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Allylic alcohols in borrowing hydrogen catalysis: from simple substrates to complex molecules

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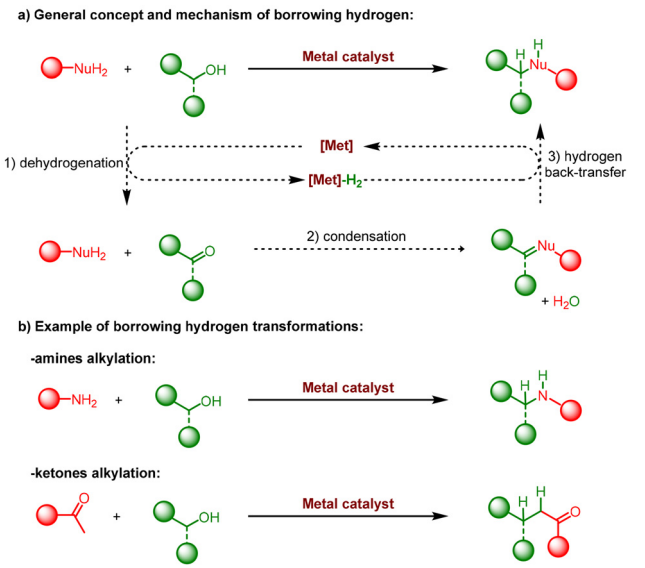
Borrowing hydrogen reactions are among the greenest approaches for creating complex molecules from simple materials. The most established borrowing hydrogen transformations are the alkylation of amines and ketones using alcohols as alkylating agents. Beyond this classical reactivity, new categories of borrowing hydrogen processes have emerged, notably those involving allylic alcohols, which have opened a distinct and rapidly growing research direction within the field. Since the first pioneering studies over a decade ago, allylic alcohol-based borrowing hydrogen reactions have garnered significant attention, particularly in recent years, leading to the development of numerous methodologies that enable rapid access to structurally diverse and valuable molecular architectures.

(I) Introduction

In order to address the ever-increasing eco-compatibility concerns for the modern synthesis of complex organic frameworks, reactions fulfilling the principle of redox-economies are becoming gold standards.[1] Such processes, by limiting unnecessary stoichiometric oxidation or reduction reactions, reduce the consumption of chemicals, avoid waste generation and decrease the number of steps. Among these, borrowing hydrogen catalysis has emerged as one of the most prominent tools.[2] In borrowing hydrogen transformations, a metal complex is able, through a catalytic cycle, to induce the direct redox-neutral transformation of saturated organic compounds such as alcohols, or less commonly amines or alkanes, into functionalised products of higher complexity (Scheme 1a). In the general mechanism, the first step of the catalytic cycle involves alcohol dehydrogenation by the catalyst, generating a reactive carbonyl compound on one side and a metal-dihydrogen complex on the other. This carbonyl compound is now reactive to engage in a condensation with another partner (here a nucleophile) to form a new unsaturated species. To close the catalytic cycle, the metal-dihydrogen complex gives back hydrogen, regenerating the necessary metal dehydrogenation complex and forming the final saturated compound.

Among the classical transformations involving borrowing hydrogen principles, the alkylation of amines or ketones using alcohols as partners is the most established one (Scheme 1b). Aside from this traditional use of alcohols as alkylating reagents, other classes of borrowing hydrogen have emerged, notably using allylic alcohols, which have opened an all-new area of research for borrowing hydrogen. Since the pioneering results more than a decade ago, they have attracted considerable interest in recent years with the development of numerous reactions to rapidly access a wide array of molecules of interest (Scheme 2).

Allylic alcohols are easily accessible, simple substrates with great potential for the rapid generation of high molecular com-



Scheme 1 General concept and mechanism of borrowing hydrogen catalysis and classical borrowing hydrogen transformations.

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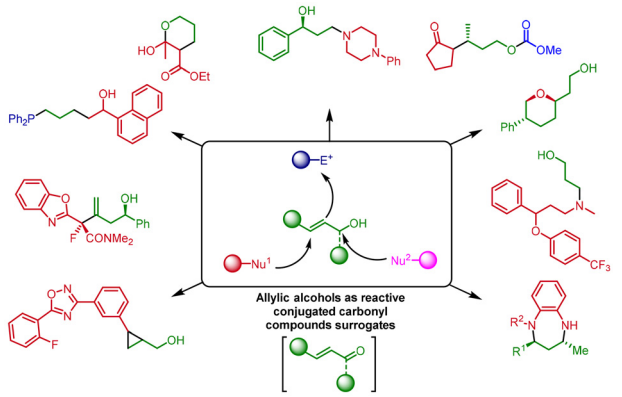
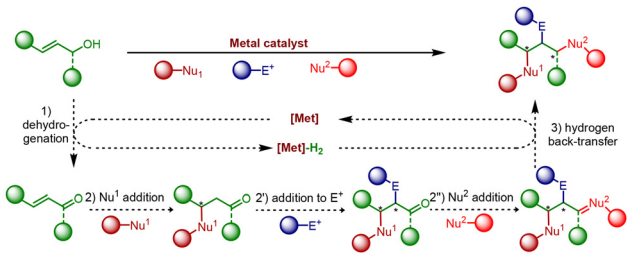


Scheme 2 Potential of allylic alcohols in borrowing hydrogen.



Scheme 3 General pathway for allylic alcohol functionalisation at different positions.

plexity and are particularly useful versatile substrates in borrowing hydrogen. Traditional methods for the transformation of allylic alcohols have mainly involved exploiting the electron-rich character of the double bond, or the activation of the alcohol through the formation of a leaving group, as in Tsuji–Trost type allylic alkylation.[3] Upon the first step of the borrowing hydrogen catalytic cycle (Scheme 3), the metal-catalysed dehydrogenation generates an α,β-unsaturated compound, inverting the polarity of the C=C double bond. This enables a wide array of transformations, notably involving 1,2 or more interestingly 1,4-conjugate addition to this newly generated electrophile. Upon 1,4-addition, a nucleophilic enol or enolate is generated, which can trigger a subsequent functionalisation with an electrophile. Finally, from the carbonyl compound, another nucleophilic 1,2-addition can occur, followed by back-hydrogen transfer. As a result, allylic alcohols can potentially react with three different partners in a single catalytic cycle, rapidly increasing molecular complexity. The 1,4-nucleophilic addition to the generated α,β-unsaturated compound can also be promoted by a second catalyst in a multicatalytic manner. This provides a handle to control the newly generated stereocentre, independently from the metal catalyst responsible for the reversible hydrogen transfers.

When following a mechanism involving the 1,4-addition to the intermediate carbonyl compound, one of the remarkable features of allylic alcohols in borrowing hydrogen is linked to the globally favoured hydrogen-transfer pathways. Indeed, in classical alkylations such as direct amine alkylation of Scheme 1, all processes are equilibrated, and particularly high temperatures are required to enable the borrowing hydrogen reaction to reach completion. Using allylic alcohols, the different kinetics and thermodynamics associated with the metal-hydrogen transfer are generally favoured, enabling the reaction to proceed at much lower temperatures.[4] This parameter is of key importance for enhancing substrate compatibility but also for enabling possible control over the stereoselectivity of the reactions. Indeed, depending on the metal complex used, the kinetics of the initial alcohol dehydrogenation are much faster than for other alcohols, notably benzylic or aliphatic ones, which facilitates the formation of the initial and more stable conjugated α,β-unsaturated compound.[5] Upon 1,4-addition to this Michael acceptor, a new carbonyl compound is generated featuring at least one aliphatic chain on one side. As a result, its hydrogenation is largely thermodynamically favoured, further assisting the overall borrowing hydrogen process. As a partial limitation, catalysts that induce the faster isomerisation of the double bond to the corresponding ketone are not tolerated in such borrowing hydrogen reactions.

It must be pointed out that, as for all borrowing hydrogen mechanisms, one of the key fundamental aspects is that the intermediate carbonyl compounds are formed transiently within the catalytic cycle and not generated sequentially. As a result, these reactive carbonyls are only present in small amounts, at a maximum concentration corresponding to the catalyst loading in the metal complex. This strongly influences the kinetics of reactions with nucleophiles or electrophiles,

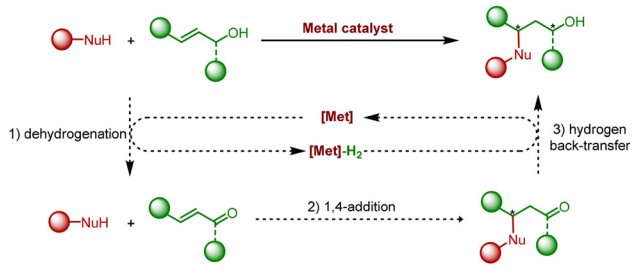
Michaël Vaglio-Pret (second person from the left), Mattéo Favre (third person from the left) and Milly Ogden (fourth person from the left) are part of ajoint team led by Dr. Amélie Kochem (CEA–CNRS) (first person from the left) and Dr. Adrien Quintard (UGA–CNRS) (right on the picture). This collaboration aims todevelop new catalytic borrowing-hydrogen methodologiesand to discover new active metal complexes, particularly iron-based systems, for hydrogen transfer reactions.

since the reactive carbonyl is present only in small amounts at a time. Therefore, these reactions display a different behaviour notably kinetics than the corresponding reactions performed with stoichiometric amounts of reactants. Another challenge in developing such borrowing hydrogen reactions from allylic alcohols is avoiding metal-catalysed allylic alcohol isomerisation, a common side reaction for various metal complexes. Finally, since different stereocentres can be generated throughout the overall catalytic cycle, several strategies have been identified to control the different stereodetermining steps of the reactions.

The availability and ease of functionalization have made allylic alcohols key precursors for borrowing hydrogen transformations.[6] In this review, we will highlight the particular reactivities that have been developed since the pioneering examples by Williams and our group, emphasising the structural diversity that can be accessed through the different strategies. These transformations encompass the use of a wide array of partners such as nucleophiles adding in a 1,4-fashion to the α,β-unsaturated carbonyl compound, electrophiles reacting with the generated enolate upon 1,4-addition, or, finally, nucleophiles adding in a 1,2-manner. This makes borrowing hydrogen from allylic alcohols a rich field of research with great potential for the synthesis of complex scaffolds.

(II) 1,4-Addition on the transient α,β-unsaturated compound

As mentioned in the introduction, the borrowing hydrogen strategy using allylic alcohols enables the inversion of the polarity of the C=C double bond, generating a transient electron-poor Michael acceptor. As a result, it is logical that researchers have sought to take advantage of this electrophilicity to perform additions of different classes of nucleophiles (Scheme 4). Since the 1,4-addition can be co-catalysed by a variety of catalysts, it is unsurprising that different multicatalytic strategies have been developed to favour nucleophilic addition. This can notably be applied to control the stereochemistry of the final product (Scheme 4). Another strategy to control the chirality of the obtained product consists in taking advantage of a chiral metal complex able to perform a stereoselective back-hydrogen transfer. Both strategies have been developed and can also be combined to further enhance stereocontrol, or to independently control all the generated stereocentres.



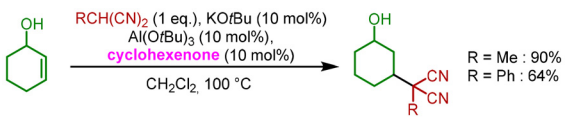
Scheme 4 General pathway for allylic alcohol functionalisation through transient 1,4-addition.

(IIa) 1,4-Addition of carbon-centred nucleophiles

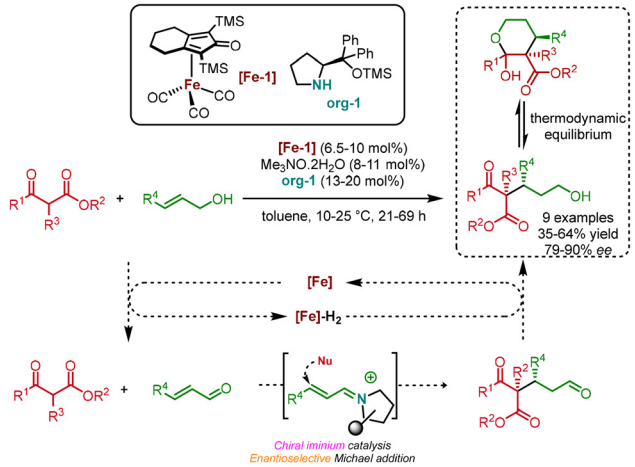
(IIa-1) Historical perspective. In 2001, the group of Williams reported the first example of the use of allylic alcohols in borrowing hydrogen. In this report, nucleophilic malonitrile derivatives were added to a cyclic alcohol such as cyclohexenol (Scheme 5).[7]

This reaction required a particular approach to induce the necessary changes in the oxidation state of the alcohol to enable the 1,4-addition of the malonitrile to the transient conjugated ketone, distinct from a mechanism involving metal-catalysed borrowing hydrogen. Using either a strong base (*t*-BuOK) or a strong Lewis acid Al(O*t*-Bu)$_3$, together with 10 mol% of a sacrificial ketone as a hydride acceptor, a Meerwein–Ponndorf–Verley-type hydride transfer could occur between the allylic alcohol and the sacrificial ketone, inducing an overall borrowing hydrogen type mechanism, converging to the functionalized aliphatic alcohol products.

This reaction remained a scientific curiosity, limited to two examples of cyclic alcohols, until 2013, when our group advanced the field through the development of a multicatalytic combination enabling the first catalytic borrowing hydrogen enantioselective addition of nucleophiles to allylic primary alcohols (Scheme 6).[8] Key to success was the merging of the iron complex **Fe-1**, activated by Me_3NO and triggering the reversible change in oxidation state from alcohol to aldehyde, with the organocatalyst, which enabled the addition of the nucleophile to the transient α,β-unsaturated aldehyde through iminium-type catalysis, hence controlling the stereochemistry of the generated adduct. The proof of concept for this multicatalytic principle was obtained in the reaction of keto-esters with allylic primary alcohols. Remarkably, the aliphatic aldehyde is back-hydrogenated much faster than the ketone during the process allowing the formation of the desired product. In addition, as mentioned in the introduction, the ease of dehydrogenation of allylic alcohols and hydrogen-back transfer to the final aliphatic aldehydes allow the borrowing hydrogen reaction to be conducted at low temperatures at which the organocatalyst can control the enantioselectivity of the 1,4-addition (10–25 °C). As a result, the final adducts, obtained under thermodynamic equilibrium between open and closed forms, are obtained in up to 90% ee. Interestingly, starting from substituted keto-esters, challenging quaternary stereocentres can be generated during the borrowing hydrogen transformation.



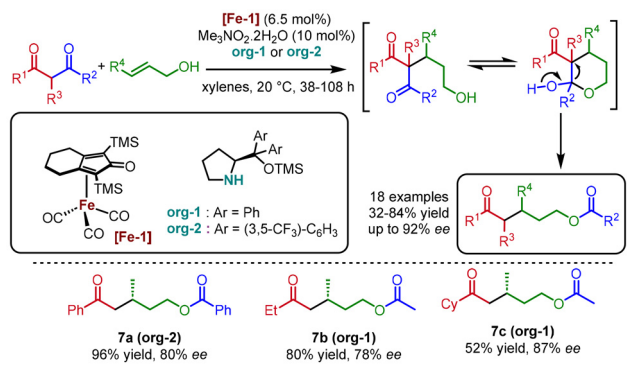
Scheme 5 Williams' first example of use of allylic alcohol in borrowing hydrogen.



Scheme 6 Development of the first multicatalytic borrowing hydrogen functionalisation of allylic alcohols.

This multicatalytic approach provides a new strategy to enable the functionalisation of the α,β-unsaturated carbonyl intermediate and to potentially control the stereochemistry of borrowing hydrogen transformations. It has since been employed to numerous applications in other transformations, using different catalysts to activate either the incoming nucleophile or the α,β-unsaturated carbonyl compound.[9]

(IIa-2) 1,4-Addition starting from allylic primary alcohols. From this result, using the same iron complex and organocatalyst combination, it was later demonstrated that diketones are excellent substrates in the borrowing hydrogen addition to allylic primary alcohols (Scheme 7).[10] This reaction is particularly interesting as the second ketone enables the activation of the pro-nucleophile for the 1,4-addition and is transferred through Claisen fragmentation during the borrowing hydrogen process, to directly protect the alcohol as an ester while liberating a mono-ketone. The iron complex **Fe-1** also proved optimal for driving the borrowing hydrogen cycle. Once again, the use of a chiral secondary amine organocatalyst ensures enantiocontrol of the overall process through iminium-type addition (up to 92% ee).

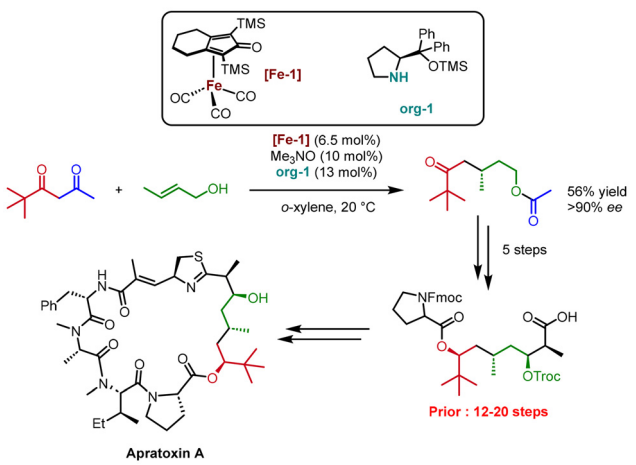


Scheme 7 Multicatalytic addition of diketones to allylic alcohols.

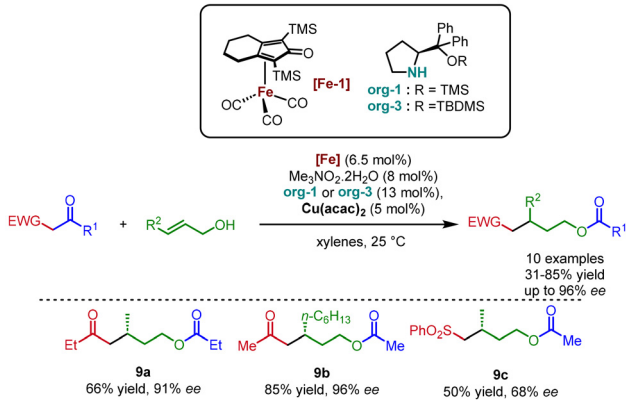
Demonstrating the value of nucleophilic addition of diketones to allylic alcohols, this multicatalytic reaction was applied to the synthesis of the polyketide fragment of apratoxin A, a naturally occurring molecule with reported anticancer activity.[11] The application of this strategy considerably reduced the number of steps required to prepare this complex polyketide, from literature approaches requiring 12–20 steps to only six steps from commercially available materials (Scheme 8). This synthetic shortcut highlights the potential of borrowing hydrogen in total synthesis.

The mechanism of the multicatalytic borrowing hydrogen was demonstrated in a subsequent study, which enabled the confirmation of several important general aspects of this reactivity.[12] First, it established the independent roles of the two catalysts: the iron complex, responsible for the dehydrogenation and back-hydrogen transfer, and the organocatalyst, responsible for the nucleophilic addition. Most importantly, this study confirmed that in borrowing hydrogen, the generation of only very low concentration of the intermediate carbonyl compounds – at most corresponding to the metal catalyst loading – has a considerable impact on the kinetics of the 1,4-addition, which in this case is the rate-determining step, and therefore on the overall borrowing hydrogen catalytic cycle. This important observation regarding the impact of intermediate carbonyl concentration holds for all borrowing hydrogen kinetics. It led our group to improve the process through the incorporation of a third catalyst, a copper salt, presumably activating the pro-nucleophile through coordination. This results in increased yields and enantiocontrol for the addition of keto-esters, diketones and nitrosulfones to allylic alcohols (Scheme 9). It should be noted that, to avoid the requirement for activation of the iron complex by trimethylamine-*N*-oxide, our group also recently developed a photoactivated iron complex which, upon irradiation by light, generates the active dehydrogenation catalyst.[13]

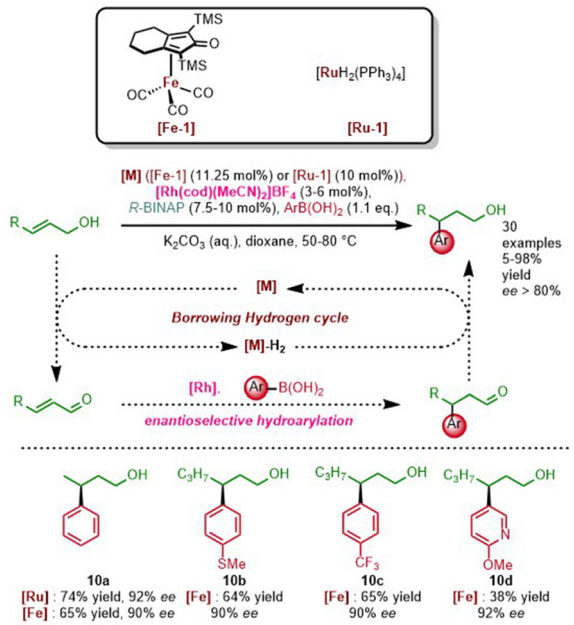
Based on the multicatalytic principle, in 2019 Dydio and coworkers extended this approach to the rhodium-catalysed addition of arylboronic acids (Scheme 10).[14] Using the same



Scheme 8 Multicatalytic synthesis of apratoxin A polyketide fragment.



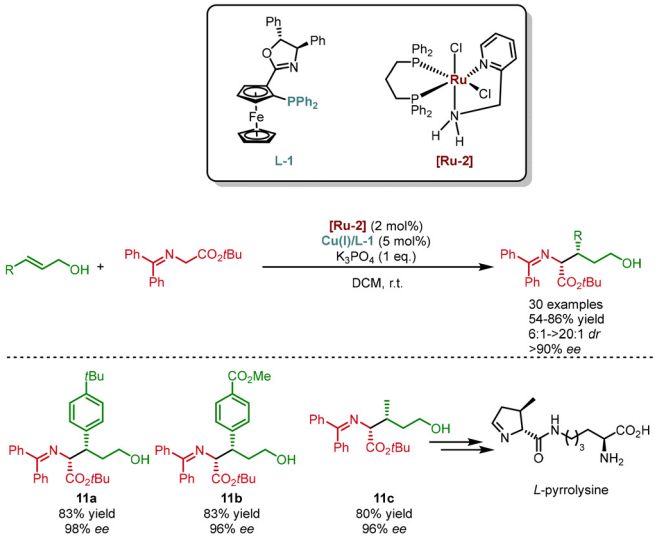
Scheme 9 Triple-catalytic functionalisation of allylic alcohols.



Scheme 10 Enantioselective rhodium catalysed 1,4-addition/borrowing hydrogen.

type of iron complexes or $RuH_2(PPh_3)_4$, the borrowing hydrogen activation of allylic primary alcohols could be efficiently merged with the enantioselective 1,4-addition of various aryl boronic acids to the transient α,β-unsaturated aldehydes. Using (*R*)-BINAP as the ligand for the rhodium complex, the newly created stereogenic centre was efficiently controlled in up to 96% ee. This reaction is particularly noteworthy, as it expands the scope of C–C bond formation on allylic alcohols to the direct addition of a broad array of aromatic compounds. It must be pointed out that even pyridine derivatives can be tolerated in the process.

Recently, the teams of Dong and Wang applied the multicatalytic approach to the addition of ketoimine esters (Scheme 11).[15] The key to success was the combination of the ruthenium complex **Ru-2** with a chiral copper complex. As for

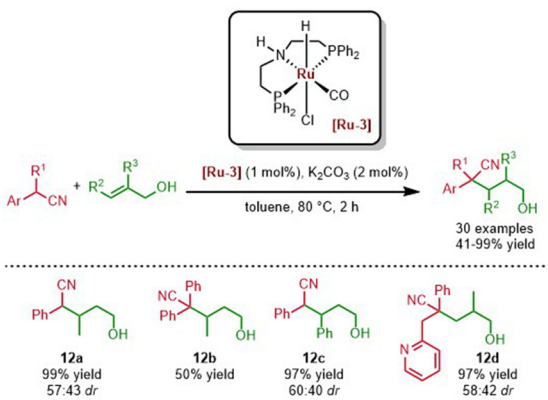


Scheme 11 Enantioselective copper-catalysed 1,4-addition/borrowing hydrogen.

the above-mentioned reactions, the Michael addition on the transient α,β-unsaturated aldehyde is the rate-limiting and stereodetermining step and is governed by the chiral copper complex.

Through this multicatalytic combination, a wide array of chiral alcohols featuring two controlled contiguous stereocentres are obtained in up to 98% ee. Importantly, the resulting adducts can be derivatised, notably towards the key fragment of L-pyrrolysine, which is accessed in only three steps compared to six steps in the literature. This further highlights the synthetic economies that can be achieved by appropriately using allylic alcohols in borrowing hydrogen chemistry.

In 2022, the group of Gunanathan reported that nitriles could add to allylic primary alcohols (Scheme 12).[16] For this purpose, they identified **Ru-3** as an appropriate metal catalyst for the borrowing hydrogen pathway. A catalytic amount of K_2CO_3 or *t*-BuOK was used to activate the ruthenium complex



Scheme 12 Ruthenium-catalysed addition of nitriles on allylic primary alcohols.

and deprotonate the isonitrile, thereby facilitating the 1,4-addition; however, control experiments also revealed that the ruthenium complex itself accelerated this 1,4-addition reaction. Importantly, the nitrile is not reduced by the metal hydride under the reaction conditions, even though relatively high temperatures (80 °C) are required for full conversion. Given the absence of activation by a chiral catalyst, only racemic compounds are obtained through this approach. Moreover, no diastereocontrol is observed when multiple stereogenic centres are generated. Importantly, demonstrating the utility of this method, the authors also showed that various small bioactive molecules could be easily prepared in only a few steps using this borrowing hydrogen strategy.

The last example of nucleophilic addition to allylic primary alcohols concerns a reaction related to Williams' hydride transfer.[17] In this reaction, *t*-BuONa induces hydride transfers between allylic alcohols and aliphatic aldehydes, presumably through ionic Meerwein–Ponndorf–Verley-type mechanism (Scheme 13). It is suggested that the small amount of aldehyde required to initiate the catalytic cycle arises from isomerisation of the allylic alcohol to the corresponding aliphatic aldehyde. Indoles add to the transient α,β-unsaturated aldehydes to generate intermediate aliphatic aldehydes, reduced to the aliphatic alcohols upon thermodynamically favoured hydride transfer from another molecule of allylic alcohol. This reaction, which proceeds under simple conditions at 120 °C, affords substituted indoles of significant value. Although this represents a formal borrowing hydrogen process, it enables the direct incorporation of key indole nucleophiles on allylic alcohols.

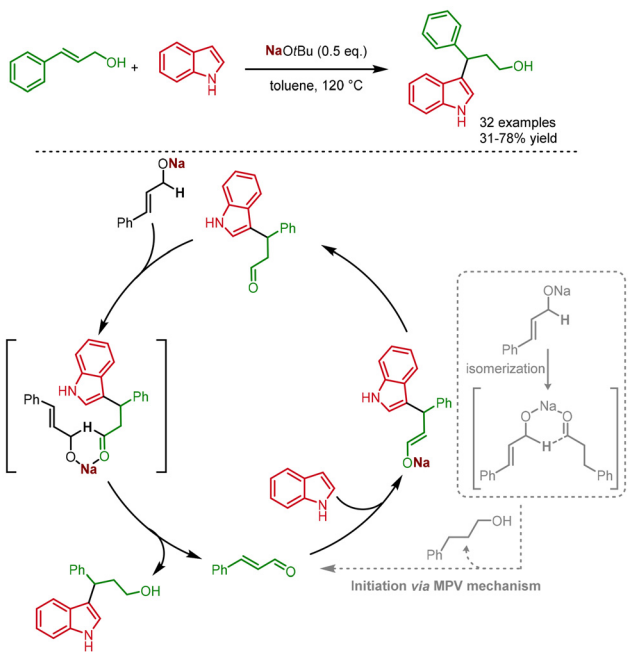
(IIa-3) 1,4-Addition starting from allylic secondary alcohols. Secondary allylic alcohols represent another important class of substrates in borrowing hydrogen methodology. Once efficient metal-catalysed dehydrogenation of the alcohol has occurred, the main challenges arises from the lower reactivity of the resulting α,β-unsaturated ketone, and from the difficulty of controlling the stereochemistry of the newly generated secondary alcohol during the final back-hydrogen transfer.

Following their addition of nitriles to allylic primary alcohols (see Scheme 12), the team of Gunanathan reported that nitriles could also be added to allylic secondary alcohols (Scheme 14).[16] The reaction also proceeds efficiently with **Ru-3**; however, the use of isopropanol is required to drive the process towards formation of the final secondary alcohol by reducing the minor amount of ketone formed during the reaction. As a limitation, and as observed in Scheme 12, no diastereocontrol is achieved for the hydrogen back-transfer. Of particular interest, a bidirectional multiple addition to two allylic alcohols was developed, affording compound **14c** in 45% yield.

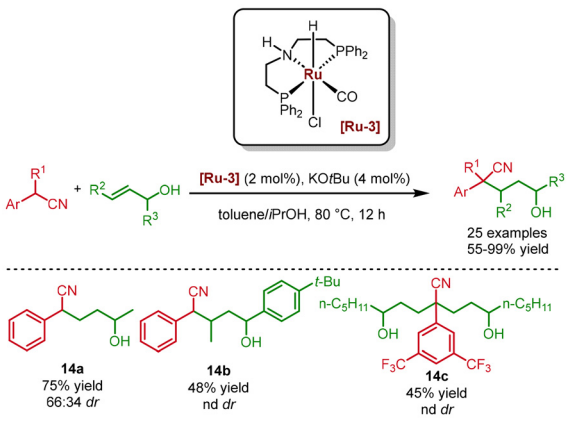
Extending the potential of this approach, the same team reported in 2024 that 2-naphthols could also participate in a borrowing hydrogen strategy with allylic secondary alcohols (Scheme 15).[18] Using the same **Ru-3** complex, various 2-naphthols were efficiently added to the transiently generated enone. As observed previously, the borrowing hydrogen process leaves a partial amount of unreduced ketone, and the use of isopropanol is required to achieve complete reduction to the secondary alcohol. This extension to another class of nucleophiles provided the desired functionalised aromatic compounds in 47–90% yield, although with the limitation that only racemic mixtures of alcohols were obtained.

Since a new stereocentre is created when allylic secondary alcohols are used in borrowing hydrogen reactions, considerable efforts have been devoted to developing different strategies capable of controlling the stereochemistry of these reactions.

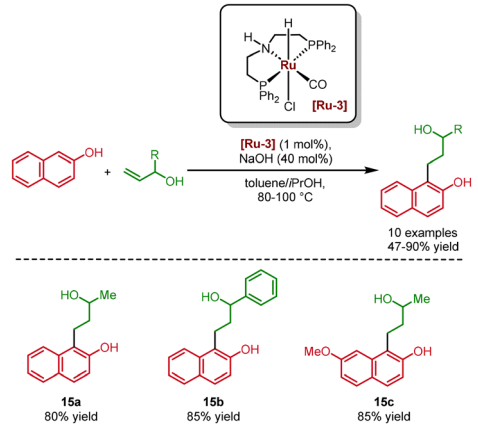
In 2022, the group of C. Wang reported that a chiral ruthenium complex could be employed to control the stereoselectivity during the addition of a Schiff base to allylic secondary alcohols (Scheme 16).[19] Starting from racemic alcohols, the first step of the catalytic cycle generates the reactive transi-



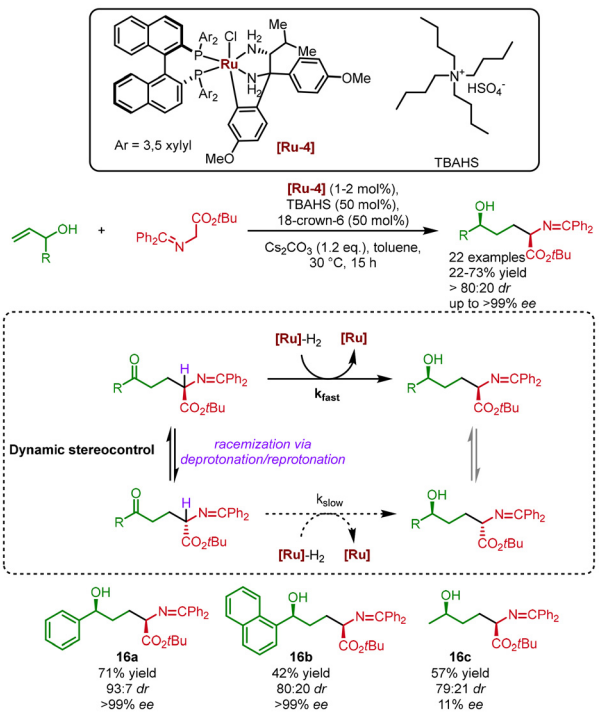
Scheme 13 Base-induced functionalisation of allylic alcohols by indoles.



Scheme 14 Ruthenium-catalysed addition of nitriles on secondary allylic alcohols.



Scheme 15 Ruthenium-catalysed addition of 2-naphthols on secondary allylic alcohols.

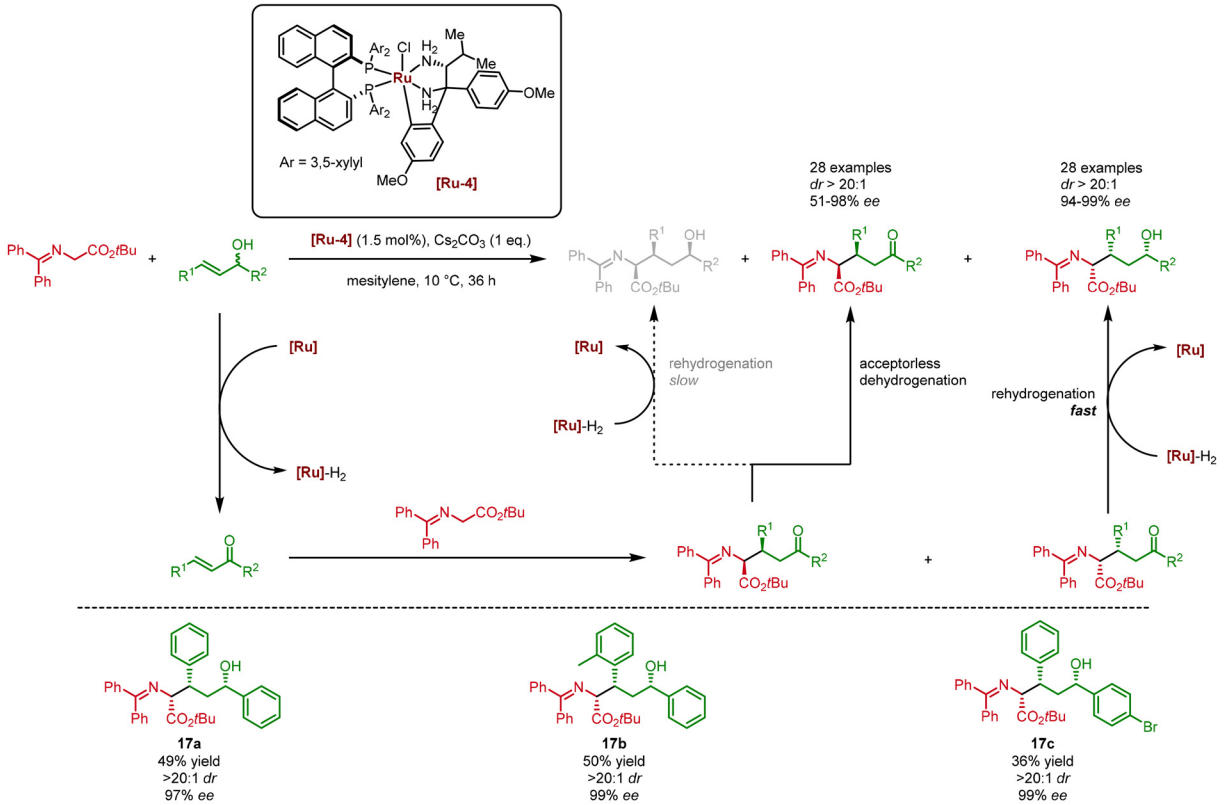


Scheme 16 Ruthenium-catalysed enantioselective addition of Schiff base on secondary allylic alcohols through dynamic kinetic asymmetric transformation.

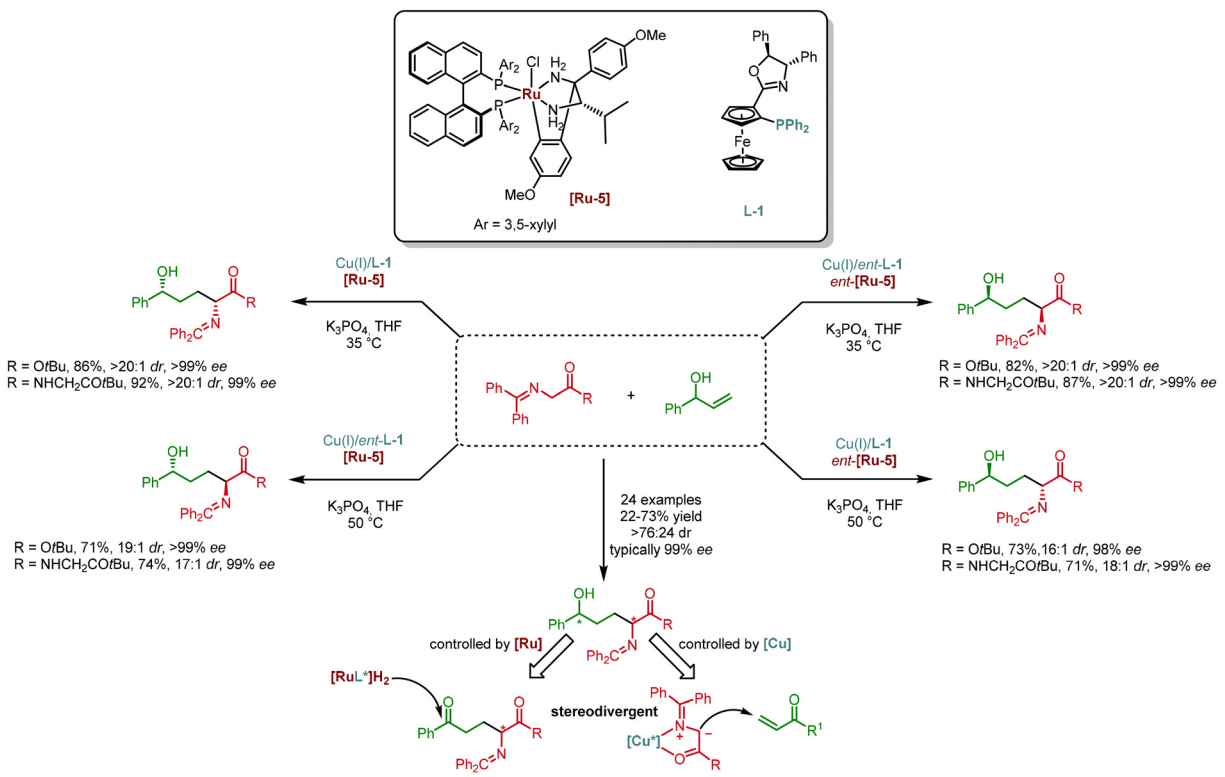
ent enone, which then undergoes base-induced 1,4-addition by the Schiff base to afford a racemic ketone. From this racemic ketone, the key step of the process is a dynamic kinetic asymmetric transformation that occurs during the back-hydrogen transfer mediated by the chiral ruthenium hydride complex. The pre-existing ester-stereocentre rapidly racemises through deprotonation/re-protonation, and only one enantiomer undergoes ketone reduction by the [Ru]-H_2 to generate the final major stereoisomer of the alcohol. Additionally, it was also found that the minor diastereomer of the final product also equilibrates to the major one. Starting from different allylic alcohols, 21 examples of secondary alcohols were prepared with typically more than 80 : 20 dr and >98% ee, demonstrating the high efficiency of stereocontrol by the ruthenium complex. A limitation arises when aliphatic ketones are hydrogenated in the final step, leading to only moderate enantiocontrol as observed for compound **16c**. Of interest, the reaction could be further applied to the concise synthesis of challenging 2,5-disubstituted pyrrolidines.

Starting from secondary allylic alcohols featuring a substituted terminal olefin, a different mechanistic scenario was observed in the reaction with ketimine-esters (Scheme 17).[20] In this example, an achiral base is used to activate the pro-nucleophile, leading to racemic Michael adducts upon 1,4-addition to the substituted enone. From this transient ketone, a divergent kinetic resolution pathway is observed when a chiral ruthenium catalyst is employed. One enantiomer is rapidly back-hydrogenated, leading to the enantioenriched alcohol. In contrast, the other enantiomer does not undergo reduction; instead, it leads to the expulsion of hydrogen from the metal coordination sphere in an acceptorless manner, providing the enantioenriched ketone. This highlights the diversity of mechanistic potential through which stereocontrol can arise in these borrowing hydrogen transformations of allylic alcohols. As a consequence of this kinetic resolution mechanism, both pseudo-enantiomeric products (ketones and alcohols) can be isolated in excellent diastereo- and enantioselectivity (>20 : 1 dr and >93% ee) with the alcohol products featuring three stereocentres, all of which are controlled during the last back-hydrogenation step by the chiral ruthenium complex.

Interestingly, the team of C.-J. Wang discovered that pro-nucleophilic ketimine esters could be activated by a chiral copper complex, enabling a valuable stereodivergent borrowing hydrogen strategy (Scheme 18).[21] This reaction follows the multicatalytic principles described previously, with a metal complex responsible for the reversible hydrogen transfer and a second catalyst promoting the nucleophilic addition. As a result, the stereochemistry of the 1,4-addition to the enone is exclusively controlled by the chiral copper complex. The chiral ruthenium complex operates through the same borrowing hydrogen mechanism as above, but in this case, it exclusively controls the stereoselectivity of the newly formed secondary alcohol upon back-hydrogen transfer. Of importance and in contrast with the previous examples, using a weaker base (K_3PO_4), the stereoinformation on the potentially stereochemically labile acidic stereocentre is preserved in the final product. Consequently, the two catalysts independently control each newly formed stereocentre, resulting in a fully stereodivergent transformation that provides access to all possible stereoisomers (diastereoisomers and enantiomers) with equal efficiency, simply by switching the chirality of one of the catalysts. Notably, in addition to esters, peptides were also tolerated as side chains of the pro-nucleophile, demonstrating the robustness and tolerance of the catalytic conditions and yielding valuable chiral molecules typically in more than 10 : 1 dr and 98% ee.



Scheme 17 Ruthenium-catalyzed addition of ketimine-esters on secondary allylic alcohols with kinetic resolution of the intermediate Michael adduct.



Scheme 18 Stereodivergent multicatalytic addition on secondary allylic alcohols.

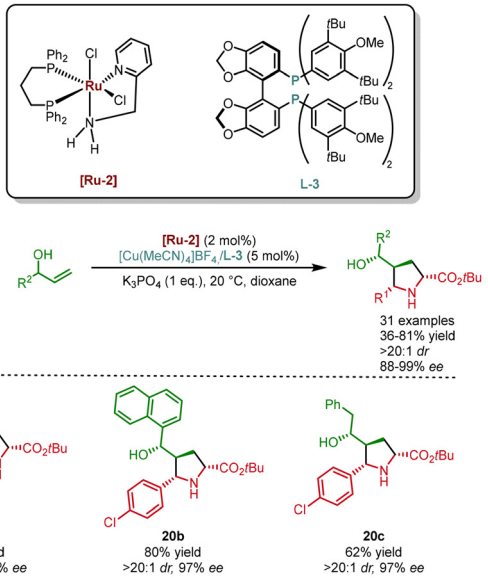
Following the same approach, the same team also reported that racemic cyclic ketimine esters are effective nucleophiles for reactions with allylic secondary alcohols (Scheme 19).[22] Once again, the system is fully stereodivergent, thanks to the combined use of a chiral ruthenium complex and a chiral copper complex, each independently controlling one of the newly created stereocentres. Importantly, challenging tetrasubstituted stereocentres are generated during the borrowing hydrogen process. The efficiency of the two catalysts in controlling the stereochemical outcome is reflected in the excellent levels of stereocontrol observed across all the chiral complex scaffolds obtained (typically >10 : 1 dr and 98% ee). Once again, aliphatic chains on the intermediate ketone provide lower stereocontrol, as often observed in enantioselective ketone hydrogenation.

Starting from aldimine pro-nucleophiles instead of ketimines, the potential of this multicatalytic approach could be extended to the direct cascade synthesis of substituted chiral pyrrolidines (Scheme 20).[23] The reduced number of substituents on the imine enables the aldimine esters to engage in a copper-catalysed enantioselective [3 + 2] cycloaddition with the transient enone generated upon ruthenium-catalysed dehydrogenation of the allylic alcohol. This cycloaddition controls the three new stereocentres formed on the pyrrolidine. Subsequent back-hydrogen transfer to the ketone forms the final secondary alcohol. Because an achiral ruthenium complex is used for this borrowing hydrogen step, the diastereoselective back-hydrogen transfer is governed by the chirality already present on the pyrrolidine ring, which dictates the stereoselectivity of the newly formed alcohol stereogenic centre. Such a reaction, which controls four stereogenic centres within a single catalytic cycle, demonstrates the power of multicatalytic borrowing hydrogen transformations on allylic alcohols.

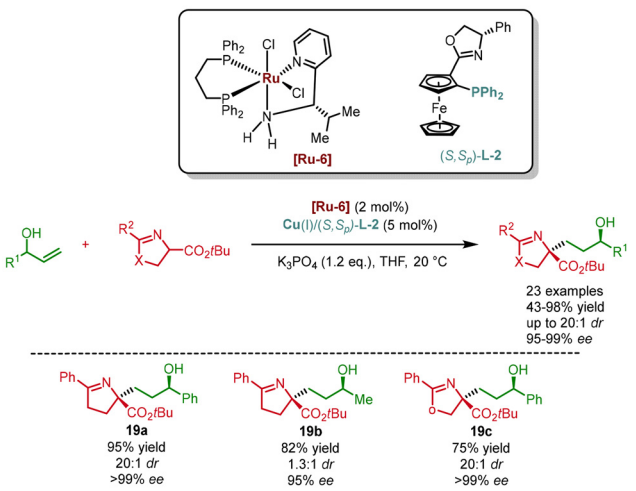
Recently, the groups of Dong, Wang and Kong independently extended the scope of nucleophiles to include the use of azaaryl acetates (Scheme 21).[24] The corresponding copper-enolate reactive intermediate is readily formed by additional coordination with the pyridine substituent. When using a chiral copper complex, the resulting 1,4-addition to the enone controls the stereochemistry of the formed challenging quaternary centre. As already demonstrated on other substrates above, the process is fully stereodivergent, thanks to the independent control by the chiral ruthenium complex during the back-hydrogenation step that leads to the formation of the alcohol.

The value of this approach is that methyl-esters are used as pro-nucleophiles, which under the reaction conditions undergo *in situ* cyclisation to the corresponding δ-valerolactones, a scaffold of great interest known for the significant bioactivity of numerous derivatives. Once again, the independent stereocontrol by the two catalysts enables access to all possible stereoisomers of the δ-valerolactones with equal efficiency and high dia- and enantio-control (>10 : 1 dr and >95% ee).

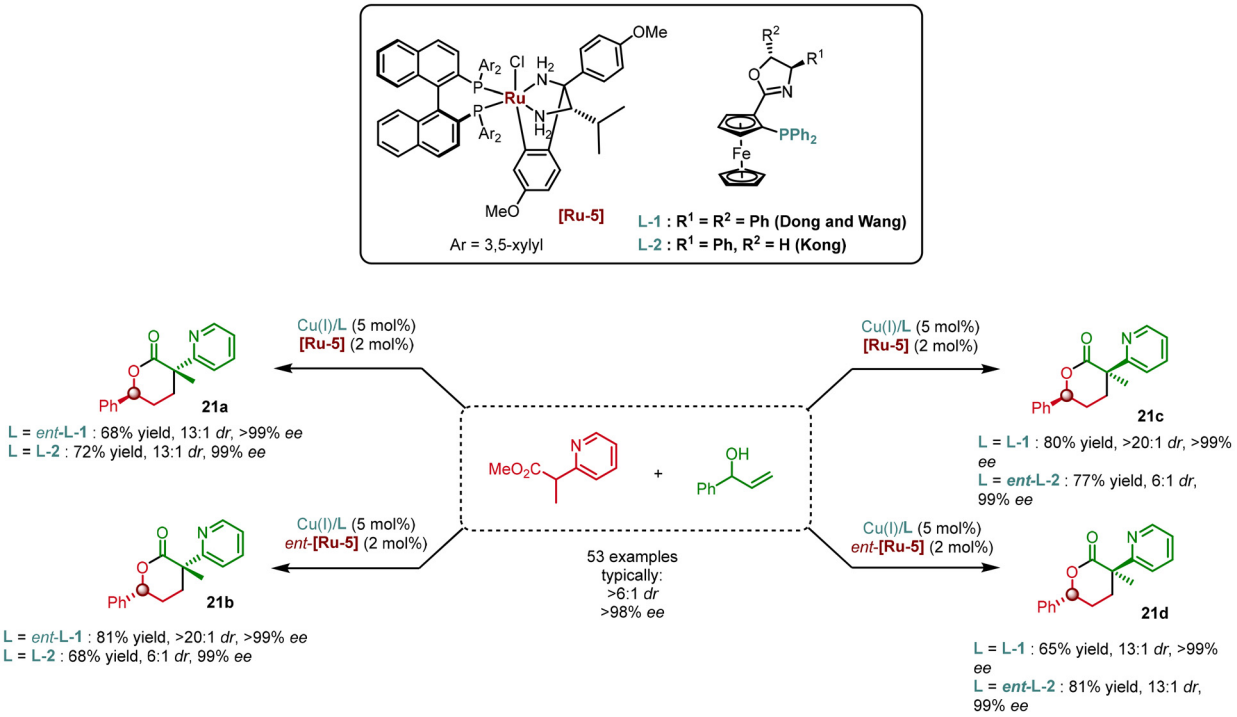
In 2025, the team of Dong and Wang used allenic alcohols – another class of secondary allylic alcohols – in a multicatalytic stereodivergent borrowing hydrogen method (Scheme 22).[25] This represents a challenging class of substrates, notably because of the potential ease with which the double bond can isomerise both in the starting alcohol and in the obtained final products. It was discovered that a particular class of pro-nucleophiles, α-fluoro azaaryl acetamides/acetates, could react efficiently with these allenic alcohols, producing the corresponding borrowing hydrogen products. Using K_3PO_4 as the base, the product, featuring a fluorinated tetra-substituted stereocentre, was isolated, with the two stereocentres independently controlled by the chiral copper and ruthenium complexes. Significantly, when switching conditions by modulating



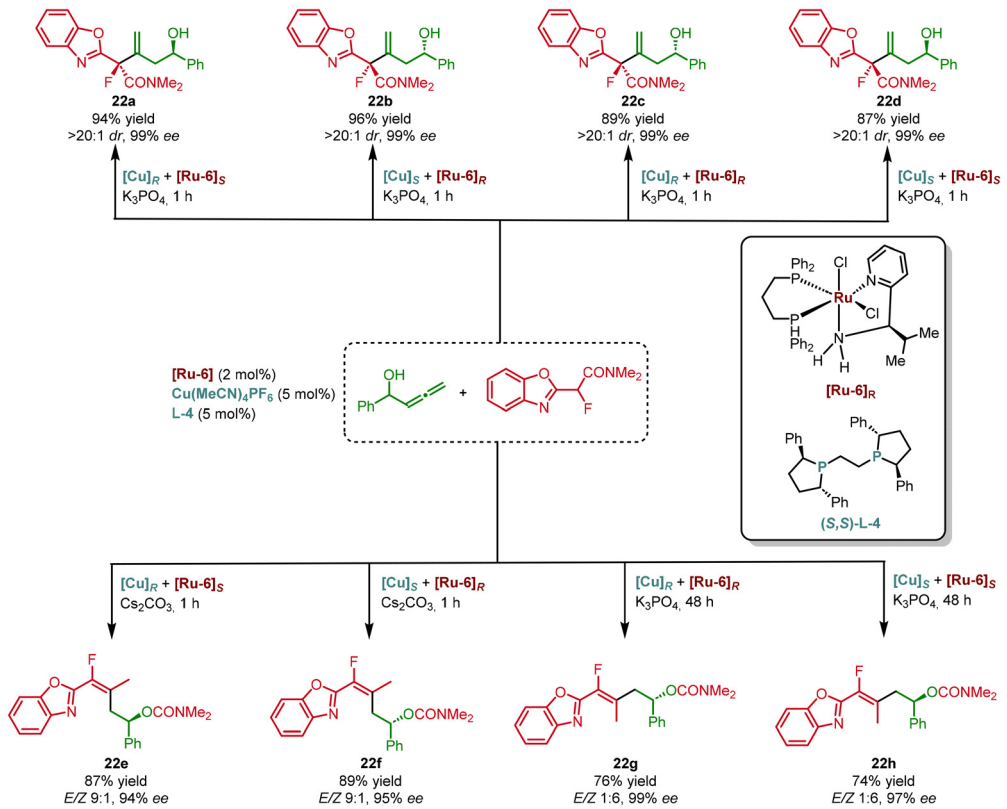
Scheme 20 Multicatalytic cycloaddition of aldimine-esters on secondary allylic alcohols.



Scheme 19 Stereodivergent multicatalytic addition of cyclic ketimine esters on secondary allylic alcohols.



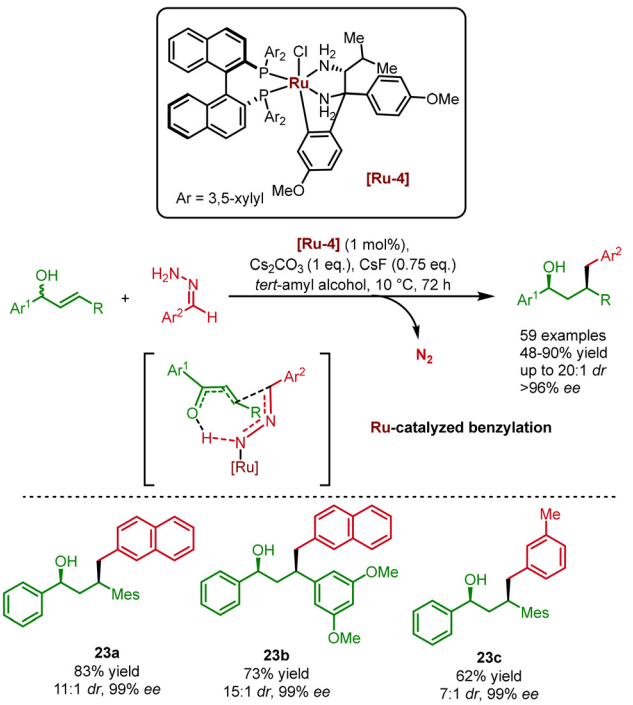
Scheme 21 Stereodivergent multicatalytic addition of aza-aryl acetates on secondary allylic alcohols.



Scheme 22 Stereodivergent multicatalytic addition on allenic allylic alcohols.

the base used (Cs_2CO_3), a retro-Claisen fragmentation followed by double bond isomerisation was observed, leading to *E* alkenes. Moreover, when K_3PO_4 was used, and the reaction was stirred for a longer time (48 hours *vs.* 1 h), the *Z*-alkenes could be isolated selectively. This discovery highlights the diversity of substrates accessible through simple changes in the reaction conditions and catalyst's chirality, in this case, enabling access to all four possible stereoisomers of the non-rearranged products, as well as the four possible stereoisomers of the rearranged alkenes.

The last example of carbonyl nucleophile addition to secondary allylic alcohols took advantage of the particular reactivity of hydrazones (Scheme 23).[26] Hydrazones are pro-nucleophiles that can be activated to induce aryl transfer upon N_2 liberation. The team of Wang discovered that secondary allylic alcohols could react with hydrazones in the presence of a chiral ruthenium complex. From the transiently generated enone, the chiral ruthenium complex catalyses the hydrazone addition through coordination to the terminal nitrogen atom, thereby controlling the stereochemistry of the newly formed stereocentre. Subsequent back-hydrogen transfer to the ketone, controlled by the same ruthenium complex, generates the final stereocontrolled alcohol. It must be noted that no hydrogenation of the hydrazone is observed under these reaction conditions. Overall, this reaction is of great interest since it allows the addition of benzyl nucleophile equivalents, which are impossible to access by borrowing hydrogen using other methods.



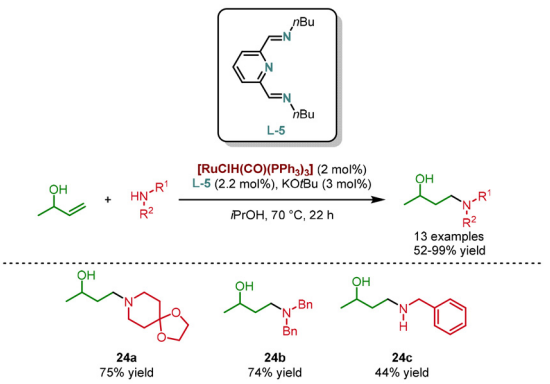
Scheme 23 Addition of benzyl nucleophile equivalents to allylic alcohols.

(IIb) 1,4-Addition of nitrogen-centered nucleophiles

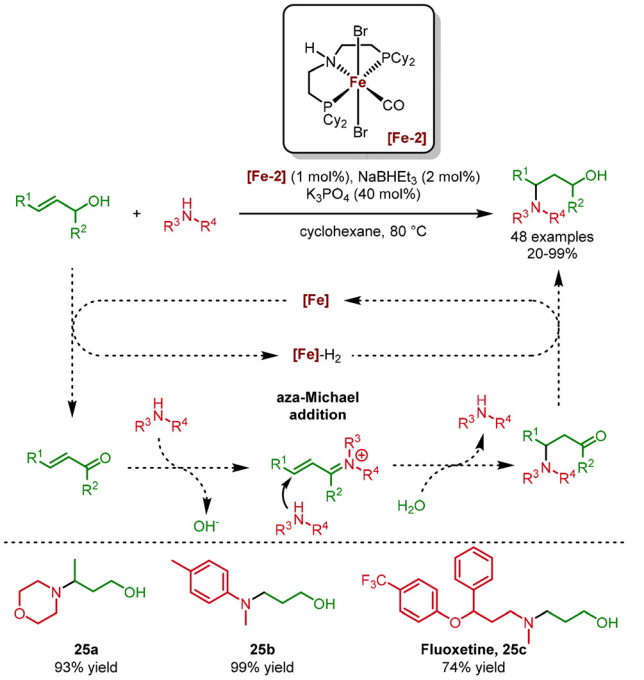
Heteroatoms-centred nucleophiles, such as amines, represent another important class of partners used with allylic alcohols in borrowing hydrogen reactions. Following 1,4-addition to the α,β-unsaturated compound and subsequent back hydrogen transfer, they provide access to 1,4-amino-alcohols, which are otherwise difficult to obtain. However, the development of such transformations faces numerous challenges. Most notably, competition between 1,4-addition to the α,β-unsaturated compound and 1,2-addition leading to imine formation can occur. Additionally, the 1,4-addition of nitrogen-centred nucleophiles is also highly reversible, creating a considerable challenge when trying to control the enantioselectivity of this step.

In 2015, the group of Ohta first focused on this challenging transformation using an achiral ruthenium complex (Scheme 24).[27] Starting from secondary allylic alcohols with terminal alkenes, a range of primary and secondary amines reacted efficiently (52–99% yield). This reaction represents an interesting formal *anti*-Markovnikov hydroamination of alkenes, providing in a single step the key 1,4-amino-alcohols from simple substrates. Of importance, a large excess of isopropanol is used, which is necessary to reduce, through hydrogen transfer, the small amounts of undesired ketones formed. Relatively high temperatures (typically 80 °C) are also necessary to drive the reaction to completion using this ruthenium catalyst. More recently, the team of Zhang, Hao and Lin have shown that using an alternative ruthenium pincer complex promoted the reaction on a wider scope of allylic alcohols, notably substituted alkenes, albeit without diastereocontrol.[28]

In 2019, the teams of Xiao and Wang found that the reaction could be effectively promoted by using a non-noble metal-based iron complex (Scheme 25).[29] Applying only 1–2 mol% of this iron complex, activated by $NaHBEt_3$, the formal hydroamination was efficiently carried out on a broad range of allylic alcohols and secondary amines. Mechanistic investigations revealed that the amines also potentially catalysed the 1,4-addition through iminium ion formation. This borrowing hydrogen was notably applied to the synthesis of fluoxetine **25c**.

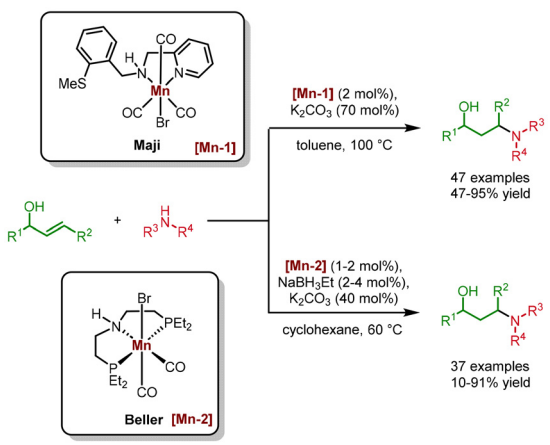


Scheme 24 Ruthenium-catalysed 1,4-amino-alcohol synthesis through reaction of amines with allylic alcohols.



Scheme 25 Iron-catalysed 1,4-amino-alcohol synthesis through reaction of amines with allylic alcohols.

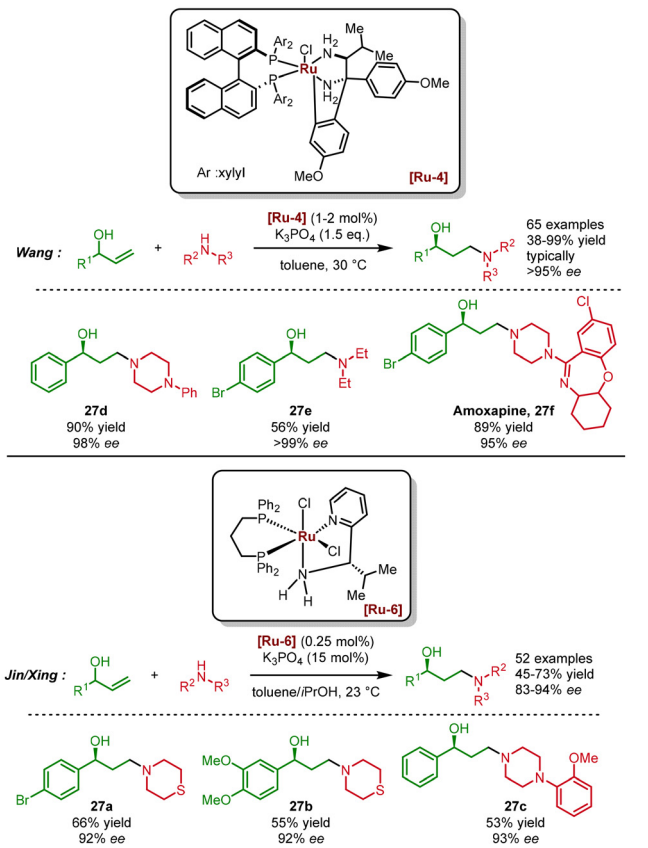
In 2021, the groups of Maji and Beller independently reported that manganese complexes could be efficient to catalyse such formal hydroamination of allylic alcohols (Scheme 26).[30] For this purpose, the group of Maji used a diamine manganese complex, while Beller and co-workers identified an efficient PNP pincer manganese catalyst. Both complexes were active in the borrowing hydrogen–nitrogen 1,4-addition, tolerating various substitutions on the allylic alcohols. However, when using these substituted alcohols (disubstituted alkenes or secondary alcohols), only highly nucleophilic secondary amines were tolerated in the borrowing hydrogen process.



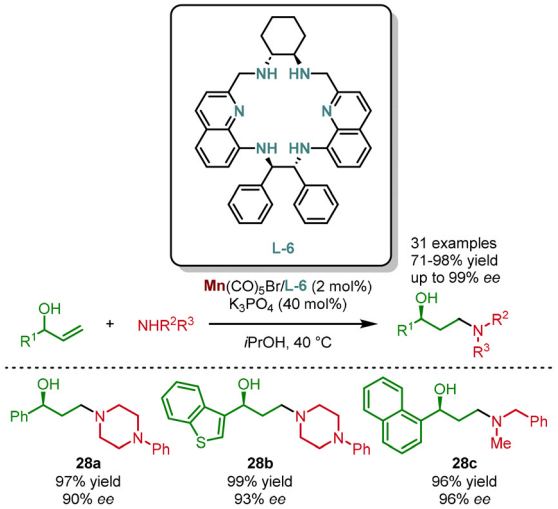
Scheme 26 Manganese-catalysed 1,4-amino-alcohol synthesis through reaction of amines with allylic alcohols.

While the previously mentioned studies led to racemic compounds, the groups of Wang and Jin and Xing independently found in 2020 that chiral ruthenium complexes could be used to control the stereochemistry of the newly generated secondary alcohols in such reactions (Scheme 27).[31] Wang used the ruthenacycle **Ru-4**, and Jin and Xing used **Ru-6**. Both catalysts feature a diphosphine and a chiral amine chelating ligand, ensuring optimal reactivity for the borrowing hydrogen cycle and good enantiocontrol during the back-hydrogen transfer to the generated ketone (typically >90% ee). The reaction was limited to terminal alkene-allylic alcohols, but a variety of secondary amines, both cyclic and acyclic, could be used. Moreover, using **Ru-4**, it has been shown that primary amines were also good nucleophiles in this reaction. Compared to the previous results using ruthenium complexes, no extra isopropanol as a hydrogen donor was required for optimal reactivity, indicating that no dihydrogen was lost from the metal coordination spheres. The strong synthetic potential of this transformation was highlighted in the concise synthesis of various bioactive molecules, such as cytisine, amoxapine or fluoxetine.

In 2022, Chen and Fan designed a new, elegant non-precious chiral manganese complex based on a N_6-macrocyclic ligand (Scheme 28).[32] This complex was highly active and



Scheme 27 Ruthenium-catalysed enantioselective 1,4-amino-alcohol synthesis through reaction of amines with allylic alcohols.



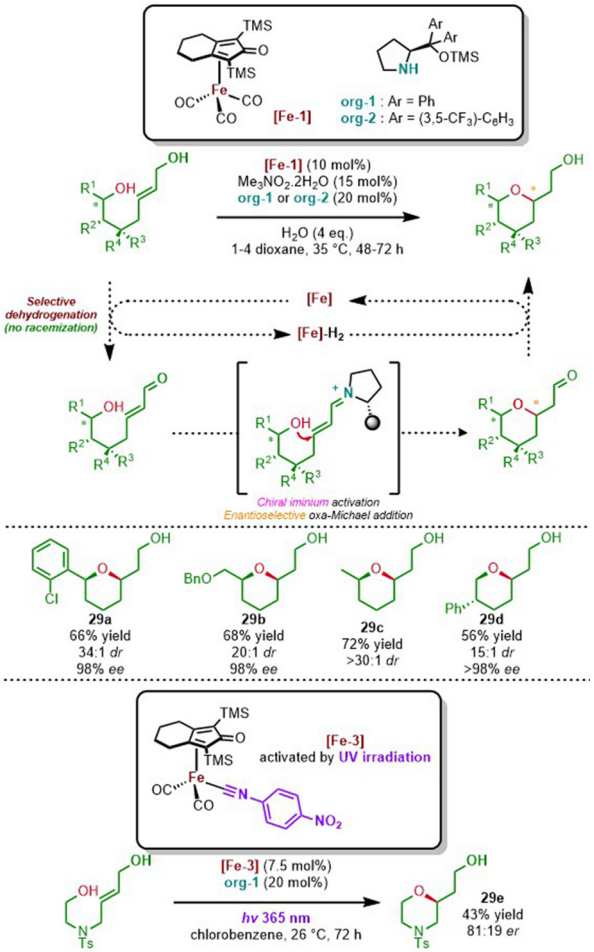
Scheme 28 Manganese-macrocyclic ligand complex for enantioselective 1,4-amino-alcohol synthesis.

selective in the formal hydroamination by reaction of primary and secondary amines with secondary allylic alcohols bearing terminal alkenes. A considerable effect of the macrocyclic structure is observed in this reaction, since non-macrocyclic complexes did not provide any reactivity in the borrowing hydrogen process. This effect was explained by a possible macrocyclic template effect with additional H-bonds between the ligands and the substrate. Isopropanol is also required here to facilitate back-hydrogen transfer to the non-reduced ketone. Overall, this study shows the potential of borrowing hydrogen enantioselective transformations using easily accessible and cheap, non-precious metal complexes. Recently, the team of Li, He and Hou also applied another chiral manganese complex to the same transformation, providing the chiral 1,4-amino-alcohols in up to 92% ee, even though enantiocontrol was generally lower than using the macrocyclic ligand.[33]

(IIc) 1,4-Addition of oxygen-centred nucleophiles

Despite the crucial synthetic prevalence of 1,3-di-oxygenated motifs in natural products and drugs, the 1,4-addition of alcohols to α,β-unsaturated carbonyl compounds is even more challenging, given its high reversibility, thus considerably limiting the potential of oxa-Michael additions in synthesis. Given the potential irreversible nature of the back-hydrogen transfer in borrowing hydrogen reactions involving allylic alcohols, this approach could serve as a handle to promote otherwise challenging transient 1,4-addition of alcohols to α,β-unsaturated carbonyl compounds. However, a major difficulty in the development of an addition reaction of an alcohol to an allylic alcohol *via* borrowing hydrogen is the selective dehydrogenation of the allylic alcohol.

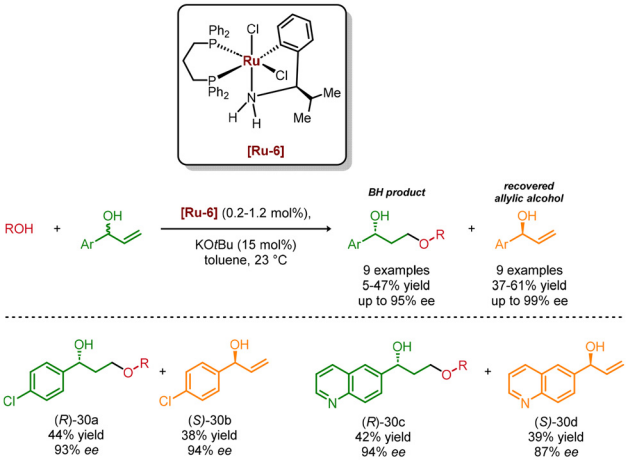
The concept of addition of alcohols to allylic alcohols was demonstrated in 2024 by our group in an intramolecular fashion (Scheme 29).[34] This method provides rapid access to functionalised tetrahydropyranes, another class of crucial



Scheme 29 Multicatalytic reaction of alcohols with allylic alcohols.

motifs present in numerous bioactive compounds. The key to success was the application of a multicatalytic system combining the iron complex and a chiral pyrrolidine organocatalyst. Of interest, the iron complex selectively induces the allylic alcohol dehydrogenation to the reactive α,β-unsaturated aldehyde without affecting the nucleophilic primary or secondary alcohols. The chiral organocatalyst controls the stereoselectivity during the oxa-Michael addition, with a process that could be diastereoselective starting from chiral nucleophilic alcohols or enantioselective starting from achiral starting materials. In the latter case, light-activated complex **[Fe-3]** had to be used for success. Importantly, the irreversible back-hydrogen transfer prevented any racemisation of the product through retro-oxa-Michael addition.

Following their investigation of intermolecular aza-Michael additions on allylic alcohols, the team of Yu and Xing discovered that the chiral ruthenium complex selectively dehydrogenated one enantiomer over the other of starting secondary allylic alcohols (Scheme 30).[35] Combined with simple alcohols (methanol, ethanol or benzyl alcohol), an enantioselective borrowing hydrogen could occur providing the desired 1,3-di-oxygenated desired products. As a limitation, given the observed



Scheme 30 Enantioselective oxa-Michael through kinetic resolution of allylic alcohols.

kinetic resolution mechanism, only half of the racemic starting allylic alcohol reacted and the other enantiomer of the allylic alcohol was recovered.

In 2025, He, Fan and co-workers identified that the chiral macrocyclic manganese complex could promote with great efficiency the enantioselective addition of alcohols to secondary-allylic alcohols (Scheme 31).[36] The reaction worked the best notably using large excess of simple alcohols such as methanol, providing the 1,3-di-oxygenated compounds in >80% ee. Further derivatizations indicated that the methyl substituent could be removed from the ether to generate the 1,3-diol.

To date, these limited examples represent the only additions of nucleophilic alcohols to allylic alcohols processing through borrowing hydrogen mechanism, which despite their great synthetic utility have been poorly studied.

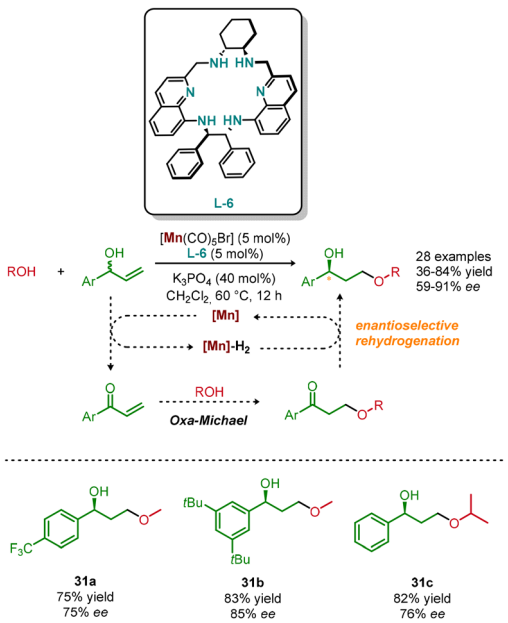
(IId) 1,4-Addition of hydrogen-centred nucleophiles

The last class of nucleophiles used in 1,4-additions *via* borrowing hydrogen functionalisation of allylic alcohols is hydride donors. In 2024, Morrill and co-workers identified isopropanol as a hydrogen source to effectively promote the reduction of allylic alcohols to aliphatic alcohols (Scheme 32).[37] In contrast to classical alkene hydrogenations, the mechanism involves an iron-catalysed initial dehydrogenation to an α,β-unsaturated aldehyde, followed by double hydride addition through 1,4- then 1,2-addition. This allows the use of an iron-cyclopentadienone complex as a cheap, available catalyst, which is usually inactive in C=C bond hydrogenation.

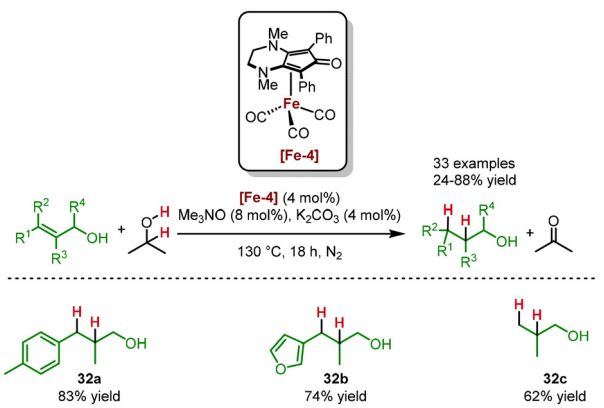
(III) Direct alcohol functionalisation through 1,2-addition to the transient carbonyl

(IIIa) 1,2-Addition using amines as nucleophiles

While all the above-mentioned reactions involving allylic alcohols focused on the reactivity of the intermediate α,β-unsaturated compounds in a 1,4-addition, different groups have explored 1,2-additions on the intermediate electrophiles. Such mechanisms based on borrowing hydrogen reactivities are complementary to Tsuji–Trost allylic substitutions, avoiding the requirement for additives that are often necessary to activate the hydroxyl group in the starting allylic alcohols.[38] However, in contrast with most of the above-mentioned reactions involving a 1,4-addition, the use of borrowing hydrogen for formal allylic substitution typically requires higher temperatures to reach completion. This might be due to the higher temperature required to drive the reaction to completion through back-hydrogen transfer to the intermediate unsaturated compound.



Scheme 31 Manganese-macrocyclic ligand complex for oxa-Michael reaction.



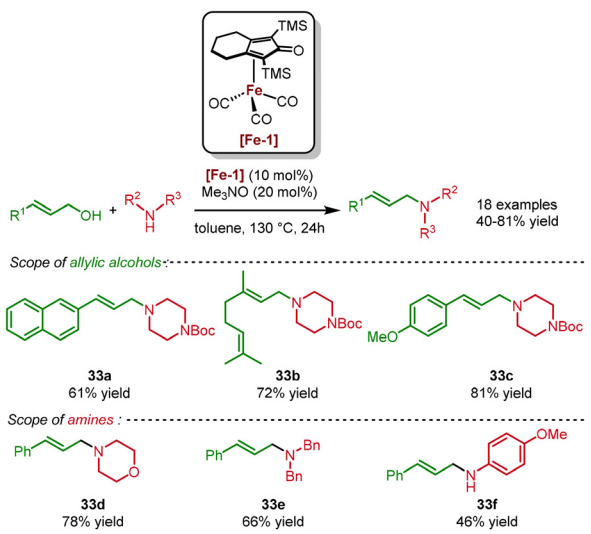
Scheme 32 Iron-catalysed reduction of allylic alcohols through borrowing hydrogen.

In this context, the team of Sundararaju disclosed a borrowing hydrogen type allylic amination of primary allylic alcohols (Scheme 33).[39] The interest of this method lies in the application of a cheap iron-cyclopentadienone complex activated by Me_3NO, even though 10 mol% of the iron complex is required for optimal reactivity. At 130 °C, a broad range of secondary and primary amines reacted efficiently to generate useful allylic amines in 40–81% yield. Interestingly, no side isomerisation of the double bond, or 1,4-addition of the amine to the intermediate α,β-unsaturated aldehydes were observed under the reaction conditions. Control experiments confirmed that the reaction processes through a borrowing hydrogen mechanism and not through a conventional direct allylic substitution.

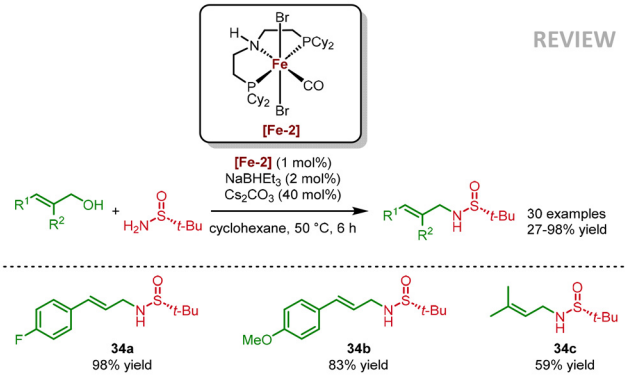
The group of Ma and Wang subsequently applied a Fe-PNP complex **Fe-2** in the allylic substitution of chiral *tert*-butylsulfinamide with primary allylic alcohols (Scheme 34).[40] This enantiopure sulfinamide reacted efficiently with primary allylic alcohols, affording the desired allylic sulfinamides with yields typically higher than 80%. As a limitation of this methodology, a glovebox was required to carry out the reaction due to the ligands used being rather oxygen sensitive. Even though at first glance the use of a chiral auxiliary may not appear relevant in this reaction, considering it does not create any stereogenic centre, the high potential of the obtained chiral molecules was demonstrated in the use of the enantiopure allylic amine as a chiral ligand for a rhodium complex. The resulting chiral complex can catalyse an enantioselective addition of boronic acid to cyclohexanone, leading to a high enantiomeric excess of 97% for the obtained product.

Aside from non-noble metals, in 2021, Luo and co-workers found that the iridium N,N-complex **Ir-1** was highly reactive for the reaction of amines on primary allylic alcohols (Scheme 35).[41]

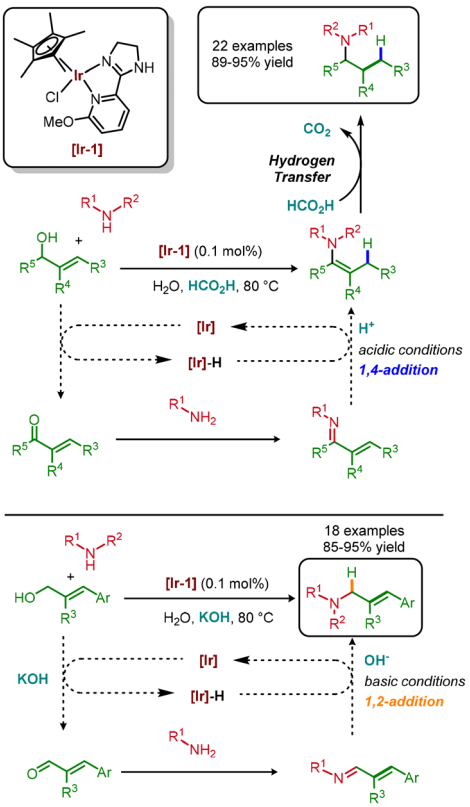
Under basic conditions, the borrowing hydrogen mechanism through imine or iminium formation and 1,2-hydrogen back transfer was favoured, providing 18 examples of variously



Scheme 33 Iron-catalysed allylic amination of primary allylic alcohols.



Scheme 34 Iron-catalysed allylic amination of primary allylic alcohols using *tert*-butylsulfinamide.



Scheme 35 Iridium-catalysed allylic amination of primary allylic alcohols.

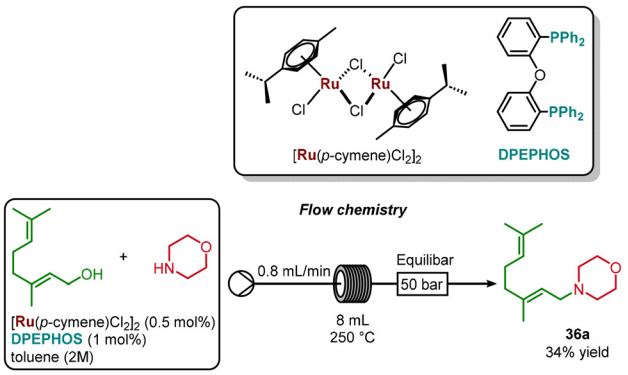
substituted secondary or tertiary allylic amines, all obtained in more than 85% yield. However, under acidic conditions (HCOOH), an alternative mechanistic pathway involving 1,4-hydrogen back-transfer to the conjugated imine, followed by another hydrogen transfer, led to the obtention of a saturated amine. In this case, formic acid acts as an additional hydrogen source to obtain the fully reduced product. As a result, it is possible to obtain, with equal efficiency, both allylic and aliphatic amines, simply by changing conditions (acidic or basic).

Aside from this example using an iridium complex, in 2019, the group of Ley reported a ruthenium-catalysed amination using one example of primary allylic alcohol in flow (Scheme 36).[42] Using only 0.5 mol% of a commercial ruthenium complex ([Ru(*p*-cymene)Cl_2]$_2$), a single example of allylic amine **36a** was prepared with 34% NMR yield.

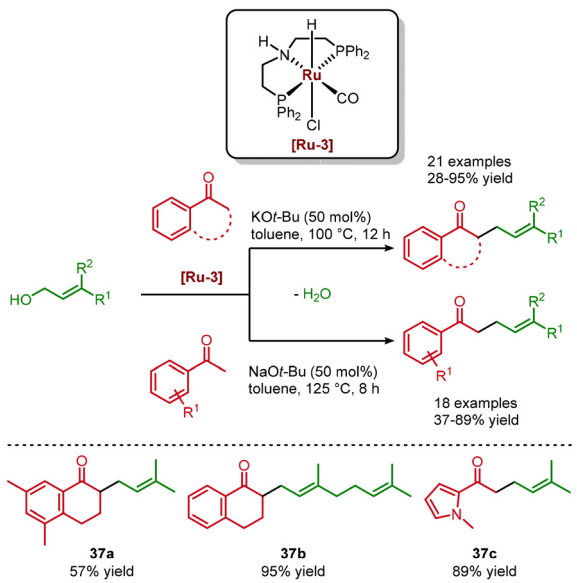
(IIIb) 1,2-Addition using carbonyls as pro-nucleophiles

Aside from amines as nucleophiles, the group of Gunanathan also reported that ketones could be reacted with primary allylic alcohols, through a 1,2-addition to the intermediate α,β-unsaturated aldehyde (Scheme 37).[43]

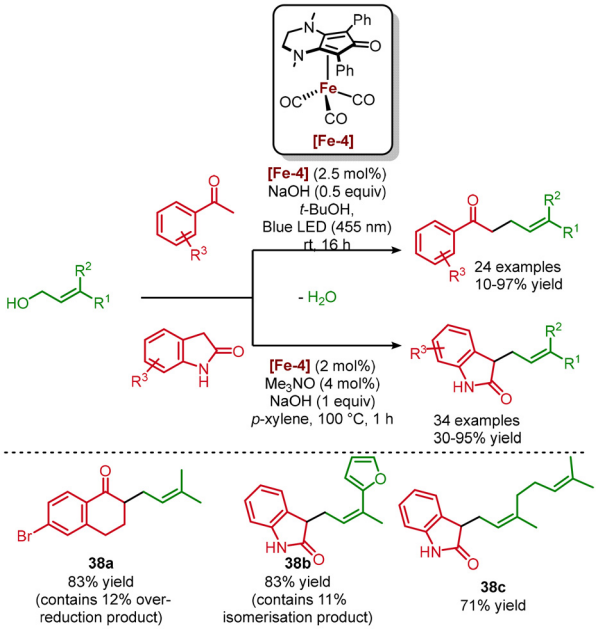
The reaction could be efficiently carried out using only 0.1 to 1 mol% of ruthenium pincer catalyst **Ru-3** and a base, generating the alkylated ketone products with typically more than 65% yield. While a broad range of cyclic ketones and acetophenone derivatives could be efficiently condensed on primary allylic alcohols, the scope of allylic alcohols only focused on tri-substituted alkenes, leading to prenylated ketones of interest. The mechanistic pathway *via* a borrowing hydrogen process could also be confirmed by different mechanistic observations.



Scheme 36 Ruthenium-catalysed 1,2-amination using flow chemistry.



Scheme 37 Ruthenium-catalysed reaction of ketones with primary allylic alcohols through 1,2-addition.



Scheme 38 Iron-catalysed reaction of ketones and oxindoles with primary allylic alcohols through 1,2-addition.

The teams of Poater and Renaud and the one of Sundararaju exploited the reactivity of iron complex [Fe-4] to perform similar formal 1,2-addition of different nucleophiles with allylic alcohols.[44] Under blue-light irradiation, 2.5 mol% of this simple iron complex could be activated through one CO removal, to catalyse efficiently the borrowing hydrogen condensation of a broad array of acetophenones in up to 97% yield. Using Me_3NO as activating reagent for the iron complex, it was shown that substituted oxindoles were efficient nucleophiles, leading to the selective *C*-functionalisation without any *N*-alkylation. In both cases, as limitations, tri-substituted alkenes were used to limit the potential side-reactions such as over reduction and final double-bond isomerisation, observed in most cases in minor amounts together with the desired products (Scheme 38).

Despite its interest for the easy prenylation of ketones, the cited reactions represent so far, the only examples of C–C bond formation through 1,2-addition in borrowing hydrogen using allylic alcohols which should find other applications within the next years.

(IV) Di-functionalisation through cascade 1,4-addition and additional trapping

One of the great advantages of using allylic alcohols in borrowing hydrogen is the possibility to functionalise different posi-

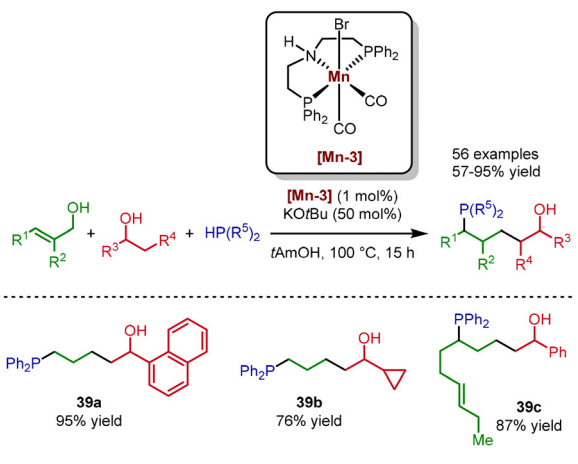
tions *via* cascade reactions, further increasing the generated molecular complexity. Indeed, the transient α,β-unsaturated aldehyde can react in cascades with nucleophiles through 1,4- and 1,2-additions leading to a 1,3-difunctionalisation of allylic alcohols. In addition, the enolate generated upon 1,4-addition can also react with another electrophile, leading to a 1,2-difunctionalisation of the starting allylic alcohol. Once the challenges of compatibility between the substrates and selectivity of the additions are solved, these cascade transformations offer the possibility to generate greater molecular complexity through a single reaction. The first examples of such cascades were only reported recently, and to this day, despite the great interest in this approach, only three different transformations have been reported.

In 2024, the teams of Liu and Zhao used a pincer PNP-manganese complex to trigger a cascade 1,3-carbophosphination through the multicomponent reaction of primary allylic alcohols, diarylphosphine and an aliphatic alcohol chain (Scheme 39).[45]

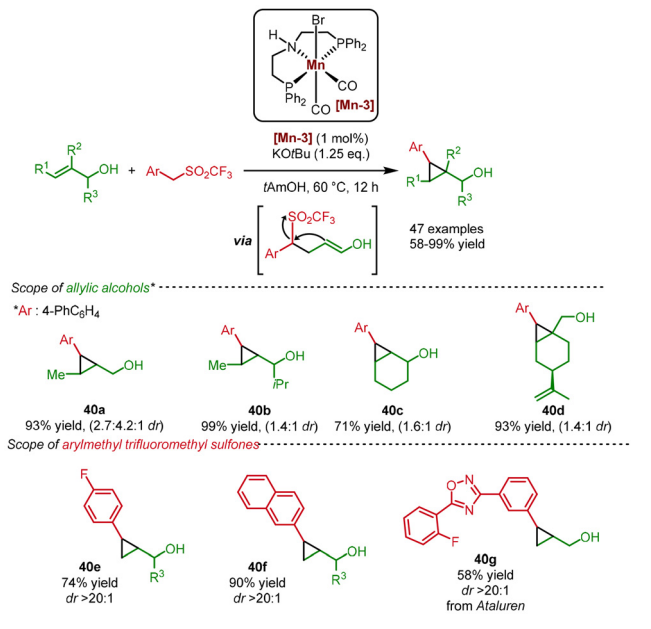
The catalytic cycle of this 1,3-difunctionalisation starts with an initial dehydrogenation of the allylic alcohol by the manganese complex, forming the intermediate α,β-unsaturated aldehyde. The other alcohol is also dehydrogenated to generate the pro-nucleophilic ketone, in this case an acetophenone derivative. The α,β-unsaturated aldehyde then reacts through 1,4-addition with the diarylphoshine to generate an aldehyde, trapped by condensation with the enolate of the ketone. The newly formed α,β-unsaturated ketone is then back-hydrogenated twice to generate the new secondary alcohol chain. As a result, through this cascade, a new C–P and a C–C bond are created from two initially unreactive alcohols, demonstrating the interest of borrowing hydrogen cascades. The interest of the obtained 1,3-difunctionalised ε-hydroxy phosphine was demonstrated through subsequent transformations of the different alcohols and diarylphosphines, highlighting the versatility of the products in synthesis. Mechanistic studies showed that the manganese-catalysed dehydrogenation of the secondary alcohol was involved in the rate-determining step, confirming the relative ease of allylic alcohol dehydrogenation.

The same year, Liu and co-workers reported the difunctionalisation of allylic alcohols through the reaction of sulfones and secondary or primary allylic alcohols, catalysed by the same manganese pincer complex (Scheme 40).[46] This reaction makes use of the dual reactivity of aliphatic sulfones, acting both as a nucleophile performing a 1,4-addition on the intermediate α,β-unsaturated carbonyl compound, and then as an electrophile in a subsequent cyclisation. As a result, in this cascade, the double bonds of allylic alcohols are readily transformed into substituted cyclopropanes. The products were obtained as racemates, but while the cyclisation was perfectly diastereoselective, the back hydrogen transfer to ketones only resulted in modest diastereocontrol (2.8 : 1 dr to 6.7 : 1 dr). Additionally, when starting from substituted allylic alcohols, the diastereoselectivity was also low during the 1,4-addition. Highlighting the broad substrate tolerance of the borrowing hydrogen reaction, this 1,2-difunctionalisation could be applied in the late-stage functionalisation of complex molecules such as commercial drug fragments.

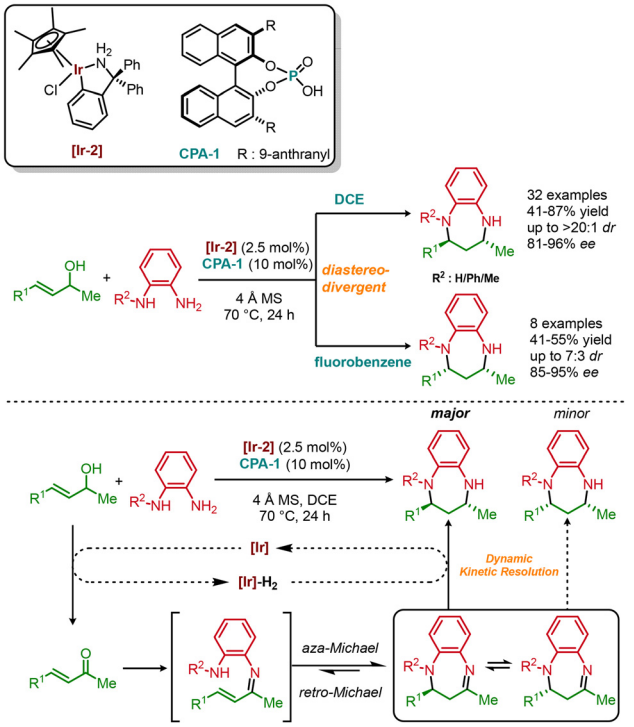
The last example of allylic alcohol difunctionalisation is an enantioselective borrowing hydrogen strategy, which was developed by the groups of Yang and Zhao. For this purpose, they reacted aromatic 1,2-dianilines with secondary allylic alcohols under dual iridium and phosphoric acid catalysis (Scheme 41).[47] Upon iridium-catalysed allylic alcohol dehydrogenation, the diamine undergoes double addition to the formed enone. This condensation is reversible, and the back-hydrogen transfer, co-catalysed by the chiral iridium complex and chiral phosphoric acid activating the imine, controls the stereoselectivity of the reaction. The result of this dynamic



Scheme 39 Manganese-catalysed 1,3-carbophosphination of allylic alcohols.



Scheme 40 Manganese-catalysed difunctionalisation of allylic alcohols.



Scheme 41 Enantioselective 1,3-diamination of secondary allylic alcohols.

asymmetric diamination of allylic alcohols is the efficient preparation of challenging tetrahydrobenzodiazepines, obtained with excellent stereocontrol (typically above 80 : 20 dr and 90% ee). Interestingly, a remarkable switch in diastereocontrol between *trans* and *cis* tetrahydrobenzodiazepines was observed simply by switching solvent from dichloroethane to fluorobenzene, even though no clear explanation could be provided for this behaviour. Overall, this study demonstrates the potential of allylic alcohol difunctionalisation in the stereoselective preparation of challenging substrates such as 7-membered ring heterocycles.

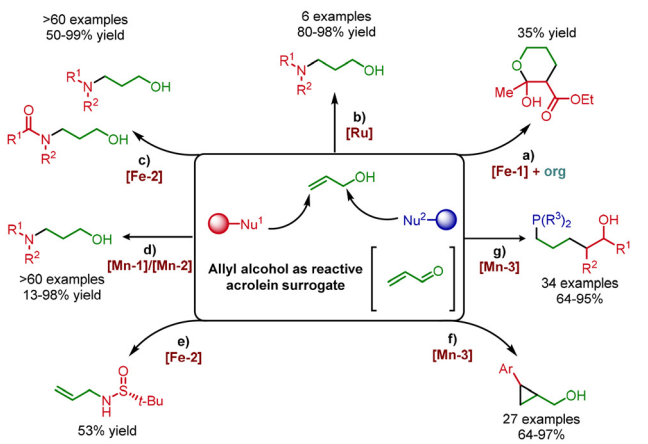
As seen from these examples, the investigation of difunctionalisation of allylic alcohols only started recently but offers broad perspectives for the development of other reactions, rapidly generating high molecular complexity in a single catalytic cycle. To date, no example of triple 1,2,3-functionalisation of allylic alcohols has been reported, even though such multicomponent cascades offer great potential for the construction of complex molecular architectures.

(V) Allyl alcohol as an acrolein surrogate

As a final remark, we would like to highlight a particularly useful application of the reactivity of allylic alcohols in borrowing hydrogen processes in the case of reactions involving the unsubstituted allyl alcohol. Indeed, during such borrowing hydrogen processes, metal-catalysed dehydrogenation of allyl alcohol transiently generates acrolein. Acrolein is a highly useful synthetic building block, which, despite its broad use, suffers from numerous drawbacks such as poor stability with a polymerisation tendency, and high toxicity. Moreover, its commercial availability was discontinued in recent years, which makes it necessary to find new broadly applicable acrolein surrogates.

In this context, borrowing hydrogen using the simple allyl alcohol is a smart solution to generate *in situ* the transient reactive acrolein and trap it before its polymerisation. This approach presents the advantage of requiring a cheap, less toxic starting material, to generate a poorly stable intermediate and directly transform it, prior to its decomposition. Many of the reactions presented in this review have also been applied to allyl alcohol and will be briefly presented in this section. These applications highlight one of the interesting applications of borrowing hydrogen, further demonstrating the usefulness of the approach from allylic alcohols.

Our group was the first to report the reaction of allyl alcohol with a keto-ester in the multicatalytic iron-complex/secondary amine system shown in Scheme 6, leading to the functionalized alcohol in a moderate 35% yield (Scheme 42a).[8] The alcohol formed is in equilibrium between the open and closed lactol form (shown). Later, Ohta and co-workers applied the ruthenium-catalysed reaction of nucleophilic secondary amines of Scheme 24 to allyl alcohol (Scheme 42b).[27] Upon transient acrolein generation, the amines could undergo a 1,4-aza-Michael reaction, to generate, after the back hydrogen transfer, six examples of useful 1,3-aminoalcohols. Generalising this reaction, the team of Xiao and Wang applied the iron complex in Scheme 25 for the functionalisation of allyl alcohols with nitrogen-centred nucleophiles (Scheme 42c).[29] The reaction tolerated an impressive scope of primary and secondary amines, but also amides, with more than 60 examples of products for the reaction on allyl alcohol described. In addition, it was also used in the late-stage func-



Scheme 42 Overview of borrowing hydrogen reactions on allyl alcohol.

tionalisation of natural products and drugs, demonstrating the robustness and strong potential of the method. Following this report, the two manganese complexes of Scheme 26 could also be applied to the hydroamination of allyl alcohol, once again with a large substrate scope with respect to the amine nucleophiles that can be used in the process, encompassing all kinds of primary or secondary amines (Scheme 42d).[30] Similarly, the manganese complex could be applied in the late-stage condensation of different complex, drug-like molecules with allyl alcohol.[30] Ma, Wang and co-workers also demonstrated on one example, like in Scheme 34, that *tert*-butylsulfinamide could perform a 1,2-addition on the transient acrolein starting from allyl alcohol to generate the allylated sulfonamide, obtained in 53% yield (Scheme 42e).[40]

More interestingly, the difunctionalisation of allyl alcohol through borrowing hydrogen methodology could be performed using different partners. Using arylmethyl trifluoromethyl sulfones and a manganese complex as in Scheme 40, the cyclopropanation of allyl alcohol led to 24 examples of substituted cyclopropanes, obtained in 64–97% yield, and more importantly, as single diastereomers (Scheme 42f).[46] Finally, the manganese multicomponent 1,3-carbophosphination shown in Scheme 39 could also be efficiently performed on allyl alcohol, leading to complex molecules bearing alcohol and phosphine functions (Scheme 42g).[45]

Overall, all of these examples demonstrate that applying allyl alcohol within borrowing hydrogen is a general method to bypass the problematic use of acrolein, with a variety of applications in the synthesis of numerous molecules of interest.

(VI) Conclusions

In summary, throughout recent years, borrowing hydrogen reactions involving allylic alcohols have evolved from a conceptual curiosity to a powerful modern platform for efficient molecular construction, avoiding unnecessary steps and stoichiometric activation reagents. The polarity inversion of allylic alcohol substrates upon the first step of dehydrogenation of the borrowing hydrogen catalytic cycle unlocks access to transient α,β-unsaturated carbonyl intermediates. The unique reactivity of allylic alcohols, stemming from their facile dehydrogenation and favourable hydrogen-return kinetics, enables borrowing hydrogen catalysis to operate often under milder conditions than classical alcohol alkylations, notably allowing the development of stereocontrolled versions of these reactions. This review highlights all the possibilities offered by borrowing hydrogen reactions using allylic alcohols through the reaction of the α,β-unsaturated carbonyl intermediates. In a 1,4-addition pathway on the intermediate, a wide array of carbon-, nitrogen-, oxygen-, and hydrogen-based nucleophiles can be incorporated, offering unmatched structural diversity. Importantly, multicatalytic strategies have emerged as the cornerstone for reactivity and stereocontrol, potentially allowing each step of the catalytic cycle to be optimised. In this context, the combinations of borrowing hydrogen catalysts with organocatalysts, copper complexes, and rhodium or ruthenium-based systems can generate products of remarkable complexity, including quaternary and tetrasubstituted stereocentres. The success of stereodivergent transformations illustrates the depth of stereochemical control now achievable in borrowing hydrogen processes, with potential access to all stereoisomers of the products. In a 1,2-addition pathway to the intermediate, the borrowing hydrogen reaction from allylic alcohols leads to an allylic alkylation of different nucleophiles, which is complementary to traditional allylic substitutions involving π-allyl intermediates.

Furthermore, the use of allylic alcohols in borrowing hydrogen chemistry enables cascade reactions that can functionalise multiple positions, greatly increasing molecular complexity through sequential additions. Although this strategy holds significant promise, it remains in its early stages, with only a few cascade transformations reported to date due to significant challenges, notably within partner compatibility and selectivity control. Nevertheless, these recent developments demonstrate that allylic alcohols can serve as platforms for multicomponent transformations, greatly expanding bond-forming opportunities in a single catalytic sequence and resulting in maximised molecular complexity using minimal stoichiometric reagents and steps.

Finally, aside from synthetic economies, all these approaches also reveal how borrowing hydrogen from allylic alcohols enables reactivities that would otherwise be impossible, such as the transient formation and derivatisation of unstable intermediates like acrolein, or stereocontrol in substrates susceptible to rapid racemisation.

In addition, increasingly sustainable catalyst systems based on iron and manganese are helping to shift the field away from precious metals, merging redox-economy and sustainability ideals. Applications to the streamlined synthesis of bioactive molecules and complex natural product fragments highlight the significant step and redox economies enabled by this chemistry.

Despite these achievements, other challenges remain, including solving compatibility issues between the reaction partners and avoiding undesired side reactions arising from the undesired transfer of hydrogen from the generated metal hydride to the other partners. To enable industrial applications, efforts to reduce catalyst loadings and use inexpensive catalysts should be an important research field in the coming years. While different systems allowed control of enantioselectivity of the borrowing hydrogen reactions, discovering new stereocontrolled reactions, notably stereodivergent ones, is also highly desirable. Finally, one-step multiple functionalisations of allylic alcohols are only beginning to emerge, and future works should unveil numerous other borrowing hydrogen cascade reactions transforming allylic alcohols into valuable complex scaffolds of interest.

Overall, borrowing hydrogen reactions from allylic alcohols stands as a rapidly advancing field with exceptional promise for the future of catalysis and sustainable processes, and we hope that this review will help design new reactions of interest based on these principles.

Author contributions

Conceptualisation, A. Q.; methodology, A. Q., investigation, M. V. P., M. F., M. O., A. K., A. Q.; writing – review and editing, M. V. P., M. F., M. O., A. K., A. Q.; supervision, A. Q. All authors have read and agreed to the published version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Data availability

This is a review. All datas are accessible through the original articles.

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