

Electro-Redox Process: A Long-Overlooked Mode of Single-Electron Transfer in Organic Synthesis

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Abstract: Single electron transfer (SET) is a fundamental step in radical-mediated organic transformations, enabling unique bond-forming and cleavage that are difficult to access via traditional two-electron pathways. Electrochemical redox directly drives single electron transfer processes through heterogeneous electron transfer at the electrode-electrolyte interface without external catalysts such as transition metals and precious metals. Anodic single-electron oxidation activates inert C–H bonds, generating carbon-centered radicals for selective functionalization, whereas cathodic reduction enables homolytic cleavage of C–X bonds, generating radical anions or carbanions for reductive coupling and dehalogenation. Electrochemical single electron transfer (SET) has emerged as a powerful, sustainable alternative to metal-catalyzed and photo-redox systems. By eliminating stoichiometric redox agents, transition metals, and photocatalysts, electro-synthesis utilizes precise potential control and a traceless electron supply under mild conditions to avoid metal contamination, the generation of by-products, and reduce environmental impact. Mediator-assisted SET and hydrogen-atom transfer enable selective oxidation of unactivated aliphatic C–H bonds, while electrochemical radical cyclization constructs C–C and C–heteroatom bonds. In this review, we summarized the fundamental principles, general mechanism and technical characteristics of the electrochemically driven by single electron transfer process. Advances in anodic C–H functionalization, cathodic reduction, cyclization and mediator-assisted oxidation are highlighted, alongside electrode materials and reactor engineering. We aim to provide a comprehensive overview of recent advancements in this field, highlighting key mechanistic insights and future opportunities for sustainable synthesis via single electron transfer. Remaining challenges such as selectivity, scale-up, and emerging directions are also discussed.

Keywords: electro-redox; single-electron transfer; cathodic reduction; anodic oxidation; sustainable synthesis

1. Introduction

Organic synthesis involving free radicals has become an indispensable and practical tool for constructing complex molecular skeletons, offering distinct reactivity patterns from traditional polar two-electron pathways. Single electron transfer (SET) is a fundamental step for radical transformations, driving homolytic activation of chemical bonds, generation of active radical species, and new bond formation, which remains inaccessible through classical polar ionic pathways. Over the past few decades, strategies centered on SET have revolutionized complex molecule synthesis, enabling the streamlined construction of structurally diverse pharmaceutical scaffolds, natural prod-

uct cores, and advanced organic functional materials.^{1,2}

Traditional single-electron transfer (SET) chemistry has been anchored by two mature paradigms: transition metal-catalyzed redox processes and photo-redox catalysis.^{3–7} Transition metal catalysts have long dominated radical synthesis due to their reliable redox tunability and broad substrate compatibility.^{8–12} However, transition metal-mediated redox processes typically rely on the use of stoichiometric chemical oxidants or reductants, generating substantial chemical waste streams and imposing a heavy environmental burden.^{13–15} While photo-redox processes enable single-electron transfer under mild room-temperature conditions, which relies on expensive pho-

tosensitizers prone to photobleaching and long-term degradation under prolonged irradiation.^{16,17} Although transition metal and photo-redox platforms remain widely employed, their inherent economic and ecological limitations continue to drive the pursuit of sustainable redox activation strategies in synthetic chemistry.^{18–21}

Electrochemical organic synthesis has experienced a profound renaissance, establishing a sustainable paradigm for steering precise single-electron transfer (SET) pathways.^{22–24} Moreover, electro-synthesis achieves precise oxidation and reduction through heterogeneous charge transfer at the electrode–electrolyte interface, employing the electron as a traceless, sustainable reagent. This eliminates the need for transition metals, photosensitizers, and stoichiometric reagents, preventing metal contamination and reducing waste. Furthermore, precise electrode potential modulation facilitates the realization of exceptional chemo-selectivity and functional group tolerance unattainable through conventional pathways.²⁵ Despite recent advances, electrochemically driven organic synthesis still remained relegated to the periphery of mainstream organic chemistry, historically dismissed as an empirical “black

box.” This developmental lag primarily stemmed from poorly defined interfacial electron-transfer kinetics, a lack of standardized screening protocols for electrode and electrolyte selection, and the inherent complexity of regulating open-shell intermediates within heterogeneous electrical double layers.

Recently, the upgrade of modular, standardized electrolysis hardware, sophisticated *in-situ* spectroscopic and spectrometric characterization, and quantum-chemical modeling of interfacial electric fields have elucidated the reaction mechanism. Therefore, electro-redox processes involving single-electron transfer (SET) pathways enable diverse organic transformations, such as direct anodic oxidation, cathodic reduction, and redox-neutral paired electrolysis (Figure 1).²⁶ In this review, we provide a rigorous examination of the fundamental principles, mechanistic classifications, and frontier developments in electrochemically driven SET transformations (Table 1). We evaluate the distinct advantages of electrochemical SET over conventional transition-metal and photo-redox platforms (Table 2), delineate core challenges in interfacial efficiency and selectivity control, and outline future horizons of technological innovation for scalable organic synthesis.

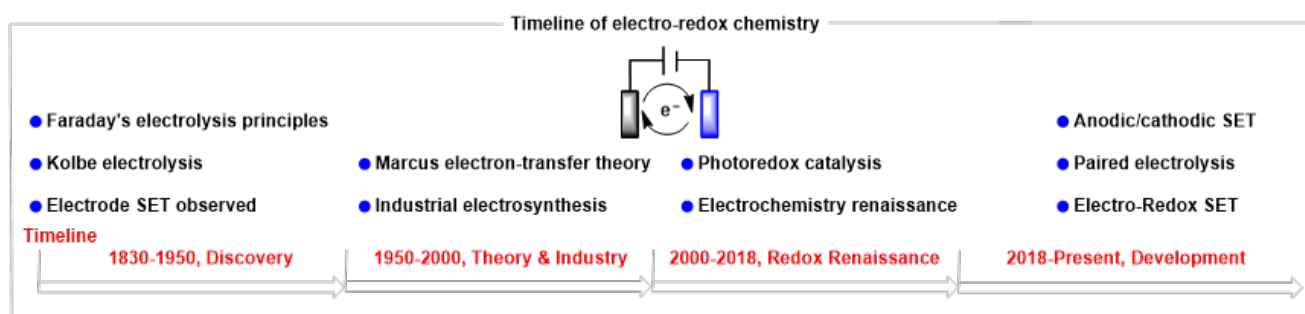


Figure 1. Timeline of electro-redox chemistry.

Table 1. Advances in electro-redox processes via SET.

Reaction types
C–C bond formation Electrocatalytic homo-/cross-coupling of alkenes ²⁷ Ni-catalyzed electrochemical reductive relay cross-coupling ²⁸ Electroreductive olefin-ketone coupling ²⁹ Pd-catalyzed electrochemical carboxylation ³⁰ Iodide-promoted electro-redox NHC organocatalysis ³¹ Asymmetric NHC-catalyzed (3+3) annulation ³² Electrochemically driven oxidative Strecker reaction ³³
C–N bond formation Electrochemical tandem difunctionalization of olefins for α -tertiary amines ³⁴ Site-selective electrochemical arene C–H amination ³⁵ Continuous-flow electrochemical arene C–H amination ³⁶ Diphenyl diselenide-mediated metal-free electrochemical allene cascade cyclization ³⁷ Supporting-electrolyte-free [2+2+1] annulation via hydrogen-bond pre-assembly ³⁸ Electrochemically driven Ugi-azide reaction via tertiary-amine C(sp ³)–H activation ³⁹ DDQ-mediated formal [3+2] cycloaddition for tetrazoloquinoxalinones ⁴⁰ Indirect electrosynthesis of 1,3,4-oxadiazoles from N-acylhydrazones ⁴¹
C–O bond formation Electrode-controlled divergent functionalization of styrenes ⁴² Cl ₄ NHPI-mediated scalable electrochemical allylic C–H oxidation ⁴³ Quinuclidine-mediated oxidation of unactivated aliphatic C(sp ³)–H bonds ⁴⁴ ABNO-mediated electrochemical Shono-type α -oxygenation of cyclic carbamates ⁴⁵ Electrosynthesis of sp ³ -rich heterocycles via mesolytic fragmentation of anodically generated aryl radical cations ⁴⁶

Table 1. Cont.

Reaction types	
C-O bond formation	
Electrochemical oxidative ring-opening of indoles ⁴⁷	
Biomimetic iron-catalyzed electrochemical benzylic C-H hydroxylation ⁴⁸	
C-X bond formation	
Paired-electrolysis shuttle reaction for reversible vicinal dihalogenation ⁴⁹	
Plasticizer-mediated electro(de)chlorination from waste PVC ⁵⁰	
Catalyst-free electrochemical hydrodehalogenation of aryl halides ⁵¹	

Table 2. Comprehensive comparison of three types of SET processes.

Dimension	Electrochemical SET	Transition-metal-mediated SET	Photo-redox SET
Catalyst/mediator cost	Electron as mediator, lower cost; inexpensive electrodes	Expensive metal catalysts; stoichiometric reagents	Expensive photosensitizers, prone to photobleaching
Metal contamination	No metal residues	Metal residues requiring extra purification	Noble-metal sensitizers leave residues; organic sensitizers costly
Functional-group tolerance	Tunable potential, broad substrate compatibility	Prone to poisoning	Good functional group tolerance and selectivity control
Scalability	Gram to kilogram scale; continuous-flow	Industrially mature; higher scale-up cost	Limited by light penetration and photo-bleaching
Over potential/energy	Indirect electrolysis lowers overpotential; electricity only	Higher energy requirement	Room temperature; light-source energy
Representative E-factor	No stoichiometric reagents, few by-products, low E-factor	Stoichiometric reagents; salt waste, high E-factor	Without stoichiometric oxidant; higher solvent load

2. Electro-redox mediated C-H functionalization via SET

C-H functionalization is a research hotspot in modern organic synthesis, and anodic oxidative SET provides a green and efficient solution for inert C-H bond activation. Electron-rich aromatic C-H bonds and aliphatic C(sp³)-H bonds can be selectively activated via anodic single-electron oxidation to generate carbon-centered radicals, realizing selective arylation, amination, and oxygenation reactions. In 2025, the Gong group developed a concise and efficient one-step electrocatalytic strategy for the direct reductive coupling of alkenes, providing a novel green synthetic route for the efficient construction of C-C bonds from readily available bulk alkene feedstocks (Figure 2).²⁷ Compared with traditional synthetic methods relying on stoichiometric and hazardous organolithium reagents to

generate key active intermediates, the electro-redox process enabled the *in-situ* generation of highly reactive alkene radical anion intermediates under mild, metal-free, and exogenous oxidant/reductant-free conditions, which overcomes the limitations of conventional protocols. This reaction underwent radical addition, followed by protonation and hydrogen atom transfer to afford the target coupling products. Moreover, both homocoupling and cross-coupling of alkenes demonstrate broad substrate applicability, and allowed one-step synthesis of biologically active 1,4-diphenylbutane moieties. By harnessing the abundant presence of alkenes as substrates, this strategy overcame the traditional synthetic limitations of highly reactive radical anion intermediates. It provided a mild, redox-neutral, and atom-economical platform to streamline the modular construction of complex fine chemicals and pharmacologically active molecular scaffolds via electrocatalysis.

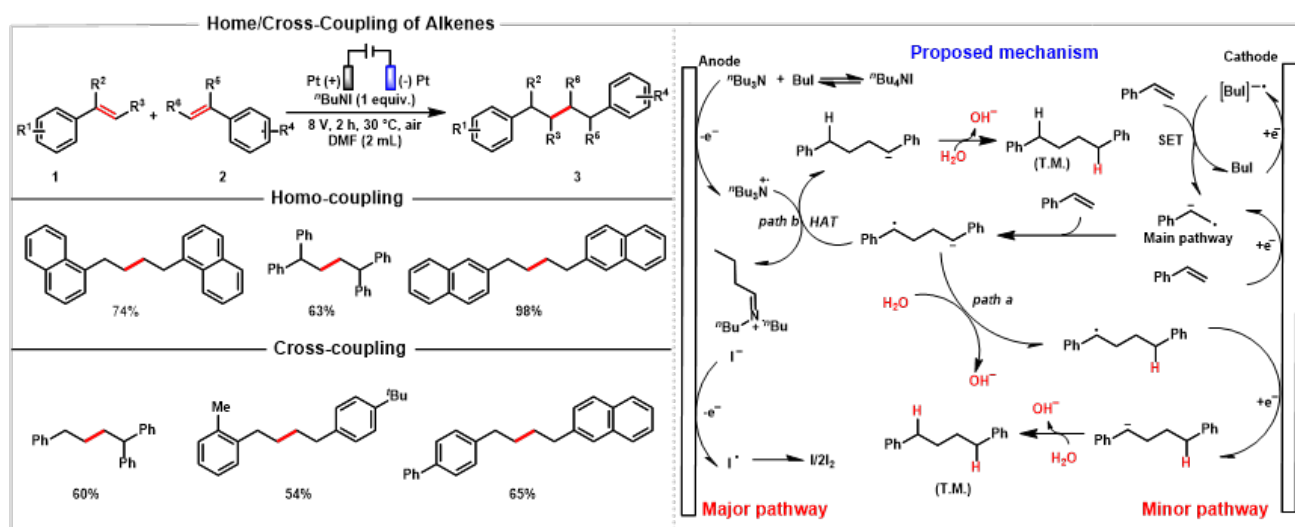


Figure 2. Electrocatalytic homo/cross coupling of alkenes.

In 2021, the Morandi group established a versatile electrochemical platform (e-shuttle) for the reversible interconversion of alkenes and vicinal dihalides without involving hazardous elemental halogens (Figure 3).⁴⁹ Utilizing inexpensive graphite electrodes, the e-shuttle process enabled the direct dihalogenation of a broad range of alkenes using readily available 1,2-dibromoethane, 1,2-dichloroethane and 1,1,1,2-tetrachloroethane as halogen sources under mild conditions.

Furthermore, this electrochemical process also realized step-wise dechlorination of the persistent organochlorine pollutant lindane ($C_6H_6Cl_6$) to benzene in complex soil matrices, utilizing terminal alkenes as selective chlorine acceptors. By coupling environmental remediation with organic synthesis, this electrocatalytic platform met hazardous waste disposal requirements and converted toxic pollutants into valuable halogenated building blocks.

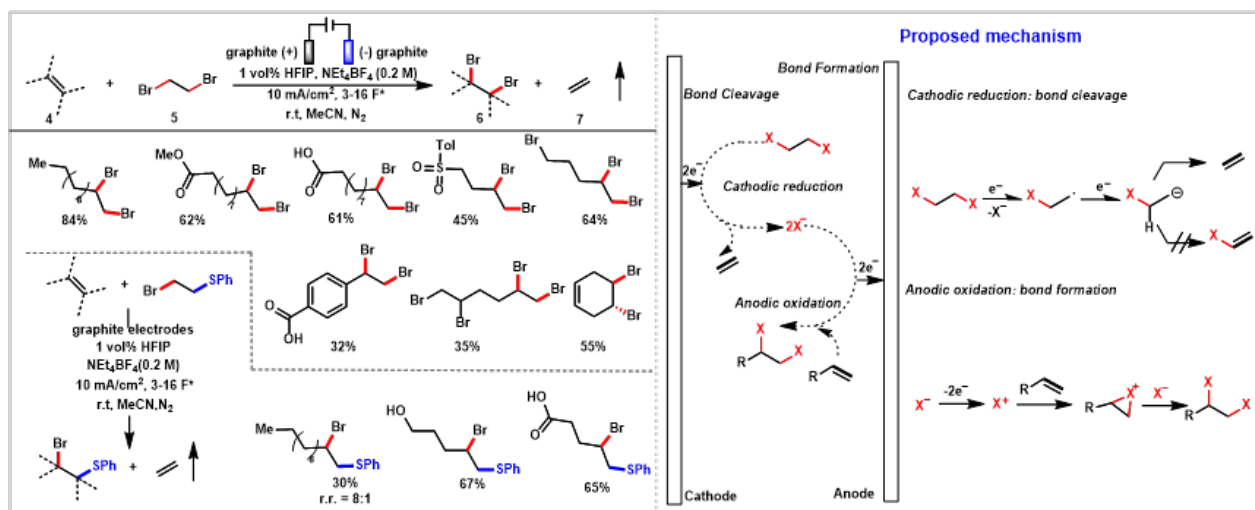


Figure 3. Electrochemical e-shuttle process.

Nitrogen atom-containing quaternary carbon centers represent privileged architectural scaffolds in drug discovery, which impart three-dimensional configuration, target selectivity and higher metabolic stability. However, the construction of α -tertiary amines (α -TPAs) is still challenging, mainly due to the steric hindrance of tetrasubstituted carbon centers and the nucleophilic properties of primary amines. Although traditional strategies, such as nucleophilic α -amination, α -C–H functionalization and photocatalytic α -NH radical amination, can access α -amino compounds, they often suffer poor functional group tolerance and lack of stereo-control.

To overcome these limitations, Banerjee et al. developed an electrochemical C–H functionalization of olefins without using any oxidant in 2026, which directly converted 1,1-disubstituted olefins into $C(sp^3)$ -rich α -tertiary amines. This protocol employed bench-stable, inexpensive ammonium surrogates as nitrogen sources and readily accessible thiophenols as thiol reagents, eliminating the requirement for preactivated sulfur precursors to achieve one-pot aminosulfonylation and aminosulfonylation of alkenes (Figure 4).³⁴ Furthermore, the reaction was compatible with a variety of nitrogen sources, including ammonia reagents, amino acids, dipeptides, aliphatic amines, and nitrogen-containing heterocycles. Notably, the gram-scale electrosynthesis (up to 10.0 mmol) was successfully conducted to highlight its potential for practical synthesis. Mechanistic studies indicated a radical-polar crossover pathway triggered by thiophenol, which was essential for the efficient formation

of congested α -tertiary amine skeletons.

Aromatic amines are abundant in pharmaceuticals, agrochemicals, natural products and organic functional materials.⁵² Traditional cross-coupling reactions relies on pre-functionalized substrates such as halogenated aromatic hydrocarbons or aromatic boronic acids with the production of salt waste.^{53–56} Since the early 2000s, direct C–H amination has emerged as an efficient method to prepare aromatic amines. Despite significant advances, current catalytic approaches remain constrained by narrow substrate scopes, poor regiocontrol, and limited scalability.^{57–59} In 2024, the Malapit group established an electrochemical $C(sp^2)$ –H amination reaction enabled by *in-situ* generated mono-cationic radical (Figure 5).³⁵ Compared with conventional strategies, the generation of electrophilic monocationic *N*-radical intermediates was crucial to achieve $C(sp^2)$ –H functionalization efficiently, delivering diverse aryl DABCONium salts in excellent yields with *para*-selectivity. The reaction exhibited exceptional functional group tolerance, well accommodating aryl halides, carbonyl compounds, sulfonamides, and various N-heteroarenes. Moreover, it was compatible with electron-rich, electron-neutral, and electron-deficient arenes, and enabled the late-stage modification of pharmaceutical molecules, showcasing remarkable substrate scope and synthetic application. Furthermore, the resulting aromatic DABCONium salts served as versatile building blocks for the synthesis of diverse aryl piperazines.

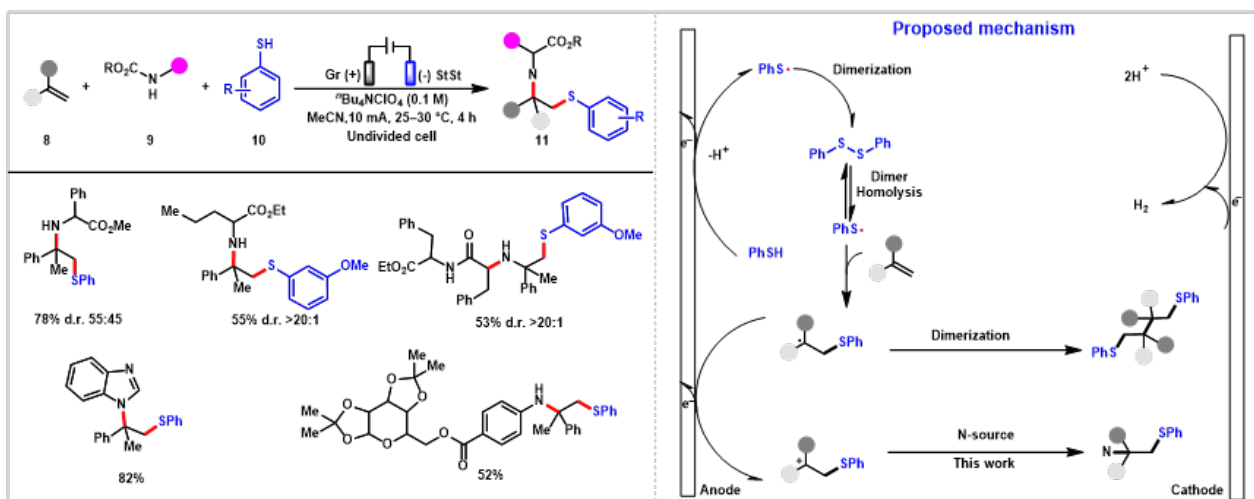


Figure 4. Electrochemical C–H functionalization of olefins with ammonia surrogates and amino acids.

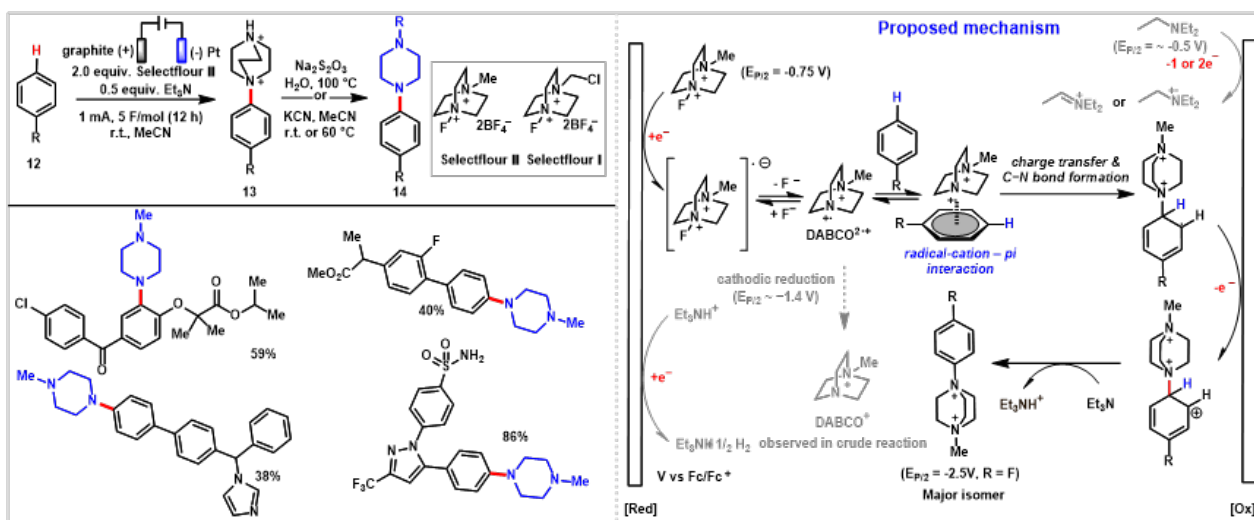


Figure 5. Electrochemical selective C(sp²)–H amination of arenes.

The Xu group developed a continuous flow protocol of electrochemical C(sp²)–H amination through the pyridine-aminolysis cascade pathway.³⁶ Leveraging the enhanced mass transport, high electrode-to-volume ratio, and precise residence-time control of continuous-flow electrochemical microreactors, this protocol achieved a continuous-flow synthesis of diverse aromatic amines. Mechanistic studies disclosed aromatic substrates were first anodized to generate radical cations *in-situ*, then reacted with pyridine derivatives to form stable aryl pyridinium salt intermediates, followed by direct amination to afford the target aromatic amines (Figure 6).³⁶

As one of the highest-volume yet least recycled thermoplastics, poly (vinyl chloride) (PVC) traditionally poses severe disposal hazards due to corrosive hydrogen chloride (HCl) and toxic plasticizers.^{60–63} In 2023, the McNeil group introduced a paired-electrolysis strategy for the chemical upcycling of PVC, addressing the persistent environmental burdens of chlorinated plastic waste. In this protocol, chlorine radicals generated at the anode surface played a pivotal role by me-

diating hydrogen atom abstraction and polymer backbone activation. Moreover, the plasticizer DEHP acted as a redox mediator to accelerate charge-transfer kinetics, enabling the selective transformation of PVC into value-added chemical feedstocks (Figure 7).⁵⁰

Key points in this part

- Anodic oxidative SET provides a green route to inert C–H activation: electron-rich aromatic C–H and aliphatic C(sp³)–H bonds are converted to carbon-centered radicals for selective arylation, amination and oxygenation.
- Electrogenated alkene radical anions enable mild, metal-free, exogenous oxidant/reductant-free linear homo-/cross-coupling of alkenes, affording bioactive 1,4-diarylbutane motifs in one step (Figure 2).²⁷
- An electrochemically assisted shuttle platform makes alkene–vicinal dihalide interconversion reversible, combining green dihalogenation (from 1,2-dihaloethanes) with complete dechlorination of persistent pollutants such as

lindane in soil (Figure 3).⁴⁹

- Metal- and oxidant-free electrochemical difunctionalization of 1,1-disubstituted olefins with ammonia surrogates and thiophenols delivers congested α -tertiary amines (verified on >71 substrates, up to 82% yield, gram-scale to 10.0 mmol) via a radical-polar crossover pathway (Figure 4).³⁴
- Arene C–H amination is achieved via two complementary electrochemical routes. The first is a cathodic monocationic N-radical-mediated pathway that delivers para-selective

aryl DABCONium salts (Figure 5),³⁵ while the second is a continuous-flow pyridine-aminolysis cascade system compatible with both electron-rich and electron-deficient arenes (Figure 6).³⁶

- Paired electrolysis upcycles PVC waste as a solid chlorine source for aromatic chlorination, with the DEHP plasticizer serving as a redox mediator; this route cuts global-warming potential by 71% versus HCl-based protocols (Figure 7).⁵⁰

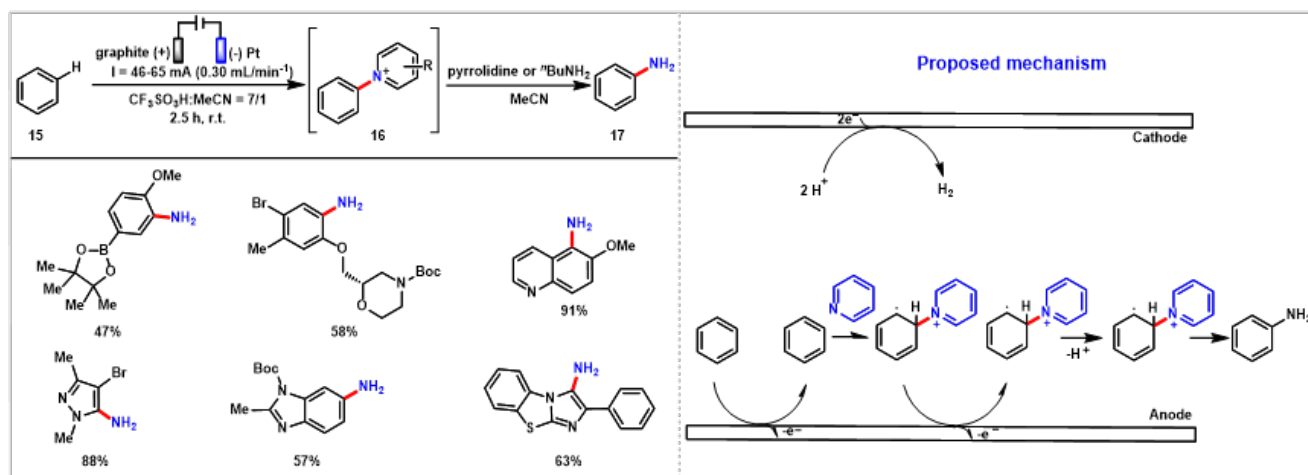


Figure 6. Electrochemical selective C(sp²)–H amination of arenes via pyridine-aminolysis.

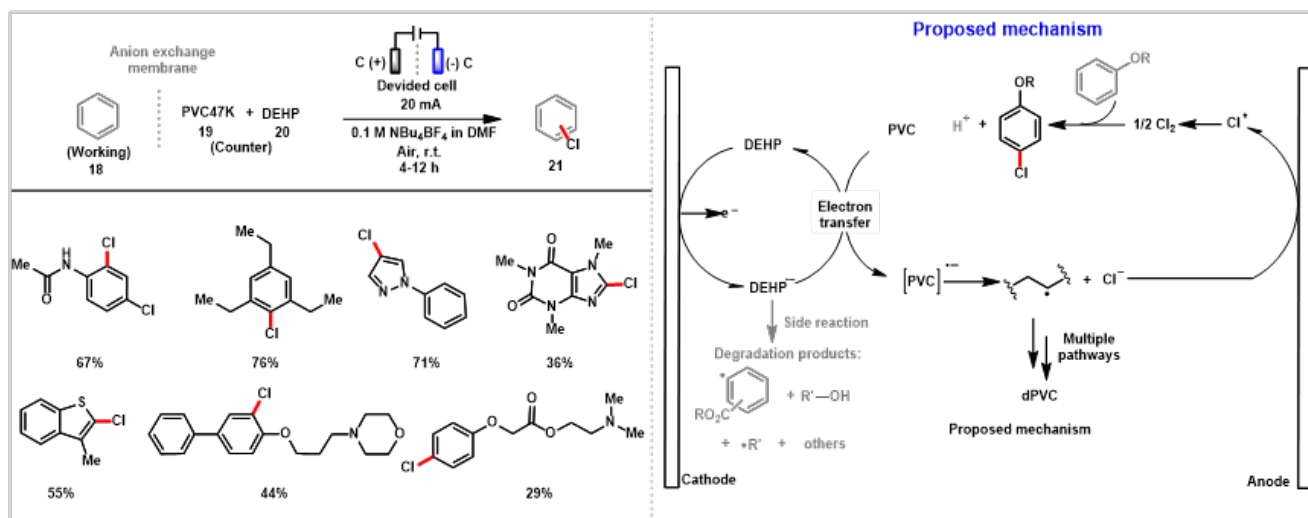


Figure 7. Paired-electrolysis strategy for upcycling of poly(vinyl chloride).

3. Electro-redox mediated cathodic reduction via SET

Cathodic reduction constitutes a cornerstone of catalyst-free electrosynthesis, wherein substrates undergo direct single-electron transfer (SET) at the electrode surface to generate reactive intermediates, such as radical anions, neutral radicals, or carbanions, circumventing the need for stoichiometric metal reductants (Zn, Mn, etc.). Alkyl and aryl halides are widely employed as versatile synthetic building blocks. Conventional re-

ductive dehalogenation typically relies on stoichiometric quantities of metal-based reductants or toxic tin hydride reagents. In contrast, cathodic single-electron transfer enables direct homolytic cleavage of the C–X bond, generating carbon-centered radicals that can undergo subsequent hydrogen abstraction, cyclization, or coupling reactions.

In 2020, the Mei group reported a nickel-catalyzed electrochemical reductive relay cross-coupling between aryl halides and alkyl bromides (Figure 8).²⁸ The reaction proceeded ef-

ficiently in an undivided electrolytic cell without additional equivalent metal reducing agent. The catalytic cycle was directly driven by current and this protocol accommodated both aryl bromides and chlorides to deliver 1,1-diarylethanes in good yields and with high regioselectivity.

The Chi group developed a catalyst- and transition-metal-free electrochemical hydrodehalogenation of aryl halides using an undivided cell equipped with inexpensive graphite rod elec-

trodes (Figure 9).⁵¹ In this electro-reductive process, trialkylamines ($n\text{Bu}_3\text{N}/\text{Et}_3\text{N}$) served dual roles as both the terminal reducing agent and the hydrogen atom donor, eliminating the need for external hydrogen sources or redox mediators. The protocol exhibited broad substrate scope, efficiently converting aryl bromides as well as less reactive aryl chlorides and fluorides under mild, current-driven conditions, establishing a cost-effective and sustainable platform for halide reduction.

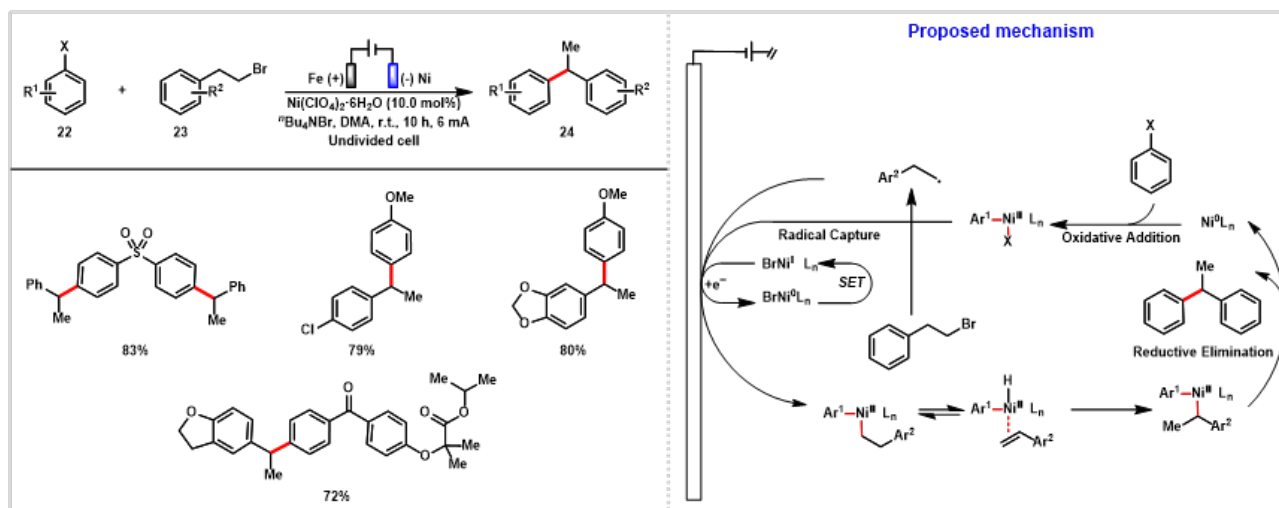


Figure 8. Electro-redox mediated cross-coupling of aryl halides and alkyl bromides.

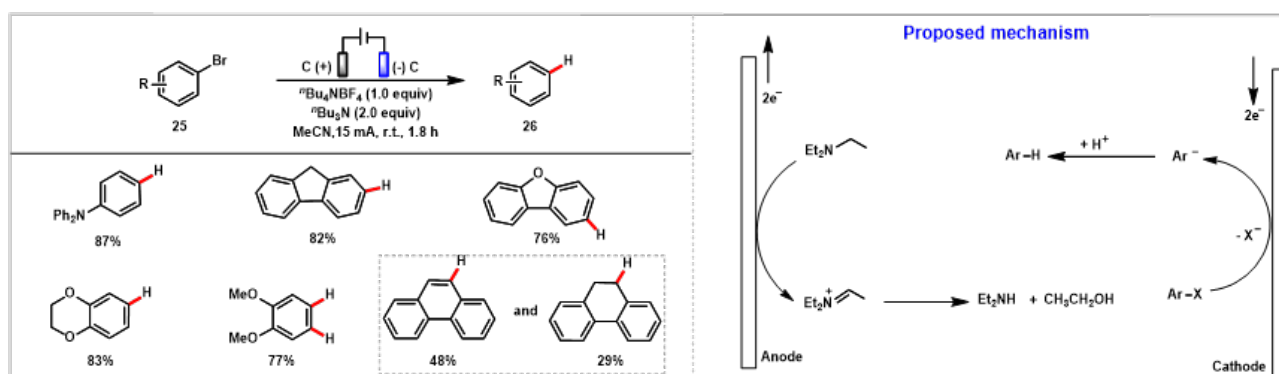


Figure 9. Electro-redox hydrodehalogenation of aryl halides.

Cathodic single-electron reduction of carbonyl compounds generates reactive carbonyl radical anion intermediates that undergo subsequent protonation, radical dimerization, or addition to unsaturated π -systems for complex oxygenate synthesis. By bypassing traditional two-electron Grignard pathways and eliminating stoichiometric metal reductants, direct cathodic single-electron transfer overcomes long-standing mechanistic limitations, offering a sustainable and controllable approach for the polarity-reversal coupling of unactivated ketones. In 2020, the Baran group developed an electro-redox protocol for the reductive coupling of unactivated olefins and ketones, bypassing the strict functional-group constraints of traditional Grignard-based strategies (Figure 10).²⁹ The reaction proceeded under mild conditions in an undivided electrochemical

cell and was readily performed on gram scale, while accommodating a broad range of structurally diverse ketones and alkenes. Mechanistic studies revealed an electrochemically driven pathway initiated by cathodic single-electron reduction of the ketone to generate a transient ketyl radical. Subsequent addition of this electrophilic species to the unactivated olefin generated a carbon-centered radical, which underwent a second cathodic reduction to a carbanion prior to final protonation. By harnessing precise electrode-potential regulation to drive challenging reductions without stoichiometric chemical reductants, this protocol highlighted the distinct advantage of electrosynthesis in forging bonds inaccessible through classical thermochemical routes.

Reductive radical-radical coupling provides a complemen-

tary cathodic single-electron-transfer (SET) strategy in which two radical species, generated by sequential or parallel cathodic reductions, undergo C–C bond formation. In 2018, the Mei group reported a Pd-catalyzed electrochemical regioselective carboxylation of allylic esters with CO₂ as the C1 carbon source, providing branched α -aryl carboxylic acids with high regioselectivity (Figure 11).³⁰ Moreover, the use of chiral bidentate phosphine ligands enabled asymmetric induction, affording the corresponding carboxylation products with up to 67% ee, establishing a precedent for enantioselective electrochemical carboxylation. Cyclic voltammetry showed significant changes in the electrochemical response upon addition

of the allylic substrate and CO₂, consistent with their involvement in the Pd-mediated catalytic process. Mechanistic studies revealed that steric repulsion between the ligand-bound Pd center and the aryl substituent favored isomerization of the cationic π -allyl-Pd(II) intermediate to the terminal η^1 -allyl-Pd(II) isomer, inducing formation of the branched product. Subsequent two-electron cathodic reduction of the η^1 -allyl-Pd(II) species generated a nucleophilic η^1 -allyl-Pd(0) intermediate. In the presence of Mg²⁺ generated by anodic oxidation of the magnesium electrode, this low-valent Pd intermediate underwent CO₂ incorporation to furnish the α -aryl carboxylate and regenerate the Pd(0) catalyst.

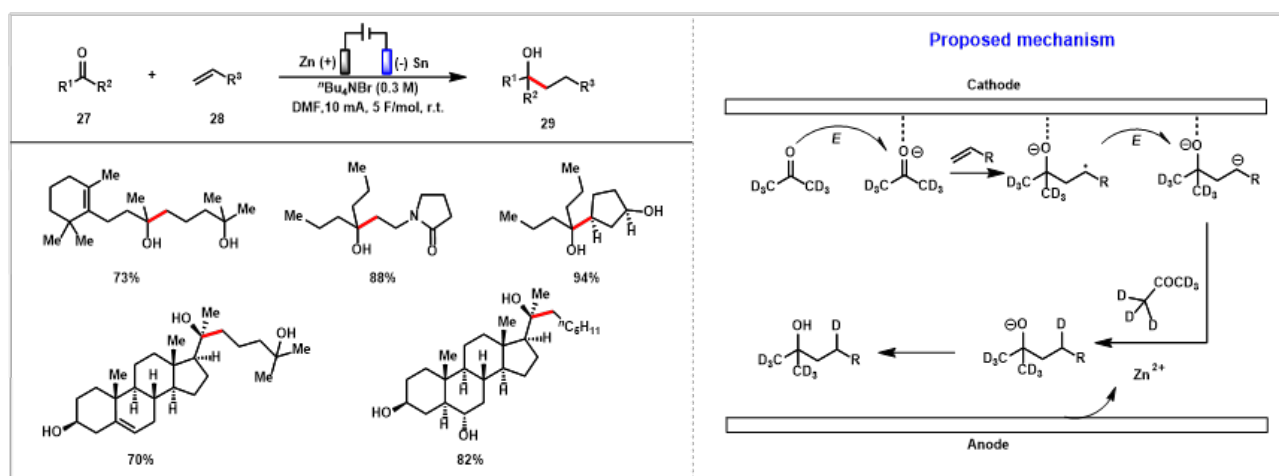


Figure 10. Electro-reductive coupling of unactivated olefins and ketones.

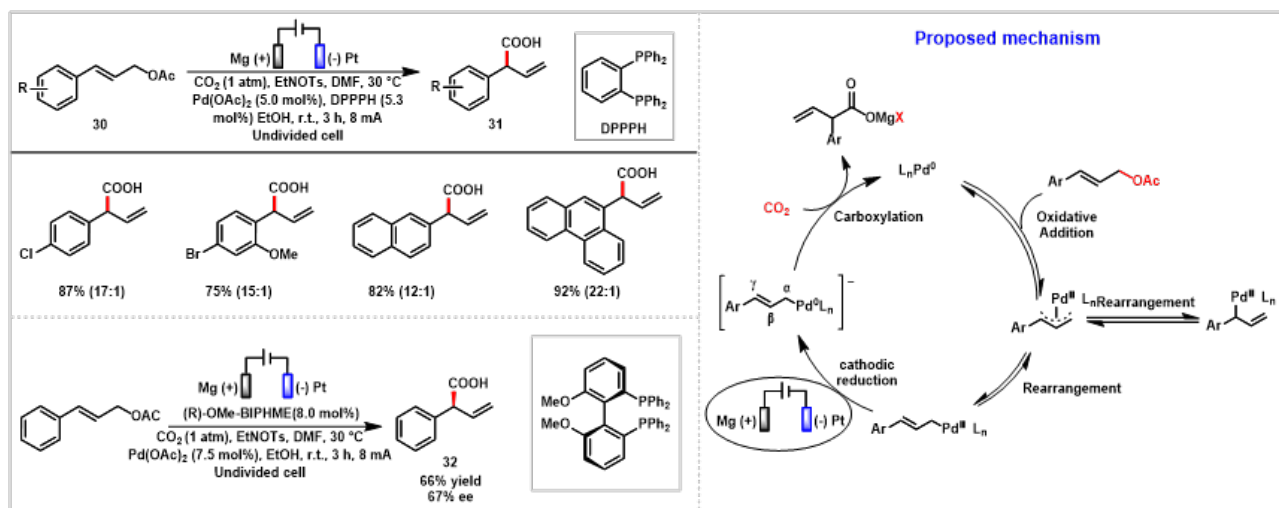


Figure 11. Electro-redox-induced Pd-catalyzed carboxylation of allylic esters with CO₂.

Key points in this part

- Cathodic single-electron reduction lets substrates accept electrons directly at the cathode to generate radical anions, neutral radicals or carbanions, avoiding stoichiometric metal reductants (Li, Na, Zn) and expensive photoreductive systems.
- Cathodic homolytic C–X cleavage of alkyl/aryl halides generates carbon-centered radicals for hydrogen abstraction, cyclization or coupling; aryl chlorides, bromides, iodides and activated alkyl halides react under mild, metal-free conditions.
- Nickel-catalyzed electrochemical reduction relay cross-coupling of aryl halides and alkyl bromides runs in an

undivided cell without stoichiometric metal reductant, giving 1,1-diaryllalkanes with good yields and excellent regioselectivity (Figure 8).²⁸

- Catalyst-free electrochemical hydrodehalogenation uses only graphite electrodes and trialkylamines ($^n\text{Bu}_3\text{N}/\text{Et}_3\text{N}$) that serve as both terminal reductant and hydrogen-atom donor, even converting low-reactivity aryl chlorides and fluorides (Figure 9).⁵¹
- Cathodically generated carbonyl radical anions enable direct reductive coupling of unactivated olefins and ketones via radical addition–second-electron reduction–protonation, avoiding Grignard-type reagents and achieving gram-scale amplification (Figure 10).²⁹
- Palladium-catalyzed electrochemical carboxylation of styrene derivatives achieves regioselective α -aryl carboxylic acid synthesis with up to 67% ee (Figure 11).³⁰

4. Electro-redox mediated cyclization via SET

Electrochemical single-electron-transfer (SET) radical cyclization enables C–C and C–heteroatom bond formation with-

out using stoichiometric redox reagents.^{64–68} Allenes, with their cumulated $\text{C}=\text{C}=\text{C}$ framework and three nonequivalent carbon centers, are versatile but challenging substrates for radical addition, leading to several regioisomers.^{69–73} Electrochemical control of radical generation therefore provides an attractive strategy for addressing this selectivity problem,^{74–78} although allene radical functionalization still remains underdeveloped.^{79–83} Recently, Volla et al. reported an electrochemical cascade using diphenyl diselenide to enable regioselective allene functionalization through selenium-radical addition at the central carbon, followed by anodic oxidation and intramolecular nucleophilic cyclization to afford oxazoline and oxazolidin-2-imine scaffolds under mild conditions (Figure 12).³⁷ Cyclic voltammetry, radical-trapping experiments, electrolysis on–off studies and DFT calculations supported the proposed mechanism and rationalized the regioselective radical addition. This work established an electrochemical radical–polar crossover as an effective strategy for controlling allene regioselectivity, enabling direct access to biologically relevant heterocycles.

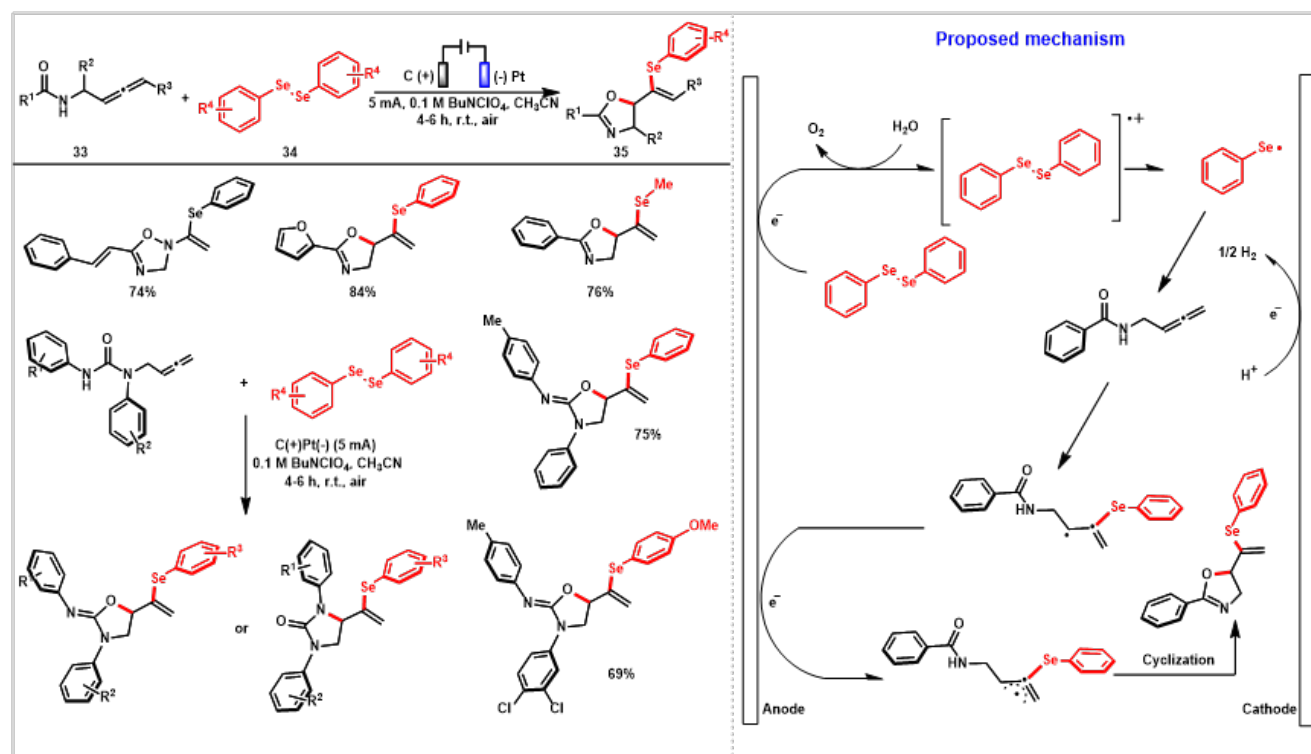


Figure 12. Electro-redox-induced regioselective allene functionalization.

The synergistic activation with the electrode and hydrogen-bond enables additive-free electrochemical decarboxylative cascade cyclization by coupling substrate preorganization with controlled cathodic and anodic electron transfer. In 2024, He and co-workers developed a hydrogen-bond-mediated electrochemical [2+2+1] cyclization of benzo[d]isothiazole 1,1-dioxide, *N*-aryl glycine and paraformaldehyde, affording fused benzo[d]isoth-

iazolo[1,1-b]imidazole 5,5-dioxide derivatives under mild conditions in the absence of a transition-metal catalyst, redox mediator or supporting electrolyte (Figure 13).³⁸ Mechanistic studies disclosed that hydrogen-bond association with water facilitated the formation of a readily reduced charge-transfer complex, enabling cathodic electron transfer and generation of the glycine-derived carboxylate/aminomethyl radical pathway. First, de-

carboxylation of *N*-aryl glycine produced the corresponding aminomethyl radical, which reacted with the benzoisothiazole. Subsequent hydrogen-atom transfer, Mannich-type C–N bond formation and intramolecular cyclization, followed by anodic dehydrogenative oxidation, afforded the aromatized fused heterocycle.

This strategy demonstrated a model of hydrogen-bond-assisted electrochemical activation that replaced conventional electrolyte- and redox-mediated activation, enabling efficient amino-acid decarboxylative functionalization for fused sulfone-heterocycle synthesis without exogenous additives.

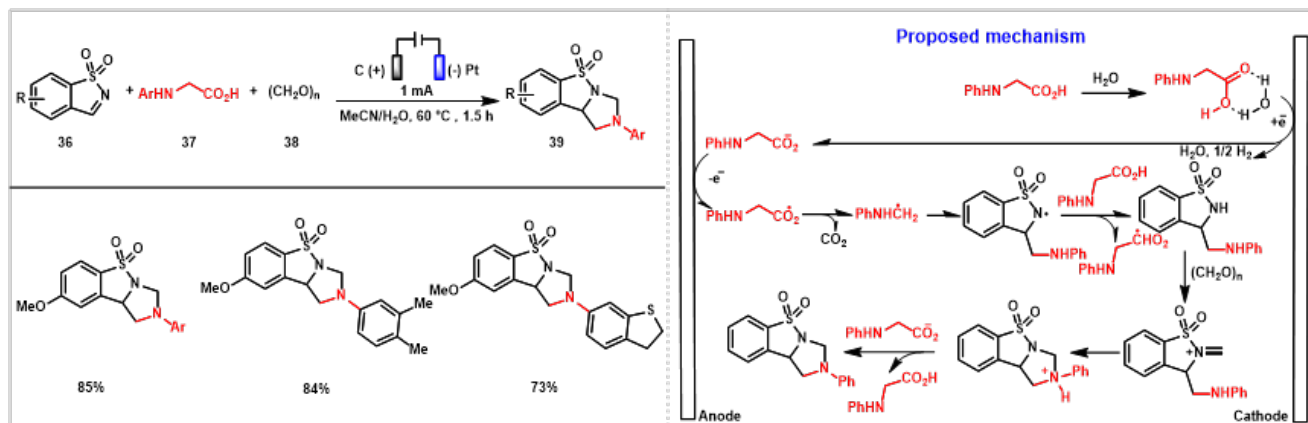


Figure 13. Hydrogen-bond-mediated electrochemical [2+2+1] cyclization.

Nitrogen-containing heterocycles are ubiquitous pharmacophores in pharmaceuticals and bioactive molecules, driving continued efforts to develop efficient and sustainable methods for their selective synthesis and functionalization. In 2025, Zhang and co-workers reported a mild electrochemical Ugi–azide reaction that enabled direct functionalization of the C(sp³)–H bonds of tertiary amines to synthesize α -aminomethyl tetrazoles. In contrast to conventional Ugi–azide reactions that typically required metal catalysts, iodine-based additives or stoichiometric oxidants, this traceless electrochemical protocol operated under ambient conditions and com-

pleted in 2.5 h, while tolerating diverse functional groups and remaining effective on preparative scale. Mechanistic studies supported an anodic single-electron-transfer pathway in which oxidation of the tertiary amine generated an α -aminoalkyl radical, followed by radical addition to the reaction partners and intramolecular [3+2] cycloaddition to establish the tetrazole ring (Figure 14).³⁹ By replacing externally supplied oxidants with electrode-driven electron transfer, this method coupled direct C(sp³)–H activation with radical cyclization, providing a concise and operationally simple route to α -aminomethyl tetrazoles under mild conditions.

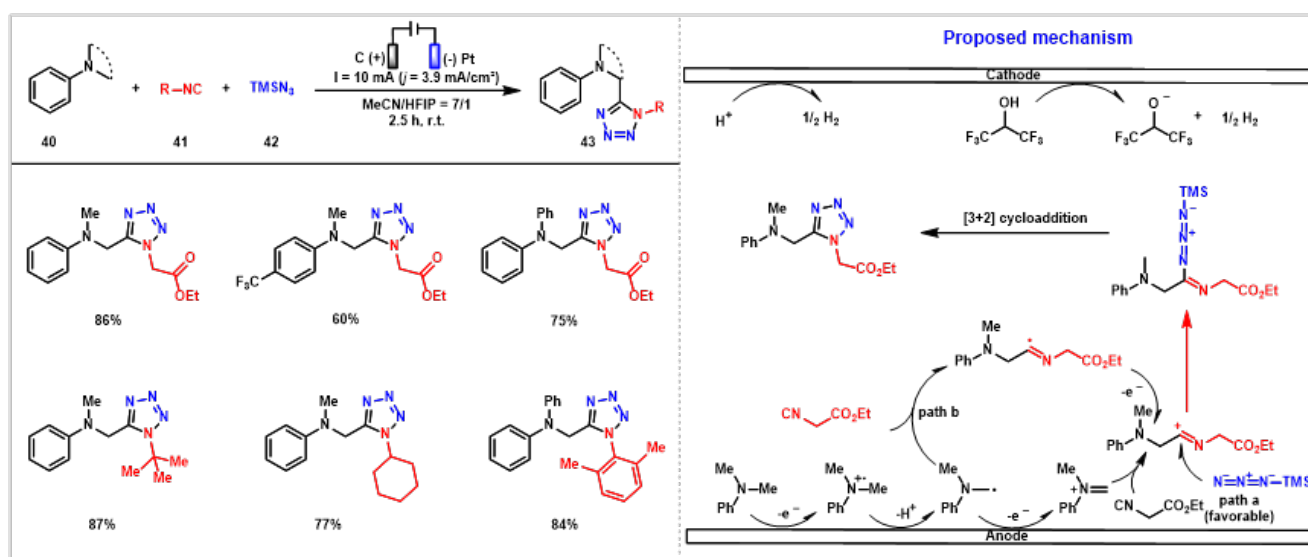


Figure 14. Electro-redox-induced Ugi–azide reaction.

In 2026, Sarkar and co-workers reported a DDQ-catalyzed electrochemical formal [3+2] cycloaddition for the synthesis of tetrazolo[1,5-a]quinoxalin-4(5H)-one derivatives (Figure 15).⁴⁰ The reaction employed a catalytic amount of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) as a redox mediator and sodium azide as an inexpensive azide source, enabling the transformation without using stoichiometric external oxidants. Mechanistic studies supported a DDQ-mediated radical pathway in which electrochemically regenerated DDQ facilitated

single-electron transfer to generate azidyl radicals, which subsequently underwent radical addition to the quinoxalinone substrate and intramolecular cyclization to construct the fused tetrazole ring. The method tolerated diverse substituents on the quinoxalinone framework to access a broad range of tetrazoloquinoxalinone derivatives in good yields. By integrating catalytic redox mediation with electrode-driven radical generation, this protocol provided a practical approach to tetrazole-fused heterocycle synthesis under electrochemical conditions.

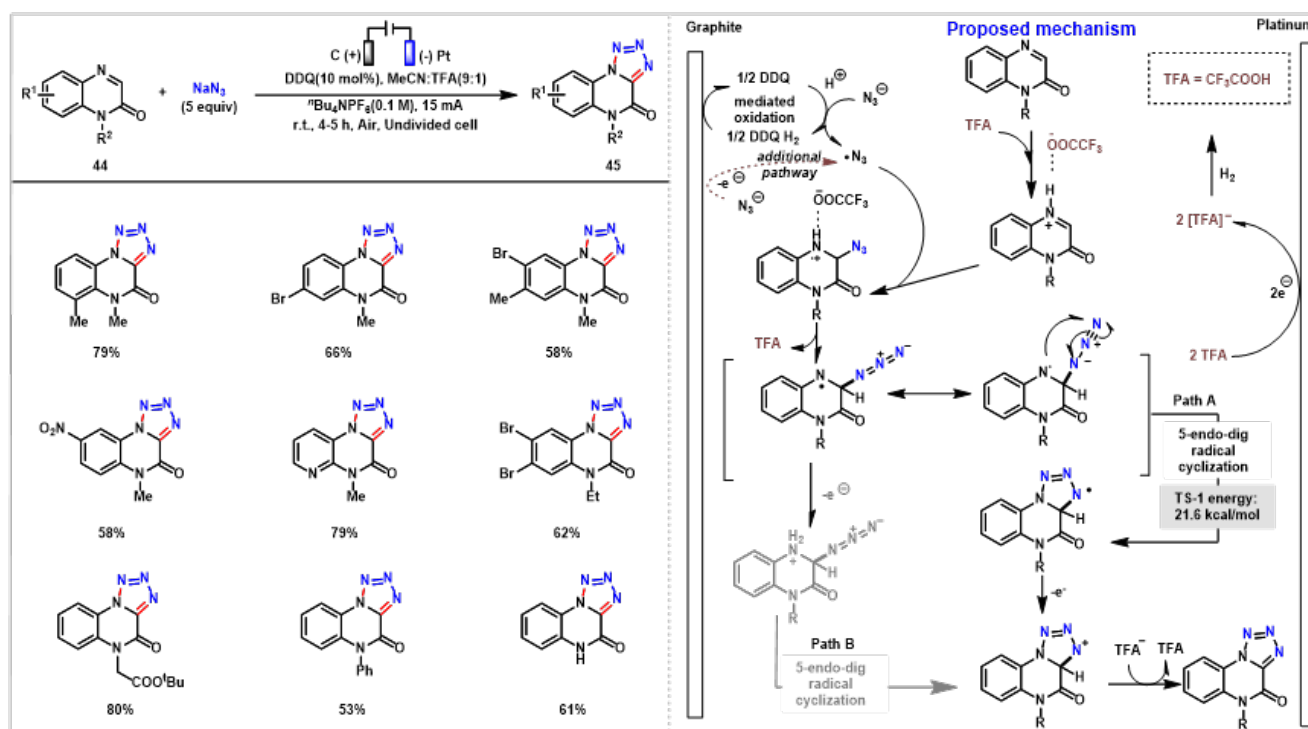


Figure 15. Electro-redox-mediated formal [3+2] cycloaddition.

The electrode material is a key determinant of electrochemical reaction pathways because electrode–substrate interfacial interactions can modulate electron-transfer kinetics,^{84–87} intermediate stabilization and product selectivity, enabling divergent transformations under otherwise identical reaction conditions.^{88,89} In 2019, Chiba and co-workers demonstrated this principle through an electrode-controlled divergent electrochemical oxidation of styrene derivatives using molecular oxygen as the sole oxygen source (Figure 16).⁴² Notably, the reaction pathways were switched by using different electrode materials. This reaction tolerated a broad range of styrene substrates, allowing two distinct product classes to be accessed from the same starting materials without changing the bulk reaction conditions. Mechanistic studies attributed this divergence to differences in electrode–substrate interfacial properties. Relative to platinum, carbon electrodes facilitated styrene oxidation and promoted substrate adsorption, thereby altering the reaction pathway of the resulting styrene radical cations. At the carbon interface, the radical cations preferen-

tially reacted with neutral styrene to initiate C–C bond formation and subsequent cyclization, whereas at the platinum interface they were preferentially intercepted by superoxide ($\text{O}_2^{\bullet-}$), leading to oxidative C=C bond cleavage and carbonyl formation. This study demonstrated that electrode-surface properties controlled the reaction pathways of electrochemically generated radical cations, providing a mechanistically defined strategy for switching product selectivity through electrode selection.

Inspired by the vitamin B1-dependent conversion of pyruvate to acetyl-CoA, N-heterocyclic carbene (NHC) catalysis has emerged as a versatile platform for the selective functionalization of unsaturated aldehydes. Oxidative NHC catalysis has enabled functionalization at the α -, β -, γ -, δ - and carbonyl positions of aldehyde substrates.⁹⁰ Compared with established chemical and photo-redox promoted NHC catalysis, electro-redox-mediated NHC catalysis remains relatively underexplored.⁹¹ In 2022, Zhu and co-workers developed an iodide-promoted electro-redox NHC catalytic platform that enabled

single-electron oxidation of *in-situ* generated Breslow intermediates, providing a general entry to NHC-catalyzed radical transformations (Figure 17).³¹ Radical-clock experiments and cyclic voltammetry supported an anodic radical-coupling pathway distinct from conventional oxidative NHC catalysis. The integration of iodide co-catalysis with paired electrolysis eliminated the need for stoichiometric chemical oxidants while

enabling diverse reaction manifolds, including α -, β -, γ -, δ - and carbonyl functionalization, and cyclization. The broad substrate scope and scalability of this platform demonstrated the potential of electro-redox control to expand NHC catalysis beyond conventional two-electron reactivity and provided direct access to radical transformations from NHC-based intermediates.

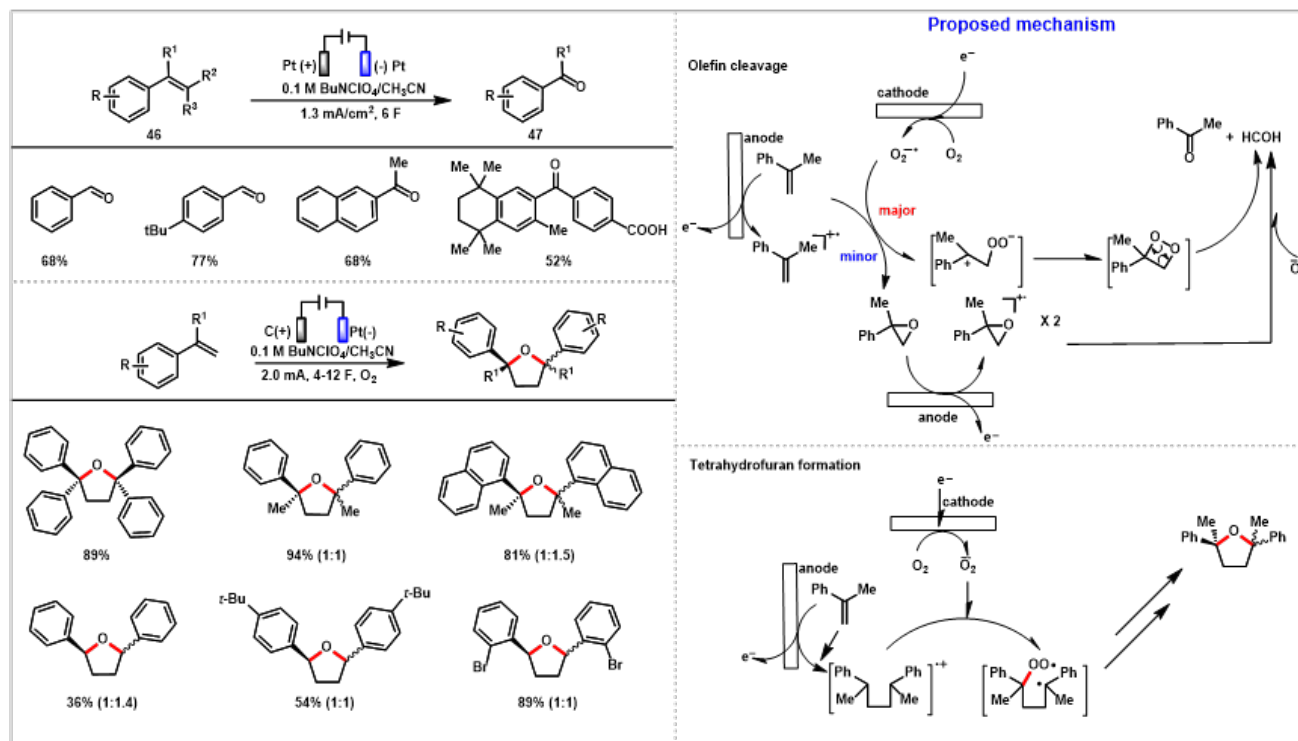


Figure 16. Electrode-controlled divergent oxidation of styrene derivatives.

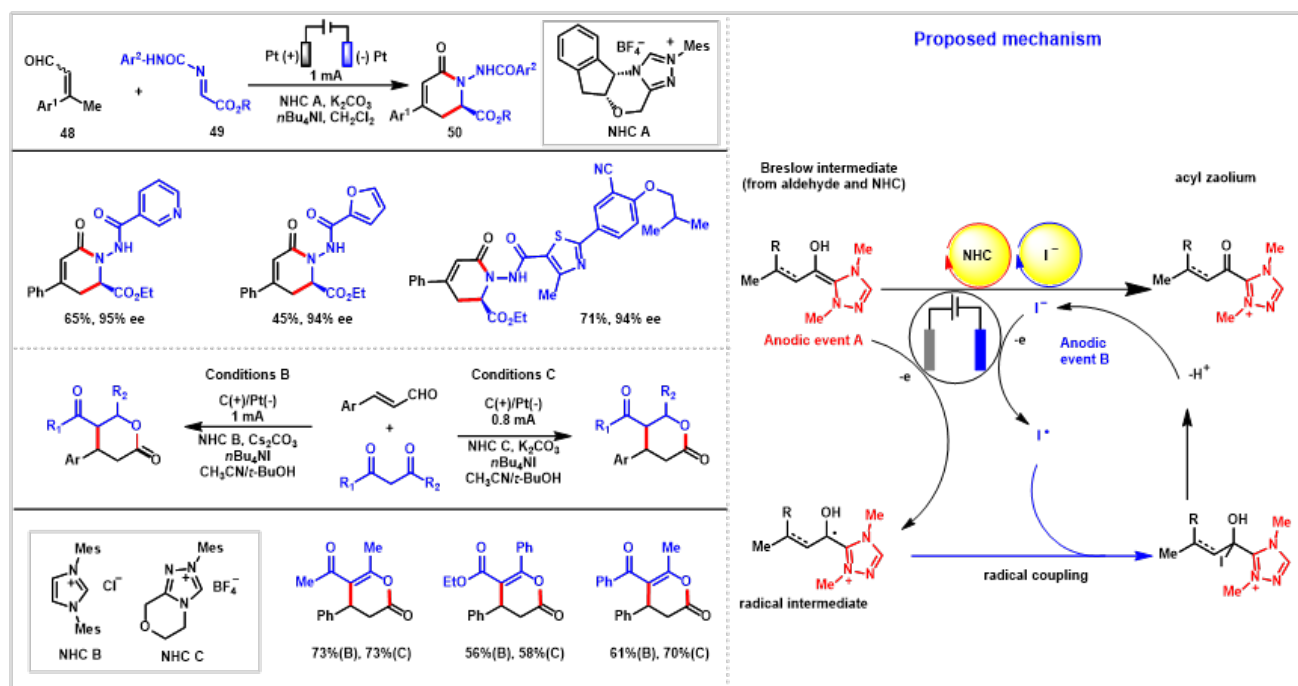


Figure 17. Electro-redox-mediated NHC catalysis.

In 2025, Banerjee and co-workers reported an asymmetric electro-redox mediated NHC-catalyzed radical cyclization enabled by β -carbon LUMO-lowering activation of enals and coupled to *in-situ* hydrogen evolution (HER) (Figure 18).³² By replacing stoichiometric oxidants with electrochemical electron transfer, this protocol enables enantioselective synthesis of chiral naphthopyran-3-one frameworks and β -arylsplitomicin derivatives in up to 93% yield and 99% ee. Mechanistic studies and cyclic voltammetry supported direct single-electron oxida-

tion of the catalytically generated Breslow intermediate, initiating the radical cyclization cascade. Concurrent HER converted the cathodic reduction equivalent into molecular hydrogen, avoiding stoichiometric chemical oxidants and minimizing waste. This protocol accommodated diverse substrates and enabled the enantioselective synthesis of structurally diverse products, demonstrating the potential of electro-redox control to extend NHC catalysis from conventional polar reactivity to asymmetric radical cyclization.

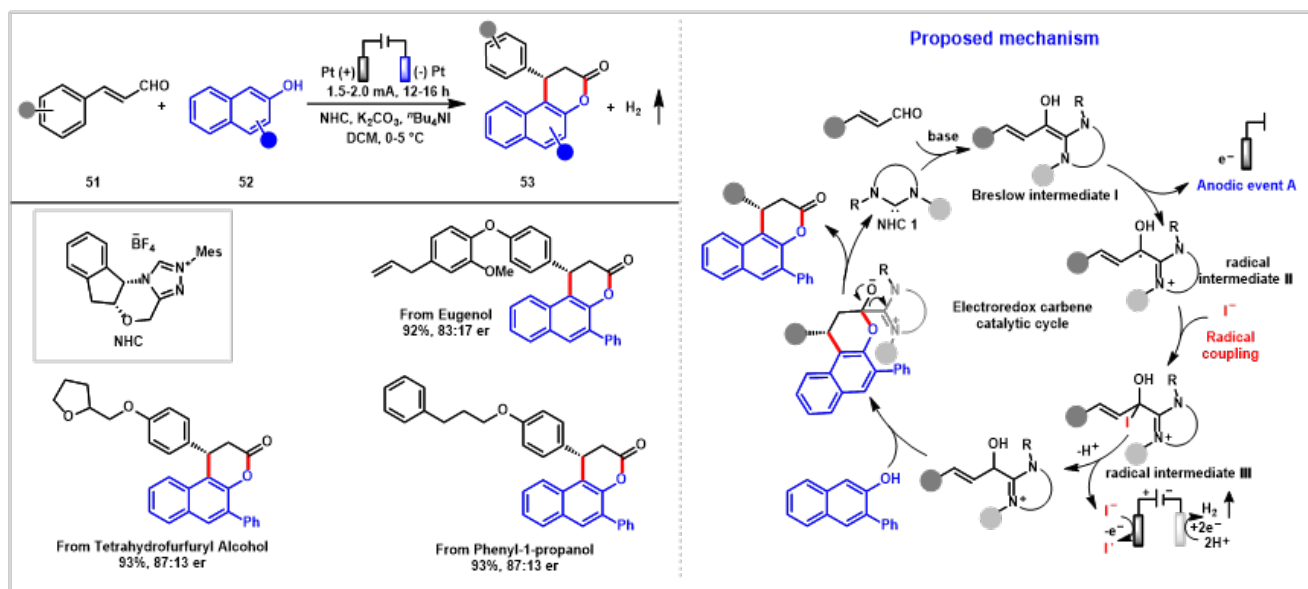


Figure 18. Electro-redox mediated NHC-catalyzed radical cyclization.

Key points in this part

- Electro-redox SET-mediated radical cyclization constructs diverse cyclic skeletons without stoichiometric redox reagents or harsh conditions.
- Diphenyl diselenide mediates a metal-free electrochemical allene cascade cyclization, which proceeds through sequential selenium-radical addition to the central allene carbon, anodic oxidation and intramolecular nucleophilic cyclization, to construct oxazolines and oxazolidine-2-imines under mild conditions. (Figure 12).³⁷
- Hydrogen-bond pre-association between substrate and water enables additive-free electro-cascade [2+2+1] cyclization, constructing fused benzo[d]imidazothiazole dioxide skeletons with lowered activation potential (Figure 13).³⁸
- Electrochemically driven Ugi-azide reactions via anodic C(sp³)-H activation of tertiary amines furnish α -aminomethyl tetrazoles within 2.5 h under ambient conditions (Figure 14);³⁹ recyclable DDQ as an electro-redox mediator enables transition-metal-free formal [3+2] cycloaddition to tetrazoloquinolines (Figure 15).⁴⁰
- Electrode material itself can steer selectivity: switching from Pt, which mediates oxidative C=C cleavage to generate carbonyls, to carbon electrodes that enable intramolecu-

lar cyclization to afford tetrahydrofurans diverges styrene functionalization under identical conditions (Figure 16).⁴²

- Iodide-promoted electroredox NHC organocatalysis oxidizes Breslow intermediates via a distinct anodic radical-coupling pathway, covering α -, β -, γ -, δ - and carbonyl activation modes without stoichiometric oxidants (Figure 17);³¹ an asymmetric variant delivers chiral naphthopyran-3-ones in up to 93% yield and 99% ee with H₂ as the only byproduct (Figure 18).³²

5. Electro-redox-mediated oxidation via SET

Direct electrolysis enables substrates to undergo electron transfer at the electrode surface, whereas indirect electrolysis uses a redox mediator that undergoes preferential electron transfer at the electrode and subsequently shuttles electrons between the electrode and substrates. In the presence of a redox mediator, this molecule is first oxidized by single-electron transfer (SET) at the anode to generate a reactive oxidizing species, which then undergoes homogeneous SET with the substrate to initiate C-H bond cleavage. This strategy circumvents the high overpotential required for direct anodic oxidation of otherwise inert C-H bonds, while minimizing electrode passivation and overoxidation and improving chemo-selectivity in late-

stage C–H functionalization. In 2016, Baran and co-workers reported a scalable Cl_4NHPI -mediated electrochemical allylic C–H oxidation (Figure 19).⁴³ Compared with conventional allylic oxidation that relies on the use of stoichiometric amounts of chromium reagents or selenium-based oxidants or precious-metal catalysts, this metal-free protocol employed electrolysis

to generate the reactive oxidant species at the electrode surface and enabled sequential SET and hydrogen-atom-transfer (HAT) steps. The method exhibited broad substrate compatibility and was demonstrated on a 100-g scale, underscoring the scalability of electrolysis for preparative C–H functionalization.

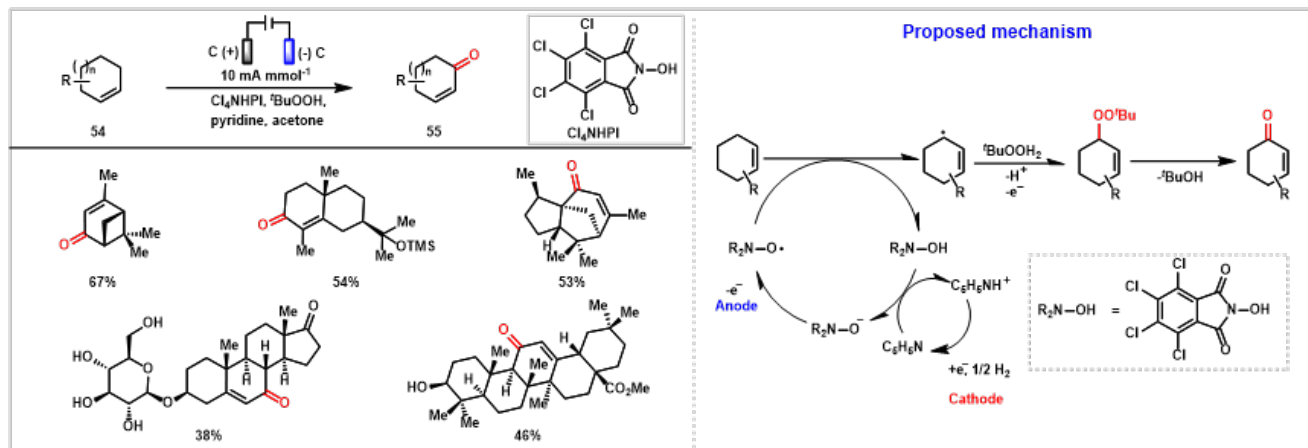


Figure 19. Electrochemical allylic C–H oxidation.

Beyond allylic C–H oxidation, the electroredox-mediated SET/HAT process has been extended to the selective activation of otherwise challenging unactivated aliphatic $\text{C}(\text{sp}^3)$ –H bonds. Direct anodic oxidation of methylene and methine sites generally requires high overpotentials, resulting in solvent oxidation and compromising site selectivity. In 2017, Baran and co-workers developed a quinuclidine-mediated electrochemical strategy for the selective oxidation of unactivated $\text{C}(\text{sp}^3)$ –H bonds (Figure 20).⁴⁴ The reaction employed inexpensive carbon and nickel electrodes, with anodic oxidation of

quinuclidine generating a reactive radical cation that mediates hydrogen-atom transfer from a remote $\text{C}(\text{sp}^3)$ –H bond in solution, away from the electrode surface. This protocol exhibited broad substrate scope and high functional-group tolerance, and its scalability was demonstrated by the oxidation of perillalactone on a 50-g scale. By generating the reactive oxidant electrochemically rather than using stoichiometric chemical oxidants, this electrolysis provided a scalable approach to selective aliphatic $\text{C}(\text{sp}^3)$ –H oxidation for late-stage functionalization.

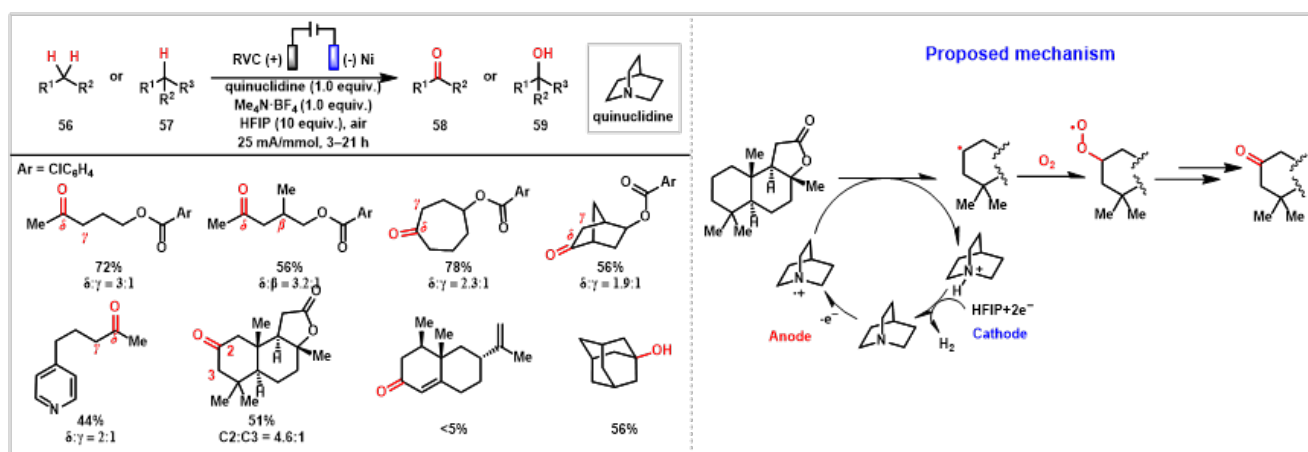


Figure 20. Electrochemical oxidation of unactivated $\text{C}(\text{sp}^3)$ –H bond.

Conventional Shono oxidation often requires direct anodic oxidation of carbamate substrates at relatively high potentials, leading to functional-group incompatibility. In 2028, Stahl and co-workers addressed this limitation by developing an

ABNO-mediated electrochemical Shono-type α -oxygenation of cyclic carbamates (Figure 21).⁴⁵ The bicyclic aminoxyl mediator ABNO underwent anodic oxidation to the corresponding oxoammonium species, enabling C–H oxidation at

an operational potential nearly 1 V lower than that required for direct electrolysis. The oxoammonium species then oxidized the α -C–H bond through concerted hydride transfer, directly forming the α -oxygenated product without a discrete carbon-centered radical intermediate. Therefore, the reaction mechanism was distinct from the SET/HAT manifold described above for aliphatic hydrocarbon oxidation. In the ABNO-mediated reaction, anodically generated oxoammonium species directly abstracted a hydride equivalent from the α -C–H bond of the cyclic carbamate through a concerted two-electron process, avoiding the formation of a discrete α -amino carbon radical. By contrast, hydrocarbon oxidation

involved sequential single-electron oxidation and hydrogen-atom transfer, in which the oxidized mediator abstracted H• from an aliphatic C–H bond to generate a carbon-centered radical that underwent subsequent oxidation or functionalization. These studies demonstrated that mediator structure directly influenced the selectivity and mechanism of C–H oxidation by controlling both the redox potential and the reactivity of the electrogenerated intermediate. The oxoammonium functionality of ABNO enabled selective, concerted hydride transfer from α -amino C–H bonds, whereas mediators capable of generating radical cations promote stepwise HAT from unactivated aliphatic C–H bonds.

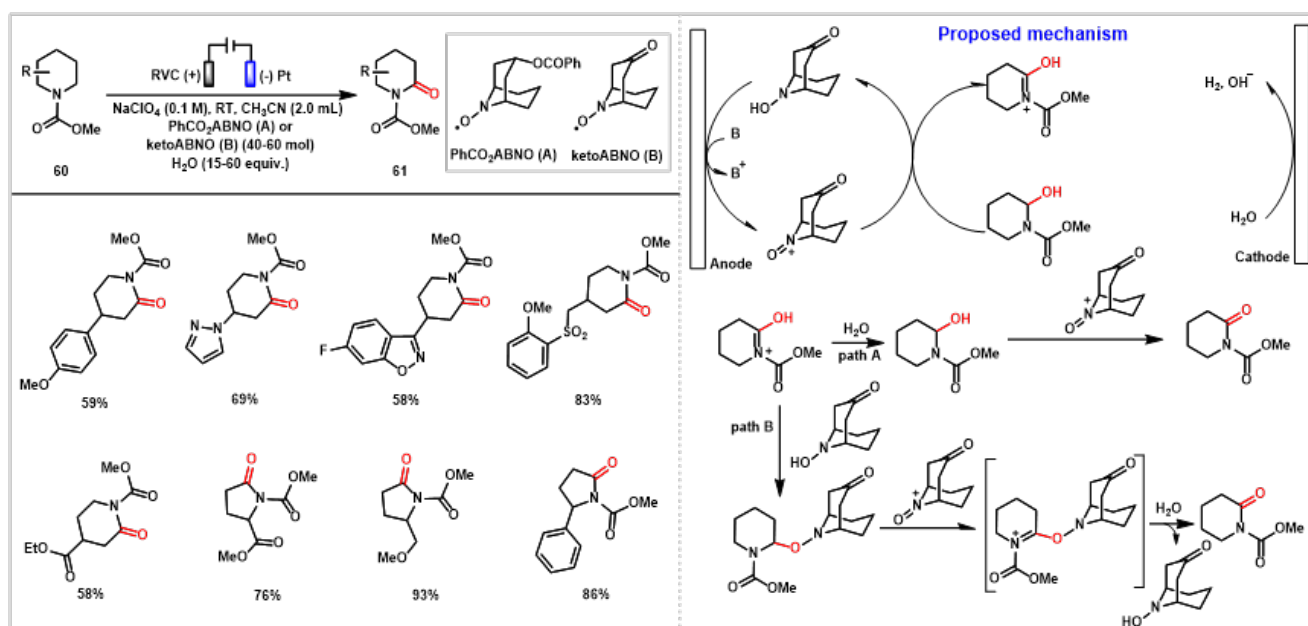


Figure 21. Electrochemical Shono-type oxidation of cyclic carbamates.

Selective cleavage of carbon–carbon σ bonds provides a direct strategy for skeletal editing, but controlling C–C bond fragmentation while preserving other functional groups remains challenging. In 2024, Morrill and co-workers summarized electrochemical deconstructive functionalization of arylcycloalkanes, highlighting C–C bond cleavage of anodically generated aromatic radical cations as a versatile entry to skeletal reconstruction.⁹² Moreover, this group developed an electrochemical deconstructive cyclization for synthesis of heterocycles (Figure 22).⁴⁶ Mechanistic studies disclosed that an aromatic radical cation was generated via anodic single-electron oxidation of the arylcycloalkane, while following fragmentation to produce a carbon-centered cation and a neutral radical fragment. The resulting carbocation was rapidly intercepted by a tethered nucleophile, converting the transient fragmentation intermediate to form a C–O or C–N bond and yielding heterocyclic products such as tetrahydrofurans, tetrahydropyrroles and pyrrolidines. This radical-cation-mediated fragmentation–cyclization sequence demonstrated

broad functional-group compatibility and enabled direct conversion of saturated arylcycloalkanes into structurally differentiated heterocycles. The method was further applied to single-pass continuous-flow electrolysis on a 5-mmol scale, which required a lower supporting-electrolyte loading and delivered higher productivity than the corresponding batch process. Continuous-flow operation addressed several limitations associated with mass transfer, electrode utilization and throughput in batch electrolysis, providing a practical route to scale radical-cation-mediated C–C bond fragmentation.

Beyond electrochemical C–C bond cleavage, electrochemical SET has also enabled new approaches to classical reactions for the sustainable synthesis of value-added building blocks. α -Aminonitriles are versatile intermediates in pharmaceutical synthesis,^{93–97} but the conventional Strecker reaction relies primarily on aldehydes or imines and can require metal catalysts or stoichiometric additives.^{98–100} In 2024, Feng and co-workers developed an electrochemical oxidative Strecker reaction that uses readily available alcohols as alkylating reagents to access

α -aminonitriles (Figure 23).³³ The metal- and external-oxidant-free protocol operated under ambient conditions and accommodated aromatic primary amines, secondary amines and aliphatic amines, with broad functional-group tolerance. The reaction was scaled up to gram level by adjusting the electrolysis parameters. Mechanistic studies combining cyclic voltam-

metry, control experiments and DFT calculations implicated a hydroxymethyl radical ($\bullet\text{CH}_2\text{OH}$), providing a distinct radical pathway for alcohol-to-nitrile coupling. This strategy replaced conventional aldehyde or imine substrates with alcohols and uses electrochemical oxidation to generate the reactive hydroxymethyl radical, enabling scalable access to α -aminonitriles.

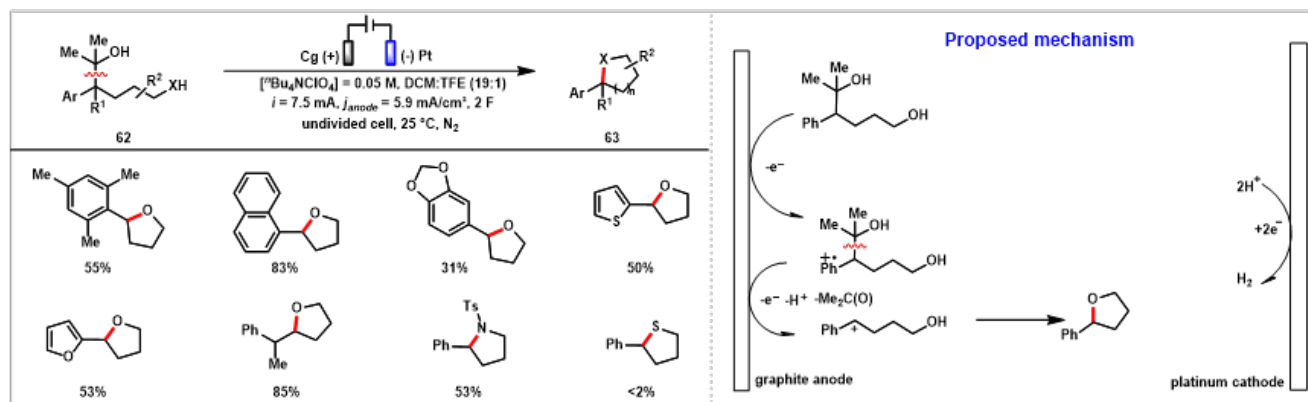


Figure 22. Electro-redox mediated C–C bond fragmentation.

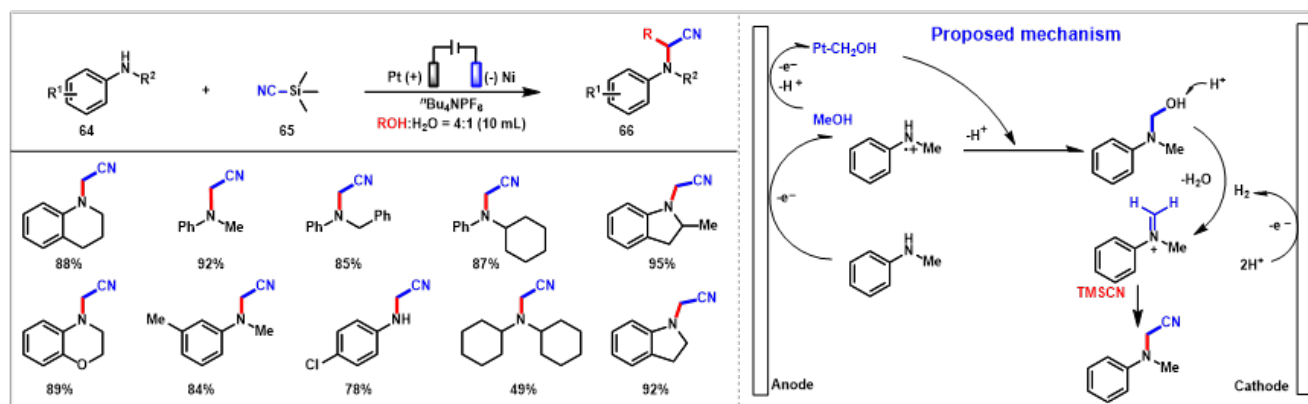


Figure 23. Electro-redox mediated oxidative Strecker reaction of alcohol.

Indoles are prevalent heterocyclic scaffolds in natural products and pharmaceuticals.^{101–105} Oxidative cleavage of the C–C bond provides direct access to o-formyl, o-acyl and anthranilic acid derivatives, which serve as useful intermediates for pharmaceutical synthesis.^{106,107} Conventional approaches such as Witkop oxidation, however, generally require strong oxidants or transition-metal catalysts and are most effective with N-protected or electron-rich indoles, with limited efficiency for free or electron-deficient substrates.^{108–112} In 2021, Guo and co-workers developed a catalyst- and external-oxidant-free electrochemical oxidative ring-opening of indoles in an undivided cell, directly converting indoles to anthranilic acid derivatives (Figure 24).⁴⁷ This method operated under mild conditions and accommodated a broader range of indole substrates, including free and electron-deficient indoles, avoiding prefunctionalization and minimizing the use of stoichiometric oxidants.

1,3,4-Oxadiazoles are important heterocyclic motifs in phar-

maceuticals, functional materials and agrochemicals. Conventional routes to these structures commonly require stoichiometric or excess oxidants for the oxidative cyclization of N-acylhydrazones, which can compromise functional-group tolerance and generate oxidative by-products that complicate purification and scale-up. Jamieson and co-workers developed an indirect electrochemical route to 2,5-disubstituted 1,3,4-oxadiazoles from N-acylhydrazones (Figure 25).⁴¹ In this process, DABCO served as a redox mediator, undergoing anodic oxidation to generate the active oxidizing species that converted the N-acylhydrazone to the 1,3,4-oxadiazole, while cathodic reduction regenerated DABCO to sustain the mediator cycle. Subsequently, they developed a one-pot process that generated the N-acylhydrazone intermediate *in-situ* by condensation of readily available aldehydes with hydrazine derivatives, followed by electrochemical oxidative cyclization to the corresponding 1,3,4-oxadiazoles. The strategy demonstrated that electrochemical regeneration of a redox mediator

was integrated with precursor formation *in-situ* and oxidative heterocycle construction, providing a practical framework

for replacing stoichiometric oxidants with catalytic electron transfer in multistep synthesis.

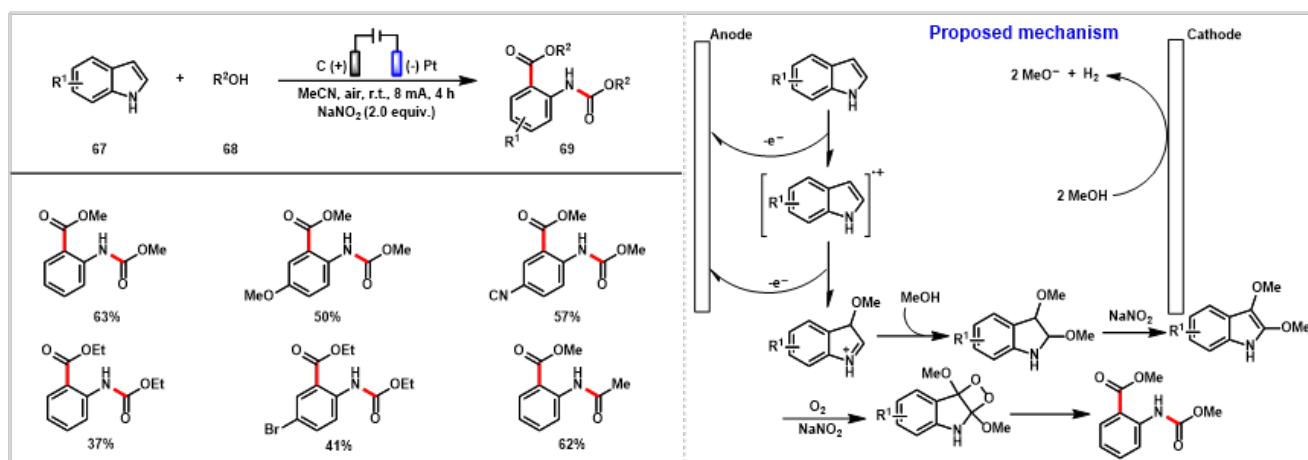


Figure 24. Electro-redox mediated oxidative ring-opening of indoles.

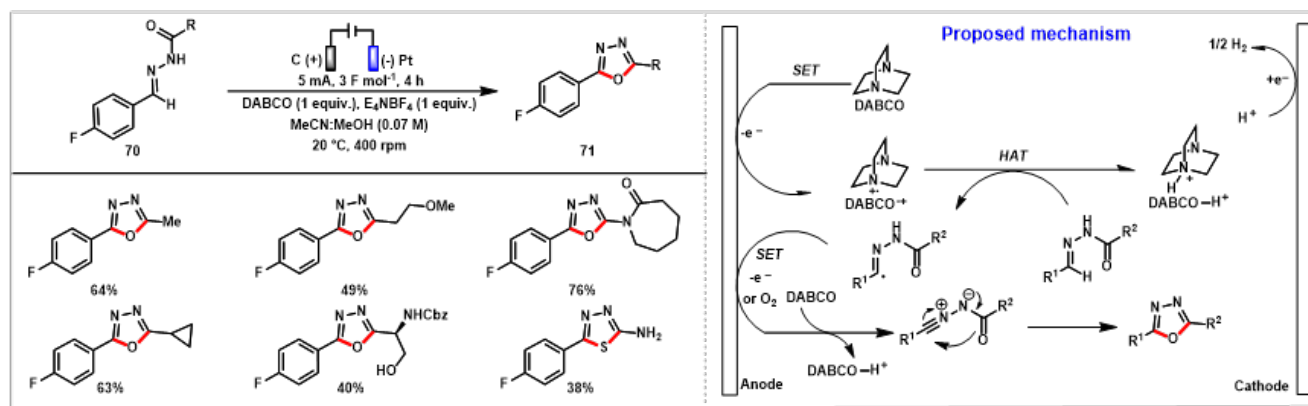


Figure 25. Electrochemical synthesis of 2,5-disubstituted-1,3,4-oxadiazoles.

Electrochemical C–H oxidation offers a direct route to selectively functionalize otherwise inert C–H bonds, but controlling site selectivity and avoiding overoxidation remain challenging. Qiu and co-workers developed a biomimetic iron-catalyzed electrochemical benzylic C–H hydroxylation, using water as the oxygen source through a water-activation strategy (Figure 26).⁴⁸ In this process, electrochemical oxidation promoted the formation of high-valent iron–oxygen intermediates *in-situ*, which mediated hydrogen-atom abstraction and subsequent oxygen transfer at the benzylic C–H bond to furnish the corresponding alcohols. The controlled generation of these reactive iron–oxygen species enabled benzylic C–H functionalization while suppressing unselective oxidation pathways. The reaction accommodated primary, secondary and tertiary benzylic substrates and showed broad functional-group compatibility, including late-stage hydroxylation of structurally complex bioactive molecules. By coupling anodic electron transfer with water activation at an iron center, this strategy provided a mild approach to site-selective benzylic C–H hydroxylation without involving stoichiometric chemical oxidants and enabled

direct installation of hydroxyl groups into complex molecular frameworks.

Key points in this part

- Indirect electrosynthesis uses redox mediators as electron-transfer shuttles, avoiding the high overpotentials, electrode passivation and over-oxidation of direct anodic C–H oxidation while improving chemoselectivity for late-stage functionalization.
- Cl₄NHPI-mediated electrochemical allylic C–H oxidation shows broad substrate compatibility and high chemoselectivity, validated on a 100 g scale (Figure 19).⁴³
- Quinuclidine-mediated indirect electrolysis selectively oxidizes “deep-seated” unactivated C(sp³)–H bonds via remote hydrogen-atom transfer, demonstrated by 50 g-scale oxidation of perilla lactone (Figure 20).⁴⁴
- Electro-redox C–H oxidation falls into two mechanistic classes, SET/HAT for aliphatic hydrocarbons and concerted hydride transfer for α -amino C–H bonds; the ABNO-mediated Shono-type α -oxygenation of cyclic carbamates

lowers the operating potential by nearly 1 V versus direct electrolysis (Figure 21).⁴⁵

- Anodically generated aromatic radical cations trigger mesolytic C–C cleavage for deconstructive functionalization, enabling modular synthesis of C(sp³)-rich heterocycles, further boosted by single-pass continuous-flow electrolysis at 5 mmol scale (Figure 22).⁴⁶
- The electrochemical oxidative Strecker reaction uses cheap alcohols as alkylating agents to synthesize α -aminonitriles metal- and oxidant-free at room temperature, proceed-

ing via a distinctive hydroxymethyl radical (CH₂·OH) intermediate—an unprecedented bridge between fuel-cell chemistry and organic electrosynthesis (Figure 23).³³

- Green oxidative manifolds further include electrochemical ring-opening of indoles to o-aminobenzoic acid derivatives without oxidant or catalyst (Figure 24),⁴⁷ DABCO-mediated indirect synthesis of 2,5-disubstituted-1,3,4-oxadiazoles from N-acylhydrazones (Figure 25),⁴¹ and biomimetic iron-catalyzed benzylic C–H hydroxylation via water activation for site-selective late-stage modification (Figure 26).⁴⁸

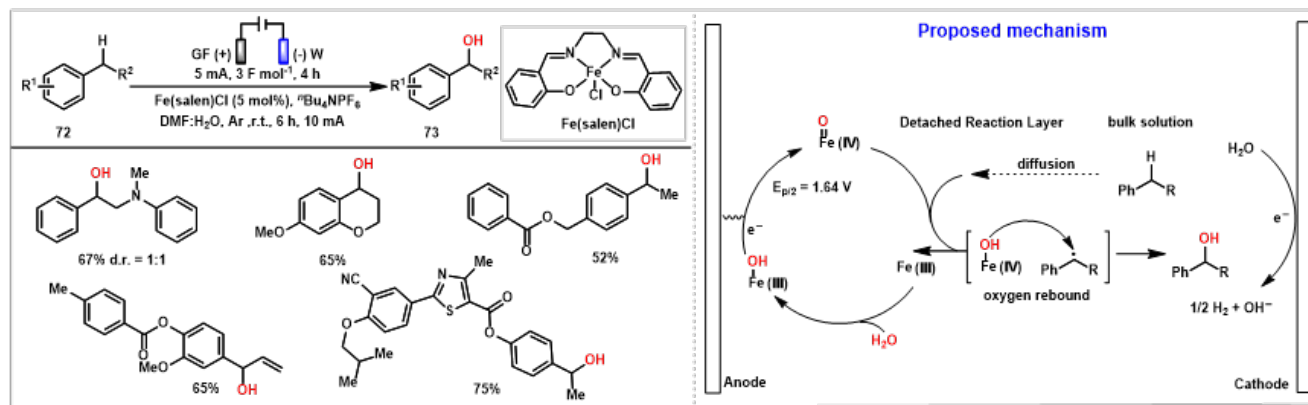


Figure 26. Electro-redox benzylic C–H hydroxylation.

6. Electrode material and reactor engineering

Beyond molecular mechanisms and substrate scope, the practical performance of electro-redox reactions via SET is strongly governed by electrode properties and reactor configuration. Electrode composition, surface characteristics and cell architecture directly influence electron-transfer kinetics, interfacial mass transport and reaction selectivity, while reactor design determines current distribution, mixing and scala-

bility.^{113,114} As a highly feasible green sustainable technology in the field of modern organic synthesis, electrochemistry relies on the gradual maturity of high-throughput micro-electrochemical reactor technology to provide technical support for its large-scale industrial application. Despite their central role in electrochemical reaction performance, these engineering parameters have been discussed in many reviews of electro-synthesis (Table 3).

Table 3. Recent reviews concerning electrode materials and reactor engineering.

Electrode material
The related research progress of carbon felt-based electrodes was reviewed from four aspects: material basic characteristics, modification strategies, functional characterization and application scenarios. The advantages of various carbon felt electrode modification methods were summarized.¹¹⁵ The research progress of surface functional group modification of nitrogen doping, nitrogen-sulfur/nitrogen-boron co-doping and surface catalytic modification of metal/ion and metal oxide was reviewed. The comprehensive properties of the two types of modified electrodes were compared, and the future development direction of graphite felt activation modification was prospected.¹¹⁶ The latest progress in the preparation of doped graphene by electrochemical exfoliation of graphite in an aqueous-phase system was reviewed, and the regulation of different preparation parameters on the physical properties and energy storage properties of the products was analyzed.¹¹⁷ The synthesis technology and hierarchical pore structure of single-chip electrodes from wood, bamboo and other plant sources were systematically reviewed. The regulation of structural characteristics on electrocatalytic performance was analyzed. The application progress of such electrodes in small molecule conversion electrocatalytic scenarios such as water electrolysis, oxygen reduction, carbon dioxide reduction and nitrogen reduction was summarized.¹¹⁸ The latest application progress of anode materials in the field of Kolbe and non-Kolbe electrocatalytic decarboxylation of carboxylic acids was reviewed. The research progress in the preparation of fuel and high value-added chemicals by electrocatalytic oxidation of carboxylic acids under different electrode systems was summarized. The performance characteristics and application performance of various electrode catalytic materials such as Pt-based catalysts and carbon-based catalysts were introduced.¹¹⁹ The research progress of binder-free independent oxygen electrodes with various fiber structures such as electrospun nanofibers, bacterial cellulose, cellulose fibers, carbon cloth/paper, metal nanowires, and metal mesh was systematically reviewed.¹²⁰ The oriented design strategies of metal-organic frameworks (MOFs) materials (original MOFs, MOF composites and their derivatives) are reviewed, and their frontier applications in supercapacitor energy storage and fuel cell oxygen reduction electrocatalysis are summarized.¹²¹

Table 3. Cont.

Electrode material
Various synthesis methods and reaction mechanisms of graphene quantum dots (GQDs) -based nanomaterials are systematically reviewed. The frontier applications of GQDs-based composites in electrochemical energy storage fields such as supercapacitors and batteries, as well as in electrocatalytic fields such as fuel cells, water splitting and CO₂ reduction are summarized.¹²² Focusing on hollow carbon-based nanomaterials with the advantages of internal voids and fast mass transfer paths, the application progress of these materials in the fields of electrocatalytic oxygen evolution/oxygen reduction, hydrogen evolution, CO₂ reduction and so on is systematically reviewed.¹²³ The material types involved in 3D electrodes (3D carbon-based materials, 3D metal-based materials) were systematically classified, and the conventional preparation process of corresponding materials and the doping modification control strategy of active metal/non-metal components were summarized.¹²⁴ The key research progress of dynamic intelligent control under the four dimensions of atom, structure, interface and manufacturing is reviewed. The frontier development directions such as dynamic evaluation system, adaptive electrode development and green intelligent manufacturing are summarized.¹²⁵ The regulation and optimization mechanism of various surface and interface modification strategies such as size limitation, doping, surface reconstruction, interface regulation and defect engineering on the electrocatalytic performance of inorganic low-dimensional electrode materials are summarized.¹²⁶
Reactor engineering
The coupling law between the surface structure, ion distribution and local electric field at the electrocatalytic interface was summarized. The feasible technical path of directional transformation of local reaction environment by electrode physical structure and reaction cell configuration was discussed.¹²⁷ The existing design of electrochemical reactor (ECR) electrolyzers was reviewed, and five typical electrochemical devices including membrane electrode assembly (MEA), flow cell (FC), rotating disk electrode (RDE), rotating ring disk electrode (RRDE) and rotating cylindrical electrode (RCE) were discussed.¹²⁸ The application progress of high-voltage electrochemical reactor (HP ECR) in water electrolysis, N₂ reduction reaction and CO₂ reduction reaction is summarized.¹²⁹ The research progress of various polymer materials and corresponding alkaline solid polymer membranes used in anion exchange membrane (AEM) electrolyzers was reviewed, and the performance indices such as ion exchange capacity and ionic conductivity were analyzed.¹³⁰ In order to reduce the cost of green hydrogen production, the research progress of proton exchange membrane (PEM) electrolyzers was reviewed.¹³¹ The research progress of electrolytic cell systems coupled with the hydrogen evolution reaction, oxygen reduction reaction, carbon dioxide reduction reaction, nitrogen reduction reaction and other cathode reduction reactions suitable for small molecules was reviewed.¹³² The related research in the field of photoelectrochemical reactors was systematically reviewed, and the adaptation characteristics of various photoelectrochemical reactor configurations such as sequencing batch, hybrid, separated/unseparated electrolytic cells, flow cells, and stirred tanks were classified.¹³³ The technological evolution path from traditional batch reactors to advanced continuous flow reactors such as gas convection electrode reactors and staged three-phase diffusion reactors is summarized. The emerging frontiers such as data-driven catalyst discovery and integrated system design are prospected.¹³⁴

7. Conclusion

Electrochemical single-electron transfer (SET) provides a catalyst-free route to radical generation in which electron transfer is driven directly at the electrode–solution interface. By replacing molecular redox catalysts and stoichiometric oxidants or reductants with electrical input, electrochemical SET enables tunable redox control while avoiding metal residues and catalyst-derived waste. This platform supports diverse radical transformations, including C–C and C–heteroatom bond formation, C–H functionalization, cyclization and cascade reactions, with reactivity complementary to conventional catalytic and photoredox methods. Emerging implementations, including battery-powered electrosynthesis, further enhance the portability and accessibility of electrochemical SET.

Despite these advances, electrochemical SET remains constrained by interfacial control, selectivity and scalability. Electrode composition, surface properties and local current density govern heterogeneous electron transfer, substrate adsorption and radical generation, whereas mass transport, electrode spacing and cell architecture influence competing pathways and reaction reproducibility. These effects become more pronounced

during scale-up, where electrode passivation, ohmic losses and concentration gradients can limit productivity. Mechanistically, the coupling of interfacial electron transfer with solution-phase radical reactions also complicates prediction and control of chemo-, regio- and site selectivity. Asymmetric electrochemical SET presents an additional challenge because transient radical intermediates must be generated and stereo-controlled within a heterogeneous electrochemical environment.

Addressing these limitations will require advances in electrode engineering, reactor design and automated reaction discovery. Continuous-flow electrolysis can improve mass transfer, reduce concentration gradients and enable precise control of residence time and current density, providing a route toward scalable electrosynthesis. High-throughput platforms such as HTe-Chem enable systematic screening of electrode materials, applied potential, current and electrolyte composition, while integration with machine learning offers opportunities for data-driven optimization of multidimensional reaction spaces. Photoelectrochemical coupling provides an additional strategy for accessing reactivity beyond conventional electrolysis by combining photon excitation with electrochemical redox

control. Together, these developments could establish catalyst-free electrochemical SET as a more predictable, selective and scalable platform for sustainable radical synthesis.

Author Contributions

L.W., Y.H., L.L., H.L., and P.C.: Original Draft Preparation; Z.J.: Supervision and Revision. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement

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

AI Use Statement

During the preparation of this work, the authors used ChatGPT (OpenAI) for language polishing, improving clarity and readability. The authors subsequently reviewed and edited the content as necessary and take full responsibility for the final content of the published article.

Conflict of Interest

The authors declare no conflict of interest.

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