

Supporting Information for

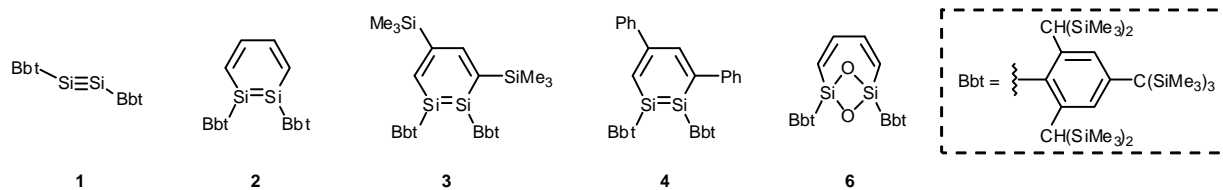
Reactivity of an aryl-substituted silicon–silicon triple bond: 1,2-Disilabenzenes from the reaction of a 1,2-diaryldisilyne with alkynes

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Experimental Section

General Procedure. All experiments were performed under an argon atmosphere unless otherwise noted. All solvents were purified by standard methods and/or The Ultimate Solvent System (Glass Contour Company)^{S1} prior to use. NMR spectra were recorded on a JEOL JNM AL-300 spectrometer (300 MHz for ^1H ; 75 MHz for ^{13}C NMR; 59 MHz for ^{29}Si NMR) using a C_6D_6 as a solvent. The chemical shifts are given in ppm relative to the standard as follows: residual $\text{C}_6\text{D}_5\text{H}$ 7.16 ppm for ^1H NMR spectra, C_6D_6 central transition 128.0 ppm for ^{13}C NMR spectra, and external SiMe_4 0.0 ppm for ^{29}Si spectra. Multiplicity of signals in ^{13}C NMR spectra was determined by DEPT technique. High-resolution mass spectral data were obtained on a JEOL JMS-700 spectrometer (FAB) or a Bruker micrOTOF (APPI-TOF). UV/Vis spectra were measured by a JASCO Ubest V-570. Melting points (uncorrected) were measured with a Yanaco micro melting point apparatus using sealed capillary tubes. Compound **1** was prepared according to the reported procedure.^{S2}

Reaction of 1 with acetylene. Acetylene gas was generated by treating calcium carbide with degassed water under anaerobic condition, and dried through a column of phosphorus pentoxide. A valved NMR tube was charged with 20.2 mg (15.5 μmol) of **1** and 0.4 mL of *n*-hexane, and the solution was degassed by freeze-pump-thaw cycles. The solution was exposed to acetylene gas (1 atm) and shaken briefly at room temperature. The dark yellow color of the solution faded, and a light-yellow solution was obtained after 5 min. Volatiles were removed under vacuum, and the light-yellow residue

was checked by NMR. The crude product was recrystallized from *n*-hexane. 13.2 mg (9.73 μmol , 63%) of **2** was afforded as light-yellow needles. **2**: Light-yellow crystals mp 317–318 $^{\circ}\text{C}$ (dec.); ^1H NMR (400 MHz, C_6D_6) δ 0.297, 0.301 (s, 72H, $\text{CH}(\text{SiMe}_3)_2$), 0.40 (s, 54H, $\text{C}(\text{SiMe}_3)_3$), 2.98 (s, 4H, CHSi), 7.05 (s, 4H, Bbt ArH), 7.61–7.68 (m, 2H, $\text{CH}=\text{CH}$), 7.72–7.79 (m, 2H, $\text{CH}=\text{CH}$); ^1H NMR (300 MHz, C_6D_{12}) δ 0.10, 0.11 (s, 72H, $\text{CH}(\text{SiMe}_3)_2$), 0.33 (s, 54H, $\text{C}(\text{SiMe}_3)_3$), 2.77 (s, 4H, CHSi), 6.89 (s, 4H, Bbt ArH), 7.46 (s, 4H, $\text{CH}=\text{CH}$); ^{13}C NMR (75 MHz, C_6D_6) δ 2.6, 3.1 ($\text{CH}(\text{SiMe}_3)_2$), 5.9 ($\text{C}(\text{SiMe}_3)_3$), 22.7 ($\text{C}(\text{SiMe}_3)_3$), 37.2 (CHSiMe_3), 127.2 (BbtC(3,5)), 135.3 (BbtC(1)), 135.8 ($\text{CH}=\text{CH}$), 146.3 ($\text{CH}=\text{CH}$), 148.0 (BbtC(4)), 152.6 (BbtC(2,6)); ^{13}C NMR (75 MHz, C_6D_{12}) δ 2.8, 3.3 ($\text{CH}(\text{SiMe}_3)_2$), 6.2 ($\text{C}(\text{SiMe}_3)_3$), 23.5 ($\text{C}(\text{SiMe}_3)_3$), 37.6 (CHSiMe_3), 127.7 (BbtC(3,5)), 135.9 (BbtC(1)), 136.0 ($\text{CH}=\text{CH}$), 146.7 ($\text{CH}=\text{CH}$), 148.3 (BbtC(4)), 153.0 (BbtC(2,6)); ^{29}Si NMR (59 MHz, C_6D_6) δ 1.0 ($\text{C}(\text{SiMe}_3)_3$), 1.5, 2.4 ($\text{CH}(\text{SiMe}_3)_2$), 57.1 ($\text{Si}=\text{Si}$); ^{29}Si NMR (59 MHz, C_6D_{12}) δ 0.9 ($\text{C}(\text{SiMe}_3)_3$), 1.4, 2.3 ($\text{CH}(\text{SiMe}_3)_2$), 56.8 ($\text{Si}=\text{Si}$); UV/Vis (*n*-hexane) λ_{max} (*n*-hexane)/nm 378 ($\epsilon/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ 1.1×10^4); HRMS (ESI, $[\text{M}+\text{H}]^+$, m/z) Calcd for $\text{C}_{64}\text{H}_{139}\text{Si}_{16}$ 1355.7180, obsd: 1355.7129.

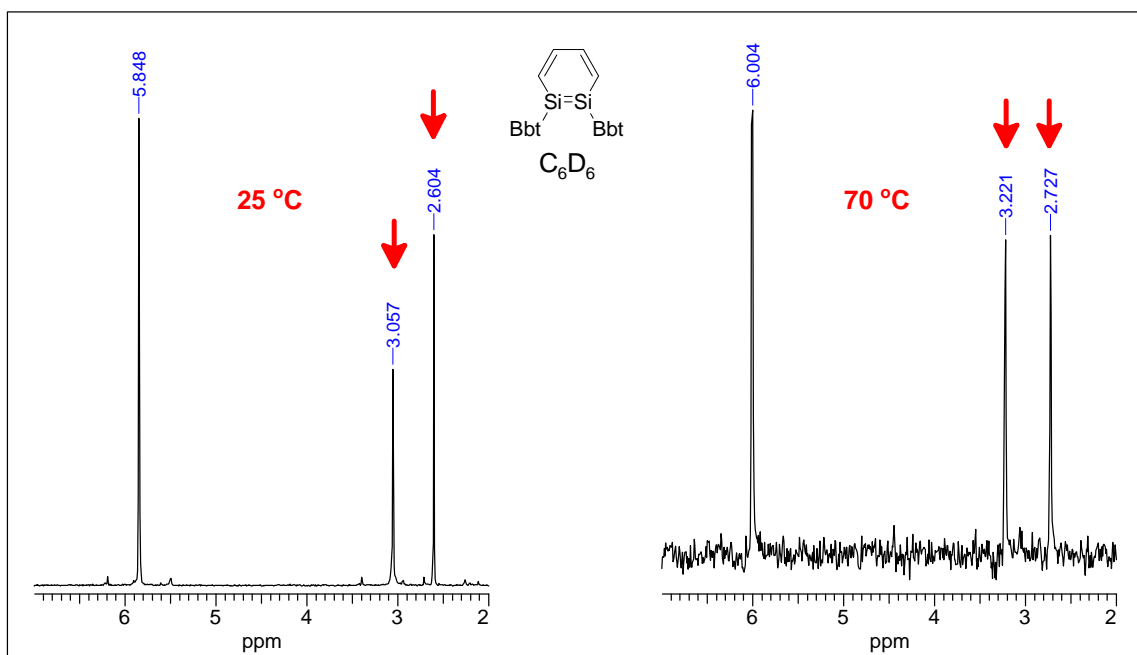


Fig. S-1. ^{13}C NMR spectra for **2** (trimethylsilyl regions) at room and elevated temperatures. The trimethylsilyl groups on *ortho* positions of Bbt groups were observed as two peaks due to the trans-bent character of **2**.

Reaction of 1 with trimethylsilylacetylene. To a *n*-hexane solution (0.4 mL) of **1** (20.2 mg, 15.5 μmol) was added 8.7 μL (61.9 μmol) of trimethylsilylacetylene. After the solution was stood at room temperature for 4 hr, an orange-yellow solution was obtained. Volatiles were removed under vacuum and the residue was analyzed by NMR (C_6D_6). Its NMR spectra suggested the formation of **3** as a major product. The crude product was recrystallized from *n*-hexane. 57.0 mg (38.0 μmol , 25%) of pure **3** was afforded as orange-yellow crystals. **3**: Orange-yellow crystals slowly changed to a green solid over 179 $^\circ\text{C}$; ^1H NMR (300 MHz, C_6D_6) δ 0.24 (s, 27H, $\text{CH}(\text{SiMe}_3)_2$, ring SiMe_3), 0.27 (s, 18H, $\text{CH}(\text{SiMe}_3)_2$), 0.38 (br s, 45H, $\text{CH}(\text{SiMe}_3)_2$, $\text{C}(\text{SiMe}_3)_3$), 0.40 (s, 18H, $\text{CH}(\text{SiMe}_3)_2$), 0.43 (s, 27H, $\text{C}(\text{SiMe}_3)_3$), 0.48 (br s, 9H, ring SiMe_3), 2.65 (br s, 2H, CHSi), 2.84 (br s, 2H, CHSi), 7.00 (s, 2H, Bbt ArH), 7.02 (s, 2H, Bbt ArH), 8.28 (s, 1H, ring CH), 8.35 (s, 1H, ring CH); ^{13}C NMR (75 MHz, C_6D_6) δ 0.6, 3.3, 3.5, 3.97, 4.01, 4.3, ($\text{CH}(\text{SiMe}_3)_2$, ring SiMe_3), 5.4, 6.0 ($\text{C}(\text{SiMe}_3)_3$), 22.1, 22.6 ($\text{C}(\text{SiMe}_3)_3$), 36.2 (CHSiMe_3), 127.2 (d, Bbt $\text{C}(3,5)$), 128.3 (d, Bbt $\text{C}(3,5)$), 128.7 (s), 133.9 (s), 134.8 (s), 144.8 (d, ring CH), 147.1 (s), 148.0 (s), 148.4 (s), 150.3 (s), 153.0 (s), 153.3 (d, ring CH); ^{29}Si NMR (59 MHz, C_6D_6) δ 0.87, 0.93 ($\text{C}(\text{SiMe}_3)_3$), -2.2, 0.3, 0.8, 2.2, 2.5, 3.6 ($\text{CH}(\text{SiMe}_3)_2$, ring SiMe_3), 64.1, 65.4 ($\text{Si}=\text{Si}$); HRMS (ESI, $[\text{M}+\text{H}]^+$, m/z) Calcd for $\text{C}_{70}\text{H}_{155}\text{Si}_{18}$ 1499.7970, obsd: 1499.7985.

Reaction of 1 with phenylacetylene. To a *n*-hexane solution (0.4 mL) of **1** (15.9 mg, 12.2 μmol) was added 5.4 μL (48.7 μmol) of phenylacetylene. After the solution was stood at room temperature for 2 hr, an orange solution was obtained. Volatiles were removed under vacuum and the residue was analyzed by NMR (C_6D_6). Its NMR spectra suggested formation of 3,5-diphenyl-1,2-bis(Bbt)-1,2-

disilabenzene (**4**) as a major product. All attempts for isolation of the product by recrystallization were failed due to high solubility and low crystallinity. The NMR data of **4** were collected from the crude mixture. **4**: ^1H NMR (300 MHz, C_6D_6) δ 0.07, 0.25, 0.29, 0.34 (s \times 4, 18 \times 4H, $\text{CH}(\text{SiMe}_3)_2$), 0.38, 0.40 (s \times 2, 27 \times 2H, $\text{C}(\text{SiMe}_3)_3$), 2.83 (s, 2H, CHSi), 2.93 (br s, 2H, CHSi), 7.03 (s, 4H, Bbt ArH), 6.96-7.13 (m, 4H, PhH), 7.24–7.31 (m, 4H, PhH), 7.51 (d, $^3J = 7.5$ Hz, 2H, PhH), 7.76 (d, $^3J = 7.2$ Hz, 2H, PhH), 8.21 (d, $^4J = 2.2$ Hz, 1H, ring CH), 8.26 (d $^4J = 2.2$ Hz, 1H, ring CH); ^{13}C NMR (75 MHz, C_6D_6) δ 2.7, 2.8, 3.7, 4.0 ($\text{CH}(\text{SiMe}_3)_2$), 5.8, 6.0 ($\text{C}(\text{SiMe}_3)_3$), 22.8, 22.9 ($\text{C}(\text{SiMe}_3)_3$), 35.8, 35.9 (CHSiMe_3), 126.4 (s), 126.6 (s), 127.8 (d), 128.8 (d) 129.1 (d), 131.4 (s), 131.7 (d), 132.5 (s), 134.0 (s), 139.5 (d), 145.7 (s), 146.2 (s), 147.7 (s), 148.0 (s), 148.2 (s), 148.5 (s), 152.6 (s), 153.3 (s), 157.3 (s); ^{29}Si NMR (59 MHz, C_6D_6) δ 0.8, 1.0 ($\text{C}(\text{SiMe}_3)_3$), 1.1, 1.3, 2.2, 3.4 ($\text{CH}(\text{SiMe}_3)_2$), 55.0, 61.7 ($\text{Si}=\text{Si}$).

Reaction of 1 with 1,7-octadiyne. To a *n*-hexane solution (0.4 mL) of **1** (29.6 mg, 22.7 μmol) was added 5.9 μL (45 μmol) of 1,7-octadiyne. After the solution was stood at 3 $^\circ\text{C}$ for 12 hr, a light-yellow solution was obtained. Volatiles were removed under vacuum and the residue was analyzed by NMR (C_6D_6). Its NMR spectra suggested formation of a complex mixture.

Reaction of 1 with bis(trimethylsilyl)acetylene. By the similar procedure for **1** with trimethylsilylacetylene, a *n*-hexane solution of **1** was reacted with 4 equiv of bis(trimethylsilyl)acetylene. After 8 hr at room temperature, volatiles were removed under vacuum. No change was observed in ^1H NMR spectrum.

Reaction of 2 with oxygen. A valved NMR tube was charged with 10.5 mg (7.74 μmol) of **2** and 0.4 mL of C_6D_6 , and the solution was degassed by freeze-pump-thaw cycles. The solution was exposed to dry oxygen gas (1 atm) and shaken briefly at room temperature. The dark yellow color of the solution

faded immediately, and a colorless solution was obtained after 1 min. The reaction mixture was checked by NMR, and it was confirmed that **2** changed to **6** quantitatively. **6**: Colorless crystals mp 340–1 °C; ¹H NMR (300 MHz, C₆D₆) δ 0.33 (s, 27H, C(SiMe₃)₃), 0.37 (s, 27H, C(SiMe₃)₃), 0.38 (s, 72H, CH(SiMe₃)₂), 2.64 (s, 4H, CHSi), 6.12–6.19 (m, 2H, CH=CH), 6.64–6.71 (m, 2H, CH=CH), 6.97 (s, 4H, ArH); ¹³C NMR (75 MHz, C₆D₆) δ 2.2, 2.6 (CH(SiMe₃)₂), 5.8 (C(SiMe₃)₃), 22.8 (C(SiMe₃)₃), 29.8 (CH₂), 127.4 (ArC(3,5)), 128.8 (ArC(1)), 135.9 (CH=CH), 142.6 (CH=CH), 148.9 (ArC(4)), 151.8 (ArC(2,6)); ²⁹Si NMR (59 MHz, C₆D₆) δ –10.1 (SiO), 1.1 (C(SiMe₃)₃), 2.0, 2.7 (CH(SiMe₃)₂); HRMS (FAB, M⁺, *m/z*) Calcd for C₆₄H₁₃₈O₂Si₁₆ 1386.7000, obsd: 1386.7007.

X-ray crystallographic analyses of 2 and 6. The intensity data were collected on a Rigaku/MS Mercury CCD diffractometer with graphite monochromated MoK α radiation ($\lambda = 0.71070$ Å). Single crystals suitable for X-ray analysis were obtained by cooling down the concentrated solutions (toluene solution for **2**; toluene and hexane mixed solution for **6**). A single crystal suitable for X-ray analysis was mounted on a glass fiber. In the case of air-sensitive compound, mounting was made in a glove-box (Ar). The structures were solved by a direct method (SIR-97^{S3}) and refined by full-matrix least-squares procedures on F^2 for all reflections (SHELXL-97^{S4}). All hydrogen atoms were placed using AFIX instructions, while all other atoms were refined anisotropically.

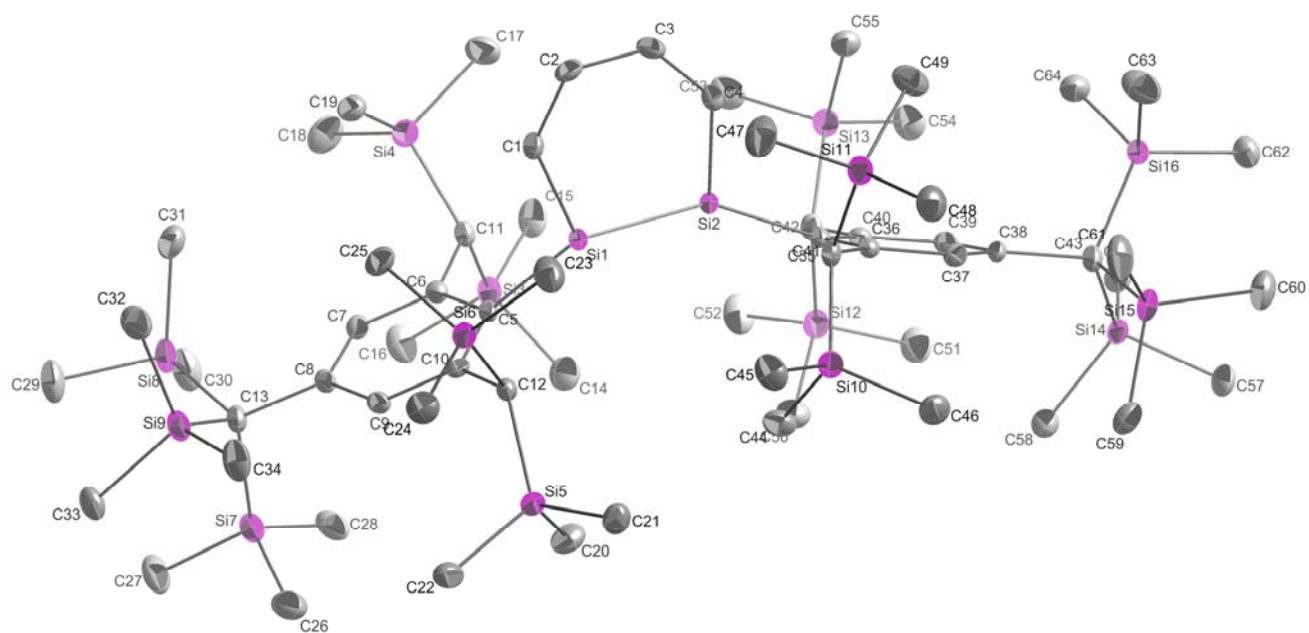


Figure S-2. Thermal ellipsoid (50%) drawing of $[2 \cdot 0.5(C_7H_8)]$. Hydrogen atoms and solvate are omitted for clarity. Tris(trimethylsilyl)methyl group attached to C(38) is disordered, and one of them is shown.

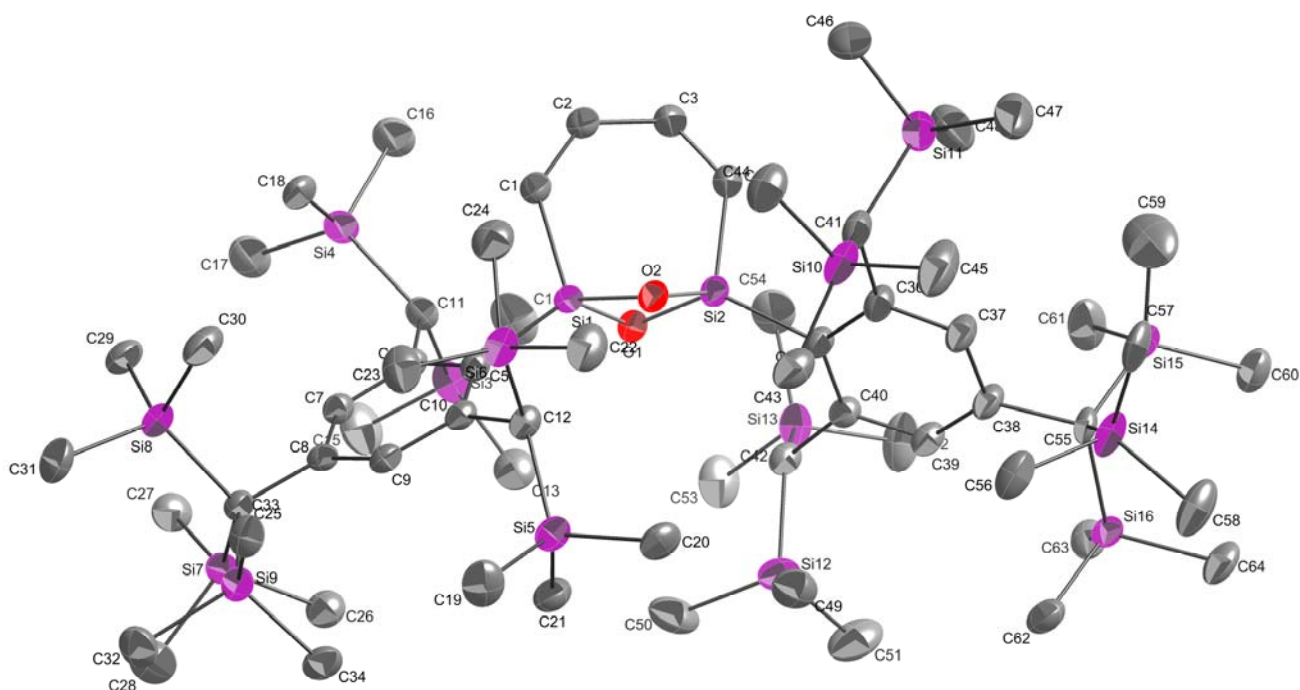


Figure S-3. Thermal ellipsoid (50%) drawing of $[6 \cdot C_7H_8 \cdot C_6H_{14}]$. Hydrogen atoms and solvates are omitted for clarity. Tris(trimethylsilyl)methyl group attached to C(38) is disordered, and one of them is shown.

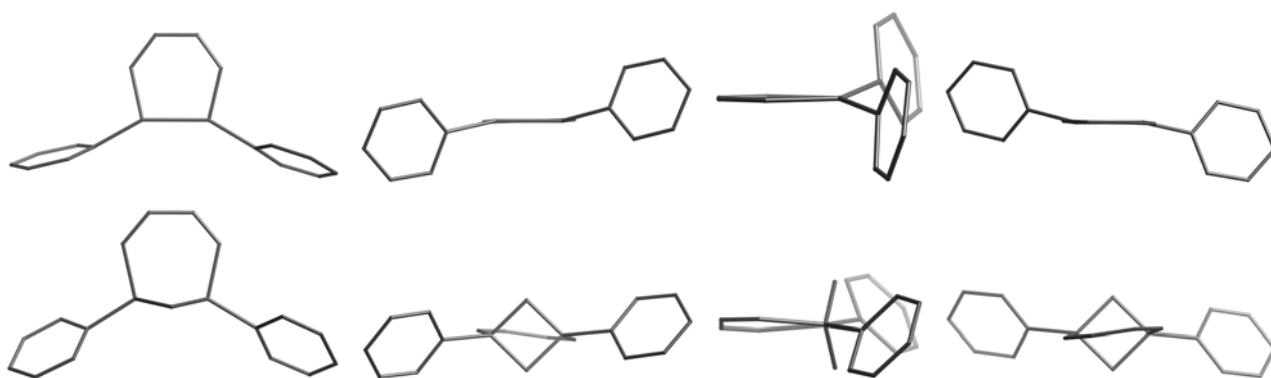


Figure S-4. Stick plots of **2** (top) and **6** (bottom) for geometrical comparison between the two compounds. Only skeletal structures were drawn for clarity.

Table S-1. Crystal data and structure refinement for [2·0.5(C₇H₈)].

Empirical formula	C _{67.50} H ₁₄₂ Si ₁₆	
Formula weight	1403.25	
Temperature	103(2) K	
Wavelength	0.71075 Å	
Crystal system	monoclinic	
Space group	P2 ₁ /c (#14)	
Unit cell dimensions	$a = 18.524(2)$ Å	$\alpha = 90^\circ$.
	$b = 12.0037(14)$ Å	$\beta = 101.5916(14)^\circ$.
	$c = 40.568(5)$ Å	$\gamma = 90^\circ$.
Volume	8836.5(19) Å ³	
Z	4	
Density (calculated)	1.055 Mg/m ³	
Absorption coefficient	0.264 mm ⁻¹	
F(000)	3084	
Crystal size	0.20 × 0.20 × 0.10 mm ³	
θ range for data collection	2.84 to 25.00°.	
Index ranges	-22 ≤ h ≤ 22, -14 ≤ k ≤ 14, -47 ≤ l ≤ 48	
Reflections collected	80148	
Independent reflections	15370 [$R(\text{int}) = 0.0709$]	
Completeness to $\theta = 25.00^\circ$	98.8 %	
Max. and min. transmission	0.9741 and 0.9492	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15370 / 0 / 879	
Goodness-of-fit on F^2	1.057	
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0441$, $wR_2 = 0.1243$	
R indices (all data)	$R_1 = 0.0492$, $wR_2 = 0.1284$	
Largest diff. peak and hole	1.134 and -0.389 e.Å ⁻³	

Table S-2. Crystal data and structure refinement for [6·C₇H₈·C₆H₁₄].

Empirical formula	C ₇₇ H ₁₆₀ O ₂ Si ₁₆	
Formula weight	1567.49	
Temperature	103(2) K	
Wavelength	0.71075 Å	
Crystal system	triclinic	
Space group	<i>P</i> $\bar{1}$ (#2)	
Unit cell dimensions	<i>a</i> = 16.8221(2) Å	α = 92.6933(4)°.
	<i>b</i> = 17.7685(2) Å	β = 111.9361(5)°.
	<i>c</i> = 18.7611(2) Å	γ = 107.5178(12)°.
Volume	4879.28(10) Å ³	
<i>Z</i>	2	
Density (calculated)	1.067 Mg/m ³	
Absorption coefficient	0.246 mm ⁻¹	
<i>F</i> (000)	1724	
Crystal size	0.10 × 0.05 × 0.02 mm ³	
θ range for data collection	2.78 to 25.00°.	
Index ranges	-19 ≤ <i>h</i> ≤ 19, -21 ≤ <i>k</i> ≤ 19, -22 ≤ <i>l</i> ≤ 22	
Reflections collected	40744	
Independent reflections	16924 [<i>R</i> (int) = 0.0296]	
Completeness to θ = 25.00°	98.5 %	
Max. and min. transmission	0.9951 and 0.9758	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	16924 / 108 / 1119	
Goodness-of-fit on <i>F</i> ²	1.039	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0452, w <i>R</i> ₂ = 0.1196	
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0496, w <i>R</i> ₂ = 0.1244	
Largest diff. peak and hole	0.498 and -0.543 e.Å ⁻³	

References

- (S1) A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen and F. J. Timmers, *Organometallics*, 1996, **15**, 1518.
- (S2) T. Sasamori, J. S. Han, K. Hironaka, N. Takagi, S. Nagase and N. Tokitoh, *Pure Appl. Chem.*, 2010, **82**, 603-612.
- (S3) A. Altomare, M. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. Moliterni, G. Polidori and R. Spagna, *J. Appl. Cryst.*, 1999, **32**, 115.
- (S4) (a) G. M. Sheldrick, *Acta Crystallogr. Sect. A* 1990, **46**, 467. (b) G. Sheldrick, SHELX-97 Program for Crystal Structure Solution and the Refinement of Crystal Structures, Institut für Anorganische Chemie der Universität Göttingen, Tammanstrasse 4, D-3400 Göttingen, Germany, 1997.

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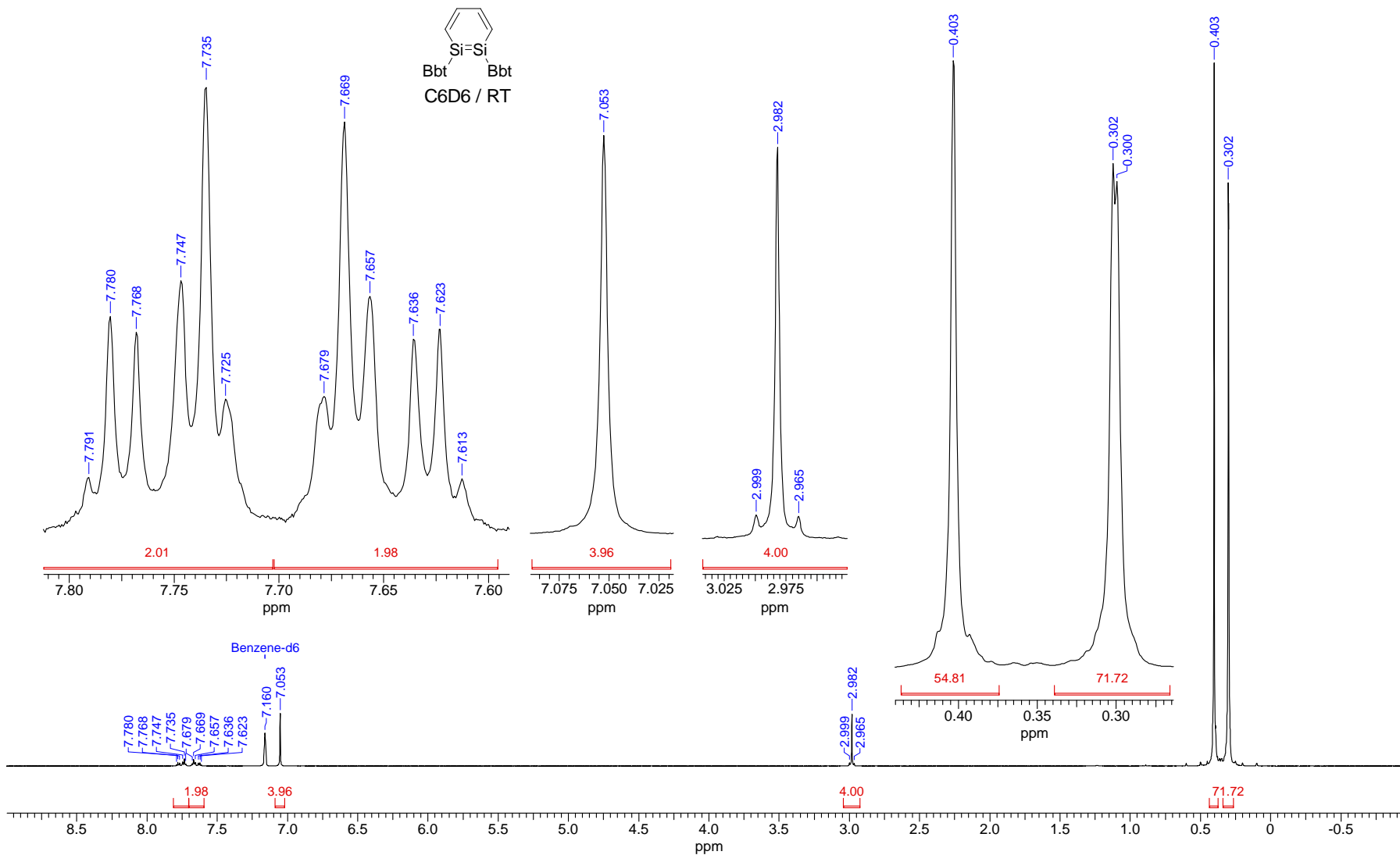


Fig. S-5. ¹H NMR spectrum of 2.

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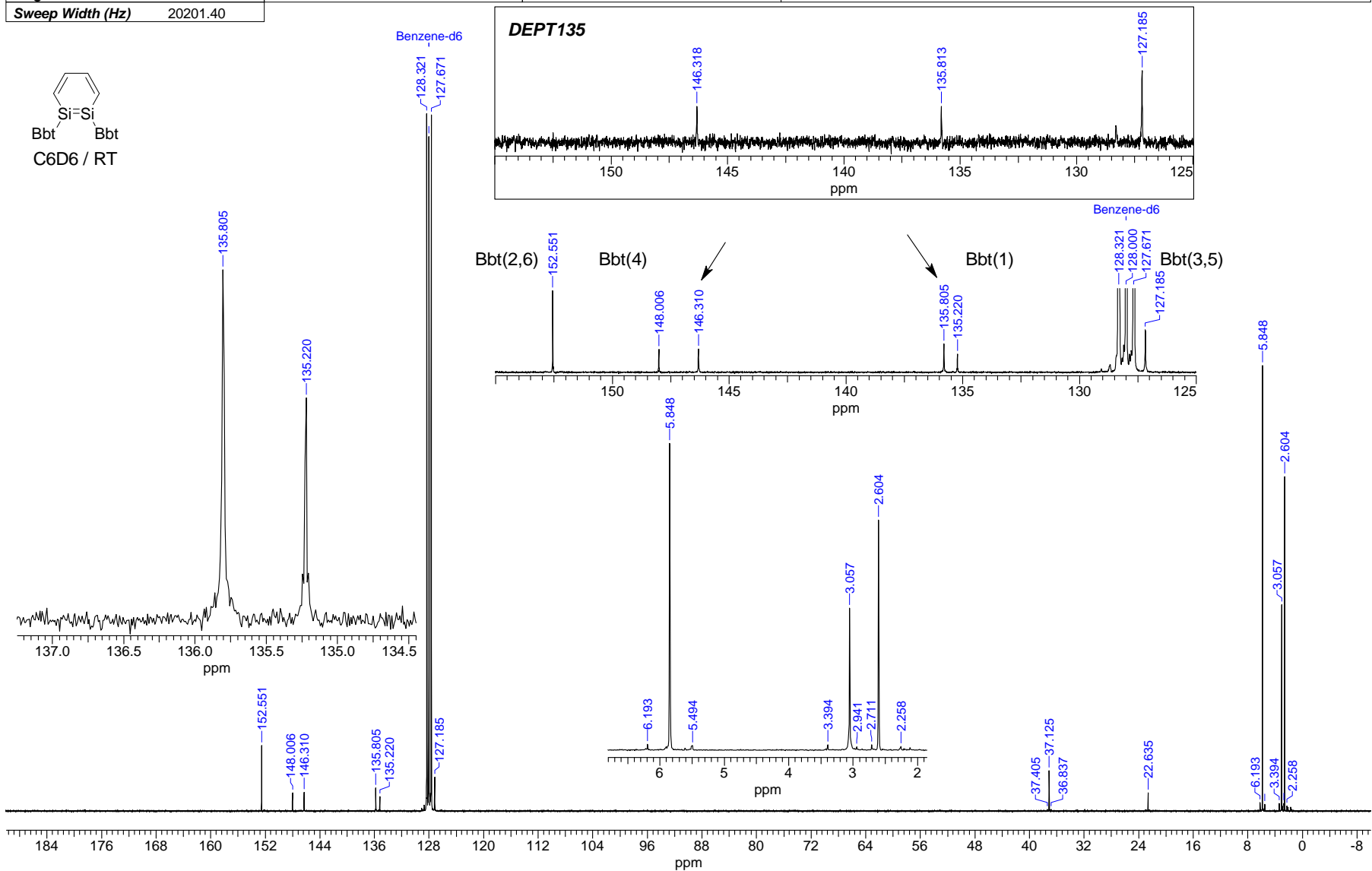


Fig. S-6. $^{13}\text{C}\{^1\text{H}\}$ and ^{13}C DEPT135 NMR spectra of **2**.

