Green Chemistry

ROYAL SOCIETY OF CHEMISTRY

PAPER

View Article Online
View Journal

Check for updates

Cite this: DOI: 10.1039/d1gc00716e

Visible-light-initiated catalyst-free oxidative cleavage of (*Z*)-triaryl-substituted alkenes containing pyridyl motif under ambient conditions†‡

Wenjing Li,[a] Shun Li,[a] Lihua Luo,[a] Yicen Ge,[b] Jiaqi Xu,[a] Xueli Zheng,[a] Maolin Yuan,[a] Ruixiang Li,[a] Hua Chen[a] and Haiyan Fu*[a]

Received 24th February 2021,
Accepted 6th April 2021

DOI: 10.1039/d1gc00716e

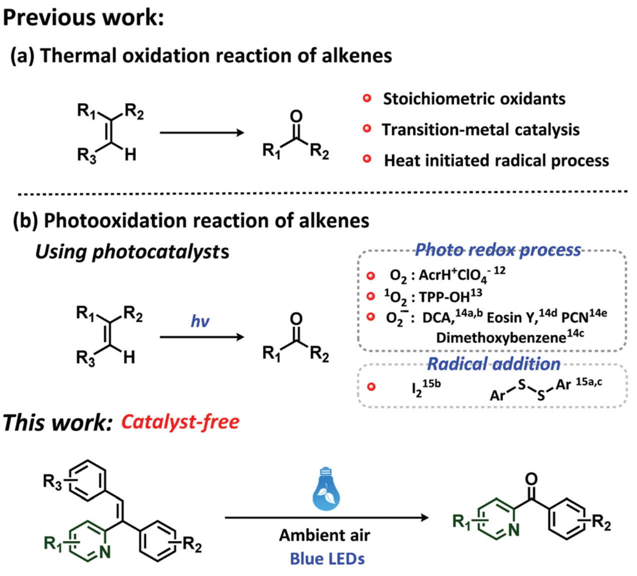
rsc.li/greenchem

The catalyst-free oxidative cleavage of (*Z*)-triaryl-substituted alkenes bearing a pyridyl motif in ambient air under the irradiation of blue LEDs at room temperature has been developed. The reaction was facile and scalable, and proceeded with good functional group tolerance, affording pharmaceutically useful 2-acyl pyridines. The electron paramagnetic resonance (EPR) studies together with control experiments showed that the singlet oxygen ($^1O_2$) and superoxide anion ($O_2^{\bullet-}$) are the reactive oxidants. The $^1O_2$ generation mechanism correlated well with the photophysical properties of the substrate (*Z*)-triaryl-substituted alkenes, the excited state of which was proved to serve as the triplet sensitizer for the generation of $^1O_2$.

Introduction

Compounds bearing the carbonyl moiety, such as aldehydes and ketones, are of great synthetic interest in pharmaceutical development, chemical biotechnology, industrial processes and materials science.[1] Among various synthetic approaches, direct oxidative cleavage of unsaturated bonds of alkenes is a classic and facile way to acquire carbonyl compounds.[2] Traditionally, C=C bonds can be cleaved by ozonolysis,[3] Lemieux–Johnson oxidation,[4] transition metal (Ru,[5] Au,[6] Pd,[7] Pt,[8] Fe,[9] Cu[10]) catalyzed oxidation, or thermally initiated radical processes[11] (Scheme 1, eqn (a)). However, these methods often employ super-stoichiometric oxidants, a series of specific additives, or heavy metals as catalysts under harsh reaction conditions. As a result, large amounts of hazardous and toxic waste are generated afterwards, which does not meet the requirements of green and sustainable chemistry.

Due to the increasing demand for environmentally friendly synthesis, molecular O_2 as an abundant, clean, cheap, and safe oxidant has become a good choice for C=C bond oxidation, especially activated by clean and renewable light irradiation. The existing protocols of alkene photooxidation typically require external photocatalysts, such as Fukuzumi catalyst 10-methylacridinium perchlorate ($AcrH^+ClO_4^-$),[12] 5,10,15-triphenyl-20-(4-hydroxy-phenyl)-21*H*,23*H*-porphyrin (TPP-OH),[13] 9,10-dicyanoanthracene (DCA),[14a,b] dimethoxybenzene,[14c] Eosin Y,[14d] polymeric carbon nitrides (PCN),[14e]



Scheme 1 Methodologies for the oxidative C=C bond cleavage of the alkene.

---

[a] *Key Laboratory of Green Chemistry & Technology, Ministry of Education College of Chemistry, Sichuan University, Chengdu, 610064, P. R. China. E-mail: scufhy@scu.edu.cn*

[b] *College of Materials, Chemistry and Chemical Engineering, Chengdu University of Technology, No.1 3rd Erxian Road East, Chengdu, 610059, P. R. China. E-mail: geyicen@cdut.edu.cn*

† Dedicated to Prof. Christian Bruneau for his outstanding contribution to catalysis.

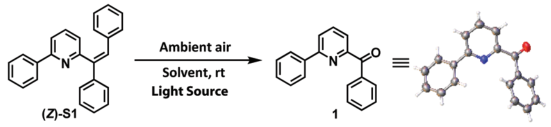
‡ Electronic supplementary information (ESI) available. CCDC 2055782. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1gc00716e

disulfide,[15a,c] and I_2 [15b] (Scheme 1, eqn (b)). Under the irradiation of light, the photocatalysts are excited to higher energy states from their ground states, thereby exhibiting stronger oxidizing ability. The excited photocatalysts oxidize the alkene to give the corresponding radical cation, which then reacts with either molecular O_2 [12] or reactive oxygen species such as singlet oxygen ($^1O_2$)[13] and superoxide anion ($O_2^{\bullet-}$),[14] thus facilitating the oxidative cleavage of C═C bonds. Alternatively, the alkene oxidation reaction could also occur *via* photoinitiated radical addition processes, for example, visible-light-mediated I_2 and disulfide catalytic systems.[15] However, the requirement of an external photosensitizer in these systems makes them less attractive owing to economic and environmental concerns. In this regard, the development of reactions without external photocatalysts or photomediators is attracting growing interest. Recently, several elegant organic transformations have been successfully achieved in the absence of a photocatalyst with photoactive substrates.[16] For example, in 2018, Wang[17] reported a selective remote C–H trifluoro-methylation of aminoquinolines with CF_3SO_2Na under visible-light irradiation in air without an external photocatalyst. Later, Wei[18] described the visible-light-driven reaction of aryldiazo sulfones with thiols to synthesize unsymmetrical sulfoxides by employing O_2 as an oxidant. Most recently, He[19] developed the visible-light-induced decarboxylative acylation of quinoxalin-2(1*H*)-ones with α-oxo carboxylic acids in ambient air. The reactivity of this transformation was attributed to the singlet $^1O_2$ formed from the ground state triplet O_2 ($^3O_2$) *via* energy transfer with the photoexcited substrate. Nevertheless, further explanations about the reason why the substrate could act as a photosensitizer of $^3O_2$ to produce $^1O_2$ are still lacking.

Herein, we describe an oxidative cleavage of (*Z*)-triaryl-substituted alkenes containing a pyridyl motif in ambient air as a green oxidant. The reaction gave rise to a series of 2-acyl pyridines under the irradiation of blue LEDs without an external photocatalyst. To the best of our knowledge, it represents the first catalyst-free alkene photooxidation system. Mechanistic studies revealed that the reaction was enabled by photoinduced $^1O_2$ and $O_2^{\bullet-}$ which were produced *via* the energy transfer and single electron transfer (SET) process, respectively, between the triplet excited state of the substrate and molecular O_2.

2-Pyridyl containing triaryl-substituted alkenes were synthesized by using our previously developed pyridinium salts alkenylation reaction.[20] We initiated our investigations by irradiating the solution of (*Z*)-2-(1,2-diphenyl-vinyl)-6-phenylpyridine (*Z*)-**S1** with a 30 W blue LEDs (380–410 nm) in ambient air at room temperature. As shown in Table 1, solvents had a great influence on the reaction. Polar solvents such as dimethyl sulfoxide (DMSO), *N*,*N*-dimethylacetamide (DMAc), and *N*,*N*-dimethylformamide (DMF) showed moderate activities, affording the desired product phenyl(6-phenylpyridin-2-yl)methanone **1** in 52–67% yields (Table 1, entries 1–3). Non-polar solvents, such as dichloroethane (DCE), tetrahydrofuran (THF), acetonitrile (CH_3CN), 1,4-dioxane, and toluene, were found to be not suitable for this reaction and only led to the formation of a trace amount of the product (entries 4–8). In contrast, alcohol solvents such as ethanol (EtOH), isopropanol (IPA), and methanol (MeOH) could increase the yields over 70% (entries 9–11). The highest yield obtained was 83% in MeOH. It should be noted that benzaldehyde was always detected along with compound **1** in around 40–60% yields. When the reaction was irradiated under UV light, however, only 39% yield of the product was formed (entry 12). The control experiments showed that both light and O_2 in air play a crucial role in the process, as no reaction occurred either without light or in a nitrogen atmosphere (entries 13 and 14). It was noteworthy that besides the oxidation product there is also a small amount of (*Z*)-**S1** which was isomerized to its *E*-isomer under photooxidation conditions (Table S2‡). In the case of pure (*E*)-**S1** as the substrate, while the *E* → *Z* isomerization of alkenes also occurred to a different extent, no C═C oxidation product was detected (Table S3‡). In addition, triphenylethylene and other *Z*-configurational heteroaryl substituted alkenes failed to be photooxidized under the optimal conditions (Table S4‡). These results revealed that both the *Z*-configuration and pyridyl motif were responsible for the realization of the present external catalyst-free photooxidation reaction.

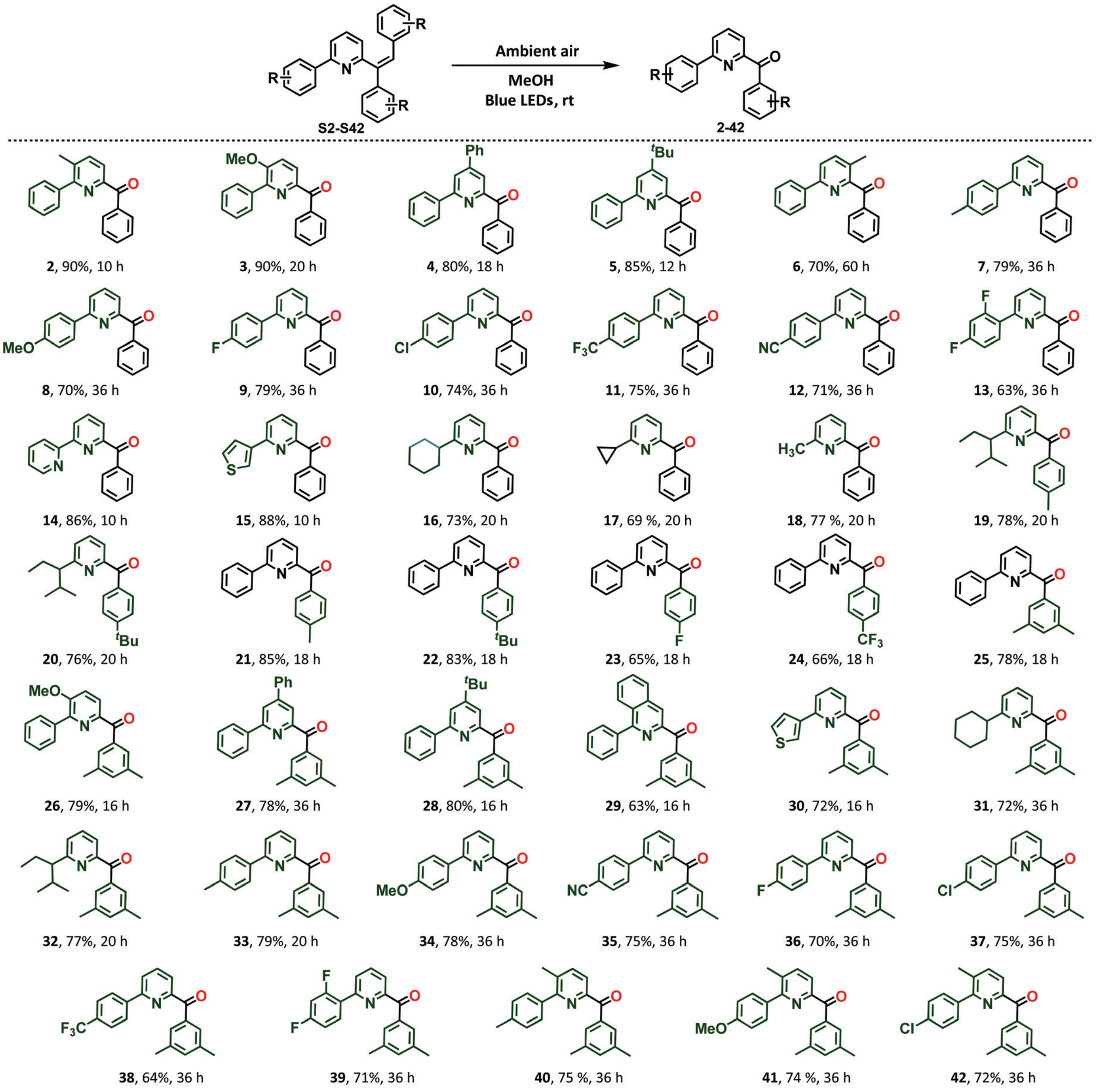
Table 1 Optimization of the reaction conditions[a]



Entry	Light source	Solvent	Yield[b] (%)	Benzaldehyde
1	Blue LEDs	DMSO	60	42
2	Blue LEDs	DMAc	67	45
3	Blue LEDs	DMF	52	40
4	Blue LEDs	DCE	Trace	NR
5	Blue LEDs	THF	Trace	NR
6	Blue LEDs	CH_3CN	Trace	NR
7	Blue LEDs	1,4-Dioxane	Trace	NR
8	Blue LEDs	Toluene	Trace	NR
9	Blue LEDs	EtOH	81	58
10	Blue LEDs	Isopropanol	70	50
11	Blue LEDs	MeOH	83	63
12	UV lamps	MeOH	39	Trace
13	Dark	MeOH	NR	NR
14[c]	Blue LEDs	MeOH	NR	NR

[a] Reaction conditions: (*Z*)-**S1** (0.10 mmol), solvent (1 mL), ambient air, 30 W blue LEDs, room temperature, time. [b] Isolated yields. [c] N_2 atmosphere.

With the optimal reaction conditions in hand, we next examined the substrate scope (Scheme 2). In general, this protocol was highly efficient with a broad substrate scope. The use of various electron-rich substituents in the 3-, 4-, or 5-position of the pyridine ring had little influence on the oxidation process and the desired 2-acyl pyridine **2–6** were formed in 70–90% yields. Notably, the substrate bearing a methyl group in the 5-position of the pyridine ring required a longer time to afford ketone **6** in moderate yield, probably due to the increased steric hindrance around the reaction centre. A series

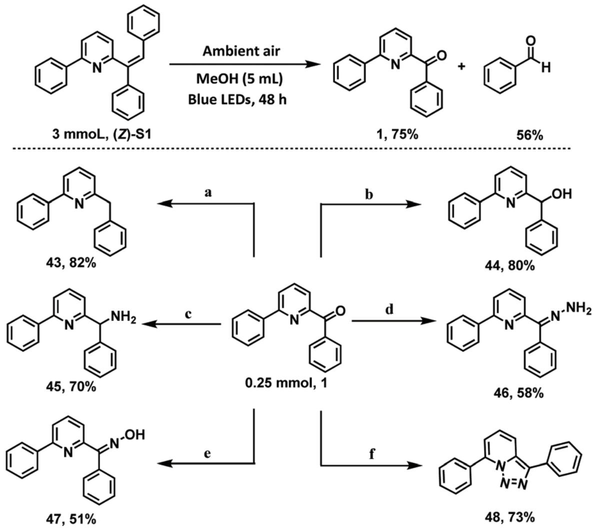


Scheme 2 The substrate scope of (*Z*)-triaryl-substituted alkenes. Reaction conditions: **S2–S42** (0.10 mmol), MeOH (1–3 mL), ambient air, 30 W blue LEDs, room temperature, time. Isolated yields.

of electron-rich and electron-poor functional groups on the adjacent phenyl rings were well tolerated, which delivered the desired 2-acyl pyridine **7–13** in 63–79% yields. In addition, substrates with heterocyclic, cyclohexyl, methyl, or branched alkyl groups at the 2-position of the pyridine moiety were reacted smoothly, providing the corresponding products **14–20** in moderate to excellent yields (69–88%). Meanwhile, the electronic properties of the 1-aryl group had a negligible effect on the reaction, delivering moderate to high yields of the corresponding 2-acyl pyridine **21–24.**

Even for the steric demanding substrates with the bulkier 3,5-dimethylphenyl group, the C=C bonds were still cleaved efficiently to give the corresponding 2-acyl pyridine **25–42** in good yields. Again, various functional groups, such as –F, –Cl, –CN, –OMe, $-CF_3$, alkyls, and heterocycles were well tolerated on the 1-pyridyl motif.

To exemplify the potential applications of the developed process, (*Z*)-2-(1,2-diphenylvinyl)-6-phenylpyridine (*Z*)-**S1** was reacted in MeOH on a 30-times scale under the standard conditions with a prolonged reaction time, and the desired product phenyl(6-phenylpyridin-2-yl)methanone **1** was isolated in a moderate yield of 75%, demonstrating the good scalability of this method. Inconsistent with its versatile derivatization in pharmaceutical synthesis,[21] the resulting 2-acyl pyridine was efficiently converted into the corresponding alfa-pyridyl-substituted phenylmethane **43**,[22a] benzyl alcohol **44**,[22b] benzylic amine **45** [22c] by reduction, hydrogenation, and reductive amination in good yields (Scheme 3a–c). In addition, pyridyl hydra-



Scheme 3 Large-scale synthesis of **1** and its further derivatization. Reaction conditions: (a) NaI (0.5 mmol), HBr (0.625 mmol), CH_3COOH (0.5 mL), H_3PO_2 (0.75 mmol), 115 °C, 12 h; (b) AgOTf (6 mol%), KHMDS (20 mol%), H_2 (20 bar), Toluene (1 mL), 80 °C, 72 h; (c) NH_4OAc (0.5 mmol), $NH_3{\cdot}H_2O$ (0.75 mL), Zn (0.25 mmol), EtOH (1 mL)/H_2O (0.5 mL), 80 °C, 3 h; (d) $NH_2NH_2{\cdot}H_2O$ (0.5 mmol), CH_3COOH (5 μL), EtOH (0.5 mL), 80 °C, 12 h; (e) $NH_2OH{\cdot}HCl$ (0.5 mmol), NaOAc (0.5 mmol), H_2O (0.5 mL)/MeOH (50 μL), 60 °C, 12 h; (f) 1) $NH_2NH_2{\cdot}H_2O$ (0.375 mmol), CH_3COOH (0.025 mmol), EtOH (1 mL), 80 °C, 6 h; (2) Cu $(OAc)_2$ (0.0125 mmol), EtOAc (2 mL), 80 °C, 12 h.

zone **46** and oxime **47** were also readily prepared by the condensation of **1** with hydrazine and hydroxylamine in moderate yields of 58% and 51%, respectively (Scheme 3d and e).[22d,e] Interestingly, the treatment of **1** with $NH_2NH_2.H_2O$ followed by Cu(II)-promoted cyclization gave rise to a triazolo-fused pyridine derivative **48** in 73% overall yield (Scheme 3f).[22f]

To understand this transformation, some control experiments were conducted and the results are shown in Table 2. First, when the typical radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPO) or 2,6-ditertbutyl-4-methylphenol (BHT) was added into the reaction system, the yield was dramatically decreased, revealing that the reaction was likely to proceed involving the radical species (Table 2, entries 1 and 2). Furthermore, when performing the model reaction in the presence of 2 equiv. of $^1O_2$ scavengers, such as 1,4-diazabicyclo[2,2,2]octane (DABCO) and NaN_3,[23] only a trace amount of oxidation product **1** was obtained (entries 3 and 4). In addition, endoperoxide **49** as the [4 + 2] cycloaddition product was detected in a reaction system containing the $^1O_2$ trapping reagent anthracene (entry 5, see the ESI‡ for details).[24] Moreover, the yield of the photooxidation product of (*Z*)-**S1** decreased significantly to 36%, when an $^1O_2$ consuming reagent 1,3-diphenylisobenzofuran (DPBF) was present (Fig. 1).[25] The above experimental results strongly suggested that $^1O_2$ was generated during the transformation. In addition, a superoxide radical anion ($O_2^{\bullet-}$) might also be involved in this oxidation process, since none of the desired product was detected in the presence of $O_2^{\bullet-}$ scavengers, such as 2,2-diphenyl-1-picrylhydrazyl (DPPH) and benzoquinone (entries 6 and 7).[26] Finally, light on–off experiments showed that the product formation was completely suppressed in the absence of light, ruling out a radical chain pathway (Fig. S3‡).

Table 2 Quenching experiments for the oxidative C=C bond cleavage of the alkene[a]

Entry	Quenchers	Yield[b]	Verified reactive species
1	TEMPO	Trace	Radical
2	BHT	Trace	Radical
3	DABCO	NR	$^1O_2$
4	NaN_3	Trace	$^1O_2$
5[c]	Anthracene	6	$^1O_2$
6	DPPH	NR	$O_2^{\bullet-}$
7	Benzoquinone	Trace	$O_2^{\bullet-}$

[a] Reaction conditions: (*Z*)-**S1** (0.10 mmol), quenchers (0.20 mmol), MeOH (1 mL), ambient air, 30 W blue LEDs, room temperature, 12 h. [b] Yields were determined by GC-MS. [c] Endoperoxide **49** was detected.

Electron paramagnetic resonance (EPR) studies were performed to further probe the nature of the radical species formed during the reaction (Fig. 2). With the addition of the

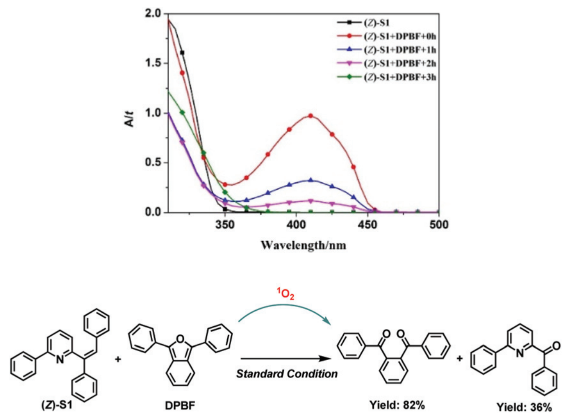


Fig. 1 UV-vis absorption spectra of (*Z*)-**S1** (5×10^{-5} M^{-1}) and DPBF (5×10^{-5} M^{-1}) in MeOH under blue LEDs irradiation.

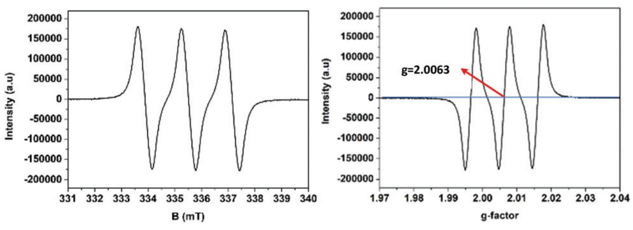


Fig. 2 EPR spectra of the $^1O_2$ adduct with TEMP: magnetic induction intensity B (mT) (Left); *g*-factor (Right).

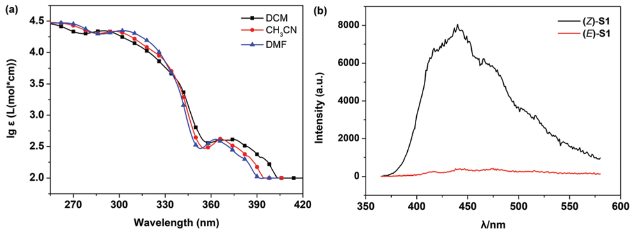


Fig. 3 (a) UV-vis absorption of (*Z*)-**S1** (1×10^{-5} M^{-1}) in DCM (black line), CH_3CN (red line) and DMF (blue line); (b) phosphorescence spectra of (*Z*)-**S1** and (*E*)-**S1** (1×10^{-5} M^{-1}) in 2-MeTHF, 77 K.

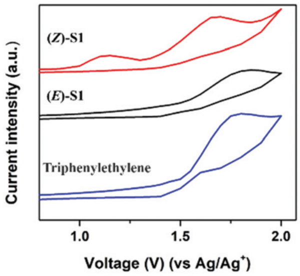
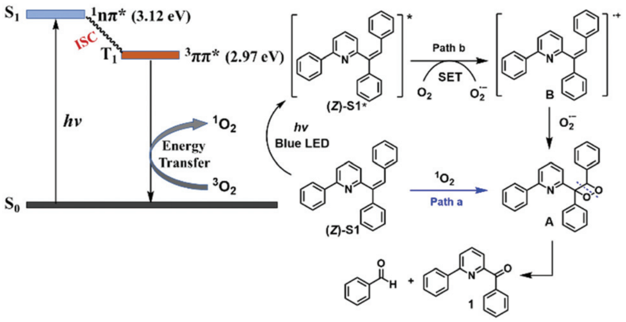


Fig. 4 Cyclic voltammogram.

radical spin trapping reagent 2,2,6,6-tetra-methylpiperidine (TEMP) to the methanol solution of (*Z*)-**S1** (pre-treated by irradiation with blue-LEDs), a triplet EPR signal with a *g*-value of 2.0063 and an a_N value of 16.2 G was observed, and it was assigned to the TEMP-trapped $^1O_2$ species.[17,27] The same signal was also detected in the solution of (*E*)-**S1** under identical conditions (Fig. S11‡). However, no EPR signal was detected in the case of triphenylethylene (Fig. S12‡).

To elucidate the mechanism of $^1O_2$ generation, the UV-vis absorption spectra of (*Z*)-**S1** in dilute DCM (dichloromethane), CH_3CN, and DMF solution (1×10^{-5} M^{-1}) were obtained as shown in Fig. 3a. Negative solvatochromism (namely, the absorption wavelength blue-shifted with increasing solvent polarity) was observed in the weak absorption band (355 nm-400 nm), which was tentatively assigned to $^1n\pi^*$. In addition, the hyperfine structure of the phosphorescence spectrum was assigned to a triplet state with $^3\pi\pi^*$ character. The energy levels of the $^1n\pi^*$ (3.12 eV) and $^3\pi\pi^*$ (2.97 eV) states for (*Z*)-**S1** were determined from the highest energy peak of its phosphorescence emission band at 77 K in 2-MeTHF (Fig. 3b), and the onset of the $^1n\pi^*$ band in more polar DMF, respectively. Thus, from the absorption and emission spectra, the energy difference between the singlet $^1n\pi^*$ and triplet $^3\pi\pi^*$ excited states (ΔE_{ST}) was calculated as 0.15 eV. According to the El-Sayed's rules,[28] such a low ΔE_{ST} value enabled the facile intersystem crossing (ISC) process from the $^1n\pi^*$ to $^3\pi\pi^*$ excited state. Nevertheless, the transition of $^3\pi\pi^*$ to the ground state was spin-forbidden, and thus the lifetime of the triplet $^3\pi\pi^*$ excited states was long enough for the sensitization of $^3O_2$ to $^1O_2$ *via* the energy transfer process. In contrast, the phosphorescence of (*E*)-**S1** was very weak, which indicated a lower triplet yield in the case of (*E*)-**S1**. The different phosphorescence between the two isomers might be ascribed to their structural difference (Fig. S8 and S9‡). The maximum wavelength of the UV-vis absorption spectra of (*E*)-**S1** exhibited a pronounced red-shift in comparison with that of (*Z*)-**S1** (326 nm *vs.* 290 nm) (Fig. S5‡), suggesting that (*E*)-**S1** has a more conjugated π system, which might be caused by the more co-planarity of (*E*)-**S1** (Fig. S7‡). The relatively localized $^1n\pi^*$ state should have a similar energy level for both *Z* and *E* isomers, but the $^3\pi\pi^*$ energy level of (*E*)-**S1** is even lower due to its more conjugational feature, thus resulting in higher ΔE_{ST}.



Scheme 4 The proposed mechanism.

In addition, the cyclic voltammetry (CV) measurement (Fig. 4) demonstrated the oxidation peaks (*vs.* Ag/Ag^+) at 1.00 V, 1.38 V for (*Z*)-**S1**, 1.56 V for (*E*)-**S1**, and 1.52 V for triphenylethylene, respectively. Evidently, (*Z*)-**S1** could be easily oxidized, while the oxidation of (*E*)-**S1** and triphenylethylene was difficult.

Based on the above mechanistic studies and the related literature results,[13,14,29] a plausible mechanism is proposed in Scheme 4. First, the substrate (*Z*)-**S1** (S_0) was excited with light to produce a singlet-excited state (S_1) with $^1n\pi^*$ character, which readily underwent intersystem crossing to the triplet state (T_1) (denoted as (*Z*)-**S1***) due to their small singlet–triplet energy gap. Then the long-lived $^3\pi\pi^*$-featured triplet (*Z*)-**S1*** state sensitized the ground-state triplet oxygen $^3O_2$ to highly reactive singlet $^1O_2$ *via* the energy transfer (ET) process.[30] Subsequently, the resultant $^1O_2$ underwent [2 + 2] cycloaddition with (*Z*)-**S1** to give dioxetane **A** (path a). Alternatively, a SET process occurred between (*Z*)-**S1*** and molecular O_2 to generate a superoxide radical anion ($O_2^{\bullet -}$) and the (*Z*)-**S1**$^{\bullet +}$ **B**,[14] combination of them could also afford dioxetane **A** (path b). Finally, the cleavage of dioxetane **A** generated the desired product **1** and benzaldehyde.

Conclusions

In conclusion, the first external catalyst-free oxidative cleavage of C=C bonds with (*Z*)-triaryl-substituted alkenes has been developed in ambient air under the irradiation of blue LEDs. This oxidation reaction was enabled by employing photoactive

(*Z*)-triaryl-substituted alkenes bearing a 2-pyridyl group, thus affording a variety of pharmaceutically important 2-acyl pyridines with high efficiency. Mechanistic studies revealed that the photoactivated substrate served as a triplet sensitizer to react with $^3O_2$ to produce highly reactive $^1O_2$ or $O_2^{\bullet-}$, which afterwards oxidatively cleaved the C═C bonds of the substrate. The main advantages of this process include using aerobatic air as the oxidant, catalyst-free and mild conditions, and sustainable light as the energy resource.

Author contributions

Wenjing Li: Conceptualization, methodology, investigation, writing – original draft, and visualization. Shun Li: validation and visualization. Lihua Luo: investigation and validation. Yicen Ge: methodology. Jiaqi Xu: resources. Xueli Zheng: resources. Maolin Yuan: resources and methodology. Ruixiang Li: methodology and resources. Hua Chen: resources, supervision, and project administration. Haiyan Fu: conceptualization, writing – review & editing, supervision, project administration, and funding acquisition.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We thank the National Natural Science Foundation of China (No. 22072099 and 21871187) and the Collaborative Fund of Luzhou Municipal Government and Sichuan University (No. 2018CDLZ-13) for financial support. We also thank Professor Zhiyun Lu from Sichuan University for helpful discussions of the $^1O_2$ sensitization mechanism and Chunchun Zhang from the Centre of Testing & Analysis, Sichuan University, for NMR measurements.

Notes and references

1 A. Rajagopalan, M. Lara and W. Kroutil, *Adv. Synth. Catal.*, 2013, **355**, 3321–3335.

2 (*a*) K. Sato, M. Aoki and R. Noyori, *Science*, 1998, **281**, 1646–1647; (*b*) J. P. Wan, Y. Gao and L. Wei, *Chem. – Asian J.*, 2016, **11**, 2092–2102.

3 (*a*) R. Criegee, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 745–752; (*b*) C. E. Schiaffo and P. H. Dussault, *J. Org. Chem.*, 2008, **73**, 4688–4690; (*c*) M. O'Brien, I. R. Baxendale and S. V. Ley, *Org. Lett.*, 2010, **12**, 1596–1598; (*d*) R. Willand-Charnley, T. J. Fisher, B. M. Johnson and P. H. Dussault, *Org. Lett.*, 2012, **14**, 2242–2245; (*e*) K. C. Basavaraju, S. Sharma, R. A. Maurya and D.-P. Kim, *Angew. Chem., Int. Ed.*, 2013, **52**, 6735–6738.

4 R. Pappo, D. S. Allen Jr., R. U. Lemieux and W. S. Johnson, *J. Org. Chem.*, 1956, **21**, 478–479.

5 (*a*) D. Yang and C. Zhang, *J. Org. Chem.*, 2001, **66**, 4814–4818; (*b*) E. A. Nyawade, H. B. Friedrich, B. Omondi and P. Mpungose, *Organometallics*, 2015, **34**, 4922–4931; (*c*) Y.-Q. Zhong, H.-Q. Xiao and X.-Y. Yi, *Dalton Trans.*, 2016, **45**, 18113–18119; (*d*) C. Mi, L. Li, X.-G. Meng, R.-Q. Yang and X.-H. Liao, *Tetrahedron*, 2016, **72**, 6705–6710; (*e*) T. S. Manikandan, R. Ramesh and D. Semeril, *RSC Adv.*, 2016, **6**, 97107–97115; (*f*) D. D. Joarder, S. Gayen, R. Sarkar, R. Bhattacharya, S. Roy and D. K. Maiti, *J. Org. Chem.*, 2019, **84**, 8468–8480.

6 D. Xing, B. Guan, G. Cai, Z. Fang, L. Yang and Z. Shi, *Org. Lett.*, 2006, **8**, 693–696.

7 F. V. Singh, H. M. S. Milagre, M. N. Eberlin and H. A. Stefani, *Tetrahedron Lett.*, 2009, **50**, 2312–2316.

8 (*a*) K. Feng, M.-L. Peng, D.-H. Wang, L.-P. Zhang, C.-H. Tung and L.-Z. Wu, *Dalton Trans.*, 2009, **44**, 9794–9799; (*b*) H. Hong, L. Hu, M. Li, J. Zheng, X. Sun, X. Lu, X. Cao, J. Lu and H. Gu, *Chem. – Eur. J.*, 2011, **17**, 8726–8730.

9 (*a*) A. Dhakshinamoorthy and K. Pitchumani, *Tetrahedron*, 2006, **62**, 9911–9918; (*b*) F. Shi, M. K. Tse, M.-M. Pohl, A. Brckner, S. Zhang and M. Beller, *Angew. Chem., Int. Ed.*, 2007, **46**, 8866–8868; (*c*) A. D. Chowdhury, R. Ray and G. K. Lahiri, *Chem. Commun.*, 2012, **48**, 5497–5499; (*d*) P. Spannring, V. Yazerski, P. C. A. Bruijnincx, B. M. Weckhuysen and R. J. M. KleinGebbink, *Chem. – Eur. J.*, 2013, **19**, 15012–15018; (*e*) A. Gonzalez-de-Castro and J. Xiao, *J. Am. Chem. Soc.*, 2015, **137**, 8206–8218; (*f*) C. P. Yap, J. K. Ng, S. Madrahimov, A. A. Bengali, T. S. Chwee and W. Y. Fan, *New J. Chem.*, 2018, **42**, 11131–11136; (*g*) B.-J. Xiong, X.-Q. Zeng, S.-H. Geng, S. Chen, Y. He and Z. Feng, *Green Chem.*, 2018, **20**, 4521–4527.

10 (*a*) M. M. Hossain and S.-G. Shyu, *Tetrahedron*, 2014, **70**, 251–255; (*b*) M. M. Hossain, W.-K. Huang, H.-J. Chen, P.-H. Wang and S.-G. Shyu, *Green Chem.*, 2014, **16**, 3013–3017; (*c*) D. D. Joarder, S. Gayen, R. Sarkar, R. Bhattacharya, S. Roy and D. K. Maiti, *J. Org. Chem.*, 2019, **84**, 8468–8480.

11 (*a*) R. Lin, F. Chen and N. Jiao, *Org. Lett.*, 2012, **14**, 4158–4161; (*b*) G.-Z. Wang, X.-L. Li, J.-J. Dai and H.-J. Xu, *J. Org. Chem.*, 2014, **79**, 7220–7225; (*c*) T. Wang, X. Jing, C. Chen and L. Yu, *J. Org. Chem.*, 2017, **82**, 9342–9349; (*d*) Z. Cheng, W. Jin and C. Liu, *Org. Chem. Front.*, 2019, **6**, 841–845.

12 K. Suga, K. Ohkubo and S. Fukuzumi, *J. Phys. Chem. A*, 2003, **107**, 4339–4346.

13 R. S. Murthy, M. Bio and Y. You, *Tetrahedron Lett.*, 2009, **50**, 1041–1044.

14 (*a*) J. Eriksen, C. S. Foote and T. L. Parker, *J. Am. Chem. Soc.*, 1977, **99**, 6455; (*b*) J. Eriksen and C. S. Foote, *J. Am. Chem. Soc.*, 1980, **102**, 6083–6088; (*c*) T. Mori, M. Takamoto, Y. Tate, J. Shinkuma, T. Wada and Y. Inoue, *Tetrahedron Lett.*, 2001, **42**, 2505–2508; (*d*) A. K. Singh, R. Chawla and L. D. S. Yadav, *Tetrahedron Lett.*, 2015, **56**, 653–656; (*e*) Y. Zhang, N. Hatami, N. S. Lange, E. Ronge,

W. Schilling, C. Joossc and S. Das, *Green Chem.*, 2020, **22**, 4516–4522.

15 (*a*) X. Baucherel, J. Uziel and S. Juge, *J. Org. Chem.*, 2001, **66**, 4504–4510; (*b*) A. Fujiya, A. Kariya, T. Nobuta, N. Tada, T. Miura and A. Itoh, *Synlett*, 2014, **25**, 884–888; (*c*) Y. Deng, X.-J. Wei, H. Wang, Y. Sun, T. No and X. Wang, *Angew. Chem., Int. Ed.*, 2017, **56**, 832–836.

16 (*a*) Q.-H. Teng, Y. Yao, W.-X. Wei, H.-T. Tang, J.-R. Li and Y.-M. Pan, *Green Chem.*, 2019, **21**, 6241–6245; (*b*) L. Tang, F. Yang, Z. Yang, H. Chen, H. Cheng, S. Zhang, Q. Zhou and W. Rao, *Org. Lett.*, 2021, **23**, 519–524; (*c*) J. Yang, B. Sun, H. Ding, P.-Y. Huang, X.-L. Tang, R.-C. Shi, Z.-Y. Yan, C.-M. Yu and C. Jin, *Green Chem.*, 2021, **23**, 575–581; (*d*) L. Lu, Y. Li and X. Jiang, *Green Chem.*, 2020, **22**, 5989–5994.

17 L. Zhao, P. Li, X. Xie and L. Wang, *Org. Chem. Front.*, 2018, **5**, 1689–1697.

18 Q. Liu, L. Wang, H. Yue, J.-S. Li, Z. Luo and W. Wei, *Green Chem.*, 2019, **21**, 1609–1613.

19 L.-Y. Xie, Y.-S. Bai, X.-Q. Xu, X. Peng, H.-S. Tang, Y. Huang, Y.-W. Lin, Z. Cao and W.-M. He, *Green Chem.*, 2020, **22**, 1720–1725.

20 W. Li, J. Tang, S. Li, X. Zheng, M. Yuan, B. Xu, W. Jiang, H. Fu, R. Li and H. Chen, *Org. Lett.*, 2020, **22**, 7814–7819.

21 (*a*) D. C. Reis, M. C. X. Pinto, E. M. S. Fagundes, S. M. S. V. Wardell, J. L. Wardell and H. Beraldo, *Eur. J. Med. Chem.*, 2010, **45**, 3904–3910; (*b*) I. Karthikeyan, S. K. Alamsetti and G. Sekar, *Organometallics*, 2014, **33**, 1665–1671; (*c*) L. Ren, L. Wang, Y. Lv, G. Li and S. Gao, *Org. Lett.*, 2015, **17**, 2078–2081.

22 (*a*) G. G. Wu, F. X. Chen, D. LaFrance, Z. Liu, S. G. Greene, Y.-S. Wong and J. Xie, *Org. Lett.*, 2011, **13**, 5220–5223; (*b*) S. Wang, H. Huang, S. Tsareva, C. Bruneau and C. Fischmeistera, *Adv. Synth. Catal.*, 2019, **361**, 786–790; (*c*) Y.-M. Cai, X. Zhang, C. An, Y.-F. Yang, W. Liu, W.-X. Gao, X.-B. Huang, Y.-B. Zhou, M.-C. Liu and H.-Y. Wu, *Org. Chem. Front.*, 2019, **6**, 1481–1484; (*d*) Z. Zhang, D. Yadagiri and V. Gevorgyan, *Chem. Sci.*, 2019, **10**, 8399–8404; (*e*) D. Olbert, H. Görls, D. Conrad and M. Westerhausen, *Eur. J. Inorg. Chem.*, 2010, **2010**, 1791–1797; (*f*) D. Rawat, C. Ravi, A. Joshi, E. Suresh, K. Jana, B. Ganguly and S. Adimurthy, *Org. Lett.*, 2019, **21**, 2043–2047.

23 (*a*) J. Kollmann, Y. Zhang, W. Schilling, T. Zhang, D. Riemer and S. Das, *Green Chem.*, 2019, **21**, 1916–1920; (*b*) Y. Li, T. Mou, L. Lua and X. Jiang, *Chem. Commun.*, 2019, **55**, 14299–14302; (*c*) Y. Li, S. A.-e-A. Rizvi, D. Hu, D. Sun, A. Gao, Y. Zhou, J. Li and X. Jiang, *Angew. Chem., Int. Ed.*, 2019, **58**, 13499–13506; (*d*) L. Lu, Y. Lia and X. Jiang, *Green Chem.*, 2020, **22**, 5989–5994; (*e*) M. B. Reddy, N. Neerathilingam and R. Anandhan, *Org. Chem. Front.*, 2021, **8**, 87–93.

24 (*a*) M. Fu, X. Ji, Y. Li, G.-J. Deng and H. Huang, *Green Chem.*, 2020, **22**, 5594–5598; (*b*) K. Liu, J.-H. Deng, J. Yang, S.-F. Gong, Y.-W. Lin, J.-Y. He, Z. Cao and W.-M. He, *Green Chem.*, 2020, **22**, 433–438.

25 Y. Zhou, W. Liu, Z. Xing, J. Guan, Z. Song and Y. Peng, *Org. Chem. Front.*, 2020, **7**, 2405–2413.

26 H. Lv, R. D. Laishram, J. Li, Y. Zhou, D. Xu, S. More, Y. Daia and B. Fan, *Green Chem.*, 2019, **21**, 4055–4061.

27 (*a*) V. Gómez-Vidales, G. Granados-Oliveros, A. Nieto-Camacho, M. Reyes-Solís and M. Jiménez-Estrada, *RSC Adv.*, 2014, **4**, 1371–1377; (*b*) L.-Y. Xie, T.-G. Fang, J.-X. Tan, B. Zhang, Z. Cao, L.-H. Yang and W.-M. He, *Green Chem.*, 2019, **21**, 3858–3863.

28 J. Zhou, P. Chen, X. Wang, Y. Wang, Y. Wang, F. Li, M. Yang, Y. Huang, J. Yu and Z. Lu, *Chem. Commun.*, 2014, **50**, 7586–7589.

29 D. Wei and F. Liang, *Org. Lett.*, 2016, **18**, 5860–5863.

30 (*a*) S. P. McIlroy, E. Cló, L. Nikolajsen, P. K. Frederiksen, C. B. Nielsen, K. V. Mikkelsen, K. V. Gothelf and P. R. Ogilby, *J. Org. Chem.*, 2005, **70**, 1134–1146; (*b*) C. B. Nielsen, J. Arnbjerg, M. Johnsen, M. Jørgensen and P. R. Ogilby, *J. Org. Chem.*, 2009, **74**, 9094–9104.