N-Silylation of Amines Mediated by Et3SiH/KO*t*Bu

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Dedicated to Professor Philippe Renaud on the occasion of his 60th birthday

Silylation of primary and secondary amines is reported, using triethylsilane as the silylating reagent in the presence of potassium *tert*-butoxide (KOtBu). The reaction proceeds well in the presence of 0.2 equiv of KO*t*Bu. In competition experiments, aniline is selectively silylated over aliphatic amines. Computational studies support a catalytic mechanism which is initiated by KOtBu interacting with the silane to form KH and silylated amine. The KH then takes over the role of base in the propagation of the cyclic mechanism, and deprotonates the amine. This reacts with R3SiH to afford the product R3SiNR'R" and regenerate KH.

Keywords: KOtBu • N-silylation • dehydrogenation • transition metal-free • catalysis

Introduction

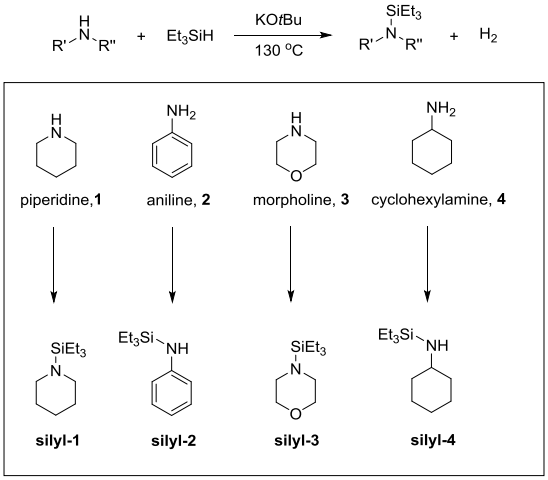
Silicon chemistry plays a significant role in modern industry, with silicon being used extensively to make silicones as well as alloys, including aluminum-silicon and iron-silicon. It is also widely used as a semiconductor in electronic devices.[1] Recently, significant attention has focused on the formation of silicon-heteroatom (nitrogen, oxygen, sulfur) bonds. Silazanides, featuring silicon-nitrogen bonds, have been used as bases,[2] ligands in coordination chemistry[3] and protecting groups in chemical synthesis.[4-7] Historical approaches for formation of silazanides, based on condensation between chlorosilanes and amines, present the drawback of generating corrosive HCl as by-product and considerable amounts of salts.[8] In recent years, these methods are complemented by protocols based on a cross-dehydrogenative coupling of hydrosilanes and amines, with H_2 being the exclusive by-product of the catalytic process. In this regard, a comprehensive review of catalytic bond formation reactions for silicon-nitrogen (and other heteroatoms) has been published by Kuciński and Hreczycho in 2017.[9] Several catalytic processes have been developed over the years to obtain compounds containing the Si-N bond. These include processes mediated by alkali metals and alkaline earth metals (such as Ba, Mg, Ca and Sr)[10-16] transition metals (Rh, Zn, Ru),[5,6,17] metal nanoparticles[18,19] and main group compounds.[20,21] Generating O-Si bonds by mild cross dehydrogenative methods has also been the focus of recent attention. Weickgenannt and Oestreich showed in 2009 that potassium *tert*-butoxide can act catalytically in the dehydrocoupling of hydrosilanes with alcohols[22] while Grubbs et al have exploited similar couplings with NaOH[23,24] and Vanucci et al. have likewise used K2CO3.[25]
The most intriguing recent development in silicon chemistry may well be the use of the Et_3SiH/KO*t*Bu system, which has been extensively developed by Stoltz, Grubbs et al. to address a number of remarkable reactions, such as the conversion of arenes and heteroarenes into regioselectively silyl-substituted products and the reductive cleavage of C-S and C-O bonds in aryl thioethers and aryl ethers, respectively.[26-31] The combination of Et_3SiH and KO*t*Bu leads to triethylsilyl radicals which are very likely to play a major role in these reactions, although non-radical routes may also contribute, especially in the silylation process. Although a broad network of reactions involving several intermediates and mechanisms has been proposed, the mechanistic diversity of this pair of reagents is still puzzling. We recently reported the Et_3SiH/KO*t*Bu reagent in reductions of arenes and in cleavage of C-N bonds.[32] In this paper, we report our experimental and computational studies on the use of this reagent pair to silylate amines. Our publication at this stage is prompted by the appearance of a very recent patent in this area.[33]

Results and Discussion

Initially, representative (aliphatic, aromatic and heterocyclic) primary and secondary amines (substrates **1**-**4**, Scheme 1, inset) were treated with Et_3SiH and KO*t*Bu at 130 °C for different durations. All amines were silylated on the N atom in good yields (55 - 64 %) after 18 h using 3 equiv. of both KO*t*Bu and Et_3SiH. The products are known to be unstable to routine chromatography and so they were characterized by NMR, GC-MS and IR spectroscopy.
The cross-dehydrogenative coupling of triethylsilane and all the substrates also took place when only 0.2 equiv. of KO*t*Bu were used, indicating that the *tert*-butoxide base acts catalytically or acts as initiator of a chain reaction. In these cases, higher yields were obtained (70-87 %), but as the lower quantity of base allows the reaction mixture to be more easily stirred (less solid is present), this may be due to a more effective stirring of the reaction mixture.
N-silylation of **1**-**4** also occurred on decreasing reaction time to 3 h (Table 1). Interestingly, disilylation of the nitrogen atom on primary amines **2** and **4** was possible, but was not observed in any case under our conditions, as confirmed by GCMS and ^{1}H NMR. The ^{1}H NMR signals corresponding to N-

H were seen in the spectra of **silyl-2** and **silyl-4** and the integrals of the silyl groups indicate monosilylated product.

When the reactions were carried out with NaO*t*Bu as base, no silylated products were produced, while NaH was found to be effective, although in low-to-moderate yields (see Table S1 in SI file). Interestingly, KH was also ineffective in producing silylated products and this point comes up for comment later in the paper.[34-36]



Scheme 1. Potassium *tert*-butoxide-mediated N-silylation of amines **1-4**[1]

Table 1. N-silylation of amines by the Et_3SiH/KO*t*Bu system.

Entry	Substrate	Time	Base equiv.	Silylated product[a]	Remaining substrate
1	**1**	18 h	3	64 %	-
2	**1**	18 h	0.2	75 %	-
3	**1**	3 h	0.2	66 %	traces
4	**2**	18 h	3	62 %	-
5	**2**	18 h	0.2	87 %	-
6	**2**	3 h	0.2	74 %	traces
7	**3**	18 h	3	58 %	-
8	**3**	18 h	0.2	80 %	-
9	**3**	3 h	0.2	67 %	-
10	**4**	18 h	3	55 %	-
11	**4**	18 h	0.2	72 %	-
12	**4**	3 h	0.2	71	-

[a] Conversion of substrates was determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene as an internal standard.

The conversion of the amines **1-4** to silyl derivatives as a function of time in the presence of KO*t*Bu (0.2 equiv), was monitored by ^{1}H-NMR. Different reaction profiles were observed for the various amines (Figure 1) with piperidine **1** and morpholine **3** being fully converted into **silyl-1** and **silyl-3**, respectively, within 1 h of reaction start, whereas it took 2 h for cyclohexylamine, **4**, to be completely monosilylated.

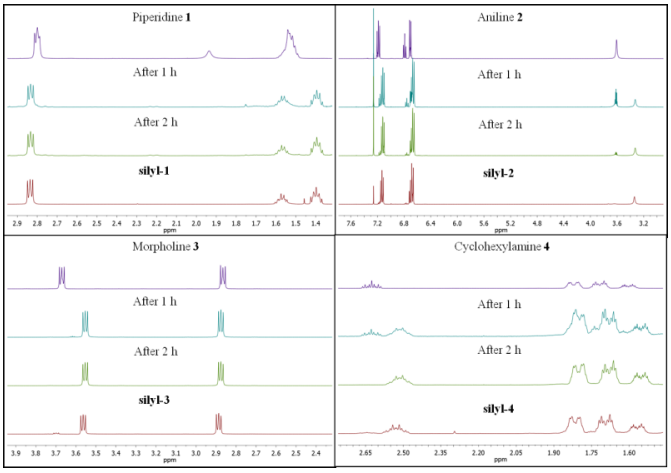


Figure 1. Conversion profiles displayed by amines **1-4**, and followed by ^{1}H-NMR, using 3 equiv. of Et_3SiH and 0.2 equiv. of KO*t*Bu.

To probe for selective silylations, competitive reactions using two different amines from our list were carried out. The results are shown in Table 2. When aniline **2** (1 equiv) was mixed with any other amine (1 equiv), KO*t*Bu (0.2 equiv) and silane (3 equiv), only aniline was silylated (Entries 1-3). To check whether a rapidly silylated aliphatic amine could transfer a silyl group to aniline in these mixtures, competitive reactions were performed involving (**silyl-1** or **silyl-4**) together with aniline **2** to investigate a possible transfer of the triethylsilyl group from **silyl-1** or **silyl-4** to **2**. However, the desilylation of piperidine or cyclohexylamine and the subsequent silylation of aniline did not occur.

Table 2. Competitive reactions between two substrates using 3 equiv. of Et_3SiH and 0.2 equiv. of KO*t*Bu, 3h, 130 °C

Entry	Amine **A**	Amine **B**	Silylated amine **A**	Silylated amine **B**
1	**2**	**1**	73 %	0 %
2	**2**	**3**	68 %	0 %
3	**2**	**4**	78 %	0 %
4	**1**	**3**	76 %	74 %
5	**1**	**4**	74 %	77 %
6	**3**	**4**	72 %	63 %

The proposed mechanisms for the silylation of amines with alkaline earth metal catalysts typically include a deprotonation step of the amine substrate before the nitrogen-silicon bond is formed.[7] In analogy to this class of reactions, several pathways leading to the deprotonation of the aliphatic amine substrates were investigated computationally (Scheme 2; as a starting point trimethylsilane was used instead of triethylsilane for computational economy). It was found, as expected, that the direct deprotonation of aliphatic amines with KO*t*Bu is thermodynamically unfavourable[37] (Scheme 2 'Direct Deprotonation' and Table S3). A more accessible energy profile was identified for the reaction of potassium *tert*-butoxide **8** with trimethylsilane **5** to generate potassium hydride **9**. The subsequent deprotonation of the amine substrates **6** with this hydride is

highly efficient (Step A in Scheme 2). (The direct deprotonation of an amine with potassium *tert*-butoxide **8** is only possible for aniline substrates, see SI). This finding suggests that the silylation of aliphatic amines with the KO*t*Bu-Et_3SiH reagent system critically hinges on potassium hydride. Thus, it appears plausible to draw the mechanism of this reaction with potassium hydride as the actual catalytic species. This may initially seem curious, as commercial KH was not effective in promoting the reactions in the laboratory. However, a strong difference in reactivity between a free KH molecule and the commercial solid aggregate is expected.[34-36]

The energy profile of the proposed mechanism has been calculated for four model substrates, **2** and **6a-c**. Aniline **2** and dimethylamine **6a** represent typical aromatic and aliphatic amines, while the silylated amines **6b** , **6c** can be used to explore the energetics of further silylation.

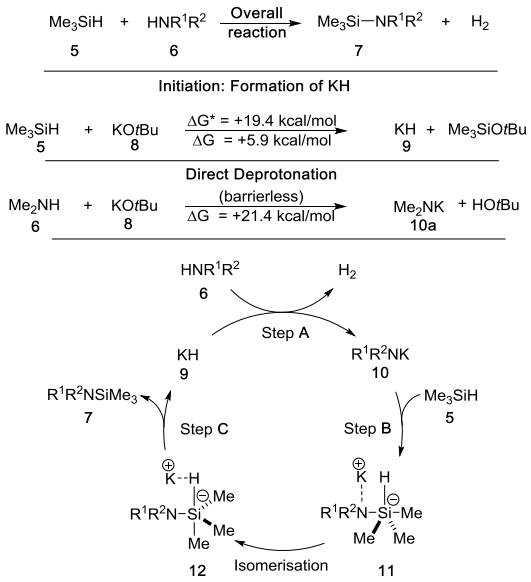
$PhNH_2$	Me_2NH	$(Me_3Si)MeNH$	$(Me_3Si)PhNH$
2	**6a**	**6b**	**6c**

As has been discussed, potassium hydride **9** efficiently deprotonates the amine substrates **6**. The potassium amide **10** then adds to the silane reagent **5** (step B) to form the pentavalent silicate species **11**. After an isomerization that features a nearly thermoneutral Berry pseudorotation (which moves the attacking amide nitrogen atom out of the axial position and the leaving hydrogen atom of the departing hydride into an axial position) to **12**, this species eliminates potassium hydride **9**. Thereby, the silylated product **7** is formed and the catalytic cycle is closed.

Comparing the energy profiles for the model substrates **2** and **6a** (Table 3) gives a clear explanation for the selective silylation of aniline reported above. The silylation of each aliphatic amine is dependent on the formation of the corresponding potassium amide. The deprotonation of aniline **2** is much more favourable than the deprotonation of **6a** and can even be achieved by KOtBu. In a direct competition experiment between aniline and an aliphatic primary or secondary amine, it is aniline **2** that is deprotonated and subsequently silylated.

The computational model based on the simple substrates provides interesting information. For anilines, while the first silylation to give **6c** + KH from **2** is possible, no feasible energy profile was found for the second silylation to give **7c** (R^1 = Ph, R^2 = $SiMe_3$) + KH. In fact, the intermediate **11c** is not a stable structure (i.e. there is no local minimum on the hyper energy surface that would correspond to **11c**). This implies that the reaction cannot proceed. On the other hand, in relation to the aliphatic amine, methylamine, conversion of its monosilylated derivative **6b** to its disilylated derivative **7b** + KH is shown. Step B is endergonic but it features a valid transition state, and rapid subsequent use of KH in the next cycle can make it viable.

These experimental findings indicate that it depends on the exact nature of the amine substrate whether the reaction stops after the first silylation or proceeds to a second silylation. To better understand the factors influencing the balance between mono and double silylation of primary



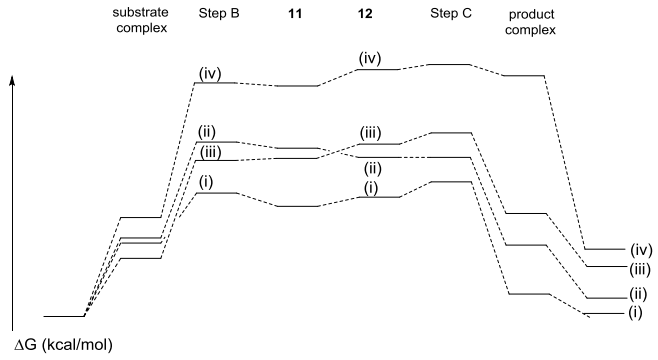
Amine Step **A**	**2** R^1=H; R^2=Ph	**6a** R^1=R^2=Me	**6b** R^1=Me; R^2=$SiMe_3$	**6c** R^1=$SiMe_3$, R^2=Ph
ΔG*	2.7	9.8	7.2	2.0
ΔG	-18.2	0.2	-7.6	-18.3
Step **B**				
ΔG*	16.1	7.9	13.9	No T.S.
ΔG	15.6	2.2	12.4	**11c** not stable
Step **C**				-
ΔG*	5.9	1.8	2.3	-
ΔG	-6.4	-11.7	-13.3	
Overall Reaction				
ΔG*	20.1	9.8	15.4	n.a.
ΔG	-9.8	-7.9	-7.6	-6.3

(All energies are in kcal mol^{-1}).

Scheme 2 and Table 3. Proposed mechanism for the silylation of amines with the KO*t*Bu-Et_3SiH reagent system. [a] **11c** is not a stable structure. Thus, the reaction cannot proceed.

aliphatic amines, a more extensive computational model was employed (see Figure 2 and also Figure S2 and S5). It was found that steric factors have a critical impact on the reaction. As can be expected, the energy barrier increases with increasing steric bulk. But only a moderate increase was observed when increasing the steric bulk on the silyl groups; changing the methyl groups for ethyl groups led to a moderate increase of the rate determining step from 15.4 kcal/mol to 17.6 kcal/mol, respectively [Path (i) and Path (ii)]. A marked increase of the rate-determining barrier height was observed for *n*-propyl (iii) as a larger aliphatic residue on the amine. The activation barrier for the analogous reaction with *i*-propylamine (iv) was found to be even higher. In fact, the second silylation of the *i*-propylamine substrate is predicted to have a barrier that is 5.1 kcal/mol

higher than the second silylation of the *n*-propylamine substrate, which makes this reaction >500-times slower.



(i)	0.00	8.7	13.9*	12.4	13.1	**15.4***	5.0	0.0
(ii)		8.8	**19.1***	18.3	17.2	17.6*	8.3	1.8
(iii)		7.1	16.6*	17.0	20.1	**22.5***	10.7	5.6
(iv)		9.5	25.7*	25.6	27.2	**27.6***	26.8	10.3

Figure 2. The four most accessible energy profiles for the key steps B and C as shown in Scheme 2 for substrates with increasing steric bulk; (i): $Me_3SiN(Me)H$ and Me_3SiH, (ii): Et_3SiH and $Et_3SiN(Me)H$ (iii): Et_3SiH and $Et_3SiN(nPr)H$, (iv): $Et_3SiN(iPr)H$ and Et_3SiH

In summary, computational studies align with laboratory experiments in supporting the feasibility of silylation of primary and secondary amines with KOtBu as base and with a trialkylsilane as silylating agent. The reaction is somewhat sensitive to steric effects and likely proceeds through a catalytic cycle in which KH is generated.

Experimental Section

General Text

All chemicals were commercially available and used without additional purification. ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ as solvent on a Bruker AV3 at 400 and 100 MHz, respectively, and the NMR chemical shifts are referenced in ppm from an internal solvent peak. Signal multiplicities are abbreviated as: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; bs, broad singlet. Coupling constants are given in Hertz (Hz)

The silylation reactions were performed in a glove box (Innovative Technology Inc., USA) under nitrogen atmosphere (O_2 < 1 ppm). All reagents introduced into the glove box were transferred through the port, which was evacuated and purged with nitrogen ten times before entry.

The mass spectra were recorded by gas-phase chromatography (GC-MS) using electron ionization (EI). Low resolution GC-MS data were recorded using an Agilent Technologies 7890A GC system coupled to a 5975C inert XL EI/CI MSD detector. Separation was performed using the DB5MS-UI column (30 m x 0.25 mm x 0.25 µm) at a temperature of 320 °C, using helium as the carrier gas. Chloroform was used as a solvent in all GC-MS analyses.

Infra-Red spectra were recorded on an ATR-IR spectrometer. High-resolution mass spectrometry (HRMS) was performed at the National Mass Spectrometry Centre, Swansea. Accurate mass was obtained using atmospheric pressure chemical ionisation (APCI), electron ionisation (EI) and nanospray ionisation (NSI) with an LTQ Orbitrap XL mass spectrometer.

General procedure for N-silylation of substrates 1-4

The amine (0.50 mmol, 1.0 equiv.), triethylsilane (0.24mL, 1.5mmol, 3.0equiv.) and potassium *tert*-butoxide (168 or 11 mg , 1.50 or 0.1 mmol, 3.0 or 0.2 equiv.) were sealed in a pressure tube in a glove box under nitrogen. The tube was removed and heated at 130 °C for different durations behind a safety shield. After cooling to room temperature, the mixture was diluted with water and extracted into diethyl ether. The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. When only 0.2 equiv. of the base were used, reactions were quenched by addition to $CDCl_3$ without doing any extraction with water in order to obtain more accurate conversion values.

This general procedure has been also followed when other bases (NaH, KH, NaO*t*Bu) were used in place of KO*t*Bu. Samples for GCMS experiments were prepared by dissolving a small amount (< 1 mg/mL) of the crude reaction mixture in chloroform.

Procedure for N-silylation of amines **1-5** as a function of time followed by ^1H-NMR

The amine (0.50 mmol, 1.0 equiv.), triethylsilane (0.24mL, 1.5mmol, 3.0equiv.) and potassium *tert*-butoxide (11 mg , 0.1 mmol, 0.2 equiv.) were sealed in a pressure tube in a glove box under nitrogen. The reaction was entirely performed in the glovebox at 130 °C and ^1H-NMR spectra of reaction mixture aliquots were acquired every 30 min.

Procedure for competitive reactions

Amine A (0.50 mmol, 1.0 equiv.), amine B (0.50 mmol, 1.0 equiv.), triethylsilane (0.24mL, 1.5mmol, 3.0equiv.) and potassium *tert*-butoxide (11 mg , 0.1 mmol, 0.2 equiv.) were sealed in a pressure tube in a glove box under nitrogen. The tube was removed and heated at 130 °C for different durations behind a safety shield. After cooling to room temperature, the mixture was diluted with water and extracted into diethyl ether. The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure.

Procedure for competitive reactions involving (**silyl-1** or **silyl-4**) together with aniline **2**

Silyl-1 or **silyl-4** (1 mmol, 2.0 equiv.), aniline **2** (0.50 mmol, 1.0 equiv.), and potassium *tert*-butoxide (11 mg , 0.1 mmol, 0.2 equiv.) were sealed in a pressure tube in a glove box under nitrogen. The tube was removed and heated at 130 °C for different durations behind a safety shield. After cooling to room temperature, the mixture was diluted with water and extracted into diethyl ether. The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure.

Conversion of substrates

Conversion of substrates was determined by ^{1}H-NMR using 1,3,5-trimethoxybenzene (10 %) as internal standard. Reactions were directly quenched by adding to $CDCl_3$. The quantity of each product was determined as follows:

- (example calculation Table 1, Entry 2): for the product **silyl-1** the integration of the methoxy signals of the internal standard in the ^{1}H-NMR spectrum (δ3.78 ppm) was set to 9 units.

The integration of the signal corresponding to the two methylene groups next to the N atom of **silyl-1** at δ2.85 ppm (2 × CH_2, 4 H) was then measured and the following calculation gave the amount of **silyl-1** present: (30.15/4) x 10 = 75 %

- (example calculation Table 1, Entry 5): for the product **silyl-2** the integration of the methoxy signals of the internal standard in the ^{1}H-NMR spectrum (δ3.78 ppm) was set to 9 units.

The integration of the signal corresponding to the two *ortho* aromatic protons of **silyl-2** at δ7.18 – 7.14 ppm (2 H) was then measured and the following calculation gave the amount of **silyl-2** present: (17.45/2) x 10 = 87 %

- (example calculation Table 1, Entry 8): for the product **silyl-3** the integration of the methoxy signals of the internal standard in the ^{1}H-NMR spectrum (δ3.78 ppm) was set to 9 units.

The integration of the signal corresponding to the two methylene groups next to the O atom of **silyl-3** at δ3.58 – 3.55 ppm (2 × CH_2, 4 H) was then measured and the following calculation gave the amount of **silyl-3** present: (31.84/4) x 10 = 80 %

- (example calculation Table 1, Entry 11): for the product **silyl-4** the integration of the methoxy signals of the internal standard in the ^{1}H-NMR spectrum (δ3.78 ppm) was set to 9 units.

The integration of the signal corresponding to proton next to the amino group of **silyl-4** at δ2.57 – 2.49 ppm (1 H) was then measured and the following calculation gave the amount of **silyl-4** present: (7.18/1) x 10 = 72 %

Characterisation of products

N-triethylsilylpiperidine (Silyl-**1**). The general procedure was followed ,using piperidine **1** (42.6 mg, 49.4 µL). δ_H (400 MHz, $CDCl_3$): 2.85 – 2.82 (4H, m, 2 × *CH*$_2$), 1.59 – 1.55 (2H, m, *CH*$_2$), 1.43 – 1.37 (4H, m, 2 × *CH*$_2$), 0.94 (9H, t, *J* = 7.6 Hz, 3 × *CH*$_3$), 0.54 (6H, q, *J* = 8.0 Hz, 3 × *CH*$_2$). δ_C (100 MHz, $CDCl_3$): 3.6, 6.8, 25.2, 27.6, 46.3. IR (NEAT) ν (cm^{-1}) = 667, 688, 725, 851, 949, 1003, 1059, 1236, 2874, 2911, 2932, 2951. GC-MS [*m/z* (%)]: 199.2 (20, M^+), 170.2 (100), 142.2 (22), 112.1 (11), 87.1 (37), 59.1 (63). The data are consistent with the literature.[38]

N-triethylsilylaniline (Silyl-**2**.) The general procedure was followed using aniline **2** (46.6 mg, 45.6 µL). δ_H (400 MHz, $CDCl_3$): 7.18 – 7.14 (2H, m, Ar*H*), 6.75 – 6.68 (3H, m, Ar*H*), 3.36 (1H, s, *NH*), 1.02 (9H, t, *J* = 7.6 Hz, 3 × *CH*$_3$), 0.79 (6H, q, *J* = 8.0 Hz, 3 × *CH*$_2$). δ_C (100 MHz, $CDCl_3$): 4.1, 6.5, 115.6, 116.9, 128.7, 147.2. IR (NEAT) ν (cm^{-1}) = 671, 691, 720, 746, 770, 887, 997, 1290, 1385, 1476, 1497, 1601, 2874, 2953. GC-MS [*m/z* (%)]: 207.2 (43, M^+), 178.2 (100), 150.1 (68), 122.1 (70), 120.1 (76), 92.2 (18), 79.1 (30), 59.1 (15). The data are consistent with the literature.[39]

N-triethylsilylmorpholine (Silyl-**3**). The general procedure was followed, using morpholine **3** (43.6 mg, 43.7 µL). δ_H (400 MHz, $CDCl_3$): 3.58 – 3.55 (4H, m, 2 × *CH*$_2$), 2.88-2.90 (4H, m, 2 × *CH*$_2$), 0.95 (9H, t, *J* = 8.0 Hz, 3 × *CH*$_3$), 0.56 (6H, q, *J* = 8.0 Hz, 3 × *CH*$_2$). δ_C (100 MHz, $CDCl_3$): 3.3, 6.7, 45.5, 68.2. IR (NEAT) ν (cm^{-1}) = 677, 723, 839, 970, 1015, 1101, 1238, 1458, 2874, 2911, 2953. GC-MS [*m/z* (%)]: 201.2 (16, M^+), 172.2 (100), 144.1 (19), 114.1 (45), 87.1 (70), 59.1 (91). The data are consistent with the literature.[40]

N-triethylsilylcyclohexylamine (Silyl-**4**). The general procedure was followed, using cyclohexylamine **4** (49.6 mg, 57.2 µL). δ_H (400 MHz, $CDCl_3$): 2.57 – 2.49 (1H, m, *CH*), 1.85 – 1.82 (1H, m, *CH*), 1.81 – 1.79 (1H, m, *CH*), 1.72 – 1.71 (1H, m, *CH*), 1.69 – 1.67 (1H, m, *CH*), 1.59 – 1.54 (1H, m, *CH*), 1.31 – 1.27 (1H, m, *CH*), 1.25 – 1.21 (1H, m, *CH*), 1.17 - 1.09 (1H, m, *CH*), 1.07 - 1.02 (2H, m, 2 × *CH*), 0.95 (9H, t, *J* = 8.0 Hz, 3 × *CH*$_3$), 0.52 (6H, q, *J* = 8.0 Hz, 3 × *CH*$_2$), 0.33 (1H, bs, *NH*). δ_C (100 MHz, $CDCl_3$): 4.6, 6.7, 25.2, 25.4, 38.6, 50.1. IR (NEAT) ν (cm^{-1}) = 667, 685, 715, 724, 822, 858, 1011, 1117, 1234, 1406, 1449, 2851, 2874, 2926, 2949. GC-MS [*m/z* (%)]: 213.3 (15, M^+), 184.2 (100), 170.2 (48), 142.1 (6), 128.1 (8), 115.2 (7), 100.1 (7), 87.1 (14), 59.1 (15). HRMS (APCI) calcd for $C_{12}H_{26}NSi$ $[M-H]^+$: 212.1829, found: 212.1828.

Supplementary Material

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/MS-number.

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Author Contribution Statement

FP performed the laboratory experiments and SR performed the computational experiments. JAM and TT supervised the work. FC, SR and JAM wrote the article. All authors commented on the manuscript.

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Entry for the Table of Contents

N-Silylation of Amines Mediated by Et_3SiH/KO*t*Bu

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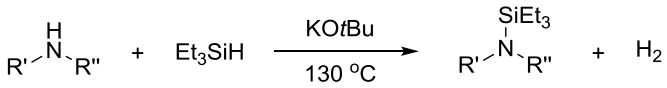

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