# ON THE SYNTHESIS AND DEPROTONATION OF BIPYRROMETHYL SILANES

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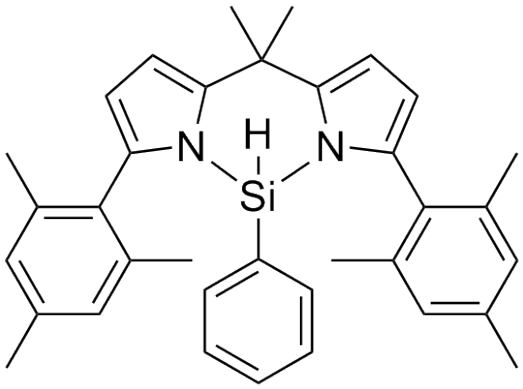


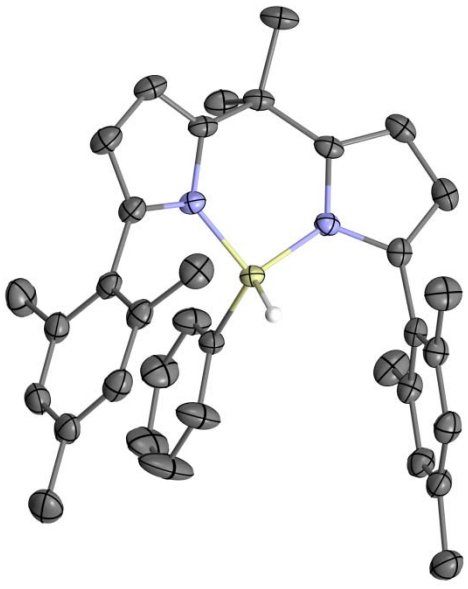

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# TABLE OF CONTENTS


ABSTRACT 3

I. INTRODUCTION 4

1. HOMOGENEOUS CATALYSIS 4

2. SILYL LIGANDS 4

3. PYRROLES AND BIPYRROMETHYL COMPOUNDS 5

4. IRON SILANES AND THEIR USE AS CATALYSTS 7

5. AIM 7

II. DESIGN OF THE SCAFFOLDS 8

1. THE TWO SCAFFOLDS 8

III. RESULTS 9

1. SYNTHESIS OF THE SCAFFOLDS 9

2. SYNTHESIS OF THE SILANES 12

IV. DEPROTONATION OF THE SILANE 17

1. FIRST BASE: KHMDS 17

2. SECOND BASE: KH 19

V. OXIDATIVE ADDITION TO PLATINUM 21

VI. HALOGENATED SILANES 22

1. SYNTHESIS OF PHENYL(TRIBROMO)SILANE 23

2. SILYLATION OF THE SCAFFOLD 23

3. DIRECT HALOGENATION OF THE BIPYRROMETHYL SILANE 23

VII. CONCLUSIONS 25

VIII. OUTLOOK 25

IX. ACKNOWLEDGEMENTS 25

X. EXPERIMENTALS 26

XI. REFERENCES 31

XII. APPENDIX: ANALYTICAL DATA 33

# ABSTRACT

An important field in catalysis is transition-metal (TM) based carbon-carbon cross coupling. As noble metals are scarce, efforts are made to use first-row transition metals for these catalytic conversions instead. However, due to their current design, some base metal TM complexes contain phosphine ligands. These ligands are prone to dissociation, making these complexes difficult to characterize. The use of strongly binding anionic silyl ligands, isoelectronic to phosphines, might aid in the stability of the complex and thus allow for more facile characterisation. This would lead to a better understanding of the mechanism behind carbon-carbon cross coupling, and will eventually allow for better catalyst design.

In this work, 1,9-diphenyl-5,5-dimethylbipyrromethane ($H_2$dpbpm) and 1,9-dimesityl-5,5-dimethylbipyrromethane ($H_2$dmbpm) are synthesized in a three-step synthesis, largely according to literature procedures. These compounds are then silylated in a two-step synthesis *via* lithiation, of which 1,9-dimesityl-5,5-dimethylbipyrromethyl phenyl silane is isolated in good yields. The crystal structure of this compound is presented as well. Attempts to deprotonate the silane are made, but most led to degradation of the scaffold and desilylation of the silane, if the reagents reacted at all. The potassium salt of the siloxane was synthesized and crystallized serendipitously by reaction of PhSi(dmbpm)H in the presence of potassium hydride, 18-crown-6 and traces of moisture.

Methods to circumvent the problem of deprotonation included oxidative addition to platinum(0) tetrakis(triphenylphosphine), as well as incorporating halogens into the designed silane for subsequent reduction. These methods proved to be unsuccessful as well, as oxidative addition did not occur, and silylation with trihalogenated silanes resulted in an incomprehensible mixture of compounds, often not representing the bipyrromethyl backbone, from which no single compound could be isolated.

# I. INTRODUCTION

## 1. HOMOGENEOUS CATALYSIS

The importance of catalysis for society and industry is supported by the large majority of chemical processes that involve the use of a catalyst in one or more of the reaction steps, whether on small or industrial scale. A large part of the homogeneous catalysts involve a transition metal, and within that class second- and third row transition metals like platinum, palladium, osmium and iridium are well represented. Examples include Vaska's complex, Wilkinson's catalyst and Adam's catalyst.

However, the natural abundance of these noble metals is low. This, combined with their chemical significance, makes them very valuable. An interesting alternative would be the use of first-row transition metals like iron, cobalt and nickel, which are abundant and thus an attractive economical option.

The aforementioned noble metals are not yet fully replaced by their first-row analogues due to several reasons ranging from weak metal-ligand bonds to the ability of these metals to acquire a high spin state, complicating catalyst design. This is because electrons in high spin-state metal-complexes populate the anti-bonding orbital of the metal-ligand bond, lengthening and thus weakening this bond.

## 2. SILYL LIGANDS

A commonly used ligand in homogeneous catalysis is phosphine (general formula $PR_3$), because it binds strongly to (transition) metals and can dissociate with relative ease in favour of other ligands. Silyl ligands, however, besides being potent σ-donors, are good π-acceptors, as well. Furthermore, the bond between the metal centre and a silyl ligand ($R_3Si^-$), has more of an ionic character. This makes silanide-based ligands interesting compounds to explore. Moreover, $R_3Si$-ligand is a stronger field ligand than the isolelectronic phosphines and can possibly inhibit Fe(II) from becoming high spin, as it increases the energy gap between the $t_{2g}$ and $e_g$ orbitals. Even if the $e_g$ orbitals are occupied, which would promote dissociation of the ligand (as these electrons occupy antibonding orbitals), the strong ionic character of the Si-M bond is expected to prevent dissociation.

Because the silyl-ligands are expected not to dissociate from metal complexes as easily as phosphines do, this allows for better characterisation of the homogeneous catalysts that are designed to perform carbon-carbon cross coupling, given that they are able to replace the isoelectronic phosphines. This allows for better understanding of the mechanisms involved in this process, and will subsequently lead to better catalyst design.

The silyl-ligands that will be described in this project are intended for iron-based catalysis. Notable examples of this kind of catalysis include C-H-bond oxidation[1] and Kumada cross-coupling[2, 3]. An important downside to iron-based catalysts, however, is its tendency to partake in one-electron processes. Iron has lots of possible oxidation states (-2 to +5), where palladium, another known metal in heterogeneous catalysis, has 0, +2 and +4, only allowing two-electron processes. This prevents any paramagnetism and, more importantly, radical chemistry. In general, it makes for more well-behaved reactions.

An example of an anionic silyl ligand is tripyrrolylsilanide[4]. Its electron-accepting orbitals are shown in figure 1. These are similar to those of the isoelectronic phosphine (figure 2). The nature of the N-substituent on silicon is important[4]. Pyrrolyl substituents are effective electron-withdrawing groups as a result of aromatic delocalisation of the lone pair on nitrogen into the heterocycle. Pyrroles, and other similar five-membered ringstructures in which the nitrogen atom is part of an aromatic ring, cannot donate this lone pair because that would break the aromaticity. This makes the p-orbital on silicon more available for bonding and thus increasing its π-acidity.

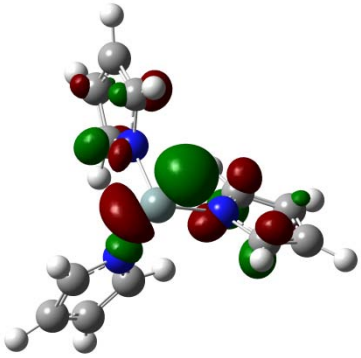


FIGURE 1: TRISPYRROLYL SILANIDE (LUMO) [5]

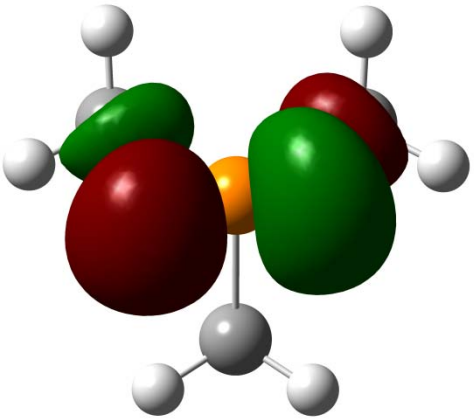


FIGURE 2: TRIMETHYL PHOSPHINE (LUMO+1) [5]

Studies with molybdenum[6] and rhodium and iridium[7] showed that, although the metal-silyl bond is strong, the monodentate ligand is susceptible to cleavage by nucleophiles and electrophiles, as well as insertion of certain molecules, including alkenes, carbon monoxide and compounds containing carbonyl groups. All these pathways involve the reagent to closely approach the Si-M bond leading to its cleavage.

A way to circumvent this lability is to use a chelating scaffold to bind the silicon with two covalent bonds. In a recent study by Tanaka and Osuka[8], silanes were synthesized which adapt a boat-shaped 2,7-diaza-1-silepin structure in a butterfly-like conformation (the structure is presented in figure 3). It was shown that the chelating effect of the scaffold greatly enhances the stability of the bipyrrosilane, to the point where it becomes stable under aerobic conditions. Besides the chelating effect, the authors claim the alkyl-substituents on the silicon are responsible for additional kinetic stabilisation. These silicon complexes were also found to exhibit blue emissions in both solution and in the solid-state, which might make these compounds exploitable as fluorophores.

Besides a chelating effect, adding sterically demanding substituents on the 2-position of the pyrrole (the 1- and 9-positions of the bipyrromethane backbone) creates steric bulk and thus provides additional protection for the metal-ligand bond.

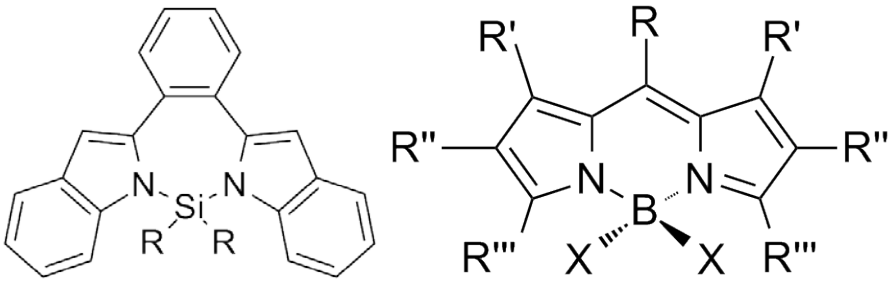



FIGURE 3: LEFT: THE STRUCTURE OF A INDOLE-BASED SILANE, AS SYNTHESIZED BY TANAKA AND OSUKA [8] (R = ME, ET, PH, TOL). ON THE RIGHT, THE GENERAL STRUCTURE OF A BODIPY, A USEFUL DYE AND PROTEIN MARKER.

## 3. PYRROLES AND BIPYRROMETHYL COMPOUNDS

An important research field where pyrrolyl and bipyrromethyl compounds are being exploited is that of fluorescence and spectroscopy. Notable among the compounds used here are boron dipyrromethenes, or BODIPYs (figures 3 and 4). They are being applied as molecular-scale probes for monitoring real-time events in nanoscopic environments[9]. They offer insight in physical and chemical events where conventional imaging proves impossible. They are exploited as protein markers[10], selective ion sensors[11] and solar sell sensitizers[12], among other examples.

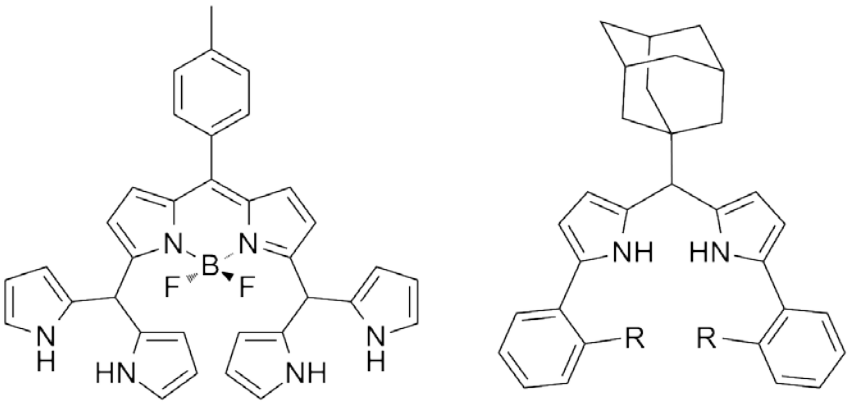
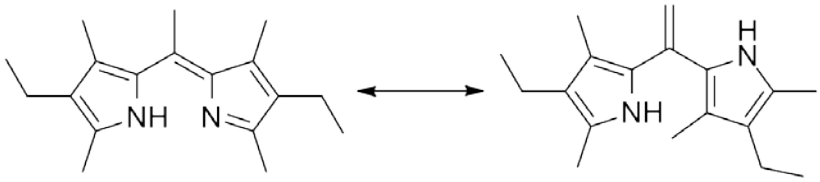



**FIGURE 4: EXAMPLES OF PYRROLE-BASED SCAFFOLDS. ADAPTED FROM [11] (LEFT) AND [13] (RIGHT).**

Different communications use different substituents on the aromatic heterocycles of the BODIPY backbone.[13,14] Beside complexation to boron, the bipyrromethyl scaffolds also found their way into organometallic chemistry, *e.g.* a chelating triphosphine for transition-metal complexation while sustaining its fluorescent properties.[15] The group of Wagler[14] used their scaffold to bind a silane *via* lithiation and subsequent reaction with a suitable organochlorosilane. The structure discussed in Wagler's work has one methyl group on the bridge connecting the heterocycles, resulting in a scaffold-precursor that undergoes a tautomerisation, shown in scheme 1. The authors chose to use *n*-butyl lithium to enhance the reactivity of the bipyrromethane scaffold, because, referring to the work of Sakamoto[16], mixing the bare scaffold with $SiCl_4$ in the presence of triethylamine left the starting materials unreacted.

The two tautomers coexist in equilibrium in solution: they were isolated from similar solvents yet at different temperatures. This was also confirmed by computational methods, which also revealed there is an energy difference of only 0.96 kcal per mole between the two structures. Unexpectedly, variable temperature NMR studies in *n*-$C_6D_{14}$ provided no evidence for an equilibrium, and only a set of signals characteristic for the molecule on the right-hand side of the double-sided arrow were observed in the range between -55 and +18 °C.

The right-hand side of the equilibrium appeared to be more stable upon lithiation as well. Reaction of this compound with *n*-butyl lithium thus yielded the dilithiated species which allowed for easy conversion into the silicon-containing bipyrromethene by reaction with a suitable silane. The silanes used in that publication were dimethyldichlorosilane, diphenyldichlorosilane and 1,1-dichlorosilacyclobutane.




**SCHEME 1: TAUTOMERS OF A PREVIOUSLY SYNTHESIZED BIPYRROMETHENE. ADAPTED FROM [14].**

## 4. IRON SILANES AND THEIR USE AS CATALYSTS

One of the very first transition metal-silane compounds was a iron-silane complex.[17] But it wasn't until 1965 that other (cobalt-based) silanes were synthesized, which also led to the discovery of transition metal catalyzed hydrosilylation of olefins.[18] Interest in silylmetallic compounds grew steadily, and nowadays nearly all the transition metals know silyl derivatives.[19]

Reactivity and chemistry of silylmetallic compounds are similar to those of organometallic analogues. An important difference, however, is that silylmetallic compounds, notably those of the late transition metals, are not likely to undergo insertion reactions. This is perhaps explained by the $\pi$-backbonding capabilities of the silyl-group, which shortens the bond to the metal below the expected value for covalent single bonds and thus strengthening it. However, silylmetallic compounds are more prone to dissociation via addition/elimination reactions.

There is still much to learn on silylmetallic compounds, and research in both stoichiometric and catalytic fields with transition metal-silyl derivatives continues.

## 5. AIM

The aim of the project was to synthesize silanes using chelating pyrrole-based scaffolds and a suitable silane precursor. Afterwards, attempts were made to deprotonate the silane at the silicon-atom using a non-coordinating base to produce the anionic silanide.

The bipyrromethyl scaffold will be synthesized from free pyrrole in  a three-step synthesis, largely according to literature procedures. Afterwards, the pyrroles will be deprotonated using an organolithium reagent, followed by silylation with dichlorophenylsilane. Finally, deprotonation of the silicon will be attempted using potassium bis(trimethylsilyl)amide and potassium hydride.

# II. DESIGN OF THE SCAFFOLDS

Following the ideas outlined in the previous chapter, two silanes were designed that likely possess the wanted qualities. The steric bulk of both the scaffold and the substituents on the silicon itself would prevent addition/elimination reactions taking place at the silicon atom, and two pyrrole-like moieties will create a chelating effect, strongly enhancing the stability of the silane.

## 1. THE TWO SCAFFOLDS

Two bipyrromethane scaffolds are of particular interest. These are 1,9-diphenyl-5,5-dimethylbipyrromethane ($H_2$dpdpm, **1a**) and 1,9-dimesityl-5,5-dimethylbipyrromethane ($H_2$dmbpm, **1b**). The structures are presented in figure 5.

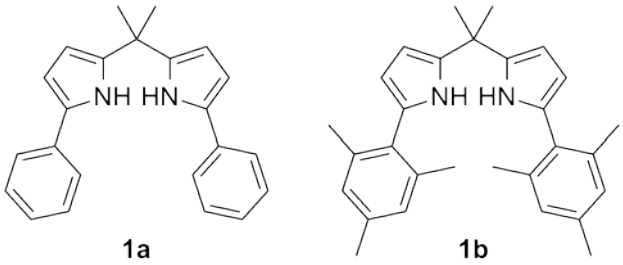



**FIGURE 5: THE STRUCTURES OF THE TWO SCAFFOLDS SYNTHESIZED IN THIS RESEARCH.**

The two pyrrole-moieties provide an excellent basis for a chelating effect, creating a six-membered ring with the silicon-atom upon silylation. The two aryl substituents will provide the steric bulk that will protect the future silicon-metal-bond.

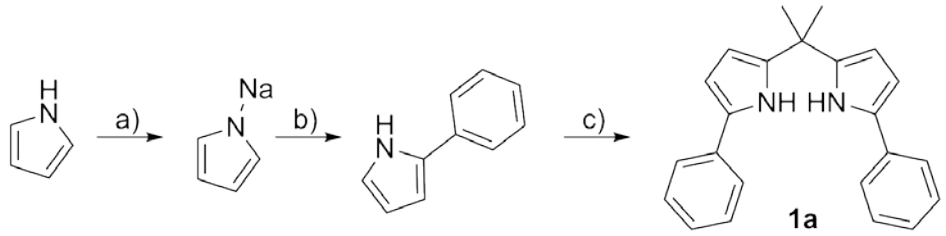
The aryl pyrroles that make up the scaffold have been synthesized before in the pursuit of a general method for the arylation of pyrrolides with large aryl-moieties in the positions adjacent to the nitrogen atom[20]. Arylpyrroles are useful precursors in the synthesis of fluorescent dyes[21a], pharmaceuticals[21b] and insecticides.[21c] Phenyl pyrrole has been used for the synthesis of a bipyrromethane scaffold, albeit using adamantane-type ketones and aldehydes[13] to bridge the pyrrole-moieties (the use of carbonyl-containing reagents for the condensation of pyrroles is explained in the next chapter). In their research, these bipyrromethane molecules were synthesized to function as anion receptors. They found that different substituents on the phenylrings lead to a change in photophysical properties and thus different spectroscopic responses in the presence of anions from tetrabutylamonium salts. These anions interacted *via* hydrogenbonds with the N-H-protons from the pyrrolides, thus creating fluorescent anion sensors.

Compound **1b** has been synthesized before for complexation to transition metals, albeit without the incorporation of the silicon.[22] In that study, $H_2$dmbpm was lithiated with PhLi and subsequently metallated by reaction with a stoichiometric amount of divalent metal precursor (i.e. $MCl_2(py)_2$; M = Fe, Zn, Co, Ni, Mn) to yield a metal complex of the type M(dmbpm)$(py)_2$. Differential pulse voltammetry was used to reveal a two-electron oxidation pathway which is entirely ligand-based and shared among the metal centers prepared, regardless of their d-electron configuration. This indicates that the highest occupied molecular orbitals belong to the ligand and are as such above the partially filled 3d-orbitals of the metal.

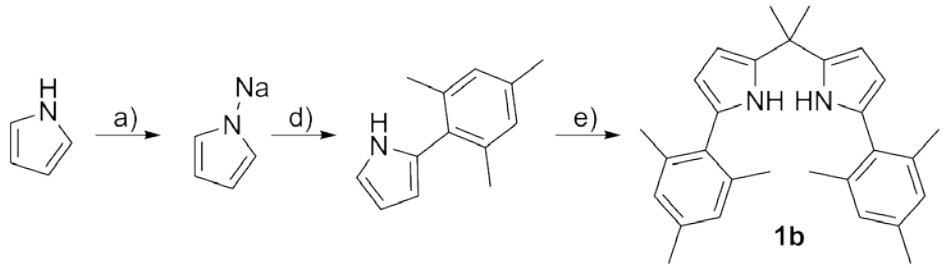
# III. RESULTS

## 1. SYNTHESIS OF THE SCAFFOLDS

Compounds **1a** and **1b** were synthesized from free pyrrole in a three step synthesis (schemes 2 and 3). First, pyrrole reacted with sodium hydride in tetrahydrofuran to give the sodium pyrrolide (step a[20]). This then reacted with zinc chloride and iodobenzene or 2-bromomesitylene in dioxane in the presence of a catalytic amount of palladium diacetate and 2-ditertbutylphosphinobiphenyl (otherwise known as "JohnPhos") as a supporting ligand (steps b and d[20]). Lastly, the resulting 2-arylpyrroles condensated to $H_2$dpbpm (**1a**) and $H_2$dmbpm (**1b**) by reaction with either acetone or 2,2-dimethoxypropane and a catalytic amount of either trifluoroacetic acid (TFA) or pyridinium *p*-toluene sulphonate (PPTS) in dichloromethane (steps c and e).[22]




**SCHEME 2: THE SYNTHESIS OF THE BIPYRROMETHYL SCAFFOLD FROM PYRROLE. REAGENTS: (A) SODIUM HYDRIDE, THF. (*QUANT.*). (B) IODOBENZENE, ZINC CHLORIDE, PALLADIUM-CATALYST, DIOXANE (35%). (C) ACETONE, TRIFLUOROACETIC ACID, DICHLOROMETHANE (24%).**

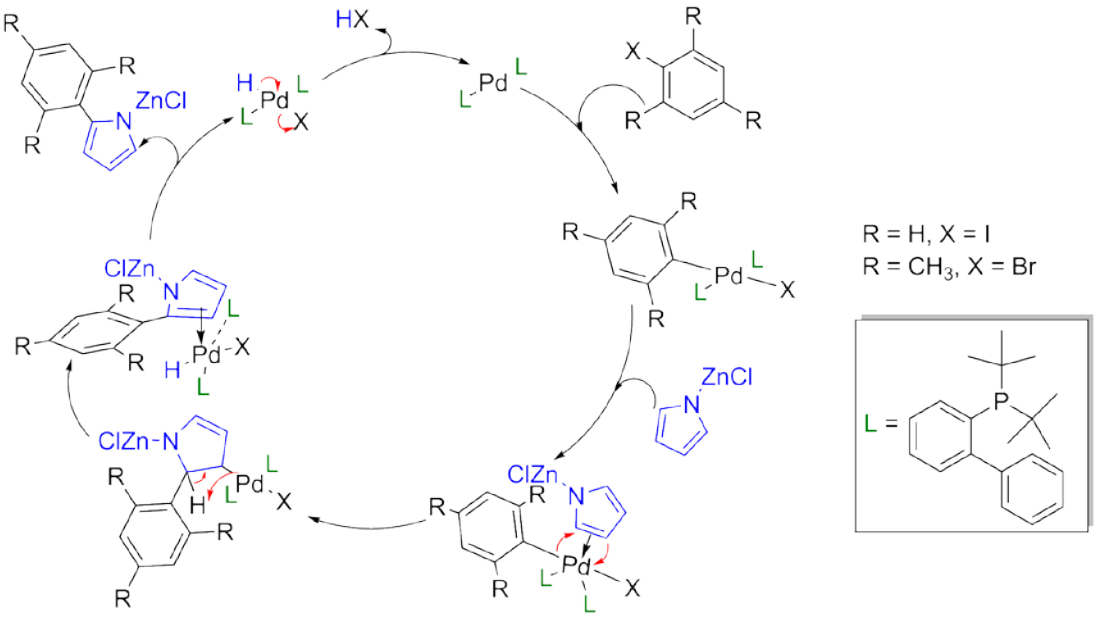



**SCHEME 3: THE SYNTHESIS OF THE BIPYRROMETHYL SCAFFOLD FROM PYRROLE. REAGENTS: (A) SODIUMHYDRIDE, THF. (*QUANT.*). (D) 2-BROMOMESITYLENE, ZINC CHLORIDE, PALLADIUM-CATALYST, DIOXANE (47%). (E) 2,2-DIMETHOXYPROPANE, PYRIDINIUM *P*-TOLUENE SULPHONATE, DICHLOROMETHANE (92%).**

After the deprotonation of the pyrrole, a Pd-catalyzed Heck-type arylation takes place. The general mechanism of the arylation is shown in scheme 4.

Although the reagents resemble those used in Negishi-type cross-coupling reactions, it is hard to defend that this reaction has a Negishi-type mechanism. In the Negishi cross-coupling, an organozincchloride reacts with a halogenated aryl species over a palladium catalyst to yield the arylated organic compound and the dihalogenated zinc(II) salt.[23] The (carbon-)atom that is bound to the zinc-cation is the atom that is cross-coupled. However, in this reaction, the sodium pyrrolide is transmetallated *in situ* to give the zinc(II)chloric pyrrolide. This means that the zinc-cation is bound to the deprotonated nitrogen-atom of the pyrrole. According to the mechanism of the Negishi-type cross-coupling, the pyrrole becomes arylated at the nitrogen-atom; however, this is not observed, as the pyrrole is arylated on the carbon-atom adjacent to the nitrogen-atom (the 2-position). Resonance structures of the pyrrolide anion would place the negative charge on one of the carbon-atoms, but this is of course less desirable/stable than the case where it is on the nitrogen-atom. Even if the pyrrolide would attack the palladium with a negatively charged carbanion, this would mean the nitrogen-atom of the heterocycle has a double bond with one carbon and a single bond to another, which is not observed. Therefore, I propose this reaction takes place using a Heck-type mechanism of arylation.

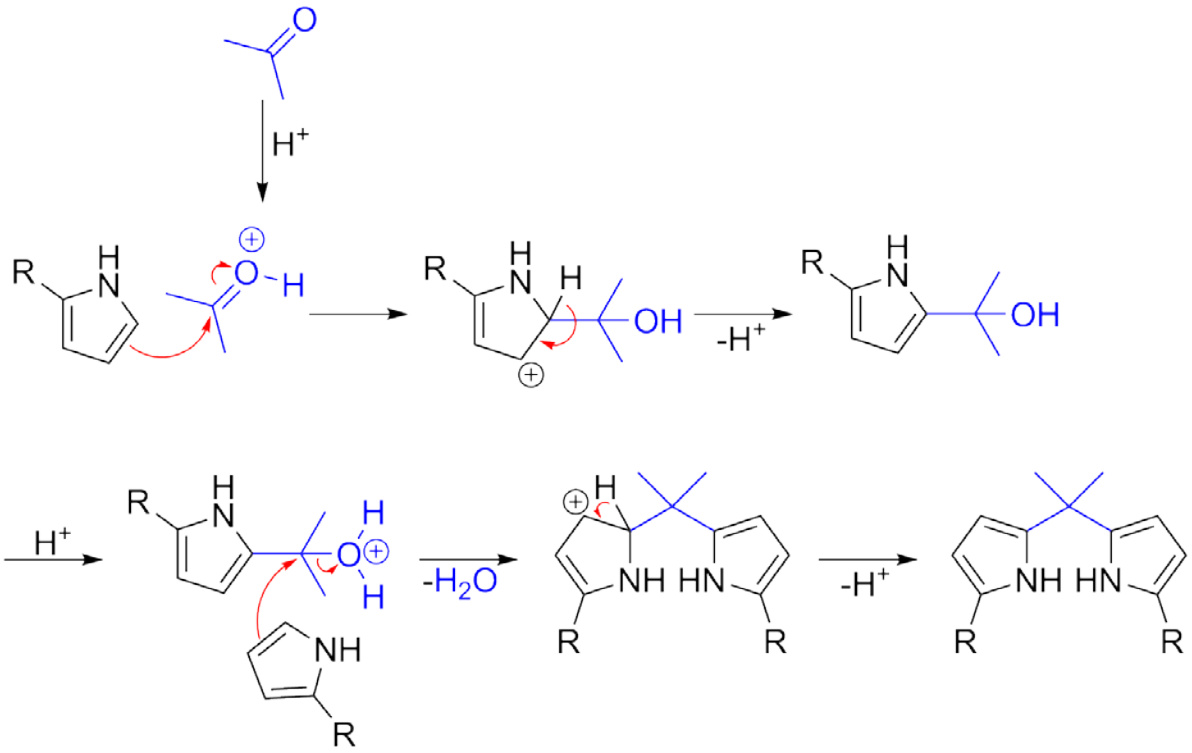
The (pyrrolyl)zinc chloride is made *in situ* from the sodium pyrrolide. The arylhalogenide (either iodobenzene or 2-bromomesitylene) reacts with the palladium catalyst *via* oxidative addition. In case of iodobenzene, the catalyst is palladium(ii) acetate; in the case of 2-bromomesitylene, the catalyst is tris(dibenzylideneacetone) dipalladium(0). In both cases, the supporting ligand is the JohnPhos compound. As the pyrrolide approaches the catalyst, the aryl-group leaves the palladium and σ-bond metathesis occurs. After the arylpyrrole leaves the molecule, reductive elimination of the hydrogenhalogenide restores the catalyst. This can react with the zincchloric arylpyrrolide to form the dihalogen zinc salt and 2-aryl pyrrole (the water used in the aqueous workup also forms the arylpyrrolide from the salt). An important observation in this step is that, in the case of iodobenzene, 2,5-diphenylpyrrole is synthesized while, when using 2-bromomesitylene, little to no 2,5-dimesitylpyrrole is found. Based on this observation, it is concluded that that steric bulk prevents or severely limits double arylation.




**SCHEME 4: ARYLATION OF (PYRROLYL)ZINC CHLORIDE, USING A PALLADIUM CATALYST.**

Dioxane is chosen *in lieu* of tetrahydrofuran because of its higher boiling point. This way, the reaction can be carried out in regular glassware, rather than in a pressure vessel. Due to the insolubility of the zinc- and sodium salts, yields in this step were much lower than expected. During the aqueous workup, 2-phenylpyrrole and 2,5-diphenylpyrrole are recovered as the organic compounds in step (b) and 2-mesitylpyrrole in step (d). The zinc- and sodium salts are discarded. GCMS analysis reveals traces of biphenyl, the result of homo-coupling; no bimesityl was observed due to its bulkiness. The arylpyrroles can be separated and isolated using column chromatography.

Step (c) and (e) involve the acid-catalyzed condensation of arylpyrrole with acetone (in the case of 2-phenylpyrrole) or 2,2-dimethoxypropane (in the case of 2-mesitylpyrrole). The mechanism is shown in scheme 5 for step (c). This method follows the one designed by Swartz II and Odom[24], which they adapted from Lindsey and coworkers.[25] King and Betley[22] used a variation of this procedure by using PPTS and 2,2-dimethoxypropane, rather than TFA and acetone.

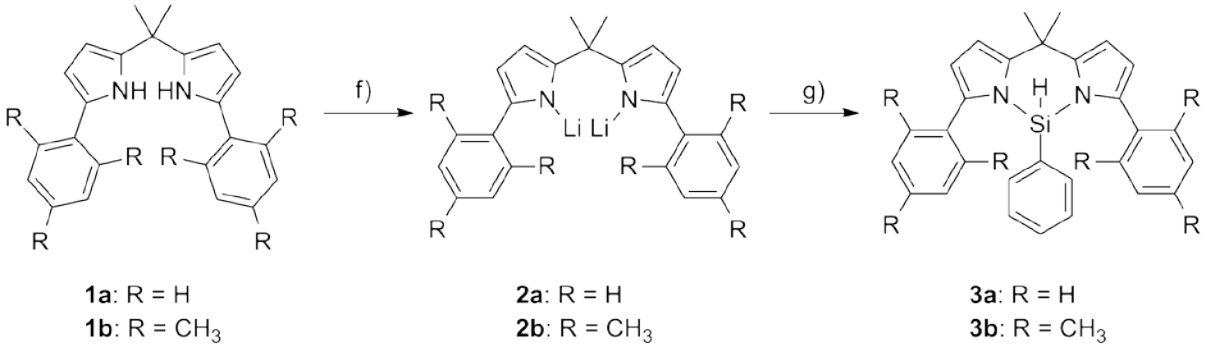



**SCHEME 5: THE CONDENSATION OF SUBSTITUTED PYRROLES USING $H^+$ AND ACETONE (R = PH).**

This reaction and isolation of 2-phenylpyrrole with acetone and TFA (step c) proceeded with low yields (24% pure compound, due to impure fractions during the column purification), but the reaction between 2-mesitylpyrrole and 2,2-dimethoxypropane (step e) proceeded with excellent results (88%-92%). Suspected is that 2,2-dimethoxypropane is a much more reactive compound than acetone, or that a lot of material is lost during the workup of step (c), which involves a large amount of NaOH solution (step (e) requires no aqueous workup, only a filtration of the solid PPTS).

## 2. SYNTHESIS OF THE SILANES

With the bipyrromethyl scaffold in hand, this material could now be silylated in a two-step process. These steps are shown in scheme 6; the lithiation of **1b** is adapted from [22] and the silylations are adapted from [14].




**SCHEME 6: THE SYNTHESIS OF THE SILANE *VIA* THE LITHIUM SALT. REAGENTS FOR 1A: (F) PHENYLLITHIUM, DIETHYL ETHER (34%). (G) DICHLOROPHENYL SILANE, TETRAHYDROFURAN. REAGENTS FOR 1B: (F) *N*-BUTYL LITHIUM, DIETHYL ETHER (62%). (G) DICHLOROPHENYL SILANE, TETRAHYDROFURAN (82%).**

The lithiation of **1a** proceeded with the use of phenyl lithium. This was added as a 1.5 M solution in dibutyl ether. The lithiation of **1b** used an 1.6 M solution of *n*-butyl lithium in diethyl ether. Preliminary $^{1}$H-NMR analysis of the crude product showed that **2a** had dibutyl ether still present, which was coordinated to the lithium salt in a 4:5 ratio (ether:salt). The material of **2b**, however, had diethyl ether coordinated in a 2:3 ratio.

During the silylation, the organolithium compounds reacted with dichlorophenyl silane. This displaces the lithium from the scaffold in favor of the silicon. Although the Si-Cl bond is slightly stronger than the Si-N bond (456(42) kJ/mol *versus* 439(38) kJ/mol[26]), the formation of lithium chloride and the stability of the chelating effect of the pyrrole-moieties are the driving force of this reaction. After silylation was complete, excess dichlorophenyl silane was evaporated, along with the solvent, and the residue was transferred to the glovebox. Here, toluene was added to dissolve the organosilane and disperse the lithium chloride, which was filtered away and discarded.

All attempts to precipitate or crystallize a solid from the crude reaction of **3a** were unsuccessful. Although $^{1}$H-NMR analysis showed promising results, it proved to be impossible to isolate any relevant material that was void of toluene. However, **3b** was isolated in good yields (82%). The crude mixture could be washed with hexane, and the silane crystallized from a saturated solution of diethyl ether or hexane in a freezer overnight. The obtained crystals were analyzed with X-ray diffraction; the results are shown in figure 6.

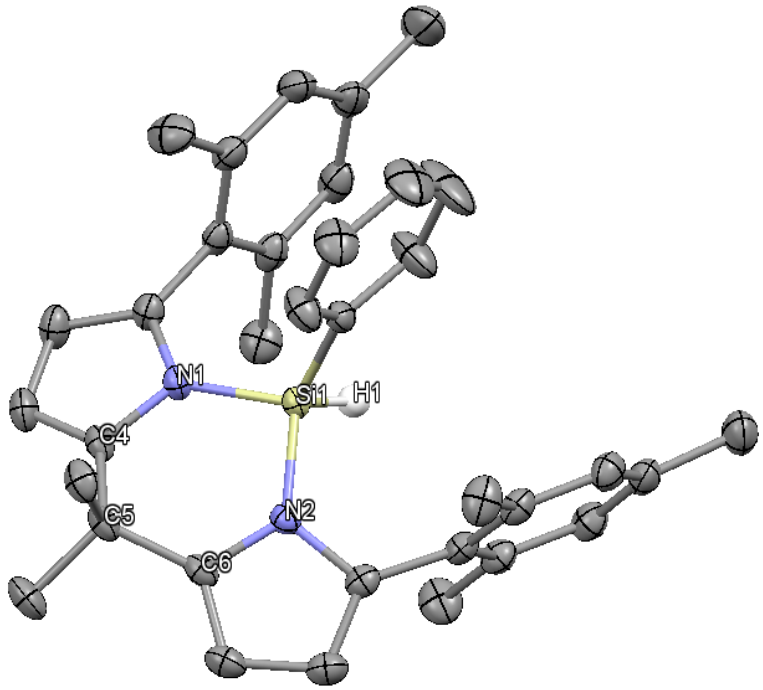



**FIGURE 6: CRYSTAL STRUCTURE OF COMPOUND 3B. CO-CRYSTALLIZED HEXANE AND HYDROGEN ATOMS (SAVE FOR THE SI-H) ARE OMITTED FOR CLARITY.**

| Angle | Value (degrees) | Bond/Distance | Length (Å) |
|---|---|---|---|
| C4-C5-C6 | 112.2(1) | Si1-N2 | 1.747(1) |
| C6-N2-Si1 | 126.78(8) | N2-C6 | 1.398(1) |
| N2-Si1-N1 | 99.59(5) | C5---Si1 | 3.262(1) |

**TABLE 1: SELECTED BOND ANGLES AND DISTANCES IN COMPOUND 3B.**

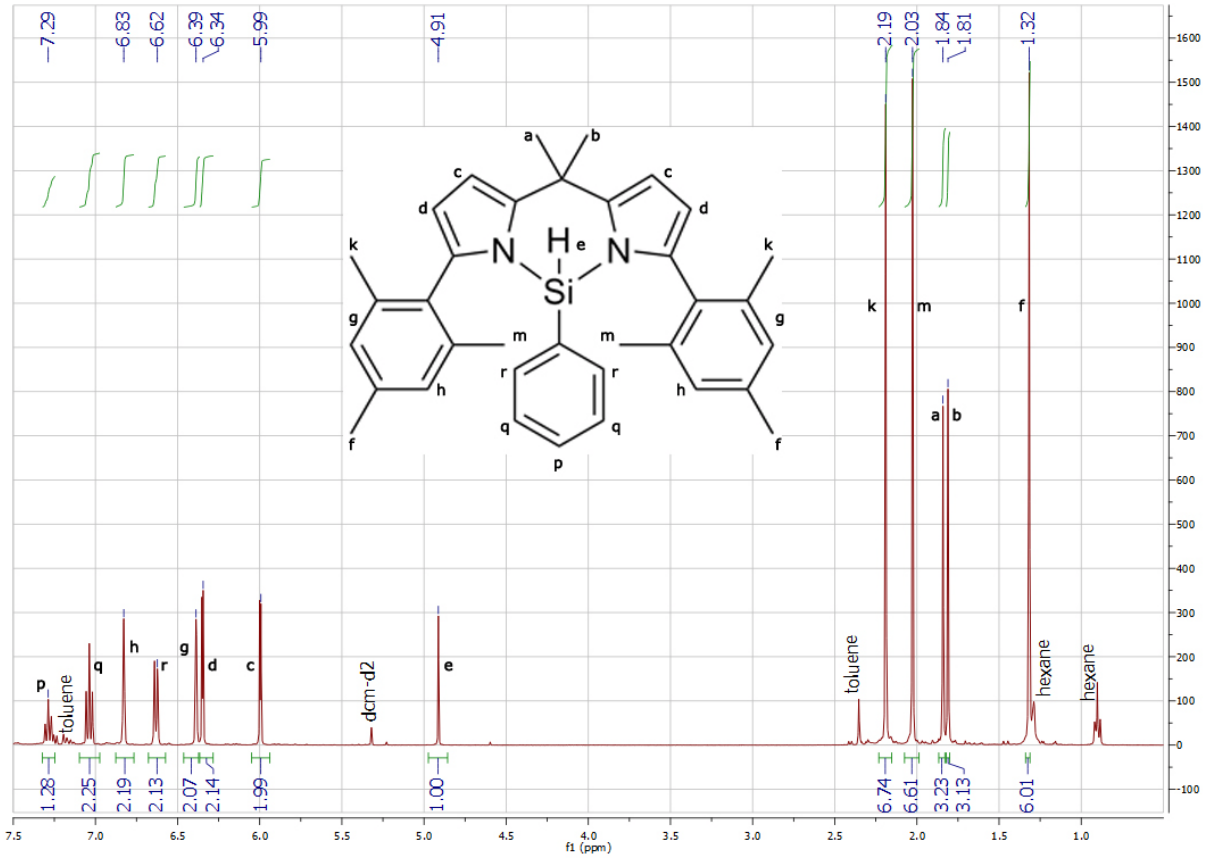



**FIGURE 7: $^{1}$H-NMR SPECTRUM OF COMPOUND 3B ($CD_2CL_2$, 25 °C).**

Figure 7 shows the $^{1}$H-NMR spectrum of **3b**. The hydrogen atoms labeled "a" and "b" belong to the methyl-groups on the "bridge"-methyl carbon. They appear as two singlets as a result of a slightly different chemical environment. The tetrahedral silicon-atom actually creates two distinct faces of the molecule: one with the phenyl ring and one with the hydrogen-atom (figure 6). This also leads to two different peaks in the aromatic region (labeled "h" and "g") assigned to the protons directly on the mesityl rings, as two are oriented above the plane and two are oriented below it. The same is true for the *ortho*-methyl groups on the mesityl rings (labeled "k" and "m").

Dissolving the material in $C_7D_8$ allowed for NMR measurements at various temperatures, in this case -85 °C to 80 °C. This could show whether the "bridge"-methyl groups become indistinguishable due to more rapid ring flipping of the six-membered ring containing the silicon-atom. This flipping would cause the two separate peaks to merge together. However, all methyl groups (those on the bridge, as well as those on the *ortho*-positions of the mesityl rings) remain on the same ppm-shift as they are observed at room temperature. This means that, on this temperature scale, the conformation is locked and the structure is rigid.

Save for the slight "butterfly"-effect of the bipyrromethyl backbone, the two mesityl-rings and the phenyl-ring are orientated parallel to each other and they are orientated perpendicular to the bipyrromethyl backbone (figure 6). The phenyl-ring is pointing out of the molecule, resulting in the aforementioned different faces of the molecule.

In table 1, several bond lengths and angles of the bipyrromethyl backbone of **3b** are presented. The bond length between silicon and the nitrogen is 1.747 Å. This is much lower than the N-M bonds (M = Mn, Fe, Co, Ni, Zn) in the compounds synthesized by King and Betley[22] (0.131 Å lower for Ni to 0.306 Å lower for Mn). Except for Zn, as the number of d-electrons increase in these metals, the M-N bond becomes shorter.

When comparing these compounds to **3b**, it also appears that the length of the nitrogen-carbon bond in the ring is slightly longer than the same bond in the molecules containing the transition metals[27] (between 0.008 Å for Fe and 0.022 Å for Co).

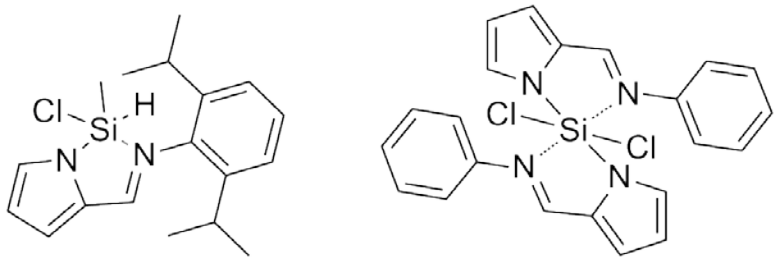



**FIGURE 8: TWO EXAMPLES OF PYRROLE-BASED LIGANDS ON A SILICON CENTRE.**

In our group, compounds were synthesized containing pyrrole-based ligands coordinated around a silicon atom in a penta- or hexa-coordinated fashion. Besides a covalent bond with the pyrrole-nitrogen, these compounds contain one or more dative bonds to an imine-nitrogen. Two examples are shown in figure 8. Silicon-nitrogen (pyrrole) distances are 1.788 Å for the penta-coordinated species and 1.841 Å for the hexa-coordinated species. These bonds are slightly longer than those found in **3b**. This is probably due to an electronic effect: the chlorine atom behaves as a covalently bound nitrogen[4], but the electron donating character of the datively bound nitrogen of the imine leads to an increase in the length of the Si-bond to the pyrrole. In **3b**, the pyrrole substituents on the silicon atom are electron withdrawing and thus shorten the Si-N bond. The work of Korkin[28] supports these observations and show that Si-N bondlengths are very variable, as they depend strongly on the character (covalent *versus* dative) and on the substitution at the silicon atom.

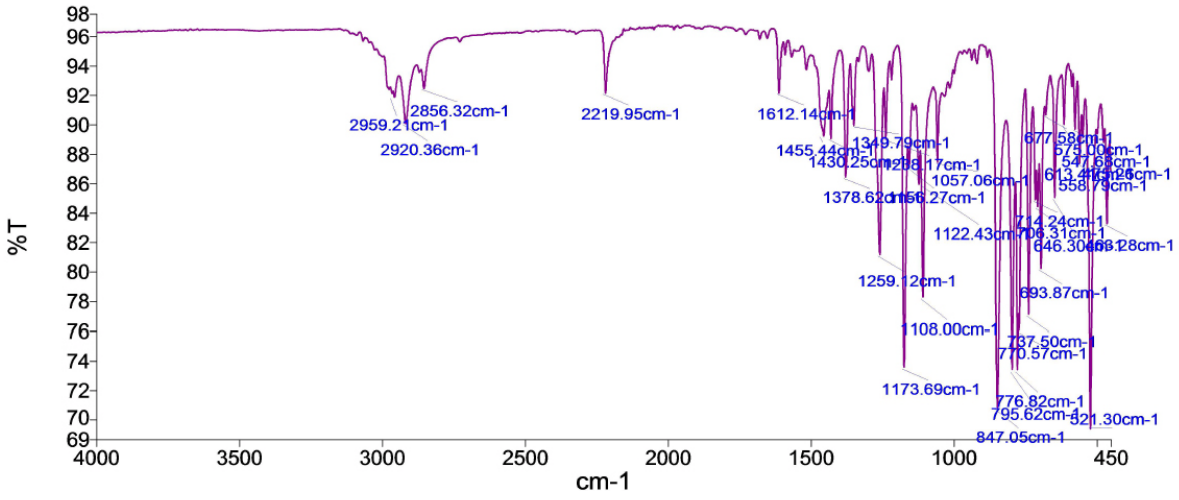



**FIGURE 9: THE IR SPECTRUM OF 3B (ATR, 25 °C).**

In figure 9, the IR spectrum of **3b** is presented. One of the most notable features of this spectrum is the sharp band at 2220 $cm^{-1}$. This band belongs to the Si-H stretch vibration. Comparing the spectrum of **3b** to those of similar compounds leads to interesting conclusions. The penta-coordinated compound in figure 8 shows a similar band at 2211 $cm^{-1}$. The work of Tour and co-workers[29] focused on the synthesis of a wide array of organosilanes, of which some had a silicon-hydrogen bond and others had a silicon-alkoxy bond. In the 1600-2800 $cm^{-1}$ range, no bands are observed in the spectra of organosilanes that did not feature a Si-H bond. The organosilanes that did contain the Si-H bond (while retaining identical substitutions on the silicon-atom) showed bands in the 2100-2200 $cm^{-1}$ range, thus making these bands excellent hallmarks for the presence of the Si-H bond. Some Si-H vibration wavelengths are presented in table 2 for the organosilanes. It shows that the observed frequency of the Si-H vibration in **3b** is slightly higher than the Si-H vibration of similar compounds; the work of Smith and Angelotti[30] confirms that electron withdrawing substituents on the silicon atom increase the vibrational frequency of the silicon-hydrogen bond, from 2097 $cm^{-1}$ for triethyl silane to 2258 $cm^{-1}$ for trichloro silane. The Si-H vibration frequency of **3b** falls nicely in the range of frequencies presented in that work: some selected compounds and their Si-H frequencies are presented in table 2.

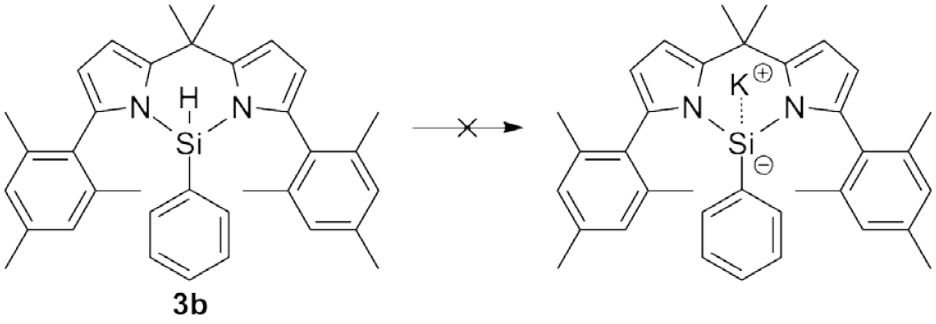
| Organosilane [29] | Vibration wavelength(s) [$cm^{-1}$] | Organosilane [30] | Vibration wavelength(s) [$cm^{-1}$] |
|---|---|---|---|
| (Tri-*n*-butyl)silane | 2099.9 | Triethylsilane | 2097.2 |
| Dimethyl(phenyl)silane | 2120.2 | Diphenyl(methyl)silane | 2120.5 |
| Dimethyl(1-naphtyl)silane | 2120.0 | Trimethoxysilane | 2203.2 |
| Di-*n*-butyl(1-naphtyl)silane | 2111.4 | Difluoro(methyl)silane | 2227.5 |
| Triphenylsilane | 2123.5 | Tribromosilane | 2236.0 |
| Di-4-methylphenylsilane | 2134.2 | Trichlorosilane | 2258.3 |

**TABLE 2: A COLLECTION OF ORGANOSILANES AND THE FREQUENCY OF THEIR SI-H VIBRATIONS.**

Following the results in this chapter, we conclude that we found a successful pathway for the synthesis of PhSi(dmbmp)H (**3b**). It was synthesized in an overall yield of 10% in 5 steps (averaging 60% for each step). NMR analysis ($^{1}H$, $^{13}C$, $^{29}Si$), as well as IR spectrometry and X-ray crystallography, confirm the identity of the novel silane. Unfortunately, PhSi(dpbmp)H (**3a**) could not be isolated. To convert the silane into a silanide ligand for complexation to transition metals, the silane has to be deprotonated at the silicon atom. In the next chapter, we will discuss our attempts at deprotonation.

# IV. DEPROTONATION OF THE SILANE

Having found a successful synthetic route to the designed silane, methods to deprotonate it can be investigated (scheme 7).




**SCHEME 7: SYNTHESIS OF THE SILYL ANION, USING A NON-COORDINATING (BRØNSTED) BASE.**

The potassium salt of the silyl anion is considered to be very unstable and will degrade immediately upon contact with air and moisture. This, in combination with the steric bulk of the scaffold and the weak acidity of the hydrogen, would make the deprotonation challenging. Two bases were investigated for this deprotonation step: potassium hydride and potassium bis(trimethylsilyl)amide (KHMDS).

## 1. FIRST BASE: KH

Potassium hydride is a strong base (pKa ≈ 35 for KH, *versus* pKa ≈ 26 for KHMDS) and is non-nucleophilic. Besides adding KH, an equal amount of 18-crown-6 was added to stabilize the designed cation. A preliminary small scale reaction (using 40 mg of **3b**) was carried out: the reagents were dissolved in THF and the container was put on a Schlenkline to stir under nitrogen atmosphere at room temperature. After 20 hours, the solvent became pinkish/terra cotta, and a fine suspension had formed. After evacuation of the volatiles, the residue was transferred to a glovebox. Here, toluene was added to suspend the solid, insoluble material, and to solve any leftover starting material. This could then be separated by filtration. $^{1}$H-NMR analysis of the filtrate (in $C_6D_6$) revealed no relevant material. This means that all the starting material had reacted.

The filter was washed with acetonitrile, which dissolved the residue. Evacuation of the solvent and redissolvement in $CD_3CN$ allowed for $^{1}$H-NMR analysis, which resulted in the spectrum shown in figure 10.

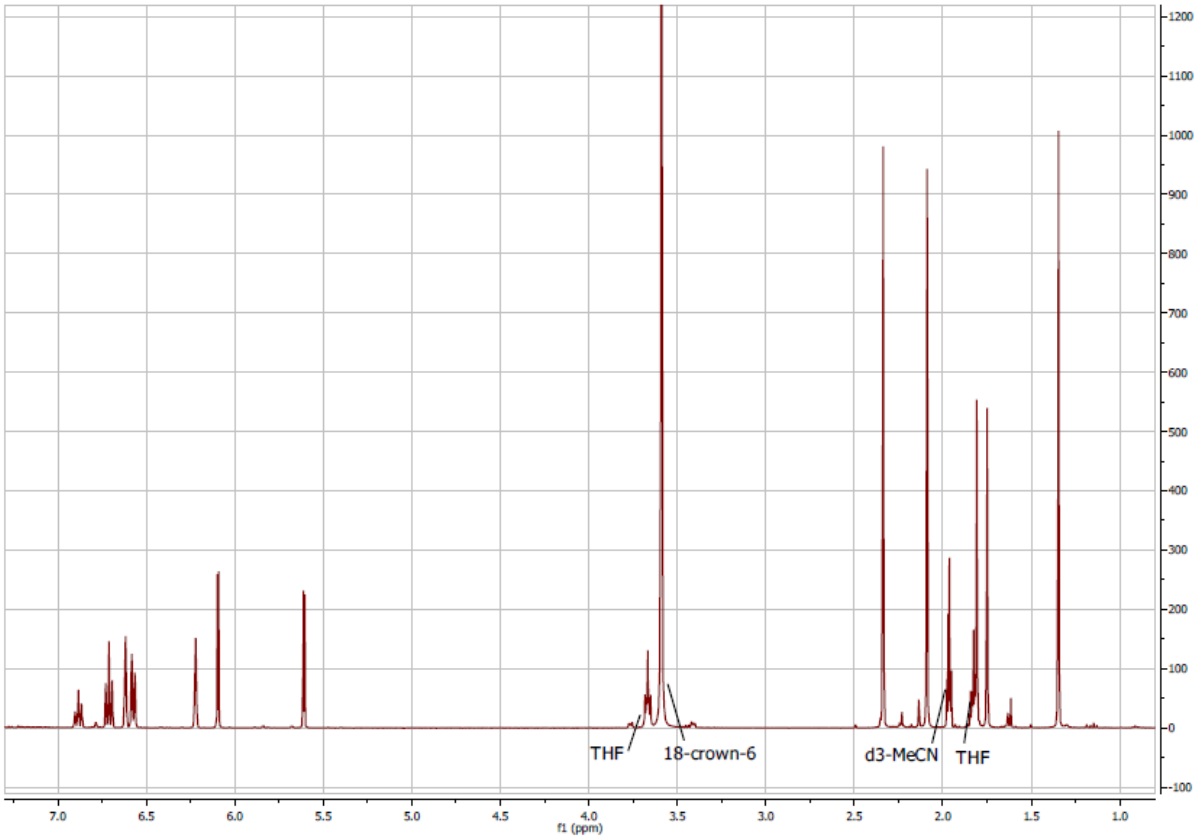



**FIGURE 10: $^{1}$H-NMR SPECTRUM ($CD_3CN$, 25 °C) OF THE PRODUCT OF THE DEPROTONATION ATTEMPT, USING POTASSIUM HYDRIDE AND 18-CROWN-6.**

Besides crown ether and tetrahydrofuran the spectrum shows the presence of a single compound, resembling the asymmetric compound **3b**, without the Si-H proton or any N-H protons. Compared to the $^{1}$H NMR spectrum of **3b** presented in figure 7, the peaks have only slightly moved.[31] Further, this material shows perfectly the splitting pattern of the *para*-, *meta*- and *ortho*-protons on the phenyl ring attached to the silicon atom. The presence of the Si-Ph, combined with the absence of silicon- and nitrogen-bound protons, pointed towards the presence of a deprotonated silane, and $^{29}$Si-NMR (proton decoupled) analysis revealed a singlet at -60.9 ppm. This is a large difference with the $^{29}$Si-NMR shift of **3b** (-27.3 ppm). This pointed towards an increase in electron density around the silicon centre[32] (and thus the success of the deprotonation), although the exact shift is influenced by solvent molecules binding to the cation, which alters the shift  10 ppm.[33, 34] *In summa*, All NMR data was consistent with a compound resembling PhSi(dmbmp)K, stabilized with 18-crown-6.

A diffusion crystallization from acetonitrile with toluene yielded colorless crystals, which were analyzed using x-ray diffraction. The crystal structure of this material is presented in figure 11.

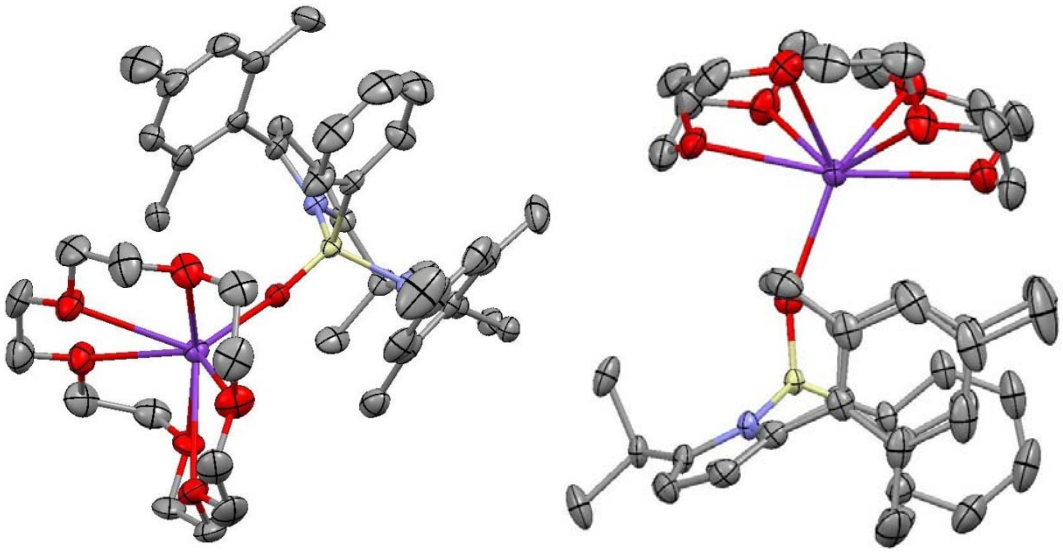


**FIGURE 11: CRYSTAL STRUCTURE OF THE PRODUCT OF THE DEPROTONATION ATTEMPT, USING POTASSIUM HYDRIDE AND 18-CROWN-6. HYDROGEN ATOMS AND CO-CRYSTALLIZED TOLUENE ARE OMITTED FOR CLARITY. RIGHT, THE CONFORMATION OF THE METHYL BRIDGE OF THE BIPYRROMETYL BACKBONE AND THE ECLIPSING OF THE PHENYL RING BY THE MESITYL RINGS ARE CLEARLY VISIBLE.**

Instead of the desired product, potassium phenyl(1,9-dimesityl-5,5-dimethylbipyrromethyl)siloxide crownetherate, or Ph(dmbpm)SiOK · $C_{12}H_{24}O_6$, had formed. This means that, somewhere during the reaction or the work up, either the silane or the potassium hydride had reacted with water (either traces in the solvents used or traces in the nitrogen gas). Repeating the reaction with similar conditions and reagents, but in a closed vessel (solvent bomb) using purified nitrogen (as used in the glovebox), yielded no reaction.[35] This indicates that the silane did not react with the tetrahydrofuran, as was shown to be possible by Prince and coworkers[36] using similar conditions. This means that traces of water from the nitrogen gas used the first time caused the formation of the siloxyl salt, probably *via* hydrolyzing potassium hydride to potassium hydroxide, followed by attack of the hydroxide on the silicon. The silol is subsequently deprotonated by the excess potassium hydride.

An interesting feature of this structure is the changed conformation of the six-membered ring containing the silicon and the two nitrogen atoms: where, in the protonated silane, it is slightly shaped as an envelope (pointing the methyl bridge towards the phenyl ring); in the current structure it adopts a boat conformation (pointing the methyl bridge towards the oxygen atom). Also, the Si-phenyl ring used to point outside the stacking of the mesityl rings, while in the current structure the phenyl ring is half-eclipsed by the two mesityl moieties (figure 11).

## 2. Second Base: KHMDS

The second attempt to deprotonate **3b** involved the use of potassium bis(trimethylsilyl)amide, or KHMDS (figure 12). This base is chosen as it is non-coordinating and non-nucleophilic. Three equivalents were added as a 0.5 M solution in toluene to a solution of **3b** in THF, and the mixture was heated to reflux temperatures. NMR samples were collected during the synthesis but they degraded during preparation, required too much THF to make a clear solution and/or were too diluted to subtract any reliable information. After 40 hours, the solvent was evacuated and the residue was transferred to the glovebox, where diethyl ether was added to the residue. The resulting suspension was filtered and the residue was dissolved in THF. Because the reaction predicts a potassium salt, obtaining material that is insoluble in diethyl ether was a promising observation.

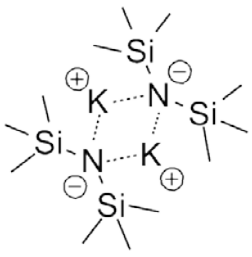



**FIGURE 12: THE STRUCTURE OF THE KHMDS DIMER.**

Both filtrate and residue were dried *in vacuo* to yield solid material. $^1$H-NMR-analysis of this material (filtrate in $C_6D_6$, residue in $C_4D_8O$) revealed that the filtrate contained a compound resembling the symmetrical **1b**, albeit without the N-H protons. This could mean that **3b** was desilylated in this deprotonation attempt, and that the bare scaffold **1b** was subsequently deprotonated by the excess of base to become $K_2$(dmbpm). The $^1$H-NMR spectrum of this desilylation is presented in the appendix.

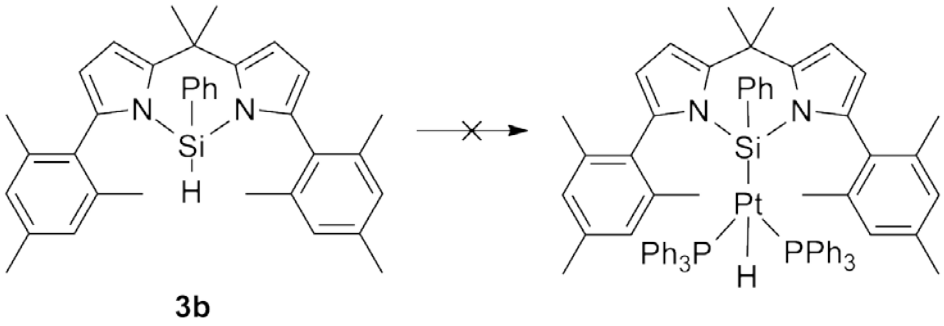
The residue, besides tetrahydrofuran and toluene, contained two compounds. One of them is **1b**, recognizable from the broad N-H signals, the signal accounting for 4 protons in the aromatic region (belonging to the symmetric mesityl protons) and the large signal in the aliphatic area accounting for 12 protons (belonging to the 4 *ortho*-methyl groups on the mesityl rings). The other compound in the sample resembles the asymmetric **3b**, albeit without the signal for the silicon-proton. Again, the presence of the Si-phenyl ring is clear from the splitting pattern of the *ortho*-, *meta*- and *para*-hydrogens. It is believed that this, too, is the potassium salt of the siloxide, as was observed with the deprotonation attempt using potassium hydride. The $^1$H NMR spectra for these compounds, although recorded in different solvents ($CD_3CN$ for the deprotonation attempt with KH *versus* $C_4D_8O$ for the deprotonation attempt using KHMDS), reveal that the peaks belonging to the siloxane are present in both spectra. The $^1$H-NMR spectra of the residue are presented in the appendix.

The presence of water (probably from the nitrogen gas used, or by diffusion *via* an insufficiently greased stopper) can account for the observed results. The KHMDS could react with water, forming bis(trimethylsilyl)amide and potassium hydroxide. The hydroxide can attack the silicon, forming the silol. This can then be deprotonated to form the potassium siloxide, or the silol-moiety is completely liberated from the scaffold to form $K_2$(dmbpm) (which can be hydrolysed by the moisture to restore the scaffold **1b**).

Following the failed deprotonation experiments performed and discussed in this chapter, it was concluded that this hydrogen-atom has too little of a proton-character to allow for a facile deprotonation. The lability of the compounds towards trace amounts of water proved to be detrimental. Other ways have to be explored to realize either the removal of this atom or the introduction of a metal atom on this position.

# V. OXIDATIVE ADDITION TO PLATINUM

After the failed attempts to deprotonate the silane using a base, a method was explored where the silane reacts with platinum(0) tetrakis(triphenylphosphine). This way, a Si-M bond could be formed directly from **3b**, thus circumventing the problems encountered in the previous chapter. Furthermore, this experiment could prove whether it is possible for **3b** to undergo oxidative addition; if it is possible with platinum, it might be possible with iron as well. However, if no oxidative addition takes place on the noble metal, it limits the possibilities of reaction with a base metal like iron. Scheme 8 shows the oxidative addition.




**3b**

**SCHEME 8: OXIDATIVE ADDITION OF 3B ON PLATINUM. REAGENTS: PLATINUM(0) TETRAKIS(TRIPHENYLPHOSPHINE), TOLUENE.**

The oxidative addition of a Si-H bond to a coordinatively unsaturated metal complex has proved to be a successful method in the preparation of silylmetal complexes[37] and plays a role in many metal-catalyzed silylation reactions.[38] Examples include hydrosilylation, dehydrogenative silylation and polysilane production.[39] Chan and co-workers[37] were successful in synthesizing an array of silylplatinum compounds by reacting the substituted hydrosilane with di(tricyclohexylphosphine) platinum(0). These substitutions included aliphatic moieties (both saturated and unsaturated) as well as aromatic hydrocarbons.

The platinum compound we used was platinum(0) tetrakis(triphenylphosphine). It is a yellow solid, and is used as a precursor to other platinum complexes.[40] The work of Belluco[41] focused on complexes of platinum(II) and platinum (0) with group IV elements, including silicon. The synthesis of the Pt-Si bond included reactions between the aforementioned platinum(0) precursor and trichlorosilane, as well as reactions with silanes of the type $(C_6H_5X)_3SiH$, where X = *p*- or *m*-F or $-CH_3$.

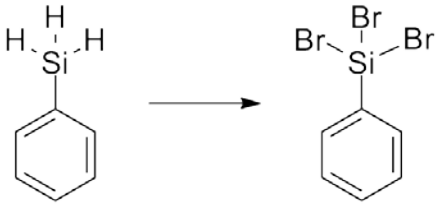
Hübler and co-workers[4] designed and synthesized *N*-pyrrolylsilanes that they managed to react with osmium and ruthenium precursors *via* an oxidative addition. The influence of pyrrolyl fragments as potent electron-withdrawing groups was previously established by Moloy and Petersen when they used *N*-pyrrolylphosphines and observed decreased bondlengths between the metal centre and the phosphorus atom in their transition metal-complexes.[42] Extrapolating from their success, a transition-metal silyl complex based on platinum and a bipyrromethyl silane should be feasible.

Considering the results of previous attempts with similar compounds, an attempt was made to perform an oxidative addition of compound **3b** over tetrakis(triphenylphosphine)platinum(0).

In a glovebox, silane **3b** was dissolved in dry toluene. The platinum precursor was also dissolved in dry toluene, and the solutions were combined. The combined solution was stirred under nitrogen atmosphere for 16 hours at 88 °C and, in another experiment, for 24 hours at 55 °C. After evacuation of the solvents, the residue is redissolved in $C_6D_6$ for $^1$H-NMR analysis. This revealed that no reaction had occurred under either circumstance. Suspected is that the silane and the ligands on the metal complex are too sterically demanding to allow for a facile oxidative addition over this particular platinum(0) precursor.

# VI. HALOGENATED SILANES

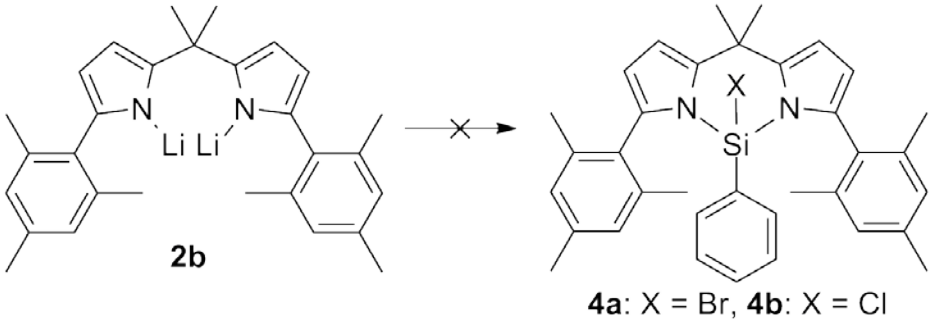
Considering the difficulties concerning the deprotonation and the oxidative addition encountered in the previous chapters, a new method was designed that could lead to the desired silyl anion. This new method involved the silylation of the lithium salt **2b** using a trihalogenated phenylsilane. The resulting compound would have a halogenated silicon centre. It should be possible to reduce the halogenated silane *via* an Umpolung-type reaction, in which the halosilane is solved in THF and allowed to react with metallic lithium, resulting in the alkali metal-silicon bond.[43] This could subsequently react with a suitable iron-precursor to form the iron-silicon bond. Alternatively, the halogenated silane could be added to $\pi$-$C_5H_5Fe(CO)_2Na$ (synthesized by reacting $Fe_2Cp_2(CO)_4$ with sodium), which creates the Fe-Si bond by liberating sodium chloride.[17, 44] Cundy and Lappert[45] were able to synthesize a Fe-Si-containing compound using the same iron-complex and a halogenated silacyclobutane. *In summa*, halogenated silanes show to be valuable precursors in the synthesis of silylferrous compounds. Two silanes were chosen for the silylation: phenyl(trichloro)silane and phenyl(tribromo)silane. Due to the lack of commercial availability of the latter, this was synthesized according to the method of Iwata.[46] This reaction is presented in scheme 9.




**SCHEME 9: THE BROMINATION OF PHENYLSILANE. REAGENTS: ALLYL BROMIDE, PALLADIUM(II) DICHLORIDE (42%).**

Iwata prepared a method for halogenating silanes in good to high yields. The procedure involves reacting alkylated silanes with halogenated hydrocarbons (e.g. allylbromide) in the presence of a catalytic amount of palladium(II) dichloride or nickel(II) dichloride, liberating alkanes in favor of the hydrogen-halogen exchange. The reactions appeared to proceed more rapidly when allylbromide was used in favor of ethyl- or *n*-propyl bromide. The same trend was observed when switching from nickel(II) dichloride to palladium(II) dichloride.

When the tribrominated silane is available, this can be used to silylate the bipyrromethyl scaffold, following similar conditions as in the silylation of **2b**. This reaction is presented in scheme 10.




**SCHEME 10: THE SILYLATION OF THE BIPYRROMETHYL SCAFFOLD. REAGENTS: PHENYL(TRIBROMO)SILANE (FOR COMPOUND 4A) AND PHENYL(TRICHLORO)SILANE (FOR 4B), TETRAHYDROFURAN.**

## 1. Synthesis of phenyl(tribromo)silane

The synthesis of phenyl(tribromo)silane followed the literature procedure by Iwata.[46] Allylbromide and a catalytic amount of palladium(II) dichloride were added to phenylsilane and heated to reflux temperatures (70°C at atmospheric pressure for allylbromide). This mixture was allowed to stir and reflux under nitrogen atmosphere for 60 hours. Evacuation of the volatiles at room temperature and 0.23 Torr pressure removed the starting material and the monobrominated species of the silane, as their boiling points are below room temperature at this pressure. Vacuum distillation of the residue yielded phenyl(tribromo)silane as the sole product (110 °C at 0.23 Torr).

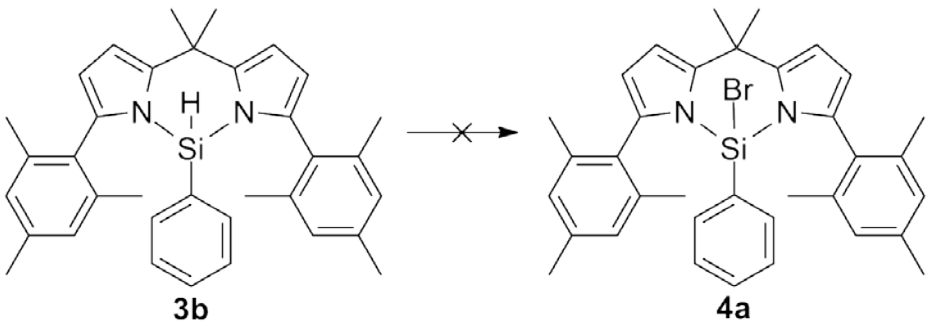
## 2. Silylation of the scaffold

Now both trihalogenated silanes are available, attempts can be pursued as to silylate **2b** using these new silanes. In the synthesis of **4a**, phenyl(tribromo)silane was added to $Li_2$(dmbpm) at -80 °C in tetrahydrofuran. Further, in the synthesis of **4b**, the solution was allowed to stir for 18 hours, as opposed to 3 hours in the reaction between **2b** and phenyl(tribromo)silane. After the reaction, the solvent and excess silane were evacuated and the residue was transferred to a glovebox for further work up. There, toluene was added to suspend the lithium salt. This could then be filtered. The filtrate was dried *in vacuo*. This yielded a purple residue for the chloro-species and dark red residue for the bromo-species. Solving these residues in $C_6D_6$ allowed for $^1$H-NMR analysis.

Unfortunately, this revealed a complex mixture of compounds. In the case of the bromo-species, the mixture still contained phenyl(tribromo)silane, which proved to be difficult to evacuate (see Appendix). This is in concordance with the isolation of phenyl(tribromo)silane described above, which required very low pressure and high temperature for its distillation. Also, the pyrrole-peaks (found in the region between 5.85 ppm and 6.25 ppm) revealed that two similar bipyrromethyl compounds had formed, neither of which resembled the asymmetric structure of **3b** (regarding the mesityl-protons). As for the chloro-species, the pyrrole-peaks have strong correlation with a peak in the crowded aromatic region (TOCSY, included in the Appendix), a counter-intuitive feature which was previously absent. Also, their multiplicity changed from doublets to triplets, a feature which was last observed in **1b**. The absence of signals in $^{29}$Si-NMR further confirms that **2b** was not silylated in the synthesis attempt of **4b**.

## 3. Direct halogenation of the bipyrromethyl silane

Following the unsuccessful attempts at silylating the bipyrromethyl scaffold **2b** using trihalogenated silanes, an effort was made to directly halogenate compound **3b**, using the same method as for the bromination of phenylsilane. The reaction is presented in scheme 11.




**SCHEME 11: DIRECT HALOGENATION OF THE DESIGNED BIPYRROMETHYL SILANE. REAGENTS: ALLYLBROMIDE, PALLADIUM(II) DICHLORIDE.**

Silane **3b** was dissolved in allylbromide and, after addition of the catalyst, was allowed to reflux under nitrogen atmosphere for 67 hours. The mixture became a dark blue suspension. After evacuating the excess allylbromide, the residue was transferred to a glovebox where the residue was dissolved in toluene. This gave a light blue suspension of dark blue flakes, which were separated by filtration. Evacuation of the solvent and redissolvement in $C_6D_6$ allowed for $^1$H-NMR analysis. Unfortunately, this revealed that the crude material contained a complex mixture of compounds, none of which seemed to resemble the bipyrromethyl scaffold. $^1$H-NMR analysis of the dark flakes in $CD_2Cl_2$, too, revealed that this did not contain any material that resembles the bipyrromethyl scaffold.

Following the results mentioned in this chapter, no successful pathway to the halogenated silane was found. Tribromo(phenyl)silane was successfully synthesized according to a literature procedure. However, we were unable to use a trihalogenated phenyl silane in the silylation of the lithiated compound $Li_2$(dmbpm). From the absence of signals in the $^{29}$Si-NMR spectra, one can conclude that either (1) the designed compounds **4a** and **4b** are unstable and deteriorate under ambient conditions or (2) the third halogen substitution on the silicon atom in the silane alters its reactivity in such a way that the predicted pathway, in which one halogen ion removes one lithium ion to form the Si-N bond in the scaffold, does not occur. Also, the dosage of the trihalogenated phenyl silane and the catalyst proved to be problematic on this small scale (which was required due to the insufficient amount of lithium salt). However, if one could use an excess of lithium salt in this silylation, it would remove the problems encountered during the evacuation of any excess *i.e.* unreacted silane, aiding in the isolation of the halogenated bipyrromethyl phenyl silane.

# VII. Conclusions

The aim of the project as stated in I.5 was partly realized. Silane **3b** was successfully synthesized, isolated and crystallized in good yields, starting from free pyrrole (10% yield over 5 steps). Silane **3a** could not be isolated. Attempts at deprotonation of **3b** resulted in desilylation and hydrolysis in the case of KHMDS. Attempts at deprotonation using KH resulting in hydrolysis of the Si-H bond, if the reagents reacted at all. Reaction of **3b** with an excess of potassium hydride in the presence of 18-crown-6 and traces of water resulted in the crownetherate of the potassium salt of the siloxyl species. The silicon-bound hydrogen apparently has too little of a proton character to allow for a facile deprotonation. A preliminary attempt at complexation to platinum by oxidative addition resulted in unreacted starting material, possibly due to the steric bulk of the reagents.

Silylation with trihalogenated silanes resulted in a complex mixture of compounds from which no single compound could be isolated. It seems that the inertia of the Si-H bond towards halogenation, deprotonation and oxidative addition prevents the clean conversion from the bipyrromethyl silane into the halosilane, silanide or silyl-platinum complex, respectively. Other methods have to be explored to either obtain the anion of **3b** or synthesize a metal complex with **3b** as a ligand.

# VIII. Outlook

The synthesis of phenyl(1,9-diphenyl-5,5-dimethylbipyrromethyl) silane (**3a**) can be repeated, using King's method of condensation and lithiation[22], as it proved to be quite successful for the synthesis of phenyl(1,9-dimesityl-5,5-dimethylbipyrromethyl) silane (**3b**). Decreasing the steric bulk on the bipyrromethyl scaffold could lead to a successful oxidative addition on platinum(0) using the reaction conditions discussed in chapter V; alternatively, one could use a different (smaller) metal complex for this oxidative addition. Further, the synthesis of an ironsilyl compound can be explored, where the pyrrolide-based ligand is built on the silicon-atom *after* the Fe-Si-bond has formed (*e.g.* by oxidative addition of trichlorosilane to a suitable iron precursor).

# IX. Acknowledgements

First, I want to thank prof. dr. Bert Klein Gebbink for offering me the opportunity to perform my masterthesis in his research group. Dr. Marc-Etienne Moret, our fruitful discussions on this subject were indispensable, as was sharing your knowledge and experiences on this matter, as you are the first to explore pyrrole-based chemistry within our group. Prof. dr. Leo Jenneskens, thank you for being the second corrector for my report. Your knowledge and spirit both are refreshing and inspirational.

Secondly, I'd like to thank Léon Witteman for his daily supervision. Although Johann Jastrzebski introduced me to NMR, you helped a lot with advanced heteronuclear and two-dimensional spectra – to you I owe my knowledge on this subject, as well as my prowess with advanced synthetic chemical techniques. Furthermore, you helped me out when I experienced practical as well as theoretical difficulties, and your patience prevented us both from losing our minds.

I thank Martin Lutz for performing crystallography experiments and Adri van den Hoogenband for assisting with GCMS experiments in the beginning of the research. Lastly, I'd like to thank the entire group at OCC, for making my stay as pleasant as it was educational.

(2-Biphenyl)di-tert-butylphosphine (97%), sodium hydride (60% dispersion in mineral oil), potassium hydride (30 wt%) platinum(0) tetrakistriphenylphosphine and dipalladium(0) tris(dibenzylideneacetone) and phenyl lithium (*ca*. 1.8M solution in di-*n*-butyl ether) were purchased from Sigma Aldrich. Palladium(II) acetate (47.5% Pd basis), palladium(II) chloride (60% Pd basis), zinc(II) chloride (98+%), pyrrole (99%), trifluoroacetic acid (99%), acetone (99+%), iodobenzene (98%), 2-bromomesitylene (99%), *n*-butyllithium (1.6M solution in hexanes), allylbromide (99%) and 18-crown-6 (99%) were purchased from Acros. Pyridinium *p*-toluenesulphonate (99+%) was purchased from Fluka. All reagents were used without further purification, unless stated otherwise.

Tetrahydrofuran and 1,4-dioxane were distilled over sodium and benzophenon before use. Acetonitrile, dichloromethane, tetrahydrofuran and toluene were degassed and stored over molecular sieves before use. Solvents used for column purification were technical grade and were used as purchased.

All NMR measurements were performed at room temperature at 400 MHz with tetramethylsilane as reference. Sodium pyrrole[20], 1,9-dimesityl-5,5-dimethylbipyrromethane (**1b**), 1,9-dimesityl-5,5-dimethylbipyrromethyl lithium (**2b**)[22] and phenyl(tribromo)silane[46] were synthesized according to literature procedures. The syntheses of 2-mesitylpyrrole and 2-phenylpyrrole are adaptions from a literature procedure.[20]

## SODIUM PYRROLE

Sodium hydride (13.4 g, 60% in mineral oil, 335 mmol) was washed with hexanes (100 mL) under nitrogen atmosphere to remove the mineral oil. The hexanes were then removed *via* cannula filtration. The sodium hydride was redispersed in tetrahydrofuran (150 mL). Pyrrole (11.1 g, 11.5 mL, 166 mmol) was added dropwise, promoting violent effervescence of hydrogen gas. Reaction allowed to stir for 3 hours. Excess sodium-hydride was removed with a swivel-type glass frit and quenched with isopropanol and ethanol. Sodium pyrrole solution was dried *in vacuo* to yield the title compound as an off-white to pale yellow solid (17.2 g, *quant*.).

$^1$H NMR ($C_6D_6$): δ/ppm 7.10 (t, $^3J_{HH}$ = 1.25 Hz, 2H, $NaNC_4H_4$), 6.41 (t, $^3J_{HH}$ = 1.25 Hz, 2H, $NaNC_4H_4$).

## 2-PHENYLPYRROLE

Zinc chloride (10.2 g, 75.0 mmol) and sodium pyrrolide (6.7 g, 75.3 mmol) were weighed under inert atmosphere. These were then transferred to the fume hood where dry dioxane (50 mL) was added. A yellow suspension formed. The catalyst palladium(II) acetate (31.8 mg, 142 μmol) and the supporting ligand 2-ditertbutylphosphinebiphenyl (45.0 mg, 152 μmol) were added and magnetic stirring was replaced with mechanic stirring. Iodobenzene (2.9 mL, 26.3 mmol) was added and reaction was left to stir overnight under nitrogen atmosphere at 100° C. The solution coloured green over time.

Continued stirring while suspension was allowed to come to room temperature. Mechanic stirring was halted and removed and the suspension was dissolved in water and the organic compounds were extracted with diethyl ether. Organic fractions were collected, combined, dried on anhydrous magnesium sulphate and filtered through cotton wool before drying *in vacuo* to yield the crude compound as a dark green residue.

This was coated on 300 $cm^3$ of silicagel and purified *in columnae* with 1500 $cm^3$ of silicagel and using an elouent consisting of a 9:1 ratio of petroleum ether and ethyl acetate. This afforded the title compound (2.28 g, 9.3 mmol, 35%, $R_f$ 0.3).

$^1$H NMR ($(CD_3)_2CO$): δ/ppm 9.74 (s, 1H, N*H*), 6.89 (d, $^3J_{HH}$ = 7.66 Hz, 2H, *o*-$C_6H_5$), 6.60 (t, $^3J_{HH}$ = 7.81 Hz, 2H, *m*-$C_6H_5$), 6.42 (t, $^3J_{HH}$ = 7.42 Hz, 1H, *p*-$C_6H_5$), 6.12 (s, 1H, $NHC_4H_3$), 5.79 (s, 1H, $NHC_4H_3$), 5.43 (s, 1H, $NHC_4H_3$).

## 2-MESITYLPYRROLE

Zinc chloride (6.25 g, 45.8 mmol) and sodium pyrrolide (4.1 g, 46.1 mmol) were weighed under inert atmosphere. These were then transferred to the fume hood where dry dioxane (180 mL) was added. A yellow suspension was formed. The catalyst tris(benzylideneacetone)palladium(0) (45 mg, 48 μmol) and the supporting ligand 2-ditertbutylphosphinebiphenyl (29.1 mg, 98 μmol) were added and magnetic stirring was replaced with mechanic stirring. 2-Bromo-mesitylene (2.4 mL, 15.7 mmol) was added and reaction was left to stir overnight under nitrogen at 100° C. The suspension turned green over time.

The stirring was continued while suspension was allowed to come to room temperature. Mechanic stirring was halted and removed and the suspension was dissolved in water (700 mL) and the organic compounds were extracted with diethyl ether (400 mL). Organic fractions were collected, combined, dried on anhydrous magnesium sulphate and filtered through cotton wool before drying *in vacuo* to yield the crude compound as a dark green residue.

This was coated on 80 $cm^3$ of silicagel and purified *in columnae* with 800 $cm^3$ of silicagel and using an elouent consisting of a 9:1 ratio of petroleum ether and ethyl acetate. This afforded the title compound (1.3 g, 7.0 mmol, 46%, $R_f$ 0.3).

$^1$H NMR ($CDCl_3$): δ/ppm 7.86 (1H, N*H*), 6.94 (2H, $C_6H_2(o\text{-}CH_3)_2(p\text{-}CH_3)$), 6.82 (q, $^3J_{HH}$ = 3.33 Hz, $^4J_{HH}$ = 0.71 Hz, 1H, $NHC_4H_3$), 6.32 (q, $^3J_{HH}$ = 4.29 Hz, $^4J_{HH}$ = 1.42 Hz, 1H, $NHC_4H_3$), 6.04 (q, $^3J_{HH}$ = 3.53 Hz, $^4J_{HH}$ = 1.51 Hz,1H, $NHC_4H_3$), 2.32 (3H, $C_6H_2(o\text{-}CH_3)_2(p\text{-}CH_3)$), 2.14 (6H, $C_6H_2(o\text{-}CH_3)_2(p\text{-}CH_3)$).

## 1,9-DIPHENYL-5,5-DIMETHYLBIPYRROMETHANE (1A)

In a roundbottom schlenk, acetone (460 μL, 6.3 mmol) and 2-phenyl pyrrole (1.8 g, 12.6 mmol) were combined and solved in dichloromethane (40 mL). Trifluoroacetic acid (50 μL, 647 μmol) was added, which initiated a color change from orange-red to bright purple. Solution is left to stir under nitrogen for 80 hours.

Afterwards, a 0.1 solution of sodium hydroxide is added to quench the reaction and bring the solution to pH = 7. The aqueous layer is extracted with dichloromethane. The organic fractions are collected, combined and dried over anhydrous magnesium sulphate. The material is filtered through cotton wool and dried *in vacuo* to yield the crude material. This is purified using column chromatography with a 9:1 mixture of petroleum ether and ethyl acetate as an elouent. The title compound is obtained as a purple solid (510 mg, 1.56 mmol, 24%).

$^1$H NMR ($C_6D_6$): δ/ppm 8.06 (2H, N*H*), 7.38 (d, $^3J_{HH}$ = 6.39 Hz, 4H, $(o\text{-}C_6H_5)_2$), 7.31 (t, $^3J_{HH}$ = 6.09 Hz, 4H, $(m\text{-}C_6H_5)_2$), 7.17 (t, $^3J_{HH}$ = 7.47 Hz, 2H, $(p\text{-}C_6H_5)_2$), 6.46 (d, $^3J_{HH}$ = 2.38 Hz, 2H, $NHC_4H_2$), 6.21 (d, $^3J_{HH}$ = 2.38 Hz, 2H, $NHC_4H_2$), 1.74 (s, 6H, $C(CH_3)_2$).

## 1,9-DIMESITYL-5,5-DIMETHYLBIPYRROMETHANE (1B)

In a roundbottom schlenk, 2,2-dimethoxypropane (3.18 mL, 30 mmol) and 2-mesitylpyrrole (500 mg, 2.7 mmol) were combined and solved in dichloromethane (60 mL). The resulting salmon-coloured solution is stirred for 15 minutes under nitrogen atmosphere. Then, pyridinium *p*-toluenesulphonate (68 mg, 272 μmol) is added, which initiates a slight colour change to pink. Solution is left to stir under nitrogen for 24 hours.

Overnight, a vermilion colour persisted, which turned red as the reaction was running for 24 hours. Solvents and volatiles were dried *in vacuo*, and residue was redissolved in diethyl ether (50 mL), which precipitates the pyridinium *p*-toluenesulphonate. This suspension is then filtered through cotton wool and the clear orange solution was dried *in vacuo* to yield the crude product as a dark purple oil. Co-evaporation with toluene removed impurities and yielded the title compound as a pink powder (510 mg, 1.24 mmol, 92%).

$^1$H NMR ($C_6D_6$): δ/ppm 7.58 (2H, N*H*), 6.88 (4H, $C_6H_2$(*o*-$CH_3$)$_2$(*p*-$CH_3$)), 6.12 (d, $^3J_{HH}$ = 4.15 Hz, 2H, $NHC_4H_2$), 5.88 (d, $^3J_{HH}$ = 4.15 Hz, 2H, $NHC_4H_2$), 2.29 (s, 6H, $C_6H_2$(*o*-$CH_3$)$_2$(*p*-$CH_3$)), 2.06 (s, 12H, $C_6H_2$(*o*-$CH_3$)$_2$(*p*-$CH_3$)), 1.49 (s, 6H, C($CH_3$)$_2$).

## 1,9-DIPHENYL-5,5-DIMETHYLBIPYRROMETHYL LITHIUM (2A)

Compound **1a** (0.5 g, 1.53 mmol) was dissolved in diethyl ether (2 mL). While stirring under nitrogen atmosphere, Phenyllithium (2 mL, 1.5 M in dibutyl ether) was dissolved in diethyl ether. Both solutions were cooled using liquid nitrogen until they are both partially frozen. Phenyllithium solution were added to **1a** while thawing. Solution was allowed to stir for 2 hours while warming to room temperature. The resulting solution was dried *in vacuo* and the residue was redissolved in hexane and the suspension of **2a** was filtered. This solid was washed with hexanes and dried further to remove all traces of dibutyl ether. The title compound was isolated as a pale yellow powder (175 mg, 518 μmol, 34%).

$^1$H NMR ($C_6D_6$): δ/ppm 7.63 (d, $^3J_{HH}$ = 7.77 Hz, 4H, (*o*-$C_6H_5$)$_2$), 7.10 (t, $^3J_{HH}$ = 6.99 Hz, 4H, (*m*-$C_6H_5$)$_2$), 6.84 (t, $^3J_{HH}$ = 6.99 Hz, 2H, (*p*-$C_6H_5$)$_2$), 6.75 (d, $^3J_{HH}$ = 2.38 Hz, 2H, $NHC_4H_2$), 6.39 (d, $^3J_{HH}$ = 2.38 Hz, 2H, $NHC_4H_2$), 1.81 (s, 6H, C($CH_3$)$_2$).

## 1,9-DIMESITYL-5,5-DIMETHYLBIPYRROMETHYL LITHIUM (2B)

Compound **1b** (510 mg, 1.24 mmol) was dissolved in diethyl ether (5 mL). While stirring under nitrogen atmosphere, *n*-butyllithium (1.86 mL, 1.6 M in hexanes) was added dropwise. Solution was stirred for 2 hours in a water bath at room temperature. The resulting yellow solution was dried *in vacuo* upon which a yellow solid was formed. This solid was washed with hexanes to yield the title compound as a pale yellow powder (325 mg, 770 μmol, 62%).

$^1$H NMR ($C_6D_6$): δ/ppm 6.78 (4H, $C_6H_2$(*o*-$CH_3$)$_2$(*p*-$CH_3$)), 6.52 (d, $^3J_{HH}$ = 2.66 Hz, 2H, $NLiC_4H_2$), 6.08 (d, $^3J_{HH}$ = 2.57 Hz, 2H, $NLiC_4H_2$), 2.17 (18H, $C_6H_2$(*o*-$CH_3$)$_2$(*p*-$CH_3$)), 1.96 (6H, C($CH_3$)$_2$).

## ATTEMPT: PHENYL(1,9-DIPHENYL-5,5-DIMETHYLBIPYRROMETHYL) SILANE (3A)

Under inert atmosphere, **4** (175 mg, 518 μmol) was dissolved in tetrahydrofuran (6 mL). Solution was then transferred to a fume hood, where, while stirring, dichlorophenylsilane (120 μL, 821 μmol) was added under a flow of nitrogen. Solution was allowed to stir for another 2 hours. Solvents and excess silane were evacuated and residue is transferred to a glovebox. Toluene was added to precipitate lithium salts. Suspension was filtered and the toluene is evacuated to afford the crude product as a brown residue (238 mg). Attempts to isolate and characterize the compound remained fruitless.

## PHENYL(1,9-DIMESITYL-5,5-DIMETHYLBIPYRROMETHYL) SILANE (3B)

Under inert atmosphere, **2b** (290 mg, 678 μmol) was dissolved in tetrahydrofuran (10 mL). Solution was then transferred to a fume hood, where, while stirring, dichlorophenylsilane (151 μL, 1.01 mmol) was added under a flow of nitrogen. Solution was allowed to stir for another 3 hours. Solvents and excess silane was evacuated and residue is transferred to a glovebox. Toluene was added to precipitate lithium salts. Suspension was filtered and the toluene was evacuated to afford the crude product as a brown residue (250 mg, 485 μmol, 71%). A crystallization at -40° C from a saturated solution of hexanes or diethyl ether afforded the title compound as colourless crystals.

$^1$H NMR ($C_6D_6$): δ/ppm 6.95 (s, 1H, $C_6H_5$-*p*-Si), 6.79 (s, 4H,$C_6H_5$-*o*-*m*-Si), 6.62 (d, $^3J_{HH}$ = 3.22 Hz, 2H, $NSiC_4H_2$), 6.46 (2H, $C_6H_2$(*o*-$CH_3$)$_2$(*p*-$CH_3$)), 6.38 (d, $^3J_{HH}$ = 3.22 Hz, 2H, $NSiC_4H_2$), 6.19 (s, 2H, $C_6H_2$(*o*-$CH_3$)$_2$(*p*-$CH_3$)), 5.32 (s, $^1J_{SiH}$ = 125.7 Hz, $^1J_{SiC}$ = 8.6 Hz, 1H, Si*H*), 2.20 (s, 6H, $C_6H_2$(*o*-$CH_3$)$_2$(*p*-$CH_3$)), 1.96 (s, 6H, $C_6H_2$(*o*-$CH_3$)$_2$(*p*-$CH_3$)), 1.91 (s, 3H, C($CH_3$)$_2$), 1.88 (s, 3H, C($CH_3$)$_2$), 1.53 (s, 6H, $C_6H_2$(*o*-$CH_3$)$_2$(*p*-$CH_3$)).

$^{13}$C NMR ($C_6D_6$): δ/ppm 144.4, 139.7, 138.8, 137.6, 134.5, 133.9, 131.4, 130.6, 130.1, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.0, 111.6, 107.1, 36.4, 36.3, 31.2, 20.7, 20.4, 20.0.

$^{29}$Si NMR (inept, $C_6D_6$, *J* = 255 Hz): δ/ppm -27.34.

## Attempt: potassium (phenyl(1,9-dimesityl-5,5-dimethylbipyrromethyl)) silanide

Under inert atmosphere, **3b** (52 mg, 100 μmol) was weighed and solved in dry tetrahydrofuran (5 mL). Potassium bis(trimethylsilyl)amide (300 μL, 0.5 M in toluene, 150 μmol) was added and the solution was then transferred to a fume hood, where it was allowed to stir and reflux for 40 hours under nitrogen. Then, the volatiles were evacuated and the crude residue was transported to a glove box, where toluene was added. The resulting suspension was filtered and the residue is solved in tetrahydrofuran. Both solutions were dried *in vacuo*. $^1$H NMR analysis revealed that the starting material was desilylated.

In another attempt, **3b** (33 mg, 64 μmol) was weighed and solved in dry tetrahydrofuran (1 mL). Potassium hydride (10.5 μL, 262 μmol) was suspended in dry tetrahydrofuran (1 mL) and was added to **3b** before it could settle. The suspension is then transferred to a fume hood, where it was allowed to stir for 16 hours under nitrogen. After evacuation of the solvent, residue was redissolved in $C_6D_6$ for $^1$H-NMR analysis. This revealed that the starting material had not reacted.

In a third attempt, **3b** (40 mg, 78 μmol) was dissolved in dry tetrahydrofuran (1 mL) under inert atmosphere. 18-Crown-6 (50 mg, 200 μmol) was dissolved in 1 mL dry tetrahydrofuran. Potassium hydride (6 mg, 170 μmol) was suspended in 1 mL and the two solutions and the suspension were mixed before the potassium hydride could settle. The resulting suspension was allowed to stir under nitrogen atmosphere at room temperature for 16 hours. The suspension became pinkish/terra cotta over time. The solvent was evacuated and the residue was transferred to a glovebox. Here, toluene was added, and the resulting suspension was filtered. Acetonitrile was added to the residue, which resulted in a pale yellow solution. The filter was washed with acetonitrile to dissolve all material. Evacuation of the solvent and redissolvement in $CD_3CN$ allowed for $^1$H-NMR analysis. A vapour-type crystallization from acetonitrile with toluene yielded colourless crystals. ESI-MS and crystallography analysis revealed that, rather than the title compound, the crownetherate of Ph(dmbmp)SiOK had formed.

$^1$H NMR ($CD_3CN$): δ/ppm 6.80 (t, $^3J_{HH}$ = 7.80 Hz, 1H, $C_6H_5$-*p*-Si), 6.62 (t, $^3J_{HH}$ = 7.33 Hz, 2H, $C_6H_5$-*o*-Si), 6.53 (s, 2H, $C_6H_2$(*o*-$CH_3$)$_2$(*p*-$CH_3$)), 6.49 (d, $^3J_{HH}$ = 7.33 Hz, 2H, $C_6H_5$-*m*-Si), 6.13 (s, 2H, $C_6H_2$(*o*-$CH_3$)$_2$(*p*-$CH_3$)), 6.00 (d, $^3J_{HH}$ = 2.86 Hz, 2H, NSi$C_4H_2$), 5.52 (d, $^3J_{HH}$ = 3.28 Hz, 2H, NSi$C_4H_2$), 3.50 (s, 24H, $(C_2H_4O)_6$), 2.25 (s, 6H, $C_6H_2$(*o*-$CH_3$)$_2$(*p*-$CH_3$)), 2.00 (s, 6H, $C_6H_2$(*o*-$CH_3$)$_2$(*p*-$CH_3$)), 1.72 (s, 3H, C($CH_3$)$_2$), 1.66 (s, 3H, C($CH_3$)$_2$), 1.26 (s, 6H, $C_6H_2$(*o*-$CH_3$)$_2$(*p*-$CH_3$)).

$^{13}$C NMR ($CD_3CN$): δ/ppm 146.10, 142.27, 141.92, 138.72, 136.17, 135.54, 134.33, 127.60, 127.53, 127.27, 126.20, 70.87, 68.25, 37.84, 36.94, 29.82, 26.22, 22.39, 21.01.

$^{29}$Si NMR ($CD_3CN$): δ/ppm -60.9.

## Attempt: bis(triphenylphosphine) (phenyl(1,9-dimesityl-5,5-dimethylbipyrro-methyl))silyl) platinum(II) hydride

In a glovebox, compound **3b** (14.5 mg, 28.1 μmol) was dissolved in dry toluene (1 mL). Tetrakis(triphenylphosphine)platinum(0) (38.6 mg, 31.0 μmol) was dissolved in dry toluene (1 mL). The two solutions were combined. The resulting orange solution were transferred to a fumehood where it was stirred for another 18h at 88 °C without a reflux condenser under active nitrogen atmosphere. Afterwards, the solvent was evacuated and the residue redissolved in $C_6D_6$ for $^1$H-NMR analysis. This revealed that the starting material had not reacted.

## PHENYL(TRIBROMO)SILANE

Allylbromide (14 mL, 162 mmol) and a catalytic amount of palladium(II) dichloride (80 mg, 450 μmol) were added to phenylsilane (5 mL, 40 mmol) and allowed to stir under nitrogen atmosphere at reflux temperatures for 63 hours. Afterwards, the reaction was allowed to cool down to room temperature. Subsequent evacuation of the volatiles at room temperature and 0.23 Torr removed the starting material and the monobrominated species of the silane, as their boiling points are below room temperature at this pressure. Distillation of the residue yielded the title compound as the sole product (5.89 g, 42%).

$^{1}$H NMR ($C_6D_6$): δ/ppm 7.56 (dd, 2H, $^{3}J_{HH}$ = 1.78 Hz, $^{5}J_{HH}$ = 1.82 Hz, o-*H*$_2$), 6.98 (m, 3H, m-*H*$_2$ & p-*H*).

## ATTEMPT: BROMO(PHENYL(1,9-DIMESITYL-5,5-DIMETHYLBIPYRROMETHYL) SILANE (4A)

Lithium salt **2b** (100 mg, 197 μmol) was dissolved in dry tetrahydrofuran (3 mL). The solution was cooled to -80°C, and phenyl(tribromo)silane (350 mg, 1.01 mmol) was added. The solution was allowed to stir for 3 hours. After the reaction, the solvent and excess silane were evacuated and the residue was transferred to a glovebox for further work up. There, toluene was added to suspend the lithium salt. This could then be filtered. The filtrate was dried *in vacuo*. This yielded a dark red residue. Solving this residue in $C_6D_6$ allowed for $^{1}$H-NMR analysis. Unfortunately, this revealed a complex mixture of compounds, which did not resemble the bipyrromethyl scaffold.

In another attempt to synthesize the title compound, compound **3b** (101 mg, 197 μmol) was dissolved in allylbromide (1 mL, 11.5 mmol). Palladium(II) dichloride (8 mg, 45 μmol) was added to the solution and the resulting suspension was allowed to stir for 67 hours. After evacuating the excess allylbromide, the residue was transferred to a glovebox where the residue was dissolved in toluene. This gave a light blue suspension of dark blue flakes, which are removed by filtration. Evacuation of the solvent and redissolvement in $C_6D_6$ allows for $^{1}$H-NMR analysis. The dark flakes were dissolved in $CD_2Cl_2$ for $^{1}$H NMR analysis. Unfortunately, this revealed that the material contained a complex mixture of compounds, none of which resembled the bipyrromethyl scaffold.

## ATTEMPT: CHLORO(PHENYL(1,9-DIMESITYL-5,5-DIMETHYLBIPYRROMETHYL) SILANE (4B)

Lithium salt **2b** (105 mg, 248 μmol) was dissolved in dry tetrahydrofuran (3 mL). Phenyl(trichloro)silane (70 μL, 436 μmol) was added and the solution is allowed to stir for 66 hours. Over time, the solution turned dark red. After the reaction, the solvent and excess silane were evacuated and the residue was transferred to a glovebox for further work up. There, toluene was added to suspend the lithium salt. This could then be filtered. The filtrate was dried *in vacuo*. This yielded a purple residue. Solving these residues in $C_6D_6$ allowed for $^{1}$H-NMR analysis. Unfortunately, this revealed a complex mixture of compounds. The absence of a silicon-peak in $^{29}$Si-NMR confirms that **2b** was not silylated in this synthesis attempt.

# XI. REFERENCES


[1]. M.C. White (2012), *Science*, **335**, pp 807 et seq.

[2]. M. Tamura & J. Kochi (1971), *Synthesis (Stuttg.)*, **6**, pp 303 et seq.

[3]. R. Jana, T.P. Pathak, M.S. Sigman (2011), *Chem. Rev.*, **111**, pp 1417 et seq.

[4]. K. Hübler, W.R. Roper, L.J. Wright (1997), *Organometallics,* **16**, pp 2730-2735.

[5]. T. Evers (2013), *Studies on indolyl- and pyrrolylsilanes as potential precursors for Si-centred ligands* (internal communication).

[6]. A.A. Dahy, N. Koga, H. Nakazawa (2013), *Organometallics* **32**, pp 2725-2735.

[7]. M. Esteruelas, M. Oliván, A. Vélez (2013), *Inorg. Chem.* **52**.

[8]. T. Tanaka & A. Osuka (2015), *Chem. Commun.* **51**, pp 8123-8125.

[9]. A.C. Benniston, G. Copley, K.J. Elliott, R. Harrington, W. Clegg (2008), *Eur. J. Org. Chem.*, **10**, pp 2705-2713.

[10]. Ö. Dilek & S.L. Bane (2009), *Bioorg. Med. Chem. Lett.*, **19**, pp 6911-6913.

[11]. S. Madhu & M. Ravikanth (2012), *Inorg. Chem.,* **51**, pp 4285-4292.

[12]. C.Y. Lee & J.T. Hupp (2010), *Langmuir*, **26**, pp 3760-3765.

[13]. M. Aleskovic *et al*. (2013), *Tetrahedron*, **69**, 2013, pp 1725-1734.

[14]. A. Kämpfe, E. Kroke, J. Wagler (2014), *Organometallics*, **33**, pp 112-120.

[15]. L.J. Higham *et al.* (2012), *Angew. Chem., Int. Ed.*, **51**, pp 4921-4924.

[16]. N. Sakamoto, C. Ikeda, M. Yamamura, T. Nabeshima (2011), *J. Am. Chem. Soc.* **133**, pp 4726−4729.

[17]. T. S. Piper, D. Lemal, G. Wilkinson (1956), *Naturwiss.* **43**, p 129.

[18]. J.L. Speier, J.A. Webster, G.H. Barnes (1957), *J. Am. Chem. Soc.* **79**, pp 974 et seq.

[19]. T.D. Tilley (1989), *The Chemistry of Organic Silicon Compounds*, pp 1415 et seq.

[20]. R.D. Rieth, N.P. Mankad, E. Calimano, J.P. Sadighi (2004), *Org. Lett.*, 6, **22**, pp 3981-3983

[21]. Selected references (as selected and mentioned by Rieth and co-workers [20]):

[21a]. L.B.-Å Johansson *et al.* (2000), *Chem. Commun.*, pp 2203-2204.
[21b]. P. La Colla *et al*. (2001), *Chem. Pharm. Bull.* **49**, pp 1406-1411.
[21c]. D.A. Hunt (1996), *Pest. Sci.*, **47**, pp 201-202.

[22]. E.R. King & T.A. Betley (2009), *J. Am. Chem. Soc.*, **131**, pp 14374-14380.

[23]. J. Soloducho (1999), *Synthetic Materials* **99**, pp 181-189.

[24]. D.L. Swartz II & A.L. Odom (2006), *Organometallics*, **26**, pp 6125-6133.

[25]. J.S. Lindsey *et al*. (1999), *J. Org. Chem*., **64**, p 1391.

[26]. J.A. Dean, *Lange's Handbook Of Chemistry* (1992), **14**, pp 4.41 et seq. Both energies refer to the elementary "MX → M + X" reaction in the gaseous state at 298 K.

[27]. Except in the case of Ni, where the six-membered ring is distorted and one nitrogen-carbon bond is 1.402 Å and the other is 1.372 Å.

[28]. A.A. Korkin, J.V. Cole, D. Sengupta, J.B. Adams (1999), *J. Electrochem. Soc.*, **11**, pp 4203-4212.

[29]. J.M. Tour, J.A. John, E.B. Stephens (1992), *J. Organomet. Chem.* **429**, pp 301-310.

[30]. A.L. Smith & N.C. Angelotti (1959), *Spectrochimica Acta* **15**, pp 412-420.

[31]. However, since these spectra are recorded in different solvents ($CD_2Cl_2$ *versus* $CD_3CN$), this part of the comparison isn't too reliable.

[32]. M. Flock & C. Marschner (2002), *Chem. Eur. J.* **8**, pp 1024-1030.

[33]. H. V. R. Dias, M. M. Olmsted, K. Ruhlandt-Senge, P. P. Power (1993), *J. Organomet. Chem.* **1** pp 492 et seq.

[34]. C. Marschner (1998), *Eur. J. Inorg. Chem.* **2**, pp 221 et seq.

[35]. Repeating the reaction in benzene, too, yielded no reaction. Although benzene is not a polar solvent, it is capable of stabilizing cations due to cation-$\pi$ interactions. Kebarle [Kebarle *et al.* (1981), *J. Chem. Phys.* **85**, pp 1814 et seq.] and Meot-Ner [Meot-Ner *et al.* (1985), *J. Am. Chem. Soc.* **107**, pp 469 & 474] find that $-\Delta H_{exptl}$ = 19.2 kcal/mol for benzene and $K^+$, which is higher than water and $K^+$ ($-\Delta H_{exptl}$ = 17.9 kcal/mol).

[36]. P.D. Prince, M.J. Bearpark, G.S. McGrady, J.W. Steed (2008), *Dalton Trans.*, pp 271–282.

[37]. D. Chan *et al.* (2004), *Organometallics* **23**, pp 5744-5756.

[38]. J.L. Speier (1979), *Adv. Organomet. Chem.* **17**, p 407 et seq.

[39]. Selected references (as selected and mentioned by Chan and co-workers [29]):

(a) J.A. Reichl & D.H. Berry (1999), *Adv. Organomet. Chem.* **43**, pp 197 et seq.
(b) F. Gauvin, J.F. Harrod, H.G. Woo (1998), *Adv. Organomet. Chem.* **42**, pp 363 et seq.
(c) M.E. Wright & B.B. Cochran (1996), *Organometallics* **15**, pp 317 et seq.
(d) I. Matsuda, Y Kukuta, T. Tsuchihashi, H. Nagashima, K. Itoh (1997), *Organometallics* **16**, pp 4327 et seq.

[40]. R. Ugo, F. Cariati, G. La Monica (1968), *Inorganic Syntheses* **11**, pp 115–108.

[41]. U. Belluco, G. Deganello, R. Pietropaolo, P. Uguagliati (1970), *Inorganica Chimica Acta Reviews* **4**, pp 7-39.

[42]. K.G. Moloy & J.L. Petersen (1995), *J. Am. Chem. Soc.* **462**, pp 331 et seq.

[43]. E.W. Turnblom, R.J. Boettcher, K. Mislow (1975), *J. Am. Chem. Soc.*, **7**, pp 1766-1772.

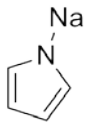
[44]. However, the use of the $\pi$-$C_5H_5$ (Cp) ligand would not be preferred in our case, as this ligands binds so strongly to the metal centre it would hinder further ligand exchange, limiting the scope of catalyst design.

[45]. C.S. Cundy & M.F. Lappert (1973), *Journal of Organometallic Chemistry* **57**, pp C72-C74.

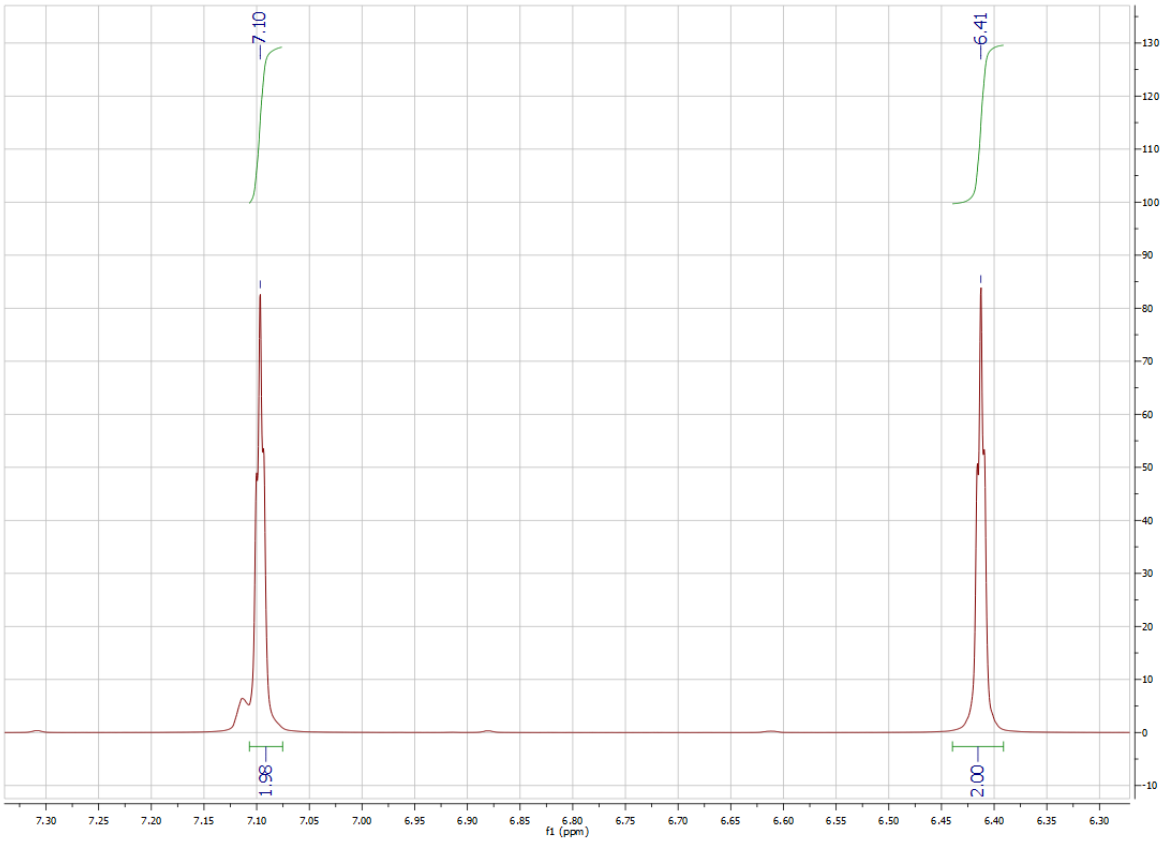
[46]. A. Iwata *et al.* (2003), *Journal of Organometallic Chemistry* **667**, pp 90-95.

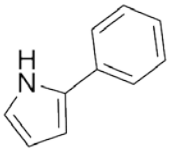
# XII. Appendix: Analytical Data

This chapter contains all analytical data of the compounds discussed in this work that were referred to and/or not presented in the main text.




$^{1}$H-NMR ($C_6D_6$, 25°C)





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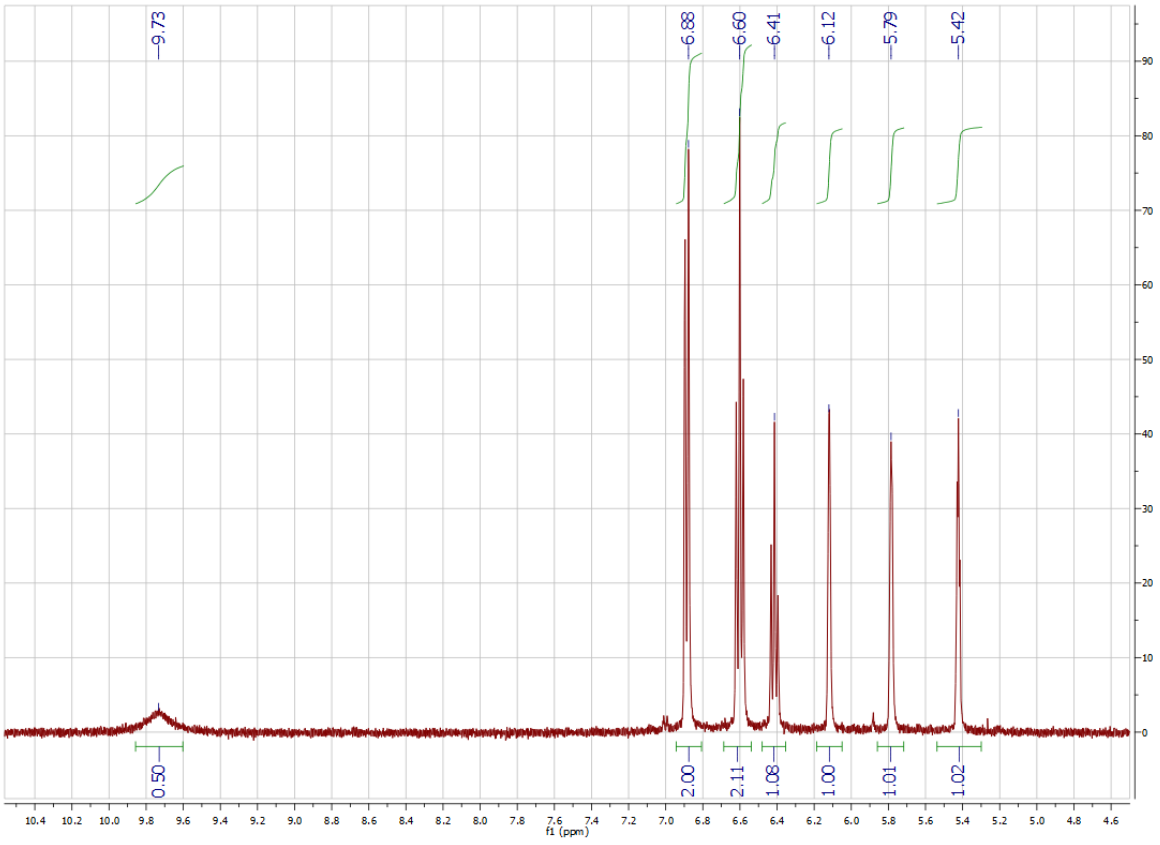
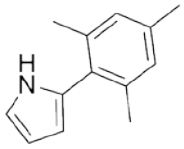
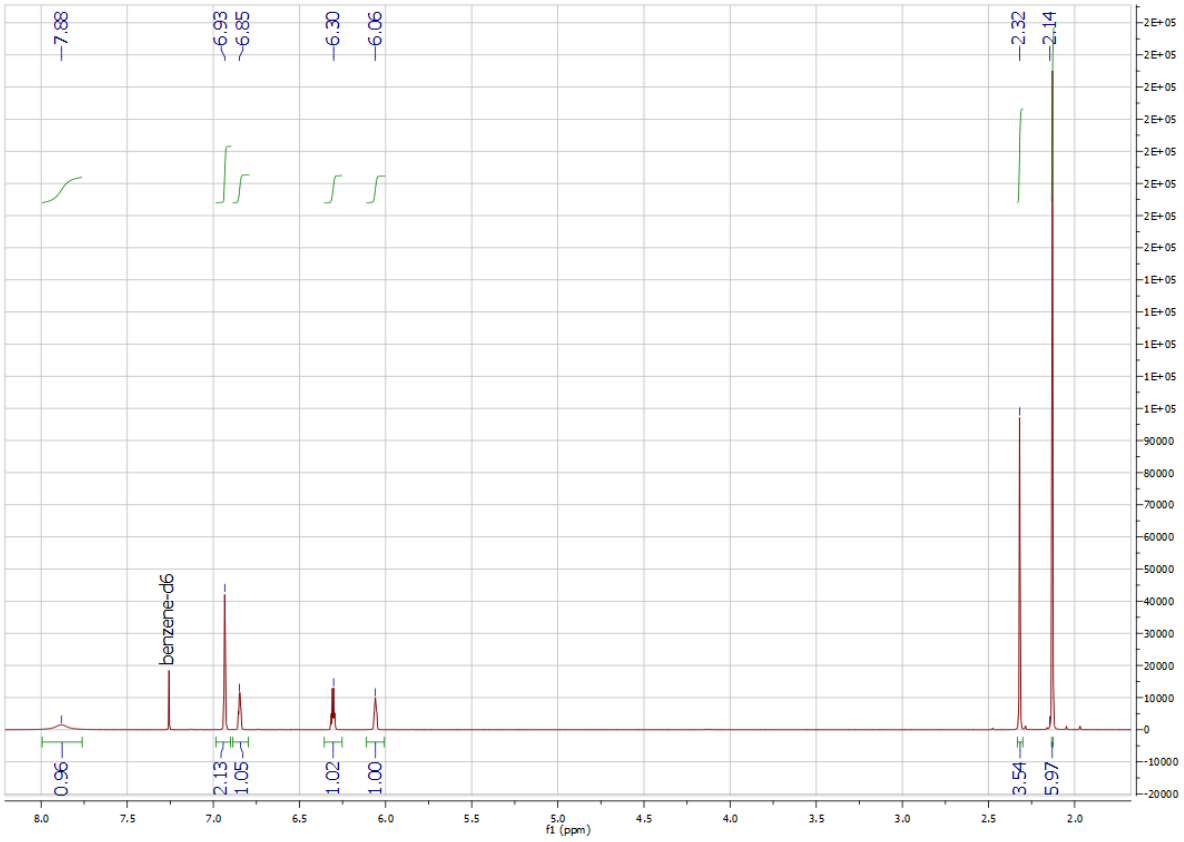
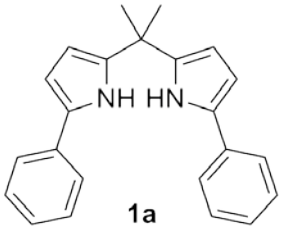




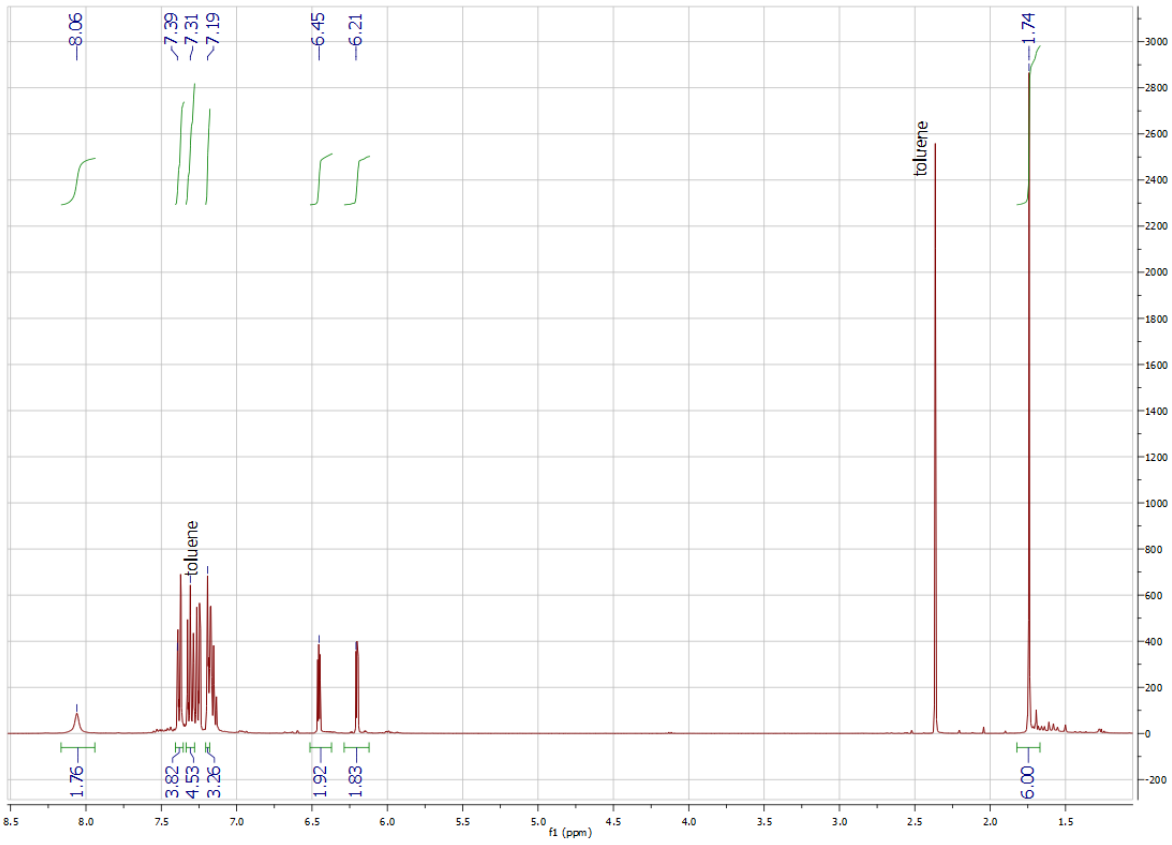
$^{1}$H-NMR ($CDCl_3$, 25°C)

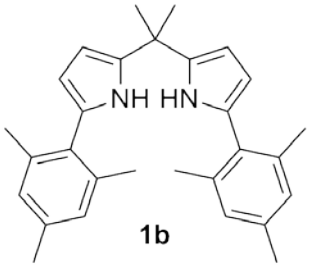





**1a**

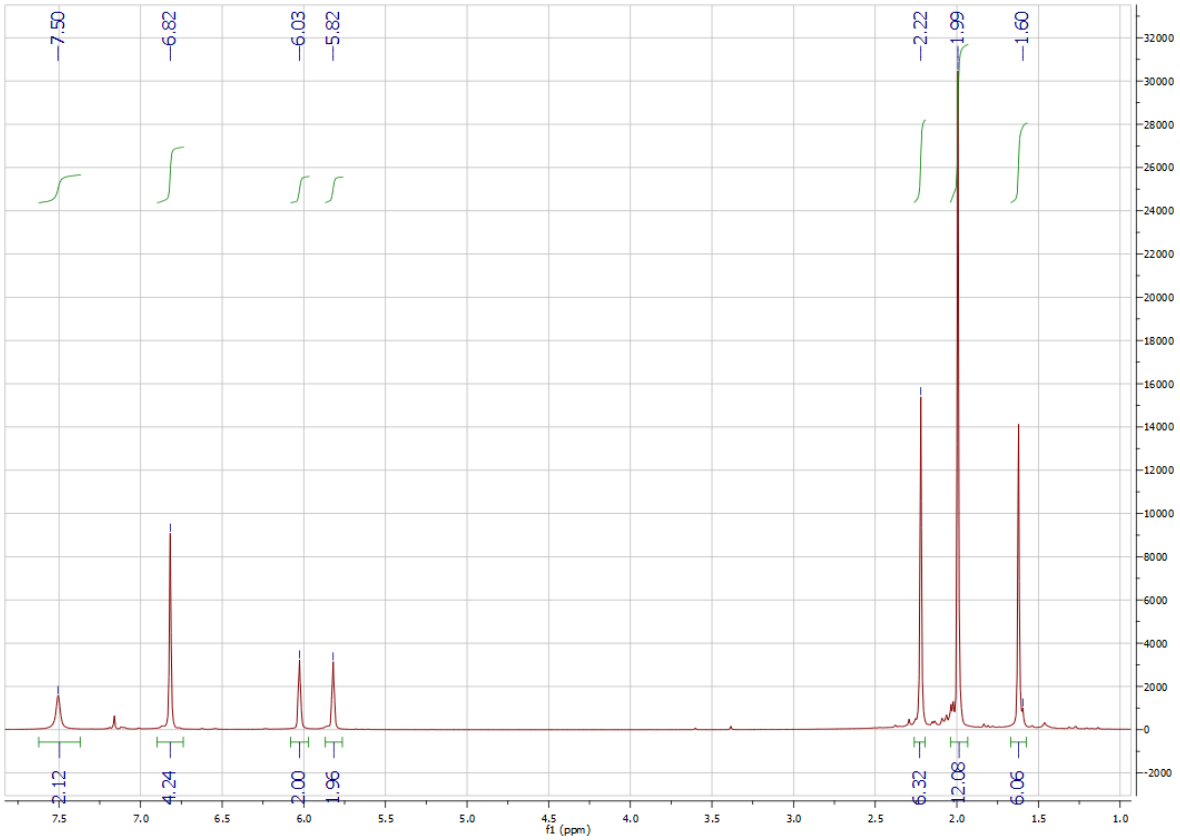
$^{1}$H-NMR ($CDCl_3$, 25°C)

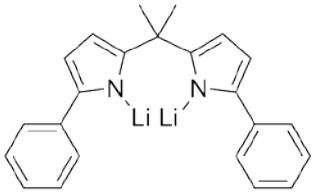





**1b**

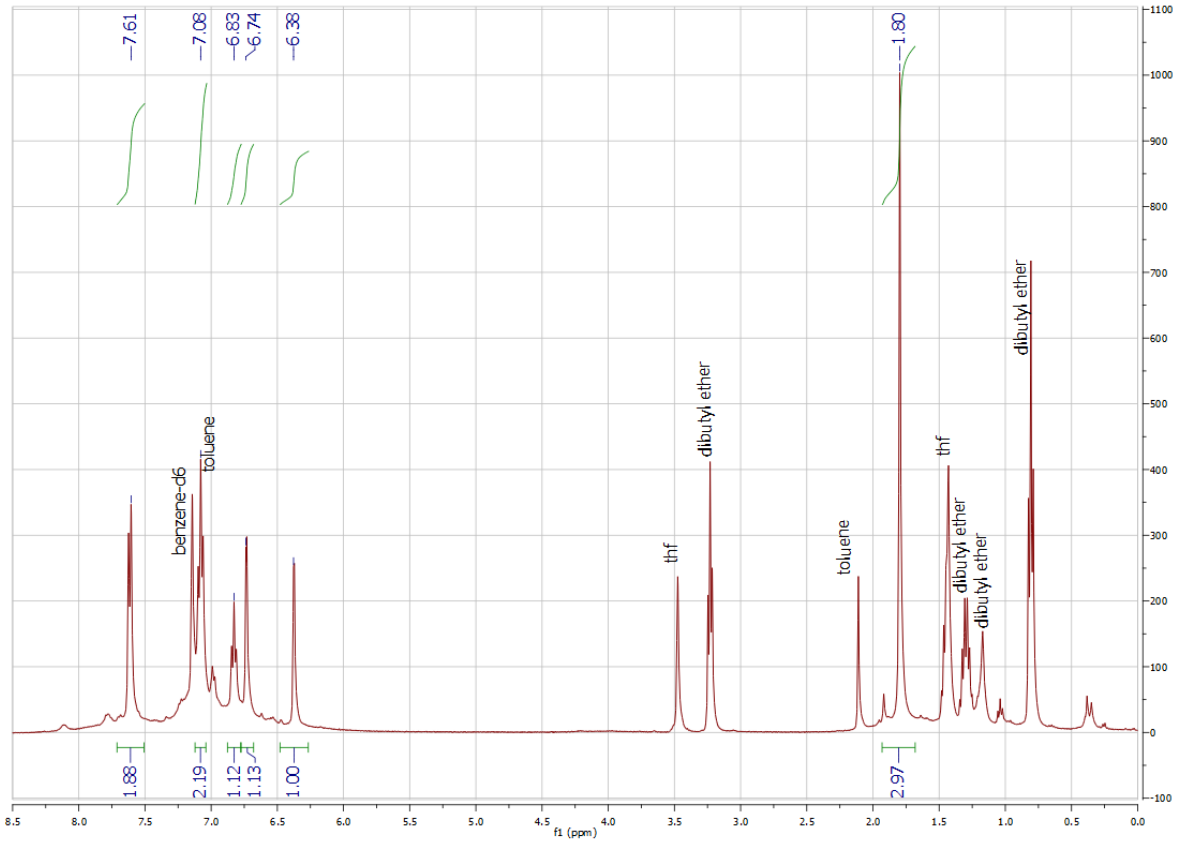
$^{1}$H-NMR ($C_6D_6$, 25°C)

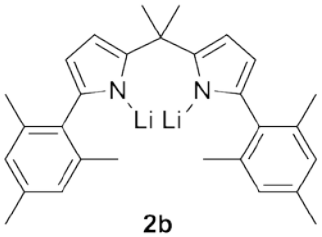





**2a**

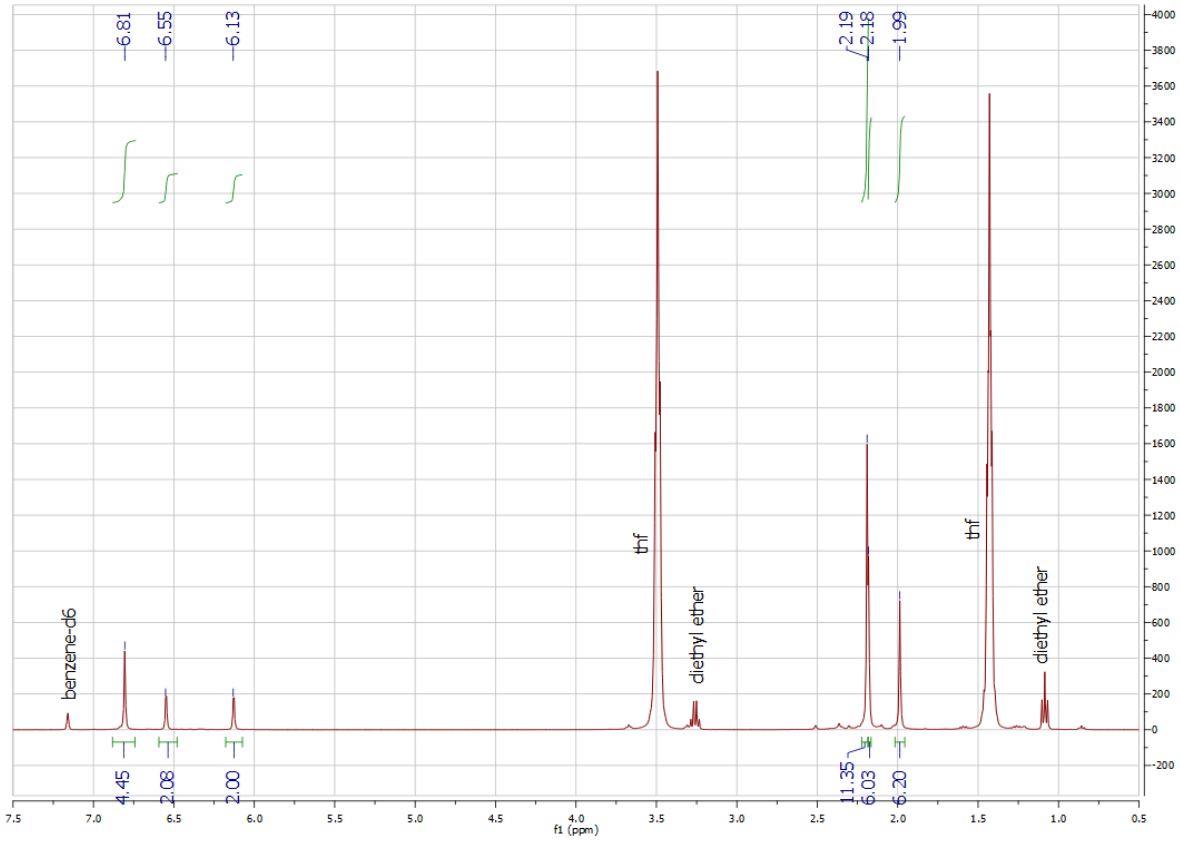
$^{1}$H-NMR ($C_6D_6$ & $C_4D_8O$, 25°C)

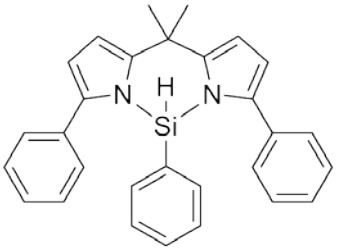





**2b**

$^{1}$H-NMR ($C_6D_6$, 25°C)

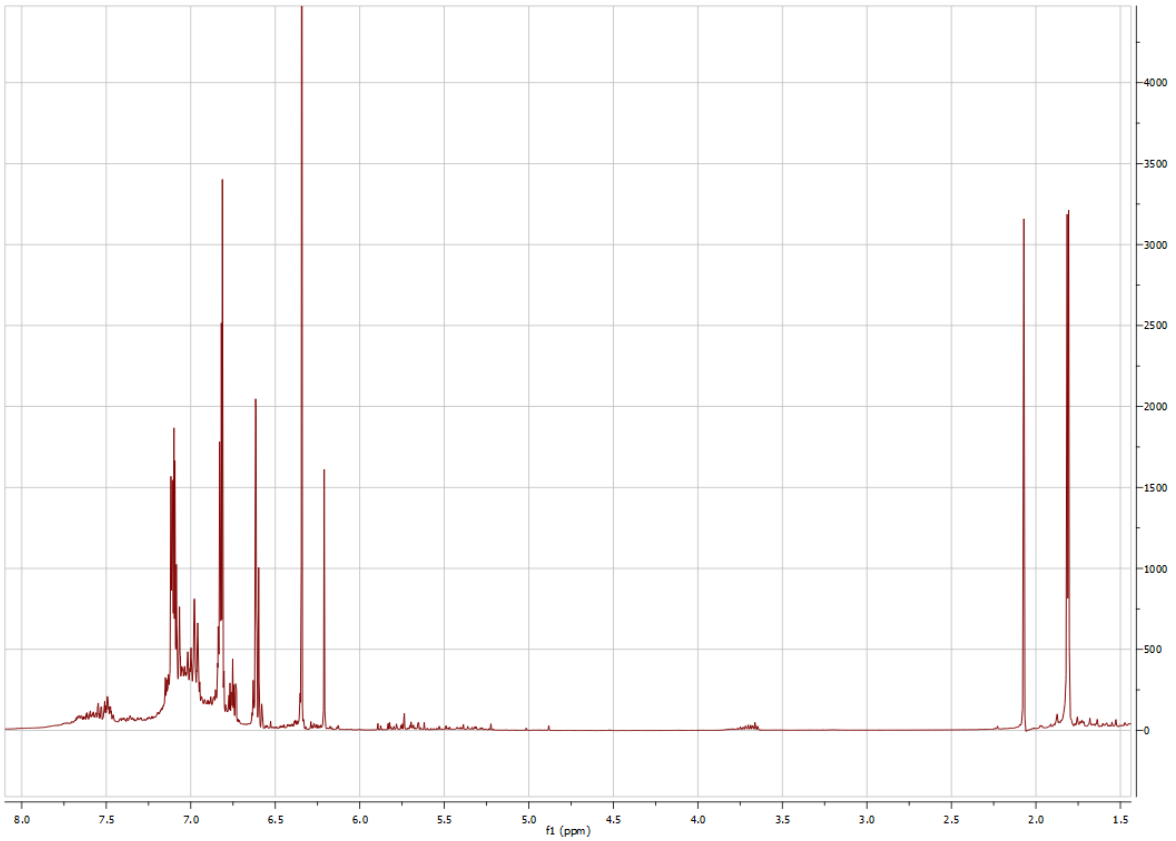


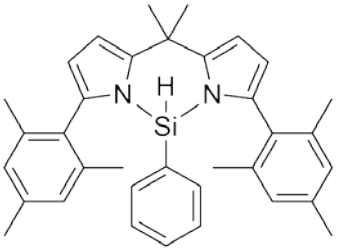



**3a**

(*Not isolated*)

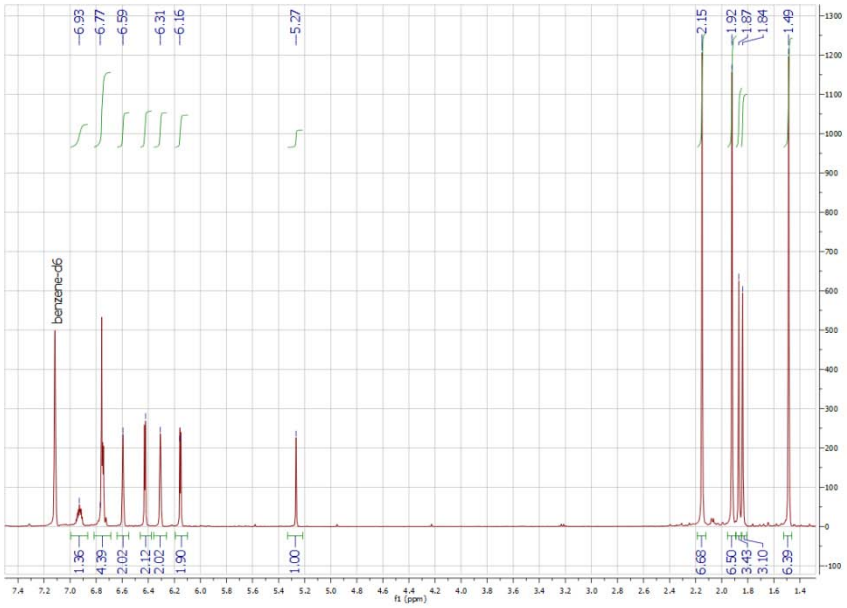
$^{1}$H-NMR ($C_6D_6$, 25°C)



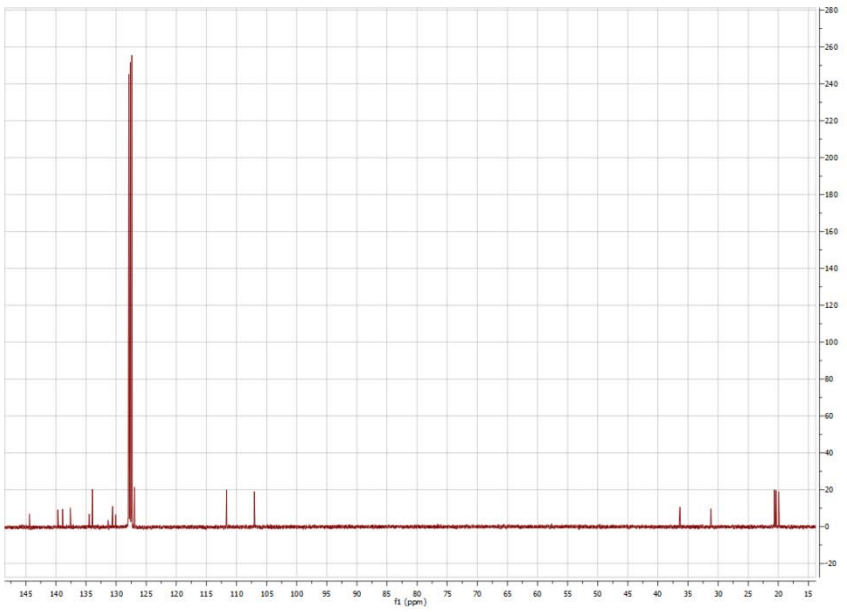



**3b**

$^{1}$H-NMR ($C_6D_6$, 25°C)

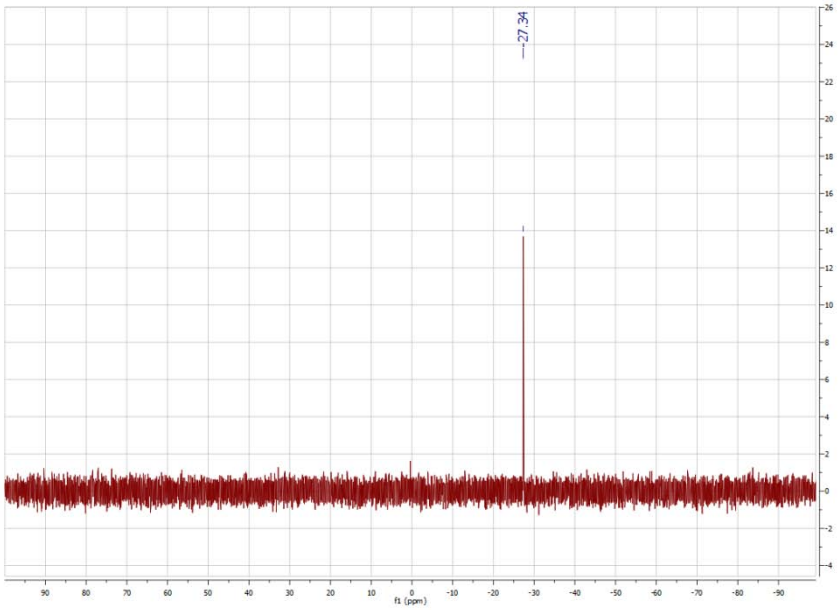



$^{13}$C-NMR ($C_6D_6$, 25°C)

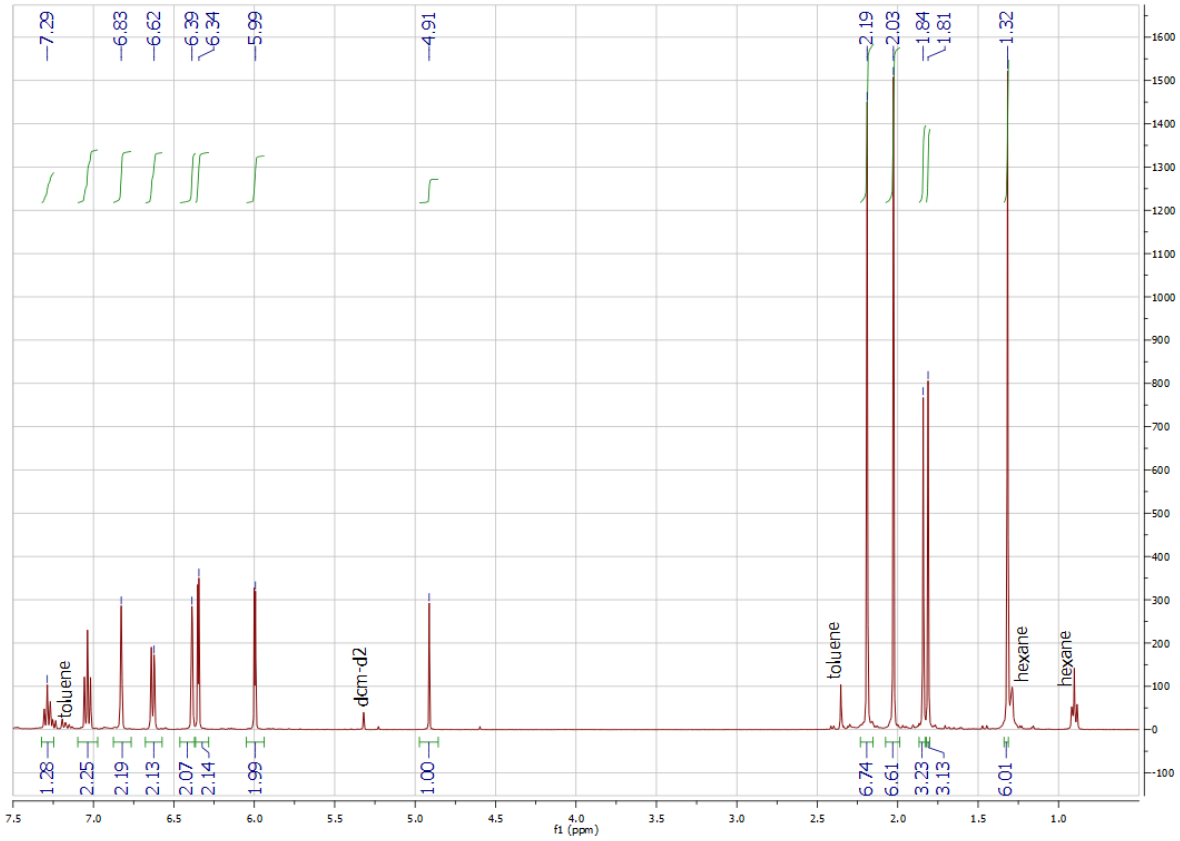


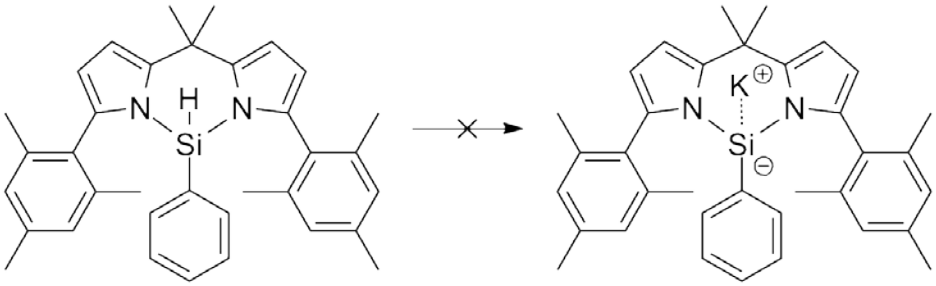

(*Cont'd*)

$^{29}$Si-NMR {$^{1}$H decoupled} ($C_6D_6$, 25°C)



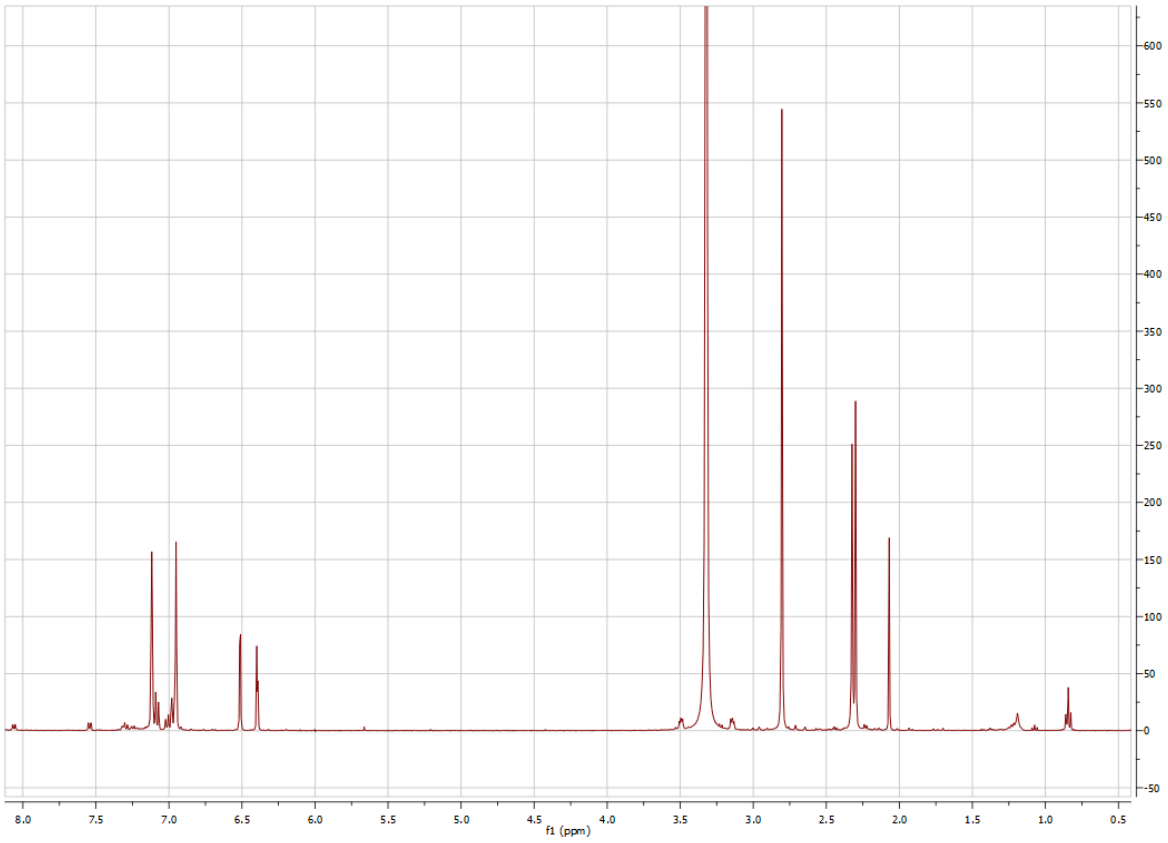

$^{1}$H-NMR ($CD_2Cl_2$, 25°C)



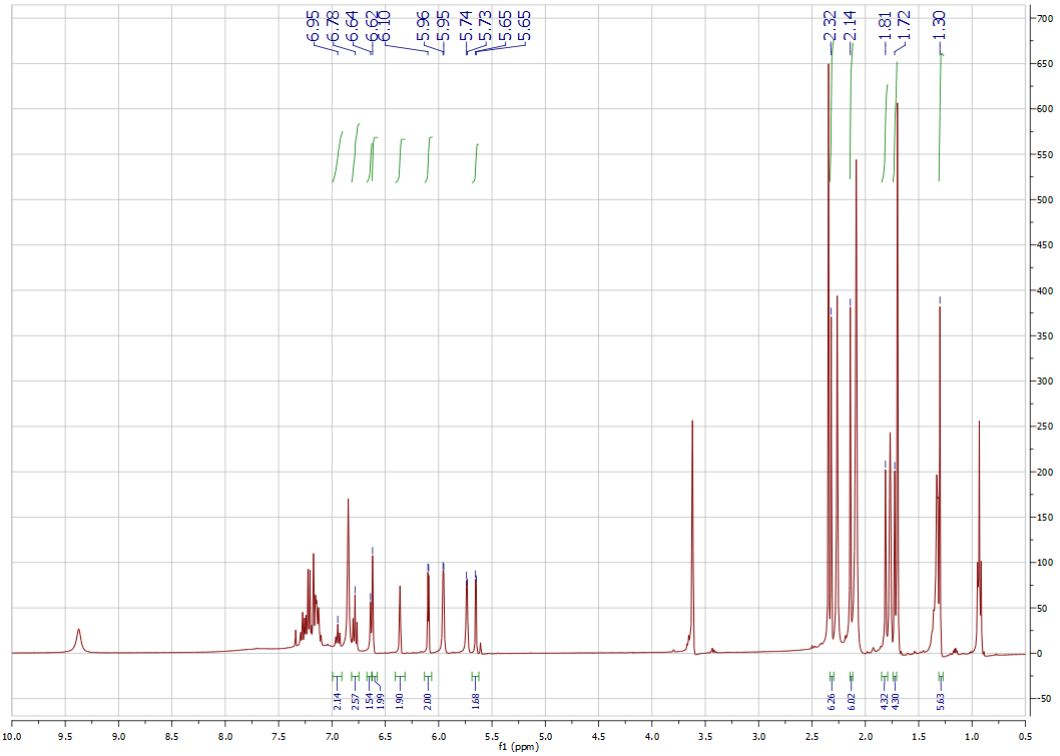



**3b** (*Attempt*)

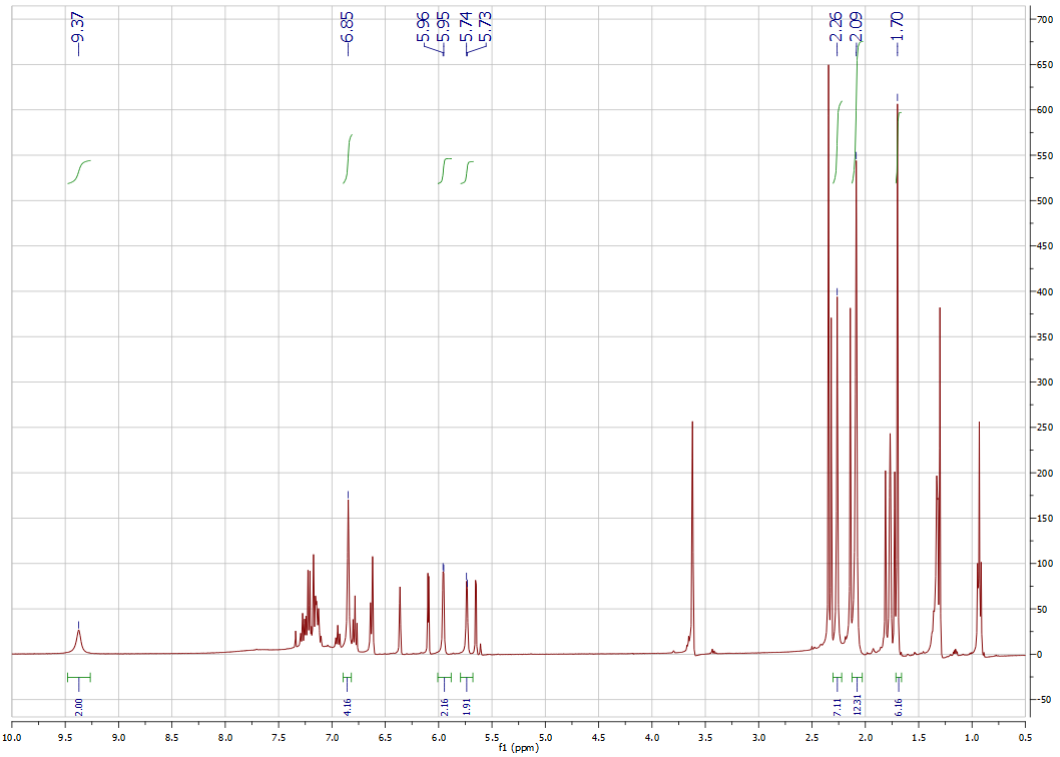
$^{1}$H-NMR ($C_6D_6$)



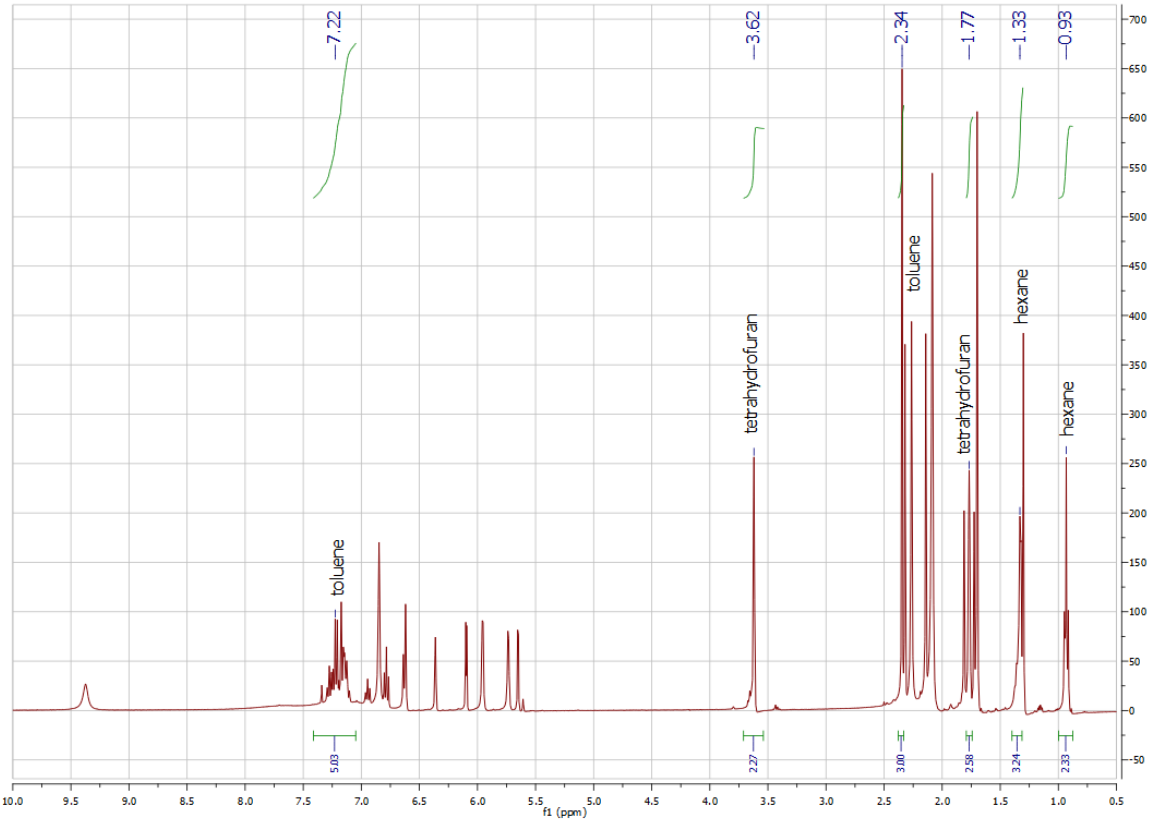

The $^{1}$H-NMR spectrum of the filtrate of the workup in the deprotonation attempt of **3b** using KHMDS reveals the presence of the desilylated scaffold.



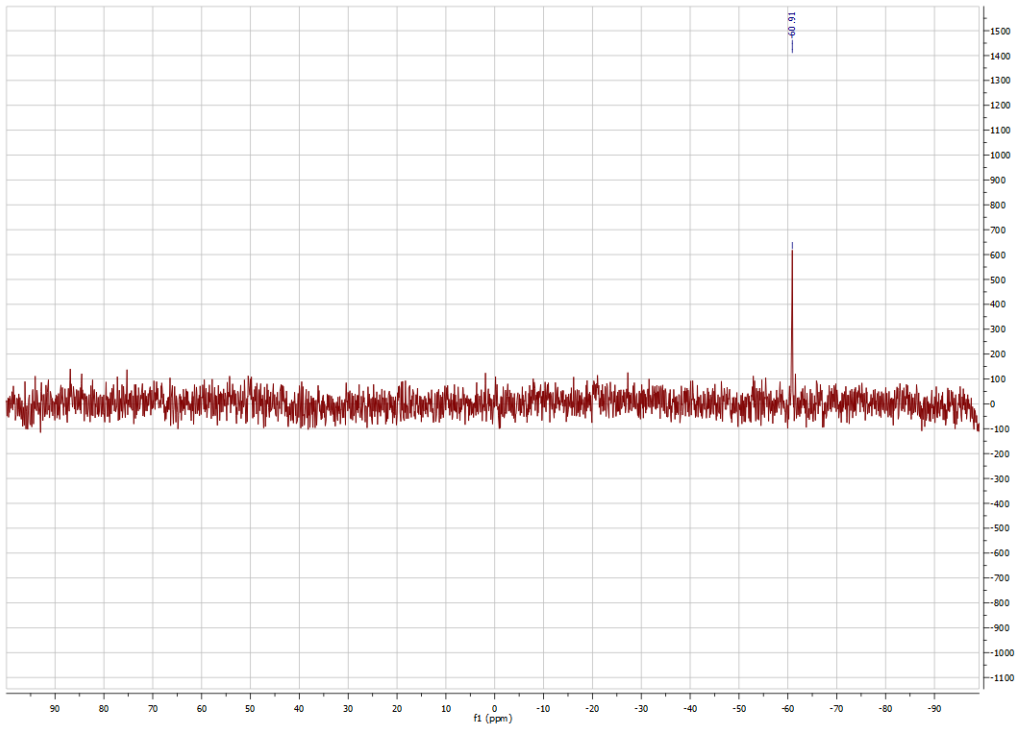

The $^{1}$H-NMR spectrum ($C_4D_8O$, 25° C) of the residue of the workup in the deprotonation attempt of **3b** using KHMDS reveals the presence of multiple compounds. Highlighted in the above spectrum are the peaks belonging to the siloxane.



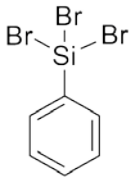

Highlighted in the above $^{1}$H-NMR spectrum ($C_4D_8O$, 25° C) are the peaks belonging to the hydrogen-signals of the free scaffold **1b**.



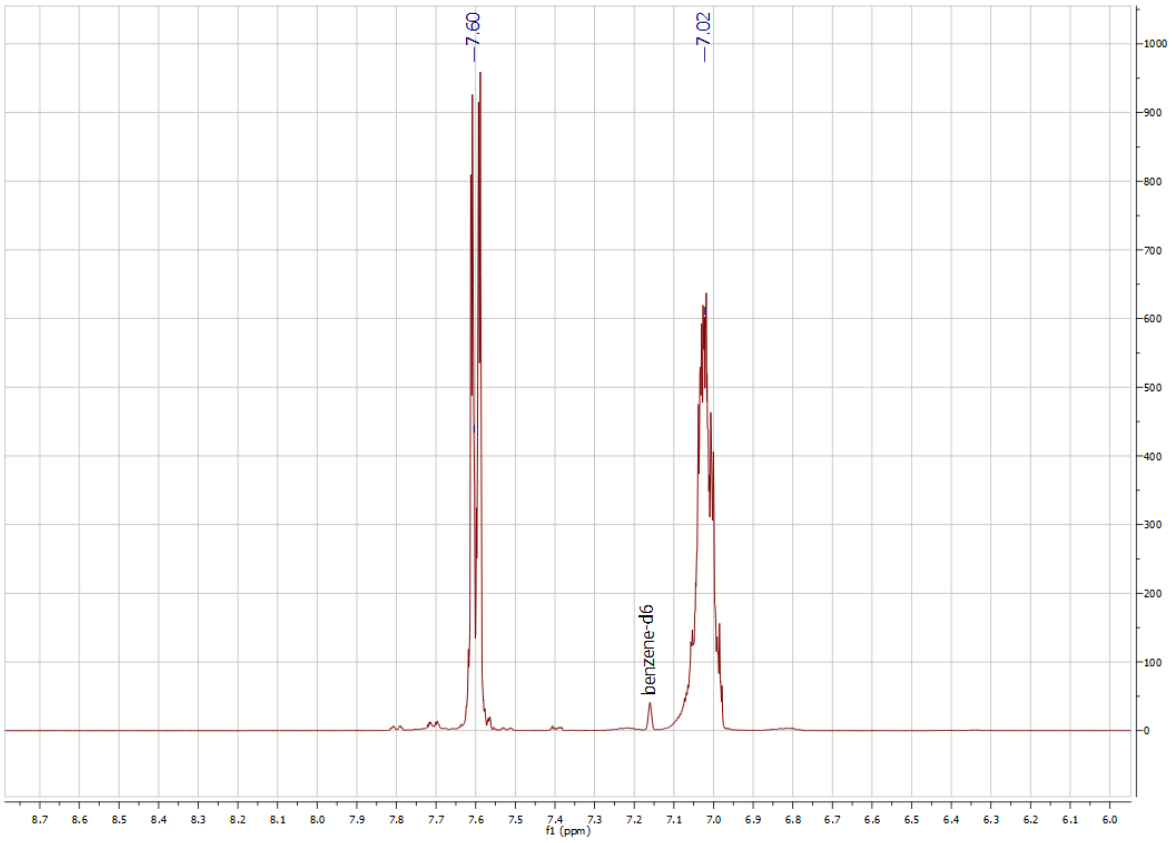

Highlighted in the above $^{1}$H-NMR spectrum ($C_4D_8O$, 25° C) are the hydrogen-signals belonging to the solvents present in the residue of the workup of the deprotonation attempt of **3b** using KHMDS. They are toluene, tetrahydrofuran and hexane.

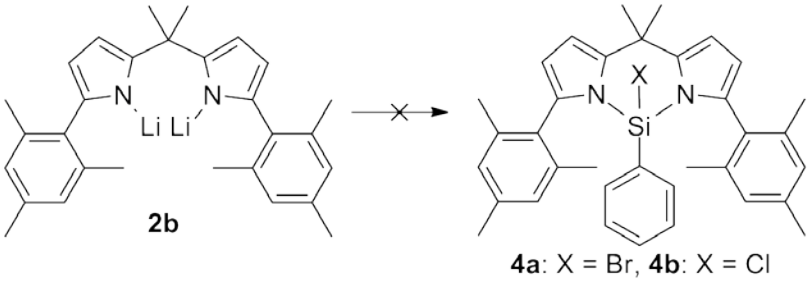



Presented above is the $^{29}$Si-NMR spectrum ($CD_3CN$, 25 °C) of the deprotonation attempt of **3b** using KH. The silicon-signal belongs to potassium phenyl(1,9-dimesityl-5,5-dimethylbipyrromethyl)siloxide crownetherate.



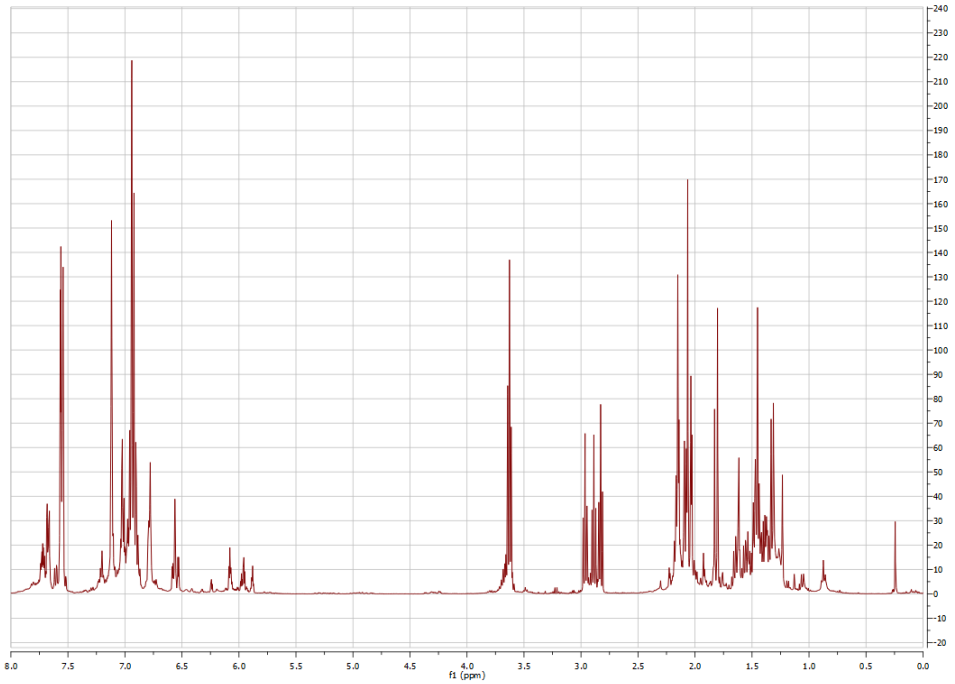

$^{1}$H-NMR ($C_6D_6$ , 25°C)



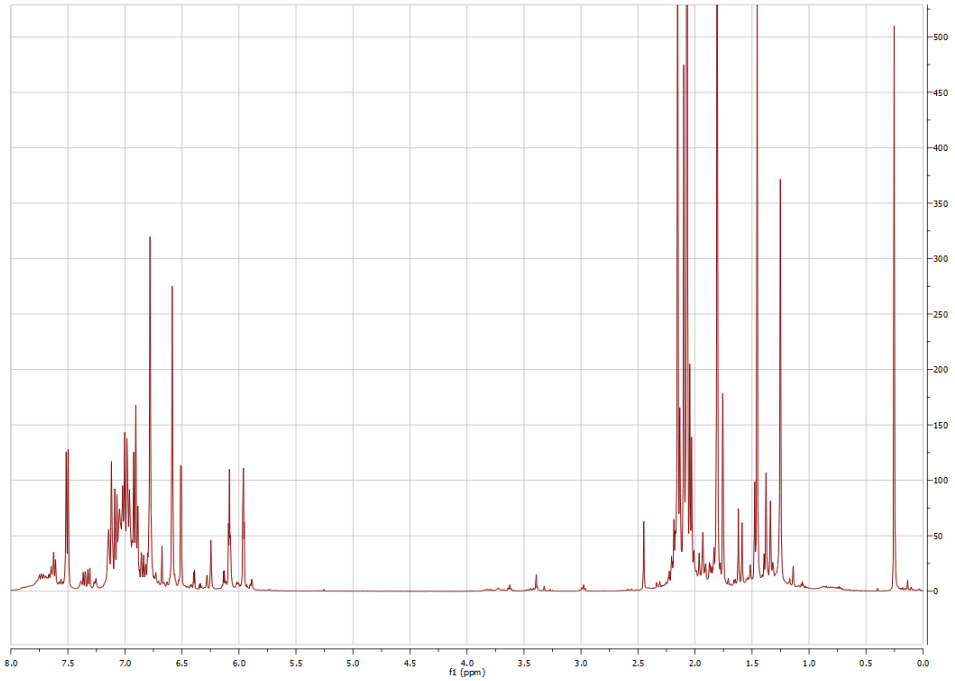



(*Attempt*)

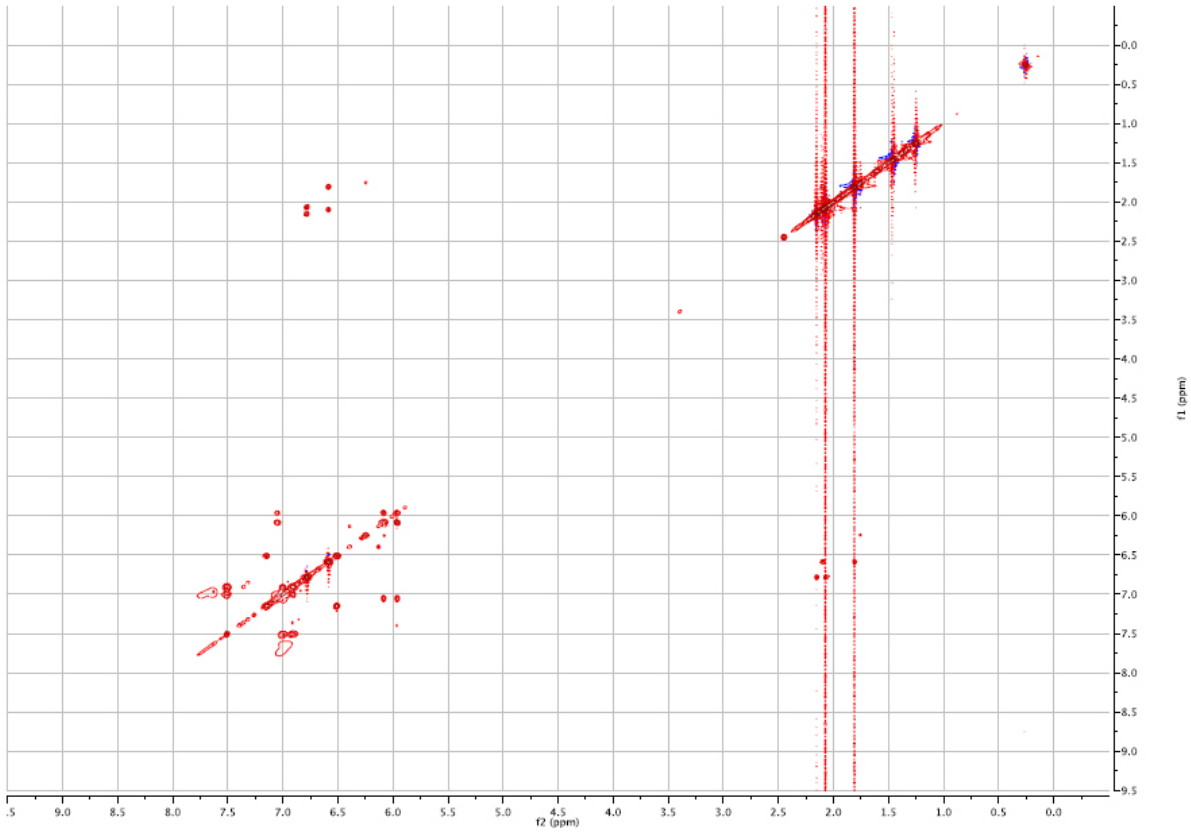
**4a**, $^{1}$H-NMR ($C_6D_6$, 25°C)

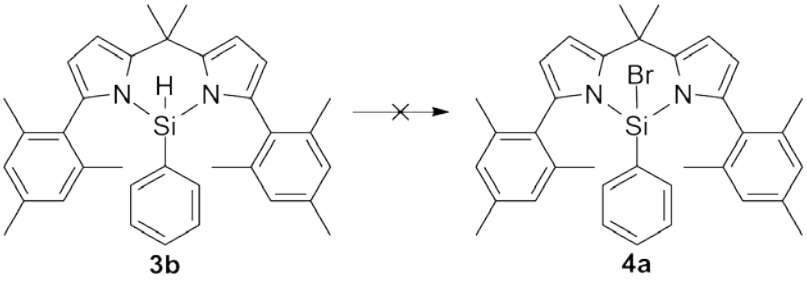



**4b**, $^{1}$H-NMR ($C_6D_6$, 25°C)



**4b**, 2D $^{1}$H-TOCSY ($C_6D_6$, 25 °C)






**3b** **4a**

(*Attempt*)

$^{1}$H-NMR ($C_6D_6$, 25°C)