

**Ruthenium-Catalysed Double *trans*-Hydrosilylation of 1,4-Diarylbuta-1,3-diyne  
Leading to 2,5-Diarylsiloles**

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**General.** All manipulations were carried out in a nitrogen-filled gloved box and with standard Schlenk techniques under an argon atmosphere. Column chromatography was performed with silica gel 60N (Kanto). Preparative thin-layer chromatography was performed with silica gel 60 PF<sub>254</sub> (Merck). Gel permeation chromatography was carried out on a JAI LC-908. NMR spectra were recorded on a Varian Gemini 2000 (<sup>1</sup>H at 300.77 MHz and <sup>13</sup>C NMR at 75.46 MHz), a JEOL JNM-A400 (<sup>11</sup>B at 128.15 MHz and <sup>29</sup>Si at 79.30 Hz), or a JEOL JNM-ECA600 (<sup>13</sup>C NMR at 150.92 MHz). Proton chemical shifts were referenced to the residual proton signals in CDCl<sub>3</sub> ( $\delta$  7.26 ppm) and C<sub>6</sub>D<sub>6</sub> ( $\delta$  7.16 ppm). Carbon chemical shifts were referenced to the carbon signals in CDCl<sub>3</sub> ( $\delta$  77.00 ppm) and C<sub>6</sub>D<sub>6</sub> ( $\delta$  128.00 ppm). Boron and silicon chemical shifts were referenced to external standards BF<sub>3</sub>·OEt<sub>2</sub> ( $\delta$  0.0 ppm) and SiMe<sub>4</sub> ( $\delta$  0.0 ppm), respectively. High resolution mass spectra were recorded on a JEOL JMS-SX102A. UV-vis spectra were recorded on a JASCO V-550. Fluorescence spectra were recorded on a JASCO FP-777. Thermal data were obtained using an SII EXSTAR6000 DSC6220 at a heating rate 10 °C/min. The molecular weights of polymers were determined by gel permeation chromatography measured in CHCl<sub>3</sub> at 40 °C with a system consisting of a TOSOH 8020 series and Shodex columns (K-805L and K-804L).

**Materials.** [Cp\**Ru*(MeCN)<sub>3</sub>]PF<sub>6</sub> (**1**)<sup>1</sup> and 9-Silafluorene (**3d**)<sup>2</sup> were prepared according to literature procedures. 1,2-Dichloroethane was distilled from calcium hydride. All other reagents and solvents were used as received without further purification.

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### Preparation of 1,3-Diynes 2.

**I. Palladium-Catalysed Homo-Coupling<sup>3</sup> (for 2a,<sup>4</sup> 2b,<sup>5</sup> 2c,<sup>6</sup> 2d,<sup>7</sup> 2f,<sup>8</sup> 2h, and 2k<sup>9</sup>).** To a solution of ethynylbenzene (5.1 g, 50.0 mmol) in diisopropylamine (500 mL) were added PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.70 g, 1.00 mmol, 2.0 mol %), CuI (0.19 g, 1.00 mmol, 2.0 mol %), and I<sub>2</sub> (6.35 g, 25.0 mmol), and the reaction mixture was stirred at room temperature for 2 h. The precipitate was filtrated off, and the volatile materials were removed under reduced pressure. The crude product was purified by column chromatography on silica gel (hexane) to give 1,4-diphenylbuta-1,3-diyne (**2a**, 3.06 g, 61%).

**1,4-Bis[4-(trimethylsilyl)phenyl]buta-1,3-diyne (2h).** <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.27 (s, 18H), 7.49 (s, 8H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ -1.3, 74.3, 81.9, 122.0, 131.5, 133.2, 142.4; HRMS (EI) calcd for C<sub>22</sub>H<sub>26</sub>Si<sub>2</sub> (M<sup>+</sup>) 346.1573, found 346.1573.

**II. Eglinton Coupling<sup>10</sup> (for 2e<sup>11</sup> and 2g).** A mixture of 1-bromo-3-ethynylbenzene (1.81 g, 10 mmol) and Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (2.85 g, 14.3 mmol) in pyridine–MeOH (1:1, 10 mL) was heated under reflux for 2 h. After cooling to room temperature, the insoluble materials were filtered off. To the filtrate was added HCl aqueous solution, and extracted with Et<sub>2</sub>O. The extract was passed through a plug of Florisil<sup>®</sup> and evaporated. The residue was subjected to column chromatography on silica gel to afford 1,4-bis(3-bromophenyl)buta-1,3-diyne (**2g**, 0.95 g, 53%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.18–7.27 (m, 2H), 7.46 (dt, *J* = 7.8, 1.2 Hz, 2H), 7.52 (dq, *J* = 7.8, 1.2 Hz, 2H), 7.67 (t, *J* = 1.7 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 74.8, 80.5, 122.2, 123.5, 129.8, 131.0, 132.5, 135.1; HRMS (EI) calcd for C<sub>16</sub>H<sub>8</sub>Br<sub>2</sub> (M<sup>+</sup>) 357.8993, found 357.8994.

**III. Glaser Coupling<sup>12</sup> (for 2i).** A mixture of 2-(3-ethynylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.82 g, 8.0 mmol) and CuCl (79 mg, 0.8 mmol) in pyridine (200 mL) was heated under an oxygen atmosphere at 40 °C for 2.5 h. The solvent was removed under reduced pressure. To the residue was added 3N HCl aqueous solution, and extracted with Et<sub>2</sub>O and CH<sub>2</sub>Cl<sub>2</sub>, dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated. The residue was subjected to column chromatography on silica gel to afford 1,4-bis[3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]buta-1,3-diyne (**2i**, 0.57 g, 32%). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.35 (s, 24H), 7.34 (t, *J* = 7.8 Hz, 2H), 7.60 (d, *J* = 7.8 Hz, 2H), 7.78 (dd, *J* = 7.2, 0.9 Hz, 2H), 7.99 (s, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 24.9, 74.0, 81.4, 84.1, 121.4, 127.7, 134.9, 135.1, 138.9 [carbon attached to boron was not observed due to quadrupole broadening caused by the boron nucleus]; <sup>11</sup>B NMR (CDCl<sub>3</sub>, 128.15 MHz) δ 30.5; HRMS (EI) calcd for C<sub>28</sub>H<sub>32</sub>B<sub>2</sub>O<sub>4</sub> (M<sup>+</sup>) 454.2487, found 454.2489.

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(5) [20199-36-4].

(6) [22666-07-5].

(7) [22779-05-1].

(8) [55606-94-5].

(9) [2979-05-7].

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#### IV. Hay Coupling<sup>13</sup> (for **2j**<sup>14</sup>)

To a suspension of CuCl (182 mg, 1.85 mmol) in DME (10 mL) was added TMEDA (322 mg, 0.41 mmol). After stirring at room temperature for 10 min, 3-ethynylthiophene (1.0 g, 9.24 mmol) was added, and the mixture was kept at 30–35 °C for 1 h while air was bubbled through the solution. The reaction was quenched with water, and the mixture was extracted with Et<sub>2</sub>O. The organic layer was dried over MgSO<sub>4</sub> and concentrated. The residue was purified by column chromatography on silica gel (hexane:AcOEt = 10:1) to give 1,4-di(3-thienyl)buta-1,3-diyne (**2j**, 739 mg, 75%).

**V. Cadiot–Chodkiewicz Coupling<sup>15</sup> (for **2l**<sup>16</sup> and **6**<sup>17</sup>).** To a solution of 1-ethynyl-4-vinylbenzene (1.40 g, 10.9 mmol) in MeOH–H<sub>2</sub>O (2:1, 6.0 mL) was added *n*-butylamine (2.39 g, 32.7 mmol), CuCl (0.16 g, 1.64 mmol), and NH<sub>2</sub>OH·HCl (0.23 g, 3.27 mmol) at room temperature. To the mixture was added slowly a solution of (bromoethynyl)benzene (1.97 g, 10.9 mmol) in MeOH (2.0 mL) at 0 °C. After stirring at room temperature for 24 h, the reaction was quenched with water, and the mixture was extracted with Et<sub>2</sub>O. The organic layer was dried over MgSO<sub>4</sub> and concentrated. The residue was purified by column chromatography on silica gel (hexane) to give 1-(phenylbuta-1,3-diynyl)-4-vinylbenzene (**2l**, 1.59 g, 70%).

#### VI. Sonogashira Coupling (for **2m**<sup>18</sup>)

To a solution of 4-iodoanisole (947 mg, 4.05 mmol) in THF (10 mL) were added diisopropylamine (1.5 mL), buta-1,3-diynylbenzene<sup>19</sup> (563 mg, 4.45 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (142 mg, 0.203 mmol, 5.0 mol %), and CuI (77.3 mg, 0.406 mmol, 10 mol %), and the reaction mixture was stirred at room temperature for 10 h. The precipitate was filtered off, and the volatile materials were removed under reduced pressure. The crude product was purified by column chromatography on silica gel (hexane:AcOEt = 10:1) to give 1-methoxy-4-(phenylbuta-1,3-diynyl)benzene (**2m**, 161 mg, 17%).

**VII. Copper-Catalysed Cross-Coupling<sup>20</sup> (for **2n**).** A mixture of trimethyl(phenylethynyl)silane (1.33 g, 7.65 mmol), 1-(chloroethynyl)-4-(trifluoromethyl)benzene (2.43 g, 11.9 mmol), and CuCl (80 mg, 0.81 mmol) in DMF (45 mL) was heated at 120 °C for 1 day. The reaction was quenched with 3N HCl aqueous solution, and the mixture was extracted with Et<sub>2</sub>O. The organic layer was washed with saturated NaHCO<sub>3</sub> aqueous solution and brine, dried over MgSO<sub>4</sub>, and evaporated. An aliquot of the crude product was purified by GPC to give 1-(phenylbuta-1,3-diynyl)-4-(trifluoromethyl)benzene (**2n**). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.32–7.40 (m, 3H), 7.53–7.56 (m, 2H), 7.60 (d, *J* = 8.9 Hz, 2H), 7.63 (d, *J* = 8.9 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 73.4, 76.2, 79.8, 82.8, 121.3, 123.7 (<sup>1</sup>*J*<sub>C–F</sub> = 272.1 Hz), 125.3 (<sup>3</sup>*J*<sub>C–F</sub> = 3.5 Hz), 125.7, 128.5, 129.5, 130.7 (<sup>2</sup>*J*<sub>C–F</sub> = 32.4 Hz), 132.5, 132.7; HRMS (EI) calcd for

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(16) [106643-22-5].

(17) [37902-13-9].

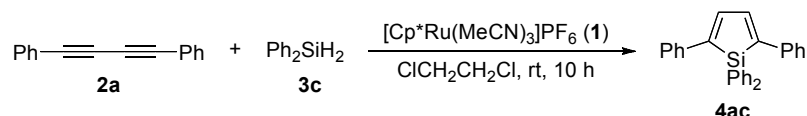
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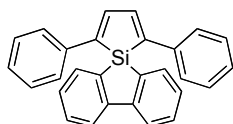
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C<sub>17</sub>H<sub>9</sub>F<sub>3</sub> (M<sup>+</sup>) 270.0656, found 270.0657.

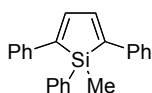
### General Procedure for Ruthenium-Catalysed Double *trans*-Hydrosilylation of 1,3-Diynes



To a solution of [Cp<sup>\*</sup>Ru(MeCN)<sub>3</sub>]PF<sub>6</sub> (**1**, 25.2 mg, 0.050 mmol) in 1,2-dichloroethane (1.5 mL) was added a solution of 1,4-diphenylbuta-1,3-diyne (**2a**, 50.6 mg, 0.250 mmol) and diphenylsilane (**3c**, 138.2 mg, 0.750 mmol) in 1,2-dichloroethane (1.0 mL). After being stirred under an argon atmosphere for 10 h at room temperature, the reaction mixture was concentrated under reduced pressure. The residue was purified by thin-layer chromatography (hexane:AcOEt = 10:1) to give 1,1,2,5-tetraphenylsilole<sup>21</sup> (**4ac**, 49.7 mg, 51%). Mp 169 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.13-7.27 (m, 6H), 7.32-7.44 (m, 10H), 7.49 (s, 2H), 7.67-7.72 (m, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 126.8, 127.0, 128.4, 128.6, 130.2, 131.6, 135.8, 138.6, 140.3, 143.2; <sup>29</sup>Si NMR (CDCl<sub>3</sub>, 79.30 MHz) δ -9.2; HRMS (CI) calcd for C<sub>28</sub>H<sub>22</sub>Si (M<sup>+</sup>) 386.1491, found 386.1491.



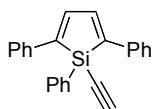
**2',5'-Diphenylspiro[9-silafluorene-9,1'-silole] (4ad)**. The title compound (91.4 mg, 79%) was prepared from **2a** (60.7 mg, 0.30 mmol) and **3d** (164.1 mg, 0.90 mmol). Mp 197 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.07-7.18 (m, 10H), 7.21-7.28 (m, 2H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.66 (s, 2H), 8.00 (d, *J* = 7.5 Hz, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 121.5, 126.4, 127.1, 128.1, 128.5, 131.2, 132.4, 134.1, 137.8, 138.4, 141.7, 149.3; HRMS (EI) calcd for C<sub>28</sub>H<sub>20</sub>Si (M<sup>+</sup>) 384.1334, found 384.1334.



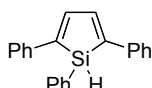
**1-Methyl-1,2,5-triphenylsilole (4ab)**.<sup>22</sup> To a solution of [Cp<sup>\*</sup>Ru(MeCN)<sub>3</sub>]PF<sub>6</sub> (30.3 mg, 0.060 mmol) in 1,2-dichloroethane (1.5 mL) was added a solution of **1a** (60.7 mg, 0.30 mmol) and chloro(phenyl)silane (128.4 mg, 0.90 mmol) in 1,2-dichloroethane (1.5 mL). After being stirred under an argon atmosphere for 10 h at room temperature, the solvent was removed under reduced pressure to give crude 1-chloro-1,2,5-triphenylsilole (**4ae**). To a solution of **4ae** in Et<sub>2</sub>O was added slowly methyllithium (2.2 M in Et<sub>2</sub>O, 0.61 mL) at -78 °C, and the reaction was allowed to warm to room temperature. After 12 h, the reaction was quenched with a NaH<sub>2</sub>PO<sub>4</sub>-Na<sub>2</sub>HPO<sub>4</sub> buffer (pH = 6.8), and the mixture was extracted with Et<sub>2</sub>O, dried over MgSO<sub>4</sub>, and concentrated. The residue was purified by thin-layer chromatography (hexane:AcOEt = 20:1) to give 1-methyl-1,2,5-triphenylsilole (**4ab**, 59.8 mg, 61%). Mp 74 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.82 (s, 3H), 7.14-7.28 (m, 5H), 7.33-7.44 (m, 8H), 7.43 (s, 2H), 7.64-7.68 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ -5.6, 126.3, 126.9, 128.3, 128.6, 129.9, 133.4, 134.4, 138.5, 139.2, 144.0; HRMS (CI) calcd for C<sub>23</sub>H<sub>20</sub>Si (M<sup>+</sup>) 324.1334, found 324.1334.

(21) [51531-22-7].

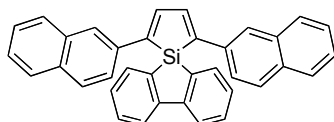
(22) [49538-70-7].



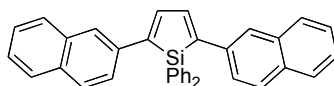
**1-Ethynyl-1,2,5-triphenylsilole (5).** The title compound was obtained in 40% analogously by the reaction of **4ae** with ethynylmagnesium bromide (0.5 M in THF). Mp 98 °C.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  2.78 (s, 1H), 7.15-7.22 (m, 2H), 7.23-7.41 (m, 7H), 7.45 (s, 2H), 7.49 (d,  $J = 7.7$  Hz, 4H), 7.77 (dd,  $J = 7.7, 1.4$  Hz, 2H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  82.4, 98.7, 126.7, 127.4, 128.4, 128.6, 129.7, 130.6, 134.8, 137.4, 140.5, 140.6; HRMS (EI) calcd for  $\text{C}_{24}\text{H}_{18}\text{Si}$  ( $\text{M}^+$ ) 334.1178, found 334.1175.



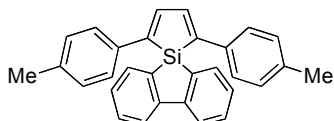
**1,2,5-Triphenylsilole.**<sup>23</sup> The title compound was isolated in 30% as a by-product of the ethynylation reaction.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  5.46 (s, 1H), 7.14-7.44 (m, 15H), 7.65-7.68 (m, 2H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  126.7, 127.2, 128.5, 128.6, 130.3, 130.5, 135.5, 138.2, 140.5, 141.6; HRMS (EI) calcd for  $\text{C}_{22}\text{H}_{18}\text{Si}$  ( $\text{M}^+$ ) 310.1178, found 310.1182.



**2',5'-Di(2-naphthyl)spiro[9-silafluorene-9,1'-silole] (4bd).** The title compound (42.7 mg, 59%) was prepared from **2b** (45.4 mg, 0.15 mmol) and **3d** (82.0 mg, 0.45 mmol). Mp 201 °C.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.21-7.37 (m, 6H), 7.40-7.60 (m, 8H), 7.60-7.71 (m, 6H), 7.82 (s, 2H), 8.08 (d,  $J = 7.8$  Hz, 2H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  121.5, 124.1, 125.6, 125.9, 126.1, 127.4, 128.0, 128.2, 131.3, 132.6, 132.7, 133.5, 134.1, 135.3, 138.6, 142.1, 149.3 [one carbon missing due to overlap]; HRMS (EI) calcd for  $\text{C}_{36}\text{H}_{24}\text{Si}$  ( $\text{M}^+$ ) 484.1647, found 484.1648.



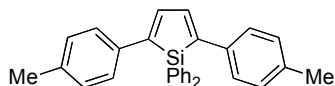
**2,5-Di(2-naphthyl)-1,1-diphenylsilole (4bc).** The title compound (107.3 mg, 55%) was prepared from **2b** (120.9 mg, 0.40 mmol) and **3c** (221.2 mg, 1.20 mmol). Mp 106 °C.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.32-7.46 (m, 10H), 7.62-7.81 (m, 16H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  124.6, 125.6, 126.0, 126.4, 127.5, 128.1, 128.2, 128.4, 130.3, 131.7, 132.7, 133.7, 135.9, 136.2, 140.8, 143.4 [one carbon missing due to overlap]; HRMS (EI) calcd for  $\text{C}_{36}\text{H}_{26}\text{Si}$  ( $\text{M}^+$ ) 486.1804, found 486.1809.



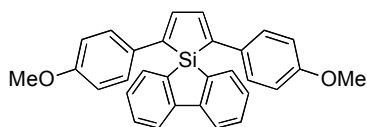
**2',5'-Bis(4-methylphenyl)spiro[9-silafluorene-9,1'-silole] (4cd).** The title compound (47.8 mg, 77%) was prepared from **2c** (34.5 mg, 0.15 mmol) and **3d** (82.0 mg, 0.45 mmol). Mp 210 °C.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  2.22 (s, 6H), 6.93 (d,  $J = 8.3$  Hz, 4H), 7.06

(23) [19923-44-5].

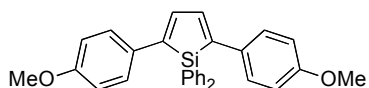
(d,  $J = 8.3$  Hz, 4H), 7.24 (t,  $J = 7.2$  Hz, 2H), 7.52 (dt,  $J = 7.5, 1.2$  Hz, 4H), 7.61 (s, 2H), 8.00 (d,  $J = 7.8$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  21.1, 121.4, 126.2, 128.0, 129.2, 131.0, 132.7, 134.1, 135.1, 136.8, 137.7, 140.8, 149.2; HRMS (EI) calcd for  $\text{C}_{30}\text{H}_{24}\text{Si}$  ( $\text{M}^+$ ) 412.1647, found 412.1647.



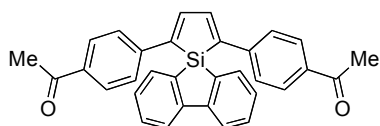
**2,5-Bis(4-methylphenyl)-1,1-diphenylsilole (4cc).** The title compound (54.2 mg, 65%) was prepared from **2c** (46.1 mg, 0.20 mmol) and **3c** (110.6 mg, 0.60 mmol). Mp 147 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.28 (s, 6H), 7.03 (d,  $J = 8.1$  Hz, 4H), 7.28-7.41 (m, 10H), 7.44 (s, 2H), 7.67-7.70 (m, 4H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  21.2, 126.6, 128.3, 129.3, 130.1, 131.9, 135.8, 136.8, 139.5, 142.5, [one carbon missing due to overlap]; HRMS (EI) calcd for  $\text{C}_{30}\text{H}_{26}\text{Si}$  ( $\text{M}^+$ ) 414.1804, found 414.1803.



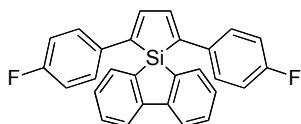
**2',5'-Bis(4-methoxyphenyl)spiro[9-silafluorene-9,1'-silole] (4dd).** The title compound (52.2 mg, 78%) was prepared from **2d** (39.3 mg, 0.15 mmol) and **3d** (82.0 mg, 0.45 mmol). Mp 167 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.66 (s, 6H), 6.63 (d,  $J = 8.4$  Hz, 4H), 7.06 (d,  $J = 8.4$  Hz, 4H), 7.22 (t,  $J = 7.2$  Hz, 2H), 7.46-7.54 (m, 4H), 7.58 (dd,  $J = 6.9, 0.6$  Hz, 2H), 7.98 (d,  $J = 8.1$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  55.1, 114.0, 121.4, 127.4, 128.0, 130.8, 131.1, 133.0, 134.1, 136.5, 139.8, 149.2, 158.7; HRMS (EI) calcd for  $\text{C}_{30}\text{H}_{24}\text{O}_2\text{Si}$  ( $\text{M}^+$ ) 444.1546, found 444.1548.



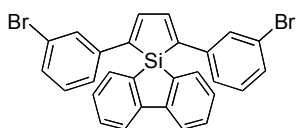
**2,5-Bis(4-methoxyphenyl)-1,1-diphenylsilole (4dc).** The title compound (66.9 mg, 75%) was prepared from **2d** (52.5 mg, 0.20 mmol) and **3c** (110.6 mg, 0.60 mmol). Mp 207 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.76 (s, 6H), 6.75-6.81 (m, 4H), 7.32-7.42 (m, 12H), 7.69 (d,  $J = 8.4$  Hz, 4H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  55.2, 114.0, 127.8, 128.3, 130.1, 131.5, 132.0, 135.8, 138.5, 141.4, 158.7; HRMS (EI) calcd for  $\text{C}_{30}\text{H}_{26}\text{O}_2\text{Si}$  ( $\text{M}^+$ ) 446.1702, found 446.1703.



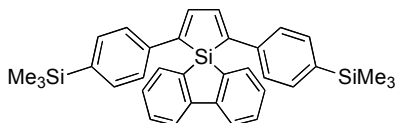
**2',5'-Bis(4-acetylphenyl)spiro[9-silafluorene-9,1'-silole] (4ed).** The title compound (35.4 mg, 25%) was prepared from **2e** (85.9 mg, 0.30 mmol) and **3d** (164.1 mg, 0.90 mmol). Mp 221 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.46 (s, 6H), 7.19 (d,  $J = 8.1$  Hz, 4H), 7.24-7.28 (m, 2H), 7.52-7.57 (m, 4H), 7.70 (d,  $J = 8.4$  Hz, 4H), 7.76 (s, 2H), 8.00 (d,  $J = 8.4$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  26.4, 121.8, 126.5, 128.3, 128.8, 131.2, 131.7, 134.0, 135.6, 139.1, 142.1, 143.8, 149.3, 197.2; HRMS (FAB) calcd for  $\text{C}_{32}\text{H}_{24}\text{O}_2\text{Si}$  ( $\text{M}^+$ ) 468.1546, found 468.1547.



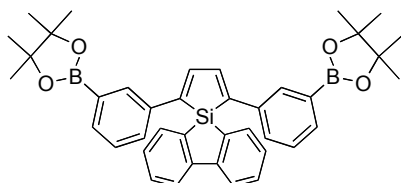
**2',5'-Bis(4-fluorophenyl)spiro[9-silafluorene-9,1'-silole] (4fd).** The title compound (41.1 mg, 65%) was prepared from **2f** (35.7 mg, 0.15 mmol) and **3d** (82.0 mg, 0.45 mmol). Mp 173 °C.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  6.79 (t,  $J = 8.7$  Hz, 4H), 7.06-7.11 (m, 4H), 7.25 (t,  $J = 7.4$  Hz, 2H), 7.49-7.59 (m, 6H), 7.99 (d,  $J = 7.8$  Hz, 2H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  115.5 ( $^2J_{\text{C-F}} = 22.0$  Hz), 121.6, 127.8 ( $^3J_{\text{C-F}} = 8.1$  Hz), 128.2, 131.4, 132.0, 133.9 ( $^4J_{\text{C-F}} = 3.5$  Hz), 134.0, 137.1, 141.2, 149.3, 161.9 ( $^1J_{\text{C-F}} = 247.0$  Hz); HRMS (EI) calcd for  $\text{C}_{28}\text{H}_{18}\text{F}_2\text{Si}$  ( $\text{M}^+$ ) 420.1146, found 420.1147.



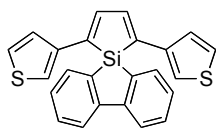
**2',5'-Bis(3-bromophenyl)spiro[9-silafluorene-9,1'-silole] (4gd).** The title compound (77.3 mg, 71%) was prepared from **2g** (72.6 mg, 0.20 mmol) and **3d** (109.4 mg, 0.60 mmol). Mp 157 °C.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  6.81 (d,  $J = 7.5$  Hz, 2H), 6.89 (t,  $J = 8.0$  Hz, 2H), 7.18 (dd,  $J = 8.1, 0.9$  Hz, 2H), 7.23-7.28 (m, 2H), 7.45 (s, 2H), 7.53 (t,  $J = 8.1$  Hz, 4H), 7.60 (s, 2H), 7.98 (d,  $J = 7.5$  Hz, 2H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  121.7, 122.7, 125.9, 128.3, 128.4, 130.0, 130.1, 131.2, 131.6, 134.0, 137.9, 139.7, 142.6, 149.4; HRMS (EI) calcd for  $\text{C}_{28}\text{H}_{18}\text{Br}_2\text{Si}$  ( $\text{M}^+$ ) 539.9545, found 539.9543.



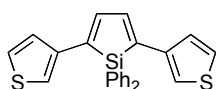
**2',5'-Bis[4-(trimethylsilyl)phenyl]spiro[9-silafluorene-9,1'-silole] (4hd).** The title compound (49.2 mg, 62%) was prepared from **2h** (52.0 mg, 0.15 mmol) and **3d** (82.0 mg, 0.45 mmol). Mp 203 °C.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  0.18 (s, 18H), 7.14 (d,  $J = 8.4$  Hz, 4H), 7.20-7.30 (m, 6H), 7.48-7.58 (m, 4H), 7.68 (s, 2H), 8.00 (d,  $J = 7.8$  Hz, 2H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  -1.2, 121.5, 125.6, 128.1, 131.2, 132.5, 133.6, 134.1, 138.2, 138.5, 139.3, 142.0, 149.3; HRMS (EI) calcd for  $\text{C}_{34}\text{H}_{36}\text{Si}_3$  ( $\text{M}^+$ ) 528.2125, found 528.2125.



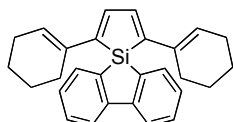
**2',5'-Bis[3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]spiro[9-silafluorene-9,1'-silole] (4id).** The title compound (92.2 mg, 72%) was prepared from **2i** (90.8 mg, 0.20 mmol) and **3d** (109.4 mg, 0.60 mmol). Mp 154 °C.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  1.30 (s, 24H), 6.89 (d,  $J = 7.4$  Hz, 2H), 6.99 (t,  $J = 7.5$  Hz, 2H), 7.20 (t,  $J = 7.2$  Hz, 2H), 7.46-7.55 (m, 6H), 7.69 (s, 2H), 7.89 (s, 2H), 7.80 (d,  $J = 7.8$  Hz, 2H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  24.8, 83.7, 121.4, 127.98, 128.01, 130.5, 131.0, 131.7, 132.5, 133.2, 134.0, 137.2, 138.2, 142.0, 149.4 [carbon attached to boron was not observed due to quadrupole broadening caused by the boron nucleus];  $^{11}\text{B NMR}$  ( $\text{CDCl}_3$ , 128.15 MHz)  $\delta$  31.1; HRMS (EI) calcd for  $\text{C}_{40}\text{H}_{42}\text{B}_2\text{O}_4\text{Si}$  ( $\text{M}^+$ ) 636.3038, found 636.3042.



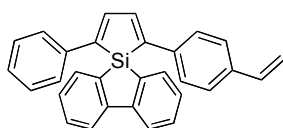
**2',5'-Di(3-thienyl)spiro[9-silafluorene-9,1'-silole] (4jd).** The title compound (45.2 mg, 76%) was prepared from **2j** (32.1 mg, 0.15 mmol) and **3d** (82.0 mg, 0.45 mmol). Mp 233 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  6.60-6.65 (m, 2H), 7.11-7.16 (m, 4H), 7.26 (t,  $J = 7.2$  Hz, 2H), 7.44 (s, 2H), 7.54 (t,  $J = 7.7$  Hz, 2H), 7.60 (d,  $J = 6.9$  Hz, 2H), 7.99 (d,  $J = 7.5$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  121.4, 121.8, 125.0, 125.7, 128.1, 131.4, 131.7, 132.2, 134.3, 139.6, 141.0, 149.3; HRMS (EI) calcd for  $\text{C}_{24}\text{H}_{16}\text{S}_2\text{Si}$  ( $\text{M}^+$ ) 396.0463, found 396.0463.



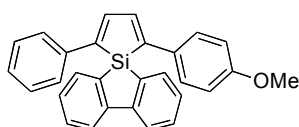
**1,1-Diphenyl-2,5-di(3-thienyl)silole (4jc).** The title compound (80.2 mg, 67%) was prepared from **2j** (64.3 mg, 0.30 mmol) and **3c** (165.9 mg, 0.90 mmol). Mp 146 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  7.04-7.05 (m, 2H), 7.23-7.27 (m, 4H), 7.30 (s, 2H), 7.33-7.43 (m, 6H), 7.67-7.70 (m, 4H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  121.8, 125.5, 125.6, 128.4, 130.3, 131.3, 135.9, 136.5, 139.7, 140.5; HRMS (EI) calcd for  $\text{C}_{24}\text{H}_{18}\text{S}_2\text{Si}$  ( $\text{M}^+$ ) 398.0619, found 398.0617.



**2',5'-Dicyclohexenylspiro[9-silafluorene-9,1'-silole] (4kd).** The title compound (39.4 mg, 50%) was prepared from **2k** (42.1 mg, 0.20 mmol) and **3d** (109.4 mg, 0.60 mmol) as oil.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.39-1.46 (m, 4H), 1.56-1.62 (m, 4H), 1.70-1.79 (m, 4H), 2.14-2.22 (m, 4H), 5.08 (t,  $J = 3.6$  Hz, 2H), 6.91 (s, 2H), 7.22-7.30 (m, 2H), 7.46 (t,  $J = 7.7$  Hz, 2H), 7.56 (d,  $J = 6.3$  Hz, 2H), 7.89 (d,  $J = 8.1$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  22.3, 22.6, 25.7, 26.2, 121.1, 127.6, 129.1, 130.4, 130.7, 133.8, 135.1, 135.7, 138.0, 148.6; HRMS (EI) calcd for  $\text{C}_{28}\text{H}_{28}\text{Si}$  ( $\text{M}^+$ ) 392.1960, found 392.1958



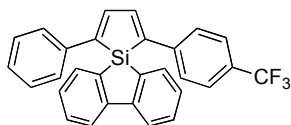
**2'-Phenyl-5'-(4-vinylphenyl)spiro[9-silafluorene-9,1'-silole] (4ld).** The title compound (38.7 mg, 63%) was prepared from **2l** (34.2 mg, 0.15 mmol) and **3d** (82.0 mg, 0.45 mmol). Mp (decomp.) 89 °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.12 (d,  $J = 11.0$  Hz, 1H), 5.60 (d,  $J = 17.6$  Hz, 1H), 6.56 (dd,  $J = 17.6, 11.1$  Hz, 1H), 7.05-7.16 (m, 9H), 7.23 (t,  $J = 7.5$  Hz, 2H), 7.47-7.59 (m, 4H), 7.64 (s, 2H), 7.98 (d,  $J = 7.8$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  113.4, 120.9, 121.5, 126.40, 126.44, 126.5, 127.1, 128.1, 128.6, 131.2, 132.4, 134.1, 136.3, 137.3, 137.8, 138.1, 138.4, 141.4, 141.8, 149.3; HRMS (EI) calcd for  $\text{C}_{30}\text{H}_{22}\text{Si}$  ( $\text{M}^+$ ) 410.1491, found 410.1490.



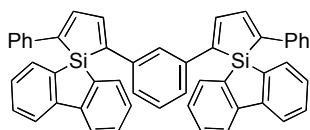
**2-(4-Methoxyphenyl)-5-phenylspiro[9-silafluorene-9,1'-silole] (4md).** The title



compound (33.4 mg, 56%) was prepared from **2m** (33.2 mg, 0.14 mmol) and **3d** (78.2 mg, 0.43 mmol) as oil.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  3.66 (s, 3H), 6.63 (d,  $J = 8.7$  Hz, 2H), 7.03-7.15 (m, 7H), 7.22 (t,  $J = 7.1$  Hz, 2H), 7.46-7.64 (m, 6H), 7.98 (d,  $J = 7.8$  Hz, 2H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  55.1, 114.1, 121.5, 126.3, 126.8, 127.6, 128.1, 128.5, 130.6, 131.1, 132.7, 134.1, 137.0, 137.9, 139.4, 142.1, 149.2, 158.8 [one carbon missing due to overlap]; HRMS (EI) calcd for  $\text{C}_{29}\text{H}_{22}\text{OSi}$  ( $\text{M}^+$ ) 414.1440, found 414.1440.

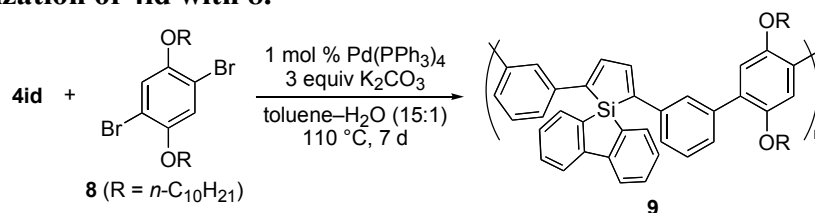


**2'-Phenyl-5'-[4-(trifluoromethyl)phenyl]spiro[9-silafluorene-9,1'-silole] (4nd).** The title compound (62.1 mg, 69%) was prepared from **2n** (54.1 mg, 0.20 mmol) and **3d** (109.4 mg, 0.60 mmol). Mp 74 °C.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.08-7.24 (m, 9H), 7.33 (d,  $J = 8.1$  Hz, 2H), 7.50-7.57 (m, 4H), 7.62-7.72 (m, 2H), 7.98 (d,  $J = 7.5$  Hz, 2H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  121.7, 124.1 ( $^1J_{\text{C-F}} = 271.8$  Hz), 125.5 ( $^3J_{\text{C-F}} = 3.8$  Hz), 126.4, 126.5, 127.5, 128.2, 128.6, 131.5, 131.7, 134.0, 137.1, 137.5, 140.0, 141.3, 144.0, 149.3 [one carbon (*ipso* to  $\text{CF}_3$ ) missing due to overlap]; HRMS (EI) calcd for  $\text{C}_{29}\text{H}_{19}\text{F}_3\text{Si}$  ( $\text{M}^+$ ) 452.1208, found 452.1209.



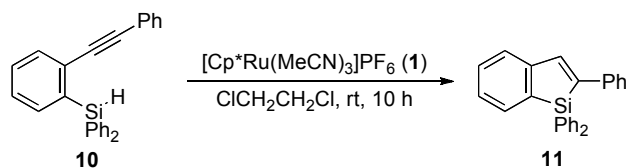
**1,3-Bis(2'-phenylspiro[9-silafluorene-9,1'-silole]-5'-yl)benzene (7).** The title compound (133.3 mg, 72%) was prepared from **6** (87.5 mg, 0.27 mmol) and **3d** (293.5 mg, 1.6 mmol). Mp (decomp.) 232 °C.  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  6.64-6.71 (m, 2H), 7.02-7.15 (m, 10H), 7.15-7.25 (m, 8H), 7.46-7.56 (m, 10H), 7.99 (d,  $J = 7.8$  Hz, 4H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  121.4, 123.4, 125.7, 126.4, 127.0, 128.1, 128.5, 128.9, 131.2, 132.5, 134.1, 137.7, 137.8, 138.1, 138.2, 141.4, 141.8, 149.2; HRMS (EI) calcd for  $\text{C}_{50}\text{H}_{34}\text{Si}_2$  ( $\text{M}^+$ ) 690.2199, found 690.2198.

#### Polymerization of **4id** with **8**.



To a solution of  $\text{Pd}(\text{PPh}_3)_4$  (1.3 mg, 1.2  $\mu\text{mol}$ ) in toluene (0.57 mL) were added 1,4-dibromo-2,5-bis(decyloxy)benzene (**8**, 63.8 mg, 0.116 mmol), **4id** (74.0 mg, 0.116 mmol),  $\text{K}_2\text{CO}_3$  (48.1 mg, 0.348 mmol), and water (0.038 mL). After being stirred at 110 °C for 1 week, the reaction mixture was poured into an excess of MeOH. The precipitate was collected by filtration, washed with MeOH, and dried under vacuum to give black polymer **9** (89.6 mg, 99%).  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  0.78-0.91 (br, 6H), 1.03-1.30 (br, 24H), 1.32-1.46 (br, 4H), 1.61-1.78 (br, 4H), 3.74-4.05 (br, 4H), 6.57-6.86 (m, 3H), 6.90-7.12 (br, 4H), 7.14-7.57 (br, 11H), 7.64-7.74 (br, 2H).  $M_n = 4.66 \times 10^3$ ,  $M_w = 1.66 \times 10^4$ ,  $M_w/M_n = 3.57$ .

**Reaction of 10.**



To a solution of  $[\text{Cp}^*\text{Ru}(\text{MeCN})_3]\text{PF}_6$  (20.2 mg, 0.040 mmol) in 1,2-dichloroethane (0.5 mL) was added a solution of diphenyl[2-(phenylethynyl)phenyl]silane<sup>24</sup> (**10**, 72.1 mg, 0.200 mmol) in 1,2-dichloroethane (1.5 mL). After being stirred for 10 h at room temperature, the reaction mixture was concentrated under reduced pressure. The residue was purified by thin layer chromatography (hexane:AcOEt = 10:1) to give 1,1,2-triphenyl-1-silaindene<sup>25</sup> (**11**, 51.9 mg, 72%). Mp (decomp.) 97 °C. <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  7.19-7.46 (m, 12H), 7.52-7.55 (m, 2H), 7.62-7.70 (m, 5H), 7.77 (s, 1H); <sup>13</sup>C NMR ( $\text{CDCl}_3$ )  $\delta$  124.7, 127.0, 127.2, 128.2, 128.6, 130.2, 130.5, 132.1, 132.9, 135.7, 136.1, 138.9, 142.8, 143.8, 149.6 [one carbon missing due to overlap]; HRMS (EI) calcd for  $\text{C}_{26}\text{H}_{20}\text{Si}$  ( $\text{M}^+$ ) 360.1334, found 360.1334.

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(24) [141240-76-8].

(25) [141240-81-5].

**Table.** Photophysical and Thermal Properties of Siloles

		UV-vis <sup>a</sup>		fluorescence <sup>b</sup>		<i>T</i> <sub>g</sub> (°C)	<i>T</i> <sub>m</sub> (°C)
		$\lambda_{\text{abs}}$ (nm)	log $\epsilon$	$\lambda_{\text{em}}$ (nm)	$\Phi_{\text{F}}$		
<b>4ac</b>		382	4.26	467	0.64	35	169
<b>4ad</b>		391	4.12	490	0.35	65	197
<b>4bd</b>		418	4.29	510	0.16	83	201
<b>4cd</b>		–	–	501	0.11	70	210
<b>4dd</b>		414	4.05	513	0.07	81	167
<b>4ed</b>		411	4.22	501	0.30	–	–
<b>4gd</b>		390	4.24	488	0.65	52	157
<b>4hd</b>		401	4.34	500	0.31	90	203
<b>4jd</b>		398	3.95	493	0.26	81	233
<b>4nd</b>		391	4.14	496	0.26	–	–
<b>7</b>		396	4.33	494	0.29	– <sup>c</sup>	– <sup>c</sup>

<sup>a</sup> Measured in CHCl<sub>3</sub>. <sup>b</sup> Measured in hexane. Determined with reference to quinine sulfate in 0.1 N H<sub>2</sub>SO<sub>4</sub> and anthracene in EtOH (excited at 250 nm). <sup>c</sup> Decomposed.