

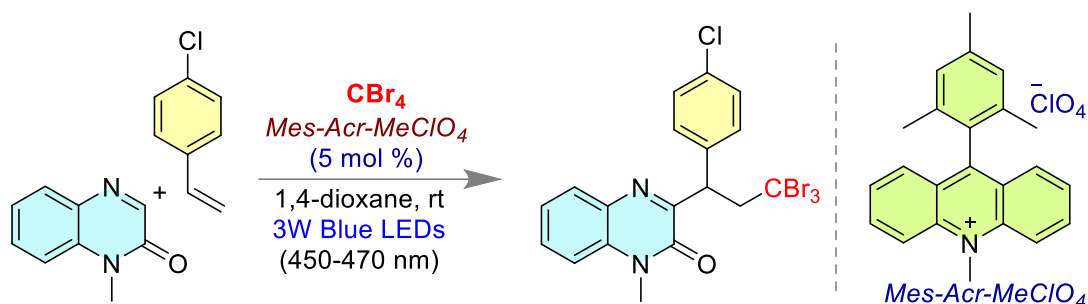
# Atom Transfer Radical Addition to Alkenes using Fukuzumi Photocatalyst for Regioselective Functionalization of Quinoxalin-2(*I*H)-ones

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## GRAPHIC FOR TOC



## ABSTRACT

The atom transfer radical addition (ATRA) reaction is defined as a method for introducing halogenated compounds into alkenes *via* a radical mechanism. In this study, we present an ATRA approach for achieving regioselective functionalization of quinoxalin-2(*I*H)-ones by activating C-Br bonds of  $\text{CBr}_4$ , and subsequent trihaloalkyl-carbofunctionalization of styrenes employing the 9-mesityl-10-methylacridinium perchlorate (Fukuzumi) photocatalyst under 3W blue LED (450-470 nm) irradiation. This three-component radical cascade process demonstrates remarkable efficiency in the synthesis of 1-methyl-3-(3,3,3-tribromo-1-(4-chlorophenyl)propyl)quinoxalin-2(*I*H)-one derivatives.

## KEYWORDS

Atom Transfer Radical Addition (ATRA); 9-Mesityl-10-methylacridinium Perchlorate Photocatalyst; Quinoxalin-2(1H)-one; Three Component Reaction (3-CR); Visible light photocatalysis

## INTRODUCTION

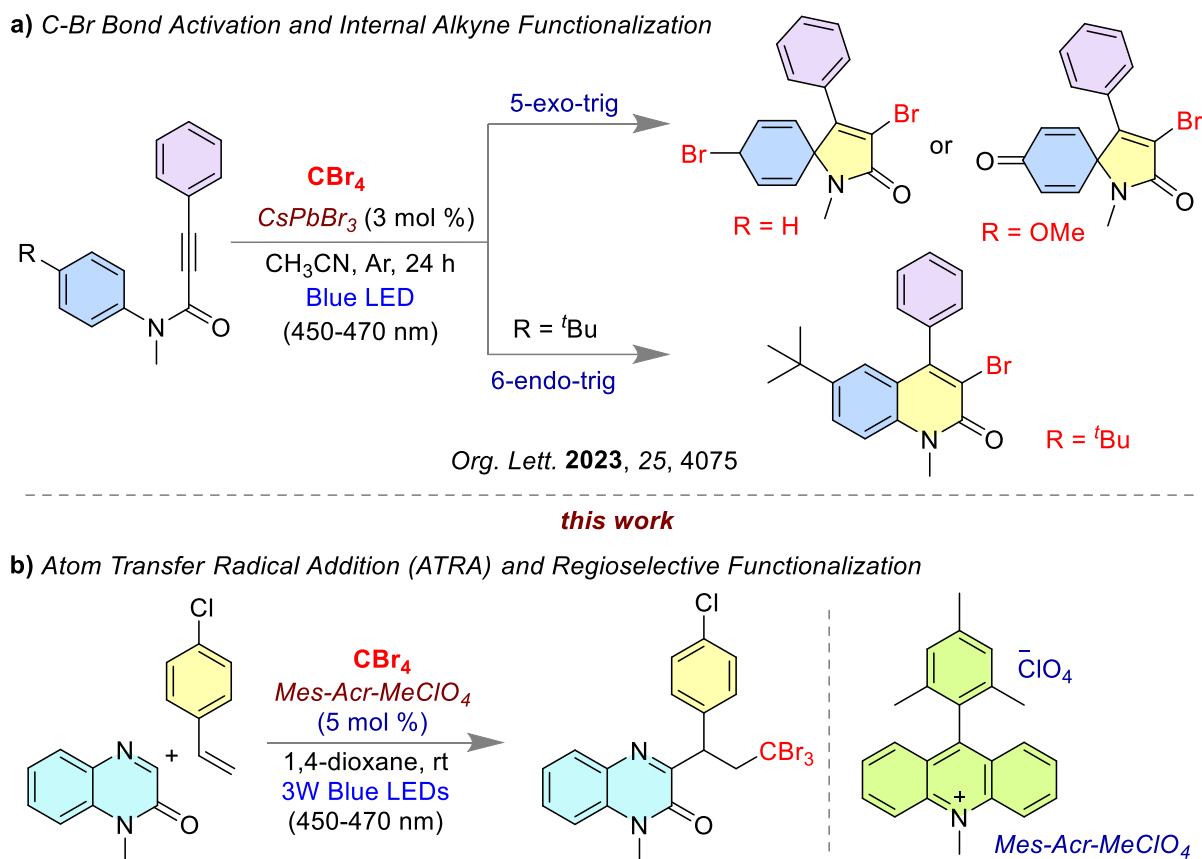
The Atom Transfer Radical Addition (ATRA) reaction is a versatile method for incorporating halogenated compounds into alkenes through a radical mechanism. Recent research has underscored the significance of ATRA as a valuable synthetic tool. ATRA facilitates the efficient functionalization of alkynes and alkenes, traditionally relying on radical initiators or transition metal catalysts.<sup>1</sup> Remarkably, recent advancements have harnessed visible light-mediated catalysts to execute ATRA under mild conditions, thus reducing the occurrence of side reactions, enhancing catalytic efficiency, and simplifying the purification process.<sup>2-3</sup> Nevertheless, it is worth noting that many established ATRA methods still entail harsh conditions, employ toxic reagents, and exhibit limited compatibility with various functional groups.<sup>4-5</sup>

In recent years, visible light photocatalysis has emerged as a promising frontier in organic synthesis.<sup>6-7</sup> This approach boasts numerous advantages, including high atom and step economy, along with innovative synthesis strategies.<sup>6</sup> A particularly exciting breakthrough in this field is the utilization of organic dyes as photocatalysts. Compared to transition metal complexes,<sup>8</sup> these dyes are cost-effective, readily available, and less toxic, positioning them as excellent alternatives for photocatalysis.<sup>9</sup> Consequently, the incorporation of organic dyes as photocatalysts<sup>7, 10-12</sup> has significantly broadened the landscape of photocatalytic organic transformations, presenting a promising and sustainable avenue for organic synthesis.<sup>13-14</sup>

A regioselective multicomponent reaction (MCR) is a chemical process in which three or more reactants undergo simultaneous reactions to yield a single product. What sets a regioselective MCR apart from other MCRs is its specificity in targeting particular reaction sites where new chemical bonds are formed.<sup>15-16</sup> In quinoxalin-2(*I*H)-ones, there are typically two reactive sites, namely C-3 and C-7. In this context, functionalization at the C-3 positions involves the concurrent formation of two C-C bonds.<sup>17</sup> In synthetic chemistry, regioselective MCRs streamline complex molecule synthesis, minimize steps, enable diverse molecular structures, and support compound library creation for materials and drug research.<sup>18-19</sup> In the context of functionalization of quinoxalin-2(*I*H)-ones *via* multicomponent reactions, Wei and co-workers documented the utilization of Langlois reagent (CF<sub>3</sub>SO<sub>2</sub>Na) as a radical precursor in the presence of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, with heating at 80 °C, in an ACN: H<sub>2</sub>O (4:1) solvent mixture to yield 3-trifluoroalkylated quinoxalin-2(*I*H)-ones.<sup>20</sup> Studer and co-workers have introduced a visible-light-induced  $\alpha$ -perfluoroalkyl- $\beta$ -heteroarylation of diverse alkenes using perfluoroalkyl iodides and quinoxalin-2(*I*H)-ones.<sup>21</sup>

Mal and co-workers reported a chemodivergent functionalization approach for *N*-methylalkanamides. They employ C-Br bond activation of CBr<sub>4</sub> with a CsPbBr<sub>3</sub> perovskite photocatalyst under blue LED irradiation (Figure 1a).<sup>22</sup> The selectivity between a 5-*exo*-trig spiro cyclization and a 6-*endo*-trig cyclization hinges on the stability of the radical intermediate generated during the reaction.<sup>22</sup> However, in this study, we introduce an ATRA (Atom Transfer Radical Addition) approach to achieve selective functionalization of quinoxalin-2(*I*H)-ones. This involves activating C-Br bonds in CBr<sub>4</sub> and subsequently conducting a trihaloalkyl-carbofunctionalization of styrenes. We employ the 9-mesityl-10-methylacridinium perchlorate or Mes-Acr-MeClO<sub>4</sub> (Fukuzumi) photocatalyst<sup>23-24</sup> in conjunction with 3W blue LED (450-

470 nm) irradiation. This three-component radical cascade process demonstrates high efficiency in synthesizing derivatives of 1-methyl-3-(3,3,3-tribromo-1-(4-chlorophenyl)propyl)quinoxalin-2(1H)-one (Figure 1b).



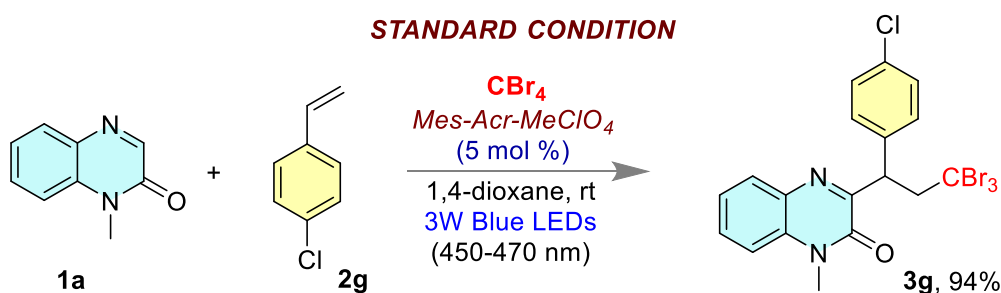
**Figure 1.** a) A chemodivergent synthesis using  $\text{CsPbBr}_3$  photocatalyst *via* C-Br bond activation of  $\text{CBr}_4$ .<sup>22</sup> b) ATRA and multicomponent reaction of quinoxalin-2(1H)-ones with terminal alkene using Mes-Acr-MeClO<sub>4</sub> photocatalyst for the formation of 1-methyl-3-(3,3,3-tribromo-1-(4-chlorophenyl)propyl)quinoxalin-2(1H)-one.

## RESULTS AND DISCUSSION

In this investigation, we subjected 1-methylquinoxalin-2(1H)-one **1a** to a reaction with 1-chloro-4-vinylbenzene **2g** and  $\text{CBr}_4$ , resulting in the synthesis of a variety of quinoxalin-2(1H)-ones with yields spanning from 35% to 95%. Detailed analysis, including X-ray studies and

$^{13}\text{C}$  NMR, provided significant evidence that tribromomethane radical was generated from  $\text{CBr}_4$ , and served as a nucleophile in the multicomponent regioselective ATRA reaction. The reaction conditions shown in Table 1, which are deviations from the standard condition, shed light on the crucial role of both photocatalysts and solvents in the outcomes of the photocatalytic reactions. Entry 1 highlights that without a specific photocatalyst, the reaction in 1,4-dioxane yields no product. Entry 2, employing Eosin Y as the photocatalyst in the same solvent, yielded only trace amounts of the product. In contrast, Entry 3 showcased a significant improvement in yield (20%) when  $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$  was used in 1,4-dioxane, emphasizing its suitability as a photocatalyst. Notably, Entries 4 and 5 demonstrated that the choice of solvent, DCE versus DCM, can substantially impact the yield. Entry 6, using acetone as the solvent, yielded only trace amounts of the product. Similarly, entries 7, 9, 10, 12, 13, 14, and 15, employing MeCN, DMSO, Toluene, EtOH, TFE, HFIP, and NMP as solvents respectively, resulted in no detectable product, underscoring their unsuitability for this reaction. Entries 8 and 11 showed moderate yields (34% and 44%, respectively) when DMF and MeOH were used as solvents. Finally, entries 16 and 17 employed 1,4-dioxane as the solvent, while varying the equivalence of  $\text{CBr}_4$ , resulting in distinct outcomes. Entry 16 achieved a high yield of 65% when 1.5 equiv of  $\text{CBr}_4$  was used, while a slightly lower yield of 37% was obtained when employing 1.0 equiv of  $\text{CBr}_4$  (Entry 17).

**Table 1.** Reaction condition optimization by deviating from standard condition.<sup>a</sup>

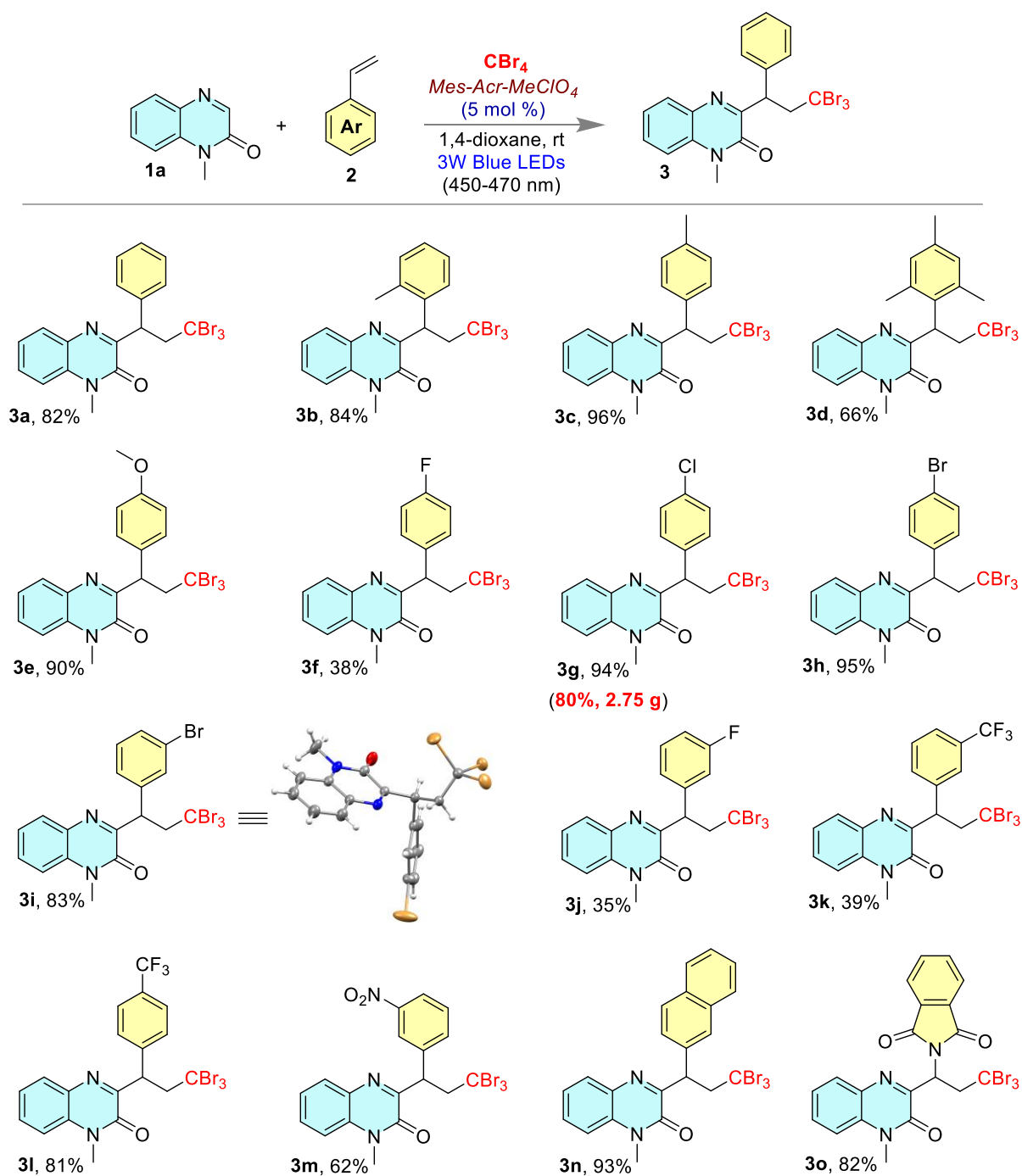


Entry	Photocatalyst	Solvent	Yield(%)
1	-	1,4-Dioxane	0
2	Eosin Y	1,4-Dioxane	trace
3	Ru(bpy) <sub>3</sub> (PF <sub>6</sub> ) <sub>2</sub>	1,4-Dioxane	20
4	Mes-Acr-MeClO <sub>4</sub>	DCE	47
5	Mes-Acr-MeClO <sub>4</sub>	DCM	39
6	Mes-Acr-MeClO <sub>4</sub>	Acetone	trace
7	Mes-Acr-MeClO <sub>4</sub>	MeCN	0
8	Mes-Acr-MeClO <sub>4</sub>	DMF	34
9	Mes-Acr-MeClO <sub>4</sub>	DMSO	trace
10	Mes-Acr-MeClO <sub>4</sub>	Toluene	trace
11	Mes-Acr-MeClO <sub>4</sub>	MeOH	44
12	Mes-Acr-MeClO <sub>4</sub>	EtOH	0
13	Mes-Acr-MeClO <sub>4</sub>	TFE	0
14	Mes-Acr-MeClO <sub>4</sub>	HFIP	0
15	Mes-Acr-MeClO <sub>4</sub>	NMP	0
16	Mes-Acr-MeClO <sub>4</sub>	1,4-dioxane	65 <sup>b</sup>
17	Mes-Acr-MeClO <sub>4</sub>	1,4-dioxane	37 <sup>c</sup>

<sup>a</sup>Reaction Conditions: **1a** (0.3 mmol, 1 equiv), 1-chloro-4-vinylbenzene **2g** (0.4 mmol, 1.2 equiv), **CBr<sub>4</sub>** (0.7 mmol, 2 equiv), and Mes-Acr-Me-ClO<sub>4</sub> (0.018 mmol 5 mol %), under air atmosphere for 1-10 h using Blue LEDs, <sup>b</sup>using 1.5 equiv of CBr<sub>4</sub>, <sup>c</sup>using 1 equiv of CBr<sub>4</sub>.

The quinoxalin-2(*I*H)-one scaffold an important *N*-heterocyclic compound that has a wide range of applications including industrial and pharmaceutical industries.<sup>25-27</sup> Figures 2 and 3 show the substrate scope for the synthesis of derivatives **3f** and **5a** via ATRA under the optimized conditions (Table 1). These reaction conditions prove compatible and yield satisfactory results for compounds bearing both electron-donating (EDG) and electron-

withdrawing (EWG) groups. Notably, the lowest yield is achieved when employing fluorinated styrene under ideal conditions. We further explored the substrate scope by varying both the styrene moiety and the *N*-1 substituted methyl group of quinoxalin-2(*1H*)-ones, as depicted in Figure 2. Styrene and substituted styrenes, bearing 2-methyl, 4-methyl, 1,3,5-trimethyl, and 4-methoxy groups, demonstrated excellent reactivity, yielding the desired products in high yields of 82% (**3a**), 84% (**3b**), 96% (**3c**), 66% (**3d**), and 90% (**3e**), respectively. Additionally, para-halogenated derivatives **3f**, **3g**, and **3h** were isolated with yields ranging from 38% to 95%. However, the introduction of *meta*-halogen groups resulted in compounds **3i** and **3j** with yields of 83% and 35%, respectively. When a trifluoromethyl group was present at the *meta*-position of the styrene (**3k**) moiety, the product yield decreased to 39%. Notably, electron-withdrawing groups, such as  $-\text{CF}_3$  (**3l**) and  $-\text{NO}_2$  (**3m**) at the para position, yielded products with satisfactory yields of 81% and 62%, respectively. Moreover, a comparable yield of 82% was achieved with the phthalimide-containing heterocyclic moiety in **3o**. This synthesis also successfully yielded the compound **3g** on a gram scale (2.75 g), achieving the target yield of 80%, as depicted in Figure 2.

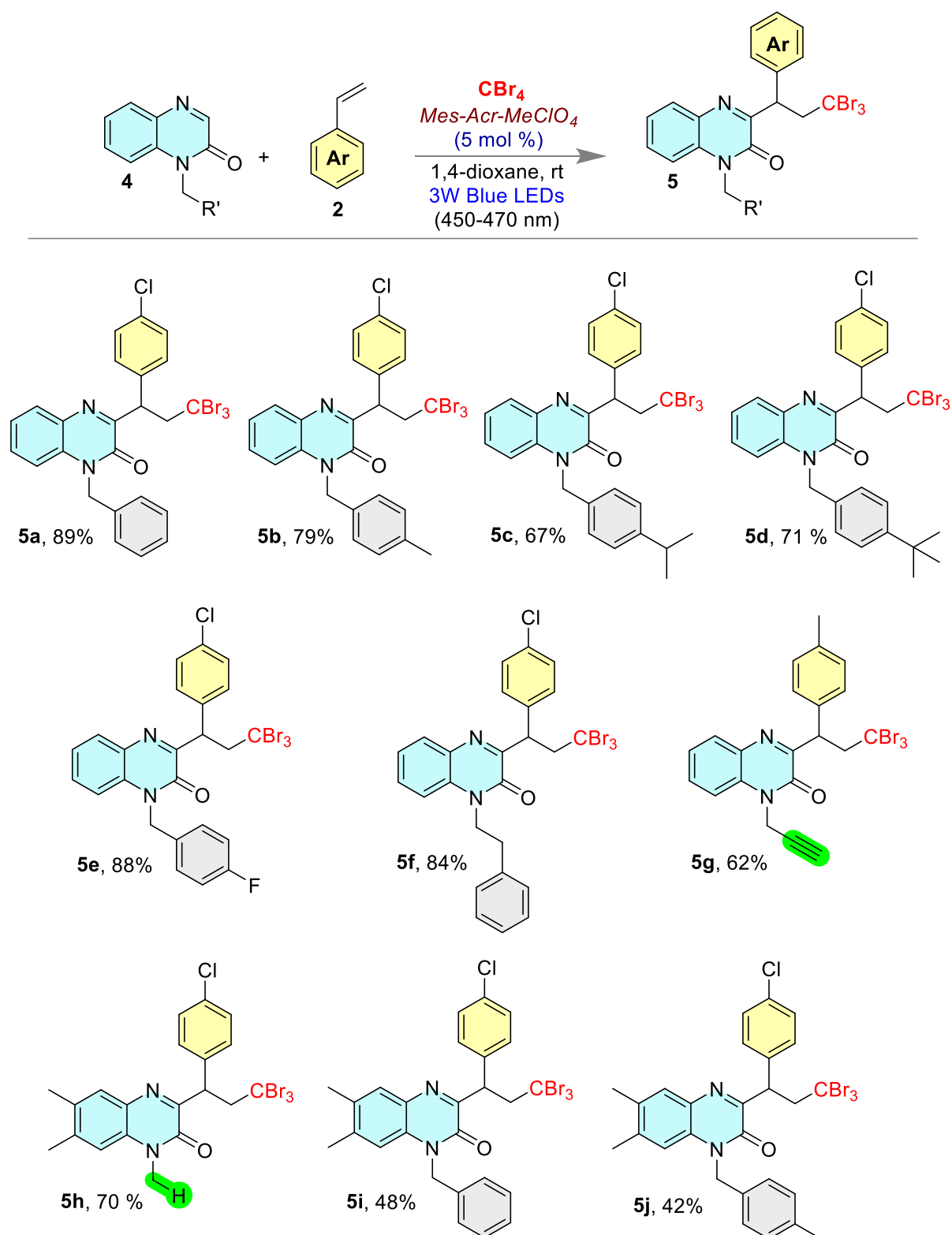


**Figure 2.** Substrate scope for 1-methylquinoxalin-2(1H)-one **1a** with different styrenes and gram scale synthesis of 1-methyl-3-(3,3,3-tribromo-1-(4-chlorophenyl)propyl)quinoxalin-2(1H)-one (**3g**).

Subsequently, we expanded the substrate scope by investigating various substituents at the N-1 position of quinoxalin-2(1H)-ones (Figure 3). When *N*-benzyl-protected quinoxalin-2(1H)-

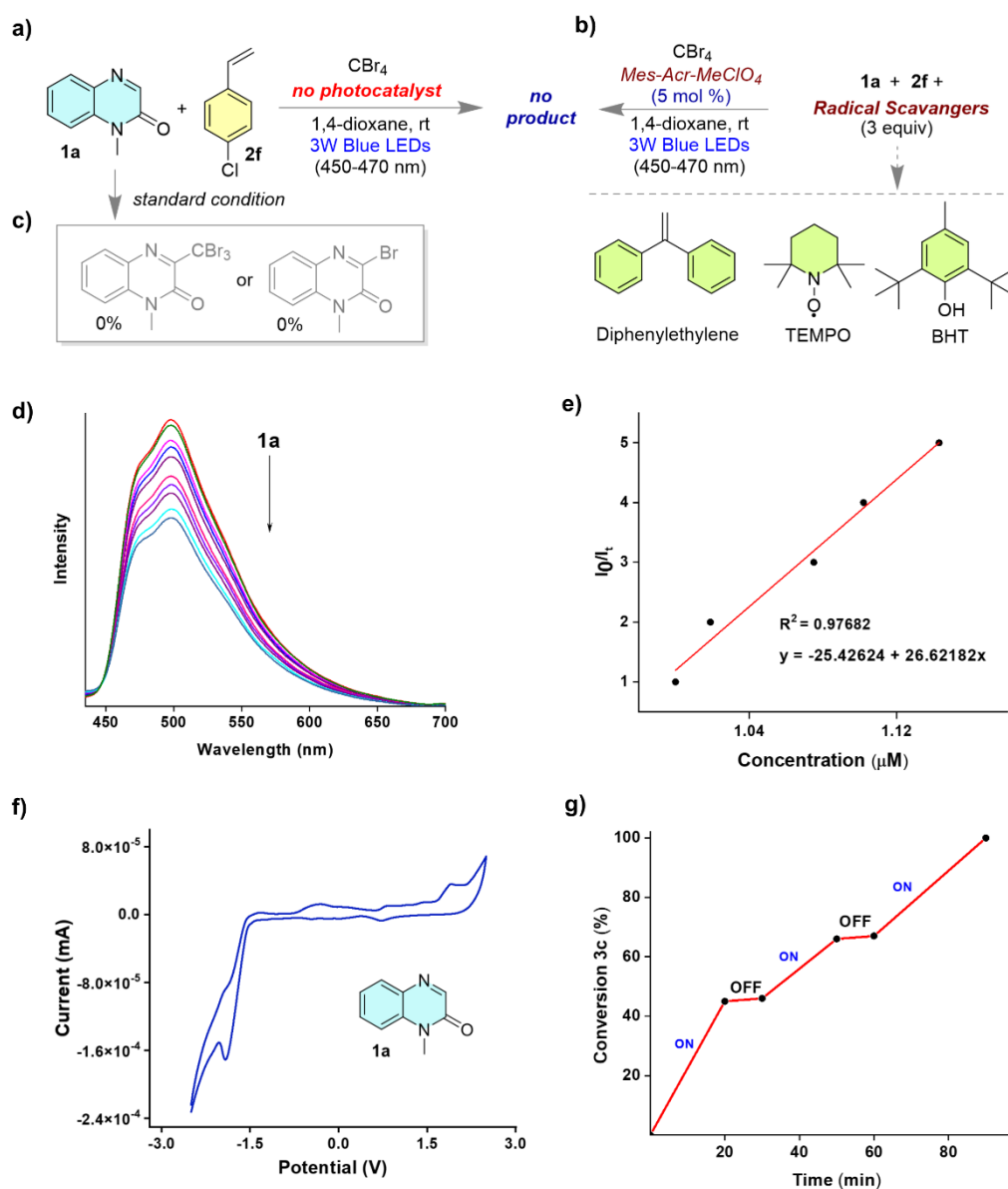


ones (**5a**) were utilized, a notable yield of 89% was achieved. Especially, introducing –Me, –<sup>i</sup>Pr, and –<sup>t</sup>Bu groups at the para position of the benzylic moiety yielded the desired products **5b**, **5c**, and **5d** with reasonable yields of 79%, 67%, and 79%, respectively. In addition, the reaction displayed excellent tolerance for electron-withdrawing groups as well. In particular, the N-benzyl group with a para-positioned –F yielded a satisfactory 88% yield for compound **5e**. Furthermore, the presence of alkyl and alkynyl functionalities at the N-1 position led to the formation of **5f** and **5g**, with yields of 84% and 62%, respectively. The versatility of the reaction was further demonstrated with disubstituted *o*-phenylenediamine derivatives. When –Me, benzyl, and 4-methylbenzyl groups occupied the N-1 position of quinoxalin-2(*1H*)-ones, the corresponding products **5h**, **5i**, and **5j** were isolated with yields ranging from 42% to 70%.



**Figure 3.** Substrate scope with different substitution at *N*-1 position and different *o*-phenylenediamine.

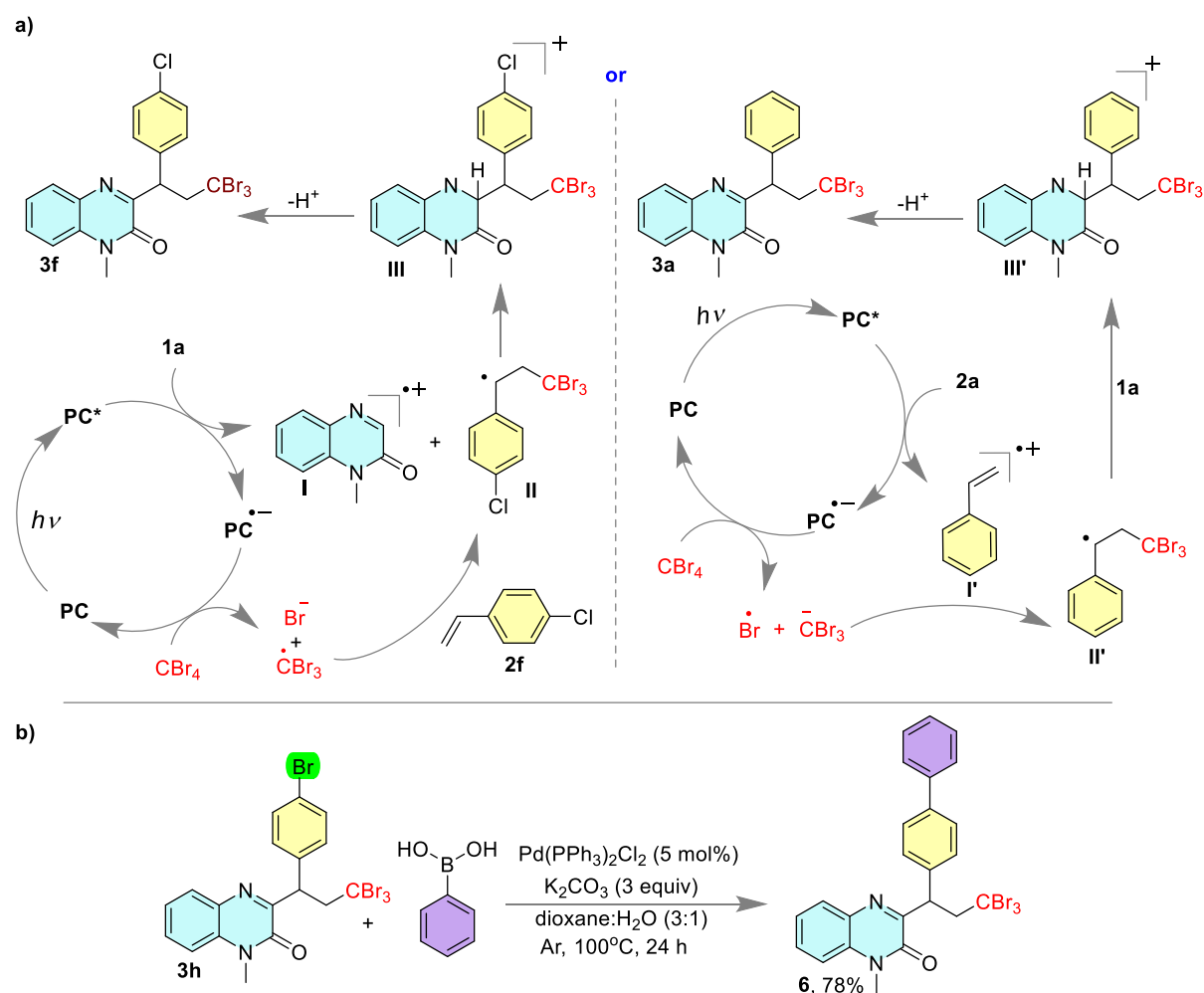
The control experiments (Figure 4) helped to establish the reaction mechanism. To assess the role of the photocatalyst, we conducted an initial reaction in the presence of light but without the Mes-Acr-Me-ClO<sub>4</sub> photocatalyst. Notably, this control experiment revealed that in the absence of the photocatalyst, no desired product was observed, leaving only the starting material intact (Figure 4a).<sup>28</sup> Furthermore, in the presence of radical inhibitors known to support the radical process, such as 1,1-diphenylethylene, TEMPO (2,2,6,6-tetramethylpiperidine-1-oxyl), and BHT (butylated hydroxytoluene), no desirable product was observed (Figure 4b). We conducted a competitive analysis comparing tribromomethane's attack on either the C=N of quinoxalin-2(*I*H)-ones or the C=C center of the alkene. However, we observed no formation of either methyl-3-(tribromomethyl)quinoxalin-2(*I*H)-one or 3-bromo-1-methylquinoxalin-2(*I*H)-one from tribromomethane radical or bromo radical (Figure 4c). This suggests that the tribromomethane radical was initially captured by the C=C center of the alkene (styrenes), forming a nucleophilic radical that subsequently attacked the electrophilic center of quinoxalin-2(*I*H)-one, completing the reaction. Fluorescence quenching occurred upon the introduction of 1-methylquinoxalin-2(*I*H)-one **1a** to Mes-Acr-MeClO<sub>4</sub> (Figure 4d), and analysis using a Stern-Volmer plot (Figure 4e) indicated that the excited state of Mes-Acr-MeClO<sub>4</sub> was quenched by **1a** through a single electron transfer process. The cyclic voltammetry (CV) diagram of **1a** is shown in the Figure 4f. We conducted a light ON–OFF–ON experiment to assess the reaction's light dependency. This experiment involved running the reaction with the light ON, OFF, and then ON again (Figure 4g).<sup>29</sup> The results unequivocally demonstrate that the reaction occurs exclusively when the light is ON, confirming the essential role of visible light in the process.



**Figure 4.** a) In absence of Mes-Acr-MeClO<sub>4</sub> Photocatalyst. b) Radical trapping experiments using diphenylethylene, TEMPO, BHT. c) In absence of 1-chloro-4-vinylbenzene. d) Fluorescence quenching experiment of Mes-Acr-MeClO<sub>4</sub> by 1-methylquinoxalin-2(1H)-one. e) SV plot. f) CV diagram of 1-methylquinoxalin-2(1H)-one. g) Light ON-OFF-ON experiment.

We propose a plausible reaction mechanism based on control experiments and literature reports (Figure 5a).<sup>30-31</sup> The oxidation and reduction potentials of key compounds were compared: Mes-Acr-MeClO<sub>4</sub> exhibited an excited state reduction potential of +2.06 V vs. SCE,<sup>32</sup> while

1-methylquinoxalin-2(*H*)-one **1a** and styrene **2a** had oxidation potentials of +1.9 V<sup>33</sup> and +1.97 V vs. SCE, respectively. Interestingly, the oxidation potential of CBr<sub>4</sub> was found to be +1.21 V vs. SCE. Therefore, the electron transfer might be feasible only from **PC** to **1a** or **2a** upon irradiation. Initially, Mes-Acr-MeClO<sub>4</sub> is excited to **PC**<sup>\*</sup> and underwent a single electron transfer (SET) to form intermediate **I** or **I'** (**1a** or **2a** radical cation), while **PC** itself is reduced to **PC**-radical anion. The CBr<sub>4</sub> accepts electrons from **PC**-radical anion, leading to the formation of bromide anion and tribromo radical. The tribromo radical might have reacted with the C=C bond of styrene to generate a benzylic radical intermediate **II** or **II'**. Intermediate **II** or **II'** could combine with intermediate **III** or **III'**, followed by deprotonation, led to **3f** or **3a**.



**Figure 5.** a) Plausible mechanism (two possible pathways are shown). b) Chemical modification of **3h** via Suzuki coupling.

The compound **3h**, as depicted in Figure 5b, served as the starting material for a synthetic application. A Suzuki coupling reaction was carried out using 1-methyl-3-(3,3,3-tribromo-1-(4-bromophenyl)propyl)quinoxalin-2(*1H*)-one (**3h**) and phenylboronic acid in the presence of Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (5 mol %), K<sub>2</sub>CO<sub>3</sub> (3 equiv), and a mixed solvent of dioxane: H<sub>2</sub>O (3 : 1) at 100°C for 24 h.

In summary, we introduce an ATRA approach for achieving regioselective functionalization of quinoxalin-2(*1H*)-ones. This process involves the activation of C-Br bonds using CBr<sub>4</sub>, followed by tribromomethyl-carbofunctionalization of styrenes and a subsequent radical cascade addition to quinoxalin-2(*1H*)-ones. We used the 9-mesityl-10-methylacridinium perchlorate (Fukuzumi) photocatalyst under 3W blue LED (450-470 nm) irradiation. This reaction proceeded through a three-component one pot coupling *via* radical cascade process. This interdisciplinary approach, uniting the realms of organic chemistry and photochemistry, holds great potential for advancing the field of organic chemistry significantly.

## ACKNOWLEDGMENT

B.P. and S.S. thank NISER for the fellowship.

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