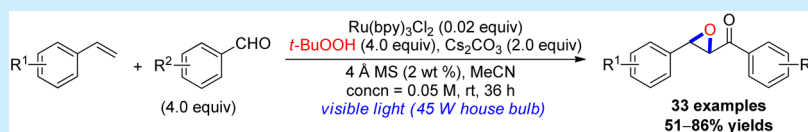


Visible-Light-Promoted Photoredox Syntheses of α,β -Epoxy Ketones from Styrenes and Benzaldehydes under Alkaline Conditions

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S Supporting Information



ABSTRACT: A range of styrenes and benzaldehydes were smoothly combined to form α,β -epoxy ketones under the synergistic actions of photocatalyst $Ru(bpy)_3Cl_2$, *tert*-butyl hydroperoxide (*t*-BuOOH), cesium carbonate (Cs_2CO_3), and visible light irradiation. The process likely proceeds through visible-light-enabled photocatalytic generations of acyl radicals as key intermediates.

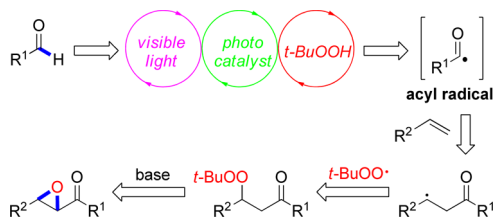
α,β -Epoxy ketones are important intermediates and precursors in modern synthetic organic chemistry.¹ Meanwhile, alkenes and aldehydes are both abundant chemical feedstocks and organic building blocks, and their direct functionalizations represent remarkably versatile means to access complex molecular entities.² As α,β -epoxy ketones are a structurally formally oxidative combination of their corresponding alkenes and aldehydes,^{3–7} not surprisingly, conceptual design as well as experimental realization of such an approach stands out as a highly sought after synthetic goal. Within this context, a radical chemistry-based scenario seems to serve as the logical connection between α,β -epoxy ketones syntheses^{8–11} and visible light photoredox catalysis, which has witnessed tremendous growth in recent years in uncovering both new catalysis concepts and robust synthetic applications^{12–15} and has particular strengths in initiating radical-based mechanistic networks. In turn, such opportunities serve as the key motivation for us to tackle a visible light-mediated protocol for the direct and mild merging of alkene and aldehyde partners to produce desired α,β -epoxy ketone product.

As shown in Scheme 1, our design concept envisions that a hydrogen abstraction event occurring on an aldehyde substrate might be initiated via synergistic interactions of visible light

stimulation, photocatalysis, and external oxidation, thereby generating relatively long-lived acyl radicals species.¹⁶ Subsequent radical addition to alkenes would accomplish C–H to C–C bond conversion and then furnish new acyl-functionalized radicals, followed by radical coupling with an alkylperoxy radical leading to the key intermediate β -peroxy ketones that are labile for producing α,β -epoxy ketones under alkaline conditions. The choice of an external oxidant is crucial in this design scenario since it should conceivably operate as a multifunctional reagent, i.e., as a radical precursor, a hydrogen acceptor, and an oxygen donor. Thus, the challenge in experimental demonstration of this proposal evidently relies on screening and identifying optimal reaction conditions that are capable of nurturing simultaneously all of the above-mentioned events.

With 1-chloro-4-vinylbenzene **1f** and benzaldehyde **2a** as the model substrates and a 45 W household bulb as the visible light source, we initially discovered that the desired α,β -epoxy ketone **3f** was produced in 39% yield (entry 1, Table 1) in a solvent of MeCN (concn = 0.05 M) at room temperature, together with $Ru(bpy)_3Cl_2$ (0.02 equiv), *t*-BuOOH (4.0 equiv, 5.5 M in decane), and K_2CO_3 (2.0 equiv) under an argon balloon atmosphere for 36 h. When an organic base Et_3N (entry 2) was employed, the reaction was found to be completely inhibited. To our delight, the yield of **3f** was improved to 61% when Cs_2CO_3 was employed as the base (entry 3). As a comparison, a lower loading of Cs_2CO_3 was shown to be less effective (46% yield, entry 4), and the Lewis acid $Mg(ClO_4)_2$ completely inhibited the reaction (entry 5). Interestingly, when 4 Å molecular sieves were employed as the additive, a respectable 82% yield of **3f** was observed (entry 6). Furthermore, the solvent effects were shown to be significant in the reaction, and the product was all furnished in lower yields

Scheme 1. Visible-Light-Promoted Photoredox Preparations of α,β -Epoxy Ketones from Styrenes and Benzaldehydes under Alkaline Conditions



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Table 1. Identification of the Optimal Reaction Conditions

entry	base	additive	solvent	oxidant ^e	yield ^f (%)
1	K ₂ CO ₃		MeCN	<i>t</i> -BuOOH	39
2	Et ₃ N		MeCN	<i>t</i> -BuOOH	trace
3	Cs ₂ CO ₃		MeCN	<i>t</i> -BuOOH	61
4 ^a	Cs ₂ CO ₃		MeCN	<i>t</i> -BuOOH	46
5 ^b	Cs ₂ CO ₃	Mg(ClO ₄) ₂	MeCN	<i>t</i> -BuOOH	trace
6	Cs ₂ CO ₃	4 Å MS	MeCN	<i>t</i> -BuOOH	82
7	Cs ₂ CO ₃	4 Å MS	DMSO	<i>t</i> -BuOOH	trace
8	Cs ₂ CO ₃	4 Å MS	DMF	<i>t</i> -BuOOH	37
9	Cs ₂ CO ₃	4 Å MS	toluene	<i>t</i> -BuOOH	trace
10	Cs ₂ CO ₃	4 Å MS	CH ₂ Cl ₂	<i>t</i> -BuOOH	trace
11	Cs ₂ CO ₃	4 Å MS	Et ₂ O	<i>t</i> -BuOOH	21
12	Cs ₂ CO ₃	4 Å MS	MeOH	<i>t</i> -BuOOH	trace
13	Cs ₂ CO ₃	4 Å MS	THF	<i>t</i> -BuOOH	35
14	Cs ₂ CO ₃	4 Å MS	MeCN	(BzO) ₂	0
15	Cs ₂ CO ₃	4 Å MS	MeCN	(<i>t</i> -BuO) ₂	0
16	Cs ₂ CO ₃	4 Å MS	MeCN	K ₂ S ₂ O ₈	0
17 ^c	Cs ₂ CO ₃	4 Å MS	MeCN	<i>t</i> -BuOOH	0
18 ^d	Cs ₂ CO ₃	4 Å MS	MeCN	<i>t</i> -BuOOH	0
19	Cs ₂ CO ₃	4 Å MS	MeCN		0

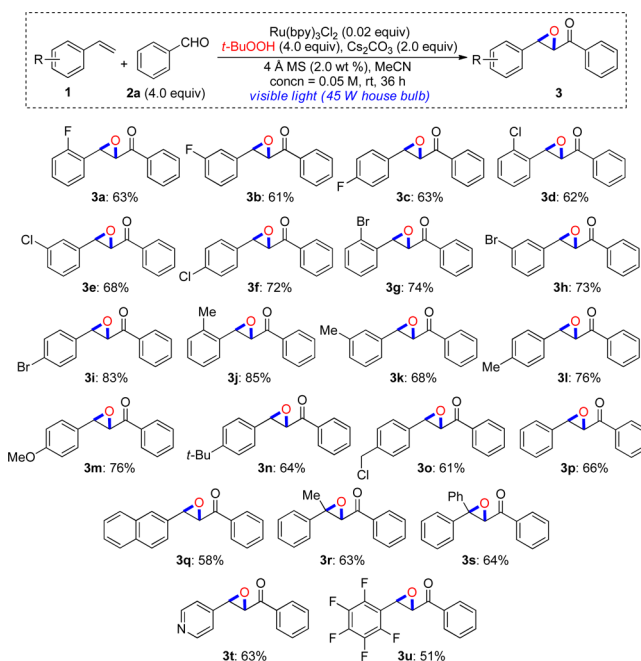
^aCs₂CO₃ (0.5 equiv) was used. ^bMg(ClO₄)₂ (1.0 equiv) was used. ^cNo light. ^dNo Ru(bpy)₃Cl₂. ^e*t*-BuOOH 5.5 M in decane. ^fYield was determined by ¹H NMR.

under otherwise identical reaction conditions when MeCN was replaced by dimethyl sulfoxide (DMSO), dimethylformamide (DMF), toluene, CH₂Cl₂, Et₂O, MeOH, or tetrahydrofuran (THF) (entries 7–13). As anticipated, the choice of an oxidant was evidently most critical, and the employment of benzoyl peroxide (BPO), (*t*-BuO)₂, and K₂S₂O₈ all drastically inhibited the reactivity (entries 14–16). Subsequently, control experiments operated under the absence of either a photocatalyst, or visible light, or an oxidant (entries 17–19) unambiguously pointed to complete inhibition of the reactivity. Thus, these screening results helped establish the optimal reaction conditions to be the following: 0.02 equiv of Ru(bpy)₃Cl₂, 2 wt % of activated powdered 4 Å molecular sieves, 4.0 equiv of *t*-BuOOH, and 2.0 equiv of Cs₂CO₃ in the solvent of MeCN and under a balloon–argon atmosphere at room temperature.

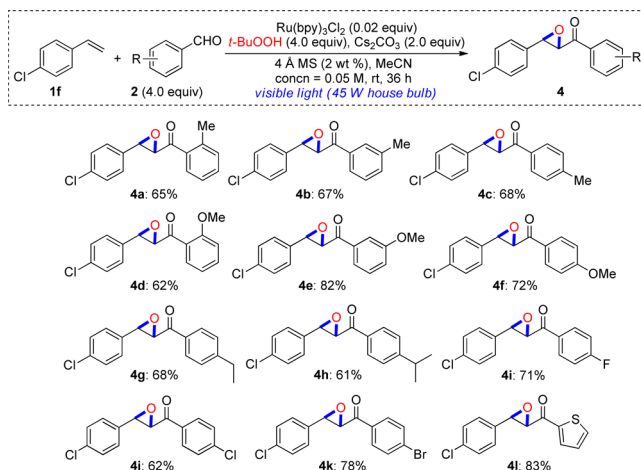
With the identified optimal reaction conditions in hand, we next sought to examine the scope of aromatic alkenes **1**. As shown in Scheme 2, the transformations generally proceed to produce the corresponding α,β -epoxy ketones **3** in moderate to good isolated yields (51–85%). Neither electron-withdrawing nor donating properties, or the substitution patterns (*ortho*, *meta*, *para*) on the aryl rings (**3a–3o**), seemed to have a significant influence on the reaction efficiency. Moreover, the aryl ring with benzyl chloride (**3o**), without substitution (**3p**), or with more conjugation (**3q**) was each shown to be comparably competent substrate. Remarkably, 1,1-disubstituted alkenes bearing α -methyl (**3r**) or phenyl substituent (**3s**) and alkenes featuring heteroatom (**3t**) or pentafluorinations (**3u**) were all found to be well accommodated, thereby significantly expanding the reaction scope and synthetic usefulness.

We next focused our attention on the scope of the aromatic aldehydes **2**. As exemplified in Scheme 3, a range of substrates were readily implementable, and the reactivities were confirmed to be broadly compatible, regardless of electron-withdrawing or

Scheme 2. Reactivity Screenings on Styrenes



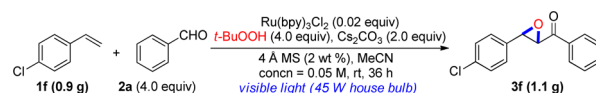
Scheme 3. Reactivity Screenings on Benzaldehydes



-donating properties and the substitution patterns (*ortho*, *meta*, *para*) on the aryl rings, as their corresponding products (**4a–k**) were all consistently produced in 61–82% isolated yields. Furthermore, an aryl ring with heteroatom (**4l**) was also successful in this protocol, allowing direct access to desired product in 83% isolated yield.

The synthetic application of this new visible-light-promoted photoredox C–H functionalization technology was further demonstrated through a gram-scale preparation of α,β -epoxy ketone. As illustrated in Scheme 4, under the standard conditions, 1-chloro-4-vinylbenzene **1f** (0.9 g) and benzaldehyde **2a** were smoothly converted to **3f** (1.1 g) in 66% isolated yield. This representative transformation helps manifest

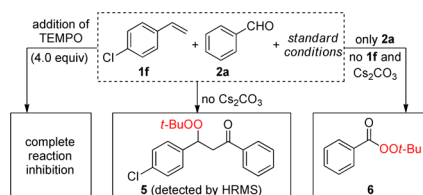
Scheme 4. Synthetic Application in Gram-Scale Preparation



practical value that this method may offer for rapid and reliable access of α,β -epoxy ketone substances and under very mild reaction conditions.

Mechanistic experiments were next conducted to help shed light on the potential reaction pathways. As summarized in Scheme 5, using 1-chloro-4-vinylbenzene **1f** and benzaldehyde

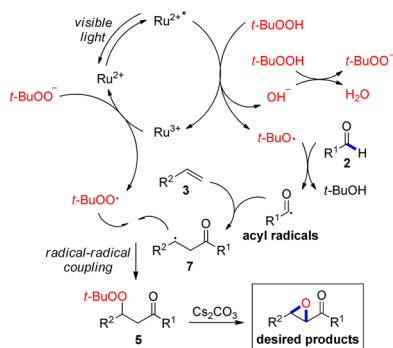
Scheme 5. Experimental Probes on Reaction Mechanism



2a as the model reaction, the addition of a widely known radical-scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) led to complete inhibition of the intended reactivity, implying strongly involvement of radical intermediates. Furthermore, structure **5** was detected by high-resolution mass spectrum (HRMS) analysis of the reaction mixture when the base Cs_2CO_3 was absent. Finally, *tert*-butyl benzoperoxoate **6** was isolated when neither **1f** nor Cs_2CO_3 was added to the reaction.

The observed reactivities coupled with the above investigations collectively point to a plausible mechanistic network shown in Scheme 6. The sequence would be initiated through

Scheme 6. Proposed Mechanistic Network



catalytic visible light irradiation of Ru^{2+} to its excited state Ru^{2+*} ,¹⁷ whose electron transfer to *t*-BuOOH would in turn induce scission of its weak O–O bond to generate simultaneously two species: hydroxyl anion HO^- and *tert*-butoxy radical *t*-BuO•. Subsequently, *t*-BuO• may abstract a hydrogen from aldehydes to produce the key acyl radical which may be captured by alkenes to produce intermediate **7**. Meanwhile, HO^- would capture one proton from another *t*-BuOOH to generate *tert*-butyl peroxide anion *t*-BuOO[−] which may be reduced to *tert*-butyl peroxide radical *t*-BuOO• in a single-electron-transfer process.¹⁸ Followed by radical–radical combination of *t*-BuOO• and **7**, β -peroxy ketone **5** was thus formed and further underwent elimination of *t*-BuOH to produce the corresponding final product under alkaline condition. The beneficial roles of 4 Å molecular sieves in the context is likely attributable to scavenging water that could have been formed when the HO^- abstracts proton from *t*-BuOOH.

In conclusion, stimulated by an initial design concept of exploring direct oxidative coupling through combining the

possibility of C–H functionalization and visible light photo-redox catalysis, we have established a straightforward protocol for α,β -epoxy ketone syntheses that directly employed abundantly available styrenes and benzaldehydes as substrates and operated under very mild conditions. Of central importance to this discovery is likely the identification of multiple synergistic parameters allowing for reliable generations of acyl radical intermediates. Further mechanism studies and new developments will thus be continuously explored and reported in due course.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b02629.

Experimental procedures and spectral data for all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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