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Review

Catalytic asymmetric synthesis of silicon-stereogenic organosilanes

Yichen Wu,[1,5] Long Zheng,[1,5] Yan Wang,[4,*] and Peng Wang[1,2,3,*]

SUMMARY

Silicon-stereogenic organosilanes have attracted heightened attention in various scientific communities including synthetic chemistry, material chemistry, and medicinal chemistry, along with the rapid developments in the catalytic construction of various Si-stereogenic architectures more recently. This review offers a comprehensive overview of catalytic preparation of Si-stereogenic organosilanes by categorizing prochiral starting materials (such as dihydrosilanes, dialkylsilanes, diarylsilanes, dialkenylsilanes, dialkynylsilanes, and other precursors).

INTRODUCTION

The silicon element belongs to the carbon group and is located below carbon in the periodic table. Although it is the second most abundant element in Earth's crust, no organosilicon compounds have been discovered in nature yet.[1,2] Since the first organosilicon compound ($SiEt_4$) was prepared by Friedel and Crafts from the reaction between silicon tetrachloride and diethyl zinc in 1863, organosilicons have been extensively utilized as sealants and adjuvants on the scale of megatons/year in the fields of agriculture, construction, automotive, cosmetic, high-performance aerospace, etc.[3,4] More and more functional organosilanes possessing unique optoelectronic properties or bioactivities have been developed in the last decades. The σ^*-π^* conjugation in silicon-containing conjugated molecules typically results in low lowest unoccupied molecular orbital (LUMO)-highest occupied molecular orbital (HOMO) gap, which has been widely leveraged in the development of novel optoelectronic materials.[5–15] The "carbon/silicon switch" strategy has emerged in medicinal chemistry, where the silicon analogs could alter the physicochemical and biological properties owing to the fundamental differences (such as covalent radii, electronegativity, and structural features) between carbon and silicon.[16–23]

Over the last decades, enantioenriched Si-stereogenic organosilanes attract increasing attention since they are considered as versatile chiral precursor, chiral auxiliary, chiral catalyst, and mechanism probe in synthetic chemistry (Scheme 1A).[24–34] For instance, Oestreich and co-workers have demonstrated a configurationally constrained Si-stereogenic cyclic monohydrosilane, which could be utilized for the efficient resolution of alcohols and as a mechanistic probe in transition-metal-catalyzed reactions.[35,36] Wang and co-workers have empowered Si-centered spirocyclic scaffolds as promising platforms for the development of chiral ligands with superior performance in transition-metal-catalyzed asymmetric reactions.[37–40] Along with the advances in the development of silicon-containing functional materials and bioactive molecules, Si-stereogenic optoelectronic materials and bioactive compounds have also appeared in the literature. Song group reported that (−)-sila-mesembranol, containing a Si-stereogenic quaternary center, exhibits better antidepressant effects in mice than its carbon counterpart.[41] In light of the importance and increasing demand

THE BIGGER PICTURE

Silicon-stereogenic organosilanes play more and more important roles in diverse fields including synthetic chemistry, medicinal chemistry, and material chemistry. This review summarizes the preparation of various Si-stereogenic organosilanes via catalytic asymmetric synthesis, providing the growing inventory of this class of functional compounds with novel architectures. This comprehensive summary not only provides overall and further perspectives in this area but also gives an application blueprint of diverse novel silicon-chirality-containing architectures.

for Si-stereogenic functional organosilanes, the construction of Si-stereogenic organosilanes becomes one of the important targets in the asymmetric catalysis.

The study on the construction of the optically active Si-stereogenic compound was initiated by Kipping et al. at the turn of the 20th century.[42,43] Despite a large number of experimental results, few conclusions could be drawn due to the lack of the available analytic tools. The revival of this chemistry thanks to the development of methodologies for the determination of absolute configuration and resolution procedures. Since the pioneering studies by Sommer and Corriu's group in the middle of 20th century, various chiral reagents and chiral auxiliaries have been utilized to access countless optically active Si-stereogenic compounds, leading to the numerous applications of this class of chiral molecules in organic chemistry.[44–49] However, traditional strategies for the construction of the silicon-centered chirality generally required stoichiometric chiral regents or auxiliaries. For the purpose of maximizing efficiency and minimizing waste production, catalytic approaches are still highly sought after. Since the pioneering studies on catalytic asymmetric synthesis of chiral Si-stereogenic silanes reported by Corriu[50] and Kumada[51] independently, the creation of chirality on the silicon center in a catalytic manner gains traction, especially as asymmetric catalysis improves by leaps and bounds.[36,52–54] However, strategies for the construction of Si-stereogenic silanes lag behind those for the construction of carbon congeners despite of the structural similarity.

Well-established carbon-centered chiral chemistry largely relied on the stereoselective conversion of carbon–carbon and carbon–heteroatom multiple bonds. In contrast, the low stability of silicon–carbon or silicon–heteroatom multiple bonds, which originates from the larger covalent atomic radius of silicon and less effective overlap of the more diffused 3p orbitals relative to that of 2p orbitals, results in the construction of Si-stereogenic silanes largely relying on the desymmerization of sp^3-silicon center. In addition, the larger atomic radius of silicon and the longer C–Si bond (Si vs. C: 111 vs. 67 pm; C–Si vs. C–C: ca 1.87 Å vs. ca. 1.53 Å) generally lead to a looser transition state in the chiral induction step, in comparison with the transition state in the preparation of carbon-centered chirality. For these reasons, catalytic systems developed with carbon-centered chirality in mind may not be suitable for the construction of silicon-centered chirality. The inaccessibility of feedstock chiral silicon precursors also significantly hinders progress in this area.

Despite of these challenges, a variety of novel strategies have been developed for the preparation of this class of chiral compounds with diverse novel architectures. For now, the main effort has focused on the catalytic desymmetrization of prochiral organosilanes, with two identical substitutes attached to the silicon atom, such as dihydrosilanes, dialkylsilanes, diarylsilanes, etc. Very recently, elegant examples on the dynamic kinetic asymmetric transformation (DYKAT) of racemic silanes have emerged, presenting a promising alternative for the construction of Si-stereogenic silanes (Scheme 1B). Given the importance of Si-stereogenic organosilanes in material chemistry and medicinal chemistry and the rapid development in the preparation of these chiral molecules, this review intends to offer a comprehensive overview on the catalytic synthesis of Si-stereogenic organosilanes as well as a future perspective. In particular, this review presents this topic by categorizing prochiral starting materials (such as dihydrosilanes, dialkylsilanes, diarylsilanes, dialkenylsilanes, dialkynylsilanes, and other precursors) used in the asymmetric synthesis, hoping to provide a comprehensive guide regarding the construction of various functional Si-stereogenic monohydrosilanes, silanols, and other organosilanes.

[1]State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, CAS, 345 Lingling Road, Shanghai 200032, China

[2]School of Chemistry and Material Sciences, Hangzhou Institute for Advanced Study University of Chinese Academy of Sciences, Hangzhou 310024, China

[3]College of Material Chemistry and Chemical Engineering, Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education, Hangzhou Normal University, Hangzhou 311121, China

[4]CAS-Key Laboratory of Synthetic Biology, CAS Center for Excellence in Molecular Plant Sciences, CAS, Shanghai 200032, China

[5]These authors contributed equally

*Correspondence:
wangyan@cemps.ac.cn (Y.W.),
pengwang@sioc.ac.cn (P.W.)

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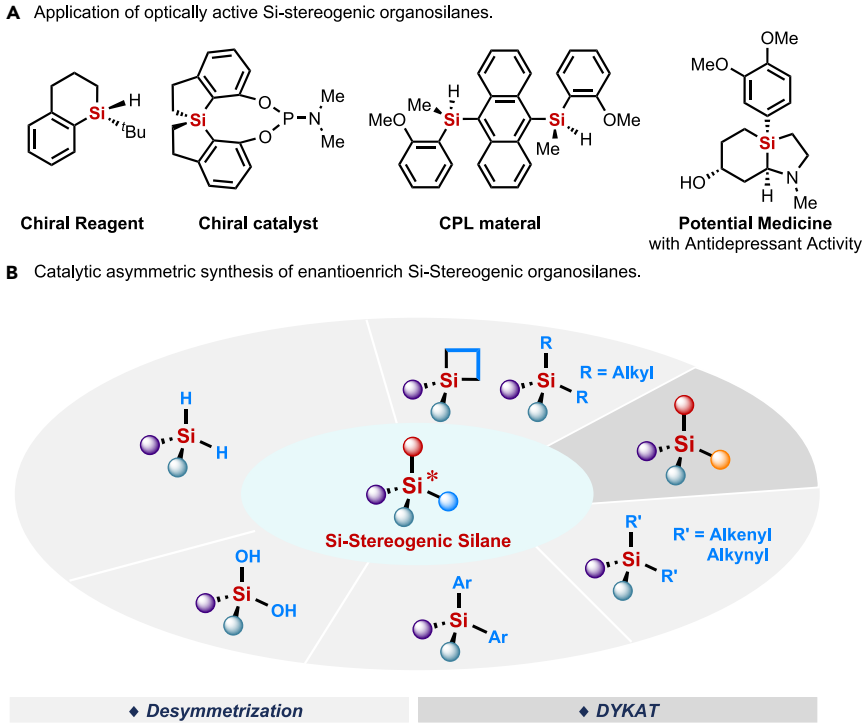

Scheme 1. Application and catalytic asymmetric synthesis of Si-stereogenic organosilanes
(A) Application of optically active Si-stereogenic organosilanes.
(B) Catalytic asymmetric synthesis of enantioenrich Si-stereogenic organosilanes.

CATALYTIC ASYMMETRIC DESYMMETRIZATION OF DIHYDROSILANES

The preparation of Si-stereogenic organosilanes via the desymmetrization of dihydrosilanes is the most well-studied approach for the synthesis of Si-stereogenic organosilanes, which could provide the corresponding trisubstituted monohydrosilanes and axially chiral spirosilacycles in high efficiency and stereoinduction. In this context, we classified the section by the formation of Si–C or Si–X bonds, which is related to the synthetic values of targeted Si-stereogenic organosilanes.

Si-stereogenic organosilanes construction via Si–C bond formation

Via hydrosilylation of carbon–carbon unsaturated bonds

The first catalytic preparation of Si-stereogenic monohydrosilanes via silicon–carbon bond formation reaction of dihydrosilanes was reported by Curriu and Kumada independently.[50,51] Since then, significant progress has been made in this direction. Currently, the widely studied strategies for construction of Si–C bond from dihydrosilanes include hydrosilylation of unsaturated carbon–carbon double or triple bond, dehydrogenative C–H silylation, carbenoid insertion, transition-metal-catalyzed Si–H coupling reaction, etc.[55] Among those strategies, catalytic asymmetric hydrosilylation is one of the most straightforward processes to construct enantioenriched organosilanes incorporating chiral silicon centers. The pioneering work was performed by Tamao and co-workers to synthesize axially chiral spirosilane **2** for material science pursuits (Scheme 2).[56] Later, they showed that this thiophene-containing spirosilacycle could be used for construction of the chiral molecular square **3** with D_4 symmetry as the angular unit.[57]

In 2020, Wang group developed a catalytic system to prepare various chiral spirosilabiindanes **5** in high enantioselectivities and diastereoselectivities by adopting a

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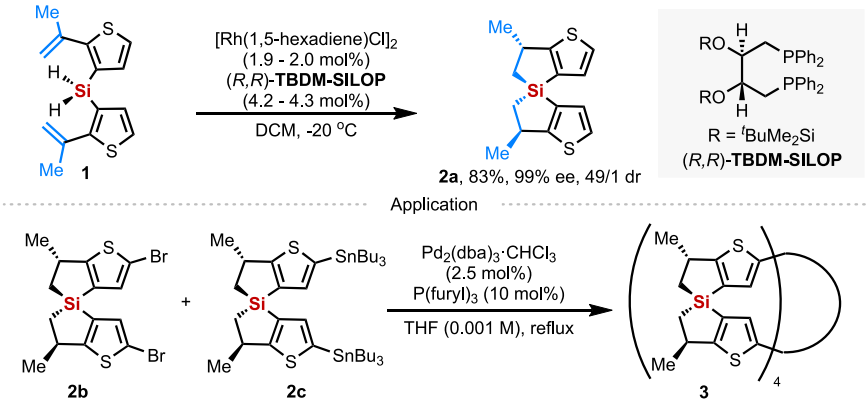

Scheme 2. Synthesis of axially chiral spirosilane via catalytic asymmetric hydrosilylation
Synthesis (Tamao et al.[56]); application (Tamao et al.[57]).

Rh-catalyzed intramolecular dihydrosilylation reaction (Scheme 3).[37] A new type of chiral spirosilacycle-based chiral scaffolds, SPSiOLs, were prepared under this newly developed procedure with high yields and high enantioselectivities in the presence of a low catalyst loading. Notably, this novel chiral scaffold has been employed for the development of a series of SPSiOL-based chiral ligands, including SPSiP, SPSiPhos, and SPSiPO ligands, which have been proven as promising chiral ligands in transition-metal-involved asymmetric catalysis due to the longer C–Si bond, larger Si atomic radius, and the vertical rigid configuration.[39,40] For example, a Ni-catalyzed regioselective and enantioselective hydrosilylation of 1,1-disubstituted alkenes **8** has been realized for the first time with broad substrate scope and up to 96% ee thanks to the SPSiPO ligand.

This intramolecular hydrosilylation could also be utilized to reach enantioenriched Si-stereogenic monohydrosilanes with the chirality on the silicon center. In 2022, Wang group demonstrated the first construction of Si-stereogenic cyclic monohydrosilanes **11** by the utilization of Rh-catalyzed intramolecular hydrosilylation, which are highly useful as chiral reagents for alcohol resolution and mechanism probes (Scheme 4).[58] Moreover, the construction of both carbon-centered and silicon-centered chirality in one reaction has been realized, producing a wide range of five- and six-membered cyclic monohydrosilanes in excellent diastereoselectivities, regioselectivities, and enantioselectivities. The reaction also proceeded in high efficiency ($\lesssim$5 min in most cases) and the catalyst loading could be lowered to 0.1 mol % on a large scale. Further applications of this cyclic monohydrosilane were also demonstrated to access cyclic tetrasubstituted Si-stereogenic derivatives via stereospecific conversion of Si–H bond.

In the same year, Meng group reported a tandem hydrosilylation of enynes for the synthesis of chiral cyclic alkenylsilanes **14** bearing both C-stereogenic and Si-stereogenic centers by utilizing earth-abundant cobalt catalysts (Scheme 5).[59] Mechanistic studies unveiled that the target products were reached via a key Ojima-Crabtree isomerization after Co(I)–H addition, and the enantiodiscrimination and diastereodiscrimination events occurred in the second hydrosilylation step.

Asymmetric intermolecular hydrosilylation has also been developed for the creation of Si-stereogenic centers. In 2018, Hou and co-workers reported an elegant asymmetric intermolecular hydrosilylation of hydrosilanes with a wide range of alkenes

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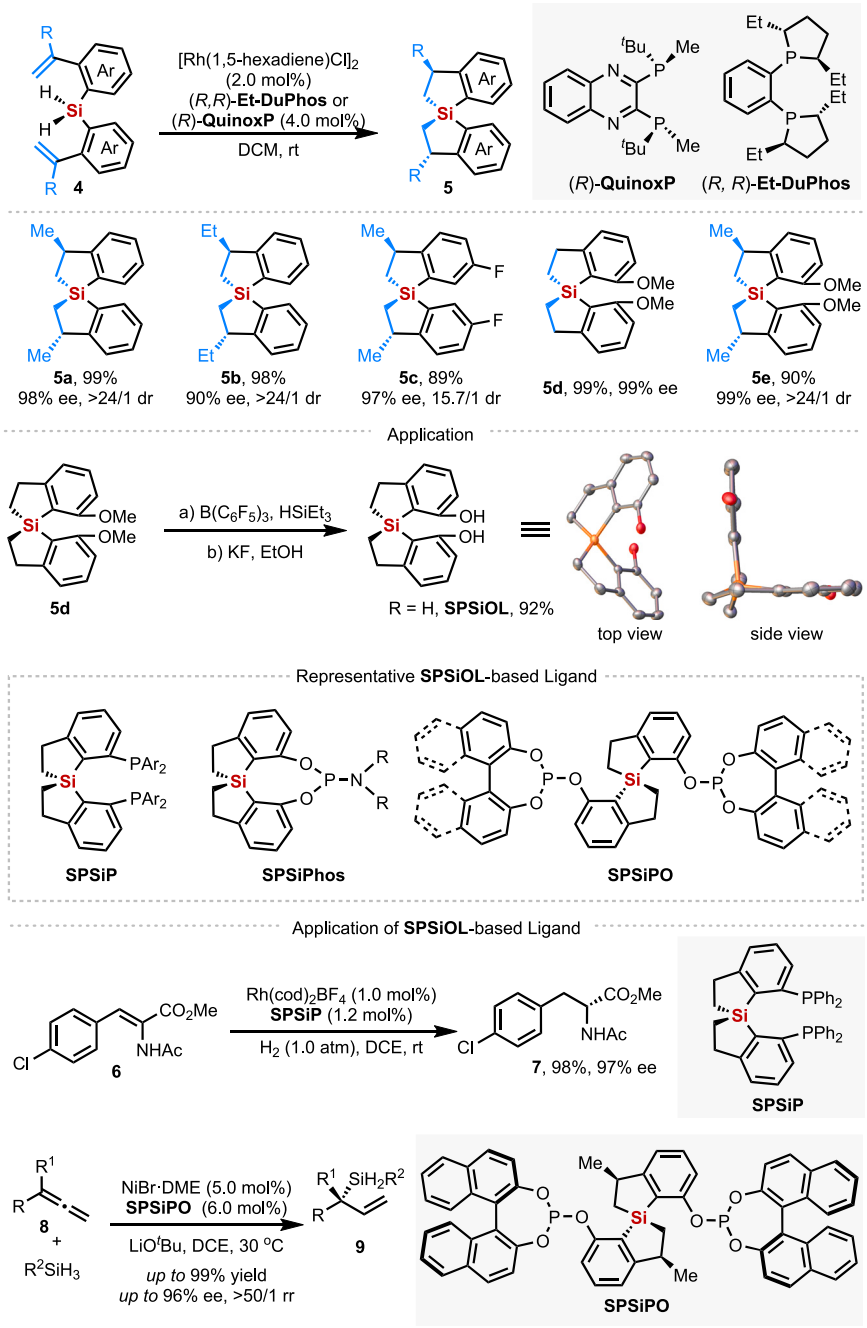
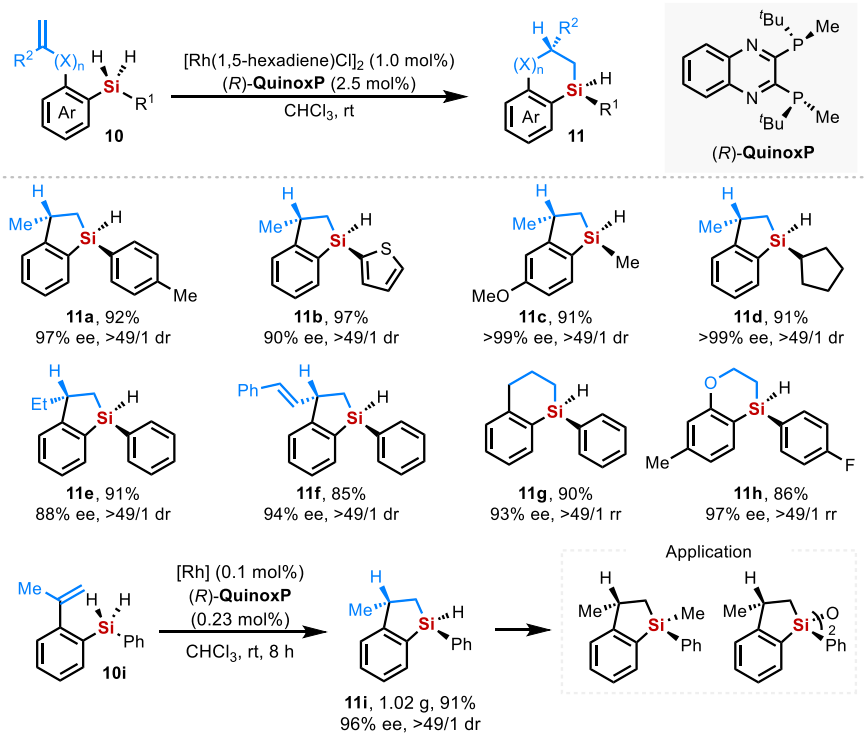


Scheme 3. Synthesis of chiral spirosilabiindanes via catalytic asymmetric dihydrosilylation
Synthesis of chiral spirosilabiindanes and SPSiPhos (Wang and Li et al.[37]); SPSiPO (Wang and Xu et al.[39]); SPSiP (Wang et al.[40]).

for the first time, compatible with both styrenes and unactivated alkenes (Scheme 6).[60] With a chiral half-sandwich scandium catalyst **Sc1**, both cyclic and acyclic dihydrosilanes **15** are suitable substrates, providing the corresponding chiral monohydrosilanes **17** with good to high enantioselectivities. Importantly, the σ-metathesis between a Si–H and a Sc–alkyl bond was proposed as the stereo-determining step, which is different from the typical mechanisms in other noble metal-catalyzed hydrosilylation reactions.



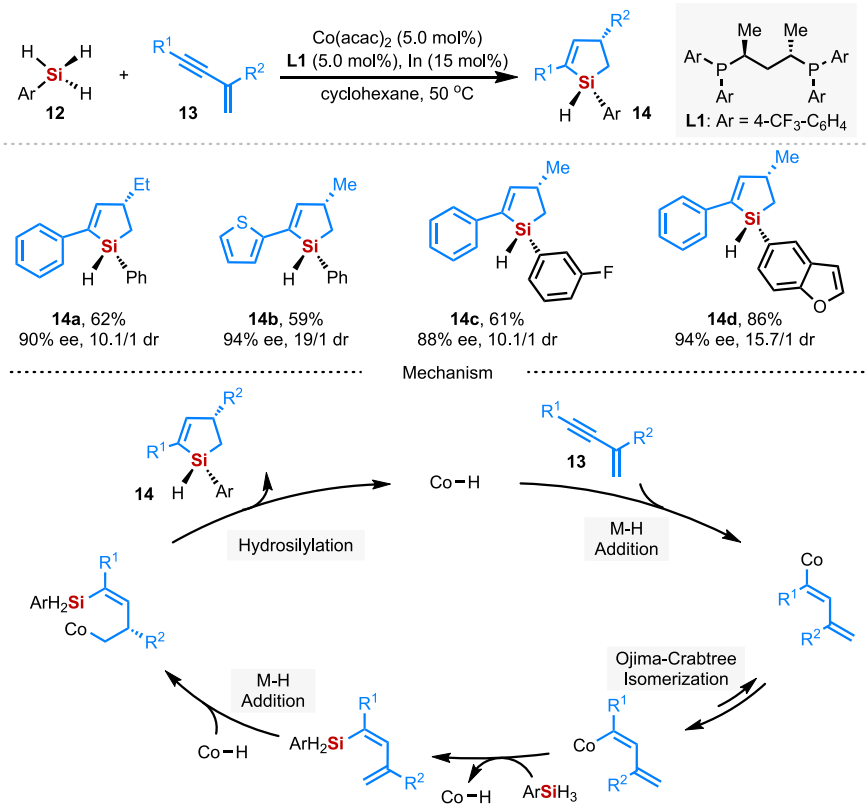
Scheme 4. Synthesis of Si-stereogenic cyclic monohydrosilanes via catalytic asymmetric hydrosilylation

Wang and Peng et al.[58]

In 2020, W. He and Zhang group presented a Rh-catalyzed intermolecular hydrosilylation of allylic ethers and allylic amines with prochiral dihydrosilanes, yielding Si-stereogenic monohydrosilanes **20** in moderate enantioselectivities (Scheme 7).[61] Here, a specific environment on the Si atom of dihydrosilanes **18** was required for the achievement of good enantioinduction, and the weak coordination with the alkenes **19** was also essential for high reactivities. Although the ultimate enantioselectivity leaves room for improvement, this report represents the first example of noble metal-catalyzed intermolecular hydrosilyaltion with unactivated alkenes for the construction of silicon-centered chirality.

Recently, a cobalt-catalyzed asymmetric intermolecular hydrosilylation of 1,3-diene for the preparation of the chiral organosilanes **23** containing adjoining Si-stereogenic center and C-stereogenic center was realized by Meng and Chong group (Scheme 8).[62] With the combination of $Co(acac)_2$ and chiral bisphosphine (*S,S*)-**L3**, a wide range of allylic monohydrosilanes were synthesized in high regioselectivities, enantioselectivities, and diastereoselectivities by adopting a similar catalytic system to their tandem hydrosilylation with enynes.

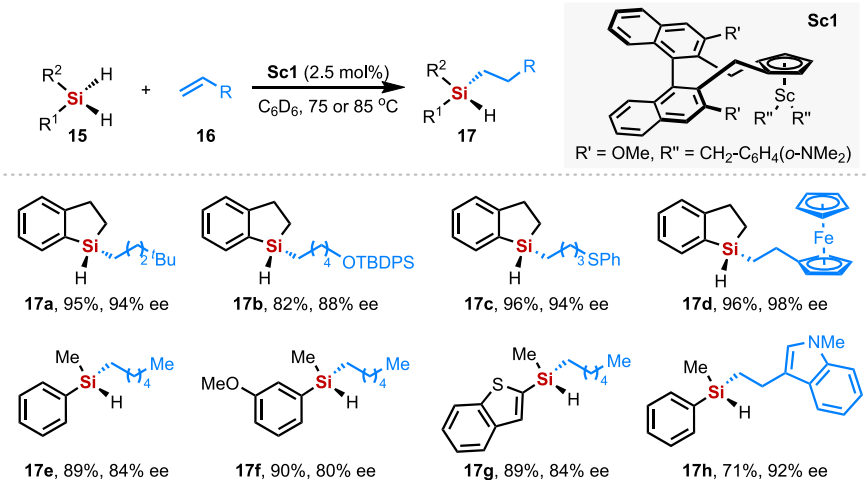
In addition to the asymmetric hydrosilylation of alkenes, the enantioselective hydrosilylation of alkynes with prochiral dihydrosilanes is another appealing process for the access of Si-stereogenic alkenylsilanes bearing both an alkene motif and a Si–H group. The resultant chiral alkenylsilanes are synthetic useful for further derivatizations. In 2012, Tomooka group reported the first transition-metal-catalyzed hydrosilylation of alkynes for the preparation of enantioenriched vinylhydrosilanes in the presence of $Pt(dba)_3$ and a TADDOL-derived phosphonite ligand (**L4** or **L5**) (Scheme 9).[63] Under the optimal conditions, the symmetric internal alkenes **25** were reacted with prochiral dihydrosilanes **24** to give the target products **26** with up to 86% ee.



Scheme 5. Synthesis of chiral cyclic alkenylsilanes via Co-catalyzed tandem hydrosilylation with enynes

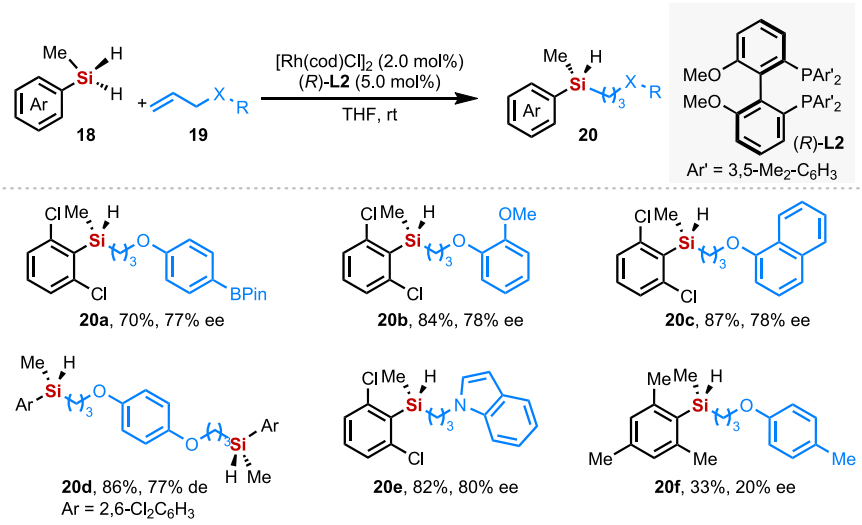
Meng et al.[59]

By taking advantage of 3d transition-metal catalysis, Huang group realized the preparation of Si-stereogenic vinyl hydrosilanes **29** via a Co-catalyzed asymmetric hydrosilylation of terminal alkynes and unsymmetric internal alkynes (Scheme 10).[64] With chiral pyridine-bis(oxazoline) (PyBox) ligand, the hydrosilylation proceeded



Scheme 6. Synthesis of chiral monohydrosilanes via Sc-catalyzed intermolecular hydrosilylation with alkenes

Hou et al.[60]

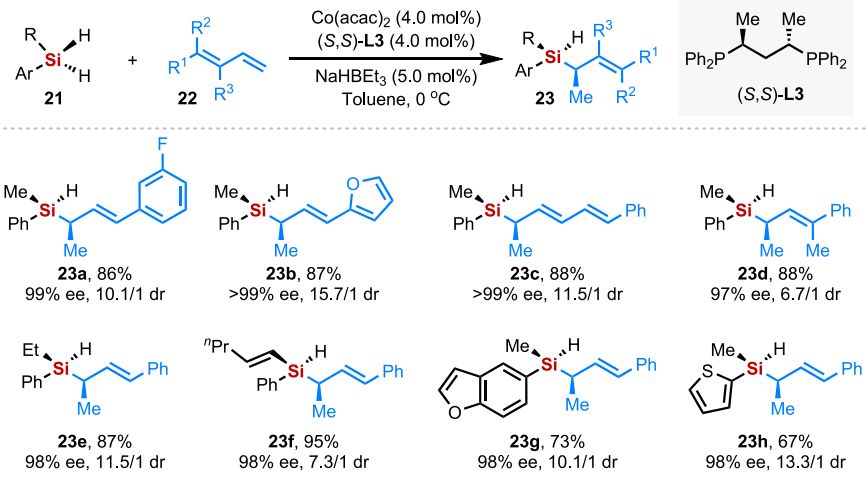


Scheme 7. Synthesis of chiral monohydrosilanes via Rh-catalyzed intermolecular hydrosilylation with unactivated alkenes

He and Zhang et al.[61]

smoothly in high branch-regioselectivities and enantioselectivities for terminal alkynes. In the case of internal alkynes, target products were yielded efficiently with the Si-substituents mainly located on the aryl side (**29g**). It should be pointed out that the steric environment around the Si atom of the dihydrosilanes is crucial for the high level of stereoinduction, while the dihydrosilane bearing a smaller aryl substituent (*o*-toyl) resulted in a dramatic decrease in enantioselectivity (**29h**).

In 2021, Xu group reported a Pd-catalyzed asymmetric hydrosilylation of ynones, producing a series of Si-stereogenic silylenones in the presence of a chiral binaphthyl phosphoramidite ligand **L6** (Scheme 11, above).[65] It should be mentioned that *ortho*-substituents on the aryl group of ynones affect the regioselectivities (**32a** vs. **32b**). The density functional theory (DFT) calculations indicated that the chirality of this reaction is largely controlled by multiple X-H-π interactions, including the one



Scheme 8. Synthesis of chiral allylic monohydrosilanes via Co-catalyzed intermolecular hydrosilylation with 1,3-dienes

Meng and Chong et al.[62]

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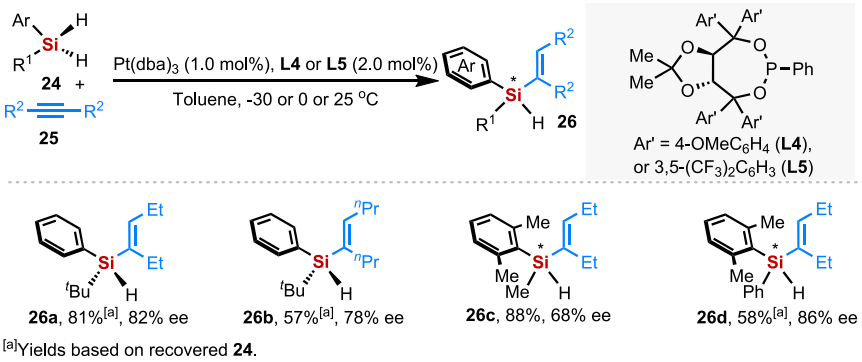
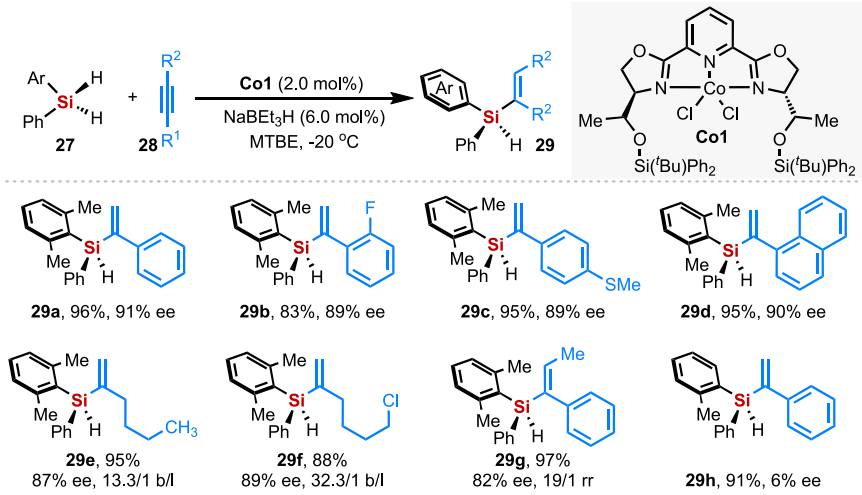


Scheme 9. Synthesis of chiral vinylhydrosilanes via Pt-catalyzed intermolecular hydrosilylation with alkynes

Tomooka et al.[63]

between the C–H bond of ligand and aromatic ring of hydrosilane, and the one between Si–H bond of hydrosilane and naphthyl ring of ligand. Recently, the same group further employed this synthetic strategy for the construction of Si-stereogenic enynes by the hydrosilylation of dialkynes (Scheme 11, below).[66] With a systematic evaluation of chiral P-ligands, the BINOL-derived **L7** was found to create a suitable cavity for the high level of chiral induction. A variety of unsymmetric 1,3-diynes were utilized to yield the corresponding hydrosilylated products **32e–32j** in high regioselectivities and enantioselectivities. Mechanistic investigations revealed that product-involving catalyst aggregation and autocatalysis were possibly involved in this reaction.

Very recently, Lan and Shen group reported a Cu-catalyzed enantioselective 1,4-hydrosilylation of 1,3-enynes **34** (Scheme 12).[67] With the combination of CuOAc and (*S,S*)-**Ph-BPE**, Si-stereogenic silylallenes **35a–35c** featuring both axial chirality and silicon-centered chirality have been accessible in high enantioselectivities and good diastereoselectivities using dihydrosilanes as substrate. Notably, the axial configurations of **35a–35c** are different from the one (**35d**) derived from trihydrosilane



Scheme 10. Synthesis of chiral vinylhydrosilanes via Co-catalyzed intermolecular hydrosilylation with alkynes

Huang et al.[64]

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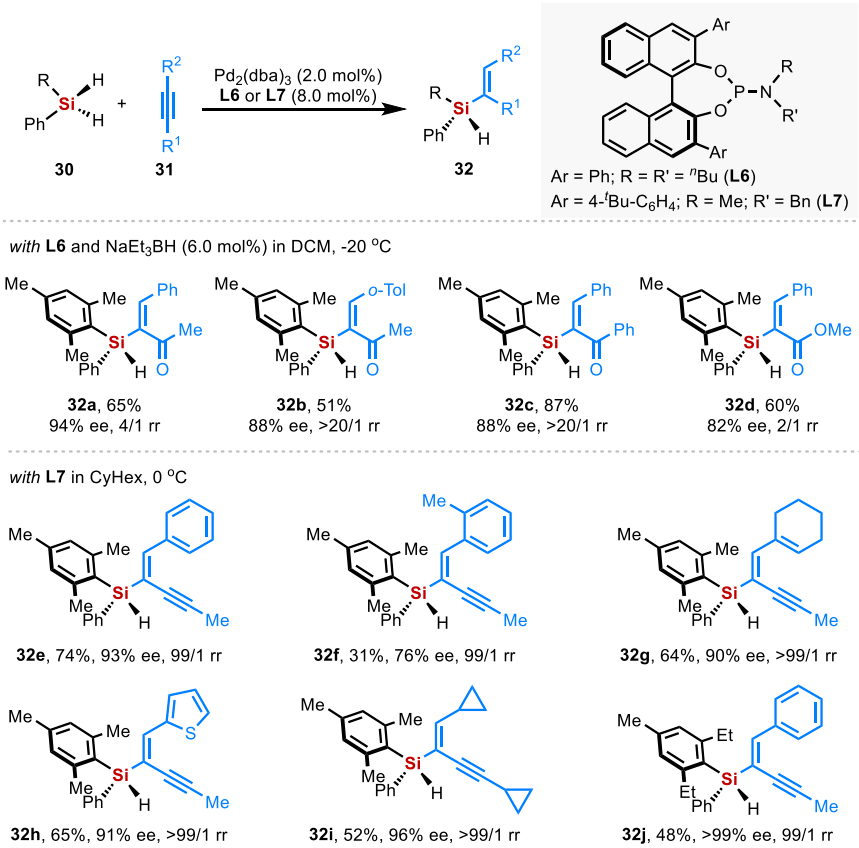

Scheme 11. Synthesis of chiral vinylhydrosilanes via Pd-catalyzed intermolecular hydrosilylation with ynones or dialkynes

Hydrosilylation of ynones (Xu et al.[65]); hydrosilylation of dialkynes (Xu et al.[66]).

which was rationalized by the involvement of epimerization of the chiral allenyl-Cu intermediates during the process.

Via dehydrogenative silylation of C–H bonds

Transition-metal-catalyzed intramolecular dehydrogenative silylation of C–H bonds is another charming strategy for the creation of Si-stereogenic organosilanes due to its step- and atom-economy, where H_2 is the sole byproduct. The pioneering work by Kuninobu and Takai group in 2013 demonstrated the synthesis of axially chiral spiro-9-silabifluorene derivatives **37** with moderate to good enantiomeric excess by employing $[Rh(cod)Cl]_2$ in the presence of the chiral diphosphine ligand (*R*)-**BINAP** (Scheme 13).[68] 3 years later, the same group revisited this reaction and further improved the chiral induction to up to 95% ee by lowering the reaction temperature from 135°C to 70°C.[69] Moreover, mechanistic studies revealed that monohydrosilane constitutional isomers **Int 1** and **Int 8** were involved and the interconversion between two isomers occurred with retention of stereochemistry. Meanwhile, a Si-stereogenic chirality to axial chirality conversion was observed in this reaction for the first time. The identification of enantioenriched monohydrosilane **Int 1** bearing a silicon-centered chirality also indicates the possibility of preparation of Si-stereogenic monohydrosilanes via the same approach.

In 2020, C. He group developed a Rh-catalyzed tandem enantioselective intramolecular C–H silylation/intermolecular alkene hydrosilylation to construct various Si-stereogenic

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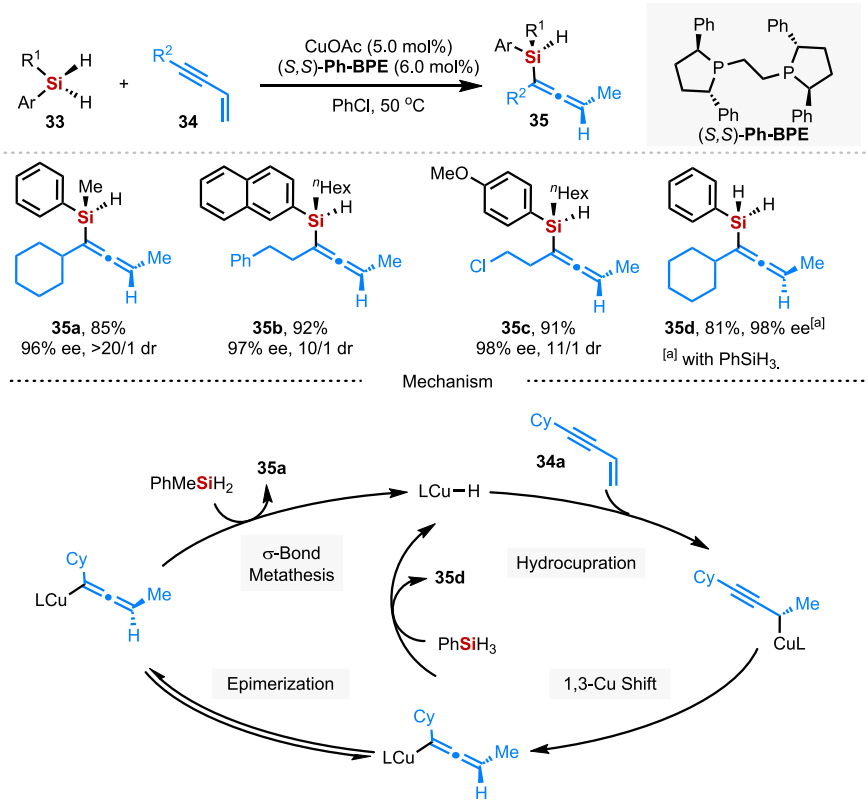

Scheme 12. Synthesis of Si-stereogenic silylallenes via Cu-catalyzed enantioselective 1,4-hydrosilylation of 1,3-enynes

Shen and Lan et al.[67]

silanes (Scheme 14).[70] By again taking advantage of $[Rh(cod)Cl]_2$ and the chiral diphosphine, 9-silanfuorenes (**39a–39d**), Si-bridged ladder compounds (**39e–39g**) and benzosilolometallocenes (**39h** and **39i**) have been accessible in high enantioselectivities by the stereospecific hydrosilylation of alkene with *in situ* formation of monohydrosilane by asymmetrical C–H silylation.

Soon after, W. He group applied the Rh-catalyzed asymmetric intramolecular C(sp^2)-H silylation strategy in the synthesis of chiral monohydrosilanes (Scheme 15).[71] A wide range of Si-stereogenic spirosilabifluorene-cored and ferrocene-based monohydrosilanes **41** could be obtained in high yields and excellent enantioselectivities under mild reaction conditions. Downstream applications of monohydrosilanes proceeded via stereospecific transformations of the Si–H bond, including alcoholysis with alcohol (**42**) and hydrosilylation with alkyne (**43**).

C. He and co-workers also reported an asymmetric rhodium-catalyzed intramolecular C–H silylation to access 1*H*-benzosiloles (BSs) (**45a–45d**) and 1*H*-benzosilolometallocenes (**45e–45h**) (Scheme 16).[72] Similar to W. He's protocol, Segphos was efficient for the intramolecular C(sp^2)–H silylation, giving cyclic monohydrosilanes in good yields and excellent enantioselectivities. This strategy has been successfully applied by the same group in the construction of six- and seven-membered cyclic monohydrosilanes **47** bearing a chiral silicon center (Scheme 17).[73] Notably, the investigation on the photophysical properties of the corresponding π-conjugated enantioenriched monohydrosilanes (such as **47c**, **47f**, and **47g**) indicates the

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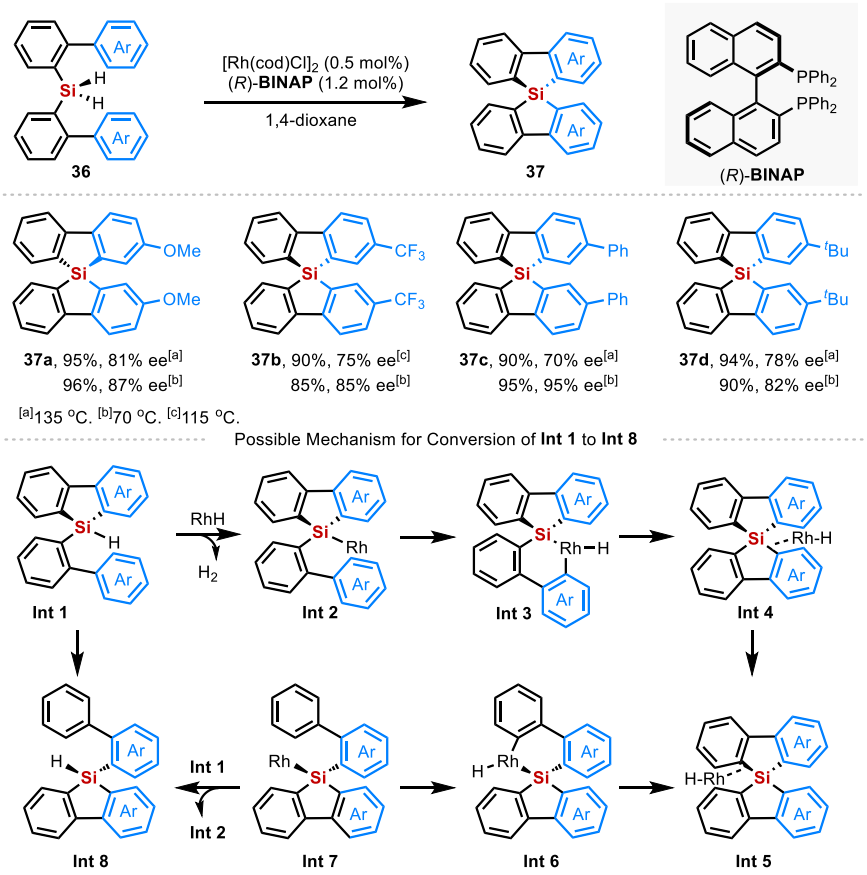
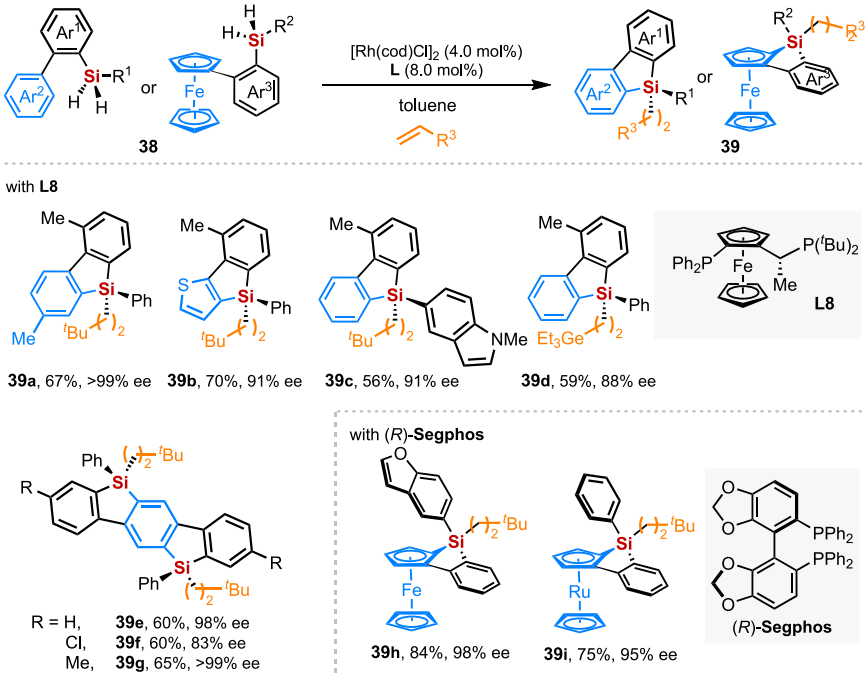


Scheme 13. Synthesis of axially chiral spiro-9-silabifluorene derivatives via Rh-catalyzed intramolecular dehydrogenative silylation

Pioneering work (Kuninobu and Takai et al.[68]); mechanist studies (Murai and Takai et al.[69]).

potential of this class of compounds as the optoelectronic materials due to their bright blue fluorescence under UV light irradiation.

Although transition-metal-catalyzed intermolecular C–H silylation is normally less efficient and more challenging than its intramolecular version, C. He and co-workers have realized such intermolecular Rh-catalyzed dehydrogenative process with reactive heteroarenes, including thiophene, furan, benzothiophene, and benzofuran (Scheme 18).[74] With the combination of $[Rh(cod)Cl]_2$, chiral diphosphine ligand (**L8** or **L10**) and NBE-OMe, organosilanes **50a–50c** containing two Si-stereogenic centers were delivered in excellent enantioselectivities. The dehydrogenative silylation also occurred between dihydrosilanes and substituted (hetero)arenes, affording mono-stereogenic monohydrosilanes **50d–50f** in moderate yields and good enantioselectivities. In addition, examples with simple arenes were demonstrated in moderate chiral induction by using a large excess of arenes (**50g**). The photophysical properties of **50c** were valued. The circular dichroism (CD) spectra showed clear Cotton effects at around 332 nm. In addition, the solution of **50c** is circularly polarized luminescence (CPL)-active and the CPL maxima of **50c** in DCM solution are at 504 nm with g_{lum} being -3.7×10^{-3}. Moreover, the author demonstrated that the utilization of these bis-Si-stereogenic monohydrosilanes as monomers in polymerization. For example, the polymerization between **50a** and 1,4-bis(dimethyl(vinyl) silyl)benzene **51** proceeded smoothly via Pt-catalyzed stereospecific hydrosilyation



Scheme 14. Synthesis of Si-stereogenic silanes via Rh-catalyzed tandem enantioselective C–H silylation/alkene hydrosilylation

C. He et al.[70]

to produce the polymer **52** in good yield with moderate molecular weight and promising PDI.

Soon after, Chen and Huang group also presented similar outcomes of a rhodium-catalyzed intermolecular dehydrogenative C–H silylation between prochiral dihydrosilanes and heteroarenes (Scheme 19).[75] Si-stereogenic monohydrosilanes **55** were obtained in high enantioselectivity in the presence of chiral ligand **L9**. Preliminary mechanistic investigation revealed that the steric hindrance of dihydrosilanes plays a crucial role in ensuring high enantioselectivity in C–H silylation.

The dehydrogenative C(sp^3)–H silylation for the preparation of chiral Si-stereogenic organosilanes has also been developed. A pioneering work was conducted by Takai and Murai group where 1,1′-spirosilabiindane **57** with axial chirality was obtained via 2-fold dehydrogenative silylation, albeit with low enantioselectivity (40% ee) (Scheme 20, above).[76] This strategy was further applied by C. He group in 2020 to access enantioenriched dihydrobenzosiloles. To avoid the decomposition or racemization of the monohydrosilane intermediate, a sequential enantioselective aliphatic C–H silylation/stereospecific hydrosilylation of active alkenes (such as styrene and vinyl derivatives) employing [Rh(cod)Cl]$_2$ and (*R*,Sp)-Josiphos (**L7**) was devised (Scheme 20, below).[77] A variety of chiral dihydrobenzosiloles **60** formed in up to 97% ee, including ones containing pendent bioactive molecules and pharmaceuticals (**60f** and **60g**).

This C(sp^3)–H silylation strategy was further deployed on biphenyldihydrosilanes containing both silicon central and axial prochiralities. By the addition of the hydrogen acceptor (NBE-OMe), dihydrosilane substrates **61** underwent efficient intramolecular benzylic C(sp^3)–H silylation to produce **62** in high enantioselectivities, where a novel silicon center-to-axial chirality relay phenomenon was observed

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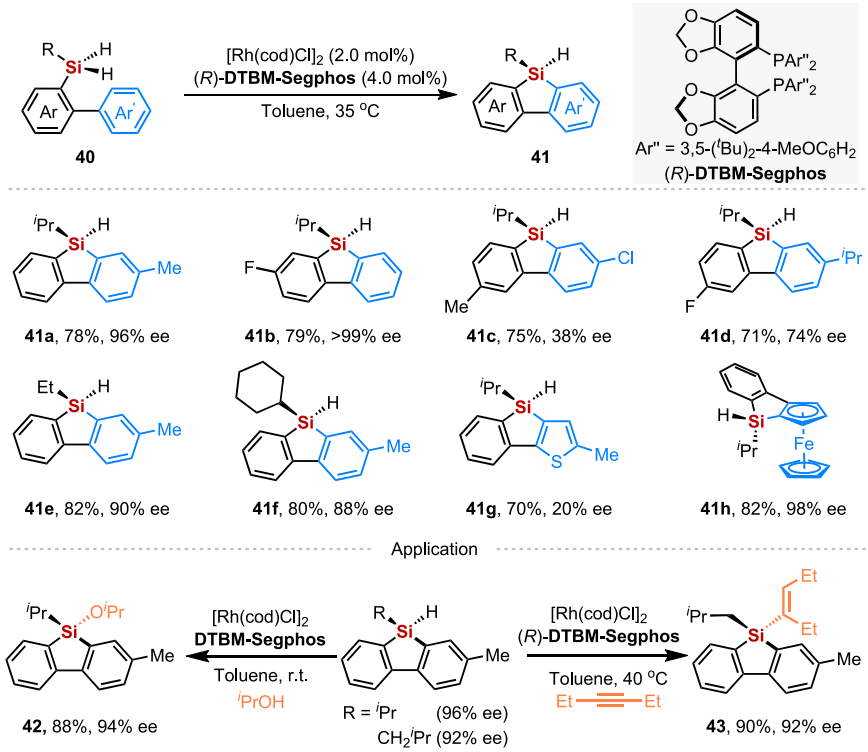
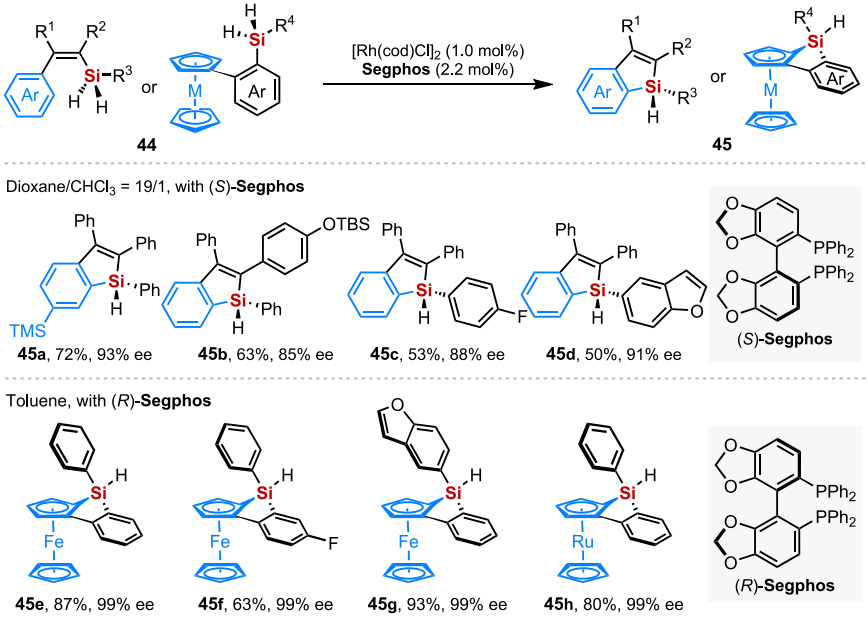


Scheme 15. Synthesis of chiral monohydrosilanes via Rh-catalyzed intramolecular dehydrogenative silylation

W. He et al.[71]

(Scheme 21).[78] In addition to the efficient construction of C–C axial chirality, C–N axial chirality could also be realized with high enantioselectivity (**62c**). With dihydrosilanes bearing non-symmetric *ortho*-substituents on the reacting benzene ring, the



Scheme 16. Synthesis of chiral 1*H*-benzosiloles and 1*H*-benzosilolometallocenes via Rh-catalyzed intramolecular dehydrogenative silylation

C. He et al.[72]

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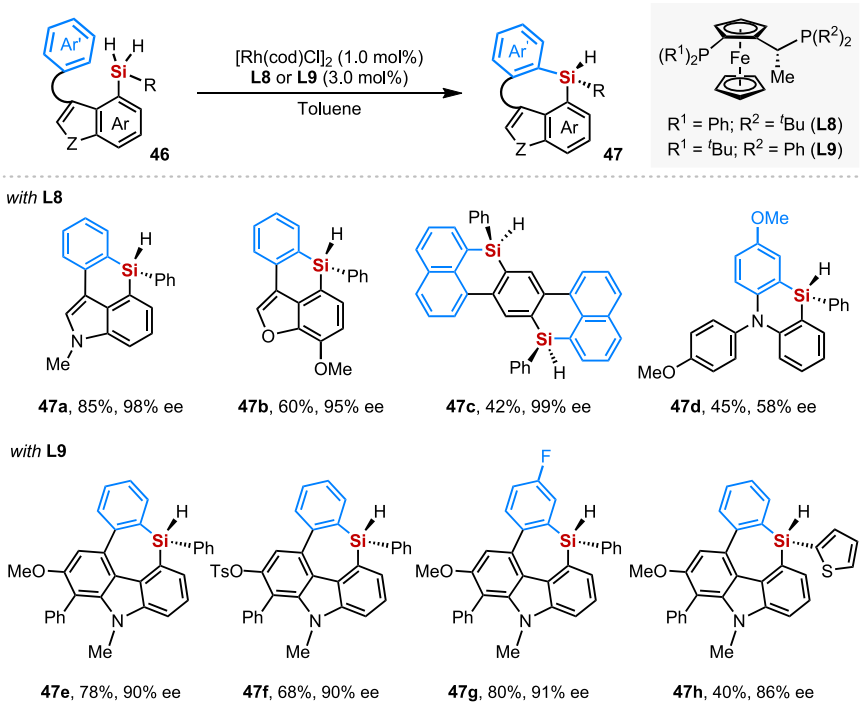

Scheme 17. Synthesis of chiral six- and seven membered cyclic monohydrosilanes via Rh-catalyzed intramolecular dehydrogenative silylation
C. He et al.[73]

desired products were afforded in good enantiopurity through kinetic resolution (**62g** and **62h**).

Via carbene insertion into Si–H bonds

The asymmetric carbene insertion into Si–H bond represents another straightforward and attractive strategy. The construction of enantioenriched organosilanes containing a chiral silicon center via this strategy was initiated by the Katsuki group, using a chiral iridium(III)-salen complexes as the carbene-transfer catalyst (Scheme 22, above).[79] Simultaneous construction of a carbon-stereogenic center and a Si-stereogenic center was achieved in good diastereoselectivities and high enantioselectivities when prochiral dihydrosilanes reacted with donor/acceptor carbenes (α-aryl-α-diazoacetates). In 2017, Iwasa and Chanthamath group revisited this transformation using a chiral Ru(II)-Pheox catalyst. Although diastereoselectivities were low in all demonstrated cases, good to excellent enantioselectivities were obtained for both stereoisomers (**65e–65g**) (Scheme 22, middle).[80] Recently, donor/donor carbene precusors (diaryldiazomethane) have been successfully utilized to produce Si-stereogenic benzhydroyl silanes by Franz, Shaw, and coworkers (**65h–65k**) (Scheme 22, below).[81] Improvements in enantioselectivity were afforded by installation of an *ortho* substituent on one aryl ring of the diazo precursor (**65j** and **65k**).

Via transition-metal-catalyzed cross-coupling reactions with halides

Transition-metal-catalyzed cross-coupling of aryl halides and their analogs with dihydrosilanes has been developed to create C–Si bond and was also applied to access Si-stereogenic organosilane. In 2012, optically enriched monohydrosilanes were afforded by Yamanoi and Nishihara group via the palladium-catalyzed arylation of prochiral dihydrosilanes with aryl iodides (Scheme 23, above).[82] By using a

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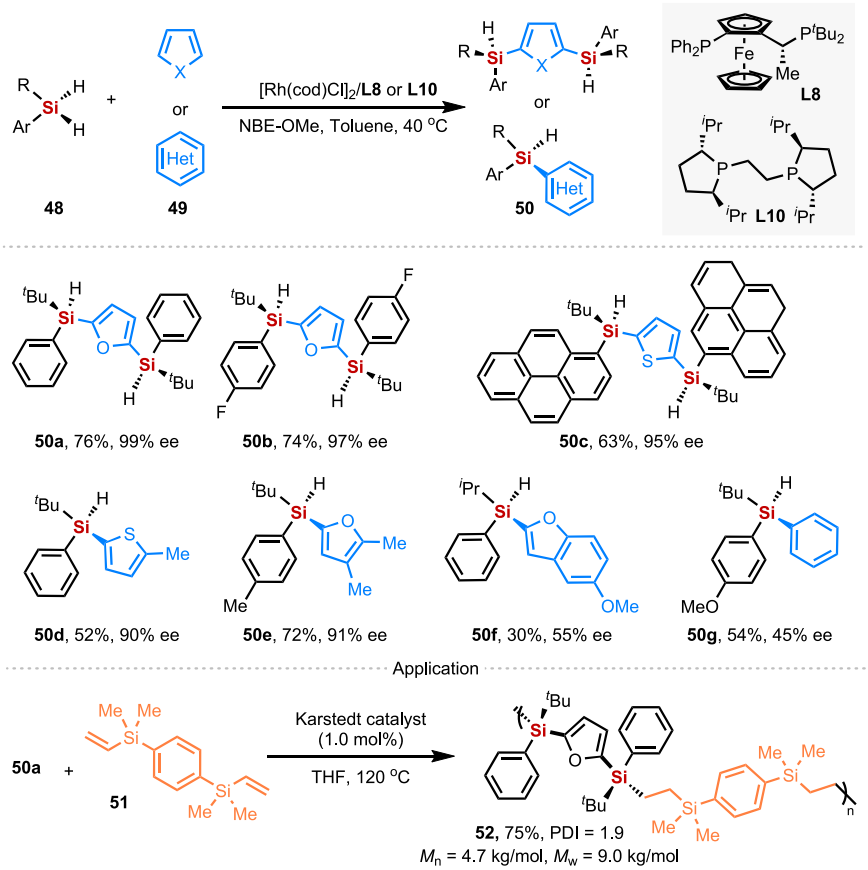
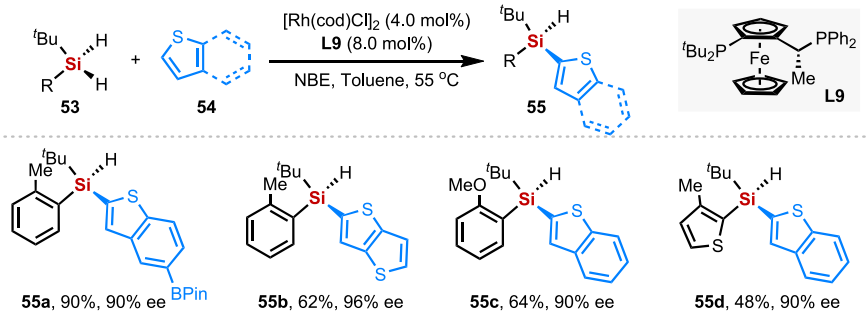


Scheme 18. Synthesis of chiral monohydrosilanes via Rh-catalyzed intermolecular dehydrogenative silylation

C. He et al.[74]

chiral phosphoramidite ligand **L11**, the products **68a–68d** were formed in up to 77% ee. Later, the same group demonstrated the synthesis of low-molecular-weight CPL materials through the same approach.[84] During the investigation of the relationship between the structure and optical properties, they found that these materials could be used to developed small organic CPL dyes (**68k** and **68l**) (Scheme 23, middle). Similar strategy has been applied by Xu and Yang group with the combination of $Pd_2(dba)_3$/TADDOL-derived phosphoramidite ligand **L12**



Scheme 19. Synthesis of Si-stereogenic monohydrosilanes via Rh-catalyzed intermolecular dehydrogenative silylation

Cheng and Huang et al.[75]

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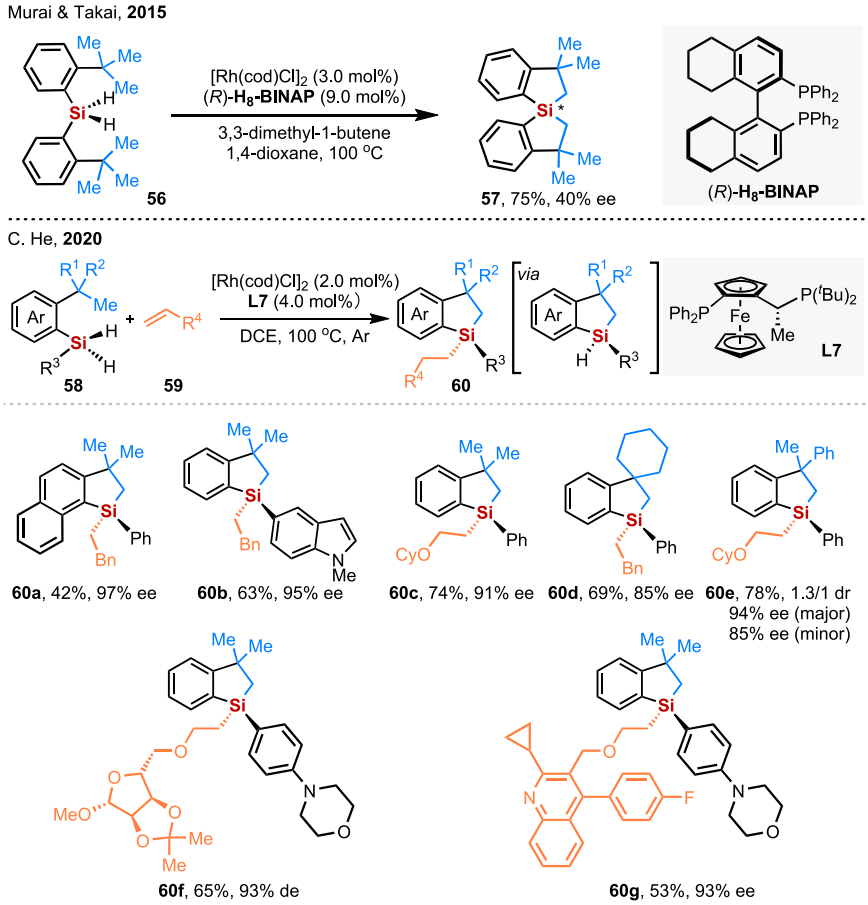

Scheme 20. Synthesis of Si-stereogenic organosilanes via Rh-catalyzed intramolecular dehydrogenative C(sp^3)–H silylation

Synthesis of spirosilabiindane (Murai and Takai et al.[76]); synthesis of dihydrobenzosiloles (C. He et al.[77]).

(Scheme 23, below).[83] By systematically revaluating TADDOL-based phosphoramidite ligands, the enantioselectivities of the arylated products **68m–68p** were improved to up to 86% ee.

Recently, L.-W. Xu, Hong, and Z. Xu et al. reported a Pd-catalyzed cross-coupling of alkynyl bromides with organosilanes (Scheme 24).[85] In this work, the asymmetric version was also evaluated for the preparation of Si-stereogenic alkynylsilane **71**, albeit in moderate enantioselectivities with a chiral xantphos-type ligand **L13**.

Construction of Si-stereogenic monohydrosilanes via Si–X bond formation

Other than Si–C bond formation in the desymmetrization of dihydrosilanes, the construction of Si-stereogenic organosilanes via Si–X (X = O, N, etc.) bond formation has also been explored, providing a series of siloxanes, silanols, and silazanes. The pioneering work was reported by Corriu group, in which rhodium-catalyzed dehydrogenative coupling occurred between prochiral dihydrosilanes and alcohols. Although 3%–19% optical purity was obtained with achiral alcohol utilizing (+)-DIOP as chiral ligand, the enantioinduction was improved by utilization of (−)-menthol as the alcohol source (**74c** and **74d**) (Scheme 25, above).[50] A breakthrough has been outlined by C. He and co-workers recently. The use of Josiphos-type ligand **L9**

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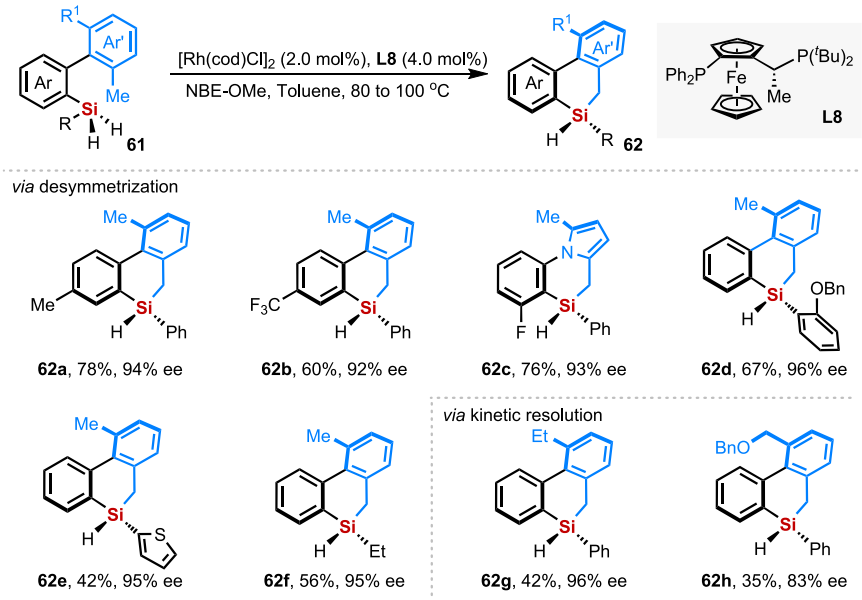

Scheme 21. Synthesis of chiral cyclic monohydrosilanes via Rh-catalyzed intramolecular dehydrogenative C(sp^3)–H silylation

C. He et al.[78]

enabled the construction of Si-stereogenic siloxanes in high enantioselectivities (Scheme 25, below).[86,87] This dehydrogenative coupling between arylalkyldihydrosilanes and alcohols or silanols proceeded smoothly, delivering the corresponding products **77** in up to 99% ee. Application-wise, the product **77e** containing pyrene displayed large g_{lum} values with high emission efficiency, indicating potency in becoming optoelectronic materials.

The next year, this strategy was further expanded to the coupling with water by the same group (Scheme 26).[88] With $[Rh(cod)Cl]_2$ and (*S*,*S*)-**Ph-BPE**, Si-stereogenic monohydrosilanols **79** could be obtained in good yields with high chemo- and stereoselectivities. Further applications of the chiral silanols were demonstrated and the modifications on both hydroxyl and hydro motifs in a stereospecific manner delivered various Si-stereogenic derivatives (**80**, **81**).

In 2003, Leighton group reported a Cu-catalyzed alcoholysis of prochiral dihydrosilanes (Scheme 27).[89] With the combination of chiral BDPP ligand (**L3** or **L14**) and chiral alcohols **83**, monohydrosilanes **84** were obtained in good diastereoselectivities. Of note, the chirality on the silane atom relied on the ligand and the diastereomers could be accessible with (*R*,*R*)-**L3** or (*S*,*S*)-**L3**. Further improvement on the diastereoselectivity (32.3/1 dr) was realized by the utilization of the 3,5-difluorophenyl analog of (*R*,*R*)-BDPP (**L14**).

In 2022, Liu, Gu, and Wang et al. reported the asymmetric dehydrogenative Si–O coupling with water, catalyzed by copper for the first time.[90] By using a chiral *N*,*N*,*P*-ligand (**L15**), a wide range of Si-stereogenic monohydrosilanols **86** were readily synthesized via the coupling of *tert*-butylaryldihydrosilanes with water in good yields and high enantioselectivities using **87** as a SET oxidant (Scheme 28). However, the replacement of aryl group on silicon atom by a triphenyl alkenyl group significantly decreases both efficiency and stereoselectivity (**86g**). The bulky *tert*-butyl group is also essential for the stability of the monohydrosilanols and efficiency.

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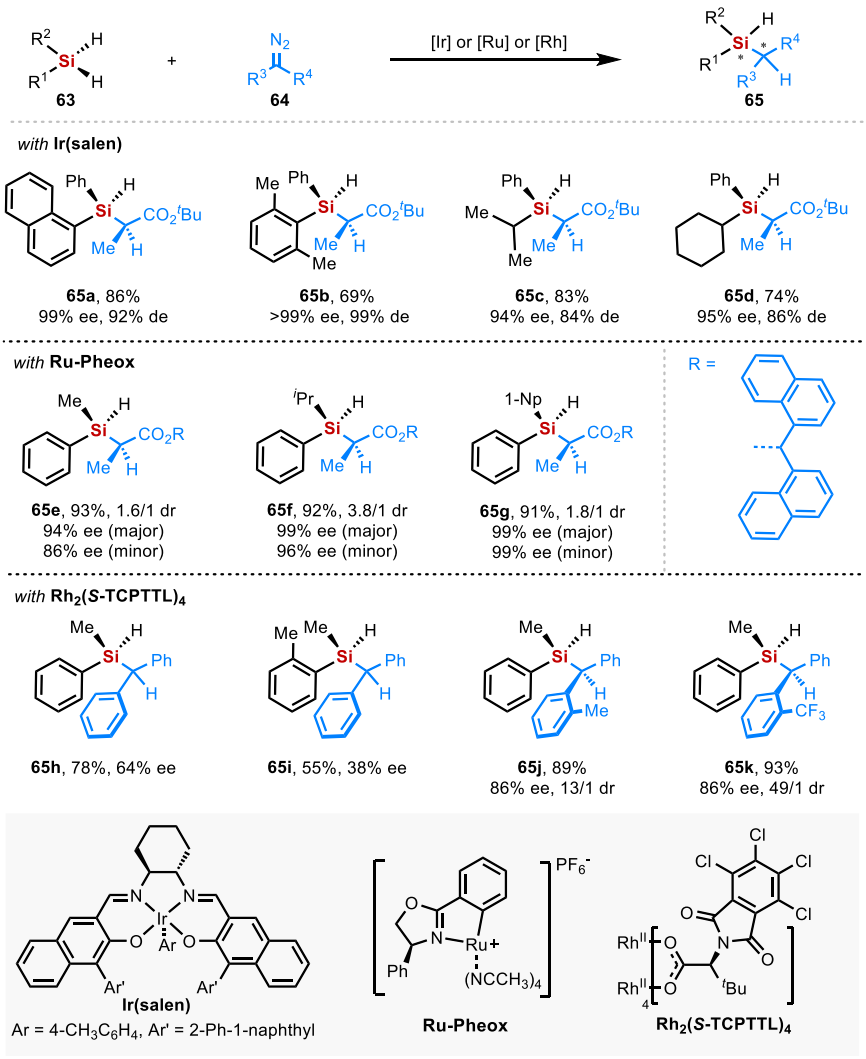

Scheme 22. Synthesis of chiral acyclic monohydrosilanes via asymmetric carbene insertion into Si–H bond

Ir catalysis (Katsuki et al.[79]); Ru catalysis (Iwasa and Chanthamath et al.[80]); Rh catalysis (Franz and Shaw et al.[81]).

A smaller cyclohexyl group resulted in 25% yield and 67% ee (**86h**). Preliminary mechanistic studies unveiled that the reaction was initiated by the SET process with alkyl bromide **87** to given **Int 10**, followed by base-promoted hydrolysis to reach **Int 11**. The subsequent σ-metathesis with dihydrosilanes occurred through a four-membered cyclic transition state to give the final silanol product.

In polymer chemistry, this dehydrogenative construction strategy has been employed to access the chiral-at-silicon main chain polymer by Kawakami group in 2000 (Scheme 29).[91] Three bis(silane) monomers, 1,2-bis(phenyldihydrosilyl)ethane (**BSE**), 1,4-bis(phenyldihydrosilyl)benzene (**BSB**) or 1,4-bis(phenyldihydrosilyl)naphthalene (**BSN**), were engaged with cyclohexanediol (**CHDOL**), giving the corresponding chiral polymers **88** in the presence of Rh[(*R*)-**BINAP**]Cl. The enantioselectivities could be determined (average 1.5%∼39.8% ee) by the cleavage of chiral polymers with MeMgBr.

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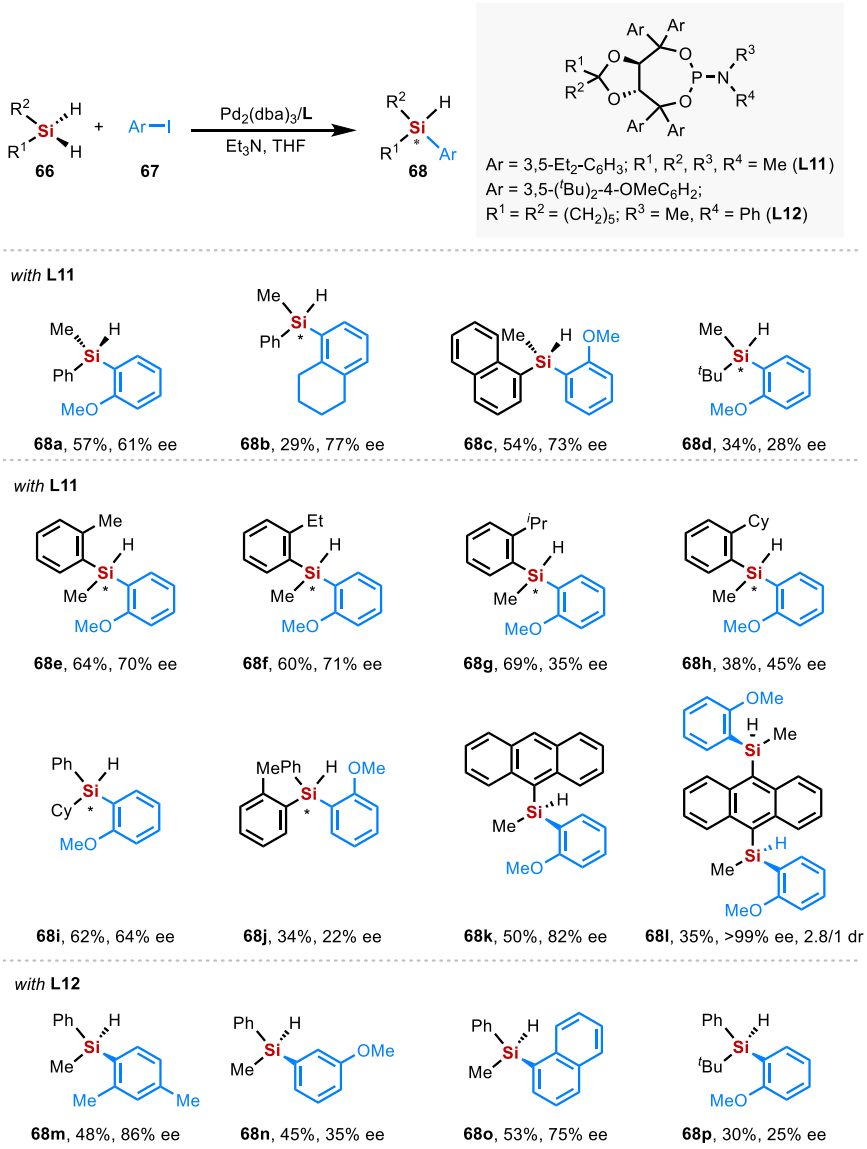
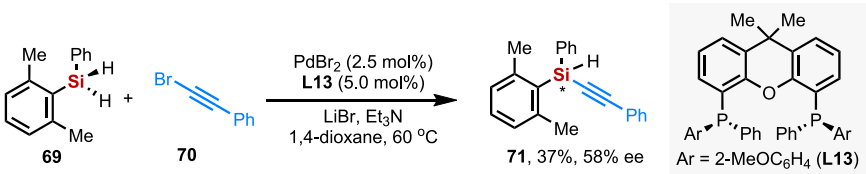


Scheme 23. Synthesis of chiral acyclic monohydrosilanes via Pd-catalyzed cross-coupling of aryl halides

Pioneering work (Yamanoi and Nishihara et al.[82]); further investigation (Xu et al.[83]).

Si-stereogenic siloxanes could also be reached by the asymmetric hydrosilylation of ketones via the silicon–oxygen bond formation. Back in the 1970s, Corriu group and Kumada group independently reported a Rh-catalyzed hydrosilylation of ketones, affording the corresponding products **92a–92g** in low to moderate enantioselectivities by the employment of chiral phosphine ligand (Scheme 30, above).[51,92,93] The chiral induction was largely improved by Takaya and co-workers in 1994 by the utilization of (*R*)-**Cybinap** (Scheme 30, below).[94] The optically active chiral siloxanes **92e–92g** were prepared in up to >99% ee from (1-naphthyl)phenylsilane.

In 2018, L.-W. Xu and Z. Xu group reported the synthesis of six-membered silyloxycycles and cyclic siloxanes via platinum-catalyzed sequential hydrosilylation and cyclization (Scheme 31).[95] Using the chiral diphosphine ligand **L17** developed by

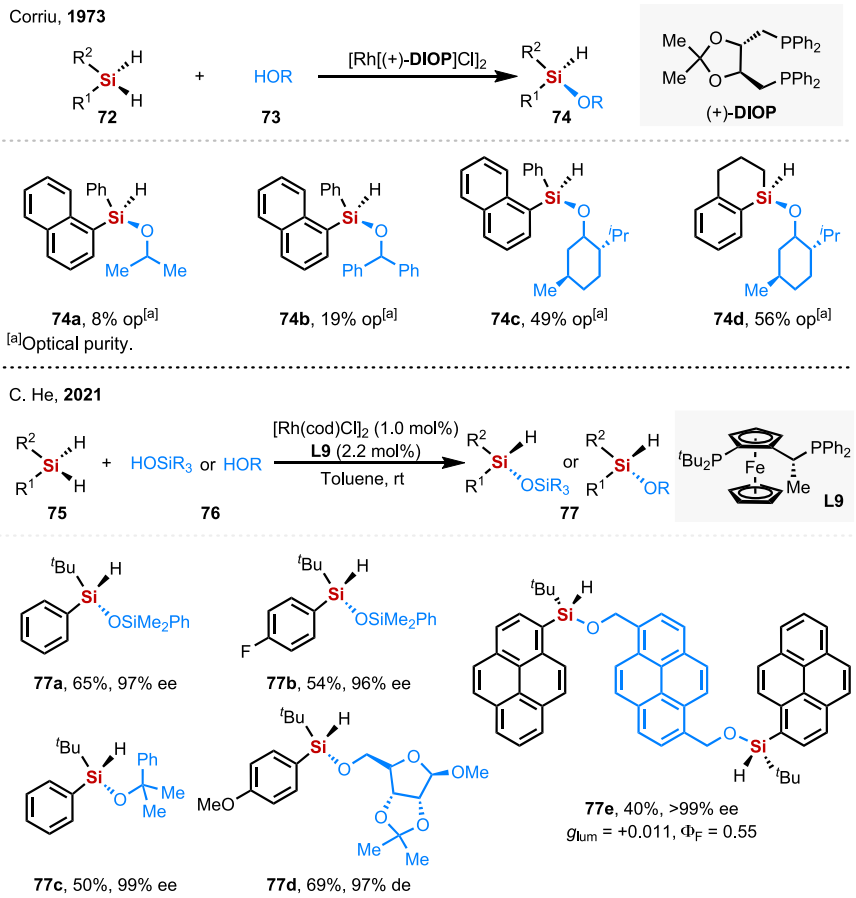


Scheme 24. Synthesis of Si-stereogenic alkynylsilane via Pd-catalyzed cross-coupling of alkynyl bromides

L.-W. Xu, Hong, and Z. Xu et al.[85]

the same group, they also attempted the chiral version of this reaction, albeit up to 32% ee was obtained therein.

Besides Si–O bond formation, the construction of silicon-nitrogen bond can also give access to Si-stereogenic organosilanes. In 2017, Guan group first reported a proof-of-concept yttrium-catalyzed cross-dehydrogenative coupling of amines with prochiral silanes (Scheme 32).[96] With the novel yttrium-iminophosphonamide complex (**Y1**), chiral silylamine **97** could be obtained efficiently in up to 23% ee via one-pot dehydrogenation/borylation process. 2 years later, the same group introduced a calcium catalyst into this coupling reaction and the same product **97** was



Scheme 25. Synthesis of Si-stereogenic siloxanes via Rh-catalyzed dehydrogenative coupling reaction

Rh/(+)-**DIOP** (Corriu et al.[50]); Rh/Josiphos (C. He et al.[86]).

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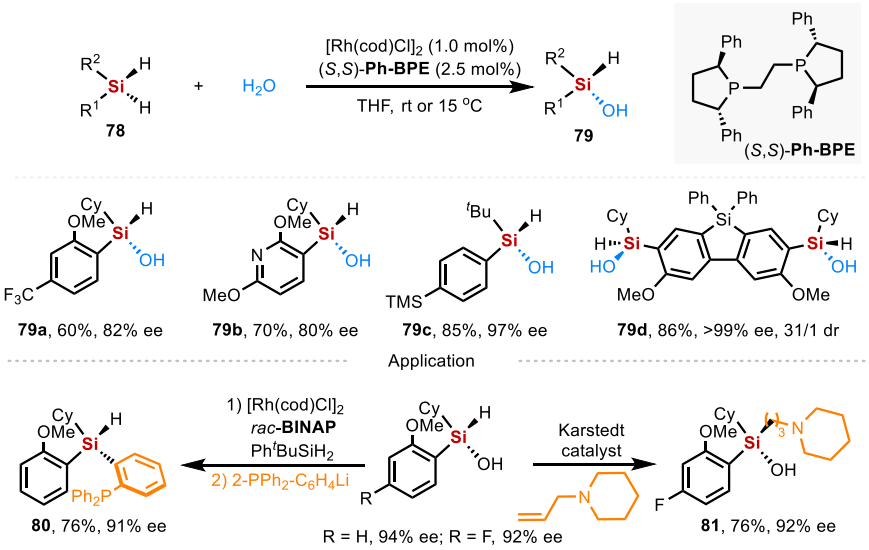
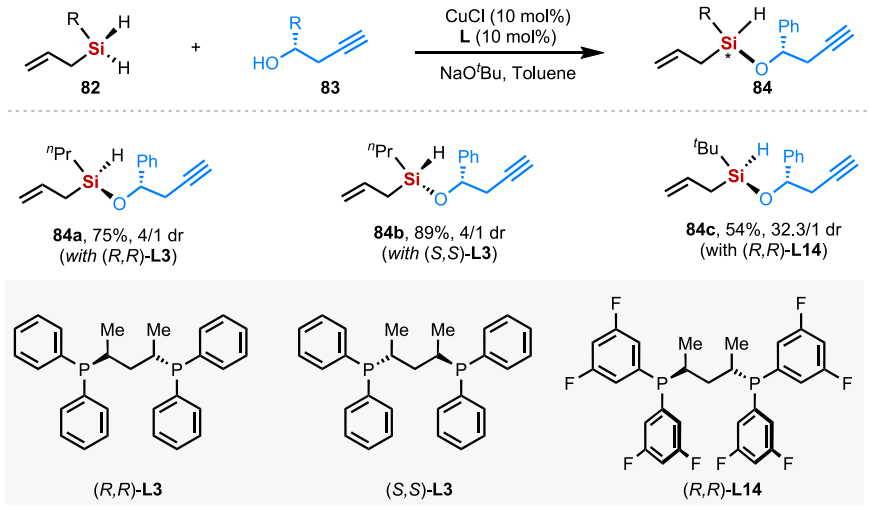


Scheme 26. Synthesis of Si-stereogenic monohydrosilanols via Rh-catalyzed dehydrogenative coupling reaction with water
C. He et al.[88]

afforded in a slightly increased enantioselectivity in the presence of the chiral N-heterocyclic carbene (NHC) ligand (**L18**).[97]

Very recently, the synthesis of Si-stereogenic silazanes in high enantioselectivity has been shown by C. He and co-workers (Scheme 33).[98] Employing Rh/diphosphine ligand (**L9**) as catalyst, the dehydrogenative coupling proceeded smoothly, delivering the target products **100** in high yields and good stereoselectivities. Moreover, this protocol could also be utilized for preparation of Si-stereogenic polycarbosilazanes, producing **100h** and **100i** in good yields and excellent enantioselectivities.

Switching the nitrogen source, the same group presented the application of this chiral catalyst system in the *N*-silylation of sulfoximine, where a variety of Si-stereogenic



Scheme 27. Synthesis of Si-stereogenic siloxanes via Cu-catalyzed alcoholysis
Leighton et al.[89]

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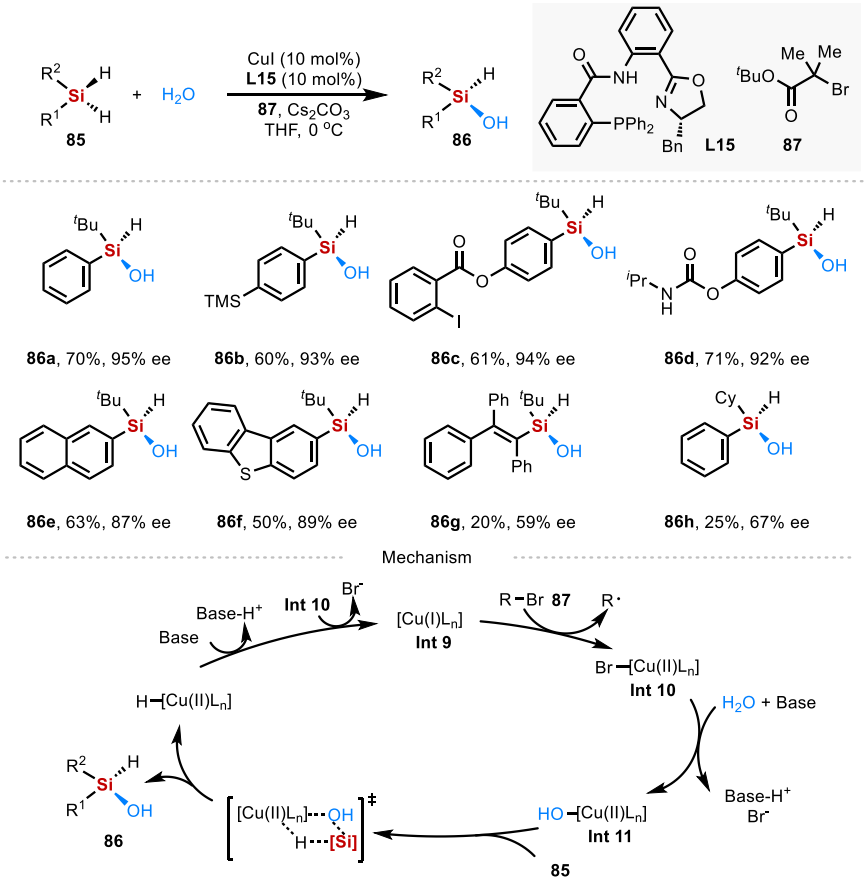
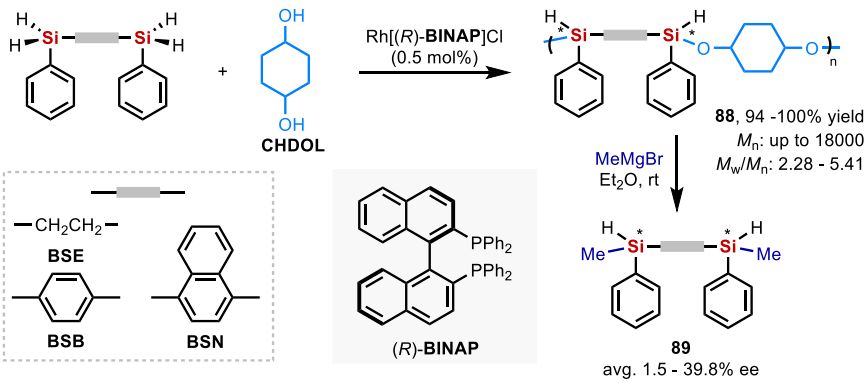


Scheme 28. Synthesis of Si-stereogenic monohydrosilanols via Cu-catalyzed asymmetric dehydrogenative Si–O coupling with water

Liu, Gu, and Wang et al.[90]

103 were reached in high enantioselectivities (Scheme 34).[99] Product 103e containing a 9,9-dimethyl-9,10-dihydroacridine unit features a large Stokes shift of 220 nm and was thought to have potential usage as TADF materials. The chiral *N*-silylated sulfoximine 103f was further utilized in polymerization to afford 104 efficiently with small polymer dispersity index.



Scheme 29. Synthesis of chiral-at-silicon main-chain polymer via Rh-catalyzed asymmetric dehydrogenation

Kawakami et al.[91]

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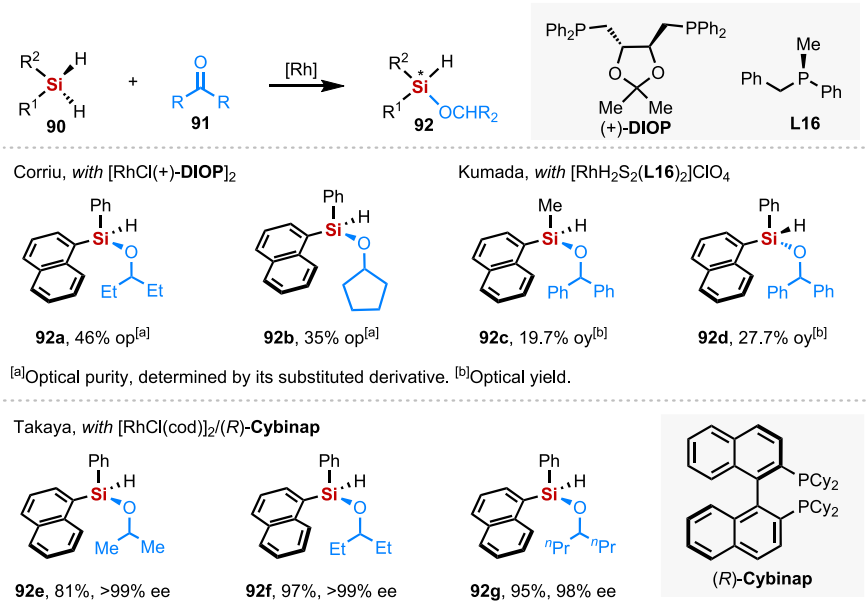
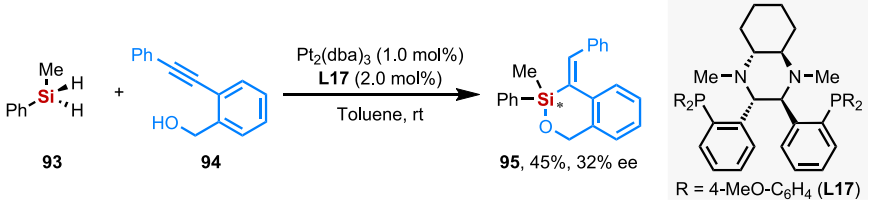


Scheme 30. Synthesis of chiral Si-stereogenic silanols via Rh-catalyzed hydrosilylation of ketones
Rh/(+)-**DIOP** (Corriu et al.[51]); Rh/**L16** (Kumada et al.[92,93]); Rh/(*R*)-**Cybinap** (Takaya et al.[94]).

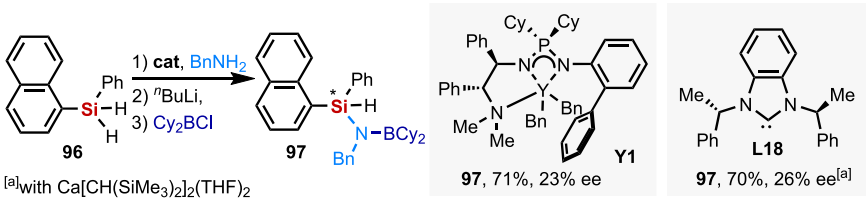
CATALYTIC ASYMMETRIC DESYMMETRIZATION OF CYCLIC AND ACYCLIC DIALKYLSILANES

Silacyclobutanes (SCBs) and their derivatives have long been known as a versatile linchpin involved in ring-opening or ring-expansion processes due to the incorporation of their C(alkyl)–Si bonds in a strained four-numbered-ring system (150 kJ/mol) and enhanced Lewis acidity. Although the research on this chemistry could be traced back to the late 19th century,[100] the first example of asymmetric construction of silicon stereocenters from SCBs was reported by Shintani, Hayashi, and co-workers in 2011 (Scheme 35).[101] Here, the intramolecular ring expansion reaction of alkyne-tethered SCBs was developed in the presence of PdCp(η^3-C_3H_5)/chiral phosphoramidite ligand [(*S,S,S*)-**L19**], delivering the corresponding products **106** in moderate to high enantioselectivities. The reaction was also reproducible on a larger scale with a reduced catalyst loading (3.0 mol % Pd catalyst), and the ee value was further improved after treating with activated carbon and trituration. As an exemplary functionalization of this ring expansion product, hydroboration with BH_3·THF was carried out in a regio- and diastereoselective manner to deliver **107** with contiguous two-carbon and one quaternary silicon stereocenters.

Thereafter, the same group expanded this asymmetric ring expansion reaction to the intermolecular version. With the same catalyst system, 1-sila-2-cyclohexenes



Scheme 31. Synthesis of chiral cyclic siloxanes via Pt-catalyzed sequential hydrosilylation and cyclization
L.-W. Xu and Z. Xu et al.[95]

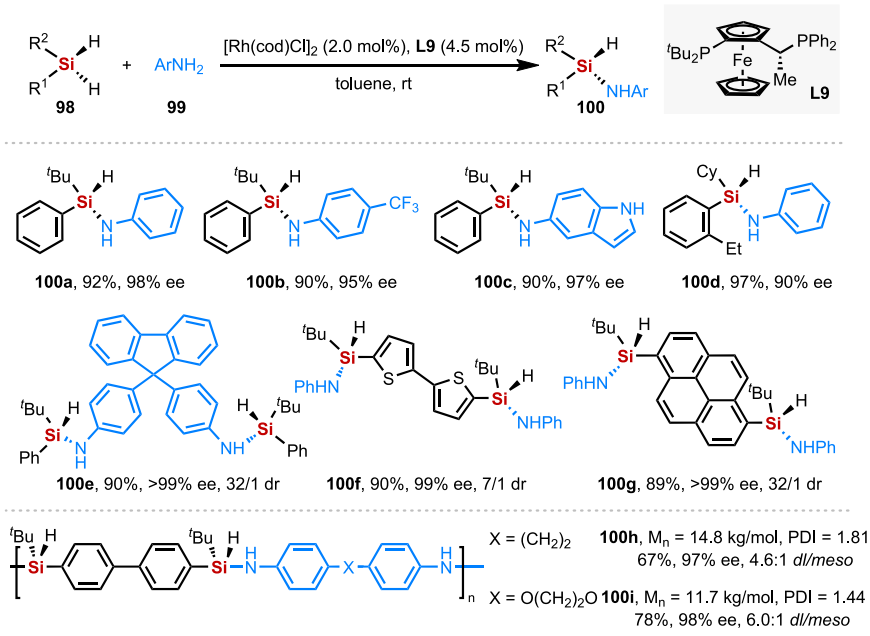


Scheme 32. Synthesis of chiral silylamine via catalytic asymmetric dehydrogenation
Yttrium catalysis (Guan et al.[96]); calcium catalysis (Guan et al.[97]).

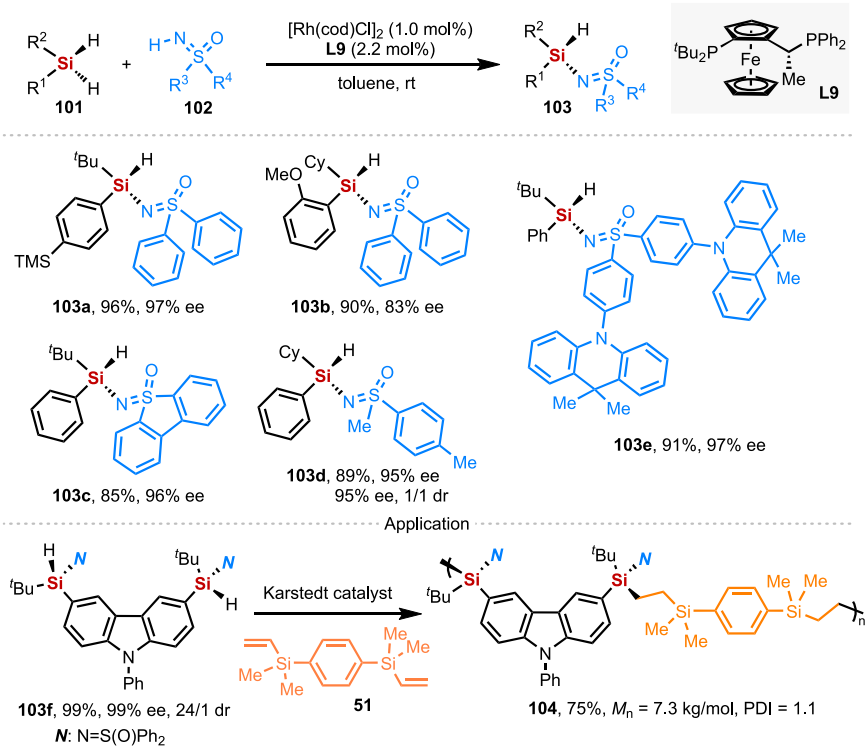
110 were synthesized in high yields and good enantioselectivities though the reaction between SCBs and electron-deficient alkynes (Scheme 36).[102] It is noteworthy that a single regioisomer was obtained when unsymmetrical alkynes were used (109b). Instead of the initial oxidative addition of Pd to SCB, experimental evidence indicated that the catalyst preferred to coordinate to alkyne (oxidative cyclization), followed by transmetalation (σ-bond metathesis) and reductive elimination to afford the final product. Lastly, chemo- and diastereoselective transformations on Si-stereogenic 1-sila-2-cyclohexenes could yield bicyclic lactone 112 via olefin hydrogenation and reduction.

In 2019, Song group revisited the above reaction and realized an intermolercular cycloaddition of SCBs with unactivated terminal alkynes 114 in the presence of a Rh catalyst (Scheme 37).[103] An array of silacyclohexenes 115 were constructed in good yields and enantioselectivities. Moreover, this methodology could be applied in the synthesis of (−)-sila-mesembranol bearing a quaternary silicon chiral center, which possesses better antidepressant effects in comparison with its natural analog (−)-mesembranol in mice.[41]

In 2021, this asymmetric ring expansion reaction of SCBs with alkynes was further explored by Xu group (Scheme 38).[104] Employing a chiral Ar-BINMOL-Phos (*S*,*R*)-L21 as ligand, multi-substituted 1-sila-2-cyclohexenes 118, bearing an aryl α,β-unsaturated



Scheme 33. Synthesis of Si-stereogenic silazanes via Rh-catalyzed asymmetric dehydrogenation
C. He et al.[98]



Scheme 34. Synthesis of *N*-silylated sulfoximines c via Rh-catalyzed asymmetric dehydrogenation
C. He et al.[99]

ester moiety, have been yielded in excellent chemoselectivities, moderate to good yields and enantioselectivities in the presence of a bimetallic system (Rh/Cu).

More recently, axially chiral 6/6-silaspiranes have been successfully accessed via the dual ring expansion of spirosilabicyclobutane **119** by Song, Yang, and Lan group (Scheme 39).[105] With electron-rich alkenes and the bulky chiral binaphthyl phosphoramidite ligand (*R*)-**L22**, this Rh-catalyzed asymmetric reaction proceeded in good enantioselectivities (**121a–121d**). Observing deactivation after the first ring expansion when using alkenes with electron-deficient groups, the authors also developed a stepwise process, which could be further applied for the construction of heterodisubstituted spirosilabicyclohexenes from two different alkynes (**121g** and **121h**). To evaluate the chiroptical properties of this 6/6-spiro skeleton, further transformation of **121b** via the Suzuki-Miyaura cross-coupling reaction was performed to afford pyrene-bearing **123**, which shows promising CPL activity.

Following this lead, the same group then reported the construction of Si-stereogenic 6/5-spirosilafluorenes utilizing a similar catalyst system (Scheme 40). With substrate type **124** containing the SCB-spirofused structure unit, this Rh-catalyzed asymmetric ring expansion reaction with terminal alkenes proceeded smoothly to afford **126** in excellent enantioselectivities.[106] The authors noted that *ortho*-substituents in spirosilafluorene-fused SCBs are required to reach the high stereoinduction (**126a–126c** vs. **126d**). When the product was decorated with the tetraphenylethylene (TPE) groups (**127**), aggregation-induced emission (AIE) property could be observed.

In 2022, Song and Su groups reported a palladium-catalyzed asymmetric ring expansion of SCBs with allenoates **129**, affording chiral silacyclohexanes **130**

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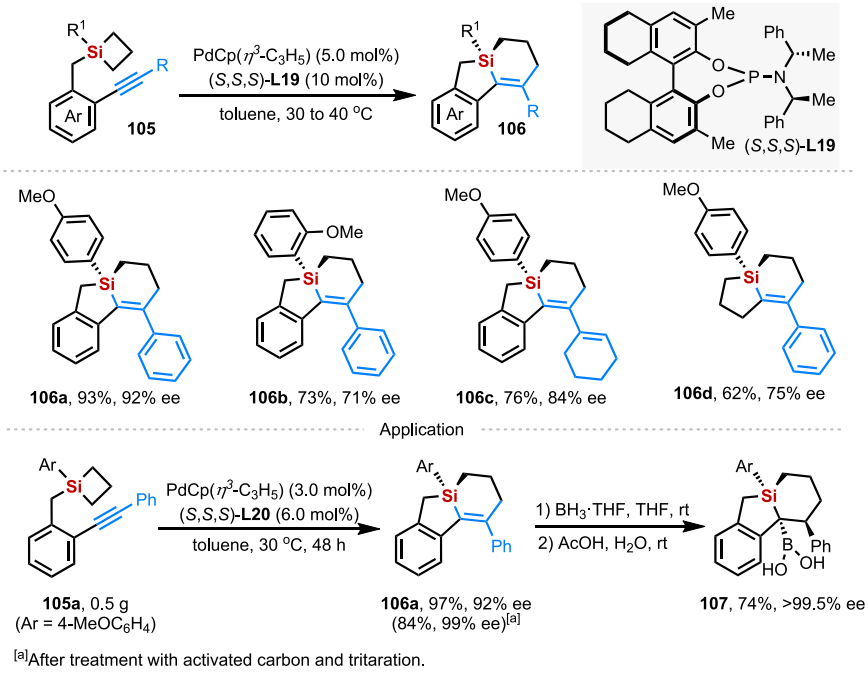


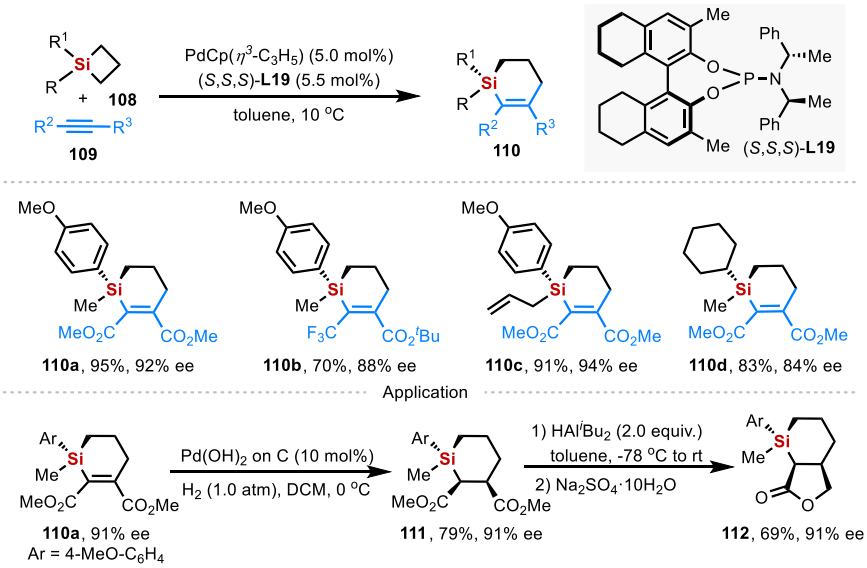
[a]After treatment with activated carbon and tritaration.

Scheme 35. Synthesis of silacycles possessing tetraorganosilicon stereocenters via Pd-catalyzed asymmetric intramolecular ring-expansion reaction

Shintani and Hayashi et al.[101]

possessing silicon-stereogenic centers (Scheme 41).[107] The excellent regioselectivity and good enantioselectivity were given in the presence of $Pd(OAc)_2$ and a TADDOL-derived ligand (*R,R*)-**L24**.

In addition to the annulation products, acyclic chiral silanes could also be formed via the intermolecular reaction between SCBs and alkynes. Exploiting the fact that β-H



Scheme 36. Synthesis of Si-stereogenic 1-sila-2-cyclohexenes via Pd-catalyzed asymmetric intermolecular ring-expansion reaction

Shintani and Hayashi et al.[102]

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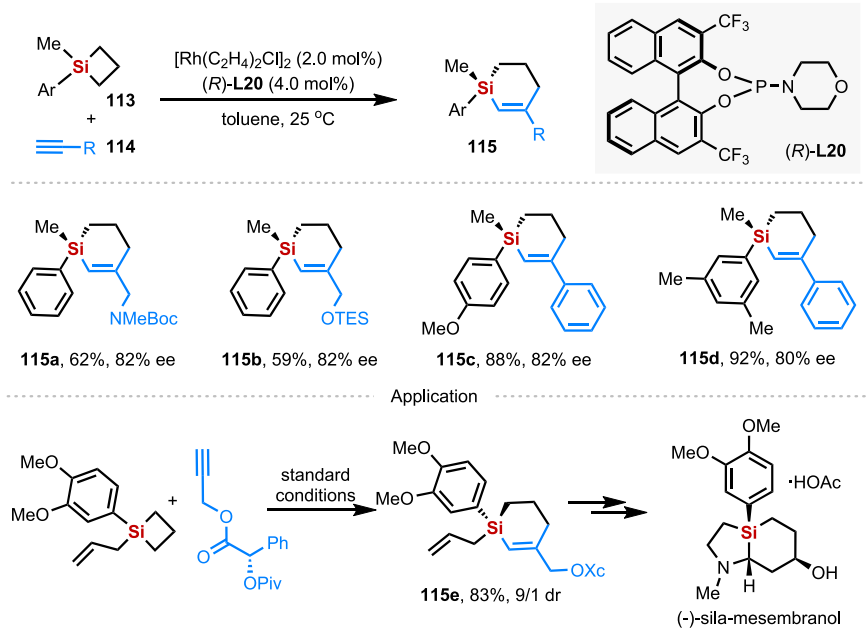
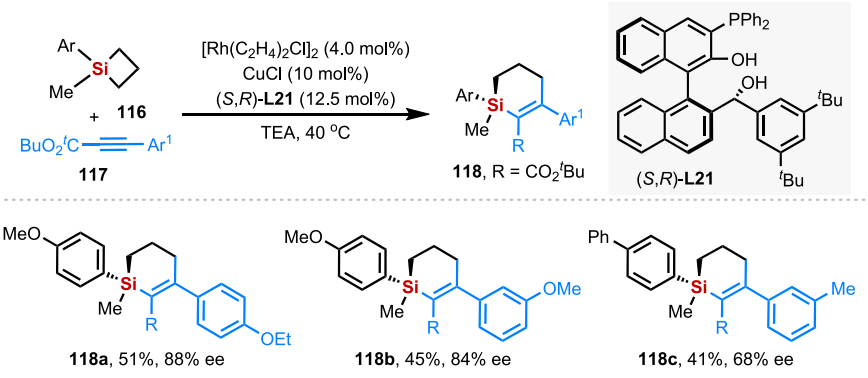


Scheme 37. Synthesis of Si-stereogenic silacyclohexenes via Rh-catalyzed asymmetric intermolecular cycloaddition

Cycloaddition of SCBs with terminal alkynes (Song et al.[103]); synthesis of (−)-sila-mesembranol (Song et al.[41]).

elimination is often more feasible at Ni-center than Pd or Rh-center, Zhao and co-workers realized the ligand-controlled chemodivergent reaction of SCBs with alkynes using nickel as catalyst, in which Si-stereogenic allyl vinylsilanes **133** have been prepared in high enantioselectivities in the presence of a TADDOL-derived phosphonite ligand (*R,R*)-**L25** (Scheme 42).[108]

In 2017, W. He group reported the asymmetric synthesis of dibenzosiloles **136** with a silicon-stereogenic center via Rh-catalyzed desymmetrization of SCBs/intermolecular dehydrogenative silylation with (hetero)arenes (Scheme 43).[109,110] In particular, exclusive regioselectivity was found with 3-substituted thiophene (**136b**). Moreover, a large excess of simple arenes is required to obtain the synthetic useful yields due to the low reactivity of simple arenes in the event of transition-metal-catalyzed C–H



Scheme 38. Synthesis of Si-stereogenic 1-sila-2-cyclohexenes via Rh/Cu-catalyzed asymmetric ring-expansion reaction

Xu et al.[104]

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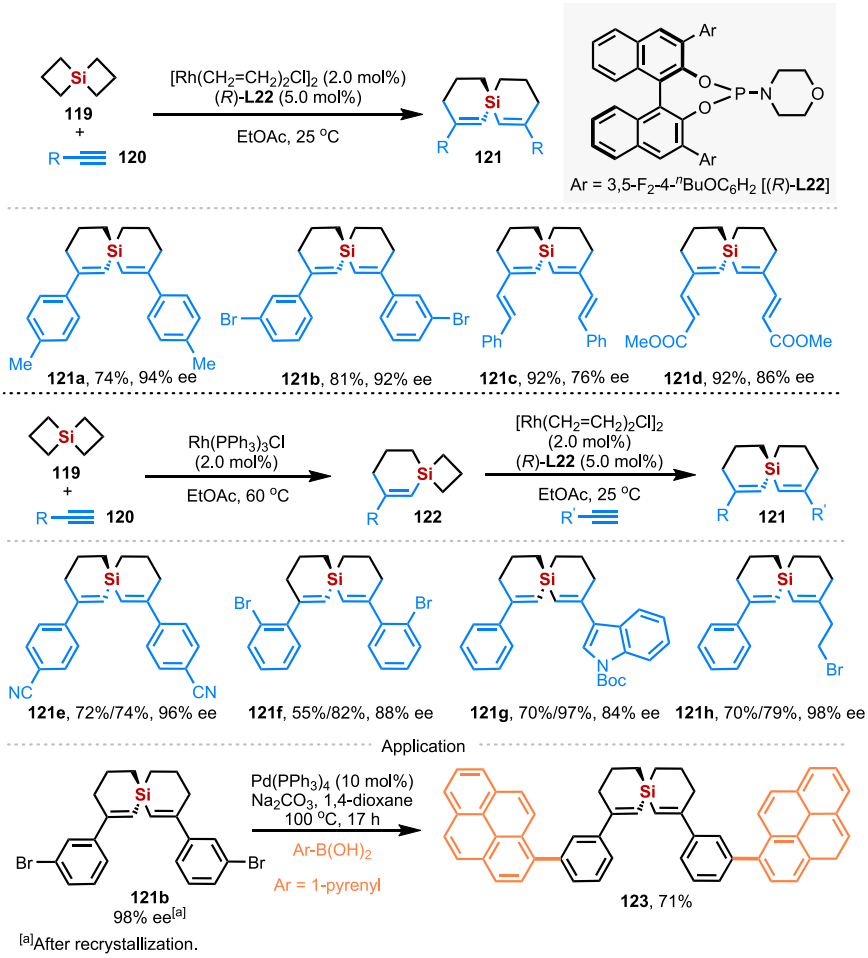

Scheme 39. Synthesis of axially chiral 6/6-silaspiranes via Rh-catalyzed asymmetric dual ring expansion

Song, Yang, and Lan et al.[105]

activation reaction (**136c**). The ferrocene substituted SCB (**134e**) was also a suitable substrate, affording the corresponding product as a single diastereomer with 91% ee. Interestingly, the removal of *ortho*-aryl group led to the formation of chiral acyclic monohydrosilanes with good chiral induction (Scheme 44). With $[Rh(C_2H_4)_2Cl]_2$/(S)-MeO-Biphep catalyst system, the enantioselective intermolecular C–H silylation of (benzo)thiophenes proceeded well (**139a–139d**).[111] For example, the Si-stereogenic monohydrosilane **139d** bearing two heterocycles was afforded in 91% ee. The steric bulky group next to silicon atom was essential to inhibit the oligomerization of SCBs.

Asymmetric reactions of SCBs with other π-units have also been explored recently. In 2021, Zhao group presented the access of enantioenriched Si-stereogenic BSs **141** via the intramolecular ring expansion of SCBs **140** containing 2-alkenylaryl group (Scheme 45).[112] The employment of a *P*-chiral monophosphorus ligand (*R*)-**L26** developed by Tang's group,[113] high enantioinduction could be reached in this nickel-catalyzed asymmetric reaction. Moreover, the molecule **141f** bearing Si-stereogenic bis-silicon-bridged π-extended system was also constructed, which displayed strong positive and negative signals at around 244 nm in the CD spectra. **141f** was also CPL-active and the value of the dissymmetry factor at the emission maxian (g_{lum}) was estimated to be 4.86×10^{-4}.

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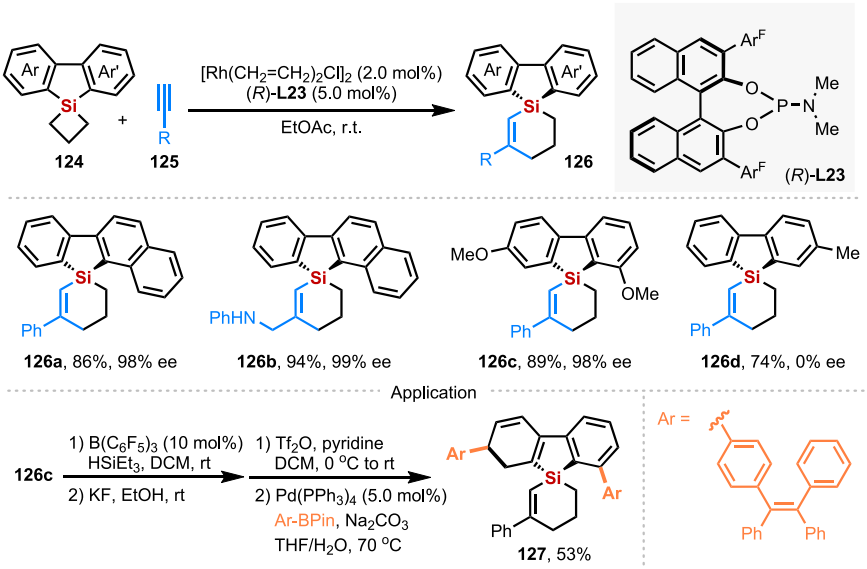
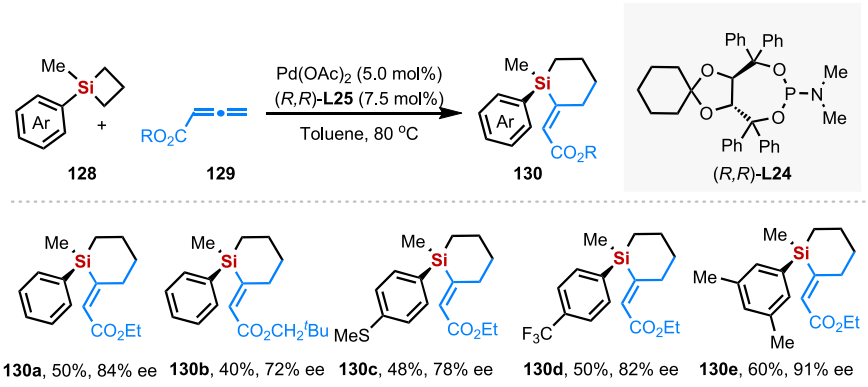


Scheme 40. Synthesis of Si-stereogenic 6/5-spirosilafluorenes via Rh-catalyzed asymmetric ring expansion

Song and Wang et al.[106]

In 2022, Zhao and Li developed a methodology to synthesize chiral sila-bridged bicyclic skeletons bearing both C- and Si-stereocenters via an intramolecular Heck-type cyclization (Scheme 46).[114] By utilizing silacyclopentenes **142** tethered the *ortho*-bromo benzyl group as the starting material and Pd/(R_p,*R*)-^{t}Bu-FOXAP as the optimal catalyst, sila-bridged compounds **143** could be prepared with high ee values. DFT calculation revealed the high enantioselectivity was attributed to ligand-controlled kinetic stereo-differentiation in the migratory insertion step.

Besides the utilization of cycloalkylsilanes to realize enantioselective synthesis of Si-stereogenic molecules, several examples starting with the acyclic dialkylsilanes have also been reported. In those cases, acyclic dialkylsilanes normally contain functional groups that could be converted. Back to the 1990s, Blanco group reported an enzyme-catalyzed esterification of prochiral dialkylsilanes **144** bearing two hydroxyl groups (Scheme 47, left).[115,116] Two Si-stereogenic silylmethanols haven been obtained in the moderate enantioselectivities using lipase from *Candida cylindracea*



Scheme 41. Synthesis of chiral silacyclohexanes via Pd-catalyzed asymmetric ring expansion

Song and Su et al.[107]

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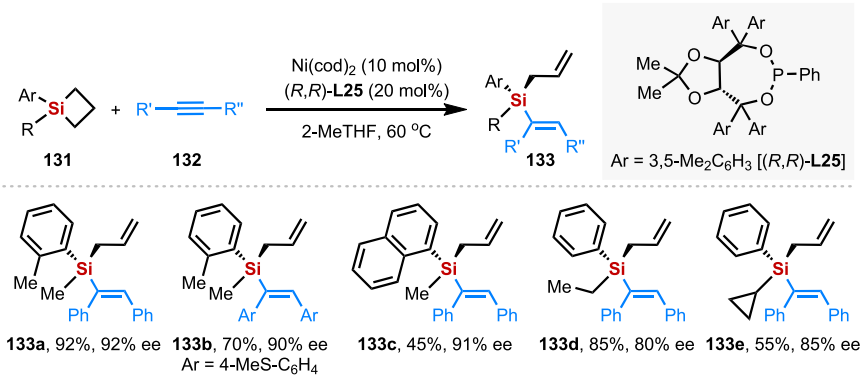


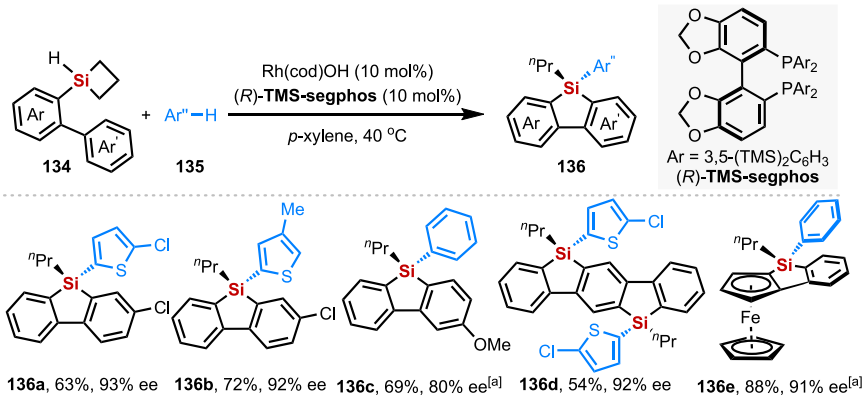
Scheme 42. Synthesis of chiral allyl vinylsilanes via Ni-catalyzed asymmetric ring-opening reaction

Zhao et al.[108]

(LCC) or lipase from *Chromobacterium viscosum* (LCV) as the catalyst (**147a** and **147b**). In comparison with transition-metal catalysis, the enzymatic system is low toxic and can tolerate moisture and oxygen. Recently, Xu, Ye, and co-workers revisited this reaction with a copper/pyridinebisoxazoline catalytic system (Scheme 47, right).[117] Various silylmethanols have been accessed in good yields and moderate enantioselectivities via the monoesterification of 2-sila-1,3-propanediols with benzoyl chlorides **146**.

Desymmetrization of dialkylsilanes by cleaving the Si–C bond was another efficient manner for construction of optical Si-stereogenic compounds. In 2012, Chatani, Tobisu, and co-workers reported a Rh-catalyzed C(sp^3)–Si bond activation reaction with symmetric alkyne **149** for the synthesis of BS in an enantioselective manner (Scheme 48).[118] With (*S*,*S*)-**QuinoxP** as the ligand, Si-stereogenic BS **150** was formed in 98% ee.

In 2022, Wang and co-workers developed a methodology to synthesize chiral α-trifluoromethyl cyclic ketones via a Sc-catalyzed homologation reaction of cyclic ketone with 2,2,2-trifluorodiazoethane (CF_3CHN_2) as the trifluoromethyl source (Scheme 49).[119] When silacyclohexanones **151** were employed as the starting materials, a variety of chiral



[a]Arene was used as solvent.

Scheme 43. Synthesis of chiral dibenzosiloles via Rh-catalyzed desymmetrization of SCBs/intermolecular dehydrogenative silylation

W. He et al.[109,110]

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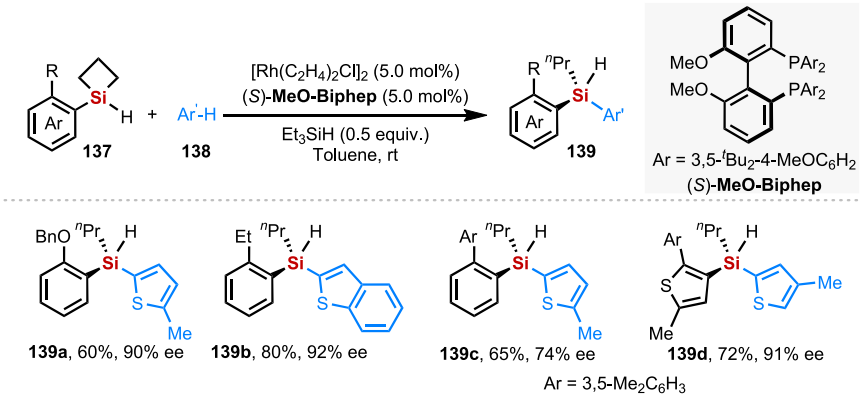
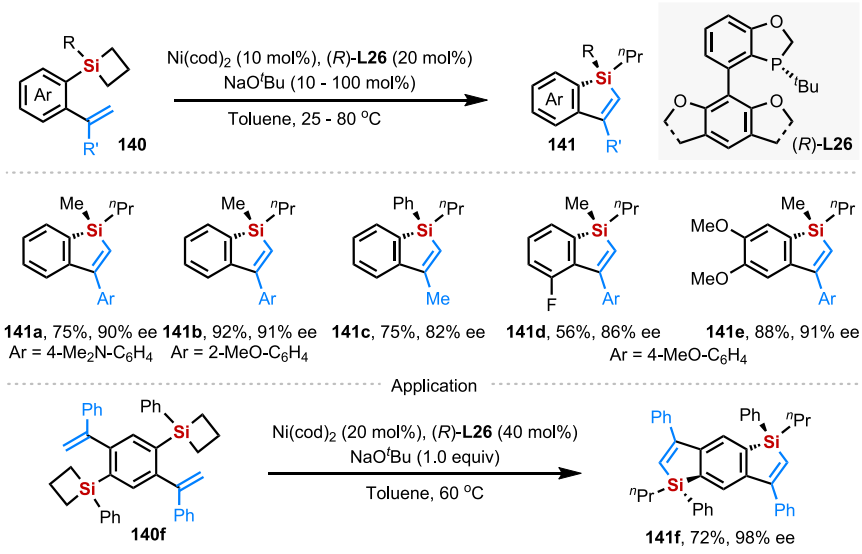


Scheme 44. Synthesis of chiral acyclic monohydrosilanes via Rh-catalyzed intermolecular C–H silylation
W. He et al.[111]

α-trifluoromethyl silacycloheptanones **153** owning two chiral centers were afforded in high enantioselectivities and moderate diastereoselectivities.

In 2022, organocatalyzed enantioselective synthesis of tertiary silyl ether **156** bearing a chiral silicon center has been first reported by List group (Scheme 50).[120] The reaction between bis(methallyl)silanes **154** and 2,6-dimethylphenol **155** proceeded smoothly with their well-studied imidodiphosphorimidate (IDPi) catalysts via a desymmetrizing C–C bond forming silicon-hydrogen exchange process (see **Int 12** to **Int 13**). The mechanism was proposed as follows, that is, **154** was first protonated by IDPi, followed by cation-π cyclization and subsequent Si–C bond cleavage to afford silylium-based ion pair **Int 14** which reacted with phenol to reach product and regenerate the catalyst.

In 2023, Yu group demonstrated the construction of Si-stereogenic cyclic 1,2,5,6-tetrahydrosilines via the enamine-catalyzed desymmetrically intramolecular



Scheme 45. Synthesis of Si-stereogenic benzosiloles via Ni-catalyzed ring-opening reaction
Zhao et al.[112]

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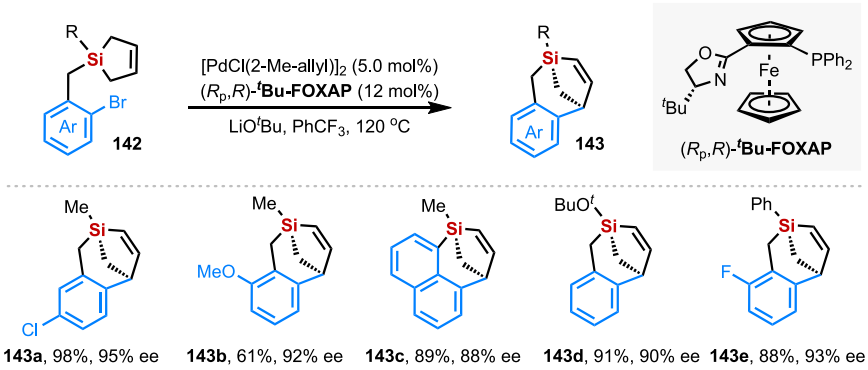


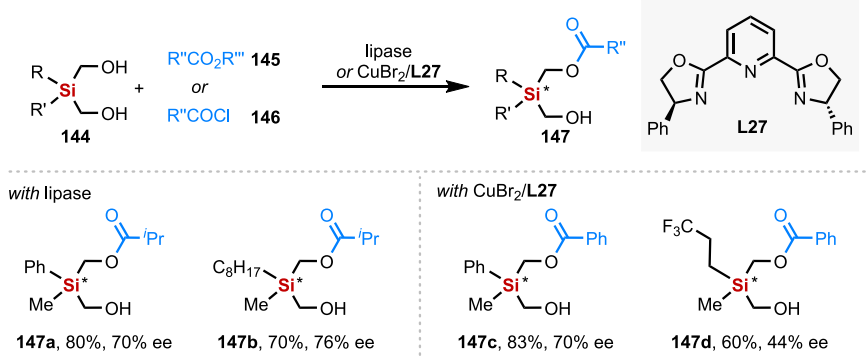
Scheme 46. Synthesis of chiral sila-bridged bicyclic skeletons via Pd-catalyzed intramolecular Heck-type cyclization
Zhao and Li et al.[114]

aldolization of prochiral siladials (Scheme 51).[121] This remote enantioinduction performed smoothly with a combination of chiral imidazolidinone (**cat1** or **cat2**) and 2,6-dichlorobenzoic acid **159**, affording 1,2,5,6-tetrahydrosilines **158** featuring an enal moiety in high yields. Of note, TfOH was required to workup the reaction, which could accelerate the dehydration process of aldol products.

CATALYTIC ASYMMETRIC DESYMMETRIZATION OF DIARYLSILANES

Since dibenzosiloles are one of the widely used motifs in optical materials, their chiral analogs are highly demanded in the development of chiral silicon-containing materials. In 2012, Shintani and Hayashi group, for the first time, reported a strategy for the construction of Si-stereogenic dibenzosiloles in an asymmetric manner (Scheme 52).[122] A $Pd(OAc)_2$/Josiphos-type ligand (**L29**) catalyst system was employed to reach the target dibenzosiloles **161** via intramolecular C–H arylation of prochiral (arylsilyl)aryl triflates **160**. It should be mentioned that C–H functionalization was occurred selectively at the less steric hinder position (**161c**). Moreover, 2-fold C–H arylations proceeded enantioselectively in 97% ee, when aryl ditriflates was used as the substrate (**161d**).

In 2017, the same group disclosed that Si-stereogenic 5,10-dihydrophenazasilines could be produced using 3-amino-substituted (arylsilyl)aryl triflates **162** (Scheme 53).[123] The high enantioselectivities were achieved when chiral bis(trimethylsilyl)-substituted BINAP [(*R*)-**L30**] was utilized as the optimal ligand. Both experimental



Scheme 47. Synthesis of Si-stereogenic silylmethanols via catalytic asymmetric esterification
Enzymatic esterification (Blanco et al.[115,116]); Cu-catalyzed esterification (Xu et al.[117]).

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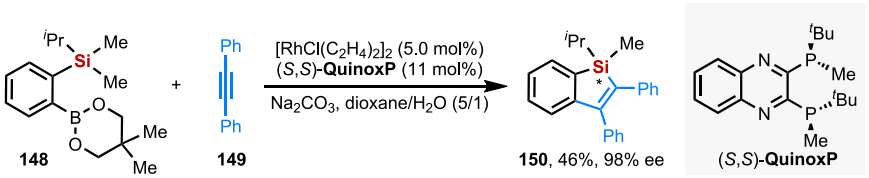


Scheme 48. Synthesis of Si-stereogenic benzosiloles via Rh-catalyzed asymmetric C(sp^3)–Si bond activation reaction

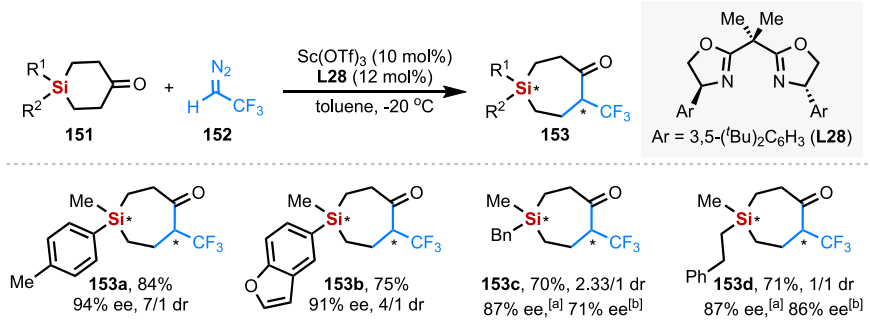
Xu et al.[118]

and theoretical studies indicated that this process underwent a sequence of oxidative addition, 1,5-palladium migration and intermolecular coordination of the amino group to the palladium center, followed by deprotonation and reductive elimination. Mechanistic studies also unveiled that 1,5-palladium migration was the enantio-determining step.[124]

Following the above strategy utilizing 1,5-metal migration for Si-stereogenic molecule construction, Shintani group reported the synthesis of 5*H*-dibenzo[*b*,*f*]silepin derivatives, which was triggered by 1,5-palladium migration in 2021 (Scheme 54).[125] In this report, one example was demonstrated in the asymmetric version when (*R*)-**BINAP** was used as the ligand, giving the chiral 13*H*-benzo[*f*]fluoreno[1,9-*bc*]silepin **165** in a promising enantioselectivity. The multiple 1,n-palladium migrations were involved in this reaction which allows to reach the complicated structure motif in one single operation.

Very recently, the same group developed a palladium-catalyzed intramolecular Hiyama coupling to synthesize 4-sila-4*H*-benzo[*d*][1,3]oxazines (Scheme 55).[126] They also offered the asymmetric version where Josiphos-type **L31** was employed as the chiral ligand to afford the corresponding products **167** in good enantioselectivities. The mechanistic study on this reaction disclosed that intramolecular transmetalation via chiral inversion at silicon center was proceeded after oxidative addition, followed by reductive elimination.

In 2021, Zhao and co-workers utilized an intramolecular Ir-catalyzed enantioselective dehydrogenation in constructing cyclic siloxanes **170** containing the chiral silicon-stereogenic center, which could be further transformed to a Si-stereogenic chiral phenolic silanol (**PSiOL**) by Tamao-Fleming oxidation with the stereospecific ring opening (Scheme 56).[127] Furthermore, with the obtained non-C_2-symmetric chiral



[a]For major isomer. [b]For minor isomer.

Scheme 49. Synthesis of Si-stereogenic silacyclic ketones via Rh-catalyzed asymmetric C(sp^3)–Si bond activation reaction

Wang et al.[119]

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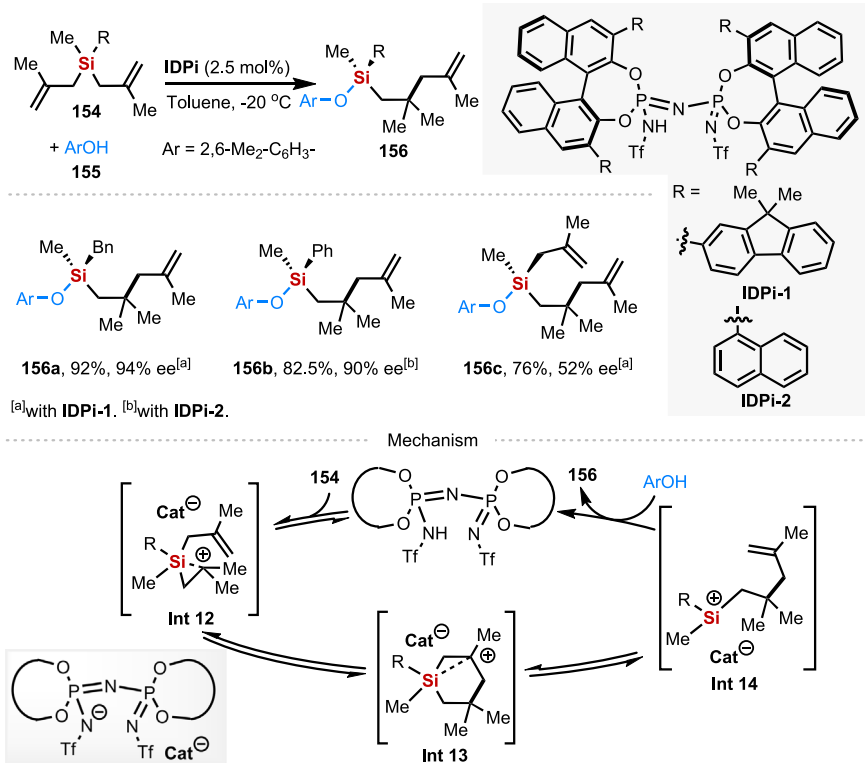
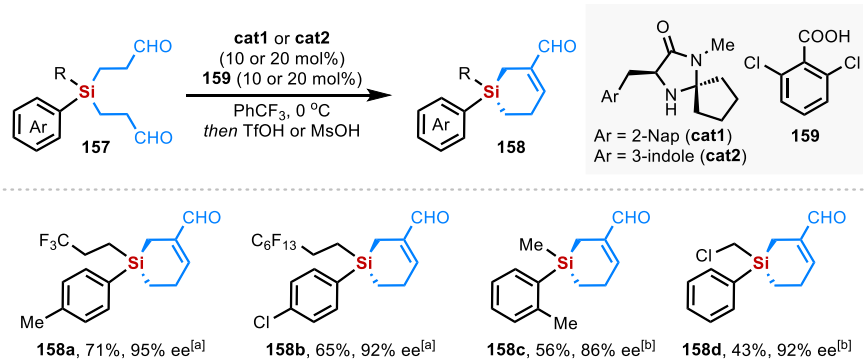


Scheme 50. Synthesis of Si-stereogenic tertiary silyl ethers via asymmetric organocatalysis
List et al.[120]

diol scaffold, the authors developed a series of PSiOL-derived chiral monodentate phosphoramidites (**171a–171c**) and preliminary studies indicated the good enantioinduction in Rh-catalyzed 1,4-addition reaction.

Catalytic strategy of Si–C bond cleavage of prochiral tetraorganosilanes has also been demonstrated by several groups. In 2012, Shintani and Hayashi reached silicon-streogenic dibenzooxasilines **176** from prochiral diphenylsilanes with Rh/(S,S)-Me-**Duphos** where enantiodiscriminating transmetalation was realized for the first



Scheme 51. Synthesis of Si-stereogenic cyclic 1,2,5,6-tetrahydrosilines via the enamine-catalyzed desymmetrically intramolecular aldolization
Yu et al.[121]

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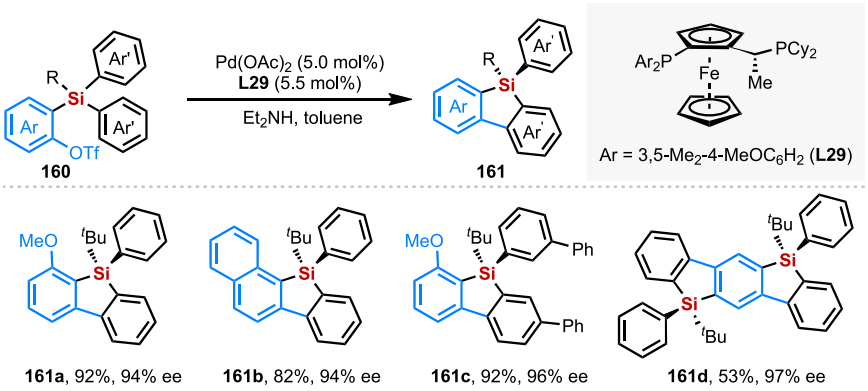
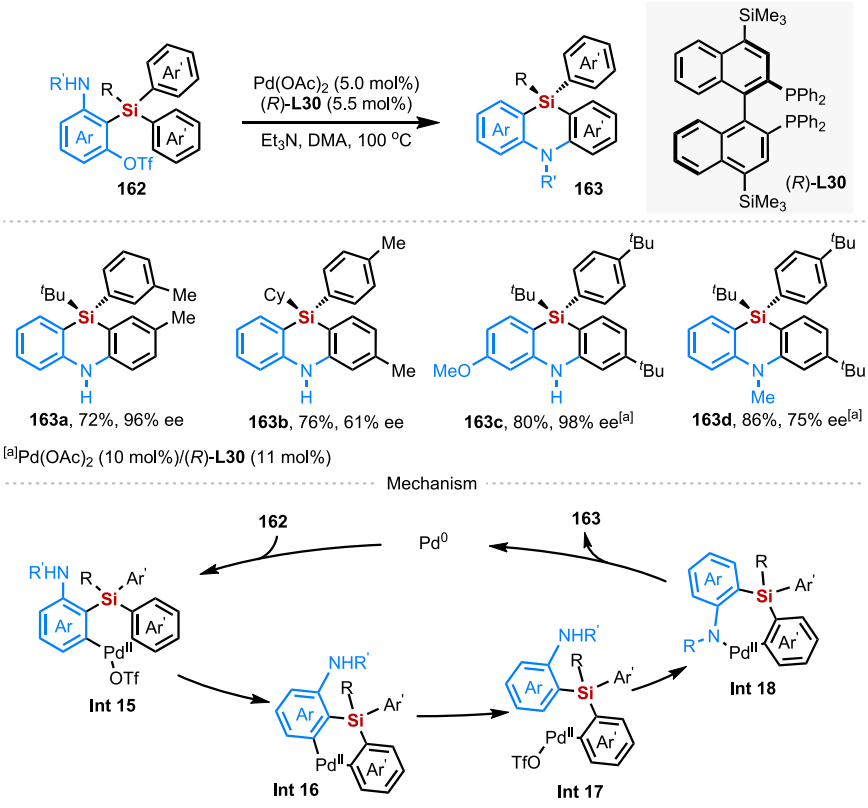


Scheme 52. Synthesis of Si-stereogenic benzosiloles via Pd-catalyzed intramolecular C–H arylation

Shintani and Hayashi et al.[122]

time (Scheme 57).[128,129] In this reaction, both reactivity and enantioselectivity highly depended on the size of the alkyl group (**176a** vs. **176e**).

In 2015, Ogoshi and co-workers introduced the aryl-transfer process into the synthesis of chiral benzoxasiloles (Scheme 58).[130] The simultaneous construction of carbon- and



Scheme 53. Synthesis of Si-stereogenic 5,10-dihydrophenazasilines via enantioselective 1,5-palladium migration

1,5-palladium migration (Shintani and Nozaki et al.[123]); mechanistic studies (Shintani, Yamashita, and Nozaki et al.[124]).

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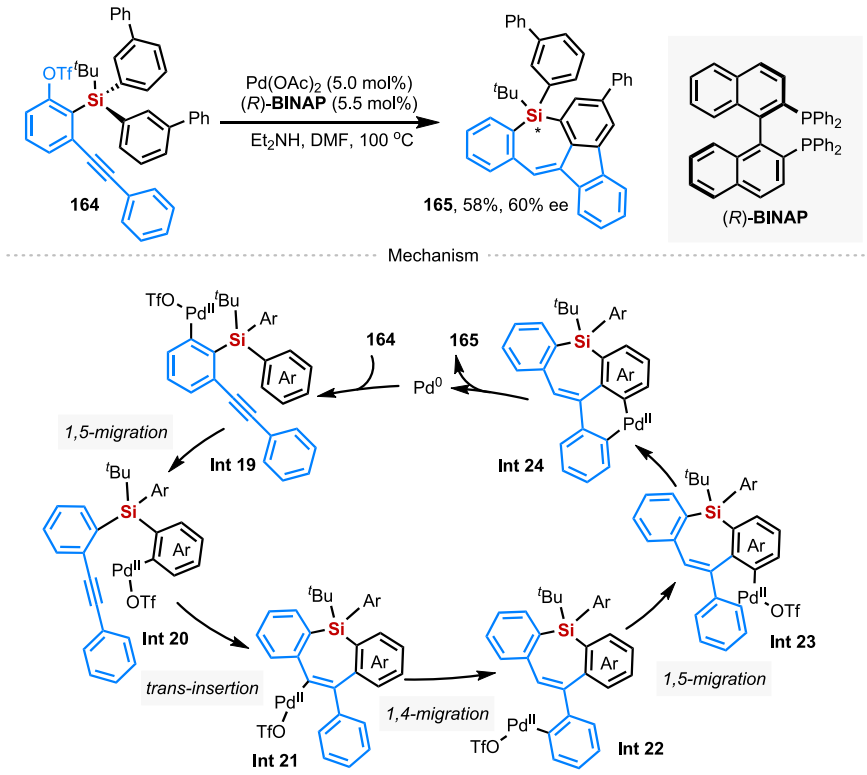
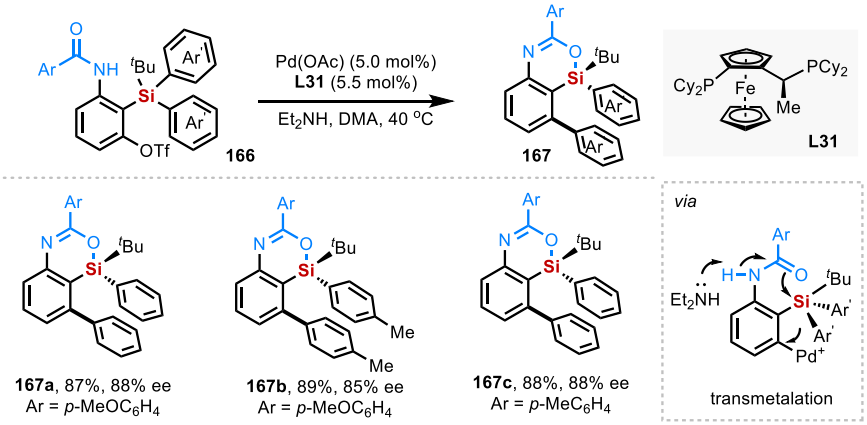


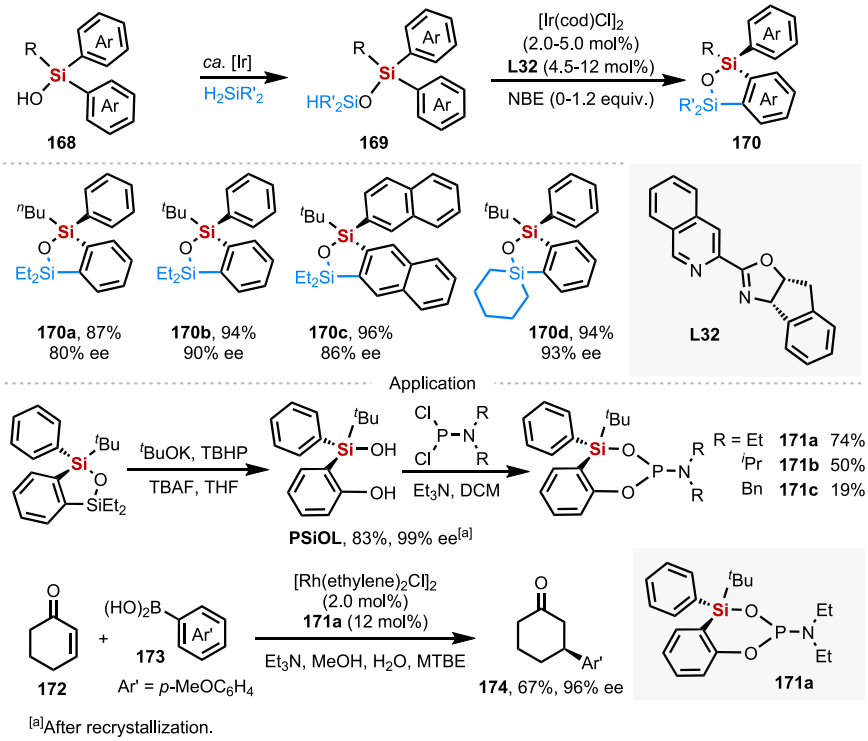
Scheme 54. Synthesis of Si-stereogenic 13*H*-benzo[*f*]fluoreno[1,9-*bc*]silepin via multiple 1,n-palladium migration
Shintani et al.[125]

Si-stereogenic center in one molecule was reached by nickel-catalyzed enantioselective addition to the aldehyde. With the chiral NHC ligand (*R,R*)-**L33**·HBF_4, the target products (**178**) were formed in high enantioselectivities and diastereoselectivies, where intramolecular aryl-migration took place by the benefit to the coordination pattern of Ni(NHC) complexes to the substrate.



Scheme 55. Synthesis of Si-stereogenic 4-sila-4*H*-benzo[*d*][1,3]oxazines via Pd-catalyzed intramolecular Hiyama coupling
Shintani et al.[126]

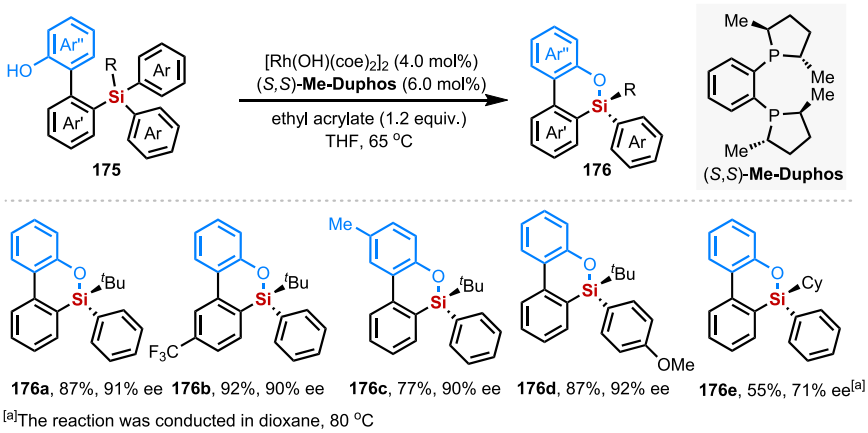
Please cite this article in press as: Wu et al., Catalytic asymmetric synthesis of silicon-stereogenic organosilanes, Chem (2023), https://doi.org/10.1016/j.chempr.2023.09.024



Scheme 56. Synthesis of Si-stereogenic cyclic siloxanes via intramolecular Ir-catalyzed enantioselective dehydrogenation

Zhao et al.[127]

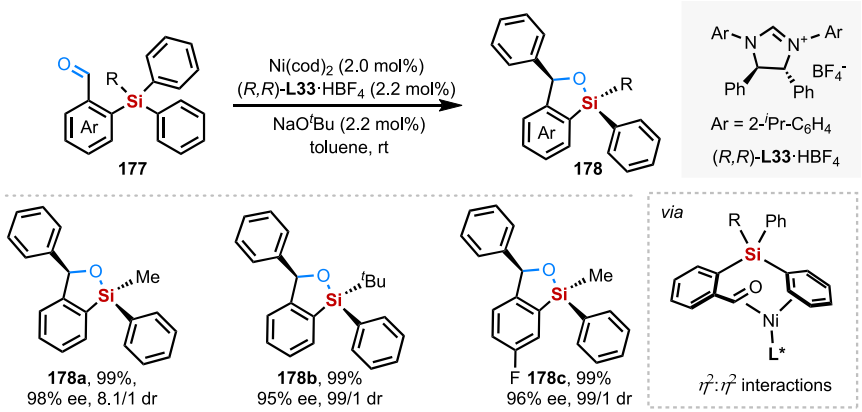
In 2021, Gu group expanded their previous research on the enantioselective aryl-Narasaka acylation for the creation of axial chirality and point chirality in one step (Scheme 59).[131,132] The Rh-catalyzed ring opening/acylation of distorted silafluorenes **179** with acid anhydride have been achieved in high enantioselectivities and diastereoselectivities with a TADDOL-based bulky phosphoramidite ligand (**L34**). Notably, the axially chiral compound with a Si-stereogenic silanol motif was synthesized for the first time.



Scheme 57. Synthesis of Si-stereogenic dibenzooxasilines via enantioselective transmetalation

Shintani and Hayashi et al.[128,129]

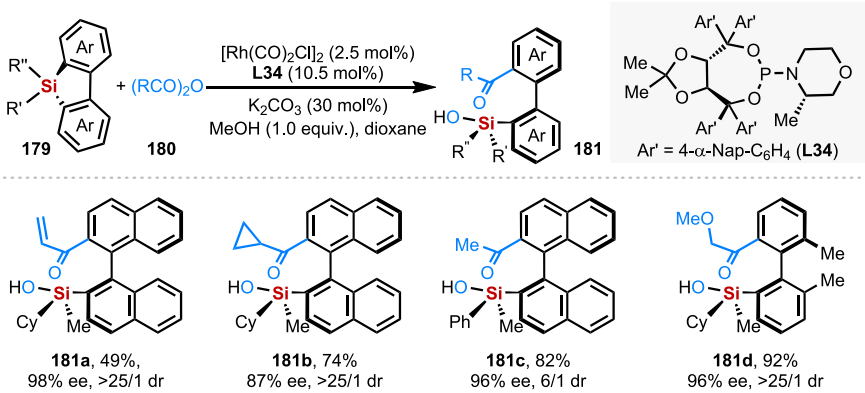
Please cite this article in press as: Wu et al., Catalytic asymmetric synthesis of silicon-stereogenic organosilanes, Chem (2023), https://doi.org/10.1016/j.chempr.2023.09.024



Scheme 58. Synthesis of Si-stereogenic benzoxasiloles via Ni-catalyzed enantioselective addition to the aldehyde
Ogoshi et al.[130]

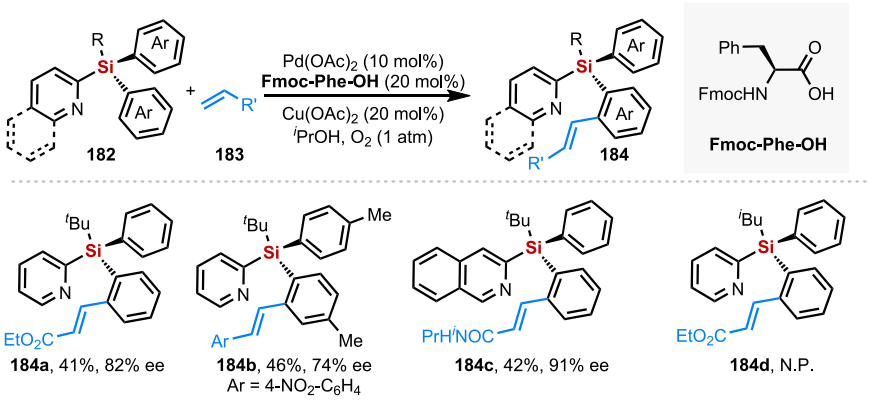
Inspired by positive affect of amino acid on the directed C(sp^2)–H functionalization using silicon-linked directing group, Xu and Cui group developed a Pd-catalyzed C–H Heck-type olefination to reach Si-stereogenic silane **184** from diaryl-substituted tetraorganosilicons **182** (Scheme 60).[133] With pyridine or quinoline as the directing group, C–H olefination proceeded smoothly in good enantioselectivities in the presence of the mono-*N*-protected amino acid (MPAA) ligand. Of note, the *tert*-butyl group was crucial for this reaction where the silane containing less bulky substituent than *tert*-butyl group attached to silicon center could not give the corresponding product (**184d**). In addition, this reaction normally gave moderate yields, probably due to the instability of the pyridine-attached organosilanes under the optimal conditions.

Hydrosilylation is a common and economic approach for the access to chiral Si-stereogenic molecules. Recently, the enantioselective rhodium-catalyzed trans-selective hydrosilylation of aryl-tethered alkynes has been introduced by Xu group to give optical BSs (Scheme 61).[15] With their developed chiral Ar-BINMOL-Phos ligand (**L35**) bearing hydrogen-bond donors, the Rh-catalyzed intramolecular reaction underwent in good to high enantioselectivities where the additive KO^{t}Bu was responsible for the formation of the active Rh species. Moreover, the fluorescence property



Scheme 59. Synthesis of Si-stereogenic organosilane bearing axial chirality and point chirality via enantioselective aryl-Narasaka acylation
Gu et al.[131,132]

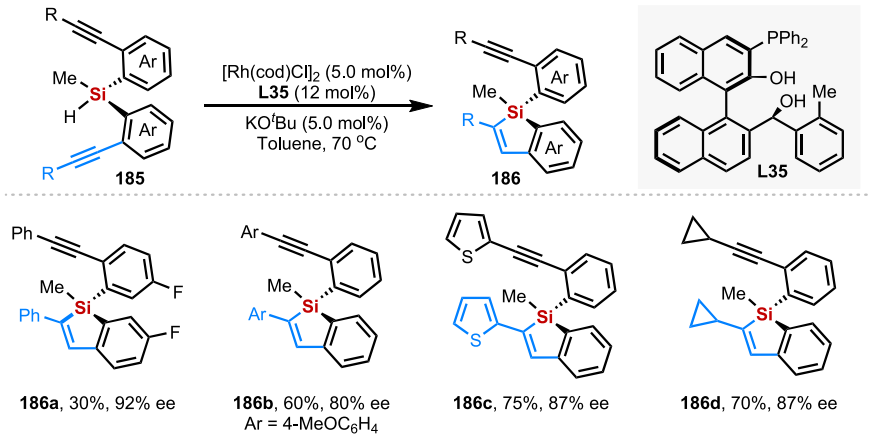
Please cite this article in press as: Wu et al., Catalytic asymmetric synthesis of silicon-stereogenic organosilanes, Chem (2023), https://doi.org/10.1016/j.chempr.2023.09.024



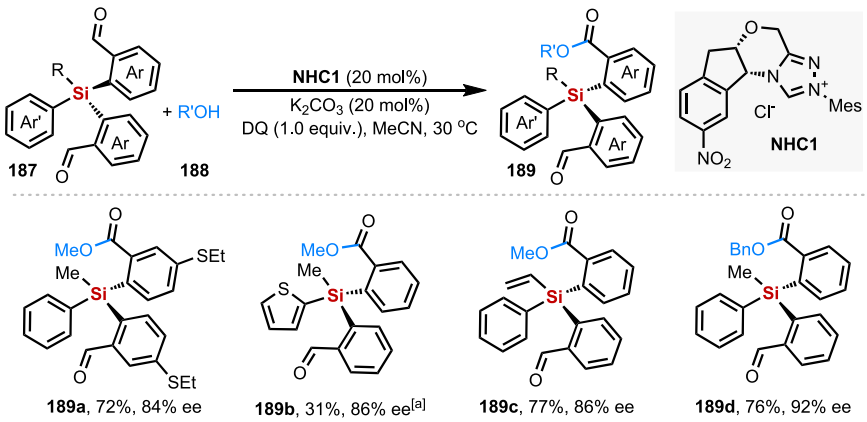
Scheme 60. Synthesis of Si-stereogenic organosilane via Pd-catalyzed C–H Heck-type olefination
Xu and Cui et al.[133]

was evaluated with these BSs derivatives and the enhancement of the BS emission was detected with the structure bearing electron-donating group (**186b**). In addition, the intensive CPL signs were also observed with **186b**.

Metal-free organocatalyzed asymmetric approaches have also been demonstrated in the construction of enantioenriched silanes via the desymmetrization of diarylsilanes. Recently, the utilization of chiral NHC has attracted the certain attention. In 2022, Chi, Zheng, and co-workers have developed an NHC-catalyzed desymmetrization of diarylsilanes **187** bearing two formyl groups (Scheme 62).[134] Chiral tetrasubstituted silanes **189** were obtained via the conversion of one of the two aldehydes to a carboxylic ester where the carbene addition to form Breslow intermediate was the enantio-determining step. In the meantime, Xu, Yang, Chen, and co-workers realized Si-stereogenic silanes with the similar substrates **190** via a carbene-catalyzed stereoselective intramolecular benzoin reaction (Scheme 63).[135] Dibenzo[*b*,*f*]silepin-10-ones **191** containing carbon- and Si-stereogenic centers were obtained in good to excellent enantioselectivities and moderate to excellent diastereoselectivities by employing a *L*-phenylalaninol-derived NHC precatalyst (**NHC2**). The difference on the substrates (R and R′) was required for reaching the high diastereoselectivity (**191a–191c** vs. **191d**).



Scheme 61. Synthesis of Si-stereogenic benzosiloles via Rh-catalyzed trans-selective hydrosilylation of alkynes
Xu et al.[15]



[a]THF was used as solvent.

Scheme 62. Synthesis of chiral tetrasubstituted silanes via NHC-catalyzed desymmetrization approach

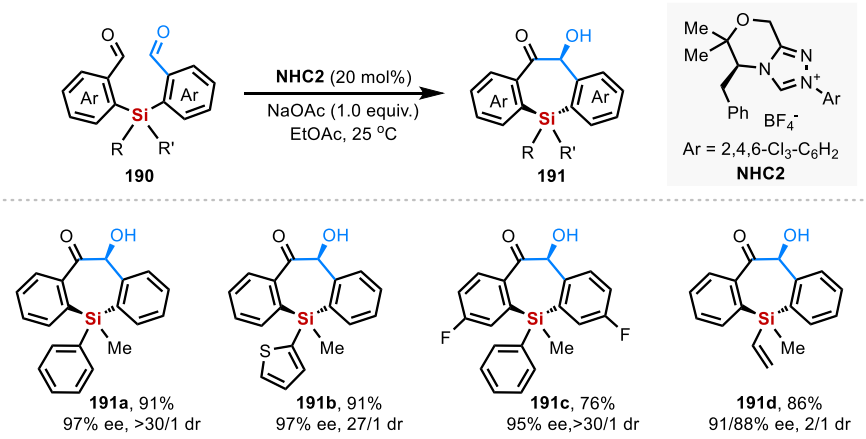
Chi and Zheng et al.[134]

The spirocyclic chiral phosphoric acid (CPA) has also been introduced as the organocatalyst for the synthesis of Si-stereogenic compounds by Yang and Xue group via the desymmetrization of 5,10-dihydrophenazasilines **192** (Scheme 64).[136] High enantioselectivities were given via this asymmetric electrophilic aromatic amination with azodicarboxylate **193**.

Enzymatic approach is another strategy in asymmetric preparation of enantiomerically Si-stereogenic compounds. Xu group reported the potential of creating chiral silanes **197** via a remote desymmetrization of prochiral silicon-centered diols **195** with *Candida antarctica* lipase B (CAL-B) as catalyst (Scheme 65).[137] In this enzymatic reaction, the moderate to good enantioselectivities could be achieved by the acylation of alcohols.

CATALYTIC ASYMMETRIC DESYMMETRIZATION OF DIALKENYLSILANES AND DIALKYNYLSILANES

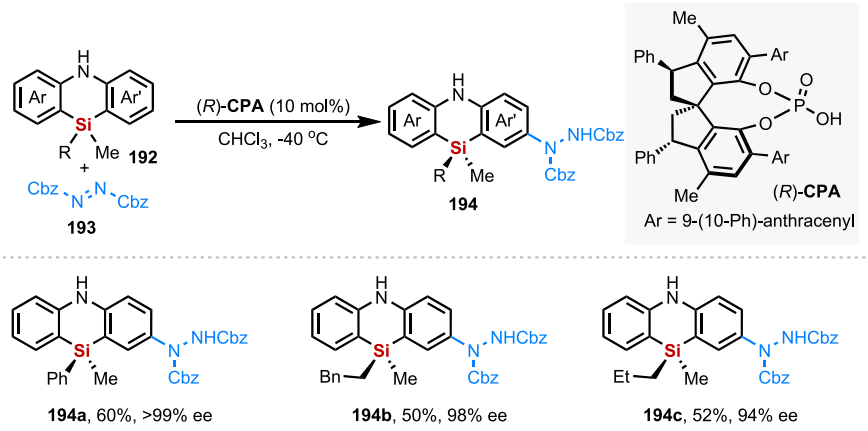
Catalytic asymmetric desymmetrization of dialkenylsilanes and dialkynylsilanes has also been studied for constructing chiral Si-stereogenic silanes. In 2015, Naganawa,



Scheme 63. Synthesis of chiral dibenzo[*b,f*]silepin-10-ones via NHC-catalyzed stereoselective intramolecular benzoin reaction

Xu, Yang, and Chen et al.[135]

Please cite this article in press as: Wu et al., Catalytic asymmetric synthesis of silicon-stereogenic organosilanes, Chem (2023), https://doi.org/10.1016/j.chempr.2023.09.024



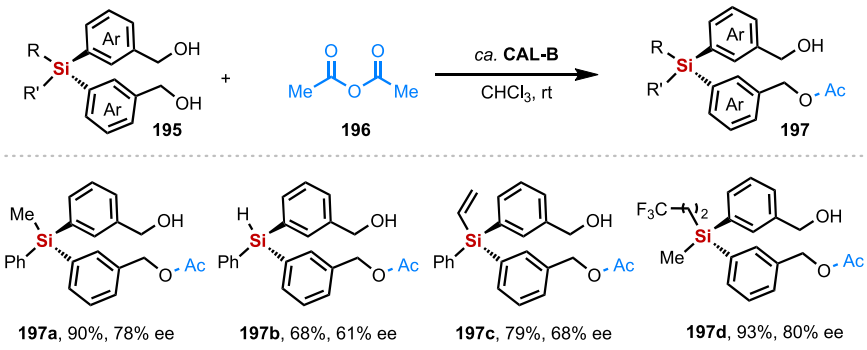
Scheme 64. Synthesis of Si-stereogenic silanes via CPA-catalyzed asymmetric electrophilic aromatic amination

Yang and Xue et al.[136]

Nishiyama, and co-workers reported a rhodium-catalyzed intramolecular hydrosilylation of 1,3-diene[138] for the preparation of Si-stereogenic molecules employing an axially chiral phenanthroline ligand BinThro (**L36**)[139] (Scheme 66). Five-membered chiral products **199** were accessed in high yields and good to high enantioselectivities. Moreover, **199d** could be obtained in moderate enantioselectivities from diarylsilanes. It should be noted that the efficient chiral environment was introduced by a *N,N,O*-tridentate coordination to metal.

In 2020, Xiong and co-workers developed a copper-catalyzed enantioselective hydroboration of vinylsilanes, producing boronate-substituted alkenylsilanes with contiguous silicon and carbon stereocenters in generally excellent enantioselectivities (**201a–201e**) (Scheme 67).[140] Notably, this method provides α-borylated alkenylsilanes, which could be further decorated via the stereospecific C–B conversion.

Shintani and Nozaki group have developed a series of asymmetric [2 + 2 + 2] cycloaddition of silicon-containing diynes using rhodium catalyst.[141,142] In this chemistry, an axially chiral monophosphine ligand [(*R*)-**L37**], which was initially reported by Hayashi group,[143] has been employed. Chiral dibenzosiloles (**204a** and **204b**) have been prepared when internal alkynes were used as the substrate (Scheme 68, above left).[141] The chiral **204c** containing two BSs, which are fused with a benzene core, was also given via 2-fold cycloaddition, whose optical property was also investigated



Scheme 65. Synthesis of Si-stereogenic silanes via enzymatic acylation of alcohols

Xu et al.[137]

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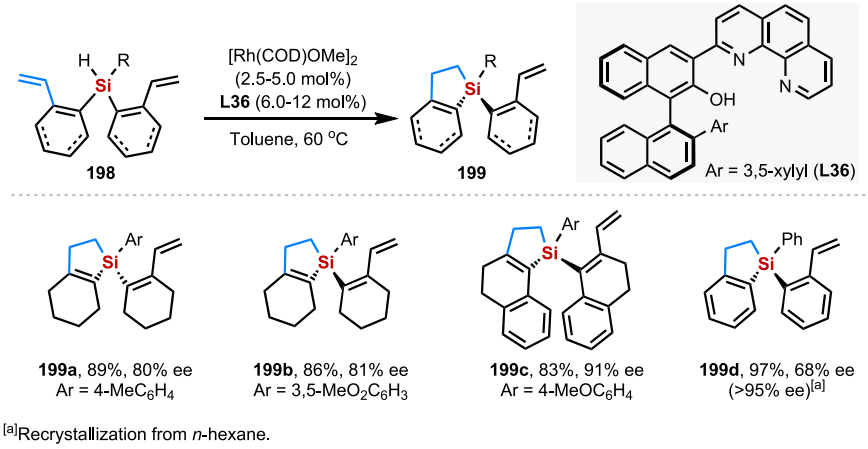


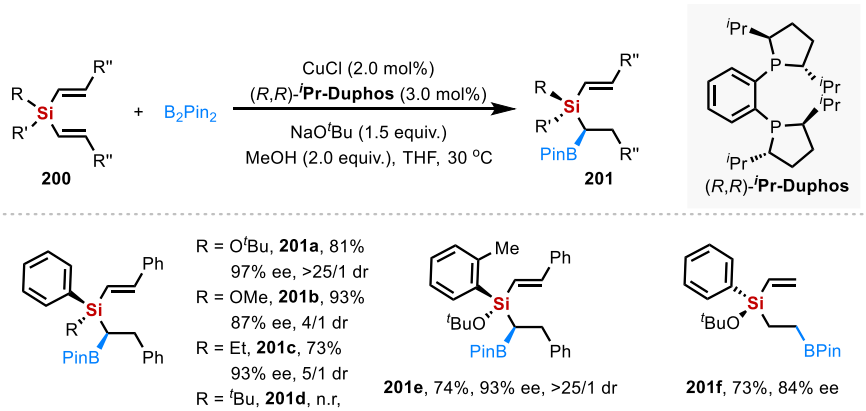
[a]Recrystallization from *n*-hexane.

Scheme 66. Synthesis of Si-stereogenic cyclic silanes via Rh-catalyzed intramolecular hydrosilylation

Naganawa and Nishiyama et al.[138]

showing a strong positive and negative Cotton effects at 282 (Δ_ε = +7.3 M^{-1} cm^{-1}) and 256 nm (Δ_ε = −10.8 M^{-1} cm^{-1}), respectively. When the same type of prochiral dialkynyl silanes reacted with isocyanate under the same reaction conditions, dihydrobenzosilolopyridinones (**204d** and **204e**) were achieved with high regioselectivities and enantioselectivities (Scheme 68, above right).[142] Si-stereogenic chiral polymer was also prepared using a trimethylsilylethynyl-substituted dialkynyl silane. With desilylation and subsequent Sonogashira coupling, the chiral conjugated polymer **205** was obtained with the average molecular weight of 19,000 g mol^{-1}. The CD spectrum showed negative Cotton effects at 287 (Δ_ε = −10.7 M^{-1} cm^{-1}) and 237 nm (Δ_ε = −22.4 M^{-1} cm^{-1}). The same strategy was later employed by Shintani group in 2020, where chiral benzonaphthosilanes (**204f** and **204g**) containing a six-membered silacycle were formed with 8-alkylnyl-1-naphthyl substituted silane (Scheme 68, below).[144]

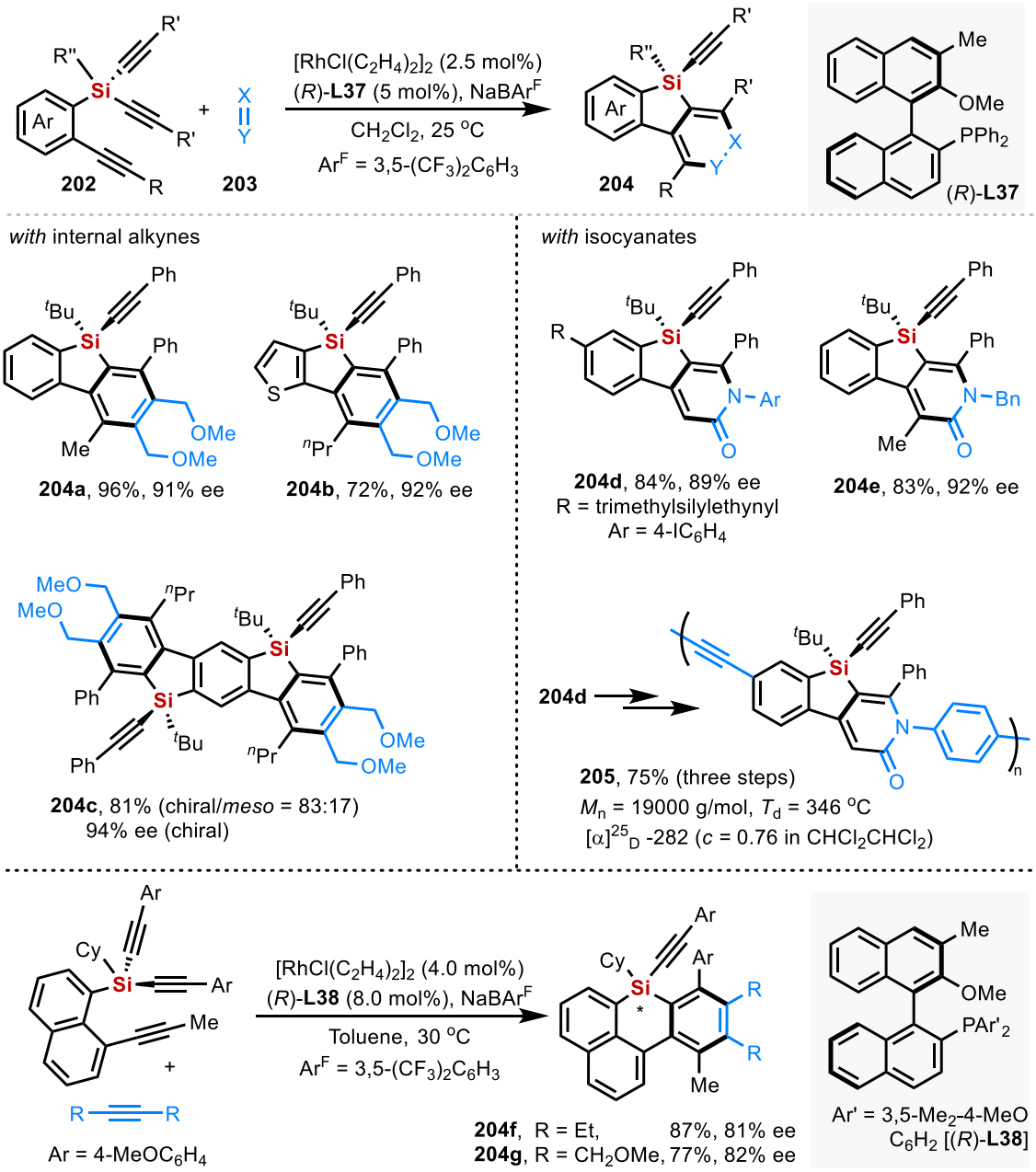
In 2017, this Rh-catalyzed [2 + 2 + 2] cycloaddition strategy has been utilized for achieving silicon-centered axially chiral spirocyclic compounds (Scheme 69).[145] The silicon-containing tetrayne **206** was employed to react with nitrile, and spirosilacycles **208** were



Scheme 67. Synthesis of chiral boronate-substituted alkenylsilanes via Cu-catalyzed enantioselective hydroboration

Xiong et al.[140]

Please cite this article in press as: Wu et al., Catalytic asymmetric synthesis of silicon-stereogenic organosilanes, Chem (2023), https://doi.org/10.1016/j.chempr.2023.09.024



Scheme 68. Synthesis of chiral cyclic silanes via Rh-catalyzed asymmetric [2+2+2] cycloaddition

Asymmetric [2 + 2 + 2] cycloaddition with internal alkynes (Shintani and Nozaki et al.[141]); asymmetric [2 + 2 + 2] cycloaddition with isocyanates (Shintani and Nozaki et al.[142]); synthesis of benzonaphthosilanes (Shintani et al.[144]).

produced via Rh-catalyzed asymmetric cycloaddition with (*R*)-**L39** and sequential cycloaddition with (±)-**L40**. The CPL of these compounds were measured and showed a comparable range to those of the common CPL molecules (**208a** and **208b**). Moreover, axially chiral **208c** and **208d** containing pyridone motif were also synthesized in high enantioselectivities with isocyanates under the same asymmetric conditions.

1 year later, Tanaka group reported the construction of benzofuranylmethyl-idene-benzoxasiloles **210** via the cascade process including 1,2-Si-migration, 1,3-C-migration and oxycyclization (Scheme 70).[146] Moderate enantioselectivities were induced

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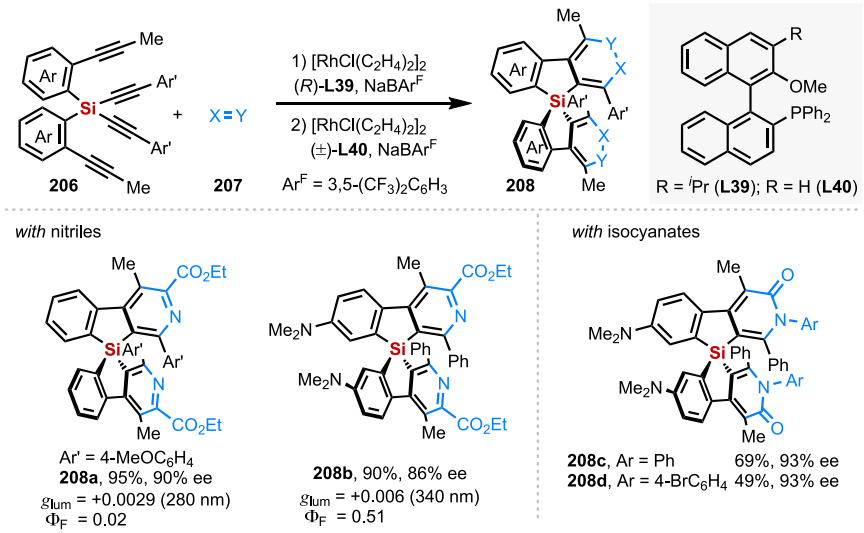
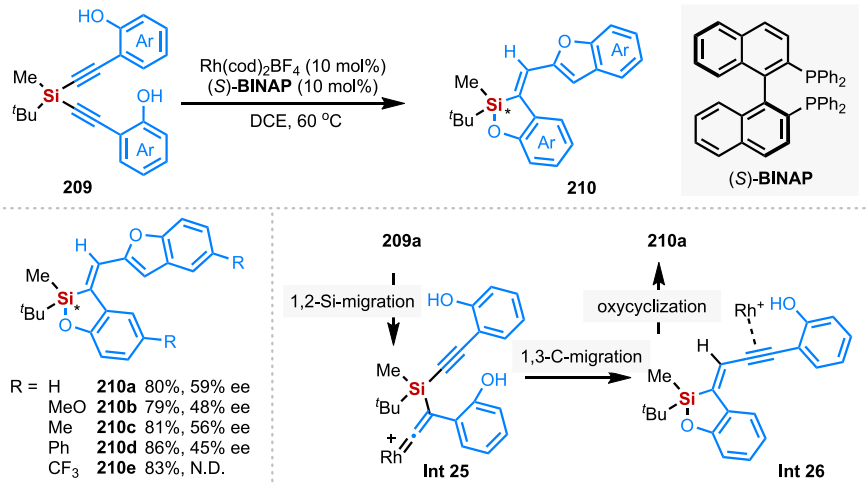


Scheme 69. Synthesis of chiral spriosilacycles via Rh-catalyzed asymmetric [2 + 2 + 2] cycloaddition

Shintani and Nozaki et al.[145]

using a $Rh(cod)_2BF_4$/(*S*)-**BINAP** catalyst. Photophysical properties of these chiral cyclic compounds were then evaluated and the ones with electron-donating groups were detected with red shifts of absorption and emission maxima. Moreover, the mirror-image relationships of (+)-**210c** and (−)-**210c** were found according to the electronic CD (ECD) spectra.

In 2020, L.-W. Xu and Z. Xu group tried to apply the Pt-catalyzed mono-lateral functionalization of dialkynylsilane for accessing Si-stereogenic alkynylsilanes (Scheme 71).[147] One example was demonstrated by the utilization of their developed Ar-NNP (**L42**). Diborated products (*Z*-**212** and *E*-**212**) were formed and a promising enantioselectivity was reached in *E*-**212**.



Scheme 70. Synthesis of chiral benzofuranylmethyl-idenebenzoxasiloles via Rh-catalyzed asymmetric cascade process

Tanaka et al.[146]

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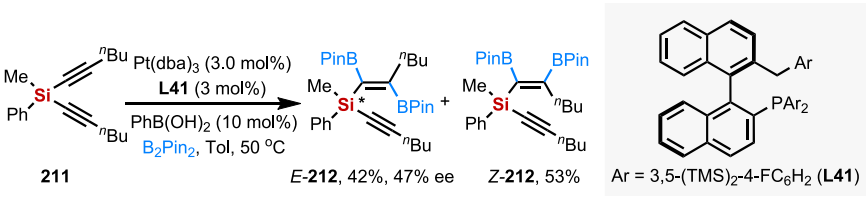


Scheme 71. Synthesis of Si-stereogenic silanes via Pt-catalyzed mono-lateral diboration of dialkynylsilanes

L.-W. Xu and Z. Xu et al.[147]

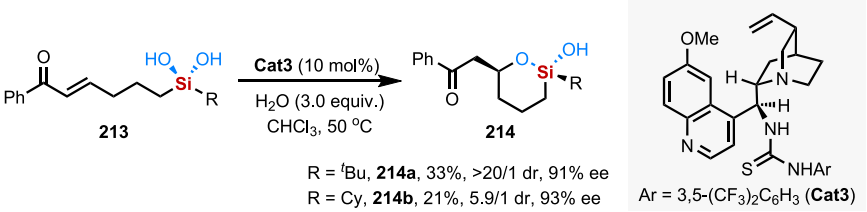
CATALYTIC ASYMMETRIC DESYMMETRISZATION OF SILANEDIOLS

Prochiral silanediols are not the common substrates for the access of enantioenriched Si-stereogenic silanes. In 2020, Matsubara and Asano et al. applied their developed methodology on the synthesis of optically active tetrahydropyrans (Scheme 72).[148] The desymmetrization of silanediols **213** proceeded smoothly via organocatalyzed cycloetherfication, giving the target products **214** in high enantioselectivities and moderate to good diastereoselectivities. Notably, this work represents the first example of constructing Si-stereogenic silanes via asymmetric organocatalysis.

C. He and Li et al. reported a Cu-catalyzed asymmetric Si–H/O–H dehydrogenative coupling of silanediols with hydrosilanes in 2022 (Scheme 73).[149] Optical Si-stereogenic silanols were obtained via a desymmetric σ-bond metathesis process in an intermolecular fashion. Of note, the steric hindrance around the Si atom was demanded for the high enantioselectivity (**217a** and **217b**). Moreover, further investigation on the photophysical properties revealed that the DCM solution of **217c** displays the clear Cotton effects at 334 and 349 nm and intense CPL signals from 320 to 650 nm.

OTHERS

Development of the catalytic synthesis of chiral Si-stereogenic organosilanes generally focused on the desymmetrization of prochiral silanes bearing two identical substituents. However, strategies on dynamic kinetic resolution (DKR) or DYKAT[150,151] of racemic silanes, which will considerably widen the access of Si-stereogenic molecules, are rarely investigated mainly due to the lack of the efficient way to deracemization on silicon center. Very recently, L.-W. Xu and Z. Xu group realized the first dynamic kinetic asymmetric intramolecular hydrosilylation (DyKAH). The deracemization of "silicon-centered" racemic hydrosilanes **218** bearing three different substituents were performed to afford Si-stereogenic BSs **219** in good to high enantioselectivities by the utilization of their newly developed non-diastereopure-type mixed phosphine-phosphoramidite ligand (**SiMOS-Phos**) (Scheme 74).[152] DFT calculation indicated that (*R*)-**218** went through the



Scheme 72. Synthesis of chiral silicon-containing oxacyclic compounds via organocatalyzed cycloetherfication

Matsubara and Asano et al.[148]

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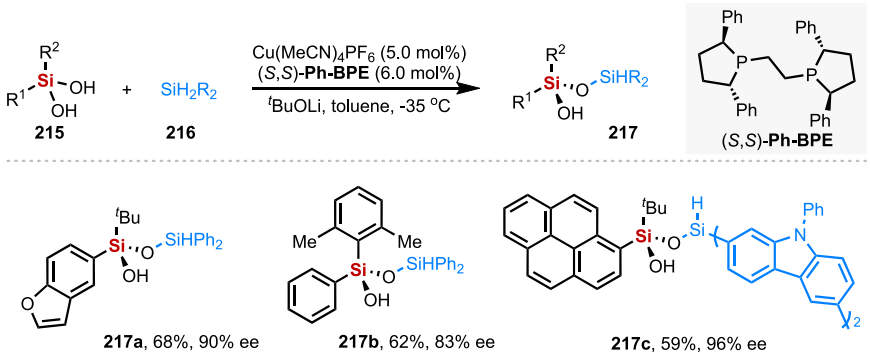
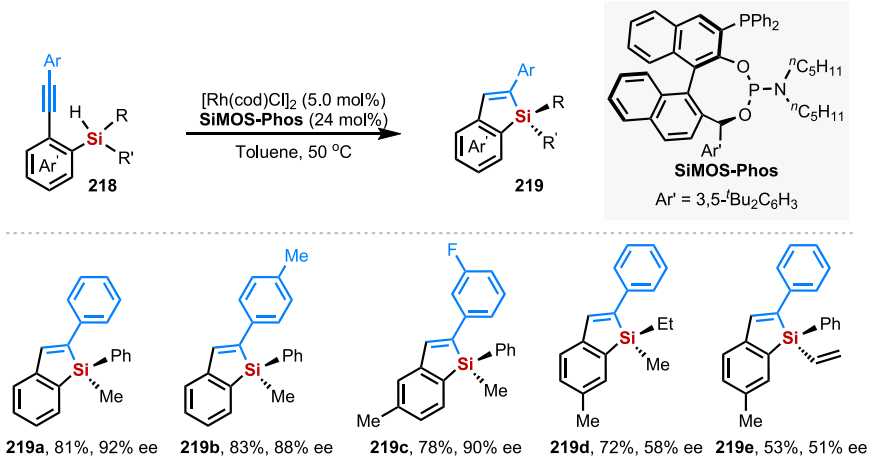


Scheme 73. Synthesis of chiral silanols via Cu-catalyzed asymmetric Si–H/O–H dehydrogenative coupling
C. He and Li et al.[149]

Chalk-Harrod pathway while (*S*)-**218** was via the ligand-assisted chiral inversion, leading to the product with the same stereoselectivity.

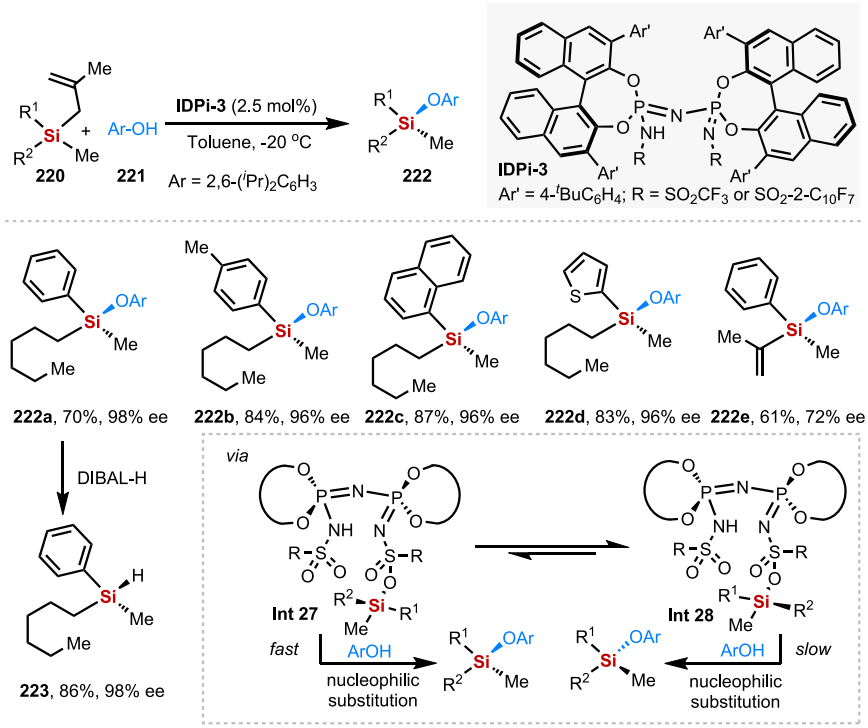
Shortly after, List group outlined a DYKAT using their developed organic IDPi catalyst (Scheme 75).[153] The reaction proceeded between racemic allylsilanes **220** and phenols **221**, delivering Si-stereogenic silyl ethers **221** in good enantioselectivities. **222a** could be further reduced by DIBAL-H to reach the useful monohydrosilane **223** in a stereospecific manner. Mechanistic studies disclosed that the epimerization of silyl-catalyst species with the combination of the different rates of the subsequent nucleophilic substitution for the two epimers led to the good outcome of the enantioselectivity.

A few other approaches to access of chiral Si-stereogenic compounds using racemic silanes containing four different substituents have also been evaluated. In 2020, Xu developed a palladium-catalyzed ring expansion/insertion of benzosilacyclobutanes to form various silabicyclo[4.1.0]heptanes containing three continuous chiral carbon stereocenters (Scheme 76).[154] The authors also tested the reaction between Me(Et)Si-containing benzosilacyclobutane **224** and cyclopropylene **225**, giving moderate chiral induction with unsatisfied diastereoselectivity.



Scheme 74. Synthesis of Si-stereogenic benzosiloles via Rh-catalyzed dynamic kinetic asymmetric intramolecular hydrosilylation
L.-W. Xu and Z. Xu et al.[152]

Please cite this article in press as: Wu et al., Catalytic asymmetric synthesis of silicon-stereogenic organosilanes, Chem (2023), https://doi.org/10.1016/j.chempr.2023.09.024

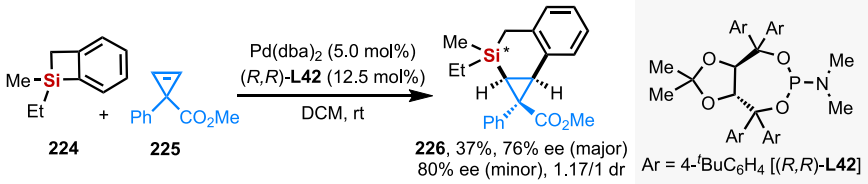


Scheme 75. Synthesis of Si-stereogenic silyl ethers via a dynamic kinetic asymmetric transformation process
List et al.[153]

In 2022, Su group reported a Ni-catalyzed reductive coupling of chlorohydrosilanes, affording aryl- and alkenylhydrosilanes via unconventional Si–Cl cleavage (Scheme 77).[155] In this paper, the author attempted to proceed the reaction in an enantioselective fashion, however, only moderate enatioinduction was reached (**229**). Moreover, the observed unchanged ee values during the reaction progress disfavored the direct kinetic resolution of a racemic chlorohydrosilane.

CONCLUSIONS AND OUTLOOK

This review summarizes the catalytic preparation of various Si-stereogenic silanes via catalytic asymmetric synthesis to date. These efficient methodologies significantly enriched the diversity of Si-stereogenic organosilanes, providing a growing inventory of this class of functional compounds with various novel architectures. Along with the rapid developments of synthetic methodologies, applications of Si-stereogenic organosilanes in synthetic chemistry, medicinal chemistry and material chemistry start to emerge in the literature.



Scheme 76. Synthesis of Si-stereogenic silabicyclo[4.1.0]heptane via Pd-catalyzed ring expansion/insertion
Xu et al.[154]

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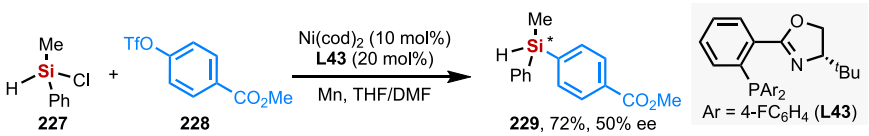

Scheme 77. Synthesis of Si-stereogenic monohydrosilane via Ni-catalyzed reductive coupling
Su et al.[155]

Although astonishing progress has been made, catalytic strategies are largely limited to the desymmetrization of dihydrosilanes, diarylsilanes and dialkylsilanes to date. The desymmetrization reactions based on dialkenylsilanes, dialkynylsilanes, silanesdiols, and other organosilanes are relatively less mentioned. Meanwhile, the access of Si-stereogenic compound largely relied on the desymmetrization of symmetric organosilane precursors, which significantly diminish the structural diversity and synthetic values of those compounds. From the perspective of reaction type, synthetic strategies mainly focus on transition-metal-catalyzed hydrosilylation, dehydrogenative silylation with C–H and X–H bonds. There are still much room for the development of new methodologies to create Si-stereogenic silanes with novel reaction processes including transition-metal catalysis, organocatalysis, and biocatalysis.

Further investigations will aim at the development of novel reaction patterns, including introduction of earth-abundant metal catalysts and organocatalysts, which will provide new catalytic modes and reaction patterns to deliver Si-stereogenic silanes with novel architectures. Moreover, the asymmetric reaction could be explored with the combination of other catalytic platforms, such as photoredox catalysis or electrocatalysis by virtue of the rapid advance of the related chemistry. Very recently, a few elegant DKR processes have been demonstrated for the construction of enantioenriched Si-stereogenic silanes. The continuing effort on the development of efficient DYKAT, including the deeply understanding on mechanism of rapid racemization of organic silicon center, will provide the powerful approach for the access of Si-stereogenic silanes. It could be envisioned that further development of catalytic asymmetric reactions for the access of chiral Si-stereogenic silanes will enrich the armory of Si-stereogenic silanes, leading to the exploration of new applications with enriched diverse novel architectures, such as optoelectronic materials and Si-containing chiral drugs, in material science and pharmaceutical chemistry.

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AUTHOR CONTRIBUTIONS

Y. Wu. and L.Z. investigated the literature and wrote the manuscript, Y. Wang and P.W. proposed the topic of the review and revised the manuscript. All authors read, discussed, and approved the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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