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Solvent-Controlled Electrochemical Cyclization of Areneazo-2-(2-nitro)propanes to Benzo[c]cinnolines

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ABSTRACT

Modulating the redox potential of organic substrates is a powerful strategy for steering electrochemical reaction pathways, particularly for systems capable of undergoing both oxidation and reduction. Herein, we report the first electrochemical cyclization of areneazo-2-(2-nitro)propanes to benzo[c]cinnolines enabled by solvent-mediated redox pathway control. Careful selection of the reaction medium, especially mixed solvent systems containing hexafluoroisopropanol (HFIP) and alcohol additives, not only widens the redox potential gap between oxidation and reduction events but also stabilizes key intermediates through hydrogen-bonding interactions, thereby favoring oxidative intramolecular cyclization over competing denitrogenative reduction pathways. Cyclic voltammetry reveals a clear correlation between solvent-dependent redox windows and reaction outcomes, underscoring the decisive role of solvent effects in governing electrochemical selectivity. Under optimized constant current conditions using graphite electrodes, a broad range of areneazo-2-(2-nitro)propanes undergo efficient cyclization to afford benzo[c]cinnolines in good yields. Mechanistic studies support a pathway involving MeOH-stabilized diazonium intermediates and controlled redox fragmentation, demonstrating how strategic solvent engineering can unlock new electrochemical transformations of redox-active organic substrates.

1 | Introduction

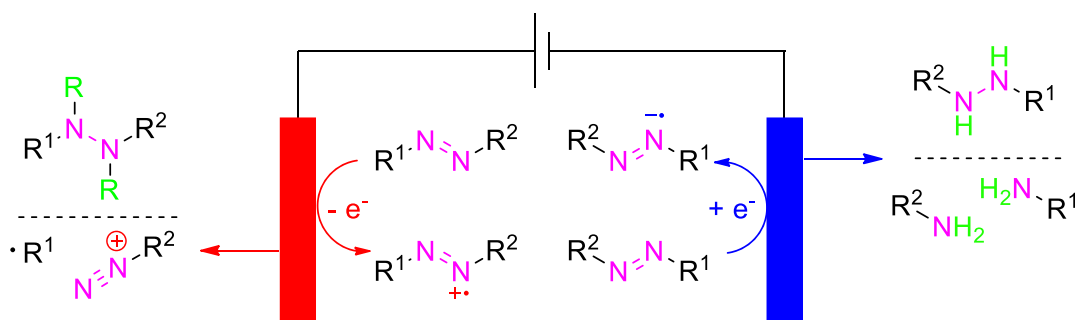
The ability to modulate the redox potential of organic substrates is a powerful strategy for steering the outcome of electrochemical transformations [1–3]. This is especially important for compounds capable of undergoing both oxidative and reductive processes, where closely spaced redox potential windows allow access to multiple competing pathways. A critical yet often underappreciated factor in this control is the choice of reaction solvent [4], which influences not only solubility and nucleophilicity but also the thermodynamics and kinetics of electron transfer. Among these, the distinction between protic and aprotic solvents has emerged as a key parameter in governing reaction selectivity for substrates with multiple redox-active sites or accessible oxidation states [5–8]. In particular, fluorinated protic solvents can stabilize charged intermediates via hydrogen bonding and solvation, effectively shifting

redox potentials and enabling or suppressing specific mechanistic pathways [9, 10]. While this concept of redox modulation applies broadly to various redox-active organic systems, azo compounds can offer a clear and illustrative case study, engaging in both oxidative and reductive electrochemical reactions [11], each with multiple possible outcomes (Scheme 1a). Upon reduction, the azo group may undergo sequential one- or two-electron transfer to yield hydrazines or cleaved amine products, while oxidation can produce radical cations, leading to diazonium ion or N-centered radical coupling. Building on the premise that the dominant electrochemical pathway is fundamentally governed by the redox potential of the substrate [12, 13], the choice of solvent emerged as a strategic lever for modulating the electrochemical redox behavior of azo compounds and, ultimately, for optimizing the preferential reductive or oxidative pathway. Areneazo-2-(2-nitro)propanes

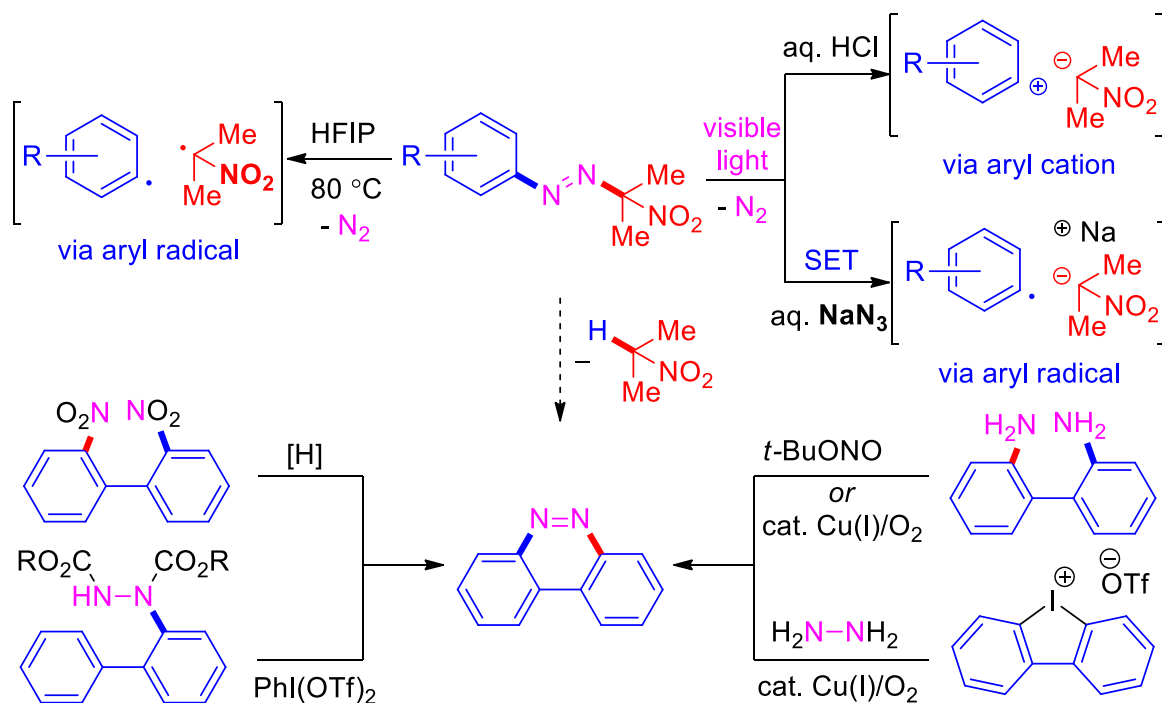
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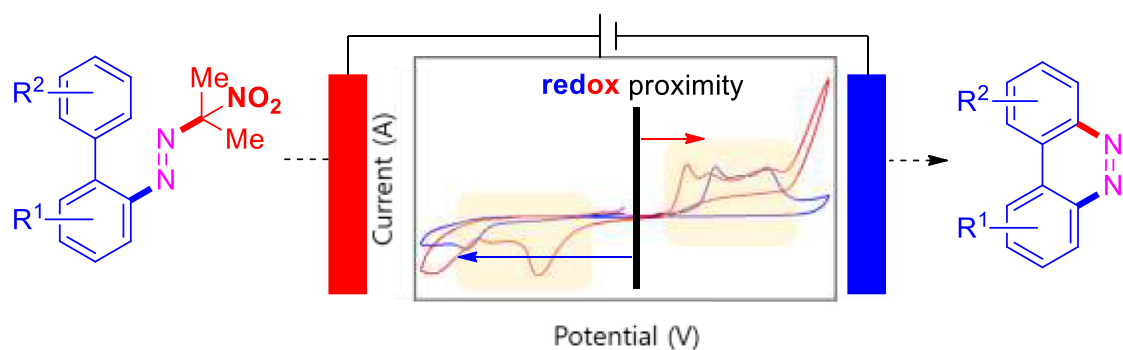
(a) Electrochemical Reductive and Oxidative Reaction Pathways of Azo Compounds



(b) Photochemical and Thermal Fragmentation Pathways of Areneazo-2-(2-nitro)propanes



(c) Proposed Electrochemical Cyclization *via* Solvent-Mediated Oxidative Pathway



SCHEME 1 | Reductive and oxidative pathway of azo compounds and proposed solvent-mediated oxidative pathway of areneazo-2-(2-nitro)propanes.

serve as safer and more stable alternatives to diazonium salts without impact sensitivity or explosive propagation behavior [14], readily undergoing radical fragmentation under photochemical [15, 16] and thermal [17] conditions (Scheme 1b). Given the proximity of their redox potentials, we envisioned that solvent-mediated redox pathways could enable the electrochemical

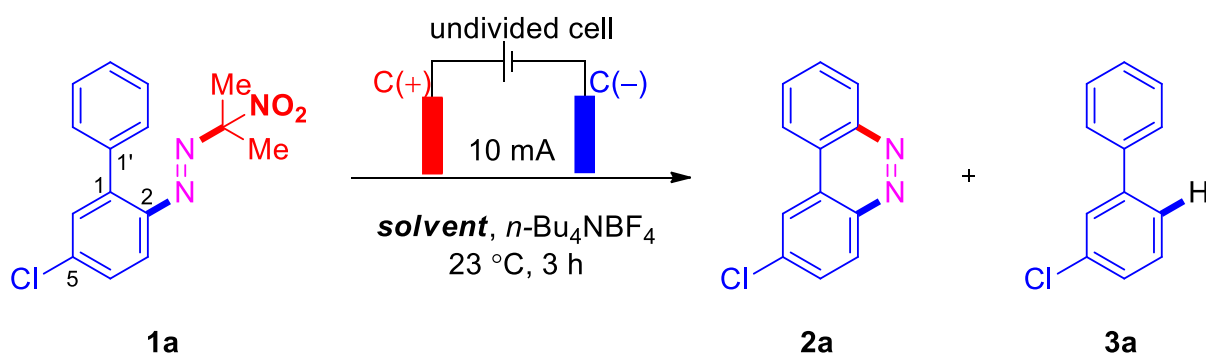
cyclization of areneazo-2-(2-nitro)propanes to yield benzo[c]cinoline derivatives, emerging redox catalysts [18, 19] and promoters [20–22]. While previous synthetic approaches to benzo[c]cinnolines relied on the reductive coupling of 2,2'-dinitro-1,1'-biaryls [23–25], the oxidative cyclization of biphenylhydrazine-1,2-dicarboxylates using $\text{PhI}(\text{OTf})_2$ [26, 27], the oxidative

dehydrogenative coupling of 1,1'-biphenyl-2,2'-diamines [28, 29], the Cu-catalyzed tandem dual C–N coupling between hydrazines and cyclic diphenyliodonium salts [30–32], Rh-catalyzed C–H activation strategies toward cinnoline frameworks [33–35], no electrochemical strategy has yet been reported [36]. Herein, we report the first electrochemical cyclization of areneazo-2-(2-nitro)propanes to benzo[c]cinnolines, where careful modulation of redox windows under different reaction media directed the oxidative intramolecular cyclization pathway (Scheme 1c). The relevance and significance of electrochemical solvent systems in modulating the redox pathways of areneazo-2-(2-nitro)propanes were supported by cyclic voltammetric analysis [37, 38], mechanistic studies, and correlations between solvent environment and product outcomes. These findings highlighted how solvent engineering could be strategically employed to control the redox pathways and direct complex organic transformations.

2 | Results and Discussion

The electrochemical cyclization of areneazo-2-(2-nitro)propanes to benzo[c]cinnolines was investigated under a constant current of 10 mA, using *n*-Bu₄NBF₄ as the electrolyte and graphite carbon electrodes as both the anode and cathode (Table 1). Initially, 5-chloro-1,1'-diphenyldiazene **1a** was selected as a model substrate, exhibiting a half-peak oxidation potential ($E^{\text{ox}}_{\text{p/2}}$) of 1.63 V versus Ag/AgNO₃ and a half-peak reduction potential ($E^{\text{red}}_{\text{p/2}}$) of –1.81 V versus Ag/AgNO₃, as determined by cyclic voltammetry. The solvent window of **1a** was evaluated using various solvents with high oxidation potentials (entries 1–4) and a strong reduction potential (entry 5) [39]. Electrochemical cyclization of **1a** to the desired benzo[c]cinnoline **2a** proceeded in CH₂Cl₂ and MeOH, yielding **2a** in 3% and 10%, respectively. However, across all tested solvents (entries 1–5), the reaction

TABLE 1 | Optimization of electrochemical cyclization of areneazo-2-(2-nitro)propane.



Entry ^a	Solvent system	Variations	Yield, % ^b 2a/3a
1	CH ₂ Cl ₂	—	3/33
2	CH ₃ CN	2 h	0/6
3	MeOH	4 h	10/26
4	HFIP	1 h	0/10
5	DMSO	2 h	0/26
6	CH ₂ Cl ₂ /HFIP (3:3)	2 h	20/18
7	CH ₃ CN/HFIP (3:3)	—	62/0
8	DMSO/HFIP (3:3)	—	0/20
9	CH ₃ CN/HFIP (5:1)	—	54/0
10	CH ₂ Cl ₂ /HFIP (4:1)	—	50/13
11	CH ₂ Cl ₂ /HFIP (5:1)	—	73/0
12	CH ₂ Cl ₂ /MeOH (5:1)	6 h	26/11
13	CH ₂ Cl ₂ /HFIP (5:1)	5 mA, 5 h	64/trace
14	CH ₂ Cl ₂ /HFIP (5:1)	Ni(–)	66/0
15	CH ₂ Cl ₂ /HFIP (5:1)	Zn(–)	47/10
16	CH ₂ Cl ₂ /HFIP (5:1)	0.1 mL MeOH	73/12
17	CH ₂ Cl ₂ /HFIP (5:1)	0.1 mL EtOH	69/trace
18	CH ₂ Cl ₂ /HFIP (5:1)	0.1 mL <i>i</i> -PrOH	50/30
19	CH ₂ Cl ₂ /HFIP (5:1)	0.1 mL <i>t</i> -BuOH	56/trace
20	CH ₂ Cl ₂ /HFIP (5:1)	0.2 mL MeOH	54/20

^aReaction conditions: **1a** (0.3 mmol) and *n*-Bu₄NBF₄ (0.3 mmol) in solvent (0.05 M) using graphite carbons at 23°C for 3 h.

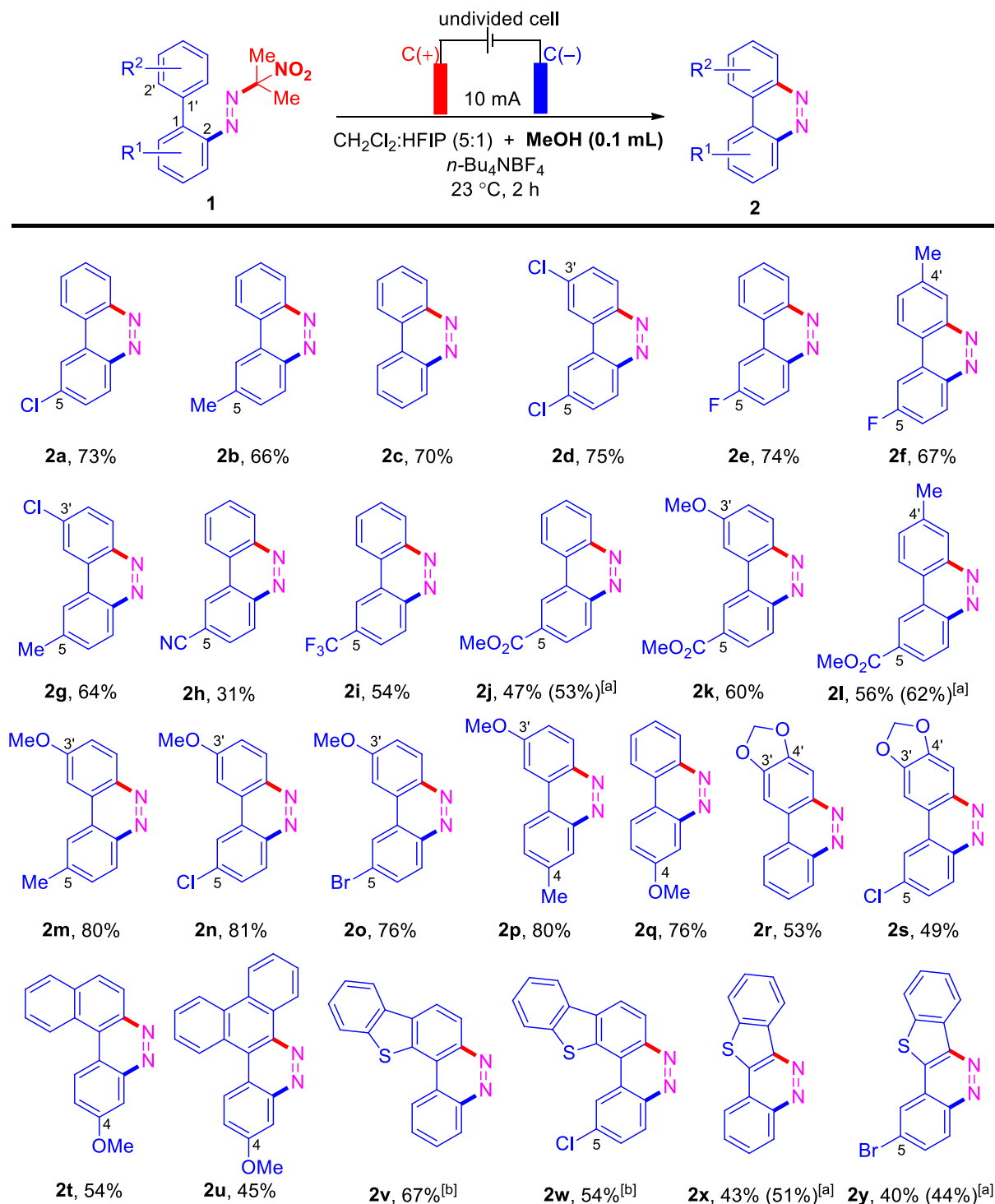
^bYields based on ¹H NMR using internal standard, CH₂Br₂.

preferentially afforded the denitrogenative reduction product **3a**. This prompted the exploration of mixed solvent systems, which led to the identification of CH₃CN/HFIP and CH₂Cl₂/HFIP mixtures (entries 6–8). Notably, the CH₃CN/HFIP system improved the yield of **2a** to 62% without the formation of **3a** (entry 7). Further tuning of solvent ratios identified a 5:1 mixture of CH₂Cl₂ and HFIP as optimal (entries 9–11), giving **2a** in 73% yield. A control experiment using MeOH instead of HFIP confirmed the crucial role of HFIP in the electrochemical pathway (entry 12). Reducing the applied current to 5 mA led to a slight decrease in product yield (entry 13), whereas replacing the graphite cathode with metallic alternatives such as Ni(–) or Zn(–) resulted in decreased yields of 47%–66% (entries 14–15). The optimized electrochemical conditions were further evaluated by incorporating alcohol additives (entries 16–19). The addition of 1–2 vol% MeOH was found to be broadly beneficial; however, increasing the MeOH content beyond 2 vol% promoted the formation of the reduced product **3a** and resulted in a decreased yield of **2a** to 54% (entry 20).

With the optimized conditions for the electrochemical cyclization of areneazo-2-(2-nitro)propanes to benzo[*c*]cinnolines in hand, the substrate scope of areneazo-2-(2-nitro)propanes was investigated (Scheme 2). Under standard conditions in CH₃CN, the half-peak oxidation potentials ($E_{p/2}^{\text{ox}}$) and half-peak reduction potentials ($E_{p/2}^{\text{red}}$) of areneazo-2-(2-nitro)propanes were found to be closely aligned with only different signs. However, the optimized electrochemical conditions with MeOH as an additive revealed more pronounced potential gaps between $E_{p/2}^{\text{ox}}$ and $E_{p/2}^{\text{red}}$, which significantly influenced cyclization efficiency. For example, 5-methyl-1,1'-diphenyldiazene **1b** underwent smooth cyclization to give benzo[*c*]cinnoline **2b** in 53% yield under MeOH-free conditions, while the presence of 1 vol% MeOH improved the yield to 66%. Similarly, unsubstituted 1,1'-diphenyldiazene **1c** gave **2c** in 70% yield with MeOH additive, compared to 50% without MeOH additive. Thus, the MeOH additive markedly improved the yields of **2** across the substrate scope; for example, 3',5'-dichloro-1,1'-diphenyldiazene **1d** afforded **2d** in 75% yield, underscoring the importance of achieving sufficient redox potential separation (See the Supporting Information for detail). This correlation between redox potential gaps and reaction efficiency guided the further exploration of substrates. Substrates bearing fluorine **1e–1f**, chlorine **1g**, strong electron-withdrawing groups such as nitrile **1h** and trifluoromethyl **1i**, and ester groups **1j–1l** were well tolerated, delivering the corresponding benzo[*c*]cinnolines **2e–2j** in moderate to good yields. Methoxy-substituted substrates showed minor reduction peaks, yet still afforded products **2m–2p** in 76%–81% yields. The method proved effective for a wide range of areneazo-2-(2-nitro)propanes, including those with electronically different substitution patterns **1q–1s**. More complex aromatic frameworks such as naphthyl **1t**, phenanthrenyl **1u**, dibenzothiophenyl **1v–1w**, and benzothiophenyl **1x–1y** were also successfully incorporated, furnishing the corresponding benzo[*c*]cinnoline products **2t–2y** in 43%–67% yields. Once again, the presence of MeOH additive played a critical role in promoting efficient electrochemical cyclization across this broad substrate scope.

As shown in our optimization studies, a larger difference between the absolute redox potentials preferentially leads to the formation of **2a**. In CH₃CN, product **2a** was not formed, and significant decomposition of **1a** was observed. Considering that **2a** remained

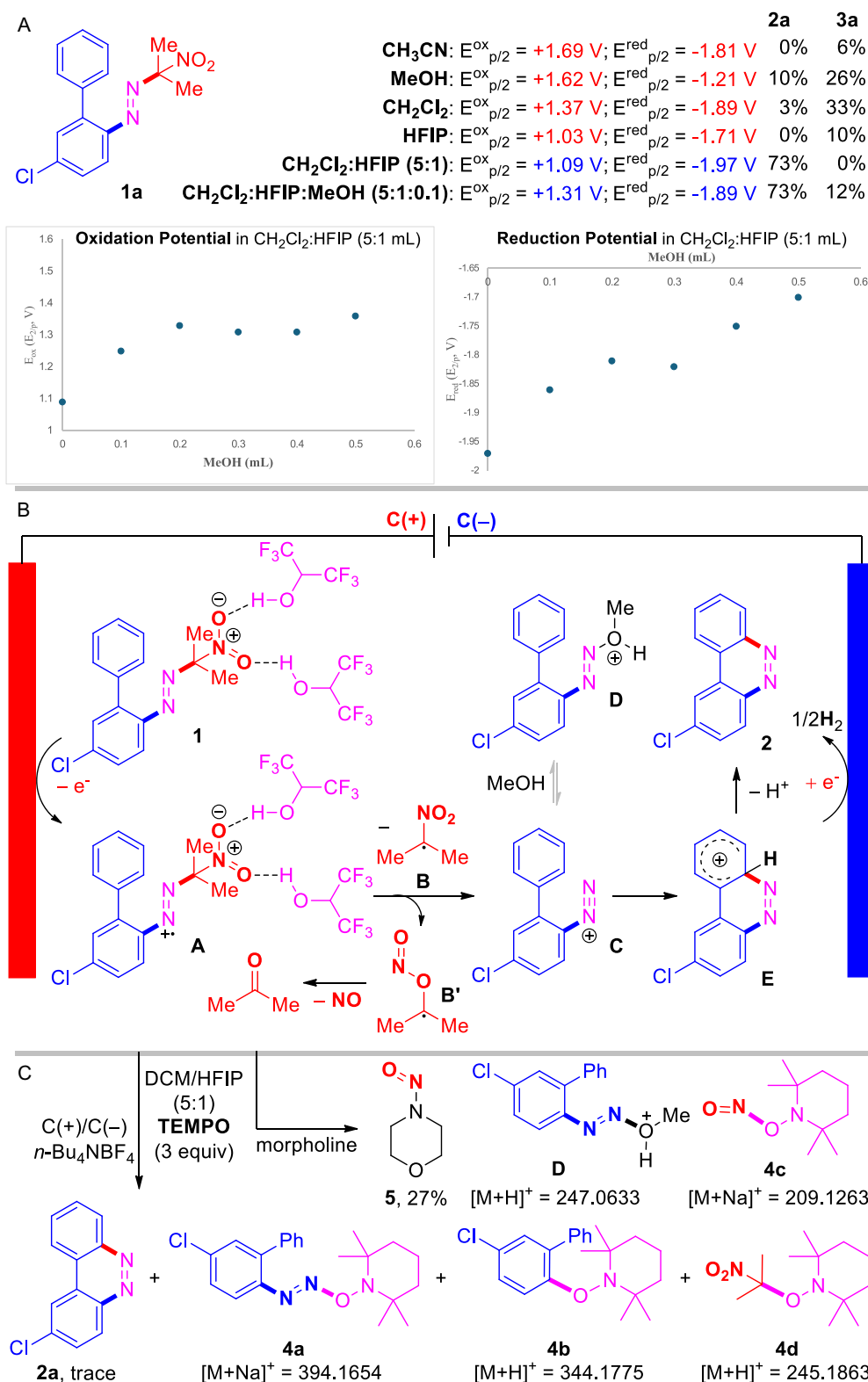
86% intact over 30 min under the CH₃CN reaction conditions (see the Supporting Information), this decomposition was most likely due to reduction of **1a** at the cathode rather than decomposition of **2a** formed by oxidation at the anode. When the solvent was changed to CH₂Cl₂, which has a lower oxidation potential, substrate oxidation was confirmed, resulting in the formation of over 30% of **2a** and **3a**. However, because CH₂Cl₂ exhibits a reduction potential similar to CH₃CN, cathodic decomposition of **1a** still occurred. These observations indicate that improving the product yield requires lowering the oxidation potential of the substrate (approaching 0 V) while shifting the reduction potential to more negative values to prevent cathodic decomposition. In other words, a strategy that increases the redox potential gap, the difference between the anodic and cathodic processes, is essential. The influence of redox potential gaps was examined further using 5-chloro-1,1'-diphenyldiazene **1a** in various solvents (Scheme 3A). Smaller redox gaps were observed in CH₃CN (~0.12 V) and MeOH (~0.41 V), where the substrate decomposition predominated. In CH₃CN, only a small amount of the reduction product **3a** (6%) was obtained, while in MeOH, **2a** and **3a** were formed in 10% and 26% yields, respectively. Although CH₂Cl₂ offered a slightly wider redox gap (~0.52 V), **2a** was formed in only 3% yield, while **3a** was obtained in 33% yield. The measured redox gap in HFIP was about 0.68 V, the $E_{p/2}^{\text{red}}$ peak showed another broad peak at around –0.71 V, thus the redox gap in HFIP may be less than 0.68 V, thus leading to a mere reduction product **3a** in 10% yield. A more pronounced gap (0.88 V) was observed in a CH₂Cl₂/HFIP (5:1) mixture, delivering **2a** exclusively in 73% yield. When 1.7 vol% of MeOH was added to this mixture, the redox gap narrowed to 0.58 V, yet **2a** was still formed in 73% yield, along with 12% of **3a**. These results suggested that while large redox gaps promoted the benzo[*c*]cinnoline formation, the additive, MeOH, might play an additional role in stabilizing reactive intermediates [40, 41]. Notably, increasing the amount of MeOH additive in the CH₂Cl₂/HFIP (5:1) solvent mixture significantly shifted the redox potentials of **1a**, with the $E_{p/2}^{\text{ox}}$ increasing from 1.09 to 1.36 V and the $E_{p/2}^{\text{red}}$ shifting from –1.97 to –1.70 V. While the electrochemical cyclization behaviors of areneazo-2-(2-nitro)propanes are consistent with our potential gap theory, several substrates (**1e**, **1r**, **1x**) under CH₂Cl₂/HFIP with a MeOH additive exhibited higher reaction efficiencies compared to those in CH₃CN, despite similar or even smaller potential gaps. This discrepancy likely indicates that both redox potential modulation and intermediate stabilization cooperatively contribute to productive electrocyclization, highlighting the dual role of MeOH. While MeOH may slightly lower both oxidation and reduction potentials, it simultaneously stabilizes the diazonium intermediate and/or mitigates solvent-derived proton reduction at the cathode, thereby facilitating a more efficient overall redox process. In contrast, under CH₂Cl₂/HFIP without MeOH, all substrates showed higher efficiencies only when larger potential gaps were observed compared to the CH₃CN condition. It should be noted that areneazo-2-(2-nitro)propanes are capable of undergoing both oxidation and reduction, which can lead to the misassignment of a reduction peak when the scan is initiated in the positive direction. This peak does not correspond to the intact substrate, but rather to a species formed through substrate oxidation followed by fragmentation. Notably, this peak is absent when the scan begins in the negative direction, allowing for accurate determination of the true reduction potential of the intact substrate. Based on these data, a plausible electrochemical cyclization mechanism is proposed (Scheme 3B). A hydrogen-bonding



SCHEME 2 | Substrates scope of electrochemical cyclization of areneazo-2-(2-nitro)propanes ([a] without MeOH. [b] 5 mA for 5 h).

interaction between HFIP and the nitro group of the areneazo-2-(2-nitro)propane facilitates the formation of radical cation **A**, which fragments into the 2-nitropropyl radical **B** and the diazonium species **C** [17]. As previously reported [14–17], the 2-nitropropyl radical **B** undergoes *nitro-to-nitrite* rearrangement, ultimately forming acetone and nitric oxide via fragmentation of the isopropyl nitrite radical **B'**. The diazonium species **C** can be stabilized by MeOH to form **D** [42, 43], but MeOH can also promote reduction to **3a** [44]. The stabilizing effect of MeOH has proven essential for some substrates; for instance, no product was obtained from **1r** and **1s** in its

absence. The combination of a widened redox potential gap and MeOH-mediated stabilization of **C** enables intramolecular cyclization to benzo[*c*]cinnolines via intermediate **E**, with H^+ reduction to H_2 completing the redox cycle. The hydrogen-bonding interaction between HFIP and the nitro group of **1a** is supported by ^1H and ^{19}F NMR spectroscopic analyses performed at varying ratios of **1a** and HFIP (see the Supporting Information for details). Additional mechanistic support was provided by NMR detection of acetone and radical inhibition/capture experiments using TEMPO, where the proposed intermediate **D** (in the presence of MeOH), azo



SCHEME 3 | Cyclic voltammetry studies and proposed mechanism for electrochemical cyclization of areneazo-2-(2-nitro)propanes.

radical species **4a**, dediazotized aryl radical **4b**, transient NO radical **4c**, and nitroalkyl radical **4d** were detected by HRMS analysis (Scheme 3C). In addition, the presence of NO was also confirmed by the formation of N-nitrosomorpholine **5** from morpholine under electrochemical reaction conditions. While the stoichiometric generation of NO gas could raise safety concerns, its rapid oxidation in air (to NO₂) and subsequent reaction with moisture (to

HNO₂/HNO₃) make the accumulation of toxic gaseous species during the reaction unlikely. Under our electrochemical conditions, NO_x species are further expected to undergo facile redox processes, forming HNO at the anode and N₂O at the cathode; thus, direct release of hazardous levels of NO is not anticipated. If the formation of other potentially toxic species, such as NO₂ under O₂ and electrochemical conditions, remains a concern, the reaction can

readily be conducted under an argon atmosphere in comparable yields. Notably, comparable yields are obtained under both argon and air conditions. The calculated Faraday efficiency of the current electrochemical reaction remained around 20%, likely due to multiple redox side reactions involving aryl radicals and NO species, as well as electrochemical decomposition pathways of the benzo[*c*]cinnoline derivatives (see Supporting Information for details). It should be noted that these mechanistic findings highlight the critical roles of solvent composition, redox potential modulation, and MeOH additives in governing the electrochemical reactivity of areneazo-2-(2-nitro)propanes. Thus, the MeOH additive modulates the redox gap of the system and can also function as a proton (or hydrogen) donor under the electrochemical conditions (Table 1, entry 16). Consistent with this interpretation, the use of other alcohol additives, particularly *i*-PrOH, more strongly promoted the reductive pathway leading to byproduct **3a** (entry 18), supporting the involvement of proton/hydrogen transfer processes. In addition to possible protonation effects, HRMS analysis of the reaction mixture provided evidence that MeOH participates in stabilizing reactive intermediates through nucleophilic trapping of the diazonium species **C**. These observations suggest that the promotional effect of MeOH likely arises from a combination of roles, including modulation of redox properties, proton donation, and intermediate stabilization, rather than from protonation-facilitated cyclization alone. While solvent effects are central to tuning reactivity, they alone cannot fully account for the observed solvent-dependent outcomes, as certain media lead predominantly to substrate decomposition rather than productive cyclization. Given that these substrates can undergo both oxidation and reduction, enforcing pathway selectivity requires strategies that widen the redox potential gap while stabilizing key intermediates, likely through hydrogen-bonding interactions.

3 | Conclusion

In summary, we have developed an electrochemical cyclization of areneazo-2-(2-nitro)propanes to benzo[*c*]cinnolines through a solvent-controlled oxidative pathway. Using graphite electrodes and *n*-Bu₄NBF₄ as the electrolyte under constant current, we demonstrated the critical role of redox potential gaps between oxidation and reduction half-peaks ($E_{p/2}^{ox}$ and $E_{p/2}^{red}$), which are effectively modulated by solvent systems and MeOH additives. Given the growing interest in redox-guided electrochemical construction of heterocycles, our approach, guided by cyclic voltammetry, offers a systematic framework for tuning oxidative and reductive electrochemical pathways. Ongoing studies are focused on applying this solvent-mediated redox pathway control to other redox-active organic scaffolds, and the results will be reported in due course.

4 | Experimental Section

4.1 | General Procedure for Electrochemical Cyclization of Areneazo-2-(2-nitro)propanes to Benzo[*c*]cinnolines

Electrochemical reactions were carried out using an IKA ElectraSyn 2.0. Compound **1** (0.30 mmol), tetrabutylammonium tetrafluoroborate (0.30 mmol), and 6 mL of a DCM/HFIP mixture

(5:1, 0.05 M) were added to a 10 mL undivided IKA vial. The electrochemical cell was equipped with a graphite working electrode (WE) and a graphite counter electrode (CE), and a constant current of 10 mA was applied for 2–4 h. Upon the reaction completion, the mixture was concentrated in vacuo and purified by column chromatography on silica gel using EtOAc in hexanes to give the desired product **2a–2y**. The same procedure was performed in a separate setup except for the addition of MeOH (0.1 mL). The reaction without MeOH was designated as condition **A**, and the reaction with MeOH (0.1 mL) as condition **B**.

4.2 | 2-Chlorobenzo[*c*]cinnoline (**2a**)

The compound was synthesized by using **1a** with a reaction time of 3 h. The product was isolated by silica gel flash column chromatography using ethyl acetate/hexanes (1:4) eluent. Yellow solid; m.p.: 214–215°C; (**A**): 47.0 mg (73%), (**B**): 47.2 mg (73%). ¹H NMR and ¹³C NMR spectra for this compound were consistent with previously reported literature data [28] ¹H NMR (600 MHz, CDCl₃): δ 8.73–8.71 (m, 1H), 8.65 (d, *J* = 8.4 Hz, 1H), 8.48 (d, *J* = 1.8 Hz, 1H), 8.45–8.44 (m, 1H), 7.93–7.89 (m, 2H), 7.81 (dd, *J* = 9.0, 1.8 Hz, 1H); ¹³C NMR (150 MHz, CDCl₃): δ 145.3, 143.6, 138.0, 133.0, 131.9, 131.4, 130.1, 130.0, 122.1, 121.4, 121.1, 119.8.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data underlying this study are available in the published article and its online supplementary material.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.