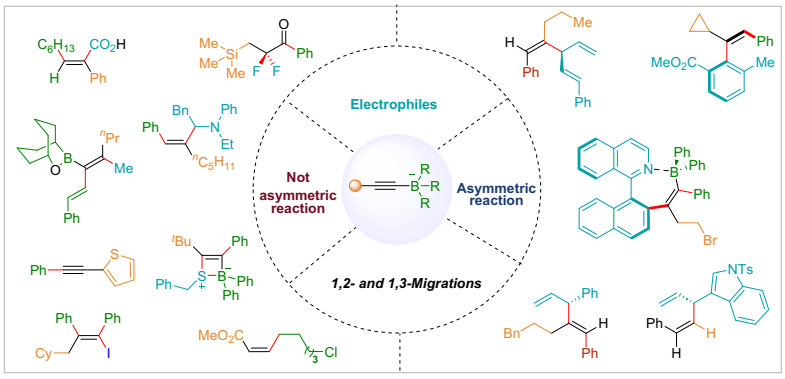
Short Review

Electrophile-Promoted Stereospecific 1,2- and 1,3-Migrations of Alkynylboronates

Fengya He, Dongyang Zhang, Nan Wei, Hui Wang

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GRAPHICAL ABSTRACT



ABSTRACT

The 1,2-migration of tetracoordinate boron compounds represents a powerful strategy for the construction of C–C bonds and stereogenic centers, enabling the efficient synthesis of complex organic molecules under mild conditions. In recent years, substantial progress has been made in this field through the 1,2-migration of alkynylboronates, affording a diverse array of alkenylboron and allylic boron derivatives. In this context, electrophilic reagents readily induce the 1,2-migration of alkynylboronates, while high-oxidation-state π-acidic late-transition-metals, such as Pd^{2+} and Ni^{2+}, have also proven effective as catalysts in reactions involving alkynylboronates. This review systematically summarizes the advances in the 1,2- and 1,3-migration processes of alkynylboronates, as well as transformations involving three-component coupling reactions. Key developments include the reactions of alkynylboronates with a variety of electrophiles (protons, halogens, sulfur species, and iodonium species, etc.) to access tetrasubstituted alkenes, alkenyl halides, benzothiophenes, boracycles, and allylamines; the development of cascade and one-pot strategies that streamline synthetic routes from simple alkynes; and the integration of asymmetric catalysis for the stereoselective construction of carbon stereocenters and axially chiral motifs. The discussion also extends to the reaction scope, mechanistic studies, and synthetic utility of the methodologies described herein.

Keywords alkynylboronates, 1,2-/1,3-migration, electrophiles, asymmetric catalysis, allylations

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1 Introduction

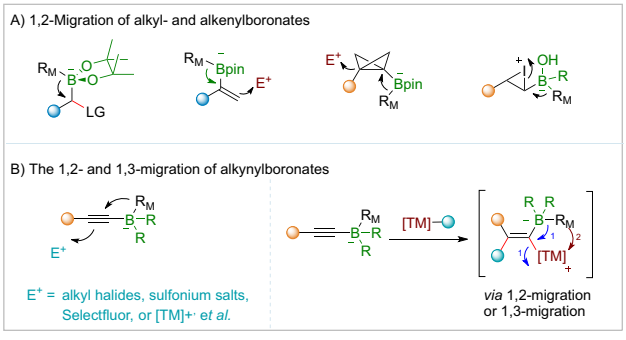
The 1,2-migration of tetracoordinate boron compounds constitutes an important class of transformations in organoboron chemistry for the synthesis of various boron compounds. The origins of this reactivity can be traced to seminal contributions from the reactions of Brown's hydroboration–oxidation,[1] Matteson's boron-mediated homologation,[2] and Zweifel's alkyl/aryl migration in alkenyl boron "ate" complexes.[3] Mechanistically, the vacant *p*-orbital of tricoordinate organoboron compounds can undergo nucleophilic addition by organolithium or Grignard reagents, or by alkoxides, to generate tetracoordinate boronate intermediates. In the presence of an adjacent leaving group or electrophilic site, a substituent on the boron atom can migrate to the neighboring atom, simultaneously regenerating the tricoordinate boron center (**Scheme 1A**).[4] This process commonly proceeds in a highly stereospecific manner and provides an efficient entry to C–C and C–heteroatom bonds, including C–O and C–N bonds. These developments have turned classical Matteson homologation and Zweifel olefination into versatile asymmetric synthesis tools, capable of constructing both central and axial chirality. Accordingly, borate 1,2-migration has become a reliable strategy for the synthesis of natural products, bioactive molecules, and functional materials, while continuing to reveal distinctive features of boron-mediated bond reorganization.[5]

Despite the considerable body of work in this area, systematic reviews focused on stereospecific 1,2-migration reactions of alkynylboronates remain scarce.[6] This review summarizes recent advances in electrophile-induced stereospecific 1,2- or 1,3-migrations of alkynylboronates (**Scheme 1B**). Particular emphasis is placed on metal-free electrophile-induced 1,2-migration reactions and transition-metal-catalyzed coupling reactions involving alkynylboronates through 1,2- or 1,3-migration processes.

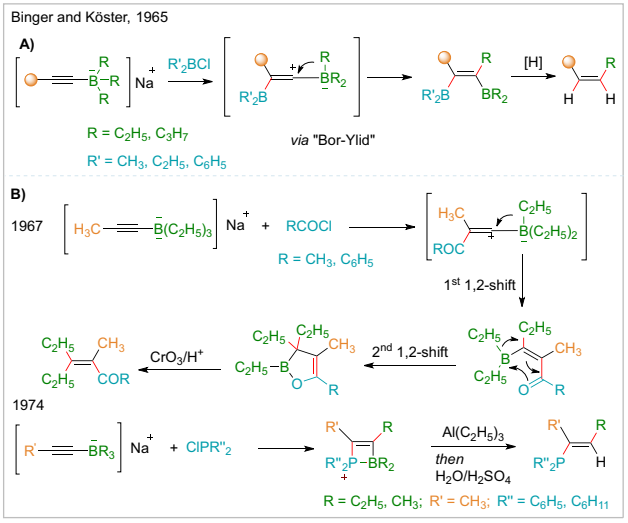
2 Electrophile-Promoted Stereospecific 1,2- and 1,3-Migration of Alkynylboronates

2.1 1,2-Migration of Alkynylboronates Induced by Electrophiles under Noncatalytic Conditions

The reaction of alkynylboronates with electrophiles, proceeding via a 1,2-migration of an organyl group from boron to the adjacent α-carbon, is a powerful method for the synthesis of multiply substituted alkenylboranes. This protocol, pioneered by Binger and Köster in 1965, employs R_2BCl as an electrophile to afford *cis*-1,2-bis(dialkylboryl)alkenes in good yields. And subsequent reduction of these products could provide the corresponding *Z*-alkenes (**Scheme 2A**).[7] Later, they extended this chemistry to acyl chlorides and chlorodiorganophosphanes, which led to the formation of substituted oxaboroles and organo-1,2-phosphaboret-3-enes, respectively (**Scheme 2B**).[8]



Scheme 1 The stereospecific 1,2- and 1,3-migration of boron "ate" compounds.



Scheme 2 1,2-Migration of alkynylboronates with R_2BCl, acyl chlorides, and chlorodiorganophosphanes.

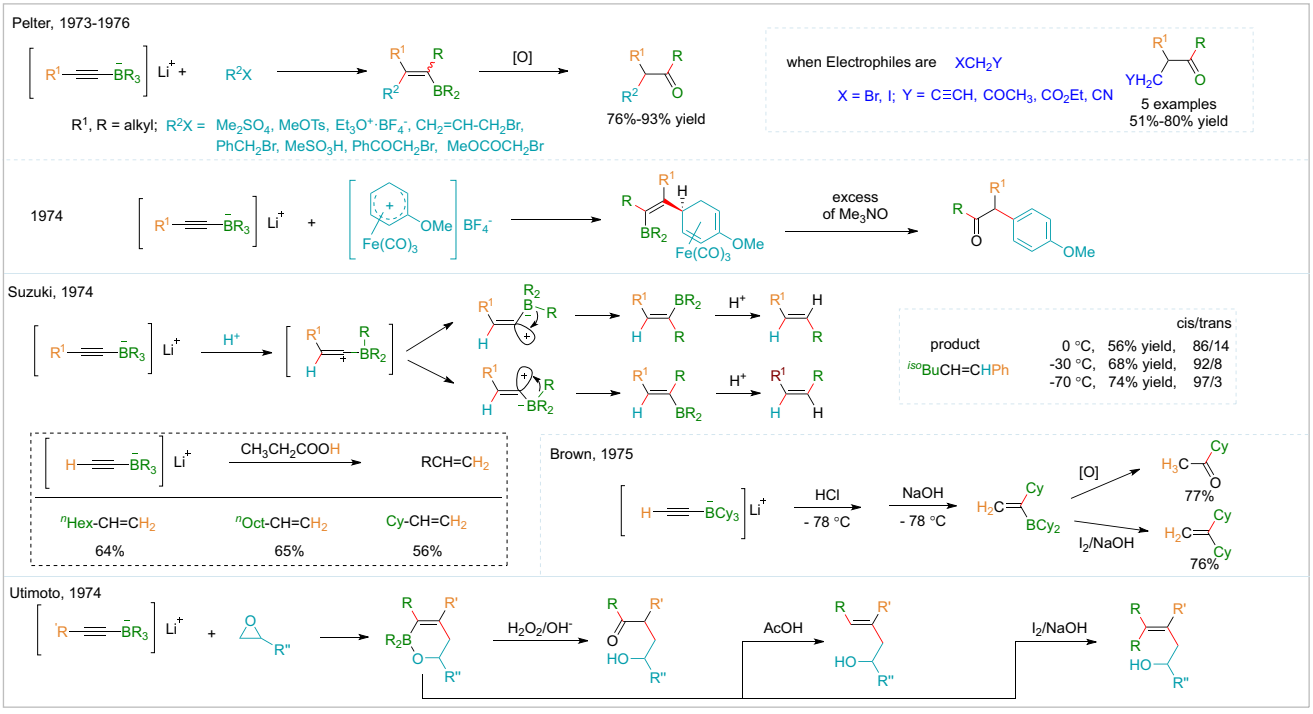
Subsequently, a diverse range of electrophiles was developed for reactions with alkynylboronates. Notable contributions in the 1970s came from Pelter,[9] Suzuki,[10] Brown,[11] Utimoto,[12] and Hooz,[13] who explored electrophiles including protons,[9a,10,11] alkyl halides[9b,c,f,g] acyl chlorides,[8a] allyl bromides,[9h] oxiranes,[12] cationic metal complexes,[9d] and sulfenyl chlorides.[13] Interestingly, the stereochemical outcome is highly dependent on the electrophile's nature: when the electrophile bears a heteroatom capable of coordinating to boron, such as oxygen, sulfur, or selenium, only products arising from *anti*-addition of the electrophile and the migrating group across the triple bond were observed. In contrast, electrophiles such as protons, chlorosilanes, and alkyl halides give nonstereospecific mixtures of addition products (*Z*- and *E*-alkenes). Despite this variability, the alkenylborane products can be conveniently oxidized to the corresponding ketones (**Scheme 3**).

In 1984, Deng and coworkers further investigated the reaction with carbon dioxide, which proceeds through a stereospecific *syn*-addition of the electrophile and the migrating group across the triple bond; after acidic work-up, this method provides α,β-unsaturated carboxylic acids with exclusive *Z*-configuration in high yields (**Scheme 4**).[14]

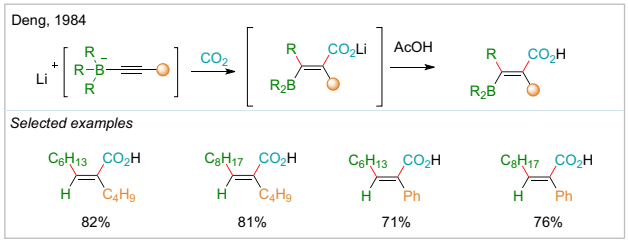
Although this chemistry showed promise for alkene synthesis, it received little further attention over the ensuing decades. The field has recently been reinvigorated by independent contributions from the Song and Aggarwal groups. In 2025, Aggarwal and coworkers reported that treatment of an alkynyl-9-BBN

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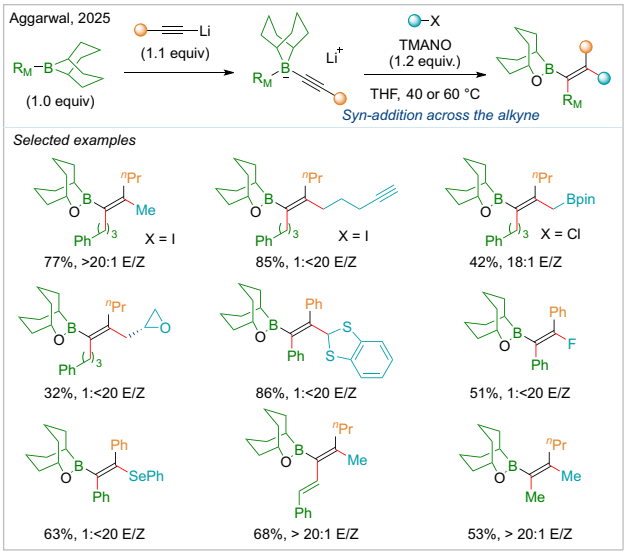
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Scheme 3 1,2-Migration of alkynylboronates with different electrophiles.



Scheme 4 The reaction of alkynylboronates with CO_2.



Scheme 5 Boron-mediated modular assembly of tetrasubstituted alkenes.

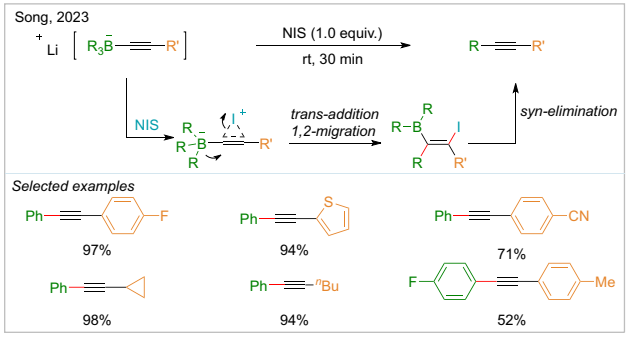
boronate complex with a range of electrophiles, including alkyl halides, sulfonium salts, Selectfluor, phenylselenyl chloride, and dimethyl(methylthio)sulfonium tetrafluoroborate, induced highly *cis*-selective 1,2-migration to furnish the corresponding alkenylboron species as single stereoisomers (**Scheme 5**).[15] Subsequent oxidation with trimethylamine *N*-oxide (TMANO) converts these labile alkenylboranes into stable borinic esters, which serve as versatile linchpins for further transformations en route to various positional and stereoisomers of tetrasubstituted alkenes. Of particular note, the reaction with phenylselenyl chloride proceeds with *syn*-selectivity, in stark contrast to the *anti*-selective outcome reported by Hooz in 1976 using trialkylalkynylborate salts.[13] This work offers a practical and general solution to the long-standing challenge of stereocontrolled tetrasubstituted alkene synthesis.

In contrast to the 9-BBN-based system employed by Aggarwal, the Song group has predominantly utilized triphenylborane-derived alkynylboronates in reactions with electrophiles. For example, in 2023, they reported the reaction of Ar_3B-alkynylboronates with NIS as the electrophile. In this coupling, aryl-substituted unsymmetrical alkynes are obtained in high yields via an electrophilic iodination-induced 1,2-migration of alkynylboronates, followed by *syn*-elimination of the tetrasubstituted alkenyl monoiodide intermediate (**Scheme 6**).[16]

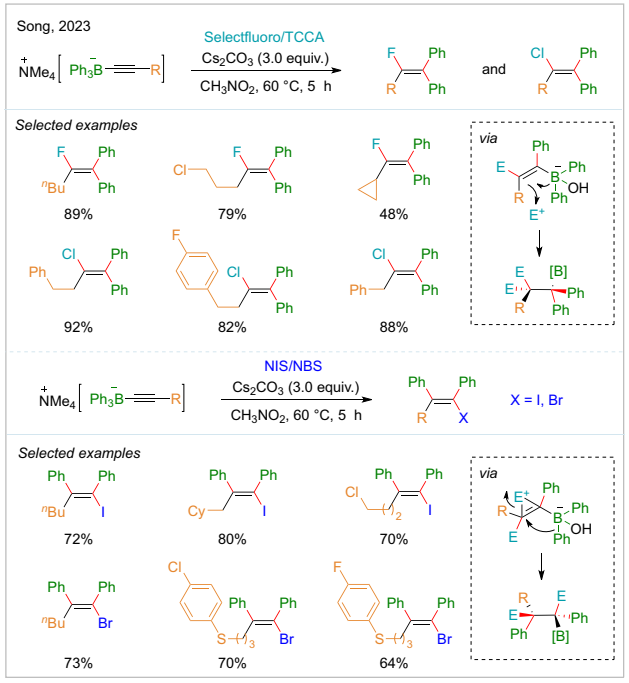
Subsequently, Song and coworkers successfully achieved the synthesis of tetrasubstituted alkenyl monohalides through the reaction of Ar_3B-alkynylboronates with various electrophilic halogenating reagents. Specifically, by utilizing common, inexpensive

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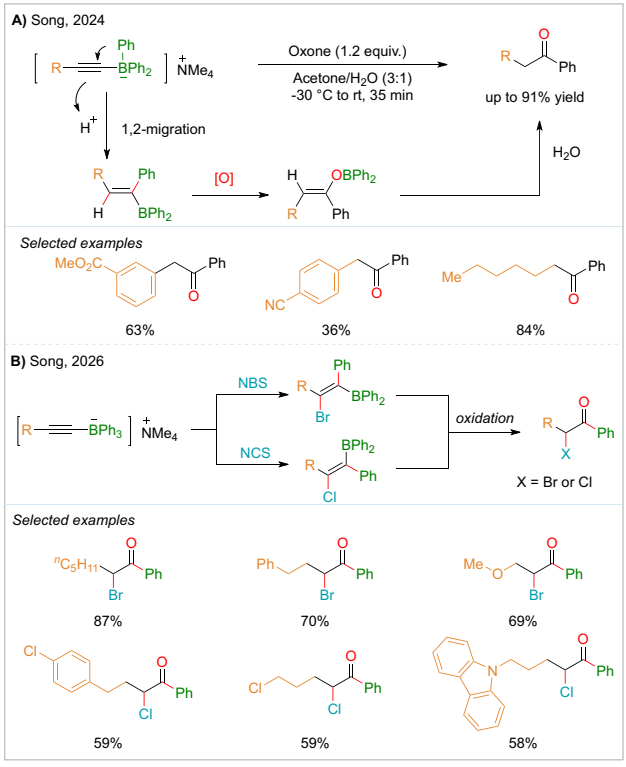


Scheme 6 Transition-metal free Sonogashira-type couplings of Ar_3B-alkynylboronates.



Scheme 7 Synthesis of tetrasubstituted monohaloalkenes via two migrations from alkynylboronates.

sources, Selectfluor, TCCA, NIS, and NBS, they efficiently obtained all four halogenated derivatives (F, Cl, Br, and I) under transition-metal-free conditions (**Scheme 7**).[17] Remarkably, the identity of the halogen dictates the migratory pathway: Selectfluor and TCCA promote sequential 1,2-/1,2-aryl migrations, whereas NIS and NBS trigger 1,2-/1,3-aryl shifts via halonium ion intermediates, thereby furnishing distinct regioisomeric products with exceptional stereoselectivity. The authors explain that the 1,3-shift is presumably feasible owing to steric hindrance arising from the large size of the Br^+ or I^+ ion, given the stability of the final products. In addition, the resulting alkenyl monohalides could serve as versatile synthetic intermediates, engaging in a wide range of palladium-catalyzed cross-coupling reactions to construct C–C, C–B, C–N, C–O, C–P, and C–Si bonds.



Scheme 8 1,1-Oxycarbonation of terminal alkynes.

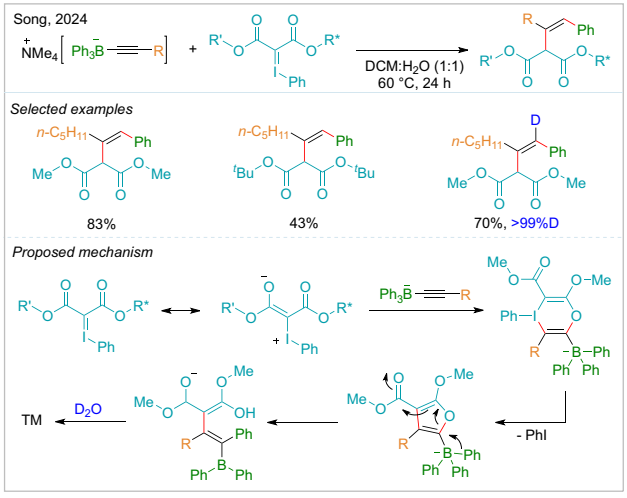
Moreover, in 2024, they disclosed a one-pot protocol that involves a 1,2-migration of Ph_3B-alkynylboronates followed by oxidation to deliver ketones.[18] In this transformation, Oxone plays a pivotal dual role: it initially serves as a proton source to trigger the 1,2-shift of the tetracoordinated borate species, and subsequently acts as an oxidant to convert the resulting alkenylborane intermediate into the corresponding ketone products (**Scheme 8A**). Then, the same group developed a similar approach in which NBS and NCS were used to induce the 1,2-migration of Ph_3B-alkynylboronates; subsequent oxidation provided a highly convenient method for synthesizing α-bromo and α-chloro ketones (**Scheme 8B**).[19]

In the same year, Song and coworkers extended this reactivity to iodonium ylides as electrophilic partners for Ar_3B-alkynylboronates, providing access to multisubstituted olefins (**Scheme 9**).[20] The reaction involves *cis*-addition to generate a six-membered cyclic intermediate, followed by 1,2-phenyl migration from the furanboronate intermediate and protodeboronation to furnish tri- and tetrasubstituted alkenes with excellent stereospecificity. Substitution of H_2O with D_2O enabled the efficient preparation of deuterated trisubstituted alkenes with high deuterium incorporation, providing a practical entry to isotopically labeled building blocks for drug discovery and mechanistic studies.

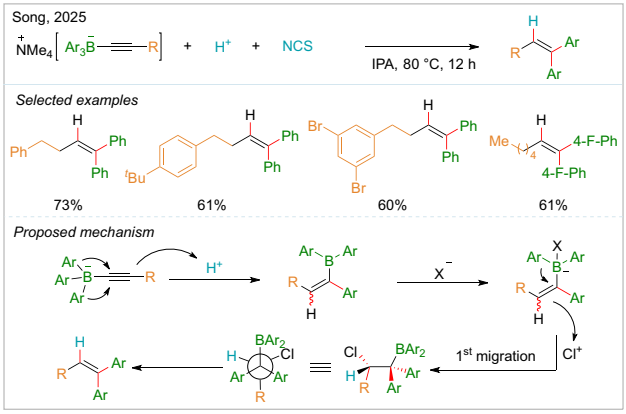
Subsequently, the authors developed a series of reactions that use Ar_3B-alkynylboronates with different fluorinating reagents to construct α,α-difluoroketones, monofluoroalkenes, (deuterated) α-SCF_3 ketones, and SCF_3-bearing alkenes in the presence of oxidants or acetic acid (as well as D_2O and CH_3COOD) (**Scheme 10**).[21] In the presence of Selectfluor and

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Scheme 9 Synthesis of polysubstituted olefins from alkynylboronates and iodonium ylides.



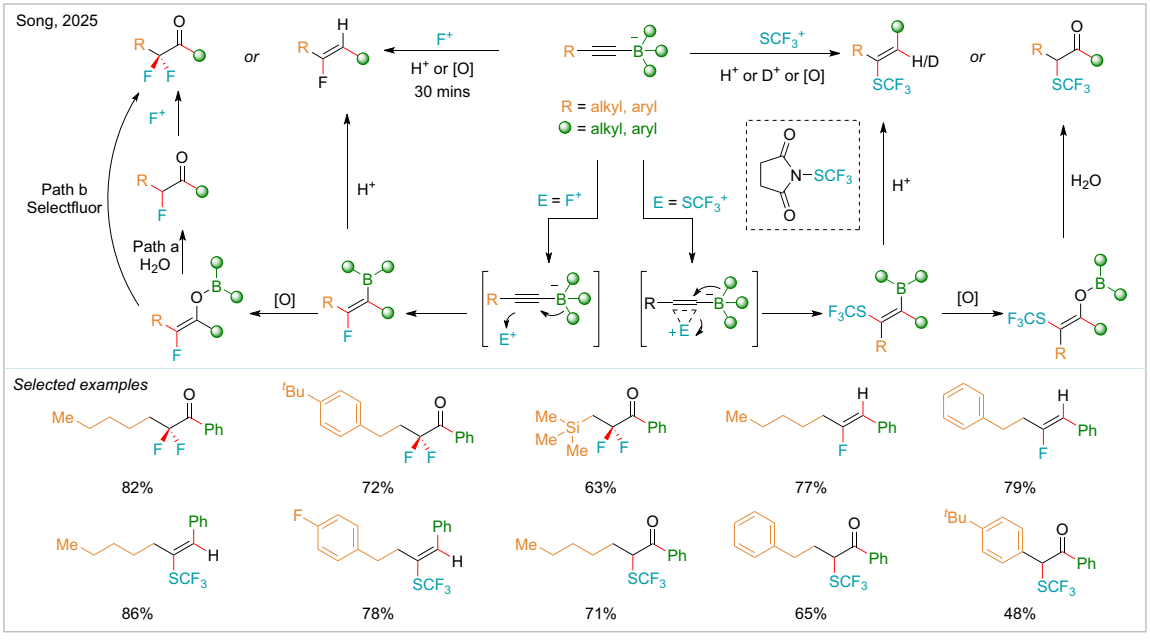
Scheme 11 HCl/NCS enabled sequential dual migrations of alkynylboronates.

H_2O_2, the alkenyl boronates are oxidatively fluorinated to give α,α-difluoroketones in good yields. Under acidic conditions (CH_3COOH), the reaction favors monofluoroalkenes with excellent stereoselectivity. After that, they employ different SCF_3 sources to react with Ar_3B-alkynylboronates. Under acidic conditions (CH_3CO_2H/D), *N*-(trifluoromethylthio)succinimide as the SCF_3-containing electrophile, facilitates the formation of SCF_3-substituted alkenes with excellent stereoselectivity. In contrast, when the reaction is conducted in the presence of $NaBO_3{\cdot}4H_2O$, the product is transformed into α-SCF_3 ketones.

Taking advantage of the multistep, one-pot strategy, the Song group further developed a useful protocol for the synthesis of trisubstituted alkenes from Ar_3B-alkynylboronates under HCl/NCS conditions (**Scheme 11**).[22] In this manifold, HCl serves as the primary electrophile, initiating the first 1,2-migration of alkynylboronates. Subsequently, NCS promotes a second 1,2-aryl migration, followed by *syn*-elimination of $PhBX_2$ to deliver the corresponding alkenes efficiently.

Subsequently, Song and coworkers expanded the synthetic utility of this platform by employing a diverse array of sulfur-based electrophiles in reactions with Ar_3B-alkynylboronates, enabling the divergent construction of sulfur-containing compounds through distinct migratory pathways (either a single 1,2-migration or consecutive dual 1,2-migrations) (**Scheme 12**).[23]

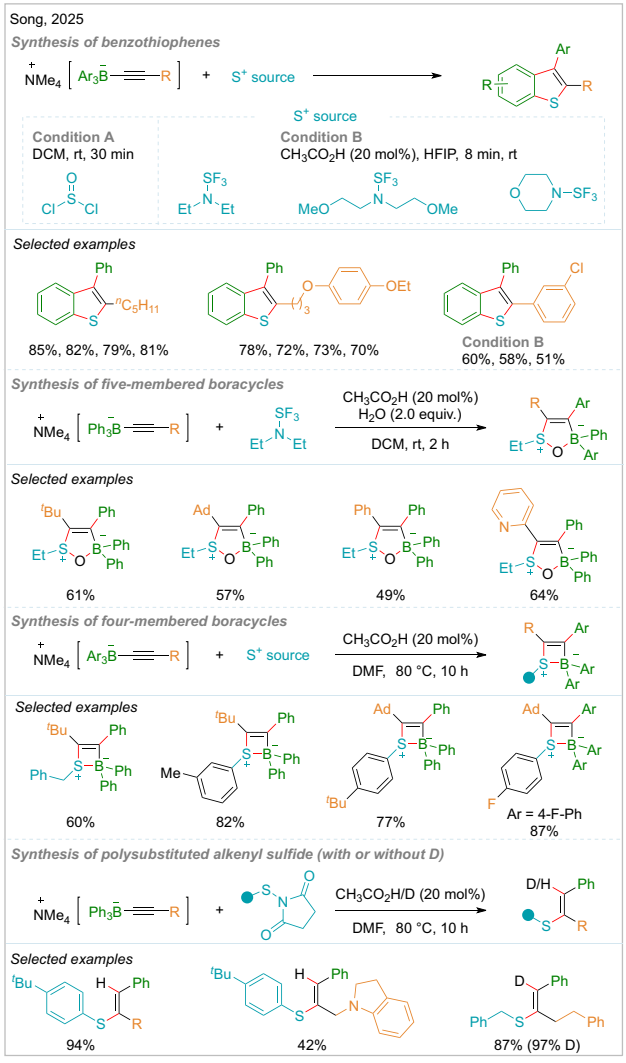
Specifically, the DAST-type reagents and $SOCl_2$ promote sequential dual 1,2-aryl migrations, followed by intramolecular electrophilic substitution, to deliver substituted benzothiophenes. By precise



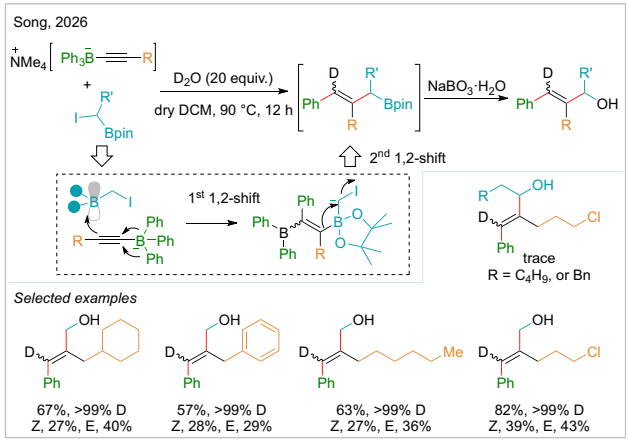
Scheme 10 Synthesis of α,α-difluoroketones, monofluoroalkenes, α-SCF_3 ketones, and (deuterated) SCF_3-containing alkenes.

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Scheme 12 Reactions of Ar_3B-alkynylboronates with sulfur electrophiles.



Scheme 13 Synthesis of deuterated tetrasubstituted allylboronates via consecutive dual 1,2-migration.

modulation of steric hindrance and reaction conditions, five- and four-membered boracycles (via single migration followed by B(sp^2)-heteroatom capture) and polysubstituted alkenyl sulfides (via single migration and subsequent protodeboronation) could also be selectively obtained. Overall, through multiple migration steps, these transformations simultaneously incorporate both aryl groups on the boron center into the final product, significantly improving atom economy.

Recently, the same group revealed an elegant protocol that, through dual 1,2-migration of Ar_3B-alkynylboronates with α-iodoboronates, using D_2O as the deuterium source, delivers deuterated tetrasubstituted allylboronates with quantitative deuterium incorporation (>99% D) (**Scheme 13**).[24] The initial 1,2-migration of the alkynylborate is nonstereospecific, providing a mixture of *Z*/*E* alkenyl boron intermediates (*Z*/*E* ratio around 1:1 to 2:1). A subsequent stereospecific Matteson-type 1,2-migration then affords a diborylated alkene, which undergoes selective protodeboronation of the alkenyl boronate upon treatment with D_2O. Final oxidative workup could furnish the corresponding allylic alcohol products. The authors were able to isolate both *Z*- and *E*-configurations using silica gel chromatography, overcoming the typical challenges associated with separating such highly substituted isomers. Unfortunately, this transformation did not proceed with α-alkyl-substituted iodoboronic esters, likely due to steric hindrance.

Allylamines are privileged structural motifs in pharmaceuticals, agrochemicals, and functional materials;[25] however, their stereoselective synthesis remains a significant challenge. Recently, the Song group developed a conceptually elegant strategy that leverages Ar_3B-alkynylboronates to generate alkenyl anion equivalents in situ via a 1,2-metallate shift. These intermediates then undergo a Brønsted acid-promoted cascade with a wide variety of amines and aldehydes, producing allylamines with exclusive *Z*-selectivity and exceptional chemo- and regioselectivity (**Scheme 14**).[26] The substrate scope is exceptionally broad, encompassing primary and secondary aromatic/aliphatic amines, enamines, ammonia surrogates (Boc-NH_2), chiral amines, amino acids, and esters, as well as complex drug molecules. Notably, when chiral partners are employed, excellent diastereocontrol (>20:1 d.r.) is achieved. A variety of aldehydes are also tolerated. In this process, alkynylboronates serve as masked, stable alkenyl anion equivalents that react with iminium salts.

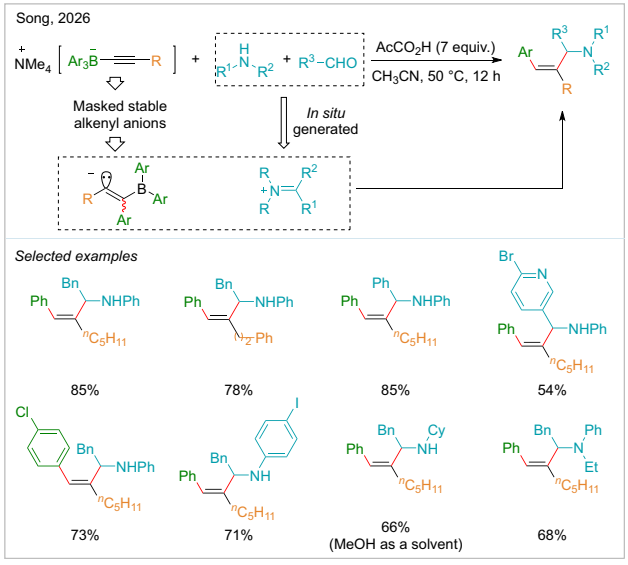
2.2 Transition-Metal-Catalyzed Allylations of Alkynylboronates

Transition-metal-catalyzed allylation represents a powerful strategy for C–C bond formation, offering precise regio- and stereochemical control over allyl introduction.[27] When applied to alkynylboronates via a 1,2-migration process, this platform could enable modular and highly stereoselective access to skipped 1,4-dienes, which are structural motifs widespread in natural products and bioactive compounds.[28]

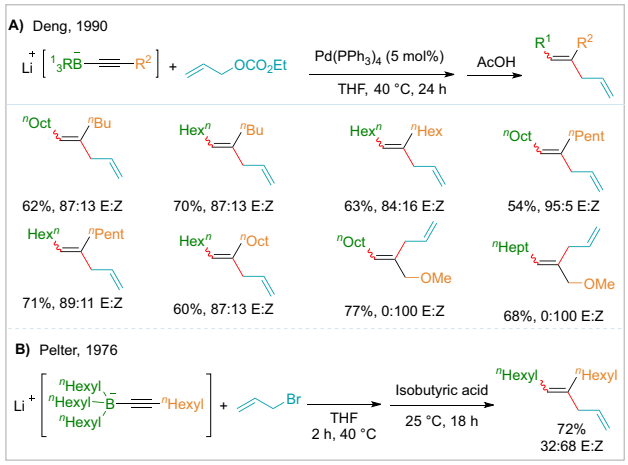
In 1990, Deng and coworkers reported the first palladium-catalyzed allylation of allyl carbonates with lithium trialkylalkynylboronates, which upon reduction afforded 1,4-dienes in good yields (**Scheme 15A**).[29] In that study, alkyl-substituted

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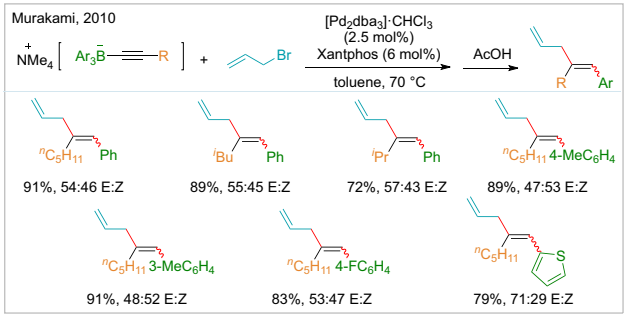
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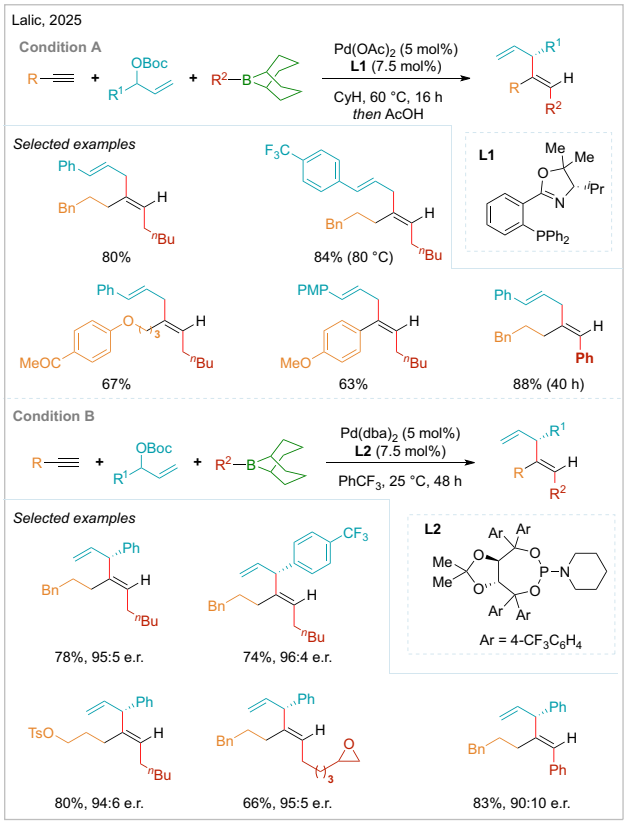
Scheme 14 Synthesis of *Z*-allylamines from alkynyl tetracoordinate boron compounds.



Scheme 15 The allylation reactions of allyl carbonates with lithium trialkylalkynylboronates.



Scheme 16 The palladium-catalyzed allylation reactions of alkynyl(aryl)(diorganyl)borates with allylic bromides.



Scheme 17 The palladium-catalyzed enantioselective trifunctionalization of terminal alkynes.

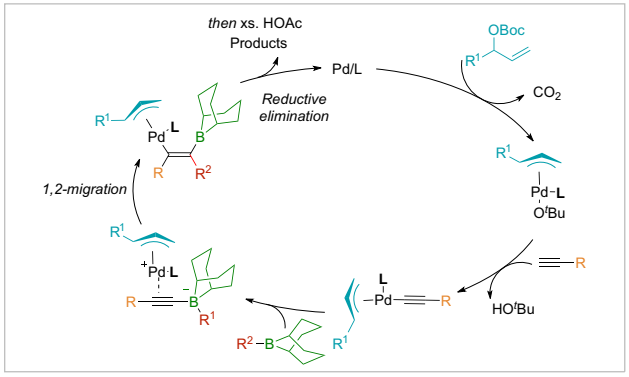
alkynylboronates predominantly gave *E*-alkenes (*E*/*Z*: 84/16 to 95/5), whereas alkoxy-substituted substrates furnished *Z*-alkenes exclusively (100% selectivity), a result ascribed to the oxygen-boron interaction. Notably, an earlier report by Pelter in 1976 showed that, under metal-free conditions, alkyl-substituted alkynylboronates could react with allyl bromide to produce 1,4-dienylboranes with *Z*-alkene as the major product (*Z*/*E*: 68/32) (**Scheme 15B**).[9h]

Subsequently, in 2010, Murakami and coworkers also reported a palladium-catalyzed allylation reaction of alkynyl(aryl)(diorganyl)borates with allylic bromides (**Scheme 16**).[30] Under noncatalytic conditions, alkynyltriarylborates exhibited lower reactivity than their trialkyl counterparts; however, in the presence of $[Pd_2dba_3]\cdot CHCl_3$ and Xantphos ligand, the reaction efficiency could be markedly enhanced, although the *E*/*Z* selectivity remained unsatisfactory. Notably, the reaction utilized air-stable alkynyltriphenylborate salts, and mechanistic experiments revealed that the process proceeded via an intramolecular 1,2-migration mechanism.

Very recently, Lalic and coworkers have demonstrated a palladium-catalyzed trifunctionalization of terminal alkynes, organoboranes, and allylic carbonates as coupling partners (**Scheme 17**).[31] This transformation provides efficient access to highly substituted tri- and tetrasubstituted alkenes with excellent regioselectivity and diastereoselectivity. The reaction relies on

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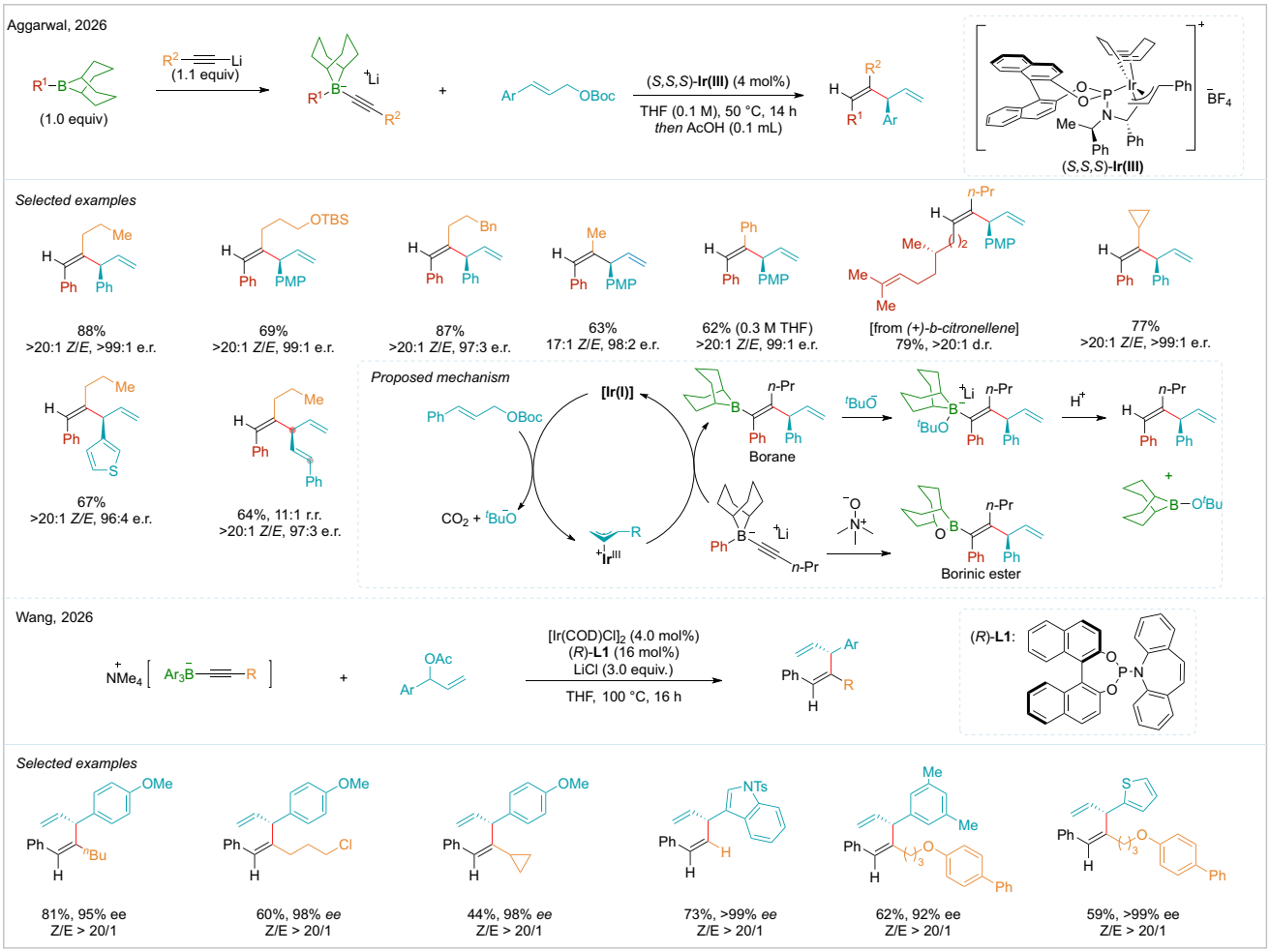


Scheme 18 The proposed mechanism of enantioselective trifunctionalization of terminal alkynes.

the in situ generation of alkynylboronates from the terminal alkyne and organoborane. Notably, judicious tuning of the ligand allows for a divergent switch in regioselectivity between the branched and linear products, while also enabling high enantiocontrol in the branched adducts. Moreover, the polysubstituted alkenylboronates readily undergo subsequent cross-coupling and nucleophilic substitution at the boron moiety, thereby broadening access to tetrasubstituted alkenes.

The reaction is proposed to begin with the oxidative addition of Pd(0) into the allylic carbonate to give a Pd(II) complex and CO_2. The resulting Pd(II) species then deprotonates the terminal alkyne to form a palladium acetylide. Reaction of this intermediate with the Lewis-acidic organoborane affords a Pd(II) alkynyl borate complex, which undergoes a 1,2-metallate shift to generate a tetrasubstituted alkenyl–palladium intermediate. Finally, reductive elimination furnishes the tetrasubstituted alkene product and regenerates Pd(0).

Concurrently, Aggarwal and Wang independently disclosed the iridium-catalyzed 1,2-migration/allylation reactions of alkynylboronates (**Scheme 19**). Aggarwal and coworkers utilized 9-BBN-derived alkynyl boronate complexes in combination with chiral π-allyliridium species generated in situ from allylic carbonates.[32] Wang and coworkers, by contrast, employed air-stable alkynyltriphenylborate salts as substrates together with allylic acetates.[33] Both protocols delivered structurally diverse skipped 1,4-dienes in high yields, with excellent *E*/*Z* ratios and exceptional regio- and enantioselectivities (>20:1 r.r.; >99:1 e.e.). The substrate scope in



Scheme 19 Iridium-catalyzed enantioselective allylation of terminal alkynylboronate complexes.

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both systems was found to be broad, allowing for a variety of alkynyl substituents that included both simple alkyl and aryl groups as well as more complex functional units. Additionally, various allylic electrophiles with aryl, alkenyl, alkynyl, or alkyl components were also accommodated. It is worth noting that Carreira and coworkers had previously shown that potassium alkynyltrifluoroborates react with π-allyliridium complexes to furnish direct alkynylation products rather than the 1,2-migration adducts.[34] Mechanistically, in Aggarwal's work, ^{11}B NMR spectroscopy supported a concerted migration/allylation pathway. And the DFT calculations by Wang also elucidated the origins of the high chemo- and stereoselectivity: the favored transition state features a T-shaped π–π interaction with the cationic π-allyl-Ir(III) complex, which facilitates *syn*-addition of the migrating group and the Ir(π-allyl) fragment across the alkyne. Finally, both reactions enabled further derivatization of the diene products. Their broad substrate scope and stereochemical fidelity of both reactions highlight their potential in the synthesis and derivatization of complex natural products and pharmaceutically relevant molecules.

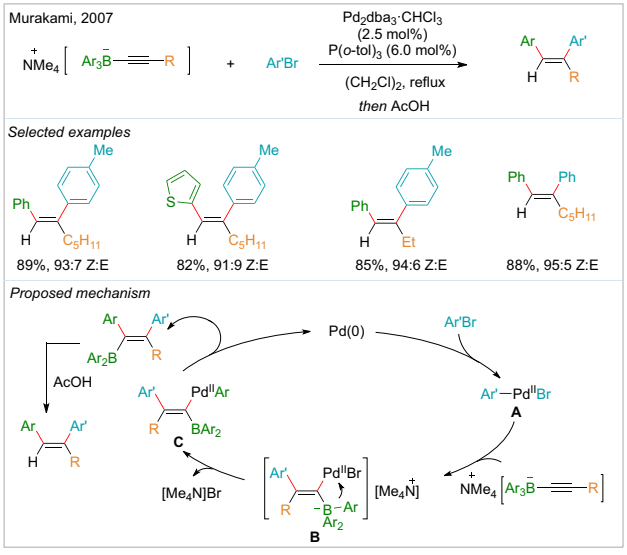
2.3 Other Transition-Metal-Catalyzed Reactions of Alkynylboronates

π–Acidic late transition-metal complexes in high oxidation states, such as Pd^{II} and Ni^{II}, are highly electrophilic and exhibit strong affinity for π-bonds. In 2007, Murakami and coworkers disclosed a palladium-catalyzed coupling of alkynyl triarylborates with aryl halides that affords trisubstituted alkenylboranes with good yields and excellent *Z*/*E* selectivity (*Z*/*E* ratio up to >99/1) (**Scheme 20**).[35] The catalytic cycle is initiated by oxidative addition of arylboromide to Pd(0), generating arylpalladium species **A**. Then, regioselective carbopalladation across the alkyne moiety of alkynylboronate furnishes intermediate **B**, followed by a 1,3-migration of the phenyl group from boron to palladium to give alkenyl-palladium species **C**. Reductive elimination from the resulting palladium complex delivers the alkenylborane products and regenerates the Pd(0) catalyst.

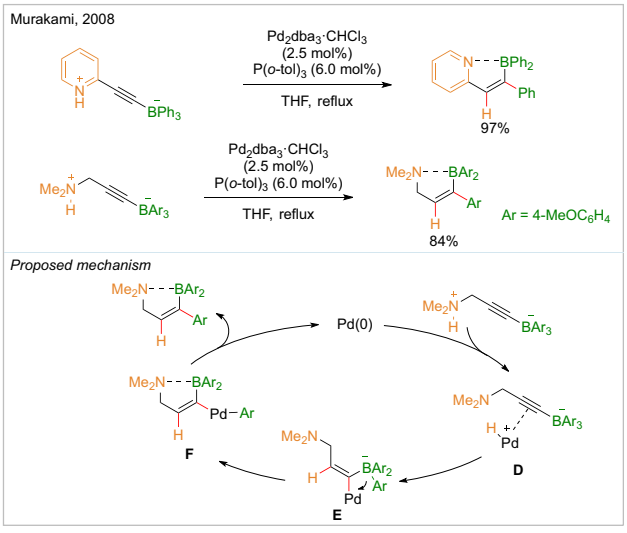
Subsequently, in 2008, they also described a palladium-catalyzed rearrangement of ammonioalkynyltriarylborates that provides intramolecular amine-borane complexes (**Scheme 21**).[36] This transformation achieves stereoselective *trans* installation of hydrogen and boron across the newly formed C=C bond, affording cyclic amine-borane adducts. Mechanistically, first, proton transfer from the tertiary ammonium group to Pd(0) generates cationic palladium species **D**. Regioselective *cis*-hydropalladation of the C≡C bond then delivers zwitterionic intermediate **E**. Subsequent migration of the aryl group from boron to palladium (1,3-migration) produces the alkenyl-palladium intermediate **F**. Reductive elimination of **F** releases the cyclic amine-boranes and regenerates the Pd(0) catalyst.

In 2011, Murakami and coworkers also extended this palladium-catalyzed strategy to 2-bromopyridine *N*-oxides and azaaromatic halides as coupling partners with alkynyltriarylborates, affording a diverse array of π-conjugated compounds (**Scheme 22**).[37] The mechanism of this transformation, however, diverges from that of the previously described system. Owing to the coordinating ability of the nitrogen and oxygen atoms toward boron, the arylpalladium intermediate, following *cis*-carbopalladation of the alkyne, undergoes a 1,2-migration in which the migrating phenyl group attacks from the backside of the α-carbon–Pd bond. This pathway results in an inversion of stereochemistry at the α-sp^2-carbon, in contrast to the retention observed in the earlier reaction.

Before above work, they also reported a palladium-catalyzed cross-coupling for 9-BBN-derived alkynylboronates (in 2009), which were conveniently accessed by the addition of alkynyllithium reagents to Ph-9-BBN (**Scheme 23A**).[38] Notably, the ligand was found to exert decisive control over the migratory pathway, thereby dictating the stereochemical outcome of the



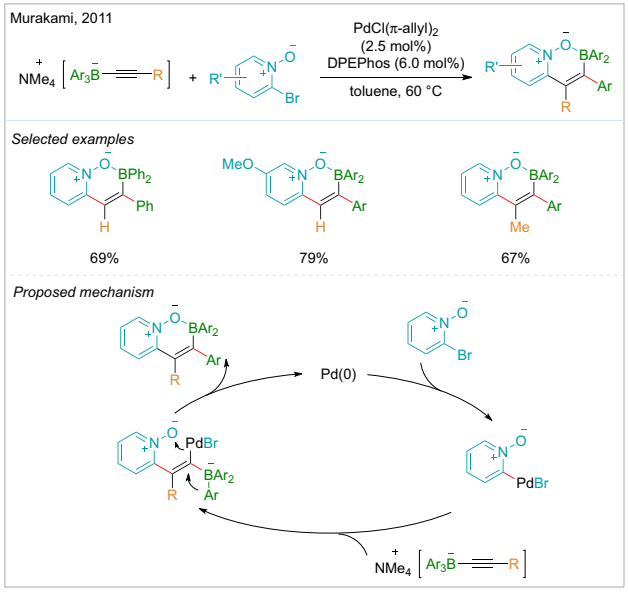
Scheme 20 Palladium-catalyzed reaction of alkynyltriarylborates with aryl halides.



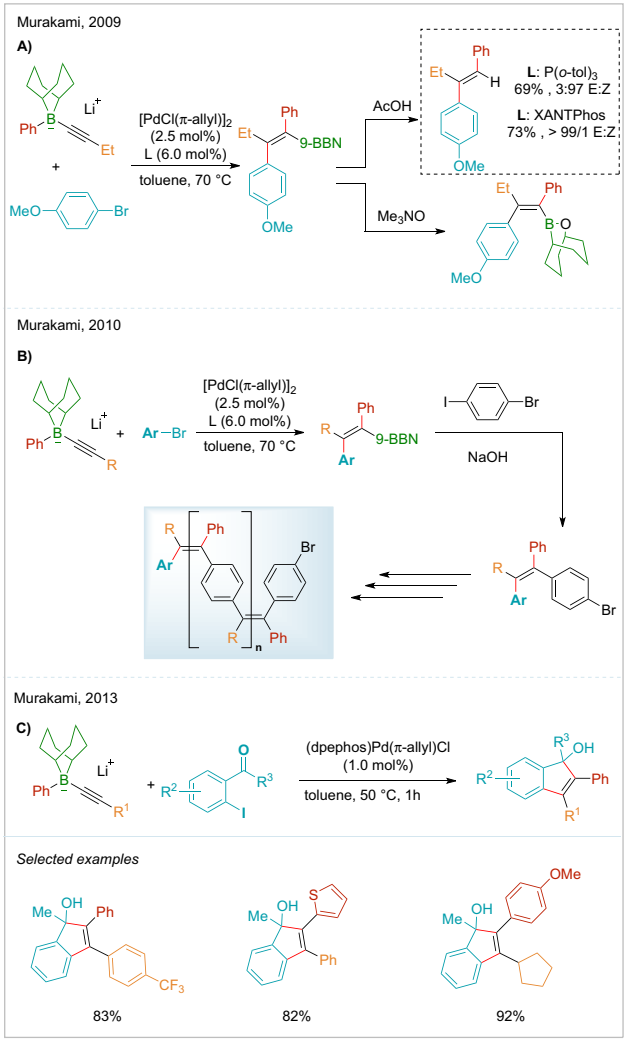
Scheme 21 Palladium-catalyzed rearrangement of ammonioalkynyltriarylborates.

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Scheme 22 Palladium-catalyzed reaction of azaaromatic halides with alkynyl(triaryl)borates.



Scheme 23 Palladium-catalyzed cross-coupling for 9-BBN-derived alkynylboronates via 1,2-migration process.

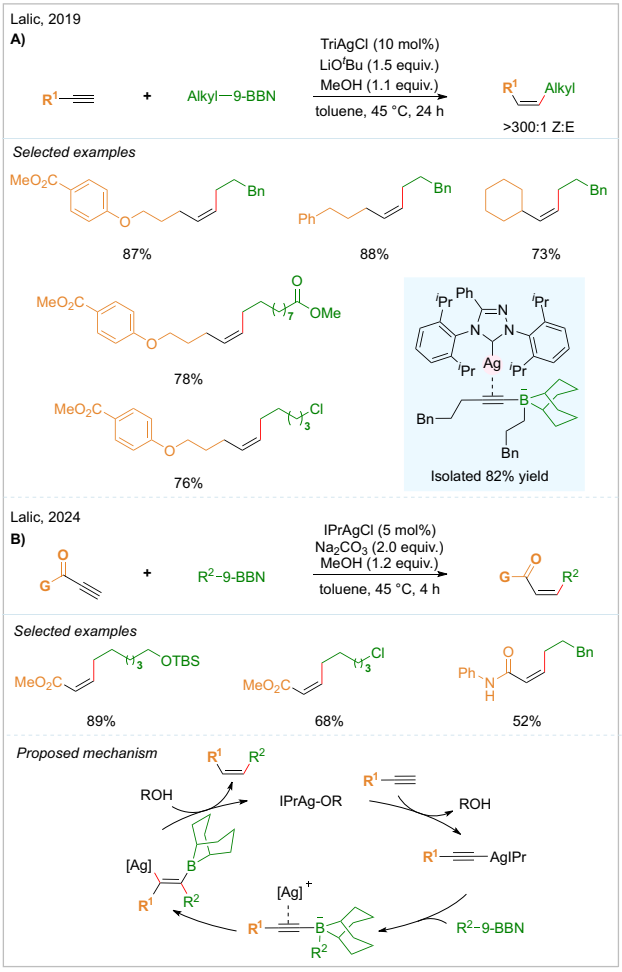
reaction. Specifically, with tri(*o*-tolyl)phosphine as a ligand, a selective 1,3-migration of the phenyl group from boron to palladium occurred, affording the (*Z*)-alkenylborane with high stereoselectivity (*E*/*Z*: 3/97). In contrast, when the steric bulk of monodentate phosphine ligands was increased, formation of the (*E*)-isomer was progressively favored; for instance, XANTPhos steered the reaction toward a 1,2-migration pathway, ultimately delivering the alkenylborane products with *E*/*Z* ratio >99:1. The resulting organoboron products could be stereospecifically oxidized with TMANO to furnish trisubstituted alkenyl borinic esters, a transformation that proceeds via migration of the 9–BBN bridgehead sp^3 carbon to oxygen. Importantly, the sequential palladium-catalyzed transformations could also be conducted in a one-pot fashion: after completion of the migration coupling, addition of a base such as NaOH or Cs_2CO_3 triggered a second coupling event, providing oligo(arylenevinylene)s that feature tetrasubstituted vinylene units (**Scheme 23B**).[39] The catalytic manifold was also amenable to *o*-iodophenyl ketones as electrophilic partners, which underwent a regioselective annulation process to furnish substituted indenols (**Scheme 23C**).[40]

In addition to the palladium-catalyzed migration reaction described above, silver catalysts can also promote the 1,2-migration of alkynyl boronate complexes. In 2019, the Lalic group reported a silver-catalyzed hydroalkylation of terminal alkynes with alkylboranes, which enables the efficient and highly selective synthesis of *Z*-disubstituted alkenes (*Z*/*E*: >300/1) (**Scheme 24A**).[41] The success of this method relies on a 1,2-metalate rearrangement of the silver boronate intermediate, which is the key step governing the stereochemical outcome. The reaction proceeds under mild conditions and exhibits a broad substrate scope, tolerating a wide range of functional groups, including alcohols, aldehydes, ketones, esters, nitriles, halides, and heterocycles. In their further mechanistic study,[42] the authors isolated and characterized the key silver alkynyl boronate complex, confirming its structure by X-ray single-crystal diffraction. DFT calculations validated the transition state of the 1,2-migration, while kinetic experiments along with KIE measurements were performed to elucidate the reaction pathway, indicating that the 1,2-migration is the rate-determining step. In 2024, the same strategy was applied by the authors to access *Z*-Michael acceptors from conjugated alkynes (**Scheme 24B**).[43] Subsequently, they proposed the catalytic cycle: the silver acetylide reversibly forms an alkynylboronate complex with the alkylborane, which then undergoes a silver-promoted 1,2-migration to generate a tetrasubstituted alkenylboron intermediate, ultimately affording the *Z*-alkene through protodeboration and protodeargentation.

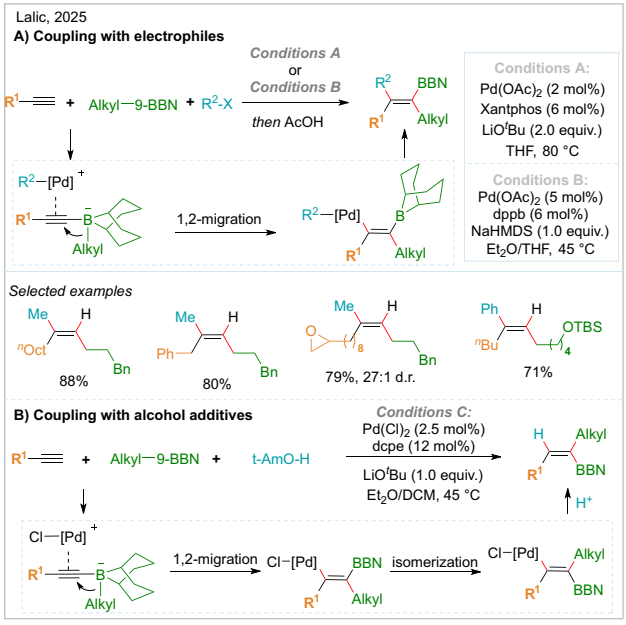
In 2025, Lalic and coworkers also developed a palladium-catalyzed coupling reaction of terminal alkynes with alkylboranes and organohalides, enabling the diastereodivergent and highly regioselective synthesis of tri- and tetrasubstituted alkenes (**Scheme 25A**).[44] The reaction involves a key alkynylboronate

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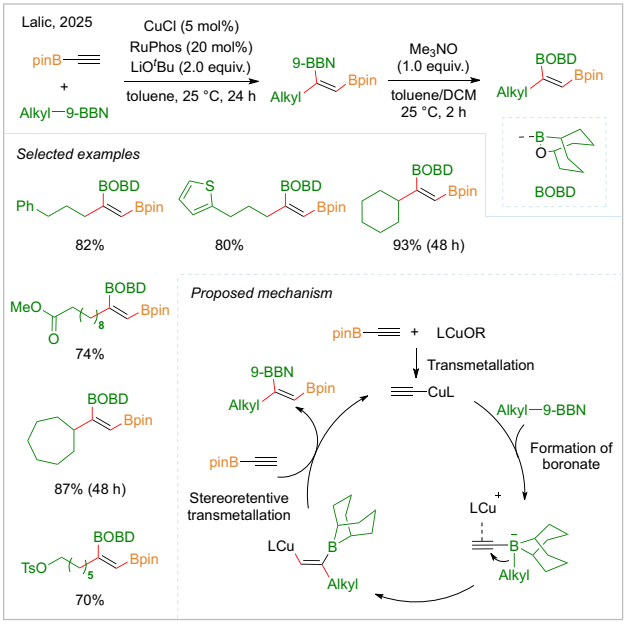
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Scheme 24 Palladium-catalyzed trifunctionalization of terminal alkynes for the synthesis of highly substituted alkenes.



Scheme 25 Palladium-catalyzed trifunctionalization of terminal alkynes for the synthesis of highly substituted alkenes.



Scheme 26 Copper-catalyzed C(sp^2) homologation of alkylboranes.

complex, which undergoes a cationic palladium-mediated 1,2-metallate shift. As a result, different isomers of highly substituted alkenes can be prepared simply by changing the sequence in which the coupling partners are introduced. Notably, when a proton source is used in place of the organohalide, complementary *E*-selectivity is observed in the formation of trisubstituted alkenes, attributed to a sterically driven isomerization of the alkenyl-palladium intermediate (**Scheme 25B**). Compared to Murakami's two-component system, Lalic's three-component approach is more convergent and modular, which could provide a practical route to structurally diverse, highly substituted alkenes and their isomers.

Lalic and coworkers have also reported a related copper-catalyzed C(sp^2)-insertion homologation of alkylboranes with alkynyl boronic esters, enabling efficient, highly regioselective, and diastereoselective access to a range of trisubstituted diborylalkenes (**Scheme 26**).[45] Mechanistic studies support the formation of a boronate complex, which could undergo a copper-induced 1,2-metallate shift to deliver a heterobimetallic alkene intermediate. Subsequently, an unusual transmetalation between the alkenyl copper species and the alkynyl boronic ester installs the second boryl group and regenerates the active catalyst. Experimental mechanistic validation by the authors confirmed this pathway, affording the diborylalkene product in 87% yield. More importantly, the resulting diboryl alkenes could serve as versatile synthetic handles, enabling convenient access to alkenylboronates and, following further functionalization, to a variety of trisubstituted alkenes.

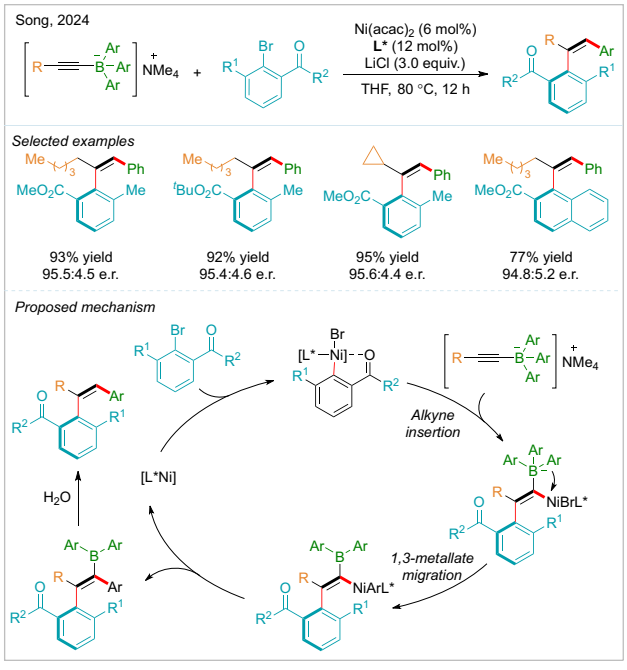
Axially chiral molecules, including alkenes and biaryls, are important structural motifs in natural products, chiral ligands,

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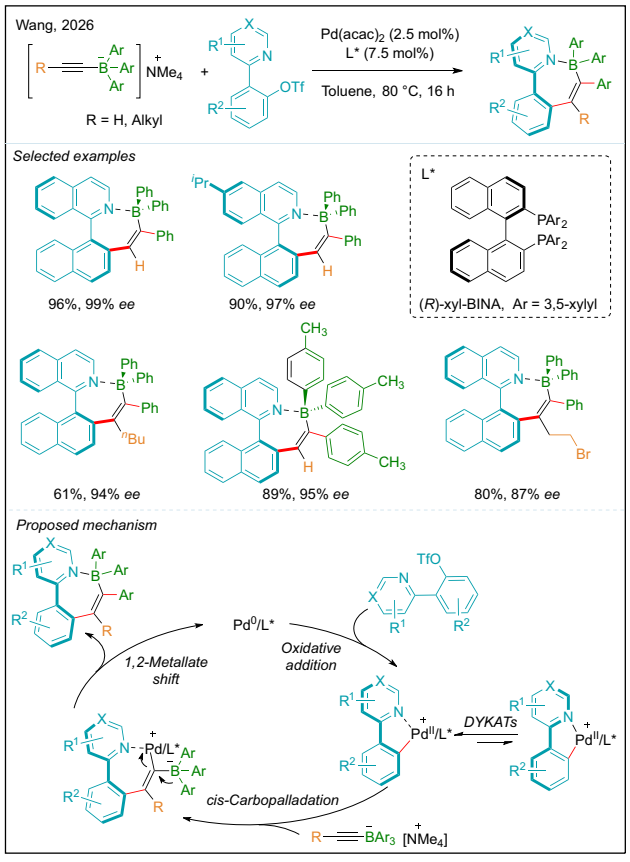
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and catalysis,[46] but their efficient asymmetric synthesis has long-faced challenges. Among the various strategies developed, transition-metal-catalyzed migratory reactions of alkynylboronates have emerged as a powerful and versatile platform. In 2023, Song and coworkers reported a nickel-catalyzed atroposelective synthesis of axially chiral alkenes from alkynylboronates and aryl halides (**Scheme 27**).[47] With a chiral pyridine-BOX ligand and $Ni(acac)_2$, a range of aryl bromides and alkynylboronates couple to give substituted styrenes and naphthyl alkenes in good yields and high enantiomeric ratios (94:6–96:4 e.r.), with broad functional group tolerance. Mechanistic studies indicate that the enantioselectivity arises from a *syn*-addition of the aryl-Ni intermediate to the alkyne, followed by a subsequent 1,3-phenyl shift.

In 2026, Wang and coworkers reported a palladium-catalyzed atroposelective cyclization of racemic *N*-heterobiaryl triflates with alkynylboronates, providing access to axially chiral seven-membered 1,2-BN-bridged biaryls (**Scheme 28**).[48] The method operates under mild conditions and delivers the desired products in up to 99% yield with excellent enantioselectivities (up to 99% ee), while accommodating a broad range of aryl- and alkyl-substituted alkynylboronates and various functional groups. The transformation proceeds through a palladium-catalyzed dynamic kinetic asymmetric transformation (DyKAT), followed by *cis*-carbopalladation of the alkyne and 1,2-migration of the alkynylboronate. The resulting axially chiral BN-heterocycles display promising circularly polarized luminescence with dissymmetry factors up to 5.7×10^{-3}, pointing to their potential as chiral optoelectronic materials. The synthetic value of this protocol is further demonstrated by gram-scale synthesis and diverse derivatizations of the chiral BN-embedded products, all of which proceed with complete retention of enantiopurity.



Scheme 27 Ni-catalyzed assembly of axially chiral alkenes from alkynyl tetracoordinate borons via 1,3-metallate shift.



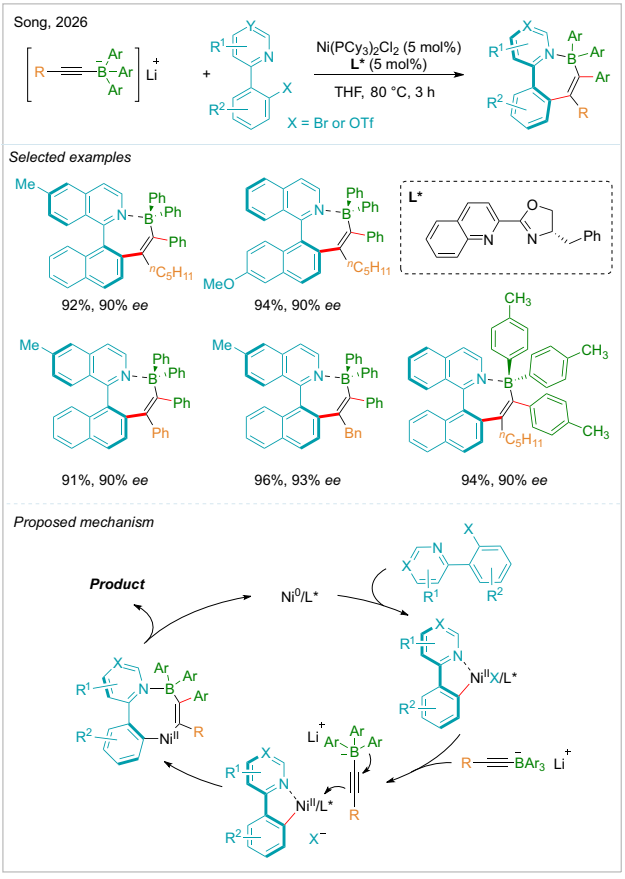
Scheme 28 Palladium-catalyzed cyclization of *N*-heterobiaryl triflates with alkynylboronates.

Subsequently, Song and coworkers reported a nickel-catalyzed enantioselective cascade reaction of *N*-heterobiaryl bromides or triflates with alkynylboronates, which also enabled the synthesis of a series of axially chiral seven-membered 1,2-BN-bridged biaryls (**Scheme 29**).[49] Under the optimized conditions, the products were also obtained in high yields with excellent enantioselectivities (up to 98% yield, 98% ee). Unlike the aforementioned palladium-catalyzed system, this reaction was proposed to proceed through a distinct mechanism. Oxidative addition of the *N*-heterobiaryl electrophile to Ni(0) generates an Ar-Ni(II) species, which acts as an electrophile and directly induces aryl migration from the boron center of the alkynylboronate. This pathway avoids the *cis*-carbometalation of the alkyne followed by 1,2-migration proposed for the palladium-catalyzed reaction. A series of control experiments, including studies of the nitrogen-directing group, radical-trapping experiments, time-course monitoring, and nonlinear-effect analysis, were also performed by the authors to verify the mechanism.

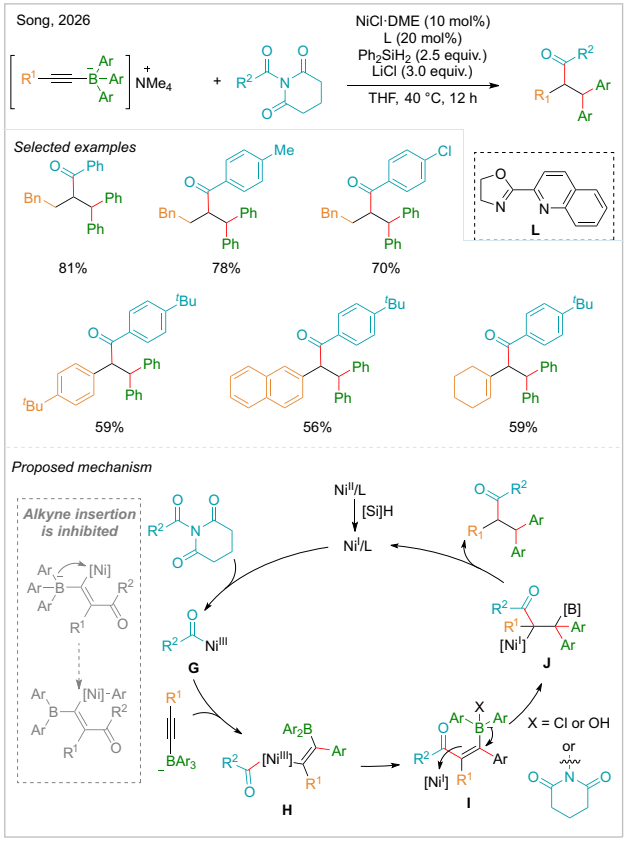
Moreover, Song and coworkers recently reported a nickel-catalyzed coupling reaction of alkynyl borates with *N*-acyl glutarimides (**Scheme 30**).[50] This transformation proceeds through a cascade of two successive 1,2-migrations, which collectively enable a trifunctionalization of the alkynes. Mechanistic studies ruled out the involvement of a nickel hydride species and a direct *cis*-addition pathway. Instead, the proposed catalytic cycle begins

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Scheme 29 Nickel-catalyzed cyclization of *N*-heterobiaryl electrophiles with alkynylboronates.



Scheme 30 Nickel-catalyzed boron-mediated trifunctionalization of alkynes.

with the reduction of Ni(II) to Ni(I) by Ph_2SiH_2. Then, oxidative addition of the *N*-acyl glutarimide to Ni(I) generates the Ni(III) intermediate **G**, which induces the 1,2-migration of alkynylboronates to afford **H**. Reductive elimination of **H** releases the vinylboron intermediate **I** and regenerates Ni(I). In the presence of Cl^-, OH^-, or glutarimide anions, **I** is converted into a tetracoordinate alkenylboron intermediate. A second nickel-mediated 1,2-migration then gives **J**, which undergoes hydrolysis to furnish the desired product. The success of this transformation relies on the preferential hydrolysis of **J** over competing β-boron elimination, which would otherwise generate an alkene byproduct.

3 Conclusion

In summary, the 1,2- and 1,3-migrations of alkynylboronates have provided a valuable strategy for the construction of multisubstituted alkenes and complex molecules. In these transformations, the reaction proceeds through an electrophile-induced migration of an aryl, alkyl, or alkenyl group from the boron center to the alkyne moiety, which could enable the formation of various C–C and C–X bonds (X = O, S, Se, P, etc.) under mild conditions. Over the past decades, the scope of this transformation has expanded considerably from the classical electrophile-induced 1,2-migration, pioneered by Binger, Pelter, Brown, Utimoto, Hooz, and others, to transition-metal-catalyzed processes, allowing greater control over the migratory selectivity and stereoselectivity. Murakami, Aggarwal, Song, Lalic, and Wang have made notable contributions to the field, including palladium-catalyzed migration reactions, metal-catalyzed asymmetric couplings, and cascade reactions.

Although research on electrophile-induced 1,2-migrations of alkynyl boronate complexes has progressed rapidly in recent years, the field remains highly dynamic and continues to expand. Future developments could extend the migration chemistry of alkynylboronates to as-yet unexplored asymmetric organocatalytic transformations. Song and coworkers reported the route in 2026 to access allylamines from alkynylboronates, amines, and aldehydes, providing a valuable foundation for subsequent asymmetric catalysis.[25] Beyond this, the development of new electrophilic triggers for diverse alkynylboronate complexes should further broaden the synthetic scope of the methodology. Equally worthwhile is the design of more efficient chiral catalytic systems that enable highly selective construction of quaternary carbon centers and remote stereogenic centers. Finally, it is remarkable that the seminal work on alkynylboronate 1,2-migrations from the 1960s has inspired a wealth of new methodologies with broad-ranging applications in modern synthetic chemistry.

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Statements and Additional Information

Conflict of Interest The authors declare that they have no conflict of interest.

Contributors' Statement Fengya He: Writing - original draft. Dongyang Zhang: Conceptualization, Investigation, Methodology, Project administration, Supervision, Writing - original draft, Writing - review & editing. Wei Nan: Formal analysis, Validation, Writing - review & editing. Hui Wang: Conceptualization, Funding acquisition, Investigation, Methodology, Project administration, Resources, Supervision, Writing - original draft, Writing - review & editing.

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