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Harnessing the synergistic power of light and electricity: an emerging frontier in catalytic heterocycle synthesis

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The strategic integration of photochemistry and electrochemistry in organic synthesis has opened new avenues for catalytic heterocycle synthesis. This highlight provides a comprehensive overview of photoelectrocatalytic heterocycle forming strategies, discussing the mechanistic aspects and offering insights into the future prospects of this emerging field. Based on the distinct mechanistic pathways, the transformations herein have been preliminarily classified into four categories: (1) photoexcitation of electrochemically generated radical ion catalysts, (2) electrochemically mediated photoredox catalysis, (3) electrochemically mediated photoinduced ligand-to-metal charge transfer catalysis, and (4) interfacial photoelectrocatalysis and others.

1. Introduction

In the field of modern organic synthesis, chemists have never stopped exploring more environmentally benign synthetic methodologies. In this context, both organic photochemistry[1] and electrochemistry[2] have come into their sight, being promising alternatives to conventional thermochemistry. When a compound absorbs light energy and transitions to an excited state, significant changes occur in its electronic distribution and configuration, thereby initiating the following chemical transformations. This distinct mechanism makes photochemical reactions, especially those driven by visible-region light, particularly attractive, owing to their unique reactivity, mild conditions and high selectivity.[3] In electrochemical organic transformations, traceless electrons serve as intrinsic redox agents, replacing hazardous chemical oxidants/reductants and thereby reducing both costs and waste generation. By precisely tuning the applied electric potential and introducing appropriate mediators, it is feasible to control selectivity and suppress undesirable side reactions.[4]

While the use of either light irradiation or electrical potential to achieve organic transformations has been extensively studied during the last one or two decades, the integration of both, known as photoelectrocatalysis (PEC) or elec-

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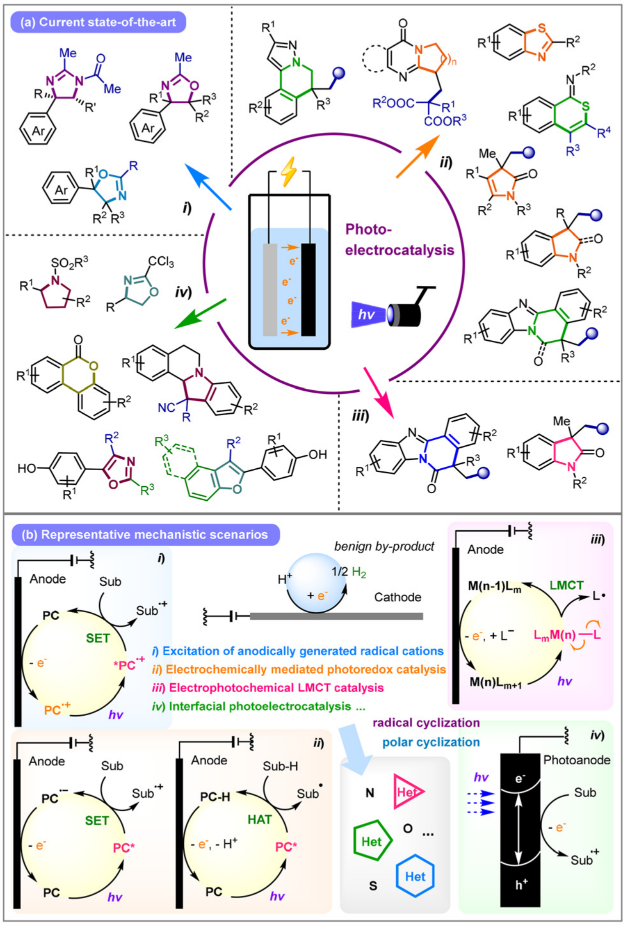
trophotocatalysis (EPC), represents a relatively recent development.[5] The synergistic combination of light and electricity enables novel catalytic pathways, reduces the reliance on external chemical oxidants/reductants, and significantly broadens substrate compatibility, thereby improving both the versatility and sustainability of synthetic methodologies. Since 2019, an increasing number of photoelectrocatalytic systems have been introduced for achieving selective organic transformations, with particular emphasis on cross-coupling reactions (for C–B,[6] C–C,[7] C–N,[8] C–O,[9] C–P,[10] and other[11] bond formation) and (di)functionalization of unsaturated moieties,[12] among others.[13]

Heteroatom-containing cyclic frameworks, commonly referred to as heterocycles, are widely present as key structural motifs in pharmaceuticals, natural products, and agricultural chemicals.[14] Therefore, the efficient, economical, and sustainable construction of heterocycles has long been a central research focus in both academic and industrial settings. Since the traditional approaches often involve harsh reaction conditions and hazardous reagents, light-induced and electrochemically driven alternatives have emerged in recent years, providing innovative, selective, and environmentally benign methods for the synthesis of diverse heterocycles.[15] However, in the more advanced field of organic photoelectrochemistry, cyclization strategies for heterocycle formation have received relatively limited attention compared to other transformation types,[6–13] and thus remain largely underdeveloped.

This highlight focuses on the current advancements made in photoelectrocatalytic heterocycle synthesis, discussing the synthetic aspects of these protocols (Scheme 1a). Typically, under concurrent light-irradiation and electrolysis, cyclization reactions involve the photoexcitation of ground-state photocatalysts (PCs) to initiate the subsequent chemical processes, with anodic oxidation for the (re)generation of key catalytic species or ground-state PCs and cathodic reduction serving as a counter reaction for hydrogen gas evolution. Based on the distinct mechanistic pathways, these transformations can be preliminarily classified into four categories (Scheme 1b): (1) photoexcitation of electrochemically generated radical ion catalysts (Scheme 1b, i), (2) electrochemically mediated photoredox catalysis (Scheme 1b, ii), (3) electrochemically mediated photoinduced ligand-to-metal charge transfer (LMCT)[16] catalysis (Scheme 1b, iii), and (4) interfacial photoelectrocatalysis (i-PEC)[17] and others (Scheme 1b, iv). It is worth noting that alkene epoxidation, a fundamental organic transformation used for synthesizing three-membered epoxide rings, has recently been employed as a model reaction in interfacial photoelectrochemical research studies.[18] However, such studies are primarily rooted in physical chemistry and materials science, focusing on the efficient conversion of light energy into electrical energy, featuring only preliminary synthetic applications. As a consequence, these protocols are excluded from the scope of this highlight, except for those involving the formation of more complex heterocyclic structures with more significant



Scheme 1 Photoelectrocatalytic heterocycle synthesis: an overview of the current advances.

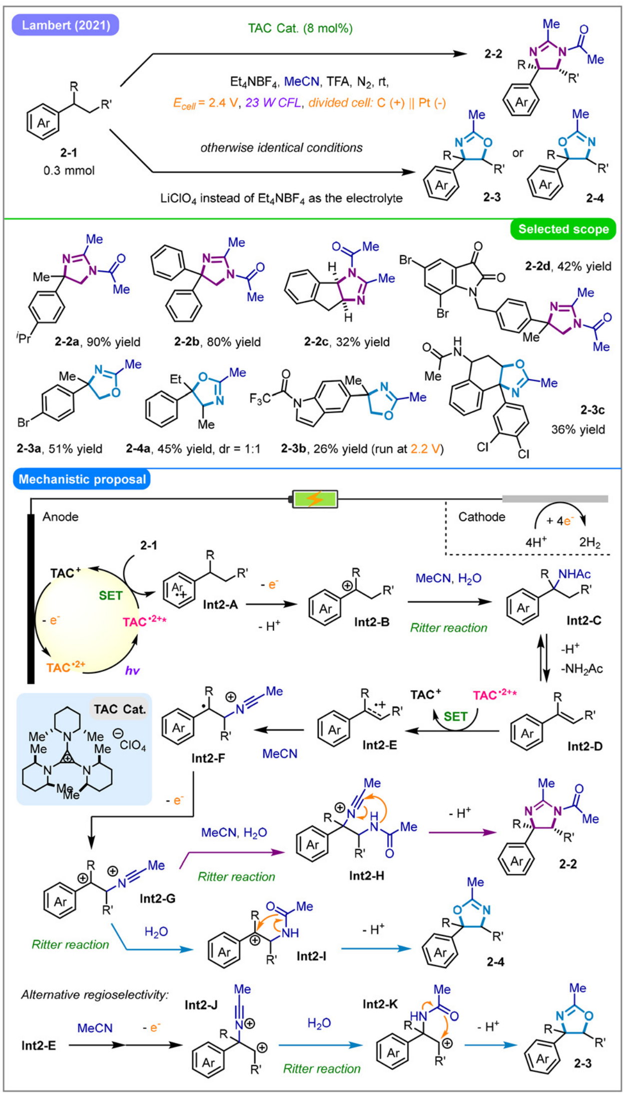
implications for organic chemistry. By systematically examining the detailed reaction conditions, representative substrate scopes, and plausible mechanistic proposals, this highlight discusses the advantages and limitations of current methodologies, with the intention of inspiring future research in this field.

2. Photoexcitation of electrochemically generated radical ion catalysts

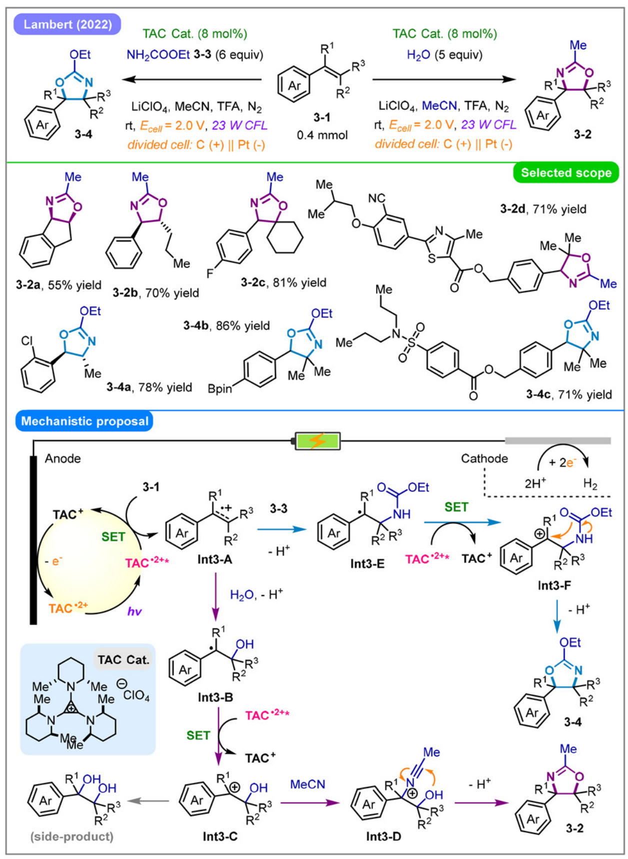
This innovative strategy primarily employs a specially designed catalytic species, termed an electrophotocatalyst, which first undergoes facile single-electron oxidation/reduction at a moderate potential to form a radical ion. Upon absorbing light of specific wavelengths, this radical ion further undergoes photoexcitation to an excited state, featuring strong oxidizing/reducing capability to facilitate the formation of the desired heterocycle. Such a strategy allows certain high-potential-demanding transformations to occur under milder potentials, thereby ensuring better functional group tolerance.

In 2019, the Lambert group developed a trisaminocyclopropenium ion (TAC^+) electrophotocatalyst, which is prone to oxidation at the anode ($E_{1/2}$ = 1.26 V *vs.* SCE) to form a stable red-colored radical dication ($TAC^{•2+}$) for further photoexcitation (λ_{max} = 450, 500, and 550 nm), thereby producing a strongly oxidizing species $TAC^{•2+}$* (E_{ox} = 3.33 V *vs.* SCE).[19] Based on this study, in 2021, they introduced an electrophotocatalytic vicinal C–H diamination or oxyamination of alkylated arenes (**2-1**), affording either 3,4-dihydroimidazoles (**2-2**) or oxazolines (**2-3** or **2-4**) as products with acetonitrile serving as both the solvent and nitrogen source (Scheme 2).[20] The reactions were carried out in a divided cell under controlled potential, irradiated with a white compact fluorescent lamp (CFL), in the presence of 8 mol% TAC catalyst and trifluoroacetic acid (TFA) as a co-solvent. Notably, changing the electrolyte would significantly influence product selectivity: Et_4NBF_4 favored the formation of 3,4-dihydroimidazoles (**2-2**), whereas $LiClO_4$ favored oxazolines (**2-3** or **2-4**). Mechanistically, TAC-facilitated electrophotocatalytic oxidation and deprotonation events generate the benzylic cation **Int2-B**. This intermediate is proposed to undergo a Ritter-type reaction followed by acid-catalyzed elimination, yielding α-methylstyrene **Int2-D**. Subsequent single-electron oxidation of **Int2-D**, followed by trapping with acetonitrile and further oxidation, leads to the formation of the dicationic intermediate **Int2-G** or **Int2-J**. These intermediates then undergo another Ritter-type transformation and nucleophilic cyclization to yield either dihydroimidazole **2-2** or oxazoline (**2-3** or **2-4**) as the product.

In the following year, the same research group further demonstrated a regiodivergent electrophotocatalytic aminooxygenation of aryl olefins (**3-1**) for the synthesis of oxazoline derivatives (**3-2** or **3-4**) using either water or urethane (**3-3**) as the inexpensive nucleophilic reagent (Scheme 3).[21] A similar TAC-based system was used, generating the radical cation intermediate **Int3-A** from **3-1** under photoelectrochemical conditions. This intermediate is readily attacked by either the O- or N-centered nucleophile, followed by electrophotocatalytic oxidation, yielding the corresponding benzylic cation **Int3-C** or **Int3-F**, respectively. Intramolecular polar cyclization of **Int3-F** affords the 2,1-aminooxygenation product (**3-4**), whereas intermolecular attack by the solvent MeCN on **Int3-C**, in compe-



Scheme 2 Electrophotocatalytic diamination and oxyamination of vicinal C–H bonds for the synthesis of N-heterocycles.



Scheme 3 Regiodivergent electrophotocatalytic aminooxygenation of aryl olefins.

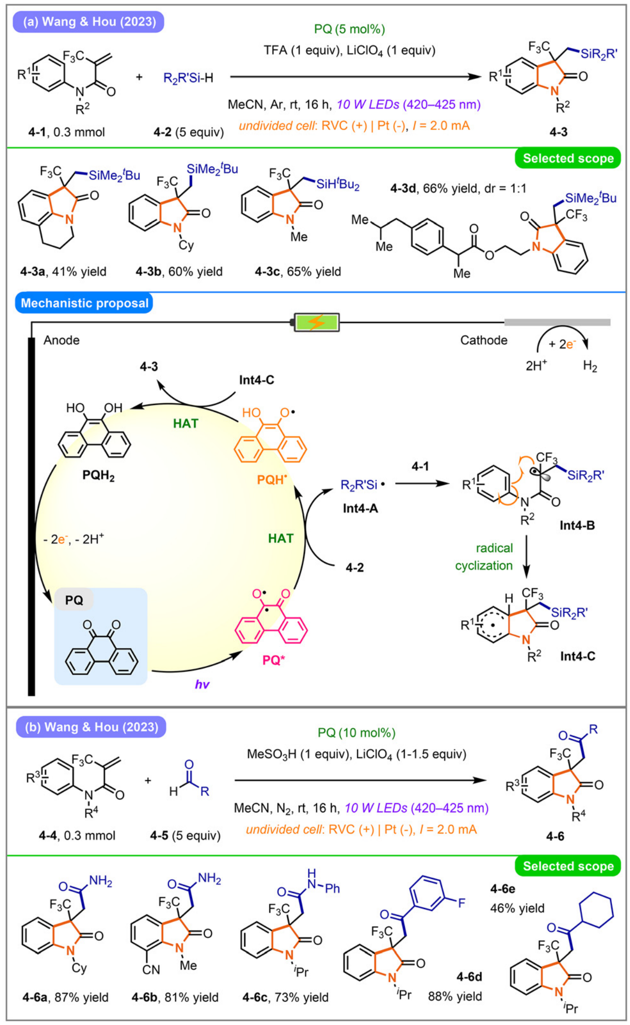
tition with water, leads to the formation of **Int3-D**, which subsequently cyclizes to yield the 1,2-aminooxygenation product (**3-2**). The mild reaction conditions enable broad functional group tolerance, including compatibility with various heterocycles and complex molecular architectures. Furthermore, the protocol exhibits favorable *syn*-diastereoselectivity and demonstrates promising applicability.

In addition to these oxidative annulation strategies from Lambert's group, it is noteworthy that one of Wickens' works also included a reductive cyclization of an alkene-tethered aryl chloride.[10b] The cyclization proceeds through the capture of an aryl radical, generated *via* the reductive cleavage of the C_{Ar}–Cl bond by $NpMI^{\bullet -}*$, an excited-state fused organic species formed through a sequential cathodic reduction and photoexcitation process, ultimately leading to the formation of a dihydrobenzofuran framework.

3. Electrochemically mediated photoredox catalysis

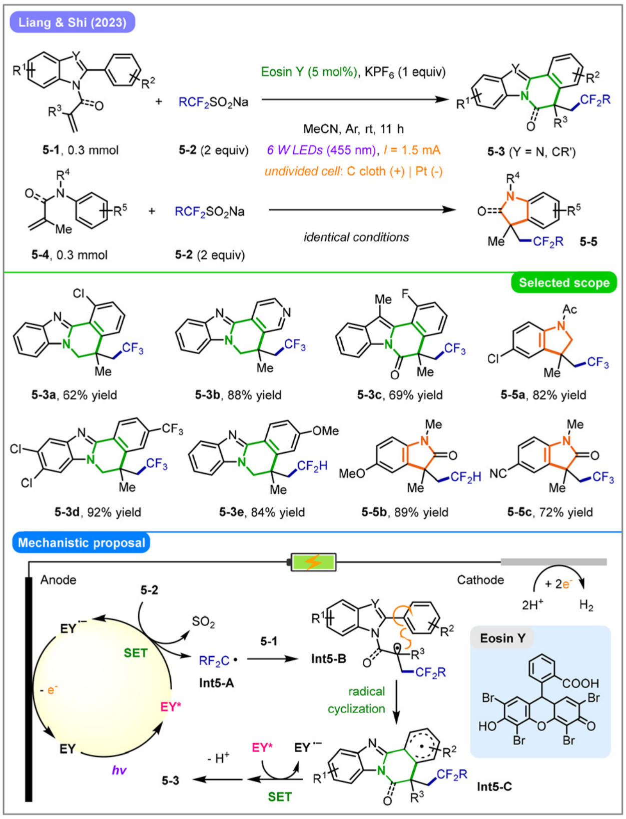
This paradigm utilizes the classical photoredox catalysis, in which the photoexcited photocatalyst undergoes processes such as single-electron transfer (SET), energy transfer (EnT), and hydrogen atom transfer (HAT)[22] to generate radical-type intermediates that participate in the following cyclization reactions. The regeneration of the ground-state photocatalyst is usually achieved through anodic oxidation, thereby eliminating the requirement for an external chemical oxidant. Meanwhile, cathodic evolution of environmentally benign molecular hydrogen serves as the counter reaction. This approach provides a more sustainable alternative to conventional photochemical reactions.

The incorporation of silyl groups into organic molecules through photo- or electrochemical methods has attracted significant research focus over the past few decades.[23] In 2023, the research group led by Wang and Hou disclosed an organo-photoelectrochemical approach for silylative cyclization of CF_3-substituted *N*-arylacrylamides (**4-1**) with organosilanes (**4-2**), employing 9,10-phenanthrenequinone (PQ) as a photocatalyst (Scheme 4a).[24] Under the irradiation at 420–425 nm, PQ is excited to a diradical state (PQ*), which demonstrates strong HAT capability. This enables the abstraction of a hydrogen atom from silane **4-2**, generating a silyl radical intermediate (**Int4-A**) and $PQH^{\bullet}$. Subsequent radical addition of **Int4-A** to substrate **4-1**, followed by intramolecular cyclization, leads to the formation of the radical intermediate **Int4-C**. Finally, the silylated 3-CF_3-2-oxindole product (**4-3**) is afforded through a second HAT reaction between **Int4-C** and $PQH^{\bullet}$, concomitantly regenerating the reduced photocatalyst PQH_2. In this system, electro-oxidation facilitates the regeneration of ground-state PQ, while proton reduction at the cathode obviates the need for external chemical oxidants. Later that year, the same group further applied this photoelectrocatalytic system to generate acyl radicals from formamides or aldehydes (**4-5**) (Scheme 4b).[25] A wide range of acylated 3-CF_3-2-oxindoles (**4-6**) were synthesized from CF_3-substituted *N*-arylacrylamides (**4-4**) through a similar tandem radical cyclization pathway.

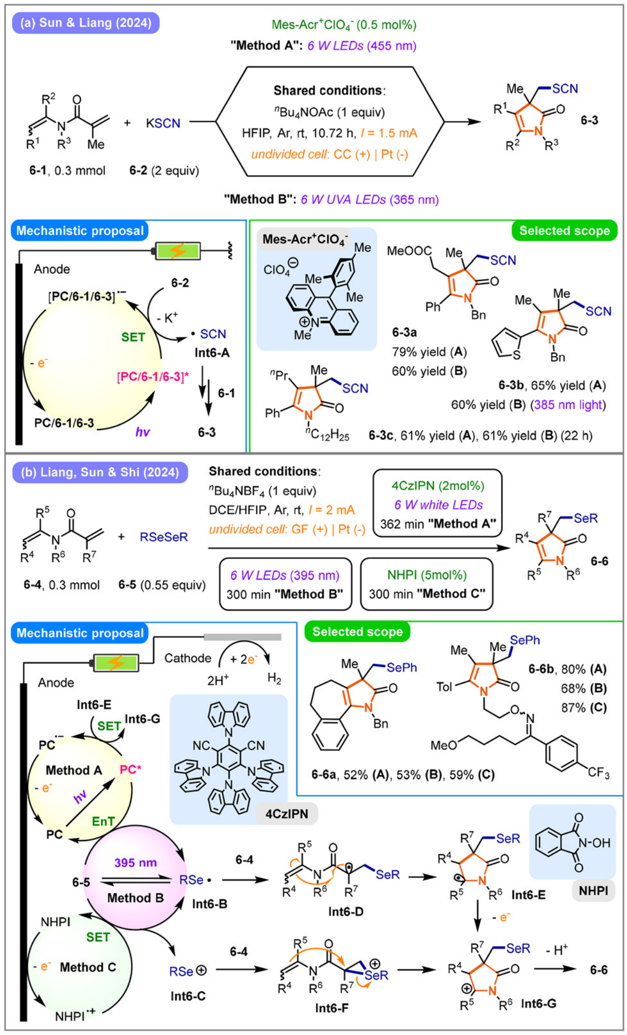


Scheme 4 Organo-photoelectrocatalytic protocols for the synthesis of 3-CF_3-2-oxindoles.

Synthetic methods for the efficient incorporation of fluoroalkyl groups, such as $-CF_3$ and $-CF_2H$, are of significant interest in medicinal chemistry.[26] Employing N-heterocycle-tethered alkenes (**5-1**) as cyclization precursors, the team led by Liang and Shi developed a tri- or difluoromethylative cyclization with fluoromethanesulfinate salts (**5-2**), using Eosin Y as a photocatalyst under photoelectrochemical conditions (Scheme 5).[27] Notably, both activated and unactivated terminal alkenes were proven as competent substrates, enabling the synthesis of a broad range of fused N-heterocyclic compounds (**5-3**) through an electrochemically mediated photoredox catalytic cycle in which the excited-state photocatalyst (EY*) functioned as a mild single-electron oxidant. Moreover, this methodology was also demonstrated to be applicable to the synthesis of various other fluoroalkylated nitrogen-containing heterocycles, including compounds **5-5**.



Scheme 5 Photoelectrocatalytic tri- or difluoromethylative cyclization of alkenes.

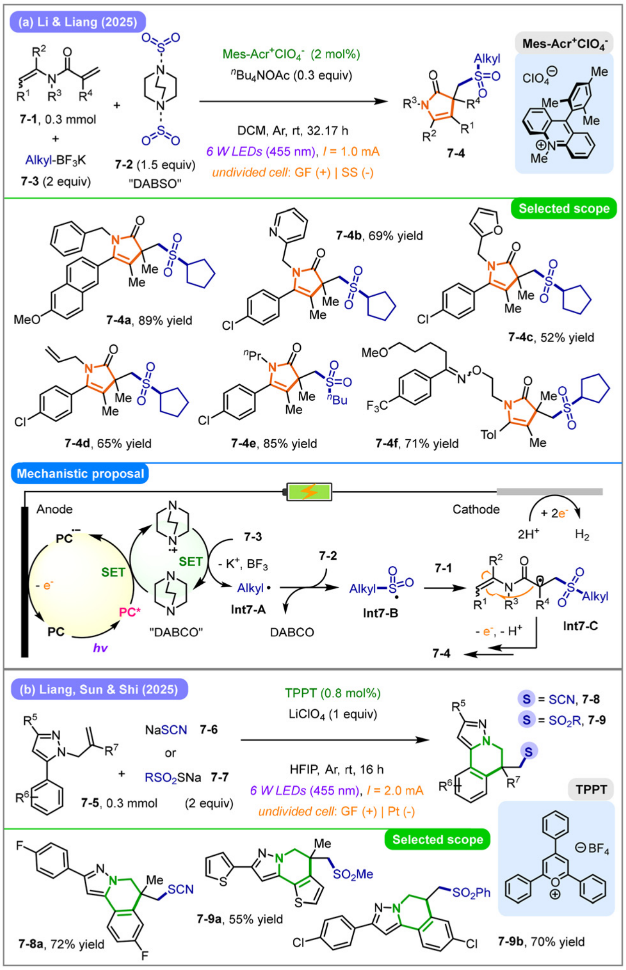


Scheme 6 Photoelectrocatalytic cyclization of 3-aza-1,5-dienes for the construction of 4-pyrrolin-2-one skeletons.

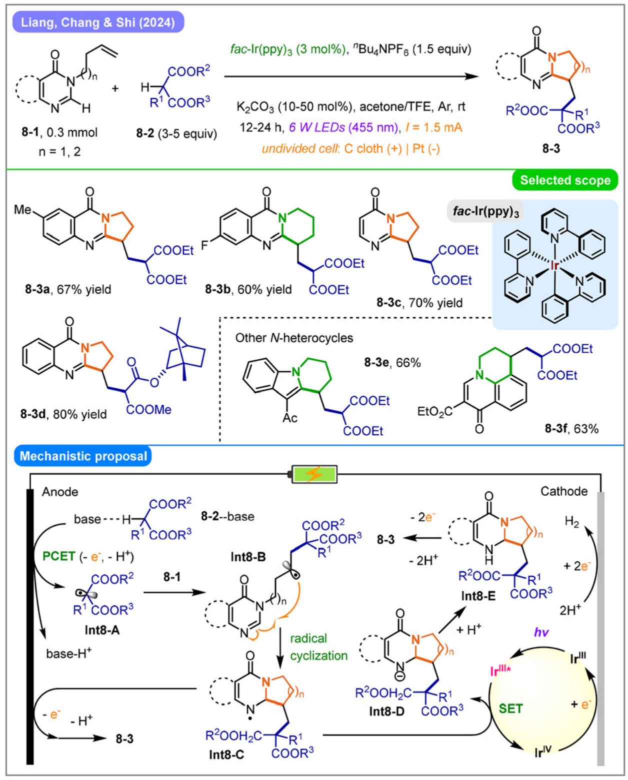
Given the significance of heterocycles containing sulfur- and selenium-based substituents,[28] in 2024 and 2025, Liang and colleagues sequentially developed three photoelectrocatalytic strategies for the construction of 4-pyrrolin-2-one frameworks with simultaneous incorporation of thiocyanate,[29] aryl/alkylselenyl,[30] and alkyl sulfonyl[31] groups. By means of self- or acridinium-photoelectrocatalysis, Sun, Liang, and their coworkers achieved an external-oxidant-free thiocyanocyclization of various activated alkenes, yielding a broad array of thiocyanated heterocycles (Scheme 6a).[29] Interestingly, in this system, the acridinium salt, substrates **6-1**, and products **6-3** are all capable of undergoing photoexcitation, followed by single-electron reduction by KSCN (**6-2**), thereby generating the key radical species $^{\bullet}$SCN to initiate cyclization. In the same year, the team led by Liang, Sun, and Shi reported a selenocyclization *via* three hybrid (photo)electrochemical protocols, using diorganyl diselenides (**6-5**) as the selenyl sources (Scheme 6b).[30] Under 4CzIPN-photoelectrocatalysis (method A), PC-free photoelectrochemical conditions (method B), or NHPI-mediated electrochemical conditions (method C), the selenocyclization could be realized through both radical-based (**Int6-D**) and cation-based (**Int6-F**) pathways.

To date, various sulfur dioxide surrogates have emerged as versatile and sustainable alternatives to the troublesome gaseous SO_2 for the synthesis of SO_2-containing compounds, among which the 1,4-diazabicyclo[2.2.2]octane bis(sulfur dioxide) adduct (DABSO) has received particular attention.[32] In 2025, the research group of Li and Liang developed a three-component net-oxidative sulfonylation of 3-aza-1,5-dienes (**7-1**) with DABSO (**7-2**) and organotrifluoroborates (**7-3**) through photoelectrocatalysis (Scheme 7a).[31] Mechanistic investigations revealed that DABSO undergoes *in situ* conversion to 1,4-diazabicyclo[2.2.2]octane (DABCO) after donation of SO_2, which acts as an electron shuttle between the acridine-based photoelectrocatalytic cycle and **7-3**, thereby facilitating the oxidative generation of the alkyl radical intermediate **Int7-A** for triggering cyclization.

In line with their previous studies,[29–31] in 2025, Liang, Sun, Shi, and colleagues disclosed a photoelectrochemical cyclization of nitrogen-containing unactivated alkenes, including pyrazole-derived ones (**7-5**), for the construction of various N-heterocycles bearing sulfur-containing substituents, employing 2,4,6-triphenylpyrylium tetrafluoroborate (TPPT) as the organic photocatalyst (Scheme 7b).[33] In this work, NaSCN (**7-6**)



Scheme 7 Photoelectrochemical cyclization for the synthesis of N-heterocycles with sulfur-substituent introduction.



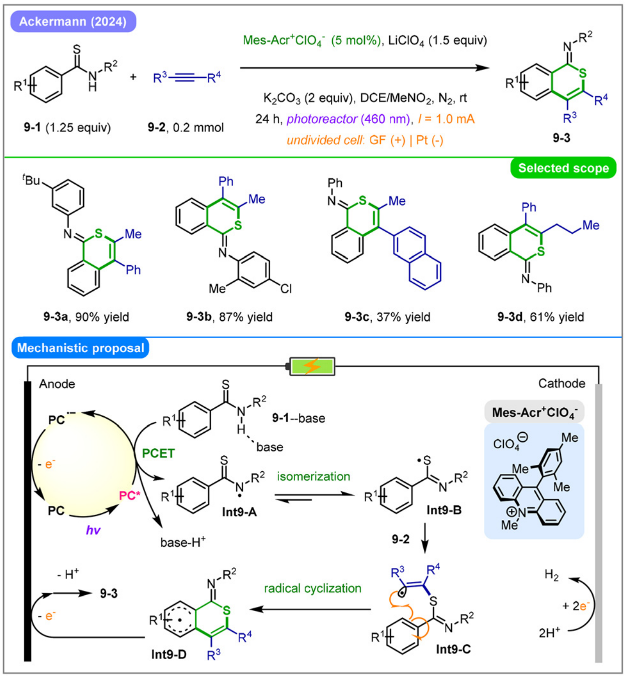
Scheme 8 Photoelectrochemical synthesis of polycyclic pyrimidin-4-ones from unactivated alkenes and malonates.

and $NaSSO_2R$ (**7-7**) served as the sources of $^{•}CN$ and $^{•}SO_2R$, respectively, enabling the formation of various heterocyclic frameworks such as 5,6-dihydropyrazolo[5,1-*a*]isoquinoline derivatives (**7-8** and **7-9**).

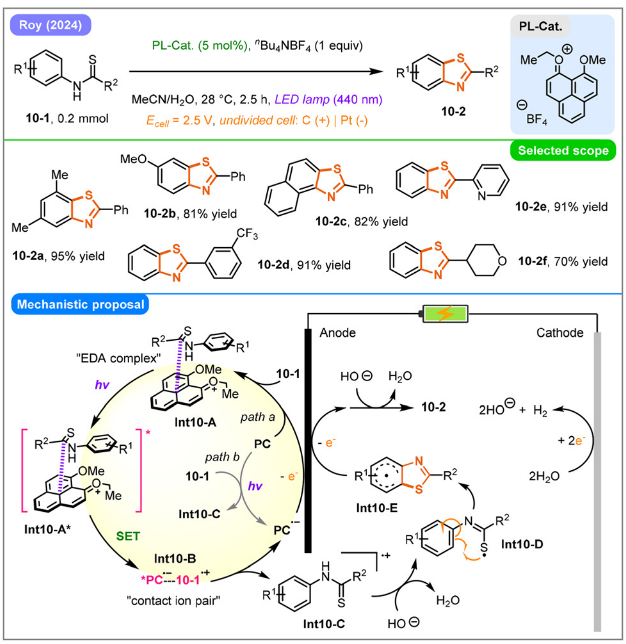
Selective activation of C(sp^3)–H bonds for direct functionalization has emerged as a prominent focus in both organic photo- and electrochemical synthesis.[34] In 2024, the research team led by Liang, Chang, and Shi introduced a hybrid system integrating electrolysis, photocatalysis, and a Brønsted base to synthesize polycyclic pyrimidin-4-ones (**8-3**) through dehydrogenative carbocyclization of unactivated alkenes (**8-1**) with simple malonates (**8-2**) (Scheme 8).[35] The proposed mechanism involves a base-mediated proton-coupled electron transfer (PCET)[36] process, which plays a pivotal role in the generation of the carbon-centered radical **Int8-A** from **8-2**. Subsequent addition of **Int8-A** to the alkene moiety of **8-1** produces the radical **Int8-B**, which further cyclizes to form the heterocyclic scaffold (**Int8-C**). This intermediate can either undergo anodic oxidation followed by deprotonation to yield the final product **8-3** or proceed *via* a photoredox-mediated reduction and protonation pathway to afford **Int8-E**, which subsequently undergoes anodic dehydrogenation to produce **8-3**. The authors proposed that the synergistic interaction between light and electricity arises from the rapid anchoring of **Int8-C** by the oxidative quenching photoredox cycle of *fac*-Ir$(ppy)_3$ at the cathode.

Alkynes have been utilized as versatile moieties for achieving cyclization transformations to access heterocyclic compounds.[37] In 2024, the Ackermann group reported a [4 + 2] annulation between benzothioamides (**9-1**) and alkynes (**9-2**) for the synthesis of functionalized isothiochromenes (**9-3**), enabled by a photoelectrochemical PCET strategy (Scheme 9).[38] Detailed spectroscopic studies and control experiments revealed that the hydrogen bonding interaction between the strong N–H of **9-1** and the base K_2CO_3, coupled with photoelectrocatalytic electron transfer, promotes the formation of the nitrogen radical **Int9-A**, which rapidly isomerizes into the sulfur radical **Int9-B**. The subsequent radical oxidative annulation with alkyne **9-2** delivers the six-membered S-heterocycle product **9-3**. This work represents a breakthrough in photoelectrocatalytic mono-sulfur-containing heterocycle synthesis.

The *in situ* formed electron donor–acceptor (EDA) complexes have been strategically exploited to promote various visible-light induced organic transformations.[39] In 2024, Roy and colleagues combined EDA complex formation with photoelectrochemical conditions to catalyze intramolecular C–S bond formation for the synthesis of diverse sulfur-containing heterocycles, including benzo[*d*]thiazoles (**10-2**), using a phenalenyl-



Scheme 9 Photoelectrochemical [4 + 2] annulation for S-heterocycle synthesis.



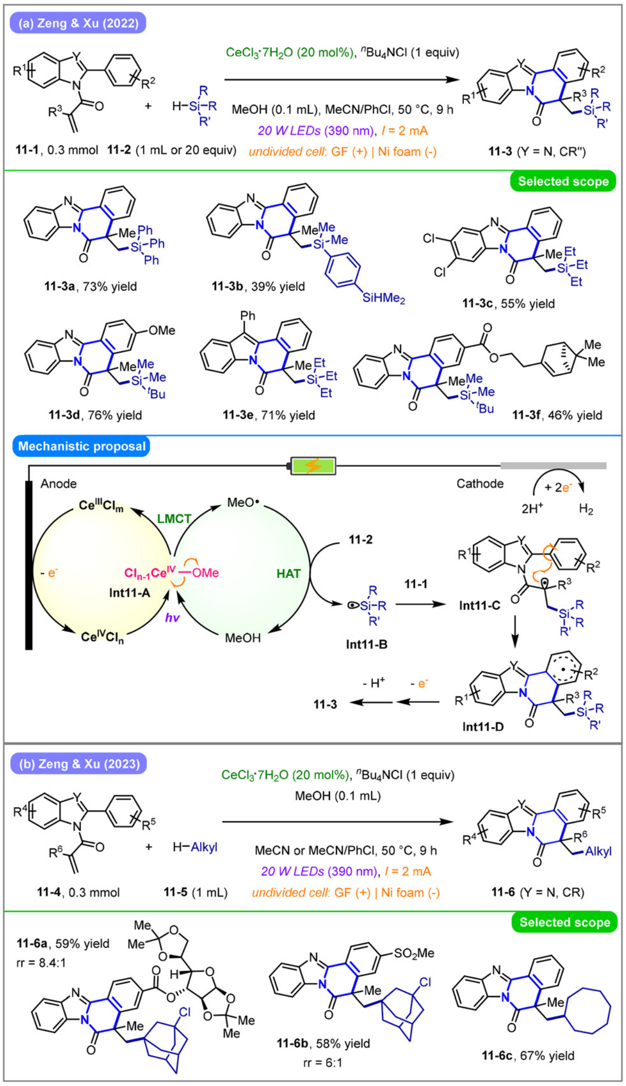
Scheme 10 Photoelectrocatalytic intramolecular C–S bond formation using a phenalenyl-based photocatalyst.

based photocatalyst (PL-Cat.) developed by their research group (Scheme 10).[40] Mechanistically, PL-Cat. engages in a noncovalent interaction with substrate **10-1** through ion pair–π interactions to generate an EDA complex (**Int10-A**), as evidenced by mechanistic investigations involving UV-visible spectroscopic analysis, cyclic voltammetry experiments, and computational calculations (path a). Upon visible-light irradiation, complex **Int10-A** is excited to form **Int10-A***, which subsequently undergoes intramolecular SET to yield a contact ion pair (**Int10-B**), which then collapses into $PC^{\bullet-}$ and the radical cation **Int10-C**. This radical cation is deprotonated by HO^{-} generated at the cathode, resulting in the formation of an S-centered radical (**Int10-D**). Further anodic oxidation and deprotonation of **Int10-D** led to the final aromatic N-,S-heterocycle **10-2**. Alternatively, direct excitation of the PC ($E^{*}_{1/2} = +2.61$ V *vs.* Ag/AgCl) followed by reductive quenching with **10-1** to generate **Int10-C** and $PC^{\bullet-}$ may also be a plausible pathway (path b). The ground-state PC can be efficiently regenerated *via* anodic oxidation of $PC^{\bullet-}$, thereby closing the catalytic cycle.

4. Electrochemically mediated photoinduced LMCT catalysis

The rapidly emerging photoinduced LMCT catalysis has also been successfully integrated into photoelectrochemical systems, offering more sustainable strategies for organic synthesis, including heterocycle formation.[16c] This photocatalytic mode begins with the coordination of a nucleophilic ligand to an electron-deficient metal center, forming a metal–ligand complex. Upon photoexcitation, the coordinate bond undergoes homolytic cleavage, yielding a reduced metal center and an oxidized, ligand-centered radical. In contrast to the well-developed photoredox catalysis, the primary conceptual advantage of LMCT lies in its ability to readily generate highly reactive radical species (such as $Cl^{\bullet}$, $Br^{\bullet}$, and $RO^{\bullet}$)[41] upon irradiation at specific wavelengths, without the necessity for precise redox potential matching. Similar to the strategies outlined in the previous section, electrochemical oxidation is utilized as an alternative to costly and hazardous chemical oxidants for regenerating high-valent metal catalysts, with the cathodic reduction of protons serving as a benign counter reaction.

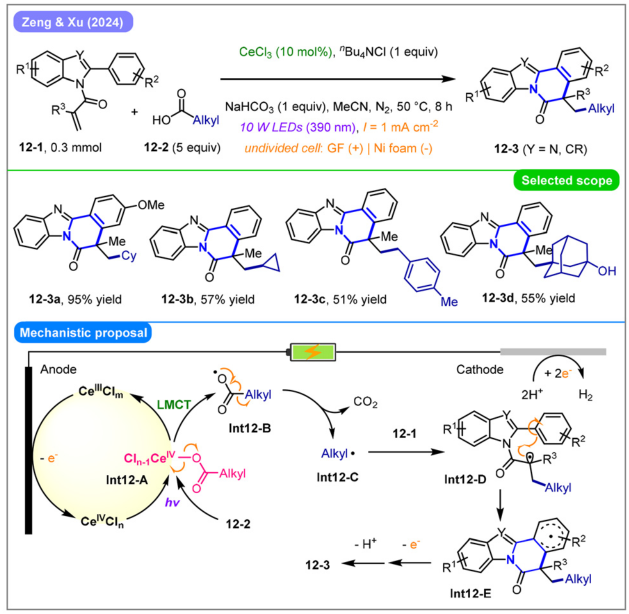
During the period from 2022 to 2024, the group of Zeng and Xu sequentially disclosed three electrophotochemical LMCT protocols for the construction of diverse benzimidazo-fused isoquinolinones, using cerium trichloride (or its hydrate) as a cost-effective photocatalyst.[42–44] In 2022, they first applied this strategy to achieve selective activation of Si–H bonds, which is governed by polarity-matching effects, generating silyl radicals that initiate cyclization and ultimately yield Si-functionalized benzimidazo-fused isoquinolinones (**11-3**) (Scheme 11a).[42] The efficient formation of reactive $MeO^{\bullet}$ (or $[Cl-OHCH_3]^{\bullet}$) is accomplished through the homolytic cleavage of the excited-state complex **Int11-A**, which subsequently acts as an electrophilic HAT agent to selectively activate more hydridic Si–H bonds rather than C–H bonds, thereby producing the silyl radical **Int11-B**. In the following year, their group further extended this electrophotochemical Ce-LMCT catalytic system to direct alkane C–H activation, enabling the synthesis of a broad range of alkyl-substituted benzimidazo-fused isoquinolinones (**11-6**) (Scheme 11b).[43] Compared to earlier



Scheme 11 Electrophotochemical Ce-LMCT catalyzed Si–H and C–H activation for N-heterocycle synthesis.

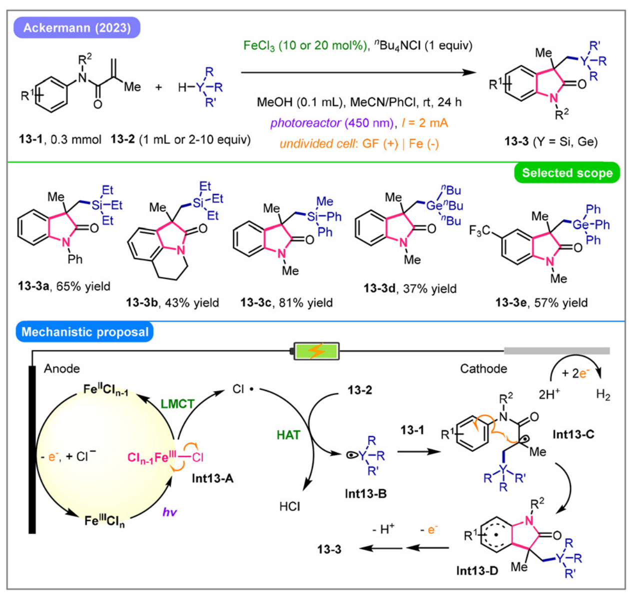
approaches that rely on prefunctionalized Si- or C-centered radical precursors, these photoelectrocatalytic methodologies offer significant advantages in terms of both atom efficiency and step economy, and do not require the use of external chemical oxidants.

Decarboxylative functionalization of bench-stable, readily available, and cost-effective carboxylic acids has attracted considerable interest among researchers in the fields of organic photo- and electrochemistry.[45] To address the limitations in substrate compatibility and chemoselectivity identified in their prior work,[43] in 2024, Zeng, Xu, and coworkers used a range of primary, secondary, and tertiary aliphatic carboxylic acids (**12-2**) as alkyl radical precursors, successfully achieving decarboxylative carbocyclization through electrophotochemical Ce-LMCT catalysis (Scheme 12).[44] Mechanistically, the Ce(IV) species generated at the anode coordinates with carboxylic acid **12-2**, forming a complex which upon irradiation at 390 nm transitions to an excited state (**Int12-A**). This excited complex subsequently undergoes homolytic cleavage, yielding reduced Ce(III) and an acyloxy radical intermediate (**Int12-B**), which proceeds to participate in the following decarboxylative cyclization process, finally delivering the alkylated benzimidazo-fused isoquinolinone (**12-3**).



Scheme 12 Electrophotochemical Ce-LMCT catalyzed decarboxylative cyclization.

Apart from carbon and silicon, their congener germanium has also garnered increasing interest within the synthetic chemistry community due to its distinctive properties when



Scheme 13 Photoelectrochemical Si–H and Ge–H activation for indolin-2-one synthesis.

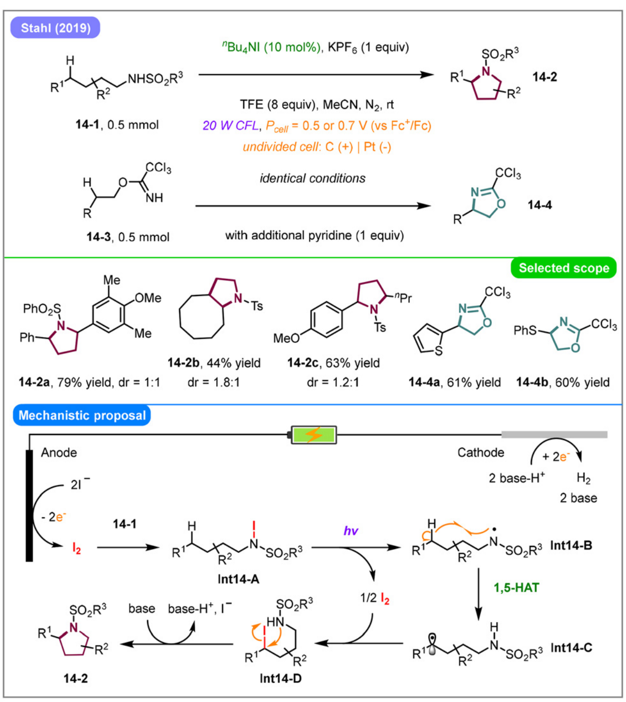
integrated into molecular architectures.[46] In 2023, Ackermann's group employed photoinduced Fe-LMCT catalysis to activate Si–H and Ge–H bonds of hydrosilanes and hydrogermanes (**13-2**), thereby enabling radical cyclization of α,β-unsaturated amides (**13-1**) to selectively furnish a range of silyl- or germyl-substituted indolin-2-ones (**13-3**) under photoelectrochemical conditions (Scheme 13).[47] The photoinduced LMCT process in the excited iron(III)–Cl complex (**Int13-A**) facilitated the generation of the chlorine radical (Cl•), followed by a crucial HAT event to yield a HCl molecule. This sequence enabled selective activation of Si–H and Ge–H bonds through a radical-polarity-matched mechanism, effectively overcoming the challenge posed by the similar redox potentials of Si/Ge–H and C–H bonds.

5. Interfacial photoelectrocatalysis and others

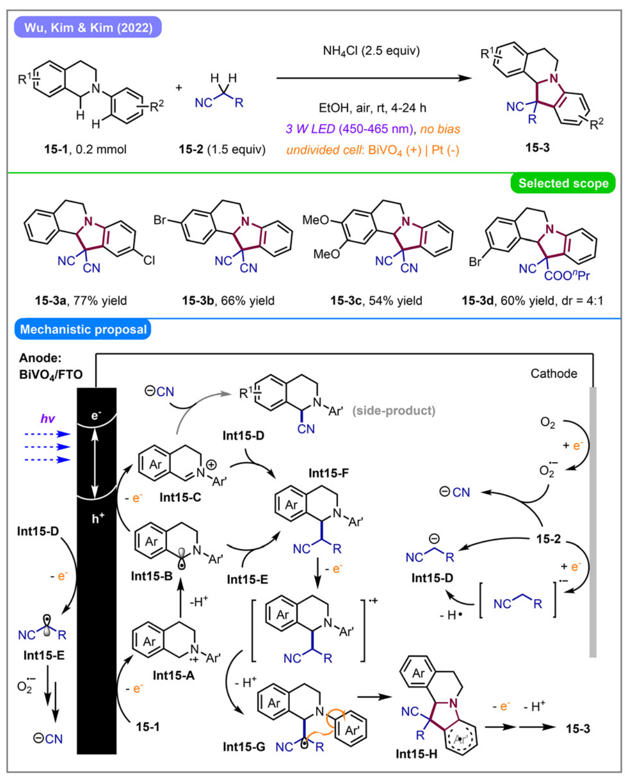
Reactions proceeding through mechanisms distinct from the aforementioned types have been summarized in this section.

Intramolecular 1,*n*-HAT has been strategically applied in organic synthesis for the precise activation of specific remote $C(sp^3)$–H bonds.[48] As an early endeavor in constructing heterocyclic frameworks through the synergistic use of photo- and electrochemical catalysis, in 2019, Stahl's group developed a dehydrogenative $C(sp^3)$–H/N–H coupling protocol, enabling the efficient synthesis of a broad scope of pyrrolidines (**14-2**) and oxazolines (**14-4**) (Scheme 14).[49] As a variant of the classical Hofmann–Löffler–Freytag (HLF) reaction, this protocol employed iodide as an electrochemical mediator, the regeneration of which (0.3–0.7 V *vs.* Fc/Fc$^+$) substantially reduced the required electrochemical potential, thereby overcoming the limited functional group tolerance observed in earlier studies. Mechanistically, electrochemical oxidation of iodide generates molecular iodine, which subsequently reacts with the sulfonamide substrate **14-1** to form an N–I intermediate (**Int14-A**). Upon visible-light irradiation, the N–I bond of **Int14-A** undergoes homolytic cleavage, yielding a nitrogen-centered radical (**Int14-B**), which readily undergoes intramolecular 1,5-HAT to generate a remote carbon-centered radical (**Int14-C**). This radical is then intercepted by iodine to form an alkyl iodide intermediate (**Int14-D**), which undergoes Brønsted base-promoted nucleophilic displacement by the pendant nitrogen nucleophile, ultimately furnishing the pyrrolidine product **14-2**. Compared to other electrochemical C–H amination reactions, this strategy exhibited significantly enhanced functional group tolerance, as exemplified by its ability to accommodate electron-rich aromatic moieties that typically engage in undesirable side reactions under high-potential conditions.

In recent years, interfacial photoelectrochemistry has garnered increasing attention as a promising approach for organic synthesis, offering significant advantages such as cost-effectiveness, reusability and stability of photoelectrodes as heterogeneous catalysts.[17] In 2022, the research group led by Wu, Kim, and Kim reported a self-biasing interfacial photo-



Scheme 14 Photoelectrochemical synthesis of pyrrolidines and oxazolines through intramolecular dehydrogenative coupling.

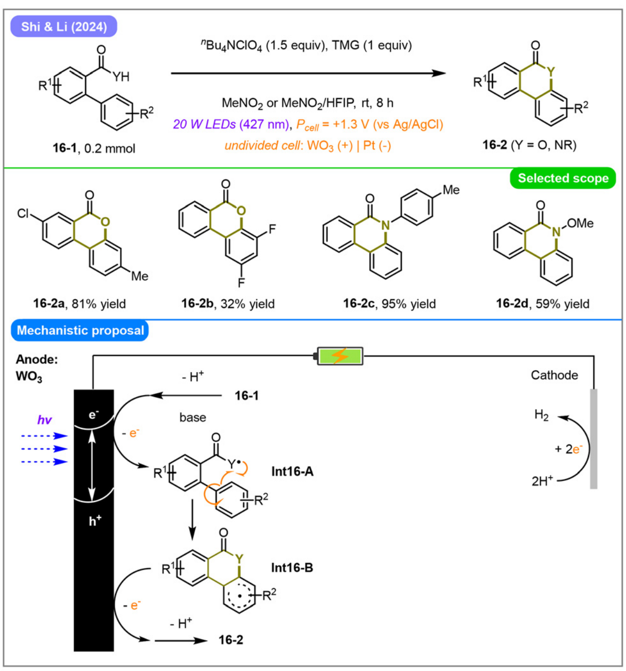


Scheme 15 Unbiased photoelectrocatalyzed synthesis of *N*-bearing fused rings.

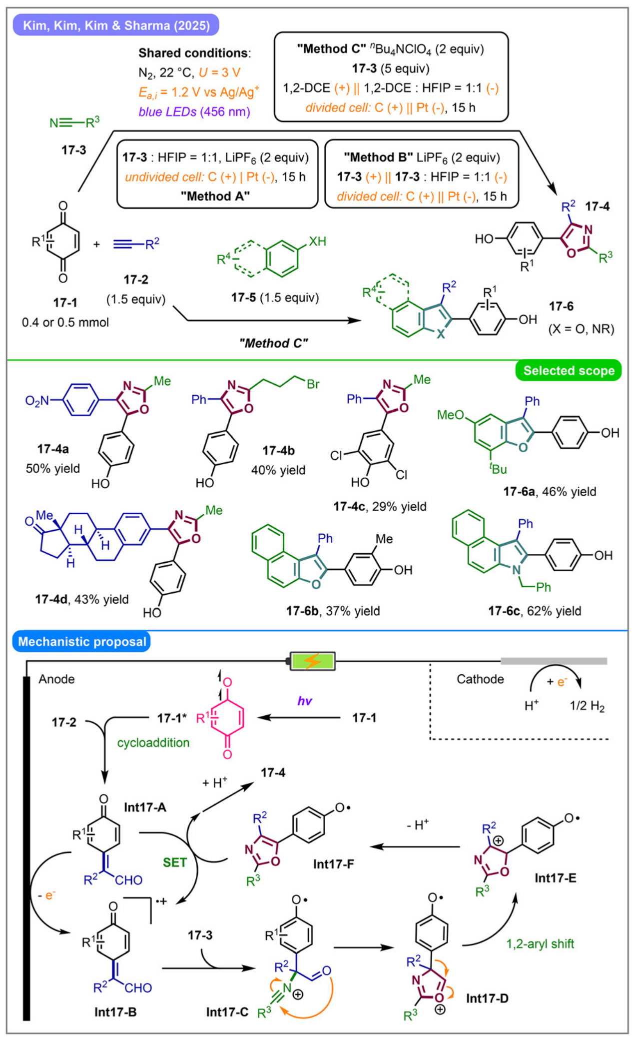
electrocatalytic strategy for the cascade C–H activation/cyclization of *N*-aryl tetrahydroisoquinolines (**15-1**) with malononitrile derivatives (**15-2**), enabling the construction of nitrogen-containing fused cyclic compounds (**15-3**), using an *m*-$BiVO_4$ film as the photoanode (Scheme 15).[50] Under visible-light irradiation, the photoanode is excited, generating high-energy electron–hole pairs that facilitate the oxidation of substrates and intermediates without the need for an external bias and with a minimal overpotential. According to the proposed mechanism, the key intermediate **Int15-F** may form either through radical–radical cross-coupling between **Int15-B** and **Int15-E** or *via* a nucleophilic attack of **Int15-D** on **Int15-C**. Subsequent oxidation–deprotonation of **Int15-F** yields the radical intermediate **Int15-G**, which undergoes radical cyclization followed by further oxidation–deprotonation to afford the target fused N-heterocyclic compound **15-3**. Notably, the photoanode in this work can be readily recovered after cleaning with dichloromethane and reused for more than ten cycles while retaining comparable catalytic activity, a clear advantage over homogeneous photoelectrochemical methods.

In 2024, Shi, Li, and their colleagues described a photoelectrochemical dehydrogenative cyclization of 2-arylbenzoic acids and 2-arylbenzamides (**16-1**) in a PEC cell, employing a mesoporous WO_3 photoanode in combination with a platinum cathode (Scheme 16).[51] The reaction is initiated by TMG (tetramethylguanidine)-mediated deprotonation of **16-1**, followed by single-electron oxidation mediated by the photo-excited photoanode, leading to the formation of the O- or N-centered radical intermediate **Int16-A**. This radical undergoes intramolecular capture by the adjacent aryl group to form a six-membered ring (**Int16-B**), which subsequently undergoes oxidation–deprotonation to yield the corresponding lactone or lactam product **16-2**.

Very recently, the research team led by Kim *et al.* disclosed a catalyst-free photon-primed organic electrosynthetic strategy for the efficient synthesis of various substituted oxazoles (**17-4**) and fused furans/pyrroles (**17-6**) (Scheme 17).[52] Mechanistically, the quinone substrate **17-1** is readily excited to its triplet state (**17-1***) upon visible-light irradiation, which initiates a subsequent photocycloaddition with alkyne **17-2**, generating a highly reactive *p*-quinone methide intermediate (**Int17-A**). This species undergoes facile anodic oxidation to form a highly electrophilic radical cation **Int17-B**, capable of reacting with weak nucleophiles such as **17-3** (also phenols/anilines **17-5**). The resulting intermediate **Int17-C** subsequently undergoes polar cyclization, a 1,2-aryl shift, and deprotonation to yield **Int17-F**, which then engages in an SET process with **Int17-A**, producing the final product **17-4** and regenerating **Int17-B**. Such a redox-chain mechanism signifi-



Scheme 16 Photoelectrochemical dehydrogenative cyclization of 2-arylbenzoic acids and 2-arylbenzamides.



Scheme 17 Photon-primed organic electrosynthesis of oxazoles and fused furans/pyrroles.

cantly enhances the overall efficiency of the transformation, leading to an apparent faradaic efficiency exceeding 100%. A broad substrate scope was demonstrated, including the late-stage modification of bioactive scaffolds, thereby highlighting the synthetic utility and potential of this photoelectrocatalytic methodology.

6. Summary and outlook

Over the past few years, the rapidly emerging field of organic photoelectrocatalysis has demonstrated preliminary applications in novel and sustainable heterocycle synthesis. These promising approaches not only expand the synthetic toolbox, but also inspire the innovative design of new cyclization paradigms.

Despite the notable advances, significant challenges and opportunities remain to be addressed. First, the majority of current studies have focused on the synthesis of nitrogen-containing heterocycles, featuring rather limited structural diversity, with considerably fewer reports on the construction of other heterocycles, such as those containing oxygen and sulfur, among others. Second, the existing reactions usually exhibit stringent structural requirements for radical addition, thereby limiting their practical applicability in the synthesis of complex molecules. Furthermore, current strategies have predominantly focused on the synthesis of saturated or partially saturated heterocycles, with limited progress in the construction of aromatic ones.

In conclusion, the rapid emergence of organic photoelectrocatalysis has led to the establishment of diverse innovative cyclization strategies for heterocycle synthesis. It is anticipated that continued efforts from the synthetic community will focus on the development of more efficient and sustainable methodologies for constructing a wider variety of heterocyclic frameworks from readily available starting materials.

Conflicts of interest

There are no conflicts to declare.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

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