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Iron-mediated reactions of gem-dihaloalkanes with α,β-unsaturated carbonyl compounds

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The ability to harness divergent reactivity and selectively dictate product outcomes from simple precursors has been a longstanding challenge in organic chemistry, especially in radical chemistry. Herein, we developed a sustainable reaction model leveraging earth-abundant iron as a reductant and gem-dihaloalkanes as radical donors to convert commodity α,β-unsaturated compounds into β,γ-unsaturated compounds or cyclopropanes in a tunable manner. The formation of the former involves unusual radical-mediated 1,2-acyl migrations and the generation of the latter involves an intramolecular radical–radical coupling. Moreover, the chemoselectivity could be effectively controlled by the solvent effects. This study not only provides a practical platform for synthesizing functionalized building blocks but also unlocks novel reactivity modes for gem-dihaloalkanes, positioning them as key tools for sustainable radical-involved transformations.

Introduction

The selective manipulation of divergent reactivity from simple starting materials to access structurally distinct molecular scaffolds represents one of the most enduring challenges in organic synthesis. Radical-mediated transformations offer unparalleled versatility in skeletal remodelling, enabling the construction of complex molecular architectures from readily available precursors.[1–7] Gem-dihaloalkanes are attractive synthons in synthetic chemistry, as they are not only readily available and inexpensive bulk chemicals but also excellent precursors for carbenes and two mono-radicals, among which their application as carbene precursors has been well-developed, while their use as two mono-radical donor precursors remains relatively underdeveloped.

On the one hand, radical-mediated acyl migrations have emerged as a powerful strategy for carbon–carbon bond reorganization. Despite their synthetic utility, radical-mediated 1,2-acyl migrations, exemplified by the classic Dowd–Beckwith reaction, are predominantly restricted to cyclic ketone substrates.[8–12] In contrast, flexible linear analogues often lack the conformational rigidity required for efficient radical cyclization, necessitating the formation of strained three-membered ring intermediates that are prone to unproductive fragmentation or intermolecular side reactions, ultimately leading to low yields and undesired byproducts (Fig. 1a).[13]

To date, there have been few reported cases of radical-mediated 1,2-carbonyl migrations in linear systems. Furthermore, these limited examples are restricted to the specialized 1,2-formyl migrations of β,γ-unsaturated enals.[14–16] Therefore, the development of 1,2-acyl migration methods for linear substrates is highly desirable, especially for the challenging task of constructing β,γ-unsaturated enals *via* a reverse process.

On the other hand, cyclopropane motifs are ubiquitous in medicinal chemistry and drug discovery, representing one of the most prevalent ring systems in biologically active compounds (Fig. 1b).[17] The Simmons–Smith reaction has long served as a classic and fundamental method for the construction of cyclopropanes.[18–20] Nevertheless, it relies on strict operating conditions and potentially hazardous zinc–copper couple reagents, and usually requires relatively electron-rich alkenes.[21,22] Moreover, these carbenoid intermediates are incompatible with polar or protic solvents, further limiting their application potential.[23] The newly developed cyclopropanation reactions in recent years have made remarkable progress in overcoming these inherent limitations.[24–30] Despite these advances, these strategies still rely on the combined mode of complex transition metal catalysts and stoichiometric reducing agents, which increases reaction costs and limits scalability (Fig. 1c). Thus, the development of a simplified and cost-effective method remains a critical requirement.

Herein, we report a tunable reaction model that uses earth-abundant, non-noble iron as a reductant and gem-dihaloalkanes as two mono-radical donors to achieve either 1,2-acyl migration or cyclopropanation of simple linear α,β-

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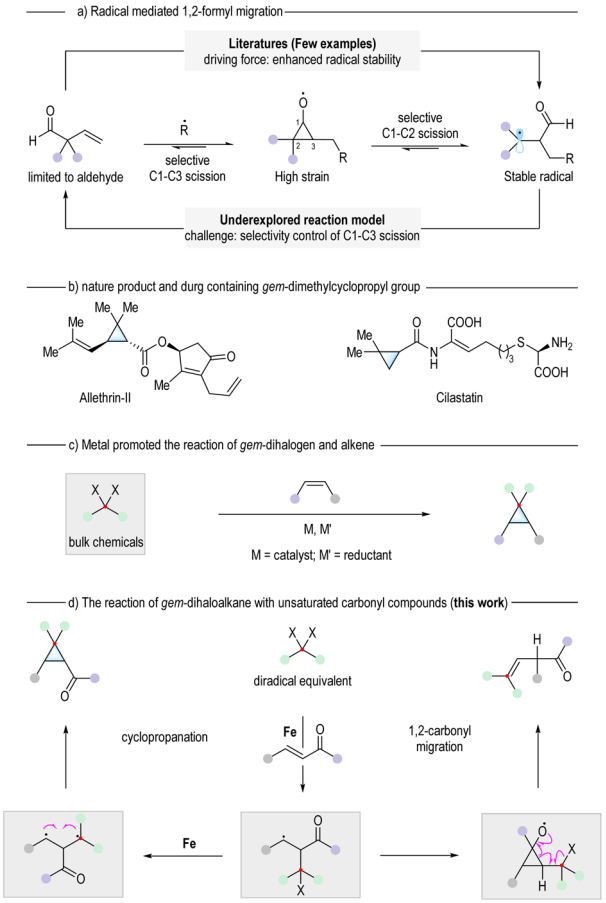


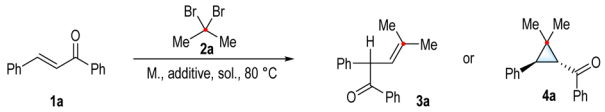
Fig. 1 Background and our proposal.

unsaturated compounds under distinct reaction conditions (Fig. 1d). It is worth noting that the current radical 1,2-acyl migration proceeds with an unprecedented reverse process to construct β,γ-unsaturated carbonyl compounds rather than using them as substrates, and cyclopropanation involves an intramolecular two mono-radical coupling rather than *via* a carbenoid intermediate. This approach will build on foundational work in radical-mediated acyl migrations and cyclopropanations by using only a simple reductant to unlock novel reactivity modes for gem-dihaloalkanes.

Results and discussion

To implement this method, we initially selected chalcone **1a** and 2,2-dibromopropane **2a** as the model substrates to evaluate a range of earth-abundant metals such as Zn, Mn, In, and Fe as single-electron reductants. Among them, we were pleased to observe successful reactions by using iron powder (entries 1–4). The desired 1,2-acyl migration product **3a** (ref. 31) and cyclopropanation product **4a** (ref. 32) were afforded by treating **1a** and **2a** with iron powder in toluene at 80 °C (entry 4). To our delight, when LiCl was used as an additive, the reaction yield of **3a** could be effectively improved to 67% (entry 5). To further elevate the yield and selectivity, a variety of solvents were investigated (Table 1).

Table 1 Condition screening[a]



Entry	M	Solvent	Additive	Yield[b] **3a**/**4a** (%)
1	Zn	PhMe	None	N.D.
2	Mn	PhMe	None	N.D.
3	In	PhMe	None	N.D.
4	Fe	PhMe	None	12/<5
5	Fe	PhMe	LiCl	67/20
6	Fe	ACN	LiCl	46/28
7	Fe	THF	LiCl	61/20
8	Fe	DME	LiCl	75/22
9	Fe	H_2O	LiCl	0/43
10	Fe	ACN/H_2O[c]	LiCl	0/36
11	Fe	EtOH/H_2O[c]	LiCl	0/74

[a] All reactions were conducted using **1a** (0.2 mmol, 1.0 equiv.), **2a** (0.6 mmol, 3.0 equiv.), additive (0.6 mmol, 3.0 equiv.) and metal (0.6 mmol, 3.0 equiv.) in solvent (2.0 mL). [b] Isolated yield. [c] Ratio is 10 : 1. N.D. is not detected.

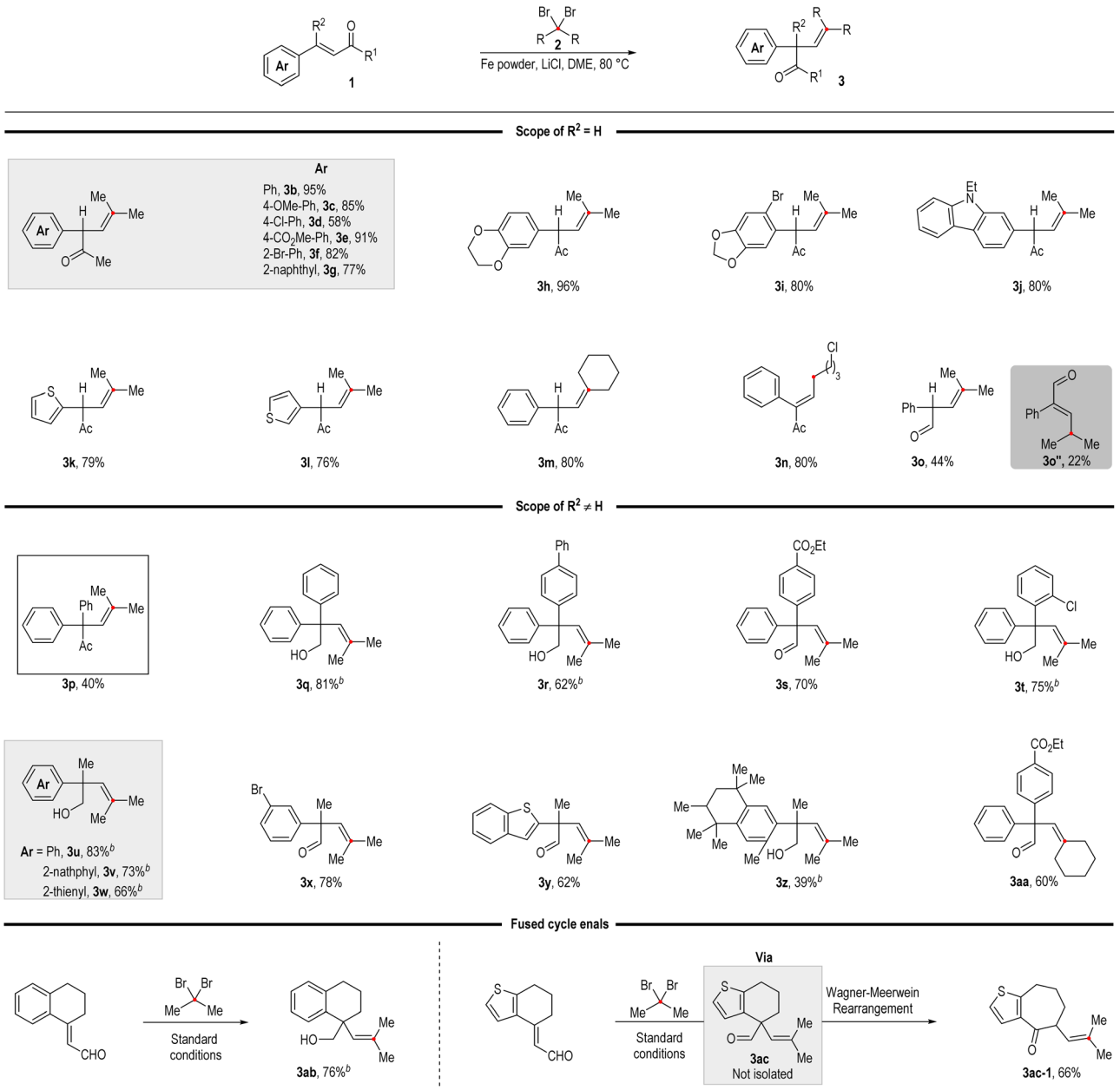
These results revealed that 1,2-dimethoxyethane (DME) significantly outperformed other solvents, improving the yield of **3a** to 75% (entries 6–8). Delightfully, when employing water as a solvent, selectivity was reversed to give only product **4a**. Moreover, when using ethanol/water as the mixed solvent, the yield of product **4a** could be increased to 74% (entry 11).

With the optimized reaction conditions established, we systematically investigated the substrate scope of the 1,2-acyl migration reaction (Scheme 1). First, we tried to replace the benzoyl group with an acetyl group. Surprisingly, the cyclopropanation product was completely suppressed, while the rearrangement product **3b** could be obtained in 95% yield.

In contrast, replacing it with a *tert*-butyl group resulted in no rearrangement product being observed. Then, the various aryl substitutions, including *p*-methoxy (**3c**), *p*-chlorine (**3d**), *p*-ester (**3e**) and *o*-bromo (**3f**) phenyl groups, at the β-position of unsaturated ketone, were found to be readily accommodated. Beyond that, a variety of aromatic rings (**3g–3l**) which occupied the β-position were tested, generating the target products in good to high yields.

To diversify the scope of β,γ-unsaturated ketone, other geminal dihalides were also employed in this reaction. When the cyclohexyl geminal dihalide was subjected to this protocol, the desired product **3m** was produced in 80% yield. More importantly, gem-dihalide bearing alkyl chloride was examined and the rearrangement product **3n** could be afforded in 80% yield with the alkyl chloride preserved. However, alkyl geminal dihalides cannot be replaced by benzyl geminal dihalides, because they would rapidly dimerize, resulting in no rearrangement product being observed.

The retention of the alkyl chloride can be attributed to the higher bond dissociation energy and lower reduction potential of the monoalkyl halide relative to the gem-dihalide.[33] Having



Scheme 1 Scope of β,γ-unsaturated ketone or aldehyde. [a] All reactions of α,β-unsaturated ketone or aldehyde **1** (0.2 mmol, 1.0 equiv.), gem-dihaloalkanes **2** (0.6 mmol, 3.0 equiv.), LiCl (0.6 mmol, 3.0 equiv.), and iron powder (0.6 mmol, 3.0 equiv.) were stirred in dry DME (2.0 mL) at 80 °C. [b] The aldehyde was reduced by using DIBAL-H as the reductant.

established the reactivity of ketones, we then extended the investigation to aldehyde analogues. Fortunately, the corresponding product **3o** could be obtained in 44% yield. The low yield may be due to its instability toward olefin isomerization, allowing **3o″** to be isolated in 22% yield. The construction of quaternary carbon centers especially with three or even four sp^2-carbons poses significant challenges.[34,35] Notably, our strategy demonstrates promising potential for accessing such structure units. To pursue the synthesis of quaternary carbon centers with four sp^2-carbons, β,β-diaryl substituted enones and enal were investigated and the products **3p–3t** were afforded in moderate to high yields.

Furthermore, for constructing quaternary carbon centers with three sp^2-carbons, β-methyl-β-aryl group substituted α,β-unsaturated aldehydes were prepared and tested, which afforded products **3u–3y** in good yields. Importantly, tonalide is a highly renowned and extensively utilized synthetic musk species in the fragrance industry,[36] and product **3z** featuring the tonalide core scaffold was successfully obtained in 39% yield, which underscored the promise of the methodology for synthetic modification in fragrance materials development. (Some products such as **3q**, **3r**, **3t–3w**, **3z**, and **3ab** were reduced with DIBAL-H due to their tendency to decompose).

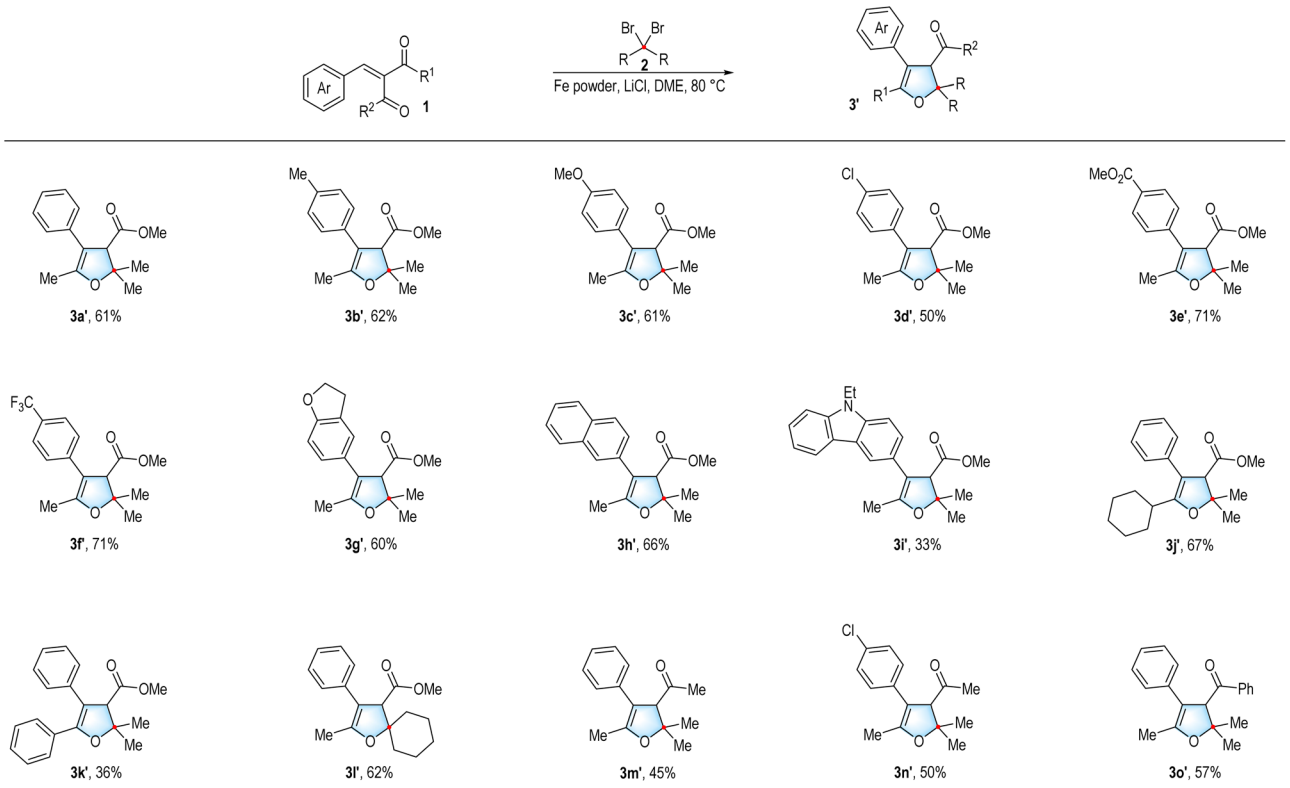
Of note, gem-dihalide was not limited to 2,2-dibromopropane and replacement of it with cyclohexyl gem-dihalides still led to smooth reaction progression, affording product **3aa** in 60% yield under the standard condition. When phenyl-fused cyclohexyl enal was investigated, it underwent successful transformation to the corresponding product **3ab** in 76% yield. Notably, the thienyl-fused cyclohexyl enal afforded the ring-expanded product (**3ac-1**) in 66% yield. This outcome might be attributed to the enhanced electron richness of the thiophene ring relative to the benzene ring, which facilitated the Wagner–Meerwein rearrangement of **3ac** catalyzed by $FeBr_2$ as the Lewis acid.

Subsequently, to further explore the substrate scope, we envisaged installing a group at the α-position of unsaturated ketone **1**. Interestingly, after introducing an ester group at this position, a dihydrofuran product **3a′** was constructed in of 61% yield under standard conditions. Given the pharmaceutical importance of dihydrofuran derivatives,[37] we studied the generality of the cascade sequence, as shown in Scheme 2. Various β-substituted enones with an α-ester substituent reacted well, yielding the desired products **3b′** to **3f′** in moderate to good yields. Furthermore, several β-aryl substituted enones were also compatible, furnishing the corresponding products **3g′–3i′** in good yields.

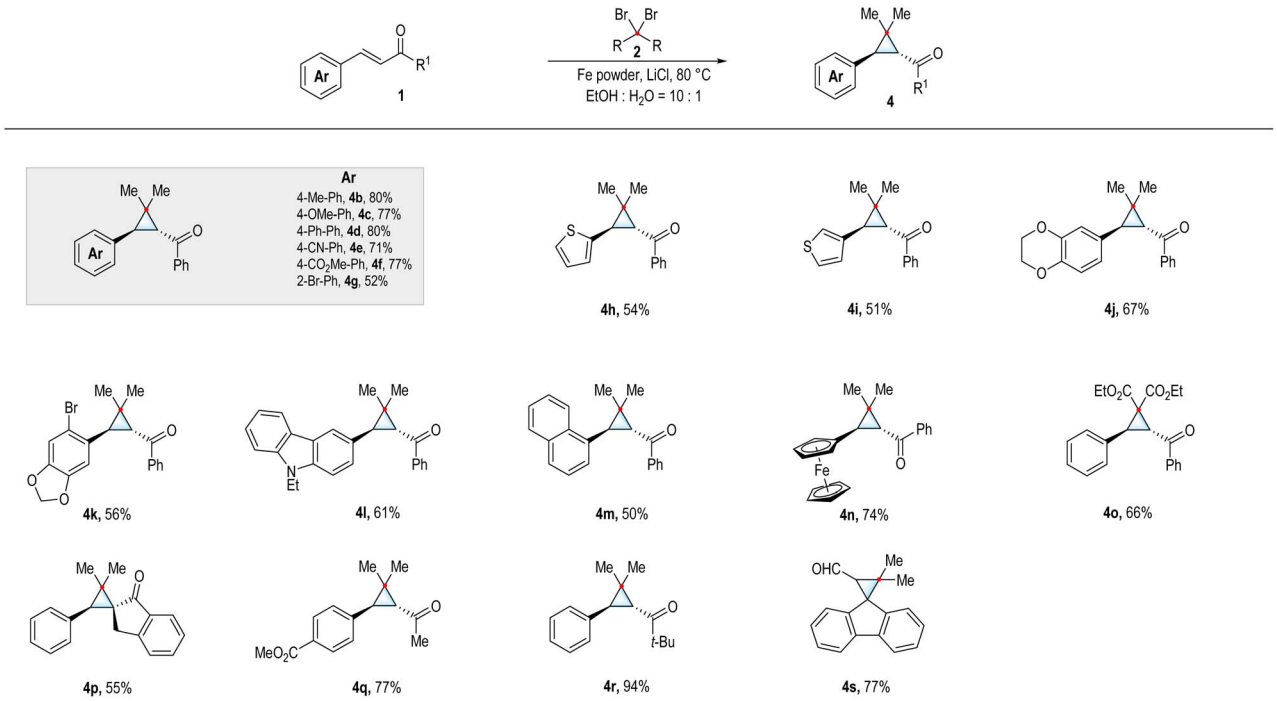
Additionally, to further evaluate functional group tolerance, both cyclohexyl ketone and aryl ketone were examined, affording the expected products **3j′** and **3k′** in 67% and 36% yields, respectively. Meanwhile, a cyclohexyl geminal dihalide could also be used in place of 2,2-dibromopropane, affording the spirocyclic product **3l′** in 62% yield. Besides, the 1,3-diketone consistent of enone also delivered the expected products (**3m′–3o′**) in moderate to good yields. Nevertheless, after installing cyano and aldehyde groups at the α-position of α,β-unsaturated compounds, the reactions resulted in a complex mixture and the desired product could not be observed. Next, we studied the scope of the cyclopropanation reaction under the standard condition as shown in Scheme 3. A series of electronically dissimilar α,β-unsaturated compounds were tested. Various substituents on the benzene rings at the chalcone β-position (**4b–4g**) were well tolerated.

In addition, enones with heterocyclic, fused aromatic, or ferrocenyl substituents at the β-carbon proved to be effective substrates in the reaction (**4h–4n**). Specifically, gem-dihaloalkane could be replaced with dibromomalonates, providing the desired **4o** in 66% yield. Remarkably, with the goal of synthesizing a pentasubstituted cyclopropane, we attempted to employ the cyclic enone, resulting in the smooth formation of the spirocyclic product **4p** in acceptable yield. Moreover, alkyl ketones were tested under this condition, affording the expected products **4q** and **4r** in 77% and 94% yields, respectively. Finally, β,β-disubstituted enal was employed as a substrate and product **4s** was successfully obtained in 77% yield.

To validate the scalability and practicality of the developed protocols, gram–scale reactions and synthetic transformations were further conducted (Scheme 4). The syntheses of **3b**, **3a′** and



Scheme 2 Scope of the dihydrofuran derivative. [a] All reactions of enone **1** (0.2 mmol, 1.0 equiv.), gem-dihaloalkanes **2** (0.6 mmol, 3.0 equiv.), LiCl (0.6 mmol, 3.0 equiv.), and iron powder (0.6 mmol, 3.0 equiv.) were stirred at 80 °C in dry DME (2.0 mL).



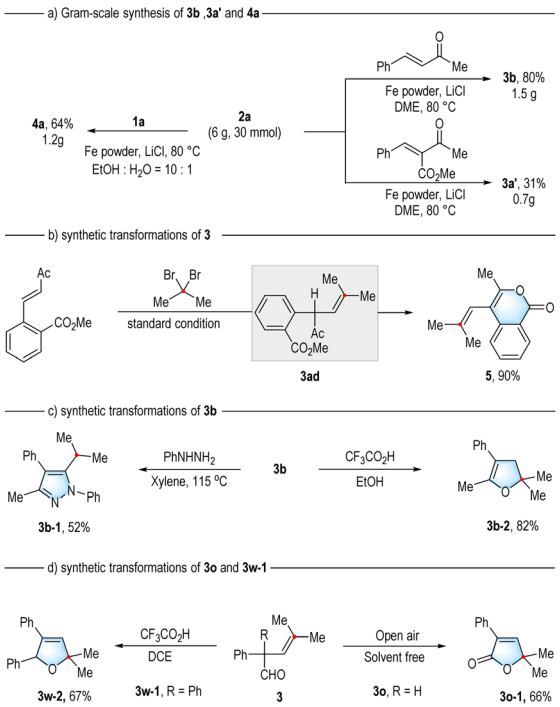
Scheme 3 Scope of the cyclopropane derivative. [a] All reactions of enone **1** (0.2 mmol, 1.0 equiv.), gem-dihaloalkanes **2** (0.6 mmol, 3.0 equiv.), LiCl (0.6 mmol, 3.0 equiv.), and iron powder (0.6 mmol, 3.0 equiv.) were stirred at 80 °C in ethanol (2.0 mL) and water (0.2 mL).

4a were on a 10 mmol scale, affording the target products **3b**, **3a′**, and **4a** in 80%, 31% and 64% yields, respectively (Scheme 4a). β,γ-unsaturated compounds are valuable. Herein, we demonstrated several effective transformations of our reaction products into heterocycles that are highly valuable scaffolds in drug discovery.[38,39] As shown in Scheme 4b, the compound **3ad** may further undergo an ester exchange of enol generated from an acetyl group *in situ*, affording the isocoumarin derivative **5** in 90% yield. Simultaneously, pyrazole derivative **3b-1** was obtained from **3b** and phenylhydrazine *via* olefin isomerization/6π-electrocyclization. Alternatively, **3b** could be converted into the dihydrofuran derivative **3b-2** *via* enol isomerization/intramolecular *oxa*-alkylation prompted by trifluoroacetic acid.

Encouraged by our recent research on acid promoted 1,2-migration of the aryl group of β,γ-unsaturated aldehyde,[40] we sought to investigate whether this reaction could be applicable to the current substrate. Fortunately, acid promoted a *retro*-semipinacol rearrangement of **3w-1** to afford a stable carbocation which would further undergo an oxygen alkylation, forming the final dihydrofuran derivative **3w-2**. Likewise, γ-lactones comprise a structural moiety frequently present in biologically active natural products.[41] Significantly, β,γ-unsaturated aldehydes **3o** could be smoothly transformed into γ-butyrolactones **3o-1** incorporating *gem*-dimethyl substituted quaternary carbon in open air.[42]

In general, the transformation process demonstrates remarkable efficiency and selectivity, highlighting the potential of these compounds in synthetic chemistry. The structural diversity achieved through these efficient transformations offers new avenues for drug development, particularly in constructing complex molecule skeletons containing gem-dimethyl groups.

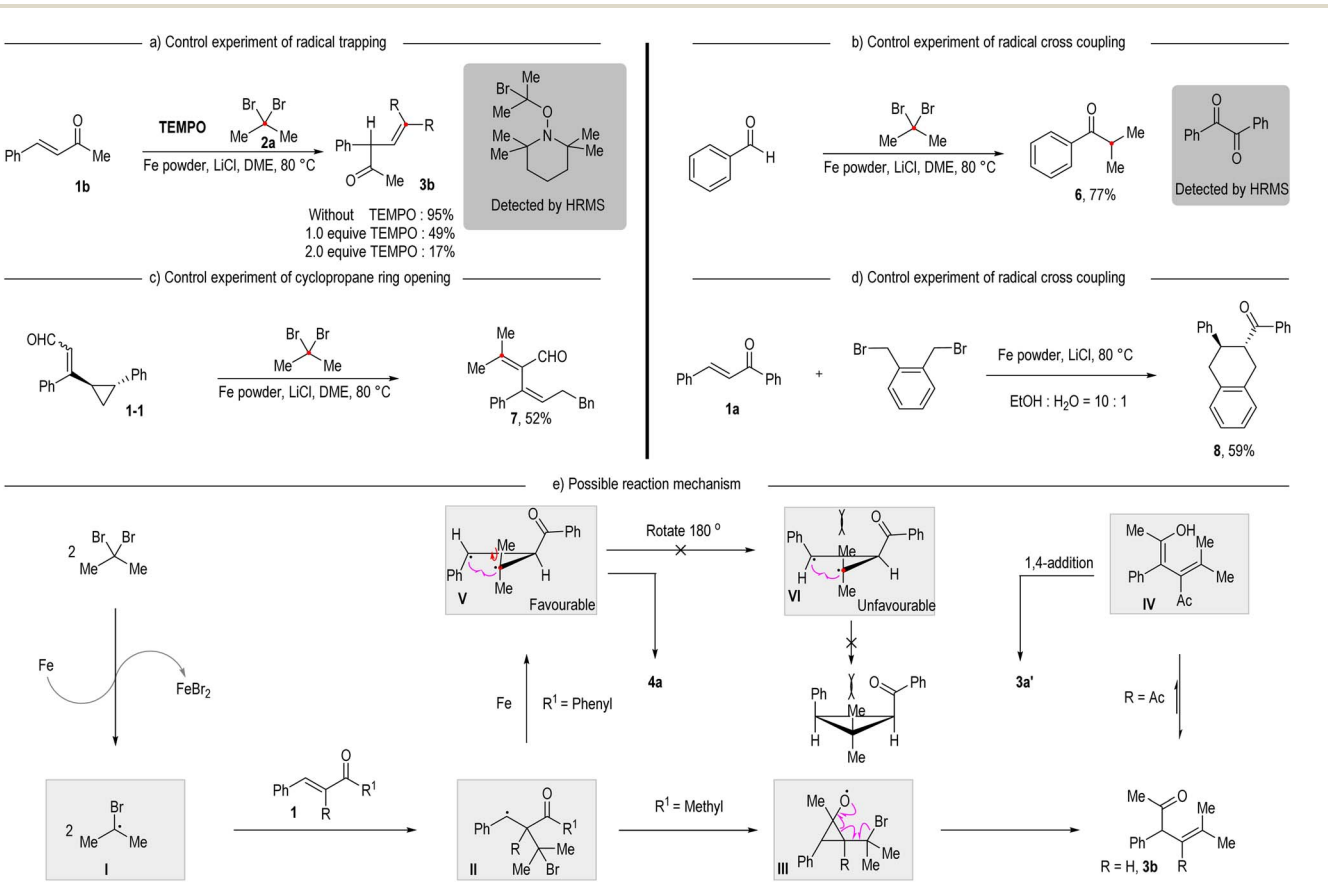
Subsequently, we conducted some control experiments to further investigate the reaction pathway. Initially, we performed



Scheme 4 Scale up synthesis and synthetic transformations.

a control reaction with TEMPO to probe for the formation of the $\cdot CBr(CH_3)_2$ radical. For our model system of acyl migration, increasing concentrations of TEMPO decreased the formation of rearrangement product **3b**, and HRMS analysis of the reaction mixture identified the formation of the TEMPO-$CBr(CH_3)_2$ adduct, supporting the formation of $\cdot CBr(CH_3)_2$ radicals (intermediate I) under our reaction conditions. To further verify the plausibility, a cross coupling experiment of an acyl radical and isopropyl radical was designed and conducted. Pleasingly, when we subjected 2,2-dibromopropane to benzaldehyde under optimized conditions, it led to the expected ketone **6** as the isolated product and bimolecular termination product of an acyl radical could detected by HRMS. (For a proposed mechanistic scheme, please see the SI). This sequence provides supplementary evidence for the existence of an acyl radical and isopropyl radical. Next, radical probes were evaluated. α,β-unsaturated aldehyde contains a 2-aryl-cyclopropyl moiety at the β-position of **1-1**, which could be used as a radical clock coupling partner.[43,44] The reaction of β-phenylcyclopropyl alkenal gave the ring-opening product **7** under the standard condition. This result suggests that the transformation might involve a radical pathway and the radical might initially undergo addition at the α-position of α,β-unsaturated carbonyl compounds (intermediate II). Additionally, when 1,2-bis(bromomethyl)benzene was used as the substrate instead of a gem-dihalide, the cyclization reaction still took place, leading to the formation of a dihydronaphthalene derivative **8** in 59% yield, which supports the formation of the key two mono-radical intermediate V.

According to the results of the above control experiments, a plausible reaction mechanism is illustrated in Scheme 5. Initially, tertiary free radical species I was generated from 2,2-dibromopropane under promotion of iron powder. Then, the intermediate I underwent an addition reaction at the α-position of the α,β-unsaturated ketone to form more stable benzyl radical II that might proceed through two distinct reaction pathways. On the one hand, within polar solvents, the radical could be stabilized due to an increased weighting of zwitterionic canonical contributors within the resonance description.[45] The stabilized radical would be more favorable for a subsequent cyclization process. After another radical was formed by homolytic cleavage of the C–Br bond, two radicals were directly coupled to generate the cyclopropane **4a**. On the other hand, the radical would mainly attack the carbonyl group to form cyclopropanyl oxygen radical III. Subsequently, a radical initiated Grob fragmentation delivers β,γ-unsaturated product **3b**. Notably, when the substituent (R) at the α-position of unsaturated ketones was an electron-withdrawing group, the product tended to undergo enolization, followed by an *oxa*-Michael reaction to form a dihydrofuran product **3a′** bearing gem-dimethyl-substituted quaternary carbon.



Scheme 5 Control experiments and the proposed mechanism.

Conclusions

In conclusion, we reported radical-mediated 1,2-acyl migrations of linear α,β-unsaturated ketone to generate the β,γ-unsaturated ketone. When electron-withdrawing groups were present at the α-position of α,β-unsaturated ketone, the product could form a dihydrofuran bearing gem-dimethyl-substituted quaternary carbon center. This strategy enables the direct conversion of commercial raw materials into high-value compounds, including β,γ-unsaturated compounds, dihydrofuran and cyclopropane. Rooted in foundational radical-mediated acyl migration chemistry, it pioneers new synthetic routes to versatile building blocks. We foresaw the versatility of this protocol expanding considerably across diverse facets of synthetic chemistry.

Author contributions

Guangshen Wang: writing – original draft, conceptualization, investigation, methodology, data curation. Baosheng Li: funding acquisition, resources, project administration, supervision, writing – review & editing. The others: validation and providing resources.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data that support the findings of this study are available in the supplementary information (SI) of this article. Supplementary information: experimental procedures, mechanistic studies and data analysis, and characterization data and spectra of all new compounds. See DOI: https://doi.org/10.1039/d6sc01614f.

Acknowledgements

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