

# Visible-light-induced regioselective bifunctionalization of $\alpha$ -olefin: Development of one-pot photo-synthesis of C<sub>3</sub>-substituted dihydrobenzofurans

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## Abstract

A method for the catalytic regioselective synthesis of C<sub>3</sub>-substituted dihydrobenzofurans (DHBs) via [2+2] photocycloaddition of alkene and *p*-benzoquinone is developed. This method realizes the rapid synthesis of DHBs with readily available substrates and simple reaction conditions by using Lewis acid B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and Lewis base P(*o*-tol)<sub>3</sub> as a catalyst in combination with the classical Paternò–Büchi reaction. This reaction is of interest in terms of bifunctionalization by formal [2+3] cycloaddition of olefins and applies to a wide range of  $\alpha$ -olefins.

## Introduction

Dihydrobenzofurans (DHBs) are an important structural unit in bioactive natural molecules and have been used for synthesizing oxygen-containing pharmaceutical candidates.<sup>1</sup> In particular, pharmaceuticals with C<sub>3</sub>-substituted DHB structures are known to have a glucose-lowering action.<sup>2</sup> Although several approaches to synthesize the DHB structure have been developed recently,<sup>3–5</sup> the development of a regioselective and efficient synthesis method of C<sub>3</sub>-substituted DHB remains a challenge. Perhaps the most attractive and robust synthesis approach for synthesizing C<sub>3</sub>-substituted DHB is to use the intramolecular Heck-type arylation reactions of an aryl halide (or its isosteres) that bear the allyl ether group using Pd-,<sup>6</sup> Ni-<sup>7</sup>, and Cu-catalyst<sup>8</sup> (Scheme 1a). Although this approach is reliable for obtaining the desired regioselective products, it requires preliminary prefunctionalization of substrates and is unsuitable for generating structural diversity in the

products.

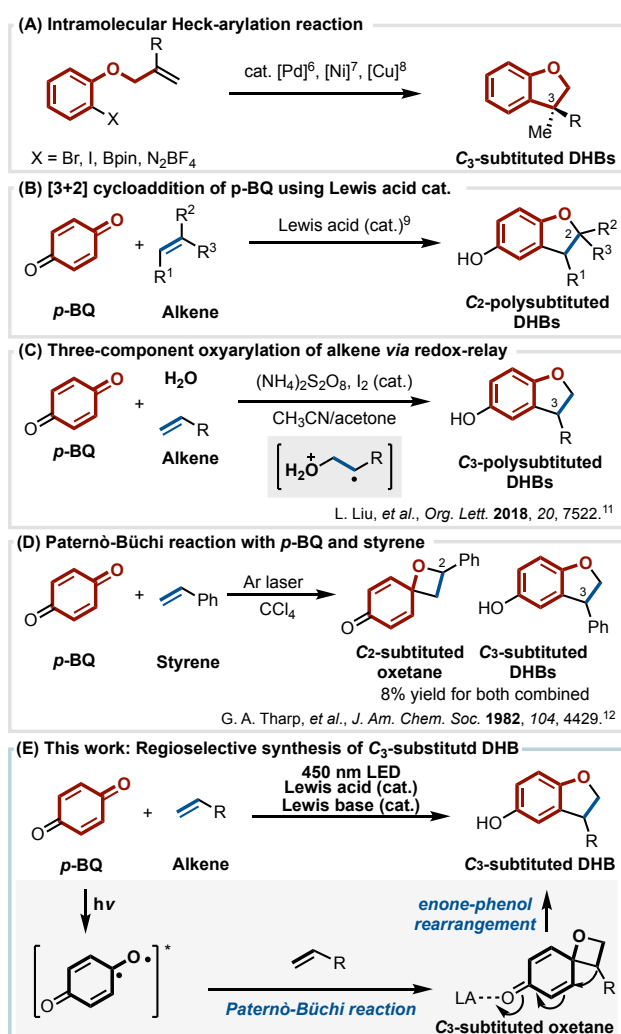
Intermolecular cycloaddition reactions in which two bonds are formed simultaneously are the ideal methods to solve the aforementioned issues, and they are a powerful tool to rapidly and diversely construct DHB structures. Among them, the [3+2] cycloaddition reactions of *p*-benzoquinone (*p*-BQ) with an alkene using Lewis acids provides efficient access to DHBs<sup>9</sup> (Scheme 1b). Because the regioselectivity of the alkene double-bond carbon reaction site follows Markovnikov's rule in this reaction process,<sup>10</sup> C<sub>2</sub>-substituted DHBs with an oxygen forming a bond with a more highly substituted alkene carbon are obtained. In contrast, synthesizing C<sub>3</sub>-substituted DHB (anti-Markovnikov products) via a polar reaction between carbonyl derivatives and alkenes is a challenge. Therefore, different synthetic strategies have to be explored to obtain C<sub>3</sub>-substituted DHB with enhanced structural diversity from versatile compounds. For example, Liu and coworkers reported a metal-free methodology of three-component oxyarylation using *p*-BQ, an alkene, and H<sub>2</sub>O to rapidly and regioselectively construct a C<sub>3</sub>-substituted DHB structure via a redox-relay process using (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>O<sub>8</sub> as an oxidant (Scheme 1c).<sup>11</sup> Although the key to the hydration of the alkene radical cation species proceeds according to the anti-Markovnikov rule in this reaction, problems related to the reaction performance, such as the overall low yield rates of all products, persist.

Considering this background, we decided to adopt a different strategy to achieve efficient and regioselective C<sub>3</sub>-substituted DHB synthesis. Our strategy is based on the classical Paternò-Büchi reaction,<sup>12</sup> which is the photochemical [2+2] cycloaddition reaction of a carbonyl with an alkene to afford an oxetane compound. The regioselectivity and stereoselectivity of the Paternò-Büchi reaction has been well discussed, and it is known to be determined generally by the steric or electronic factors of the substrate used.<sup>12b,c, 13</sup> For example, when using *p*-BQ and styrene as substrates in the Paternò-Büchi reaction, C<sub>2</sub>-substituted oxetane is obtained in a low yield.<sup>14</sup> In addition, a small amount of C<sub>3</sub>-substituted DHB, not C<sub>3</sub>-substituted oxetane, is generated in this reaction (Scheme 1d). This C<sub>3</sub>-substituted DHB is attributed to the dienone-phenol rearrangement of C<sub>3</sub>-substituted oxetane.<sup>15</sup> We hypothesized that if the efficient dienone-phenol rearrangement of

the C<sub>3</sub>-substituted oxetane can be promoted using a suitable catalyst, C<sub>3</sub>-substituted DHB can be synthesized with remarkable convenience and complete regioselectivity. Thus, we developed a new strategy for regioselective C<sub>3</sub>-substituted DHB synthesis by using Lewis acid and Lewis base pairs (LPs) as a catalyst in the Paternò–Büchi reaction of *p*-BQ with various alkenes as the substrate (Scheme 2).

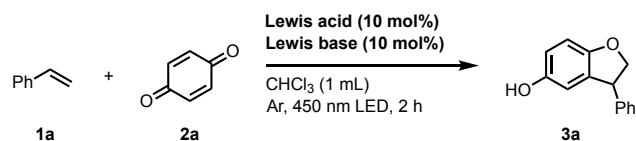
**Scheme 1. Dihydrobenzofuran (DHB) synthesis in previous works: A) TM catalysis. B) [3+2] cycloaddition by Lewis acid. C)**

**Oxyarylation of an alkene. D) Traditional Paternò–Büchi reaction. E) DHB synthesis in this work.**



## Result and Discussion

To optimize the reaction conditions, we evaluated the synthesis of C<sub>3</sub>-substituted DHB by externally irradiating styrene (**1a**), *p*-BQ (**2a**), and various Lewis acids (10 mol%) with a 450 nm LED for 2 h (Table 1). Initially, various Lewis acids were examined to accelerate the dienone–phenol rearrangement reaction in oxetane. The reaction proceeded and generated DHB (**3a**) in 20%–30% yield when a Lewis acid such as AlCl<sub>3</sub> or FeCl<sub>3</sub> was used (Table 1, entry 1, 2). Although the addition of B-based Lewis acids such as B(OPh)<sub>3</sub> and B(O<sup>*i*</sup>Pr)<sub>3</sub> furnished the desired **3** albeit in low yield, the use of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, which exhibits stronger Lewis acidity, improved the yields of the desired product **3** (Table 1, entry 3-5).<sup>16</sup> Interestingly, bulky Lewis base such as phosphine or amine were added in equal amounts as B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, and the desired product was obtained in 70% yield when P(*o*-tol)<sub>3</sub> was applied (entry 8). Surprisingly, the reaction proceeded smoothly even with only 1 mol% both of Lewis acid B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and Lewis base P(*o*-tol)<sub>3</sub> catalysts, and the desired product (**3a**) was obtained in 94% isolated yield (entry 11). Gram-scale reaction was also possible, and the desired DHB (**3a**) was isolated in 77% yield, 1.6 g (entry 12). However, the reaction did not proceed under dark conditions or without catalyst conditions, and the starting material was recovered (entry 13, 14).

**Table 1. Optimization of Reaction Conditions<sup>a</sup>**

entry	Lewis acid	Lewis base	<b>3a</b> <sup>b</sup> (%)
1	AlCl <sub>3</sub>	-	36
2	FeCl <sub>3</sub>	-	17
3	B(C <sub>6</sub> H <sub>5</sub> O) <sub>3</sub>	-	21
4	B( <i>i</i> -PrO) <sub>3</sub>	-	18
5	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	-	58
6	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	P( <i>n</i> -Bu) <sub>3</sub>	60
7	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	P(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	55
8	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	P( <i>o</i> -tol) <sub>3</sub>	70
9	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	dppe	0
10	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	Ph <sub>3</sub> N	59
11	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> (1 mol%)	P( <i>o</i> -tol) <sub>3</sub> (1 mol%)	94 <sup>c</sup>
12 <sup>d</sup>	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> (1 mol%)	P( <i>o</i> -tol) <sub>3</sub> (1 mol%)	77 <sup>c</sup> (1.6 g)
13 <sup>e</sup>	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> (1 mol%)	P( <i>o</i> -tol) <sub>3</sub> (1 mol%)	0
14	-	-	0

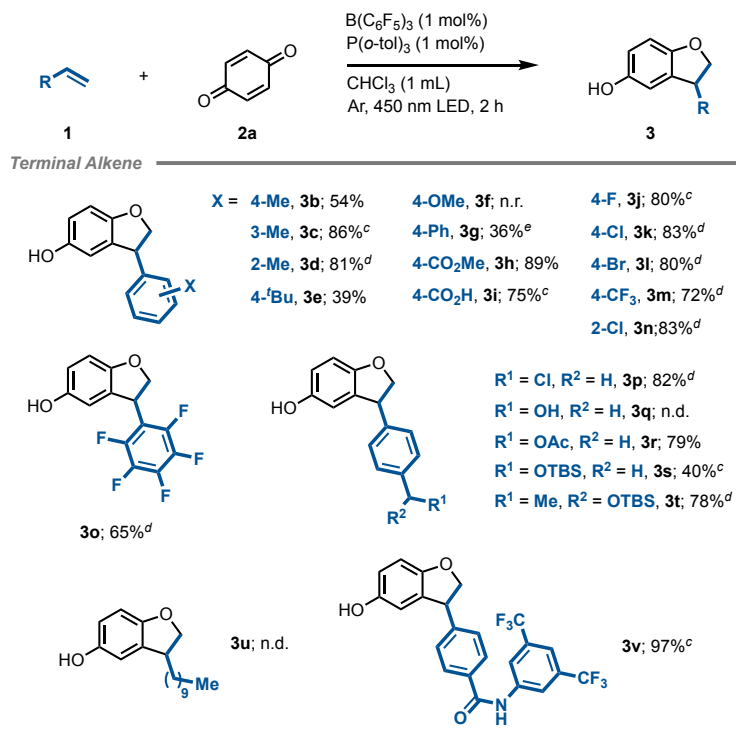
<sup>a</sup>Reaction conditions: *p*-Benzoquinone (*p*-BQ) **2a** (0.1 mmol), styrene **1a** (3.0 equiv), Lewis acid (10 mol%), and/or Lewis base (10 mol%)

in CHCl<sub>3</sub> (1 mL) stirred at room temperature irradiated with a 1 W/450 nm LED for 2 h. <sup>b</sup><sup>1</sup>H nuclear magnetic resonance (NMR) yield. <sup>c</sup>

Isolated yield. <sup>d</sup>The gram-scalable reaction. Reaction conditions: *p*-BQ **2a** (10 mmol), styrene **1a** (3.0 equiv), B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (1 mol%), and P(*o*-tol)<sub>3</sub> (1 mol%) in CHCl<sub>3</sub> (50 mL) stirred at room temperature irradiated with a 50 W/450 nm LED light for 24 h. <sup>e</sup> The reaction under the dark condition.

After determining the optimized conditions, we focused on exploring the substrate scope of the series of terminal alkenes, as shown in Scheme 2. Styrene bearing alkyl substituents (**1b–1e**) furnished C<sub>3</sub>-substituted DHBs **3b–3e** in moderate to good yields. In the case of styrene bearing the electron-rich methoxy group (**1f**), the reaction did not proceed, and *p*-BQ (**2a**) and 4-methoxy styrene (**1f**) were recovered quantitatively. 4-Vinyl biphenyl (**1g**) was not a suitable substrate for this reaction because of its low solubility in the solvent. In contrast, substrates with electron-withdrawing groups such as esters, carboxylic acids, and halogen-containing styrene (**3h–3n**) reacted smoothly with **2a** to produce DHBs **3h–3n** in 72%–89% yield. The desired DHB **3o** was obtained in good yield when 2,3,4,5,6-pentafluorostyrene (**1o**) that has extremely strong electron-withdrawing capacity was used. Although styrene bearing a Cl-group at the benzylic position (**1p**) gave DHB **3p** in 82% yield, styrene bearing the free OH-group (**1q**) produced a complex mixture and yielded only a trace amount of DHB **3q**. However, the reaction performed using benzyl alcohol substrates protected by Ac (**3r**) or TBS (**3s** and **3t**) could tolerate well under the reaction conditions, and the corresponding DHBs **3r–3t** were obtained. Aliphatic 1-dodecane (**1u**) formed oxetane by [2+2] photocycloaddition but not by the formation of DHB **3u**. Finally, the reaction efficiency did not decrease when using styrene with the amide group (**1v**), and the desired DHB **3v** was afforded in excellent yield (97%). Note that all DHBs **3** obtained were C<sub>3</sub>-substituted with complete regioselectivity.

**Scheme 2. Reaction with Various Terminal Alkenes 1 Using *p*-Benzoquinone (*p*-BQ) **2a**<sup>a,b</sup>.**



<sup>a</sup> Reaction conditions: *p*-BQ **2a** (0.1 mmol), terminal alkenes **1** (3.0 equiv.), B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (1 mol%) and P(*o*-tol)<sub>3</sub> (1 mol%) in CHCl<sub>3</sub> (1 mL) stirred at room temperature irradiated with a 450 nm LED light for 2 h. <sup>b</sup> Isolated yield. <sup>c</sup> Using 5.0 equivalents of alkenes. <sup>d</sup> Using 0.5 mL of CHCl<sub>3</sub>. <sup>e</sup> Using 1.5 mL of CHCl<sub>3</sub>.

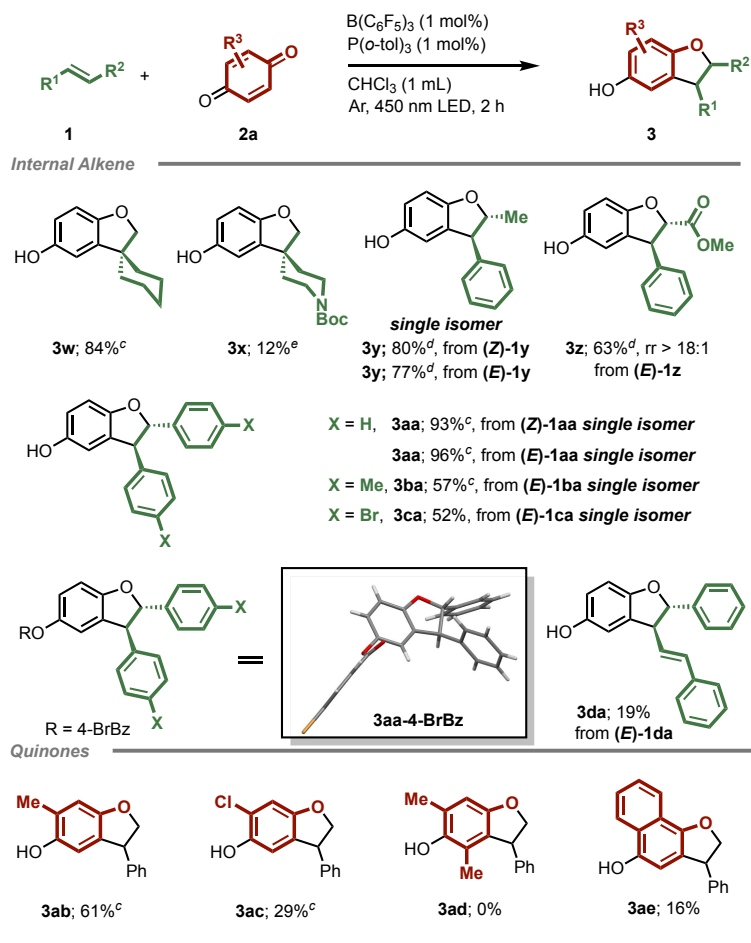
Following the terminal alkenes, a variety of internal and polysubstituted alkenes **1w–1da** were applied for synthesizing structurally diverse DHBs **3** (Scheme 3). The reaction proceeded smoothly with aliphatic methylcyclohexane (**1w**) to give the desired C<sub>3</sub>-disubstituted spiro-DHB compound **3w**. Furthermore, this method can also be used to synthesize C<sub>3</sub>-disubstituted spiro-piperidinyl DHBs such as **3x**, which are known to exhibit important biological activities,<sup>17</sup> with complete regioselectivity. Both (*E*)- and (*Z*)-β-methyl styrene (**1y**) were smoothly adducted with *p*-BQ (**2a**) under the optimized conditions. Interestingly, C<sub>2</sub>- and C<sub>3</sub>-disubstituted DHBs **3y** were generated with a single diastereomer with complete regioselectivity, indicating that the stereoselectivity of the product was not affected by the conformation of the starting materials. This result suggests that the reaction proceeds via a sequential, rather than concerted, reaction

mechanism. Providing further support to this result, DHB **3z** bearing the methyl ester group at C<sub>2</sub>-position was obtained at regioisomeric ratio (rr) > 18:1 with a single diastereomer from the reaction using (**e**)-**1Z**. In all cases of use of an internal alkene, such as the stilbene derivative **1aa–1ca**, the reaction proceeded well, and the corresponding DHB was obtained as a single diastereomer. Single crystal X-ray crystallography of **3aa–Bz** revealed that its relative conformation is trans. Although a more conjugated substrate such as trans, trans-1,4-diphenyl-1,3-butadiene (**1da**) provided the desired DHB **3da**, many byproducts derived from unstable dienes were obtained after the reaction was completed.

Finally, the range of accessible quinones was investigated. The mono-substituted form such as *p*-tolquinone (**2b**) or *p*-Cl quinone (**2c**) was tolerated, but the di-substitution at the *p*-position such as 2,6-dimethyl-benzoquinone (**2d**) formed a complex mixture, and the target product was not obtained. Finally, the range of accessible quinones was investigated. Therefore, mono-substituted forms such as *p*-tolquinone (**2b**) and *p*-Cl quinone (**2c**) were tolerated, but compounds with di-substitution at the *p*-position, such as 2,6-dimethylbenzoquinone (**2d**), formed a complex mixture, and the target product was not obtained. When naphthoquinone (**2e**) was used as a substrate, undesired [2+2] cycloaddition proceeded in competition with the formation of the desired product **3ae**.<sup>18</sup>

**Scheme 3. Reaction with Various Internal Alkenes **1** and Quinones **2**<sup>a,b</sup>.**





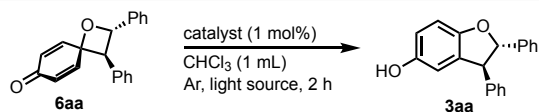
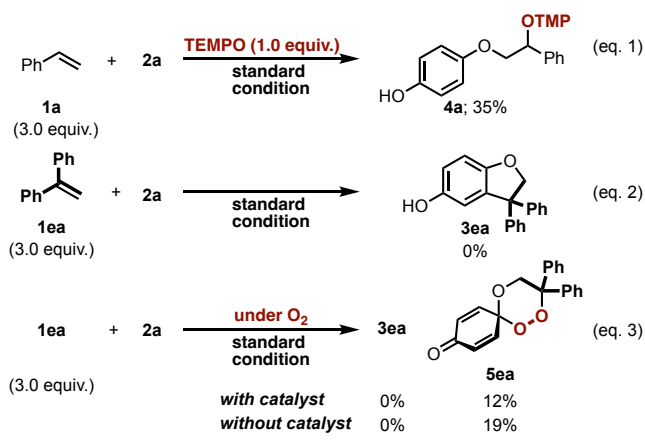
<sup>a</sup> Reaction conditions: Quinones **2** (0.1 mmol), olefins **1** (3.0 equiv.), B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (1 mol%), and P(*o*-tol)<sub>3</sub> (1 mol%) in CHCl<sub>3</sub> (1 mL) stirred at room temperature irradiated with a 450 nm LED light for 2 h. <sup>b</sup> Isolated yield. <sup>c</sup> Using 5.0 equivalents of olefins. <sup>d</sup> Using 0.5 mL of CHCl<sub>3</sub>. <sup>e</sup> Only using B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> catalyst.

To gain an insight into the synthesis mechanism, several control experiments were performed. Initially, a radical-trapping experiment using 2,2,6,6-tetramethyl piperidine-1-yl-oxyl (TEMPO) as a radical scavenger was performed (Scheme 4, eq.1). In this experiment, **4a**, which is the intermolecular adduct of p-BQ (**2a**) with styrene trapped by TEMPO, was generated in a 35% yield. This indicated that benzyl radical was generated as an intermediate for the radical addition of p-BQ (**2a**) and styrene. 1,1-Diphenylethylene, which is known as a radical scavenger, was used instead of styrene in an Ar atmosphere, and the desired photoreaction was completely suppressed (Scheme 4,

eq.2). In contrast, when the reaction was carried out in an oxygen atmosphere, the formation of trioxane **5ea** with triplet oxygen trapped by p-BQ (**2a**) and styrene was confirmed in the presence or absence of LP catalysts (Scheme 4, eq.3). This means that the triplet biradical intermediate was generated by the excitation of C=O ( $n-\pi^*$ ) bonds by visible light, or via the formation of a CT-excipient intermediate with alkenes.<sup>14, 19</sup> Moreover, these experimental insights indicate that the triplet biradical intermediate is also generated in Ar atmosphere, and it is suggested that the intermolecular radical addition of carbonyl to alkene proceeds reversibly in this reaction (eq. 2, 3). Note that the LP catalyst was not involved in this photoaddition reaction step between p-BQ (**2a**) with alkene (eq. 3).

To reveal the intermediate and role of the LP catalyst in this reaction, further experiment was performed (Scheme 4. bottom). First, we set out to synthesize oxetane **6aa**, the assumed intermediate for the PB reaction. Oxetane **6aa** was obtained in high yield with a single diastereomer when the reaction under standard conditions was performed without adding LPs catalyst and by using p-BQ (**2a**) and trans-stilbene (**(E)-1aa**) (for See SI). The result suggests that the initial addition process between the carbonyl and alkene proceeds via a catalyst-independent [2+2] photocycloaddition (Paternò-Büchi reaction). To investigate whether oxetane **6aa** acts as an intermediate, the reaction was performed using an LP catalyst under irradiation with a 450 nm LED light (entry 1). Therefore, oxetane **6aa** was converted to the desired DHB **3aa**, and the stereo configuration was retained. Thus, oxetane **6aa** is predicted to be an intermediate for the reaction, and it is suggested that the LPs catalysts have a remarkable effect on the conversion of oxetane to DHB. The same reaction was examined under conditions of shielding from the LED light with or without LP catalysts, and the reaction proceeded smoothly even without light irradiation if the LP catalyst was added (entries 2, 3, and 4). This means that the LP catalyst is essential for converting oxetane to DHB, and light is not involved in this conversion. Furthermore, the reaction proceeds to give **3aa** in 45% yields without the Lewis base (entry 4); thus, the Lewis acid  $B(C_6F_5)_3$  independently, rather than the frustrated Lewis pairs, probably promote the conversion of oxetane to DHB *via* dienone-phenol rearrangement.

#### Scheme 4. Control experiments.

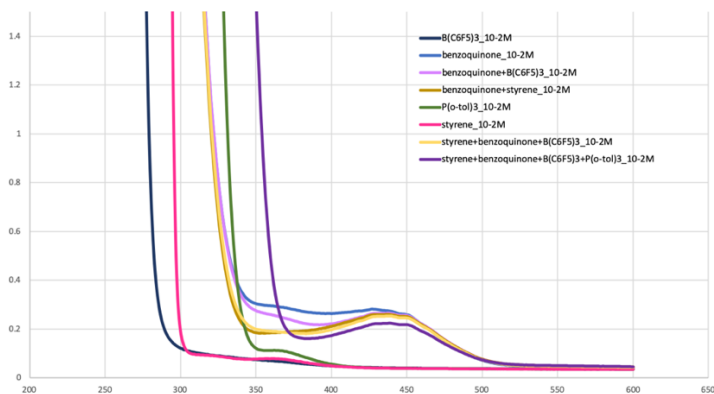


entry	catalyst	light source	3aa (%)
1	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> / P( <i>o</i> -tol) <sub>3</sub>	450 nm	70
2	none	450 nm	17
3	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> / P( <i>o</i> -tol) <sub>3</sub>	dark	76
4	none	dark	45
5	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	dark	10

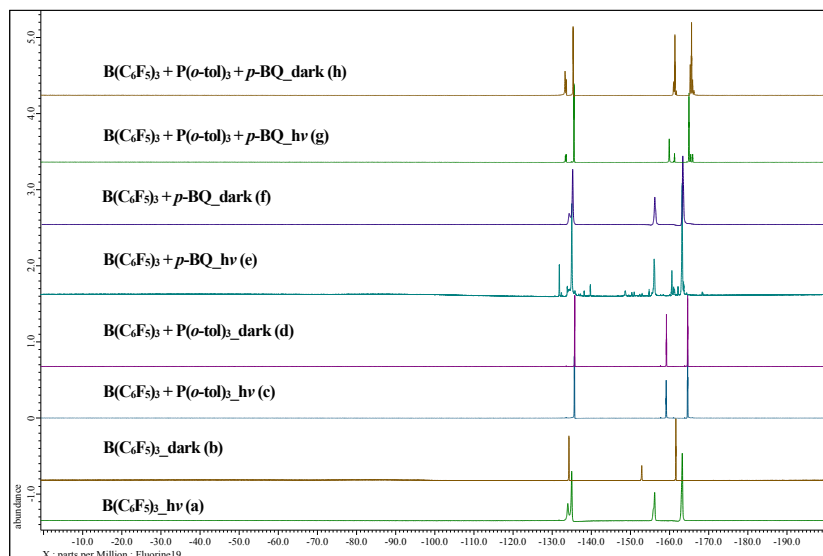
Upon mixing equimolar ( $10^{-2}$  M) amounts of *p*-BQ (**2a**) and/or various reagents in CHCl<sub>3</sub> at room temperature, the UV/Vis absorption spectrum of *p*-BQ (light blue line) exhibited a local absorption maximum of nearly 440 nm with a broad shoulder (Figure 1a). This absorption is caused by the  $n-\pi^*$  transition of carbonyls.<sup>20</sup> However, the addition of some reagents used in this reaction, such as B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and P(*o*-tol)<sub>3</sub>, did not change the maximum UV/Vis absorption wavelength (lavender-purple, brown, yellow, and purple lines). These spectra were in good agreement with the results of the aforementioned experiments that the Lewis acid or Lewis base catalysts are not involved in the photoreaction and that *p*-BQ (**2a**) itself was absorbed and excited by the 450 nm LED illumination, which provides the driving force of the reaction.

When the interaction between the Lewis acid B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> and Lewis base P(*o*-tol)<sub>3</sub> or *p*-BQ (**2a**) was observed from <sup>19</sup>F nuclear magnetic resonance (NMR) measurements, we gained an insight into the role of Lewis bases (Figure 1b). Equimolar mixtures ( $10^{-2}$  M) of *p*-BQ

(**2a**),  $B(C_6F_5)_3$ , and  $P(o\text{-tol})_3$  in  $CDCl_3$  were irradiated by 450 nm LED light or shielded from the light for 2 h; thereafter, the  $^{19}F$  NMR measurements were made. The samples of only  $B(C_6F_5)_3$  (spectra a, b) and those containing  $P(o\text{-tol})_3$  (spectra c, d) showed a slight chemical shift regardless of the presence or absence of visible light, and severe decomposition of  $B(C_6F_5)_3$  did not occur. In contrast,  $B(C_6F_5)_3$  decomposed greatly when irradiated by the LED light and mixed with *p*-BQ (**2a**) (spectrum e). However, for the samples containing the LP catalyst and *p*-BQ (**2a**), multiple decompositions of  $B(C_6F_5)_3$  after LED light irradiation did not occur (spectrum g). Based on these investigations, we envisioned that one of the roles of the Lewis base is to protect the Lewis acid from decomposition by forming a complex.<sup>21, 22b</sup> In addition, some of the findings from experimental results are as follows: (1) When only the Lewis base was used as a catalyst, DHB did not form, and the reaction stopped at oxetane (see SI and Table 1). (2) Bulky Lewis bases tend to promote conversion to DHB (see SI Table S1), suggesting that the Lewis base is not directly involved in the reaction but is likely to affect the reaction indirectly through interaction with the Lewis acid. (It is not clear whether the complex is a frustrated Lewis pairs or LPs<sup>22-24</sup>).



**Figure 1 (a) UV/Vis absorption spectrum**



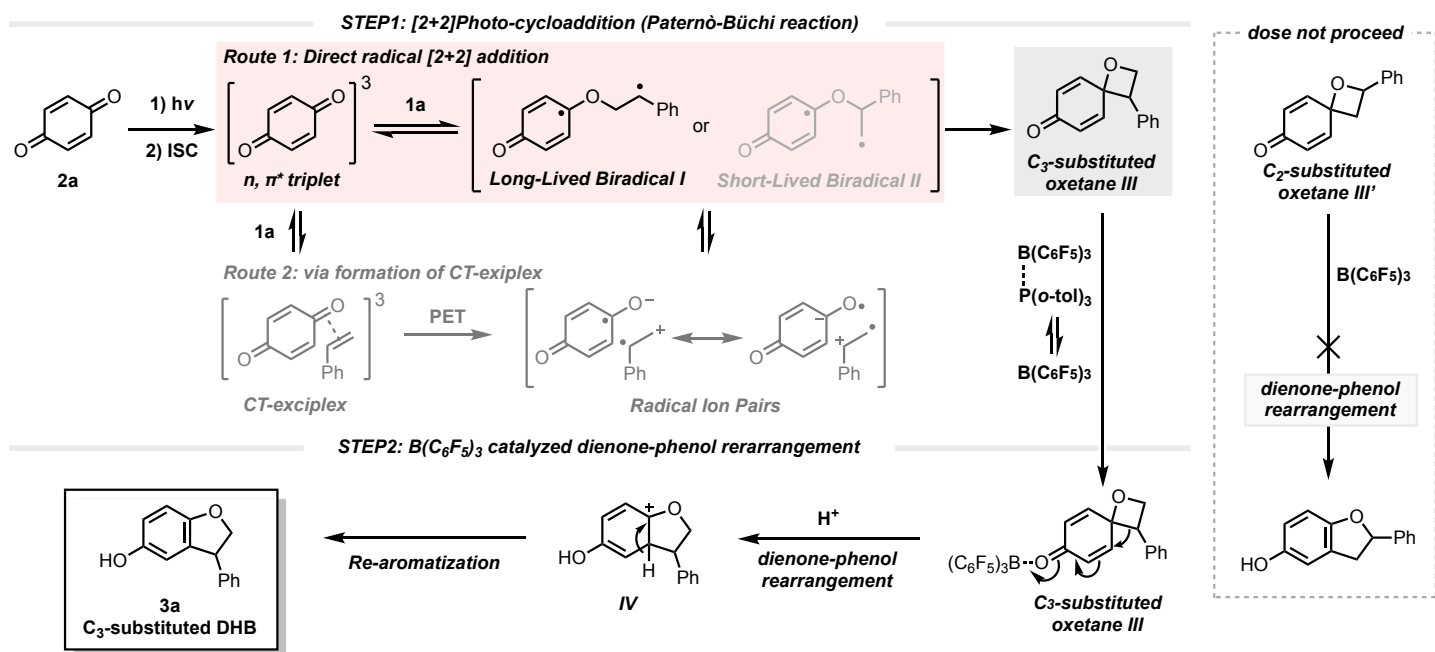
**Figure 1. (b)  $^{19}\text{F}$  NMR spectrum**

Based on these findings, we envisioned the plausible mechanism as shown Scheme 5. Initially, *p*-BQ (**2a**) was excited by 450 nm LED light and undergoes intersystem crossing to generate the excited  $n-\pi^*$  triplet species.<sup>17</sup> Subsequently, the [2+2] photocycloaddition reaction (Paternò-Büchi reaction) with styrene **1a** proceeds to selectively generate  $\text{C}_3$ -substituted oxetane **III**.<sup>12, 14, 19</sup> There are two possible mechanisms leading to the formation of  $\text{C}_3$ -substituted oxetane **III**: (1) the direct radical addition of the excited  $n-\pi^*$  triplet carbonyl oxygen diradical<sup>19a,b</sup> to styrene leads to the formation of the long-lived diradical **I** species or short-lived diradical **II** species, and (2) the formation of a CT-excimer<sup>14, 23c, 25</sup> between the excited triplet *p*-BQ (**2a**) and styrene **1a** proceeds to generate the aforementioned diradicals **I** or **II** via one-electron transfer. In this research, the first pathway is predicted to be the main pathway because the stabilizing effect of solvation on radical ion pairs is small owing to the use of nonpolar solvents.<sup>26</sup> However, it is clear from the radical-scavenging experiment shown in Scheme 5 (eq. 1) that either pathway ultimately produces the diradical species **I** or **II**. As discussed in the results of the mechanistic experiments described in Schemes 5 and 6, the full regioselectivity in the formation of the  $\text{C}_3$ -substituted DHBs are attributed to the following reasons: the long-lived diradical **I** species is more likely to give  $\text{C}_3$ -substituted oxetane **III** in the reversible diradical species

generation process up to oxetane formation,<sup>14, 19a</sup> and the subsequent dienone-phenol rearrangement proceeds irreversibly, and the dienone-phenol rearrangement of C<sub>2</sub>-substituted oxetane **III'** did not occur (See for SI). In addition, C<sub>2</sub>-substituted oxetane **III'** was not obtained in most reactions.

Finally, C<sub>3</sub>-substituted DHB **3a** was obtained by the Lewis acid B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-catalyzed dienone-phenol rearrangement. Here, the state that forms by the complexing of the Lewis acid B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> with the Lewis base P(*o*-tol)<sub>3</sub> or *p*-BQ (**2a**) is unclear, but the Lewis base P(*o*-tol)<sub>3</sub> is considered to play a protective role of the Lewis acid B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> in this reaction. Further investigations into this LP-catalyzed reaction mechanism under visible light are ongoing.

### Scheme 5. Plausible mechanism.



In conclusion, we explored synthetically valuable applications of the classical Paternò-Büchi reaction and established a rapid and efficient methodology for the synthesis of C<sub>3</sub>-substituted dihydrobenzofurans. The reaction is accelerated by visible light and a very small amount of LP catalyst and can be completed in as little time as 1 h. From a broader perspective, the development of a practical photocatalytic

reaction system that enhances the utilization value of classical reactions as done in this research is of great academic significance. We also expect to demonstrate significant advances in many industries, including the pharmaceutical industry.

### Conflicts of interest

There are no conflicts to declare.

### Acknowledgments

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