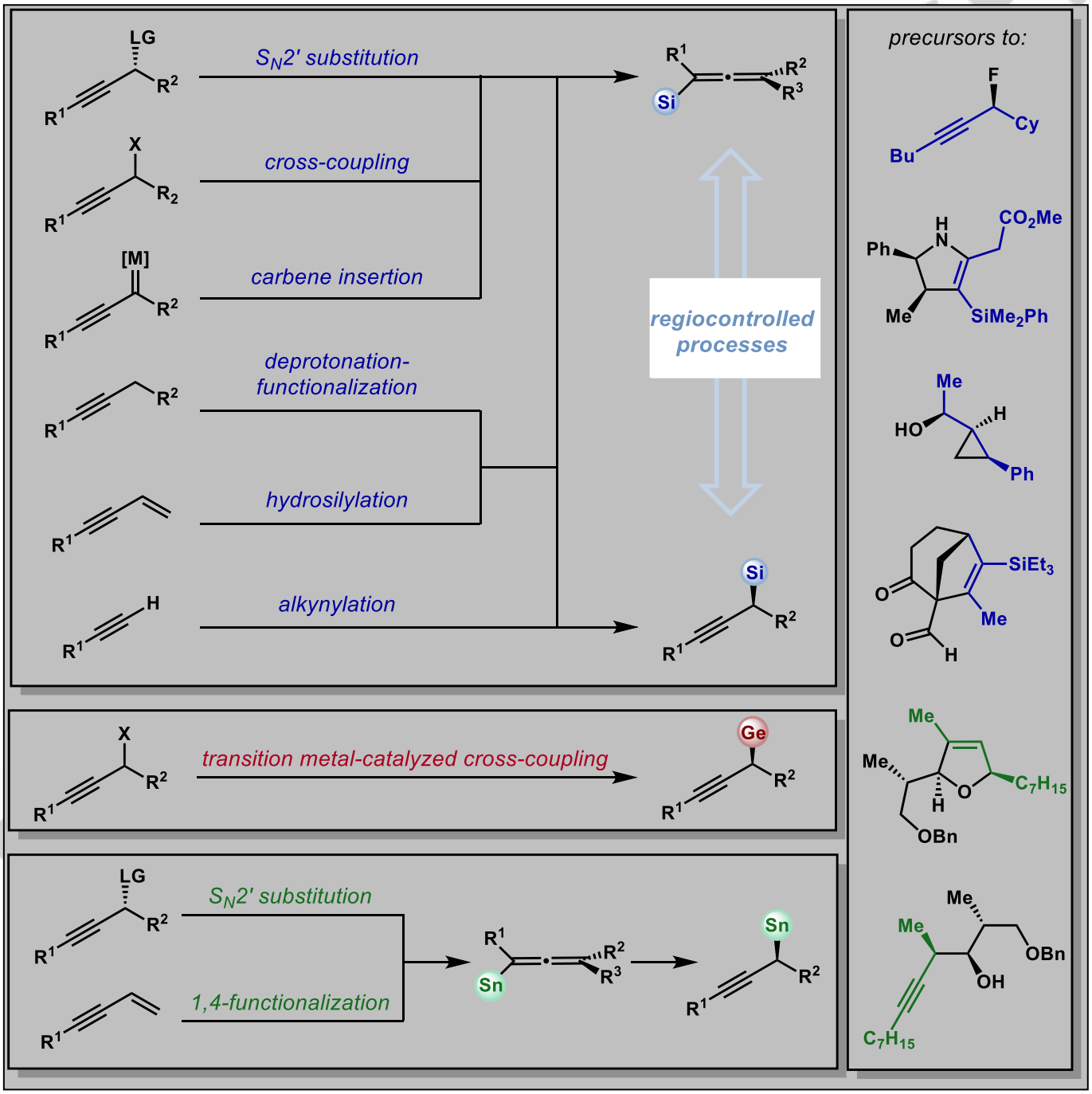
# Asymmetric Synthesis of Propargylic and Allenic Silanes, Germanes and Stannanes

Hai Chang,[#[a]] Ruihan Wang,[#[a]] and Yi-Ming Wang*[[a]]

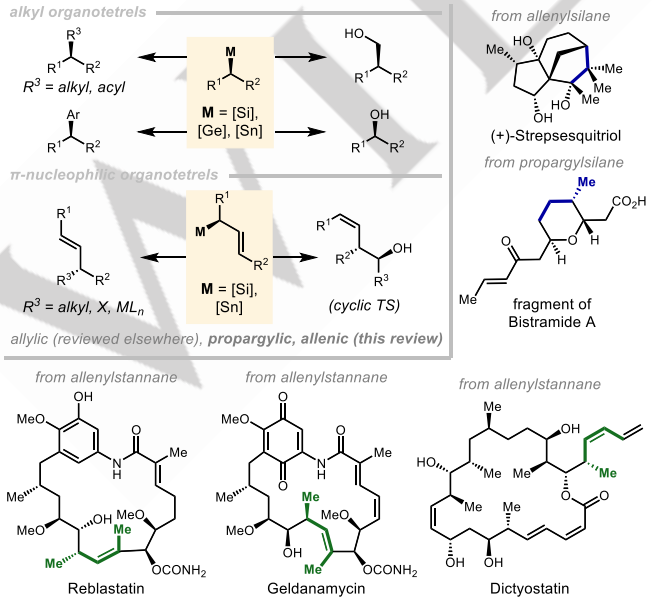


[a] H. Chang, R. Wang, Dr. Y.-M. Wang
Department of Chemistry
University of Pittsburgh
Pittsburgh, Pennsylvania 15260, United States
E-mail: ym.wang@pitt.edu
[#] H.C. and R.W. contributed equally to this manuscript.

**Abstract:** Enantioenriched propargylic and allenic derivatives of silicon, germanium, and tin are versatile building blocks for stereoselective synthesis. Consequently, considerable efforts toward their efficient and selective synthesis have been made, both through classical approaches for chirality transfer and catalytic enantioselective strategies that employ the latest developments in transition metal catalysis, organocatalysis, and photoredox catalysis. In this review, we survey broadly applicable synthetic strategies and discuss the scope and mechanistic details for specific protocols that afford these compounds in a regio- and stereoselective manner.

## 1. Introduction

As congeners of carbon in Group 14 of the Periodic Table, the heavier tetrels (Si, Ge, Sn and Pb) form organometallic compounds that played important historic roles and continue to see important applications in chemical industry and academic research. Due to the moderate electropositivity of these elements (1.9 to 2.0 on the Pauling electronegativity scale) and their electron-precise bonding (leaving behind no vacant orbitals or lone pairs), organotetrel compounds are generally characterized by stability to air and water and compatibility with a range of reagents and catalysts.[1] Consequently, they serve as valuable reagents in a variety of synthetic protocols. In particular, organosilicon and organotin compounds have become well-established reagents in C–C bond formation reactions, including metal-catalyzed cross-coupling, olefination, and carbonyl/imine addition reactions.



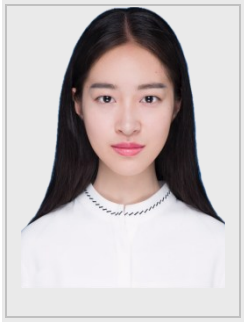

**Scheme 1.** Synthetic applications of enantioenriched organotetrel compounds.

Organic synthesis using these organometallic reagents in enantioenriched form has allowed for the construction of functionally complex molecules with precise control of stereochemistry.[2] A variety of transformations have enabled the conversion of enantioenriched silanes and stannanes into products containing new C–C or C–X bonds in a stereospecific manner (Scheme 1).[3] Germanes, including their enantioenriched derivatives, are far less explored compared to silanes and stannanes but have recently received increased attention due to their potential to serve as lower-toxicity alternatives to stannanes.[4] Among these organometallic derivatives, π-nucleophilic reagents that typically react with $S_E2'$ selectivity stand out as a particularly versatile family of reagents.[5] In enantioenriched form, these reagents, which include allylic, propargylic, and allenic organotetrels, have been used as chiral building blocks for the enantioselective synthesis of natural products and other complex bioactive compounds, due to their utility in forging contiguous stereocenters with nearby sites of unsaturation.[6]

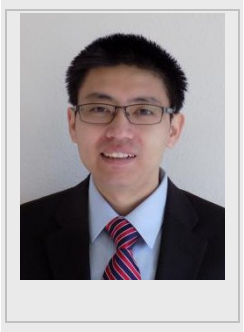
While the synthesis of enantioenriched allylmetal reagents, including allylsilanes and allylstannanes, is well-documented,[7] the synthesis of enantioenriched allenyl- and propargylmetal derivatives of Si, Ge, Sn has yet to be surveyed in a systematic manner. We felt that it was worthwhile to discuss the synthesis of these reagents collectively herein, as propargyl- and allenylmetal reagents are regioisomeric counterparts of one another and are often prepared from the same or closely related starting materials.[8] Consequently, the effective control of propargyl vs. allenyl regioselectivity is a crucial feature of useful protocols for their synthesis, in addition to control of stereochemistry.[8a–b] Although general methods for the synthesis of enantioenriched propargyl and allenyl derivatives of Si, Ge, and Sn are highly sought after due to their aforementioned synthetic utility,[9] only a small collection of strategies have been successfully deployed for the enantioselective assembly of these molecular architectures.

In this review, we summarize these strategies and provide a critical examination of existing protocols for the synthesis of these closely related classes of compounds. We first provide an overview of the broad approaches and major strategies that have been employed for stereoinduction, followed by details of reported protocols, including a delineation of their scope and notable features, organized into sections by specific types of transformations.

Hai Chang obtained Bachelor's degree from Nankai University in 2022, where he worked under the supervision of Prof. Gong Chen. He entered Ph.D. program at University of Pittsburgh and conducted research under supervision of Prof. Yiming Wang. His main research area is focused on catalytic C($sp^3$)–H functionalization and organotetrel chemistry.



Ruihan Wang obtained her Bachelor's degree at China Pharmaceutical University in 2019, where she studied pharmacy and conducted research under the supervision of Prof. Bo Zhang. In 2019, she entered the Ph.D. program at the University of Pittsburgh and conducted research under the supervision of Prof. Yiming Wang. Her main research area is focused on the development of new methodologies for catalytic C($sp^3$)–H functionalization.



Yiming Wang obtained an AB/AM degree in chemistry & physics and mathematics from Harvard University in 2008 after conducting research in the group of Professor Andrew Myers. In 2013, he obtained his PhD degree at the University of California, Berkeley, where he conducted research under the supervision of Professor Dean Toste. In the same year he conducted postdoctoral research in the laboratory of Professor Stephen Buchwald at the Massachusetts Institute of Technology as a National Institutes of Health Postdoctoral Fellow. He joined the Department of Chemistry at the University of Pittsburgh in the Fall of 2017 and is currently Associate Professor.

## 2. Overview of strategies for stereoinduction

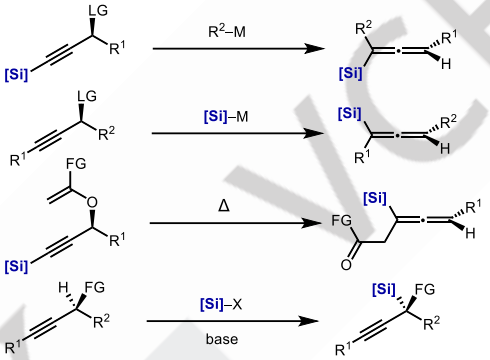
Enantioenriched organosilanes constitute the major class of chiral organotetrel compounds employed in stereoselective synthesis. Accordingly, we provide an overview of stereoinduction strategies for installing tetrels on the alkyne and allene moieties, using organosilanes as the basis for discussion.[10]

### 2.1. Chirality transfer

A common approach for the preparation of enantioenriched allenylsilanes employs alkynes bearing a stereodefined leaving group at the propargylic position in stereospecific $S_N2'$ process. In this type of process, an organometallic reagent attacks the more distal carbon of the alkyne to displace the leaving group and generate an allene bearing a new axis of chirality, through which high levels of chirality transfer with 1,3-*anti*-stereospecificity can be achieved. In this fashion, the silyl group can either arise from a preexisting substituent on the alkyne substrate or be introduced as the attacking nucleophile using an external silylmetal reagent. Such a process may take place in a single concerted $S_N2'$ transition state or take place in a multistep fashion through one or more organometallic intermediates, aided by a transition metal catalyst (a formal $S_N2'$ substitution). In a similar manner, central-to-axial chirality transfer in the Claisen rearrangement of substituted propargyl vinyl ethers leads to the formation of functionalized allenylsilanes with very high levels of stereospecificity.

The synthesis of enantioenriched propargylsilanes from enantioenriched alkynes is uncommon, as reported examples of nucleophilic substitution of alkynes carrying propargylic leaving groups by silylmetal reagents have all strongly favored substitution with $S_N2'$ regioselectivity over $S_N2$. The same is true for most instances of transition metal-catalyzed substitution reactions using carbon nucleophiles as coupling partners. Under limited circumstances (for α,β-epoxyalkynes specifically), enantioenriched α-chiral alkynes have been employed as starting materials. These substrates are reported to undergo metalation and subsequent electrophilic silylation at the propargylic position with retention of configuration (Scheme 2).

Although the abovementioned methods are effective for the enantioselective synthesis of allenylsilanes, the requirement for alkyne starting materials of high enantiopurity can render structurally complex substrates less practically accessible, thereby limiting the synthetic utility of a chirality transfer approach. Furthermore, the access to propargylsilanes is severely limited. Synthetic methods using achiral or racemic starting materials have enabled access to a broader range of products.

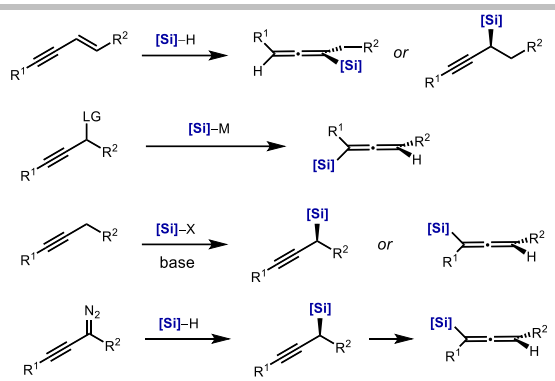



**Scheme 2.** Asymmetric synthesis from chiral starting materials.

### 2.2. Enantioselective silylation

The introduction of a silyl group in an enantioselective manner is a direct and increasingly important approach for the asymmetric synthesis of propargyl and allenylsilanes. In this approach, the stereocenter is introduced to a prochiral or chiral but racemic alkyne through the attack of a nucleophilic or electrophilic silylating reagent. Four general methods under this scenario are outlined below (Scheme 3):

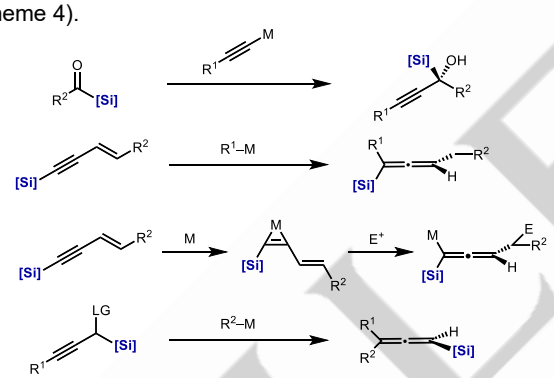
1. Enantioselective hydrosilylation of enynes. In this approach, achiral enyne substrates undergo enantioselective hydrosilylation enabled by transition metal catalysts and chiral ligands. Hydrosilylation of the double bond yields enantioenriched propargylsilane products, while hydrosilylation across the 1,3-enyne moiety affords enantioenriched allenylsilane products.
2. Catalytic propargylic silylation. Enabled by transition metal catalysts and chiral ligands, racemic alkynes carrying a leaving group at the α position can be used as substrates to undergo stereoconvergent cross-coupling with nucleophilic silylmetal reagents, giving enantioenriched allenylsilane derivatives.
3. Enantioselective deprotonation-silylation. Internal alkynes with propargylic protons can undergo deprotonation by strong organolithium base in the presence of stoichiometric chiral promoter or through transition metal catalysis in the presence of amine base, generating nucleophilic intermediates which react with electrophilic silyl sources, resulting in the formation of enantioenriched propargylsilane or allenylsilane products.
4. Metal catalyzed Si–H insertion. Starting with a metal carbene precursor (e.g., a tosylhydrazone-derived diazoalkane), direct insertion into the Si–H bond of a silane reagent in the presence of a chiral ligand affords enantioenriched propargylsilane products, which could subsequently be converted stereospecifically into allenylsilanes under metal catalysis.



**Scheme 3.** Enantioselective silylation from achiral or racemic starting materials.

### 2.3. Enantioselective alkyne functionalization

In addition to installing silyl group on the alkyne substrates in an asymmetric fashion, enantioenriched organosilanes can also be synthesized by forging a new C–C bond to the achiral or racemic alkynes bearing a pre-installed silyl group. Methods falling under this category include 1) nucleophilic addition of a terminal alkyne to an acylsilane via a metal acetylide intermediate, either in the presence of a chiral ligand or chiral auxiliary, 2) asymmetric 1,4-functionalization of 1,3-enynes catalyzed by transition metals in the presence of a chiral ligand, 3) reductive metalation by low-valent metal followed by electrophilic trapping using a reagent carrying a chiral auxiliary, and 4) enantioconvergent cross-coupling of α-silylated propargyl halides and organometallic reagents proceeding through radical intermediates in the presence of a chiral transition metal catalyst (Scheme 4).



**Scheme 4.** Enantioselective synthesis from achiral or racemic silicon-containing starting materials.

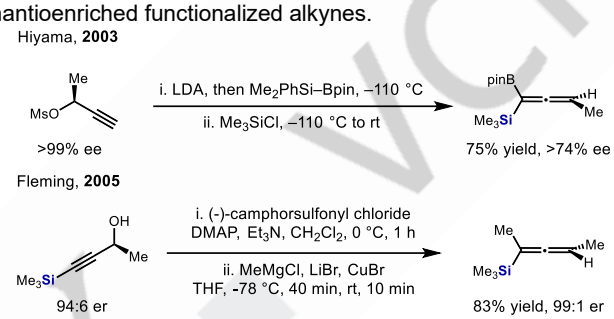
## 3. Propargylic substitution

### 3.1. $S_N2'$ and $S_N1'$ substitution

Asymmetric $S_N2'$ substitution of alkynes bearing a stereodefined leaving group at the propargylic position is the most straightforward and mechanistically simple approach for the preparation of allenyl tetrels in their enantioenriched forms. This approach relies on chirality transfer, which results from the stereoelectronic preference for orienting the attacking nucleophile and leaving group in a 1,3-*anti* configuration in the transition state. On the other hand, for reactions proceeding through an $S_N1'$ mechanism, in which leaving group departure generates a stabilized carbocation, racemic substrates may potentially give an enantioconvergent outcome.

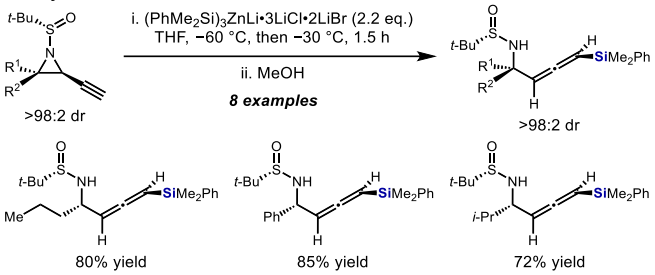
In 2003, Hiyama and coworkers reported a synthesis of 1-boryl-1-silylallenes from terminal propargylic mesylates or acetates using a transmetalation/silyl migration strategy. In the reported protocol, treatment of the enantioenriched terminal alkyne with BuLi is used to generate a lithium acetylide. Upon addition of $Me_2PhSiBpin$, the alkynylboronate species is formed, which in turn undergoes boron-to-carbon migration with $S_N2'$ displacement of the leaving group to give the allene product with moderate levels of stereospecificity.[11]

Subsequently, the Fleming group reported an enantioselective synthesis of allenylsilane through an $S_N2'$ process employing a methyl Grignard reagent (Scheme 5).[12] They began with moderately enantioenriched propargyl alcohol substrate, prepared by asymmetric alkynone reduction with Alpine-Borane, and converted it into a camphorsulfonate for further upgrading of stereoisomeric purity. A single diastereomer (>99.5:0.5 dr) of which was obtained after three rounds of recrystallizations. Then treatment with methyl Grignard reagent afforded the allenylsilane product with high enantiomeric purity (99:1 er). The authors also performed derivatizations of the allenylsilane compound through electrophilic substitution reactions, generating several enantioenriched functionalized alkynes.



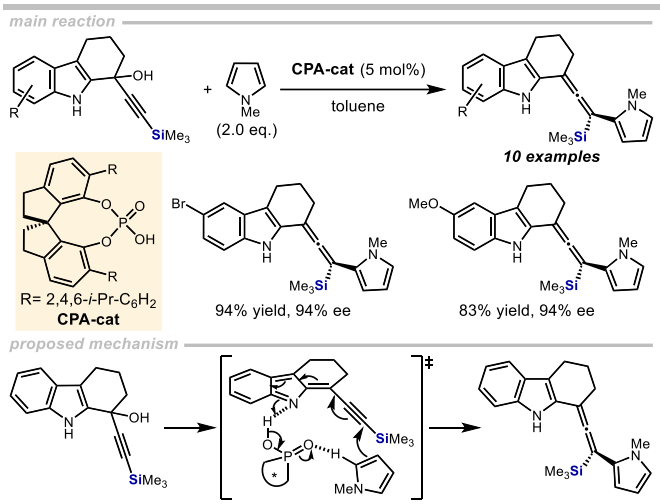
**Scheme 5.** Synthesis of enantioenriched allenylsilane by $S_N2'$.

More recently, Chemla, Ferreira, Pérez-Luna, and co-workers developed a nucleophilic ring-opening of *N-tert*-butanesulfinyl ethynylaziridines by lithium tris(phenyldimethylsilyl)zincate (Scheme 6).[13] The reaction was demonstrated to proceed through an *anti*-$S_N2'$ pathway in a stereoselective and stereospecific fashion. Diverse 4-amino-1-allenylsilanes were obtained in good yields (up to 85%) and high levels of enantioselectivity (>98:2 dr). The *N-tert*-butanesulfinyl group was shown to be readily removed under acidic conditions to afford amine hydrochloride salts. Earlier, the same group reported that this strategy could be applied to the corresponding epoxides for the synthesis of the analogous stereodefined 4-hydroxy-1-allenylsilanes.[14]



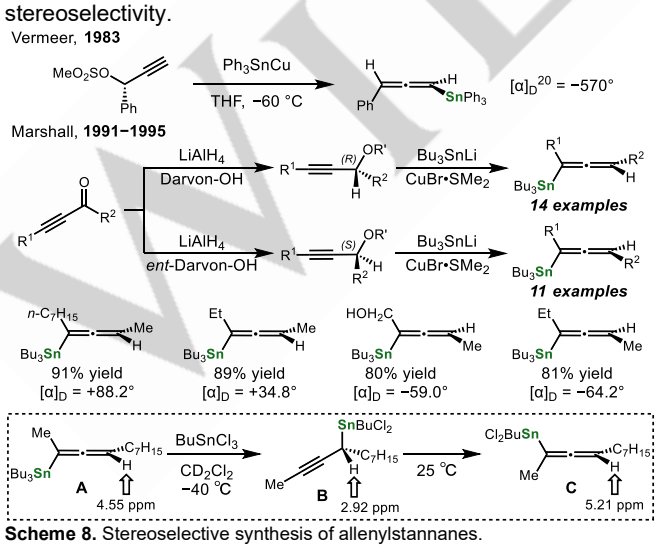
**Scheme 6.** Stereoselective access to 4-amino-1-allenylsilanes.

In a variant of this strategy, Terada demonstrated a stereoconvergent substitution reaction proceeding through an $S_N1'$ mechanism catalyzed by a chiral phosphoric acid, which converted racemic indolylmethanols bearing tetrahydrocarbazoles into enantioenriched allenylsilanes with *N*-methyl-2-pyrrolyl substituents (Scheme 7).[15] In this reaction, the substrate undergoes an exclusive 1,8-addition across the extended conjugated system in good yields (43–94%) and high enantioselectivities (up to 95% ee).




**Scheme 7.** Chiral Brønsted acid catalyzed enantioconvergent substitution of indolylalkynyl silanes with *N*-methylpyrrole.

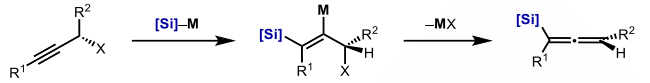
The $S_N2'$ reaction is also a common and conventional approach for the synthesis of enantioenriched allenylstannanes. In 1983, Vermeer and coworkers reported the use of a stannylcopper(I) reagent to convert a chiral acetylene into an allenylstannane compound in a stereospecific fashion.[16] In the 1990s, Marshall disclosed the use of chiral alkynes with a propargyl leaving group, which were prepared by stereoselective reduction of alkynones with the $LiAlH_4$–(*ent*-)Darvon alcohol complex, for the synthesis of enantioenriched allenylstannanes through stereospecific $S_N2'$ substitution using a stannyllithium reagent.[17] In the course of their investigations, the authors also uncovered a chlorostannane mediated interconversion of allenyl- and propargylstannanes in a $^1H$ NMR study. When allenylstannane **A** was treated with $BuSnCl_3$ at –40 °C, a signal at 2.92 ppm appeared with concomitant disappearance of allenic proton at 4.55 ppm, indicating the formation of an alkyne. The resulting propargylstannane species **B** remained stable in the mixture for 2 h at –40 °C. Upon warming to ambient temperature, a new allenic proton signal corresponding to stannane **C** appeared at 5.21 ppm and gradually intensified, while the propargyl proton signal diminished over a period of 5 h. The treatment of stannane **B** or **C** with carbaldehydes yielded enantioenriched alcohols, suggesting that this allene isomerization process is stereospecific (Scheme 8). In addition, the authors demonstrated the preparation of compound **A** on 8.90 mmol scale without significant loss in yield and stereoselectivity.




**Scheme 8.** Stereoselective synthesis of allenylstannanes.

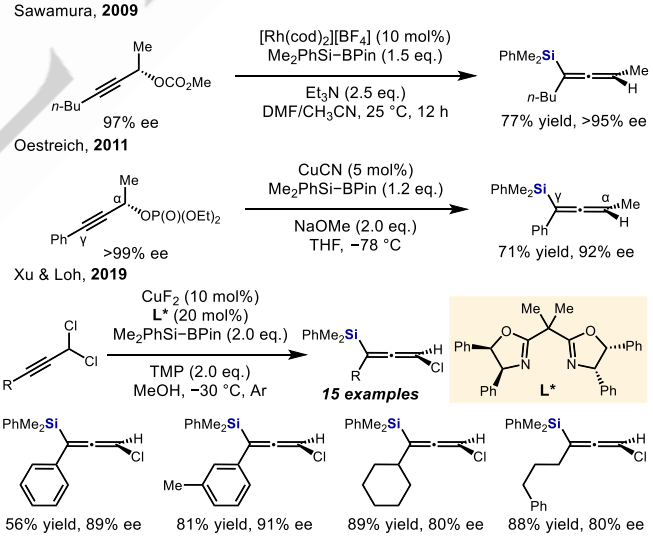
### 3.2. Metal-catalyzed formal $S_N2'$ by metalation–elimination

Functionalization of alkynes with metal–silane reagents is another common strategy for the synthesis of chiral allenylsilanes. The silylmetal reagents can be employed stoichiometrically or generated in situ through catalytic transmetalation between silylboronates and metal catalysts. As illustrated in Scheme 9, this process features a site-selective addition to the triple bond and subsequent β-O or Cl elimination.



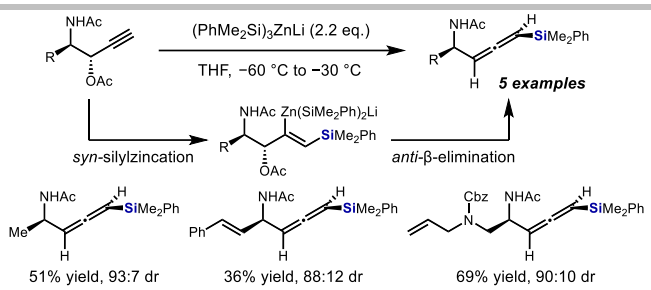

**Scheme 9.** Mechanism of silylation–elimination for the generation of enantioenriched allenylsilanes.

In 2009, Sawamura developed a Rh-catalyzed silylation of propargyl carbonates for the synthesis of racemic tri- and tetrasubstituted allenylsilanes.[18] This method tolerated various functionalized propargyl carbonates and allowed the reaction to proceed at ambient temperature. In this work, the authors demonstrated one example of asymmetric synthesis, in which an enantioenriched starting material was employed to generate axially chiral allenylsilane product in excellent enantioselectivity (>95% ee). Under a similar mechanistic paradigm, Oestreich reported the Cu(I)-catalyzed enantio- and regioselective propargylic substitution of α-chiral phosphates in 2011.[19] The initial Cu(I)-catalyzed Si–B bond activation generates a catalytic nucleophilic Si–Cu species, which undergoes propargylic substitution with $S_N2'$ selectivity. The α-branched propargylic systems were found to give superb γ-selectivity (γ:α > 99:1), and the enantioenriched propargyl phosphate substrate reacted with good central-to-axial chirality transfer (92% es). Building on this work, Xu and Loh reported a copper-catalyzed silylation of propargyl dichlorides.[20] These prochiral substrates react with moderate to good enantioselectivity to give trisubstituted allenylsilanes when a copper catalyst based on a chiral BOX ligand was used (Scheme 10).



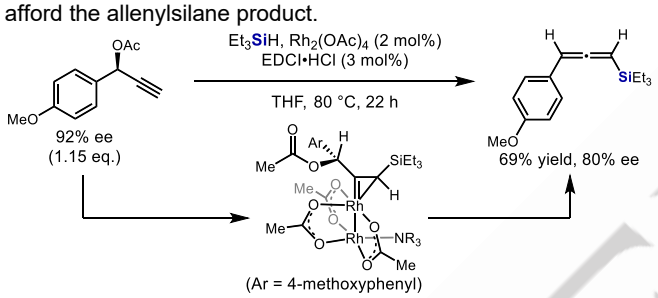

**Scheme 10.** Transition-metal-catalyzed enantioselective propargylic substitution with silylboronate.

In 2016, Pérez-Luna and co-workers reported a stereospecific and stereoselective synthesis of a range of functionalized allenylsilanes containing both an axially chiral allenylsilane, as well as an adjacent nitrogen-substituted stereocenter, through the diastereocontrolled reaction of stereodefined 4-aminopropargylic acetates with lithium tris(phenyldimethylsilyl)zincate (Scheme 11).[21] Mechanistic experiments suggested that this reaction is not likely to proceed through the *anti*-$S_N2'$ displacement of the acetate group. More likely, it involves a *syn*-silylzincation of the carbon–carbon triple bond followed by an *anti*-β-elimination.




**Scheme 11.** Stereospecific silylzincation-elimination.

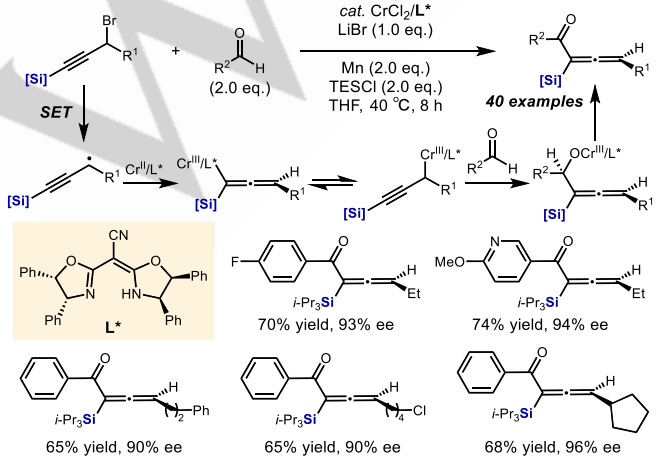
Hydrosilanes are an alternative class of silylating reagents used for the synthesis of allenylsilanes by metalation–elimination $S_N2'$ reaction. In a very recent report, Zhu and Sun demonstrated a new application of dirhodium(II) complexes, fine-tuned with amine ligands, in the catalytic transformation of aryl-substituted propargyl acetates (Scheme 12).[22] The authors performed a chirality transfer experiment using a chiral propargyl ester as the starting material, generating an enantioenriched allenylsilane product in 69% yield with slightly reduced enantiomerically purity (80% ee). Experimental results and DFT calculations suggested that the mechanistic pathway of this process involves a σ-alkenyl rhodium intermediate, which undergoes β-oxygen elimination to afford the allenylsilane product.




**Scheme 12.** Rh-catalyzed $S_N2'$-type silylation of propargyl esters.

### 3.3. Transition metal-catalyzed cross-coupling

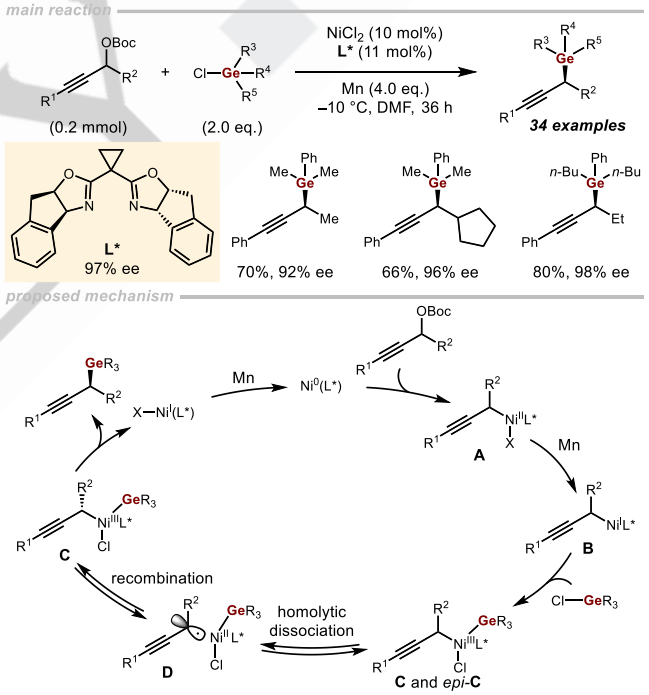
In 2023, the Wang group at the Westlake University reported an effective chromium-catalyzed stereoconvergent coupling of racemic propargyl halides bearing an alkynyl silyl group to access chiral α-keto allenylsilanes under mild conditions.[23] A wide array of aromatic aldehydes with electronically distinct substituents, as well as alkyl groups of propargyl bromides with diverse steric profiles were well tolerated, exhibiting good to moderate yields (up to 77%) and high enantioselectivities (96% ee). This process goes through an unprecedented Cr-catalyzed asymmetric reductive radical–polar crossover/Oppenauer oxidation sequence, which represents a novel strategy for the synthesis of enantioenriched ketonic allenes (Scheme 13).




**Scheme 13.** Cr-catalyzed asymmetric allenylsilane synthesis via sequential radical–polar crossover and Oppenauer oxidation.

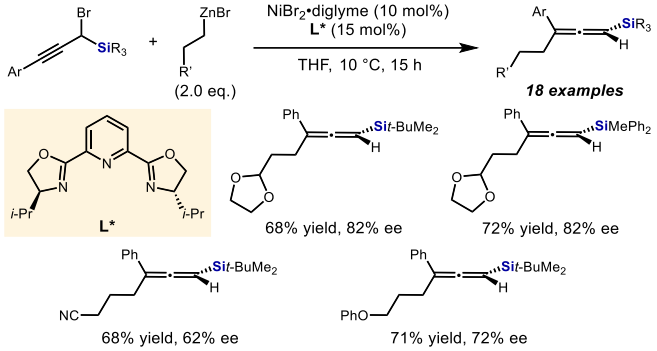
Germanium, considered as a bioisostere of carbon in medicinal chemistry, holds significant value for biological and pharmacological studies.[24] Enantioenriched organogermanes with diverse and complex structures have seen increased application potential, the access to which is highly appealing yet challenging and underexplored.[25] In 2024, Shu reported an enantioselective nickel-catalyzed reductive coupling of propargyl esters and tertiary chlorogermanes (Scheme 14, top).[26] A chiral BOX ligand was utilized to achieve excellent stereoinduction (up to 98% ee). A variety of electronically and structurally distinct alkynes were efficiently tolerated in this process.

Mechanistic studies revealed that Ni−C homolysis takes place to give propargylic radicals to allow for a stereoconvergent process. Notably, the source of this radical is a propargylic carbonate ester, an unusual and rarely reported radical precursor. The authors proposed a catalytic cycle, as shown at the bottom of Scheme 14, in which oxidative addition of Ni(0) to the carbonate ester is followed by reduction with Mn to generate a propargylnickel(I) species **B**. This intermediate undergoes a second oxidative addition with chlorogermane to form a Ni(III) complex **C**, which is subject to rapid epimerization at the propargylic position through the intermediacy of a propargylic radical. Selective reductive elimination of one particular stereoisomer of **C** leads to the desired propargylgermane product in highly enantioenriched form through an enantioconvergent process.




**Scheme 14.** Enantioconvergent and propargyl-selective cross-coupling of propargylesters with chlorogermanes by nickel catalysis.

A nickel-catalyzed cross coupling strategy also found application in the synthesis of enantioenriched allenylsilanes. In 2021, Oestreich developed an enantioconvergent and regioselective synthesis of allenylsilanes from racemic α-silylated propargyl bromides and primary alkylzinc reagents (Scheme 15).[27] In this process, the bulky silyl group installed at the α-position directed the cross coupling to occur exclusively at the γ-position of the alkyne moiety. A chiral PyBOX ligand contributed to the enantiocontrol at a moderate level (up to 82% ee). The yield and enantioselectivity remained consistent on a 1.0 mmol scale.



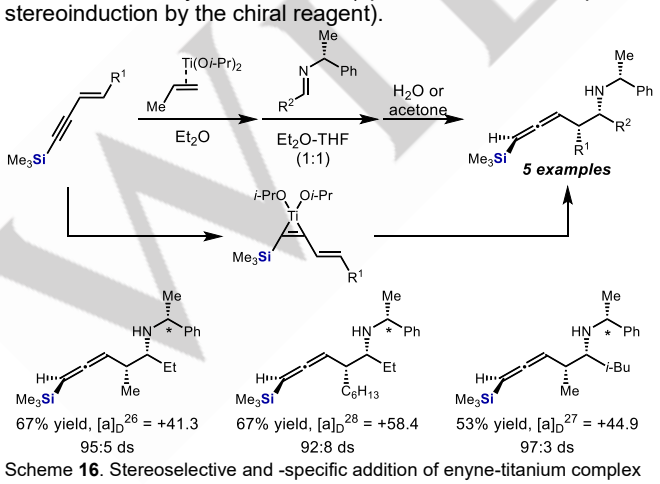

**Scheme 15.** Nickel-catalyzed C($sp^2$)−C($sp^3$) cross-coupling starting from racemic α-silylated propargyl bromides.

## 4. Enyne functionalization

1,3-Enyne derivatives are versatile and accessible precursors for the preparation of unsaturated products, including ones that carry additional readily functionalizable chemical handles at nearby positions.[8h][28] Earlier work on transition metal-free methods using chiral promoters, as well as more recent advances in asymmetric transition metal catalysis, have made them valuable substrates for enantioselective 1,2- and 1,4-functionalization reactions, allowing them to be employed in a number of general protocols for the synthesis of enantioenriched allenyl and propargyl tetrels.

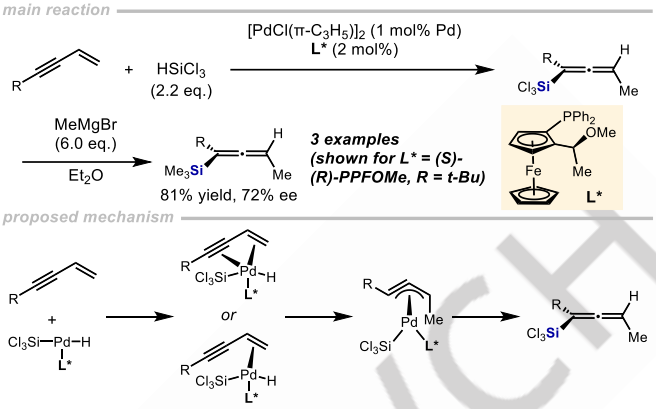
### 4.1. Transition metal-catalyzed hydrofunctionalization

In an early report, Sato described a stereoselective and -specific addition of nucleophilic enyne−titanium complexes to chiral imines, generating enantioenriched allenylsilanes with three consecutive stereocenters (Scheme 16).[29] In this approach, (*Z*)-enynes with a TMS group pre-installed at the alkynyl position were treated with ($\eta^2$-propene)Ti(O-*i*-Pr)$_2$ to generate the enyne−titanium complex, as evidenced by protonolysis and deuteriolysis experiments. The addition to imines proceeded at the remote olefinic carbon to give the β-aminoallenylsilane with excellent control of the relative stereochemistry of the allene stereoaxis and α and β stereocenters. Although yields of this transformation were moderate (up to 67%), high diastereoselectivity was achieved (up to 97:3 ds, with respect to stereoinduction by the chiral reagent).



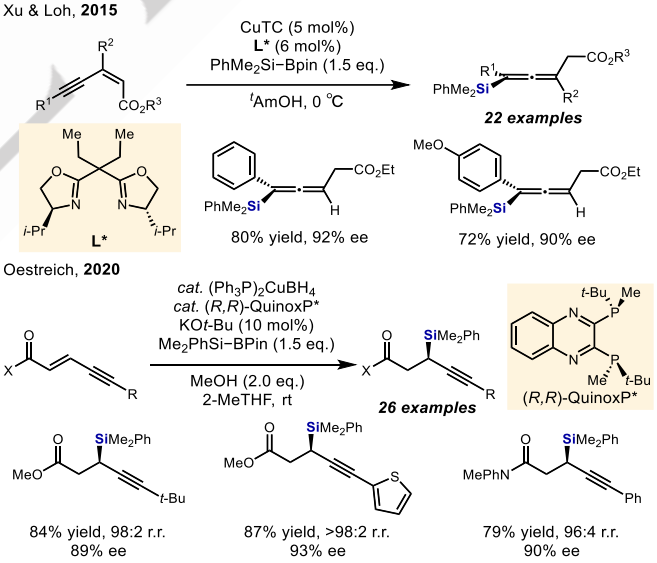

Scheme **16**. Stereoselective and -specific addition of enyne-titanium complex

In 2011, Hayashi reported a palladium-catalyzed asymmetric hydrosilylation of 1-buten-3-ynes to obtain axially chiral allenylsilanes (Scheme 17).[30] This process was proposed to proceed by hydropalladation across the enyne moiety through a π-propargyl(silyl)palladium intermediate. Chiral ferrocenylphosphine ligands were employed to achieve stereoinduction. While it represents an early example of 1,4-selective catalytic asymmetric hydrosilylation of enynes for the synthesis of allenylsilanes, this protocol was limited to enynes with sterically bulky substituents, and only moderate control of enantioselectivity (up to 77% ee) was achieved.



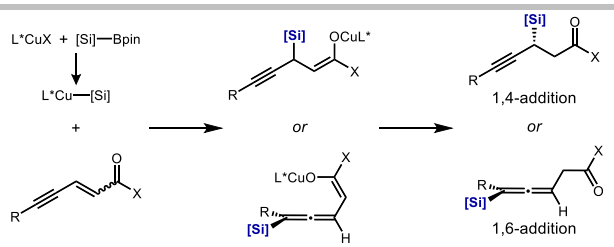

**Scheme 17.** Palladium-catalyzed asymmetric hydrosilylation of 4-substituted 1-buten-3-ynes.

In 2015, Xu and Loh reported a copper-catalyzed hydrosilylation of (*Z*)-enynoates with silylboronates that proceeded with exclusive 1,6-selectivity to give enantioenriched allenylsilane products.[31] A chiral BOX ligand was used to achieve high levels of enantioselectivity (up to 94% ee). Prompted by this work, Oestreich further modified this copper catalysis system and developed a method to achieve the 1,4-selective addition of silylboronic ester to (*E*)-enynoates, leading to a range of α-chiral propargylsilanes.[32] Ligand screening experiments revealed (*R,R*)-QuinoxP* to be an exceptional ligand for effective control over both enantioselectivity and 1,4- versus 1,6-selectivity (Scheme 18).



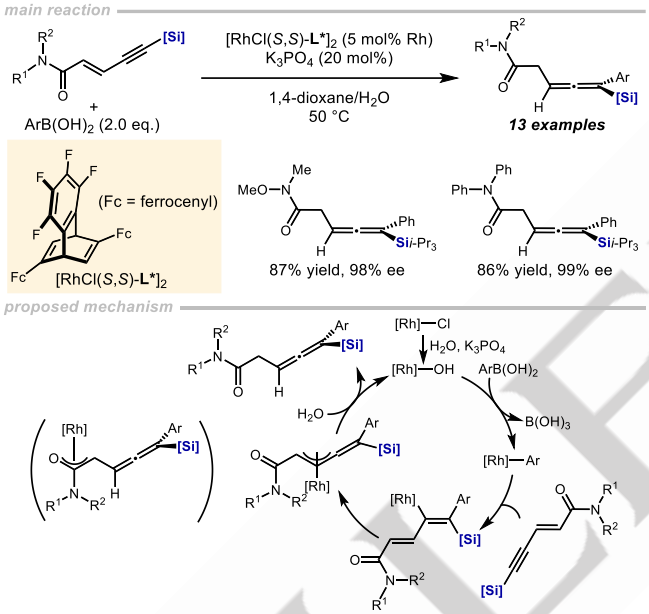

**Scheme 18.** Enantioselective copper-catalyzed deconjugative addition of silicon nucleophiles to enynoates.

Scheme 19 depicts the general mechanistic pathways of this copper-catalyzed silylation process. First, a Cu−Si species is generated from the silylboronate with the assistance of an alcohol. Then upon coordination with the enynoate, 1,4- or 1,6-silyl addition occurs to afford a copper enolate intermediate. Finally, protonation by the alcohol releases the desired silylated product.




**Scheme 19.** Mechanistic synopsis of copper-catalyzed hydrosilylation of enynoates.

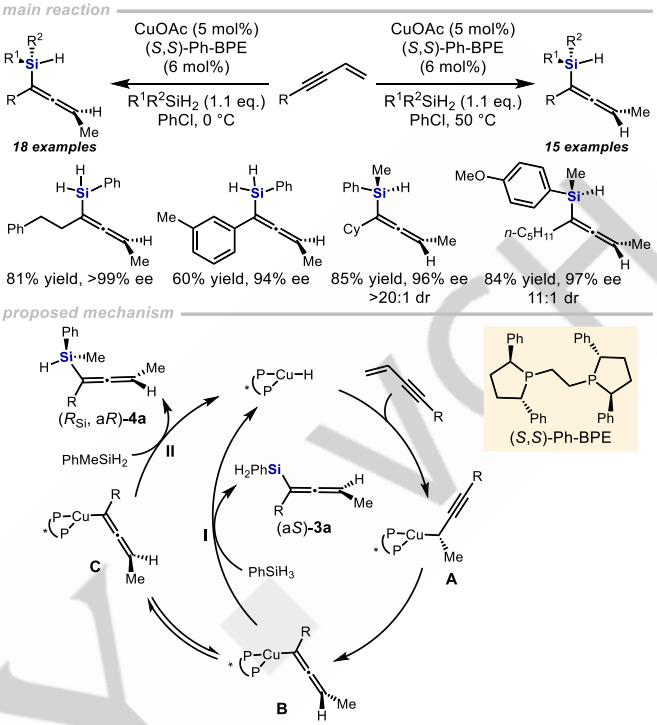
In a mechanistically similar approach to aforementioned Cu-catalyzed hydrosilylation, Hayashi developed a rhodium-catalyzed asymmetric hydroarylation of β-alkynyl acrylamides substituted with a silyl group on the alkynyl carbon, yielding allenylsilanes with exclusive 1,6-selectivity and high enantioselectivity (94−99% ee).[33] The proposed mechanism involves the insertion of an alkyne moiety into the rhodium−aryl bond in which the aryl is placed proximal to the silyl group, generating an alkenyl rhodium intermediate. This intermediate undergoes rhodium migration along the π-system followed by hydrolysis to deliver the allenylsilane product and regenerate the active hydroxorhodium species (Scheme 20).




**Scheme 20.** Rhodium-catalyzed enantioselective hydroarylation of enynamides.

As an advancement of enhancing the synthetic utility of the hydrosilylation approach, Shen and Lan disclosed a mild and efficient system catalyzed by copper in 2023, enabling the synthesis of chiral allenylsilanes from simple 4-substitued 1-buten-3-ynes.[34] This transformation, which used (*S*,*S*)-Ph-BPE as the ligand, proceeded with excellent levels of enantioselectivity in most cases (95 to >99% ee, 30 examples). Moreover, the construction of allenylsilanes with a second stereogenic center at the silicon was explored, demonstrating both high enantioselectivity (90−98% ee) and good diastereoselectivity (9:1 to >20:1 dr). When the reaction was conducted on a gram scale, both yield and enantiopurity of the allenylsilane product remained consistently high. Contemporaneously, Xu and Zhao disclosed a very similar copper-catalyzed system for conversion of enynes to allenylsilanes and investigated the effect of ligand on 1,2- vs. 1,4-regioselectivity.[35]

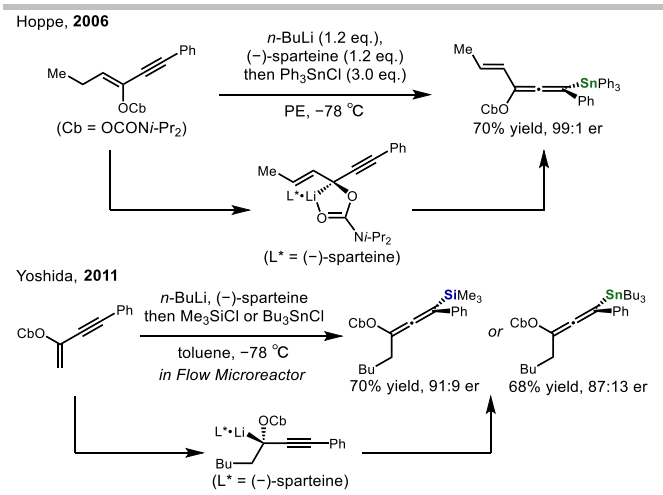
Combining experimental results and DFT calculations, Shen and Lan proposed a catalytic cycle as illustrated in Scheme 21. Starting from a CuH species, olefin insertion into the Cu–H bond generates a propargylcopper intermediate **A**, which isomerizes to an allenylcopper intermediate **B** through 1,3-Cu shift. When $PhSiH_3$ is used (pathway I), σ-bond metathesis occurs to generate ($S_a$)-**3a** with the retention of axial chirality of **B**. On the other hand, when $PhMeSiH_2$ is used (pathway II), intermediate **B** first isomerizes to intermediate **C** (with the opposite sense of axial chirality) via a dynamic kinetic asymmetric process before undergoing a diastereoselective σ-bond metathesis to produce ($R_{Si}$,$R_a$)-**4a**.




**Scheme 21.** Copper catalyzed enantioselective access to allenylsilanes of axial chirality and chirality at the silicon stereogenic center.

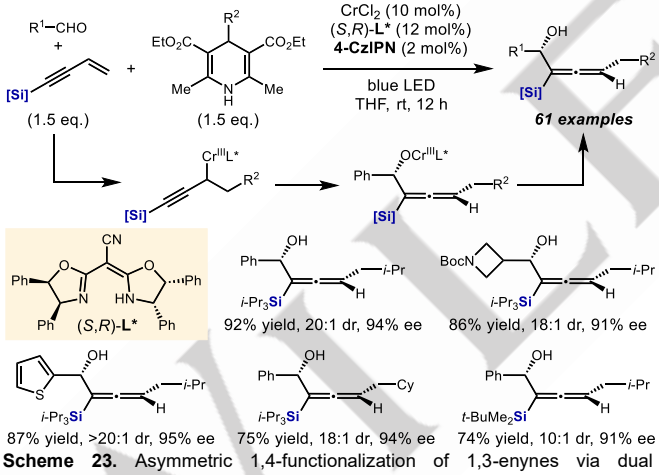
### 4.2. 1,4-Difunctionalization

In early studies on allenyltetrel synthesis through enyne functionalization, transition metal-free stoichiometric 1,4-difunctionalization was employed as a straightforward and convenient approach. In 2006, Hoppe reported a synthesis of enantioenriched allenylstannanes through (–)-sparteine-mediated lithiation.[36] This reaction proceeded through deprotonation of the (*Z*)-1-alken-1-yl *N*,*N*-diisopropylcarbamate at the allylic position by BuLi/(–)-sparteine with high enantiotopic differentiation, leading to a configurationally stable lithium chelate. Trapping this intermediate with electrophilic stannylating reagent resulted in the highly enantioenriched allenylstannane product (70% yield, 99:1 er). Using a similar approach, Yoshida established a flow microreactor system for asymmetric allenylsilane and allenylstannane synthesis in 2011.[37] Notably, this system enabled the use of a configurationally unstable chiral organolithium intermediate, generated via carbolithiation of the enyne, in a reaction with an electrophilic Si or Sn reagent before epimerization could occur (Scheme 22).




**Scheme 22.** Asymmetric synthesis of allenyltetrels through (–)-sparteine-mediated lithiation.

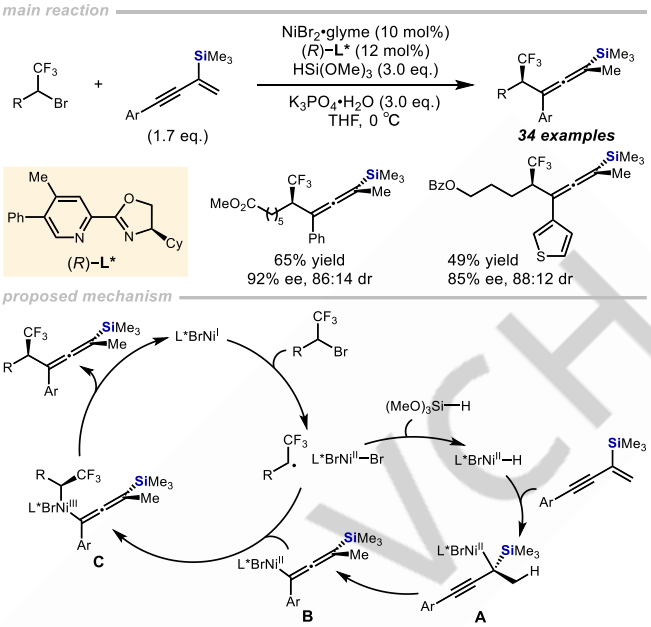
In recent years, newly emergent transition metal-catalyzed methodologies based on single-electron processes have also been employed in 1,4-difunctionalization of enynes, enabling transformations of readily prepared starting materials under mild conditions. In 2022, Wang group at the Westlake University reported an asymmetric three-component 1,4-dialkylation of 1,3-enynes via dual photoredox and chromium catalysis to provide chiral α-hydroxylallenylsilanes.[38] This method allowed for the generation of a broad range of products in good yield, high diastereo- and enantioselectivity. The proposed mechanistic pathway involves the formation of a propargyl chromium intermediate via radical capture, followed by subsequent nucleophilic addition to aldehydes leading to the desired allenylsilane product (Scheme 23).




**Scheme 23.** Asymmetric 1,4-functionalization of 1,3-enynes via dual photoredox and chromium catalysis.

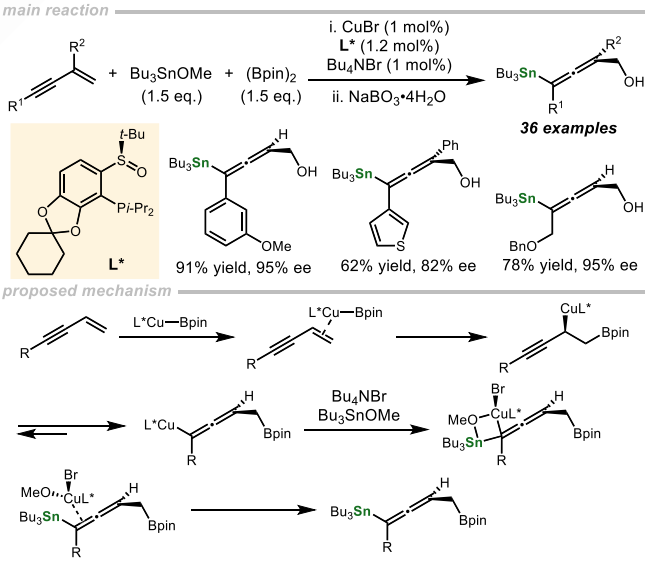
In 2024, Fu reported a new approach to the synthesis of enantioenriched allenylsilanes through nickel-catalyzed enantioconvergent and diastereoselective cross-coupling between racemic alkyl halides and prochiral 1,3-enynes in the presence of a hydride reagent.[39] A chiral oxazoline ligand was employed for enantioinduction. Similar to Wang's work described above, this method enabled the challenging and seldom reported simultaneous control of vicinal central and axial elements of chirality under catalytic conditions, and all the reactions could be carried out on 0.8 mmol scale.

Scheme 24 outlines the plausible mechanism of this nickel catalysis process. A chiral nickel hydride species undergoes a regio- and stereoselective migratory insertion into the prochiral double bond of the 1,3-enyne to form a propargyl nickel complex **A**. This is followed by the stereospecific 1,3-migration of nickel to give an allenyl nickel complex **B**, establishing the axis of chirality. Finally, the coupling of intermediate **B** with the alkyl halide via a trifluoromethyl-substituted secondary radical affords the desired product.




**Scheme 24.** Nickel-catalyzed enantioconvergent and diastereoselective allenylation of alkyl electrophiles.

The transition metal-catalyzed enyne 1,4-difuntionalization strategy could also be applied to the asymmetric synthesis of chiral allenyl stannes. In 2021, Liao and coworkers reported a Cu-catalyzed asymmetric 1,4-borylstannation of 1,3-enynes.[40] $Bu_3SnOMe$ and bis(pinacolato)diboron ($B_2pin_2$) were chosen as reaction partners to achieve 1,4-borylstannation, oxidation by $NaBO_3•4H_2O$ gave the desired allenylic alcohols. Analogous to the nickel system, the proposed mechanism of this process also involves a stereospecific isomerization of propargylmetal species to form an allenylmetal intermediate. This intermediate coordinates with the bromide ion (from $Bu_4NBr$) and $Bu_3SnOMe$ to form a stable four-membered ring intermediate, generating the desired allenylstannane product via stereoretentive transmetallation (Scheme 25).

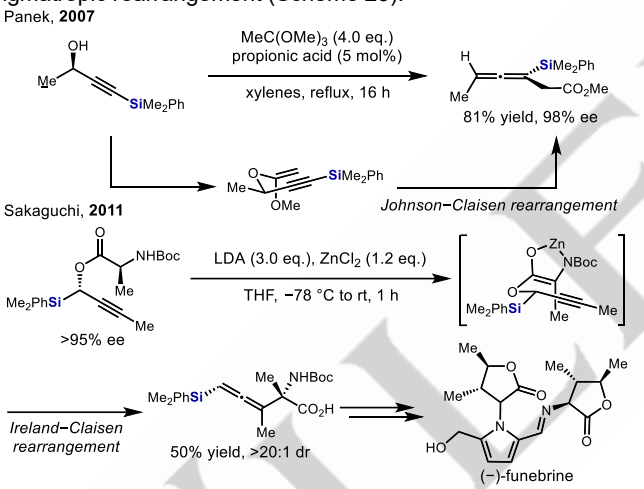



**Scheme 25.** Asymmetric 1,4-functionalization of 1,3-enynes via dual photoredox and chromium catalysis.

## 5. Claisen rearrangement

As a complement to the extensively developed substitution and addition-based methods discussed above, the Claisen rearrangement of enantioenriched silicon-containing alkynes is also a reliable and convenient approach for the preparation of chiral allenylsilanes.

In 2007, Panek demonstrated an enantioselective synthesis of a chiral allenylsilane by the Johnson orthoester variant of the Claisen rearrangement.[41] Refluxing xylenes was found to be crucial for the high conversion to the allenylsilane product in this transformation. Starting from a highly enantioenriched 1-silyl propargyl alcohol, the ester substituted allenylsilane was obtained in good yield (81%) and excellent levels of chirality transfer (98% ee). The authors employed the stereodefined allenylsilane products prepared using this method as the carbon nucleophile in Lewis acid mediated addition to oxocarbenium ions for the synthesis of a range of homopropargylic ethers bearing contiguous stereocenters with high levels of chirality transfer and diastereoselectivity. In order to demonstrate the practicality of this approach, Panek reported a similar operating procedure for conducting this reaction on a gram scale in 2012, with no significant loss in yield and stereoselectivity.[42] In this work, In 2011, Sakaguchi reported the stereoselective total synthesis of (–)-funebrine in 14 steps.[43] The crucial steps in the synthesis involve a stereoselective Ireland−Claisen rearrangement of the (*S*)-α-acyloxy-α-alkynylsilane, which gave the allenylsilane product as a single diastereomer (50% yield, >20:1 dr). It was suggested in their previous study that the high diastereoselectivity can be attributed to the preferential formation of the *Z*-enolate and equatorial orientation of the silyl group in the transition state of the sigmatropic rearrangement (Scheme 26).[44]



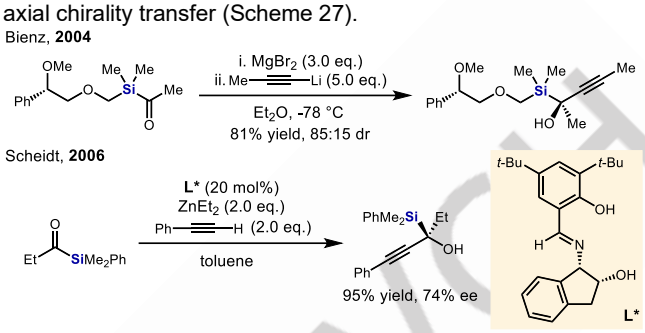

**Scheme 26.** Asymmetric synthesis of allenylsilanes through Claisen rearrangement.

## 6. Alkynylation

Compared to the synthesis of allenylsilanes with effective stereoinduction, the incorporation of a silyl group at the propargylic position in an enantioselective fashion is a challenging process. Instead, a more common and important strategy for synthesizing enantioenriched proparylsilanes is to alkynylate at the α position of a silane, using simple terminal alkynes, either pre-metalated or metalated *in situ*, as the alkyne source in an asymmetric alkynylation reaction.

### 6.1. Addition to acylsilanes

In early reports, asymmetric addition of acetylides to acylsilanes was discovered as a mechanistically simple approach for the synthesis of α-hydroxy propargylsilanes. In 2004, Bienz reported a stereospecific reaction of an acylsilane bearing a chiral auxiliary with the nucleophilic lithium acetylide reagent.[45] The use of $Et_2O$ as the solvent gave the best stereochemical outcome (85:15 dr). In a significant advance, which eliminated the need for the chiral auxiliary, Scheidt reported a catalytic asymmetric addition of alkynes to acylsilanes.[46] This approach utilized a tridentate Schiff base ligand for enantioinduction, yielding the α-hydroxy propargylsilane product in 74% ee. The authors further converted the propargylsilane product into a silyloxyallene via the Brook rearrangement, which resulted in good (94% es) point-to-axial chirality transfer (Scheme 27).

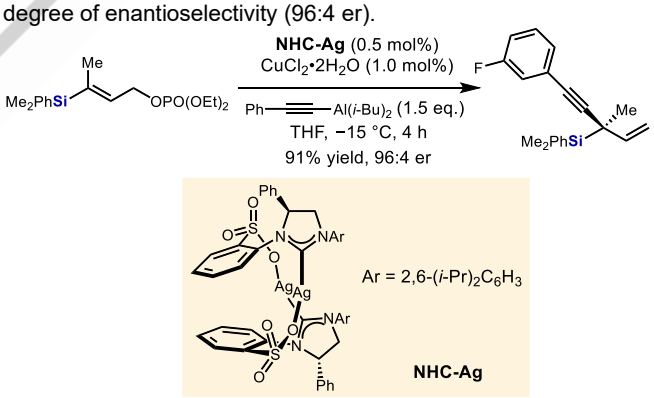



**Scheme 27.** Asymmetric addition of acetylides to acylsilanes.

### 6.2. Transition metal-catalyzed coupling reactions

In recent years, enantioselective synthesis of propargylsilanes by transition metal catalyzed alkynylation has gained increased attention as a successful approach to access this class of products in high levels of enantioselectivity. Most transformations of this type involve the *in situ* formation of copper acetylides as key intermediates.

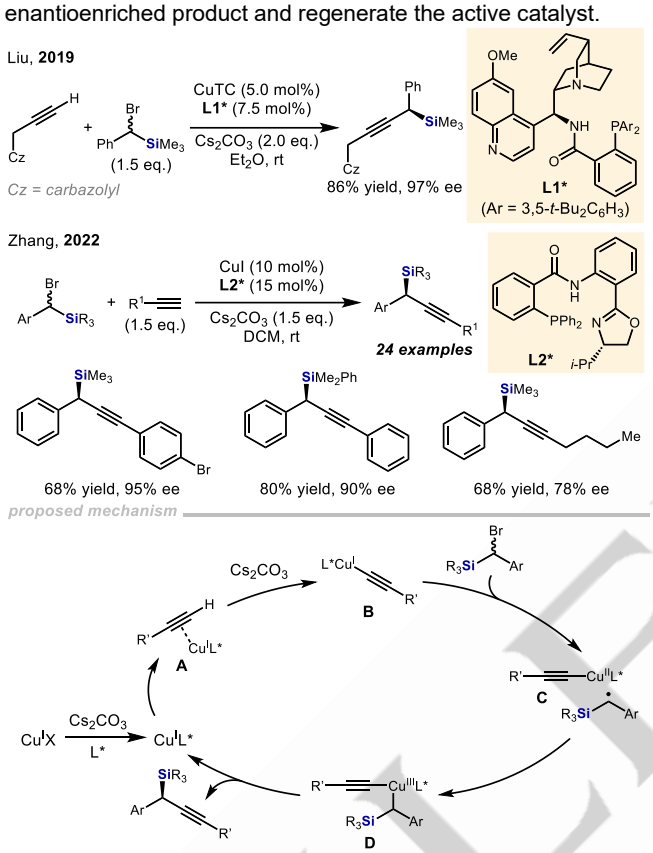
In 2011, Hoveyda reported a catalytic enantioselective method for the formation of the propargylsilanes bearing tetrasubstituted stereogenic centers (Scheme 28).[47] The chiral NHC–Cu complex efficiently promoted transfer of the alkyne group from the alkynylaluminum reagent to the silyl-substituted allylic phosphate substrate via an enantioselective allylic substitution (EAS) process, affording the $S_N2'$ product in high yield (91%) and high degree of enantioselectivity (96:4 er).




**Scheme 28.** NHC–Cu-Catalyzed enantioselective allylic substitutions with alkynylaluminum reagent.

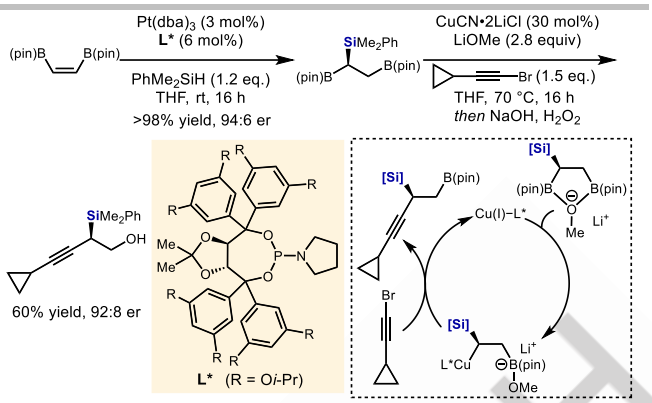
More recently, Liu developed an asymmetric copper-catalyzed C($sp^3$)–C(sp) coupling in 2019 by combining a copper catalyst with a cinchona alkaloid-based chiral P,N-ligand.[48] This approach enabled the Sonogashira-type cross-coupling of a broad range of terminal alkynes with racemic alkyl halides. The authors demonstrated one example of the coupling of α-silylbenzyl bromide, generating a carbazole-containing propargylsilane product in 86% yield and 97% ee. In 2022, Zhang and coworkers extended this strategy to the synthesis of a broader range of enantioenriched propargylsilanes in a study in which they developed a novel phosphino-oxazoline ligand to achieve good to excellent stereocontrol (up to 95% ee).[49] In their exploration of substrate scope, the authors carefully examined a broad range of functionalized substituents on the alkyne, as well as the aryl and silyl groups on the electrophilic coupling partner (Scheme 29).

Both research groups performed thorough investigations to probe the reaction mechanism. Many of their observations, along with literature support, led to the insight that this copper catalyzed process undergoes a mechanism involving the coupling of an alkyl radical with a copper acetylides species. In one possible pathway, that the reaction starts with the formation of monomeric Cu(I) acetylide **B** from the reaction of Cu(I)L* complex **A** with the terminal alkyne in the presence of base. Subsequent stepwise one-electron oxidative addition of **B** with alkyl halide through either inner- or outer-sphere electron transfer followed by coupling of Cu(II) acetylide **C** with the α-silyl benzylic radical results in the formation of a Cu(III) complex **D**. Finally, C($sp^3$)–C(sp) bond coupling occurs via reductive elimination to furnish the enantioenriched product and regenerate the active catalyst.




**Scheme 29.** Copper-catalyzed coupling of alkynes with α-silyl benzyl halides.

In 2023, Morken reported a copper-catalyzed site-selective coupling of a 1,2-diboryl-1-silylalkane to an alkynyl bromide proceeding through a mechanistic pathway distinct from the one previously described.[50] The enantioenriched diboronate starting material was prepared from a Pt-catalyzed enantioselective hydrosilylation of (*Z*)-1,2-diborylethylene enabled by a chiral phosphoramidite ligand. In the subsequent copper-catalyzed reaction, coupling with an alkynyl bromide took place α to the silyl group which gave the product with high levels of regioselectivity and stereospecificity. The general mechanism of this type of transformations is depicted in Scheme 30, in which a transmetallation between the Cu(I) complex and the silylboronate was suggested to occur as a requisite event, followed by trapping of the organocopper product by the alkynyl bromide to release the product and the copper salt. As demonstrated in their previous studies, lithium methoxide likely served as an activator for the silylboronate substrate by forming a cyclic chelated ate complex.[51]



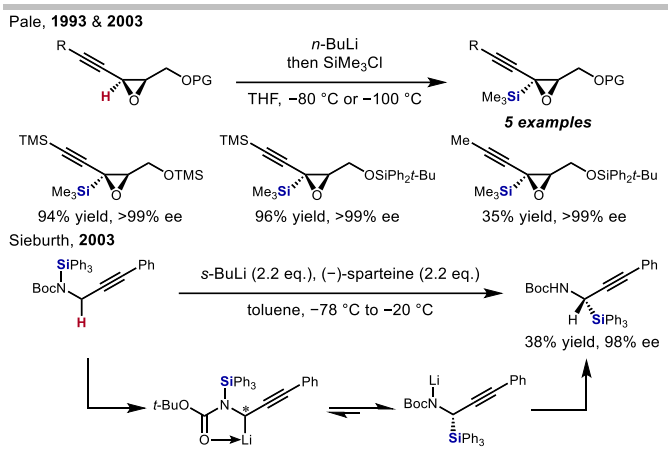

**Scheme 30.** Enantioselective synthesis of 1,2-diborylsilanes and copper-catalyzed site-selective cross-coupling.

## 7. Direct C($sp^3$)–H silylation

In contrast to monosubstituted acetylenes and metal acetylides, internal alkynes are a less common class of starting materials for the synthesis of enantioenriched propargylsilanes. Yet, as substrates for direct asymmetric C($sp^3$)–H silylation, they hold considerable potential as precursors that are particularly versatile and synthetically accessible. While still underdeveloped, this retrosynthetically straightforward strategy has found successful applications in stoichiometric lithiation chemistry, as well as a recent catalytic study. The mechanisms of these transformations all involve organic base-mediated deprotonation at the propargylic position, followed by functionalization with electrophilic silylating reagents.

### 7.1. Organolithium base-mediated deprotonation

In early reports, Pale reported an asymmetric propargylic silylation of ethynyl oxiranes with chiral C($sp^3$) centers, a structural motif commonly found in natural products (Scheme 31).[52] This process proceeds through initial deprotonation of enantioenriched ethynyl oxiranes using *n*-butyllithium. The propargylic oxiranyl anions were then trapped with trimethylsilyl chloride as the electrophile to produce silylated ethynyl oxiranes in excellent enantioselectivities (>99% ee). Due to the difficulty of stabilizing oxiranyl anions, the scope of this reaction is limited to a small number of specialized substrates. In 2003, Sieburth developed an asymmetric synthesis of a *tert*-butoxycarbonyl (Boc) protected propargylaminosilane from a racemic propargylamine derivative.[53] The use of (–)-sparteine–*n*-butyllithium complex enables propargylic deprotonation to form the *N*-silylated carbanion intermediate, which undergoes a reverse aza-Brook rearrangement to give the *C*-silylated product. The Boc group allows for the formation of a configurationally stable carbanion and also provides a driving force for the rearrangement by stabilization of the *N*-lithio product. The product was obtained in excellent enantioselectivity, albeit in modest yield (38%, 98% ee).

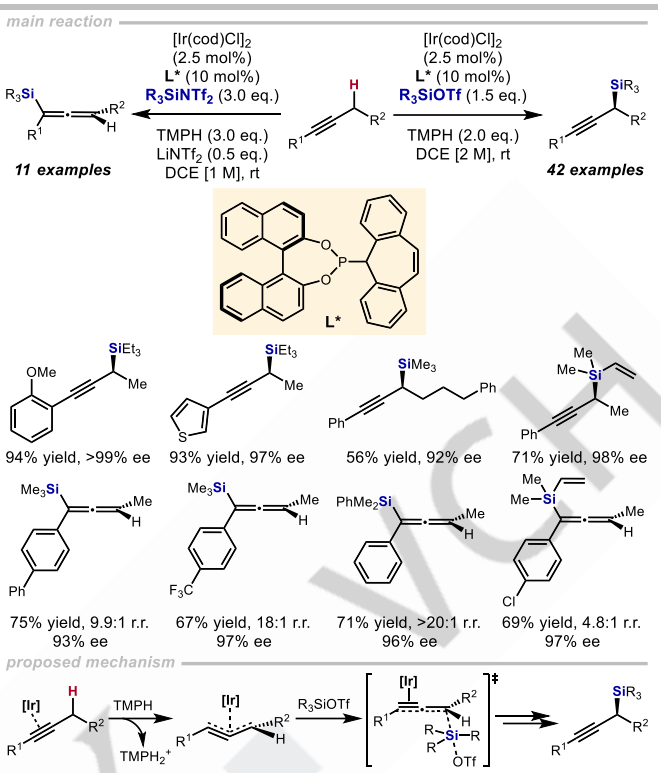



**Scheme 31.** Asymmetric organolithium-mediated propargylic deprotonation-silylation.

### 7.2. π-Complexation-assisted deprotonation

In 2024, Wang and Liu reported a system for asymmetric propargylic silylation under ambient conditions demonstrating broad functional group tolerance, in which internal alkynes undergo asymmetric and regioselective C($sp^3$)–H functionalization catalyzed by a phosphoramidite-ligated iridium catalyst.[54] Notably, this process allowed for direct catalytic C($sp^3$)–H silylation of alkynes without pre-functionalization or specialized silylating reagents. Notably, the use of different electrophilic silyl sources ($R_3SiOTf$ or $R_3SiNTf_2$) allowed for the regiodivergent synthesis of silylated compounds with good to excellent control of regioselectivity. On a 5.0 mmol scale, propargylic silanes could be obtained without significant loss in yield and stereoselectivity.

The mechanistic synopsis of the likely pathway towards propargylsilane products is depicted in Scheme 32. Initially, upon addition of silyl triflate and alkyne into a catalyst mixture containing Ir[**L***]$_2$Cl, halide abstraction and coordination with the alkyne takes place to give a cationic Ir–alkyne complex. This allows for deprotonation at the propargylic position by mild organic base 2,2,6,6-tetramethylpiperidine (TMPH) to afford an $\eta^3$-allenyliridium intermediate. Kinetic data and DFT computations support a mechanism in which the subsequent C–Si bond formation occurs via outer-sphere attack by the electrophilic silylating reagent.

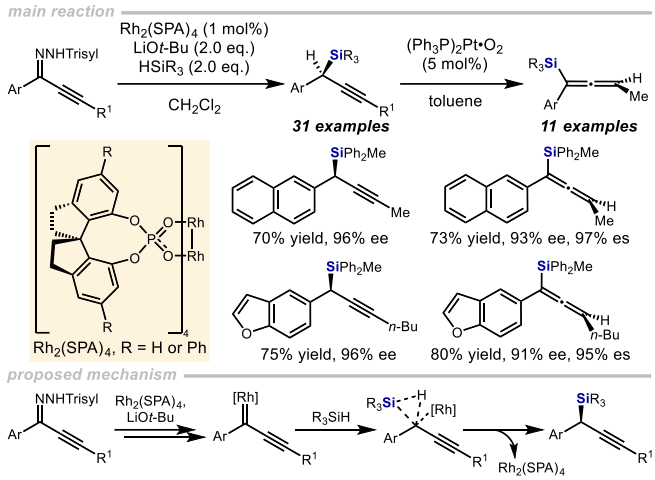



**Scheme 32.** Ir-catalyzed enantioselective and regiodivergent synthesis of propargyl and allenylsilanes.

## 8. Carbene insertion

In 2021, a seminal report by Zhou and Zhu described an enantioselective synthesis of propargylsilanes and allenylsilanes by a Rh-catalyzed carbene insertion strategy.[55] In this work, chiral spiro phosphate-ligated dirhodium complexes were used to catalyze the asymmetric insertion of aryl alkynyl carbenes into the Si−H bonds of silanes with excellent enantioselectivities (up to 98% ee) under mild conditions. In addition, the authors developed mild and general conditions for the stereospecific isomerization of propargylsilanes to give axially chiral allenylsilanes with excellent levels of stereospecificity. Although the method is limited to aryl-substituted carbene precursors, this report represents an alternative strategy for asymmetric propargylsilane synthesis and describes the first example of a highly enantioselective insertion reaction of alkynyl carbenes. In addition, the reaction could be performed on a gram scale in good yield (75%) and good enantioselectivity (94% ee).

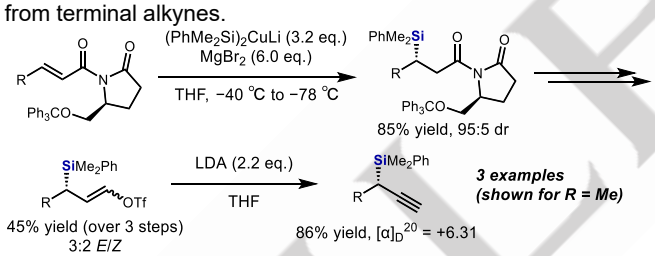
The proposed mechanism is outlined in Scheme 33. Treatment of alkynyl *N*-trisylhydrazones with base and rhodium catalyst leads to the formation of the active alkynyl rhodium carbene. This carbene intermediate undergoes concerted insertion into the Si−H bond of the silane to furnish the desired silylated product. Mechanistic studies pointed to platinum nanoparticles as the active catalyst for the reported conditions for the stereospecific isomerization of propargylsilanes to allenylsilanes.




**Scheme 33.** Rh-catalyzed enantioselective insertion of alkynyl carbenes into Si−H bonds.

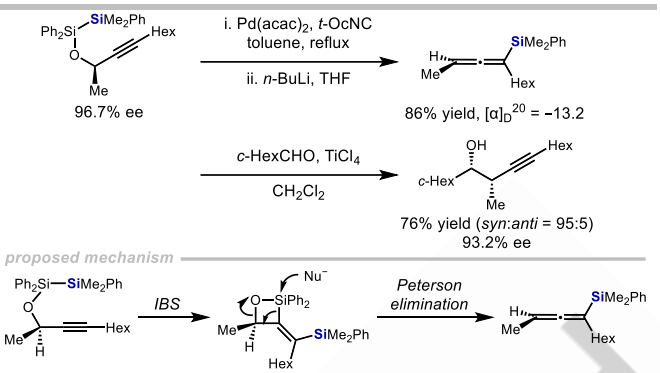
## 9. Miscellaneous methods

In 1998, Fleming reported an unusual approach for the synthesis of enantioenriched propargylsilanes without employing alkyne substrates (Scheme 34).[56] In this five-step route, which starts with α,β-unsaturated carbonyl fragments attached to Koga's chiral auxiliary, conjugate addition of the silylcopper reagent gives imides bearing a β-silyl stereogenic center with high levels of diastereoselectivity. Removal of the auxiliary, triflation, and elimination of HOTf using lithium diisopropylamide (LDA) furnished the enantioenriched propargylsilane products. Despite its lengthy synthesis, this method represents a rare example of a process that is suitable for accessing propargylsilanes derived from terminal alkynes.



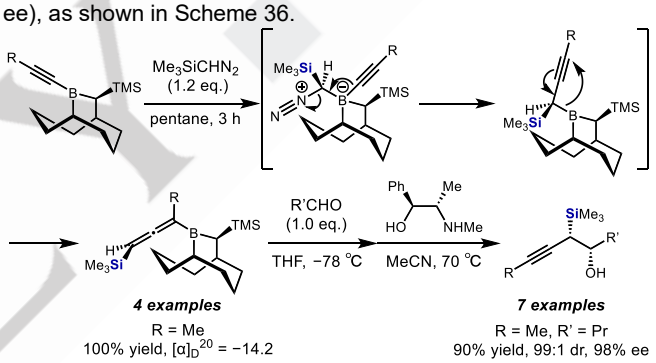

**Scheme 34.** Synthesis of enantioenriched propargylsilanes from α,β-unsaturated imides with chiral auxiliary.

In 2003, Suginome described a stereoselective access to an enantioenriched allenylsilane via palladium-catalyzed intramolecular bis-silylation (IBS).[57] As illustrated in Scheme 35, the palladium−isocyanide catalyst was used to establish the IBS process through Si−Si activation, generating the oxasiletane product. Subsequent Peterson-type elimination enabled by treatment with *n*-BuLi led to the allenylsilane product in 86% yield. Although the enantiopurity of the allenylsilane could not be determined, its derivatization product obtained after treatment of cyclohexanecarboxaldehyde in the presence of $TiCl_4$ exhibited high enantiopurity (93.2% ee). The IBS step proceeded with high *syn*-selectivity, which, combined with the *syn*-stereospecific silyloxy elimination of the oxasiletane, enabled the efficient overall transfer of point chirality to axial chirality in this strategically distinct approach to the synthesis of enantioenriched allenylsilanes.



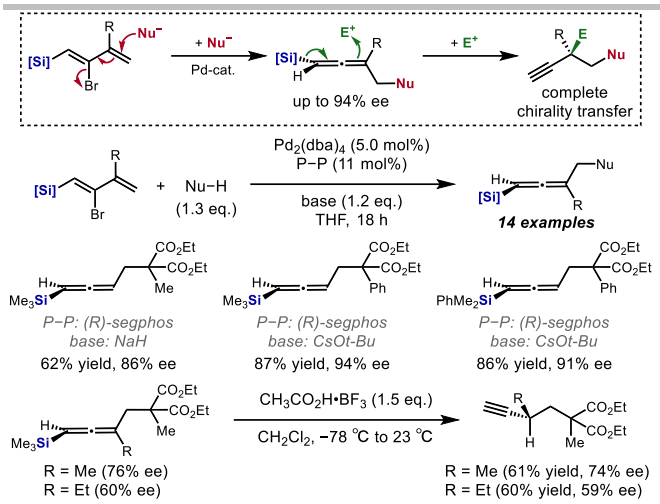

**Scheme 35.** Asymmetric allenylsilane synthesis via Pd-catalyzed IBS/elimination sequence.

In 2007, Soderquist described an asymmetric synthesis of boron-containing allenylsilanes and their conversion to enantioenriched propargylsilanes.[58] In this approach, *B*-alkynyl 10-TMS-9-BBDs (10-trimethylsilyl-9-borabicyclo[3.3.2]decane) in optically pure form were treated with $TMSCHN_2$ to give isomerically pure γ-boryl allenylsilanes through stereoselective insertion of a $Me_3SiCH$ group into the alkynyl B−C bonds in a Matteson-type process, followed by spontaneous 1,3-borotropic rearrangement. These, in turn, react with aldehydes to give β-hydroxy propargylsilanes (upon removal of the borabicyclic fragment with the aid of pseudoephedrine) in good yields (80−96%) and with excellent levels of chirality transfer (94−99% ee), as shown in Scheme 36.



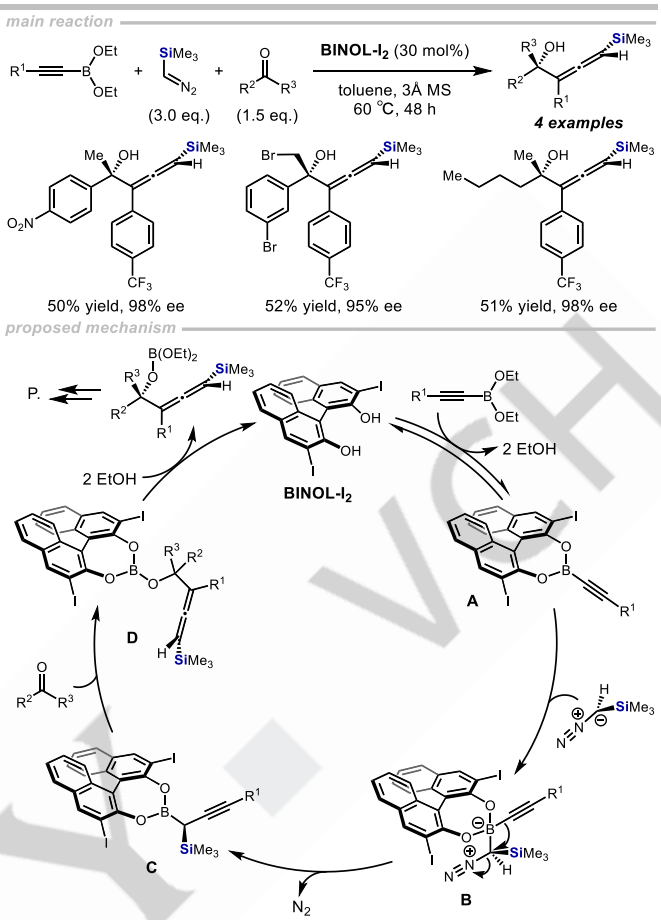

**Scheme 36.** Asymmetric synthesis of allenylsilanes from alkynyl boranes through a 1,2-insertion–1,3-borotropic rearrangement.

In 2010, Ogasawara and Takahashi reported the conversion of 2-bromo-1-silyl-1,3-dienes, which were prepared by bromination of β-silylenals/enones followed by Peterson olefination, into axially chiral allenylsilanes via asymmetric Pd-catalyzed $S_N2'$ reaction.[59] Subsequent carbo-, fluoro-, and protodesilylation of the 3,3-dialkylallenylsilanes took place via the *anti* $S_E2'$ pathway and resulted in the formation of terminal alkynes bearing a propargylic tertiary stereogenic center, proceeding with complete axial-to-central chirality transfer (Scheme 37).




**Scheme 37.** Asymmetric Pd-catalyzed $S_N2'$ reaction and the desilylative $S_E2'$ reaction to the ambivalent 2-bromo-1-silyl-1,3-dienes.

In a 2023 report, Szabó developed an organocatalytic three-component coupling reaction of alkynyl boronates, diazomethanes (including the trifluoromethyl and trimethylsilyl derivatives), and aliphatic/aromatic ketones for the synthesis of enantioenriched allenes (including examples of allenylsilanes) through the catalysis by a BINOL derivative.[60] Though the yields are moderate (40−52%), this transformation gave excellent enantioselectivities (95−98% ee) and only a single diastereomer was formed. It was suggested that this reaction proceeds via a transesterification of the alkynyl boronate with **BINOL-I$_2$** to generate a BINOL boronate **A**. This species reacts with the diazomethane derivative to form an ate complex **B**, which undergoes 1,2-migration of the alkynyl group with loss of $N_2$ to give the stereodefined α-SiMe$_3$ propargyl boronate **C**. Reaction of **C** with the ketone substrate through a closed transition state then gives boronic ester **D**, which regenerates the catalyst upon transesterification with EtOH to give the diethoxy boronic ester, the hydrolysis of which affords the allenylic alcohol product upon workup (Scheme 38).




**Scheme 38.** Asymmetric organocatalytic homologation of alkynyl boronates.

## 3. Summary and Outlook

In addition to continued investigation and exploitation of classical stoichiometric approaches, developments in catalytic methods in recent years have resulted in a significant expansion of the range of synthetically accessible propargylic and allenic derivatives of Si, Ge, and Sn. This is especially true for enantioenriched allenylsilanes, with an assortment of both unadorned and functionalized derivative now being readily accessible in enantioenriched form. Nevertheless, stereodefined allenylsilanes of certain substitution patterns, including those that are 1,3-disubstituted or tetrasubstituted, are accessible only in special cases. Access to enantioenriched propargylsilanes also remains somewhat limited. In contrast, the catalytic enantioselective synthesis of propargylic and allenic stannanes remains virtually unexplored, while few enantioenriched germanes of any kind have been prepared so far. Thus, in spite of their known and potential synthetic utility, a vast range of stereodefined propargylic and allenic organotetrels remains nontrivial to access. More widespread availability and utilization of these compounds await further conceptual advances in synthetic technology, as well as the ingenuity and effort of the synthetic community.

## Acknowledgements

We thank the National Science Foundation (CHE-2400082) for generous financial support.

**Keywords:** Organotetrels • Asymmetric synthesis • Alkynes • Allenes • Catalysis

[1] a) S. J. Blunden, A. H. and Chapman, *Environ. Technol. Lett.* **1982**, *3*, 267–272; b) M. Hoch, *Appl. Geochem.* **2001**, *16*, 719–743; c) S. E. Denmark, R. F. Sweis, *Chem. Pharm. Bull.* **2002**, *50*, 1531–1541; d) M. J. Curtis-Long, Y. Aye, *Chem. Eur. J.* **2009**, *15*, 5402–5416; e) T. Hiyama, *Organosilicon and Relating Organotin Chemistry.* In *Organometallics in Synthesis*, **2013**, pp. 373–544; f) S. E. Denmark, R. F. Sweis, *Organosilicon Compounds in Cross-Coupling Reactions.* In *Metal-Catalyzed Cross-Coupling Reactions*, **2014**, pp. 475–532; g) C. Fricke, F. Schoenebeck, *Acc. Chem. Res.* **2020**, *53*, 2715–2725.

[2] a) H. E. Burks, J. P. Morken, *Chem. Commun.* **2007**, *45*, 4717–4725; b) B. Su, J. F. Hartwig, *Angew. Chem. Int. Ed.* **2022**, *61*, e202113343; c) W. C. Xue, M. Oestreich, *ACS Cent. Sci.* **2020**, *6*, 1070–1081; d) L. Li, W. S. Huang, Z. Xu, *Sci. China Chem.* **2023**, *66*, 1654–1687; e) M. Zhang, S. Gao, J. Tang, L. Chen, A.Liu, S. Sheng, A. Q. Zhang, *Chem. Commun.* **2021**, *57*, 8250–8263; f) N. Kranidiotis-Hisatomi, M. Oestreich, *Synthesis* **2023**, *55*, 1497-1506; g) J. W. Han, T. Hayashi, *Tetrahedron: Asymmetry* **2014**, *25*, 479-484.

[3] a) J. A. Marshall, *Chemical Reviews* **1996**, *96*, 31-48; b) J. A. Marshall, J. Org. Chem. **2007**, *72*, 8153–8166; c) M. Curtis-Long, Y. Aye, *Chem. Eur. J.* **2009**, *15*, 5402–5416; d) A. W. Schmidt, H. Knölker, *Synlett.* **2010**, *15*, 2207-2239; e) S. E. Denmark, T. W. Wilson, *Angew. Chem. Int. Ed.* **2012**, *51*, 9980-9992; f) *Comprehensive Organic Synthesis (Second Edition)* (Eds.: P. Knochel), Elsevier, **2014**, pp. 27-48.

[4] a) G. B. Gerber, A. Léonard, *Mutation Research/Reviews in Mutation Research* **1997**, *387*, 141–146; b) E. Lukevics, L. Ignatovich, in *Metallotherapeutic Drugs and Metal*‐*Based Diagnostic Agents*, **2005**, pp. 279–295.

[5] C. E. Masse, J. S. Panek, *Chem. Rev.* **1995**, *95*, 1293–1316.

[6] a) S. K. Ghosh, *Helv. Chim. Acta.* **2023**, *106*, e202300141; b) V. Coeffard, I. Beaudet, J. Quintard, E. le Grognec, *Chirality*, **2010**, *22*, 864-869; c) W. H. Pearson, P. Stoy, *Synlett* **2003**, *7*, 903-921; d) J. A. Marshall, *Main Group Metal Chemistry*, **1994**, *17*, 259-268.

[7] a) G. Li, X. Huo, X. Jiang, W. Zhang, *Chem. Soc. Rev.* **2020**, *49*, 2060–2118; b) W. Ming, X. Liu, L. Mao, X. Gu, Q. Ye, *Chin. J. Chem.* **2021**, *39*, 1716–1725; c) F. Ferreira, O. Jackowski, R. Pérez Sevillano, *Synthesis* **2023**, *55*, 2609–2638; d) J. Li, J. Huang, Y. Wang, Y. Liu, Y. Zhu, H. You, F. E. Chen, *Chem. Sci.* **2024**, *15*, 8280–8294.

[8] a) I. Fleming, K. Takaki, A. P. Thomas, *J. Chem. Soc., Perkin Trans. 1*, **1987**, 2269–2273. b) J. Kjellgren, H. Sundén, K. J. Szabó, *J. Am. Chem. Soc.* **2005**, *127*, 1787–1796; c) I. E. Wrona, J. T. Lowe, T. J. Turbyville, T. R. Johnson, J. Beignet, J. A. Beutler, J. S. Panek, *J. Org. Chem.* **2009**, *74*, 1897–1916; d) S. Shah, B. G. Das, V. K. Singh, *Tetrahedron* **2021**, *93*, 132238; e) W. Xiao, J. Wu, *Org. Chem. Front.* **2022**, *9*, 5053–5073; f) M. Yus, C. Nájera, F. Foubelo, J. M. Sansano, *Chem. Rev.* **2023**, *123*, 11817–11893; g) L. Z. Li, Y. R. Huang, Z. X. Xu, H. S. He, H. W. Ran, K. Y. Zhu, J. C. Han, C. C. Li, *J. Am. Chem. Soc.* **2024**, *146*, 24782–24787; h) S. Li, K. Yuan, G. Zhang, R. Guo, *Eur. J. Org. Chem.* **2024**, *27*, e202301316; i) Q. Ran, K.-F. Wu, Y.-H. Xu, *Org. Lett.* **2024**, *26*, 3767–3771.

[9] a) M. E. Jung and S. Min, *J. Am. Chem. Soc.* **2005**, *127*, 10834–10835; b) I. E. Wrona, J. T. Lowe, T. J. Turbyville, T. R. Johnson, J. Beignet, J. A. Beutler, J. S. Panek, *J. Org. Chem.* **2009**, *74*, 1897–1916; c) S. Yu, S. Ma, *Angew. Chem. Int. Ed.* **2012**, *51*, 3074–3112; d) X. Liu, G. Dong, *Chem* **2024**, *10*, 22–23.

[10] X. Kuang, C. Ding, Y. Wu, P. Wang, *Chin. J. Org. Chem.* **2023**, *43*, 3367–3387.

[11] M. Shimizu, T. Kurahashi, H. Kitagawa, T. Hiyama, *Org Lett.* **2003**, *5*, 225–227.

[12] a) M. J. C. Buckle, I. Fleming, S. Gil, K. L. C. Pang, *Org. & Biomol. Chem.* **2004**, *2*, 749–769; b) M. J. C. Buckle, I. Fleming, *Tetrahedron Lett.* **1993**, *34*, 2383–2386.

[13] V. N. Bochatay, Y. Sanogo, F. Chemla, F. Ferreira, O. Jackowski, A. Pérez-Luna, *Adv. Synth. Catal.* **2015**, *357*, 2809–2814.

[14] T. Leung, G. Zweifel, *J. Am. Chem. Soc.* **1974**, *96*, 5620-5621.

[15] S. Umemiya, K. Lingqi, Y. Eto, M. Terada, *Chem. Lett.* **2022**, *51*, 391–394.

[16] K. Ruitenberg, H. Westmijze, J. Meijer, C. J. Elsevier, P. Vermeer, *J. Organomet. Chem.* **1983**, *241*, 417–422.

[17] a) J. A. Marshall, X. J. Wang, *J. Org. Chem.* **1991**, *56*, 3211–3213; b) J. A. Marshall, X. J. Wang, *J. Org. Chem.* **1992**, *57*, 1242–1252; c) J. A. Marshall, R. H. Yu, J. F. Perkins, *J. Org. Chem.* **1995**, *60*, 5550–5555.

[18] H. Ohmiya, H. Ito, M. Sawamura, *Org. Lett.* **2009**, *11*, 5618–5620.

[19] D. J. Vyas, C. K. Hazra, M. Oestreich, *Org. Lett.* **2011**, *13*, 4462–4465.

[20] Z. L. Liu, C. Yang, Q. Y. Xue, M. Zhao, C. C. Shan, Y. H. Xu, T. P. Loh, *Angew. Chem. Int. Ed.* **2019**, *58*, 16538–16542.

[21] V. Bochatay, Z. Neouchy, F. Chemla, F. Ferreira, O. Jackowski, A. Pérez-Luna, *Synthesis* **2016**, *48*, 3287–3300.

[22] W. Li, R. Wu, H. Ruan, B. Xiao, X. Gao, H. Jiang, K. Chen, T. Y. Sun, S. Zhu, *Angew. Chem. Int. Ed.* **2024**, *63*, e202409332.

[23] X. Zeng, F.-H. Zhang, Z. Wang, *Org. Chem. Front.* **2023**, *10*, 310–316.

[24] a) E. Lukevics, L. Ignatovich, in *The Chemistry of Organic Germanium, Tin and Lead Compounds*, **2002**, pp. 1653–1683; b) L. G. Menchikov, M. A. Ignatenko, *Pharm. Chem. J.* **2013**, *46*, 635–638; c) T. Takeda, S. Doiyama, J. Azumi, Y. Shimada, Y. Tokuji, H. Yamaguchi, K. Nagata, N. Sakamoto, H. Aso, T. Nakamura, *Sci. Rep.* **2019**, *9*, 13637.

[25] a) H. Arii, T. Amari, J. Kobayashi, K. Mochida, T. Kawashima, *Angew. Chem. Int. Ed.* **2012**, *51*, 6738–6741; b) J. Levi Knippel, A. Z. Ni, A. W. Schuppe, S. L. Buchwald, *Angew. Chem. Int. Ed.* **2022**, *61*, e202212630; c) D. Brosamlen, M. Oestreich, *Org. Lett.* **2023**, *25*, 1901–1906; d) M. Y. Xu, W. T. Jiang, M. Z. Xia, Z. L. An, X. Y. Xie, B. Xiao, *Angew. Chem. Int. Ed.* **2024**, *63*, e202317284; e) A.-C. Han, X.-G. Zhang, L.-L. Yang, J.-B. Pan, H.-N. Zou, M.-L. Li, L.-J. Xiao, Q.-L. Zhou, *Chem. Catal.* **2024**, *4*, 100826; f) A. C. Han, L. J. Xiao, Q. L. Zhou, *J. Am. Chem. Soc.* **2024**, *146*, 5643–5649; g) S.-H. Chen, S. Zhang, Z.-Y. Chen, Y. Wu and P. Wang, *ChemRxiv*, **2024**, https://doi.org/10.26434/chemrxiv-2024-105l3.

[26] G.-Y. Han, P.-F. Su, Q.-Q. Pan, X.-Y. Liu, X.-Z. Shu, *Nat. Catal.* **2023**, *7*, 12–20.

[27] Y. Xu, H. Yi, M. Oestreich, *Organometallics* **2021**, *40*, 2194–2197.

[28] a) B. M. Trost, J. T. Masters, *Chem. Soc. Rev.* **2016**, *45*, 2212–2238; b) Y. Hu, M. Bai, Y. Yang, Q. Zhou, *Org. Chem. Front.* **2017**, *4*, 2256–2275; c) M. Holmes, L. A. Schwartz, M. J. Krische, *Chem. Rev.* **2018**, *118*, 6026–6052; d) L. Fu, S. Greßies, P. Chen, G. Liu, *Chin. J. Chem.* **2019**, *38*, 91–100; e) Q. Dherbassy, S. Manna, F. J. T. Talbot, W. Prasitwatcharakorn, G. J. P. Perry, D. J. Procter, *Chem. Sci.* **2020**, *11*, 11380–11393.

[29] T. Hamada, R. Mizojiri, H. Urabe, F. Sato, *J. Am. Chem. Soc.* **2000**, *122*, 7138–7139.

[30] J. W. Han, N. Tokunaga, T. Hayashi, *J. Am. Chem. Soc.* **2001**, *123*, 12915–12916.

[31] M. Wang, Z. L. Liu, X. Zhang, P. P. Tian, Y. H. Xu, T. P. Loh, *J. Am. Chem. Soc.* **2015**, *137*, 14830–14833.

[32] W. Mao, M. Oestreich, *Org. Lett.* **2020**, *22*, 8096–8100.

[33] T. Nishimura, H. Makino, M. Nagaosa, T. Hayashi, *J. Am. Chem. Soc.* **2010**, *132*, 12865–12867.

[34] C. Jin, X. He, S. Chen, Z. Guo, Y. Lan, X. Shen, *Chem* **2023**, *9*, 2956–2970.

[35] Z. L. Wang, Q. Li, M. W. Yang, Z. X. Song, Z. Y. Xiao, W. W. Ma, J. B. Zhao, Y. H. Xu, *Nat. Commun.* **2023**, *14*, 5048.

[36] R. Bou Chedid, M. Brümmer, B. Wibbeling, R. Fröhlich, D. Hoppe, *Angew. Chem. Int. Ed.* **2007**, *46*, 3131–3134.

[37] Y. Tomida, A. Nagaki, J. Yoshida, *J. Am. Chem. Soc.* **2011**, *133*, 3744–3747.

[38] F. H. Zhang, X. Guo, X. Zeng, Z. Wang, *Nat. Commun.* **2022**, *13*, 5036.

[39] A. Hossain, R. L. Anderson, C. S. Zhang, P. J. Chen, G. C. Fu, *J. Am. Chem. Soc.* **2024**, *146*, 7173–7177.

[40] J. Ye, Y. Liao, H. Huang, Y. Liu, D. Fang, M. Wang, L. Hu, J. Liao, *Chem. Sci.* **2020**, *12*, 3032–3038.

[41] R. A. Brawn, J. S. Panek, *Org. Lett.* **2007**, *9*, 2689–2692.

[42] R. A. Brawn, J. S. Panek, *Org. Synth.* **2012**, *89*, 420–431.

[43] T. Okada, K. Sakaguchi, T. Shinada, Y. Ohfune, *Tetrahedron Lett.* **2011**, *52*, 5744–5746.

[44] T. Okada, N. Oda, H. Suzuki, K. Sakaguchi, Y. Ohfune, *Tetrahedron Lett.* **2010**, *51*, 3765–3768.

[45] B. K. Guintchin, S. Bienz, *Organometallics* **2004**, *23*, 4944–4951.

[46] T. E. Reynolds, A. R. Bharadwaj, K. A. Scheidt, *J. Am. Chem. Soc.* **2006**, *128*, 15382–15383.
[47] J. A. Dabrowski, F. Gao, A. H. Hoveyda, *J. Am. Chem. Soc.* **2011**, *133*, 4778–4781.
[48] X. Y. Dong, Y. F. Zhang, C. L. Ma, Q. S. Gu, F. L. Wang, Z. L. Li, S. P. Jiang, X. Y. Liu, *Nat. Chem.* **2019**, *11*, 1158–1166.
[49] R. Guo, J. Sang, H. Xiao, J. Li, G. Zhang, *Chin. J. Chem.* **2022**, *40*, 1337–1345.
[50] Z. Kong, W. Hu, J. P. Morken, *ACS Catal.* **2023**, *13*, 11522–11527.
[51] N. Xu, Z. Kong, J. Z. Wang, G. J. Lovinger, J. P. Morken, *J. Am. Chem. Soc.* **2022**, *144*, 17815–17823.
[52] a) G. P. Pale, J. Chuche, *Tetrahedron: Asymmetry* **1993**, *4*, 1991–1994; b) S. Klein, J. H. Zhang, M. Holler, J.-M. Weibel, P. Pale, *Tetrahedron* **2003**, *59*, 9793–9802.
[53] S. M. Sieburth, H. K. O'Hare, J. Xu, Y. Chen, G. Liu, *Org. Lett.* **2003**, *5*, 1859–1861.
[54] J. Zhu, H. Xiang, H. Chang, J. C. Corcoran, R. Ding, Y. Xia, P. Liu, Y. M. Wang, *Angew. Chem. Int. Ed.* **2024**, *63*, e202318040.
[55] L. L. Yang, J. Ouyang, H. N. Zou, S. F. Zhu, Q. L. Zhou, *J. Am. Chem. Soc.* **2021**, *143*, 6401–6406.
[56] I. Fleming, J. M. Mwaniki, *J. Chem. Soc., Perkin Trans. 1* **1998**, 1237–1248.
[57] M. Suginome, Y. Ito, *J. Organomet. Chem.* **2003**, *685*, 218–229.
[58] E. Canales, A. Z. Gonzalez, J. A. Soderquist, *Angew. Chem. Int. Ed.* **2007**, *46*, 397–399.
[59] M. Ogasawara, A. Okada, V. Subbarayan, S. Sörgel, T. Takahashi, *Org. Lett.* **2010**, *12*, 5736–5739.
[60] M. Deliaval, R. Jayarajan, L. Eriksson, K. J. Szabo, *J. Am. Chem. Soc.* **2023**, *145*, 10001–10006.