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Letter

Electrocatalytic Synthesis of Aryl-Propargyl Alcohols from Arylacetylenes with *N*,*N*-Dimethylacetamide and Water

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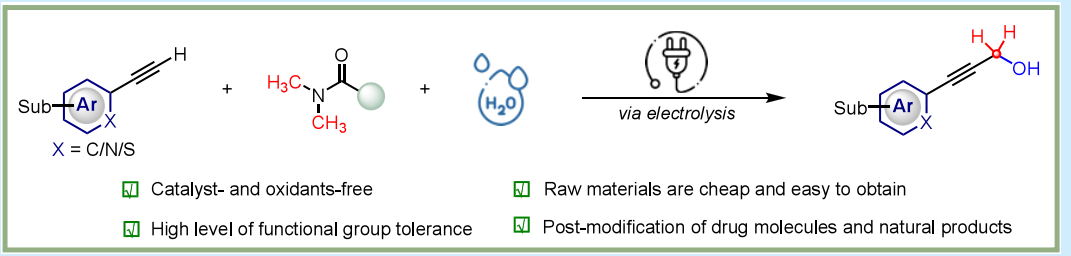

ABSTRACT: Propargyl alcohols serve as important building blocks in pharmaceuticals and materials science, yet their traditional synthesis often involves hazardous reagents and produces significant waste. Herein, we present an electrochemical hydroxymethylation of arylacetylenes that enables the direct and efficient synthesis of aryl-propargyl alcohols under mild conditions. This protocol uniquely employs water as the oxygen source and the solvent (DMA or DMF) as the methylene donor, eliminating the need for external oxidants or additional carbon sources. The reaction proceeds smoothly in an undivided cell, tolerates a broad range of functional groups, and is readily scalable to gram quantities as well as adaptable to continuous flow processes. Mechanistic studies, including isotope labeling and DFT calculations, confirm the incorporation of both the hydroxyl and methylene units from water and solvent, respectively, via an anodic oxidation pathway. This approach provides a practical and efficient route for constructing aryl-propargyl alcohols using simple, readily available components in an electrochemical setting.

Propargyl alcohols are highly valuable building blocks in organic synthesis, serving as key intermediates in the preparation of pharmaceuticals, natural products, and advanced functional materials. Their versatile reactivity enables the efficient construction of diverse heterocycles and complex molecular scaffolds through cyclization,[1] rearrangement,[2] and addition reactions[3] (Scheme 1a). Since these compounds are rare in nature and mainly obtained synthetically, sustainable synthesis methods are increasingly important. Among current strategies, transforming terminal alkynes into propargyl alcohols is a straightforward route, incorporating all atoms from the alkyne with minimal byproducts (Scheme 1b). Conventional protocols, such as nucleophilic addition of alkynes to formaldehyde, often require strong bases, organometallic reagents, and low temperatures, resulting in significant waste and limited substrate scopes.[4] Copper-catalyzed methods using paraformaldehyde or aqueous formaldehyde improve upon these protocols but still need harsh conditions, including strong bases and elevated temperatures.[5] Driven by the need for greener alternatives, rongalite (sodium hydroxymethanesulfinate) has been utilized as a practical C1 (CH_2OH) source for hydroxymethylation of alkynes.[6] However, this strategy still requires stoichiometric amounts of strong base, elevated temperature and generates stoichiometric sulfite ion (SO^{2-}) as byproduct (Scheme 1b). Beyond these methods, Favorskii-type reactions have also been explored with recent progress including the use of Cs_2CO_3 and Et_3N as weak bases to promote the transformation of aliphatic aldehydes and terminal alkynes into the corresponding propargyl alcohols.[7] More recently, a direct alkynylation protocol of aldehydes or ketones catalyzed by triisopropylsilanol (i-Pr_3SiOH) in conjunction with a strong base (KOH) has been reported, enabling efficient synthesis of propargyl alcohols under mild conditions.[8] Nevertheless, the development of direct and selective hydroxymethylation of terminal alkynes under mild, metal-free, and atom-economic conditions remains highly desirable.

In pursuit of such sustainable synthesis, organic electrosynthesis has emerged as a powerful green tool for redox transformations. It leverages electrons as traceless reagents, avoiding toxic oxidants/reductants while enabling precise

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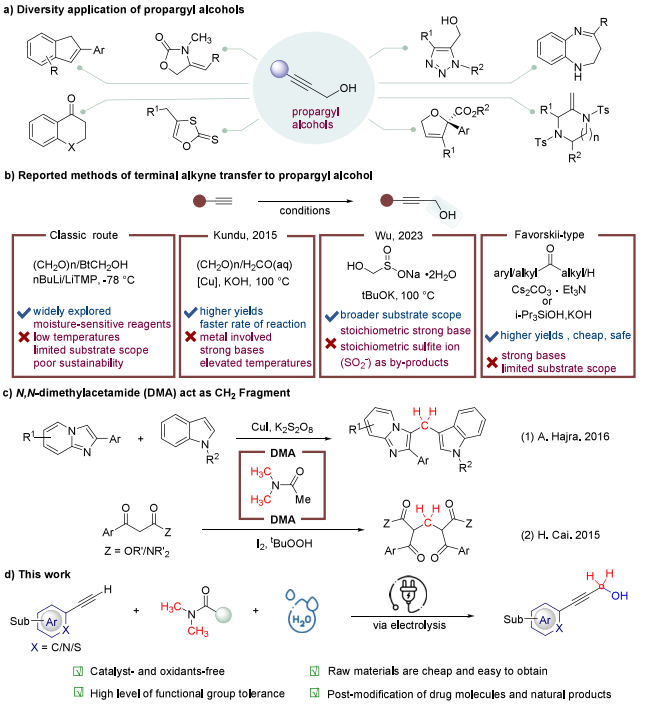
Scheme 1. Electrochemical Oxidation of Arylacetylenes to Aryl-Propargyl Alcohols

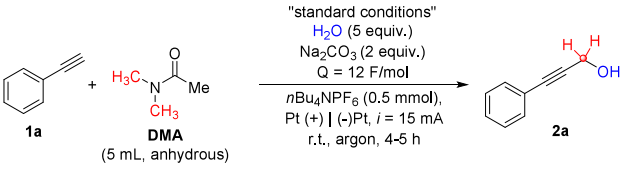


reaction control under mild conditions.[9] Recent advances have demonstrated that electrochemical activation of terminal alkynes offers a robust avenue for sustainable transformations. For example, copper- and quaternary ammonium salt-promoted electrochemical protocols have achieved C−H functionalization and homocoupling of terminal alkynes under mild, oxidant-free conditions.[10] Recently, Dapkekar and Gedu developed an electrochemical reductive coupling of terminal acetylenes and aldehydes to deliver diverse α-substituted propargyl alcohols and, using formaldehyde, access primary propargyl alcohols as well.[11] Despite this progress, sustainable C1 sources beyond formaldehyde remain highly desirable. One such promising C1 source is *N*,*N*-dimethylacetamide (DMA), a commonly used solvent once considered chemically inert but recently recognized as a versatile C1 synthon delivering fragments such as NC,[12] C,[13] CH,[14] and CH_2 fragment in C−C bond-forming reactions. For example, Cai and co-workers achieved the metal-free Csp^3−N bond-cleavage of DMA using I_2 as the catalyst to generate methylene-bridged β-keto esters in moderate yield,[15] while Hajra and co-workers reported copper-catalyzed synthesis of heterodiarylmethanes by employing DMA as a methylenating reagent to bridge imidazo[1, 2-a]pyridines with indoles[16] (Scheme 1c). These studies illustrate DMA's valuable role as a methylene source with sustainable credentials. Given these advances, combining DMA as a sustainable C1 source with the precise and mild activation provided by electrochemical methods offers a powerful and atom-economical strategy for the sustainable hydroxymethylation of terminal alkynes.

Building on these insights, we report a metal-free electrochemical strategy for the direct hydroxymethylation of arylacetylenes into aryl-propargyl alcohols, utilizing DMA as both a solvent and methylene source, with water as a green hydroxyl group donor (Scheme 1d). By using water as the sole oxygen donor[17] and DMA's dual role as solvent and methylene source, the protocol enhances sustainability through improved atom economy and minimized use of auxiliary reagents. This mild and efficient protocol eliminates the need for external oxidants, strong bases, or precious metal catalysts, and features a broad substrate scope that enables the one-step conversion of inexpensive, readily available starting materials into valuable propargyl alcohols. Mechanistic investigations, supported by DFT calculations, reveal that the reaction proceeds via anodic oxidation of DMA followed by base-mediated nucleophilic addition of water. This work highlights the potential of electrochemical methods to enable selective and efficient direct hydroxymethylation of arylacetylenes—achieving C−C bond formation under mild, metal-free conditions without harsh reagents—thereby expanding the synthetic toolbox for access to valuable propargyl alcohol building blocks.

The feasibility of electrocatalytic hydroxymethylation of arylacetylenes was investigated using phenylacetylene (**1a**) as a model substrate in a simple two-electrode undivided cell (Table 1). Optimal conditions were established as constant

Table 1. Reaction Optimization[a]



entry	variation from "standard conditions"	yield (%)[b]
1	none	74
2	without electricity	0
3	without H_2O	<10
4	without Na_2CO_3	61
5	Et_3N instead of Na_2CO_3	23
6	DMF (anhydrous) as solvent	50
7	CH_3CN, DCM and 1,4-dioxane (anhydrous) as solvent	0
8	*i* = 10 mA	65
9	*i* = 20 mA	70
10	C(+)/(-)Pt instead of Pt(+)/(-)Pt	57
11[c]	Flow (i = 60 mA, rate = 5 mL/min, 2.0 h)	50

[a]Conditions: **1a** (0.2 mmol, 1 equiv), H_2O (10 equiv), Na_2CO_3 (2 equiv), nBu_4NPF_6 (0.5 mmol), DMA (5 mL), Pt anode, Pt cathode (current intensity = 3.3 mA/cm^2), r.t. and *i* = 15 mA, undivided cell; [b]Isolated yields; [c]Reactor volume: 3 mL, isolated yields

current electrolysis at 15 mA in DMA at room temperature, with water (5 equiv) and Na_2CO_3 (2 equiv). Under these conditions (entry 1), the desired 3-phenylprop-2-yn-1-ol (**2a**) was obtained in a 74% isolated yield. Control experiments underscored the essential roles of each component: no product was detected without electricity (entry 2), and omitting water resulted in >10% yield (entry 3). Na_2CO_3 improves reaction efficiency, as evidenced by a slightly decreased yield upon its omission (entry 4). In contrast, the use of Et_3N gave significantly poorer outcomes (entry 5), underscoring the critical role of water as the oxygen source and the beneficial effect of Na_2CO_3. Solvent choice was also crucial—substituting DMA with DMF moderately decreased in yield (entry 6), while no reaction occurred in CH_3CN, DCM, or 1,4-dioxane, with complete recovery of starting material (entry 7). These results suggest that DMA functions not only the reaction medium but also participate directly in the transformation. Electrolysis parameters also influenced the outcome: both

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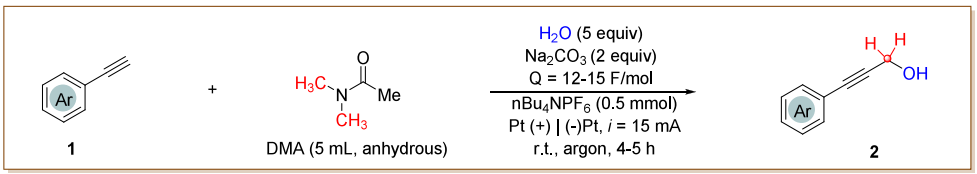
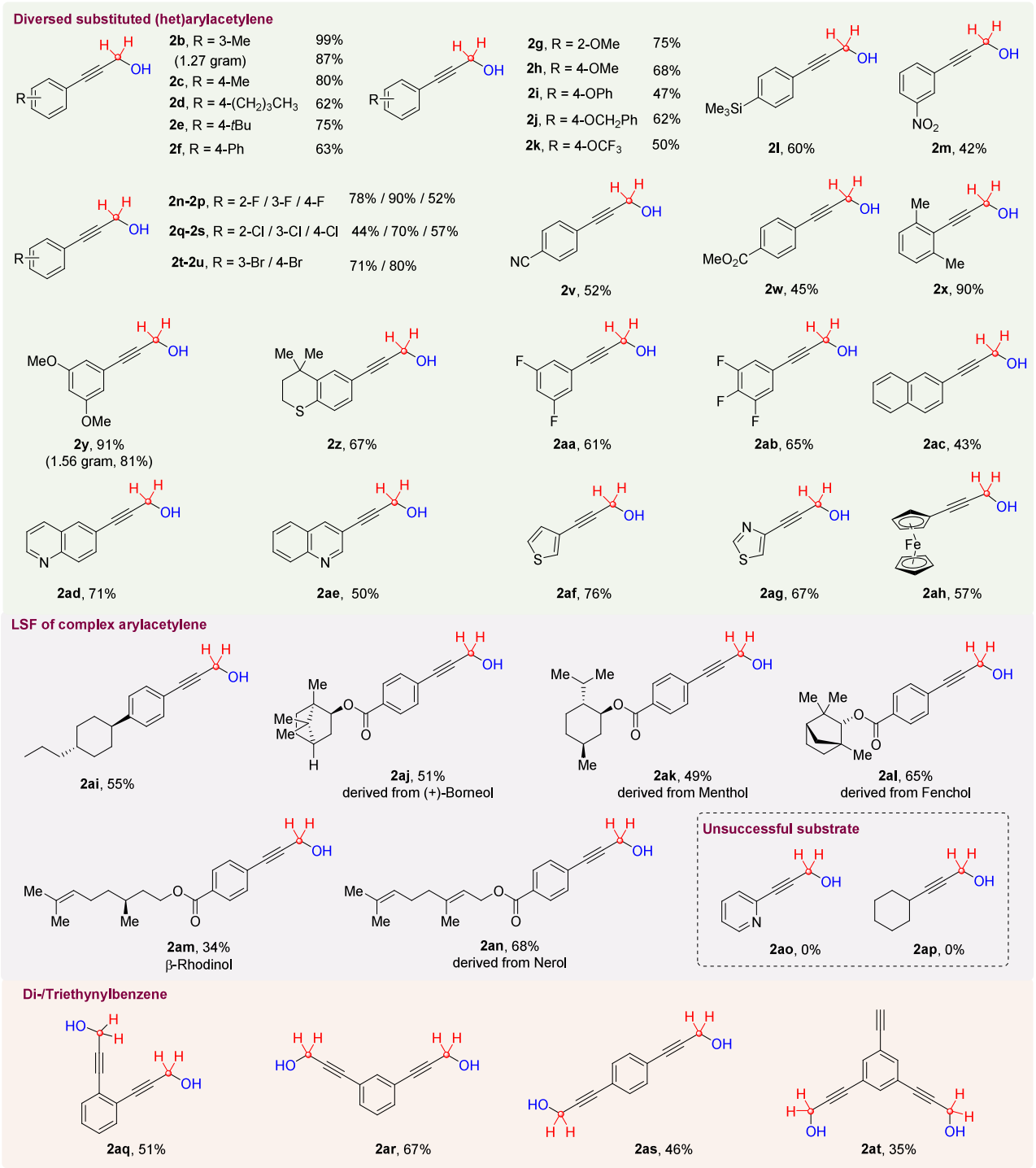
Scheme 2. Substrates Scope[a]





[a]Conditions: alkyne (0.2 mmol, 1 equiv), H_2O (5 equiv), nBu_4NPF_6 (0.5 mmol), DMA (5 mL), Pt anode, Pt cathode (current intensity = 10 mA/cm^2), r.t. and *i* = 15 mA, undivided cell. Isolated yields are reported, unless noted otherwise

lower (10 mA) and higher (20 mA) currents reduced yields (entries 8 and 9), and replacing the platinum anode with graphite led to a lower yield (entry 10). We further explored the applicability of this electrochemical hydroxymethylation in a circulation flow-cell reactor and were pleased to find that

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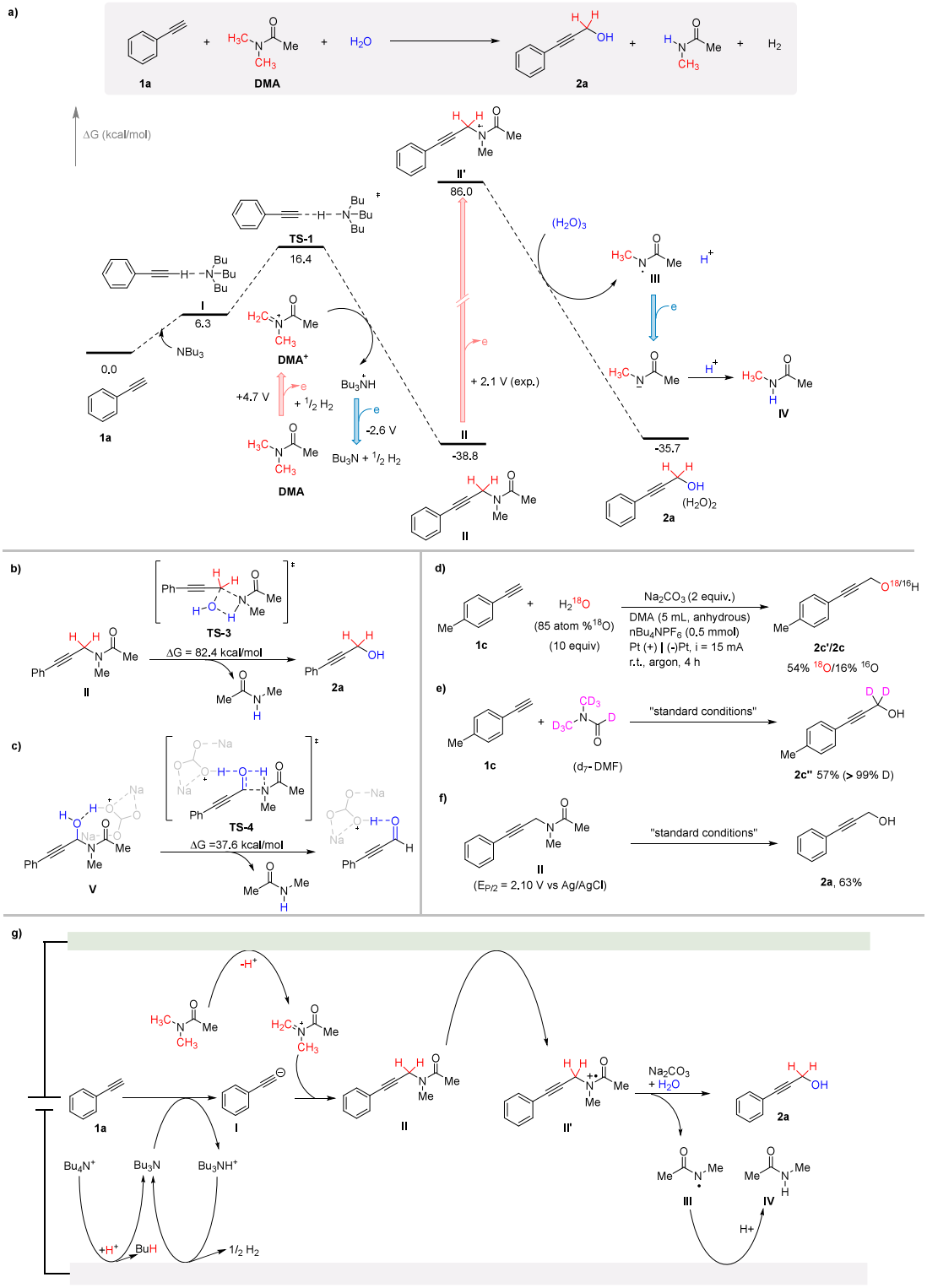
Scheme 3. Computational Studies and Plausible Mechanisms



propargyl alcohol **2a** could still be obtained in 50% isolated yield. (entry 11, see Supporting Information Section 6).

With the optimized conditions in hand, we explored the substrate scope of this electrocatalytic hydroxymethylation using a diverse array of arylacetylenes (Scheme 2). The reaction demonstrated broad compatibility, accommodating a wide range of functional groups and substitution patterns on the aromatic ring. Monosubstituted aryl group bearing electron-donating groups such as methyl, *tert*-butyl, methoxy, OPh, OCH_2Ph, OCF_3, long-chain alkyl, and silyl groups all reacted smoothly to provide the corresponding propargyl alcohols (**2b**−**2k**) in moderate to high yields (47−99%). Halide substituents (F, Cl, Br, and I) were well tolerated, providing products **2l**−**2s** with good yields (68−81%). Substrates bearing electron-withdrawing groups such as cyano, nitro, and ester groups at either para- or meta-position

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also reacted smoothly to afford the desired products **2t**−**2w** in moderate yields. Disubstituted aryl group, including dimethyl (**2x**), dimethoxy (**2y**), dialkyl (**2z**), and difluoro (**2aa**) derivatives, were successfully converted, and a trifluoro-substituted arylacetylene (**1ab**) furnished the product in a 65% yield. Importantly, the gram-scale synthesis of **2y**, delivering 1.56 g of product in 81% yield, underscores the practicality of the approach for preparative applications and large-scale synthesis. Moreover, this method was also effective for heteroaryl substrates often challenging under electrochemical conditions with naphthyl, quinolinyl, thienyl, thiazolyl, and even ferrocene derivatives all affording the corresponding propargyl alcohols (**2ac**−**2ah**) in moderate to high yields (43−76%). The protocol was further applied to late-stage functionalization of complex molecules. Arylacetylenes bearing chiral centers, such as compound **2ai**, as well as those derived from bioactive compounds including (+)-borneol (**2aj**), menthol (**2ak**), fenchol (**2al**), *β*-rhodinol (**2am**) and nerol (**2an**) were successfully converted into their corresponding products in good yields (68−81%).We also examined substrates bearing multiple alkynyl groups on the aromatic ring. Dialkynylbenzenes, regardless of the substitution pattern (ortho, meta, or para), yielded corresponding bis-(propargyl alcohol) products in moderate yields. In contrast, for trialkynylbenzene, hydroxymethylation occurred at only two positions, likely because electronic effects after the initial transformations hindered reaction at the third site (**2at**). Notably, pyridylacetylene (**2ao**) and cyclohexylacetylene (**2ap**) did not yield the desired products; DFT calculations (see Supporting Information Section 8) indicate that the lack of reactivity for alkyl-substituted alkynes arises from unfavorable electronic properties under the reaction conditions.

Density functional theory (DFT) calculations were performed, (Scheme 3a). At the outset, nBu_4N^+ cation undergoes elimination to generate nBu_3N,[10] forming a hydrogen-bonded complex (intermediate **I**, endergonic by 6.3 kcal/mol) with phenylacetylene (**1a**). Subsequently, nBu_3N abstracts the terminal hydrogen from **1a** via transition state **TS-1** with a 10.1 kcal/mol barrier, generating the phenylacetylene anion. DMA is oxidized at the anode, releasing an electron and hydrogen atom to form cationic species DMA^+, requiring +4.7 V. DMA^+ then replaces the nBu_3NH^+ cation from **TS-1** to form a stable intermediate **II**. Dissociated nBu_3NH^+ is then reduced at the cathode, regenerating nBu_3N and releasing hydrogen gas. A direct nucleophilic substitution of water with intermediate **II** to yield 3-phenylpropargyl alcohol and *N*-methylacetamide is unfavorable, as indicated by a prohibitive energy barrier of 82.4 kcal/mol (**TS-3**, Scheme 3b). A more feasible pathway involves further anodic oxidation of intermediate **II** ($E_{p/2}$ = 2.10 V vs Ag/AgCl) under the applied electric field to form cationic radical intermediate **II′**. This activated species undergoes hydroxylation with water clusters $[(\mathbf{H_2O})_3]$, yielding product **2a** complexed with water molecules and *N*-methylacetamide radical (**III**). Subsequently, intermediate **III** is reduced at the cathode to form *N*-methylacetamide (**IV**) after protonation. Frontier molecular orbital (FMO) analysis further supports these mechanistic assignments summarized in Figure S6. Finally, an alternative pathway involving intramolecular decomposition of the intermediate **V** to form phenylpropargyl aldehyde and *N*-methylacetamide is unlikely (Scheme 3c), given the high activation barrier (**TS-4**, 37.6 kcal/mol) and experimental evidence showing no conversion of the aldehyde to 3-phenylprop-2-yn-1-ol under the standard conditions (Figure S4).

To further verify the reaction mechanism, we confirmed water as the O-source by isotope labeling (Scheme 3d): $H_2{}^{18}O$ gave **2c′** in 54% yield with full ^{18}O incorporation, while residual water likely accounts for 16% unlabeled product. Using d_7-DMF as solvent, **2c′′** was obtained in 57% yield with full deuterium incorporation, confirming DMA or DMF as the methylene source (Scheme 3e). Furthermore, synthesis and successful conversion of the putative intermediate *N*-methyl-*N*-(3-phenylprop-2-yn-1-yl) acetamide (**II**) to **2a** (63% yield, Scheme 3f) support its viability and the proposed mechanism.

Based on the above findings and supporting literature, a plausible reaction mechanism is proposed (Scheme 3g). The process begins with anodic oxidation of DMA, generating an iminium ion that reacts with phenylethynyl anion **I**, formed via deprotonation by nBu_4N^+,[10] to yield intermediate **II**. Subsequent anodic oxidation of intermediate **II** forms cation radical **II′**, which undergoes nucleophilic attack by a water cluster, releasing amide radical **III** to produce 3-phenylprop-2-yn-1-ol (**2a**)—a process potentially accelerated by Na_2CO_3. Finally, radical **III** is reduced to the corresponding anion to yield *N*-methylacetamide (**IV**) upon protonation. Throughout the electrochemical process, protons are reduced at the cathode, generating H_2 as a byproduct. Another possible mechanism involving S_N2 attack by the phenylethynyl anion on a water-trapped DMA^+ intermediate was considered, but DFT calculations show prohibitively high barriers under our conditions (see Supporting Information 8.2).

In summary, we have established a robust and sustainable electrochemical protocol for the synthesis of aryl-propargyl alcohols from arylacetylenes. This method features the unique utilization of water as the oxygen source and the reaction solvent as the methylene donor, eliminating the need for external oxidants and maximizing atom economy. The transformation proceeds under mild conditions with broad substrate scope and excellent functional group tolerance, consistently affording the desired propargyl alcohols in good yields. The practicality of the protocol is further highlighted by successful gram-scale synthesis and its efficient translation to a flow-cell system, enabling continuous and scalable production. Overall, this strategy provides a powerful and practical platform for the streamlined construction of valuable aryl-propargyl alcohols. Continued optimization and expansion of this methodology are expected to broaden its applicability in complex molecule synthesis and related organic transformations.

■ ASSOCIATED CONTENT

Data Availability Statement

The data underlying this study are available in the published article and its Supporting Information.

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.5c03363.

General procedures, tables of reaction optimizations, analytical data, and characterization data for all the products (PDF)

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Notes

The authors declare no competing financial interest.

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