



Recent progress of organosilicon compound: synthesis and applications

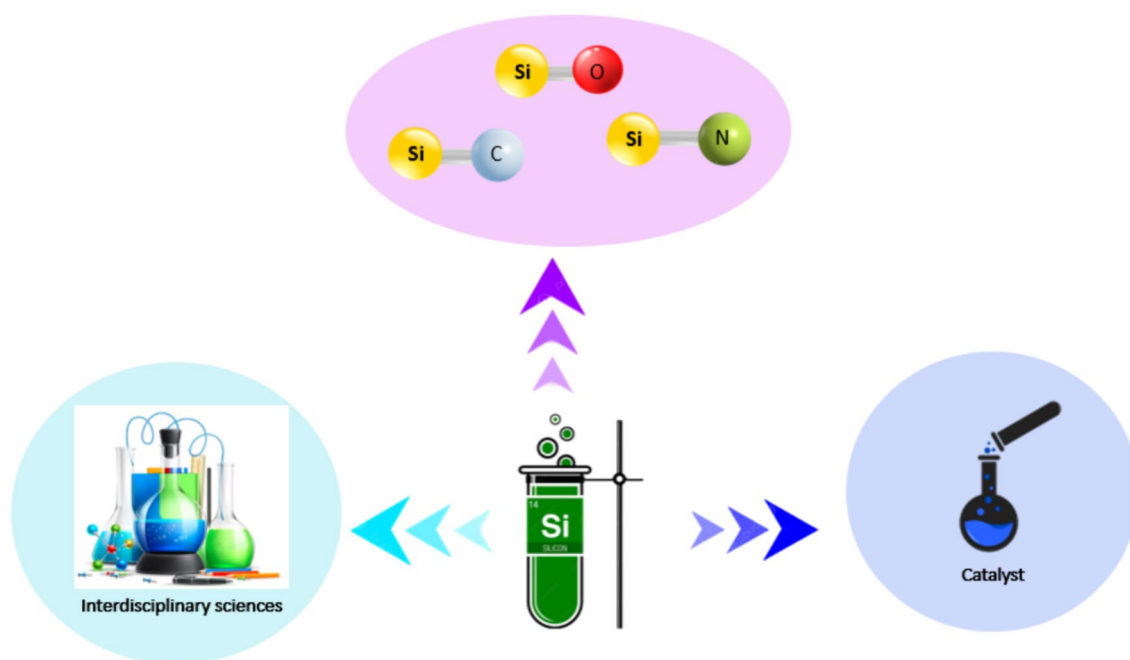
Hoda Mollabagher¹ · Mohammad M. Mojtahedi¹ · Seyed Amir Hossein Seyed Mousavi¹

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Abstract

Organosilicon compounds play a crucial role as essential building blocks and valuable organic molecules in various materials. They are extensively utilized as synthetic intermediates in chemical synthesis processes. Recent studies have highlighted the multifaceted role of silicon compounds, showcasing their significance not only as reactive participants or products but also as potent catalysts in various chemical reactions, as reported by researchers. In this comprehensive review, our objective is to provide a summary of recent advancements in synthesizing various organosilicon compounds in formation of silicon–carbon, silicon–oxygen, silicon–nitrogen and explore the applications of siliconic materials as catalysts in polymerization, reduction, and isomerization processes. Emphasizing the significant potential of this methodology, we aspire to inspire further research and applications in this rapidly emerging field. Furthermore, this review covers over 50 years of research on organosilicon chemistry in CCERCI under supervision of Prof. Seyed Mohammad Bolourtchian.

Graphical Abstract



Keywords Organosilicon · Si–O bond cleavage · Si–C bond formation · Si–N bond formation · Protection

Abbreviations

DFT Density functional theory
DHP Dihydropyridines

Extended author information available on the last page of the article

GDP	Gross domestic product
H ₃ btb	1,3,5-Tris(4-carboxyphenyl)benzene acid
H ₂ hipamifba	4-(((4 ((Carboxymethyl)carbamoyl) phenyl)amino)methyl)benzoic acid
H ₂ TDC	2,5-Thiophene dicarboxylic acid
HMDS	Hexamethyldisilane
HMPA	Hexamethylphosphoramide
JACS	Journal of the American Chemical Society
KHMDS	Potassium bis(trimethylsilyl)amide
LiAlH ₄	Lithium aluminum hydride
LiClO ₄	Lithium perchlorate
MSS	Martin's spiroisilane
MW	Microwave
NC	Nanocube
PCy ₃	Tricyclohexylphosphine
RT	Room temperature
THF	Tetrahydrofuran
TMSCI	Trimethylsilyl chloride

Introduction

Over the past few decades, silicon has emerged as a crucial element in both research and applications, marking a significant journey in the field of organosilicon chemistry since the late nineteenth century [1]. Organosilicons play a crucial role in both academic research and industrial applications [2, 3]. Their flexibility is evident across variety scientific disciplines, contributing significantly to fields such as materials science [4–7], pharmaceuticals [8–10], chemosensor [11], catalysis [12, 13] and polymer chemistry [14]. Additionally, these compounds are indispensable in synthesizing complex molecules and play a pivotal role in drug discovery endeavors and biomedical engineering applications [15] (Fig. 1).

The trend of researchers' inclination toward organosilicon compounds from Scopus as a source, based on the number of articles published by them in the period from 1945 to 2024, has been depicted in a bar chart. From this (Fig. 2), it can be inferred that initially, the study of these compounds had mainly an academic and laboratory aspect, resulting in a limited number of research studies. However, with the continuous advancement of science and the discovery of new applications for these compounds, especially after the

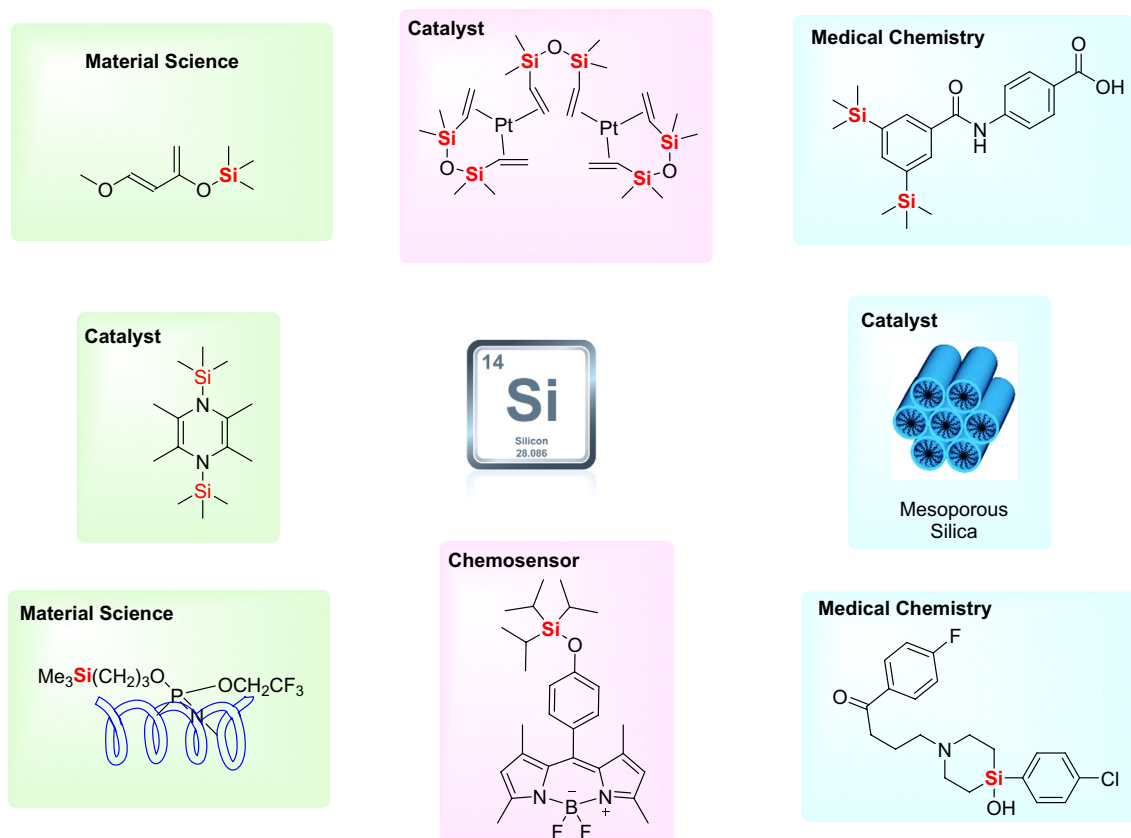


Fig. 1 Silicon-containing functional molecules: applications in catalysis, chemosensors, medicinal chemistry, and materials Science

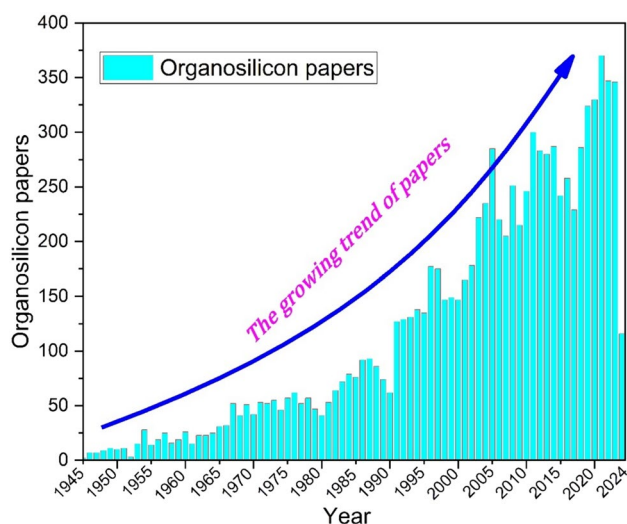


Fig. 2 The published articles on the subject of organosilicon compounds worldwide from 1945 to 2024 extracted from Scopus

1980s in areas such as the synthesis of herbicides and fungicides, researchers' interest has increased. Gradually, with the entry of organosilicon compounds into fields such as the

manufacture of temperature-resistant industrial adhesives, sealants, and, most importantly, anti-foaming agents used in petrochemical processes, the inclination toward research in this area has seen a significant rise since the 1990s.

These compounds, as anti-foaming agents, contribute to the stability of equipment such as distillation towers. In recent years, the entry of these compounds into pharmaceutical areas has led to a growing interest from major pharmaceutical companies to invest in this field. Overall, by studying reputable scientific articles and examining the volume of investments, it can be stated that research in this field has a bright and growing future.

The statistical representation in (Fig. 3) clearly indicates the volume of articles published in reputable journals in the field of chemistry, specifically on organosilicon compounds. The publication of 382 articles on organosilicon compounds by Journal of the American Chemical Society demonstrates the placement of this topic at the forefront of novel scientific advancements. Moreover, reputable journals, Journal of Organometallic Chemistry, Tetrahedron Letters, and Journal of Organic Chemistry, with 377, 206, and 107 articles published in this field, respectively, are also among the pioneers in publishing articles on organosilicon compounds

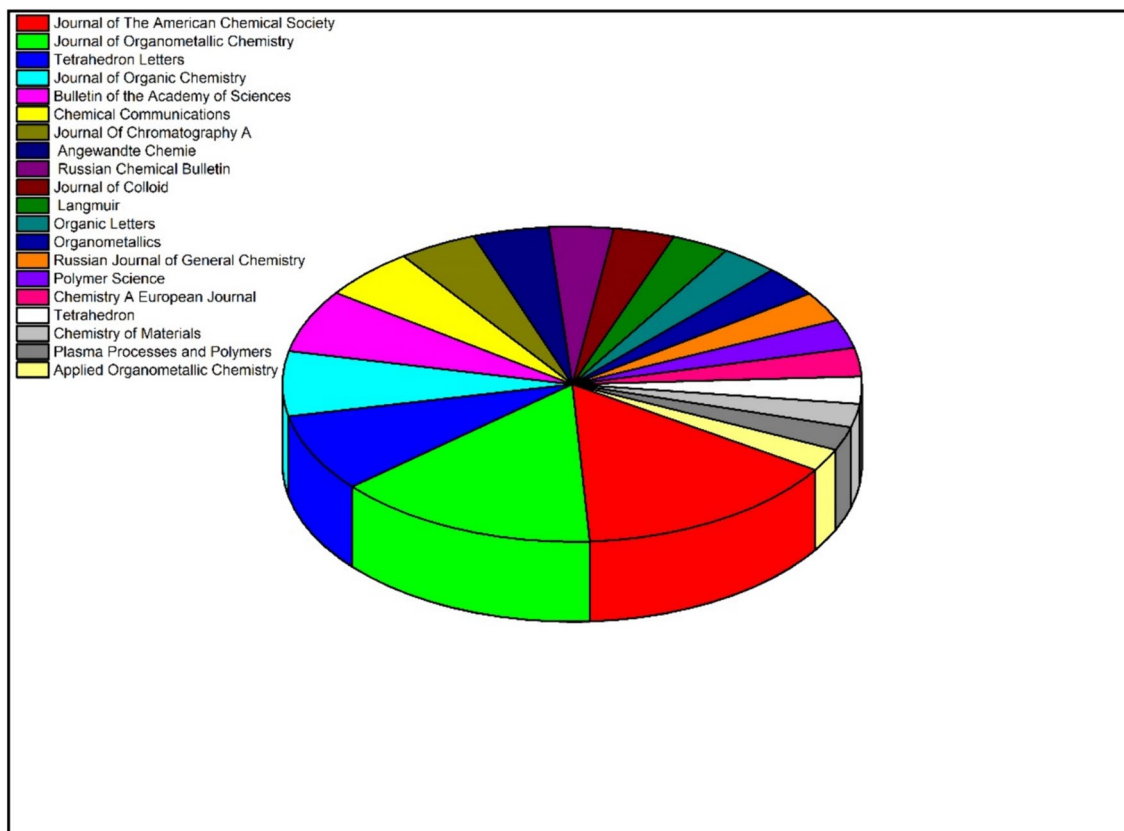


Fig. 3 Classification of reliable journals based on the volume of articles they have published in the field of organosilicon compounds using the Scopus database

worldwide. The substantial interest of these prestigious journals in this area can serve as a strong incentive for young researchers to engage in experimental research in this field.

Professor Seyed Mohammad Bolourtchian is the founder of organosilicon in Iran. Bolourtchian, an expert in pharmacy and chemistry (silicon chemistry) with a Ph.D. in Pharmacy from Tabriz University and a Ph.D. in Chemistry from French National Centre for Scientific Research (CNRS), has been an active and continuous member of the Academy of Sciences and has received the honor of receiving the First Class Medal of Science from the President. He is considered among the winners of the first round of lasting faces (2013) in the fields of chemistry, pharmacy, and medicine. In addition, he is also the founder of the Iranian Institute of Chemistry and Chemical Engineering.

An attempt has been made to graphically depict the distribution of scientific concepts related to silicon organic compounds in various research sources for a better understanding of the research landscape, provides an elegant depiction in this field (Fig. 4). As predicted earlier, the majority of scientific documents are published in the form of Scopus articles in reputable scientific journals. The high inclination of scientists toward publishing journal articles has multiple reasons. Among these reasons, the short time required to prepare the necessary infrastructure for publishing an article and the possibility of focusing on a specialized topic within a few pages of a scientific document can be highlighted. Additionally, the availability of free access for researchers from some scientific centers is another factor contributing to the abundance of journal articles. Furthermore, the role of open-access articles and their contribution to encouraging researchers to publish scientific documents in the form of journal articles should not be overlooked [16].

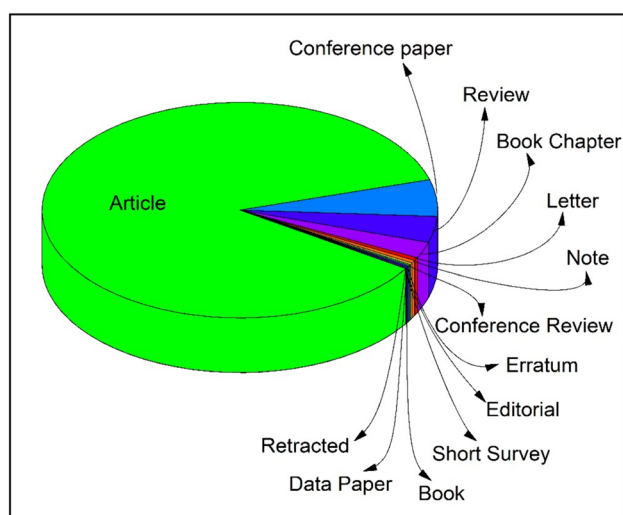


Fig. 4 How to distribute organosilicon articles in the Scopus database among different scientific sources

Formation of silicon–carbon bond

In recent decades, there has been extensive investigation into activation using metal catalysts and functionalization of C–H or C–C bonds [17–20]. Considering the high reactivity observed in C–SiR₃ bonds, current research endeavors have been directed toward the selective conversion of C–H bonds into the more versatile C–Si bonds, employing a series of successive metal-catalyzed C–H bond activations.

Silylation reaction of unsaturated olefines

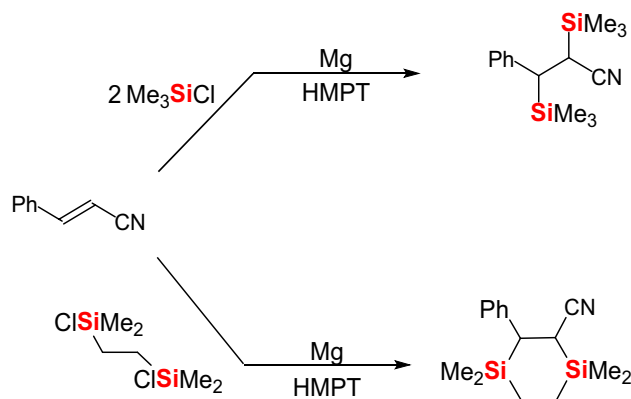
In 1971, Bolourtchian and coworkers reported the reaction of trimethylchlorosilane (TMSCl) with cinnamitrile, leading to the 1,2-addition in the presence of magnesium. Also Adding 1,2-bis(chlorodimethylsilyl)ethane to cinnamitrile results in a similar reaction leading to the formation of a six-membered cyclic structure [21]. Magnesium has been chosen as the catalyst in this process, aligning with recent findings reported by researchers [22] (Scheme 1).

In the case of cinnamitrile, the conjugated double bond system with –C≡N functional group is active and carbon–silicon bond creation in two neighboring carbon atoms.

This outcome is generally different in α -ethylenic aldehydes/ketones compounds featuring a conjugated double bond with a carbonyl group, where 1,4-disilylation takes place, and C-silylated in β position with corresponding aldehydes/ketone structure obtained after hydrolysis [23].

Silylation reaction of α,β -unsaturated carbonyl

In 1996, Bolourtchian and colleagues [24] reported the synthesis of β -silylated olefins. This was achieved through the reaction of α,β -unsaturated aldehydes and ketones with trimethylsilyl chloride and lithium in THF, followed by



Scheme 1 1,2-Addition to cinnamitrile in the presence of magnesium

hydrolyzing the intermediate in acidic media and the addition of a Wittig reagent (Scheme 2).

Researches have indicated that reactions with *N,N*-disubstituted cinnamic or methacrylic amides have shown similar products, resulting 1,4 addition to conjugated group and the formation of a C–S bond [25]. Finally, the obtained carbonyl group was successfully reduced with LiAlH_4 to obtain the corresponding alcohol (Scheme 3).

In light of the extensive Bolourtchians research group findings involving aldehydes, ketones, esters, nitriles, and acyl chlorides, they proposed a mechanism that is applicable to the case of α -ethyl ketones. Consistent with similar instances, the process entails the formation of a radical ion [25] (Scheme 4).

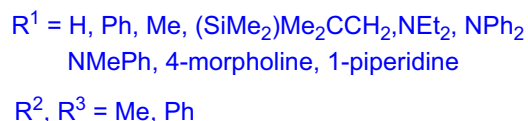
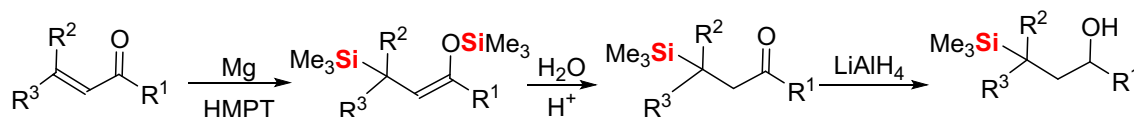
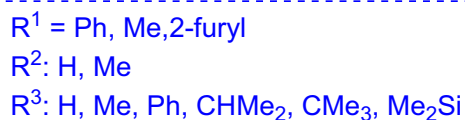
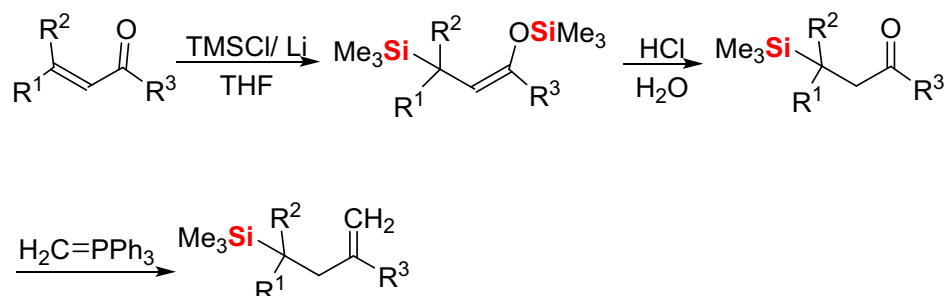
As reported, efficient 1,4-disilylation has been indicated to require conjugation of the α - β unsaturated carbonyl system with another group.

Compounds such as phorone, β -ionone, and pseudo-ionone were reported that examined as substances possessing dual functional groups conjugated with other groups for investigation.

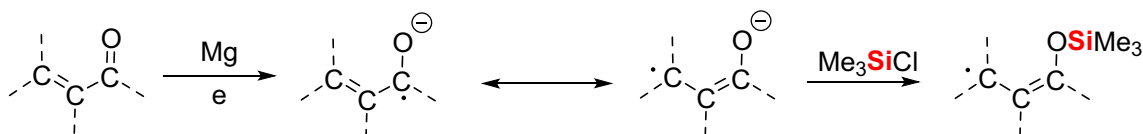
When the α - β unsaturated carbonyl system conjugated with double bond, compounds such as aldehydes, ketones, and cinnamic esters shown good yield in 1,4-disilylation. In fact, the reports associated with cinnamic amides have also exhibited results aligned with these same findings (Scheme 5).

ketones with α -ethylene-like structures wherein the $\text{C}=\text{C}-\text{C}=\text{O}$ system is not conjugated with another group (like α -ionone, cyclohexene-2-one...) specifically

Scheme 2 Reaction of α,β -unsaturated carbonyl group with TMSCl in presence of lithium as catalyst followed by addition of a Wittig reagent



Scheme 3 Reaction of α,β -unsaturated carbonyl group with TMSCl in presence of magnesium followed by reduction with LiAlH_4



Scheme 4 Mechanism formation of a radical ion in α,β -unsaturated carbonyl group with TMSCl

highlighting that methylbutenone mainly undergoes reductive duplication. Meanwhile, methacrylic amides predominantly exhibit 1,4-disilylation, suggesting the participation of the nitrogen atom's lone pair in conjugation [26].

Based on the comprehensive findings gathered from aldehydes, ketones, esters, nitriles, and α -ethylene acid chlorides, the Bolourtchian's group proposed mechanism specifically for α -ethylene amides. Similar to other analogous cases, it suggests the initiation of a radical ion (Scheme 6):

The radical, although stabilized by conjugation, will be represented as type (a) for simplicity, considering position 4 (rather than 2) as the active position in this case.

The radical (a) could then either duplicate itself or, in an electron-rich environment, form an anion.

The potential results can be summarized as follows in (Scheme 7). The progress of (1) is favored in a solvent with a low electron density. Then it was reported by replacing HMPT with THF occurred duplication over C-silylation. Progress (2) should be favored in HMPT where the reaction medium is more electron-rich. However, two concurrent reactions, (2') and (2''), exist here: (2') will be unfavorable when the $\delta+$ charge on position 4 decreases due to delocalization.

In 1976, three types of amides, including (furyl-2)-3 and (thienyl-2)-3 acrylamides, along with sorbamides, were investigated. Subsequently, the silicon-substituted amides prepared were reduced to their corresponding amines using lithium aluminum hydride [27]. In recent studies, scientists have also explored heterocyclic compounds for the synthesis of pharmaceutical intermediates [28] (Scheme 8).

Bolourtchian have reported that in the case of sorbamides, in the presence of trimethylsilyl chloride and magnesium, both disilylation regarding 1,4 and 1,6 positions have been

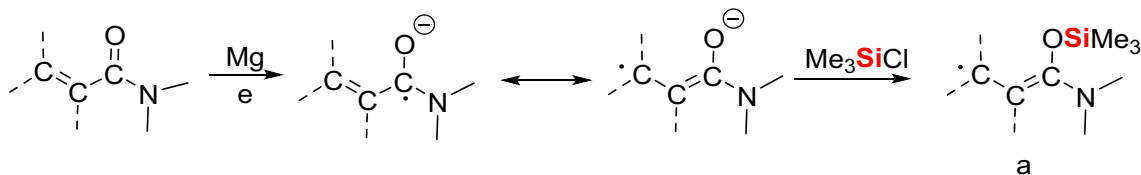
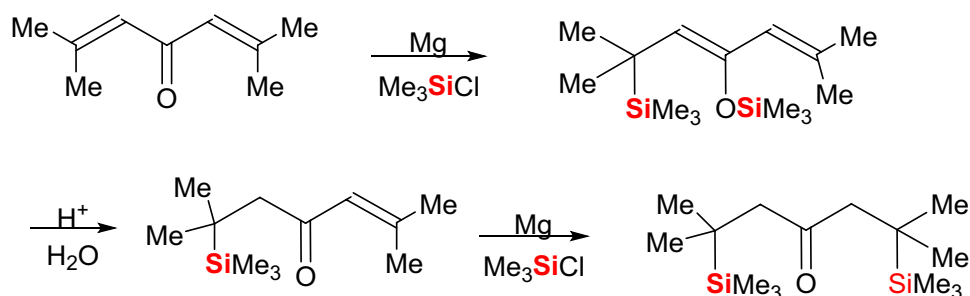
observed, with its NMR spectrum confirming this finding (Scheme 9).

In 2003, the Bolourtchian research group developed a new synthetic method for producing organosilicon compounds via silylation reactions [29]. They stated that the reaction of α,β -epoxy esters with TMSCl/Mg in the presence of HMPA as a solvent resulted in the production of the related β -silylesters. TMSCl has also been described to serve three fundamental roles: activating the epoxide ring by coordinating with its oxygen atom, stabilizing the ensuing anion intermediates, and activating the magnesium metal (Scheme 10).

Zhao et al. in 2023 reported a visible-light-induced photocatalysis by utilizing the reactivity of pentacoordinate silylsilicates derived from Martin's spiro-silane (MSS) as precursors for silyl radicals [30]. The process is demonstrated for the hydrosilylation of a broad range of alkenes and alkynes, as well as the C–H silylation of heteroarenes (Scheme 11). Importantly, they confirmed that Martin's spiro-silane exhibits its stability and can be recovered through a simple workup procedure. Additionally, the reaction shown efficacy when conducted in water as the solvent or utilizing low-energy green LEDs as an alternative energy source.

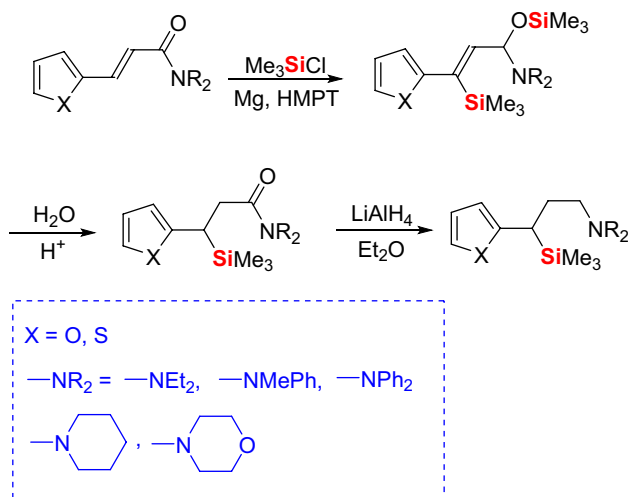
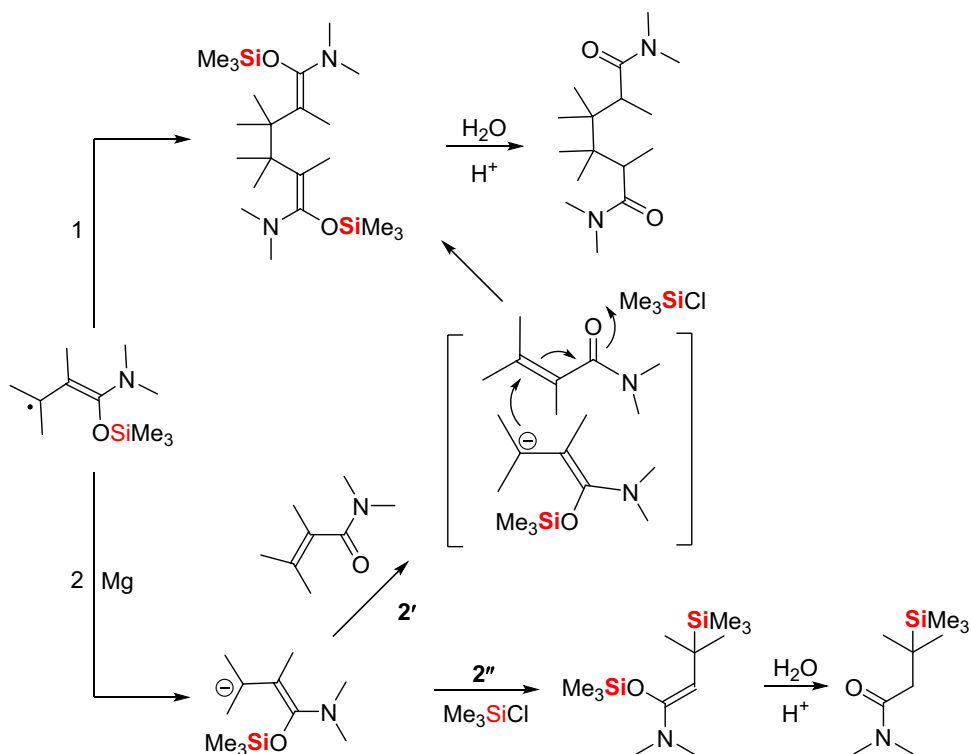
In 2023, the Xu group introduced a method where they revealed the hydrosilylation of 1,3-diyne with dihydrosilanes, utilizing the palladium catalyst $\text{Pd}_2(\text{dba})_3$ [31]. They reported that by employing this method, Si-stereogenic enynes and a polyenyne were synthesized with excellent enantiomeric excesses (up to > 99%) through desymmetrization. In this approach, newly developed chiral ligands were utilized, leading to the synthesis of a diverse array of chiral silanes. Additionally, a Si-containing polymer featuring a Si-stereogenic center, which is typically challenging to access,

Scheme 5 1,4-Addition of α - β unsaturated carbonyl system conjugated with double bond



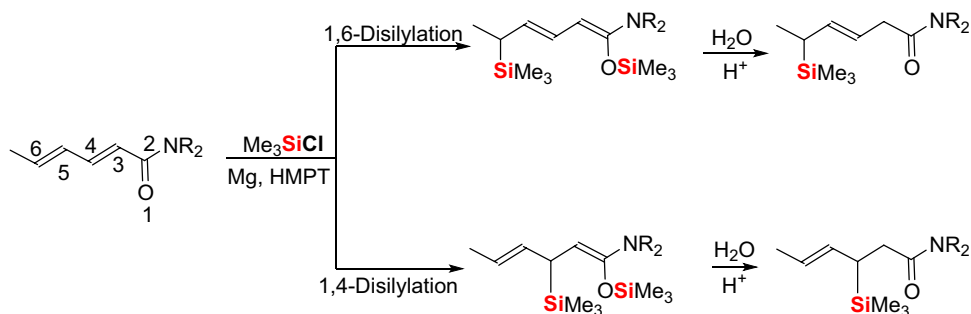
Scheme 6 Propose a mechanism of production of radical ion in α,β -unsaturated amide silylation

Scheme 7 The overall pathway of silylation of α,β -unsaturated amide



Scheme 8 Preparation of silicon-substituted amides followed by reduction to their corresponding amines using LiAlH₄

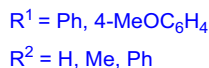
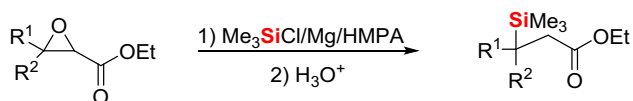
Scheme 9 Silylation of sorbamides in both 1,4 and 1,6 position



was produced. Also, only 2 mol% of Pd₂(dba)₃ was used as the catalyst incorporation of 8 mol% of chiral ligands at 0 °C to give desired product with up to 91% yield (Scheme 12).

Xu and coworkers demonstrated the use of a Heterogeneous copper nitride nanocubes (Cu₃N NCs) for the protosilylation of unsaturated compounds with silylboronate [32] (Scheme 13). However, the use of organic ligands or bases is inevitable in this process. This method provides additive-free conditions by applying Cu₃N NCs. Different substrates, including alkynes, alkenes, and imines, were effectively converted into the corresponding organosilanes under additive-free conditions.

Liu and colleagues made a noteworthy discovery by finding that copper(I) chloride exhibits catalytic activity in the silylation process of propargyl carbonates with silylboranes [33]. The simplicity of this catalyst is highlighted by its ability to effectively handle a diverse range of propargyl carbonates, accommodating variations in substitution patterns,



Scheme 10 Silylation of α,β -epoxy esters in presence of catalytic amount of magnesium

encompassing both primary and terminal propargyl carbonates. The authors reported a variety of silyllallenes, including those with three or four substitutions, as well as those with substitutions at positions 1,1- or 1,3-disubstituted, were efficiently synthesized. This process exhibited a high level of compatibility with various functional groups. Substantial modifications in terms and structure were crucial for the effectiveness of this reaction. Additionally, the involvement of a copper catalyst, a specific ligand, and a base proved to be essential for this reaction. The bulky and strongly

donating PCy_3 ligand exhibited excellent performance, leading to a high yield of product (Scheme 14).

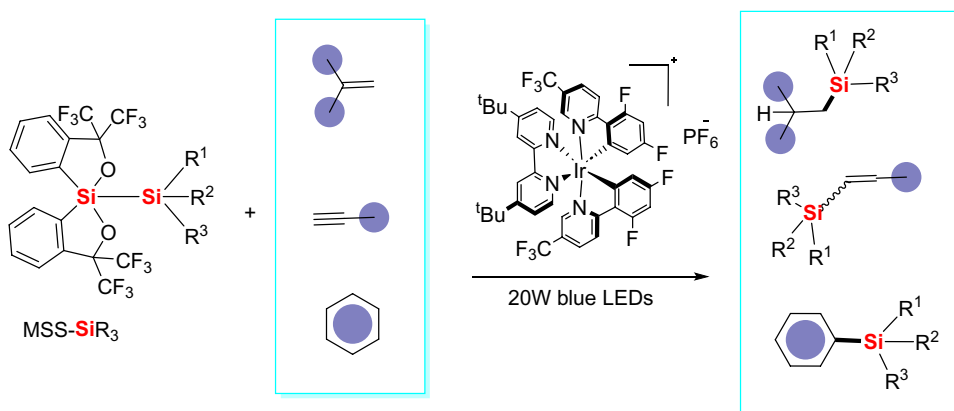
Silylation reaction of C=N

Silylamines exhibit a notable shift in reactivity compared to typical imines. While imines commonly act as electrophiles, silylamines display nucleophilic behavior specifically at the carbonyl carbon. This transformation in their chemical behavior is quite significant since it enables silylamines to participate in reactions that were previously inaccessible to them before undergoing silylation [34].

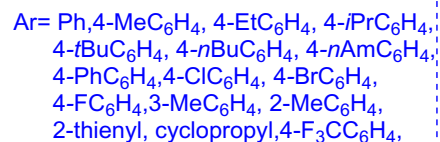
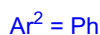
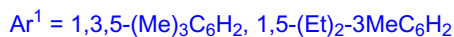
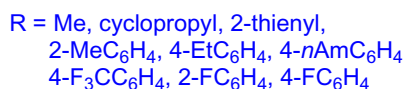
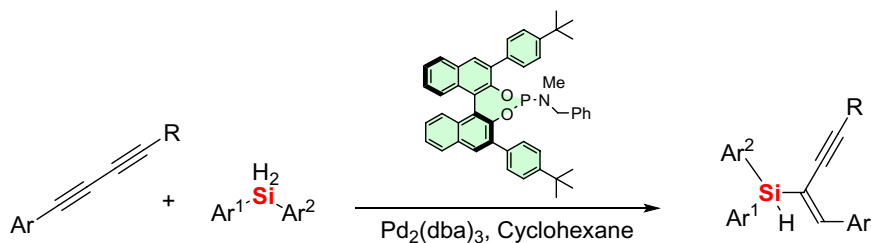
In this contest, Bolourtchian and Galeassadi showed their efforts for the synthesis of variety of α -silylamine via reaction TMSCl with both aromatic and aliphatic imide in presence of lithium and THF as a solvent [35].

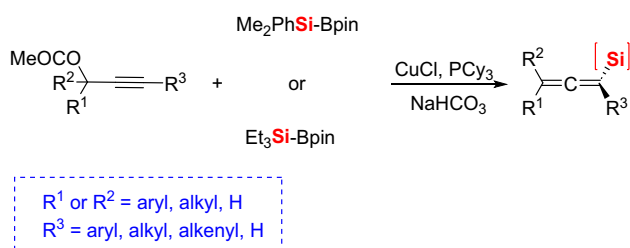
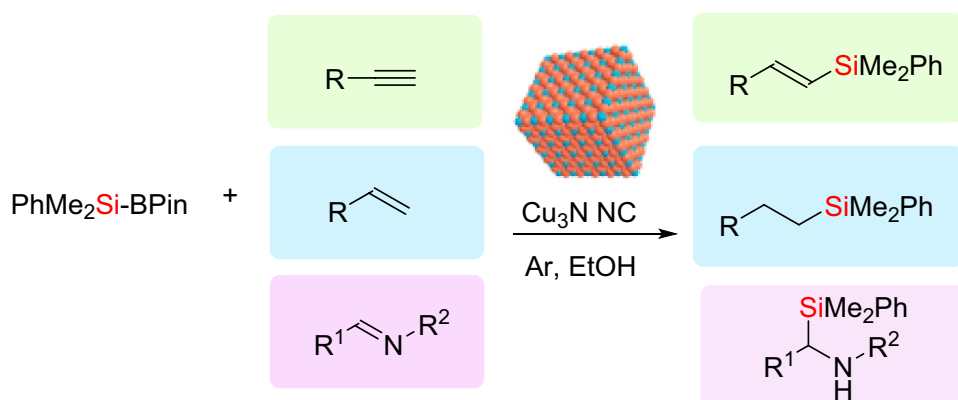
Further in 1997, Bolourtchian and Saednya [36] repeated the reaction of imines with TMSCl by using magnesium, obtaining products with a 70–75% yield upon hydrolysis (Scheme 15).

Scheme 11 Hydrosilylation of a broad range of alkenes, alkynes and heteroarenes in presence of MSS-SiR_3



Scheme 12 Pd-catalyzed hydrosilylation of 1,3-diyne for the synthesis of silicon-stereogenic



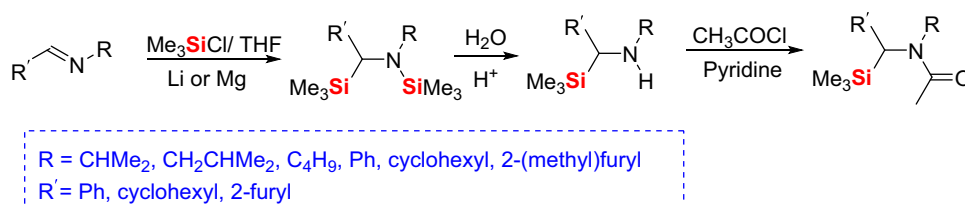
Scheme 13 Protosilylation of unsaturated compounds using $\text{Cu}_3\text{N NC}$ as catalyst under Ar**Scheme 14** The silylation of diverse propargyl carbonates

Silylation reaction of acyl allynes

Silylation of substituted acyl chloride was first reported in 1995 by Saidi and coworkers, where up to 1 equiv of acyl chloride was added to 1 equiv bis(trimethylsilyl) acetylene in presence of anhydrous aluminum chloride to formation polyfunctional mono acyl trimethyl silylacetylene [37]. They examined acyl chlorides with dual bonds in furan and thiophene rings, along with other compounds. They observed that the presence of a furan ring resulted in lower product efficiency, while the presence of an aromatic ring containing an electron-donating substituent in the *para* position led to the highest product yields (Scheme 16).

Direct silylation of C–H bonds

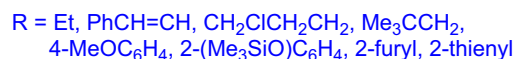
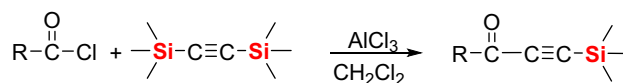
Initially, silylated aryldiazenes were employed as equivalents to aryl anions. This method involved the formation of nucleophilic species in situ through the interaction with a *Lewis* base. The versatility of this approach was demonstrated

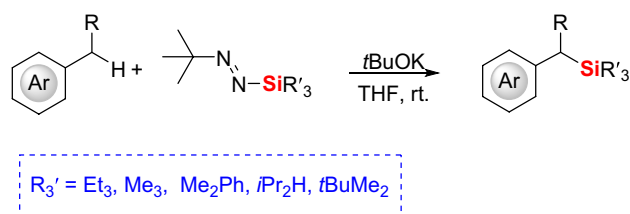
Scheme 15 Reaction of imines with TMSCl in presence of lithium as catalyst in THF as solvent

in various synthetically useful protocols, including the 1,2-arylation of carbonyl compounds [38] and imines [39]. Additionally, it facilitated the assembly of fluorinated systems through nucleophilic substitutions [40, 41].

Neil et al. recently introduced a novel transition metal-free catalytic method for the direct silylation of benzylic $\text{C}(\text{sp}^3)\text{-H}$ bonds at room temperature [42]. In this innovative approach utilized stable *tert*-butyl-substituted silyldiazenes ($t\text{Bu-N}=\text{N-SiR}_3$) as the source of silicon (Scheme 17).

Formation of a carbon–silicon bond holds significant appeal in organic synthesis owing to the utility and significance of organosilicon compounds. Silylated amines, pivotal intermediates in organic synthesis, have drawn attention due to their biological activities and therapeutic potential. Among the common approaches for converting a $\text{C}=\text{N}$ bond into an amine, the hydrosilylation reaction is frequently employed. In this reaction, the *N*-silylated product, derived from an imine, can undergo facile hydrolysis, resulting in a final product to the hydrogenation of a $\text{C}=\text{N}$ bond [43].

**Scheme 16** Silylation of substituted acyl chloride



Scheme 17 The direct silylation of benzylic C–H bonds using *t*BuOK as catalyst

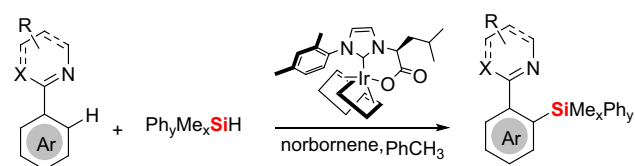
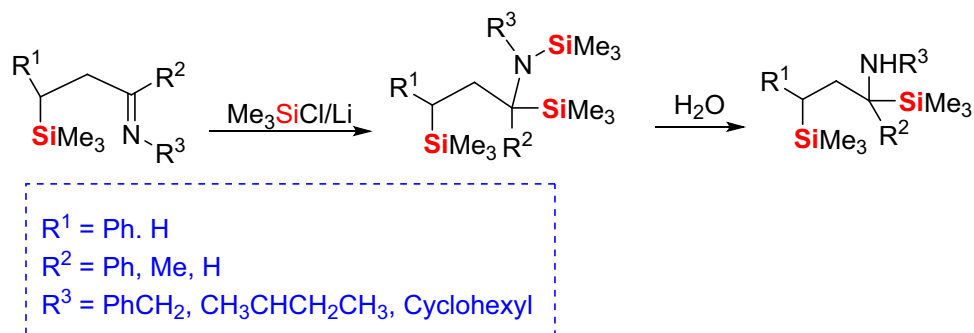
Silylation reactions of β -silylated imines resulting in facile reduction to yield the corresponding α,γ -disilylated amines are being reported by Bolourtchian et al., introducing both novel organosilicon compounds: α,γ -disilylated amines, and β -silylated imines [44] (Scheme 18).

Vignesh and colleagues documented an exciting application of new chiral iridium(I) complexes featuring LX-type bidentate NHC–carboxylate ligands derived from amino acids. These complexes were utilized for the ortho-directed dehydrogenative silylation of both sp^2 C–H and sp^3 C–H bonds in the presence of norbornene as a hydrogen acceptor [45] (Scheme 19). Heterocyclic compounds have diverse applications in the pharmaceutical industry [46]. Despite the use of bulky aromatic silylating agents, the developed catalytic system offers precise control over the regioselectivity of the silylation reaction, representing the primary objective of this research in synthesizing heterocyclic derivatives. It successfully stops competing functionalization of both the heterocyclic directing group and the aromatic solvent.

Formation of silicon–oxygen bond

Phenol and its derivatives, due to their wide-ranging applications in the synthesis of polymers, pesticides, analgesics, and resins, hold a special industrial significance [47]. For this reason, researchers have paid special attention to these compounds in their studies. In 2002, Mojtahedi and coworkers presented the silylation of phenols and alcohols using Hexamethyldisilane (HMDS) as the silylating agent [48].

Scheme 18 Silylation reactions of β -silylated imines



Scheme 19 Iridium(I) complexes catalyzing in directed C–H silylation

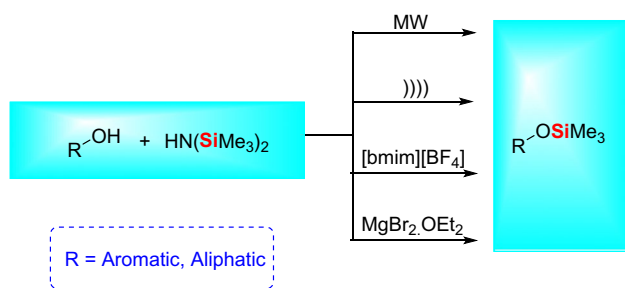
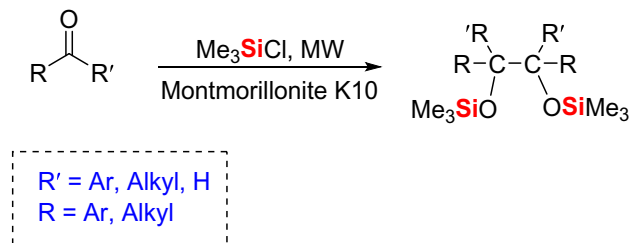
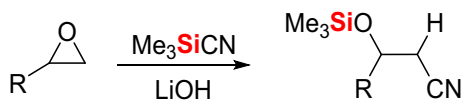
They also reported that the utilization of microwave irradiation yielded remarkable results in enhancing the reaction efficiency and decreasing the reaction time. In addition, he indicated in another investigation that this reaction is achievable under ultrasonic irradiation [49] (Scheme 20). In another research, Mojtahedi's research group claimed benzylic and primary alcohols were effectively shielded using HMDS in good to excellent yields at room temperature within [bmim][BF₄] ionic liquid. Furthermore, the ionic liquid was retrieved completely and employed efficiently in subsequent reactions by Mojtahedi's group. This procedure was also adeptly utilized for phenols protections [50]. This group have also reported MgBr₂·OEt₂ as an effective catalyst for this reaction, functioning as a bidentate chelating Lewis acid [51].

In 1998, the research group led by Bolourtchian [52] informed the reductive coupling of carbonyl compounds. They described the coupling in the presence of TMSCl and montmorillonite K10 clay under microwave irradiation, resulting in the production of bis(trimethylsilyl) pinacols in quantitative yields (Scheme 21).

In 2010, Azizi and his research group developed an efficient and straightforward methodology for the ring opening of epoxides with TMSCN, granting access to valuable and synthetically challenging β -hydroxy nitriles [53] (Scheme 22).

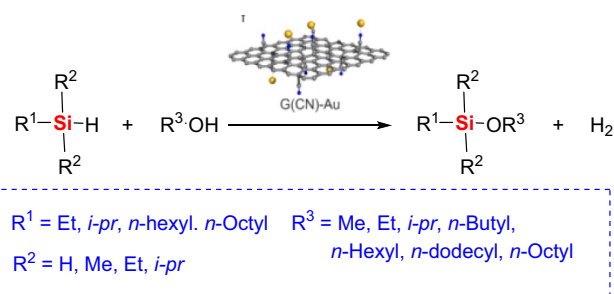
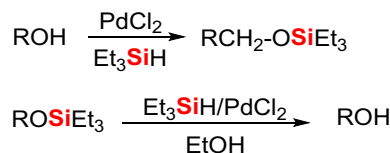
They declared lithium hydroxide as an essential factor for the progression of the reaction, and in its absence, the reaction does not occur.

The Ravishankars group in 2023 [54] presented a method using G(CN)–Au as catalyst for coupling of organosilanes

**Scheme 20** Silylation of phenols and alcohols using HMDS**Scheme 21** Reductive coupling of carbonyl compounds in presence of TMSCl and montmorillonite K10 clay under microwave irradiation**Scheme 22** Ring opening of epoxides with TMSCN in presence of LiOH

with alcohols. They described that a gold-based single-atom catalyst (SAC) is obtained through a one-step, reduction of Au(III) salt followed by stabilization of Au(I) ions on nitrile-functionalized graphene, known as cyanographene (G-CN). The G(CN)-Au catalyst, supported by graphene exhibits a distinctive linear structure of the Au(I) active sites under mild reaction conditions. This particular structure enhances a multistep mode of action in the dehydrogenative coupling of organosilanes with alcohols (Scheme 23).

In 2005, Mirza-Aghayans research group demonstrated new procedure for converting of alcohols to silyl ethers by using palladium(II) chloride/organosilane system. Moreover, they investigated into the subsequent deprotection of triethylsilyl ethers to regenerate the parent alcohol [55] (Scheme 24). They confirmed that utilizing Et₃SiH and incorporation of palladium(II) chloride into a blend of alcohol and silane yielded the respective silyl ether. Furthermore, the generation of the corresponding alcohol was occurred by addition of palladium (II) chloride to a mixture of triethylsilyl ether in dry ethanol.

**Scheme 23** Coupling of organosilanes with alcohols using G-CN as catalyst**Scheme 24** Protection and deprotection of alcohol with Et₃SiH-PdCl₂

Deprotection silicon–oxygen bond

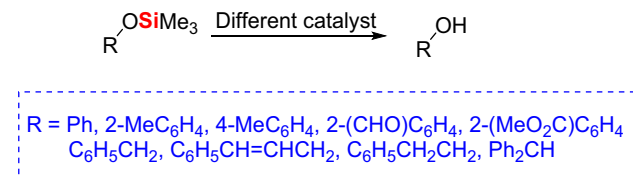
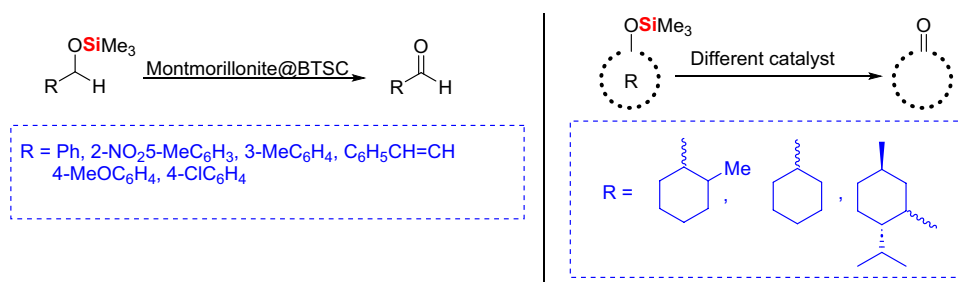
Removing protective groups, modifying, and restructuring functional groups are significant challenges in organic chemistry. These processes are essential for practical chemical synthesis of potential molecules, playing a pivotal role in both academic research and industrial applications [56]. Indeed, Hydroxy groups play a significant role in organic molecules, and managing their manipulation is crucial in multistep synthesis. One of the most effective approaches to safeguard hydroxy groups is by converting them into trialkylsilyl ethers.

Heravi et al. described Montmorillonite K10 supported bis(trimethylsilyl)chromate (Montmorillonite@BTSC) as a catalyst for the direct oxidative deprotection of various trimethylsilyl ethers into their respective carbonyl compounds [57].

Later in 1999, Mojtahedi and coworkers utilized a combination of iron (III) nitrate and montmorillonite K10 for the oxidative deprotection of trimethylsilyl ethers into their respective carbonyl compounds [58] (Scheme 25).

A highly effective method of deprotection of trimethylsilyl ethers was reported by Mojtahedi and co-workers [59] in 1999. They presented a desilylation method for various phenols and alcohols, achieving almost quantitative yields under solvent-free conditions, employing a microwave oven with montmorillonite K10 clay as a support. They also explored the trimethylsilyl group's deprotection using PdCl₂(PhCN)₂ as a catalyst under microwave irradiation. A notable observation was the improved efficiency when adding a drop of

Scheme 25 Oxidative deprotection of trimethylsilyl ethers into their respective carbonyl compounds



Scheme 26 Deprotection of trimethylsilyl ethers

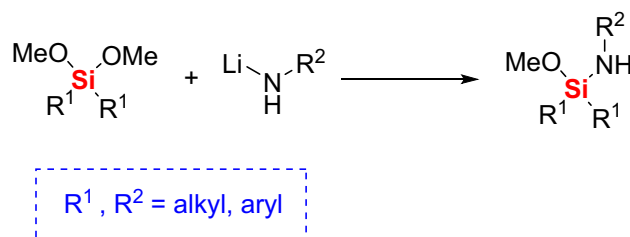
water before heating, as the reaction failed without water (Scheme 26).

Formation of silicon–nitrogen bond

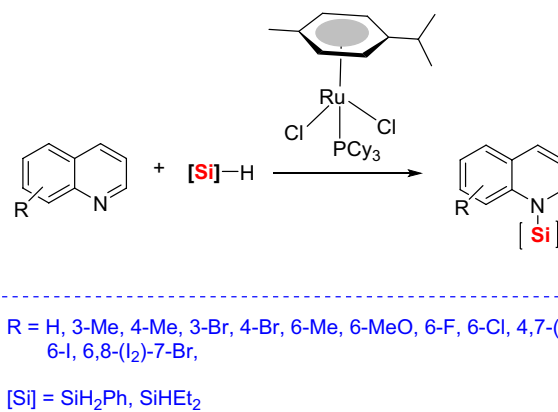
The Si–N bond is widely utilized across diverse fields due to its versatility. It serves as a fundamental component in organic synthesis, acts as ligands for both transition-metal and main group compounds, and functions as protective groups for alcohols, aldehydes, and ketones. The primary approach to creating a silicon–nitrogen bond typically involves the reaction of an amino group with silane [60], hydrosilane [61–64], chlorosilanes [65].

In a recent 2021 publication by Achternbosch et al., a highly selective substitution of silicon-bound methoxy groups with primary lithium amides is detailed [66]. The process involved addition of an amine solution in *n*-pentane to a solution of *n*-butyllithium in *n*-hexane at –30 °C. Subsequently, the mixture was warmed to 0 °C before adding dimethoxysilane at –60 °C. This unique reactivity arises from the formation of remarkably stable lithium methoxide, compensating for the reduced Si–N bond enthalpy in comparison to Si–O bonds. In contrast to substitution reactions involving halosilanes, this method allows for exceptionally selective monosubstitutions under mild conditions, even in the presence of additional reactive methoxy groups (Scheme 27).

Behera and his research team reported the regioselective dearomatization of *N*-heteroarenes in the presence of the catalyst [Ru-(*p*-cymene)(PCy₃)Cl₂] [67] (Scheme 28). DFT studies have shown the complete catalytic cycle, indicating that product formation is driven by *N*→Si tetrel bonding. Initially, PCy₃ dissociates from catalyst, and subsequent



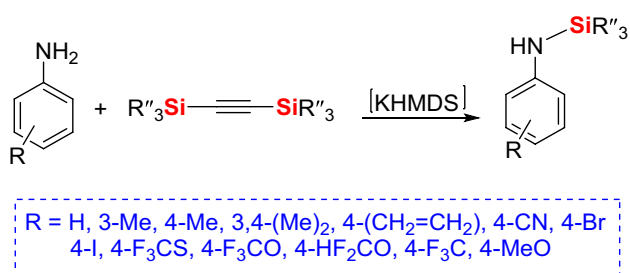
Scheme 27 Alkoxyaminosilane synthesis via primary lithium amides



Scheme 28 [Ru-(*p*-cymene)(PCy₃)Cl₂] catalyzed dearomatization of *N*-heteroarenes

reaction of [(*p*-cymene)RuCl₂] with silane generates the catalytically active intermediate [(*p*-cymene)RuHCl].

In 2022, Kuciński and Hreczycho achieved the efficient protocol for catalytic N–H silylation of aromatic primary amines using KHMDS as catalyst and bis(trimethylsilyl) acetylene acted as silylating agent [68] (Scheme 29). KHMDS played a crucial role in the dealkynative coupling in this procedure. Additionally, they asserted that the amine's acidity significantly influences the deprotonation step, ultimately impacting the efficiency of the final products. They reported successful reactions with Halo-substituted anilines, electron-deficient ones with fluorinated functionalities, and the cyano derivative, all yielding high-product yields. Additionally, heterocyclic primary amines, essential in synthetic



Scheme 29 N–H silylation of aromatic amines

and biological applications, were observed to be compatible with the reaction conditions.

In 2023, Sahoo and Nembenna developed a zinc-catalyzed chemoselective mono-hydrosilylation reaction of nitriles [69] (Scheme 30). In their research, nitriles with a diverse range of functional groups, including electron-donating, electron-withdrawing, and mixed electron-donating/electron-withdrawing groups, as well as heteroaryl, alkyl, and alkene moieties, were successfully converted into their corresponding *N*-silylimines and/or *N,N'*-silyldiimines with high conversion rates. The reported mechanism initiates with the coordination of silane to zinc hydride, leading to the formation of an intermediate. Subsequently, this intermediate undergoes a reaction with nitriles through a 6-membered cyclic transition state, ultimately yielding the desired silylated product.

Silicon in carbon chemistry

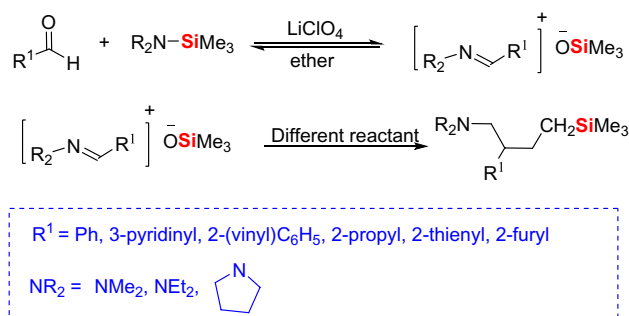
In 1995, Saidi and his research group described a new method for synthesis of β -silylated *N,N*-dialkyl amine derivatives by applying LiClO₄ as *Lewis* acid in Mannich type

reaction of aldehyde with *tertiary* amines to obtain iminium salt followed by addition of trimethylsilylmethylmagnesium chloride [70] (Scheme 31).

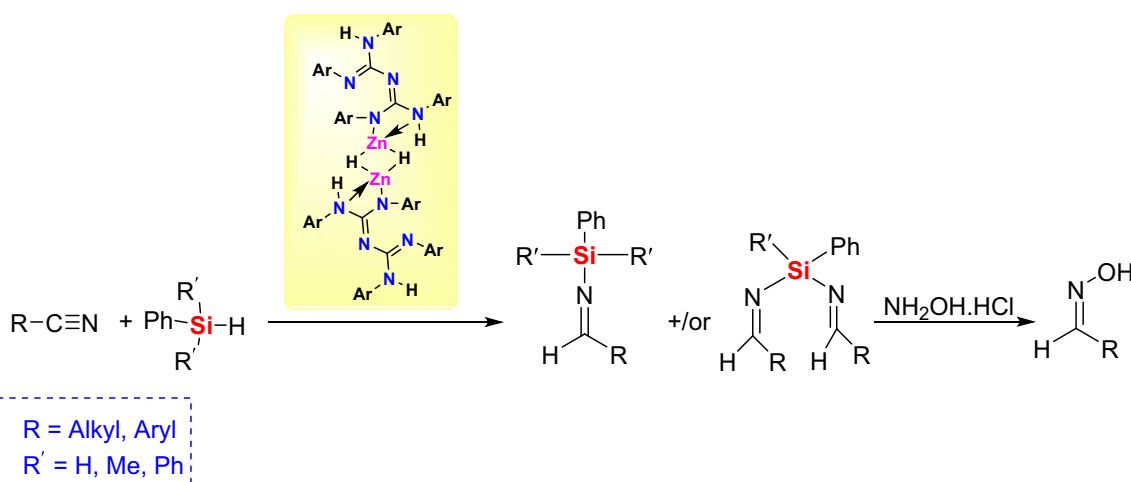
Furthermore, Saidi mentioned in another report that by employing lithium (trimethylsilyl)acetylide or (trimethylsilyl)propargyl magnesium bromide, the formation of β -silylated *N,N*-dialkyl amine can be conducted in one-step procedure [71].

In the presence of lithium ions and within a highly polar medium, the interaction of R₂NSiMe₃ with aldehydes in a lithium perchlorate diethyl ether solution gives rise to the generation of an iminium salt [72].

Parallely the same group has described a three-component reaction for synthesis silylated primary amines by using aldehydes, lithium hexamethyldisilazane and lithium(trimethylsilyl)acetylide or trimethylsilylmethylmagnesium chloride as an organosilicon nucleophile in presence of lithium perchlorate [73]. A little later, in 1999, Mojta-hedi and colleagues employed organolithium reagents and



Scheme 31 Mannich type reaction of aldehyde with tertiary amines derivatives using LiClO₄ followed by addition of trimethylsilylmethylmagnesium chloride



Scheme 30 Chemoselective formation of *N*-silylimine

magnesium-based nucleophiles for the synthesis of primary amines [74] (Scheme 32).

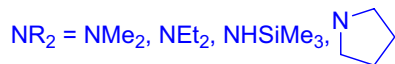
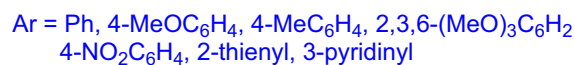
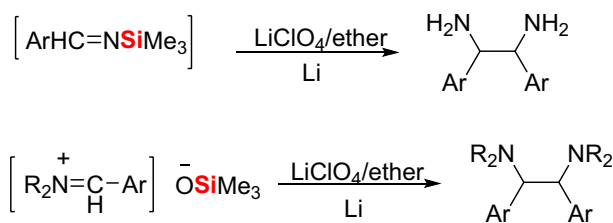
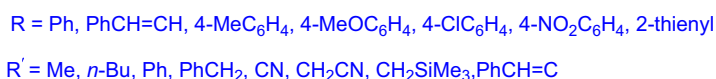
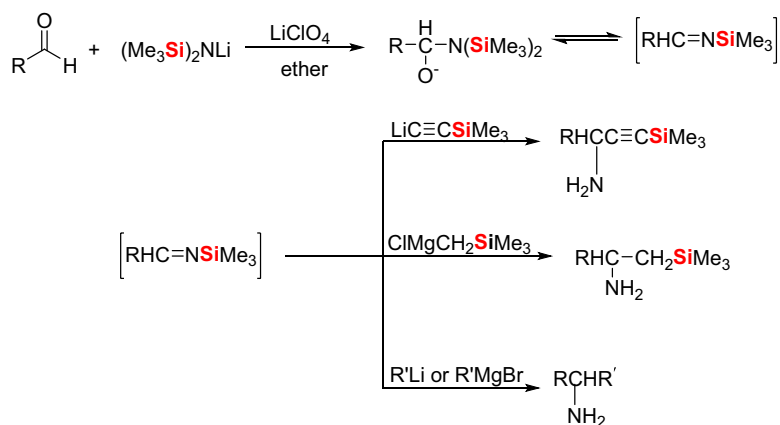
In another report, it was detailed by Mojtahedi that the reductive coupling of iminium ions occurs in an ethereal environment in the presence of lithium metal using lithium perchlorate [75]. It has been reported that the use of high-energy wave irradiation such as ultrasonic or microwave radiation leads to an improvement in the efficiency of chemical processes [76–78]. The utilization of ultrasound irradiation has played a significant role in reducing reaction times and acceleration. Moreover, under these conditions, diamines were formed with notable diastereoselectivity (Scheme 33).

Strecker reaction

The renowned Strecker reaction was initially reported in 1850 by the German chemist Adolph Strecker (1822–1871) [79]. This pivotal discovery marked a significant contribution by Strecker to the field of organic chemistry. The Strecker reaction, named in his honor, has since become a fundamental synthesis method. It stands out as one of the earliest one-pot and atom-economic multi-component reactions ever uncovered. This feature underscores its efficiency and environmental friendliness, aligning with the principles of green chemistry. The Strecker reaction's ability to combine multiple reactants in a single reaction vessel, minimizing waste and maximizing resource utilization, has contributed to its enduring significance in organic synthesis. The combination of aldehyde, amine, and cyanide is commonly referred to as the Strecker reaction [80].

In 2006, Mojtahedi and his colleagues applied [bmim][ClO₄] an efficient catalyst for the Strecker reaction in the

Scheme 32 Synthesis silylated primary amines

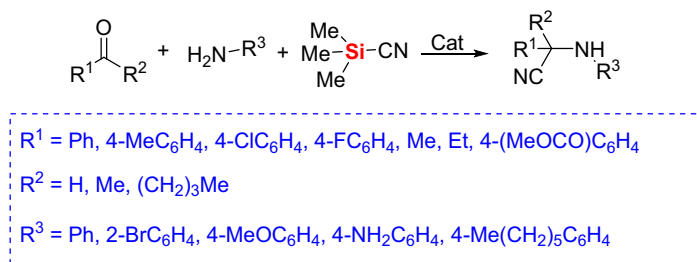


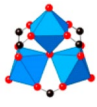
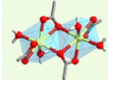
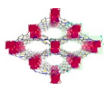
Scheme 33 Reductive coupling of iminium ions using LiClO₄ in ether

presence of aldehyde, amine, and TMSCN as starting materials [81].

Later, in 2009, this research group applied Superparamagnetic Fe₃O₄ as an efficient catalyst in the same reaction [82]. This approach aimed to synthesize α-aminonitriles. They also assessed the diastereoselectivity of the product by employing a chiral amine, (S)-1-phenylethylamine. Their observations, based on NMR spectroscopy, revealed the formation of diastereomers in a 4:1 ratio. This investigation into diastereoselectivity adds a stereochemical dimension to their study, providing valuable insights into the chiral aspects of the synthesized products.

Researchers and chemists widely favor heterogeneous catalysts due to their easy separation and high activity [83]. Recent reports have indicated a growing interest in MOFs due to their high surface area and the presence of active sites capable of interacting with reactive substances. MOFs have

Scheme 34 Strecker reaction in different in different condition

[bmim][ClO ₄]	2006
	2009
Fe ₃ O ₄	
	2016
In-MOF	
	2023
Cd-MOF	
	2023
Co-MOF	

gained particular attention and found numerous applications in synthesis processes and adsorption due to these unique attributes [84, 85].

In 2016, Reinares-Fisac and his research group introduced metal organic framework with indium as the metal center for the one-pot Strecker reaction of ketones, leading to the formation of substituted α -aminonitriles [86]. Notably, In-MOF ($[In_3O(bt b)_2(HCOO)(L)]$, (L = methanol, water, or ethanol) stands out among other catalysts for this reaction, requiring small catalyst loadings and eliminating the need for heat or solvents. They found In-MOF to be an effective catalyst for both linear and cyclic ketones and showed typically, the formation of the imine intermediate is thought to involve the activation of the carbonyl group by the *Lewis* acid site (Scheme 34).

Recently, Khan group demonstrated that Cd-MOFs could efficiently act as *Lewis* acid in the C–N bond-forming Strecker reaction involving aldehyde and ketone carbonyl compounds with amines and TMS-CN [87]. The Cd-MOF, with the formula $[Cd(hipamifba)(H_2O)_2] \cdot 2H_2O$, incorporates an asymmetric amide-functionalized dicarboxylic acid, H₂hipamifba.

In 2023, Sahoo, in a report, provided insight into the mechanism of Strecker reactions utilizing the robust 3D cobalt-based MOFs known as IITKGP-50 [88]. The Co-MOF, denoted by the formula $[Co_2(\mu_2-O)(TDC)_2(L)(H_2O)_2] \cdot 2DMF$ (L = 3,3'-azobispyridine), demonstrated exceptional framework robustness, maintaining stability not only in water but also in a broad range of aqueous pH solutions (pH = 2–12).

In their proposed mechanism, they suggest that the oxygen connected to the benzaldehyde ring interacts with *Lewis* acidic sites in the catalyst, leading to an increase in the electrophilicity of the carbonyl carbon. This electrophilic nature of the carbonyl carbon is then subjected to nucleophilic attack by an amine.

Alkynyl alcohols, featuring a terminal alkynyl carbon shielded with a trimethylsilyl (TMS) group, function as versatile organic building blocks, owing to their reactivity and broad utility in various synthetic transformations. This functional group provides an excellent platform for subsequent modifications. Silylated alkynols, a subset of these compounds, often exhibit significant biological activity along with low toxicity, contributing to their pharmacological importance. Ongoing research efforts focus on developing synthetic methodologies in this domain. Notably, the selective removal of a terminal trimethylsilyl group from bistrimethylsilylated alkynols allows for further tailored transformations, harnessing the discriminative cleavage of silicon–carbon bonds.

In 1998, the group of Bolourtchian described a reaction between Lithium trimethylsilyl acetaldehyde with silylated aldehydes and ketones to prepare the diastereomers of bis-trimethylsilylated hydroxy alkynes [89, 90] (Scheme 35).

The synthesis of silylated alcohols has garnered attention due to their utility in synthesis and potential therapeutic benefits owing to lower toxicity [91]. One method to prepare these compounds involves reducing trimethylsilyl carbonyl compounds using a suitable reducing agent.

In 1998, Zadnabad and co-workers reported a various β -trimethylsilylated alcohols were obtained in good yields and within a short duration by reducing β -trimethylsilyl carbonyl compounds using sodium borohydride under microwave irradiation [92] (Scheme 36).

Silicon as catalyst

While the extensive use of silicon-containing mineral catalysts such as silica [93], nanosilica [94, 95], zeolites [96, 97], SBA [98–100], and aluminosilicates [101] has been widely reported in scientific literature by researchers, the approach shifts when it comes to organosilicon compounds. Organosilicon, or silicon-containing organic compounds, offer a distinct perspective compared to their mineral counterparts.

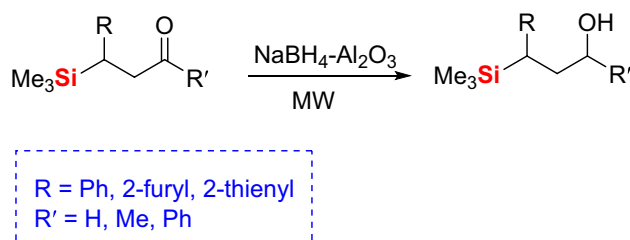
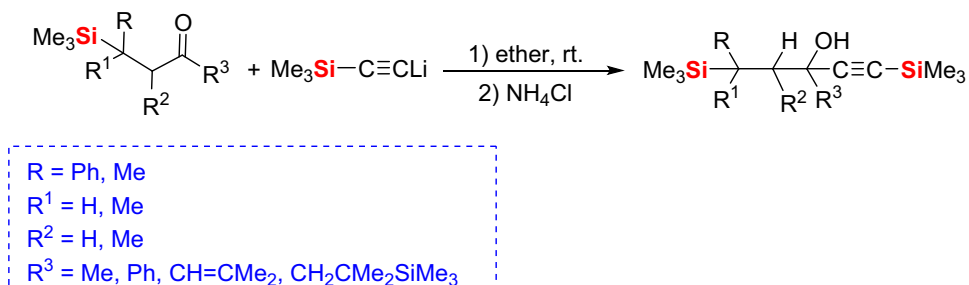
Silicon hydrides have found successful applications in substitution, hydrogenation [102], polymerization [103], and addition processes. A significant number of these reactions are catalyzed by transition metal complexes. The application of organosilicon reagents in conjunction with palladium (Pd) complexes further exemplifies the versatility of organosilanes as valuable precursors in the field of organic chemistry [104].

Isomerization

In 2003, Mirza-Aghayan et al. conducted an investigation into the reactivity of the system $\text{Et}_3\text{SiH}/\text{PdCl}_2$ in the presence of α -olefins [105]. They reported the utilization of the $\text{Et}_3\text{SiH}/\text{PdCl}_2$ system as an exceedingly efficient method for the isomerization of α -olefins under mild solvent-free conditions.

Based on the proposed mechanistic pathway, it is postulated that the reactivity of Et_3SiH in the presence of palladium chloride follows the subsequent sequence. Initially, metallic Pd is formed through the reduction of palladium dichloride utilizing Et_3SiH , as illustrated in (Scheme 37). This Pd(0) species acts as the catalytically active entity in the isomerization reaction, facilitating the generation of the corresponding alkane. The succeeding step involves the establishment of a palladium complex via oxidative addition

Scheme 35 Reaction between lithium trimethylsilyl acetaldehyde with silylated carbonyl compound



Scheme 36 Reduction of β -trimethylsilyl carbonyl compounds using $\text{NaBH}_4-\text{Al}_2\text{O}_3$

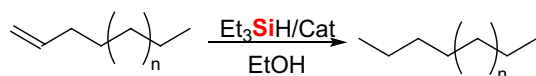
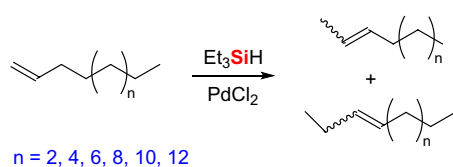
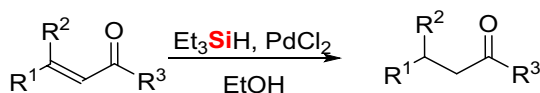
of Et_3SiH to metallic palladium, followed by a reductive elimination process incorporating a 1,2-hydride shift.

Reduction

Also, Mirza-Aghayans research group, in another report, declared the successful demonstration of high efficiency in reducing alkenes to their corresponding alkanes using PdCl_2 , Et_3SiH , and ethanol as a solvent at room temperature. It is important to note that the hydrogenation process did not entail any hydrosilylation reactions, and only the desired alkanes were obtained in significant yields (Scheme 38).

In 2006, the investigation of hydrogenation and isomerization of carbon–carbon double bonds in 1-alkenes was conducted utilizing palladium(II) acetate and palladium on activated charcoal catalysts in combination with Et_3SiH [106]. Under ambient conditions, the reduction of 1-alkenes was carried out in the presence of Et_3SiH , ethanol, and a catalytic quantity of either $\text{Pd}(\text{OAc})_2$ or Pd/C . High yields were achieved with this efficient method in the hydrogenation of unsaturated alkenes to their alkanes. Following that, the isomerization of $\text{C}=\text{C}$ bonds in 1-alkenes was reported by utilizing the same catalytically system, in the absence of solvent. At room temperature, the $\text{Pd}(\text{OAc})_2/\text{Et}_3\text{SiH}$ system demonstrated superior effectiveness compared to the $\text{Pd}/\text{C}-\text{Et}_3\text{SiH}$ system, while comparable results were obtained at 50°C for both catalysts.

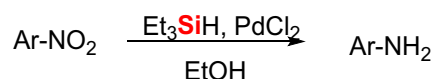
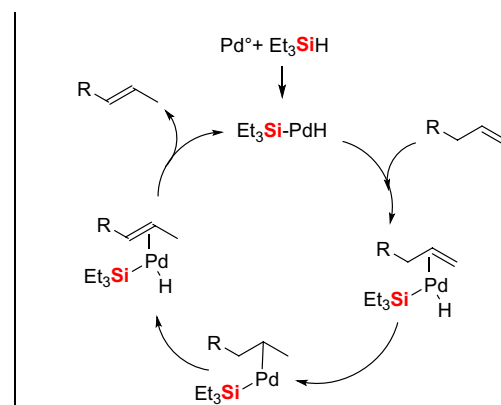
Further, the group also applied the $\text{PdCl}_2/\text{Et}_3\text{SiH}$ system for the selective hydrogenation of the $\text{C}=\text{C}$ bond of α,β -unsaturated ketones, resulting in the formation of the corresponding saturated carbonyl compounds [107] (Scheme 39).

Scheme 37 The isomerization of α -olefins with $\text{Et}_3\text{SiH}/\text{PdCl}_2$ **Scheme 38** The reduction of 1-alkenes**Scheme 39** selective hydrogenation of α,β -unsaturated ketones

In 2010, another important work concerning reduction of nitroaromatic compounds to the corresponding anilines was reported by Mirza-Aghayan [108] who used triethylsilane as reducting agent in the presence of catalytic amounts of palladium chloride. This report extends the scope of her prior research on the utilization of the $\text{Et}_3\text{SiH}-\text{PdCl}_2$ system for the chemical transformation of organic functional groups. They presented their preliminary findings, highlighting the versatility of the $\text{PdCl}_2-\text{Et}_3\text{SiH}$ combination in the reduction of nitroaromatic compounds to the corresponding amines under mild conditions (Scheme 40).

In 2010, Azizi and coworkers [109] presented the one pot reductive amination of aldehydes using metal-free system as a catalyst. This report details the effective one-pot synthesis of diverse amines with structural variations, employing Hantzsch ester as the hydrogen source. The desired product is formed by using a DHP as a reducing agent in conjunction with a catalytic quantity of trimethylsilyl chloride (Scheme 41).

Utilizing its multifaceted properties, CCl_4 has proven to be a versatile reagent, demonstrating efficacy as a dehydrating agent for the synthesis of hydrazides [110], amides, carboxyamides [111, 112], and heterocycles and also in ethylene polymerization [113].



Ar = Ph, 4-MeC₆H₄, 4-NH₂C₆H₄, 2-naphthyl
3,4-(CH₂OH)₂C₆H₃, 4-(CH₃CO)C₆H₄,
3-(HCO)C₆H₃, 4-HOC₆H₄,
2,6-(Me)₂-3-pyridinyl

Scheme 40 Reduction of nitroaromatic compounds to the corresponding anilines using $\text{Et}_3\text{SiH}-\text{PdCl}_2$

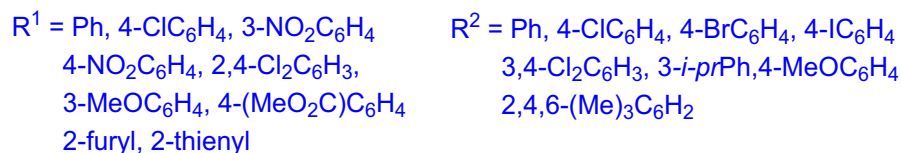
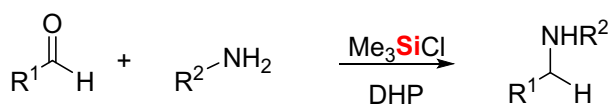
In 2010, Azizi and co-workers [114] developed a silicon tetrachloride catalyzed method as described aromatic and aliphatic amines are treated with α,β -unsaturated carbonyl compounds in the presence of catalytic amount of silicon tetrachloride. The interaction of both aryl and alkyl amines with various Michael acceptors yielded the respective Michael adducts, utilizing a straightforward catalyst, and achieving yields ranging from good to excellent (Scheme 42).

In 2012, Azizi and collaborators identified that Mannich reactions with different aromatic aldehydes catalyzed by SiCl_4 , when conducted in a solvent-free condition, exhibited a smooth progression [115]. Also, they mentioned that using Silicon tetrachloride in absent of solvent led to the Mannich-type reaction produced the desired product with excellent yields and demonstrated excellent anti-selectivity (Scheme 43).

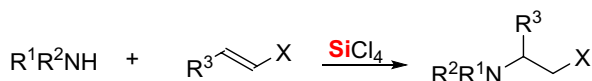
The novel applications of organosilicon compounds in interdisciplinary sciences

Silicon organic compounds, known for their versatile chemical properties [116] have opened up exciting avenues for various applications across different fields [117]. The unique structural characteristics of silicon-based organic

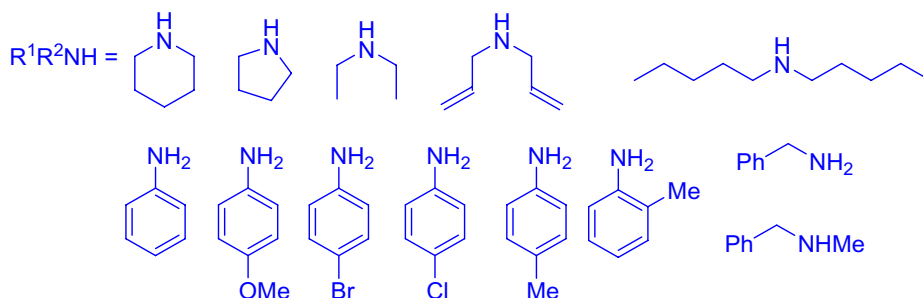
Scheme 41 Reductive amination of aldehydes with DHP as reduction agent and catalytical amount of TMSCl



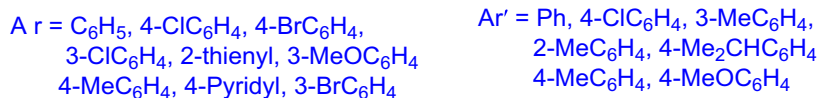
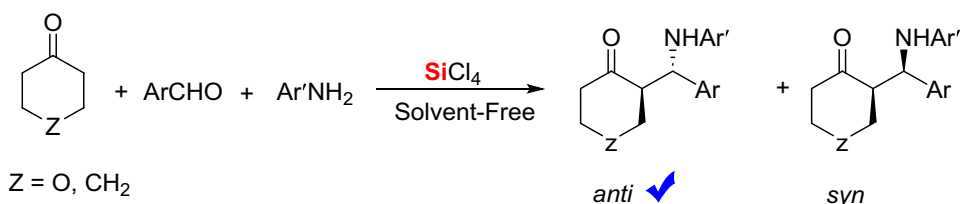
Scheme 42 Reaction of amines with α,β -unsaturated carbonyl compounds using SiCl_4



$X = \text{CN}, \text{COOMe}, \text{CONH}_2, \text{COR}$



Scheme 43 Mannich-type reaction using SiCl_4 as catalyst



compounds [118] contribute to their wide range of uses, including but not limited to the following:

Silicones in biomedical engineering

Silicones, derived from silicon organic compounds, have found applications in biomedical engineering. These materials are utilized in the development of medical adhesives

[119], prosthetics [120], and various medical devices due to their biocompatibility and flexibility [121].

Silicon-based polymers for advanced materials

The synthesis of silicon-based polymers has led to the creation of advanced materials with remarkable properties. These polymers find applications in industries such as aerospace [122], electronics [123], and construction, where their

unique thermal and mechanical characteristics are highly valuable.

Energy storage devices

Recent energy crises worldwide have prompted researchers to intensify their focus on the fields of phase change materials and batteries more than ever before [124]. The increasing demand for sustainable energy solutions has underscored the importance of developing innovative materials and energy storage technologies. Silicon organic compounds play a crucial role in the development of materials for energy storage devices. Silicon-based anode materials in lithium-ion batteries [125], for example, demonstrate enhanced performance and capacity, contributing to the improvement of energy storage systems [126].

Solar energy technology

In today's world, sustainable energy supply is one of the main power indicators for developed countries [127]. Solar light is known as the cleanest source of energy production in the world and it has been found that it can be used as a sustainable source of energy production without the slightest damage to the environment [128]. Organosilicon compounds play a crucial role in solar energy technology, primarily as essential components in the production of semiconductor-based solar cells. These compounds are used as additives or coatings in solar cells to enhance their performance and efficiency. Some of these applications in the field of making solar cells are: water-repellent coatings [129], dust-resistant coatings [130], anti-scratch coatings [131], anti-reflective coatings [132].

Hydrogen production

Hydrogen production holds significant importance in terms of energy and the environment [133]. Hydrogen, as a clean and renewable energy source, can play a crucial role in power generation, carbon-neutral transportation, and efficient energy storage [134]. Additionally, hydrogen finds extensive applications in the chemical industry, fertilizer production, and metal processing. It serves as a green and sustainable solution to global energy and environmental challenges. It can be said that the most key part in the production of hydrogen is the process catalyst [135] which organosilicon compounds are among the most efficient materials for making these catalysts [136].

Silica nanoparticles in drug delivery

The use of silica nanoparticles, derived from silicon compounds, has gained attention in drug delivery systems. These

nanoparticles offer a promising platform for controlled drug release and targeted delivery [137], enhancing the efficacy of pharmaceutical treatments [138].

Organosilicon compounds in green chemistry

Organosilicon compounds contribute to the principles of green chemistry by providing alternatives to traditional organic synthesis routes [139]. The use of silicon reagents in various chemical transformations reduces environmental [140] impact and enhances the efficiency of synthetic processes [141].

Silicones in personal care products

Silicones are widely employed in the formulation of personal care products, such as shampoos [142], conditioners [143], and skincare items. Their unique properties, including water repellency and smooth texture, enhance the performance and sensory aspects of these products [144].

Silicon-containing surfactants

Silicon-containing surfactants play a vital role in formulations for industrial and household cleaning products. Their surface-active properties contribute to improved wetting, emulsification, and dispersing capabilities in various applications [145]. The continuous exploration of silicon organic compounds is likely to unveil even more innovative applications [146], further expanding their role in shaping advancements across diverse scientific and industrial domains [147].

Conclusions and outlook

The field of organosilicon compounds is rapidly expanding, exerting a profound and enduring influence across various domains of synthetic chemistry. A fundamental reaction in silicon chemistry involves the creation of carbon–silicon bonds, typically through the cleavage of carbon–carbon or carbon–hydrogen bonds. Researchers commonly observe that the majority of carbon–silicon bond formations take place in the presence of metal catalysts.

This comprehensive review delineates significant advancements in organosilicon chemistry spanning from 1940 to 2023, emphasizing the material's crucial role in organic synthesis. Its versatility extends beyond being a starting material or final product, as it also functions adeptly as a catalyst.

The impactful presence of these compounds as catalysts in Strecker, Mannich, reduction, isomerization, and carbonyl protection and deprotection reactions has garnered significant attention from researchers. Furthermore, this report

meticulously details the substantial impact of organic silicon compounds on the progression of synthetic and catalytic chemistry. The applications of their properties have played a pivotal role in shaping the landscape of these scientific fields. This continuous advancement not only underscores the significance of organosilicon chemistry but also holds the promise of a vibrant and promising future for its continued exploration.

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Declarations

Conflict of interest The authors declare no competing interests.

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Authors and Affiliations

Hoda Mollabagher¹ · Mohammad M. Mojtahedi¹  · Seyed Amir Hossein Seyed Mousavi¹

✉ Mohammad M. Mojtahedi
mojtahedi@ccerci.ac.ir

¹ Faculty of Organic Chemistry and Natural Products,
Chemistry and Chemical Engineering Research Center
of Iran, Pajohesh Blvd, Tehran 1496813151, Iran