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Visible-Light Carbon Nitride-Catalyzed Aerobic Cyclization of Thiobenzanilides under Ambient Air Conditions

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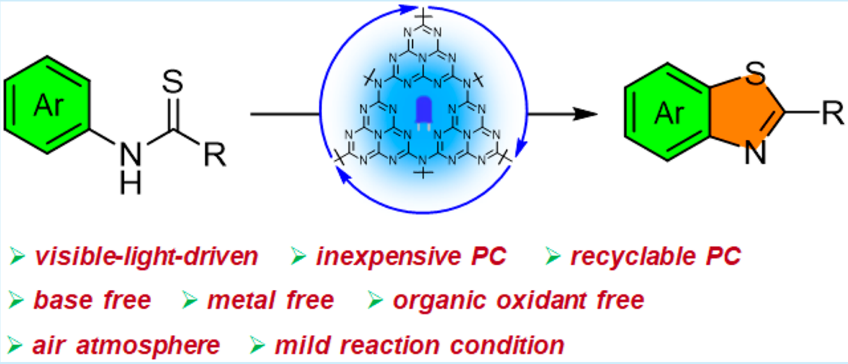
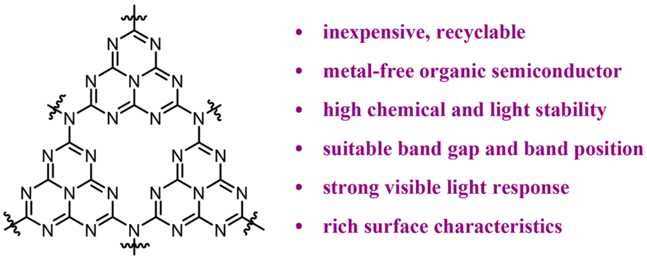


ABSTRACT: A metal-free heterogeneous photocatalysis has been developed for the synthesis of benzothiazoles via intramolecular C−H functionalization/C−S bond formation of thiobenzanilides by inexpensive graphitic carbon nitride (g-C_3N_4) under visible-light irradiation. This reaction provides access to a broad range of 2-substituted benzothiazoles in high yields under an air atmosphere at room temperature without addition of a strong base or organic oxidizing reagents. In addition, the catalyst was found to be stable and reusable after five reaction cycles.

The visible-light-driven photocatalysis not only offers an appealing approach to a green chemical process but also provides a vast opportunity to develop new synthetic methodologies for organic synthesis.[1] The past decades have witnessed the rapid development of photoredox catalysis, especially in homogeneous catalysis with transition metal complexes based on Ru and Ir,[2] as well as with organic dyes like acridinium salts,[3] riboflavins,[4] and chromones.[5] Heterogeneous photocatalysts, which have been often used in water splitting,[6] organic pollutant degradation,[7] and CO_2 reduction,[8] have found increasing applications in organic transformations in recent years due to their low cost, recyclability, and excellent thermal and chemical stability.[9] Among heterogeneous photocatalysts, graphite carbon nitride materials (g-CNs) are particularly prominent because of their unique properties as described here[10] (Scheme 1). (1) g-CNs are metal-free organocatalysts, which can avoid the introduction of transition metals into the reaction.[10a] (2) g-CNs can be easily synthesized from commodity chemicals, and their properties can be readily tuned by synthetic modifications.[10b] (3) g-CNs have a suitable band gap (2.7 eV, corresponding to 460 nm) and favorable positions of the valence and conduction band, allowing for controlled oxidation and reduction of many substrates.[10a] (4) g-CNs display exceptionally high chemical stability in the presence of reactive nucleophiles, electrophiles, and radicals.[10b] (5) g-CNs as heterogeneous photocatalysts are two-dimensional materials with rich surface characteristics and have catalytic properties comparable to those of homogeneous photocatalysts.[10a] Because of these advantages, g-CNs have received a great deal of attention recently as a synthetically useful heterogeneous photocatalyst.[11]

Scheme 1. Properties of Carbon Nitride Materials



Benzothiazole is a privileged structure frequently found in pharmaceuticals and biologically active natural products.[12]

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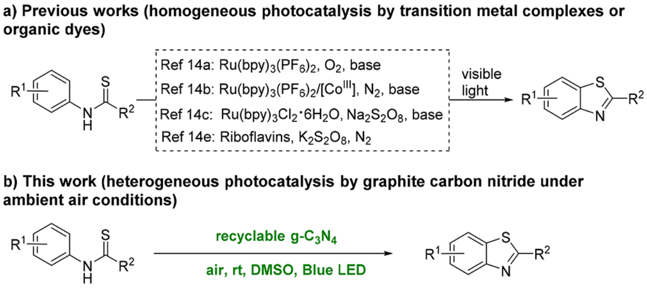
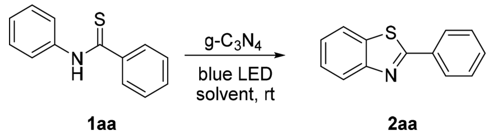
Generally, benzothiazoles are prepared via oxidative cyclization of thiobenzanilides using various oxidants such as hypervalent iodine, bromine, or metal salt.[13] Though convenient, the synthetic method often displays low functional group tolerance or requires stoichiometric or excess amounts of toxic oxidants. In recent years, visible-light-driven synthesis as a green approach to this kind of compound has attracted an increasing amount of attention (Scheme 2a).[14] Li et al. reported a visible-light-driven synthesis of benzothiazoles using $Ru(bpy)_3(PF_6)_2$ as a photocatalyst, dioxygen as the terminal oxidant, and DBU as a base.[14a] Lei et al. developed an external oxidant-free oxidative coupling for the synthesis of benzothiazoles by the $Ru(bpy)_3(PF_6)_2$/Co dual catalytic system.[14b] Gustafson et al. reported a similar synthesis of benzothiazoles using $Ru(bpy)_3Cl_2·6H_2O$ as a photocatalyst and $Na_2S_2O_8$ as an oxidant.[14c] By using TEMPO as an oxidant, Li and Lang et al. achieved a visible-light-driven cyclization of thiobenzanilides without addition of a photosensitizer.[14d] Schmidt et al. employed riboflavin as a photocatalyst and potassium peroxydisulfate as a sacrificial oxidizing agent to synthesize 2-substituted benzothiazoles via cyclization of thiobenzanilides.[14e] Despite these advances, there is still a great demand for photoredox synthesis of benzothiazoles using a green oxidant and a recyclable catalyst under mild conditions. Herein, we report the first heterogeneous visible-light-driven aerobic synthesis of benzothiazoles via intramolecular C−H functionalization/C−S bond formation of thiobenzanilides under ambient air conditions using carbon nitride as a photocatalyst.

Scheme 2. Synthesis of 2-Substituted Benzothiazoles via Visible-Light Photocatalysis



At the outset, we chose *N*-phenylbenzothioamide (**1aa**) as the substrate and $g\text{-}C_3N_4$ as the photocatalyst to optimize the conditions. $g\text{-}C_3N_4$ can be readily prepared by thermal polycondensation of urea (for details, see the Supporting Information). Initially, the photoredox cyclization of **1aa** was performed under an air atmosphere and irradiation of a 10W blue LED (410 nm) at room temperature with dimethylformamide (DMF) as the solvent. To our delight, cyclization product 2-phenyl benzothiazole **2aa** was obtained in 39% yield (Table 1, entry 1). Solvent screening showed that dimethyl sulfoxide (DMSO) was the best, giving **2aa** in 95% yield (entries 2−9). It is worth noting that when H_2O was used as the solvent, **2aa** was obtained in 78% yield (entry 9). Under a N_2 atmosphere, no reaction was observed, indicating O_2 in air is essential for the cyclization reaction (entry 10). No reaction occurred in the absence of blue-light irradiation, and a 6% product yield was obtained in the absence of $g\text{-}C_3N_4$ (entries 11 and 12). The two experiments revealed that $g\text{-}C_3N_4$ and light are indispensable in the photochemical C−H thiolation reaction. Interestingly, $Ru(bpy)_3Cl_2$ and $Ir(ppy)_3$, which are commonly used in homogeneous photocatalysis, were found to be less efficient under the same condition (entries 13 and 14, respectively).

Table 1. Optimization of Reaction Conditions

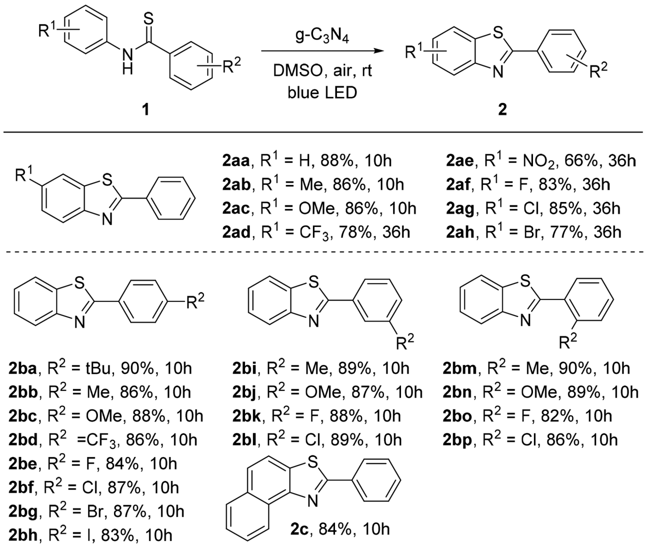


entry[a]	catalyst	solvent	atmosphere	yield (%)
1	$g\text{-}C_3N_4$	DMF	air	39
2	$g\text{-}C_3N_4$	CH_3CN	air	18
3	$g\text{-}C_3N_4$	$CHCl_3$	air	trace
4	$g\text{-}C_3N_4$	DCE	air	20
5	$g\text{-}C_3N_4$	DMSO	air	95
6	$g\text{-}C_3N_4$	THF	air	57
7	$g\text{-}C_3N_4$	CH_3OH	air	80
8	$g\text{-}C_3N_4$	EtOH	air	69
9	$g\text{-}C_3N_4$	H_2O	air	78
10	$g\text{-}C_3N_4$	DMSO	N_2	trace
11[b]	$g\text{-}C_3N_4$	DMSO	air	no reaction
12	–	DMSO	air	6
13	$Ru(bpy)_3Cl_2$ (5 mol %)	DMSO	air	12
14	$Ir(ppy)_3$ (5 mol %)	DMSO	air	17

[a]Reaction conditions: **1aa** (0.1 mmol) and $g\text{-}C_3N_4$ (10 mg) in solvent (3 mL) irradiated by a 10 W blue LED for 8 h at rt. Yields were determined by HPLC. [b]Without irradiation.

With the optimized condition in hand, we investigated the scope of this reaction (Table 2). We first examined the substituent (R^1) effect of the *N*-aryl group of **1aa** on the reaction. Both electron-donating and electron-withdrawing groups are well tolerated to afford the desired products (**2aa**−**2ah**) in 66−88% yields. The reactivity of the electron-donating groups is higher than that of electron-withdrawing groups, completing the reaction in shorter period of time. The reaction showed excellent combability with halogen groups (F, Cl, and

Table 2. Synthesis of Substituted 2-Arylbenzothiazoles[a]



[a]Reaction conditions: **1** (0.1 mmol) and $g\text{-}C_3N_4$ (10 mg) in DMSO (3 mL) irradiated by a 10 W blue LED under an air atmosphere at rt. Isolated yields are shown.

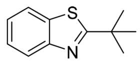
Br) without dehalogenation being observed. It is worth noting that p-NO_2-containing thiobenzanilide, which is a challenging substrate for the synthesis of the corresponding benzothiazole,[14e] reacted efficiently under our condition to provide the desired product (**2ae**) in 66% yield. When an *N*-aryl ring was replaced with a naphthyl ring, the reaction gave the corresponding product in 84% yield.

We further investigated the substitution (R^2) effect of the 2-aryl group on the reaction (Table 2, **2ba−2bp**). Excellent yields were obtained with both electron-rich and electron-poor substituents on the 2-phenyl ring (82−90%). All of the substituent positions (*ortho*, *meta*, and *para*) are compatible with the reaction (82−90%).

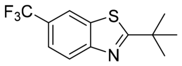
Heterogeneous photocatalysis can also be applied to *N*-aryl alkylthioamides for the synthesis of 2-alkylbenzothiazoles. As shown in Table 3, both bulky and small alkyl substituents are compatible with our protocol, leading to the desired products in excellent yields. It is worth noting that thioamides with a small alkyl group are poor substrates for the synthesis of the corresponding 2-alkylbenzothiazoles in previous reports.[14b,d,e]

Table 3. Synthesis of Substituted 2-Alkylbenzothiazolesa[a]

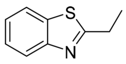
1d **2d**



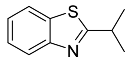
2da, 90%, 10h



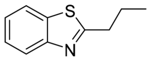
2db, 85%, 10h



2dc, 85%, 10h



2dd, 86%, 10h

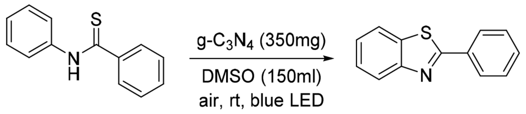


2de, 85%, 10h

[a]Reaction conditions: **1d** (0.1 mmol) and g-C_3N_4 (10 mg) in DMSO (3 mL) irradiated by a 10 W blue LED under an air atmosphere at rt. Isolated yields are shown.

To demonstrate the practicality of this method, a gram-scale reaction with **1aa** was performed. Treatment of **1aa** (1.00 g) with g-C_3N_4 by irradiation of blue LED under an air atmosphere gave desired product **2aa** in 62% yield (Scheme 3).

Scheme 3. Gram-Scale Reaction



1aa
1.00 g, 4.69 mmol

2aa, 62% yield
0.62 g, 2.93 mmol

To get insight into the reaction mechanism, several control experiments were carried out. Light on/off experiments were performed to investigate the effect of light irradiation on the reaction (Figure 1). It was found that the cyclization proceeded smoothly under blue-light irradiation, but no reaction occurred when the light was turned off. This experiment revealed that light is indispensable for the reaction and the reaction should not be a radical chain reaction initiated by light.

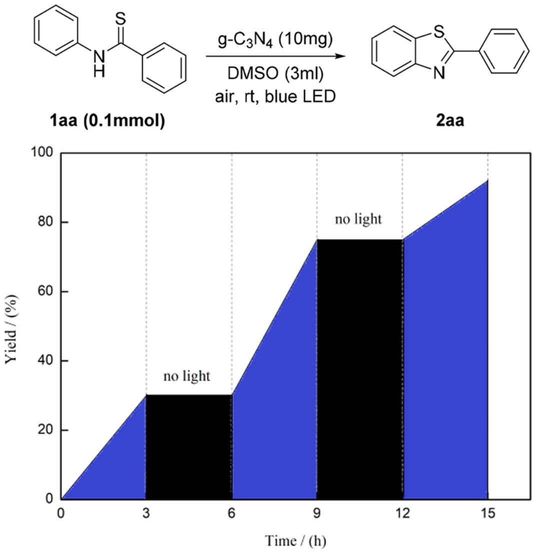


Figure 1. Light on/off experiments.

Furthermore, the steady-state emission of g-C_3N_4 is conducted in the presence of *N*-phenylbenzothioamide (see Figure S8). The red shift was observed with the increase in the concentrations of *N*-phenylbenzothioamide in the experiment, indicating *N*-phenylbenzothioamide adsorbs on the surface of g-C_3N_4 to form a complex that has a new electron donor level above the original valence band of g-C_3N_4.[9a,b,15]

The effect of different scavengers was investigated to gain further information about the reaction mechanism (Table 4).

Table 4. Active Species Trapping Reaction for the Cyclization of Thiobenzanilides[a]

1aa **2aa**

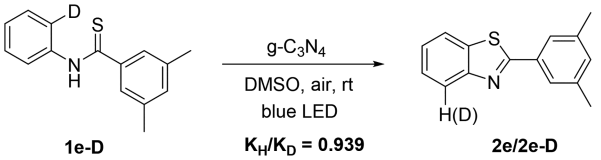
entry	quencher	equiv	atmosphere	quenching group	yield (%)
1	benzoquinone	1.0	air	$O_2^{\bullet -}$	93
2	$AgNO_3$	3.0	N_2	e	90

[a]Reaction conditions: **1aa** (0.1 mmol) and g-C_3N_4 (10 mg) in DMSO (3 mL) irradiated by a 10 W blue LED for 10 h at rt. Yields were determined by HPLC.

When superoxide radical ($O_2^{\bullet -}$) scavenger benzoquinone was added,[11] the product yield was not obviously changed. Our EPR experiment has demonstrated the existence of superoxide radical in the reaction (see Figure S10). Furthermore, when the reaction was performed under a N_2 atmosphere with 3 equiv of $AgNO_3$, an electron scavenger,[16] product **2aa** was obtained in 90% yield. These two experiments indicated that molecular oxygen in air acts as an electron scavenger to promote the photoredox reaction.

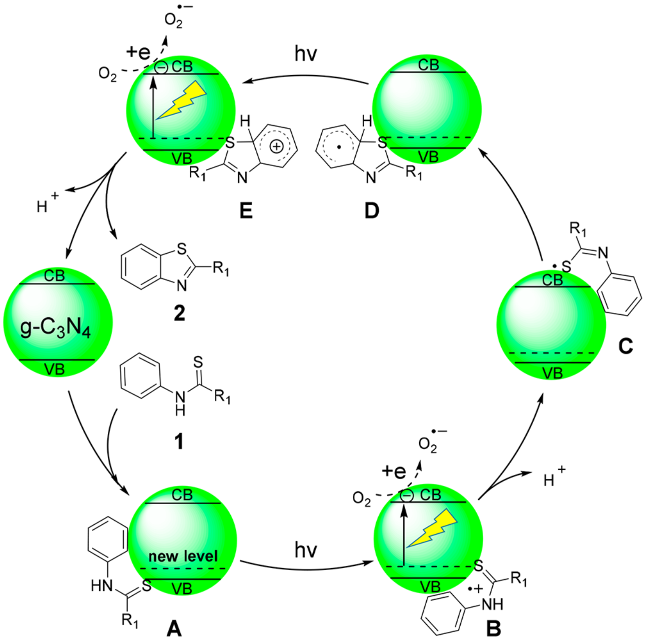
The intramolecular kinetic isotope effect (K_H/K_D = 0.939) was obtained by using deuterated substrate **1e-D** (Scheme 4), which suggests that the C−H bond cleavage might not be the rate-determining step. In addition, no reaction occurred when *N*-methyl-*N*-phenylbenzothioamide **1f** was used as a substrate under the same reaction condition (Scheme 5), indicating that the deprotonation of the N−H bond is involved in the photoredox cyclization.

Scheme 4. Intramolecular Kinetic Study



Scheme 5. Control Experiment

Scheme 6. Proposed Reaction Mechanism



According to the experiments described above and the literature,[14a,b] a plausible reaction mechanism is proposed (Scheme 6). Initially, N-substituted benzothioamide **1** adsorbs to the surface of g-C_3N_4 to form a complex **A** with the formation of a new donor level above the valence band of g-C_3N_4. Visible-light irradiation of **A** drives the promotion of an electron to the conduction band of g-C_3N_4 with the generation of radical cation **B**. The photogenerated electron quenching by O_2 and loss of a proton from **B** produce radical **C**. The sulfur-centered radical of **C** intramolecularly attacks the benzene ring to form aryl radical **D**, which releases an electron to the conduction band of g-C_3N_4 to generate a cation **E** under visible-light irradiation. **E** undergoes deprotonation and rearomatization to provide final product **2**, which is consistent with the KIE study and previous findings.[14b] It has been reported that the direct conversion of aryl radical **D** to **2** via hydrogen atom transfer (HAT) with $HOO^\bullet$ has a KIE of 5, where cleavage of the C−H bond is considered to be the rate-determining step.[14a] In our reaction, O_2 acts as an electron scavenger to be reduced to $O_2^{\bullet-}$ that may react with protons to form $HOO^\bullet$; the latter is eventually converted to H_2O_2 and O_2.[17]

Table 5. Recyclability of Catalyst g-C_3N_4

no. of cycles	1	2	3	4	5
yield (%)	95	96	95	93	94

The recyclability of g-C_3N_4 was investigated (Table 5). Treatment of **1aa** with g-C_3N_4 gave **2aa** in 95% yield in the first run. The heterogeneous photocatalyst can be separated easily from the reaction mixture by simple centrifugation. The recovered catalyst was reused five times without a loss of catalytic activity. Furthermore, the stability of g-C_3N_4 was investigated by comparison of the recycled catalyst and the fresh catalyst. Examination of the two catalysts by X-ray powder diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM) shows that a recycled catalyst did not change obviously in morphology or structure after five recycling steps (see Figure S5).

In conclusion, we have developed a metal-free, heterogeneous photocatalysis for the synthesis of 2-substituted benzothiazoles via C−H functionalization/C−S bond formation of thiobenzanilides using inexpensive graphitic carbon nitride (g-C_3N_4) as the catalyst and visible light as the energy source. This reaction is tolerant to a variety of functional groups and can be carried out under an air atmosphere at room temperature without the need for a strong base or an organic oxidizing agent. In addition, the catalyst was found to be stable and reusable. A mechanistic study revealed that absorption of the substrate to g-C_3N_4 took place and facilitated the photoredox transformation; cleavage of the C−H bond of thiobenzanilides may not be the rate-determining step, and O_2 in air acts as an electron scavenger to promote the photoredox reaction. We believe that this green protocol would find applications in the pharmaceutical industry.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c01571.

Experimental procedures, characterization data, and ^1H and ^{13}C NMR spectral data of products (PDF)

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Notes

The authors declare no competing financial interest.

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(17) $O_2^{\bullet -}$ acts as a proton quencher rather than a base that removes the N-H hydrogen from **B** because the loss of a proton from radical cation **B** and cation **E** could be facile because of generation of more stable radical **C** and product **2**, respectively, and may be facilitated by solvent (DMSO) or basic g-C_3N_4.