Enamines of Acylsilanes: Electrochemical Synthesis, Structure, and Use as a Source of α-(Trimethylsilyl)alkylamines†

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α-(Trimethylsilyl)alkylamines ("RSMA"), **1**, have been prepared with good yields from enamines of acylsilanes, **2**, through reduction of the corresponding iminium salts, **5**, with sodium borohydride. The entire process constitutes an original way to homologate a carbonyl compound into the next RSMA, as the starting enamine was obtained through reductive silylation of the *O*-silyl-protected cyanohydrin, **3**, of this carbonyl compound. In this occasion, the electrochemical procedure for the reductive silylation was proven to be as effective as the chemical one, giving **2** in yields of the same order of magnitude. ^{29}Si NMR spectroscopic studies allowed the complete assignment of the *E* and *Z* structures of these isomeric enamines.

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Introduction

Because of the easy cleavage of silicon−carbon bonds to create carbon−carbon or carbon−heteroelement bonds, the use of C-silylated compounds in organic synthesis have received increasing attention in the last decades.[1] Consequently, there arose the constant need of newer silylated synthons. Among these, compounds having the Si−C−N sequence in their skeleton ("**s**ilyl**m**ethyl**a**mines") have gained a peculiar importance as they were proven to be excellent precursors for α-nitrogen carbanions[2] and nitrogen heterocycles (*via* nonstabilized azomethine ylides).[3] Moreover, biological activity has often been associated with this sequence.[4]

If preparative methods exist for (aminomethyl)silanes [**m**ono(**s**ilyl**m**ethyl)**a**mines, "MSMA", ≡SiCH$_2$NH$_2$],[5] α-silylbenzylamines [**a**ryl(**s**ilyl)**m**ethyl**a**mines, "ASMA", Ar(≡Si)CHNH$_2$],[6] or **b**is(**s**ilyl)**m**ethyl**a**mines ["BSMA", (≡Si)$_2$CHNH$_2$],[7−9] general synthetic methods for α-silylalkylamines [**a**lkyl(**s**ilyl)**m**ethyl**a**mines, "RSMA", R(≡Si)CHNH$_2$], **1**, were lacking. Only the preparation of one such RSMA, by alkylation of an (aminomethyl)-silane, has been described in the literature.[10]

Transformation of enamines into the corresponding amines being a known synthetic process, we made the assumption that, possessing the same skeleton, the desired amines could be obtained from enamines of acylsilanes, **2**, compounds for which preparation exists.[11,12]

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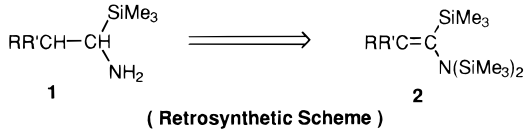


This paper reports on the conversion of enamines **2** into RSMA **1**. Also reported is complementary information on the synthesis and the structure of **2**.

Results

Synthesis of Enamines 2. A few years ago, we published the synthesis of **2** through the reductive silylation of *O*-trimethylsilyl-protected cyanohydrins **3** by means of lithium in the presence of trimethylsilyl chloride in tetrahydrofuran (THF).[11,12] The key point was the decisive and unavoidable use of hexamethylphosphoramide (HMPA) as a cosolvent, which made the transformation complete. However, having gained experience in electroreductive silylation,[9] we tested this technique (sacrificial anode)[13] with the aim to avoid the use of lithium, on the one side, and to try to limit the amount of HMPA, on the other.

Cyanohydrins **3** were treated, at room temperature (instead of 0 °C in the case of the chemical process)[12] with trimethylsilyl chloride in THF in the presence of 1 equiv of HMPA (instead of 4)[12] in an undivided cell equipped with an aluminum-made sacrificial anode. After 4.4 faradays were passed through the reaction mixture, enamines **2** were obtained in good to excellent yields comparable to those given by the chemical route[12] (Table 1 and Scheme 1).

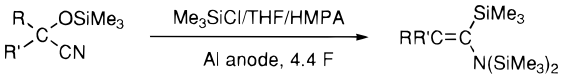
Structural Studies of 2. Compounds **2** were obtained, when R ≠ R′, as a mixture of the *Z* and *E* isomers in variable ratio. But the difficulty was to assign the correct geometry to each isomer, a task which had not been undertaken previously.[11,12] Although attempted separation of these isomers failed, clear assignment was made possible by using spectroscopic methods.

NMR Spectroscopy. In the ^{1}H, ^{13}C, and ^{29}Si NMR spectra of most of the enamines **2** prepared, the intensities of the signals due to one isomer appeared clearly as being different from the ones related to the other isomer. This allowed us to assign each set of signals to one isomer, without, however, the possibility of determining its geometry. This problem was solved by studying the coupling constants of the silicon atoms with the neighboring protons, using a selective population transfer technique.[14,15] Because molecules **2** possessed $SiMe_3$ groups, analysis of the complex information obtained was very difficult but was made possible with the help of a simulation program allowing determination of coupling constants with good precision (0.1 Hz).[16]

Table 1. Synthesis of 2

2	R	R′	yield, %	*E*/*Z*	yield, %[12]
a	H	Me	59	88/12	
b	H	Et	75	67/33	
c	H	^{t}Bu	78	80/20	68
d	Me	Me	70		82
e	Me	^{n}Pr	82	58/42	80
f	Me	$SiMe_3$	66	73/27	
g		C_5H_9	68		80
h		C_6H_{11}	75		

Scheme 1. Electrochemical Synthesis of Enamine 2



Scheme 2. $^nJ(^{29}Si-^1H)$ Coupling Constants in Enamines 2

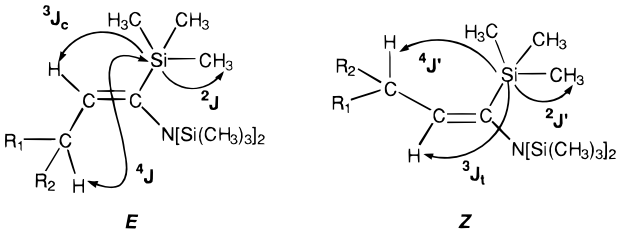


Table 2. Coupling Constants $^nJ(^{29}Si-^1H)$ in Enamines 2

2	$^2J(E)$	$^2J'(Z)$	$^3J_c(E)$	$^3J_t(Z)$	$^4J(E)$	$^4J'(Z)$
a	6.3	6.4	4.9	10.5	1.2	1.2
b	6.5	6.5	4.9	10.4	1.0	1.4
c	6.3	6.3	5.8	11.8		
e	6.5	6.4			1.1	1.3
f	6.4	6.4			1.2	1.6

Coupling constants $^nJ(^{29}Si-^1H)$, where *n* represents the number of bonds between a silicon atom and the considered proton(s), have been measured for a series of structurally defined vinyltrimethylsilanes,[15] and the authors established that (a) $^2J = 6.3 \pm 0.2$ Hz was characteristic of the $SiMe_3$ group, (b) ^4J did not afforded any information related to the geometry of the molecule, and (c) ^3J was largely greater (approximately two times) for the *Z* isomer (^3J_t) than for the *E* isomer (^3J_c)[17] (Scheme 2).

The measurements we have made on spectra of molecules **2a**−**c** were in good agreement with these findings (Table 2). Correlating the ^nJ values with the intensities of the corresponding NMR signals allowed the complete assigment of the spectra to each isomer, the *E* being the major isomer formed (Table 1). Consequently it was established that the *Z* isomer had a shorter retention time in GLC. This property was used to identify respectively the *E* and *Z* isomers of enamines **2e** and **2f**, a determination which was not possible by ^{29}Si NMR because of the absence of any $^3J(^{29}Si-^1H)$ coupling and of the weakness of the $^4J(^{29}Si-^1H)$ couplings. However, this constant can be used (with some precautions) for determining the *E* or *Z* nature of **2** (R, R′ ≠ H) as it is smaller for the *E* isomer (Table 2). This is true also with **2b**.

IR and Mass Spectrometries. The techniques used were mass spectrometry and Fourier transformed in-

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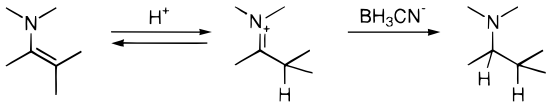
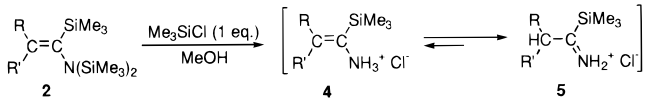
Scheme 3. Borohydride Reduction of Enamines



Scheme 4. Protolysis of Enamines 2



frared spectrometry coupled with gas chromatography (respectively GC/MS and GC/FTIR). If on the MS spectra of *E* and *Z* isomers no appreciable difference could be noted in the fragmentation patterns and in the intensities, clear differences appeared in their IR spectra: a characteristic $\nu_{C=C}$ absorption was observed only for the *E* isomer (~1580 cm^{-1}),[18] except for **2f** where this band was present for both isomers and shifted to lower values (probably because of the influence of the vinylic silicon atom), respectively at 1506 cm^{-1} (*Z*) and 1522 cm^{-1} (*E*).

Synthesis of α-(Trimethylsilyl)alkylamines (RSMA), 1. It was already known that reduction of enamines through catalytic hydrogenation[19,20] could serve as a method for preparing amines. In our case, catalytic hydrogenation of enamines **2** in the presence of palladium[19] on charcoal (10%) or Raney nickel[20] did not lead to any reaction, probably for steric and electronic reasons.

Durst and co-workers have shown that enamines, in acidic medium, were easily converted into amines by reduction of the corresponding iminium salt using sodium cyanoborohydride as the reducing agent[21] (Scheme 3).

Some years ago, we reported the facile conversion of **2** into the corresponding enaminium salt **4**, which isomerized slowly into the iminium salt **5**, by action of 1 equiv of trimethylsilyl chloride in methanol, whereas hydrochloric acid was ineffective[11,12] in the same solvent (Scheme 4).

So, iminium salts **5** were first obtained from **2** and, then, treated with sodium cyanoborohydride in an acidic THF/methanol mixture. The corresponding RSMA **1** were obtained in good yields after neutralization of the reaction mixture.

The two steps of this synthesis could be performed in a one-pot fashion, trimethylsilyl chloride being added to the solution of the enamine and cyanoborohydride in a methanol/THF mixture. Comparable yields were obtained (Table 3).

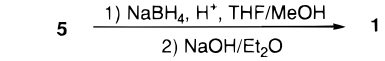
Finally, the use of sodium borohydride (less expensive) instead of sodium cyanoborohydride was tested successfully as it gave equivalent results (Scheme 5).

None of these processes allowed the obtention of amine **1f** from enamine **2f**, as **1a** was formed instead. This was probably due to the presence in **5f** of a silyl group in the β position from the C=N bond, which made this group easy to cleave off through protolysis (Scheme 6).

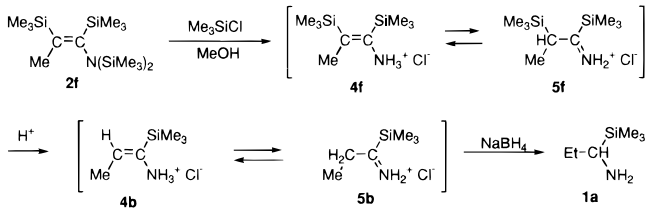
Table 3. Synthesis of RSMA 1

				yields from **2** ("one-pot"), %	
1	R	R′	yields from **5**, %	$NaBH_3CN$	$NaBH_4$
a	H	Me	68	63	64
b	H	Et	65	58	61
c	H	^{t}Bu	62	65	63
d	Me	Me	66	61	57
e	Me	^{n}Pr	58	60	59
g	C_5H_9		56	55	52
h	C_6H_{11}		65	58	60

Scheme 5. Conversion of Iminium Salts 5 into 1

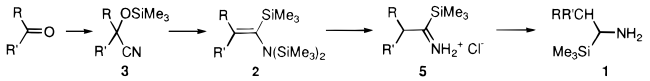


Scheme 6. Formation of Amine 1a from Enamine 2f



Conclusions

This study has allowed us to achieve access to a series of original RSMA **1** compounds. Moreover, it has been shown the following. (a) Electrosynthesis constitutes an elegant alternative to the chemical process to synthesize enamines **2** from *O*-silylcyanohydrins **3**. (b) Isomers **2*E*** and **2*Z*** can be fully characterized by means of spectroscopic methods, particularly by analysis of the NMR $^nJ(^{29}Si-^1H)$ coupling constants. (c) *N*,*N*-Disilyl enamines of acysilanes **2** are excellents precursors for α-alkyl(silyl)methylamines (RSMA) **1**; an original one-pot procedure using sodium borohydride has been set up to realize the transformation. (d) Finally, the sequence of transformations, i.e. cyanosilylation, reductive silylation, and borohydride reduction, constitutes an original homologation process of a carbonyl compound into the next α-(trimethylsilyl)alkylamine:



Experimental Section

General Data. Gas chromatographic (GC) analyses were performed on a Hewlett-Packard 5890 (series II) temperature programmable chromatograph equipped with capillary columns (CPSIL, 25 m × 0.25 μm). Infrared spectra of neat compounds (film on NaCl pellets for liquids and 1% dispersion in KBr for solids) were obtained from a Perkin-Elmer 1420 ratio recording infrared spectrometer, and Fourier transformed infrared spectra were registered using a Nicolet 20SXC spectrometer connected to a Carlo Erba GC 6000 Vega chromatograph equipped with PTE 5 capillary columns (25 m, 0.25 μm). ^1H NMR spectra were recorded using a Hitachi R-1200 (60 MHz, solvent CCl_4 and CH_2Cl_2 at δ = 5.33 ppm[22] as internal reference) or a Bruker AC250 (250 MHz, solvent $CDCl_3$) or AC200 (200 MHz, solvent $CDCl_3$). These two last

(18) In *N*-alkyl enamines, $\nu_{C=C}$ absorption occurs usually at higher values (1660−1620 cm^{-1}). See: Leonard, N. J.; Gash, V. W. *J. Am. Chem. Soc.* **1954**, *76*, 2781.
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Table 4. Preparation of Cyanohydrins 3

3	R	R′	yield, %
a	H	Me	80
b	H	Et	74
c	H	^{t}Bu	95
d	Me	Me	98
e	Me	^{n}Pr	95
f	Me	Me_3Si	83
g	C_5H_9		85
h	C_6H_{11}		80

spectrometers were also used for recording ^{13}C and ^{29}Si NMR spectra ($CDCl_3$ at 77.39 ppm and TMS at 0 ppm, respectively, as internal reference). Mass spectra were registrered on a VG Micromass 16 F (70 eV) connected with a Data System 2040 station and an Intersmat IGC 121 M gas chromatograph equipped with BP1 (25 m, 0.25 μm) columns. Elemental analyses were performed by the Service Central d'Analyse of the CNRS.

Starting Materials. Reagent-grade aldehydes, ketones, trimethylsilyl cyanide,[23] HMPA,[24] THF, and tetrabutylammonium bromide were used without purification. Trimethylsilyl chloride, kindly supplied by Rhône-Poulenc Co., was distilled over magnesium turnings prior to use and kept under an argon atmosphere.

Preparation of Cyanohydrins 3. The Evans[25] procedure was used. It consisted in reacting commercial aldehyde or ketone (1 equiv) with trimethylsilyl cyanide (11 g, 1.1 equiv) in the presence of a catalytic amount of anhydrous zinc iodide (250 mg), at room temperature (aldehydes) or upon warming at 60 °C for 1 h (ketones). Evaporation of the excess of the cyanide under vacuum left, in quantitative yields, a raw material which was purified by distillation. Tables 4 and 5 list the yields of purified products and some physicochemical data. It should be noted in IR spectra that the ν_{CN} absorption was very weak and sometimes not visible (**3c**). ^1H NMR data were in good agreement with those reported previously: **3c**,[11] **3d**,[11,26] **3e**,[11] **3f**,[27] **3g**,[11,26] and **3h**.[11]

Electrochemical Reductive Silylation of 3: Synthesis of 2. The electrolysis procedure has already been published.[9] Using the equipment described, cyanohydrins **3** (150 mM) were mixed with THF (150 mL), trimethylsilyl chloride (240 g, 2.3 M, 300 mL), HMPA (36 g, 0.2 M, 40 mL), and tetrabutylammonium bromide (300 mg). After 4.4 faradays/mol were passed into the 500 mL undivided cell equipped with an aluminum-made sacrificial anode, the organic layer was extracted with dry pentane (500 mL). Low-boiling materials were evaporated under vacuum, and the residue was taken into 100 mL of pentane. After washing with water until neutral, drying over sodium sulfate and evaporating the solvent, a viscous liquid was recovered which consisted in a mixture of the *E* and *Z* enamines **2**. This mixture was purified by distillation and analyzed by GC (GC traces from the GC/MS and GC/FTIR; see General Data above) and ^1H NMR to determine the *E*/*Z* ratio (Table 1). Assigment of an *E* or *Z* structure to each isomer was made by ^{29}Si NMR (Table 2). Physicochemical data of **2** were in good agreement with those from the literature, when they were available: **2c**−**e**,**g**,**h**.[11]

1-(Trimethylsilyl)-1-[bis(trimethylsilyl)amino]prop-1-ene (2a). Anal. Calc for $C_{12}H_{31}NSi_3$ (M: 273.64): C, 52.67; H, 11.42; N, 5.12; Si, 30.79. Found: C, 52.71; H, 11.39; N, 5.09; Si, 30.72.

(*E*)-1-(Trimethylsilyl)-1-[bis(trimethylsilyl)amino]prop-1-ene (2a*E*): ^1H NMR δ 0.10 [s, 9H, Si(C**H**$_3$)$_3$], 0.11 [s, 18H, N(Si(C**H**$_3$)$_3$)$_2$], 1.64 [d (^3J = 6.5), 3H, C**H**$_3$], 5.75 [q (^3J = 6.5), 1H, =C**H**]; ^{13}C NMR δ 0.0 [Si(**C**H$_3$)$_3$], 2.6 [N(Si(**C**H$_3$)$_3$)$_2$], 14.4 [**C**H$_3$], 134.0 [=**C**H]; 150.1 [Si−**C**−N]; ^{29}Si NMR δ −6.7 [$^2J_{SiMe_3}$ = 6.3 (9H), $^3J_{SiC=CH}$ = 4.9 (1H), $^4J_{SiC=CCH_3}$ = 1.2 (3H), C−**Si**(CH$_3$)$_3$], 1.8 [$^2J_{SiMe_3}$ = 6.5 (9H), $^4J_{SiNC=CH}$ = 1.2 (1H), $^5J_{SiNC=CCH_3}$ = 1.1 (3H), N−**Si**(CH$_3$)$_3$]; IR $\nu_{C=C}$ (cm^{-1}) 1596 (very weak); MS (70 eV) *m*/*z* 273 (M$^+$, 2.5), 258 (M$^+$ − Me, 5.6), 200 (M$^+$ − SiMe$_3$, 100), 172 (22.3), 73 (98.6).

(*Z*)-1-(Trimethylsilyl)-1-[bis(trimethylsilyl)amino]prop-1-ene (2a*Z*): ^1H NMR δ 0.10 [s, 9H, Si(C**H**$_3$)$_3$], 0.11 [s, 18H, N(Si(C**H**$_3$)$_3$)$_2$], 1.73 [d (^3J = 7.3), 3H, C**H**$_3$], 5.86 [q (^3J = 7.3), 1H, =C**H**]; ^{13}C NMR δ 0.0 [Si(**C**H$_3$)$_3$], 2.6 [N(Si(**C**H$_3$)$_3$)$_2$], 15.3 [**C**H$_3$], 137.0 [=**C**H]; 150.1 [Si−**C**−N]; ^{29}Si NMR δ −7.7 [$^2J_{SiMe_3}$ = 6.4 (9H), $^3J_{SiC=CH}$ = 10.5 (1H), $^4J_{SiC=CCH_3}$ = 1.2 (3H), C−**Si**(CH$_3$)$_3$], 2.3 [$^2J_{SiMe_3}$ = 6.5 (9H), $^4J_{SiNC=CH}$ = 1.8 (1H), $^5J_{SiNC=CCH_3}$ = 1.5 (3H), N−**Si**(CH$_3$)$_3$]; IR $\nu_{C=C}$ (cm^{-1}) invisible; MS (70 eV) *m*/*z* 273 (M$^+$, 1.8), 258 (M$^+$ − Me, 13.2), 200 (M$^+$ − SiMe$_3$, 100), 172 (19.3), 73 (28.0).

1-(Trimethylsilyl)-1-[bis(trimethylsilyl)amino]but-1-ene (2b). Anal. Calc for $C_{13}H_{33}NSi_3$ (M: 287.67): C, 54.28; H, 11.56; N, 4.87; Si, 29.29. Found: C, 54.31; H, 11.58; N, 4.84; Si, 29.21.

(*E*)-1-(Trimethylsilyl)-1-[bis(trimethylsilyl)amino]but-1-ene (2b*E*): ^1H NMR δ 0.11 [s, 18H, N(Si(C**H**$_3$)$_3$)$_2$], 0.12 [s, 9H, Si(C**H**$_3$)$_3$], 0.96 [t (^3J = 7.5), 3H, C**H**$_3$], 2.11 [m, 2H, C**H**$_2$], 5.59 [t (^3J = 6.7), 1H, =C**H**]; ^{13}C NMR δ 0.0 [Si(**C**H$_3$)$_3$], 2.6 [N(Si(**C**H$_3$)$_3$)$_2$], 13.6 [**C**H$_3$], 21.4 [**C**H$_2$], 142.0 [=**C**H]; 148.0 [Si−**C**−N]; ^{29}Si NMR δ −6.7 [$^2J_{SiMe_3}$ = 6.5 (9H), $^3J_{SiC=CH}$ = 4.9 (1H), $^4J_{SiC=CCH_2}$ = 1.4 (2H), C−**Si**(CH$_3$)$_3$], 1.6 [$^2J_{SiMe_3}$ = 6.5 (9H), $^4J_{SiNC=CH}$ = 1.3 (1H), $^5J_{SiNC=CCH_2}$ = 0.9 (2H), N−**Si**(CH$_3$)$_3$]; IR $\nu_{C=C}$ (cm^{-1}) 1588 (weak); MS (70 eV) *m*/*z* 287 (M$^+$, 2.4), 272 (M$^+$ − Me, 4.6), 214 (M$^+$ − SiMe$_3$, 95.5), 172 (20.8), 73 (100).

(*Z*)-1-(Trimethylsilyl)-1-[bis(trimethylsilyl)amino]but-1-ene (2b*Z*): ^1H NMR δ 0.12 [s, 18H, N(Si(C**H**$_3$)$_3$)$_2$], 0.13 [s, 9H, Si(C**H**$_3$)$_3$], 1.00 [t (^3J = 7.5), 3H, C**H**$_3$], 2.16 [m, 2H, C**H**$_2$], 5.80 [t (^3J = 6.7), 1H, =C**H**]; ^{13}C NMR δ 0.4 [Si(**C**H$_3$)$_3$], 2.6 [N(Si(**C**H$_3$)$_3$)$_2$], 14.5 [**C**H$_3$], 23.3 [**C**H$_2$], 145.0 [=**C**H]; 146.0 [Si−**C**−N]; ^{29}Si NMR δ −7.6 [$^2J_{SiMe_3}$ = 6.5 (9H), $^3J_{SiC=CH}$ = 10.4 (1H), $^4J_{SiC=CCH_2}$ = 1.0 (2H), C−**Si**(CH$_3$)$_3$], 2.2 [$^2J_{SiMe_3}$ = 6.5 (9H), $^4J_{SiNC=CH}$ = 1.3 (1H), $^5J_{SiNC=CCH_2}$ = 1.2 (2H), N−**Si**(CH$_3$)$_3$]; IR $\nu_{C=C}$ (cm^{-1}) invisible; MS (70 eV) *m*/*z* 287 (M$^+$, 2.3), 272 (M$^+$ − Me, 5.1), 214 (M$^+$ − SiMe$_3$, 89.3), 172 (18.6), 73 (100).

3,3-Dimethyl-1-(trimethylsilyl)-1-[bis(trimethylsilyl)-amino]but-1-ene (2c). Anal. Calc for $C_{15}H_{37}NSi_3$ (M: 315.72): C, 57.06; H, 11.81; N, 4.44; Si, 26.69. Found: C, 57.01; H, 11.82; N, 4.41; Si, 26.63.

(*E*)-3,3-Dimethyl-1-(trimethylsilyl)-1-[bis(trimethylsilyl)amino]but-1-ene (2c*E*): ^1H NMR δ 0.10 [s, 9H, Si(C**H**$_3$)$_3$], 0.16 [s, 18H, N(Si(C**H**$_3$)$_3$)$_2$], 1.12 [s, 9H, C(C**H**$_3$)$_3$], 5.25 [s,1H, =C**H**]; ^{13}C NMR δ 0.6 [Si(**C**H$_3$)$_3$], 3.1 [N(Si(**C**H$_3$)$_3$)$_2$], 30.6 [C(**C**H$_3$)$_3$], 34.7 [**C**(CH$_3$)$_3$], 146.7 [=**C**H]; 156.2 [Si−**C**−N]; ^{29}Si NMR δ −5.2 [$^2J_{SiMe_3}$ = 6.3 (9H), $^3J_{SiC=CH}$ = 5.8 (1H), C−**Si**(CH$_3$)$_3$]; 1.6 [$^2J_{SiMe_3}$ = 6.3 (9H), N−**Si**(CH$_3$)$_3$]; MS (70 eV) *m*/*z* 315 (M$^+$, 0.9), 300 (M$^+$ − Me, 0.9), 242 (M$^+$ − SiMe$_3$, 100), 186 (21.4), 73 (67.3).

(*Z*)-3,3-Dimethyl-1-(trimethylsilyl)-1-[bis(trimethylsilyl)amino]but-1-ene (2c*Z*): ^1H NMR δ 0.08 [s, 18H, N(Si-(C**H**$_3$)$_3$)$_2$], 0.17 [s, 9H, Si(C**H**$_3$)$_3$], 1.12 [s, 9H, C(C**H**$_3$)$_3$], 5.96 [s,1H, =C**H**]; ^{13}C NMR δ 2.6 [Si(**C**H$_3$)$_3$], 3.5 [N(Si(**C**H$_3$)$_3$)$_2$], 31.3 [C(**C**H$_3$)$_3$], 34.7 [**C**(CH$_3$)$_3$], 144.7 [=**C**H]; 156.2 [Si−**C**−N]; ^{29}Si NMR δ −7.6 [$^2J_{SiMe_3}$ = 6.3 (9H), $^3J_{SiC=CH}$ = 11.8 (1H), C−**Si**(CH$_3$)$_3$], 2.4 [$^2J_{SiMe_3}$ = 6.3 (9H), N−**Si**(CH$_3$)$_3$]; MS (70 eV) *m*/*z* 315 (M$^+$, 0.2), 300 (M$^+$ − Me, 1.4), 242 (M$^+$ − SiMe$_3$, 100), 186 (19.5), 73 (63.3).

(22) Pretsch, E.; Clerc, T.; Seibl, J.; Simon, W. *Tabellen zur Struktur aufklärung organischer Verbindungen mit spectroskopischen Metoden;* Springer Verlag: Berlin, 1976.

(23) This reagent was also prepared by following a described procedure where potassium cyanide was reacted with bis(trimethylsilyl) sulfate. See ref 11 and references cited therein.

(24) Due to the suspected toxicity of this material, the use of various solvents proposed as substitutes for HMPA was checked. Either they gave very poor yields (1,3-dimethyl-2-imidazolinone, DMEU, and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidone, DMPU) or they reacted themselves (DMF, TMU, for example).

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Table 5. Physicochemical Data of 3

3	bp, °C/Torr	^{1}H NMR, ppm (J, Hz)				^{13}C NMR, ppm						IR: ν_{CN}, cm^{-1}
		$SiMe_3$	CH_3	CH_2	CH	$SiMe_3$	CH_3	CH_2	CH	C	CN	
a	68/30	0.08	1.40 (6.7)		4.42 (6.7)	−0.4	22.9		57.2		120.1	2245
b	82/30	0.06	0.89 (7.5)	1.67 (7.5, 6.4)	4.23	−0.5	8.9	29.5	62.7		120.1	2241
c	110/30	0.24	1.04		4.04	−0.5	24.9		70.8	35.8	119.3	
d	51/30	0.08	1.44			1.2	30.8			66.1	122.5	2231
e	73/30	0.17	0.91 (7.2), 1.49	1.41−1.67		1.2	13.8, 17.6	28.9, 45.5		69.5	122.0	2235
f	53/20	0.11, 0.17	1.48			−5.1, 1.3	23.5			61.0	122.8	2210
g	81/25	0.17	1.68−1.80, 1.87−2.06			1.0		22.6, 41.7		74.4	122.5	2233
h	112/30	0.17	1.45−1.72, 1.96−2.02			1.4		22.6, 24.5, 39.4		70.7	121.9	2232

2-Methyl-1-(trimethylsilyl)-1-[bis(trimethylsilyl)amino]prop-1-ene (2d): ^{1}H NMR δ 0.0 [s, 18H, N(Si(C**H**$_3$)$_3$)$_2$], 0.08 [s, 9H, Si(C**H**$_3$)$_3$], 1.60 [s, 3H, C**H**$_3$], 1.68 [s, 3H, C**H**$_3$]; ^{13}C NMR δ 1.1 [Si(**C**H$_3$)$_3$], 2.8 [N(Si(**C**H$_3$)$_3$)$_2$], 21.9 [**C**H$_3$], 22.2 [**C**H$_3$], 140.6 [=**C**<]; 142.5 [Si−**C**−N]; ^{29}Si NMR δ −8.2 [$^2J_{SiMe_3}$ = 6.4 (9H), $^4J_{SiC=CCH_3}$ = 1.0 (3H), C−**Si**(CH$_3$)$_3$], 2.2 [$^2J_{SiMe_3}$ = 6.4 (9H), $^5J_{SiNC=CCH_3}$ = 0.8 (3H), N−**Si**(CH$_3$)$_3$]; IR $\nu_{C=C}$ (cm^{-1}) 1587; MS (70 eV) m/z 287 (M$^+$, 5.0), 214 (M$^+$ − SiMe$_3$, 92.1), 172 (14.1), 100 (15.4), 73 (100). Anal. Calc for $C_{13}H_{33}NSi_3$ (M: 289.69): C, 54.28; H, 11.56; N, 4.87; Si, 29.29. Found: C, 54.31; H, 11.54; N, 4.85; Si, 29.21.

2-Methyl-1-(trimethylsilyl)-1-[bis(trimethylsilyl)amino]pent-1-ene (2e). Anal. Calc for $C_{15}H_{37}NSi_3$ (M: 315.73): C, 57.06; H, 11.81; N, 4.44; Si, 26.99. Found: C, 57.09; H, 11.79; N, 4.45; Si, 26.95.

(*E*)-2-Methyl-1-(trimethylsilyl)-1-[bis(trimethylsilyl)amino]pent-1-ene (2e*E*): ^{1}H NMR δ 0.12 [s, 18H, N(Si(C**H**$_3$)$_3$)$_2$], 0.20 [s, 9H, Si(C**H**$_3$)$_3$], 0.95 [t (^3J = 7.2), 3H, C**H**$_3$−CH$_2$], 1.34−1.51[m, 2H, C**H**$_2$], 1.71 [s, 3H, =C−C**H**$_3$], 2.08−2.19 [m, 2H, =C−C**H**$_2$]; ^{13}C NMR δ 1.5 [Si(**C**H$_3$)$_3$], 2.8 [N(Si(**C**H$_3$)$_3$)$_2$], 14.7 [=C−**C**H$_3$], 20.0 [**C**H$_3$−CH$_2$], 21.0 and 38.5 [**C**H$_2$], 141.0 [=**C**−CH$_3$]; 147.3 [Si−**C**−N]; ^{29}Si NMR δ −8.2 [$^2J_{SiMe_3}$ = 6.4 (9H), $^4J_{SiC=CCH_3}$ = 1.1 (3H), C−**Si**(CH$_3$)$_3$], 2.3 [$^2J_{SiMe_3}$ = 6.5 (9H), N−**Si**(CH$_3$)$_3$]; IR $\nu_{C=C}$ (cm^{-1}) 1577 (very weak); MS (70 eV) m/z 315 (M$^+$, 1.7), 300 (M$^+$ − Me, 3.8), 242 (M$^+$ − SiMe$_3$, 93.8), 172 (19.7), 100 (9.3), 73 (100).

(*Z*)-2-Methyl-1-(trimethylsilyl)-1-[bis(trimethylsilyl)amino]pent-1-ene (2e*Z*): ^{1}H NMR δ 0.12 [s, 18H, N(Si(C**H**$_3$)$_3$)$_2$], 0.19 [s, 9H, Si(C**H**$_3$)$_3$], 0.96 [t (^3J = 7.2), 3H, C**H**$_3$−CH$_2$], 1.34−1.51 [m, 2H, C**H**$_2$], 1.78 [s, 3H, =C−C**H**$_3$], 2.08−2.19 [m, 2H, =C−C**H**$_2$]; ^{13}C NMR δ 1.4 [Si(**C**H$_3$)$_3$], 2.8 [N(Si(**C**H$_3$)$_3$)$_2$], 14.3 [=C−**C**H$_3$], 19.6 [**C**H$_3$−CH$_2$], 22.1 and 36.7 [**C**H$_2$], 140.3 [=**C**−CH$_3$]; 146.4 [Si−**C**−N]; ^{29}Si NMR δ −7.9 [$^2J_{SiMe_3}$ = 6.4 (9H), $^4J_{SiC=CCH_3}$ = 1.3 (3H), C−**Si**(CH$_3$)$_3$], 2.3 [$^2J_{SiMe_3}$ = 6.5 (9H), N−**Si**(CH$_3$)$_3$]; IR $\nu_{C=C}$ (cm^{-1}) invisible; MS (70 eV) m/z 315 (M$^+$, 2.1), 300 (M$^+$ − Me, 3.2), 242 (M$^+$ − SiMe$_3$, 97.3), 172 (21.4), 100 (11.2), 73 (100).

1,2-Bis(trimethylsilyl)-1-[bis(trimethylsilyl)amino]prop-1-ene (2f). Anal. Calc for $C_{15}H_{39}NSi_4$ (M: 345.83): C, 52.09; H, 11.37; N, 4.05; Si, 32.49. Found: C, 52.01; H, 11.42; N, 4.07; Si, 32.43.

(*E*)-1,2-Bis(trimethylsilyl)-1-[bis(trimethylsilyl)amino]-prop-1-ene (2f*E*): ^{1}H NMR δ 0.15 [s, 18H, N(Si(C**H**$_3$)$_3$)$_2$], 0.17 [s, 9H, Si(C**H**$_3$)$_3$], 0.22 [s, 9H, Si(C**H**$_3$)$_3$], 1.85 [s, 3H, C**H**$_3$]; ^{13}C NMR δ 1.7 [Si(**C**H$_3$)$_3$], 2.9 [N(Si(**C**H$_3$)$_3$)$_2$], 3.5 [Si(**C**H$_3$)$_3$], 21.1 [**C**H$_3$], 144.9 [=**C**−]; 156.0 [Si−**C**−N]; IR $\nu_{C=C}$ (cm^{-1}) 1522; MS (70 eV) m/z 330 (M$^+$ − Me, 2.2), 272 (M$^+$ − SiMe$_3$, 100), 218 (14.5), 184 (16.9), 73 (61.8).

(*Z*)-1,2-Bis(trimethylsilyl)-1-[bis(trimethylsilyl)amino]-prop-1-ene (2f*Z*): ^{1}H NMR δ 0.11 [s, 18H, N(Si(C**H**$_3$)$_3$)$_2$], 0.19 [s, 9H, Si(C**H**$_3$)$_3$], 0.21 [s, 9H, Si(C**H**$_3$)$_3$], 1.85 [s, 3H, C**H**$_3$]; ^{13}C NMR δ 1.3 [Si(**C**H$_3$)$_3$], 2.0 [Si(**C**H$_3$)$_3$], 2.8 [N(Si(**C**H$_3$)$_3$)$_2$], 20.4 [**C**H$_3$], 144.9 [=**C**−]; 156.0 [Si−**C**−N]; IR $\nu_{C=C}$ (cm^{-1}) 1506; MS (70 eV) m/z 330 (M$^+$ − Me, 0.9), 272 (M$^+$ − SiMe$_3$, 100), 218 (24.2), 184 (15.8), 73 (56.4).

{**[Bis(trimethylsilyl)amino](trimethylsilyl)methylene**}-**cyclopentane (2g):** ^{1}H NMR δ 0.10 [s, 18H, N(Si(C**H**$_3$)$_3$)$_2$], 0.14 [s, 9H, Si(C**H**$_3$)$_3$], 1.55−1.67 [m, 4H, C**H**$_2$], 2.12−2.36 [m, 4H, C**H**$_2$]; ^{13}C NMR δ 0.0 [Si(**C**H$_3$)$_3$], 2.9 [N(Si(**C**H$_3$)$_3$)$_2$], 25.2, 26.9, 30.9, and 32.9 [**C**H$_2$], 137.7 [=**C**<]; 155.1 [Si−**C**−N]; ^{29}Si NMR δ −8.2 [$^2J_{SiMe_3}$ = 6.4 (9H), $^4J_{SiC=CCH_2}$ = 1.6 (2H), C−**Si**(CH$_3$)$_3$], 1.9 [$^2J_{SiMe_3}$ = 6.4 (9H), $^5J_{SiNC=CCH_2}$ = 1.6 (2H), N−**Si**(CH$_3$)$_3$]; IR $\nu_{C=C}$ (cm^{-1}) 1589; MS (70 eV) m/z 313 (M$^+$, 5.3), 298 (M$^+$ − Me, 3.4), 240 (M$^+$ − SiMe$_3$, 100), 172 (18.7), 73 (85.4). Anal. Calc for $C_{15}H_{35}NSi_3$ (M: 313.71): C, 57.43; H, 11.25; N, 4.46; Si, 26.86. Found: C, 57.47; H, 11.28; N, 4.43; Si, 26.79.

{**[Bis(trimethylsilyl)amino](trimethylsilyl)methylene**}-**cyclohexane (2h):** ^{1}H NMR δ 0.11 [s, 18H, N(Si(C**H**$_3$)$_3$)$_2$], 0.17 [s, 9H, Si(C**H**$_3$)$_3$], 1.54−1.57 [m, 6H, C**H**$_2$], 2.21−2.28 [m, 4H, C**H**$_2$]; ^{13}C NMR δ 1.2 [Si(**C**H$_3$)$_3$], 2.8 [N(Si(**C**H$_3$)$_3$)$_2$], 27.0, 27.7, 28.3, 30.9, and 33.4 [**C**H$_2$], 137.3 [=**C**<]; 148.0 [Si−**C**−N]; ^{29}Si NMR δ −8.1 [$^2J_{SiMe_3}$ = 6.3 (9H), C−**Si**(CH$_3$)$_3$], 2.3 [$^2J_{SiMe_3}$ = 6.4 (9H), N−**Si**(CH$_3$)$_3$]; IR $\nu_{C=C}$ (cm^{-1}) 1587; MS (70 eV) m/z 327 (M$^+$, 5.6), 312 (M$^+$ − Me, 5.2), 254 (M$^+$ − SiMe$_3$, 100), 73 (78.4). Anal. Calc for $C_{16}H_{37}NSi_3$ (M: 327.74): C, 58.64; H, 11.38; N, 4.27; Si, 25.71. Found: C, 58.69; H, 11.42; N, 4.25; Si, 25.70.

Synthesis of α-Alkyl(silyl)methylamines 1. In a 250 mL two-necked round-bottomed flask equipped with a condenser connected to a dryer (potash), a magnetic stirring bar, and a 100 mL pressure-equalizing dropping funnel were introduced enamine **2** (0.1 M), sodium borohydride (0.2 M, 8.8 g), and 100 mL of methanol. From the funnel, trimethylsilyl chloride (0.2 M, 22 g, 30 mL) was dropwise added over a 2 h period. After 4 h of stirring at room temperature, low-boiling materials (methanol, methoxysilane, and excess silyl chloride) were evaporated under vacuum to yield a solid which was dissolved in water (50 mL). Organic impurities were extracted with ether and discarded, and the aqueous layer was basified with solid sodium hydroxide (4 g). The resulting amine was extracted with ether, the solution dried over potassium hydroxide, and the solvent evaporated. Pure amines **1** were obtained through distillation.

1-(Trimethylsilyl)-1-propylamine (1a): bp 48 °C (25 mmHg); ^{1}H NMR δ −0.23 [s, 9H, Si(C**H**$_3$)$_3$], 0.72 [t (^3J = 7.3), 3H, C**H**$_3$], 0.84 [s, D$_2$O exchangeable, N**H**$_2$], 0.98−1.11 [m, 2H, C**H**$_2$], 1.79 [dd (^3J = 9.9 and ^3J = 3.9), 1H, Si−C**H**−N]; ^{13}C NMR δ −3.8 [Si(**C**H$_3$)$_3$], 11.7 [**C**H$_3$], 26.8 [**C**H$_2$]; 43.0 [Si−**C**H−N]; ^{29}Si NMR δ 2.81 [$^2J_{SiMe_3}$ = 6.4 (9H), $^2J_{SiMe_3}$ = 5.7 (1H), $^3J_{SiMe_3}$ = 3.5 (1H), $^3J_{SiMe_3}$ = 2.3 (1H), **Si**(CH$_3$)$_3$]; IR $\nu_{C=C}$ (cm^{-1}) 3306 (NH$_2$); MS (70 eV) m/z 131 (M$^+$, 1.7), 116 (M$^+$ − Me, 5.0), 74 (65.3), 73 (27.6), 58 (M$^+$ − SiMe$_3$, 100). Anal. Calc for C_6H_{17}-NSi (M: 131.29): C, 54.89; H, 13.05; N, 10.67. Found: C, 54.72; H, 12.96; N, 10.48.

1-(Trimethylsilyl)-1-butylamine (1b): bp 63 °C (25 mmHg); ^{1}H NMR δ −0.23 [s, 9H, Si(C**H**$_3$)$_3$], 0.67 [t (^3J = 6.9), 3H, C**H**$_3$], 0.86 [s, D$_2$O exchangeable, N**H**$_2$], 0.99−1.16 [m, 2H, C**H**$_2$],], 1.19−1.33 [m, 2H, C**H**$_2$], 1.9 [dd (^3J = 9.9 and ^3J = 3.5), 1H, Si−C**H**−N]; ^{13}C NMR δ −4.0 [Si(**C**H$_3$)$_3$], 13.8 [**C**H$_3$], 20.0 [**C**H$_2$]; 36.0 [**C**H$_2$]; 43.7 [Si−**C**H−N]; ^{29}Si NMR δ 3.01 [$^2J_{SiMe_3}$ = 6.3 (9H), $^2J_{SiMe_3}$ = 5.8 (1H), $^3J_{SiMe_3}$ = 2.9 (1H), $^3J_{SiMe_3}$ = 3.0 (1H), **Si**(CH$_3$)$_3$]; IR $\nu_{C=C}$ (cm^{-1}) 3300 (NH$_2$); MS (70 eV) m/z 145 (M$^+$, 1.5), 130 (M$^+$ − Me, 0.9), 116 (19.7), 74 (72.3), 73 (48.2), 72 (M$^+$ − SiMe$_3$, 100). Anal. Calc for $C_7H_{19}NSi$ (M: 145.32): C, 57.85; H, 13.18; N, 9.64. Found: C, 57.63; H, 12.99; N, 9.37.

3,3-Dimethyl-1-(trimethylsilyl)-1-butylamine (1c): bp 83 °C (25 mmHg); ^{1}H NMR δ −0.08 [s, 9H, Si(C**H**$_3$)$_3$], 0.84 [s,

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9H, C(C**H**$_3$)$_3$], 1.05 [dd (^2J = 14.7 and ^3J = 8.3), 1H, C**H**$_2$], 1.20 [s, D_2O exchangeable, N**H**$_2$], 1.38 [dd (^2J = 14.7 and ^3J = 1.4), 1H, C**H**$_2$], 2.20 [dd, 1H, (^2J = 8.9 and ^3J = 1.5), 1H, Si−C**H**−N]; ^{13}C NMR δ −4.1 [Si(**C**H$_3$)$_3$], 29.9 [C(**C**H$_3$)$_3$], 31.7 [**C**(CH$_3$)$_3$], 37.8 [**C**H$_2$]; 47.8 [Si−**C**H−N]; ^{29}Si NMR δ 3.6 [$^2J_{SiMe_3}$ = 6.3 (9H), $^2J_{SiMe_3}$ = 5.2 (1H), $^3J_{SiMe_3}$ = 0.9 (1H), $^3J_{SiMe_3}$ = 0.8 (1H), **Si**(CH$_3$)$_3$]; IR $\nu_{C=C}$ (cm^{-1}) 3300 (NH$_2$); MS (70 eV) *m*/*z* 173 (M$^+$, 0.9), 116 (M$^+$ − ^{t}Bu, 100), 100 (M$^+$ − SiMe$_3$, 47.4), 74 (99.5), 73 (87), 57 (74.1). Anal. Calc for $C_9H_{23}NSi$ (M: 173.37): C, 62.35; H, 13.37; N, 8.08. Found: C, 62.11; H, 13.02; N, 7.89.

2-Methyl-1-(trimethylsilyl)-1-propylamine (1d): bp 56 °C (25 mmHg); ^{1}H NMR δ −0.01 [s, 9H, Si(C**H**$_3$)$_3$], 0.83 [d (^3J = 6.9), 3H, C**H**$_3$], 0.89 [d (^3J = 6.9), 3H, C**H**$_3$], 1.76 [m, 1H, MeC**H**], 1.79 [s, D_2O exchangeable, N**H**$_2$], 1.99 [dd (^3J = 4.5), 1H, Si−C**H**−N]; ^{13}C NMR δ −2.3 [Si(**C**H$_3$)$_3$], 18.6 [**C**H$_3$], 21.1 [**C**H$_3$], 31.1 [Me$_2$**C**H], 48.1 [Si−**C**H−N]; ^{29}Si NMR δ 1.99 [$^2J_{SiMe_3}$ = 6.3 (9H), $^2J_{SiMe_3}$ = 6.8 (1H), $^3J_{SiMe_3}$ = 3.1 (1H), **Si**(CH$_3$)$_3$]; IR $\nu_{C=C}$ (cm^{-1}) 3310 (NH$_2$); MS (70 eV) *m*/*z* 145 (M$^+$, 0.7), 130 (M$^+$ − Me, 9.7), 102 (25.4), 74 (M$^+$ − SiMe$_3$, 94.7), 73 (37.7), 72 (100). Anal. Calc for $C_7H_{19}NSi$ (M: 145.32): C, 57.85; H, 13.18; N, 9.64. Found: C, 57.64; H, 13.03; N, 9.41.

2-Methyl-1-(trimethylsilyl)-1-pentylamine (1e): bp 90 °C (25 mmHg); two diastereoisomers were seen on NMR spectra, ^{1}H NMR δ −0.01 and 0.00 [2s, 9H, Si(C**H**$_3$)$_3$], 0.77−0.88 [m, 2 × 3H + 2 × 3H, 2C**H**$_3$], 0.99 [s, 2H, D_2O exchangeable, N**H**$_2$], 1.06−1.44 [m, 4H, C**H**$_2$], 1.55−1.92 [m, 1H, C**H**], 2.03 and 2.13 [2d (^3J = 4.5 and ^3J = 3.1), 1H, Si−C**H**−N]; ^{13}C NMR δ −2.3 and −2.1 [Si(**C**H$_3$)$_3$], 14.2, 14.3, 15.7 and 17.6 [**C**H$_3$], 20.5, 20.5, 35.3 and 35.3 [**C**H$_2$], 36.8 and 36.9 [**C**H], 45.4 and 48.0 [Si−**C**H−N]; ^{29}Si NMR δ 2.1 and 2.3 [**Si**(CH$_3$)$_3$]; IR $\nu_{C=C}$ (cm^{-1}) 3311 (NH$_2$); MS (70 eV) *m*/*z* 173 (M$^+$, 0.7), 158 (M$^+$ − Me, 1.6), 102 (12.3), 100 (56.7), 74 (94.7), 73 (37.7), 72 (M$^+$ − SiMe$_3$, 100). Anal. Calc for $C_9H_{23}NSi$ (M: 173.37): C, 62.35; H, 13.37; N, 8.08. Found: C, 62.21; H, 13.24; N, 7.96.

(Cyclopentyl)(trimethylsilyl)methylamine (1g): bp 75 °C (25 mmHg); ^{1}H NMR δ −0.23 [s, 9H, Si(C**H**$_3$)$_3$], 1.27−1.69 [m, 11H, 9H$_{ring}$ + N**H**$_2$], 1.81 [d (^3J = 7.1), 1H, Si−C**H**−N]; ^{13}C NMR δ −2.9 [Si(**C**H$_3$)$_3$], 25.1, 25.4, 29.6 and 30.2 [**C**H$_{2ring}$], 44.0 [**C**h$_{ring}$], 45.6 [Si−**C**H−N]; ^{29}Si NMR δ 2.8 [$^2J_{SiMe_3}$ = 6.2 (9H), $^2J_{SiMe_3}$ = 5.6 (1H), $^3J_{SiMe_3}$ = 2.6 (1H), **Si**(CH$_3$)$_3$]; IR $\nu_{C=C}$ (cm^{-1}) 3307 (NH$_2$); MS (70 eV) *m*/*z* 171 (M$^+$, 2.5), 102 (M$^+$ − C_5H_9, 100), 74 (86.4), 73 (41.9), 69 (47.6). Anal. Calc for C_9H_{21}-NSi (M: 171.36): C, 63.08; H, 12.35; N, 8.17. Found: C, 62.91; H, 12.04; N, 7.96.

(Cyclohexyl)(trimethylsilyl)methylamine (1h): bp 84 °C (25 mmHg); ^{1}H NMR δ −0.00 [s, 9H, Si(C**H**$_3$)$_3$], 0.98−1.72 [m, 13H, 11H$_{ring}$ + N**H**$_2$], 1.97 [d, (^3J = 4.3), 1H, Si−C**H**−N]; ^{13}C NMR δ −2.2 [Si(**C**H$_3$)$_3$], 26.3, 26.5, 29.1 and 31.3 [**C**H$_{2ring}$], 41.9 [**C**H$_{ring}$], 47.6 [Si−**C**H−N]; ^{29}Si NMR δ 2.3 [$^2J_{SiMe_3}$ = 6.4 (9H), $^2J_{SiMe_3}$ = 6.9 (1H), $^3J_{SiMe_3}$ = 2.9 (1H), **Si**(CH$_3$)$_3$]; IR $\nu_{C=C}$ (cm^{-1}) 3306 (NH$_2$); MS (70 eV) *m*/*z* 185 (M$^+$, 1.5), 112 (M$^+$ − SiMe$_3$, 100), 102 (M$^+$ − C_6H_{11}, 50.3), 74 (86.4), 73 (41.9), 69 (47.6). Anal. Calc for $C_{10}H_{23}NSi$ (M: 185.38): C, 64.79; H, 12.51; N, 7.56. Found: C, 64.64; H, 12.36; N, 7.34.

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