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Electronic Supplementary Information

The Selective Formation of a 1,2-Disilabenzene from the Reaction of a Disilyne with Phenylacetylene

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1. General Remarks.

All manipulations were carried out under an argon atmosphere using either Schlenk line techniques or glove boxes. All solvents were purified by standard methods and/or the Ultimate Solvent System, Glass Contour Company.[S1] Trace amounts of water and oxygen remaining in the solvents were thoroughly removed by bulb-to-bulb distillation from potassium mirror prior to use. ^{1}H, ^{13}C, and ^{29}Si NMR spectra were measured on a JEOL JNM-ECA600 (^{29}Si: 119 MHz) or on a JEOL AL-300 spectrometer (^{1}H: 300 MHz; ^{13}C: 75 MHz; ^{29}Si: 59 MHz) in the Joint Usage/Research Center (JURC, Institute for Chemical Research, Kyoto University). A signal arising from residual C_6D_5H (7.15 ppm) in C_6D_6 was used as the internal standard for the ^{1}H NMR spectra, while that of C_6D_6 (128.0 ppm) was used for the ^{13}C NMR spectra, and external $SiMe_4$ (0.0 ppm) for the ^{29}Si NMR spectra. High-resolution mass spectra (HRMS) were obtained from a Bruker micrOTOF focus-Kci mass spectrometer (DART). All melting points were determined on a Büchi Melting Point Apparatus M-565 and are uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory (Institute for Chemical Research) of Kyoto University. Tbb(Br)Si=Si(Br)Tbb (Tbb = 1-Br-2,6-[$CH(SiMe_3)_2]_2$-4-*t*-Bu-C_6H_2) was prepared according to literature procedures.[S2]

2. Experimental Details.

Synthesis of 1,2-Tbb$_2$-disilyne (1): Potassium graphite (KC_8, 10.5 mg, 77.7 μmol) was added to a benzene solution (1.5 mL) of 1,2-dibromodisilene **1** (39.1 mg, 35.0 μmol) at room temperature. After stirring the reaction mixture for 30 minutes, the solvent was removed under reduced pressure and *n*-hexane was added. The resulting suspension was filtered to remove graphite and inorganic salts. The filtrate was condensed and recrystallized from *n*-hexane to afford 1,2-Tbb$_2$-disilyne **1** (27.8 mg, 29.1 μmol, 83%). **1**: yellow crystals, mp 80.0–81.0 °C (dec); ^{1}H NMR (300 MHz, C_6D_6, 298 K) δ 0.28 (s, 72 H, CH(Si*Me*$_3$)$_2$), 1.27 (s, 18 H, C(*Me*)$_3$), 3.26 (s, 4H, C*H*Si), 6.93 (s, 4H, Ar*H*); ^{13}C NMR (75 MHz, C_6D_6, 298 K) δ 0.79 (q), 31.23 (q), 34.59 (s), 38.70 (d), 120.41 (d), 137.43 (s), 150.16 (s), 151.35 (s); ^{29}Si NMR (59 MHz, C_6D_6, 298 K) δ 2.74 (*Si*Me$_3$), 16.16 (*Si*≡Si). UV–vis (*n*-hexane) λ_{max} (nm, ε) = 371 (16,000), 478 (1,900). Anal. Calcd for $C_{48}H_{98}Si_{10}$: C, 60.23; H, 10.39. Found: C, 60.30; H, 10.33. MS

(DART-TOF, positive mode): *m*/*z* calcd for $C_{48}H_{99}Si_{10}$ 955.5434 ($[M+H]^+$), found 955.5424 ($[M+H]^+$).

Synthesis of 1,2-Tbb$_2$-disilabenzene (3): Acetylene gas was generated by treating calcium carbide with degassed water at room temperature under anaerobic conditions and leading the thus produced gas through a column of phosphorus pentoxide. In a *J*-Young NMR tube (5ϕ), an *n*-hexane solution (0.5 mL) of **1** (21.9 mg, 22.9 μmol) was degassed by freeze-pump-thaw cycles. Then, the solution was exposed to acetylene gas that generated as described above (1 atm) and the tube was shaken at room temperature. The color of the solution changed from dark to light yellow after ~10 minutes of shaking. All volatiles were removed under reduced pressure, and the pale-yellow residue was recrystallized from benzene to afford 1,2-Tbb$_2$-disilabenzene **3** (22.5 mg, 22.9 μmol, quant). **3**: yellow crystals, mp 130.0-131.0 °C (dec); ^{1}H NMR (300 MHz, C_6D_6, 298 K) δ 0.20 (s, 36H, CH(Si*Me*$_3$)$_2$), 0.22 (s, 36 H, CH(Si*Me*$_3$)$_2$), 1.34 (s, 18 H, C(*Me*)$_3$), 2.89 (s, 4H, C*H*Si), 7.02 (s, 4H, Ar(Tbb)*H*), 7.72 (AA'BB', *J* = 3.6, 13.5 Hz, 2H, Si–CH=C*H*), 7.84 (AA'BB', *J* = 3.6, 13.5 Hz, 2H, Si–C*H*=CH); ^{13}C NMR (75 MHz, C_6D_6, 298 K) δ 1.53 (q), 2.12 (q), 31.16 (q), 34.54 (s), 34.58 (d), 122.38 (d), 128.75 (s), 135.30 (d), 145.81(d), 151.65 (s), 151.83 (s); ^{29}Si NMR (59 MHz, C_6D_6, 298 K) δ 2.36 (*Si*Me$_3$), 3.36 (*Si*Me$_3$), 61.67 (*Si*=Si). UV−vis (*n*-hexane) λ_{max} (nm, ε) = 363 (8,400), 397 (5,100, sh). MS (DART-TOF, positive mode): *m*/*z* calcd for $C_{52}H_{103}Si_{10}$ 1007.5752 ($[M+H]^+$), found 1007.5691 ($[M+H]^+$).

Synthesis of 3,5-diphenyl-1,2-Tbb$_2$-disilabenzene (4): An *n*-hexane solution (0.3 mL) of **1** (11.2 mg, 11.7 μmol) in a *J*-Young NMR tube was treated with phenylacetylene (4.0 mg, 39.2 μmol, 3.4 equiv) for 10 min. Thereafter, all volatiles were removed under reduced pressure and the pale-yellow residue was recrystallized from *n*-hexane to afford 3,5-diphenyl-1,2-Tbb$_2$-disilabenzene **4** as stable yellow crystals (13.5 mg, 11.6 μmol, 99%). **4**: yellow crystals, mp 137.0-138.0 °C (dec); ^{1}H NMR (300 MHz, C_6D_6, 298 K) δ −0.12 (s, 18H, CH(Si*Me*$_3$)$_2$), 0.03 (s, 18H, CH(Si*Me*$_3$)$_2$), 0.06 (s, 18H, CH(Si*Me*$_3$)$_2$), 0.07 (s, 18H, CH(Si*Me*$_3$)$_2$), 1.24 (s, 9H, C(*Me*)$_3$), 1.28 (s, 9H, C(*Me*)$_3$), 2.60 (s, 2H, C*H*Si), 2.87 (s, 2H, C*H*Si), 6.85 (s, 2H, Ar(Tbb)*H*), 6.88 (s, 2H, Ar(Tbb)*H*), 7.01-7.09 (m, 2H, Ph*H*), 7.16-7.21 (m, 4H, Ph*H*), 7.50-7.53 (m, 4H, Ph*H*), 7.93 (d, 1H, *J* = 2.0 Hz), 8.06 (d, 1H, *J* = 2.0 Hz); ^{13}C NMR (75 MHz, C_6D_6): δ 1.37 (q), 1.97 (q), 2.86 (q), 2.88 (q), 31.31 (d), 31.35 (d), 32.98 (q), 33.58 (q), 34.60 (s), 34.68 (s), 122.47 (d), 123.06 (d), 126.33 (d), 127.09 (d), 127.77 (d), 128.18 (d), 128.66 (d), 129.36 (d), 130.93 (s), 131.61 (d), 138.47 (s), 144.16 (d), 145.67 (s), 148.63 (s), 149.37 (s), 151.25 (s), 152.10 (s), 152.14 (s), 152.86 (s), 161.05 (s); ^{29}Si NMR (119 MHz, C_6D_6, 298 K) δ 1.26 (*Si*Me$_3$), 1.88 (*Si*Me$_3$), 4.39 (*Si*Me$_3$), 4.48 (*Si*Me$_3$), 59.72 (*Si*=Si), 72.66 (Si=*Si*). UV−vis (*n*-hexane) λ_{max} (nm, ε) = 385 (11,000), 442 (9,300). MS (DART-TOF, positive mode): *m*/*z* calcd for $C_{64}H_{110}Si_{10}$ 1159.6378 ([M+H]$^+$), found 1159.6341 ([M+H]$^+$).

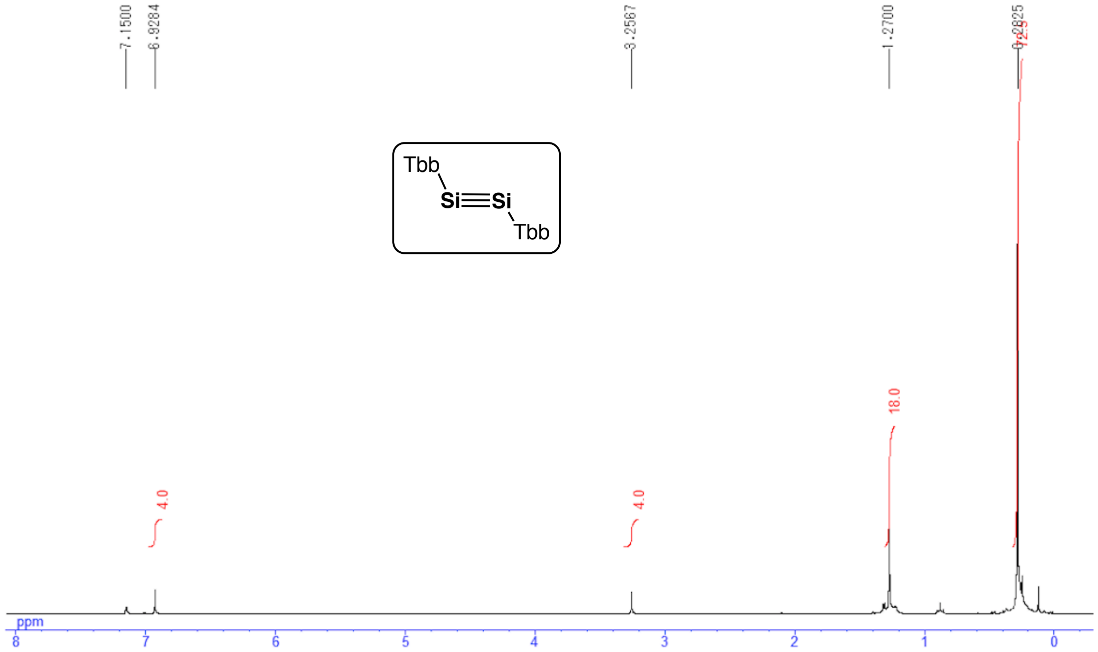

Figure S1. ^{1}H NMR spectrum of **1** in C_6D_6.

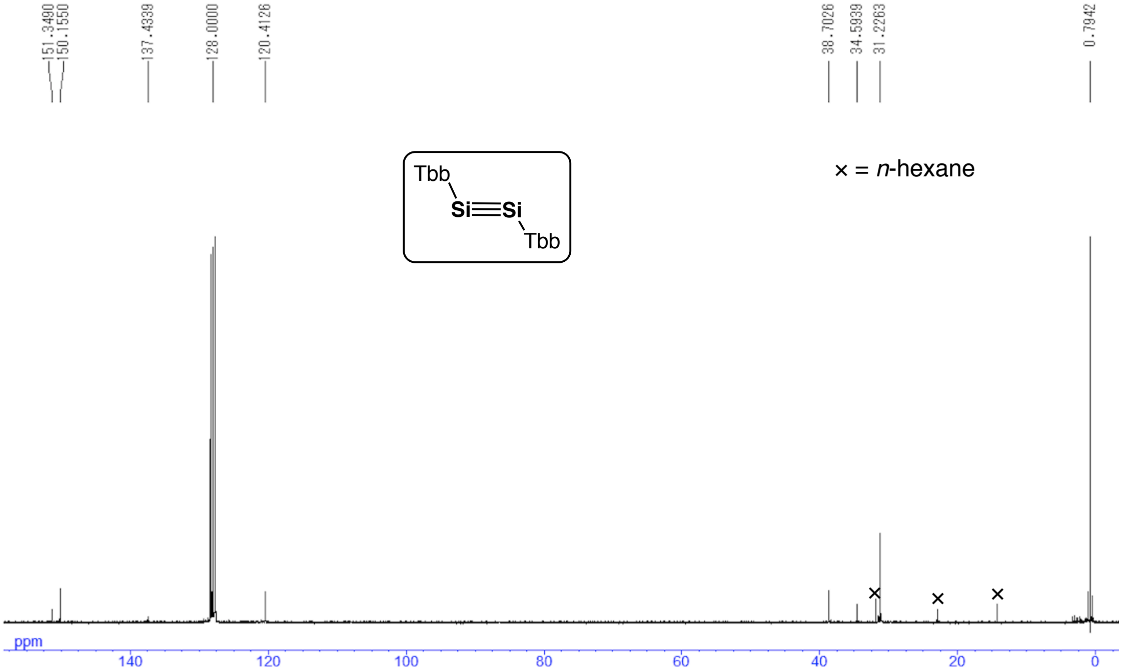

Figure S2. ^{13}C NMR spectrum of **1** in C_6D_6.

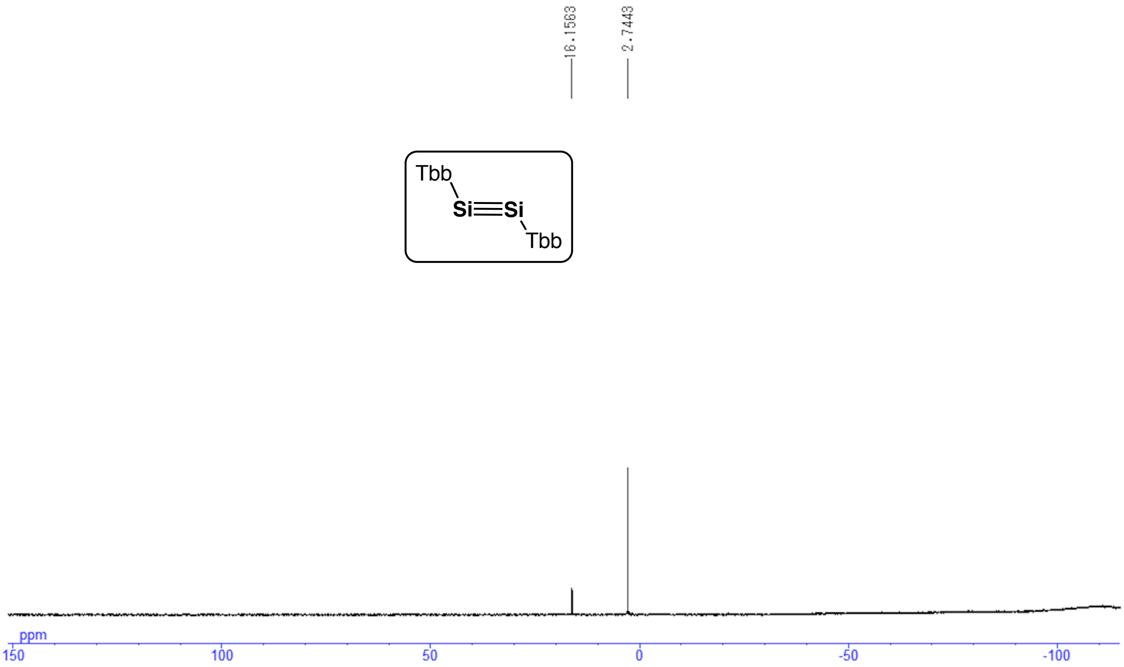

Figure S3. ^{29}Si NMR spectrum of **1** in C_6D_6.

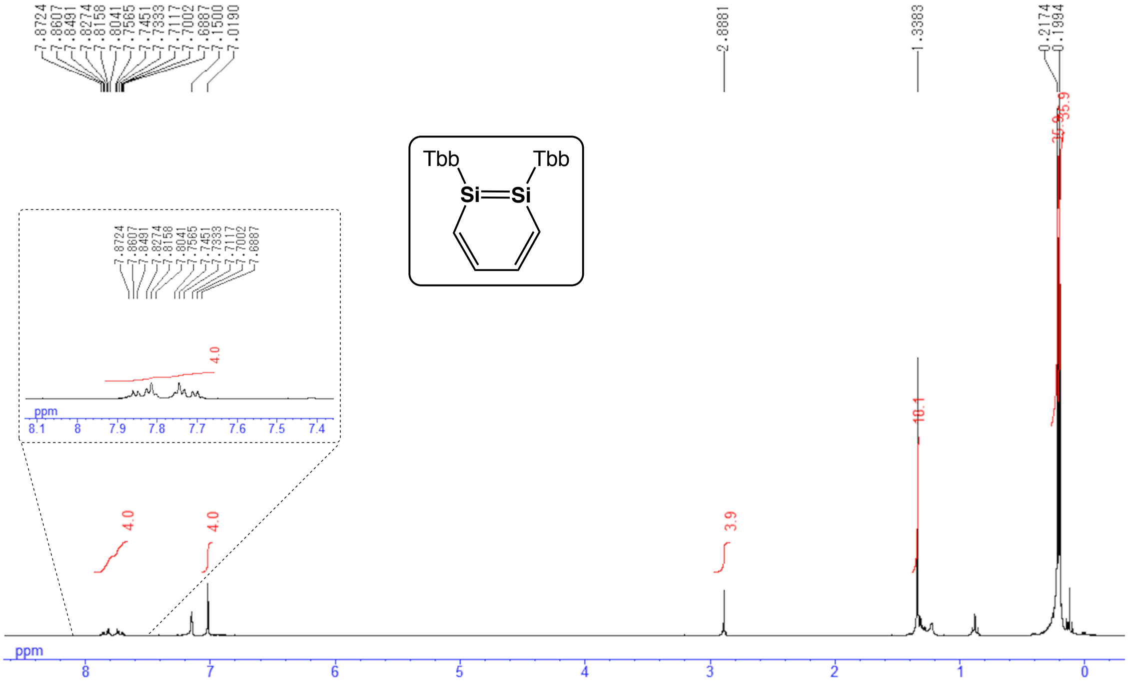

Figure S4. ^{1}H NMR spectrum of **3** in C_6D_6.

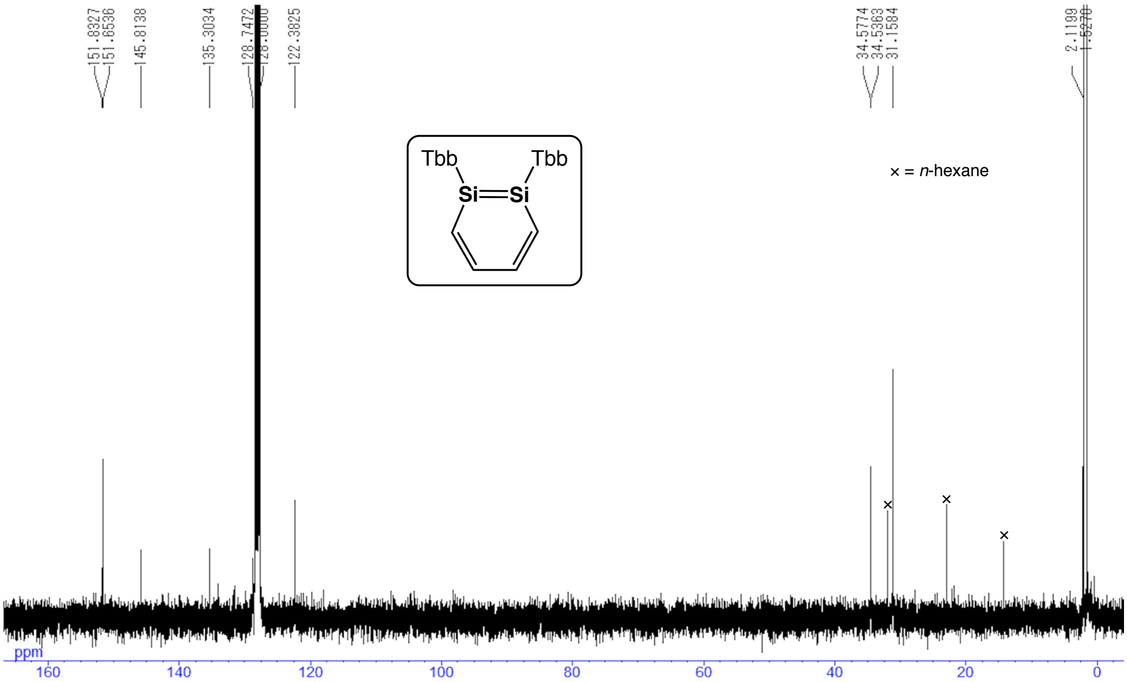

Figure S5. ^{13}C NMR spectrum of **3** in C_6D_6.

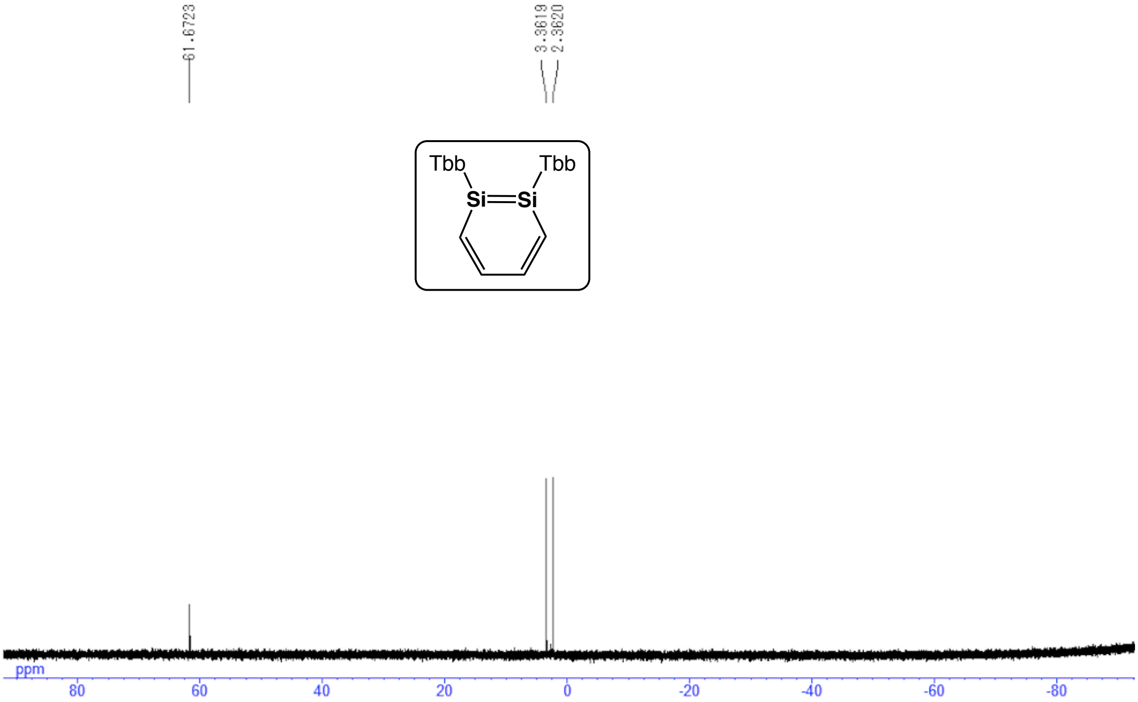

Figure S6. ^{29}Si NMR spectrum of **3** in C_6D_6.

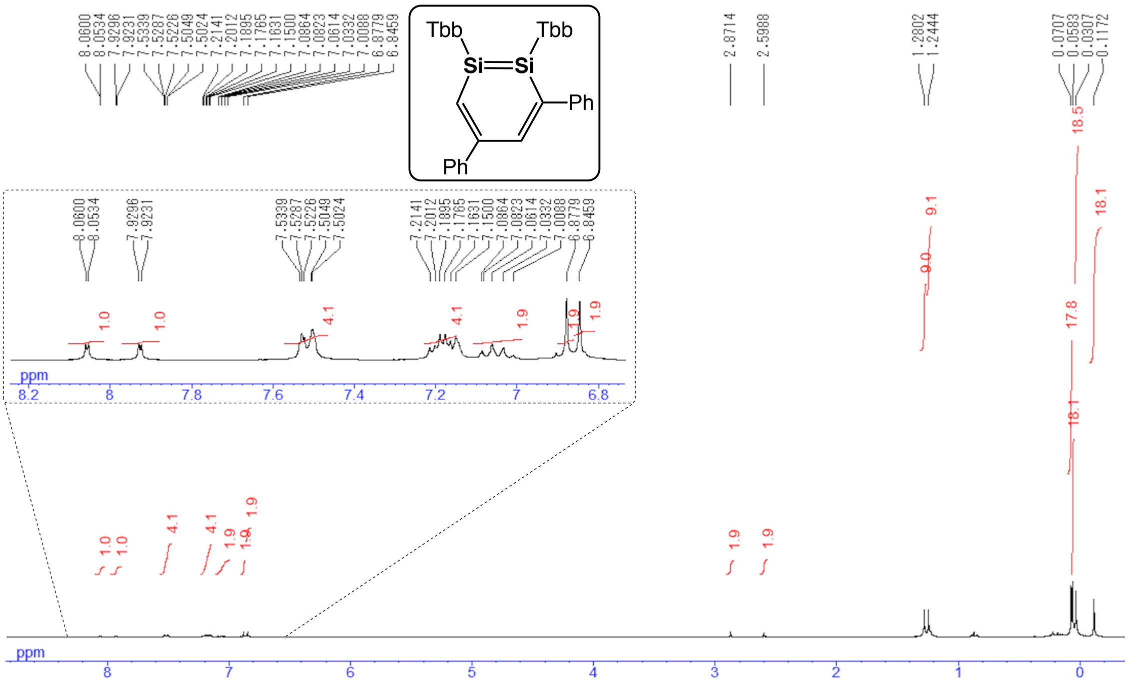

Figure S7. ^{1}H NMR spectrum of **4** in C_6D_6.

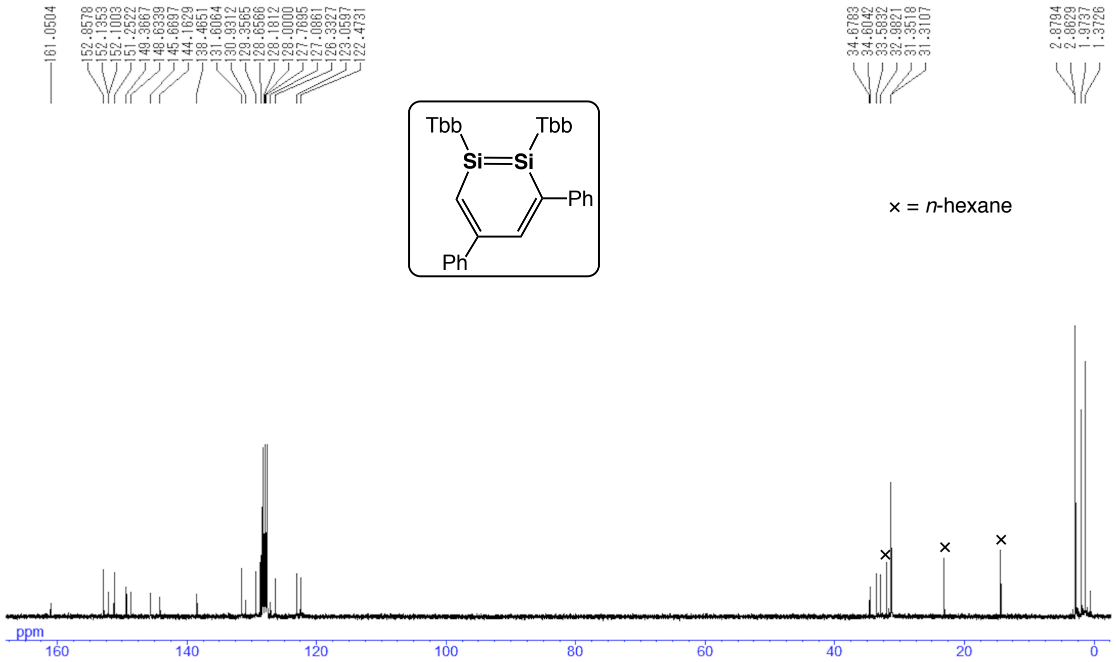

Figure S8. ^{13}C NMR spectrum of **4** in C_6D_6.

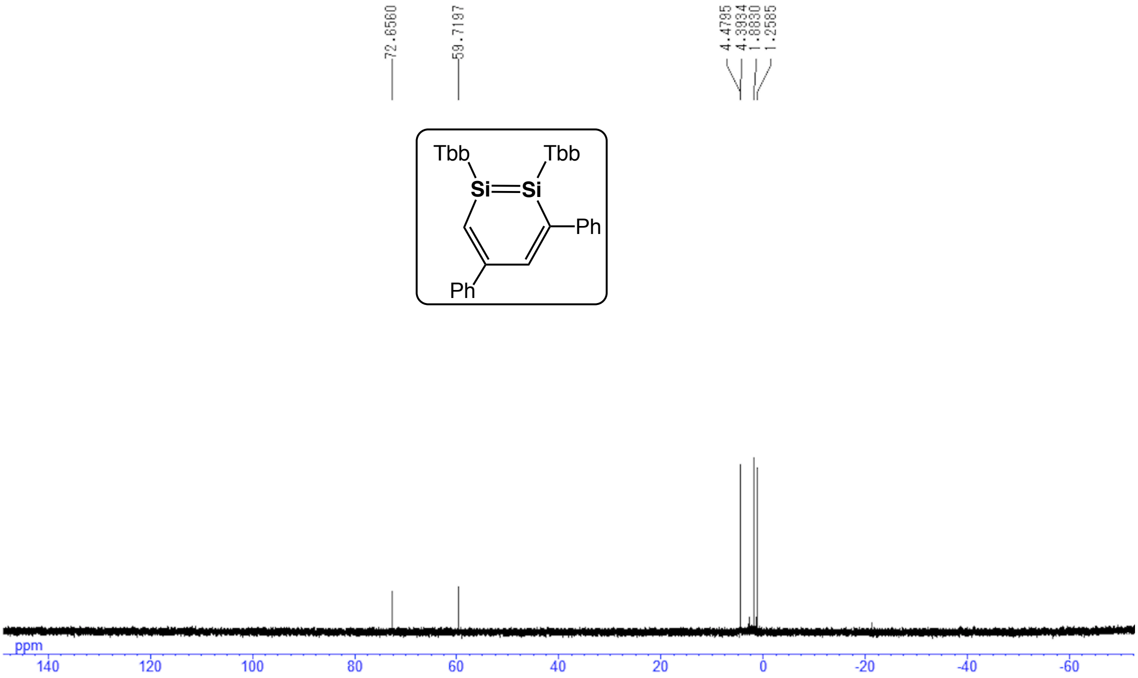

Figure S9. ^{29}Si NMR spectrum of **4** in C_6D_6.

3. X-Ray Crystallographic Analyses.

Single crystals of **1**, [**3**·C_6H_6], and **4** were obtained from recrystallization in *n*-hexane (**1** and **4**) or benzene ([**3**·C_6H_6]) at –20 ºC (**1** and **4**) or room temperature ([**3**·C_6H_6]) in an argon-filled glove box. Intensity data for **1** and **4** were collected on a RIGAKU Saturn70 CCD(system) with VariMax Mo Optics using Mo-Kα radiation (λ = 0.71073 Å), while those for [**3**·C_6H_6] were collected at the BL02B1 beamline of SPring-8 (2016B1716) on a large cylindrical camera using synchrotron radiation (λ = 0.3024(1) Å). The structures were solved using a direct method (SIR2004[S3]) and refined by a full-matrix least-squares method on F^2 for all reflections using the programs of SHELXL-97[S4] for **1** and **4**, and SHELXL-2016/4[S5] for [**3**·C_6H_6]. All non-hydrogen atoms were refined anisotropically. The positions of all hydrogen atoms for **1** and **4** were calculated geometrically, while those for [**3**·C_6H_6] were located on difference Fourier maps, and were refined as riding models. Supplementary crystallographic data were deposited at the Cambridge Crystallographic Data Centre (CCDC) under deposition numbers CCDC-1830586-1830588, and can be obtained free of charge from *via* www.ccdc.cam.ac.uk/data_request.cif.

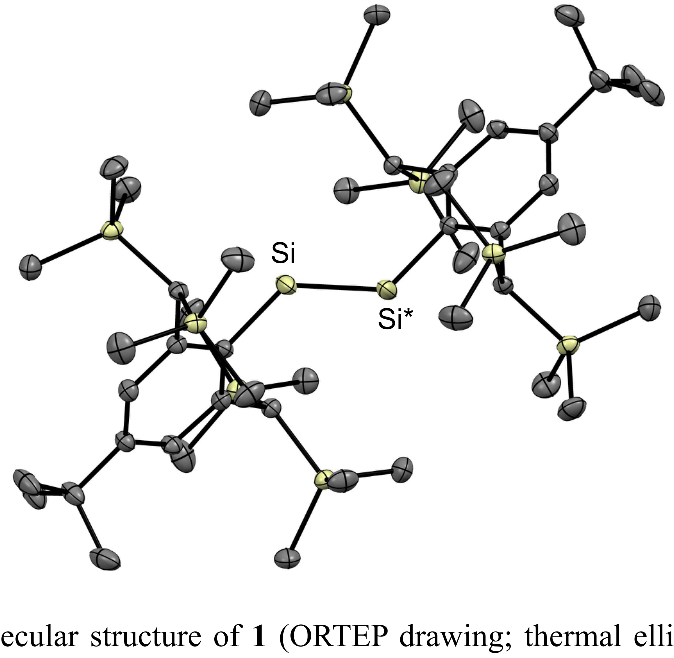

Figure S10. Molecular structure of **1** (ORTEP drawing; thermal ellipsoids set to 50% probability). Hydrogen atoms are omitted for clarity.

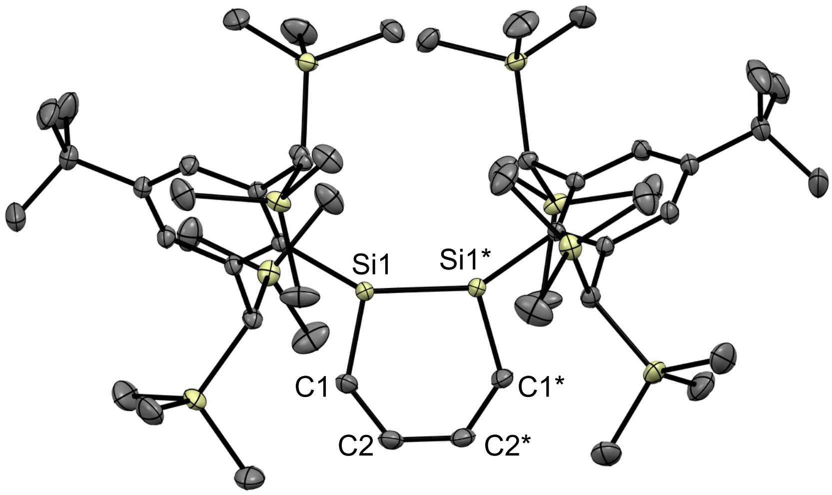

Figure S11. Molecular structure of **3** (ORTEP drawing; thermal ellipsoids set to 50% probability). Hydrogen atoms and one molecule of benzene are omitted for clarity.

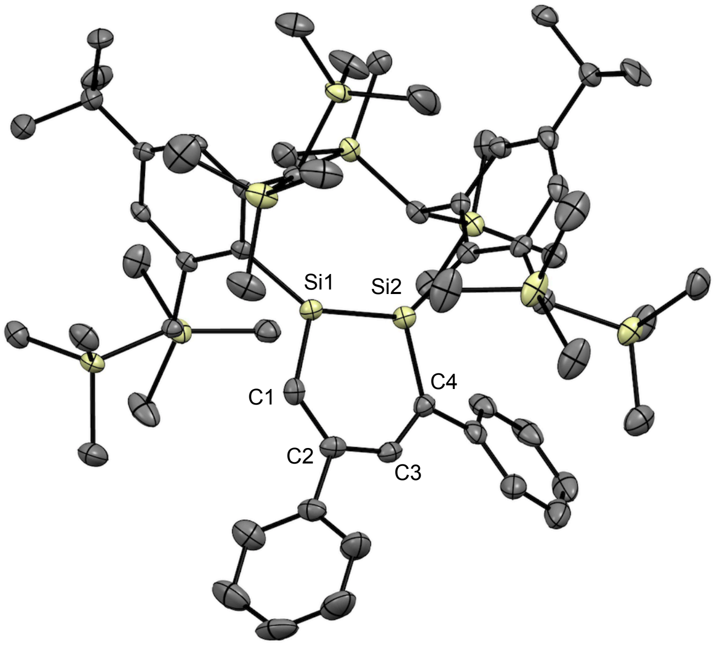

Figure S12. Molecular structure of **4** (ORTEP drawing; thermal ellipsoids set to 50% probability). Hydrogen atoms are omitted for clarity.

4. Computational calculations.

All calculations were carried out using the *Gaussian 09* (Revision E.01) program package.[S6] Geometry optimizations and vibrational frequencies were calculated in the gas phase at the theoretical level indicated in the main text. Computational time was generously provided by the Supercomputer Laboratory of the Institute for Chemical Research at Kyoto University. Optimized geometries are availabe as the .xyz file.

- **NICS-scan calculations**

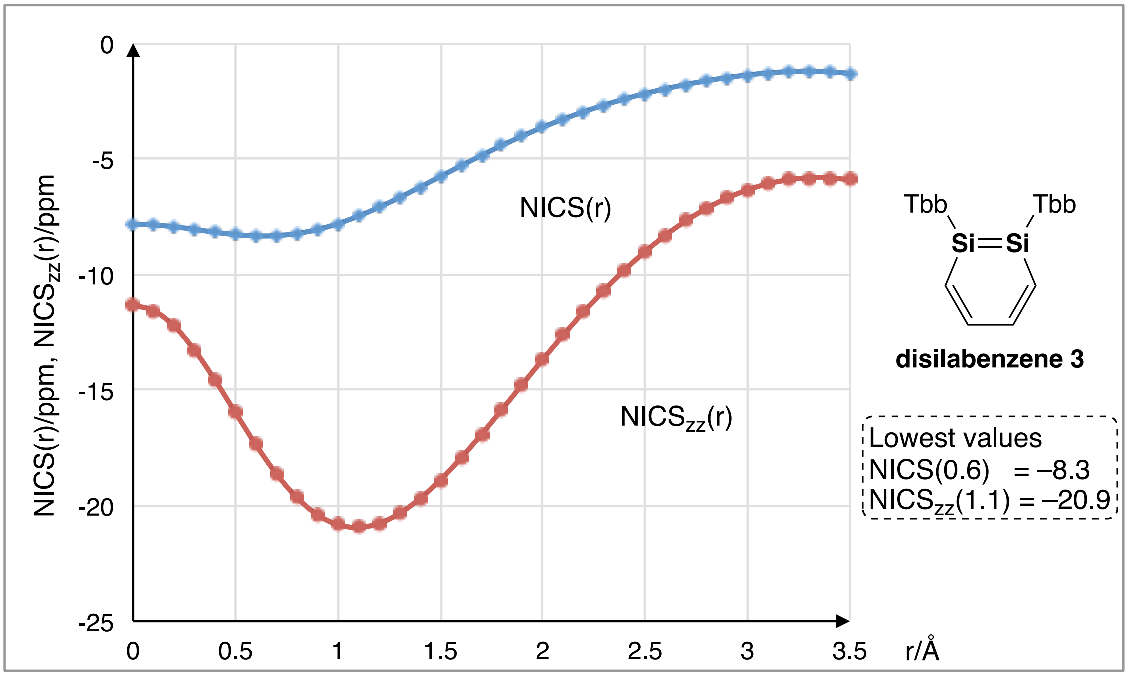

Figure S13. NICS(r) and NICS$_{zz}$(r) values for 1,2-disilabenzene **3**, calculated at the GIAO-B3PW91/6-311(3df,p)//B3PW91/6-31G(2d,p) level of theory.

5. References

S1) A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, F. J. Timmers, *Organometallics*, 1996, **15**, 1518-1520.

S2) T. Agou, N. Hayakawa, T. Sasamori, T. Matsuo, D. Hashizume, N. Tokitoh, *Chem.-Eur. J.,* 2014, **20**, 9246-9249.

S3) M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, R. Spagna, *J. Appl. Cryst.,* 2005, **38**, 381-388.

S4) G. M. Sheldrick, *Acta Crystallogr. Sect. A,* 2008, **64**, 112-122.

S5) G. M. Sheldrick, *Acta Crystallogr. Sect. C*, 2015, **71**, 3-8.

S6) Gaussian 09, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, 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, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2013**.