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RECENT ADVANCES IN TRANSITION-METAL-CATALYSED REGIOSELECTIVE ORTHO C-H FUNCTIONALIZATION STRATEGY- A COMPREHENSIVE REVIEW

KEY WORDS:

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ABSTRACT

Metal-catalyzed C-H allylation has emerged as a powerful strategy for the direct installation of allyl groups into inactivated C-H bonds, offering streamlined access to complex molecules with improved atom and step economy. Unlike classical allylation methods that rely on prefunctionalized substrates, direct C-H allylation eliminates extra synthetic steps and enhances functional-group compatibility. Advances in noble and first-row transition-metal catalysis, directing-group strategies, ligand design, and photoredox systems have enabled selective activation of both C(sp²)-H and C(sp³)-H bonds under mild conditions. The allyl moiety serves as a versatile handle for further transformations, making this approach valuable in natural product synthesis, late-stage functionalization of pharmaceuticals, and materials chemistry. Ongoing challenges include regioselective control, asymmetric variants, and scalable protocols. Continued development of sustainable catalysts and novel allyl sources is expected to expand the scope, efficiency, and selectivity of C-H allylation, reinforcing its central role in modern synthetic chemistry.

1. INTRODUCTION

The activation and functionalization of inert C-H bonds have revolutionized organic synthesis, providing unprecedented opportunities to construct complex molecules from simple and abundant precursors with enhanced atom and step economy.¹⁻³ Among the diverse C-H bond transformations, metal-catalyzed C-H allylation has emerged as a particularly powerful strategy for the direct installation of synthetically versatile allyl groups.⁴⁻⁶ The allyl moiety is a fundamental structural motif in numerous natural products, agrochemicals, pharmaceuticals, and fine chemicals, and it serves as a valuable synthetic handle for subsequent functionalization through oxidation, cyclization, or substitution reactions.⁷⁻⁸ Consequently, the development of efficient and selective methods for direct C-H allylation has become a central focus in modern catalysis.

1.1 Background and Mechanistic Overview

Traditionally, allylation reactions relied on prefunctionalized substrates such as allyl halides, allyl carbonates, or allyl acetates, proceeding through π -allyl metal intermediates via the classical Tsuji-Trost mechanism.⁹ Although highly effective, these methods often suffer from poor atom economy and require multiple preparative steps. In contrast, metal-catalyzed C-H allylation enables the direct incorporation of an allyl fragment into an inactivated C-H bond, eliminating the need for substrate pre activation and significantly simplifying synthetic routes.¹⁰⁻¹²

These reactions typically proceed through metal-mediated C-H bond cleavage, formation of a metal-carbon intermediate and subsequent coupling with an allyl donor such as an allyl halide, allyl ether, or vinyl epoxide.¹³ The involvement of π -allyl or σ -allyl intermediates provides diverse reactivity pathways, enabling precise control over regioselectivity and functional-group compatibility. Advances in directing-group strategies, ligand design, and oxidation-state management have further expanded the versatility of C-H allylation, allowing selective activation of C(sp²)-H and even C(sp³)-H bonds under increasingly mild conditions.¹⁴

1.2 Catalytic Systems and Recent Developments

Early developments in C-H allylation predominantly employed noble metals such as palladium, rhodium, iridium, and ruthenium, which offered high reactivity and excellent selectivity.¹⁵⁻¹⁷ However, growing sustainability concerns have driven a shift toward earth-abundant first-row transition metals, including cobalt, manganese, nickel, and iron.¹⁸⁻²⁰ These metals are attractive due to their low cost, reduced toxicity, and tuneable redox properties, aligning well with the principles of green chemistry.

In addition, the emergence of dual catalysis and metallaphotoredox systems has further expanded the scope of C-H allylation, enabling reactions under visible-light irradiation and redox-neutral conditions.²¹⁻²³ the development of novel allyl sources—such as vinyl ethylene carbonate, allyl phenyl ethers, and allyl alcohols—has enabled new oxidative and redox-neutral pathways with improved selectivity and broader substrate tolerance.²⁴

1.3 Synthetic Applications

The strategic incorporation of allyl groups via C-H allylation has found widespread application in synthetic methodology and late-stage functionalization.²⁵⁻²⁷ The allyl unit can be readily transformed into a wide range of functional groups, including alcohols, aldehydes, carboxylic acids, and conjugated dienes, thereby serving as a versatile entry point for the construction of biologically active scaffolds and complex natural products.²⁸⁻³⁰ Late-stage allylation, in particular, enables rapid diversification of drug-like molecules without extensive protecting-group manipulations, a feature highly valued in medicinal chemistry and materials science.³¹

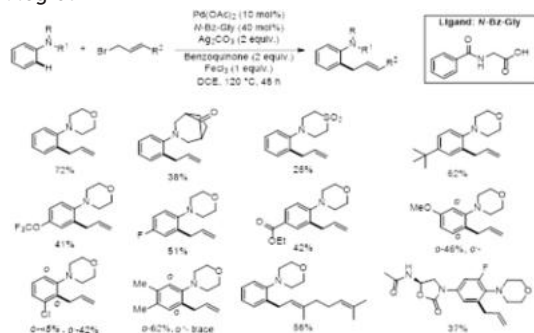
Furthermore, C-H allylation has been successfully applied to the functionalization of heterocycles, amides, anilines, and indoles, highlighting its broad functional-group tolerance.³²⁻³⁴ in materials chemistry, allylated intermediates serve as key precursors for polymer synthesis, photoactive materials, and functional coatings, underscoring the interdisciplinary importance of this transformation.³⁵

1.4 Outlook

Despite significant advances, several challenges remain, including regioselective differentiation among multiple C-H bonds, the development of asymmetric variants, and the translation of these methods to scalable and industrially viable processes.³⁶⁻³⁸ Future research is expected to focus on improving catalyst sustainability, incorporating renewable oxidants, and expanding enantioselective and photochemical allylation strategies.³⁹

Metal-catalyzed C-H allylation represents a paradigm shift in modern organic synthesis, combining fundamental mechanistic innovation with broad synthetic utility. Continued exploration of new metals, ligands, and activation strategies promises to further expand its scope, bringing chemists closer to the long-standing goal of selective, efficient, and sustainable C-H bond functionalization.

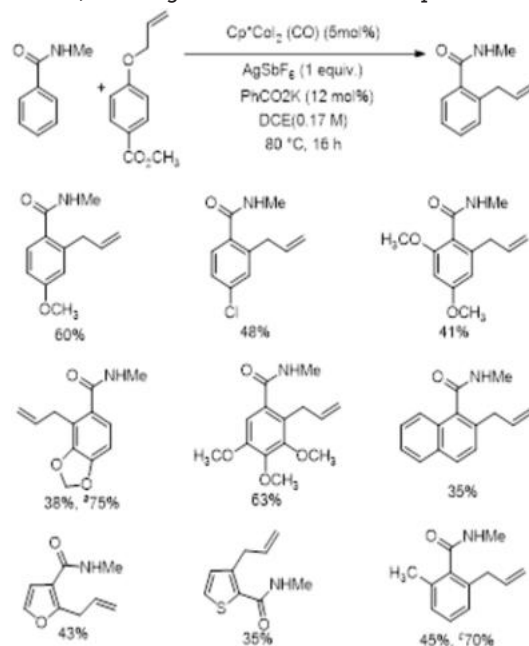
In 2025, Yuan and co-workers⁴⁰ reported an *ortho* C-H allylation-reaction of tertiary-anilines catalyzed by palladium. They reacted tertiary anilines with allyl halides in the presence of 10 mol% Pd(OAc)₂, 40 mol% N-Bz-Gly, 2 equiv. BQ and 1 equiv. FeCl₃ in DCE at 120 °C for 48 hours, furnished the corresponding *ortho* allylated tertiary anilines in good to moderate yields (Scheme 1).⁴⁰ This *ortho* C-H allylation reaction efficiently accommodated a collection of tertiary-anilines, including phenyl morpholine, 1-phenylpiperidine, *N,N*-dimethylaniline, substituted phenylpiperidines, and a spirocyclic substrate, all providing the desired *ortho*-allylated products. Allyl bromide proved more effective than allyl chloride or iodide, which showed lower reactivity. The reaction tolerated a broad range of functional groups, including sulfonyl, sulphur ether, esters, ketones, trifluoromethyl, and amides. *Para*-substituted anilines with alkyl, -OCF₃, phenyl, or halogens were compatible. Regioselectivity in *meta*-substituted substrates was influenced by electronic effects, favouring the *ortho* position adjacent to electron-withdrawing groups and the position *para* to electron-donating groups. Various alkyl-substituted allyl bromides also participated smoothly in the transformation. Furthermore, the weak stabilizing interactions between the amino groups and ligand, generated through the transition state, offer a more appropriate explanation for the observed *ortho* selectivity in the C-H activation. This method was successfully applied to the late-stage allylation of complex molecules, including derivatives of ibuprofen, linezolid, ketoprofen, naproxen, and dehydro abietic acid. Notably, it manages the limitations typically associated with conventional amide-directing group strategies.



(Scheme 1). Palladium-catalyzed allylation of tertiary-anilines at the *ortho* C-H position.

In 2024, Sotomayor and co-workers⁴¹ introduced the directed C-H allylation approach for aromatic carboxamides with allyl aryl ethers, utilizing Cp*Co (III) as a catalyst. The reaction of *N*-methyl benzamide with methyl 4-(allyloxy) benzoate conducted by 5 mol% Cp*CoI₂(CO), 1 equiv. AgSbF₆, 12 mol% PhCO₂K in DCE at 80 °C for 16 hours, led to the formation of 2-allyl-*N*-methylbenzamide in moderate to good yields (Scheme 2). The Cp*Co (III)-catalyzed allylation is compatible with electron-donating and electron-

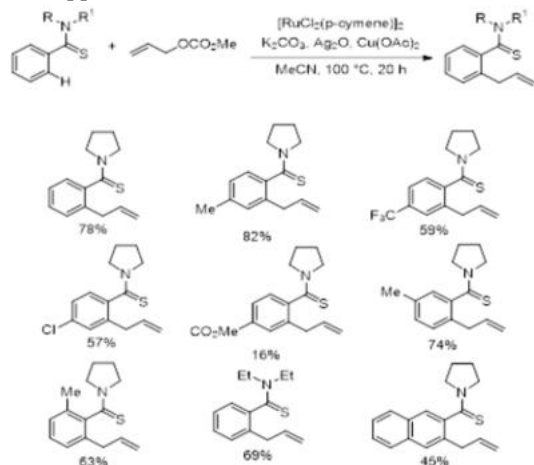
withdrawing groups, as well as halides, at the C-4 position of the aromatic ring. Allylation of 4-fluorocarboxamide was carried out with allyl-methyl-carbonate. *Ortho*-substituents, including methyl and methoxy, afforded moderate reactivity, while nitro, trifluoromethyl, and halide groups at the *ortho*-position inhibited the reaction due to steric effects. *Meta*-substituents mainly influenced regioselectivity through electronic effects, with steric factors also playing a role. The reaction was successful with 3,5-dimethoxy amide, but no conversion was observed with other 3,5-disubstituted amides (dimethyl, dinitro, ditrifluoromethyl). The method was also applicable to naphthalene-derived amides, yielding C3 and C2 allylated products regio selectively. Furthermore, heteroarenes such as furan and thiophene were also allylated. The obtained allylated compounds have been utilized in the synthesis of various intriguing carbocyclic and heterocyclic structures, including isochromanones and isoquinolones.



(Scheme 2). Cp*Co (III)-catalyzed allylation of aromatic carboxamides with allyl aryl ethers via directed C-H activation.

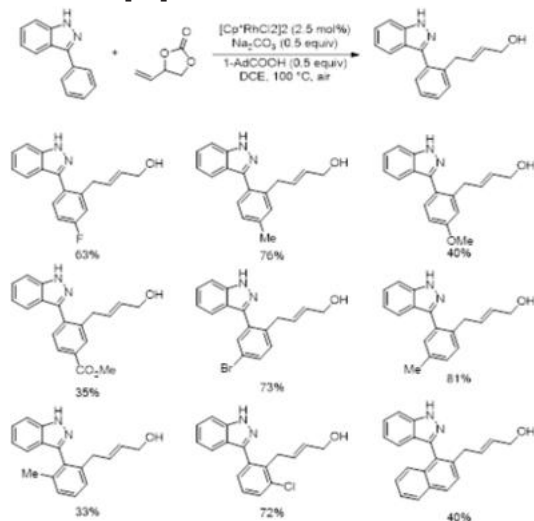
In 2024, Zhao and co-workers⁴² developed a C-H functionalization strategy for *N,N*-dialkyl thiobenzamides using a ruthenium (II) catalyst, with allyl methyl carbonate serving as the allyl donor. They reacted *N,N*-dialkyl thiobenzamides using allyl-methyl-carbonate carried out by 10 mol% [RuCl₂(p-cymene)]₂, 0.5 equiv. Ag₂O, 2.0 equiv. Cu(OAc)₂, 2.0 equiv. K₂CO₃ in acetonitrile at a temperature of 100 °C for a period of 20 hours under argon atmosphere and obtained the corresponding 2-allyl-*N,N*-dimethyl benzothioamide in good yields and with excellent regioselectivity (Scheme 3). Substrates featuring electron-withdrawing or electron-donating groups at the *para* position of the benzene ring underwent smooth reactions, while a strongly electron-donating methoxy group at the *para* position resulted in only trace amounts of the product. The reaction demonstrated tolerance for halide substituents like chloro, bromo, and iodo. Additionally, substrates with electron-deficient groups at the *ortho*- or *meta*-positions also participated in the reaction, yielding the corresponding allylation products. Furthermore, the method proved effective for polyaromatic substrates, including naphthyl derivatives, highlighting the broad applicability of the approach. The coupling of *para*-substituted thiobenzamides with allyl methyl carbonate favoured the formation of the desired products with high regioselectivity. This method is the first instance of a Ru-catalyzed C-H allylation guided by a sulfur-containing group, with the added benefit of using the

sustainable and eco-friendly solvent MeCN. This reaction operates under mild conditions and utilizes inexpensive, readily available materials, making it highly practical for various applications.



(Scheme 3). Ruthenium (II)-catalyzed C–H allylation of *para*-substituted thiobenzamides using allyl methyl carbonate.

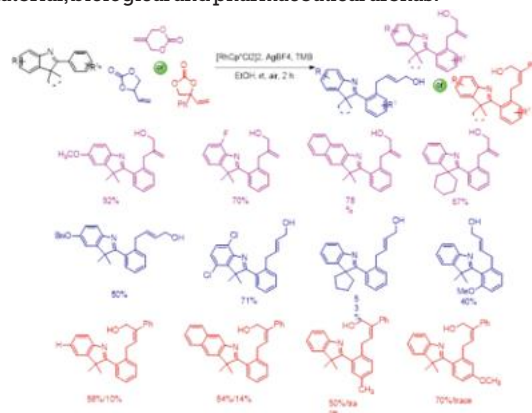
In 2023, Cui and his co-workers⁴³ reported a rhodium-catalyzed protocol enables selective C–H allylation of 1*H*-indazoles using vinyl ethylene carbonate providing a direct and efficient strategy for the incorporation of allylic alcohol functionality. They reacted 3-aryl-1-*H* indazoles with vinyl ethylene carbonate in the presence of 2.5 mol% [Cp**Rh*Cl₂]₂, 0.5 equiv. Na₂CO₃, 0.5 equiv. 1-AdCOOH in DCE at 100 °C for 12 hours under air, affording the corresponding allyl alcohol functionalized products in good yields (Scheme 4). The reaction tolerated methyl substituents at the *ortho*-, *meta*-, and *para*-positions of the 3-phenyl ring in 3-aryl-1*H*-indazoles, although steric hindrance at the *ortho*-position had a noticeable effect on the transformation. A range of *para*-substituted electron-donating groups (Me, OMe, *i*-Pr, *t*-Bu) were well accommodated. Electron-withdrawing groups (CF₃, NO₂, CN, COOMe) and halogens (Cl, F, Br) on the aryl ring were also compatible. Substrates bearing *meta*- or *ortho*-halogen substituents, as well as 6-fluoro-substituted indazoles, participated effectively under the standard reaction conditions. Various aryl and heteroaryl substituted 1*H*-indazoles, including 3-(naphthalen-1-yl), 3-(pyridin-4-yl) and 3-(thiophen-2-yl) derivatives with the standard reaction conditions. This method offers a powerful strategy for the late-stage C–H allylation of indazole-based substrates, enabling selective activation of C–H and C–O bonds in a one-pot process.



(Scheme 4). Rhodium catalyzed one-pot C–H allylation of 1*H*-

indazoles using vinyl ethylene carbonate as an efficient allyl donor.

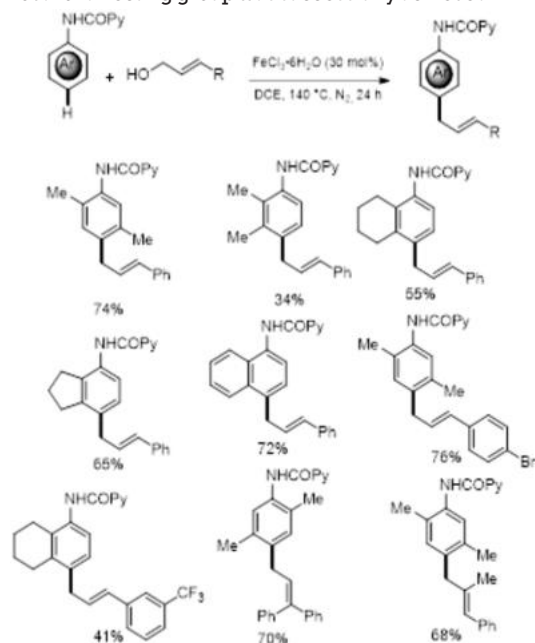
In 2024, Li and his co-workers⁴⁴ developed the C–H allylation of 2-aryl-3*H*-indoles with vinyl cyclic carbonates for the synthesis of linear and branched aryl allylic alcohols. They allylated 2-aryl-3*H* indoles with 5-methylene-1,3-dioxan-2-one or 4-vinyl-1,3-dioxolan-2-one in the presence of 5 mol% [RhCp*Cl₂]₂, 20 mol% AgBF₄, 1 equiv. TMB in EtOH at room temperature under air for 2 hours and obtained the corresponding product in moderate to good yields (Scheme 5). A wide range of 2-aryl-3*H*-indoles, bearing both electron-donating and electron-withdrawing groups at various positions, were compatible with the reaction, producing the desired products. Halogen-substituted substrates and spirocyclic indoles were also well-tolerated, demonstrating the mild reaction conditions. Additionally, substrates with functional groups at the *para*- and *meta*-positions of the phenyl ring underwent selective allylation, with steric effects influencing regioselectivity. Further extension of the methodology to 4-vinyl-1,3-dioxolan-2-one enabled the synthesis of hybrid compounds with linear aryl allylic alcohol moieties. The reaction was also applicable to a variety of functionalized indole derivatives, including those with alkyl, halogen, and benzyl groups, as well as indoles substituted at different positions on the 3*H*-indole scaffold. This mild, scalable method enables efficient access to allylic alcohol-tethered 3*H*-indoles, making it valuable for applications in material, biological and pharmaceutical arenas.



(Scheme 5). C–H functionalization strategy for synthesizing aryl allylic alcohols from 2-aryl-3*H*-indoles and vinyl carbonates.

In 2023, Tan and co-workers⁴⁵ developed Para-selective C–H allylation reaction with aniline derivatives mediated by an iron catalyst. They reacted various aniline derivatives with allyl alcohols by using 30 mol% FeCl₃·6H₂O in DCE under conditions of 140 °C for 24 hour and obtained the corresponding allylic-arenes in moderate to favourable yields under N₂ (Scheme 6). Cinnamyl alcohols bearing electron-withdrawing substituents such as chloro, bromo, fluoro, and trifluoromethyl groups participated effectively in the reaction, demonstrating the method's broad halogen tolerance and its potential utility for subsequent functional modifications. Cycloalkane-fused aniline derivatives were also compatible under the optimized conditions. Notably, no products resulting from *para*-alkenylation or *ortho*-allylation were detected. Furthermore, the protocol successfully accommodated disubstituted allylic alcohols, highlighting its versatility. Initially, the first aniline derivative reacts with FeCl₃·6H₂O to form intermediate (A), releasing HCl. Simultaneously, allyl alcohol 2 forms the (E)-allyl-Fe species (B) in the presence of HCl. A nucleophilic attack occurring between (A) and (B) generates intermediate (C), which undergoes deprotonation as well as rearomatization to give the final product, with FeCl₃ (A) regenerated to complete the catalytic cycle (Scheme 7). These reactions typically rely on valuable transition-metal-catalysts and are largely restricted

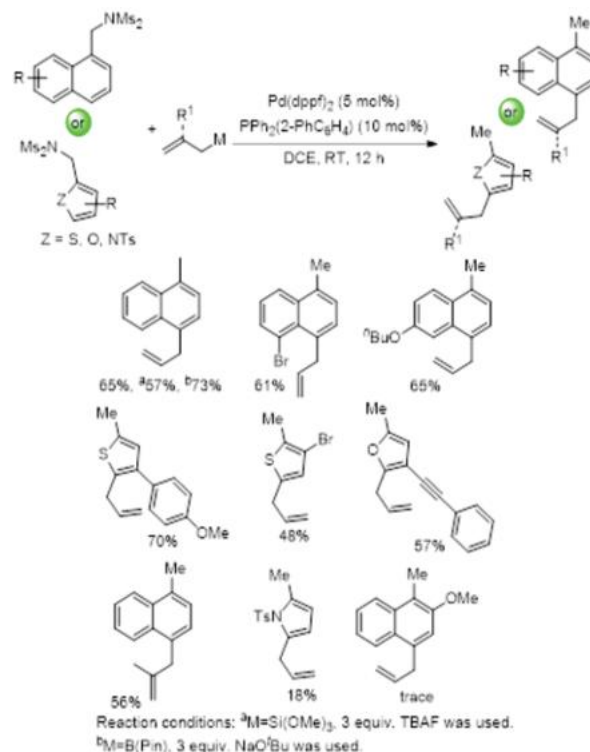
to *ortho*-C H bond allylation in arenes, yielding various allylic arenes with high regio- and chemoselectivity. To further demonstrate the practical applicability of this approach, a scale-up reaction was performed, and the removal of directing group was successfully achieved.



Scheme 6. Para-selective C–H allylation reaction with aniline derivatives enabled by iron catalysis.

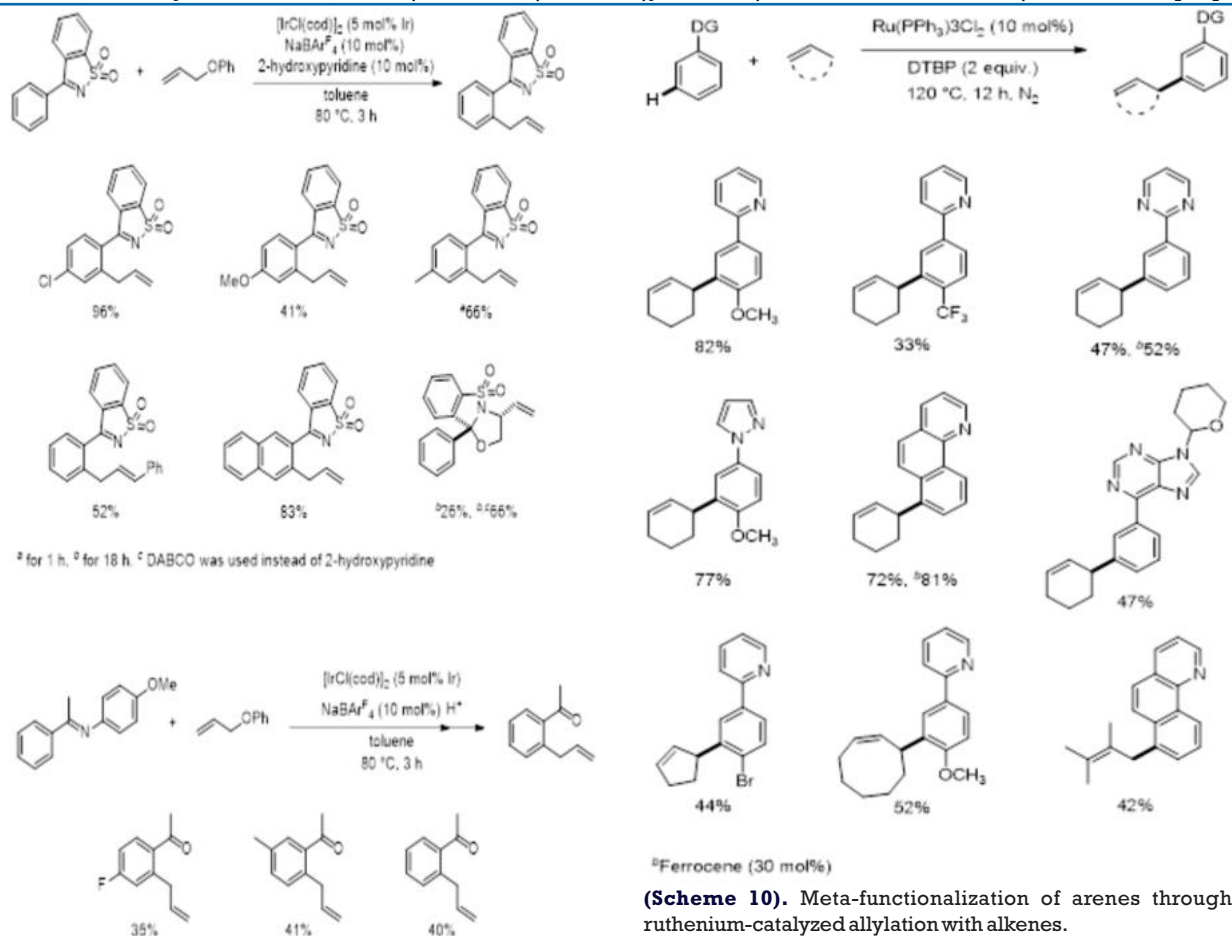
In 2021, Tian and his colleagues⁴⁶ reported an excellent regioselective method for the allylation of aromatic C–H bonds of *N*-(Arylmethyl) sulfonimides using allyl Grignard Reagents, proceeding through benzylic C–N bond Cleavage. Utilizing 5 mol% Pd(dppf)₂Cl₂ and 10 mol% PPh₃(2-PhC₆H₄)₂ as the catalytic system in DCE at room-temperature, the reaction afforded substituted allyl naphthalenes in excellent to good-yields after 12 hours (Scheme 8). The methodology accommodated various *N*-(1-naphthylmethyl) sulfonimides, though substitution at the C-2 position, such as with bromo or methyl groups, led to diminished site selectivity due to competing benzylic allylation. This underscores the reaction's sensitivity to steric and electronic effects on the naphthalene ring. Specifically, bulky C-2 substituents promoted dual reactivity at both aromatic and benzylic sites, while electron-donating groups like methoxy favoured benzylic allylation, likely through coordination with the nucleophile. Introduction of a C-4 methyl group enabled dearomative allylation and quaternary centre formation, though the product proved unstable and required oxidative conversion. In contrast, simple benzyl sulfonimides lacking aromatic extension were unreactive, emphasizing the role of aromatic stabilization in facilitating C–H functionalization. The reaction was effectively extended to heteroaryl substrates: thiophene and furan derivatives underwent highly selective aromatic allylation, whereas pyrrole analogsfavoured benzylic pathways, likely driven by sulfonyl–Grignard coordination. A broad range of allyl nucleophiles were compatible; however, those with significant steric bulk or altered electronic properties often failed to induce C–N bond cleavage and instead led to desulfonylation. Based on experimental observations and prior studies, the proposed mechanism involves initial oxidative addition of the *N*-(arylmethyl) sulfonimide to in situ-generated Pd(0), forming a π -benzylpalladium intermediate (A). Subsequent transmetalation with the allyl Grignard reagent yields a σ -allyl- π -benzylpalladium species (B), which can undergo reductive elimination to form a dearomatized intermediate (C) along with the catalyst regeneration. (C) undergoes

isomerization to yield the desired product. Parallely, the intermediate (A) can undergo benzylic substitution in sterically hindered cases to furnish the allylation product (Scheme 9). The developed method offers a regioselective and mild approach to synthesizing allyl(hetero)arenes from readily available starting materials, with potential applications in pharmaceuticals, dyes, catalysis, and organic electronics. Notably, substituting *N*-(arylmethyl)sulfonimides with alternative benzyl electrophiles significantly reduces regioselectivity, highlighting the unique effectiveness of sulfonimides in this transformation.



(Scheme 7). Aromatic C–H bond allylation of *N*-(Arylmethyl)sulfonimides enabled by cleavage of the benzylic C–N linkage with allyl grignard reagents.

In 2021, Nishimura and colleagues⁴⁷ reported an iridium-catalyzed method for the C–H bond transformation in *N*-sulfonyl ketimines. Utilizing allyl-phenyl-ether or allyl alcohol as the allyl source, the reaction proceeded efficiently with 5 mol% [IrCl(cod)]₂, 10 mol% NaBARF₄, and 10 mol% 2-hydroxypyridine under toluene reflux conditions at 80 °C for 3 hours, delivering the desired allylated products in moderate to excellent yields (Scheme 8). The methodology was applicable to various *para*- and *meta*-substituted *N*-sulfonyl ketimines, including substrates bearing naphthyl groups, demonstrating good functional group tolerance and regioselectivity. Cinnamyl alcohols also served as effective allyl donors. Additionally, reactions with butadiene monoepoxide led to oxazolidine formation under standard conditions, and the use of DABCO significantly enhanced this transformation. The protocol was further extended to imines derived from *p*-methoxyaniline and benzophenones, enabling *ortho*-selective allylation, although pyridine additives were found to inhibit these reactions due to the higher basicity of the imine substrates. The study demonstrated the crucial role of pyridine derivatives as catalysts in promoting the C–H functionalization strategy applied to *N*-sulfonyl ketimines. Notably, the methodology was also applicable to ketimines generated from *p*-methoxyaniline and benzophenone, which underwent direct C–H bond allylation using allyl phenyl ether even in the absence of pyridine additives, furnishing the corresponding ketones after hydrolysis.

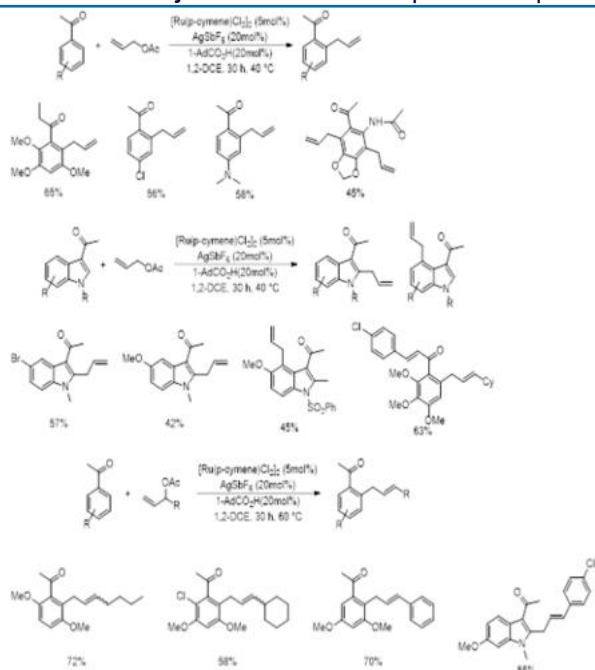


(Scheme 9). C–H Bond allylation of ketimines using an iridium catalyst.

In 2022, Li and co-workers⁴⁸ developed a ruthenium-catalyzed strategy for introducing allyl groups at the *meta*-position of arenes through cross-dehydrogenative coupling with alkenes. The reaction carried out with 10 mol% Ru(PPh₃)₃Cl₂ and 2 equiv. di-*tert*-butyl peroxide (DTBP) at 120 °C under a nitrogen atmosphere for 12 hours, delivered the *meta*-allylated arenes in good to moderate yields (Scheme 10). The ruthenium-catalyzed *meta*-allylation showed broad applicability with arenes bearing electron-donating, halogen, or fluorinated groups, while electron-withdrawing groups reduced reactivity. Aryl-substituted substrates did not significantly influence the reaction outcome. Heterocyclic auxiliaries, such as pyrimidine, pyrazole, and purine, were successfully employed, indicating the method's utility for late-stage functionalization of bioactive scaffolds. Benzo[*h*]quinoline derivatives also participated effectively in the reaction. Both cyclic and acyclic alkenes served as effective coupling partners, demonstrating the method's versatility. The catalytic cycle begins with a nitrogen-assisted *ortho*-selective reversible C(sp²)-H ruthenation of arenes, forming the active ruthenium intermediate (A). Parallely, DTBP-assisted H-abstraction of the alkene gives the allyl radical (B), which then adds to the *para*-position of C_{Ar}-Ru bond, forming (C). The addition of (B) is *para*-selective due to the *ortho*-/ *para*-directing ability of the C_{Ar}-Ru bond. The species (C) undergoes deprotonation-aromatization with the help of DTBP to yield the stable complex (D) that furnishes the meta-allylated product following a ligand exchange with the arenes (Scheme 11). The developed protocol was successfully applied to gram-scale synthesis under optimized conditions, demonstrating its practicality.

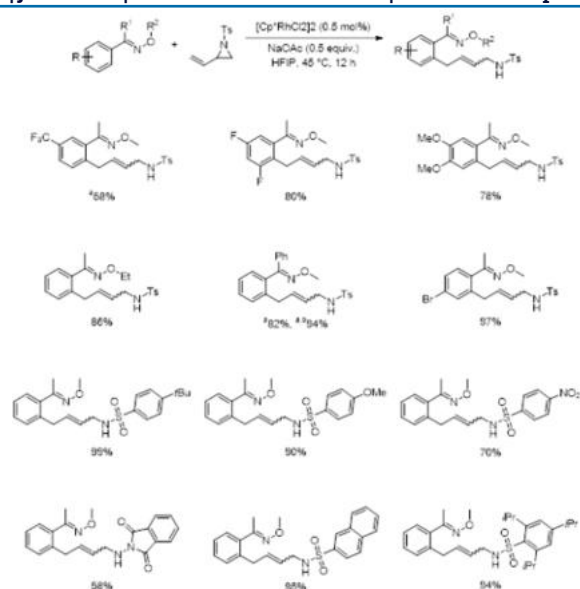
(Scheme 10). Meta-functionalization of arenes through ruthenium-catalyzed allylation with alkenes.

In 2021, Dethle and colleagues⁴⁹ reported a redox-neutral, carboxylic acid-assisted Ru-catalyzed C–H allyl functionalization of aromatic ketones. They reacted aromatic ketones using allyl acetate in the presence of 5 mol% [Ru(p-cymene)Cl]₂, 20 mol% of AgSbF₆ and 20 mol% 1-AdCO₂H in 1,2-dichloroethane at 40 °C for 30 h, afforded the corresponding C-4 and C-2 allylated indoles or *ortho*-allylated chalcones in fair to good yields (Scheme 12). The allylation reaction demonstrated a broad and diverse substrate scope. Electron-rich aromatic ketones bearing methoxy, methyl, amino, or halogen substituents reacted efficiently, with the position of substituents showing minimal effect on reactivity. In contrast, substrates with electron-withdrawing groups and aromatic aldehydes did not undergo allylation, likely due to weak coordination ability or susceptibility to oxidative side reactions. Indole-based substrates, particularly N-protected 3-acetylindoles, underwent regioselective C–H allylation, where electronic and steric influences dictated product distribution; notably, electron-withdrawing N-protecting groups shifted the regioselectivity toward the C-4 position. Substrates such as chalcones were also compatible under the standard conditions. Additionally, an acetophenone bearing two coordinating groups successfully underwent double allylation, resulting in a bis-functionalized product. The reaction also accommodated a range of α -functionalized secondary allyl acetates including linear, branched, and cyclic variants frequently affording products with good stereoselectivity. However, primary allyl acetates with similar carbon frameworks remained unreactive, underscoring the method's preference for sterically hindered secondary allyl donors. The developed catalytic method operates efficiently under mild conditions and offers a valuable approach for synthesizing a range of terminal olefin derivatives in fair to good yields, highlighting its utility in the construction of synthetically relevant molecular frameworks.



(Scheme 11). Ru-catalyzed allyl group incorporation into aromatic ketones via C–H activation under redox-neutral conditions, assisted by a carboxylic acid.

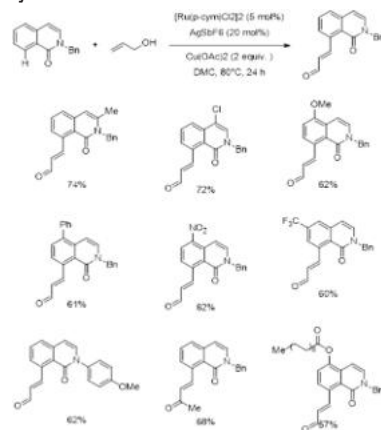
In 2024, Wang and co-workers⁵⁰ reported a Rhodium (III)-catalyzed method for the direct C–H functionalization of aromatic ketoximes using 2-vinylaziridines as allylating reagents. The transformation proceeded under mild conditions, employing 0.5 mol% $[\text{Cp}^*\text{RhCl}_2]_2$ and 0.5 equivalents of NaOAc in hexafluoroisopropanol (HFIP) at 45 °C for 12 hours, afforded the desired allylated arenes in moderate to excellent yields (Scheme 13). Aromatic ketoximes bearing *para*-substituted electron-donating groups generally showed higher reactivity compared to those with electron-withdrawing substituents, which often required increased catalyst loading and elevated temperature. *Meta*-substituted ketoximes followed a similar trend, although steric hindrance in certain cases affected the reaction efficiency. Substituents at the *ortho*-position significantly hindered reactivity, supporting the hypothesis that steric bulk near the reactive site limits mono allylation. Variations on the oxime oxygen and imine carbon further indicated that bulkier substituents reduced the reaction efficiency, while extended aromatic systems such as naphthyl derivatives remained well tolerated. A diverse set of 2-vinylaziridines, particularly those with aryl sulfonyl and alkyl sulfonyl groups, were successfully employed in the transformation. Electron-withdrawing groups on the sulfonyl aryl rings tended to enhance the formation of the E-isomer in the product mixture. In contrast, less activated vinylaziridines such as those bearing phthalimide or ester functionalities showed limited or no reactivity under the standard conditions. The proposed mechanism begins with the generation of $\text{Cp}^*\text{Rh}(\text{OAc})$ from Cp^*RhCl_2 and NaOAc. C–H activation of the aryl ketoxime by $\text{Cp}^*\text{Rh}(\text{OAc})_2$ forms intermediate (A). Coordination of the vinyl aziridine to (A) yields intermediate (B), which undergoes migratory insertion to generate intermediate (C). β -Elimination from (C) produces the monoallylated product and regenerates the Rh catalyst. The E-selectivity is attributed to a favourable conformation of intermediate C1 over C2, leading predominantly to the E-isomer (Scheme 14). This method offers mild conditions, high efficiency, broad substrate scope, and excellent functional group tolerance, with selective *ortho*-mono allylation and retention of amine groups in cyclic systems. It is also suitable for gram-scale synthesis, highlighting its synthetic practicality. However, it consistently yields mixtures of Z/E isomers.



Reaction conditions: *The reactions were performed at 65 °C using 1 mol % $[\text{Rh}(\text{Cp}^*)\text{Cl}_2]_2$. *2.4 Equiv of 2a was employed.

(Scheme 12). Selective C–H activation and allylation of aromatic ketoximes mediated by rhodium (III) catalysis.

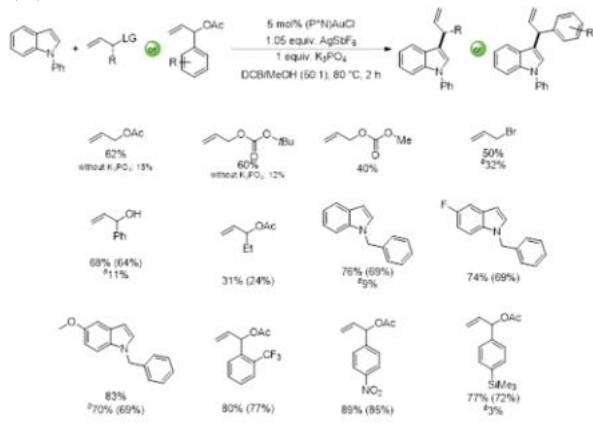
In 2024, Sharma and co-workers⁵¹ reported C8-selective alkenylation of Isoquinolones via Ruthenium (II) catalysis using allyl alcohol. The transformation involved the reaction of N-benzylisoquinolone with allyl alcohol in the presence of 5 mol% $[\text{Ru}(\text{p-cym})\text{Cl}_2]_2$, 20 mol% AgSbF_6 , 2 equiv. Cu(OAc)₂ in DMC at 80 °C over 24 hours, afforded C8-alkenylated isoquinolones bearing aldehyde functionalities in moderate to good yields (Scheme 15). The reaction exhibited a wide tolerance for various isoquinolone derivatives under Ru (II) catalysis. Halogens at C4 and various electron-donating or -withdrawing groups at C5 and C6 were well tolerated. Methoxyphenyl-protected and complex conjugated isoquinolones also reacted efficiently. α , β -Unsaturated carbonyl compounds served as alternative alkenylating agents. However, C7-substituted isoquinolones and other heterocycles like N-benzylquinolones and N-pyrimidylindolines were unreactive, likely due to steric or electronic factors. The reaction begins with the formation of active Ru (II) species (A), which coordinates with isoquinolone to promote C–H activation, forming ruthenacycle (B). Coordination with the *in-situ* generated enone gives intermediate (C), which undergoes 1,2-migratory insertion to produce seven-membered ruthenacycle (D). Final β -hydride elimination from (D) affords the alkenylated product (Scheme 16). The use of dimethyl carbonate as a green solvent enhances the environmental sustainability of the method, which was further validated by successful scale-up, demonstrating its practical applicability.



(Scheme 13). C8-selective functionalization of isoquinolones

via Ru (II)-catalyzed alkenyl group incorporation from allyl alcohol.

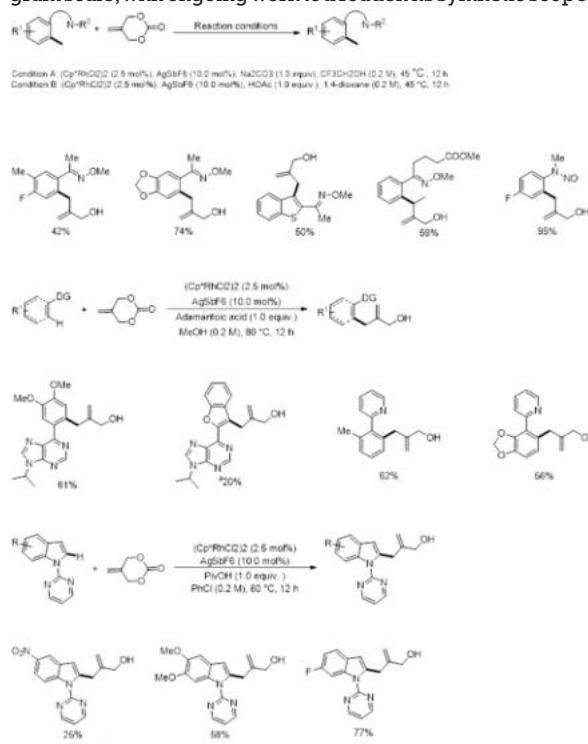
In 2022, Bourissou and colleagues⁸² reported a gold (I)/gold (III) catalytic system for the allylation of *N*-phenyl indole using α - and γ -substituted allyl substrates. The reaction was carried out with 5 mol% (P N) AuCl, along with 1.05 equiv. AgSbF₆ and 1 equiv. K₃PO₄ as additives, in a DCB/MeOH solvent mixture at 80 °C for 2 hours, affording the desired allylated products in good yields (Scheme 14). A variety of allyl substrates bearing different leaving groups were evaluated, with allyl alcohols, acetates, carbonates, and phosphates showing good reactivity, while phosphonates were unreactive. Reactions performed without an external base gave significantly reduced efficiency, suggesting the leaving group may play a dual role. Both allyl halides also proved competent, though side products were observed with bromide. The reaction showed high selectivity for C3-branched allylation of indoles, regardless of whether linear or branched allyl substrates were used, supporting the involvement of a common Au (III) π -allyl intermediate. Substitution at the α - or γ -position of the allyl group with alkyl or aryl groups consistently gave branched products. The method tolerated a broad range of indole derivatives including those with *N*-substitution and functional groups on the aromatic core were compatible with the reaction, highlighting the versatility and functional group tolerance of this π -allyl-based gold catalytic system. Mechanistic studies suggest an Au(I)/Au (III) catalytic cycle, where the initial coordination of the allyl substrate to form π -alkene Au(I) complex (A), followed by oxidative addition to form a π -allyl Au (III) intermediate (B). The indole then undergoes nucleophilic attack at the terminal position of the π -allyl moiety, completing the C-C bond formation (Scheme 14). This gold-catalyzed allylation methodology demonstrates broad functional group tolerance and high selectivity for branched C3-allylated indole products. It showcases the utility of hemilabile P^N ligands in stabilizing both Au (I) and Au (III) species, enabling mild and efficient C(sp³)-X bond activation without the need for strong oxidants or photoredox conditions. This strategy extends gold catalysis to allylation reactions traditionally dominated by metals like Pd, Ru, and Ir, offering a new avenue for C-C bond formation via π -allyl Au (III) intermediates.



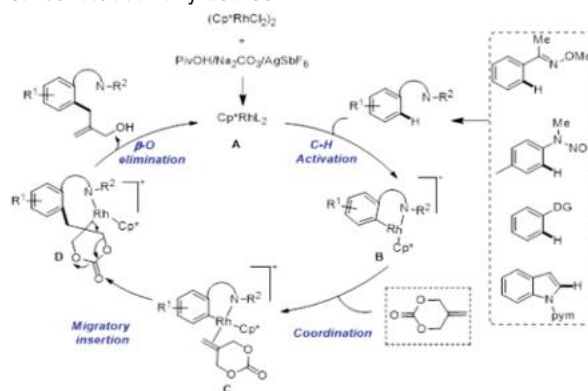
(Scheme 14). Au (I)/Au (III)-catalyzed allylation via π -allyl Au (III) intermediates.

In 2021, Zhang and co-workers⁸³ developed access to branched allylarenes via Rhodium (III)-catalyzed C-H Allylation of (Hetero)arenes with 2-Methylidenetrimethylene Carbonate. They reacted (hetero)arenes with 2-methylidenetrimethylene carbonate in the presence of (Scheme 15). The rhodium-catalyzed allylation showcased broad substrate versatility. Aryl oxime ethers bearing both electron-donating and electron-withdrawing groups were well tolerated, with *meta*-substituted systems showing regioselectivity for the less

hindered position. Carbonyl-derived oximes and heteroarenes like benzothiophene were compatible, whereas *ortho*-substitution impeded reactivity. The reaction was also effective for *N*-nitroanilines, 6-arylpyridines, and 2-phenylpyridines, accommodating a range of functional groups with minimal influence from electronic effects. Notably, a wide range of *N*-pyrimidylindoles bearing substituents such as halogens, alkyl, formyl, ester, nitro, and aryl groups at various positions underwent efficient allylation. Even disubstituted indoles and a pyrrole derivative reacted smoothly, highlighting the method's strong functional group tolerance and applicability to complex heterocycles. The catalytic cycle begins with C-H activation between the active rhodium catalyst (A) and the substrate, forming the cyclometalated intermediate (B). Coordination with the alkene to form (C), and subsequent migratory insertion generate intermediate (D), which undergoes β -oxygen elimination and decarboxylation. Finally, protodemetalation delivers the allylic alcohol product and regenerates catalyst (A) (Scheme 16). The method supports various directing groups and enables efficient synthesis of branched allylic alcohols. It introduces 2-methylidenetrimethylene carbonate as a novel allyl source in C-H allylation and is applicable on a gram scale, with ongoing work to broaden its synthetic scope.



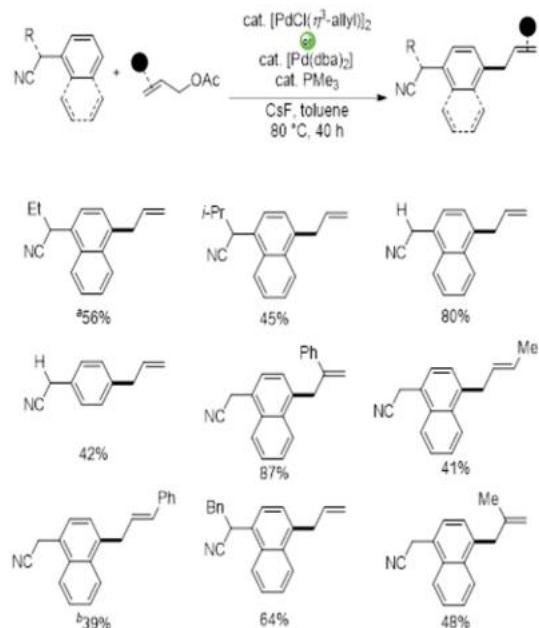
(Scheme 15). Branched allylarene synthesis via Rh (III)-catalyzed C-H allylation using 2-methylidenetrimethylene carbonate as an allyl source.



(Scheme 16). Proposed mechanism involving Rh (III)-

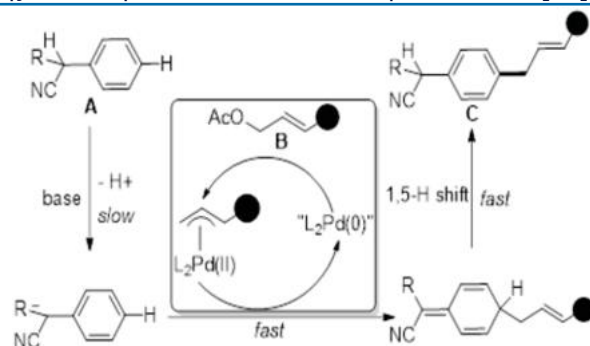
catalyzed C–H activation, alkene insertion, β -oxygen elimination, and protodemetalation to form branched allylic alcohols.

In 2023, Ueno and co-workers⁵⁴ developed a method for para-Selective C–H functionalization of 1-(Cyanomethyl)arenes via palladium catalysis, employing allyl acetates as the allyl source. The reaction, carried out with 5.0 mol% $[\text{PdCl}(\eta^3\text{-allyl})]$, 20 mol% PMe_3 , and 4.0 equivalents of CsF in toluene at 80 °C over 40 hours, enabled the allylation of 1-(cyanomethyl) naphthalenes, affording the corresponding *para*-allylated products in moderate to good yields (Scheme 17). The substrate scope demonstrated good tolerance for 1-(cyanomethyl)arenes bearing small alkyl or benzyl groups, with *para*-selective allylation proceeding efficiently. Bulkier α -substituents led to lower reactivity and minor byproduct formation, while the α -unsubstituted substrate showed enhanced selectivity. Substrates with linear alkyl chains occasionally produced minor amounts of α -dehydrogenated byproducts, indicating competing side reactions. Functionalization occurred preferentially on naphthalene over phenyl rings, and simple cyanomethylbenzene gave modest results. Heteroaromatic and sterically hindered substrates, as well as those bearing other electron-withdrawing groups, showed limited reactivity. Substituted allyl acetates were also compatible, and reactions favoured linear products, consistent with typical Tsuji–Trost-type regioselectivity. The mechanism begins with oxidative addition of allyl acetate to $\text{Pd}(0)$, generating an η^3 -allylpalladium (II) complex. Deprotonation of the substrate (A) by base forms a cyano-stabilized carbanion, which increases nucleophilicity at the *para*-position of the arene. This leads to selective attack on the less hindered terminus of the π -allyl complex, followed by a 1,5-hydrogen shift that restores aromaticity and delivers the *para*-allylated product (C), while regenerating the $\text{Pd}(0)$ catalyst (Scheme 18). The resulting products retain an α -hydrogen adjacent to the nitrile group, enabling further α -functionalization, thus offering valuable opportunities for sequential transformations. Notably, the methodology was successfully applied to gram-scale synthesis, demonstrating its practicality and potential for broader synthetic applications.



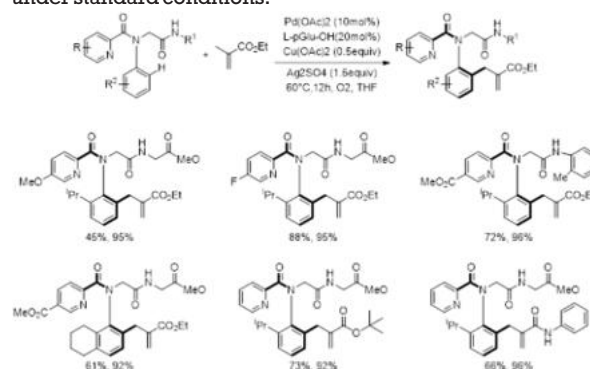
Reaction conditions: ^aA mixture of the desired product C and the corresponding α - β -dehydrogenated product was obtained. ^bA mixture of *ortho*-allylated product was obtained.

(Scheme 17). Selective *para*-allylation of 1-(cyanomethyl)arenes using allyl acetates under palladium catalysis.



(Scheme 18). Mechanistic pathway for the Pd-catalyzed *para*-allylation of 1-(cyanomethyl)arenes using allyl acetates as the allyl source.

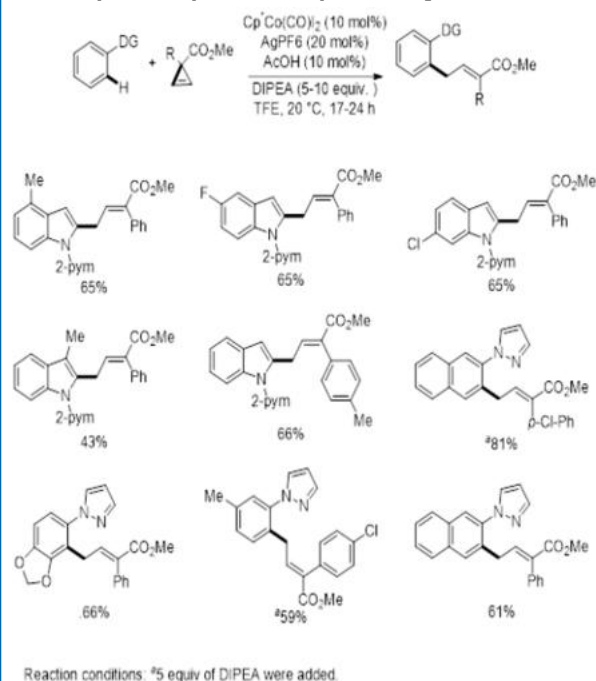
In 2021, Zhang and co-workers⁵⁵ reported an atroposelective C–H allylation enabled by Pd (II) catalysis for the synthesis of chiral *N*-Aryl peptidatrop isomers. The reaction between *N*-aryl peptoids and ethyl methacrylate was conducted using 10 mol% $\text{Pd}(\text{OAc})_2$, 20 mol% *L*-pGlu-OH, 0.5 equivalents of $\text{Cu}(\text{OAc})_2$, and 1.5 equivalents of Ag_2SO_4 in THF under an O_2 atmosphere at 60 °C for 12 hours, affording the desired products in good to excellent yields (Scheme 19). The reaction tolerated a wide range of *N*-aryl peptoids, with pyridine-based directing groups proving most effective. Electron-withdrawing substituents on the pyridine ring enhanced reactivity, whereas electron-donating groups led to diminished yields but retained high enantioselectivity, while backbone and aryl ring variations were well accommodated, maintaining high enantioselectivity. A broad array of methacrylates and other olefins also performed well, and conformational studies confirmed the formation of stable atropisomers. To demonstrate the synthetic utility and scalability of the allylation strategy, a gram-scale reaction was carried out, successfully delivering the desired product under standard conditions.



(Scheme 19). Pd (II)-catalyzed C–H allylation enabling the synthesis of enantioenriched *N*-aryl peptoid-based atropisomers.

In 2021, Kim and colleagues⁵⁶ reported a method for Cobalt (III)-catalyzed C–H allylation of *N*-pyrimidyl indoles using cyclopropenes, achieved through a sequential C–C and C–H bond activation strategy. The reaction was carried out under an argon atmosphere using 10 mol% $\text{Cp}^*\text{Co}(\text{CO})_2$ as the catalyst, along with 20 mol% AgPF_6 , 10 mol% AcOH , and 5–10 equivalents of DIPEA in trifluoroethanol (TFE) at 20 °C for 17–24 hours, yielding the allylated (hetero)arene products in good efficiency (Scheme 20). A broad range of substrates was well tolerated under the optimized conditions, demonstrating the versatility of the transformation. Both electron-rich and electron-deficient *N*-pyrimidyl indoles bearing substituents at various positions participated effectively in the reaction. Additionally, *N*-aryl pyrazoles and cyclopropenes also proved to be compatible coupling partners. The reaction consistently afforded the corresponding allylated

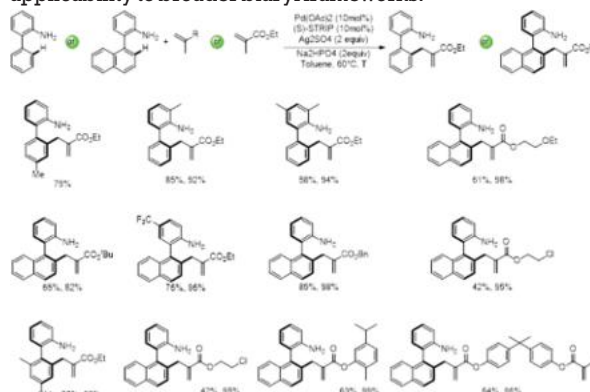
(hetero)arenes with high efficiency and excellent stereoselectivity. The proposed mechanism begins with the formation of a cationic cobalt (III) complex (A) in the presence of Ag(I) and AcOH. This active species undergoes reversible, directed C–H activation with the substrate to form cobaltacycle (B). Coordination of (B) with cyclopropene generates π -complex (C), which then undergoes olefin insertion to afford cyclopropyl–cobalt intermediate (D). A subsequent β -carbon cleavage opens the cyclopropene ring, producing intermediate (E), which is stabilized by its tautomeric enolate form (F). Proto-demetalation of (F) yields the alkenylated product, with regeneration of cobalt complex (A). An alternative pathway involving Co–carbenoid intermediate (G) and its migratory insertion to form (H) was considered less likely. Finally, under basic conditions, the alkenylated product undergoes isomerization to the thermodynamically favoured allylated compound



(Scheme 20). Cobalt (III)-catalyzed sequential activation of C–H and C–C bonds enabling allylation with cyclopropenes.

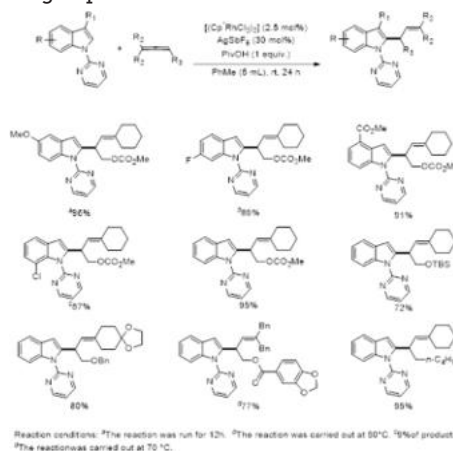
In 2020, Shi and co-workers⁵⁷ reported a palladium-catalyzed, atroposelective C–H allylation of biaryl-2-amines using methacrylates as allyl surrogates. The reaction, promoted by 10 mol% Pd(OAc)₂, 2 equiv. Ag₂SO₄, and 10 mol% (S)-STRIP in the presence of 2 equiv. Na₂HPO₄ in toluene at 60 °C, proceeded via β -hydride elimination and delivered the allylated products in good to excellent yields (Scheme 21). The methodology demonstrated broad applicability across various biaryl-2-amines, including those bearing electron-donating, electron-withdrawing, or multiple substituents, all delivering allylated products with high enantioselectivity. Both naphthyl- and biphenyl-based amines were compatible with the catalytic system. A wide range of methacrylates also participated efficiently, including alkyl, aryl, heteroaryl, and functionalized derivatives. While sterically hindered methacrylates showed reduced enantioselectivity, most substrates afforded products in high optical purity. Mono allylation was selectively achieved even in substrates with multiple reactive sites, and stereochemistry was assigned based on established analogs. The developed C–H allylation strategy was successfully applied to gram-scale synthesis, highlighting its practicality and scalability. The resulting axially chiral biaryl products serve as versatile intermediates, as the amine functionality offers a handle for further synthetic transformations. This approach represents an efficient method for the late-stage functionalization of

biaryl scaffolds, with ongoing efforts aimed at extending its applicability to broader biaryl frameworks.



(Scheme 21). Directed C–H allylation for atroposelective biaryl functionalization employing 1,1-disubstituted alkenes as surrogates under Pd catalysis.

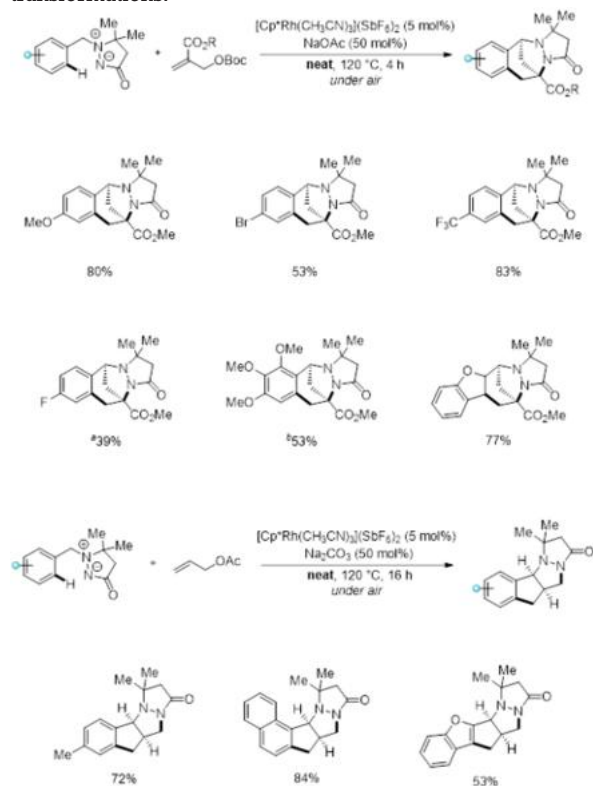
In 2022, Zhai and co-workers⁵⁸ reported a rhodium-catalyzed stereoselective C–H functionalization of indoles through intermolecular coupling with trisubstituted allenes. The reaction was conducted under mild conditions using 2.5 mol% [Cp*RhCl₂]₂ as the catalyst, along with 30 mol% AgSbF₆ and 1 equiv. PivOH in toluene under room temperature, delivered the allylated indole products in moderate to excellent yields (Scheme 22). The methodology displayed broad tolerance toward various indole derivatives, including those with electron-donating, electron-withdrawing, and sterically demanding substituents. A wide range of trisubstituted allenes bearing alkyl, cyclic, polycyclic, and functionalized groups including acid-sensitive moieties were also compatible, highlighting the versatility and robustness of the transformation. Furthermore, the reaction was successfully extended to acyclic allene substrates, including those bearing dibenzyl groups and aromatic substituents. A plausible Rh(III)-catalyzed mechanism involves initial C–H activation of the indole substrate via a concerted metalation-deprotonation (CMD) pathway, assisted by the 2-pyrimidinyl directing group, to generate a five-membered rhodacycle intermediate (A). Regioselective syn-insertion of the trisubstituted allene into the Rh–C bond then occurs, forming a key organometallic intermediate (B). Subsequent stereospecific proto demetalation delivers the allylated product, with Z-selectivity attributed to steric hindrance that disfavors the alternative intermediate (C). The synthetic utility of this method was demonstrated through a gram-scale reaction, confirming its practicality for larger-scale synthesis. Additionally, trisubstituted allenes incorporating fragments derived from natural products and pharmaceuticals were successfully employed. The transformation was notable for its high atom economy, regio- and stereoselectivity, and strong functional group tolerance.



(Scheme 22). Stereoselective C–H functionalization of

indoles using allenes under rhodium catalysis.

In 2025, Zhang and co-workers⁶⁹ developed a Rh (III)-catalyzed strategy for synthesizing fused and bridged tetracyclic compounds via C–H activation and [3+2] cycloaddition of azomethine imines. The reaction employed aryl azomethine imines, MBH adducts, and allyl acetates with 5 mol% [Cp*Rh(CH₃CN)₃](SbF₆)₂ and 50 mol% NaOAc at 120 °C for 4 hours under air, yielded the products in moderate to excellent efficiency (Scheme 23). The reaction exhibited broad substrate scope with respect to both azomethine imines and MBH adducts. Electron-donating and electron-withdrawing substituents at the *para*-position of the aryl ring were well-tolerated. *Meta*-substituted imines showed regioselectivity influenced by steric effects, while substrates containing ether groups favoured activation at more hindered positions. *Ortho*-substituted and heteroaryl azomethine imines, including (benzo) furan and (benzo) thiophene, effectively participated in the reaction to afford heterocyclic tetra cycles, whereas indole and pyridine analogs were unreactive. The method also enabled the construction of complex bridged tetracyclic frameworks. MBH adducts bearing ethyl and benzyl groups served as efficient partners, and substitution with allyl acetates allowed access to fused tetracyclic indenopyrazolones. This transformation was compatible with a variety of aryl, naphthyl, and heteroaryl azomethine imines, further demonstrating its synthetic versatility. A plausible catalytic mechanism involves initial C–H activation by a cationic Rh (III) species, assisted by azomethine coordination, to generate a six-membered rhodacycle intermediate (A). This intermediate undergoes migratory insertion with the MBH adduct to obtain the intermediate (B), followed by β-O elimination form (C) and an *exo*-selective [3+2] cycloaddition occurs, ultimately forming the N-heterocyclic tetracycle and regenerating the Rh (III) catalyst (Scheme 23). This method enables the efficient synthesis of bridged pyrazolone frameworks with high diastereo selectivity and has demonstrated practical utility through successful scale-up and downstream synthetic transformations.

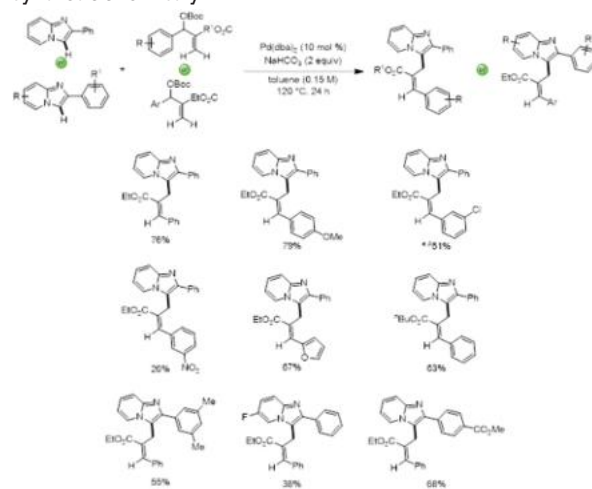


Reaction conditions: *The reaction was conducted at 80 °C for 16 hours.

*The reaction was carried out for 16 hours.

(Scheme 23) Efficient synthesis of bridged pyrazolone frameworks with high diastereoselectivity

In 2023, Kaliyamoorthy and colleagues⁶⁰ developed a palladium-catalyzed method for the regioselective C3-allylation of 2-aryl imidazopyridines using Morita-Baylis-Hillman (MBH) carbonates. The reaction was carried out with 10 mol% Pd(dba)₃ and 2 equivalents of NaHCO₃ in toluene conducted at 120 °C over a period of 24 hours, the reaction yielded the desired allylated products in moderate to good efficiencies (Scheme 24). The C3-allylation strategy demonstrated broad substrate tolerance. A variety of MBH carbonates bearing aryl, heteroaryl, halogen, electron-donating, and electron-withdrawing groups were effectively employed. The ester moiety within the carbonates could also be varied without significantly affecting the reaction outcome. In contrast, simple allyl sources such as allyl bromides and esters were ineffective. On the nucleophilic side, diverse 2-aryl imidazopyridines including those with electron-donating, halogen, and electron-withdrawing substituents on either the aryl ring or the imidazopyridine core were compatible with the reaction conditions, highlighting the versatility and functional group tolerance of the method. The proposed mechanism begins with coordination of Pd (0) to the alkene moiety of the MBH carbonate, forming complex (A). Oxidative addition then generates the π-allyl-Pd (II) intermediate (B), along with the release of CO and *tert*-butoxide. The imidazopyridine nucleophile attacks the less hindered end of II, forming intermediate (C). Subsequent deprotonation at the C3 position by *tert*-butoxide yields the final allylated product and regenerates Pd (0). Alternatively, a pathway involving C–H activation of the imidazopyridine by (B) to give intermediate (D), followed by reductive elimination, is also considered plausible. Imidazopyridine represents a privileged scaffold found in numerous pharmaceutically active compounds. Notably, the developed allylation protocol is amenable to gram-scale synthesis, and the resulting products offer valuable handles for further synthetic transformations, highlighting their utility in medicinal and synthetic chemistry.

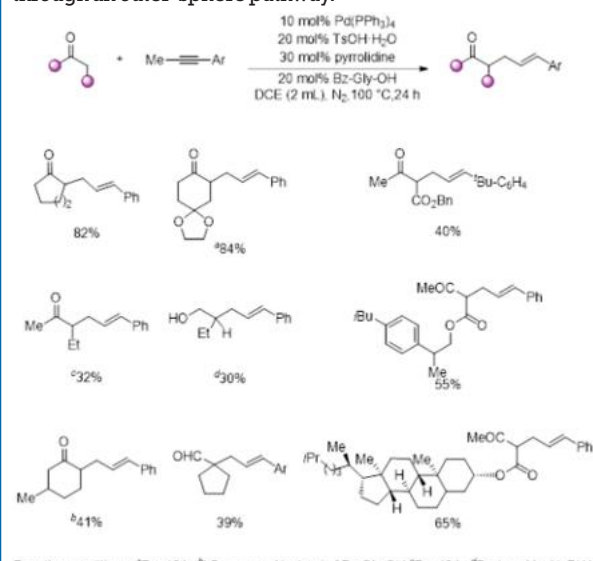


Reaction conditions: *4 equiv of the allylic source was employed *The reaction was carried out at 150 °C.

(Scheme 24). Palladium-catalyzed C3-selective allylic alkylation of 2-aryl imidazopyridines using Morita-Baylis-Hillman carbonates as allylating agents.

In 2022, Ganguly and co-workers⁶¹ developed a synergistic effect between substrates and ligands in allylic alkylation catalyzed by palladium with 1-Aryl-1-propynes. The reaction involved various carbonyl compounds and was conducted using 10 mol% Pd(PPh₃)₄, 20 mol% TsOH·H₂O, 30 mol% pyrrolidine, and 20 mol% Bz-Gly-OH in 1,2-dichloroethane (DCE) under a nitrogen atmosphere at 100 °C for 24 hours, afforded the corresponding α-allylated carbonyl products in moderate to good yields (Scheme 25). The reaction demonstrated broad substrate compatibility, efficiently transforming cyclic ketones (five- to eight-membered rings),

including substituted cyclohexanones, which underwent regioselective α -allylation at the less hindered position. Acyclic ketones reacted selectively at the α -methylene site, while a variety of aldehydes also underwent α -functionalization. β -ketoesters were mono-allylated at the active methylene position, and complex β -ketoester-containing frameworks delivered diastereomerically pure products. The methodology showed good selectivity and broad scope across diverse carbonyl substrates but was ineffective with aliphatic alkynes such as 2-hexyne. The synthetic utility of this methodology was highlighted by its successful application on a gram scale, exemplified through the allylic alkylation of cyclohexanone. Notably, this study represents the first instance of an MPAA (mono-protected amino acid) ligand facilitating a transformation beyond traditional C–H activation pathways. Mechanistic insights from DFT calculations suggest that Bz-Gly-OH promotes enamine formation, which subsequently engages the π -allylpalladium intermediate through an outer-sphere pathway.



Reaction conditions: ^aFor 16 h. ^b5 was used instead of Bz-Gly-OH. ^cFor 48 h. ^dReduced by NaBH₄.

(Scheme 25). The role of substrate and ligand cooperation in Palladium-mediated allylic alkylation involving 1-aryl-1-propynes.

In 2024, Soulé and his team⁶² introduced a nickel/iridium-based metalla photo redox catalytic system for the allylic C–H arylation of *N*-allyl heterocycles. Using *N*-allyl carbazole as the model substrate, they combined chloro arenes or allyl amines with 2 mol% IrF₃, 2 equiv. NiCl₂(dtbbpy) and 2 equiv. 2,6-lutidine in DMF, carrying out the reaction at room temperature under 440 nm light for 15 hours, and obtained the corresponding product in moderate to good yields. The substrate scope revealed that aryl chlorides with various electron-withdrawing groups, such as acyl, cyano, and trifluoromethyl, generally provided high *Z*-selectivity, though the stereochemical outcome was strongly influenced by the specific substituent and its position on the aromatic ring. In some cases, like with aldehyde-containing aryl chlorides or *ortho*-substituted benzonitriles, the *E*-isomer was favoured, suggesting substrate-dependent stereoselectivity likely governed by a photo induced *E*→*Z* isomerization mechanism. Attempts with electron-deficient allyl amines such as *N*-allylbenzamide were unsuccessful due to redox incompatibility with the photo catalyst. The reaction was tolerant to substitution on the carbazole ring and could be extended to *N*-allyl indoles, where the electronic nature and position of substituents on the indole significantly influenced the *Z*:*E* ratio. The method enables regioselective γ -amino radical arylation under mild conditions, producing enamines with controllable *Z* or *E* configurations based on the substrate. This approach offers a valuable strategy for constructing complex amine structures with high regio- and stereo-selectivity.

2.0 CONCLUSION

Metal-catalyzed C–H allylation has emerged as a transformative strategy in modern organic synthesis, enabling the direct installation of allyl groups into inactivated C–H bonds with high efficiency, selectivity, and atom economy. This methodology overcomes limitations of classical allylation approaches by eliminating the need for pre functionalized substrates and allowing precise control over regioselectivity and functional-group compatibility. Advances in noble- and first-row transition-metal catalysis, directing-group strategies, ligand design, and dual photo redox systems have expanded the reaction scope to both C(sp²)–H and C(sp³)–H bonds under mild conditions.

The strategic incorporation of allyl groups has found broad applications in natural product synthesis, late-stage functionalization of pharmaceuticals, and materials chemistry, providing versatile handles for further transformations. Despite significant progress, challenges such as regioselective differentiation, asymmetric variants, and scalable industrial processes remain. Future research focusing on sustainable catalysts, renewable oxidants, and enantioselective or photochemical strategies is expected to further enhance the utility of C–H allylation.

In conclusion, C–H allylation represents a paradigm shift in synthetic chemistry, merging mechanistic innovation with broad synthetic applicability and offering a sustainable pathway toward efficient and selective C–H bond functionalization.

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