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Harnessing electrochemical proton-coupled electron transfer for radical generation from diazo compounds

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Although diazo compounds are privileged reagents in organic synthesis, sustainable methods for their radical engagement remain scarce, with most existing protocols relying on costly photocatalysts or stoichiometric reductants. Herein, we report an electrochemical proton-coupled electron transfer (PCET) strategy for the reductive activation of diazo compounds, granting access to electrophilic radicals in the absence of transition metals and exogenous reductants. This versatile platform enables diverse transformations, including hydroalkylation of alkenes, carboxylation with CO_2, and multicomponent Minisci-type alkylations, all of which exhibit high efficiency and broad functional group tolerance. Mechanistic investigations support a paired electrolysis scenario wherein the anodic oxidation of methanol serves as the proton source to facilitate the cathodic activation of diazo compounds *via* PCET. This sustainable protocol broadens the synthetic repertoire of diazo compounds and represents a significant advancement in green electrochemical synthesis.

Green foundation

1. This work advances green chemistry *via* an electrochemical PCET strategy that eliminates transition metals, exogenous reductants/oxidants, and heavy-metal contamination. It operates under mild room-temperature, low-current conditions, maximizes atom economy with dual-role methanol, enables broad substrate scope, CO_2 valorization, and scalable gram-scale synthesis.
2. Qualitatively: we established a metal- and exogenous-reductant-free electrochemical PCET platform for diazo compound activation, using dual-role methanol to minimize waste and avoid toxic reagents. Quantitatively: target transformations afford up to 82% isolated yield (gram-scale) under mild rt, 5–10 mA constant current, with no heavy-metal contamination.
3. Replace Pt electrodes with earth-abundant, fully recyclable electrode materials; develop continuous-flow systems to realize solvent and electrolyte recycling; improve stereoselectivity and substrate compatibility for broader synthetic applications.

Introduction

Diazo compounds represent privileged building blocks in organic synthesis.[1–5] Conventionally, their electron-rich resonance structures enable polarity-matched cycloadditions[6–8] or electrophilic additions[9–12] (Fig. 1a, left panel). Beyond these intrinsic reactivities, transition metal-catalyzed metal carbene transformations,[13–15] alongside light-[2,16–18] or heat-induced[19–21] free carbene reactions, have significantly expanded their synthetic repertoire, enabling challenging transformations such as cyclopropanations and X–H insertion reactions (Fig. 1a, right panel). More recently, the emergence of radical chemistry has redefined diazo compounds as potent radical precursors.[3,22] For instance, Zhang[23–25] and Gryko[26] demonstrated the generation of carbon-centered radicals *via* metalloradical intermediates, facilitating C(sp^2)–H alkylation and cyclopropanation (Fig. 1b, I). In a distinct approach, the Doyle group reported the formation of diazomethyl radicals *via* an Fe(II)/TBHP-induced hydrogen atom transfer (HAT) process for alkene cycloaddition[27] (Fig. 1b, II). Furthermore, photochemical reduction of diazo compounds—including α-diazosulfonium salts,[28] α-diazoiodonium salts,[29–31] and pre-protonated species[32–40]—has emerged as a mild strategy for radical generation (Fig. 1b, III). However, these photochemical

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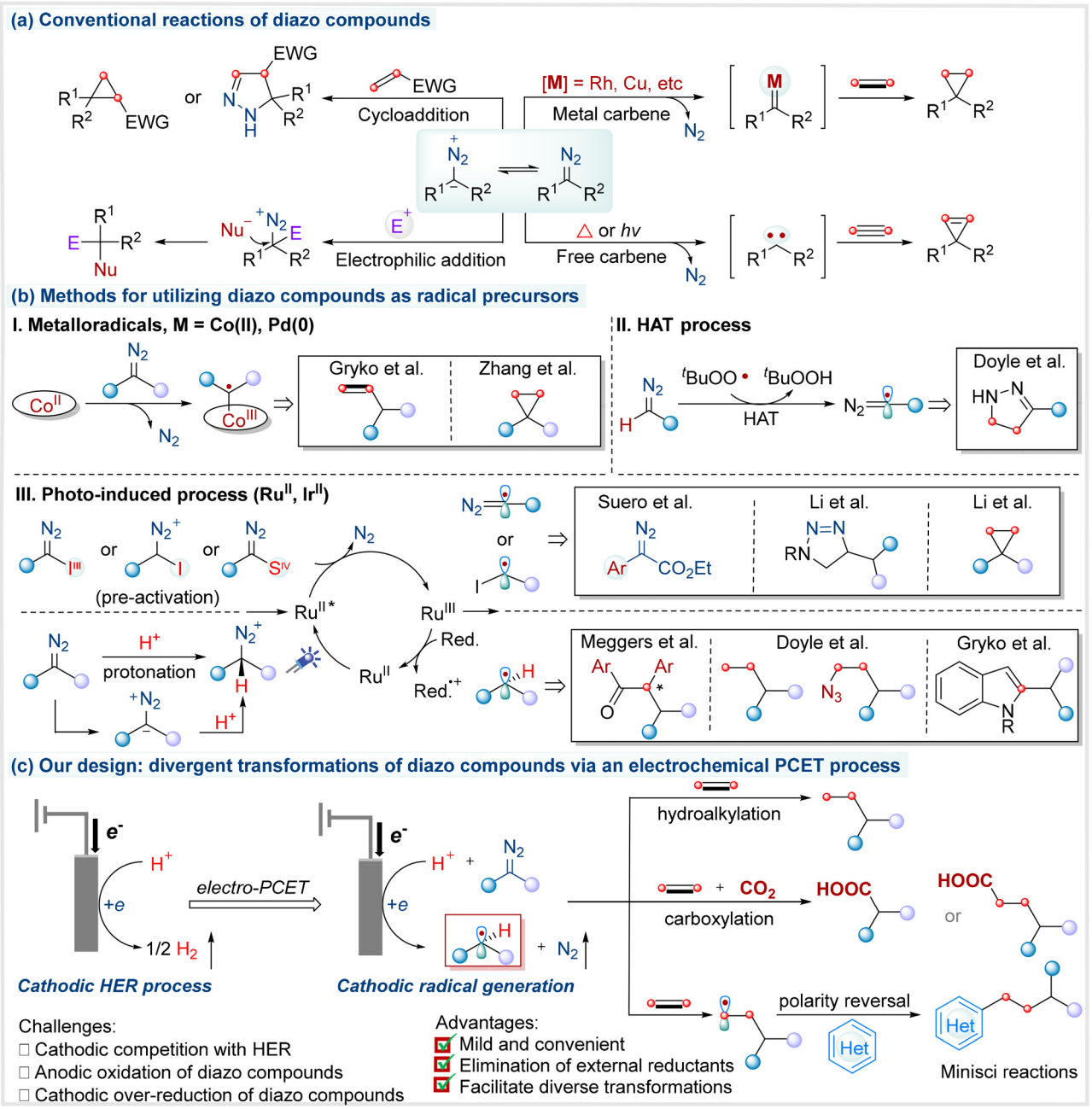


Fig. 1 Reactions of diazo compounds: (a) conventional reaction of diazo compounds; (b) methods of utilizing diazo compounds as radical precursors; (c) this work: divergent transformations of diazo compounds *via* an electrochemical PCET process. HER: hydrogen evolution reaction.

protocols often suffer from inherent limitations, such as the requirement for expensive photocatalysts, stoichiometric reducing agents, and elaborate pre-activation steps, which restrict their reaction diversity and scalability. Therefore, the development of robust and atom-economical strategies for radical generation from diazo compounds remains highly desirable.

In this context, electrochemical synthesis has emerged as a sustainable platform, enabling efficient redox reactions without exogenous oxidants or reductants.[41–45] Consequently, strategies harnessing the direct single-electron reduction of diazo compounds under electrochemical conditions are particularly attractive. While sparse reports have implicated diazo compounds in electrochemical reactions,[46–51] protocols that exploit anodic oxidation to synergistically supply both protons and electrons for a cathodic proton-coupled electron transfer (PCET) process remain elusive. Herein, we propose a design in which protic solvents (*e.g.*, methanol or water) serve a dual role as both solvent and sacrificial electron/proton donor: anodic oxidation supplies the necessary electrons and concurrently releases protons to activate diazo compounds for PCET reduction at the cathode (Fig. 1c). This method obviates the need for external reductants. Crucially, unlike traditional

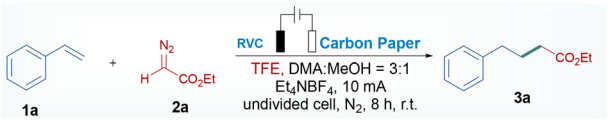
systems where the cathodic hydrogen evolution reaction (HER) dominates under protic conditions, this approach preferentially diverts protons toward diazo activation, enabling the efficient generation of electrophilic radicals and significantly expanding the synthetic utility of diazo compounds.

In this work, we present an efficient electrochemical strategy for the reduction of protonated diazo compounds, enabling the generation of carbon-centered radicals that participate in a diverse array of transformations—including olefin hydroalkylation, multicomponent carboxylation using CO_2, and Minisci-type alkylations (Fig. 1c). Notably, this protocol operates under mild, metal-free, and external-reductant-free conditions, demonstrating broad functional group tolerance and high efficiency. Furthermore, the incorporation of CO_2 in carboxylation reactions represents a meaningful step toward carbon valorization, addressing the pressing need for sustainable decarbonization strategies in synthetic chemistry.[52–54]

Results and discussion

The direct generation of carbon-centered radicals from diazo compounds *via* an electrochemical PCET strategy presents distinct opportunities and challenges. We envisaged that the cathodic reduction of protonated ethyl diazoacetate (**2a**) would generate an α-ester-substituted carbon-centered radical, which could undergo addition to styrene to form a benzyl radical intermediate. Subsequent cathodic reduction of this intermediate, followed by protonation, would afford the desired hydroalkylation product. Preliminary screening of reaction conditions using styrene and **2a** revealed three primary challenges (Table 1): (i) competitive rapid anodic oxidation of **2a**, visually evidenced by gas bubble formation; (ii) potential over-reduction of the formed radical intermediate due to the electron-withdrawing ester group (–CO_2Et); and (iii) the critical need for an effective protic additive to activate **2a** without triggering excessive hydrogen evolution at the cathode. Pleasingly, despite these hurdles, we obtained the target product **3a** in 68% yield under optimized conditions (entry 1): using DMA/MeOH as the solvent, Et_4NBF_4 as the electrolyte, trifluoroethanol (TFE) as the protic additive, and a constant current of 10 mA in an undivided cell equipped with a reticulated vitreous carbon (RVC) anode and a carbon paper cathode at room temperature. Control experiments underscored the necessity of both electrical current and TFE: omitting either resulted in no conversion or a significantly reduced yield (entries 2 and 3). Employing alternative protic additives, such as trifluoroacetic acid (TFA) or hexafluoroisopropanol (HFIP), afforded markedly lower yields (entries 4 and 5). Substituting the solvent with MeCN/MeOH or acetone/MeOH decreased the yields to 13% and 36%, respectively (entries 6 and 7). Electrochemical parameters also proved critical. Replacing the RVC anode with carbon paper or a graphite plate decreased the reaction yields to 20–35% (entries 8 and 9). Replacing the cathode material with graphite felt or RVC also failed to afford improved yields (15–35%, entries 10 and 11). Notably, using $^nBu_4NI$ as the electrolyte led to no product formation, likely due to the rapid decomposition of **2a** by anodically generated iodine (entry 12). Deviating from the optimal current intensity (either higher or lower) resulted in diminished yields (entries 13 and 14). Furthermore, the reaction exhibited sensitivity to air, as performing it under an ambient atmosphere reduced the yield to 37% (entry 15). Overall, this hydroalkylation system operates under mild, metal-free conditions and eliminates the need for sacrificial reductants or metal anodes, highlighting the advantages of the electrochemical PCET strategy for the reduction of diazo compounds.

Table 1 Optimization of electrochemical reaction conditions[a]



Entry	Variation from standard conditions	Yield (%)
1	None	68[b]
2	w/o electricity	0
3	w/o TFE	34
4	HFIP instead of TFE	27
5	TFA instead of TFE	18
6	MeCN : MeOH = 3 : 1 as solvent	13
7	Acetone : MeOH = 3 : 1 as solvent	36
8	Carbon paper (+) instead of RVC (+)	35
9	Graphite plate (+) instead of RVC (+)	20
10	Graphite felt (−) instead of carbon paper (−)	35
11	RVC (−) instead of carbon paper (−)	15
12	$^nBu_4NI$ instead of Et_4NBF_4	0
13	5 mA, 16 h	44
14	15 mA, 5.4 h	51
15	Air instead of N_2	37

[a] Conditions: **1a** (0.6 mmol, 1.0 equiv.), **2a** (1.8 mmol, 3.0 equiv.), DMA : MeOH = 3 : 1 (6.0 mL), TFE (1.0 mmol), Et_4NBF_4 (0.6 mmol, 0.1 M), Reticulated Vitreous Carbon (RVC, 1.0 × 1.5 × 0.1 cm) as the anode, carbon paper (1.0 × 1.5 × 0.01 cm) as the cathode, constant current = 10 mA, 8 h, under N_2 and in an undivided cell. Yields were determined by ^1H NMR measurement of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. [b] Isolated yield.

With the optimized conditions in hand, we systematically evaluated the substrate scope for the hydroalkylation of alkenes with α-diazo compounds (Fig. 2). A diverse range of monosubstituted styrenes bearing alkyl, halogen, or trifluoromethyl substituents at the *para*-, *meta*-, and *ortho*-positions were efficiently converted into the corresponding products **3a–3m** in moderate to good yields. Notably, the electron-rich 2-methoxy-substituted styrene was well-tolerated despite its susceptibility to anodic oxidation (due to its low oxidation potential), affording **3k** in a moderate yield (40%). Interestingly, replacing TFE with H_2O (40 equiv.) proved beneficial for 4-vinylbiaryl substrates (**1n–1s**), delivering products **3n–3s** in good to excellent yields. In contrast, 2-vinylnaphthalene and disubstituted styrenes exhibited diminished reactivity, furnishing **3t–3w** in 22–67% yields. Heteroaryl alkenes containing thiophene, pyridine, or thiazole rings were also suit-

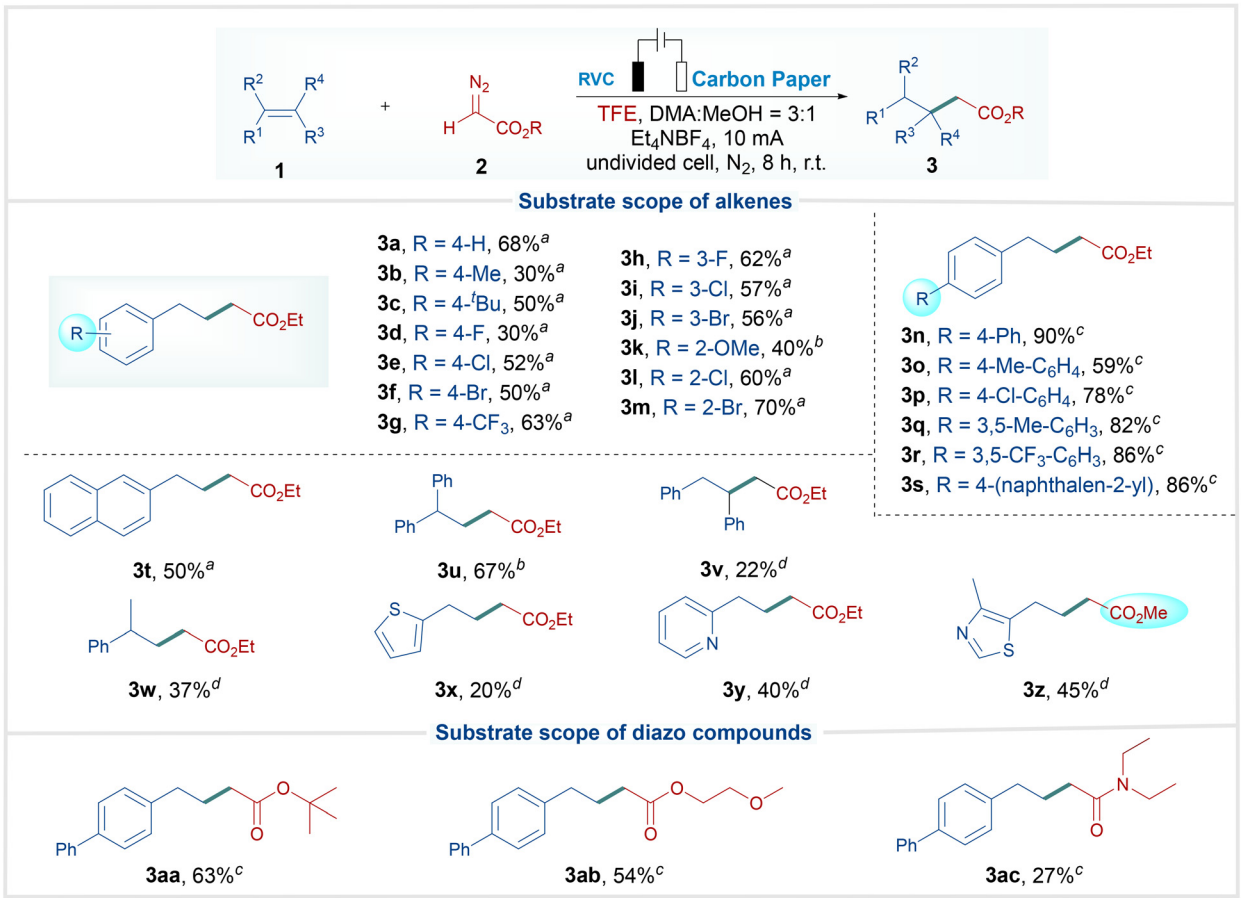


Fig. 2 Substrate scope of alkenes and diazo compounds for the electrochemical hydroalkylation reaction.[a] Undivided cell, **1** (1.0 equiv.), **2** (3.0 equiv.), DMA : MeOH = 3 : 1, TFE (1.0 mmol), Et_4NBF_4 (0.1 M), RVC anode, carbon paper cathode, 10 mA, r.t., N_2, 8 h. [b] Undivided cell, **1** (3.0 equiv.), **2** (1.0 equiv.), $^nBu_4NClO_4$ (0.15 M), DMA : MeOH = 3 : 1, graphite plate anode, carbon paper cathode, r.t., N_2, 10 mA, 2.5 h. [c] Undivided cell, **1** (1.0 equiv.), **2** (8.0 equiv.), H_2O (40 equiv.), $^nBu_4NOAc$ (0.05 M), DMA : MeOH = 3 : 1, foam stainless steel anode, carbon paper cathode, N_2, 5 mA, r.t., 12 h. [d] Undivided cell, **1** (3.0 equiv.), **2** (1.0 equiv.), $^nBu_4NClO_4$ (0.15 M), DMF : MeOH = 3 : 1, Mg plate anode, carbon paper cathode, 10 mA, r.t., N_2, 2.5 h. Isolated yields.

able substrates, affording **3x–3z** in 20–45% yields. Intriguingly, the methyl ester product **3z** was exclusively obtained when 4-methyl-5-vinylthiazole was employed, presumably resulting from a thiazole-mediated transesterification with methanol. The protocol also demonstrated compatibility with α-diazo esters bearing *tert*-butyl or ether groups, affording the corresponding products (**3aa–3ab**) in 54–63% yields, whereas the α-diazo amide substrate delivered **3ac** in 27% yield.

Encouraged by the success of the electrochemical hydroalkylation of alkenes with α-diazo esters, we sought to extend this platform to the more synthetically formidable direct 1,3-carboxylation of olefins using **2a** and CO_2. While the 1,2-dicarboxylation of alkenes to form succinic acid derivatives is well-established,[55–59] the homologous 1,3-carboxylation remains largely unexplored, despite its potential to access valuable structurally diverse acid derivatives. Furthermore, the direct fixation of CO_2 in this transformation not only expands the synthetic utility of diazo compounds but also highlights the capability of electrochemical strategies in sustainable carbon valorization. Mechanistically, we hypothesized that the benzylic anion intermediate, generated *via* cathodic reduction of the benzylic radical, could be selectively intercepted by CO_2 (rather than undergoing protonation). This diversion would enable a three-component dicarboxylation involving olefins, diazo compounds, and CO_2 to afford 1,3-dicarboxylate scaffolds in a one-pot process (Fig. 3).

However, the realization of this transformation faced three critical challenges: (i) the conflicting solvent requirements: efficient CO_2 activation typically demands aprotic conditions, whereas the protonation of diazo compounds requires protic additives, which paradoxically favor the competing hydroalkylation pathway; (ii) the competitive over-reduction of the α-ester-substituted carbon-centered radical, potentially compromising both conversion efficiency and product selectivity; and (iii) the necessity to suppress the known electrochemical dicarboxylation of olefins with CO_2.[55] Gratifyingly, the desired 1,3-carboxylation product **4a** was obtained in 45% yield from 4-phenylstyrene and ethyl diazoacetate using a divided cell equipped with optimized electrodes, employing triethylamine as a sacrificial electron donor in the anode compartment, and

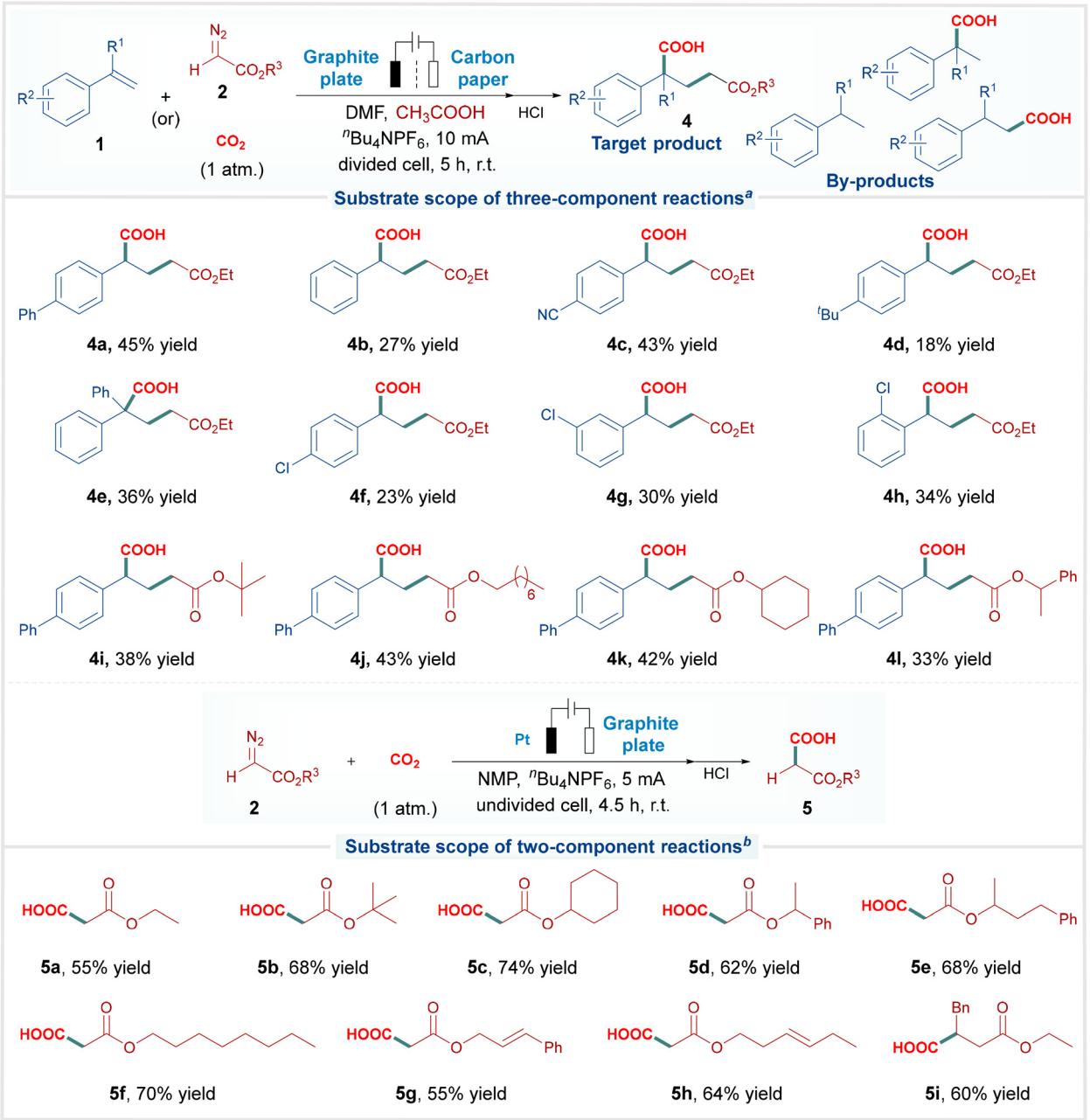


Fig. 3 Substrate generality of two- and three-component electrochemical carboxylation reactions. [a] Divided cell, graphite plate anode, carbon paper cathode, $^{n}Bu_4NPF_6$ (0.2 M), constant current = 10 mA, r.t., 5 h. Cathodic chamber: **1** (0.3 mmol, 1.0 equiv.), **2** : AcOH (1 : 1, 3.0 equiv.), CO_2 (1 atm), DMF (6.0 mL); anodic chamber: Et_3N (1.0 mmol), DMF (6.0 mL). [b] Undivided cell, Pt anode, graphite plate cathode, **2** (0.4 mmol, 1.0 equiv.), CO_2 (1 atm), $^{n}Bu_4NPF_6$ (0.05 M), constant current = 5 mA, r.t., 4.5 h.

a pre-mixed ethyl diazoacetate/acetic acid solution (1 : 1 molar ratio) in the cathode chamber (Fig. 3). The substrate scope of this novel 1,3-carboxylation with α-diazoesters was subsequently evaluated. Styrene afforded product **4a** in a diminished yield of 27%. *para*-Substituted styrenes bearing cyano or *tert*-butyl groups, as well as 1,1-diphenylethylene, yielded products **4b–4e** in 18–43% yields. *ortho*-, *meta*-, and *para*-Chlorostyrenes afforded products **4f–4h** in 23–34% yields. Additionally, α-diazo compounds bearing diverse ester substituents (*e.g.*, *tert*-butyl, octyl, and cyclohexyl) yielded products **4i–4l** in comparable yields, indicating that the steric nature of the ester groups has a negligible impact. It is worth noting that this complex reaction system generated competing byproducts derived from olefin hydroalkylation, hydrocarboxylation, and hydrogenation (Fig. 3), which not only complicates product purification but also contributes to the modest yields obtained. Serendipitously, the isolation of the unexpected product **5a**—formed *via* direct deaminative carboxylation of **2a**

(involving N_2 extrusion and CO_2 capture)—prompted further exploration of this two-component carboxylation. Employing NMP as the solvent in an undivided cell under a CO_2 atmosphere, a variety of oxopropanoic acids (**5a–5i**) were efficiently obtained from mono- and disubstituted diazo compounds in moderate to good yields in the absence of exogenous proton sources. We propose that NMP serves a dual function: it acts as both a sacrificial electron donor (undergoing anodic oxidation) and a proton donor (concomitantly releasing protons) to facilitate the activation of diazo compounds. This self-sufficient dual functionality constitutes a key advantage of the protocol.

Having established protocols for alkene hydroalkylation and 1,3-carboxylation, we subsequently extended this strategy to a multicomponent, electrochemical Minisci-type alkylation reaction involving diazo compounds, alkenes, and heteroarenes. The design hinges on a radical polarity reversal strategy: electrophilic carbon-centered radicals, generated *via* the electrochemical reduction of diazo compounds, undergo addition to olefins. This process generates a nucleophilic alkyl radical intermediate, which is then capable of being trapped by electron-deficient heteroarenes. Subsequent anodic oxidation of the resulting radical intermediates, followed by deprotonation, completes the oxidative aromatization to yield functionalized aromatic hydrocarbons. After systematic optimization, we obtained the three-component adduct **7a** in 56% yield from styrene **1a**, ethyl diazoacetate **2a**, and 1-methylquinoxalin-2(1*H*)-one **6a** in a DMF/MeOH mixture at room

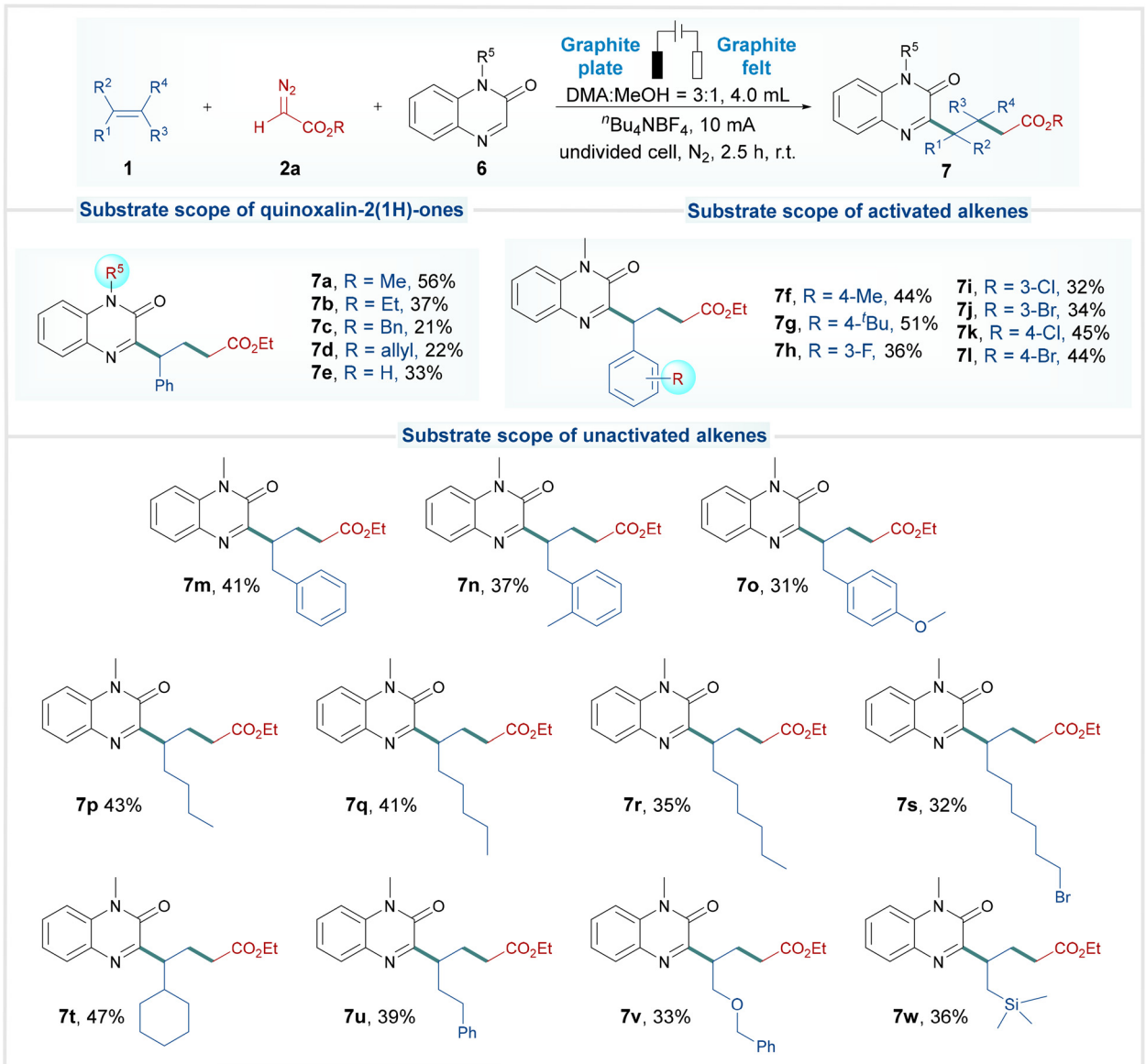


Fig. 4 The substrate scope of the electrochemical redox-neutral multicomponent Minisci-type alkylation reaction. Undivided cell, graphite plate anode, graphite felt cathode, $^nBu_4NBF_4$ (0.1 M), DMA : MeOH (3 : 1, 4.0 mL) as the solvent, 1-methylquinoxalin-2(1*H*)-one **6** (0.2 mmol, 1.0 equiv.), olefin **1** (2.0 equiv.), ethyl diazoacetate **2a** (3.0 equiv.), constant current = 10 mA, N_2, r.t., 2.5 h.

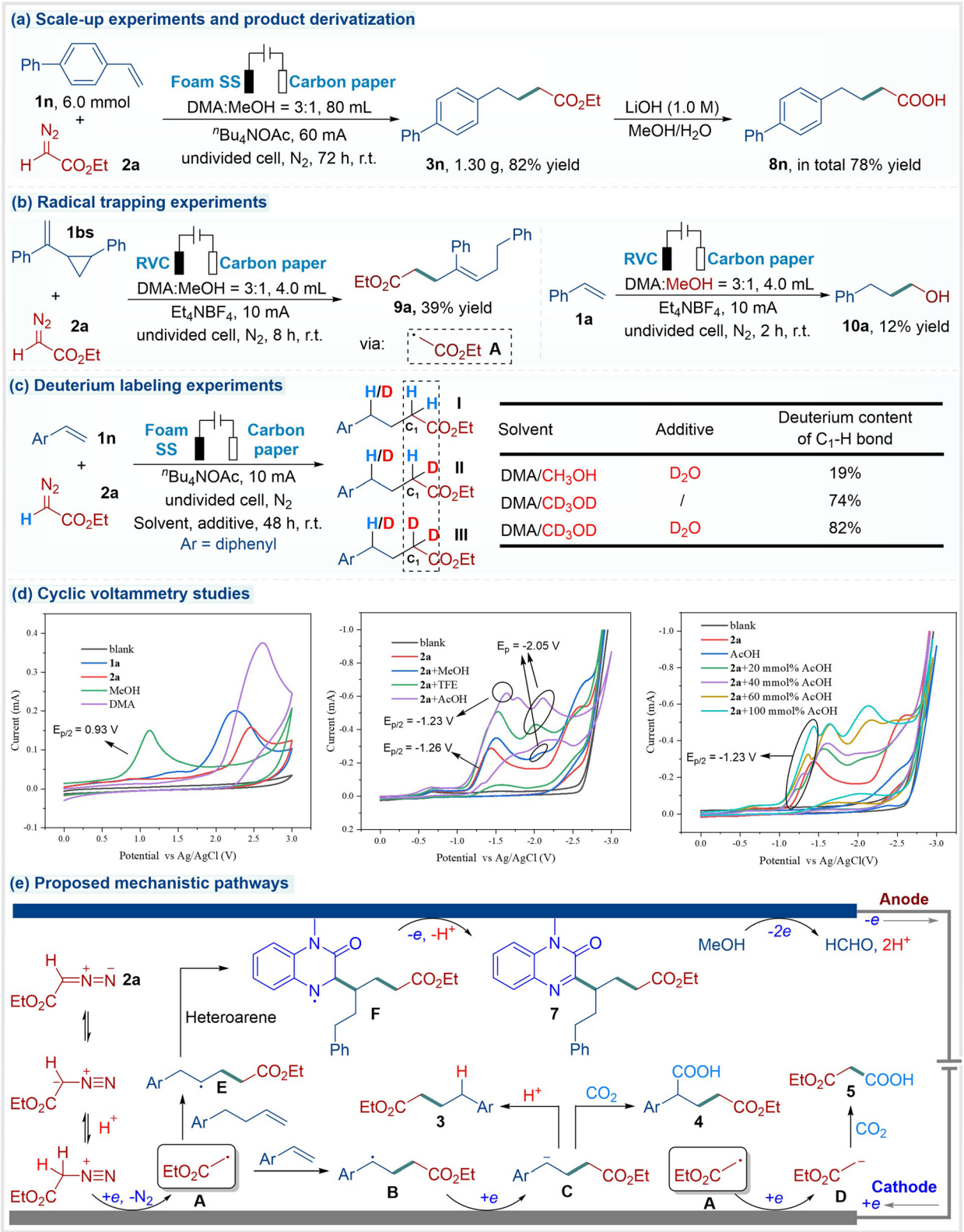


Fig. 5 Mechanistic investigations: (a) gram-scale synthesis; (b) radical trapping experiments; (c) deuterium labeling experiments; (d) cyclic voltammetry studies; (e) proposed mechanistic pathways.

temperature under a constant current of 10 mA, using a graphite plate anode and a graphite felt cathode (Fig. 4). Notably, methanol alone sufficed as the proton source to activate the quinoxalinone or protonate **2a**, obviating the need for external acidic additives. With the optimized conditions established, we explored the substrate scope of this electrocatalytic multicomponent cascade reaction (Fig. 4). Evaluation of various *N*-substituted quinoxalinone derivatives revealed that the methyl-substituent (**6a**) afforded the highest yield (56%), while ethyl, benzyl, and allyl substituents resulted in diminished yields (21–37%). The mild reaction conditions demonstrated broad functional group tolerance, accommodating various substituents on the styrene aryl ring—including fluoro, chloro, bromo, methyl, and *tert*-butyl groups—yielding products **7f–7l** in 32–51% yields. Expanding the scope to unactivated alkenes, allylbenzene underwent successful transformation to form adduct **7m** in moderate yield. Electron-donating groups such as methyl and methoxy on the phenyl ring of allylbenzene exerted minimal impact on reactivity, with products **7n** and **7o** obtained in 37% and 31% yields, respectively. In addition, aliphatic alkenes bearing various alkyl chains, including sensitive ether and silane substituents, were also compatible, affording products **7p–7w** in 32–47% yields.

Mechanistic studies

To demonstrate the scalability and synthetic potential of our protocol, the hydroalkylation of **1n** with **2a** was conducted on a gram scale (6.0 mmol), affording product **3n** in 82% isolated yield (Fig. 5a). Subsequent hydrolysis of **3n** with LiOH in a MeOH/H_2O mixture furnished the corresponding monocarboxylic acid **8n** in 78% yield (over two steps), further underscoring the method's practical utility. To gain deeper mechanistic insights, a radical clock experiment employing 1bs and **2a** yielded the ring-opened product **9a**. This result corroborates the involvement of the key radical intermediate **A** and confirms the cathodic generation of the α-ester-substituted carbon-centered radical from ethyl diazoacetate (Fig. 5b). Separately, subjecting styrene (**1a**) to standard conditions in the absence of **2a** afforded product **10a** in 12% yield. This suggests the *in situ* generation of formaldehyde *via* the anodic oxidation of MeOH—a process that concurrently supplies both electrons and protons for the reaction, thereby accounting for the efficient transformation in the DMF/MeOH mixture without additional sacrificial reducing agents. Deuterium-labeling experiments were conducted to elucidate the proton source for ethyl diazoacetate activation and evaluate the relative contributions of MeOH and H_2O (Fig. 5c). ^{1}H NMR analysis revealed that the use of MeOH/D_2O resulted in 19% deuterium incorporation at the α-position. In contrast, the exclusive use of CD_3OD increased this value to 74%, and combining CD_3OD and D_2O further elevated it to 82%. These results confirm that while both MeOH and H_2O can act as proton sources, MeOH serves as the primary proton donor in this system. Cyclic voltammetry (CV) experiments revealed that MeOH exhibits a lower oxidation potential ($E_{p/2}$ = 0.93 V *vs.* Ag/AgCl) compared to styrene (**1a**, 1.95 V), ethyl diazoacetate (**2a**, 2.22 V), and DMF (2.26 V), substantiating its role as the anodic electron donor (Fig. 5d, left). Regarding the cathodic process, **2a** exhibited a distinct reduction peak at −1.26 V. The addition of MeOH or TFE significantly enhanced the reduction current, indicating that protonation facilitates the reduction of ethyl diazoacetate (Fig. 5d, middle). Introduction of acetic acid (AcOH), a stronger acid, resulted in a further current increase and the emergence of a new reduction peak at −1.23 V. Crucially, an additional peak around −2.05 V—observed in the presence of MeOH, TFE, or AcOH—is indicative of the over-reduction of radical species **A**. Concentration-dependent CV studies using AcOH (Fig. 5d, right) further validated its role in activating **2a** *via* protonation, as peak currents increased proportionally with acid concentration.

Based on above results and previous reports,[35] we propose a plausible reaction mechanism (Fig. 5e). The reaction initiates with the protonation of **2a**, which exists in equilibrium with its protonated form in the presence of a proton donor. At the cathode, the protonated species undergoes single-electron reduction concomitant with N_2 extrusion, forming the key electron-deficient radical **A**. Radical **A** adds to styrene (**1a**) to generate benzylic radical intermediate **B**, which is further reduced to yield carbanion intermediate **C**. Intermediate **C** can either undergo protonation to yield the hydroalkylation product **3** or be intercepted by CO_2 to afford the dicarboxylated product **4**. Alternatively, radical **A** can undergo direct cathodic reduction to form anion **D**, which affords the monocarboxylate product **5** following CO_2 capture. Throughout these transformations, the anodic oxidation of methanol plays a pivotal role by furnishing both electrons and protons. This process not only facilitates the activation of diazo compounds but also sustains the acid–base equilibrium and charge neutrality of the system. In the redox-neutral Minisci manifold, the electrophilic radical **A** exhibits distinct chemoselectivity, preferentially adding to the alkene rather than reacting with the electron-deficient heteroarene. This addition generates the nucleophilic alkyl radical **E**. Subsequent interception of radical **E** by the heteroarene forms radical **F**, which undergoes anodic oxidation and aromatization to yield the final three-component coupling product **7**.

Conclusions

In summary, we have established an efficient and mild electrochemical protocol for the reduction of diazo compounds *via* a proton-coupled electron transfer (PCET) strategy. This platform unlocks access to electrophilic radicals from diazo compounds, facilitating diverse transformations, including olefin hydroalkylation, two- or three-component carboxylation with CO_2, and redox-neutral three-component Minisci alkylation reactions. Distinguishing features of this strategy include its operational simplicity, broad functional group tolerance, and superior sustainability, as it obviates the need for stoichiometric metal reductants. Mechanistic investigations elucidate

that the anodic oxidation of methanol synergistically supplies both the electrons and protons necessary for the activation of diazo compounds, highlighting the atom-economic nature of our approach. Collectively, these findings underscore the cost-effectiveness, sustainability, and practicality of the strategy, paving the way for the expanded electrochemical application of diazo compounds and substantially broadening their synthetic repertoire.

Author contributions

D. Zhang and J. Wu conceived the idea for this work and designed the experiments. Y. Min, L. Wang, H.-Y. Sun, and D. Zhang performed and analyzed the experiments. D. Zhang, P. O'Neill, Srinivas Reddy Dubbaka and J. Wu supervised the entire project. J. Wu, D. Zhang, Hwee Ting Ang discussed the results and wrote the manuscript.

Conflicts of interest

The authors declare that they have no conflict of interest.

Data availability

The data Experimental procedures, full spectroscopic data for all new compounds, and copies of ^{1}H and ^{13}C NMR spectra that support the findings of this study are available in the supplementary information (SI) of this article. Supplementary information is available. See DOI: https://doi.org/10.1039/d6gc01103a.

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