ChemComm

FEATURE ARTICLE

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Cite this: *Chem. Commun.*, 2025, **61**, 18327

Carbon monoxide as the key: carbonylation triggered (hetero)aryl migration transformations

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This review summarizes recent advances in carbonylative functionalization strategies enabled by free radical mediated carbon monoxide (CO) insertion, with a focus on its role in facilitating carbon chain elongation and activating challenging allylic alcohol substrates *via* radical-mediated migration reactions. The article systematically discusses a range of radical triggers-including CF_3, diazo-derived, oxygen-centered, trifluoromethylthio, alkoxycarbonyl, phosphinyl, nitrogen-centered, cobalt-hydride, and hydrogen-bonding-assisted species-that promote intermolecular and intramolecular functional group migrations under mild conditions. Key to these transformations is the synergistic interplay between CO insertion and migration events, which collectively enable remote aryl or heteroaryl transfer to carbonyl carbons, yielding valuable 1,4-dicarbonyl compounds, lactones, and other functionalized scaffolds. The review also highlights mechanistic insights, substrate adaptability, and the ability to overcome traditional limitations in selectivity and reactivity. Despite significant progress, challenges remain in expanding migration scope, simplifying substrate design, and achieving asymmetric catalysis. This work aims to inspire further innovation in CO-mediated synthetic methodologies.

Received 6th October 2025,
Accepted 28th October 2025

DOI: 10.1039/d5cc05720e

rsc.li/chemcomm

1. Introduction

Compounds containing carbonyl groups are regarded as "privileged scaffolds" in synthetic chemistry due to their diverse reactive sites and ease of modification. They are widely used in the construction of various functional molecules. As an important class of such structures, 1,4-diketones often serve as key precursors for the synthesis of diverse biologically active molecules, such as pyrroles, furans, thiophenes, diols, diamines, and cyclopentenones.[1] These structural motifs are also widely found in natural products, as exemplified by herquline A, amphidinolide F, and among others.[2] Furthermore, heteroarenes are also prevalent in natural products, pharmaceuticals,

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Xiao-Feng Wu

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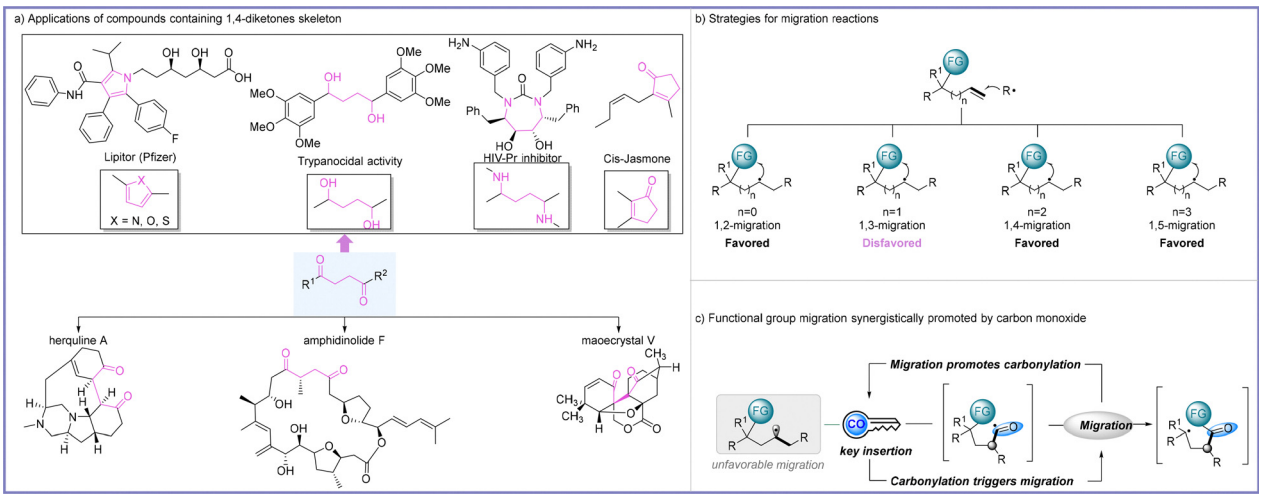
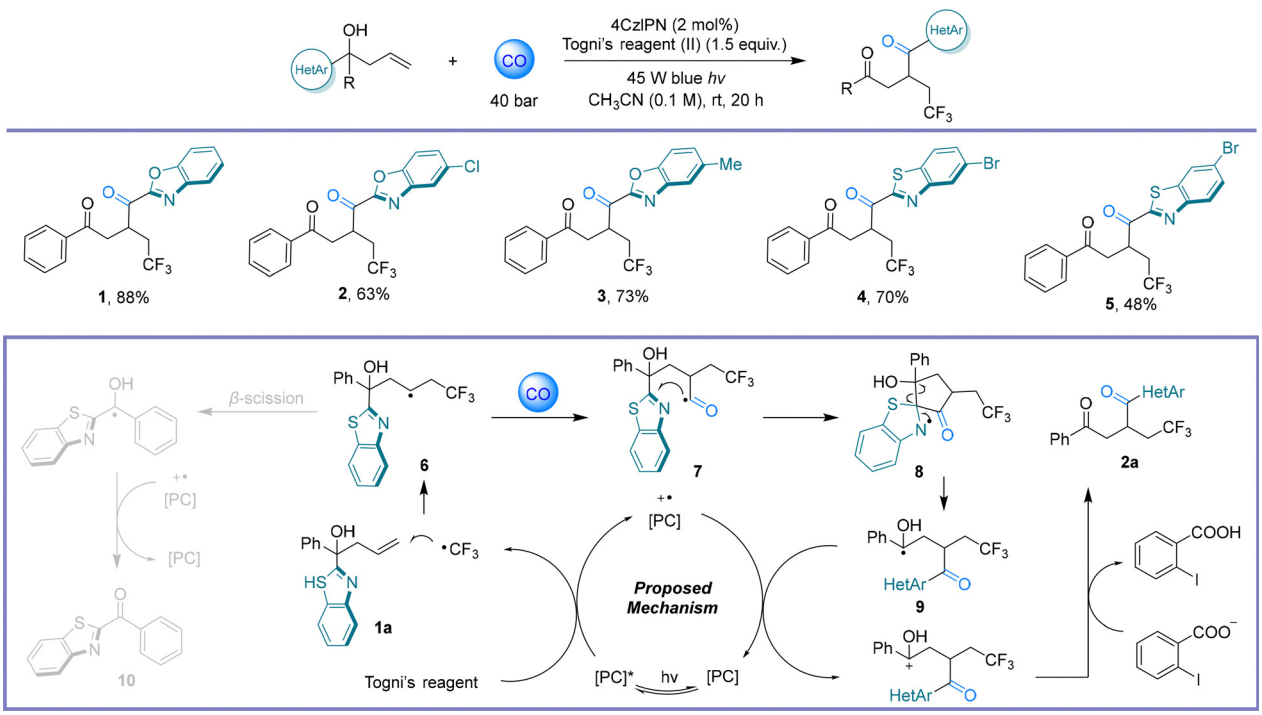


Fig. 1 (a) Applications of compounds containing 1,4-diketones skeleton. (b) Strategies for migration reactions. (c) Functional group migration synergistically promoted by carbon monoxide.

and various synthetic compounds.[3] The construction of heteroaryl architectures has long been an important research direction in synthetic chemistry (Fig. 1a). Over the past century, significant progress has been made in this field, with synthetic strategies primarily relying on classical methods such as transition-metal-catalyzed cross-coupling,[4] nucleophilic addition,[5] and Friedel–Crafts reactions.[6] In recent years, with the rapid development of radical chemistry, this strategy has increasingly become a highly efficient and reliable approach for the synthesis of complex molecules.

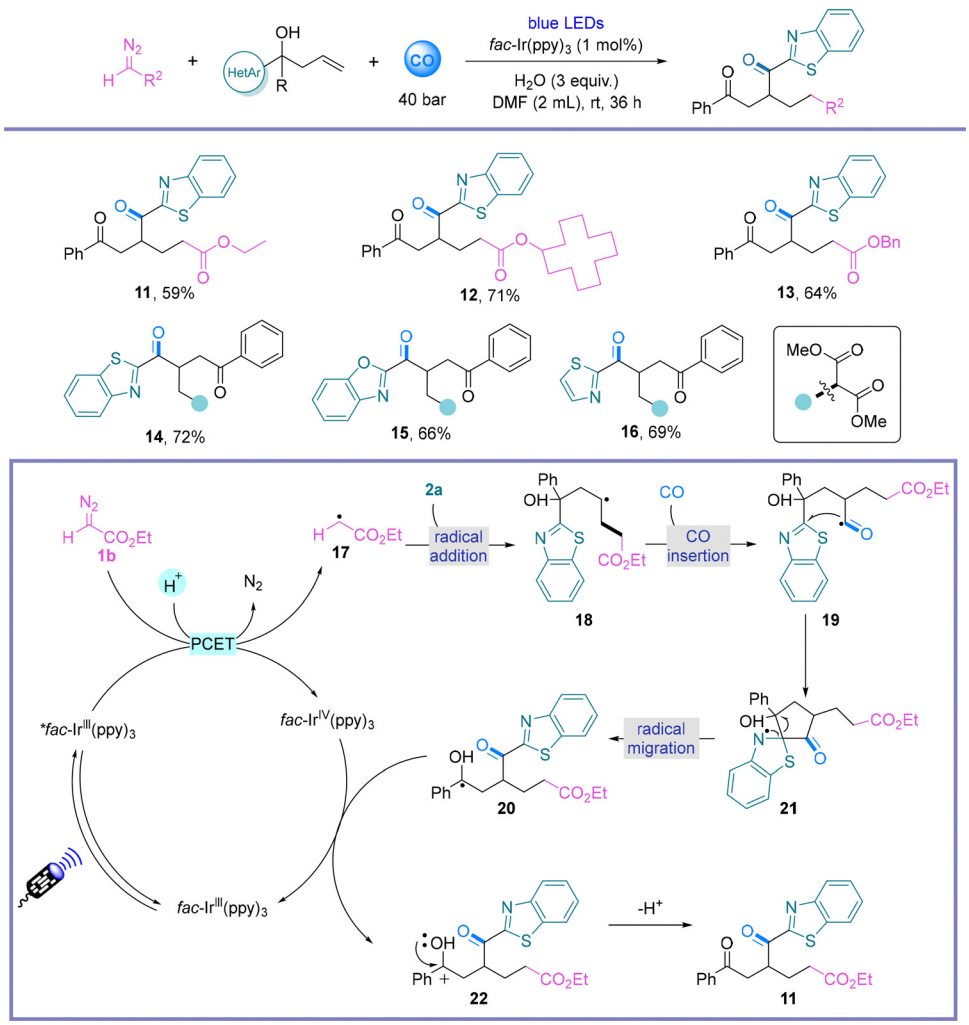
Rearrangement reactions, which enable the precise introduction of specific functional groups into target molecules through controlled bond cleavage and reorganization, represent a class of highly important transformations in organic synthesis. Over the past century, research on rearrangement reactions has continued to evolve; however, progress in radical-mediated rearrangements has been relatively slow due to the high reactivity and uncontrolled nature of radical intermediates. Since Wieland's first report of a radical-mediated aryl migration in 1911, functional group migration (FGM) reactions have gradually gained attention.[7] Nevertheless, such reactions have long been limited by the narrow scope of migratable groups and short migration distances (*e.g.*, classical 1,2-aryl shifts), which restricted their broader application in synthesis.



Scheme 1 Migration triggered by CF_3 radicals.

In recent years, with continuous advances in radical chemistry, remarkable progress has been made in remote functional group migration strategies.[8] These transformations typically involve three key steps: (1) generation of a radical intermediate at a distal site of the molecule; (2) migration of the functional group *via* a cyclic transition state, accompanied by bond cleavage and formation, resulting in a new radical species; and (3) interception and quenching of the newly formed radical. The efficiency of the overall process is influenced by multiple factors: the electronic nature of the migrating group directly affects the feasibility of migration; the change in state from the initially formed distal radical to the new radical after migration provides the driving force, while the distance between the two radical sites also critically determines the migration mode. 1,4- or 1,5-functional group migrations are kinetically favored, proceeding *via* five- or six-membered ring transition states, whereas 1,3- or 1,6-migrations through four- or seven-membered ring transition states are generally disfavored (Fig. 1b).

Carbon chain elongation represents one of the central strategies in organic synthesis.[9] Carbon monoxide (CO), as an inexpensive and readily available endogenous carbonyl source, is widely used in both industrial and academic research and is regarded as one of the most practical and efficient C1 synthons.[10] Since Roelen's first report of a well-defined carbonylative transformation in 1937, the application of CO in organic synthesis and industrial production has gradually evolved into a core research direction.[11] With continuous advances in methodologies such as transition metal catalysis,[12] visible-light photocatalysis,[13] and electrochemistry,[14] a variety of efficient carbonylative strategies have been developed for constructing carbonyl-containing molecular frameworks, and the mechanisms underlying these catalytic reactions have been progressively elucidated. Based on the unique electronic structure of CO, reactions involving CO can be broadly categorized into four types: (1) transition-metal-mediated oxidative addition yielding electrophilic acyl metal species;[15] (2) generation of acyl cations under strongly acidic conditions;[16] (3) formation of acyl anions in strongly basic environments;[17] and (4) capture of acyl intermediates generated *via* radical pathways.[18] From a methodological perspective, exploring novel transformation pathways for reactive carbonyl intermediates is of great significance, as these species can initiate new processes such as



Scheme 2 Migration triggered by diazo compounds.

the activation and transformation of inert reactants *via* carbonylative functionalization.

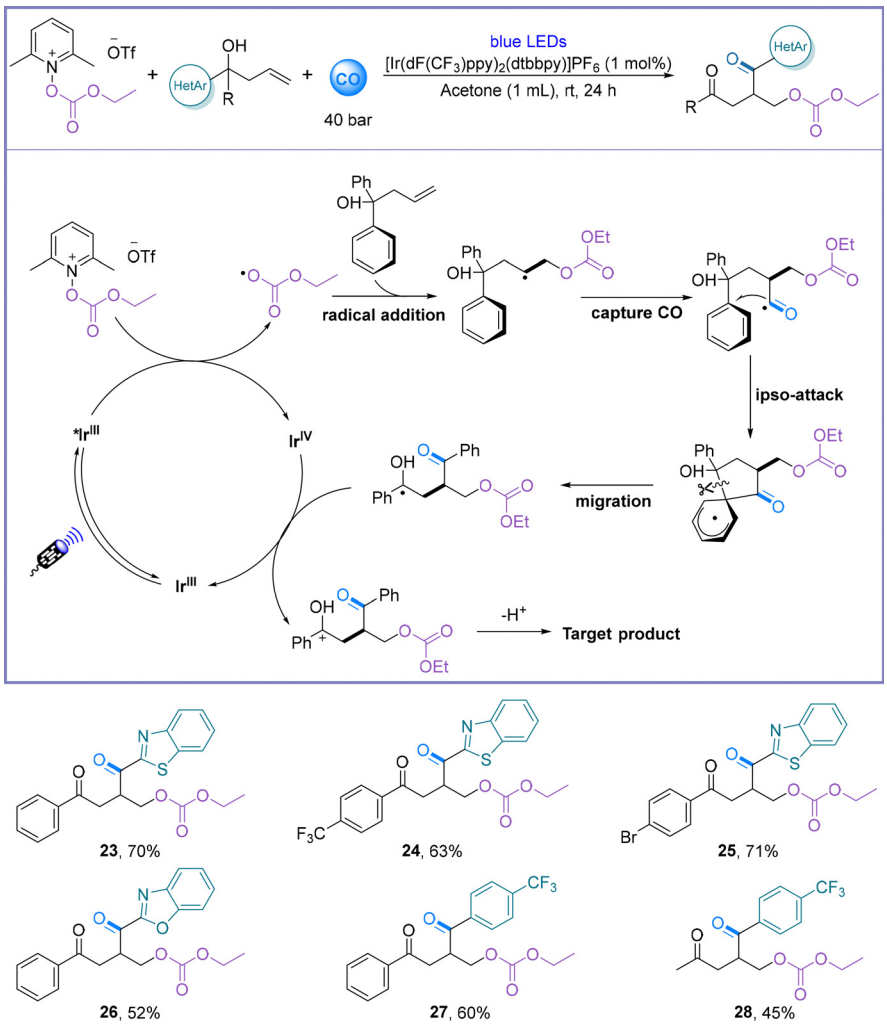
In this review, we summarize and discuss how the introduction of CO enables carbon chain elongation, unlocking transformations of otherwise challenging allylic alcohol skeletons *via* migration reactions, thereby fully demonstrating the role and significance of CO (Fig. 1c). The selective insertion of CO constructs a bridging pathway for functional group migration, while the migration process in turn facilitates efficient capture of CO by carbon radicals. The insertion and migration steps operate through a synergistically promoted mechanism, collectively driving the remote migration of aryl or heteroaryl groups to the carbonyl carbon. The content is divided into two parts: (1) intermolecular heteroaryl migration involving carbon monoxide (CO); and (2) intramolecular heteroaryl migration involving carbon monoxide (CO).

2. Intermolecular heteroaryl migration involving carbon monoxide (CO)

In recent years, significant progress has been made in controlling the chemoselectivity and regioselectivity of radical-based reactions. Radical-mediated difunctionalization of alkenes, as an efficient strategy for utilizing olefins, has attracted widespread attention in the chemical community.[19] Against this backdrop, the emergence of the intramolecular remote functional group migration (FGM) strategy has further broken through the limitations of traditional alkene difunctionalization, significantly expanding its reaction scope and synthetic potential.[20] In this section, we discuss the difunctionalization of alkenes for the synthesis of 1,4-dicarbonyl compounds *via* external radical attack, selective CO insertion, and subsequent heteroaryl group migration.

2.1. Migration triggered by CF_3 radicals

The combination of carbonylation and rearrangement reactions demonstrates unique synthetic value. Exploration in this direction offers the following key advantages: (1) the CO-involved chain-elongation strategy is expected to overcome the limitations of existing carbonylative transformations, expanding the scope and conceptual framework of their functionalization applications; (2) enabling (hetero)aryl migration in homoallylic alcohols provides a new pathway for introducing



Scheme 3 Migration triggered by oxygen-centered radicals.

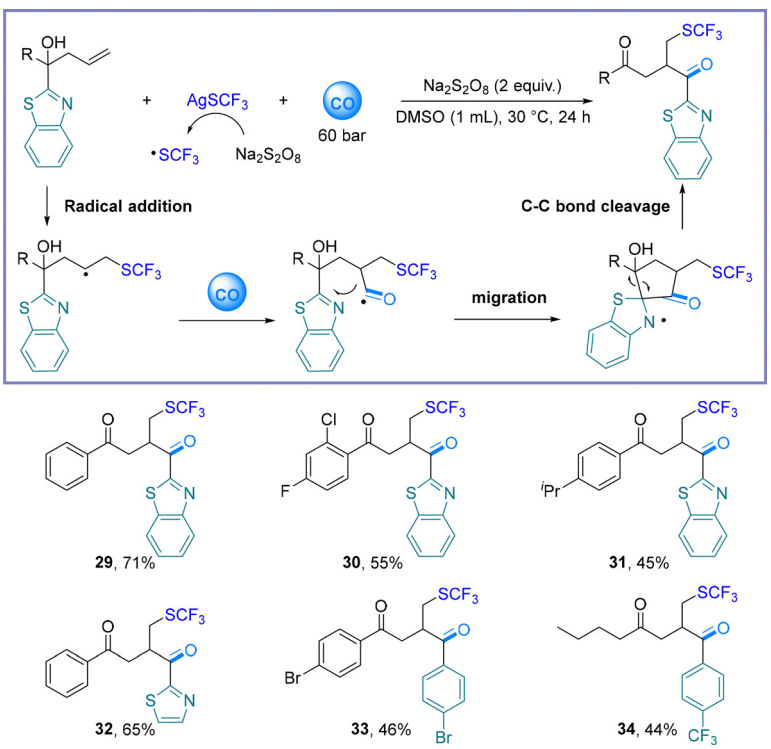
diaryl/heteroaryl groups to carbonyl carbon centers; (3) using CO as a carbonyl source allows the synthesis of 1,4-dicarbonyl compounds containing fluoroalkyl and heterocyclic motifs under milder conditions compared to conventional radical carbonylations. These products can be further transformed into bis(hetero)aryl structural units.[21] In 2024, Wu's team reported a visible-light-photocatalyzed radical relay carbonylative reaction enabling the migration of heteroaryl groups (Scheme 1).[22] This method employs CO as a C1 synthon, which inserts a carbonyl unit into the molecular framework to extend the carbon chain and facilitate the migration of a distal functional group. The strategy offers an efficient route for constructing 1,4-dicarbonyl skeletons bearing fluoroalkyl and heterocyclic motifs. Its broad functional group tolerance further highlights the practical utility of CO-based carbonylation in complex organic synthesis. Notably, the key insertion of CO significantly reduces the energy barrier of the cyclic transition state, enabling the migration transformation of previously challenging homoallylic alcohol substrates. Related mechanistic studies are described in Scheme 1.

2.2. Migration triggered by diazo compounds

Due to their high reactivity and broad applicability, diazo compounds are widely recognized as valuable carbene precursors under transition metal catalysis or direct photoexcitation.[23] In contrast, studies reporting diazo compounds as radical precursors remain relatively limited.[24] The conversion of diazo compounds into carbon radicals *via* a proton-coupled electron transfer (PCET) process could offer a promising solution.[25] In this context, Wu's team developed a mild and efficient method for heteroaryl migration and carbonylative functionalization of unactivated alkenes using carbon monoxide, enabling the synthesis of a diverse range of polycarbonyl compounds in good yields (Scheme 2).[26] In the proposed mechanism, the diazo compound is reduced by the excited-state photocatalyst and undergoes a proton-coupled electron transfer (PCET) process, releasing nitrogen gas to generate an alkyl radical **17**. This radical subsequently adds to the alkene, forming a new carbon-centered radical intermediate **18**, which then captures carbon monoxide and proceeds through the formation and cleavage of a cyclic transition state to afford intermediate **21**. Finally, the product **11** is obtained *via* an aryl migration quenching step.

2.3. Migration triggered by oxygen-centered radicals

The difunctionalization of alkenes holds significant value in synthetic chemistry. Although substantial progress has been made in carbonylative functionalization of alkenes—such as hydroformylation, borocarbonylation, polyfluoroalkylcarbonylation, and arylcarbonylation[27] their corresponding oxycarbonylation remains unreported. Oxygen-centered radicals, known for their high reactivity, have played a key role in organic transformations since their discovery.[28] The addition of such radicals to unsaturated systems is regarded as an efficient strategy for constructing new C–O bonds. In response to this challenge, in 2024, Wu and team members reported an oxygen-centered radical-mediated oxycarbonylation of unactivated alkenes using carbon monoxide (Scheme 3).[29] The reaction



Scheme 4 Migration triggered by trifluoromethylthio radical.

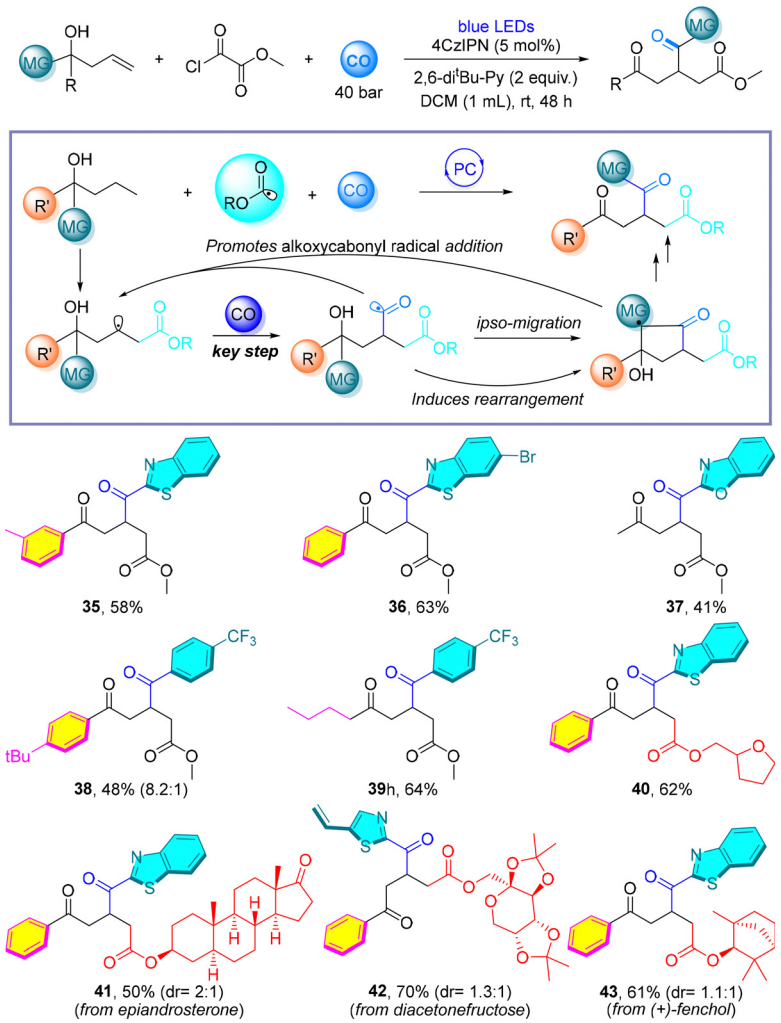
was achieved by modulating the reactivity of both the oxygen-centered radicals and the resulting carbon radicals. Meanwhile, the effective participation of carbon monoxide suppressed competitive hydrogen atom abstraction pathways, offering a new direction for the further utilization of CO in radical carbonylative transformations.

2.4. Migration triggered by trifluoromethylthio radical

Sulfur-containing compounds represent an important class of organic molecules widely found in pharmaceuticals, biologically active substances, and functional materials.[30] Introducing sulfur-based functional groups into organic frameworks can effectively enhance biological activity and expand molecular diversity.[31] As a result, the construction of C–S bonds have become a prominent research focus in organic synthesis, leading to the development of numerous efficient synthetic strategies. Therefore, the incorporation of both carbonyl and sulfur-containing groups *via* difunctionalization of alkenes is of particular interest. In 2024, Wu's team reported a novel strategy for the difunctional carbonylative reaction of unactivated alkenes involving a sulfur-centered radical and carbon monoxide (Scheme 4).[32] In this system, $AgSCF_3$ is oxidized to generate the trifluoromethylthio radical, which adds to the alkene. Subsequently, with the participation of carbon monoxide, an intramolecular migration process takes place, efficiently constructing a variety of sulfur-containing 1,4-dicarbonyl skeletons. This approach expands the scope of carbonylative difunctionalization of alkenes and offers new perspectives for developing intermolecular migration reactions based on sulfur radical addition to alkenes.

2.5. Migration triggered by alkoxycarbonyl radicals

Alkyl esters represent an important class of structural motifs widely found in natural products, agrochemicals, and biologically active molecules. They are frequently employed in drug design to modulate target affinity and membrane permeability.[33] Among existing synthetic approaches, alkoxycarbonylation of alkenes offers a straightforward route to ester formation; alternatively, aliphatic esters can also be accessed *via* alkoxycarbonyl addition to alkenes.[34] However, reported methods are largely limited to activated alkenes, and examples of alkoxycarbonyl radical-mediated difunctionalization of

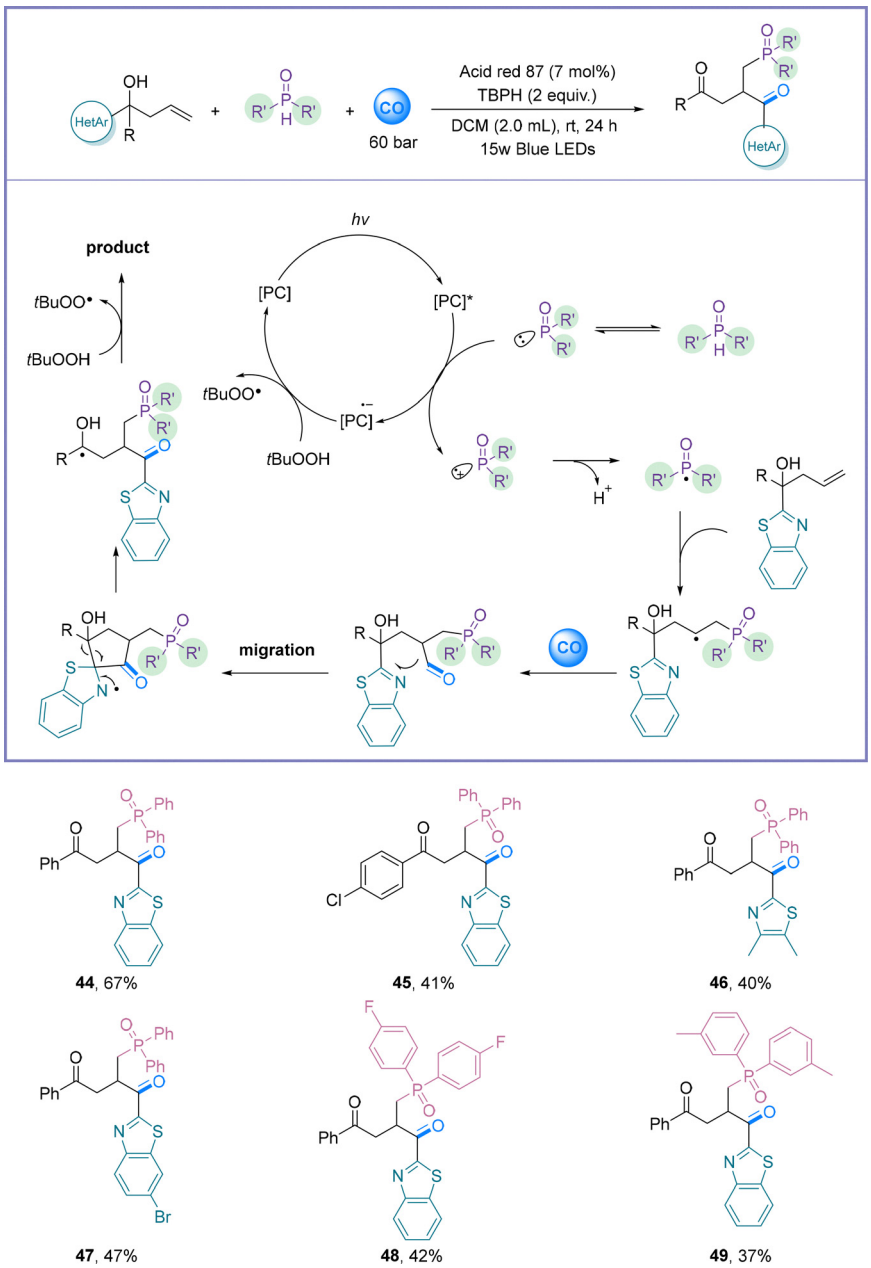


Scheme 5 Migration triggered by alkoxycarbonyl radicals.

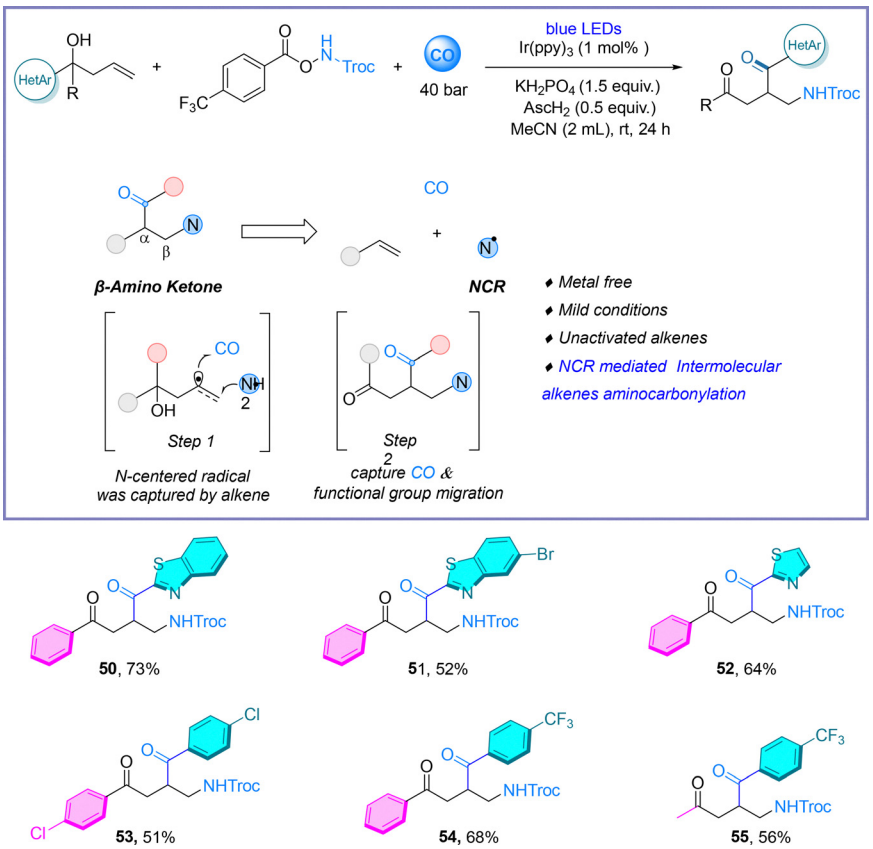
unactivated alkenes remain scarce. To address this, Wu and colleagues reported a strategy involving the addition of alkoxycarbonyl radicals to unactivated alkenes under photoredox conditions, facilitated by carbon monoxide (CO) (Scheme 5).[35] This approach leverages CO to rapidly capture nucleophilic alkyl intermediates, effectively suppressing β-hydride elimination and decomposition side reactions. Meanwhile, CO insertion promotes intramolecular functional group migration and acyl quenching, enabling the successful construction of a diverse range of unsymmetrical 1,4-dicarbonyl compounds and expanding the structural library of such skeletons. It is noteworthy that this work represents the first example of carbonylative difunctionalization of unactivated alkenes involving exogenous alkoxycarbonyl radicals.

2.6. Migration triggered by phosphinyl radicals

Organophosphorus compounds, as a distinct class of structural motifs, are widely employed as ligands in transition-metal-catalyzed organic reactions due to their unique coordination properties.[36] Since the pioneering work by Hirao's team in the 1980s on palladium-catalyzed C–P bond formation,[37] significant progress has been made in the development of transition-metal-catalyzed strategies for constructing C–P bonds. However, these methods often require expensive metal catalysts,



Scheme 6 Migration triggered by phosphinyl radicals.



Scheme 7 Migration triggered by nitrogen-centered radical.

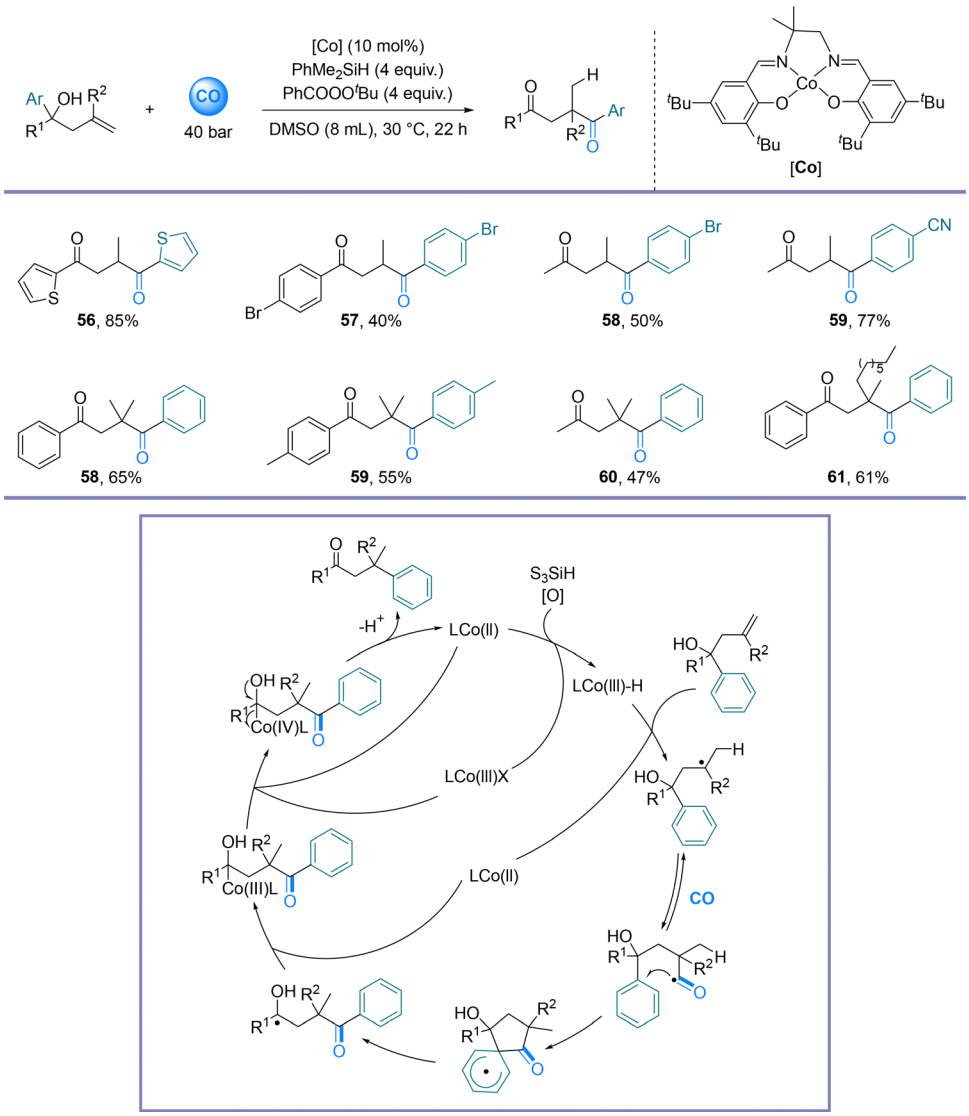
specialized ligands, and elevated reaction temperatures, which somewhat limit their broader applicability. On the other hand, with the advancement of organic chemistry, visible-light photocatalysis has emerged as a sustainable synthetic strategy. In 2024, Wu and colleagues developed a photo-mediated phosphoryl-carbonylative migration reaction of alkenes (Scheme 6).[38] A key feature of this reaction is that the incorporation of carbon monoxide not only facilitates carbon chain elongation but also suppresses the formation of hydro-phosphinylation byproducts. This method provides a milder and more sustainable approach to direct C–P bond construction.

2.7. Migration triggered by nitrogen-centered radical

The β-aminocarbonyl structural unit is an important functional unit, widely present in various bioactive molecules. It also serves as a key intermediate in the synthesis of nitrogen-containing compounds such as β-amino alcohols, β-amino acids, and β-lactams, demonstrating broad synthetic utility.[39] The 1,2-difunctionalization of alkenes represents an effective strategy for constructing complex molecules and offers a promising route for the preparation of nitrogen-containing compounds. However, due to the high kinetic barrier associated with intermolecular amination of alkenes, the development of aminocarbonylation reactions remains underexplored, with limited studies reported so far.[40] Furthermore, in the few existing examples, the alkene substrates are largely restricted to styrene derivatives, and carbonyl sources are mainly limited to aldehydes and anhydrides, indicating notable limitations in substrate scope. Building on previous work, Wu and colleagues reported a photocatalytic aminocarbonylation of unactivated alkenes mediated by nitrogen-centered radicals (Scheme 7).[41] The generation of nitrogen-centered radicals in this process proceeds without the need for exogenous oxidants, and the final quenching step occurs without requiring external nitrogen nucleophiles.

2.8. Migration triggered by Co–H

Metal hydride (MH, M = Co, Fe, Mn, *etc.*)-catalyzed hydrogen atom transfer (HAT) has become an efficient strategy for the hydrofunctionalization of alkenes, demonstrating excellent Markovnikov selectivity.[42] It is particularly noteworthy that the research groups of Pronin, Carreira, Teskey, and Johnstone, among others,[43] have independently developed cobalt-catalyzed HAT processes that successfully achieve the hydro-semipinacol rearrangement of allylic alcohols, providing a novel pathway for the efficient synthesis of α-aryl ketones. Building on these advances, in 2025, Cheng and colleagues reported a cobalt-hydride-catalyzed remote aryl migration strategy to achieve Markovnikov hydroarylcarbonylation of unactivated alkenes.[44] By integrating HAT catalysis with distal aryl migration, this method realizes Markovnikov-selective

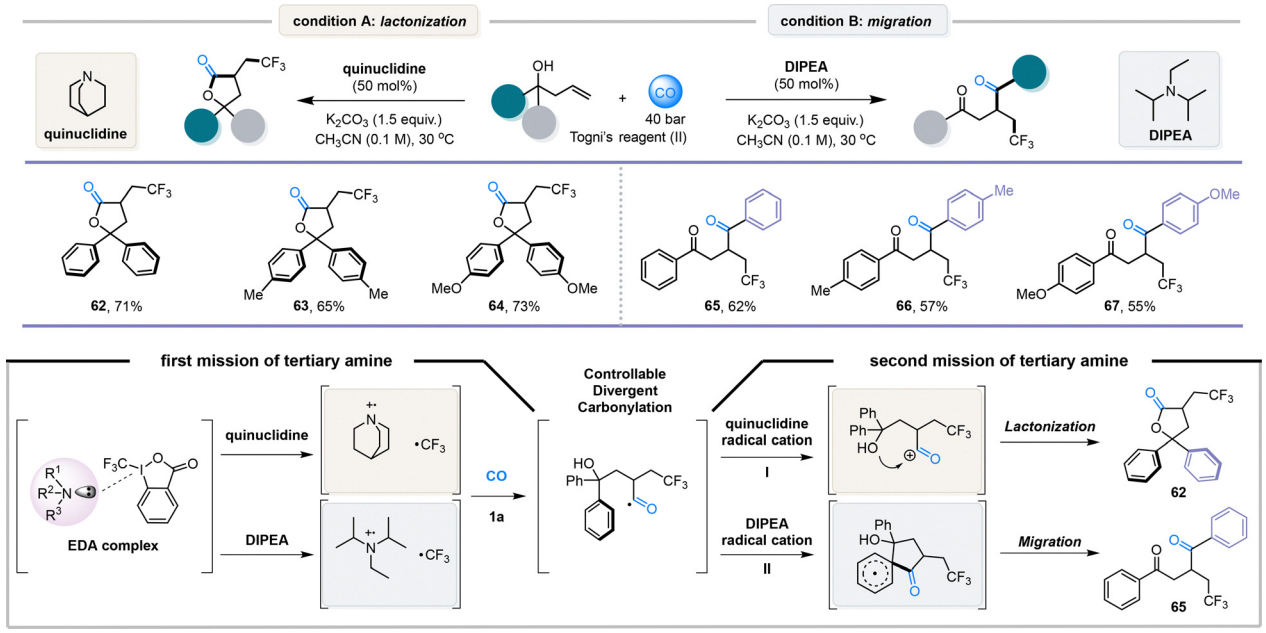


Scheme 8 Migration triggered by Co–H.

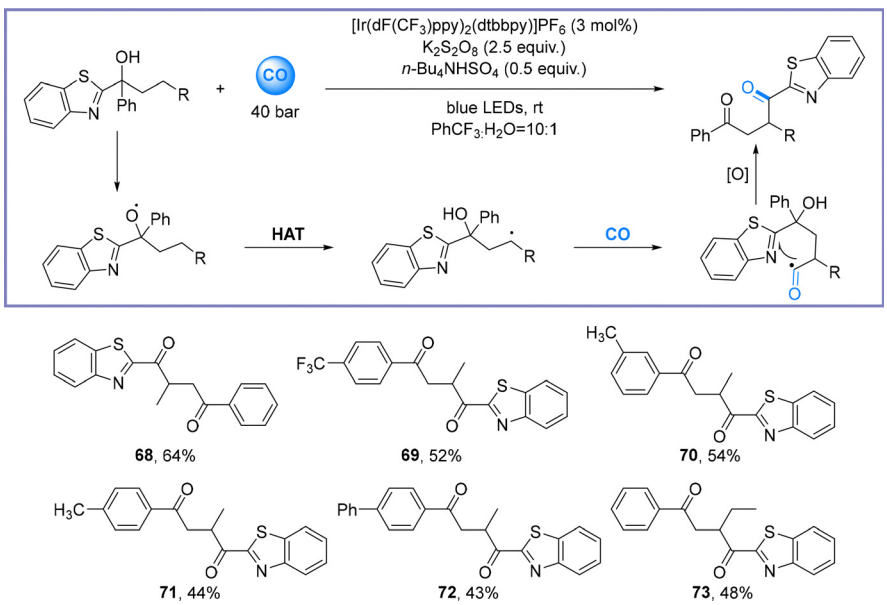
hydroarylcarbonylation of unactivated alkenes. Specifically, the reaction proceeds *via* a HAT-generated radical intermediate from homoallylic alcohols. Under a CO atmosphere, this intermediate forms an acyl species, which then triggers a remote aryl migration through a kinetically favored five-membered ring transition state. Subsequent C–C bond cleavage affords α-alkylated 1,4-dicarbonyl compounds efficiently (Scheme 8).

2.9. Amine-tuned selective migration and ring formation

With the continuous advancement of carbonylative reactions, the issue of selectivity has become increasingly prominent. In particular, the effective control of regioselectivity and chemoselectivity has emerged as a central challenge in this field of research.[45] In ligand-assisted metal-catalytic systems, achieving selective activation at different sites often relies on ligands with specific steric and electronic properties, a requirement that significantly increases the complexity and difficulty of methodological development. Therefore, the development of innovative strategies for selective carbonylation without transition metals is particularly urgent. In 2025, Wu and colleagues reported a controllable carbonylative synthesis of γ-lactones and 1,4-diketones *via* an electron donor–acceptor (EDA) complex strategy tuned by amines (Scheme 9).[46] Specifically, carbon radicals generated from the EDA complex undergo CO trapping to form acyl species. Simultaneously, the amine donor undergoes single-electron oxidation to yield an aminium radical cation, whose structural and electronic properties dictate the subsequent reactivity of the acyl intermediate. Under conditions of low steric hindrance, the acyl species tends to be oxidized to an acyl cation, whereas under sterically congested environments, the acyl radical remains stable. When both a nucleophilic hydroxyl group and a radical-accessible aryl group are present within the same molecule, the acyl intermediate reacts selectively with one of the functional groups: electrophilic acyl cations favor lactonization with the hydroxyl



Scheme 9 Amine-tuned selective migration and ring formation.



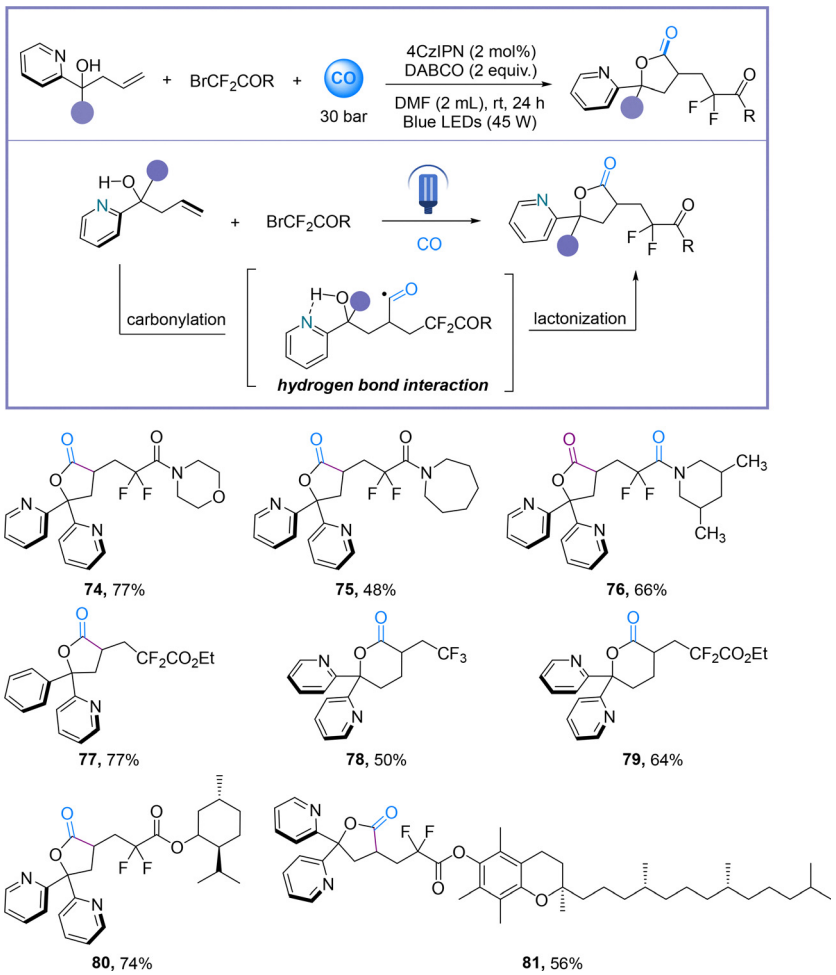
Scheme 10 Intramolecular hydrogen atom transfer (HAT)-induced migration.

group, while nucleophilic acyl radicals promote long-range radical aryl migration.

3. Intramolecular heteroaryl migration mediated by carbon monoxide (CO)

3.1. Intramolecular hydrogen atom transfer (HAT)-induced migration

Selective C–H functionalization represents a powerful strategy for the direct transformation of inert C(sp^3)–H bonds, offering a creative approach to modify complex natural products and pharmaceutical molecules without the need for *de novo* synthesis.[47] As a complement to well-established transition-metal-catalyzed methods, radical-mediated hydrogen atom transfer (HAT) provides a distinct functionalization pathway that can achieve selectivities and site preferences sometimes inaccessible *via* traditional metal catalysis. The use of oxygen- or nitrogen-centered radicals to initiate 1,5-hydrogen atom transfer (1,5-HAT) enables direct functionalization of remote C(sp^3)–H bonds. This process involves the transfer of a



Scheme 11 Effect of hydrogen bond chelation on the migration of homoallyl alcohol substrates.

hydrogen atom from carbon to an oxygen or nitrogen radical, generating a highly reactive carbon radical intermediate, which is subsequently captured by a radical trapping agent to install a functional group at a distal carbon site. However, unlike 1,5-HAT, which proceeds through a more stable six-membered ring transition state, 1,4-hydrogen atom transfer must occur *via* a higher-energy five-membered ring transition state, making it thermodynamically less favorable. As a result, studies on 1,4-HAT are far less common than those on 1,5-HAT. In 2024, Wu and team reported a study on remote migration reactions *via* a HAT strategy at γ-C(sp^3)–H bonds using tertiary alcohols bearing heteroaromatic groups as substrates. By employing carbon monoxide to extend the carbon chain, the reaction enabled otherwise disfavored 1,4-HAT processes (Scheme 10).[48]

4. Effect of hydrogen bond chelation on the migration of homoallyl alcohol substrates

The hydrogen bond is a type of non-covalent interaction characterized by electrostatic attraction, widely observed across diverse fields such as electrochemistry, biomimetic catalysis, biomedical science, and materials science.[49] Its functions include enhancing molecular reactivity, improving stereoselectivity, and stabilizing molecular architectures. Furthermore, the presence of heteroatoms (*e.g.*, nitrogen, oxygen) facilitates the formation of hydrogen bonds. Consequently, molecular systems containing heteroaromatic rings often exhibit a pronounced tendency for hydrogen-bonding interactions. In 2025, Wu's team reported a novel carbonylative approach for the efficient synthesis of a series of lactones using tertiary alcohols bearing both pyridyl and allylic groups as substrates (Scheme 11).[50] In this strategy, the nitrogen atom of the 2-pyridyl group acts as a hydrogen-bond acceptor, forming an intramolecular hydrogen bond with the adjacent hydroxyl group. This interaction significantly enhances the nucleophilicity of the hydroxyl group. Following carbonylation, the strengthened nucleophile facilitates intramolecular cyclization, preferentially leading to lactone formation over alternative migration pathways.

5. Summary and outlook

In this review, we have highlighted the role of carbon monoxide (CO) in enabling carbon chain elongation, thereby unlocking

the transformation of otherwise challenging allylic alcohol skeletons *via* migration reactions. These advances further demonstrate the practical utility and value of CO in synthetic chemistry. The article provides a detailed discussion of various transformations and their underlying mechanisms, offering a solid foundation for further research into remote functional group migration and CO insertion. Furthermore, we elaborate on the synergistic mechanism between CO insertion and functional group migration, which collaboratively drives the remote migration of aryl or heteroaryl groups to carbonyl carbon centers. Additionally, we summarize various radical activation strategies that enable selective CO insertion, facilitating heteroaryl migration for the synthesis of 1,4-dicarbonyl compounds.

Despite these advances in CO-involved migratory carbonylations, several challenges remain to be addressed: (1) expanding the scope of migrating groups: current systems are largely limited to heteroaryl migrations; broader migration motifs remain underexplored. (2) Simplifying substrate accessibility: Developing novel migration modes-such as docking migration-could eliminate the need for pre-functionalized alkenes and streamline substrate synthesis. (3) Enabling asymmetric carbonylative migration: Implementing chiral catalytic modes in remote functional group migration could provide efficient strategies for constructing enantioenriched scaffolds relevant to pharmaceutical applications. We hope that this review will stimulate further development in the field of carbonylative migration reactions.

Conflicts of interest

There are no conflicts to declare.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

Acknowledgements

Financial support from National Key R&D Program of China (2023YFA1507500) and DICP are appreciated.

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