

## Electronic Supplementary Information

### Reactions of an Isolable Dialkylsilylene with Aromatic Nitriles Providing a New Type of Heterosilole

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## 1. Experimental Section

### *General*

All synthetic experiments were performed under argon or nitrogen in a standard vacuum system unless otherwise noted. Tetrahydrofuran (THF), hexane, and toluene were distilled from sodium-benzophenone.  $^1\text{H}$  (400 MHz),  $^{13}\text{C}$  (100 MHz),  $^{29}\text{Si}$  (80 MHz), and  $^{19}\text{F}$  NMR (376 MHz) spectra were recorded with TMS as an internal standard on a BRUKER AV-400 MHz instrument. MS were measured with a Trance 2000 DSQ mass spectrometer. High-resolution MS were measured on a Thermo Scientific LTQ Orbitrap XL spectrometer. Melting points are uncorrected. Dialkylsilylene **1** was prepared according to the literature procedures.<sup>S1</sup> Dialkylsilylene **1** and other air-sensitive materials were handled in an MBraun glovebox. All products were purified by flash chromatography or GPC (LC-9101, Japan Analytical Industry Co. Ltd).

*General procedure for the reactions of dialkylsilylene 1 with nitriles 6a-6e:* A hexane solution of a nitrile (0.42 mmol) was added to a solution of dialkylsilylene **1** (75 mg, 0.2 mmol) in hexane at -30 °C. The reaction mixture was allowed to stir for 30 min at -30 °C. Then the solvent was removed under vacuum. The product was isolated as pure substance from the resulting residue by flash chromatography or GPC (toluene).

**7a:** yellow solid (94 mg, 81%); mp 148-150 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.08 (s, 18H), 0.14 (s, 18H), 2.20-2.27 (m, 2H), 2.32-2.40 (m, 2H), 7.47-7.54 (m, 6H), 7.89-7.90 (m, 2H), 8.52-8.54 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.81, 4.28, 13.02, 33.80, 128.00, 128.39, 129.55, 130.44, 130.66, 131.51, 136.14, 141.00, 169.27, 204.68;  $^{29}\text{Si}$  NMR (80 MHz,  $\text{CDCl}_3$ )  $\delta$  1.91, 5.25, 45.58; MS(EI),  $m/z$  (%): 578( $\text{M}^+$ , 6); ESI-HRMS[ $\text{M}+\text{H}$ ] $^+$   $m/z$  Calcd for  $\text{C}_{30}\text{H}_{51}\text{N}_2\text{Si}_5$ : 579.2899. Found: 579.2893.

**7b:** yellow solid (1.04g, 82%); mp 164-166 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 0.09 (s, 18H), 0.13 (s, 18H), 2.24-2.28 (m, 2H), 2.34-2.37 (m, 2H), 3.88-3.89 (d, 6H), 6.94-6.96 (d,  $J = 8.0$  Hz, 2H), 6.99-7.02 (d,  $J = 12$  Hz, 2H), 7.95-7.97 (d,  $J = 8.0$  Hz, 2H), 8.49-8.51 (d,  $J = 8.0$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  3.92, 4.35, 13.08,

33.69, 55.36, 55.43, 113.29, 113.68, 129.40, 132.00, 132.51, 133.35, 161.93, 162.36, 169.08, 202.64;  $^{29}\text{Si}$  NMR (80 MHz,  $\text{CDCl}_3$ )  $\delta$  1.71, 5.13, 44.64; ESI-HRMS  $[\text{M}+\text{H}]^+$   $m/z$  Calcd for  $\text{C}_{32}\text{H}_{55}\text{N}_2\text{O}_2\text{Si}_5$ : 639.3110. Found: 639.3104.

**7c**: yellow solid (1.14g, 85%); mp 168-170°C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 0.19 (s, 18H), 0.24 (s, 18H), 2.36-2.39 (m, 2H), 2.46-2.49 (m, 2H), 7.58-7.60 (m, 4H), 7.93-7.96 (m, 3H), 7.99-8.01 (m, 2H), 8.08 (s, 1H), 8.26 (s, 1H), 8.55-8.58 (m, 2H), 9.31 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  4.02, 4.52, 13.41, 33.89, 126.18, 126.27, 126.64, 126.72, 127.38, 127.64, 127.83, 127.89, 127.99, 128.32, 129.63, 131.57, 132.43, 132.50, 133.22, 133.66, 134.60, 135.24, 138.17, 169.46, 204.20;  $^{29}\text{Si}$  NMR (80 MHz,  $\text{CDCl}_3$ )  $\delta$  2.05, 5.40, 45.66; ESI-HRMS  $[\text{M}+\text{H}]^+$   $m/z$  Calcd for  $\text{C}_{38}\text{H}_{55}\text{N}_2\text{Si}_5$ : 679.3212. Found: 679.3211.

**8d**: yellow solid (1.2g, 75%); mp (decomp.) 110-112°C;  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ),  $\delta$ : 0.25(s, 36H), 2.35(s, 4H), 7.17-7.19 (d,  $J = 8.0$  Hz, 4H), 7.42-7.44 (d,  $J = 8.0$  Hz, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  3.43, 13.83, 33.44, 116.39, 122.77, 124.95, 128.02, 133.2, 136.5;  $^{29}\text{Si}$  NMR (80 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  4.02, 59.47; ESI-HRMS  $[\text{M}+\text{H}]^+$   $m/z$  Calcd for  $\text{C}_{32}\text{H}_{49}\text{F}_6\text{N}_2\text{Si}_5$ : 715.2646. Found: 715.2655.

**8e** yellow solid (1.05g, 66%); mp (decomp.) 128-133°C;  $^1\text{H}$  NMR (400 MHz,  $\text{C}_6\text{D}_6$ ),  $\delta$ : 0.23(s, 36H), 2.21(s, 4H), 6.73-6.78(m, 4H), 7.15-7.22(m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  3.48, 14.09, 33.54, 113.55, 116.99, 129.15, 131.79, 134.67, 138.60, 171.37;  $^{29}\text{Si}$  NMR (80 MHz,  $\text{C}_6\text{D}_6$ ):  $\delta$  4.02, 59.64; ESI-HRMS  $[\text{M}+\text{H}]^+$   $m/z$  Calcd for  $\text{C}_{34}\text{H}_{47}\text{F}_{12}\text{N}_2\text{Si}_5$ : 851.2394. Found: 851.2415.

**9e** yellow solid (1.25g, 72%); mp 138-140°C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 0.08(s, 9H), 0.13(s, 9H), 0.25(s, 9H), 0.28(s, 9H), 2.39-2.19(m, 4H), 2.64(s, 1H), 2.65(s, 1H), 7.79(s, 1H), 7.84(s, 1H), 7.91(s, 2H), 8.37 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.91, 3.16, 3.79, 4.18, 8.83, 11.54, 31.95, 33.41, 92.11, 121.60, 121.67, 122.19, 124.18, 124.32, 124.38, 126.08, 128.60, 129.53, 131.53, 131.87, 132.00, 132.34, 135.31, 138.86, 146.04, 174.41;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$ , -62.82, -63.39;  $^{29}\text{Si}$  NMR (80 MHz,  $\text{CDCl}_3$ ):  $\delta$  2.28, 2.36, 3.58, 4.02, 39.73; ESI-HRMS  $[\text{M}+\text{H}]^+$   $m/z$  Calcd for  $\text{C}_{34}\text{H}_{49}\text{F}_{12}\text{N}_2\text{OSi}_5$ : 869.2500. Found: 869.2522.

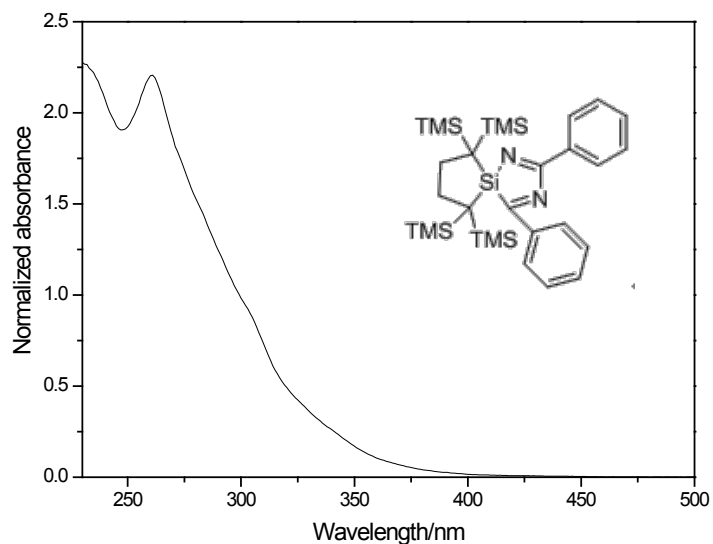
## 2. Crystal structure determination

Single crystals of **7b** and **9e** suitable for X-ray analysis were obtained by the recrystallization from hexane. The X-ray diffraction data were collected on a Bruker Smart Apex CCD diffractometer with graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) using the  $\omega$ - $2\theta$  scan mode. The structure was solved by direct methods and refined on  $F^2$  by full-matrix least-squares methods using SHELX-2000.<sup>S2</sup> All calculations and molecular graphics were carried out on a computer using the SHELX-2000 program package and Diamond. All the structural data are deposited with CCDC. The reference numbers are: 941168(**7b**) and 941167 (**9e**).

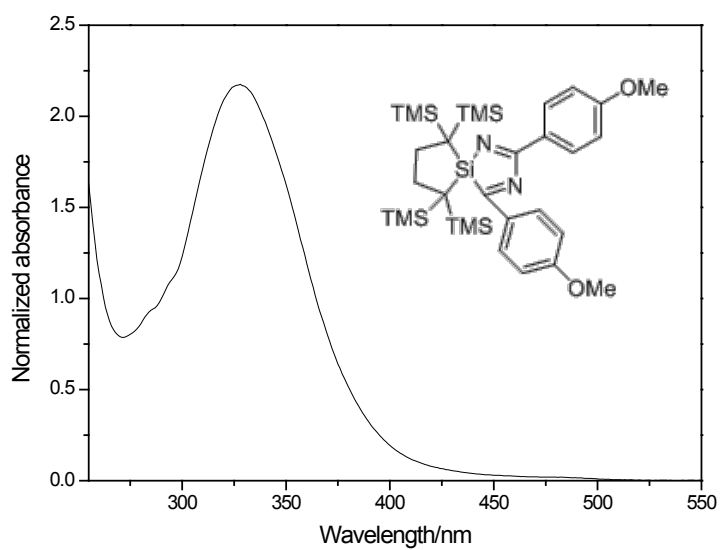
**Table S1.** Crystal and refinement data for **7b** and **9e**

Parameters	<b>7b</b>	<b>9e</b>
Empirical formula	C <sub>32</sub> H <sub>54</sub> N <sub>2</sub> O <sub>2</sub> Si <sub>5</sub>	C <sub>32</sub> H <sub>50</sub> F <sub>6</sub> N <sub>2</sub> O Si <sub>5</sub>
Formula weight	639.22	733.19
Crystal system, Space group	Monoclinic, P2(1)/c	Triclinic, P-1
<i>a</i> [Å]	17.9250(19)	11.9145(7)
<i>b</i> [Å]	19.611(2)	13.3510(8)
<i>c</i> [Å]	11.0217(12)	14.5688(9)
$\alpha$ [deg]	90	115.7100(10)
$\beta$ [deg]	102.677(2)	108.8790(10)
$\gamma$ [deg]	90	90.4120(10)
<i>V</i> [Å <sup>3</sup> ]	3779.9(7)	1945.9(2)
<i>Z</i> , <i>D</i> <sub>calcd</sub> [g cm <sup>-3</sup> ]	4, 1.123	2, 1.251
$\mu$ [mm <sup>-1</sup> ]	0.218	0.239
<i>F</i> (000)	1384	776
Reflections collected	20530	24141
Independent Reflections	6639	8905
<i>R</i> (int)	0.0507	0.0277
Data/restraints	6639 / 0 / 384	8905 / 0 / 487
/parameters		
final <i>R</i> indices	0.0561	0.0463
[ <i>I</i> >2 $\sigma$ ( <i>I</i> )] <i>R</i> <sub>1</sub>		
<i>R</i> indices (all data) <i>wR</i> <sub>2</sub>	0.1871	0.1576

### 3. UV- visible spectra of 7a and 7b



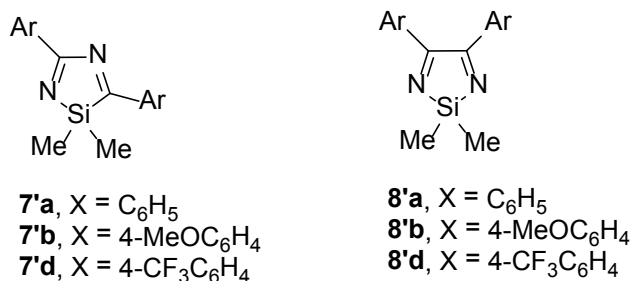
**Figure S1.** Uv/Vis ( $\text{CH}_2\text{Cl}_2$ ) of **7a**.  $\lambda_{\text{max}} (\epsilon) = 260 \text{ nm} (17102 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$



**Figure S2.** Uv/Vis ( $\text{CH}_2\text{Cl}_2$ ) of **7b**.  $\lambda_{\text{max}} (\epsilon) = 328 \text{ nm} (17262 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$

#### 4. Theoretical Calculations

**Calculation Details.** The calculations in this work were performed for the compounds **7'a-7'c** and **8'a-8'c** shown in Chart 1S using the density functional B3LYP methods as implemented in Gaussian 03 package.<sup>S3</sup> The ground-state geometries were optimized at the B3LYP/6-311+G(d,p) level with no symmetry constraints. The vibrational analysis for the relative compounds does not yield any imaginary frequencies, indicating that the structure of each molecule corresponds to at least a local minimum on the potential energy surface. TD-DFT calculations were performed using B3LYP functional in conjugation with 6-31G(d,p) basis set. For the goal of approaching available experimental results, we have performed 12 allowed transitions (nstates = 12) in our TD-DFT calculation process.



**Chart 1S.**

**Table 2.** Relative Stability of **7'** to the Corresponding **8'**, Frontier Orbital Energies, and Absorption Maxima of **7'a-c** Calculated at the B3LYP/6-311+G(d,p) Level

	Compound		
	<b>7'a</b> (X = H)	<b>7'b</b> (X = OMe)	<b>7'c</b> (X = CF <sub>3</sub> )
Relative Energy <sup>a</sup>	3.47	4.55	4.71
Orbital Energy <sup>b</sup>			
LUMO ( $\pi^*$ )	-5.364	-4.834	-5.218
HOMO (n, N <sup>4</sup> )	-8.969	-8.972	-8.983
HOMO-1 (n, N <sup>1</sup> )	-10.620	-10.646	-10.582
HOMO-2 ( $\pi$ )	-14.153	-12.060	-14.007 <sup>c</sup>
$\lambda_{\max}/\text{nm}$ ( $f$ ) <sup>d</sup>	379.8 (0.127) n $\rightarrow$ $\pi^*$ 333.8 (0.180) $\pi$ $\rightarrow$ $\pi^*$ 331.2 (0.184) n $\rightarrow$ $\pi^*$ 258.1 (0.315) n $\rightarrow$ $\pi^*$	372.5 (0.633) $\pi$ $\rightarrow$ $\pi^*$ 261.3 (0.425) n $\rightarrow$ $\pi^*$	373.1 (0.161) n $\rightarrow$ $\pi^*$ 328.9 (0.132) $\sigma$ $\rightarrow$ $\pi^*$ 326.1 (0.233) $\pi$ $\rightarrow$ $\pi^*$ 266.6 (0.442) n $\rightarrow$ $\pi^*$

- a. Energy relative to the corresponding **8'** type isomer in kcal/mol. Positive value means **7'x** is less stable than **8'x** (**x** = **a-c**). b. In eV. c. HOMO-4. HOMO-2 and 3 (-13.315, -13.414 eV) is a  $\sigma$ -type orbital. d. Calculated using a TD-DFT method at the B3LYP/6-31+G(d) level.  $f$  denotes oscillator strength. Excitations with  $f < 0.1$  are omitted.

## 5. $^1\text{H}$ , $^{13}\text{C}$ , and $^{29}\text{Si}$ NMR spectra of silaaziridines 7a-7c, 8a-8b and 9e

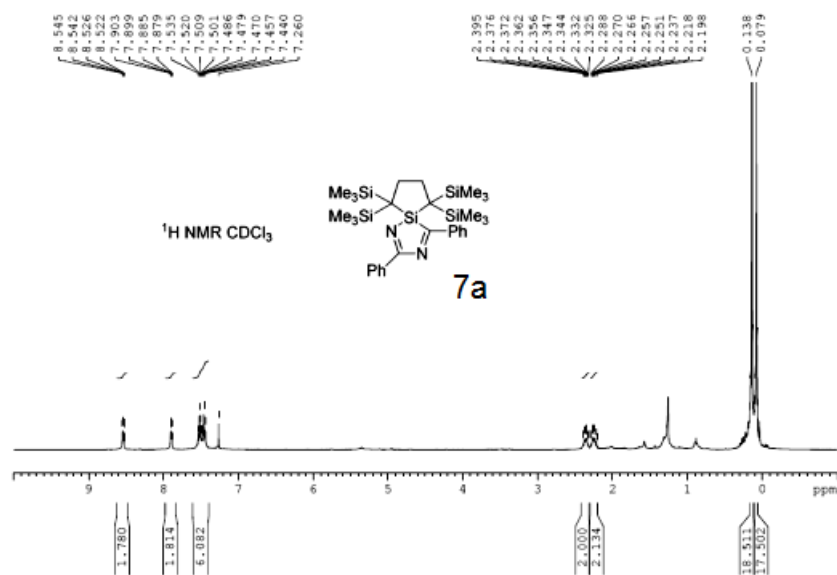


Figure S3.

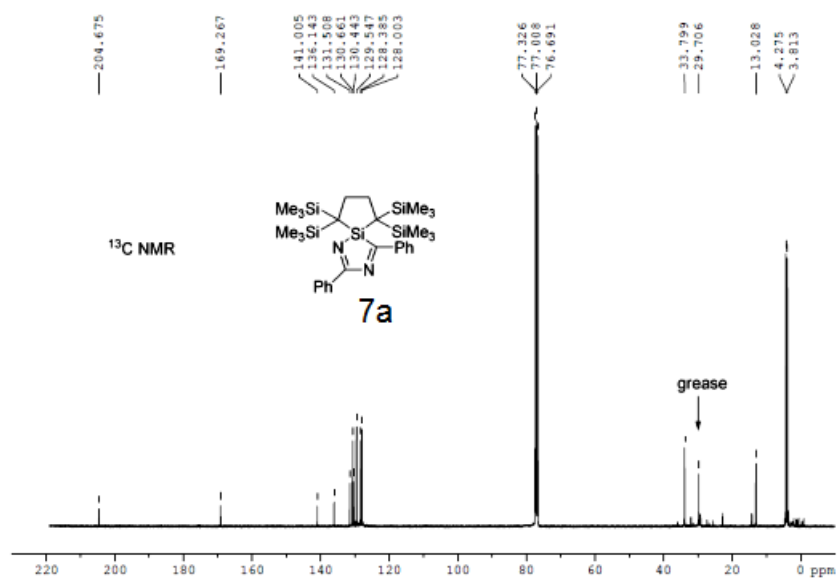


Figure S4.



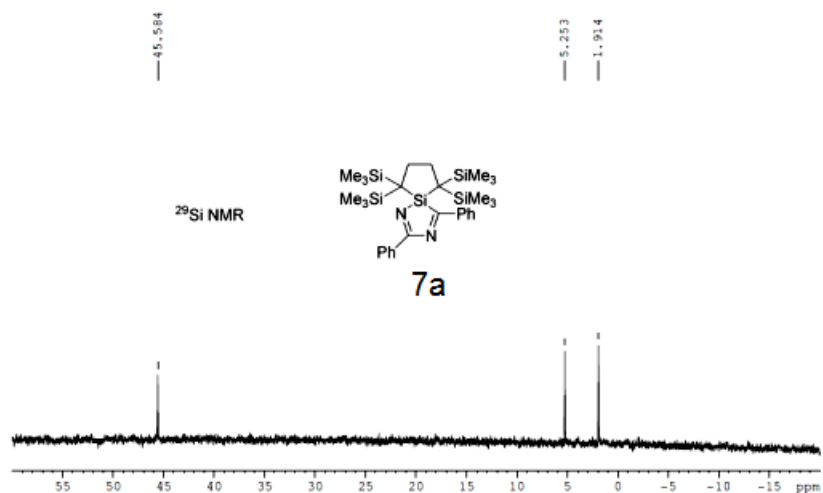


Figure S5.

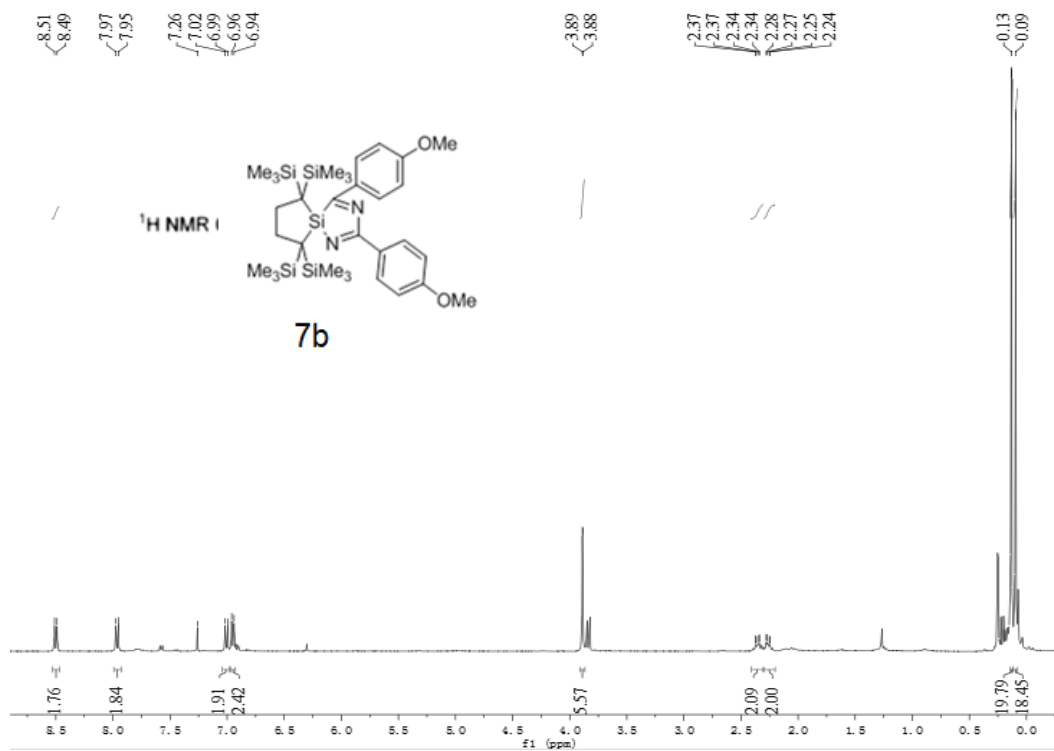


Figure S6.

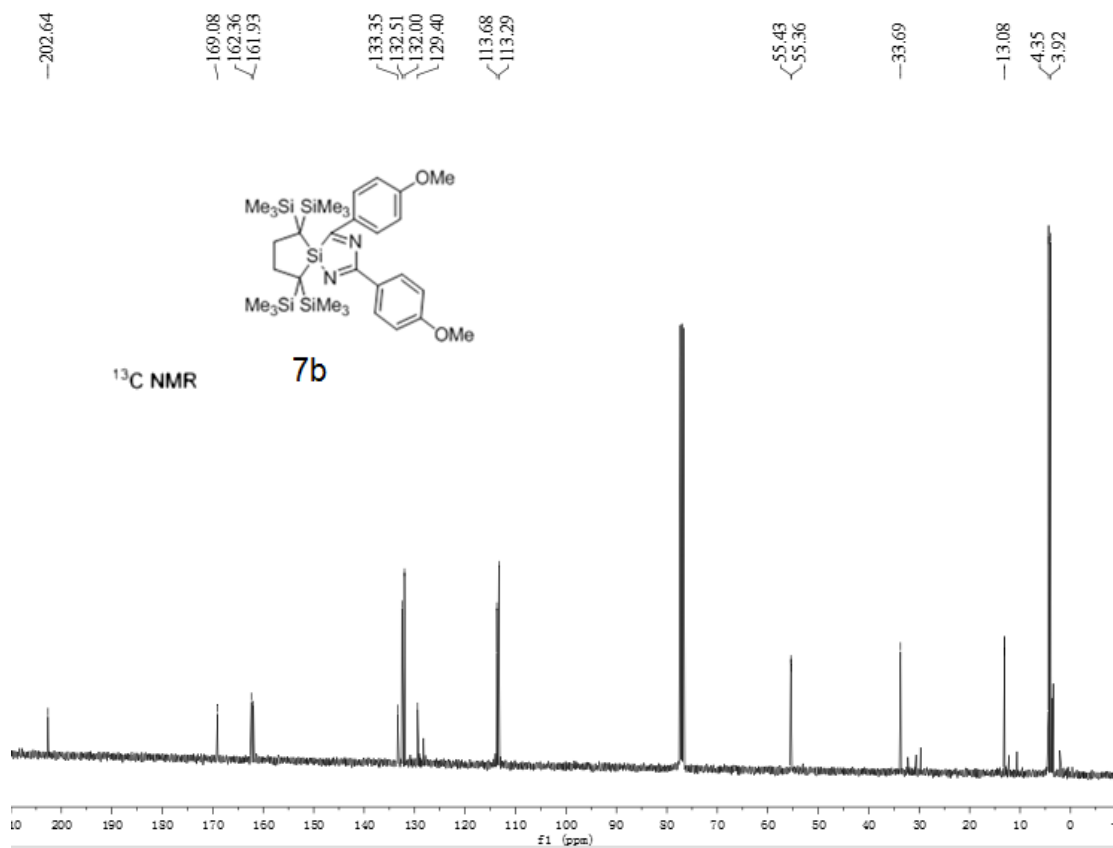


Figure S7.

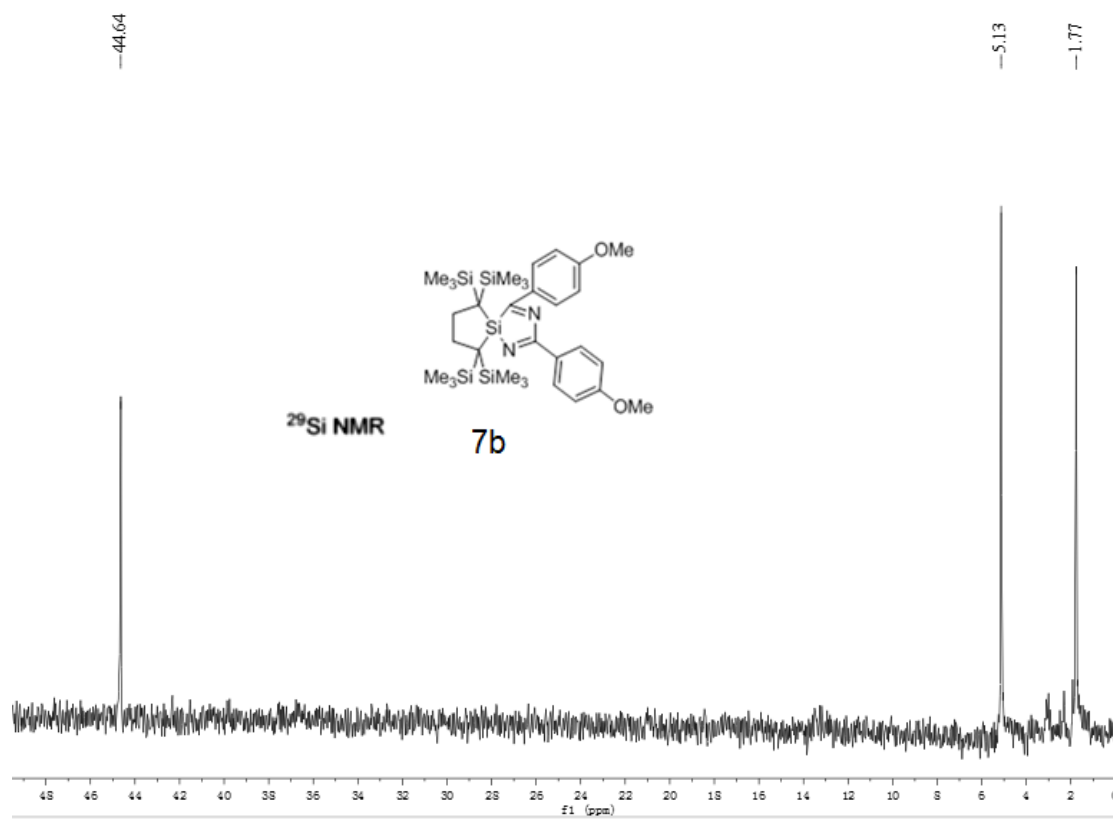


Figure S8.

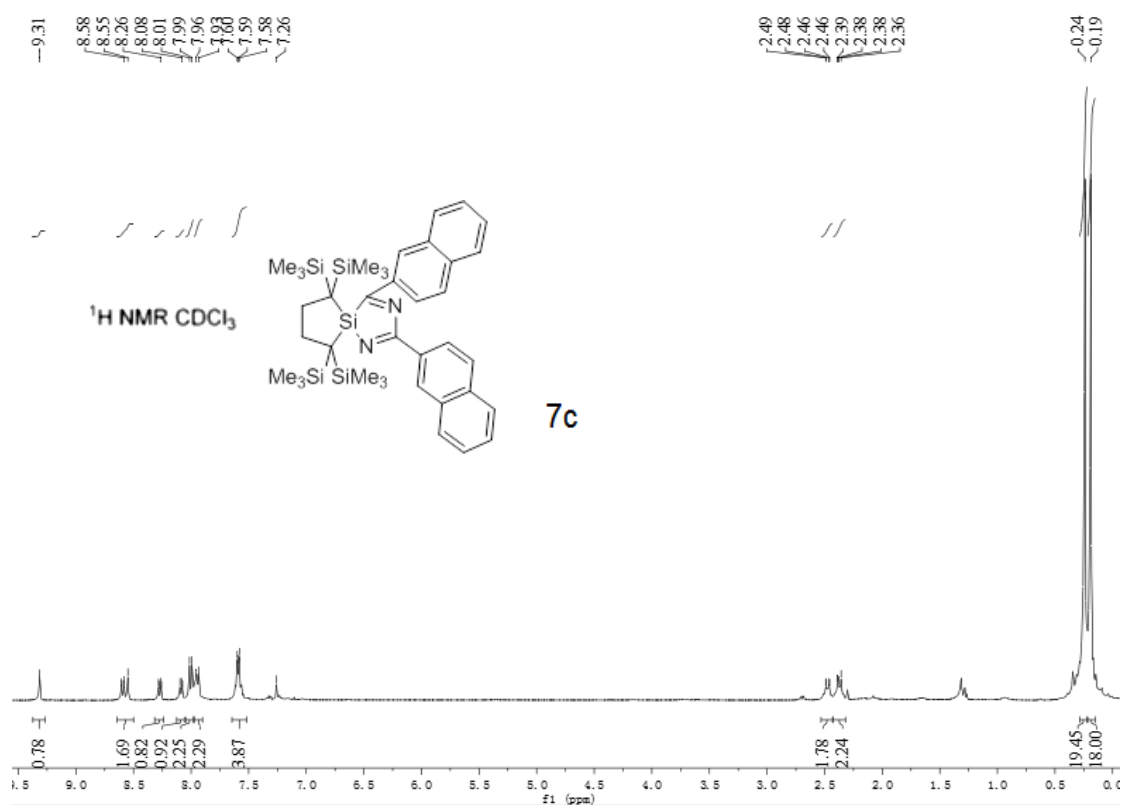


Figure S9.

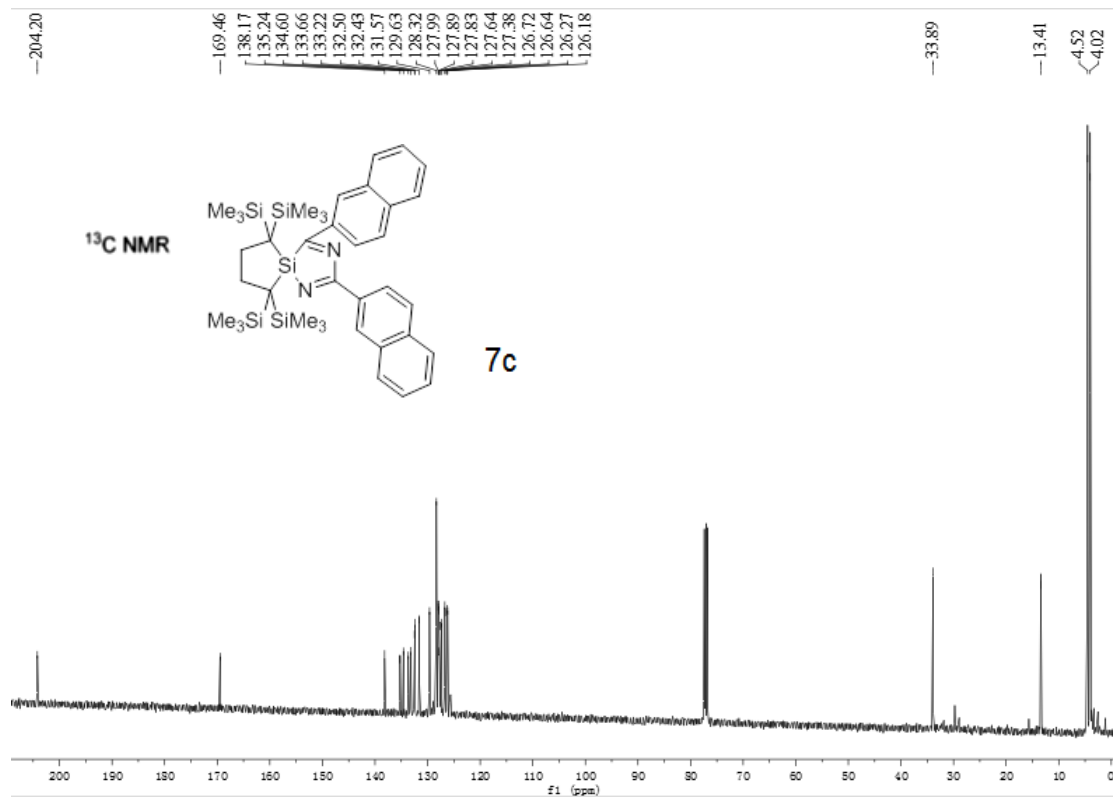


Figure S10.



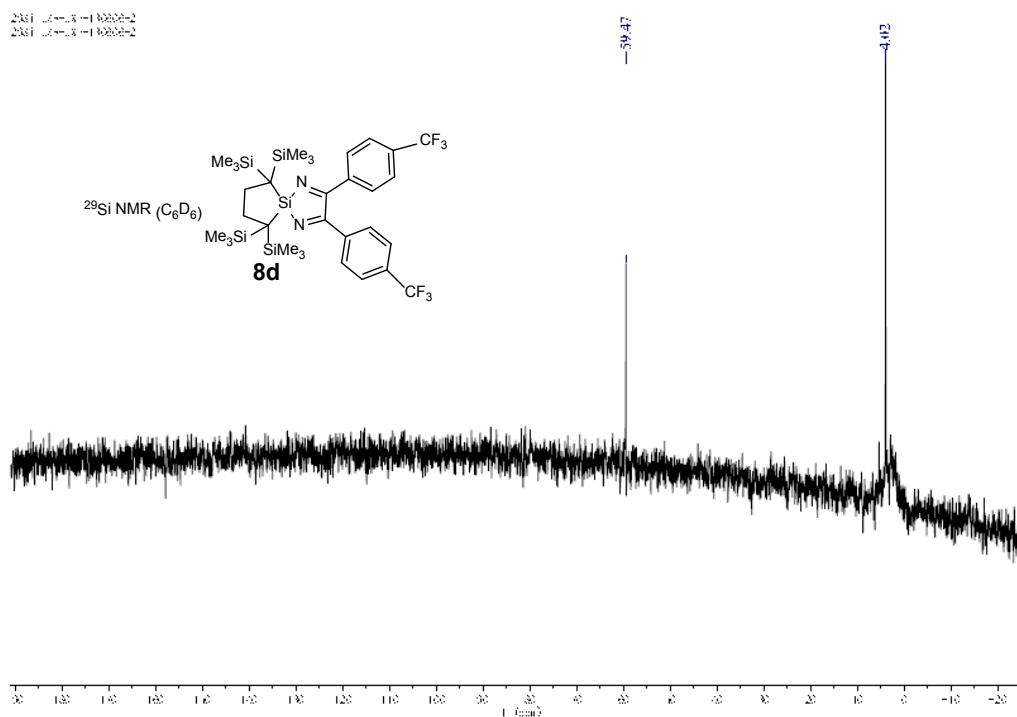


Figure S13.

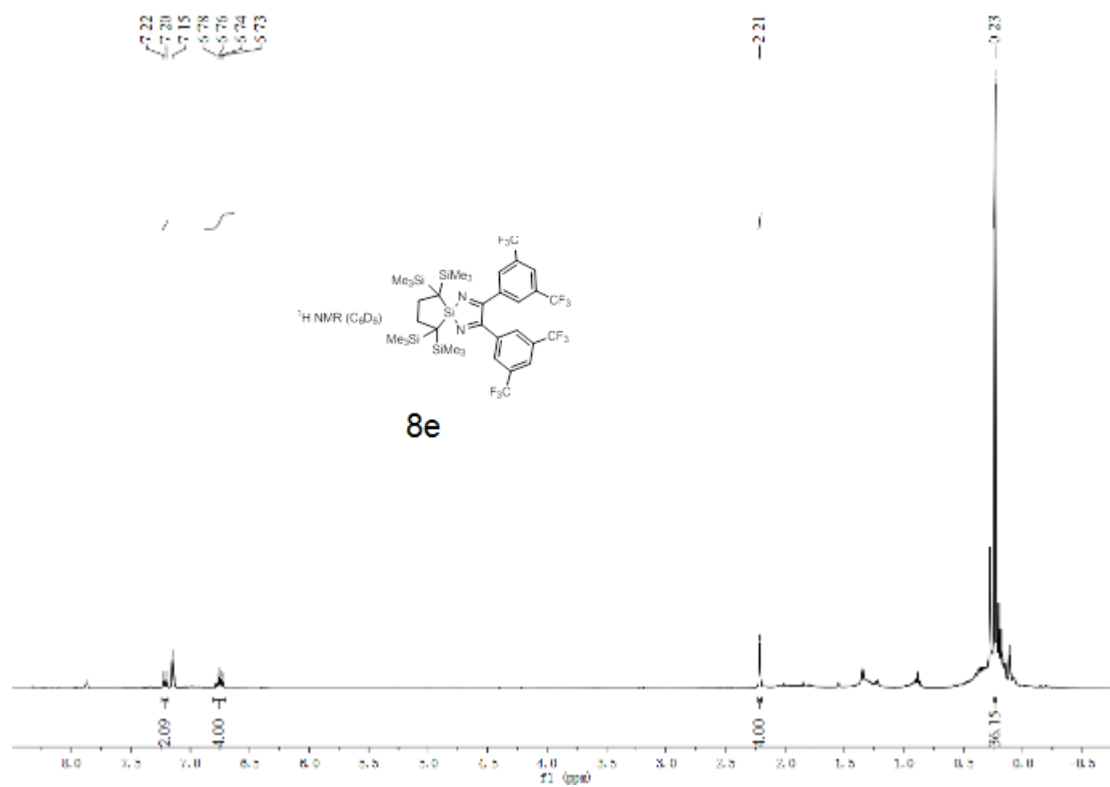


Figure S14.

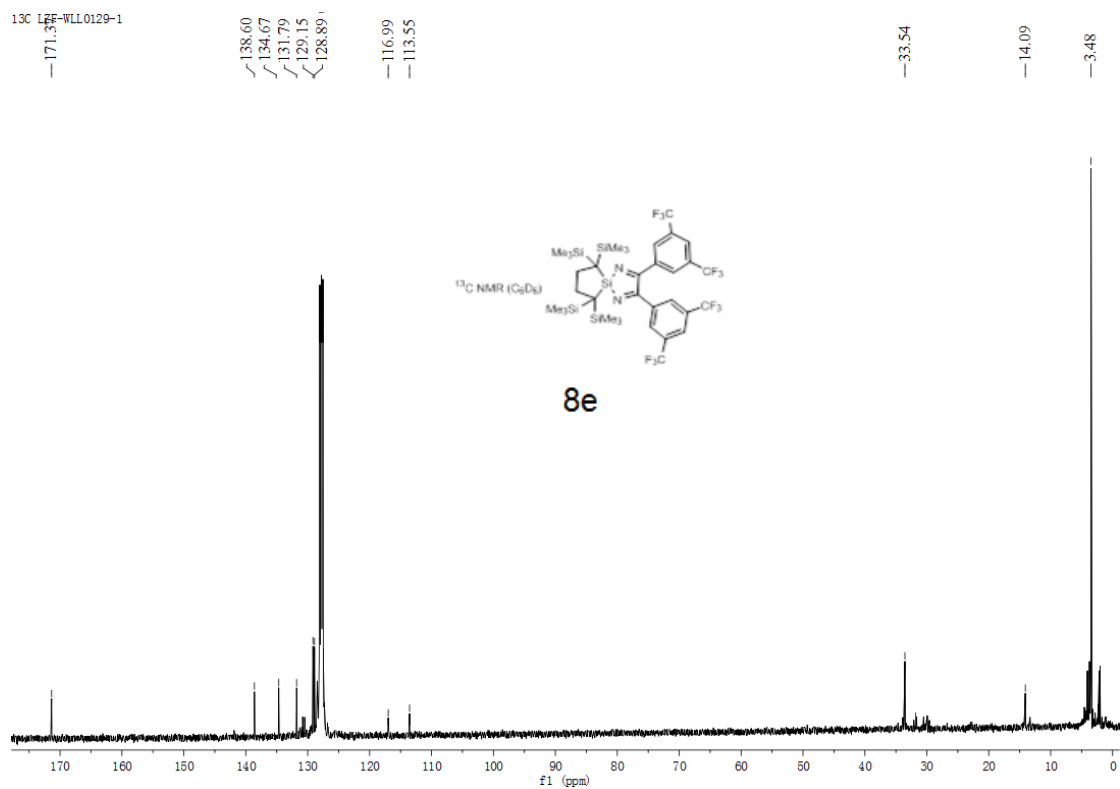


Figure S15.

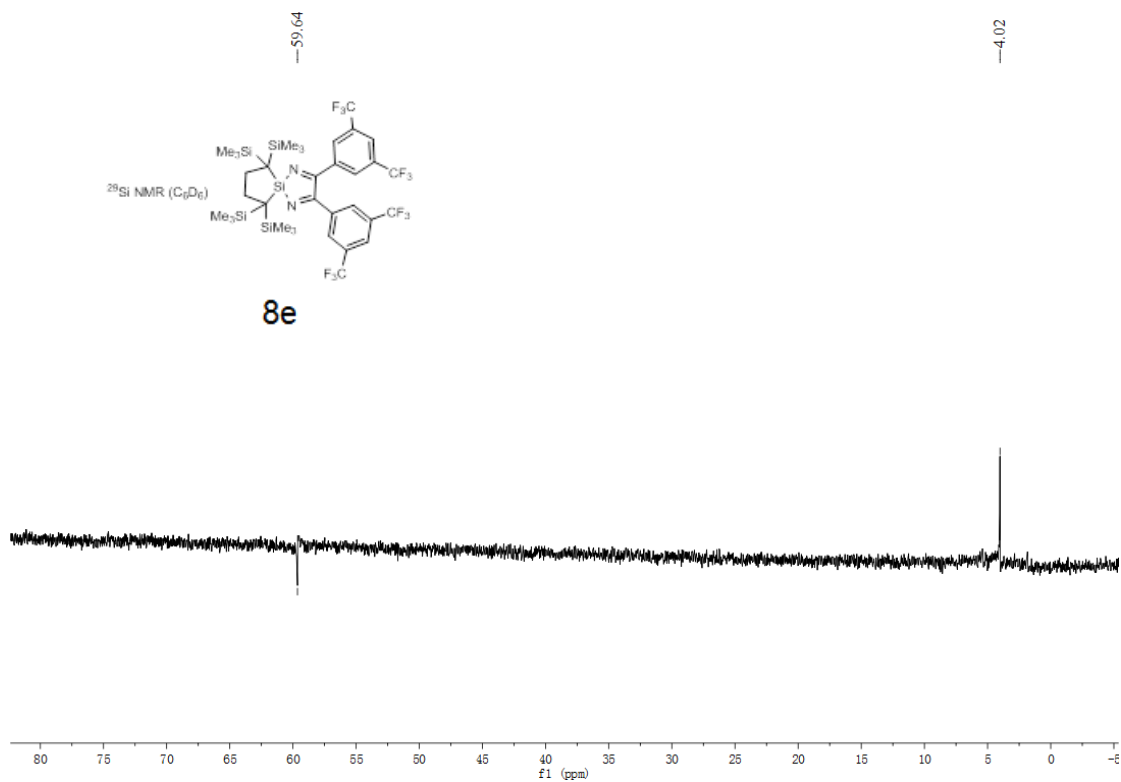


Figure S16.

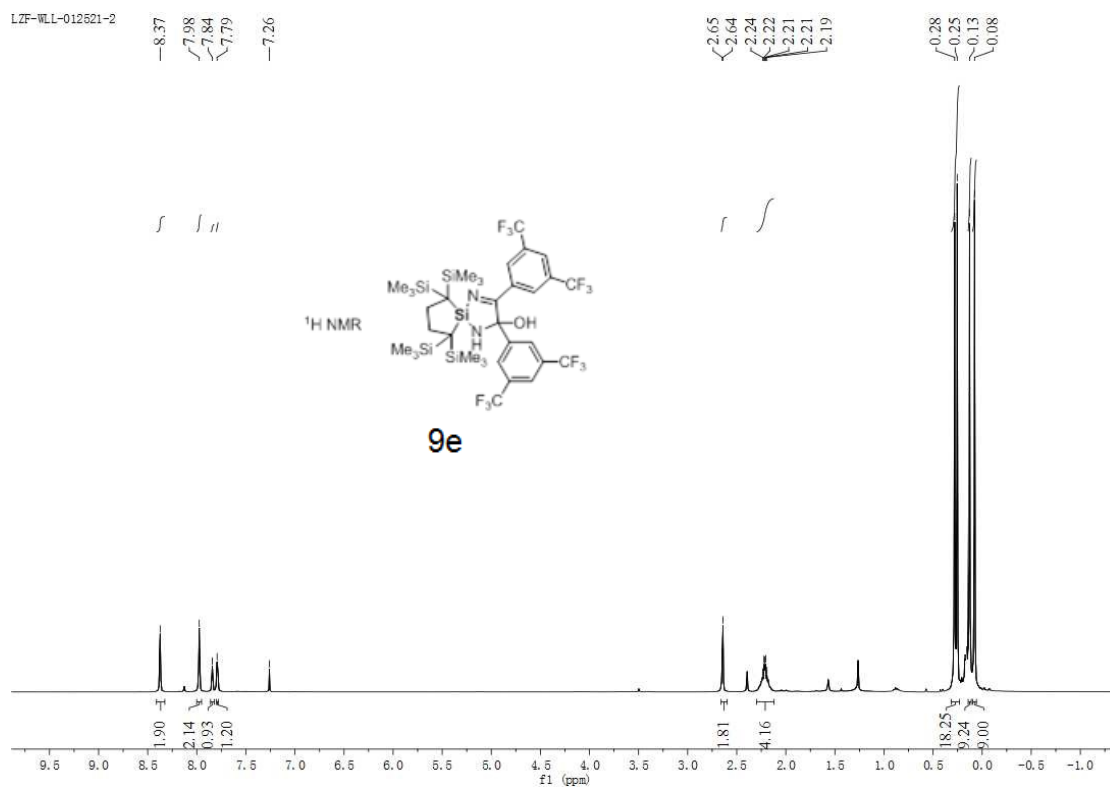


Figure S17.

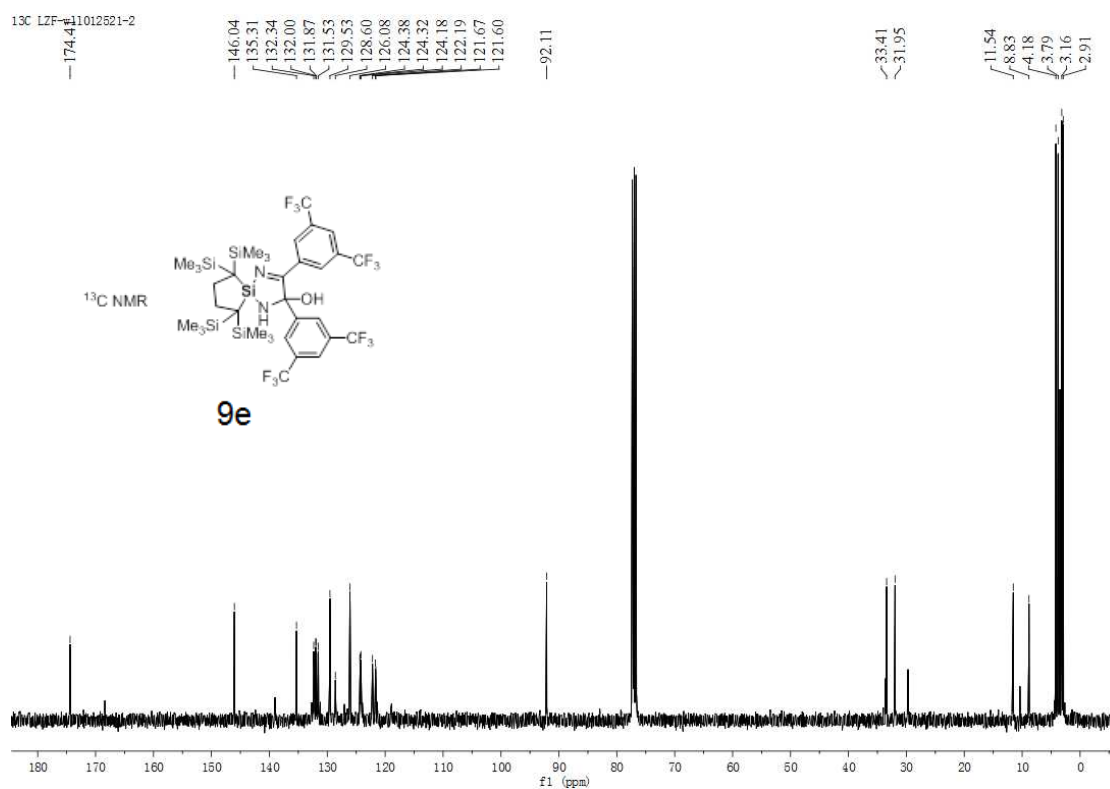


Figure S18.

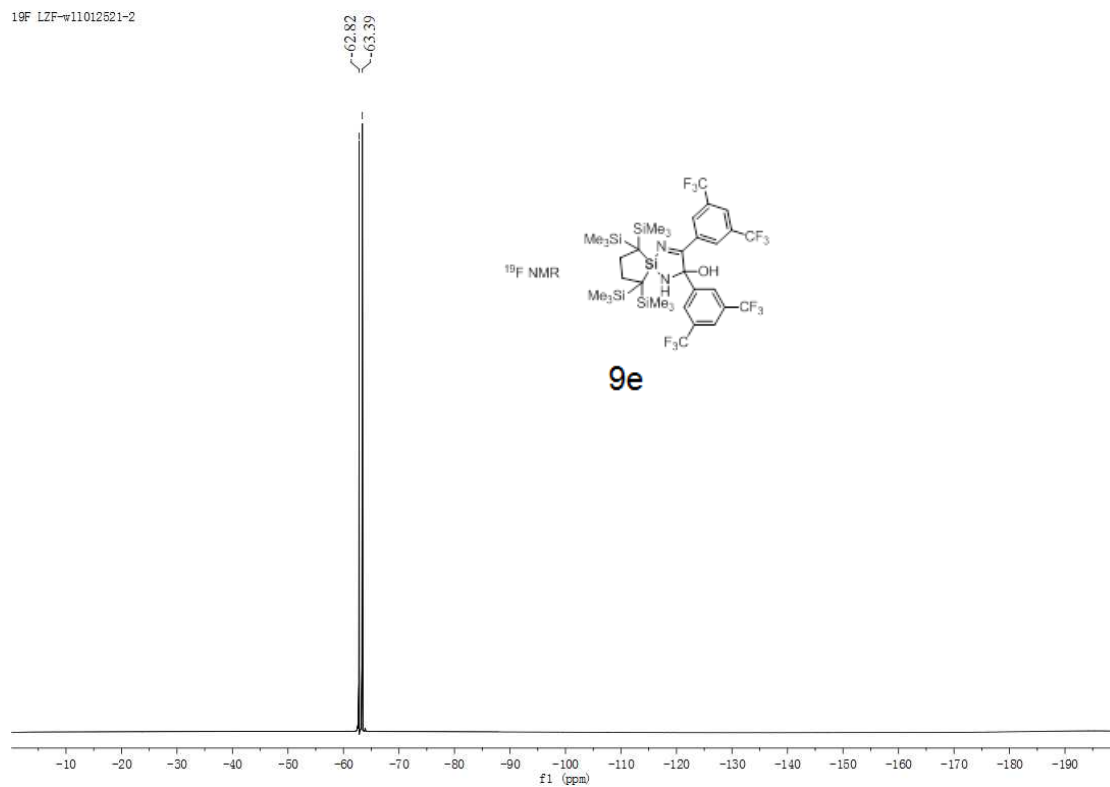


Figure S19.

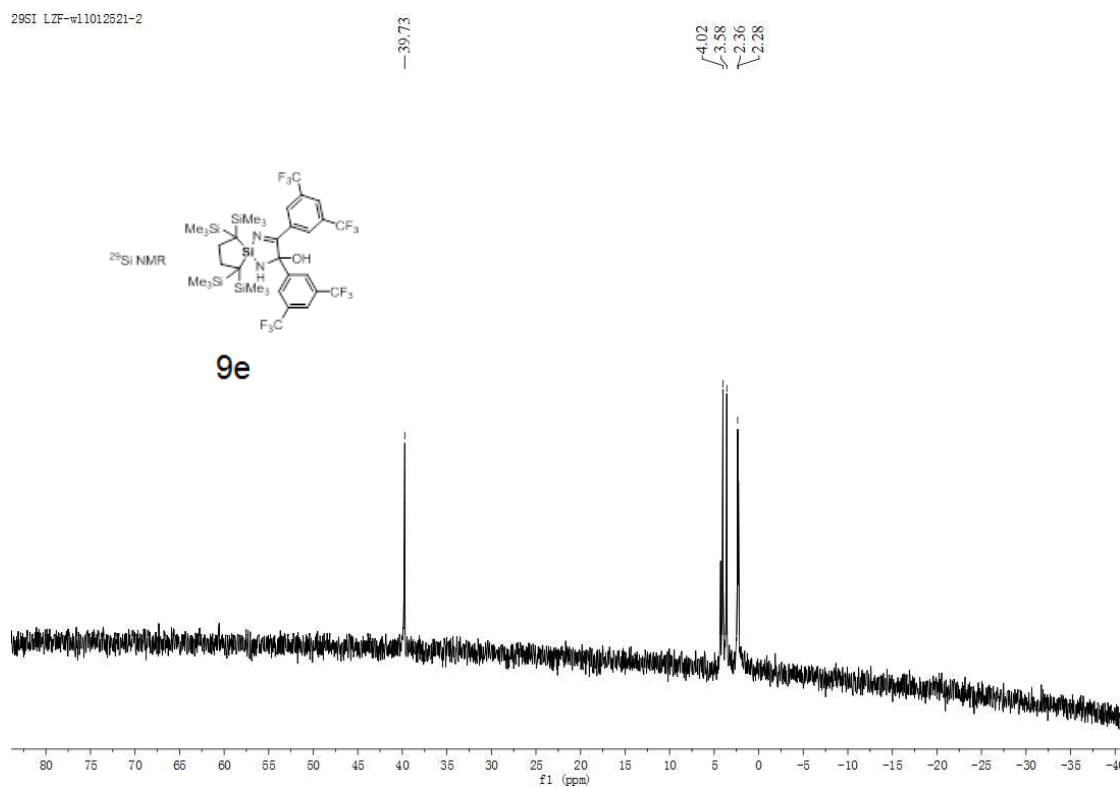


Figure S20.



## 6. References

- (S1) M. Kira; S. Ishida; T. Iwamoto and C. Kabuto, *J. Am. Chem. Soc.*, 1999, **121**, 9722.
- (S2) (a) C. L. Picou, E. D. Stevens, M. Shah, J. H. Boyer, *Acta Crystallogr. Sect. C* 1990, **46**, 1148. (b) SMART, SAINT, SADABS and SHELXTL, Bruker AXS Inc., Madison, 2000.
- (S3) Gaussian 03 (Revision D.01), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.