Photocatalytic selective 1,2-hydroxyacylmethylation of 1,3-dienes with sulfur ylides as source of alkyl radicals

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Exploration of the zwitterionic property of sulfur ylides has long been known as a flexible strategy in a wide range of chemical transformations for different ring-sized construction. By contrast, their use in radical synthetic chemistry has been significantly limited due to dearth of general activation methods. Herein, a convenient strategy of visible light-driven proton-coupled electron transfer was reported to enable sulfur ylides to decompose into the corresponding α-carbonyl carbon radicals. With this method, a highly selective 1,2-hydroxyacylmethylation between 1,3-dienes, sulfur ylides and water under photoredox catalysis is thus achieved (>40 examples). Preliminary mechanistic studies and theoretical calculations shed light on the mechanism and the origin of regioselectivity.

Exploration of the zwitterionic property of sulfur ylides has long been known as a versatile strategy in a wide range of chemical transformations for different ring-sized construction.[1] Some of the these thermal reactions have also become textbook knowledge. In comparision to these ionic chemistry, use of sulfur ylides in radical synthetic chemistry has been significantly limited due to dearth of general activation methods, though direct photolysis of sulfur ylides[2] and theoretical studies[3] on sulfur ylide radical cations have been the subject of studies for more than five decades. Some of these early studies also disclosed that the chemical reactivity of sulfur ylide radical cations, generated from sulfur ylides by single electron transfer (SET) oxidation, were highly dependent on their substitution patterns. For instance, a pioneering study of Schuster revealed that stabilized sulfur ylides could undergo visible light-driven SET-oxidation to form sulfur ylide radical cations, when using 9,10-dicyanoanthracene (DCA) as a photocatalyst.[4] However, mixtures of different products consisting of cyclopropanes and alkenes were observed. Building on this work and by employing the reactivity of sulfur ylide radical cations, we have recently developed a range of photoredox-catalyzed radical coupling reactions of sulfur ylides.[5] Key to the success of these processes is the controlled generation of sulfur ylide radical cations through a SET-oxidation event under photocatalyic conditions (Scheme 1a). On the basis of these studies, we attempted to further explore the synthetic potential of sulfur ylides in radical chemistry. Thus, we envisioned development of a distinct catalytic activation platform for decomposion of sulfur ylides into their corresponding neutral alkyl radicals rather than radical cations, given the wide applications of carbon-centred radicals in radical transformations.[6]

With the introduction of visible light photoredox catalytic methods for the generation of various open-shell species under mild conditions,[7] sulfonium salts have been indentified to be a versatile class of precursors to form the relevant carbon-centred radicals upon SET-reduction-triggered C-S bond cleavage (Scheme 1a).[8,9] A series of outstanding works from the groups of Ritter,[10] Wang,[11] Procter,[12] Shi,[13] Alcarrazo,[14] and Yang[15] established that a range of aryl, alkyl, and α-diazo sulfonium salts could serve as competent source of functionalized aryl and alkyl radicals to particiapte in diverse C-C and C-heteroatom bond-forming reations through photoredox cycles. Despite these impressive contributions, to our knowledge, less reactive and stabilized sulfur ylides such as these derived from α-bromocarbonyl compounds, have yet to been exploited for the generation of the relevant α-carbonyl carbon radicals. As part of our interest in the photoredox catalysis[16] and sulfur ylide chemistry,[5] we wondered whether the merger of visible light photoredox catalysis and proton-coupled electron transfer (PCET)[17] would provide a new approach for conversion of sulfur ylides to the corresponding alkyl radicals in a controlled manner (Scheme 1a). Since the work of Kellogg on the photoinduced SET-reduction-mediated generation of α-carbonyl carbon radicals from the α-bromocarbonyl compounds,[18] α-carbonyl alkyl bromides have found extensive in numerous photoredox catalyzed radical cross-couplings.[19,20] However, such compound class, in some instances, have been plagued by their low reactivity and susceptibility to thermal nucleophilic substitution due to the good leaving ability of bromide. The resultant bromide anions are also oxidation labile species. To overcome these potential challenges, MacMillan[21a,b] and Zeitler[21c] documented that α-acetoxy acetophenones provided an elegant alternative class of precursors towards α-carbonyl carbon radicals. If successful, thus, our method would complement existing methods for catalytic generation of α-carbonyl carbon radicals, while circumventing the possible side reactions and efficiency issues

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encountered in the direct use of sulfonium salts or α-bromo carbonyl compounds.
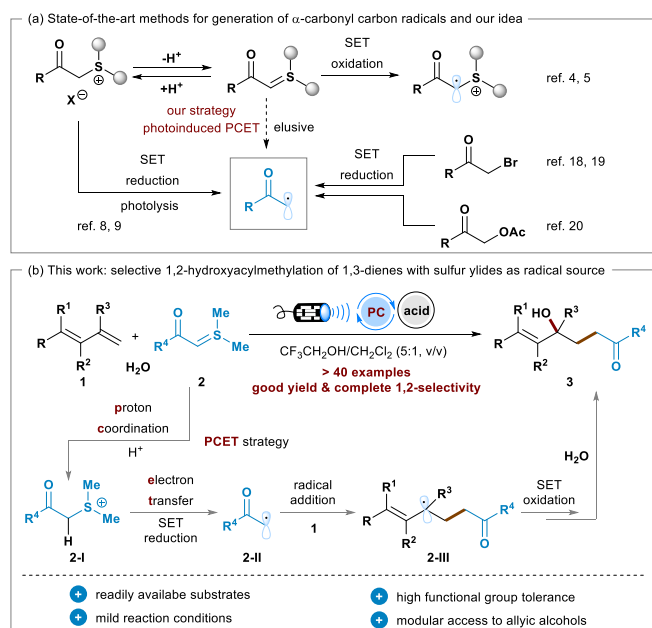
Scheme 1 Background. (a) State-of-the-art light-induced methods for the generation of α-carbonyl carbon radicals and our methods. (b) Our reaction design and working hypothesis. SET = single electron transfer. PC = photocatalyst.

With the evolvement of photoredox catalysis,[7] visible light-driven radical-mediated 1,4- and 1,2-difunctionalization of 1,3-dienes and derivatives has emerged as a powerful paradigm for simultaneous installation of carbon-carbon and/or carbon-heteroatom bonds.[22] The resultant allylic compounds are useful synthetic building blocks because of their unique structural characteristics. The majority of these reactions were triggered by addition of photogenerated carbon-centred radicals to the terminal alkene moiety. Notwithstanding the impressive advances, some challenges still remain, such as expansion of the current pool of radical precursors and coupling partners, as well as selectivity caused by the inherent structural property of 1,3-dienes. Building our recent achievements on tandem radical addition and C-O coupling reactions of 1,3-dienes[23] and design plan for activation of sulfur ylides (Scheme 1a), we became interested in investigating selective 1,2-hydroxyacylmethylation of 1,3-dienes with sulfur ylides as source of alkyl radicals and water as a nucleophile (Scheme 1b). The achievement of this reaction would provide a practical method for preparation of valuable ketone-containing allylic alcohols, complementing the existing radical-involved allylic functionalization.[24] In addition to activation of sulfur ylides, however, several other challenges might also be considered, such as efficient trap of α-carbonyl carbon radical by 1,3-dienes, control of the regioselectivity during the couping between nucleophile and allylic radical intermediate that was often met in the radical reactions of 1,3-dienes. Herein, we report how this idea was translated into experimental reality, enabling the target selective 1,2-hydroxyacylmethylation reaction of 1,3-dienes.

Table 1 Condition optimisation[a]

Entry	Variation	Yield[b] (%)
1	none	59
2	H_2O (1.0 equiv)	19
3	H_2O (5.0 equiv)	43
4	H_2O (20.0 equiv)	57
5	$Ru(bpy)_3Cl_2 \cdot 6H_2O$	< 5
6	Eosin Y, 20 W green LED	< 5
7	Ph-PTZ, 20 W purple LED	10
8	fac-[Ir(ppy)₃] (1.0 mol%)	40
9	fac-[Ir(ppy)₃] (5.0 mol%)	64
10	HFIP	8
11	EtOH, DMF, or CH_3CN	< 5
12	**1a**/**2a**/H_2O = 1/3/15	63
13	**1a**/**2a**/H_2O = 1/3/15, 10 W blue LED	46
14	**1a**/**2a**/H_2O = 1/3/15, 40 W blue LED	55
15	**1a**/**2a**/H_2O = 1/3/15, CF_3CH_2OH/CH_2Cl_2 (2.5 + 0.5 mL)	74
16	**1a**/**2a**/H_2O = 1/3/15, CF_3CH_2OH/CH_2Cl_2 (2.5 + 0.5 mL) Et₃N·3HF (1.0 equiv)[c]	94 (90)[d]

[a] Reaction conditions: **1a** (0.60 mmol, 3.0 equiv), **2a** (0.20 mmol), H_2O (3.0 mmol, 15.0 equiv), and fac-[Ir(ppy)₃] (0.004 mmol, 2.0 mol%), in CF_3CH_2OH (2.0 mL) at rt under argon atmosphere and the irradiation of 20 W blue LED (450-460 nm, distance ca. 3 cm) for 24 h. [b] Determined by ¹H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. [c] Reaction time shortened to 7 h. [d] Isolated yield. HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol.

Initially, we examined the feasibility of the designed three-component 1,2-hydroxyacylmethylation reaction using 1-phenylbutadiene **1a**, sulfur ylide **2a** and H_2O as the model substrates with 3/1/15 equivalent ratio (Table 1).[25] The representative optimization results are highlighted in Table 1. Pleasingly, the desired reaction could indeed work smoothly to form 1,2-adduct product **3aa** exclusively in 59% NMR yield, when using fac-[Ir(ppy)₃] as the photocatalyst in CF_3CH_2OH as solvent under irradiation of a 20 W blue LED at room temperature for 24 h (entry 1). During optimization studies, it was found that the reaction was very sensitive to the amounts of H_2O, photocatalysts and reaction media. As shown in entries 2-4, varying stoichiometry of H_2O has an obvious effect on the reaction effciency, and a fifteenfold amount of H_2O was the best of choice. Next, we screened several other commonly used Ir(III) and Ru(II) photocatalysts as well as organic photocatalysts. Among them, only organic photocatalyst 10-phenylphenothiazine (Ph-PTZ) gave a 10% yield of **3aa** (entry 7),

while the others resulted in very low conversion or messy mixture. As 1 mol% or 5 mol% loading of photocatalyt *fac*-[Ir(ppy)$_3$] did not lead to significant improvement of the yield (entries 8 and 9), a 2 mol% loading was used for further optimisation in terms of cost and efficiency. An extensive survey of solvents was also performed and it was found that CF$_3$CH$_2$OH was still optimal. Other solvents such as EtOH, DMF and CH$_3$CN completely inhibited the desired reactivity (entry 11), while 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) resulted in trace amount of **3aa** (entry 10). These results implied that CF$_3$CH$_2$OH might serve as a proton source to participate in the activation of sulfur ylide **2a**.

Upon further screening of various equivalent ratios of **1a**, **2a** and H$_2$O, it was established that the yield was increased to 63%, when using 1-phenylbutadiene **1a** as limiting reagent with threefold and fifteenfold excess of **2a** and H$_2$O, respectively (entry 12). Using such a ratio of three reaction components, we proceeded to screen other parameters regarding light intensity, concentration and additives. Though the decrease and increase of light intensity both resulted in an decrease of yield (entries 13 and 14), a mixture solvent system of CF$_3$CH$_2$OH/CH$_2$Cl$_2$ (5/1, v/v) and a concentration of 0.067 M increased the yield to 74% (entry 15). Interestingly, we found that the reaction outcome was also greatly influenced by the acidity/basicity of the reaction mixture. An extensive screen of additives identified Et$_3$N·3HF (1.0 equiv) to be optimal, with **3aa** being isolated in 90% yield (entry 16). Finally, a series of control experiments confirmed that photocatalyst and visible light irradiation are both critical to the reaction.[25]

Having established effective conditions for selective 1,2-hydroxyacylmethylation of 1-phenylbutadiene **1a**, we first investigated the scope of 1,3-dienes. The results are highlighted in Table 2. As for 1-aryl-1,3-butadienes, there is no obvious requirement for electronic properties or specific substitution patterns in this system. For instance, in addition to **1a**, a range of 1-aryl-1,3-butadiene derivatives **1b-p** bearing an electron-donating (e.g., Me, OMe, *t*-Bu) or electron-withdrawing (e.g., F, Cl, Br, CF$_3$ and OCF$_3$) substituent at *para*-, *ortho*- or *meta*-position of the aromatic ring all react smoothly to give **3ba-pa** with generally good efficiency (51-96% yield). Moreover, 1,3-dienes **1q** having 3-thiophenyl and **1r** with 2-naphthyl group also prove to be compatible with the reaction, affording the expected products **3qa** and **3ra** in 74% and 65% yields, respectively. Notably, as shown in the case of substrates **1s** and **1t** with disubstituted phenyl ring, the increased steric hindrance of phenyl ring has no deleterious effect on the reaction, with the corresponding product **3sa** and **3ta** being obtained with good yields. Note that these products (e.g., **3ea-ga**, **3ia-ja** and **3oa-pa**) bearing halogen functionalities such as F, Br, and Cl, offer excellent handles for further synthetic elaborations. Encouraged by these results, we extended the protocol to some disubstituted 1,3-dienes to construct structurally more complex allylic alcohols. Under the standard conditions, 1,1-diphenyl substituted **1u**, and **1v** and **1w** having a methyl group at the C2 and C3 position are all well tolerated, furnishing the expected products **3ua-wa** in satisfactory yields (54-91% yields). Remarkably, the current catalytic system also proved to be suitable for challenging alkyl-substituted 1,3-diene **1x**, allowing exclusive formation of the desired 1,2-hydroxyacylmethylated

product **3xa** in 63% yield. Such type of 1,3-dienes typically resulted in formation of mixtures of 1,2-and 1,4-adducts in our previously reported photo-induced copper-catalyzed C-O cross-coupling reactions.[23]
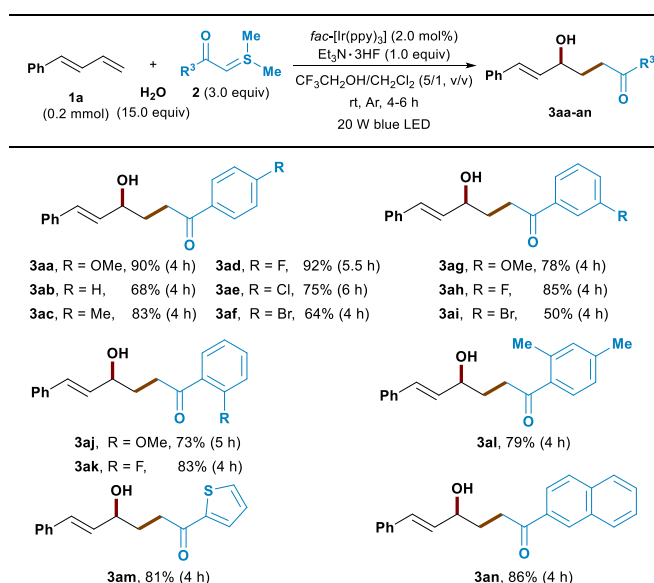
Table 2 Scope of 1,3-dienes[a,b]
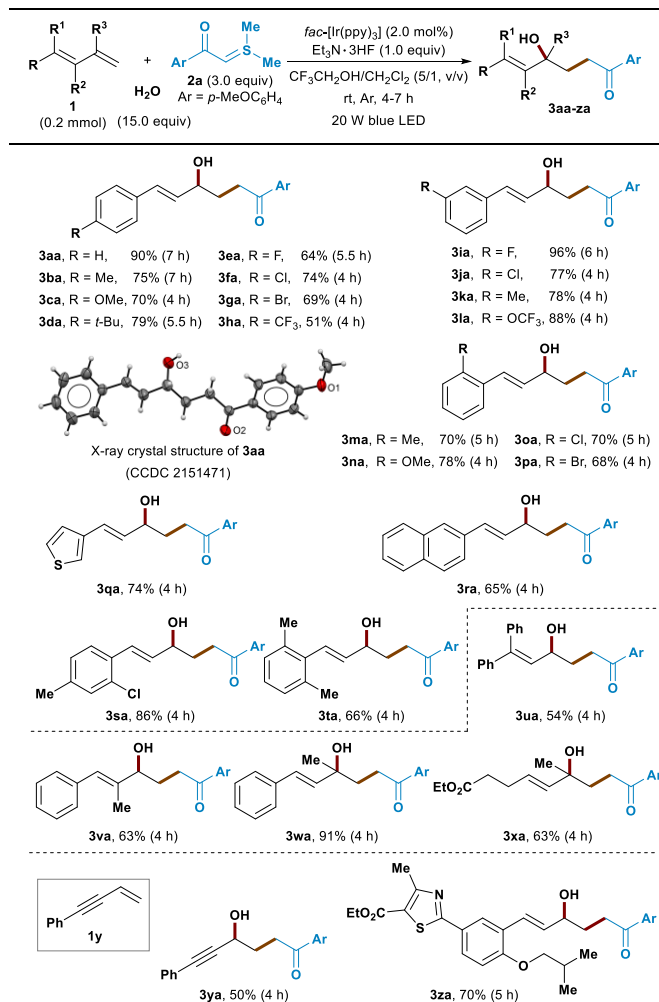
[a] Reaction conditions: **1** (0.20 mmol), **2a** (0.60 mmol, 3.0 equiv), H$_2$O (3.0 mmol, 15.0 equiv), Et$_3$N·3HF (0.2 mmol, 1.0 equiv), and *fac*-[Ir(ppy)$_3$] (0.004 mmol, 2.0 mol%), in a mixture of CF$_3$CH$_2$OH (2.5 mL) and CH$_2$Cl$_2$ (0.5 mL) at rt under argon atmosphere and the irradiation of 20 W blue LED (450-460 nm, distance ca. 3 cm) for 4-7 h. [b] Isolated yield.

Notably, as for the radical acceptors, the current protocol is not limited to 1,3-dienes. Under the optimal reaction conditions, 1-phenyl-1,3-enylene **1y** also works well to give propargylic alcohol **3ya** in 50% yield. A pharmaceutical febuxostat-derived 1,3-diene **1z** also proves to be compatible with the reaction system, producing **3za** in 70% yield.

Then, we turned our attention to explore the generality of the protocol by reacting a representative set of stabilized sulfur ylides **2** with **1a** and H$_2$O under the standard conditions (Table 3). Again, it was found that the electronic characteristics and the substitution patterns of the aromatic ring of sulfur ylides do not have any obvious effect on the three-component reaction. For

instance, aside from model substrate **2a**, an array of α-bromocarbonyl compound-derived sulfur ylides **2b-k** bearing neutral (**2b**), electron-donating (e.g., Me, OMe) and electron-withdrawing (e.g., F, Cl, Br) at the *para-*, *meta-* or *ortho-*position of the phenyl ring are all well accommodated. Products **3ab-ak** are thus achieved in yields ranging from 50-92%. As shown in the synthesis of **3al**, sterically demanding multiply substituted sulfur ylide **2l** also reacts to give a 79% yield. Markedly, both 2-thiophene- and 2-natphthyl-substituted sulfur ylides **2m** and **2n** are also competent radical precursors, giving rise to the corresponding products **3am** and **3an** in 81% and 86% yields, respectively. As a limitation of the current reaction system, alkyl-substituted sulfur ylides do not react under the standard conditions, which might await further condition optimisation.

Table 3 Scope of sulfur ylides[a,b]

[a] Reaction conditions: **1a** (0.20 mmol), **2** (0.60 mmol, 3.0 equiv), H$_2$O (3.0 mmol, 15.0 equiv), Et$_3$N·3HF (0.2 mmol, 1.0 equiv), and *fac*-[Ir(ppy)$_3$] (0.004 mmol, 2.0 mol%), in a mixture of CF$_3$CH$_2$OH (2.5 mL) and CH$_2$Cl$_2$ (0.5 mL) at rt under argon atmosphere and the irradiation of 20 W blue LED (450-460 nm, distance ca. 3 cm) for 4-6 h. [b] Isolated yield.
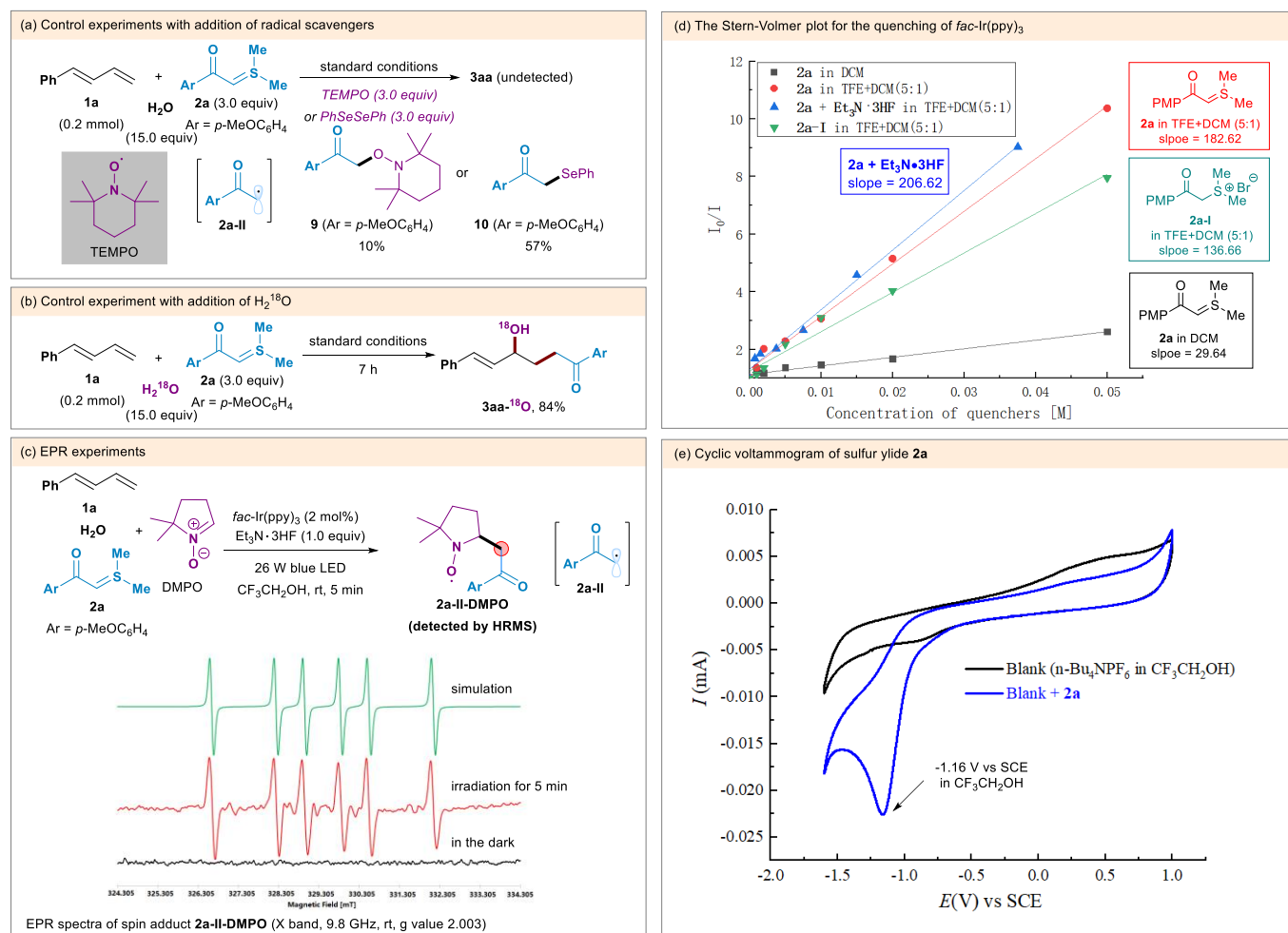
To demonstrate the synthetic potential of this protocol, we also performed the three-component reaction of **1a**, **2a** and H$_2$O on a 5.0 mmol scale, and comparable results can still be achieved (**3aa**, 1.38 g, 88% yield) (Scheme 2a). As the allylic alcohol and ketone are versatile handles for synthetic transformations, several derivatizations product **3aa** were carried out (Scheme 2b). For example, upon routine oxidation of the free alcohol moiety with DMP, the corresponding

valuable building block 1,4-dione **4** can be isolated in 80% yield. Surprisingly, under Appel reaction conditions,[26a] dehydration product, 1,3-diene **5**, is obtained in 72% yield after 24 h rather than the proposed allylic halide. Moreover, further treatment of **3aa** with CF$_3$CH$_2$OH as both a nucleophile and solvent in the presence of Et$_3$N·3HF gives the trifluoroethoxylation product **6** in 90% yield.[26b] With Fernandes' Pd-catalyzed intramolecular *O*-allylation methodology,[26c] the *γ*-acetoxy-*δ,ε*-unsaturated ketoxime **7** easily derived from **3aa** can undergo intramolecular *6-exo O*-allylation efficiently to provide biologically relevant oxazine **8** in 68% yield.
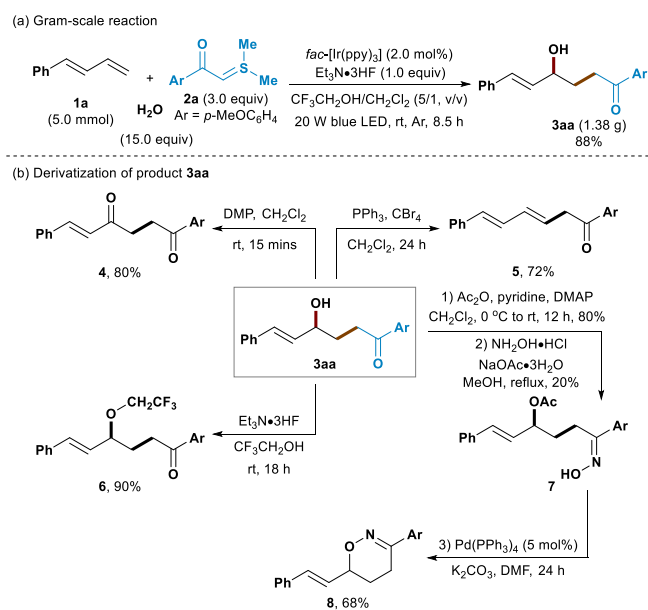
Scheme 2 Synthetic utility. DMP = 1,1,1-Triacetoxy-1,1-dihydro-1,2-benziodoxol-3(1*H*)-one. DMAP = 4-(Dimethylamino)pyridine. (a) Gram-scale reaction. (b) Derivatization of product.

In order to gain some insight into the reaction mechanism, we carried out a range of mechanistic studies. First, when stoichiometric radical scavengers 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (3.0 equiv) or PhSeSePh (3.0 equiv) were added to the model reaction, the formation of desired product **3aa** was completely inhibited; instead, radical trapping TEMPO-adduct **9** and PhSe-adduct **10** could be isolated with 10% and 57% yield, respectively (Scheme 3a). These results suggest that the α-carbonyl carbon radical **2a-II** and a radical process might be involved in our reaction. Moreover, when replacing H$_2$^{16}O with H$_2$^{18}O, the model reaction also reacts well to give the corresponding ^{18}O-labelled product **3aa-^{18}O** in 84% yield (Scheme 3b). This outcome confirms that hydroxy oxygen atom in the product should stem from water.

(a) Control experiments with addition of radical scavengers

Ph—CH=CH—CH=CH₂ **1a** (0.2 mmol) + H₂O (15.0 equiv) + **2a** (3.0 equiv) Ar = p-MeOC₆H₄

standard conditions → **3aa** (undetected)

TEMPO (3.0 equiv) or PhSeSePh (3.0 equiv)

TEMPO / **2a-II**

9 (Ar = p-MeOC₆H₄) 10%   or   **10** (Ar = p-MeOC₆H₄) 57%

(b) Control experiment with addition of H₂¹⁸O

Ph **1a** (0.2 mmol) + H₂¹⁸O (15.0 equiv) + **2a** (3.0 equiv) Ar = p-MeOC₄H₄

standard conditions, 7 h → Ph—CH=CH—CH(¹⁸OH)—CH₂—C(O)Ar **3aa-¹⁸O**, 84%

(c) EPR experiments

Ph **1a**, H₂O + **2a** (Ar = p-MeOC₆H₄) + DMPO

fac-Ir(ppy)₃ (2 mol%), Et₃N·3HF (1.0 equiv), 26 W blue LED, CF₃CH₂OH, rt, 5 min → **2a-II-DMPO** (detected by HRMS)   [**2a-II**]

simulation / irradiation for 5 min / in the dark

324.305 325.305 326.305 327.305 328.305 329.305 330.305 331.305 332.305 333.305 334.305 Magnetic Field [mT]

EPR spectra of spin adduct **2a-II-DMPO** (X band, 9.8 GHz, rt, g value 2.003)

(d) The Stern-Volmer plot for the quenching of fac-Ir(ppy)₃

- ■ 2a in DCM
- ● 2a in TFE+DCM (5:1)
- ▲ 2a + Et₃N·3HF in TFE+DCM (5:1)
- ▼ 2a-I in TFE+DCM (5:1)

I_0/I vs Concentration of quenchers [M]

2a + Et₃N·3HF slope = 206.62

2a in TFE+DCM (5:1) slope = 182.62

2a-I in TFE+DCM (5:1) slope = 136.66

2a in DCM slope = 29.64

(e) Cyclic voltammogram of sulfur ylide 2a

I (mA) vs E(V) vs SCE

— Blank (n-Bu₄NPF₆ in CF₃CH₂OH)
— Blank + **2a**

-1.16 V vs SCE in CF₃CH₂OH

Scheme 3 Mechanistic studies. (a) Radical trapping studies. (b) Control experiment with H₂¹⁸O. (c) EPR studies. (d) Stern-Volmer quenching plot of fac-Ir(ppy)₃ with **2a** (in CH₂Cl₂), **2a-I** (in TFE/CH₂Cl₂), **2a** (in TFE/CH₂Cl₂), and **2a**/Et₃N·3HF (in TFE/CH₂Cl₂). (e) Cyclic voltammetry.

Next, we utilized electron paramagnetic resonance (EPR) technique with 5,5-dimethyl-pyrroline N-oxide (DMPO) as a spin trap to investigate radical species possibly engaged in the process. In a mixture of sulfur ylide **2a** and DMPO in CF₃CH₂OH under irradiation with blue LED for 5 min, the formation of persistent radical adduct **2a-II-DMPO** was confirmed by EPR spectroscopy, a sextet signal with a g value = 2.003, A_N = 1.597 mT, and A_H = 2.307 mT, which was coincident with the carbon-centred radical adduct. The simulation EPR spectrum (green trace) was in perfectly agreement with the experimental one (red trace). The adduct **2a-II-DMPO** was also confirmed by ESI-HRMS spectrometry (Scheme 3c).[25] Collectively, these outcomes suggest the involvement of α-carbonyl carbon radical **2a-II** in our reaction.

To further probe the reaction pathway, we then performed the Stern-Volmer luminescence quenching experiments of the photocatalyst fac-[Ir(ppy)₃] by gradually increasing the amount of sulfur ylide **2a**, its precursor sulfnonium salt **2a-I** and relevant mixture in CF₃CH₂OH and/or CH₂Cl₂ (Scheme 3d). The results reveal that the solutions of sulfur ylide **2a** in the presence or absence of the additive Et₃N·3HF in CF₃CH₂OH/CH₂Cl₂ mixture all can quench the excited photocatalyst more efficiently than the sulfonium salt **2a-I** does, though sulfonium salt **2a-I** shows somewhat quenching effect. Notably, the combination of **2a** and Et₃N·3HF has the strongest quenching effect for photocatalyst. In contrast, sulfur ylide **2a** in CH₂Cl₂ shows the weakest quenching effect. To get a deeper insight into the mechanism, we measured reduction potential of the ground states of **2a** to be -1.16 V (vs SCE in CF₃CH₂OH),[25] which is inside the redox window of the excited state photocatalyst *fac-Ir(ppy)₃ ($E_{1/2}$*III/IV = -1.73V vs SCE), revealing that our three-component reaction may undergo oxidative quenching cycle of

photocatalyst.[27] Finally, we determined the quantum yield of the model reaction of **1a**, **2a** and H_2O to be 0.03. A value significantly below unit implies that the reaction mainly proceeds through sequential redox events rather than by a radical chain process.[25]
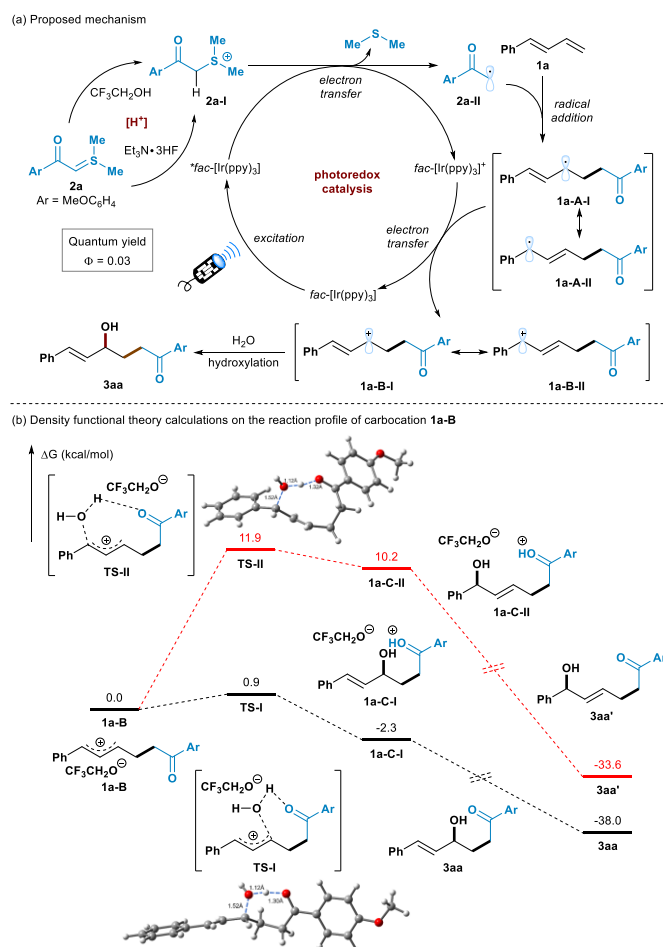
Scheme 4 The proposed mechanism and DFT calculations.

On the basis of these mechanistic studies and literature reports,[10-15, 27] we then proposed a plausible mechanism with the model reaction of **1a**, **2a** and H_2O as an example (Scheme 4a). Given the weak basicity of the sulfur ylide **2a**, it reversibly interacts with CF_3CH_2OH and/or $Et_3N\cdot3HF$ to favour formation of certain amount of the adduct sulfonium salt **2a-I**,[28] which is susceptible to SET reduction. Then, sulfonium salt **2a-I** undergoes SET reduction by the excited state *fac-[Ir^{III}(ppy)$_3$], also known as an oxidative quenching event, giving the oxidizing sate fac-[Ir^{IV}(ppy)$_3$] and α-carbonyl carbon radical **2a-II** with release of dimethyl sulfide. Subsequently, electrophilic **2a-II** undergoes intermolecular radical addition across the terminal alkene of 1-phenylbutadiene **1a** to furnish new relatively stable carbon radical **1a-A-I** or **1a-A-II**, which is further oxidized by the oxidizing sate fac-[Ir^{IV}(ppy)$_3$] species via another SET process to provide carboncation **1a-B** with concurrent regeneration of the ground state photocatalyst fac-[Ir^{III}(ppy)$_3$], completing the photoredox catalytic cycle. Finally, an off-photocatalytic cycle nucleophilic attack of H_2O to the allylic carbocation **1a-B** occurs

in a highly regioselective manner to afford the corresponding 1,2-hydroxyacylmethylation product **3aa**.

To better understand the origin of the regioselectivity involved in the nucleophilic attack of H_2O to the intermediate carbocation **1a-B**, we conducted density functional theory (DFT) calculations on the Gibbs free energy profile of **1a-B** at the ωb97xD/6-311+G**//6-31+G(d) level of theory (Scheme 4b).[25] As allylic carbocation **1a-B-I** is in fast equilibrium with benzylic carbocation **1a-B-II**, in principle, H_2O could undergo nucleophilic addition to these two intermediates to form the corresponding 1,2- and 1,4-adducts. Calculations indicated that the attack of H_2O at the allylic position of **1a-B-I**, which goes through H-bond-assisted transition state **TS-I**, generates 1,2-adduct **3aa** with a Gibbs free energy barrier of only 0.9 kcal/mol. In contrast, the attack of H_2O at benzylic position **1a-B-II** goes through transition state **TS-II** and affords 1,4-adduct **3aa'** with a Gibbs free energy barrier of 11.9 kcal/mol. The Gibbs free energy gap of **TS-I** and **TS-II** is determined to be 11.0 kcal/mol, which is significantly enough to produce the 1,2-adduct exclusively at room temperature and is in good accordance with the experimental facts. Taken together, sulfur ylides used in the current study not only serve as precursors to α-carbonyl carbon radicals, the carbonyl moiety might also act as a H-bond donor to direct the attack of nucleophilic water, thus enabling 1,2-difunctionalization as the favoured pathway.

In summary, we have reported a convenient strategy of visible light-driven proton-coupled electron transfer to enable sulfur ylides to decompose into the corresponding α-carbonyl carbon radicals. This method allows achievement of a selective 1,2-hydroxyacylmethylation among 1,3-dienes, sulfur ylides and water under photoredox catalysis. This three-component reaction is distinguished by mild conditions, exquisite regioselectivity and broad substrate scope, thus offering a practical complementary method for construction of allylic alcohols. Experimental observations and theoretical calculations shed light on the mechanism and the origin of regioselectivity. The discovered H-bond-activation mode for control of regioselectivity should be of potential use in related synthetic radical chemistry of 1,3-dienes. Work on further expansion of the scope of sulfur ylides and nucleophiles is currently in progress in our laboratory.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

Notes and references

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