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Olefins from alcohols *via* catalytic acceptorless dehydrogenation coupling reactions

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Olefins serve as essential building blocks for creating a wide range of molecular structures, including pharmaceuticals, polymers, and various natural products. In recent years, homogeneous transition-metal catalysis has emerged as a highly efficient method for synthesizing carbon–carbon double bonds in a cascade manner. Among the various approaches to introducing unsaturation, the catalytic acceptorless dehydrogenation coupling (ADC) reactions stand out due to their atom economy and eco-benign characteristics. By dehydrogenating alcohol, ADC produces aldehydes or ketones, which then undergo a condensation reaction with another molecule to yield an unsaturated product. The only byproducts of this process are H_2 and H_2O, which make the ADC reaction superior to the traditional way of producing chemicals. Surprisingly, despite the significance of olefins, there is currently no dedicated review article that specifically addresses catalytic routes to olefins from alcohols (A2O) *via* the ADC method. This review article aims to highlight the latest advancements in olefination reactions involving various substrates, including carbonyl compounds, phosphorus ylides and substrates with acidic α-hydrogens (such as sulfones, alkyl-substituted N-heteroarenes, and nitriles). Various aspects of metal–ligand cooperation (MLC) and their application are also discussed in brief detail. MLC involving bi-functional catalysts, where the metal center and the ligand jointly participate in the reaction, has shown great potential in ADC reactions. By exploring these catalytic pathways, we hope to inspire researchers to develop novel methods for olefin synthesis using abundant feedstocks.

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1. Introduction

Olefins are versatile building blocks that are essential for the construction of molecular frameworks such as drugs, polymer compounds, and natural products. They are also widely used for sensitization, electroluminescence, and organic dyes.[1] Many styrene derivatives exhibit critical biological activities, including resistance to cardiovascular and cancerous diseases.[2] Historically, alkyl halide dehydrohalogenation and alcohol dehydration were the primary methods for producing alkenes.[3] In 1953, Wittig pioneered a reliable method to form C=C bonds that became a classic in organic chemistry to form C=C bonds by treating carbonyl compounds with phosphorus ylides to give the corresponding alkenes and phosphorus oxide (Fig. 1).[4] The Wittig olefination reaction has since undergone stereoselective modifications, such as the *E*-selective Horner–Wadsworth–Emmons (HWE) olefination and the *Z*-selective Still–Gennari olefination. Peterson introduced a seminal methodology for olefination, employing alpha-silyl carbanions in conjunction with ketones.[5] In 1973, Julia introduced a novel approach to olefin synthesis utilizing sulfones.[6] The Tebbe olefination reaction,[7] a major breakthrough for the efficient synthesis of olefinic compounds, followed these advancements. Ir, Ru, Os, and Rh-based metal catalysts can also dehydrogenate abundant alkanes to produce alkenes with high efficiency.[8] Furthermore, various methods for alkene functionalization have emerged, such as olefin metathesis reactions,[9] which enable the synthesis of diverse and complex olefins from simple alkenes. A legacy of the era of cross-coupling is the Heck reaction,[10] which inserts substituted olefins into a molecular framework in the presence of a base and a Pd-catalyst.

Traditional synthesis of alkenes requires highly nucleophilic and reactive aldehydes, super stoichiometric amounts of strong bases, heavy transition metal catalysts, and phosphine ligands, which often face selectivity and functional group compatibility issues. In recent times, there has been an increasing demand for synthesizing effective

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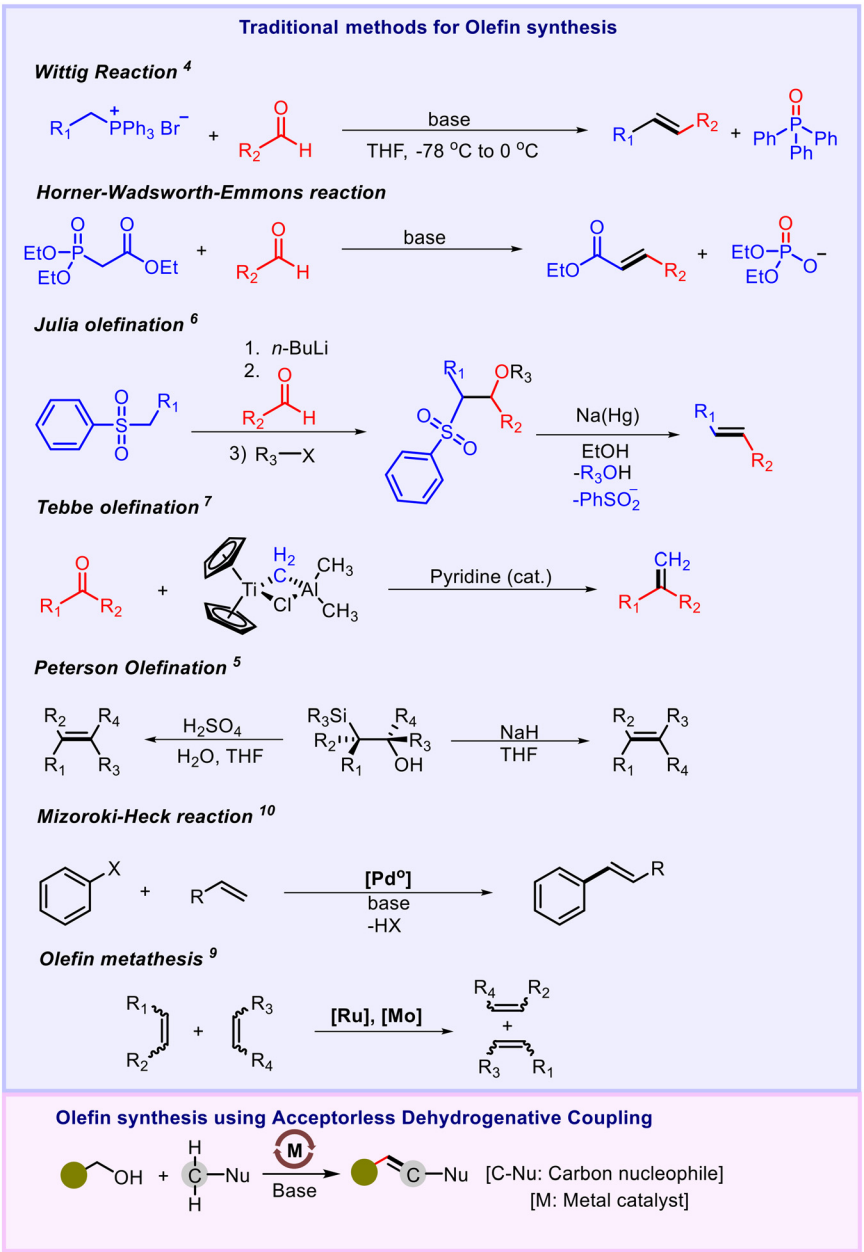


Fig. 1 Various approaches to access olefin.

and environmentally friendly processes for diverse chemicals (Fig. 1). Transition metal catalysis has been shown to be a potent tool for accomplishing this goal by facilitating the production of eco-friendly synthetic methods. Thus, there is considerable interest in searching for biomass outside the food chain and non-petroleum waste materials as carbon sources to establish cost-effective and environment-friendly synthetic methods.[11] Lignocellulose is a readily available plant biomass, generally out of food chain competition, and can be processed into alcohol.[12,13] In modern chemistry, alcohol has emerged as a crucial electrophile for the synthesis of coupling compounds *via* the hydrogen auto-transfer approach and the ADC (acceptorless dehydrogenation coupling) strategies.[14] In 2021, Maiti and co-workers reported recent progress in the transition metal-catalyzed oxidative olefination of sp^2 and sp^3 C–H bonds.[15] This review article focuses on the acceptorless dehydrogenation coupling strategy among various olefination methodologies. This strategy enables the formation of olefin compounds using alcohol as a reagent.

Dehydrogenation and related reactions of fundamental feedstocks[16] is a valuable approach employed in organic synthesis to activate unreactive molecules (Fig. 2). In particular, ADC of alcohols involves the use of a metal catalyst to dehydrogenate alcohols, resulting in the formation of highly reactive aldehydes or ketones along with a metal hydride complex. The resulting active carbonyl intermediates can further participate in coupling reactions with other

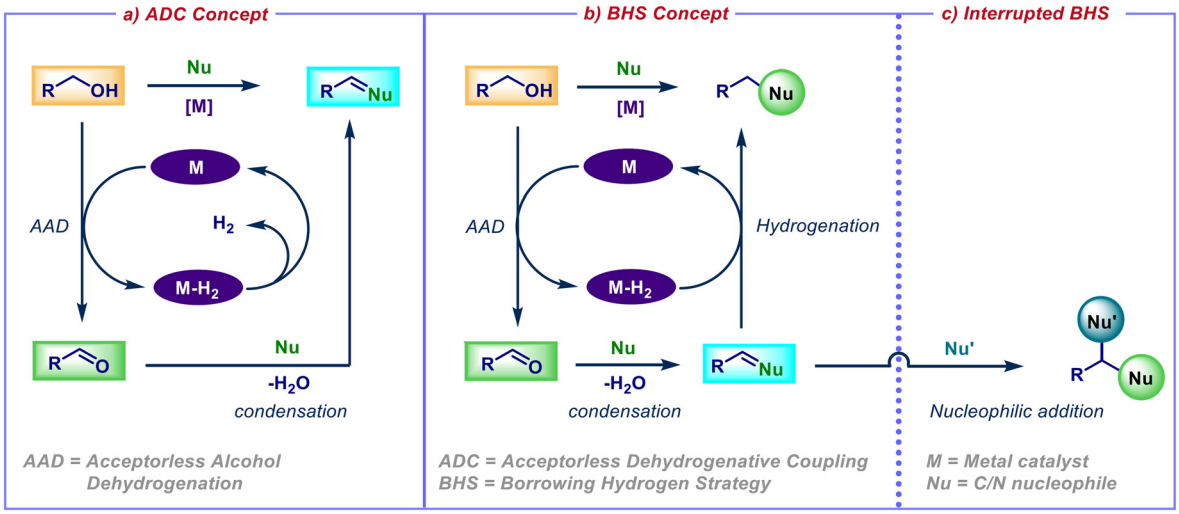


Fig. 2 Three main approaches to AAD reactions: (a) acceptorless dehydrogenative coupling (ADC), (b) borrowing hydrogenation strategy (BHS), and (c) interrupted borrowing hydrogen strategy.

molecules, leading to the formation of complex compounds featuring unsaturated bonds. The metal hydride species releases hydrogen when it reacts with another molecule, regenerating the active catalyst and enabling continuous catalytic cycles. Recently, the ADC strategy has garnered significant attention from numerous research groups, particularly in the synthesis of olefin compounds with the generation of water as a by-product. Furthermore, the absence of external hydrogen acceptors simplifies the reaction conditions and reduces reagent costs. The ADC strategy has emerged as a versatile strategy for alkene synthesis, employing various noble transition metal catalysts such as Ru, Ir, Rh, Ru-nanoparticles, Pd heterogeneous catalysts, and base metals such as Ni, Mn, and Co. The electronic and steric properties of the coordinating ligands profoundly influence the reactivity and properties of these transition metal complexes. The concept of metal–ligand cooperation (MLC) involving bi-functional catalysts, where the metal center and the ligand jointly participate in the reaction, has shown great potential in ADC reactions.

2. General reaction mechanism of olefination using alcohol *via* ADC pathway

The acceptorless dehydrogenative coupling of a nucleophile using alcohol as a precursor enables the olefination reaction, as illustrated in Fig. 2 and 3. This process involves the transfer of hydrogen from alcohol **A** to a metal catalyst, forming the corresponding carbonyl compound **B** and a metal hydride intermediate species **C**. Subsequently, the acidic hydrogen-bearing compound **D** loses its acidic hydrogen, transforming into a nucleophile. The nucleophile then engages in a condensation reaction with the aldehyde, leading to the formation of the olefin compound **E**. The metal hydride species can be protonated to release hydrogen gas or accepted by an oxidant to complete the catalytic cycle.

3. Wittig type olefination using alcohol

One of the most common and widely used C=C bond-forming transformations in organic synthesis is the Wittig olefination reaction (Scheme 1a).[17] Over the years, there has been considerable interest in the development of efficient and easy-to-operate alternative strategies, as Wittig transformation requires carbonyls for the ylides to react, and carbonyls show less reactivity and selectivity.[18] Using alcohols instead of carbonyls, Williams and co-workers reported an indirect Wittig-type olefination reaction that yielded alkane as the final product. The iridium or ruthenium catalyst followed an elegant borrowing hydrogen pathway, but the reduction of alkene could not be controlled in the final step.[19]

Milstein and co-workers developed a Ru-catalyzed Wittig-type reaction of an alcohol with a ylide that produces an olefin and hydrogen gas without using any oxidant

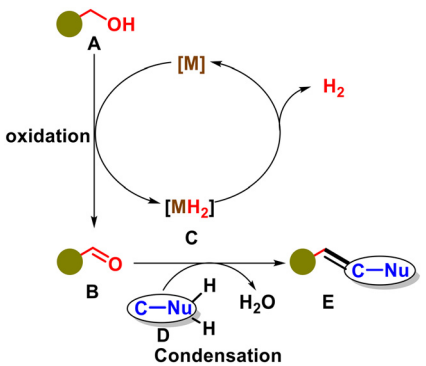
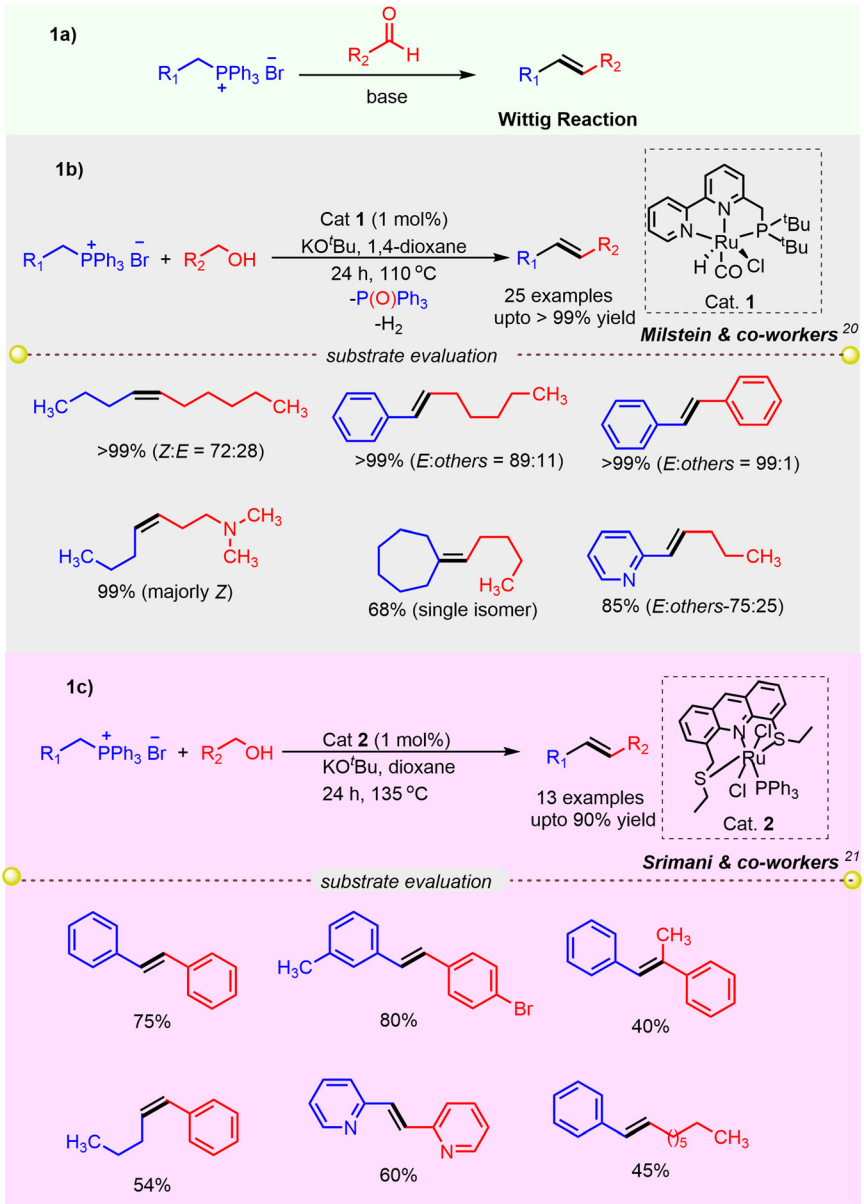
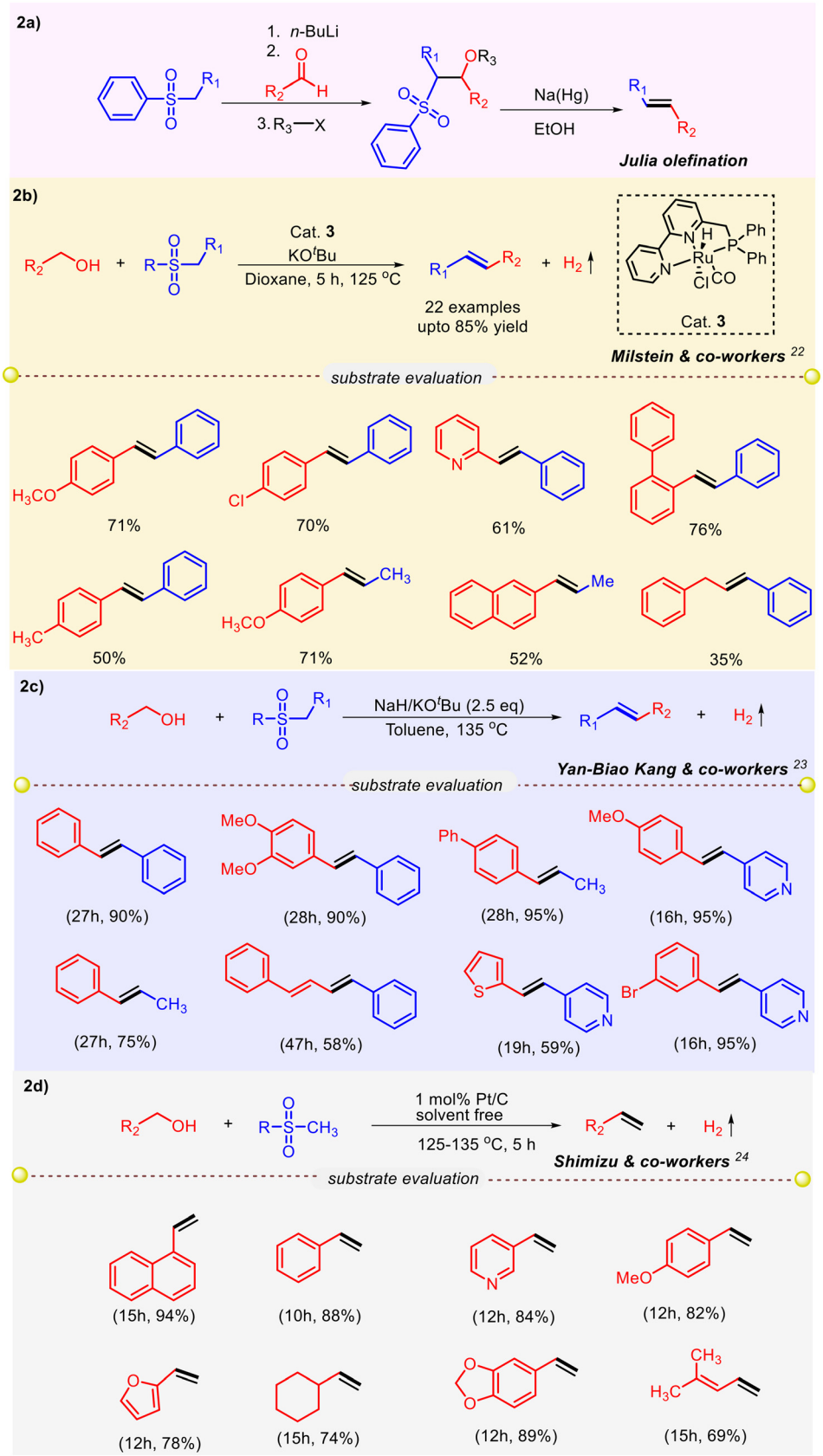


Fig. 3 General procedure for olefination *via* acceptorless dehydrogenation coupling.



Scheme 1 Wittig-type olefination reactions: (1a) classical Wittig reaction. (1b and c) Wittig-type olefination reactions using alcohol by (1b) the research group of Milstein, and (1c) Srimani and co-workers.

(Scheme 1b).[20] After several optimization studies, it was observed that *n*-hexanol as a limiting reagent with an excess of Wittig salt *n*-butyl-triphenylphosphonium bromide (1.1 eq.) in the presence of 1.2 eq. of base and 1 mol% ruthenium catalyst (Cat. **1**) provided the final olefin product with 85% yield. NMR studies revealed that the *Z*-isomer of the olefin product formed as a major diastereomer with a 72 : 28 ratio over the *E*-isomer. The reaction was compatible with various functional groups, such as aliphatic alcohols, heterocycles, amines, halides, and aromatic rings with different electronic properties. The study revealed that the formation of olefin in the benzylic position exhibited a predominant *E* selectivity, whereas the formation of olefin in the unstabilized position exhibited a *Z* selectivity. The reaction mechanism involved the dehydrogenation of alcohol by the catalyst to form aldehyde and H_2, followed by a Wittig-type olefination with the non-stabilized ylide. Using a Ru-pincer complex (Cat. **2**) with an acridine-based SNS ligand, Srimani and co-workers achieved a Wittig-type olefination of alcohols with phosphonium salts under oxidant-free conditions (Scheme 1c).[21] They used alcohol as a limiting reagent, KO^{t}Bu as a base, and various aromatic and aliphatic phosphonium salts as coupling reagents. A diverse range of benzyl alcohols exhibiting different electronic properties, heteroaryl alcohols, aliphatic alcohols, as well as both aromatic and aliphatic phosphonium salts, have been successfully employed in the reaction resulting in the formation of the desired product with moderate to good yields. The olefin products showed a preference for the *E* isomer over the *Z* isomer in most cases, with moderate to good yields. The reaction mechanism involved the dehydrogenation of alcohol by



Scheme 2 Olefination reactions using sulfones: (2a) classical Julia olefination, (2b) Julia-type olefination reaction using alcohol by (2b) the research group of Milstein, (2c) the research group of Yan-Biao Kang, and (2d) by Shimizu and co-workers.

the catalyst to form aldehyde and H_2, followed by a Wittig-type olefination with the phosphonium salt.

4. Direct olefination of alcohol with sulfones *via* ADC

In 1973, Marc Julia reported the multistep classical olefination *via* the formation of β-acyloxy alkyl sulfones from aldehydes and phenyl sulfones followed by the reductive elimination with sodium amalgam to furnish the olefin (Scheme 2a).[6a] In 2014, the research group of Milstein reported the single-step Julia-type olefination of alcohols using sulfones, catalyzed by the PNN-based ruthenium pincer complex (Cat. **3**) *via* the ADC strategy (Scheme 2b).[22] Following a series of optimization studies, it was determined that the reaction of dimethyl sulfones (1.06 mmol) with alcohol (1 mmol) in the presence of catalyst **3** (0.025 mmol) and KO^{t}Bu (1.1 eq.) base in refluxing dioxane for 5 hours at 125 °C resulted in the formation of desired product styrenes in good to excellent yields, accompanied by the release of hydrogen gas. A number of electron-donating and electron-withdrawing alcohols underwent this catalytic protocol successfully. The formation of *E*-stilbenes was observed when benzyl phenyl sulfones were utilized as alkenylating reagents in combination with various benzyl alcohols. The findings of mechanistic experiments indicate that the reactions proceed through a complex pathway that differs significantly from the conventional Julia-type olefination. The investigation of a potential reaction intermediate has suggested that the reaction may proceed *via* metal–ligand cooperation. However, a definitive depiction of the mechanistic pathway could not be ascertained. Dehydroxy-methylation of alcohol reagents was observed when the reaction was conducted under mild H_2 pressure in the presence of dimethylsulfone.

In 2015, Yan-Biao Kang and co-workers successfully implemented a novel method for base-mediated *E*-specific direct Julia olefination,[23] utilizing aryl alcohols without the aid of any transition metal catalyst (Scheme 2c). The efficacy of several bases, including NaO^{t}Bu, KO^{t}Bu, NaH, KOH, *n*-BuLi, and LiHMDS, was evaluated, and it was found that NaH exhibited the most favorable conversion with excellent yield. A range of styrenes was synthesized using this base-promoted protocol in good to excellent yield by using different alcohols in conjunction with phenyl methyl sulfone. Notably, the utilization of alkyl phenyl sulfones as alkenylating reagents in combination with various aromatic alcohols resulted in the formation of diverse internal alkenes exhibiting *E*-stereoselectivity. Remarkably, many functional groups, including methoxy, halides, heterocycles, and amines, remained intact throughout the reaction and yielded the final product.

The proposed plausible mechanism of base-mediated olefination reaction is discussed below (Fig. 4). In the presence of a base, alcohol (**A-1**) generates a trace amount of aldehyde (**A-2**) by thermal dehydrogenation. On the other hand, the base abstracts a proton from **B-1** and forms sulfone

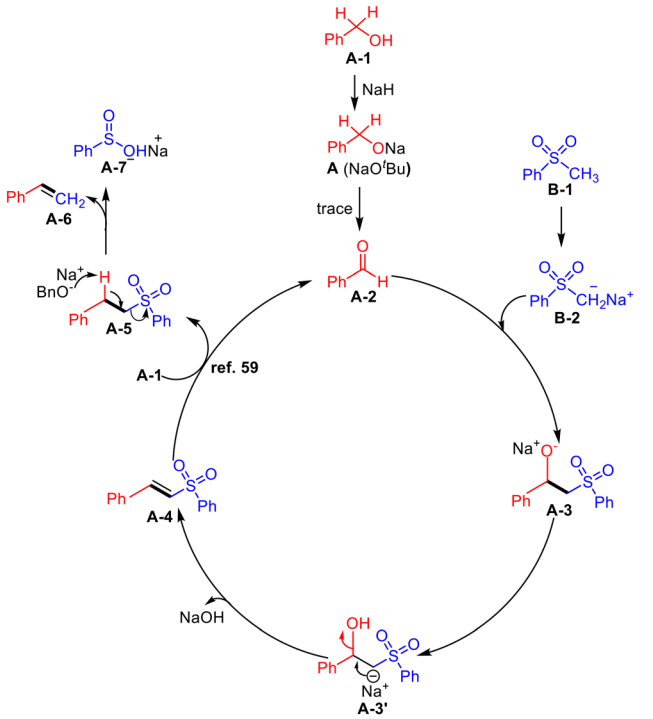


Fig. 4 Mechanistic cycle for base-mediated olefination using sulfone.

salt **B-2**, which subsequently reacts with aldehyde and forms **A-3**. Then, **A-3** isomerizes to **A-3′**, followed by the elimination of NaOH to lead to the intermediate **A-4**. Later, another molecule of alcohol reacts with intermediate **A-4**, and a hydride transfer from alcohol to intermediate **A-4** results aldehyde **A-2** and alkyl phenyl sulfone intermediate **A-5**. Aldehyde **A-2** triggers a fresh catalytic cycle initiation, while intermediate **A-5** undergoes an elimination step mediated by a base to produce the ultimate product olefin.

Using heterogeneous Pt nanoparticles on carbon (Pt/C), Shimizu *et al.* achieved the direct olefination of various primary and secondary alcohols with sulfones through heterogeneous catalysis (Scheme 2d).[24] The authors examined various carbon-supported Pt-catalysts that were pre-reduced with H_2 at 300 °C. Benzyl alcohol (1.5 mmol) and dimethyl sulfone (1 mmol) were chosen as model substrates. The Pt/C catalyst effectively converted dimethyl sulfone to styrene with 88% yield. Noteworthy that the reaction of benzyl alcohol and dimethyl sulfone with 0.02 mol% of Pt/C catalyst (TON = 3950) increased the efficiency by 150 times compared to the other previously reported catalyst for the olefination of benzyl alcohol with dimethyl sulfone.

The development of new methods for olefination reactions using base metal catalysts is a challenging area of research. Balaraman and co-workers reported a Ni-metal-catalyzed direct olefination of primary alcohols with sulfones, which afforded various terminal and internal olefins with the liberation of hydrogen gas.[25] It was observed that a Ni(II) NNN-type complex (Cat. **4**) effectively catalyzed the direct Julia-type olefination of alcohols to *E*-stilbenes in excellent yield in the presence of base KO^{t}Bu at 110 °C (Fig. 5,

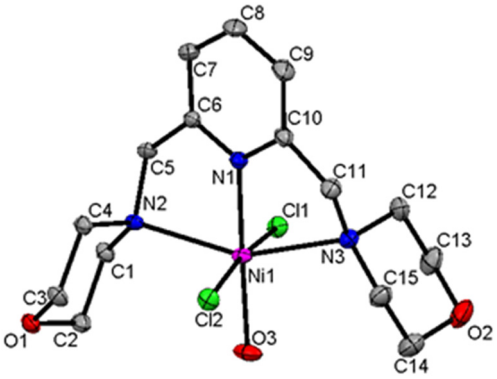


Fig. 5 Single crystal X-ray structure of catalyst **4**.

Scheme 3). A range of benzylic alcohols with diverse functional groups, such as electron-donating, electron-withdrawing, ether, aryl, alkyl, and halides (fluoro, chloro, and bromo), was successfully employed in the olefination reaction with sulfones. The reaction proceeded smoothly and delivered the desired olefins in high yields. The application of this strategy was extended to the stereo-selective synthesis of biologically relevant molecules, such as DMU-212 (used for breast cancer treatment) and resveratrol.

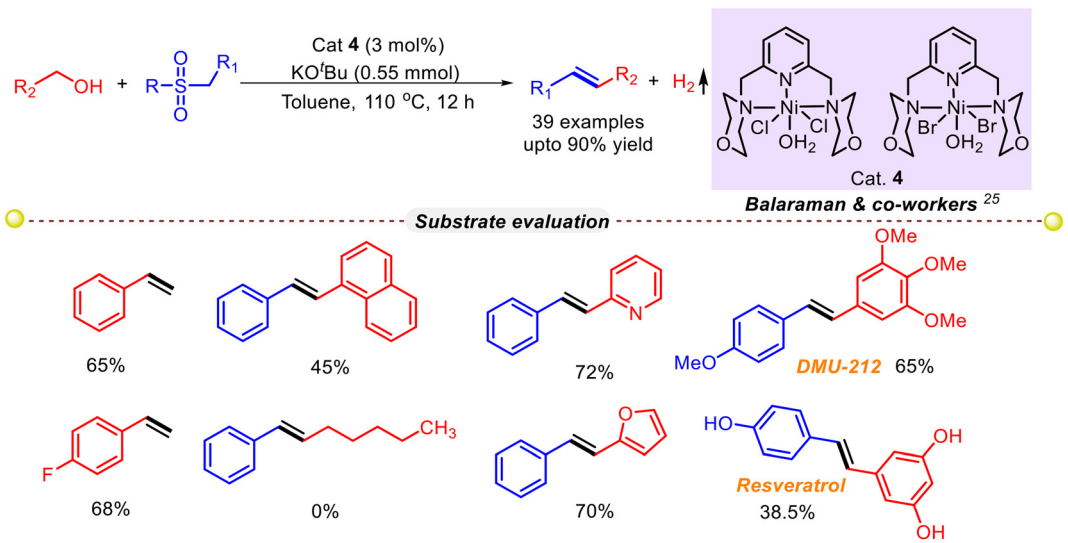
A possible mechanism for the olefination of alcohols using an NNN–Ni catalyst is shown in Scheme 4. The precatalyst reacts with a base to generate complex **C-1**, which undergoes β-hydride elimination to produce the corresponding aldehyde and Ni–H species **C-2**. The aldehyde then participates in a Julia-type olefination with sulfone to afford the desired alkene product, while the Ni–H species **C-2** is converted to intermediate **C-4** by metal–ligand cooperation (MLC) mediated dehydrogenation of intermediate **C-3**, thus completing the catalytic cycle.

Using commercially available $FeCl_2$ and 1,10-phenanthroline as a catalytic system, KO^{t}Bu as base, and toluene as solvent at 120 °C, both primary and secondary alcohols underwent direct Julia-type olefination with dimethyl sulfone to afford various olefin products in good to excellent yields (Scheme 5a).[26] This reaction was compatible with different electron-donating and withdrawing groups on the benzyl or heteroaryl alcohols. A remarkable case was the conversion of 1,2,3,4-tetrahydronaphthalene-1-ol to 1-methylnapthalene as the only product. This protocol was also applicable to other functional groups containing 1,2,3,4-tetrahydronaphthalene-1-ol, such as cyclic ether, aliphatic, and substituted benzylic groups. Control experiments and labelling studies suggested the reaction proceeded *via* the ADC of 1,2,3,4-tetrahydronaphthalene-1-ol followed by the formation of terminal alkene by Julia-type olefination using dimethylsulfone. In the presence of Fe-catalyst, the terminal alkene isomerized to an internal alkene, and subsequent dehydrogenations lead to the formation of an aromatic final product. The rate-determining step was found to be the C–H bond cleavage of the alcohol, with a K_H/K_D value of 2.53.

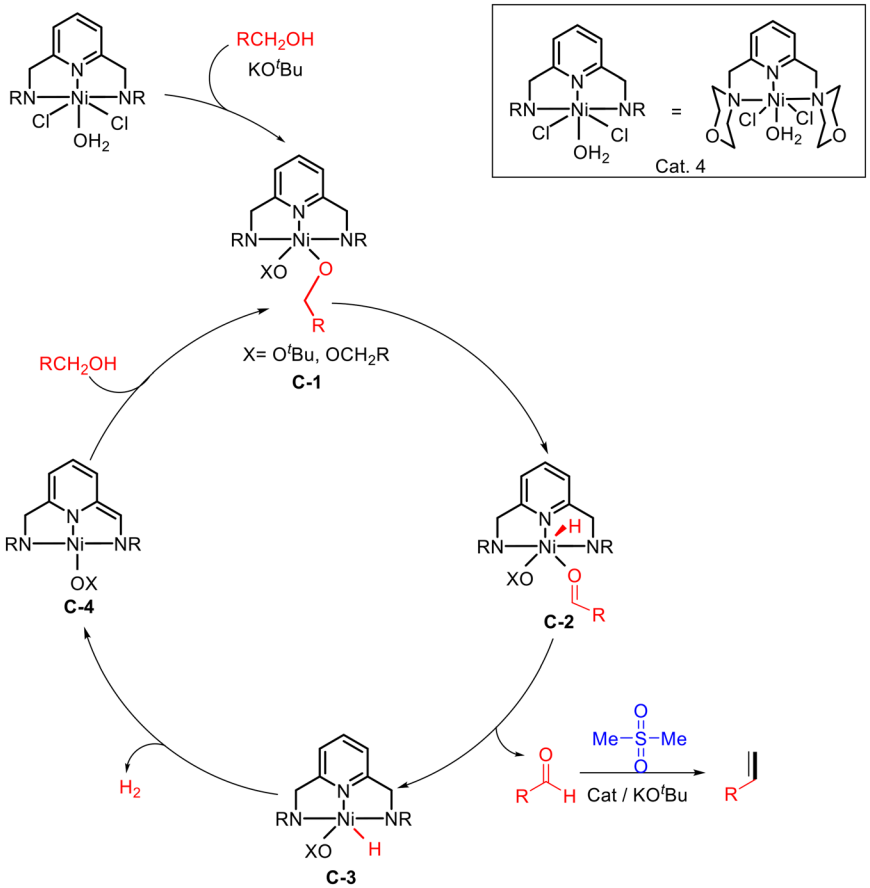
Of late, Maji and co-workers also reported a similar type of olefination reactions using alcohol and sulfones with Ni catalyst ($NiBr_2$) and bidentate nitrogen ligands (1,10-phenanthroline and neocuproine), which showed a good to excellent formation of stilbene derivatives with a predominant *E*-selectivity (Scheme 5b).[27] Performed mechanistic studies indicated the reaction follows an ADC-type pathway.

5. Olefination of alkyl substituted *N*-heteroarenes with alcohols

Aryl-substituted olefins bearing *N*-heteroarenes are important scaffolds in various biologically active drug molecules and agrochemicals.[28] *E*-selective conjugated *N*-heteroarenes are used in the synthesis of conducting polymers and have wide applications in material sciences as emissive layers in organic



Scheme 3 The Ni–NNN catalyzed Julia-type olefination of alcohols using sulfones.



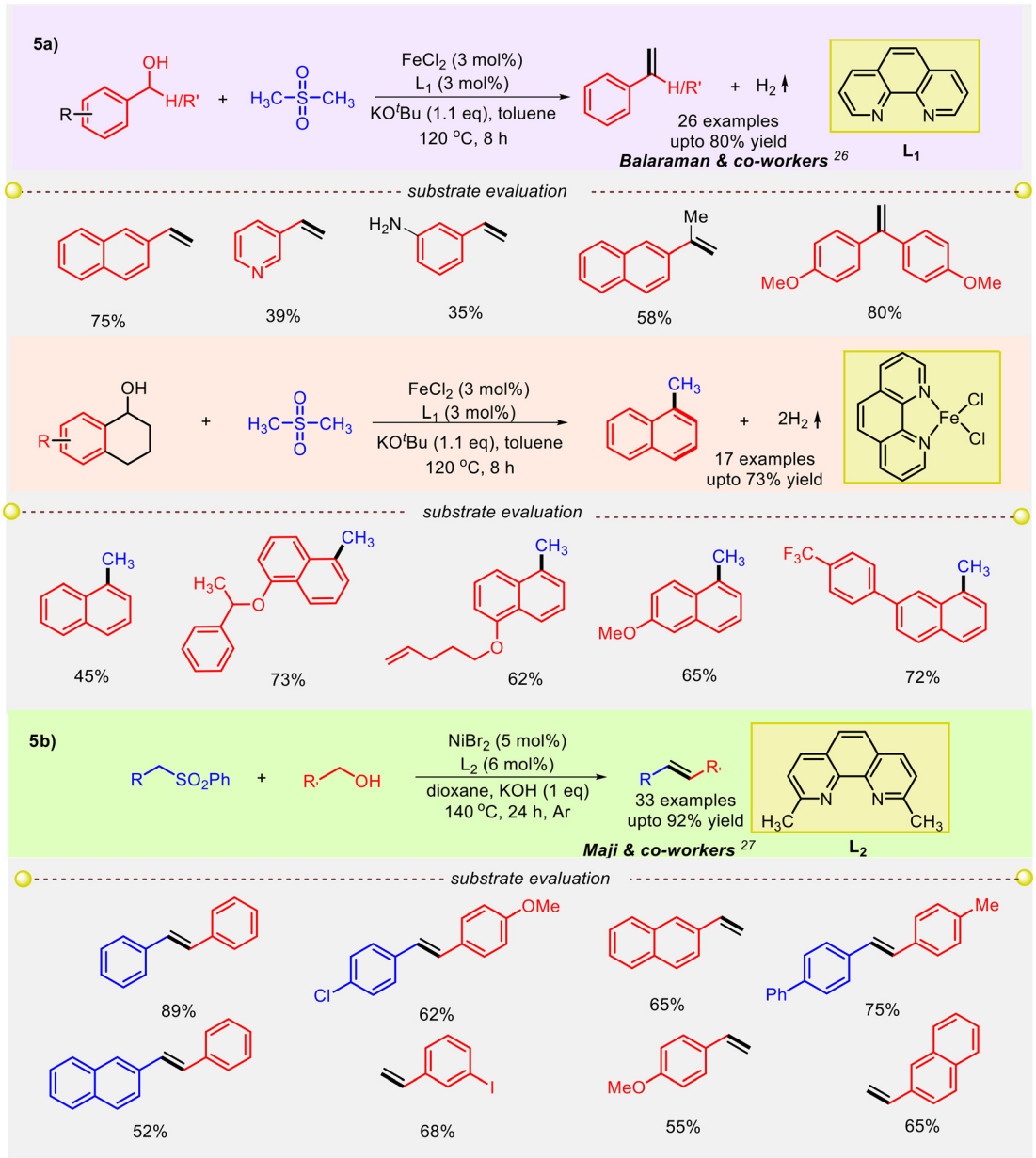
Scheme 4 A plausible mechanism for Ni–NNN catalyzed olefination using sulfones.

light-emitting diodes.[29] An Mn-catalyzed protocol for the α-olefination of alkyl-substituted *N*-heteroarenes with alcohols *via* dehydrogenation coupling was recently reported by Kempe and co-workers (Scheme 6).[30] Using an Mn complex (Cat. **5**) stabilized by a triazine-based ligand (PN_5P type ligand) with a *para*-methyl substituent as a catalyst and KOH as a base at 135 °C, the authors successfully synthesized (*E*)-2-styrylquinoline from 2-methyl quinoline and benzyl alcohol. In this case, the olefin/alkane selectivity was greater than 20 : 1, with alkane as a minor side product. The NMR analysis confirmed that the final alkene product was obtained with *E*-stereoselectivity. The reaction was compatible with various alkyl-substituted *N*-heteroarenes and alcohols bearing different functional groups, such as thiophene, methoxy, bromide, chloride, and iodide. The protocol also enabled the synthesis of an imaging agent (STB-8) for the detection of Alzheimer's disease β-amyloid plaques.

According to previous literature reports and mechanistic studies, the base-mediated dehalogenation of the Mn-precatalyst (Scheme 7) leads to the dearomatization of the triazine ring and the formation of the active catalyst **D-1**. The active catalyst **D-1** then reacts with alcohol *via* MLC-mediated O–H activation to yield the Mn–alkoxy complex **D-2**, which undergoes β-hydride elimination to produce aldehyde and the manganese–hydride complex **D-3**. The aldehyde then participates in a base-mediated aldol condensation-type reaction to afford the desired olefin product, while the complex **D-3** releases hydrogen gas and regenerates the active catalyst **D-1**.

Maji and co-workers reported the catalytic olefination of methyl-substituted *N*-heteroarenes with primary alcohols.[31] 2-Methylpyrazine and benzyl alcohol were used as model substrates to optimize the reaction condition. The reaction of these substrates with $Mn(CO)_5Br$ (5 mol%) and NNN type ligand **L-3** (5 mol%) in the presence of KO^tBu at 110 °C for 16 h afforded the olefinated product (*E*)-2-styrylpyrazine with 96% yield (Scheme 8a). The reaction was compatible with various *N*-heteroarenes and primary alcohols bearing different functional groups and steric and electronic effects. Using this catalytic protocol, the author also synthesized the *in vivo* imaging reagent STB-8 and the core structures of molnekulast and heparin blue. The mechanistic finding revealed that the reaction follows an ADC-type pathway; H_2 and water are the only two by-products of this synthetic protocol.

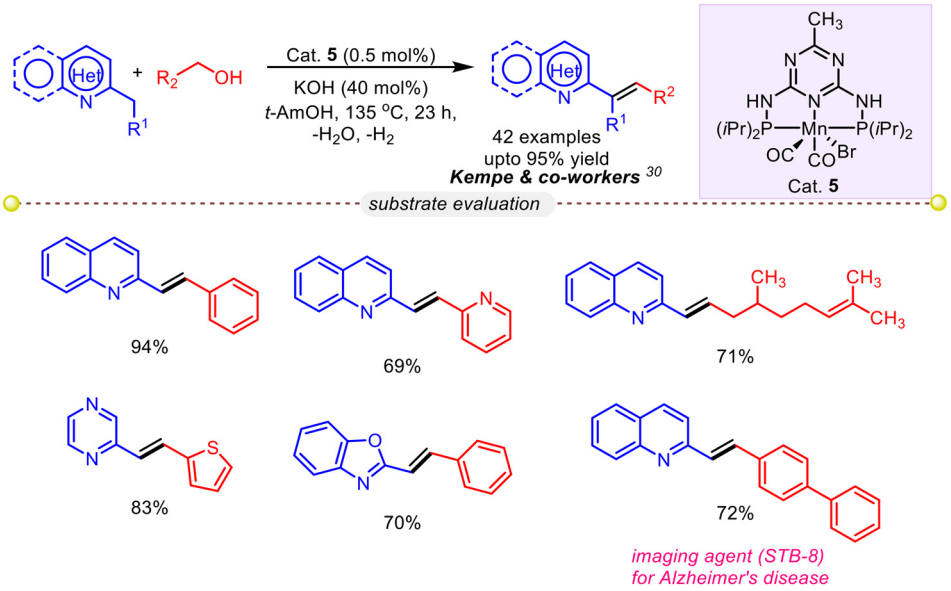
Recently, the research groups of Banerjee,[32] Baidya,[33] and Ramesh[34] independently reported alternative procedures for the α-olefination of alkyl-substituted *N*-heteroarenes with the aid of Ni catalysts. Banerjee and coworkers have used 2-methylquinoline, methylpyrazine, and other *N*-heteroarenes



Scheme 5 Ni and Fe-catalyzed olefination using sulfones. Research work conducted by (5a) Balaraman & co-workers, and (5b) Maji & co-workers.

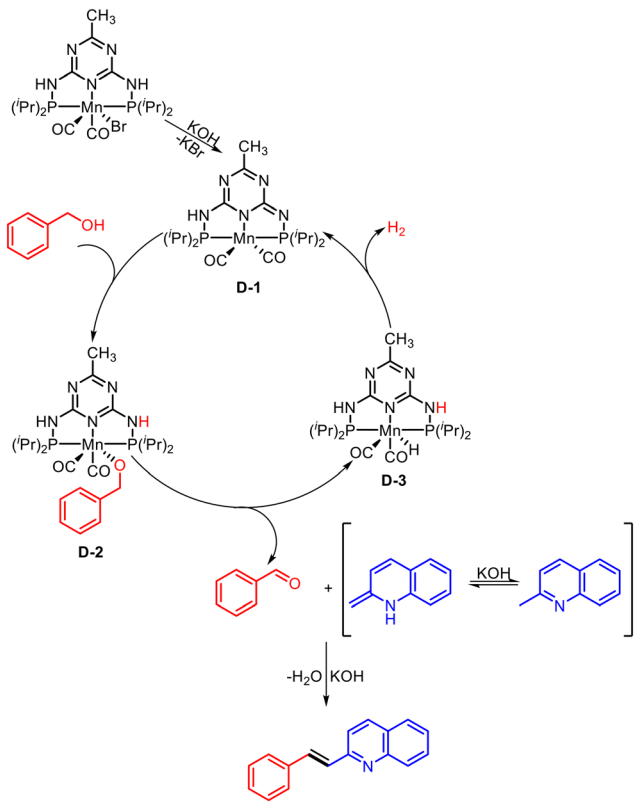
as substrates. They observed that 5 mol% of $NiBr_2$ and 6 mol% of 1,10-phenanthroline ($\mathbf{L_1}$) ligand effectively catalyzed the reaction of alcohols with 2-methyl *N*-heteroarenes to give the corresponding olefin products in good yields (Scheme 8b).[32] Several alcohol-containing natural products, such as oleyl alcohol, and citronellol, successfully delivered the corresponding olefin product upon reaction with alkyl-substituted *N*-heteroarenes in good yield. The synthetic utility of this ADC reaction was showcased in the synthesis of STB-8 and galipinine (shows antimalarial activities). The mechanistic study indicated that the reaction was proceeding through an enamine intermediate by dearomatization of 2-alkyl heteroarenes with the generation of water and dihydrogen as by-products.

Baidya and his co-workers have used Ni-catalysts in combination with different N-based amide ligands for the olefination reaction. In a typical example, 2-methylquinoline reacted with benzyl alcohol in the presence of base KO^{t}Bu and *in situ* generated catalyst from $NiBr_2$ and 8-aminoquinoline picolinic amide ligand $\mathbf{L_4}$ at 140 °C gave the final product (*E*)-2-styrylquinoline with 88% yield (Scheme 8c).[33] This protocol provided the olefinated products with excellent *E*-selectivity and good to very high yields. Mechanistic studies suggested that the catalytic protocol follows the ADC-type pathway. Recently, Ramesh and co-workers also achieved olefination of 2-methylheteroarenes with benzyl alcohols using Ni(II)–N, S chelating complex (Cat. **6**) as a catalyst which provided the product yield up to 93% (Scheme 8d).[34]



Scheme 6 An Mn–PNP catalyzed α-olefination of alkyl-substituted *N*-heteroarenes.

Gnanaprakasam and co-workers reported an acceptorless dehydrogenative α-olefination of 2-oxindole with diaryl methanols using Ru–NHC as a catalyst to synthesize a wide variety of arylidene-2-oxindole derivatives (Scheme 9).[35] This methodology was successfully applied for the synthesis of a bioactive drug *i.e.* TAS-301. The biological activities of the synthesized 3-(diphenylmethylene)indolin-2-one derivatives were investigated against the plasmodium falciparum parasite and showed significant activity with IC50 = 2.24 μM.

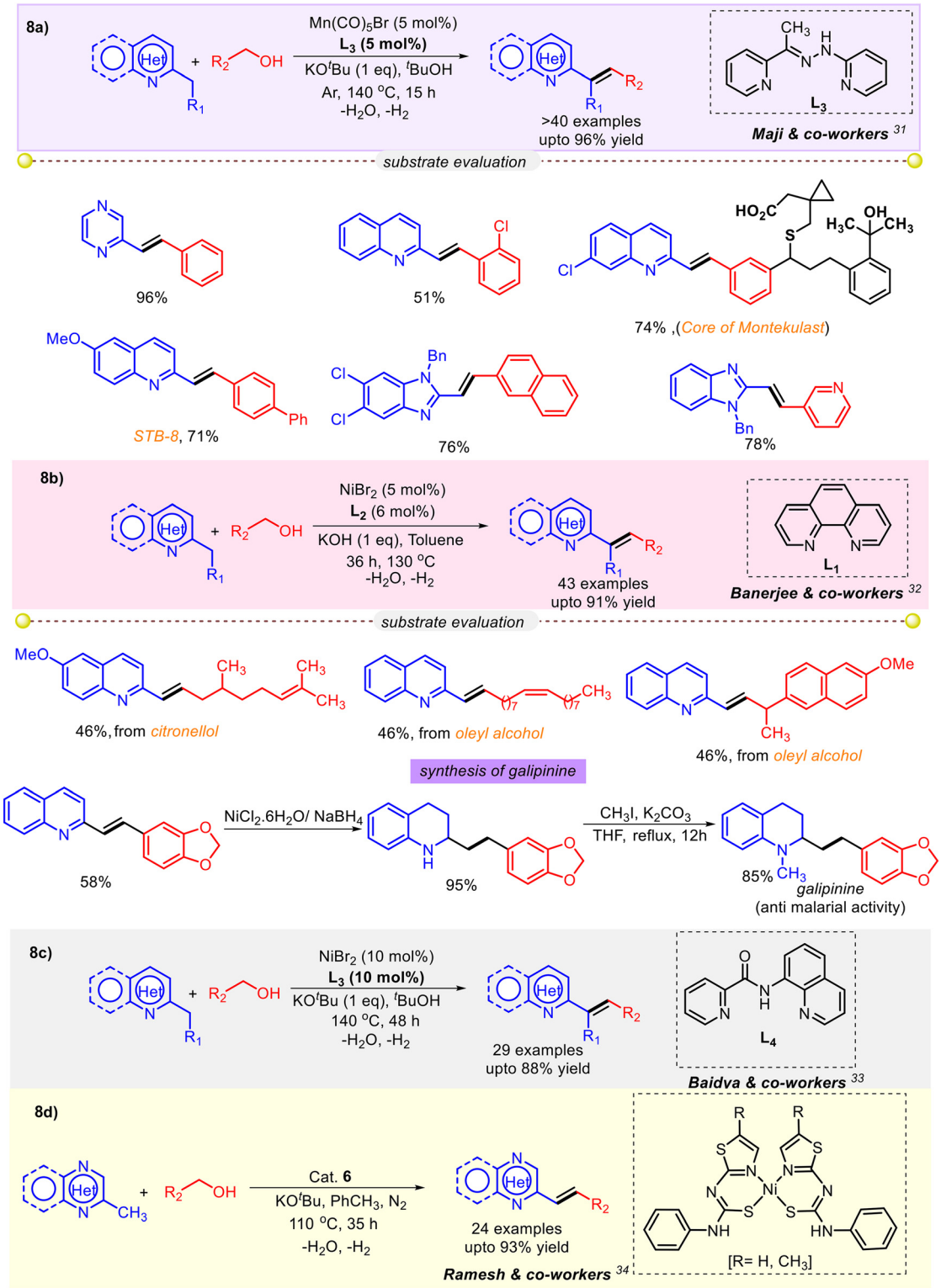


Scheme 7 Plausible catalytic cycle for Mn–PNP catalyzed α-olefination of alkyl-substituted *N*-heteroarenes.

6. Alkenation of alcohols *via* ADC with hydrazine/hydrazone

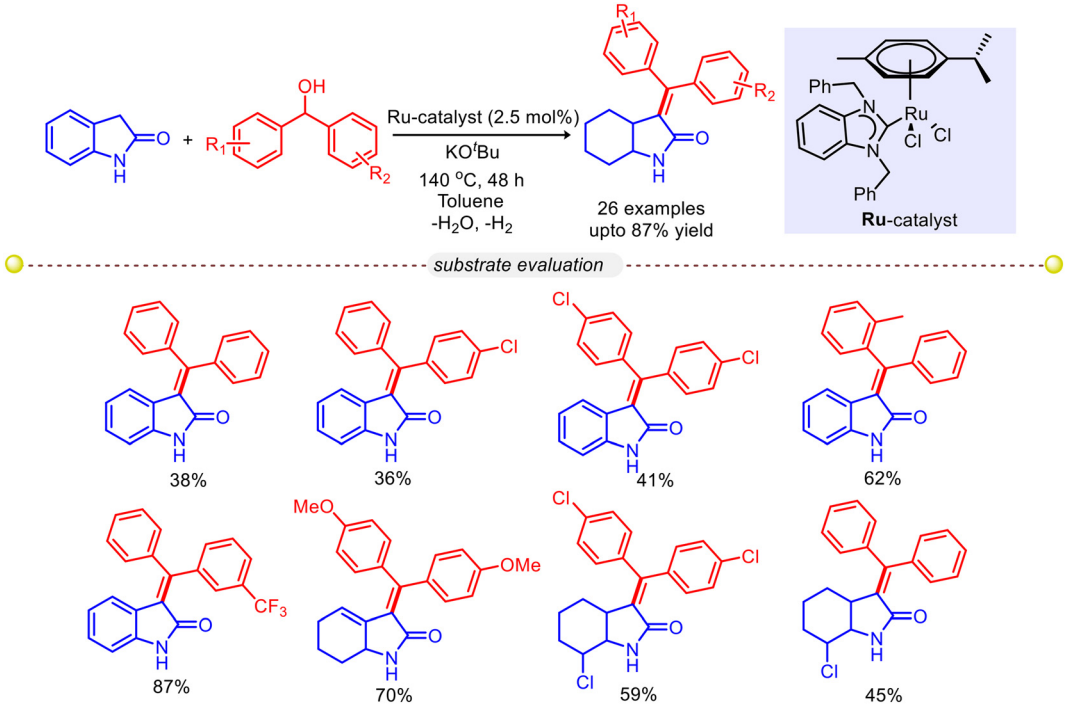
Li and co-workers successfully introduced a new strategy for deoxygenation reaction using alcohols and hydrazine by Ru or Ir catalyst.[36] The research group of Milstein reported a similar reaction using a manganese pincer complex, which produced alkenes from alcohols and hydrazine/hydrazone under base-free conditions with the formation of H_2, N_2, and water as the only byproducts.[37] In a closed Schlenk tube, benzyl alcohol and hydrazine in THF were treated with catalyst 7 (3 mol%) at 120 °C, resulting in the conversion of alcohol to stilbene (91% yield) after 24 h (Scheme 10a). A variety of benzyl alcohols bearing electron-donating and -withdrawing groups participated in the Mn-catalyzed olefination reaction and gave good to excellent yields, whereas heteroaryl alcohols and nitro-substituted alcohol failed to produce the desired product. Notably, the protocol was further extended to synthesize mixed alkenes from the coupling of alcohol and hydrazone (Scheme 10b). A broad range of aromatic and aliphatic alcohols reacted with the THF solution of benzylidenehydrazine in the presence of catalyst 7 at 120 °C, providing *E*-selective mixed alkenes in moderate to good yields.

The plausible pathway for olefination by coupling of alcohols with hydrazones in the presence of an Mn catalyst is discussed in Scheme 11. Under thermal conditions, the precatalyst **E-1** liberates hydrogen and forms complex **E-2**, which activates the O–H bond of alcohol *via* MLC and produces an alkoxy intermediate **E-3**. This intermediate undergoes β-hydride elimination and generates the corresponding

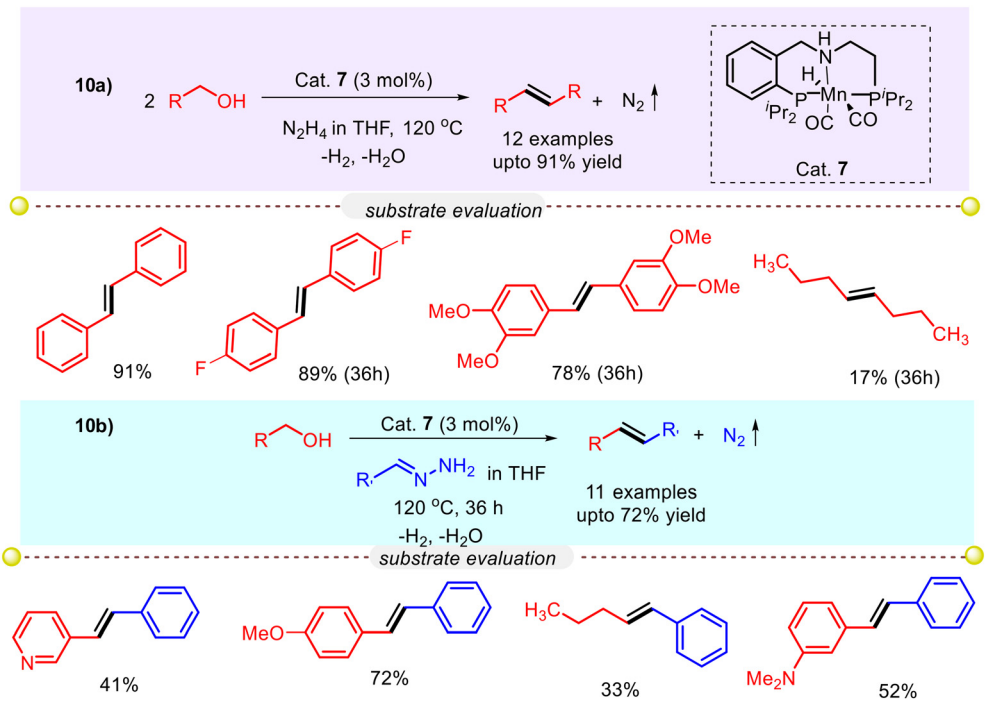


Scheme 8 Mn and Ni-catalyzed α-olefination of alkyl-substituted *N*-heteroarenes. Research work conducted by (8a) Maji & co-workers, (8b) Banerjee & co-workers, (8c) Baidva & co-workers, and (8d) Ramesh & co-workers.

aldehyde. The aldehyde, synthesized *de novo*, reacts with excess hydrazine to form a hydrazone. The hydrazone then reacts with intermediate **E-2** *via* N–H activation and forms complex **E-4**. This complex undergoes an Mn-catalyzed concerted reaction with an aldehyde and yields the final product of olefin, N_2, and Mn–hydroxo complex **E-5**. Finally, the complex **E-5** releases H_2O regenerates the intermediate complex **E-2**, and continues the catalytic cycle.



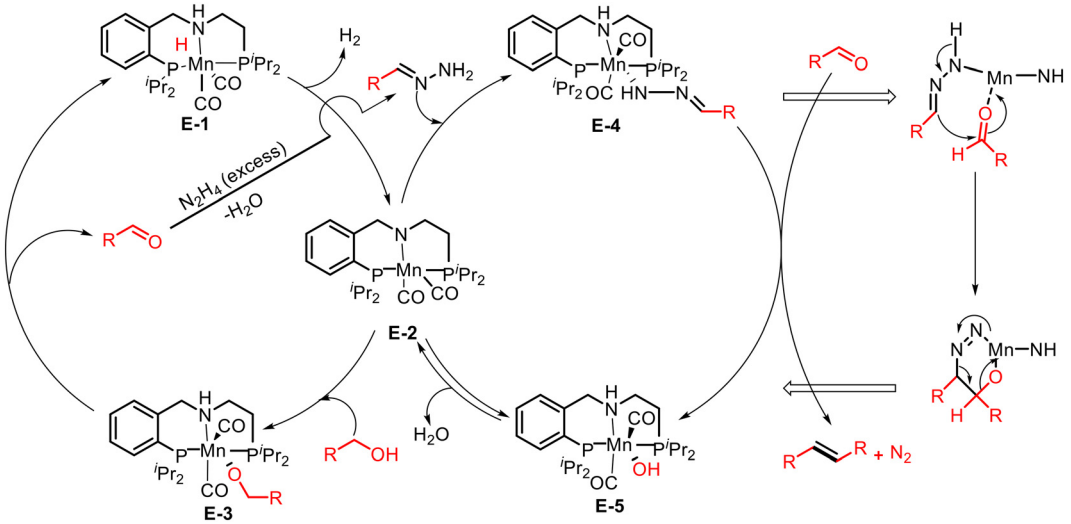
Scheme 9 Ru–NHC-catalyzed α-olefination of 2-oxindole with diaryl methanols.[35]



Scheme 10 Olefination of (10a) hydrazine and (10b) hydrazone *via* ADC strategy.[37]

7. Transition metal-catalyzed α-olefination of nitriles

α,β-Unsaturated acrylonitriles are used as building blocks to synthesize a variety of drug molecules, herbicides, and natural products.[38] Notably, vinyl nitriles have applications in optoelectronic materials and the synthesis of light-emitting diodes.[39] The conventional approach to make vinyl nitriles is a base-mediated Knoevenagel reaction using carbonyl compounds and nitriles as starting materials. Base-mediated condensation reactions have several drawbacks like side reactions including self-



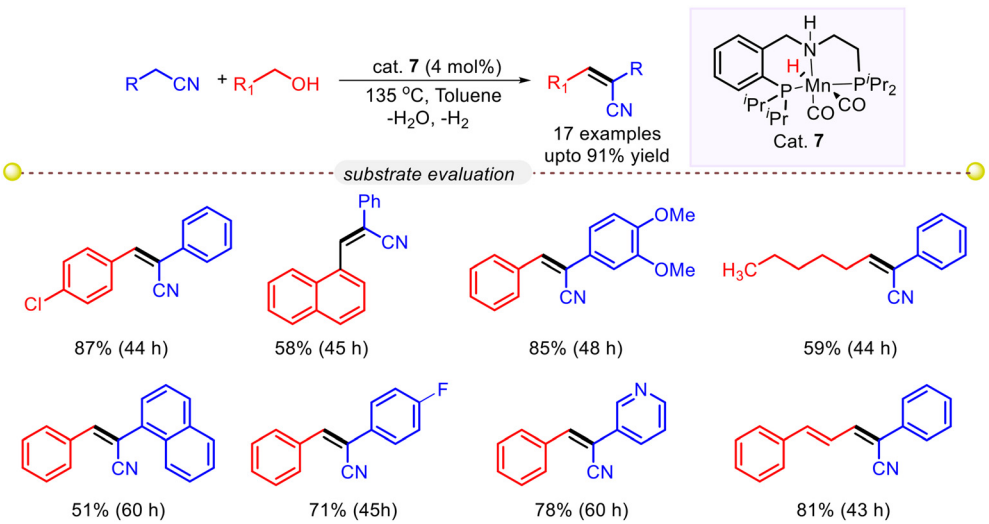
Scheme 11 Plausible catalytic cycle for olefination of hydrazine and hydrazone *via* ADC strategy.

condensation, Cannizzaro reaction, and aldol condensation, *etc.*[40,41]

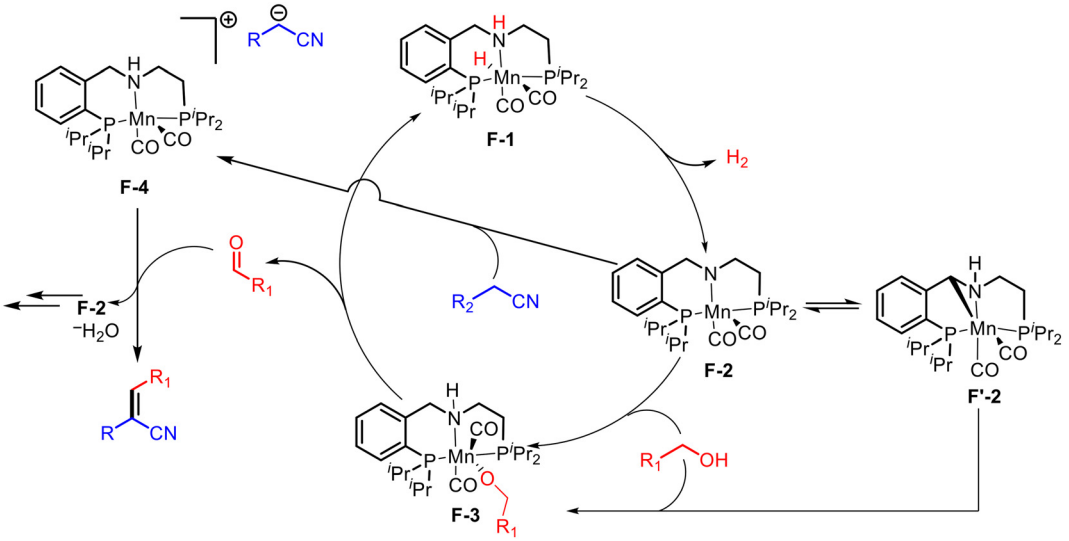
In 2017, Milstein and co-workers reported an α-olefination of nitriles with alcohols *via* a dehydrogenation coupling pathway. The reaction is catalyzed by a molecularly defined Mn–PNP pincer complex (Cat. 7).[42] A reaction mixture of benzyl alcohol (0.25 mmol), benzyl cyanide (0.25 mmol), and catalyst 7 in 1 mL of toluene at 135 °C produced 2,3-diphenylacrylonitrile in 87% isolated yield with complete *Z*-isomer selectivity. The reaction is general and various benzyl alcohols bearing electron-donating and withdrawing groups at the *para* position and substituted benzyl cyanides were employed under reaction conditions. The protocol was successfully extended to aliphatic alcohols. The by-products of these reactions are H_2 and H_2O (Scheme 12).

The proposed mechanism for α-olefination of alcohols is illustrated in Scheme 13. The proposed mechanism for α-olefination of alcohols involving Mn–pincer complex **F-1** is initiated with hydrogen liberation and formation of amido complex **F-2**. After C–H activation complex **F-2** transformed to thermodynamically more stable complex **F′-2**. The O–H activation of alcohol through proton transfer to either the nitrogen of complex **F-2** or benzylic carbon of **F′-2** giving alkoxy complex following β-hydride elimination releases the aldehyde. In a simultaneous pathway α-hydrogen bearing nitrile generates a nitrile carbanion *via* deprotonation. Control experiments and NMR studies suggested that complex **F-2** abstracts a proton from nitriles bearing α-hydrogen and generates a nitrile carbanion. The nucleophilic attack of carbanion **F-4** at the aldehyde leads to the formation of α,β-unsaturated nitrile, and amido complex with the liberation of water.

Wang and co-workers observed that vinyl nitriles can be synthesized *via* dehydrogenative coupling of alkylnitriles and alcohols using bi-nuclear Rh-complex as a catalyst.[43] Notably, an atmosphere-controlled chemoselectivity was observed.



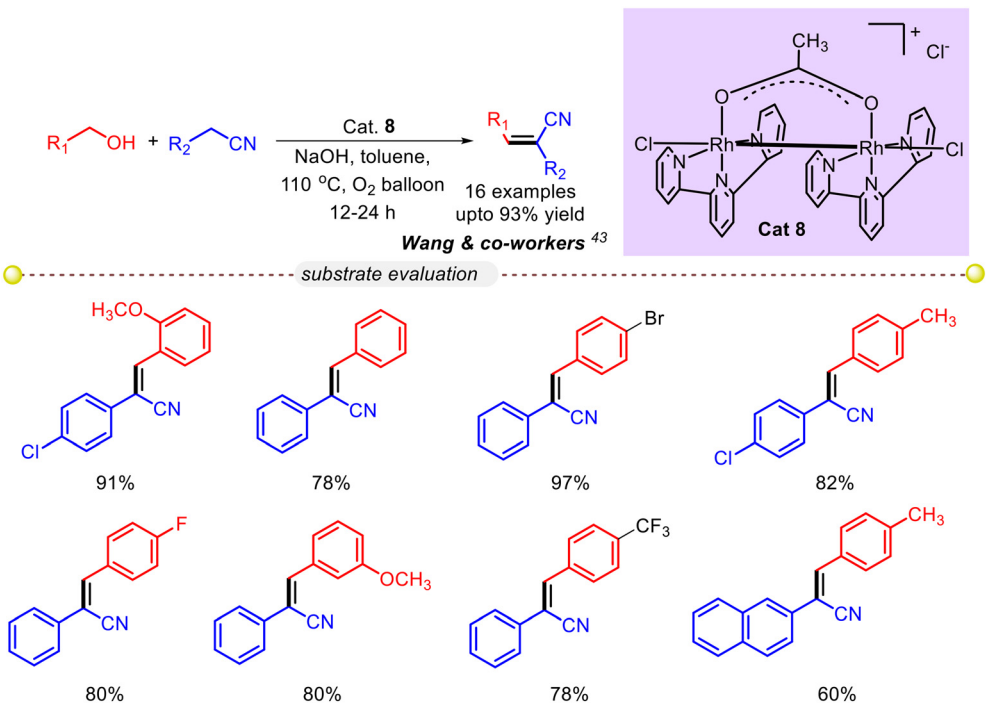
Scheme 12 An Mn–PNP catalyzed α-olefination of nitriles with alcohols.[42]



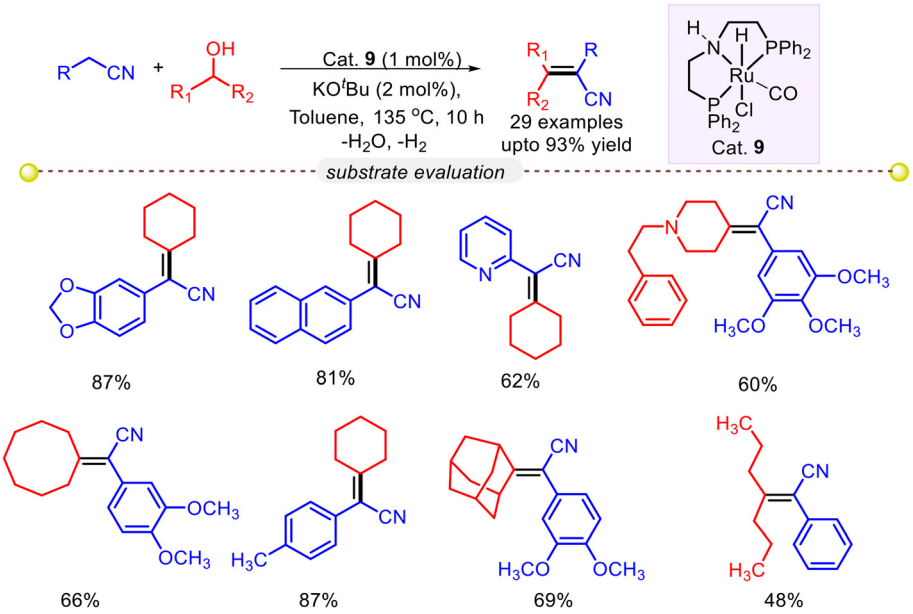
Scheme 13 Plausible catalytic cycle for Mn–PNP complex catalyzed α-olefination of nitriles with alcohols.

Reaction under inert Argon atmosphere resulted in alkylation *via* borrowing hydrogen pathway whereas, reaction under oxygen atmosphere assisted in dehydrogenation process and noticed the formation of olefins as final product. The isolated yield of olefinated product was found to be optimum using binuclear rhodium catalyst (Cat. **8**) and base NaOH in toluene at 110 °C (Scheme 14). The reaction was carried out in a Radleys Carousel tube equipped with an O_2 balloon.

After the initial report of olefination of nitriles using primary alcohol by Milstein and Wang groups,[42,43] Gunanathan and co-workers reported Ru(II)-pincer complex (Cat. **9**) catalyzed synthesis of β-disubstituted vinyl nitriles using secondary alcohols (Scheme 15).[44] One equiv. of phenyl acetonitrile with a two equiv. of cyclohexanol in the presence of Ru-MACHO (1 mol%), KO^{t}Bu as a base in toluene at 135 °C resulted in the formation of a final olefin product with 84% yield. Electron-donating, electron-withdrawing, halo-substituted phenyl acetonitriles, nitriles bearing heterocycles, and aliphatic side chains provided the corresponding alkene products in moderate to good yield under the optimized reaction conditions. The protocol was further extended to various cyclic and acyclic secondary alcohols. Notably,

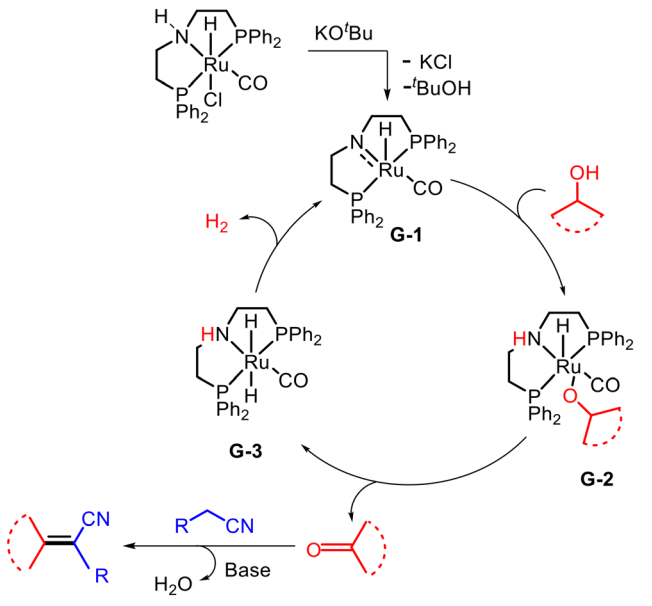


Scheme 14 Rh-binuclear complex catalyzed α-olefination of nitriles using alcohols.[43]



Scheme 15 Ru–PNP complex catalyzed synthesis of alkenyl nitriles using alcohols.[44]

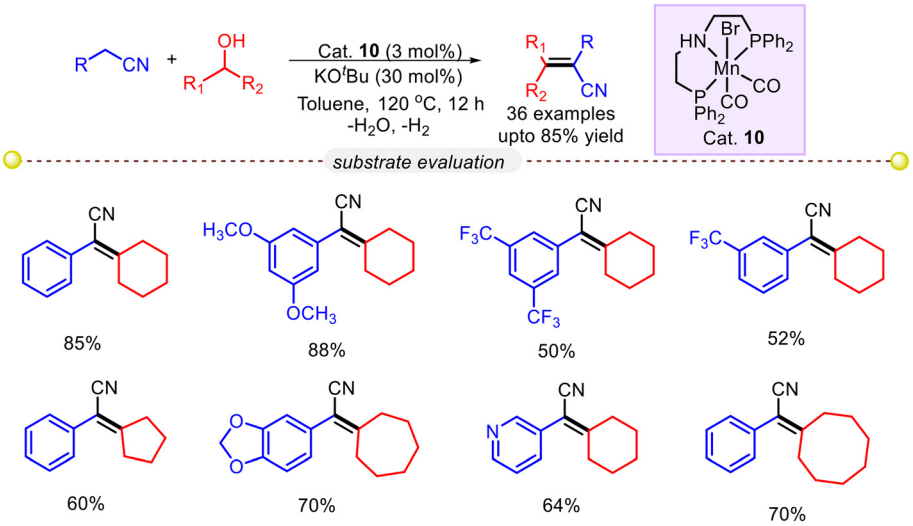
cycloheptanol, cyclooctanol, and sterically bulky 2-adamantanol are amenable and enable product formation under the optimized reaction condition. From the kinetic studies, it was confirmed that the reaction follows first-order kinetics. Mechanistic findings suggested a plausible catalytic cycle (Scheme 16) where in the presence of base precatalyst forms coordinatively unsaturated complex **G-1**. Complex **G-1** reacts with secondary alcohol and generates alkoxy-ligated Ru-complex **G-2** upon MLC-mediated O–H bond activation of a secondary alcohol. Subsequently, the ketone is generated through a β-hydride elimination reaction, concomitant with the release of a ruthenium dihydride complex **G-3**. Hydrogen liberation from complex **G-3** regenerates active catalyst **G-1**.



Scheme 16 Plausible catalytic cycle for Ru–PNP complex catalyzed synthesis of substituted alkenyl nitriles using alcohols.

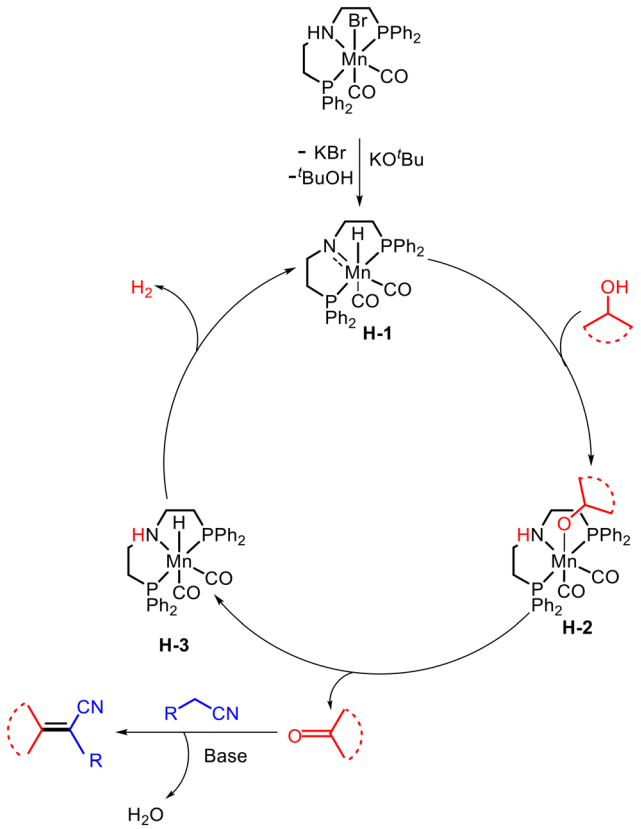
Since the replacement of precious metals with non-precious metals is one of the prime goals in modern chemistry, Balaraman and co-workers came up with an elegant method for synthesizing vinyl nitriles from nitriles and secondary alcohols using a well-defined manganese catalyst. KO^{t}Bu was used as a base, and Mn(I)–PNP pincer precatalyst (Cat. **10**) was used in toluene solvent at 120 °C to selectively olefinate a number of acetonitriles with different secondary alcohols (Scheme 17).[45] The olefination reaction of acetonitrile, incorporating both electron-donating and electron-withdrawing groups, as well as halides, exhibited excellent reactivity, yielding the desired products in good to excellent isolated yields. The kinetic studies indicated that the reaction follows first-order kinetics concerning both phenyl acetonitrile and cyclohexanol, while the catalyst showed a fractional order. Additionally, a kinetic deuterium-labeling experiment revealed a k_H/k_D ratio of 2.53, indicating that the rate-determining step involves the activation of the C–H bond in secondary alcohol.

The proposed catalytic cycle for the Mn–PNP complex catalyzed synthesis of substituted alkenyl nitriles using secondary alcohols is shown in Scheme 18. Initially, the Mn-precatalyst is subjected to a base and transforms to a coordinatively unsaturated intermediate, denoted as **H-1**. Subsequently, the alcohol undergoes O–H activation *via* a proton transfer to the amido nitrogen of intermediate **H-1**, leading to the formation of an intermediate of the alkoxy-type, referred to as **H-2**. Next, the dehydrogenation reaction proceeds through the favorable pathway of base-promoted β-hydrogen abstraction. This intramolecular metal–ligand cooperation facilitates the formation of ketones and the manganese hydride complex **H-3**, which subsequently



Scheme 17 An Mn–PNP complex catalyzed the synthesis of substituted alkenyl nitriles using secondary alcohols.[45]

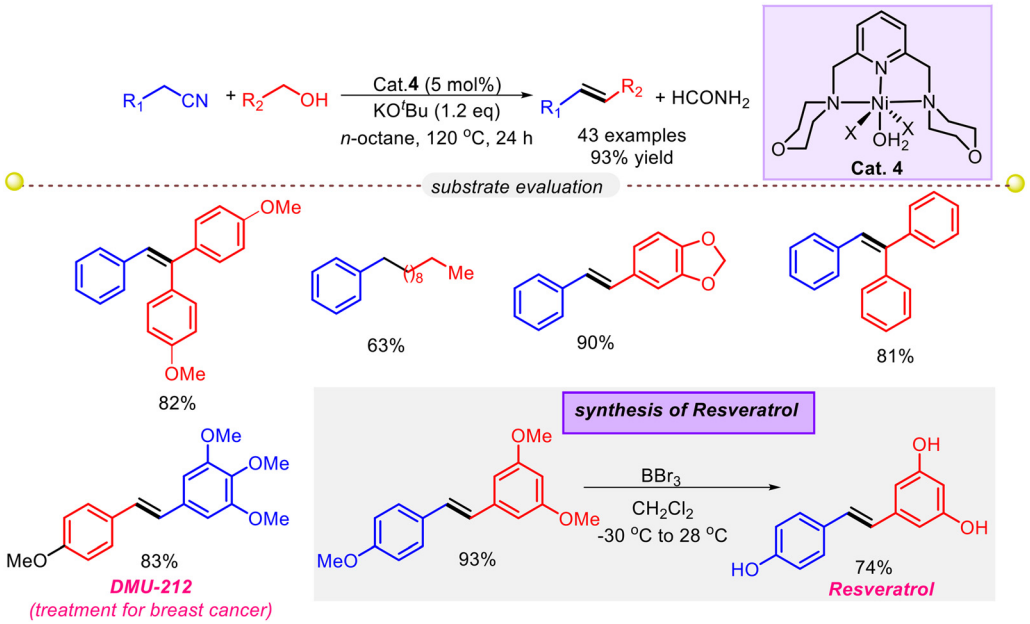
liberates hydrogen gas to regenerate the catalytically active intermediate **H-1**. Eventually, through Knoevenagel condensation between the *in situ* generated ketones and nitriles, vinyl nitriles are formed, with the elimination of a water molecule.



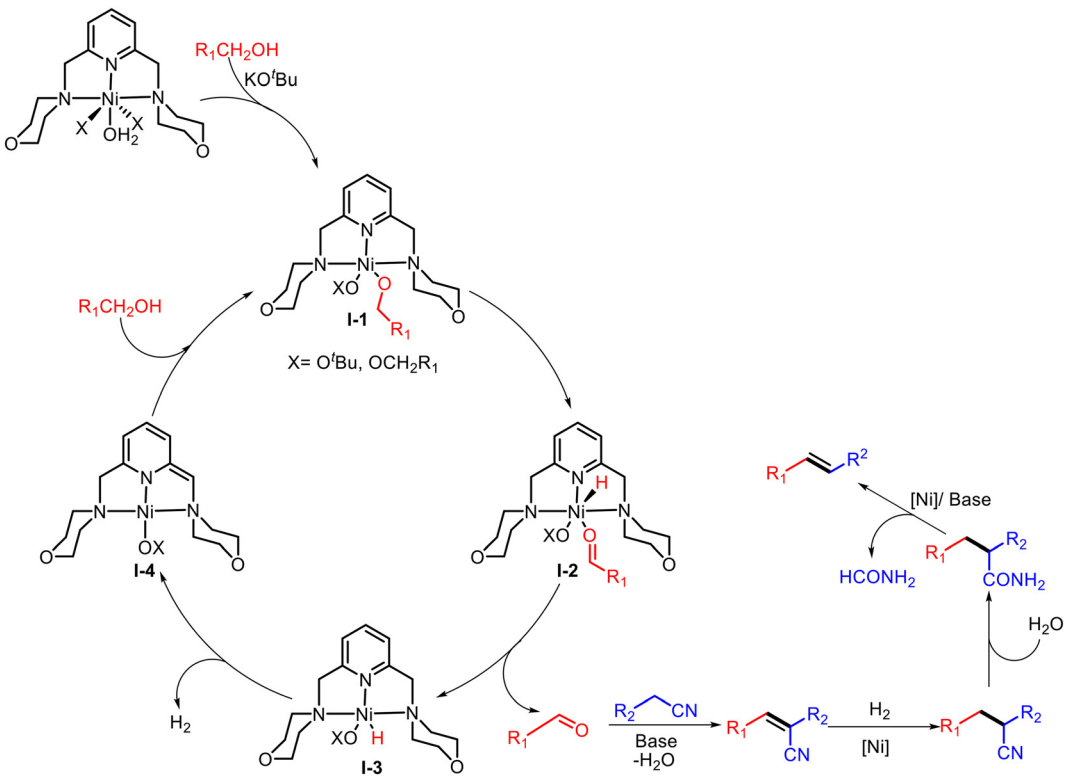
Scheme 18 Plausible catalytic cycle for Mn–PNP complex catalyzed synthesis of substituted alkenyl nitriles using secondary alcohols.

In 2021, Balaraman and co-workers disclosed an unprecedented olefin (*E*) synthesis using nickel-catalyzed acceptorless dehydrogenative coupling of alcohols with nitriles *via* a decyanation pathway,[46] where previous reports had shown α-alkylated/alkenylated products with the same starting materials. After screening several reaction conditions, the optimization experiments revealed that 4-methoxybenzyl alcohol and 2-phenylacetonitrile underwent a Ni-catalyzed (Cat. **4**) dehydrogenative coupling to form (*E*)-1-methoxy-4-styrylbenzene with 87% yield when KO^{t}Bu, *n*-octane solvent and Cat. **4** was used under refluxing temperature at 120 °C (Scheme 19). The reaction conditions were well tolerated and provided good to excellent yield for *ortho*, *para*, and *meta*-substituted benzyl alcohol and phenyl acetonitriles. The reaction protocol was equally viable for heteroaryl systems, sterically demanding *ortho*-substituted alcohols, and sterically hindered secondary alcohols. The reaction methodology was applied to synthesize DMU-212 (a drug for breast cancer treatment) and resveratrol (pan-assay interference compound) with an excellent yield of 83% and 74%, respectively under the present Ni-catalyzed conditions. To get a mechanistic elucidation, deuterium labeling experiments, and several control experiments were performed. The experimental results suggested that the reaction proceeds *via* a tandem acceptorless dehydrogenative coupling decyanation pathway.

Based on the mechanistic insights, the catalytic cycle (Scheme 20) started with a displacement reaction where the alcohol displaced the chloride ligand from the Ni-metal center of the pre-catalyst in the presence of KO^{t}Bu followed by a β-hydride elimination which led to an aldehyde and Ni–H species. The Ni–H species regenerated the active catalyst **I-1** *via* H_2 liberation followed by reacting with the alcohol. The *in situ* generated aldehyde underwent the Knoevenagel condensation with a nitrile and led to vinyl-



Scheme 19 Ni–NNN complex catalyzed decyanative olefination of nitriles using alcohol.[46]



Scheme 20 Plausible catalytic cycle for Ni–NNN complex catalyzed decyanative olefination of nitriles using alcohol.

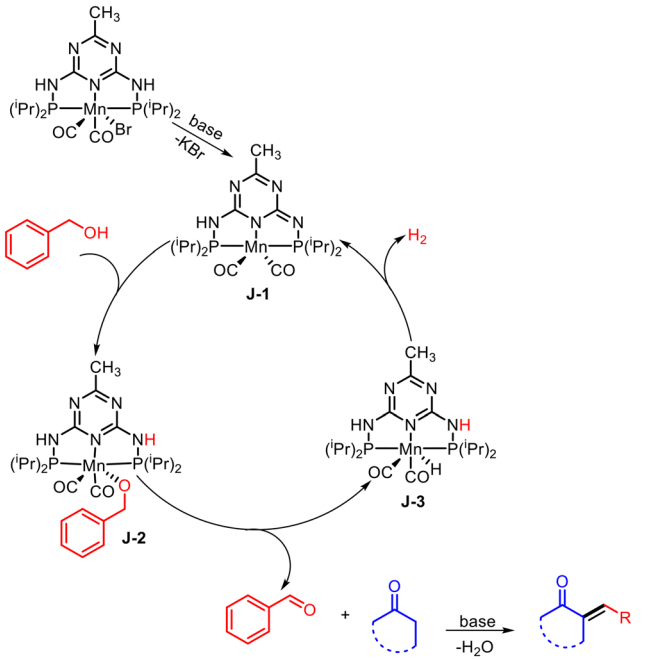
nitrile by eliminating a water molecule, and subsequent hydrogenation in the presence of Ni-catalyst followed by condensation resulted in α-alkylated arylacetamide. In the final step, the elimination of formamide from α-alkylated arylacetamide resulted in (*E*)-stilbene product.

8. Synthesis of α,β-unsaturated ketone using alcohol

α,β-Unsaturated ketones have broad applications in the synthesis of pharmaceuticals, biologically active compounds,

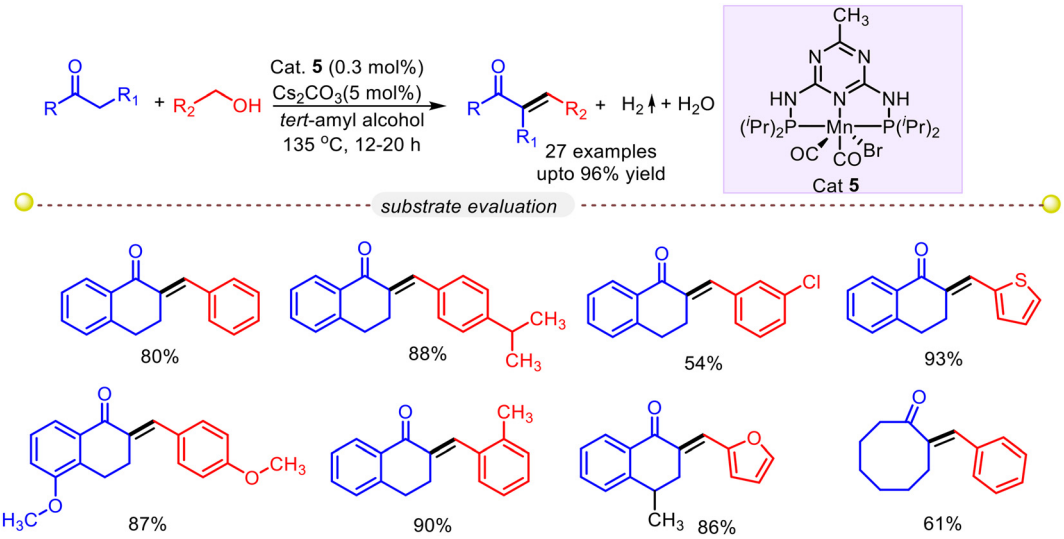
pesticides, food additives, and other functional materials.[47] Conventionally, α,β-unsaturated ketones are synthesized *via* aldol condensation using ketones or aldehydes with a stoichiometric amount of strong bases under cryogenic conditions.[48] As an alternative, the acceptorless dehydrogenative coupling method of alcohols with ketones is one of the most suitable methods to form α,β-unsaturated ketones. In recent years, compared to precious noble metal catalysts, the use of earth-abundant, economically feasible, and less toxic base metals has been highly demanded.

Recently Gunanathan and co-workers reported an atom-economical dehydrogenative coupling reaction of alcohols and ketones to α,β-unsaturated ketone using a manganese pincer complex (Cat. **5**).[49] In a representative example, 1-tetralone was reacted with a small excess of benzyl alcohol at 135 °C for 12 hours using catalyst **5** in the presence of a catalytic amount of base Cs_2CO_3. Spectroscopic analyses revealed that 1-tetralone effectively converted to 80% alkenyl product (Scheme 21) with a selectivity of 97 : 3 over alkane product. Under these catalytic conditions, heteroaryl, aliphatic, and benzylic primary alcohols featuring various functional groups (such as chloride, bromide, and methoxy) and various activated ketones furnished the desired product in good to moderate yield. Deuterium labelling studies and other experimental analyses predicted the reaction protocol follows the ADC pathway (Scheme 22). In the presence of a base, the precatalyst generates coordinatively unsaturated dearomatized intermediate **J-1**. The formation of alkoxy-ligated complexes **J-2** is observed upon the reaction of intermediate **J-1** with primary alcohols. Subsequently, a β-hydride elimination from **J-2** resulted in an aldehyde with an Mn–hydride complex **J-3**. The *de novo* synthesized aldehyde underwent a base-promoted olefination with 1-tetralone to yield the final α,β-unsaturated ketone product, whereas Mn–hydride complex **J-3** liberates hydrogen and regenerates dearomatized intermediate **J-1**.

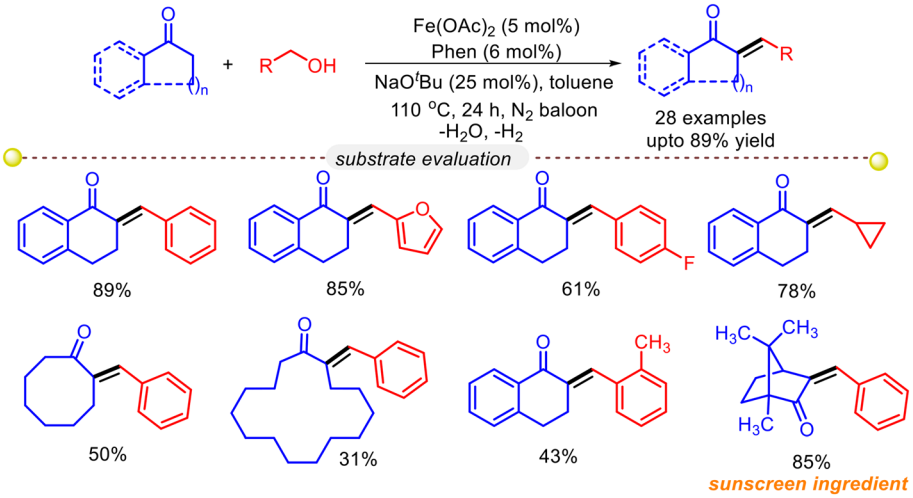


Scheme 22 Plausible catalytic cycle for Mn–PNP complex catalyzed synthesis of α,β-unsaturated ketones using alcohol.

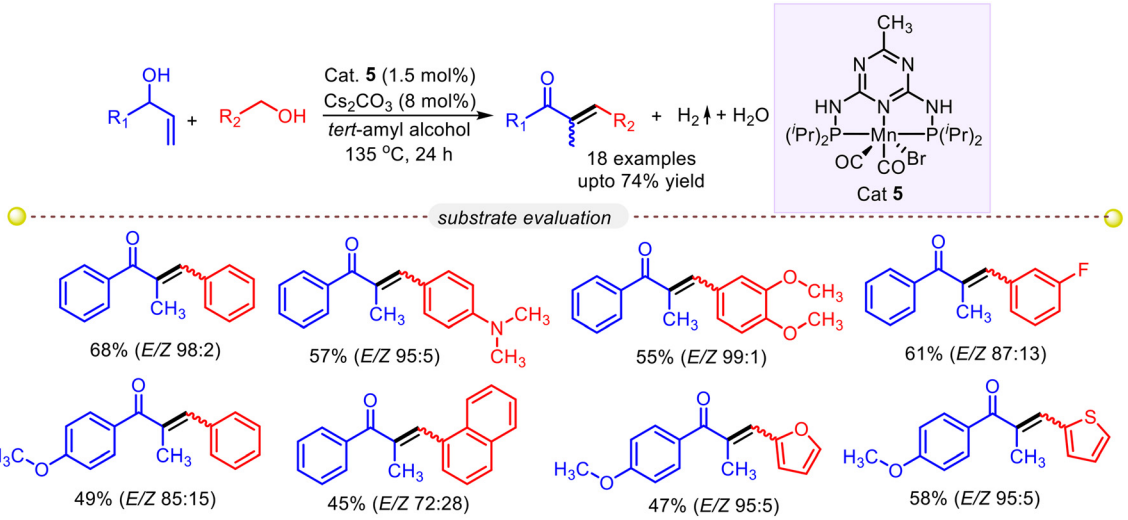
The research group of Banerjee reported iron-catalyzed dehydrogenative coupling of alcohols and ketones to obtain α,β-unsaturated ketones.[50] Iron(II) acetate in combination with 1,10-phenanthroline and base ^{t}BuONa in toluene at 110 °C provided the corresponding *E*-selective (>25 : 1) olefins from α-tetralone and 4-methoxybenzyl alcohol with 75% yield. A number of cyclic (C7, C8, C15 membered cyclic ketones) and acyclic ketones, as well as benzyl alcohols with delicate functional groups such as nitro, nitrile, trifluoromethyl, fluoro, chloro, 1,3-dioxolone, alkyl, and alkoxy, including heterocycles (furan functionality), were tolerated by the established catalytic process. The protocol



Scheme 21 An Mn–PNP complex catalyzed synthesis of α,β-unsaturated ketones *via* the ADC strategy.[49]



Scheme 23 Iron-catalyzed synthesis of α,β-unsaturated ketones using alcohol.[50]

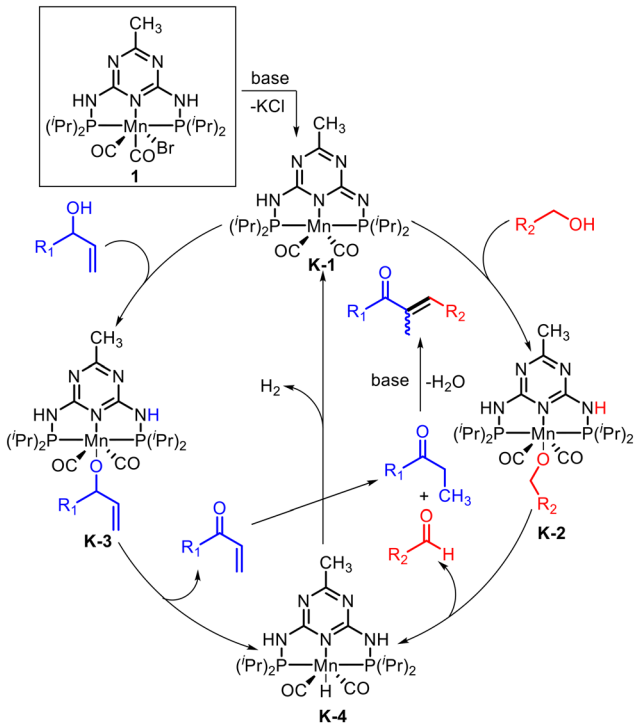


Scheme 24 Mn-complex catalyzed cross-coupling of secondary allylic alcohols and primary alcohols.[51]

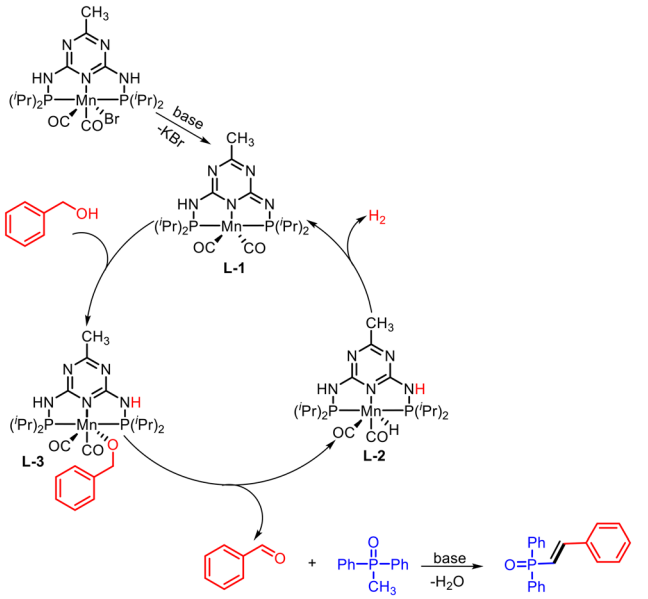
was also applied for the synthesis of a sunscreen component (Scheme 23). Mechanistic experiments such as deuterium labeling studies, determination of the rate and order of the reaction, and quantitative determination of H_2 gas suggested that the reaction followed the ADC-type pathway.

Allylic alcohols are versatile **C-3** precursors that can be used to synthesize various organic compounds with different applications. In 2021, Gunanathan and co-workers devised a method to produce α-alkenyl and α-alkyl ketones by directly cross-coupling primary alcohols and secondary allylic alcohols with a PNP–Mn(I) pincer complex catalyst. The best yield of the olefinated product was obtained with precatalyst 1 and a mild base Cs_2CO_3 for 24 h, giving a 97 : 3 ratio of alkenyl and alkylation products (Scheme 24).[51]

The cross-coupled olefin product was formed in moderate to good yield as a mixture of *E* and *Z* isomers from benzyl alcohols with electron-donating, electron-withdrawing, or halo substituents, as well as activated alcohols with heterocycles and secondary allyl alcohols with electron-donating groups. Based on several experimental studies, a plausible catalytic pathway for the PNP–Mn(I) pincer complex catalyzed olefination reaction is shown in Scheme 25. In the presence of a base, the Mn-precatalyst generates coordinatively unsaturated dearomatized intermediate **K-1**. The formation of alkoxy-ligated complexes **K-2** and **K-3** is observed upon the reaction of intermediate **K-1** with secondary allylic alcohols and primary alcohols, respectively. This reaction proceeds through the facile O–H activation of alcohol functionalities. Subsequently, a β-hydride elimination from **K-2** and **K-3** resulted in α,β-unsaturated ketone and aldehyde, respectively with an Mn–hydride complex **K-4**. The Mn–hydride complex **K-4** has been found to facilitate the selective hydrogenation of α,β-unsaturated ketone and produces propiophenone which subsequently reacts (in an aldol condensation pathway) with aldehyde and yields a final olefin product in the presence of base.



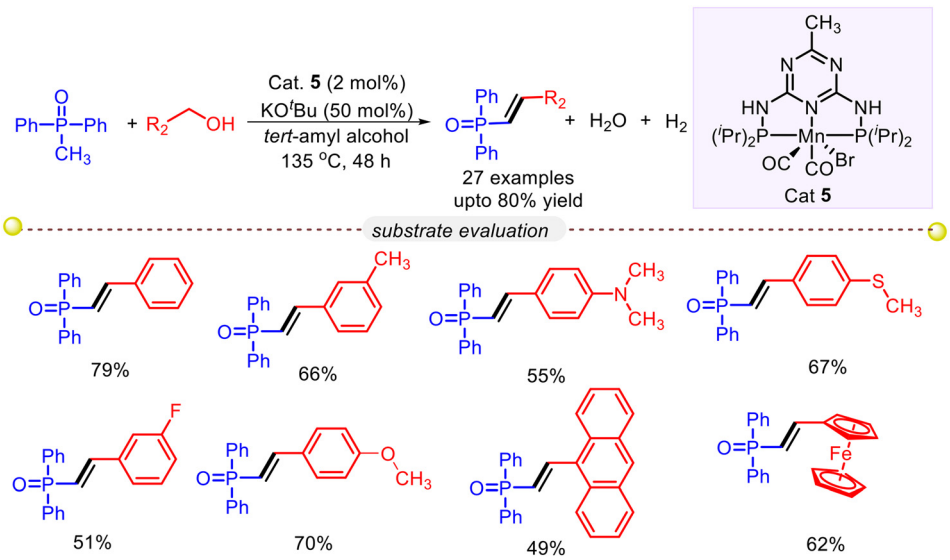
Scheme 25 Plausible catalytic cycle for Mn–PNP complex catalyzed cross-coupling of secondary allylic alcohols and primary alcohols.



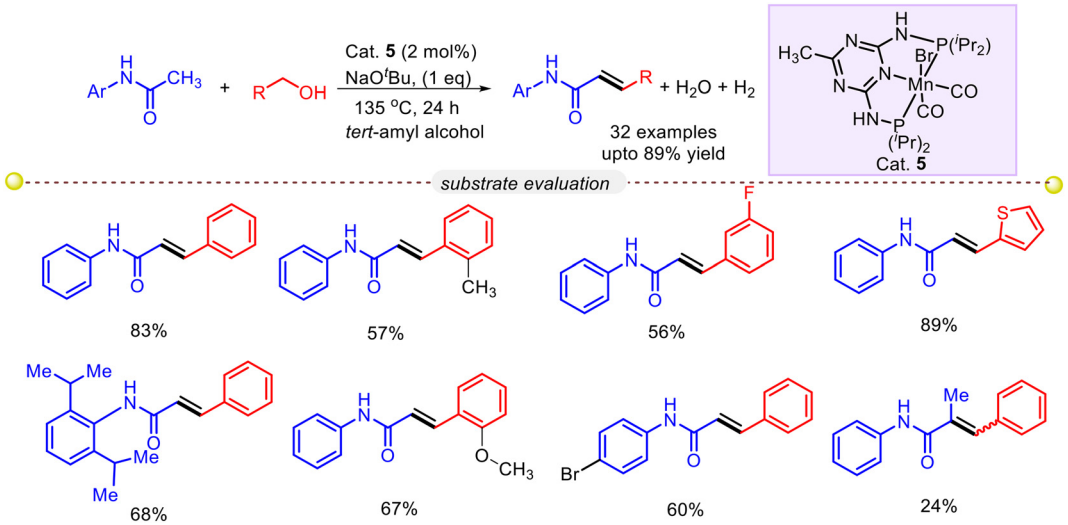
Scheme 27 Plausible catalytic cycle for Mn–PNP complex catalyzed α-olefination of alkenylphosphine oxides using alcohol.

9. α-Olefination of alkenyl phosphine oxides using alcohol

Alkenylphosphine oxides are widely used in synthetic chemistry as the unsaturated C–C bond can be tamed to various modifications further. The unsaturation-containing phosphine oxides have widespread utility in agricultural, medicinal, and industrial chemistry.[52] Pandia *et al.* devised an excellent method for the synthesis of alkenylphosphine oxides *via* dehydrogenative coupling of methyldiphenylphosphine oxide and arylmethyl alcohols using PNP–Mn(I) pincer complex (Scheme 26).[53] A broad range of neutral, electron-donating, electron-withdrawing aromatic systems underwent the reaction using KO^{t}Bu as a base in *tert*-amyl alcohol solvent at 135 °C. In the presence of a base, the Mn-precatalyst generates coordinatively unsaturated dearomatized intermediate **L-1** (Scheme 27). The formation of alkoxy-ligated complexes **L-2** is observed upon the reaction of intermediate **L-1** with primary alcohols. Subsequently, a β-hydride elimination from **L-2** resulted in an aldehyde with a Mn–hydride complex **L-3**. The *de novo* synthesized aldehyde underwent a base-promoted olefination



Scheme 26 Mn-catalyzed α-olefination of alkenylphosphine oxides using alcohol.[53]

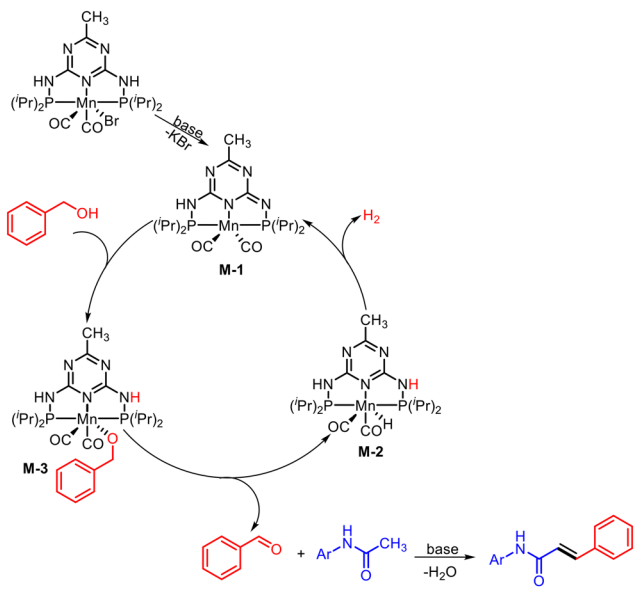


Scheme 28 An Mn–PNP complex catalyzed α-olefination of alkenylamides using alcohol.[55]

to yield the final alkenylphosphine oxides, whereas the Mn–hydride complex liberates hydrogen and generates dearomatized intermediate **L-1**.

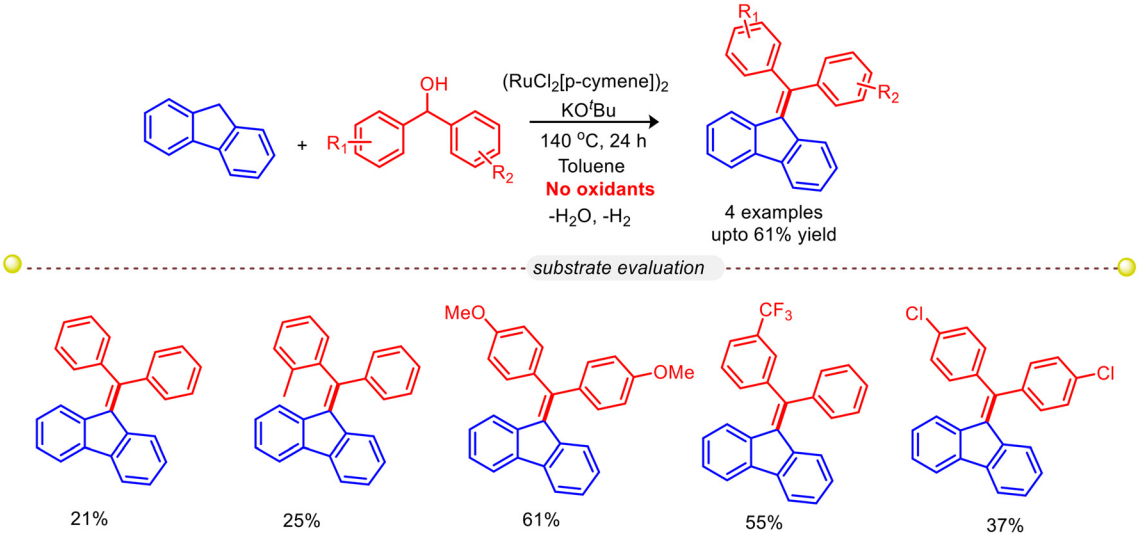
10. α-Olefination of alkylamides using alcohol

Unsaturated amides play a crucial role in a wide range of applications, including natural products, bioactive molecules, polymeric materials, and pharmaceuticals.[54] The traditional method for synthesizing α,β-unsaturated amides involves nucleophilic substitution of α,β-unsaturated carboxylic acids with amines, which often requires excessive reagents and suffers from limited compatibility with different functional groups. To address these challenges and pave the way for a sustainable future, chemists have been exploring various catalytic methods to introduce unsaturation alongside the amide functional group. However, there is a pressing need for a simple, selective, cost-effective, and efficient synthesis strategy. Gunanathan and co-workers developed a synthetic protocol for α-alkenylation of amides using primary alcohol as an alkenylation reagent and earth-abundant base metal manganese complex as a catalyst. Precatalyst **1** and base NaO^{t}Bu were determined to be the best combination for the isolated yield of olefinated product when used for 24 hours at 135 °C in a *tert*-amyl alcohol solvent (Scheme 28).[55] A wide range of C(α)-olefinated amides were prepared using this Mn-catalyzed protocol by employing various primary alcohols and amides. Electron-donating benzyl alcohols and heteroaryl alcohols produced *E*-selective α,β-unsaturated amides with moderate to good yield. In the case of benzyl alcohols bearing electron-withdrawing group the yield of the expected olefinated product was only moderate, whereas secondary alcohols and aliphatic alcohols failed to provide desired alkene product. The catalytic reaction was found to be applicable to tertiary amides, although it resulted in a combination of alkenylation and alkylation products. A series of control experiments and deuterium labeling experiments were performed to get a mechanistic insight (Scheme 29).

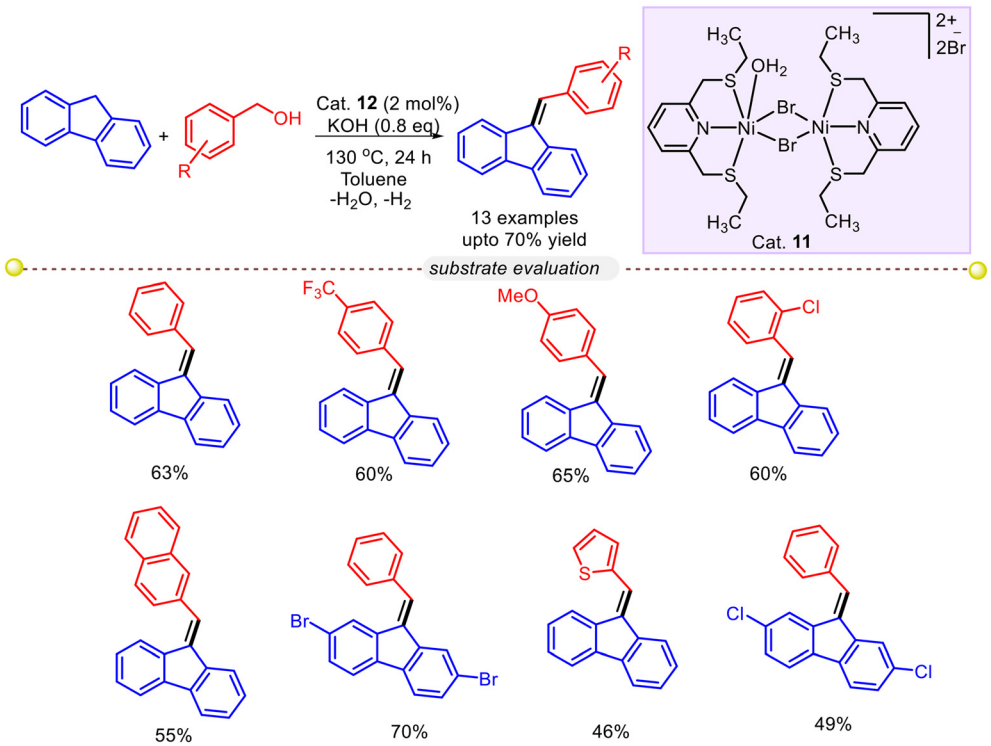


Scheme 29 Plausible catalytic cycle for Mn–PNP complex catalyzed α-olefination of alkenylamides using alcohol.

Mechanistic studies indicate, in the presence of a base, precatalyst generates coordinatively unsaturated dearomatized intermediate **M-1**. The formation of alkoxy-ligated complexes **M-2** is observed upon the oxidative addition of primary alcohols with intermediate **M-1**. Subsequently, a β-hydride elimination from **M-2** resulted in an aldehyde with an Mn–hydride complex **M-3**. The *in situ* generated aldehyde underwent a base-promoted olefination with corresponding amide to yield the final α,β-unsaturated amide product, whereas the Mn–hydride complex liberates hydrogen and generates dearomatized intermediate **M-1**.



Scheme 30 Reaction scheme and substrate scopes for Ru-catalyzed α-olefination of alkenylamides using benzhydrols.[57]



Scheme 31 Reaction scheme for Ni-catalyzed C(sp^3)–H olefination of 9*H*-fluorene.

11. C(sp^3)–H olefination of 9*H*-fluorene

Organic compounds generated from fluorene molecules have potential use in optoelectronics, solar cell, and semiconductor properties and have medicinal applications.[56] Realising the importance of alkylated and olefinated fluorene derivatives, Gnanaprakasam and co-workers reported the sp^3 C–H alkylation of 9*H*-fluorene using primary alcohol and a Ru catalyst *via* the borrowing hydrogen strategy.[57] However, this reaction with secondary alcohols in the absence of any external oxidants furnished the tetrasubstituted alkene as the major product. Hence, a reaction of 9*H*-fluorene 1 with substituted benzhydrols such as methyl-, methoxy-, chloro and trifluoromethyl in the presence of 5 mol% [Ru(*p*-cymene)Cl_2]$_2$ and 2 equiv. of KO^{t}Bu at 140 °C afforded the respective alkene products in good yield. A higher selectivity for the formation of alkene in the case of secondary alcohols, can be due to the fact that it is difficult for the sterically hindered alkene to coordinate with the Ru catalyst for a further hydrogenation reaction (Scheme 30).

Srimani and co-workers devised the BH (borrowing hydrogen) and ADC method where benzyl alcohols were used as alkylating and alkenylating sources (Scheme 31).[58] After careful investigation of several reaction parameters, it was found that treating fluorene and 3-methoxybenzylalcohol in the presence of Cat. **11** and toluene with base KOH at 130 °C provided corresponding 9-alkylidenefluorene product with 65% yield. The formation of an alkylated side product (after the reduction of the olefin bond) was also observed. Electron-donating, electron-withdrawing, halo-substituted benzyl alcohols, activated alcohols bearing heterocycles, and substituted fluorene derivatives were well-acquainted with the reaction protocol and delivered the desired product with moderate to excellent yield. Control experiments and kinetic studies suggested that the reaction protocol follows an ADC-type pathway, whereas the reduced alkylated product was formed *via* the BH approach.

Outlook and conclusion

Olefination stands out as one of the paramount reactions for the formation of C=C bonds. Acceptorless dehydrogenation (ADH) is a novel strategy for synthesizing alkenes from various substrates, such as nitriles, sulfones, phosphorus ylides, and carbonyl compounds. This review discusses the environmental benefits of ADH-based olefinations that use alcohols as the hydrogen source, producing only H_2O and H_2 as the waste. This review holds significant importance, as olefins serve as crucial feedstocks or intermediates in both industrial and laboratory. We also showcase the diverse catalytic systems that have been developed for this purpose and their industrial relevance. However, there are still many challenges and opportunities for further improvement. This review aims to inspire researchers in this area to design more effective catalysts that can lower the reaction temperature, base amount, and reaction time, and increase the selectivity. By overcoming the current drawbacks and promoting innovative solutions, we can make the field of acceptorless dehydrogenation coupling for direct olefination more efficient and practical.

Conflicts of interest

The authors declare that they have no known competing financial interests.

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