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手性烯丙基硅烷的催化对映选择性合成

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摘要 手性烯丙基硅烷作为多功能试剂被广泛应用于不对称合成中, 因而, 发展高效的方法构建该类化合物受到了大家的广泛关注. 伴随着不对称催化领域的快速发展, 催化不对称合成手性烯丙基硅烷已经取得了重要的进展. 详细总结了手性烯丙基硅烷催化不对称合成的进展, 并展示了其在有机合成中的应用.
关键词 手性烯丙基硅烷; 不对称合成; 催化合成

Catalytic Enantioselective Preparation of Chiral Allylsilanes

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Abstract Chiral allylsilanes, a versatile linchpin, are widely used in the area of asymmetric synthesis. Therefore, the development of efficient methodologies for the preparation of the enantioenriched allylsilanes has attracted great attention. Significant advances have been made in the catalytic enantioselective preparation of chiral allylsilanes by virtue of the rapid developments in asymmetric catalysis. The advances in the construction of chiral allylsilanes and their synthetic applications are summarized.
Keywords chiral allylsilanes; asymmetric catalysis; catalytic synthesis

1 Introduction

Organosilane compounds play increasingly important roles in multiple areas due to their stability and low toxicity, and have been extensively utilized in complex-molecule synthesis,[1] material science[2] and pharmaceutical chemistry.[3] Among those organosilanes, chiral allylsilanes have been long-known as a versatile linchpin, and have been widely utilized in area of asymmetric synthesis.[4] First, chiral allylsilanes are versatile synthetic precursors for the synthesis of chiral homoallylic alcohols via stereospecific Hosomi-Sakurai reaction.[5] The silyl group in chiral allylsilanes normally serves as a masked hydroxyl group involving in a variety of functionalization processes. Second, chiral allylsilanes can react with a wide range of electrophiles, which allows the preparation of various optically active molecules.[6] Moreover, the multifarious transformations on the carbon-carbon double bond could also significantly enhance the chemical space of those reagents.

In light of the importance of enantioenriched allylsilanes, the construction of this class of chiral compounds has attracted much attention.[7] Traditional synthetic routes for the preparation of enantioenriched allylsilanes normally starts from the optically active substrates via stoichiometric reactions, including Wittig olefination with optically active

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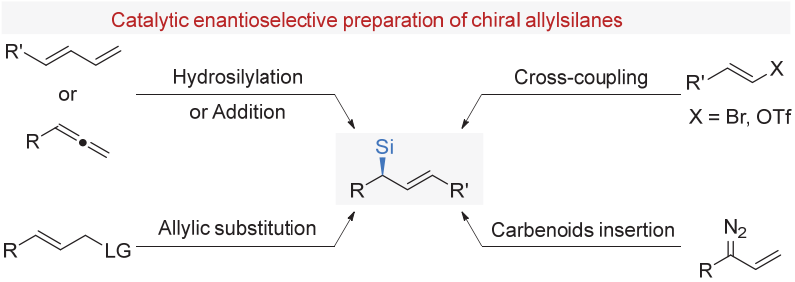
α-silylaldehydes,[8] allylic rearrangement (S_N2' reaction)[9] and Claisen rearrangement.[10] In addition, catalytic methods with the chiral auxiliary,[11] chiral substrate,[12] or chiral silicon reagent[13] are also demonstrated in the literature. However, these methodologies normally require unstable synthetic precursors, stoichiometric amount of chiral auxiliary or substrates, or harsh reaction conditions.

Along with the rapid progresses in asymmetric catalysis, the emerge of transition metal catalyzed asymmetric technologies invoke scientists to the direct synthesis of enantioenriched allylsilanes in the catalytic manner. The first catalytic asymmetric synthesis of chiral allylsilanes was reported by Kumada *et al.*[14] in 1982 via asymmetric cross-coupling reaction. Since then, much effort has been paid in catalytic asymmetric preparation of chiral allylsilanes, which has significantly accelerated their applications in synthetic chemistry. Despite of the importance of chiral allylsilanes in synthetic chemistry and the significant advances in the preparation of this class of chiral compounds, systematical summary on the catalytic asymmetric synthesis of allylsilanes has not be presented. One review on the synthesis of allylsilanes was published almost thirty years ago by Sarkar,[7] and some excellent professional reviews have appeared periodically over the past few decades.[15] Accordingly, the lack of a comprehensive review on catalytic synthesis of chiral allylsilanes prompts us to present this review. In this review, we mainly aim at the catalytic preparation of optically active allylsilanes via asymmetric hydrosilylation, allylic substitution, cross-coupling, insertion of metal carbenoids into Si—H bonds, addition and other methods (Scheme 1), and the catalytic processes with chiral reagents or substrates do not fall into the scope of current perspective.

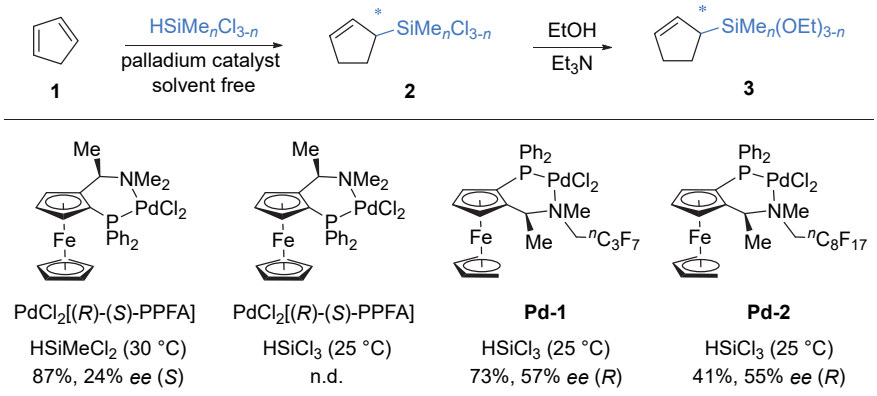
2 Asymmetric hydrosilylation with 1,3-dienes or allenes

Enantioselective hydrosilylation of unsaturated carbon-carbon bonds is a versatile synthetic route to form chiral allylsilanes, which has been extensively studied for decades. Back to 1983, Hayashi and co-workers[16] have presented a pioneering work for the preparation of cyclic allylsilanes with dichloromethylsilane as the hydrosilylating reagent, employing $PdCl_2$[(*R*)-(*S*)-PPFA] as the optimal chiral catalyst with very low catalyst loading (0.01 mol%) (left, Scheme 2). The optical purity was determined by converting the unstable hydrosilylated product **2** to the corresponding diethoxymethylsilane **3**. However, the current catalyst was less efficient in enantioselectivity, and was inactive with other silane sources, such as trichlorosilane (middle left, Scheme 2). The higher chiral induction was given when polyfluoroalkyl groups were introduced onto the amine donor of the original palladium catalyst (right, Scheme 2).[17] The author hypothesized that the high activity was partially attributed to the improved solubility of palladium catalysts **Pd-1** and **Pd-2**. In 1995, Hiyama group[18] further evaluated the $PdCl_2$[(*R*)-(*S*)-PPFA] catalyst in the asymmetric reaction with difluoro(phenyl)silane. The corresponding allylsilane was given in moderate enantioselectivity (77% *ee*) by employing the combination of [PdCl(η^3-C_3H_5)]$_2$ and **L1** (Scheme 3).

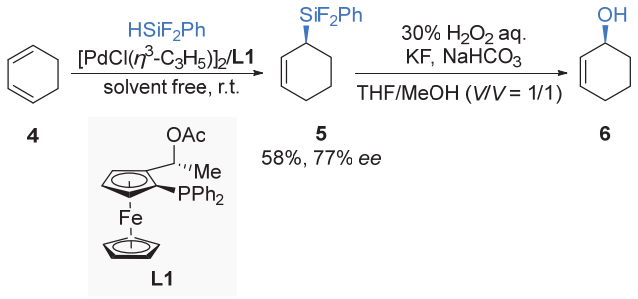
In 1990, Achiwa and co-workers[19] developed a new type



Scheme 1 Catalytic enantioselective preparation of chiral allylsilanes



Scheme 2 Early examples on Pd-catalyzed asymmetric hydrosilylation



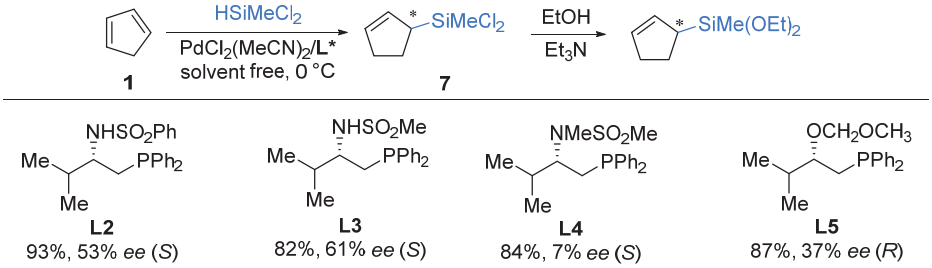
Scheme 3 Pd-catalyzed asymmetric hydrosilylation with difluoro(phenyl)silane

of chiral monophosphine ligand, chiral (*β*-*N*-sulfonylaminoalkyl)phosphine, and evaluated its enantio-inducing ability in Pd-catalyzed asymmetric hydrosilylation of cyclopentadiene with dichloromethylsilane (Scheme 4). Although moderate enantioselectivity was obtained, the reaction was performed efficiently even at low temperature (up to 93% at 0 ℃). It should be mentioned that the NH group in the chiral ligand was crucial for the high enantioselectivity (**L3** vs **L4**), and the replacement of amino group with ether group on the ligand (**L5**) resulted in a reverse stereo-configuration.

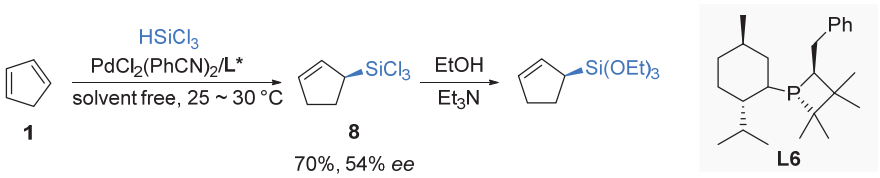
In 1994, Marinetti[20] designed a new class of chiral phosphines, *P*-menthylphosphetane (**L6**), which was later used in Pd-catalyzed asymmetric hydrosilylation (Scheme 5). Excellent efficiency and moderate enantioselectivity were found with the combination of $Pd(PhCN)_2Cl_2$/**L6** (1/1).

Another type of chiral monodentate phosphine ligand (MOP) designed by Hayashi group[21] was employed to the palladium catalyzed asymmetric hydrosilylation of 1,3-cyclopentadiene with trichloroshilane in 2001 (Scheme 6). The great improvement on the enantioselectivity was observed by the employment of **L7** with an axially chiral binaphthyl moiety. It should be mentioned that the aryl group at the 2' position of **L7** affected the stereochemical outcomes, where 90% *ee* could be afforded when electron-rich and steric hindered Ar-MOP was used. The next year, the same group[22] further modified this binaphthyl based ligand by installation of *n*-octyl group on 6 and 6' positions (**L8**), which resulted in a higher enantioselectivity under the same reaction conditions compared to that with **L7**. Subsequently, Han *et al.*[23] reported the utilization of a chiral phosphoramidite ligand **L9** derived from (*S*)-1,1-bi(2-naphthol) [(*S*)-BINOL] and a secondary amine in the palladium-catalyzed asymmetric hydrosilylation of cyclohexadiene, yielding the enantioenriched cyclic allylsilane **9** in 87% *ee* (Scheme 7).

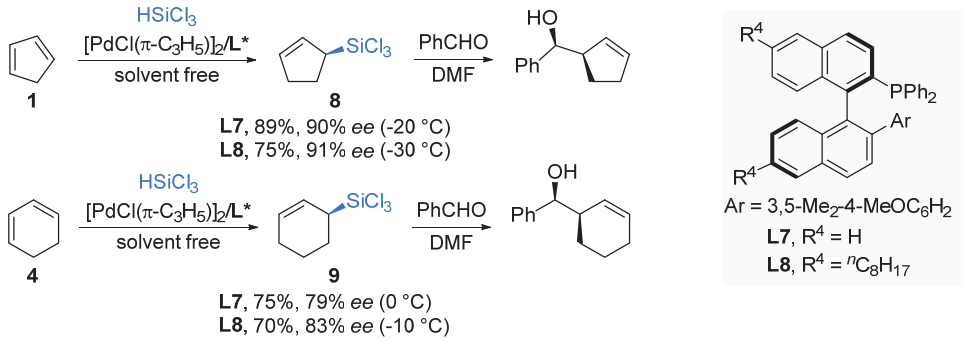
The evolution of catalytic system promotes the develop-



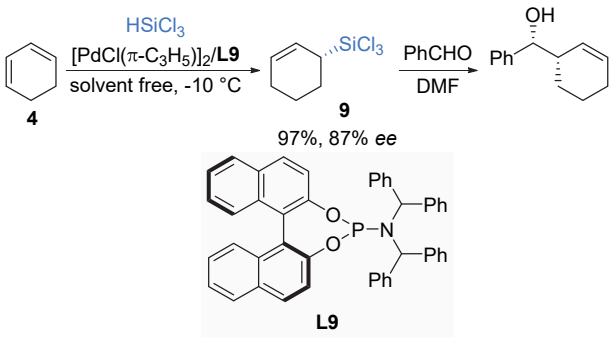
Scheme 4 Pd-catalyzed asymmetric hydrosilylation using chiral (*β*-*N*-sulfonylaminoalkyl)phosphine ligand



Scheme 5 Pd-catalyzed asymmetric hydrosilylation using *P*-menthylphosphetane ligand



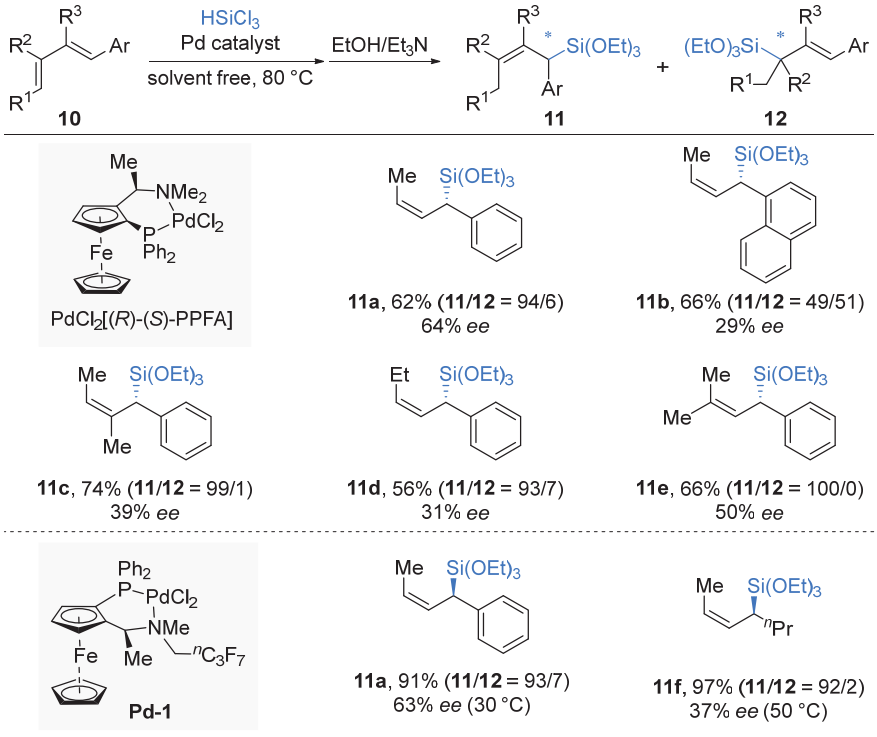
Scheme 6 Pd-catalyzed asymmetric hydrosilylation of cyclic 1,3-dienes with monodentate phosphine ligand



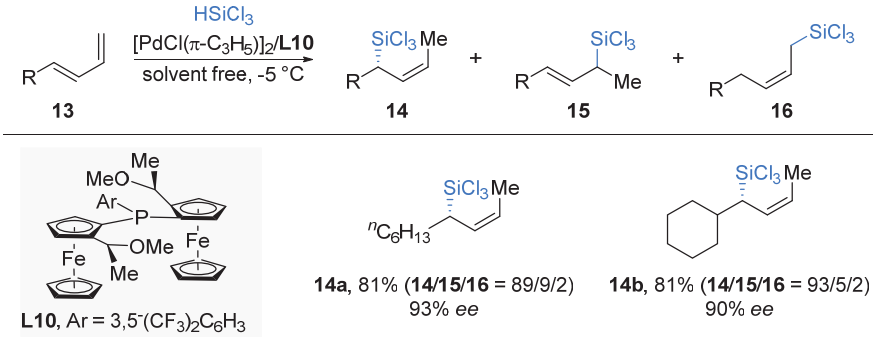
Scheme 7 Pd-catalyzed asymmetric hydrosilylation of cyclic 1,3-dienes with chiral phosphoramidite ligands

ment of asymmetric hydrosilylation of cyclic 1,3-diene. Meanwhile, the enantioselective hydrosilylation of acyclic 1,3-diene has also been investigated. In 1985, Hayashi and co-workers[24] realized the enantioselective hydrosilylation of acyclic 1,3-diene with trichlorosilane in the presence of $PdCl_2$[(*R*)-(*S*)-PPFA] (Scheme 8). (*Z*)-1-Silyl-2-butenes, which could barely be accessible by the previous asymmetric Grignard cross-coupling, was reached in high regioselectivities with moderate chiral induction, when the (*E*)-1-phenylbutadiene and its derivatives with methyl substituent were involved. However, hydrosilylation of (*E*)-1-(1-naphthyl)butadiene (**10b**) delivered the corresponding product with low regioselectivity. The introduction of fluoroalkyl group into the catalyst (**Pd-1**) further expanded the scope of the acyclic 1,3-diene, producing the 1-alkyl/aryl allylsilane in high regioselectivities albeit with moderate enantioselectivities.[17]

In 2002, a new ferrocenylmonophosphine ligand containing two chiral ferrocenyl units (**L10**) was developed by the same group.[25] The enantioselectivity was further improved to 93% with this newly developed ligand (Scheme 9).



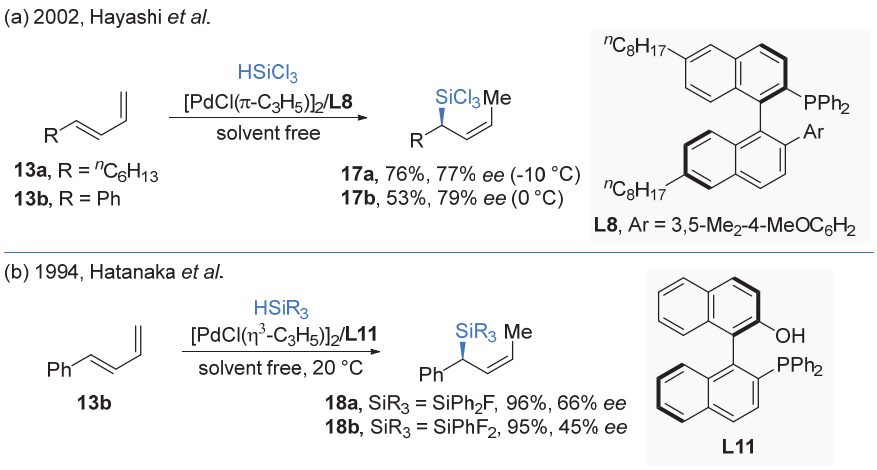
Scheme 8 Pd-catalyzed asymmetric hydrosilylation with 1,3-dienes



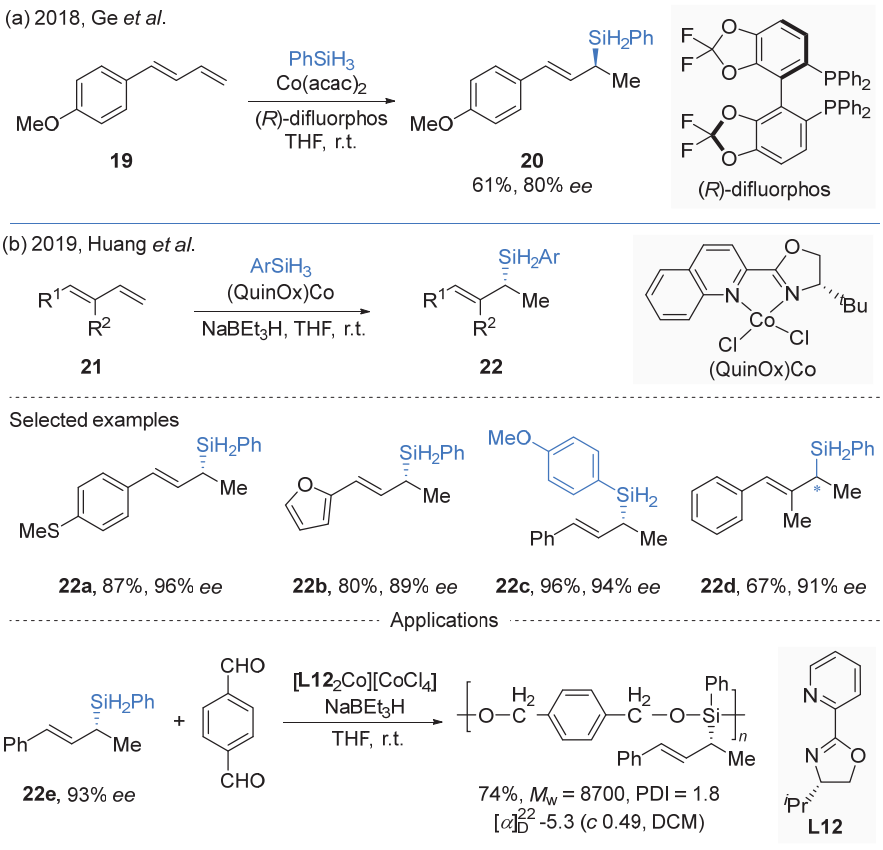
Scheme 9 Pd-catalyzed asymmetric hydrosilylation with acyclic 1,3-diene

The chiral ligands with an axially chiral binaphthyl moiety have also been valued in the asymmetric hydrosilylation of linear 1,3-diene. Although good enantioinduction was found with MOP ligand (**L8**) with cyclodiene (Scheme 6), moderate enantioselectivity was given with linear ones (Scheme 10, a)[22]. In 1994, Hatanaka and co-workers[26] evaluated the chiral (*R*)-2-diphenylphosphino-1,1'-binaphthyls (**L11**) in the hydrosilylation of linear conjugated diene. The substituents on the silane highly affected the chiral induction and the highest enantioselectivity was obtained with $HSiPh_2F$ (96% yield, 66% *ee*) (Scheme 10, b).

In 2018, Ge group[27] developed a cobalt-catalyzed 1,2-Markovnikov hydrosilylation of conjugated dienes in the stereoconvergent manner for the first time (Scheme 11, a), which gave the chiral allylsilanes in good yields and enantioselectivities by utilizing (*R*)-difluorphos as the optimal ligand. The next year, Huang group[28] systematically explored this asymmetric 1,2-Markovnikov hydrosilylation by employing a quinoline-oxazoline cobalt complex (Scheme 11, b). The hydrosilylation of various 1,3-dienes, such as 1,3-dienes with thioether or heterocycle, and 1,2-disubstituted dienes, proceeded smoothly, yielding the corres-



Scheme 10 Pd-catalyzed asymmetric hydrosilylation with 1,3-dienes

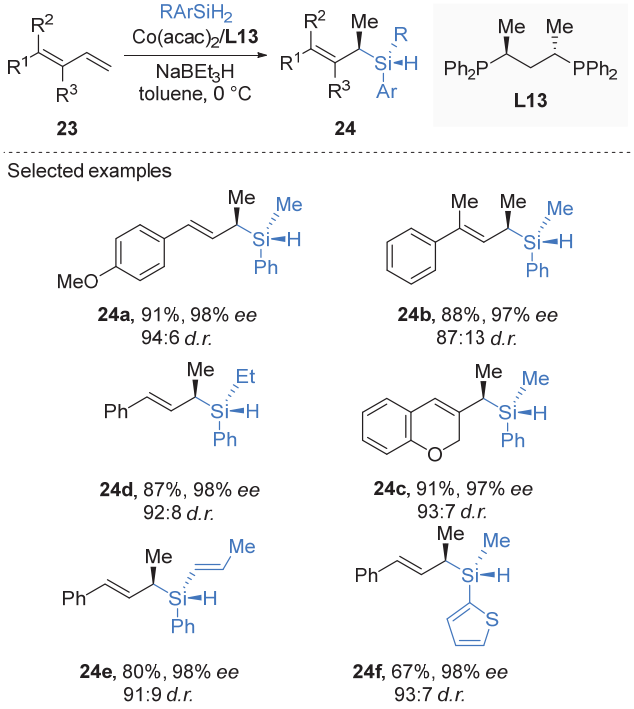


Scheme 11 Co-catalyzed asymmetric hydrosilylation with 1,3-dienes

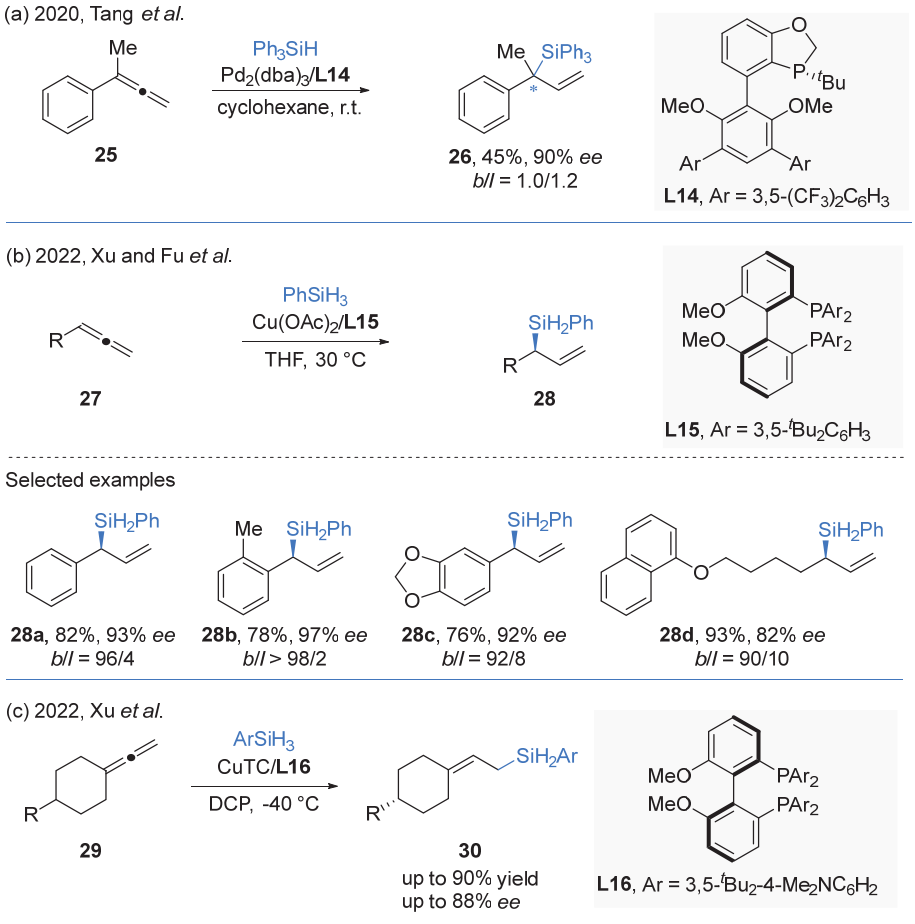
ponding chiral allylsilanes in high regioselectivity and enantioselectivity. Furthermore, the applications of the chiral product **22e** were also demonstrated, including utilization as monomer in cobalt-catalyzed step-growth polymerization.

Despite of rapid advances in the area of asymmetric hydrosilylation reaction, the construction of both carbon-centered and silicon-centered chirality in one reaction is largely less mentioned. In 2022, the Wang group[29] achieved the construction of both chiral centers via intramolecular hydrosilylation with high diastereoselectivities and enantioselectivities. Following this lead, Meng, Chong and co-workers[30] published a Co-catalyzed intermolecular hydrosilylation of 1,3-dienes with prochiral silane, which could afford the products bearing both a carbon-stereogenic and a silicon-stereogenic center with high regio-, diastereo- and enantioselectivities in the presence of bisphosphine **L13** (Scheme 12).

Recently, the asymmetric hydrosilylation of allenes has been explored as the alternative approach to access of various chiral allylsilanes (Scheme 13, a).[31] Tang group demonstrated the first example of asymmetric hydrosilylation of allenes **25** with a combination of $Pd_2(dba)_3$ and a mono-phosphine ligand. Utilization of a P-chiral monophosphorus ligand **L14**, the high enantioselectivity with moderate regioselectivity was found when monohydrosilane was used as substrate.



Scheme 12 Co-catalyzed asymmetric hydrosilylation of 1,3-dienes for the construction of Si-stereogenic allylsilanes



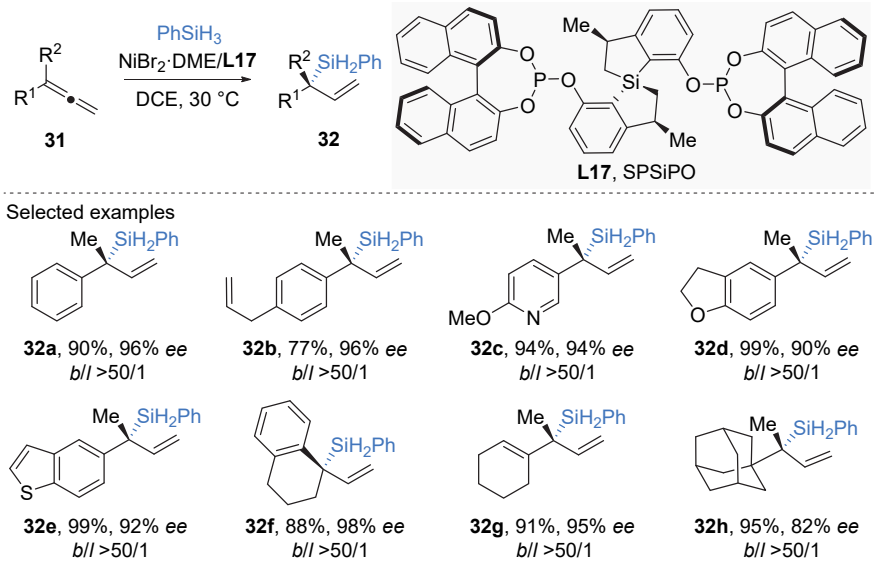
Scheme 13 Pd- and Cu-catalyzed asymmetric hydrosilylation of allenes

In 2022, Xu and Fu group[32] developed a copper-catalyzed hydrosilane of monosubstituted allenes **27**. In this work, the regioselectivity could be controlled by the choice of solvent, and the branched chiral allysilanes **28** were obtained in tetrahydrofuran (THF) with high regioselectivities and enantioselectivities (up to 98/2 *r.r.*, 97% *ee*) with the aid of $Cu(OAc)_2$ and C_2-symmetric bisphosphine ligand **L15** (Scheme 13, b). A series of aromatic-, aliphatic-substituted chiral allylsilanes were accessible in moderate to high yields (74%～98%) and excellent regio- and enantioselectivities. They further applied this catalyst system in the asymmetric hydrosilylation of 4-substituted vinylidenecyclohexanes **29**, delivering the allylsilanes **30** featuring an axial charity (Scheme 13, c).[33]

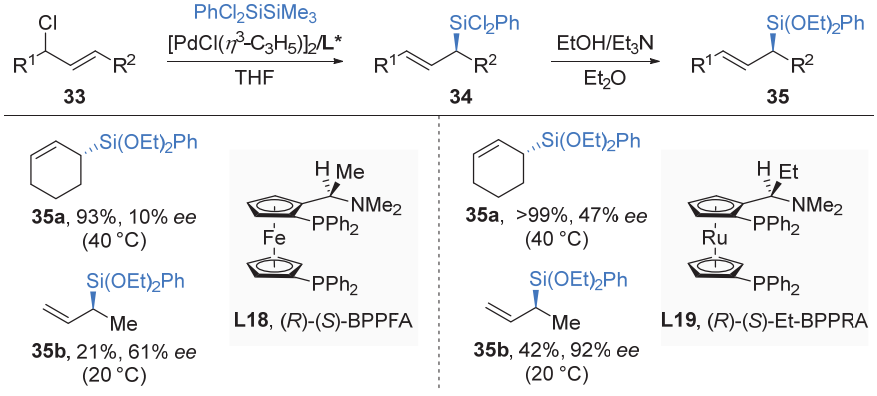
Recently, Wang group[34] presented an elegant protocol for the preparation of chiral tertiary allylsilanes **32** in excellent enantioselectivities and regioselectivities via nickel-catalyzed asymmetric hydrosilylation of 1,1-disubstituted allenes **31** (Scheme 14). The key to achieve this stereoselective hydrosilylation reaction was the employment of their developed SPSiOL-derived bisphosphite ligand (SPSiPO, **L17**).[35] 1,1-Disubstituted allenes containing (hetero)aryl groups were well compatible. Notably, the chemoselectivity was evaluated with the substrate bearing a terminal alkene motif (**32b**), and the enantioselective hydrosilylation selectively occurred on the allene motif rather than the alkenyl group. Furthermore, the allylsilane bearing a cyclic tertiary carbon center **32f** was also accessible in excellent enantioselectivity (98% *ee*). Density functional theory (DFT) calculations revealed the detailed reaction mechanism and the origins of the high enantioselectivity.

3 Asymmetric Allylic Substitution with Nucleophiles

In addition to the transition metal catalyzed asymmetric hydrosilylation of dienes and allenes, the asymmetric allylic substitution with silicon nucleophiles is another well-known process for the preparation of chiral allylsilanes. The early research on this field was performed by Hayashi and co-workers[36] via palladium-catalyzed silylation of linear allylic chlorides. The asymmetric version was also demonstrated by the employment of the chiral ligand (*R*)-(*S*)-BPPFA (**L18**, left, Scheme 15). Due to the instability of the



Scheme 14 Synthesis of chiral α-tertiary allylsilanes via nickel/SPSiPO catalyzed hydrosilylation

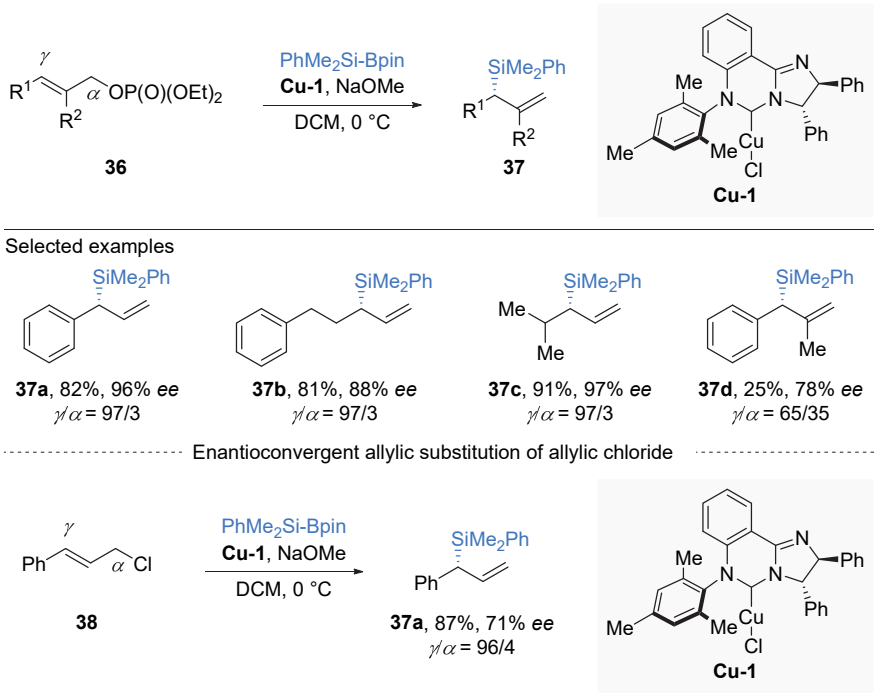


Scheme 15 Palladium-catalyzed asymmetric allylic substitution with disilanes

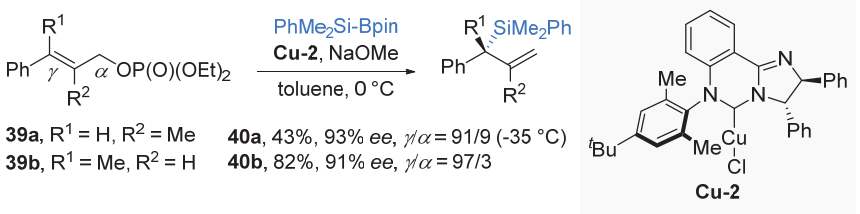
direct silylation product **34**, the further transformation was performed, producing **35** in low to moderate enantioselectivities (up to 61% *ee*). The following year, Yanagi *et al.*[37] developed a new chiral bisphosphine (*R*)-(*S*)-Et-BPPRA (**L19**) bearing a 1,1'-bis(diphenylphosphino)ruthenocene skeleton, which possesses a wider P—Pd—P bite angle in the complex of $PdCl_2$ than that of the corresponding ferrocene analog. The modification on the chiral backbone resulted in a better chiral induction in the above asymmetric palladium-catalyzed silylation reactions, yielding the same chiral silylated products **35** in significantly higher enantioselectivities (right, Scheme 15).

In 2013, Oestreich group[38] reported a copper-catalyzed allylic substitution of linear allylic chlorides and phosphates with silylborane reagent ($PhMe_2Si$-Bpin) (Scheme 16). The branched silylated products **37** were achieved in high regio- and enantioselectivities in the presence of the chiral *N*-heterocyclic carbene (NHC)-Cu(I) complex (**Cu-1**), which was first developed by McQuade group.[39] Compared to the allylic chlorides, the reaction with the phosphates presented in higher enantioselectivity (96% *ee* vs 71% *ee* for **37a**). It should be mentioned that the substitute on the *β*-position of **37d** affected both the regioselectivity and enantioselectivity (γ/α = 65/35, 78% *ee*). To overcome this limitation, the same group employed a sterically more demanding NHC-Cu(I) complex (**Cu-2**). After systematically examination of the influence of ligand, solvent and temperature (Scheme 17),[40] the enantioselectivity of **40a** was improved to 93% *ee* with **Cu-2** in toluene at −35 ℃. The substrate bearing a *γ*-methyl group (**39b**) could also provide the corresponding allylic silane **40b** in good isomeric purity (91% *ee* and γ/α = 97/3). Later, they also applied the chiral complex **Cu-1** in the silylation of cyclic phosphates, which could deliver the cyclic allylsilane **42** with high *γ*-selectivity (Scheme 18). The mechanistic studies unveiled that both enantiomers of cyclic phosphate underwent the same S_N2' pathway but with opposite diastereofacial selectivity, leading to the direct enantioconvergent silylation.[41]

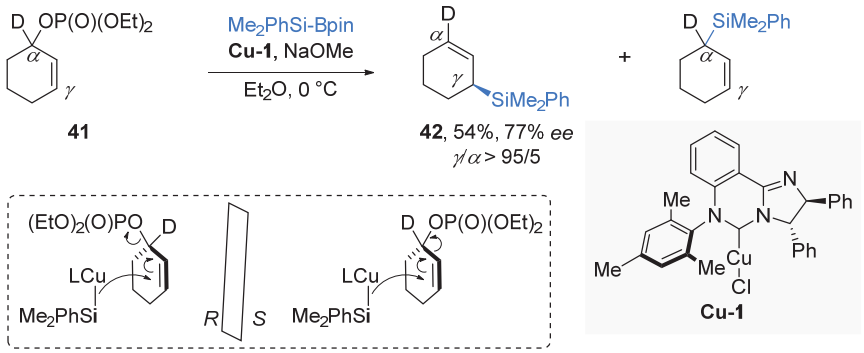
In the same year, Hayashi and Shintani *et al.*[42] also reported the same reaction with the aid of new chiral NHC ligand **L20** (Scheme 19). The reaction had good functional groups tolerance, such as naphthyl, thienyl, and alkyl groups. Moreover, the tetrasubstituted carbon stereocenters were accessed in high enantioselectivities by utilization of *γ*,*γ*-disubstituted allyl phosphates. The application of the chiral allylic silanes was also presented, producing the enantioenriched homoallylic alcohols in high enantioselectivities.



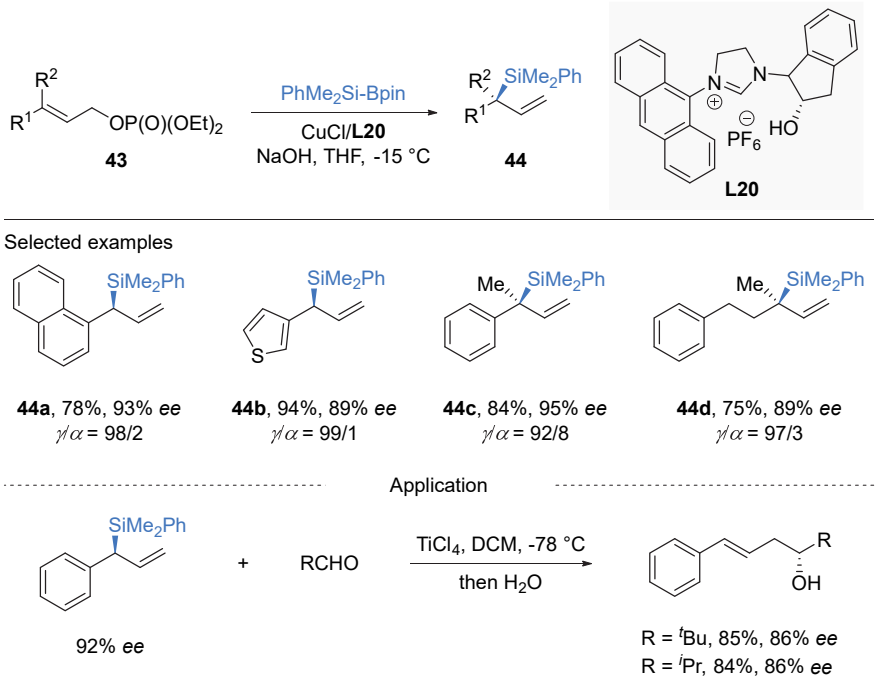
Scheme 16 **Cu-1** catalyzed asymmetric allylic substitution



Scheme 17 **Cu-2** catalyzed asymmetric Si-allylic substitution



Scheme 18 Asymmetric Si-allylic substitution with McQuade's catalyst

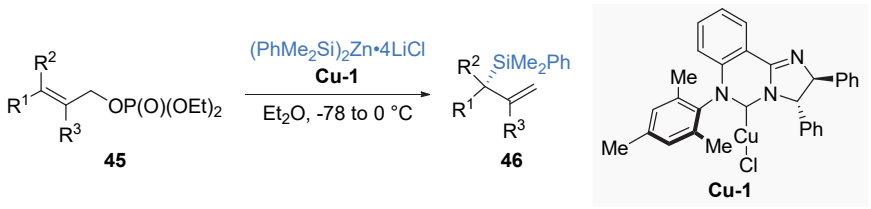


Scheme 19 Cu/**L20**-catalyzed asymmetric allylic substitution

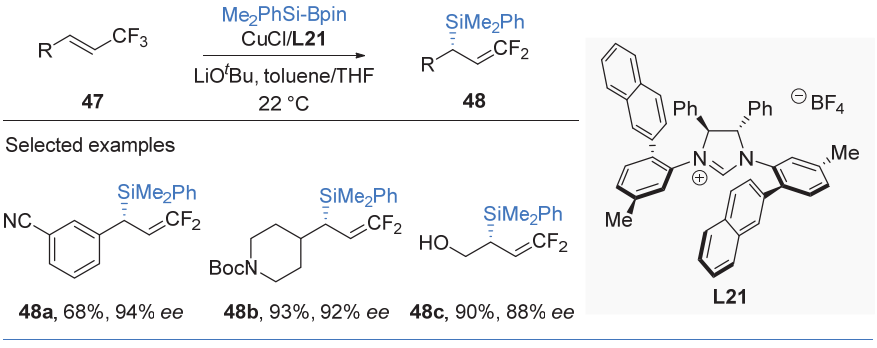
In 2015, Oestreich group[43] revisited this Cu-catalyzed asymmetric allylic substitution of acyclic allyl phosphates employing the soft bis(triorganosilyl) zinc reagent[44] as the silicon nucleophile (Scheme 20). With Cu-NHC complex (**Cu-1**), the allylic silylated products **46** were reached in high regioselectivities and enantioselectivities. It should be noteworthy that the variant substitutions on silicon atom could be achieved due to the easy access of zinc reagents, albeit with lower enantioselectivities when steric bulk group was attached to silicon.

Except for using allyl chlorides and phosphates as the substrates, trifluoromethyl substituted alkenes were also valued in this asymmetric allylic silylation reaction, producing the chiral *gem*-difluroalkene in high efficiency.[45] In 2019, Hoveyda and Torker group[46] introduced the Cu/chiral NHC ligand **L21** as the catalyst in approaching *γ*-silyl-*α*,*α*-difluroalkenes in good enantioselectivities (Scheme 21, a). The mechanistic investigation revealed that Cu—F elimination was the slow step, which could be speeded up by the addition of a mild Lewis acid to associate with the departing fluoride anion. Subsequently, Shi, Li and co-workers[47] realized the similar reaction employing chiral triazolium-based NHC ligands **L22**, producing a series of the enantioenriched *gem*-difluoroallylsilanes **50** in 42%～93% *ee* (Scheme 21, b). The *β*-difluoromethyl alcohol could be accessed via the stereospecific oxidation of the enantioenriched *gem*-difluoroallylsilane.

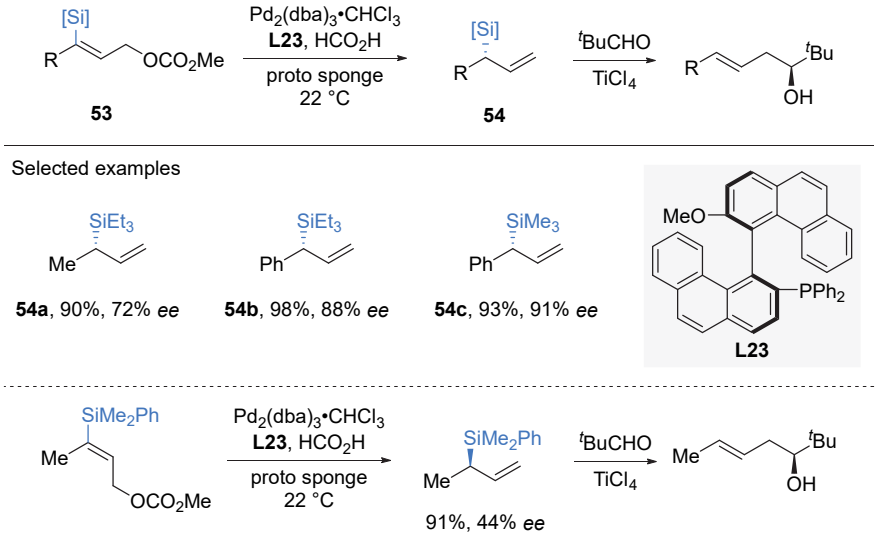
The asymmetric reduction or allylic substitution reaction of the *γ*-silylated allylic alcohol derivatives provides another alternative access to the chiral allylsilanes. The initiate study was carried out by Hayashi and his co-workers[48] in 1994 with the catalyst system of palladium catalyst combined with axially chiral monodentate phosphine ligand **L23** (Scheme 22). This asymmetric hydride addition of silyl substituted allylic esters (reduction) with formic acid as the hydride source proceeded smoothly, furnishing the allylsilanes **54** in high regio- and enantio-selectivities.



Scheme 20 Synthesis of chiral allylsilanes with bis(triorganosilyl)zinc compounds



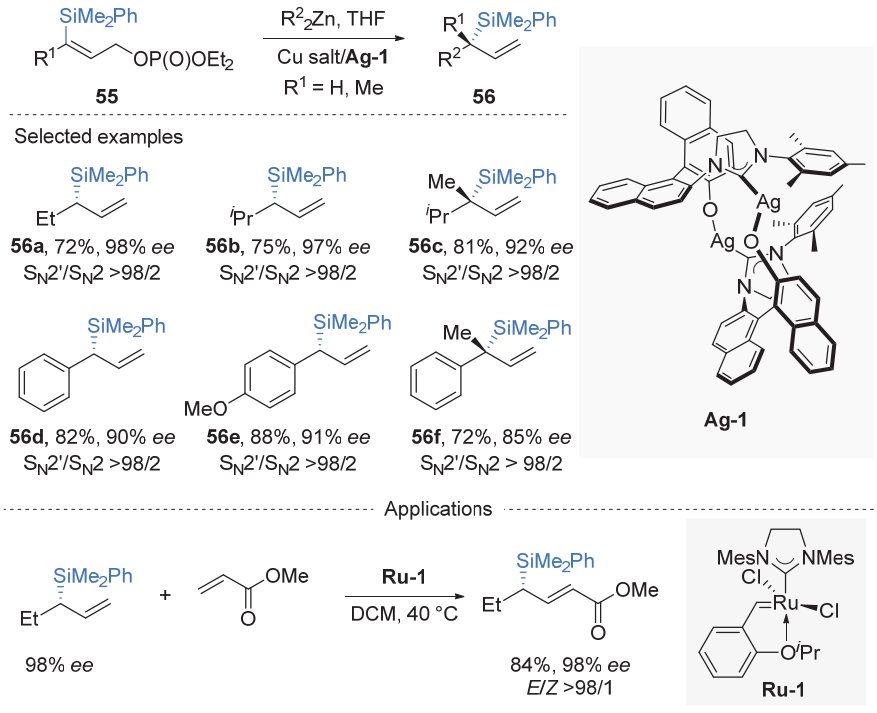
Scheme 21 Catalytic enantioselective silyl-substitution with trifluoromethyl alkenes



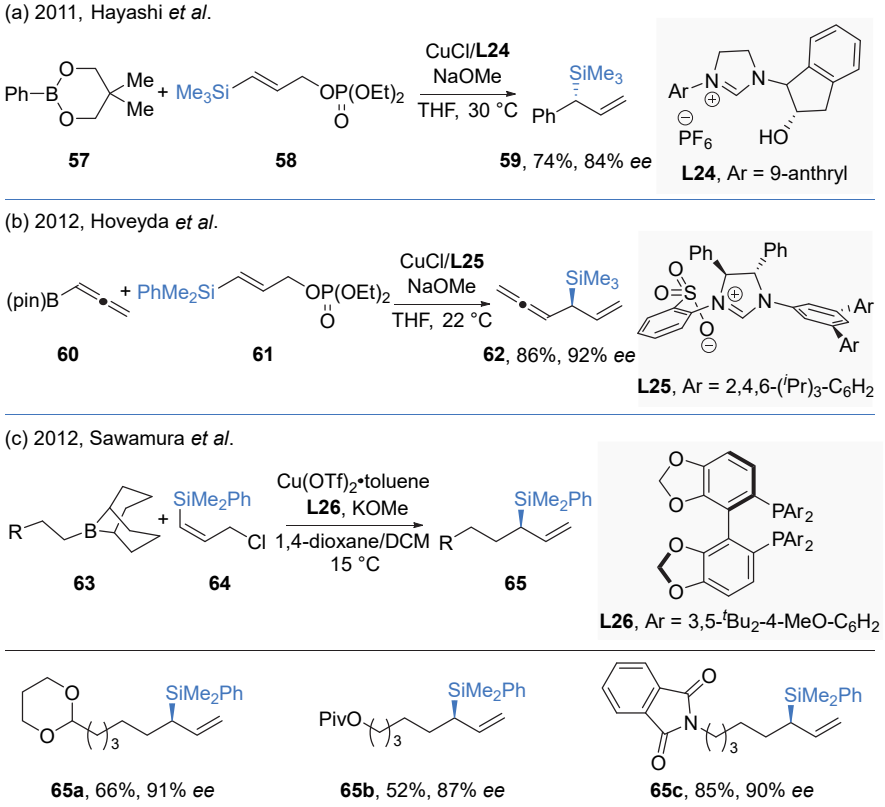
Scheme 22 Asymmetric reduction of the γ-silylated allylic alcohol derivatives

In 2007, Hoveyda group[49] outlined the catalytic asymmetric allylic substitution with organozinc reagents as the nucleophiles for the first time (Scheme 23). A variety of the allylsilanes were afforded in up to 98 % *ee* with greater than 98% site-selectivity (S_N2'/S_N2) in the presence of Cu/chiral bidentate NHC ligand with a low catalyst loading. It was worth noting that silanes with quaternary carbon stereogenic centers could also be accessible, which was difficult to construct. Moreover, the product was demonstrated to utilize in the olefin metathesis.

In 2011, Hayashi and co-workers[50] developed the Cu-catalyzed asymmetric allylic substitution of γ-silylated allyl phosphates with arylboronic acid neopentylglycol esters. When γ-silylated allylic alcohol derivative **58** was employed, chiral allylsilane **59** could be prepared in 74% yield with 84% *ee* by utilizing chiral NHC-based ligand **L24** (Scheme 24, a). The following year, Hoveyda and co-worker[51] employed allenylboronic acid pinacol ester as the nucleophile in Cu-catalyzed enantioselective allylic substitutions with allylic phosphates, which could provide the allenyl-substituted chiral allylsilane **62** in 86% yield and 92% *ee* (Scheme 24, b). Subsequently, Sawamura group[52] introduced the alkylboron compounds (alkyl-9-BBN, **63**) to the Cu-catalyzed enantioselective allylic substitution reaction (Scheme 24, c). With (*Z*)-allyl chloride **64**, enantioenriched α-stereogenic chiral allylsilanes **65** were afforded in good enantioselectivities with good functional tolerance including ester, phthalimide, or chlorine moieties.



Scheme 23 Cu-catalyzed asymmetric allylic substitution with organozinc reagents

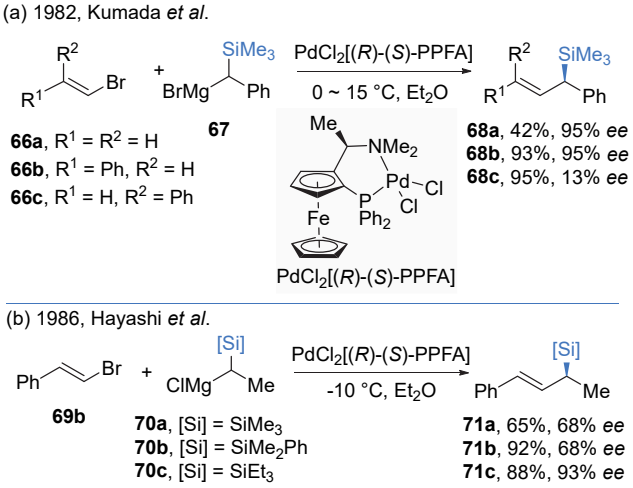


Scheme 24 Cu-catalyzed asymmetric allylic substitution with Si-containing allyl partners

4 Catalytic asymmetric cross-coupling with vinyl bromides or enol triflates

The first access to the enantioenrich chiral allylsilanes through catalytic asymmetric cross-coupling reaction was demonstrated by Kumada and co-workers[14] in 1982 (Scheme 25, a). The high enantioselective allylsilane **68** was afforded by the reaction between vinyl bromide **66** and (trimethylsilyl)benzylmagnesium bromide **67** in the presence of PdCl$_2$[(*R*)-(*S*)-PPFA]. In 1986, the same group[53] revisited this reaction (Scheme 25, b), and found that the silyl substituents of the Grignard reagent affected the enantioselectivities.

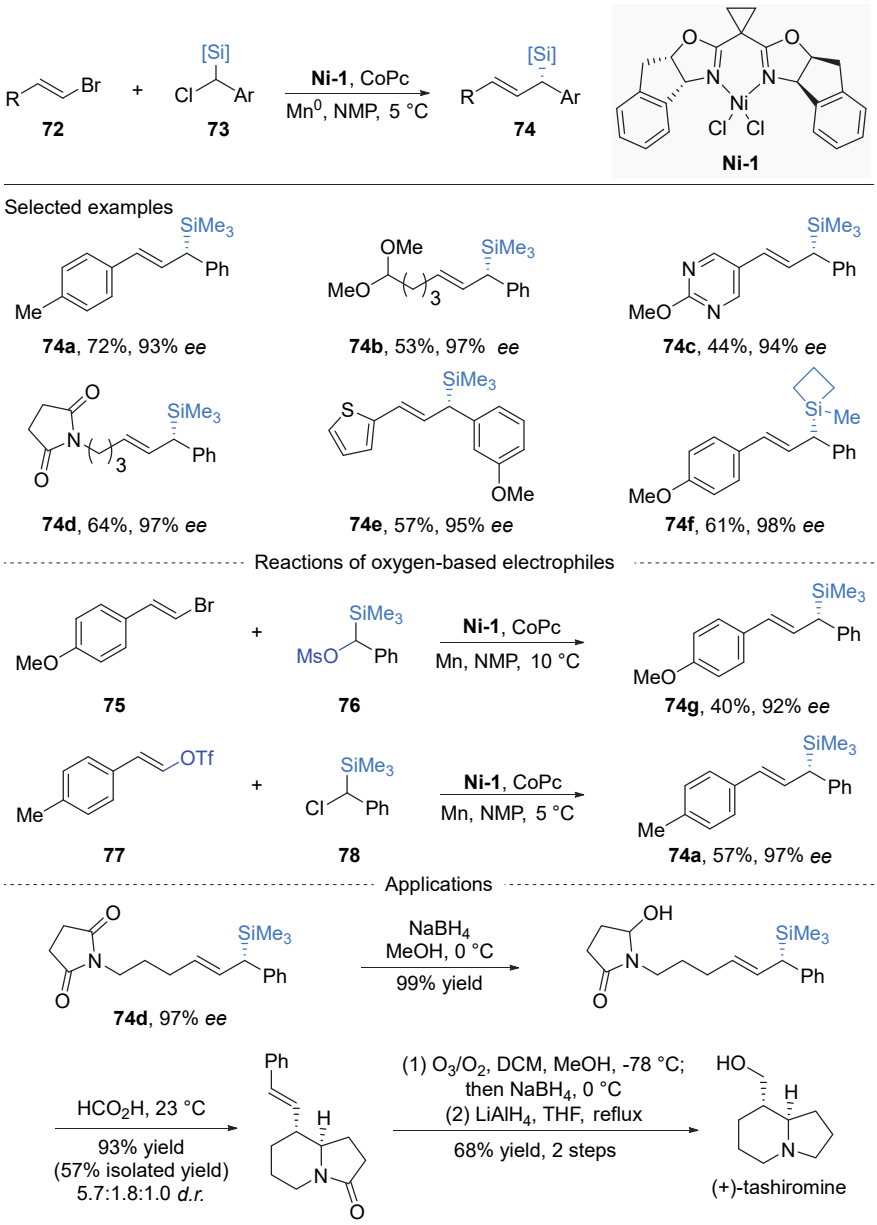
The research on transition metal-catalyzed reductive coupling between two electrophiles has recently attracted considerable attention,[54] which has also been utilized in the synthesis of chiral allylic silanes since 2018. Reisman group[55] reported the asymmetric Ni-catalyzed reductive cross-coupling between vinyl bromide **72** and chlorobenzyl silane **73** (Scheme 26). Employing chiral bis(oxazoline) ligand, the reaction proceeded smoothly with good functional group and heterocycle compatibility. Moreover, the products **74** with various decoration on silane atom were also accessible. It should be mentioned that *cis*-alkenyl bromides, tri- and tetra-substituted alkenyl bromides could not react under this reaction conditions. The preliminary investigations with other electrophiles (benzyl mesylate (**76**) or enol triflate (**77**)) further highlighted the generality of this protocol, leading to high enantioselectivities with



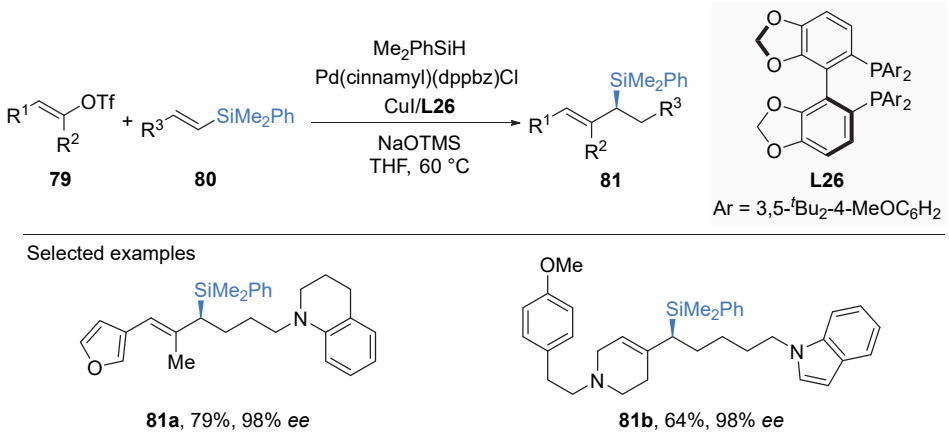
Scheme 25 Palladium-catalyzed asymmetric Kumada-type alkenylation

moderate yields. Furthermore, the author demonstrated the concise synthesis of (+)-tashiromine by utilizing their current method for the construction of the key intermediate **74d**.

In 2022, Buchwald and co-workers[56] developed a general protocol for the access of the chiral *α*-stereogenic allyl metalloids, including the allylic silanes (Scheme 27). With (*S*)-DTBM-Segphos (**L26**), the asymmetric hydroalkenylation of vinyl metalloids could be achieved via the CuH and Pd relay catalysis, affording the silylated product **81** in good



Scheme 26 Nickel-catalyzed enantioselective reductive alkenylation of α-chloro benzylsilanes



Scheme 27 CuH/Pd-catalyzed asymmetric hydroalkenylation of vinyl metalloids

to high enantioselectivities. It should be noted that the substituents attached on the silicon atom highly affected the efficiency of the reaction.

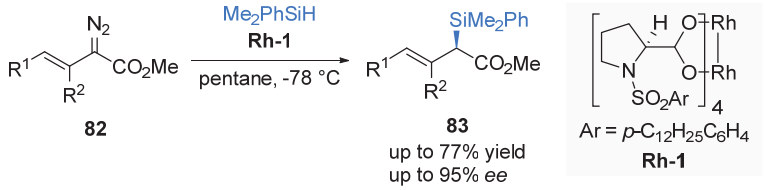
5 Enantioselective insertion of carbenoids into Si—H bond

The insertion of metal carbenoids into Si—H bond is an attractive process to reach the *α*-silyl-substituted carbon-stereogenic center, which could be traced back to 1988 by the Doyle group.[57] In 1997, this strategy has been successfully introduced in the construction of enantioselective allylsilanes by Davies group (Scheme 28).[58] By the employment of rhodium(II) (*S*)-*N*-(*p*-(dodeeylphenyl)sulfonyl)prolinate (**Rh-1**), the asymmetric insertion of alkenyl *α*-diazoesters delivered the target products **83** in up to 95% *ee*.

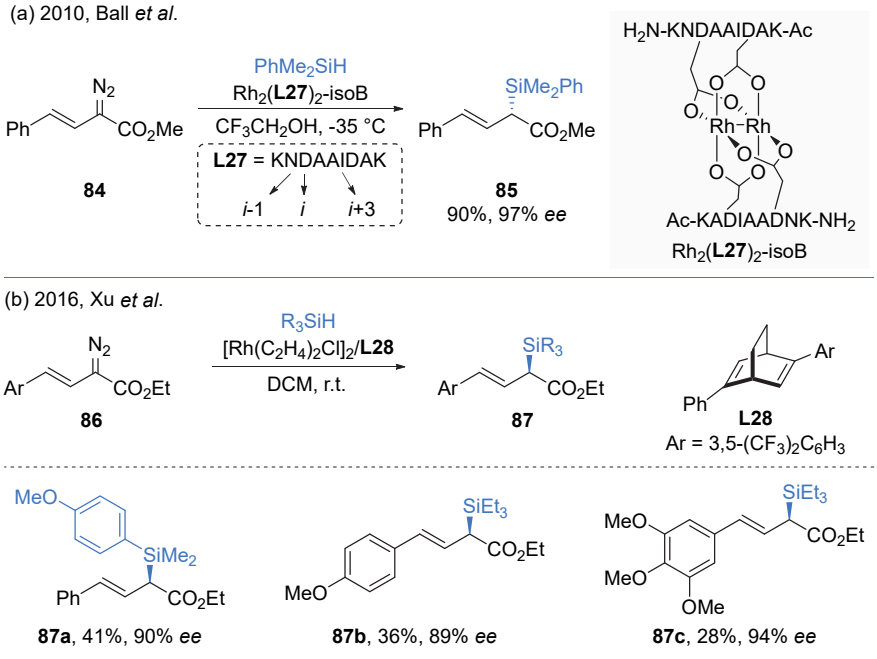
In 2010, Ball and co-workers[59] evaluated the rhodium-catalyzed asymmetric insertions into Si—H with various natural peptide-derived carboxylate ligands. The systematical study on the peptide ligands indicated *i*−1 and *i*+3 positions have significant influence on the chiral induction mainly because the binding between rhodium and the above two positions in ligand resulted in strongly helical. And the high enantioselectivities could be reached to afford the chiral allylsilane **85** when Rh_2(**L27**)$_2$-isoB was employed as catalyst (Scheme 29, a).

Following their studies on the asymmetric B—H insertion of *α*-diazo carbonyl compounds,[60] Xu group[61] extended their newly developed rhodium(I)-diene catalyst to the reaction of Si—H insertion (Scheme 29, b). The enantioselective insertion of alkenyl *α*-diazoesters and alkenyl *α*-diazophosphonates into Si—H bond proceeded smoothly under mild conditions by the utilization of the C_1-symmetric chiral diene ligand **L28** bearing a bicyclo[2.2.2]octadiene skeleton. With the optimal conditions, three examples regarding the preparation of chiral allylsilanes were demonstrated by the reaction of vinyl substituted diazoesters **87** in 89%～94% *ee*.

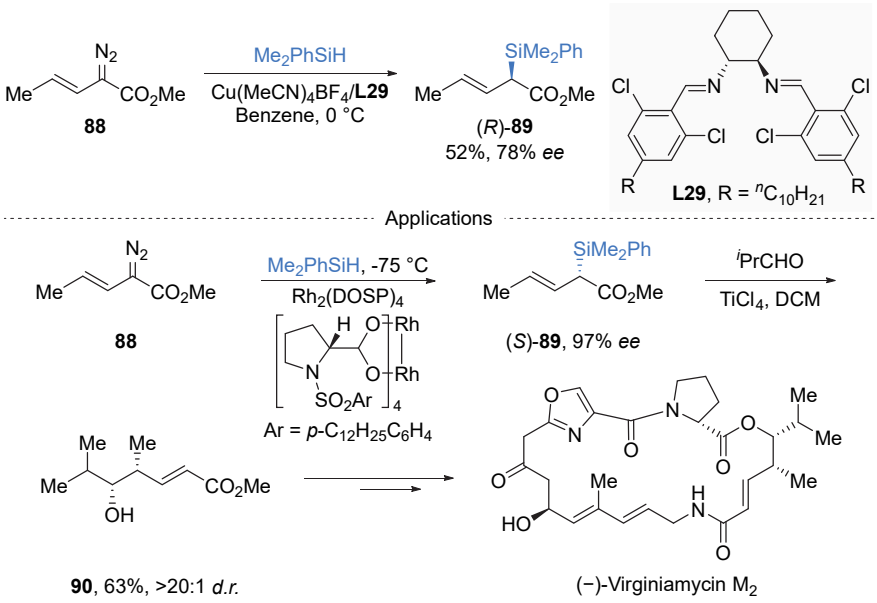
In addition to the wide exploration of rhodium catalyst in asymmetric metal-carbene or carbenoid insertion into Si—H bond, other transition metals were also evaluated. In 2010, Panek group[62] investigated the asymmetric metal-carbene or carbenoid insertion reaction with C_2-symmetric copper(I) diimine complexes (Scheme 30). Although a slightly high chiral induction was found with $Rh_2(DOSP)_4$, this Cu(I)-catalyzed reaction could be considered as the economical alternative. Moreover, the author[63] presented the stereoselective synthesis of antibiotic (−)-virginiamycin M_2 with the chiral allylic silane (*S*)-**89** as the key intermediate.



Scheme 28 Rh(II)-prolinate catalyzed enantioselective insertion of allylic carbenoids into Si—H bond



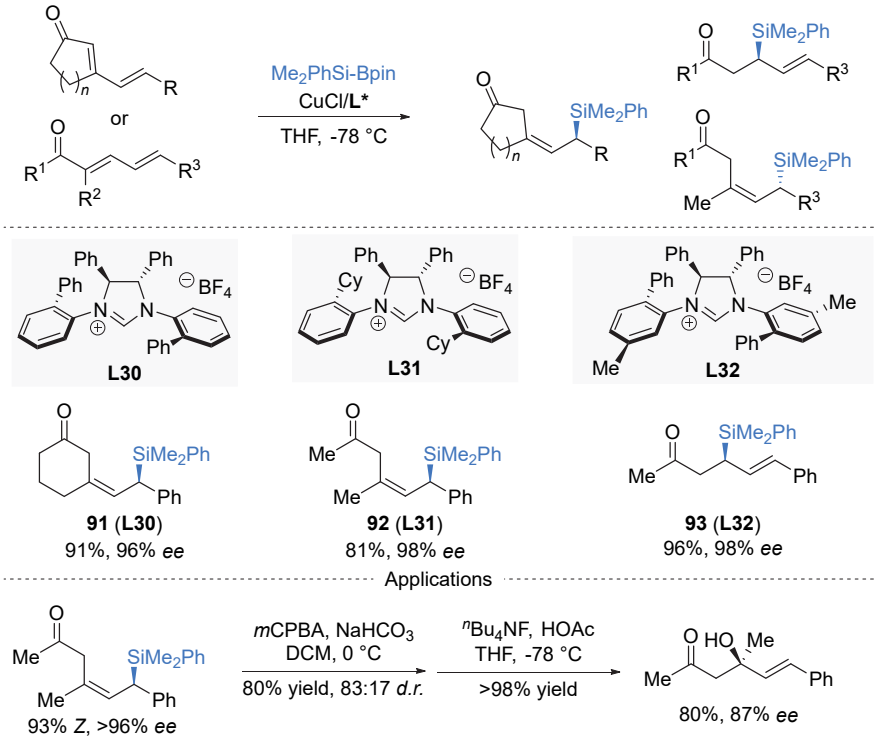
Scheme 29 Rh-catalyzed asymmetric insertion of allylic carbenoids into Si—H bond



Scheme 30 Asymmetric insertion of allylic carbenoids into Si—H bond

6 Asymmetric addition reaction with Si-nucleophiles

In addition to widely studied strategies including hydrosilylation of alkenes, allylic substitution, and carbene insertion, the asymmetric conjugated addition reaction of Michael acceptors or imines with a silicon nucleophile represents another efficient approach for the preparation of enantioenriched allylsilanes. In 2010, Hoveyda *et al.*[64] developed a Cu-catalyzed enantioselective silyl-conjugate addition reaction to *α*,*β*-unsaturated carbonyls. In this work, the chiral carbonyl-containing allylsilane **91** was prepared via 1,6-addition of cyclic *α*,*β*,*γ*,*δ*-dienones in the presence of the chiral NHC ligand **L30**. Following this discovery, they outlined the construction of a series of enantioenriched carbonyl-containing allylsilane in high regioselectivity via the silyl-conjugate addition to dienones and dienoates catalyzed with active NHC-Cu-SiMe$_2$Ph species.[65] The 1,6-addition product **92** was obtained in high enantioselectivity using *β*-substituted acyclic dienones, while 1,4-addition occurred in the reaction of acyclic dienones with no substituents on *β*-position (Scheme 31). Moreover, the further



Scheme 31 Cu-catalyzed enantioselective 1,4- or 1,6-addition reaction with silylboranes

application of the chiral allylsilanes was illustrated via a sequence of epoxidation and fluorine anion-initiated desilylative ring-opening process, affording the chiral *β*-hydroxyl ketone in high efficiency.

In 2014, Sato group[66] mentioned the access of chiral *α*-amino allylsilanes via Cu-catalyzed asymmetric addition of silicon nucleophile with alkenyl *N*-*tert*-butylsulfonylimines **94**, which could be further converted to corresponding enantioenriched *α*-amino carboxylate methyl ester **96** via stereospecific desilylative carboxylation with CO_2 (Scheme 32).

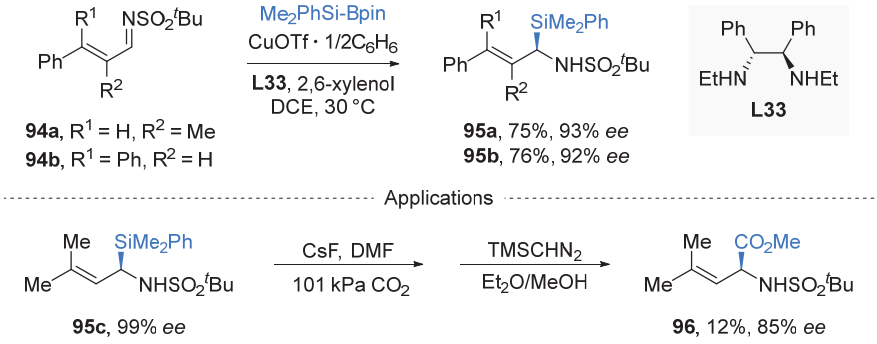
Later, Xu group[67] reported Cu-catalyzed conjugate addition of *α*,*β*-unsaturated sulfonyl ketimines with silylborane reagent (Me_2PhSi-BPin). The asymmetric version was realized by the utilization of the Pybox ligand **L34**, offering the cooresponding (*E*)-*β*-tosylamine-substituted allylsilanes **98** in high enantioselectivities (Scheme 33).

In 2018, Xu and co-workers[68] developed a Cu-catalyzed double silicon-addition of electron-deficient conjugated enynes **99** for the synthesis of 1,3-bis(silyl)propenes **100** (Scheme 34). In its asymmetric version, the chiral pyridine-oxazoline ligand **L35** was utilized to yield *Z*-specific bis(silyl)propene products in up to 98% yield and 95% *ee* with silylboronate reagent under mild reaction conditions.

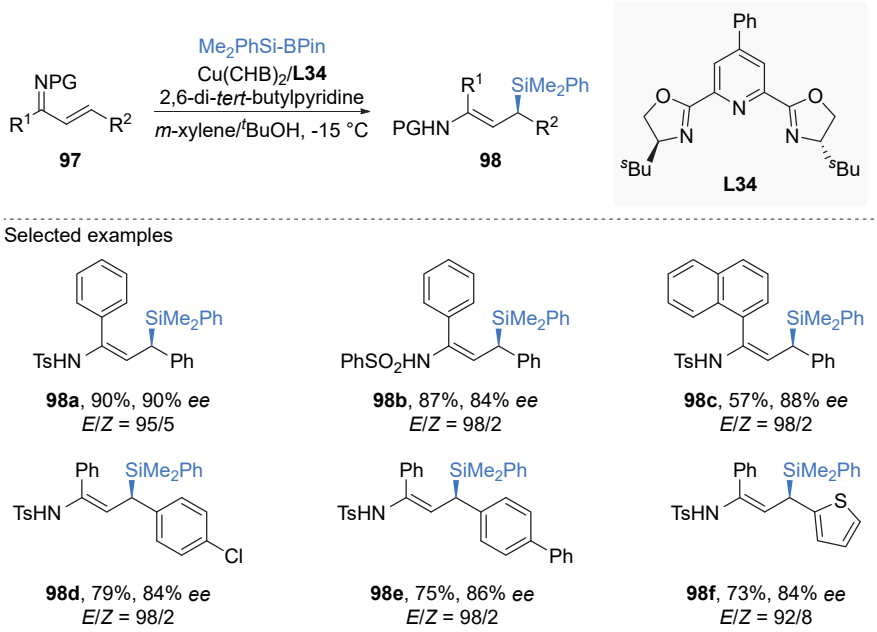
Recently, Yin group[69] reported a Cu-catalyzed asymmetric 1,4-conjugate silylation of *α*,*β*-unsaturated sulfones by virtue of a modified McQuade's six-membered NHC-Cu(I) complex (**Cu-3**). With the subsequent Julia-Kocienski olefination, the enantioenriched allylsilanes **103** were accessible. Moreover, the one-pot process was demonstrated, providing the product without the decrease of enantioselectivity (Scheme 35).

7 Silylfunctionalization of unsaturated bonds for the preparation of chiral allylsilanes

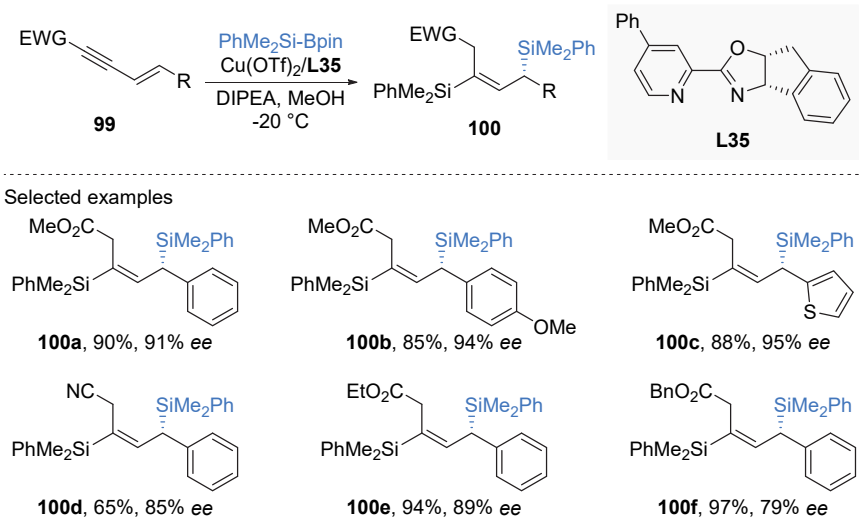
In 2005, Moberg and co-worker[70] explored the enantioselective silaboration of 1,3-cyclohexadiene with Me_2PhSi-BPin (Scheme 36). After the systematical evaluation of various chiral ligands, the desired product **106** was obtained in 70% *ee* in the presence of $Pt(acac)_2$ and **L36**.



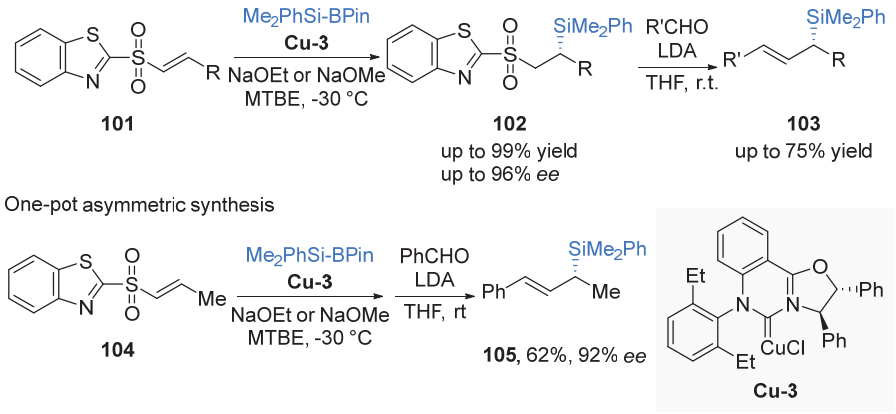
Scheme 32 Cu-catalyzed asymmetric 1,2-addition of alkenyl *N*-*tert*-butylsulfonylimines with silylboranes



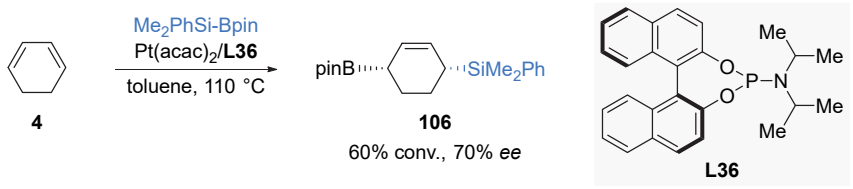
Scheme 33 Cu-catalyzed asymmetric 1,4-addition of *α*,*β*-unsaturated sulfonyl ketimines with silylboranes



Scheme 34 Cu-catalyzed double silicon-addition of electron-deficient conjugated enynes with silylboranes



Scheme 35 Copper(I)-catalyzed asymmetric addition of α,β-unsaturated sulfones with silylboranes



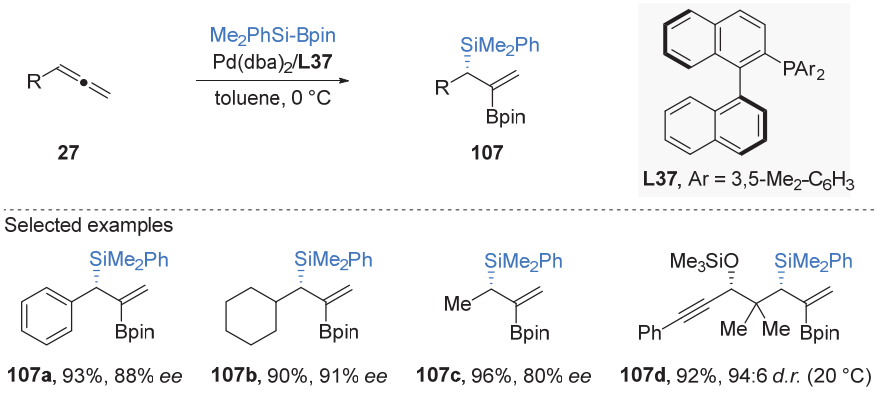
Scheme 36 Pt-catalyzed silaboration with 1,3-cyclohexadiene with silylboranes

This silaboration strategy has been further explored to construct the chiral allylsilane by Suginome and co-workers in 2006 (Scheme 37).[71] With allenes as the substrates, the target products **107**, β-borylallylsilanes, were afforded efficiently in high chemo-, regio- and enantioselectivities with the combination of $Pd(dba)_2$ and a chiral monodentate phosphine ligand **L37**. Notably, the monosubsituted allenes bearing both aryl and alkyl groups were suitable for this protocol.

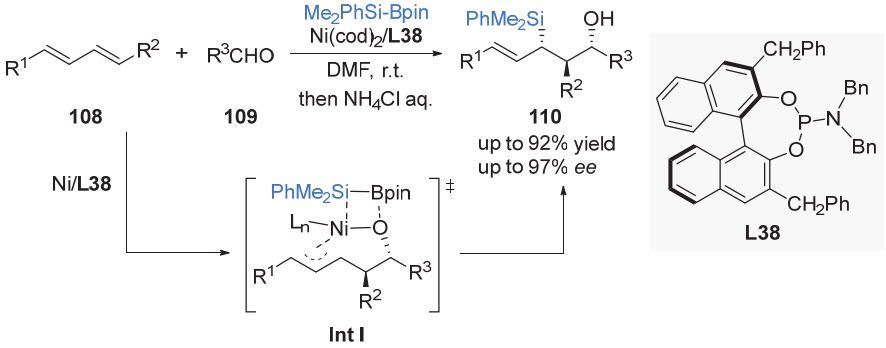
In 2011, a Ni-catalyzed asymmetric three-component coupling reaction among 1,3-dienes, aldehydes, and silylborane was reported by Sato and co-workers (Scheme 38).[72] With **L38** as chiral ligand, simultaneous construction of three consecutive carbon-stereogenic centers through a single process was realized, affording the α-chiral allylsilanes **110** in high enantioselectivity. Mechanistic studies suggested that oxanickelacycle intermediate (**Int 1**)[73] was involved in continuous σ-bond metathesis, giving the desired products **110**.

8 Other catalytic asymmetric methods

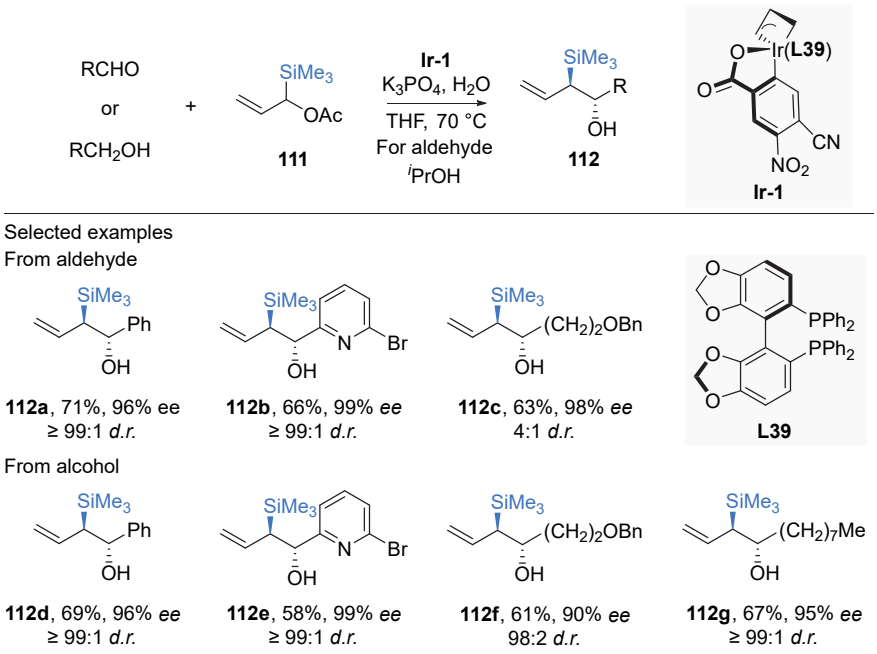
In addition to the catalytic asymmetric methods mentioned above, several examples by using silicon-containing substrates with different reaction patterns have been mentioned in the literature. In 2010, Krische and co-workers[74] showed iridium-catalyzed carbonyl (trimethylsilyl)allylation employing **Ir-1** as the optimal catalyst (Scheme 39). The target products **112** were available in good yields with an



Scheme 37 Palladium-catalyzed asymmetric silaboration of allenes with silylboranes



Scheme 38 Ni-catalyzed asymmetric three-component coupling reaction of 1,3-dienes, aldehydes and silylboranes



Scheme 39 Iridium-catalyzed carbonyl (trimethylsilyl)allylation

exceptional level of diastereo- and enantioselectivity in most cases via the reaction between *α*-(trimethylsilyl)allyl acetate **111** and aldehydes or alcohols.

In 2018, Huang and Fu *et al.*[75] reported NHC-catalyzed formal [4+2] annulation of enals with *β*-silyl enones. The organosilanes containing two consecutive carbon-stereogenic centers were afforded in a diastereo- and enantioselective manner (Scheme 40). The functional groups such as naphthyl, heteroaryl, as well as other substituted silyls (Me_2PhSi and $MePh_2Si$) were compatible with excellent diastereoselectivity (>20∶1 *d.r.*) and enantioselectivity (96%～99 % *ee*). The proposed mechanism was showed in

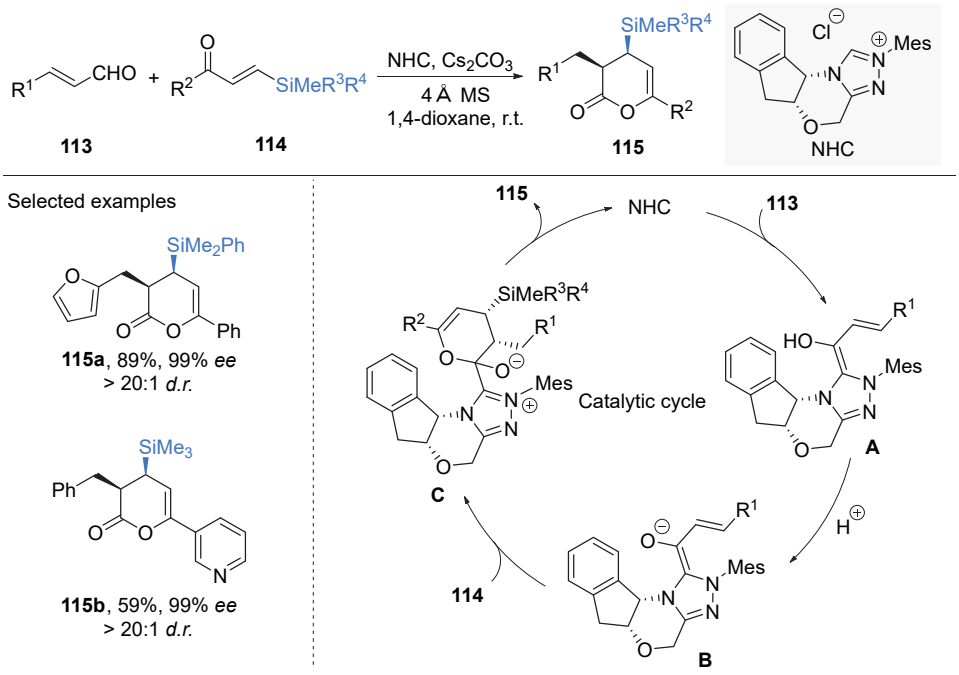
Scheme 40. Mechanistically, the Breslow intermediate **B** was formed first, followed by the continuous endo-Diels-Alder cycloaddition, which could release NHC catalyst to give product **115**.

In 2007, Hiyama group[76] reported the application of their new disclosed organo[2-(hydroxymethyl)phenyl]dimethylsilanes **116** as nucleophiles in the rhodium-catalyzed 1,4-addition reactions. The proposed formation of five-membered pentacoordinated silicate species **Si-1** in the presence of a weak base allowed the activation of the organosilicon compounds under the fluoride-free conditions. With this alkenylsilane reagents, the asymmetric 1,4-addition to *β*-silyl *α*,*β*-unsaturated ketones delivered the corresponding allylsilanes **117** in moderate to high enantioselectivities by the employment of chiral diene ligand **L40** (Scheme 41).[77] The derivatization of the chiral allylsilane **116a** was also performed, producing the intramolecular allylated product **118** in a stereospecific manner.

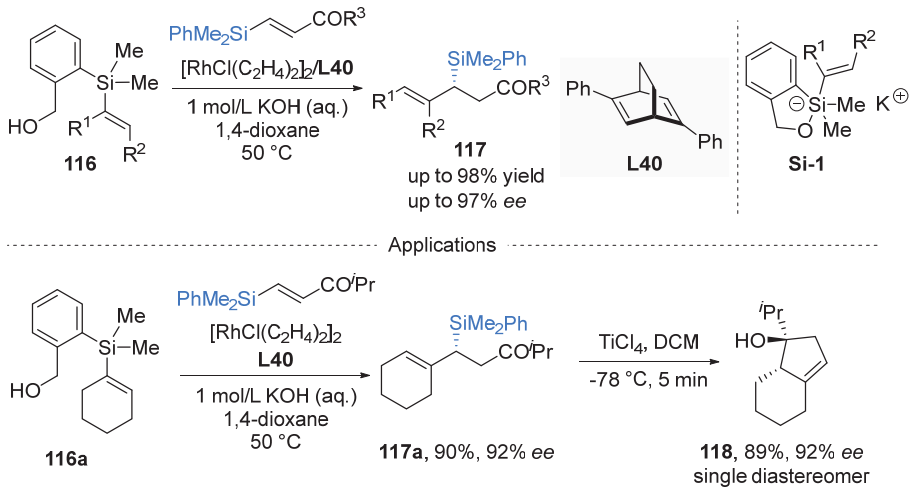
9 Conclusion

The advances in the catalytic preparation of enantioenriched allylsilanes, versatile synthetic intermediate in synthetic chemistry, were systematically summarized. These methodologies are highly efficient and synthetically useful, thus significantly promoting the synthetic applications of the title chiral compounds. For example, (−)-virginiamycin M_2 was synthesized using chiral allylsilane derivative as the key intermediate.

Although visible progress has been made in this field, challenges still remain. The current catalytic synthetic app-



Scheme 40 NHC-catalyzed formal [4+2] annulation of enals with *β*-silyl enones



Scheme 41 Rh-catalyst asymmetric 1,4-addition of *β*-silyl *α*,*β*-unsaturated ketones

roaches are largely limited to the asymmetric addition and substitution, which hamper the access of, for example, the α-stereogenic tertiary allylsilanes, a good precursor for the valuable tertiary alcohols. Currently, the reaction mainly focuses on the utilization of precious metal (such as palladium and rhodium) as the catalyst, despite of several elegant examples with Cu and Co catalysts. Further efforts should aim at the development of the novel reaction patterns for the construction of chiral allylsilanes by the employment the earth-abundant metal catalysts. Moreover, more general approaches will be explored by taking advantage of the asymmetric organocatalysis or cooperative catalysis. These further developments will predictably enlarge the structure diversity of enantioenriched allylsilanes which will serve as the versatile linchpin for the access of the more complicate chiral structures. The efficient synthesis of natural products and pharmaceuticals with this versatile reagent will also be flourished over the coming years. Undoubtably, the increasing inventory of the title chiral reagents will further promote the development in pharmaceutical chemistry and material science.

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