Supporting Information

for

# One-pot Synthesis of Heavier Group 14 *N*-Heterocyclic Carbene using Organosilicon Reductant

Ravindra K. Raut, Sheikh Farhan Amin, Padmini Sahoo, Vikas Kumar and Moumita Majumdar*

## Contents



Department of Chemistry,
Indian Institute of Science, Education and Research, Pune
Pune-411008, Maharashtra India
E-mail: moumitam@iiserpune.ac.in

## 1. Plots of NMR Spectra

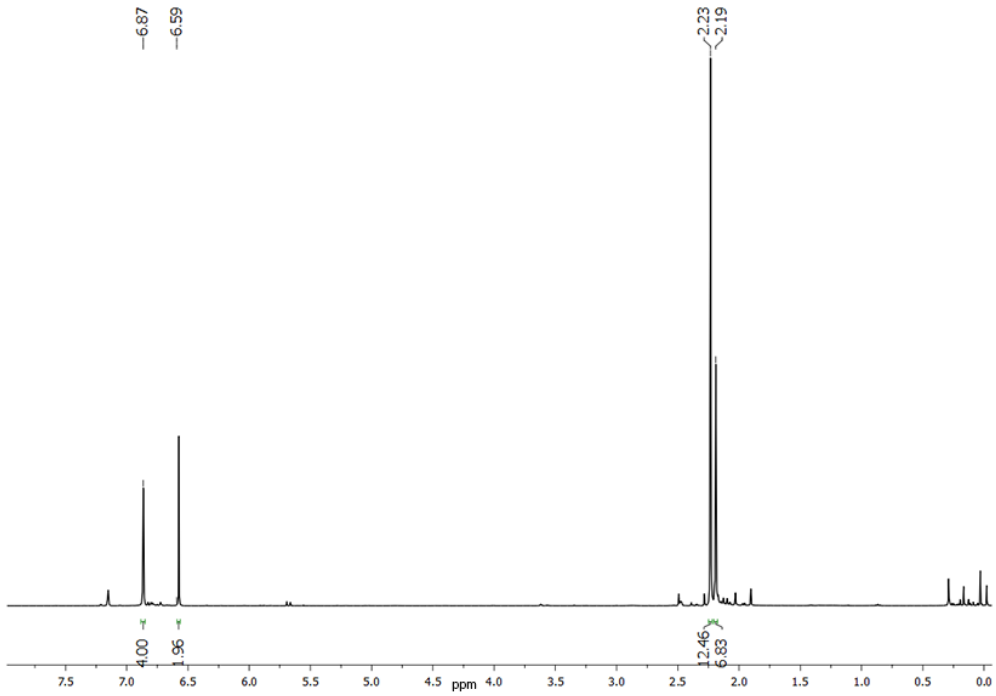



**Figure S1.** $^{1}$**H NMR of Compound 1 (crude reaction mixture, before crystallization)**

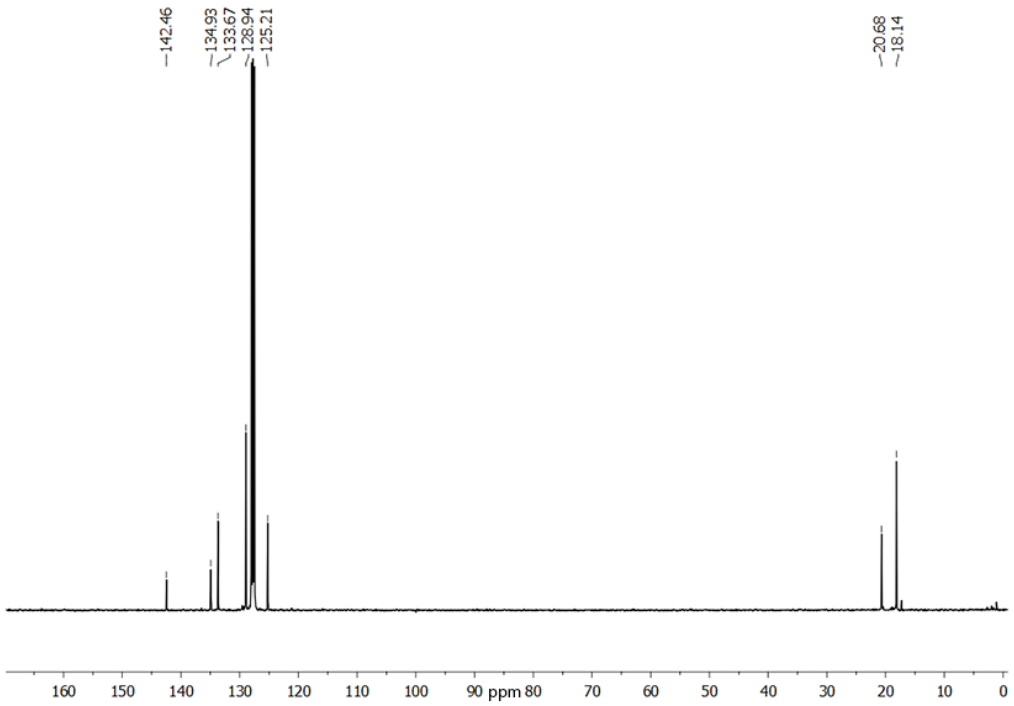



**Figure S2.** $^{13}$**C NMR of Compound 1 (crude reaction mixture, before crystallization)**

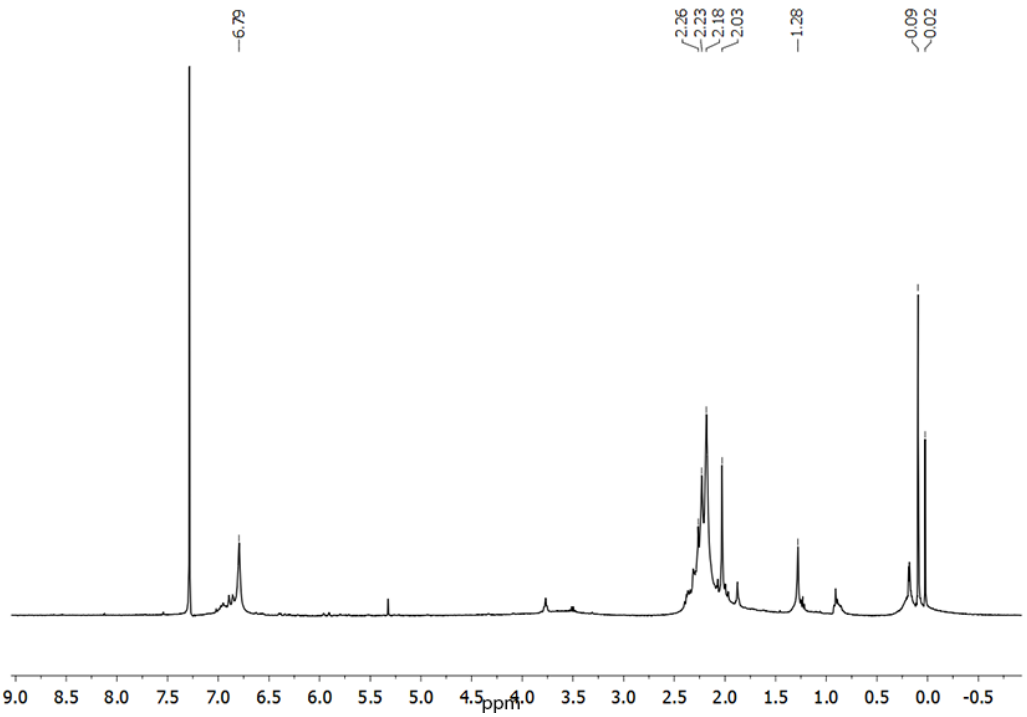



**Figure S3.** **$^{1}$H NMR in $CDCl_3$ of the hexane insoluble solid residue from the crude reaction mixture of compound 1**

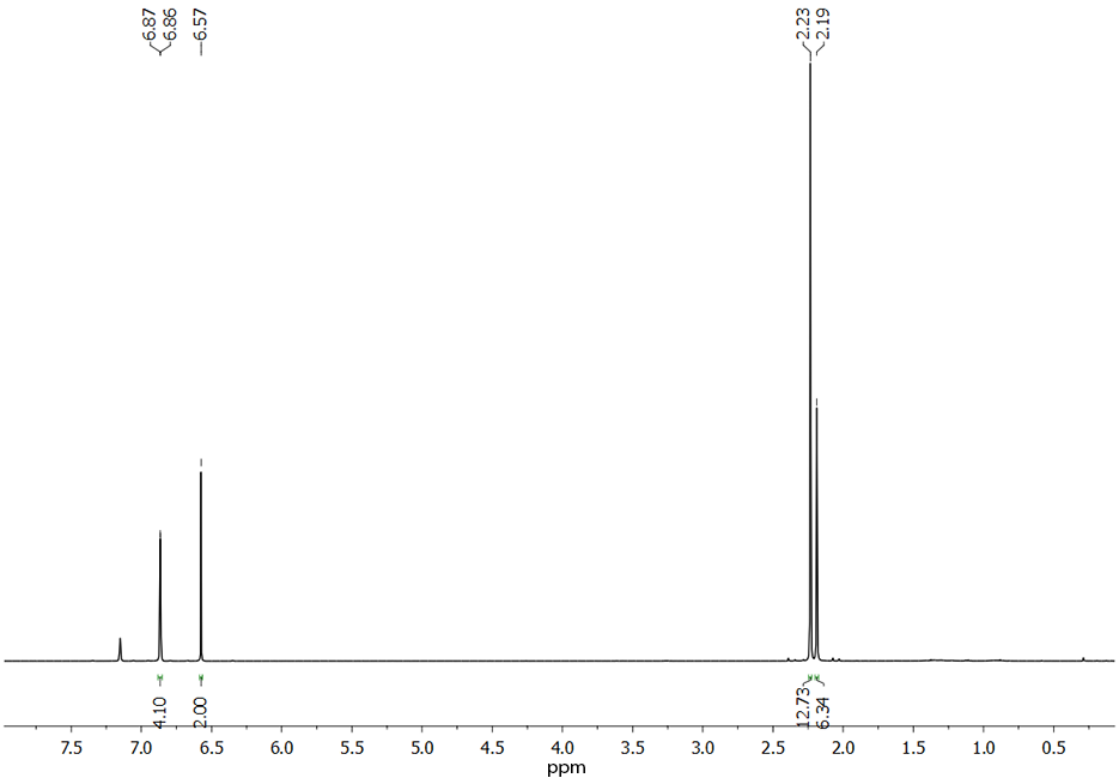



**Figure S4. $^{1}$H NMR of Compound 1**

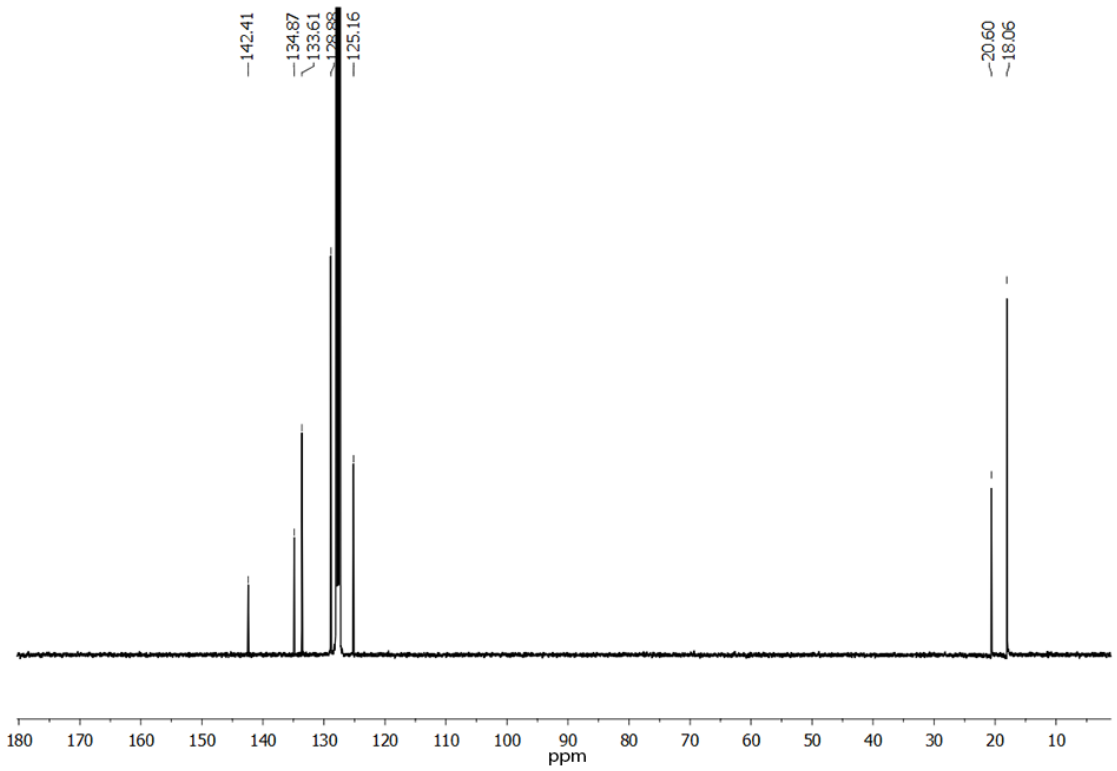



**Figure S5. $^{13}$C NMR of Compound 1**

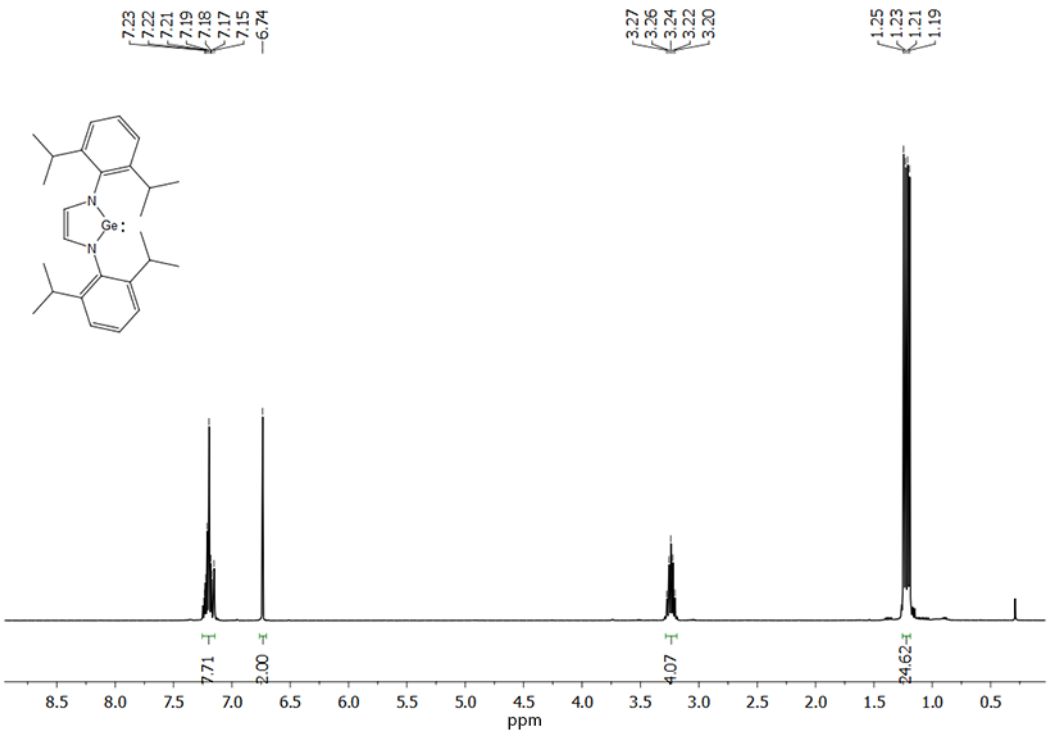



**Figure S6. $^{1}$H NMR**

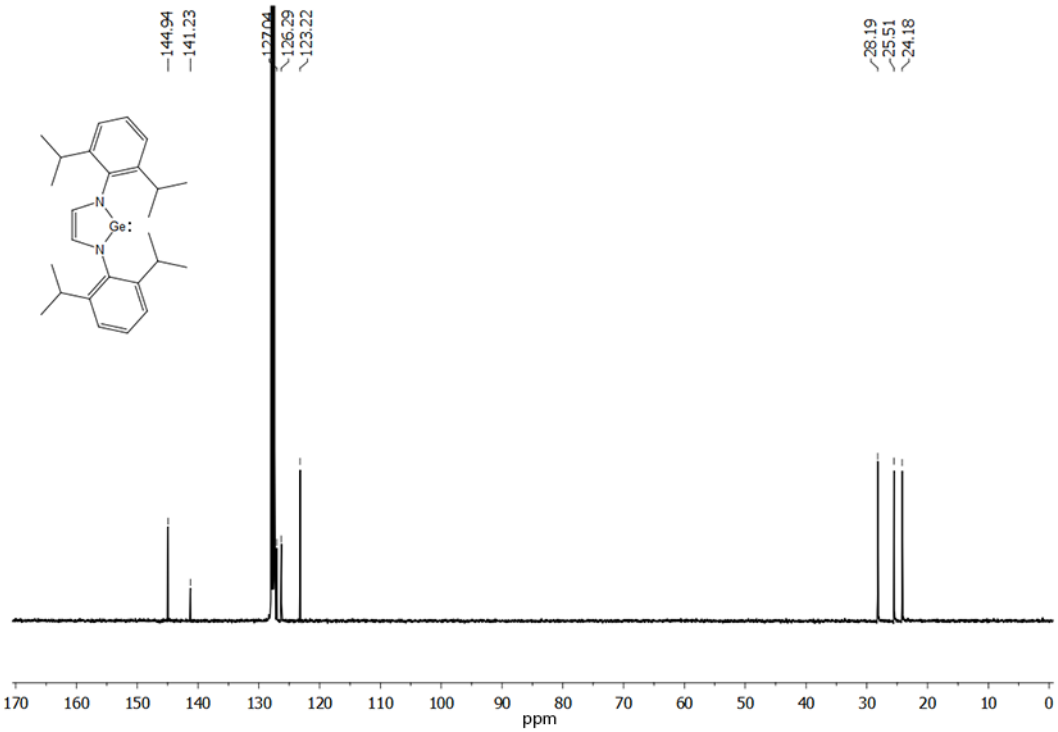



**Figure S7. $^{13}$C NMR**

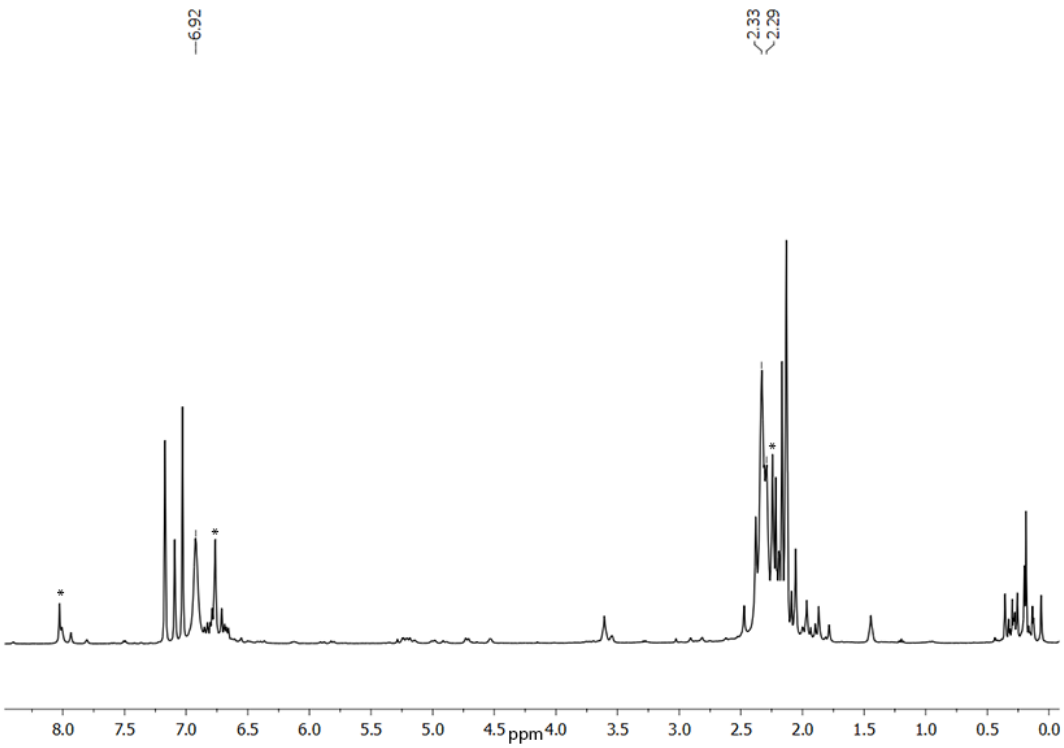



**Figure S8.** **$^{1}$H NMR of Compound 2 (crude reaction mixture, before crystallization); * = free ligand**

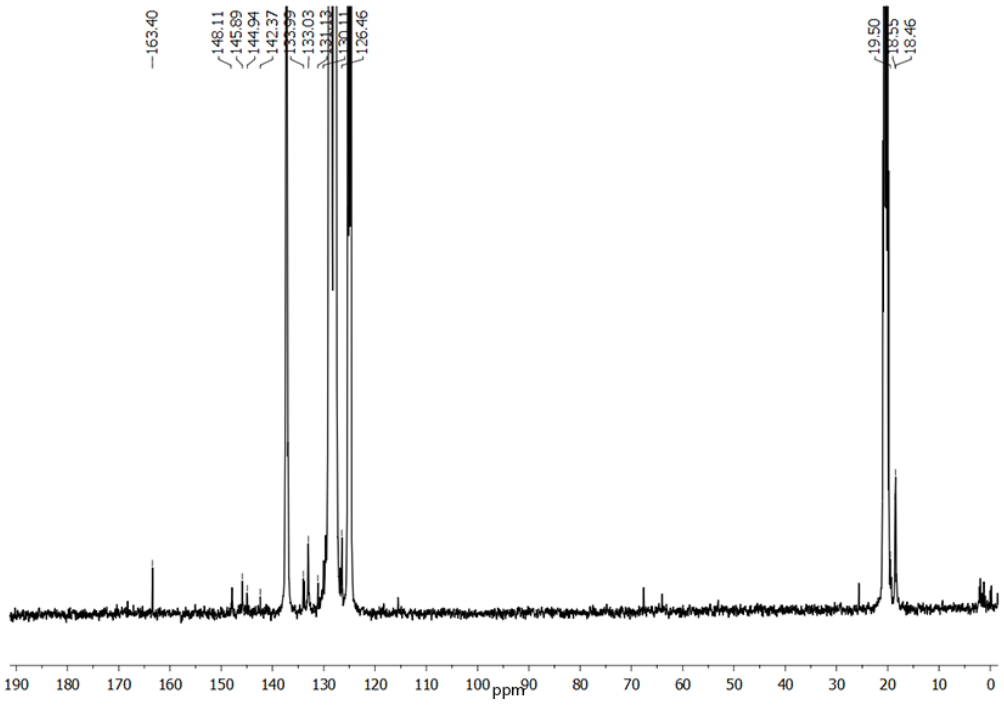



**Figure S9.** **$^{13}$C NMR of Compound 2 (crude reaction mixture, before crystallization)**

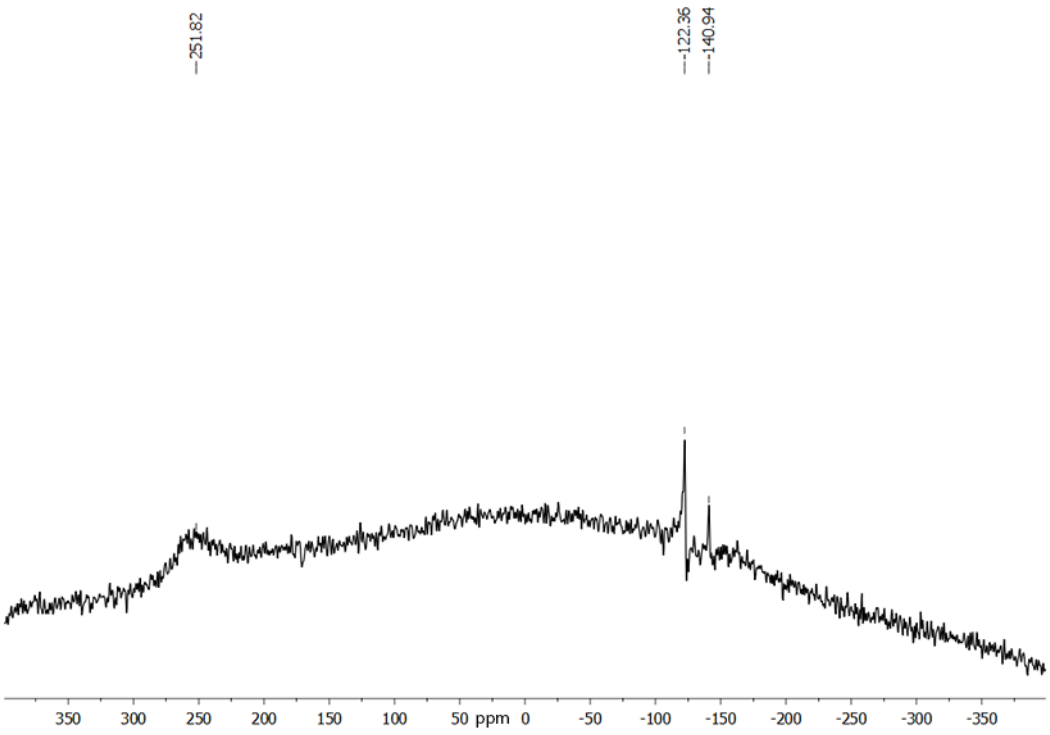



**Figure S10.** **$^{119}$Sn NMR of Compound 2 (crude reaction mixture, before crystallization)**

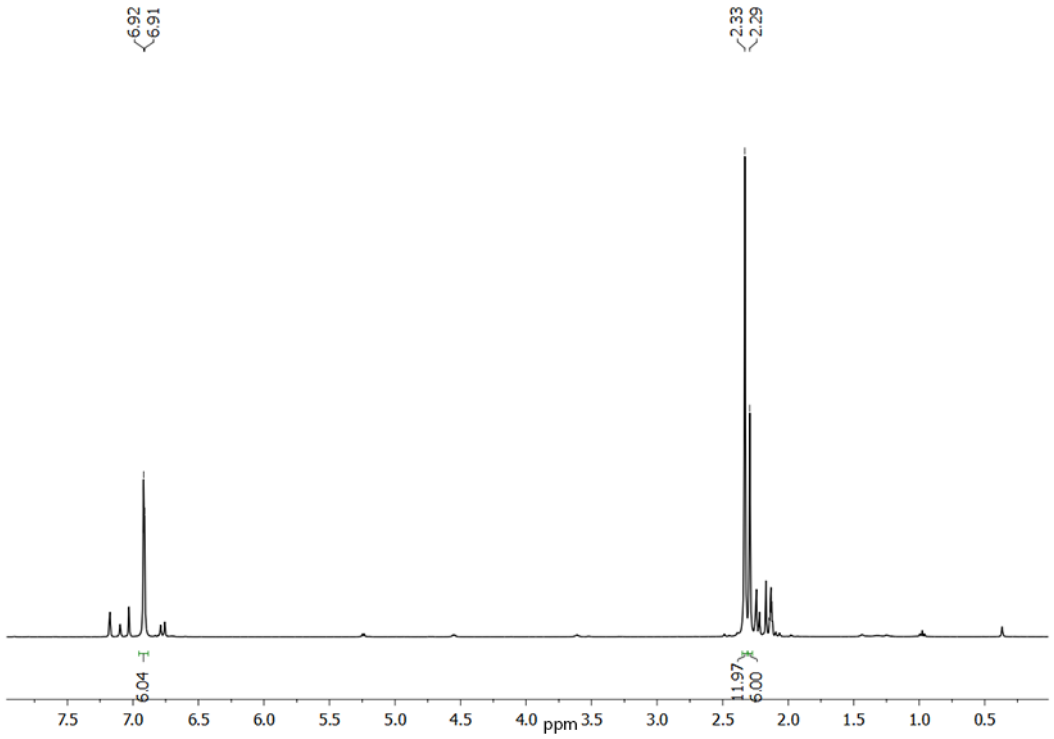



**Figure S11.** **$^{1}$H NMR of Compound 2**

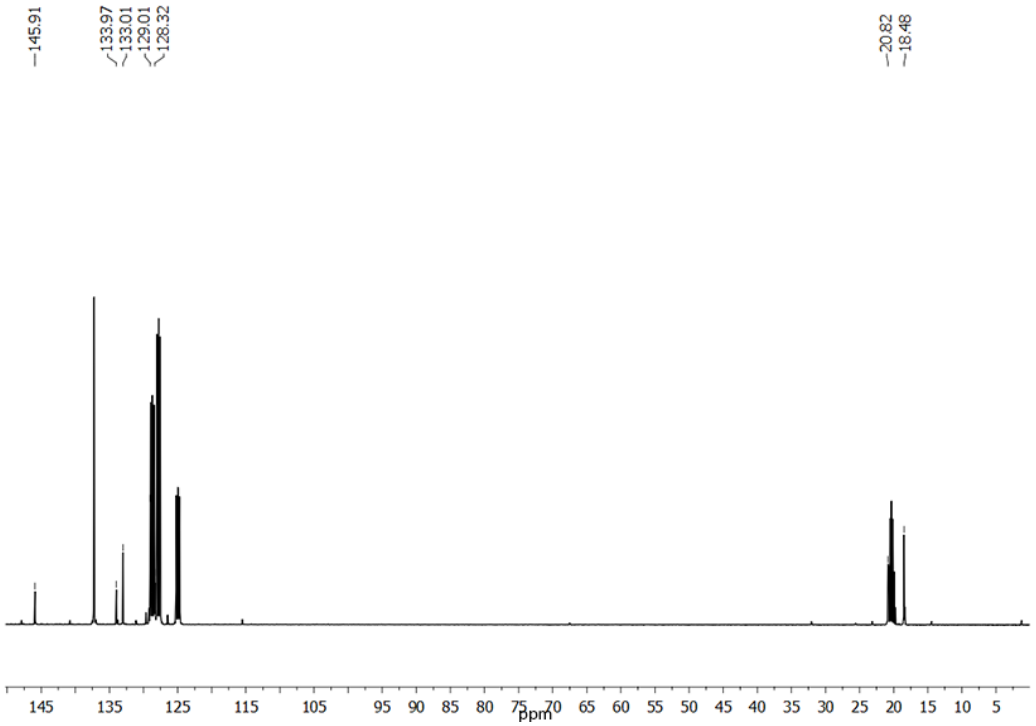



**Figure S12. $^{13}$C NMR of Compound 2**

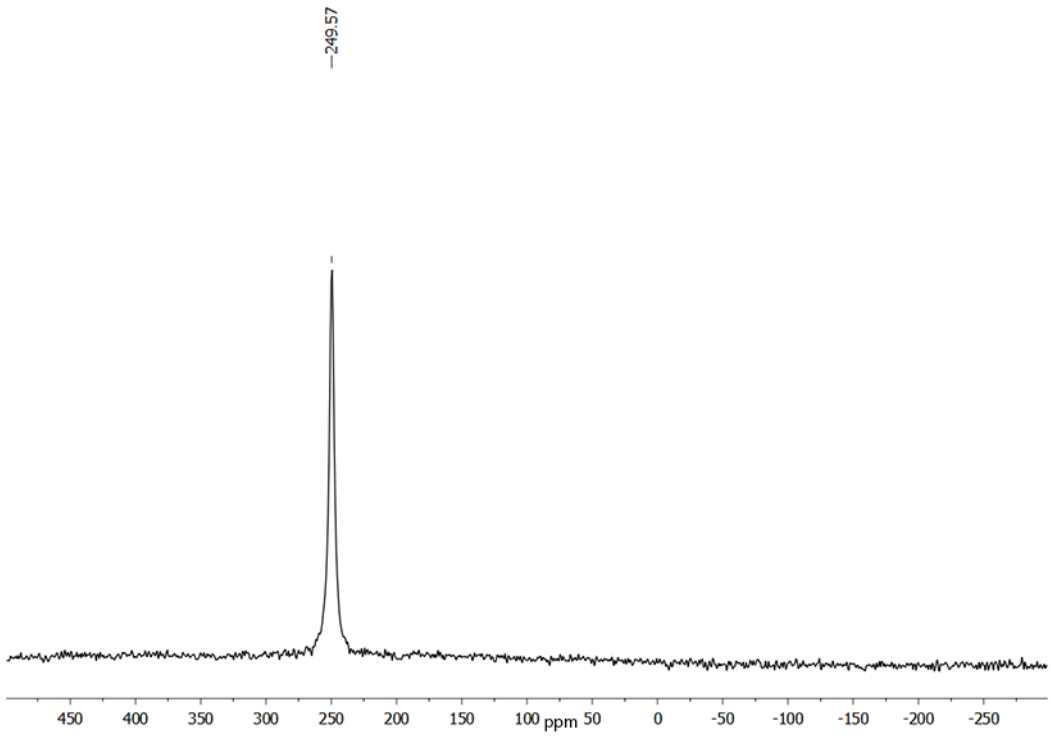
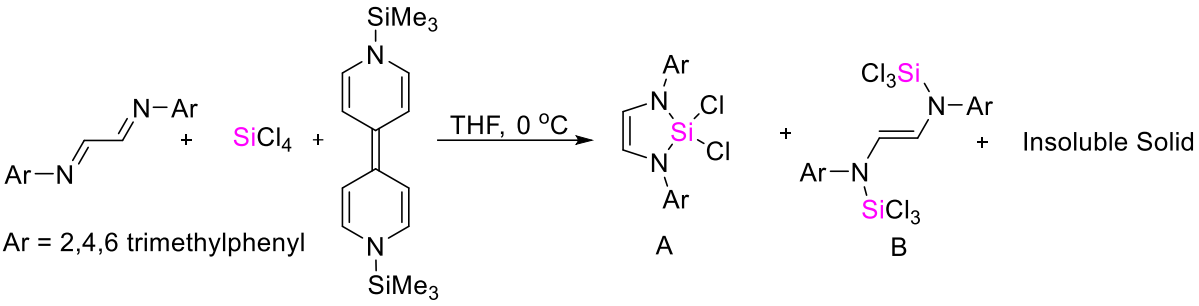



**Figure S13. $^{119}$Sn NMR of Compound 2**

## Attempts to synthesize *N*-Heterocyclic Silylene:

### Trial 1:




To a mixture of $N^1$,$N^2$-dimesitylethane-1,2-diimine (0.254 g, 0.865 mmol) and 1,1'-bis(trimethylsilyl)-1,1'-dihydro-4,4'-bipyridine (0.528 g, 1.74 mmol) taken in 20 mL of tetrahydrofuran maintained at 0 ºC, was added drop-wise 5 mL tetrahydrofuran solution of $SiCl_4$ (0.1 mL, 0.865 mmol). The red reaction mixture was warmed to room temperature and stirred for 12 hours. The volatiles were removed under vacuum giving a brown solid. Hexane was added to it and filtered. Subsequently, the filtrate was evaporated under vacuum giving orange sticky solid.

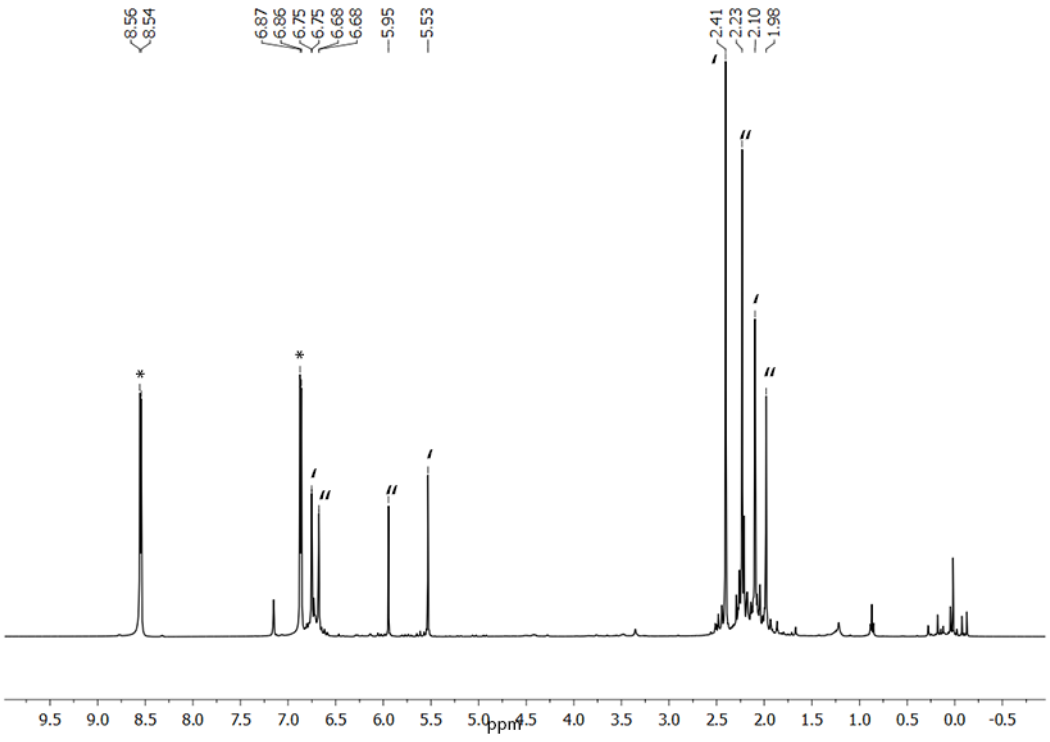



**Figure S14. $^1$H NMR plot of Trial 1 (* = 4,4'-Bipyridine, ' = A, '' = B)**

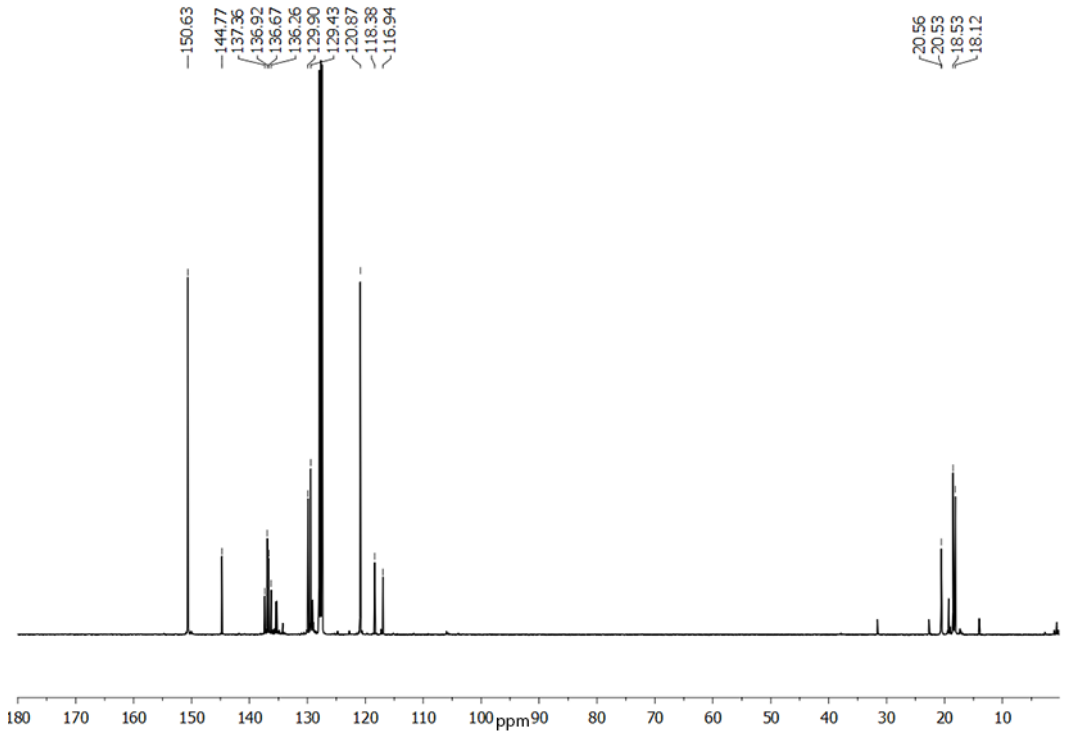
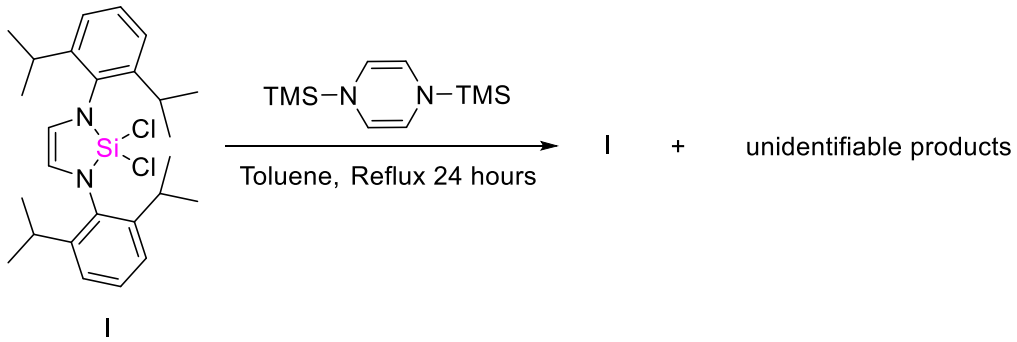



**Figure S15.** **$^{13}$C NMR Plot of Trial 1**

**Trial 2:**




20 mL of toluene was added to mixture of 2,2-dichloro-1,3-bis(2,6-diisopropylphenyl)-2,3-dihydro-1H-1,3,2-diazasilole [S1] (0.3 g, 0.631 mmol) and 1,4-bis(trimethylsilyl)-1,4-dihydropyrazine (0.142 g, 0.631 mmol) at room temperature. The yellow reaction mixture was refluxed for 24 hours. Volatiles were removed under vacuum giving yellow viscous liquid.

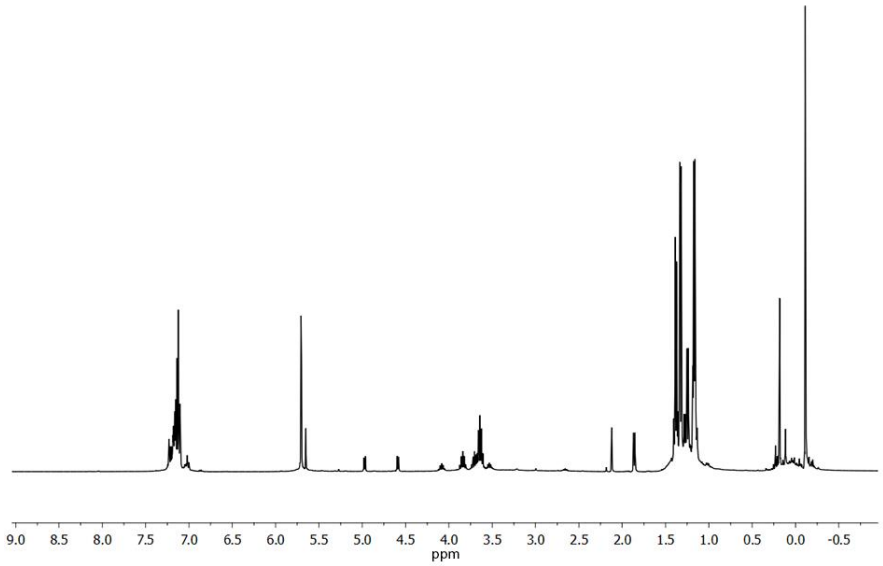



**Figure S16. $^{1}$H NMR of Trial 2**

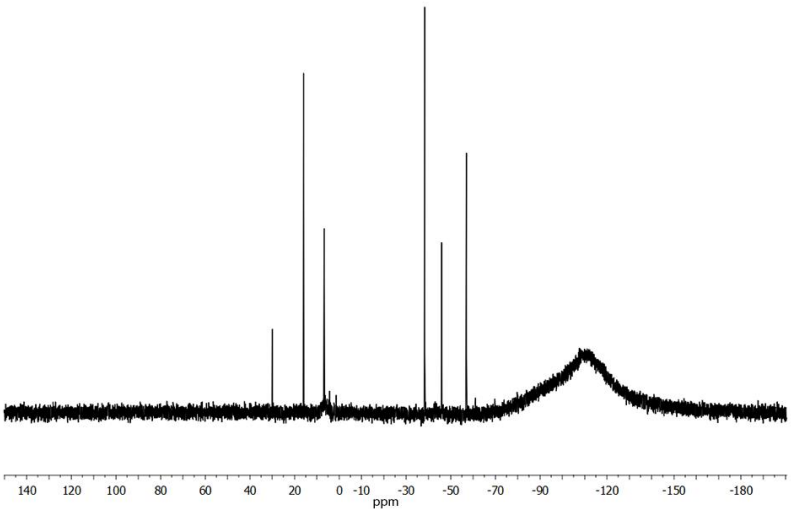
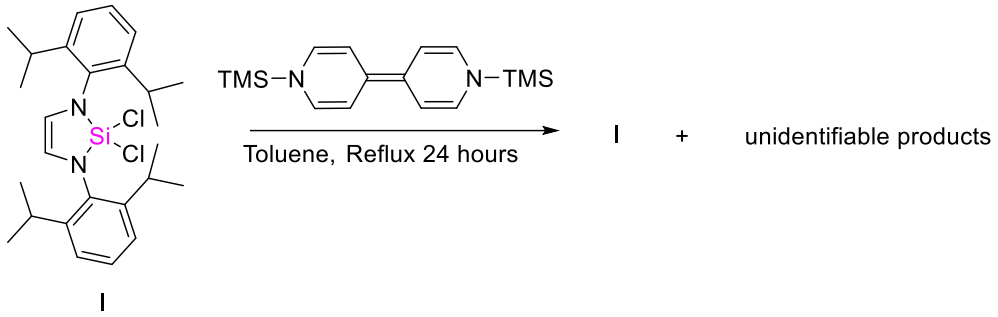



**Figure S17. $^{29}$Si NMR of Trial 2**

**Trial 3:**




I

20 mL of toluene was added to mixture of 2,2-dichloro-1,3-bis(2,6-diisopropylphenyl)-2,3-dihydro-1H-1,3,2-diazasilole (0.3 g, 0.631 mmol) and 1,1'-bis(trimethylsilyl)-1H,1'H-4,4'-bipyridinylidene (0.191 g, 0.631 mmol) at room temperature. The orange reaction mixture was refluxed for 24 hours. Volatiles were removed under vacuum giving orange yellow viscous liquid.

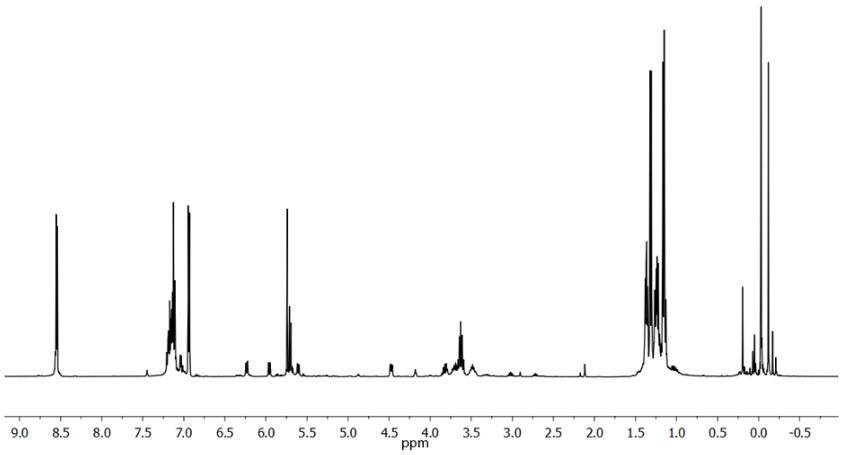



**Figure S18. $^{1}$H NMR of Trial 3**

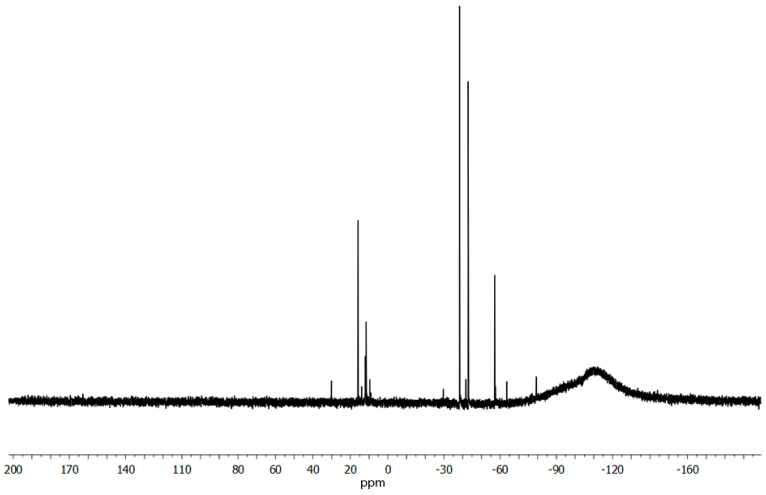
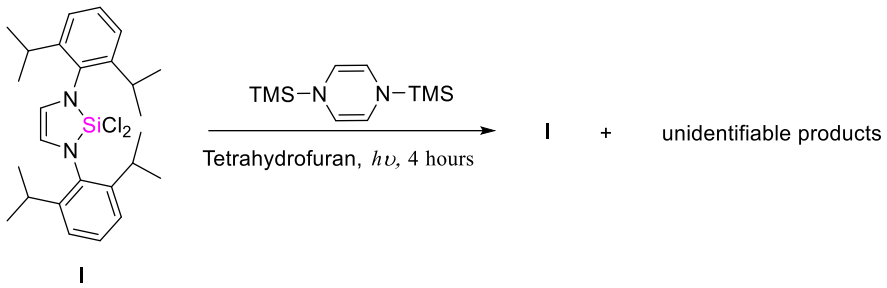



**Figure S19. $^{29}$Si NMR of Trial 3**

**Trial 4:**




I

Photochemical reactor was charged with 70 mL tetrahydrofuran solution of 2,2-dichloro-1,3-bis(2,6-diisopropylphenyl)-2,3-dihydro-1H-1,3,2-diazasilole (0.238 g, 0.5 mmol) and 1,4-bis(trimethylsilyl)-1,4-dihydropyrazine (0.113 g, 0.5 mmol). The yellow reaction mixture was irradiated with ultrviolet light for 4 hours. The volatiles were removed under vacuum giving yellow viscous liquid.

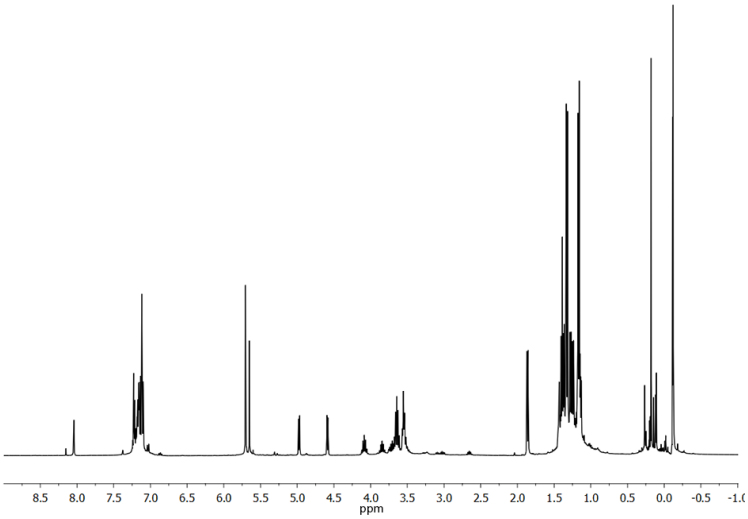



**Figure S20. $^{1}$H NMR**

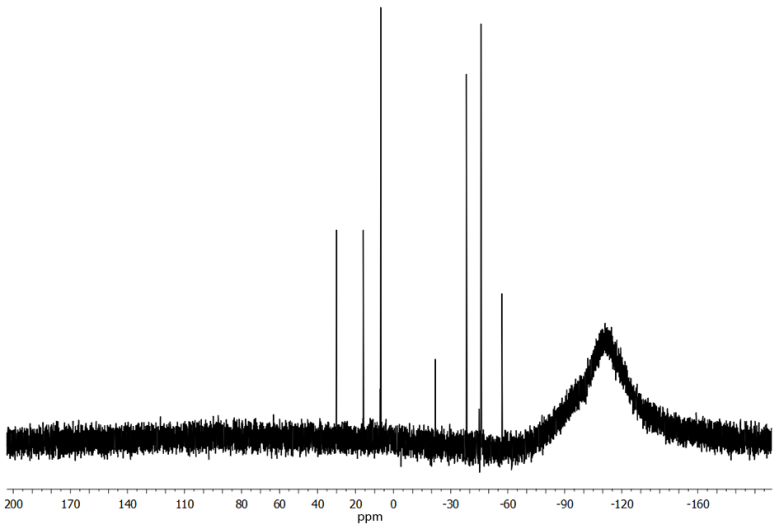
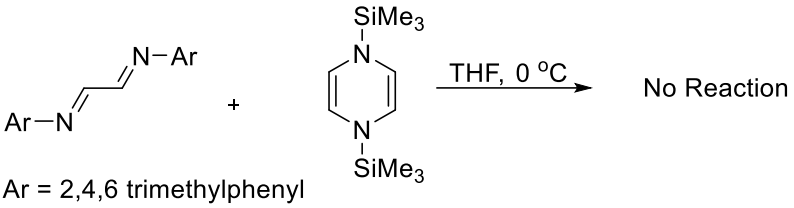



**Figure S21. $^{29}$Si NMR**

## Reaction of Diazabutadiene with Organosilicon Reductant




10 mL of tetrahydrofuran was added to a mixture of $N^1$,$N^2$-dimesitylethane-1,2-diimine (0.1 g, 0.342 mmol) and 1,4-bis(trimethylsilyl)-1,4-dihydropyrazine (0.077g, 0.342 mmol) at room temperature. The yellow reaction mixture was stirred for 12 hours at room temperature. Solvent was removed under vacuum giving yellow solid.

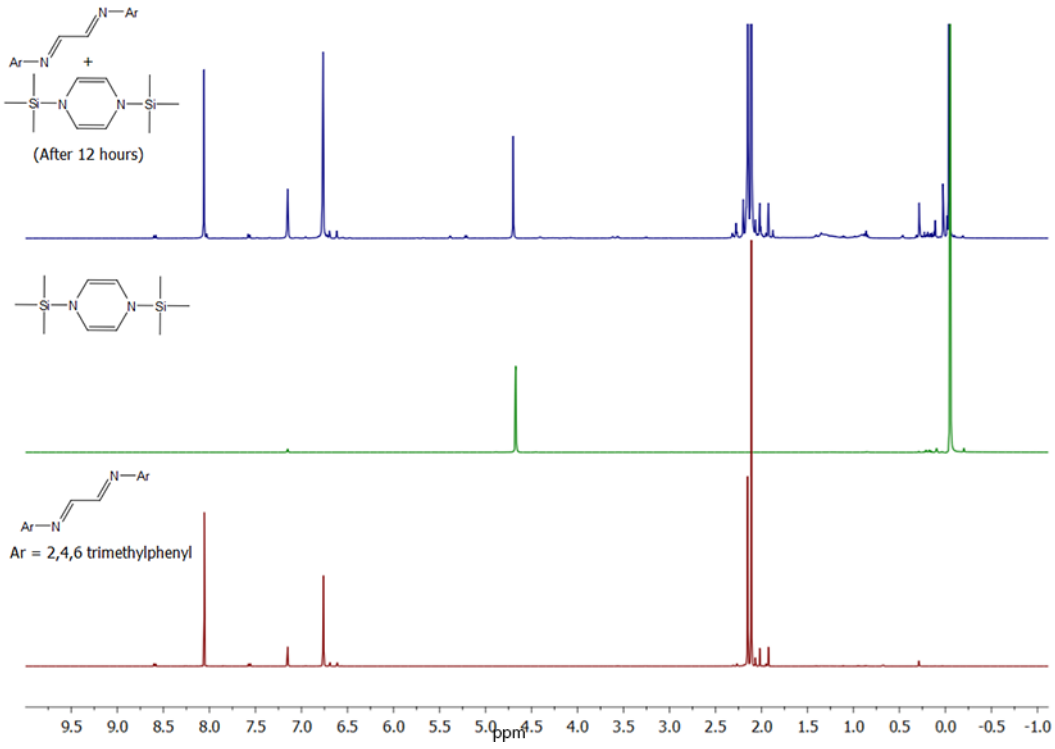



**Figure S22. $^1$H NMR study for the reaction between diazabutadiene and organosilicon reductant.**

## 2. X-ray Data

**Table S1. Crystal data and structure refinement for Compound 1.**

| | |
|---|---|
| Empirical formula | $C_{20}H_{24}N_2Ge$ |
| Formula weight | 365.00 |
| Temperature | 100 K |
| Wavelength | 1.54178 Å |
| Crystal system | Triclinic |
| Space group | P -1 |
| Unit cell dimensions | a = 8.1542 (4) Å α = 76.988 (2) |
| | b = 10.2525 (4) Å β = 75.233 (2) |
| | c = 12.5214 (6) Å γ = 67.180 (2) |
| Volume | 923.58 (7) $Å^3$ |
| Z | 2 |
| Density (calculated) | 1.312 $g/cm^3$ |
| Absorption coefficient | 2.241 $mm^{-1}$ |
| F(000) | 380 |
| Crystal size | 0.09 x 0.08 x 0.07 $cm^3$ |
| Theta range for data collection | 4.727 to 66.731°. |
| Index ranges | -9<=h<=9, -12<=k<=12, -14<=l<=14 |
| Reflections collected | 5992 |
| Independent reflections | 3188 [R(int) = 0.0371] |
| Completeness to theta = 66.731° | 97.3 % |
| Absorption correction | Multi-scan |
| Max. and min. transmission | 0.817 and 0.855 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 3188 / 0 / 214 |
| Goodness-of-fit on $F^2$ | 1.088 |
| Final R indices [I>2sigma(I)] | R1 = 0.0359, wR2 = 0.0969 |
| R indices (all data) | R1 = 0.0371, wR2 = 0.0979 |
| Largest diff. peak and hole | 0.629 and -0.404 $e.Å^{-3}$ |

**Table S2. Crystal data and structure refinement for Compound 2**

| | |
|---|---|
| Empirical formula | $C_{20}H_{24}N_2Sn$ |
| Formula weight | 411.10 |
| Temperature | 100 K |
| Wavelength | 1.54178 Å |
| Crystal system | Triclinic |
| Space group | P -1 |
| Unit cell dimensions | a = 8.1203 (5) Å α = 92.139 (2) |
| | b = 10.3254 (6) Å β = 104.427 (2) |
| | c = 12.4256 (7) Å γ = 111.697 (2) |
| Volume | 927.74 (10) $Å^3$ |
| Z | 2 |
| Density (calculated) | 1.472 $g/cm^3$ |
| Absorption coefficient | 10.943 $mm^{-1}$ |
| F(000) | 416 |
| Crystal size | 0.1 x 0.08 x 0.06 $cm^3$ |
| Theta range for data collection | 3.712 to 66.644°. |
| Index ranges | -9<=h<=9, -12<=k<=12, -14<=l<=14 |
| Reflections collected | 9456 |
| Independent reflections | 3260 [R(int) = 0.0512] |
| Completeness to theta = 66.644° | 99.2 % |
| Absorption correction | Multi-scan |
| Max. and min. transmission | 0.402 and 0.519 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 3260 / 0 / 214 |
| Goodness-of-fit on $F^2$ | 1.132 |
| Final R indices [I>2sigma(I)] | R1 = 0.0493, wR2 = 0.1215 |
| R indices (all data) | R1 = 0.0512, wR2 = 0.1234 |
| Largest diff. peak and hole | 2.874 and -2.247 $e.Å^{-3}$ |

## 3. Molecular Structure

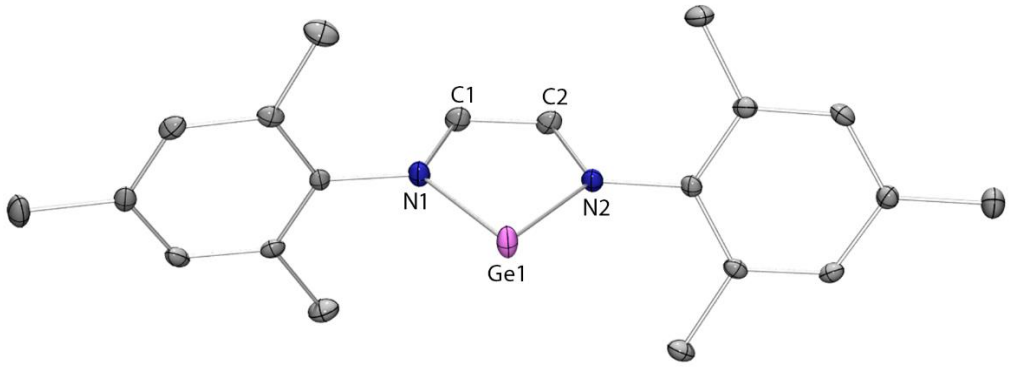



**Figure S23.** Molecular structure of **1** in the solid state (thermal ellipsoids at 30%, H atoms omitted for clarity). Selected bond lengths [Å] and bond angle [º]: Ge1-N1 = 1.8679 (18) Å, Ge1-N2 = 1.8786 (18); N1-Ge-N2 = 83.62 (8).

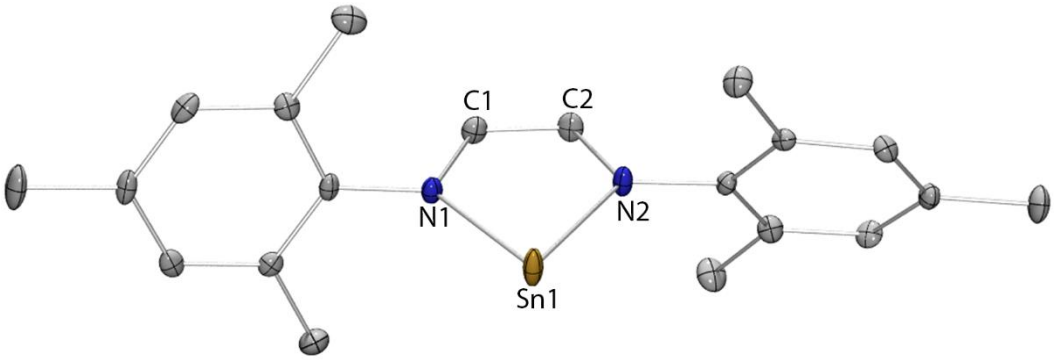



**Figure S24.** Molecular structure of **2** in the solid state (thermal ellipsoids at 30%, H atoms omitted for clarity). Selected bond lengths [Å] and bond angle [º]: Sn1-N1 = 2.089 (4) Å, Sn1-N2 = 2.096 (4); N1-Sn-N2 = 77.95 (16).

## References

[S1] Park, P.; Schäfer, A.; Mitra. A.; Haase, D.; Saak, W.; West, R.; Müller, T. Synthesis and reactivity of *N*-aryl substituted *N*-heterocyclic silylenes. *J. Organomet. Chem.* **2010**, *695*, 398-408, DOI: 10.1016/j.jorganchem.2009.10.034.