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COUNTERATTACK REAGENTS: HEXAMETHYLDISILANE AND 1,2-DIMETHYL-1,1,2,2-TETRAPHENYLDISILANE IN THE SYNTHESIS OF POLYSILYLATED HYDRAZINES

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Abstract — Polysilylated hydrazines have wide applicability. It is tedious to prepare these compounds by classic means. However, using hexamethyldisilane and 1,2-dimethyl-1,1,2,2-tetraphenyldisilane as counterattack reagents, we synthesized polysilylated hydrazines under alkaline conditions in good to excellent yields. This one-pot method is expedient and more efficient than other procedures. Polysilylated hydrazines were found to react with aldehydes or ketones in the presence of a catalytic amount of trimethylsilyl trifluoromethanesulfonate to give the corresponding hydrazones under anhydrous conditions.

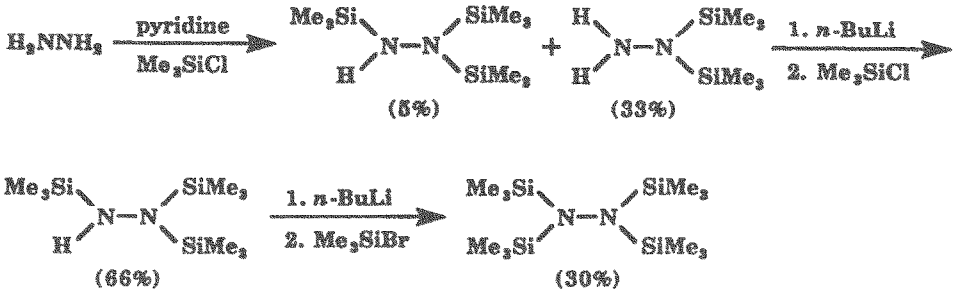
INTRODUCTION

Polysilylated hydrazines are ideal starting materials for the generation of various organic species. Examples of their application include photolysis of tetrakis(trimethylsilyl)-hydrazine to provide bis(trimethylsilyl)aminyl radical;[1] condensation of 1,1-bis-(trimethylsilyl)-2,2-dimethylhydrazine with chloroformate, phosgene,[2] or fluorophosgene[3] to give hydrazodicarboxylates; reaction of disilylated 4-amino-1,2,4-triazole with thionyl chloride to afford a (sulfinylamino)triazole;[4] and metallation of fully silylated hydrazine to produce dinitrogen-containing organometallic complexes.[5]

In spite of the wide applicability of polysilylated hydrazines, their preparation is tedious. The typical procedure involves sequential silylations of the nitrogens by separate reactions.[6-11] Furthermore, strong bases such as *n*-butyl- or phenyllithium are commonly employed.[6-9] Scheme 1 depicts a classic method for the preparation of tetrakis(trimethylsilyl)hydrazine.[8] It includes three steps, utilizes two different bases, requires the strong silylating agent Me_3SiBr, and gives the desired product in ~ 8% overall yield. Herein we report an efficient, "one-pot" method for the synthesis of a variety of

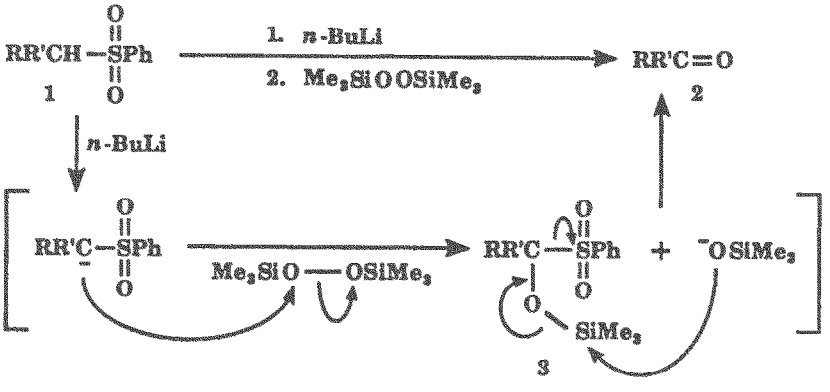
silylated hydrazines under mild conditions. This method employs hexamethyldisilane and 1,2-dimethyl-1,1,2,2-tetraphenyldisilane as "counterattack reagents."

Scheme 1



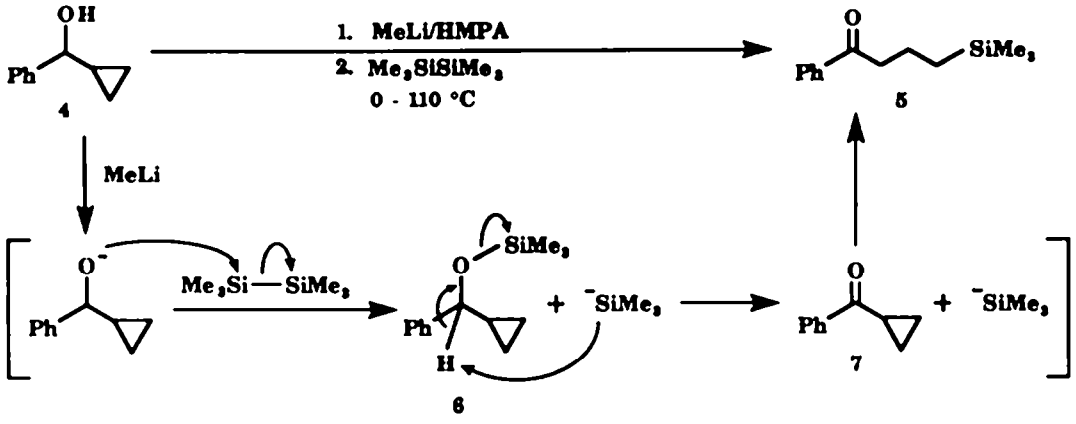
Counterattack reagents generally contain a leaving group that reattacks a stable intermediate generated in situ.[12] Through the use of a counterattack reagent, two or more reactions can be made to occur in a single pot. The reattacking species, i.e. the original leaving group, can be a nucleophile. An example is Me_3SiO^- in the oxidative desulfonylation of phenyl sulfones (1) to ketones or aldehydes (2) (Scheme 2).[13] This nucleophile, liberated from the counterattack reagent $Me_3SiOOSiMe_3$, reattacks the stable intermediate α-siloxy sulfone (3) to give 2 in 66-91% yield.

Scheme 2



On the other hand, the reattacking species can also be a strong base. Then it removes acidic protons from the intermediate. In the "one-pot" conversion of α-cyclopropylbenzyl alcohol (4) into γ-trimethylsilylbutyrophenone (5) via cyclopropyl phenyl ketone (7) (Scheme 3),[12] Me_3Si^- first serves as a leaving group in the counterattack reagent $Me_3SiSiMe_3$. Subsequently Me_3Si^- abstracts an acidic proton in the intermediate benzyl silyl ether (6) to afford ketone 7. With the same strategy, we were able to polysilylate hydrazines in one reaction.

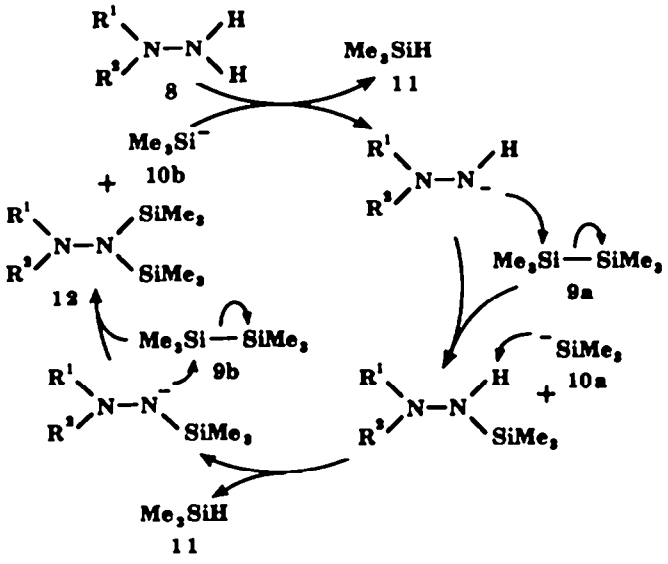
Scheme 3



RESULTS AND DISCUSSION

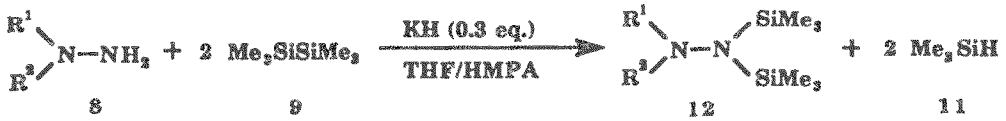
Scheme 4 illustrates our design for the preparation of polysilylated hydrazines **12** (Scheme 5) from hydrazines **8** and $Me_3SiSiMe_3$ (**9**) under alkaline conditions. The disilane, $Me_3SiSiMe_3$, plays a dual role in this reaction: silylating agent and source of base. In the overall process, proton abstraction alternates with silylation. This alternation repeated four times would convert H_2NNH_2 to $(Me_3Si)_2NN(SiMe_3)_2$ without isolation of any intermediate.

Scheme 4



The entire process shown in Scheme 4 constitutes a catalytic cycle. Trimethylsilyl anion (**10b**), resulting from **9b**, could trap a proton from the starting material (**8**).[14,15] Thus, only a catalytic amount of base should be required to complete the reaction shown in Scheme 5.

Scheme 5



According to the design shown in Scheme 4, we have successfully prepared a variety of silylated hydrazines in good to excellent yields (Table I). A typical experimental procedure is as follows.

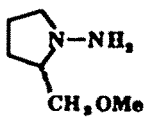
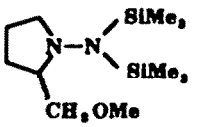
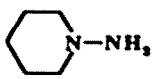
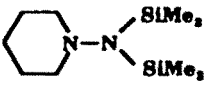
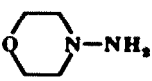
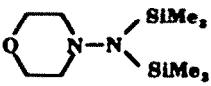
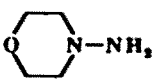
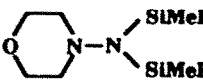
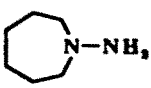
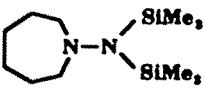
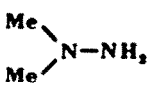
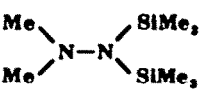
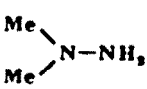
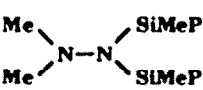
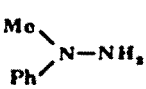
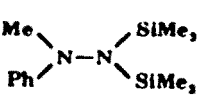
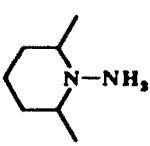
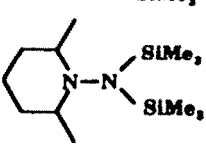
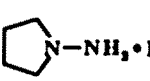
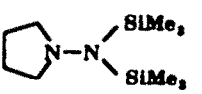
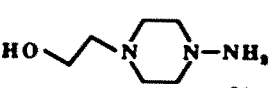
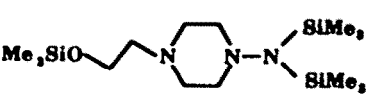
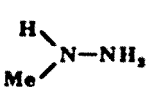
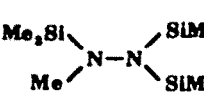
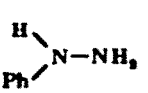
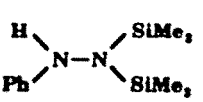
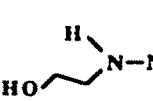
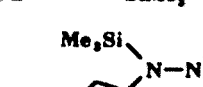
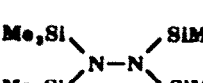
A solution of hydrazine (**8**) in THF under an atmosphere of nitrogen was treated with 0.3 equivalent of KH at 0 °C, followed by warming to room temperature for one hour. To this pale yellow suspension were added HMPA[16] and a slight excess of $Me_3SiSiMe_3$. The number of equivalents of $Me_3SiSiMe_3$ employed was based on the number of acidic protons in substrate **8** (see Table I). After 24 hours, the reaction was worked up under normal conditions and the crude product was chromatographed through silica gel to provide the pure polysilylated product (**12**).

We obtained excellent yields for the silylation of hydrazines with one nitrogen atom in a ring (see Table I, entries 1-5). Examples include (*S*)-(-)-1-amino-2-(methoxymethyl)pyrrolidine (**13a**, 94%), 1-aminopiperidine (**14a**, 92%), 4-aminomorpholine (**15a**, 90%), and 1-aminohomopiperidine (**16a**, 97%). For acyclic substrates, 1,1-dimethylhydrazine (**17a**, entry 6) was silylated almost quantitatively (99%); however the yield for 1-methyl-1-phenylhydrazine (**18a**, entry 8) was only 51%. The lower yield may be attributable to competing reactions: abstraction of an ortho proton in the benzene ring[17] by Me_3Si^- and transfer of an electron from Me_3Si^- to the aromatic nucleus of the substrate.[18,19] To test the latter assumption, 4-nitrophenylhydrazine was subjected to the same reaction conditions. Kornblum et al. have shown that the nitrophenyl group is an excellent electron acceptor.[20] As expected, we did not detect any silylated products.

We extended this efficient silylation method to a hindered hydrazine, 1-amino-2,6-dimethylpiperidine (**19a**, entry 9, 91%). For the hydrochloride salt of a hydrazine, potassium hydride was not capable of liberating the free hydrazine. Consequently, we used *n*-butyllithium in the silylation of 1-aminopyrrolidine hydrochloride (**20a**, entry 10). The corresponding silylated compound (**20b**) was obtained in 87% yield.

Use of hexamethyldisilane via a repetitive counterattack process can exhaustively silylate hydrazines that contain more than two acidic protons. These hydrogens may be attached to nitrogen or oxygen atoms. Thus 1-amino-4-(2-hydroxyethyl)piperazine (**21a**, entry 11) and methylhydrazine (**22a**, entry 12) underwent a "double-counterattack" process to give trisilylated products **21b** (70%) and **22b** (93%), respectively.

Table I. Silylation of Hydrazines by Use of Disilanes as Counterattack Reagents[a]

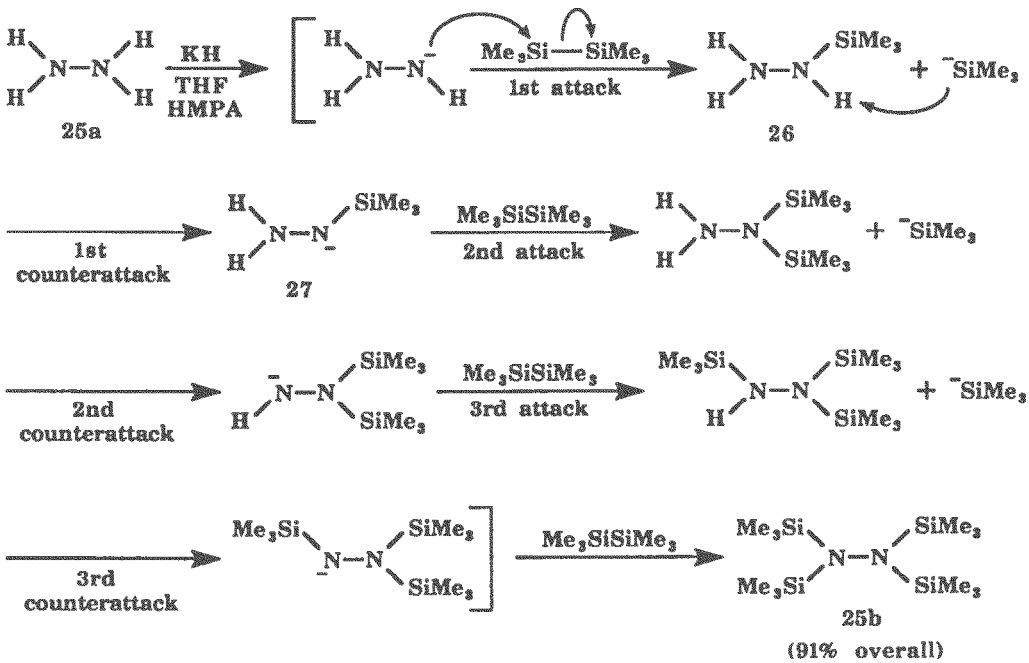
entry	hydrazine		disilane	equiv.	product		% yield
1		**13a**	$Me_3SiSiMe_3$	2.1		**13b**	94
2		**14a**	$Me_3SiSiMe_3$	2.1		**14b**	92
3		**15a**	$Me_3SiSiMe_3$	2.1		**15b**	90
4		**15a**	$Ph_2MeSiSiMePh_2$	2.1		**15c**	93[b]
5		**16a**	$Me_3SiSiMe_3$	2.1		**16b**	97
6		**17a**	$Me_3SiSiMe_3$	2.1		**17b**	99
7		**17a**	$Ph_2MeSiSiMePh_2$	2.1		**17c**	83[b]
8		**18a**	$Me_3SiSiMe_3$	2.1		**18b**	61
9		**19a**	$Me_3SiSiMe_3$	2.1		**19b**	91
10		**20a**	$Me_3SiSiMe_3$	2.1		**20b**	87[c,d]
11		**21a**	$Me_3SiSiMe_3$	3.1		**21b**	70[b]
12		**22a**	$Me_3SiSiMe_3$	3.1		**22b**	93
13		**23a**	$Me_3SiSiMe_3$	3.1		**23b**	69
14		**24a**	$Me_3SiSiMe_3$	4.2		**24b**	65[b]
15	H_2N-NH_2	**25a**	$Me_3SiSiMe_3$	4.2		**25b**	91

[a]Unless otherwise indicated, the reaction was carried out at room temperature for 24 hr with KH as the base. [b]The reaction time was 3 days. [c]The reaction time was 40 hr. [d]*n*-BuLi (1.3 eq) was used as the base.

Phenylhydrazine (**23a**, entry 13) contains three NH hydrogens. However, the reaction of **23a** with 3.1 equivalents of $Me_3SiSiMe_3$ under alkaline conditions did not afford the corresponding trisilylated product. Instead, a 1,1-disilylated hydrazine (**23b**) was obtained in 69% yield. In the hydrazine system, West et al. found it difficult to trimethylsilylate a nitrogen with a phenyl group attached.[21] This resistance to silylation could result from a steric interaction between the phenyl and the silyl substituents. Additionally, an electronic effect disfavoring the formation of this type of N-Si bond should be considered.[21]

We tetrasilylated 2-hydroxyethylhydrazine (**24a**, entry 14) and hydrazine (**25a**, entry 15) to give **24b** (65%) and **25b** (91%), respectively. Scheme 6 illustrates a one-pot preparation of tetrakis(trimethylsilyl)hydrazine (**25b**) via a "triple-counterattack" pathway. The Me_3Si^- generated in the first attack should counterattack (trimethylsilyl)hydrazine (**26**) to produce silyl hydrazide **27** as the major intermediate; the negative charge resides on the nitrogen bearing a trimethylsilyl group. The stabilization of the α-nitrogen anion by silicon in **27** is by analogy to the α-effect in silyl carbanions.[22] This analysis agrees to the results of the first silylation step in Scheme 1; 1,1-bis(trimethylsilyl)hydrazine is obtained as the main product.[8] Regarding the manipulation and the yield (91% *versus* 8%), the counterattack method shown in Scheme 6 is much more efficient than the classic procedure depicted in Scheme 1.

Scheme 6



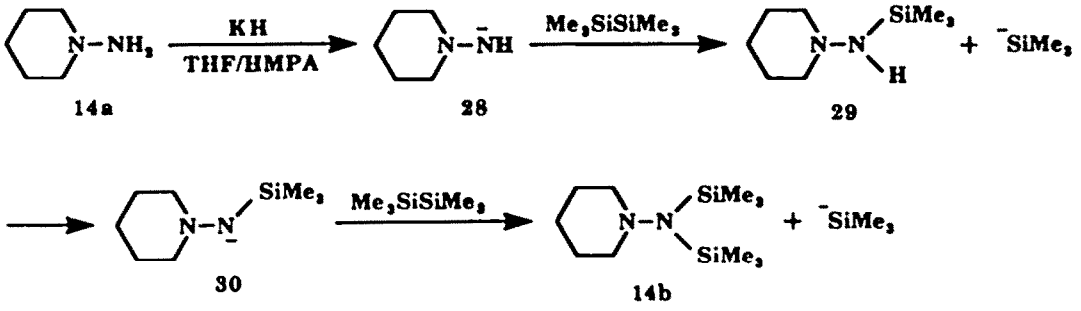
The by-product of the reaction shown in Scheme 5 is trimethylsilane (**11**). This compound was not isolated because of its volatility (b.p. 6.7 °C). When using another counterattack reagent $Ph_2MeSiSiMePh_2$ to react with 4-aminomorpholine (**15a**), we

obtained Ph_2MeSiH and disilyl hydrazine **15c** in 96% and 93% yields, respectively. This disilane also efficiently silylated 1,1-dimethylhydrazine (**17a**, 83%). However, we found it impractical to use a related compound, $Ph_3SiSiPh_3$, for the silylation. Hexaphenyldisilane has low solubility in most organic solvents and dissolves sluggishly in HMPA.

We performed the newly developed process for polysilylation of hydrazines on scales ranging from milligrams to multigrams. The stoichiometry of KH to initiate the reaction on a gram scale can be reduced from 0.3 to 0.1 equivalent. In addition, our experiments showed that this silylating reaction benefits from HMPA as a cosolvent. In the absence of HMPA, the reaction produced a significant amount of the corresponding 2-tetrazene, RR'N-N=N-NRR'.[23]

In a control experiment, we treated hydrazine **14a** with 1.0 equivalent of KH in THF/HMPA (4:1) in order to convert **14a** completely to hydrazide **28** (Scheme 7). We then added 1.3 equivalents of $Me_3SiSiMe_3$ to the reaction mixture. Hydrazide **28** was expected to react with 1.0 equivalent of $Me_3SiSiMe_3$ to give monosilylated hydrazine **29**. The remaining 0.3 equivalent of $Me_3SiSiMe_3$ could transfer only up to 30% of **29** to disilylated hydrazine **14b** via **30**. Under such conditions, we expected to observe both **29** and **14b** after workup. Through product analysis with GC and NMR spectroscopy, we did not detect any monosilylated hydrazine **29**. Instead, disilylated hydrazine **14b** was isolated in 75% yield based on the amount of $Me_3SiSiMe_3$ added. These results indicate that silylation of **28** with $Me_3SiSiMe_3$ in THF/HMPA is slower than silylation of **30**.

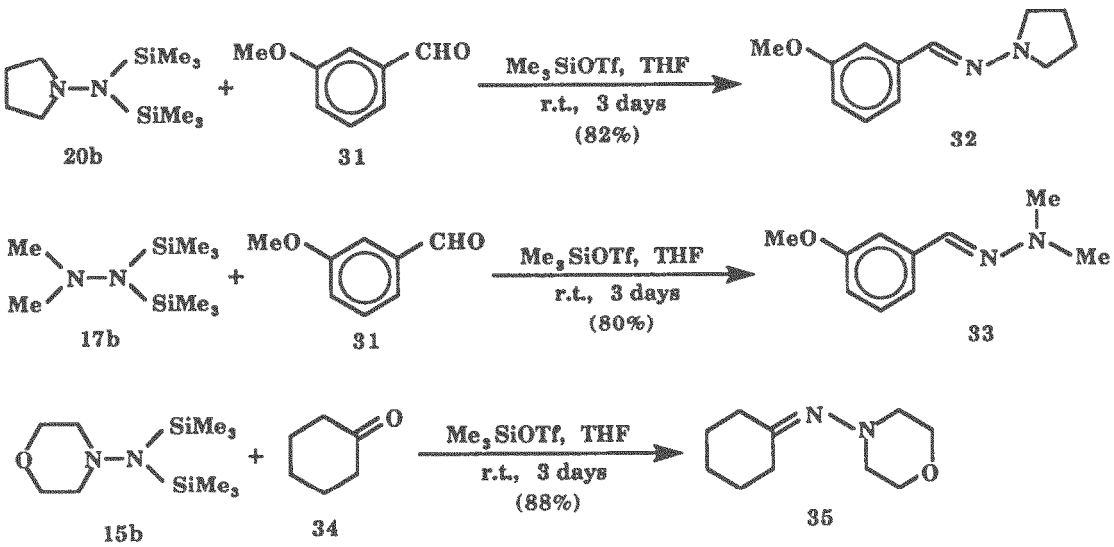
Scheme 7



In contrast with most silylated nitrogen compounds,[24] we found that polysilylated hydrazines are stable under mild hydrolytic conditions. Routinely the silylations were worked up with aqueous sodium chloride solution, and the products were purified by chromatography with silica gel and a mixture of EtOAc/hexanes as eluant. Among products **13b-25b**, slight hydrolysis occurred during chromatography only with the silyl ether moieties in **21b** and **24b**. We conclude that trimethylsilyl ethers are more susceptible to hydrolysis than are trimethylsilylated hydrazines. This susceptibility accounts for the lower yields in the conversions of **21a** to **21b** and **24a** to **24b** (entries 11 and 14, respectively).

We used polysilylated hydrazines to synthesize hydrazones in the presence of a catalyst. Reaction of an aldehyde (e.g. **31**) or a ketone (e.g. **34**) with 1.1 equivalents of a silylated hydrazine (e.g. **15b**, **17b** or **20b**) and 0.2 equivalent of trimethylsilyl trifluoromethanesulfonate (Me_3SiOTf) in THF gave the corresponding hydrazone (e.g. **32**, **33** and **35**) in very good yield (≥ 80%, Scheme 8). The volatile by-product $Me_3SiOSiMe_3$ is inert and easy to remove. This new procedure efficiently provides hydrazones under aprotic conditions.

Scheme 8



In conclusion, we have developed an efficient and expedient method for the synthesis of polysilylated hydrazines. The counterattack method used in this synthesis involves single-, double-, and triple-counterattack processes. Disilanes, $Me_3SiSiMe_3$ and $Ph_2MeSiSiMePh_2$, are employed as counterattack reagents.

EXPERIMENTAL

All reactions were carried out in oven-dried glassware (120 °C) under an atmosphere of nitrogen. Ethyl acetate and hexanes from Tilley Chemical Co. were dried and distilled over CaH_2. THF from J. T. Baker Chemical Co. was freshly distilled from Na/benzophenone. Hexamethylphosphoramide was dried over molecular sieves, type 13X. Other commercially available chemicals were used directly without purification except otherwise indicated. *m*-Anisaldehyde, *n*-butyllithium (2.5 M in hexanes), cyclohexanone, HMPA, potassium hydride (35%, dispersion in mineral oil), trimethylsilyl trifluoromethanesulfonate, and all hydrazines were purchased from Aldrich Chemical Co. Hexamethyldisilane and 1,2-dimethyl-1,1,2,2-tetraphenyldisilane were purchased from Petrarch Systems. Melting points were obtained with a Büchi 510 melting point apparatus

and are not corrected. Analytical TLC was performed on precoated plates purchased from Analtech, Inc. (silica gel GHLF) by using UV light or 2.5% phosphomolybdic acid in ethanol with heating for visualization. Mixtures of ethyl acetate and hexanes were used as eluants. GC analyses were performed on a Hewlett-Packard 5794A instrument equipped with a 12.5-m cross-linked methylsilicone gum capillary column (0.2-mm i.d.). Purification by gravity column chromatography was carried out by using EM Reagents Silica Gel 60 (particle size 0.063-0.200 mm, 70-230 mesh ASTM). Chromatotron separations were performed on a model 7924T chromatotron from Harrison Research. The plates (1, 2, or 4 mm thickness) were coated with EM Reagents Silica Gel 60 PF_{254} containing gypsum. Infrared (IR) spectra were measured on a Perkin-Elmer 599B or 710B spectrophotometer. The wavenumbers reported are referenced to the polystyrene 1601 cm^{-1} absorption. Proton NMR spectra were obtained on a Varian CFT-20 spectrometer with chloroform-*d* as solvent and tetramethylsilane as an internal standard. Proton NMR multiplicities are recorded by using the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad; *J*, coupling constant (hertz). High-resolution mass spectra were obtained with a VG Analytical 70-S mass spectrometer.

Standard Procedure for the Preparation of Polysilylated Hydrazines

Potassium hydride was added to a dry, one-necked round-bottomed flask equipped with a stirring bar and a rubber septum, and was washed with hexanes (3 × 5 mL). Hexanes were removed to give KH as a white powder. The hydrazine in THF was added to the flask at 0 °C under an atmosphere of nitrogen. After one hour of stirring, the suspension was warmed to room temperature and HMPA and a disilane were added. Stirring was continued for 24 hours. Then the reaction was quenched with water (2 mL) and the solution was extracted with diethyl ether (3 × 15 mL). The combined organic layers were washed with water (4 × 10 mL) and brine (2 × 10 mL), dried over $MgSO_4$, filtered, and concentrated to give an oil. The crude product was chromatographed to afford a pure polysilylated hydrazine.

(*S*)-1-*Bis*(*trimethylsilyl*)*amino*-2-(*methoxymethyl*)*pyrrolidine* (**13b**)

The standard procedure was followed. Reagents added into the reaction flask included KH (35% in mineral oil, 40 mg, 0.35 mmol, 0.3 equiv.), (*S*)-(-)-1-amino-2-(methoxymethyl)pyrrolidine (**13a**, 150 mg, 1.15 mmol, 1.0 equiv.), THF (12 mL), HMPA (3.0 mL), and $Me_3SiSiMe_3$ (354 mg, 2.42 mmol, 2.1 equiv.). After workup and purification by gravity column chromatography (10% EtOAc in hexanes as eluant), disilylated hydrazine **13b** was obtained as a colorless oil (298 mg, 1.08 mmol, 94%): GC (injector temperature 260 °C; column temperature 130 °C) t_R 4.58 min.; ^1H NMR ($CDCl_3$) δ 0.09 (s, 9H, $NSi(CH_3)_3$), 0.21 (s, 9H, $NSi(CH_3)_3$), 1.35-2.05 (m, 4H, CH_2CH_2), 2.80-3.60 (m, 5H, OCH_2NCH and NCH_2), 3.35 (s, 3H, OCH_3); IR (neat) 2955, 2895, 2820, 1450 (C-N), 1400, 1250 (Si-CH_3), 1198 (N-Si), 1125 (C-O), 953 (N-Si), 878, 845 (Si-CH_3), 763, 683 cm^{-1}; exact mass calcd for $C_{12}H_{30}N_2OSi_2$: 274.1897; found (70 eV): 274.1899.

1-[*Bis*(*trimethylsilyl*)*amino*]*piperidine* (**14b**)

The standard procedure was followed. Reagents added into the reaction flask included KH (35% in mineral oil, 48 mg, 0.42 mmol, 0.3 equiv.), 1-aminopiperidine (**14a**, 136 mg, 1.36 mmol, 1.0 equiv.), THF (14 mL), HMPA (3.5 mL), and $Me_3SiSiMe_3$ (427 mg, 2.92 mmol, 2.1 equiv.). After workup and purification by gravity column chromatography (5% EtOAc in hexanes as eluant), disilylated hydrazine **14b** was obtained as a colorless oil (305 mg, 1.25 mmol, 92%): TLC R_f 0.80 (20% EtOAc in hexanes); GC (injector temperature 260 °C; column temperature 110 °C) t_R 5.04 min.; ^{1}H NMR ($CDCl_3$) δ 0.10 (s, 18H, 2 × $Si(CH_3)_3$), 1.08-1.72 (m, 6H, $(CH_2)_3$), 2.68-2.93 (m, 4H, CH_2NCH_2); IR (neat) 2938, 2860, 2838, 1447 (C-N), 1402, 1250 (Si-CH_3), 1070, 1003, 968, 870, 840 (Si-CH_3), 823, 793, 762, 688 cm^{-1}; exact mass calcd for $C_{11}H_{28}N_2Si_2$: 244.1791; found (70 eV): 244.1790.

1-[*Bis*(*trimethylsilyl*)*amino*]*morpholine* (**15b**)

The standard procedure was followed. Reagents added into the reaction flask included KH (35% in mineral oil, 88 mg, 0.77 mmol, 0.3 equiv.), 1-aminomorpholine (**15a**, 262 mg, 2.57 mmol, 1.0 equiv.), THF (26 mL), HMPA (6.5 mL), and $Me_3SiSiMe_3$ (789 mg, 5.39 mmol, 2.1 equiv.). After workup and purification by gravity column chromatography (10% EtOAc in hexanes as eluant), disilylated hydrazine **15b** was obtained as a colorless oil (571 mg, 2.32 mmol, 90%): TLC R_f 0.60 (10% EtOAc in hexanes); GC (injector temperature 260 °C; column temperature 130 °C) t_R 2.95 min.; ^{1}H NMR ($CDCl_3$) δ 0.13 (s, 18H, 2 × $Si(CH_3)_3$), 2.74-2.98 (m, 4H, CH_2NCH_2), 3.38-3.73 (m, 4H, CH_2OCH_2); IR (neat) 2980, 2945, 2920, 2878, 11468, 1420 (C-N), 1400, 1372, 1310, 1255 (Si-CH_3), 1120 (C-O), 1042, 968 (N-Si), 867, 843, (Si-CH_3), 769, 683 cm^{-1}; exact mass calcd for $C_{10}H_{26}N_2OSi_2$: 246.1584; found (70 eV): 246.1585.

1-[*Bis*(*diphenylmethylsilyl*)*amino*]*morpholine* (**15c**) and *Diphenylmethylsilane*[25]

The standard procedure was followed, except that the reaction mixture was stirred for 72 hours. Reagents added into the reaction flask included KH (35% in mineral oil, 88 mg, 0.77 mmol, 0.3 equiv.), 1-aminomorpholine (**15a**, 262 mg, 2.57 mmol, 1.0 equiv.), THF (26 mL), HMPA (6.5 mL), and $Ph_2MeSiSiMePh_2$ (2.13 g, 5.39 mmol, 2.1 equiv.). After workup and purification with a chromatotron (2 mm plate; 3% EtOAc in hexanes as eluant), the desired product (**15c**) was obtained as wax (1.18 g, 2.38 mmol, 93%): melts ~ 46 °C; TLC R_f 0.42 (10% EtOAc in hexanes); GC (injector temperature 260 °C; column temperature 250 °C) t_R 23.26 min.; ^{1}H NMR ($CDCl_3$) δ 0.48 (s, 6H, 2 × $SiCH_3$), 2.55-2.83 (m, 4H, CH_2NCH_2), 3.15-3.41 (m, 4H, CH_2OCH_2), 7.16-7.75 (m, 20H, ArH); IR (CCl_4) 3062, 3042 (Ar-H), 2958, 2915, 2890, 2850, 1952, 1881, 1815, 1763, 1590, 1488, 1452, 1428 (C-N), 1258 (Si-CH_3), 1112 (C-O), 1032, 1003, 955 (N-Si), 865, 792, 740, 717, 703, 652 cm^{-1}; exact mass calcd for $C_{30}H_{34}N_2OSi_2$: 494.2210; found (70 eV): 494.2215.

The by-product Ph_2MeSiH was isolated as a colorless, irritant liquid (974 mg, 4.92 mmol, 96%): TLC R_f 0.64 (10% EtOAc in hexanes); GC (injector temperature 260 °C; column temperature 250 °C) t_R 4.88 min.; ^{1}H NMR ($CDCl_3$) δ 0.57 (s, 3H, $SiCH_3$), 7.16-7.57 (m, 10H, ArH); Si-H signal was not observed in the NMR spectrum; IR (neat) 3069, 3023 (Ar-H), 2964 (Si-CH_3), 2123 (Si-H),1954, 1885, 1819, 1763, 1597 (C=C), 1491, 1432, 1260

(Si-CH_3), 1118, 1056, 1030, 1004, 838, 795, 729, 703 cm^{-1}; exact mass calcd for $C_{13}H_{14}Si$: 198.0865; found (70 eV): 198.0860.

1-[*Bis(trimethylsilyl)amino]homopiperidine* (**16b**)

The standard procedure was followed. Reagents added into the reaction flask included KH (35% in mineral oil, 56 mg, 0.49 mmol, 0.3 equiv.), 1-aminohomopiperidine (**16a**, 187 mg, 1.64 mmol, 1.0 equiv.), THF (16 mL), HMPA (4.5 mL), and $Me_3SiSiMe_3$ (503 mg, 3.44 mmol, 2.1 equiv.). After workup and purification by gravity column chromatography (10% EtOAc in hexanes as eluant), disilylated hydrazine **16b** was obtained as a colorless oil (413 mg, 1.60 mmol, 97%): TLC R_f 0.78 (5% EtOAc in hexanes); GC (injector temperature 260 °C; column temperature 130 °C) t_R 4.45 min.; ^1H NMR ($CDCl_3$) δ 0.12 (s, 18H, 2 × $Si(CH_3)_3$), 1.33-1.70 (m, 8H, $(CH_2)_4$), 2.79-3.13 (m, 4H, CH_2NCH_2); IR (neat) 2940, 2862, 2845, 1452 (C-N), 1403, 1254 (Si-CH_3), 1062, 970, 845 (Si-CH_3), 763, 688 cm^{-1}; exact mass calcd for $C_{12}H_{30}N_2Si_2$: 258.1948; found (70 eV): 258.1948.

1,1-*Bis(trimethylsilyl)*-2,2-*dimethylhydrazine* (**17b**)[6,10,26,27]

The standard procedure was followed. Reagents added into the reaction flask included KH (35% in mineral oil, 134 mg, 1.16 mmol, 0.3 equiv.), 1,1-dimethylhydrazine (**17a**, 232 mg, 3.86 mmol, 1.0 equiv.), THF (39 mL), HMPA (9.5 mL), and $Me_3SiSiMe_3$ (1.19 g, 8.12 mmol, 2.1 equiv.). After workup and purification by gravity column chromatography (5% EtOAc in hexanes as eluant), disilylated hydrazine **17b** was obtained as a colorless oil (779 mg, 3.82 mmol, 99%): TLC R_f 0.78 (5% EtOAc in hexanes); GC (injector temperature 260 °C; column temperature 80 °C) t_R 2.87 min.; ^1H NMR ($CDCl_3$) δ 0.12 (s, 18H, 2 × $Si(CH_3)_3$), 2.62 (s, 6H, 2 × NCH_3); IR (neat) 2940, 2895, 2850, 2818, 2768, 1440 (C-N), 1400, 1238 (Si-CH_3), 1015, 956 (N-Si), 863 (Si-CH_3), 822, 750, 672 cm^{-1}; exact mass calcd for $C_8H_{24}N_2Si_2$: 204.1478; found (70 eV): 204.1480.

1,1-*Bis(diphenylmethylsilyl)*-2,2-*dimethylhydrazine* (**17c**) and *Diphenylmethylsilane*[25]

The standard procedure was followed, except that the reaction mixture was stirred for 72 hours. Reagents added into the reaction flask included KH (35% in mineral oil, 67 mg, 0.58 mmol, 0.3 equiv.), 1,1-dimethylhydrazine (**17a**, 116 mg, 1.93 mmol, 1.0 equiv.), THF (19 mL), HMPA (5.0 mL), and $Ph_2MeSiSiMePh_2$ (1.60 g, 4.06 mmol, 2.1 equiv.). After workup and purification with a chromatotron (2 mm plate; hexanes as eluant), the desired product (**15c**) was obtained as a colorless oil (725 mg, 1.60 mmol, 83%): TLC R_f 0.64 (10% EtOAc in hexanes); GC (injector temperature 260 °C; column temperature 250 °C) t_R 11.13 min.; ^1H NMR ($CDCl_3$) δ 0.49 (s, 6H, 2 × $SiCH_3$), 2.45 (s, 6H, NCH_3), 7.04-7.77 (m, 20H, ArH); IR (neat) 3052 (ArH), 2998, 2975, 2925, 2864, 2833, 2782, 2749, 1927, 1854, 1786, 1735, 1552, 1447 (C-N), 1383, 1267 (Si-CH_3), 1212, 1181, 1148, 1065, 977 (N-Si), 908, 792, 741, 688 cm^{-1}; exact mass calcd for $C_{28}H_{32}N_2Si_2$: 452.2104; found (70 eV): 452.2110.

The by-product Ph_2MeSiH was isolated as a colorless, irritant liquid (682 mg, 3.44 mmol, 89%). Its physical properties are identical to those listed in the preparation of **15c**.

1,1-Bis(trimethylsilyl)-2-methyl-2-phenylhydrazine (**18b**)[8]

The standard procedure was followed. Reagents added into the reaction flask included KH (35% in mineral oil, 57 mg, 0.49 mmol, 0.3 equiv.), 1-phenyl-1-methylhydrazine (**18a**, 201 mg, 1.65 mmol, 1.0 equiv.), THF (17 mL), HMPA (4.3 mL), and $Me_3SiSiMe_3$ (507 mg, 3.46 mmol, 2.1 equiv.). After workup and purification by gravity column chromatography (10% EtOAc in hexanes as eluant), disilylated hydrazine **18b** was obtained as pale yellow oil (224 mg, 0.84 mmol, 51%): TLC R_f 0.75 (10% EtOAc in hexanes); GC (injector temperature 260 °C; column temperature 150 °C) t_R 3.39 min.; ^1H NMR ($CDCl_3$) δ 0.10 (s, 18H, 2 × $Si(CH_3)_3$), 3.17 (s, 3H, NCH_3), 6.52-7.43 (m, 5H, ArH); IR (neat) 3096, 3060, 3020 (Ar-H), 2942, 2898, 2083, 1582, 1485, 1324, 1240, (Si-CH_3), 1187, 1109, 1075, 936 (N-Si), 830 (Si-CH_3), 778, 739, 688 cm^{-1}; exact mass calcd for $C_{13}H_{26}N_2Si_2$: 266.1634; found (70 eV): 266.1629.

1-Bis(trimethylsilyl)amino-2,6-dimethylpiperidine (**19b**)

The standard procedure was followed. Reagents added into the reaction flask included KH (35% in mineral oil, 42 mg, 0.36 mmol, 0.3 equiv.), 1-amino-2,6-dimethylpiperidine (**19a**, 156 mg, 1.21 mmol, 1.0 equiv.), THF (12 mL), HMPA (3.0 mL), and $Me_3SiSiMe_3$ (373 mg, 2.55 mmol, 2.1 equiv.). After workup and purification by gravity column chromatography (5% EtOAc in hexanes as eluant), disilylated hydrazine **19b** was obtained as a pale yellow oil (301 mg, 1.10 mmol, 91%): TLC R_f 0.75 (5% EtOAc in hexanes); GC (injector temperature 260 °C; column temperature 140 °C) t_R 4.02 min.; ^1H NMR ($CDCl_3$) δ 0.14 and 0.21 (2 × s, 18H, $NSi(CH_3)_3$), 1.10 (d, J = 6.1 Hz, 6H, 2 × CH_3), 0.95-1.86 (m, 6H, $(CH_2)_3$), 2.49-3.03 (m, 2H, CHNCH); IR (neat) 2945, 2923, 2848, 2783, 1450 (C-N), 1370, 1312, 1250 (Si-CH_3), 1024, 987, 932 (N-Si), 913, 875, 836 (Si-CH_3), 759, 678 cm^{-1}; exact mass calcd for $C_{13}H_{32}N_2Si_2$: 272.2104; found (70 eV): 272.2105.

1-[Bis(trimethylsilyl)amino]pyrrolidine (**20b**)

In a dry, 50 ml one-necked round-bottomed flask equipped with a stirring bar and a rubber septum, 1-aminopyrrolidine hydrochloride (**20a**, 200 mg, 1.60 mmole, 1.0 equiv.) was suspended in THF (16 mL) under nitrogen atmosphere. To the mixture was added *n*-butyllithium (2.5 M in hexanes, 0.83 mL, 2.1 mmole, 1.3 equiv.) at -78 °C and it was stirred for 30 min. Hexamethylphosphoramide (4.0 mL) and $Me_3SiSiMe_3$ (692 mg, 3.36 mmole, 2.1 equiv.) were added into the reaction solution after it was warmed to room temperature. The reaction mixture was stirred at room temperature for 40 hours. It was then quenched with water (2 mL) and the mixture was extracted with diethyl ether (3 × 15 mL). The ether layers were combined and washed with water (4 × 10 mL) and brine (2 × 10 mL), dried over $MgSO_4$, and filtered. The filtrate was then concentrated and chromatographed to afford pure disilylated hydrazine **20b** as a pale yellow oil (319 mg, 1.38 mmol, 87%): TLC R_f 0.88 (20% EtOAc in hexanes); GC (injector temperature 260 °C; column temperature 110 °C) t_R 3.23 min.; ^1H NMR ($CDCl_3$) δ 0.10 (s, 18H, 2 × $Si(CH_3)_3$), 1.52-1.87 (m, 4H, $(CH_2)_2$), 2.73-3.03 (m, 4H, CH_2NCH_2); IR (neat) 2958, 1254 (Si-CH_3), 980, 881, 845 (Si-CH_3), 761 cm^{-1}; exact mass calcd for $C_{10}H_{26}N_2Si_2$: 230.1635; found (70 eV): 230.1633.

1-*Bis(trimethylsilyl)amino*-4-[2-(*trimethylsiloxy)ethyl]piperazine* (**21b**)

The standard procedure was followed. Reagents added into the reaction flask included KH (35% in mineral oil, 46 mg, 0.40 mmol, 0.3 equiv.), 1-amino-4-(2-hydroxyethyl)piperazine (**21a**, 192 mg, 1.32 mmol, 1.0 equiv.), THF (12 mL), HMPA (3.0 mL), and $Me_3SiSiMe_3$ (600 mg, 4.10 mmol, 3.1 equiv.). After workup and filtration through Celite (10% EtOAc in hexanes as eluant), trisilylated product **21b** was obtained in pure form as a pale yellow oil (334 mg, 0.92 mmol, 70%): GC (injector temperature 260 °C; column temperature 180 °C) t_R 3.82 min.; ^1H NMR ($CDCl_3$) δ 0.11 (s, 27H, $OSi(CH_3)_3$ and 2 × $NSi(CH_3)_3$), 2.35-2.58 (m, 6H, NCH_2), 2.78-3.02 (m, 4H, $NNCH_2$), 3.69 (t, J = 6.5 Hz, 2H, $SiOCH_2$); IR (neat) 2958, 2898, 2804, 1456 (C-N), 1253 (Si-CH_3), 1105 (C-O), 1072 Si-O), 1018, 965 (N-Si), 869, 843 (Si-CH_3), 758, 675 cm^{-1}; exact mass calcd for $C_{15}H_{39}N_3OSi_3$: 361.2401; found (70 eV): 361.2412.

1-*Methyl*-1,2,2-*tris(trimethylsilyl)hydrazine* (**22b**)[7]

The standard procedure was followed. Reagents added into the reaction flask included KH (35% in mineral oil, 95 mg, 0.83 mmol, 0.3 equiv.), methylhydrazine (**22a**, 127 mg, 2.77 mmol, 1.0 equiv.), THF (28 mL), HMPA (7.0 mL), and $Me_3SiSiMe_3$ (1.25 g, 8.57 mmol, 3.1 equiv.). After workup and purification by gravity column chromatography (10% EtOAc in hexanes as eluant), trisilylated hydrazine **22b** was obtained as a colorless oil (677 mg, 2.58 mmol, 93%): GC (injector temperature 260 °C; column temperature 110 °C) t_R 3.43 min.; ^1H NMR ($CDCl_3$) δ 0.10 (s, 9H, $CNSi(CH_3)_3$), 0.13 (s, 18H, 2 × $NSi(CH_3)_3$, 2.64 (s, 3H, NCH_3); IR (neat) 2957, 2902, 2798, 1252 (Si-CH_3), 1011, 956 (N-Si), 846 (Si-CH_3), 680 cm^{-1}; exact mass calcd for $C_{10}H_{30}N_2Si_3$: 262.1717; found (70 eV): 262.1719.

1,1-*Bis(trimethylsilyl)*-2-*phenylhydrazine* (**23b**)[10,28]

The standard procedure was followed. Reagents added into the reaction flask included KH (35% in mineral oil, 68 mg, 0.59 mmol, 0.3 equiv.), phenylhydrazine (**23a**, 213 mg, 1.97 mmol, 1.0 equiv.), THF (20 mL), HMPA (5.0 mL), and $Me_3SiSiMe_3$ (895 mg, 6.11 mmol, 3.1 equiv.). After workup and purification by gravity column chromatography (10% EtOAc in hexanes as eluant), disilylated hydrazine **23b** was obtained as a colorless oil (254 mg, 1.36 mmol, 69%): TLC R_f 0.76 (20% EtOAc in hexanes); GC (injector temperature 260 °C; column temperature 150 °C) t_R 3.39 min.; ^1H NMR ($CDCl_3$) δ 0.10 (s, 18H, 2 × $Si(CH_3)_3$), 4.95-5.30 (broad, s, 1H, NH), 6.55-7.25 (m, 5H, ArH); IR (neat) 3340 (N-H), 3039 (Ar-H), 2943, 2894, 1602 (C=C), 1493 (C-N), 1302, 1251 (Si-CH_3), 958 (N-Si), 845 (Si-CH_3), 752, 695 cm^{-1}; exact mass calcd for $C_{18}H_{24}N_2Si_2$: 252.1478; found (70 eV): 252.1487.

1-[2-(*Trimethylsiloxy)ethyl*-1,2,2-*tris(trimethylsilyl)]hydrazine* (**24b**)

The standard procedure was followed, except that the reaction time was 72 hours. Reagents added into the reaction flask included KH (35% in mineral oil, 98 mg, 0.86 mmol, 0.3 equiv.), 2-hydroxyethylhydrazine (**24a**, 224 mg, 2.86 mmol, 1.0 equiv.), THF (28 mL), HMPA (7.0 mL), and $Me_3SiSiMe_3$ (1.75 g, 12.0 mmol, 4.2 equiv.). After workup and filtration through Celite (10% EtOAc in hexanes as eluant), tetrasilylated product **24b** was obtained in pure form as a pale yellow oil (676 mg, 1.85 mmol, 65%): TLC R_f 0.72 (5%

EtOAc in hexanes); GC (injector temperature 260 °C; column temperature 150 °C) t_R 4.83 min.; ^{1}H NMR ($CDCl_3$) δ 0.02-0.25 (36H, 4 × $Si(CH_3)_3$), 2.63-3.22 (m, 2H, NCH_2), 3.42-3.97 (m, 2H, OCH_2); IR (neat) 2963, 1260 (Si-CH_3), 1052 (C-O and Si-O), 940 (N-Si), 847 (Si-CH_3), 805, 762, 688 cm^{-1}; exact mass calcd for $C_{14}H_{40}N_2OSi_4$: 364.2218; found (70 eV): 364.2229.

Tetrakis(trimethylsilyl)hydrazine (**25b**)[1,8,29]

The standard procedure was followed. Reagents added into the reaction flask included KH (35% in mineral oil, 108 mg, 0.95 mmol, 0.3 equiv.), anhydrous hydrazine (**25a**, 101 mg, 3.15 mmol, 1.0 equiv.), THF (32 mL), HMPA (8.0 mL), and $Me_3SiSiMe_3$ (1.94 g, 13.2 mmol, 4.2 equiv.). After workup and purification by gravity column chromatography (10% EtOAc in hexanes as eluant), tetrasilylated hydrazine **25b** was obtained as a white solid (920 mg, 2.87 mmol, 91%): mp 289-291 °C (sublimed; lit.[1] 290-292 °C); GC (injector temperature 260 °C; column temperature 150 °C) t_R 3.32 min.; ^{1}H NMR ($CDCl_3$) δ 0.17 (s, $Si(CH_3)_3$); IR (CCl_4) 2943, 1252 (Si-CH_3), 922 (N-Si), 841 (Si-CH_3), 820, 667 cm^{-1}; exact mass calcd for $C_{12}H_{36}N_2Si_4$: 320.1956; found (70 eV): 320.1961.

3-*Methoxybenzalaminopyrrolidine* (**32**)

To a solution of *m*-anisaldehyde (**31**, 42 mg, 0.31 mmol, 1.0 equiv.), 1-[bis(trimethylsilyl)amino]pyrrolidine (**20b**, 79 mg, 0.34 mmol, 1.1 equiv.) and THF (3.0 mL) at 0 °C was added trimethylsilyl trifluoromethanesulfonate (14 mg, 0.062 mmol, 0.2 equiv.). The mixture was stirred at 0 °C under an atmosphere of nitrogen for 30 min. and then at room temperature for 72 hours. The reaction mixture was filtered through silica gel with 5% EtOAc in hexanes as eluant. After the solvent was removed by rotary evaporation, purification of the residue with a chromatotron (1 mm plate; 2.5% EtOAc in hexanes as eluant) gave hydrazone **32** as a colorless oil (52 mg, 0.25 mmol, 82%): TLC R_f 0.17 (5% EtOAc in hexanes); GC (injector temperature 260 °C; column temperature program: initial temperature 110 °C, duration 3 min.; increment rate 15 °C/min.; final temperature 250 °C) t_R 9.50 min.; ^{1}H NMR ($CDCl_3$) δ 1.81-2.04 (m, 4H, $(CH_2)_2$), 3.24-3.45 (m, 4H, CH_2NCH_2), 3.81 (s, 3H, OCH_3), 6.59-6.80 (broad s, 1H, N=CH), 6.94-7.36 (m, 4H, ArH); IR (neat) 3057 (Ar-H), 2968, 2840, 1593 (C=C), 1560 (C=N), 1482, 1458, 1429, 1376, 1336, 1270 (Ar-O), 1140, 1045, 892, 876, 770 (Ar), 697 (Ar) cm^{-1}; exact mass calcd for $C_{12}H_{16}N_2O$: 204.1263; found (70 eV): 204.1261.

3-*Methoxybenzaldehyde N,N-Dimethylhydrazone* (**33**)

To a solution of *m*-anisaldehyde (**31**, 100 mg, 0.73 mmol, 1.0 equiv.), 1,1-bis(trimethylsilyl)-2,2-dimethylhydrazine (**17b**, 165 mg, 0.81 mmol, 1.1 equiv.) and THF (15 mL) at 0 °C was added trimethylsilyl trifluoromethanesulfonate (33 mg, 0.15 mmol, 0.2 equiv.). The mixture was stirred at 0 °C under an atmosphere of nitrogen for 30 min. and then at room temperature for 72 hours. The reaction mixture was filtered through silica gel and eluted with 5% EtOAc in hexanes. After the solvent was removed by rotary evaporation, purification of the residue with a chromatotron (1 mm plate; 2.5% EtOAc in hexanes as eluant) gave hydrazone **33** as a colorless oil (104 mg, 0.58 mmol, 80%): TLC R_f 0.21 (5% EtOAc in hexanes); GC (injector temperature 260 °C; column temperature

program: initial temperature 110 °C, duration 3 min.; increment rate 15 °C/min.; final temperature 250 °C) t_R 6.83 min.; ^1H NMR ($CDCl_3$) δ 2.96 (s, 6H, NCH_3), 3.82 (s, 3H, OCH_3), 6.60-6.81 (broad, s, 1H, N=CH), 6.92-7.30 (m, 4H, ArH); IR (neat) 3058 (Ar-H), 2998, 2957, 2839, 2796, 1594 (C=C), 1564 (C=N), 1469, 1365, 1261 (Ar-O), 1158 (C-O), 1039, 897, 784, 767 (Ar), 698 (Ar) cm^{-1}; exact mass calcd for $C_{10}H_{14}N_2O$: 178.1106; found (70 eV): 178.1107.

Cyclohexylideneaminomorpholine (**35**)

To a solution of cyclohexanone (**34**, 119 mg, 1.22 mmol, 1.0 equiv.), 1-[bis(trimethylsilyl)amino]morpholine (**15b**, 330 mg, 1.34 mmol, 1.1 equiv.) and THF (12 mL) at 0 °C was added trimethylsilyl trifluoromethanesulfonate (54 mg, 0.24 mmol, 0.2 equiv.). The mixture was stirred at 0 °C under an atmosphere of nitrogen for 30 min. and then at room temperature for 72 hours. The reaction mixture was filtered through silica gel and eluted with 5% EtOAc in hexanes. After the solvent was removed by rotary evaporation, purification of the residue with a chromatotron (1 mm plate; 2.5% EtOAc in hexanes as eluant) gave hydrazone **35** as a colorless oil (195 mg, 1.07 mmol, 88%): TLC R_f 0.55 (10% EtOAc in hexanes); GC (injector temperature 260 °C; column temperature 130 °C) t_R 4.09 min.; ^1H NMR ($CDCl_3$) δ 1.46-1.87 (m, 6H, $(CH_2)_3$), 2.13-2.77 (m, 8H, 2 × $N{=}CCH_2$ and CH_2NCH_2), 3.68-3.87 (m, 4H, CH_2OCH_2); IR (neat) 2920, 2840, 1626 (C=N), 1248 (C-N), 1102 (C-O), 1058, 983, 955, 843, 830 cm^{-1}; exact mass calcd for $C_{10}H_{18}N_2O$: 182.1419; found (70 eV): 182.1421.

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