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ARTICLE

Visible-Light-Enabled Three-Component Carboamidation of Alkenes with Aryl Thianthrenium Salts

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Herein, we report a visible-light-enabled strategy for activating aryl thianthrenium salts that enables a three-component Ritter-type carboamidation of alkenes with nitriles/H_2O. Under neutral and mild irradiation, C-C and C-N bonds are sequentially formed in a single operation to deliver diverse benzylamides with broad functional-group tolerance. A wide range of aryl thianthrenium salts as well as diverse styrenes are compatible, and late-stage diversification of pharmaceutically relevant motifs is readily achieved. Mechanistic studies suggest that a single-electron transfer (SET) pathway is likely operative, involving reductive quenching of the excited Ir(III) photocatalyst by thianthrene, followed by reduction of the arylthianthrenium salt by the resulting Ir(II) species to generate an aryl radical. This work expands the synthetic utility of aryl thianthrenium salts and provides a modular entry to architecturally complex benzylamides from simple alkene feedstocks.

Introduction

Amide motifs are ubiquitous in natural products, pharmaceuticals, and functional materials, and benzylamides represent one of the most prevalent privileged scaffolds in medicinal chemistry (Scheme 1a).[1,2] For example, S11-1038 is a highly selective, subnanomolar inhibitor of butyrylcholinesterase (BChE) with potential for Alzheimer's disease.[3] p38α MAP kinase inhibitors have been widely pursued for inflammation-related disorders as well as metabolic and neurodegenerative diseases associated with cellular stress.[4] Muraglitazar has been investigated for the management of type 2 diabetes and comorbid conditions associated with metabolic syndrome.[5] Consequently, considerable efforts have been devoted to the development of efficient synthetic methods to access these privileged scaffolds.[6-8] Among the various strategies for assembling such frameworks, transformations employing alkenes as feedstocks are particularly appealing. On the one hand, alkenes are abundantly available, inexpensive, and readily functionalized.[9-12] On the other hand, incorporating a nitrogen source across the carbon-carbon double bond enables rapid access to structurally complex substrates from simple starting materials.[13-15]

The classical Ritter reaction can construct these frameworks by generating carbocation intermediates from olefins under strongly acidic conditions, followed by nucleophilic addition of a nitrile and subsequent hydrolysis.[16,17] Despite its operational simplicity and broad substrate generality, the reliance on strong acids and elevated temperatures markedly restricts the accessible structural diversity. To address these limitations, a number of elegant alternatives have been developed. For example, in 2019, Tobisch and co-workers reported an enantioselective CuH-catalyzed hydroamidation of styrenes with dioxazolones and silanes, enabling access to benzylamide derivatives.[18] However, this protocol typically relies on a narrow subset of dioxazolone substrates. In 2025, Zuo and co-workers developed a metal-free, oxidant-free three-component assembly of amides with two distinct aldehydes to construct polysubstituted benzylamide frameworks.[19] However, this transformation relies on a strong Brønsted acid (HBr) and typically requires elevated temperatures. Consequently, the development of new, mild and modular approaches that transform simple alkenes into benzylamides remains highly desirable.

In recent years, visible-light-mediated photocatalysis has witnessed rapid advancement, providing an innovative and environmentally benign platform for chemical bond construction under mild conditions.[20,21] These photocatalytic protocols typically proceed via the generation of highly reactive open-shell species, which serve as key intermediates for assembling a wide range of chemical bonds. In 2021, Chen and co-workers reported an efficient visible-light/Ir-catalyzed three-component Ritter-type aminoalkylation of alkenes with nitriles.[22] In 2023, Hu and co-workers developed an elegant visible-light-induced four-component Ritter-type reaction of CF_3Br, alkenes, carboxylic acids, and nitriles.[23] Although these methods can be applied to assemble benzylamide frameworks, they typically require bromides as radical precursors, which imposes limitations on substrate generality (Scheme 1b).

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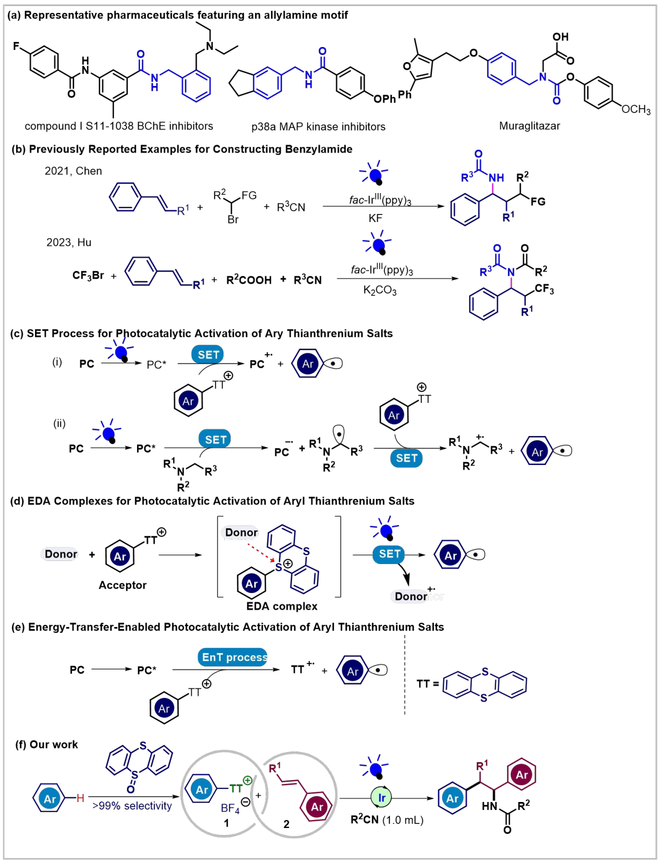

Scheme 1 Context and strategy to access benzylamides.

Aryl thianthrenium salts, as versatile aryl radical precursors, have attracted considerable attention, owing to their excellent stability, operational simplicity, and straightforward preparation without the need for column purification.[24-28] Extensive efforts have focused on activating these salts under photocatalytic conditions, typically via photocatalyst-mediated single-electron transfer (SET) pathways (Scheme 1c).[29-33] In addition, the formation of electron donor-acceptor (EDA) complexes has provided an alternative strategy for photoinduced electron transfer and subsequent C-S bond cleavage (Scheme 1d).[34-38] More recently, energy-transfer (EnT)-mediated activation of aryl thianthrenium salts has also been disclosed, gradually emerging as a highly attractive strategy (Scheme 1e).[39-41] These activation modes have been successfully applied to the construction of a wide range of C-C bonds as well as C-X (S, O, N, P) bonds. However, the synthetic potential of aryl thianthrenium salts in the construction of benzylamide frameworks has remained underexplored. Motivated by these precedents, we herein report a visible-light-enabled activation strategy for aryl thianthrenium salts, enabling the three-component carboamidation of alkenes with nitriles and water via a Ritter-type pathway. Using $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ as the photocatalyst, this protocol efficiently delivers polysubstituted benzylamide products under neutral conditions with excellent functional-group tolerance and broad substrate scope. This method provides a more sustainable route to architecturally complex scaffolds, including pharmaceutically relevant molecules (Scheme 1f).

Results and discussion

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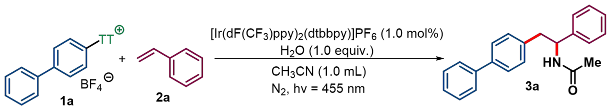
To identify the optimal reaction conditions, we began our studies using aryl thianthrenium salt **1a** and styrene **2a** as model substrates in acetonitrile (Table 1). After systematic optimization of the photocatalyst, solvent, and irradiation wavelength, we identified the optimal conditions as 1 mol% $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ in MeCN with H_2O as an additive under N_2, and irradiation with a 25 W 455 nm blue LED at room temperature for 12 h afforded **3a** in 71% isolated yield (Table 1, entry 1). Notably, a range of commercially available photocatalysts was evaluated, among which $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ exhibited the highest catalytic activity (Table 1, entry 2). Furthermore, solvent screening showed that replacing MeCN with other solvents (e.g., DMF, DCM, DCE, or DMA) led to diminished yields, even when MeCN (20 equiv.) was added as an additive (Table 1, entry 3). In addition, replacing 455 nm with other irradiation wavelengths failed to improve the reaction outcome (Table 1, entry 4). Control experiments further revealed that both light irradiation and the photocatalyst are indispensable for this transformation (Table 1, entries 5-6).

Table 1 Optimization of reaction conditions [a]



Entry	Variations from standard conditions	Yield (%) [b]
1	None	71
2	Photocatalysts other than [Ir][c]	N.R. to 24
3	Solvents other than CH_3CN	N.R. to 67[d]
4	Wavelengths other than 455 nm	N.R. to 64
5	Without blue LED irradiation	N.R.
6	Without [Ir]	N.R.

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (1 mol%), H_2O (1.0 equiv.), MeCN (1 mL) at room temperature under irradiation with a 25 W blue LED (455 nm) for 12 h. [b]Isolated yield. [c][Ir]: $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$. [d]MeCN as an additive (20 equiv.)

Encouraged by the optimized reaction conditions, the generality and substrate scope of this transformation were investigated. We were pleased to observe that various aryl thianthrenium salts **1** featuring both electron-rich and electron-deficient substituents on the aryl ring reacted smoothly with aromatic alkenes **2**, providing the corresponding benzylamides in moderate to good yields (**3c**-**3e**). In addition, substrates bearing sensitive functional groups such as ester and cyano groups were also compatible, furnishing the expected products in moderate to good yields (**3f**-**3g**). Furthermore, a broad range of halo-substituted aryl thianthrenium salts proved to be suitable substrates for this transformation, affording the corresponding products in good yields and underscoring the utility of this protocol for structural diversification (**3h**-**3l**). Additionally, several heteroatom-containing substrates were also well tolerated, engaging efficiently with styrene derivatives to furnish the corresponding benzylamides (**3m**-**3p**). Moreover, pharmaceutically relevant cores, including bifenthrin, gemfibrozil, pyriproxyfen, flurbiprofen, boscalid and isoprocarb were all well tolerated under the standard reaction conditions,

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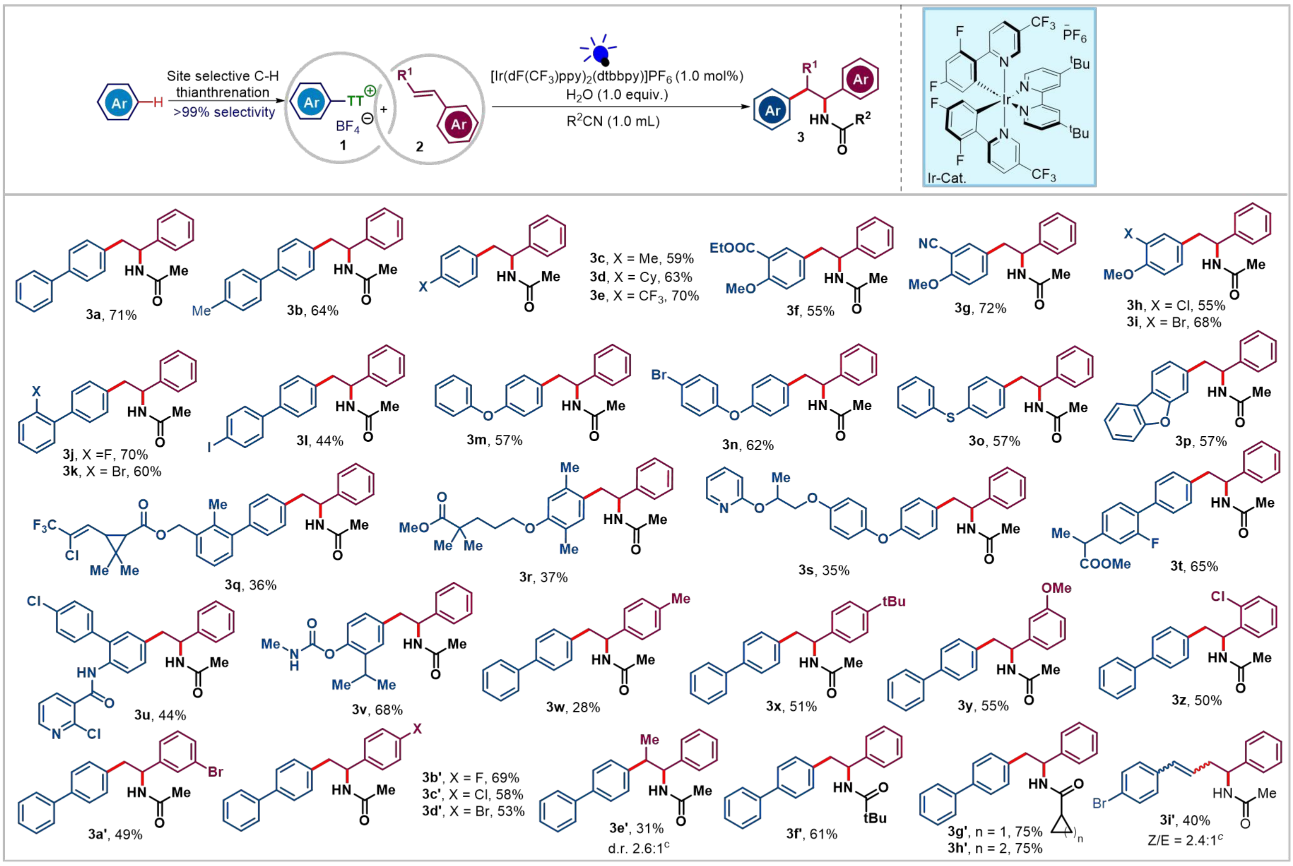
thereby clearly demonstrating the practicality of this method (**3q**-**3v**). Next, we explored the scope of the alkenes. A range of substituted styrene derivatives bearing either electron-rich (Me, *t*Bu, OMe) or electron-deficient (F, Cl, Br) substituents was evaluated, and all proved suitable for this transformation, delivering the corresponding products in moderate to good yields (**3w**-**3d'**). 1,2-Disubstituted alkenes (**3e'**) as well as other alkyl-substituted nitriles (**3f'**-**3h'**) were found to be compatible, proceeding smoothly under the optimized conditions to give the desired products. Notably, selected alkenyl thianthrenium salts were also compatible under the standard conditions, affording the corresponding products in moderate yields (**3i'**), although the efficiency and selectivity were substrate-dependent (see the Supporting Information for details).

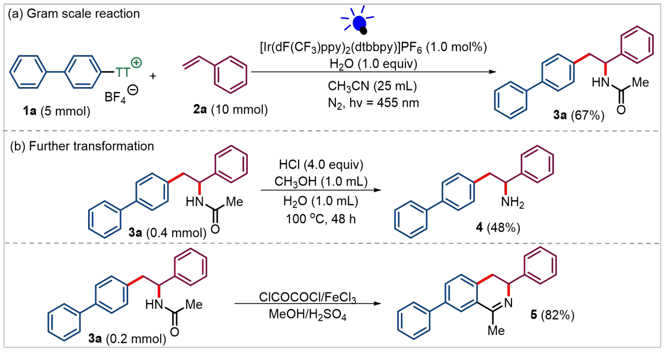
Scheme 2 Substrate scope of three-component carboamidation of alkenes[a, b]



[a]Reaction conditions: **1** (0.2 mmol), **2** (0.4 mmol), $[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (1 mol%), H_2O (1.0 equiv.), R^2CN (1 mL) at room temperature under irradiation with a 25 W blue LED (455 nm) for 12 h. [b]Isolated yield. [c]Isolated ratio.

To demonstrate the operational practicality of the method, a scale-up reaction was conducted using aryl thianthrenium salt **1a** and styrene **2a** under irradiation from two 25 W blue LED lamps, affording **3a** in 67% yield (Scheme 3a, see the SI for details). To further highlight the synthetic utility of this protocol, we carried out derivatization of the resulting benzylamides, as depicted in Scheme 3b. Treatment of **3a** with HCl in a 1:1 $MeOH/H_2O$ mixture at 100 °C furnished the free amine **4** in moderate yield. In addition, **3a** can be converted to 1-methyl-3,7-diphenyl-3,4-dihydroisoquinoline **5** using oxalyl chloride and $FeCl_3$.[42]

To gain preliminary mechanistic insight into the reaction, a series of control experiments were carried out as shown in Figure 1. First, a series of radical trapping experiments were conducted by adding 2,2,6,6-tetramethylpiperidin-1-yl-oxidanyl (TEMPO) or 1,1-diphenylethylene under the standard reaction conditions (Figure 1a). The addition of these radical scavengers markedly suppressed the reaction. Moreover, the detection of TEMPO-adduct **6** by high-resolution mass spectrometry (HRMS), together with the isolation of compound **7** in 63% yield, is consistent with the involvement of an aryl radical intermediate in this transformation. Notably, although the thianthrenium cationic intermediate **8** could not be isolated, its presence in solution was detected by HRMS (Figure 1b). Furthermore,



Scheme 3 Synthetic applications

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fluorescence quenching experiments were carried out to separately investigate the interactions of thianthrenium salt **1a** and thianthrene (TT) with the photocatalyst [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$. As shown in Figure 1c, both **1a** and TT can quench the emission of the excited Ir(III) photocatalyst, and good linear relationships were observed in the corresponding Stern-Volmer plots. Notably, TT exhibited a higher quenching efficiency toward the excited Ir(III) photocatalyst than **1a**, indicating that TT can effectively interact with the excited photocatalyst. This result is consistent with the feasibility of a thianthrene-mediated reductive quenching pathway, in which TT reduces the excited Ir(III) species to generate a reduced Ir intermediate. Furthermore, on/off photochemical experiments confirmed that continuous irradiation is crucial for this transformation (Figure 1d). Finally, the calculated apparent quantum yield (AQY) at 455 nm indicates that this transformation does not proceed through a radical chain process (see the Supporting Information for details).

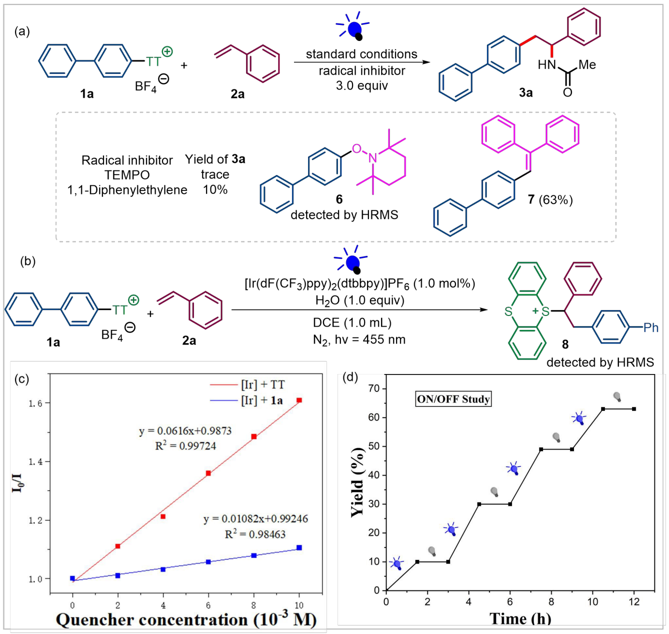
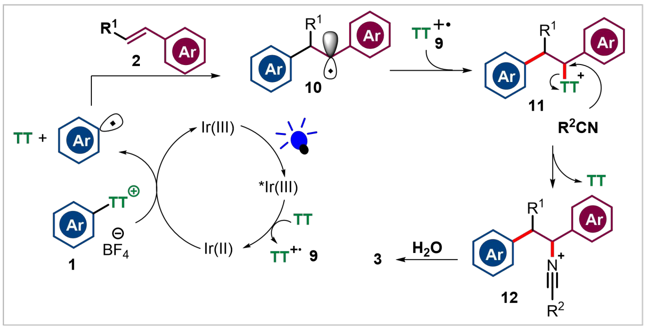


Figure 1 Investigations of the reaction mechanism. (a) Radical trapping experiments. (b) Intermediate trapping by HRMS. (c) The emission quenching of [Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)]PF$_6$ by thianthrenium salt **1a** and TT, respectively. (d) Visible light irradiation on/off experiment.

On the basis of these preliminary results obtained above, a plausible reaction pathway is proposed in Scheme 4. Upon visible-light irradiation, thianthrene is proposed to reductively quench the excited Ir(III) photocatalyst to yield a reduced Ir(II) species, together with the thianthrene radical cation **9**. The feasibility of the subsequent reduction step is supported by the fact that arylthianthrenium salts generally possess more accessible reduction potentials than many aryl halides [E^0(ArTT$^+$/ArTT$^\bullet$) ≈ −1.5 V vs SCE in CH$_3$CN].[43] Thus, the reduced Ir(II) species can readily reduce arylthianthrenium salt **1** to form the aryl radical intermediate. Then, the aryl radical adds to styrene **2** to form benzyl radical **10**, which may recombine with the thianthrene radical cation **9** to afford the key thianthrenium cationic intermediate **11**. Subsequent attack of nitrile on intermediate **11** gives nitrilium intermediate **12**, which undergoes in situ hydrolysis to deliver the target benzylamide product **3**.



Scheme 4 Plausible mechanism

Conclusions

In summary, we have developed a visible-light-enabled strategy for the activation of aryl thianthrenium salts, enabling a three-component Ritter-type carboamidation of alkenes with nitriles/H$_2$O. The reaction proceeds under neutral and mild conditions, provides polysubstituted benzylamides in a modular fashion, and exhibits broad functional-group tolerance as well as applicability to the late-stage diversification of complex motifs. Mechanistic experiments support the involvement of aryl radical intermediates and suggest that a thianthrene-mediated SET pathway may operate under the reaction conditions. Given its operational simplicity and synthetic versatility, this protocol is expected to further expand the application scope of thianthrenium salts in photocatalytic alkene difunctionalization chemistry.

Author contributions

Y. S. and D. Y. conceived and supervised the project. K. F., X. L., Y. W., L. Z., and J. L. performed the experiments. K. F. analyzed the data. Y. S. and D. Y. wrote the manuscript with input from all authors. All authors approved the final version of the manuscript.

Conflicts of interest

The authors declare no competing financial interest.

Data availability

The data underlying this study are available in the published article and its Supporting Information.

Supplementary information (SI) available: General experimental procedures, characterization data and copies of ^{1}H, ^{13}C and ^{19}F NMR spectra.

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Data availability statements

The data supporting this article have been included as part of the Supplementary Information.