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Facile generation of [bis(2-pyridyldimethylsilyl)methyl]lithium and its reaction with carbonyl compounds. New method for the stereoselective synthesis of vinylsilanes

Kenichiro Itami, Toshiki Nokami and Jun-ichi Yoshida*

Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Yoshida, Kyoto 606-8501, Japan

Dedicated to Professor Barry M. Trost on the occasion of his 60th birthday

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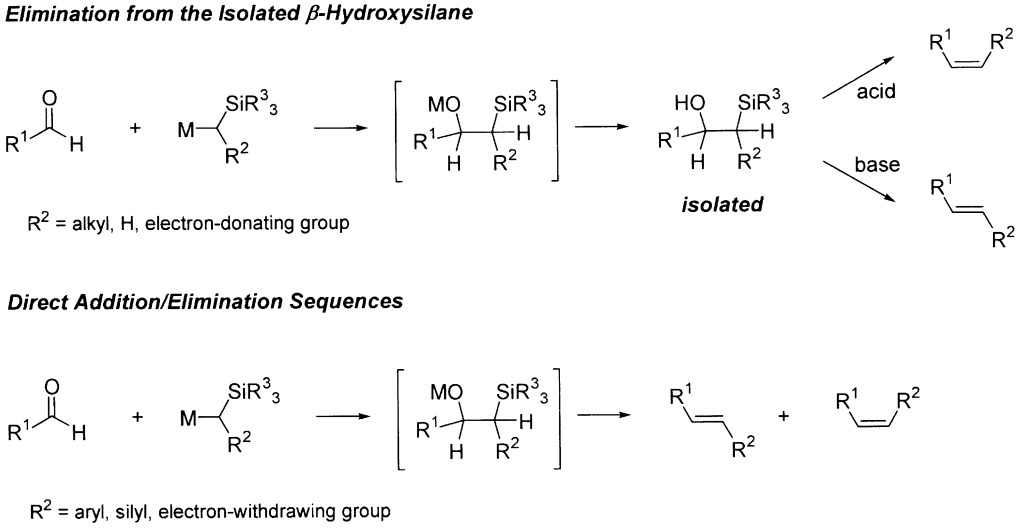
Abstract—The generation of $(2\text{-PyMe}_2\text{Si})_2\text{CHLi}$ was easily accomplished by the deprotonation of $(2\text{-PyMe}_2\text{Si})_2\text{CH}_2$ using *n*-BuLi in Et_2O. The ^1H NMR analysis of $(2\text{-PyMe}_2\text{Si})_2\text{CHLi}$ in Et_2O-d_{10} revealed the coordination of both pyridyl groups to lithium. Thus generated $(2\text{-PyMe}_2\text{Si})_2\text{CHLi}$ was found to react with a variety of aldehydes and ketones to give the corresponding vinylsilanes in extremely high yields with complete stereoselectivities (>99% *E*).

1. Introduction

The Peterson-type olefination reaction has emerged as an extremely useful method for the preparation of alkenes from carbonyl compounds.[1,2] Although the exact mechanism of the Peterson-type olefination is not clear at the present time, it has been generally accepted that the reaction occurs with the intermediacy of β-silyl alkoxide or β-silyl alcohol.[2] The interesting aspect of the Peterson-type olefination is that the course of the reaction is highly dependent on the substituents on α-carbon. In the case of the reaction of α-silyl carbanions bearing alkyl, hydrogen, or electron-donating substituents on α-carbon, β-silyl alcohols are usually isolated.[2] Treatment of thus isolated β-silyl alcohols with



Scheme 1. Two types of reaction modes of Peterson-type olefination.

Keywords: Peterson-type olefination reaction; vinylsilanes; silyl alcohols.

* Corresponding author. Tel.: +81-75-753-5651; fax: +81-75-753-5911; e-mail: yoshida@sbchem.kyoto-u.ac.jp

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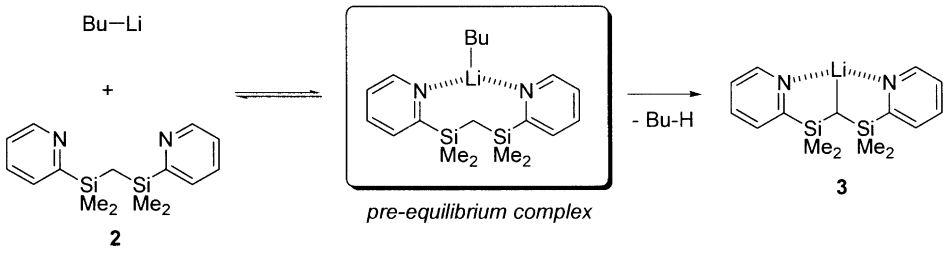
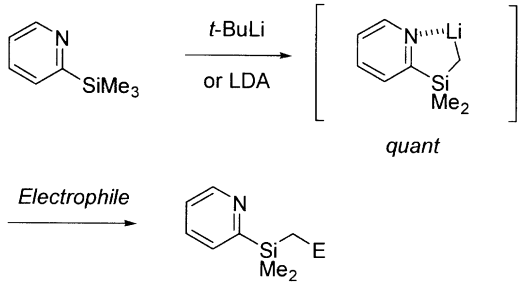


Scheme 2. Complex induced proximity effect in the deprotonation of **2**.

acid or base leads to the formation of alkenes (Scheme 1).[3,4] The benefit of this procedure is that the stereoselectivity (*E* or *Z*) can be controlled by the choice between acid and base. On the other hand, the reaction of α-silyl carbanions bearing aryl or electron-withdrawing group on α-carbon leads to the direct formation of alkenes, in which the initial intermediate undergoes spontaneous elimination reaction (Scheme 1).[2] In this case, the stereoselectivity of the reaction is dependent on the steric and electronic nature of the substituents on α-carbon and silicon.[2] By using the Peterson-type olefination reaction, synthetically useful vinylsilanes can be prepared by the reaction of bis(silyl)-methylmetal with carbonyl compounds using the later direct addition/elimination process.[4–6]

Despite many practical advantages of Peterson-type olefination reactions over the conventional carbonyl olefination reactions,[7] such as Wittig reaction, Tebbe reaction, Nozaki reaction, and Julia coupling, there exist several significant disadvantages to be overcome before the Peterson-type olefination becomes to be enlisted into service in a real sense. For example, there is no general route for the generation of α-silyl carbanion and this chemistry still suffers from its substrate dependence.[8]

Recently, we have embarked on a program directed towards the development of a general method for the generation of synthetically useful α-silyl carbanion. We paid particular attention to the silane deprotonation methodology because of its convenience compared with the other α-silyl carbanion-generating methods such as metal–halogen exchange reaction, metal–heteroatom exchange reaction, and alkyllithium–vinylsilane addition reaction.[8] Our approach was to append the potentially coordinating pyridyl group on silicon thereby enabling the facile deprotonation. For example, the facile deprotonation of otherwise difficult methyl group on silicon[9] was achieved by utilizing pyridyl group as the intramolecular ligand (Eq. (1)).[10–12] Thus generated 2-$PyMe_2SiCH_2Li$ was found to be an excellent nucleophilic hydroxymethylating reagent for various electrophiles.[11]



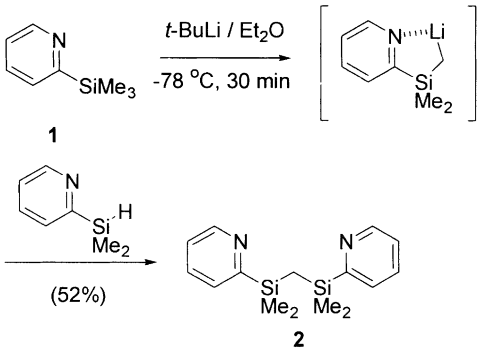
(1)

In ongoing efforts to exploit 2-$PyMe_2Si$ group in the α-silyl carbanion chemistry, we envisioned that appending multiple 2-$PyMe_2Si$ groups should lead to interesting reactivity. Recently, we reported the facile deprotonation of $(2\text{-}PyMe_2Si)_2CH_2$ and the reaction of thus generated $(2\text{-}PyMe_2Si)_2CHLi$ with carbonyl compounds, which leads to the stereoselective synthesis of vinylsilanes.[13] In this paper, we report on the full details of this study.

2. Results and discussion

2.1. Deprotonation of bis(2-pyridyldimethylsilyl)-methane

The synthesis of starting material $(2\text{-}PyMe_2Si)_2CH_2$ (**2**) can be easily accomplished in one-pot by the reaction of 2-$PyMe_2SiCH_2Li$, which is easily generated by the deprotonation of 2-pyridyltrimethylsilane **1** with 2-$PyMe_2SiH$ as reported previously (Eq. (2)).[11]



(2)

At the outset, we examined the deprotonation of **2** to generate $(2\text{-}PyMe_2Si)_2CHLi$ (**3**). We have already reported that the deprotonation of **1** is highly dependent on the lithiating agent employed: *t*-BuLi leads to quantitative deprotonation; *n*-BuLi leads to a complex mixture.[10] As in the case for **1**, the deprotonation of **2** was successfully accomplished by 1.1 equiv. of *t*-BuLi in Et_2O at −78°C and subsequent reaction with allyl bromide gave the corresponding adduct

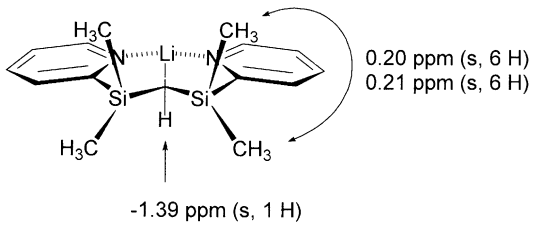


Figure 1. ^1H NMR of **3** in Et_2O-d_{10} at −78°C.

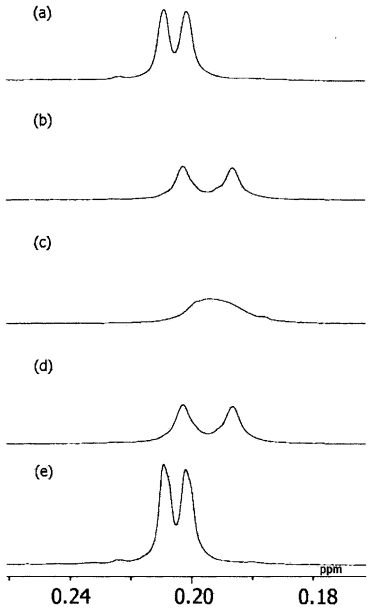
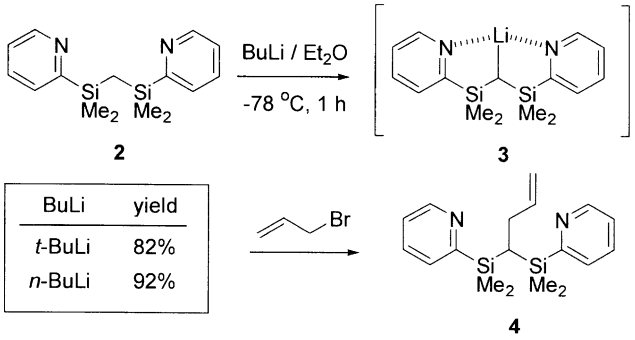


Figure 2. ^{1}H NMR of methyl groups on silicon of **3** in Et_2O-d_{10}: (a) at −78°C; (b) raised to −30°C from −78°C; (c) raised to 0°C from −30°C; (d) re-cooled to −30°C from 0°C; (e) re-cooled to −78°C from 30°C.

$(2\text{-}PyMe_2Si)_2CHCH_2CH{=}CH_2$ (**4**) in 82% yield (Eq. (3)). Anticipating the increased reactivity of **2**, we next employed *n*-BuLi under otherwise identical conditions and **4** was isolated in 92% yield (Eq. (3)). Simple alkyl bromides were not applicable as electrophiles in this reaction because of their lower reactivities toward nucleophiles. We assume that the steric hindrance of **3** is also responsible for its low reactivity toward alkyl bromides, since $2\text{-}PyMe_2SiCH_2Li$ possesses sufficient reactivity toward various alkyl bromides.[11]



(3)

The realization of extremely efficient deprotonation of **2** under very mild conditions might be worth mentioning. As already reported by several groups, the deprotonation of $(Me_3Si)_2CH_2$[4,14] or related bis(silyl)methane[15,16] requires very forcing conditions such as *t*-BuLi/THF/HMPA/−40°C/7.5 h[4] or *n*-BuLi/TMEDA/rt/1 week.[14] On the other hand, in the case of **2**, the deprotonation does not require *t*-BuLi or polar solvent system. These results clearly suggest the enhanced reactivity of **2** toward base. We assume that the deprotonation of **2** proceeded through the agency of what Beak and Meyers have termed 'complex induced proximity effect (CIPE)'.[17] In the reaction, there must be a pre-equilibrium complex of **2** and *n*-BuLi prior to the subsequent deprotonation (Scheme 2). As a result, the formation of the pre-equilibrium complex renders the deprotonation event intramolecular in nature and this might be the reason for the increased reactivity of **2**.

In addition to the kinetic preference for the deprotonation of **2** by CIPE, we presume that the thermodynamic stabilization of generated organolithium **3** by the intramolecular pyridyl group coordination is also responsible for the efficiency of this deprotonation process. In order to ascertain whether the pyridyl group is coordinating to lithium or not, we next examined the structure of **3** in solution using ^{1}H NMR spectroscopy in Et_2O-d_{10} at −78°C (Fig. 1). The ^{1}H NMR spectrum showed two singlets (0.20 and 0.21 ppm) due to the two methyl groups on each silicon atom and one singlet (−1.39 ppm) due to a proton on α-carbon. The observed non-equivalence of the methyl groups on silicon is most likely attributed to the coordination induced rigid five-membered cyclic structure of **3**. Moreover, the observed two singlets indicate that both pyridyl groups are coordinating to the lithium and that the two $2\text{-}PyMe_2Si$ groups are equivalent. In line with these assumptions, two pyridyl groups were equivalent in the ^{1}H NMR spectrum (see Section 4).

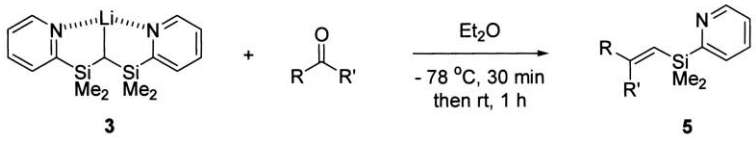
Next, we examined the variable-temperature ^{1}H NMR experiments for **3** at intervals of 15 min (raising: −78, −30, 0°C; re-cooling: 0, −30, −78°C) (Fig. 2). It was found that the two singlets for the methyl groups on silicon coalesced at 0°C (Fig. 2c), which implies that the ring flipping of 5-membered cyclic structure becomes rapid around 0°C. In addition, re-cooling of the sample to −78°C (Fig. 2e) showed identical spectrum with the original one (Fig. 2a), which indicates the reasonable stability of **3** at 0°C.

2.2. Reaction of [bis(2-pyridyldimethylsilyl)methyl]-lithium with carbonyl compounds

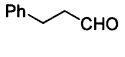
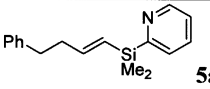
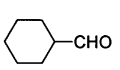
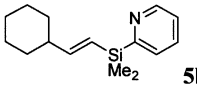
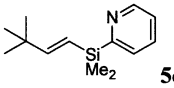
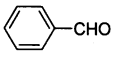
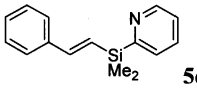
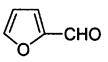
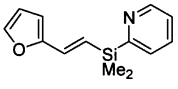
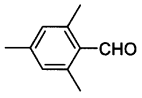
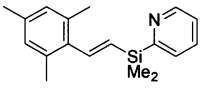
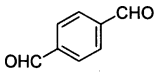
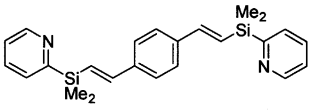
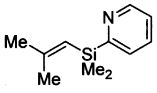
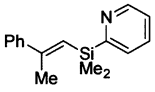
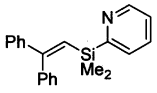
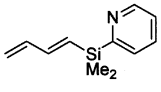
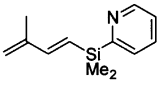
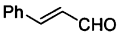
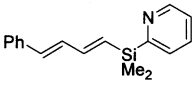
Having established the facile deprotonation of **2**, we further investigated the reactions of $(2\text{-}PyMe_2Si)_2CHLi$ (**3**) with various carbonyl compounds. It has been reported that the reactions of $2\text{-}PyMe_2SiCH_2Li$ with aldehydes and ketones gave the β-silyl alcohols without formation of alkenes by the Peterson-type elimination.[11] However, in the case of **3**, the Peterson-type olefination was found to take place, after or concurrently with the addition, to give the corresponding vinylsilanes **5** stereoselectively. The results are depicted in Table 1.

The reactions with primary, secondary, and tertiary aliphatic and aromatic aldehydes gave the corresponding vinylsilanes in quantitative yields (entries 1–7). Noteworthy is that the reaction is also applicable to the sterically hindered aldehydes (entries 3 and 6) and bis-aldehyde (entry 7). Ketones gave the disubstituted vinylsilanes with somewhat lower yields (entries 8–10). For enolizable ketones such as acetophenone, proton transfer presumably competed with addition where **3** serves as the base (entry 9). The reaction can be applied to the stereoselective synthesis of dienylsilanes as well (entries 11–13). In all cases, virtually complete stereoselectivities (>99% *E*) were observed.

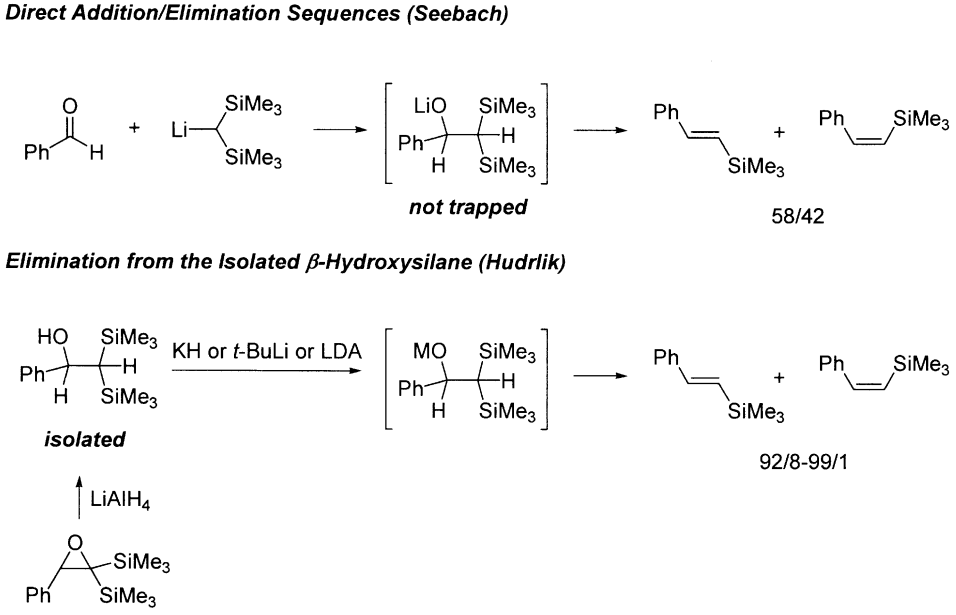
Table 1. Reactions of $(2\text{-PyMe}_2\text{Si})_2\text{CHLi}$ with carbonyl compounds[a]



3 **5**

entry	carbonyl compound	vinylsilane (5)	yield (%)[b]	selectivity[c]
1		 **5a**	quant	>99% *E*
2		 **5b**	quant	>99% *E*
3		 **5c**	quant	>99% *E*
4		 **5d**	90	>99% *E*
5		 **5e**	quant	>99% *E*
6		 **5f**	94	>99% *E*
7[d]		 **5g**	98	>99% *E*
8		 **5h**	73	-
9		 **5i**	56	>99% *E*
10		 **5j**	84	-
11		 **5k**	53	>99% *E*
12		 **5l**	quant	>99% *E*
13		 **5m**	79	>99% *E*

[a] Unless otherwise noted, the reactions were performed in dry Et_2O using **3** and carbonyl compounds (1.5 equiv.) at −78°C for 30 min and then room temperature for 1 h under argon.
[b] Isolated yields based on **3**.
[c] Determined by ^1H, ^{13}C NMR analysis, and NOE experiments.
[d] The reaction was performed using **3** (2.5 equiv) and carbonyl compound (1.0 equiv).



Scheme 3. Two reaction modes in the Peterson-type synthesis of vinylsilane.

2.3. The origin of stereoselectivity

It has been well documented that the acid- or base-mediated elimination from the isolated β-silyl alcohol is highly stereoselective.[3] However, this is not the case for the direct addition/elimination sequences. Hudrlik has elegantly revealed this somewhat puzzling phenomenon (Scheme 3).[4] For example, consistent with the original report by Seebach,[5] the condensation of $(Me_3Si)_2CHLi$ with benzaldehyde gave vinylsilane with a mixture of stereoisomers (*E*/*Z*=58/42).[18] On the other hand, the treatment of the isolated β-silyl alcohol with a variety of bases and additive led to vinylsilane with very high stereoselectivities (*E*/*Z*=92/8–99/1). He concluded that β-silyl alkoxide is not a major intermediate in the direct addition/elimination sequences and suggested that the reaction of bis(silyl)-methyllithium and aldehydes may involve nearly simultaneous formation of C–C and Si–O bonds to give oxasiletane anion directly. Consistent with these results, many reported direct addition/elimination reactions of bis(silyl)methylmetal and carbonyl compounds lead to the formation of vinylsilanes with lower *E* selectivities.[6]

However, we observed complete *E*-selectivity in the direct

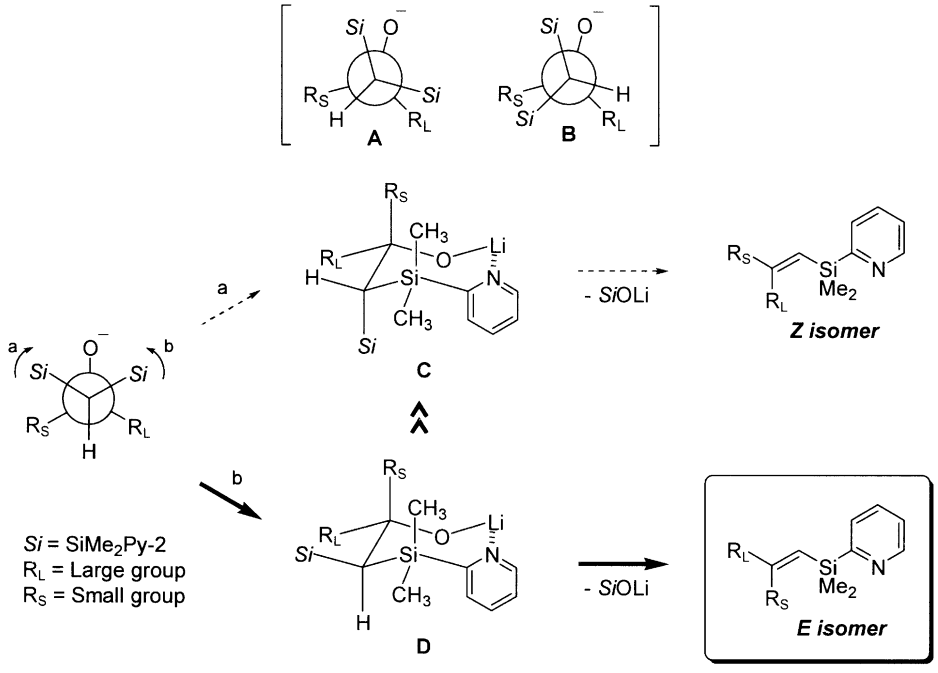
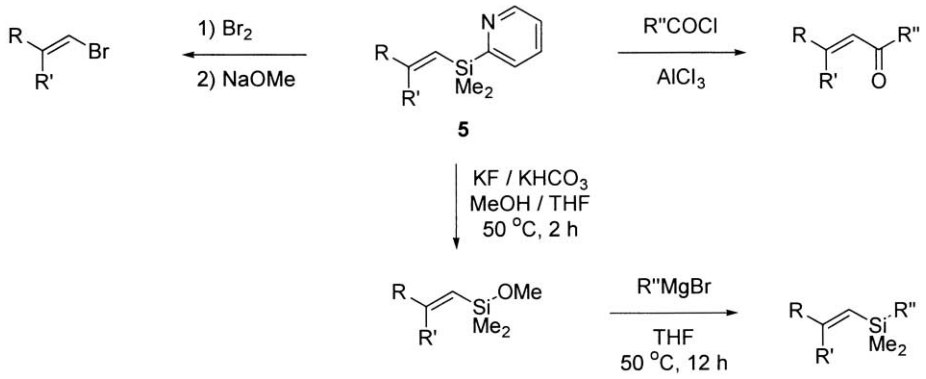


Figure 3. The origin of stereoselectivity.

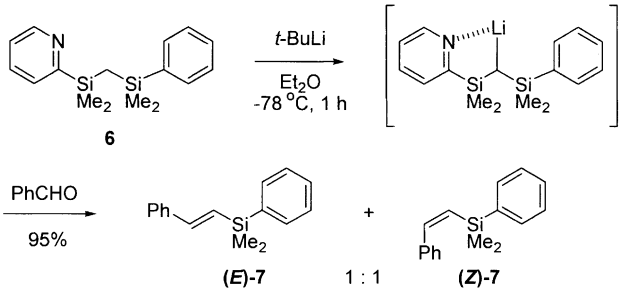


Scheme 4. Synthetic transformations of 2-pyridyl-substituted vinylsilanes.

addition/elimination reaction of $(2\text{-PyMe}_2\text{Si})_2\text{CHLi}$ with various carbonyl compounds. To the best of our knowledge, this is the first general method for the stereoselective synthesis of vinylsilane, which proceeds with direct addition/elimination sequences. If the selectivities are governed by the well-accepted *syn*-elimination from the β-silyl alkoxide (**A** or **B**),[2] the selectivity differences between $(2\text{-PyMe}_2\text{Si})_2\text{CHLi}$ and $(\text{Me}_3\text{Si})_2\text{CHLi}$ should not be dramatic as it is (Fig. 3). Moreover, Hudrlik has already established that the use of more sterically demanding *t*-BuMe_2Si group instead of Me_3Si group only led to a slight increase in the *E* selectivity, indicating that the steric factor is not a sole decisive factor for the high selectivity.[4] There must be some contributions of pyridyl group in the observed high stereoselectivity. We surmise that, before the elimination of the siloxy group, the chair-like conformer (**C** or **D**) might be involved as a stereo-determining intermediate where the intramolecular coordination of the pyridyl group locks the conformation.[19] Of the two, **D** should be preferred over **C**, since both silyl and R_L groups can occupy the equatorial positions. Thus, preferred conformer **D** may lead to the observed *E*-isomer. However, we must stress that these discussions are purely speculative with no experimental evidence.

2.4. Elimination aptitude of 2-PyMe_2Si group

In order to assess the elimination aptitude of the 2-PyMe_2Si group in the Peterson-type olefination, we next conducted the control experiment using $2\text{-PyMe}_2\text{SiCH}_2\text{SiMe}_2\text{Ph}$ (**6**) that can be prepared in 99% yield by the reaction of $2\text{-PyMe}_2\text{SiCH}_2\text{Li}$ with PhMe_2SiCl. The generation of $2\text{-PyMe}_2\text{SiCH(Li)SiMe}_2\text{Ph}$ was successfully accomplished by the reaction of **6** with *t*-BuLi in Et_2O. Thus generated carbanion was subsequently allowed to react with benzaldehyde to give the PhMe_2Si-substituted styrene **7** in 95% yield (Eq. (4)). The formation of a 1/1 mixture of two stereoisomers (*E* and *Z*) strongly denotes that the addition process is non-selective giving the two diastereomeric intermediates. Moreover, it should be noted that the formation of 2-PyMe_2Si-substitued styrene was not detected at all in this reaction. This observation underscores greater elimination aptitude of 2-PyMe_2Si group and we assume the following as the plausible explanations: (i) the coordination of pyridyl group may force the conformation as in **C** or **D** (Fig. 3), thereby making 2-PyMe_2Si group to eliminate; and (ii) greater electrophilicity of 2-PyMe_2Si group renders the alkoxide attack more readily.[15]



(4)

2.5. Synthetic transformations of 2-pyridyl-substituted vinylsilanes

We conducted several synthetic transformations of 2-pyridyl-substituted vinylsilanes **5** that we prepared (Scheme 4). Subjection of 2-pyridyl-substituted vinylsilanes into the action of KF/MeOH led to the formation of methoxy(vinyl)silane by 2-Py–Si bond cleavage.[12b] The resultant methoxysilane can be further allowed to react with Grignard reagents such as PhMgBr to give the corresponding vinylsilane that can be used for further transformations.[20]

More practically, 2-pyridyl-substituted vinylsilane itself can be directly subjected to the reactions with various electrophiles. For example, treatment of **5d** with CH_3COCl in the presence of AlCl_3 afforded 4-phenyl-3-buten-2-one in 91% yield. Bromination of **5d** afforded β-bromostyrene in 54% yield.

3. Conclusions

In conclusion, we have established that $(2\text{-PyMe}_2\text{Si})_2\text{CH}_2$ undergoes extremely facile deprotonation by *n*-BuLi to give $(2\text{-PyMe}_2\text{Si})_2\text{CHLi}$ quantitatively. The ^1H NMR analysis of $(2\text{-PyMe}_2\text{Si})_2\text{CHLi}$ in Et_2O-d_{10} revealed the coordination of both pyridyl groups to lithium. Thus generated $(2\text{-PyMe}_2\text{Si})_2\text{CHLi}$ was found to react with a variety of aldehydes and ketones affording the corresponding vinylsilanes and dienylsilanes in extremely high yields with complete stereoselectivities (>99% *E*). This expeditious

and versatile protocol will find use in many organic reactions using vinylsilanes and dienylsilanes.[20]

4. Experimental

4.1. General

NMR spectra were recorded on Varian GEMINI-2000 (^{1}H 300 MHz, ^{13}C 75 MHz) and JEOL A-500 (^{1}H 500 MHz, ^{13}C 125 MHz) spectrometers in $CDCl_3$ with internal standards (7.26 ppm ^{1}H, 77.0 ppm ^{13}C). Mass spectra (EI) were recorded with a JMS-SX102A spectrometer. Infrared spectra were recorded on a Shimadzu FTIR-8100 spectrophotometer. Gel permeation chromatography was carried out with Japan Analytical Industry LC-918. Unless otherwise noted, all materials were obtained from commercial suppliers and used without further purification. Diethyl ether (Et_2O) was freshly distilled under argon from sodium benzophenone ketyl prior to use.

4.1.1. Bis(2-pyridyldimethylsilyl)methane (2). To a solution of 2-pyridyltrimethylsilane **1** (6.13 g, 40.5 mmol) in dry Et_2O (40 mL) was added dropwise a solution of *t*-BuLi (40.0 mmol, 1.38 M solution in pentane) at −78°C. The mixture was stirred for additional 30 min. To the resultant solution of (2-pyridyldimethylsilyl)methyllithium was added a solution of 2-pyridyldimethylsilane (5.49 g, 40.0 mmol) in dry Et_2O (20 mL) at −78°C and stirred for 30 min. After stirring the reaction mixture at room temperature for 12 h, the reaction was quenched with a saturated aqueous solution of NH_4Cl. Extractive work-up and subsequent distillation afforded **2** (5.99 g, 52%) as colorless oil: bp 127°C/0.15 mmHg. ^{1}H NMR (300 MHz) δ 0.22 (s, 12H), 0.38 (s, 2H), 7.08 (ddd, *J*=7.5, 4.8, 1.5 Hz, 2H), 7.38 (ddd, *J*=7.5, 1.5, 1.2 Hz, 2H), 7.46 (td, *J*=7.5, 1.8 Hz, 2H), 8.68 (ddd, *J*=4.8, 1.8, 1.2 Hz, 2H); ^{13}C NMR (75 MHz) δ −1.2, 0.1, 122.5, 128.6, 133.8, 150.0, 168.7. IR (neat) 2955, 1576, 1559, 1451, 1418, 1248, 1051 cm^{-1}. Anal. Calcd for $C_{15}H_{22}N_2Si_2$: C, 62.88; H, 7.74; N, 9.78. Found: C, 62.61; H, 7.78; N, 9.79. HRMS *m/z* calcd for $C_{14}H_{19}N_2Si_2$ $(M-CH_3)^+$: 271.1087; found: 271.1079.

4.1.2. [Bis(2-pyridyldimethylsilyl)methyl]lithium (3). To a solution of **2** (14.5 mg, 0.05 mmol) in dry Et_2O (0.2 mL) and Et_2O-d_{10} (0.3 mL) was added dropwise a solution of *n*-BuLi (0.06 mmol, 1.56 M solution in hexane) at −78°C. The mixture was left for additional 30 min to afford an orange ether solution of [bis(2-pyridyldimethylsilyl)-methyl]lithium (**3**). ^{1}H NMR (500 MHz, Et_2O-d_{10}, −78°C) δ −1.39 (s, 1H), 0.20 (s, 6H), 0.21 (s, 6H), 7.26 (ddd, *J*=7.5, 5.0, 1.0 Hz, 2H), 7.60 (dd, *J*=7.5, 1.0 Hz, 2H), 7.68 (td, *J*=7.5, 1.0 Hz, 2H), 8.69 (dd, *J*=5.0, 1.0 Hz, 2H).

4.1.3. 4,4-Bis(2-pyridyldimethylsilyl)butene (4). To a solution of **2** (60 mg, 0.21 mmol) in dry Et_2O (1 mL) was added dropwise a solution of *n*-BuLi (0.23 mmol, 1.55 M in hexane) at −78°C. After stirring for an additional 1 h, allyl bromide (38 mg, 0.31 mmol) was added and stirred for 1 h at 0°C. After being stirred at room temperature for 17 h, the mixture was washed with H_2O (2×10 mL). The organic phase was additionally extracted with 1N aq HCl (3×10 mL). The aqueous phase was basified to pH 14 by adding NaOH pellet and was extracted with Et_2O (2×10 mL). Drying over $MgSO_4$ and removal of the solvents under reduced pressure afforded **3** (63 mg, 92%) as a pale yellow oil: ^{1}H NMR (300 MHz): δ 0.21 (s, 6H), 0.28 (s, 6H), 0.86 (t, *J*=6.0 Hz, 1H), 2.26–2.34 (m, 2H), 4.67 (ddt, *J*=9.9, 1.8, 1.5 Hz, 1H), 4.72 (ddt, *J*=16.8, 1.8, 1.5 Hz, 1H), 5.55 (ddt, *J*=16.8, 9.9, 6.9 Hz, 1H), 7.09 (ddd, *J*=7.5, 4.8, 1.5 Hz, 2H), 7.37 (ddd, *J*=7.5, 1.5, 1.2 Hz, 2H), 7.46 (td, *J*=7.5, 1.5 Hz, 2H), 8.69 (ddd, *J*=4.8, 1.5, 1.2 Hz, 2H); ^{13}C NMR (75 MHz): δ −2.6, −2.1, 10.9, 30.2, 113.8, 122.5, 129.2, 133.7, 140.7, 149.9, 168.3. HRMS *m/z* calcd for $C_{18}H_{26}N_2Si_2$: 326.1635; found: 326.1635.

4.2. General procedure for the synthesis of vinylsilanes (5)

To a solution of **2** (143 mg, 0.5 mmol) in dry Et_2O (1 mL) was added dropwise a solution of *n*-BuLi (0.55 mmol, 1.50 M in hexane) at −78°C. After being stirred for an additional 1 h, a carbonyl compound (0.75 mmol) was added and the mixture was stirred for 30 min at −78°C and 1 h at room temperature. The reaction was quenched with a saturated aqueous solution of NH_4Cl. Extractive work-up and subsequent silica gel chromatography (hexane/EtOAc=10/1 to 5/1 as eluent) afforded vinylsilanes **5**. Yields are given in Table 1.

4.2.1. (*E*)-2-Pyridyldimethyl(4-phenyl-1-butenyl)silane (5a). ^{1}H NMR (300 MHz) δ 0.38 (s, 6H), 2.43–2.53 (m, 2H), 2.70–2.79 (m, 2H), 5.86 (dt, *J*=18.6, 1.5 Hz, 1H), 6.24 (dt, *J*=18.6, 6.3 Hz, 1H), 7.14–7.22 (m, 4H), 7.24–7.31 (m, 2H), 7.44 (ddd, *J*=7.5, 1.5, 0.9 Hz, 1H), 7.56 (td, *J*=7.5, 1.8 Hz, 1H), 8.79 (ddd, *J*=4.8, 1.8, 0.9 Hz, 1H); ^{13}C NMR (75 MHz) δ −3.3, 34.9, 38.4, 122.8, 125.8, 127.3, 128.3, 128.5, 129.5, 134.0, 141.9, 148.9, 150.3, 167.5. HRMS *m/z* calcd for $C_{17}H_{21}NSi$: 267.1443; found: 267.1431.

4.2.2. (*E*)-2-Pyridyldimethyl(2-cyclohexylethenyl)silane (5b). ^{1}H NMR (300 MHz) δ 0.36 (s, 6H), 1.00–1.35 (m, 5H), 1.58–1.80 (m, 5H), 1.94–2.08 (m, 1H), 5.75 (dd, *J*=18.9, 1.2 Hz, 1H), 6.13 (dd, *J*=18.9, 5.7 Hz, 1H), 7.16 (ddd, *J*=7.5, 4.8, 1.8 Hz, 1H), 7.50 (ddd, *J*=7.5, 1.8, 1.2 Hz, 1H), 7.55 (td, *J*=7.5, 1.8 Hz, 1H), 8.77 (ddd, *J*=4.8, 1.8, 1.2 Hz, 1H); ^{13}C NMR (75 MHz) δ −3.3, 25.9, 26.1, 32.2, 43.9, 122.7, 123.1, 129.4, 133.9, 150.3, 155.5, 167.9. IR (neat) 2924, 1612, 1574, 1449, 1418, 1244 cm^{-1}. HRMS *m/z* calcd for $C_{15}H_{23}NSi$: 245.1600; found: 245.1604.

4.2.3. (*E*)-2-Pyridyldimethyl(3,3-dimethylbut-1-enyl)-silane (5c). ^{1}H NMR (300 MHz) δ 0.38 (s, 6H), 1.01 (s, 9H), 5.71 (d, *J*=18.9 Hz, 1H), 6.18 (d, *J*=18.9 Hz, 1H), 7.18 (ddd, *J*=7.5, 4.8, 1.5 Hz, 1H), 7.48 (dt, *J*=7.5, 1.2 Hz, 1H), 7.57 (td, *J*=7.5, 1.8 Hz, 1H), 8.78 (dm, *J*=4.8 Hz, 1H); ^{13}C NMR (75 MHz) δ −3.2, 28.9, 35.2, 119.6, 122.7, 129.5, 134.1, 150.2, 160.3, 167.9. HRMS *m/z* calcd for $C_{13}H_{20}NSi$ $(M-H)^+$: 218.1365; found: 218.1368.

4.2.4. (*E*)-2-Pyridyldimethylstyrylsilane (5d). ^{1}H NMR (300 MHz) δ 0.50 (s, 6H), 6.65 (d, *J*=19.2 Hz, 1H), 7.02 (d, *J*=19.2 Hz, 1H), 7.21 (ddd, *J*=6.9, 4.8, 2.1 Hz, 1H), 7.26–7.36 (m, 3H), 7.44–7.49 (m, 2H), 7.54–7.62 (m, 2H), 8.81 (dt, *J*=5.1, 1.2 Hz, 1H); ^{13}C NMR (75 MHz) δ

−3.4, 122.9, 126.1, 126.6, 128.3, 128.6, 129.5, 134.1, 138.2, 145.9, 150.4, 167.0. IR (neat) 2959, 1605, 1574, 1495, 1449, 1418, 1246 cm^{-1}. HRMS *m/z* calcd for $C_{15}H_{17}NSi$: 239.1131; found: 239.1122.

4.2.5. (*E*)-2-Pyridyldimethyl(2-furan-2-ylethenyl)silane (5e). ^1H NMR (300 MHz) δ 0.47 (s, 6H), 6.30 (d, *J*=3.3 Hz, 1H), 6.37 (dd, *J*=3.3, 1.8 Hz, 1H), 6.48 (d, *J*=18.9 Hz, 1H), 6.79 (d, *J*=18.9 Hz, 1H), 7.19 (ddd, *J*=7.2, 4.8, 2.1 Hz, 1H), 7.36 (d, *J*=1.8 Hz, 1H), 7.51–7.62 (m, 2H), 8.79 (dm, *J*=4.8 Hz, 1H); ^{13}C NMR (75 MHz) δ −3.4, 108.7, 111.5, 122.9, 124.1, 129.6, 133.2, 134.1, 142.5, 150.4, 154.0, 166.8. IR (neat) 2959, 1617, 1576, 1545, 1478, 1417, 1248 cm^{-1}. HRMS *m/z* calcd for $C_{13}H_{15}NOSi$: 229.0923, found 229.0927.

4.2.6. (*E*)-2-Pyridyldimethyl[2-(2,4,6-trimethylphenyl)-ethenyl]silane (5f). ^1H NMR (300 MHz) δ 0.52 (s, 6H), 2.28 (s, 3H), 2.29 (s, 6H), 6.12 (d, *J*=19.8 Hz, 1H), 6.87 (s, 2H), 7.04 (d, *J*=19.8 Hz, 1H), 7.17–7.25 (m, 1H), 7.56–7.62 (m, 2H), 8.81 (dt, *J*=4.8, 1.2 Hz, 1H); ^{13}C NMR (75 MHz) δ −3.3, 20.6, 20.8, 122.8, 128.7, 129.5, 132.3, 134.0, 135.4, 136.2, 136.3, 144.9, 150.3, 167.3. HRMS *m/z* calcd for $C_{18}H_{23}NSi$: 281.1600, found 281.1591.

4.2.7. (*E*,*E*)-Bis{1,4-[2-(2-pyridyldimethylsilyl)ethenyl]}-benzene (5g). ^1H NMR (300 MHz) δ 0.49 (s, 12H), 6.64 (d, *J*=19.2 Hz, 2H), 6.99 (d, *J*=19.2 Hz, 2H), 7.17–7.24 (m, 2H), 7.43 (s, 4H), 7.52–7.63 (m, 4H), 8.80 (dm, *J*=5.1 Hz, 2H); ^{13}C NMR (75 MHz) δ −3.4, 122.9, 126.3, 126.8, 129.5, 134.1, 138.0, 145.4, 150.3, 166.9. IR (KBr) 1603, 1574, 1557, 1509, 1451, 1420, 1248 cm^{-1}. HRMS *m/z* calcd for $C_{24}H_{28}N_2Si_2$: 400.1791; found: 400.1793.

4.2.8. 2-Pyridyldimethyl(2-methylpropenyl)silane (5h). ^1H NMR (300 MHz) δ 0.40 (s, 6H), 1.72 (s, 3H), 1.88 (d, *J*=1.5 Hz, 3H), 5.41 (br, 1H), 7.17 (ddd, *J*=7.5, 4.8, 1.8 Hz, 1H), 7.50–7.60 (m, 2H), 8.78 (dm, *J*=4.8 Hz, 1H); ^{13}C NMR (75 MHz) δ −1.8, 23.6, 29.4, 121.1, 122.6, 129.3, 134.0, 150.3, 154.6, 168.3. HRMS *m/z* calcd for $C_{11}H_{17}NSi$: 191.1130; found: 191.1139.

4.2.9. (*E*)-2-Pyridyldimethyl(2-phenylpropenyl)silane (5i). ^1H NMR (300 MHz) δ 0.52 (s, 6H), 2.17 (d, *J*=0.6 Hz, 3H), 6.12 (d, *J*=0.6 Hz, 1H), 7.19–7.24 (m, 1H), 7.28–7.35 (m, 3H), 7.50 (dt, *J*=6.9, 1.8 Hz, 2H), 7.59 (dt, *J*=4.5, 1.2 Hz, 2H), 8.81 (dt, *J*=4.8, 1.5 Hz, 1H); ^{13}C NMR (75 MHz) δ −1.8, 21.4, 122.8, 124.0, 125.6, 127.7, 128.2, 129.5, 134.2, 144.0, 150.3, 154.0, 167.7. IR (neat) 3061, 2959, 1597, 1574, 1493, 1445, 1418, 1246, 1138 cm^{-1}. HRMS *m/z* calcd for $C_{16}H_{19}NSi$: 253.1287; found: 253.1284.

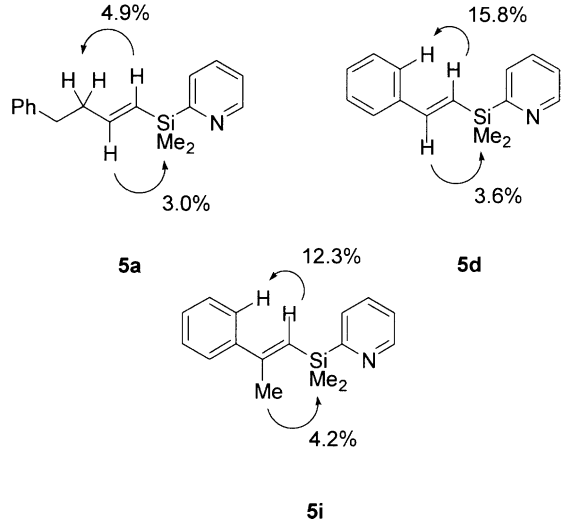
4.2.10. 2-Pyridyldimethyl(2,2-diphenylethenyl)silane (5j). ^1H NMR (300 MHz) δ 0.16 (s, 6H), 6.55 (s, 1H), 7.10–7.19 (m, 3H), 7.22–7.36 (m, 8H), 7.37–7.45 (m, 1H), 7.53 (td, *J*=7.5, 1.8 Hz, 1H), 8.78 (dm, *J*=5.1 Hz, 1H); ^{13}C NMR (125 MHz) δ −2.0, 122.5, 126.34, 126.35, 127.3, 127.4, 127.8, 128.0, 129.3, 129.6, 133.9, 142.3, 142.9, 150.0, 158.8, 167.8. IR (neat) 3058, 2957, 1574, 1489, 1443, 1418, 1246 cm^{-1}. HRMS *m/z* calcd for $C_{21}H_{21}NSi$: 315.1443; found: 315.1444.

4.2.11. (*E*,*E*)-2-Pyridyldimethyl(buta-1,3-dienyl)silane (5k). ^1H NMR (300 MHz) δ 0.42 (s, 6H), 5.15 (ddd, *J*=9.9, 1.5, 0.6 Hz, 1H), 5.25 (ddd, *J*=16.8, 1.5, 0.6 Hz, 1H), 6.05 (dd, *J*=18.3, 0.9 Hz, 1H), 6.39 (dtd, *J*=16.8, 9.9, 0.9 Hz, 1H), 6.64 (ddt, *J*=18.3, 9.9, 0.6 Hz, 1H), 7.18 (ddd, *J*=7.5, 4.8, 1.8 Hz, 1H), 7.50 (ddd, *J*=7.5, 1.8, 1.2 Hz, 1H), 7.57 (td, *J*=7.5, 1.8 Hz, 1H), 8.78 (ddd, *J*=4.8, 1.8, 1.2 Hz, 1H); ^{13}C NMR (75 MHz) δ −3.5, 118.6, 122.9, 129.5, 131.2, 134.1, 139.7, 146.8, 150.4, 167.0. IR (neat) 2959, 1574, 1256 cm^{-1}. Anal. Calcd for $C_{11}H_{15}NSi$: C, 69.78; H, 7.99; N, 7.40. Found: C, 69.69; H, 8.17; N, 7.37. HRMS *m/z* calcd for $C_{11}H_{15}NSi$: 189.0974, found 189.0977.

4.2.12. (*E*,*E*)-2-Pyridyldimethyl(3-methylbuta-1,3-dienyl)-silane (5l). ^1H NMR (300 MHz) δ 0.43 (s, 6H), 1.86 (s, 3H), 5.04 (d, *J*=1.5 Hz, 1H), 5.09 (d, *J*=1.5 Hz, 1H), 6.00 (d, *J*=18.9 Hz, 1H), 6.74 (d, *J*=18.9 Hz, 1H), 7.19 (ddd, *J*=7.5, 4.8, 1.8 Hz, 1H), 7.51 (ddd, *J*=7.5, 1.8, 1.2 Hz, 1H), 7.58 (td, *J*=7.5, 1.8 Hz, 1H), 8.79 (ddd, *J*=4.8, 1.8, 1.2 Hz, 1H); ^{13}C NMR (75 MHz) δ −3.4, 17.8, 118.0, 122.8, 125.9, 129.5, 134.0, 143.5, 148.8, 150.3, 167.2. IR (neat) 2988, 1576, 1246 cm^{-1}. HRMS *m/z* calcd for $C_{12}H_{17}NSi$: 203.1130; found: 203.1121.

4.2.13. (*E*,*E*)-2-Pyridyldimethyl(4-phenylbuta-1,3-dienyl)-silane (5m). ^1H NMR (300 MHz) δ 0.46 (s, 6H), 6.16 (dm, *J*=17.1 Hz, 1H), 6.60 (dt, *J*=14.7, 6.0 Hz, 1H), 6.76–6.89 (m, 2H), 7.19–7.26 (m, 2H), 7.29–7.34 (m, 2H), 7.38–7.42 (m, 2H), 7.54 (ddd, *J*=7.5, 1.5, 1.2 Hz, 1H), 7.60 (td, *J*=7.5, 1.5 Hz, 1H), 8.80 (ddd, *J*=5.4, 1.8, 1.2 Hz, 1H); ^{13}C NMR (75 MHz) δ −3.3, 122.7, 126.5, 127.7, 128.5, 129.3, 131.0, 131.3, 133.6, 133.9, 136.9, 146.1, 150.1, 166.7. IR (neat) 2956, 1576, 1246, 1001 cm^{-1}. HRMS *m/z* calcd for $C_{17}H_{19}NSi$: 265.1287; found: 265.1291.

The *E* stereochemistry of **5** was assigned based on the NOE experiments and the coupling constants between the two vinylic protons (17.1–19.8 Hz) in ^1H NMR. The selected NOE data are as follows:



4.2.14. 2-Pyridyldimethyl[(phenyldimethylsilyl)methyl]-silane (6). To a solution of 2-pyridyltrimethylsilane **1** (3.03 g, 20 mmol) in dry Et_2O (20 mL) was added dropwise a solution of *tert*-butyllithium (20 mmol, 1.31 M solution in pentane) at −78°C. The mixture was stirred for additional

30 min. To the resultant solution of (2-pyridyldimethylsilyl)methyllithium was added chlorodimethylphenylsilane (3.76 g, 22 mmol) at −78°C and the mixture was stirred for 1 h. After stirring for 3 h at room temperature, the reaction was quenched with H_2O (20 mL). Extractive work-up and subsequent silica gel chromatography (hexane/EtOAc=10/1 as eluent) afforded **6** (5.64 g, 99%) as colorless oil: ^{1}H NMR (300 MHz) δ 0.23 (s, 6H), 0.27 (s, 6H), 0.35 (s, 2H), 7.16 (ddd, J=7.5, 4.8, 1.5 Hz, 1H), 7.29–7.33 (m, 3H), 7.42–7.49 (m, 3H), 7.54 (td, J=7.5, 1.8 Hz, 1H), 8.76 (ddd, J=4.8, 1.8, 1.2 Hz, 1H); ^{13}C NMR (75 MHz) δ −1.1, −0.5, 1.1, 122.6, 127.7, 128.68, 128.71, 133.4, 134.0, 140.9, 150.1, 168.9. IR (neat) 3067, 2955, 1576, 1559, 1428, 1248, 1113 cm^{-1}. HRMS m/z calcd for $C_{16}H_{23}NSi_2$: 285.1369; found: 285.1358.

4.2.15. 1-Phenyl-2-(dimethylphenylsilyl)ethylene (7). To a solution of **6** (294 mg, 1.03 mmol) in dry Et_2O (1 mL) was added dropwise a solution of *t*-BuLi (1.10 mmol, 1.31 M in pentane) at −78°C and the mixture was stirred for 30 min. To the resultant solution of carbanion was added benzaldehyde (127 mg, 1.20 mmol) at −78°C and the mixture was stirred for 30 min. After stirring overnight at room temperature, the reaction was quenched with H_2O (5 mL). Extractive work-up and subsequent silica gel chromatography (hexane as eluent) afforded **7** (234 mg, 95%) as a mixture of stereoisomers (E/Z=1/1). These isomers were separated by gel permeation chromatography. ***E*-isomer**:[21] ^{1}H NMR (300 MHz) δ 0.46 (s, 6H), 6.61 (d, J=18.9 Hz, 1H), 6.97 (d, J=18.9 Hz, 1H), 7.27–7.40 (m, 6H), 7.47 (d, J=6.9 Hz, 2H), 7.58–7.62 (m, 2H); ^{13}C NMR (75 MHz) δ −2.7, 126.6, 127.1, 127.9, 128.2, 128.6, 129.1, 134.0, 138.2, 138.6, 145.4; IR (neat) 3067, 3022, 2957, 1605, 1574, 1495, 1248, 1113, 990 cm^{-1}. ***Z*-isomer**:[21] ^{1}H NMR (300 MHz) δ 0.26 (d, J=0.6 Hz, 6H), 6.01 (d, J=15.0 Hz, 1H), 7.22 (s, 5H), 7.32–7.36 (m, 3H), 7.50 (d, J=15.0 Hz, 1H), 7.52–7.57 (m, 2H); ^{13}C NMR (75 MHz) δ −1.1, 127.4, 127.8 (two peaks as judged by integration), 128.2, 128.8, 130.2, 133.7, 139.58, 139.61, 148.1; IR (neat) 2961, 1592, 1570, 1493, 1428, 1248, 1111 cm^{-1}.

4.3. Acylation of pyridyl-substituted vinylsilane

To a mixture of CH_3COCl (79 mg, 1.0 mmol) and $AlCl_3$ (133 mg, 1.0 mmol) in CH_2Cl_2 (2 mL) was added slowly a solution of **5d** (72 mg, 0.3 mmol) in CH_2Cl_2 (1 mL). After stirring the mixture for 2 h at room temperature, the reaction mixture was washed with saturated aqueous $NaHCO_3$ solution and brine. Drying over $MgSO_4$ and subsequent silica gel chromatography (hexane/EtOAc=10/1 as eluent) afforded (*E*)-4-phenyl-3-buten-2-one (40 mg, 91%) as pale yellow oil.

4.4. Bromination of pyridyl-substituted vinylsilane

To a solution of **5d** (120 mg, 0.5 mmol) in CH_2Cl_2 (1 mL) was added a solution of Br_2 (101 mg, 0.63 mmol) in CH_2Cl_2 (1 mL) at −78°C and the mixture was stirred for 5 min. To the resulting mixture were added MeOH (10 mL) and $Na_2S_2O_3$ (250 mg) and the mixture was stirred for additional 5 min. The reaction mixture was then poured into 15% aqueous $Na_2S_2O_3$ solution. After extractive work-up, the combined organic layer was dried over $MgSO_4$ and the solvents were removed under reduced pressure to give the crude 1,2-dibromide. The crude 1,2-dibromide was dissolved in ice-cold MeOH (5 mL) and treated with NaOMe (41 mg, 0.75 mmol) in MeOH (0.75 mL) at 0°C. The resulting mixture was stirred at 0°C for 1 h and then at room temperature for 12 h. Extractive work-up and subsequent silica gel chromatography (hexane as eluent) afforded β-bromostyrene (40 mg, 54%, E/Z=67/33) as colorless oil.

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