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Metal-Free, Room-Temperature, Radical Alkoxycarbonylation of Aryldiazonium Salts through Visible-Light Photoredox Catalysis**

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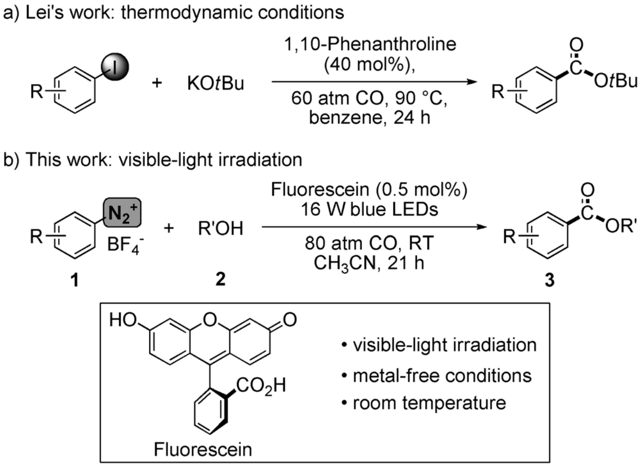
Abstract: *The first radical alkoxycarboxylation of aryldiazonium salts using CO gas through visible-light-induced photoredox catalysis (16 W blue LEDs) has been developed. This reaction is entirely metal-free, is carried out at room temperature with a low loading of an organic dye as a photocatalyst (0.5 mol %), and provides a wide range of arylcarboxylic acid esters in high yields. Importantly, this photocatalytic system can be successfully extended to other carboxylation reactions.*

Over the last century, the ester moiety has emerged as an important structural unit in a great number of natural isolates and synthetic materials. Not surprisingly, ester synthesis has become one of the most important and fundamental tasks in chemical science, and many elegant methods have been established in both industrial and academic settings. One approach towards efficient ester synthesis is direct alkoxycarbonylation utilizing carbon monoxide (CO). This approach relies on the development of a wide range of robust metal catalysts which elegantly combine many central transition metals (i.e., palladium, ruthenium, rhodium, cobalt, etc.) and diverse organic ligands (mainly organic phosphine, nitrogen and carbene compounds).[1] In the last two decades, radical alkoxycarbonylations[2] have attracted the attention of the synthetic community because of their mild reaction conditions (ambient temperature). In the 1990s, the groups of Watanabe[3] and Miyaura[4] reported two isolated examples of alkoxycarbonylation reactions of aliphatic iodides promoted by photoirradiation in the presence of metal catalysts such as platinum, rhenium, osmium, ruthenium, manganese, and cobalt complexes. Recently, Ryu[5] and co-workers have made substantial contributions to photocatalysis methodology with mechanistic insights into the role of acyl radicals. Not only have they significantly expanded the scope of organic halides which can react with palladium and manganese catalysts, but they have also identified a reasonable reaction mechanism of these metal-catalyzed radical alkoxycarbonylations. Despite these advances, the vast majority of room-temperature radical alkoxycarbonylations are generally limited to highly reactive aliphatic iodides. In addition, high-energy light sources such as 200 W high-pressure mercury lamps or 500 W xenon lamps are necessary to efficiently promote the generation of reactive radicals. Therefore, radical alkoxycarbonylation has yet to reach its full potential[6] with respect to diversity of substrate and product, as well as energy economy.

Interest in transition-metal-free cross-coupling reactions of aryl halides[7,8] has increased since the first unexpected finding from the group of Itami in 2008.[8a] Shortly thereafter, Lei and co-workers[9] disclosed the first example of radical alkoxycarbonylation of aryl iodides in the absence of a transition-metal catalyst, thereby providing a range of aromatic carboxylic *tert*-butyl esters under thermodynamic conditions (Scheme 1 a). In this transformation, potassium *tert*-butoxide was critical, thus acting as a reducing agent and the ester alkoxy component. The organocatalyst 1,10-phenanthroline (40 mol %) was also necessary to facilitate the generation of aryl radicals from the organic halides. Although this work represents an impressive advance, the development of a general alkoxycarbonylation process which involves aryl radicals and diverse alcohol components at room temperature remains an important goal.



Scheme 1. Radical alkoxycarbonylation for aryl carboxylic acid esters.

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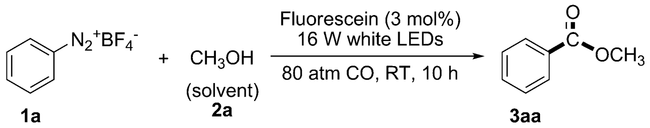
Since 2008, visible-light-induced photocatalysis has been a powerful platform for the development of novel radical synthetic methods because of the natural abundance of visible light, thus inspiring potential applications and sustainability.[10] By using these methods, readily available, reactive arenediazonium salts[11] have been widely utilized as a convenient aryl radical source.[12] As a result, many unusual transformations of these reagents have been carried out by photocatalysis[13] or the combination of photocatalysis with palladium[14] or gold catalysis.[15] Importantly, within the realm of photoredox catalysis, some organic dyes have been identified as efficient visible-light catalysts capable of promoting numerous radical reactions under metal-free conditions.[16] Continuing our work on visible-light-induced photocatalysis,[13d,17] we herein report a catalytic photoredox radical alkoxycarbonylation of aryldiazonium salts using a low loading of an organic photosensitizer and low-energy visible light (Scheme 1b). By using this method, aryl carboxylic acids esters having a wide variety of aliphatic alcohol components can be easily obtained in high yields and with high selectivities under metal-free and room-temperature conditions.

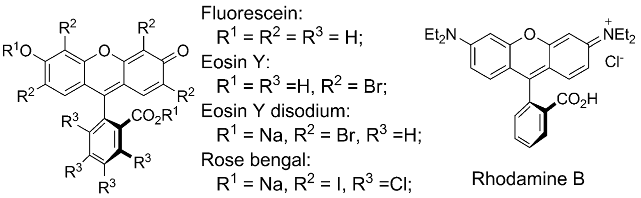
Initially, we examined this radical alkoxycarbonylation reaction using phenyl diazonium tetrafluoroborate (**1a**, 0.2 M in methanol) as a model substrate in the presence of 3 mol % of fluorescein as a photocatalyst under irradiation with 16 W white LED and a CO pressure of 80 atm. To our delight, the anticipated reaction did indeed proceed smoothly, thus delivering the desired product, benzoyl methyl ester **3aa**, in high yield (Table 1, entry 1). The results of control experiments showed that the reaction efficiency decreased noticeably in the absence of either light irradiation or a photosensitizer (entries 2 and 3). In addition to fluorescein, other organic dyes such as eosin Y, its sodium salt, rose Bengal, and rhodamine B were also successful in accelerating this alkoxycarbonylation process, albeit with somewhat lower efficiencies (entries 4–7). Other reaction parameters such as the substrate concentration, the CO pressure, and the visible-light source were investigated.[18] As a result, the yield improved to 79 % when the reaction was performed in dilute methanol under irradiation by 16 W blue LEDs instead of white light (entry 10). Notably, the loading of the photocatalyst can be reduced to 0.5 mol % and gave the product in a better yield by extending the reaction time (entry 11).

Table 1: Optimization of reaction conditions.



Entry	Variation from the initial conditions[a]	Yield [%][b]
1	none	76
2	without light	3
3	without Fluorescein	22
4	Eosin Y, instead of Fluorescein	66
5	Eosin Y disodium, instead of Fluorescein	67
6	Rose bengal, instead of Fluorescein	46
7	Rhodamine B, instead of Fluorescein	63
8	60 atm of CO	62
9	0.1 M in CH_3OH	78
10	16 W blue LEDs, 0.1 M in CH_3OH	79
11	*0.5 mol% Fluorescein, 16 W blue LEDs 0.1 M in CH_3OH, 21 h*	*81*

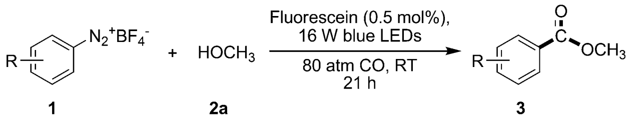
[a] Initial conditions: **1a** (0.2 mmol, 0.1 M) and Fluorescein (0.006 mmol, 3 mol%) were added into CH_3OH. After flushing the autoclave three times with CO, a pressure of 80 atm CO was set and the reaction was performed under the irradiation of 16 W white LEDs for 10 h at RT. [b] Determined by GC analysis using dimethyl terephthalate as an internal standard.

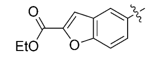
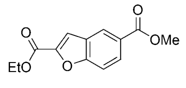


With the optimal reaction conditions in hand, we probed the scope of this photocatalytic radical alkoxycarbonylation reaction. As summarized in Table 2, a series of aryldiazonium salts was successfully applied to this reaction. Variation of the electronic properties of substituents on the benzene ring had little influence on the catalytic efficiency. Both electron-donating groups (MeO, PhO, Me, and OH) and electron-withdrawing groups (Br, SO_3^-, CN, NO_2, and CO_2Et) were successfully introduced at the *para* position of the benzene ring, thus delivering the corresponding substituted benzoyl methyl esters in good yields (entries 2–10). Additionally, variation of the postion of the substituent on the benzene ring of the diazonium salt was also explored. For example, when 3-nitro- and 2-iodophenyl diazonium salts were used as substrates, the corresponding 3-nitro- and 2-iodobenzoyl methyl esters were conveniently formed with 60 and 50 % yields, respectively. Significantly, the sensitive functional groups in traditional transition-metal-catalyzed alkoxycarbonylation, such as bromo and iodo, were compatible with this process, thus allowing subsequent transformation by cross-coupling technologies.[19] This compatibility demonstrated the complementarity of this radical route with numerous other palladium-catalyzed alkoxycarboxylation protocols. In addition, this photocatalytic radical alkoxycarbonylation tolerated heteroaryl diazonium salts. For example, the 2-(ethoxycarbonyl)benzofuran derivative **1m** was converted into the corresponding ester product **3am** in good yield (entry 13).

Next, we turned our attention to the generality of the alcohol coupling partner of this transformation. As highlighted in Figure 1, a broad range of aliphatic alcohols readily participate in this radical alkoxycarboxylation reaction, regardless of the steric bulk of the substituents around the reactive hydroxy group (**3bb–bh**). For example, when sterically hindered isopropyl, cyclohexyl, and *tert*-butyl alcohols were employed, the corresponding esters were obtained in moderate to good yields (**3be–bg**). Notably, a wide range of functional groups was compatible with these photoredox catalysis conditions, including ether, free hydroxy, chloride, alkyne, and alkene moieties. Through this approach, a series of functionalized arylcarboxyl acid esters was synthesized with good efficiency and selectivity (**3bi–bm**). Notably, terminal alkenes and alkynes, which are known to be good

Table 2: Radical alkoxycarbonylation of different aryl diazonium salts.[a]



Entry	Aryl source	Product	Yield [%][b]
1	**1a:** C_6H_5	**3aa**	81[c]
2	**1b:** 4-$CH_3OC_6H_5$	**3ab**	75
3	**1c:** 4-$PhOC_6H_5$	**3ac**	80
4[d]	**1d:** 4-OH-C_6H_5	**3ad**	73
5	**1e:** 4-$CH_3C_6H_5$	**3ae**	62
6	**1f:** 4-BrC_6H_5	**3af**	64
7[e]	**1g:** 4-(SO_3^-)-C_6H_5	**3ag**	80
8[f]	**1h:** 4-CNC_6H_5	**3ah**	68
9[f]	**1i:** 4-$NO_2C_6H_5$	**3ai**	65
10	**1j:** 4-(CO_2Et)-C_6H_5	**3aj**	66
11[f]	**1k:** 3-$NO_2C_6H_5$	**3ak**	60
12[f]	**1l:** 2-IC_6H_3	**3al**	50
13[f]	 **1m**	 **3am**	58

[a] Unless otherwise noted, the reaction was carried out on a scale of 0.4 mmol under the standard reaction conditions as given in Table 1, entry 11. [b] Yield of the isolated products. [c] Determined by GC analysis using dimethyl terephthalate as an internal standard. [d] EtOH was used as the solvent, and the product is the corresponding ethyl ester. [e] 4-Diazophenylsulfonic acid was used as the substrate. [f] A mixture of 0.2 mL of MeOH and 3.8 mL of CH_3CN was used as the solvent.

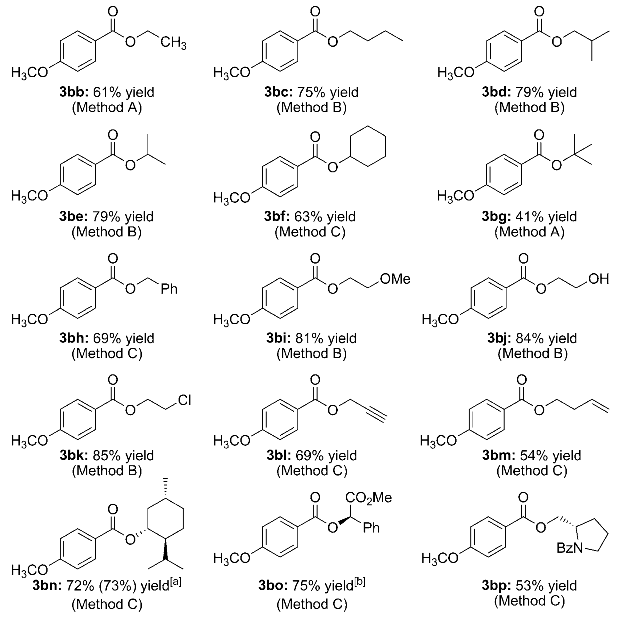
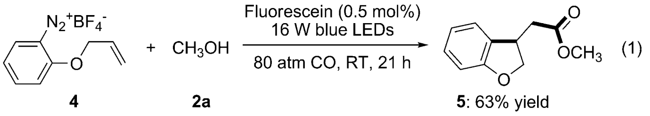
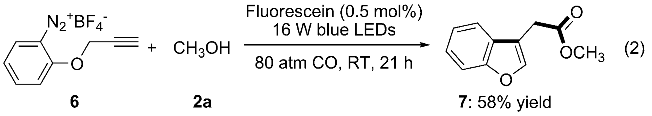

3bb: 61% yield (Method A)
3bc: 75% yield (Method B)
3bd: 79% yield (Method B)
3be: 79% yield (Method B)
3bf: 63% yield (Method C)
3bg: 41% yield (Method A)
3bh: 69% yield (Method C)
3bi: 81% yield (Method B)
3bj: 84% yield (Method B)
3bk: 85% yield (Method B)
3bl: 69% yield (Method C)
3bm: 54% yield (Method C)
3bn: 72% (73%) yield[a] (Method C)
3bo: 75% yield[b] (Method C)
3bp: 53% yield (Method C)

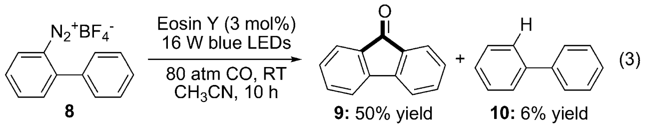
Figure 1. Generality of alcohols. Method A: **1b** (0.4 mmol) in 4.0 mL corresponding alcohol. Method B: **1b** (0.4 mmol) and 0.2 mL alcohol in 3.8 mL CH_3CN. Method C: **1b** (0.4 mmol) and 2 equivalents alcohol in 4.0 mL CH_3CN. Yield is that of the isolated product. [a] Yield of 6 mmol scale reaction given within parentheses. [b] Alcohol **3o**: 98% *ee*; the product **3bo**: 98% *ee*.

acceptors in radical reactions, remained intact, thereby indicating the high selectivity for CO in this process. Significantly, the success of this photocatalytic radical carboxylation protocol extended to chiral alcohols. For example, when the natural isolate (−)-menthol (**2n**), methyl D-(−)-mandelate (**2o**), and *N*-benzoyl L-(+)-prolinol (**2p**) were subjected to standard photocatalytic reaction conditions (Method C), the resultant ester products (**3bn**–**bp**) were obtained in satisfactory yields. Notably, a gram-scale reaction with 6 mmol of the 4-methoxybenzenediazonium tetrafluoroborate (**1b**) and 2 equivalents of **2n** was implemented under the visible-light photoredox catalysis conditions and it proceeded in a similar efficiency, thus providing the corresponding ester product **3bn** in 73% yield.

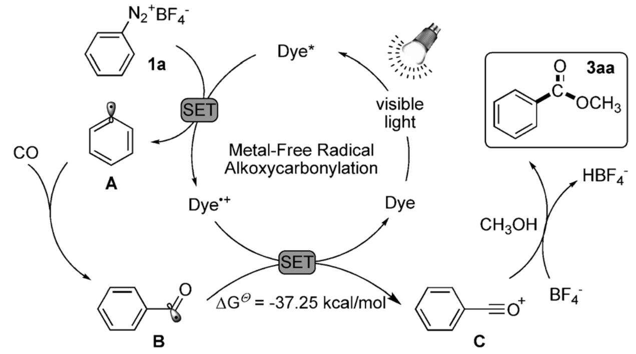
Moreover, this visible-light-induced photocatalysis strategy can be further applied to other radical carboxylation reactions. For example, when *ortho*-allyl-substituted benzenediazonium **4** and *ortho*-propargyl-substituted benzenediazonium **6** were subjected to the standard reaction conditions, methyl 2-(2,3-dihydrobenzofuran-3-yl)acetate (**5**) and methyl 2-(benzofuran-3-yl)acetate (**7**), respectively, were obtained in good yields through a radical addition/alkoxycarboxylation sequence [Eq. (1) and (2)]. Beyond radical alkoxycarboxylation, the use of the (1,1′-biphenyl)-2-diazonium salt **8** resulted in 9*H*-fluoren-9-one (**9**) in moderate yield with minimal formation of the competitive byproduct **10** [Eq. (3)]. We believe that our findings will open a new avenue for novel reaction design utilizing visible-light-induced photocatalyzed radical carboxylation protocols.







As shown in Scheme 2, a plausible mechanism is proposed using radical methoxycarboxylation of benzenediazonium salt (**1a**) as an example of this novel photocatalytic process. The initial single-electron reduction of the substrate with the excited state of the Dye photocatalyst to generate the phenyl radical **A** and simultaneously deliver the oxidized Dye radical cation (Dye$^{\bullet+}$) has been elegantly demonstrated in previous reports. Trapping of a CO molecule by this reactive intermediate forms the new benzoyl radical **B**. Further oxidation of **B** by Dye$^{\bullet+}$ results in the benzylidyneoxonium **C**, thus completing the visible-light-induced photoredox catalysis cycle. Finally, electronic trapping of **C** by methanol gives the desired **3aa** with concomitant generation of fluoroboric acid. The byproduct of the radical carbonylation is the corresponding arene, which was generated through the



Scheme 2. Plausible reaction mechanism. Dye = fluorescein.

abstraction of hydrogen by the aryl radical.[20] Control experiments indicated that high CO pressure could significantly inhibit the formation of the byproduct. In addition, biphenyl cannot be detected even with increasing amounts of fluorescein (10 mol %, 50 mol %, 100 mol %).[21] It means that in the presence of a certain amount of CO, phenyl radicals can be easily and efficiently converted into acyl radicals.[22]

In contrast, we postulated that Dye$^{\cdot+}$ is capable of oxidizing **B** to **C**. The DFT calculations indicated that the Gibbs free energy of the oxidation of a phenyl radical to phenyl cation by Dye$^{\cdot+}$ is 0.14 kcal mol^{-1} while the energy for the formation of **C** is -37.25 kcal mol^{-1}. This data means that the oxidation of benzoyl radical is much more favorable.[23] Perhaps more importantly, preliminary results of a radical quenching experiment with 2,2,6,6-tetramethylpiperidinooxy (TEMPO) confirmed that the reaction proceeds by a radical mechanism. Importantly, the fact that the enantiopurities of chiral alcohols remained unchanged after this transformation (i.e., **3bo**) shows that this process has no influence on the chiral center of the alcohol. Accordingly, it is reasonable that the hydroxy group of the alcohol functions as the nucleophile which attacks **C** to afford the ester product.

In conclusion, by using visible-light-induced photoredox catalysis, we have developed the first radical alkoxycarboxylation of aryldiazonium salts using CO gas. This reaction was entirely metal free and was carried out at room temperature with low loading of the organic photocatalyst to deliver a range of esters using various aryl carboxylic acid and alcohol partners in moderate to good yields. Importantly, the application of this protocol to chiral alcohols has also been proven to be feasible, including natural isolates such as (−)-menthol and their derivatives such as methyl D-(−)-mandelate and *N*-benzoyl L-(+)-prolinol. Further studies focused on expanding on the success of this visible-light-induced photocatalytic carboxylation are currently underway, and the results will be reported in the near future.

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