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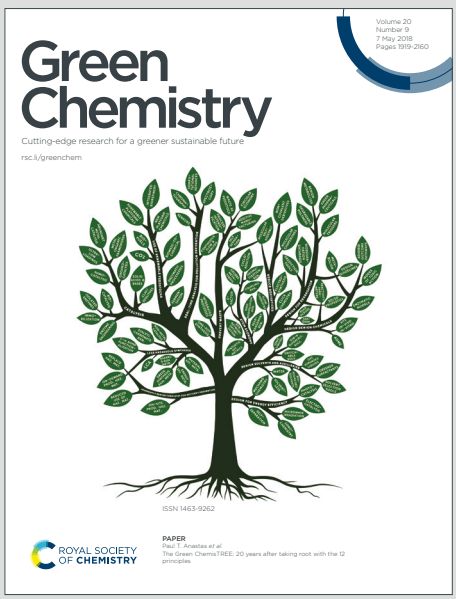

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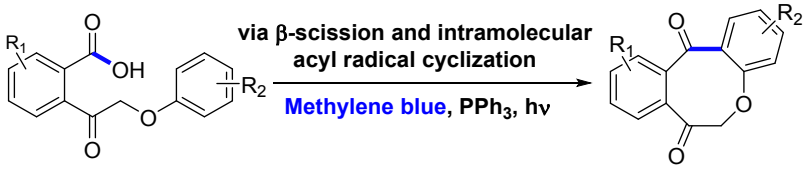

- Metal-free
- Mild conditions
- Methylene blue as photocatalyst
- Carboxylic acids as substrate

33 examples
49%-83%

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ARTICLE

Synthesis of Dibenzocycloketones by Acyl Radical Cyclization from Aromatic Carboxylic Acids via Methylene Blue as Photocatalyst

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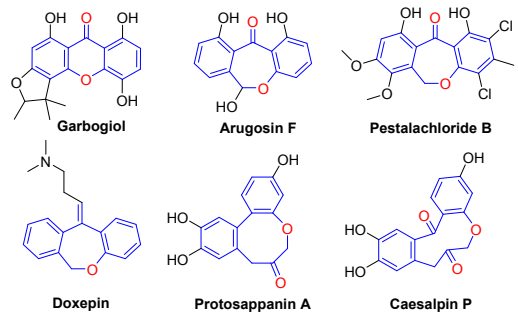
An efficient intramolecular radical cyclization reaction via photoredox catalysis was developed for synthesis of dibenzocycloketone derivatives by using methylene blue as photosensitizer proceeds. This strategy could be widely used to synthesize large heterocycles by the unique reactivity of phosphoranyl radicals formed by the polar/SET crossover between aromatic carboxylic acid and phosphine radical cation. Attractive features of this process include generation of acyl radical by inexpensive and metal-free photocatalyst, which effectively undergoes cyclization process.

Introduction

Dibenzocycloketone derivatives are ubiquitous structural motifs found in natural products, biologically active molecules, as well as functional materials (**Scheme 1**).[1] More specifically, with the feature of anti-HIV-1,[2] anti-cancer[3] and anti-inflammatory,[4] the study of dibenzocycloketone derivatives has become a promising field of organic chemistry.



Scheme 1. Dibenzocyclocketones natural products and drugs.

Therefore, there are a few synthetic strategies available for the preparation of dibenzocycloketone. In general, this kind of compounds is synthesized through Friedel-Crafts acylation via electrophilic aromatic substitution catalyzed by Lewis-acid or Brønsted-acid.[5] However, excess stoichiometric acid catalyst was required in this reaction because of forming complexation between the ketone product and the acid catalyst, which resulted in the waste of the catalyst and the production of acidic wastewater in the process of post-treatment.[6] In this circumstance, cross-couplings involving C–H bond activation catalyzed by transition-metal has been emerged as a good method for the construction of a carbon–carbon skeleton.[7] Nevertheless, transition metal catalysis requires the substrate with a suitable structure for connecting the metal center and reaction site, which limits the selection range of the substrate.[8] Moreover, there are reports of other methods of building this skeleton structure such as intramolecular Minisci acylation,[9] intramolecular dehydrogenative cyclization,[10] trifluorotoluene hydrodefluorination reaction,[11] and intramolecular homolytic acylation by corresponding selenoesters.[12] Despite of the advances in the synthesis of dibenzocycloketone derivatives, these methods still suffered from the need for harsh reaction conditions, the limited structural diversity and the functional group tolerability.

Carboxylic acids is attractive and widely by using synthon to make acyl radical, because carboxylic acids as starting materials are not only abundant and inexpensive but also readily available in great structural diversity. [13] In recent years, the novel application of visible-light photoredox catalysis to organic synthesis has emerged as an efficient tool, and novel strategies targeting carboxylic acids as building blocks have been developed.[14] In particular, it has attracted attention as an ideal way to generate radicals from decarboxylation of carboxylic acids by photoredox catalysis.[15] At present, many valuable transformations of this carboxylic acid mode were reported. In 2015, Bergonzini and co-workers reported carboxylic acids were used to generate acyl radicals via single-electron transfer (SET) by means of visible-light photoredox catalysis (**Scheme 2A, a**).[16] In 2017, Zhu and co-workers reported the first photocatalytic intramolecular acyl radical coupling for constructing carbon−carbon bond using a readily available carboxylic acids as the acyl source via photoredox catalysis, which expanded new applications of carboxylic acids in organic synthesis(**Scheme 2A, b**).[17] These methods can afford the acyl radical by a single electron reduction of a mixed acid anhydride formed in situ

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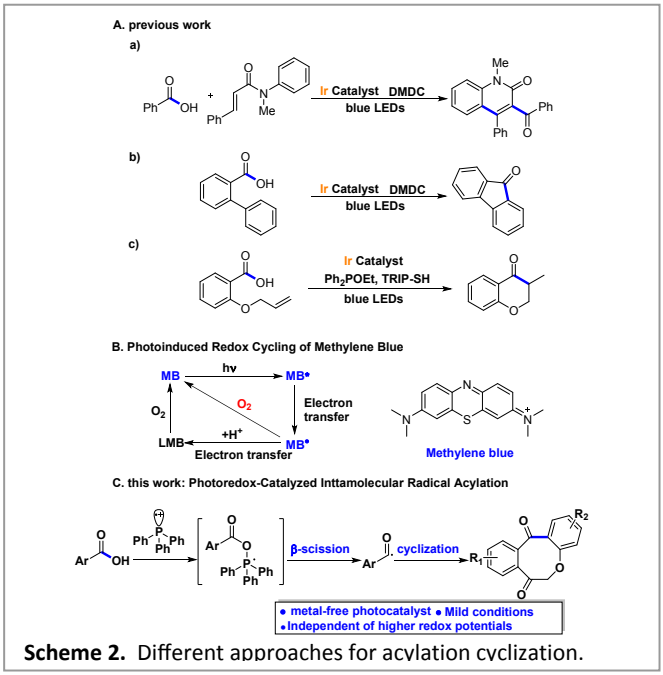
from an aromatic acid by a highly reducing iridium photocatalyst. In 2018, Doyle and colleagues reported the Intramolecular acyl radical cyclizations of carboxylic acids by using β-scission of phosphoranyl radicals to produce acyl radicals via expensive iridium photocatalyst (**Scheme 2A, c**).[18] This method was independent of higher substrate redox potentials. It is a promising advancement in photocatalytic strategies. Therefore, the development of effective and inexpensive strategies for direct preparation of dibenzocycloketone from carboxylic acid will be a valuable goal.

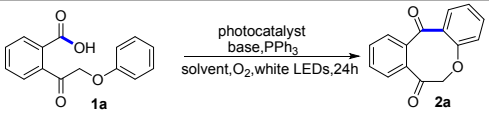
Methylene blue (MB) has seen as an organic photosensitizer in diverse biological and medical applications.[19] Since MB is a member of the thiazine dye family having a triplet state, the triplet sensitizer MB and the substrate interact to form a radical, or in the case of oxygen, produce singlet oxygen. Flash photolysis studies have indicated that the photoreduction occurs by electron transfer (ET) steps, producing a semireduced MB radical (MB•) as an intermediate (**Scheme 2B**).[20] With this knowledge, our aim is to use methylene blue ($E_{1/2}^{ox}$ = +1.13 V versus SCE (Saturated Calomel Electrode))[21] as photocatalyst to develop an effective acyl intramolecular cyclization ， which would undergo single-electron transfer (SET) process with triphenylphosphine (E_{ox} = +0.98 versus SCE)[22] to afford a phosphine radical cation under visible light.



Scheme 2. Different approaches for acylation cyclization.

To our knowledge， intramolecular acyl radical reactions is widely used in the synthesis of five- and six-membered dibenzocycloketones, while the synthesis of seven- and eight-membered dibenzocycloketones is rare, especially the eight-membered ring.[23] We wondered if carboxylic acid substrates would produce acyl radical, followed formation of dibenzocycloketones with more complex and diverse structural backbones by intramolecular radical cyclization. Herein, we report a practical and simple process of acyl radical cyclization using MB as a photocatalyst, carboxylic acid derivatives as an acyl radical source by tetravalent phosphinecentered radicals to prepare dibenzocycloketone derivatives (**Scheme 2C**). In this process phosphoranyl radicals could be accessed via nucleophilic addition of an acid to a phosphine radical cation generated by photoinduced single-electron transfer.[24] The phosphoranyl radical could undergo β-scission to form a strong P–O double bond and acyl radical and then undergo intramolecular acyl radical cyclization.[25] In addition, we anticipated that this strategy would complete the direct conversion to the corresponding acyl radical, independent of substrate-dependent redox potential and functional group properties. Ultimately, this method could be applied to construct large heterocyclic compounds by intramolecular acylation reaction.

Table 1. Optimization of reaction conditions[a]



entry	catalyst	base	solvent	yield (%)[b]
1	Methylene blue	2,6-lutidine	DMA	64
2	Eosin Y	2,6-lutidine	DMA	0
3	Fluorescein	2,6-lutidine	DMA	0
4	Rhodmine B	2,6-lutidine	DMA	0
5	$[Ir(dFCF_3ppy)_2dtbbpy]PF_6$	2,6-lutidine	DMA	50
6	Methylene blue	K_2HPO_4	DMA	38
7	Methylene blue	Cs_2CO_3	DMA	26
8	Methylene blue	DABCO	DMA	39
9	Methylene blue	TMEDA	DMA	42
10	Methylene blue	**2,4,6-collidine**	**DMA**	**76**,70[c],0[d,e]
11	Methylene blue	2,4,6-collidine	DMF	67
12	Methylene blue	2,4,6-collidine	DMSO	61
13	Methylene blue	2,4,6-collidine	CH_3CN/H_2O	42
14	Methylene blue	2,4,6-collidine	DCM/H_2O	45
15	--	2,4,6-collidine	DMA	0

[a] Reaction conditions: **1a** (0.2 mmol), photocatalyst (2.0 mol%), PPh_3 (1.5 eq.) and base (1.0 eq.) in solvent 2 ml, irradiation with white light LEDs at 25 °C for 24 h, the reaction completed (monitored by TLC). [b] isolated yield by flash column chromatography. [c] Control experiment Ph_2POEt instead of PPh_3. [d] Control experiment without white LEDs. [e] Control experiment without PPh_3.

Results and discussion

According to previous studies on the photoredox catalysis, the conditions for the reaction were investigated by used 2-(2-phenoxyacetyl)benzoic acid (**1a**) as model substrate, and the experimental results were summarized in **Table 1**. As a preliminary experiment, **1a** as the substrate was irradiated

under visible light from a white LEDs in DMA at room temperature in presence of 2,6-lutidine and PPh_3 with methylene blue as photocatalyst. The reaction gave desired product **2a** in a 64% yield in 24 h (**Table 1**, entry 1), showing that this intramolecular radical cyclization is feasible. This experimental result encouraged us to study the reaction conditions by optimizing photocatalysts, bases and solvents.

Firstly, the photocatalyst as a crucial factor was investigated. Dye photocatalyst was used including Eosin Y ($E_{1/2}^{ox}$ = +0.76 V versus SCE), Fluorescein ($E_{1/2}^{ox}$ = +0.87 V versus SCE) and Rhodmine B ($E_{1/2}^{ox}$ = +0.91 V versus SCE), no product was found (**Table 1**, entries 2-4). While $[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ ($E_{1/2}^{ox}$ = +0.97 V versus SCE) was used as photocatalyst, the reaction only gave a 50% yield (**Table 1**, entry 5). Next, bases including organic bases and inorganic bases were also been screened. The use of inorganic bases K_2HPO_4 and Cs_2CO_3 gave relatively low yields (38% and 26%) of **2a** (**Table 1**, entries 6-7). The use of organic bases such as triethylenediamine (DABCO) and tetramethylethylenediamine (TMEDA) gave relatively low yields (39% and 42%) of **2a** (**Table 1**, entries 8-9). Use of 2,4,6-collidine as the base in place of 2,6-lutidine gave a good yield of 76% (**Table 1**, entry 10). Some aprotic solvents were also screened as reaction solvents. Polar aprotic solvents such as DMF and DMSO gave good yields in 67% and 61%, respectively (**Table 1**, entries 11-12). The use of CH_3CN/H_2O (v/v=4:1) gave a low yield in 42% (**Table 1**, entry 13). The use of DCM/H_2O (v/v=4:1) gave also a low yield in 45% (**Table 1**, entry 14). When Ph_2POEt was used instead of PPh_3, the product yield was slightly reduced (**Table 1**, entry 10[c]). There was not desired product was detected in the control experiment without PPh_3 or the light source or the photocatalyst (**Table 1**, entries 10[d,e] and 15), which indicated PPh_3, the light source and the photocatalyst were essential in the reaction.

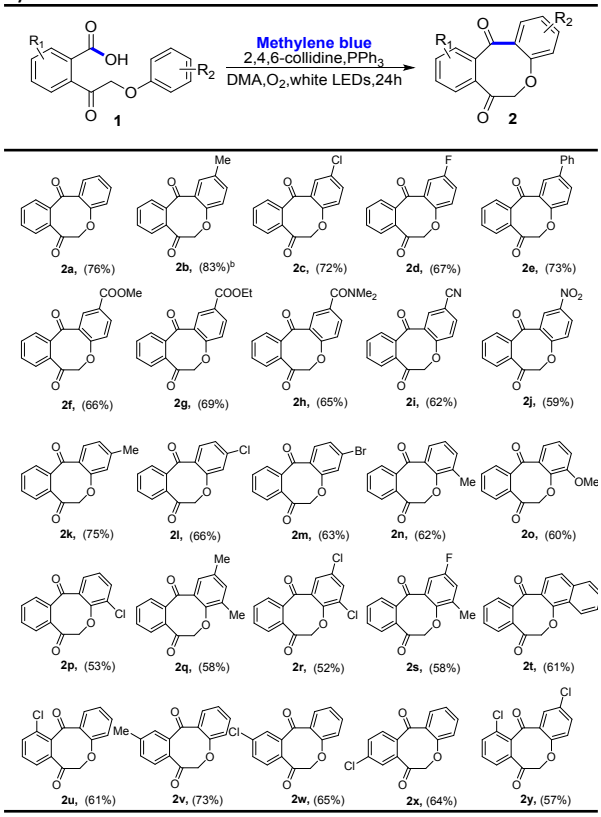
Based on the above results, optimized conditions of the intramolecular radical cyclization were 2.0 mol% MB as the photocatalyst, 1.5 equiv. of PPh_3 as additive, 1.0 equiv. of 2,4,6-collidine as base in DMA under irradiation visible light from white LEDs at room temperature.

Having conditions optimized, we investigated a variety of different carboxylic acids to expand the scope of the reaction. Representative examples were shown in **Table 2**.

First, the compound **1a** without substituent group gave desired product **2a** with 76% yield. Next, based on the characteristics of the intramolecular acylation reaction, we focus on the expansion of acylated aromatic ring (phenol part). The substituents on para-position of the phenolic hydroxyl group afforded the desired products **2b**-**2j** in medium to good yields (59–83%). By contrast, the electron-donating substituent (-Me, **2b**, 83%) was more favorable to the reaction compared with electron-drawing substituent (-NO_2, **2j**, 59%). The substituents (-Me, -Cl and -Br) on meta-position of the phenolic hydroxyl group also gave the desired products **2k**, **2l** and **2m** in medium to good yields (63–75%). However, no regioisomer formation was observed in the reaction. This may be due to the fact that the aromatic radical cyclization process rarely exhibits regioselectivity. While the substituents were at the ortho position, the products (**2n**, **2o** and **2p**) were only obtained in moderate yields (53–62%). Compared with the above experimental results such as **2n** and **2b**, this reduction of yields may be caused by the steric-hindrance effect. The carboxylic acids with two substituents (**2q**, **2r** and **2s**) also participated in the reaction providing similarly moderate yields (52–58%). Furthermore, the substrate containing naphthalene (**2t**) also produced the desired products in 61% of yields. Substituents on the aromatic moiety of carboxylic acids were also tolerated. Compared to the yields of **2u**, **2w** and **2x**, the substituent position showed little influence on the reaction efficiency (61%, 65% and 64%, respectively). Compared with the electron-rich group –Me (**2v**), electron-deficient group –Cl (**2w**) on the meta position of the carboxyl showed an obviously low reaction activity and yield (73% and 65%, respectively). Finally, the substituents on different aromatic rings also gave the target product **2y** in 51% of yields.

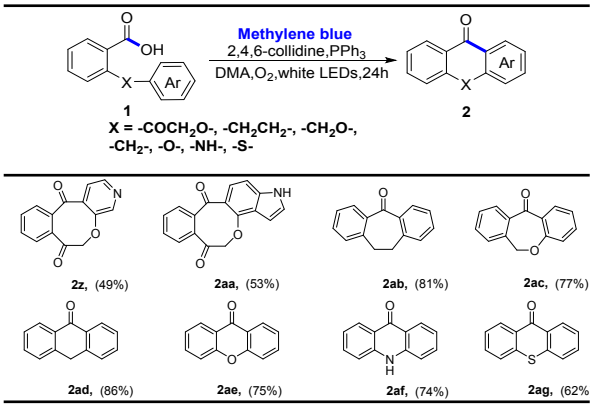
Next, we investigated the scope of heteroaromatic substrates. 3-Position of pyridine (**2z**) was tested and resulted in promising yield (49%). It was noteworthy that 2- and 4- positions of the pyridine ring gave no products. This phenomenon may be due to the electron-deficient effect of the 2- and 4-positions relative to the 3-position (**2z**).[9a] Moreover, heterocyclic carboxylic acid with the indole moiety also participated in the process with

Table 2. Substrates scope of the intramolecular radical cyclization reaction[a]



[a] Reaction conditions: Compound **1** (0.2 mmol), methylene blue (2.0 mol%), PPh_3 (1.5 eq.) and 2,4,6-collidine (1.0 eq.) in DMA 2 ml, irradiation with white light LEDs at 25 °C for 24 h, the reaction completed (monitored by TLC). Isolated yield after purification by column chromatography. [b] The reaction was carried out on a 4 mmol gram-scale with under standard condition (63% yield, 0.64g).

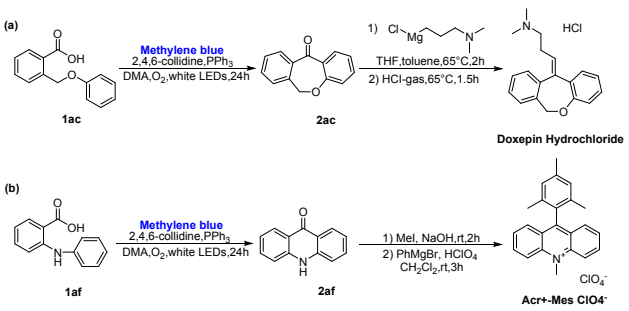
Table 3. Substrates scope of heteroaromatic substrates and other linkers[a]



[a] Reaction conditions: Compound **1** (0.2 mmol), methylene blue (2.0 mol%), PPh_3 (1.5 eq.) and 2,4,6-collidine (1.0 eq.) in DMA 2 ml, irradiation with white light LEDs at 25 °C for 24 h, the reaction completed (monitored by TLC). Isolated yield after purification by column chromatography.

medium yield of product **2aa** (53%). Finally, we directed our attention to delineating the scope of other linkers than alfa-keto ethers. Pleasantly, we found that this strategy could be applied to other linker substrates to readily build dibenzocycloketone skeletons (**2ab-2ag**) in medium to good yields (62–86%). The carbon atom linkers (**2ab**, 81%; **2ad**, 86%) had higher yields compared to the heteroatom linkers (**2ac**, 77%; **2ae**, 75%; **2af**, 74%; **2ag**, 62%). We compared the ^{1}H NMR data of known compounds with previous studies, proving the correct assignment of the proposed dibenocycloketone structure.[26]

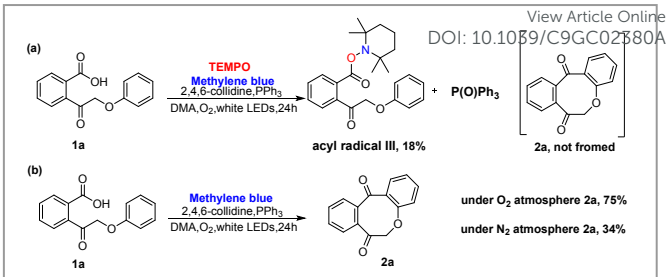
A further demonstration of the value of this plan was tested



Scheme 3. Preparation of Doxepin Hydrochloride and 9-Mesityl-10-methylacridinium Perchlorate (Acr$^+$-Mes

by the preparation of tricyclic antidepressants Doxepin Hydrochloride, which was widely used in the treatment of chronicpain and depression (**Scheme 3a**).[27] We also synthesized 9-Mesityl-10-methylacridinium Perchlorate (Acr$^+$-Mes ClO_4^-) in a similar way, which was a dual sensitizer with the capacity of efficient singlet oxygen formation and electron-transfer reaction (**Scheme 3b**).[28]

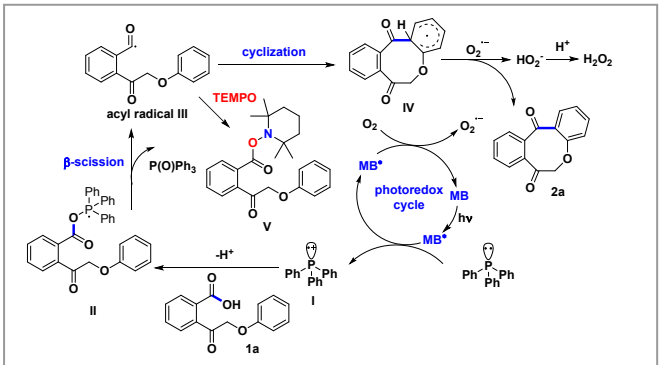
Two control experiments (shown in **Scheme 4**) were conducted to insight into the acylation cyclization process. When 2.0 equiv. of TEMPO was added as a radical quencher, the reaction under standard conditions did not give desired product. However, the formation of Acyl-TEMPO adduct and the by-product triphenylphosphine oxide were observed in low yield



Scheme 4. Mechanism research.

(**Scheme 4a**). The above experiment implied the involvement of a radical species in this process. When the reaction was carried out under O_2 atmosphere, the reaction effect was hardly affected. However, when the reaction is in an N_2 atmosphere, the reaction is inhibited (**Scheme 4b**). This showed that an appropriate amount of oxygen is necessary in the reaction system.

Based on the above experiments, a plausible mechanism for



Scheme 5. A Plausible Mechanism.

the intramolecular radical cyclization is proposed in **Scheme 5**. According to the literature reported, the intramolecular radical cyclization tends to the ortho-position of aryl C–H component compared to ipso position of alkyl phenol.[29] The photocatalyst **MB** is excited to generate **MB*** under irradiation of white light. Next, a SET process of the triphenylphosphine (**PPh_3**) is caused by **MB*** to give **MB•** and phosphine radical cation **I**. Polar nucleophilic addition to the cation with carboxylic acid would generate phosphoranyl radical **II**, which upon β-scission would generate the corresponding acyl radical **III** and triphenylphosphine oxide. If excess TEMPO is add in the reaction, the acyl radical **III** can be trapped to obtain the compound **V**. Acyl radical **III** undergoes intramolecular addition to deliver the intermediate **IV**. The reduced **MB•** was then oxidized by the residue oxygen from the air in the reaction tube to regenerate the ground state **MB** to complete the catalytic cycle. At the same time, the generated **$O_2^{\bullet-}$** abstracted a hydrogen atom from **IV** to provide **2a** and **HO_2^-**. Finally, **HO_2^-** anion was protonated to form **H_2O_2**.

Conclusions

In conclusion, a convenient acyl radical cyclization reaction is developed to synthesize dibenzocycloketone derivatives via photoredox catalysis under irradiation of white light. Our research shows that sensitizers using organic dyes as

photocatalysts can use low-cost materials that are environmentally friendly in line with the concept of green chemistry. Moreover, this method could be extended to the gram-scale due to good functional-group compatibility and no harsh condition. Finally, based on some experimental results and literatures, a plausible mechanism for the intramolecular cyclization of acyl radical is proposed. The further reactivity and applicability of acyl radicals for the synthesis of other heterocyclic structures by photoredox catalyzed transformation is currently underway in our laboratory.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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