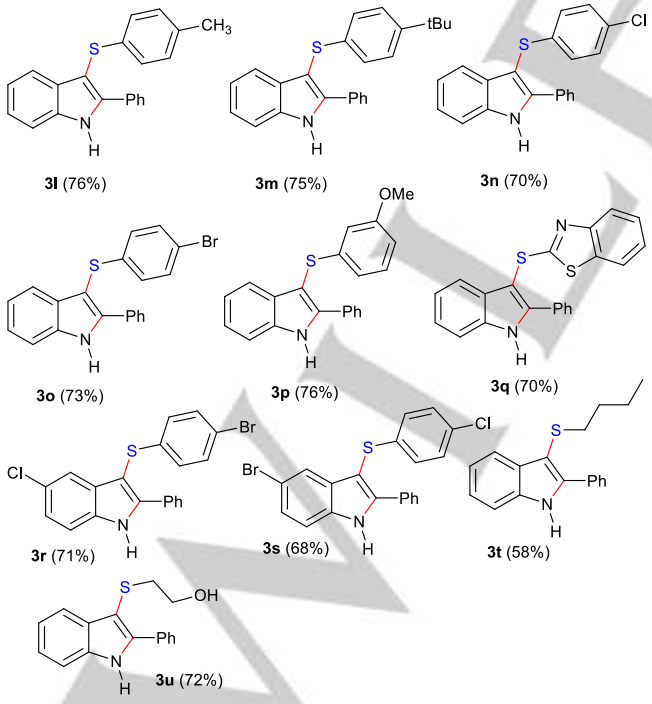
[a]Reaction conditions: **1a** (0.114 mmol), **2a** (0.171 mmol), photo-catalyst (5 mol %), solvent (1.5 mL), ambient air, blue LED, rt, 12h. [b]Isolated yield. [c]1.0 equiv. of **2a** was used. [d]2.0 equiv. of **2a** was used. [e]under N_2. [f]under oxygen atmosphere.

reaction was carried out under nitrogen atmosphere only 10% yield of **3a** was isolated with recovered starting material **1a** (entry 14). When reaction was performed under oxygen atmosphere, no further improvment in the yield was observed (56%, entry 15). With these optimized reaction conditions in hand, the substrate scope of 2-alkynyl-azidoarenes and thiophenols were examined (Scheme 2/3). Several 2-alkynyl-azidoarenes were prepared using the literature procedure[12] and reacted with benzene thiol (**2a**). The reaction was effectively amenable to a wide range of substrate scope of 2-phenylethynyl aryl azides (**1a-e**) such as methyl, chloro, bromo and trifluoromethyl to provide the desired 3-sulfenylindoles **3a-e** in 70-80% yields. The scope of azido benzenes with aryl alkynyl was further investigated. A range of arylethynyl i.e., *p*-Me, *p*-Et, *p*-^{n}Bu, *p*-Br, *p*-OEt proceeded fine in the reaction to provide the corresponding 3-sulfenylindoles products **3f-j** in very good yields (77-86%). Azidobenzenes of alkynyl with ethynylcyclopropane (**1k**) was reacted with benzene thiol under the optimized condition, provided corresponding product **3k** in 62% yield. Next, the scope of aryl thiols was explored. A variety of thiophenols were applied under the optimized reaction condition with 1-azido-2-(phenylethynyl)benzene **1a** (Scheme 3). Aryl thiols such as *p*-Me, *p*-^{t}Bu, *p*-Cl, *p*-Br, *m*-OMe proceeded smoothly to deliver the products **3l-p** in 73-76% yields. Interestingly, the



Scheme 2. Scope of 2-Alkynyl Arylazides. Reaction conditions: **1** (0.114 mmol), **2** (0.171 mmol), eosin Y (5 mol %), CH_3CN (1.5 mL), ambient air, blue LED, rt, 12h.

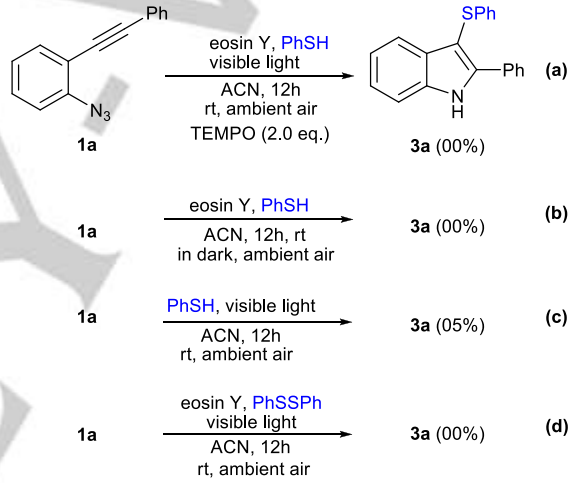
benzothiazole-2-thiols also worked well and afforded the targeted products **3q** in 70% yield. In view of chemo-selective functionalization in either ring, 3-sulfenylindoles with chloro and bromo groups on two different aromatic rings were prepared (**3r**



Scheme 3. Scope of thiols. Reaction conditions: **1** (0.114 mmol), **2** (0.171 mmol), eosin Y (5 mol %), CH_3CN (1.5 mL), ambient air, blue LED, rt, 12h.

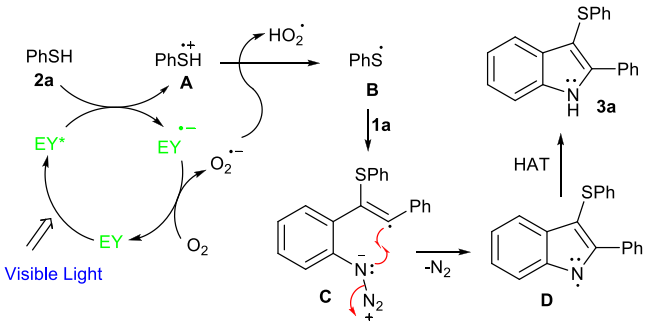
and **3s**) in 71 and 68% yields. When aliphatic thiols such as butane-1-thiol and 2-mercaptoethan-1-ol were treated with 1-azido-2-(phenylethynyl)benzene, the corresponding products **3t** and **3u** were formed in good yields (58 and 72%, respectively).

Some control experiments were carried out to have mechanistic insight in the reaction. When the reaction was performed under the standard condition in the presence of classical radical inhibitor TEMPO, the formation of product was not observed and starting material **1a** was recovered which suggest radical pathway involved in the reaction (Scheme 4, eq. a). In absence of visible light (eq. b), no product formation was observed whereas in absence of photo-redox catalysts (eq. c) only 5% of product was obtained, which suggests the necessity of photoredox catalyst and visible light for the reaction to occur. Under the nitrogen atmosphere reaction afforded only 10% of **3a** with recovered **1a** (table 1, entry 14) which suggest the necessity of oxygen for the reaction. When the reaction was performed with diphenyldisulfide instead of thiophenol, the formation of **3a** was not observed (eq. d).



Scheme 4 Control experiment

From above control experiments and the literature[13] following plausible radical cascade reaction pathway has been suggested (Scheme 5). Visible light mediated photo-excitation of Eosin Y (**EY**) produces Eosin Y (**EY***). One electron oxidation of thiophenol by this excited state **EY*** affords radical species (**A**) with reduction of **EY*** to **EY**$^{\bullet-}$ which could re-oxidized to its



Scheme 5 A plausible mechanism pathway

ground state by air oxygen to EY and $O_2^{\bullet-}$. Deprotonation of radical **A** gives radical **B**. Regioselective addition of radical **B** on the triple bond of **1a** gives radical intermediate **C**. Intramolecular radical cyclization and release of N_2 from intermediate **C** delivers *N*-centered radical intermediate **D**. Hydrogen radical transfer from hydrogen source present in the reaction mixture provides **3a**.

Conclusions

In summary, an efficient and mild photo-redox catalyzed, visible light induced radical cascade annulation strategy via vicinal thioamination of alkyne for the synthesis of 3-sulfenylindoles using organic dye as photo-redox catalyst and air as mild and greenest oxidant has been developed. Reaction does not require any sacrificial acceptor or donor and proceed at room temperature.

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Keywords: Photoredox catalysis • Organic dye • 3-sulfenylinodles • visible light • cascade annulation

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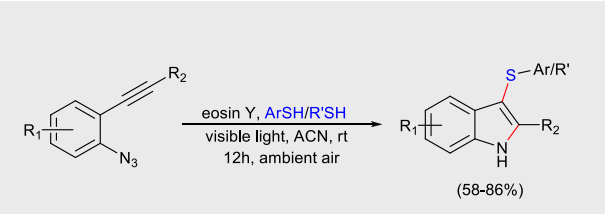

An efficient, mild and metal free, radical cascade annulation strategy for 2-substituted-3-sulfenylindoles from 2-alkynyl-azidoarenes via vicinal thioamination of alkyne catalyzed by eosin Y photoredox catalyst mediated by visible light in the presence of air as mild oxidant.

Key Topic* Photo-redox catalysis

*Shrikant D. Tambe, Rajendra S. Rohokale and Umesh A. Kshirsagar**

Page No. – Page No.

Visible Light Mediated Eosin Y Photo-redox Catalyzed Vicinal Thioamination of Alkynes: Radical Cascade Annulation Strategy for 2-Substituted-3-sulfenylindoles