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Visible Light Induced Aerobic Epoxidation of α,β-Unsaturated Ketones Mediated by Amidines

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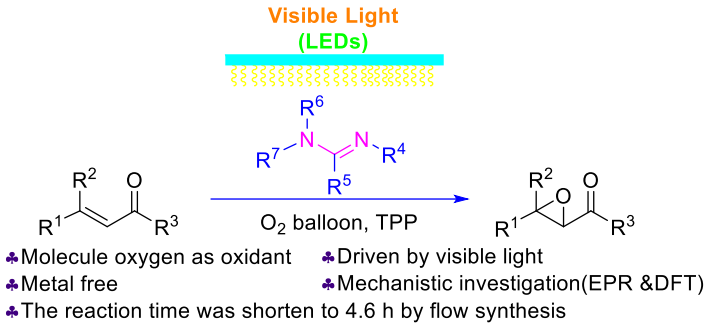
Supporting Information Placeholder



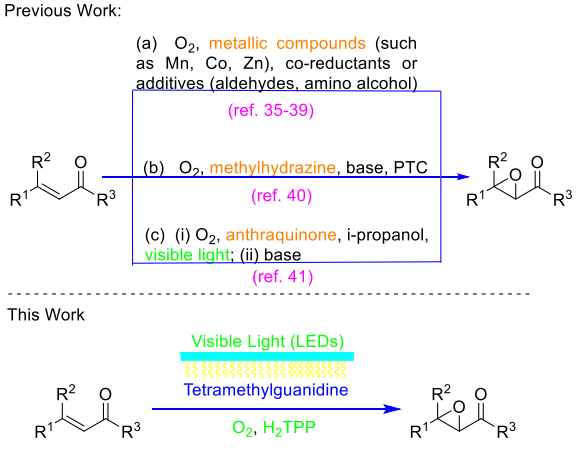
ABSTRACT: An aerobic photoepoxidation of α,β-unsaturated ketones driven by visible light in the presence of tetramethylguanidine (**3b**), tetraphenylporphine (H_2TPP) and molecular oxygen under mild conditions was revealed. The corresponding α,β-epoxy ketones were obtained in yields of up to 94% in 96 h. The reaction time was shortened to 4.6 h by flow synthesis. The mechanism related to singlet oxygen was supported by experiments and density functional theory (DFT) calculations.

■ INTRODUCTION

Visible light driven photocatalysis is a promising route for 21st century organic chemistry and has attracted much attentions in recent years[1-4]. Epoxy ketones are among the most versatile building blocks in organic synthesis and provide intermediates for natural products or biologically active compounds[5,6], such as manumycin A[7,8], epoxyquinol[9], panepophenanthrin[10] and nisamycin[11]. This wide range of interesting applications has promoted the development of methodologies for the synthesis of epoxy ketones[12-18]. Catalytic epoxidation using molecular oxygen as oxidant[19-25] is an attractive and potential method, which is inexpensive, convenient and environmentally benign.

Using molecular oxygen as an oxidant is a longstanding strategic subject[26-29] and significant achievements in aerobic epoxidation have been made[30-34]. Nevertheless, most reports[35-39] have used metallic compounds / additives or metallic catalysts / coreductants (such as Et_2Zn / amino alcohol[35], Co(II)TPP-OCH_3 / isobutyraldehyde[36], Mn(TPP)OAc / isobutyraldehyde [37]) (Scheme 1, (a)), which always lead to metal residue and poor atom economy. Only a limited number of reports[40,41] related to the catalytic epoxidation of α,β-unsaturated ketones with molecular oxygen as the oxidant in the absence of metallic compounds have been reported. In 2013, Norio Shibata and his coworkers reported an aerobic epoxidation of β-trifluoromethyl-β,β-disubstituted enones induced by methylhydrazine[40]. They proposed that the key to this success was the unique behavior of H_2NNHMe for generating hydrogen peroxide in the presence of molecular oxygen and a base (Scheme 1, (b)). H_2NNHMe was ultimately converted into methane. In the same year, Akichika Itoh and his coworkers developed another method for the epoxidation of α,β-unsaturated ketones in two steps. First, *i*-propanol was oxidized by molecular oxygen catalyzed by anthraquinone-2-carboxylic acid in the presence of visible light. Synchronously, hydrogen peroxide was generated and used as the direct oxidant for the following oxidation of α,β-unsaturated ketones after adding a base and substrates (Scheme 1, (c))[41].

Scheme 1. Aerobic epoxidation of α,β-unsaturated ketones using molecular oxygen as the oxidant

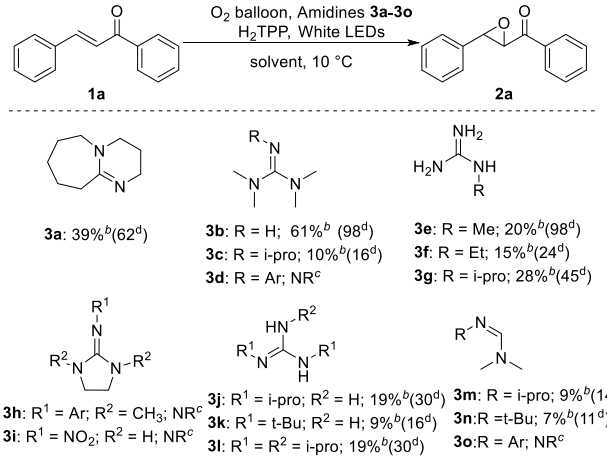


Photosensitization is an effective method to generate excited singlet oxygen ($^1O_2$) and provides great opportunities to make the protocol simpler, greener and sustainable, having a bright prospect for its various applications[42-50]. Especially, the reactions of alkenes with singlet oxygen are familiar[51-55], such as Schenck–ene reactions[56,57], [2+2]-cycloadditions[58], [4+2]-cycloadditions[59-61], and epoxidations[62-64]. However, to the best of our knowledge, there is still a lack of methods for the one-step epoxidation of α,β-unsaturated ketones with molecule oxygen as the oxidant by photocatalysis in the absence of metallic compounds. Here, an epoxidation of α,β-unsaturated ketones in the presence of tetramethylguanidine, H_2TPP and molecular oxygen under visible light is reported (Scheme 1).

■ RESULTS AND DISCUSSION

As a part of our ongoing study on photooxidation[65,66], we attempted to extend the methods reported[65,66] to the epoxidation of α,β-unsaturated ketones by using molecular oxygen as the oxidant. First, we attempted to undertake the enantioselective epoxidation of chalcone **1a** (0.1 mmol) in toluene in the presence of PTC (10 mol %, reported in the literature[65]), H_2TPP (1 mol %, 0.001 mmol), K_2HPO_4 (50% aq), molecular oxygen and visible light. However, the reaction did not go on. Subsequently, some inorganic bases and organic bases, such as Cs_2CO_3, KOH, Na_2CO_3, Et_3N, DMAP, DABCO, morpholine, pyridine and iminazole, were further demonstrated to have none or poor effect. Fortunately, **3a** and **3b** were discovered to be effective and gave **2a** in yields of 39% and 61%, respectively, in the presence of H_2TPP, O_2 and visible light (Scheme 2). This exciting result spurred us to explore the nature of this epoxidation.

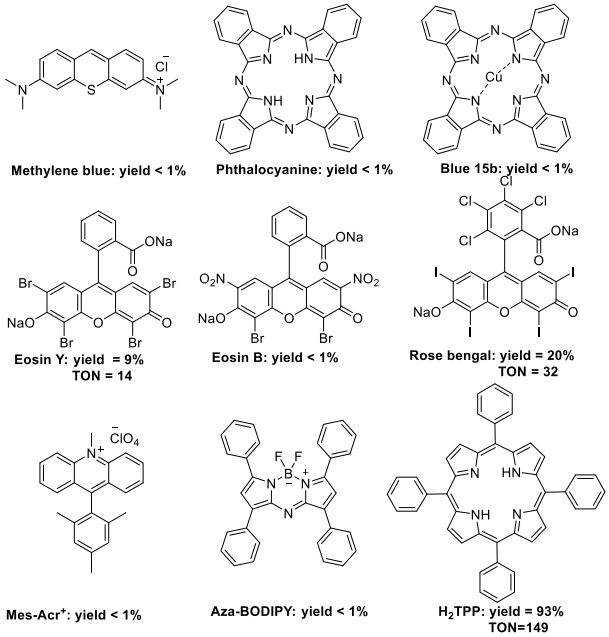
Scheme 2. Amidines screening for the photoepoxidation of chalcone[a].



[a]Reaction conditions: **1a** (83.32 mg, 0.4 mmol), amidine (1.2 mmol), H_2TPP (1.5 mg, 0.0025 mmol), toluene (2 mL), oxygen balloon, white LEDs (10 W), 72 h, 10 °C. [b]Yields of isolated product. [c]NR-not reaction.[d]Turnover number (TON) = moles of the oxidation product / moles of H_2TPP.

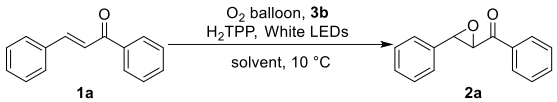
To improve the epoxidation, a series of derivatives of amidines were synthesized and applied to the photoepoxidation of chalcone **1a** (Scheme 2). We began our studies by choosing **1a** as the model substrate, using H_2TPP as the photosensitizer, and using LEDs (Light Emitting Diode, white light, 10 W, 4000 K) to provide light. Low yields (8% - 19%) of **2a** were obtained when **3c**, **3j**, **3k**, **3l**, **3m** and **3n** were used instead of **3b**. Moreover, no reaction occurred when **3d**, **3h**, **3i** and **3o** were used. Interestingly, all of those amidines were beared an electron-withdrawing group or a conjugated group in the N' position, such as a benzyl group or a nitro group. Side reactions occurred when **3e**, **3f** and **3g** were used and **2a** was obtained in low yields (15% - 28%). Therefore, **3b** is the best choice among the amidines listed in Scheme 2.

Scheme 3. Photosensitizers screening for the photoepoxidation of chalcone[a].



[a]Reaction conditions: **1a** (83.32 mg, 0.4 mmol), **3b** (1.6 mmol), photosensitizer (0.0025 mmol), dioxane (2 mL), oxygen balloon, white LEDs (10 W), 96 h, 10 °C. Yields of isolated product. TON = moles of the oxidation product / moles of the photosensitizer.

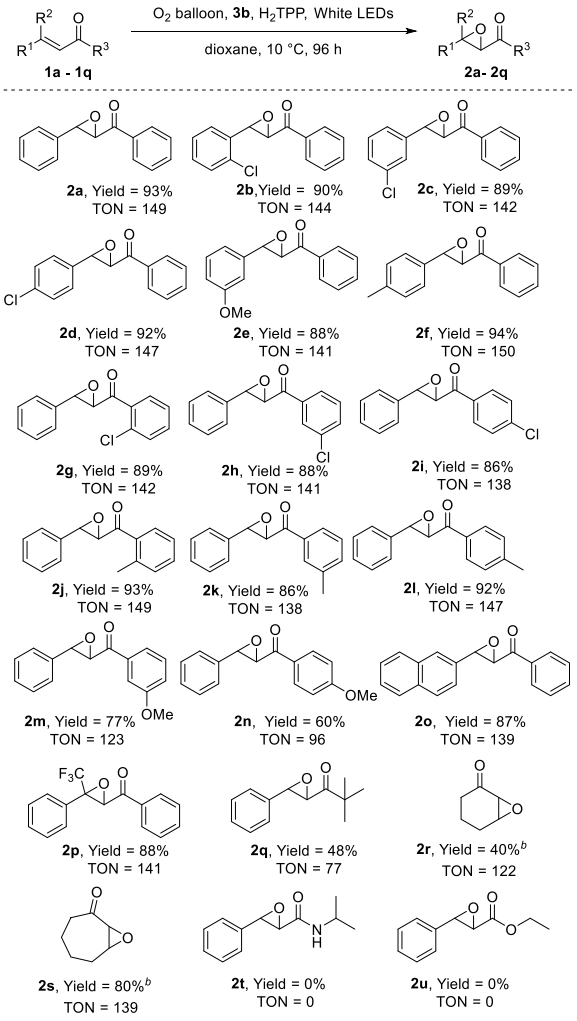
Table 1. Optimization for the photoepoxidation of chalcone[a]



Entry	1a (mmol)	3b (mmol)	Solvent	T (°C)	Time (h)	Yield[b] (%)	TON[c]
1	0.4	1.6	Toluene	10	96	89	142
2	0.4	1.6	Dioxane	10	96	93	149
3	0.4	1.6	$CHCl_3$	10	96	88	146
4	0.4	1.6	THF	10	96	77	123
5	0.4	1.6	Ethanol	10	96	36	58
6	0.4	1.6	Toluene	-15	96	30	64
7	0.4	1.6	dioxane	42	96	40	102
8	0.4	1.6	dioxane	30	96	64	131
9	0.4	1.6	dioxane	20	96	82	141
10	0.4	1.6	dioxane	4	96	88	128
11	0.2	0.8	dioxane	10	96	90	63
12	0.4	0.4	dioxane	10	240	79	149
13	0.4	3.2	dioxane	10	96	93	123
14	0.4	1.6	dioxane	10	48	80	144
15[d]	0.4	1.6	dioxane	10	96	77	146
16[e]	5	15	dioxane	10	96	91	455

[a]Reaction conditions: H_2TPP (1.5 mg, 0.0025 mmol), solvent (2 mL), oxygen balloon, white LEDs (10 W). [b]Yields of isolated product. [c]TON = moles of the oxidation product / moles of H_2TPP. [d]In air. [e]H_2TPP (6.0 mg, 0.01 mmol), dioxane (4 mL).

Scheme 4. Substrate scope of the photoepoxidation mediated by **3b**[a]

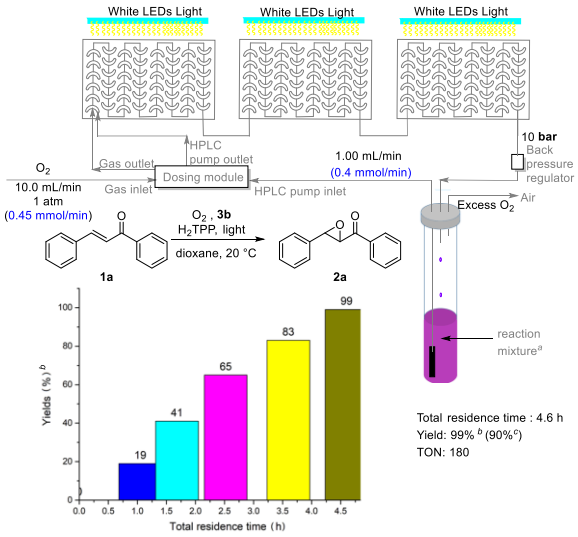


[a]Reaction conditions: **1** (0.4 mmol), **3b** (184 mg, 1.6 mmol), H_2TPP (1.5 mg, 0.0025 mmol), dioxane (2 mL), oxygen balloon, white LEDs (10 W), 96 h, 10 °C, yields of isolated product; TON = moles of the oxidation product / moles of H_2TPP. [b]The crude yield was determined by GC - MS.

After a suitable amidine **3b** had been identified, further reaction optimization was explored (Table 1). Among the different solvents shown in Table 1 (entries 1 - 5), toluene, dioxane and $CHCl_3$ could give yields of 88% - 93% (Table 1, entries 1 - 3). Especially, dioxane gave **2a** in a yield of 93% (Table 1, entry 2). THF gave 2a in a moderate yield of 77% (Table 1, entry 4). Ethanol proved to be less efficient in a yield of 36% (Table 1, entry 5). H_2TPP is the best photosensitizer among the photosensitizers shown in Scheme 3. It was evident to find that extremely low temperature was bad for the reaction rate through the comparison of the yield in toluene at 10 °C to that at -15 °C (Table 1, entries 1 and 6, 89% and 30%, respectively). Further increasing the temperature was not conducive to improving the yields as expected (Table 1, entries 2, 7 - 10, 93% (10 °C) > 82% (20 °C) > 64% (30°C) > 40% (42°C)). Reducing the concentration of **3b** and **1a** to half resulted in a slightly lower yield (Table 1, entry 11, 90%). A 79% yield value could be obtained after 240 h when the ratio of **3b** / **1a** was reduced from 4 to 1 (Table 1, entry 12). Furthermore, there was no significant improvement to the yield value by further increasing the ratio of **3b** / **1a** from 4 to 8 (Table 1, entry 13). The yield decreased clearly from 93% to 80% when the reaction time was shortened to 48 h (Table 1, entry 14). **2a** could be obtained in a yield of 77% by using air oxygen as the oxidant (Table 1, entry 15). Furthermore, **2a** was obtained in a yield of 91% for the scale-up experiment when amplified it to the gram scale with 1.05 g of **1a** (5 mmol), 15 mmol of **3b**, 0.01 mmol of TPP in dioxane (4 mL) (Table 1, entry 16).

With the optimal reaction conditions in hand (Table 1, entry 2), the substrate scope of the aerobic epoxidation mediated by **3b** was explored (Scheme 4). Satisfactorily, most of the chalcone derivatives bearing a halogen or alkyl group exhibited excellent yields (**2a** - **2l** and **2o**, 86% - 94%) except for **1m** and **1n** bearing the OMe group (**2m** and **2n**, yields of 77% and 60%, respectively). **2p** bearing the CF_3 group was obtained in a yield of 88%. **2q** was also obtained in a yield of 48%. It is worth mentioning that the reaction also proceeded for cyclohexenone **1r** and 2-cycloheptenone **1s** (crude yields of 40% and 80%, respectively). Unfortunately, it doesn't suit for N-isopropylcinnamamide **1t** and ethyl cinnamate **1u**.

Scheme 5. Photoepoxidation by flow synthesis[a].



[a]Reaction mixture was prepared by dissolving **1a** (1.67 g, 8 mmol), **3b** (3.68 g, 32 mmol) and H_2TPP (24 mg, 0.04 mmol) in dioxane (total volume: 20 mL); Reaction mixture : 1.00 mL/min; O_2 : 10.0 mL/min (calculated at standard state (298.15 K, 1 atm)); 10 bar. [b]Yield was determined by ^{1}H-NMR analysis. [c]Yield of isolated product.

In contrast to conventional batch processing, microreactor technology exhibits salient advantages for its large specific surface area, enhanced heat- and mass-transfer rates, reduced safety hazards and high degree of control over photochemical transformations[67,68]. To accelerate the reaction, Corning Advanced Flow Reactors (Lab Reactors, Figure S2) were used for the reaction investigation (Scheme 5). **2a** was obtained in a yield of 99% (NMR) and an isolated yield of 90% after a total residence time of 4.6 h. The reaction processed

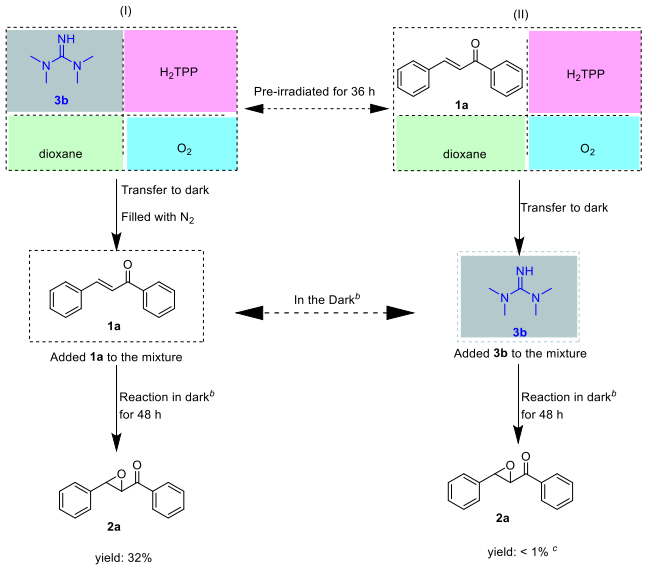
in microreactors (Figure S5) was clearly faster than that in reaction tubes (Figure S4).

Table 2. Mechanism exploration experiments[a]

Entry	3b (mmol)	Additive	Time (h)	Yield[b] (%)
1[c]	1.6	none	48	0 (0[f])
2[d]	1.6	none	48	0 (0[f])
3[e]	1.6	none	96	11 (<1%[f,g])
4	0	DMAP 1.0 mmol	48	0
5[g]	1.6	DABCO 1.0 mmol	96	< 1%
6	1.6	NaN_3 1.0 mmol	96	28

[a]Reaction conditions: **1a** (83.32 mg, 0.4 mmol), H_2TPP (1.5 mg, 0.0025 mmol), dioxane (2 mL), oxygen balloon, white LEDs (10 W), 10 °C. [b]Yields of isolated product. [c]Reaction under the nitrogen protection. [d]Reaction in the dark. [e]Without photosensitizer. [f]In toluene. [g]Yield was determined by ^{1}H-NMR analysis.

Scheme 6. Mechanism exploration experiments[a]

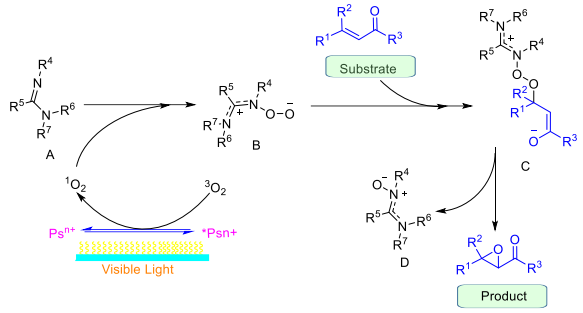


[a]Reaction conditions : **1a** (83.32 mg, 0.4 mmol), **3b** (184 mg, 1.6 mmol), H_2TPP (1.5 mg, 0.0025 mmol), dioxane (2 mL), oxygen ballon, white LEDs (10 W), 10 °C, yield of isolated product. [b]Dark condition: The reaction tube was wrapped with aluminium foil and then covered with black cloth. [c]Yield was determined by ^{1}H-NMR analysis.

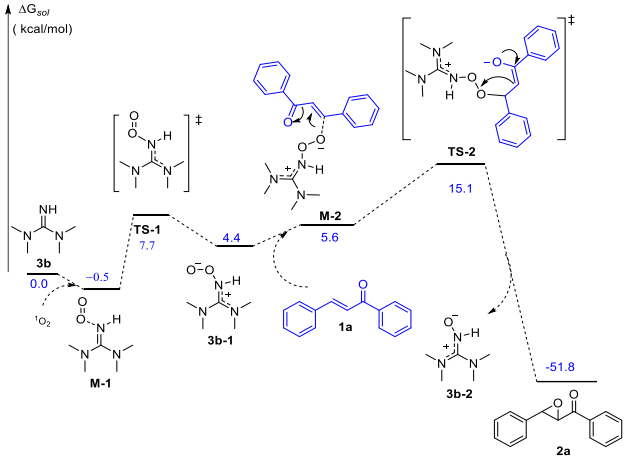
In order to investigate the mechanism of this epoxidation, control experiments without O_2, light, H_2TPP and amidines were conducted (Table 2, entries 1 - 4). Epoxidation did not proceed under a N_2 atmosphere (Table 2, entry 1). This result indicates that the origin of incorporated oxygen atom in the epoxides came from molecular oxygen. The reaction did not occur in the dark (Table 2, entry 2) or did not proceed effectively without the photosensitizer (Table 2, entry 3). This suggests that light was the indispensable driving force for this epoxidation. Additionally, no product was obtained when using DMAP instead of **3b** (Table 2, entry 4). Therefore, tetramethylguanidine, O_2, H_2TPP and light are imperative. The reaction was suppressed in the presence of the singlet oxygen inhibitors 1,4-diazabicyclo[2,2,2] octane [69,70](DABCO) and NaN_3[71] (Table 2, entries 5 and 6). Therefore, singlet oxygen may account for the epoxidation. In addition, according to the results of Scheme 6 (I), **2a** can be obtained in a yield of 32% when the mixture of **3b** and H_2TPP in dioxane was pre-irradiated under an O_2 atmosphere for 36 h, and then moved to the dark conditions and filled with N_2. The reaction was completed by adding the substrate **1a** and stirring it under a N_2 atmosphere for another 48 h. In contrast, little product (scheme 6 (II), < 1% yield) was obtained when the mixture of **1a** and H_2TPP in dioxane was pre-irradiated under an O_2 atmosphere for 36 h, and then moved to the dark conditions, where the substrate **3b** was added, and stirred under an O_2 atmosphere for an additional 48 h. Therefore, the key to this reaction was the change of **3b** under light. Furthermore, the information regarding to [**3a**+O](M-3), [**3b**+O](3b-2) and [**3a**+2O](M-4) was found in the HRMS spectra (Figures S7 and S8). Additionally, the information regarding to H_2O_2 could not be found in the ^{1}H NMR spectra after irradiated the mixture of **3b**, H_2TPP in $CDCl_3$ or DMSO-d6 (Figures S9 and S10).

On the basis of all the above results, a plausible mechanism is described as Scheme 7. Under irradiation, the photosensitizer Ps^n is excited to its excited state $^*Ps^n$. Singlet oxygen ($^1O_2$) is produced from the ground state ($^3O_2$) through energy transfer with the excited state photosensitizer $^*Ps^n$. $^1O_2$ reacts with amidine **A** to give amidine peroxide **B**, which is then oxidized the substrate to yield an epoxy ketone (product) via the formation of a C–O bond to form transition state **C** and the breakage of the O-O bond in **C**. Amidine oxide **D** is generated simultaneously.

Scheme 7. A proposed reaction mechanism



Scheme 8. Calculated energy profile for the epoxidation of **1a** mediated by tetramethylguanidine (**3b**).



In addition, density functional theory (DFT) calculations (Scheme 8) were carried out to judge whether the epoxidation could proceed as suggested. Here, the reaction of chalcone (**1a**) with singlet oxygen mediated by tetramethylguanidine (**3b**) was chosen as the model reaction. First, $^1O_2$ reacts with tetramethylguanidine

(**3b**) via the transition state **TS-1** to give tetramethylguanidine peroxide (**3b-1**). This step only needs to overcome a low energy barrier of 8.2 kcal/mol. Subsequently, the newly formed **3b-1** reacts with **1a** to yield product **2a** via **TS-2** featuring C–O bond formation and O–O cleavage. Tetramethylguanidine oxide **3b-2** is released at the same time. This step has a free energy barrier of only 15.6 kcal/mol, suggesting a feasible process. The whole reaction is exergonic by 51.8 kcal/mol. Overall, the reaction could feasibly take place from the view of DFT calculations.

■ CONCLUSIONS

In conclusion, we reveal an aerobic epoxidation of α,β-unsaturated ketones in excellent yields of up to 94% driven by visible light in the presence of tetramethylguanidine (**3b**), O_2 and H_2TPP at 10 °C, in which no metallic compounds participated. The reaction time was shortened from 96 h to 4.6 h by flow synthesis. Tetramethylguanidine, O_2, H_2TPP and light are indispensable. The reaction was suppressed in the presence of the singlet oxygen inhibitors DABCO and NaN_3, which demonstrated the reaction proceeded through a singlet oxygen process. The detailed reaction mechanisms involving the formation of tetramethylguanidine peroxide (**3b-1**) and oxidation of chalcone were further computationally investigated to show a relatively low activation barrier of 15.6 kcal/mol. The method expands the utility of amidines to the aerobic oxidation.

■ EXPERIMENTAL SECTION

General Unless otherwise stated, all commercial reagents and solvents were used without further purification. Analytical TLC was visualized with UV light at 254 nm and 365 nm. Thin layer chromatography analysis was carried out on TLC glass sheets with silica gel 60 F254. Purification of reaction products was carried out with chromatography on silica gel 60 (200 - 300 mesh). Microreactors type was Corning advanced flow reactors with two lab reactor reaction modules (internal volume: 2.7 mL, with extra white LEDs light strip 20 W) and a lab photo reaction module (internal volume: 3 mL). High resolution mass spectra (HRMS) were taken at liquid chromatograph/mass spectrometers (Thermo Scientific LTQ Orbitrap XL or Agilent G6224A). Gas chromatography mass spectra (GC - MS) were taken at gas chromatograph mass spectrometer (Agilent 5975C). ^{1}H NMR (400 MHz or 500 MHz) spectra and ^{13}C NMR (126 MHz or 110 MHz) spectra were recorded on a Bruker Avance II 400 or Bruker Avance III 500 spectrometer.

General Procedure to prepare substrates 1a-1q: To a stirred solution of benzaldehyde (2.12 g, 20 mmol) and acetophenone (2.40 g, 20 mmol) in ethanol (50 mL) at room temperature, $Ba(OH)_2$ (0.06 g, 0.02 mmol) was added. The reaction were conducted at room temperature (or refluxed if not reacted at room temperature). After complete consumption of one of the starting materials as indicated by TLC (usually within 60 min), added 20 mL of water, extracted with CH_2Cl_2 (20 ml × 3), washed with saturated brine, dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The crude product was purified by recrystallization (or by silica-gel column chromatography).

(E)-chalcone (**1a**)[72]: Purification by recrystallization (petroleum ether/ethyl acetate = 20 : 1, v/v), afforded **1a** as light yellow solid (3.77g, 90.7% yield), mp: 57 - 58 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.05 – 7.99 (m, 2H), 7.81 (d, *J* = 15.7 Hz, 1H), 7.64 (m, *J* = 6.6, 2.9 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.56 – 7.47 (m, 3H), 7.42 (m, *J* = 5.0, 1.9 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.6, 144.9, 138.3, 135.0, 132.9, 130.6, 129.0, 128.7, 128.6, 128.5, 122.2. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{15}H_{13}O$ 209.0961; Found 209.0958.

(E)-3-(2-chlorophenyl)-1-phenylprop-2-en-1-one (**1b**)[73]: Purification by recrystallization (petroleum ether/ethyl acetate = 20 : 1, v/v), afforded **1b** as light yellow solid (4.18 g, 86.1% yield), mp: 50 – 52 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18 (d, *J* = 15.6 Hz, 1H), 8.09 – 7.91 (m, 2H), 7.80 – 7.68 (m, 1H), 7.64 – 7.54 (m, 1H), 7.54 – 7.39 (m, 4H), 7.38 – 7.27 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.4, 140.6, 138.0, 135.5, 133.3, 133.0, 131.2, 130.3, 128.7 (d, *J* = 5.6 Hz), 127.8, 127.2, 124.8.

(E)-3-(3-chlorophenyl)-1-phenylprop-2-en-1-one (**1c**)[74]: Purification by recrystallization (petroleum ether/ethyl acetate = 20 : 1, v/v), afforded **1c** as light yellow solid (3.01 g, 62.0% yield), mp: 75 -77 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 7.5 Hz, 2H), 7.74 (d, *J* = 15.7 Hz, 1H), 7.68 – 7.57 (m, 2H), 7.57 – 7.45 (m, 4H), 7.42 – 7.31 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 190.1, 143.1, 138.0, 136.8, 135.1, 133.1, 130.3 (d, J = 8.9 Hz), 128.7 (d, J = 16.1 Hz), 128.0, 126.9, 123.3.

(E)-3-(4-chlorophenyl)-1-phenylprop-2-en-1-one (**1d**)[72]: Purification by column separation (petroleum ether/ethyl acetate = 20 : 1, v/v), afforded **1d** as light yellow solid (4.60 g, 94.8% yield), mp: 56 -58 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (m, *J* = 8.5, 4.4 Hz, 2H), 7.95 – 7.77 (m, 1H), 7.75 – 7.38 (m, 8H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.5, 144.8, 138.2, 134.9, 132.8, 130.6, 129.0 (d, *J* = 2.5 Hz), 128.7 (d, *J* = 2.5 Hz), 128.7 – 128.3 (m), 122.1.

(E)-3-(3-methoxyphenyl)-1-phenylprop-2-en-1-one (**1e**)[73]: Purification by column separation (petroleum ether/ethyl acetate = 20 : 1, v/v), afforded **1e** as light yellow solid (3.89 g, 94.8% yield), mp: 58 - 59 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (m *J* = 7.4, 1.9, 1.0 Hz, 2H), 7.77 (d, *J* = 15.7 Hz, 1H), 7.65 – 7.56 (m, 1H), 7.55 – 7.46 (m, 3H), 7.38 – 7.30 (m, 1H), 7.26 (m, *J* = 1.9, 1.1 Hz, 1H), 7.16 (m, *J* = 2.9, 1.4 Hz, 1H), 7.04 – 6.91 (m, 1H), 3.86 (d, *J* = 0.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.5, 156.0, 144.7, 138.2, 136.3, 132.8, 130.0, 128.6 (d, *J* = 11.7 Hz), 122.4, 121.1, 116.3, 113.5, 55.3.

(E)-1-phenyl-3-(p-tolyl)prop-2-en-1-one (**1f**)[75]: Purification by column separation (petroleum ether/ethyl acetate = 20 : 1, v/v), afforded **1f** as light yellow solid (2,73 g, 61.4% yield), mp: 96 - 97 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 – 7.92 (m, 2H), 7.78 (d, *J* = 15.7 Hz, 1H), 7.52 (m, *J* = 15.5, 10.5, 3.2 Hz, 6H), 7.22 (t, *J* = 7.3 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 190.7, 145.0, 141.2, 138.5, 132.8, 132.3, 129.8, 128.7, 128.6 (d, J = 2.0 Hz), 121.2, 21.6.

(E)-1-(2-chlorophenyl)-3-phenylprop-2-en-1-one (**1g**)[72]: Purification by column separation (petroleum ether/ethyl acetate = 20 : 1, v/v), afforded **1g** as light yellow oil (4.46 g, 91.8% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 – 7.51 (m, 2H), 7.50 – 7.32 (m, 8H), 7.12 (m, *J* = 16.1, 2.4 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 193.8, 146.3, 139.1, 134.4, 131.5, 130.9, 130.3, 129.4, 129.0, 128.6, 126.9, 126.3.

(E)-1-(3-chlorophenyl)-3-phenylprop-2-en-1-one (**1h**)[76]: Purification by recrystallization (petroleum ether/ethyl acetate = 20 : 1, v/v), afforded **1h** as light yellow solid (4.31 g, 88.8% yield), mp: 97 – 98 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 1.9 Hz, 1H), 7.90 (m, *J* = 7.8, 1.4 Hz, 1H), 7.83 (d, *J* = 15.7 Hz, 1H), 7.66 (m, *J* = 6.7, 3.1 Hz, 2H), 7.59 – 7.53 (m, 1H), 7.51 – 7.39 (m,

5H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 188.9, 145.6, 139.8, 134.9, 134.6, 132.7, 130.8, 130.0 (d, *J* = 2.1 Hz), 129.0, 128.6 (d, *J* = 2.7 Hz), 126.6, 121.4.

(E)-1-(4-chlorophenyl)-3-phenylprop-2-en-1-one (**1i**)[72]: Purification by recrystallization (petroleum ether/ethyl acetate = 20 : 1, v/v), afforded **1i** as light yellow solid (4.00 g, 82.4% yield), mp: 101 – 103 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 8.00 (d, J = 8.2 Hz, 2H), 7.85 (d, J = 15.7 Hz, 1H), 7.67 (m, J = 6.4, 3.0 Hz, 2H), 7.58 – 7.47 (m, 3H), 7.49 – 7.42 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 189.2, 145.4, 139.3, 136.6, 134.8, 130.8, 130.0 (d, *J* = 3.7 Hz), 129.1 (dd, *J* = 7.1, 3.4 Hz), 128.6 (d, *J* = 3.4 Hz), 121.60.

(E)-3-phenyl-1-(o-tolyl)prop-2-en-1-one (**1j**)[77]: Purification by column separation (petroleum ether/ethyl acetate = 20 : 1, v/v), afforded **1j** as light yellow oil (4.10 g, 92.3% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.53 (m, 2H), 7.53 – 7.47 (m, 1H), 7.46 – 7.35 (m, 5H), 7.33 – 7.24 (m, 2H), 7.14 (d, *J* = 16.1 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.6, 145.9, 139.2, 137.0, 134.7, 131.4, 130.7, 130.5, 129.0, 128.5, 128.2, 126.8, 125.6, 20.3.

(E)-3-phenyl-1-(m-tolyl)prop-2-en-1-one (**1k**)[77]: Purification by recrystallization (petroleum ether/ethyl acetate = 20 : 1, v/v), afforded **1k** as light yellow solid (3.51 g, 78.9% yield), mp: 62 – 64 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 – 7.75 (m, 3H), 7.65 (m, *J* = 6.6, 2.9 Hz, 2H), 7.53 (d, *J* = 15.7 Hz, 1H), 7.41 (m, *J* = 8.5, 4.9, 2.8 Hz, 5H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.7, 144.7, 138.5, 138.3, 135.0, 133.7, 130.6, 129.1, 129.0, 128.6, 128.5, 125.8, 122.3, 21.5.

(E)-3-phenyl-1-(p-tolyl)prop-2-en-1-one (**1l**)[72]: Purification by recrystallization (petroleum ether/ethyl acetate = 20 : 1, v/v), afforded **1l** as light yellow solid (2.97 g, 66.8% yield), mp: 56 -58 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 – 7.89 (m, 2H), 7.81 (d, *J* = 15.7 Hz, 1H), 7.64 (m, *J* = 6.6, 3.0 Hz, 2H), 7.54 (d, *J* = 15.7 Hz, 1H), 7.41 (m, *J* = 5.0, 2.0 Hz, 3H), 7.30 (d, *J* = 7.8 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 189.9, 144.3, 143.6, 135.6, 135.0, 130.4, 129.3, 128.9, 128.7, 128.4, 122.1, 21.7.

(E)-1-(3-methoxyphenyl)-3-phenylprop-2-en-1-one (**1m**)[78]: Purification by column separation (petroleum ether/ethyl acetate = 20 : 1, v/v), afforded **1m** as colorless oil (4.33 g, 91.0% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (m, *J* = 15.6, 2.1 Hz, 1H), 7.61 (m, *J* = 15.5, 7.5, 2.6 Hz, 3H), 7.56 – 7.47 (m, 2H), 7.41 (m, *J* = 5.7, 2.4 Hz, 4H), 7.12 (m, *J* = 8.2, 2.7 Hz, 1H), 3.87 (s, *J* = 3.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.3, 160.0, 144.9, 139.7, 135.0, 130.6, 129.7, 129.0, 128.5, 122.2, 121.1, 119.4, 113.0, 55.6.

(E)-1-(4-methoxyphenyl)-3-phenylprop-2-en-1-one (**1n**)[72]: Purification by recrystallization (petroleum ether/ethyl acetate = 20 : 1, v/v), afforded **1n** as white solid (3.74 g, 78.6% yield), mp: 107 - 109 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (m, *J* = 8.9, 3.9 Hz, 2H), 7.93 – 7.73 (m, 1H), 7.71 – 7.53 (m, 3H), 7.48 – 7.34 (m, 3H), 6.99 (m, *J* = 9.0, 3.7 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 188.8, 163.6, 144.1, 135.2, 131.2, 130.9, 130.4, 129.0, 128.5, 122.0, 114.0, 55.6.

(E)-3-(naphthalen-2-yl)-1-phenylprop-2-en-1-one (**1o**)[79]: Purification by recrystallization (petroleum ether/ethyl acetate = 20 : 1, v/v), afforded **1o** as yellow solid (4.37 g, 84.7% yield), mp: 87 - 89 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.71 (d, *J* = 15.4 Hz, 1H), 8.35 – 8.22 (m, 1H), 8.18 – 8.05 (m, 2H), 8.00 – 7.86 (m, 3H), 7.73 – 7.47 (m, 7H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 190.3, 141.8, 138.3, 133.8, 133.0, 132.4, 131.9, 130.9, 128.9, 128.8, 128.7, 127.1, 126.4, 125.5, 125.2, 124.7, 123.6.

1p was prepared according to literature[80]. *(Z)-4,4,4-trifluoro-1,3-diphenylbut-2-en-1-one* (**1p**): yellow oil at room temperature, yellow solid at 0 - 8 °C (2.29 g, 83% yield), mp: 0 - 4 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 7.8 Hz, 1H), 7.63 – 7.50 (m, 1H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.37 – 7.23 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 192.2, 139.2, 138.9, 136.2, 134.0, 131.0, 129.5, 129.2, 129.0, 128.8, 128.5, 124.4, 121.6.

(E)-benzylidenepinacolone (**1q**)[81]: The reactant of pinacolone is 2.0 eq. Purification by column separation (petroleum ether/ethyl acetate = 25 : 1, v/v), afforded **1q** as light yellow solid (3.78 g, 99% yield), mp: 40 – 42 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (d, *J* = 15.6 Hz, 1H), 7.57 (dd, *J* = 6.7, 2.9 Hz, 2H), 7.38 (m, *J* = 4.9, 1.9 Hz, 3H), 7.13 (d, *J* = 15.6 Hz, 1H), 1.23 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 204.3, 143.0, 135.1, 130.3, 129.0, 128.4, 120.9, 43.4, 26.5.

N-isopropylcinnamamide (**1t**)[82]: white solid, mp: 39 – 41 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 15.6 Hz, 1H), 7.53 – 7.44 (m, 2H), 7.33 (m, *J* = 5.1, 2.2 Hz, 3H), 6.40 (m, *J* = 15.6, 8.7, 2.5 Hz, 1H), 5.74 (d, *J* = 57.3 Hz, 1H), 4.23 (m, *J* = 8.0, 6.5 Hz, 1H), 1.22 (d, *J* = 6.5 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.2, 140.8, 140.8, 135.1, 129.7, 129.6, 128.9, 127.8, 121.3, 121.2, 41.7, 23.0, 22.9.

Ethyl cinnamate (**1u**)[83]: light yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 16.0 Hz, 1H), 7.51 (m, *J* = 6.1, 3.5 Hz, 2H), 7.44 – 7.29 (m, 3H), 6.44 (d, *J* = 16.0 Hz, 1H), 4.26 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.1, 144.7, 134.6, 130.3, 129.0, 128.2, 118.4, 60.6, 14.5.

General Procedure to prepare products 2a-2q : **3b** (200 ul, 1.6 mmol) was added to the mixture solution of **1a** (83.32 mg, 0.4 mmol) and H_2TPP (1.5 mg, 0.0025 mmol) in dioxane (2 mL) in a Schlenk tube equipped with a stir bar and oxygen balloon. The mixture was irradiated by white light (LEDs light strip, 10 W/m, 10 W, 4000 K) and stirred under an O_2 atmosphere at 10 °C for 96 h. Then purified it by chromatography (silica gel, PE / CH_2Cl_2 / EtOAc = 25 : 1 :1) to afford the product.

phenyl(3-phenyloxiran-2-yl)methanone (**2a**)[84]: white solid (83.20 mg, 93% yield), mp: 87-88 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (m, *J* = 5.0, 2.4 Hz, 2H), 7.63 (m, *J* = 7.7, 2.6 Hz, 1H), 7.51 (m, *J* = 7.8, 6.4, 3.5 Hz, 2H), 7.40 (q, *J* = 5.3, 4.6 Hz, 5H), 4.39 – 4.26 (m, 1H), 4.17 – 4.03 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 193.1, 135.5, 134.0, 129.1, 128.9, 128.8, 128.7, 128.3, 128.2, 125.8, 125.7, 61.0, 59.4. HRMS (ESI-TOF) *m/z*: [M + H]$^+$ Calcd for $C_{15}H_{13}O_2$ 225.0910; Found 225.0910.

(3-(2-chlorophenyl)oxiran-2-yl)(phenyl)methanone (**2b**)[85]: light yellow solid (96.81 mg, 90%), mp: 71-73 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.17 – 8.00 (m, 3H), 7.63 (m, *J* = 7.6, 4.0 Hz, 1H), 7.57 – 7.47 (m, 2H), 7.40 (m, *J* = 6.9, 2.8, 2.2 Hz, 2H), 7.37 – 7.28 (m, 1H), 4.41 (t, *J* = 2.2 Hz, 1H), 4.19 (t, *J* = 2.3 Hz, 1H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 192.8, 135.4, 134.1, 133.8, 133.3, 129.8, 129.4, 128.9, 128.4, 127.3, 126.2, 60.1, 57.2.

(3-(3-chlorophenyl)oxiran-2-yl)(phenyl)methanone (**2c**)[79]: yellow solid (92.50 mg, 89% yield), mp: 59 – 61 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.19 – 8.07 (m, 2H), 7.81 – 7.70 (m, 1H), 7.61 (t, *J* = 7.8 Hz, 2H), 7.54 – 7.42 (m, 3H), 7.38 (m, *J* = 4.8, 2.1 Hz, 1H), 4.39 (t, *J* = 2.7 Hz, 1H), 4.17 (d, *J* = 1.9 Hz, 1H).^{13}C NMR (101 MHz,

Chloroform-*d*) δ 192.6, 137.7, 135.4, 134.9, 134.2, 130.1, 129.2, 129.0, 128.4, 125.8, 124.2, 60.8, 58.5.

(3-(4-chlorophenyl)oxiran-2-yl)(phenyl)methanone (**2d**)[85]: light yellow solid (95.27 mg, 92% yield), mp: 87 – 89 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (d, *J* = 8.2 Hz, 2H), 7.70 – 7.58 (m, 1H), 7.58 – 7.47 (m, 2H), 7.45 – 7.28 (m, 4H), 4.32 (d, *J* = 2.2 Hz, 1H), 4.09 (d, *J* = 2.1 Hz, 1H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 193.1, 135.5, 134.0, 129.1, 128.9, 128.8, 128.4, 127.2, 125.8, 61.0, 59.4.

(3-(3-methoxyphenyl)oxiran-2-yl)(phenyl)methanone (**2e**)[86]: light yellow solid (89.80 mg, 88% yield), mp: 75 – 77 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 8.1 Hz, 2H), 7.77 – 7.20 (m, 4H), 6.94 (m, *J* = 22.5, 7.0 Hz, 3H), 4.30 (s, 1H), 4.05 (s, 1H), 3.81 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 193.0, 160.1, 137.2, 135.4, 134.0, 129.9, 128.9, 128.3, 118.2, 114.7, 110.9, 60.9, 59.3, 55.3.

phenyl(3-(p-tolyl)oxiran-2-yl)methanone (**2f**)[79]: white solid (88.38 mg, 94% yield), mp: 82 - 84 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 – 7.98 (m, 2H), 7.71 – 7.58 (m, 1H), 7.58 – 7.45 (m, 2H), 7.37 – 7.17 (m, 4H), 4.32 (t, *J* = 1.9 Hz, 1H), 4.06 (d, *J* = 2.0 Hz, 1H), 2.40 (d, *J* = 4.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 193.2, 139.0, 135.5, 134.0, 132.5, 129.5, 128.9, 128.3, 125.8, 61.0, 59.5, 21.3.

(2-chlorophenyl)(3-phenyloxiran-2-yl)methanone (**2g**)[86,87]: light yellow solid (95.48 mg, 89% yield), mp: 69 - 71 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 – 7.59 (m, 1H), 7.52 – 7.29 (m, 8H), 4.17 (d, *J* = 1.9 Hz, 1H), 4.11 (d, *J* = 1.9 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.2, 136.5, 135.2, 133.0, 132.1, 130.4, 130.1, 129.0, 128.7, 127.2, 125.8, 62.9, 60.4.

(3-chlorophenyl)(3-phenyloxiran-2-yl)methanone (**2h**)[88]: yellow oil (102.72 mg, 88% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 2.1 Hz, 1H), 7.91 (d, *J* = 7.9 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.55 – 7.31 (m, 6H), 4.26 (d, *J* = 2.2 Hz, 1H), 4.10 (d, *J* = 2.1 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 192.1, 136.9, 135.3, 135.2, 133.9, 130.3, 129.2, 128.9, 128.4, 126.6, 125.9, 61.0, 59.6.

(4-chlorophenyl)(3-phenyloxiran-2-yl)methanone (**2i**)[85]: light yellow soild (88.67 mg, 86% yield), mp: 121 - 124 °C; ^{1}H NMR (400 MHz, Chloroform-d) δ 7.94 (d, J = 8.3 Hz, 2H), 7.50 – 7.31 (m, 7H), 4.23 (d, J = 1.8 Hz, 1H), 4.06 (d, J = 1.8 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 192.1, 140.6, 135.3, 133.7, 129.8, 129.2, 129.2, 128.8, 125.8, 61.1, 59.4.

(3-phenyloxiran-2-yl)(o-tolyl)methanone (**2j**)[86]: yellow oil (84.74 mg, 93% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (t, *J* = 8.1 Hz, 1H), 7.62 – 7.05 (m, 8H), 4.10 (m, *J* = 29.7, 7.8 Hz, 1H), 2.57 (d, *J* = 8.3 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.5, 138.8, 135.5, 135.4, 132.3, 132.0, 129.0, 129.0, 128.8, 125.8, 62.4, 59.5, 21.0.

(3-phenyloxiran-2-yl)(m-tolyl)methanone (**2k**)[88]: light yellow solid (81.17 mg, 86% yield), mp: 58 – 59 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.90 – 7.77 (m, 2H), 7.42 (m, *J* = 10.5, 9.8, 4.7 Hz, 7H), 4.32 (t, *J* = 2.3 Hz, 1H), 4.09 (d, *J* = 2.0 Hz, 1H), 2.42 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 193.2, 138.8, 135.6 (d, *J* = 4.5 Hz), 134.8, 129.1, 128.8 (d, *J* = 2.2 Hz), 125.8, 125.6, 60.9, 59.4, 21.4.

(3-phenyloxiran-2-yl)(p-tolyl)methanone (**2l**)[85]: light yellow solid (89.76 mg, 92% yield), mp: 86 – 87 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 7.8 Hz, 2H), 7.40 (p, *J* = 7.3, 6.1 Hz, 5H), 7.29 (d, *J* = 7.8 Hz, 2H), 4.30 (d, *J* = 1.9 Hz, 1H), 4.14 – 4.03 (m, 1H), 2.44 (d, *J* = 4.9 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 192.6, 145.1, 135.6, 133.0, 129.6, 129.0, 128.8, 128.5, 125.8, 60.9, 59.3, 21.8.

(3-methoxyphenyl)(3-phenyloxiran-2-yl)methanone (**2m**)[88]: yellow oil (85.76 mg, 77% yield); ^{1}H NMR (400 MHz, Chloroform-d) δ 7.71 – 7.50 (m, 2H), 7.50 – 7.29 (m, 6H), 7.27 – 7.06 (m, 1H), 4.30 (s, 1H), 4.18 – 4.00 (m, 1H), 3.86 (m, J = 15.9, 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 192.9, 160.0, 136.8, 135.5, 129.9, 129.1, 128.8, 125.8, 121.0, 120.5, 112.5, 61.0, 59.4, 55.5.

(4-methoxyphenyl)(3-phenyloxiran-2-yl)methanone (**2n**)[79]: yellow oil (61.70 mg, 60% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 – 7.79 (m, 2H), 7.47 – 7.27 (m, 5H), 6.93 (d, *J* = 8.9 Hz, 2H), 4.25 (d, *J* = 1.9 Hz, 1H), 4.06 (d, *J* = 1.9 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.4, 164.3, 135.7, 130.8, 129.0, 128.8, 128.6, 125.8, 114.1, 60.9, 59.2, 55.6.

(3-(naphthalen-2-yl)oxiran-2-yl)(phenyl)methanone (**2o**)[79]: white solid (96.81 mg, 87% yield), mp: 113 – 115 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 – 8.04 (m, 2H), 8.00 (m, *J* = 7.4, 1.9 Hz, 1H), 7.96 – 7.84 (m, 2H), 7.70 – 7.59 (m, 2H), 7.57 – 7.44 (m, 5H), 4.73 (d, *J* = 1.9 Hz, 1H), 4.31 (d, *J* = 2.0 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 193.4, 135.6, 134.2, 133.4, 131.8, 131.3, 129.1, 129.0, 128.6, 126.9, 126.3, 125.6, 122.7, 122.6, 60.3, 58.0.

phenyl(3-phenyl-3-(trifluoromethyl)oxiran-2-yl)methanone (**2p**)[89]: white solid (104.86 mg, 88% yield), mp: 81 – 82 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 – 7.78 (m, 2H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.37 – 7.30 (m, 2H), 7.21 (m, *J* = 14.5, 8.4, 6.2 Hz, 3H), 4.71 (s, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 189.5, 135.0, 134.4, 130.0, 129.0, 128.5, 128.3, 128.2, 126.9, 124.1, 121.4, 63.0, 62.7, 60.2.

2,2-dimethyl-1-(3-phenyloxiran-2-yl)propan-1-one (**2q**)[90]: colourless oil (39.24 mg, 48% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.34 (m, 3H), 7.33 – 7.28 (m, 2H),3.86 (s, 2H), 1.23 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 208.2, 135.7, 129.0, 128.8, 125.7, 59.4, 59.2, 43.7, 25.8.

Procedure to investigate the reaction of 1r and 1s: **3b** (1.6 mmol) was added to the mixture solution of **1r** (38.45 g, 0.4 mmol) and H_2TPP (1.5 mg, 0.0025 mmol) in dioxane (2 mL) in a Schlenk tube equipped with a stir bar and O_2 balloon. The mixture was irradiated with white light (LEDs, 10 W, 4000 K) and stirred under an O_2 atmosphere at 10 °C for 96 h. Added 20 mL CH_2Cl_2 to the reaction mixture, washed with HCl aqueous solution (1 mmol/mL) and brine, and dried over anhydrous Na_2SO_4. The mixture solution was filtered before injecting to the gas chromatograph mass spectrometer (Agilent 5975C). The crude yield was determined by GC-MS adopting the area normalization method. **1r**: MS Calcd for C_6H_8O 96.1; Found 96.0; **2r**: MS calcd for $C_6H_8O_2$ 112.1, Found 112.0; **1s**: MS Calcd for $C_7H_{10}O$ 110.1; Found 110.1; **2r**: MS calcd for $C_7H_{10}O_2$ 126.1, Found 126.0.

Procedure to prepare amidines 3c-3o[91]: Vilsmeyer salt tetramethylchloroformamidinium hexafluorophosphate (3.36g, 12 mmol) in MeCN (20 mL) was slowly added to a mixture solution of amine (isopropylamine, 0.80 g, 12 mmol) and Et_3N (2.4 g, 24 mmol) in MeCN (20 mL) under cooling in an ice bath and a N_2 atmosphere. After 30 min. the mixture was refluxed for 3 h. Then 2 eq. of NaOH dissolved in a minimum amount of water was added under vigorous stirring in order to deprotonate. The mixture was extracted with CH_2Cl_2, dried over $MgSO_4$. After remove the solvent as well as excess Et_3N, the residue was distilled under reduced pressure to afford the final product.

2-isopropyl-1,1,3,3-tetramethylguanidine (**3c**)[92]: light yellow oil (1.16 g, 73.8% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.58 (m, *J* = 6.4 Hz, 1H), 2.97 (s, 12H), 1.27 (d, *J* = 6.4 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.0, 77.4, 47.9, 39.9, 23.2. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_8H_{20}N_3$ 158.1652; Found 158.1652.

1,1,3,3-tetramethyl-2-phenylguanidine (**3d**)[93]: yellow oil (1.64 g, 85.7% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.12 (t, *J* = 7.7 Hz, 2H), 6.76 (t, *J* = 7.3 Hz, 1H), 6.64 (d, *J* = 7.8 Hz, 2H), 2.61 (s, 12H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 158.3, 151.9, 128.4, 121.2, 119.1, 39.3.

Procedure to prepare amidines 3e-3f: A solution of *S*-methylisothiourea sulfate (5.53 g, 20 mmol) in water (30 mL) was cooled with an ice bath. Amine (100 mmol) was added dropwise with stirring. Stirred the mixture at room temperature for 16 h and then refluxed for 4-5 h. The solution was evaporated under reduced pressure and the residue was crystallized from 95% EtOH to give guanidine sulfate. Dissolved the guanidine sulfate with water (50 mL), and added $Ba(OH)_2$ (6.94 g, 22 mmol). Stirred it for 1 h at 50 °C to deprotonate, added EtOH (50 mL), filtered to remove the $BaSO_4$, and evaporated under reduced pressure to give the crude product. Dissolved the crude product to CH_2Cl_2 and removed the impurity by filtering. The filtrate was evaporated under reduced pressure, dried in vacuo to afford the final product.

1-methylguanidine (**3e**)[94]: light yellow waxy solid (2.77 g, 94.8% yield);^{1}H NMR (400 MHz, Deuterium Oxide) δ 2.69 (s, 3H).^{13}C NMR (101 MHz, DMSO-d_6) δ 158.7, 28.6. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_2H_8N_3$ 74.0713; Found 74.0709.

1-ethylguanidine (**3f**)[95]: light yellow oil (3.21 g, 92.0% yield); ^{1}H NMR (400 MHz, Deuterium Oxide) δ 3.08 (q, *J* = 7.3 Hz, 2H), 1.10 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 157.8, 36.0, 15.3. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_3H_{10}N_3$ 88.0869; Found 88.0879.

1-isopropylguanidine (**3g**)[96]: yellow oil (3.37 g, 83.3% yield); 1H NMR (400 MHz, Deuterium Oxide) δ 3.55 (m, J = 9.9, 6.3, 3.6 Hz, 1H), 1.09 (m, J = 6.2, 2.7 Hz, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 157.2, 42.0, 23.3. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_4H_{12}N_3$ 102.1026; Found 102.1024.

Procedure to prepare amidines 3h[97]: First step: DMC was prepared according to the literature[98]: To a solution of DMI (2.28 g, 20 mmol) in CCl_4 (50 mL) was added trichlormethychlorlformate (1.96 g, 6.6 mmol) at room temperature and stirred it for 5 h. Filtered, washed with CCl_4 and n-hexane, and dried to afford DMC (2.43 g, 72.0% yield). Second step: **3h** was prepared according to the literature[97]: A solution of amine (0.93 g, 10 mmol) in CH_2Cl_2 (10 mL) was slowly added to a solution of DMC (1.69 g, 10 mmol) and Et_3N (2.01g, 20 mmol) in CH_2Cl_2 (10 mL) at 0-5 °C under a N_2 atmosphere. Then the mixture was stirred at room temperature for 5 h and the solvent was evaporated. The residue was dissolved in H_2O (4 mL), basified with aqueous NaOH (20%) to pH = 12, and extracted with toluene (5 x 30 mL). The combined organic layers was washed with H_2O (10 x 5 mL) and brine (5 x 10 mL), dried over $MgSO_4$, filtered, evaporated under reduced pressure, and dried in vacuo to give *1,3-dimethyl-2-phenylimino-1,3-diazolidine* (**3h**) as a yellow oil (0.98 g, 52.3% yield). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.10 (t, *J* = 7.8 Hz, 2H), 6.79 (m, *J* = 24.6, 7.6 Hz, 3H), 3.17 (d, *J* = 3.0 Hz, 4H), 2.55 (d, *J* = 3.2 Hz, 6H). ^{13}C NMR (101 MHz, DMSO-*d6*) δ 154.8, 150.2, 128.3, 122.0, 119.4, 48.0, 34.8.

2-(nitroimino)imidazolidine[99] (**3i**): white solid, mp: 215 – 217 °C; ^{1}H NMR (400 MHz, DMSO-*d6*) δ 8.40 (s, 2H), 3.57 (s, 4H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 163.2, 42.0. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_3H_7N_4O_2$ 131.0564; Found 131.0565.

Procedure to prepare amidines 3j-3k*[100]*: A stirred mixture of carbodiimide (N, N-diisopropylcarbodiimide, 2.52g, 20 mmol) and NH_4Cl (2.14 g, 40 mmol) in dry acetonitrile (10 mL) was heated under reflux for 24 h. Then cooled the mixture (0 °C) and obtained the colorless crystals (guanidinium chloride) by filtering. The crystals were suspended in dichloromethane (50 mL) and basified with aqueous NaOH (40%, 30 mL). The aqueous layer was extracted with dichloromethane (3 × 50 mL). The combined organic layer was dried over powder KOH, filtered, evaporated under reduced pressure and dried in vacuo to give the product.

(E)-1,2-diisopropylguanidine (**3j**)[100]: white solid (1.718 g, yield 60.0%), mp: 62 – 64 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.64 (p, *J* = 6.3 Hz, 2H), 1.14 (d, *J* = 6.4 Hz, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.0, 77.4, 43.0, 23.4. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_7H_{18}N_3$ 144.1495; Found 144.1495.

(E)-1,2-di-tert-butylguanidine (**3k**)[100]: white solid (1.64 g, yield 47.8%), mp: 136 – 138 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 1.31 (s, 24H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 157.8, 77.4, 50.2, 30.0. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_9H_{22}N_3$ 172.1808; Found 172.1807.

3l was prepared according to literature[100]: A stirred solution of N, N-diisopropylcarbodiimide (2.52 g, 20 mol) and isopropylammonium chloride (2.39 g, 25 mmol) in ethanol (10 mL) was heated under reflux for 24 h, followed by distillation of the solvent in vacuo. The residue was dissolved in water and the solution made basic with aq. NaOH (20%). Extracted with dichloromethane, dried of the combined org. layers with K_2CO_3, filtered evaporated under reduced pressure and dried *in vacuo* to give the product.

1,2,3-triisopropylguanidine (**3l**) white solid (2.33 g, 63% yield), mp: 57 – 59 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.62 – 3.25 (m, 3H), 1.08 (m, *J* = 6.4, 1.8 Hz, 18H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.2, 44.5, 23.9. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ Calcd for $C_{10}H_{24}N_3$ 186.1965; Found 186.1962.

Procedure to prepare amidines 3m - 3o[101]: A mixture of amine (isopropylamine, 1.18 g, 20 mmol) and DMF dimethyl acetal (3.57 g, 30 mmol) in methanol (30 mL) was heated to 70 °C with stirring under a N_2 atmosphere for 3 h or until completion as indicated by TLC. The mixture was cooled to room temperature, and the product was isolated via evaporated to dryness to give the crude product **3m - 3o**. Purified it by distillation or column separation to obtained the product.

(E)-N′-isopropyl-N,N-dimethylformimidamide (**3m**)[102]: Colorless transparent liquid (reduced pressure distillation, 1.48 g, 64.9% yield); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.35 (s, 1H), 3.23 (p, *J* = 6.3 Hz, 1H), 2.71 (s, 6H), 1.00 (d, *J* = 6.3 Hz, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 152.6, 55.1, 36.5, 25.9.

(E)-N′-tert-butyl-N,N-dimethylformimidamide (**3n**)[103]: Colorless transparent liquid (reduced pressure distillation, 1.86 g, 72.4% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 (s, 1H), 2.83 (s, 6H), 1.18 (s, 9H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.3, 52.3, 36.3, 31.3.

(E)-N,N-dimethyl-N′-phenylformimidamide (**3o**)[104]: Purification by column separation (CH_2Cl_2/MeOH = 20/1, v/v), light yellow oil (2.76 g, 93.2% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.52(s,

1H), 7.30 – 7.23 (m, 2H), 7.01 (m, *J* = 7.3, 1.1 Hz, 1H), 6.98 – 6.94 (m, 2H), 3.02 (s, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 153.4, 152.0, 128.7, 121.5, 120.8, 33.9.

Characterization for Photosensitizers:

10-methyl-9-phenylacridin-10-ium perchlorate (Mes-Acr$^+$)[105]: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.81 (m, *J* = 9.3, 2.0 Hz, 2H), 8.41 (m, *J* = 8.8, 6.6, 1.8 Hz, 2H), 7.85 (m, *J* = 8.7, 1.8 Hz, 2H), 7.83 – 7.74 (m, 2H), 7.16 (s, 2H), 5.11 (d, *J* = 2.0 Hz, 3H), 2.48 (d, *J* = 2.0 Hz, 3H), 1.73 (d, *J* = 2.0 Hz, 6H).

3,3′,5,5′-tetraphenyl-ms-aza-2,2′-dipyrrolylmethene difluoroborate (Aza-BODIPY)[106]: ^{1}H NMR (400 MHz, Chloroform-d) δ 8.07 (td, J = 7.2, 6.7, 2.1 Hz, 8H), 7.68 – 7.33 (m, 12H), 7.04 (s, 2H).

Reaction in microreactors: A Corning Advanced Flow Reactors (Lab reactors) were used for the reaction investigation. To guarantee sufficient light and reaction time, two lab reactor reaction modules (internal volume: 2.7 mL, L × W × H : 155 mm × 125 mm ×8 mm, with an extra white LEDs light strip 20 W, 4000 K) and a lab photo reaction module (internal volume: 3 mL, L × W × H : 155 mm × 125 mm ×8 mm; equipped with an original LEDs Light module, 20 W, 4000 K) were used (Figures S2 and S3,). Total power of the LEDs light was 40 W. The total internal volume of reaction modules is 8.4 mL. A circulating temperature bath (thermostat) pumped oil through an integrated heat-exchanger to maintain the reaction temperature at 20 °C. A back pressure regulator (0-20 bar) was added to the outlet of the lab photo reaction module to increase the solubility of O_2. O_2 was inlet to the reaction modules with the gas dosing line in the dosing module (including a mass flow gas controller). The reaction mixture was inlet to the reaction modules with the liquid dosing line in the dosing module.

The reaction in microreactors was a recirculating reaction. The reaction mixture was prepared by dissolving **1a** (1.67g, 8 mmol), **3b** (3.68 g, 32 mmol) and H_2TPP (24 mg, 0.04 mmol) in dioxane (total volume of 20 mL) in a reaction tube (Tube #1, 50 mL) with the assist of ultrasound. Then, inlet the reaction mixture (1.00 mL/min) and O_2 (10.0 mL/min, calculated at standard state (298.15 K, 1 atm)) to the microreactors with the dosing module. A back pressure regulator (0-20 bar) connected to the outlet of the lab photo reaction module was used to maintain the pressure at 10 bar. The outlet of the back pressure regulator was directly attached to the original reaction tube (Tube #1, the reaction tube was connected to air with a pipe to release the excess O_2 and relieve pressure quickly) and the reaction mixture was circulated. O_2 was continuously inlet to the microreactors in the full process (without reuse).

$$\text{Total residence time} = \mathrm{N} \times \frac{\mathrm{V}_1}{v_{liq,R} + v_{gas,R}}$$

$$\text{Total time} = \mathrm{N} \times \frac{\mathrm{V}_2}{v_{liq,R}}$$

Therefore,

$$\text{Total residence time} = \text{Total time} \times \frac{\mathrm{V}_1}{\mathrm{V}_2} \times \frac{v_{liq,R}}{v_{liq,R} + v_{gas,R}}$$

N reafers to the number of the reaction cycles. $v_{liq,R}$ and $v_{gas,R}$ refer to the flow rate of the reaction mixture and O_2 (at 10 bar), respectively, $v_{liq,R} = 1.00$ mL/min and $v_{gas,R} = 1.0$ mL/min (10 bar). V_1 refers to the total volume of the reaction module, $V_1 = 8.4$ mL. V_2 refers to the total volume of the reaction mixture including the reaction mixture in the reaction module, in the pipe and in the reaction tube, $V_2 = 20$ mL.

Therefore,

$$\text{Total residence time} = \text{Total time} \times 0.21$$

The product was isolated by the following experimental procedures: firstly added 200 mL CH_2Cl_2 to the reaction mixture, then washed with HCl aqueous solution (1 mol/L) and saturated brine solution, dried over anhydrous sodium sulfate, filtered, removed the solvent by evaporating under reduced pressure and dried in vacuo to obtained the crude product (yield of 94%). Removed the H_2TPP by adding mixture solution of MeOH / CH_2Cl_2 (to remove the H_2TPP). Filtered and removed the solvent by evaporating under reduced pressure. Purified it by chromatography (silica gel) to afford the final product (yield of 90%).

Method to determine the crude yields: The NMR yield was determined by the normalization method of peaks area shown in Figure S1.

Singlet oxygen quantum yields: The Singlet oxygen quantum yields (Table S3) were determined according to Zhao's literature[107]. The quantum yield of singlet oxygen of the each photosensitizer was obtained by measuring the degradation of 1,3-diphenylisobenzofuran (DPBF) in the presence of the photosensitizers and light. A mixed solution of the photosensitizer (5 μM) and DPBF (50 μM) in DMF was irradiated with a white light (LEDs, 10 W) and the absorption value at 417 nm was determined by using a UV-vis spectrophotometer (UV-9000S, China) every 20 s in 2 min. The control group of adding methylene blue was conducted under the same conditions ($\Phi_{\mathrm{ref}} = 0.49$). The singlet oxygen quantum yield was calculated by the equation: $\Phi_{\mathrm{PS}} = \Phi_{\mathrm{ref}} \times \frac{k_{\mathrm{PS}}}{k_{\mathrm{ref}}}$. The observed rate constants (k_{obs}) were calculated from $\ln(\mathrm{A}_0/\mathrm{A}) = k_{\mathrm{obs}} \times t$ where A_0 and A represent the ultraviolet visible absorbance at time 0 and time *t*, respectively.

■ CALCULATION SECTION

General All calculations were performed with Gaussian 09 program[108]. The M06 functional[109,110] was used for geometry optimization and frequency calculations without any symmetry or geometrical constraints. The 6-31+G(d, p) basis set was used for C, H, N and O atoms. To obtain more accurate energies, single-point energy calculations were performed with larger basis set viz., 6-311++G(d,p) for C, H, N and O atoms. The solvation energies were calculated on the basis of gas-phase optimized geometries by using the CPCM solvation model and toluene was taken as the solvent ($\boldsymbol{\varepsilon}$ = 2.37)[111]. The free energy in solution obtained from such a single-point calculation, including Gibbs free energy correction from the frequency calculation, was used for description of energy profiles.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI *****.

Table S1-S2; Figure S1 – S10; Cartesian coordinates of optimized all stationary points together with their single-point energy (a.u.) in solution and the imaginary frequencies (cm^{-1}) of transition states; GC – MS for the reaction system of **1r** and **1s**; copies of ^{1}H and ^{13}C NMR spectra of **1a** – **1q**, **1t**- **1u**, **2a** – **2q**, **3c** – **3o**; HRMS spectra of **1a**, **2a**, and **3c**, **3e**-**3g**, **3i** -**3l**; copies of ^{1}H NMR spectra of **Mes-Acr$^+$**, **Aza-BODIPY**. (PDF)

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Notes

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