SYNTHESIS OF SILYLANILINE PRECURSORS TO ORGANIC-INORGANIC HYBRID POLYMERS

by

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ABSTRACT

A broad spectrum of derivative chemistry has originated from the study of boron compounds containing silicon-nitrogen functional groups. Small molecules that contain various silicon-nitrogen moieties are synthetically useful due to the reactivity of the Si-N bond. Some of our current research is focused on the development of a variety of 4-substituted aniline derivatives containing one or more silicon-nitrogen bonds. These molecules hold potential as precursors to novel organic-inorganic hybrid polymeric systems involving alternating borazine (-BR-NR'-) and phenylene ($-C_6H_4-$) moieties. The work presented here involves the synthesis, purification, and characterization of a small library of silylaniline derivatives.

ACKNOWLEDGEMENTS

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INTRODUCTION

The polymer industry has catapulted our civilization to new heights of productivity and leisure, producing many of the household and industry standards for our way of life. Most tools, games, utilities, and necessities either contain or are made entirely out of one or more different kinds of polymers. Traditional polymers that one would usually encounter are typically organic polymeric systems developed for their utility. However, the chemical intrigue of polymeric systems lies outside of the practicality of these plastics. The nature of the polymeric backbone and testing the possibilities of replacing organic moieties with their inorganic analogues is the basis of the work presented here.

Typically, polymer synthesis falls under the realm and classification of organic chemistry, as most polymers involve a stable carbon-carbon backbone. Well-developed examples include polyethylene[1], polyvinylchloride[1] (PVC), or polystyrene[1] (Styrofoam).

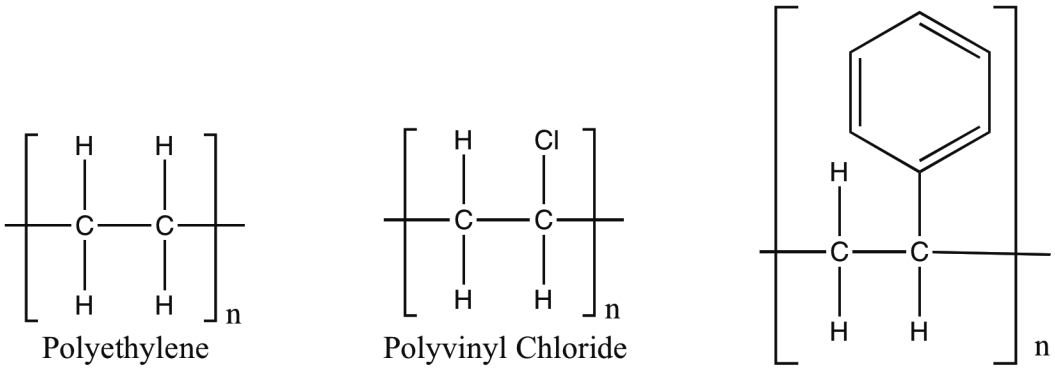


Figure 1. Common Organic Polymers

These polymers are all important and have been designed to display specific characteristics, such as structural integrity, flexibility, chemical and thermal stability, and

a lack of toxicity to humans. During recent decades, inorganic chemists have been interested in the development of new polymers, both as scaffolds for inorganic reactions, and in synthesizing polymers with an inorganic backbone. Inorganic polymers have sometimes displayed enhanced properties over organic polymers. These properties include bonds that are more resistant to free radical cleavage and the incorporation of elements with different valencies than carbon, which would affect the compound's flexibility, reactivity, thermal stability, and solvent interactions.[2]

A common backbone of an organic polymer consists of carbon atoms with tetravalency, containing eight valence electrons for every two carbon atoms. If, instead of carbon, alternating boron-nitrogen bonds were to be incorporated, the result would be an identical number of valence electrons. This indicates that the boron-nitrogen bond is isoelectronic to the carbon-carbon bond. This supports the hypothesis that a polymer consisting of an alternating boron-nitrogen structure would behave similarly to its carbon-carbon analogue.

The boron-nitrogen bond shares many of the same characteristics of a carbon-carbon bond. As stated above, the number of valence electrons is the same. In addition, the boron-nitrogen analogues of alkanes (amine-boranes, $X_3B\text{-}NR_3$), alkenes (aminoboranes $X_2B{=}NR_2$), and alkynes (iminoboranes, $XB{\equiv}NR$) share similar bond distances and properties.[3] This suggests that a polymeric system consisting of a boron-nitrogen backbone is possible.

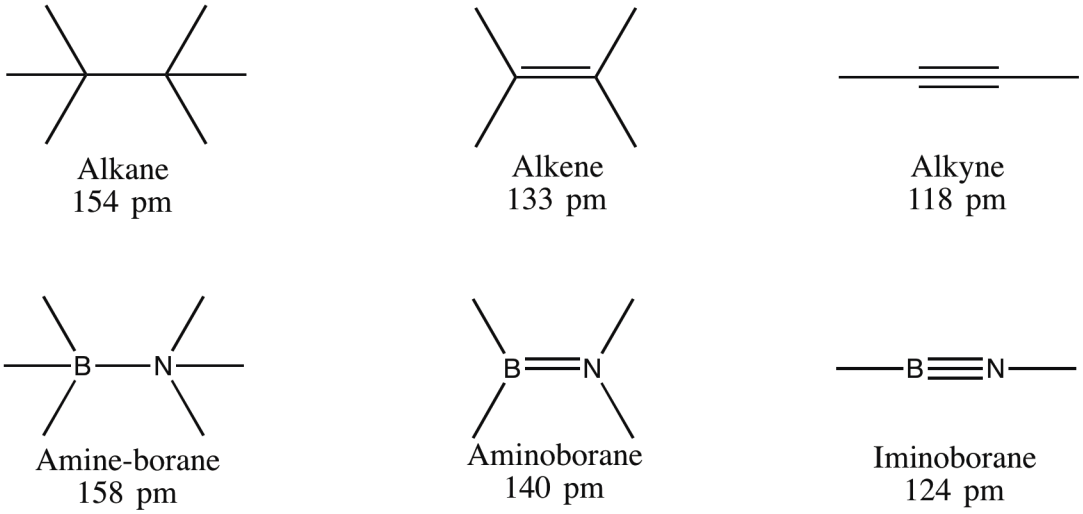


Figure 2. Comparative Structures and Bond Lengths of C-C and B-N Moieties

One of the problems associated with producing polymers with a boron-nitrogen backbone, is the generation of a cyclic trimeric by-product called borazine.[4] Borazine is such a stable structure that its formation acts as a thermodynamic sink. With this in mind, a different synthetic technique was necessary in order to design a polymer that did not degenerate into borazine. Understanding this challenge, the Neilson group has spent a number of years investigating various synthetic strategies in order to develop potential precursors to boron-nitrogen polymeric systems.

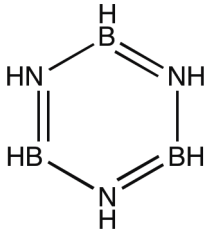


Figure 3. The Cyclic Boron-Nitrogen Trimer: Borazine

In 1984, Li and Neilson[5] showed, through various derivatives of alkyl[bis(trimethylsilyl)amino]boranes, that when both a silylated and an alkylated amine were bound to a boron atom, only one N atom participated in pi-bonding, while the boron atom was protected from nucleophilic attack (Figure **4**). This novel use of bulky groups resulted in the formation of stable B-N bonds and also served as a model of how to help prevent a boron-nitrogen containing compound from degenerating into borazine.

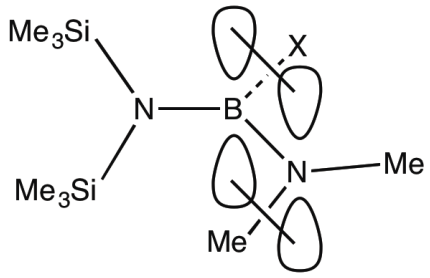


Figure 4. Stabilization of the Boron-Nitrogen Bond

In 1986, Li and Neilson[6] improved on their previous design. They not only used alkylated amines on single boron atoms, but also managed to prepare stable diborylamines, producing an as-yet-unknown boron nitrogen system containing both B-Cl and Si-N bonds. This was a rare observation due to the high thermal stability afforded by the steric protection of the bulky tert-butyl substituent on boron, as shown in Figure **5** below.

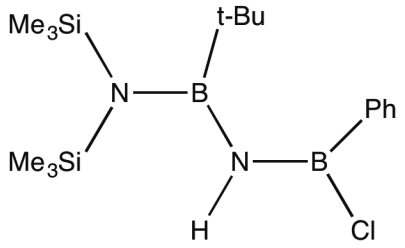


Figure 5. Linear Boron-Nitrogen Compound with Si-N and B-Cl Bonds

In an attempt to prevent the production of borazine Shaw and Neilson[7] synthesized precursors with the strategy of using acyclic diborylamines containing Si-N and B-X groups as starting compounds and to link the nitrogen atoms of the N-B-N-B backbone through bridging $-(CH_2)_n-$ by use of the 1,3,2-diazoboracycloalkane ring system. This cyclic element of the precursor would allow a linear polymeric chain to form without the risk of the formation of borazine as it would be sterically hindered. This approach also led Shaw to produce a linear boron-nitrogen chain length of six, as depicted in Figure **6** below.

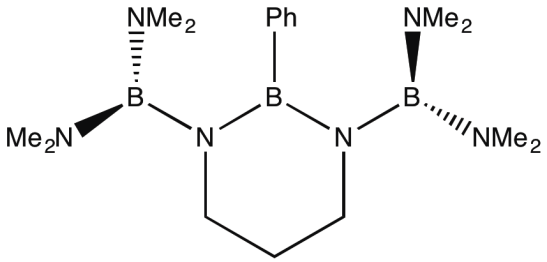


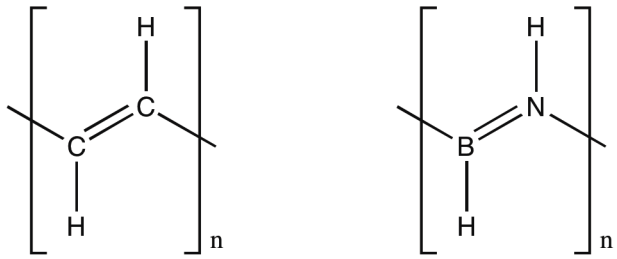
Figure 6. Sterically Hindered Boron-Nitrogen Precursor

Shaw and Neilson[8] then reported in 1994 more research on this cyclic monomer for a linear polymeric chain. They found that it was possible to derivatize this diazaboracyclohexane ring system by silylating any amino groups. These discoveries along with the possible condensation reactions of the monomers serve as a guide for future research.

In the work presented here, we wish to build on the previous work of the Neilson group. As Li and Shaw have reported, the formation of the cyclic trimer borazine prevents any traditional linear condensation reaction with aminoboranes. Instead, we have chosen to use Li's technique of stabilizing a prospective boron atom with silylated

amine moieties because of their stabilizing pi-bonding. In addition, we have chosen to provide a steric hindrance to the formation of borazine, as suggested by Shaw. In an attempt to prevent borazine formation, we have also elected to explore the possibility of an organic/inorganic hybrid polymeric chain, interspersing the borazine (-BR-NR'-) groups with phenylene ($-C_6H_6-$) moieties. This polymeric chain then reduces the chance of producing a cyclic trimer.

Due to its similarity in structure to polyacetylene and the extended pi-network, polyiminoboranes would be expected to share the properties of increased stability and electrical conductivity: useful attributes for a novel polymeric system. Since the proposed synthesis would insert a phenylene moiety into the polymeric chain, this could cause some concern that resonance would be broken. However, the phenylene group also consists of sp^2 hybridized carbon atoms that can contribute to this resonance.



Polyacetylene Polyiminoborane

Figure 7. Polyacetylene vs. Polyiminoborane

With this overarching goal in mind, this specific project has focused on the development of individual precursor compounds, their functionalization, and characterization. These compounds were all synthesized with the idea of the possibility of functionalization with a boron atom and condensation to produce a prospective polymer. The synthetic route and plan are now reported.

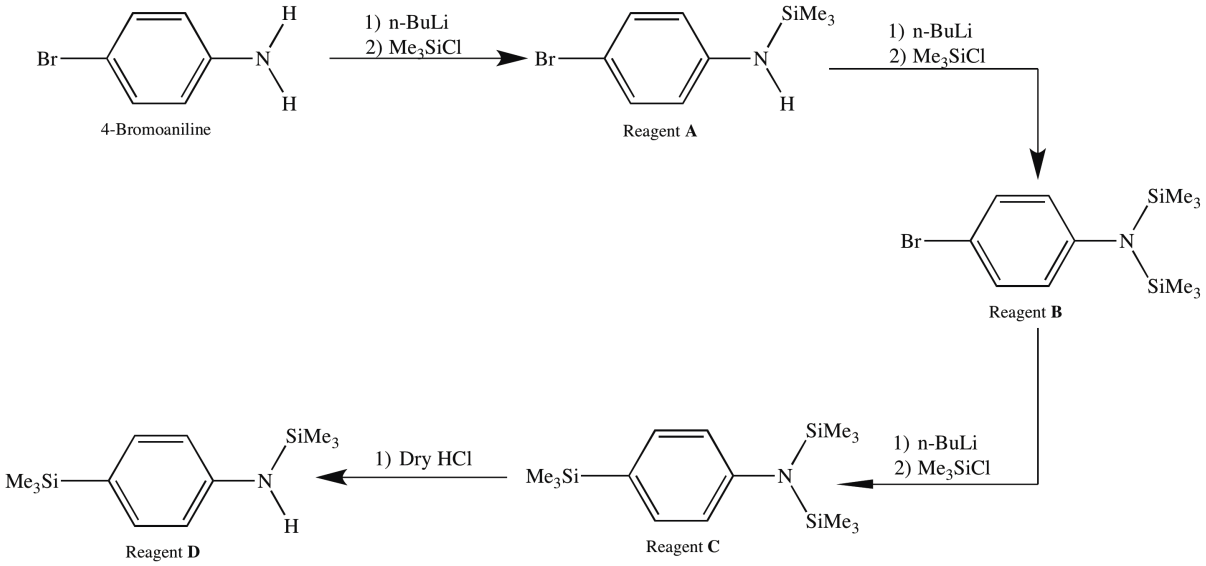
RESULTS AND DISCUSSION

Synthesis of Silylaniline Reagents

All of the syntheses to be discussed have started with the preparation of silylaniline derivatives of 4-bromoaniline, producing mono-, di-, and tri-silylaniline reagents (Scheme **1**). This method has resulted in simple, high yield preparative chemistry. The process involves three main reaction types: (1) deprotonation at the N-H site; (2) metal-halogen exchange at the aryl bromide site; and (3) Si-N bond cleavage.

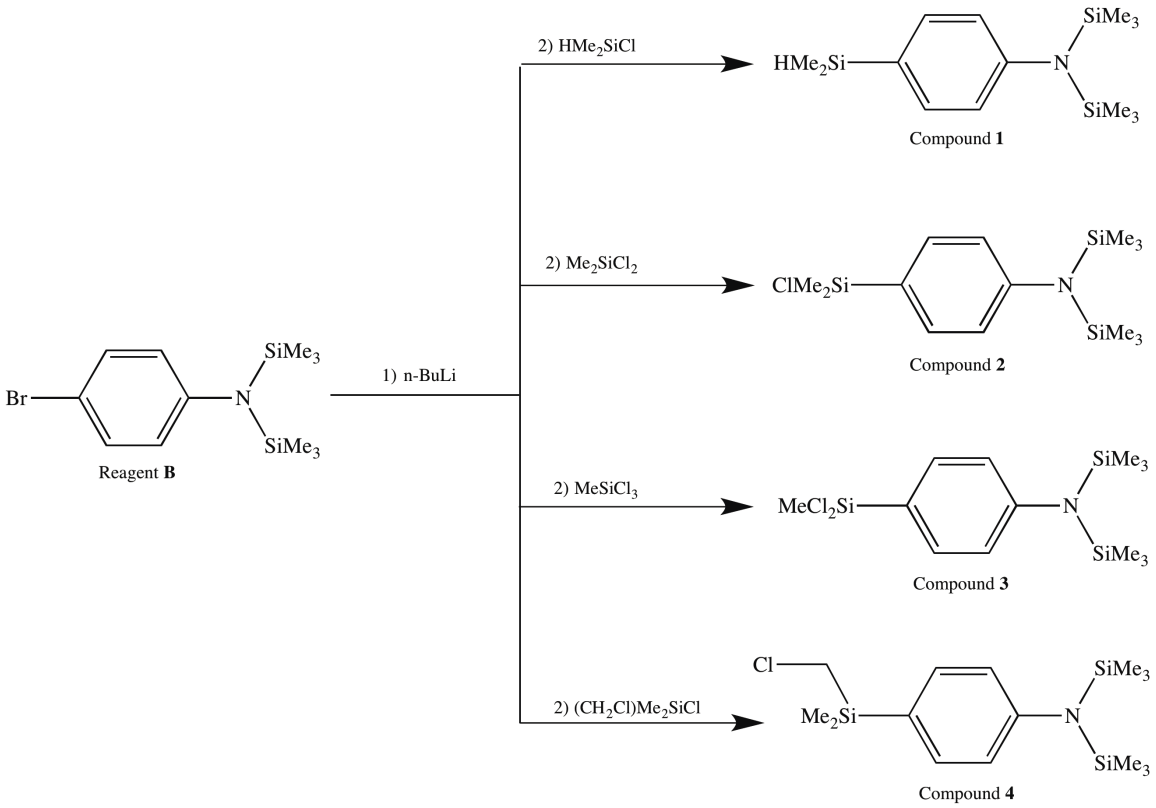
The first silylaniline compound was achieved when 4-bromoaniline was deprotonated with *n*-butyllithium and silylated with chlorotrimethylsilane to produce silylaniline reagent **A**. Reagent **A** was then deprotonated again with *n*-butyllithium and again reacted with chlorotrimethylsilane to produce reagent **B**. Reagent **B** was able to undergo lithium halogen exchange with *n*-butyllithium and was reacted with chlorotimethylsilane to produce reagent **C**. Reagent **C** was then reacted with dry hydrochloric acid to cleave the labile silicon-nitrogen bond and yield reagent **D**. The silylaniline reagents **A** to **D** were synthesized in good yields as moisture sensitive, colorless to light yellow, distillable liquids. Compounds **A**-**D** have been characterized by ^{1}H and ^{13}C NMR spectroscopy (Table **1**-**4**).

Scheme 1. Synthesis of Silylaniline Reagents



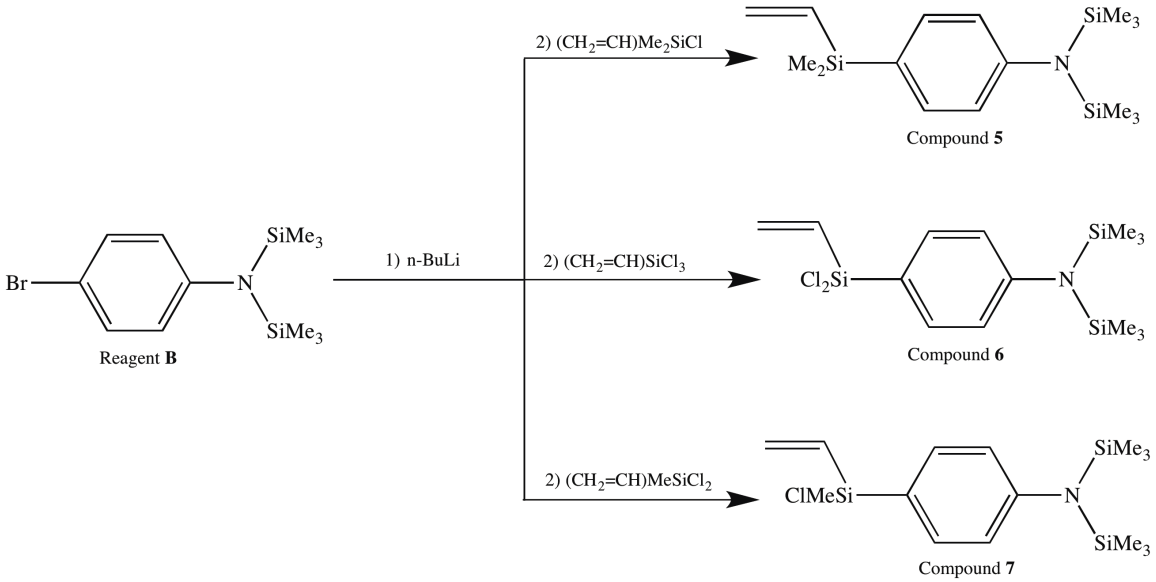
From here the synthesis of additional compounds from reagent **B** involves lithium halogen exchange and reaction with a small library of commercially available chlorosilanes (Scheme **2**). The first group of derivatives produced involves silanes linked to halogens or short alkanes. When reacted with different chlorosilanes, the lithiated intermediate produces the corresponding compounds. The lithiated intermediate is reacted with chlorodimethylsilane, dichlorodimethylsilane, trichloromethylsilane, and chloro(chloromethyl)dimethylsilane to produce new compounds **1**-**4** (respectively), collected as distillable liquids in good yields. All have been characterized by ^{1}H and ^{13}C NMR spectroscopy (Table **5**-**8**).

Scheme 2. Synthesis of Alkane-linked Derivatives 1-4



A similar procedure was utilized to react the lithiated intermediate of reagent **B** with silanes linked to a vinyl group (Scheme **3**). This subcategory of compounds is only distinct from the previous category by the presence of the vinyl functional group and the possibility of its synthetic utility for future work. The lithiated intermediate can be reacted with chlorodimethylvinylsilane, trichlorovinylsilane, and dichloromethylvinylsilane to produce compounds **5-7**, respectively. The Si-N derivatives labeled **5-7** were collected as distillable liquids in good yields. All have been characterized by ^{1}H and ^{13}C NMR spectroscopy (Table **9-11**).

Scheme 3. Synthesis of Vinyl Derivatives 5-7



The vinyl group present in these compounds has the potential to open the possibility of a different type of polymerization, using the vinyl functionality rather than strictly using the condensation by elimination of a silane group. This possibility further expands the research avenues for this project, allowing for multiple polymerization methods.

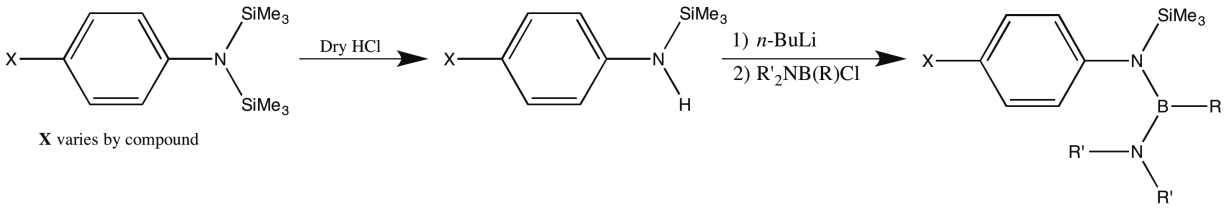
A variety of Ph-N-B-N derivatives have been prepared. It is notable that the polymerization of most of these starting units would yield a product that not only contains borazine (-BR-NR'-) and phenylene (-C_6H_4-) groups but also silicon atoms in the backbone. As such, we would expect that any polymeric system with this structure or any system that would utilize the vinyl functionality (resulting in an alkane) would break the resonance in the backbone of the structure and yield a non-conducting polymer.

CONCLUDING REMARKS

This project focused mainly on the development of precursor molecules of possible monomers of a novel polymeric system. In fact, all of the precursors explored in this project are devoid of any B-N bonds or boron atoms. As such, this work has been for the purpose of laying a solid foundation and groundwork for future synthesis.

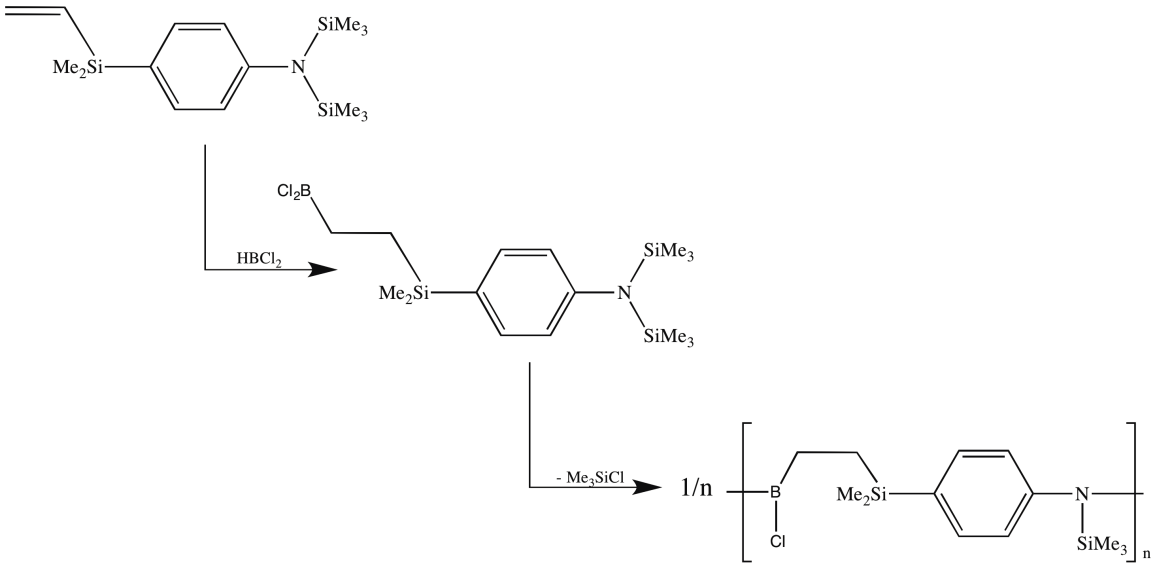
With any of the compounds **1**-**7** described above, the functionalization of the nitrogen with a boron atom (Scheme **4**) would allow for a possible condensation reaction. In order to do so, it would be necessary to eliminate one of the trimethylsilyl groups from this nitrogen and replace it with a proton. This can be accomplished by treatment with dry HCl. Then, by replacing the proton with an aminochloroborane, it is possible to introduce a boron-nitrogen bond into the molecule. This functionality allows for a variety of new reactions and further exploration.

Scheme 4. Introduction of a Boron Atom at the Aniline Site



In addition, it is possible that the vinyl group present on compounds **5**-**7** has the potential to undergo hydroboration to produce an alkane-linked boron atom attached to the molecule (Scheme **5**). This boron, if attached to a chlorine atom, could undergo an elimination of Me_3SiCl to result in a novel linear polymeric system.

Scheme 5. The Potential Polymerization via Hydroboration of Vinyl Functionality



While the work reported here is important for the continuation of this project, the future work holds much promise for the synthesis of a novel organic/inorganic hybrid polymeric system. This work starts with the functionalization of the reported compounds with a boron atom at some site, and hopefully results in the eventual formation of a polymer from the resulting compound.

EXPERIMENTAL SECTION

Materials And General Procedures. These reagents were purchased and used without any further purification: *n*-BuLi (2.5 M hexane solution), Me_3SiCl, HCl (1.0 M diethyl ether solution), Me_2SiHCl, Me_2SiCl_2, $MeSiCl_3$, $MeSiCl_3$, $CH_2ClSiCl(Me)_2$, $H_2C{=}CHSi(CH_3)_2Cl$, $H_2C{=}CHSiCl_3$, $H_2C{=}CHSiMeCl_2$. A Bruker-400 spectrometer was used to collect all NMR (^1H and ^{13}C) spectra using $CDCl_3$ as a solvent. Unless stated otherwise, all reactions were carried out under a dry nitrogen atmosphere or under vacuum.

Preparation of Silylaniline Reagent A. In a 500-mL, 3-neck flask, with a N_2 inlet, a 250-mL addition funnel, and a stirring mechanism, Et_2O (200 mL) and $BrC_6H_4NH_2$ (17.2 g, 100 mmol) were combined. The solution was cooled to 0 °C, followed by the addition of *n*-BuLi (44 mL, 110 mmol, 10 % excess) dropwise via the addition funnel. The mixture was then allowed to stir and warm to room temperature for ca. 2 hrs. The mixture was cooled to 0 °C, followed by the addition of Me_3SiCl (14 mL, 110 mmol, 10 % excess) dropwise via the addition funnel. The mixture was again allowed to stir and warm to room temperature for ca. 5 hrs. Ether was then removed at reduced pressure. Upon bringing the solution to atmospheric pressure in a N_2 environment, hexanes (125 mL) were added to precipitate the lithium salt. The mixture was then filtered, the filtrate collected, and the solvent removed under reduced pressure.

The product distilled as a pale yellow liquid.

Yield: 86 %. bp: 73-77 °C (0.65 mmHg).

^{1}H NMR: δ 0.325 (s, N-SiMe$_3$), 3.506 (s, N-H), 6.585 (d, N-C$_6$H$_4$, J_{HH} = 8.8), 7.275 (d, N-C$_6$H$_4$, J_{HH} = 8.8). ^{13}C NMR: δ 0.17 (Me$_3$Si), 109.44 (N-C$_6$H$_4$), 117.58 (N-C$_6$H$_4$), 132.18 (N-C$_6$H$_4$), 146.77 (N-C$_6$H$_4$).

Preparation of Silylaniline Reagent B. In a 1.0-L, 3-neck flask, with a N_2 inlet, a 250-mL addition funnel, and a stirring mechanism, hexanes (350 mL) and Reagent **A** (24.4 g, 100 mmol) were combined. The solution was cooled to 0 °C, followed by the addition of *n*-BuLi (48 mL, 120 mmol, 20 % excess) dropwise via the addition funnel. The mixture was then allowed to stir and warm to room temperature for ca. 2 hrs. The mixture was cooled to 0 °C, followed by the addition of Me$_3$SiCl (15 mL, 120 mmol, 20 % excess) dropwise via the addition funnel. The mixture was heated at reflux for ca. 8 hrs. The mixture was then filtered, the filtrate collected, and the solvent removed under reduced pressure. The product distilled as a pale yellow liquid.

Yield: 61 %. bp: 80-85 °C (0.80 mmHg).

^{1}H NMR: δ 0.093 (s, N-(SiMe$_3$)$_2$), 6.801 (d, N-C$_6$H$_4$, J_{HH} = 8.4), 7.348 (d, N-C$_6$H$_4$, J_{HH} = 8.4). ^{13}C NMR: δ 2.04 (N-(SiMe$_3$)$_2$), 116.84 (N-C$_6$H$_4$), 131.77 (N-C$_6$H$_4$), 132.07 (N-C$_6$H$_4$), 147.28 (N-C$_6$H$_4$).

Preparation of Silylaniline Reagent C. In a 1.0-L, 3-neck flask, with a N_2 inlet, a 250-mL addition funnel, and a stirring mechanism, Et$_2$O (300 mL) and Reagent **B** (15.8 g, 50 mmol) were combined. The solution was cooled to 0 °C, followed by the addition of *n*-BuLi (24 mL, 60 mmol, 20 % excess) dropwise via the addition funnel.

The mixture was then allowed to stir and warm to room temperature for ca. 2 hrs. The mixture was cooled to 0 °C, followed by the addition of Me_3SiCl (7.6 mL, 60 mmol, 20 % excess) dropwise via the addition funnel. The mixture was again allowed to stir and warm to room temperature for ca. 5 hrs. Ether was then removed at reduced pressure. Upon bringing the solution to atmospheric pressure in a N_2 environment, hexanes (200 mL) were added to precipitate the lithium salt. The mixture was then filtered, the filtrate collected, and the solvent removed under reduced pressure. The product distilled as a colorless liquid.

Yield: 75 %. bp: 80-84 °C (0.60 mmHg).

^{1}H NMR: δ 0.120 (s, N-$(SiMe_3)_2$), 0.301 (s, Ph-$SiMe_3$), 6.921 (d, N-C_6H_4, J_{HH} = 8.0), 7.386 (d, N-C_6H_4, J_{HH} = 8.0). ^{13}C NMR: δ -0.85 (N-$(SiMe_3)_2$), 2.19 (Ph-$SiMe_3$), 122.01 (N-C_6H_4), 133.77 (N-C_6H_4), 129.79 (N-C_6H_4), 148.80 (N-C_6H_4).

Preparation of Silylaniline Reagent D. In a 500-mL, 3-neck flask, with a N_2 inlet, a 125-mL addition funnel, and a stirring mechanism, Et_2O (150 mL) and Reagent **C** (6.193 g, 20 mmol) were combined. The solution was cooled to 0 °C, followed by the addition of dry HCl solution (15 mL, 15 mmol, 7 % excess) dropwise via the addition funnel. The mixture was allowed to stir at 0 °C for ca. 4 hrs. The mixture was then allowed to stir and warm to room temperature overnight. Ether was then removed at reduced pressure. The product distilled as a colorless liquid.

Yield: 76 %. bp: 60-79 °C (0.23 mmHg).

^{1}H NMR: δ 0.299 (s, N-$SiMe_3$), 0.349 (s, Ph-$SiMe_3$), 3.570 (s, N-H), 6.742 (d, N-C_6H_4, J_{HH} = 8.4), 7.383 (d, N-C_6H_4, J_{HH} = 8.4). ^{13}C NMR: δ -0.68 (N-$SiMe_3$), 0.18 (Ph-$SiMe_3$), 115.77 (N-C_6H_4), 127.07 (N-C_6H_4), 134.68 (N-C_6H_4), 148.27 (N-C_6H_4).

Preparation of Compound 1. In a 500-mL, 3-neck flask, with a N_2 inlet, a 125-mL addition funnel, and a stirring mechanism, Et_2O (250 mL) and Reagent **B** (13.0 g, 41 mmol) were combined. The solution was cooled to 0 °C, followed by the addition of *n*-BuLi (18 mL, 45 mmol, 10 % excess) dropwise via the addition funnel. The mixture was then allowed to stir and warm to room temperature for ca. 2 hrs. The mixture was cooled to -78 °C, followed by the addition of Me_2SiClH (6 mL, 54 mmol, 30 % excess) dropwise via the addition funnel. The mixture was allowed to stir at -78 °C ca. 4 hrs. and then allowed to warm to room temperature while stirring overnight. Ether was removed at reduced pressure. Upon bringing the solution to atmospheric pressure in a N_2 environment, hexanes (150 mL) were added to precipitate the lithium salt. The mixture was then filtered, the filtrate collected, and the solvent removed under reduced pressure.

The product distilled as a colorless liquid.

Yield: 81 %. bp: 65-76 °C (0.24 mmHg).

^{1}H NMR: δ 0.114 (s, N-$(SiMe_3)_2$), 0.378 (s, Ph-SiH-Me_2), 4.467 (m, Ph-$SiMe_2$-H), 6.932 (d, N-C_6H_4, J_{HH} = 8.0), 7.409 (d, N-C_6H_4, J_{HH} = 8.0). ^{13}C NMR: δ -3.57 (N-$(SiMe_3)_2$), 2.16 (Ph-$SiHMe_2$), 116.74 (N-C_6H_4), 129.71 (N-C_6H_4), 134.71 (N-C_6H_4), 149.71 (N-C_6H_4).

Preparation of Compound 2. In a 500-mL, 3-neck flask, with a N_2 inlet, a 125-mL addition funnel, and a stirring mechanism, Et_2O (250 mL) and Reagent **B** (6.33 g, 20 mmol) were combined. The solution was cooled to 0 °C, followed by the addition of *n*-BuLi (9 mL, 22.5 mmol, 12.5 % excess) dropwise via the addition funnel. The mixture was then allowed to stir and warm to room temperature for ca. 2 hrs. The mixture was cooled to -78 °C, followed by the addition of Me_2SiCl_2 (3 mL, 25 mmol, 20 % excess) dropwise via the addition funnel. The mixture was allowed to stir at -78 °C ca. 4 hrs. and then allowed to warm to room temperature while stirring overnight. Ether was removed at reduced pressure. Upon bringing the solution to atmospheric pressure in a N_2 environment, hexanes (150 mL) were added to precipitate the lithium salt. The mixture was then filtered, the filtrate collected, and the solvent removed under reduced pressure.

The product distilled as a colorless liquid.

Yield: 55 %. bp: 55-88 °C (0.20 mmHg).

^{1}H NMR: δ 0.127 (s, N-$(SiMe_3)_2$), 0.718 (s, Ph-SiCl-Me_2), 6.983 (d, N-C_6H_4, J_{HH} = 8.2), 7.509 (d, N-C_6H_4, J_{HH} = 8.2). ^{13}C NMR: δ 0.09 (N-$(SiMe_3)_2$), 2.19 (Ph-$SiClMe_2$), 115.84 (N-C_6H_4), 134.31 (N-C_6H_4), 129.74 (N-C_6H_4), 149.14 (N-C_6H_4).

Preparation of Compound 3. In a 500-mL, 3-neck flask, with a N_2 inlet, a 125-mL addition funnel, and a stirring mechanism, Et_2O (150 mL) and Reagent **B** (6.33 g, 20 mmol) were combined. The solution was cooled to 0 °C, followed by the addition of *n*-BuLi (9 mL, 22.5 mmol, 12.5 % excess) dropwise via the addition funnel. The mixture was then allowed to stir and warm to room temperature for ca. 2 hrs. The

mixture was cooled to -78 °C, followed by the addition of $MeSiCl_3$ (2.6 mL, 22 mmol, 10 % excess) dropwise via the addition funnel. The mixture was allowed to stir at -78 °C ca. 4 hrs. and then allowed to warm to room temperature while stirring overnight. Ether was removed at reduced pressure. Upon bringing the solution to atmospheric pressure in a N_2 environment, hexanes (75 mL) were added to precipitate the lithium salt. The mixture was then filtered, the filtrate collected, and the solvent removed under reduced pressure.

The product distilled as a colorless liquid.

Yield: 45 %. bp: 63-94 °C (0.45 mmHg)

^{1}H NMR: δ 0.164 (s, N-$(SiMe_3)_2$), 1.076 (s, Ph-$SiCl_2Me$), 7.065 (d, N-C_6H_4, J_{HH} = 8.4), 7.645 (d, N-C_6H_4) J_{HH} = 8.4). ^{13}C NMR: δ 2.24 (N-$(SiMe_3)_2$), 5.85 (Ph-$SiCl_2Me$), 119.59 (N-C_6H_4), 132.33 (N-C_6H_4), 133.62 (N-C_6H_4), 142.94 (N-C_6H_4).

Preparation of Compound 4. In a 500-mL, 3-neck flask, with a N_2 inlet, a 125-mL addition funnel, and a stirring mechanism, Et_2O (150 mL) and Reagent **B** (6.33 g, 20 mmol) were combined. The solution was cooled to 0 °C, followed by the addition of *n*-BuLi (9 mL, 22.5 mmol, 12.5 % excess) dropwise via the addition funnel. The mixture was then allowed to stir and warm to room temperature for ca. 2 hrs. The mixture was cooled to -78 °C, followed by the addition of $CH_2ClSiCl(Me)_2$ (2.9 mL, 22 mmol, 10 % excess) dropwise via the addition funnel. The mixture was allowed to stir at -78 °C ca. 4 hrs. and then allowed to warm to room temperature while stirring overnight. Ether was removed at reduced pressure. Upon bringing the solution to atmospheric pressure in a N_2 environment, hexanes (75 mL) were added

to precipitate the lithium salt. The mixture was then filtered, the filtrate collected, and the solvent removed under reduced pressure.

The product distilled as a colorless liquid.

Yield: 62.5 %. bp: 79-96 °C (0.14 mmHg)

^{1}H NMR: δ 0.088 (s, N-($SiMe_3$)$_2$), 0.427 (s, Ph-Si(CH_2Cl)Me_2), 2.959 (s, Ph-$SiMe_2$(CH_2Cl)), 6.917 (d, N-C_6H_4, J_{HH} = 8.2), 7.380 (d, N-C_6H_4) J_{HH} = 8.2). ^{13}C NMR: δ –4.37 (N-($SiMe_3$)$_2$), 2.17 (Ph-Si(CH_2Cl)Me_2), 30.82 (Ph-$SiMe_2$(CH_2Cl)), 115.83 (N-C_6H_4), 129.77 (N-C_6H_4), 134.02 (N-C_6H_4), 149.71 (N-C_6H_4).

Preparation of Compound 5. In a 500-mL, 3-neck flask, with a N_2 inlet, a 125-mL addition funnel, and a stirring mechanism, Et_2O (250 mL) and Reagent **B** (11.1 g, 35 mmol) were combined. The solution was cooled to 0 °C, followed by the addition of *n*-BuLi (17 mL, 42.5 mmol, 20 % excess) dropwise via the addition funnel. The mixture was then allowed to stir and warm to room temperature for ca. 2 hrs. The mixture was cooled to -78 °C, followed by the addition of H_2C=CH$Si(CH_3)_2Cl$ (6 mL, 43.5 mmol, 24 % excess) dropwise via the addition funnel. The mixture was allowed to stir at -78 °C ca. 4 hrs. and then allowed to warm to room temperature while stirring overnight. Ether was removed at reduced pressure. Upon bringing the solution to atmospheric pressure in a N_2 environment, hexanes (150 mL) were added to precipitate the lithium salt. The mixture was then filtered, the filtrate collected, and the solvent removed under reduced pressure.

The product distilled as a colorless liquid.

Yield: 83 %. bp: 50-87 °C (0.30 mmHg).

^{1}H NMR: δ 0.139 (s, N-($SiMe_3$)$_2$), 0.402 (s, Ph-Si-Me_2), 5.798 (m, Si-(CH=CH_2)), 6.107 (m, Si-(CH=CH_2)), 6.361 (m, Si-(CH=CH_2)), 6.950 (d, N-C_6H_4, J_{HH} = 8.2), 7.413 (d, N-C_6H_4) J_{HH} = 8.2). ^{13}C NMR: δ –2.65 (N-($SiMe_3$)$_2$), 2.08 (Ph-Si-Me_2), 129.62 (Si-(CH=CH_2)), 138.64 (Si-(CH=CH_2)), 116.88 (N-C_6H_4), 131.55 (N-C_6H_4), 134.14 (N-C_6H_4), 148.88 (N-C_6H_4).

Preparation of Compound 6. In a 1.0-L, 3-neck flask, with a N_2 inlet, a 125-mL addition funnel, and a stirring mechanism, Et_2O (300 mL) and Reagent **B** (9.48 g, 30 mmol) were combined. The solution was cooled to 0 °C, followed by the addition of *n*-BuLi (14 mL, 36 mmol, 20 % excess) dropwise via the addition funnel. The mixture was then allowed to stir and warm to room temperature for ca. 2 hrs. The mixture was cooled to -78 °C, followed by the addition of H_2C=$CHSiCl_3$ (5 mL, 39 mmol, 31 % excess) dropwise via the addition funnel. The mixture was allowed to stir at -78 °C ca. 4 hrs. and then allowed to warm to room temperature while stirring overnight. Ether was removed at reduced pressure. Upon bringing the solution to atmospheric pressure in a N_2 environment, hexanes (200 mL) were added to precipitate the lithium salt. The mixture was then filtered, the filtrate collected, and the solvent removed under reduced pressure.

The product distilled as a colorless liquid.

Yield: 33 %. bp: 90-112 °C (0.30 mmHg).

^{1}H NMR: δ 0.143 (s, N-($SiMe_3$)$_2$), 5.988 (m, Si-(CH=CH_2)), 6.196 (m, Si-(CH=CH_2)), 6.365 (m, Si-(CH=CH_2)), 7.042 (d, N-C_6H_4, J_{HH} = 8.4), 7.632 (d, N-C_6H_4) J_{HH} = 8.4). ^{13}C

NMR: δ 2.19 (N-($SiMe_3$)$_2$), 130.00 (Si-(CH=CH_2)), 138.21 (Si-(CH=CH_2)), 117.18 (N-C_6H_4), 132.26 (N-C_6H_4), 134.28 (N-C_6H_4), 152.42 (N-C_6H_4).

Preparation of Compound 7. In a 1.0-L, 3-neck flask, with a N_2 inlet, a 125-mL addition funnel, and a stirring mechanism, Et_2O (300 mL) and Reagent **B** (9.48 g, 30 mmol) were combined. The solution was cooled to 0 °C, followed by the addition of *n*-BuLi (14 mL, 36 mmol, 20 % excess) dropwise via the addition funnel. The mixture was then allowed to stir and warm to room temperature for ca. 2 hrs. The mixture was cooled to -78 °C, followed by the addition of H_2C=CHSi$MeCl_2$ (4.7 mL, 36 mmol, 20 % excess) dropwise via the addition funnel. The mixture was allowed to stir at -78 °C ca. 4 hrs. and then allowed to warm to room temperature while stirring overnight. Ether was removed at reduced pressure. Upon bringing the solution to atmospheric pressure in a N_2 environment, hexanes (200 mL) were added to precipitate the lithium salt. The mixture was then filtered, the filtrate collected, and the solvent removed under reduced pressure.

The product distilled as a colorless liquid.

Yield: 52 %. bp: 91-112 °C (0.30 mmHg)

^{1}H NMR: δ 0.146 (s, N-($SiMe_3$)$_2$), 0.795 (s, Ph-Si-Me), 6.013 (m, Si-(CH=CH_2)), 6.246 (m, Si-(CH=CH_2)), 6.357 (m, Si-(CH=CH_2)), 7.011 (d, N-C_6H_4, J_{HH} = 8.2), 7.536 (d, N-C_6H_4) J_{HH} = 8.2). ^{13}C NMR: δ –0.81 (N-($SiMe_3$)$_2$), 2.21 (Ph-Si-Me), 128.53 (Si-(CH=CH_2)), 135.60 (Si-(CH=CH_2)), 129.87 (N-C_6H_4), 133.55 (N-C_6H_4), 134.86 (N-C_6H_4), 150.78 (N-C_6H_4).

Table 1. NMR Spectroscopic Data for Silylaniline Reagent **A**

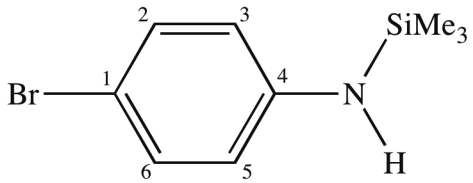
	^{1}H NMR			^{13}C NMR	
Compound	Signal	δ	J_{HH}		δ
 Reagent **A**	N-$SiMe_3$	0.33 (s)		0.17	
	N-H	3.51 (s)			
	N-C_6H_4	6.59 (d)	8.8	C_1	109.44
		7.28 (d)	8.8	$C_{2,6}$	117.58
				$C_{3,5}$	132.18
				C_4	146.77

Table 2. NMR Spectroscopic Data for Silylaniline Reagent **B**

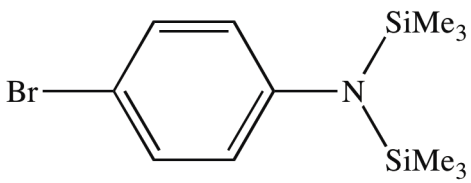
	^{1}H NMR			^{13}C NMR	
Compound	Signal	δ	J_{HH}		δ
 Reagent **B**	N-$(SiMe_3)_2$	0.09 (s)		2.04	
	N-C_6H_4	6.80 (d)	8.4	C_1	116.84
		7.35 (d)	8.4	$C_{2,6}$	131.77
				$C_{3,5}$	132.07
				C_4	147.28

Table 3. NMR Spectroscopic Data for Silylaniline Reagent **C**

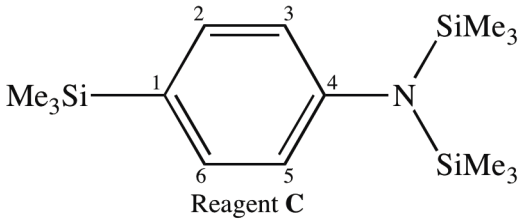
Compound	^{1}H NMR Signal	δ	J_{HH}	^{13}C NMR	δ
 Reagent **C**	N-$(SiMe_3)_2$	0.12 (s)			-0.85
	Ph-$SiMe_3$	0.30 (s)			2.19
	N-C_6H_4	6.92 (d)	8.0	C_1	122.01
		7.39 (d)	8.0	$C_{2,6}$	133.77
				$C_{3,5}$	129.79
				C_4	148.80

Table 4. NMR Spectroscopic Data for Silylaniline Reagent **D**

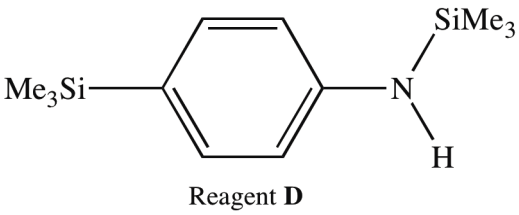
Compound	^{1}H NMR Signal	δ	J_{HH}	^{13}C NMR	δ
 Reagent **D**	N-$SiMe_3$	0.30 (s)		-0.68	
	Ph-$SiMe_3$	0.35 (s)		0.18	
	N-H	3.57 (s)			
	N-C_6H_4	6.74 (d)	8.4	C_1	115.77
		7.38 (d)	8.4	$C_{2,6}$	127.07
				$C_{3,5}$	134.68
				C_4	148.27

Table 5. NMR Spectroscopic Data for Compound **1**

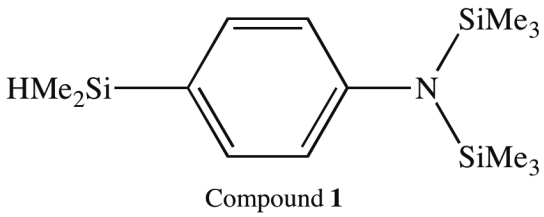
	^{1}H NMR			^{13}C NMR	
Compound	Signal	δ	J_{HH}	δ	
 Compound **1**	N-$(SiMe_3)_2$	0.11 (s)		-3.57	
	Ph-SiH-Me_2	0.38 (d)	3.6	2.16	
	Ph-$SiMe_2$-H	4.47 (m)			
	N-C_6H_4	6.93 (d)	8.0	C_1	116.74
		7.41 (d)	8.0	$C_{2,6}$	129.71
				$C_{3,5}$	134.71
				C_4	149.71

Table 6. NMR Spectroscopic Data for Compound **2**

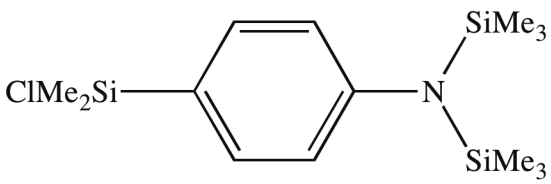
Compound	^{1}H NMR			^{13}C NMR	
	Signal	δ	J_{HH}		δ
 Compound **2**	N-$(SiMe_3)_2$	0.13 (s)		0.09	
	Ph-$SiClMe_2$	0.72 (s)		2.19	
	N-C_6H_4	6.98 (d)	8.4	C_1	115.84
		7.51 (d)	8.4	$C_{2,6}$	129.74
				$C_{3,5}$	134.31
				C_4	149.14

Table 7. NMR Spectroscopic Data for Compound **3**

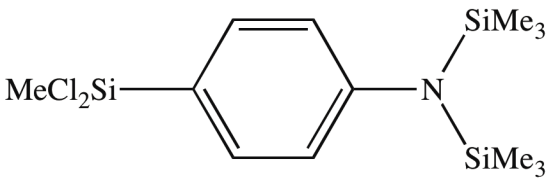
	^{1}H NMR			^{13}C NMR	
Compound	Signal	δ	J_{HH}	δ	
 Compound **3**	N-$(SiMe_3)_2$	0.16 (s)		2.24	
	Ph-$SiCl_2Me$	1.08 (s)		5.85	
	N-C_6H_4	7.07 (d)	8.4	C_1	119.59
		7.65 (d)	8.4	$C_{2,6}$	132.33
				$C_{3,5}$	133.62
				C_4	142.94

Table 8. NMR Spectroscopic Data for Compound **4**

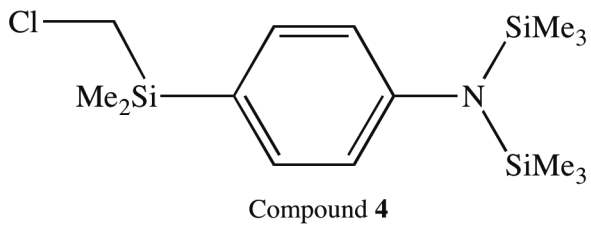
Compound	^{1}H NMR Signal	δ	J_{HH}	^{13}C NMR	δ
 Compound **4**	N-$(SiMe_3)_2$	0.09 (s)		-4.37	
	Ph-Si$(CH_2Cl)Me_2$	0.43 (s)		2.17	
	Ph-$SiMe_2(CH_2Cl)$	2.96 (s)		30.82	
	N-C_6H_4	6.92 (d)	8.2	C_1	115.83
		7.38 (d)	8.2	$C_{2,6}$	129.77
				$C_{3,5}$	134.02
				C_4	149.71

Table 9. NMR Spectroscopic Data for Compound **5**

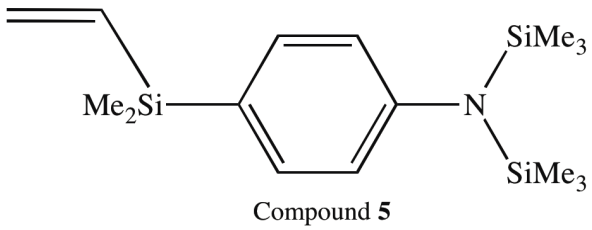
Compound	^{1}H NMR Signal	δ	J_{HH}	^{13}C NMR	δ
 Compound **5**	N-$(SiMe_3)_2$	0.14 (s)			-2.65
	Ph-Si-Me_2	0.40 (s)			2.08
	Si-$(CH=CH_2)$	5.80 (m)			129.62
		6.11 (m)			138.64
		6.36 (m)			
	N-C_6H_4	6.95 (d)	8.2	C_1	131.55
		7.41 (d)	8.2	$C_{2,6}$	134.14
				$C_{3,5}$	116.88
				C_4	148.88

Table 10. NMR Spectroscopic Data for Compound **6**

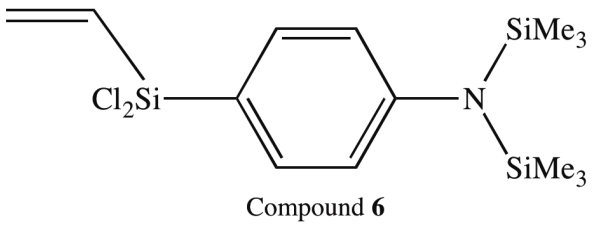
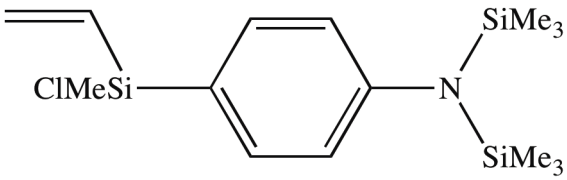
Compound	^{1}H NMR Signal	δ	J_{HH}	^{13}C NMR	δ
 Compound **6**	N-$(SiMe_3)_2$	0.14 (s)			2.19
	Si-$(CH{=}CH_2)$	5.99 (m)			130.00
		6.20 (m)			138.21
		6.37 (m)			
	N-C_6H_4	7.04 (d)	8.4	C_1	117.18
		7.63 (d)	8.4	$C_{2,6}$	132.26
				$C_{3,5}$	134.28
				C_4	152.42

Table 11. NMR Spectroscopic Data for Compound **7**

Compound	^{1}H NMR Signal	δ	J_{HH}	^{13}C NMR	δ
 Compound **7**	N-$(SiMe_3)_2$	0.15 (s)		-0.81	
	Ph-Si-Me	0.80 (s)		2.21	
	Si-$(CH=CH_2)$	6.01 (m)		128.53	
		6.25 (m)		135.60	
		6.36 (m)			
	N-C_6H_4	7.01 (d)	8.2	C_1	129.87
		7.54 (d)	8.2	$C_{2,6}$	133.55
				$C_{3,5}$	134.86
				C_4	150.78

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