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Photoinitiated multicomponent cascade reaction of *N*—heteroarenes with unactivated alkenes and trimethylsilyl azide

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ABSTRACT

A visible-light-mediated multicomponent cascade reaction of heteroarenes with unactivated alkenes and $TMSN_3$ has been developed. This approach gives a practical solution for the eco-friendly modification of *N*-heteroarenes with a high functional group tolerance and a broad substrate scope. This efficient, green strategy provides access to functional compounds that contain both a heteroarene skeleton and an organic azide structure.

Introduction

Over the past decade, photocatalysis has emerged as an efficient platform to develop robust and valuable organic transformations, especially for alkene difunctionalization [1]. Photo-induced radical--mediated difunctionalization of alkenes provides an environmental sustainability strategy to increase molecular and functional complexity from simple and readily available starting materials [2]. In those reactions, active alkyl radical intermediates have been employed in various alkene functionalization, giving valuable compounds in an atom-economical fashion. For instance, *N*-heteroarenes and their derivatives are crucial motifs in bioactive natural products and synthetic pharmaceuticals [3]. In recent decades, various methods have been developed to introduce different functional groups into *N*-heterocycles [4]. A representative approach is direct arylation of heteroarenes with unactivated bromoalkanes and alkenes using a photoredox gold catalyst reported by Barriault's group in 2016 (Scheme 1a) [4]. Recently, Nagib and co-workers demonstrated an efficient photocatalytic method to enable heteroarene phosphinylalkylation using iridium as the photocatalyst [4]. Despite the broad substrate scope and good yields, these methods require expensive metal catalysts, increasing experimental costs and product toxicity. Considerable efforts have been devoted to metal-free reactions without toxic transition metals. For example, Studer presented a visible-light-initiated α-perfluoroalkyl-β-heteroarylation of alkenes with perfluoroalkyl iodides and quinoxalin-2(1*H*)-ones [4]. In 2021, Chu's group reported an efficient, metal-free protocol for three-component sulfonylative pyridylation of styrenes *via* organic photoredox catalysis [4].

Orangoazides are important organic compounds due to their transformation diversity, and they are widely applied in building pharmaceutical molecules or chemical libraries [5]. Therefore, introduction of an azide group into organic molecules has attracted much attention [6]. In 2017, Liu and co-workers reported an intermolecular azidoheteroarylation of simple alkenes based upon a radical polar effect *via* a metal-free, radical-mediated, multicomponent cascade process [7]. Nagib et al. disclosed the multicomponent, radical-mediated addition that enabled difunctionalization of alkenes with heteroarenes and a variety of radical precursors [8]. Meanwhile, our group described a hypervalent iodine(III)-promoted rapidly three-component cascade reaction of quinoxalinones with unactivated alkenes and trimethylsilyl azide ($TMSN_3$) (Scheme 1b). However, from the perspective of green chemistry, the requirement of stoichiometric amounts of oxidants is still a major restriction hindering broad application of these reactions. Therefore, it is of high synthetic value to develop simple and practical methods for the introduction of an azide group into organic molecules [9].

To develop efficient and straightforward strategies for synthesizing valuable compounds [10], we report a protocol for intermolecular

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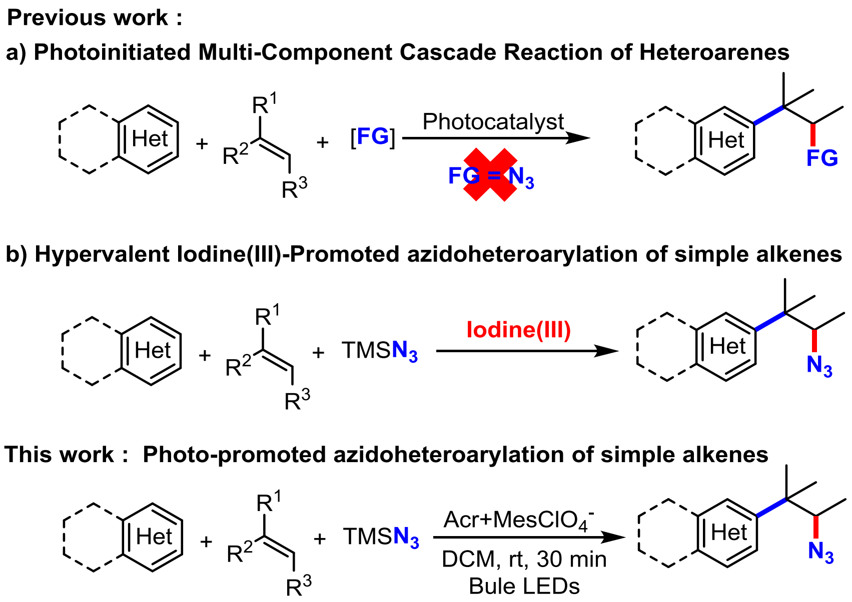
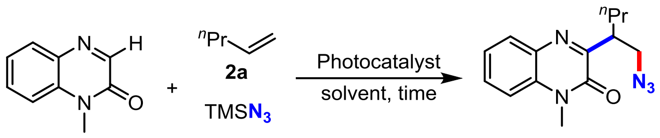


Scheme 1. The Multicomponent Cascade Reaction of Heteroarenes.

Table 1
Screening of Reaction Conditions for the Multicomponent Cascade Reaction[a,b].



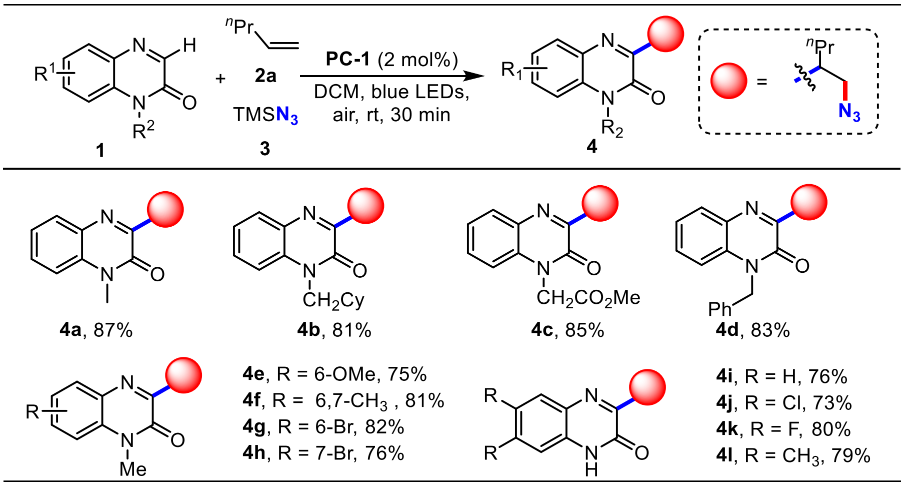
N-Me-9-Mes-Acr-ClO_4 **PC-1**; Eosin Y **PC-2**; Acid Red 94 **PC-3**; Rose Bengal **PC-4**

Fluorenone **PC-5**; Rhodamine B **PC-6**; Ir(ppy)$_2$(dtb-bpy)PF_6 **PC-7**

Entry	Photocatalyst	Solvent	Time	Yield (%)
1	**PC-1**	DCM	1 h	88
2	**PC-2**	DCM	1 h	24
3	**PC-3**	DCM	1 h	38
4	**PC-4**	DCM	1 h	34
5	**PC-5**	DCM	1 h	77
6	**PC-6**	DCM	1 h	69
7	**PC-7**	DCM	1 h	47
8	**PC-1**	THF	1 h	35
9	**PC-1**	toluene	1 h	45
10	**PC-1**	DMSO	1 h	52
11	**PC-1**	DMF	1 h	38
12	**PC-1**	DCM	2 h	88
13	**PC-1**	DCM	30 min	86
14	**PC-1**	DCM	15 min	63
15[c]	**PC-1**	DCM	30 min	trace
16[d]	**PC-1**	DCM	30 min	84
17[e]	**PC-1**	DCM	30 min	87
18[f]	**PC-1**	DCM	1 h	68
19[e]	**PC-1, dark**	DCM	30 min	0
20[g]	–	DCM	30 min	0

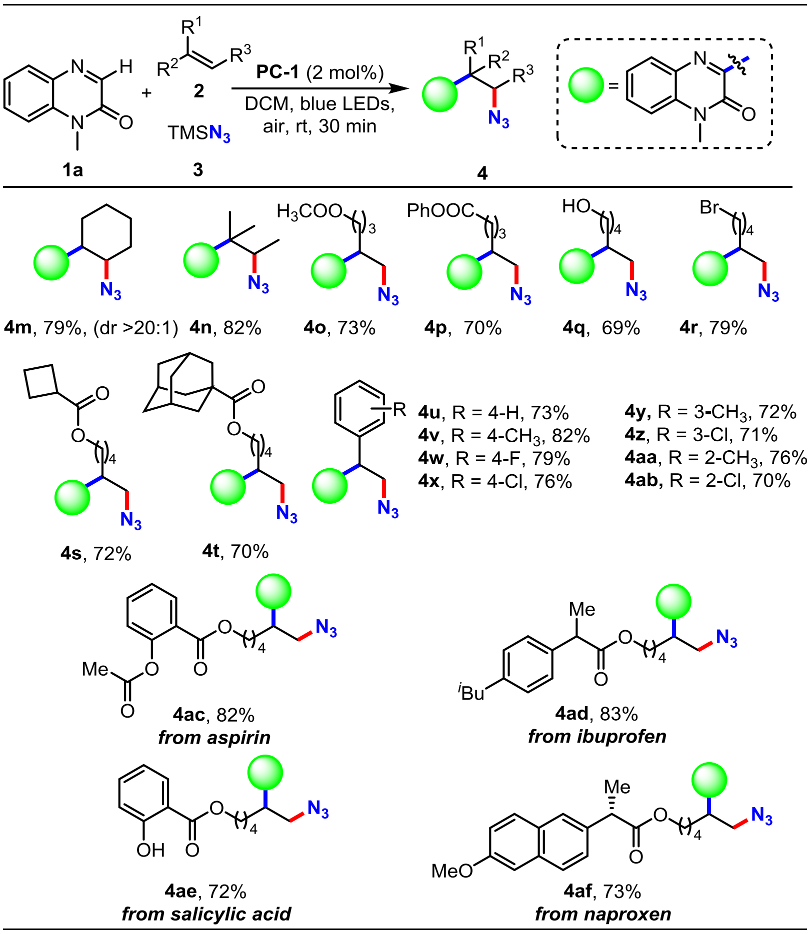
[a] **1a** (0.2 mmol), **2a** (1.3 equiv), **3** (1.3 equiv), photocatalyst (4 mol%), solvent (1.0 mL), rt, irradiation with 6 W blue LEDs (420 nm) under air.
[b] Isolated yields.
[c] Under N_2.
[d] Under O_2.
[e] **PC-1** (2 mol%).
[f] **PC-1** (1 mol%).
[g] No **PC-1**.

Table 2
Substrate Scope of Quinoxalin-2(1H)-ones for the Multicomponent Cascade Reaction[a,b].



[a] **1** (0.2 mmol), **2a** (1.3 equiv), **3** (1.3 equiv), **PC-1** (2 mol%), DCM (1.0 mL), rt, irradiation with 6 W blue LEDs under air.
[b] Isolated yields.

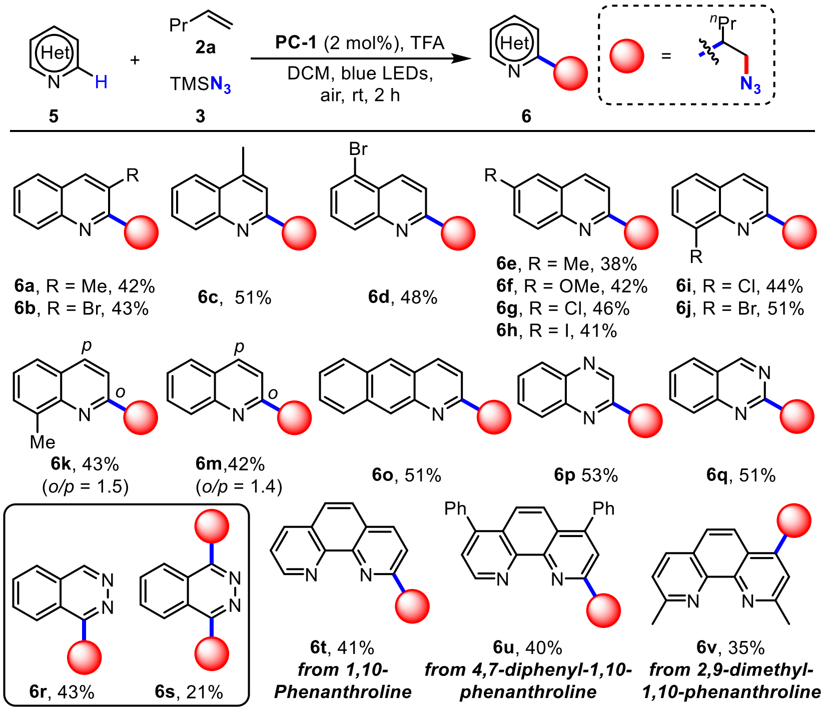
Table 3
Substrate Scope of Alkenes for the Multicomponent Cascade Reaction[a,b].



[a] **1a** (0.2 mmol), **2** (1.3 equiv), **3** (1.3 equiv), **PC-1** (2 mol%), DCM (1.0 mL), rt, irradiation with 6 W blue LEDs under air.
[b] Isolated yields.

Table 4

Substrate Scope of N—Heteroarenes for the Multicomponent Cascade Reaction[a,b].



[a] 5 (0.2 mmol), 2a (1.3 equiv), 3 (1.3 equiv), TFA (1.1 equiv), PC-1 (2 mol%), DCM (1.0 mL), rt, irradiation with 6 W blue LEDs under air.
[b] Isolated yields.

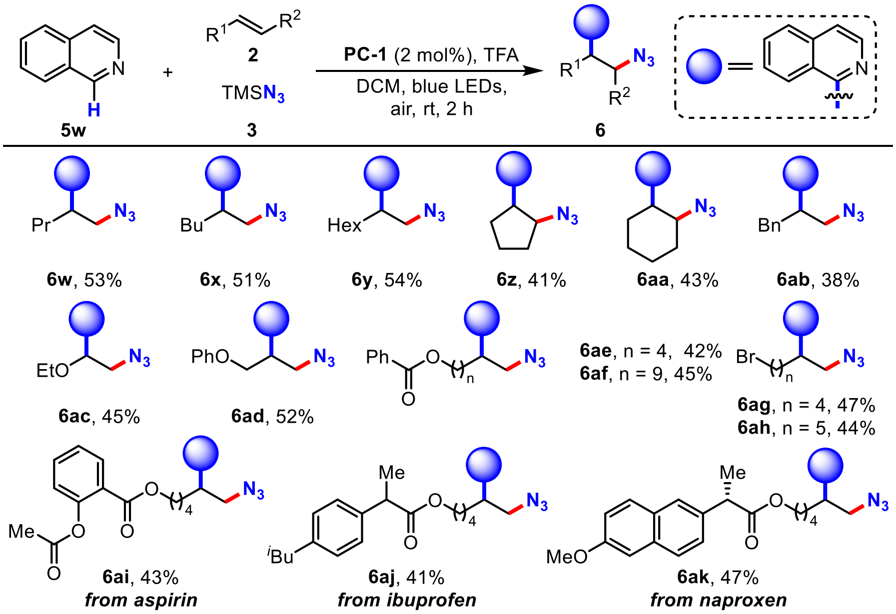
azidoheteroarylation of unactivated alkenes based on visible light stimulation. Importantly, our method can be performed at room temperature in a sustainable fashion, unlike traditional reactions that typically require hypervalent iodine(III) for azide radical generation from $TMSN_3$ [11].

Results and discussion

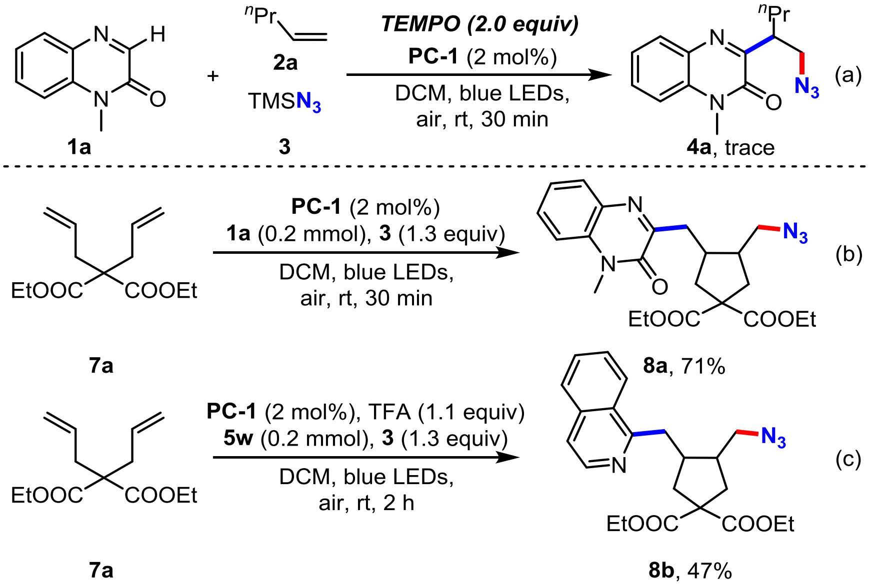
We commenced our study by examining the reaction of quinoxalinone (**1a**), 1-amylene (**2a**), and $TMSN_3$ (**3**) in the presence of 5 mol% of $Acr^+MesClO_4^-$(**PC-1**) and dichloromethane (DCM) under irradiation with a 6 W LED. From this versatile test reaction, the desired product (**4a**) was generated in 88% yield (Table 1, entry 1). To optimize reaction

Table 5

Substrate Scope of Alkenes with Isoquinoline for the Multicomponent Cascade Reaction[a,b].



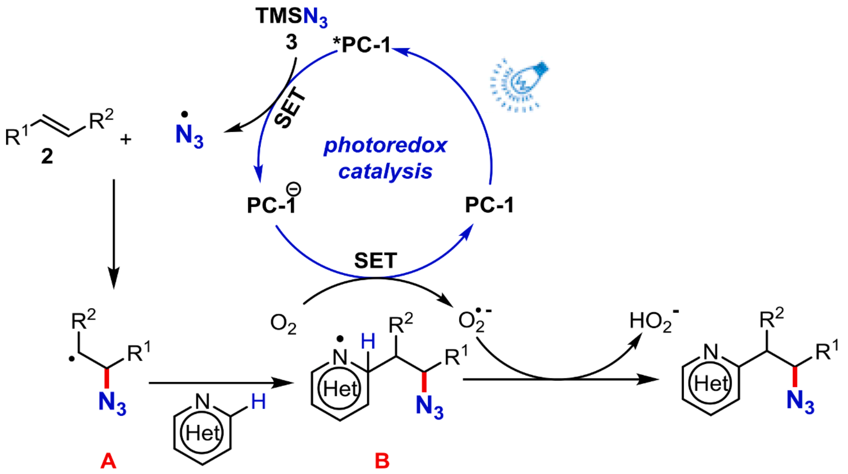
[a] 5v (0.2 mmol), 2 (1.3 equiv), 3 (1.3 equiv), TFA (1.1 equiv), PC-1 (2 mol%), DCM (1.0 mL), rt, irradiation with 6 W blue LEDs under air.
[b] Isolated yields.



Scheme 2. Control Experiments of the Multicomponent Cascade Reaction.

conditions, we investigated the effect of photocatalyst and solvent on the reaction yield. As shown in entries 1–11, the highest yield was 88% when the reaction was carried out using $Acr^{+}MesClO_4^{-}$(**PC-1**) as the photocatalyst in dichloromethane (DCM). The reaction was finished within 30 min (Table 1, entries 12–14). No desired product was detected when the model reaction was conducted under a nitrogen atmosphere, implying that O_2 might play an essential role in this transformation (Table 1, entry 15). However, when the model reaction was conducted under a O_2 atmosphere, the yield of desired product would not be enhanced (Table 1, entry 16). When the catalyst loading was reduced to 2 mol%, the reaction afforded **4a** in 87% yield (Table 1, entry 17). Further reduction of catalyst loading to 1 mol% decreased the product yield, even after one hour of reaction (Table 1, entry 18). Moreover, transformation did not occur in the absence of light stimulation and **PC-1** (Table 1, entries 19–20).

Under the optimized condition, we studied the substrate scope of the multicomponent cascade reaction (Table 2). We first examined the compatibility of different quinoxalin-2(1*H*)-ones. Quinoxalin-2(1*H*)-ones with a wide range of *N*-substituents such as methyl, cyclopropylmethyl, acetyl ester, and benzyl groups, were well tolerated, giving corresponding products (**4a-4d**) in 81–87% yields. Quinoxalin-2(1*H*)-ones bearing methoxy-, methyl-, and bromo- groups on the benzene ring were also compatible, yielding products (**4e-4 h**) in 75–82% yields. It is worth noting that unsubstituted *N*—H substrates with methyl- and halo- moieties on the benzene ring could also be transformed into corresponding products in acceptable yields (**4i-4l**). These results show that the multicomponent cascade reaction is compatible with a wide range of quinoxaline derivatives. Furthermore, the substrate scope of alkenes was explored (Table 3). The reaction was suitable for the cyclic and multiply substituted alkenes, providing corresponding products (**4 m** and **4n**) in 79% and 82% yields. Subsequently, various alkenes with different functional groups, such as ester, hydroxy and halo, were well tolerated, giving target products (**4o-4t**) in 69–79% yields. Of note, a wide range of styrenes containing both electron-donating and electron-withdrawing groups proceeded smoothly, affording corresponding products (**4u-4ab**) in moderate to high yields. To further test the scalability of this method, alkenes containing aspirin, ibuprofen, salicylic acid, and naproxen moieties were examined, with



Scheme 3. Plausible Mechanism for the Multicomponent Cascade Reaction.

corresponding products (**4ac-4af**) in good yields.

N-heteroarenes are essential in biological synthesis, especially in research for new therapeutic agents. To this end, we investigated the scope of *N*-heteroarenes for three-component coupling (Table 4). A series of quinolines with diverse substituents, such as alkyl, halo and alkoxy, gave corresponding products (**6a-6 m**) in 38–51% yields. Quinoxaline, quinazoline, phthalazine, phenanthroline and its derivatives were also effective substrates (**6o-6v**) for transformation. To further examine the substrate scope, a variety of alkenes were studied (**Table 5**). Nonfunctionalized linear and cyclic alkenes reacted with isoquinoline smoothly, affording desired products (**6w-6aa**) in 41–54% yields. Diverse functional groups, such as benzyl, ether, ester, and halo, were well tolerated (**6ab-6ah**). It is noteworthy that privileged scaffolds in relevant antiphlogistic drugs, such as aspirin, ibuprofen and naproxen, were amenable to this protocol, giving target products (**6ai-6ak**) in 41–47% yields.

To probe the mechanism underlying the multicomponent cascade reaction, a series of control experiments were performed (Scheme 2). First, the addition of 2.0 equivalents of radical scavenger TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) led to complete inhibition of transformation (Scheme 2a). In addition, the radical clock experiments provided the desired products (**8a** and **8b**) in 71% and 47% yields. These results strongly support that a radical mechanism is involved in this cascade reaction (Scheme 2bc).

According to above results and previous literature, [12] a plausible mechanism for this cascade reaction was proposed in Scheme 3. Firstly, the excited ***PC-1** was generated from **PC-1** under visible light irradiation (Ered* = 2.06 V vs. SCE)[9].[a] Then, $TMSN_3$ (**3**) reacted with ***PC-1** to produce the azido radical and **PC-1**$^-$ *via* a single electron transfer (SET) process. The oxidation potential of the free azide anion was found to be +1.32 V (NHE) [9]. Subsequently, the azido radical attacked alkene **2** to produce alkyl radical (**A**), which then reacted with *N*-heteroarene to furnish a nitrogen radical intermediate (**B**). Meanwhile, another SET process took place between **PC-1**$^-$ and O_2, providing an $O_2^{\bullet -}$ species with the regeneration of **PC-1** [13]. Finally, the $O_2^{\bullet -}$ species oxidized the intermediate (**B**) to afford the corresponding coupling product.

Conclusions

In conclusion, we have developed a visible-light-mediated method for the cascade reaction of *N*-heteroarenes with unactivated alkenes and $TMSN_3$. The mildness of the strategy permits high tolerance of functional groups and enables the synthesis of diverse heteroarenes with medicinal relevance.

Supplementary Materials

Supplementary material associated with this article can be found, in the online version, at XXX.

CRediT authorship contribution statement

Jiabin Shen: Investigation, Writing – original draft. **Lei He:** Investigation, Writing – original draft. **Chenfeng Liang:** Conceptualization. **Yani Ouyang:** Conceptualization. **Xiaoguang Yue:** Conceptualization. **Haifeng Wu:** Writing – review & editing. **Jun Xu:** Writing – review & editing. **Xiaogang Liu:** Project administration, Writing – review & editing. **Qing Zhu:** Project administration, Writing – review & editing. **Pengfei Zhang:** Project administration, Writing – review & editing.

Declaration of Competing Interest

We have no conflict of interest to declaration.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.mcat.2022.112330.

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