Green Chemistry

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Cite this: *Green Chem.*, 2024, **26**, 4199

Photoredox streamlines electrocatalysis: photoelectrosynthesis of polycyclic pyrimidin-4-ones through carbocyclization of unactivated alkenes with malonates†

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Both polycyclic pyrimidin-4-one synthesis and the dehydrogenative coupling of malonates often require a redox agent, an elevated temperature, large amounts of transition-metal salts, and/or highly acidic/basic conditions, and the promising photoelectrocatalysis suffers from limited reaction patterns. We present herein a new photoelectrocatalytic mode and an electrolysis–photocatalysis–Brønsted base hybrid system for the synthesis of polycyclic pyrimidin-4-ones through dehydrogenative carbocyclization of unactivated alkenes with simple malonates under very mild and external-oxidant-free conditions. The reaction exhibits a good functional-group tolerance and is amenable for a gram-scale synthesis, and the sunlight could serve as the light source. Mechanistic studies suggest that the synergistic effect of light and electricity originates from the fast anchoring of an active electrochemical intermediate by the oxidative quenching photocatalytic cycle of $Ir(ppy)_3$.

Received 21st January 2024,
Accepted 27th February 2024

DOI: 10.1039/d4gc00352g

rsc.li/greenchem

Published on 28 February 2024. Downloaded on 11/12/2025 10:40:43 AM.

Introduction

Polycyclic pyrimidin-4-ones are found in the skeletons of many pharmaceuticals (Fig. 1a)[1,2] and alkaloids (Fig. 1b),[3–6] such as vibegron,[1] risperidone,[2] (−)-aglaroxin C,[3] vasicinone,[4] anisotin,[5] and auranthine,[6] and exhibit a broad range of important bioactivities. Tremendous efforts have been devoted to the construction of this structural motif, and conventionally the cycloaddition of 2-arylquinazolin-4-ones with one-[7] or two-carbon synthons[8] could afford 2,3-fused pyrimidin-4-ones (Scheme 1a). Alternatively, they could be prepared through the [4 + 2]-annulation of 1,4-dipoles such as isatoic anhydrides,[9] isatins[10–12] and 2-aminobenzoyls[13–15] with 1,2-dipoles[16] like 1,2,3,4-tetrahydroisoquinolines,[11,13] isatins[9,10] and pyridines (Scheme 1b).[12,14] Both methodologies are rather appealing, yet generally proceed with a chemical oxidant and large amounts of transition-metal salts at a high temperature. Over the past decade, the alkene difunctionalization[17] and cyclization[18] have proven to be particularly fruitful lines of research, and it has been found recently that *N*-tethered alkenyl group quinazolin-4-ones[19–23] and *N*-cyanobenzamides[24] could undergo intriguing cyclizations to give fused quinazolin-4-ones, often at an elevated temperature and in the presence of a redox agent. On the other hand, the C–C bond formation is of fundamental interest in synthetic chemistry, and the dehydrogenative coupling of a C–H bond is most fascinating due to its atom- and

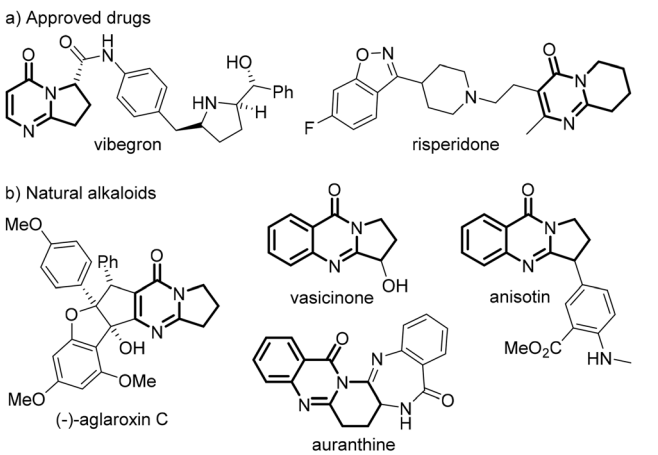

Fig. 1 (a) Selected examples of pyrimidin-4-one pharmaceuticals; (b) Selected examples of pyrimidin-4-one alkaloids.

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†Electronic supplementary information (ESI) available: Experimental details, spectral data, and copies of NMR spectra. See DOI: https://doi.org/10.1039/d4gc00352g

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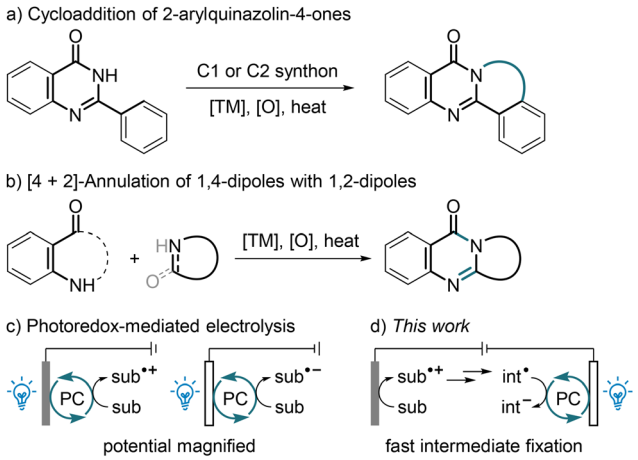

Scheme 1 Synthesis of polycyclic pyrimidin-4-ones and electrophotocatalysis.

step-economy.[25] Malonates are readily available C–H feedstocks, and they could serve as nucleophiles to react with electrophiles usually using a stoichiometric excess of a base in the absence[26] or presence of a noble-metal catalyst.[27] Recent reports have revealed that a polarity-reversed malonate radical could be furnished upon the oxidation of the corresponding enolate, and such an electrophilic 1,3-dicarbonyl radical could be coupled with a wide range of acceptors[28–31] as well as persistent radicals.[32] Notwithstanding the extraordinary discoveries, these reactions frequently require as well high transition-metal loadings and/or highly acidic/basic conditions. Furthermore, it seems that the net-oxidative coupling of a malonate radical[28–30] is more challenging than a redox-neutral one,[31] because the former usually proceeds at an elevated temperature and is often restricted to fluoro-[28] or alkyl-activated malonates.[29] As a result, the development of green and mild protocols for the synthesis of polycyclic pyrimidin-4-ones and for the dehydrogenative coupling of simple malonates is still highly desirable.

Photocatalytic and electrochemical techniques have revolutionized modern organic synthesis over the past decade.[33] In addition, enterprising pioneers, including Lambert[34] and Xu,[35] combined the two techniques to harness the powers of both light and electricity, spawning a new paradigm of electrophotocatalysis and pushing the boundaries of redox chemistry.[36] Using a photocatalytic cycle as the electron shuttle between the reactants and an anode[34,35,37–41] or cathode,[42] a mild yet heterogeneous electrode potential might be turned into a homogeneous and highly biased excited-state potential, thus enabling the coupling of an inactive radical precursor, or enabling an improved reaction efficiency and/or a better functional-group tolerance (Scheme 1c). In some cases, the radical-photogeneration process involved the photoinduced ligand-to-metal charge transfer of $CeCl_3$ [37] or $FeCl_3$,[38] or involved the hydrogen-atom transfer to an excited aryl ketone,[39] decatungstate[40] or riboflavin.[41] In the case reported by Li and coworkers, light and electricity induced the same reaction sequence simultaneously and independently.[43] It was also reported that visible light could be introduced to electrolysis to cleave a C/N/Cl–halogen bond[44] or to illuminate a photoanode.[45] Despite these exciting advances, to date photoelectrosynthesis is still rather underdeveloped, and its reaction types are very limited. Considering its characteristics of sustainability, mildness and robustness, such a hybrid strategy is highly promising, and the development of new reaction modes is of great significance. As a part of our ongoing interest in the green synthesis of heterocycles,[46] we report herein a photoelectrocatalytic construction of polycyclic pyrimidin-4-ones through the dehydrogenative carbocyclization of unactivated alkenes with simple malonates under mild conditions, wherein the diffusion issue, which is related to electrochemistry, of a key transient intermediate might be addressed through fast fixation by an oxidative quenching photocatalytic cycle (Scheme 1d). Similar synergistic effects were observed in two photoreductant-assisted electrochemical alkylations of quinolines, wherein the photocatalysts (PCs) were not regenerated at an electrode.[47,48]

Results and discussion

Exploration of the photoelectrocatalytic carbocyclization was begun using 7-fluoro-3-homoallylquinazolin-4-one **1a** and diethyl malonate **2a** as model substrates (Table 1; see the ESI† for full details). The desired product alkylated dihydropyrroloquinazolinone **3a** was obtained in 54% NMR yield when the reaction was conducted in an undivided cell having a C cloth (CC) anode and a Pt plate cathode with K_2CO_3 (40 mol%) as the base, 4CzIPN (5 mol%) as the PC, Bu_4NPF_6 (1 equiv.) as the supporting electrolyte in acetone/2,2,2-trifluoroethanol (TFE, 9 : 1, v/v) under blue-light irradiation and 2.0 mA constant current conditions at room temperature for 9 h (Q = 2.24 F mol^{-1}, entry 1). While *t*BuOK worked as well as K_2CO_3 (entry 2), the use of a weaker base such as $KHCO_3$ led to a depreciation in the yield (entry 3). A base catalyst is essential for this transformation, and we failed to access the desired product **3a** under base-free conditions (entry 4). A survey of solvents was then conducted. The use of acetone alone had a slightly deleterious effect on the reaction efficiency (entry 5), and the reaction in CH_3CN gave a poor yield of **3a** (entry 6). 1,2-Dichloroethane (DCE) proved ineffective for this transformation, probably due to the poor solubility of K_2CO_3 (entry 7). A comparable yield of 55% was achieved upon varying the ratio of acetone to TFE to 11 : 1 (entry 8). Interestingly, a slightly better yield was obtained when the photoreductant of $Ir(ppy)_3$ was used as the PC (entry 9), whereas the use of Mes-$Acr^+ClO_4^-$, a potent photooxidant, furnished **3a** in a very low yield (entry 10). The yield was improved to 69% on reducing the current to 1.5 mA and prolonging the irradiation time to 12 h, suggesting the importance of the synchronization of electrocatalytic and photocatalytic steps (entry 11). Further increases in the yield were achieved by reducing the loadings of K_2CO_3 and $Ir(ppy)_3$ and increasing the dosage of the electrolyte (entry 12). Whereas the absence of electricity led to no

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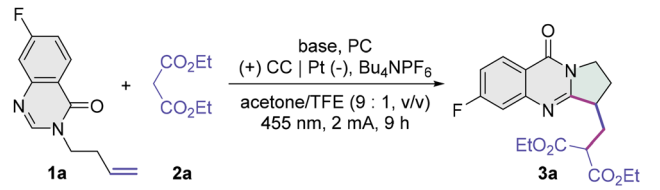
Table 1 Optimization of the reaction conditions[a]



Entry	Base	PC	Solvent	Yield[b] (%)
1	K_2CO_3	4CzIPN	Acetone/TFE	54
2	*t*BuOK	4CzIPN	Acetone/TFE	50
3	$KHCO_3$	4CzIPN	Acetone/TFE	20
4		4CzIPN	Acetone/TFE	0
5	K_2CO_3	4CzIPN	Acetone	47
6	K_2CO_3	4CzIPN	CH_3CN	28
7	K_2CO_3	4CzIPN	DCE	0
8	K_2CO_3	4CzIPN	Acetone/TFE[c]	55
9	K_2CO_3	$Ir(ppy)_3$	Acetone/TFE[c]	59
10	K_2CO_3	Mes-Acr$^+$$ClO_4^-$	Acetone/TFE[c]	16
11[d]	K_2CO_3	$Ir(ppy)_3$	Acetone/TFE[c]	69
12[e]	K_2CO_3	$Ir(ppy)_3$	Acetone/TFE[c]	75 (68)[f]

Entry	Deviation from entry 12	Yield[b] (%)
13	No electric current	0
14	No light	40
15	No PC	38

[a] Reaction conditions: **1a** (0.3 mmol), **2a** (0.9 mmol), base (40 mol%, 0.12 mmol), PC (5 mol%, 0.015 mmol), Bu_4NPF_6 (0.3 mmol), acetone/TFE (9 : 1, v/v, 6.0 mL), 6 W blue LEDs (λ_{max} = 455 nm), CC anode (15 × 15 mm), platinum plate cathode (15 × 15 mm), undivided cell, 2.0 mA, Ar, room temperature, 9 h. [b] Yields were determined by ^{19}F NMR analysis using trifluorotoluene as an internal standard. [c] acetone/TFE (11 : 1, v/v). [d] 1.5 mA, 12 h. [e] K_2CO_3 (10 mol%, 0.03 mmol), $Ir(ppy)_3$ (3 mol%, 0.009 mmol), Bu_4NPF_6 (1.5 equiv., 0.45 mmol), 1.5 mA, 12 h. [f] Isolated yield.

reactivity (entry 13), and pyrroloquinazolinone **3a** was afforded in poor yields upon the removal of light (entry 14) or PC (entry 15) under otherwise optimized conditions.

With the optimal conditions in hand, we evaluated the scope of this transformation (Table 2). While unsubstituted 3-homoallyl quinazolin-4-one reacted with diethyl malonate **2a** to afford the desired product **3b** in 72% yield, a variety of alkylated dihydropyrroloquinazolinones bearing an electron-releasing or electron-withdrawing unit at the 5- (**3c1** and **3c2**), 6- (**3d1–3d5**), 7- (**3e1** and **3e2**) or 8-position (**3f1–3f6**) could be prepared from the corresponding 3-homoallyl quinazolin-4-ones in moderate to high yields. The tested functionalities include methyl, methoxy, fluoro, chloro, bromo and trifluoromethyl groups, and their substituent effects are subtle and poorly characterized. Brominated quinazolin-4-ones (**3d5** and **3f5**) might be challenging substrates and prone to reductive dehalogenation (see the ESI†). These halide products possess complementary functional handles for subsequent cross-coupling. Such a photoelectrocatalytic protocol also tolerates disubstituted substrates such as 6,7-dimethoxy (**3g1**), 6,7-difluoro (**3g2**), 6-chloro-8-methyl (**3h1**), 6,8-dichloro (**3h2**) and 7,8-dimethyl quinazolin-4-ones (**3i**). Tetrahydropyridoquinazolinone **3j** with a newly formed six-membered ring was furnished in a good yield from 3-(4-pentenyl) quinazolin-4-one with a five-carbon alkenyl chain. Using a longer alkenyl chain, we failed to obtain the desired seven- or eight-membered ring product (see the ESI†). As for C–H radical precursors, dimethyl, dibenzyl, diisopropyl, dibutyl and di-*tert*-butyl malonates (**3k–3n**), as well as asymmetric precursors like benzyl methyl malonate (**3o1** and **3o2**) and *tert*-butyl methyl malonate (**3p1** and **3p2**), were all competent to react with a quinazolin-4-one unit having an *N*-tethered alkene moiety, with the corresponding dihydropyrrolo- or tetrahydropyridoquinazolinones provided. A poor yield of the cyclized product **3q** was obtained when dimethyl 2-fluoromalonate was used, probably owing to the steric effect. The potential for the late-stage editing of complex molecules was demonstrated by the carbocyclization of a malonate derived from (−)-borneol (**3r**). It is noteworthy that the photoelectrocatalytic conditions were mild enough to tolerate a thienoquinazolinone substrate (**3s**), and the alkenes linked to a monocyclic pyrimidin-4-one (**3t**) or 6-(trifluoromethyl)pyrimidin-4-one motif (**3u**) were productively engaged in this cyclization as well. Unfortunately, the phenylethynyl, homoallyl, (*tert*-butoxycarbonyl)amino and hydroxy substituents on the aryl moiety were not tolerated (see the ESI†) and represent some limitations of the present methodology.

This new electrophotocatalytic strategy can be applied to a variety of unactivated alkenes (Table 3). Benzoimidazolic alkenes were first assessed, and with diethyl malonate **2a** as the carbon radical precursor under optimal conditions, polycyclic product benzopiperidinoimidazole **4a** was furnished in 86% yield from the *N*-(4-pentenyl) benzoimidazole. *N*-Homoallyl benzoimidazoles participated in this cyclizative cascade to afford modest yields of the corresponding benzopyrroloimidazoles **4b** and **4c**, which might be somewhat strained due to the fusion of two five-membered rings. The attempt to extend the reaction to *N*-homoallyl isoquinolin-1-one gave rise to the formation of pyrroloisoquinolinone **4d** in a moderate yield, and pyrrolopyridinone **4e** was also prepared from the corresponding 1-homoallyl pyridin-2-one. We then moved on to investigate the carbocyclization of indolic alkenes. Indolic substrates bearing an electron-withdrawing motif, such as carbethoxy, acetyl or cyano group, at the C3-position all worked well, providing the desired tetrahydropyridoindoles **4f–4h** in good to high yields. The substrates featuring a pyrazole-4-carboxylate or pyrrole-2-carboxylate are both compatible with this transformation, and the desired pyridopyrazole **4i** and 5,6,7,8-tetrahydroindolizine **4j** were provided in 84% and 59% yields, respectively. While this carbocyclization is applicable to *N*-(2-methylallyl)-2-phenylbenzoimidazole, giving 5,6-dihydrobenzoimidazo[2,1-*a*]isoquinoline **4k** in a very high yield, the use of *N*-allyl acetanilide afforded indoline **4l** in 54% yield. Interestingly, when *O*-allyl salicylaldehyde was used as the substrate, the carbonyl group served as the inbuilt radical trap to furnish the chroman-4-one **4m** albeit in a modest yield. The 6,7-dihydropyrido[3,2,1-*ij*]quinolin-1-one **4n** rather than a 2,3-dihydropyrrolo[1,2-*a*]quinolin-5-one product was delivered when an *N*-homoallyl quinolin-4-one was employed. With the tosyl-protected diallylamine, the redox-

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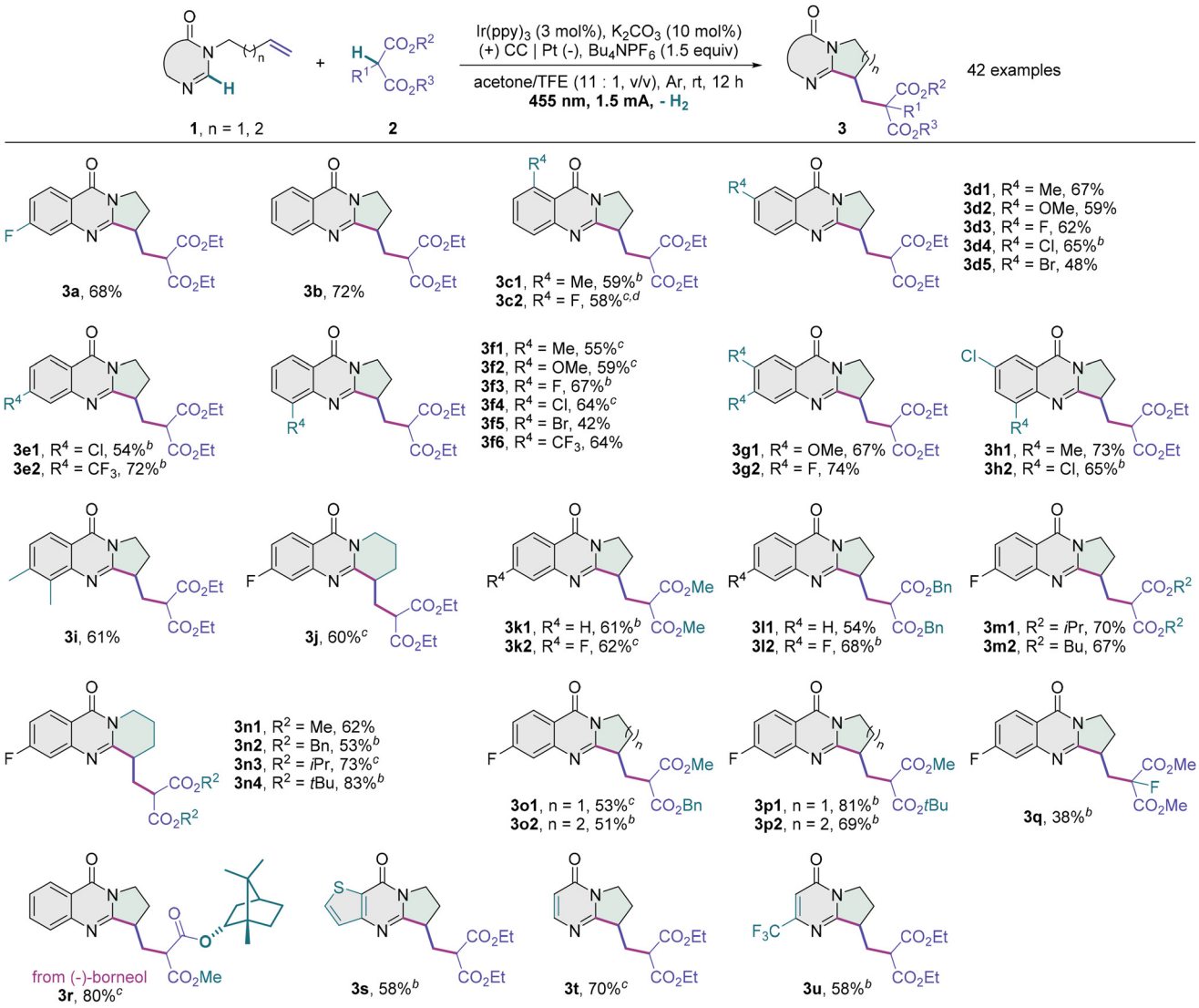
Table 2 Substrate scope[a]



[a] Reaction conditions: **1** (0.3 mmol), **2** (0.9 mmol), K_2CO_3 (0.03 mmol), Ir(ppy)$_3$ (0.009 mmol), Bu_4NPF_6 (0.45 mmol), acetone/TFE (11 : 1, v/v, 6.0 mL), 6 W blue LEDs (λ_{max} = 455 nm), CC anode (15 × 15 mm), platinum plate cathode (15 × 15 mm), undivided cell, 1.5 mA, Ar, room temperature, 12 h. [b] 1.5 mmol of **2** was used. [c] 0.15 mmol of K_2CO_3 was used. [d] 24 h.

neutral product 3,4-dialkylpyrrolidine **4o** was afforded. Although we failed to extend this electrophotocatalytic protocol to several activated alkenes (see the ESI†), indolin-2-one **4p** was obtained in an excellent yield from the parent *N*-arylacrylamide.

A gram-scale reaction of 6-methyl-3-homoallyl quinazolin-4-one **1d1** and diethyl malonate **2a** was performed (Scheme 2a), and the fused quinazolin-4-one product **3d1** was delivered in a comparable yield. The yield of **3d1** was not compromised using sunlight as the light source (Scheme 2b). These results highlight the feasibility of the present protocol in practical utilization.

Attention was then turned towards gaining insight into the mechanism of this transformation (Scheme 3). Kinetic profiles were recorded using ^{19}F NMR spectroscopy of the reactions run under standard, electrochemical or photoredox conditions (Scheme 3a and Fig. S4†). While the carbocyclization did not proceed in the absence of electric current (gray line), much lower reaction rates were observed in the electrolyses under dark conditions (dark yellow and dark cyan lines), confirming the unique catalytic power of this hybrid system and highlighting the importance of simultaneously harnessing the powers of both light and electricity (violet line). A mechanism of indirect electrolysis using ground-state Ir(ppy)$_3$ as an electron shuttle could be ruled out, as comparable results were obtained in the electrochemical reactions with or without the PC (dark yellow and dark cyan lines). Similar trends were observed in the on/off experiments (Scheme 3b and Fig. S5†), in which the carbocyclization became slower under dark conditions and stopped in electricity-off cycles, suggesting a short

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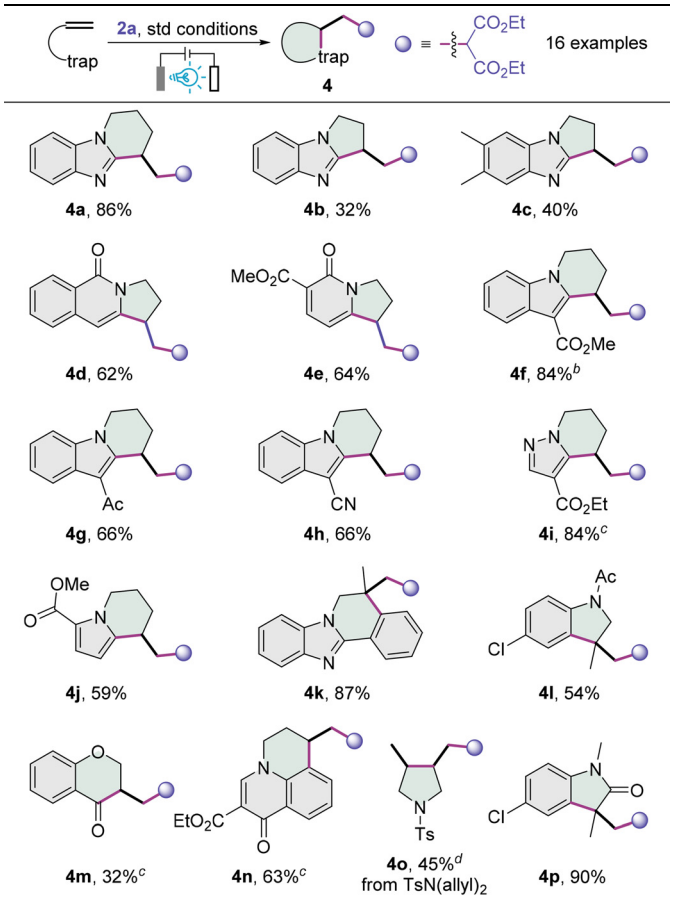
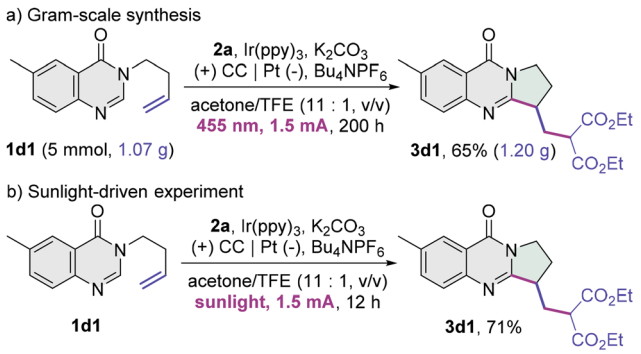
Table 3 Strategy extension[a]

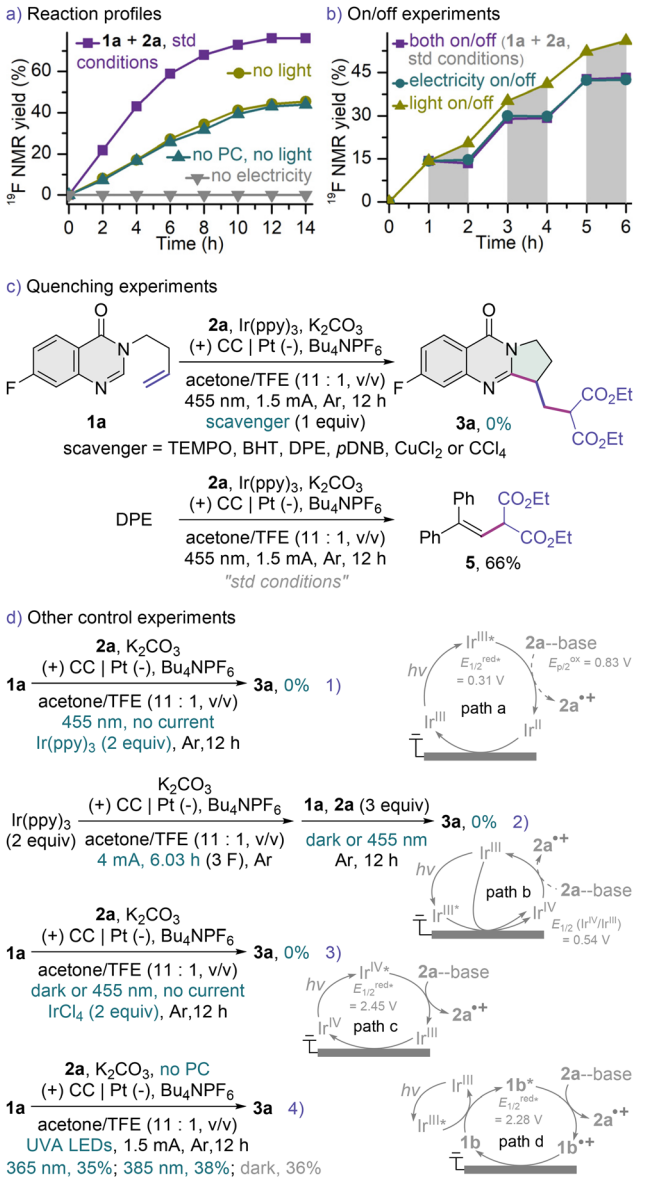


[a] Reaction conditions: alkene substrate (0.3 mmol), **2a** (0.9 mmol), K_2CO_3 (0.03 mmol), $Ir(ppy)_3$ (0.009 mmol), Bu_4NPF_6 (0.45 mmol), acetone/TFE (11 : 1, v/v, 6.0 mL), 6 W blue LEDs (λ_{max} = 455 nm), CC anode (15 × 15 mm), platinum plate cathode (15 × 15 mm), undivided cell, 1.5 mA, Ar, room temperature, 12 h. [b] 24 h. [c] 0.15 mmol of K_2CO_3 were used. [d] 0.45 mmol of K_2CO_3 were used.



Scheme 2 Synthetic utility.

chain mechanism. The radical and single-electron transfer (SET) nature of this protocol was evidenced by quenching experiments (Scheme 3c), in which the model reaction under otherwise optimal conditions ceased upon the addition of a quencher, and the tested quenchers include radical scavengers



Scheme 3 Mechanistic investigations.

such as 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), butylated hydroxytoluene (BHT) and 1,1-diphenylethylene (DPE), a SET inhibitor of *p*-dinitrobenzene (*p*DNB), and electron scavengers like $CuCl_2$ and CCl_4. Subjecting DPE to our standard conditions afforded the malonate-DPE adduct **5** in 66% yield, indicating that the malonate radical might be involved in this transformation. Cyclic voltammetry (CV) tests revealed that the unactivated alkene **1a** ($E_{p/2}$ = 1.92 V *vs.* SCE, Fig. S12†)[22] has a higher oxidation potential than the base-activated diethyl malonate **2a** ($E_{p/2}$ = 0.83 V *vs.* SCE, Fig. S10 and S11†),[32,49] thus it is unlikely that **1a** undergoes a preferential oxidation followed by the nucleophilic addition of **2a** to the resulting alkene radical cation.[50]

The excited-state reduction potential of $Ir(ppy)_3$ is only 0.31 V *vs.* SCE (see the ESI†),[51] thus precluding a proton-coupled electron transfer (PCET) from diethyl malonate **2a** to excited

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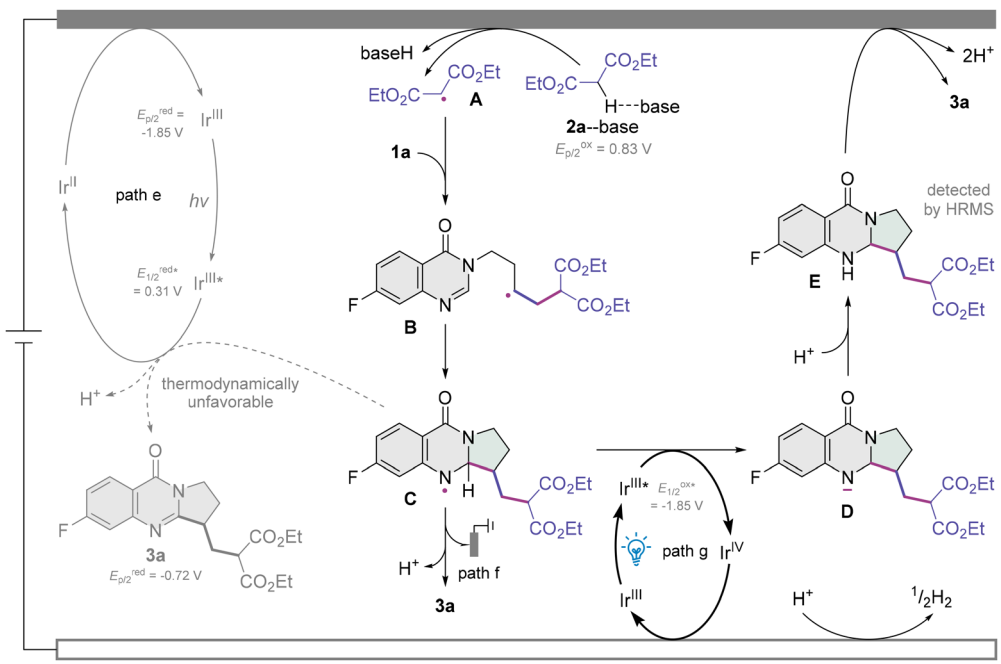
PC in the presence of a base. Such results are in accordance with the facts that in Stern–Volmer quenching experiments **2a** hardly quenched excited Ir(ppy)$_3$ in acetone in the presence or absence of K_2CO_3 (Fig. S19†),[32] and that 2 equiv. of Ir(ppy)$_3$ as the photooxidant failed to promote the desired carbocyclization without electricity (Scheme 3d1). These combine to rule out the merging of electrolysis with the reductive quenching photocatalytic cycle of Ir(ppy)$_3$ (path a).[52] Although a transient photoexcited catalyst has not been reported to be heterogeneously oxidized at the anode,[36] we still assessed the possibility of the oxidative quenching photocatalytic cycle[53] serving as an electron shuttle between the anode and the reactants (path b). No reaction occurred using an excess of either electrochemically generated Ir^{IV} species (Scheme 3d2)[54] or $IrCl_4$ (Scheme 3d3) as the oxidant in the absence of the electric current, suggesting that an Ir^{IV} complex might not be a key oxidizing intermediate in this transformation. This was further evidenced by the CV tests of Ir(ppy)$_3$, wherein the reduction wave for Ir^{IV}/Ir^{III} (Fig. S13 and S14†) and the oxidation peak of Ir^{IV}/Ir^{V} (Fig. S13†) did not disappear or significantly decrease upon the addition of **2a** and K_2CO_3.[28b,55] Considering that the SET from base-activated **2a** to the related Ir^{IV} complex ($E_{1/2}$ (Ir^{IV}/Ir^{III}) = 0.54 V *vs.* SCE, Fig. S7 and S8†)[51] is thermodynamically unfavorable, a highly oxidized excited-state Ir^{IV} complex might be involved (path c).[56] Although the excited-state reduction potential of the *in situ* electrochemically generated Ir^{IV} complex was estimated to be 2.45 V *vs.* SCE (see the ESI†), visible light failed to induce the excess Ir^{IV}-promoted carbocyclization (Schemes 3d2 and d3), suggesting that such an electron-primed photocatalytic mechanism (path c)[34,37,42] is less likely yet could not be completely ruled out. Quinazolin-4-ones can absorb to some extent ultraviolet-A (UVA) light and serve as a photosensitizer,[20] and the excited-state reduction potential of quinazolin-4-one **1b** was estimated to be 2.28 V *vs.* SCE (see the ESI†). Nonetheless, an energy-transfer process leading to the triplet sensitization of **1b** by excited Ir(ppy)$_3$ might not be a productive pathway as well (path d), because no beneficial effect was observed when the electrochemical reaction without a PC was irradiated with UVA LEDs (Scheme 3d4). These negative results concerning the two highly oxidizing photooxidants (paths c and d) coupled to the PC screening data (Table S4†) revealed that the title reaction might not be excited-state reduction potential-dependent. The malonate radical might be generated at the anode.[57]

A mechanistic proposal consistent with these studies is presented in Scheme 4. In the beginning, diethyl malonate **2a** undergoes a PCET to the anode to afford the malonate radical **A**, and such a polarity-reversed 1,3-dicarbonyl radical adds to the tethered alkene moiety, which is nucleophilic, of 3-homoallyl quinazolin-4-one **1a** to give the alkyl radical intermediate **B**. **B** cyclizes to the ring closure N-radical **C** through the intramolecular radical trapping by the amidine moiety of the heterocyclic ring. Two factors weighed heavily against the oxidation of **C** by the reductive quenching photocatalytic cycle of Ir(ppy)$_3$ followed by a deprotonation to furnish the pyrroloquinazolinone product **3a** (path e). One is the extremely low excited-state reduction potential of the PC ($E_{1/2}$ = 0.31 V *vs.* SCE),[51] and the other is its much lower reduction potential ($E_{p/2}$ = −1.85 V *vs.* SCE, Fig. S9†)[51] than that of product **3a** ($E_{p/2}$ = −0.72 V *vs.* SCE, Fig. S15 and S16†), making the SET from intermediate **C** to excited Ir(ppy)$_3$ thermodynamically unfavorable.[47,48] On the other hand, the anodic oxidation of



Scheme 4 The proposed mechanism.

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C and subsequent deprotonation could occur to deliver pyrroloquinazolinone **3a** (path f).[58] Nonetheless, because of the heterogeneous nature of electrochemistry, radical **C** might not be long-lived enough and might experience difficulty in wandering to the anode surface. In such a case, **C** is reduced by the oxidative quenching photocatalytic cycle ($E_{1/2}^{ox*} = -1.85$ V *vs.* SCE, see the ESI†)[51] to give the nitranion intermediate **D**,[47,48,59] and the Ir^{III} catalyst is regenerated at the cathode (path g). The protonation of **D** gives tetrahydropyrroloquinazolinone **E**, which was detected by high-resolution mass spectrometry (HRMS, Fig. S22 and S23†). **E** is readily oxidized to pyrroloquinazolinone **3a** after migrating to the anode.[60] Therefore, we consider that the synergistic effect of this photoelectrocatalytic system originates from the fast anchoring of an active electrochemical intermediate by a photocatalytic cycle with a homogeneous, transient, fixed and highly biased excited-state potential. Significant hydrogen evolution was confirmed by the hydrogen detection experiments (Fig. S24†), which is associated with the cathodic reduction of protons to hydrogen to maintain electron conservation.

Conclusions

The work herein describes in detail the development of polycyclic pyrimidin-4-one synthesis using an electrolysis–photocatalysis–Brønsted base hybrid system through the dehydrogenative carbocyclization of unactivated alkenes with simple malonates. The reaction is mild, external-oxidant-free and atom-economical with H_2 serving as the sole by-product, and exhibits a good functional-group tolerance. This new photoelectrocatalytic mode, which benefits from the fast anchoring of an active electrochemical intermediate by the oxidative quenching photocatalytic cycle, might provide clues for further development of novel photoelectrocatalytic reactions.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We gratefully acknowledge the financial support from the National Natural Science Foundation of China (22061024), the Yunnan Ten Thousand Talent Program for Young Top-Notch Talents (YNWR-QNBJ-2018-133), the Open Project of Yunnan Precious Metals Laboratory (YPML-2023050262), the Scientific Research Funds of Yunnan Education Department (2023J0838), the Frontier Research Team of Kunming University 2023, and the Scientific Research Funds of Kunming University (XPZJ2204 and YJL23020). In addition, Minglin Tao would like to thank her family, especially her grandma Ms Wu, because she has always been deeply loved.

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