

# **Photochemical Isomerisation of Boryl-Substituted Silole Derivatives**

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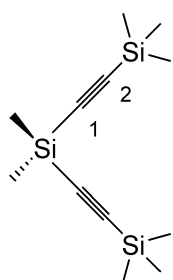
## **Supporting Information**

**General Procedures.** Reactions with air- and moisture sensitive compounds were carried out under an argon atmosphere using Schlenk-type glassware or a glovebox. Solvents were dried with the procedure reported by *Grubbs* (Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics*, 1996, 15, 1518-1520) or, particularly deuterated solvents, were distilled from appropriate drying agents and stored under an argon atmosphere. The following instruments were used for physical characterization of the compounds: NMR: Varian Inova 500 ( $^1\text{H}$ : 500 MHz;  $^{11}\text{B}$ : 161 MHz;  $^{13}\text{C}$ : 126 MHz;  $^{19}\text{F}$ : 470 MHz;  $^{29}\text{Si}$ : 99 MHz {using INEPT pulse sequence based on  $J_{\text{Si,H}} = 7$  Hz}). Most NMR assignments were supported by additional 2D experiments. The IR spectra were obtained with a Varian 3100 FT-IR (EXCALIBUR Series) spectrometer, the MS GC-EI with Triplequad TSQ (Thermo-Finnigan-MAT, Bremen). Elemental analyses were performed with a Foss-Heraeus CHN-O-Rapid instrument. Irradiation: Pyrex filtered UV light Philips-Hg-high pressure lamp (125 W: HPK 125).

X-ray Crystal Structure Analysis: Data sets were collected with Nonius KappaCCD diffractometers, in case of Mo-radiation equipped with a rotating anode generator. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods in Enzymology*, 1997, 276, 307-326), absorption correction Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Cryst.* 2003, A59, 228-234), structure solution SHELXS-97 (G.M. Sheldrick, *Acta Cryst.* 1990, A46, 467-473), structure refinement SHELXL-97 (G.M. Sheldrick, *Acta Cryst.* 2008, A64, 112-122), graphics XP (BrukerAXS, 2000).

**Bis(trimethylsilylethynyl)dimethylsilane (1a)** [R. Köster, G. Seidel, J. Süß, B. Wrackmeyer, *Chem. Ber.*, 1993, 126, 1107].

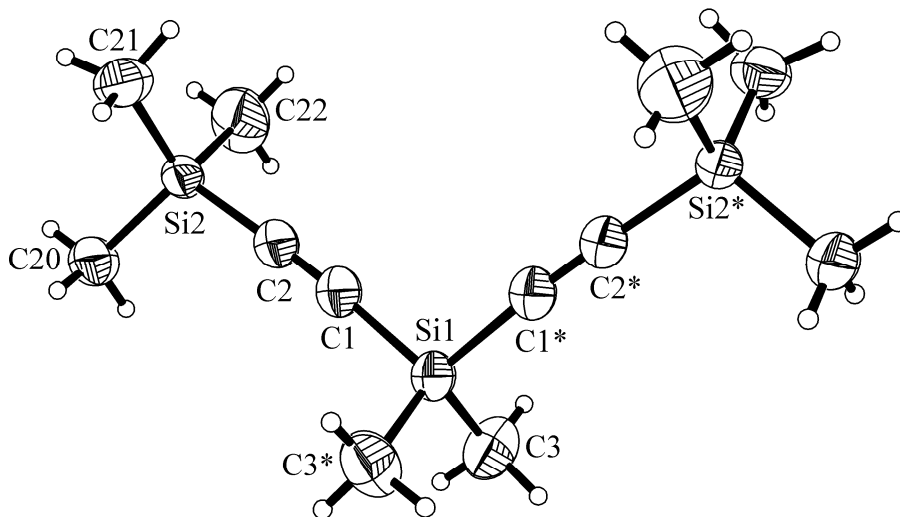
Trimethylsilylethynyllithium (3.5 g, 33.6 mmol) was dissolved under argon in 100 mL diethylether in a 300 mL Schlenk flask with stirring. The flask was then cooled to -30 °C, and dichlorodimethylsilane (2.4 mL, 24.5 mmol) was added to the cold solution with a syringe, under argon. The white suspension was stirred at low temperature for 1 hour and at room temperature overnight. Filtration over celite afforded a colourless liquid that was purified by distillation (60 °C, 10<sup>-1</sup> mbar). Isolated yield = 57% (2.45 g). The product crystallized on standing, forming crystals suitable for X-ray diffraction.



<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, TMS): δ 0.32 (s, <sup>2</sup>J<sub>Si,H</sub> = 7.6 Hz, 3 H, SiMe<sub>2</sub>), 0.07 (s, <sup>2</sup>J<sub>Si,H</sub> = 7.1 Hz, 9 H, SiMe<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, TMS): δ 115.5 (<sup>1</sup>J<sub>Si,C</sub> = 89.6 Hz, <sup>2</sup>J<sub>Si,C</sub> = 12.1 Hz, C2), 110.2 (<sup>1</sup>J<sub>Si,C</sub> = 75.9 Hz, <sup>2</sup>J<sub>Si,C</sub> = 14.8 Hz, C1), 0.5 (<sup>1</sup>J<sub>Si,C</sub> = 61.8 Hz, SiMe<sub>2</sub>), -0.3 (<sup>1</sup>J<sub>Si,C</sub> = 56.2 Hz, SiMe<sub>3</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, TMS): δ -20.6 (SiMe<sub>3</sub>), -44.6 (SiMe<sub>2</sub>). <sup>1</sup>H, <sup>13</sup>C GHSQC (126 / 500 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, TMS): δ <sup>13</sup>C / δ <sup>1</sup>H 0.5 / 0.32 (SiMe<sub>2</sub>), -0.3 / 0.07 (SiMe<sub>3</sub>). <sup>1</sup>H, <sup>13</sup>C GHMBC (500 / 126 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, TMS): δ <sup>1</sup>H / δ <sup>13</sup>C 0.32 / 110.2 (SiMe<sub>2</sub> / C1), 0.07 / 115.5 (SiMe<sub>3</sub> / C2). <sup>29</sup>Si, <sup>1</sup>H GHMQC (99 / 500 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, TMS): δ <sup>29</sup>Si / δ <sup>1</sup>H -20.6 / 0.07 (SiMe<sub>3</sub>), -44.6 / 0.32 (SiMe<sub>2</sub>).

FT-IR (KBr, cm<sup>-1</sup>): 2963, 2902, 2106 (C≡C), 1252, 1053, 842, 785, 761, 700.

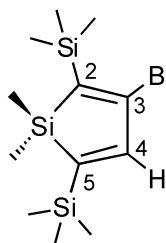
Crystal data for  $C_{12}H_{24}Si_3$  (**1a**),  $M = 252.58$ , orthorhombic, space group  $Fdd2$  (No. 43),  $a = 18.3002(4)$ ,  $b = 32.3093(7)$ ,  $c = 5.8892(1)$  Å,  $V = 3482.09(12)$  Å<sup>3</sup>,  $D_c = 0.964$  g cm<sup>-3</sup>,  $\mu = 2.299$  mm<sup>-1</sup>,  $Z = 8$ ,  $\lambda = 1.54178$  Å,  $T = 223(2)$  K, 6100 reflections collected ( $\pm h, \pm k, \pm l$ ),  $[(\sin\theta)/\lambda] = 0.60$  Å<sup>-1</sup>, 1473 independent ( $R_{int} = 0.037$ ), and 1460 observed reflections [ $I \geq 2\sigma(I)$ ], 75 refined parameters,  $R = 0.027$ ,  $wR^2 = 0.071$ ; CCDC 765606.



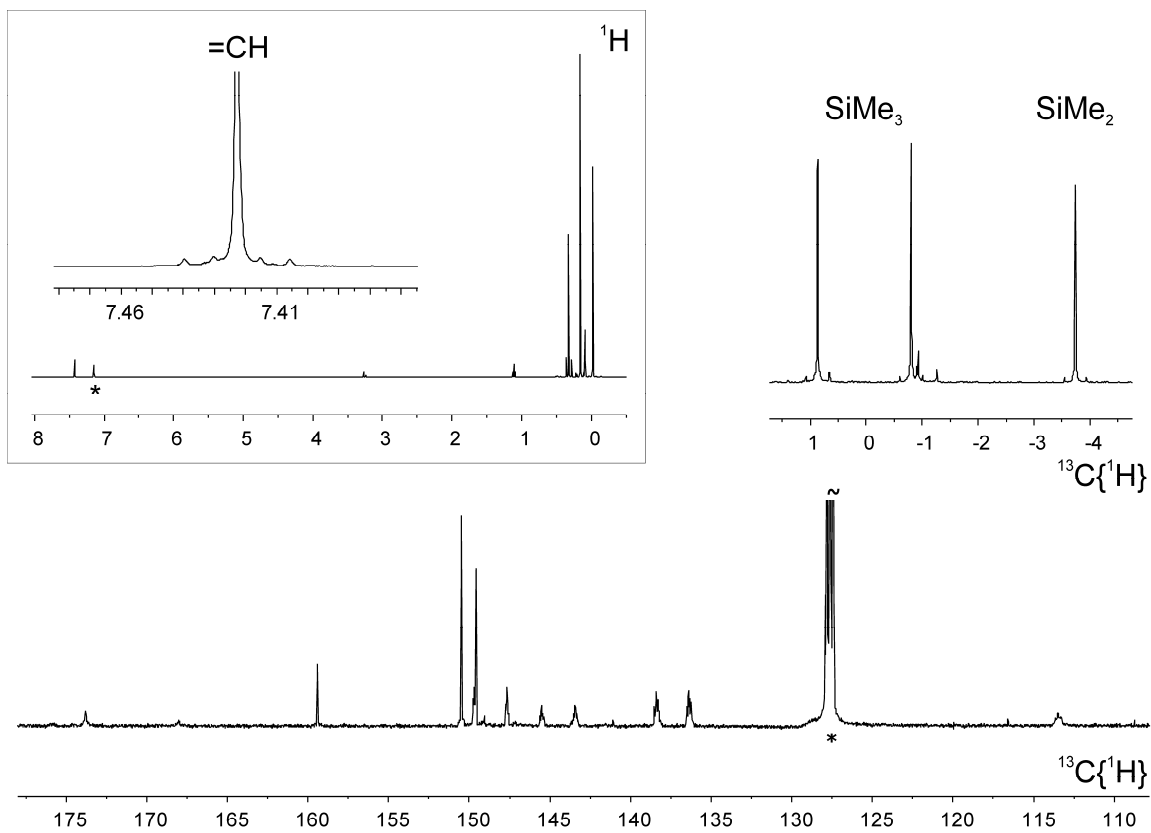
50% probability of thermal ellipsoids

### 3-[Bis(pentafluorophenyl)boryl]-2,5-bis(trimethylsilyl)dimethylsilole (3a).

Bis(trimethylsilylethynyl)dimethylsilane (1a) (438 mg, 1.734 mmol), and bis(pentafluorophenyl)borane<sup>1</sup> (600 mg, 1.734 mmol), were weighed in an argon-filled glove-box and put into a 300 mL Schlenk flask. Toluene (100 mL) was added at room temperature by cannula under argon and the resulting bright yellow solution was stirred overnight. The day after, the volatiles were removed under high vacuum leaving a yellow oily product. The product was washed with pentane (3x30 mL), and no further purification was performed. Yield 78% (815 mg).



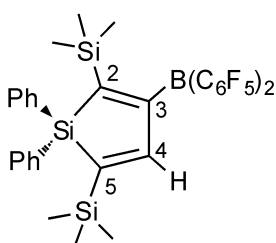
<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, TMS):  $\delta$  7.42 (s, <sup>3</sup>J<sub>Si,H</sub> = 16.9 Hz, <sup>3</sup>J<sub>Si,H</sub> = 7.5 Hz, 1 H, 4-H), 0.32 (s, <sup>2</sup>J<sub>Si,H</sub> = 6.7 Hz, 6 H, SiMe<sub>2</sub>), 0.16 (s, <sup>2</sup>J<sub>Si,H</sub> = 6.6 Hz, 9 H, 5-SiMe<sub>3</sub>), -0.02 (s, <sup>2</sup>J<sub>Si,H</sub> = 6.5 Hz, 9 H, 2-SiMe<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, TMS):  $\delta$  174.2 (br, C3), 159.8 (C2), 150.9 (C4), 149.9 (C5), 149.0 (dm, <sup>1</sup>J<sub>F,C</sub>  $\approx$  252 Hz, C<sub>6</sub>F<sub>5</sub>), 144.8 (dm, <sup>1</sup>J<sub>F,C</sub>  $\approx$  261 Hz, C<sub>6</sub>F<sub>5</sub>), 137.7 (dm, <sup>1</sup>J<sub>F,C</sub>  $\approx$  253 Hz, C<sub>6</sub>F<sub>5</sub>), 113.8 (br, *i*-C<sub>6</sub>F<sub>5</sub>), 1.2 (<sup>1</sup>J<sub>Si,C</sub> = 51.9 Hz, 2-SiMe<sub>3</sub>), -0.4 (<sup>1</sup>J<sub>Si,C</sub> = 52.2 Hz, 5-SiMe<sub>3</sub>), -3.4 (<sup>1</sup>J<sub>Si,C</sub> = 48.2 Hz, SiMe<sub>2</sub>). <sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, BF<sub>3</sub>·OEt<sub>2</sub>):  $\delta$  64 (br,  $\nu_{1/2} \approx$  1500 Hz). <sup>19</sup>F NMR (470 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, CFCl<sub>3</sub>):  $\delta$  -126.4 (m, 2 F, *o*-F), -143.6 (tt, <sup>3</sup>J<sub>F,F</sub> = 20.8 Hz, <sup>4</sup>J<sub>F,F</sub> = 6.3 Hz, 1 F, *p*-F), -160.7 (m, 2 F, *m*-F). <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, TMS):  $\delta$  25.6 (SiMe<sub>2</sub>), -7.1 (5-Si), -9.6 (2-Si). <sup>13</sup>C, <sup>1</sup>H GHSQC (126 / 500 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, TMS):  $\delta$  <sup>13</sup>C /  $\delta$  <sup>1</sup>H 150.9 / 7.42 (4-CH), 1.2 / -0.02 (2-SiMe<sub>3</sub>), -0.4 / 0.16 (5-SiMe<sub>3</sub>), -3.4 / 0.32 (SiMe<sub>2</sub>). <sup>1</sup>H, <sup>13</sup>C GHMBC (500 / 126 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, TMS):  $\delta$  <sup>1</sup>H /  $\delta$  <sup>13</sup>C 7.42 / 174.2, 159.8, 149.9 (4-H / C3, C2, C5), 0.32 / 159.8, 149.9 (SiMe<sub>2</sub> / C2, C5), 0.16 / 149.9 (5-SiMe<sub>3</sub> / C5), -0.02 / 159.8 (2-SiMe<sub>3</sub> / C2). <sup>19</sup>F, <sup>19</sup>F GCOSY (470 / 470 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, CFCl<sub>3</sub>):  $\delta$  <sup>19</sup>F /  $\delta$  <sup>19</sup>F -126.3 / -160.7 (*o*-F / *m*-F), -143.6 / -160.7 (*p*-F / *m*-F). <sup>29</sup>Si, <sup>1</sup>H GHMQC (99 / 500 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, TMS):  $\delta$  <sup>29</sup>Si /  $\delta$  <sup>1</sup>H 25.6 / 7.42, 0.32 (SiMe<sub>2</sub> / 4-H, SiMe<sub>2</sub>), -7.1 / 7.42, 0.16 (5-Si / 4-H, 5-SiMe<sub>3</sub>), -9.6 / 7.42, -0.02 (2-Si / 4-H, 2-SiMe<sub>3</sub>).



$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ , 298 K) and  
 $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ , 298 K) spectra (\* solvent).

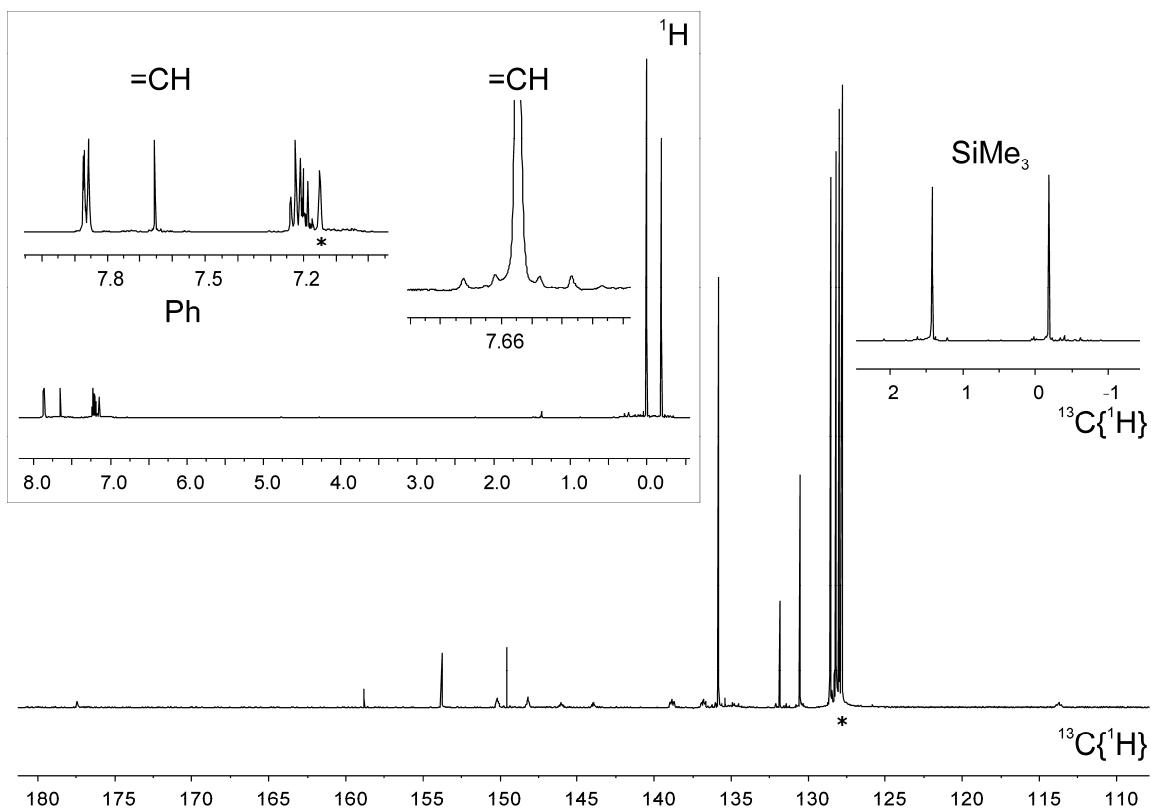
### 3-[Bis(pentafluorophenyl)boryl]-2,5-bis(trimethylsilyl)diphenylsilole (3b).

Bis(trimethylsilylethynyl)diphenylsilane<sup>2</sup> (**1b**) (421 mg, 1.118 mmol), and bis(pentafluorophenyl)borane<sup>1</sup> (381 mg, 1.101 mmol), were placed in an argon-filled glove-box into a 100 mL Schlenk flask. Toluene (40 mL) was added at room temperature by cannula under argon and the resulting bright yellow solution was stirred overnight. The day after, the volatiles were removed under high vacuum leaving a yellow glue-like product, which was washed with pentane (2 x 30 mL). Yield 78% (412 mg).



<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, TMS):  $\delta$  7.87 (m, 4 H, *o*-Ph), 7.65 (<sup>3</sup>J<sub>Si,H</sub> = 17.8 Hz, <sup>3</sup>J<sub>Si,H</sub> = 7.3 Hz, 4-H), 7.22 (m, 4 H, *m*-Ph), 7.19 (m, 2 H, *p*-Ph), 0.01 (s, <sup>2</sup>J<sub>Si,H</sub> = 6.6 Hz, 9 H, 5-SiMe<sub>3</sub>), -0.18 (s, <sup>2</sup>J<sub>Si,H</sub> = 6.6 Hz, 9 H, 2-SiMe<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, TMS):  $\delta$  177.4 (br, C3), 158.8 (C2), 153.8 (C4), 149.6 (<sup>1</sup>J<sub>Si,C</sub> = 58.7 Hz, <sup>1</sup>J<sub>Si,C</sub> = 49.5 Hz, C5), 149.2 (dm, <sup>1</sup>J<sub>F,C</sub>  $\approx$  252 Hz, C<sub>6</sub>F<sub>5</sub>), 145.0 (dm, <sup>1</sup>J<sub>F,C</sub>  $\approx$  262 Hz, C<sub>6</sub>F<sub>5</sub>), 137.8 (dm, <sup>1</sup>J<sub>F,C</sub>  $\approx$  253 Hz, C<sub>6</sub>F<sub>5</sub>), 135.8 (*o*-Ph), 131.8 (<sup>1</sup>J<sub>Si,C</sub> = 67.1 Hz, *i*-Ph), 130.5 (*p*-Ph), 128.6 (*m*-Ph), 113.7 (br, *i*-C<sub>6</sub>F<sub>5</sub>), 1.4 (<sup>1</sup>J<sub>Si,C</sub> = 51.8 Hz, 2-SiMe<sub>3</sub>), -0.2 (<sup>1</sup>J<sub>Si,C</sub> = 52.2 Hz, 5-SiMe<sub>3</sub>). <sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, BF<sub>3</sub>·OEt<sub>2</sub>):  $\delta$  64 (br,  $\nu^{1/2} \approx 1800$  Hz). <sup>19</sup>F NMR (470 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, CFCl<sub>3</sub>):  $\delta$  -126.0 (m, 2 F, *o*-F), -143.0 (tt, <sup>3</sup>J<sub>F,F</sub> = 21.1 Hz, <sup>4</sup>J<sub>F,F</sub> = 6.5 Hz, 1 F, *p*-F), -160.5 (m, 2 F, *m*-F). <sup>29</sup>Si{DEPT} NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, TMS):  $\delta$  13.2 (SiPh<sub>2</sub>), -6.2 (5-Si), -8.8 (2-Si). <sup>13</sup>C, <sup>1</sup>H GHSQC (126 / 500 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, TMS):  $\delta$  <sup>13</sup>C /  $\delta$  <sup>1</sup>H 153.8 / 7.65 (4-CH), 135.8 / 7.87 (*o*-Ph), 130.5 / 7.19 (*p*-Ph), 128.6 / 7.22 (*m*-Ph), 1.4 / -0.18 (2-SiMe<sub>3</sub>), -0.2 / 0.01 (5-SiMe<sub>3</sub>). <sup>1</sup>H, <sup>13</sup>C GHMBC (500 / 126 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, TMS):  $\delta$  <sup>1</sup>H /  $\delta$  <sup>13</sup>C 7.87 / 131.8, 130.5, 128.6 (*o*-Ph / *i*-Ph, *p*-Ph, *m*-Ph), 7.65 / 177.4, 158.8, 149.6, 131.8 (4-H / C3, C2, C5, *i*-Ph), 7.21 / 135.8, 131.8, 130.5 (*m*-Ph / *o*-Ph, *i*-Ph, *p*-Ph), 7.20 / 135.8, 128.6 (*p*-Ph / *o*-Ph, *m*-Ph), 0.01 / 149.6 (5-SiMe<sub>3</sub> / C5), -0.18 / 158.8 (2-SiMe<sub>3</sub> / C2). <sup>19</sup>F, <sup>19</sup>F GCOSY (470 / 470 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, CFCl<sub>3</sub>):  $\delta$  <sup>19</sup>F /  $\delta$  <sup>19</sup>F -126.0 / -160.5 (*o*-F / *m*-F), -143.0 / -160.5 (*p*-F / *m*-F). <sup>29</sup>Si, <sup>1</sup>H GHMQC (99 /

500 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, TMS):  $\delta$  <sup>29</sup>Si /  $\delta$  <sup>1</sup>H 13.2 / 7.87, 7.65 (SiPh<sub>2</sub> / o-Ph, 4-H), -6.2 / 7.65, 0.01 (5-Si / 4-H, 5-SiMe<sub>3</sub>), -8.8 / -0.18 (2-Si / 2-SiMe<sub>3</sub>).

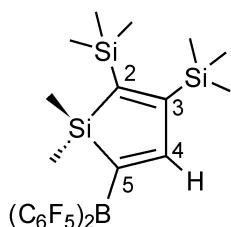


<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K)  
and <sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) spectra (\* solvent).



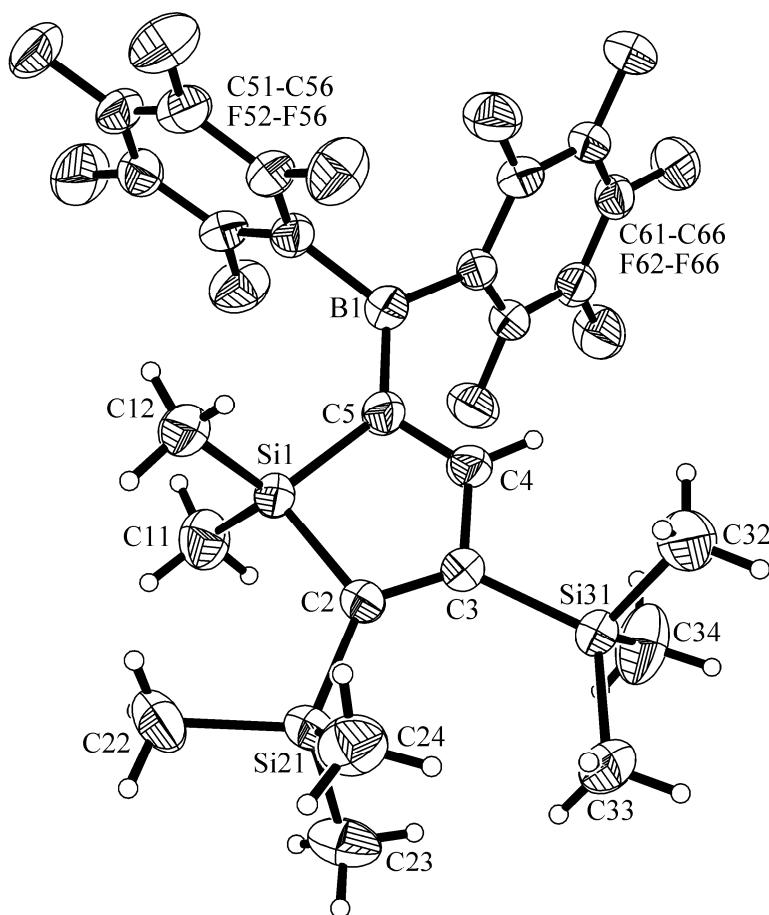
### 5-[Bis(pentafluorophenyl)boryl]-2,3-bis(trimethylsilyl)dimethylsilole (4a).

Bis(trimethylsilylethynyl)dimethylsilane (**1a**) (365 mg, 1.445 mmol), and bis(pentafluorophenyl)borane<sup>1</sup> (500 mg, 1.445 mmol), were put into a 300 mL Schlenk flask under argon. Toluene (50 mL) was added at room temperature by cannula and the resulting bright yellow solution was stirred overnight. The day after, the solution was irradiated with UV lamp for 4 hours. The solution remained yellow but slightly darker. The solvent was then removed by vacuum, and the yellow-brown solid was washed with pentane (20 mL). Yield 79% (685 mg). Crystals suitable for X-ray diffraction were obtained from a concentrated pentane solution at -30 °C.



<sup>1</sup>H NMR (500 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, TMS): δ 8.11 (s, <sup>3</sup>J<sub>Si,H</sub> = 14.3 Hz, 1 H, 4-H), 0.20 (s, 9 H, 2-SiMe<sub>3</sub>), 0.16 (s, 9 H, 3-SiMe<sub>3</sub>), 0.14 (br s, 6 H, SiMe<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (151 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, TMS): δ 181.1 (<sup>1</sup>J<sub>Si,C</sub> = 58.3 Hz, <sup>1</sup>J<sub>Si,C</sub> = 42.2 Hz, C2), 172.1 (C4), 171.5 (<sup>1</sup>J<sub>Si,C</sub> = 61.7 Hz, C3), 151.6 (br, C5), 146.3 (dm, <sup>1</sup>J<sub>F,C</sub> ≈ 245 Hz, C<sub>6</sub>F<sub>5</sub>), 142.6 (dm, <sup>1</sup>J<sub>F,C</sub> ≈ 260 Hz, C<sub>6</sub>F<sub>5</sub>), 137.7 (dm, <sup>1</sup>J<sub>F,C</sub> ≈ 250 Hz, C<sub>6</sub>F<sub>5</sub>), 115.4 (br, *i*-C<sub>6</sub>F<sub>5</sub>), 1.7 (<sup>1</sup>J<sub>Si,C</sub> = 51.9 Hz, 2-SiMe<sub>3</sub>), 0.6 (<sup>1</sup>J<sub>Si,C</sub> = 51.7 Hz, 3-SiMe<sub>3</sub>), -3.9 (<sup>1</sup>J<sub>Si,C</sub> = 48.9 Hz, SiMe<sub>2</sub>). <sup>19</sup>F NMR (470 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, CFCl<sub>3</sub>): δ -130.9 (m, 2 F, *o*-F), -149.8 (t, <sup>3</sup>J<sub>F,F</sub> = 20.7 Hz, 1 F, *p*-F), -161.2 (m, 2 F, *m*-F). <sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, BF<sub>3</sub>·OEt<sub>2</sub>): δ 61 (br, *v*<sub>1/2</sub> ≈ 1000 Hz). <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, TMS): δ 24.3 (SiMe<sub>2</sub>), -7.2 (3-Si), -10.1 (2-Si). <sup>13</sup>C, <sup>1</sup>H GHSQC (151 / 600 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, TMS): δ <sup>13</sup>C / δ <sup>1</sup>H 172.1 / 8.11 (4-CH), 1.7 / 0.20 (2-SiMe<sub>3</sub>), 0.6 / 0.16 (3-SiMe<sub>3</sub>), -3.9 / 0.14 (SiMe<sub>2</sub>). <sup>1</sup>H, <sup>13</sup>C GHMBC (600 / 151 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, TMS): δ <sup>1</sup>H / δ <sup>13</sup>C 8.11 / 181.1, 171.5, 151.6, -3.9 (4-H / C2, C3, C5, SiMe<sub>2</sub>), 0.20 / 181.1 (2-SiMe<sub>3</sub> / C2), 0.16 / 171.5 (3-SiMe<sub>3</sub> / C3), 0.14 / 181.1, 151.6 (SiMe<sub>2</sub> / C2, C5). <sup>29</sup>Si, <sup>1</sup>H GHMQC (99 / 500 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K, TMS): δ <sup>29</sup>Si / δ <sup>1</sup>H 24.3 / 8.11, 0.14 (SiMe<sub>2</sub> / 4-H, SiMe<sub>2</sub>), -7.2 / 8.11, 0.16 (3-Si / 4-H, 3-SiMe<sub>3</sub>), -10.1 / 8.11, 0.20 (2-Si / 4-H, 2-SiMe<sub>3</sub>). C<sub>24</sub>H<sub>25</sub>BF<sub>10</sub>Si<sub>3</sub> (598.5): calcd. C 48.16, H 4.21; found C 47.69, H 4.25.

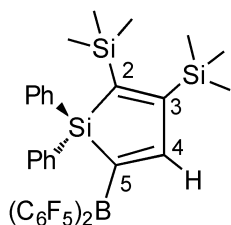
Crystal data for  $C_{24}H_{25}BF_{10}Si_3$  (**4a**),  $M = 598.52$ , monoclinic, space group  $C2/c$  (No. 15),  $a = 26.7841(7)$ ,  $b = 6.5724(2)$ ,  $c = 33.4388(9)$  Å,  $\beta = 107.519(1)^\circ$ ,  $V = 5613.4(3)$  Å<sup>3</sup>,  $D_c = 1.416$  g cm<sup>-3</sup>,  $\mu = 0.248$  mm<sup>-1</sup>,  $Z = 8$ ,  $\lambda = 0.71073$  Å,  $T = 223(2)$  K, 21439 reflections collected ( $\pm h, \pm k, \pm l$ ),  $[(\sin\theta)/\lambda] = 0.66$  Å<sup>-1</sup>, 6379 independent ( $R_{int} = 0.071$ ), and 4407 observed reflections [ $I \geq 2\sigma(I)$ ], 351 refined parameters,  $R = 0.068$ ,  $wR^2 = 0.157$ ; CCDC 765607.



50% probability of thermal ellipsoids

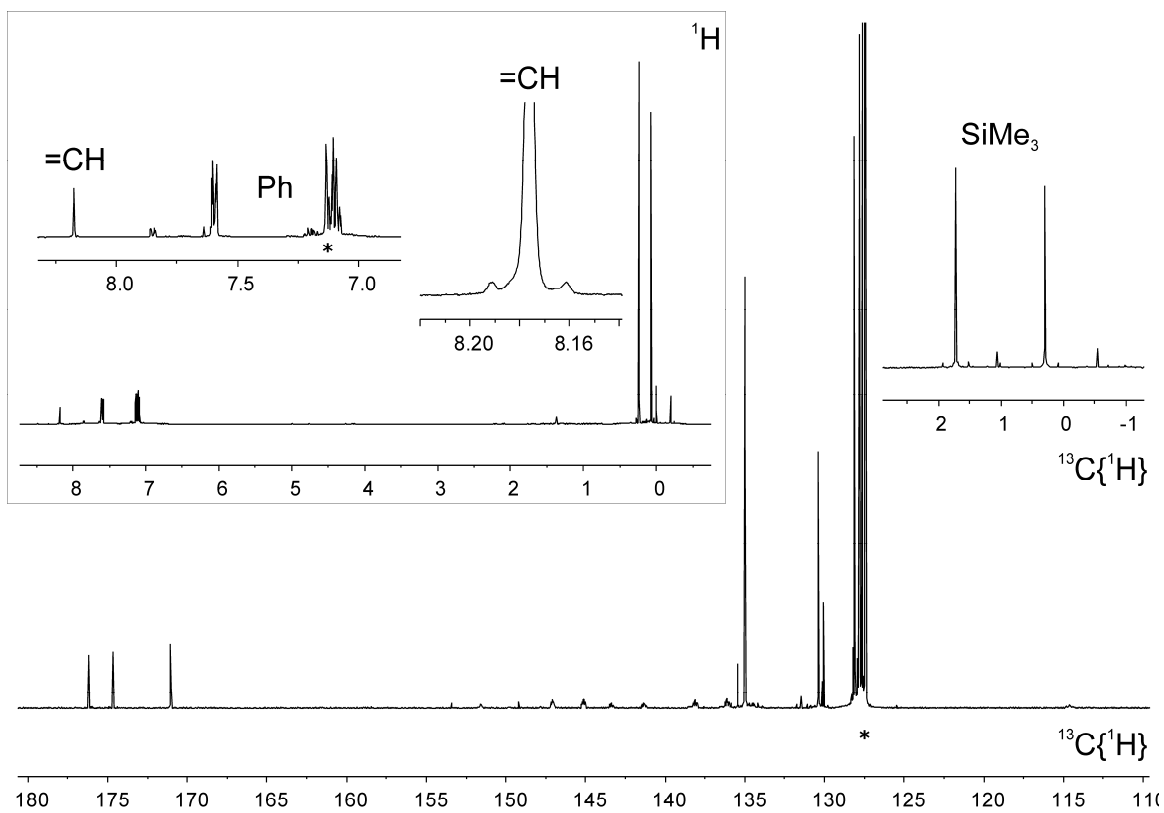
### 5-[Bis(pentafluorophenyl)boryl]-2,3-bis(trimethylsilyl)-diphenylsilole (**4b**)

3-[Bis(pentafluorophenyl)boryl]-2,5-bis(trimethylsilyl)-diphenylsilole (**3b**) (250 mg, 0.346 mmol) was dissolved by 10 mL toluene in a 50 mL Schlenk flask under argon with stirring, and the flask was irradiated with UV lamp for 2 hours. The volatiles were then removed and the yellow product washed with pentane (1x10 mL). Isolated yield 71% (569 mg).



$^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ , 298 K, TMS):  $\delta$  8.19 ( $^3J_{\text{Si,H}} = 14.3$  Hz, 4-H), 7.61 (m, 4 H, *o*-Ph), 7.12 (m, 2 H, *p*-Ph), 7.11 (m, 4 H, *m*-Ph), 0.25 (s,  $^2J_{\text{Si,H}} = 6.6$  Hz, 9 H, 3-SiMe<sub>3</sub>), 0.08 (s,  $^2J_{\text{Si,H}} = 6.6$  Hz, 9 H, 2-SiMe<sub>3</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ , 298 K, TMS):  $\delta$  176.6 ( $^1J_{\text{Si,C}} = 58.7$  Hz,  $^1J_{\text{Si,C}} = 43.8$  Hz, C2), 175.0 ( $^1J_{\text{Si,C}} = 61.1$  Hz, C3), 171.4 ( $^3J_{\text{Si,C}} = 9.9$  Hz,  $^3J_{\text{Si,C}} = 9.9$  Hz, C4), 152.0 (br, C5), 146.5 (dm,  $^1J_{\text{F,C}} \approx 247$  Hz,  $\text{C}_6\text{F}_5$ ), 142.7 (dm,  $^1J_{\text{F,C}} \approx 256$  Hz,  $\text{C}_6\text{F}_5$ ), 137.5 (dm,  $^1J_{\text{F,C}} \approx 252$  Hz,  $\text{C}_6\text{F}_5$ ), 135.4 (*o*-Ph), 130.8 (*p*-Ph), 130.4 ( $^1J_{\text{Si,C}} = 67.5$  Hz, *i*-Ph), 128.5 (*m*-Ph), 115.0 (br, *i*- $\text{C}_6\text{F}_5$ ), 2.1 ( $^1J_{\text{Si,C}} = 52.1$  Hz, 2-SiMe<sub>3</sub>), 0.7 ( $^1J_{\text{Si,C}} = 51.9$  Hz, 3-SiMe<sub>3</sub>).  $^{11}\text{B}\{^1\text{H}\}$  NMR (161 MHz,  $\text{C}_6\text{D}_6$ , 298 K,  $\text{BF}_3\cdot\text{OEt}_2$ ):  $\delta$  62 (br,  $\nu_{1/2} \approx 1400$  Hz).  $^{19}\text{F}$  NMR (470 MHz,  $\text{C}_6\text{D}_6$ , 298 K,  $\text{CFCl}_3$ ):  $\delta$  -130.1 (m, 2 F, *o*-F), -150.1 (t,  $^3J_{\text{F,F}} = 20.7$  Hz, 1 F, *p*-F), -161.5 (m, 2 F, *m*-F).  $^{29}\text{Si}\{^1\text{H}\}$  NMR (99 MHz,  $\text{C}_6\text{D}_6$ , 298 K, TMS):  $\delta$  13.6 (SiPh<sub>2</sub>), -6.7 (3-Si), -9.2 (2-Si).  $^{13}\text{C}$ ,  $^1\text{H}$  GHSQC (126 / 500 MHz,  $\text{C}_6\text{D}_6$ , 298 K, TMS):  $\delta$   $^{13}\text{C}$  /  $\delta$   $^1\text{H}$  171.4 / 8.19 (4-CH), 135.4 / 7.61 (*o*-Ph), 130.8 / 7.12 (*p*-Ph), 128.5 / 7.11 (*m*-Ph), 2.1 / 0.08 (2-SiMe<sub>3</sub>), 0.7 / 0.25 (3-SiMe<sub>3</sub>).  $^1\text{H}$ ,  $^{13}\text{C}$  GHMBC (500 / 126 MHz,  $\text{C}_6\text{D}_6$ , 298 K, TMS):  $\delta$   $^1\text{H}$  /  $\delta$   $^{13}\text{C}$  8.19 / 176.6, 175.0, 152.0, 130.4 (4-H / C2, C3, C5, *i*-Ph), 7.61 / 130.8, 130.4, 128.5 (*o*-Ph / *p*-Ph, *i*-Ph, *m*-Ph), 7.12 / 135.4, 130.4, 128.5 (*p*-Ph / *o*-Ph, *i*-Ph, *m*-Ph), 7.11 / 135.4, 130.8, 130.4 (*m*-Ph / *o*-Ph, *i*-Ph, *p*-Ph), 0.25 / 175.0 (3-SiMe<sub>3</sub> / C3), 0.08 / 176.6 (2-SiMe<sub>3</sub> / C2).  $^{29}\text{Si}$ ,  $^1\text{H}$  GHMQC (99 / 500 MHz,  $\text{C}_6\text{D}_6$ , 298 K, TMS):  $\delta$   $^{29}\text{Si}$  /  $\delta$   $^1\text{H}$  13.6 / 8.19, 7.61 (SiPh<sub>2</sub> / 4-H, *o*-Ph), -6.7 / 8.19, 0.25 (3-Si / 4-H, 3-SiMe<sub>3</sub>), -9.2 / 8.19, 0.08 (2-Si / 4-H, 2-SiMe<sub>3</sub>).  $^1\text{H}\{^{19}\text{F}$ , NOE}:  $\delta_{\text{irr}}(^{19}\text{F})$

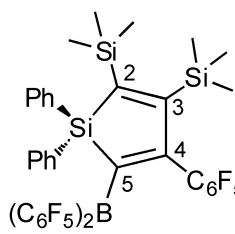
$\delta_{\text{res}}(^1\text{H})$  -130.1 / 8.19, 7.61 (o-F / 4-H, o-Ph).  $^{19}\text{F}\{^1\text{H}, \text{NOE}\}$ :  $\delta_{\text{irr}}(^1\text{H})$  /  $\delta_{\text{res}}(^{19}\text{F})$  8.19 / -130.1 (4-H / o-F), 7.61 / -130.1 (o-Ph / o-F).



$^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz,  $\text{C}_6\text{D}_6$ , 298 K)  
and  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ , 298 K) spectra (\* solvent).

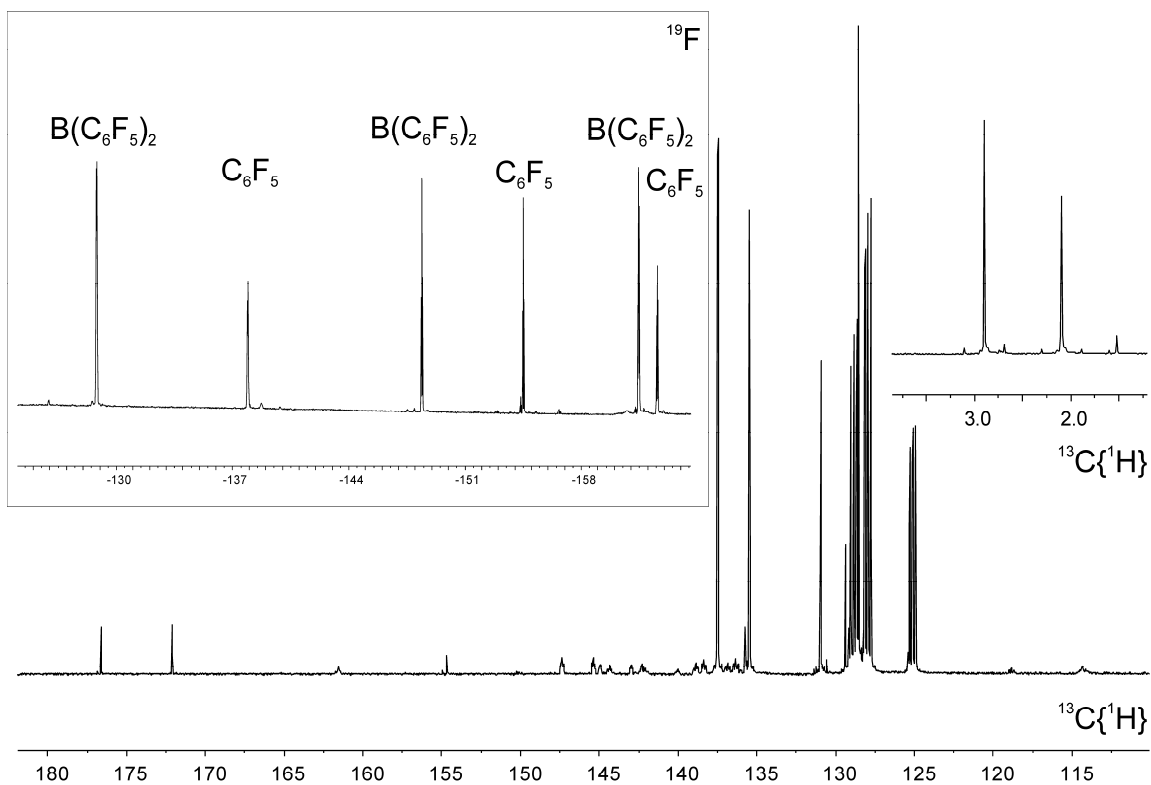
### 5-[Bis(pentafluorophenyl)boryl]-2,3-bis(trimethylsilyl)-4-pentafluorophenyl-diphenylsilole (5)

Bis(trimethylsilylethynyl)diphenylsilane (**1b**) (294 mg, 0.780 mmol), and tris(pentafluorophenyl)borane<sup>1</sup> (400 mg, 0.781 mmol), were weighed under argon a 100 mL Schlenk flask and dissolved by 30 mL toluene. After 2 hours stirring at room temperature, the flask was irradiated with UV lamp for 6 hours in order to achieve complete isomerisation. During irradiation, the solutions turned from pale-yellow to bright-green. After irradiation the volatiles were removed by vacuum and the green sticky product washed with pentane (1x10 mL). Isolated yield 58% (402 mg).



<sup>1</sup>H NMR (500 MHz, C<sub>7</sub>D<sub>8</sub>, 298 K, TMS): δ 7.58 (m, 4 H, *o*-Ph), 7.05 (m, 2 H, *p*-Ph), 7.03 (m, 4 H, *m*-Ph), 0.01 (s, <sup>2</sup>J<sub>Si,H</sub> = 6.5 Hz, 9 H, 2-SiMe<sub>3</sub>), -0.03 (s, <sup>2</sup>J<sub>Si,H</sub> = 6.4 Hz, 9 H, 3-SiMe<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>7</sub>D<sub>8</sub>, 298 K, TMS): δ 176.6 (<sup>1</sup>J<sub>Si,C</sub> = 61.1 Hz, C3), 172.1 (<sup>1</sup>J<sub>Si,C</sub> = 58.5 Hz, <sup>1</sup>J<sub>Si,C</sub> = 42.6 Hz, C2), 161.6 (br, C5), 154.7 (C4), 146.4 (dm, <sup>1</sup>J<sub>F,C</sub> ≈ 246 Hz, B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>), 143.9 (dm, <sup>1</sup>J<sub>F,C</sub> ≈ 246 Hz, C<sub>6</sub>F<sub>5</sub>), 143.3 (dm, <sup>1</sup>J<sub>F,C</sub> ≈ 257 Hz, B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>), 141.0 (dm, <sup>1</sup>J<sub>F,C</sub> ≈ 257 Hz, C<sub>6</sub>F<sub>5</sub>), 137.9 (dm, <sup>1</sup>J<sub>F,C</sub> ≈ 254 Hz, C<sub>6</sub>F<sub>5</sub>), 137.3 (dm, <sup>1</sup>J<sub>F,C</sub> ≈ 251 Hz, B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>), 135.5 (*o*-Ph), 130.9 (*p*-Ph), 129.4 (<sup>1</sup>J<sub>Si,C</sub> = 68.6 Hz, *i*-Ph), 128.5 (*m*-Ph), 118.8 (*i*-C<sub>6</sub>F<sub>5</sub>), 114.3 (br, *i*-B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>), 2.9 (<sup>1</sup>J<sub>Si,C</sub> = 52.7 Hz, 2-SiMe<sub>3</sub>), 2.1 (<sup>1</sup>J<sub>Si,C</sub> = 52.0 Hz, 3-SiMe<sub>3</sub>). <sup>11</sup>B{<sup>1</sup>H} NMR (160 MHz, C<sub>7</sub>D<sub>8</sub>, 298 K, BF<sub>3</sub>·OEt<sub>2</sub>): δ 65 (br, *v*<sub>1/2</sub> ≈ 1600 Hz). <sup>19</sup>F NMR (470 MHz, C<sub>7</sub>D<sub>8</sub>, 298 K, CFC<sub>3</sub>): δ -128.8 (m, 4 F, *o*-F), -148.4 (t, <sup>3</sup>J<sub>FF</sub> = 19.8 Hz, 2 F, *p*-F), -161.5 (m, 4 F, *m*-F)(B(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>), -137.9 (m, 2 F, *o*-F), -154.5 (t, <sup>3</sup>J<sub>FF</sub> = 20.7 Hz, F, *p*-F), -162.6 (m, 2 F, *m*-F)(C<sub>6</sub>F<sub>5</sub>). <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz, C<sub>7</sub>D<sub>8</sub>, 298 K, TMS): δ 14.9 (SiPh<sub>2</sub>), -6.9 (3-Si), -9.4 (2-Si). <sup>13</sup>C, <sup>1</sup>H GHSQC (126 / 500 MHz, C<sub>7</sub>D<sub>8</sub>, 298 K, TMS): δ <sup>13</sup>C / δ <sup>1</sup>H 135.5 / 7.58 (*o*-Ph), 130.9 / 7.05 (*p*-Ph), 128.5 / 7.03 (*m*-Ph), 2.9 / 0.01 (2-SiMe<sub>3</sub>), 2.1 / -0.03 (3-SiMe<sub>3</sub>). <sup>1</sup>H, <sup>13</sup>C GHMBC (500 / 126 MHz, C<sub>7</sub>D<sub>8</sub>, 298 K, TMS): δ <sup>1</sup>H / δ <sup>13</sup>C 7.58 / 130.8, 129.4 (*o*-Ph / *p*-Ph, *i*-Ph), 7.05 / 135.5, 128.5 (*p*-Ph / *o*-Ph, *m*-

Ph), 7.03 / 135.5, 129.4 (*m*-Ph / *o*-Ph, *i*-Ph), 0.01 / 172.1 (2-SiMe<sub>3</sub> / C2), -0.03 / 176.6 (3-SiMe<sub>3</sub> / C3). <sup>29</sup>Si, <sup>1</sup>H GHMQC (99 / 500 MHz, C<sub>7</sub>D<sub>8</sub>, 298 K, TMS): δ <sup>29</sup>Si / δ <sup>1</sup>H 14.9 / 7.58, 7.03 (SiPh<sub>2</sub> / *o*-Ph, *m*-Ph), -6.9 / -0.03 (3-Si / 3-SiMe<sub>3</sub>), -9.4 / 0.01 (2-Si / 2-SiMe<sub>3</sub>).



<sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>7</sub>D<sub>8</sub>, 298 K)  
and <sup>19</sup>F NMR (470 MHz, C<sub>7</sub>D<sub>8</sub>, 298 K) spectra (\* solvent).

<sup>1</sup> D. J. Parks, W. E. Piers and G. P. A. Yap, *Organometallics*, 1998, **17**, 5492.

<sup>2</sup> G. Dierker, J. Ugolotti, G. Kehr, R. Fröhlich and G. Erker, *Adv. Synth. Catal.*, 2009, **351**, 1080.