

## Supporting Information

### Base-Mediated Borylsilylation/Silylation of Ammonium Salts with Silylborane

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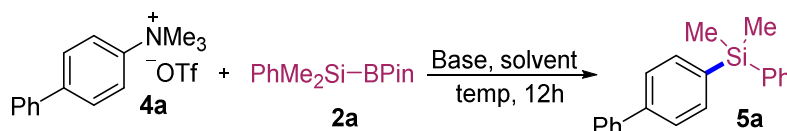
## 1. General information

All experiments were performed using standard Schlenk techniques under nitrogen atmosphere. All anhydrous solvents, commercial reagents, and organic bases were purchased from Adamas-Beta Co. or Bidepharm Co. and used as received. PhMe<sub>2</sub>Si-Bpin<sup>1</sup> and Et<sub>3</sub>Si-Bpin<sup>2</sup> were prepared according to the method reported previously. All products were identified using NMR analysis and comparison with authentic samples. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> or DMSO-*d*<sub>6</sub> on Bruker spectrometers at 400 or 500 MHz. All shifts are reported in parts per million (ppm) relative to residual CHCl<sub>3</sub> peak (7.26 and 77.0 ppm, <sup>1</sup>H NMR and <sup>13</sup>C NMR, respectively). Abbreviations are: s, singlet; d, doublet; t, triplet; q, quartet; brs, broad singlet. High Resolution Mass Spectra were obtained on a Waters Synapt G2-Si (ESI, Q-TOF) or Thermofisher Q Exactive GC (EI, Orbitrap). All flash chromatography was performed using silica gel, 300-400 mesh. TLC analysis was carried out on glassplates coated with silica gel 60 F254, 0.2 mm thickness. The plates were visualized using a 254 nm ultraviolet lamp or iodine cylinder. The following compounds have previously been described in the literature: **1a**<sup>3</sup>, **1b**<sup>3</sup>, **1c**<sup>4</sup>, **1d**<sup>4</sup>, **1e**<sup>4</sup>, **1f**<sup>5</sup>, **1h**<sup>3</sup>, **1i**<sup>3</sup>, **1j**<sup>3</sup>, **1k**<sup>4</sup>, **1l**<sup>4</sup>, **1m**<sup>4</sup>, **1n**<sup>6</sup>, **1o**<sup>4</sup>, **1p**<sup>7</sup>, **1q**<sup>3</sup>, **1s**<sup>5</sup>, **1u**<sup>8</sup>, **4a**<sup>9</sup>, **4b**<sup>10</sup>, **4c**<sup>10</sup>, **4d**<sup>10</sup>, **4e**<sup>10</sup>, **4f**<sup>6</sup>, **4g**<sup>6</sup>, **4h**<sup>9</sup>, **4i**<sup>6</sup>, **4j**<sup>6</sup>, **4l**<sup>11</sup>, **4n**<sup>12</sup>, **4p**<sup>13</sup>, **4t**<sup>14</sup>, **4w**<sup>10</sup>, **4x**<sup>14</sup>, **4y**<sup>15</sup> and **10**<sup>16</sup>.

## 2. Table S1. Optimization of reaction conditions of silylation of aryl ammonium salt **4a**<sup>a</sup>

LiHMDS was found to mediate the reaction of aryl ammonium triflate **4a** and silylborane **2a**, affording the desired product **5a** in 30% yield at room temperature (entry 1). KO<sup>t</sup>Bu and NaO<sup>t</sup>Bu exhibited no obvious difference in reactivity compared with LiHMDS (entries 2 and 3). A weaker base LiOtBu resulted in 46% isolated yield of **5a**, giving the best result in screening of bases. The product **5a** was furnished with 83% yield at 55 °C, while further elevation of the temperature didn't show any

improvement (entries 5 and 6). Other solvents, such as NMP, 1,4-dioxane, DMSO, and DME, were also tested, and no better results were observed (entries 7-10).

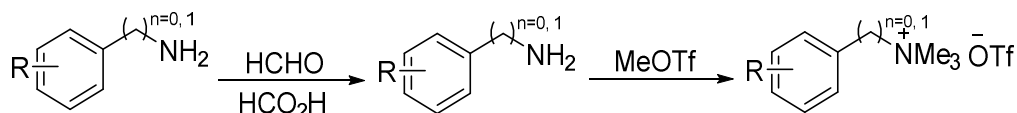


entry	base	temp (°C)	solvent	yield (%)
1	LiHMDS	25	THF	30
2	KO <sup>t</sup> Bu	25	THF	33
3	NaO <sup>t</sup> Bu	25	THF	25
4	LiO <sup>t</sup> Bu	25	THF	46
5	LiO <sup>t</sup> Bu	55	THF	83
6	LiO <sup>t</sup> Bu	75	THF	83
7	LiO <sup>t</sup> Bu	55	NMP	64
8	LiO <sup>t</sup> Bu	55	1,4-dioxane	78
9	LiO <sup>t</sup> Bu	55	DMSO	80
10	LiO <sup>t</sup> Bu	55	DME	72

<sup>a</sup>Reaction conditions: **4a** (0.2 mmol), **2a** (0.4 mmol), base (0.4 mmol), solvent (0.5 mL).

### 3. Experiment procedures

#### 3.1. General procedure (GP1) for Substrates



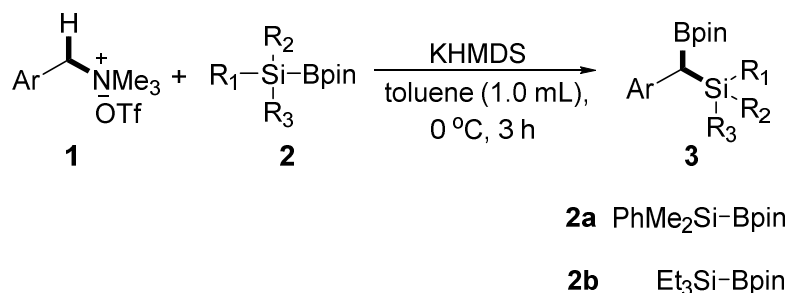
**Step 1:** Following the literature procedure<sup>17</sup>. To a mixture of formic acid (5.0 equiv.) and primary amine (5.0 mmol) was added formaldehyde (36% aqueous solution, 2.2 equiv.) at 0 °C. The reaction mixture was refluxed overnight in an oil bath. After cooling to room temperature, 1.0 mL of aqueous HCl (2 M) was added. The remaining formic acid and formaldehyde were evaporated under reduced pressure. 5.0 mL of aqueous HCl (2 M) was then added and the mixture was washed with ethyl acetate (10 mL × 3). The aqueous layer was basified with aqueous buffer solution of NH<sub>3</sub> (1 M)/NH<sub>4</sub>Cl (1 M) and extracted with dichloromethane (10 mL × 3). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated under

reduced pressure. The crude residue was purified by silica gel column to give dimethyl benzyl amine.

**Step 2:** Following the literature procedure<sup>18</sup>. To a solution of the above dimethyl benzyl amine (5 mmol) in Et<sub>2</sub>O (15 mL) was dropwise added MeOTf (0.7 mL, 6 mmol) at 0 °C. The reaction mixture was stirred for an additional 20 minutes at 0 °C, and then warm to rt. for another 2 h. The precipitate was collected by filtration and washed with Et<sub>2</sub>O (20 mL ×3). The resulting solid was dried in vacuum to give benzyl ammonium salts **1** and ammonium salts **4**.

**Notes:** All aryldimethylamines and ammonium salt **6** were purchased from Adamas-Beta Co. or Bidepharm Co. and used as received. All aryltrimethylammonium triflates were prepared on 10.0 mmol scale (of *N,N*-dimethylarylamine) as described above in the General Procedure. Yields and spectral data are given below for all products.

### 3.2. General procedure (GP2) for borylsilylation of benzylic ammonium salts

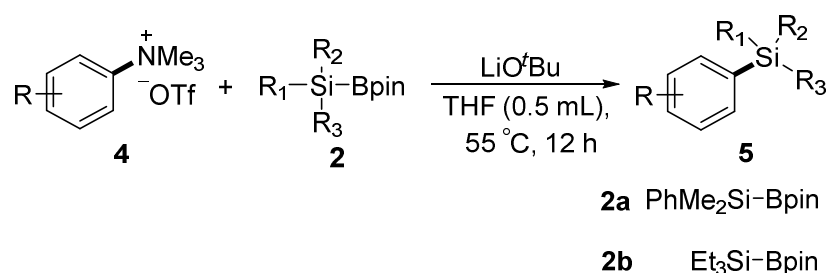


A flame-dried Schlenk tube equipped with a magnetic stir bar was charged with the ammonium salt **1** (0.20 mmol), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling cycles (three times) before toluene (1.0 mL) was added. Then, this tube was cooled to 0 or -20 °C. **2** (0.24 mmol) and base (KHMDS or LiHMDS, 0.22 mmol) were injected sequentially with stirring. After 3 hours, the reaction was quenched with NH<sub>4</sub>Cl aqueous solution and extracted with ethyl acetate (20 mL ×2). After filtration and evaporation of the solvents in vacuo, the crude product **3** was purified by column chromatography.

**The procedure for the 1 mmol scale synthesis of 3i**

A 50 mL round-bottom flask equipped with a magnetic stir bar was charged with the ammonium salt **1i** (364.1 mg, 1.0 mmol), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling cycles (three times) before toluene (5.0 mL) was added. Then, this tube was cooled to 0 °C. **2a** (314.6 mg, 1.2 mmol) and KHMDS (1.1 mL, 1.1 mmol, 1.0 M in THF) were injected sequentially with stirring. After 3 hours, the reaction was quenched with NH<sub>4</sub>Cl aqueous solution and extracted with ethyl acetate (30 ml\*2). After filtration and evaporation of the solvents in vacuo, the crude product **3i** was purified by column chromatography (301.7 mg, 75% yield, petroleum ether/EtOAc = 50/1).

### 3.3. General procedure (GP3) for silylation of aryl ammonium salts



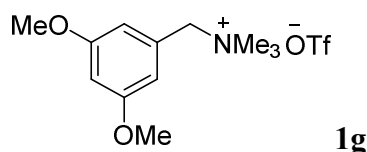
A flame-dried Schlenk tube equipped with a magnetic stir bar was charged with the aryl ammonium salts **4** (0.20 mmol), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling cycles (three times) before THF (0.5 mL) was added. Then **2** (0.40 mmol) and LiO<sup>t</sup>Bu (0.40 mmol, 2.2 M in THF) was injected sequentially into the tube. The whole reaction mixture was stirred at room temperature or reacted in an oil bath at 55°C for 12 h. After that, the reaction was quenched with NH<sub>4</sub>Cl aqueous solution and extracted with ethyl acetate (20 ml\*2). After filtration and evaporation of the solvents in vacuo, the crude product **5** was purified by column chromatography.

#### The procedure for the 1 mmol scale synthesis of **5e**

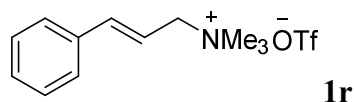
A flame-dried Schlenk tube equipped with a magnetic stir bar was charged with the aryl ammonium salts **4e** (350.4 mg, 1.0 mmol), sealed with a septum, and degassed by alternating vacuum evacuation and argon backfilling cycles (three times) before THF (2.5 mL) was added. Then **2a** (524.4 mg, 2.0 mmol) and LiO<sup>t</sup>Bu (0.91 mL, 2.0 mmol,

2.2 M in THF) was injected sequentially into the tube. The whole reaction mixture was stirred in an oil bath at 55°C for 12 h. After that, the reaction was quenched with NH<sub>4</sub>Cl aqueous solution and extracted with ethyl acetate (30 ml\*2). After filtration and evaporation of the solvents in vacuo, the crude product **5e** was purified by column chromatography (204.7 mg, 78% yield, petroleum ether/EtOAc = 100/1).

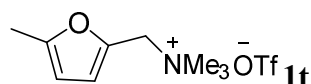
#### 4. Characterization data of starting materials



**1g** was synthesized following the general procedure (**GP1**) and obtained in 83% yield. 3.01 g, white solid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.64 (d, *J* = 2.2 Hz, 2H), 6.53 (d, *J* = 2.3 Hz, 1H), 4.50 (s, 2H), 3.79 (s, 6H), 3.17 (s, 9H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 161.3, 129.0, 120.6 (q, *J* = 315.0 Hz), 110.7, 102.7, 69.7, 55.6, 52.8. HRMS (ESI) *m/z*: [M-OTf]<sup>+</sup> Calcd for C<sub>12</sub>H<sub>20</sub>NO<sub>2</sub> 210.1494; found: 210.1491.

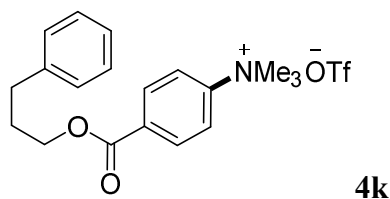


**1r** was synthesized following the general procedure (**GP1**) and obtained in 90% yield. 2.93 g, light yellow solid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.47-7.43 (m, 2H), 7.38-7.33 (m, 3H), 7.02 (d, *J* = 15.6 Hz, 1H), 6.27-6.18 (m, 1H), 4.19 (d, *J* = 7.6 Hz, 2H), 3.20 (s, 9H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 144.7, 134.4, 129.8, 128.9, 127.4, 120.7 (q, *J* = 315.0 Hz), 113.5, 68.4, 52.7. HRMS (ESI) *m/z*: [M-OTf]<sup>+</sup> Calcd for C<sub>12</sub>H<sub>18</sub>N 176.1439; found: 176.1441.



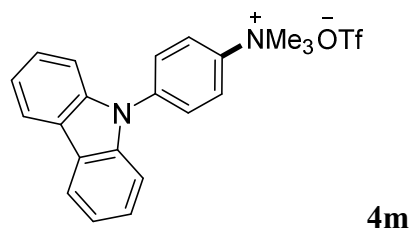
**1t** was synthesized following the general procedure (**GP1**) and obtained in 66% yield. 1.18 g, white solid (at 0°C), <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.69 (d, *J* = 3.0 Hz, 1H), 6.04 (d, *J* = 3.2 Hz, 1H), 4.52 (s, 2H), 3.15 (s, 9H), 2.29 (s, 3H). <sup>13</sup>C NMR (126 MHz,

**CDCl<sub>3</sub>**)  $\delta$  151.2, 135.7, 115.9 (q,  $J$  = 320.0 Hz), 113.6, 102.9, 57.3, 47.8, 8.8. **HRMS** (ESI)  $m/z$ : [M-OTf]<sup>+</sup> Calcd for C<sub>9</sub>H<sub>16</sub>NO 154.1232; found: 154.1236.



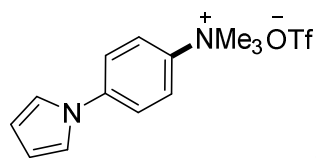
**4k** was synthesized following the general procedure (**GP1**) and obtained in 89% yield.

3.98g, white solid, **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  8.21 (d,  $J$  = 8.6 Hz, 2H), 7.92 (d,  $J$  = 8.7 Hz, 2H), 7.29 (t,  $J$  = 7.5 Hz, 2H), 7.21 (d,  $J$  = 6.8 Hz, 3H), 4.37 (t,  $J$  = 6.4 Hz, 2H), 3.79 (s, 9H), 2.77 (t,  $J$  = 7.5 Hz, 2H), 2.16-2.08 (m, 2H). **<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**  $\delta$  164.4, 149.9, 140.9, 132.8, 132.1, 128.6, 128.4, 126.2, 119.96, 120.6 (q,  $J$  = 322.5 Hz), 65.3, 57.5, 32.3, 30.1. **HRMS (ESI)**  $m/z$ : [M-OTf]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>24</sub>NO<sub>2</sub> 298.1807; found: 298.1809.



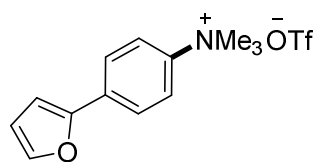
**4m** was synthesized following the general procedure (**GP1**) and obtained in 91% yield.

4.11 g, white solid, **<sup>1</sup>H NMR (400 MHz, DMSO)**  $\delta$  8.31-8.25 (m, 4H), 7.97 (d,  $J$  = 9.1 Hz, 2H), 7.51-7.41 (m, 4H), 7.38-7.32 (m, 2H), 3.74 (s, 9H). **<sup>13</sup>C NMR (126 MHz, DMSO)**  $\delta$  146.1, 140.2, 138.7, 128.3, 127.0, 123.5, 123.2, 121.2, 121.1, 121.16 (q,  $J$  = 322.5 Hz), 110.0, 57.1. **HRMS (ESI)**  $m/z$ : [M-OTf]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>21</sub>N<sub>2</sub> 301.1705; found: 301.1704.



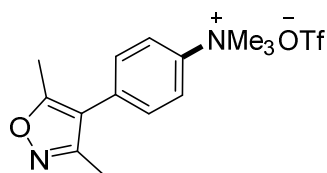
**4o**

**4o** was synthesized following the general procedure (**GP1**) and obtained in 92% yield. 3.24 mg, white solid,  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  8.03 (d,  $J$  = 9.2 Hz, 2H), 7.86 (d,  $J$  = 9.2 Hz, 2H), 7.53 (t,  $J$  = 2.2 Hz, 2H), 6.33 (t,  $J$  = 2.2 Hz, 2H), 3.63 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz, DMSO)  $\delta$  144.2, 141.0, 122.5, 121.16 (q,  $J$  = 323.8 Hz), 120.1, 119.7, 111.8, 57.0. HRMS (ESI)  $m/z$ :  $[\text{M-OTf}]^+$  Calcd for  $\text{C}_{13}\text{H}_{17}\text{N}_2$  201.1392; found: 201.1393.



**4q**

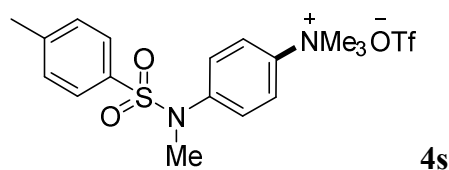
**4q** was synthesized following the general procedure (**GP1**) and obtained in 82% yield. 2.88 mg, white solid,  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  8.02 (d,  $J$  = 9.0 Hz, 2H), 7.93 (d,  $J$  = 9.0 Hz, 2H), 7.85 (s, 1H), 7.19 (d,  $J$  = 3.4 Hz, 1H), 6.67 (t,  $J$  = 2.7 Hz, 1H), 3.63 (s, 9H).  $^{13}\text{C}$  NMR (126 MHz, DMSO)  $\delta$  151.6, 146.2, 144.6, 132.1, 124.9, 121.7, 121.16 (q,  $J$  = 323.8 Hz), 112.9, 108.7, 56.9. HRMS (ESI)  $m/z$ :  $[\text{M-OTf}]^+$  Calcd for  $\text{C}_{13}\text{H}_{16}\text{NO}$  202.1232; found: 202.1229.



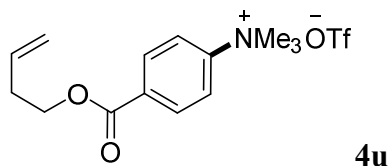
**4r**

**4r** was synthesized following the general procedure (**GP1**) and obtained in 92% yield. 3.52 mg, white solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.94 (d,  $J$  = 8.9 Hz, 2H), 7.53 (d,  $J$  = 9.0 Hz, 2H), 3.83 (s, 9H), 2.45 (s, 3H), 2.30 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  166.3, 158.2, 145.8, 133.8, 131.2, 120.6 (q,  $J$  = 321.3 Hz), 120.2, 114.6, 57.5, 11.7, 10.8. HRMS (ESI)  $m/z$ :  $[\text{M-OTf}]^+$  Calcd for  $\text{C}_{14}\text{H}_{19}\text{N}_2\text{O}$  231.1497; found: 231.1500.

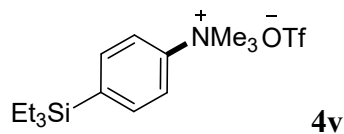




**4s** was synthesized following the general procedure (**GP1**) and obtained in 88% yield. 4.11 mg, white solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 (d,  $J$  = 8.8 Hz, 2H), 7.49-7.39 (m, 4H), 7.33 (d,  $J$  = 8.0 Hz, 2H), 3.77 (s, 9H), 3.18 (s, 3H), 2.46 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz, DMSO)  $\delta$  145.6, 144.5, 142.8, 133.6, 130.4, 127.9, 127.2, 121.7, 57.0, 38.0, 21.5 (The  $\text{CF}_3$  quartet for the triflate group didn't show up.). HRMS (ESI)  $m/z$ :  $[\text{M-OTf}]^+$  Calcd for  $\text{C}_{17}\text{H}_{23}\text{N}_2\text{O}_2\text{S}$  319.1480; found: 319.1483.



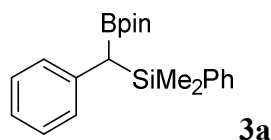
**4u** was synthesized following the general procedure (**GP1**) and obtained in 94% yield. 3.62 mg, white solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.26 (d,  $J$  = 8.5 Hz, 2H), 7.96 (d,  $J$  = 8.7 Hz, 2H), 5.92-5.81 (m, 1H), 5.25-5.10 (m, 2H), 4.43 (t,  $J$  = 6.7 Hz, 2H), 3.81 (s, 9H), 2.55 (q,  $J$  = 6.8 Hz, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  164.4, 149.9, 133.6, 132.7, 132.1, 120.6 (q,  $J$  = 320.0 Hz), 120.0, 117.8, 64.8, 57.4, 33.0. HRMS (ESI)  $m/z$ :  $[\text{M-OTf}]^+$  Calcd for  $\text{C}_{14}\text{H}_{20}\text{NO}_2$  234.1494; found: 234.1491.



**4v** was synthesized following the general procedure (**GP1**) and obtained in 84% yield. 3.36 mg, white solid,  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  8.02-7.90 (m, 2H), 7.76-7.71 (m, 1H), 7.68-7.57 (m, 1H), 3.61 (d,  $J$  = 1.5 Hz, 9H), 0.93 (t,  $J$  = 7.5 Hz, 9H), 0.88-0.76 (m, 6H).  $^{13}\text{C}$  NMR (126 MHz, DMSO)  $\delta$  153.0, 144.9, 140.8, 135.3, 125.9

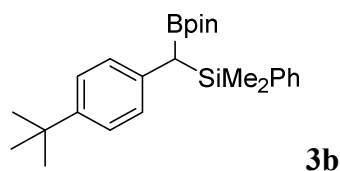
(q,  $J = 322.2$  Hz), 61.5, 12.4, 7.8. **HRMS (ESI)**  $m/z$ :  $[M-OTf]^+$  Calcd for  $C_{15}H_{28}NSi$  250.1991; found: 250.1994.

## 5. Characterization data of products 3



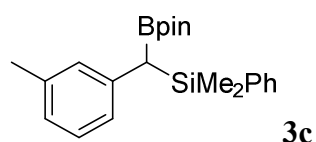
**3a**<sup>19</sup> was synthesized following the general procedure **GP2**. After purification by preparative thin-layer chromatography using petroleum ether/EtOAc (50/1) as the eluent, **3a** was obtained in 82% yield.

58.1 mg, colorless oil, **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.42-7.36 (m, 2H), 7.31-7.24 (m, 3H), 7.13 (t,  $J = 7.6$  Hz, 2H), 7.08 – 7.00 (m, 3H), 2.19 (s, 1H), 1.16 (s, 6H), 1.10 (s, 6H), 0.33 (s, 3H), 0.24 (s, 3H). **<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**  $\delta$  145.5, 140.0, 138.2, 134.1, 129.0, 128.9, 127.8, 127.4, 123.1, 113.6, 83.1, 25.1, 24.8, -2.9, -3.4.



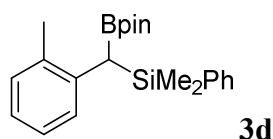
**3b**<sup>19</sup> was synthesized following the general procedure **GP2**. After purification by preparative thin-layer chromatography using petroleum ether/EtOAc (50/1) as the eluent, **3b** was obtained in 92% yield.

75.2 mg, colorless oil, **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.42-7.34 (m, 2H), 7.31-7.21 (m, 3H), 7.15 (d,  $J = 8.4$  Hz, 2H), 7.00 (d,  $J = 8.4$  Hz, 2H), 2.16 (s, 1H), 1.28 (s, 9H), 1.15 (s, 6H), 1.09 (s, 6H), 0.33 (s, 3H), 0.23 (s, 3H). **<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)**  $\delta$  146.2, 138.4, 136.6, 134.1, 128.8, 128.5, 127.3, 124.7, 83.0, 34.2, 31.5, 25.1, 24.9, 2.7, -3.4.



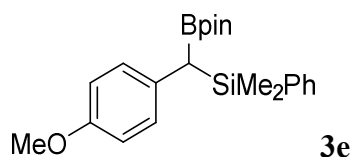
**3c**<sup>19</sup> was synthesized following the general procedure **GP2**. After purification by preparative thin-layer chromatography using petroleum ether/EtOAc (50/1) as the eluent, **3c** was obtained in 76% yield.

55.6 mg, colorless oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.45-7.35 (m, 2H), 7.31-7.21 (m, 3H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.85 – 6.75 (m, 2H), 2.22 (s, 3H), 2.14 (s, 1H), 1.16 (s, 6H), 1.10 (s, 6H), 0.33 (s, 3H), 0.24 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 139.8, 138.3, 137.1, 134.1, 129.9, 128.9, 127.6, 127.3, 125.9, 124.4, 83.0, 25.1, 24.8, 21.5, -2.9, -3.4.



**3d**<sup>19</sup> was synthesized following the general procedure **GP2**. After purification by preparative thin-layer chromatography using petroleum ether/EtOAc (50/1) as the eluent, **3d** was obtained in 69% yield.

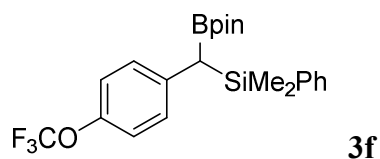
42.7 mg, colorless oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.37-7.33 (m, 3H), 7.31-7.27 (m, 1H), 7.26-7.22 (m, 2H), 7.07 (m, 1H), 7.01-6.92 (m, 2H), 2.39 (s, 1H), 1.98 (s, 3H), 1.16 (s, 6H), 1.10 (s, 6H), 0.33 (s, 3H), 0.24 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 138.5, 138.4, 135.1, 134.0, 130.0, 129.0, 128.9, 127.4, 125.3, 123.6, 83.1, 25.1, 24.8, 20.6, -2.6, -3.1.



**3e**<sup>19</sup> was synthesized following the general procedure **GP2**. After purification by preparative thin-layer chromatography using petroleum ether/EtOAc (50/1) as the eluent, **3e** was obtained in 65% yield.

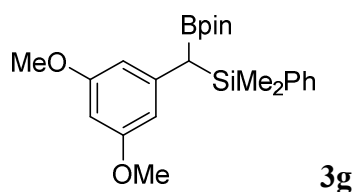
49.1 mg, colorless oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.40 (d, *J* = 6.8 Hz, 2H), 7.34-7.23 (m, 3H), 6.98 (d, *J* = 8.1 Hz, 2H), 6.70 (d, *J* = 8.1 Hz, 2H), 3.74 (s, 3H), 2.12 (s, 1H), 1.16 (s, 6H), 1.10 (s, 6H), 0.32 (s, 3H), 0.24 (s, 3H). <sup>13</sup>C NMR (126

**MHz, CDCl<sub>3</sub>)**  $\delta$  156.3, 138.3, 134.1, 131.8, 129.7, 128.9, 127.4, 113.3, 83.0, 55.2, 25.0, 24.8, -2.9, -3.3.



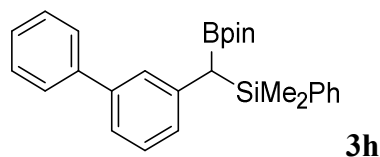
**3f** was synthesized following the general procedure **GP2**. After purification by preparative thin-layer chromatography using petroleum ether/EtOAc (50/1) as the eluent, **3f** was obtained in 79% yield.

68.3 mg, colorless oil, **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  7.36 – 7.23 (m, 5H), 7.07-6.99 (m, 2H), 6.96 (d,  $J$  = 8.4 Hz, 2H), 2.19 (s, 1H), 1.16 (s, 6H), 1.10 (s, 6H), 0.33 (s, 3H), 0.24 (s, 3H). **<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**  $\delta$  145.9, 145.9, 139.0, 137.5, 134.0, 129.8, 129.1, 127.5, 120.3, 120.6 (q,  $J$  = 255.8 Hz), 83.3, 25.0, 24.8, -3.1, -3.4. **HRMS (EI)**  $m/z$ : [M-CH<sub>3</sub>]<sup>+</sup> Calcd for C<sub>21</sub>H<sub>25</sub>O<sub>3</sub>BF<sub>3</sub>Si 421.1613; found: 421.1609.



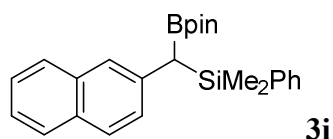
**3g** was synthesized following the general procedure **GP2**. After purification by preparative thin-layer chromatography using petroleum ether/EtOAc (50/1) as the eluent, **3g** was obtained in 77% yield.

63.8 mg, colorless oil, **<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**  $\delta$  7.46-7.37 (m, 2H), 7.33-7.22 (m, 3H), 6.30 – 6.10 (m, 3H), 3.65 (s, 6H), 2.13 (s, 1H), 1.16 (s, 6H), 1.10 (s, 6H), 0.33 (s, 3H), 0.24 (s, 3H). **<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)**  $\delta$  160.1, 142.3, 138.2, 134.1, 128.9, 127.4, 107.1, 96.4, 83.1, 55.0, 25.1, 24.8, -2.9, -3.3. **HRMS (EI)**  $m/z$ : [M]<sup>+</sup> Calcd for C<sub>23</sub>H<sub>33</sub>O<sub>4</sub>BSi 412.2236; found: 412.2233.



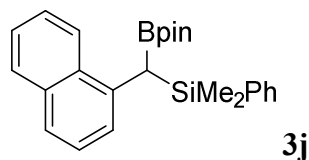
**3h** was synthesized following the general procedure **GP2**. After purification by preparative thin-layer chromatography using petroleum ether/EtOAc (50/1) as the eluent, **3h** was obtained in 73% yield.

61.3 mg, colorless oil,  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.46 – 7.33 (m, 6H), 7.32–7.19 (m, 7H), 7.13 – 7.09 (m, 1H), 2.26 (s, 1H), 1.16 (s, 6H), 1.10 (s, 6H), 0.33 (s, 3H), 0.24 (s, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  141.8, 140.5, 140.4, 138.1, 134.2, 129.0, 128.5, 128.1, 128.0, 127.9, 127.5, 127.1, 126.8, 122.6, 83.2, 25.1, 24.8, -3.0, -3.3. **HRMS (EI)**  $m/z$ :  $[\text{M}-\text{CH}_3]^+$  Calcd for  $\text{C}_{26}\text{H}_{30}\text{O}_2\text{BSi}$  413.2103; found: 413.2101.



**3i**<sup>19</sup> was synthesized following the general procedure **GP2**. After purification by preparative thin-layer chromatography using petroleum ether/EtOAc (50/1) as the eluent, **3i** was obtained in 83% yield.

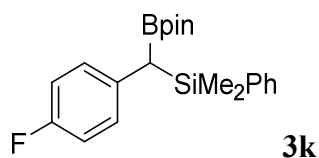
66.8 mg, colorless oil,  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 (d,  $J = 7.5$  Hz, 1H), 7.77 (d,  $J = 7.5$  Hz, 1H), 7.57–7.51 (m, 2H), 7.42 (d,  $J = 7.7$  Hz, 2H), 7.37–7.21 (m, 6H), 3.06 (s, 1H), 1.15 (s, 6H), 1.11 (s, 6H), 0.33 (s, 3H), 0.19 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  138.1, 137.9, 134.2, 133.8, 130.9, 129.0, 128.9, 127.5, 127.5, 127.2, 127.1, 126.2, 125.5, 124.2, 83.2, 25.1, 24.8, -2.7, -3.2.



**3j** was synthesized following the general procedure **GP2**. After purification by preparative thin-layer chromatography using petroleum ether/EtOAc (50/1) as the eluent, **3j** was obtained in 74% yield.

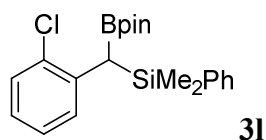
59.1 mg, colorless oil,  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.75–7.59 (m, 3H), 7.50 (s, 1H), 7.42 (d,  $J = 7.7$  Hz, 2H), 7.37–7.21 (m, 6H), 2.37 (s, 1H), 1.17 (s, 6H), 1.11 (s, 6H), 0.36 (s, 3H), 0.28 (s, 3H).  $^{13}\text{C NMR}$  (126 MHz,  $\text{CDCl}_3$ )  $\delta$  140.5, 138.7, 136.3, 136.2,

135.3, 134.2, 131.1, 130.8, 129.8, 129.5, 128.2, 127.4, 127.0, 126.5, 126.4, 85.3, 27.1, 26.9, 0.0, -1.0. **HRMS (EI)**  $m/z$ :  $[M]^+$  Calcd for  $C_{25}H_{31}O_2BSi$  402.2181; found: 402.2174.



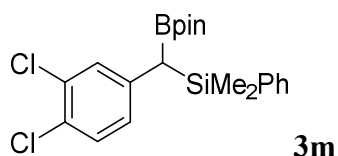
**3k** was synthesized following the general procedure **GP2**. After purification by preparative thin-layer chromatography using petroleum ether/EtOAc (50/1) as the eluent, **3k** was obtained in 62% yield.

45.8 mg, colorless oil,  **$^1H$  NMR (400 MHz,  $CDCl_3$ )**  $\delta$  7.40-7.34 (m, 2H), 7.32-7.24 (m, 3H), 7.01-6.94 (m, 2H), 6.81 (t,  $J$  = 8.8 Hz, 2H), 2.15 (s, 1H), 1.17 (s, 6H), 1.11 (s, 6H), 0.32 (s, 3H), 0.25 (s, 3H).  **$^{13}C$  NMR (100 MHz,  $CDCl_3$ )**  $\delta$  160.2 (d,  $J$  = 240.0 Hz), 137.8, 135.5 (d,  $J$  = 3.0 Hz), 134.1, 130.0 (d,  $J$  = 7.0 Hz), 129.0, 127.5, 114.4 (d,  $J$  = 21.0 Hz), 83.2, 25.1, 24.8, -3.1, -3.3. **HRMS (EI)**  $m/z$ :  $[M-CH_3]^+$  Calcd for  $C_{20}H_{25}O_2BFSi$  355.1695; found: 355.1693.



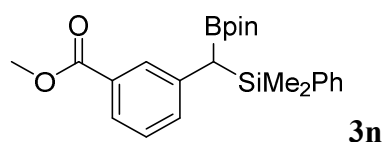
**3l** was synthesized following the general procedure **GP2**. After purification by preparative thin-layer chromatography using petroleum ether/EtOAc (50/1) as the eluent, **3l** was obtained in 58% yield.

44.4 mg, colorless oil,  **$^1H$  NMR (400 MHz,  $CDCl_3$ )**  $\delta$  7.44 (d,  $J$  = 6.5, 2H), 7.36 (m, 1H), 7.32-7.23 (m, 4H), 7.09 (m, 1H), 6.95 (m, 1H), 2.91 (s, 1H), 1.16 (s, 6H), 1.10 (s, 6H), 0.33 (s, 3H), 0.24 (s, 3H).  **$^{13}C$  NMR (101 MHz,  $CDCl_3$ )**  $\delta$  140.8, 140.2, 136.6, 135.7, 132.8, 131.5, 131.4, 129.8, 128.4, 127.2, 85.6, 27.4, 27.2, 0.0, -1.0. **HRMS (EI)**  $m/z$ :  $[M-CH_3]^+$  Calcd for  $C_{20}H_{25}O_2BClSi$  371.1400; found: 371.1399.



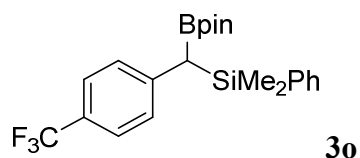
**3m** was synthesized following the general procedure **GP2**. After purification by preparative thin-layer chromatography using petroleum ether/EtOAc (50/1) as the eluent, **3m** was obtained in 78% yield.

65.4 mg, colorless oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36-7.30 (m, 5H), 7.16-7.10 (m, 2H), 6.86 (s, 1H), 2.13 (s, 1H), 1.16 (s, 6H), 1.10 (s, 6H), 0.33 (s, 3H), 0.28 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  140.8, 137.1, 134.0, 131.4, 130.5, 129.5, 129.3, 128.4, 127.6, 127.3, 83.4, 25.0, 24.7, -3.2, -3.3. HRMS (EI)  $m/z$ :  $[\text{M}-\text{CH}_3]^+$  Calcd for  $\text{C}_{20}\text{H}_{24}\text{O}_2\text{BCl}_2\text{Si}$  405.1010; found: 405.1011.



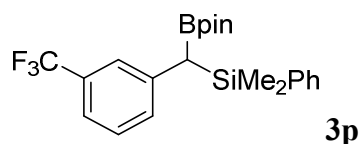
**3n** was synthesized following the general procedure **GP2**. After purification by preparative thin-layer chromatography using petroleum ether/EtOAc (40/1) as the eluent, **3n** was obtained in 66% yield.

54.2 mg, colorless oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88-7.74 (m, 2H), 7.47-7.45 (m, 2H), 7.41 – 7.25 (m, 5H), 3.96 (s, 3H), 2.34 (s, 1H), 1.26 (s, 6H), 1.21 (s, 6H), 0.42 (s, 3H), 0.36 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  167.6, 140.6, 137.6, 134.0, 133.5, 130.0, 129.6, 129.0, 127.7, 127.5, 125.0, 83.3, 51.9, 25.0, 24.7, -3.0, -3.4. HRMS (EI)  $m/z$ :  $[\text{M}]^+$  Calcd for  $\text{C}_{23}\text{H}_{31}\text{O}_4\text{BSi}$  410.2079; found: 410.2080.



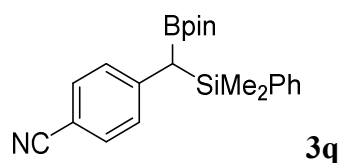
**3o** was synthesized following the general procedure **GP2**. After purification by preparative thin-layer chromatography using petroleum ether/EtOAc (50/1) as the eluent, **3o** was obtained in 80% yield.

67.3 mg, colorless oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.40-7.25 (m, 7H), 7.14 (m, 2H), 2.27 (s, 1H), 1.18 (s, 6H), 1.12 (s, 6H), 0.34 (s, 3H), 0.27 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  144.8, 137.3, 134.0, 129.2, 128.9, 127.5, 125.8 (q,  $J$ = 33.8 Hz), 124.7 (q,  $J$ = 272.2 Hz), 124.6 (q,  $J$ = 3.8 Hz), 83.4, 25.0, 24.8, -3.1, -3.4. HRMS (EI)  $m/z$ :  $[\text{M}-\text{CH}_3]^+$  Calcd for  $\text{C}_{21}\text{H}_{25}\text{O}_2\text{BF}_3\text{Si}$  405.1663; found: 405.1667.



**3p** was synthesized following the general procedure **GP2**. After purification by preparative thin-layer chromatography using petroleum ether/EtOAc (50/1) as the eluent, **3p** was obtained in 67% yield.

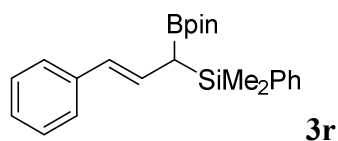
56.4 mg, colorless oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.38 -7.18 (m, 9H), 2.24 (s, 1H), 1.19 (s, 6H), 1.13 (s, 6H), 0.34 (s, 3H), 0.27 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  141.2, 137.2, 134.0, 132.1, 129.9 (q,  $J$ = 31.0 Hz), 129.2, 128.0, 127.5, 125.5 (q,  $J$ = 3.0 Hz), 124.4 (q,  $J$ = 273.7 Hz), 123.1, 120.4 (q,  $J$ = 4.0 Hz), 83.4, 25.1, 24.7, -3.3, -3.5. HRMS (EI)  $m/z$ :  $[\text{M}-\text{CH}_3]^+$  Calcd for  $\text{C}_{21}\text{H}_{25}\text{O}_2\text{BF}_3\text{Si}$  405.1663; found: 405.1662.



**3q** was synthesized following the general procedure **GP2**. After purification by preparative thin-layer chromatography using petroleum ether/EtOAc (40/1) as the eluent, **3q** was obtained in 40% yield.

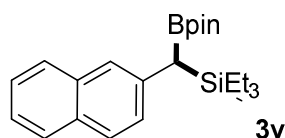
29.7 mg, colorless oil,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 (d,  $J$ = 8.4 Hz, 2H), 7.34 - 7.31 (m, 3H), 7.28 (m, 2H), 7.10 (d,  $J$ = 8.4 Hz, 2H), 2.28 (s, 1H), 1.19 (s, 6H), 1.14 (s, 6H), 0.35 (s, 3H), 0.29 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  146.9, 136.8, 133.9, 131.6, 129.44, 129.35, 127.6, 119.7, 107.1, 83.6, 25.0, 24.8, -3.26, -3.28. HRMS (EI)  $m/z$ :  $[\text{M}]^+$  Calcd for  $\text{C}_{22}\text{H}_{28}\text{O}_2\text{NBSi}$  377.1977; found: 377.1975.





**3r**<sup>20</sup> was synthesized following the general procedure **GP2**. After purification by preparative thin-layer chromatography using petroleum ether/EtOAc (30/1) as the eluent, **3r** was obtained in 53% yield.

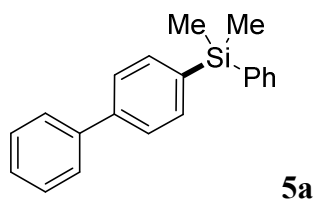
40.1 mg, colorless oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.57-7.49 (m, 2H), 7.35-7.29 (m, 3H), 7.27 – 7.22 (m, 4H), 7.15-7.10 (m, 1H), 6.33-6.27 (m, 1H), 6.08 (d, *J* = 15.7 Hz, 1H), 1.91 (d, *J* = 10.6 Hz, 1H), 1.17 (s, 6H), 1.13 (s, 6H), 0.39 (s, 3H), 0.37 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 138.8, 138.0, 134.1, 129.0, 128.5, 128.3, 127.8, 127.6, 126.0, 125.6, 83.1, 24.95, 24.90, -2.95, -2.98.



**3v** was synthesized following the general procedure **GP2**. After purification by preparative thin-layer chromatography using petroleum ether/EtOAc (55/1) as the eluent, **3v** was obtained in 53% yield.

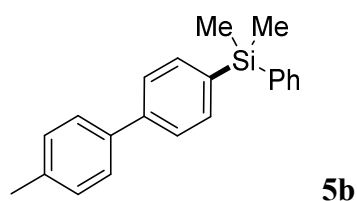
40.8 mg, colorless solid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ .69-7.55 (m, 3H), 7.51 (s, 1H), 7.36-7.21 (m, 3H), 2.17 (s, 1H), 1.17 (d, *J* = 13.9 Hz, 12H), 0.85 (t, *J* = 7.9 Hz, 9H), 0.50 (q, *J* = 8.1 Hz, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 138.8, 133.8, 130.8, 128.9, 127.5, 127.2, 127.0, 126.0, 125.4, 124.1, 83.1, 25.3, 24.8, 7.5, 3.6. HRMS (EI) *m/z*: [M]<sup>+</sup> Calcd for C<sub>23</sub>H<sub>35</sub>O<sub>2</sub>BSi 382.24939; found: 382.24933.

## 6. Characterization data for products 5



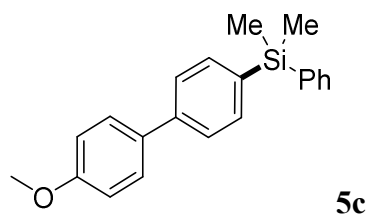
**5a**<sup>21</sup> was synthesized following the general procedure **GP3**. After purification by preparative thin-layer chromatography using petroleum ether/EtOAc (100/1) as the eluent, **5a** was obtained in 83% yield.

47.9 mg, colorless oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.68-7.55 (m, 8H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.44 – 7.34 (m, 4H), 0.64 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 144.2, 143.4, 140.5, 139.3, 137.0, 136.5, 131.5, 131.1, 130.2, 129.7, 129.5, 128.9, 0.0.



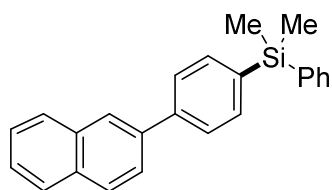
**5b**<sup>21</sup> was synthesized following the general procedure **GP3**. After purification by preparative thin-layer chromatography using petroleum ether/EtOAc (100/1) as the eluent, **5b** was obtained in 73% yield.

44.2 mg, colorless oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.60-7.50 (m, 6H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.35 (m, 3H), 7.23 (d, *J* = 7.9 Hz, 2H), 2.38 (s, 3H), 0.57 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 144.1, 140.5, 140.5, 139.5, 138.9, 137.0, 136.5, 131.8, 130.2, 129.3, 128.7, 23.4, 0.0.



**5c**<sup>21</sup> was synthesized following the general procedure **GP2**. After purification by preparative thin-layer chromatography using petroleum ether/EtOAc (100/1) as the eluent, **5c** was obtained in 65% yield.

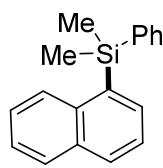
41.0 mg, colorless oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.58-7.50 (m, 8H), 7.37-7.31 (m, 3H), 6.96 (d, *J* = 8.7 Hz, 2H), 3.81 (s, 3H), 0.57 (s, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 161.6, 143.8, 140.6, 138.5, 137.0, 136.54, 136.51, 135.8, 131.4, 130.5, 130.2, 128.4, 57.6, 0.0.



**5d**

**5d** was synthesized following the general procedure **GP3**. After purification by preparative thin-layer chromatography using petroleum ether/EtOAc (100/1) as the eluent, **5d** was obtained in 92% yield.

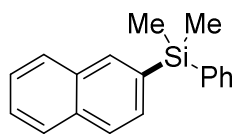
64.0 mg, colorless oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.03 (s, 1H), 7.92-7.79 (m, 3H), 7.75-7.66 (m, 3H), 7.63 (d,  $J$  = 8.2 Hz, 2H), 7.59 – 7.54 (m, 2H), 7.46 (m, 2H), 7.39-7.32 (m, 3H), 0.59 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  144.0, 140.7, 140.4, 139.4, 137.1, 136.5, 136.0, 135.0, 131.5, 130.7, 130.5, 130.2, 130.0, 129.1, 128.6, 128.3, 128.2, 127.8, 0.0. HRMS (EI)  $m/z$ :  $[\text{M}]^+$  Calcd for  $\text{C}_{24}\text{H}_{22}\text{Si}$  338.1485; found: 338.1487.



**5e**

**5e**<sup>22</sup> was synthesized following the general procedure **GP3**. After purification by preparative thin-layer chromatography using petroleum ether/EtOAc (100/1) as the eluent, **5e** was obtained in 92% yield.

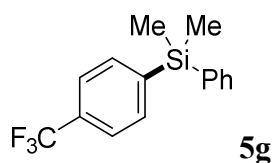
50.9 mg, colorless oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.93 (d,  $J$  = 8.4 Hz, 1H), 7.89-7.80 (m, 2H), 7.71 (d,  $J$  = 6.7 Hz, 1H), 7.56-7.49 (m, 2H), 7.46-7.38 (m, 2H), 7.36- 7.27 (m, 4H), 0.70 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  139.8, 137.9, 136.6, 135.6, 135.1, 134.3, 131.1, 130.0, 129.9, 129.5, 128.8, 126.6, 126.3, 126.0, 0.0.



**5f**

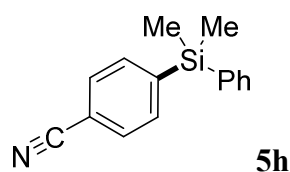
**5f**<sup>22</sup> was synthesized following the general procedure **GP3**. After purification by preparative thin-layer chromatography using petroleum ether/EtOAc (100/1) as the eluent, **5f** was obtained in 94% yield.

51.8 mg, colorless oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.02 (s, 1H), 7.81 (d, *J* = 7.8 Hz, 3H), 7.61-7.53 (m, 3H), 7.47 (m, 2H), 7.39-7.32 (m, 3H), 0.63 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 140.5, 138.0, 137.2, 136.6, 136.1, 135.2, 132.7, 131.5, 130.4, 130.2, 130.0, 129.3, 128.7, 128.2, 0.0.



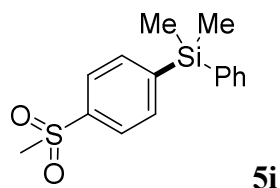
**5g**<sup>23</sup> was synthesized following the general procedure **GP3**. After purification by preparative thin-layer chromatography using petroleum ether/EtOAc (100/1) as the eluent, **5g** was obtained in 88% yield.

49.4 mg, colorless oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.62 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.53-7.47 (m, 2H), 7.40-7.35 (m, 3H), 0.58 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 143.5, 137.2, 134.6 (d, *J* = 30.1 Hz), 133.9, 129.6, 128.1, 127.8, 124.4 (q, *J* = 4.0 Hz), 124.2 (q, *J* = 271.0 Hz), -2.5.



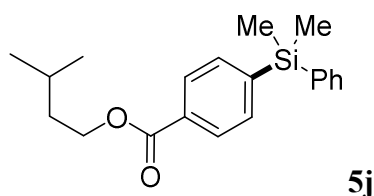
**5h**<sup>24</sup> was synthesized following the general procedure **GP3**. After purification by preparative thin-layer chromatography using petroleum ether/EtOAc (50/1) as the eluent, **5h** was obtained in 79% yield.

37.2 mg, colorless oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.60 (m, 4H), 7.52-7.46 (m, 2H), 7.38 (m, 3H), 0.57 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 145.4, 136.5, 134.6, 134.1, 131.0, 129.7, 128.1, 119.0, 112.7, -2.7.



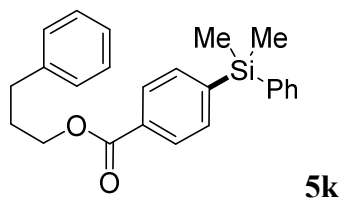
**5i**<sup>25</sup> was synthesized following the general procedure **GP3**. After purification by preparative thin-layer chromatography using petroleum ether/EtOAc (40/1) as the eluent, **5i** was obtained in 69% yield.

40.0 mg, colorless oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.89 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.50 (m, 2H), 7.39-7.37 (m, 3H), 3.04 (s, 3H), 0.60 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 146.4, 141.0, 136.5, 135.0, 134.1, 129.7, 128.1, 126.2, 44.4, -2.6.



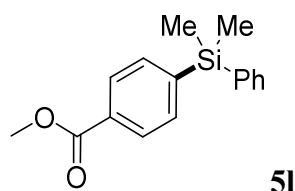
**5j** was synthesized following the general procedure **GP3**. After purification by preparative thin-layer chromatography using petroleum ether/EtOAc (50/1) as the eluent, **5j** was obtained in 87% yield.

56.6mg, colorless oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.99 (d, *J* = 7.8 Hz, 2H), 7.59 (d, *J* = 7.7 Hz, 2H), 7.52-7.47 (m, 2H), 7.35 (d, *J* = 5.4 Hz, 3H), 4.35 (t, *J* = 6.7 Hz, 2H), 1.84-1.82 (m, 1H), 1.65 (m, 2H), 0.96 (d, *J* = 6.6 Hz, 6H), 0.57 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.8, 144.5, 137.4, 134.2, 131.0, 129.4, 128.5, 128.0, 63.6, 37.4, 25.2, 22.5, -2.5. HRMS (EI) *m/z*: [M-CH<sub>3</sub>]<sup>+</sup> Calcd for C<sub>19</sub>H<sub>23</sub>O<sub>2</sub>Si 311.14618; found: 311.14627.



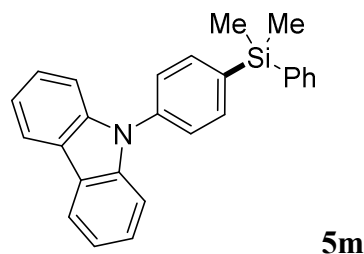
**5k** was synthesized following the general procedure **GP3**. After purification by preparative thin-layer chromatography using petroleum ether/EtOAc (50/1) as the eluent, **5k** was obtained in 61% yield.

45.3 mg, colorless oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02-7.95 (m, 2H), 7.63-7.58 (m, 2H), 7.53-7.48 (m, 2H), 7.39-7.33 (m, 3H), 7.31 – 7.26 (m, 2H), 7.22-7.17 (m, 3H), 4.33 (t,  $J$  = 6.4 Hz, 2H), 2.77 (t,  $J$  = 7.6 Hz, 2H), 2.13 – 2.05 (m, 2H), 0.57 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.7, 144.7, 141.2, 134.2, 134.2, 130.8, 129.4, 128.6, 128.5, 128.5, 128.0, 126.1, 64.2, 32.3, 30.4, -2.5. HRMS (EI)  $m/z$ :  $[\text{M}-\text{CH}_3]^+$  Calcd for  $\text{C}_{23}\text{H}_{23}\text{O}_2\text{Si}$  359.14618; found: 359.14619.



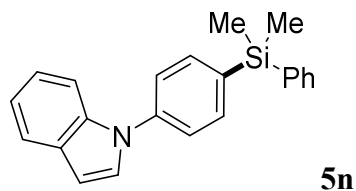
**5l**<sup>24</sup> was synthesized following the general procedure **GP3**. After purification by preparative thin-layer chromatography using petroleum ether/EtOAc (50/1) as the eluent, **5l** was obtained in 71% yield.

38.3 mg, colorless oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 (d,  $J$  = 8.1 Hz, 2H), 7.59 (d,  $J$  = 8.2 Hz, 2H), 7.50 (m, 2H), 7.36 (m, 3H), 3.90 (s, 3H), 0.57 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.3, 144.7, 137.3, 134.2, 134.1, 130.6, 129.4, 128.6, 128.0, 52.1, -2.5.



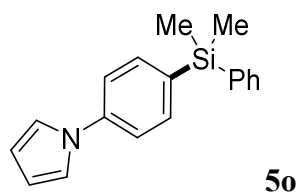
**5m**<sup>21</sup> was synthesized following the general procedure **GP3**. After purification by preparative thin-layer chromatography using petroleum ether/EtOAc (100/1) as the eluent, **5m** was obtained in 94% yield.

71.0 mg, colorless oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.11 (d,  $J = 7.7$  Hz, 2H), 7.71 (d,  $J = 8.2$  Hz, 2H), 7.63-7.56 (m, 2H), 7.52 (d,  $J = 8.2$  Hz, 2H), 7.45-7.34 (m, 7H), 7.28-7.23 (m, 2H), 0.63 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  143.0, 140.7, 140.1, 140.0, 138.0, 136.5, 131.7, 130.3, 128.5, 128.2, 125.7, 122.6, 122.3, 112.2, 0.0.



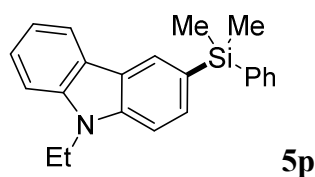
**5n** was synthesized following the general procedure **GP3**. After purification by preparative thin-layer chromatography using petroleum ether/EtOAc (100/1) as the eluent, **5n** was obtained in 83% yield.

53.9 mg, colorless oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.68-7.61 (m, 3H), 7.58-7.55 (m, 2H), 7.47 (d,  $J = 8.2$  Hz, 2H), 7.40-7.35 (m, 3H), 7.32 (d,  $J = 3.3$  Hz, 1H), 7.26 – 7.09 (m, 3H), 6.68-6.63 (s, 1H), 0.60 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  142.8, 140.1, 138.7, 138.0, 137.8, 136.5, 131.7, 131.6, 130.3, 130.1, 125.8, 124.7, 123.5, 122.7, 113.0, 106.1, 0.0. **HRMS (EI)**  $m/z$ :  $[\text{M}]^+$  Calcd for  $\text{C}_{22}\text{H}_{21}\text{NSi}$  327.1438; found: 327.1437.



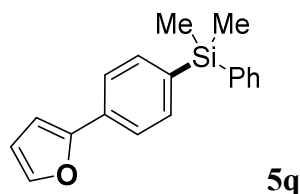
**5o**<sup>21</sup> was synthesized following the general procedure **GP3**. After purification by preparative thin-layer chromatography using petroleum ether/EtOAc (100/1) as the eluent, **5o** was obtained in 63% yield.

34.7 mg, colorless oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56-7.52 (m, 4H), 7.38-7.35 (m, 5H), 7.09 (t,  $J = 2.2$  Hz, 2H), 6.34 (t,  $J = 2.2$  Hz, 2H), 0.57 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  143.7, 140.3, 137.8, 137.6, 136.5, 131.6, 130.2, 122.1, 121.5, 112.8, 0.0.



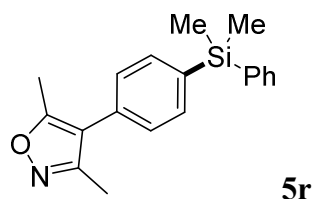
**5p** was synthesized following the general procedure **GP3**. After purification by preparative thin-layer chromatography using petroleum ether/EtOAc (100/1) as the eluent, **5p** was obtained in 71% yield.

46.6 mg, colorless oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.28 (s, 1H), 8.10 (d,  $J = 7.7$  Hz, 1H), 7.62-7.56 (m, 3H), 7.46-7.33 (m, 6H), 7.24-7.19 (m, 1H), 4.34 (q,  $J = 7.2$  Hz, 2H), 1.41 (t,  $J = 7.2$  Hz, 3H), 0.64 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  142.5, 141.7, 141.1, 136.1, 133.2, 130.7, 129.6, 128.4, 128.1, 127.4, 124.6, 122.2, 120.8, 110.2, 110.0, 39.3, 15.6, 0.0. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{22}\text{H}_{24}\text{NSi}$  330.1678; found: 330.1677.



**5q** was synthesized following the general procedure **GP3**. After purification by preparative thin-layer chromatography using petroleum ether/EtOAc (100/1) as the eluent, **5q** was obtained in 90% yield.

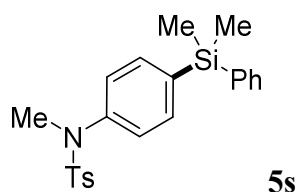
50.1 mg, colorless oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 (d,  $J = 7.9$  Hz, 2H), 7.54-7.50 (m, 4H), 7.44 (d,  $J = 1.0$  Hz, 1H), 7.36-7.32 (m, 3H), 6.67-6.64 (m, 1H), 6.46-6.43 (m, 1H), 0.55 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  156.3, 144.6, 140.5, 139.6, 136.9, 136.6, 133.8, 131.5, 130.2, 125.4, 114.0, 107.8, 0.0. HRMS (EI)  $m/z$ :  $[\text{M}]^+$  Calcd for  $\text{C}_{18}\text{H}_{18}\text{OSi}$  278.1121; found: 278.1123.





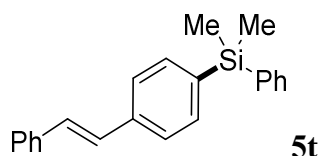
**5r** was synthesized following the general procedure **GP3**. After purification by preparative thin-layer chromatography using petroleum ether/EtOAc (100/1) as the eluent, **5r** was obtained in 55% yield.

33.8 mg, colorless oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57 (m, 4H), 7.39 (m, 3H), 7.26-7.22 (m, 2H), 2.41 (s, 3H), 2.28 (s, 3H), 0.59 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.7, 161.1, 140.3, 140.0, 137.0, 136.6, 131.7, 130.7, 130.3, 118.9, 14.1, 13.3, 0.0. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{19}\text{H}_{22}\text{NOSi}$  308.1471; found: 308.1476.



**5s** was synthesized following the general procedure **GP3**. After purification by preparative thin-layer chromatography using petroleum ether/EtOAc (50/1) as the eluent, **5s** was obtained in 52% yield.

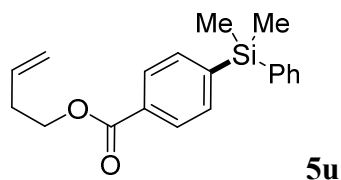
41.1 mg, colorless oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51-7.48 (m, 2H), 7.46-7.41 (m, 4H), 7.39-7.33 (m, 3H), 7.26-7.21 (m, 2H), 7.09-7.07 (m, 2H), 3.14 (s, 3H), 2.41 (s, 3H), 0.54 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  145.9, 144.8, 140.2, 139.8, 137.1, 136.5, 136.1, 131.8, 131.6, 130.3, 130.3, 128.1, 40.3, 24.0, 0.0. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{22}\text{H}_{26}\text{NO}_2\text{SiS}$  396.1454; found: 396.1455.



**5t**<sup>26</sup> was synthesized following the general procedure **GP3** with **4t** (0.4 mmol) and **2a** (0.2 mmol). After purification by preparative thin-layer chromatography using petroleum ether/EtOAc (100/1) as the eluent, **5t** was obtained in 75% yield.

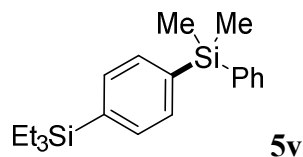
46.8 mg, colorless oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57-7.40 (m, 8H), 7.38-7.28 (m, 5H), 7.27-7.21 (m, 1H), 7.16-7.06 (m, 2H), 0.56 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,

$\text{CDCl}_3$ )  $\delta$  140.5, 140.4, 140.0, 139.6, 136.9, 136.5, 131.5, 131.0, 131.0, 130.2, 130.1, 128.9, 128.2, 0.0.



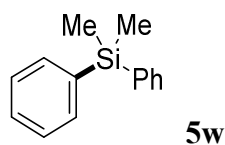
**5u** was synthesized following the general procedure **GP3** with **4u** (0.4 mmol) and **2a** (0.2 mmol). After purification by preparative thin-layer chromatography using petroleum ether/EtOAc (50/1) as the eluent, **5u** was obtained in 45% yield.

29.3 mg, colorless oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 (d,  $J = 7.6$  Hz, 2H), 7.59 (d,  $J = 7.7$  Hz, 2H), 7.53-7.46 (m, 2H), 7.36 (m, 3H), 5.92-5.80 (m, 1H), 5.29-5.07 (m, 2H), 4.37 (t,  $J = 6.6$  Hz, 2H), 2.51 (m, 2H), 0.57 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  166.7, 144.7, 137.3, 134.1, 130.8, 129.4, 128.6, 127.9, 117.4, 64.0, 33.2, -2.5. HRMS (EI)  $m/z$ :  $[\text{M}-\text{CH}_3]^+$  Calcd for  $\text{C}_{18}\text{H}_{19}\text{O}_2\text{Si}$  295.11488; found: 295.11467.



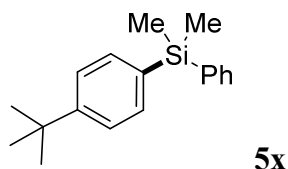
**5v** was synthesized following the general procedure **GP3**. After purification by preparative thin-layer chromatography using petroleum ether/EtOAc (100/1) as the eluent, **5v** was obtained in 60% yield.

39.2 mg, colorless oil,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.56-7.52 (m, 2H), 7.51-7.44 (m, 4H), 7.38-7.31 (m, 3H), 0.96 (t,  $J = 7.8$  Hz, 9H), 0.82-0.74 (m, 6H), 0.55 (s, 6H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.9, 140.8, 140.7, 136.6, 136.0, 135.7, 131.5, 130.2, 9.9, 5.7, 0.0. HRMS (EI)  $m/z$ :  $[\text{M}-\text{CH}_3]^+$  Calcd for  $\text{C}_{19}\text{H}_{27}\text{Si}_2$  311.1646; found: 311.1649.



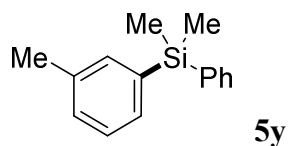
**5w**<sup>26</sup> was synthesized following the general procedure **GP3**. After purification by preparative thin-layer chromatography using petroleum ether/EtOAc (100/1) as the eluent, **5w** was obtained in 52% yield.

22.1 mg, colorless oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.55-7.46 (m, 4H), 7.38-7.29 (m, 6H), 0.55 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 140.5, 136.5, 131.4, 130.2, 0.0.



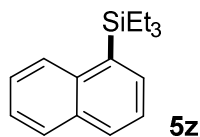
**5x**<sup>27</sup> was synthesized following the general procedure **GP3**. After purification by preparative thin-layer chromatography using petroleum ether/EtOAc (100/1) as the eluent, **5x** was obtained in 41% yield.

21.9 mg, colorless oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.54-7.51 (m, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.39-7.34 (m, 5H), 1.31 (s, 9H), 0.54 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 154.3, 140.8, 136.9, 136.5, 136.4, 131.3, 130.1, 127.1, 37.0, 33.6, 0.0.



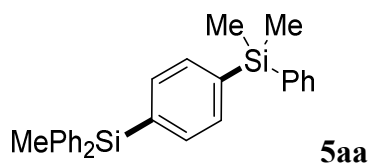
**5y**<sup>23</sup> was synthesized following the general procedure **GP3**. After purification by preparative thin-layer chromatography using petroleum ether/EtOAc (100/1) as the eluent, **5y** was obtained in 43% yield.

19.4 mg, colorless oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.53-7.50 (m, 2H), 7.35-7.30 (m, 5H), 7.24 (t, *J* = 7.3 Hz, 1H), 7.21-7.16 (m, 1H), 2.33 (s, 3H), 0.54 (s, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 140.7, 140.4, 139.5, 137.1, 136.5, 133.6, 132.3, 131.4, 130.1, 130.1, 23.9, 0.0.



**5z**<sup>28</sup> was synthesized following the general procedure **GP3**. After purification by preparative thin-layer chromatography using petroleum ether/EtOAc (55/1) as the eluent, **5z** was obtained in 32% yield.

15.9 mg, colorless oil, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.05-7.99 (m, 1H), 7.81-7.74 (m, 2H), 7.59 (dd, J = 6.8, 1.3 Hz, 1H), 7.43-7.34 (m, 3H), 0.96-0.87 (m, 15H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 137.5, 135.2, 134.8, 133.4, 129.6, 129.1, 127.9, 125.5, 125.2, 125.1, 7.7, 4.6.



**5aa** was synthesized following the general procedure **GP3**. After purification by preparative thin-layer chromatography using petroleum ether/EtOAc (100/1) as the eluent, **5aa** was obtained in 66% yield.

53.9 mg, colorless oil, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.53-7.49 (m, 10H), 7.37-7.31 (m, 9H), 0.81 (s, 3H), 0.54 (s, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 139.5, 138.0, 136.9, 136.0, 135.3, 134.5, 134.2, 133.5, 129.4, 129.1, 127.8, 127.8, -2.5, -3.5. HRMS (EI) m/z: [M-CH<sub>3</sub>]<sup>+</sup> Calcd for C<sub>26</sub>H<sub>25</sub>Si<sub>2</sub> 393.1489; found: 393.1492.

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## 8. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra

