

RESEARCH ARTICLE

View Article Online
View Journal | View IssueCite this: *Org. Chem. Front.*, 2026,
13, 147Received 21st August 2025,
Accepted 13th October 2025

DOI: 10.1039/d5qo01168j

rsc.li/frontiers-organic

An electrochemical reductive allylation and alkylation of carbonyl groups in α,β -unsaturated aldehydes and ketones

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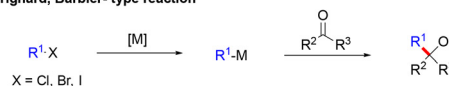
We report herein an electrochemical reductive allylation and alkylation of carbonyl groups in α,β -unsaturated aldehydes and ketones. This study provides a practical and efficient new method for synthesizing allyl alcohol, propargyl alcohol, and homoallylic alcohol.

Allyl alcohol, propargyl alcohol, and homoallylic alcohol are not only abundant in natural products and pharmaceutical molecules but also serve as important synthetic intermediates with wide applications.¹ Therefore, numerous methods have been developed to synthesize these compounds in the past decades. Among them, the reductive alkylation and allylation of carbonyl groups in enones represents one of the most effective strategies. The classic synthetic methods are shown in Scheme 1A–C. Early strategies involved Barbier–Grignard type reactions (Scheme 1A).² Subsequently, Keck, Sakurai, and Roush *et al.* successfully achieved the allylation of carbonyl groups using allyl tin, silane, and boron (Scheme 1B).³ In addition, a wide range of metals such as Mg,⁴ Ti,⁵ Mn,⁶ Zn,⁷ In,⁸ Sn⁹ and Sb¹⁰ have been explored for the reductive allylation of aldehydes and ketones with allyl halides (Scheme 1C). These classic methods often require large quantities of metal, pre-prepared allyl reagents, and display low functional group tolerance.

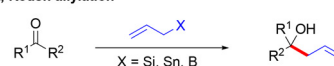
To overcome these limitations, several effective electrochemical approaches for the allylation of carbonyl groups using allyl halides have been developed (Scheme 1D). For example, Huang and co-workers reported two electrochemical allylation reactions of aldehydes and ketones in 2009–2010.¹¹ In recent years, Li's¹² group has also developed a reductive allylation of carbonyl compounds under electrochemical conditions. Very recently, Liu *et al.*¹³ achieved an electrochemical allylation of aldehydes and ketones with allylic alcohols. Despite these advances, the developed electrochemical allylation methods are largely limited to simple carbonyl substrates. The reductive functionalization of α,β -unsaturated aldehydes and ketones remains a considerable challenge due to the competing hydrogenation of the conjugated C=C bonds, which

impedes chemoselective control. In continuation of our studies toward green synthetic methods *via* electrochemistry,¹⁴ we explored an electrochemical allylation/alkylation of carbonyl groups in α,β -unsaturated aldehydes and ketones. Fortunately, we accomplished reductive C–C bond formation through coupling reactions of alkyl and allyl halides with a

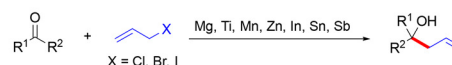
A) Grignard, Barbier-type reaction



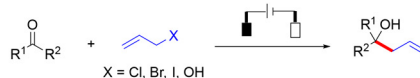
B) Sakurai, Keck, Roush allylation



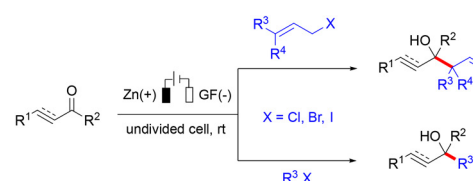
C) Traditional transition-metal mediated allylation



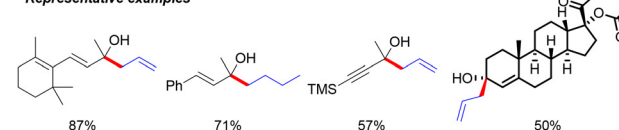
D) Electrochemical allylation of aldehydes and ketones



E) This work



Representative examples



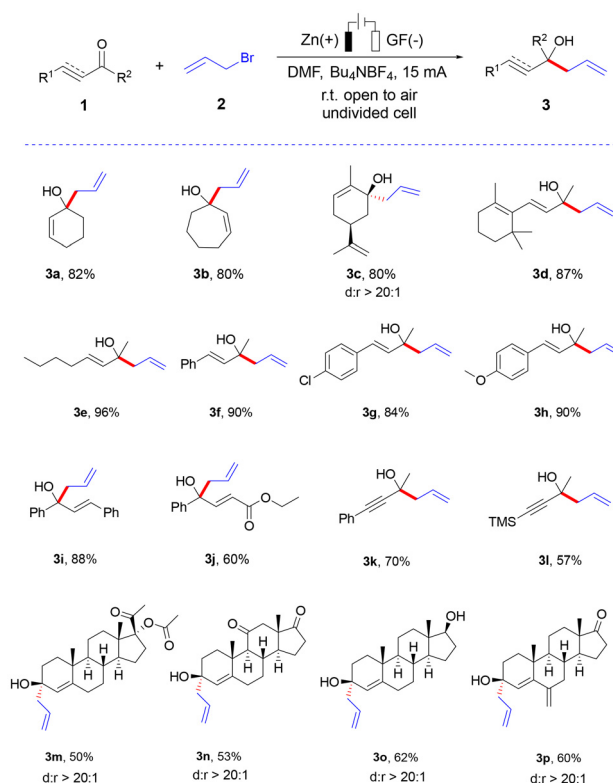
Scheme 1 Strategies for allylation/alkylation of carbonyl compounds.

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series of α,β -unsaturated aldehydes and ketones under mild electrochemical conditions (Scheme 1E).

Our investigation of electrochemical allylation commenced with using 2-cyclohexen-1-one (**1a**) and allyl bromide (**2a**) as the model substrates to optimize the reaction conditions (Table 1). To our delight, the desired product **3a** was obtained in a yield of 50% under the following conditions: zinc rod as the anode, graphite felt (GF) as the cathode, tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) as the electrolyte, *N,N*-dimethylformamide (DMF) as the solvent, and a current density of 10 mA in an open flask for 3 hours (entry 1). When the amount of allyl bromide was adjusted to 3.0 equivalents, **3a** was obtained in a yield of 74% (entry 3). Next, we examined various materials as electrodes and found that Zn/GF was more effective than the others (entries 4–6). Furthermore, increasing the current from 5 to 20 mA resulted in decreased yields of **3a** (entries 8–10). Other electrolytes, such as Et_4NBF_4 , TBAClO_4 , Bu_4NPF_6 , and LiClO_4 , resulted in relatively lower yields (entries 11–14). In addition, DMF was more effective than other solvents (entries 15–17). Finally, the control experiment confirmed that electricity is necessary (entry 18).

With the optimized conditions in hand, we next examined the substrate scope (Scheme 2). First, we evaluated six- and seven-membered enones, which afforded the corresponding products in good yields of over 80% (**3a** and **3b**). Next, we investigated *L*(–)-carvone and β -iononem, two unsaturated ketones derived from natural products, which also provided the target products in excellent yields (**3c** and **3d**). We were pleased to find that the chain enone was also compatible with



Scheme 2 Scope of α,β -unsaturated ketones. Reaction conditions: undivided cell, zinc rod as anode, **1** (0.5 mmol), **2** (1.5 mmol), Bu_4NBF_4 (0.5 mmol), DMF (5.0 mL), constant current = 15.0 mA, open to air, 2–6 h. Isolated yield.

Table 1 Optimization of the reaction conditions^a

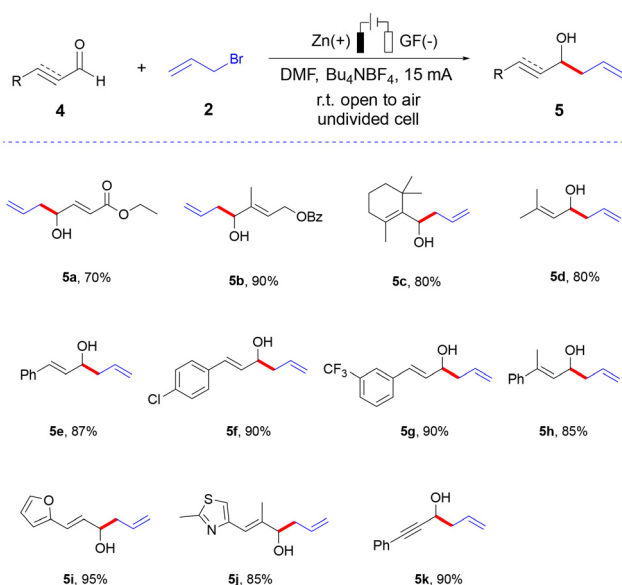
Entry	2a (eq.)	Electrode	Current (mA)	Electrolyte (0.1 M)	Solvent	Yield ^b /%	Time/h
1	1.0	Zn (+) GF (–)	10	Bu_4NBF_4	DMF	50	3.0
2	2.0	Zn (+) GF (–)	10	Bu_4NBF_4	DMF	66	3.0
3	3.0	Zn (+) GF (–)	10	Bu_4NBF_4	DMF	80	3.0
4	3.0	GF (+) GF (–)	10	Bu_4NBF_4	DMF	Trace	3.0
5	3.0	Ni (+) GF (–)	10	Bu_4NBF_4	DMF	48	3.0
6	3.0	Mg (+) GF (–)	10	Bu_4NBF_4	DMF	43	3.0
7	3.0	Sn (+) GF (–)	10	Bu_4NBF_4	DMF	19	3.0
8	3.0	Zn (+) GF (–)	5	Bu_4NBF_4	DMF	65	5.0
9	3.0	Zn (+) GF (–)	15	Bu_4NBF_4	DMF	85	2.0
10	3.0	Zn (+) GF (–)	20	Bu_4NBF_4	DMF	70	2.0
11	3.0	Zn (+) GF (–)	15	Et_4NBF_4	DMF	42	3.0
12	3.0	Zn (+) GF (–)	15	TBAClO_4	DMF	55	3.0
13	3.0	Zn (+) GF (–)	15	Bu_4NPF_6	DMF	47	3.0
14	3.0	Zn (+) GF (–)	15	LiClO_4	DMF	35	3.0
15	3.0	Zn (+) GF (–)	15	Bu_4NBF_4	DMSO	70	3.0
16	3.0	Zn (+) GF (–)	15	Bu_4NBF_4	MeCN	60	2.0
17	3.0	Zn (+) GF (–)	15	Bu_4NBF_4	THF	—	2.0
18	3.0	Zn (+) GF (–)	—	Bu_4NBF_4	DMF	N.D. ^c	2.0

^a Reaction conditions: undivided cell, zinc rod as anode, **1a** (0.5 mmol, 1.0 equiv.), electrolyte (0.5 mmol, 1.0 equiv.), solvent (5.0 mL), constant current, room temperature, open to air. ^b Isolated yield. ^c ND = not detected.

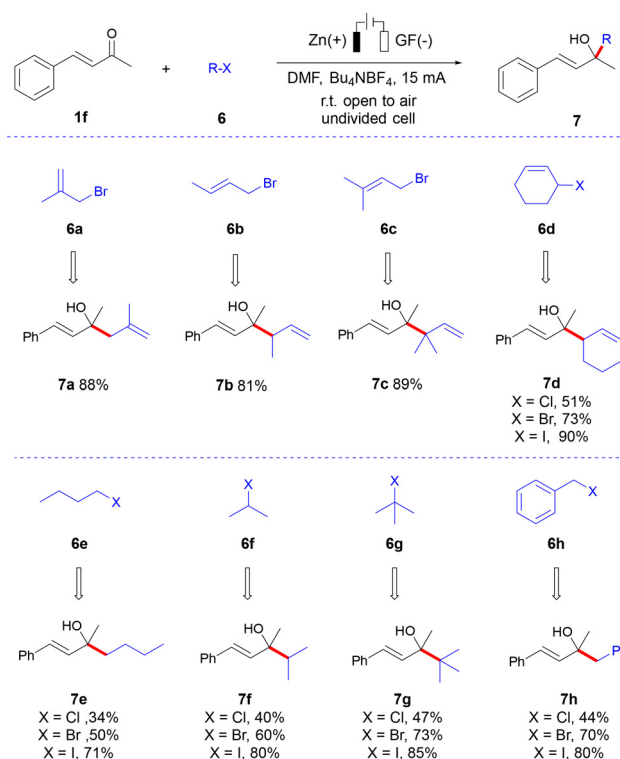
this system, affording **3e** in nearly quantitative yield in only one hour. Similarly, aryl enones gave the corresponding allyl alcohol derivatives in excellent yields (**3f–3h**). Furthermore, phenyl- and ester-substituted enones also underwent selective 1,2-addition of the allyl halide to the carbonyl group, resulting in good yields (**3i** and **3j**). Next, we also examined two unsaturated alkyneones, which afforded the target products in moderate to good yields (57–70%) (**3k** and **3l**). Finally, a series of natural steroids were also found to be effective substrates (**3m–3p**). To our surprise, reductive allylation occurred preferentially at the conjugated carbonyl groups, while the non-conjugated ones remained intact. This phenomenon assists in studying the mechanism of this reaction.

Then we examined the substrate scope of α,β -unsaturated aldehydes. As shown in Scheme 3, both alkyl (**5a–5d**) and aryl (**5e–5h**) α,β -unsaturated aldehydes gave the desired products in 85–95% yields. Additionally, heteroarene-substituted α,β -unsaturated aldehydes, which are widely utilized as core structures in medicinal chemistry, were also suitable substrates (**5i** and **5j**). Phenylpropionaldehyde was also a suitable substrate (**5k**).

Subsequently, we examined the scope of allyl halides under the standard reaction conditions (Scheme 4). Methallyl bromide (**6a**) afforded the desired homoallylic alcohol (**7a**) in 88% yield. Interestingly, crotyl bromide (**6b**) and 3,3-dimethylallyl bromide (**6c**) gave products **7b** and **7c** in 81% and 89% yields, respectively. It is noteworthy that the C=C double bonds underwent migration. Cycloallylic halides were also effective substrates (**7d**). To our delight, a series of primary, secondary and tertiary haloalkanes were found to be compatible with this system (**7e–7g**). In addition, benzyl halides also produced the allyl alcohols **7h** in moderate to high yields. In



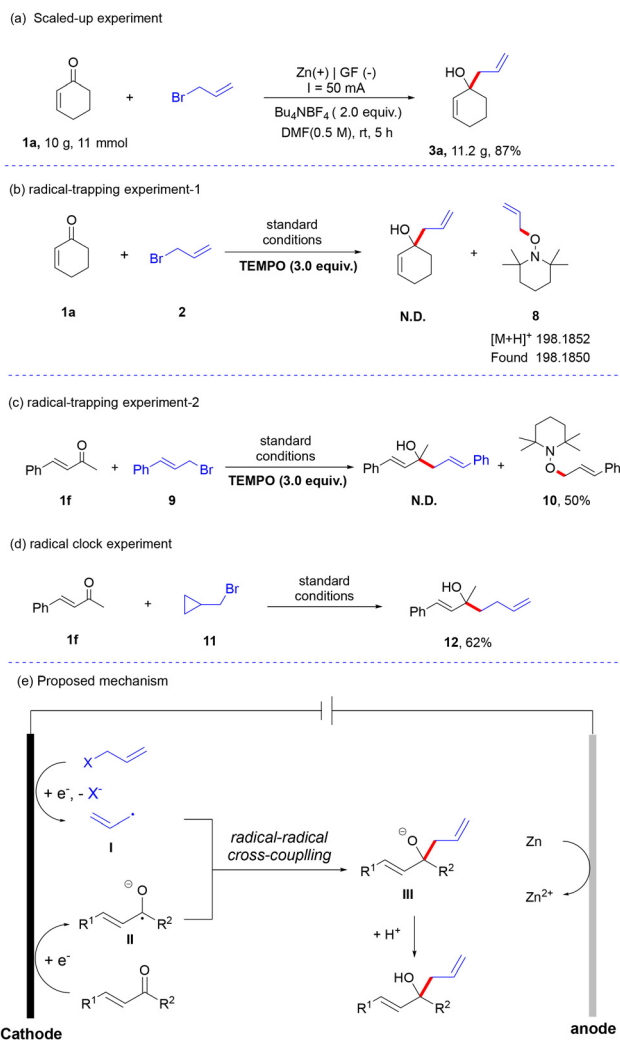
Scheme 3 Scope of α,β -unsaturated aldehydes. Reaction conditions: undivided cell, zinc rod as anode, **4** (0.5 mmol), **2** (1.5 mmol), Bu_4NBF_4 (0.5 mmol), DMF (5.0 mL), constant current = 15.0 mA, 2–6 h. Isolated yield.



Scheme 4 Scope of allyl and alkyl halides. Reaction conditions: undivided cell, zinc rod as anode, **1f** (0.5 mmol), **6** (1.5 mmol), Bu_4NBF_4 (0.5 mmol), DMF (5.0 mL), constant current = 15.0 mA, 2–6 h. Isolated yield.

the case of **6d** and **6h**, different halides such as Cl, Br and I were evaluated to compare their reactivity. From these data, the following reactivity trend was established: (1) the reactivity follows the order RI > RBr > RCl; and (2) the reactivity trend of alkyl halides is $3^\circ > 2^\circ > 1^\circ$.

To verify the scalability of this system, we conducted a scale-up experiment. As shown in Scheme 5a, under the optimal reaction conditions, 10 grams of 2-cyclohexen-1-one (**1a**) reacted with allyl bromide (**2**) and produced the target product **3a** in an isolated yield of 87%. Finally, we performed a set of mechanistic investigations. First, we performed radical trapping experiments (Scheme 5b). 2,2,6,6-Tetramethyl-1-piperidinyloxy (TEMPO) completely suppressed the reductive allylation processes, and product **3a** was not detected. Instead, two TEMPO-trapped products (**8** and **10**) were observed and identified by high-resolution mass spectrometry (HRMS). When cinnamyl bromide (**9**) was used as the allylation reagent, we successfully isolated the radical adduct **10** in 50% yield (Scheme 5c). Next, a radical clock experiment was carried out and the ring-opening product **12** was isolated in 62% yield (Scheme 5d). Based on the results obtained above, we proposed a possible mechanism for this reaction (Scheme 5e). The allyl halide is first reduced at the cathode surface to form the allyl radical (**I**), which is a transient radical. This radical readily undergoes resonance to form a more stable radical. At the same time, the enone is also reduced at the cathode to



Scheme 5 Scale-up experiments, mechanistic studies and the suggested mechanism.

form the radical anion **II**, which is a persistent radical. Radical **II** does not readily undergo resonance because the lone pair electrons on the oxygen atom stabilize the adjacent carbon-centered radical more than the π electrons of the carbon-carbon double bond. Subsequently, cross coupling of these two radicals produces an anion (**III**), which undergoes protonation to afford the final product. The anodic half-reaction involves the oxidation of Zn to Zn^{2+} .

In summary, we have developed a reductive allylation and alkylation of α,β -unsaturated aldehydes and ketones with allyl/alkyl halides in an undivided cell. This method features high reaction yields, a broad substrate scope, good functional group tolerance (with non-conjugated carbonyl groups remaining intact), scalability to gram-scale production and mild conditions.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information is available. See DOI: <https://doi.org/10.1039/d5qo01168j>.

Acknowledgements

This project was supported by the National Natural Science Foundation of China (No. 22371129) and the Science Foundation of Jiangsu Province (No. BK 20220463).

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