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Preparation of α-silyl- or α,α-bis(silyl)-substituted alkylcopper reagents and their synthetic use

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Abstract—Treatment of chlorobis(methyldiphenylsilyl)methyllithium with various alkyl and aryl Grignard reagents and CuCN·2LiCl afforded 1,1-disilylalkylcopper species. The aerobic oxidation of the resulting copper reagents provided a variety of acylsilanes in good yields. Meanwhile, treatment of dichloro(methyldiphenylsilyl)methyllithum with $Bu_2CuLi·LiCN$ provided 1-cyano-1-silylalkylcopper species via consecutive double 1,2-migration of alkyl and cyano groups.

1. Introduction

Organocuprates and organocoppers are highly important tools for organic synthesis, and numerous reports have been published on the preparative methods and reactions.[1] There are several types of copper reagents, such as the classical Gilman cuprates, cyanocuprates, hetero-cuprates, alkylcopper borontrifluoride complexes, and so on.[2] Most of them are prepared according to two approaches: (1) transmetalation from organolithium or magnesium compounds with copper salts and (2) direct metalation of organic halides with active copper.

1,2-Migration of an alkyl group on the metal center in metal carbenoid reagents is a typical reaction of an organometallic complex.[3] This process has been successfully utilized in alkylation of α-haloalkylmetals (metal=Zn, B, Al, Cu, Mn, etc.) and allows facile introduction of an alkyl group to the organometallic reagents.[4] The method would provide us with a facile route to a wide variety of metal reagents from relatively simple and easily accessible organometallics.

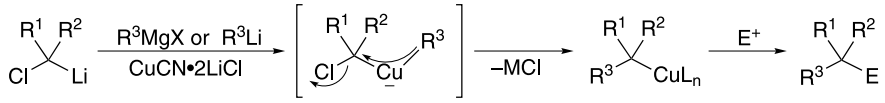
In this context, we have chosen the combination of lithium carbenoid, copper cyanide, and Grignard reagents/organolithium compounds (Scheme 1).

Here we wish to report the 1,2-migration reaction of the alkyl group from copper to the adjacent carbon bearing a chlorine atom in copper carbenoid reagents.[5] We also describe the reaction protocol in which organocuprates enable sequential introduction of two different groups into α,α-dichlorosilylmethyllithium.[6]

2. Results and discussion

2.1. Preparation of 1,1-disilylalkylcoppers and their conversion into various acylsilanes via aerobic oxidation

An addition of *n*-BuLi to a THF solution of $(Ph_2MeSi)_2CCl_2$ (**1**)[7] at −78 °C provided chlorodisilylmethyllithium **2** quantitatively via chlorine–lithium exchange in 10 min. Then, lithium carbenoid **2** was then treated with *n*-BuMgBr



Scheme 1.

Keywords: Carbenoids; 1,2-Migration; Organocopper reagents; Halogen–lithium exchange; Grignard reagents.
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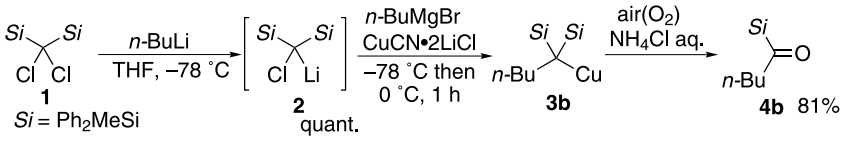


Scheme 2.

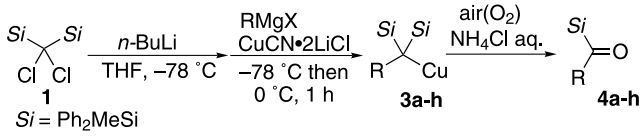
(1.2 equiv in THF) and CuCN·2LiCl (1.2 equiv in THF), and the mixture was stirred at 0 °C. After 1 h stirring in the presence of a copper salt, the requisite organocopper species **3b** was generated via a 1,2-alkyl migration (Scheme 2).[8] Hexane (5 mL) and NH_4Cl aq (10 mL) were added, and the mixture was exposed to air with stirring for 0.5 h. During this period, the aqueous layer turned blue, indicating that copper(I) was oxidized to copper(II). Extractive workup followed by purification afforded acylsilane **4b** in 81% yield.

Oxidation of the α,α-disilylalkylcopper species **3a–h** with air provided the corresponding acylsilanes in good yields (Table 1). Several features of this reaction are noteworthy. Various primary and secondary Grignard reagents can be employed in the reaction. Interestingly, the reaction with crotylmagnesium chloride yielded 3-pentenoylsilane **4h** without contamination of 2-methyl-3-butenoylsilane (entry 8). Unfortunately, these intermediary copper species did not react with electrophiles such as either alkyl halides or acyl chlorides. Aerobic oxidation of organocoppers often results in the Ullmann coupling reaction.[9] In these cases, however, the Ullmann-type coupling products were not observed at all: no dimerization reaction of the disilylalkyl group nor coupling between the disilylalkyl group and the cyano group proceeded. We presume that the reasons for the selective formation of acylsilanes would be the bulkiness of the disilylalkyl moiety and the absence of a cyano ligand on the copper(I) center in copper species **3**.

Furthermore, we found that various aromatic Grignard reagents can be employed favorably in this reaction protocol (Table 2). Unfortunately, disilylphenylmethylcopper under the standard conditions caused considerable hydrolysis due to the increased reactivity of the benzylic copper (entry 1).[10] In this case, however, oxidation of the intermediary copper species in the presence of 4 equiv of pyridine to yield benzoylsilane **6a** in 84% yield. Additionally, several features deserve to be pointed out. As shown in entries 2 and 3, *p*-FC_6H_4MgBr and C_6F_5MgBr, which are electron-deficient and less nucleophilic arylmagnesiums, can be efficiently employed. Interestingly, 2-thienyllithium which usually acts as a non-transferable or dummy ligand[1,11] in mixed homocuprates or mixed higher order cyanocuprates, provided none of acylsilanes. However, an addition of magnesium bromide to 2-thienyllithium resulted in the formation of the corresponding acylsilane **6d** in good yields (Table 2, entries 4 and 5). Furthermore, this reaction procedure can be applied to the synthesis of various aroylsilanes in entries 6–10. It enables to introduce silyl carbonyl groups into large π-conjugated system such as tolan, naphthalene, and phenanthrene.

Further application of (silyldichloromethyl)disilane **8** to the procedure described above worked well to yield benzoyldisilane **10** selectively in 51% yield (Scheme 3). Curiously, the diphenylmethylsilyl group was cleaved selectively and benzoylsilane **6a** was not obtained at all.

Table 1. Preparation of 1,1-disilylalkylcoppers and their aerobic oxidation



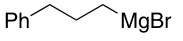
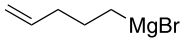
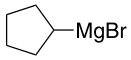
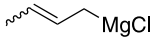
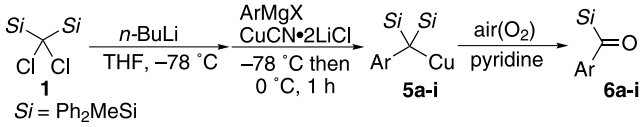
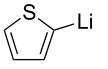
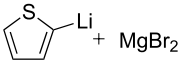
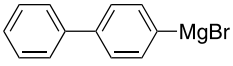
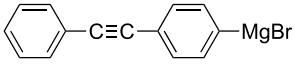
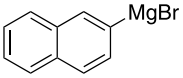
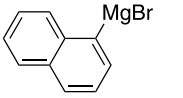
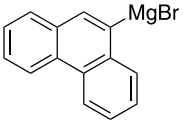
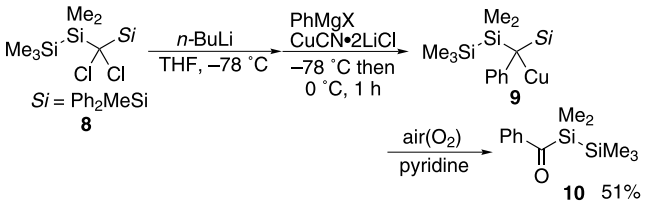
Entry	RMgX	**4** Yield/%
1	EtMgBr	**4a** 75
2	*n*-BuMgBr	**4b** 81
3		**4c** 75
4		**4d** 65
5	*i*-PrMgBr	**4e** 88
6		**4f** 84
7	MeMgBr	**4g** 47
8		**4h** 47

Table 2. Synthesis of aroylsilanes via aerobic oxidation



Entry	ArMgX	**6** Yield/%
1	PhMgBr	**6a** 84
2	*p*-FC_6H_4MgBr	**6b** 72
3	C_6F_5MgBr	**6c** 76
4		—[a]
5		**6d** 75
6		**6e** 80
7		**6f** 85
8		**6g** 82
9		**6h** 41
10		**6i** 73

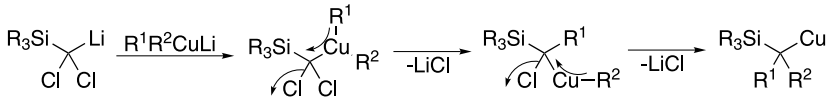
[a] Disilylacetonitrile **7** instead of silyl(2-thienyl)ketone **6d** was obtained in 81% yield.



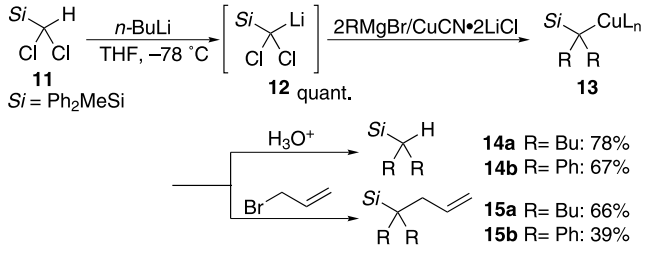
Scheme 3.

of the intermediary coppers **13** with allyl bromide proceeded successfully to furnish the allylated compounds **15a** and **15b**.

Next, we attempted double butylation of **11** by utilizing $Bu_2CuLi\cdot LiCN$ which is widely known as a cyano-Gilman cuprate. Contrary to our expectations, it turned out to provide butylation–cyanation product **16a** in good yield



Scheme 4.



Scheme 5.

2.2. Consecutive double alkylation of α,α-dichlorosilylmethyllithium by organocopper reagents

We next contemplated introduction of two different alkyl groups into dihalo carbenoids via double 1,2-migration (Scheme 4).

An addition of *n*-BuLi to a solution of dichloromethylsilane **11**[12] in THF at −78 °C resulted in the quantitative deprotonation to yield silyldichloromethyllithium **12**. Then, this dihalo-lithium carbenoid was added to organocopper reagents derived from copper cyanide. As expected from Scheme 1, the use of the copper reagent prepared by premixing butylmagnesium bromide with CuCN in a 2:1 ratio at 0 °C yielded the dibutylated product **14a** via the consecutive migration in good yield after aqueous workup (Scheme 5).[13] The use of phenylmagnesium bromide instead of BuMgBr also afforded the diphenylated product **14b** in 67% yield. The addition of allyl bromide before quenching resulted in trapping of the intermediary copper species to provide **15a** and **15b**. The nucleophilic trapping

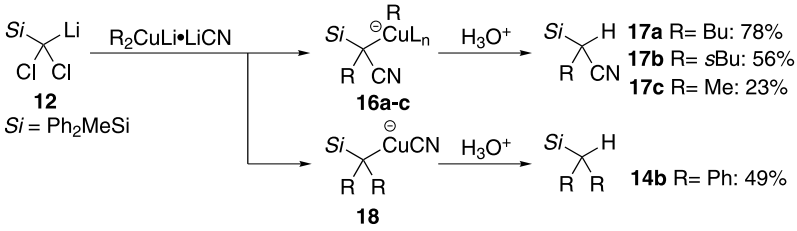
without the formation of dibutylated silane **14a** (Scheme 6). The reaction with $sBu_2CuLi\cdot LiCN$ and $Me_2CuLi\cdot LiCN$ also furnished α-cyano silanes **17b** in 56% yield and **17c** in 23% yield, respectively. Furthermore, in the case of $Ph_2CuLi\cdot LiCN$, the reaction fashion was reversed to obtain the diphenylated product **14b** in a moderate yield.

The intermediary copper species **16a** reacted with a variety of electrophiles such as allyl bromide, methyl iodide, acyl chlorides, and aldehydes.[14] Table 3 summarizes the trapping experiment of the α-cyanoalkylcopper species. The reaction with aldehydes provided α,β-unsaturated nitriles **19e** and **19f/19f′** via the Peterson elimination of the initial adducts.[15] In entry 7, aerobic oxidation of this copper reagent in the presence of pyridine afforded pentanoyl cyanide (**19g**) in a moderate yield.

In addition to alkylation–cyanation, consecutive butylation–phenylation was accomplished by sequential treatment of dichloromethyllithium **12** with BuCu and PhMgBr. The employment of BuCu derived from BuLi and copper iodide worked nicely to provide the desired butylation–phenylation product **21**. The resulting copper compound **20** can be coupled with allyl bromide and acetyl chloride to give the corresponding adducts in moderate yields. The use of a combination of BuLi and CuCN for butylation of **12** resulted in a formation of significant amount of the alkylation–cyanation product (Scheme 7).

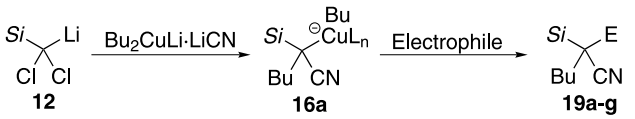
3. Conclusion

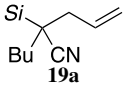
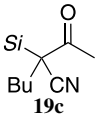
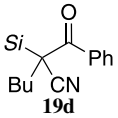
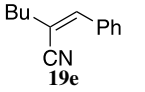
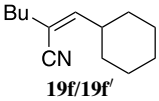
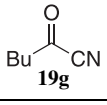
We have developed an easy and simple procedure which enables us to synthesize various kinds of acylsilanes from dichlorodisilylmethane and the corresponding Grignard



Scheme 6.

Table 3. Consecutive butylation–cyanation followed by C–C bond formation



Entry	Electrophile	Product	Yield/%
1	CH_2=$CHCH_2Br$	 **19a**	71
2	MeI	 **19b**	70
3	CH_3COCl	 **19c**	54
4	PhCOCl	 **19d**	57
5	PhCHO[a]	 **19e**	75 ($Z/E \geq 99/1$)
6	$cC_6H_{11}CHO$[b]	 **19f/19f'**	57 (Z/E=54/45)
7	air(O_2)[c]	 **19g**	51

[a] Conditions: $Bu_2CuLi \cdot LiCN$ (1.1 equiv), electrophile (2.0 equiv) were employed.
[b] $Bu_2CuLi \cdot LiCN$ (1.1 equiv), RCHO (3.0 equiv), Me_3SiCl (4.5 equiv) were employed. Me_3SiCl was used as a Lewis acid.
[c] The resultant copper reagent was exposed to air in the presence of 2 equiv pyridine at 0 °C for 30 min.

reagents. Treatment of chlorodisilylmethyllithium with various Grignard reagents and CuCN·2LiCl efficiently affords 1,1-disilylalkylcopper species. The aerobic oxidation of the resulting organocoppers provides a variety of acylsilanes in good yields. In a second part, we have also demonstrated a very different reactivity between two types of cyanocuprates prepared from CuCN and either Grignard reagents or lithium reagents. Treatment of silyldichloromethyllithium with the copper species prepared from BuMgBr and CuCN (2BuMgBr/CuCN) provides dibutylation products. On the other hand, $Bu_2CuLi \cdot LiCN$ (cyano-Gilman cuprate) yields butylation–cyanation products.

4. Experimental

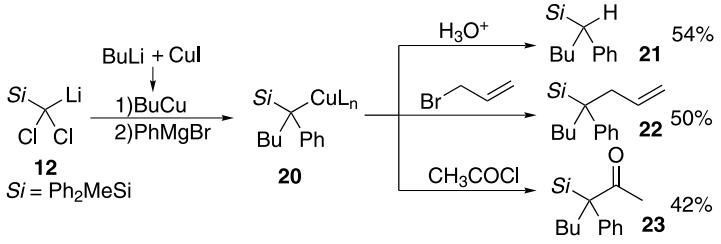
4.1. General information

Melting points were obtained a Yanako MP-50929 melting point apparatus and are uncorrected. ^{1}H NMR (300 MHz), ^{13}C NMR (75.3 MHz) and ^{19}F NMR (282.5 MHz) spectra were taken on a Varian GEMINI 300 spectrometer in $CDCl_3$ as a solvent, and chemical shifts were given in δ value with tetramethylsilane as an internal standard. IR spectra were determined on a SHIMADZU FTIR-8200PC spectrometer. Mass spectra were determined on a JEOL JMS-700 spectrometer. TLC analyses were performed on commercial glass plates bearing 0.25 mm layer of Merk Silica gel $60F_{254}$. Column chromatography was done with silica gel (Wakogel 200 mesh). The analyses were carried out at the Elemental Analysis Center of Kyoto University. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl before use. Grignard reagents were prepared from the corresponding alkyl halide and Mg turning (Nacalai tesque, INC). Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

4.1.1. Preparation of dichlorobis(methyldiphenylsilyl)-methane (1). *n*-BuLi (21 mL, 1.6 M solution in hexane, 33 mmol) was added to a solution of diisopropylamine (4.9 mL, 35 mmol) in THF (20 mL) dropwise at 0 °C, and the mixture was stirred for 0.5 h. To a pre-cooled solution of dichloromethane (0.96 mL, 15 mmol) and (chloro)methyldiphenylsilane (6.3 mL, 30 mmol) in THF (30 mL) was added the resultant solution dropwise at −78 °C via a cannula. After the mixture was stirred for 0.5 h, the cooling bath was removed. After stirring for 0.5 h at room temperature, the mixture was poured into 1 M HCl and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. Recrystallization of the residual white solid from hexane/ethyl acetate provided dichlorobis(methyldiphenylsilyl)methane (**1**, 6.1 g, 12.8 mmol) in 85% yield: Mp 138 °C; IR (nujol) 1427, 1254, 1107, 843, 802, 723, 696 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.22 (s, 6H), 7.34 (dd, J= 7.5, 8.1 Hz, 8H), 7.43 (t, J=7.5 Hz, 4H), 7.72 (d, J= 8.1 Hz, 8H); ^{13}C NMR ($CDCl_3$) δ −4.0, 71.4, 127.7, 130.1, 133.2, 136.3. Found: C, 67.91; H, 5.40%. Calcd for $C_{27}H_{26}Cl_2Si_2$: C, 67.90; H, 5.49%.

4.2. General procedure for the preparation of acylsilanes (4a) from dichlorodisilylmethane

Under argon atmosphere, to a solution of dichlorobis-(methyldiphenylsilyl)methane (**1**, 239 mg, 0.5 mmol) in



Scheme 7.

THF (3 mL) was added butyllithium (0.31 mL, 1.6 M solution in hexane, 0.5 mmol) dropwise at −78 °C and the solution was stirred for 5 min. Ethylmagnesium bromide (0.6 mL, 1.0 M solution in THF, 0.6 mmol) and CuCN·2LiCl (0.6 mL, 1.0 M solution in THF, 0.6 mmol) were added successively at −78 °C. After stirring for 1 h at 0 °C, saturated aqueous NH_4Cl (10 mL) and hexane (5 mL) were added. The mixture was stirred vigorously for 0.5 h under air at room temperature and then extracted with hexane. The organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification by silica gel column chromatography provided 1-(methyldiphenylsilyl)-1-propanone (**4b**, 95 mg, 0.37 mmol) in 75% yield as colorless oil. Spectral data for this compound were identical with those reported in the literature.[16]

4.2.1. 1-(Methyldiphenylsilyl)-1-pentanone (4b). R_f=0.58 (hexane/ethyl acetate=10/1); colorless oil; IR (neat) 3474, 2932, 1722, 1643, 1429, 1254, 1113, 793, 729, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.75 (s, 3H), 0.79 (t, J=7.5 Hz, 3H), 1.18 (tq, J=7.5, 7.5 Hz, 2H), 1.44 (tt, J=7.5, 7.5 Hz, 2H), 2.65 (t, J=7.5 Hz, 2H), 7.34–7.47 (m, 6H), 7.55–7.66 (m, 4H); ^{13}C NMR ($CDCl_3$) δ −5.4, 13.7, 22.2, 24.1, 46.4, 128.3, 130.2, 133.0, 135.1, 245.1. Found: C, 76.79; H, 7.86%. Calcd for $C_{18}H_{22}OSi$: C, 76.54; H, 7.85%.

4.2.2. 1-(Methyldiphenylsilyl)-4-phenyl-1-butanone (4c, known compound). Spectral data for this compound were identical with those reported in the literature.[17]

4.2.3. 1-(Methyldiphenylsilyl)-5-hexen-1-one (4d). R_f=0.45 (hexane/ethyl acetate=10/1); colorless oil; IR (neat) 3071, 2936, 1643, 1429, 1254, 1113, 997, 912, 793, 729, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.75 (s, 3H), 1.58 (tt, J=6.9, 7.2 Hz, 2H), 1.94 (dt, J=6.6, 6.9 Hz, 2H), 2.66 (t, J=7.2 Hz, 2H), 4.89 (d, J=11.1 Hz, 1H), 4.90 (d, J=16.2 Hz, 1H), 5.58–5.74 (m, 1H), 7.35–7.48 (m, 6H), 7.55–7.61 (m, 4H); ^{13}C NMR ($CDCl_3$) δ −5.3, 21.2, 33.0, 48.8, 115.0, 128.2, 130.1, 132.8, 135.0, 138.1, 244.4. Found: C, 77.43; H, 7.40%. Calcd for $C_{19}H_{22}OSi$: C, 77.50; H, 7.53%.

4.2.4. 2-Methyl-1-(methyldiphenylsilyl)-1-propanone (4e). R_f=0.58 (hexane/ethyl acetate=10/1); colorless oil; a paleIR (neat) 2968, 1639, 1429, 1254, 1113, 986, 793, 729, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.77 (s, 3H), 0.91 (d, J=6.9 Hz, 6H), 3.02 (sept, J=6.9 Hz, 1H), 7.34–7.47 (m, 6H), 7.56–7.62 (m, 4H); ^{13}C NMR ($CDCl_3$) δ −4.7, 16.5, 45.8, 128.1, 130.0, 133.2, 135.0, 247.1. Found: C, 76.16; H, 7.55%. Calcd for $C_{17}H_{20}OSi$: C, 76.07; H, 7.51%.

4.2.5. Cyclopentyl methyldiphenylsilyl ketone (4f). R_f=0.45 (hexane/ethyl acetate=10/1); colorless oil; IR (neat) 2957, 2866, 1638, 1429, 1254, 1111, 793, 729, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.77 (s, 3H), 1.40–1.53 (m, 6H), 1.60–1.77 (m, 2H), 3.24–3.36 (m, 1H), 7.30–7.47 (m, 6H), 7.56–7.62 (m, 4H); ^{13}C NMR ($CDCl_3$) δ −4.8, 26.0, 26.9, 56.9, 128.1, 129.9, 133.2, 135.0, 245.1. Found: C, 77.43; H, 7.53%. Calcd for $C_{19}H_{22}OSi$: C, 77.50; H, 7.53%.

4.2.6. Acetylmethyldiphenylsilane (4g, known compound). R_f=0.34 (hexane/ethyl acetate=10/1); colorless oil; IR (neat) 1643, 1429, 1340, 1254, 1113, 791, 731, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.75 (s, 3H), 2.32 (s, 3H), 7.36–7.48 (m, 6H), 7.59 (dd, J=1.5, 8.1 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ −5.6, 36.9, 128.3, 130.3, 132.7, 135.1, 243.9. Found: C, 74.71; H, 6.79%. Calcd for $C_{15}H_{16}OSi$: C, 74.95; H, 6.71%. Spectral data for this compound were identical with those reported in the literature.[18]

4.2.7. 1-(Methyldiphenylsilyl)-3-penten-1-one (*E*/*Z*=60/40) (4h). R_f=0.46 (hexane/ethyl acetate=10/1); colorless oil; IR (neat) 1645, 1429, 1254, 1113, 996, 793, 729, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.75 (s, 1.8H), 0.76 (s, 1.2H), 1.45 (d, J=6.6 Hz, 1.2H), 1.60 (d, J=4.8 Hz, 1.8H), 3.32 (dd, J=1.2, 5.4 Hz, 1.2H), 3.40 (d, J=6.9 Hz, 0.8H), 5.25–5.42 (m, 1.2H), 5.37–5.50 (m, 0.4H), 5.54–5.67 (m, 0.4H), 7.35–7.50 (m, 6H), 7.55–7.66 (m, 4H); ^{13}C NMR ($CDCl_3$) δ −5.2, −5.1, 13.1, 18.1, 48.0, 53.2, 120.7, 121.9, 128.1, 128.1, 128.2, 130.1, 130.1, 130.2, 132.6, 132.7, 135.0, 241.5, 242.1. HRMS (*m*/*z*) Found: 128.1270. Calcd for $C_{18}H_{20}OSi$: 280.1283.

4.2.8. Benzoylmethyldiphenylsilane (6a, known compound). Under argon atomosphere, to a solution of dichlorobis(methyldiphenylsilyl)methane (**1**, 239 mg, 0.5 mmol) in THF (3 mL) was added butyllithium (0.31 mL, 1.6 M solution in hexane, 0.5 mmol) dropwise at −78 °C and the solution was stirred for 5 min. Phenylmagnesium bromide (0.6 mL, 1.0 M solution in THF, 0.6 mmol) and CuCN·2LiCl (0.6 mL, 1.0 M solution in THF, 0.6 mmol) were added successively at −78 °C. After stirring for 1 h at 0 °C, pyridine (0.16 mL, 2.0 mmol) was added. The mixture was stirred for 1 h under air at 0 °C and then extracted with hexane. The organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification by silica gel column chromatography provided benzoylmethyldiphenylsilane (**6a**, 127 mg, 0.42 mmol) in 84% yield as clear, yellow oil. Spectral data for this compound were identical with those reported in the literature.[19] R_f=0.44 (hexane/ethyl acetate=10/1); IR (neat) 1612, 1589, 1576, 1447, 1429, 1252, 1209, 1173, 1111, 794, 729, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 (s, 3H), 7.31–7.50 (m, 9H), 7.60 (dd, J=1.5, 7.5 Hz, 4H), 7.77 (dd, J=1.5, 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ −3.3, 128.2, 128.2, 128.5, 130.0, 132.9, 133.7, 135.1, 141.7, 232.0. Found: C, 79.68; H, 6.06%. Calcd for $C_{20}H_{18}OSi$: C, 79.43; H, 6.00%.

4.2.9. 4-Fluorobenzoylmethyldiphenylsilane (6b). R_f=0.44 (hexane/ethyl acetate=10/1); pale yellow oil; IR (neat) 3071, 1614, 1583, 1500, 1429, 1406, 1225, 1151, 1113, 843, 729 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (s, 3H), 7.02 (t, J=9.0 Hz, 2H), 7.36–7.48 (m, 6H), 7.57–7.62 (m, 4H), 7.80 (dd, J=5.4, 9.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ −3.2, (115.4, 115.7), 128.2, 130.0, (130.6, 130.7), 133.4, 134.9, (138.1, 138.7), (163.5, 166.9), 229.5; ^{19}F NMR ($CDCl_3$) δ −105.3. Found: C, 75.11; H, 5.42%. Calcd for $C_{20}H_{17}FOSi$: C, 74.97; H, 5.35%.

4.2.10. 2,3,4,5,6-Pentafluorobenzoylmethyldiphenylsilane (6c). R_f=0.56 (hexane/ethyl acetate=10/1); yellow oil; IR (neat) 3074, 1649, 1518, 1489, 1429, 1306, 1117, 974, 731, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85 (s, 3H), 7.36–7.50 (m, 6H), 7.54–7.61 (m, 4H); ^{13}C NMR ($CDCl_3$) δ −5.5, 128.3, 130.6, 130.8, 135.0, 136.3, 138.2, 141.2, 141.6, 143.2, 143.7, 229.2; ^{19}F NMR ($CDCl_3$) δ −160.1,

−150.4, −142.9. Found: C, 61.21; H, 3.36%. Calcd for $C_{20}H_{13}F_5OSi$: C, 61.22; H, 3.34%.

4.2.11. Methyldiphenylsilyl 2-thienyl ketone (6d). R_f=0.53 (hexane/ethyl acetate=5/1); yellow oil; IR (KBr) 3068, 1570, 1512, 1428, 1406, 1230, 1113, 1051, 788, 731, 706 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (s, 3H), 6.97 (t, J=4.5 Hz, 1H), 7.34 (d, J=4.5 Hz, 1H), 7.38–7.48 (m, 6H), 7.59 (d, J=4.5 Hz, 1H), 7.61–7.65 (m, 4H); ^{13}C NMR ($CDCl_3$) δ −3.8, 128.2, 130.2, 133.2, 133.6, 134.6, 135.2, 151.2, 221.0. Found: C, 70.10; H, 5.33%. Calcd for $C_{18}H_{16}OSSi$: C, 70.09; H, 5.23%.

4.2.12. (4-Phenylbenzoyl)methyldiphenylsilane (6e). R_f=0.50 (hexane/ethyl acetate=5/1); yellow oil; IR (neat) 3069, 1593, 1556, 1429, 1217, 1177, 847, 486 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.91 (s, 3H), 7.34–7.49 (m, 6H), 7.55–7.61 (m, 4H), 7.62–7.67 (m, 4H), 7.86 (d, J=8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ −3.1, 127.0, 127.1, 128.0, 128.1, 128.6, 128.7, 129.9, 133.6, 135.0, 139.7, 140.2, 145.3, 230.8. Found: C, 82.56; H, 5.99%. Calcd for $C_{26}H_{22}OSi$: C, 82.50; H, 5.86%.

4.2.13. [4-(Phenylethynyl)benzoyl]diphenylsilane (6f). R_f=0.35 (hexane/ethyl acetate=10/1); yellow oil; IR (neat) 3071, 2957, 1589, 1427, 1209, 1111, 756, 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (s, 3H), 7.19–7.33 (m, 9H), 7.35–7.42 (m, 4H), 7.59–7.64 (m, 4H), 7.76 (d, J=8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ −3.3, 128.2, 128.2, 128.5, 130.0, 132.9, 133.7, 135.1, 141.7, 232.0. Found: C, 83.70; H, 5.41%. Calcd for $C_{28}H_{22}OSi$: C, 83.54; H, 5.51%.

4.2.14. 2-Naphthalene(methyldiphenylsilyl)methanone (6g). R_f=0.59 (hexane/ethyl acetate=5/1); yellow oil; IR (neat) 3069, 2959, 1595, 1429, 1252, 1177, 1113, 727, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.95 (s, 3H), 7.37–7.50 (m, 7H), 7.52–7.59 (m, 1H), 7.63–7.70 (m, 5H), 7.82 (d, J=8.1 Hz, 2H), 7.91 (dd, J=1.8, 8.1 Hz, 1H), 8.24 (s, 1H); ^{13}C NMR ($CDCl_3$) δ −3.1, 122.4, 126.4, 127.6, 128.1, 128.3, 128.4, 129.6, 129.9, 132.3, 132.3, 133.8, 135.0, 135.3, 139.1, 231.2. Found: C, 81.50; H, 5.96%. Calcd for $C_{20}H_{18}OSi$: C, 81.77; H, 5.72%.

4.2.15. 1-Naphthalene(methyldiphenylsilyl)methanone (6h). R_f=0.60 (hexane/ethyl acetate=5/1); yellow oil; IR (KBr) 3028, 1612, 1589, 1576, 1447, 1429, 1252, 1209, 1173, 1111, 794, 729, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (s, 3H), 7.30–7.46 (m, 7H), 7.48–7.59 (m, 2H), 7.62–7.66 (m, 4H), 7.75 (d, J=7.5 Hz, 1H), 7.85 (d, J=7.5 Hz, 1H), 7.91 (d, J=8.1 Hz, 1H), 8.70 (d, J=8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −3.1, 124.1, 125.7, 126.4, 128.1, 128.2, 128.2, 128.7, 129.9, 131.3, 132.5, 133.8, 135.0, 139.1, 236.8. Found: C, 81.63; H, 5.86%. Calcd for $C_{24}H_{20}OSi$: C, 81.77; H, 5.72%.

4.2.16. 9-Phenanthrene(methyldiphenylsilyl)methanone (6i). R_f=0.42 (hexane/ethyl acetate=5/1); yellow oil; IR (KBr) 3021, 1591, 1428, 1245, 1112, 892, 788, 722, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.94 (s, 3H), 7.37–7.49 (m, 6H), 7.52 (d, J=3.9 Hz, 2H), 7.58–7.62 (m, 1H), 7.63–7.66 (m, 1H), 7.67–7.71 (m, 4H), 7.71–7.74 (m, 1H), 8.00 (s, 1H), 8.63 (d, J=8.1 Hz, 1H), 8.68 (d, J=8.1 Hz, 1H), 8.75 (d, J=8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ −3.5, 122.6, 122.7, 126.7, 126.9, 127.2, 127.5, 127.7, 127.9, 128.3, 129.0, 130.1, 130.8, 131.8, 134.0, 134.6, 135.1, 138.2, 236.7. HRMS (m/z) Found: 402.1438. Calcd for $C_{28}H_{22}OSi$: 402.1440.

4.2.17. Bis(methyldiphenylsilyl)acetonitrile (7). R_f=0.35 (hexane/ethyl acetate=5/1); white solid; IR (neat) 2208, 1429, 1165, 1009, 816, 725, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.32 (s, 6H), 2.32 (s, 1H), 7.27–7.45 (m, 16H), 7.56–7.63 (m, 4H); ^{13}C NMR ($CDCl_3$) δ −3.9, 5.1, 71.8, 128.1, 128.2, 130.1, 130.2, 134.0, 134.7. Found: C, 77.81; H, 6.32; N, 3.17%. Calcd for $C_{28}H_{27}NSi_2$: C, 77.54; H, 6.28; N, 3.23%.

4.2.18. 1-[Dichloro-(methyldiphenylsilyl)methyl]-1,1,2,2,2-pentamethyldisilane (8). R_f=0.60 (hexane/ethyl acetate=30/1); colorless oil; IR (neat) 3072, 2953, 1429, 1400, 1248, 822 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.06 (s, 6H), 0.15 (s, 9H), 0.84 (s, 6H), 0.32 (s, 3H), 7.35–7.48 (m, 6H), 7.80–7.87 (m, 4H); ^{13}C NMR ($CDCl_3$) δ −3.2, −3.0, −0.7, 74.4, 127.7, 130.1, 133.5, 136.1. Found: C, 55.22; H, 6.93. Calcd for $C_{19}H_{28}Cl_2Si_3$: C, 55.44; H, 6.86%.

4.2.19. General procedure for the preparation of 1-benzoyl-1,1,2,2,2-pentamethyldisilane (10) from dichlorosilylmethyldisilane 8. Under argon atmosphere, to a solution of (dichlorosilylmethyl)disilane (**8**, 206 mg, 0.5 mmol) in THF (3 mL) was added butyllithium (0.31 mL, 1.6 M solution in hexane, 0.5 mmol) dropwise at −78 °C and the solution was stirred for 5 min. Phenylmagnesium bromide (0.6 mL, 1.0 M solution in THF, 0.6 mmol) and CuCN·2LiCl (0.6 mL, 1.0 M solution in THF, 0.6 mmol) were added successively at −78 °C. After stirring for 1 h at 0 °C, pyridine (0.16 mL, 2.0 mmol) was added. The mixture was stirred for 1 h under air at 0 °C and then extracted with hexane. The organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification by silica gel column chromatography provided 1-benzoyl-1,1,2,2,2-pentamethyldisilane (**10**, 61 mg, 0.27 mmol) in 51% yield. R_f=0.38 (hexane/ethyl acetate=20/1); IR (neat) 2955, 1614, 1591, 1576, 1447, 1429, 1113, 1055, 831, 799, 692 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.13 (s, 9H), 0.43 (s, 6H), 7.45–7.57 (m, 3H), 7.78 (dd, J=2.0, 13.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ −3.8, −1.8, 128.1, 132.5, 133.8, 141.9, 236.2.

4.2.20. General procedure for the preparation of 5-(methyldiphenylsilyl)nonane (14a). n-BuLi (0.31 mL, 1.6 M solution in hexane, 0.50 mmol) was added to a solution of $Ph_2MeSiCHCl_2$ (**11**, 141 mg, 0.50 mmol) in THF (5 mL) at −78 °C, and the mixture was stirred for 30 min. Then $nBu_2CuCN(MgBr)_2$ in THF, which was prepared from n-BuMgBr (1.25 mL, 1.0 M solution in THF, 1.25 mmol) and CuCN·2LiCl (0.55 mL, 1.0 M solution in THF, 0.55 mmol) at 0 °C, was added to the resulting solution at −78 °C. After stirring for 5 min, the mixture was allowed to warm gradually to 0 °C. After stirring the mixture for 1 h at 0 °C, the reaction was quenched with diluted aqueous HCl (20 mL). The mixture was extracted with hexane (10 mL×3), and the organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification by silica gel column chromatography provided 5-(methyldiphenylsilyl)nonane (**14a**, 127 mg, 0.39 mmol) in 78% yield as colorless oil: R_f=0.78

(hexane/ethyl acetate=10/1); IR (neat) 3069, 2856, 1952, 1880, 1817, 1466, 1252, 1111, 787, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.58 (s, 3H), 0.81 (t, J=7.2 Hz, 6H), 1.12–1.44 (m, 12H), 1.48–1.62 (m, 1H), 7.31–7.42 (m, 6H), 7.51–7.59 (m, 4H); ^{13}C NMR ($CDCl_3$) δ −5.06, 14.10, 23.02, 23.61, 29.65, 31.77, 127.54, 128.76, 134.63, 137.26. Found: C, 81.19; H, 9.71%. Calcd for $C_{22}H_{32}Si$: C, 81.41; H, 9.94%.

4.2.21. 4-Butyl-4-(methyldiphenylsilyl)-1-octene (15a). R_f=0.66 (hexane/ethyl acetate=10/1); colorless oil; IR (neat) 2957, 2858, 1636, 1427, 1254, 1105, 999, 910, 784, 737, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.66 (s, 3H), 0.78 (t, J=6.9 Hz, 6H), 1.06–1.24 (m, 8H), 1.44–1.60 (m, 4H), 3.32 (d, J=7.5 Hz, 2H), 4.88–4.98 (m, 2H), 5.75 (ddt, J=9.3, 16.5, 7.5 Hz, 1H), 7.30–7.38 (m, 6H), 7.60–7.66 (m, 4H); ^{13}C NMR ($CDCl_3$) δ −3.21, 13.83, 23.56, 26.64, 29.14, 35.75, 40.74, 116.69, 127.59, 128.78, 135.53, 136.21, 137.63. Found: C, 82.13; H, 9.72%. Calcd for $C_{25}H_{36}Si$: C, 82.35; H, 9.95%. HRMS (*m/z*) Found: 364.2571. Calcd for $C_{25}H_{36}Si$: 364.2586.

4.2.22. (Methyldiphenylsilyl)diphenylmethane (14b). R_f=0.59 (hexane/ethyl acetate=10/1); colorless oil; IR (neat) 3024, 1958, 1886, 1821, 1597, 1493, 1427, 1254, 1111, 999, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.53 (s, 3H), 4.14 (s, 1H), 7.0–7.21 (m, 10H), 7.24–7.40 (m, 10H); ^{13}C NMR ($CDCl_3$) δ −3.58, 44.31, 125.23, 127.51, 128.06, 129.18, 129.26, 135.21, 135.62, 141.78. Found: C, 85.39; H, 6.77%. Calcd for $C_{26}H_{24}Si$: C, 85.66; H, 6.64%.

4.2.23. 1-(Methyldiphenylsilyl)-1,1-diphenyl-3-butene (15b). R_f=0.67 (hexane/ethyl acetate=10/1); colorless oil; IR (neat) 3053, 2957, 1599, 1493, 1427, 1254, 1105, 912, 791, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.46 (s, 3H), 3.24 (d, J=6.6 Hz, 2H), 4.89 (dd, J=2.1, 10.5 Hz, 1H), 4.95 (dd, J=2.1, 17.1 Hz, 1H), 5.58 (ddt, J=10.5, 17.1, 6.6 Hz, 1H), 7.11–7.23 (m, 10H), 7.23–7.28 (m, 4H), 7.28–7.41 (m, 6H); ^{13}C NMR ($CDCl_3$) δ −3.12, 40.63, 45.66, 117.11, 125.22, 127.39, 127.45, 127.51, 128.05, 128.98, 129.17, 129.25, 129.93, 134.87, 135.20, 135.85, 135.94, 141.77, 143.42. HRMS (*m/z*) Found: 404.1954. Calcd for $C_{29}H_{28}Si$: 404.1960.

4.2.24. General procedure for the preparation of 2-(methyldiphenylsilyl)hexanenitrile (17a). *n*-BuLi (0.31 mL, 1.6 M solution in hexane, 0.50 mmol) was added to a solution of $Ph_2MeSiCHCl_2$ (**8**, 141 mg, 0.50 mmol) in THF (5 mL) dropwise at −78 °C, and the mixture was stirred for 30 min. Then $nBu_2CuLi\cdot LiCN$ in THF, which was prepared from *n*-BuLi (0.78 mL, 1.6 M solution in THF, 1.25 mmol) and $CuCN\cdot 2LiCl$ (0.55 mL, 1.0 M solution in THF, 0.55 mmol) at 0 °C, was added to the resulting solution at −78 °C. After stirring for 5 min, the mixture was allowed to warm gradually to 0 °C. And after stirring the mixture for 1 h at 0 °C, the reaction was quenched with dilute aqueous HCl (20 mL). The mixture was extracted with ethyl acetate (10 mL ×3), and the organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification by silica gel column chromatography provided 2-(methyldiphenylsilyl)hexanenitrile (**17a**, 116 mg, 0.39 mmol) in 79% yield as colorless oil: R_f=0.38 (hexane/ethyl acetate=10/1); IR (neat) 3072, 2932, 2860, 2222, 1429, 1258, 1115, 793, 729, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.76 (s, 3H), 0.85 (t, J=7.2 Hz, 3H), 1.12–1.72 (m, 6H), 2.30 (dd, J=4.2, 10.8 Hz, 1H), 7.38–7.51 (m, 6H), 7.56–7.66 (m, 4H); ^{13}C NMR ($CDCl_3$) δ −5.46, 13.90, 17.84, 22.01, 26.87, 32.01, 121.88, 128.06, 128.10, 130.16, 132.21, 132.50, 134.55. Found: C, 77.78; H, 7.80%. Calcd for $C_{19}H_{23}NSi$: C, 77.76; H, 7.90%.

4.2.25. 2-(Methyldiphenylsilyl)-3-methylpentanenitrile (17b). R_f=0.37 (hexane/ethyl acetate=10/1); colorless oil; IR (neat) 2964, 2220, 1429, 1115, 793, 732, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.77 (t, J=7.4 Hz, 3H), 0.80 (s, 3H), 0.81 (s, 3H), 0.86 (t, J=7.4 Hz, 3H), 0.93 (d, J=6.6 Hz, 3H), 1.02 (d, J=6.6 Hz, 3H), 1.20–1.77 (m, 6H), 2.38 (d, J=4.5 Hz, 1H), 2.53 (d, J=3.0 Hz, 1H), 7.36–7.51 (m, 12H), 7.56–7.62 (m,4H), 7.63–7.69 (m, 4H); ^{13}C NMR ($CDCl_3$) δ −4.41, −4.11, 11.70, 11.76, 18.12, 20.31, 23.60, 26.03, 27.78, 30.88, 33.21, 33.36, 120.33, 120.79, 128.07, 128.11, 128.14, 130.07, 130.12, 130.15, 132.65, 132.84, 133.39, 133.52, 134.50, 134.55. Found: C, 77.87; H, 8.08%. Calcd for $C_{19}H_{23}NSi$: C, 77.76; H, 7.90%.

4.2.26. 2-(Methyldiphenylsilyl)propanenitrile (17c). R_f=0.31 (hexane/ethyl acetate=10/1); colorless oil; IR (neat) 3072, 2224, 1429, 1261, 1114, 794, 731, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.78 (s, 3H), 1.33 (d, J=7.5 Hz, 3H), 2.38 (q, J=7.5 Hz, 1H), 7.40–7.52 (m, 6H), 7.59–7.69 (m, 4H); ^{13}C NMR ($CDCl_3$) δ −6.11, 10.62, 12.49, 122.82, 128.19, 128.22, 130.31, 132.11, 132.36, 134.70. Found: C, 76.19; H, 6.90%. Calcd for $C_{16}H_{17}NSi$: C, 76.44; H, 6.82%.

4.2.27. 2-Butyl-2-(methyldiphenylsilyl)-pent-4-enenitrile (19a). R_f=0.41 (hexane/ethylacetate=10/1); colorless oil; IR (neat) 2936, 2214, 1962, 1890, 1827, 1639, 1429, 1259, 1113, 922, 793, 729 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.81 (s, 3H), 0.80 (t, J=7.2 Hz, 3H), 1.13–1.30 (m, 2H), 1.30–1.50 (m, 2H), 1.50–1.72 (m, 2H), 2.29 (dd, J=7.2, 14.1 Hz, 1H), 2.48 (dd, J=7.2, 14.1 Hz, 1H), 5.02 (d, J=16.8 Hz, 1H), 5.08 (d, J=9.9 Hz, 1H), 5.82 (ddt, J=9.9, 16.8, 7.2 Hz, 1H), 7.38–7.49 (m, 6H), 7.70–7.76 (m, 4H); ^{13}C NMR ($CDCl_3$) δ −4.96, 13.82, 22.92, 27.39, 28.50, 32.71, 38.03, 118.74, 123.94, 128.03, 130.07, 132.50, 133.42, 134.61, 135.15, 135.19. Found: C, 79.34; H, 8.35%. Calcd for $C_{22}H_{27}NSi$: C, 79.22; H, 8.16%.

4.2.28. 2-Methyl-2-(methyldiphenylsilyl)hexanenitrile (19b). R_f=0.48 (hexane/ethyl acetate=5/1); colorless oil; IR (neat) 2936, 2214, 1429, 1259, 1113, 793, 729, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.76 (s, 3H), 0.86 (t, J=7.2 Hz, 3H), 1.33 (s, 3H), 1.19–1.36 (m, 3H), 1.42–1.54 (m, 2H), 1.68–1.81 (m, 1H), 7.38–7.49 (m, 6H), 7.70–7.76 (m, 4H); ^{13}C NMR ($CDCl_3$) δ −6.27, 13.98, 19.28, 22.12, 22.83, 27.36, 34.08, 125.36, 128.03, 130.09, 132.11, 132.14, 135.22, 135.24. Found: C, 77.82; H, 8.22%. Calcd for $C_{20}H_{25}NSi$: C, 78.12; H, 8.19%.

4.2.29. 2-Acetyl-2-(methyldiphenylsilyl)hexanenitrile (19c). R_f=0.52 (hexane/ethyl acetate=5/1); colorless oil; IR (neat) 2930, 2205, 1632, 1429, 1286, 1121, 797, 738, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.79 (s, 3H), 0.89 (t, J=7.2 Hz, 3H), 1.24–1.38 (m, 3H), 1.39–1.51 (m, 2H), 2.02 (s, 3H), 2.21 (t, J=7.5 Hz, 2H), 7.40–7.47 (m, 6H), 7.55–7.61 (m, 4H); ^{13}C NMR ($CDCl_3$) δ −1.49, 13.90, 18.92, 22.07,

22.23, 26.55, 30.26, 120.65, 128.11, 130.21, 130.50, 133.91, 134.17, 134.62, 162.85. HRMS (*m/z*) Found: 335.1702. Calcd for $C_{21}H_{25}NOSi$: 335.1705.

4.2.30. 2-Benzoyl-2-(methyldiphenylsilyl)hexanenitrile (19d). R_f=0.41 (hexane/ethyl acetate=5/1); colorless oil; IR (neat) 2959, 2206, 1746, 1429, 1258, 1115, 795, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.40 (s, 3H), 0.88 (t, J= 7.2 Hz, 3H), 1.23–1.36 (m, 2H), 1.38–1.51 (m, 2H), 2.29 (dd, J=7.5, 8.1 Hz, 2H), 7.32–7.38 (m, 6H), 7.43–7.50 (m, 4H); ^{13}C NMR ($CDCl_3$) δ −2.06, 13.91, 22.32, 27.80, 30.18, 97.32, 120.08. HRMS (*m/z*) Found: 397.1860. Calcd for $C_{26}H_{27}NOSi$: 397.1862.

4.2.31. (*Z*)-2-Butyl-3-phenyl-acrylonitrile (determined by NOESY) (19e). R_f=0.54 (hexane/ethyl acetate= 10/1); colorless oil; IR (neat) 2959, 2208, 1730, 1448, 926, 750, 692 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.96 (t, J=7.2 Hz, 3H), 1.33–1.47 (m, 2H), 1.65 (quint, J=7.8 Hz, 2H), 2.41 (t, J=7.8 Hz, 2H), 6.93 (s, 1H), 7.34–7.46 (m, 3H), 7.68–7.78 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.85, 21.92, 30.41, 36.04, 111.54, 118.75, 128.41, 128.66, 129.69, 133.72, 143.09. Found: C, 84.06; H, 8.20%. Calcd for $C_{13}H_{15}N$: C, 84.28; H, 8.16%. NOE (^1H difference spectrum, 300 MHz, $CDCl_3$) irradiation of δ 2.41 (CH_2)—enhancement of signals at δ 6.93 (CH, 1.6%); irradiation of δ 6.93 (CH)—enhancement of signals at δ 2.41 (CH_2, 0.9%), δ 7.68–7.78 (Ph, 0.7%)

4.2.32. (*Z*)-2-Butyl-3-cyclohexyl-acrylonitrile (*Z*/*E*= 55/45) (19f). R_f=0.62 (hexane/ethyl acetate=10/1); colorless oil; IR (neat) 2855, 2214, 1591, 1429, 1259, 1124, 858, 796, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.91 (t, J=7.5 Hz 3H), 1.20–1.24 (m, 4H), 1.24–1.42 (m, 4H), 1.45–1.55 (m, 2H), 1.62–1.78 (m, 6H), 2.18 (dt, J=1.5, 6.9 Hz, 2H), 2.44–2.60 (m, 1H), 5.95 (d, J=9.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.80, 21.77, 25.36, 25.71, 30.23, 32.28, 33.92, 40.72, 112.34, 117.84, 152.73. HRMS (*m/z*) Found: 191.1677. Calcd for $C_{13}H_{21}N$: 191.1674. NOE (^1H difference spectrum, 300 MHz, $CDCl_3$) irradiation of δ 2.18 (CH_2)—enhancement of signals at δ 5.95 (CH, 1.2%); irradiation of δ 5.95 (CH)—enhancement of signals at δ 2.18 (CH_2, 0.8%)

4.2.33. (*E*)-2-Butyl-3-cyclohexyl-acrylonitrile (*Z*/*E*= 55/45) (19f′). R_f=0.55 (hexane/ethyl acetate=10/1); colorless oil; IR (neat) 2855, 2214, 1591, 1429, 1259, 1124, 858, 797, 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.92 (t, J=7.2 Hz, 3H), 1.04–1.43 (m, 8H), 1.43–1.80 (m, 8H), 2.19 (dt, J=1.2, 7.2 Hz, 2H), 2.24–2.39 (m, 1H), 6.14 (d, J=10.2 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.87, 22.09, 25.39, 25.66, 28.39, 30.44, 31.98, 37.64, 113.12, 120.27, 152.78. HRMS (*m/z*) Found: 191.1680. Calcd for $C_{13}H_{21}N$: 191.1674. NOE (^1H difference spectrum, 300 MHz, $CDCl_3$) irradiation of δ 6.14 (CH_2)—no enhancement of signals at δ 2.19 (CH_2, 0.9%).

4.2.34. 2-Oxo-hexanenitrile (19g, known compound). Spectral data for this compound were identical with those reported in the literature.[20]

4.2.35. Preparation of 1-(methyldiphenylsilyl)-1-phenylpentane (21). *n*-BuLi (0.31 mL, 1.6 M solution in hexane, 0.50 mmol) was added to a solution of $Ph_2MeSiCHCl_2$ (**8**, 141 mg, 0.50 mmol) in THF (5 mL) dropwise at −78 °C, and the mixture was stirred for 30 min. Then *n*-BuCu in THF, which was prepared with *n*-BuLi (0.34 mL, 1.6 M solution in THF, 0.55 mmol) and CuI·LiI (0.55 mL, 1.0 M solution in THF, 0.55 mmol) at −78 °C, was added to the resultant solution at −78 °C. After stirring for 10 min., and addition of PhMgBr (0.75 mL, 1.0 M solution in THF, 0.75 mmmol), the mixture was allowed to warm gradually to −10 °C. And then the reaction was quenched with diluted aqueous HCl (20 mL). The mixture was extracted with ethyl acetate (10 mL×3), and the organic layers were dried over anhydrous Na_2SO_4 and concentrated in vacuo. Purification by silica gel column chromatography provided 1-(methyldiphenylsilyl)-1-phenylpentane (**21**, 93 mg, 0.27 mmol) in 54% yield as colorless oil: R_f=0.72 (hexane/ethyl acetate=10/1); IR (neat) 2957, 1956, 1882, 1818, 1599, 1427, 1252, 1111, 789, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.42 (s, 3H), 0.77 (t, J=6.6 Hz, 3H), 1.06–1.34 (m, 4H), 1.76–1.87 (m, 2H), 2.65 (dd, J=5.1, 10.5 Hz, 1H), 6.86–6.92 (m, 2H), 7.04–7.19 (m, 4H), 7.24–7.49 (m, 6H), 7.50–7.58 (m, 3H); ^{13}C NMR ($CDCl_3$) δ −5.22, 14.02, 22.45, 29.78, 31.43, 35.02, 124.48, 127.06, 127.43, 127.59, 127.78, 127.96, 128.36, 128.64, 128.91, 129.16, 134.54, 134.77, 135.16, 136.21, 142.34. HRMS (*m/z*) Found: 344.1963. Calcd for $C_{24}H_{28}Si$: 344.1960.

4.2.36. 4-(Methyldiphenylsilyl)-4-phenyl-1-octene (22). R_f=0.68 (hexane/ethyl acetate=20/1); colorless oil; IR (neat) 2957, 1427, 1254, 1107, 784, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.59 (s, 3H), 0.81 (t, J=7.2 Hz, 3H), 1.16–1.33 (m, 4H), 1.94–2.14 (m, 2H), 2.73–2.90 (m, 2H), 4.93 (dd, J=1.5, 10.2 Hz, 1H), 5.03 (dd, J=1.5, 17.1 Hz, 1H), 5.65–5.81 (m, 1H), 6.88–6.94 (m, 2H), 7.06–7.18 (m, 3H), 7.22–7.31 (m, 4H), 7.32–7.42 (m, 6H); ^{13}C NMR ($CDCl_3$) δ −4.42, 14.12, 23.69, 25.94, 33.53, 36.34, 38.48, 116.52, 124.35, 127.25, 128.15, 128.88, 135.36, 135.58, 136.10, 143.95. HRMS (*m/z*) Found: 384.2258. Calcd for $C_{27}H_{32}Si$: 384.2273.

4.2.37. 3-(Methyldiphenylsilyl)-3-phenyl-heptan-2-one (23). R_f=0.48 (hexane/ethyl acetate=10/1); colorless oil; IR (neat) 2957, 1659, 1429, 1217, 1119, 986, 793, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.56 (s, 3H), 0.80 (t, J=7.2 Hz, 3H), 1.13–1.37 (m, 6H), 1.99 (s, 3H), 6.84–6.90 (m, 2H), 7.13–7.19 (m, 3H), 7.22–7.36 (m, 5H), 7.37–7.42 (m, 3H), 7.56–7.60 (m, 2H); ^{13}C NMR ($CDCl_3$) δ −3.49, 13.85, 23.65, 28.05, 33.46, 59.01, 125.75, 127.23, 127.37, 127.66, 128.62, 129.02, 134.78, 135.47, 135.89, 136.01, 139.61, 212.33. HRMS (*m/z*) Found: 386.2071. Calcd for $C_{26}H_{30}OSi$: 386.2066.

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