

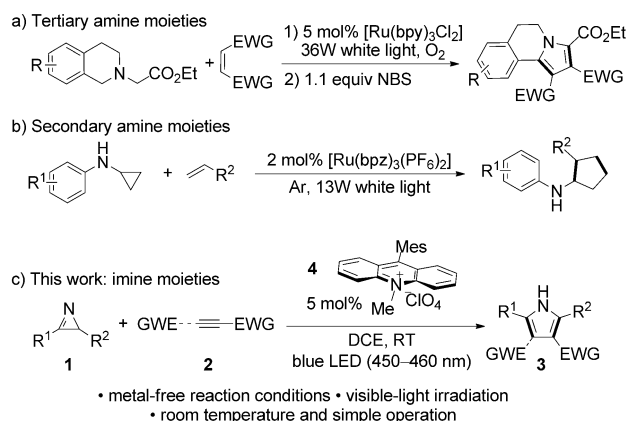
Heterocycle Synthesis

Visible-Light-Induced Formal [3+2] Cycloaddition for Pyrrole Synthesis under Metal-Free Conditions**

Jun Xuan, Xu-Dong Xia, Ting-Ting Zeng, Zhu-Jia Feng, Jia-Rong Chen, Liang-Qiu Lu,* and Wen-Jing Xiao*

Abstract: A photocatalytic formal [3+2] cycloaddition of 2*H*-azirines with alkynes has been achieved under irradiation by visible light in the presence of organic dye photocatalysts. This transformation provides efficient access to highly functionalized pyrroles in good yields and has been applied to the synthesis of drug analogues. A primary trial of photocascade catalysis merging energy transfer and redox neutral reactions was shown to be successful.

Photoredox catalysis driven by visible light has recently emerged as a flourishing research area owing to its inherent features of green chemistry and sustainability.^[1] In this context, visible-light-induced photocatalytic cycloadditions have been successfully achieved for the synthesis of structurally diverse carbo- and heterocyclic molecules.^[2] Surprisingly, however, [3+2] cycloaddition reactions proceeding through a photocatalytic amine oxidation process has received less attention. In 2011, our group^[3] and the group of Rueping^[4] independently disclosed a photocatalytic oxidation/[3+2] cycloaddition/oxidative aromatization sequence in which a metal photosensitizer catalyzed the generation of azomethine ylides from tertiary amine moieties (Scheme 1a). In addition, Zheng and co-workers elegantly developed a [3+2] cycloaddition of cyclopropylamines with olefins in the presence of a ruthenium complex and visible light, thus furnishing various cyclopentane derivatives in good yields (Scheme 1b).^[5] Despite the advances, further exploration of



Scheme 1. Visible-light-induced photocatalytic [3+2] cycloadditions. bpy = 2,2'-bipyridine, bpz = 2,2'-bipyrazine, EWG = electron-withdrawing group, DCE = 1,2-dichloroethane, NBS = *N*-bromosuccinimide.

photocatalytic cycloaddition reactions employing non-tertiary amine precursors and avoiding the use of precious metal catalysts is a highly desirable, yet challenging goal.

Polysubstituted pyrroles constitute an important family of five-membered N-containing heterocycles with diverse biological properties and synthetic applications.^[6] Not surprisingly, great efforts have been devoted to the development of practical, atom- and step-economic approaches to the pyrrole architecture.^[7] In particular, the exploitation of novel reagents and strategies has led to pyrrole syntheses using mild conditions and exhibiting good functional-group tolerance. Recently, 2*H*-azirines (**1**) were established as highly valuable synthetic intermediates for constructing different azacyclic compounds, usually by using transition-metal catalysts or UV light irradiation.^[8] From the viewpoint of green chemistry, it is significant to update the synthetic transformation of 2*H*-azirines under operationally simple and environmentally friendly conditions. As part of our ongoing research interests in developing new methods for the synthesis of carbo- and heterocycles by visible-light photoredox catalysis,^[9] we report herein a novel visible-light-induced [3+2] cycloaddition reaction of the 2*H*-azirines **1** with activated alkynes **2** (Scheme 1c). The method provides an efficient route to various polysubstituted pyrroles under very mild reaction conditions (visible-light irradiation, metal-free, and room temperature).

Initially, the formal [3+2] cycloaddition reaction was investigated under irradiation from a 3 W white LED light by using 2,3-diphenyl-2*H*-azirine (**1a**) and dimethyl but-2-yne-

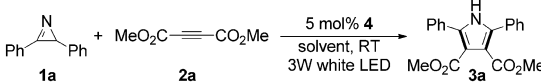
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dioate (**2a**) as model substrates. In terms of the relatively high oxidative potential of **1a** (+1.65 V),^[8d] 9-mesityl-10-methyl-acridinium perchlorate (**4**)^[10] was strategically chosen as the photoredox catalyst because of its high oxidizing power in the excited state (+2.06 V)^[11] and strong absorption band in the visible region.^[12] As shown in Table 1, either none or only

Table 1: Optimization of reaction conditions.^[a]

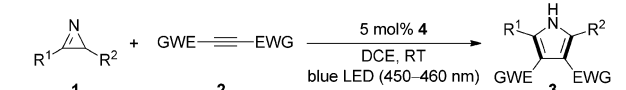
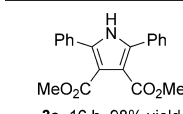
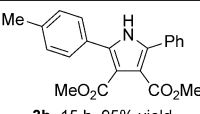
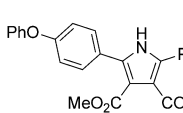
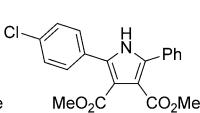
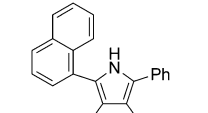
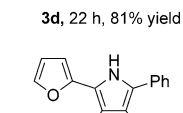
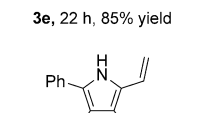
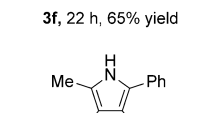
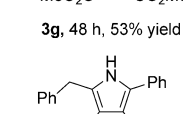
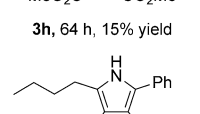
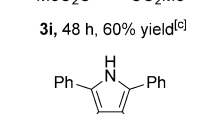
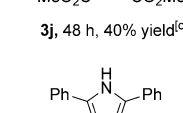
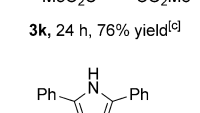
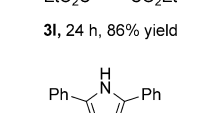
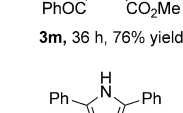
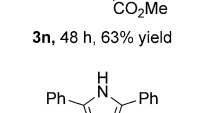
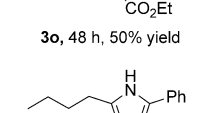
			
Entry	Solvent	t [h]	Yield [%] ^[b]
1	DMF	48	0
2	DMSO	48	0
3	MeOH	48	16
4	CH ₃ CN	48	57
5	DCE	48	61
6	CH ₂ Cl ₂	48	49
7	THF	48	25
8	CHCl ₃	48	40
9 ^[c,d]	DCE	16	98
10 ^[e]	DCE	24	0
11 ^[f]	DCE	24	0
12 ^[g]	DCE	48	0
13 ^[h]	DCE	48	0

[a] Unless otherwise noted, reaction conditions are as follows: **1a** (0.3 mmol), **2a** (1.5 mmol), photocatalyst (5 mol%), solvent (3 mL), 3 W white LED, at room temperature. [b] Yield of the isolated product. [c] 7 W blue LED (450–460 nm) was used. [d] The quantum yield was 0.066. [e] [Ru(bpy)₃Cl₂·6H₂O] was used. [f] [Ir(ppy)₂(dtbbpy)]PF₆ was used. [g] In the absence of photoredox catalyst. [h] In the absence of light source. DMF = *N,N*-dimethylformamide, DMSO = dimethylsulfoxide, THF = tetrahydrofuran.

16% yield of desired cycloaddition product **3a** was obtained when the reaction was performed in polar solvents such as DMF, DMSO, and MeOH (Table 1, entries 1–3). Further investigation revealed that the yield of **3a** could be improved to 57% when using CH₃CN as the reaction media (Table 1, entry 4). To our delight, DCE gave slightly better results than CH₃CN (Table 1, entry 5). Note that the reaction proceeded less efficiently in other solvents, including CH₂Cl₂, THF, and CHCl₃ (Table 1, entries 6–8). Importantly, the light source had a significant effect on the reaction efficiency. When a blue LED was used, the yield of isolated **3a** was dramatically improved and the reaction time was shortened to 16 hours (Table 1, entry 9). Note that this [3+2] cycloaddition process did not occur when transition-metal complexes, such as [Ru(bpy)₃Cl₂·6H₂O] or [Ir(ppy)₂(dtbbpy)]PF₆ were used as photocatalysts (Table 1, entries 10 and 11). Control experiments revealed that no reaction occurred in the absence of either the light source or the photoredox catalyst (Table 1, entries 12 and 13).

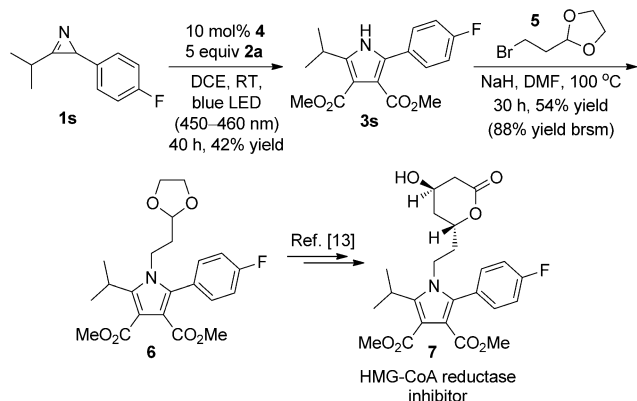
Under the optimal reaction conditions, the substrate scope of this photocatalytic [3+2] cycloaddition process was examined. As highlighted in Table 2, various substituents on the phenyl ring of **1** did not influence the catalytic efficiency. Both electron-donating (Me, OMe, PhO) and the electron-withdrawing (Cl) groups could be successfully introduced,

Table 2: Optimization of the reaction conditions.^[a,b]

		
 3a , 16 h, 98% yield	 3b , 15 h, 95% yield	 3c , 15 h, 91% yield
 3d , 22 h, 81% yield	 3e , 22 h, 85% yield	 3f , 22 h, 65% yield
 3g , 48 h, 53% yield	 3h , 64 h, 15% yield	 3i , 48 h, 60% yield ^[c]
 3j , 48 h, 40% yield ^[c]	 3k , 24 h, 76% yield ^[c]	 3l , 24 h, 86% yield
 3m , 36 h, 76% yield	 3n , 48 h, 63% yield	 3o , 48 h, 50% yield
 3p , 48 h, 58% yield	 3q , 16 h, 65% yield	 3r , 48 h, 31% yield ^[c,d]

[a] Unless otherwise noted, the reaction conditions are as follows: **1** (0.3 mmol), **2** (1.5 mmol), photocatalyst (5 mol%), DCE (3 mL), 7 W blue LED (450–460 nm), at room temperature. [b] Yield of the isolated product. [c] CH₃CN (3 mL) was used as reaction media. [d] Regioselectivity was 6.5:1.

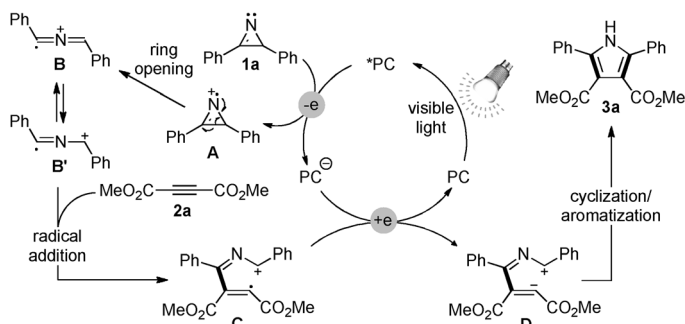
thus giving the corresponding polysubstituted pyrroles **3b–e** in excellent yields. Moreover, this reaction is also quite tolerant with respect to other functional groups, such as naphthyl, furyl, vinyl, and different kinds of alkyl groups (**3f–k**). More importantly, significant structural variation in the electron-deficient alkyne component can be realized. Both diethyl but-2-ynedioate (**2l**) and methyl 4-oxo-4-phenylbut-2-ynoate (**2m**) reacted well with **1a** to afford the corresponding tetrasubstituted pyrroles **3l** (86%) and **3m** (76%), respectively. In addition, the activated alkynes can be successfully extended to terminal alkynes. It was found that methyl and ethyl propiolate, but-3-yn-2-one, and propiolonitrile were all suitable substrates, thus providing the corresponding 3-ester, 3-keto, and 3-cyano substituted pyrroles (**3n–q**) in good yields. To our delight, the reaction showed good regioselectivity when two nonsymmetric components were involved. For instance, the reaction of the *2H*-azirine **2k** with methyl propiolate gave the corresponding pyrrole **3r** and its regioisomer with 6.5:1 regioselectivity, albeit with moderate yield.



Scheme 2. Formal synthesis of the HMG-CoA reductase inhibitor **7**.

To further demonstrate the synthetic utility of this photocatalytic formal [3+2] cycloaddition, a formal synthesis of the HMG-CoA reductase inhibitor **7** was performed (Scheme 2).^[13] In the presence of the organic dye photocatalyst **4**, the 2*H*-azirine **1s** reacted with **2a** to give the cycloaddition product **3s** in moderate yield under irradiation by a blue LED for 40 hours. Subsequently, the S_N2 substitution reaction of **3s** with 2-(2-bromoethyl)-1,3-dioxolane gave the fully substituted pyrrole **6** in 54% yield upon isolation, a compound which is the key synthetic intermediate to the target molecule **7**.^[13] This operationally simple process reveals that biologically important drug candidates can be rapidly accessed by using this unprecedented visible-light-induced formal [3+2] cycloaddition reaction as the key step.

A plausible reaction mechanism is proposed to illustrate the redox neutral reaction process (Scheme 3). The single-electron oxidation of the 2*H*-azirine in the presence of the

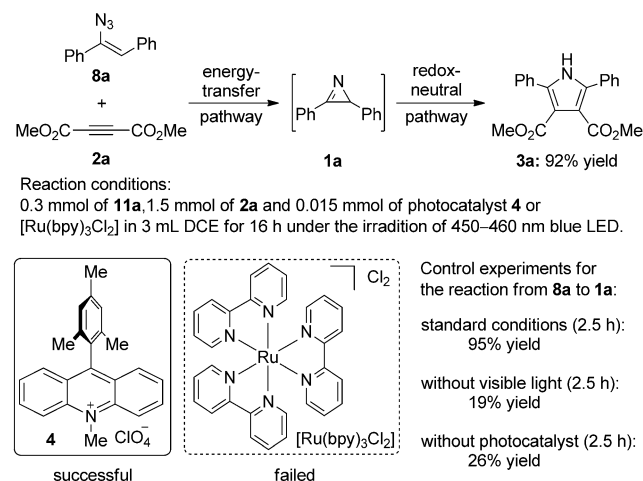


Scheme 3. Plausible reaction mechanism.

excited state of photocatalyst has proven to be feasible according to the oxidation potential of the reactants^[8d,10] and luminescence quenching experiment results.^[14] The radical cation **A** undergoes a ring-opening process to generate the 2-azaallenyl radical cation **B** and its electronic isomer **B'**.^[8a–d] Then, radical addition of **B'** to activated alkynes delivers the intermediate **C**, which subsequently undergoes an oxidation/intramolecular cyclization/aromatization sequence to give the final polysubstituted pyrroles. Moreover, the fact that this

[3+2] cycloaddition process required continuous irradiation with visible light indicated that the radical chain process might not be the predominant pathway.^[14]

Very recently, the group of Yoon^[15] disclosed that an azide group on an sp²-carbon atom can be sensitized by transition-metal photocatalysts through an energy-transfer mechanism.^[16] And the resultant nitrene intermediate generated from azide, by release of a molecule of nitrogen gas, can easily insert into the sp² C–H bonds to form a 2*H*-azirine product. Based on these observations, a photocascade catalysis merging energy transfer and redox pathways was successfully carried out (Scheme 4). To our delight, the photocatalytic



Scheme 4. The first example of a metal-free photocatalytic cascade transformation involving two different mechanisms.

cascade reaction of the azide **8a** and alkyne **2a** occurred efficiently and the desired polysubstituted pyrrole **3a** was accessed in high yield under our standard photocatalytic condition. To our knowledge, this is the first example of cascade reactions which involve two visible-light-induced processes with different mechanisms.

In conclusion, we have developed a practical pyrrole synthesis by means of a visible-light-induced photocatalytic formal [3+2] reaction of 2*H*-azirines with electron-deficient alkynes. This metal-free photocatalytic process has been successfully employed in the formal synthesis of a HMG-CoA reductase inhibitor. Notably, the first example of a visible light-induced photocascade catalysis has been realized by combining energy transfer and photoredox reactions. Additional investigations on this chemistry are ongoing in our laboratory.

Experimental Section

Representative procedure: **1a** (0.3 mmol), **2a** (1.5 mmol), 9-mesityl-10-methylacridinium perchlorate (0.015 mmol), and anhydrous DCE (3.0 mL) were added to a 10 mL Schlenk flask equipped with a magnetic stir bar. The resulting mixture was degassed by a “freeze-pump-thaw” procedure (3 times). Then the solution was stirred at a distance of ca. 5 cm from a 7 W blue LED (450–460 nm) at room temperature. Upon the completion of reaction as monitored by TLC, the solvent was removed by vacuum. The crude reaction

mixture was purified by flash chromatography on silica gel (silica: 200–300; eluent: petroleum ether/ethyl acetate (15:1–5:1) to provide the pure product **3a** as a pale yellow solid in 98 % yield.

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