

REVIEW

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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 Csp³ (alkyl), Csp² (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, Csp²- 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 allenyl⁵ or alkynyl⁶ 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

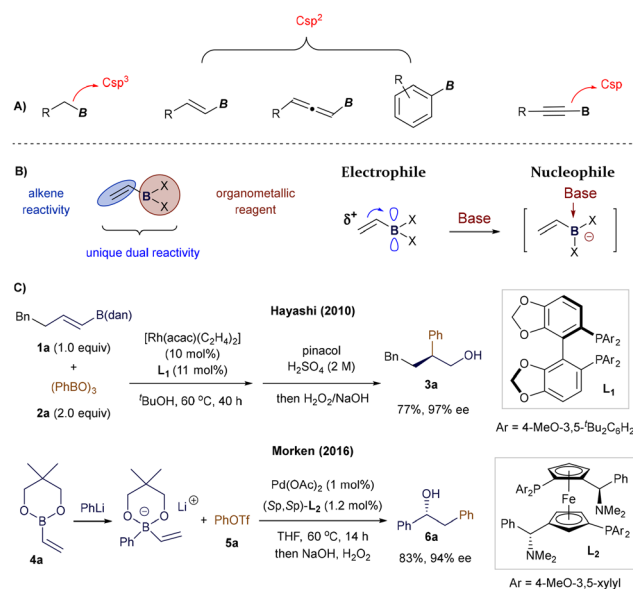


Fig. 1 Comparing the structure of different boron reagents and the typical reactivity of alkenyl boron reagents.

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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 boranes⁹ and Morken's Pd-catalyzed conjugative 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

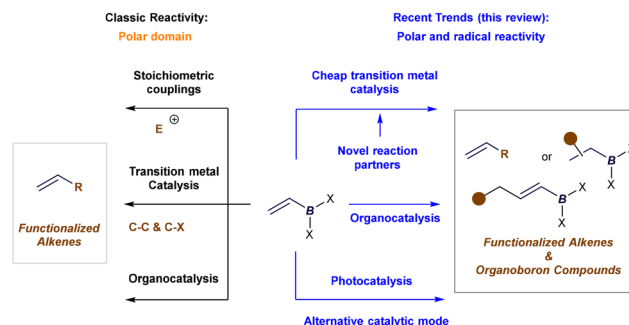


Fig. 3 Classic applications and scope of the review in the reactivity of alkenyl boron reagents in catalysis.

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).

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}

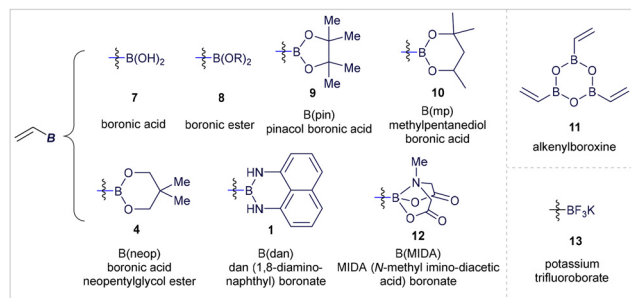
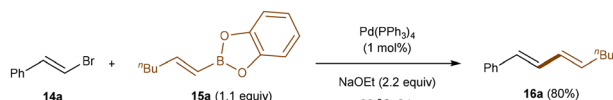


Fig. 2 Alkenyl boron reagents discussed within this review.

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 transmetalation 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

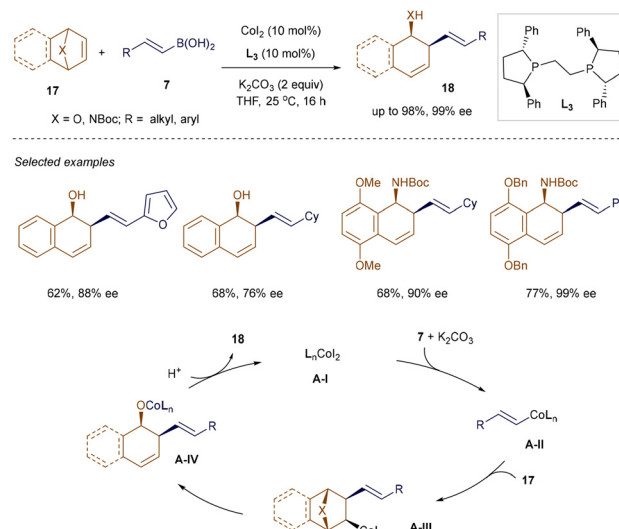
In early contributions, alkenyl boron reagents were primarily employed as organometallic partners in Pd- and Ni-catalyzed Suzuki–Miyaura-type cross-couplings, often in combination with organohalides for constructing C–C bonds.^{2a,d,16} Additionally, their use in rhodium-catalyzed Hayashi–Miyaura additions 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 CO₂²¹ as well as electron-deficient alkenes²² 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 Zhao²⁷ have disclosed the use of both Ni(II) and Co(II) catalysis to explore the asymmetric addition of alkenyl boronic acids to cyclic *N*-sulfinimines 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 alkenylation 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 CoI₂ 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 K₂CO₃, 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 $\text{Mn}_2(\text{CO})_8\text{Br}_2$, 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 $\text{Ni}(\text{acac})_2$, $\text{Pd}(\text{PPh}_3)_4$, and $[\text{Rh}(\text{COD})\text{Cl}]_2$ —failed to deliver the desired hydro-vinylation product.

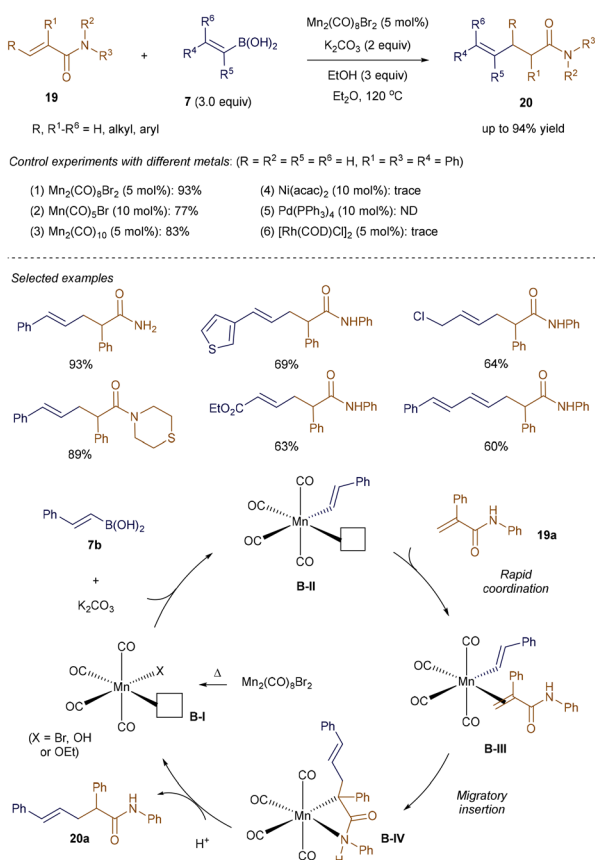
As proposed by the authors (Scheme 3), the mechanism begins with the homolysis of the dimeric manganese pre-catalyst $\text{Mn}_2(\text{CO})_8\text{Br}_2$ at 120 °C, generating the active 16-electron Mn-species **B-I**, which features a vacant coordination site. Base-assisted transmetalation of alkenyl 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

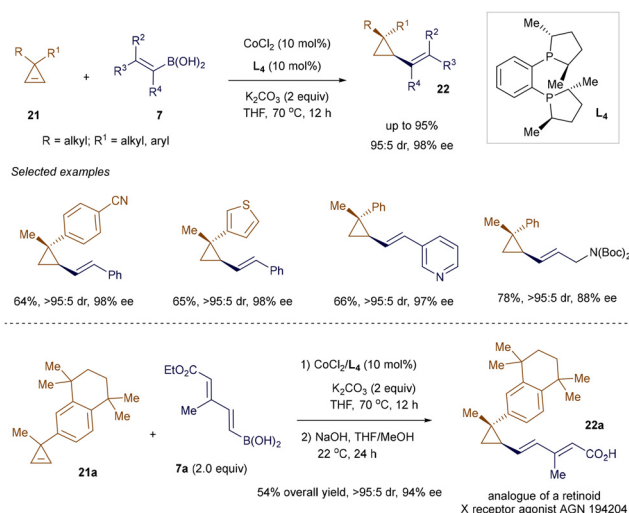
reported, facilitating the realization of hydroalkenylation processes. In these reactions, fine-tuning of the conditions is often necessary to avoid over-addition of the vinyl precursor to the alkene products. Hydroalkenylation of unsaturated hydrocarbons, such as unbiased alkenes and cyclopropenes, 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 $\text{Co}(\text{II})$ /chiral phosphine **L₄** 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.

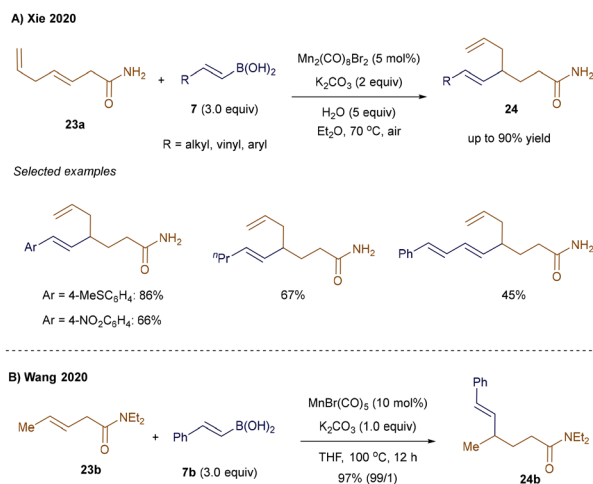


Scheme 4 Co(II)-catalyzed addition to cyclopropenes.

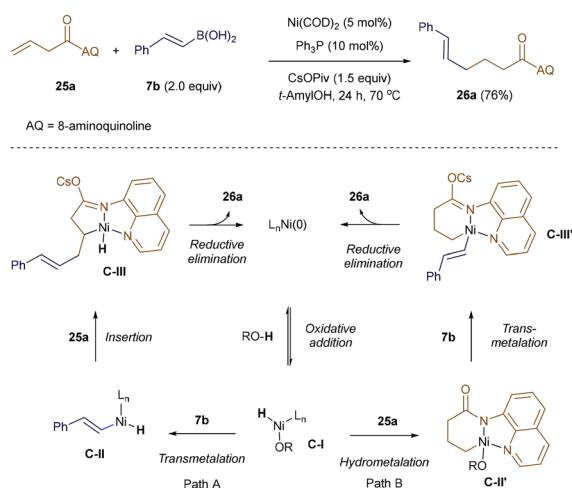


ence of terminal olefins (Scheme 5A).³⁹ This strategy was demonstrated with substrate **23a**, which contains both a terminal and an internal double bond, yielding the selectively 4,5-hydrovinylation product **24** in 45–90% yield. A similar transformation was reported by Wang and co-workers using tertiary 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



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

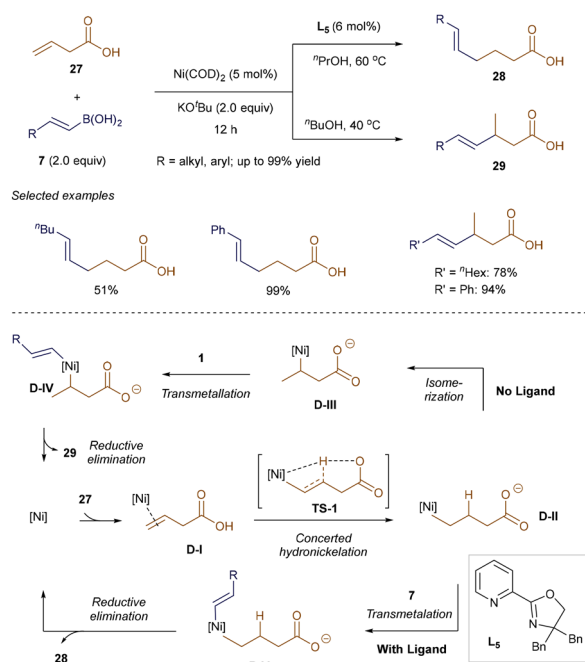


Scheme 6 Ni-catalyzed hydroalkenylation.

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 transmetalation 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 hydrometalation of intermediate **I** across the double bond of **25a** produces a six-membered nickelacycle, **C-II'**. Transmetalation 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

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 **L5**. 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 hydronicellation **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 **L5**, however, **D-II** directly undergoes transmetalation with alkenyl boronic acids **7** to form **D-V**, where steric hindrance from **L5** prevents isomerization. In both pathways, transmetalation determines the rate and selectivity of the reaction.⁴³

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

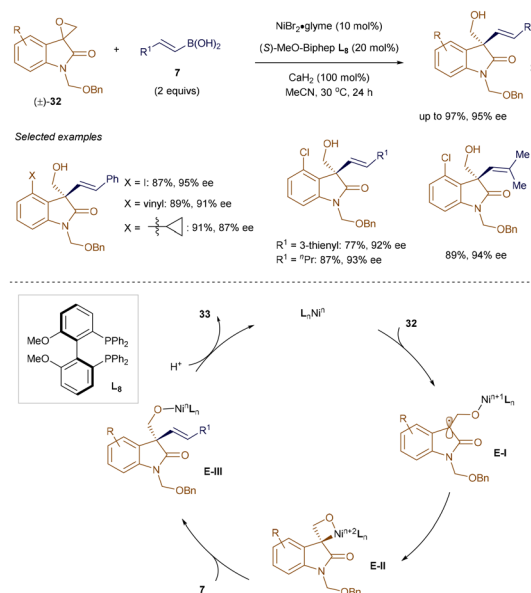


Scheme 7 Regiodivergent hydroalkenylation.



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

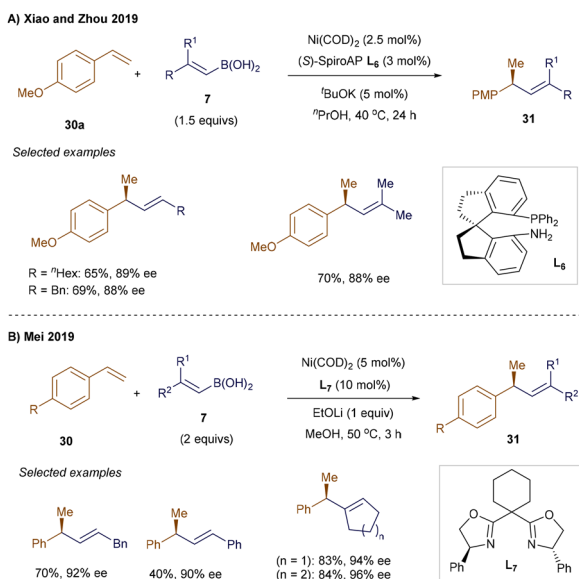
Cross-couplings. As discussed later in this section, both radical and polar pathways have been explored for challenging coupling transformations. Epoxides, due to their strained ring structure, are highly reactive intermediates and easily synthesized from alkenes and carbonyl compounds. Although transition metal-catalyzed⁴⁷ and metal-free⁴⁸ 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 NiBr₂/L₈ 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 9 Enantioconvergent coupling of spiroepoxyoxindoles with alkenyl boronic acids.

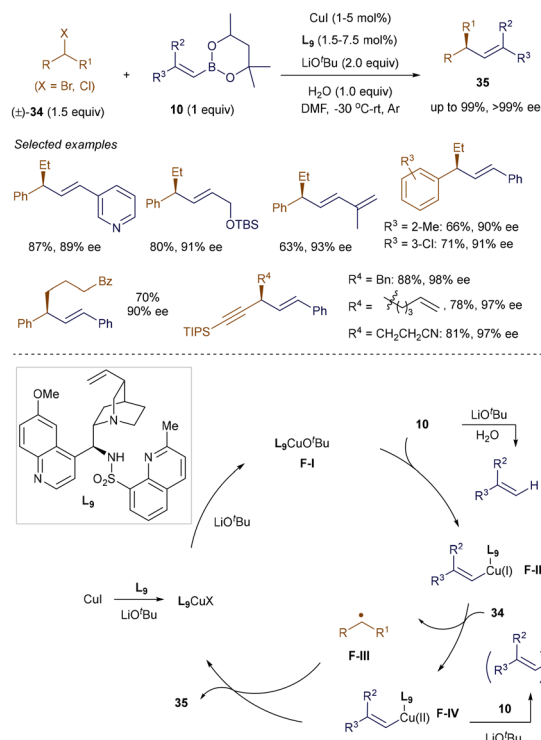
While enantioconvergent cross-coupling of racemic alkyl halides with alkenyl boronate esters is a promising strategy for constructing chiral Csp³–Csp² bonds, it remains underdeveloped due to challenges in achieving both high reactivity and enantioselectivity.⁵¹ In 2022, Liu and co-workers successfully 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, LiOtBu, and ligand **L**₉ in its tridentate form. Transmetalation 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 8 Enantioselective hydroalkenylation of styrenes.

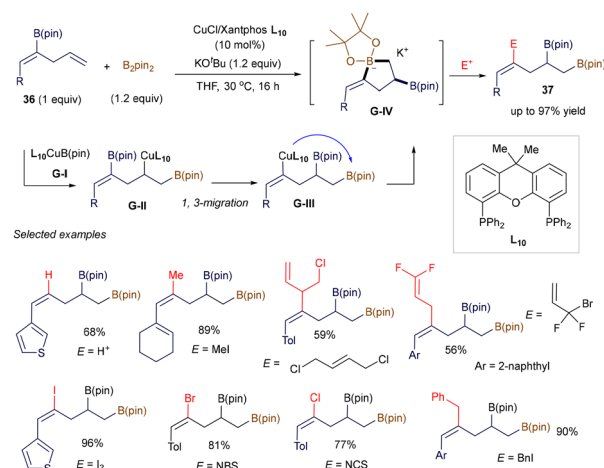




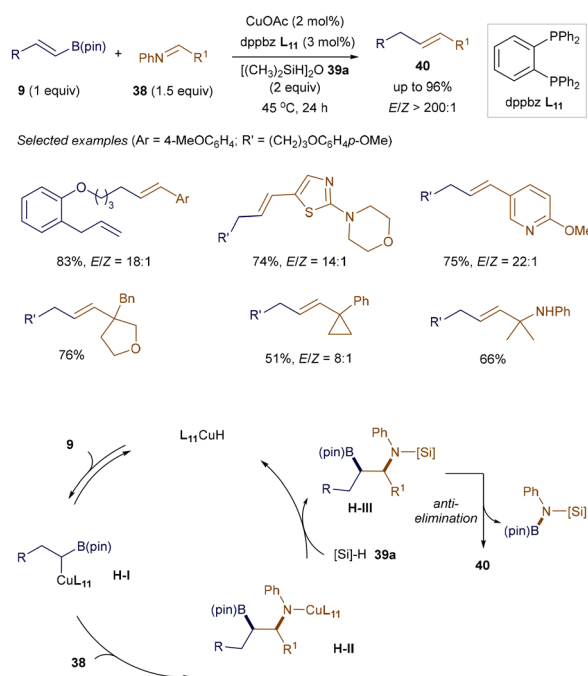
Scheme 10 Enantioconvergent coupling of secondary alkyl halides.

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, stereo-specific B/Cu 1,3-rearrangement, where the B(pin) group migrates from a Csp² to a Csp³ center (Scheme 11).⁵³ By trapping **G-IV** *in situ* with various electrophiles—such as protons, alkyl halides, I₂, 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 KOtBu or KOMe can form Lewis base adducts with intermediate **G-I**, the use of bulky *tert*-butoxide prevents stable adduct formation with L₁₀CuBpin, 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 L₉CuH to alkenyl boronates **9**, acting as an ylide



Scheme 11 Boron-copper 1,3-rearrangement.

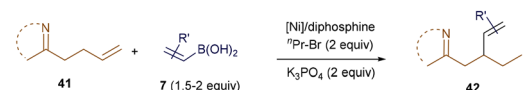


Scheme 12 Copper-catalyzed olefination of imines.

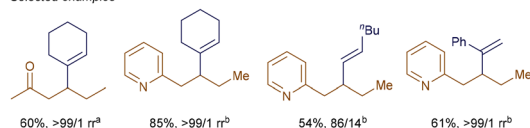
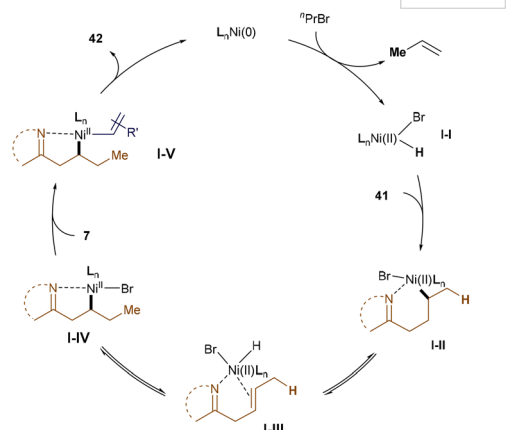
equivalent. Subsequent addition to imine **38**, followed by interaction with hydrosilane **39a**, produces intermediate **H-III**. This 1,2-boryl *N*-silylamine **H-III** then eliminates, furnishing the *E*-alkene products **40**.

NiH-involved migratory hydrofunctionalization of alkenes has emerged as an efficient method for the selective functionalization of Csp³-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



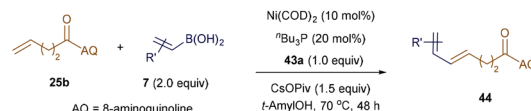


Selected examples

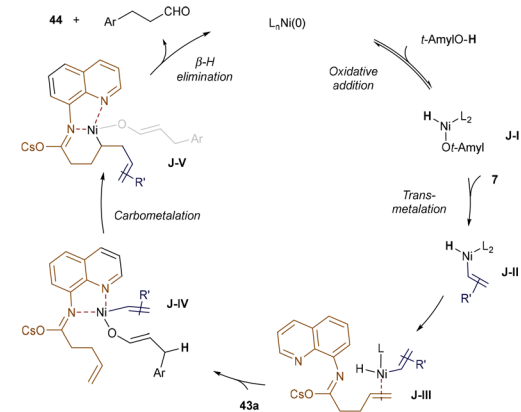
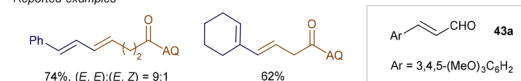
a): $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (10 mol%), $\text{Ph}_2\text{P}(\text{CH}_2)_6\text{PPh}_2$ L_{12} (15 mol%), 90 °C, 24 hb): NiI_2 (10 mol%), L_{13} (15 mol%), 100 °C, 24 hScheme 13 Ni(II)H-catalyzed β -vinylation.

the reaction involves the formation of a $\text{L}_n\text{Ni(II)Br-H}$ intermediate **I-I** via the oxidative addition of $\text{L}_n\text{Ni(0)}$ to $n\text{PrBr}$, followed by β -H elimination. After the migratory insertion of alkenes into **I-I**, assisted by nitrogen coordination, a stable nickelacycle **I-IV** is formed through a β -H elimination and reinsertion process. Transmetalation 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 transmetalation 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,



Reported examples

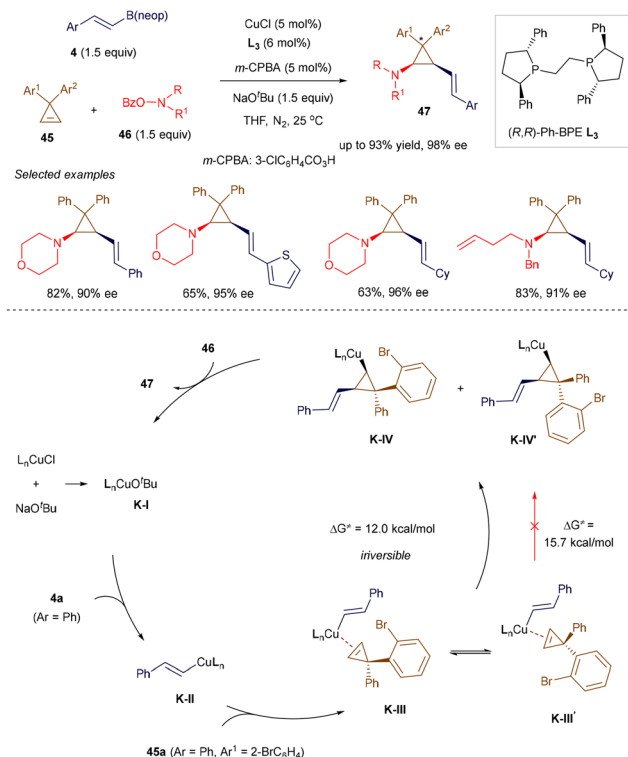


Scheme 14 Ni-catalyzed oxidative Heck reaction.

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 transmetalation. 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-BrC₆H₄ 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.

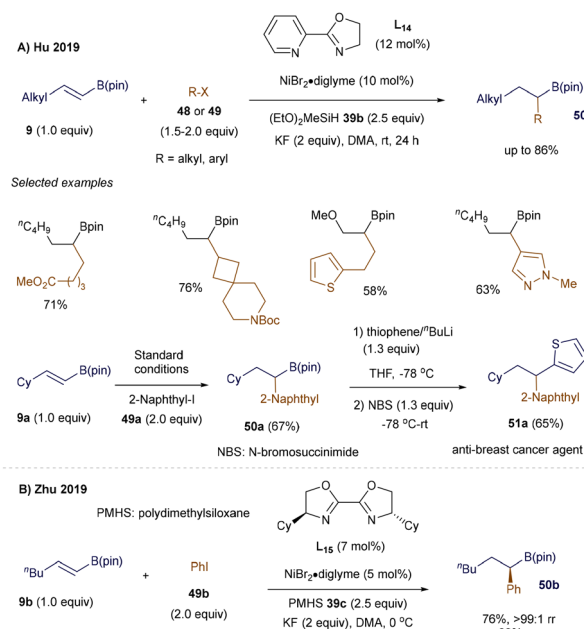
2.2 Alkenyl boron reagents as the electrophilic partner – functionalization of the olefinic moiety

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 carbocationization.⁶⁷ The second pathway focuses on conjunctive cross-coupling *via* 1,2-migrations of boronate complexes, largely pioneered by Morken and co-workers.^{27,10,68} 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).

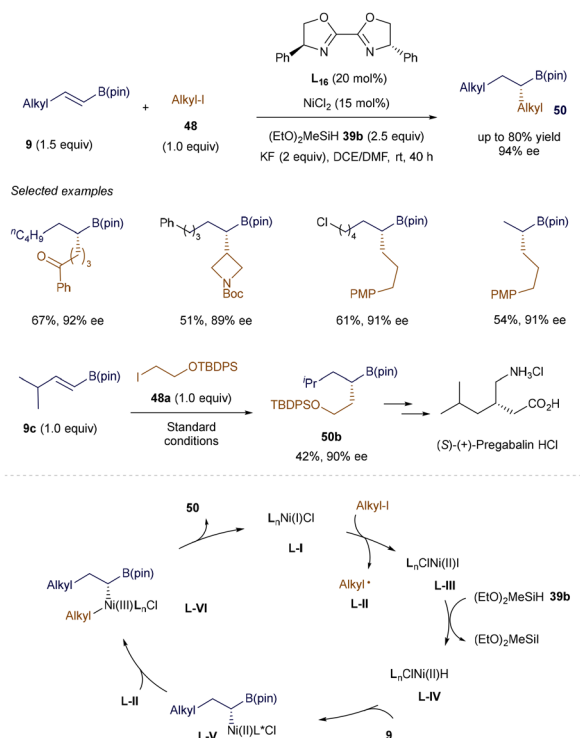
Hydroalkylation. To broaden the scope of hydroalkylation of alkenyl boronates *via* CuH catalysis, 66 organic chemists have long been intrigued by the potential to form new carbon–carbon bonds through the open-shell reactivity of alkenyl boron reagents. In 2014, Baran's group reported an FeH-catalyzed hydroalkylation of alkenyl boron reagents.⁶⁹ Around the same time, Hu⁷⁰ and Zhu⁷¹ 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.

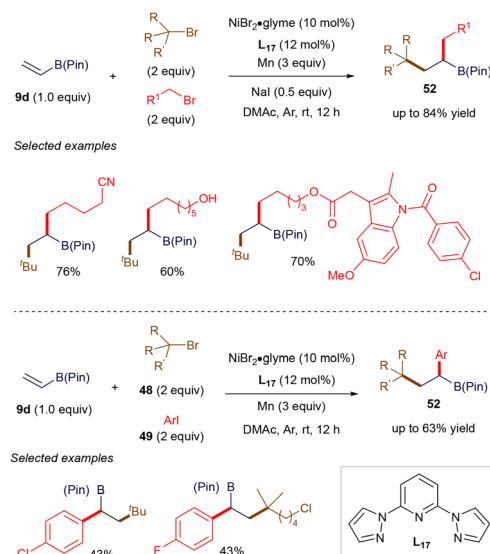




Scheme 17 NiH-catalyzed enantioselective hydroalkylation.

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 $L_nNi(I)Cl$ species **L-I**, which reduces alkyl iodide to form an alkyl radical **L-II** and $L_nClNi(II)$ **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 co-workers 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 shown

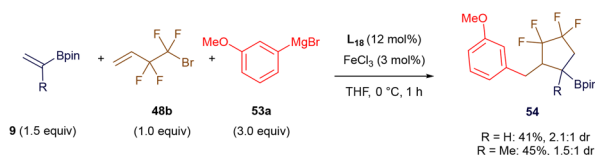
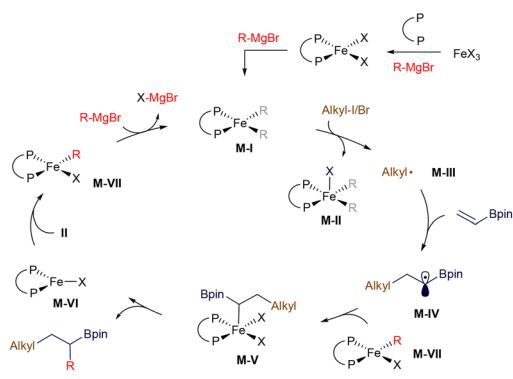
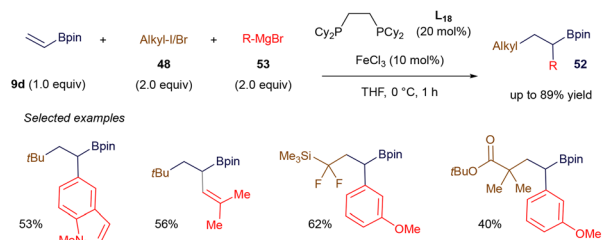


Scheme 18 Ni(I)-catalyzed selective 1,2-alkylation and 1,2-alkylarylation.

cased 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**.

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 mono-arylated 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**.

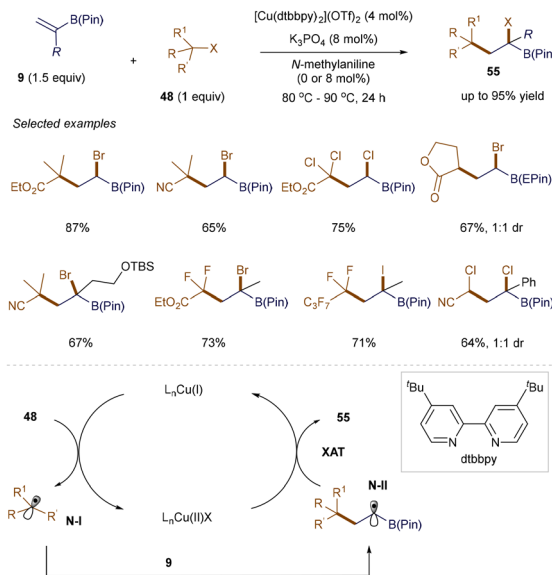




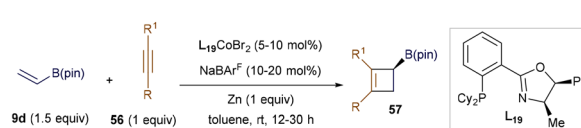
Scheme 19 Iron-catalyzed 1,2-biscarbofunctionalization.

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 $[\text{Cu}(\text{dtbbpy})_2](\text{OTf})_2$ 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 L_nCu (I), generating radical **N-I** and $\text{L}_n\text{Cu}(\text{II})\text{X}$. After radical **N-I** adds to **9**, the resulting α -boryl radical **N-II** undergoes halogen atom transfer (XAT) with $\text{L}_n\text{Cu}(\text{II})\text{X}$, forming the desired product **55** and regenerating $\text{L}_n\text{Cu}(\text{I})$.

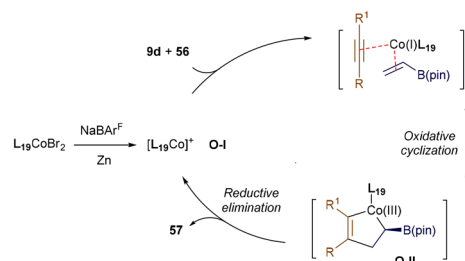
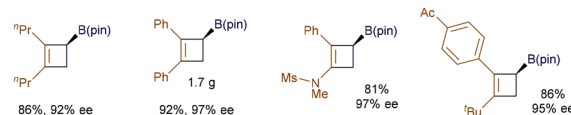
[2 + 2] cycloaddition. In 2019, Rajanbabu and co-workers introduced an excellent and practical method for the enantioselective synthesis of cyclobutyl boronates **57** *via* a Co(I)-catalyzed [2 + 2] cycloaddition between simple alkynes **56** and alkenyl boronate **9d** (Scheme 21).⁷⁶ This method demonstrated 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



Scheme 20 ATRA reaction.



Selected examples



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

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.

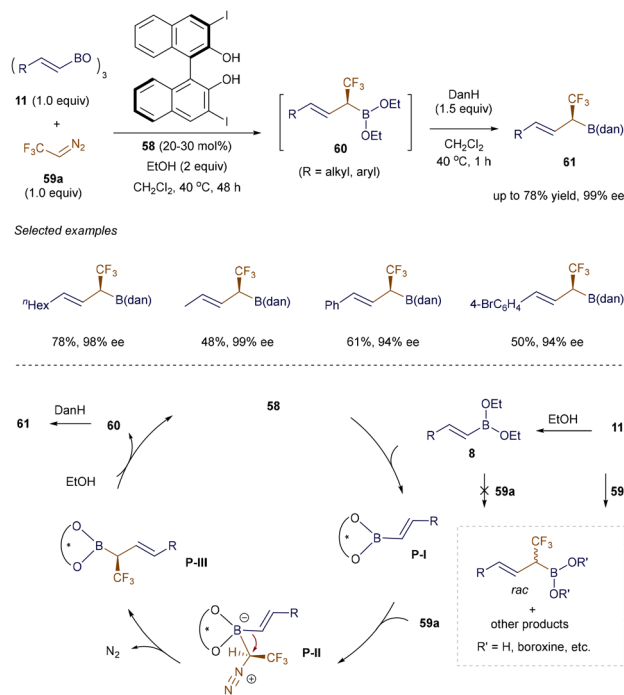
3. Organocatalysis

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



3.1 Chiral diol-catalyzed insertion reactions

In 2020, Szabó *et al.* introduced a practical method for synthesizing chiral α -CF₃ or α -SiMe₃ 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 CF₃-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

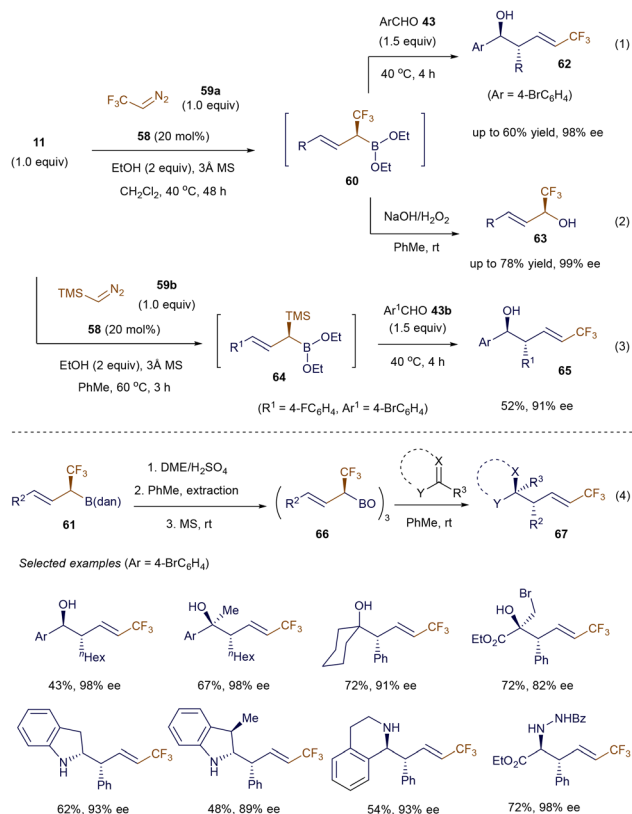


Scheme 22 Organocatalytic synthesis of α -CF₃ allylboron compounds.

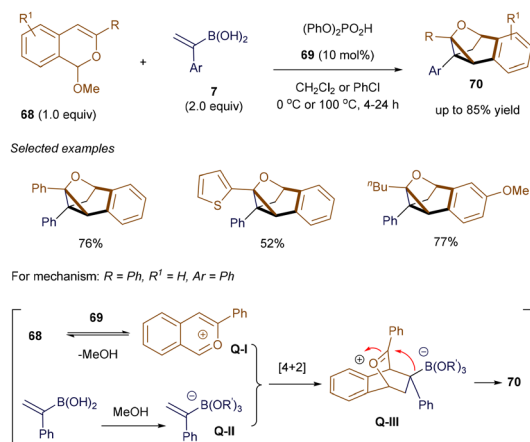
Furthermore, by reacting the chiral intermediate **60** with aldehydes **43** or under oxidative conditions ($\text{NaOH}/\text{H}_2\text{O}_2$), a variety of $\alpha\text{-CF}_3$ -substituted alcohols **62** or **63** were obtained in good to high yields with good to excellent enantioselectivities (Scheme 23, eqn (1) and (2)). Additionally, the method is compatible with Me_3Si -diazomethane **59b**, opening a new pathway for the preparation of enantioenriched $\alpha\text{-SiMe}_3$ allylboronates **64** (eqn (3)). To further demonstrate the utility of these methods, the authors presented a one-pot strategy to convert the $\alpha\text{-CF}_3$ allyl boronic derivatives **61** into $\alpha\text{-CF}_3$ 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 10 π -electron isobenzopyrylium ion as a key intermediate to facilitate cycloaddition reactions.⁹³ Soon after, Huang and Sun further demonstrated that using (1-arylviny)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)₂PO₂H **69** with appropriate acidity serves



Scheme 23 Diverse reactivities of allylic boron and silicon reagents.



Scheme 24 Synthesis of cyclopropane-containing tricyclic skeleton.

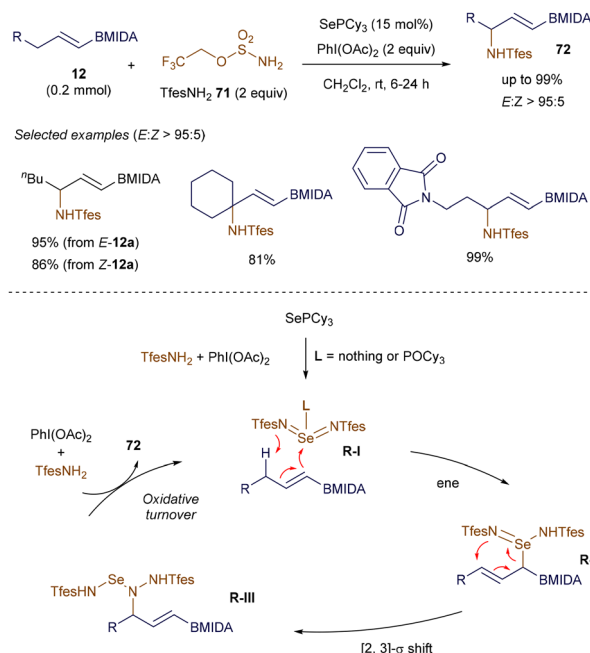
as an effective catalyst for this unusual process. A variety of highly strained products **70** were easily isolated in yields ranging from 41% to 85%, even on a gram scale. According to the proposed mechanism, the isobenzopyrylium ion **Q-I** forms through the interaction of catalyst **69** with substrate **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 gen-

erates 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 SePCy₃, forming a new C–N bond while avoiding potential issues such as transmetalation 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 SePCy₃ 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

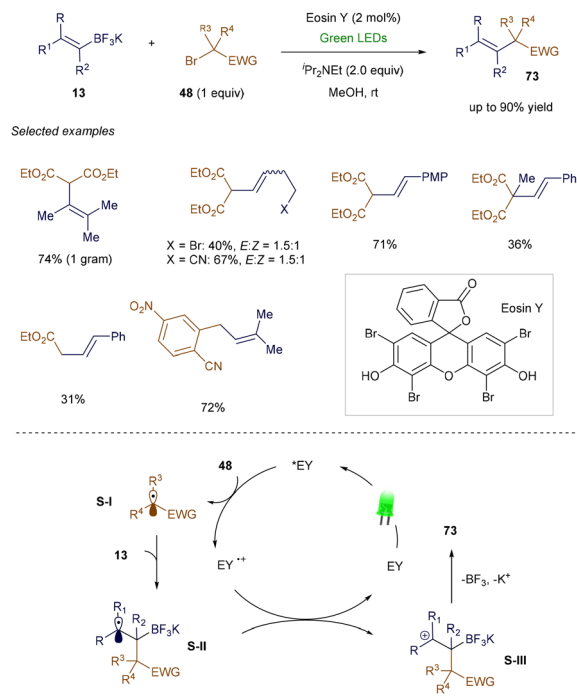
The recent resurgence of photocatalytic methods has driven the development of numerous protocols for generating highly reactive intermediates, such as free radicals and triplet states, under very mild conditions—typically through light irradiation in the presence of catalytic amounts of a photocatalyst 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 Gutierrez⁷⁴ and MacMillan⁸⁰ 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.

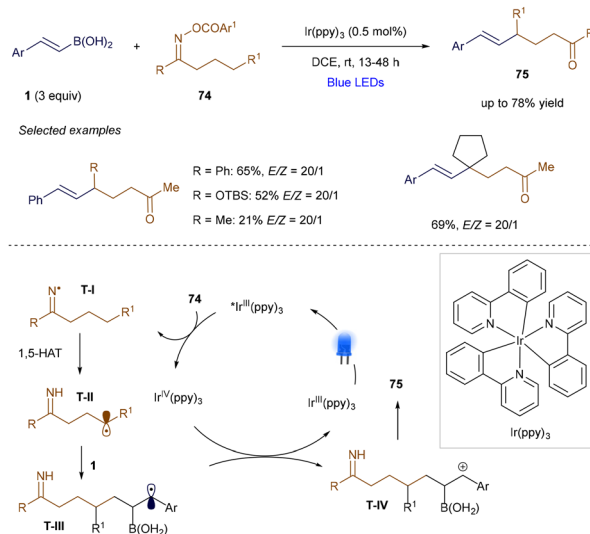
4.1 Radical addition at α position of vinyl boron reagents: synthesis of alkenes

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.

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



Scheme 26 Synthesis of functionalized alkenes from potassium vinyltrifluoroborates.



Scheme 27 Remote alkenylation.

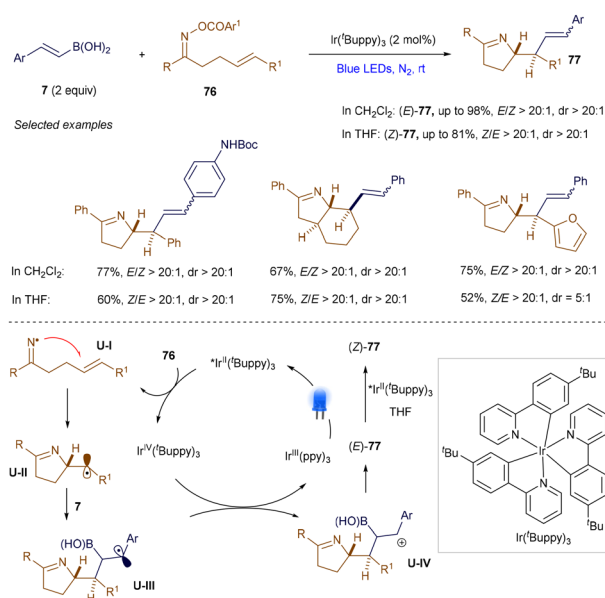
case, *O*-acyl oximes undergo photoinduced single-electron reduction, generating nitrogen-centered radical **T-I**. This radical undergoes a 1,5-hydrogen atom transfer, producing the corresponding carbon-centered radical **T-II**. Despite having a different polarity compared to the electron-poor radicals 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,



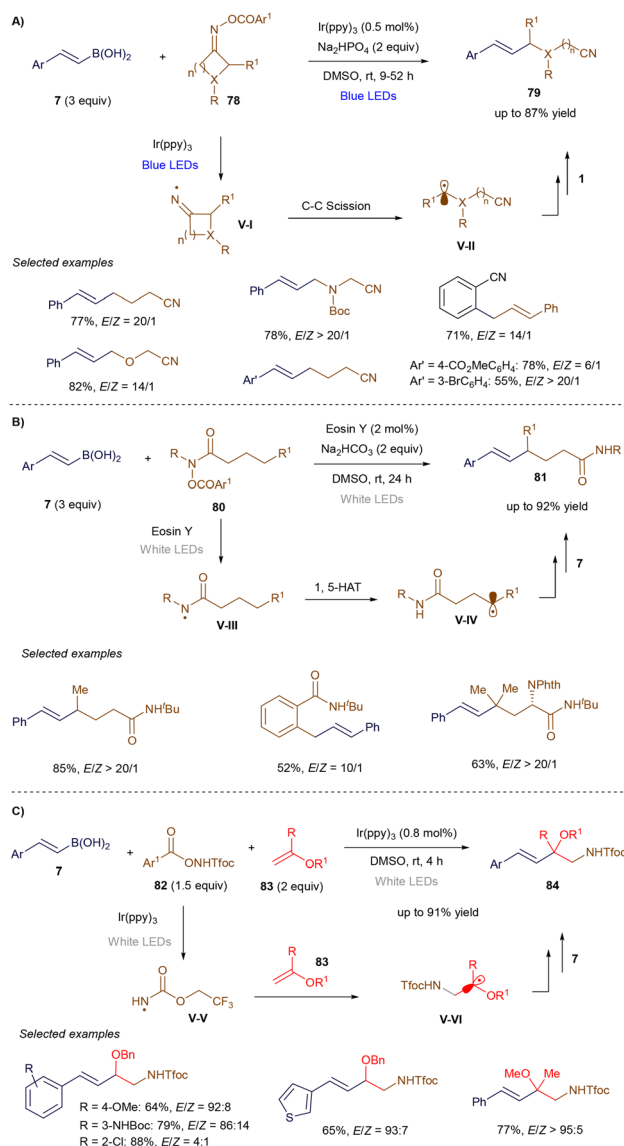
enabling the generation of primary, secondary, and tertiary alkyl radicals. However, its main limitation is that it applies primarily to styrenyl boronic derivatives, where the benzylic radical formed after addition is stabilized.

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



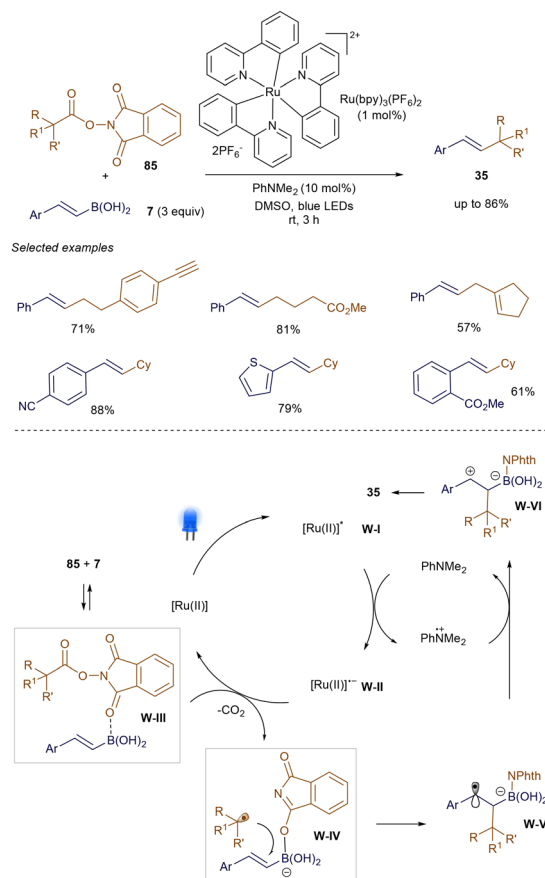
Scheme 28 Iminoalkenylation of alkenes.



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 $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$ 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**.

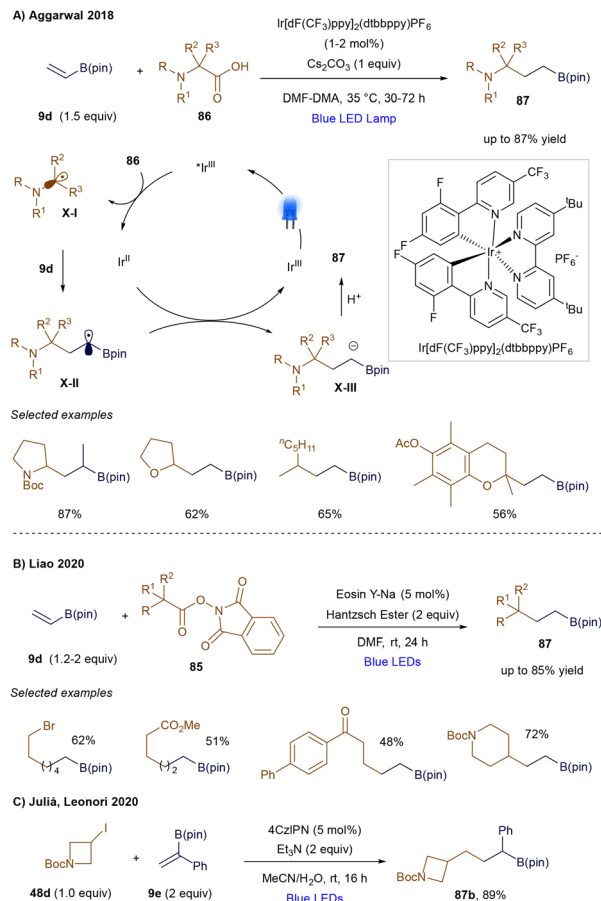




Scheme 30 Light-promoted decarboxylative cross-coupling.

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 chemistry⁸⁰ 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



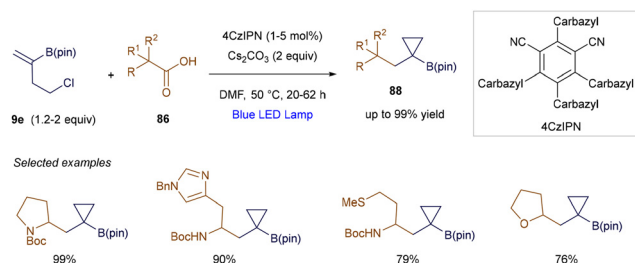
Scheme 31 1,4-Radical additions of vinyl boronic esters.

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

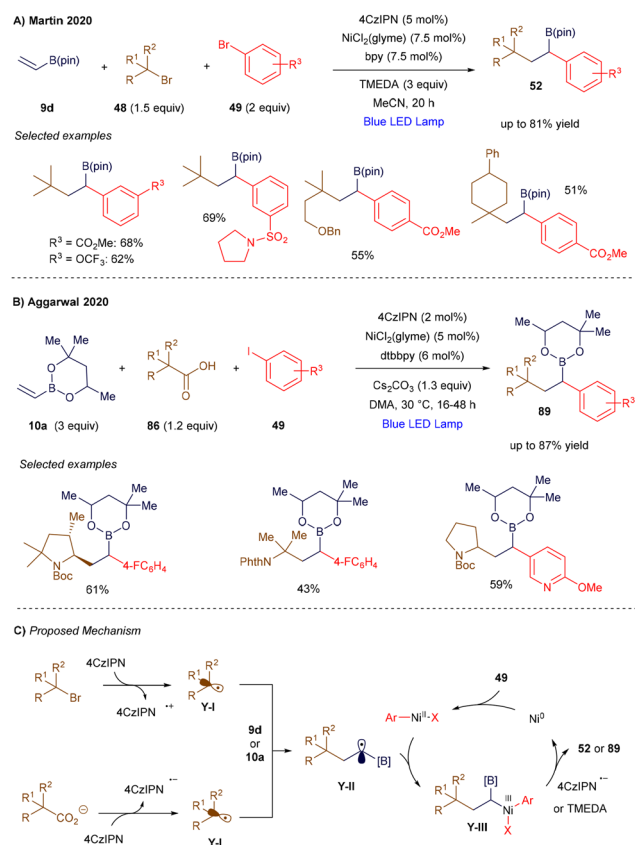
Cyclopropanation. Aggarwal's group further expanded this reactivity by developing a photocatalytic 1,2-difunctionalization of vinyl boronic esters (Scheme 32).¹¹³ The key to this method is leveraging the intermediacy of α -boryl anions, which enabled the authors to design a photochemical cyclization sequence. In this sequence, the previously generated carbon-centered anion participates in an intramolecular S_N2 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.

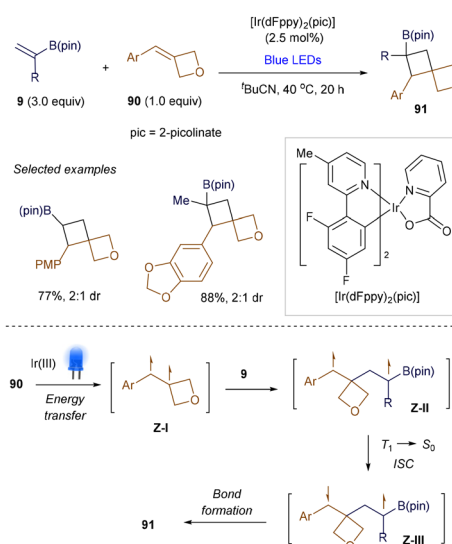
In Martin's work, the net reductive transformation required a stoichiometric amount of tetramethylethylenediamine (TMEDA) as a reductant. More recently, Noël¹¹⁶ and Chu¹¹⁷ have expanded this approach, applying it to halogen atom transfer processes and developing an asymmetric variant, respectively.

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



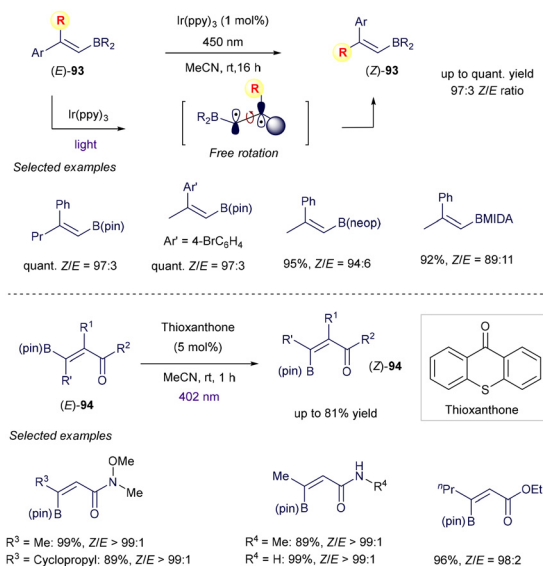
Scheme 34 Catalytic [2 + 2] photocycloaddition.



light excitation of the Ir(III) catalyst generates an excited-state complex, Ir(III)* ($E_T = 61.1 \text{ kcal mol}^{-1}$). This species can selectively sensitize oxetane **90** (Ar = Ph, $E_T = 57.4 \text{ kcal mol}^{-1}$) *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 Yoon¹²⁰ and Collins,¹²¹ offering a novel approach to constructing fused cyclobutanes.

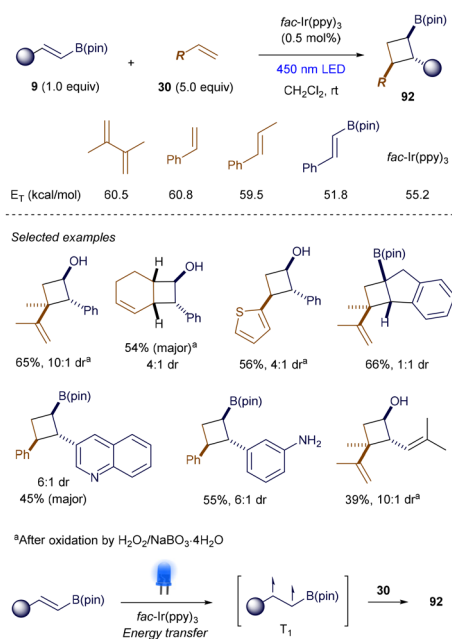
In 2022, Swierk and Brown reported that intermolecular [2 + 2] photocycloaddition reactions could also occur through energy transfer involving alkenyl boronates.¹²² The key to their success was the use of alkenyl boronates **9** with aryl or vinyl groups at the β -position, which significantly lowered 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 T₁ 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

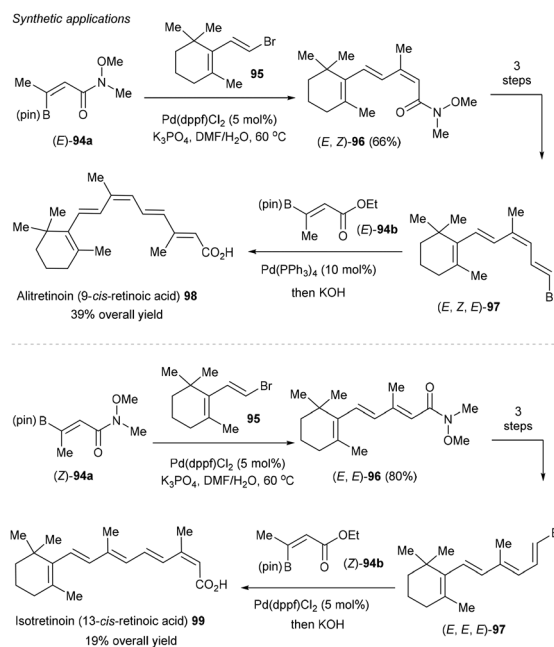


Scheme 36 Photochemical isomerization.

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 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, electrocatalysis¹²⁶ 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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References

- (a) *Boronic Acids: Preparation and Applications in Organic Synthesis, Medicine and Materials*, ed. D. G. Hall, Wiley–VCH, Weinheim, Germany, 2nd edn, 2011; (b) C. D. Entwistle and T. B. Marder, Boron Chemistry Lights the Way: Optical Properties of Molecular and Polymeric Systems, *Angew. Chem., Int. Ed.*, 2012, **41**, 2927–2931; (c) W. L. A. Brooks and B. S. Sumerlin, Synthesis and Applications of Boronic Acid-Containing Polymers: From Materials to Medicine, *Chem. Rev.*, 2016, **116**, 1375–1397; (d) B. Akgun and D. G. Hall, Boronic Acids as Bioorthogonal Probes for Site-Selective Labeling of Proteins, *Angew. Chem., Int. Ed.*, 2018, **57**, 13028–13044; (e) J. P. M. António, R. Russo, C. P. Carvalho, P. M. S. D. Cal and P. M. P. Gois, Boronic Acids as Building Blocks for the Construction of Therapeutically Useful Bioconjugates, *Chem. Soc. Rev.*, 2019, **48**, 3513–3536; (f) S. K. Mellerup and S. Wang, Boron-Based Stimuli Responsive Materials, *Chem. Soc. Rev.*, 2019, **48**, 3537–3549; (g) R. J. Grams, W. L. Santos, I. R. Scorei, A. Abad-García, C. A. Rosenblum, A. Bitá, H. Cerecetto, C. Viñas and M. A. Soriano-Ursúa, The Rise of Boron-Containing Compounds: Advancements in Synthesis, Medicinal



- Chemistry, and Emerging Pharmacology, *Chem. Rev.*, 2024, **124**, 2441–2511.
- 2 (a) N. Miyaoura and A. Suzuki, Palladium-Catalyzed Cross-Coupling Reactions of Organoboron Compounds, *Chem. Rev.*, 1995, **95**, 2457–2483; (b) T. Hayashi and K. Yamasaki, Rhodium-Catalyzed Asymmetric 1, 4-Addition and Its Related Asymmetric Reactions, *Chem. Rev.*, 2003, **103**, 2829–2844; (c) D. S. Matteson, Boronic Esters in Asymmetric Synthesis, *J. Org. Chem.*, 2013, **78**, 10009–10023; (d) A. J. J. Lennox and G. C. Lloyd-Jones, Selection of Boron Reagents for Suzuki–Miyaoura Coupling, *Chem. Soc. Rev.*, 2014, **43**, 412–443; (e) S. Roscales and A. G. Csáký, Transition-Metal-Free C–C Bond Forming Reactions of Aryl, Alkenyl and Alkynylboronic Acids and Their Derivatives, *Chem. Soc. Rev.*, 2014, **43**, 8215–8225; (f) T. N. Nguyen and J. A. May, Enantioselective Organocatalytic Conjugate Addition of Organoboron Nucleophiles, *Tetrahedron Lett.*, 2017, **58**, 1535–1544; (g) D. Chen and M.-H. Xu, Transition Metal-Catalyzed Asymmetric Addition of Organoboron Reagents to Imines, *Chin. J. Org. Chem.*, 2017, **37**, 1589–1612; (h) B. S. L. Collins, C. M. Wilson, E. L. Myers and V. K. Aggarwal, Asymmetric Synthesis of Secondary and Tertiary Boronic Esters, *Angew. Chem., Int. Ed.*, 2017, **56**, 11700–11733; (i) J. W. B. Fyfe and A. J. B. Watson, Recent Developments in Organoboron Chemistry: Old Dogs, New Tricks, *Chem*, 2017, **3**, 31–55; (j) M. Quan, L. Wu, G. Yang and W. Zhang, Pd(II), Ni(II) and Co(II)-Catalyzed Enantioselective Additions of Organoboron Reagents to Ketimines, *Chem. Commun.*, 2018, **54**, 10394–10404; (k) J. Carreras, A. Caballero and P. J. Pérez, Alkenyl Boronates: Synthesis and Applications, *Chem. – Asian J.*, 2019, **14**, 329–344; (l) S. Namirembe and J. P. Morken, Reactions of Organoboron Compounds Enabled by Catalyst-Promoted Metalate Shifts, *Chem. Soc. Rev.*, 2019, **48**, 3464–3474; (m) X. Yang, S. J. Kalita, S. Maheshuni and Y.-Y. Huang, Recent Advances on Transition-Metal-Catalyzed Asymmetric Tandem Reactions with Organoboron Reagents, *Coord. Chem. Rev.*, 2019, **392**, 35–48; (n) Z. Kuang, K. Yang, Y. Zhou and Q. Song, Base-Promoted Domino-Borylation-Protodeboration Strategy, *Chem. Commun.*, 2020, **56**, 6469–6479; (o) G. J. Lovinger and J. P. Morken, Recent Advances in Radical Addition to Alkenylboron Compounds, *Eur. J. Org. Chem.*, 2020, 2362–2368; (p) H. Wang, C. Jing, A. Noble and V. K. Aggarwal, Stereospecific 1, 2-Migrations of Boronate Complexes Induced by Electrophiles, *Angew. Chem., Int. Ed.*, 2020, **59**, 16859–16872; (q) D.-X. Zhu and M.-H. Xu, Transition Metal-Catalyzed Asymmetric Addition of Organoboron Reagents to Aldehydes and Ketones, *Chin. J. Org. Chem.*, 2020, **40**, 255–275; (r) O. O. Grygorenko, V. S. Moskvina, O. V. Hryshchuk and A. V. Tymtsunik, Cycloadditions of Alkenylboronic Derivatives, *Synthesis*, 2020, 2761–2780; (s) X. Wang, Y. Wang, W. Huang, C. Xia and L. Wu, Direct Synthesis of Multi(boronate) Esters from Alkenes and Alkynes via Hydroboration and Boration Reactions, *ACS Catal.*, 2021, **11**, 1–18; (t) C. Haldar, M. E. Hoque, J. Chaturvedi, M. M. M. Hassan and B. Chattopadhyay, *Chem. Commun.*, 2021, **57**, 13059–13074; (u) X. Ma, Z. Kuang and Q. Song, Recent Advances in the Construction of Fluorinated Organoboron Compounds, *JACS Au*, 2022, **2**, 261–279; (v) R. Bisht, C. Haldar, M. M. M. Hassan, M. E. Hoque, J. Chaturvedi and B. Chattopadhyay, *Chem. Soc. Rev.*, 2022, **51**, 5042–5100; (w) X. Li, G. Zhang and Q. Song, Recent Advances in the Construction of Tetracoordinate Boron Compounds, *Chem. Commun.*, 2023, **59**, 3812–3820; (x) C. Yin, S. Tang, J. Mei, X. Hu and H. Zhang, Electrochemical Synthesis and Transformation of Organoboron Compounds, *Org. Chem. Front.*, 2023, **10**, 3361–3377; (y) M. M. M. Hassan, S. Guria, S. Dey, J. Das and B. Chattopadhyay, Transition Metal-Catalyzed Remote C–H Borylation: An Emerging Synthetic Tool, *Sci. Adv.*, 2023, **9**, eadg3311; (z) X. Li, J. Chen and Q. Song, Recent Progress in the Catalytic Enantioselective Reactions of 1,1-Diborylalkanes, *Chem. Commun.*, 2024, **60**, 2462–2471; (aa) W. Xu and T. Xu, Dual Nickel- and Photoredox-Catalyzed Asymmetric Reductive Cross-Couplings: Just a Change of the Reduction System?, *Acc. Chem. Res.*, 2024, **57**, 1997–2011; (ab) S. Guria, M. M. M. Hassan and B. Chattopadhyay, C–H Borylation: a Tool for Molecular Diversification, *Org. Chem. Front.*, 2024, **11**, 929–953.
 - 3 (a) D. G. Hall, Boronic Acid Catalysis, *Chem. Soc. Rev.*, 2019, **48**, 3475–3496; (b) J. Lam, K. M. Szkop, E. Mosafari and D. W. Stephan, FLP Catalysis: Main Group Hydrogenations of Organic Unsaturated Substrates, *Chem. Soc. Rev.*, 2019, **48**, 3592–3612; (c) Y. Su and R. Kinjo, Small Molecule Activation by Boron-Containing Heterocycles, *Chem. Soc. Rev.*, 2019, **48**, 3613–3659.
 - 4 <https://www.nobelprize.org/prizes/lists/all-nobel-prizes-in-chemistry/>.
 - 5 (a) S. Manna, K. K. Das, D. Aich and S. Panda, Synthesis and Reactivity of Allenylboron Compounds, *Adv. Synth. Catal.*, 2021, **363**, 2444–2463 For a recent example, please see: (b) Q. Yan, C.-K. Ruan, Y.-Q. Deng, Y.-C. Pu, W.-D. Chu, C.-Y. He and Q.-Z. Liu, Copper-Catalyzed Asymmetric Propargylation of Imines Enabled by a Biphenol-Based Phosphoramidite Ligand, *Org. Chem. Front.*, 2023, **10**, 4935–4940.
 - 6 S. Nandy, S. Paul, K. K. Das, P. Kumar, D. Ghorai and S. Panda, Synthesis and Reactivity of Alkynyl Boron Compounds, *Org. Biomol. Chem.*, 2021, **19**, 7276–7297.
 - 7 For selected recent examples about the synthesis of alkenyl boron compounds, please see: (a) F. Meng, K. P. McGrath and A. H. Hoveyda, Multifunctional Organoboron Compounds for Scalable Natural Product Synthesis, *Nature*, 2014, **513**, 367–374; (b) Q. Feng, K. Yang and Q. Song, Highly Selective Copper-Catalyzed Trifunctionalization of Alkynyl Carboxylic Acids: an Efficient Route to Bis-deuterated β -borylated α,β -Styrene, *Chem. Commun.*, 2015, **51**, 15394–15397; (c) W. B. Reid, J. J. Spillane, S. B. Krause and D. A. Watson, Direct



Synthesis of Alkenyl Boronic Esters from Unfunctionalized Alkenes: A Boryl-Heck Reaction, *J. Am. Chem. Soc.*, 2016, **138**, 5539–5542; (d) K. Yeung, R. E. Ruscoe, J. Rae, A. P. Pulis and D. J. Procter, Enantioselective Generation of Adjacent Stereocenters in a Copper-Catalyzed Three-Component Coupling of Imines, Allenes, and Diboranes, *Angew. Chem., Int. Ed.*, 2016, **55**, 11912–11916; (e) Q. Xuan, Y. Wei and Q. Song, Spiro(phosphoramidite) Ligand (SIPHOS)/Cu(OTf)₂-Catalyzed Highly Regio- and Stereo-Selective Hydroborations of Internal Alkynes with Diborane in Water, *Chin. Chem. Lett.*, 2017, **28**, 1163–1166; (f) J. Liu, M. Nie, Q. Zhou, S. Gao, W. Jiang, L. M. Chung, W. Tang and K. Ding, Enantioselective Palladium-Catalyzed Diboration of 1,1-Disubstituted Allenes, *Chem. Sci.*, 2017, **8**, 5161–5165; (g) A. P. Pulis, K. Yeung and D. J. Procter, Enantioselective Copper Catalysed, Direct Functionalisation of Allenes via Allyl Copper Intermediates, *Chem. Sci.*, 2017, **8**, 5240–5247; (h) J. J. Molloy, J. B. Metternich, C. G. Daniliuc, A. J. B. Watson and R. Gilmour, Contra-Thermodynamic, Photocatalytic E/Z Isomerization of Styrenyl Boron Species: Vectors to Facilitate Exploration of Two Dimensional Chemical Space, *Angew. Chem., Int. Ed.*, 2018, **57**, 3168–3172; (i) Z. Kuang, G. Gao and Q. Song, Base-Catalyzed Diborylation of Alkynes: Synthesis and Applications of *cis*-1,2-Bis(boryl)alkenes, *Sci. China: Chem.*, 2019, **62**, 62–66; (j) M. D. Aparece, C. Gao, G. J. Lovinger and J. P. Morken, Vinylidenation of Organoboronic Esters Enabled by a Pd-Catalyzed Metallate Shift, *Angew. Chem., Int. Ed.*, 2019, **58**, 592–595; (k) K. Yeung, F. J. T. Talbot, G. P. Howell, A. P. Pulis and D. J. Procter, Copper-Catalyzed Borylative Multicomponent Synthesis of Quaternary α -Amino Esters, *ACS Catal.*, 2019, **9**, 1655–1661; (l) S. Namirembe, C. Gao, R. P. Wexler and J. P. Morken, Stereoselective Synthesis of Trisubstituted Alkenylboron Reagents by Boron-Wittig Reaction of Ketones, *Org. Lett.*, 2019, **21**, 4392–4394; (m) S. Li, J. Li, T. Xia and W. Zhao, Stereoselective Synthesis of Vinylboronates by Rh-Catalyzed Borylation of Stereoisomeric Mixtures, *Chin. J. Chem.*, 2019, **37**, 462–468; (n) L. E. Longobardi and A. Fürstner, *trans*-Hydroboration of Propargyl Alcohol Derivatives and Related Substrates, *Chem. – Eur. J.*, 2019, **25**, 10063–10068; (o) Z. Kuang, H. Chen, J. Qiu, Z. Ou, Y. Lan and Q. Song, Cu-Catalyzed Regio- and Stereodivergent Chemoselective sp^2/sp^3 1,3- and 1,4-Diborylations of CF₃-Containing 1,3-Enynes, *Chem*, 2020, **6**, 2347–2363; (p) S.-H. Yu, T.-J. Gong and Y. Fu, Three-Component Boryllallenylolation of Alkynes: Access to Densely Boryl-Substituted Ene-allenes, *Org. Lett.*, 2020, **22**, 2941–2945; (q) G.-M. Ho, L. Segura and I. Marek, Ru-Catalyzed Isomerization of ω -Alkenylboronates towards Stereoselective Synthesis of Vinylboronates with Subsequent *in situ* Functionalization, *Chem. Sci.*, 2020, **11**, 5944–5949; (r) L. Tao, X. Guo, J. Li, R. Li, Z. Lin and W. J. Zhao, Rhodium-Catalyzed Deoxygenation and Borylation of Ketones: A Combined Experimental and

Theoretical Investigation, *J. Am. Chem. Soc.*, 2020, **142**, 18118–18127; (s) S. Gao, M. Duan, Q. Shao, K. N. Houk and M. J. Chen, Development of α,α -Disubstituted Crotylboronate Reagents and Stereoselective Crotylation via Brønsted or Lewis Acid Catalysis, *J. Am. Chem. Soc.*, 2020, **142**, 18355–18368; (t) C. Wu and S. Ge, Ligand-controlled cobalt-catalyzed regiodivergent hydroboration of aryl,alkyl-disubstituted internal allenenes, *Chem. Sci.*, 2020, **11**, 2783–2789; (u) Y. Ping, R. Wang, Q. Wang, T. Chang, J. Huo, M. Lei and J. Wang, Synthesis of Alkenylboronates from *N*-Tosylhydrazones through Palladium-Catalyzed Carbene Migratory Insertion, *J. Am. Chem. Soc.*, 2021, **143**, 9769–9780; (v) S.-H. Kim-Lee, P. Mauleón, R. G. Arrayás and J. C. Carretero, Dynamic Multiligand Catalysis: A Polar to Radical Crossover Strategy Expands Alkyne Carboboration to Unactivated Secondary Alkyl Halides, *Chem*, 2021, **7**, 2212–2216; (w) A. M. Y. Suliman, E. M. A. Ahmed, T.-J. Gong and Y. Fu, Cu/Pd-Catalyzed *cis*-Borylfluoroallylation of Alkynes for the Synthesis of Boryl-Substituted Monofluoroalkenes, *Org. Lett.*, 2021, **23**, 3259–3263; (x) Z. Wang, J. Wu, W. Lamine, B. Li, J.-M. Sotiropoulos, A. Chrostowska, K. Miqueu and S.-Y. Liu, C-Boron Enolates Enable Palladium Catalyzed Carboboration of Internal 1,3-Enynes, *Angew. Chem., Int. Ed.*, 2021, **60**, 21231–21236; (y) C. You, C. G. Daniliuc, K. Bergander, S. Yamaguchi and A. Studer, Regio- and Stereoselective 1,2-Carboboration of Ynamides with Aryldichloroboranes, *Angew. Chem., Int. Ed.*, 2021, **60**, 21697–21701; (z) W. Li, S. Chen, J. Xie, Z. Fan, K. Yang and Q. Song, Synthesis of Axially Chiral Alkenylboronates through Combined Copper- and Palladium-Catalysed Atroposelective Arylboration of Alkynes, *Nat. Synth.*, 2023, **2**, 140–151; (aa) K. Liu, S. Jin and Q. Song, Base-Promoted Synthesis of Tetrasubstituted Alkenylboronates from Propargyl Amines and B₂pin₂ via dual 1,4-Metallate Shift and B–N Elimination, *Org. Chem. Front.*, 2023, **10**, 905–910; (ab) M. Chen, C. D. Knox, M. C. Madhusudhanan, T. H. Tugwell, C. Liu, P. Liu and G. Dong, Stereospecific Alkenylidene Homologation of Organoboronates by SNV Reaction, *Nature*, 2024, **631**, 328–334; (ac) M. Chen, T. H. Tugwell, P. Liu and G. Dong, Synthesis of Alkenyl Boronates through Stereoselective Vinylene Homologation of Organoboronates, *Nat. Synth.*, 2024, **3**, 337–346; (ad) H.-W. Jiang, W.-L. Yu, D. Wang and P.-F. Xu, Photocatalyzed H₂-Acceptorless Dehydrogenative Borylation by Using Amine Borane, *ACS Catal.*, 2024, **14**, 8666–8675; (ae) J. Wen, Y. Huang, Y. Zhang, H. Grötzmacher and P. Hu, Cobalt Catalyzed Practical Hydroboration of Terminal Alkynes with Time-Dependent Stereoselectivity, *Nat. Commun.*, 2024, **15**, 2208; (af) Y. Jung, S. Y. Yoo, Y. Jin, J. You, S. Han, J. Yu, Y. Park and S. H. Cho, Iridium-Catalyzed Chemo-, Diastereo-, and Enantioselective Allyl-Allyl Coupling: Accessing All Four Stereoisomers of (*E*)-1-Boryl-Substituted 1,5-Dienes by Chirality Pairing, *Angew. Chem., Int. Ed.*, 2023, **62**, e202218794; (ag) G.-L. Xu, C.-Y. Liu, X. Pang, X.-Y. Liu and



- X.-Z. Shu, Nickel-Catalyzed Cross-Electrophile Vinyl-Vinyl Coupling: An Approach to Structurally Versatile Dienylboronates, *CCS Chem.*, 2022, **4**, 864–871; (ah) Y. Ozawa, Y. Shiratori, H. Koriyama, K. Endo, H. Iwamoto and H. Ito, Synthesis of (*Z*)-Alkenyl Boronates via a Copper(I)-Catalyzed Linear-Selective Alkylboration of Terminal Allenes, *Org. Chem. Front.*, 2023, **10**, 4786–4793.
- 8 D. V. Partyka, Transmetalation of Unsaturated Carbon Nucleophiles from Boron-Containing Species to the Mid to Late d-Block Metals of Relevance to Catalytic C–X Coupling Reactions (X = C, F, N, O, Pb, S, Se, Te), *Chem. Rev.*, 2011, **111**, 1529–1595.
 - 9 K. Sasaki and T. Hayashi, Rhodium-Catalyzed Asymmetric Conjugate Addition of Arylboroxines to Borylalkenes: Asymmetric Synthesis of β -Arylalkylboranes, *Angew. Chem., Int. Ed.*, 2010, **49**, 8145–8147.
 - 10 L. Zhang, G. J. Lovinger, E. K. Edelstein, A. A. Szymaniak, M. P. Chierchia and J. P. Morken, Catalytic Conjunctive Cross-Coupling Enabled by Metal-Induced Metallate Rearrangement, *Science*, 2016, **351**, 70–74.
 - 11 For selected examples in a non-catalytic way, please see: (a) C.-V. T. Vo, T. A. Mitchell and J. W. Bode, Expanded Substrate Scope and Improved Reactivity of Ether-Forming Cross-Coupling Reactions of Organotrifluoroborates and Acetals, *J. Am. Chem. Soc.*, 2011, **133**, 14082–14089; (b) J. Kim and M. Movassaghi, Concise Total Synthesis and Stereochemical Revision of (+)-Naseaezines A and B: Regioselective Arylative Dimerization of Diketopiperazine Alkaloids, *J. Am. Chem. Soc.*, 2011, **133**, 14940–14943; (c) M. Wan, Z. Meng, H. Lou and L. Liu, Practical and Highly Selective C–H Functionalization of Structurally Diverse Ethers, *Angew. Chem., Int. Ed.*, 2014, **53**, 13845–13849; (d) Z. Xie, L. Liu, W. Chen, H. Zheng, Q. Xu, H. Yuan and H. Lou, Practical Metal-Free C(sp³)–H Functionalization: Construction of Structurally Diverse α -Substituted *N*-Benzyl and *N*-Allyl Carbamates, *Angew. Chem., Int. Ed.*, 2014, **53**, 3904–3908; (e) W. Chen, Z. Xie, H. Zheng, H. Lou and L. Liu, Structurally Diverse α -Substituted Benzopyran Synthesis through a Practical Metal-Free C(sp³)–H Functionalization, *Org. Lett.*, 2014, **16**, 5988–5991; (f) P. B. Brady and E. M. Carreira, Addition of Trifluoroborates to Oxetanyl N,O-Acetals: Entry into Spiro and Fused Saturated Heterocycles, *Org. Lett.*, 2015, **17**, 3350–3353; (g) C. Li, Y. Zhang, Q. Sun, T. Gu, H. Peng and W. Tang, Transition-Metal-Free Stereospecific Cross-Coupling with Alkenylboronic Acids as Nucleophiles, *J. Am. Chem. Soc.*, 2016, **138**, 10774–10777; (h) V. Ortega, E. del Castillo and A. G. Csáký, Transition-Metal-Free Stereocomplementary Cross-Coupling of Diols with Boronic Acids as Nucleophiles, *Org. Lett.*, 2017, **19**, 6236–6239; (i) Z. Liu, L. Chen, J. Li, K. Liu, J. Zhao, M. Xu, L. Feng, R.-Z. Wan, W. Li and L. Liu, Oxidative C–H Functionalization of *N*-Carbamoyl 1,2-Dihydroquinolines, *Org. Biomol. Chem.*, 2017, **15**, 7600–7606; (j) R. J. Armstrong, M. Nandakumar, R. M. P. Dias, A. Noble and E. L. Myers, Enantiodivergent Synthesis of Allenes by Point-to-Axial Chirality Transfer, *Angew. Chem., Int. Ed.*, 2018, **57**, 8203–8208; (k) S. Liu, X. Zeng, G. B. Hammond and B. Xu, Mild Base Promoted Nucleophilic Substitution of Unactivated sp³-Carbon Electrophiles with Alkenylboronic Acids, *Adv. Synth. Catal.*, 2018, **360**, 3667–3671; (l) S. Roscales, V. Ortega and A. G. Csáký, Selective Functionalization of Achmatowicz Rearrangement Products by Reactions with Potassium Organotrifluoroborates under Transition-Metal-Free Conditions, *J. Org. Chem.*, 2018, **83**, 11425–11436; (m) T. Fan, A. Wang, J.-Q. Li, J.-L. Ye, X. Zheng and P.-Q. Huang, Versatile One-Pot Synthesis of Polysubstituted Cyclopent-2-enimines from α , β -Unsaturated Amides: Imino-Nazarov Reaction, *Angew. Chem., Int. Ed.*, 2018, **57**, 10352–10356; (n) T. N. Nguyen, K. Setthakarn and J. A. May, Oxyallyl Cation Capture via Electrophilic Deborylation of Organoboronates: Access to α , α' -Substituted Cyclic Ketones, *Org. Lett.*, 2019, **21**, 7837–7840; (o) M. Nandakumar, B. Rubial, A. Noble, E. L. Myers and V. K. Aggarwal, Ring-Opening Lithiation–Borylation of 2-Trifluoromethyl Oxirane: A Route to Versatile Tertiary Trifluoromethyl Boronic Esters, *Angew. Chem., Int. Ed.*, 2020, **59**, 1187–1191; (p) N. Eghbarieh, N. Hanania, A. Zamir, M. Nassir, T. Stein and A. Masarwa, Stereoselective Diels–Alder Reactions of *gem*-Diborylalkenes: Toward the Synthesis of *gem*-Diboron-Based Polymers, *J. Am. Chem. Soc.*, 2021, **143**, 6211–6220; (q) A. Music, C. M. Nuber, Y. Lemke, P. Spieß and D. Didier, Electro-alkynylation: Intramolecular Rearrangement of Trialkynylorganoborates for Chemoselective C(sp²)–C(sp) Bond Formation, *Org. Lett.*, 2021, **23**, 4179–4184.
 - 12 H. Noguchi, K. Hojo and M. Sugimoto, Boron-Masking Strategy for the Selective Synthesis of Oligoarenes via Iterative Suzuki–Miyaura Coupling, *J. Am. Chem. Soc.*, 2007, **129**, 758–759.
 - 13 E. P. Gillis and M. D. Burke, Iterative Cross-Coupling with MIDA Boronates: Towards a General Platform for Small Molecule Synthesis, *Aldrichimica Acta*, 2009, **42**, 17–27.
 - 14 G. A. Molander and N. Ellis, Organotrifluoroborates: Protected Boronic Acids That Expand the Versatility of the Suzuki Coupling Reaction, *Acc. Chem. Res.*, 2007, **40**, 275–286.
 - 15 R. J. Armstrong and V. K. Aggarwal, 50 Years of Zweifel Olefination: A Transition-Metal-Free Coupling, *Synthesis*, 2017, 3323–3336.
 - 16 (a) M. Norio, K. Yamada and A. Suzuki, A New Stereospecific Cross-Coupling by the Palladium-Catalyzed Reaction of 1-Alkenylboranes with 1-Alkenyl or 1-Alkynyl Halides, *Tetrahedron Lett.*, 1979, **20**, 3437–3440 For other recent excellent work, please see: (b) X.-Y. Chen, X.-X. Nie, Y. Wu and P. Wang, *para*-Selective Arylation and Alkenylation of Monosubstituted Arenes using Thianthrene S-oxide as a Transient Mediator, *Chem. Commun.*, 2020, **56**, 5058–5061; (c) A. Chen, Y. Han, R. Wu, B. Yang, L. Zhu and F. Zhu, Palladium-Catalyzed



- Suzuki-Miyaura Cross-Couplings of Stable Glycal Boronates for Robust Synthesis of C-1 Glycals, *Nat. Commun.*, 2024, **15**, 5228.
- 17 P. Y. S. Lam, G. Vincent, D. Bonne and C. G. Clark, Copper-Promoted/Catalyzed C-N and C-O Bond Cross-Coupling with Vinylboronic Acid and its Utilities, *Tetrahedron Lett.*, 2003, **44**, 4927–4931.
 - 18 (a) T. D. Quach and R. A. Batey, Copper(II)-Catalyzed Ether Synthesis from Aliphatic Alcohols and Potassium Organotrifluoroborate Salts, *Org. Lett.*, 2003, **5**, 1381–1384; (b) Y. Bolshan and R. A. Batey, Enamide Synthesis by Copper-Catalyzed Cross-Coupling of Amides and Potassium Alkenyltrifluoroborate Salts, *Angew. Chem., Int. Ed.*, 2008, **47**, 2109–2112; (c) F. Huang, T. D. Quach and R. A. Batey, Copper-Catalyzed Nondecarboxylative Cross Coupling of Alkenyltrifluoroborate Salts with Carboxylic Acids or Carboxylates: Synthesis of Enol Esters, *Org. Lett.*, 2013, **15**, 3150–3153.
 - 19 (a) L. Chu and F.-L. Qing, Copper-Mediated Trifluoromethylation of Boronic Acids, *Org. Lett.*, 2010, **12**, 5060–5063; (b) M. Presset, D. Oehrich, F. Rombouts and G. A. Molander, Copper-Mediated Radical Trifluoromethylation of Unsaturated Potassium Organotrifluoroborates, *J. Org. Chem.*, 2013, **78**, 12837–12843; (c) J. Xu, D.-F. Luo, B. Xiao, Z.-J. Liu, T.-J. Gong, Y. Fu and L. Liu, Copper-Catalyzed Trifluoromethylation of Aryl Boronic Acids Using a CF_3^+ Reagent, *Chem. Commun.*, 2011, **47**, 4300–4302; (d) T. Liu and Q. Shen, Copper-Catalyzed Trifluoromethylation of Aryl and Vinyl Boronic Acids with An Electrophilic Trifluoromethylating Reagent, *Org. Lett.*, 2011, **13**, 2342–2345; (e) J. Liu, Y. Xiao, J. Hao and Q. Shen, Copper-Catalyzed Trifluoromethylation of (Hetero)aryl Boronic Acid Pinacol Esters with YlideFluor, *Org. Lett.*, 2023, **25**, 1204–1208; (f) C.-P. Zhang, J. Cai, C.-B. Zhou, X.-P. Wang, X. Zheng, Y.-C. Gu and J.-C. Xiao, Copper-Mediated Trifluoromethylation of Arylboronic Acids by Trifluoromethyl Sulfonium Salts, *Chem. Commun.*, 2011, **47**, 9516–9518 For the reaction by using Ir(II) catalysis, please see: (g) A. T. Parsons, T. D. Senecal and S. L. Buchwald, Iron(II)-Catalyzed Trifluoromethylation of Potassium Vinyltrifluoroborates, *Angew. Chem., Int. Ed.*, 2012, **51**, 2947–2950.
 - 20 (a) A. M. Whittaker, R. P. Rucker and G. Lalic, Catalytic $\text{S}_{\text{N}}2'$ -Selective Substitution of Allylic Chlorides With Arylboronic Esters, *Org. Lett.*, 2010, **12**, 3216–2318; (b) C.-T. Yang, Z.-Q. Zhang, Y.-C. Liu and L. Liu, Copper-Catalyzed Cross-Coupling Reaction of Organoboron Compounds with Primary Alkyl Halides and Pseudohalides, *Angew. Chem., Int. Ed.*, 2011, **50**, 3904–3907; (c) R. Shintani, K. Takatsu, M. Takeda and T. Hayashi, Copper-Catalyzed Asymmetric Allylic Substitution of Allyl Phosphates with Aryl- and Alkenylboronates, *Angew. Chem., Int. Ed.*, 2011, **50**, 8656–8659; (d) F. Gao, J. L. Carr and A. H. Hoveyda, Copper-Catalyzed Enantioselective Allylic Substitution with Readily Accessible Carbonyl- and Acetal-Containing Vinylboron Reagents, *Angew. Chem., Int. Ed.*, 2012, **51**, 6613–6617; (e) M. Yang, N. Yokokawa, H. Ohmiya and M. Sawamura, *Org. Lett.*, 2012, **14**, 816–819 For an excellent example with Ir catalysis, please see: (f) J. Y. Hamilton, D. Sarlah and E. M. Carreira, *J. Am. Chem. Soc.*, 2013, **135**, 994–997.
 - 21 (a) J. Takaya, S. Tadami, K. Ukai and N. Iwasawa, Copper (I)-Catalyzed Carboxylation of Aryl- and Alkenylboronic Esters, *Org. Lett.*, 2008, **10**, 2697–2700; (b) T. Ohishi, M. Nishiura and Z. Hou, Carboxylation of Organoboronic Esters Catalyzed by *N*-Heterocyclic Carbene Copper(I) Complexes, *Angew. Chem., Int. Ed.*, 2008, **47**, 5792–5795.
 - 22 (a) K. Takatsu, R. Shintani and T. Hayashi, Copper-Catalyzed 1,4-Addition of Organoboronates to Alkylidene Cyanoacetates: Mechanistic Insight and Application to Asymmetric Catalysis, *Angew. Chem., Int. Ed.*, 2011, **50**, 5548–5552; (b) Q. Chong, Z. Yue, S. Zhang, C. Ji, F. Cheng, H. Zhang, X. Hong and F. Meng, *N*-heterocyclic Carbene–Cu-Catalyzed Enantioselective Conjugate Additions with Alkenylboronic Esters as Nucleophiles, *ACS Catal.*, 2017, **7**, 5693–5698.
 - 23 R. Shintani, K. Takatsu and T. Hayashi, Copper-Catalyzed Asymmetric Addition of Arylboronates to Isatins: A Catalytic Cycle Involving Alkoxocopper Intermediates, *Chem. Commun.*, 2010, **46**, 6822–6824.
 - 24 (a) P.-S. Lin, M. Jeganmohan and C.-H. Cheng, Nickel-Catalyzed Mizoroki–Heck- versus Michael-Type Addition of Organoboronic Acids to α , β -Unsaturated Alkenes through Fine-Tuning of Ligands, *Chem. – Asian J.*, 2007, **2**, 1409–1416; (b) M.-H. Chen, S. Mannathan, P.-S. Lin and C.-H. Cheng, Cobalt(II)-Catalyzed 1, 4-Addition of Organoboronic Acids to Activated Alkenes: An Application to Highly cis-Stereoselective Synthesis of Aminoindane Carboxylic Acid Derivatives, *Chem. – Eur. J.*, 2012, **18**, 14918–14922.
 - 25 X. Wang, M. Quan, F. Xie, G. Yang and W. Zhang, Ni(II)/mono-RuPHOX-Catalyzed Asymmetric Addition of Alkenylboronic Acids to Cyclic Aldimines, *Tetrahedron Lett.*, 2018, **59**, 1573–1575.
 - 26 H. Wei, Y. Luo, J. Ren, Q. Yuan and W. Zhang, Ni(II)-Catalyzed Asymmetric Alkenylation and Arylation of Aryl Ketones with Organoborons via 1,5-Metalate Shift, *Nat. Commun.*, 2024, **15**, 8775.
 - 27 Y. Huang, R.-Z. Huang and Y. Zhao, Cobalt-Catalyzed Enantioselective Vinylation of Activated Ketones and Imines, *J. Am. Chem. Soc.*, 2016, **138**, 6571–6576.
 - 28 For two excellent examples by using gold catalysis, please see: (a) S. Liao, A. Porta, X. Cheng, X. Ma, G. Zanoni and L. Zhang, Bifunctional Ligand Enables Efficient Gold-Catalyzed Hydroalkenylation of Propargylic Alcohol, *Angew. Chem., Int. Ed.*, 2018, **57**, 8250–8254; (b) X. Li, M. D. Wodrich and J. Waser, Accessing Elusive σ -Type Cyclopropenium Cation Equivalents through Redox Gold Catalysis, *Nat. Chem.*, 2024, **16**, 901–921.



- 29 S. V. Kumar, A. Yen, M. Lautens and P. J. Guiry, Catalytic Asymmetric Transformations of Oxa- and Azabicyclic Alkenes, *Chem. Soc. Rev.*, 2021, **50**, 3013–3093.
- 30 (a) M. J. Fleming, H. A. McManus, A. Rudolph, W. H. Chan, J. Ruiz, C. Dockendorff and M. Lautens, Concise Enantioselective Total Syntheses of (+)-Homochelidonine, (+)-Chelamidine, (+)-Chelidonine, (+)-Chelamine and (+)-Norchelidonine by a PdII-Catalyzed Ring-Opening Strategy, *Chem. – Eur. J.*, 2008, **14**, 2112–2124; (b) M. Ito, F. Konno, T. Kumamoto, N. Suzuki, M. Kawahata, K. Yamaguchi and T. Ishikawa, Enantioselective Synthesis of Chelidonine, a B/C-*cis*, 11-hydroxyhexahydrobenzo[*c*]phenanthridine Alkaloid, *Tetrahedron*, 2011, **67**, 8041–8049.
- 31 X. J. Huang, D.-L. Mo, C.-H. Ding and X.-L. Hou, Chiral P-Containing Palladacycle-Catalyzed Asymmetric Ring-Opening Reactions of Oxabicyclic Alkenes with Alkenyl Boronic Acids, *Synlett*, 2011, 943–946.
- 32 D. Zhu, Y. Zhao, Q. Chong and F. Meng, Cobalt-Catalyzed Enantioselective Ring-Opening Reactions of Oxa- and Azabicyclic Alkenes with Alkenylboronic Acids, *Chin. J. Chem.*, 2022, **40**, 190–194.
- 33 (a) C. Wang, Manganese-Mediated C–C Bond Formation via C–H Activation: From Stoichiometry to Catalysis, *Synlett*, 2013, 1606–1613; (b) W. Liu and J. T. Groves, Manganese Catalyzed C–H Halogenation, *Acc. Chem. Res.*, 2015, **48**, 1727–1735; (c) J. R. Carney, B. R. Dillon and S. P. Thomas, Recent Advances of Manganese Catalysis for Organic Synthesis, *Eur. J. Org. Chem.*, 2016, 3912–3929; (d) Y.-Y. Hu, B.-W. Zhou and C. Wang, Inert C–H Bond Transformations Enabled by Organometallic Manganese Catalysis, *Acc. Chem. Res.*, 2018, **51**, 816–827; (e) Z. Yan, C. Zhu and J. Xie, Manganese(I)-Catalyzed Selective Functionalization of Alkynes, *Synlett*, 2019, 124–128; (f) P. Gandeepan, T. Müller, D. Zell, G. Cera, S. Warratz and L. Ackermann, 3d Transition Metals for C–H Activation, *Chem. Rev.*, 2019, **119**, 2192–2452; (g) K. Feng, R. E. Quevedo, J. T. Kohrt, M. S. Oderinde, U. Reilly and M. C. White, Late-Stage Oxidative C(sp³)-H Methylation, *Nature*, 2020, **580**, 621–627; (h) J. P. Zhao, T. Nanjo, E. C. de Lucca Jr. and M. C. White, Chemoselective Methylene Oxidation in Aromatic Molecules, *Nat. Chem.*, 2019, **11**, 213–221.
- 34 (a) Z. F. Yan, X.-A. Yuan, Y. Zhao, C. J. Zhu and J. Xie, Selective Hydroarylation of 1, 3-Diynes Using a Dimeric Manganese Catalyst: Modular Synthesis of Z-Enynes, *Angew. Chem., Int. Ed.*, 2018, **57**, 12906–12910; (b) Y. Pang, G. Liu, C. Huang, X.-A. Yuan, W. Li and J. Xie, A Highly Efficient Dimeric Manganese-Catalyzed Selective Hydroarylation of Internal Alkynes, *Angew. Chem., Int. Ed.*, 2020, **59**, 12789–12794.
- 35 D. P. Wang, J. Dong, W. Fan, X.-A. Yuan, J. Han and J. Xie, Dimeric Manganese-Catalyzed Hydroarylation and Hydroalkenylation of Unsaturated Amide, *Angew. Chem., Int. Ed.*, 2020, **59**, 8430–8434.
- 36 (a) M. Rubin, M. Rubina and V. Gevorgyan, Transition Metal Chemistry of Cyclopropenes and Cyclopropanes, *Chem. Rev.*, 2007, **107**, 3117–3179; (b) T. Hudlicky and J. Reed, Defying Ring Strain: New Approaches to Cyclopropanes, *Angew. Chem., Int. Ed.*, 2010, **49**, 486–488; (c) L. Jiao and Z.-X. Yu, Vinylcyclopropane Derivatives in Transition-Metal-Catalyzed Cycloadditions for the Synthesis of Carbocyclic Compounds, *J. Org. Chem.*, 2013, **78**, 6842–6848.
- 37 H. Zhang, W. Huang, T. Wang and F. Meng, Cobalt-Catalyzed Diastereo- and Enantioselective Hydroalkenylation of Cyclopropenes with Alkenylboronic Acids, *Angew. Chem., Int. Ed.*, 2019, **58**, 11049–11053.
- 38 X.-P. Zeng, Z.-Y. Cao, Y.-H. Wang, F. Zhou and J. Zhou, Catalytic Enantioselective Desymmetrization Reactions to All-Carbon Quaternary Stereocenters, *Chem. Rev.*, 2016, **116**, 7330–7396.
- 39 D. P. Wang, Y. He, H. Dai, C. Huang, X.-A. Yuan and J. Xie, Manganese-Catalyzed Hydrocarbofunctionalization of Internal Alkenes, *Chin. J. Chem.*, 2020, **38**, 1497–1502.
- 40 T. Liu, Y. Yang and C. Y. Wang, Manganese-Catalyzed Hydroarylation of Unactivated Alkenes, *Angew. Chem., Int. Ed.*, 2020, **59**, 14256–14260.
- 41 H. Lv, L.-J. Xiao, D. Zhao and Q.-L. Zhou, Nickel(0)-Catalyzed Linear-Selective Hydroarylation of Unactivated Alkenes and Styrenes with Aryl Boronic Acids, *Chem. Sci.*, 2018, **9**, 6839–6843.
- 42 L.-J. Xiao, L. Chen, W.-M. Feng, M.-L. Li, J.-H. Xie and Q.-L. Zhou, Nickel(0)-Catalyzed Hydroarylation of Styrenes and 1, 3-Dienes with Organoboron Compounds, *Angew. Chem., Int. Ed.*, 2018, **57**, 461–464.
- 43 Z.-Q. Li, Y. Fu, R. Deng, V. T. Tran, Y. Gao, P. Liu and K. M. Engle, Ligand-Controlled Regiodivergence in Nickel-Catalyzed Hydroarylation and Hydroalkenylation of Alkenyl Carboxylic Acids, *Angew. Chem., Int. Ed.*, 2020, **59**, 23306–23312.
- 44 X.-Y. Lv, C. Fan, L.-J. Xiao, J.-H. Xie and Q.-L. Zhou, Ligand-Enabled Ni-Catalyzed Enantioselective Hydroarylation of Styrenes and 1,3-Dienes with Arylboronic Acids, *CCS Chem.*, 2019, **1**, 328–334.
- 45 Y.-G. Chen, B. Shuai, X.-T. Xu, Y.-Q. Li, Q.-L. Yang, H. Qiu, K. Zhang, P. Fang and T.-S. Mei, Nickel-catalyzed Enantioselective Hydroarylation and Hydroalkenylation of Styrenes, *J. Am. Chem. Soc.*, 2019, **141**, 3395–3399.
- 46 D.-M. Wang, L.-Q. She, Y. Wu, C. Zhu and P. Wang, Ligand-Enabled Ni-Catalyzed Hydroarylation and Hydroalkenylation of Internal Alkenes with Organoborons, *Nat. Commun.*, 2022, **13**, 6878.
- 47 Pd catalysis: (a) N. Miyauchi, Y. Tanabe, H. Sugimoto and A. Suzuki, Cross-Coupling Reactions of 1-alkenylboranes with 3,4-Epoxy-1-butene Catalyzed by Palladium or Nickel Complexes, *J. Organomet. Chem.*, 1982, **233**, C13–C16; (b) J. Kjellgren, J. Aydin, O. A. Wallner, I. V. Saltanova and K. J. Szabó, Palladium Pincer Complex Catalyzed Cross-Coupling of Vinyl Epoxides and Aziridines with Organoboronic Acids, *Chem. – Eur. J.*, 2005, **11**, 5260–



- 5268; (c) S. Bonnet, J. H. van Lenthe, M. A. Siegler, A. L. Spek, G. van Koten and R. J. M. K. Gebbink, Bimetallic η^6 , η^1 NCN-Pincer Ruthenium Palladium Complexes with η^6 -RuCp Coordination: Synthesis, X-ray Structures, and Catalytic Properties, *Organometallics*, 2009, **28**, 2325–2333; (d) D. K. Nielsen and A. G. Doyle, Nickel-Catalyzed Cross-Coupling of Styrenyl Epoxides with Boronic Acids, *Angew. Chem., Int. Ed.*, 2011, **50**, 6056–6059; (e) G. Hamasaka, T. Muto and Y. Uozumi, Molecular-Architecture-Based Administration of Catalysis in Water: Self-Assembly of an Amphiphilic Palladium Pincer Complex, *Angew. Chem., Int. Ed.*, 2011, **50**, 4876–4878; (f) X.-Y. Lu, C.-T. Yang, J.-H. Liu, Z.-Q. Zhang, X. Lu, X. Lou, B. Xiao and Y. Fu, Cu-Catalyzed Cross-Coupling Reactions of Epoxides with Organoboron Compounds, *Chem. Commun.*, 2015, **51**, 2388–2391; (g) T. N. Nguyen and J. A. May, Tertiary and Quaternary Carbon Formation via Gallium-Catalyzed Nucleophilic Addition of Organoboronates to Cyclopropane, *Org. Lett.*, 2018, **20**, 112–115; (h) T. N. Nguyen and J. A. May, Branched Amine Synthesis via Aziridine or Azetidine Opening with Organotrifluoroborates by Cooperative Brønsted/Lewis Acid Catalysis: An Acid-Dependent Divergent Mechanism, *Org. Lett.*, 2018, **20**, 3618–3621; (i) X.-Y. Lu, L.-Y. Yan, J.-S. Li, J.-M. Li, H.-P. Zhou, R.-C. Jiang, C.-C. Liu, R. Lu and R. Hu, Base-free Ni-Catalyzed Suzuki-type Cross-Coupling Reactions of Epoxides with Boronic Acids, *Chem. Commun.*, 2020, **56**, 109–112.
- 48 (a) S. Roscales and A. G. Csáký, Metal-Free Ring-Opening of Epoxides with Potassium Trifluoroborates, *Chem. Commun.*, 2014, **50**, 454–456; (b) M. Nandakumar, B. Rubial, A. Noble, E. L. Myers and V. K. Aggarwal, Ring-Opening Lithiation–Borylation of 2-Trifluoromethyl Oxirane: A Route to Versatile Tertiary Trifluoromethyl Boronic Esters, *Angew. Chem., Int. Ed.*, 2020, **59**, 1187–1191; (c) V. Ortega and A. G. Csáký, Ring-Opening of Donor–Acceptor Cyclopropanes by Boronic Acids and Potassium Organotrifluoroborates under Transition-Metal-Free Conditions, *J. Org. Chem.*, 2016, **81**, 3917–3923.
- 49 L. Wu, G. Yang and W. Zhang, Ni-Catalyzed Enantioconvergent Coupling of Epoxides with Alkenylboronic Acids: Construction of Oxindoles Bearing Quaternary Carbons, *CCS Chem.*, 2019, **1**, 623–631.
- 50 L. Zhang, Q. Du, Y. Luo, Y. Wang, F. Gao, Y. Ye and W. Zhang, Synthesis of Skipped Aminodienes by a Ni-Catalyzed Ring-Opening/Cross-Coupling Reaction of Vinylaziridines with Multifunctional Organoboronic Acids, *Chin. J. Chem.*, 2023, **41**, 3003–3011.
- 51 For selected reviews on enantioconvergent cross-coupling of racemic alkyl (pseudo)halides, see: (a) A. H. Cherney, N. T. Kadunce and S. E. Reisman, Enantioselective and Enantiospecific Transition-Metal-Catalyzed Cross-Coupling Reactions of Organometallic Reagents To Construct C–C Bonds, *Chem. Rev.*, 2015, **115**, 9587–9652; (b) J. Choi and G. C. Fu, Transition Metal-Catalyzed Alkyl–Alkyl Bond Formation: Another Dimension in Cross-Coupling Chemistry, *Science*, 2017, **356**, eaaf7230; (c) A. Lipp, S. O. Badir and G. A. Molander, Stereoinduction in Metallaphotoredox Catalysis, *Angew. Chem., Int. Ed.*, 2021, **60**, 1714–1726.
- 52 P.-F. Wang, J. Yu, K.-X. Guo, S.-P. Jiang, J.-J. Chen, Q.-S. Gu, J.-R. Liu, X. Hong, Z.-L. Li and X.-Y. Liu, Design of Hemilabile *N*, *N*, *N*-Ligands in Copper-Catalyzed Enantioconvergent Radical Cross-Coupling of Benzyl/Propargyl Halides with Alkenylboronate Esters, *J. Am. Chem. Soc.*, 2022, **144**, 6442–6452.
- 53 P. Dominguez-Molano, R. Weeks, R. J. Maza, J. J. Carbó and E. Fernández, Boron–Copper 1,3-Rearrangement: The New Concept Behind the Boryl Migration from C(sp²) in Alkenyl Boranes to C(sp³), *Angew. Chem., Int. Ed.*, 2023, **62**, e202304791.
- 54 J. E. Baumann, C. P. Chung and G. Lalic, Stereoselective Copper-Catalyzed Olefination of Imines, *Angew. Chem., Int. Ed.*, 2024, **63**, e202316521.
- 55 (a) A. Vasseur, J. Bruffaerts and I. Marek, Remote Functionalization through Alkene Isomerization, *Nat. Chem.*, 2016, **11**, 209–219; (b) H. Sommer, F. JuliáHernández, R. Martin and I. Marek, Walking Metals for Remote Functionalization, *ACS Cent. Sci.*, 2018, **4**, 153–165; (c) D. JanssenMüller, B. Sahoo, S.-Z. Sun and R. Martin, Tackling Remote *sp*³ C–H Functionalization via Ni-Catalyzed “chain-walking” Reactions, *Isr. J. Chem.*, 2020, **60**, 195–206; (d) S. Ghosh, S. Patel and I. Chatterjee, Chain-Walking Reactions of Transition Metals for Remote C–H Bond Functionalization of Olefinic Substrates, *Chem. Commun.*, 2021, **57**, 11110–11130; (e) Y. Wang, Y. He and S. Zhu, NiH-Catalyzed Functionalization of Remote and Proximal Olefins: New Reactions and Innovative Strategies, *Acc. Chem. Res.*, 2022, **55**, 3519–3536; (f) B. C. Lee, C.-F. Liu, L. Q. H. Lin, H. Z. Yap, N. Song, C. H. M. Ko, P. H. Chan and M. J. Koh, *N*-Heterocyclic Carbenes as Privileged Ligands for Nickel-Catalysed Alkene Functionalization, *Chem. Soc. Rev.*, 2023, **52**, 2946–2991; (g) C. Romano and R. Martin, Ni-Catalysed Remote C(sp³)–H Functionalization using Chain-Walking Strategies, *Nat. Rev. Chem.*, 2024, **8**, 833–850.
- 56 H.-D. He, R. Chitrakar, Z.-W. Cao, D.-M. Wang, L.-Q. She, P.-G. Zhao, Y. Wu, Y.-Q. Xu, Z.-Y. Cao and P. Wang, Diphosphine Ligand-Enabled Nickel-Catalyzed Chelate-Assisted Inner-Selective Migratory Hydroarylation of Alkenes, *Angew. Chem., Int. Ed.*, 2024, **63**, e202313336.
- 57 H. Lv, H. Kang, B. Zhou, X. Xue, K. Engle and D. Zhao, Nickel-Catalyzed Intermolecular Oxidative Heck Arylation Driven by Transfer Hydrogenation, *Nat. Commun.*, 2019, **10**, 5025.
- 58 (a) Y. Zhang, Y. Li, W. Zhou, M. Zhang, Q. Zhang, R. Jia and J. Zhao, Assembly of Polysubstituted Chiral Cyclopropylamines via Highly Enantioselective Cu-Catalyzed Three-Component Cyclopropene Alkenylamination, *Chem. Commun.*, 2020, **56**, 12250–12253; (b) Z. Li, M. Zhang, Y. Zhang, S. Liu, J. Zhao and Q. Zhang, Multicomponent Cyclopropane Synthesis



- Enabled by Cu-Catalyzed Cyclopropene Carbometallation with Organoboron Reagent: Enantioselective Modular Access to Polysubstituted 2-Arylcyclopropylamines, *Org. Lett.*, 2019, **21**, 5432–5437.
- 59 (a) M. Ueda, A. Saitoh and N. Miyaura, Asymmetric Hydrogenation of 1-Phenylethenylboronic Acid and Esters for the Synthesis of Chiral Organoboron Compounds, *J. Organomet. Chem.*, 2002, **642**, 145–147; (b) J. B. Morgan and J. P. Morken, Catalytic Enantioselective Hydrogenation of Vinyl Bis(boronates), *J. Am. Chem. Soc.*, 2004, **126**, 15338–15339; (c) A. Paptchikhine, P. Cheruku, M. Engman and P. G. Andersson, Iridium-Catalyzed Enantioselective Hydrogenation of Vinyl Boronates, *Chem. Commun.*, 2009, 5996–5998; (d) A. Ganić and A. Pfaltz, Iridium-Catalyzed Enantioselective Hydrogenation of Alkenylboronic Esters, *Chem. – Eur. J.*, 2012, **18**, 6724–6728; (e) D. Fan, J. Zhang, Y. Hu, Z. Zhang, I. D. Gridnev and W. Zhang, Asymmetric Hydrogenation of α -Boryl Enamides Enabled by Nonbonding Interactions, *ACS Catal.*, 2020, **10**, 3232–3240.
- 60 (a) J. C. H. Lee and D. G. Hall, Chiral Boronate Derivatives via Catalytic Enantioselective Conjugate Addition of Grignard Reagents on 3-Boronyl Unsaturated Esters and Thioesters, *J. Am. Chem. Soc.*, 2010, **132**, 5544–5545; (b) J. C. H. Lee, R. McDonald and D. G. Hall, Enantioselective Preparation and Chemoselective Cross-Coupling of 1, 1-Diboron Compounds, *Nat. Chem.*, 2011, **3**, 894–899; (c) H. J. Edwards, J. D. Hargrave, S. D. Penrose and C. G. Frost, Synthetic Applications of Rhodium Catalysed Conjugate Addition, *Chem. Soc. Rev.*, 2010, **39**, 2093–2105; (d) M. Jean, B. Casanova, S. Gnoatto and P. van de Weghe, Strategy of Total Synthesis Based on the use of Rh-Catalyzed Stereoselective 1, 4-Addition, *Org. Biomol. Chem.*, 2015, **13**, 9168–9175.
- 61 (a) Y. Lee, H. Jang and A. H. Hoveyda, Vicinal Diboronates in High Enantiomeric Purity through Tandem Site-Selective NHC-Cu-Catalyzed Boron-Copper Additions to Terminal Alkynes, *J. Am. Chem. Soc.*, 2009, **131**, 18234–18235; (b) X. Feng, H. Jeon and J. Yun, Regio- and Enantioselective Copper(I)-Catalyzed Hydroboration of Borylalkenes: Asymmetric Synthesis of 1,1-Diborylalkanes, *Angew. Chem., Int. Ed.*, 2013, **52**, 3989–3992; (c) L. Dang, H. Zhao, Z. Lin and T. Marder, DFT Studies of Alkene Insertions into Cu–B Bonds in Copper(I) Boryl Complexes, *Organometallics*, 2007, **26**, 2824–2832; (d) M. Zhang, Z. Liu and W. Zhao, Rhodium-Catalyzed Remote Borylation of Alkynes and Vinylboronates, *Angew. Chem., Int. Ed.*, 2023, **62**, e202215455.
- 62 (a) D. Nishikawa, K. Hirano and M. Miura, Asymmetric Synthesis of α -Aminoboronic Acid Derivatives by Copper-Catalyzed Enantioselective Hydroamination, *J. Am. Chem. Soc.*, 2015, **137**, 15620–15623; (b) Y. Zhao, D. Qiao, M. Duan, Y. Wang and S. Zhu, Enantioselective Synthesis of α -Aminoboronates by NiH-Catalysed Asymmetric Hydroamidation of Alkenyl Boronates, *Nat. Commun.*, 2022, **13**, 5630.
- 63 (a) A. A. Szymaniak, C. Zhang, J. R. Coombs and J. P. Morken, Enantioselective Synthesis of Nonracemic Geminal Silylboronates by Pt-Catalyzed Hydrosilylation, *ACS Catal.*, 2018, **8**, 2897–2901; (b) Z. Kong, W. Hu and J. P. Morken, 1,2-Diborylsilanes: Catalytic Enantioselective Synthesis and Site-Selective Cross-Coupling, *ACS Catal.*, 2023, **13**, 11522–11527.
- 64 (a) J. R. Coombs, L. Zhang and J. P. Morken, Enantiomerically Enriched Tris(boronates): Readily Accessible Conjugative Reagents for Asymmetric Synthesis, *J. Am. Chem. Soc.*, 2014, **136**, 16140–16143; (b) H. Fang, N. Manoj, M. Popescu, A. Noble, R. Paton and V. K. Aggarwal, Platinum-Catalyzed Regio- and Enantioselective Diboration of Unactivated Alkenes with (pin)B–B(dan), *Angew. Chem.*, 2024, **64**, e202413504.
- 65 (a) D. Nishikawa, K. Hirano and M. Miura, Copper-Catalyzed Regio- and Stereoselective Aminoboration of Alkenylboronates, *Org. Lett.*, 2016, **18**, 4856–4859; (b) S. Radomkit, Z. Liu, A. Closs, M. S. Mikus and A. H. Hoveyda, Practical, Efficient, and Broadly Applicable Synthesis of Readily Differentiable Vicinal Diboronate Compounds by Catalytic Three-Component Reactions, *Tetrahedron*, 2017, **73**, 5011–5017; (c) I. Kageyuki, I. Osaka, K. Takaki and H. Yoshida, Copper-Catalyzed B(dan)-Installing Carboboration of Alkenes, *Org. Lett.*, 2017, **19**, 830–833; (d) J. Carreras, A. Caballero and P. J. Pérez, Enantio- and Diastereoselective Cyclopropanation of 1-Alkenylboronates: Synthesis of 1-Boryl-2, 3-Disubstituted Cyclopropanes, *Angew. Chem., Int. Ed.*, 2018, **57**, 2334–2338 Arnold showed that the engineering of two variants of *Rhodothermus marinus* nitric oxide dioxygenase (RmaNOD) could catalyze the stereoselective and diastereodivergent cyclopropanation of unsubstituted alkenylboronate with ethyl diazoacetate, for details, please see: (e) B. J. Wittmann, A. M. Knight, J. L. Hofstra, S. E. Reisman, S. B. J. Kan and F. H. Arnold, Diversity-Oriented Enzymatic Synthesis of Cyclopropane Building Blocks, *ACS Catal.*, 2020, **10**, 7112–7116.
- 66 (a) W. J. Jang, J. Woo and J. Yun, Asymmetric Conjugate Addition of Chiral Secondary Borylalkyl Copper Species, *Angew. Chem., Int. Ed.*, 2021, **60**, 4614–4618; (b) J. L. Knippel, A. Z. Ni, A. W. Schuppe and S. L. Buckwald, A General Strategy for the Asymmetric Preparation of α -Stereogenic Allyl Silanes, Germanes, and Boronate Esters via Dual Copper Hydride- and Palladium-Catalysis, *Angew. Chem., Int. Ed.*, 2021, **61**, e202212630; (c) J. He, C. B. Seo, W. S. Yoon and J. Yun, Asymmetric Synthesis of β -Aminoboronates via Copper-Catalyzed Reductive Coupling of Vinyl Boronates with Imines, *Org. Lett.*, 2023, **25**, 5492–5497; (d) X. Gao, X. Ren, W. Deng and X. Zhang, Copper-Catalyzed Highly Stereoselective Hydrodifluoroallylation of Cyclopropenes and Alkenyl Boronates with 3, 3-Difluoroallyl Sulfonium Salts, *Chin. J. Chem.*, 2023, **41**, 3521–3527.
- 67 C. Zhang, W. Hu, G. J. Lovinger, J. Jin, J. Chen and J. P. Morken, Enantiomerically Enriched α -Borylzinc



- Reagents by Nickel-Catalyzed Carbozincation of Vinylboronic Esters, *J. Am. Chem. Soc.*, 2021, **143**, 14189–14195.
- 68 (a) E. K. Edelstein, S. Namirembe and J. P. Morken, Enantioselective Conjunctive Cross-Coupling of Bis (alkenyl)borates: A General Synthesis of Chiral Allylboron Reagents, *J. Am. Chem. Soc.*, 2017, **139**, 5027–5030; (b) J. A. Myhill, C. A. Wilhelmsen, L. Zhang and J. P. Morken, Diastereoselective and Enantioselective Conjunctive Cross-Coupling Enabled by Boron Ligand Design, *J. Am. Chem. Soc.*, 2018, **140**, 15181–15185; (c) J. A. Myhill, L. Zhang, G. J. Lovinger and J. P. Morken, Enantioselective Construction of Tertiary Boronic Esters by Conjunctive Cross-Coupling, *Angew. Chem., Int. Ed.*, 2018, **57**, 12799–12803; (d) Y. Meng, Z. Kong and J. P. Morken, Catalytic Enantioselective Synthesis of *anti*-Vicinal Silylboronates by Conjunctive Cross-Coupling, *Angew. Chem., Int. Ed.*, 2020, **59**, 8456–8459; (e) C. Law, E. Kativhu, J. Wang and J. P. Morken, *Angew. Chem., Int. Ed.*, 2020, **59**, 10311–10315; (f) G. J. Lovinger and J. P. Morken, Ni-Catalyzed Enantioselective Conjunctive Coupling with C(sp³) Electrophiles: A Radical-Ionic Mechanistic Dichotomy, *J. Am. Chem. Soc.*, 2017, **139**, 17293–17296; (g) C. A. Wilhelmsen, X. Zhang, J. A. Myhill and J. P. Morken, Enantioselective Synthesis of Tertiary B-Boryl Amides by Conjunctive Cross-Coupling of Alkenyl Boronates and Carbamoyl Chloride, *Angew. Chem., Int. Ed.*, 2022, **61**, e202116784; (h) X. Zhang, C. Gao and J. P. Morken, Enantioselective Construction of Carbocyclic and Heterocyclic Tertiary Boronic Esters by Conjunctive Cross-Coupling Reaction, *J. Am. Chem. Soc.*, 2023, **145**, 16344–16349.
- 69 J. C. Lo, J. Gui, Y. Yabe, C.-M. Pan and P. S. Baran, Functionalized Olefin Cross-Coupling to Construct Carbon–Carbon Bonds, *Nature*, 2014, **516**, 343–348.
- 70 S. Bera and X. Hu, Nickel-Catalyzed Regioselective Hydroalkylation and Hydroarylation of Alkenyl Boronic Esters, *Angew. Chem., Int. Ed.*, 2019, **58**, 13854–13859.
- 71 Y. Zhang, B. Han and S. Zhu, Rapid Access to Highly Functionalized Alkyl Boronates by NiH-Catalyzed Remote Hydroarylation of Boron-Containing Alkenes, *Angew. Chem., Int. Ed.*, 2019, **58**, 13860–13864.
- 72 S. Bera, R. Mao and X. Hu, Enantioselective C(sp³)-C(sp³) Cross-Coupling of Non-Activated Alkyl Electrophiles via Nickel Hydride Catalysis, *Nat. Chem.*, 2021, **13**, 270–277.
- 73 X.-X. Wang, X. Lu, S.-J. He and Y. Fu, Nickel-Catalyzed Three-Component Olefin Reductive Dicarbofunctionalization to Access Alkylborates, *Chem. Sci.*, 2020, **11**, 7950–7956.
- 74 L. Liu, M. C. Aguilera, W. Lee, C. R. Youshaw, M. L. Neidig and O. Gutierrez, General Method for Iron-Catalyzed Multicomponent Radical Cascades-Cross-Couplings, *Science*, 2021, **374**, 432–439.
- 75 T. D. Ho, B. J. Lee, C. Tan, J. A. Utley, N. Q. Ngo and K. L. Hull, Efficient Synthesis of α -Haloboronic Esters via Cu-Catalyzed Atom Transfer Radical Addition, *J. Am. Chem. Soc.*, 2023, **145**, 27230–27235.
- 76 (a) M. M. Parsutkar, V. V. Pagar and T. V. Rajanbabu, *J. Am. Chem. Soc.*, 2019, **141**, 15367–15377 Ogoshi has pioneered the Co(i)-catalyzed [2 + 2] cycloaddition of vinylboronate with 1,3-enyne, albeit with low efficiency, for details, please see: (b) A. Nishimura, E. Tamai, M. Ohashi and S. Ogoshi, *Chem. – Eur. J.*, 2014, **20**, 6613–6617 For another recent work, please see: (c) K. Prysiashniuk, O. Polishchuk, S. Shulha, K. Gudzikeyvych, O. P. Datsenko, V. Kubyskin and P. K. Mykhailiuk, Borylated Cyclobutanes via Thermal [2 + 2]-Cycloaddition, *Chem. Sci.*, 2024, **15**, 3249–3254.
- 77 Z. G. Hajos and D. R. Parrish, Asymmetric Synthesis of Bicyclic Intermediates of Natural Product Chemistry, *J. Org. Chem.*, 1974, **39**, 1615–1621.
- 78 (a) B. List, R. A. Lerner and C. F. Barbas III, Proline-Catalyzed Direct Asymmetric Aldol Reactions, *J. Am. Chem. Soc.*, 2000, **122**, 2395–2396; (b) K. A. Ahrendt, C. J. Borths and D. W. C. MacMillan, New Strategies for Organic Catalysis: The First Highly Enantioselective Organocatalytic Diels–Alder Reaction, *J. Am. Chem. Soc.*, 2000, **122**, 4243–4244.
- 79 (a) M. S. Taylor and E. N. Jacobsen, Asymmetric Catalysis by Chiral Hydrogen-Bond Donors, *Angew. Chem., Int. Ed.*, 2006, **45**, 1520–1543; (b) E. A. Colby Davie, S. M. Mennen, Y. Xu and S. J. Miller, Asymmetric Catalysis Mediated by Synthetic Peptides, *Chem. Rev.*, 2007, **107**, 5759–5812; (c) T. Akiyama, Stronger Brønsted Acids, *Chem. Rev.*, 2007, **107**, 5744–5758; (d) D. Enders, O. Niemeier and A. Henseler, Organocatalysis by *N*-Heterocyclic Carbenes, *Chem. Rev.*, 2007, **107**, 5606–5655; (e) S. Mukherjee, J. W. Yang, S. Hoffmann and B. List, Asymmetric Enamine Catalysis, *Chem. Rev.*, 2007, **107**, 5471–5569; (f) K. L. Jensen, G. Dickmeiss, H. Jiang, L. Albrecht and K. A. Jørgensen, The Diarylprolinol Silyl Ether System: A General Organocatalyst, *Acc. Chem. Res.*, 2012, **45**, 248–264; (g) S. Shirakawa and K. Maruoka, Recent Developments in Asymmetric Phase-Transfer Reactions, *Angew. Chem., Int. Ed.*, 2013, **52**, 4312–4348; (h) D. Parmar, E. Sugiono, S. Raja and M. Rueping, Complete Field Guide to Asymmetric BINOL-Phosphate Derived Brønsted Acid and Metal Catalysis: History and Classification by Mode of Activation; Brønsted Acidity, Hydrogen Bonding, Ion Pairing, and Metal Phosphates, *Chem. Rev.*, 2014, **114**, 9047–9153; (i) S.-H. Xiang and B. Tan, Advances in Asymmetric Organocatalysis over the Last 10 Years, *Nat. Commun.*, 2020, **11**, 3786.
- 80 (a) S. Lee and D. W. C. MacMillan, Organocatalytic Vinyl and Friedel–Crafts Alkylations with Trifluoroborate Salts, *J. Am. Chem. Soc.*, 2007, **129**, 15438–15439; (b) H. Kim and D. W. C. MacMillan, Enantioselective Organo-SOMO Catalysis: the α -Vinylolation of Aldehydes, *J. Am. Chem. Soc.*, 2008, **130**, 398–399.
- 81 R. Nishiyabu, Y. Kubo, T. D. James and J. S. Fossey, Boronic Acid Building Blocks: Tools for Self Assembly, *Chem. Commun.*, 2011, **47**, 1124–1150.



- 82 S. Lou, P. N. Moquist and S. E. Schaus, Asymmetric Allylboration of Ketones Catalyzed by Chiral Diols, *J. Am. Chem. Soc.*, 2006, **128**, 12660–12661.
- 83 S. E. Schaus and S. Lou, Asymmetric Petasis Reactions Catalyzed by Chiral Biphenols, *J. Am. Chem. Soc.*, 2008, **130**, 6922–6923.
- 84 J. A. Bishop, S. Lou and S. E. Schaus, Enantioselective Addition of Boronates to Acyl Imines Catalyzed by Chiral Biphenols, *Angew. Chem., Int. Ed.*, 2009, **48**, 4337–4340.
- 85 T. Kodama, P. N. Moquist and S. E. Schaus, Enantioselective Boronate Additions to *N*-Acyl Quinoliniums Catalyzed by Tartaric Acid, *Org. Lett.*, 2011, **13**, 6316–6319.
- 86 (a) K. S. Barbato, Y. Luan, D. Ramella, J. S. Panek and S. Schaus, Enantioselective Multicomponent Condensation Reactions of Phenols, Aldehydes, and Boronates Catalyzed by Chiral Biphenols, *Org. Lett.*, 2015, **17**, 5812–5815; (b) Y. Luan and S. E. Schaus, Enantioselective Addition of Boronates to *o*-Quinone Methides Catalyzed by Chiral Biphenols, *J. Am. Chem. Soc.*, 2012, **134**, 19965–19968.
- 87 T. R. Wu and J. M. Chong, Asymmetric Allylboration of Acyl Imines Catalyzed by Chiral Diols, *J. Am. Chem. Soc.*, 2007, **129**, 4908–4909.
- 88 T. Inokuma, K. Takasu, T. Sakaeda and Y. Takemoto, Hydroxyl Group-Directed Organocatalytic Asymmetric Michael Addition of α , β -Unsaturated Ketones with Alkenylboronic Acids, *Org. Lett.*, 2009, **11**, 2425–2433.
- 89 (a) M. Sugiura, R. Kinoshita and M. Nakajima, *O*-Monoacyltartaric Acid Catalyzed Enantioselective Conjugate Addition of a Boronic Acid to Dienones: Application to the Synthesis of Optically Active Cyclopentenones, *Org. Lett.*, 2014, **16**, 5172–5175; (b) M. Sugiura, M. Tokudomi and M. Nakajima, Enantioselective Conjugate Addition of Boronic Acids to Enones Catalyzed by *O*-Monoacyltartaric Acids, *Chem. Commun.*, 2010, **46**, 7799–7800.
- 90 (a) B. J. Lundy, S. Jansone-Popova and J. A. May, Enantioselective Conjugate Addition of Alkenylboronic Acids to Indole-Appended Enones, *Org. Lett.*, 2011, **13**, 4958–4961; (b) P. Q. Le, T. S. Nguyen and J. A. May, A General Method for the Enantioselective Synthesis of α -Chiral Heterocycles, *Org. Lett.*, 2012, **14**, 6104–6107.
- 91 X. Liu, Z. Meng, C. Li, H. Lou and L. Liu, Organocatalytic Enantioselective Oxidative C-H Alkenylation and Arylation of *N*-Carbamoyl Tetrahydropyridines and Tetrahydro- β -carboline, *Angew. Chem., Int. Ed.*, 2015, **54**, 6012–6015.
- 92 S. J. T. Jonker, R. Jayarajan, T. Kireilis, M. Deliaval, L. Eriksson and K. J. Szabó, Organocatalytic Synthesis of α -Trifluoromethyl Allylboronic Acids by Enantioselective 1, 2-Borotropic Migration, *J. Am. Chem. Soc.*, 2020, **142**, 21254–21259.
- 93 H. Qian, W. Zhao, Z. Wang and J. Sun, Synthesis of Adjacent Quaternary Stereocenters by Catalytic Asymmetric Allylboration, *J. Am. Chem. Soc.*, 2015, **137**, 560–563.
- 94 S. Liu, H. Qian, T. Zhang, H. Xie, Z. Han, W. Guo, H. Huang and J. Sun, Mild Intermolecular Synthesis of a Cyclopropane-Containing Tricyclic Skeleton: Unusual Reactivity of Isobenzopyryliums, *Angew. Chem., Int. Ed.*, 2021, **60**, 21272–21276.
- 95 Z. Tao, K. A. Robb, J. L. Panger and S. E. Denmark, Enantioselective, Lewis Base-Catalyzed Carbosulfenylation of Alkenylboronates by 1, 2-Boronate Migration, *J. Am. Chem. Soc.*, 2018, **140**, 15621–15625.
- 96 T. P. Maloney, J. L. Berman and F. E. Michael, Metal-Free Allylic C–H Amination of Vinylsilanes and Vinylboronates using Silicon or Boron as a Regioselectivity Switch, *Angew. Chem.*, 2022, **134**, e202210109.
- 97 (a) C. K. Prier, D. A. Rankic and D. W. C. MacMillan, Visible Light Photoredox Catalysis with Transition Metal Complexes: Applications in Organic Synthesis, *Chem. Rev.*, 2016, **81**, 6898–6926; (b) N. A. Romero and D. A. Nicewicz, Organic Photoredox Catalysis, *Chem. Rev.*, 2016, **116**, 10075–10166; (c) R. C. McAtee, E. J. McClain and C. R. J. Stephenson, Illuminating Photoredox Catalysis, *Trends Chem.*, 2019, **1**, 111–125; (d) G. E. M. Crisenza and P. Melchiorre, Chemistry Glows Green with Photoredox Catalysis, *Nat. Commun.*, 2020, **11**, 803; (e) N. L. Reed and T. P. Yoon, Oxidase Reactions in Photoredox Catalysis, *Chem. Soc. Rev.*, 2021, **50**, 2954–2967.
- 98 D. M. Arias-Rotondo and J. K. McCusker, The Photophysics of Photoredox Catalysis: A Roadmap for Catalyst Design, *Chem. Soc. Rev.*, 2016, **45**, 5803–5820.
- 99 (a) D. S. Matteson, Radical Catalyzed Additions to Dibutyl Ethyleneboronate, *J. Am. Chem. Soc.*, 1959, **81**, 5004–5005; (b) D. S. Matteson, Radical-catalyzed Additions to α , β -Unsaturated Boronic Esters, *J. Am. Chem. Soc.*, 1960, **82**, 4228–4233.
- 100 M. Kischewitz, K. Okamoto, C. Mück-Lichtenfeld and A. Studer, Radical-Polar Crossover Reactions of Vinylboron Ate Complexes, *Science*, 2017, **355**, 936–938.
- 101 M. Silvi, C. Sandford and V. K. Aggarwal, Merging Photoredox with 1, 2-Metallate Rearrangements: The Photochemical Alkylation of Vinyl Boronate Complexes, *J. Am. Chem. Soc.*, 2017, **139**, 5736–5739.
- 102 Y. Yasu, T. Koike and M. Akita, Visible-Light-Induced Synthesis of a Variety of Trifluoromethylated Alkenes from Potassium Vinyltrifluoroborates by Photoredox Catalysis, *Chem. Commun.*, 2013, **49**, 2037–2039.
- 103 D. F. Reina, A. Ruffoni, Y. S. S. Al-Faiyz, J. J. Douglas, N. S. Sheikh and D. Leonori, Visible-Light-Mediated Reactions of Electrophilic Radicals with Vinyl and Allyl Trifluoroborates, *ACS Catal.*, 2017, **7**, 4126–4130.
- 104 X. Shen, J.-J. Zhao and S. Yu, Photoredox-Catalyzed Intermolecular Remote C–H and C–C Vinylation via Iminyl Radicals, *Org. Lett.*, 2018, **20**, 5523–5527.
- 105 X. Shen, C. Huang, X.-A. Yuan and S. Yu, Diastereoselective and Stereodivergent Synthesis of 2-Cinnamylpyrrolines Enabled by Photoredox-Catalyzed Iminoalkenylation of Alkenes, *Angew. Chem., Int. Ed.*, 2021, **60**, 9672–9679.



- 106 H. Chen, L. Guo and S. Yu, Primary, Secondary, and Tertiary γ -C(sp³)-H Vinylation of Amides via Organic Photoredox-Catalyzed Hydrogen Atom Transfer, *Org. Lett.*, 2018, **20**, 6255–6259.
- 107 X.-D. An, H. Zhang, Q. Xu, L. Yu and S. Yu, Stereodivergent Synthesis of α -Aminomethyl Cinnamyl Ethers via Photoredox-Catalyzed Radical Relay Reaction, *Chin. J. Chem.*, 2018, **36**, 1147–1150.
- 108 J. Brals, T. M. McGuire and A. J. B. Watson, A Chemoselective Polarity-Mismatched Photocatalytic C(sp³) C(sp²) Cross-Coupling Enabled by Synergistic Boron Activation, *Angew. Chem., Int. Ed.*, 2023, **62**, e202310462.
- 109 M. R. Heinrich, L. A. Sharp and S. Z. Zard, A Convergent Approach to γ -Carbonyl Vinyl Boronates, *Chem. Commun.*, 2005, 3077–3079.
- 110 A. Noble, R. S. Mega, D. Pflästerer, E. L. Myers and V. K. Aggarwal, Visible-Light-Mediated Decarboxylative Radical Additions to Vinyl Boronic Esters: Rapid Access to γ -Amino Boronic Esters, *Angew. Chem., Int. Ed.*, 2018, **57**, 2155–2159.
- 111 X. Shu, R. Xu, Q. Ma and S. Liao, Accessing Alkyl Boronic Esters via Visible Light-Mediated Decarboxylative Addition Reactions of Redox-Active Esters, *Org. Chem. Front.*, 2020, **7**, 2003–2007.
- 112 T. Constantin, M. Zanini, A. Regni, N. S. Sheikh, F. Juliá and D. Leonori, Aminoalkyl Radicals as Halogen-Atom Transfer Agents for Activation of Alkyl and Aryl Halides, *Science*, 2020, **367**, 1021–1026.
- 113 C. Shu, R. S. Mega, B. J. Andreassen, A. Noble and V. K. Aggarwal, Synthesis of Functionalized Cyclopropanes from Carboxylic Acids by a Radical Addition–Polar Cyclization Cascade, *Angew. Chem., Int. Ed.*, 2018, **57**, 15430–15434.
- 114 S.-Z. Sun, Y. Duan, R. S. Mega, R. J. Somerville and R. Martin, Site-Selective 1,2-Dicarbofunctionalization of Vinyl Boronates through Dual Catalysis, *Angew. Chem., Int. Ed.*, 2020, **59**, 4370–4374.
- 115 R. S. Mega, V. K. Duong, A. Noble and V. K. Aggarwal, Decarboxylative Conjunctive Cross-coupling of Vinyl Boronic Esters using Metallaphotoredox Catalysis, *Angew. Chem., Int. Ed.*, 2020, **59**, 4375–4379.
- 116 A. Luridiana, D. Mazzarella, L. Capaldo, J. A. Rincón, P. García-Losada, C. Mateos, M. O. Frederick, M. Nuño, W. J. Buma and T. Noël, The Merger of Benzophenone HAT Photocatalysis and Silyl Radical-Induced XAT Enables Both Nickel-Catalyzed Cross-Electrophile Coupling and 1,2-Dicarbofunctionalization of Olefins, *ACS Catal.*, 2022, **12**, 11216–11225.
- 117 X. Li, Y. Hu, Z. Huang, S. Zhu, F.-L. Qing and L. Chu, Metallaphotoredox-Catalyzed Three-Component Asymmetric Cross-Electrophile Coupling for Chiral Boronate Synthesis, *ACS Catal.*, 2024, **14**, 15790–15798.
- 118 (a) W. G. Hollis, W. C. Lappenbusch, K. A. Everberg and C. M. Woleben, the use of Alkenylboronate Esters in [2+2] Enone-Olefin Photocycloadditions, *Tetrahedron Lett.*, 1993, **34**, 7517–7520; (b) S. C. Coote and T. Bach, Enantioselective Intermolecular [2+2] Photocycloadditions of Isoquinolone Mediated by a Chiral Hydrogen-Bonding Template, *J. Am. Chem. Soc.*, 2013, **135**, 14948–14951; (c) O. P. Demchuk, O. V. Hryshchuk, B. V. Vashchenko, A. V. Kozytskiy, A. V. Tymtsunik, I. V. Komarov and O. O. Gryorenko, Photochemical [2 + 2] Cycloaddition of Alkenyl Boronic Derivatives: An Entry into 3-Azabicyclo [3.2.0]heptane Scaffold, *J. Org. Chem.*, 2020, **85**, 5927–5940.
- 119 P. R. D. Murray, W. M. M. Bussink, G. H. M. Davies, F. W. van der Mei, A. H. Antropow, J. T. Edwards, L. A. D'Agostino, J. M. Ellis, L. G. Hamann, F. Romanov-Michailidis and R. R. Knowles, Intermolecular Crossed [2 + 2] Cycloaddition Promoted by Visible-Light Triplet Photosensitization: Expedient Access to Polysubstituted 2-Oxaspiro[3.3]heptanes, *J. Am. Chem. Soc.*, 2021, **143**, 4055–4063.
- 120 S. O. Scholz, J. B. Kidd, L. Capaldo, N. E. Flikweert, R. M. Littlefield and T. P. Yoon, Construction of Complex Cyclobutane Building Blocks by Photosensitized [2 + 2] Cycloaddition of Vinyl Boronate Esters, *Org. Lett.*, 2021, **23**, 3496–3501.
- 121 G. Roland, K. N. Hurdal, A. Bouchouicha, N. Dowe, R. L. Davis and S. K. Collins, [2 + 2] Photocycloadditions to Form Cyclobutanes and Bicyclo[2.1.1]hexanes Employing Copper-Based Photocatalysis, *ACS Catal.*, 2024, **14**, 11490–11497.
- 122 Y. Liu, D. Ni, B. G. Stevenson, V. Tripathy, S. E. Braley, K. Raghavachari, J. R. Swierk and M. K. Brown, Photosensitized [2+2]-Cycloadditions of Alkenylboronates and Alkenes, *Angew. Chem., Int. Ed.*, 2022, **61**, e202200725.
- 123 J. J. Molloy, J. B. Metternich, C. G. Daniliuc, A. J. B. Watson and R. Gilmour, Contra-Thermodynamic, Photocatalytic E→Z Isomerization of Styrenyl Boron Species: Vectors to Facilitate Exploration of Two-Dimensional Chemical Space, *Angew. Chem., Int. Ed.*, 2018, **57**, 3168–3172.
- 124 J. J. Molloy, M. Schäfer, M. Wienhold, T. Morack, C. G. Daniluc and R. Gilmour, Boron-enabled Geometric Isomerization of Alkenes via Selective Energy-Transfer Catalysis, *Science*, 2020, **369**, 302–306.
- 125 J. J. Molloy, T. Morack and R. Gilmour, Positional and Geometrical Isomerisation of Alkenes: The Pinnacle of Atom Economy, *Angew. Chem., Int. Ed.*, 2019, **58**, 13654–13664.
- 126 For selected examples, please see: (a) P. Xiong, H. Long, J. Song, Y. Wang, J.-F. Li and H.-C. Xu, Electrochemically Enabled Carbohydroxylation of Alkenes with H₂O and Organotrifluoroborates, *J. Am. Chem. Soc.*, 2018, **140**, 16387–16391; (b) H. Yan, Z.-W. Hou and H.-C. Xu, Photoelectrochemical C–H Alkylation of Heteroarenes with Organotrifluoroborates, *Angew. Chem., Int. Ed.*, 2019, **58**, 4592–4595.

