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C_3N_4-photocatalyzed Aerobic Oxidative Cleavage of C≡C Bonds in Alkynes with Diazonium Salts Leading to Two Different Aldehydes or Esters in One Pot

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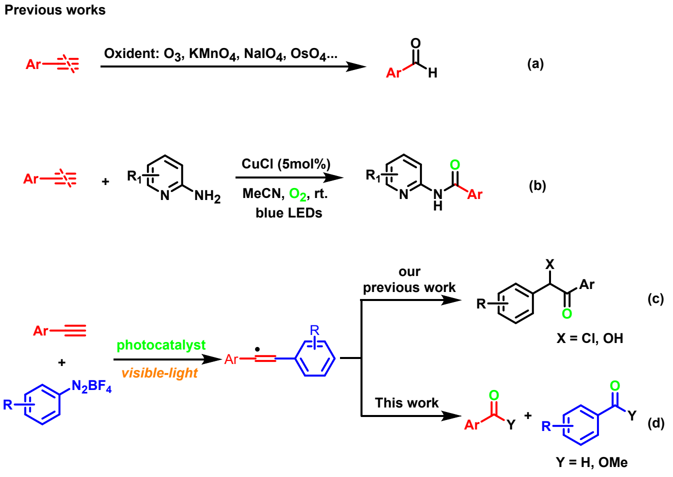
A novel photocatalyzed radical addition/oxygen oxidation/cleavage of dioxetane/HAT domino process for cleavage of C≡C bond has been described. This protocol used porous graphitic carbon nitrides (p-*g*-C_3N_4) as a metal-free recyclable photocatalyst for transformations of alkynes with diazonium salts to give two different aldehydes or esters, which enables the formation of multiple C-O bonds in a single reaction with operational simplicity. This reaction has an excellent substrate scope and give the desired products in moderate to high yields. In addition, the heterogeneous semiconductor enables easy handling and excellent recyclability with at least 6 times without any apparent loss of activity. Furthermore, this reaction could be carried out under solar light irradiation and is applicable for gram scale with satisfactory results.

Introduction

The oxidative cleavage of unsaturated bond such as C=C bond and C≡C bond is an effective method for preparing of carbonyl derivatives due to their diversity and abundance from natural sources or industrial petroleum. [1] Till now, the commonly used method in industry is most often with ozonolysis[2], which requires a high cost of special ozone generator or involve toxic and expensive reagents such as O_3. Although other oxidizing agents such as $KMnO_4$, $NaIO_4$ and OsO_4 can be used[3] (scheme 1a), most of these reagents suffer from the drawbacks in terms of toxicity, selectivity, storage, handling and cost which cannot meet the current environmental sustainable development needs. Therefore, a great effort has been dedicated to the development of sustainable catalytic oxidation processes.

Molecular oxygen can be considered as the cleanest and cheapest ideal oxidant. In the past decades, various of metal catalysts such as Pd[4], Cu[5], Fe[6], Ru[7], Ni[8], Ce[9], Co[10] and Mn[11], *et al*. have been developed for the oxygen oxidative cleavage of unsaturated bond. Although these methods can be used to synthesize the corresponding carbonyl products with high yields and excellent regioselectivity, most of them are still suffering from drawbacks such as harsh conditions or no reusability of the expensive metal catalysts. Recently, photocatalyzed oxygen oxidation cleavage of alkenes and alkynes has received extensive attentions owing to its mild condition, energy efficiency and environmental friendliness. For example, Inoue group first developed a photooxidative cleavage of aromatic alkenes using of dimethoxybenzene as photocatalyst under an O_2 atmosphere.[12] Later, You[13] and Yadav[14] exploited visible light promoted reaction with an organophotoredox catalyst for this reaction. Recently, an advantageous cleavage of styrene derivatives under white-LED visible-light irradiation using bis(4-methoxyphenyl) disulfide as a photocatalyst was also described by the group of Wang [15]. Although these methods provide attractive routes for oxidation cleavage reaction, however, most of them focus on alkenes, the direct oxidation cleavage of alkynes has been elusive.

The challenge for the oxidation cleavage of alkynes lies in how to overcome the higher dissociation energy of triple bond (C≡C BDE = 954kJ/mol *vs* C=C BDE = 728 kJ/mol). One feasible method is to use copper(I) combine with terminal alkynes to generate copper(I) phenylacetylide which can be excited by



Scheme 1. Construction of Aromatic Aldehydes via C≡C Bond Cleavage

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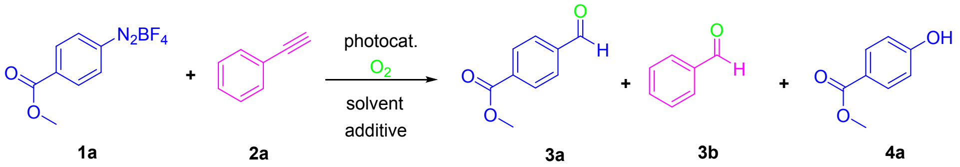
visible light.[16] For example, Hwang group reported a copper-catalyzed oxidation of terminal alkynes with 2-aminopyridines featuring a C ≡C bond cleavage with the assistance of blue light irradiation (Scheme 1b).[17]Although this method can be used to direct oxidation cleavage of alkynes with high yields and excellent regioselectivity, special amino substrates were required and the catalyst cannot be reused. The search of a simple and metal-free heterogeneous photocatalytic reaction to oxidation cleavage of alkynes is still highly desirable.

In our previous work[18] (Scheme 1c)， we found alkyne could be activate by a free radical addition to generate alkenyl radical, we envisioned whether the C=C band of alkenyl radical may be reacted with a superoxide radical to generated oxetane intermediate, which could cleavage by a typical photocatalyzed process. If possible, alkynes could be indirectly cleavaged and two different carbonyl derivatives could be obtained. On the other hand, the photocatalytic reaction have hitherto depend on homogeneous catalysts, which are usually difficult to recover from the reaction mixture. Therefore, heterogeneous photocatalysts are in high demand due to their post-reaction stability and recyclability. In this context, polymeric carbon nitride (C_3N_4)-base heterogeneous photocatalyzed organic reaction has been received much attention, due to its high thermal, chemical, and photostability, as well as favorable conduction and valence band positions.[19] Very recently, Das and co-workers developed an excellent method for selective cleavage of C=C bonds in aryl olefins using C_3N_4 as photocatalyst under an O_2 atmosphere.[20] Currently, our group also developed C_3N_4 photocatalyzed oxidative cleavage of vicinal diols,[21] Meerwein hydration reaction of alkenes[22] and hydrosulfonylation of alkynes[23]. In continuation of our interest in heterogeneous photoredox catalysis, herein, we report a mild methodology for selective oxidative cleavage of C≡C bond by means of a radical addition/oxygen oxidation/cleavage of dioxetane/HAT domino process to access aldehydes or esters under 250 W Xe lamp irradiation using p-*g*-C_3N_4 as a reusable heterogeneous photocatalyst (Scheme 1d).

Results and discussions

Table 1 Optimization of the reaction conditions[a]



Entry	Cat.	Solvent	Base	Yield/%[b]		
				3a	**3b**	**4a**
1	p-*g*-C_3N_4(20mg)	MeCN/H_2O (9:1)	-	43	30	16
2	p-*g*-C_3N_4 (20mg)	MeCN/H_2O (9:1)	Cs_2CO_3	75	72	trace
3	p-*g*-C_3N_4 (20mg)	MeCN/H_2O (9:1)	K_2HPO_4	19	trace	trace
4	p-*g*-C_3N_4 (20mg)	MeCN/H_2O (9:1)	Na_2CO_3	52	45	15
5	p-*g*-C_3N_4 (20mg)	MeCN/H_2O (9:1)	Pyridine	66	59	trace
6	p-*g*-C_3N_4 (20mg)	MeCN/H_2O (9:1)	tBuOK	28	19	trace
7	p-*g*-C_3N_4 (20mg)	MeCN/H_2O (9:1)	DBU	45	35	18
8	Fe@*g*-C_3N_4（20mg）	MeCN/H_2O (9:1)	Cs_2CO_3	58	55	trace
9	CN620 (20mg)	MeCN/H_2O (9:1)	Cs_2CO_3	71	67	trace
10	Ru(bpy)$_3$Cl$_2$ (2 mmol%)	MeCN/H_2O (9:1)	Cs_2CO_3	21	16	trace
11	Ir(ppy)$_3$ (2 mmol%)	MeCN/H_2O (9:1)	Cs_2CO_3	trace	trace	trace
12	Eosin Y (2 mmol%)	MeCN/H_2O (9:1)	Cs_2CO_3	trace	trace	trace
13	Rhodamine B (2 mmol%)	MeCN/H_2O (9:1)	Cs_2CO_3	trace	trace	trace
14	p-*g*-C_3N_4 (20mg)	Dry MeCN	Cs_2CO_3	No	No	No
15	p-*g*-C_3N_4 (20mg)	MeCN/H_2O (4:1)	Cs_2CO_3	66	61	11
16	p-*g*-C_3N_4 (20mg)	H_2O	Cs_2CO_3	55	55	15
17	p-*g*-C_3N_4 (20mg)	acetone/H_2O (9:1)	Cs_2CO_3	62	58	trace
18	p-*g*-C_3N_4 (20mg)	MeOH/H_2O (9:1)	Cs_2CO_3	48	45	11
19	p-*g*-C_3N_4 (30mg)	MeCN/H_2O (9:1)	Cs_2CO_3	72	70	trace
20	p-*g*-C_3N_4 (10mg)	MeCN/H_2O (9:1)	Cs_2CO_3	58	54	trace
21	No	MeCN/H_2O (9:1)	Cs_2CO_3	No	No	trace
22[c]	p-*g*-C_3N_4 (20mg)	MeCN/H_2O (9:1)	Cs_2CO_3	No	No	trace

a Reaction conditions: a mixture of **1a** (0.5 mmol), **2a** (0.6 mmol), base (0.2 equiv), 2 mL of solvent, O_2 atmosphere, at room temperature, under a 250 W Xe lamp irradiation, reaction for 4 hours. [b] Isolated yield. [c] Reaction was performed Without light.

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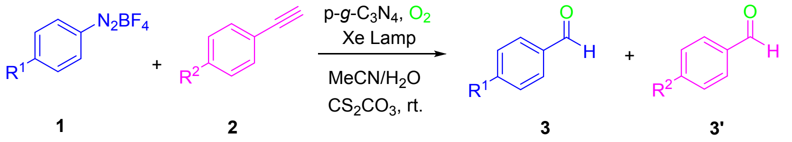
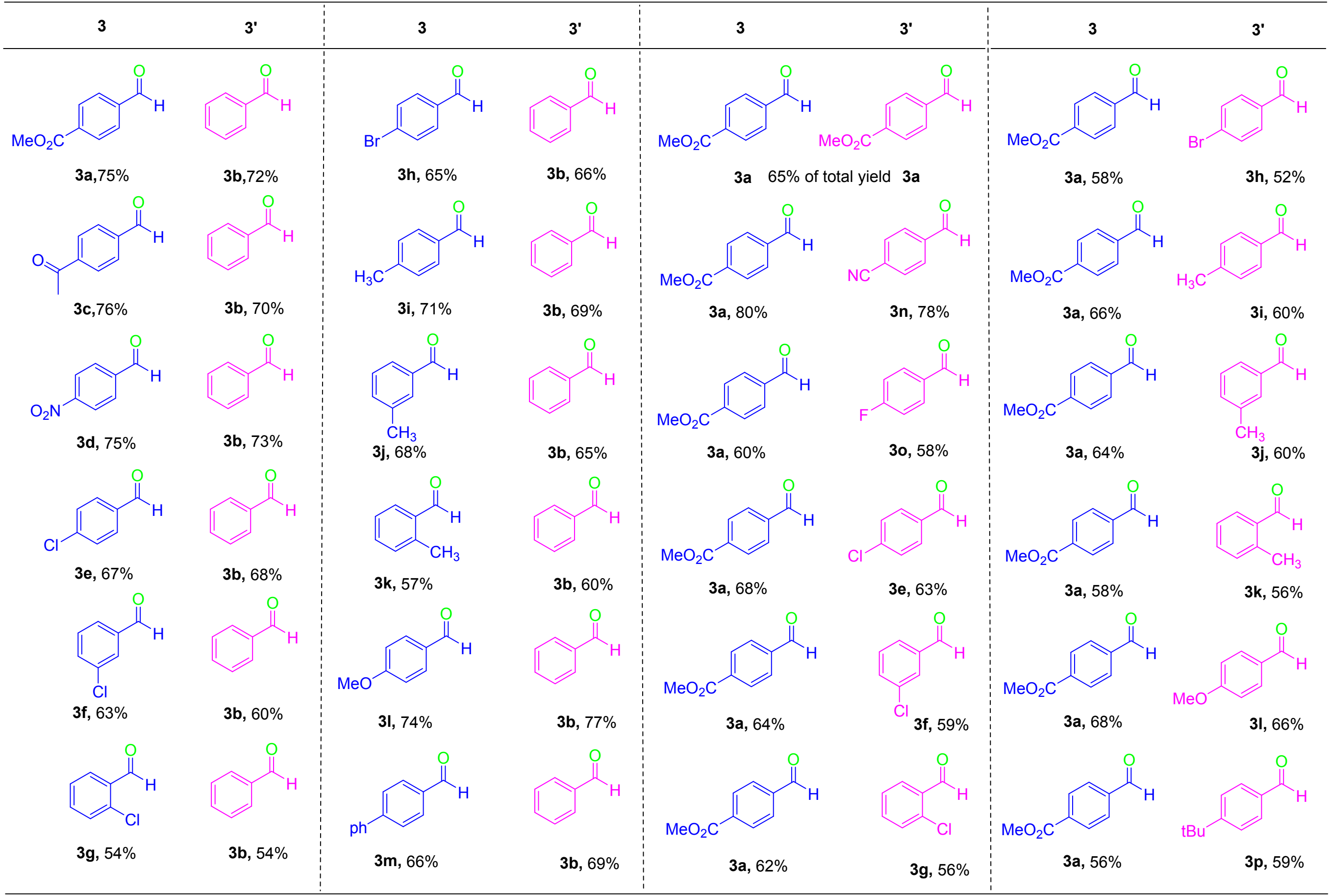
Initially, diazonium salt **1a** (0.5 mmol) and 1.2 equiv. of phenylacetylene **2a** were selected as model substrates to optimize the reaction conditions (Table 1). At first, 20 mg of p-*g*-C_3N_4 was used as catalyst in 1.8 mL of acetonitrile with 0.2 mL Of H_2O under 250 W Xe lamp irradiation for 4 h at room temperature. Gratifyingly, the desired products methyl *p*-formylbenzoate **3a** and benzaldehyde **3b** were obtained in 43% and 30% yields respectively (Table 1, entry1). However, the byproduct methyl 4-hydroxybenzoate **4a** was obtained with 16% yield at the same time (Table 1, entry1), which impelled us to search for a more efficient reaction system.

To our delight, when 0.2 equiv of Cs_2CO_3 was added, the yields of target products **3a** and **3b** increased to 75% and 72% respectively, while trace amount of byproduct **4a** was observed (Table 1, entry 2). Then a wide variety of bases such as pyridine, K_2HPO_4, Na_2CO_3, *t*BuOK, and DBU were screened, however, inferior results were obtained (Table 1, entries 3-7). Subsequently, other kind of C_3N_4-based photocatalysts such as Fe@*g*-C_3N_4 and graphitic carbon nitride with nitrogen vacancies (CN620) were tested and no better catalytic activities were showed (Table 1, entries 8 and 9). It is noticed that typical homogeneous photocatalysts such as $Ru(bpy)_3Cl_2$, $Ir(ppy)_3$, Eosin Y and Rhodamine B cannot able provide significant oxidative cleavage reaction in this condition (Table 1, entries 10–13). As expected, the transformation was hampered when anhydrous MeCN was used as a replacement (Table 1, entry 14). When the amount of water was increased, lower yields of the desired products with considerable amount of byproduct were obtained (Table 1, entries 15, 16). Organic solvents such as acetone and CH_3OH have also been applied and the results showed relatively lower yields (Table 1, entries 17, 18). Furthermore, increasing the amount of p-*g*-C_3N_4 to 30 mg cannot increase the yield (Table 1, entry 19), besides, reducing the amount of p-g-C_3N_4 to 10 mg led to a decreased yield (Table 1, entry 20). Finally, the model reaction cannot carried out without light or photocatalyst, no desired product was observed respectively (Table 1, entries 21, 22). In addition, the blue, green LED and white CFL lamps were also used,

Table 2 Scope of the reaction substrates



1 2 3 3'



3	3'	3	3'	3	3'	3	3'
3a,75%	**3b**,72%	**3h**, 65%	**3b**, 66%	**3a** 65% of total yield	**3a**	**3a**, 58%	**3h**, 52%
3c,76%	**3b**, 70%	**3i**, 71%	**3b**, 69%	**3a**, 80%	**3n**, 78%	**3a**, 66%	**3i**, 60%
3d, 75%	**3b**, 73%	**3j**, 68%	**3b**, 65%	**3a**, 60%	**3o**, 58%	**3a**, 64%	**3j**, 60%
3e, 67%	**3b**, 68%	**3k**, 57%	**3b**, 60%	**3a**, 68%	**3e**, 63%	**3a**, 58%	**3k**, 56%
3f, 63%	**3b**, 60%	**3l**, 74%	**3b**, 77%	**3a**, 64%	**3f**, 59%	**3a**, 68%	**3l**, 66%
3g, 54%	**3b**, 54%	**3m**, 66%	**3b**, 69%	**3a**, 62%	**3g**, 56%	**3a**, 56%	**3p**, 59%

[a] Reaction conditions: a mixture of **1** (0.5 mmol), **2** (0.6 mmol), Cs_2CO_3 (0.2 equiv), solvent (2 mL, MeCN/H_2O=9:1), O_2 atmosphere, at room temperature, under a 250W Xe lamp irradiation, reaction for 4 hours, isolated yield.

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however, trace amount of desired products were obtained.

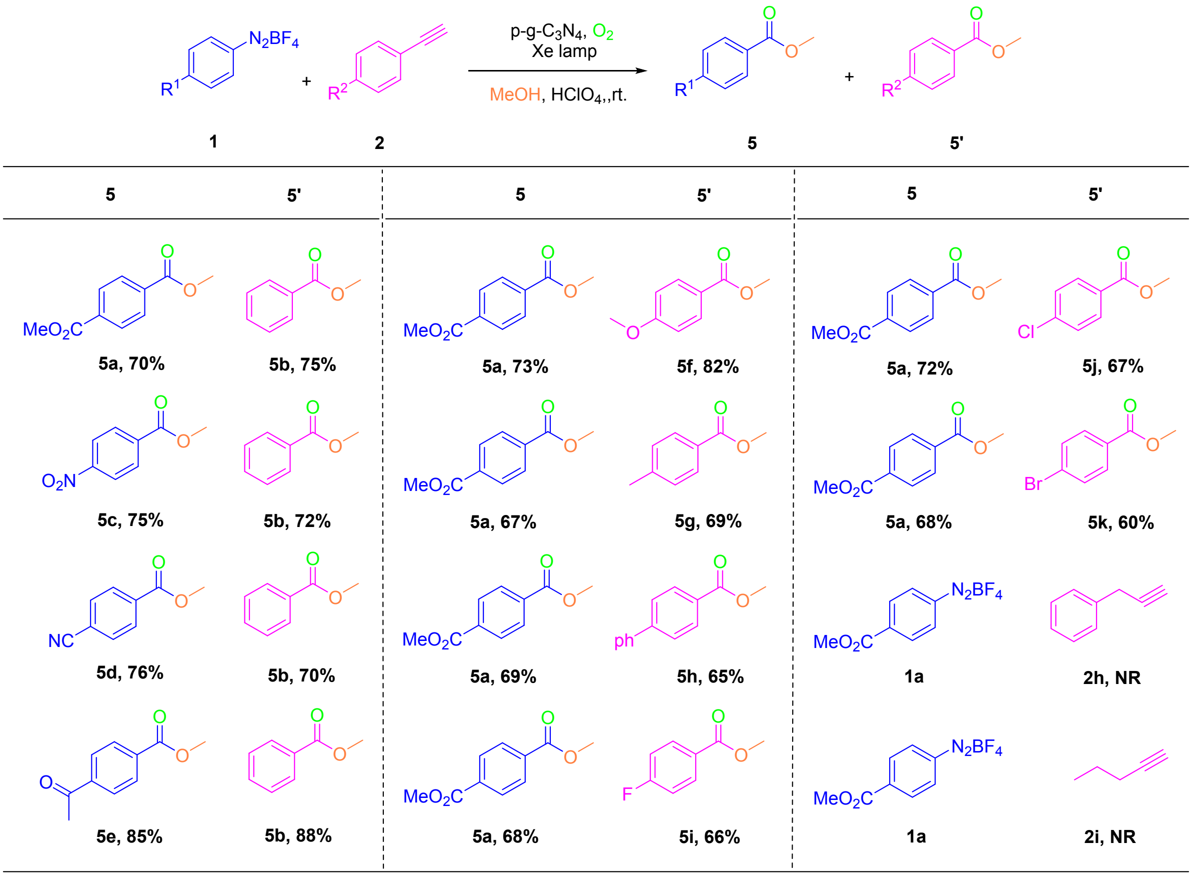
With the optimized conditions in hand, the scope of various diazonium salts was first explored (Table 2). In general, reactions of aromatic diazonium salts derivatives bearing either electron-withdrawing or electron-donating groups tolerated in the present photocatalytic transformation well to afford the desired cleavage products with moderate to good yields. Notably, a series of functional groups including halogen, nitro, ester, acyl, phenyl, methyl and methoxy groups were well compatible under the conditions, which indicated that the electronic effect had slight influence on this reaction. It was found that the steric hindrance had an obvious effect on the reaction efficiency. In comparison with the *para*-, *ortho*-, and *meta*-chloro and methyl substituted aryl diazonium salts, the ortho substituted substituents gave a relatively lower yield. Then the scope of alkynes was investigated. As we can see, most of the substrates showed good activities regardless of electron-withdrawing or -donating groups. However, the aliphatic alkynes were inert toward this transformation.

Next, we became interested in applying the photocatalytic system to synthesis aryl esters. After adjusting the reaction conditions (see Supporting Information, Table S1), 70% yield of product **5a** and 75% yield of **5b** were obtained in the presence of p-*g*-C_3N_4 (20mg) in 3mL MeOH after irradiation with a 250W Xe Lamp for 4 h, when $HClO_4$ (0.5mL) was used as additive. With these results in hand, the scopes and generality of the present method were then examined. As shown in Table 3, aryl diazonium salts containing electron-withdrawing groups such as CO_2Me, NO_2, CN and MeCO were well tolerated under the standard conditions, affording the desired products **5** and **5'** in moderate to good yields. However, substrates with electron-donating groups such as MeO and Me were unsuitable for the present reaction conditions. Different aromatic alkynes were evaluated as well. The results showed that both electron-donating groups and halogens were well tolerated under the standard conditions, while the electron-withdrawing groups cannot tolerate in such condition. Again, the aliphatic alkynes such as **2h** and **2i**, were still inert under the present reaction conditions.

Furthermore, this photocatalyzed aerobic oxidative conversion of terminal alkynes and diazonium salts could be driven by solar irradiation with satisfactory results compared with the model reaction conditions with Xe lamp irradiation. The use of solar energy makes it easily for scaling up to the gram scale. The reaction of **1a** (8mmol, 2g) was reacted with **2a** (10mmol, 1g) proceeded smoothly under the optimized conditions to provide product **3a, 3b** in 81% and 75% yields, while **5a**, **5b** in 76% and 77% yield using 300 mg of p-*g*-C_3N_4 within 6 h under solar irradiation (Scheme 2).

Finally, the reusability of this catalyst system was

Table 3 Scope of the esterification reaction substrates[a]



[a] Reaction conditions: a mixture of **1** (0.5 mmol), **2** (0.6 mmol), $HClO_4$ (0.4 mL), MeOH (3 mL), O_2 atmosphere, at room temperature, under a 250W Xe lamp irradiation, reaction for 4 hours, isolated yield.

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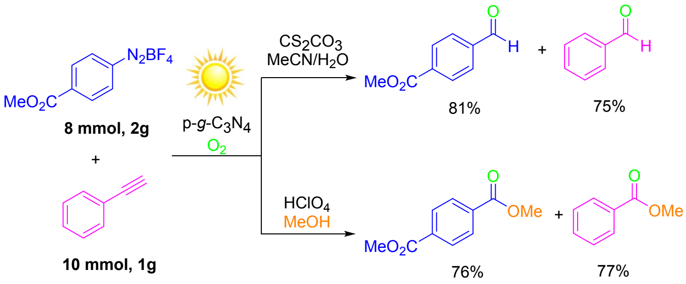


Scheme 2. Direct solar energy mediated C≡C bond cleavage on the gram scale.

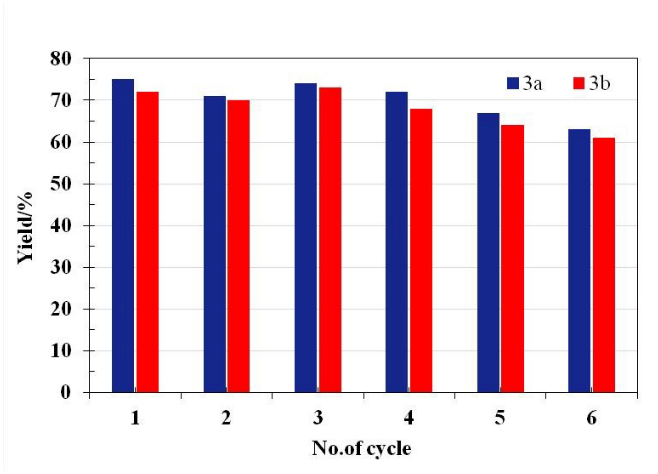
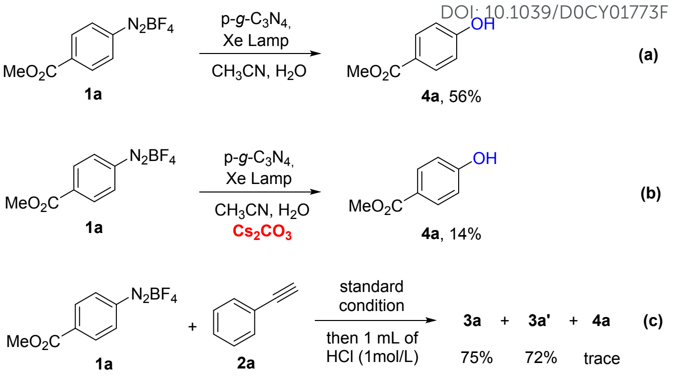


Fig.1 Recyclability of p-*g*-C_3N_4 for the synthesis of **3a** and **3b**.



Scheme 3 Controlled experiments.

Table 4 Active species trapping reactions for the photocatalyzed oxidative cleavage reaction system[a]

Entry	Quencher	Quenching group	yield (%)	
			3a	3b
1	–	–	75	71
2	TEMPO	Free radicals	trace	trace
3	*p*-Benzoquinone	$^{\cdot}O^{2-}$	trace	trace
4	CCl_4	e^-	36	31
5	$HCOONH_4$	Hole	trace	trace
6	Tertiary butanol	$^{\cdot}OH$	68	65

a mixture of **1a** (0.5 mmol), **2a** (1.2 equv.), Cs_2CO_3 (0.2 equiv), solvent (2 mL, $MeCN/H_2O=9:1$), quencher (1.2 equv.) O_2 atmosphere, at room temperature, under a 250W Xe lamp irradiation, reaction for 4 hours, isolated yield.

investigated to determine the reusability of the photocatalyst. The cyclic experiments were carried out under the first module reaction to generate aldehydes. Once the reaction was complete, p-*g*-C_3N_4 was filtered and washed with water and ethanol, dried at 105 °C, and then reused for the next reaction with a fresh batch of solvent. The results of the reuse test are shown in Fig. 1. It was obvious that p-*g*-C_3N_4 still showed excellent performance for the reaction after being reused six times.

Subsequently, a group of controlled experiments has been conducted. First, when diazonium salt reacted with p-*g*-C_3N_4 under Xe lamp irradiation with $MeCN/H_2O=9:1$ as solvent, hydrolysis product **4a** was obtained with 56% yield (Scheme 3a). While when 0.2 equiv of CS_2CO_3 was added, the yield of **4a** was dramatically decreased into 14% yield (Scheme 3b). Furthermore, when the reaction mixture has been neutralized by HCl before the purification, only trace amount of phenol was observed like the standard reaction (Scheme 3c). These results indicated the hydrolysis of diazonium salt could be significantly inhibited by base which promote the cleavage reaction.

To further explore the mechanism of the reaction, active species trapping experiments were carried out to gain a deeper understanding of the reactive oxygen species and possible intermediates in this reactions (Table 4). When 2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPO) was added, the reaction was obviously inhibited which indicated that the reaction was undergoing a radical pathway (Table 4, entry 2). Further addition of the superoxide radical quencher *p*-benzoquinone in the reaction displayed trace amount of yield of the products (Table 4, entry 3). The result suggested that the generated superoxide radicals were the major oxidative species. In addition, the yields also decreased gradually when electrons were quenched by the tetrachloromethane (Table 4, entry 4). Besides the superoxide radicals and electrons, valence band holes also had an important effect on the oxidative cleavage reaction. Quenching of valence band holes dramatically decrease the yields (Table 4, entry 5). However, the quenching of hydroxyl radical had almost no influence on the reaction (Table 4, entry 6). These results revealing that the substrates were active by valence band holes.

Based on the trapping experiments and previous literature reports, a tentative mechanism of photocatalytic oxidative cleavage of C≡C bond is depicted in Fig.2. Initially, irradiation of p-*g*-C_3N_4 with the Xe lamp creates photogenerated electrons (e^-) and holes (h^+). As a consequence, an electron reduces molecular oxygen to produce a superoxide radical $O^{2-\bullet}$. At the meantime, a single electron transfer (SET) between electrons and diazonium salt **1** to generate aryl radical **I**. Adding radical **I** to alkyne **2** generates the corresponding alkenyl radical **II**, which is oxidized by the holes to form intermediate **III**. Further reaction of intermediate **III** with $O^{2-\bullet}$ forms dioxetane intermediate Ⅳ, then the cleavage of dioxetane intermediate Ⅳ generated the aldehyde **3** and acyl radical Ⅴ. Hydrogen atom transfer (HAT) from water or

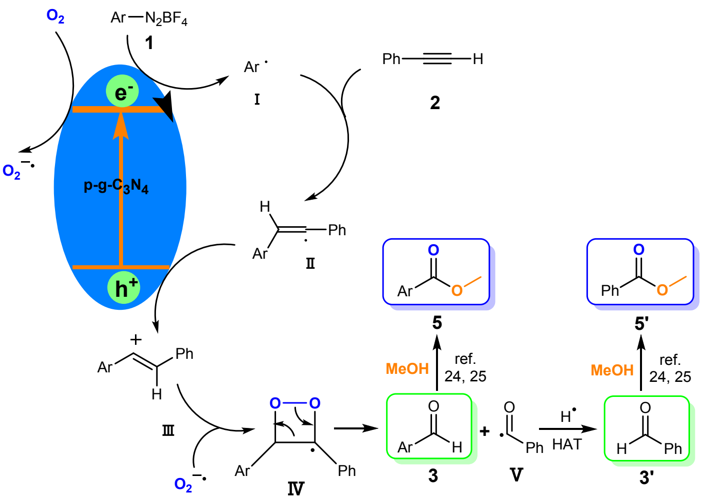


Fig. 2 Plausible reaction mechanism.

methanol to the acyl radical would give the second aldehyde **3'**. The further oxidative coupling of aldehyde and MeOH could affords methyl ester **5** and **5'** under photo-oxidative conditions.[24, 25] In addition, the another electron may be released to valence band from the water or methanol after HAT process.

Conclusions

In conclusion, we have developed a p-*g*-C_3N_4 photocatalytic system for the aerobic oxidative C≡C bond cleavage of alkynes with diazonium salts through a radical strategy under 250 W Xe lamp irradiation. A series of alkynes could be efficiently cleaved and converted into the corresponding aldehydes or esters by using O_2 as the oxidants. Mechanistic insights into the triple bond cleavage protocol reveal that this reaction may involves a sequence radical addition/oxygen oxidation/ cleavage of dioxetane/HAT process. Mild reaction conditions, non-noble metal catalyst, solar energy driven, gram scale synthesis and excellent reusability of the catalyst make the present photocatalytic system much more competitive than the existing systems.

Conflicts of interest

There are no conflicts to declare.

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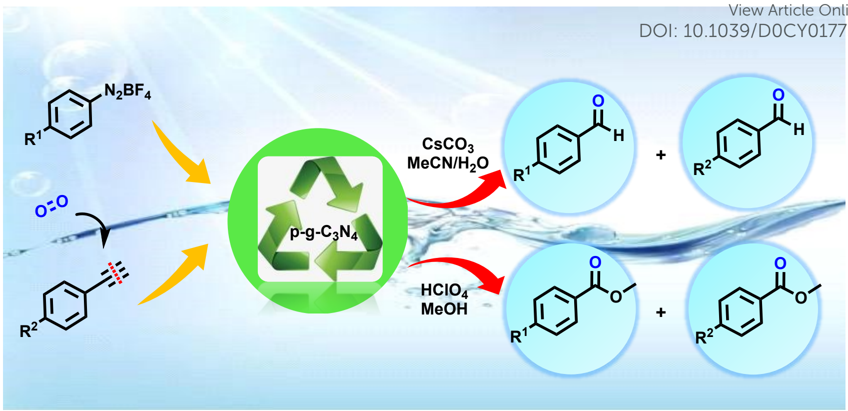
C_3N_4-photocatalyzed Aerobic Oxidative Cleavage of C≡C Bonds in Alkynes with Diazonium Salts Leading to Two Different Aldehydes or Esters in One Pot



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C_3N_4-photocatalzed oxidative cleavage of C≡C bond in alkynes with diazonium salts to access two different aldehydes or esters.