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Photoinduced deacylative epoxidation of ketone derivatives with allylic peroxides

Jiangtao Lin,[a] Mingqian Zhou,[a] Ziyang Li,[a] Jiang Duan,[a] Xiaoyu Liu,[a] Yue Wang[a] and Chao Shu *[ab]

Epoxide compounds represent a privileged scaffold with diverse applications in organic synthesis, pharmaceuticals, agrochemicals, and materials science. However, the available routes to obtain such high-value structures from feedstocks, such as ketones, remain less developed. In this work, we report an alternative deacylative epoxidation of ketones using allylic peroxides to produce fused epoxides *via* the photoinduced radical cyclization of ketone-derived pro-aromatic dihydroquinazolinones. This system operates under very mild conditions and showcases a broad substrate scope with excellent functional group tolerance (over 50 examples). Its gram-scale preparation and late-stage transformations emphasize its potential in drug discovery. A possible mechanism has been proposed based on mechanistic studies.

Introduction

Strained three-membered oxygen heterocycles, known as epoxides or oxiranes, are highly valuable motifs in the drug industry with remarkable biological and pharmaceutical activities and are commonly observed in naturally occurring substances, pharmaceutical compounds, materials and synthetic molecules, including 14 FDA-approved drugs (Scheme 1a).[1] In addition, spring-loaded oxiranes have inherent angle strain and two polar bonds, making them highly reactive and rendering them excellent reactive intermediates for constructing new bonds in larger and more complex molecules through nucleophilic ring-opening reactions in the presence of different nucleophiles, such as organolithium, amine, cyanides, thiols, halides and azides.[2,3] The global market for oxiranes is expected to reach $78 billion by 2025, fueled by various applications, such as the production of epoxy resins, surfactants, adhesives, coatings, agrochemicals, and pharmaceuticals.[4]

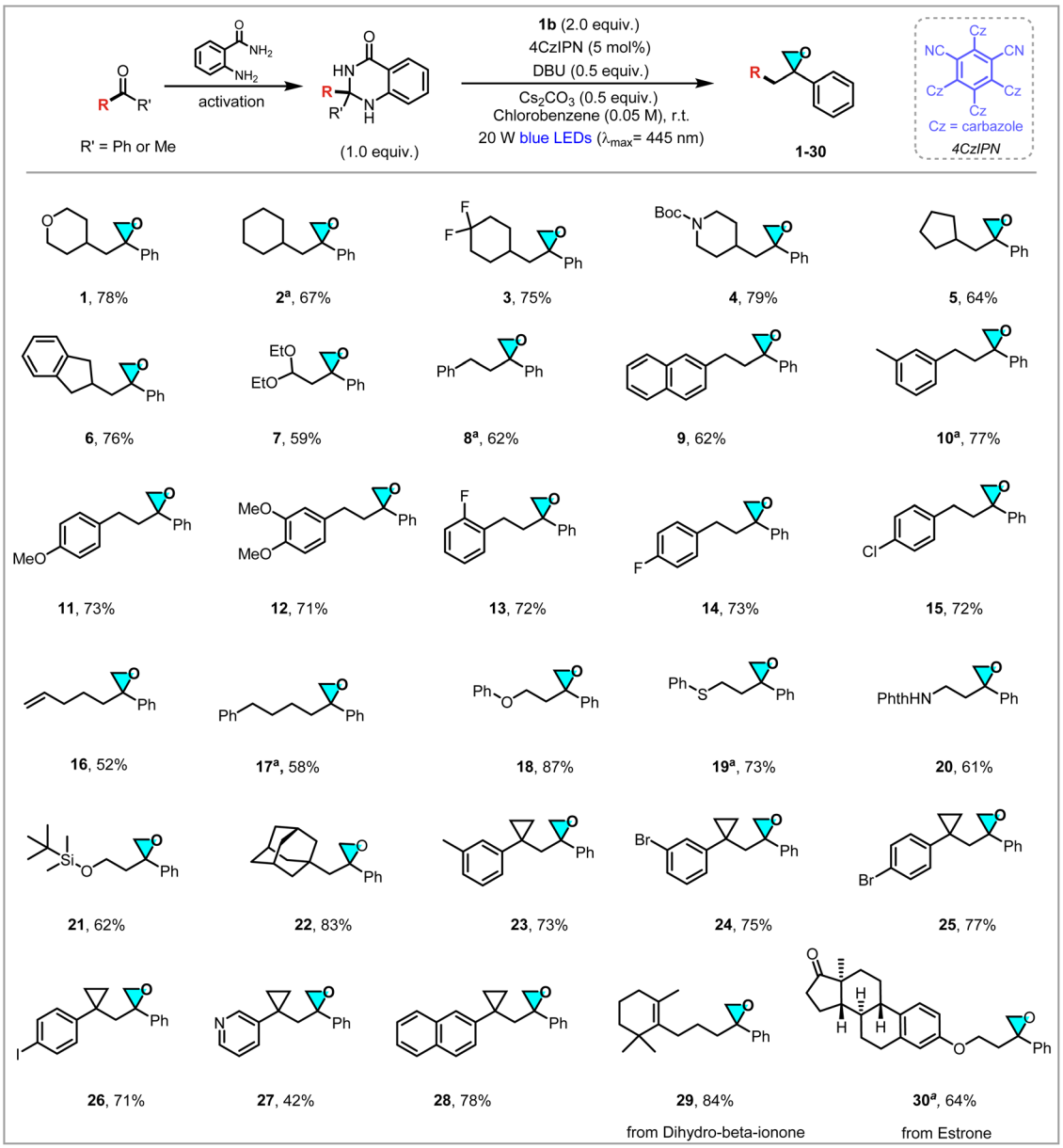
Therefore, the efficient incorporation of oxirane units into organic molecules is an important and challenging objective, particularly when utilizing abundant feedstock chemicals under simple conditions. However, the majority of state-of-the-art methodologies for synthesizing oxiranes are limited to the epoxidation of specific single alkenes using strong oxidizing agents, such as peroxy acids or hydrogen peroxide.[1,5] To explore more readily available substrates and facilitate operational processes, as well as to achieve greater structural diversity in oxiranes, it would be immensely beneficial to develop a straightforward method for converting libraries of cheap feedstocks into their corresponding oxiranes, addressing growing demands in chemical biology and drug discovery.

Among them, ketones (carbonyl compounds) are one of the most common and widely used fundamental skeletons found in many industrial chemicals and pharmaceutical architectures.[6] For example, Darzens condensation involves the reaction of aldehydes or ketones with α-mono- or dihalocarbonyl compounds in the presence of bases to form epoxides (Fig. 1b, left),[7] and the Johnson–Corey–Chaykovsky method[8] is based on the reaction of carbonyl compounds with sulfonium and sulfoxonium ylides, which are often derived *in situ* from sulfonium or sulfoxonium halides containing the mono- or disubstituted methyl group (Fig. 1b, right). However, these well-known reactions still suffer from limitations, such as the requirement for strong bases, aldehyde self-condensation, and the failure to achieve tri-alkyl sulfur ylides. The further elaboration of complex functionalities associated with ketone-containing molecules, such as amino acids, peptides and sensitive drug candidates, poses a synthetic challenge for epoxidation reactions, primarily due to the limited number of reliable methods currently available and their poor compatibility under harsh conditions.

Despite this outstanding work, the exploration of conceptually distinct strategies—especially those avoiding harsh reaction conditions, such as high temperature, excessive additives, long reaction times and limited substrate scope—remains an urgent issue. Developing alternative methods for the direct activation and functionalization of these carbonyl compounds to oxiranes is crucial for improving the quality of chemical raw materials

[a]*State Key Laboratory of Green Pesticide, Engineering Research Center of Photoenergy Utilization for Pollution Control and Carbon Reduction, CCNU-uOttawa Joint Research Centre, College of Chemistry, Central China Normal University, 152 Luoyu Road, Wuhan, Hubei, 430079, China. E-mail: chaoshu@ccnu.edu.cn*

[b]*Wuhan Institute of Photochemistry and Technology, 7 North Bingang Road, Wuhan, Hubei, 430083, China*



Scheme 1 Substrate scope for ketones. Reaction conditions: ketone derivatives (0.2 mmol, 1.0 equiv.), **1b** (0.4 mmol, 2.0 equiv.), 4CzIPN (5 mol%), DBU (0.1 mmol, 0.5 equiv.), Cs_2CO_3 (0.1 mmol, 0.5 equiv.), chlorobenzene (0.05 M), room temperature, under 20 W blue LEDs (λ_{max} = 445 nm), 24 h, in a vial. Isolated yield. The R′ group of the ketone used as the raw material is a phenyl (R′ = Ph) unless otherwise noted. The specific reaction raw materials are referenced in the Supporting Information. [a]The R′ group of the ketone used as the raw material is a methyl group (R′ = Me).

and for the late-stage modification of complex natural products and pharmaceuticals. However, due to the strong bond dissociation energy (BDE) of the C=O double bond, deoxygenation transformations of these functional groups present considerable challenges, especially for unstrained common ketones. Based on Dong's pioneering work on the deconstructive transformations of ketones,[9] alkyl radicals can be generated *via* deacylation through pre-aromatization intermediates like dihydropyrazoles and dihydrotriazoles. Recently, innovative methods have emerged for the deconstructive reactions of ketones, involving their transformation into pro-aromatic compounds known as dihydroquinazolinones (DHQZs), with related studies being reported consecutively (Fig. 1c).[10,11] Seeking a complementary route that would allow the direct transformation of unstrained ketones to oxiranes, we

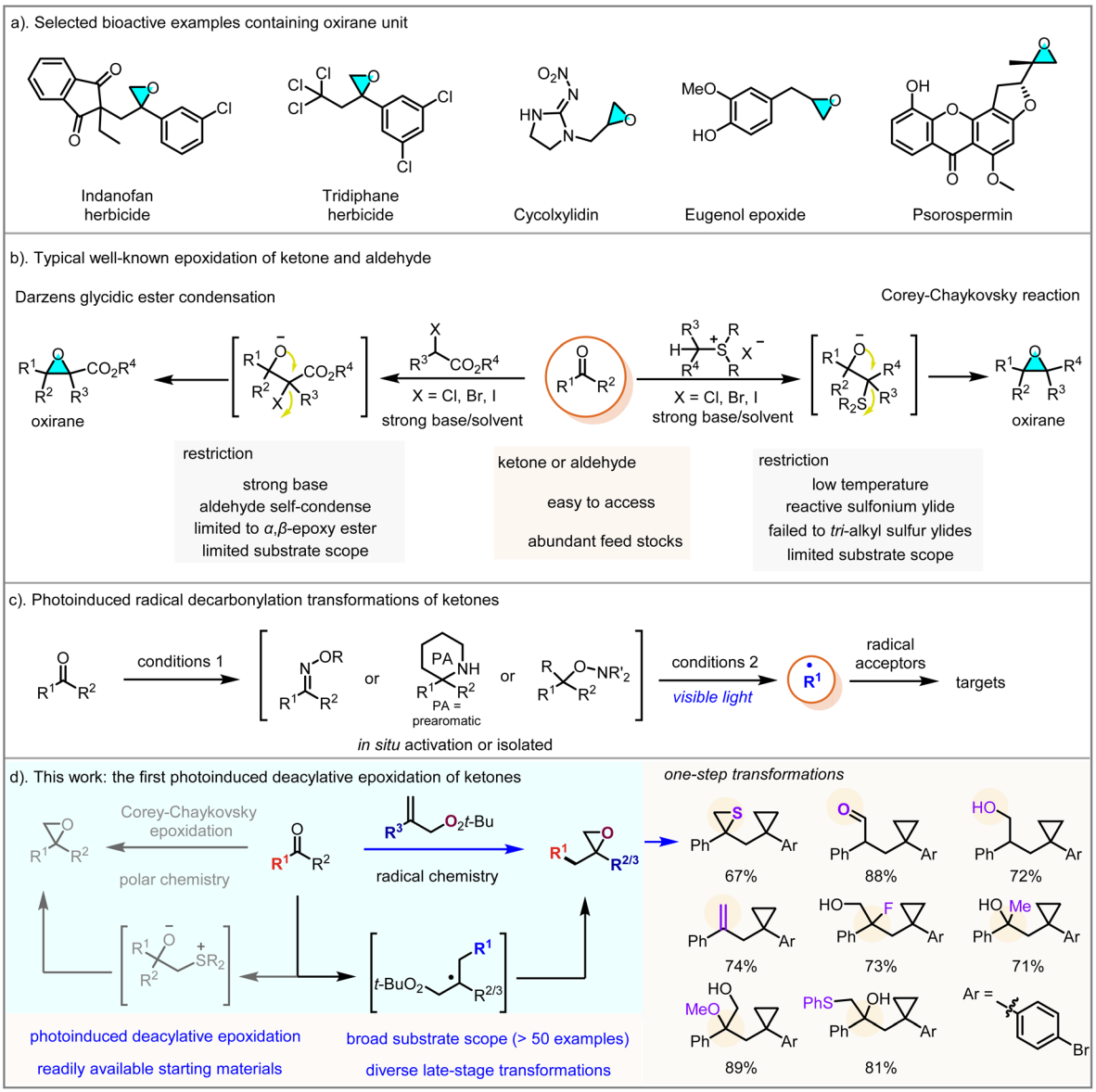


Fig. 1 Background for the synthesis of epoxides and our design. (a) Selected bioactive examples containing oxirane unit. (b) Typical well-known epoxidation of ketone and aldehyde. (c) Photoinduced radical decarbonylation transformations of ketones. (d) This work: the first photoinduced deacylative radical epoxidation of ketones.

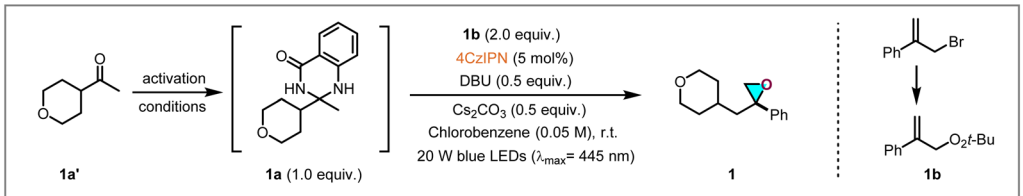
questioned whether deacylative epoxidation could occur through the aromatization-driven deconstructive reaction of ketones.

Based on our continuing interest in environmentally friendly visible-light catalytic cyclization,[12] herein, we report our efforts to develop a new method for the direct deacylative epoxidation of unstrained ketones under exceptionally mild and highly compatible conditions, providing an alternative avenue to access diverse epoxides (Fig. 1D). This versatile protocol requires no additional oxidants or organometallic reagents and features considerable substrate scope, including not only primary, secondary, and tertiary ketones, but also pharmaceutical molecules. Furthermore, the synthetic utility of this protocol is highlighted by its ability to convert epoxide into various valuable functional groups (thiirane, aldehyde, alcohol and other bulky hindered skeletons with quaternary carbon), highlighting its potential applications.

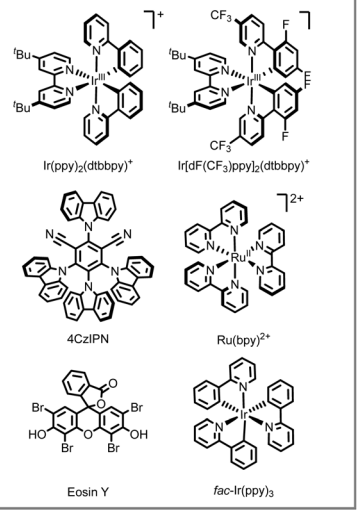
Results and discussion

At the outset of the reaction, DHQZ substrate **1a**, synthesized from a ketone feedstock through a single condensation step,

Table 1 Optimization of the reaction conditions[a]



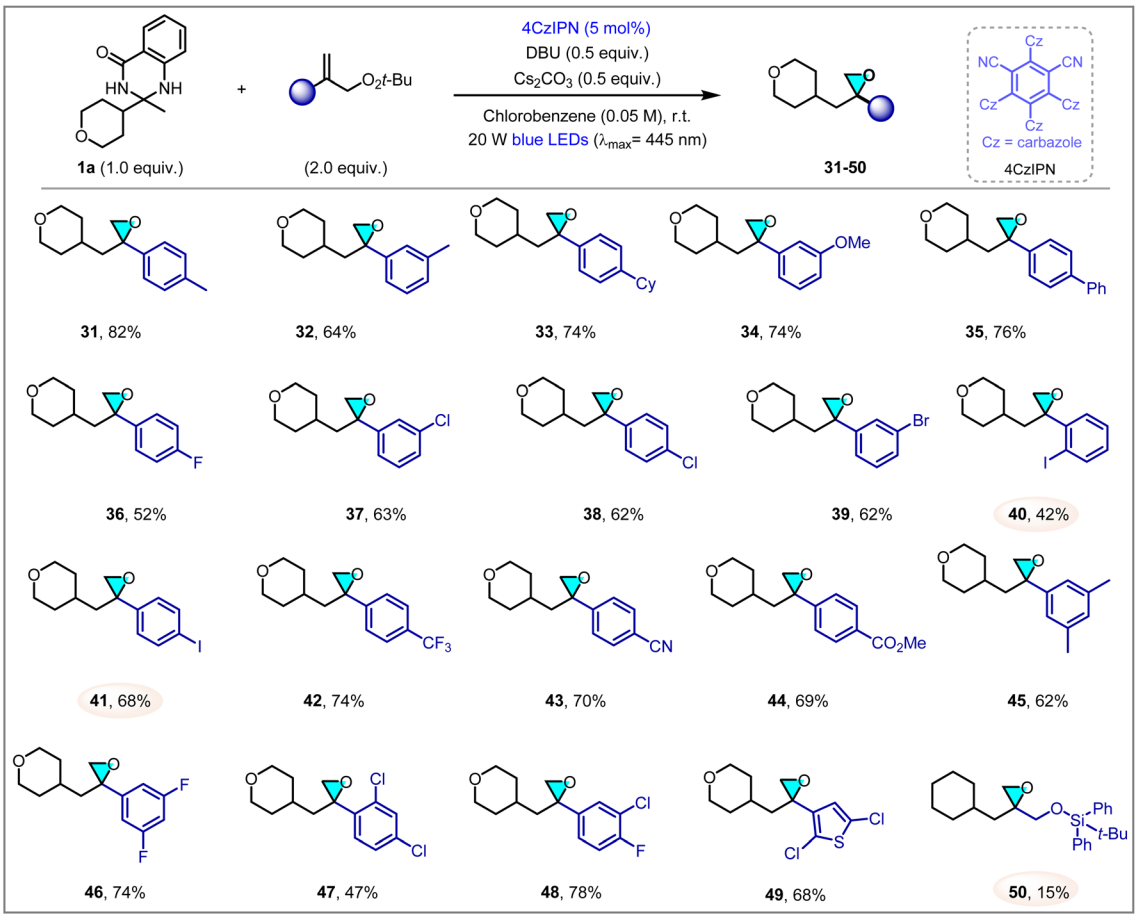
Entry	Variation from standard conditions	Yield of **1** (%)[b]	Conversion of **1a** (%)[b]	Explored photocatalysts
1	None	81	100	
2	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	32	65	
3	$Ir(ppy)_2(dtbbpy)PF_6$	25	68	
4	$Ru(bpy)_2Cl_2$	9	42	
5	Eosin Y	13	55	
6	*fac*-$Ir(ppy)_3$	17	60	
7[c]	Other solvents	<29	<57	
8[c]	Other bases	<32	<64	
9	Without DBU	60	100	
10	Without Cs_2CO_3	38	100	
11	Without light	0	0	
12	Without 4CzIPN	0	0	
13	Under air	31	84	



[a] Reaction conditions: **1a** (0.1 mmol, 1.0 equiv.), **1b** (0.2 mmol, 2.0 equiv.), photocatalyst (5 mol%), DBU (0.05 mmol, 0.5 equiv.), Cs_2CO_3 (0.05 mmol, 0.5 equiv.), chlorobenzene (0.05 M), room temperature, under 20 W blue LEDs (λ_{max} = 445 nm), 24 h, in vial. [b] ^1H NMR yield using 1,2-diethyl phthalate as the internal standard. [c] See SI for details.

and easily accessible **1b** were chosen as the model substrates to explore epoxidation conditions, and selected results are displayed in Table 1. Delightfully, after a survey of reaction conditions, it was found that when a solution of **1a** and **1b** with 0.5 equivalents of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and cesium carbonate (Cs_2CO_3) in the presence of 5 mol% of 4,5,6-tetra(9*H*-carbazol-9-yl)isophthalonitrile (4CzIPN) in chlorobenzene was stirred for 24 h under irradiation by 20 W blue LEDs (λ_{max} = 445 nm) at ambient temperature under N_2 atmosphere, the desired oxirane **1** was obtained in 81% yield (Table 1, entry 1). Other common photocatalysts, such as $Ir[(dF(CF_3)ppy)]_2(dtbbpy)PF_6$, $Ir[(ppy)_2(dtbpy)]PF_6$, $Ru(bpy)_2Cl_2$, Eosin Y or *fac*-$Ir(ppy)_3$ were screened, but provided no improvement over 4CzIPN (Table 1, entries 2–6). The screening of solvents, such as DMSO, DMC, DMA, and NMP, showed that MeCN was more suitable than others (Table 1, entry 7; for more details please see the SI). In addition, different organic or inorganic bases were examined, but no further improvement in yield was obtained (Table 1, entry 8). The developed approach still worked without the involvement of bases DBU or Cs_2CO_3, however, both leading to significantly lower efficiency (Table 1, entries 9 and 10), control experiments revealed that visible light and a photocatalyst are indispensable to the success of the reaction (Table 1, entries 11 and 12). When the reaction was carried out under air conditions, it led to **4a** in lower yield (Table 1, entry 13).

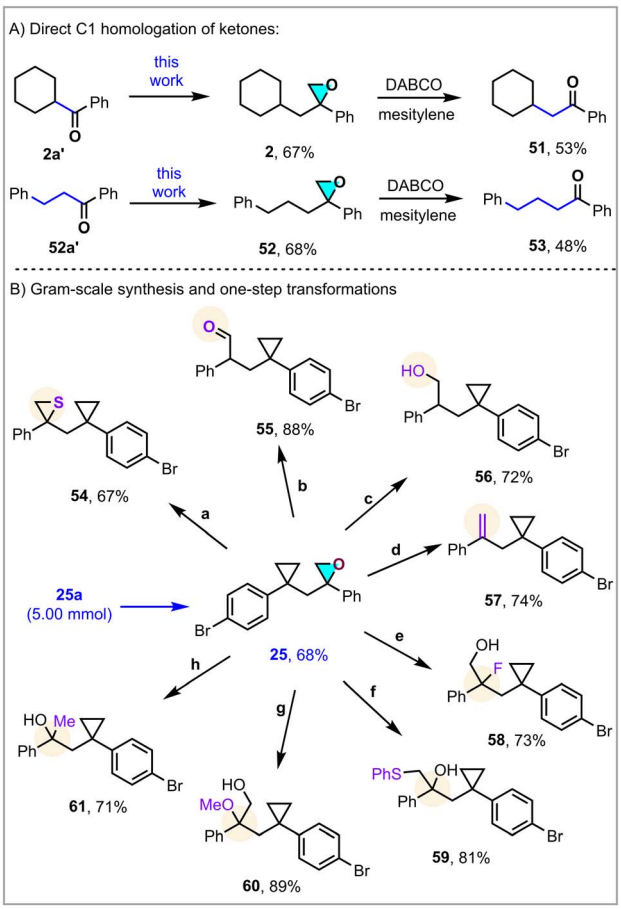
With the optimal conditions in hand for the deacylative epoxidation reaction, we first sought to explore the scope of ketones. As presented in Scheme 1, a range of structurally diverse methyl and phenyl ketones underwent epoxidation site-selectively at the nonmethyl/phenyl side with allylic peroxide to easily afford the corresponding oxiranes in generally moderate to good yields. First, various carbon cyclic and heterocyclic methyl ketones with various ring sizes reacted smoothly to generate secondary alkyl radicals and to form the desired oxiranes **1–5** in 64–79% yields. Benzo-fused cyclic methyl ketone as an indanyl radical precursor and acetal-derived 2,2-diethoxyacetophenone as a masked formyl radical source proved to be competent substrates, to give the corresponding oxiranes **6** and **7** efficiently in 76% and 59% yields, respectively. The protocol successfully accommodated different benzyl methyl ketones, and the substituted benzyl methyl ketone bearing groups, such as Me, OMe, F and Cl, on the aromatic ring were applied, yielding the corresponding oxiranes **8–15** in 56–77%



Scheme 2 The scope of allylic peroxides. Reaction conditions: **1a** (0.2 mmol, 1.0 equiv.), allylic peroxide (0.4 mmol, 2.0 equiv.), 4CzIPN (5 mol%), DBU (0.1 mmol, 0.5 equiv.), Cs_2CO_3 (0.1 mmol, 0.5 equiv.), chlorobenzene (0.05 M), room temperature, under 20 W blue LEDs (λ_{max} = 445 nm), 24 h, in vial. Isolated yields.

yields, and demonstrating that the reaction efficiency is not affected by the electronic properties of the aromatic ring. In addition, primary methyl ketones with alkene (**16**), alkyl (**17**), ether (**18**), thioether (**19**), amino (**20**) or silyl (**21**) residues were compatible partners under current reaction conditions, to deliver the targeted products in 58–87% yields. Linear alkenyl-substituted ketones undergo partial self-cyclization, leading to decreased product yield. Notably, an array of structurally diverse tertiary alkyl methyl ketones could undergo efficient deacylative epoxidation. For example, adamantyl epoxides **22** were obtained in 82% yield. Cyclopropyl ketone tethered with substituted benzene, pyridine or naphthalene also successfully furnished the desired sterically hindered epoxides **23–28** in 42–78% yields. A substrate-bearing pyridine unit is highly polar and poorly soluble in the reaction system, resulting in a lower product yield (**27**). Gratifyingly, ketone substrates derived from bioactive molecules dihydro-β-ionone and estrone afford highly functionalized epoxides **29** and **30** in 84% and 64% yields, respectively, further highlighting the high functional group tolerance and the potential for late-stage functionalization in complex systems. These results significantly expand the synthetic utility of ketones and the accessibility of epoxides, facilitating efficient deacylative epoxidation to versatile oxiranes.

Encouraged by the above results, we next investigated the scope of allylic peroxides (Scheme 2). In general, a collection of aryl allylic peroxides were proven to be viable substrates, affording the 1,1-disubstituted epoxides in moderate to good yields. Aryl substituted by different electron-donating groups, including methyl (**31**, **32**), cyclohexyl (**33**), methoxyl (**34**) and phenyl (**35**), reacted smoothly with **1a** to provide products in good yields (64–82%). Electron-withdrawing groups on the aromatic ring were tolerated as well, leading to the formation of epoxides **36–44** in 42–74% yields. Apart from various halogens (F, Cl, Br, I) on the phenyl of peroxides, giving the products efficiently, other useful substituted groups (CF_3, CN, CO_2Me) also generate the corresponding epoxides in good yields. Notably, some of these groups, such as Br, I and CN, could offer a valuable synthetic handle for further transformations. Additionally, disubstituted aryl peroxides were also tolerated to produce oxiranes **45–48** in 47–78% yield. Neither electron-



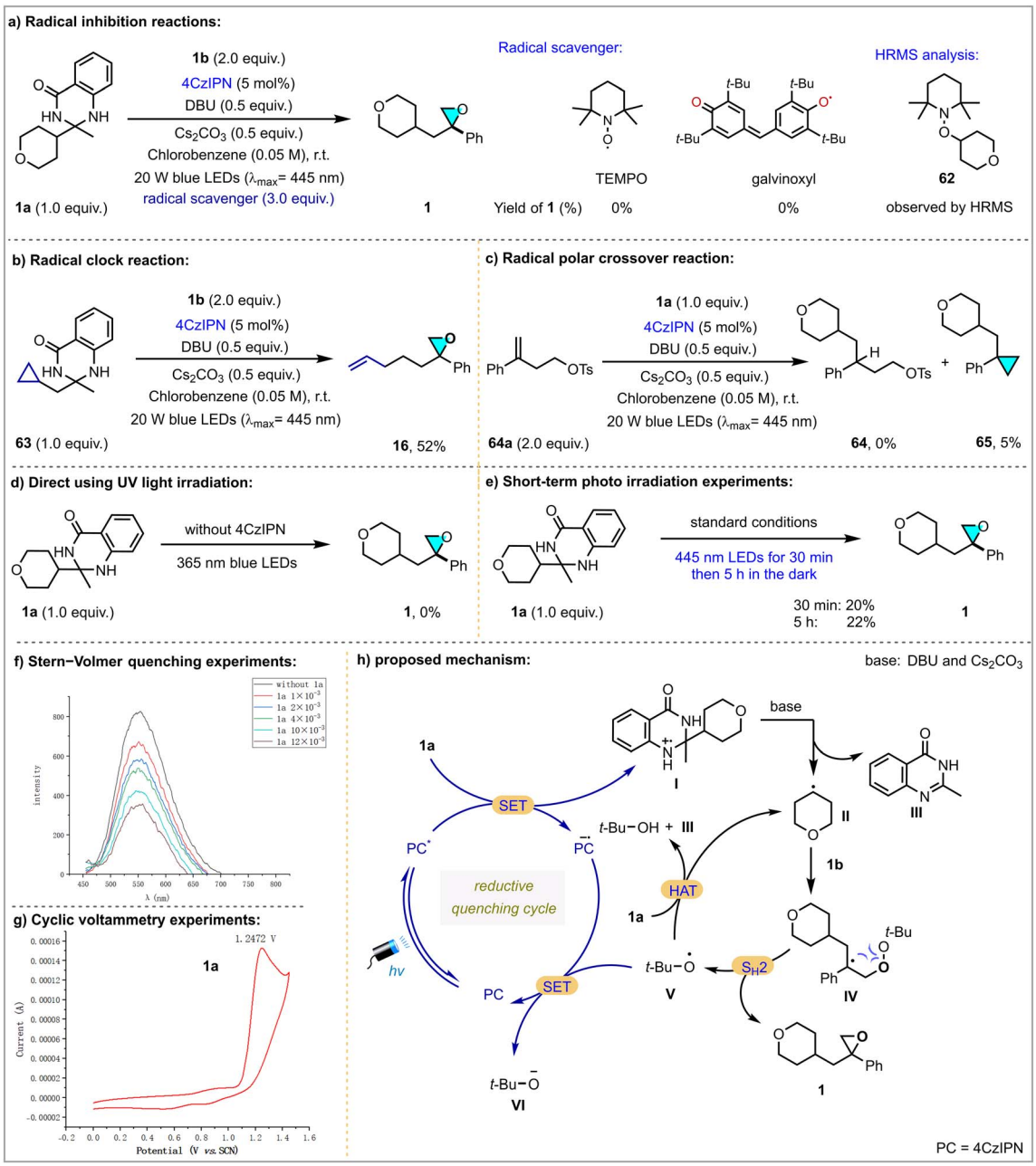
Scheme 3 Gram-scale synthesis and synthetic derivatizations of epoxide. Reaction conditions: (A) 51 : 2 (1.0 equiv.), DABCO (4.0 equiv.), mesitylene, 165 °C. 53 : 52 (1.0 equiv.), DABCO (4.0 equiv.), mesitylene, 165 °C. (B) (a) Thiourea (2.0 equiv.), **25** (0.20 mmol, 1.0 equiv.), MeOH (1.0 mL), r.t., 18 h. (b) $ZnCl_2$ (0.5 equiv.), **25** (0.20 mmol, 1.0 equiv.), toluene (2.0 mL), 110 °C, 4 h. (c) Et_2SiH (2.0 equiv.), TfOH (0.05 equiv.), **25** (0.20 mmol, 1.0 equiv.), HFIP (1.0 mL), r.t., 1 h. (d) PPh_3 (1.2 equiv.), **25** (0.20 mmol, 1.0 equiv.), *i*-PrOH (1.0 mL), 120 °C, 36 h. (e) $Et_3N{\cdot}3HF$ (2.0 equiv.), $BF_3{\cdot}Et_2O$ (0.2 equiv.), **25** (0.20 mmol, 1.0 equiv.), DCM (2.0 mL), r.t., 12 h. (f) C_6H_5SNa (1.5 equiv.), **25** (0.20 mmol, 1.0 equiv.), DMF (4.0 mL), 40 °C, 12 h. (g) HCl (37% in H_2O, 0.005 equiv.), **25** (0.20 mmol, 1.0 equiv.), MeOH (2.0 mL), r.t., 2 h. (h) $LiAlH_4$ (2.0 equiv.), **25** (0.20 mmol, 1.0 equiv.), THF (2.0 mL), r.t., 4 h.

withdrawing nor electron-donating substituents has a significant influence on the reaction. Nevertheless, *ortho*-substituted styrene peroxides markedly reduce the reaction yield, presumably owing to steric hindrance impeding the reaction pathway, as evidenced by products **40** and **47**. Heteroaryl peroxide could also be involved to form oxirane **49** in satisfactory yield (68%) under the current conditions. However, alkyl allylic peroxide resulted in a significantly reduced yield of **50**, likely due to the relatively weak reactivity of alkyl peroxides.

Homologation is a general and valuable synthetic approach used for the elongation of a carbon chain.[13] As demonstrated in Scheme 3A, one-carbon-inserted ketones **51** and **53** were obtained in 53% and 48% yields, respectively, suggesting an alternative way to achieve the one-carbon homologation of carbonyl derivatives without modification of the backbone. Moreover, to demonstrate the scalability and robustness of the method, epoxide **25** was synthesized at gram scale (5.0 mmol) with comparable efficiency (68%) (Scheme 3B). In particular, strained oxiranes, as privileged heterocyclic building blocks, are very valuable motifs in organic synthesis and drug development. By the addition of thiourea, thiirane **54** was obtained in 67% yield. Selective oxidation by $ZnCl_2$ and reduction by Et_2SiH gave primary aldehyde **55** and alcohol **56** in 88% and 72% yields, respectively. Treatment with PPh_3 led directly to the generation of terminal alkene **57** in 74% yield. Ring-opening by $Et_3N{\cdot}3HF$ formed fluorinated product **58** in 73% yield. Other nucleophiles could open the ring to give compounds **59** and **60** under basic and acidic conditions. Sterically hindered tertiary alcohol **61** was delivered with 71% yield in the presence of $LiAlH_4$.

To probe the mechanism of this deacylative epoxidation, the following control experiments were conducted, as shown in Scheme 4. First, radical scavengers 2,2,6,6-tetramethylpiperidinooxy (TEMPO) and galvinoxyl fully inhibited the reaction, and cyclohexyl radical adduct **62** was detected by high-resolution mass spectrometry (Scheme 4a). Subjecting cyclopropane-containing dihydroquinazolinone **63** to a radical clock experiment, ring-opening product **16** was isolated in 52% yield (Scheme 4b). Using alkene **64a** as a radical acceptor, no radical addition product **64** was observed, and only a trace of cyclopropanation product **65** was observed, implying that perhaps no direct radical-polar crossover process may be involved (Scheme 4c). Direct irradiation of the reaction with UV light in the absence of a photocatalyst failed to work (Scheme 4d). In addition, short-term photo-irradiation experiments suggested that a radical chain process is unlikely (Scheme 4e). Stern–Volmer fluorescence quenching experiments revealed that dihydroquinazolinone **1a** is an effective quencher for excited-state 4CzIPN* (Scheme 4f). Cyclic voltammetry (CV) studies provided compelling evidence for the ability of the photocatalyst to activate the substrate, leading to the generation of radical species (Scheme 4g).

Based on the above results and previous reports,[11] a probable catalytic cycle is proposed (Scheme 4h). Initially, photocatalyst 4CzIPN reached excited-state 4CzIPN* by irradiation with visible light. Then, single-electron transfer (SET) between **1a** ($E_{\mathbf{1a}^{\bullet+}/\mathbf{1a}}$ = +1.29 V *vs.* SCE) and 4CzIPN* ($E_{4CzIPN^*/4CzIPN^{\bullet-}}$ = +1.35 V *vs.* SCE)[14] generated $4CzIPN^{\bullet-}$ and radical cation **I**, which underwent rapid homolytic cleavage into carbon radical **II** and quinazolinone **III** under basic conditions. Carbon radical **II** was subsequently captured by allylic peroxide to form open-shell intermediate **IV**. An intramolecular radical homolytic substitution (SH_2) on the oxygen atom of **IV** furnished target oxirane **1**, alongside the release of *t*-$BuO^{\bullet}$ radical intermediate **V**. Finally, single-electron reduction of the *t*-$BuO^{\bullet}$ radical to *t*-BuO^{-} by $4CzIPN^{\bullet-}$ completed the catalytic cycle and regenerated the ground state of the photocatalyst. Meanwhile, a *t*-$BuO^{\bullet}$



Scheme 4 Mechanistic studies and proposed mechanism.

radical could also abstract a hydrogen from **1a** to form carbon radical intermediate **II**.

Conclusions

In conclusion, we introduced a unique concept of epoxidation and developed an efficient deacylative epoxidation strategy for synthesizing diverse oxirane-containing scaffolds. This method uses easily available unstrained ketones and allylic peroxides under exceptionally mild and highly compatible conditions. This transformation proceeds *via* a photoinduced aromatization-driven deconstructive reaction of ketones. This platform is particularly well-suited to the late-stage functionalization of complex natural products and pharmaceuticals with unstrained ketones, owing to its broad substrate scope and high functional group compatibility. Additionally, the ease of subsequent transformations of oxiranes, providing an appealing alternative avenue to polar Corey–Chaykovsky epoxidation for accessing diverse epoxides and their derivatives. Mechanistic investigations suggested that a deacylative radical substitution and cyclization pathway might be involved in the process.

Author contributions

C. Shu designed and directed the investigations and composed the manuscript with revisions provided by the other authors. J.

Lin and M. Zhou developed the catalytic method. Z. Li, J. Duan, X. Liu and Y. Wang studied the substrate scope. All the authors were involved the analysis of results and discussions of the project.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information: experimental procedures, characterization data, and nuclear magnetic resonance spectra. See DOI: https://doi.org/10.1039/d6sc00898d.

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