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# Facile, general allylation of unactivated alkyl halides *via* electrochemically enabled radical-polar crossover†

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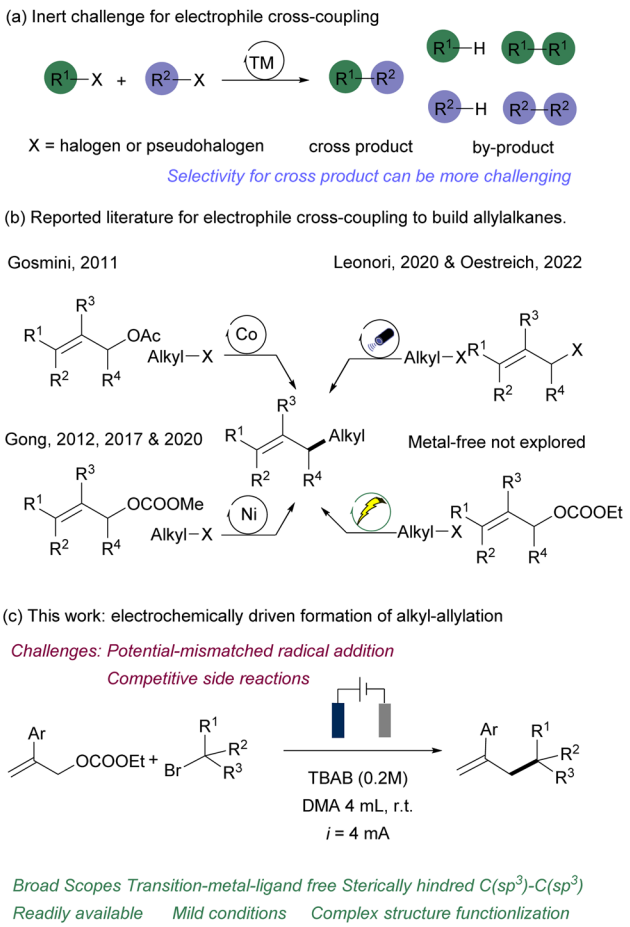
Electrochemically driven carbon–carbon formation is receiving considerable interest in organic synthesis. In this study, we present an electrochemically driven method for the formation of C($sp^3$)–C($sp^3$) bonds using readily available allylic carbonates, as well as primary, secondary, and tertiary alkyl bromides as electrophiles. This approach offers a highly selective route for synthesizing a broad range of allylic products with excellent functional group tolerance, all without the need for transition metal catalysts. Remarkably, this method also enables the smooth late-stage functionalization of various natural product- and drug-derived substrates, yielding the corresponding complex allylalkanes.

## Introduction

The development of new methodologies for constructing C($sp^3$)–C($sp^3$) bonds remains a significant challenge in the field of C–C coupling chemistry.[1–3] Transition-metal-catalyzed cross-coupling has emerged as a powerful approach for rapid construction and increasing molecular complexity.[4–8] However, traditional cross-coupling reactions often require preformed organometallic reagents, which limits their application and substrate scope.[9] To address this, reductive cross-coupling using electrophiles as coupling partners has proven to be an efficient strategy,[10–13] significantly enhancing molecular complexity by circumventing the need for activated substrates.[14–17] Recently, the metallaphotocatalyzed[18–21] and metallaelectrocatalyzed[22–28] reactions have offered alternative pathways for forming C($sp^3$)–C($sp^3$) bonds under mild conditions. Despite these advances,[29–33] constructing C($sp^3$)–C($sp^3$) bonds remains challenging due to intrinsic obstacles (Scheme 1a). For instance, these methods often rely on expensive metal–ligand catalysts or stoichiometric metal reductants.[34,35] Therefore, there is a strong demand for developing new, efficient, mild, metal–ligand-catalyst-free, and environmentally friendly strategies for C($sp^3$)–C($sp^3$) bond formation.

Electrochemistry has emerged as a versatile and powerful platform for sustainable synthesis, leveraging finely-tuned electron-transfer processes and the use of electrons as traceless redox reagents.[36–42] In this context, electroreduction has shown great promise, enabling direct interactions between substrates and electrode surfaces to generate alkyl radicals




Scheme 1 The development of electrocatalyzed directly formation of the C($sp^3$) radical.

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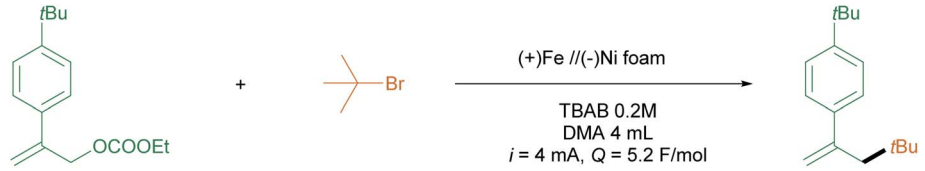
Table 1 Optimization of electrochemically driven alkyl-allylation[a]




1a 2a 3a

Optimization of reaction

| Entry | Variables | Yield[b] [%] | Entry | Variables | Yield[b] [%] |
|---|---|---|---|---|---|
| 1 | Standard | 65[c] | 10 | DMF as solvent | 50 |
| 2 | RVC(+)//Ni foam(−) w/TMEDA | 8 | 11 | MeCN as solvent | 17 |
| 3 | RVC(+)//RVC(−) w/TMEDA | 12 | 12 | 3 : 1 | 51 |
| 4 | (+)Zn//(−)Ni foam | 25 | 13 | 2 : 1 | 40 |
| 5 | (+)Fe//(−)RVC | 51 | 14 | 1 : 1 | 36 |
| 6 | (+)Zn//(−)RVC | 27 | 15 | TBACl as electrolyte | 23 |
| 7 | 1 mA | 44 | 16 | TBAI as electrolyte | 45 |
| 8 | 2 mA | 63 | 17 | w/o current | ND |
| 9 | 6 mA | 42 | 18 | w/o TBAB | 32 |

[a] Reactions were performed with 0.2 mmol of **1a**, 0.4 mmol of **2a**, 0.2 M of TBAB, 4 mL of DMA in an undivided cell at R. T. and $i = 4$ mA, 5.2 F mol$^{-1}$. [b] GC-FID yield using dodecane as internal standard. [c] Isolated yield.

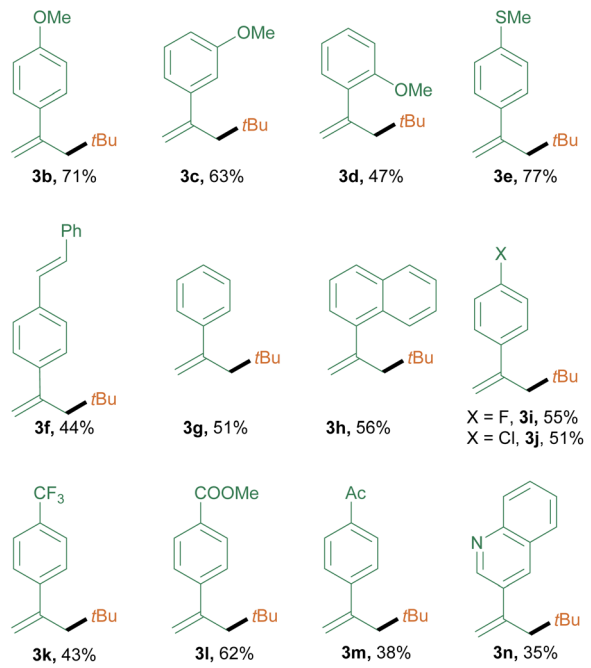



Fig. 1 Allylic carbonate scope. Reactions were performed with 0.2 mmol of 1, 0.4 mmol of 2, 0.2 M of TBAB, and 4 mL of DMA in an undivided cell at R. T. and $i = 4$ mA, 5.2 F mol$^{-1}$.

through the cathodic reduction of alkyl halides.[43–47] Elegant studies have explored this concept.[48–51] Alkyl halides play a crucial role in organic chemistry due to their diverse reactivity and ease of synthesis.[52] As a result, significant progress has been made in the electroreduction of alkyl halides, including applications such as the Giese reaction, cross-electrophile coupling (e-XEC), deuteration, borylation, and bifunctionalization of alkenes, among others.[53–57]

Allylic moieties are essential substructures in organic molecules and versatile functional groups due to their convertible C–C double bonds and allylic single bonds.[58] The allylation of various molecules *via* the construction of a C–C bond has been thoroughly investigated.[3,59] To date, transition-metal catalyzed electrophile allylation of alkyl halides is one of the most important protocols for delivering allylated-alkane compounds (Scheme 1b),[60–65] In comparison, the electrochemical allylation of alkyl halides with allylcarbonates, which benefits from transition-metal-free and sustainable conditions, has been relatively underexplored. Thus, direct electrochemical allylation of unactivated alkyl halides presents a practical and attractive alternative for the synthesis of allylated alkane compounds.

In this regard, we present a novel and versatile electroreduction protocol for the formation of allylated alkanes (Scheme 1c). This reaction offers a straightforward and efficient route to allylated products under mild conditions. Moreover, the successful late-stage functionalization of natural products highlights the potential of our methodology. This strategy not only expands the toolkit for C(sp$^3$)–C(sp$^3$) bond formation but also paves the way for future developments in this area.

## Results and discussion

We initiated the exploration with methyl 2-(4-(*tert*-butyl) phenyl) allyl ethyl carbonate (**1a**) and 2-bromo-2-methylpropane (**2a**) as the coupling partners. As outlined in Table 1, a combination of (+) iron//(−) Ni foam as electrodes, TBAB (tetrabutylammonium bromide) as an electrolyte, and DMA (dimethylacetamide) as solvent with a 4 mA current in an undivided cell delivered the

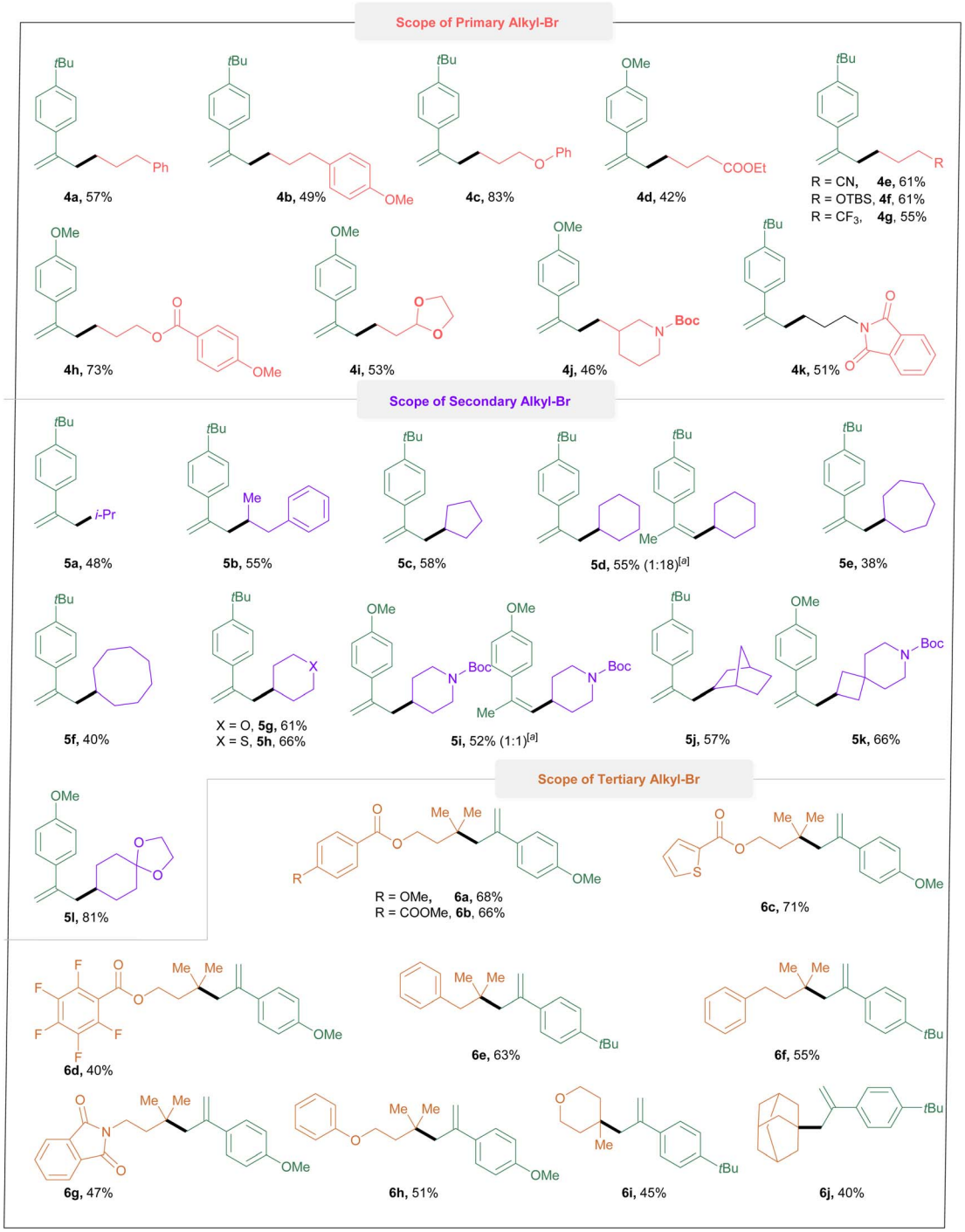



Fig. 2 Alkyl-Br substrate scope. Reactions were performed with 0.2 mmol of **1**, 0.4 mmol of **2**, 0.2 M of TBAB, and 4 mL of DMA in an undivided cell at R. T. and constant current $i = 4$ mA, 5.2 F mol$^{-1}$.[a] Detected by $^1$H NMR.

desired product **3a** in 65% isolated yield (entry 1). Altering the anode or cathode significantly decreased the reaction efficiency (entries 2–6). Adjusting the current also succeeded in this alkyl-allylation process, albeit with lower efficiency (entries 7–9). Conducting the reaction in alternative solvents, such as DMF or MeCN, did not improve the reaction outcomes (entries 10 & 11). Screening the substrates ratio also led to lower yields (entries 12–14). Applying other electrolytes did not improve the reaction efficiency (entries 15 & 16).

Control experiments revealed that the current and electrolyte were essential for obtaining high reaction results (entries 17 & 18). In order if the iron ions formed at the anode affect the reaction outcome,[66] we added different amounts of $FeBr_2$ and $FeBr_3$ as well as additional $FeBr_2$ in combination with different electrodes. However, no reaction enhancement was observed (Fig. S1 & S2†).

With the optimized condition in hand, we moved attention to evaluating the scope of this protocol. As shown in Fig. 1, the

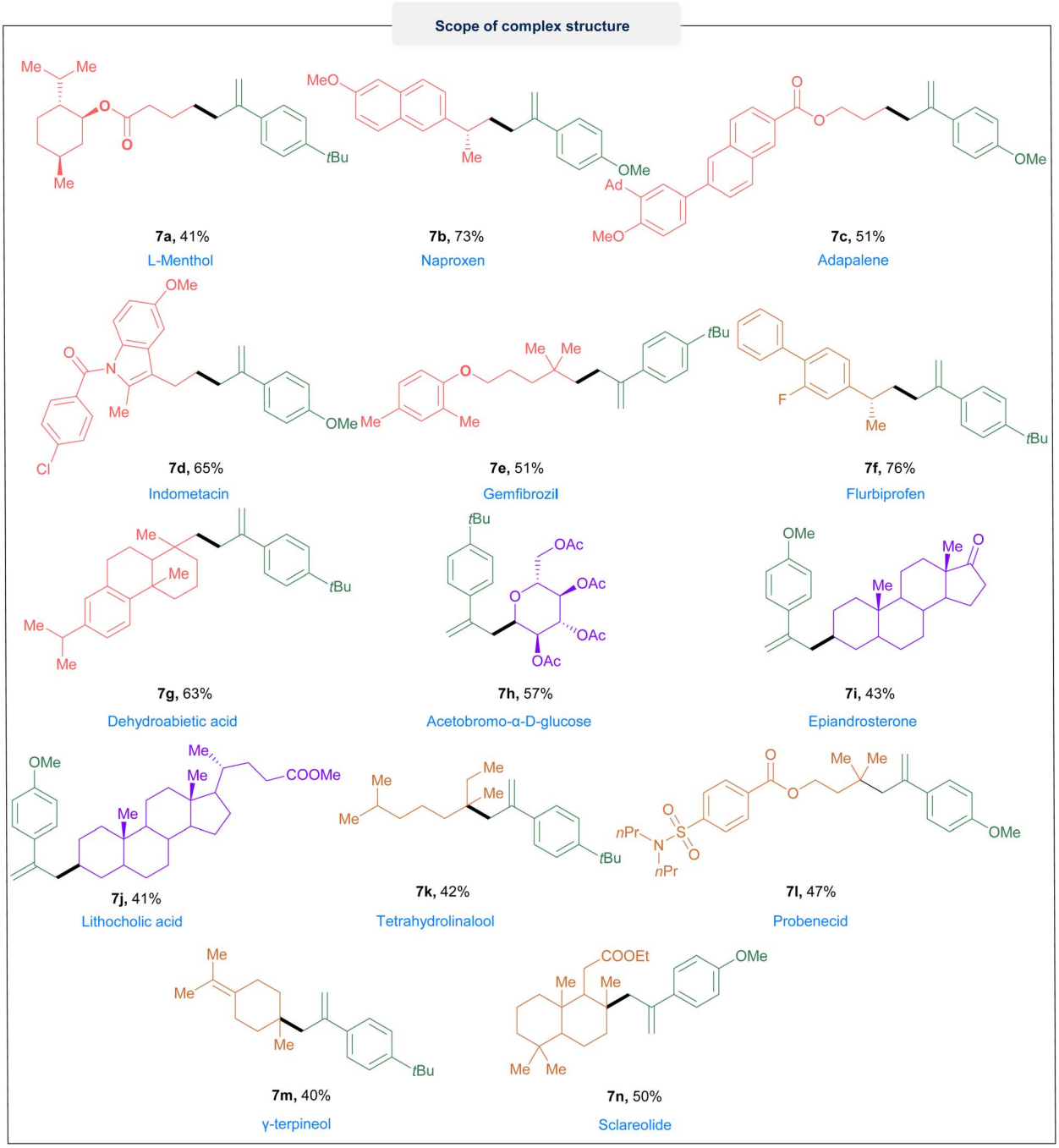



Fig. 3 Modification of structurally complex molecules. Reactions were performed with 0.2 mmol of **1**, 0.4 mmol of **2**, 0.2 M of TBAB, and 4 mL of DMA in an undivided cell at R. T. and constant current $i = 4$ mA, 5.2 F mol$^{-1}$.

installation of electro-donating (**3b–f**), electron-neutral (**3g** & **h**) and electron-withdrawing (**3i–m**) groups onto the 2-phenylallyl carbonate showed high coupling efficiency and excellent functional group compatibility. Hetero-quinoline substituted substrate also afforded the corresponding product in acceptable yield (**3n**).

Next, we investigated the scope of the alkyl halides (Fig. 2). To our delight, a series of primary, secondary and tertiary alkyl bromides, in spite of different electronic properties, all could be engaged in the reaction efficiently. For the primary alkyl bromide, alkyl bromides tethered with phenyl and methoxyl substituted phenyl, ether, ester, cyano, benzoate, acetal, trifluoromethyl, *N*-boc-piperidine and phthalimidyl groups could all be transferred to the cascade products in moderate to excellent yields (**4a–k**). The use of secondary alkyl bromides with acyclic, cyclic and heteroatoms gave good yields (**5a–5l**). Unexpectedly, isomerizations (**5d** & **5i**) were detected when bromocyclohexane and 4-bromo-*N*-boc-piperidine were used. Bicyclic and spiro compounds reacted efficiently and delivered the corresponding products (**5j–l**) in good yields. In addition, the

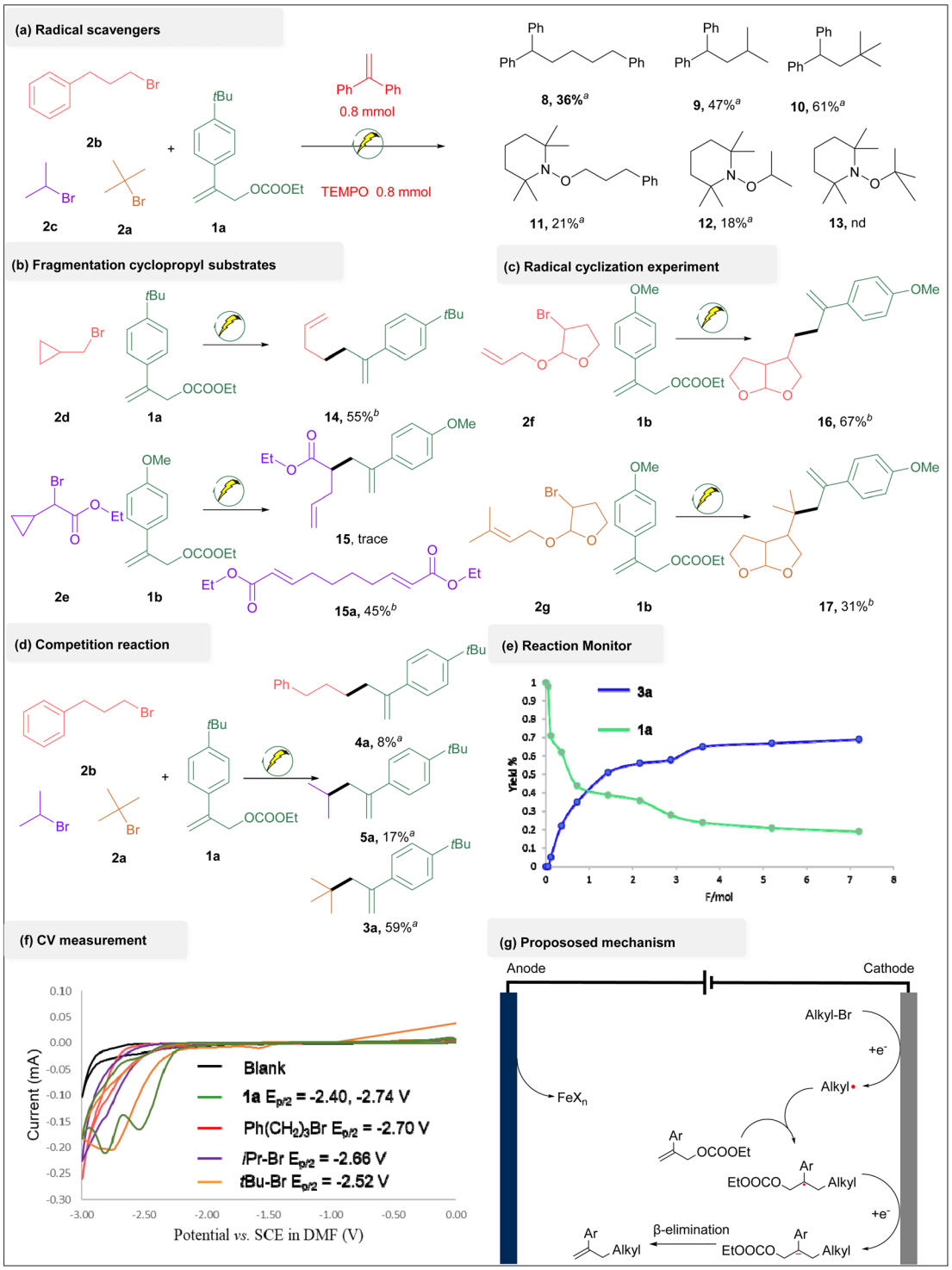



Fig. 4 Mechanistic studies. [a]GC-FID yield using dodecane as internal standard. [b]Isolated yield. (a) Radical scavengers; (b) fragmentation cyclopropyl substrates; (c) radical cyclization experiment; (d) competition reaction; (e) reaction monitor; (f) CV measurement; (g) propososed mechanism.

linear (**6a–h**) and cyclic tertiary alkyl bromides (**6i–j**) also reacted efficiently in this system. Significantly, the pentafluoro-substituted substrate could furnish the desired product (**6d**) in 40% yield. Next, our focus shifted to further demonstrating the practicability and synthetic utility of this protocol, we explored modifications on structurally complex molecules. As displayed in Fig. 3, various primary, secondary, and tertiary natural or pharmaceutical alkyl bromides derived from L-menthol (**7a**), naproxen (**7b**), adapalene (**7c**), indometacin (**7d**), gemfibrozil (**7e**), flubiprofen (**7f**), dehydroabietic acid (**7g**),

acetobromo-*a*-D-glucose (**7h**), epiandrosterone (**7i**), lithocholic acid (**7j**), tetrahydrolinalool (**7k**), probenecid (**7l**),γ-terpineol (**7m**) and sclareolide (**7n**) were effectively converted into the corresponding alkyl radical *via* this protocol, and subsequently delivered a variety of structually complex allylated-alkane derivatives in moderate to good yields.

To further elucidate the possible mechanism of this electrochemically driven formation of allylated-alkanes, a range of control experiments were performed. Firstly, the use of stoichiometric amounts of radical scavengers (1, 1- diphenyethylene and TEMPO) under the standard conditions was applied. Both desired products and alkyl radical captured products could be observed (Fig. 4a). In principle, the allylic carbonate might also be reduced by the cathode to release the allyl radical. However, we did not observe the formation. Alkyl radical clock experiments were performed by using the cyclopropyl tethered (bromomethyl) cyclopropane (**2d**) and ethyl 2-bromo-2-cyclopropylacetate (**2e**). Here, we obtained the ring-opening product **14** in 55%, although the secondary alkyl substrate only furnished the desired product **15** in trace yield and by-product **15a** was formed in 45%, which indicates that the secondary alkyl radical is involved in the reaction (Fig. 4b). Thus, radical cyclization experiments were also performed. The cyclization products **16** and **17** were obtained in 67% and 31%, respectively (Fig. 4c). These observations suggest the involvement of alkyl radicals in this protocol. To further investigate, a competition reaction was performed (Fig. 4d), yielding products **3a**, **4a**, and **5a** with yields of 59%, 8%, and 17%, respectively. These results demonstrated that the alkyl reactivity followed the sequence: tertiary > secondary > primary. Additionally, reaction monitoring indicated that the allylation reaction was completed within 7 hours (Fig. 4e). To explore the electrochemical behavior of the reactants, cyclic voltammetry (CV) measurements were conducted. As shown in Fig. 4f, the reduction peaks for 3-phenylpropyl bromide, 2-bromopropane, and *tert*-butyl bromide were observed at −2.70 V, −2.66 V, and −2.52 V *versus* the saturated calomel electrode (SCE), and the onset values were −2.4 V, −2.3 V and −2.2 V, respectively. For 2-(4-(*tert*-butyl) phenyl) allyl ethyl carbonate, two onset reduction peaks were recorded at −2.74 V and −2.40 V *versus* SCE. These findings indicate that alkyl halides can be reduced to generate the corresponding alkyl radicals under the conditions of this protocol.

### Mechanism

Based on the above analysis results and literature report,[53,65] we propose a plausible mechanism for the new electrochemical $C(sp^3)$–$C(sp^3)$ bond formation (Fig. 4g). Initially, the allylic carbonate reacts with the cathode-activated alkyl radicals, forming a stable tertiary benzyl radical. This radical is subsequently reduced at the cathode to generate a carbanion. The carbanion intermediate can then undergo β-elimination, leading to the formation of the desired products.

## Conclusions

In conclusion, we have successfully developed an efficient electrochemically-driven radical polar crossover method for the formation of allylated alkanes using allylic carbonate and unactivated alkyl bromides. This protocol operates under mild conditions, enabling the synthesis of a diverse range of synthetically valuable allylated alkanes. Given the commercial availability of the reactants and the properties of allyl and alkyl compounds, we believe that this electroreduction protocol will have broad applicability, expand the library of allylated alkanes, and inspire further exploration in the field of $C(sp^3)$–$C(sp^3)$ coupling reactions.

## Data availability

The data supporting this article have been included as part of the ESI.†

## Author contributions

H. C., and M. R. conceived the idea of this work. H. C. carried out the reaction optimization and substrate scope. H. C. and M. R. co-wrote the manuscript. M. R. directed the entire research.

## Conflicts of interest

The authors declare no competing financial interest.

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