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Merging radical-polar crossover/cycloisomerization processes: access to polyfunctional furans enabled by metallaphotoredox catalysis^{†‡}

Yongjun Liu,^b Wenping Luo,^b Tingting Xia,^a Yewen Fang,^{ID *}^{a,d} Chan Du,^a Xiaoping Jin,^{*c} Yan Li,^{*b} Li Zhang,^c Wan Lei^b and Hao Wu^a

With the radical derived from alkyl silicates or 4-alkyl-1,4-dihydropyridines as the surrogate for the nucleophile, the cyclisation of 2-(1-alkynyl)-2-alken-1-ones proceeds smoothly *via* consecutive reductive radical-polar crossover and cycloisomerization processes enabled by dual photoredox-copper catalysis. Both single-electron oxidation and reduction occur between the photocatalyst and radical precursor/adduct radical, generating the enolate ion without the need for a base and an exogenous oxidant-reducent. In contrast to the reported transition-metal catalysed cyclisation with the oxonium ion as the key intermediate, the nucleophilic attack of enolate-oxygen on the copper coordinated alkyne was proposed for this dual catalysis. This new methodology for the preparation of polyfunctional furans features mild conditions, a broad substrate scope, and good functional group tolerance.

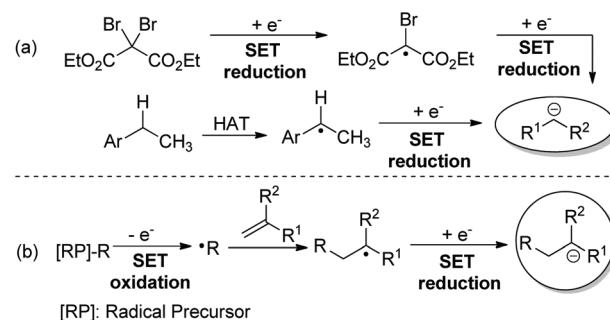
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Since Murphy and co-workers' seminal contribution to radical-polar crossover (RPC) reactions,¹ many organic transformations have been successfully developed *via* radical and ionic species in one pot.² Due to the easily available radical precursors and the generation of radicals in a sustainable way, the modern RPC process by means of photoredox catalysis³ has emerged as an attractive synthetic strategy. In many reported reductive RPC process-based transformations,^{4,5} the ionic species was generated by two consecutive reductions of the electrophile⁶ or reduction of the radical derived from hydrogen atom transfer (HAT) catalysis (Scheme 1a).⁷ Specifically, the radical doesn't engage in the new bond formation of reaction components. However, with radical addition-polar termination (RAPT) as the strategy,⁸ a carbanion was generated from single-

electron transfer (SET) reduction of the radical derived from radical addition toward a radical acceptor (Scheme 1b). Clearly, both radical and ionic species could be involved in the bond formations. Consequently, taking advantage of the high reactivity of radicals toward alkenes and tremendous well-known terminations of the ionic species, many interesting and useful reductive RAPT reactions could be designed and realized. Intrigued by the recent advances in the field of photocatalysed redox-neutral RPC reactions, the chemistry community now has a great new desire to extend the reductive RAPT strategy to more novel synthetic approaches.⁹

In the case of the base-mediated Michael reaction of α,β -unsaturated ketones, sometimes the expected 1,4-addition



Scheme 1 Generation of anionic species *via* the reductive RPC process.

^aSchool of Materials and Chemical Engineering, Ningbo University of Technology, No. 201 Fenghua Road, Ningbo 315211, China. E-mail: fang@nbu.edu.cn

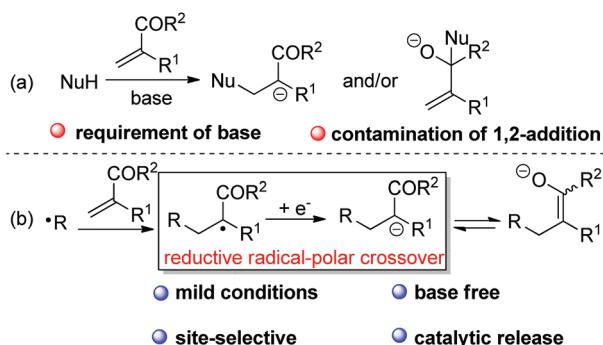
^bHubei Collaborative Innovation Center for Advanced Organic Chemical Materials and Ministry-of-Education Key Laboratory for Synthesis and Application of Organic Functional Molecules, Hubei University, No. 368 Youyi Dadao, Wuhan 430062, China. E-mail: liyanok@hubei.edu.cn

^cDepartment of Pharmaceutical Engineering, Zhejiang Pharmaceutical College, No. 888 Yinxian Avenue East, Ningbo 315100, China. E-mail: jinxp@mail.zjpc.net.cn

^dKey Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, No.345 Lingling Road, Shanghai 200032, China

[†]In memory of Prof. Kilian Muñiz.

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Scheme 2 Ketone enolate formation *via* the Michael addition or reductive RPC process.

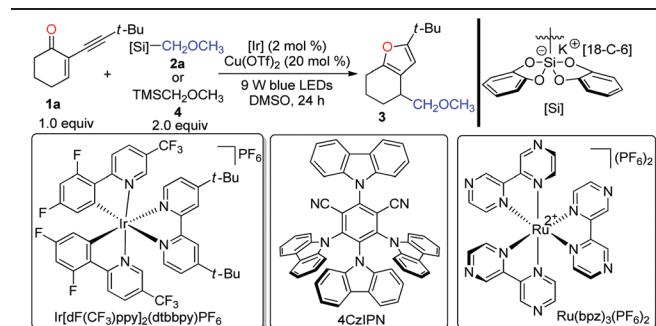
would be contaminated by 1,2-addition of the nucleophile to Michael acceptors (Scheme 2a). However, with RAPT as the strategy, it would be feasible to selectively and catalytically access ketone enolate *via* radical addition to alkene followed by SET reduction of the adduct radical (Scheme 2b). However, to the best of our knowledge, there is still no report on the synthetically useful termination of enolate-oxygen with reductive RAPT as the strategy for the formation of ketone enolate.

Highly functionalized furans are key structural units in many natural products and important pharmaceuticals.¹⁰ They also serve as useful building blocks in synthetic chemistry. For these reasons, numerous efforts have been devoted to the construction of highly functionalized furans and their further transformations.¹¹ Among the available methods to prepare furans, cyclisation of 2-(1-alkynyl)-2-alken-1-ones with various nucleophiles enabled by transition-metal catalysis is highly reliable.¹² According to the investigation by Larock and other groups, the reaction was proposed to proceed *via* the formation of an oxonium ion that is trapped by various nucleophiles to afford the corresponding furans (Scheme 3a). However, compared to the broad substrate scope of O-nucleophiles, the carbon-based nucleophiles are only limited to electron-rich arenes and indoles. Inspired by our and other groups' photo-

redox-catalysed cyclopropanations^{13,14} and Giese-type reactions,^{8,15} we envision that a carbanion could be generated *via* SET reduction of the radical derived from the Giese-type addition of the radical with 2-(1-alkynyl)-2-alken-1-one. After the generation of the enolate ion *via* the reductive RPC process, we hypothesize that a subsequent keto-enol tautomerism equilibrium would be established under base-free conditions. In the presence of a suitable catalyst, the following transition-metal-catalysed cycloisomerization of alk-3-yn-1-one would occur to furnish the expected furan (Scheme 3b). Herein, under mild and base-additive free conditions, we report that polyfunctional furans could be efficiently prepared *via* consecutive RPC and cycloisomerization processes enabled by dual photoredox–copper catalysis. With a radical as the surrogate for carbon-centered nucleophiles, this new method is nicely complementary to the well-developed transition-metal catalysed cyclisation of 2-(1-alkynyl)-2-alken-1-ones.

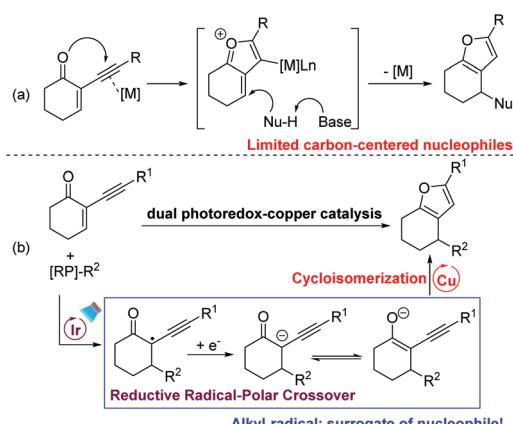
To determine whether our designed combined catalysis is feasible, we began to optimize the reaction conditions with 2-(3,3-dimethylbutynyl)-2-cyclohexen-1-one **1a** and bis-catecholatatosilicate **2a** as the model substrates. According to the results presented in Table 1, the expected polysubstituted furan **3**

Table 1 Survey of the reaction conditions^{a,b}



Entry	Deviation from the standard conditions	Yield of 3 (%)
1	None	87
2 ^c	4 instead of 2a	0
3	In DMF	57
4	In DMA	16
5	In THF	47
6	[Ru] instead of [Ir]	64
7	4CzIPN instead of [Ir]	62
8	CuCl	86
9	CuI	81
10	Cu(CH ₃ CN) ₄ PF ₆	83
11	CuOTf	47
12	CuBr ₂	18
13	Cu(OAc) ₂	81
14 ^{c,d}	Without light	0
15 ^c	No [Ir]	0
16 ^c	Without Cu(OTf) ₂	0

^a Standard reaction conditions: A reaction mixture of **1a** (0.2 mmol), **2a** (0.4 mmol), [Ir] (2 mol%), and DMSO (6.0 mL) was irradiated using 9 W blue LEDs for 24 h at room temperature (cooling with a fan). [Ir]: Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆; [Ru]: Ru(bpz)₃(PF₆)₂. ^b Yield of the isolated product **3**. ^c NMR yield (500 MHz) was reported using *p*-nitroacetophenone as an internal standard. ^d The reaction was performed in the dark.



Scheme 3 Two different pathways for accessing furans from yneones.

could be nicely isolated in 87% yield in the presence of $[\text{Ir}(\text{dF}(\text{CF}_3)\text{ppy})_2(\text{dtbbpy})\text{PF}_6]$ (2 mol%) and $\text{Cu}(\text{OTf})_2$ (20 mol%) in DMSO at room temperature upon irradiation with blue light-emitting diodes (LEDs) for 24 h (entry 1). The use of the commercially available (methoxymethyl)trimethylsilane 4 led to no formation of 3 (entry 2). Similar to our previous observation, DMSO is superior to DMF, DMA, and THF (entries 3–5). Using $\text{Ru}(\text{bpz})_3(\text{PF}_6)_2$ ¹⁶ as the photocatalyst afforded the desired furan 3 in a 64% yield (entry 6). Interestingly, with the organic photocatalyst 4CzIPN,¹⁷ the reaction also worked smoothly with a 62% yield (entry 7). Further evaluation indicated that both Cu(II) (entries 1, 12 and 13) and Cu(I) catalysts (entries 8–11) were able to promote the desired transformation. Remarkably, we found that the copper catalyst plays a critical role in this reaction, since using other Lewis catalysts resulted in a severe decrease of the efficiency (see the ESI† for more optimizations). Control experiments confirmed that visible light, a photocatalyst, and a copper catalyst were all required for this cascade reaction (entries 14–16).

With the optimized reaction conditions in hand (entry 1, Table 1), we next turned our attention to investigating the general synthetic applicability as well as the potential limitations of this novel dual photoredox–copper catalysis. As highlighted in Table 2, with 2-(3,3-dimethylbutynyl)-2-cyclohexen-1-one **1a** and 2-phenylethynyl-2-cyclohexene-1-one **1b** as the radical acceptors, a range of alkyl bis(catecholato)silicates **2** could engage in this cascade reaction to produce various furans **5** and **6** in moderate to high yields. Taking advantage of the low oxidation potential, bis-catecholato silicon compounds (E_{ox} between +0.34 and +0.87 V vs. SCE in DMF) are reliable radical precursors for the generation of reactive primary radicals.^{18,19} Pleasingly, a series of unstabilized primary radicals could be nicely engaged as shown by the formation of products **5a–d** and **6a–e**. Generally, the reactions between **1a** and **2** provided better yields compared to the corresponding

Table 2 Reaction of 2-alkynyl-cyclohexenones **1** with various alkyl bis(catecholato)silicates **2**^{a,b}

	$1 \text{a, } R^1 = t\text{-Bu}$ $1 \text{b, } R^1 = \text{Ph}$	
	$5\text{a, } R^2 = \text{Et, 73\%}$ $5\text{b, } R^2 = n\text{-Pr, 86\%}^d$ $5\text{c, } R^2 = n\text{-Hex, 68\%}^c$ $5\text{d, } R^2 = n\text{-Oct, 62\%}^d$ $5\text{e, } R^2 = i\text{-Bu, 73\%}^c$ $5\text{f, } R^2 = \text{CH}_2\text{OAc, 87\%}^d$ $5\text{g, } R^2 = c\text{-Hex, 56\%}^c$	$6\text{a, } R^2 = \text{Et, 70\%}$ $6\text{b, } R^2 = n\text{-Pr, 37\%}^d$ $6\text{c, } R^2 = n\text{-Hex, 55\%}^c$ $6\text{d, } R^2 = n\text{-Oct, 41\%}^d$ $6\text{e, } R^2 = (\text{CH}_2)_3\text{NHPH, 38\%}$ $6\text{f, } R^2 = i\text{-Bu, 22\%}^c$ $6\text{g, } R^2 = \text{CH}_2\text{OAc, 45\%}^d$ $6\text{h, } R^2 = c\text{-Hex, 51\%}^c$

^a Reaction conditions: See entry 1, Table 1. ^b Isolated yield. ^c The reaction was performed with **2** (3.0 equiv.) for 36 h. ^d The second portion of **2** (0.2 mmol), [Ir] (1 mol%), and $\text{Cu}(\text{OTf})_2$ (10 mol%) was added after 24 h and the overall reaction time was 48 h.

reactions of **1b** with **2**. Possibly, the *tert*-butyl group is much more beneficial for the stabilization of the organocopper intermediate derived from the cycloisomerization process. In addition to the linear alkyl radicals, the branched *iso*-butyl radical furnished the products **5e** and **6f** in 73% and 22% yields, respectively. Expectedly, the α -oxygenated radical reacted properly to produce **5f** (87%) and **6g** (45%). Furthermore, the secondary radical generated from bis(catecholato)cyclohexylsilicate was also converted into the corresponding products in good yields (**5g** and **6h**).

Inspired by the successful application of alkyl silicates as the alkyl radical precursors, various 4-alkyldihydropyridines (DHPs)²⁰ were used to test the generality of the radical source for this dual catalysis. Generally, the success and efficiency of this cascade reaction were highly dependent on the radical precursors. In light of the yield, the results of the reactions with alkyl-DHPs **7** as the radical precursors are inferior to those of the reactions of **1** with alkylsilicates. As listed in Table 3, methoxymethyl and *N*-Boc protected aminomethyl radicals derived from the corresponding dihydropyridine precursors could engage in the cascade reaction to afford the corresponding furans **3** and **9a** in 29% and 39% yields, respectively. However, the ethyl radical derived from 4-ethylidihydropyridine did not give the desired product. Interestingly, secondary alkyl-DHPs engaged in the cascade reactions smoothly, in which moderate yields of furans **9b** and **9c** were obtained. Pleasingly, the *tert*-butyl radical generated from Hantzsch nitrile **8** reacted well with **1a** to give furan **9d** in 33% yield. Of note, with **1a** and **1b** as the radical acceptors, it is difficult to purify the furans due to the contamination of the undesired homocoupling products of benzyl radicals. Fortunately, the purification problem could

Table 3 Reaction of 2-alkynyl-cyclohexenones **1** with various 4-alkyldihydropyridines^{a,b}

	$1 \text{a, } R^1 = t\text{-Bu}$ $1 \text{c, } R^1 = 4\text{-PhC}_6\text{H}_4$	
	$7, \text{R}^2 = \text{Et}$ $8, \text{R}^2 = \text{Ph}$	$[\text{Ir}] (2 \text{ mol } \%), \text{Cu}(\text{OTf})_2 (20 \text{ mol } \%), 9 \text{ W blue LEDs, DMSO, 24 h}$
	$3, 29\%$ $9\text{a, } 39\%$	DHP
	$9\text{b, } 50\%$ $9\text{c, } 25\%$ $9\text{d, } 33\%^c$	
	$9\text{e, } \text{Ar} = \text{Ph, 45\%}$ $9\text{f, } \text{Ar} = 4\text{-MeOC}_6\text{H}_4, 31\%$ $9\text{g, } \text{Ar} = 4\text{-ClC}_6\text{H}_4, 46\%$ $9\text{h, } \text{Ar} = 1\text{-Naphthyl, 16\%}$ $9\text{i, } 25\%$ $9\text{j, } 0\%$	

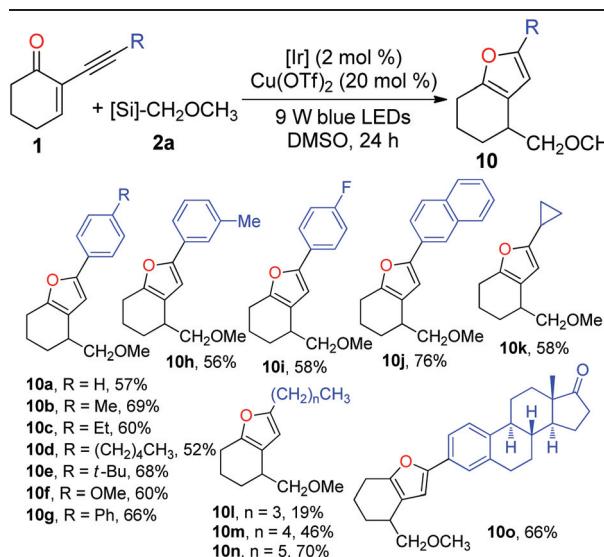
^a Reaction conditions: A reaction mixture of **1** (0.2 mmol), **7** (0.4 mmol), [Ir] (2 mol%), and DMSO (6.0 mL) was irradiated using 9 W blue LEDs for 24 h at room temperature (cooling with a fan). ^b Isolated yield. ^c 2.0 equiv. of **8** were used.

be circumvented using the reaction of enone **1c** in combination with ArCH₂-DHPs. Notably, benzylic DHPs containing not only an electron-donating group (-OMe) but also a weak electron-withdrawing group (-Cl) on the phenyl ring succeeded in delivering the target furans **9e-h** in moderate to good yields. Interestingly, the benzoyl radical generated from the acyl-DHP²¹ also successfully underwent the cascade reaction, producing **9i** in 25% yield. As a limitation, 4-carbamoyl-1,4-dihydropyridine²² failed to participate in the cascade reaction.

After investigating the scope of radical precursors, we next examined the influence of alkynes **1** using **2a** as the radical source. Generally, both aromatic and aliphatic alkynes were suitable substrates for the tandem reaction and could be readily cyclised to give the desired furans in good to high yields (Table 4). Electronic variations in the aryl ring of the alkynes have no pronounced effect on the efficiency of the tandem addition-cyclisation processes, delivering furans **10a-j** in 52–76% yields. Additionally, 5-cyclopropylfuran **10k** and a set of 5-alkyl substituted furans **10l-n** could be readily prepared using the current cascade reactions. Moreover, the reaction of the estrone derivative with **2a** successfully generated the corresponding furan **10o** in 66% yield. This demonstrates that this protocol dealing with the preparation of furans is viable in a complex molecular setting.

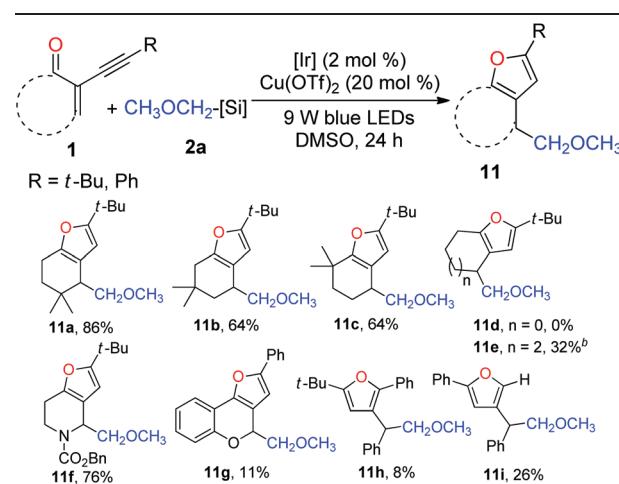
Subsequently, we focused our attention on the examination of the scope of 2-(1-alkynyl)-2-alken-1-ones **1**. As presented in Table 5, varying the steric demand on the cyclohexene ring did not diminish the efficiency of the tandem reaction, affording furans **11a-c** in 64–86% yields. Somewhat surprisingly, the reaction of the five-membered enynone with **2a** failed to give the expected furan **11d**. However, **11e** could be prepared from the seven-membered enynone in a synthetically useful yield.

Table 4 Cascade reactions of silicate **2a** with various 2-alkynylcyclohexenones **1**^a



^a Reaction conditions: See entry 1, Table 1. Isolated yields.

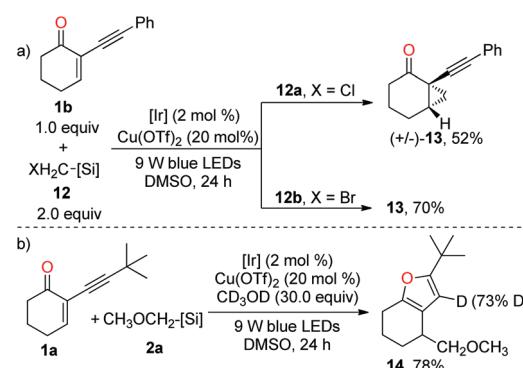
Table 5 Reactions of silicate **2a** with various 2-(1-alkynyl)-2-alken-1-ones **1**^a



^a Reaction conditions: See entry 1, Table 1. Isolated yields. ^b The reaction was conducted with **2a** (3.0 equiv.) for 36 h.

Interestingly, the nitrogen-containing six-membered enynone was readily transformed into furan **11f** in 76% yield. The benzopyran-derived enynone could likewise be used, and the resulting furan **11g** was isolated in 11% yield. Delightfully, subjecting acyclic radical acceptors to the standard reaction conditions afforded furans **11h** and **11i**, albeit in low yields.

To have a better insight into the mechanism, we have conducted several preliminary mechanistic experiments. When **1b** was subjected to the standard conditions in the presence of halomethyl silicates **12**, cyclopropane **13** was obtained instead of the furan product in both reactions (Scheme 4a), thereby supporting the involvement of the photoredox-catalysed reductive RPC process.^{13,14a} Clearly, the cyclopropanation process outcompeted the copper-catalysed cycloisomerization reaction. Moreover, in the presence of 30.0 equiv. of deuterated methanol, the furan product was obtained *via* dual catalysis instead of the copper-catalysed cyclisation of **1a** with deuterated methanol as a nucleophile, suggesting that photoredox-catalysed radical addition to alkene is more facile than the copper-



Scheme 4 Mechanistic experiments.

induced cyclisation of carbonyl oxygen onto the triple bond (Scheme 4b). According to the result of deuterium incorporation in **14**, the protonation of the carbon–copper bond was involved.

Based on these results, a prospective mechanism involving reductive RPC and copper-catalysed cycloisomerization processes is shown in Scheme 5. The initial SET oxidation of alkyl bis(catecholato)silicates **2** or 4-alkyl DHPs **7** by the photo-excited photocatalyst $^*[\text{Ir}(\text{III})]$ leads to the formation of the reduced species $[\text{Ir}(\text{II})]$ and alkyl radical **I**.^{9a} The alkyl radical reacts with the acceptor alkene **1** to provide adduct radical **II**. After SET reduction of **II** by the reduced photocatalyst, enolate ion **III** is formed and the photocatalyst is regenerated in its ground state, thus closing the redox-neutral photocatalytic cycle. After the generation of the enolate ion, subsequent keto-enol tautomerism equilibrium between **III** and **IV** would be established. Subsequent coordination of the alkynyl moiety of enolate to the copper catalyst induces a cyclisation of the enolate oxygen onto the triple bond. Protonation of the resulting organocopper intermediate **VI** produces furan **3** with simultaneous regeneration of the copper catalyst.

Lastly, we briefly evaluated the further transformation of the furan product (Scheme 6). Furan **3** was treated with DDQ in toluene to yield benzofuran **15** in 42% yield, thus providing a regioselective method for the preparation of 4-substituted benzofuran.

In summary, we have developed a mild visible-light-promoted photoredox/copper-catalysed cyclisation of 2-(1-alkynyl)-2-alken-1-ones with radicals for the preparation of polyfunctional furans. With alkyl silicates or 4-alkyl-1,4-dihydropyridines as the radical precursors, a range of alkyl radicals could

be used as the surrogate for the carbon-centered nucleophile for this cascade reaction. In addition to a broad scope of radical precursors, a set of cyclic and acyclic 2-(1-alkynyl)-2-alken-1-ones are suitable radical acceptors for this dual catalysis. This protocol tolerates a wide range of functional groups and is viable in a complex molecular setting. This methodology also features the redox-neutral RPC process and the selective formation of ketone enolate under base-free conditions. A mechanistic pathway involving consecutive photoredox-catalysed reductive RPC and copper-catalysed cycloisomerization processes is proposed. The resulting furan can be readily transformed into 4-substituted benzofuran through DDQ-promoted dehydrogenation. We anticipate that this methodology will inspire synthetic chemists with new enthusiasm for the application of the reductive RPC process in combination with transition metal catalysis for the preparation of important and useful molecules.

Conflicts of interest

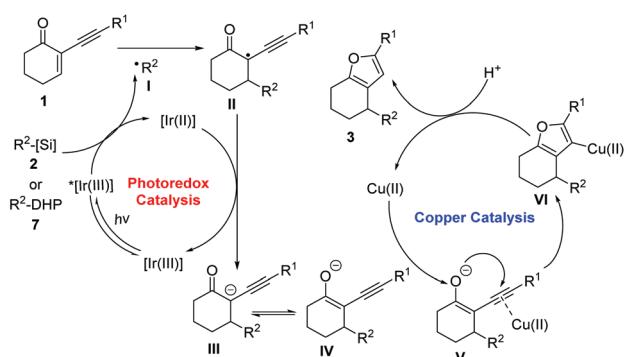
There are no conflicts to declare.

Acknowledgements

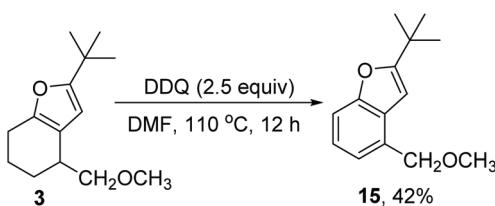
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Scheme 5 Proposed mechanistic pathway.



Scheme 6 DDQ-induced dehydrogenation of the furan product.

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