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Oxy-sulfonylation of terminal alkynes *via* C–S coupling enabled by copper photoredox catalysis†

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We report the first literature example using visible light-induced trimethylsilyl azide (TMS-N_3)-assisted copper-catalyzed oxy-sulfonylation of terminal C≡C bonds to form β-keto sulfones (C–S bond formation). TMS-N_3 promotes the reaction by facilitating the formation of sulfonyl radicals, which later decompose into N_2 gas upon light irradiation. This method involves the use of commercially available and stable starting materials. Also, a wide range of functional groups have been well-tolerated under the current photoredox process, evading the side product formation. Potent biologically active compounds, such as CES1, 11β-HSD1 inhibitors, anti-analgesic agents, and reactive synthesis intermediates were synthesized to demonstrate the synthetic utility of the current methodology. Moreover, green chemistry metrics and Eco-scale evaluation for the current photochemical method show that the protocol is eco-friendly and highly efficient.

Photoredox catalysis has emerged as a promising technique over the past decade for the activation of a wide range of small molecules to construct new chemical bonds in the field of organic chemistry.[1] The recent renaissance of photocatalysis is due to the selective excitation of light-absorbing photocatalysts (Ru, Rh, or Ir polypyridyl ligands), which upon excitation produce long lived triplet excited states and open-shell reactive intermediates *via* a single electron transfer process (SET). Furthermore, these reactive intermediates act as oxidants/reductants in the reaction (photoredox catalysis) that is not common in thermal reactions.[2]

In the past few years, copper photocatalysts have come to the forefront in the realm of photocatalysis and act as a light-absorbing species, which are further involved in the bond making and breaking process.[3] Their low cost, earth-abundant, and environmentally benign nature make these copper photoredox catalysts an ecofriendly and economically feasible alternative for the synthesis of new chemical molecules. In recent years, our group has reported various C–C, C–N, C–O coupling reactions, cyclization, and hydrogen atom transfer (HAT) reactions using a unique *in situ* generated copper(I) phenylacetylide complex as a key light-absorbing photocatalyst.[4] In this work, we present the first literature example using visible-light-induced trimethylsilyl azide ($TMSN_3$)-assisted copper-catalyzed oxy-sulfonylation of terminal C≡ bonds to form new C–S bonds (synthesis of β-keto sulfones) under blue LED irradiation at room temperature.

Sulfones are ubiquitous and versatile functional groups that are found in a wide range of biologically active moieties and pharmaceutical drugs and are considered to be valuable synthesis intermediates as they can be further functionalized with ease.[5] Traditionally, β-keto sulfones were synthesized by refluxing acyl halides and sodium sulfonate. However, this method is not an atom economical method,[6] as it requires pre-functionalization of ketones (with halides) and tedious synthesis of sulfinic acid precursors which are thermally unstable and decompose easily to form thiosulfonates and sulfinic acids.[7] Later in 2013, Lei and co-workers reported the synthesis of β-keto sulfones *via* di-functionalization of terminal C≡C bonds using oxygen (O_2) and sulfinic acids under thermal conditions using stoichiometric amounts of the base (Scheme 1a).[8] Next, various thermal and photochemical methods were developed for the synthesis of β-keto sulfones, such as (a) a two-step thermal method reported by Jiang *et al.* to synthesize β-keto sulfones by oxidative coupling of oxime acetates and sodium sulfinate at high temperatures using a copper catalyst *via* hydrolysis of vinyl amino sulfones (Scheme 1b);[9] (b) $AgNO_3/K_2S_2O_8$ catalyzed aerobic oxysulfonylation of alkenes, which needs long reaction time and a strong external oxidant;[10] (c) visible light-promoted Ru(II)-based photoredox catalyzed oxysulfonylation of terminal C≡C bonds using tosyl hydrazides, bases, and additives at RT (Scheme 1c);[11a] (d) visible light-mediated rearrangement of vinyl tosylates for the synthesis of β-keto sulfones using an

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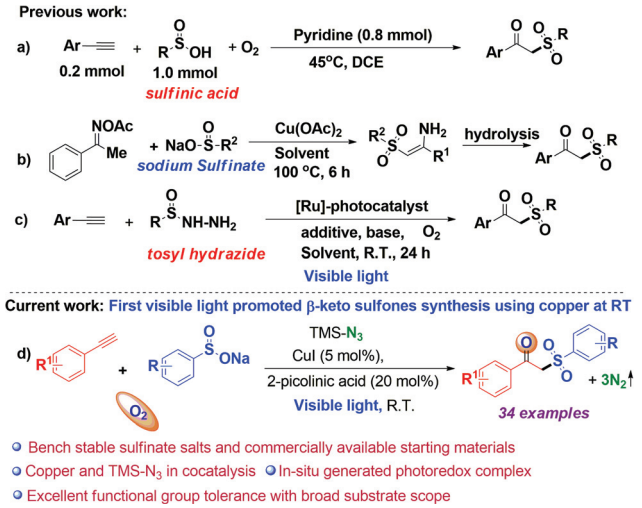


Scheme 1 Different synthesis approaches for β-keto sulfones.

organic photosensitizer (9-fluorenone);[11b] and (e) recently, the electrochemical and histidine catalyzed synthesis of β-keto sulfones, respectively, reported by S. Shaabanzadeh[12a] and A. Kumar[12b]. However, these methods use excess amounts (2.0 equiv.) of sodium sulfinate, which in turn generates large amounts of waste. Thus, the overall limitations of all the above-mentioned methods include the use of (a) pre-synthesized starting materials, (b) high reaction temperature, (c) excess amounts of external oxidants and additives, (d) expensive catalysts/photocatalysts such as 'Ru-photo-catalysts' which are known for their high price and toxicity,[13] (e) organic photosensitizers, which may have poor photostability and may involve photo-bleaching, (f) excess amounts of starting materials (sodium sulfinate), and (g) electrochemical cells (in electrochemical synthesis), which require sophisticated instrumentation and involve additional cost, and (h) the formation of unwanted waste (leading to higher E-factors).

The key features of the current oxidative coupling reaction are as follows: (a) the use of bench stable commercially available starting materials (sodium sulfinate salts and alkynes); (b) $TMSN_3$ assists in the reaction (copper catalysts and sodium sulfinate salts) to form β-keto sulfones without forming the hydroazidation products[14a,b] or triazole products[14c] (click reaction); (c) the *in situ*-generated copper complex undergoes photoexcitation and catalyzes the formation of a new C–S bond *via* the SET process with O_2 (sustainable oxidant); and (d) no formation of side products, such as sulfonic acids or homo-coupling products of terminal alkynes (1,3-diynes).

Recently, we reported a regioselective acetamidation of a terminal alkyne *via* C–N coupling[4e] under a similar photo-induced electron transfer (PET) process. By anticipating a C–S coupling reaction, we commenced our initial study by using sodium *p*-toluenesulfinate **1a**, trimethylsilyl azide ($TMSN_3$), and phenylacetylene **2a** as substrates with copper halides as a catalyst, ligands, solvent, and photo-irradiation (blue LEDs), in the presence of O_2 at room temperature to form β-keto sulfone

Table 1 Optimization of reaction conditions[a]

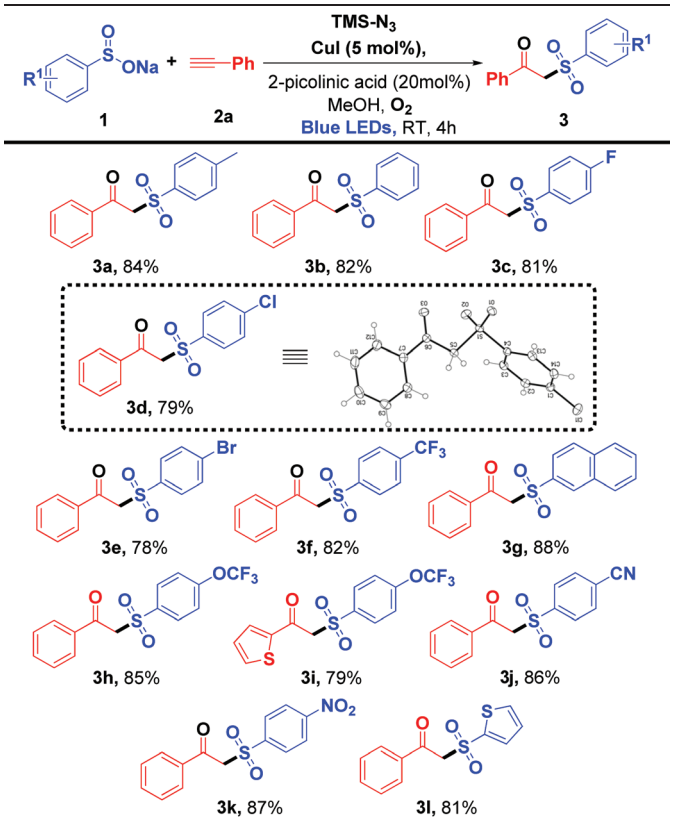
Entry	Cu [catalyst]	Ligand	Solvent	[Yield%][b]
1	CuI	2-Picolinic acid	CH_3CN–MeOH	70
2	CuBr	2-Picolinic acid	CH_3CN–MeOH	64
3	CuCl	2-Picolinic acid	CH_3CN–MeOH	53
4	CuI	2-Picolinic acid	CH_3CN	0
5	**CuI**	**2-Picolinic acid**	**MeOH**	**84**
6	CuI	2-Aminopyridine	MeOH	0
7	CuI	1,10-Phenanthroline	MeOH	62
8	CuI	2,2′-Bipyridine	MeOH	41
9[c]	CuI	None	MeOH	0
10[d]	CuI	2-Picolinic acid	MeOH	80
11[e]	CuI	2-Picolinic acid	MeOH	10
12[f]	None	2-Picolinic acid	MeOH	n.r
13[g]	CuI	2-Picolinic acid	MeOH	n.r
14[h]	CuI	2-Picolinic acid	MeOH	n.r
15[i]	CuI	2-Picolinic acid	MeOH	n.r

[a] Unless otherwise noted, reaction conditions are as follows: **1a** (0.50 mmol), **2a** (0.5 mmol), [Cu] catalyst (5 mol%), ligand (20 mol%), $TMSN_3$ (1.1 equiv.), and solvent (6 mL). The reaction mixture was irradiated with blue LEDs (40 mW cm^{-2} at 460 nm) under O_2 (1 atm) at RT. [b] Yield of the isolated product. [c] Absence of a ligand. [d] Under 1 atm air. [e] In the absence of $TMSN_3$, addition of triflic acid (1.0 equiv.). [f] In the absence of a copper catalyst. [g] Under N_2 atm (absence of O_2). [h] In the dark (absence of light). n.r = no reaction. [i] Reaction conducted in the dark at 60 °C.

3a (Table 1). First, copper iodide (5 mol%) and 2-picolinic acid (20 mol%) in CH_3CN–MeOH (1 : 1 v/v) afforded the product **3a** in 70% yield after 4 h irradiation (entry 1, Table 1). By screening various CuX (X = Cl, Br) compounds, we found that CuI was a good catalyst for this process (entries 2 and 3, Table 1). In solvent screening, we observed that in pure MeOH as a solvent, one could obtain the product **3a** in a good yield (84%), whereas using ACN as a solvent did not afford the product **3a** (entries 4 and 5). Later, the effect of other ligands, such as 2-amino pyridine, 1,10-phenanthroline, and 2,2′-bipyridine or the absence of ligands was examined. The results showed the poor formation of the product **3a** (entries 6–9). By using the current protocol, the compound **3a** could be formed in 80% yield under 1 atm air (entry 10). When using triflic acid to replace $TMSN_3$, the product **3a** was formed in only 10% yield. Overall, optimization experiments showed that CuI, O_2, and blue LED light all play a crucial role in the current photoredox protocol (entries 9–15).

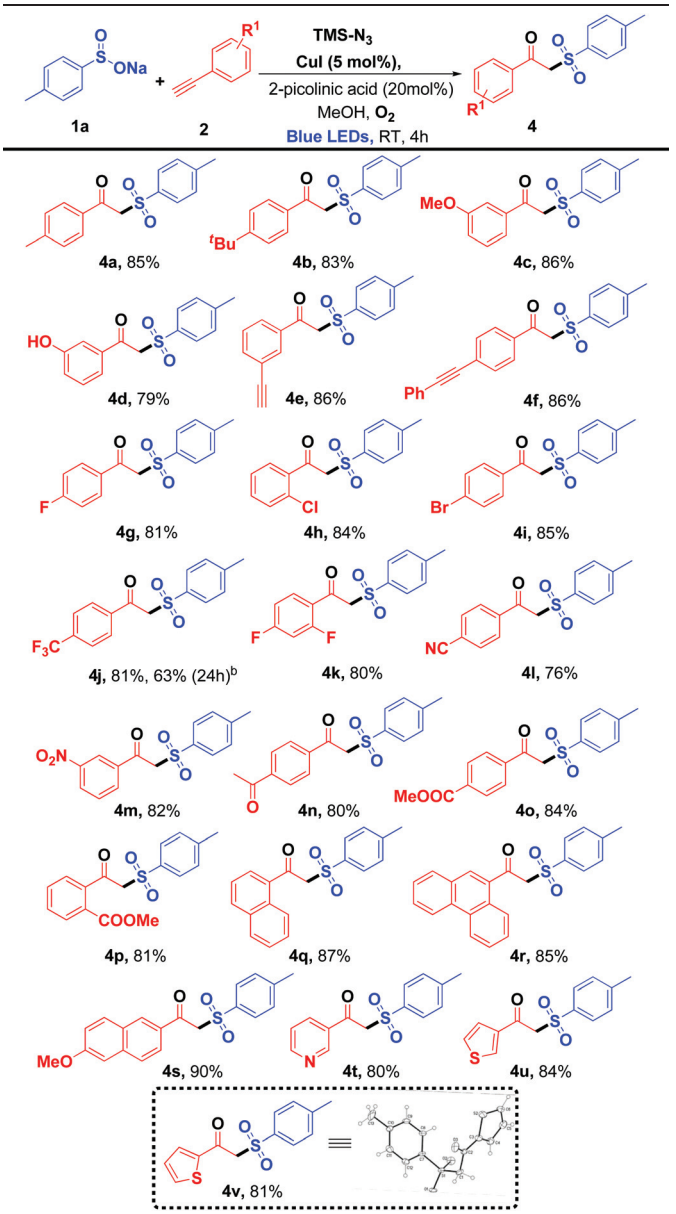
Under the optimal conditions (Table 1, entry 5) for β-keto sulfone **3**, the scope of various sodium sulfinates with phenylacetylene **2a** was examined to check the efficacy of the present photoredox system (Table 2). Sodium *p*-toluene sulfinate and benzene sulfinates showed decent reactivity with **2a**, furnishing the products **3a** and **3b** in good yields of 84% and 82%, respectively. Also, various halogens (–F, –Cl, and –Br), strong electron-withdrawing group (–CF_3, –OCF_3, –CN, –NO_2)-bearing

Table 2 Substrate scope of sodium sulfinates[a]



[a] Standard reaction conditions. Isolated yield after purification by column chromatography on SiO_2.

Table 3 Substrate scope of terminal alkynes[a]



[a] Standard reaction conditions. Isolated yield after purification by column chromatography on SiO_2. [b] Reaction performed on a 2.0 mmol scale.

sulfinates and naphthalene sulfinate reacted smoothly under the standard reaction conditions to form β-keto sulfone products (**3c–3k**) in very good yields. Interestingly, thiophene sulfonate also reacted well with **2a** to form the product 1-phenyl-2-(thiophen-2-ylsulfonyl) ethanone (**3l**) in 81% yield.

Next, the scope of terminal alkynes was explored with **1a**. Various electron-donating, withdrawing, and halo functional group substituted terminal alkynes underwent reaction with **1a** smoothly to afford β-keto sulfones (Table 3). With common electron-donating substituents such as –Me, –tBu, –OMe, and –OH, 1,3 di-alkyne **2e** reacted well with **1a** to form the corresponding sulfone analogs (**4a–4e**) in excellent yields without forming any possible side products, such as Glaser homocoupling[15] and other over-oxidation products.[7] Interestingly, when 1-ethynyl-4-(phenylethynyl) benzene **2f** was used to react with **1a**, the reaction occurred exclusively at the terminal alkyne site with no reaction at the internal alkyne site, showing good chemo-selectivity to produce **4f** in 86% yield. Furthermore, halogen-substituted (–F, –Cl, –Br, and $–CF_3$) and moderate to strong electron-withdrawing functional groups (–CN, $–NO_2$, –Ac, and –COOMe) showed exceptional functional group tolerance in forming the corresponding β-keto sulfones (**4g–4p**) in good to moderate yields.

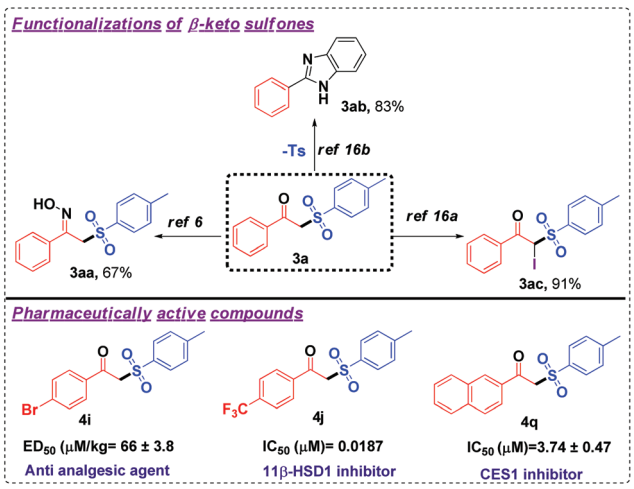
Furthermore, a gram-scale reaction of **1a** and **2q** successfully afforded **4q** in a moderate yield of 63%, after irradiation for 24 h. Pleasingly, bulky terminal alkynes, such as 1-ethynylnaphthalene and 9-ethynylphenanthrene also formed the corresponding products (**4q–4s**) in high (85–90%) yields. Moreover, heterocyclic terminal alkynes, such as 3-ethynylpyridine, 3-ethynylthiophene, and 2-ethynylthiophene, showed good reactivity to form the corresponding β-keto sulfones (**4t–4v**) in 80–84% yields. The structures of **3d** (CCDC 2057129†) and **4v** (CCDC 2008686†) were confirmed by single-crystal XRD (Fig. S5 and S6 ESI†). Unfortunately, the aliphatic alkynes failed to furnish the corresponding sulfones, and the reason is not clear.

The synthetic utility of β-keto sulfones was demonstrated by synthesizing some important intermediates/precursors (Scheme 2). First, the reaction of **3a** with hydroxylamine afforded tosylethanone oxime **3aa**, which is a potent anti-inflammatory agent.[6] Then, imidazole compound **3ab** was synthesized by de-sulfonylation[16b] of β-keto sulfones, and also, the compound **3ac**[16a] was synthesized by iodination on the active methylene group of β-keto sulfones. Moreover, the compounds **4i**, **4j**, and **4q** are found to be anti-analgesic agents,[6] 11 β-hydroxysteroid dehydrogenase type I inhibitors,[16d] and carboxylesterase 1 (CES1),[16c] respectively.

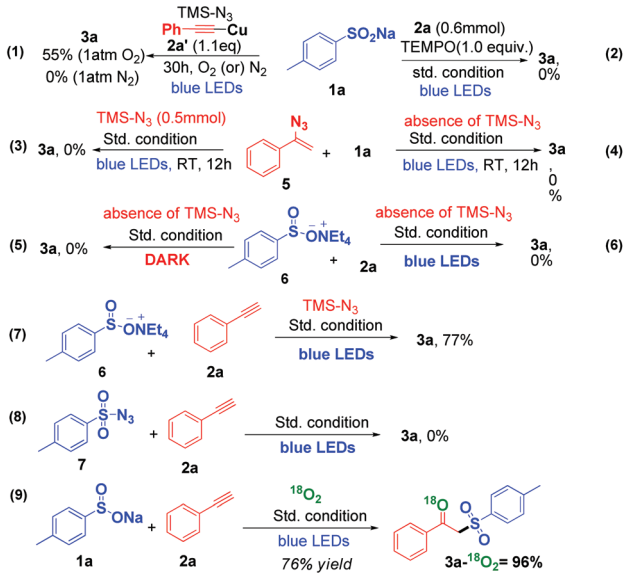
Furthermore, to demonstrate the green side of the reaction, we have evaluated the green chemistry metrics and Eco-scale for the compound **4j**. The gram-scale reaction of **1a** (2.0 mmol) with **2j** (2.0 mmol) under the standard reaction conditions and photoirradiation for 24 h at room temperature produces 0.43 g of product **4j**. Next, we evaluated Green chemistry metrics[4c,e,f,g] (Table S1, ESI†) for the current photochemical method, and the evaluation showed an E factor of 17.55, 71.4% atom economy, 45% atom efficiency, 84.2% carbon efficiency and 62.5% reaction mass efficiency. Moreover, wecompared the green chemistry metrics of the current protocol with that of a reported thermal method (Table S2, ESI†), and the results show that the current photochemical process is 1.8 times better than the thermal process.

Furthermore, we also calculated the Eco-scale[4g] (Table S4, ESI†) value for this photochemical protocol, and the calculated value of 58.5 (on the scale of 100) indicates that this method is an acceptable synthesis procedure for the preparation of β-keto sulfones.

In mechanistic investigations, a series of control experiments were carried out (Scheme 3, eqn (1)–(9)). β-keto sulfone **3a** was obtained in 55% yield when CuI and phenylacetylene were replaced by a pre-synthesized copper phenylacetylide **2a′** complex and reacted with **1a** under standard reaction conditions after 30 h blue LED irradiation (see eqn (1)). This result suggests the copper(I)-phenyl acetylide **2a**, which was



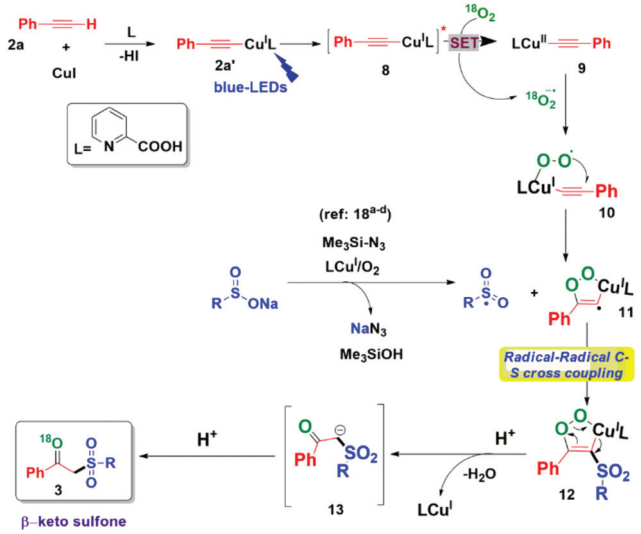
Scheme 2 Late-stage synthesis of medicinal β-keto sulfones.



Scheme 3 Mechanistic control studies.

generated *in situ*, might be the key light absorbing species.[4] On the other hand, replacing O_2 with N_2 completely suppresses the formation of **3a**, indicating that molecular O_2 is a key oxidant participating in the reaction. The addition of a radical scavenger TEMPO (1.0 equiv.) into the reaction mixture does not lead to the formation of **3a** (see eqn (2)), suggesting the involvement of radical intermediates in the reaction. We surmised that this reaction might be going through the vinyl azide intermediate **5** by hydro-azidation on terminal alkynes.[14] To confirm this possibility, we allowed **5** (instead of **2a**) to react with **1a**. However, product **3a** was not formed in both cases in the presence and absence of $TMSN_3$ under the standard conditions. Therefore, the pathway involving the formation of intermediate **5** was ruled out (see eqn (3) and (4)).

Next, we carried out a reaction using tetraethylammonium phenyl sulfonate **6** to replace sodium phenyl sulfonate. Tetraethylammonium phenyl sulfonate **6** has a bulky cation and can ionize faster than **1a**. In the absence of TMS-N_3 (light and dark), the reactions failed to produce **3a**, suggesting that TMS-N_3 plays a key role in facilitating the formation of sulfonyl radicals (see eqn (5) and (6)). However, the reaction of tetraethylammonium phenyl sulfonate **6** with **2a** in the presence of TMS-N_3 (under standard reaction conditions) under light irradiation yields the product **3a** in 77% yield (eqn (7)). Also, the reaction of **2a** with tosyl azide **7** failed to produce **3a**, suggesting that tosyl azide **7** is not a potential intermediate in the current photoredox system (see eqn (8)). Finally, to confirm the source of the O atom, we conducted the experiment under the standard reaction conditions and in the presence of labelled $^{18}O_2$ gas (97%) (instead of $^{16}O_2$) (see, eqn (9)). This experiment formed the product **3a** in 76% yield with 96% incorporation of $^{18}O_2$ in the product (Scheme S3, ESI†), confirming that the source of the O atom in the product originates from molecular O_2.



Scheme 4 Proposed mechanism.

A plausible mechanism (Scheme 4) was proposed based on the results of the above control studies and former literature reports.[4f] The *in situ* generated Cu(I)-phenyl acetylide **2a′** undergoes photo-excitation (λ_{abs} = 476 nm) and forms a long-lived triplet excited state Cu(I)-phenylacetylide **8** (τ = 15.9 μs).[4f] This photo-excited complex **8** undergoes a single electron transfer (SET) process by donating an electron to molecular O_2, as the reduction potential ($E_{1/2}$ = −2.048 V_{SCE} in CH_3CN) is adequately greater than that of O_2 ($E_{1/2}$ = +0.98 V_{SCE}).[4f] The SET process generates a superoxide radical anion, as evidenced by EPR measurements using DMPO as a radical spin trapping agent (Fig. S2, ESI†).[4f] The SET process generates a superoxide radical anion (as evidenced by the EPR measurements using DMPO as a radical spin trapping agent) (Fig. S2, ESI†) and Cu^{II}-phenylacetylide **9**.[4f] The as-formed superoxide radical anion could further react with Cu^{II}-phenylacetylide **9** and form a Cu^{I}-superoxo radical complex **10**, which further undergoes an intramolecular radical attack on C≡C to form a five-membered carbon-centered radical cyclic intermediate **11**. Meanwhile, sodium sulfinate **1a** readily reacts with TMS-N_3 in the presence of a copper(II) catalyst and oxidant O_2 (CuI reacts with O_2, and forms a Cu(II)-superoxo complex (λ_{max} = 430–510 nm)[4g,17] as evidenced by EPR, see Fig. S4, ESI†) to generate a sulfonyl radical intermediate.[18a–d,19,20] The structure of the metal-superoxo complex could have side-on and end-on geometries. Many factors can influence the oxidation ability and chemical reactivities of metal-superoxo complexes, including the types of ligands, the types of central metal ions (such as Cu(II), Ni(II), Ni(III), Fe(III), Sc(III), Mn(III), *etc.*), the oxidation state of the central metal ion, *etc*. Interested readers are referred to recent review articles.[21] Next, the cyclic intermediate **11** undergoes a radical–radical C–S cross-coupling with the sulfonyl radical intermediate to form an intermediate **12**. Concomitant isomerization of a double bond and cleavage of an O–O bond led to the formation of carbonyl carbon (intermediate **13**) and re-generated the LCu(I) complex. Furthermore, intermediate **13** abstracts the proton and forms β-keto sulfones **3**.

Conclusions

In conclusion, we report a unique copper-catalyzed photoredox method for oxy-sulfonylation (di-functionalization) of terminal alkynes (C≡C bond) by low energy visible light irradiation using commercially available inexpensive starting materials to synthesize β-keto sulfones at room temperature. Experimental evidence suggested that a SET process occurs from the *in situ*-generated triplet state excited copper complex to molecular O_2 to generate a superoxide radical anion. $TMSN_3$ promotes the reaction by forming a sulfonyl radical, leading to the formation of a new C–S bond. Also, the current photoredox protocol does not form hyper-oxidized products, namely, the Glaser homocoupling side products or unwanted waste, which is in contrast to the reported thermal procedures. Besides, the current photoredox approach can be used to synthesize various potent biologically active compounds, such as anti-analgesic agents (**4i**), 11β-HSD1 (**4j**), and CES1 inhibitors (**4q**) from simple, inexpensive, and readily available starting materials. In addition, the E-factor (the crucial parameter for green synthetic chemistry) of the current photochemical method is 1.8 times better than that of the reported thermal method. Moreover, the Eco-scale calculations scale the current protocol of 58.5 on a scale of 0–100 (shows an acceptable synthesis). Thus, overall, the present photochemical method is a green, highly efficient method and follows the various principles of green chemistry synthesis.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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