Electronic Supplementary Information for

1,2-Dialkynyldisilenes: Silicon analogues of (*E*)-enediyne

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1. Experimental detail

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) prior to use.[S1] ^{1}H NMR (400 or 300 MHz) and ^{13}C NMR (100 or 75 MHz) spectra were measured in C_6D_6 with a JEOL JNM AL-400 or AL-300 spectrometer. A signal due to C_6D_5H (7.15 ppm) was used as an internal standard in ^{1}H NMR, and that due to C_6D_6 (128 ppm) was used in ^{13}C NMR. 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. All melting points (m.p.) were determined on a Yanaco micro melting point apparatus. Elemental analyses were carried out at the Microanalytical Laboratory of the Institute for Chemical Research, Kyoto University. BbtBr were prepared according to the reported procedures.[S2]

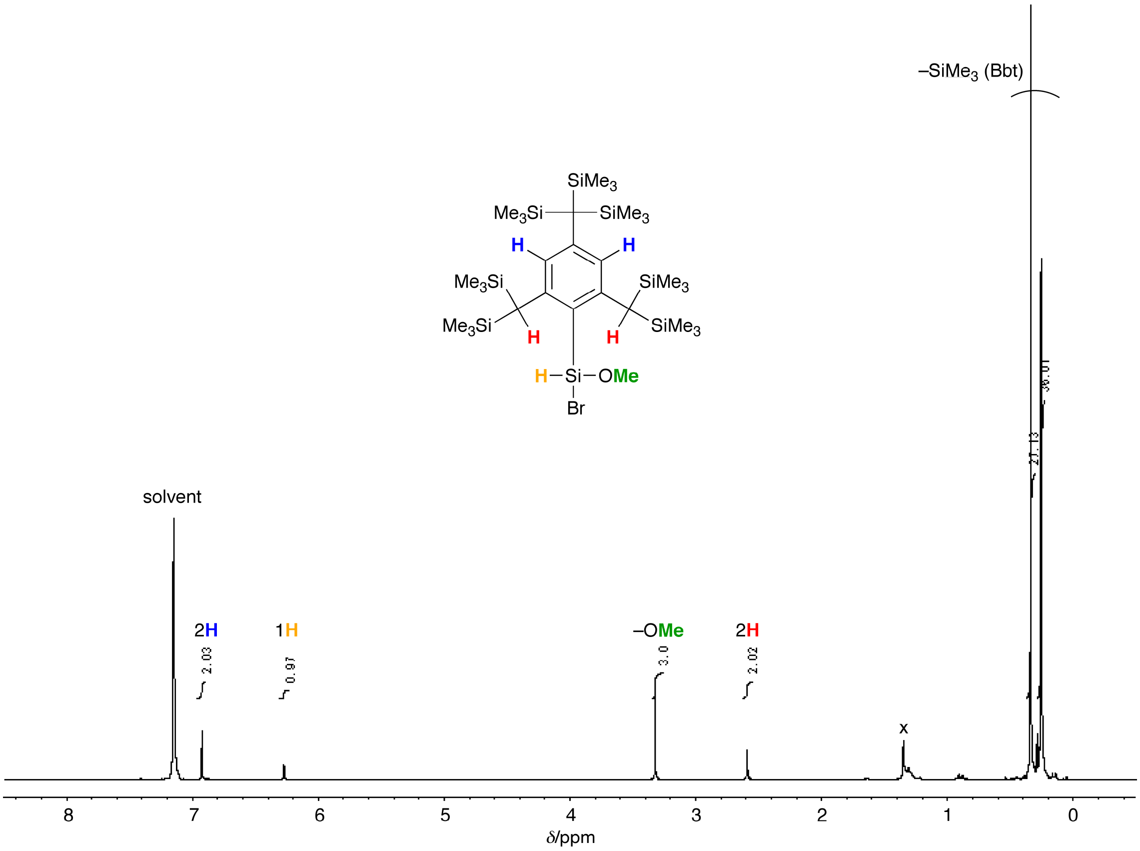
Synthesis of Bbt-substituted dimethoxysilane 3. To a THF solution (30 mL) of BbtBr (4.93 g, 7.00 mmol) at –78 °C was added *t*-BuLi (1.58 M, 4.87 mL, 7.70 mmol). After stirring for 30 min., trimethoxysilane (3.56 mL 28.0 mmol) was added to the solution followed by warm up to room temperature overnight. Then methanol was added to the reaction mixture and the solvent was removed under reduced pressure. The residue was purified with column chromatography (SiO_2, hexane/$CHCl_3$ = 90/10, rf = 0.40) to give **3** (4.08 g, 5.70 mmol, 81%) as colorless solid.

3: m.p. 200 ºC (dec.); ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 0.26 (s, 36H), 0.36 (s, 27H), 1.68 (s, 2H), 3.43 (s, 6H), 5.44 (s, 1H), 6.89 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ 1.41 (q), 5.61 (q), 22.51 (s), 28.49 (d), 51.80 (q), 126.79 (d), 127.41 (s), 147.52 (s), 151.82 (s); ^{29}Si NMR (60 MHz, $CDCl_3$, 298 K): δ –21.9, 0.9, 1.0; HRMS (FAB) *m/z* calcd for $C_{32}H_{74}O_2Si_8$ 714.3843 ($[M]^+$). Found: 714.3853 ($[M]^+$). Anal. Calcd for $C_{32}H_{74}O_2Si_8$: C, 53.71; H, 10.42. Found: C, 53.57; H, 10.33.

Synthesis of Bbt-substituted bromo(methoxy)silane 4. To a hexane (3.0 mL) solution of **3** (148 mg, 0.206 mmol) was added BBr_3 in hexane (1.0 M, 0.512 mL, 0.512 mmol) at room temperature. After stirring for 2 h at room temperature, the solvent was removed under reduced pressure. Hexane was added to the residue and the resulting suspension was filtered through Celite® to remove inorganic salts. The filtrate was pumped up to afford **4** (149.6 mg, 0.196 mmol, 95%) as colorless solid.

4: m.p. 172–174 °C; ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 0.25 (s, 18H), 0.26 (s, 18H), 0.34 (s, 27H), 2.60 (s, 2H), 3.32 (s, 3H), 6.27 (s, 1H), 6.93 (s, 2H); ^{13}C NMR (75 MHz, C_6D_6, 298 K): δ 1.46 (q), 1.53 (q), 5.56 (q), 23.06 (s), 29.13 (d), 52.30 (q), 127.16 (d), 129.92 (s), 149.44 (s), 152.55 (s); ^{29}Si NMR (60 MHz, C_6D_6, 296 K): δ –18.6, 1.0, 1.9, 2.6; HRMS (FAB) *m/z* calcd for $C_{28}H_{71}{}^{79}BrOSi_7$ 762.2842 ($[M]^+$). Found: 762.2833 ($[M]^+$).

Fig. S1. ^{1}H NMR spectrum of **4** (C_6D_6, r.t.).



Synthesis of Bbt-substituted methoxy(alkynyl)silanes 5. For **5a**, to a THF (40 mL) solution of trimethylsilylacetylene (7.2 mL, 51.1 mmol) was added *n*-BuLi in hexane (1.51 M, 46.5 mmol 30.8 mL) at 0 °C. After stirring for 30 min., the solution was cooled to –50 °C. A THF (90 mL) solution of **4** (11.9 g, 15.5 mmol) was added to the reaction mixture. After stirring for 2 h, the reaction mixture was quenched by aq. NH_4Cl and extracted with hexane/H_2O. Organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO_2) to give **5a** (9.06 g, 11.5 mmol, 74%) as colorless solid. In the similar manner using phenylacetylene as a reagent, **5b** was isolated in 64% yield.

5a: colorless solid; m.p. 138 ºC (dec.); ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 0.05 (s, 18H), 0.06 (s, 18H), 0.14 (s, 9H), 0.24 (s, 27H), 2.345 (s, 1H), 2.349 (s, 1H), 3.57 (s, 3H), 5.30 (s, 1H), 6.67 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$, 298 K) δ –0.40 (q), 1.17 (q), 1.21 (q), 5.35 (q), 22.29 (s), 28.67 (d), 52.27 (q), 109.62 (s), 117.22 (s), 124.95 (s), 126.37 (d), 147.26 (s), 151.77 (s); ^{29}Si NMR (60 MHz, $CDCl_3$, 298 K): δ –37.5, –18.3, 0.7, 1.5, 1.8; HRMS (FAB) *m/z* calcd for $C_{36}H_{80}OSi_9$ 780.4133 ($[M]^+$). Found: 780.4128 ($[M]^+$). Anal. Calcd for $C_{36}H_{80}OSi_9$: C, 55.31; H, 10.31. Found: C, 55.25; H, 10.31.

5b: colorless solid; m.p. 104 °C (dec.); ^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 0.11 (s, 18H), 0.13 (s, 18H), 0.30 (s, 27H), 2.56 (s, 2H), 3.68 (s, 3H), 5.53 (s, 1H), 6.75 (s, 2H), 7.30–7.35 (m, 3H), 7.45–7.50 (m, 2H);

^{13}C NMR (75 MHz, CDCl$_3$, 298 K): δ 1.21 (q), 1.27 (q), 5.44 (q), 22.39 (s), 28.69 (d), 52.28 (q), 91.03 (s), 107.61 (s), 122.71 (s), 125.27 (s), 126.49(d), 128.29(d), 128.92 (d), 131.99 (d), 147.41 (s), 151.85 (s); ^{29}Si NMR (60 MHz, CDCl$_3$, 298 K): δ –36.1, 0.7, 1.5, 2.1; HRMS *m/z* calcd for $C_{39}H_{76}OSi_8$ 784.4050 ([M$^+$]). Found: 784.4048 ([M$^+$]). Anal. Calcd for $C_{39}H_{76}OSi_8$: C, 59.62; H, 9.75. Found: C, 59.57; H, 9.66.

Synthesis of Bbt-substituted alkynylsilanes 6. For **6a**, to a Et$_2$O (8.0 mL) solution of **5a** (597 mg, 0.764 mmol) was added LiAlH$_4$ (232 mg, 6.11 mmol) at 0 °C. After stirring for 30 min., EtOAc was added to the reaction mixture followed by Celite® filtration to remove inorganic salts. The residue was purified by column chromatography (SiO$_2$) to afforded **6a** (567 mg, 0.754 mmol, 99%) as colorless solid. In the similar manner using **5b** as a precursor, **6b** was isolated in 97% yield.

6a: white solid; m.p. 145 °C (dec.); ^{1}H NMR (300 MHz, CDCl$_3$, 298 K): δ 0.06 (s, 36H), 0.13 (s, 9H), 0.24 (s, 27H), 2.19 (s, 2H), 4.70 (s, 2H), 6.73 (s, 2H); ^{13}C NMR (75 MHz, CDCl$_3$, 298 K): δ –0.42 (q), 1.11 (q), 5.30 (q), 22.38(s), 31.39 (d), 105.93 (s), 117.97 (s), 123.60 (s), 125.94 (d), 147.02 (s), 151.69 (s); ^{29}Si NMR (60 MHz, CDCl$_3$, 298 K): δ –75.5, –18.4, 0.7, 1.8; HRMS (FAB) *m/z* calcd for $C_{35}H_{78}Si_9$ 750.4027 ([M]$^+$). Found: 750.4033 ([M]$^+$). Anal. Calcd for $C_{35}H_{78}Si_9$: C, 55.92; H, 10.46. Found: C, 55.95; H, 10.46.

6b: white solid; m.p. 155–156 °C; ^{1}H NMR (300 MHz, C$_6$D$_6$, 298 K): δ 0.26 (s, 36H), 0.35 (s, 27H), 2.63 (s, 2H), 5.23 (s, 2H), 6.89–6.94 (m, 3H), 6.98 (s, 1H), 7.47–7.51 (m, 2H); ^{13}C NMR (75 MHz, C$_6$D$_6$, 298 K): δ 1.40 (q), 5.57 (q), 22.71 (s), 31.79 (d), 87.55 (s), 108.73 (s), 123.23 (s), 124.46 (s), 126.61 (d), 128.59 (d), 129.14 (d), 132.18 (d), 147.62 (s), 152.33 (s); ^{29}Si NMR (60 MHz, C$_6$D$_6$, 298 K): δ –73.6, 0.9, 2.1; HRMS *m/z* calcd for $C_{38}H_{74}Si_8$: 754.3945 ([M$^+$]), Found: 754.3944 ([M$^+$]). Anal. Calcd for $C_{38}H_{74}Si_8$: C, 60.40; H, 9.87. Found: C, 60.21; H, 9.72.

Synthesis of Bbt-substituted dichloro(trimethylsilylethynyl)silane 7a. NBS (171 mg, 0.962 mmol) was added to the CCl$_4$ solution (10 mL) of **6a** (344 mg, 0.458 mmol) at room temperature. After stirring at room temperature for 1 h, the solvent was removed under reduced pressure. Hexane was added to the residue and the resulting suspension was filtered to remove the inorganic salts. The filtrate was separated by GPLC (gel permeation liquid chromatography) to afford **7a** (276 mg, 0.337 mmol, 74%) as colorless crystals.

7a: white solid; m.p. 209 °C (dec.); ^{1}H NMR (300 MHz, C$_6$D$_6$, 298 K): δ 0.11 (s, 9H), 0.31 (s, 27H), 0.35 (s, 36H), 3.49 (s, 2H), 6.95(s, 2H); ^{13}C NMR (75 MHz, C$_6$D$_6$, 298 K): δ –0.78 (q), 1.83 (q), 5.68 (q), 23.18(s), 29.58 (d), 111.12 (s), 123.73 (s), 124.18 (s), 128.10 (d), 150.15 (s), 153.13 (s); ^{29}Si NMR (60 MHz, CDCl$_3$, 298 K): δ –36.2, –15.8, 1.3, 2.8; HRMS (FAB) *m/z* calcd for $C_{35}H_{76}{}^{35}Cl^{37}ClSi_9$ 818.3247 ([M]$^+$). Found: 818.3248 ([M]$^+$). Anal. Calcd for $C_{35}H_{76}Br_2Si_9$: C, 51.25; H, 9.29. Found: C, 51.22; H, 9.33.

Synthesis of Bbt-substituted dibromo(alkynyl)silanes 8. For **8a**, NBS (380 mg, 2.14 mmol) was added to the benzene solution (10 mL) of **6a** (764 mg, 1.02 mmol) at 7 °C. After stirring at room temperature for 2 h, the solvent was removed under reduced pressure. Hexane was added to the residue and the resulting suspension was filtered to remove the inorganic salts. The filtrate was recrystallized with hexane to afford **7a** (153 mg, 0.501 mmol, 49%) as colorless crystals. In the similar manner using **6b** as a precursor, **8b** was isolated in 74% yield. g

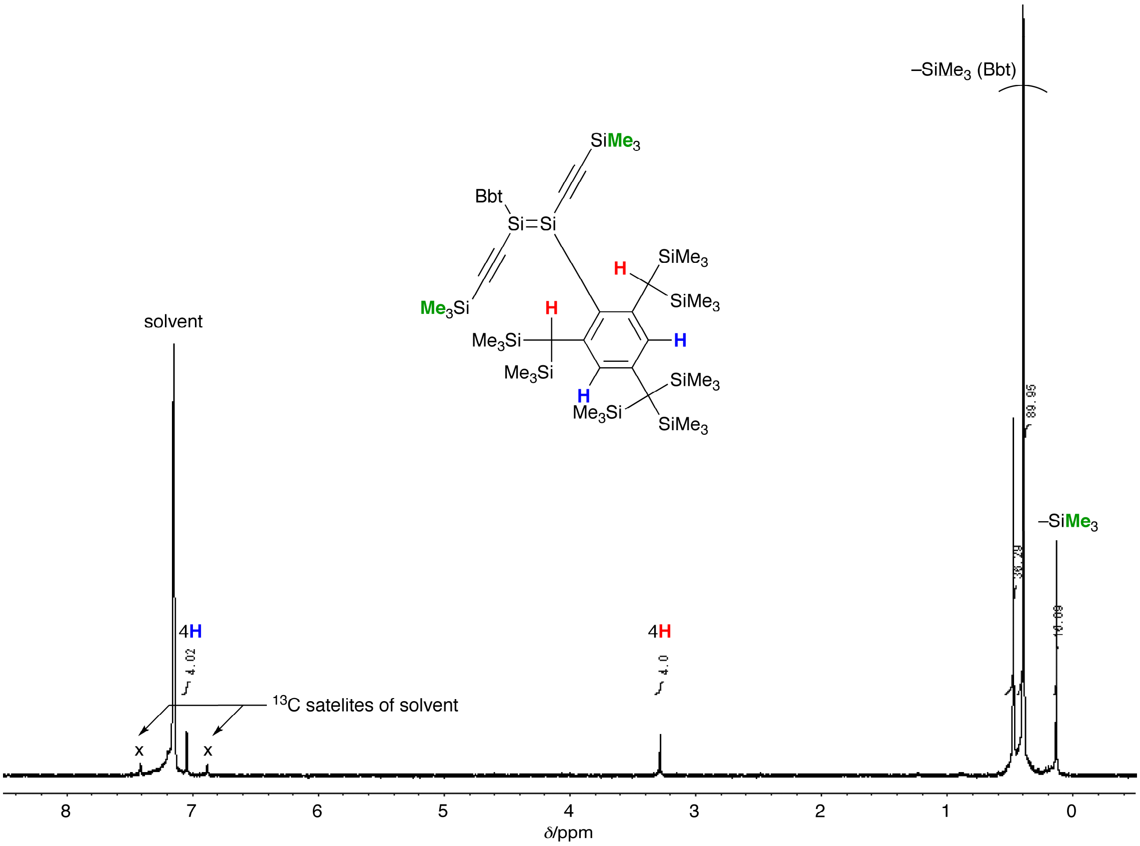
8a: white solid; m.p. 218 °C (dec.); ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 0.13 (s, 9H), 0.33 (s, 27H), 0.34 (s, 36H), 3.64 (s, 2H), 6.94 (s, 2H); ^{13}C NMR (75 MHz, C_6D_6, 298 K): δ –0.84 (q), 2.06 (q), 5.69 (q) 23.20(d), 29.71 (d), 112.07 (s), 123.60 (s), 125.88 (s), 127.19 (d), 150.31 (s), 153.16 (s); ^{29}Si NMR (60 MHz, $CDCl_3$, 298 K): δ –47.0, –15.9, 1.2, 2.7; HRMS (FAB) *m/z* calcd for $C_{35}H_{76}{}^{79}Br_2Si_9$ 906.2237 ([M]$^+$). Found: 906.2253 ([M]$^+$). Anal. Calcd for $C_{35}H_{76}Br_2Si_9$: C, 46.22; H, 8.42. Found: C, 45.97; H, 8.27.

8b: white solid; m.p. 228 °C (dec.); ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 0.32 (s, 36H), 0.34 (s, 27H), 3.77 (s, 2H), 6.89–6.98 (m, 3H), 6.97 (s, 2H), 7.43–7.45 (m, 2H); ^{13}C NMR (75 MHz, C_6D_6, 298 K): δ 2.11 (q), 5.76 (q), 23.41 (s), 29.80 (d), 93.77 (s), 114.90 (s), 121..88(s), 123.81 (s), 128.48 (d), 128.60 (d), 130.03 (d), 132.21 (d), 150.41 (s), 153.34 (s); ^{29}Si NMR (60 MHz, C_6D_6, 298 K): δ –45.0, 1.2, 2.2, 2.6. HRMS *m/z* calcd for $C_{38}H_{72}{}^{79}Br^{81}BrSi_8$: 912.2140 ([M$^+$]), Found: 912.2123 ([M$^+$]). Anal. Calcd for $C_{38}H_{72}Br_2Si_8$: C, 49.96; H, 7.94. Found: C, 49.80; H, 7.68.

Synthesis of Bbt-substituted (*E*)-1,2-dialkynyldisilenes 1. For **1a**, to a solution of **8a** (1.24 g, 1.36 mmol) in THF (15 mL) was added a THF solution of lithium naphthalenide (0.50 M, 5.5 mL, 2.7 mmol) dropwise at –78 °C. After stirring at –40 °C for 2 h, the reaction mixture was allowed to warm up to room temperature and concentrated in vacuo. Hexane was added to the residue and the resulting suspension was filtered through a plug of Celite®. The filtrate was recrystallized with hexane several times to afford **1a** (536 mg, 0.358 mmol, 53% yield) as yellow crystals. In the similar manner using **7a** and **8b**, **1a** and **1b** were isolated in 23 or 41% yield, respectively.

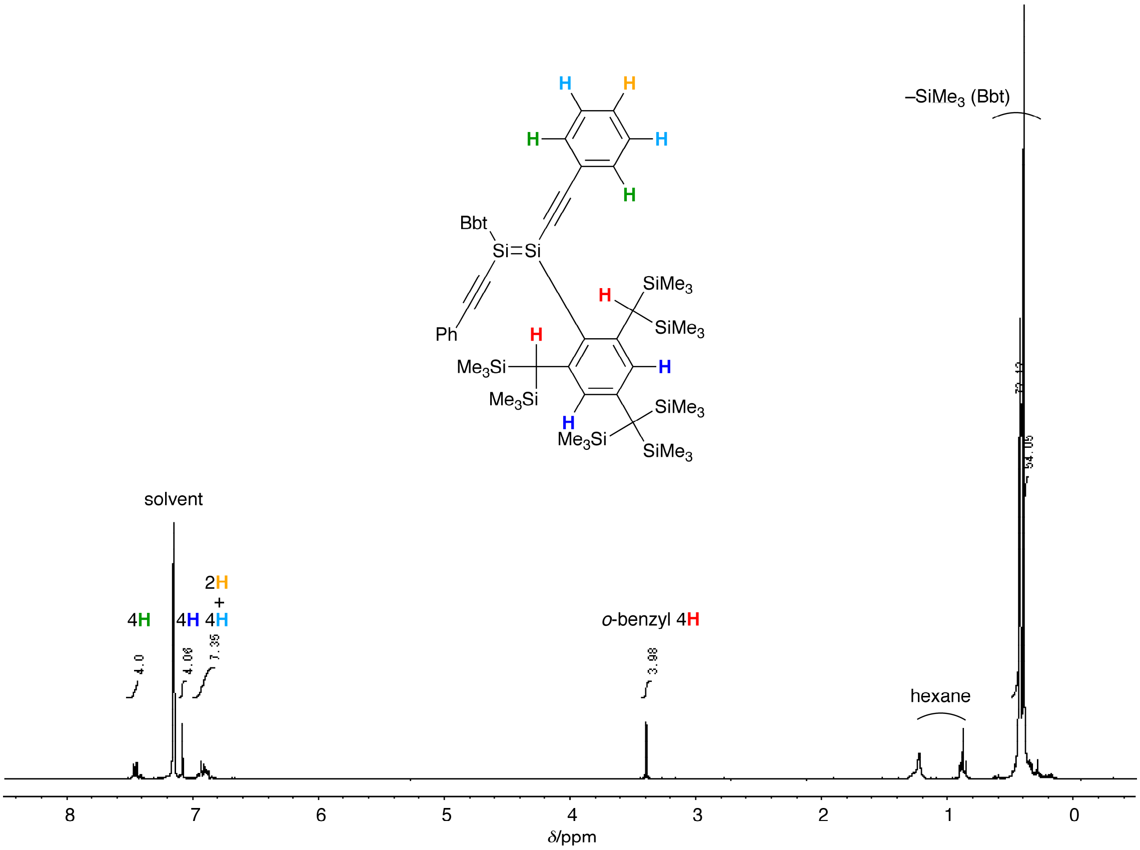
1a: yellow crystals; m.p. 251 °C (dec.); ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 0.14 (s, 18H), 0.40 (s, 90H), 0.48 (s, 36H), 3.28 (s, 4H), 7.04 (s, 4H); ^{13}C NMR (75 MHz, C_6D_6, 298 K): δ –0.15 (q), 1.59 (q), 5.70 (q) 22.56(d), 28.95 (d), 112.16 (s), 116.73 (s), 126.25 (s), 127.68 (d), 150.31 (s), 153.16 (s); ^{29}Si NMR (60 MHz, C_6D_6, 298 K): δ –19.0 (C≡C–*Si*Me$_3$), 0.9 [C(*Si*Me$_3$)$_3$], 1.2 [CH(*Si*Me$_3$)$_2$], 2.7 [CH(*Si*Me$_3$)$_2$], 44.6 (*Si*=*Si*); HRMS (FAB) *m/z* calcd for $C_{70}H_{152}Si_{18}$ 1496.7741 ([M]$^+$). Found: 1496.7736 ([M]$^+$); Anal. Calcd for $C_{70}H_{152}Si_{18}$: C, 56.07; H, 10.22. Found: C, 55.86; H, 10.05. UV/vis (hexane, r.t.): λ_{max} = 437 nm (ε = 2.4×10^4).

Fig. S2. ^{1}H NMR spectrum of **1a** (C_6D_6, r.t.).



1b: orange crystals; m.p. 280–282 °C; ^{1}H NMR (300 MHz, C_6D_6, 323 K): δ 0.40 (s, 72H), 0.43 (s, 54H), 3.39 (s, 4H), 6.86–6.96 (m, 6H), 7.08 (s, 4H), 7.41–7.47 (m, 4H); ^{13}C NMR (100 MHz, C_6D_6, 323 K): 2.41 (q), 6.06 (q), 31.87 (d), 37.46 (d), 94.97 (s), 119.57 (s), 124.35 (s), 127.21 (d), 128.50 (d), 128.62 (d), 130.83 (s), 132.26 (d), 148.13 (s), 152.63(s); ^{29}Si NMR (60 MHz, C_6D_6, 343 K): δ 1.0 [C(*Si*Me$_3$)$_3$], 2.1 ([CH(*Si*Me$_3$)$_2$]), 42.6 (*Si*=*Si*); HRMS *m/z* calcd for $C_{76}H_{144}Si_{16}$: 1504.7576 ([M$^+$]), Found: 1504.7594 ([M$^+$]). UV/vis (hexane, r.t.): λ_{max} = 469 nm (ε = 3.1 × 10^4).

Fig. S3. ^{1}H NMR spectrum of **1b** (C_6D_6, r.t.).

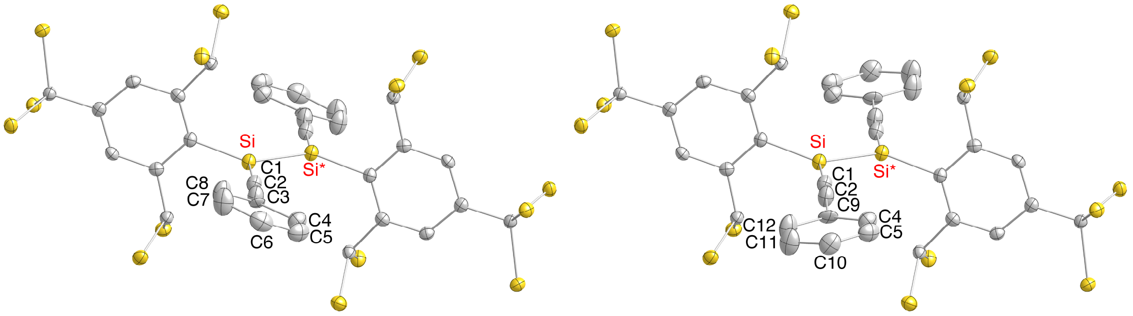


2. X-ray crystallographic analysis of 1a and 1b.

The intensity data were collected on a Rigaku/MSC Mercury CCD diffractometer with graphite monochromated MoKα radiation (λ = 0.71070 Å). Single crystals of **1a** and **1b** suitable for X-ray analysis were obtained by slow evaporation from their THF/benzene and hexane solution, respectively. The structure was 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 the other atoms were refined anisotropically.

In the case of **1b**, the phenylethynyl groups were disordered with 1:1 ratio. C1, C2, C4 and C5 atoms were shared in the two disorders (Fig. S4).

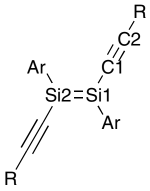
Fig. S4. Disorders in compound **1b**. Hydrogen atoms and methyl groups of $SiMe_3$ were omitted for clarity.

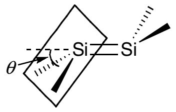


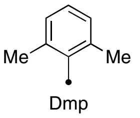
3. UV/vis spectrum of 1a and 1b.

UV/vis spectra were measured by JASCO Ubest V-570. In a glovebox filled with argon, three samples with different concentration of the solution (**1a**: 2.0 × 10^{-5}, 4.0 × 10^{-5}, 6.0 × 10^{-5} M, **1b**: 3.3 × 10^{-6}, 6.4 × 10^{-6}, 1.3 × 10^{-5} M) were prepared by the dilution of mother solution and put into UV cell (1 cm optical path length).

4. Theoretical Calculations







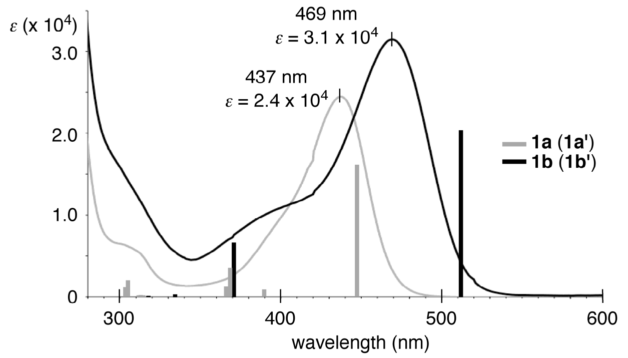
Theoretical calculations were performed by Gaussian 03[S5] program using model compounds **1a'** and **1b'**, in which all of the Bbt groups in **1a** and **1b** were replaced by 2,6-dimethylphenyl groups. The geometry optimizations of **1a'** and **1b'** were performed at the B3LYP/6-31G(d) level. The selected bond lengths and *trans*-bent angles θ were summarized in Table S1, and the Cartesian coordinates of **1a'** and **1b'** are shown in Tables S2 and S3, respectively. TD-DFT calculations for **1a'** and **1b'** were carried out at B3LYP/6-311+G(2df,2p)//B3LYP/6-31G(d) level, which results were summarized in Fig. S5, and the plots of the selected molecular orbitals of **1a'** and **1b'** are shown in Fig. S6.

Table S1. Selected bond lengths (Å) and *trans*-bent angles θ (deg).

Ar	R	Si1–Si2	Si1–C1	C1–C2	C2–R	θ
Dmp (calcd)	$SiMe_3$	2.173	1.812	1.229	1.847	15.3
Bbt (obsd)	$SiMe_3$	2.202(2)	1.811(4)	1.213(6)	1.842(5)	8.9
Dmp (calcd)	Ph	2.195	1.805	1.226	1.423	27.2
Bbt (obsd)	Ph	2.1871(10)	1.8029(19)	1.214(3)	1.453[a]	11.3

[a] The *ipso*-carbon of phenyl ring was disordered and averaged value was noted.

Fig. S5. UV/Vis spectra of **1a** and **1b** with the results of the TD-DFT calculations for **1a'** and **1b'**.



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For 1a':
 Excited State 1: 2.7631 eV  448.71 nm  f = 0.4042
    HOMO   -> LUMO          0.58974
    HOMO   -> LUMO+1        0.17229

 Excited State 2: 3.1729 eV  390.75 nm  f = 0.0219
    HOMO   -> LUMO+1        0.36798
    HOMO   -> LUMO+3        0.57871

 Excited State 3: 3.3665 eV  368.29 nm  f = 0.0892
    HOMO   -> LUMO+1        0.45282
    HOMO   -> LUMO+2       -0.37977
    HOMO   -> LUMO+3       -0.33835

 Excited State 4: 3.3709 eV  367.80 nm  f = 0.0319
    HOMO   -> LUMO+1        0.32021
    HOMO   -> LUMO+2        0.57758
    HOMO   -> LUMO+3       -0.18887

For 1b':
 Excited State 1: 2.4245 eV  511.39 nm  f = 0.7021
    HOMO   -> LUMO          0.60231

 Excited State 2: 3.3374 eV  371.50 nm  f = 0.1675
    HOMO-4 -> LUMO          0.10485
    HOMO   -> LUMO+2        0.67154
    HOMO   -> LUMO+7       -0.11419
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Fig. S6. Selected molecular orbitals of **1a’** and **1b’** (isosurface at ±0.02 a.u.).

Table S2. Coordinates (Å) of the optimized structure for **1a**´ calculated at the B3LYP/6-31G(d) level.

Atom	X	Y	Z
Si	0.579343	0.871964	-0.159929
Si	-0.640431	-0.889249	0.201433
C	-2.434720	-0.667990	0.103734
C	2.369884	0.626143	-0.034965
C	3.586485	0.457141	0.017404
C	-3.652970	-0.502095	0.109105
C	0.025713	2.670965	-0.081252
C	0.399651	3.519731	-1.156410
C	-0.733305	3.197009	0.994521
C	0.020473	4.865891	-1.135365
C	-1.092783	4.550668	0.976120
C	-0.721954	5.381602	-0.076771
C	0.310126	5.511992	-1.960540
C	-1.669626	4.954732	1.804557
C	-1.010720	6.429650	-0.071973
C	-0.010483	-2.651616	0.000396
C	-0.400465	-3.428995	-1.121350
C	0.848105	-3.214355	0.979271
C	0.064009	-4.743950	-1.237918
C	1.291750	-4.532961	0.823622
C	0.903513	-5.295488	-0.274133
H	-0.235090	-5.336980	-2.098842
H	1.946830	-4.963920	1.576863
H	1.255255	-6.318824	-0.378871
C	1.202475	3.007158	-2.332821
H	2.203823	2.677800	-2.030622
H	0.714350	2.147840	-2.811075
H	1.322843	3.786040	-3.092535
C	-1.180236	2.354678	2.169335
H	-1.966782	1.646683	1.882641
H	-0.356826	1.764050	2.585984
H	-1.579326	2.988414	2.968009
C	1.314412	-2.435022	2.190983
H	1.996239	-1.623466	1.910396

H	0.476538	-1.977255	2.730115
H	1.844884	-3.089252	2.890708
C	-1.295432	-2.875847	-2.207768
H	-2.294993	-2.635294	-1.828926
H	-0.886450	-1.949521	-2.630018
H	-1.407710	-3.596475	-3.024022
Si	-5.481555	-0.246030	0.093151
Si	5.412773	0.200077	0.102638
C	5.829898	-0.608701	1.759652
H	5.323466	-1.574339	1.868951
H	6.909470	-0.785093	1.844668
H	5.526415	0.025510	2.600101
C	5.935499	-0.923552	-1.324137
H	7.017425	-1.104321	-1.299101
H	5.431474	-1.895013	-1.270310
H	5.692629	-0.475344	-2.294113
C	6.256430	1.885405	-0.038166
H	6.017071	2.372669	-0.990032
H	5.941389	2.556138	0.768998
H	7.346945	1.779699	0.019281
C	-6.317376	-1.932216	-0.078712
H	-7.409198	-1.824761	-0.081049
H	-6.027780	-2.427676	-1.012222
H	-6.047818	-2.596618	0.749881
C	-5.990009	0.578436	1.716564
H	-5.729047	-0.045301	2.578882
H	-5.493919	1.547463	1.842095
H	-7.073259	0.750926	1.742593
C	-5.921972	0.864170	-1.371459
H	-5.421952	1.836432	-1.298286
H	-5.624499	0.406802	-2.321716
H	-7.003546	1.044681	-1.409466

Table S3. Coordinates (Å) of the optimized structure for **1b’** calculated at the B3LYP/6-31G(d) level.

Atom	X	Y	Z
Si	0.548079	0.888450	0.339761
Si	-0.548240	-0.887296	-0.339641
C	2.345411	0.783389	0.206043
C	-0.175645	2.622181	0.158677
C	-2.345602	-0.782756	-0.205945
C	0.175863	-2.620876	-0.158495
C	3.565747	0.667334	0.223914
C	-3.566013	-0.667496	-0.223878
C	-1.098287	3.091714	1.128321
C	-1.628881	4.381213	1.003913
C	-1.264313	5.205776	-0.056669
C	-0.364361	4.745314	-1.013661
C	0.187636	3.461867	-0.926499
C	1.098262	-3.090412	-1.128364
C	1.629194	-4.379766	-1.003863
C	1.265186	-5.204179	0.057027
C	0.365457	-4.743717	1.014229
C	-0.186859	-3.460413	0.926983
C	1.139296	3.006872	-2.010316
C	-1.541798	2.238978	2.299707
C	1.541122	-2.237845	-2.300121
C	-1.138256	-3.005394	2.011020
C	-4.981529	-0.526372	-0.234575
C	-5.816700	-1.661777	-0.283305
C	-7.200521	-1.514886	-0.294945
C	-7.775450	-0.241716	-0.256900
C	-6.956225	0.889462	-0.208641
C	-5.571166	0.754613	-0.198458
C	4.981155	0.525130	0.234413
C	5.817247	1.659861	0.282992
C	7.200951	1.511848	0.294422
C	7.774848	0.238214	0.256316
C	6.954703	-0.892304	0.208208
C	5.569753	-0.756334	0.198240

H	-2.332904	4.739599	1.751135
H	-1.682780	6.205853	-0.138684
H	-0.086650	5.386156	-1.847070
H	2.333027	-4.738158	-1.751261
H	1.683908	-6.204142	0.139115
H	0.088173	-5.384447	1.847867
H	1.225417	3.764128	-2.795977
H	2.142556	2.810843	-1.616729
H	0.796166	2.075010	-2.476602
H	-2.175204	2.816935	2.980608
H	-2.117042	1.366056	1.969264
H	-0.689319	1.861398	2.877073
H	2.174581	-2.815749	-2.981018
H	0.688334	-1.860792	-2.877379
H	2.116095	-1.364593	-1.970088
H	-2.141617	-2.809402	1.617672
H	-0.795023	-2.073503	2.477174
H	-1.224164	-3.762613	2.796738
H	-5.366278	-2.649081	-0.313134
H	-7.833736	-2.397133	-0.333470
H	-8.856344	-0.131679	-0.265734
H	-7.399013	1.881391	-0.180314
H	-4.930508	1.630373	-0.164072
H	5.367631	2.647531	0.312867
H	7.834887	2.393583	0.332829
H	8.855654	0.127308	0.264985
H	7.396683	-1.884591	0.179836
H	4.928376	-1.631573	0.163969

References

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

S2 Unno, M. Dissertation, The University of Tokyo, 1988.

S3 A. Altomare, M. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. Moliterni, G. Polidori, R. Spagna, *J. Appl. Cryst.* 1999, **32**, 115.

S4 (a) G. M. Sheldrick, *Acta Crystallogr. Sect. A* 1990, **46**, 467. (b) G. M. Sheldrick, SHELX-97 Program for Crystal Structure Solution and the Refinement of Crystal Structures, Institüt für Anorganische Chemie der Universität Göttingen, Tammanstrasse 4, D-3400 Göttingen, Germany, 1997.

S5 Gaussian 03, Revision E.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.