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When transition-metal-catalyzed C–H activation meets allene chemistry

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ABSTRACT

Transition-metal-catalyzed allenes-involved C–H functionalizations demonstrate unique selectivity and undergo exceptional pathways due to the existence of elusive orthogonal cumulative C═C═C bonds. As a result, it allows for a diverse array of C–H activation reactions, such as allylation, alkenylation, allenylation, dienylation, propargylation, and annulation. In this review, we comprehensively summarize the noteworthy aspects of transition-metal-catalyzed C–H functionalizations involving variously substituted allenes.

1. Introduction

The allene moiety, commonly found in a wide range of natural products, pharmaceuticals, and functional materials, exhibits distinctive reactivity in synthesis [1]. In recent decades, there has been a significant increase in the recognition and utilization of allenes as versatile building blocks for various synthetic purposes [2]. Owing to their inherent flexibility, allenes possess the capacity to engage in diverse nucleophilic and electrophilic addition reactions, as well as cycloadditions and cyclizations. As a result, they play an important role in numerous transformations facilitated by transition-metals, especially palladium and gold catalysts [3]. The intriguing characteristics of allenes as coupling partners in transition-metal-catalyzed cross-coupling reactions have been elucidated through a series of groundbreaking investigations conducted by Bäckvall, Krische, Breit, Ma, Cramer, Glorius, and other esteemed researchers [2–10]. The reactivity mode shown by allenes in carbometallation process is predominantly influenced by the generation of metal-allyl (Scheme 1, path a) or metal-alkenyl intermediates (Scheme 1, path b), distinguishing them from alkenes and alkynes. The attainment of this outcome is accomplished *via* the deliberate incorporation of an organometallic species (R-M) or related metal hydride (M−H) into the allene framework, therefore facilitating a diverse array of adaptable reactions. The manner in which C–H functionalization processes occur in allene is greatly affected by the steric and electronic characteristics of the substituents. As a consequence, the resultant regio-, chemo-, and stereoselectivity, exhibits a wide range of variations and presents significant challenges in terms of manipulation.

This article aims to provide an overview of the important advancements in allene chemistry in transition-metal-catalyzed C–H functionalization up until mid-2023. While some overlap with previous reports exists [10c-f], the substantial growth of this filed in the past five years calls for a concise review of recent discoveries and developments. The discussion of this paper will be mainly focused on the unique reactivity of allenes in these transformations, along with potential reaction mechanisms. The review is primarily organized around various transition-metal catalysts, as they play crucial roles in allene-involved C–H functionalization processes.

2. Transition-metal-catalyzed C–H functionalization with allenes

In recent years, inert C–H activation catalyzed by various transition-metals, has evolved into one of the simplest and most powerful tools for molecule editing [11]. In this regard, coupling partners containing unsaturated C–C bonds, including alkenes, alkynes, and allenes, have been extensively explored. However, achieving selectivity in C–H activation reactions with allenes represents a greater challenge compared to alkenes and alkynes due to the presence of elusive orthogonal cumulative π bonds. As a result, the reaction pathway might be varied across different transition-metal involved.

2.1. Ir-catalyzed C–H activation with allenes

The initial disclosure of the catalytic C–H activation process involving allenes is made by Krische in 2009 [12]. The pioneering work demonstrated the reaction between various aromatic/α,β-unsaturated carboxamides **1** and 1,1-dimethylallene **2**, employing cationic iridium complexes as catalysts (Scheme 2). Remarkably, this transformation

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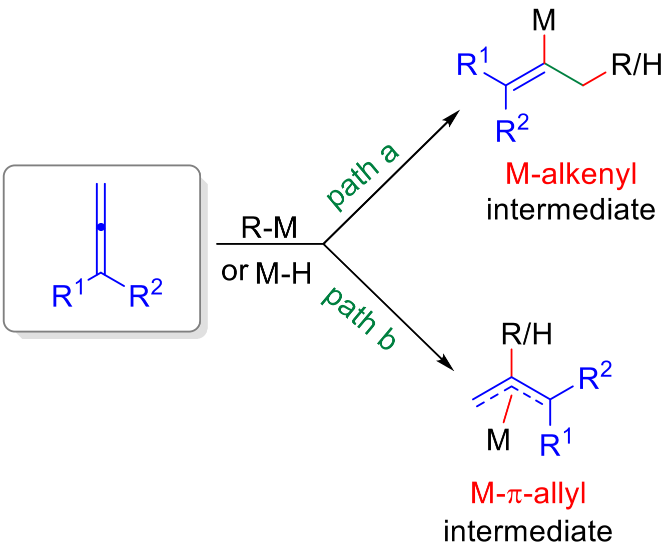
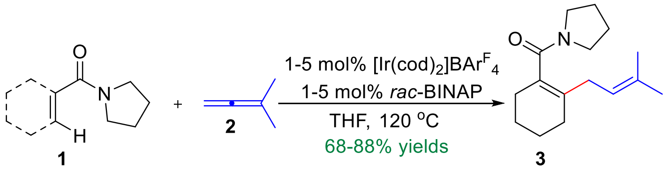


Scheme 1. The reactivity mode of allenes in carbometallation.



Scheme 2. Ir-catalyzed C–H prenylation of carboxamides.

yielded prenylated products **3** with excellent regioselectivity and high yields.

Inspired by Krische's seminal work, a multitude of C–H functionalization reactions involving allenes and other transition-metals have been progressively unveiled.

2.2. Rh-catalyzed C–H activation with allenes

Transition-metal-catalyzed hydroarylation of C–C multiple bonds, has emerged as an efficient method for generating a diverse array of important building blocks through the utilization of readily available chemicals in synthesis [13]. Among these transformations, the utilization of allene hydrometalation to generate reactive allyl metals has gained much attention [14].

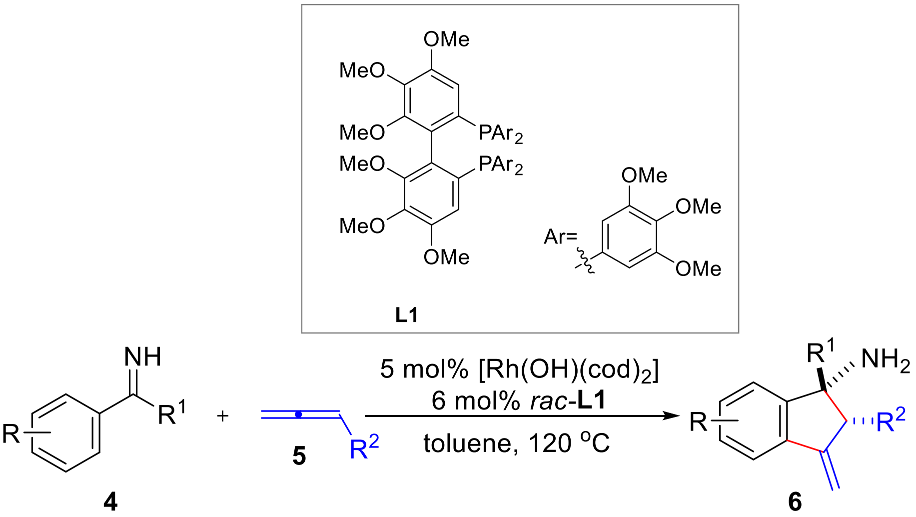
In 2010, Cramer and colleagues reported a highly regio- and diastereoselective [3 + 2] cyclization of unsubstituted ketimines **4** with terminal allenes **5** by rhodium catalysis, leading to the synthesis of methylene dihydroindenylamines **6** (Scheme 3) [5a]. In the meantime, Takai et al. got the similar results using Re catalysis without the need for P-ligands [15].

Subsequently, the Cramer group conducted further investigations into the dynamic kinetic asymmetric form of the aforementioned [3 + 2] annulation process [5b]. Mechanistic studies indicated that the geometric properties of double bonds, the diastereo- and enantioselectivity of allene insertion, and the kinetic acidity of C–H bonds all contributed to precise control over positional selectivity of C–H bond activation. Building upon their previous work, Cramer and Waldmann next demonstrated the rhodium(I)-catalyzed enantioselective C–H allylations/annulation of benzamides [5c,16]. Notably, the introduction of a new chiral Cp (cyclopentadienyl) ligand played a pivotal role in facilitating these conversions.

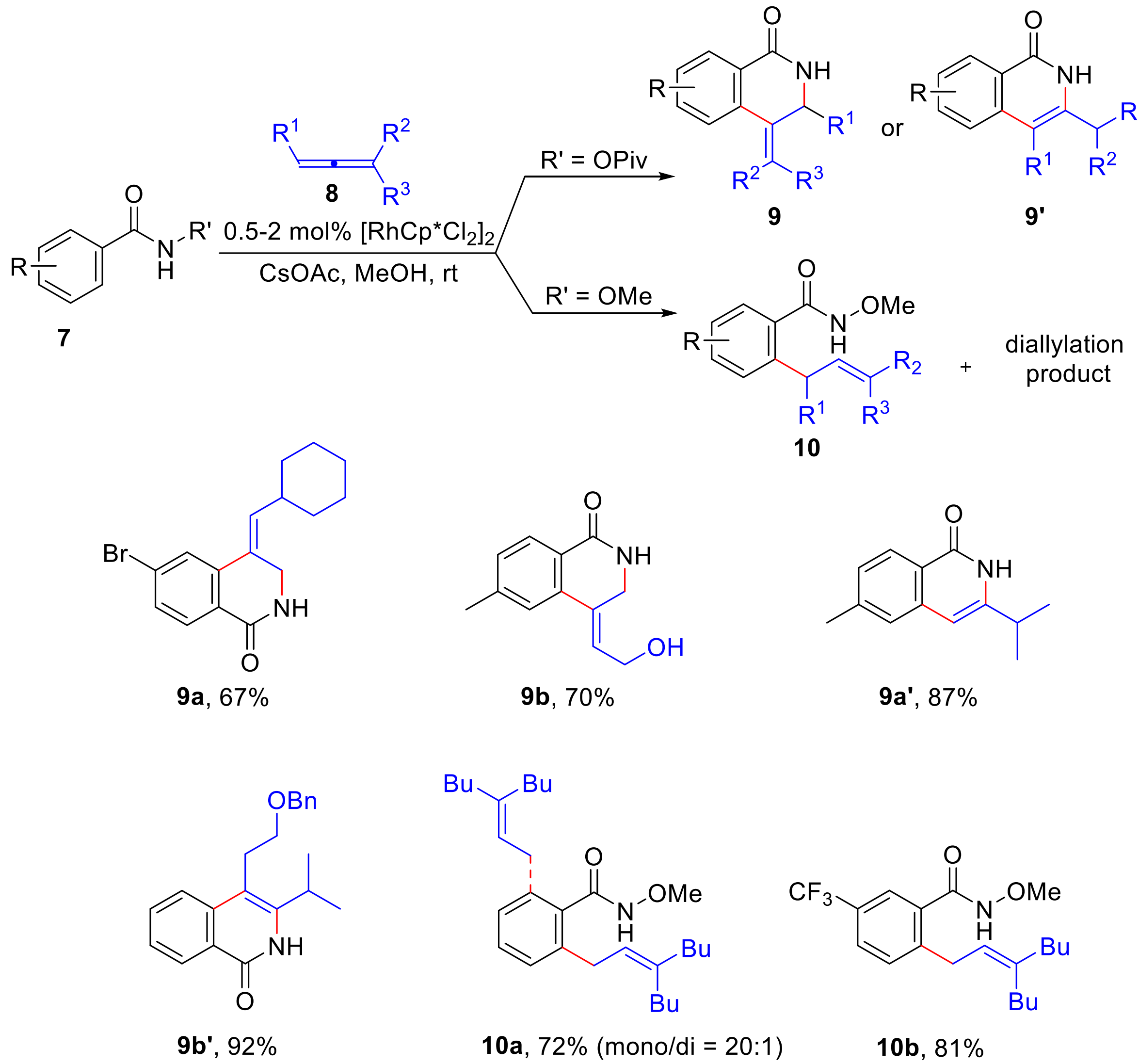
It is worth highlighting that Rh^{III} catalysts have also shown promise in achieving these allenes-mediated C–H functionalization. Remarkable redox-neutral coupling reactions between benzamide derivatives **7** and allenes **8** were separately reported by Glorius and Ma [4b,6a]. These reactions exhibited exceptional functional group tolerance and were conducted under mild conditions. (Scheme 4). Recently, similar annulation/olefination processes were also respectively disclosed by Yi and Feng, employing *gem*-difluoroallenes/*gem*–difluoromethylene allenes as related coupling partners to react with various benzamide derivatives [17].

An interesting observation made by Ma was the introducing of bulkier and synthetically more valuable trimethylsilyl-substituted allenes **11**, which led to equivalent C–H allenylation products **12** (Scheme 5) [4c]. Additionally, Ackerman et al. achieving similar results by Ru catalysis [10a]. Mechanistic investigations provided further insights into the reaction, suggesting that it potentially followed a series of steps including sequential *o*-rhodation, regioselective insertion, and β–H elimination.

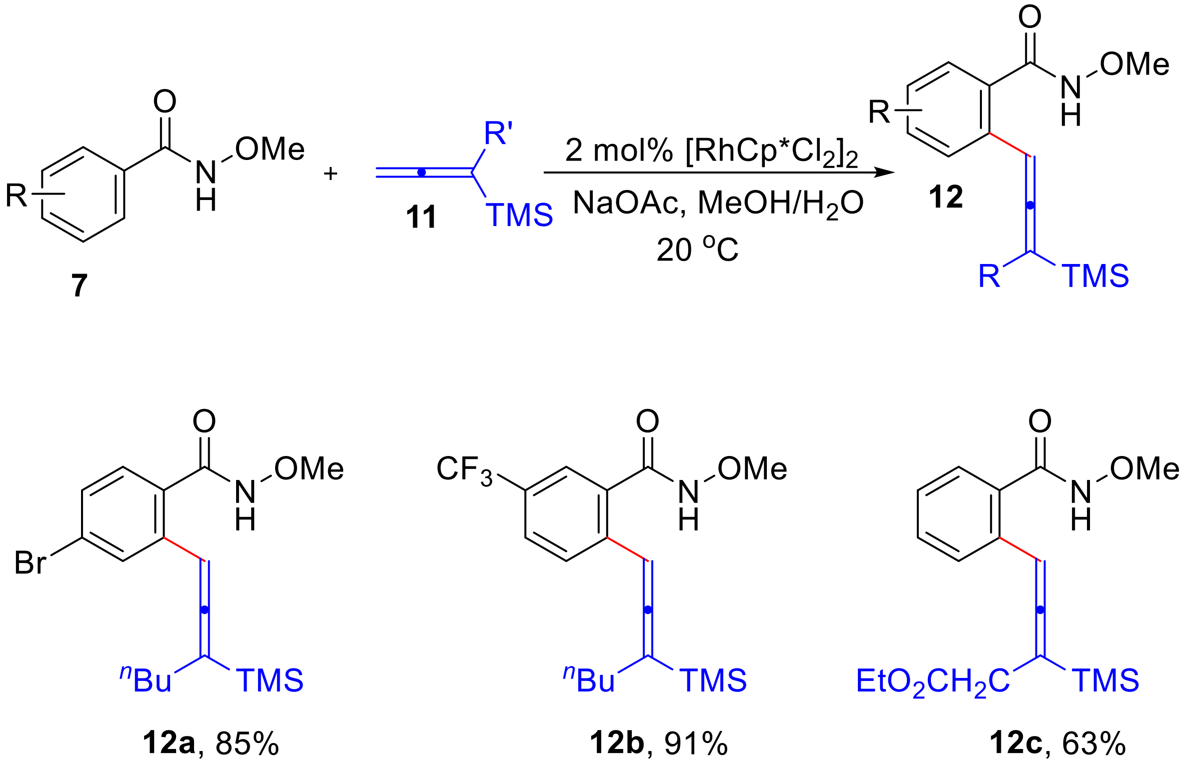
In contrast to the extensive presence of aryl C–H bond activation in enantioselective transformations catalyzed by $Cp^{x}Rh^{III}$ [18], the corresponding asymmetric functionalizations of alkenyl C–H bonds are rare and remain a considerable challenge. Cramer and co-workers made a notable breakthrough by uncovering an enantioselective [4 + 1] annulation of acrylamides **13** and allenes **14** through $Cp^{x}Rh^{III}$-catalyzed alkenyl C–H functionalization (Scheme 6) [19]. This transformative process facilitated the acquisition of α,β-unsaturated γ-lactams **15**



Scheme 3. Rh^{I}-catalyzed C–H functionalization/cyclization of ketimines with terminal allenes.



Scheme 4. Rh^{III}-catalyzed selective C–H functionalization/cyclization of benzamides with allenes.



Scheme 5. Rh^{III}-catalyzed selective Heck-type allenylation of *N*-methoxybenzamides.

bearing a quaternary stereocenter in good to excellent enantioselectivity.

Recently, there has been a growing interest in the field of dendralene chemistry, primarily due to the unique functions they exhibit in polymer chemistry, theoretical chemistry, and synthetic chemistry [20]. However, the synthesis of [3]dendralenes has been limited to a few methodologies [21]. Using an alkenyl C–H activation strategy, Glorius and coworkers successfully addressed this gap by reporting the Rh^{III}-catalyzed synthetic route to [3]dendralenes **18** from allenyl carbinol carbonates **17** (Scheme 7) [6b]. Similarly, groups led by Fu and Kapur independently reported comparable findings through oxidative coupling approaches [22].

A Rh^{III}-catalyzed mechanism was put forward for the aforementioned reaction (Scheme 8). Initially, the C–H activation procedure occurred with the assistance of the amide directing group and the addition of pivalic acid. After the allene **17** coordination, regioselective carborhodation would lead to the formation of a π-allyl rhodium(III) complex **C′**, which existed in equilibrium with the η^1-allyl rhodium(III) complex **C**. Finally, the diene products **18** were released through a formal β-oxygen elimination process, concurrently regenerating the active Rh^{III} catalyst **A**.

The current organic synthesis heavily relies on heterocycles. Many studies on the progress of annulation reactions involving allenes have been published in recent years, making them a hot topic in the chemical community [3b,10c-f]. In this context, a series of Cp^*Rh^{III}-catalyzed C–H activation/annulation with allenes (**8**, **19**–**20**, **23**, **26**–**28**) has been separately reported by Ma, Gulías, Cheng, and other researches, leading to the efficient synthesis of a wide variety of diversified heterocycles (**29**–**33**, **35**–**37**) or carboamination products (**34**) (Scheme 9) [10b,23]. These advancements have greatly expanded the synthetic toolbox for generating heterocyclic motifs, thus presenting new opportunities for their applications in diverse scientific and industrial areas.

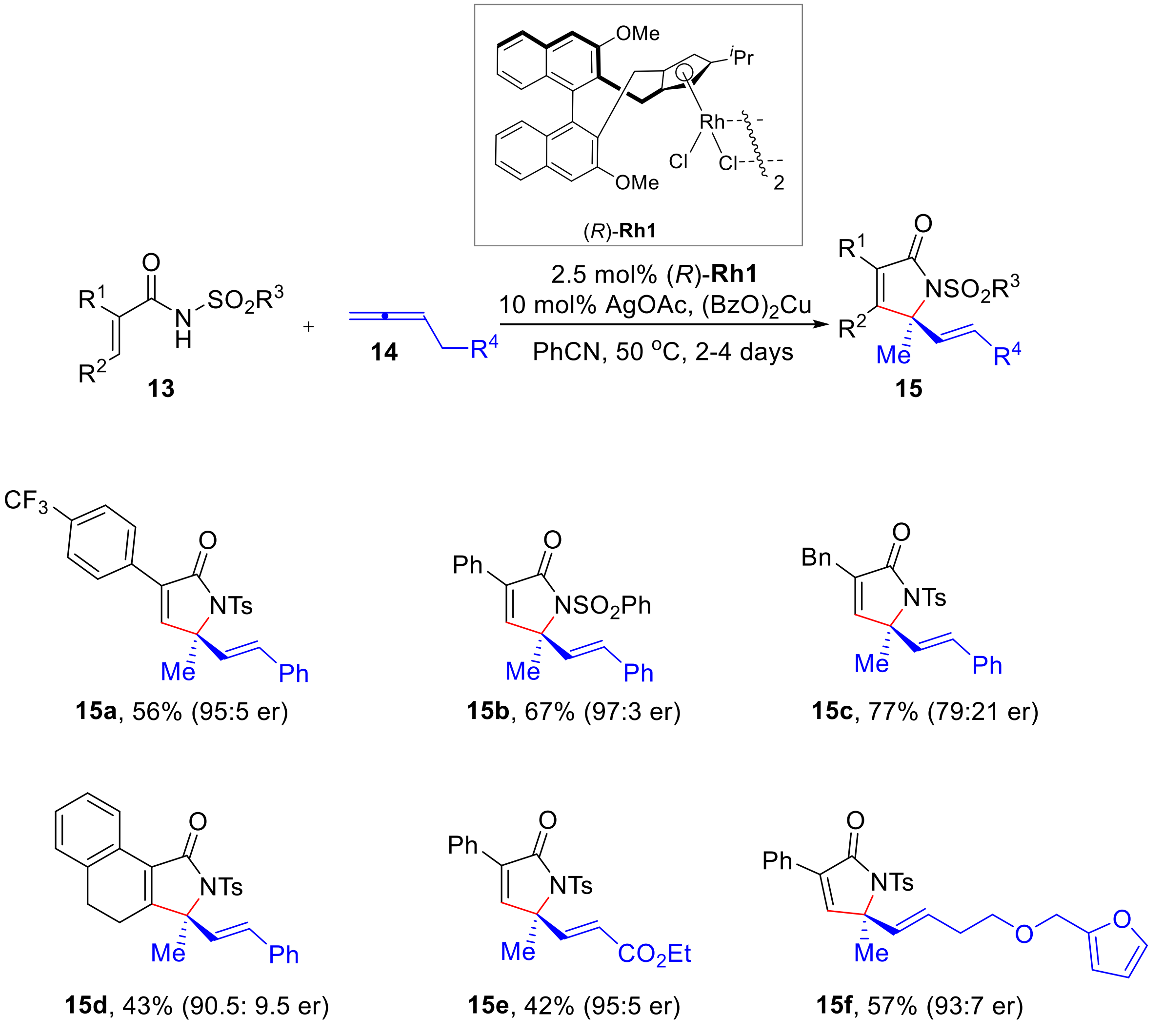
2.3. Pd-catalyzed C–H activation with allenes

Today, the use of palladium catalysis has become a highly versatile technique in organic synthesis owing to its ability to finely tune reaction parameters like as temperature, solvents, ligands, bases, and other supplementary components [24]. In addition, it shall be noted that palladium catalysts often demonstrate pronounced stereo- and regiospecificity in reactions, while also displaying a high level of tolerance towards various functional groups [25]. This characteristic significantly reduces the need for protecting groups, which makes palladium a versatile catalyst for a wide range of cross-coupling reactions. Despite the fact that Ma et al. has achieved a successful development for the palladium-catalyzed allylation of electron-rich arenes in the early part of 2010 [4a], there is a limited number of published studies on Pd-catalyzed C–H functionalization involving allenes.

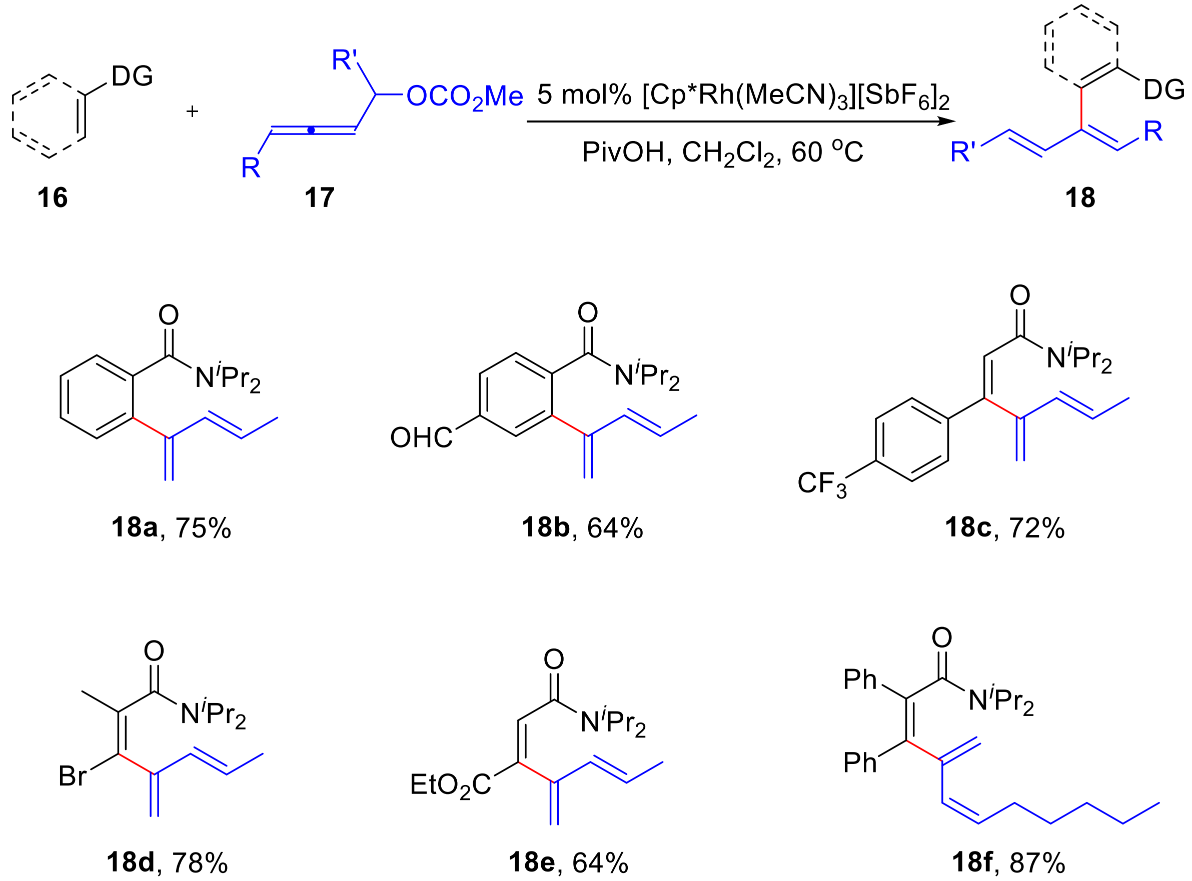
The research groups led by Liang and Nicolás independently showcased the utilization of Pd-catalyzed C–H activation and intermolecular annulation with allenes **5**/**8**, employing distinct amine derivatives **7**/**39** as direct groups (Scheme 10) [26]. Moreover, the practical use of these conversions had been significantly enhanced by the compatibility of comparable C–H functionalization procedures with ambient air and moisture. Later, Li and Xu also reported similar findings utilizing other amide derivatives [27].

Subsequently, Gulías, Zeng and their co-workers successively unmasked multiple instances of Pd-catalyzed oxidative [5 + 2] annulation between *ortho*-alkenylphenols/alkenylanilines **42** and allenes **43**, affording valuable yet synthetically challenging benzo[*b*]oxepines/benzo[*b*]azepines **44** (Scheme 11) [28]. These methodologies also boasted superior regio- and diastereoselectivities, high yields, and good functional group tolerance.

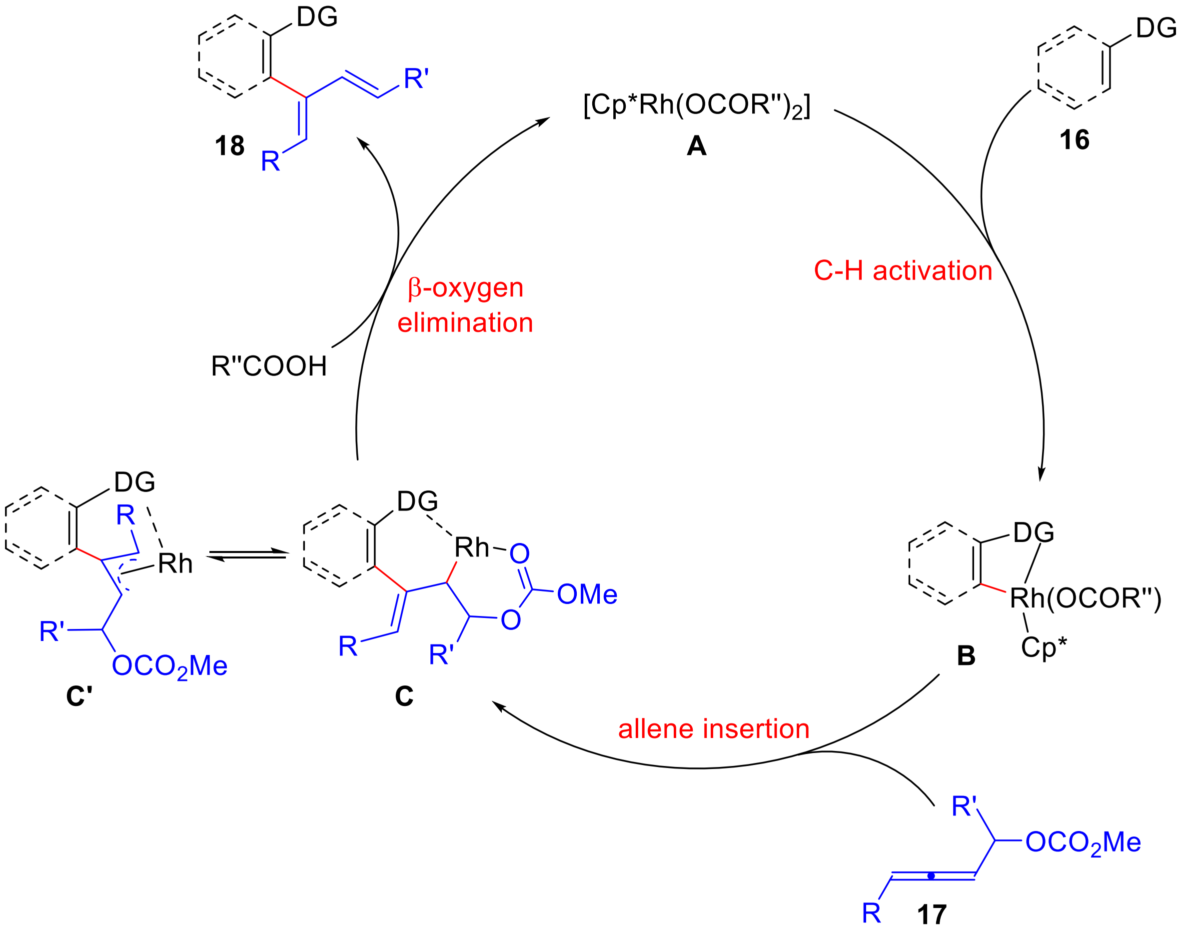
Significantly, Gulías et al. discovered a palladium-catalyzed formal [4 + 2] cycloaddition involving the activation of $C(sp^3)$–H bonds, which offered a convenient and unconventional approach to tetrahydroquinoline scaffolds **46** (Scheme 12). [29]. Furthermore, this approach could be extended to [5 + 2] annulation to facilitate the rapid



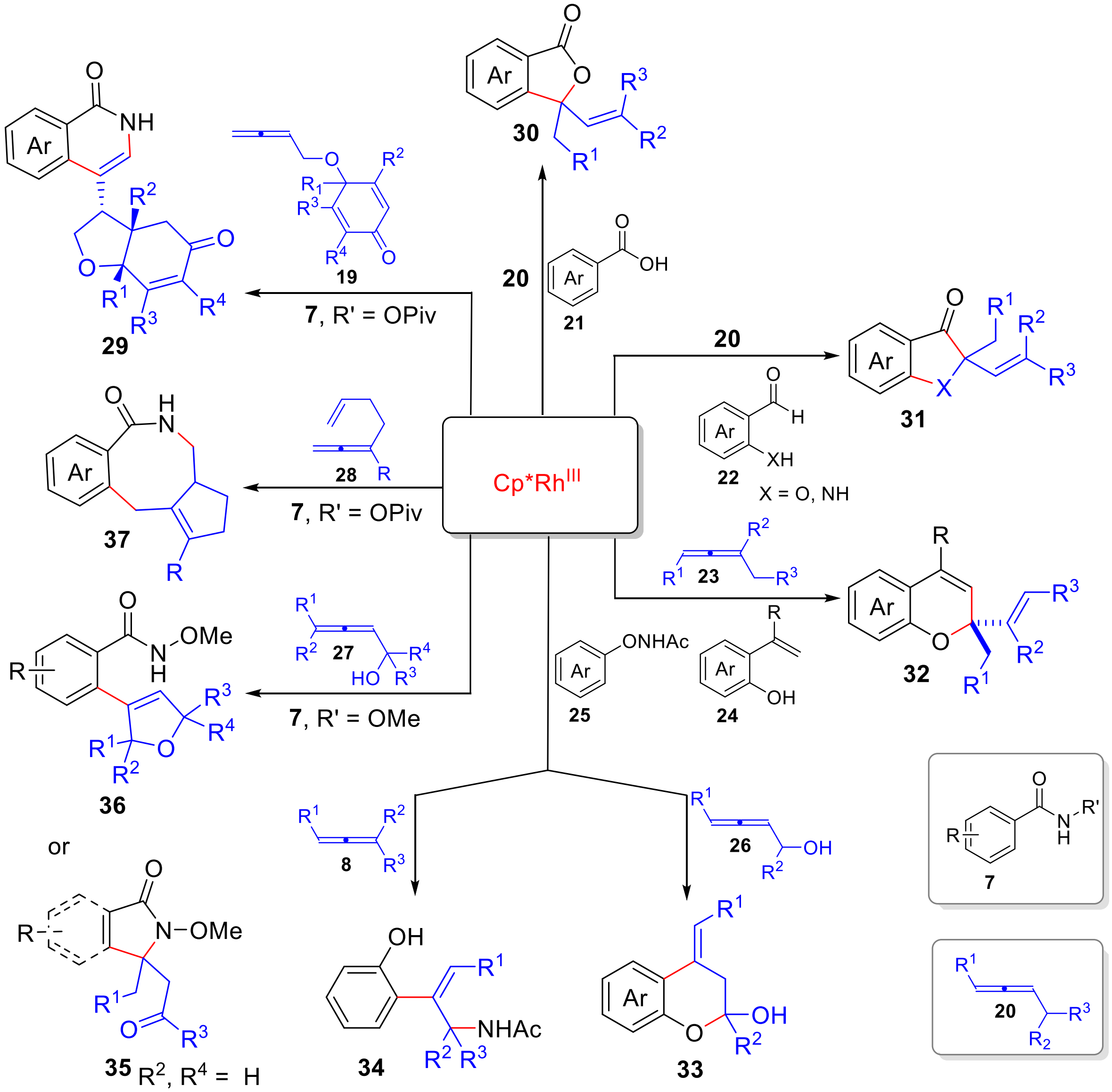
Scheme 6. Cp^{x}Rh^{III}-catalyzed enantioselective alkenyl C–H activation of acrylamides.



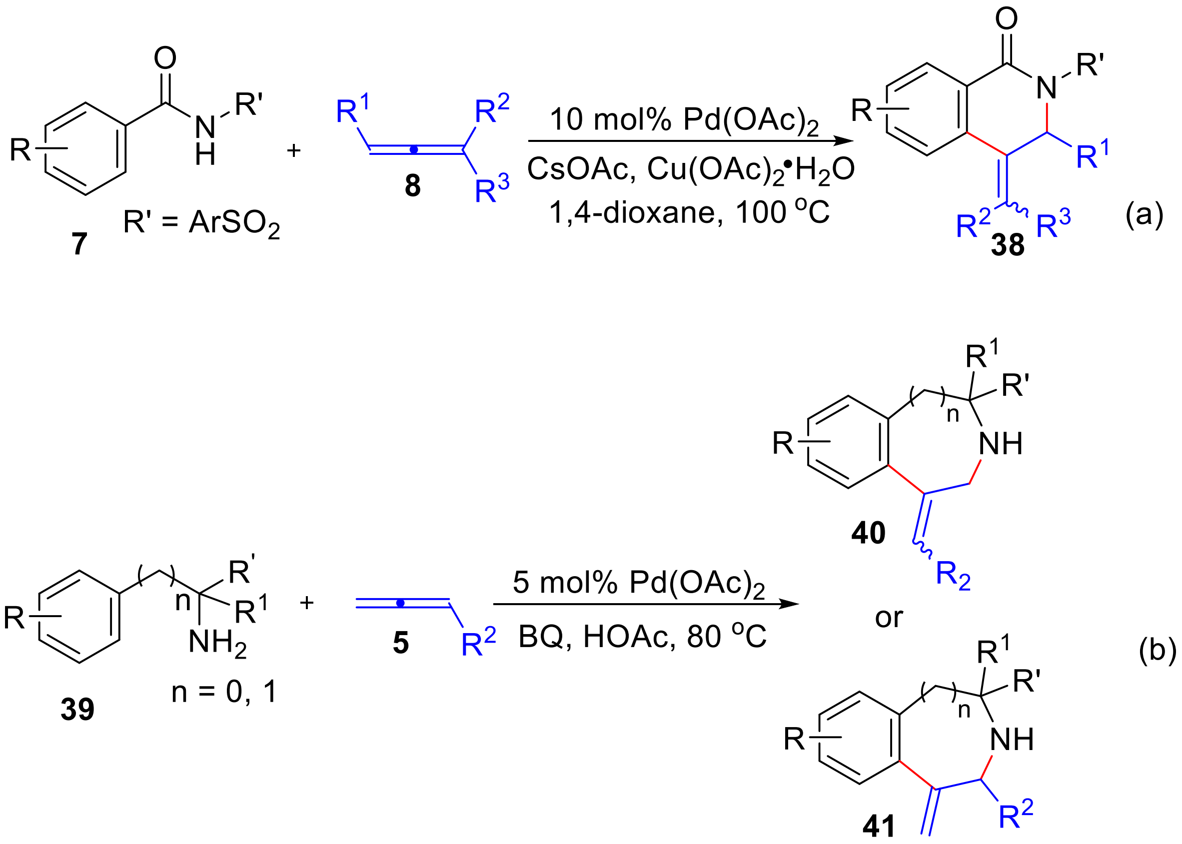
Scheme 7. Rh^{III}-catalyzed diene incorporation with allenes.



Scheme 8. Proposed mechanism for Rh^{III}-catalyzed [3]dendralene synthesis.



Scheme 9. Divergent construction of heterocycles or carboamination by $\mathrm{Rh^{III}}$-catalyzed C–H activation using allenes.



Scheme 10. Pd^{II}-catalyzed C–H activation and intermolecular annulation with allenes.

construction of attractive tetrahydro-2-benzazepines **47**.

Motivated by these promising findings, Gulías and colleagues further examined the Pd^{II}-catalyzed enantioselective C–H activation/cycloaddition reactions [29,30]. By utilizing the smartly designed chiral *mono*-N-protected amino acid (MPAA) as a ligand, they smoothly realized selective C–H cleavage of prochiral diarylmethylphenyl amides **49**, delivering the corresponding isoquinolines **53** with high *ee* values (Scheme 13, a) [30a]. Additionally, the MPAA promoted C–H activation/annulation strategy was successfully applied to the kinetic resolution of allyltriflamides **48** (Scheme 13, c) [30b]. Furthermore, it was demonstrated that other newly synthesized ligands, such as NOBINAc, also exhibited high efficacy in the palladium catalytic cycle during the asymmetric C–H activation process (Scheme 13, b) [30c].

While allenes have been widely functionalized in various ways, including as coupling partners in transition-metal-catalyzed aromatic C–H activation, direct catalytic C–H activation of allenes is unusual. The selective activation of allenyl C–H bonds using transition-metal catalysis is a tough task due to the competitive and reactive nature of C═C═C cumulated double bonds. However, Carreira et al. introduced an elegant palladium-catalyzed picolinamide directed C–H alkenylation of allenes **55** with no electronic bias [31]. This reaction enabled the formation of penta-1,2,4-triene compounds **57** with up to 94% high yields (Scheme 14). Notably, the associated amide directing group could be readily removed under mild acidic conditions without affecting the key structural motif, which further added to the versatility of this methodology.

2.4. Mn-catalyzed C–H activation with allenes

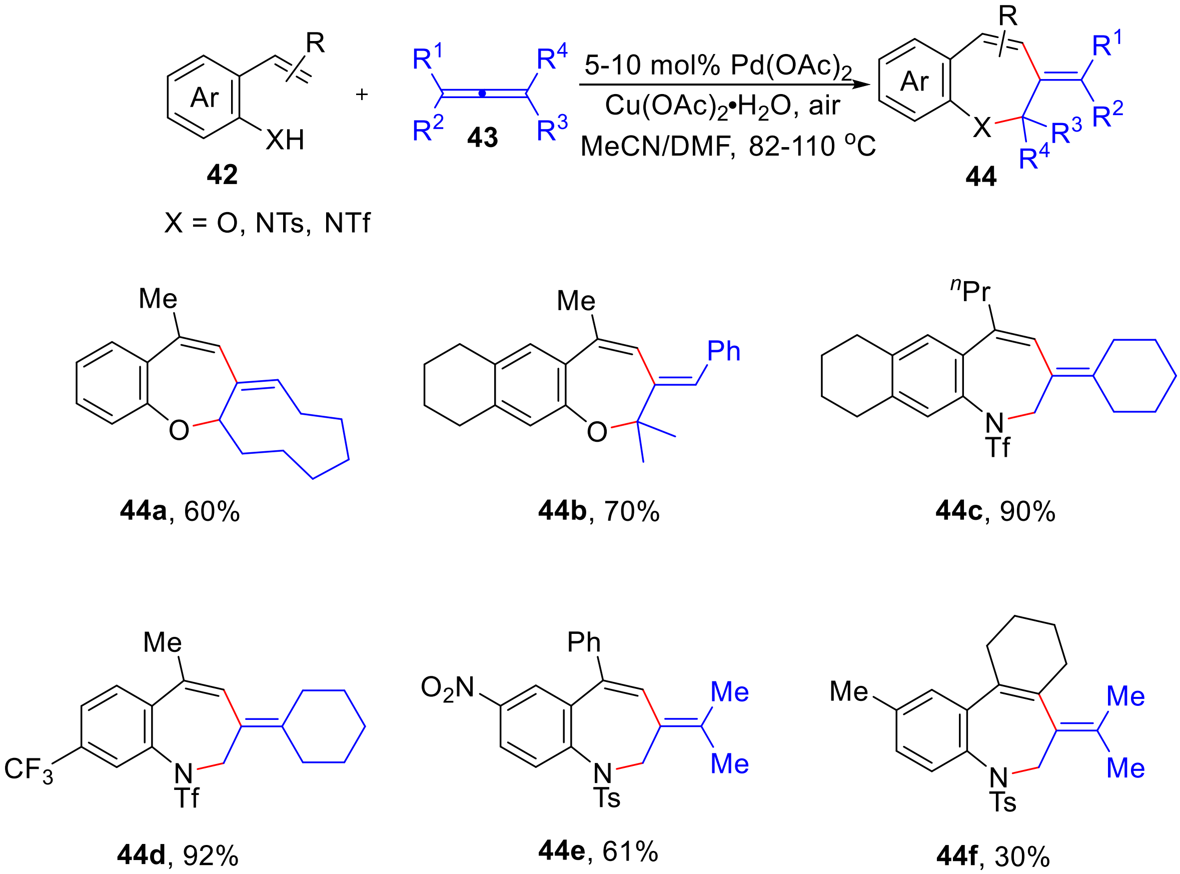
In recent decades, there has been notable attention towards first-row transition metals, such as Mn, Fe, Co, Ni, and Cu, in the field of C–H functionalization [32]. This primarily arises from their widespread availability, cost-effectiveness and low toxicity. In particular, there has been a growing interest in the utilization of manganese for C–H functionalization processes.

In 2017, the research groups of Rueping and Wang separately reported their findings on utilization of manganese(I) catalysts for achieving regio-, stereoselective hydroarylations and alkenylations from allenes (Scheme 15) [33]. It was noteworthy that the occurrence of the Smiles Rearrangement might be observed when trisubstituted allenes **8** were employed in the C–H functionalization reactions.

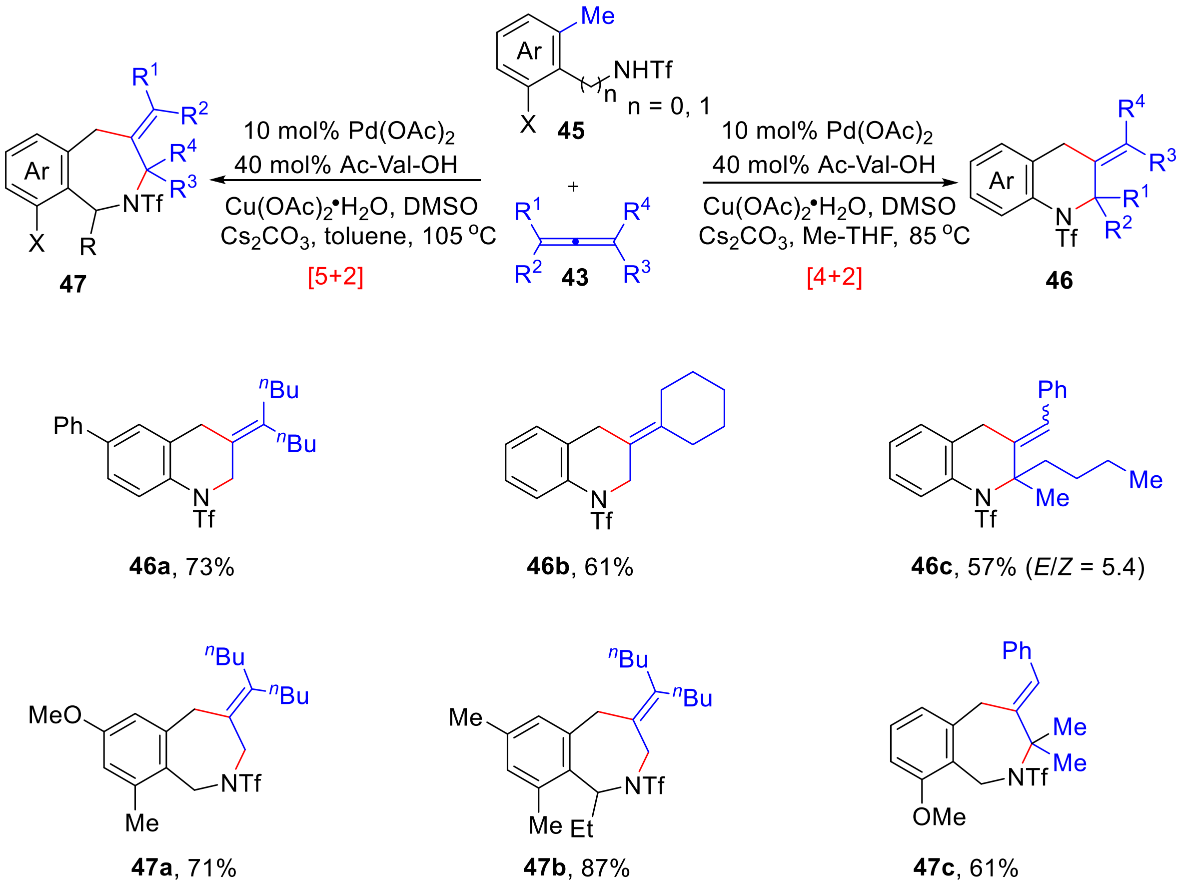
Based on related experimental studies and literature reports [32], a mechanism was proposed for the above conversion (Scheme 16). Initially, an active [Mn] species **A** was generated in the presence of $MnBr(CO)_5$ and NaOAc. Subsequently, the Mn^I-catalyzed C–H activation would occur, resulting in the formation of intermediate **B**. Thereafter, intermediate **D** is formed by a regio- and stereoselective migratory insertion, which may be determined by the electronic and steric characteristics of allene **8**. On one hand, the process of protonation of **D** may directly lead to the alkenylation product **59a**. On the other hand, the high nucleophilicity exhibited by the C–Mn bond has the potential to induce the N-to-C 1,4-migration of the pyrimidyl directing group, commonly referred to as the Smiles rearrangement, which would liberate the cyclized product **60a**.

Later, Wang et al. further conducted a study in which they demonstrated the successful application of Mn^I-catalyzed direct C–H coupling with allenes **62** (Scheme 17) [34a]. This methodology proved to be highly effective in the synthesis of various allylic arenes **63**. Moreover, the resulting allylated arenes **63** were subjected to a subsequent silver-promoted Povarov reaction, leading to the formation of structurally complex polycyclic indenoquinolines **64** [34b].

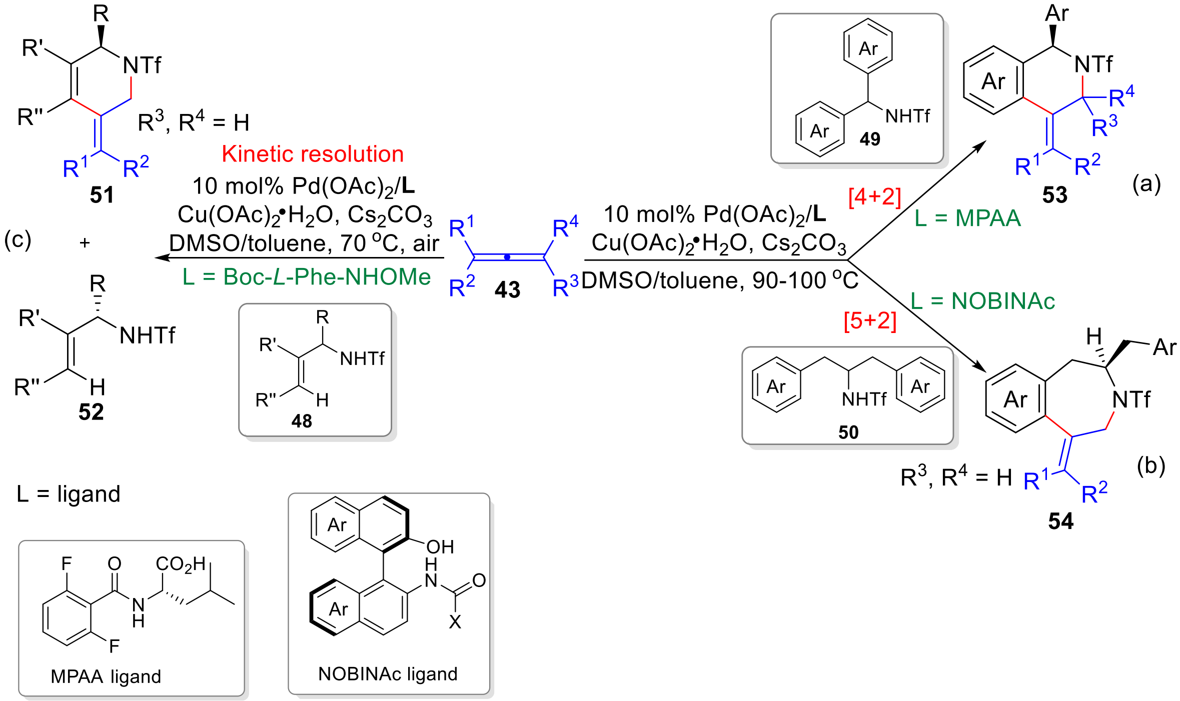
In contrast to the well-reported C–H allylation, direct C–H propargylation has not received extensive investigations, especially in processes involving unactivated C–H bonds. Glorius and co-workers revealed a novel method for the direct C–H propargylation using bromoallenes **65** with a highly selective manganese(I)/Lewis acid cocatalyst system (Scheme 18) [35]. To enhance the electrophilicity of



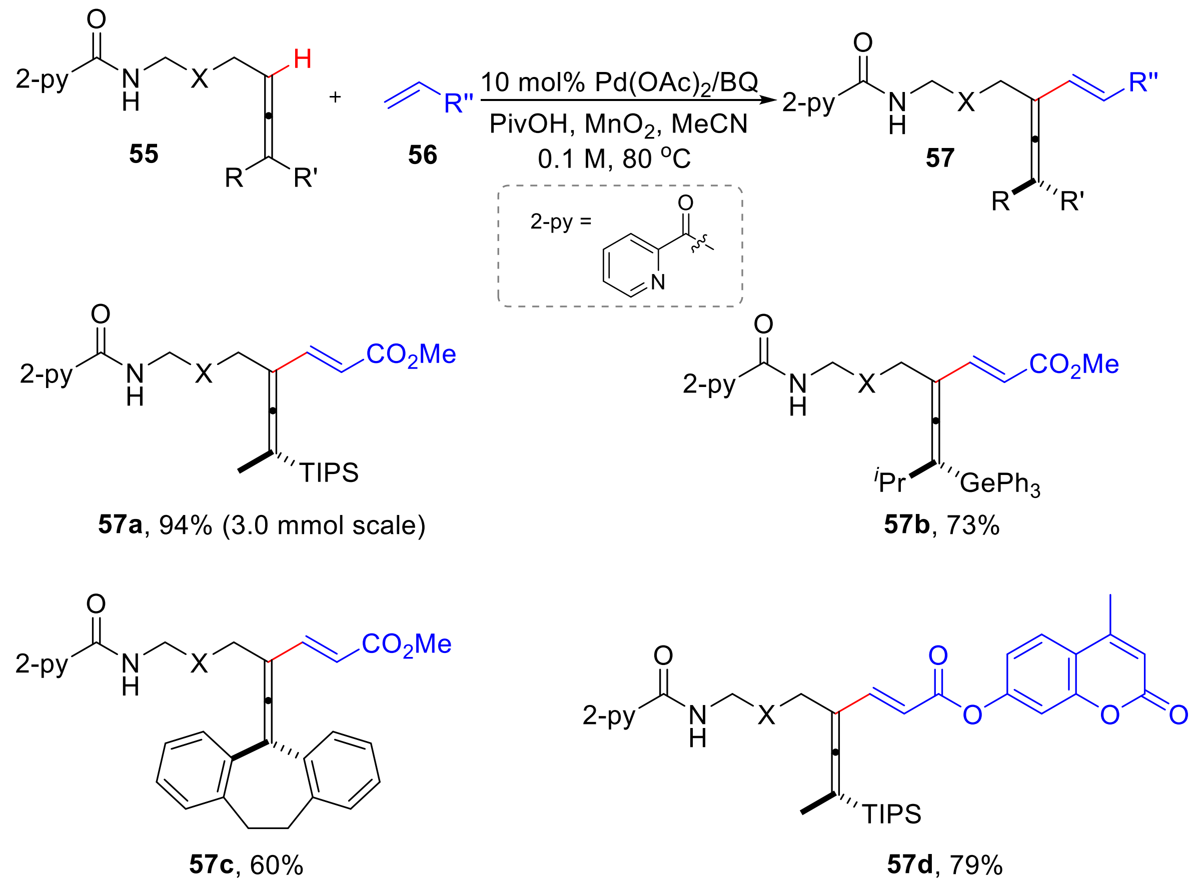
Scheme 11. Pd^{II}-catalyzed [5 + 2] annulation between *ortho*-alkenylphenols/alkenylanilines and allenes.



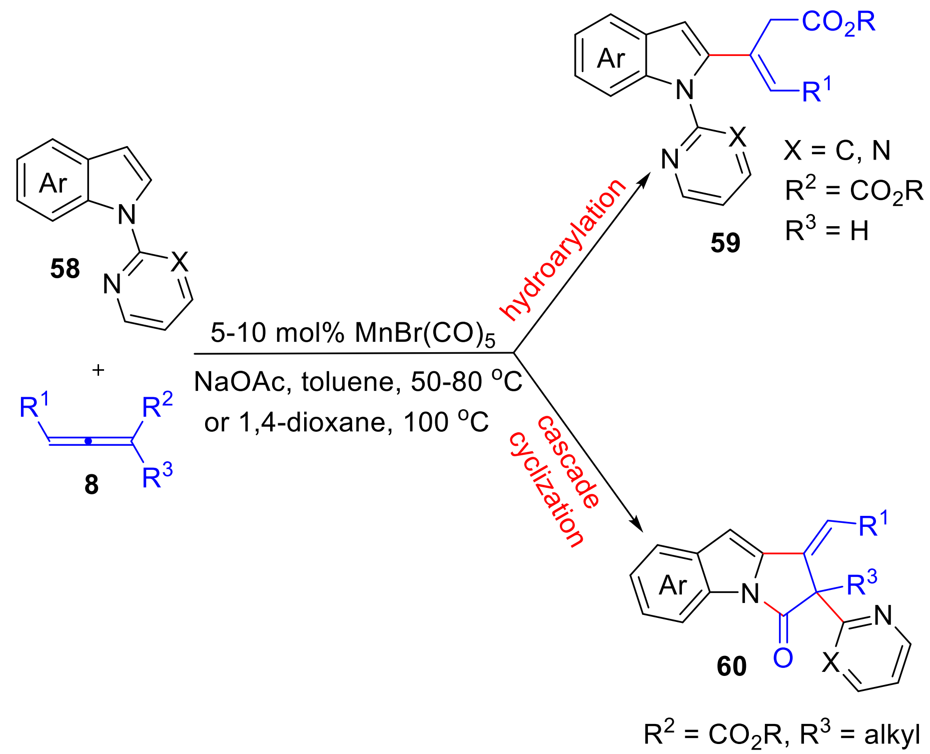
Scheme 12. Pd^{II}-catalyzed selective [4 + 2]/[5 + 2] cycloadditions with allenes.



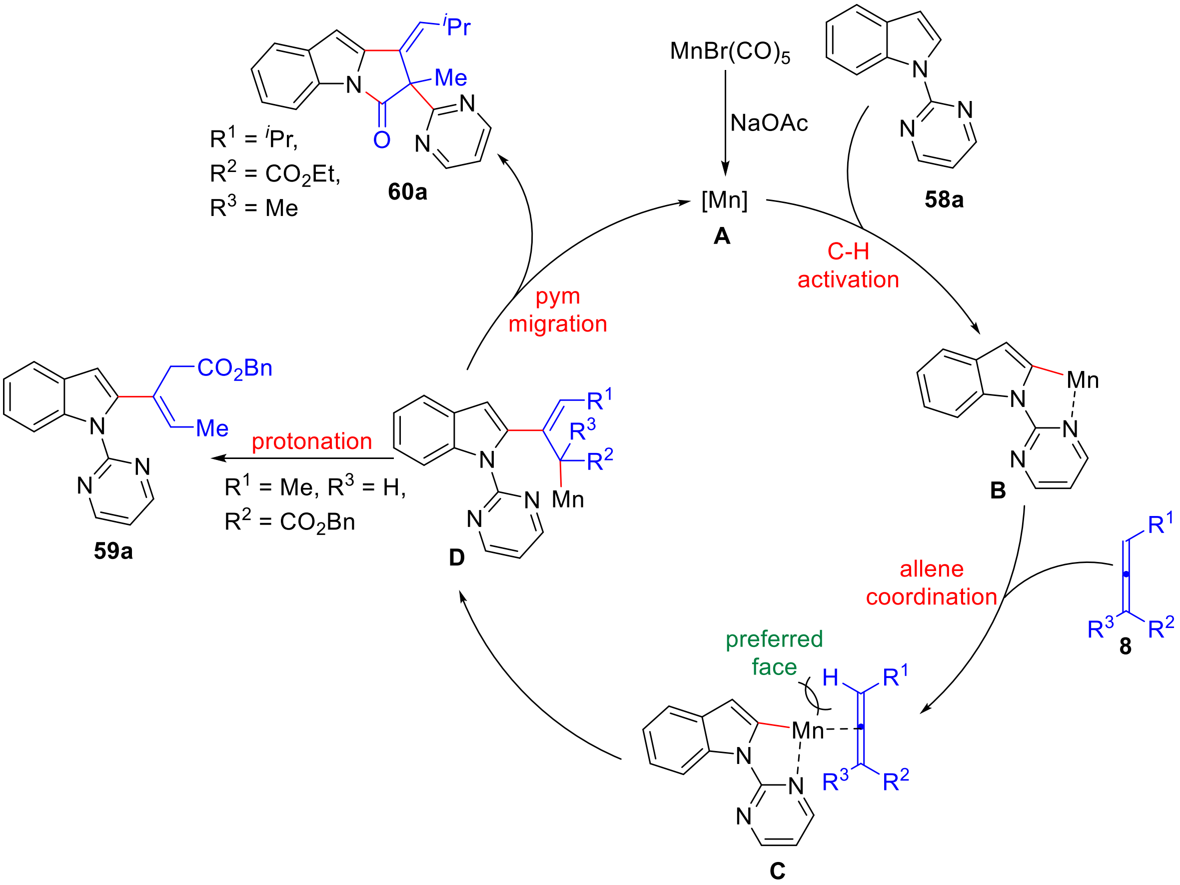
Scheme 13. Pd^{II}-catalyzed enantioselective C–H activation [4 + 2]/[5 + 2] cycloadditions with allenes.



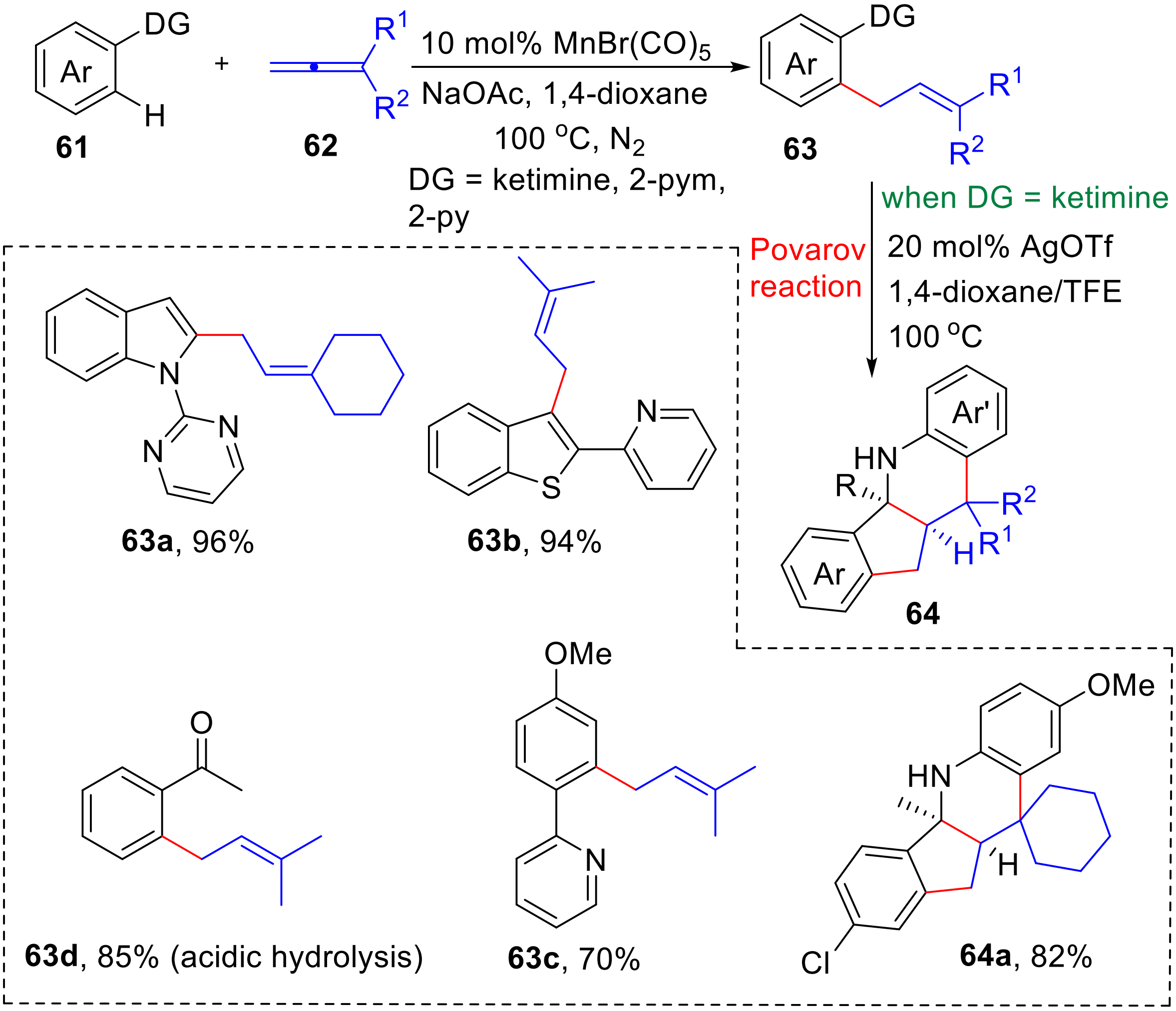
Scheme 14. Pd^{II}-catalyzed allenyl C–H alkenylation.



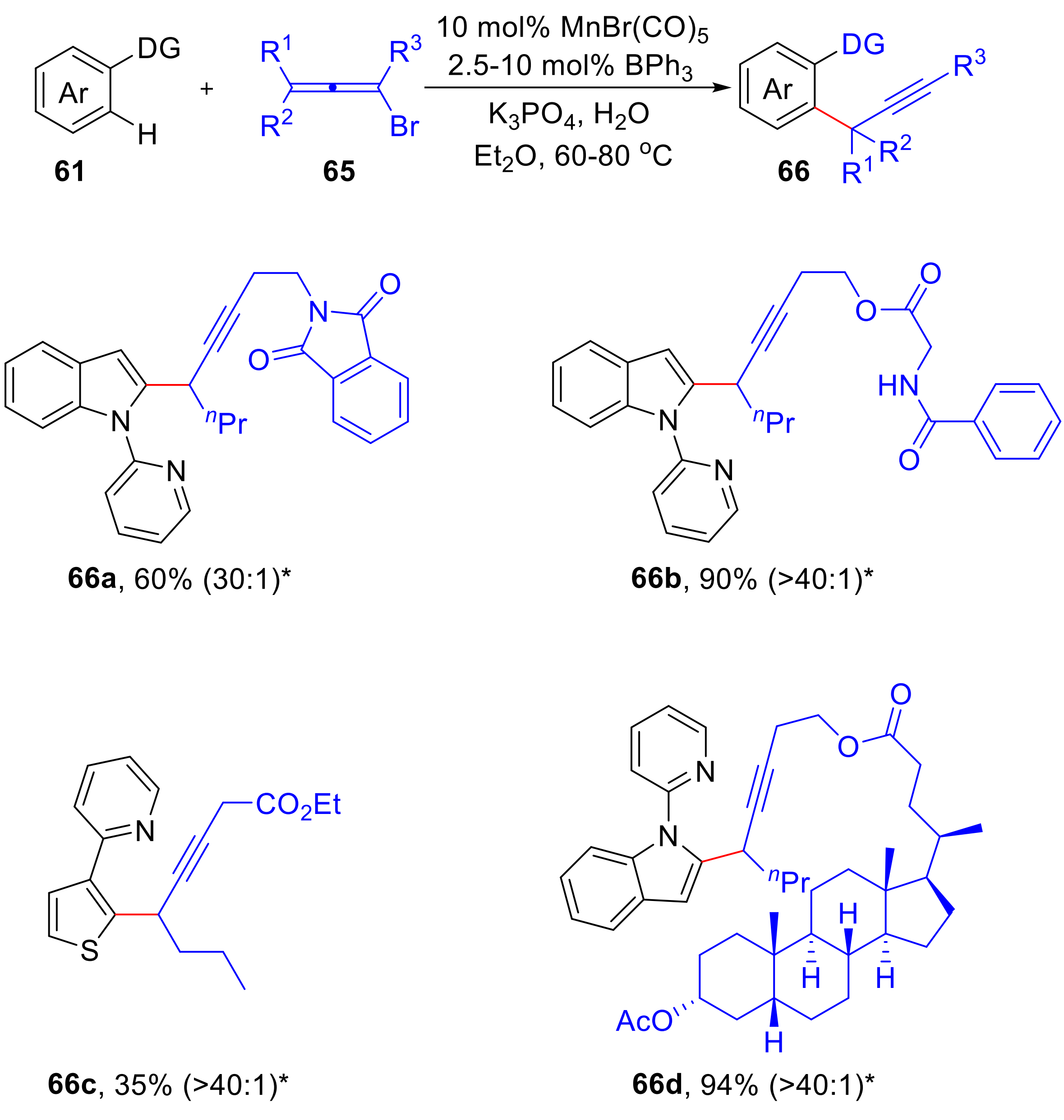
Scheme 15. Mn^{I}-catalyzed regio- and stereoselective C–H hydroarylation and alkenylation.



Scheme 16. Proposed mechanism for Mn^I-catalyzed C–H hydroarylation and alkenylation.



Scheme 17. Mn^{I}-catalyzed direct C–H allylation with allenes and silver-promoted Povarov reaction.



61 + **65** → **66**

66a, 60% (30:1)*

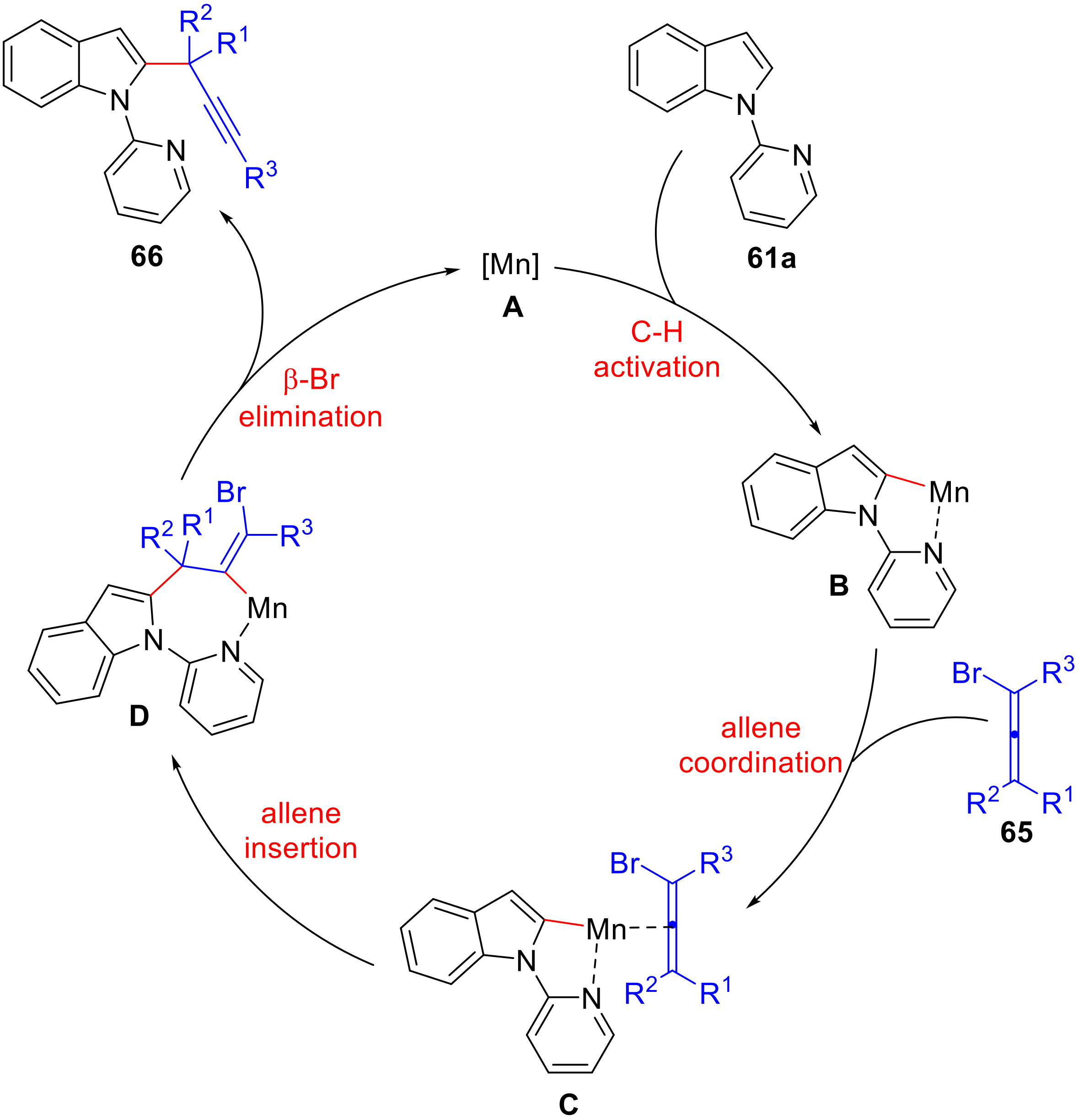
66b, 90% (>40:1)*

66c, 35% (>40:1)*

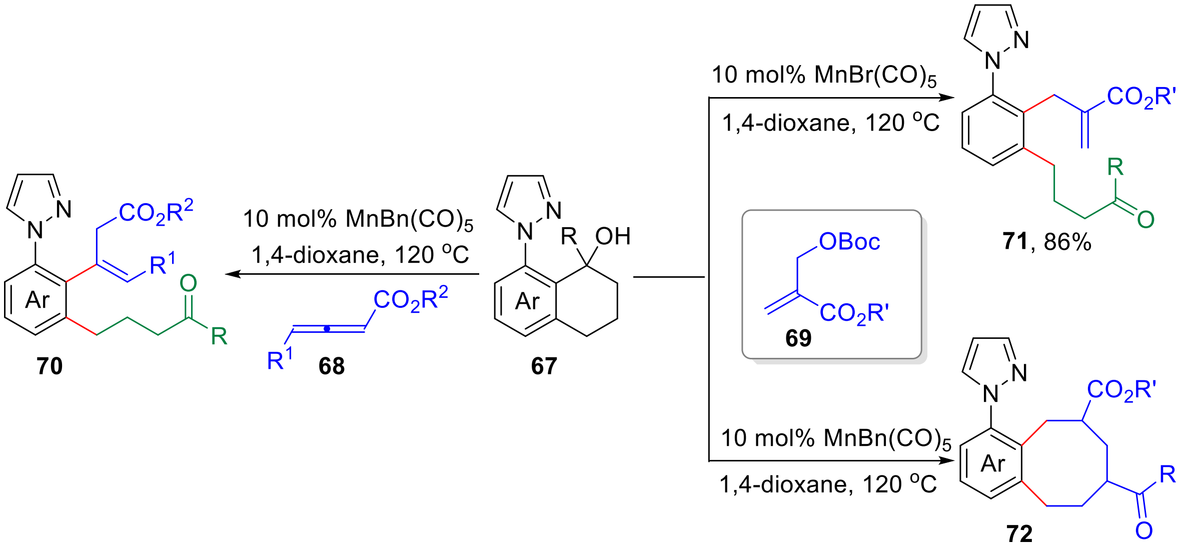
66d, 94% (>40:1)*

* The ratio herein refers to the amounts of propargylation product : allenylation product.

Scheme 18. Mn^{I}-catalyzed selective C–H propargylation using bromoallenes.



Scheme 19. Mechanism of Mn^{I}-catalyzed selective C–H propargylation using bromoallenes.



Scheme 20. The Mn^I-catalyzed C–C functionalization with allenes.

bromoallene **65** and improve both reactivity and selectivity, a Lewis acid (BPh_3) was introduced as a cocatalyst. The substrate scope exhibited favorable tolerance towards different functional groups, highlighting the potential application for late-stage diversification.

As sketched in Scheme 19, the mechanism of this regioselective propargylation generally involved the Mn^I-catalyzed C–H activation, subsequent allene coordination/insertion, and the final β-Br elimination processes.

The C–C bond functionalization has become as an adaptable and powerful tool in organic synthesis [36]. Despite significant advancements in the field of allenes chemistry in C–H functionalization achieved, the successful implementation of transition metal-catalyzed C–C activations using allenes has remained elusive. Recently, Ackermann et al. elucidated the mechanism and outcomes of the site-selective manganese(I)-catalyzed C–C hydroarylation of heteroarenes using substituted allenes **68** (Scheme 20) [37]. Aromatic compounds substituted at three positions, known as 1,2,3-tri-substituted arenes (**70–71**), were smoothly obtained with notable diastereoselectivity. It was worth noting that the ring-expansion process occurred through a cascade reaction involving C–C allylation and Michael addition. This cascade led to the formation of complex 8-membered carbocycles **72**, which showcased the distinctive property of the $MnBn(CO)_5$ complex.

The generation of compounds **70** involved a series of sequential processes (Scheme 21), including deprotonation/coordination, β-oxygen elimination, regioselective allene insertion, and protonation.

2.5. Fe-catalyzed C–H activation with allenes

The use of iron in molecular catalysis holds great appeal due to its cost-effectiveness, non-toxicity, and status as the most abundant transition-metal found on earth. Despite great progresses and developments in the field of affordable 3d base-metal catalysts [32], the utilization of iron for C–H functionalization with allenes has remained challenging until recently.

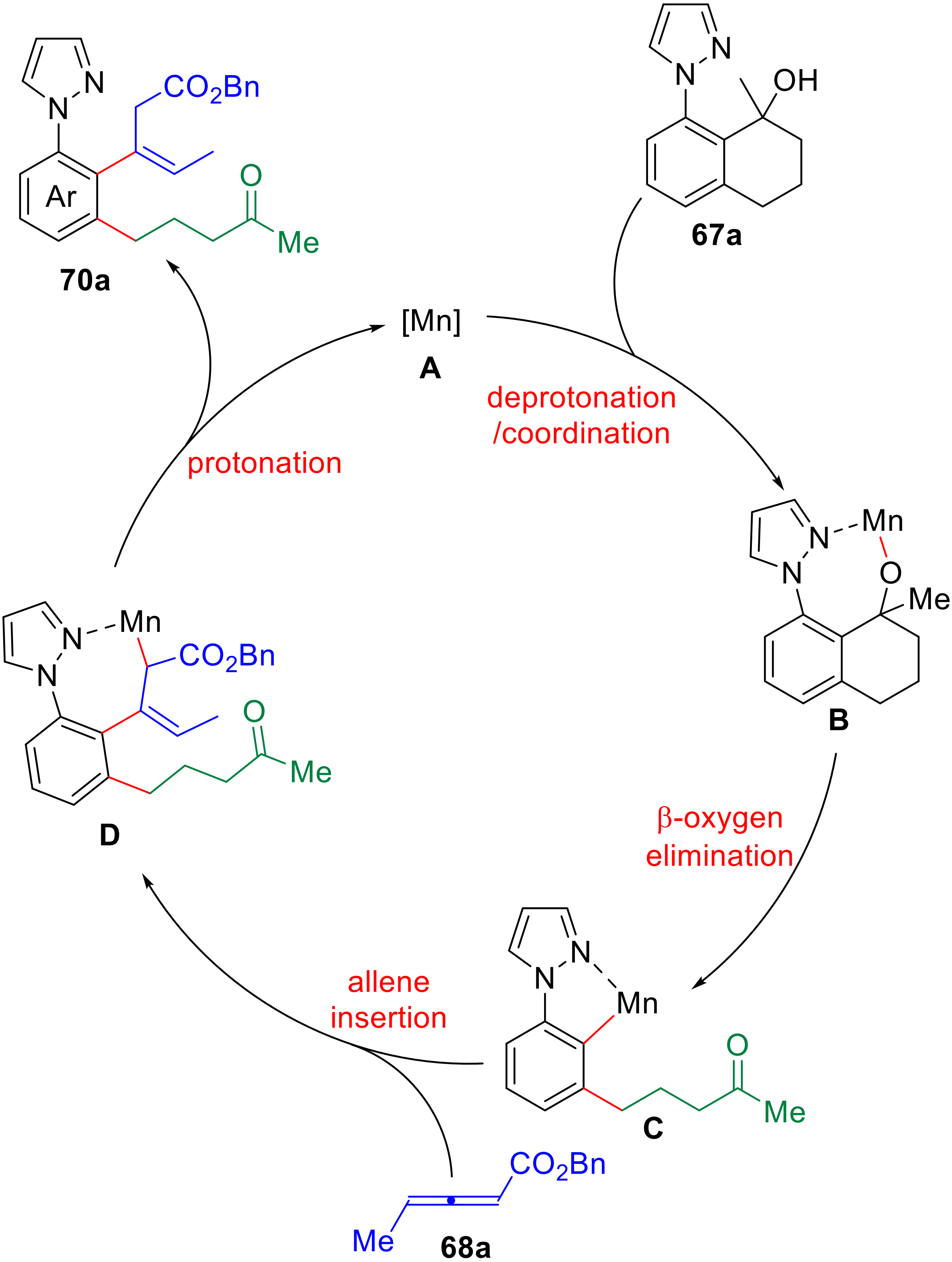
In 2018, Ackermann reported a breakthrough in C–H activation utilizing allenes, facilitated by a non-toxic iron catalyst (Scheme 22) [38]. The versatility of the iron catalyst was demonstrated through redox-neutral annulations of allenyl substrates **74**. These annulations were guided by a detachable triazole group, and involved C–H/N–H/C–O/C–H functionalizations. Importantly, these transformations occurred under mild reaction conditions, resulting in the efficient synthesis of variously substituted isoquinolones **75**.

The iron-catalyzed allene annulation discussed above was found to initiate with a straightforward C–H metalation process, along with allene migratory insertion (Scheme 23). This was subsequently followed by oxidation-induced reductive elimination, 1,4-Fe migration, and proto-demetallation processes. These mechanistic investigations provided valuable insights into the reaction.

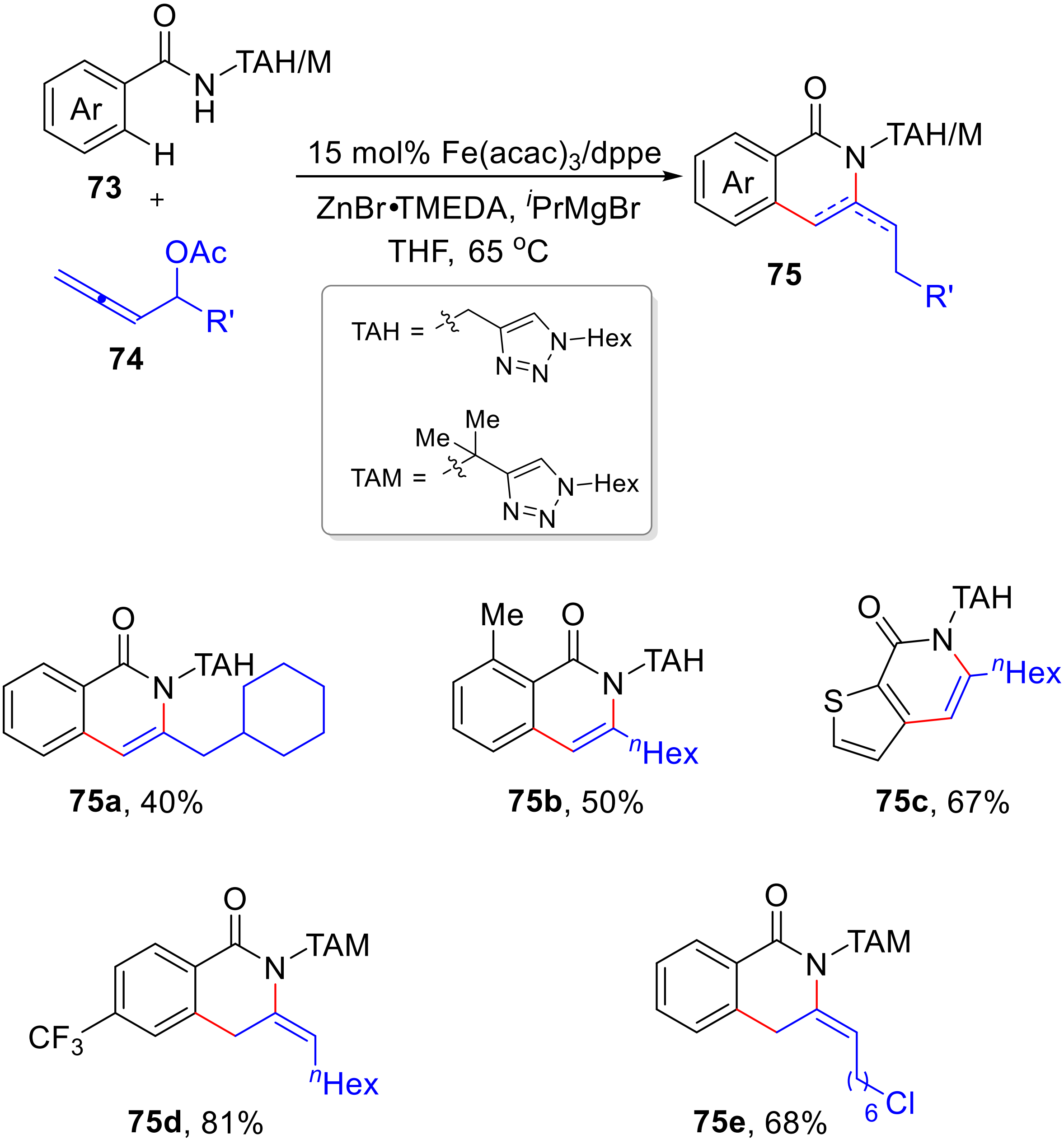
Later, the same research group documented the iron-catalyzed hydroarylation of allenes, which was facilitated by the presence of weak O-coordination (Scheme 24) [39]. The C–H activation reaction exhibited remarkable efficiency and displayed a strong preference for the *ortho*-position relative to the weakly coordinating carbonyl group. This selectivity was seen across a wide range of aryl ketones **76** and allenes **62** bearing various substituents.

While there are many established formal C–H functionalization processes involving allenes that deliver diverse olefinic products, only a limited number of methods exist for the C–H functionalization of electron-neutral allenes without causing addition to or isomerization of the delicate allene moiety [10d]. Wang et al. recently uncovered a unique approach utilizing deprotonation strategy to enable the functionalization of unactivated terminal allenes **14** through C–H activation (Scheme 25) [40]. The implementation of this approach was facilitated by the integration of a newly discovered cationic organoiron catalyst and the use of *N*,*O*-acetal reagents **73** as precursors for iminium electrophiles.

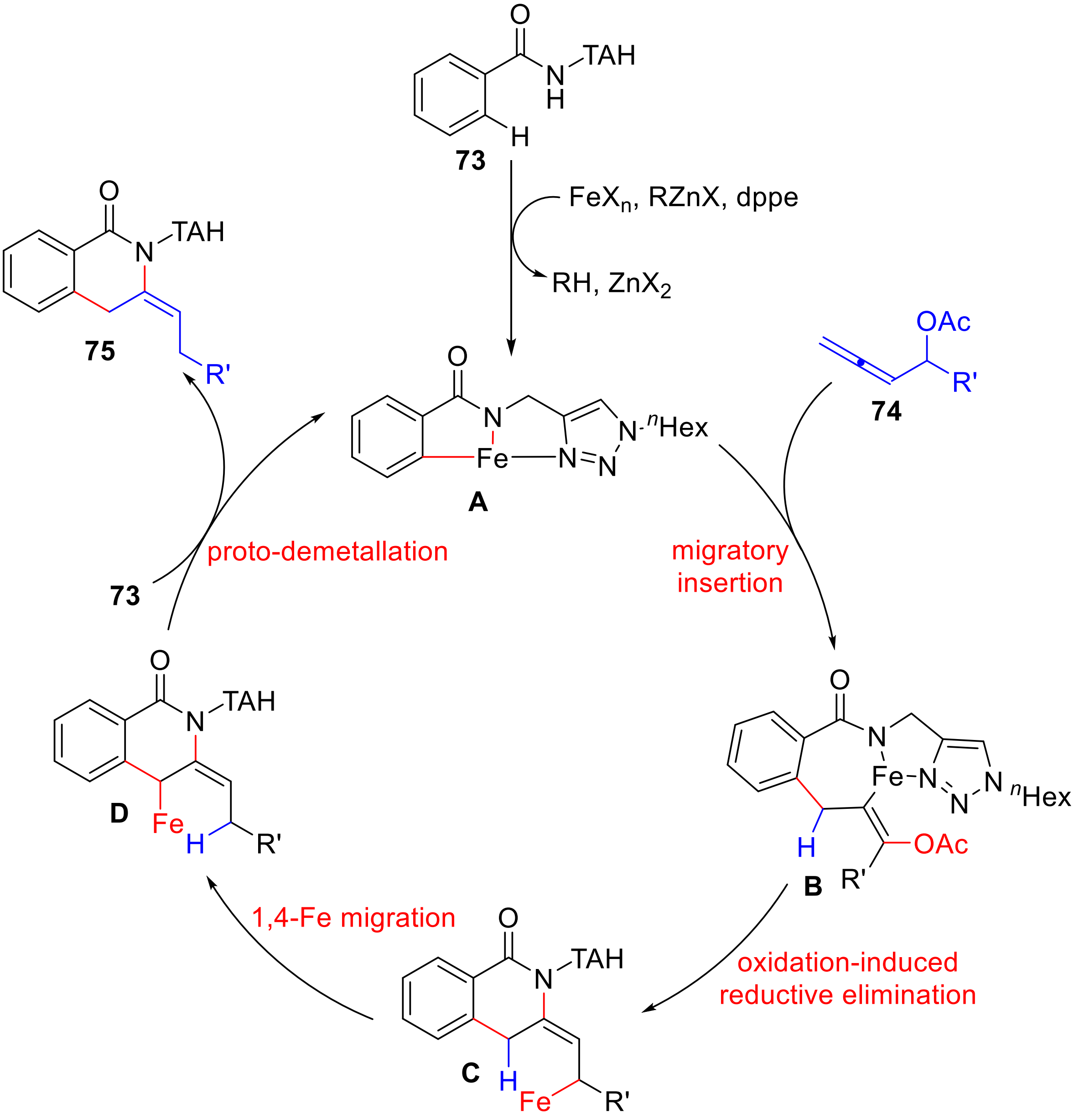
It was worth mentioning that the contrasteric C–H functionalization products **79** were generated by the selective deprotonation and S_E2'



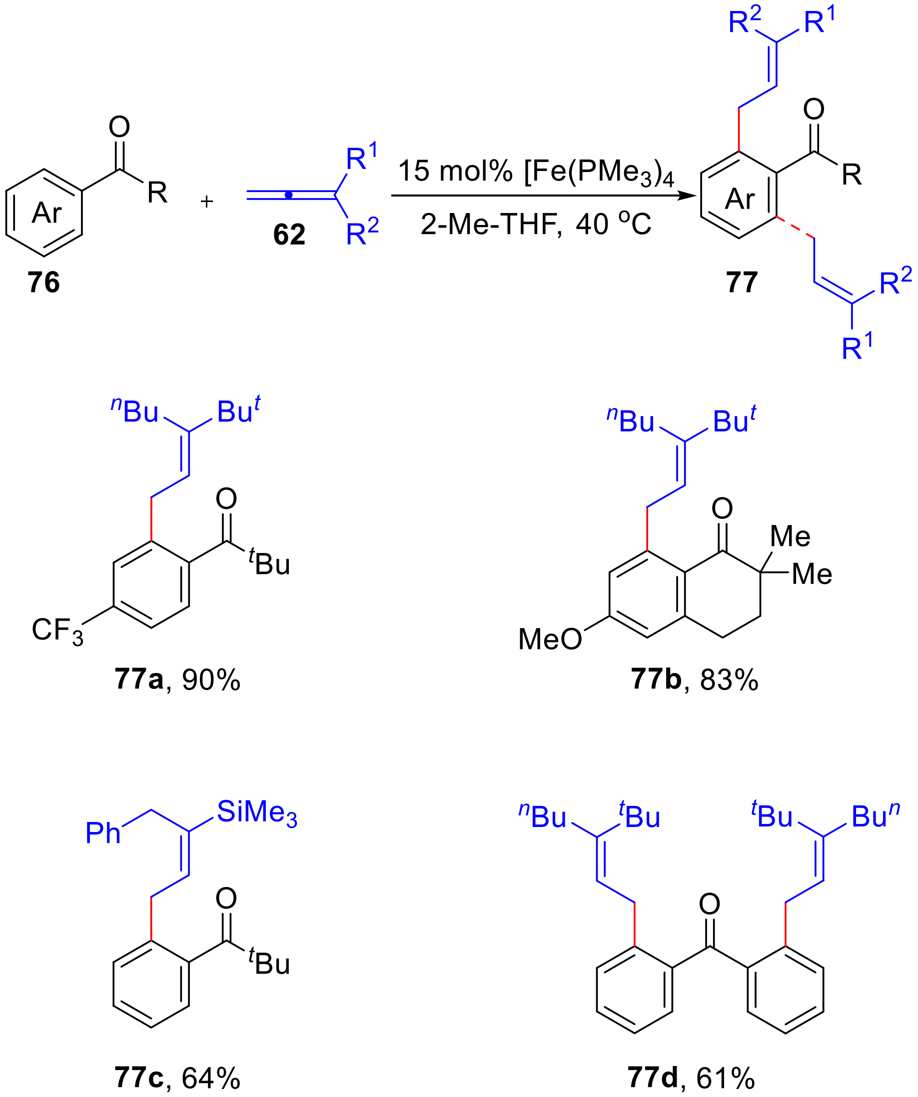
Scheme 21. Proposed mechanism of Mn^I-catalyzed C–C functionalization.



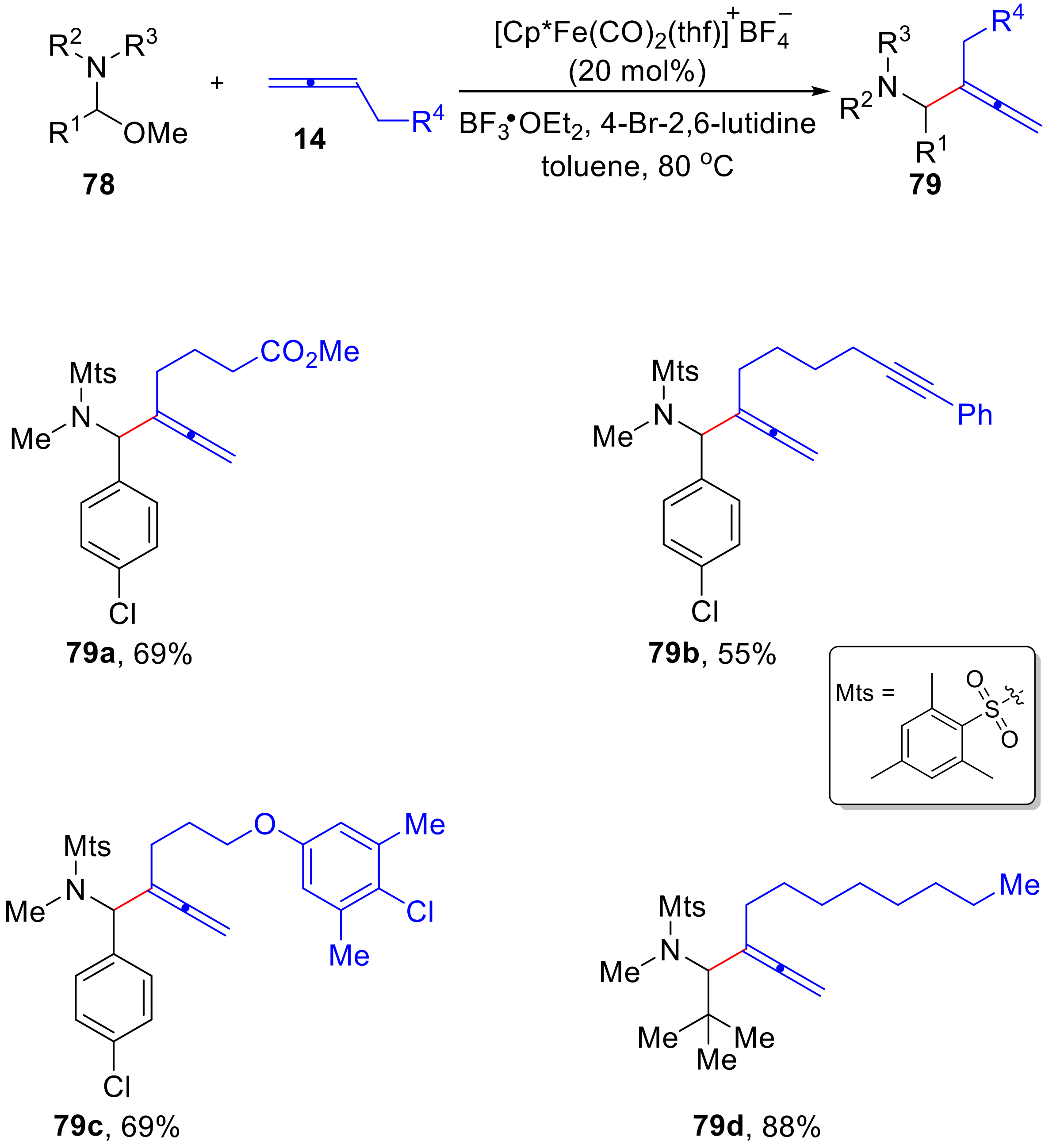
Scheme 22. Fe-catalyzed C–H/N–H annulation with allenes.



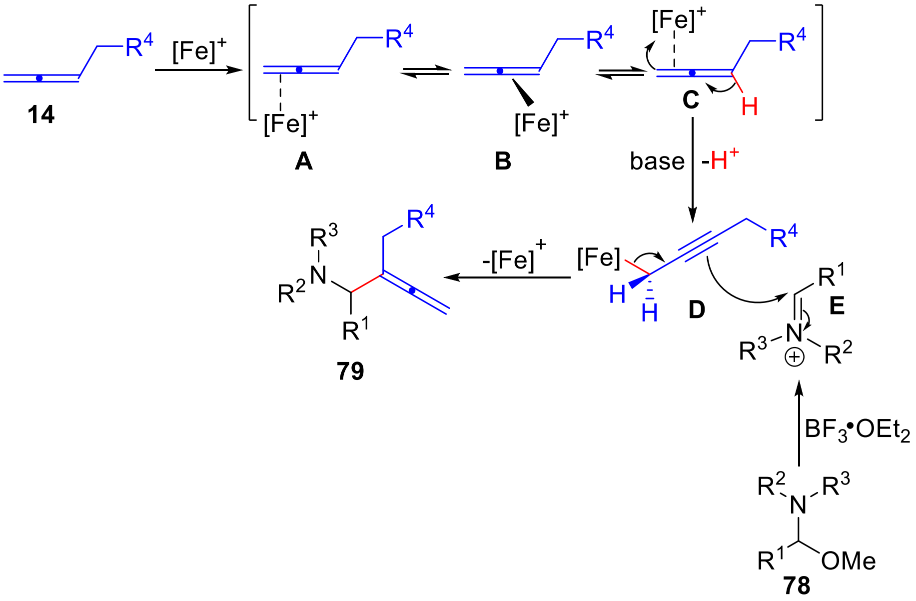
Scheme 23. Plausible catalytic cycle for the C–H/N–H/annulation.



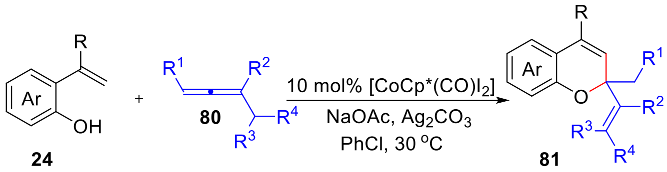
Scheme 24. Fe-catalyzed C–H allylation with allenes.



Scheme 25. Fe-catalyzed feasible approach to allenylic amines by C–H functionalization.



Scheme 26. Mechanism of Fe-catalyzed approach to allenylic amines.



Scheme 27. Co^{III}-catalyzed [5 + 1] oxidative annulation with allenes.

reaction of the stereoelectronically well-disposed isomer **C** (Scheme 26).

2.6. *Co-catalyzed C–H activation with allenes*

Significant progress has been achieved in the use of cobalt catalysts for allenes-based C–H functionalization since the groundbreaking work of Cheng in 2016. Their pioneering study demonstrated the first example of allene involvement in C–H functionalization *via* cobalt catalysis (Scheme 27) [41].

Building upon the aforementioned investigation, a diversified array of cobalt-catalyzed directed C–H activation reactions stemming from variously substituted allenes have been reported by Volla, Cheng, Ackermann, and other researchers (Scheme 28) [42]. These transformations encompassed [4 + 1], [3 + 3], and [4 + 2] annulation processes, resulting in the rapid and efficient synthesis of varied heterocyclic compounds **87–92**.

The hydroarylation of unsaturated carbon–carbon bonds offers a direct and efficient approach to valuable alkenylated/alkylated arenes. This specific process enables the formation of a carbon–carbon bond with notable effectiveness in high atom economy. In 2017, Ackermann et al. introduced the first cobalt-catalyzed hydroarylation of allenes **62**, demonstrating remarkable levels of both chemo- and regioselectivity (Scheme 29) [43]. Comprehensive investigations including kinetic studies and Hammett analysis, were conducted to unravel the catalytic cycle. The findings indicated that the cycle was commenced with a reversible dissociation of the N-ligand, followed by a kinetically significant activation of the arene C–H bond.

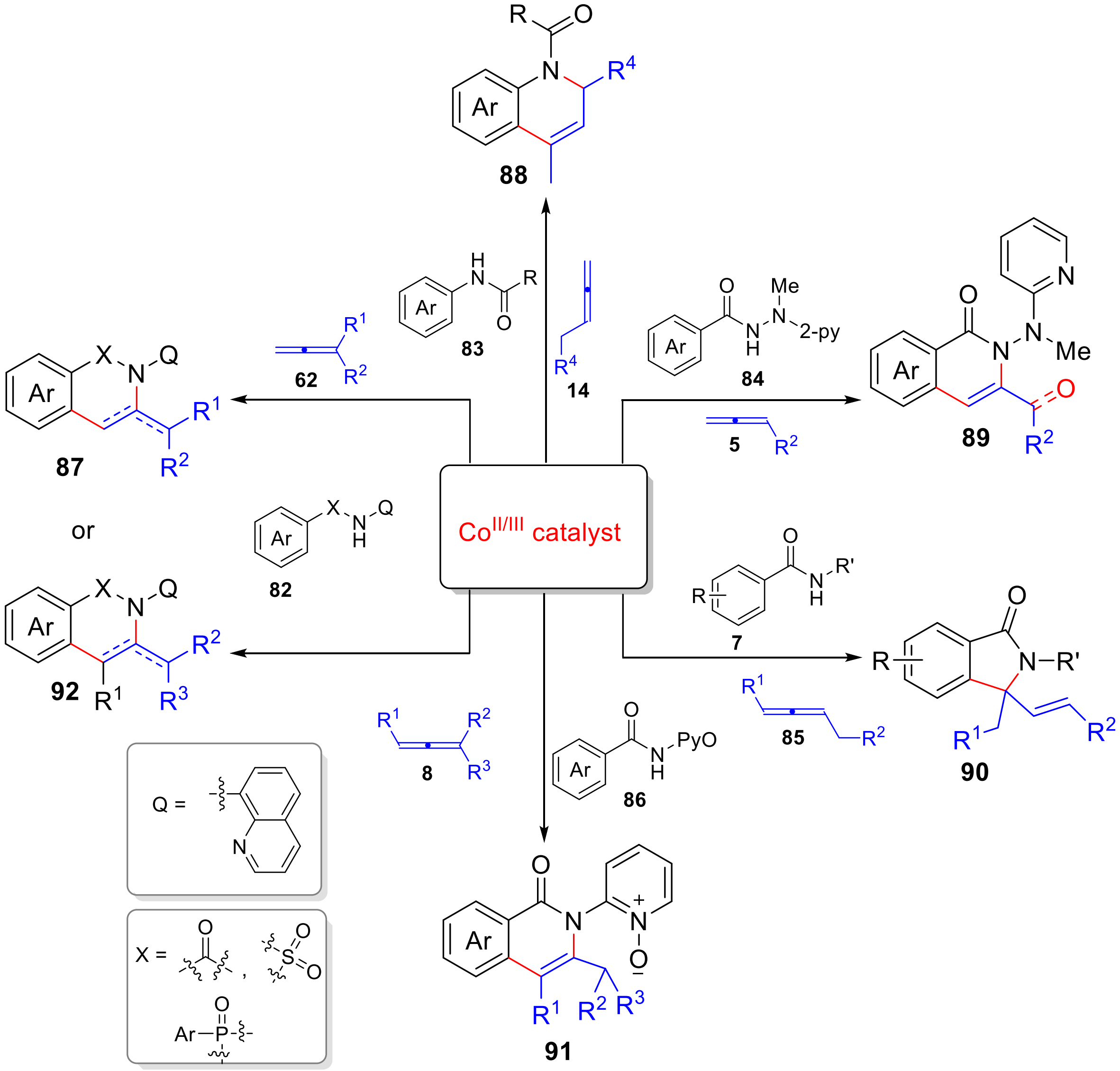
Although there has been extensive research conducted on cobalt-catalyzed C–H alkenylation and annulation processes involving allenes, the corresponding C–H dienylation reactions, which are crucial for the synthesis of functionalized 1,3-dienes and have significant implications in the fields of organic synthesis and materials science [20, 21], have received relatively less attention. Volla et al. successfully devised a novel method for regioselective C-8 dienylation of quinoline *N*-oxides **95** using cobalt catalysts (Scheme 30) [44]. This innovative approach utilized allenylcarbinol carbonates **96** as the dienylating agents. Besides, the reaction enjoyed a broad range of substrate compatibility and could be carried out under mild reaction conditions.

The use of three-component systems in C–H functionalization represents a very attractive strategy to access a diverse array of complex products in a singular reaction. This is particularly valuable when considering the extensive amounts of possible combinations of coupling partners. In line with this concept, Ellman and co-workers disclosed an innovative Co^{III}-catalyzed three-component transformation, leading to the incorporation of diversely functionalized alkenyl halides **99** in a high regio- and stereoselective manner (Scheme 31) [45].

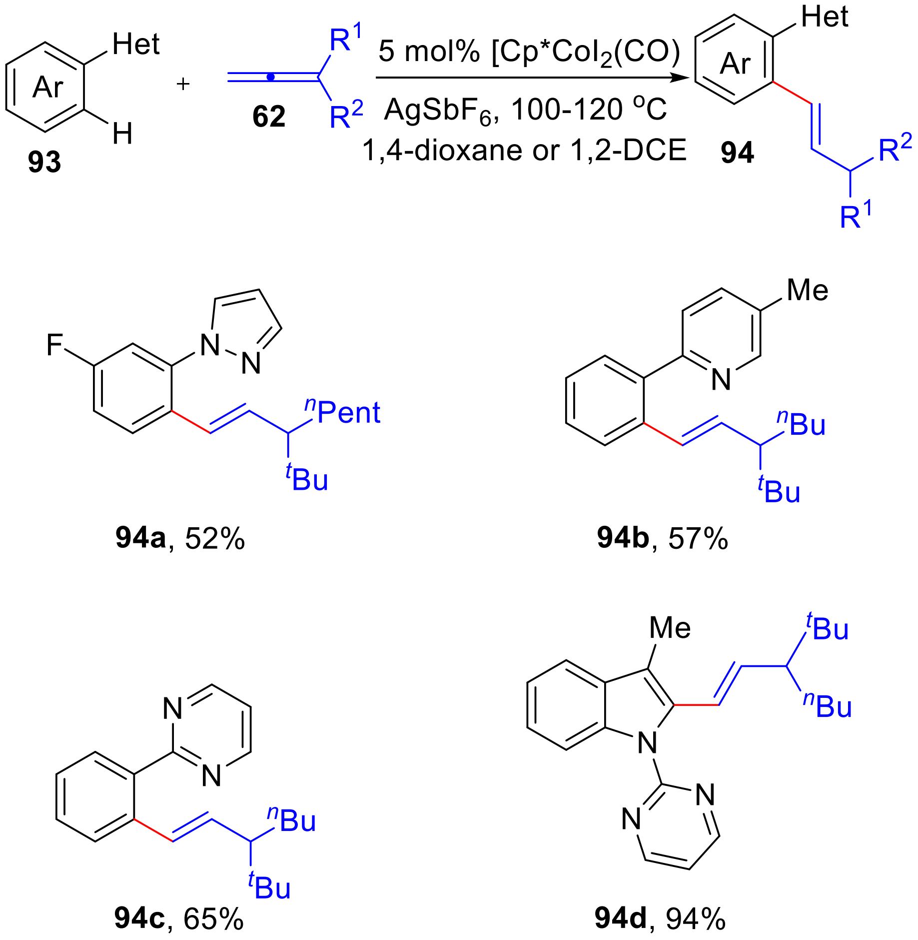
2.7. *Other transition-metal catalyzed C–H activation with allenes*

In addition to the aforementioned allene-mediated C–H functionalizations, there are also a few examples of employing other transition-metal catalysts.

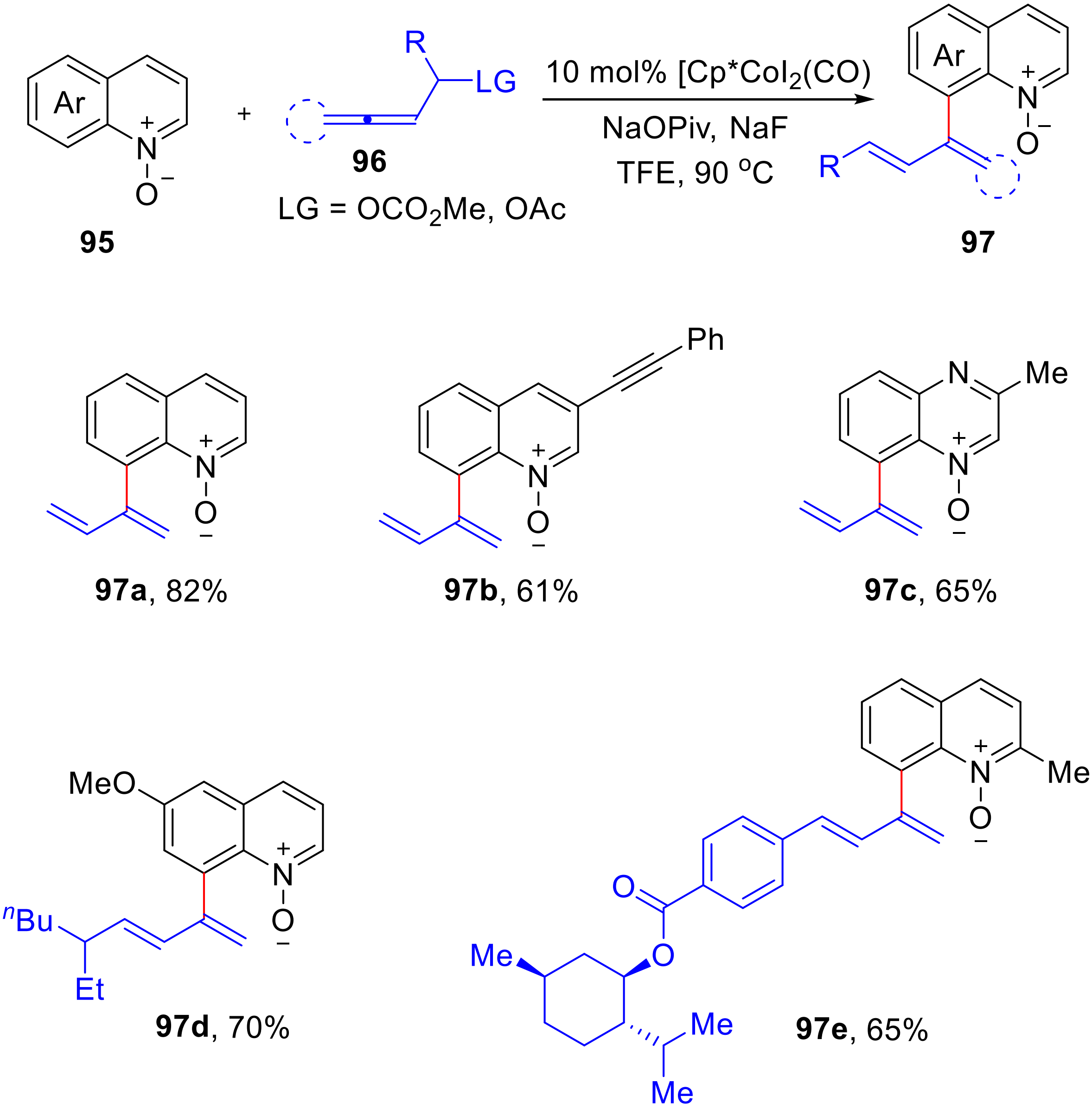
In 2017, Ackermann conducted a study detailing the initial findings of Ni^0-catalyzed C–H allylations, alkenylations, and dienylation through bifurcated C–H activation with allenes (Scheme 32) [46]. Interestingly, the allylated product **101** could be isomerized into the



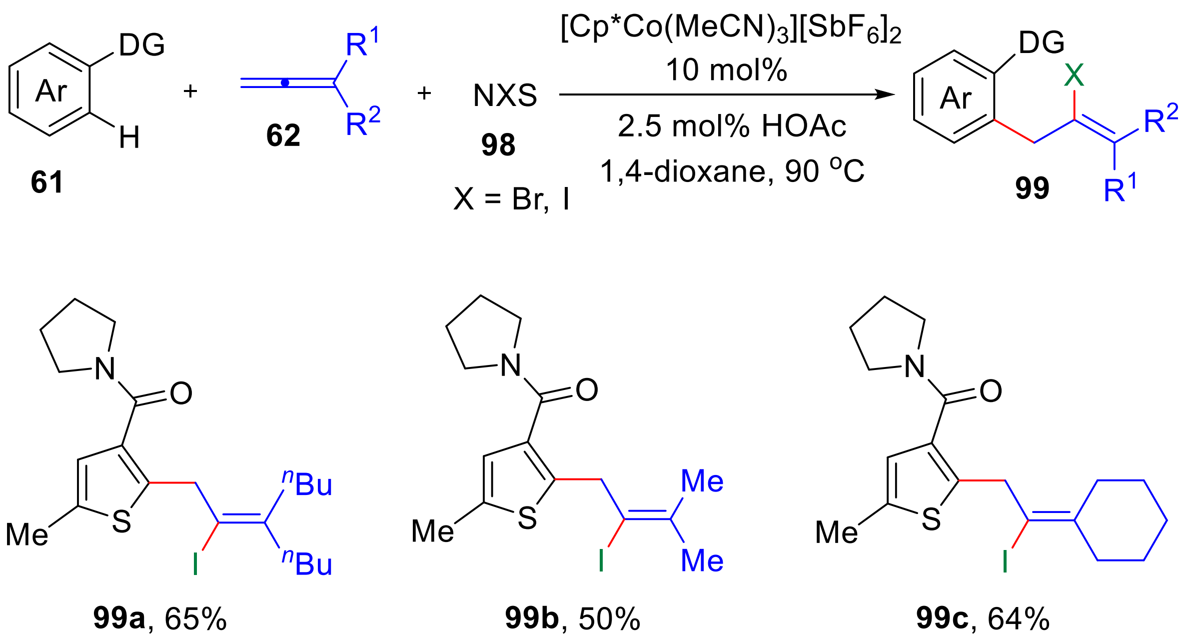
Scheme 28. Co-catalyzed diverse construction of heterocycles with allenes.



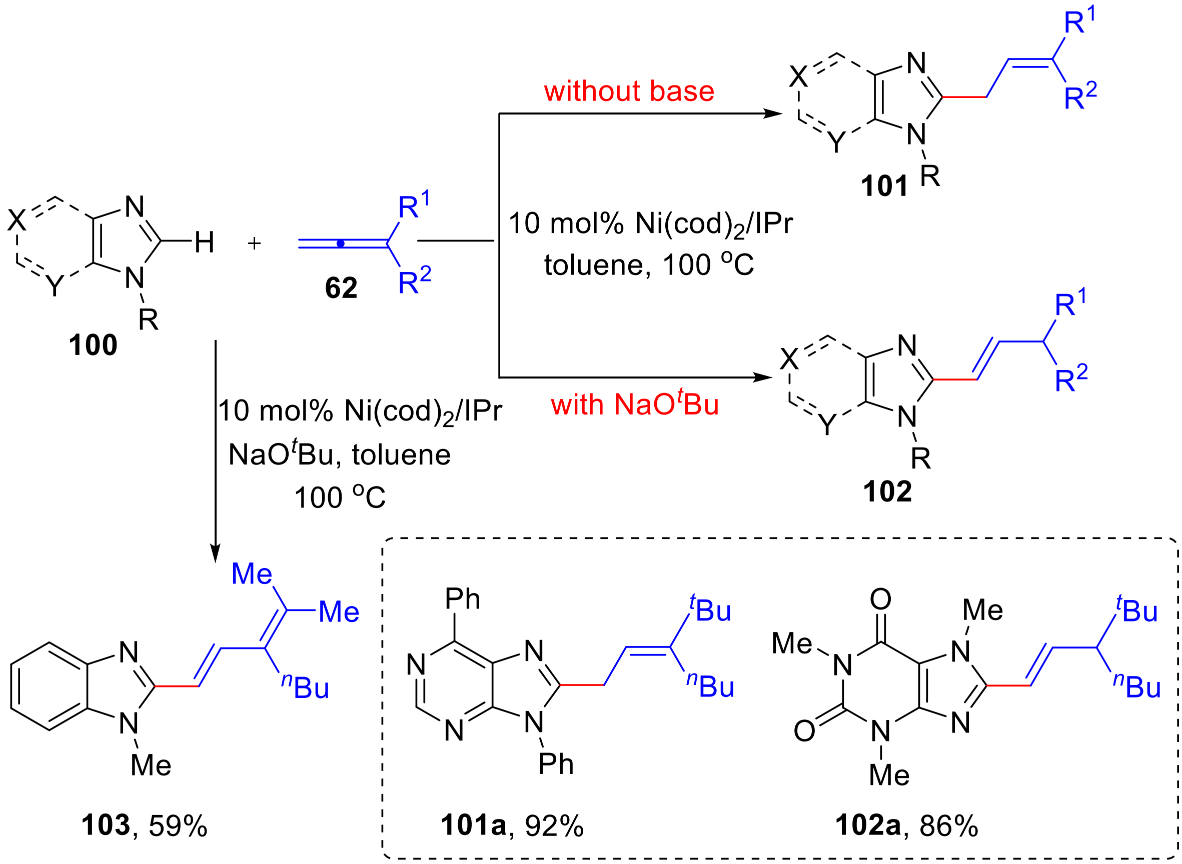
Scheme 29. Co^{III}-catalyzed C–H alkenylation with allenes.



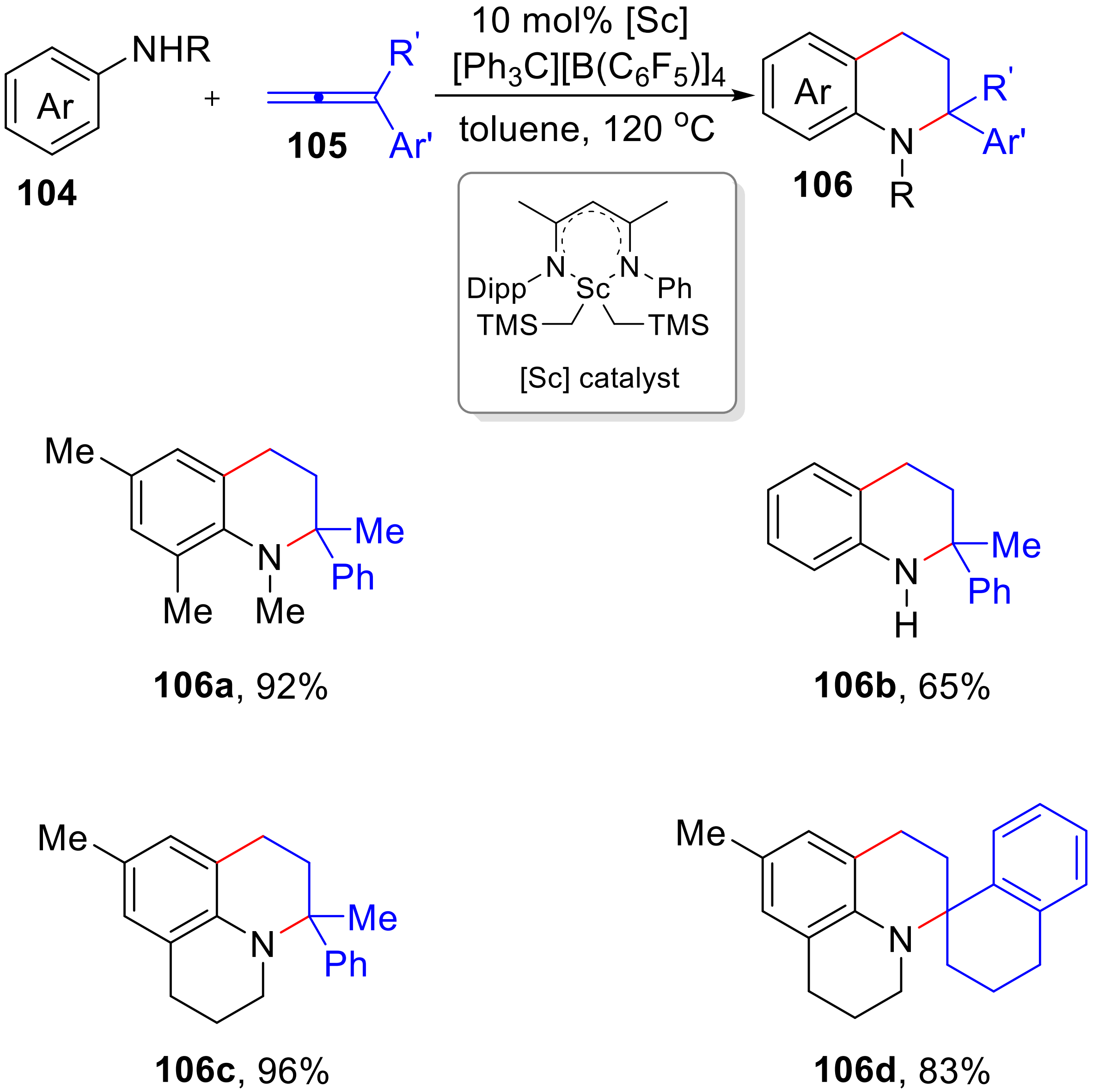
Scheme 30. Co^{III}-catalyzed C8-alkenylation of quinoline-*N*-oxides.



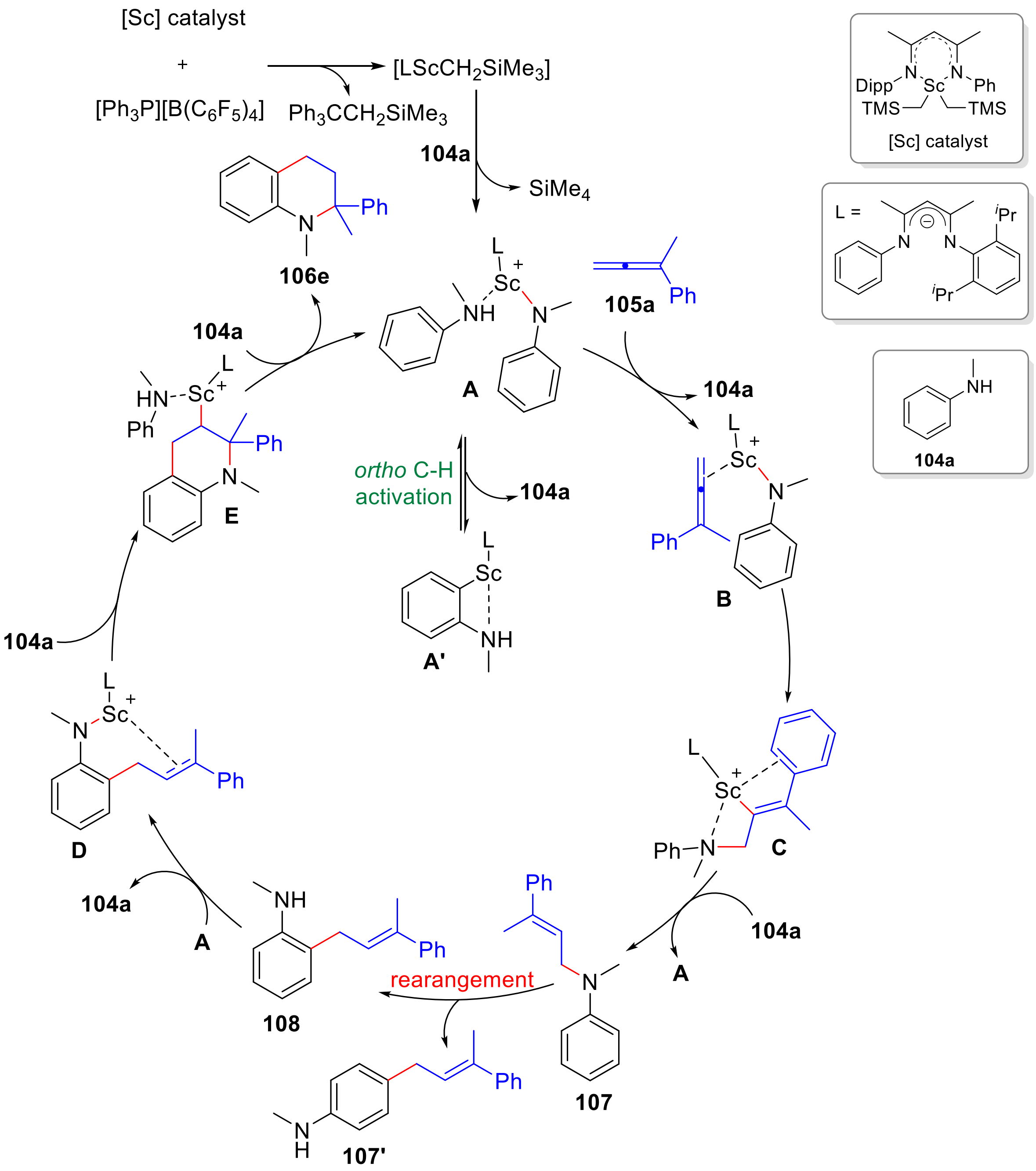
Scheme 31. Co^{III}-catalyzed three-component C–H bond functionalization.



Scheme 32. Ni^0-catalyzed heteroarene C–H activation with allenes.



Scheme 33. Scandium-catalyzed annulation of anilines with allenes.



Scheme 34. Proposed mechanism of Scandium-catalyzed annulation.

thermodynamically more stable alkenylated product **102** with the assistance of the base.

In a recent development, Xu reported a notable advancement in the field with the disclosure of a redox-neutral C–H/N–H annulation reaction between anilines **104** and allenes **105** (Scheme 33) [47]. This transformation adopted a scandium catalyst along with a simple β-diketiminato ligand. These transformations harnessed the potential of allene coupling partners as versatile three-carbon building blocks, leading to the selective construction of various tetrahydroquinolines **106** in high isolated yields. Importantly, these conversions exhibited a broad substrate scope and demonstrated high atom efficiency, further highlighting their synthetic utility.

As demonstrated in Scheme 34, a possible mechanism of the above transformation was proposed. In general, it mainly involved a series of Sc-catalyzed *N*-allylation, Hoffman-Martius rearrangement [48], and hydroamination.

3. Conclusion

In conclusion, this paper provides a comprehensive overview of recent advancements in transition-metal-catalyzed C–H activation with allenes, shedding light on the intriguing and captivating reactivities of allenes in these transformations. Further developments in this research field hold the potential to deepen our understanding of the distinct and unique reactivities exhibited by variously substituted allenes, with a particular focus on elucidating corresponding reaction mechanisms and inexpensive transition-metal catalysts developments. Next, transition-metal-catalyzed enantioselective version of C–H functionalization with allenes represents a significant challenge in achieving regio- and chemoselectivity, making it an exciting frontier in future. Besides, exploring the relatively uncharted territory of sp^3 C–H activation with allenes has the potential to significantly expand the scope of substrates available for constructing complex molecules; hence it has a great demand and is full of promising opportunities.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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