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The reactivity of alkenyl boron reagents in catalytic reactions: recent advances and perspectives

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Although organic boron reagents have found broad applications in organic synthesis, the development of new methodologies using alkenyl boron reagents has lagged behind compared to the more commonly employed aryl-substituted variants. However, in the past five years, several innovative methods have been introduced that exploit the unique reactivity of alkenyl and boron moieties. These methods, utilizing readily available alkenyl boron substrates, enable the synthesis of highly functionalized alkenes or alkyl boron products under mild conditions. This review highlights the most recent advances, focusing on the novel reactivity of alkenyl boron reagents in polar or radical pathways within catalytic reactions, employing transition metal catalysis, organocatalysis, or photocatalysis.

1. Introduction

Organoboronic acids and their derivatives are privileged scaffolds in materials science and medicinal chemistry, thanks to their unique physicochemical and biological properties.[1] In addition to their accessibility, low toxicity, and versatility, organoboron reagents have become indispensable tools for synthetic chemists. They can be selectively transformed into a variety of valuable intermediates and products,[2] or employed as Lewis acid catalysts to design novel reactions.[3] These features have led to their extensive use in organic synthesis,[2] and their significance has been underscored by the awarding of three Nobel Prizes (in 1976, 1979, and 2010).[4]

Among the various classes of organoboron compounds featuring Csp^3 (alkyl), Csp^2 (aryl, alkenyl, allenyl), or Csp (alkynyl) substituents, alkenyl boron reagents have recently garnered significant attention due to their unique reactivity, electronic properties, and structural characteristics (Fig. 1A). Unlike alkyl or aryl boron reagents, whose utility often centers around the manipulation of the boron moiety, Csp^2- and Csp-substituted alkenyl boron reagents offer broader reactivity, stemming from the presence of additional unsaturated C–C double or triple bonds.[2,5,6] Additionally, in contrast to allenyl[5] or alkynyl[6] boron compounds, a wide range of practical methods has been developed for the synthesis of diverse alkenyl boron species,[2k,7] yielding numerous derivatives with varying substitution patterns at the boron atom, thus enabling a variety of transformations.

However, alkenyl boron reagents are more prone to protodeborylation, dimerization, and polymerization pathways in the

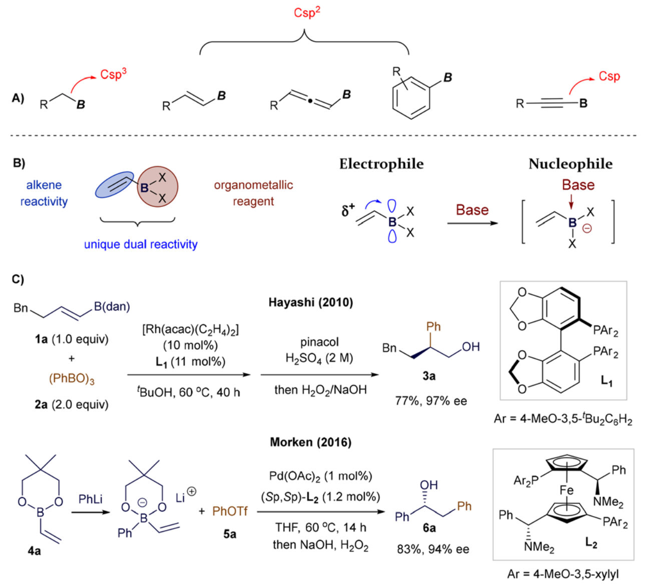

Fig. 1 Comparing the structure of different boron reagents and the typical reactivity of alkenyl boron reagents.

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presence of Brønsted acids, bases, transition metals, or oxidants, especially when compared to aryl boronic acid derivatives.[2j,8] At first glance, the dual nature of alkenyl boron reagents—bearing both a boron center and an alkene double bond—can present selectivity challenges.[2] While this increased reactivity may seem like a limitation, the synergistic interaction between the boron atom and the alkene moiety enables these compounds to exhibit unique chemical behaviours. The vacant p-orbital on the boron atom renders the adjacent double bond electron-deficient, while maintaining the boron center's Lewis acidity. As a result, alkenyl boron reagents possess ambiphilic reactivity, acting as electrophiles *via* their olefin portion and as nucleophiles when coordinated with a Lewis base (Fig. 1B). This dual reactivity is exemplified by key studies, such as Hayashi's Rh-catalyzed Michael addition to alkenyl boranes[9] and Morken's Pd-catalyzed conjunctive cross-coupling *via* 1,2-migrations of alkenyl boronates (Fig. 1C).[10] These characteristics make the chemistry of alkenyl boronates and boronic acids highly versatile, allowing for diverse modes of chemical activation and opening up exciting opportunities for designing novel synthetic protocols. The substitution at the boron center significantly impacts the reactivity and stability of the corresponding alkenyl boron compounds (Fig. 2).[2d,11] Currently, a wide range of vinyl-boron reagents is available, including the commonly used boronic acids (**7**), esters (**8**), pinacol-type esters (**9**, **10**, **4**), as well as more stable derivatives such as 1,8-diaminonaphthalene (dan) boronates (**1**),[12] *N*-methyldiaminoacetic acid (MIDA) boronates (**12**),[13] alkenylboroxines (**11**), and potassium trifluoroborates (**13**).[14]

In synthetic chemistry, classic applications of alkenyl boron reagents have traditionally centered around their use in stoichiometric coupling reactions, such as the well-known Zweifel olefination.[15] Additionally, their use in Pd- or Ni-catalyzed Suzuki–Miyaura cross-couplings—as organometallic precursors for vinyl groups—and in organocatalytic protocols has been well-documented (Fig. 3, left).[2] However, most of these transformations focused on modifying the boron functionality, leaving the alkene moiety unaltered. Recent advances in catalysis—encompassing transition metal, organocatalysis, and more recently, photocatalysis—have introduced new methods for the catalytic activation of alkenyl boron reagents. These developments have expanded reactivity at both the boron terminus and the alkene or its adjacent positions, broadening the scope in terms of polar and radical reactivity, reaction partners, and reactive intermediates. As a result, key figures in boron chemistry have revisited the synthetic potential of alkenyl boron reagents. New protocols have emerged that enable the formation of densely functionalized olefins by exploiting reactivity at the boron site or the synthesis of complex organoboron compounds through selective manipulation of the double bond, or even its allylic position (Fig. 3, right).

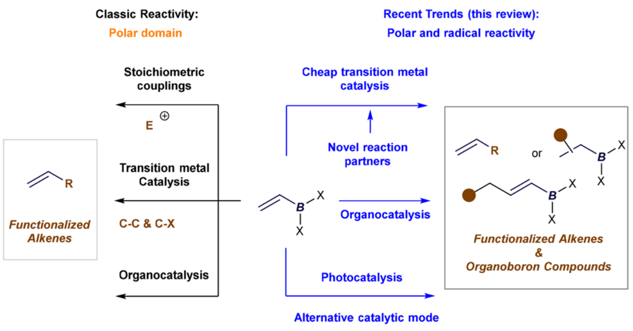


Fig. 3 Classic applications and scope of the review in the reactivity of alkenyl boron reagents in catalysis.

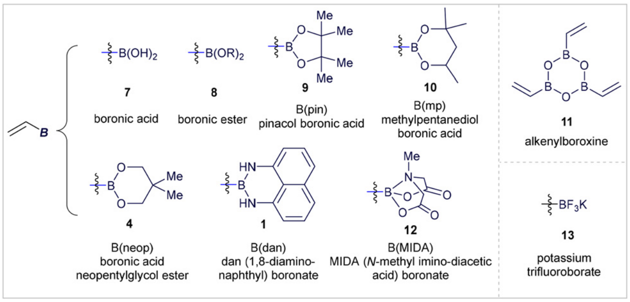
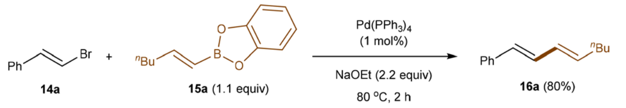


Fig. 2 Alkenyl boron reagents discussed within this review.

In this review, we highlight key catalytic protocols—primarily developed in the last five years—that have harnessed the unique reactivity of alkenyl boronates and boronic acids to advance catalytic methodologies. We will illustrate how these findings have already inspired, and will continue to inspire, the synthetic community to devise innovative solutions to long-standing challenges in synthesis. To enhance accessibility for readers, this review is structured around three major catalytic approaches—transition metal catalysis, organocatalysis, and photocatalysis—and further organized by reaction type. As discussed later, these three activation models enable efficient and versatile transformations through the selective activation of either alkenyl boron substrates or their reaction partners, yielding highly functionalized alkenes or alkyl boron products with excellent selectivity control. While several outstanding reviews on the synthetic applications of alkenyl boron reagents were published around 2020, they primarily focused on specific aspects of reactivity and do not reflect the most recent advancements in the field.[2k,l,o–r]

2. Cheap transition metal catalysis

Transition metal catalysis, recognized by several Nobel Prizes for enabling important and practical transformations,[4] has been instrumental in developing sustainable synthetic methods with exceptional control of selectivity in modern organic chemistry. As discussed below, the use of boron reagents in cost-effective transition metal-catalysis is crucial for streamlining the formation of C–C and C–heteroatom bonds. Their ability to undergo transmetallation in the presence of a metal center, coupled with their relative stability and



Scheme 1 Pioneering Suzuki–Miyaura cross-coupling by using alkenyl boron reagent.

low toxicity, makes boron derivatives a preferred choice for cross-coupling reactions. However, the reactivity of alkenyl boronates and boronic acids in transition metal-catalysis extends beyond their common role as alkenylation agents in Suzuki–Miyaura-type cross-couplings, where they act as nucleophilic partners (Scheme 1).[16] They can also be utilized in selective carbo- and hetero-functionalization of the olefin moiety, where alkenyl-boron reagents function as electrophilic partners, while preserving the boron functionality.

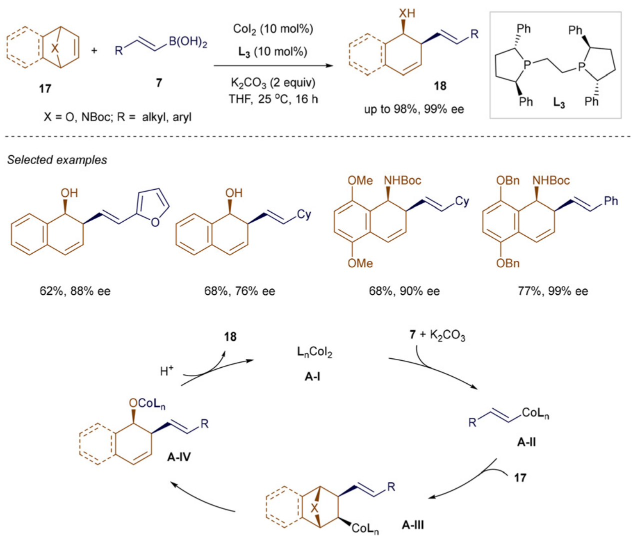
2.1 Alkenyl boron reagents as the nucleophilic partner – transmetallation through the B-atom

In early contributions, alkenyl boron reagents were primarily employed as organometallic partners in Pd- and Ni-catalyzed Suzuki–Miyaura-type cross-couplings, often in combination with organohalides for constructing C–C bonds.[2a,d,16] Additionally, their use in rhodium-catalyzed Hayashi-Miyaura additions to electron-deficient olefins has also been documented.[2b] In the context of carbon-heteroatom bond-forming couplings, inspired by Lam's work,[17] Batey and co-workers developed a set of base-free Cu-catalyzed conditions that facilitate the oxidative coupling of potassium alkenyl trifluoroborate salts with amides, phenols, and carboxylates to prepare enamides, enols, and enol esters, respectively.[18] Subsequent developments in this field have primarily focused on the use of alkenyl boron compounds for copper-catalyzed trifluoromethylation,[19] allylic substitution,[20] and addition reactions to CO_2[21] as well as electron-deficient alkenes[22] and isatins.[23] Furthermore, while investigating transition metal-catalyzed additions of boronic acids to unsaturated electrophiles, Cheng and co-workers found that Ni(II) and Co(II) salts facilitate the formation of nucleophilic organometallic intermediates from alkenyl boronic acids.[24] This observation was leveraged to implement the addition of alkenyl boronic acids to α,β-unsaturated esters and methyl oct-2-ynoate. Building on this seminal contribution, the groups of Zhang[25,26] and Zhao[27] have disclosed the use of both Ni(II) and Co(II) catalysis to explore the asymmetric addition of alkenyl boronic acids to cyclic *N*-sulfimines and ketones, respectively.

In this section, we will detail several recent and exciting examples that focus on the use of inexpensive metals, such as Co, Mn, and Ni, in catalyzed addition reactions to unsaturated bonds, cross-couplings with challenging electrophiles *via* radical or polar pathways, oxidative Heck reactions, and alkenylamination reactions.[28] Mechanistically, we will describe how transition metal-catalyzed reactions of alkenyl boron derivatives proceed *via* transmetallation of the alkenyl fragment from the boron center to the metal catalyst, leading to the formation of densely functionalized olefinic products. In all these processes, the alkenyl-boron partner serves as the nucleophilic species.

Addition to unsaturated bonds. Catalytic asymmetric ring-opening reactions of heterobicyclic alkenes have emerged as a valuable strategy for accessing enantioenriched multisubstituted cyclohexenes,[29] which are commonly found in various natural products and biologically active molecules.[30] Although Hou and co-workers pioneered the asymmetric ring-opening of oxa- and aza-bicyclic alkenes using alkenylboronic acids in Pd-catalyzed reactions, the substrate scope was limited, and the enantioselectivity was moderate at very low temperatures.[31] This limitation has been addressed by a recent method developed by Zhu, Chong, and Meng *et al.*, which employs Co-catalysis.[32] As illustrated in Scheme 2, the combination of the commercially available (*R*,*R*)-Ph-BPE **L$_3$** and CoI_2 facilitates highly enantioselective ring-opening reactions of both β-alkyl and aryl-substituted alkenyl boronic acids **7** with oxa- or aza-bicyclic alkenes **17**, yielding the corresponding products **18** with up to 98% yield and 99% enantiomeric excess (ee) at room temperature. The method demonstrates compatibility with various functional groups, including esters, chloro, bromo, and heterocycles. As proposed by the authors, the chiral phosphine-Co complex **A-I** undergoes transmetallation with alkenyl boronic acid **7** in the presence of K_2CO_3, followed by carbometallation to produce species **A-III**. β-Elimination and subsequent protonation then yields product **18** while regenerating Co complex **A-I**.

The high availability of manganese (the third most abundant transition metal in the Earth's crust), along with its low toxicity, has recently sparked renewed interest in Mn(I)-catalysis within the synthetic community.[33] In line with this trend, Xie and colleagues leveraged the ability of vinyl-boronic acids to undergo transmetallation with Mn(I)-complexes,[34] successfully applying this approach to Mn(I)-catalyzed addition reac-



Scheme 2 Co(II)-catalyzed ring-opening reactions.

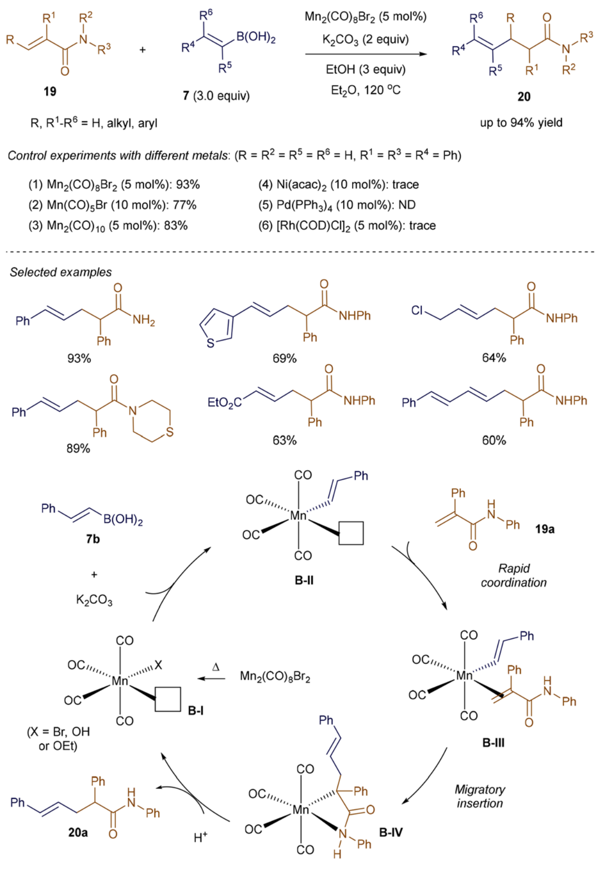
tions with α,β-unsaturated amides **19** (Scheme 3).[35] Utilizing alkenyl boronic acids **7** and 5 mol% of $Mn_2(CO)_8Br_2$, this method grants access to a diverse range of β-alkenylated amides **20** with remarkable efficiency, regio- and chemoselectivity, and high tolerance for various functional groups. The synthetic potential of this strategy is underscored by the fact that alternative metal sources—such as $Ni(acac)_2$, $Pd(PPh_3)_4$, and $[Rh(COD)Cl]_2$—failed to deliver the desired hydrovinylation product.

As proposed by the authors (Scheme 3), the mechanism begins with the homolysis of the dimeric manganese pre-catalyst $Mn_2(CO)_8Br_2$ at 120 °C, generating the active 16-electron Mn-species **B-I**, which features a vacant coordination site. Base-assisted transmetallation of alkenyl boronic acid **7b** to **B-I** forms the nucleophilic intermediate **B-II**, which then coordinates with the incoming α, β-unsaturated amides **19a** to yield complex **B-III**. Subsequent migratory insertion of the C–Mn bond across the double bond of the Michael acceptor generates **B-IV**, which upon protonation, produces the addition product **20a**, thereby regenerating the active catalyst **B-I**.[35]

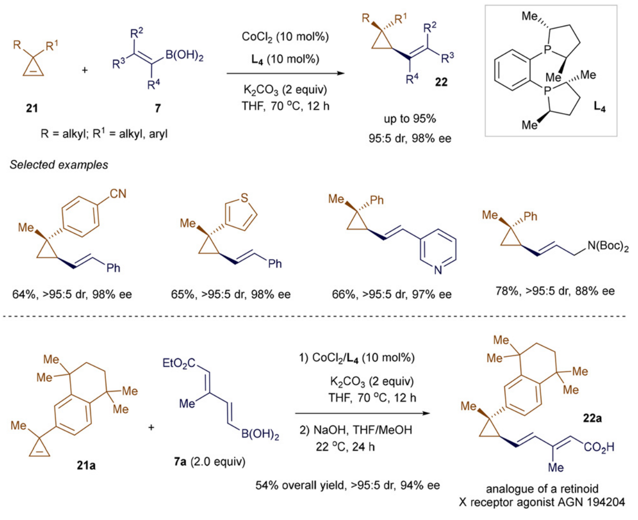
In the previous section, we discussed the ability of alkenyl boronic reagents to add to electron-deficient olefinic systems mediated by transition metals. Recently, cost-effective transition metal-catalyzed additions of alkenyl boron compounds to more challenging electron-rich double bonds have been reported, facilitating the realization of hydroalkenylation processes. In these reactions, fine-tuning of the conditions is often necessary to avoid over-addition of the vinyl precursor to the alkene products. Hydroalkenylation of unsaturated hydrocarbons, such as unbiased alkenes and cyclopropenes, has been successfully achieved using Mn, Ni, and Co catalysts, which will be reviewed in this section.

Hydroalkenylation. Alkenyl cyclopropanes have emerged as a key structural motif in medicinal chemistry and pharmaceuticals due to their presence in several biologically active natural products and drug candidates, as well as their distinct 'strained-ring' reactivity in chemical synthesis.[36] Methods to produce these compounds in a stereoselective manner are highly sought after but remain somewhat underdeveloped. Addressing this gap, Meng's group employed the conjugate addition of alkenyl boronic acids **7** to 3,3-disubstituted cyclopropenes **21**, under cobalt catalysis, to obtain enantioenriched alkenyl cyclopropanes **22** (Scheme 4).[37] A Co(II)/chiral phosphine $\mathbf{L_4}$ complex was utilized to drive this enantioselective desymmetrization reaction,[38] delivering cyclopropanes **22** with adjacent tertiary and quaternary carbon centers with both high efficiency and excellent enantioselectivity. The synthetic utility of this method was highlighted through the two-step synthesis of an analogue **22a** of the retinoid X receptor agonist AGN 194204.

Compared to the previously reported Mn(I)-catalyzed Michael addition of alkenylboronic acids to α,β-unsaturated amides (see Scheme 3),[35] the expansion of this approach to unbiased internal olefins presents a greater challenge. This difficulty arises from the rapid ligand exchange rate of the alkene, which competes with the slower migratory insertion of vinylmanganese species across unactivated alkenes.[39] Xie and colleagues addressed this issue by employing a weakly coordinating primary amide directing group, which facilitates the carbometallation step and drives the regioselective Mn(I)-catalyzed hydroalkenylation of internal alkenes, even in the pres-



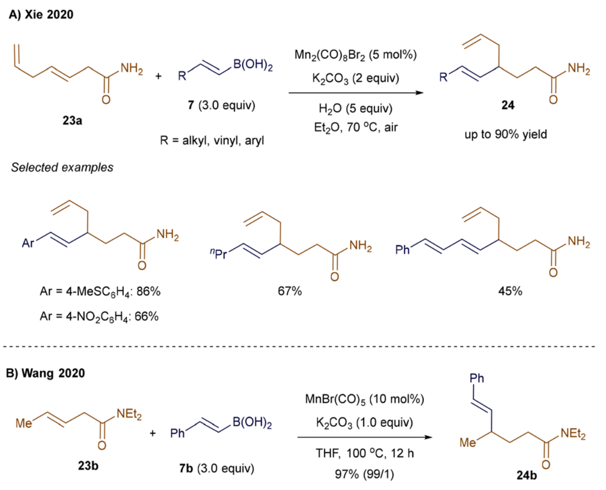
Scheme 3 Mn(I)-catalyzed addition to α,β-unsaturated amides.



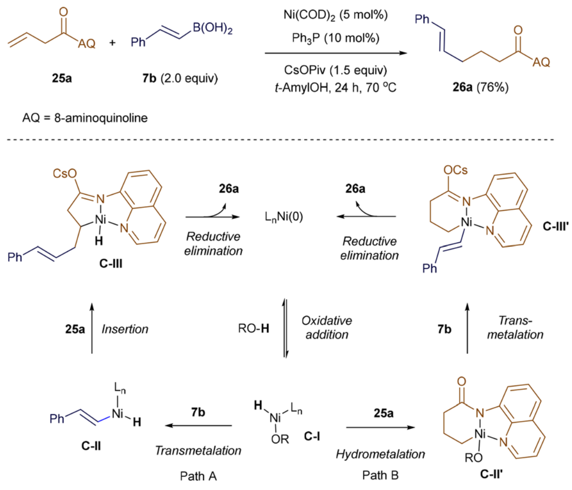
Scheme 4 Co(II)-catalyzed addition to cyclopropenes.

ence of terminal olefins (Scheme 5A).[39] This strategy was demonstrated with substrate **23a**, which contains both a terminal and an internal double bond, yielding the selectively 4,5-hydrovinylation product **24** in 45–90% yield. A similar transformation was reported by Wang and co-workers using tertiary amides as directing groups. This approach produced γ-vinylated amides **24b**—derived from substrate **23b** and boronic acid **7b**—with excellent regio- and *E*/*Z*-selectivity control (Scheme 5B).[40]

In 2018, Zhao and Zhou extended this reactivity to Ni-catalysis. They employed an 8-aminoquinoline (AQ) directing group, which enabled the linear-selective hydroalkenylation of unactivated terminal alkenes with alkenyl boronic acid 7b under redox-neutral conditions (Scheme 6).[41] The AQ template was essential for overcoming the low reactivity of aliphatic alkenes. Drawing on previous work from the Zhou group,[42] the authors proposed two potential catalytic cycles. Both cycles begin with the reversible formation of a Ni–H intermediate, **C-I**, with the alcohol additive serving as the proton source. In pathway A, the vinyl-Ni–H species **C-II** is generated through transmetallation with alkenyl boronic acid **7b**. **C-II** then undergoes directed alkene insertion, forming a five-membered nickelacycle **C-III**, which upon reductive elimination yields the linear product **26a**. Alternatively, in pathway B, sequential coordination and hydrometallation of intermediate I across the double bond of **25a** produces a six-membered nickelacycle, **C-II′**. Transmetallation of **C-II′** with boronic acid **7b** forms **C-III′**, which then undergoes reductive elimination to generate product **26a**, while regenerating the active Ni(0) catalyst.[41]



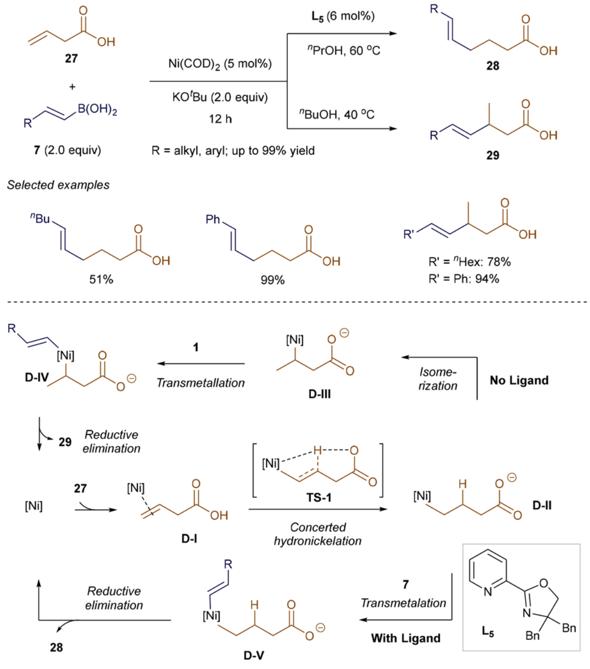
Scheme 5 Mn(I)-catalyzed hydroalkenylation of unbiased internal alkenes.



Scheme 6 Ni-catalyzed hydroalkenylation.

Liu and Engle revealed that the regioselectivity of nickel-catalyzed hydroalkenylation of β-alkenyl carboxylic acid **27** can be effectively tuned by ligands.[43] As shown in Scheme 7, both regioisomers **28** and **29** were obtained with moderate to excellent yields, depending on the presence of Pyrox ligand $\mathbf{L_5}$. DFT calculations suggest that this reaction may proceed differently from Zhao and Zhou's Ni-catalyzed hydroalkenylation. Liu and Engle proposed that the key alkylnickel(II) intermediate **D-II** forms through concerted hydronickelation **TS-1**. Without a ligand, **D-II** isomerizes into a more stable five-membered heterocyclic intermediate **D-III** *via* β-hydride elimination and alkene re-insertion, leading to Markovnikov products **29**. In the presence of ligand $\mathbf{L_5}$, however, **D-II** directly undergoes transmetallation with alkenyl boronic acids **7** to form **D-V**, where steric hindrance from $\mathbf{L_5}$ prevents isomerization. In both pathways, transmetallation determines the rate and selectivity of the reaction.[43]

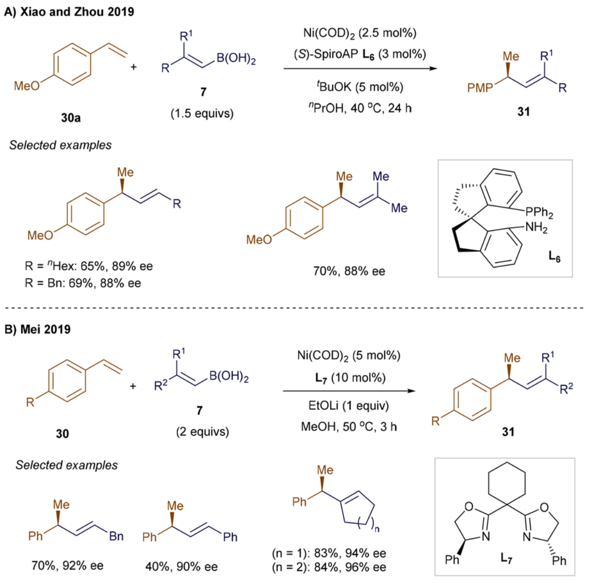
Asymmetric variants of Ni-catalyzed hydrovinylation processes using alkenyl boron nucleophiles have been developed,



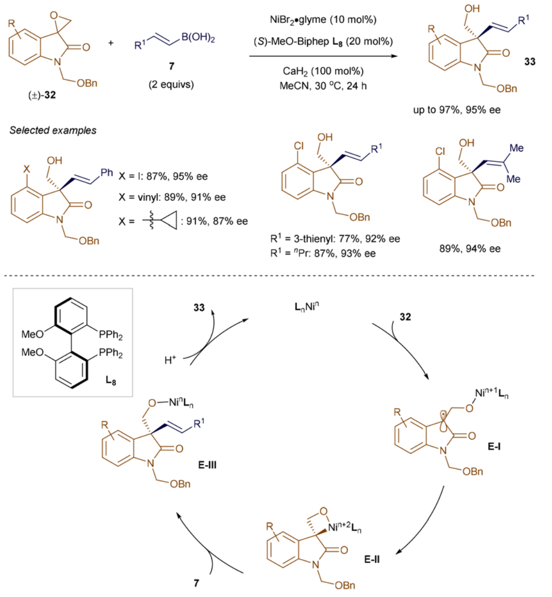
Scheme 7 Regiodivergent hydroalkenylation.

as demonstrated by Xiao and Zhou.[44] In their work, a Ni(0)-precatalyst combined with spiro-aminophosphine ligand **L_6** enabled the branched hydroalkenylation of styrenes (Scheme 8A). Mei and co-workers reported similar asymmetric reactivity (Scheme 8B), using bisoxazoline **L_7** to achieve enantioselective branched alkenylated products **31**.[45] This method's scope was extended to include β-aryl-substituted alkenyl boronic acids. Notably, in 2022, Wang and colleagues accomplished the hydroalkenylation of internal styrenes, where a simple 1,3-diketone/Ni(0) system proved crucial for achieving good selectivity.[46]

Cross-couplings. As discussed later in this section, both radical and polar pathways have been explored for challenging coupling transformations. Epoxides, due to their strained ring structure, are highly reactive intermediates and easily synthesized from alkenes and carbonyl compounds. Although transition metal-catalyzed[47] and metal-free[48] regioselective ring-opening of oxiranes with organoboron reagents is well documented, catalytic asymmetric variants have remained elusive. To address this, Zhang and colleagues developed a Ni-catalyzed enantioselective cross-coupling of racemic epoxides with alkenyl boronic acids.[49] As depicted in Scheme 9, a $NiBr_2$/**L_8** system enabled the coupling of racemic spiroepoxyoxindoles **32** with alkenyl boronic acids **7**, yielding enantioenriched homoallylic alcohols **33** with all-carbon quaternary stereocenters. Control experiments suggest the reaction initiates through single-electron transfer (SET) from the Ni-catalyst to epoxide **32**, forming a stabilized tertiary radical **E-I**. Radical recombination leads to a stereodefined Ni-oxetane adduct **E-II**, which couples with **7** to produce enantioenriched homoallylic alcohols **33**. Additionally, Zhang's group achieved nickel-catalyzed ring-opening/cross-coupling of vinylaziridines with β-substituted alkenyl boronic acids, selectively producing skipped aminodienes.[50]



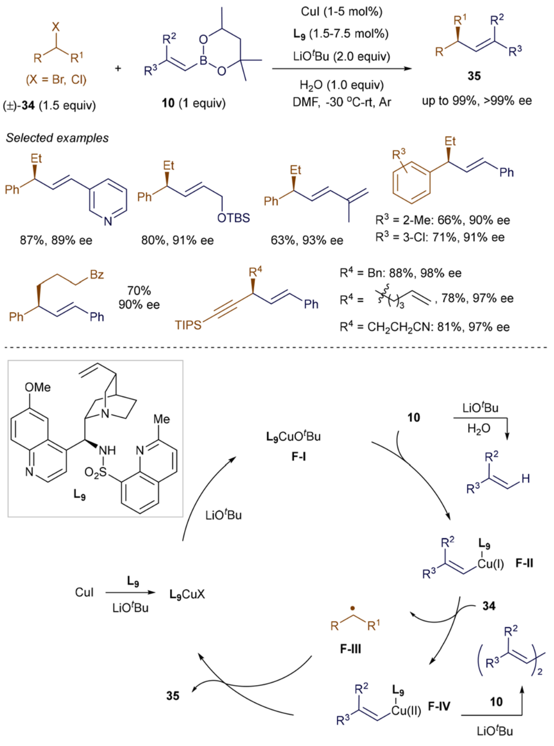
Scheme 8 Enantioselective hydroalkenylation of styrenes.



Scheme 9 Enantioconvergent coupling of spiroepoxyoxindoles with alkenyl boronic acids.

While enantioconvergent cross-coupling of racemic alkyl halides with alkenyl boronate esters is a promising strategy for constructing chiral Csp^3–Csp^2 bonds, it remains underdeveloped due to challenges in achieving both high reactivity and enantioselectivity.[51] In 2022, Liu and co-workers successfully developed a chiral copper catalyst for the enantioconvergent cross-coupling of benzyl and propargyl halides with alkenyl boronate esters (Scheme 10).[52] Control experiments revealed that a key to this success lies in the rational design of a hemilabile N,N,N-ligand **L_9** with steric hindrance at the *ortho* position of one coordinating quinoline ring. This novel ligand not only facilitates the radical cross-coupling process in its tridentate form, preventing homocoupling side reactions, but also provides high enantioselectivity by stabilizing reactive secondary alkyl radicals in its bidentate form. The system tolerated a wide variety of (hetero)benzyl and propargyl bromides and chlorides **34**, as well as mono- and di-substituted alkenyl boronate esters **10** with diverse functional groups, achieving enantioenriched alkene products **35** with up to 98% yield and over 99% ee, even at 1 mol% catalyst loading.

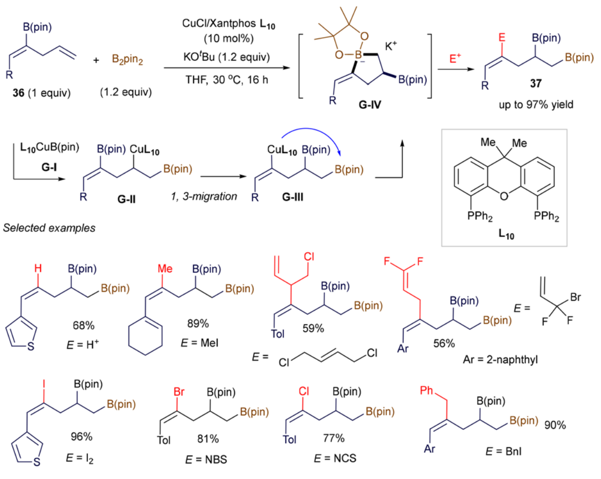
The proposed mechanism involves the formation of the active catalyst **F-I** from CuI, LiO*t*Bu, and ligand **L_9** in its tridentate form. Transmetallation of **F-I** with alkenyl boronate ester **10** generates an alkenyl-Cu(I) species **F-II** and *t*BuO-B(mp). **F-II** then reacts with alkyl halides **34**, generating a secondary alkyl radical **F-III** and an alkenyl-Cu(II) complex **F-IV** *via* a single-electron transfer process. Ligand **L_9** efficiently suppresses the undesired homocoupling of **F-IV**. The enantioconvergent coupling of **F-III** and **F-IV** produces the desired product **35** and regenerates the active catalyst **F-I**. Notably, conducting the reaction at low temperatures substantially reduces the protodeboration of **10**, aiding enantiocontrol.[52]



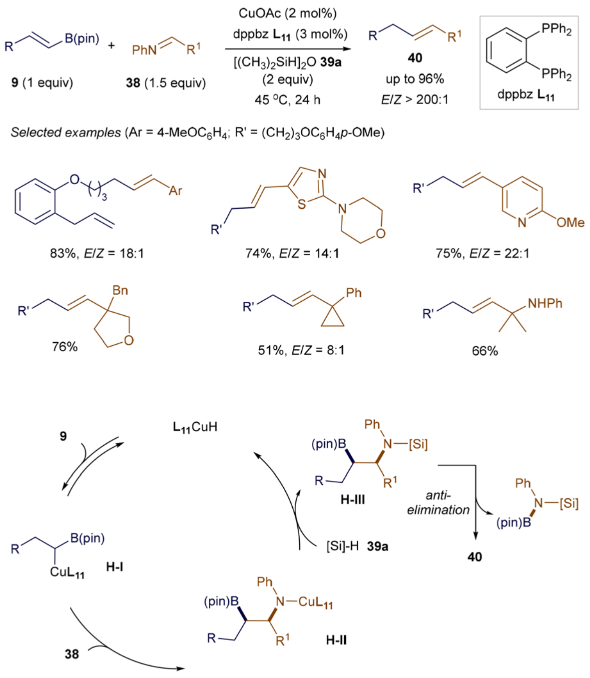
Scheme 10 Enantioconvergent coupling of secondary alkyl halides.

In addition to these radical-involved cross-coupling examples, three notable studies have recently demonstrated the use of alkenyl boronates as electrophiles *via* a polar pathway, significantly expanding the synthetic utility of these reagents. For instance, Carbó, Fernández, and co-workers revealed that the regioselective borylcupration of borylated skipped (*Z*)-dienes **36** generates the key electrophilic five-membered boracycle **G-IV** through a novel intramolecular, stereospecific B/Cu 1,3-rearrangement, where the B(pin) group migrates from a Csp^2 to a Csp^3 center (Scheme 11).[53] By trapping **G-IV** *in situ* with various electrophiles—such as protons, alkyl halides, I$_2$, NBS, or NCS—a wide range of functionalized homoallyl diborated products **37** can be easily prepared. DFT calculations suggest that, although alkoxides from bases like KO*t*Bu or KOMe can form Lewis base adducts with intermediate **G-I**, the use of bulky *tert*-butoxide prevents stable adduct formation with **L$_{10}$**CuBpin, thereby facilitating the initial borylcupration step.

Alkenes are fundamental building blocks in organic synthesis, and stoichiometric Wittig-type olefination of carbonyls or imines is among the most widely used methods for constructing functionalized alkenes. However, catalytic versions of this strategy remain underdeveloped. Recently, Lalic and co-workers reported an excellent stereoselective copper-catalyzed olefination of aryl and sterically hindered alkyl imines with various functional groups (Scheme 12).[54] The success of this method lies in the efficient generation of a copper boryl heterobimetallic complex **H-I**, formed through the regioselective addition of **L$_9$**CuH to alkenyl boronates **9**, acting as an ylide



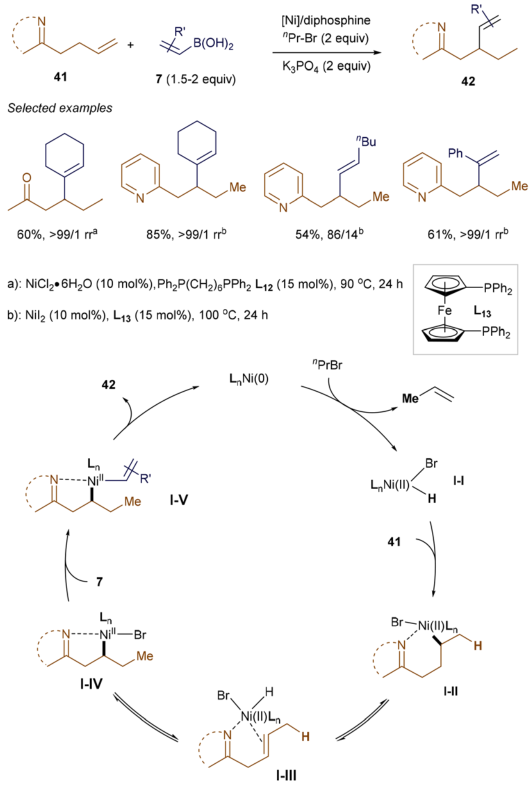
Scheme 11 Boron-copper 1,3-rearrangment.



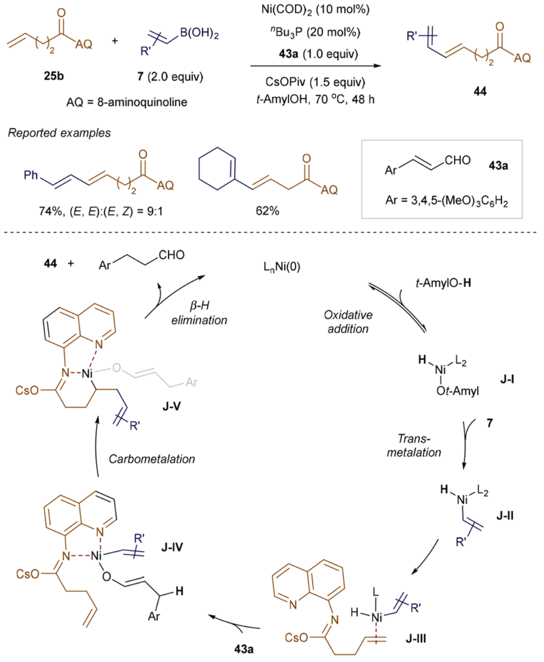
Scheme 12 Copper-catalyzed olefination of imines.

equivalent. Subsequent addition to imine **38**, followed by interaction with hydrosilane **39a**, produces intermediate **H-III**. This 1,2-boryl *N*-silylamine **H-III** then eliminates, furnishing the *E*-alkene products **40**.

NiH-involved migratory hydrofunctionalization of alkenes has emerged as an efficient method for the selective functionalization of Csp^3–H bonds.[55] Recently, Cao and Wang developed a nickel-catalyzed, chelate-assisted strategy for the regioselective migratory hydrovinylation of alkenes using diphosphine ligands.[56] As shown in Scheme 13, with imine or pyridine as directing groups, the NiH-promoted β-alkenylation proceeded smoothly, yielding vinylated products with excellent selectivity and good yields. Mechanistic studies suggest that



Scheme 13 Ni(II)H-catalyzed β-vinylation.

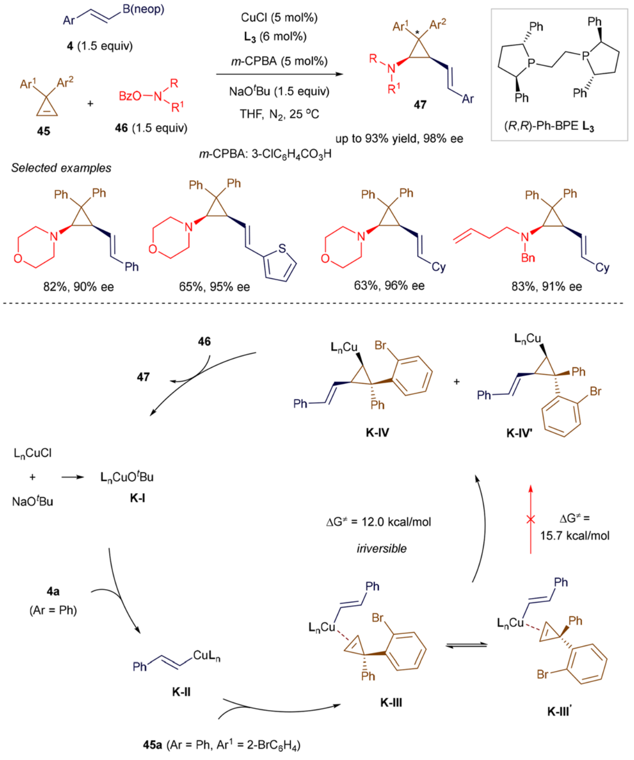


Scheme 14 Ni-catalyzed oxidative Heck reaction.

the reaction involves the formation of a **L$_n$**Ni(II)Br–H intermediate **I-I** *via* the oxidative addition of **L$_n$**Ni(0) to ^{n}PrBr, followed by β-H elimination. After the migratory insertion of alkenes into **I-I**, assisted by nitrogen coordination, a stable nickellacycle **I-IV** is formed through a β-H elimination and reinsertion process. Transmetallation with alkenyl boronic acids **7**, followed by reductive elimination, produces the desired vinylated products **42**.

Oxidative Heck. A related strategy to the hydrovinylation methods is the alkenylation of olefinic functionalities while preserving the integrity of the double bond. This was achieved in a collaboration between Xue, Engle, and Zhao, who reported a Ni(0)-catalyzed oxidative Heck reaction of unactivated alkenes with various boronic acids, using cinnamaldehyde **37a** as the terminal oxidant (Scheme 14).[57] The AQ template played a crucial role in enhancing reactivity at the unbiased alkene site. Both β-aryl and alkyl-substituted alkenyl boronic acids **7** were competent coupling partners, yielding conjugated dienoic acid derivatives **44**. Mechanistic experiments and DFT calculations suggest that the reaction proceeds through oxidative addition of the Ni(0) catalyst into the O–H bond of the alcohol, followed by transmetallation with alkenyl boronic acid **7**. Direct intramolecular carbometalation of alkene-coordinated adduct **J-III** was found to be highly endergonic, whereas the intermolecular 1,4-addition of the Ni–H bond of **J-III** to cinnamaldehyde **37a**, forming **J-IV**, was more favorable. Coordination with the enolate ligand accelerates the carbometalation of **J-IV**, producing linear intermediate **J-V**. Finally, β-hydride elimination from **J-V** generates the product **44** and regenerates the Ni(0) catalyst.

Alkenylamination. In 2020, Jia, Zhao, and co-workers introduced an elegant strategy for the highly stereoselective assembly of polysubstituted chiral cyclopropylamines.[58] Cyclopropylamine functionalities are found in various drugs and drug candidates, and they also serve as useful synthons for constructing complex carbo- and heterocycles. The authors utilized commercially available ligand **L$_3$** in combination with copper(I) chloride to promote a three-component cyclopropene alkenylamination reaction, involving hydroxyamine esters **46** and alkenyl boron reagent **5**, under mild conditions (Scheme 15). Similar to their earlier work,[58a] the addition of a catalytic amount of *m*-CPBA was crucial for successful alkenylamination. Interestingly, for cyclopropenes **45a** bearing two different aryl groups on the C3 position, the catalytic system was able to distinguish subtle differences in *ortho*-substituents, producing the product as a single diastereomer. Although the scope of the alkenyl boron reagent was limited to simple β-aryl compounds, this method enables the synthesis of polysubstituted *cis*-1,2-alkenylcyclopropylamines **47** with up to three stereogenic carbon centers. The proposed mechanism (Scheme 15) begins with the formation of alkenyl Cu(I) **K-II** *via* transmetallation. The subsequent enantioselective migratory insertion step produces cyclopropyl Cu(I) **K-IV** through intermediate **K-III**. At this stage, due to steric interactions between the incoming alkenyl group and the larger 2-BrC$_6$H$_4$ substituent, **K-III** exists as a higher-energy intermediate compared to **K-III′**. However, **K-III** undergoes faster and irreversible migratory insertion, leading to the kinetically favorable isomer **K-IV** (over **K-IV′**). Trapping with aminating reagent **46** results



Scheme 15 Cu(I)-catalyzed alkenylamination.

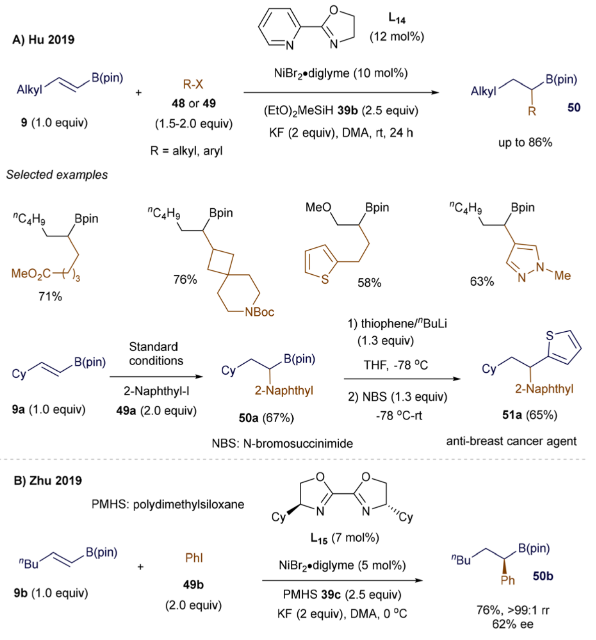
in the formation of the observed diastereomer and regenerates the Cu(I) catalyst.

2.2 Alkenyl boron reagents as the electrophilic partner – functionalization of the olefinic moiety

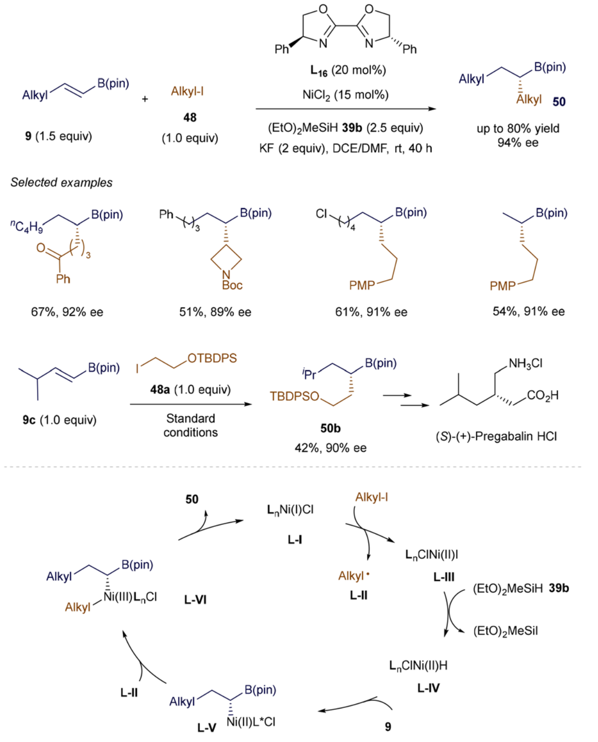
As shown in the previous transition metal-catalyzed examples, various alkenyl boron reagents have been used to incorporate carbon–carbon double bonds into products. Additionally, methods that directly functionalize the double bonds of alkenyl boron compounds have also been developed. A key feature of this strategy is that the boron moiety in the product is retained, opening new pathways for synthesizing useful alkyl boron compounds. The reactivity of the double bond in alkenyl boronates, compared to that of simple alkenes, can be unexpected and is influenced by the substituents on the boron atom, requiring careful consideration. From a bond-formation perspective, two main ionic pathways have been successfully utilized. The first pathway involves direct functionalization of the olefinic portion of alkenyl boronates through hydrogenation,[59] Michael additions,[9,60] hydroborylation,[61] hydroamination,[62] hydrosilylation,[63] diborylation,[64] Cu-mediated 1,2-difunctionalization,[65] CuH-mediated hydroalkylation,[66] and carbozincation.[67] The second pathway focuses on conjunctive cross-coupling *via* 1,2-migrations of boronate complexes, largely pioneered by Morken and co-workers.[2l,10,68] In this section, recent developments in nickel-, cobalt-, and copper-catalyzed hydroalkylation, 1,2-difunctionalization, and [2 + 2] reactions of alkenyl boronates are highlighted. In these cases, transition metals not only act as reductants to generate radicals but also mediate selective bond formation. Notably, the open-shell reactivity of alkenyl boron reagents has been applied in novel transformations under light-triggered reaction conditions (section 4).

Hydroalkylation. To broaden the scope of hydroalkylation of alkenyl boronates *via* CuH catalysis, 66 organic chemists have long been intrigued by the potential to form new carbon–carbon bonds through the open-shell reactivity of alkenyl boron reagents. In 2014, Baran's group reported an FeH-catalyzed hydroalkylation of alkenyl boron reagents.[69] Around the same time, Hu[70] and Zhu[71] simultaneously developed NiH-catalyzed regioselective hydroalkylation and hydroarylation of β-alkyl alkenyl boronic pinacol esters **9**. Directed by the B(pin) group, the strategy involves regioselective addition of the NiH intermediate to the double bond of **9**, resulting in the formation of a stable α-boryl organonickel intermediate (Schemes 16 and 17). Subsequent cross-coupling with alkyl or aryl halides **48** or **49** leads to a wide range of secondary alkyl B(pin) derivatives **50**, which serve as valuable synthetic intermediates in medicinal and materials chemistry.

As shown in Scheme 16, under Hu's optimized conditions, both hydroalkylation and hydroarylation reactions proceeded smoothly with simple starting materials, demonstrating tolerance to a variety of functional groups (Scheme 16A). Additionally, this method was successfully applied to the synthesis of an anti-breast cancer agent **51a**.[70] Meanwhile, Zhu's group achieved similar success in the NiH-catalyzed remote hydroarylation of boron-containing alkenes, utilizing nearly identical reaction conditions. They also tested an asymmetric version of the reaction, though with moderate enantioselectivity (Scheme 16B).[71]



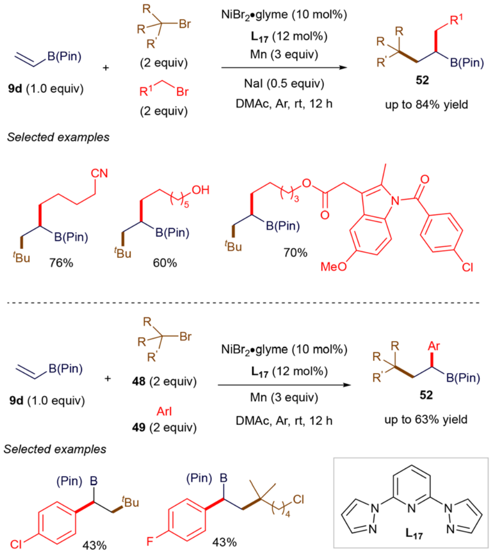
Scheme 16 NiH-catalyzed hydrocarbonation.



Scheme 17 NiH-catalyzed enantioselective hydroalkylation.

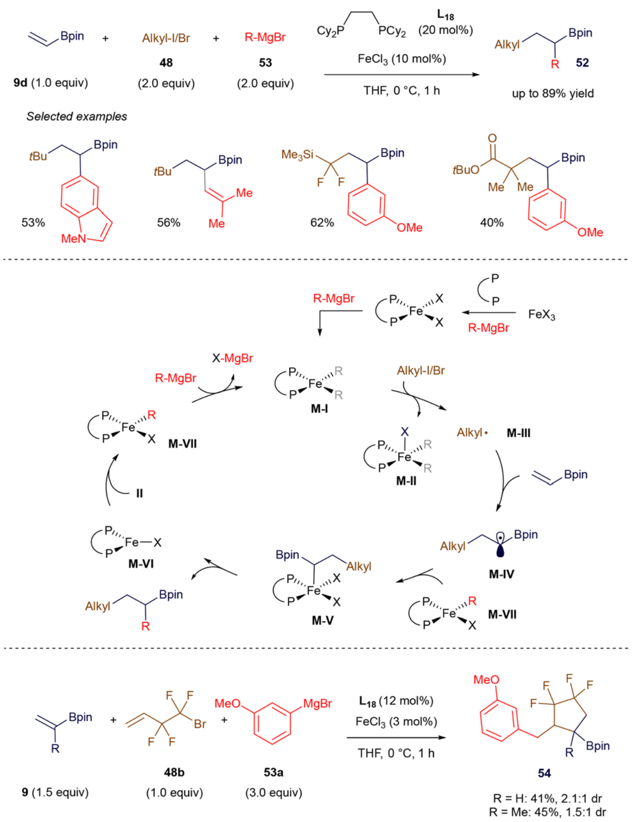
Hu's group further developed the asymmetric version of the NiH-catalyzed hydroalkylation reaction (Scheme 17).[72] This strategy allows the stereoselective union of two alkyl fragments, including secondary alkyl groups, and exhibits a broad substrate scope with excellent tolerance for various functional groups. This enables the efficient synthesis of chiral alkyl B(pin) derivatives **50** under mild conditions. Moreover, the protocol has been applied to the functionalization of natural products and drug derivatives, and was successfully used in the facile synthesis of **50b**, a key intermediate in the production of (*S*)-(+)-Pregabalin·HCl. A plausible mechanism was proposed based on a series of control experiments. It begins with the formation of a chiral **L_n**Ni(I)Cl species **L-I**, which reduces alkyl iodide to form an alkyl radical **L-II** and **L_n**ClNi(II) **L-III**. The reaction of **L-III** with $(EtO)_2MeSiH$ generates a Ni-H species **L-IV**. Subsequent regioselective insertion into alkenyl B(pin) **9** produces a Ni-alkyl intermediate **L-V**, which can recombine with the alkyl radical **L-II** to form a Ni(III) complex **L-VI**. The final reductive elimination yields the desired product **50** and closes the catalytic cycle.[72]

1,2-Difunctionalization. The open-shell reactivity of vinyl boronates plays a role in certain 1,2-carbofunctionalization reactions of vinyl boronate esters, catalyzed by inexpensive transition metals. For instance, in 2020, Lu, Fu, and coworkers reported a nickel-catalyzed three-component dialkylation and alkylarylation of vinyl boronate esters (Scheme 18).[73] The use of nickel catalysis facilitates these transformations with high coupling efficiency and excellent functional group tolerance. The synthetic utility of this method has been showcased through late-stage modifications of bioactive derivatives. Mechanistically, the nickel catalyst can distinguish between the reactivities of tertiary alkyl bromides and either primary alkyl bromides or aryl iodides, yielding products with outstanding chemo- and regio-selectivities. Notably, as illustrated later in Scheme 33A, Martin reported a similar alkylarylation involving the synergistic use of nickel and photoredox catalysis. Following a similar mechanistic pathway to Martin's, the reaction likely proceeds through the generation of tertiary alkyl radicals *via* the reduction by a Ni(I) catalyst. This is followed by a 1,4-radical addition to vinyl boronate ester **9d** and cross-coupling with primary alkyl bromides or aryl iodides, mediated by Ni(I), ultimately producing the observed product **52**.

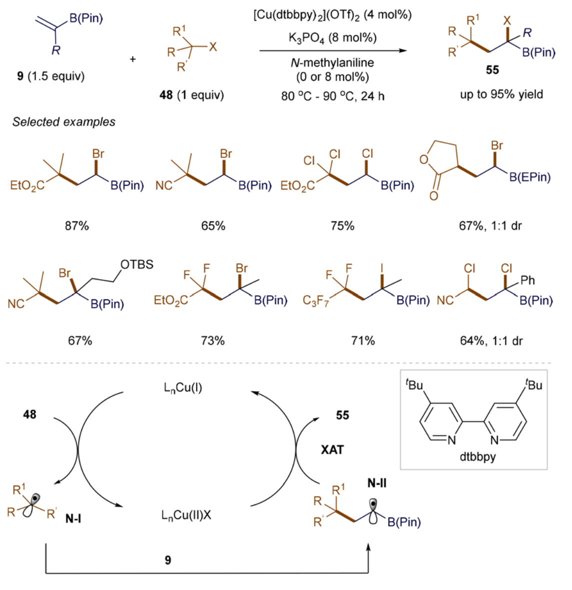


Scheme 18 Ni(I)-catalyzed selective 1,2-alkylation and 1,2-alkylarylation.

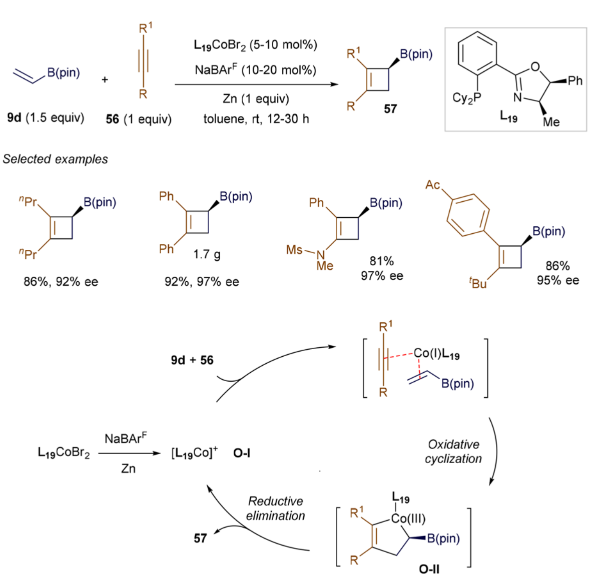
In 2021, Gutierrez's group developed an elegant Fe(II)-catalyzed three-component process involving alkyl halides, Grignard reagents, and vinyl boronate esters (Scheme 19).[74] Following a thorough investigation utilizing Mössbauer spectroscopy, electron paramagnetic resonance (EPR), X-ray crystallography, and DFT calculations, the authors proposed that the *in situ*-formed bis-arylated Fe(II) species, **M-I**, is responsible for abstracting halogen from the alkyl halide, leading to the formation of the corresponding alkyl radicals **M-III** and **M-II.** Radical **M-III** undergoes a Giese-type addition to the π-system of alkenyl boronate **9d**, generating the α-boryl radical **M-IV** (more examples of such radical additions are discussed in section 3). This radical is subsequently trapped by the monoarylated Fe(II) species **M-VII**, which facilitates C–C bond formation. Comproportionation between Fe(I) and Fe(III) species **M-VI** and **M-II** regenerates the Fe(II) species **M-VII**, allowing the catalytic cycle to continue in the presence of additional Grignard reagent. The authors further demonstrated the versatility of this method by extending it to alkyl halides with pendant olefins as radical precursors, enabling the synthesis of tetrafluoroethylene-containing cyclopentane derivatives **54**.



Scheme 19 Iron-catalyzed 1,2-biscarbofunctionalization.



Scheme 20 ATRA reaction.



Scheme 21 Co(i)-catalyzed [2 + 2] cycloaddition.

α-Haloboronic esters are valuable building blocks in organic synthesis. Their synthesis *via* atom transfer radical addition (ATRA) presents an appealing but challenging strategy due to the relative stability of the α-boryl radical, which makes efficient halogen transfer difficult except with highly electron-deficient radical precursors. To address this challenge, Hull and co-workers developed a Cu-mediated approach.[75] As illustrated in Scheme 20, using 4 mol% of $[Cu(dtbbpy)_2](OTf)_2$ as a catalyst efficiently promotes the ATRA reaction of various primary, secondary, and tertiary alkyl halides **48** with both unsubstituted and α-substituted vinyl pinacol boronic esters **9**, producing α-haloboronic esters **55** with yields of up to 95%. The proposed mechanism involves the reduction of **48** by $\mathbf{L_n}$Cu(i), generating radical **N-I** and $\mathbf{L_n}$Cu(ii)X. After radical **N-I** adds to **9**, the resulting α-boryl radical **N-II** undergoes halogen atom transfer (XAT) with $\mathbf{L_n}$Cu(ii)X, forming the desired product **55** and regenerating $\mathbf{L_n}$Cu(i).

[2 + 2] cycloaddition. In 2019, Rajanbabu and co-workers introduced an excellent and practical method for the enantioselective synthesis of cyclobutyl boronates **57** *via* a Co(i)-catalyzed [2 + 2] cycloaddition between simple alkynes **56** and alkenyl boronate **9d** (Scheme 21).[76] This method demonstrated high efficiency and selectivity under mild conditions, accommodating both symmetric and asymmetric alkynes with ease. Mechanistic studies suggest that the reaction begins with Co(i)-catalyzed selective oxidative cyclization to generate intermediate **O-II**, followed by reductive elimination to furnish the desired cyclobutyl boronate product **57**. Notably, a radical-mediated [2 + 2] cycloaddition strategy involving alkenyl boronates has also been developed for the stereoselective synthesis of cyclobutylboronates, with further examples discussed in section 4.3.

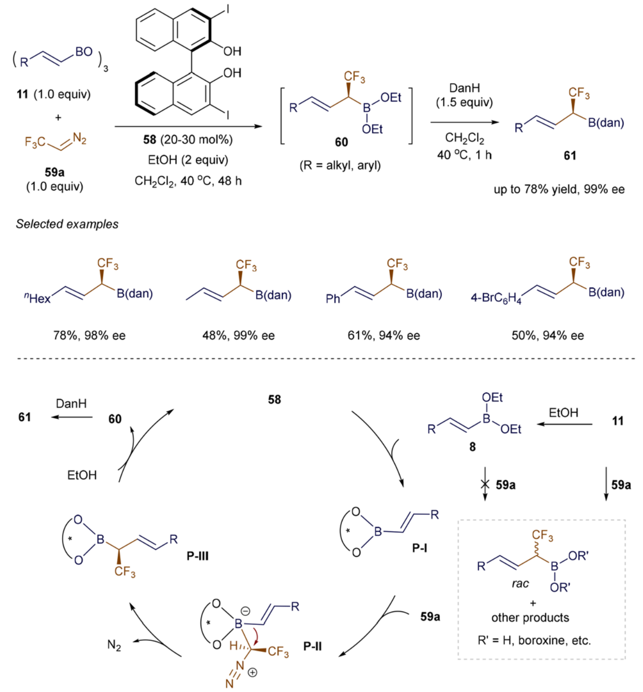
3. Organocatalysis

Although the use of simple chiral organic molecules to promote asymmetric transformations has been documented since the 1970s,[77] it wasn't until 2000 that the field experienced significant growth.[78] During this time, small chiral organic molecules with minimal functional groups were employed to mimic biocatalysts, adopting diverse catalytic modes.[79] Compared to transition-metal catalysis, organocatalysis offers several advantages, such as low toxicity, insensitivity to moisture and air, and ready availability from natural chiral sources. As a result, the field was awarded the Nobel Prize in 2021. However, organocatalytic transformations using alkenyl boron reagents have been far less explored than those using transition-metal catalysis. To date, several organocatalytic models relying on chiral diols[2c,f] and secondary amines[80] have been developed. As summarized below, alkenyl boron reagents can be directly activated by organocatalysts or used to trap reactive organic intermediates formed *in situ via* Lewis acid or Lewis base catalysis. These new protocols have been successfully applied for the facile synthesis of functionalized alkenes or alkyl boronates, including enantioselective transformations. For clarity, the discussion in this section will be organized based on the types of organocatalysts used.

3.1 Chiral diol-catalyzed insertion reactions

One exceptionally good example that uses chiral small molecules to activate boronic reagents for asymmetric organocatalysis was reported in 2006. Because of the dynamic covalent bonding ability of boron,[81] Schaus and co-workers noticed that a catalytic amount of chiral BINOL derivative can act as an exchangeable chiral ligand with neutral organoboronates, promoting the first enantioselective organocatalytic allylation of ketones *via* direct activation of allylboronates.[82] Inspired from this seminal contribution, Schaus further sought suitable organocatalytic conditions to achieve the asymmetric vinylation of *in situ* formed iminium salts (Petasis reaction) with alkenylboronates.[83] After this, the group further expanded the scope of electrophiles to acyl imines,[84] *o*-quinone methides,[85] and 1-ethoxycarbonyl-1,2-dihydroquinolines,[86] respectively. Furthermore, the groups of Chong,[87] Takemoto,[88] Sugiura,[89] May,[90] and Liu[91] also made a significant contribution to this area. Considering that these findings have been well summarized by Matteson[2c] and May,[2f] the related chemistry will not be detailed in this section.

In 2020, Szabó *et al.* introduced a practical method for synthesizing chiral α-CF_3 or α-$SiMe_3$ allylic boron molecules, which are valuable in drug design and natural product synthesis (Scheme 22).[92] Using a BINOL catalyst **58** and ethanol, the catalytic asymmetric homologation of both β-alkyl and aryl-substituted alkenyl boroxine **11** with CF_3-diazomethane **59a** proceeded smoothly under mild conditions. Notably, the reaction was scalable up to 2 mmol. The proposed mechanism begins with the formation of the unreactive ethyl alkenyl boronic ester **8**. A transesterification step with catalyst **58** then produces the chiral alkenyl boronate **P-I**, which significantly increases the Lewis acidity of the boron atom, enabling the formation of the boron ate complex **P-II** and inducing stereoselectivity. This is followed by a stereoselective 1,2-migration of the alkenyl group, resulting in **P-III**. Ethanolysis of **P-III** yields the air-sensitive intermediate **60**, which is ultimately protected with diaminonaphthalene (DanH), forming the final product **61**.

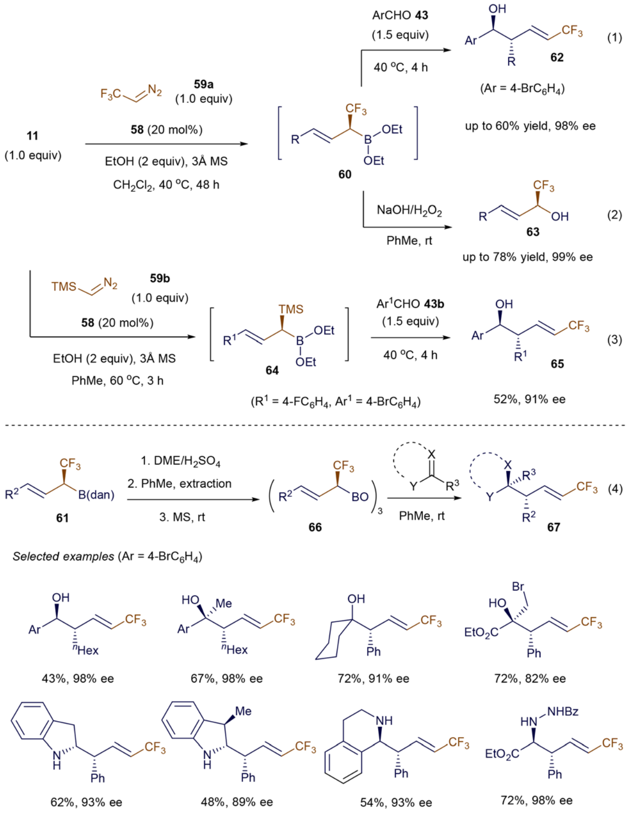


Scheme 22 Organocatalytic synthesis of α-CF_3 allylboron compounds.

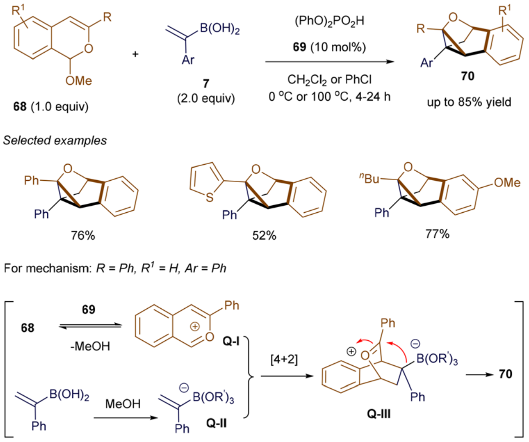
Furthermore, by reacting the chiral intermediate **60** with aldehydes **43** or under oxidative conditions (NaOH/H_2O_2), a variety of α-CF_3-substituted alcohols **62** or **63** were obtained in good to high yields with good to excellent enantioselectivities (Scheme 23, eqn (1) and (2)). Additionally, the method is compatible with Me_3Si-diazomethane **59b**, opening a new pathway for the preparation of enantioenriched α-$SiMe_3$ allylboronates **64** (eqn (3)). To further demonstrate the utility of these methods, the authors presented a one-pot strategy to convert the α-CF_3 allyl boronic derivatives **61** into α-CF_3 allylic boroxines **66**. These boroxines **66** serve as highly reactive reagents for allylation reactions with aldehydes, ketones, and imines, as well as for dearomative allylation of indoles, yielding product **67** with excellent stereoselective control (eqn (4)).[92]

3.2 Phosphoric acid-catalyzed cycloadditions

Considering the presence of double bonds in alkenyl boronic acids, the development of new catalytic examples that exploit this alkene moiety as a C2 synthon in organocatalysis has been explored. In 2015, Sun's group was among the first to utilize this reagent, employing an *in situ* generated 10π-electron isobenzopyrylium ion as a key intermediate to facilitate cycloaddition reactions.[93] Soon after, Huang and Sun further demonstrated that using (1-arylvinyl)boronic acid as the nucleophilic partner to trap the isobenzopyrylium ion enabled the formation of cyclopropane-containing tricyclic products.[94] As shown in Scheme 24, condition optimization revealed that $(PhO)_2PO_2H$ **69** with appropriate acidity serves



Scheme 23 Diverse reactivities of allylic boron and silicon reagents.



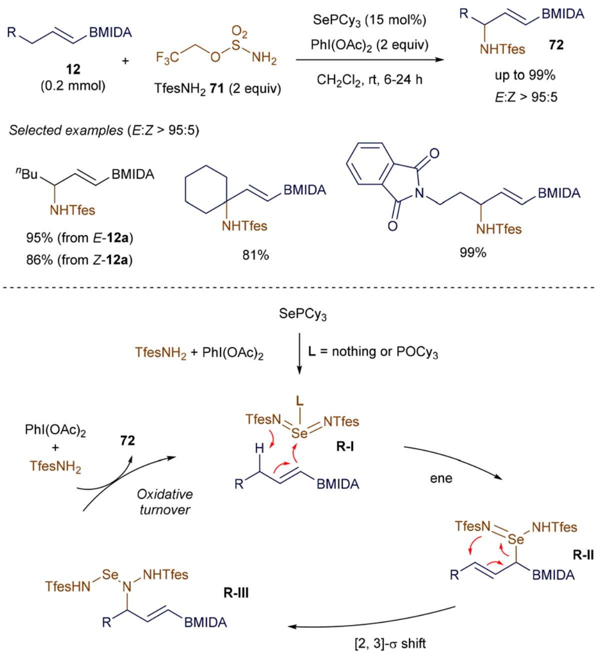
Scheme 24 Synthesis of cyclopropane-containing tricyclic skeleton.

as an effective catalyst for this unusual process. A variety of highly strained products **70** were easily isolated in yields ranging from 41% to 85%, even on a gram scale. According to the proposed mechanism, the isobenzopyrylium ion **Q-I** forms through the interaction of catalyst 69 with substrate 68, accompanied by the release of MeOH. Meanwhile, boronic acid **7** is activated by MeOH, forming borate **Q-II**. A subsequent [4 + 2] cycloaddition between these two species generates the bicyclic oxonium intermediate **Q-III**. Unlike previous examples, where the C–O bond of the oxonium bridge in **Q-III** cleaves, in this case, the nucleophilic borate preferentially attacks the electrophilic carbon of the oxonium bridge, resulting in the formation of the strained C–C bond and the observed product structure.

3.3 Lewis base-catalysed allylic amination

In addition to the stereospecific 1,2-migrations of boronate complexes induced by π-acidic transition metal complexes developed by Morken, an alternative organocatalytic 1,2-migration of alkenyl boronates was reported by Denmark in 2018. This method showcases the effectiveness of Lewis base catalysis in developing novel transformations using alkenyl boron reagents.[95] In 2022, Michael introduced a highly selective and unusual allylic C–H amination of alkenyl boronates, also employing Lewis base catalysis (Scheme 25). This novel transformation further illustrates the expanding utility of alkenyl boronates in synthetic chemistry.[96]

The allylic amination of various alkenyl B(MIDA) **12** proceeds smoothly under the catalysis of $SePCy_3$, forming a new C–N bond while avoiding potential issues such as transmetallation or alkene additions. Notably, the configuration of the double bond in substrates **12** has little impact on the outcome, and the reaction can be performed under very mild conditions. Preliminary mechanistic studies suggest that the reaction begins with the formation of a highly reactive selenium bis(imide) intermediate **R-I** through the interaction of the $SePCy_3$ catalyst with the *in situ* generated iminoiodinane. This intermediate then undergoes an *ene* reaction, followed by a [2,3]-σ rearrangement, to afford the aminated product **72** with excellent selectivity.



Scheme 25 Lewis base-catalyzed allylic amination.

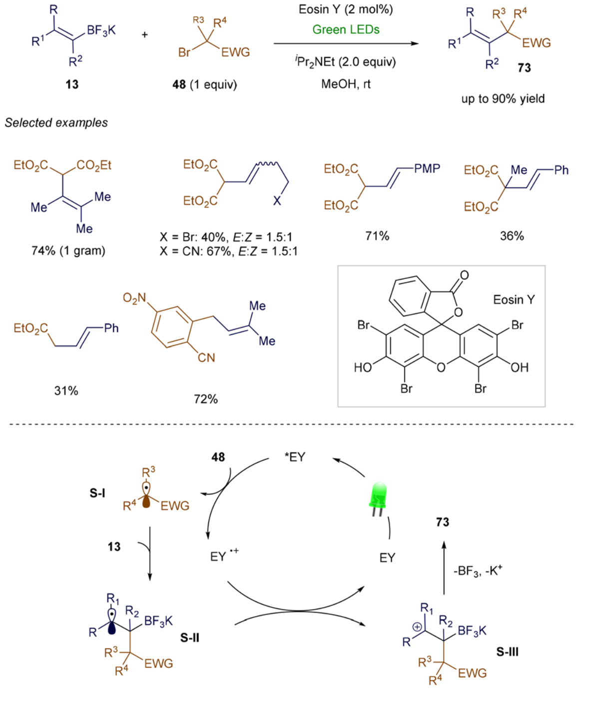
4. Photocatalysis

The recent resurgence of photocatalytic methods has driven the development of numerous protocols for generating highly reactive intermediates, such as free radicals and triplet states, under very mild conditions—typically through light irradiation in the presence of catalytic amounts of a photocatalyst at room temperature.[97] Upon photoexcitation, the photocatalyst gains enhanced redox properties, enabling it to facilitate either single-electron transfer (SET) or energy transfer (E_nT) processes with the target substrate.[98] One well-established application of this open-shell reactivity involves radical additions to alkenyl boron reagents, a strategy that has been explored for over 60 years.[99] Due to the low polarization effect of the boron-based substituent, radical addition can occur either at the α or β position of the vinyl organoboron reagent, depending on the nature of the radicals and the substituents on the alkenyl or boron moiety. For example, as previously mentioned, the groups of Gutierrez[74] and MacMillan[80] have reported selective functionalization of alkenyl boron reagents at the β position of alkenyl boronate esters or the α position of trifluoroborate salts under thermal radical conditions, respectively. The group of Studer pioneered the investigation of open-shell reactivity in vinylboronate complexes through a thermal process.[100] In 2017, Aggarwal's group reported the first light-triggered catalytic procedure for the dicarbofunctionalization of vinyl boronate complexes.[101] This work has further fuelled the development of analogous photochemical methods, driven by the resurgence of photocatalysis over the past decade.

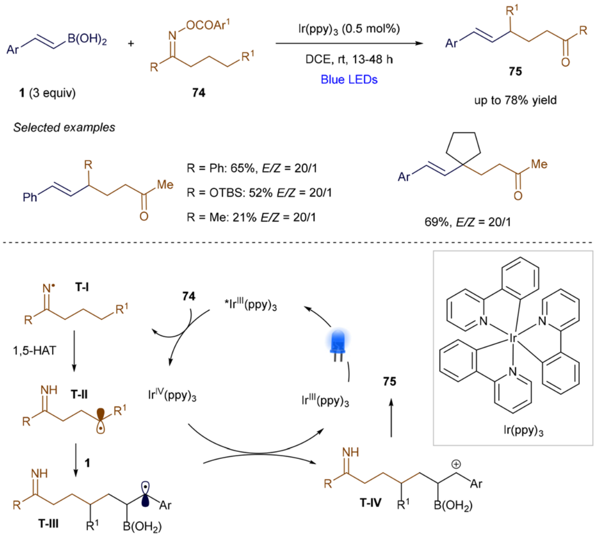
In this section, based on the types of boryl radicals formed, the discussion will be divided into three categories: radical additions at the α or β position of vinyl boronates, and the simultaneous formation of biradicals at both the α and β positions. Both single-electron transfer (SET) and energy transfer (E_nT) activation strategies have been employed in these processes, aiming to broaden the reactivity scope of alkenyl boron reagents.

4.1 Radical addition at α position of vinyl boron reagents: synthesis of alkenes

In 2013, Koike and Akita's group introduced the first photochemical strategy for synthesizing trifluoromethylated alkenes from vinyl boronates and Togni's reagent.[102] Building on this work, Leonori's group later developed a general procedure for the vinylation of various electron-poor alkyl bromide derivatives (Scheme 26).[103] In this reaction, Eosin Y, upon absorbing light, transfers an electron to electron-poor bromides **48**, generating an electrophilic radical. This radical adds to the vinyl potassium trifluoroborate **13**, forming a secondary carbon-centered radical. This radical then undergoes single-electron oxidation, resulting in a β-borato cation, which ultimately forms the desired product **73** *via* elimination.



Scheme 26 Synthesis of functionalized alkenes from potassium vinyltrifluoroborates.

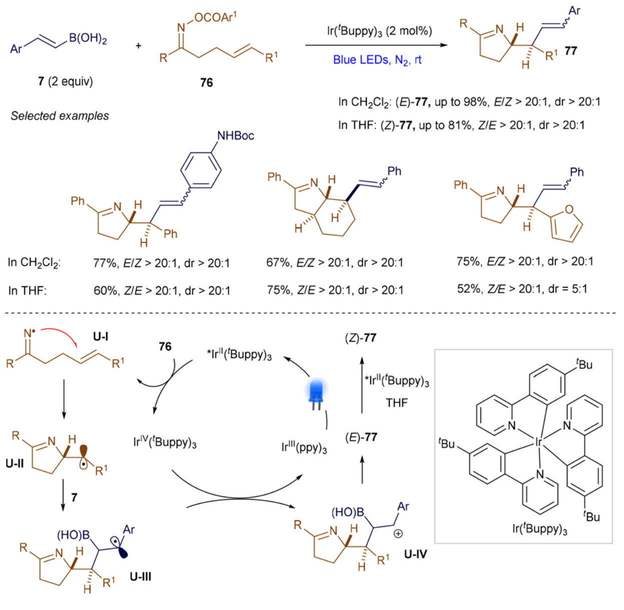


Scheme 27 Remote alkenylation.

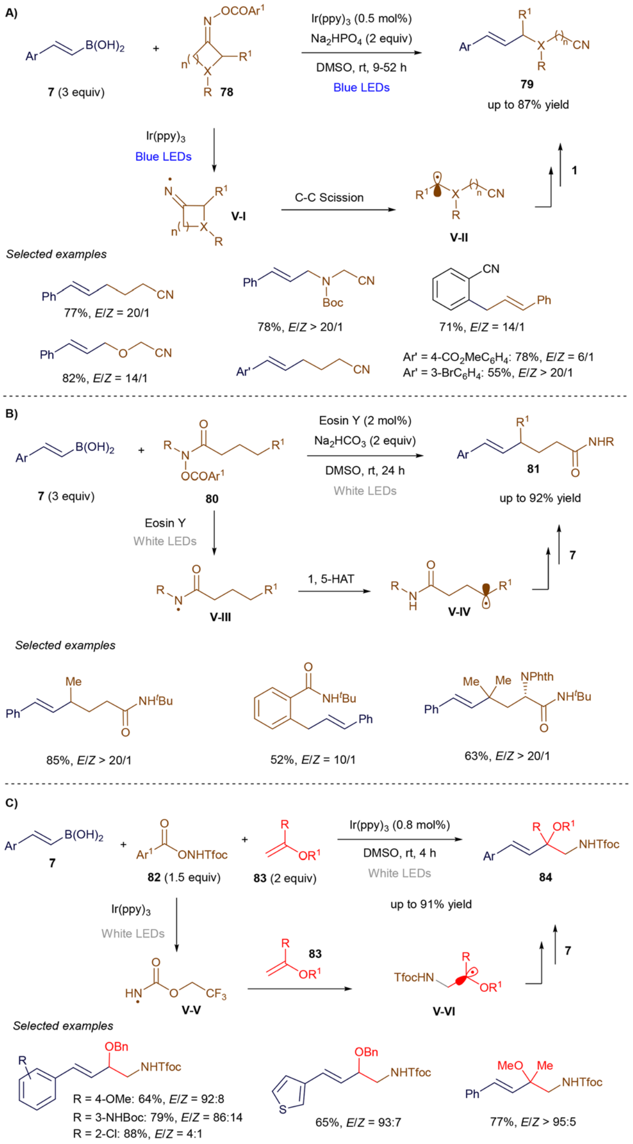
In addition to electrophilic radicals, nucleophilic radicals can also participate in α-position additions to vinyl borons, as demonstrated by Yu's group in 2018 (Scheme 27).[104] In this case, *O*-acyl oximes undergo photoinduced single-electron reduction, generating nitrogen-centered radical **T-I**. This radical undergoes a 1,5-hydrogen atom transfer, producing the corresponding carbon-centered radical **T-II**. Despite having a different polarity compared to the electron-poor radicals discussed in Scheme 25, **T-II** adds at the α-position of a styrenyl boronic acid derivative, forming benzylic radical **T-III**. After single-electron oxidation, this radical undergoes elimination, yielding the alkene product **75**. This method is versatile, enabling the generation of primary, secondary, and tertiary alkyl radicals. However, its main limitation is that it applies primarily to styrenyl boronic derivatives, where the benzyl radical formed after addition is stabilized.

Using a similar strategy, Yu and co-workers also achieved the iminoalkenylation of alkenes *via* photoredox catalysis (Scheme 28).[105] Notably, depending on the choice of solvent, both (*E*)- and (*Z*)-configurations of the alkene products **77** can be selectively obtained. Detailed mechanistic studies suggest that the formation of (*Z*)-**77** results from a photocatalytic, contra-thermodynamic *E* to *Z* isomerization, facilitated by an energy transfer (E_nT) pathway.

In the same work, Yu's group extended this process to the use of hydroxamic acid derivatives **78** (Scheme 29A). Following the photoinduced generation of a nitrogen-centered radical **V-I** *via* single-electron reduction, the radical undergoes carbon–carbon bond cleavage, yielding a carbon-centered radical **V-II**. This radical then adds at the α-position of styrenyl boronic acid **7**, and the resulting benzylic radical, after undergoing single-electron oxidation, leads to alkene product formation through elimination.[104] Later that year, the group demonstrated that amide derivatives **80** (Scheme 29B) could promote a 1,5-hydrogen atom shift to generate a carbon-centered radical **V-IV**. This radical reacts with styrenyl boronic acid **7** to ultimately produce alkene **81**.[106] Finally, Yu and co-workers expanded this methodology to a three-component reaction (Scheme 29C), where hydroxylamine derivatives **82** were combined with a photoredox catalyst to generate nitrogen-centered radicals **V-V**. These radicals were trapped in an intermolecular reaction with electron-rich enol ethers, forming nucleophilic α-oxo radicals **V-VI**, which added to styrenyl boronic acids **7**. The resulting radicals, similar to previous steps, underwent further reactions to yield alkene products **84**.[107]

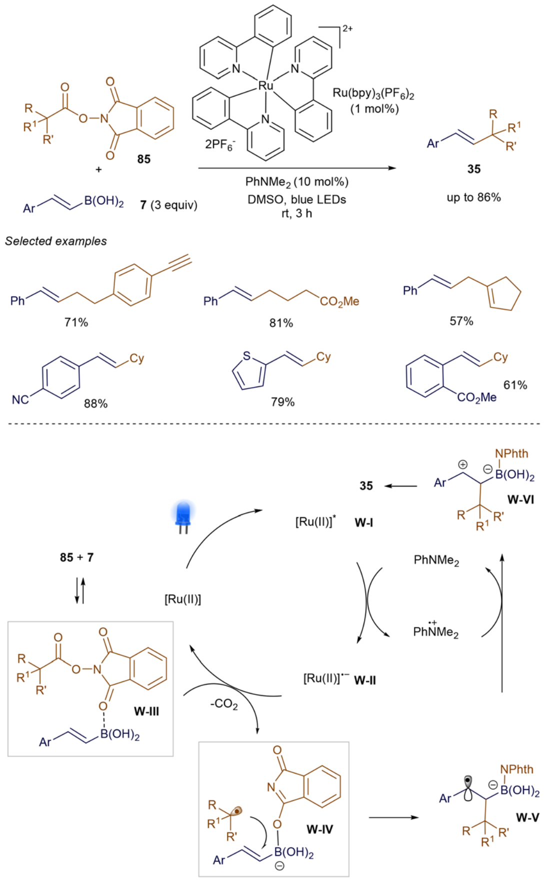


Scheme 28 Iminoalkenylation of alkenes.

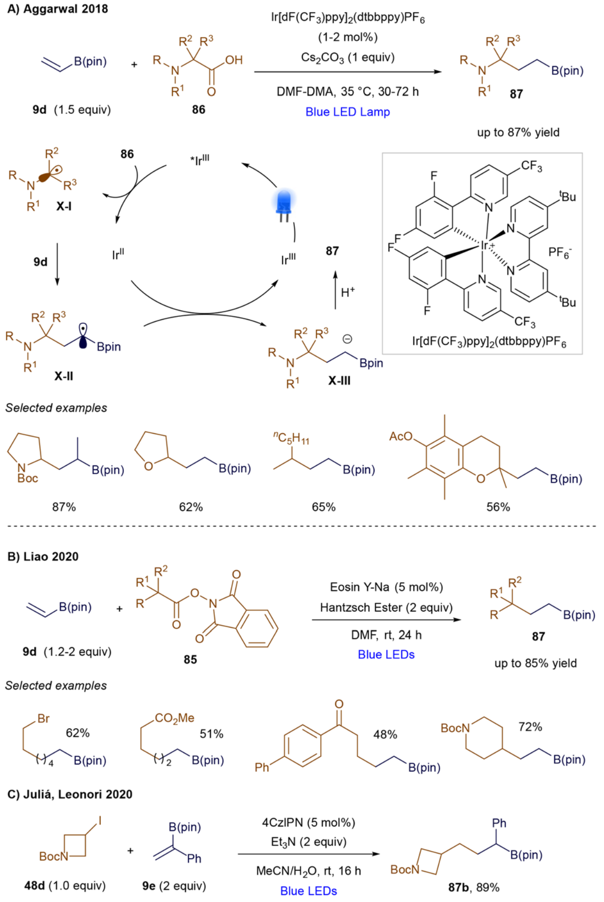


Scheme 29 Remote vinylation reactions.

Unlike Baran's earlier work using NiH catalysis,[69] Watson and co-workers recently reported that photoredox catalysis can effectively promote the decarboxylative cross-coupling of NHPI ester **85** with various styrene boronic acids **7** at room temperature.[108] As shown in Scheme 30, under blue LED irradiation, the decarboxylative coupling proceeds smoothly, catalyzed by $Ru(bpy)_3(PF_6)_2$ and $PhNMe_2$, producing product **35** with versatile functional groups. Control experiments revealed that **85** can be activated through coordination with **7**, facilitating its reduction by intermediate **W-II**. After decarboxylation of **W-III**, a nucleophilic rebound of the phthalimide anion generates the alkyl radical **W-IV** and boronate intermediate **W-V**. Subsequent radical addition, followed by radical-polar crossover *via* oxidation, forms **W-VI**, with final elimination leading to the cross-coupled product **35**.



Scheme 30 Light-promoted decarboxylative cross-coupling.



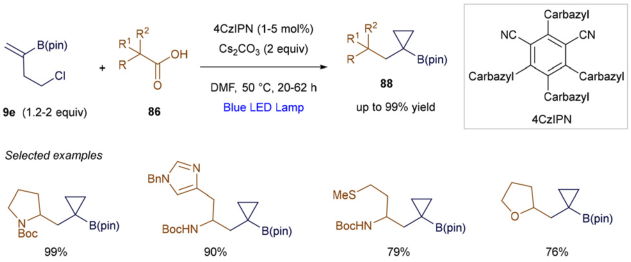
Scheme 31 1,4-Radical additions of vinyl boronic esters.

4.2 Radical addition at β position of vinyl boron reagents: synthesis of alkyl boronates

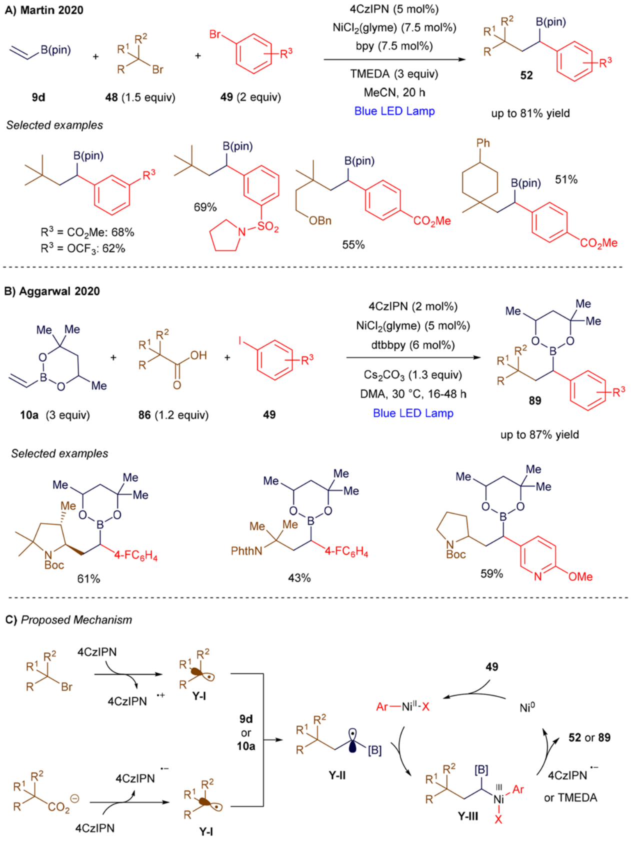
Radical addition. Despite their power, these photochemical methodologies lead to the loss of the boronic ester/acid group due to the formation of a β-borato cation followed by elimination. This group is typically useful for further synthetic modifications. In contrast, a radical addition at the β-position would prevent the formation of a vicinal carbenium ion, as the unpaired electron would now be located on the α-carbon. While this type of reactivity is well-established in thermally-promoted radical chemistry[80] and non-catalytic photochemistry,[109] the photocatalytic variant was first developed by Aggarwal's group in 2018.[110] In this pioneering example, carboxylic acids **86** are converted into the corresponding radicals **X-I** through photo-induced single-electron oxidation and subsequent decarboxylation (Scheme 31A). The radical then undergoes conjugate addition to the vinyl boronic ester **9d**, generating an α-boryl radical **X-II**, which is stabilized by delocalizing the unpaired electron into the adjacent boron's empty p-orbital. Single-electron reduction of this intermediate yields an α-boryl anion **X-III**, which, after protonation, provides the desired γ-amino boronic ester product. Subsequently, Liao's group reported that alkyl *N*-(acyloxy)phthalimides (NHPI, **85**) could also engage in this type of reactivity (Scheme 31B), with Hantzsch ester serving as the terminal reductant.[111] Moreover, Juliá and Leonori demonstrated a successful example of 1,4-radical addition using an aminoalkyl radical as a halogen atom transfer agent to activate secondary alkyl iodides, forming the key secondary alkyl radical. This radical then added to α-phenyl vinyl boronate ester **87b**, yielding the product in 89% yield (Scheme 31C).[112]

Cyclopropanation. Aggarwal's group further expanded this reactivity by developing a photocatalytic 1,2-difunctionalization of vinyl boronic esters (Scheme 32).[113] The key to this method is leveraging the intermediacy of α-boryl anions, which enabled the authors to design a photochemical cyclization sequence. In this sequence, the previously generated carbon-centered anion participates in an intramolecular S$_N$2 step. This radical-polar crossover reactivity allowed for the efficient preparation of synthetically valuable cyclopropyl boronates **88**, with yields reaching up to 99%.

1,2-Carboarylation. The versatility of vinyl borons also enabled the development of a synergistic system involving a nickel catalyst and an organic photocatalyst to promote their difunctionalization. In 2020, Martin's group (Scheme 33A)[114] and Aggarwal's group (Scheme 33B)[115] independently reported two nickel-catalyzed metallaphotoredox strategies for the difunctionalization of vinyl organoborons, each using different



Scheme 32 Cyclopropanation of vinyl boronic esters.



Scheme 33 Light-triggered 1,2-carboarylation of vinyl boronic derivatives.

radical precursors. Martin's group employed alkyl bromides, which are prone to reduction, while Aggarwal's group used carboxylic acids, which are susceptible to oxidation. In both methodologies, a photochemically generated radical (**Y-I**, Scheme 33C) is trapped by the vinyl boron reagent, resulting in an α-boryl radical **Y-II**. Concurrently, the nickel catalyst oxidatively inserts into an aryl bromide, forming a Ni(II) intermediate that intercepts the α-boryl radical, generating a nickel (III) species **Y-III**. This species undergoes reductive elimination to yield the cross-coupled product. After the reaction, the resulting nickel(I) species is regenerated to the active nickel(0) state by the reduced form of the photoredox catalyst.

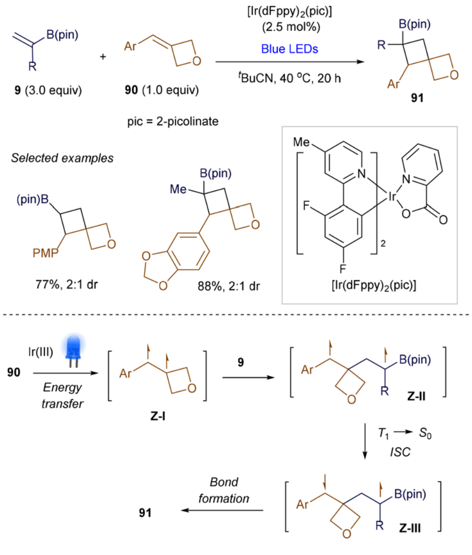
In Martin's work, the net reductive transformation required a stoichiometric amount of tetramethylethylenediamine (TMEDA) as a reductant. More recently, Noël[116] and Chu[117] have expanded this approach, applying it to halogen atom transfer processes and developing an asymmetric variant, respectively.

All the previously discussed photochemical radical additions at the β-position of vinyl boronic esters involve nucleophilic radical precursors. This is because the boron functionality makes the π-system slightly electron-deficient. However, nucleophiles can interact with the empty p-orbital of the boron atom, forming boron-ate complexes. These complexes, in turn, render the π-system electron-rich, which explains why these intermediates preferentially react with electrophilic radicals.

4.3 Triplet energy-transfer catalysis

[2 + 2] cycloadditions. In addition to established examples of synthesizing cyclobutyl boronate *via* thermal [2 + 2] cycloaddition strategies, recent studies have revealed a new approach utilizing visible light-promoted, radical-mediated strategies. Although Hollis tested UV light-mediated [2 + 2] photocycloadditions of alkenyl boronate esters with 2-cyclopentenone as early as 1993,[118] a synthetically useful, visible light-promoted catalytic version was reported by Knowles' group in 2021.[119] Two proposed pathways, discussed below, suggest the photosensitization of either styrenes or β-aryl vinyl boronates to generate key 1,2-triplet biradical intermediates. Knowles demonstrated that the intermolecular, cross-selective [2 + 2] cycloaddition between exocyclic arylidene oxetanes **90** and vinyl boronates **9** proceeds efficiently under Ir(III) photosensitizer catalysis (Scheme 34).[119]

To ensure the desired [2 + 2] reaction occurs in an intermolecular fashion, the triplet energies of the substrates must differ. Preliminary mechanistic studies revealed that visible

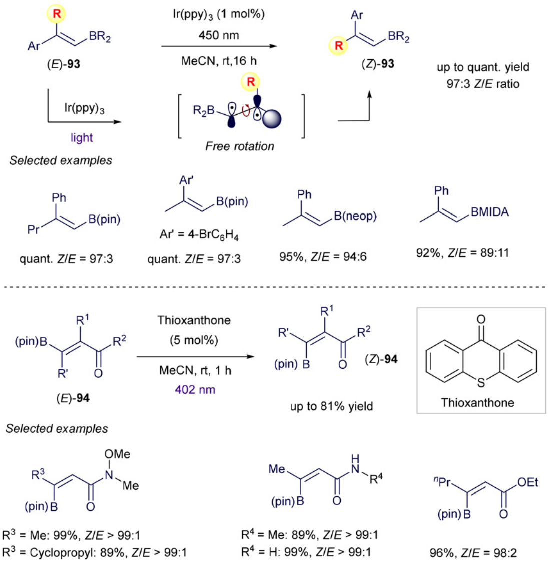


Scheme 34 Catalytic [2 + 2] photocycloaddition.

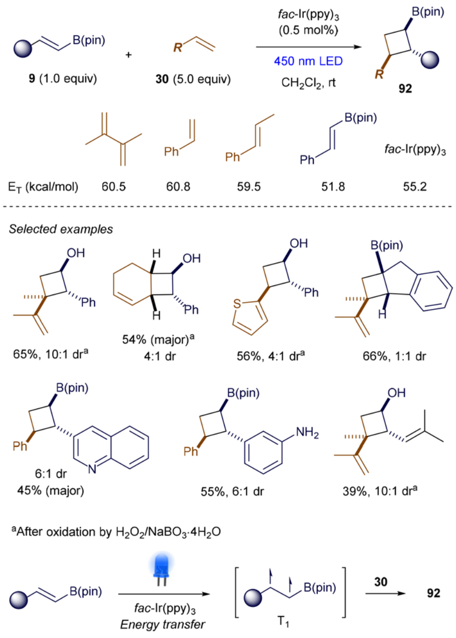
light excitation of the Ir(III) catalyst generates an excited-state complex, Ir(III)* (E_T = 61.1 kcal mol^{-1}). This species can selectively sensitize oxetane **90** (Ar = Ph, E_T = 57.4 kcal mol^{-1}) *via* energy transfer, producing the 1,2-triplet styrene intermediate **Z-I**. The subsequent [2 + 2] cycloaddition proceeds through 1,4-triplet and 1,4-singlet intermediates (**Z-II** and **Z-III**), ultimately yielding the desired products **91**. Shortly after, intramolecular versions of this reaction were also successfully demonstrated by the groups of Yoon[120] and Collins,[121] offering a novel approach to constructing fused cyclobutanes.

In 2022, Swierk and Brown reported that intermolecular [2 + 2] photocycloaddition reactions could also occur through energy transfer involving alkenyl boronates.[122] The key to their success was the use of alkenyl boronates **9** with aryl or vinyl groups at the β-position, which significantly lowered the triplet energies compared to simple styrenes or 1,3-dienes (Scheme 35). Under the catalysis of 0.5 mol% *fac*-Ir(ppy)$_3$, the cross [2 + 2] cycloaddition proceeded smoothly, producing polysubstituted cyclobutylboronates **92** with moderate to good yields and diastereoselectivity. The protocol exhibited good functional group tolerance and was scalable to 5 mmol. Mechanistic studies suggested that triplet energy transfer occurs preferentially from the photoexcited triplet state of *fac*-Ir(ppy)$_3$ to alkenyl boronates **9**, generating the crucial T$_1$ state that initiates the cycloaddition.

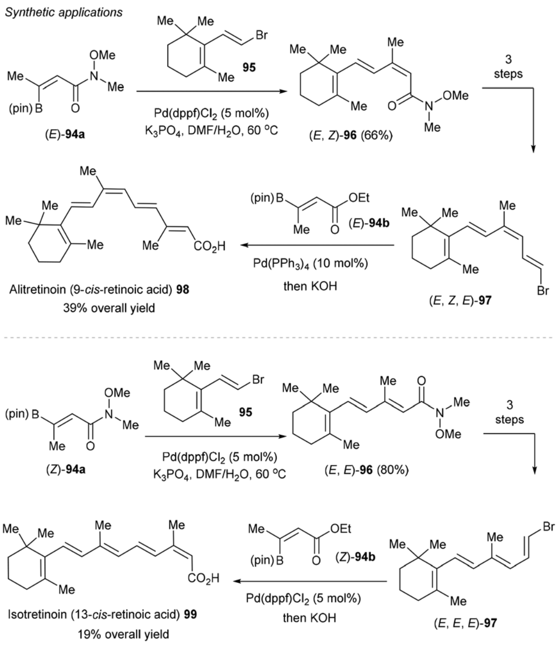
Finally, the use of vinyl boron reagents in the field of synthetic photochemistry is not limited to the above addition of radicals on the π-system, but also to photoinduced energy transfer manifold, as demonstrated by excellent examples from Gilmour and co-workers (Scheme 36).[123–125] In this case, the authors proved how photosensitized alkene isomerization, usually restricted to styrenyl chromophores because of the different absorption properties of the *E* and *Z* isomers, could be expanded to contra-thermodynamic vinyl boron reagents as well. Specifically, the authors discovered how the presence of the boron-based group within the *E* isomers extends the π-system of the whole molecule and therefore permits the energy transfer from the excited state of the simple photocatalyst. After this event and subsequent isomerization, the C–B bond in the *Z* isomer is twisted by 90° and in a dative interaction with an aryl or carbonyl group. Because of this, the *Z* isomer is blue shifted with respect to the *E* analogue and full *E* to *Z* isomerization is possible. As shown in Scheme 36, the iso-



Scheme 36 Photochemical isomerization.



Scheme 35 Catalytic [2 + 2] photocycloadditions.



Scheme 37 Synthetic applications.

merization of *cis*-α-substituted styrenyl boron reagents **93** or **94** takes place smoothly with high fidelity under visible light irradiation,[124] providing a new way for the stereoselective synthesis of sterically more hindered alkenes.

Furthermore, the method can be applied for the facile synthesis of polyene pharmaceuticals alitretinoin (9-*cis*-retinoic acid) **98** and isotretinoin (13-*cis*-retinoic acid) **99** with full control of the geometry of the alkenes, highlighting the usefulness of the methodology (Scheme 37).[124] For example, starting from easily accessible (*Z*)- and (*E*)-**94a**, stereospecific Suzuki–Miyaura cross-coupling using vinyl bromide **95** gave rise to geometrical defined (*E*,*E*)- and (*E*,*Z*)-**96** in high yields. Subsequent reduction, boron-Wittig reaction, followed by bromodeboronation furnished stereodefined intermediate (*E*,*E*,*E*)- and (*E*,*Z*,*E*)-**97**. A second Suzuki–Miyaura cross-coupling with (*E*)-**94b** worked smoothly to deliver 13-*cis*-retinoic acid **98** after hydrolysis. The analogous sequence with (*Z*)-**94a** enabled the synthesis of 9-*cis*-retinoic acid **99** (alitretinoin).

5. Conclusions

This review highlights emerging trends in catalytic synthetic methods using alkenyl boron reagents. The versatility provided by the boron atom within the olefinic system allows these reagents to function as either electrophiles or nucleophiles, depending on reaction conditions. This flexibility has been harnessed to develop metal-catalyzed processes, as detailed in section 2, where alkenyl boron compounds serve as either nucleophilic transmetallation reagents or electrophiles in various innovative transformations. Beyond metal catalysis, this versatility extends to organocatalytic protocols (section 3). Moreover, these reagents have proven useful in photocatalytic processes (section 4), demonstrating their broad reactivity, including polar and radical chemistries. These successful strategies offer new protocols for the efficient and stereoselective synthesis of valuable alkenes and alkyl boronates. The practical applications of these methods are exemplified by their use in synthesizing natural products and bioactive molecules.

Despite the progress made, many challenges and opportunities remain, offering ample room for further investigation. (1) The substrate scope is still limited. While many examples focus on aryl boron reagents, less attention is given to alkenyl boron reagents, even though the transition from aryl- to alkenyl-substituted boron reagents is non-trivial. (2) Compared to the polar reactivity of alkenyl boron reagents, their intriguing open-shell reactivity has yet to be fully explored. (3) Although several elegant examples have been reported, their asymmetric variants lag behind due to the challenge of controlling enantioselectivity, alongside chemo-, regio-, and diastereoselectivity. (4) Lastly, there is still a high demand within the synthetic community for practical methods that employ these protocols for the synthesis of highly valued molecules. We believe that the development of novel catalytic systems is crucial to addressing these challenges. For example, beyond the established metal, organo-, and photocatalytic systems, electrosynthesis[126] could further drive this chemistry forward. Additionally, DFT studies could offer deeper insights and guidance in this area. We anticipate that these findings will significantly impact this field in the near future.

Data availability

All relevant data are within the paper.

Conflicts of interest

There are no conflicts to declare.

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