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# Visible-light-enabled aerobic synthesis of benzoin bis-ethers from alkynes and alcohols†

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A new, facile, atom-economical and good regioselective method for the synthesis of benzoin bis-ethers has been developed *via* directly using readily available alkynes and alcohols as raw materials under visible light irradiation. The protocol utilizes commercial Mes-Acr<sup>+</sup>ClO<sub>4</sub><sup>-</sup> as an organophotoredox catalyst and air (O<sub>2</sub>) as a green sustainable reagent. A range of benzoin bis-ether derivatives were easily and efficiently obtained in a one-pot procedure at room temperature, and water is the by-product.

Benzoin bis-ethers and their derivatives, especially 2,2dimethoxy-2-phenylacetophenone(DMPA), are widely used in various industries, such as surface coating, photosensitive polymer materials, additives for plastic, ink, finish paints for wood products, and other various fields.<sup>1</sup> They are also important radical-type photoinitiators widely applied to polymerization reaction systems, mainly undergoing cleavage to generate benzoyl and substituted benzyl radicals upon irradiation.<sup>2</sup> As the most representative benzoin derivative, DMPA has become an important commercial photocuring agent used mainly for acrylic and unsaturated polyester resins and an effective UVcuring initiator.<sup>3</sup> Moreover, benzoin bis-ethers are significant synthons as they are widely used in constructing key structural elements.<sup>4,16</sup>

Consequently, developing green and straightforward synthetic strategies of benzoin bis-ethers has been highly anticipated for decades. Until now, the ketonization reaction is the leading approach in most methods of synthesizing benzoin bis-ethers. In 1961, Trischmann and co-workers obtained benzoin dimethyl ether from benzils with BaO.<sup>5a</sup> Later, these protocols have been reported frequently for benzoin bis-ether preparation.<sup>5</sup> In 2002, Yukio group reported that electrolytic oxidation of benzil hydrazones in MeOH could afford benzil dimethyl ketal smoothly.<sup>6</sup> More recently, a new method was reported using an aldehyde, hypertoxic KCN and trimethoxymethane to prepare benzoin bis-ethers in one pot.<sup>7</sup> Nevertheless, most of these processes still involve the use of toxic additives, excess byproducts and labile substrates, which would lead to increased cost and environmental concerns and limit their practical application (Scheme 1).

Alkynes as important, accessible raw materials are widely used for the preparation of a variety of valuable versatile organic compounds.<sup>8</sup> However, there are only two unsatisfactory methods to prepare benzoin bis-ethers from alkynes,<sup>9</sup> (i) oxidation of alkynes with excess  $H_5I0_6$  in methanol, and (ii) using stoichiometric diphenyl diselenide and ammonium peroxydisulfate in reflux. Hence, given the importance of benzoin bis-ethers and the limitations of previous approaches employing stoichiometric and hazardous oxidants, the development of a facile, efficient and eco-friendly method directly using accessible alkynes to synthesize benzoin bis-ethers is still highly desirable.

Metal-free visible-light mediated aerobic oxidation is an appealing green method marked by attractive features such as clear and sustainable reagents, handy conditions and high relevancy to solar energy, which has offered a technically



Scheme 1 Methods of the synthesis of benzoin bis-ethers.

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attractive and energy-saving platform in comparison to the traditional oxidation processes.<sup>10</sup> With increasing attention on photoredox catalysis,<sup>11</sup> the intriguing acridinium-based organic dye (Acr<sup>+</sup>-Mes,9-mesityl-10-methylacridinium) has been widely employed in organic synthesis as its mesityl group on the 9-position dramatically increases the quantum yields for the formation of the electron-transfer state,<sup>12</sup> which can effectively promote catalytic conversion. Fukuzumi and Nicewicz have used the strong oxidizing capability of Acr<sup>+</sup>-Mes to realize a range of efficient transformations.<sup>13</sup> In continuation of our interest on chemoselective transformation via visible-light-driven aerobic oxidation,<sup>14</sup> we became interested in exploring a metal-free, mild photocatalytic system to construct benzoin bis-ethers from alkynes. We envisioned that single electron transfer (SET) from alkynes to the excited state of Mes-Acr<sup>+</sup> can occur efficiently and generate the radical cation of alkynes<sup>15</sup> under photocatalytic aerobic conditions. Subsequent reaction of an alkyne radical cation with MeOH and molecular oxygen should produce the desired benzoin bisethers.

To validate our idea and optimise the reaction conditions, the reaction with diphenylacetylene as the model substrate was performed using a catalytic amount of Mes-Acr<sup>+</sup>  $ClO_4^-$  (1.5 mol%) in MeOH under irradiation with blue LEDs in open air (see the ESI<sup>†</sup>). We were delighted to obtain the desired product of 2-dimethoxy-2-phenylacetophenone (DMPA) in 82% yield (see the ESI<sup>†</sup>). Then, the control experiments were established, which show that Mes-Acr<sup>+</sup> $ClO_4^-$ , air (O<sub>2</sub>) and visible light are necessary for an efficient reaction because in the absence of any of the reagents/reaction parameters the product was not detected.

Under the established optimal conditions, we sought to evaluate the scope of the alkyne component, utilizing MeOH as the nucleophile and solvent. As shown in Table 1, excellent regioselectivity was observed which was consistent with the stability of formed radical cations and various substituted unsymmetrical and symmetrical alkynes worked well to deliver the corresponding benzoin bis-ether products in good to excellent yields. In the case of aryl-alkyl alkynes as the substrates, we only detected benzoin bis-ethers under the optimal conditions. Many versatile functional groups are readily tolerated, such as ethyl, n-heptyl, alkyl chlorides, esters, ethers, nitriles, and even steric bulky ones like cyclohexyl and perhaps most notable, unprotected alcohols (2a-2l, 44%-76%). Next, exploring the challenging scope of 1,4-diphenylbuta-1,3-diyne, we delightedly obtained the benzoin bis-ether product containing an acetylenic bond (2i, 66%). Moreover, intramolecular transformation was also tolerated under standard conditions. The expected cyclization product (21) was obtained in moderate yield. In the scope of 1,2-diaryl alkynes, we found that the difference in the substitution of the aromatic ring has an obvious influence on the conversion. When the substituent group is methyl, tert-butyl, or dimethyl, the transformation proceeded smoothly under standard conditions (2m-2n). Substitution at the ortho, metaposition of the phenyl ring was successfully incorporated as well (20-2q, 72%-75%). Furthermore, investigating the

 Table 1
 Reaction scope of alkynes<sup>a,b</sup>



<sup>*a*</sup> Reaction conditions: **1a** (0.1 mmol, 1.0 equiv.) and Mes-Acr<sup>+</sup>  $ClO_4^-$  (1.5 mol%) in MeOH (1.0 mL) were irradiated with 5 W blue LEDs for 3 h in air at room temperature. <sup>*b*</sup> Isolated yield. <sup>*c*</sup> For 10 h. <sup>*d*</sup> Only the major products are shown with the ratio of **2** to its isomer **2**' given in parentheses through the <sup>1</sup>H NMR determination of the crude product.

unsymmetrical di-aryl scope, we found that products were obtained in the *ortho*, *para*-position containing a methyl group (**2r**, **2s**). However, a mixture of products was afforded as methyl groups in the *meta*-position (**2t**). When the *para*-position of the phenyl ring has a ring electron-withdrawing group, a mixture of products was also afforded (**2u–2v**, 77%–79%). It is worth noting that certain alkynes are beyond the reach of the present catalytic systems, as anticipative products of **2w** and **2x** were not obtained.

We next turned our attention to the capacity of various alcohols in the protocol shown in Table 2. An important commercial radical-type photoinitiator of (DMPA) was provided in excellent yield with a mild methodology (**3a**, 82%). Using  $CD_3OD$  as a solvent, we also obtained the deuterium product **3b** (81%). Subsequently, a range of aliphatic alcohols including ethanol (**3c**), 1-propanol (**3d**), 1-butanol (**3e**), 1-dexanol (**3g**) and 1-octanol (**3h**) reacted smoothly with diphenylacetylene to provide the expected product under the optimal conditions in moderate to good yields. Notably, ethylene glycol could work well under the current conditions, affording the desired product **3f** in good yield. 2-Ethoxyethanol was also tolerated (**3j**, 65%). Moreover, evaluating secondary and tertiary alcohols, we found that isopropanol could convert to the expected benzoin bis-ether (**3i**) under standard conditions but *tert*-butanol failed. Finally, we obtained **3l** in 61% yield using H<sub>2</sub>O instead of an alcohol.

To demonstrate the potential utility of the mild, operationally simple strategy, a gram-scale reaction of diphenylacetylene (10 mmol, 1.78 g) was performed in MeOH for 4.0 h delivering the desired product DMPA in good yield (1.59 g, 62% yield, Scheme 2). Moreover, we found that benzoin ethers as useful building blocks could be transformed into a series of valuable compounds for organic synthesis as shown in Scheme 2.<sup>16</sup> Firstly, *N*-glycolylneuraminic acid (Neu5Gc) plays a significant role in human pathologies such as cancer and vascular disease. The intermediate (**4d**) for its synthesis was obtained from the reaction of DMPA with glucose and benzyl alcohol by two steps in excellent yield.<sup>16d</sup> As there is an orientation effect of the carbonyl group, benzoin bis-ethers were used for C–C bond formation *via* C–H bond activation in **4b** and **4f**.<sup>16b,f</sup> Finally, the ketal structure is contained in DMPA, which is a good reactive

Table 2	Reaction scope of alcohols <sup>a,</sup>	b
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<sup>*a*</sup> Reaction conditions: Diphenylacetylene (0.1 mmol, 1.0 equiv.) and Mes-Acr<sup>+</sup>  $ClO_4^-$  (1.5 mol%) in ROH/CH<sub>3</sub>CN (1.2 mL, 0.2 mL CH<sub>3</sub>CN) were irradiated with 5 W blue LEDs for 3 h in air at room temperature. <sup>*b*</sup> Isolated yield. <sup>*c*</sup> H<sub>2</sub>O/CH<sub>3</sub>CN (1:1, 1.0 mL).



Scheme 2 (a) Larger scale reaction, and (b) further synthetic application of the product.

site for further conversion such as forming **4c** by a gallium catalyst in excellent yield.<sup>16c</sup> The benzyl was obtained in 93% yield by a simple deprotection from DMPA.<sup>16a</sup> Cyclic ketal **4e** was prepared by alcoholysis in the presence of 4-MeC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H.<sup>16e</sup>

To elucidate the possible reaction mechanism, several control experiments were conducted as shown in Fig. 1. Firstly, adding 2.0 equiv. TEMPO under optimized conditions, the model reaction was completely suppressed and the trapped peak was detected at 404.1986 by HMRS in accordance with the calculation (in Fig. 1), suggesting that the present transformation might involve a diarylacetylene radical cation process. Secondly, we did not detect the desired product when the model reaction was carried out under an argon atmosphere. Finally, in the case of replacing diphenylacetylene with benzil, the desired product was not obtained, which indicates that benzyl is not necessarily an intermediate. Moreover, the reported literature has proved that the excited acridine photocatalyst (Mes-Acr<sup>+</sup>  $ClO_4^-$ ) was quenched by diphenylacetylene in fluorescence quenching (Stern–Volmer) experiments.<sup>17</sup>

Based on the above experimental results and the previous related literature,<sup>15,17,18</sup> a plausible mechanism for the reaction is outlined in Scheme 3. Under visible-light irradiation, the acridine photocatalyst is converted into the excited species  $[Acr^+-Mes ClO_4^-]^*$  ( $E_{1/2red}$  [Acr<sup>+</sup>-Mes<sup>++</sup>/Acr<sup>+</sup>-Mes] = +2.06 V vs.



Fig. 1 Control experiments for analysis of the reaction pathway.



Scheme 3 Proposed mechanism.

SCE), undergoing a SET process with diphenylacetylene  $(E^{1a \cdot +/1a} = +1.86 \text{ V } vs. \text{ SCE})$  to generate an alkyne radical cation and an Acr<sup>+</sup>-Mes ClO<sub>4</sub><sup>-</sup> radical anion. Subsequently, a nucleophilic addition of methanol to the alkene radical cation **A** generates the radical cation **B**, which could be captured by O<sub>2</sub><sup>--</sup> and populate intermediate **C**. It is also plausible that the intermediate **C** is produced by coupling radical cation **B** with O<sub>2</sub> and subsequent single electron transfer. The electron-rich alkene **C** is readily oxidized to form radical cation **D** by the excited photocatalyst. Finally, nucleophilic attack of another methanol on the radical cation **D** occurs and then the elimination of water affords the desired product **3a**. On the other hand, the photocatalyst could be regenerated by molecular oxygen  $(EO_2^{--}/O_2 = -0.87 \text{ V} vs. \text{ SCE})^{12a,19}$ 

#### Conclusions

In conclusion, we have presented an efficient metal-free visiblelight enabled methodology for synthesis of benzoin bis-ethers using air ( $O_2$ ) as an oxidant and oxygen source. The protocol with simple alkynes and alcohols as raw material constructs a range of benzoin bis-ethers in one step, utilizing commercial Mes-Acr<sup>+</sup> ClO<sub>4</sub><sup>-</sup> as an organophotoredox catalyst. This system exhibits good regioselectivity. Mechanistic insights suggested that the alkyne radical cation is the key intermediate and visible light plays a vital role in this transformation. The net reaction is very clean and water is the byproduct. Further transformations of benzoin bis-ethers indicate that they can be used as direct precursors to construct an array of important molecules, which are also widely applied in industrial production.

#### Conflicts of interest

There are no conflicts to declare.

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