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Visible Light-Catalyzed Decarboxylative Alkynylation of Arenediazonium Salts with Alkynyl Carboxylic Acids: Direct Access to Aryl Alkynes by Organic Photoredox Catalysis

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Abstract. A convenient method mediated by photoredox catalysis is developed for the direct construction of aryl alkynes. Readily available aromatic diazonium salts have been utilized as the aryl radical source to couple alkynyl carboxylic acids to feature the decarboxylative arylation. A wide range of substrates are amenable to this protocol with broad functional group tolerance, and diversely-functionalized aryl alkynes could be synthesized under mild, neutral and transition metal-free reaction conditions using visible light irradiation. Alongside synthetic sustainability associated with the photocatalytic and transition metal-free operation, another key point of this method is that the organic dye catalyst acts as an excited-state reductant, thus establishing the quenching cycle for radical addition and decarboxylative elimination.

Keywords: photocatalysis; decarboxylative alkynylation; arenediazonium salts; alkynyl carboxylic acids; transition metal-free coupling

Introduction

Functionalized aryl and heteroaryl alkynes are among the most fundamental and important p-conjugated systems in various fields. Their application permeates to not only organic synthesis but also materials science.[1] Therefore, the development of efficient methods for aryl alkyne synthesis keeps receiving the attention of synthetic chemists. Although synthetic protocol such as Sonogashira cross-coupling,[2] is well-established for the incorporation of alkyne moieties into organic molecules.[3] It is noteworthy that as a practical alternative, the use of alkynyl acids as terminal arylacetylene surrogates has in recent years won high success.

Since their successful application in decarboxylative coupling reaction in 2008,[4] alkynyl carboxylic acids have been found widespread application in various decarboxylative couplings owing to their inherent advantages such as easy storage, and low cost.[5] In addition, aryl alkynyl carboxylic acid derivatives are easy to prepare and purify.[6]

Due to the abundant source, renewability, low cost and ecofriendlinessy visible light-induced synthesis has been recognized as a powerful and green strategy.[7] Many novel visible light-mediated reactions were developed for the efficient and rapid preparation of fine chemicals over the past years.[8]

Although great success has been achieved in transition metal-catalyzed decarboxylative alkynylation reactions, it is yet highly desirable to develop more convenient and efficient methods under mild conditions. For example, the photocatalytic decarboxylative coupling strategies have recently attracted much attention (Scheme 1).[9] Chen and co-workers reported a visible-light photoredox decarboxylative coupling of N-(acyloxy)phthalimides(NOP) and alkynyl sulfones (Scheme 1, A).[10] In the same year, Xiao and Waser group independently developed the visible-light triggered decarboxylative alkynylation of carboxylic acids with benziodoxolone (BI)-alkynes (Scheme 1, B).[11] Then Li & Cheng et al. reported a similar visible light-induced decarboxylative coupling of (BI)-alkynes with alkyl carboxylic acids using DCA(9,10-dicyanoanthracene) as organic photoredox catalysts (Scheme 1, C).[12] Wang & Li's group reported a visible-light photoredox decarboxylative alkynylation of α-keto acids using bromoacetylenes as the alkynyl precursors and NHPI (N-hydroxyphthalimide) as the catalyst to give ynones under the irradiation of sunlight or blue LED light (Scheme 1, D).[13] Almost at the same time, Chen and co-workers developed a similar decarboxylative alkynylation by using a hypervalent iodine(III) reagent/photoredox dual catalytic system, with BI-alkyne as the radical acceptor and BI-OAc as the additive (Scheme 1, E).[14] Then Fu et al. developed an efficient method for the visible-light photoredox chemoselective synthesis of internal alkynes using N-phthalimidoyl oxalates with alkynyl sulfones (Scheme 1, F).[15] Then they reported a novel and efficient decarboxylative alkynylation of N-(acetoxy)phthalimides of α-amino acids with terminal alkynes by merging photoredox with copper catalysis (Scheme 1, G).[16] Although great advances have been achieved, this field still encounters some existing

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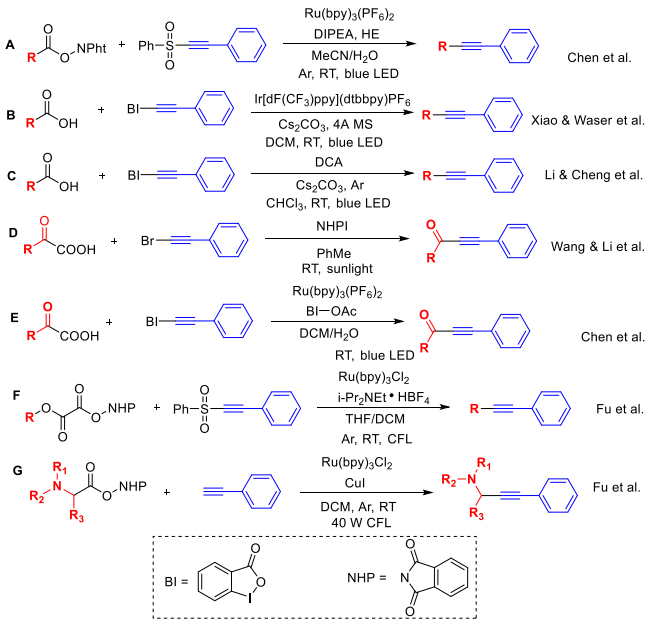
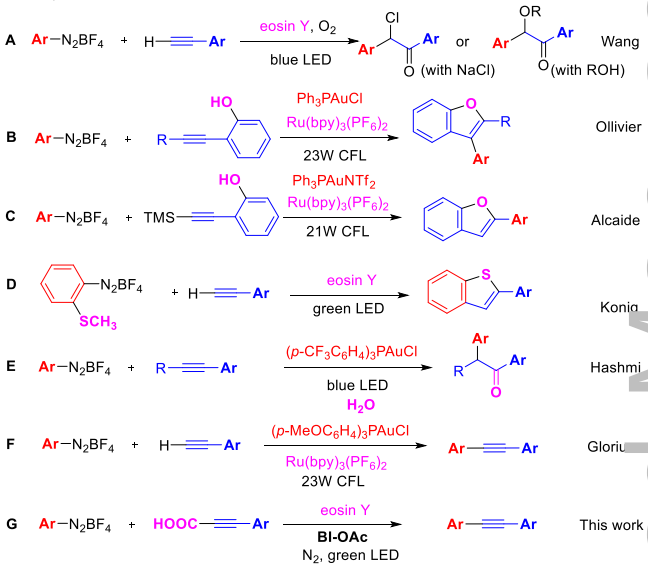
challenges, such as the low atom economy, tedious substrate preparation, super-stoichiometric and/or external oxidants/bases, which inevitably reduces their broad application. Therefore, photoredox alkynylation with alkynyl carboxylic acids is still obscured.



Scheme 1. Decarboxylative alkynylation via visible-light photoredox coupling

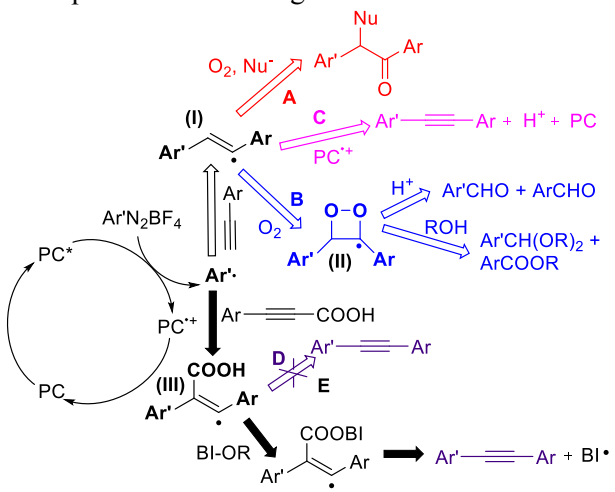
To combine the advantage aryl radical-based single electron transfer (SET) process [17] and organic dye-based photocatalysis,[18] we envision that arenediazonium salts, a class of frequently used aryl precursors in versatile organic reaction,[19-20] could be used to design a photocatalytic arylation reactions of alkynyl acids via decarboxylative coupling with organic dye as photoredox catalyst. The reaction of arenediazonium salts with internal/terminal alkynes usually through visible light-induced radical-triggered chemoselective domino process to access ketones/heterocycle (Scheme 2). Wang and co-workers reported a direct 1,2-difunctionalized approach to synthesize α-chloro or α-alkoxy aryl ketones based on the electronic properties of the substrates (Scheme 2, A).[21] Ollivier's and Alcaide's group independently developed dual photoredox/gold catalysis arylative cyclization of ortho-alkynylphenols/2-[(trimethylsilyl)ethynyl]phenol with aryl diazonium salts as flexible synthesis of benzofurans, although with different selectivity (Scheme 2, B and C).[22] König et al. first reported the photocatalytic reaction of o-methylthio-arenediazonium salts with alkynes yields substituted benzothiophenes (Scheme 2, D).[23] Hashmi et al. reported a photosensitizer-free visible light-mediated gold-catalyzed 1,2-difunctionalization of internal alkynes (Scheme 2, E).[24] However, these strategies could hardly maintain triple bond which could difficulty to apply for alkynylation. The only report was described by Glorius using terminal alkynes as alkynylated reagent by a dual gold/photoredox catalytic system. The coordinates of Au(III) intermediate as π-Lewis acid with the alkyne substrate, activating it towards the formation of the s-bonded alkynyl-Au(III) complex upon deprotonation. The Au(I)/Au(III) redox cycles facilite the alkynylation process and turn it into reality (Scheme 2, F).[25] With the goal of developing visible-light photoredox catalysis that do not require transition metal catalysts, we turned our attention to replace terminal alkynes with alkynyl carboxylic acid, the decarboxylative process might make the radical addition intermediate eliminated to rebuilt triple bond. Our group recently described the use of decarboxylative catalysis strategies to access ketones, ynones and flavones for radical acylation/alkynylation/annulation.[26] Using this concept, herein we take advantage of an organic photocatalyzed system to develop a selective radical alkynylation of terminal alkynes with arenediazonium salts to produce different diarylated alkynes (Scheme 2, G).



Scheme 2. Visible light-promoted transformations of arenediazonium salts with alkynes

Our design concept, as shown in Scheme 3, envisioned that a decarboxylative coupling event might be proceeded according to different pathways. Initially, the photocatalyst (PC) is excited under irradiation with visible light, which performs a single electron transfer (SET) to generate aryl radical from aryl diazonium salt. According to previous reports and experimental results with aryl alkynes, subsequent addition of aryl radical to aryl alkyne generates radical (I), which could either been trapped by nucleophile and oxygen to α-arylketones under path A or reacts with molecular oxygen to give peroxy radical (II) under path B. Radical II could decomposed into aldehydes as a proton acceptor, while convert to acetal and ester in the presence of alcohol. Although radical (I) might be trapped by in situ generated photocatalyst cation radical to rebuild triple bond, however, no positive results have been obtained under path C.

Leveraging recent remarkable achievements in uncovering robust synthetic reactions that relied on alkynyl carboxylic acids involved radical process,[27] it is particularly appealing to explore its possible applications in designing and identifying useful paradigms for alternative diaryl alkynes synthesis. As shown in Scheme 3, we anticipated that a decarboxylation event might be triggered on arenediazonium salt under visible-light-promoted photoredox catalysis, thereby converting it into aryl radical species, which would subsequently undergo a sequence of radical addition and decarboxylation to afford diaryl alkynes. As a representative example, arylpropiolic acids as alkynyl source with arenediazonium salts in the formation of 1,2-diarylethyne via eosin Y-catalyzed visible light-mediated arylation using BI-OAc as decarboxylation facilitated reagent was reported. In this process, cross-coupling of 3-phenylpropiolic acid and phenyl diazonium salt occurred with CO_2H acting as a leaving group in DCE under nitrogen without affect the triple bond with 3W green LED's irradiation.

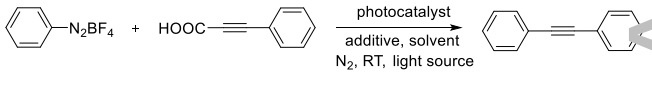


Scheme 3. Design concept of this transformation

Results and Discussion

On the basis of these previous reports, we initiated the reaction of phenylpropiolic acid and phenyl diazonium salt by using eosin Y as photocatalyst owing to its superior reduction capacity. After irradiation by 3W green LED for 12 h in DCE (1,2-dichloroethane) at room temperature, it was found that only 11% product was observed (Table 1, entry 1).[28] Within this design scenario the choice of an external oxidant is pivotal since it ideally could function as a decarboxylation-facilitated reagent but also as a radical precursor. Benziodoxole substances seem to be viable candidates fitting with this purpose, a representative structure being hydroxybenziodoxole (BI-OH). Subsequent radical addition of aryl radicals to an alkynyl carboxylic acid partner would accomplish radical (III). We propose that alkynyl carboxylic acid and BI-OH generated a benziodoxole 3-phenylpropiolate complex in situ, might facilitate C−C triple bond conversion and furnish desired product. The challenge in experimental realization of this proposal clearly lies in identifying reaction conditions that are conducive for simultaneously supporting operations of all of the above mentioned events. Gratifyingly, employing BI-OH as additive was found to substantially improve of the product yield to 45% (Table 1, entry 2). In contrast, other cyclic iodine(III) reagents methoxybenziodoxole (BI-OMe) and acetoxybenziodoxole (BI-OAc) gave even better results, while the reactivity with BI-OAc was the best (Table 1, entries 3 and 4). Inspired by this result, systematic investigation has been conducted to enhance the efficiency of the reaction. The metal complexes ($[Ru(bpy)_3]^{2+}$, fac-$[Ir(ppy)_3]$) and organic dyes (Rhodamine B, rose bengal) have been explored (Table 1, entries 5–9). The photocatalyst $Ir(ppy)_2(dtbbpy)PF_6$ (ppy = 2-phenylpyridine, dtbbpy = 4,4'-di-tert-butyl-2,2'-bipyridine) also promoted the reaction albeit in lower yield, and $[Acr^+$-Mes$]ClO_4^-$ failed to give any product (Table 1, entries 10 and 11). No product was formed in the absence of photocatalysts (Table 1, entry 12). Different light sources (blue LEDs, green LEDs and CFLs) were tested. Green LEDs (3.0 W, l = 530±10 nm) were more effective than compact blue LEDs (3.0 W, l = 450±10 nm) and fluorescent lamps (CFLs), indicating the higher photocatalytic activity of eosin Y in the presence of high-intensity green light (Table 1, entries 12–14). We also optimized the reaction time; when the reaction time was reduced to 6 h, the yield decreased slightly to 70% (Table 1, entry 15). Further control experiment indicated that no reaction took place in the absence of light, which clearly showed that the light irradiation was necessary for this transformation (Table 1, entry 16). Next, a number of solvents, such as DMF, DMSO and MeCN were screened (Table 1, entries 17–19). Replacing DCE with CH_2Cl_2 led to a slight decrease in the yield (Table 1, entry 20), while the reaction was suppressed to some extent when 1,4-dioxane was used (Table 1, entry 21). When the reaction was performed on an open air or oxygen atmospheres, no desired product was formed (Table 1, entries 22–23). Moreover, the yield only slightly diminished when the amount of the photocatalyst was decreased to 0.5 mol%, reflecting the high efficiency of this photocatalytic reaction (Table 1, entry 24).[29]

Table 1. Optimization of the photocatalytic decarboxylative alkynylation reaction conditions [a].



entry	additive	photocatalyst	light source	solvent	yield (%)
1	-	Eosin Y	Green LED	DCE	11
2	BI-OH	Eosin Y	Green LED	DCE	45
3	BI-OMe	Eosin Y	Green LED	DCE	67
4	BI-OAc	Eosin Y	Green LED	DCE	76
5	BI-OAc	$Ru(bpy)_3Cl_2$	Green LED	DCE	33
6	BI-OAc	$Ru(bpy)_3(PF_6)_2$	Green LED	DCE	41

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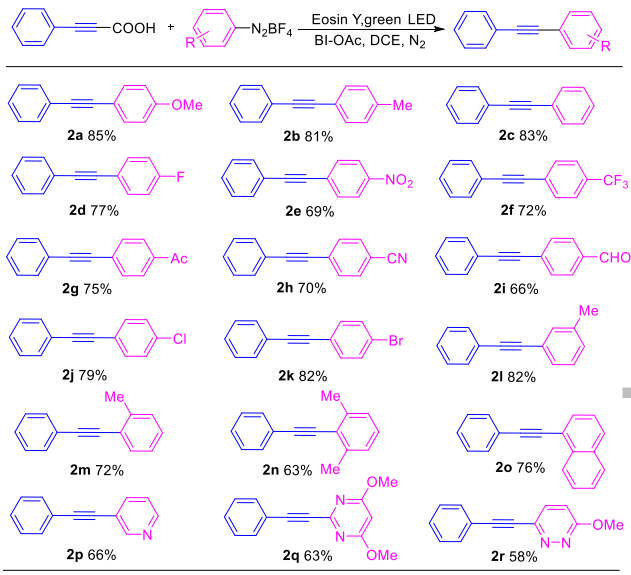
7	BI-OAc	fac-[Ir(ppy)$_3$]	Green LED	DCE	25
8	BI-OAc	Rhodamine B	Green LED	DCE	19
9	BI-OAc	Rose bengal	Green LED	DCE	36
10	BI-OAc	[Ir(dtbbpy)(ppy)$_2$][PF$_6$]	Green LED	DCE	49
11	BI-OAc	Acr$^+$-Mes	Green LED	DCE	-
12	BI-OAc	-	Green LED	DCE	-
13	BI-OAc	Eosin Y	Blue LED	DCE	71
14	BI-OAc	Eosin Y	CFL	DCE	64
15	BI-OAc	Eosin Y	Green LED	DCE	70 [c]
16	BI-OAc	Eosin Y	-	DCE	-
17	BI-OAc	Eosin Y	Green LED	DMF	23
18	BI-OAc	Eosin Y	Green LED	DMSO	40
19	BI-OAc	Eosin Y	Green LED	MeCN	55
20	BI-OAc	Eosin Y	Green LED	DCM	71
21	BI-OAc	Eosin Y	Green LED	1,4-di-oxane	39
22	BI-OAc	Eosin Y	Green LED	DCE	- [d]
23	BI-OAc	Eosin Y	Green LED	DCE	- [e]
24	BI-OAc	Eosin Y	Green LED	DCE	72 [f]

[a] Reaction conditions: phenylpropiolic acid (0.5 mmol), phenyl diazonium salt (0.5 mmol), additive (0.6 mmol), photocatalyst (1 mol%), solvent (1 mL), 25 °C, light source (3.0 W), under nitrogen, 12 h. [b] Isolated yield.[c] In 6 h. [d] Under air. [e] Under oxygen. [f] photocatalyst (0.5 mol%).

With these results in hand, the scope and generality of the present method were then examined under the optimized conditions. The reaction exhibited excellent application scope by tolerating a wide range of functional groups. Aryldiazonium salts substituted with electron-donating (MeO, Me; **2a, 2b**) and electron-withdrawing (F, NO_2; **2d, 2e**) groups were well tolerated. Aryldiazonium salts bearing other electron-withdrawing groups, including CF_3, Ac and CN on the para position reacted smoothly with 1a, delivering respectively the corresponding products in good to excellent yields (Table 2, **2f–2h**). An aryldiazonium salt containing a formyl group at the para position was also well tolerated (Table 2, **2i**). In addition to its mild, base-free nature, an important feature of the photoredox catalytic system is its compatibility with halogenated substrates. In contrast to palladium-catalyzed Sonogashira coupling, this system does not generally undergo conventional oxidative addition to aryl halides. As such, the chloridinated, brominated diaryl alkyne compounds **2j** and **2k** obtained from phenylpropiolic acid and chloro- and bromo-substituted aryldiazonium salts, respectively, were isolated with high yields using this method without competitive cleavage of the C–X bond (X = Cl, Br) (Table 2, **2j–2k**). Steric hindrance at the *meta* or *ortho*-position was also tolerated (Table 2, **2l–2m**). The sterically crowded 2,6-disubstituted aryldiazonium salt gave 2l in 63% yield (Table 2, **2n**). These synthesized compounds provide a synthetic handle for further functionalization. Furthermore, 1-(phenylethynyl)naphthalene was also accessed in 76% yield (Table 2, **2o**). It was also possible to use various heterocyclic diazonium salts with phenylpropiolic acid to deliver pyridine-functionalized, pyrimidine-functionalized and pyridazine-functionalized alkyne compounds (Table 2, **2p–2r**).

Table 2. Reaction scope of decarboxylative alkynylation with various arenediazonium salts [a,b].



[a] Reaction conditions: phenylpropiolic acid (0.5 mmol), arenediazonium salt (0.5 mmol), BI-OAc (0.6 mmol), eosin Y (1 mol%), DCE (1 mL), 25 °C, green LED (3.0 W), under nitrogen, 12 h. [b] Isolated yield.

We next varied the arylpropiolic acids reaction components (Table 3). A number of arylpropiolic acids with phenyldiazonium salts were efficiently transformed into the desired products under standard reaction conditions, including adding electron-rich (MeO and Me), electron-neutral (Ph) and electron-deficient (F, CN and NO_2) groups to the aromatic ring. Most of the substrates showed good activities regardless of electron-withdrawing or -donating groups (Table 3, **3a–3f**). Arylpropiolic acids with a *meta*- or *ortho*-methoxy/methyl substituent on the aromatic ring could be unambiguously converted into the products in good yields, respectively (Table 3, **3g–3j**). *Ortho*-chloro phenylpropiolic acid was incorporated into product **6k** with a 74% yield (Table 3, **3k**). Additionally, di-substituted diazonium salt in this coupling reaction produced the product 3l with a 70% yield (Table 3, **3l**). Some of the frequently encountered functional groups, e.g. chloro, acetyl and formyl, were demonstrated to be well-tolerated in these transformations in terms of isolated yield (74−81%) (Table 3, **3k**, **3m–3n**). Moreover, different aromatic alkynes carboxylic acids were evaluated as well, thiophenyl-substituted alkynes carboxylic acids produced good yield of product **3o** (Table 3, **3o**). The scope of the reaction was further extended to imidazo[1,2-b]pyridazine and pyrrolo[2,3-b]pyridine based heteroaryls to obtain **3p** and **3q** in 58% and 52% yields, respectively (Table 3, **3p–3q**). Interestingly, a moderate yield (43%) of propyne-1,3-diyldibenzene could be obtained when 4-phenylbut-2-ynoic acid was subjected to the reaction (Table 3, **3r**). The other aliphatic alkyne carboxylic acids such as hept-2-ynoic acid and 3-cyclohexylpropiolic acid, however, were inert toward this transformation.

Table 3. Reaction scope of various arylpropiolic acids [a,b]

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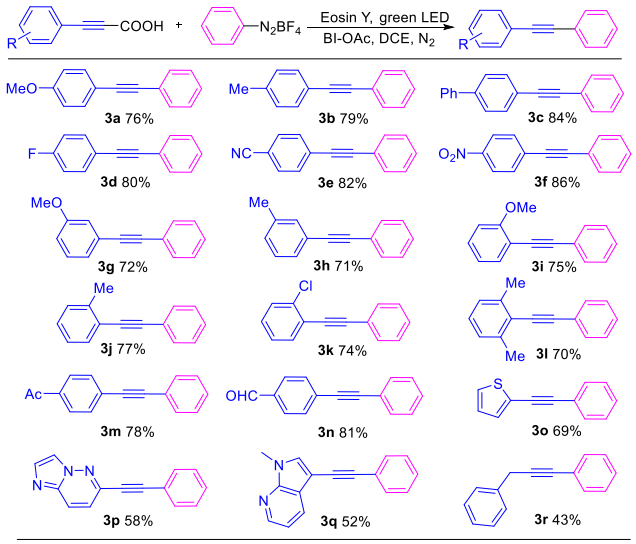
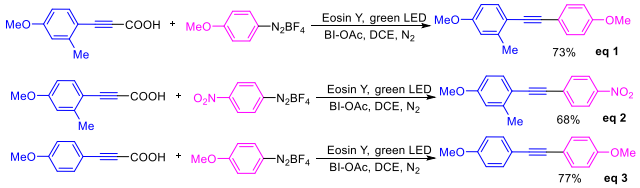


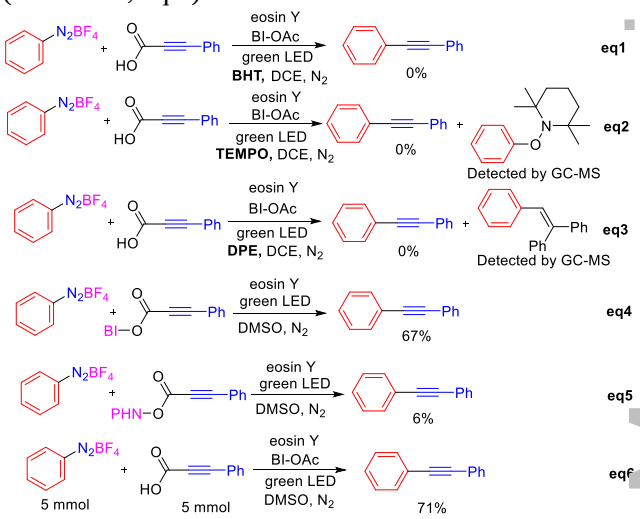
[a] Reaction conditions: arylpropiolic acid (0.5 mmol), phenyl diazonium salt (0.5 mmol), BI-OAc (0.6 mmol), eosin Y (1 mol%), DCE (1 mL), 25 °C, green LED (3.0 W), under nitrogen, 12 h. [b] Isolated yield.

In addition, some examples of asymmetric with different functional group on one side of the phenyl ring and other symmetric compound than diphenylacetylene have been tested (Scheme 5). Arylpropiolic acid substrates bearing methoxy and methyl substituents on the phenyl ring and aryl diazonium salts bearing electron-rich/electron deficient functional group at *para*-position underwent the decarboxylative alkynylation in good yields (Scheme 4, eq 1 and eq 2). Symmetric 1,2-Bis(4-methoxyphenyl)ethyne was obtained in 77% yield with *para*-methoxy group substituting on both partners (Scheme 4, eq 3).



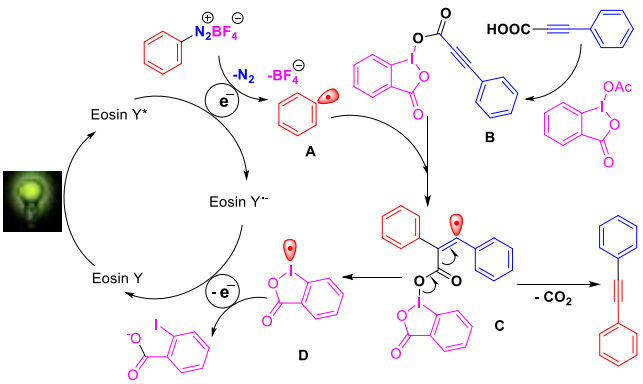
Scheme 4. Scope of the decarboxylative alkynylation

To gain mechanistic insights into this transformation, some preliminary experiments were performed (Scheme 5). The absence of either the photocatalyst eosin Y or visible light shut down the reactivity completely, thus suggesting a crucial role for both of these elements for this transformation (Table 1, entries 12 and 16). To develop a better understanding of the mechanism of this catalytic transformation, control experiments using radical scavengers such as 2,6-bis(1,1-dimethylethyl)-4-methylphenol (BHT) was conducted, and only a trace amount of the alkynylated product was obtained (Scheme 5, eq 1). This outcome indicated that the reaction was inhibited by a radical scavenger; therefore, this reaction is likely to involve a radical process. When 2 equivalents of 2,2,6,6-tetramethylpiperidyl-1-oxyl (TEMPO) or 1,1-diphenylethylene (DPE), a radical scavenger, were added to the reaction, no desired product 3aa obtained, however, we detected 2,2,6,6-tetramethyl-1-phenoxypiperidine and ethene-1,1,2-triyltribenzene by GC-MS, which indicates the presence of aryl radical intermediates (Scheme 5, eq 2 and eq 3). We speculated that an in situ generated benziodoxole 3-phenylpropiolate complex is a reactive intermediate in this present decarboxylative reaction. To support this hypothesis, a control experiment was carried out using a prepared benziodoxole 3-phenylpropiolate in advance to phenyl diazonium salt under standard condition, and 67% yield of diphenylethyne was isolated (Scheme 5, eq 4). The result showed that the yield of 2c was dramatically decreased to 6% in the presence of another decarboxyltion-facilitated substance, 1,3-dioxoisoindolin-2-yl 3-phenylpropiolate (Scheme 5, eq 5). Gram scale reaction was performed under the optimized reaction conditions to afford the 2c in 71% isolated yields (Scheme 5, eq 6).



Scheme 5. Control experiments for the decarboxylative alkynylation

Taking into account of the acquired results, a mechanism is proposed (Scheme 6). Initially, after excitation of the photocatalyst eosin Y, the aryl radical A is formed by SET from the excited state of eosin Y to aryldiazonium salt upon loss of dinitrogen. The aryl radical A incorporates to the arylpropiolic acid unit B, which was generated in situ from acetoxybenziodoxole and arylpropiolic acid in situ, to provide intermediete C. The radical C is further transformed into the target product 3 via by the elimination of CO_2 and the releases benziodoxole radical D. Finally, the reduction of the radical intermediate D by the eosin Y radical anion to give 2-iodobenzoate anion, simultaneously closing the catalytic cycle.



Scheme 6. Possible mechanism.

Conclusion

In conclusion, we have successfully accomplished an attractive strategy for direct assembly of diaryl alkynes via photocatalytic decarboxylative alkynylation of arenediazonium tetrafluoroborate with arylpropiolic acids. A variety of arenediazonium salts and arylpropiolic acids have been efficiently transformed to structurally diverse products at room temperature. The reaction uses an inexpensive and readily available organic dye, eosin Y as the photocatalyst. Moreover, no transition metal waste was generated during the process. It is thus a practical and environmentally-benign protocol toward useful aryl internal alkynes.

Experimental Section

General

Reagents and solvents were used as it is obtained from commercial vendors. Products were purified by column chromatography on silica gel (300–400 mesh). 1H and 13C NMR spectra were obtained on Bruker-400 MHz spectrometers using TMS as internal standard in CDCl3. Chemical shifts of 1H NMR and 13C NMR are reported as δ values relative to TMS and CDCl3 respectively. Chemical shifts were reported in parts per million (ppm, δ). Proton coupling patterns are described as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and broad resonances (br). HRMS (EI) data were collected on High Resolution mass spectrometer

General experimental procedure for preparation of arylpropiolic acids:

Step 1 : Triphenylphosphine (20 mmol) was added to a well-stirred solution of carbon tetrabromide (10 mmol) in dry dichloromethane (50 mL). Upon addition of aldehyde (5 mmol), the solution slowly faded away. The reaction mixture was stirred at ambient temperature for 6 hours till completion (TLC monitoring). After removal of solvent, the residue was repeatedly triturated with hexane (5 x 25 mL) and hexane solution was concentrated. This cycle was continued three times. Finally the mixture was subjected to column chromatography to afford the (2,2-dibromovinyl)arene.

Step 2 : A solution of (2,2-dibromovinyl)arene (6 mmol) in 10 mL of dry THF at –78 °C was treated with a solution of *n*-BuLi in hexane (1.6 M, 7.5 mL, 12 mmol) under nitrogen atmosphere. After stirring for 1h at –78 °C, the reaction mixture was warmed to 25 °C during 1 h, and again cooled to –60 °C. Solid carbon dioxide (5 g) was added to the above solution at –60 °C and the mixture was allowed to warm gradually to room temperature. The mixture was poured into water, and ethyl acetate was added. The aqueous layer was separated and washed further with ethyl acetate. The aqueous part was acidified with 6(N) HCl and extracted with ethyl acetate (3 x 50 mL). The organic layer was washed with brine and dried over anhydrous magnesium sulfate. Evaporation of solvent afforded pure arylpropiolic acid.

General procedure for the decarboxylative alkynylation reaction

A 10 mL reaction tube equipped with magnetic stirring bar was charged with arenediazonium tetrafluoroborate (0.5 mmol, 1 equiv), arylpropiolic acid (0.5 mmol, 1 equiv), eosin Y (1 mol %), BI-OAc (0.6 mmol, 1.2 equiv.) and DCE (1 mL). The reaction tube was sealed and the reaction mixture was degassed by bubbling with nitrogen for 5 minutes. The mixture was stirred and irradiated with green LEDs (λ = 530±10 nm) for 12 h at room temperature. After that, the solution was diluted with DCM (4 mL), and concentrated in vacuo. The mixture was purified by column chromatography on silica gel using petroleum ether/ethyl acetate as eluent to afford the desired arylalkynes, which was characterized by NMR and HRMS.

1-Methoxy-4-(phenylethynyl)benzene (2a, 3a)

White solid (88 mg, 85%). mp 57–58 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52 (dt, *J* = 4.0, 2.0 Hz, 2H), 7.49–7.45 (m, 2H), 7.36–7.28 (m, 3H), 6.88 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.5, 133.1, 131.6 128.3, 127.8, 123.6, 115.3, 114.0, 89.5, 88.1, 55.2. HRMS (EI) Calcd for $C_{15}H_{13}O$ $[M+H]^+$, 209.0961; found, 209.0970.

1-Methyl-4-(phenylethynyl)benzene (2b, 3b)

Yellow solid (78mg, 81%). mp: 73−74 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58–7.52 (m, 2 H), 7.47 (dd, *J* = 8.0, 1.6 Hz, 2 H), 7.39–7.33 (m, 3 H), 7.19 (d, *J* = 7.6 Hz, 2 H), 2.39 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 131.5, 131.5, 129.2, 128.3, 128.0, 123.5, 120.3, 89.6, 88.8, 21.5. HRMS (EI) Calcd for $C_{15}H_{13}$ $[M+H]^+$, 193.1012; found, 193.1007.

1,2-Diphenylethyne (2c)

White solid (74 mg, 83%). mp: 59−60 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (dd, *J* = 6.4, 1.6 Hz, 4H), 7.51 – 7.33 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.7, 128.4, 128.3, 123.4, 89.5. HRMS (EI) Calcd for $C_{14}H_{11}$ $[M+H]^+$, 179.0855; found, 179.0862.

1-Fluoro-4-(phenylethynyl)benzene (2d, 3d)

White solid (75 mg, 77%). mp 109–110 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.55–7.50 (m, 4H), 7.38–7.32 (m, 3H), 7.05 (t, *J* = 8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 162.5 (d, $^1J_{CF}$ = 249.2 Hz), 133.4 (d, $^3J_{CF}$ = 8.2 Hz), 131.6, 128.5, 128.4, 123.3, 119.3 (d, $^4J_{CF}$ = 3.6 Hz), 115.7 (d, $^2J_{CF}$ = 22.4 Hz), 89.2, 88.3. HRMS (EI) Calcd for $C_{14}H_{10}F$ $[M+H]^+$, 197.0761; found, 197.0755.

1-Nitro-4-(phenylethynyl)benzene (2e, 3f)

White solid (77 mg, 69%). mp 120–122 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.22 (d, *J* = 8.8 Hz, 2H), 7.68 (d, *J* = 8.8 Hz, 2H), 7.58–7.54 (m, 2H), 7.38 (dd, *J* = 5.4, 1.6 Hz,

3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 147.0, 132.3, 131.8, 130.4, 129.2, 128.6, 123.8, 122.1, 94.6, 87.6. HRMS (EI) Calcd for $C_{14}H_{10}NO_2$ $[M+H]^+$, 224.0706; found, 22.0713.

1-(Phenylethynyl)-4-(trifluoromethyl)benzene (2f)

White solid (89 mg, 72%). mp 103–104 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70–7.62 (m, 4H), 7.59 (dd, *J* = 6.4, 2.8 Hz, 2H), 7.45–7.35 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.0, 131.9, 129.0, 128.6, 125.5, 125.44, 125.41, 125.36, 122.8, 91.9, 88.1. HRMS (EI) Calcd for $C_{15}H_{10}F_3$ $[M+H]^+$, 247.0724; found, 247.0718.

1-(4-(phenylethynyl)phenyl)ethan-1-one (2g, 3m).

Yellow solid (88 mg, 75%). mp 95–96 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98–7.92 (m, 2 H), 7.62 (d, *J* = 8.4 Hz, 2 H), 7.56 (dd, *J* = 6.8, 3.2 Hz, 2 H), 7.40–7.35 (m, 3 H), 2.63 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.3, 136.3, 131.8, 131.7, 128.9, 128.5, 128.4, 128.2, 122.6, 92.7, 88.5, 26.6. HRMS (EI) Calcd for $C_{16}H_{13}O$ $[M+H]^+$, 221.0961; found, 221.0964.

4-(phenylethynyl)benzonitrile (2h, 3e).

Yellow solid (71 mg, 70%). mp 109–111 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, *J* = 8.4 Hz, 2 H), 7.62 (d, *J* = 8.4 Hz, 2 H), 7.58–7.53 (m, 2 H), 7.40 (dd, *J* = 5.2, 2.0 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.08, 132.04, 131.7, 129.1, 128.6, 128.3, 122.3, 118.6, 111.6, 93.8, 87.7. HRMS (EI) Calcd for $C_{15}H_{10}N$ $[M+H]^+$, 204.0808; found, 204.0812.

4-(phenylethynyl)benzaldehyde (2i, 3n).

Yellow solid (68 mg, 66%). mp 98–99 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.05 (s, 1 H), 7.88 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2 H), 7.60–7.50 (m, 2 H), 7.44–7.36 (m, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.19, 192.17, 136.3, 132.9, 132.5, 130.5, 130.3, 129.6, 129.2, 123.3, 94.2, 89.2. HRMS (EI) Calcd for $C_{15}H_{11}O$ $[M+H]^+$, 207.0804; found, 207.0813.

1-methyl-3-(phenylethynyl)benzene (2l, 3h).

Yellow oil (79 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62–7.57 (m, 2H), 7.45–7.36 (m, 5 H), 7.30 (td, *J* = 7.6, 1.6 Hz, 1 H), 7.21 (d, *J* = 7.6 Hz, 1 H), 2.42 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.2, 132.2, 131.5, 129.2, 128.7, 128.6, 128.4, 128.3, 128.2, 123.5, 123.1, 89.6, 89.1, 21.2. HRMS (EI) Calcd for $C_{15}H_{13}$ $[M+H]^+$, 193.1012; found, 193.1019.

1-methyl-2-(phenylethynyl)benzene (2m, 3j).

Colorless oil (69 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64–7.59 (m, 2 H), 7.57 (s, 1 H), 7.39 (dd, *J* = 9.2, 7.2 Hz, 3 H), 7.31–7.26 (m, 2 H), 7.24 (dd, *J* = 8.0, 4.4 Hz, 1 H), 2.58 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.2, 131.8, 131.6, 129.6, 128.4, 128.3, 128.2, 125.5, 123.6, 123.2, 93.4, 88.5, 20.8. HRMS (EI) Calcd for $C_{15}H_{13}$ $[M+H]^+$, 193.1012; found, 193.1007.

1,3-dimethyl-2-(phenylethynyl)benzene (2n, 3l).

Colorless oil (65 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (dd, *J* = 6.4, 2.0 Hz, 2 H), 7.43–7.32 (m, 3 H), 7.19–7.15 (m, 1 H), 7.12 (dd, *J* = 7.6, 2.4 Hz, 2 H), 2.58 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.3, 131.5, 128.4, 128.2, 127.8, 126.6, 123.9, 123.1, 97.9, 87.2, 21.2. HRMS (EI) Calcd for $C_{15}H_{13}$ $[M+H]^+$, 207.1168; found, 207.1161.

1-chloro-4-(phenylethynyl)benzene (2j).

White solid (84 mg, 79%). mp 82–83 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62–7.55 (m, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.43–7.33 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.4, 132.9, 131.7, 128.8, 128.6, 128.5, 123.1, 121.9, 90.5, 88.4. HRMS (EI) Calcd for $C_{14}H_{10}Cl$ $[M+H]^+$, 213.0466; found, 213.0473.

1-bromo-4-(phenylethynyl)benzene (2k).

White solid (105 mg, 82%). mp 82–83 °C.^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57–7.46 (m, 4H), 7.42–7.31 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.2, 131.8, 131.7, 128.7, 128.5, 123.1, 122.6, 122.4, 90.7, 88.5. HRMS (EI) Calcd for $C_{14}H_{10}Br$ $[M+H]^+$, 256.9960; found, 256.9966.

1-(phenylethynyl)naphthalene (2o).

White solid (87 mg, 76%). mp 116–119 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 (d, *J* = 8.4 Hz, 1H), 7.89 (dt, *J* = 21.2, 11.4 Hz, 3H), 7.80–7.66 (m, 3H), 7.60 (dd, *J* = 14.4, 7.2 Hz, 1H), 7.56–7.37 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.8, 133.7, 132.1, 130.8, 129.2, 128.9, 128.8, 128.7, 127.2, 126.9, 126.7, 125.7, 123.9, 121.4, 94.8, 88.0. HRMS (EI) Calcd for $C_{18}H_{13}$ $[M+H]^+$, 229.1012; found, 229.1002.

3-(phenylethynyl)pyridine (2p).

White solid (59 mg, 66%). mp 48–49 °C.^{1}H NMR (400 MHz, $CDCl_3$): δ 8.78 (s, 1 H), 8.56 (d, *J* = 4.0 Hz, 1 H), 7.83 (d, *J* = 8.0 Hz, 1 H), 7.61–7.53 (m, 2 H), 7.42–7.36 (m, 3 H), 7.30 (ddd, *J* = 8.0, 4.8, 1.0 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.3, 148.5, 138.4, 128.8, 128.6, 123.1, 122.6, 92.7, 85.8. HRMS (EI) Calcd for $C_{13}H_{10}N$ $[M+H]^+$, 180.0808; found, 180.0800.

4,6-dimethoxy-2-(phenylethynyl)pyrimidine (2q).

Yellow solid (76 mg, 63%). mp 133–135 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72–7.66 (m, 2 H), 7.44–7.36 (m, 3 H), 6.04 (s, 1 H), 4.02 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.2, 151.2, 132.7, 129.5, 128.5, 121.5, 90.1, 88.1, 86.6, 54.4. HRMS (EI) Calcd for $C_{14}H_{13}N_2O_2$ $[M+H]^+$, 241.0972; found, 241.0965.

3-methoxy-6-(phenylethynyl)pyridazine (2r).

Yellow solid (61 mg, 58%). mp 98–100 °C.^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63–7.56 (m, 2 H), 7.50 (d, *J* = 9.2 Hz, 1 H), 7.36 (dd, *J* = 5.4, 2.0 Hz, 3 H), 6.93 (d, *J* = 9.2 Hz, 1 H), 4.16 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.4, 143.6, 132.3, 132.1, 129.2, 128.3, 121.9, 116.7, 92.1, 85.6, 55.1. HRMS (EI) Calcd for $C_{13}H_{11}N_2O$ $[M+H]^+$, 211.0866; found, 211.0858.

4-(phenylethynyl)-1,1'-biphenyl (3c).

White solid (107 mg, 84%). mp 163–166 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (dt, *J* = 8.0, 6.0 Hz, 8H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.46–7.35 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.4, 140.8, 132.5, 132.1, 129.3, 128.8, 128.7, 128.1, 127.5, 123.8, 122.7, 90.6, 89.8. HRMS (EI) Calcd for $C_{20}H_{15}$ $[M+H]^+$, 255.1168; found, 255.1159.

1-methoxy-3-(phenylethynyl)benzene (3g).

Yellow solid (75 mg, 72%). mp 77–79 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63–7.55 (m, 2 H), 7.40–7.36 (m, 3 H), 7.30 (dd, *J* = 8.4, 7.6 Hz, 1 H), 7.18 (d, *J* = 7.6 Hz, 1 H), 7.12 (dd, *J* = 2.8, 1.4 Hz, 1 H), 6.94 (ddd, *J* = 8.2, 2.8, 1.0 Hz, 1 H), 3.85 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 131.6, 129.5, 128.41, 128.36, 124.3, 124.2, 123.1, 116.3, 115.1, 89.3, 89.1, 55.3. HRMS (EI) Calcd for $C_{15}H_{13}O$ $[M+H]^+$, 209.0961; found, 209.0954.

1-methoxy-2-(phenylethynyl)benzene (3i).

Yellow solid (74 mg, 71%). mp 54–56 °C.^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (dd, *J* = 8.0, 1.6 Hz, 2 H), 7.54 (dd, *J* = 7.6, 1.6 Hz, 1 H), 7.40–7.33 (m, 4 H), 7.01–6.90 (m, 2 H), 3.96 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8, 133.6, 131.6, 129.8, 128.7, 128.4, 128.3, 128.2, 126.2, 123.5, 120.4, 112.4, 110.6, 93.5, 85.8, 55.9. HRMS (EI) Calcd for $C_{15}H_{13}O$ $[M+H]^+$, 209.0961; found, 209.0966.

1-Chloro-2-(phenylethynyl)benzene (3k).

Yellow oil (78 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (td, *J* = 7.6, 3.3 Hz, 3H), 7.45 (dd, *J* = 6.9, 2.3 Hz, 1H), 7.40 – 7.37 (m, 3H), 7.30 – 7.24 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.1, 133.4, 131.9, 129.5, 129.4, 128.8, 128.5, 126.6, 123.4, 123.1, 94.7, 86.3. HRMS (EI) Calcd for $C_{14}H_{10}Cl$ $[M+H]^+$, 213.0466; found, 213.0458.

2-(phenylethynyl)thiophene (3o).

Colorless oil (63 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58–7.50 (m, 2 H), 7.36 (dd, *J* = 4.8, 3.0 Hz, 3 H), 7.33–7.29 (m, 2 H), 7.04 (ddd, *J* = 5.0, 3.2, 2.0 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.9, 131.5, 128.4, 128.3, 127.3, 127.1, 123.2, 122.9, 93.1, 82.6. HRMS (EI) Calcd for $C_{12}H_9S$ $[M+H]^+$, 185.0415; found, 185.0422.

6-(phenylethynyl)imidazo[1,2-*b*]pyridazine (3p).

Yellow solid (64 mg, 58%). mp 109–111 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, *J* = 9.6 Hz, 2 H), 7.82 (s, 1 H), 7.63 (d, *J* = 8.0 Hz, 2 H), 7.43 (m, 3 H), 7.25 (d, *J* =9.2 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.7, 137.9, 134.6, 132.0, 129.7, 128.6, 125.2, 121.3, 120.6, 117.1, 92.4, 84.9. HRMS (EI) Calcd for $C_{14}H_{10}N_3$ $[M+H]^+$, 220.0869; found, 220.0852.

1-methyl-3-(phenylethynyl)-1*H*-pyrrolo[2,3-b]pyridine (3q).

Dark yellow solid (60 mg, 52%). mp 45–47 °C.^{1}H NMR (400 MHz, $CDCl_3$): δ 8.39 (dd, *J* = 4.8, 1.6 Hz, 1 H), 8.08 (dd, *J* = 7.6, 1.6 Hz, 1 H), 7.58–7.51 (m, 2 H), 7.42 (s, 1 H), 7.38–7.28 (m, 3 H), 7.14 (dd, *J* = 7.6, 4.8 Hz, 1 H), 3.89 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.2, 144.0, 132.2, 131.3, 128.4, 128.3, 127.9, 123.9, 121.4, 116.6, 95.7, 91.2, 82.3, 31.3. HRMS (EI) Calcd for $C_{16}H_{13}N_2$ $[M+H]^+$, 220.0869; found, 220.0852.

prop-1-yne-1,3-diyldibenzene (3r).

Colorless oil (41 mg, 43%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55–7.52 (m, 1 H), 7.50–7.46 (m, 3 H), 7.41 (t, *J* = 7.6 Hz, 2 H), 7.38–7.28 (m, 5 H), 3.90 (s, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.8, 131.6, 128.6, 128.2, 128.0, 127.9, 126.6, 123.8, 87.5, 82.8, 25.9. HRMS (EI) Calcd for $C_{15}H_{13}$ $[M+H]^+$, 193.1012; found, 193.1022.

4-methoxy-1-((4-methoxyphenyl)ethynyl)-2-methylbenzene (S4, eq1).

White solid (92 mg, 73%). mp 135–137 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48–7.41 (m, 3H), 6.90 – 6.84 (m, 2H), 6.78 –6.67 (m, 2H), 3.82 (s, 3H), 3.81(s 3H), 2.49 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.4, 141.9, 133.1, 132.9, 116.1, 115.7, 115.2, 114.1, 111.3, 91.9, 87.0, 55.4, 55.3, 21.2. HRMS (EI) Calcd for $C_{17}H_{17}O_2$ $[M+H]^+$, 253.1223; found, 253.1231.

.4-methoxy-2-methyl-1-((4-nitrophenyl)ethynyl)benzene (S4, eq2)

Yellow solid (91 mg, 68%). mp 149–152 °C.^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 – 8.10 (m, 2H), 7.74 – 7.55 (m, 2H), 7.48 (s, 1H), 7.43 (s, 1H), 6.83 – 6.65 (m, 1H), 3.83 (s, 3H), 2.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.5, 146.7, 142.7, 133.8, 131.9, 131.1, 123.8, 115.4, 114.2, 111.6, 94.4, 90.6, 55.4, 21.1. HRMS (EI) Calcd for $C_{16}H_{14}NO_3$ $[M+H]^+$, 268.0968; found, 268.0977.

1,2-bis(4-methoxyphenyl)ethyne (S4, eq3)

White solid (92 mg, 73%). mp 141–143 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, *J* = 8.0 Hz, 4H), 6.87 (d, J = 8.0 Hz, 4H), 3.83 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.4, 132.9, 115.7, 113.9, 87.9, 55.3. HRMS (EI) Calcd for $C_{16}H_{15}O_2$ $[M+H]^+$, 239.1067; found, 239.1075.

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[28] We considered that BI-OAc was an efficient additive to improve the desired coupling yield from 11% to 76%. In our previous work for decarboxylative alkynylation of alkynyl carboxylic acids (ref 26a), we reported that alkynyl carboxylic acids could proceed decarboxylative alkynylation via silver-catalyzed radical process, and we speculated that it could also been reactive via photo-induced process, although in very low yield.

[29] For the scope of substrate, the alkyl acetyl acids had been investigated, however, no desired product were obtained.

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FULL PAPER

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