Regioselective Ortho C–H Functionalization via Transition-Metal Catalysis

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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(sp^2)–H and C(sp^3)–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(sp^2)–H and even C(sp^3)–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 metalla photoredox 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]

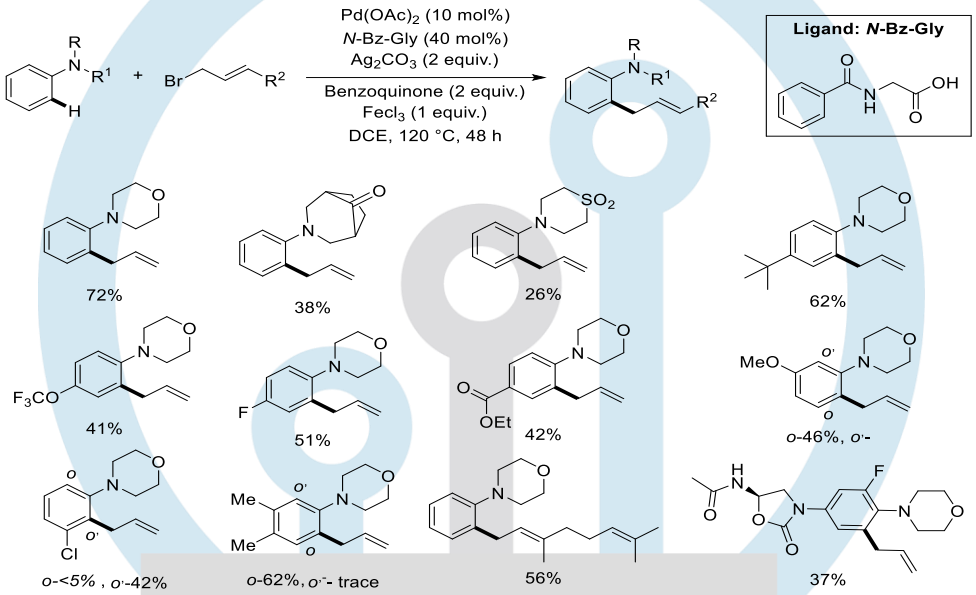
1.4 Outlook

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.

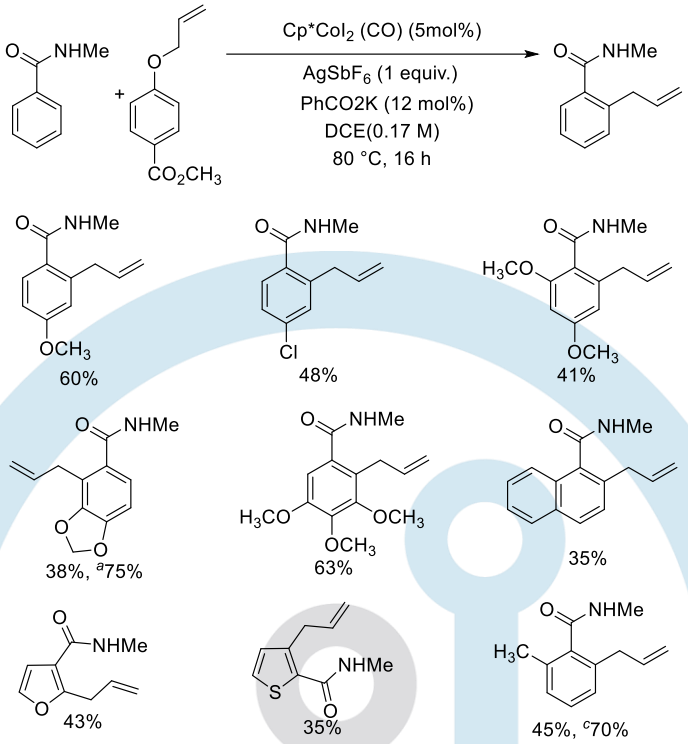
In 2025, Yuan and co-workers [40] reported an *ortho* C-H allylation-reaction of tertiary-anilines catalyzed by palladium. They reacted tertiary anilines with allyl halides in the presence of 10 mol% Pd $(OAc)_2$,40 mol% N-Bz-Gly, 2 equiv. BQ and 1 equiv. $FeCl_3$ in DCE at 120 ˚C for 48 hours, furnished 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, −OCF_3, 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.



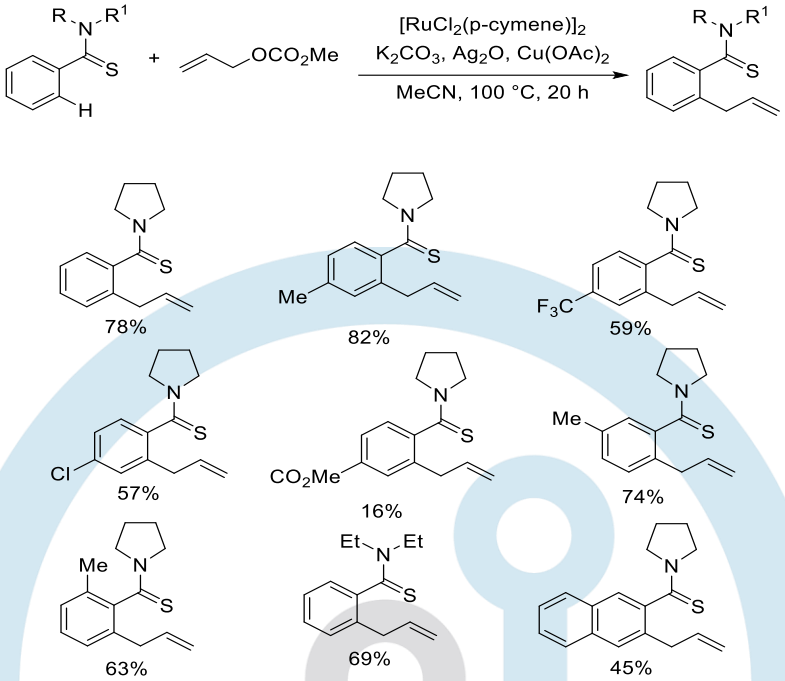
(Scheme 1). Palladium-catalyzed allylation of tertiary-anilines at the ortho C-H position.

In 2024, Sotomayor and co-workers [41] 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-(allyoxy) benzoate conducted by 5 mol% $Cp^*CoI_2(CO)$, 1 equiv. $AgSbF_6$, 12 mol% $PhCO_2K$ 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.



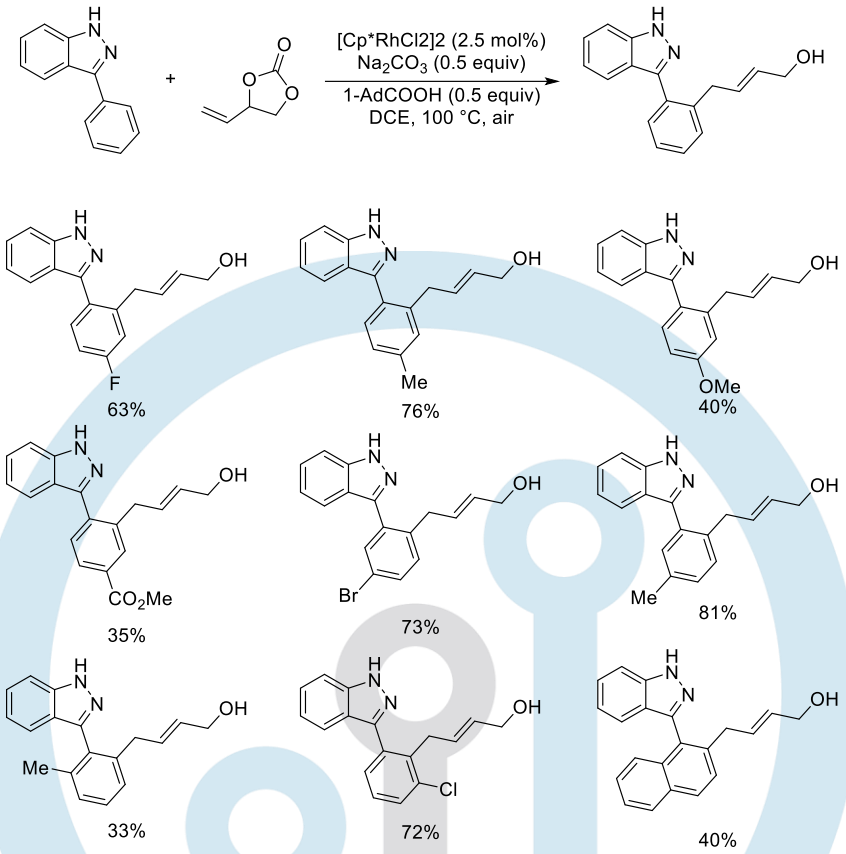
(**Scheme 2**). Cp*Co (III)-catalyzed allylation of aromatic carboxamides with allyl aryl ethers *via* directed C-H activation.

In 2024, Zhao and co-workers [42] 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% $[RuCl_2(p\text{-cymene})]_2$, 0.5 equiv. Ag_2O, 2.0 equiv. $Cu(OAc)_2$, 2.0 equiv. K_2CO_3in 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.



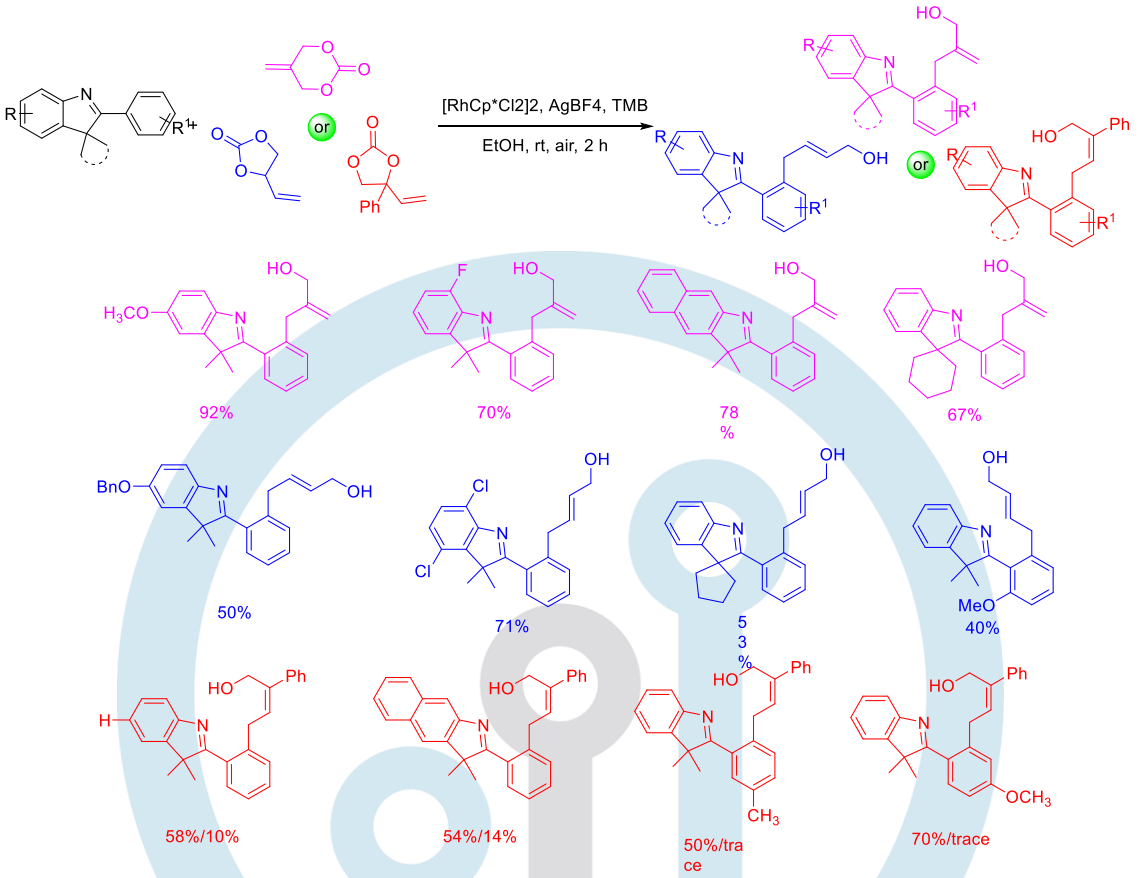
(**Scheme 3**). Ruthenium (II)-catalyzed C–H allylation of *para*-substituted thiobenzamides using allyl methyl carbonate.

In 2023, Cui and his co-workers [43] reported a rhodium-Catalysed 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% $[Cp^*RhCl_2]_2$, 0.5 equiv. Na_2CO_3, 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-1H-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 (CF_3, NO_2, 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 1H-indazoles, including 3-(naphthalen-1-yl), 3-(pyridin-4-yl) and 3-(thiophen-2-yl) derivatives, were compatible 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.



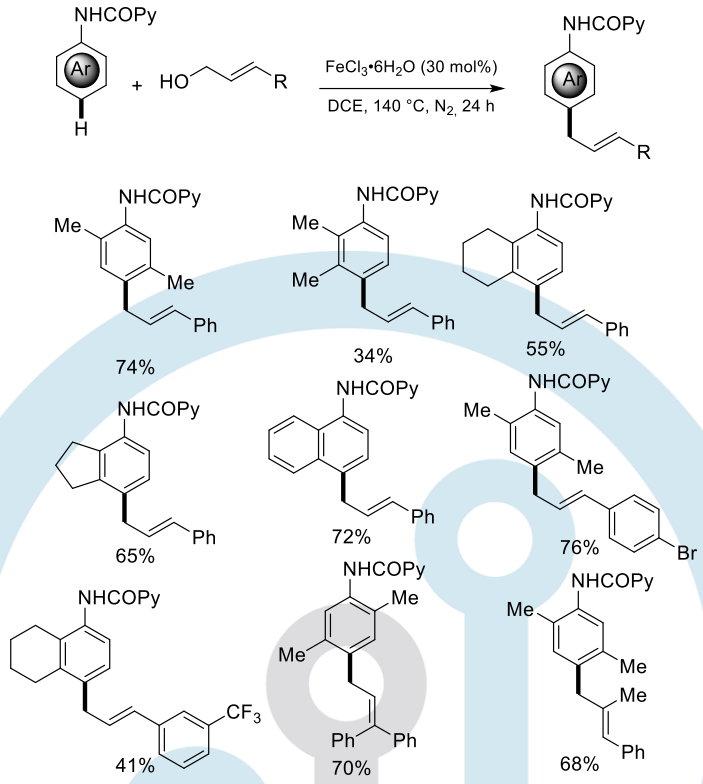
(**Scheme 4**). Rhodium catalyzed one-pot C–H allylation of 1H-indazoles using vinyl ethylene carbonate as an efficient allyl donor.

In 2024, Li and his co-workers [44] 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-3H indoles with 5-methylene-1,3-dioxan-2-one or 4-vinyl-1,3-dioxolan-2-one in the presence of 5 mol% $[RhCp^*Cl_2]_2$, 20 mol% $AgBF_4$, 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-3H-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 3H-indole scaffold. This mild, scalable method enables efficient access to allylic alcohol-tethered 3H-indoles, making it valuable for applications in material, biological and pharmaceutical arenas.



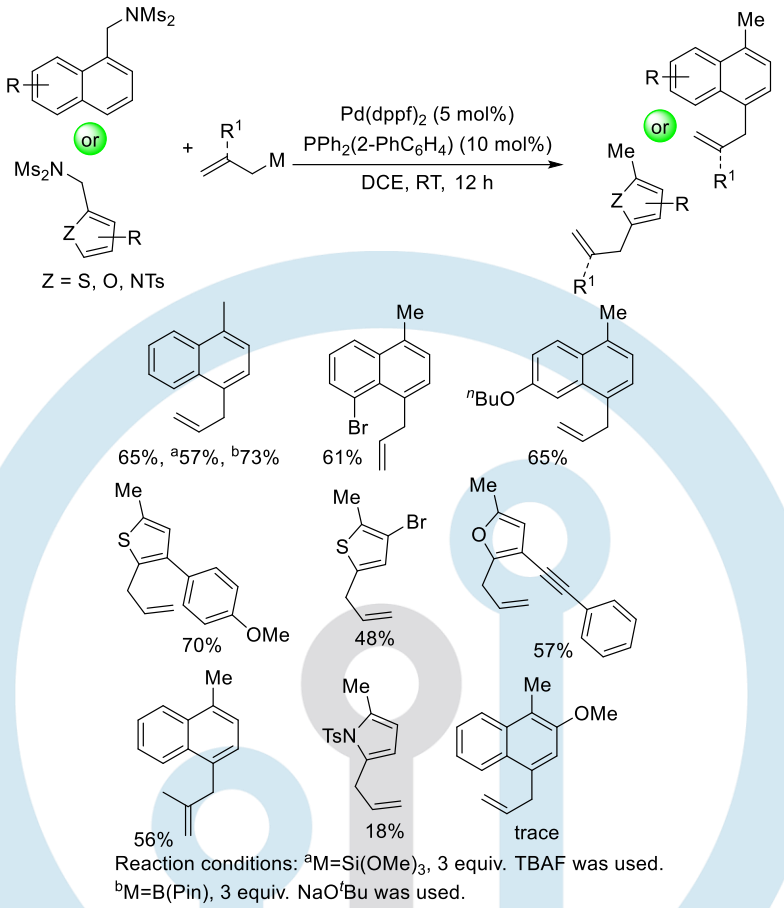
(**Scheme 5**). C–H functionalization strategy for synthesizing aryl allylic alcohols from 2-aryl-3H-indoles and vinyl carbonates.

In 2023, Tan and co-workers [45] 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% $Fecl_3.6H_2O$ in DCE under conditions of 140 ˚C for 24 hour and obtained the corresponding allylic-arenes in moderate to favourable yields under N_2 (**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 $FeCl_3 \cdot 6H_2O$ 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 and (**B**) generates intermediate (**C**), which undergoes deprotonation as well as rearomatization to give the final product, with $FeCl_3$ (**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.



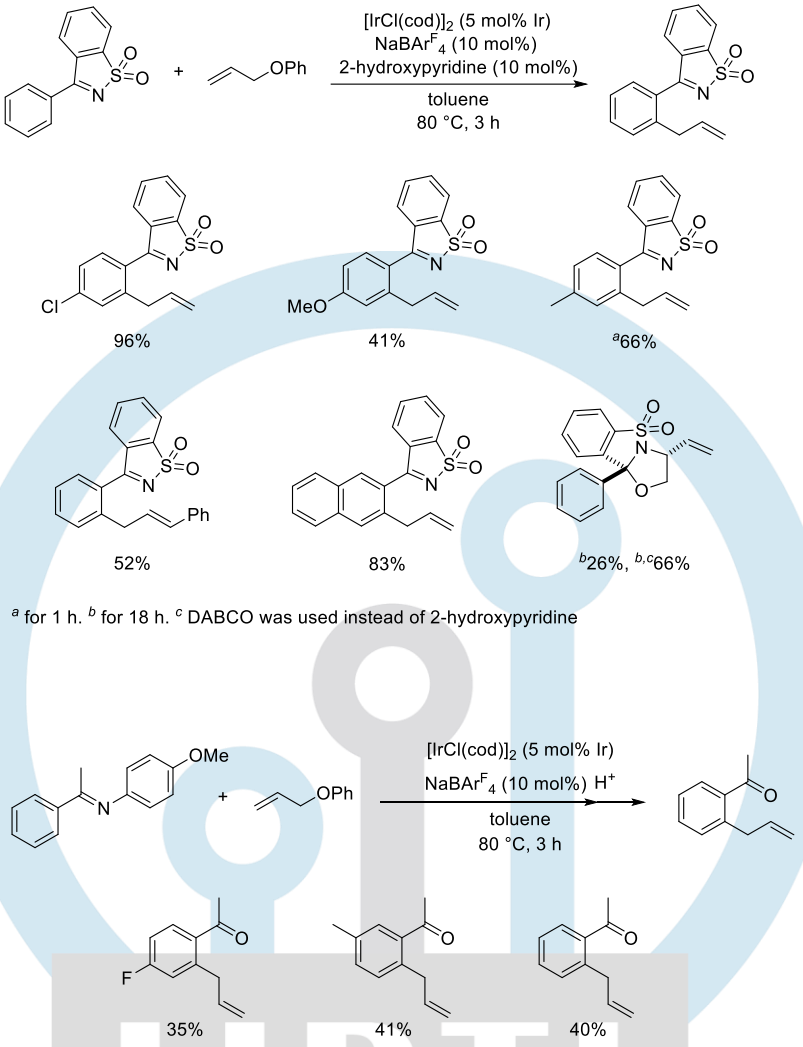
Scheme 6. Para-selective C−H allylation reaction with aniline derivatives enabled by iron catalysis.

In 2021, Tian and his colleagues [46] 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% $Pd(dppf)_2Cl_2$ and 10 mol% $PPh_2(2\text{-}PhC_6H_4)$ 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. Parallelly, 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.



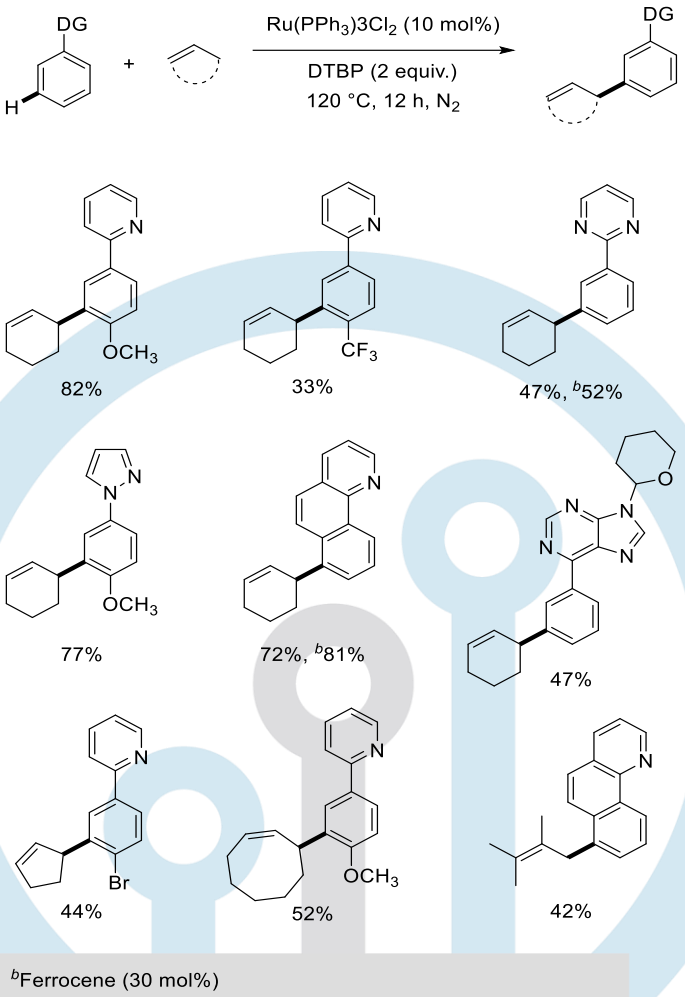
(**Scheme 7**). Aromatic C–H bond allylation of N-(Arylmethyl)sulfonimides enabled by cleavage of the benzylic C–N linkage with allyl grignard reagents.

In 2021, Nishimura and colleagues [47] 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% $NaBArF_4$, 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.



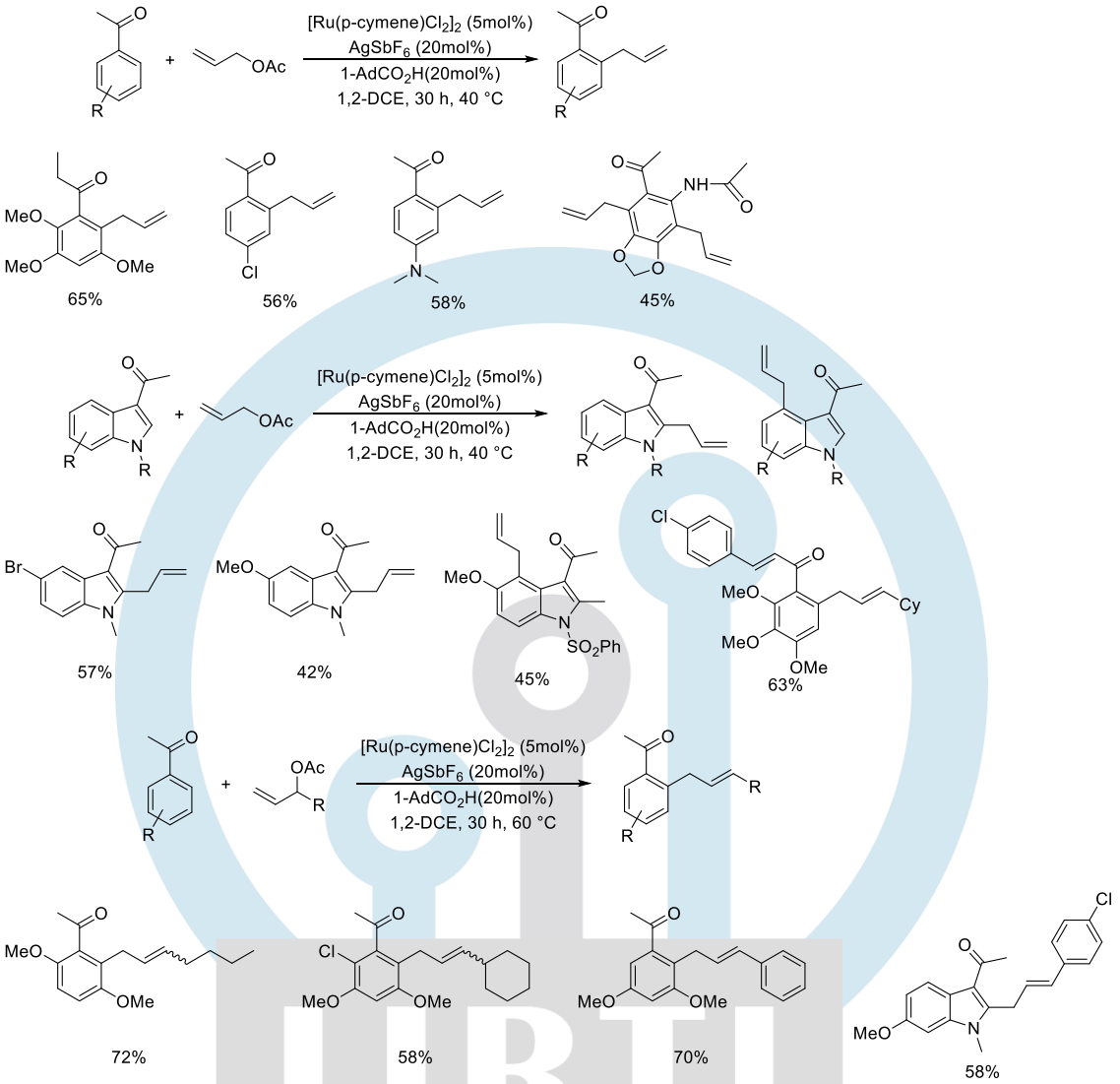
(**Scheme 9**). C–H Bond allylation of ketimines using an iridium catalyst.

In 2022, Li and co-workers [48] 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 (PPh_3)$_3Cl_2$ 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 (sp^2)-H ruthenation of arenes, forming the active ruthenium intermediate (**A**). Parallelly, DTBP-assisted α-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.

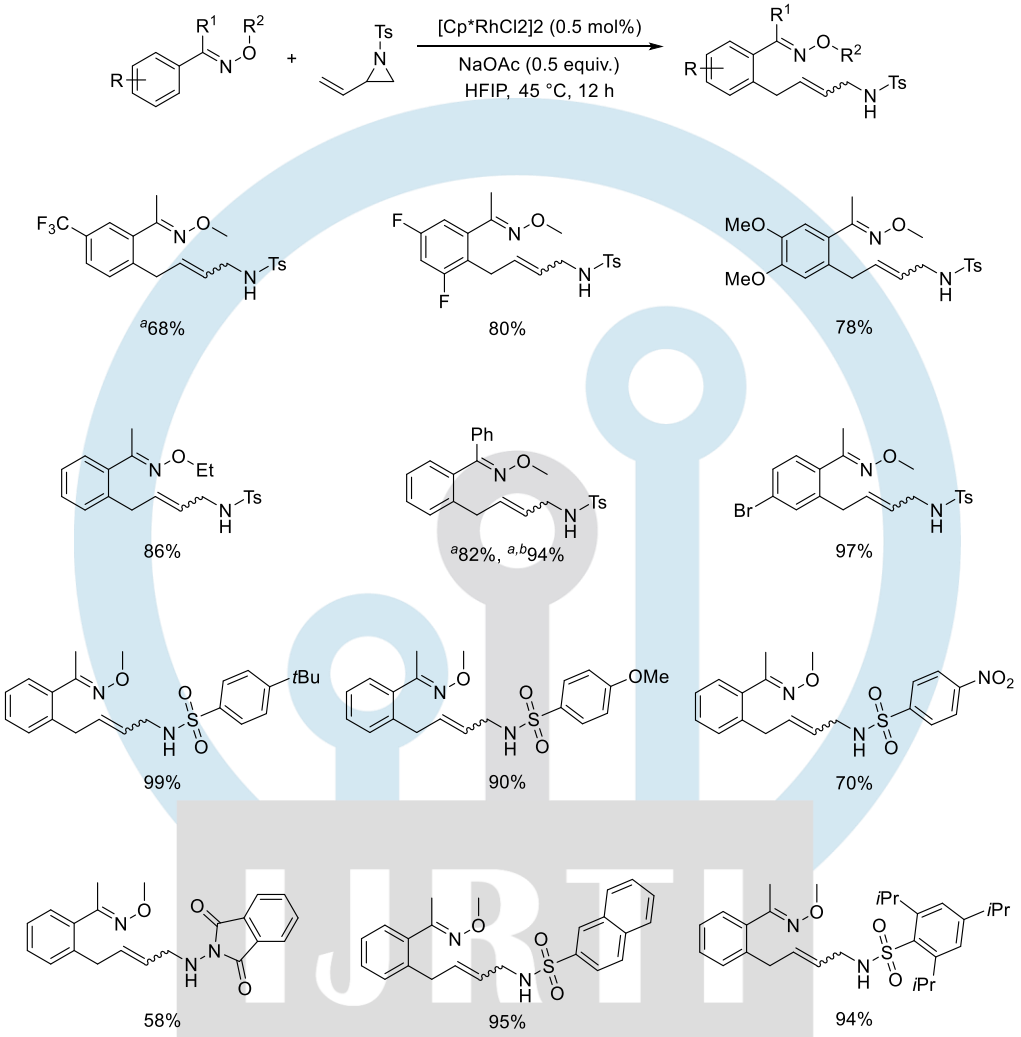
In 2021, Dethe and colleagues [49] reported a redox-neutral, carboxylic acid-assisted Ru-catalyzed C–H allyl functionalization of aromatic-ketones. They reacted aromatic ketones using allyl acetate in the presence of 5 mol% [Ru(p-cymene) $Cl_2]_2$, 20 mol% of $AgSbF_6$ and 20 mol% 1-$AdCO_2H$ in 1,2 dichloroethane at 40°Cover 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-workers [50] 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% $[Cp^*RhCl_2]_2$ 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 $CpRh(OAc)_2$ from $CpRhCl_2]_2$ and NaOAc. C–H activation of the aryl ketoxime by $Cp^*Rh(OAc)_2$ 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

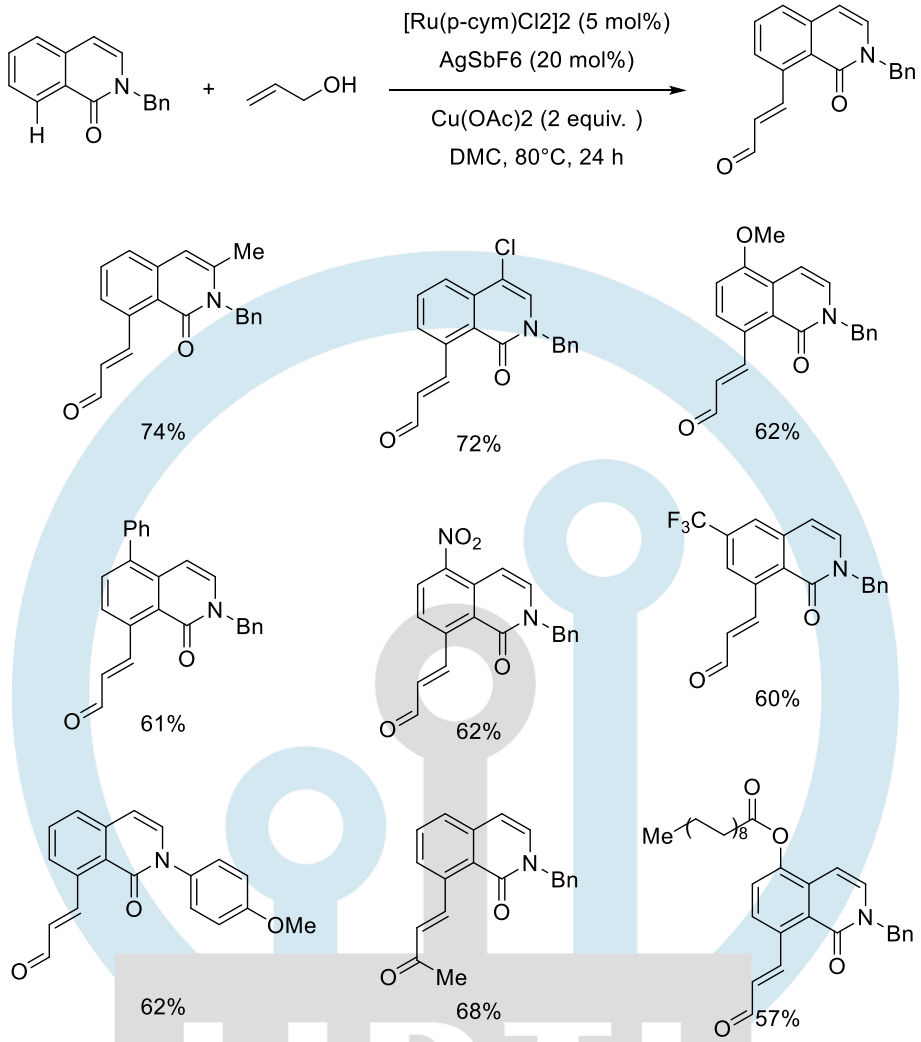
conditions, high efficiency, broad substrate scope, and excellent functional group tolerance, with selective ortho-mono allylation and retention of amine groups in cyclic systems. It is also suitable for gram-scale synthesis, highlighting its synthetic practicality. However, it consistently yields mixtures of Z/E isomers.



Reaction conditions: [a]the reactions were performed at 65 °C using 1 mol % [RhCp*Cl c2]2, [b]2.4 Equiv of 2a was employed.

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

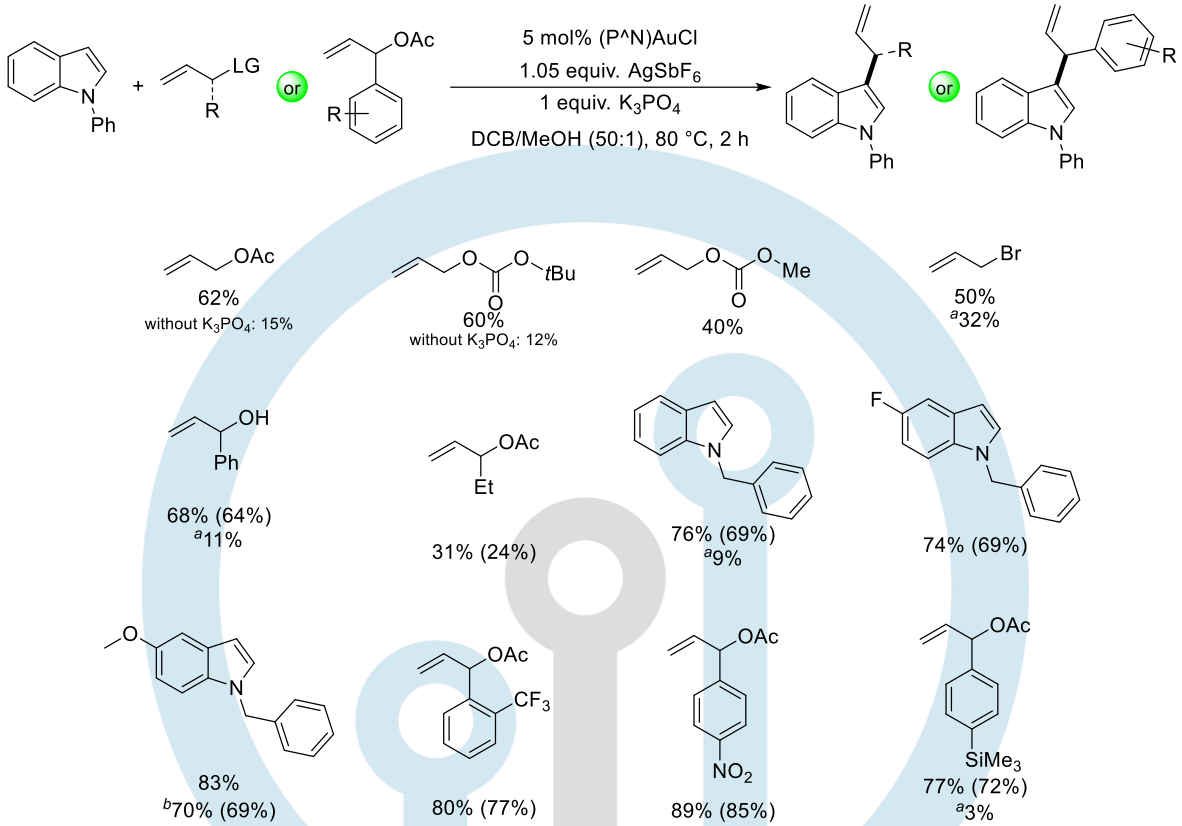
In 2024, Sharma and co-workers [51] reported C8-selective alkenylation of Isoquinolones via Ruthenium (II) catalysis using allyl alcohol. The transformation involved the reaction of N-benzylisoquinolone with allyl alcohol in the presence of 5 mol% [Ru(*p*-cym) $Cl_2]_2$, 20 mol% $AgSbF_6$, 2 equiv. Cu $(OAc)_2$ in DMC at 80 °Cover 24 hours, afforded C8-alkenylated isoquinolones bearing aldehyde functionalities in moderate to good yields (**Scheme15**). 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 colleagues [52] 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. $AgSbF_6$ and 1 equiv. K_3PO_4 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(sp^3)–X bond activation without the need for strong oxidants or photoredox conditions. This strategy extends gold catalysis to

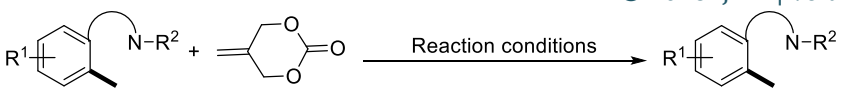
allylation reactions traditionally dominated by metals like Pd, Ru, and Ir, offering a new avenue for C–C bond formation via π-allyl Au (III) intermediates.



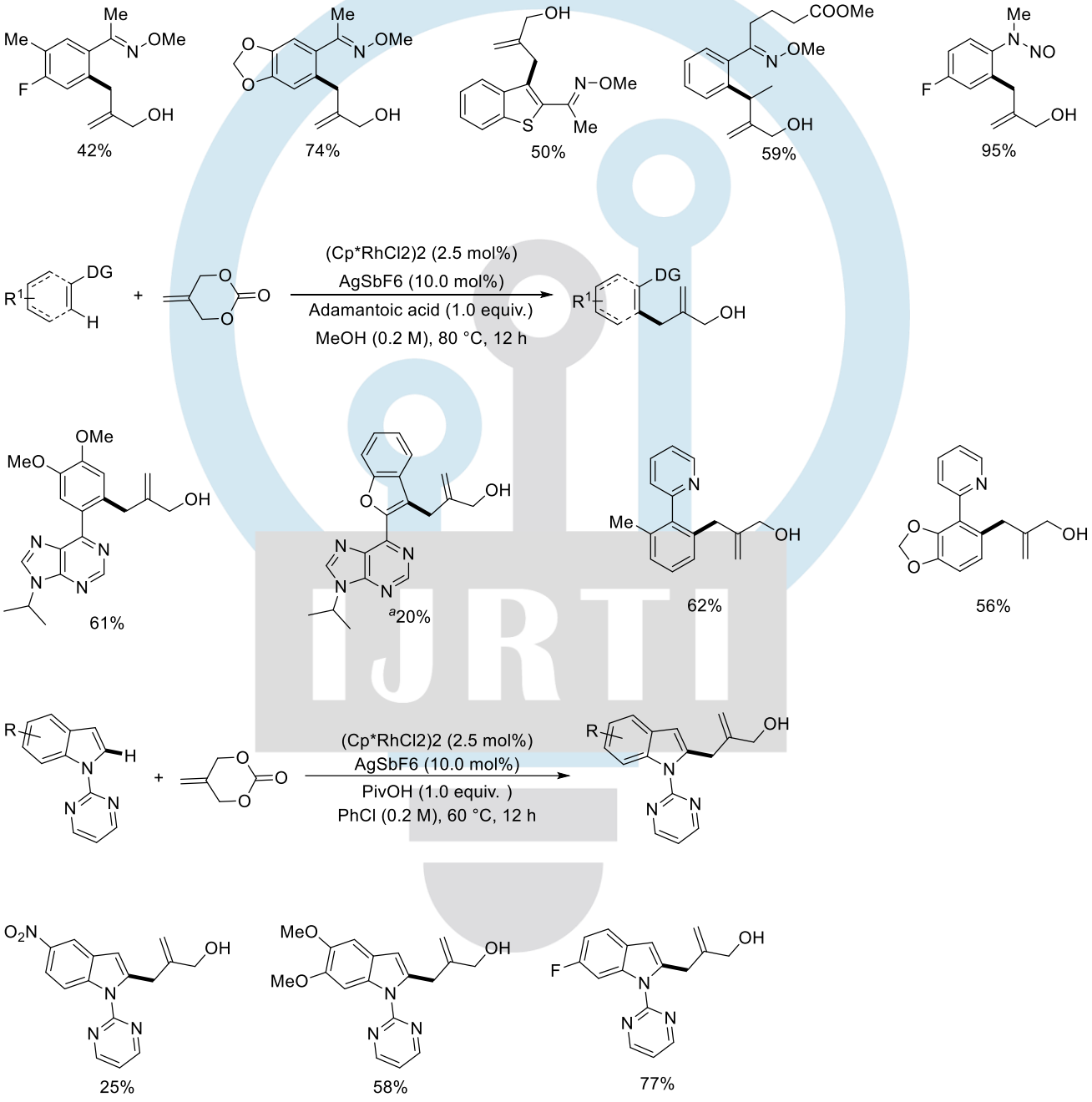
Reaction conditions: [a] In the absence of (P^N)AuCl, [b] with 1 equiv. of indole

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

In 2021, Zhang and co-workers [53] 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 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-arylpurines, 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.

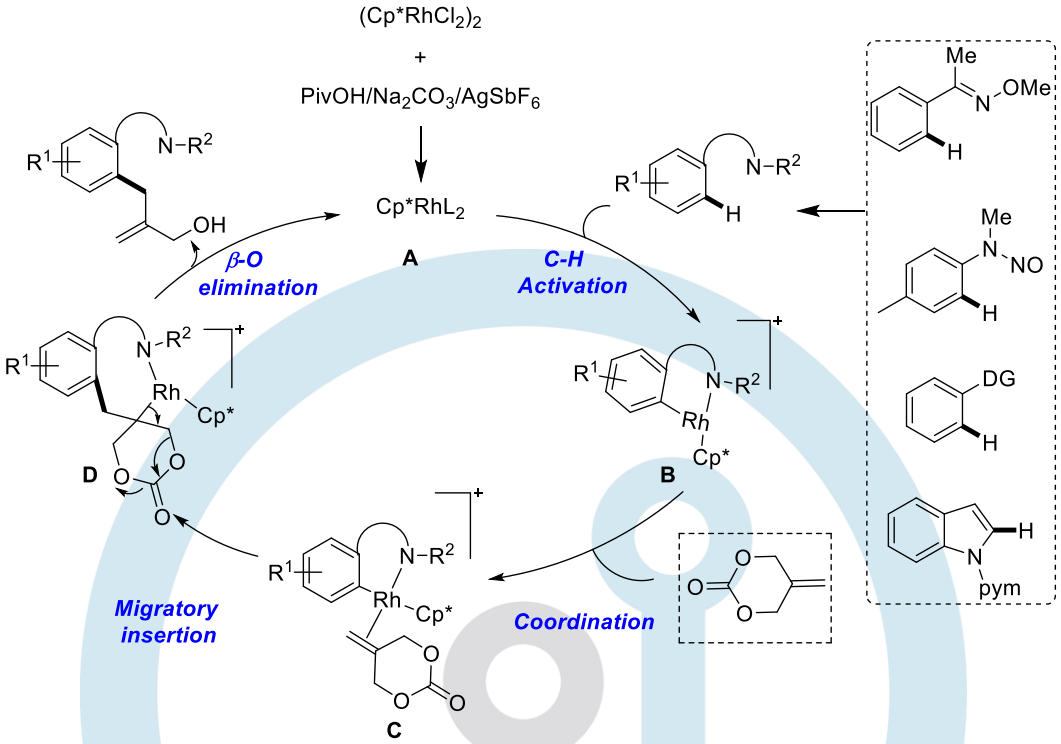


Condition A: (Cp*RhCl2)2 (2.5 mol%), AgSbF6 (10.0 mol%), Na2CO3 (1.0 equiv), CF3CH2OH (0.2 M), 45 °C , 12 h
Condition B: (Cp*RhCl2)2 (2.5 mol%), AgSbF6 (10.0 mol%), HOAc (1.0 equiv.), 1,4-dioxane (0.2 M), 45 °C, 12 h



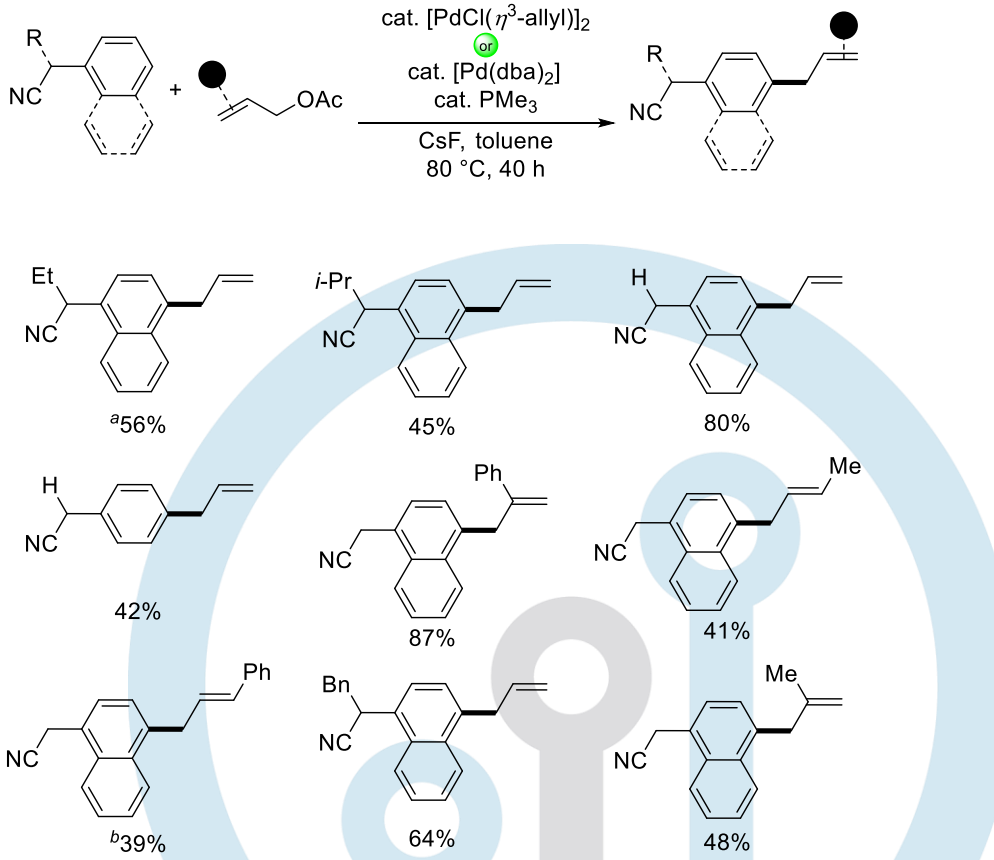
Reaction condition: [a]reaction occured at 110°C

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



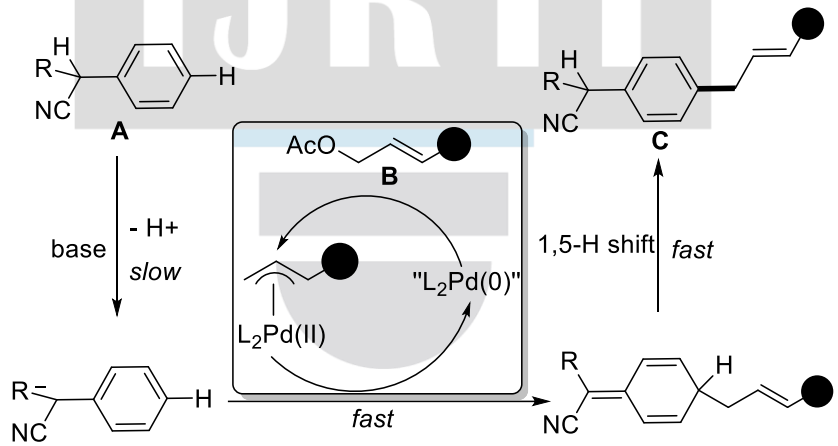
(**Scheme 16**). Proposed mechanism involving Rh (III)-catalyzed C–H activation, alkene insertion, *β*-oxygen elimination, and protodemetalation to form branched allylic alcohols.

In 2023, Ueno and co-workers [54] 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% $[PdCl(\eta^3\text{-allyl})]_2$, 20 mol% PMe_3, and 4.0 equivalents of CsF in toluene at 80 °Cover 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, β*-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 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 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: [a]A mixture of the desired product C and the corresponding,α,β-dehydrogenated product was obtained. [d]A mixture of ortho-allylated product was obtained

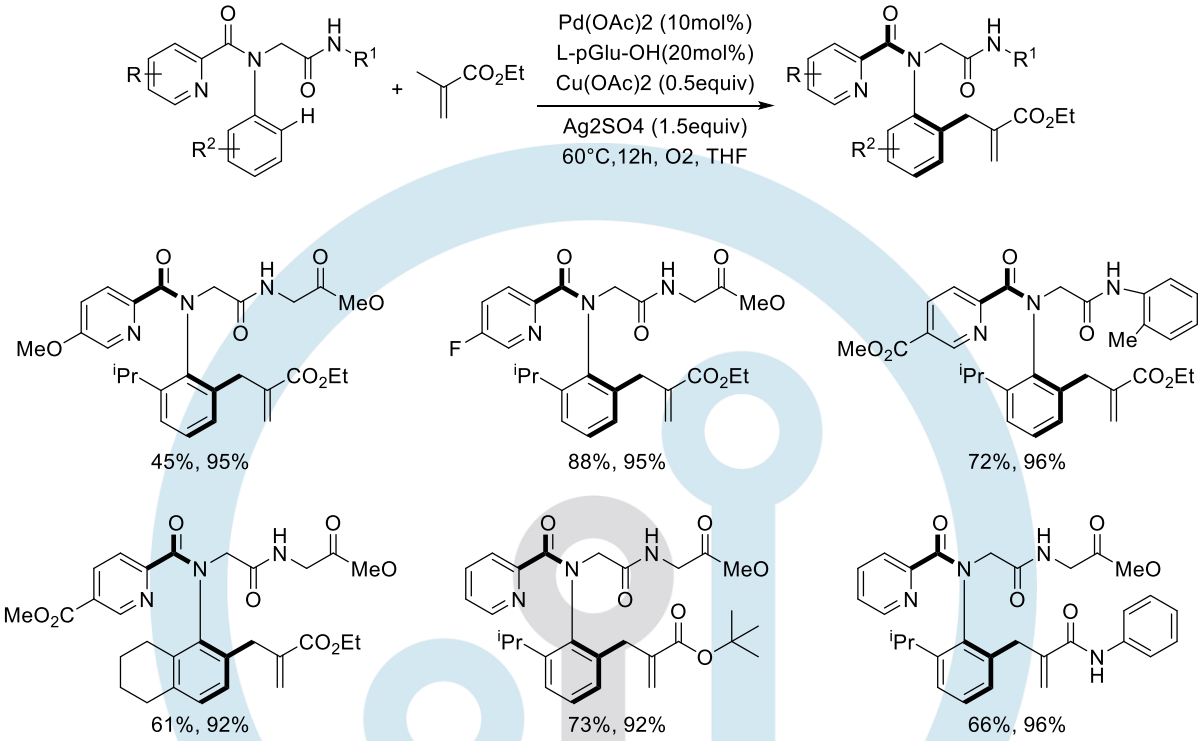
(**Scheme 17**). Selective *para*-allylation of 1-(cyanomethyl)arenes using allyl acetates under palladium catalysis.



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

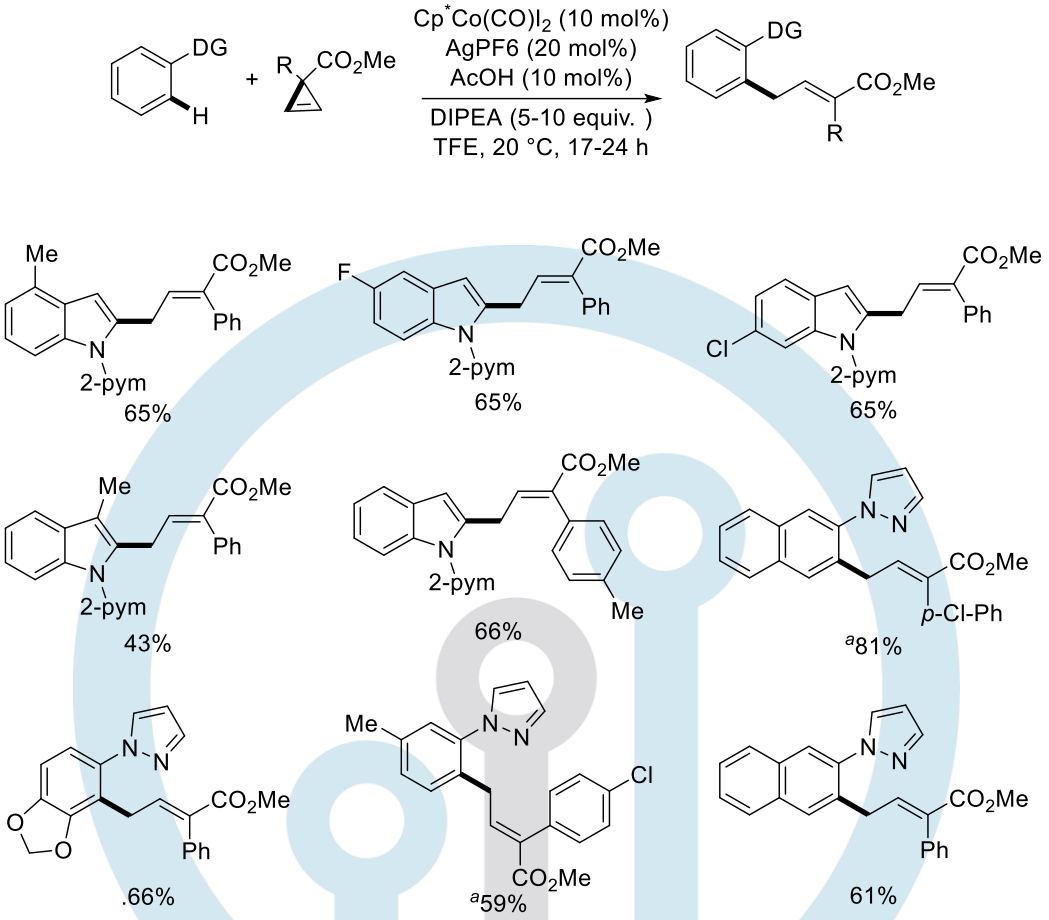
In 2021, Zhang and co-workers [55] reported an atroposelective C–H allylation enabled by Pd (II) catalysis for the synthesis of chiral N-Aryl peptoidatrop isomers. The reaction between *N*-aryl peptoids and ethyl methacrylate was conducted using 10 mol% $Pd(OAc)_2$, 20 mol% *L*-pGlu-OH, 0.5 equivalents of $Cu(OAc)_2$, 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.

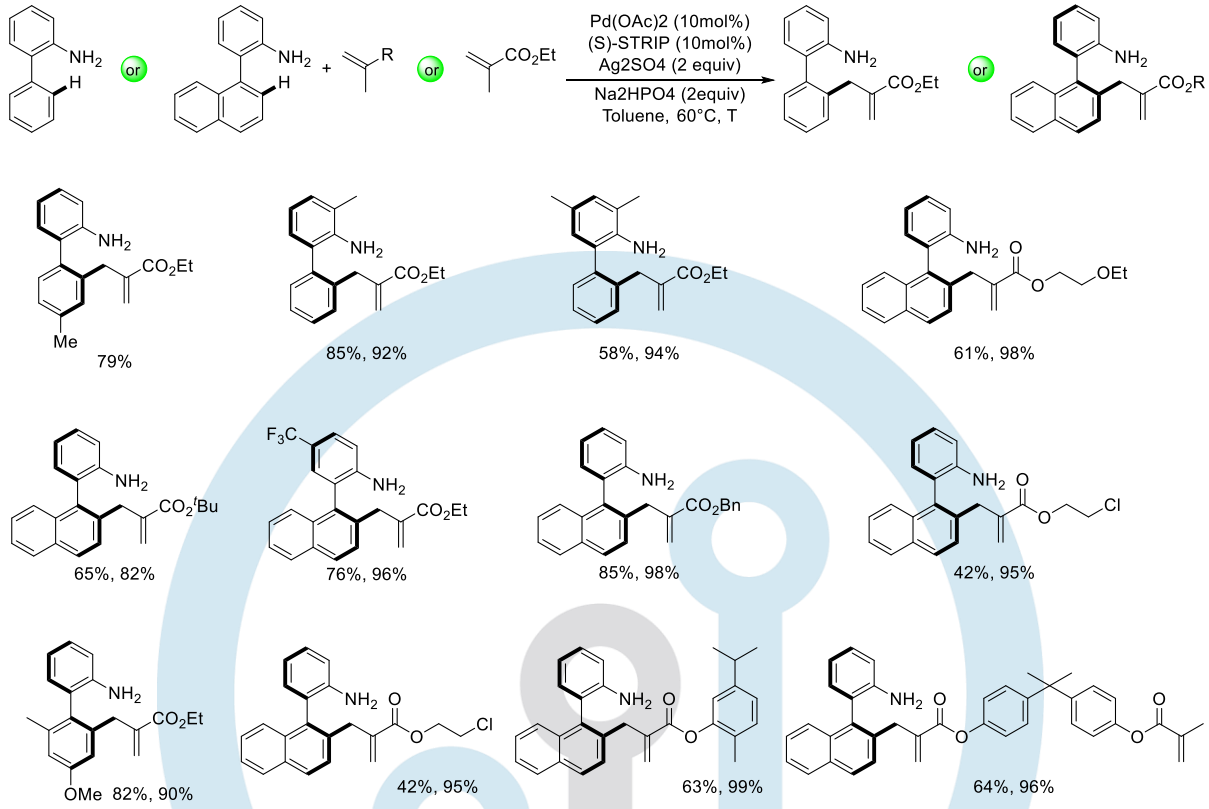
In 2021, Kim and colleagues [56] reported a method for Cobalt (III)-catalyzed C–H allylation of N-pyrimidyl indoles using cyclopropenes, achieved through a sequential C–C and C–H bond activation strategy. The reaction was carried out under an argon atmosphere using 10 mol% Cp*Co(CO)I_2 as the catalyst, 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



Reaction conditions: [a]5 equiv of DIPEA were added.

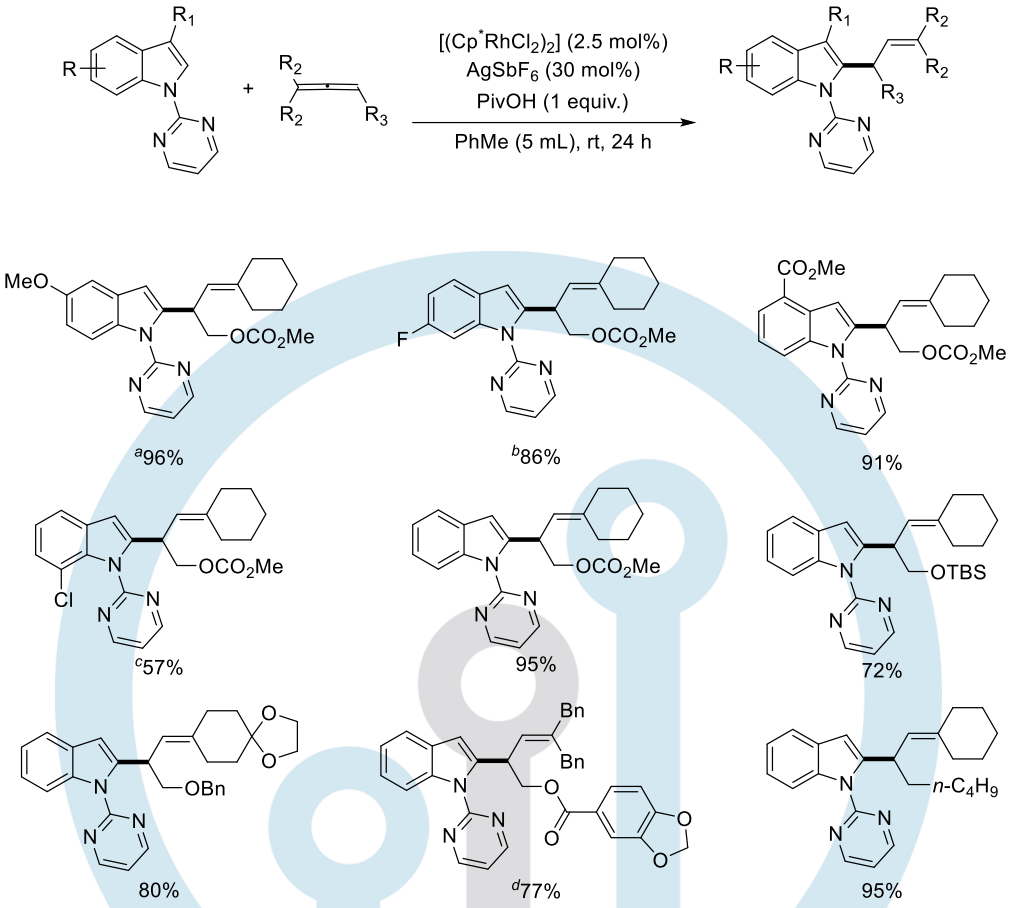
(**Scheme 20**). Cobalt (III)-catalyzed sequential activation of C–H and C–C bonds enabling allylation with cyclopropenes.

In 2020, Shi and co-workers [57] reported a palladium-catalyzed, atroposelective C–H allylation of biaryl-2-amines using methacrylates as allyl surrogates. The reaction, promoted by10 mol% Pd $(OAc)_2$,2 equiv. Ag_2SO_4, and 10 mol%(S)-STRIP in the presence of 2 equiv. Na_2HPO_4 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 enantio selectivity. 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.

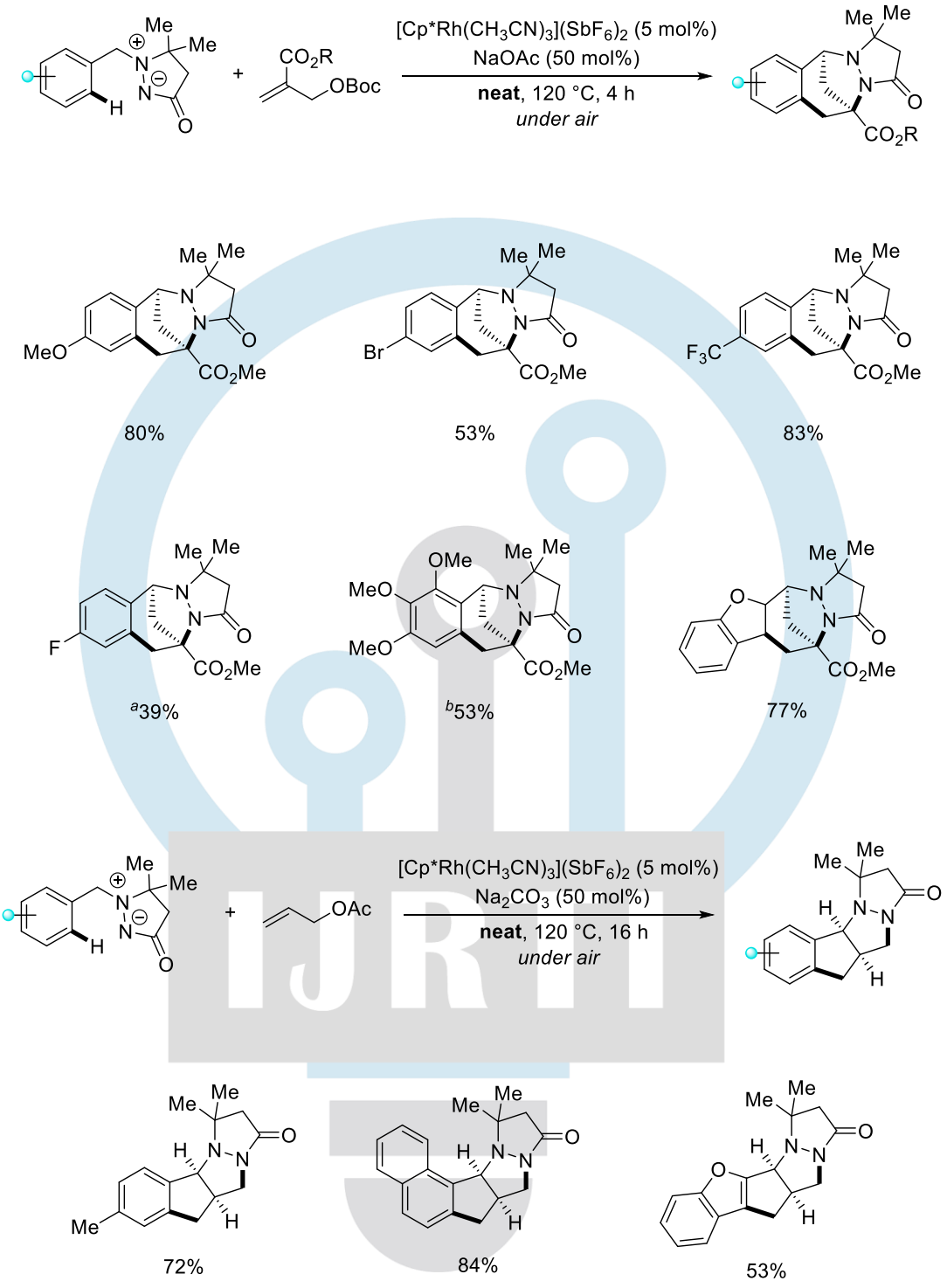
In 2022, Zhai and co-workers [58] reported a rhodium-catalyzed stereoselective C–H functionalization of indoles through intermolecular coupling with trisubstituted allenes. The reaction was conducted under mild conditions using2.5mol% $[Cp^*RhCl_2]_2$ as the catalyst, along with30mol% $AgSbF_6$ and 1 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 disfavours 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.



Reaction conditions: [a]The reaction was run for 12h. [b]The reaction was carried out at 50°C. [c]9%of product. [d]The reactionwas carried out at 70 °C.

(**Scheme 22**). Stereoselective C–H functionalization of indoles using allenes under rhodium catalysis.

In 2025, Zhang and co-workers [59] 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 $(CH_3CN)_3]$ $(SbF_6)_2$and 50 mol% NaOAc at 120 °C for 4 hours under air, yielded the products in moderate to excellent efficiency (**Scheme23**). 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.

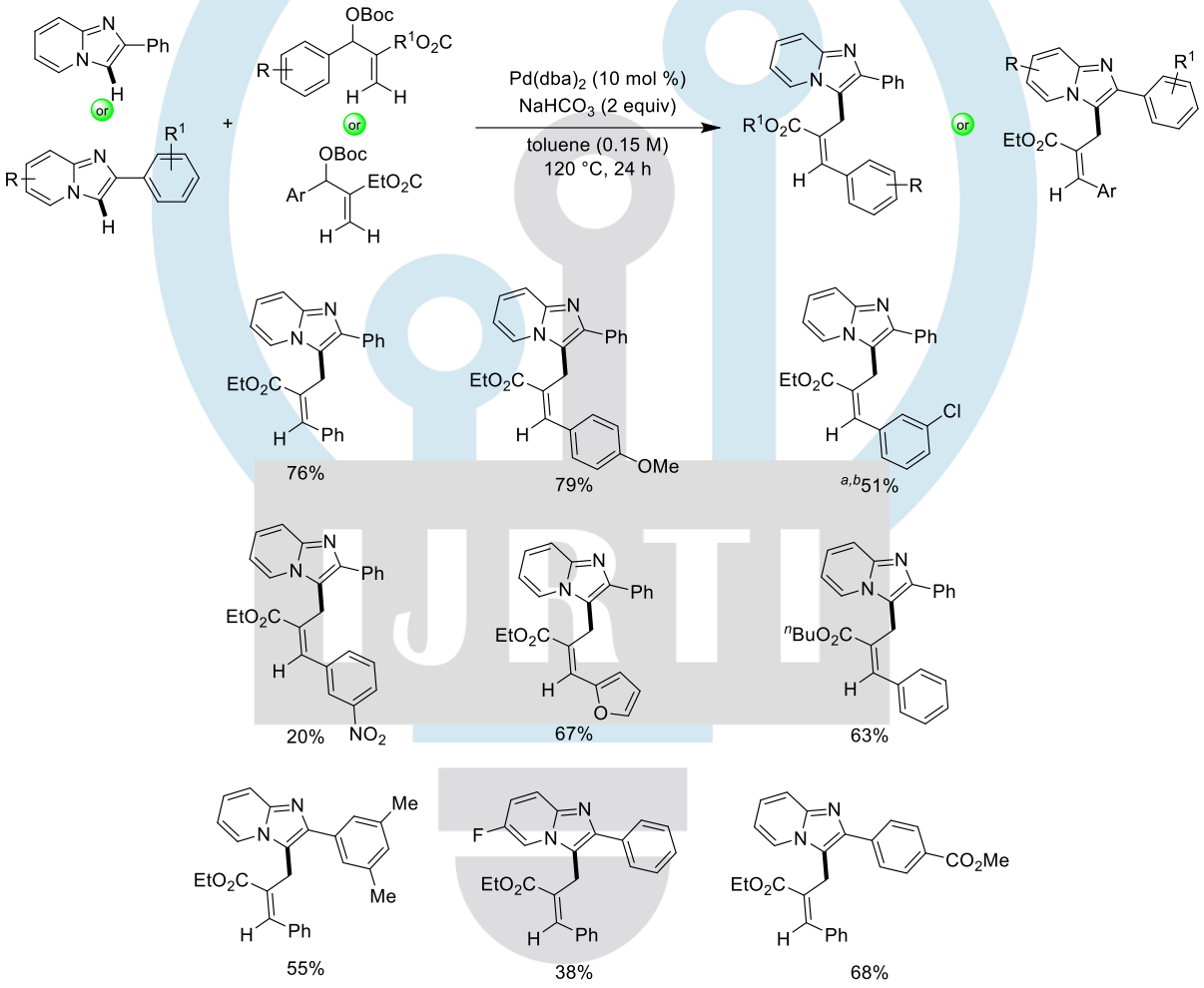


Reaction conditions: [a]The reaction was conducted at 80° C for 16 hours.
[b]The reaction was carried out for 16 hours.

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

In 2023, Kaliyamoorthy and colleagues [60] 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% $Pd(dba)_2$ and 2 equivalents of $NaHCO_3$ in toluene conducted at 120 °C over a period of 24hour, 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_2 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.

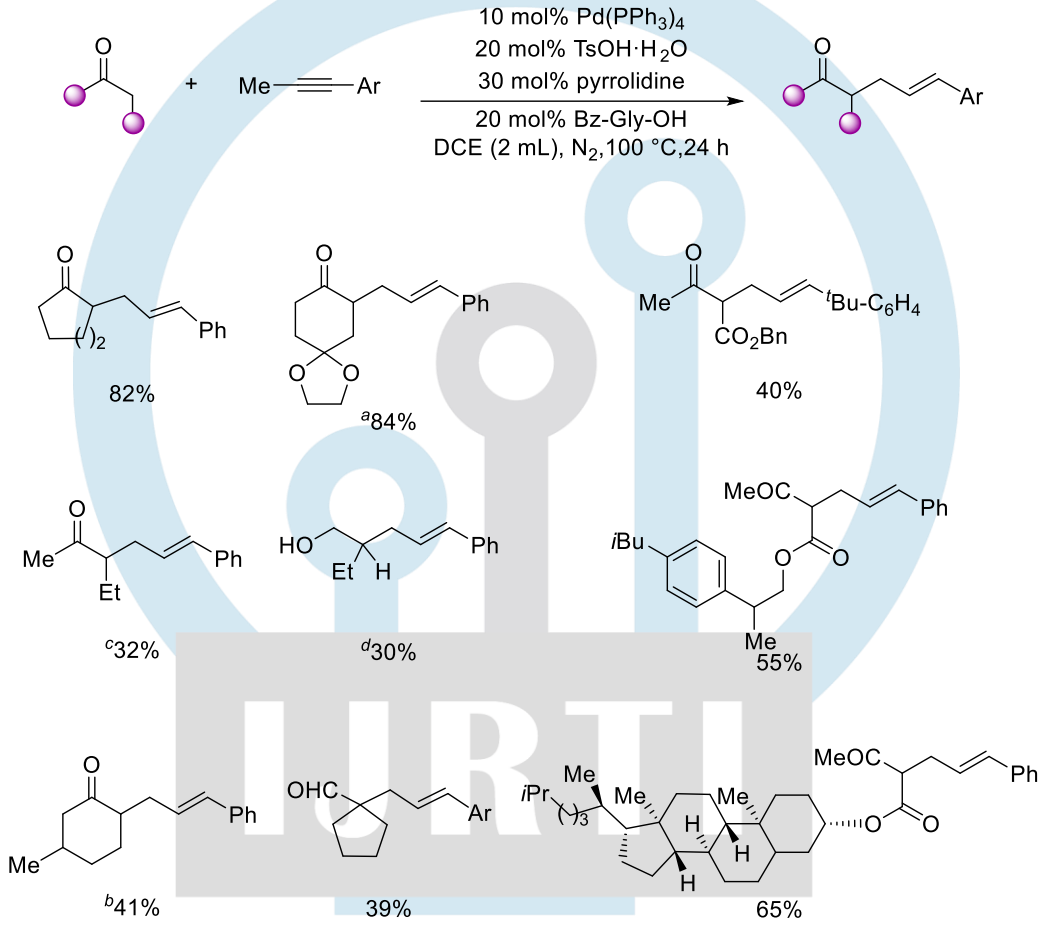


Reaction conditions: [a]4 equiv of the allylic source was employed.[b]The reaction was carried out at 150 °C.

(**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-workers [61] 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% $Pd(PPh_3)_4$, 20 mol% $TsOH{\cdot}H_2O$, 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.

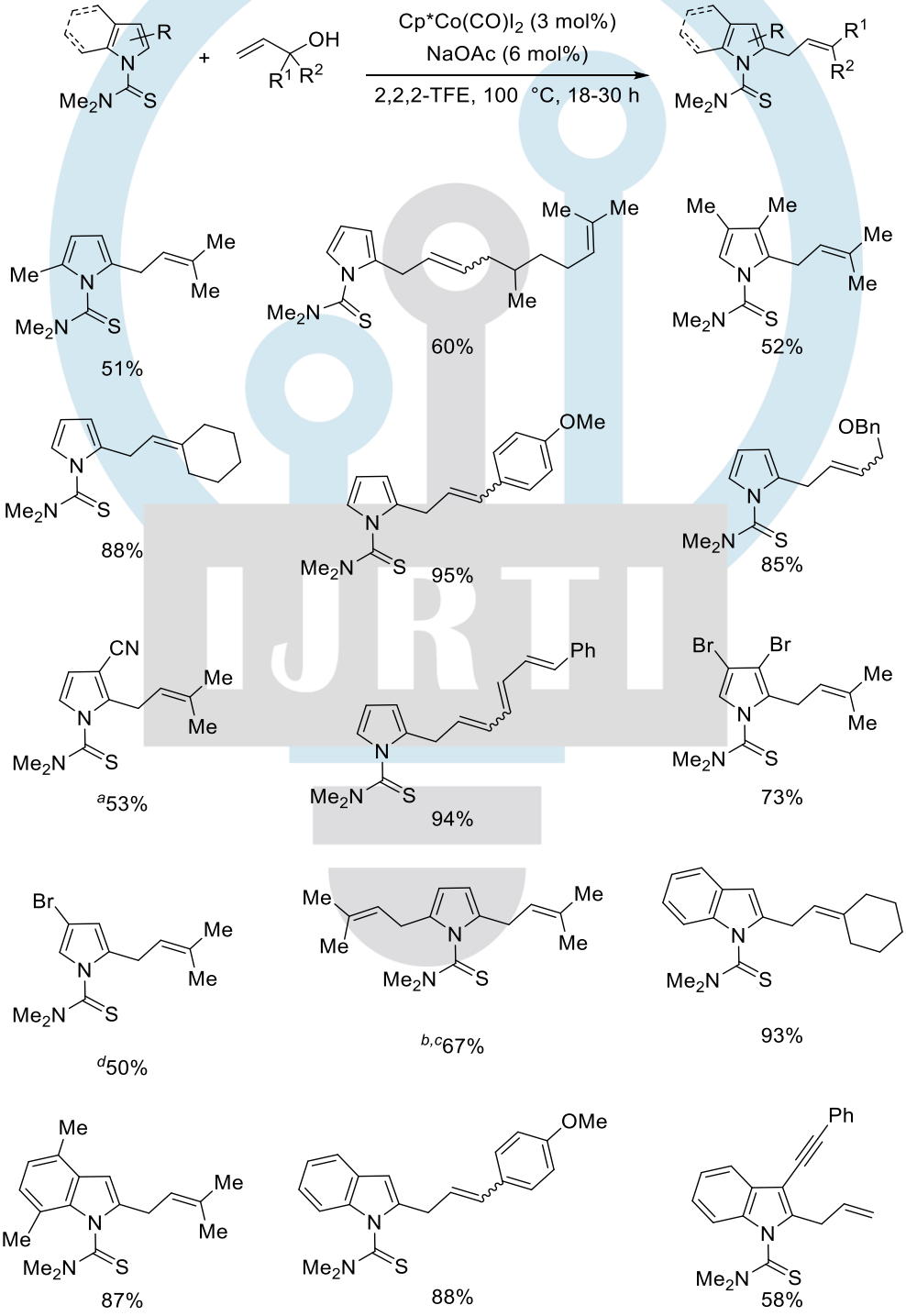


Reaction conditions: [a]For 16 h. [b]L5 was used instead of Bz-Gly-OH.[c]For 48 h. [d]Reduced by NaBH4.

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

In 2021, Maji and co-workers [62] reported a C2-prenylation of pyrrole and indole *via* Co (III)-catalyzed dehydrative reaction with allyl alcohols. They allylated various pyrroles and indoles with allyl alcohol in the presence of 3 mol% Cp*Co (CO)I 2, 6 mol% NaOAc in 2,2,2-TFE at 100 °C over18-30 hour, and obtained the corresponding product in good to high yield (**Scheme 26**). The Cp*Co (III)-catalyzed dehydrative C2-allylation displayed broad substrate compatibility with both allyl alcohols and (hetero)arenes. A variety of allyl alcohols, including prenyl, geranial-derived, cyclic (e.g., cyclohexyl, cyclopropyl), tertiary, aromatic, and simple allyl alcohols were effectively employed. Unsymmetrical allyl alcohols afforded *E/Z* mixtures favouring the (*E*)-isomer, and dialkenyl variants enabled the synthesis of 1,3-dienes with good stereoselectivity. Across all cases, mono-allylation was exclusively observed, with no evidence of di-allylation or olefin isomerization, even under high-temperature and basic conditions. Pyrrole substrates bearing electron-rich or electron-deficient groups at C2, C3, or both positions participated well, giving single regioisomeric products. Notably, sterically hindered and halogenated pyrroles were tolerated, and regioselectivity was maintained even in unsymmetrical substitution patterns. Limited reactivity was observed with bulky disubstituted pyrroles, likely due to steric hindrance. Two-fold allylation was also achieved, showcasing the potential for further diversification. For indoles, substitution at various positions

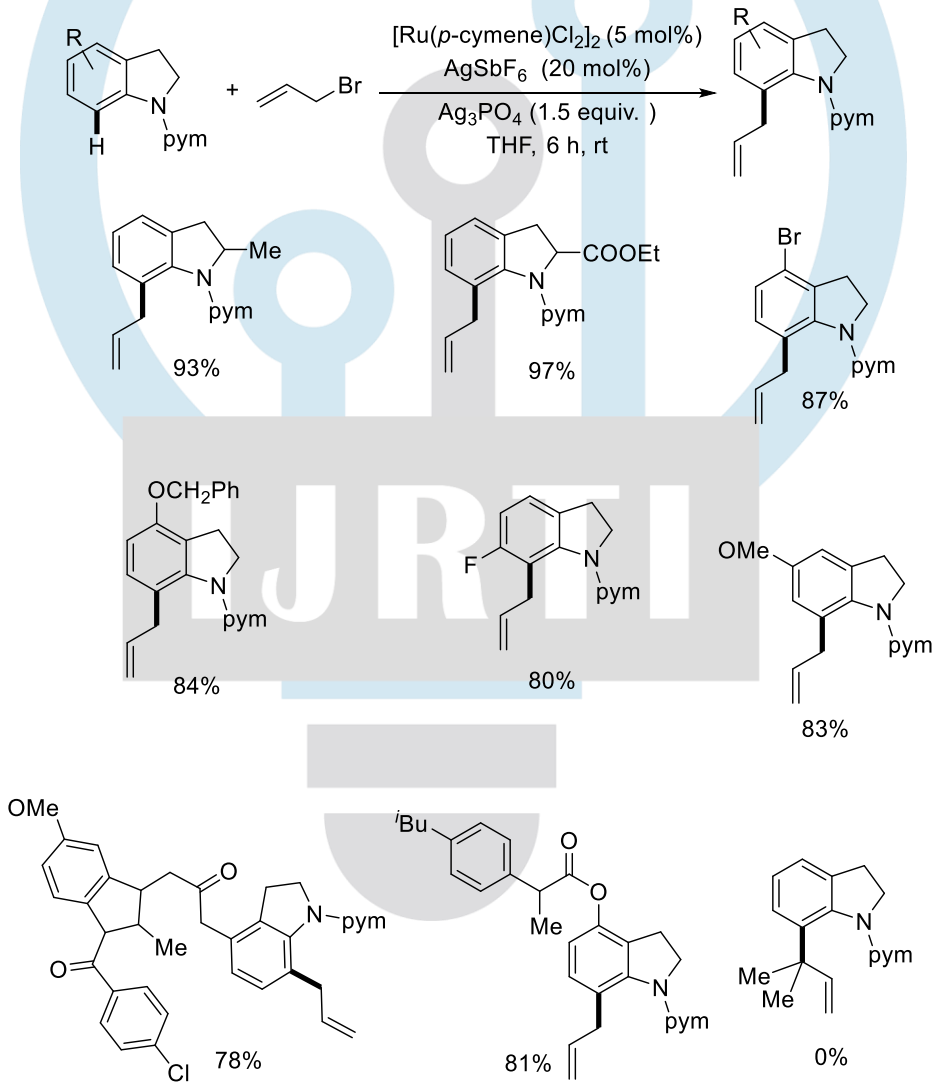
including alkyl, halogen, methoxy, cyano, and alkynyl groups were well-tolerated. C2-selective prenylation, geranylation, and other allylations proceeded efficiently, including with substrates bearing extended aliphatic or diene side chains. Importantly, steric bulk at positions like C7 did not hinder reactivity, and the inclusion of C3-alkynyl indoles demonstrated the method's applicability to the synthesis of carbazole precursors. The developed method proved to be scalable, as demonstrated by gram-scale reactions. Its broad functional group tolerance and operational simplicity such as silver-free conditions and water as the only by-product make it attractive for practical synthesis. Additionally, the directing group can be removed under mild reductive conditions, enabling access to 2-allyl pyrroles and indoles, valuable intermediates for constructing biologically active molecules, including prenylated analogs and conjugated dienes.



Reaction conditions: [a]6.0 mol% of $Cp^*Co(CO)I_2$ and 12 mol% of NaOAc were used. [b]3.0 equiv. of 2a was used. [c]27% of 3aa was isolated. [d]It was isolated as an inseparable mixture with 39% of the C5 regioisomer.

(Scheme 26). C2-prenylation of pyrrole and indole *via* Co (III)-catalyzed dehydrative reaction with allyl alcohols.

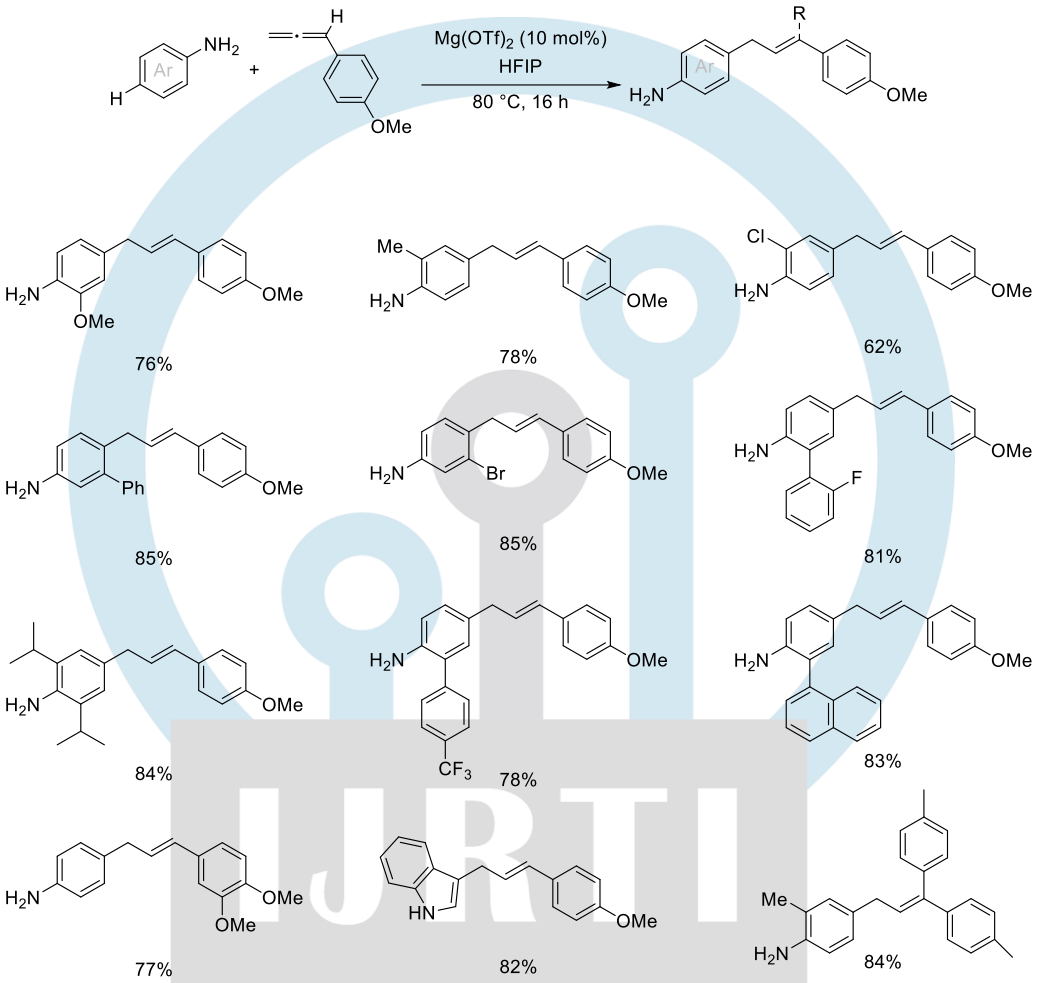
In 2023, Gupta and co-workers [63] reported a ruthenium-catalyzed C7-allylation of indolines using allyl bromide, supported by both computational and experimental studies. The reaction, carried out at room temperature for 6 hours in THF with 5 mol% [Ru(p-cymene) Cl_2] $_2$, 20 mol% $AgSbF_6$, and 1.5 equivalents of Ag_3PO_4, furnished the desired allylated products in good to excellent yields (**Scheme 27**). A variety of substituted indolines were compatible with the reaction conditions. C3-alkyl and ester-substituted indolines reacted smoothly, as did C4-bromo and benzyloxy derivatives. Both electron-donating and electron-withdrawing groups at C5 were well tolerated. A C6-fluoro substituent allowed product formation, whereas a C6-nitro group completely suppressed reactivity. Drug-conjugated indolines, including indomethacin and ibuprofen derivatives, also participated successfully. In contrast, substituted allyl alcohols showed limited reactivity, likely due to steric hindrance during the olefin insertion step. The methodology was effectively applied to a wide range of indolines, including drug-derived analogues, demonstrating good selectivity and scalability. Successful gram-scale synthesis further highlighted the practical utility of the protocol.



(**Scheme 27**). Ruthenium (II)-catalyzed C7 functionalization of Indolines using Allyl Bromide:

In 2023, Baidya and co-workers [64] developed a stereo-and regioselective method for allylating anilines using aryl allenes. The reaction was carried out using 10 mol% Mg $(OTf)_2$ in hexafluoro isopropanol at 80 °C for 16 hours, delivered the corresponding products in good yields (**Scheme 28**). The developed allylation protocol showed broad applicability across a wide range of anilines. Parent aniline, despite its inherent reactivity challenges, underwent selective *para*-allylation. *Ortho*-substituted anilines bearing alkoxy, halogen, alkyl and heteroaryl groups reacted efficiently. *Meta*-substituted anilines also provided para-selective products, and functional groups such as vinyl and hydroxyl were well tolerated. Fluorinated, trifluoromethylated, bulky aromatic, disubstituted, and N-substituted anilines were compatible, with exclusive E-selectivity observed in all cases. The reaction also accommodated a variety of aryl allenes,

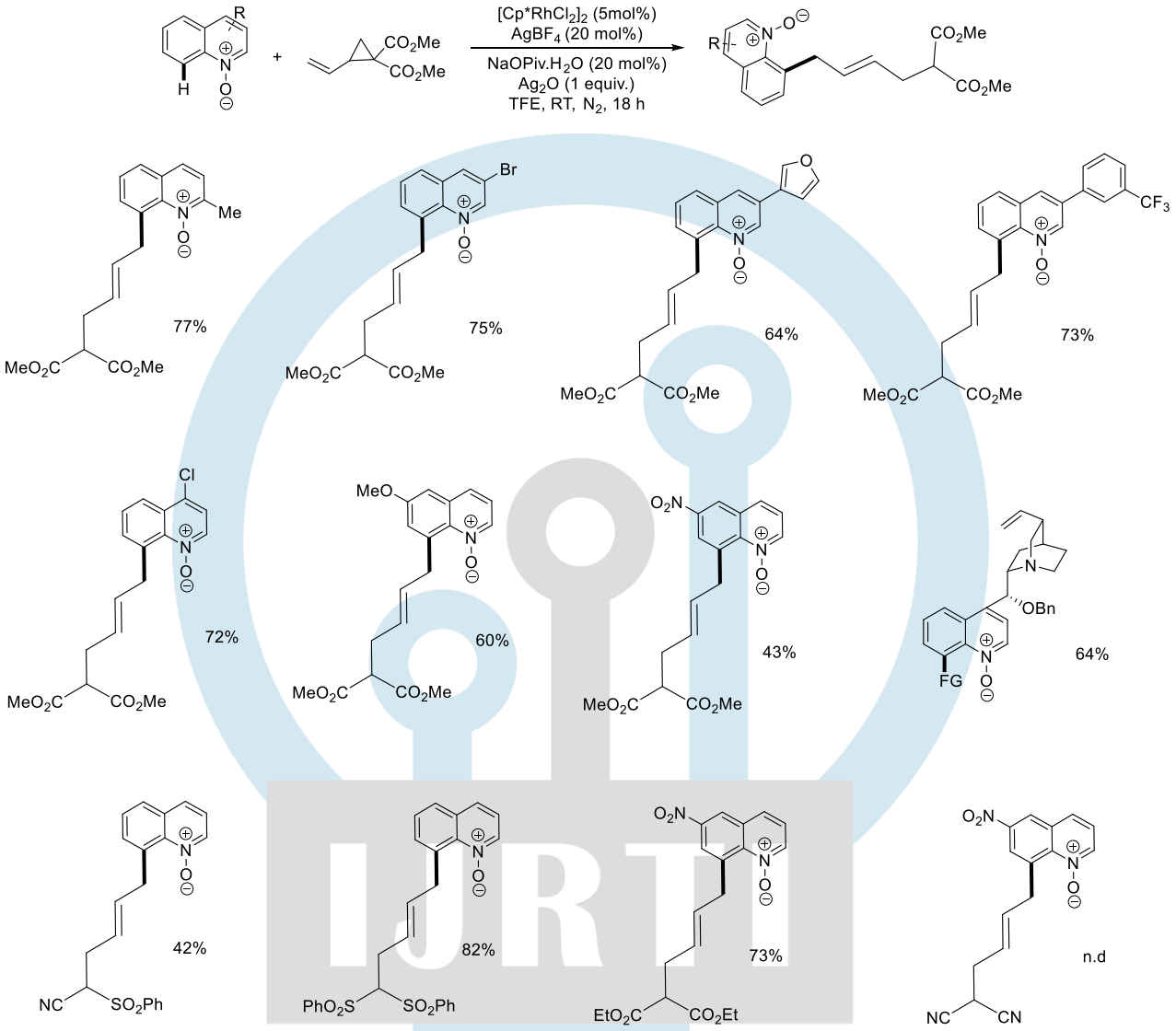
including mono-, di-, and trisubstituted types with electron-donating groups, while electron-deficient and alkyl-substituted allenes showed limited reactivity. Additionally, the methodology was successfully extended to indole substrates, demonstrating its versatility across heterocycles. The method was scalable without loss of efficiency or selectivity. The modified catalytic system facilitated a sequential allylation–hydroarylation process, providing an efficient strategy for the regioselective-di functionalization of allenes.



(**Scheme 28**). Selective allylation of anilines using aryl allenes under hexa fluoro isopropanol conditions.

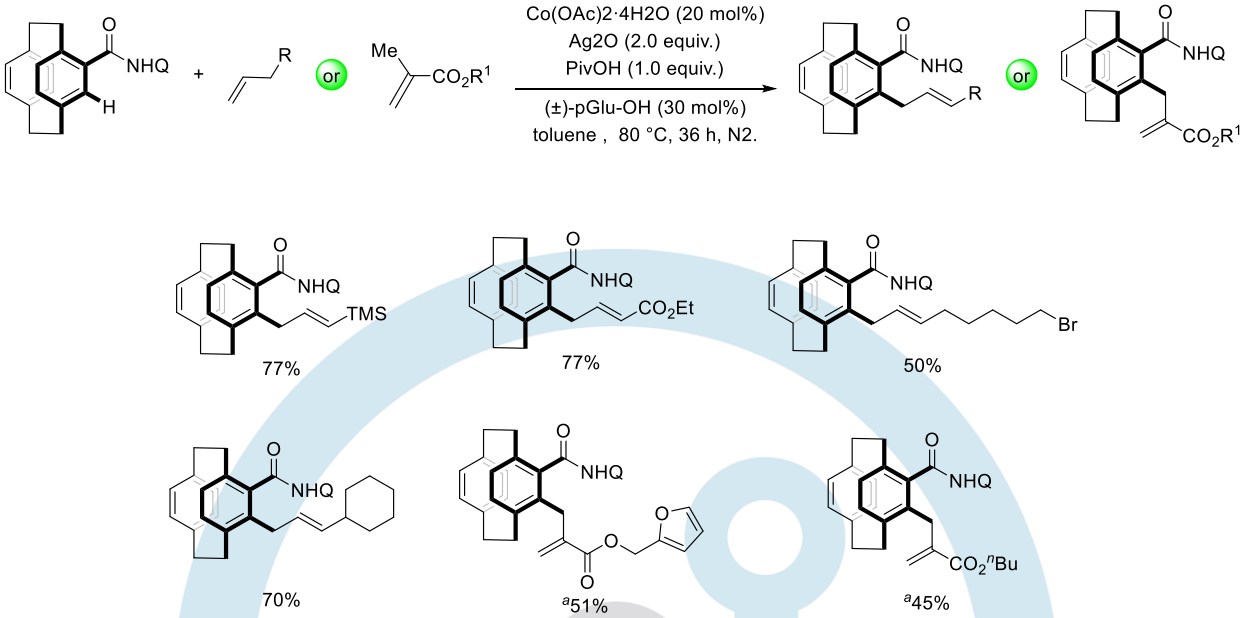
In 2023, Punniyamurthy and collaborators [65] reported a Rh (III)-catalyzed C8–H allylation of quinoline N-oxides using vinyl cyclopropanes, enabled by a sequential C–H and C–C bond activation strategy. The transformation was carried out under mild conditions employing 5 mol% $[Cp^*RhCl_2]_2$, along with20 mol% $AgBF_4$, 20 mol% $NaOPiv{\cdot}H_2O$, and 1 equiv. TFE as additives, in trifluoroethanol (TFE) at ambient temperature for 18 hours under a nitrogen atmosphere, affording the allylated products in moderate to good yields (**Scheme29**). The C8–H allylation of quinoline N-oxides exhibited broad substrate compatibility. Substituents including alkyl, aryl, halogen, heteroaryl, trifluoromethyl, nitro, and methyl groups were well tolerated, with high (Z)-selectivity observed across most cases. The reaction accommodated a variety of functional groups such as amines, ethers, and esters, and was applicable to complex molecules, including a cinchonidine derivative, highlighting its utility for late-stage diversification. The method also supported a range of vinyl cyclopropanes bearing alkyl, benzyl, aryl, sulfone, and ester groups, though reactivity decreased with strongly electron-withdrawing cyano substituents. The mechanism begins with the generation of active Rh (III) species (**A**), which promotes C8–H activation of quinoline N-oxide to form intermediate (**B**). Coordination and migratory insertion of the vinyl cyclopropane yield intermediate (**C**), followed by formation of a seven-membered Rhoda cycle (**D**), which rearranges via ester-assisted β-carbon elimination through intermediate (**E**) to give (**F**). Proto de metalation of (**F**) furnishes the allylated product, while Rh(I) is reoxidized to Rh (III) by Ag(I), completing the catalytic cycle (**Scheme 29**). This methodology showcases strong practical potential through successful scale-up, broad substrate scope, and high regio- and diastereoselectivity. Its utility in sequential C–H and C–C activation, as well as

late-stage functionalization of complex natural products, including alkaloid derivatives, underscores its value for synthetic and medicinal chemistry applications.



(**Scheme 29**). Quinoline N-oxides undergo C8–H allylation with vinyl cyclopropanes through a stepwise activation of C–H and C–C bond.

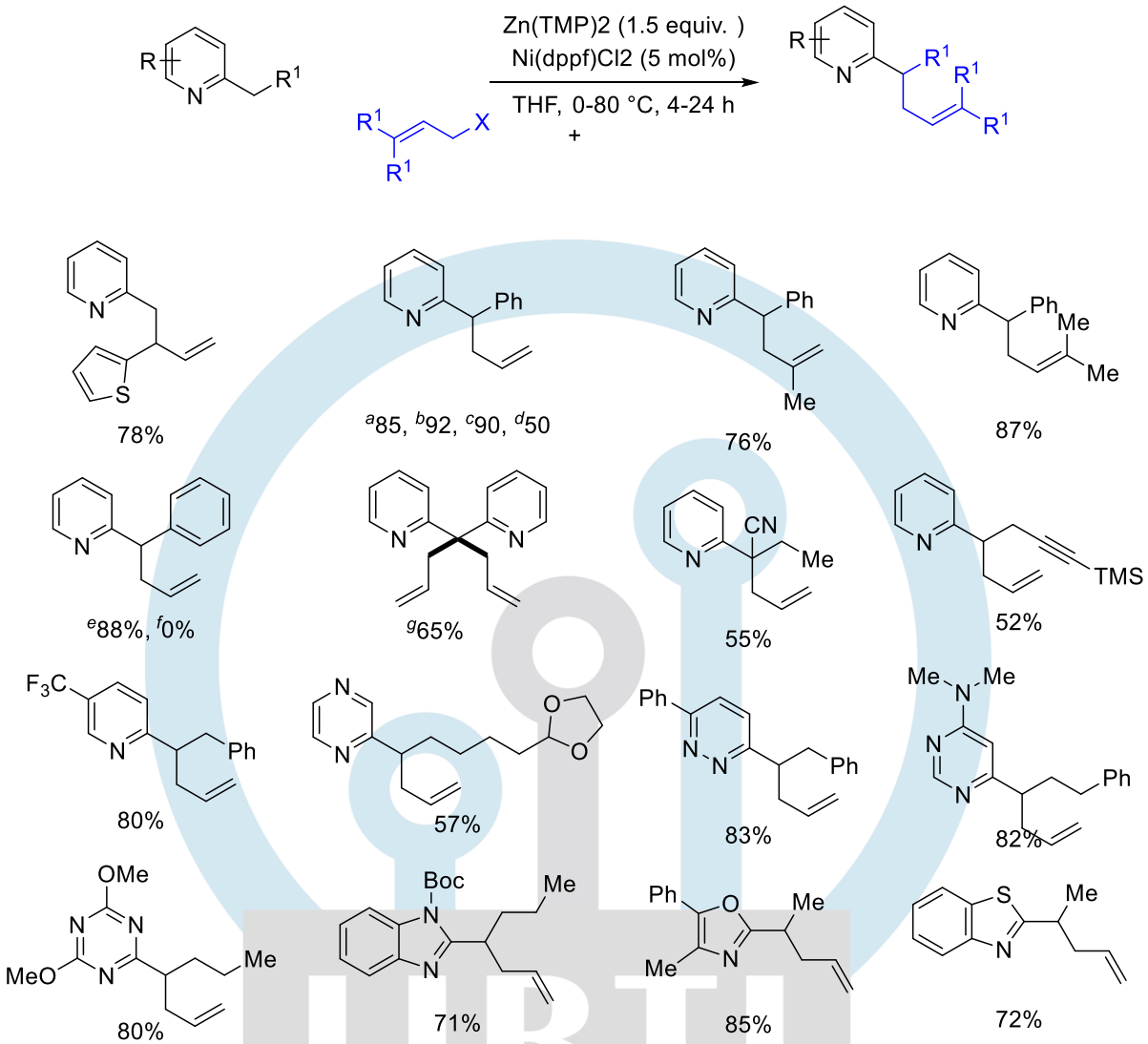
In 2022, Shi and co-workers [66] introduced a cobalt-catalyzed method for the ortho-C–H functionalization of [2.2] para cyclophane, enabling both allylation and acyloxylation. The transformation was achieved by using 20 mol% $Co(OAc)_2 \cdot 4H_2O$ as the catalyst, along with 2 equivalents of Ag_2O, 1 equivalent of pivalic acid (PivOH), and 30 mol% of (±)-pGlu-OH as a ligand in toluene at 80 °C for 36 hours under a nitrogen atmosphere, providing the desired allylated products in moderate to good yields (**Scheme30**). The cobalt-catalyzed *ortho*-allylation of [2.2] para cyclophane exhibited broad compatibility with various alkenes. Monosubstituted aliphatic alkenes reacted efficiently under the optimized conditions, tolerating functional groups such as ester, silyl and bromo moieties. Although sterically hindered substrates showed slightly reduced efficiency due to competing β-hydride elimination, the methodology remained effective. Additionally, 1,1-disubstituted alkenes, including α-methyl acrylates, were successfully employed to furnish terminally allylated products. Notably, heteroaromatic systems like furan were also well accommodated, demonstrating the reaction's versatility. The method's scalability, including gram-scale benzoyl oxylation of enantiopure substrates, highlights its potential for broader synthetic and materials applications.



reaction condition: [a] reactions were performed with Ag2SO4 (1.0 equiv.), Na2CO3 (3.0 equiv.), and PivOH (50 mol%) in 1.0 mL of DCE at 100 °C for 24 h under N2.

(**Scheme30**). Cobalt-catalyzed method for the ortho-C–H functionalization of [2.2] para cyclophane, enabling both allylation and acyl oxylation.

In 2022, Newhouse and colleagues [67] developed a nickel-catalyzed approach for introducing allyl groups at the benzylic positions of inactivated, electron-deficient heteroarenes. Using 1.5 equivalents of Zn $(TMP)_2$ and 5 mol% of $Ni(dppf)Cl_2$ as the catalyst in THF, they treated 14 different heterocyclic aromatics with allyl halides at temperatures ranging from 0 to 80 °C, over 4 to 24 hours, successfully produced the corresponding allylated derivatives in moderate to high yields (**Scheme31**). The substrate scope of the nickel-catalyzed benzylic allylation encompasses a wide range of electron-deficient heteroaromatics, including pyridines, quinolines, pyrazines, quinoxalines, pyridazines, pyrimidines, quinazolines, and triazines. Electron-withdrawing groups at the benzylic position enhanced reactivity, enabling reactions at lower temperatures. Functional groups sensitive to acid or base, as well as strained systems like cyclopropanes and silyl-protected alkynes, were well tolerated. Five-membered heterocycles such as benzimidazole, oxazole, benzoxazole, thiazole, and indole derivatives also underwent successful allylation, including diallylation in certain cases. A variety of allyl and benzyl electrophiles were compatible, including halides, esters, carbonates, and phosphates, with sterically hindered electrophiles favouring linear selectivity. The reaction proceeded with stereochemical control and required nickel catalysis, underscoring its broad applicability and robustness. This methodology offers a valuable tool for medicinal chemistry, enabling late-stage functionalization of diverse heterocyclic frameworks commonly found in pharmaceuticals. Its broad substrate and electrophile scope, mild conditions, and strong functional group tolerance make it well-suited for the synthesis of complex molecules and diversification of compound libraries. The N-directed deprotonation strategy facilitates selective activation of benzylic positions in inactivated heterocycles, and the scalability of the reaction supports its practical application in drug discovery and development.

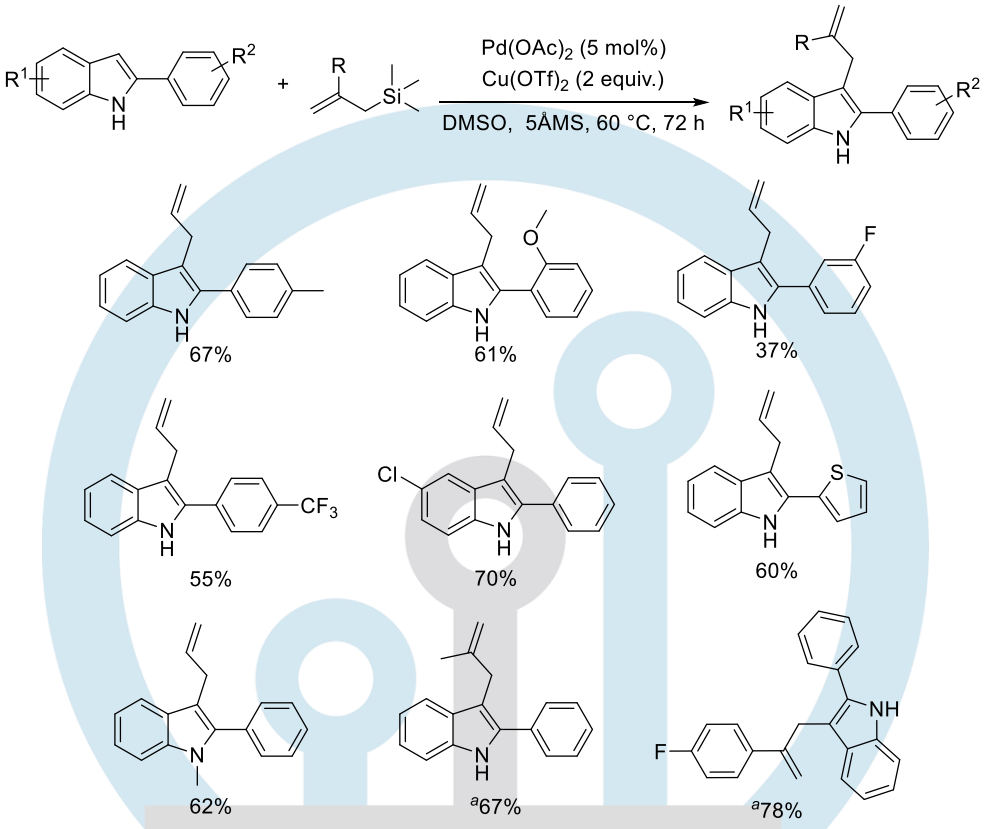


Reaction conditions: [a]X = Cl, [b]X = OPiv, [c]X = OCO2Me, [d]X = OAc. [e]1-gram scale with 1 mol% $Ni(dppf)Cl_2$. [f]3-Benzylpyridine as substrate. [g] 2.5 equivalent of $Zn(TMP)_2$ and 2.2 equivalent allyl bromide were used.

(**Scheme31**). A nickel-catalyzed approach for introducing allyl groups at the benzylic positions of electron-deficient heteroarenes.

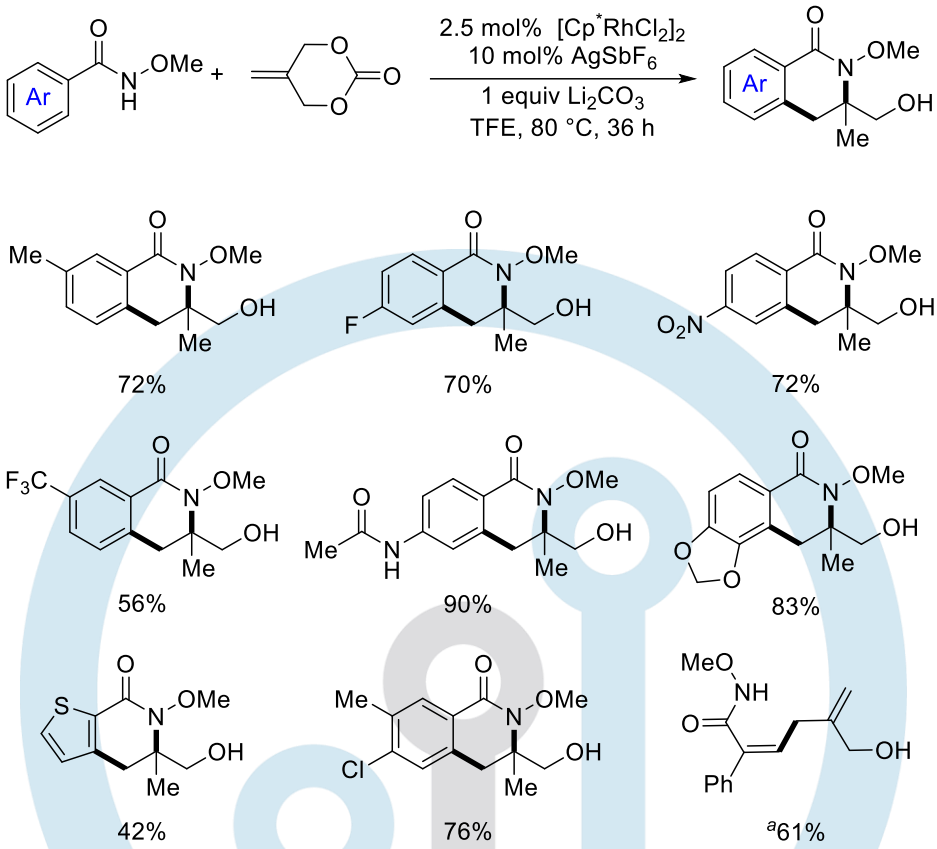
In 2023, Zhao and colleagues [68] reported a palladium-catalyzed method for the direct C–H functionalization of indole compounds using allyl trimethyl silanes. The reaction was carried out with 5 mol% Pd $(OAc)_2$, 2 equivalents of Cu $(OTf)_2$, and 5Å molecular sieves in DMSO at 60 °C over a period of 72 hours, led to the formation of the desired products in good yields (**Scheme 32**). The allylation reaction demonstrated broad substrate compatibility. Aromatic systems bearing electron-donating or electron-withdrawing groups were well-tolerated, with *ortho*-substituted arenes often performing better than *para*-substituted analogs. Electron-rich indoles showed higher reactivity, though halogenated, *alkyl*-substituted, and *N*-protected indoles also participated effectively. Heteroaromatic and polyaromatic substrates, such as thiophene and naphthyl derivatives, were compatible. Additionally, a range of 2-substituted allyl trimethyl silanes with varying electronic properties proved effective, with halogenated allyl silanes generally showing better performance than their electron-rich counterparts. The catalytic cycle is proposed to begin with coordination of the 2-substituted indole to the Pd (II) catalyst, followed by C–H activation to generate the palladacycle intermediate (**A**). This complex then undergoes trans metalation with the in situ formed pentavalent silicate species (**B**), resulting in the formation of the (allyl) (indole)palladium (II) complex (**C**). Reductive elimination from (**C**) releases the allylated indole product and regenerates the Pd (0) species, which is subsequently reoxidized by an external oxidant to complete the cycle (**Scheme 32**). This method represents a significant advancement in C–H activation by employing nontoxic, stable and user-friendly

allyl silanes as coupling partners for C–C bond formation. Notably, the reaction proceeds under mild conditions without the need for fluoride activation and accommodates a wide range of 2-substituted indoles bearing diverse functional groups.

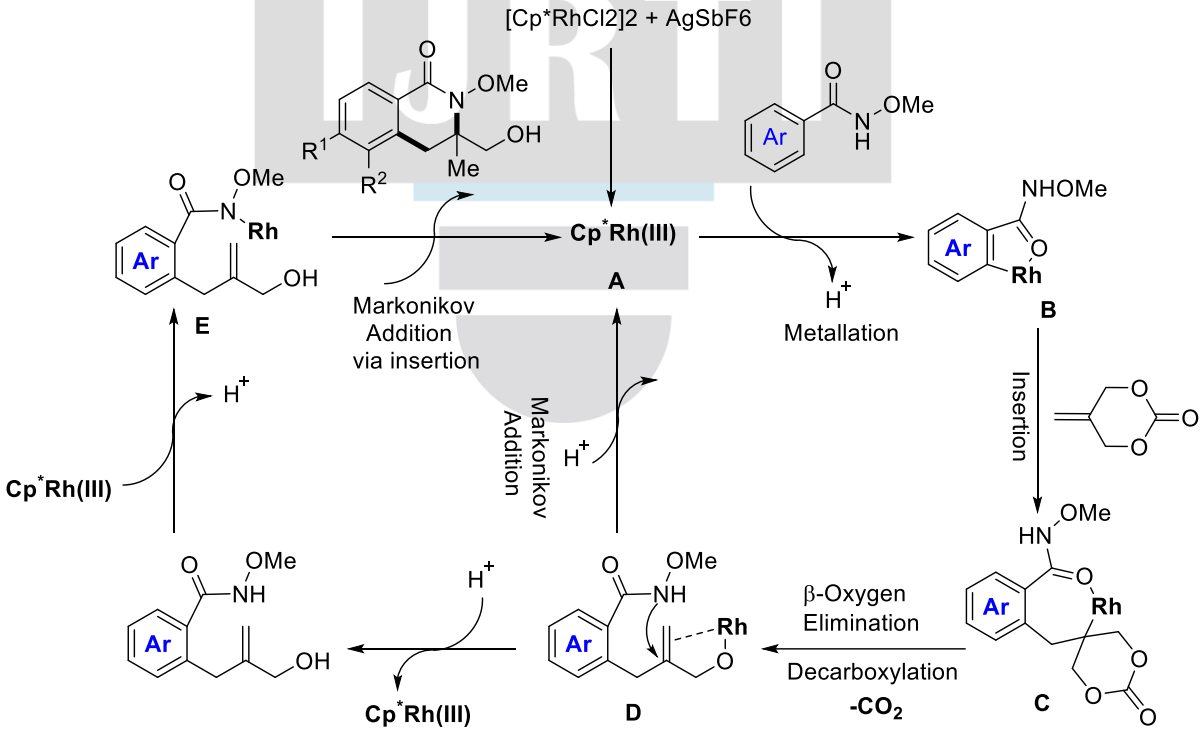


(**Scheme 32**). Palladium-catalyzed method for the direct C–H functionalization of indole compounds using allyl trimethyl silanes.

In 2021, Zhang and colleagues [69] reported a Rh (III)-catalyzed C–H allylation followed by annulative Markovnikov addition using 5-methylene-1,3-dioxan-2-one as the coupling partner. The transformation involved *N*-methoxybenzamide as the substrate and was carried out under optimized conditions using 2.5 mol% $[Cp^*RhCl_2]_2$, 10 mol% $AgSbF_6$, and 1 equivalent of Li_2CO_3 in trifluoroethanol (TFE) at 80 °C for 36 hours, afforded isoquinolinone derivatives bearing a quaternary centre at C3 in moderate to excellent yields (**Scheme 33**).[1] The reaction demonstrated a broad substrate scope, accommodating electron-donating groups such as methoxy, methyl and *N,N*-dimethyl, as well as electron-withdrawing and halogen substituents on *N*-methoxybenzamides. Coordinating groups like acetamido were well tolerated, and regioselectivity was influenced by electronic and steric effects when multiple C–H activation sites were present. Heterocyclic amides were also reactive, though less efficiently, while *ortho*-substitution was detrimental to the reaction. Additionally, acrylamide underwent direct C–H allylation rather than annulation. The catalytic cycle starts with the generation of cationic rhodium complex (**A**), which coordinates to the amide and activates the C–H bond to form rhodacycle (**B**). This is followed by insertion of the alkene into the Rh–C bond, producing intermediate (**C**), which then undergoes *β*-oxygen elimination followed by decarboxylation to give intermediate (**D**). From (**D**), the final product is formed through a Markovnikov addition pathway, either directly or after proton transfer to intermediate (**E**), involving *N*–Rh bond insertion (**Scheme 34**). This approach is compatible with diverse functional groups and has been applied to late-stage modification of *N*-methoxy amides from complex structures such as steroids and adapalene. Its effectiveness was demonstrated through a concise three-step route to access analogs of US28 inverse agonists. The strategy presents valuable potential for creating and exploring new isoquinolinone compounds.



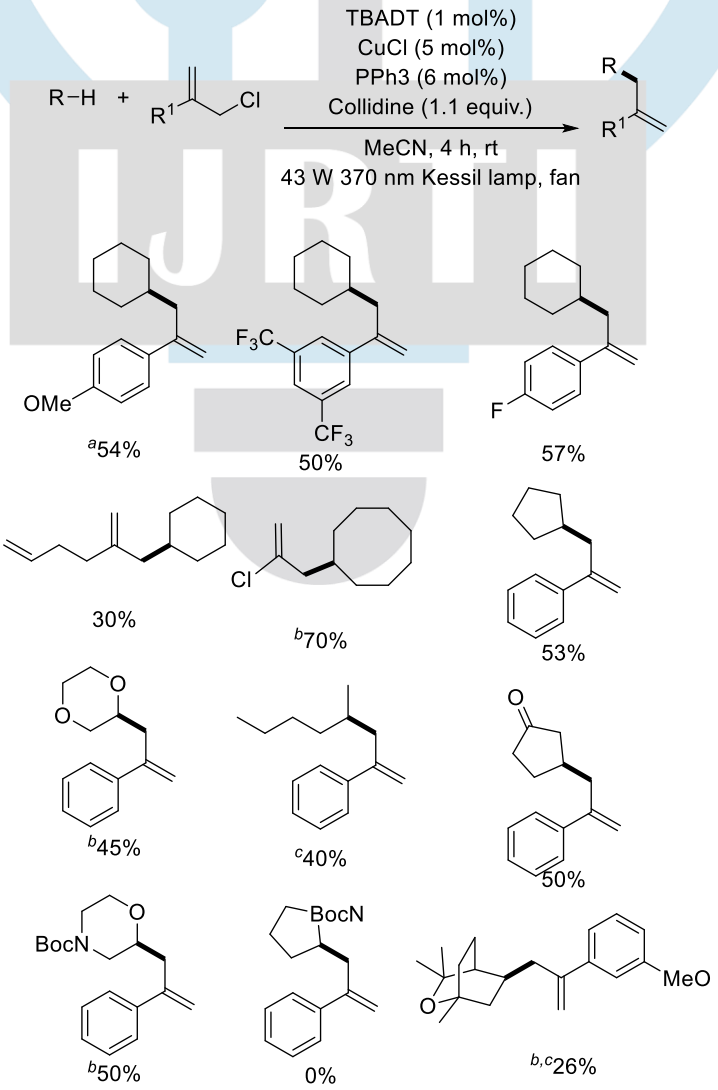
(**Scheme 33**). Rh (III)-catalyzed annulative Markovnikov addition of 5-methylene-1,3-dioxan-2-one and C–H allylation for constructing isoquinolinones bearing C3 quaternary centres.



(**Scheme 34**). Proposed mechanism for Rh (III)-catalyzed C–H activation, allylation, and annulative Markovnikov addition to form C3-quaternary isoquinolinones.

In 2022, Fananás - Mastral and colleagues [70] introduced a method for the direct C−H allylation of inert alkanes using a cooperative tungsten/copper photocatalytic system. The reaction involved treating alkanes with allylic chloride in the presence of 1 mol% TBADT, 5 mol% CuCl, 6 mol% PPh_3, and 1.1 equivalents of collidine in acetonitrile at ambient temperature for 4 hours, under near-UV light (Kessil lamp, 43 W, 370 nm) and obtained the corresponding allylated product in moderate to good yield. The W/Cu-

catalyzed C–H allylation displays broad substrate scope, accommodating a variety of allylic chlorides and alkanes. Both electron-rich and electron-deficient aryl-substituted allyl chlorides, as well as aliphatic variants like trimethyl silyl methyl and 3-butenyl derivatives, reacted selectively with cyclic alkanes. Functionalized allyl chlorides bearing halogen substituents were also compatible, enabling potential for further derivatization. A range of alkanes including cycloalkanes and linear alkanes participated effectively, with site-selectivity favouring methylene over methyl C–H bonds, and methine over methylene in branched systems. Electron-rich C–H bonds, such as the *β*-position of cyclopentanone, were selectively activated. The method extends to heterocycles, with cyclic ethers and thioethers undergoing *α*-oxy allylation with high regioselectivity. Notably, *N*-Boc morpholine favoured*α*-oxy over *α*-amino C–H activation, while *N*-Boc pyrrolidine and other stabilized radical donors were unreactive under the optimized conditions. The mechanism begins with photoexcitation of the decatung state anion (**A)** to its triplet excited state (**B),** which abstracts a H-atom from alkane to generate an alkyl radical (**D)** and the reduced decatung state species (**C**). The alkyl radical then adds to a copper(I)-allyl complex (**F)** *via* an SH2′ pathway, forming the allylated product and a Cu (II) species (**G).** Finally, a single-electron transfer from the reduced decatung state to the Cu (II) complex regenerates both the copper (I) catalyst and the ground-state decatung state, completing the catalytic cycles (**Scheme 35**). This dual catalytic approach enables efficient and rapid C–H allylation of diverse chemical feedstocks and complex natural products within mild conditions. The integration of light-induced decatung state-mediated H-atom transfer with copper catalysis ensures selective coupling while minimizing product degradation. As a result, the method provides streamlined access to synthetically valuable allylated compounds directly from simple or structurally complex substrates.



(Scheme 35) The direct C−H allylation of inert alkanes using a cooperative tungsten/copper photocatalytic system

In 2024, Sundararaju and co-workers [71] developed Manganese-catalyzed method for Z-Selective allylation of indoles using allenyl derivatives under mild conditions. Utilizing10 mol% $MnBr(CO)_5$ and 50 mol% NaOAc in 1,4-dioxane at room temperature for 36 hours and obtained the corresponding allylated product in good to excellent yield. After optimizing the reaction conditions, various *N*-pyrimidin-2-yl indoles were explored. The standard protocol was effective across a broad range of substrates, including those with electron-donating or electron-withdrawing groups. Substituents at different positions on the indole ring, such as methyl, methoxy, cyano, nitro, and aldehyde, were generally well-tolerated. Some substrates required mild heating due to solubility issues. The method also worked with extended systems like styrenyl, naphthyl, and tryptophan-based indoles. While pyrrole analogues showed limited reactivity, certain functionalized variants gave improved results. The scope was further expanded to allenes bearing aromatic and bulky substituents. Substitution at the α-position of the allene had a notable effect on stereoselectivity, with increased steric bulk favouring Z-selectivity. Tertiary allenyl alcohols proved to be particularly effective, yielding the allylated products with high selectivity under mild conditions. The reaction begins with ligand exchange between $MnBr(CO)_5$ and NaOAc, forming a manganese acetate species that coordinates with the indole substrate to give intermediate (**A**). C–H activation occurs *via* a CMD pathway, generating a mangana cycle (**B**), which then undergoes selective allene coordination and migratory insertion. The resulting seven-membered mangana cycle (**C**) undergoes proto de metalation to afford the Z-selective allylated product and regenerates the catalyst for the next cycle. This study demonstrates a mild and efficient method for C (2)-selective Z-allylation of indoles using allenes as π-coupling partners. The protocol shows broad substrate scope and excellent Z-selectivity, which can be fine-tuned through steric effects at the α-position of the allene.

In 2022, Kapur and collaborators [72] introduced a method that enabled vinylogous reactivity in vinyl diazo esters for C–H allylation of benzamides by integrating cobalt and photo redox catalysis They reacted vinyl diazo esters with benzamides in the presence of 20 mol% $Co(acac)_2$, 20 mol% Na_2[Eosin Y] and 1 equiv. $NaOPiv.H_2O$ in TFE under an oxygen atmosphere (O2 balloon) at room temperature for 48 to 72 hours isolated the corresponding allylated product in good yield. The substrate scope demonstrated broad functional group tolerance for various substituted benzoic acid derivatives. Both electron-donating and electron-withdrawing groups, including methoxy, halogens, cyano, nitro, and methyl groups, were compatible regardless of their position on the aromatic ring. Substrates bearing aryl or acetoxy groups also participated effectively in the reaction. Aliphatic carboxylic acids, including linear chains and those with remote carbonyl groups, were well tolerated. Naphthoic acid and tetra hydro naphthyl derivatives also underwent allylation smoothly. Additionally, a diverse set of vinyl diazo esters, including those with long aliphatic chains, reacted successfully, although steric hindrance in certain substituted vinyl diazo esters hindered product formation. The mechanism initiates with Co(II) undergoing ligand exchange with benzamide to form intermediate (**A**), which is oxidized by oxygen to the active Co(III) species (**B**). This species undergoes C–H activation *via* a CMD pathway to generate a cobalt cycle (**C**), which then coordinates with the diazo compound to form carbene intermediate (**D**), in equilibrium with vinylogous intermediate (**E**). Intermediate (**E**) undergoes 1,3-allylic carbene insertion to give (**F**), which through SET, protonation, and ligand exchange affords the final product and Co(I) species **G**, later reoxidized to Co (II) by Na_2 [Eosin Y] * and oxygen under green light, completing the catalytic cycle. This transformation represents a rare example of a cascade involving vinylogous reactivity of vinyl diazo compounds through C–H activation and allyl carbene migratory insertion. Its mild reaction conditions, broad functional group tolerance, and compatibility with bioactive molecules make it valuable for late-stage functionalization. The approach holds promise for further development in complex molecule synthesis.

In 2024, Soulé and his team [73] 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% IrF, 2 equiv. $NiCl_2$(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 allylamines 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 stereoselectivity.

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 $C(sp^2)$–H and $C(sp^3)$–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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