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

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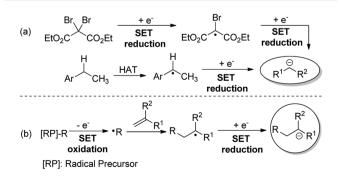
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Since Murphy and co-workers' seminal contribution to radical-polar crossover (RPC) reactions, many organic transformations have been successfully developed *via* radical and ionic species in one pot. Due to the easily available radical precursors and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

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[†]In memory of Prof. Kilian Muñiz.

(a) NuH
$$\xrightarrow{R^1}$$
 Nu $\xrightarrow{COR^2}$ \xrightarrow{PO} \xrightarrow{Nu} $\xrightarrow{R^1}$ and/or $\xrightarrow{R^1}$ \xrightarrow

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-

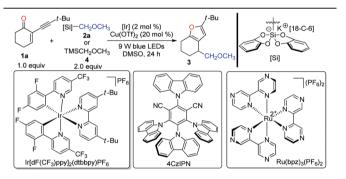
Scheme 3 Two different pathways for accessing furans from yneenones

Alkyl radical: surrogate of nucleophile!

cyclopropanations 13,14 redox-catalysed 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-catecholatosilicate 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	$Cu(CH_3CN)_4PF_6$	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. NMR yield (500 MHz) was reported using p-nitroacetophenone as an internal standard. d The reaction was performed in the

could be nicely isolated in 87% yield in the presence of Ir[dF(CF₃)ppy]₂(dtbbpy)PF₆ (2 mol%) and Cu(OTf)₂ (20 mol%) in DMSO at room temperature upon irradiation with blue lightemitting 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 Ru(bpz)₃(PF₆)₂¹⁶ 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).

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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-1one 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 ($E_{\rm ox}$ 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}

^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 Cu(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-ethyldihydropyridine 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 tertbutyl 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}

^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 vields. Interestingly, the benzovl radical generated from the acyl-DHP²¹ also successfully underwent the cascade reaction, producing 9i in 25% yield. As a limitation, 4-carbamovl-1,4dihydropyridine²² 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 100 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

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

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

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.

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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 photoexcited photocatalyst *[Ir(III)] leads to the formation of the reduced species [Ir(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 ketoenol 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

Scheme 5 Proposed mechanistic pathway

Scheme 6 DDQ-induced dehydrogenation of the furan product.

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)-2alken-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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