

Supporting Information

B(C₆F₅)₃-Catalyzed C–Si/Si–H Cross-Metathesis of Hydrosilanes

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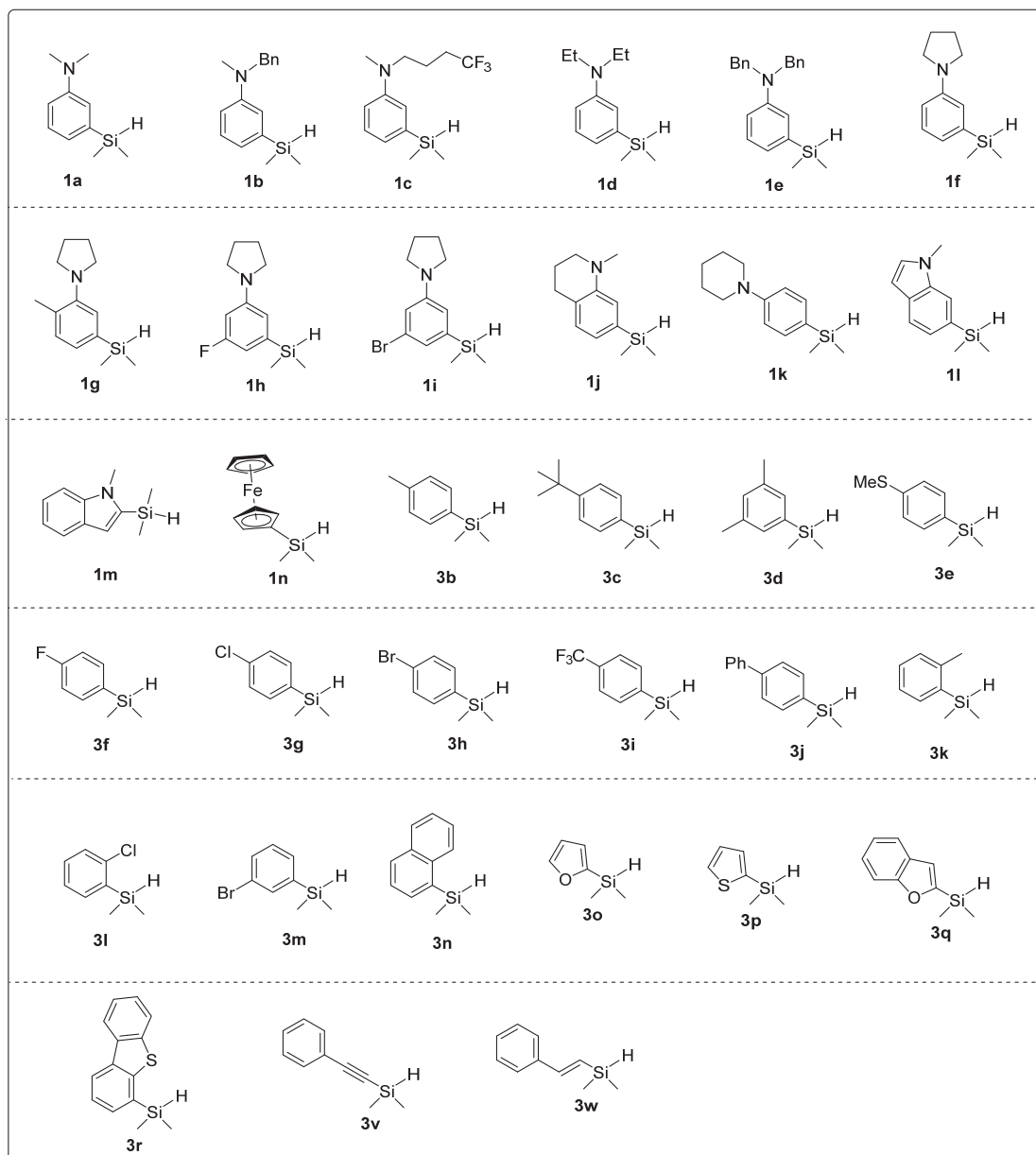
1. General Information

All manipulations of air- and moisture-sensitive compounds were performed under a nitrogen atmosphere by use of standard Schlenk techniques or a nitrogen atmosphere in a mBRAUN Labmaster130 glovebox. Nitrogen gas was purified by being passed through a Dry clean column (4Å molecular sieves, Nikka Seiko Co.) and a Gas clean GC-RX column (Nikka Seiko Co.). All ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance (500 MHz) instrument. The ^1H NMR (500 MHz) chemical shifts were measured relative to tetramethylsilane as an internal standard (TMS: $\delta = 0$ ppm). The ^{13}C NMR (126 MHz) chemical shifts were given using CDCl_3 as the internal standard (CDCl_3 : $\delta = 77.16$ ppm). High-resolution mass spectra (HR-MS) were obtained on a Bruker MicroTOF-QIII (ESI) or a JEOL JMS-T100GCV (EI). Chlorobenzene were obtained from Kanato Chemical Co., purified by an Mbraun SPS-800 Solvent Purification System and dried over fresh 3Å molecule sieves in a glovebox. Chlorobenzene- d_5 was dried over 3Å molecule sieves in a glovebox.

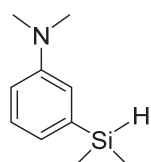
Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Most aniline derivatives and hydrosilanes were purchased from TCI and Aldrich in Japan. Tris(pentafluorophenyl)borane was purchased from TCI.

2. Synthesis of Substrates

As shows in following table, substrates **1a-n** and **3b-n, p** were prepared starting from corresponding bromo-substituted compounds according to the literature procedures or modified procedures.¹ Substrate **3o**², **3q**³ and **3r**³ were directly prepared starting from corresponding heteroarenes according to the literature procedures. Substrates **3v**⁴ and **3w**^{5,6} were prepared according to the literature procedures or modified procedures.



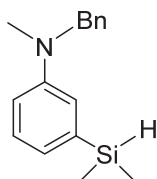
2.1 Characterization of New Compounds



3-(Dimethylsilyl)-N,N-dimethylaniline

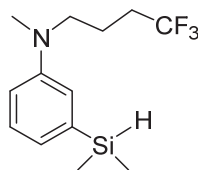
Colorless oil. ^1H NMR (500 MHz, CDCl_3): δ = 0.33 (d, J = 3.5 Hz, 6H), 2.95 (s, 6H), 4.39-4.42 (m, 1H), 6.76 (dd, J = 8.0 Hz, 2.0 Hz, 1H), 6.89-6.92 (m, 2H), 7.25 (t, J = 7.5 Hz, 1H) ppm. ^{13}C NMR (126 MHz, CDCl_3): δ = -3.5, 40.8, 113.9, 118.0, 122.3, 128.8, 138.1, 150.2 ppm. HRMS (ESI $^+$): calcd for $\text{C}_{10}\text{H}_{18}\text{NSi}^+$ $[\text{M}+\text{H}]^+$ 180.1203,

found 180.1204.



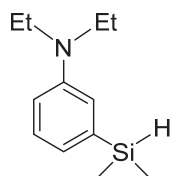
***N*-Benzyl-3-(dimethylsilyl)-*N*-methylaniline**

Colorless oil. ^1H NMR (500 MHz, CDCl_3): δ = 0.30 (d, J = 3.5 Hz, 6H), 3.00 (s, 3H), 4.38 (m, 1H), 4.51 (m, 2H), 6.75 (d, J = 7.5 Hz, 1H), 6.88 (d, J = 7.0 Hz, 1H), 6.94 (s, 1H), 7.18-7.24 (m, 4H), 7.28-7.31 (m, 2H) ppm. ^{13}C NMR (126 MHz, CDCl_3): δ = -3.57, 38.6, 56.9, 113.7, 117.8, 122.3, 126.96, 127.01, 128.7, 128.9, 138.2, 139.2, 149.3 ppm. HRMS (ESI^+): calcd for $\text{C}_{16}\text{H}_{22}\text{NSi}^+$ $[\text{M}+\text{H}]^+$ 256.1516, found 256.1512.



3-(Dimethylsilyl)-*N*-methyl-*N*-(4,4,4-trifluorobutyl)aniline

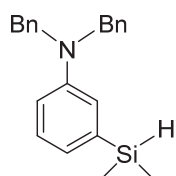
Colorless oil. ^1H NMR (500 MHz, CDCl_3): δ = 0.33 (d, J = 4.0 Hz, 6H), 1.83-1.89 (m, 2H), 2.08-2.18 (m, 2H), 2.94 (s, 3H), 3.39 (t, J = 7.5 Hz, 2H), 4.38-4.41 (m, 1H), 6.73 (d, J = 8.0 Hz, 1H), 6.88 (s, 1H), 6.90 (d, J = 7.5 Hz, 1H), 7.24 (d, J = 7.0 Hz, 1H) ppm. ^{13}C NMR (126 MHz, CDCl_3): δ = -3.6, 19.8 (q, J = 2.5 Hz, 1C), 31.5 (q, J = 29.0 Hz, 1C), 38.4, 51.7, 113.6, 117.9, 122.5, 127.3 (q, J = 276.7 Hz, 1C), 129.0, 138.5, 148.7 ppm. HRMS (ESI^+): calcd for $\text{C}_{13}\text{H}_{21}\text{F}_3\text{NSi}^+$ $[\text{M}+\text{H}]^+$ 276.1390, found 276.1388.



3-(Dimethylsilyl)-*N,N*-diethylaniline

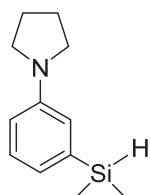
Colorless oil. ^1H NMR (500 MHz, CDCl_3): δ = 0.32-0.33 (m, 6H), 1.16 (t, J = 7.0 Hz,

6H), 3.36 (q, $J = 6.5$ Hz, 4H), 4.39-4.40 (m, 1H), 6.70 (d, $J = 6.0$ Hz, 1H), 6.81 (d, $J = 7.0$ Hz, 1H), 6.85 (s, 1H), 7.20-7.23 (m, 1H) ppm. ^{13}C NMR (126 MHz, CDCl_3): $\delta = -3.5, 12.7, 44.4, 113.0, 117.3, 121.0, 129.0, 138.1, 147.3$ ppm. HRMS (ESI^+): calcd for $\text{C}_{12}\text{H}_{22}\text{NSi}^+ [\text{M}+\text{H}]^+ 208.1516$, found 208.1518.



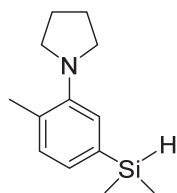
***N,N*-Dibenzyl-3-(dimethylsilyl)aniline**

Colorless oil. ^1H NMR (500 MHz, CDCl_3): $\delta = 0.22$ (d, $J = 3.5$ Hz, 6H), 4.30-4.32 (m, 1H), 4.65 (s, 4H), 6.75 (d, $J = 8.0$ Hz, 1H), 6.87 (d, $J = 7.0$ Hz, 1H), 6.93 (s, 1H), 7.17 (t, $J = 7.5$ Hz, 1H), 7.24-7.26 (m, 6H), 7.30-7.33 (m, 4H) ppm. ^{13}C NMR (126 MHz, CDCl_3): $\delta = -3.7, 54.5, 113.8, 118.1, 122.5, 126.9, 127.0, 128.8, 128.9, 138.2, 138.8, 148.7$ ppm. HRMS (ESI^+): calcd for $\text{C}_{22}\text{H}_{26}\text{NSi}^+ [\text{M}+\text{H}]^+ 332.1829$, found 332.1830.



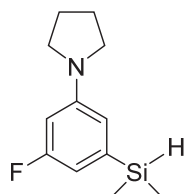
1-(3-(Dimethylsilyl)phenyl)pyrrolidine

Colorless oil. ^1H NMR (500 MHz, CDCl_3): $\delta = 0.33$ (d, $J = 3.5$ Hz, 6H), 1.98-2.00 (m, 4H), 3.28-3.30 (m, 4H), 4.39-4.41 (m, 1H), 6.57-6.59 (m, 1H), 6.73 (d, $J = 1.5$ Hz, 1H), 6.83 (d, $J = 7.0$ Hz, 1H), 7.21-7.24 (m, 1H) ppm. ^{13}C NMR (126 MHz, CDCl_3): $\delta = -3.5, 25.6, 47.7, 112.8, 117.0, 121.0, 128.9, 138.1, 147.5$ ppm. HRMS (ESI^+): calcd for $\text{C}_{12}\text{H}_{20}\text{NSi}^+ [\text{M}+\text{H}]^+ 206.1360$, found 206.1360.



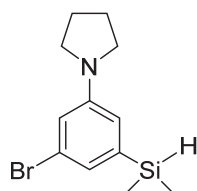
1-(5-(Dimethylsilyl)-2-methylphenyl)pyrrolidine

Colorless oil. ^1H NMR (500 MHz, CDCl_3): δ = 0.32 (d, J = 4.0 Hz, 6H), 1.91-1.93 (m, 4H), 2.31 (s, 3H), 3.19-3.21 (m, 4H), 4.39-4.42 (m, 1H), 7.00 (d, J = 7.0 Hz, 1H), 7.04 (s, 1H), 7.12 (d, J = 7.5 Hz, 1H) ppm. ^{13}C NMR (126 MHz, CDCl_3): δ = -3.4, 20.7, 25.1, 51.1, 121.1, 126.0, 130.1, 131.5, 134.8, 149.0 ppm. HRMS (ESI^+): calcd for $\text{C}_{13}\text{H}_{22}\text{NSi}^+$ $[\text{M}+\text{H}]^+$ 220.1516, found 220.1521.



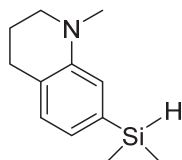
1-(3-(Dimethylsilyl)-5-fluorophenyl)pyrrolidine

Colorless oil. ^1H NMR (500 MHz, CDCl_3): δ = 0.32 (d, J = 3.5 Hz, 6H), 2.00 (t, J = 6.0 Hz, 4H), 3.28 (t, J = 6.0 Hz, 4H), 4.36-4.38 (m, 1H), 6.23 (d, J = 12.0 Hz, 1H), 6.46 (s, 1H), 6.49 (d, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (126 MHz, CDCl_3): δ = -3.6, 25.6, 47.8, 99.5 (d, J = 25.7 Hz, 1C), 106.7 (d, J = 19.4 Hz, 1C), 112.7 (d, J = 1.8 Hz, 1C), 140.3 (d, J = 6.0 Hz, 1C), 149.4 (d, J = 10.0 Hz, 1C), 164.0 (d, J = 245.4 Hz, 1C) ppm. HRMS (ESI^+): calcd for $\text{C}_{12}\text{H}_{19}\text{FNSi}^+$ $[\text{M}+\text{H}]^+$ 224.1265, found 224.1266.



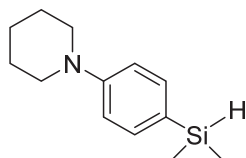
1-(3-Bromo-5-(dimethylsilyl)phenyl)pyrrolidine

Colorless oil. ^1H NMR (500 MHz, CDCl_3): δ = 0.32 (d, J = 4.0 Hz, 6H), 1.98 (m, 4H), 3.25 (m, 4H), 4.35-4.37 (m, 1H), 6.59 (s, 1H), 6.67 (s, 1H), 6.89 (s, 1H) ppm. ^{13}C NMR (126 MHz, CDCl_3): δ = -3.6, 25.6, 47.7, 115.2, 115.5, 123.0, 123.9, 140.5, 148.7 ppm. HRMS (ESI^+): calcd for $\text{C}_{12}\text{H}_{19}\text{BrNSi}^+$ $[\text{M}+\text{H}]^+$ 284.0465, found 284.0457.



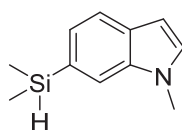
7-(Dimethylsilyl)-1-methyl-1,2,3,4-tetrahydroquinoline

Colorless oil. ^1H NMR (500 MHz, CDCl_3): δ = 0.25 (d, J = 4.0 Hz, 6H), 1.88-1.93 (m, 2H), 2.69 (t, J = 6.5 Hz, 2H), 2.84 (s, 3H), 3.15 (t, J = 5.5 Hz, 2H), 4.30-4.32 (m, 1H), 6.68 (s, 1H), 6.71 (d, J = 7.0 Hz, 1H), 6.89 (d, J = 7.0 Hz, 1H) ppm. ^{13}C NMR (126 MHz, CDCl_3): δ = -3.4, 22.5, 28.0, 39.2, 51.6, 116.3, 122.0, 124.4, 128.7, 135.7, 146.4 ppm. HRMS (ESI^+): calcd for $\text{C}_{12}\text{H}_{20}\text{NSi}^+$ $[\text{M}+\text{H}]^+$ 206.1360, found 206.1359.



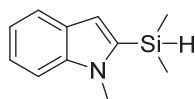
1-(4-(Dimethylsilyl)phenyl)piperidine

Colorless oil. ^1H NMR (500 MHz, CDCl_3): δ = 0.30 (d, J = 3.5 Hz, 6H), 1.55-1.60 (m, 2H), 1.66-1.71 (m, 4H), 3.19 (t, J = 5.5 Hz, 4H), 4.37-4.40 (m, 1H), 6.92 (d, J = 8.5 Hz, 2H), 7.40 (d, J = 8.5 Hz, 2H) ppm. ^{13}C NMR (126 MHz, CDCl_3): δ = -3.4, 24.5, 25.9, 50.0, 115.6, 125.5, 135.2, 152.8 ppm. HRMS (ESI^+): calcd for $\text{C}_{13}\text{H}_{22}\text{NSi}^+$ $[\text{M}+\text{H}]^+$ 220.1516, found 220.1518.



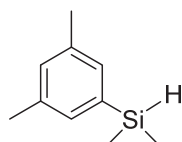
6-(Dimethylsilyl)-1-methyl-1H-indole

Colorless oil. ^1H NMR (500 MHz, CDCl_3): δ = 0.39 (d, J = 3.5 Hz, 6H), 3.77 (s, 3H), 4.54-4.56 (m, 1H), 6.46 (d, J = 3.0 Hz, 1H), 7.02 (d, J = 3.0 Hz, 1H), 7.26 (d, J = 8.0 Hz, 1H), 7.50 (s, 1H), 7.63 (d, J = 7.5 Hz, 1H) ppm. ^{13}C NMR (126 MHz, CDCl_3): δ = -3.0, 32.9, 101.0, 115.0, 120.7, 124.4, 129.2, 129.4, 129.5, 136.7 ppm. HRMS (EI^+): calcd for $\text{C}_{11}\text{H}_{15}\text{NSi}^+$ $[\text{M}]^+$ 189.0968, found 189.0976.



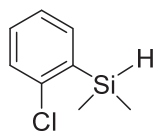
2-(Dimethylsilyl)-1-methyl-1*H*-indole

Colorless oil. ^1H NMR (500 MHz, CDCl_3): δ = 0.43 (d, J = 4.0 Hz, 6H), 3.83 (s, 3H), 4.61-4.64 (m, 1H), 6.73 (s, 1H), 7.07 (d, J = 7.0 Hz, 1H), 7.20-7.23 (m, 1H), 7.31 (d, J = 8.0 Hz, 1H), 7.60 (d, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (126 MHz, CDCl_3): δ = -3.6, 32.7, 109.2, 112.0, 119.3, 120.8, 122.3, 128.5, 138.5, 140.3 ppm. HRMS (EI^+): calcd for $\text{C}_{11}\text{H}_{15}\text{NSi}^+$ $[\text{M}]^+$ 189.0968, found 189.0979.



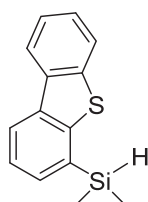
(3,5-Dimethylphenyl)dimethylsilane

Colorless oil. ^1H NMR (500 MHz, CDCl_3): δ = 0.32 (d, J = 4.0 Hz, 6H), 2.32 (s, 6H), 4.37-4.40 (m, 1H), 7.01 (s, 1H), 7.15 (s, 2H) ppm. ^{13}C NMR (126 MHz, CDCl_3): δ = -3.6, 21.4, 131.1, 131.9, 137.4 ppm. HRMS (EI^+): calcd for $\text{C}_{10}\text{H}_{16}\text{Si}^+$ $[\text{M}]^+$ 164.1016, found 164.1023.



(2-Chlorophenyl)dimethylsilane

Colorless oil. ^1H NMR (500 MHz, CDCl_3): δ = 0.42 (d, J = 3.5 Hz, 6H), 4.50-4.53 (m, 1H), 7.22-7.25 (m, 1H), 7.29-7.34 (m, 2H), 7.49 (d, J = 7.0 Hz, 1H) ppm. ^{13}C NMR (126 MHz, CDCl_3): δ = -3.7, 126.2, 129.1, 131.1, 136.4, 136.9, 141.2 ppm. HRMS (EI^+): calcd for $\text{C}_8\text{H}_{11}\text{ClSi}^+$ $[\text{M}]^+$ 170.0313, found 170.0323.



Dibenzo[*b,d*]thiophen-4-yl dimethylsilane

Colorless oil. ^1H NMR (500 MHz, CDCl_3): δ = 0.50 (d, J = 4.0 Hz, 6H), 4.72-4.75 (m, 1H), 7.44-7.48 (m, 3H), 7.61 (d, J = 6.5 Hz, 1H), 7.85-7.88 (m, 1H), 8.15-8.19 (m, 2H) ppm. ^{13}C NMR (126 MHz, CDCl_3): δ = -4.1, 121.7, 122.8, 124.1, 124.4, 126.8, 131.7, 133.0, 134.8, 135.6, 139.6, 145.9 ppm. HRMS (EI^+): calcd for $\text{C}_{14}\text{H}_{14}\text{SSi}^+ [\text{M}]^+$ 242.0580, found 242.0623.

3. The Preliminary Screening of Functional Group for $\text{B}(\text{C}_6\text{F}_5)_3$ -Catalyzed Substituent Redistribution of Tertiary Hydrosilanes

In a glovebox, tertiary hydrosilane bearing functional group **1** (0.25 mmol) was added to a solution (0.5 mL) of $\text{B}(\text{C}_6\text{F}_5)_3$ (6.4 mg, 5 mol%) in $\text{C}_6\text{D}_5\text{Cl}$ in a 20-mL Schlenk tube with a magnetic stir bar. The Schlenk tube was taken out of the glovebox and the reaction mixture was stirred at 100 °C (oil) for 24 h. After completion of the reaction, the mixture was cooled to room temperature. CH_2Br_2 was used as internal standard and the resulting mixture was subjected to ^1H NMR spectroscopy. The isolated yield was obtained by column chromatography (hexane/ CH_2Cl_2 = 4/1-2/1, v/v) on silica gel (1% Et_3N was added to eluent).

Table S1. The Screening of functional group for $\text{B}(\text{C}_6\text{F}_5)_3$ -catalyzed substituent redistribution of tertiary hydrosilanes ^{a,b}

$$2 \text{ FG}-\text{C}_6\text{H}_4-\text{Si}(\text{Me})_2\text{H} \xrightarrow[\text{C}_6\text{D}_5\text{Cl}, 100^\circ\text{C}, 24\text{ h}]{\text{B}(\text{C}_6\text{F}_5)_3 (5\text{ mol}\%)} \text{FG}-\text{C}_6\text{H}_4-\text{Si}(\text{Me})_2-\text{C}_6\text{H}_4-\text{FG} + \text{Me}_2\text{SiH}_2$$

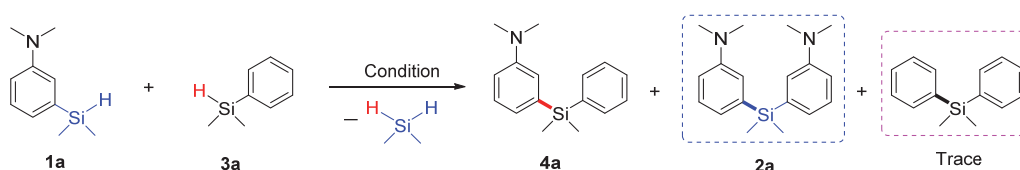
Hydrosilane	Product	Hydrosilane	Product	Hydrosilane	Product
	 Trace		 23% ^{c,f}		 11%
	 N.D. ^d		 N.D. ^d		 10%
	 81% ^c		 Trace		 11%
	 N.D. ^d				

^aReaction conditions: hydrosilane (0.25 mmol), B(C₆F₅)₃ (5 mol%) and C₆D₅Cl (0.5 mL) under N₂ at 100 °C for 24 h. ^bNMR yield. ^cIsolated yield. In this case, chlorobenzene was used as solvent. ^dThe desilylation of starting material was observed and a large amount of *N,N*-dimethylaniline could be detected. ^eThe desilylation of starting material was observed and a large amount of 1-Phenylpiperidine could be detected. FG = Fuctional group, N.D. = Not detected.

4. Optimization of B(C₆F₅)₃-Catalyzed Cross-Methathesis Reaction of Two Different Hydrosilanes

In a glovebox, hydrosilane **1a** (45 mg, 0.25 mmol) was added to a solution (0.5 mL) of boron species (5.0 mol%) in solvent in a 20-mL Schlenk tube with a magnetic stir bar. Dimethylphenylsilane **3a** (68 mg, 0.50 mmol) was then added to resulting mixture. The Schlenk tube was taken out of the glovebox and the reaction mixture was stirred at the indicated temperature (oil) during indicated time. After completion of the reaction, the mixture was cooled to room temperature. After removal of solvent, the resulting mixture was subjected to ¹H NMR spectroscopy to confirm the ratio of product **4a** and byproduct **2a** using CDCl₃ as solvent. The isolated yield was obtained by column chromatography (hexane/CH₂Cl₂ = 4/1-2/1, v/v) on silica gel (1% Et₃N was added to eluent).

Table S2. Optimization of B(C₆F₅)₃-catalyzed cross-metathesis of two hydrosilanes^a



Entry	Ratio (1a/3a)	Catalyst	Solvent	Temp./Time	Yield (4a) ^b	Ratio (4a/2a) ^b
1	1/2	B(C ₆ F ₅) ₃	THF	100 °C/24 h	N.D.	-
2	1/2	B(C ₆ F ₅) ₃	Benzene	100 °C/24 h	83%	7.4:1
3	1/2	B(C ₆ F ₅) ₃	Toluene	100 °C/24 h	85%	9.8:1
4	1/2	B(C ₆ F ₅) ₃	CHCl ₃	100 °C/24 h	86%	10:1
5	1/2	B(C ₆ F ₅) ₃	PhCl	100 °C/24 h	88% (79%)	18.3:1
6	1/2	[Ph ₃ C][B(C ₆ F ₅) ₄]	PhCl	100 °C/24 h	75%	12.5:1

7	1/2	BPh ₃	PhCl	100 °C/24 h	N.R.	-
8 ^c	1/2	B(C ₆ F ₅) ₃	PhCl	100 °C/24 h	58%	3.9:1
9	1/1.2	B(C ₆ F ₅) ₃	PhCl	100 °C/24 h	70%	4.9:1
10	1/2	B(C ₆ F ₅) ₃	PhCl	80 °C/24 h	55%	2.5:1
11	2/1	B(C ₆ F ₅) ₃	PhCl	100 °C/24 h	51% ^d	-
12	1/2	None	PhCl	100 °C/24 h	N.R.	-

^aReaction conditions: 0.25 mmol scale, boron species (5.0 mol%) and solvent (0.5 mL) under N₂ at 100 °C for 24 h. ^bDetermined by NMR using CH₂Br₂ as an internal standard. Number in parenthesis is isolated yield. ^c2.5 mol% B(C₆F₅)₃ was used. ^dIsolated yield based on **3a**. N.R. = No reaction, N.D. = Not detected.

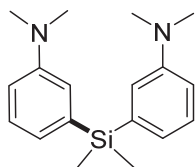
5. Experimental Procedures

Procedures A: In a glovebox, hydrosilane **1** (0.25 mmol) was added to a solution of B(C₆F₅)₃ (6.4 mg, 5.0 mol%) in chlorobenzene (0.5 mL) in a 20-mL Schlenk tube with a magnetic stir bar. The Schlenk tube was taken out of the glovebox and the reaction mixture was stirred at 100 °C (oil bath) for 24 h. After completion of the reaction, the mixture was cooled to room temperature. The mixture was diluted with 10 mL of CH₂Cl₂ and analyzed by TLC. Then, the combined organic phases were concentrated and the resulting residue was purified by column chromatography on silica gel (1% Et₃N was added to eluent) to provide the desired product.

Procedures B: In a glovebox, hydrosilane **1** (0.25 mmol) was added to a solution of B(C₆F₅)₃ (6.4 mg, 5.0 mol%) in chlorobenzene (0.5 mL) in a 20-mL Schlenk tube with a magnetic stir bar. Another hydrosilane **3** (0.50 mmol) was then added. The Schlenk tube was taken out of the glovebox and the reaction mixture was stirred at 100 °C (oil bath) for 24 h. After completion of the reaction, the mixture was cooled to room temperature. The mixture was diluted with 10 mL of CH₂Cl₂ and analyzed by TLC. Then, the combined organic phases were concentrated and the resulting residue was purified by column chromatography on silica gel (1% Et₃N was added to eluent) to provide the desired product.

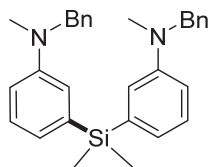
Safety Note: In view of byproduct Me_2SiH_2 as a flammable gas, please be very careful in the process of using current catalytic method.

6. Spectral Data of Products



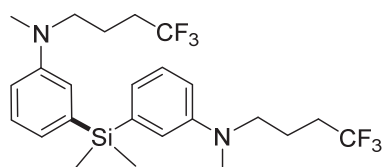
3,3'-(Dimethylsilanediyl)bis(*N,N*-dimethylaniline) **2a**

The general procedure A was followed. Purification via column chromatography on silica gel (Hexane/EtOAc = 15/1, v/v) afforded **2a** as colorless oil (30.3 mg, 81% yield). ^1H NMR (500 MHz, CDCl_3): δ = 0.53 (s, 6H), 2.91 (s, 12H), 6.75 (dd, J = 8.0 Hz, 2.0 Hz, 2H), 6.91 (d, J = 7.0 Hz, 2H), 6.93 (d, J = 2.5 Hz, 2H), 7.21-7.24 (m, 2H) ppm. ^{13}C NMR (126 MHz, CDCl_3): δ = -2.0, 40.8, 113.7, 118.5, 122.9, 128.6, 139.1, 150.1 ppm. HRMS (ESI^+): calcd for $\text{C}_{18}\text{H}_{27}\text{N}_2\text{Si}^+ [\text{M}+\text{H}]^+$ 299.1938, found 299.1940.



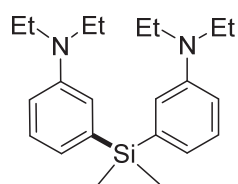
3,3'-(Dimethylsilanediyl)bis(*N*-benzyl-*N*-methylaniline) **2b**

The general procedure A was followed. Purification via column chromatography on silica gel (Hexane/EtOAc = 15/1, v/v) afforded **2b** as colorless oil (36.6 mg, 65% yield). ^1H NMR (500 MHz, CDCl_3): δ = 0.45 (s, 6H), 2.97 (s, 6H), 4.47 (s, 4H), 6.74 (d, J = 8.0 Hz, 2H), 6.86 (d, J = 7.0 Hz, 2H), 6.93 (s, 2H), 7.16-7.23 (m, 8H), 7.27-7.30 (m, 4H) ppm. ^{13}C NMR (126 MHz, CDCl_3): δ = -2.2, 38.7, 57.0, 113.5, 118.2, 122.7, 126.96, 127.0, 128.6, 128.7, 139.1, 139.3, 149.2 ppm. HRMS (ESI^+): calcd for $\text{C}_{30}\text{H}_{35}\text{N}_2\text{Si}^+ [\text{M}+\text{H}]^+$ 451.2564, found 451.2568.



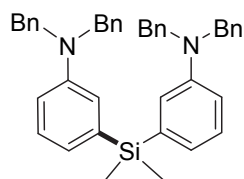
3,3'-(Dimethylsilanediyl)bis(*N*-methyl-*N*-(4,4,4-trifluorobutyl)aniline) **2c**

The general procedure A was followed. Purification via column chromatography on silica gel (Hexane/EtOAc = 15/1, v/v) afforded **2c** as colorless oil (44.5 mg, 73% yield). ^1H NMR (500 MHz, CDCl_3): δ = 0.52 (s, 6H), 1.77-1.83 (m, 4H), 2.01-2.11 (m, 4H), 2.90 (s, 6H), 3.33 (t, J = 7.5 Hz, 4H), 6.71 (d, J = 8.0 Hz, 2H), 6.83 (s, 2H), 6.91 (d, J = 7.0 Hz, 2H), 7.24 (t, J = 8.0 Hz, 2H) ppm. ^{13}C NMR (126 MHz, CDCl_3): δ = -2.2, 19.8 (q, J = 2.3 Hz, 1C), 31.5 (q, J = 29.0 Hz, 1C), 38.4, 51.7, 113.4, 118.2, 122.8, 127.3 (q, J = 276.8 Hz, 1C), 128.9, 139.3, 148.6 ppm. HRMS (ESI^+): calcd for $\text{C}_{24}\text{H}_{33}\text{F}_6\text{N}_2\text{Si}^+[\text{M}+\text{H}]^+$ 491.2312, found 491.2343.



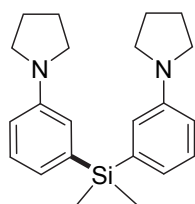
3,3'-(Dimethylsilanediyl)bis(*N,N*-diethylaniline) **2d**

The general procedure A was followed. Purification via column chromatography on silica gel (Hexane/EtOAc = 25/1, v/v) afforded **2d** as colorless oil (26.9 mg, 61% yield). ^1H NMR (500 MHz, CDCl_3): δ = 0.51 (s, 6H), 1.12 (t, J = 7.0 Hz, 12H), 3.32 (q, J = 7.0 Hz, 8H), 6.69 (d, J = 7.0 Hz, 2H), 6.83 (d, J = 7.0 Hz, 2H), 6.85 (s, 2H), 7.20 (t, J = 8.0 Hz, 2H) ppm. ^{13}C NMR (126 MHz, CDCl_3): δ = -2.1, 12.7, 44.5, 112.9, 117.9, 121.6, 128.8, 139.2, 147.2 ppm. HRMS (ESI^+): calcd for $\text{C}_{22}\text{H}_{35}\text{N}_2\text{Si}^+[\text{M}+\text{H}]^+$ 355.2564, found 355.2574.



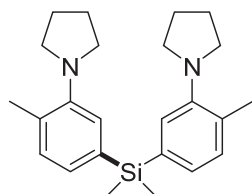
3,3'-(Dimethylsilanediyl)bis(*N,N*-dibenzylaniline) **2e**

The general procedure A was followed. Purification via column chromatography on silica gel (Hexane/EtOAc = 20/1, v/v) afforded **2e** as colorless oil (52.5 mg, 70% yield). ^1H NMR (500 MHz, CDCl_3): δ = 0.28 (s, 6H), 4.58 (s, 8H), 6.70 (d, J = 8.5 Hz, 2H), 6.76 (d, J = 7.0 Hz, 2H), 6.88 (s, 2H), 7.08 (t, J = 8.0 Hz, 2H), 7.20-7.23 (m, 12H), 7.27-7.29 (m, 8H) ppm. ^{13}C NMR (126 MHz, CDCl_3): δ = -2.5, 54.6, 113.6, 118.4, 122.7, 126.96, 126.97, 128.7, 138.9, 139.1, 148.4 ppm. HRMS (ESI^+): calcd for $\text{C}_{42}\text{H}_{43}\text{N}_2\text{Si}^+$ $[\text{M}+\text{H}]^+$ 603.3190, found 603.3188.



Dimethylbis(3-(pyrrolidin-1-yl)phenyl)silane **2f**

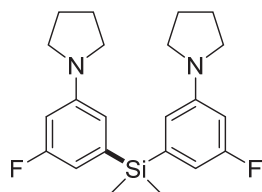
The general procedure A was followed. Purification via column chromatography on silica gel (Hexane/EtOAc = 30/1, v/v) afforded **2f** as colorless oil (33.4 mg, 76% yield). ^1H NMR (500 MHz, CDCl_3): δ = 0.52 (s, 6H), 1.97-1.98 (m, 8H), 3.26-3.27 (m, 8H), 6.57 (d, J = 7.5 Hz, 2H), 6.76 (s, 2H), 6.84 (d, J = 7.0 Hz, 2H), 7.21 (t, J = 7.5 Hz, 2H) ppm. ^{13}C NMR (126 MHz, CDCl_3): δ = -2.0, 25.6, 47.7, 112.6, 117.3, 121.6, 128.6, 139.2, 147.4 ppm. HRMS (ESI^+): calcd for $\text{C}_{22}\text{H}_{31}\text{N}_2\text{Si}^+$ $[\text{M}+\text{H}]^+$ 351.2251, found 351.2253.



Dimethylbis(4-methyl-3-(pyrrolidin-1-yl)phenyl)silane **2g**

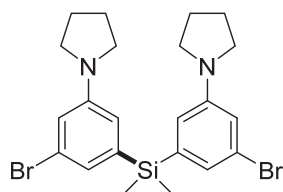
The general procedure A was followed. Purification via column chromatography on silica gel (Hexane/EtOAc = 30/1, v/v) afforded **2g** as colorless oil (34.6 mg, 73% yield). ^1H NMR (500 MHz, CDCl_3): δ = 0.50 (s, 6H), 1.89-1.91 (m, 8H), 2.31 (s, 6H), 3.15-3.17 (m, 8H), 7.00 (d, J = 7.5 Hz, 2H), 7.06 (s, 2H), 7.10 (d, J = 7.0 Hz, 2H) ppm. ^{13}C NMR (126 MHz, CDCl_3): δ = -1.8, 20.7, 25.1, 51.1, 121.4, 126.5, 129.9,

131.4, 136.0, 148.8 ppm. HRMS (ESI⁺): calcd for C₂₄H₃₅N₂Si⁺[M+H]⁺ 379.2564, found 379.2560.



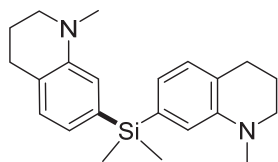
Bis(3-fluoro-5-(pyrrolidin-1-yl)phenyl)dimethylsilane **2h**

The general procedure A was followed. Purification via column chromatography on silica gel (Hexane/CH₂Cl₂ = 6/1, v/v) afforded **2h** as a white solid (30.8 mg, 64% yield). ¹H NMR (500 MHz, CDCl₃): ¹H NMR (500 MHz, CDCl₃): δ = 0.50 (s, 6H), 1.98 (m, 8H), 3.25-3.26 (m, 8H), 6.23 (d, *J* = 12.0 Hz, 2H), 6.45 (s, 2H), 6.48 (d, *J* = 8.5 Hz, 2H) ppm. ¹³C NMR (126 MHz, CDCl₃): δ = -2.3, 25.6, 47.8, 99.5 (d, *J* = 25.7 Hz, 1C), 107.1 (d, *J* = 19.4 Hz, 1C), 112.9 (d, *J* = 1.76 Hz, 1C), 140.9 (d, *J* = 6.0 Hz, 1C), 149.3 (d, *J* = 10.0 Hz, 1C), 164.0 (d, *J* = 245.2 Hz, 1C) ppm. HRMS (ESI⁺): calcd for C₂₂H₂₉F₂N₂Si⁺ [M+H]⁺ 387.2063, found 387.2061.



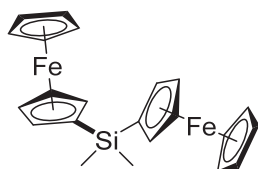
Bis(3-bromo-5-(pyrrolidin-1-yl)phenyl)dimethylsilane **2i**

The general procedure A was followed. Purification via column chromatography on silica gel (Hexane/EtOAc = 15/1, v/v) afforded **2i** as colorless oil (30.5 mg, 48% yield). ¹H NMR (500 MHz, CDCl₃): ¹H NMR (500 MHz, CDCl₃): δ = 0.50 (s, 6H), 1.96-1.99 (m, 8H), 3.22-3.25 (m, 8H), 6.57 (d, *J* = 2.5 Hz, 2H), 6.68 (d, *J* = 2.5 Hz, 2H), 6.87 (m, 2H) ppm. ¹³C NMR (126 MHz, CDCl₃): δ = -2.3, 25.6, 47.7, 115.2, 115.7, 123.3, 123.9, 140.9, 148.6 ppm. HRMS (ESI⁺): calcd for C₂₂H₂₉Br₂N₂Si⁺ [M+H]⁺ 509.0441, found 509.0477.



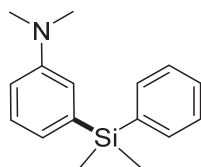
Dimethylbis(1-methyl-1,2,3,4-tetrahydroquinolin-7-yl)silane **2j**

The general procedure A was followed. Purification via column chromatography on silica gel (Hexane/EtOAc = 20/1, v/v) afforded **2j** as colorless oil (29.4 mg, 67% yield). ^1H NMR (500 MHz, CDCl_3): δ = 0.49 (s, 6H), 1.94-1.99 (m, 4H), 2.75 (t, J = 6.0 Hz, 4H), 2.86 (s, 6H), 3.20 (t, J = 5.5 Hz, 4H), 6.78-6.80 (m, 4H), 6.93 (d, J = 7.0 Hz, 2H) ppm. ^{13}C NMR (126 MHz, CDCl_3): δ = -1.9, 22.6, 28.0, 39.3, 51.6, 116.7, 122.6, 124.1, 128.5, 136.9, 146.3 ppm. HRMS (ESI^+): calcd for $\text{C}_{22}\text{H}_{31}\text{N}_2\text{Si}^+[\text{M}+\text{H}]^+$ 351.2251, found 351.2251.



Bis(ferrocenyl)dimethylsilane **2k**

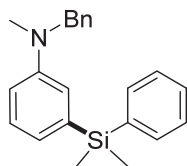
The general procedure A was followed. Purification via column chromatography on silica gel (Hexane/ CH_2Cl_2 = 10/1, v/v) afforded **2k** as an orange solid (43.6 mg, 81% yield). ^1H NMR (500 MHz, CDCl_3): δ = 0.49 (s, 6H), 4.09 (s, 10H), 4.12 (t, J = 2.0 Hz, 4H), 4.33 (t, J = 2.0 Hz, 4H) ppm. ^{13}C NMR (126 MHz, CDCl_3): δ = -0.7, 68.4, 70.8, 71.5, 73.2 ppm. HRMS (ESI^+): calcd for $\text{C}_{22}\text{H}_{25}\text{Fe}_2\text{Si}^+[\text{M}]^+$ 428.0341, found 428.0351.



3-(Dimethyl(phenyl)silyl)-*N,N*-dimethylaniline **4a**

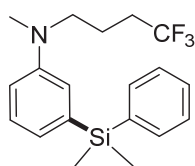
The general procedure B was followed. Purification via column chromatography on silica gel (Hexane/ CH_2Cl_2 = 3/1, v/v) afforded **4a** as colorless oil (50.2 mg, 79%

yield). ^1H NMR (500 MHz, CDCl_3): δ = 0.54 (s, 6H), 2.91 (s, 6H), 6.76 (dd, J = 8.0 Hz, 2.0 Hz, 1H), 6.88-6.90 (m, 2H), 7.24 (t, J = 8.0 Hz, 1H), 7.33-7.34 (m, 3H), 7.53-7.54 (m, 2H) ppm. ^{13}C NMR (126 MHz, CDCl_3): δ = -2.1, 40.8, 113.7, 118.4, 122.8, 127.9, 128.7, 129.1, 134.4, 138.7, 138.8, 150.1 ppm. HRMS (ESI^+): calcd for $\text{C}_{16}\text{H}_{22}\text{NSi}^+[\text{M}+\text{H}]^+$ 256.1516, found 256.1518.



***N*-benzyl-3-(dimethyl(phenyl)silyl)-*N*-methylaniline 4b**

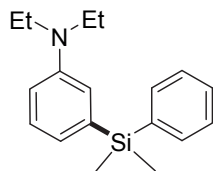
The general procedure B was followed. Purification via column chromatography on silica gel (Hexane/ CH_2Cl_2 = 4/1, v/v) afforded **4b** as colorless oil (58.8 mg, 71% yield). ^1H NMR (500 MHz, CDCl_3): δ = 0.49 (s, 6H), 2.98 (s, 3H), 4.48 (s, 2H), 6.75 (d, J = 8.5 Hz, 1H), 6.87 (d, J = 7.0 Hz, 1H), 6.90 (s, 1H), 7.19-7.23 (m, 4H), 7.27-7.31 (m, 5H), 7.49 (d, J = 7.0 Hz, 2H) ppm. ^{13}C NMR (126 MHz, CDCl_3): δ = -2.2, 38.7, 57.0, 113.5, 118.2, 122.6, 127.0, 127.8, 128.7, 128.8, 129.1, 134.3, 138.7, 138.8, 139.2, 149.2 ppm. HRMS (ESI^+): calcd for $\text{C}_{22}\text{H}_{26}\text{NSi}^+[\text{M}+\text{H}]^+$ 332.1829, found 332.1837.



3-(Dimethyl(phenyl)silyl)-*N*-methyl-*N*-(4,4,4-trifluorobutyl)aniline 4c

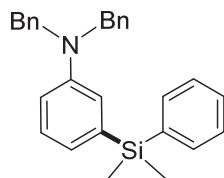
The general procedure B was followed. Purification via column chromatography on silica gel (Hexane/ CH_2Cl_2 = 5/1, v/v) afforded **4c** as colorless oil (61.5 mg, 70% yield). ^1H NMR (500 MHz, CDCl_3): δ = 0.54 (s, 6H), 1.76-1.82 (m, 2H), 1.99-2.07 (m, 2H), 2.89 (s, 3H), 3.31 (t, J = 7.5 Hz, 2H), 6.71 (d, J = 8.0 Hz, 1H), 6.80 (d, J = 2.0 Hz, 1H), 6.89 (d, J = 7.0 Hz, 1H), 7.21-7.25 (m, 1H), 7.34-7.35 (m, 3H), 7.53-7.55 (m, 2H) ppm. ^{13}C NMR (126 MHz, CDCl_3): δ = -2.2, 19.7 (q, J = 2.52 Hz, 1C), 31.5 (q, J = 29.0 Hz, 1C), 38.4, 51.7, 113.4, 118.2, 122.7, 127.3 (q, J = 276.8 Hz, 1C),

127.9, 128.9, 129.2, 134.3, 138.6, 139.2, 148.5 ppm. HRMS (ESI⁺): calcd for C₁₉H₂₅F₃NSi⁺[M+H]⁺ 352.1703, found 352.1713.



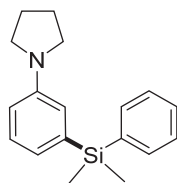
3-(Dimethyl(phenyl)silyl)-*N,N*-diethylaniline **4d**

The general procedure B was followed. Purification via column chromatography on silica gel (Hexane/CH₂Cl₂ = 4/1, v/v) afforded **4d** as colorless oil (51.8 mg, 73% yield). ¹H NMR (500 MHz, CDCl₃): δ = 0.53 (s, 6H), 1.11 (t, *J* = 7.0 Hz, 6H), 3.31 (q, *J* = 7.0 Hz, 4H), 6.68-6.70 (m, 1H), 6.80-6.81 (m, 2H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.33-7.34 (m, 3H), 7.54-7.55 (m, 2H) ppm. ¹³C NMR (126 MHz, CDCl₃): δ = -2.2, 12.7, 44.5, 112.9, 117.7, 121.4, 127.8, 128.9, 129.1, 134.4, 138.7, 138.8, 147.2 ppm. HRMS (ESI⁺): calcd for C₁₈H₂₆NSi⁺[M+H]⁺ 284.1829, found 284.1840.



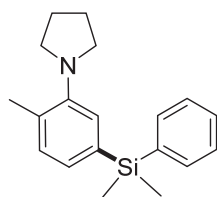
N,N-Dibenzyl-3-(dimethyl(phenyl)silyl)aniline **4e**

The general procedure B was followed. Purification via column chromatography on silica gel (Hexane/CH₂Cl₂ = 5/1, v/v) afforded **4e** as colorless oil (77.3 mg, 76% yield). ¹H NMR (500 MHz, CDCl₃): δ = 0.42 (s, 6H), 4.61 (s, 4H), 6.73-6.75 (m, 1H), 6.85 (d, *J* = 7.0 Hz, 1H), 6.88 (s, 1H), 7.15 (t, *J* = 8.0 Hz, 1H), 7.21-7.31 (m, 13H), 7.41 (d, *J* = 7.0 Hz, 2H) ppm. ¹³C NMR (126 MHz, CDCl₃): δ = -2.4, 54.8, 113.7, 118.6, 122.6, 126.9, 127.0, 127.8, 128.7, 128.8, 129.0, 134.2, 138.5, 138.8, 138.9, 148.4 ppm. HRMS (ESI⁺): calcd for C₂₈H₃₀NSi⁺[M+H]⁺ 408.2142, found 408.2164.



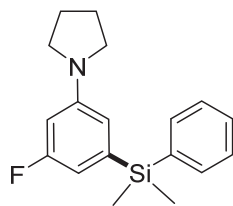
1-(3-(Dimethyl(phenyl)silyl)phenyl)pyrrolidine **4f**

The general procedure B was followed. Purification via column chromatography on silica gel (Hexane/CH₂Cl₂ = 4/1, v/v) afforded **4f** as colorless oil (56.6 mg, 81% yield). ¹H NMR (500 MHz, CDCl₃): δ = 0.53 (s, 6H), 1.96 (t, J = 6.0 Hz, 4H), 3.25 (t, J = 6.0 Hz, 4H), 6.58 (d, J = 6.5 Hz, 1H), 6.70 (s, 1H), 6.82 (t, J = 7.0 Hz, 1H), 7.21-7.24 (m, 1H), 7.32-7.33 (m, 3H), 7.53-7.55 (m, 2H) ppm. ¹³C NMR (126 MHz, CDCl₃): δ = -2.1, 25.6, 47.6, 112.7, 117.2, 121.5, 127.8, 128.8, 129.0, 134.4, 138.7, 138.9, 147.4 ppm. HRMS (ESI⁺): calcd for C₁₈H₂₄NSi⁺[M+H]⁺ 282.1673, found 282.1682.



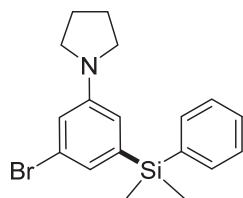
1-(5-(Dimethyl(phenyl)silyl)-2-methylphenyl)pyrrolidine **4g**

The general procedure B was followed. Purification via column chromatography on silica gel (Hexane/CH₂Cl₂ = 4/1, v/v) afforded **4g** as colorless oil (61.8 mg, 84% yield). ¹H NMR (500 MHz, CDCl₃): δ = 0.52 (s, 6H), 1.89-1.91 (m, 4H), 2.32 (s, 3H), 3.15-3.18 (m, 4H), 6.98 (d, J = 7.5 Hz, 1H), 7.02 (s, 1H), 7.11 (d, J = 7.5 Hz, 1H), 7.21-7.24 (m, 1H), 7.32-7.34 (m, 3H), 7.52-7.54 (m, 2H) ppm. ¹³C NMR (126 MHz, CDCl₃): δ = -2.1, 20.8, 25.1, 51.1, 121.3, 126.4, 127.8, 129.0, 130.0, 131.5, 134.3, 135.5, 138.9, 148.9 ppm. HRMS (ESI⁺): calcd for C₁₉H₂₆NSi⁺[M+H]⁺ 296.1829, found 296.1830.



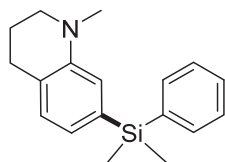
1-(3-(Dimethyl(phenyl)silyl)-5-fluorophenyl)pyrrolidine **4h**

The general procedure B was followed, but reaction was carried out at 120 °C for 48 h and 0.75 mmol PhMe₂SiH₂ was used. Purification via column chromatography on silica gel (Hexane/CH₂Cl₂ = 5/1, v/v) afforded **4h** as colorless oil (30.3 mg, 40% yield). ¹H NMR (500 MHz, CDCl₃): δ = 0.53 (s, 6H), 1.98 (t, *J* = 6.0 Hz, 4H), 3.24 (t, *J* = 6.0 Hz, 4H), 6.23 (d, *J* = 12.5 Hz, 1H), 6.43 (s, 1H), 6.48 (t, *J* = 8.0 Hz, 1H), 7.34-7.35 (m, 3H), 7.53 (d, *J* = 6.0 Hz, 2H) ppm. ¹³C NMR (126 MHz, CDCl₃): δ = -2.3, 25.6, 47.8, 99.4 (d, *J* = 25.7 Hz, 1C), 107.1 (d, *J* = 19.4 Hz, 1C), 112.9 (d, *J* = 1.76 Hz, 1C), 127.9, 129.3, 134.3, 138.2, 141.1 (d, *J* = 5.9 Hz, 1C), 149.3 (d, *J* = 10.0 Hz, 1C), 164.0 (d, *J* = 245.4 Hz, 1C) ppm. HRMS (ESI⁺): calcd for C₁₈H₂₃FNSi⁺[M+H]⁺ 300.1578, found 300.1585.



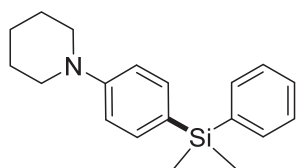
1-(3-Bromo-5-(dimethyl(phenyl)silyl)phenyl)pyrrolidine **4i**

The general procedure B was followed. Purification via column chromatography on silica gel (Hexane/CH₂Cl₂ = 10/1, v/v) afforded **4i** as colorless oil (32.5 mg, 36% yield). ¹H NMR (500 MHz, CDCl₃): δ = 0.52 (s, 6H), 1.97 (t, *J* = 6.0 Hz, 4H), 3.22 (t, *J* = 6.0 Hz, 4H), 6.56 (s, 1H), 6.68 (s, 1H), 6.88 (s, 1H), 7.34-7.35 (m, 3H), 7.52 (d, *J* = 6.0 Hz, 2H) ppm. ¹³C NMR (126 MHz, CDCl₃): δ = -2.3, 25.6, 47.7, 115.1, 115.8, 123.3, 123.9, 128.0, 129.3, 134.3, 138.1, 141.3, 148.6 ppm. HRMS (ESI⁺): calcd for C₁₈H₂₃BrNSi⁺[M+H]⁺ 360.0778, found 360.0771.



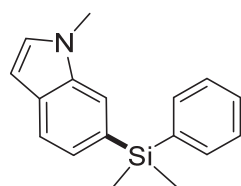
7-(Dimethyl(phenyl)silyl)-1-methyl-1,2,3,4-tetrahydroquinoline **4j**

The general procedure B was followed. Purification via column chromatography on silica gel (Hexane/CH₂Cl₂ = 4/1, v/v) afforded **4j** as colorless oil (52.8 mg, 75% yield). ¹H NMR (500 MHz, CDCl₃): δ = 0.45 (s, 6H), 1.87-1.92 (m, 2H), 2.68 (t, J = 6.0 Hz, 2H), 2.77 (s, 3H), 3.13 (t, J = 5.5 Hz, 2H), 6.65 (s, 1H), 6.69 (d, J = 7.0 Hz, 1H), 6.87 (d, J = 7.0 Hz, 1H), 7.25-7.26 (m, 3H), 7.47-7.48 (m, 2H) ppm. ¹³C NMR (126 MHz, CDCl₃): δ = -2.1, 22.5, 28.0, 39.2, 51.6, 116.6, 122.5, 124.2, 127.8, 128.6, 129.0, 134.3, 136.3, 139.0, 146.4 ppm. HRMS (ESI⁺): calcd for C₁₈H₂₄NSi⁺[M+H]⁺ 282.1673, found 282.1670.



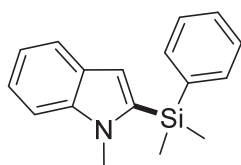
1-(4-(Dimethyl(phenyl)silyl)phenyl)piperidine **4k**

The general procedure B was followed. Purification via column chromatography on silica gel (Hexane/CH₂Cl₂ = 4/1, v/v) afforded **4k** as colorless oil (44.6 mg, 60% yield). ¹H NMR (500 MHz, CDCl₃): δ = 0.50 (s, 6H), 1.56-1.60 (m, 2H), 1.66-1.70 (m, 4H), 3.19 (t, J = 5.5 Hz, 4H), 6.90 (d, J = 8.5 Hz, 2H), 7.32-7.33 (m, 3H), 7.39 (d, J = 8.0 Hz, 2H), 7.50-7.52 (m, 2H) ppm. ¹³C NMR (126 MHz, CDCl₃): δ = -2.0, 24.5, 25.9, 49.9, 115.4, 126.1, 127.8, 129.0, 134.3, 135.4, 139.3, 152.7 ppm. HRMS (ESI⁺): calcd for C₁₉H₂₆NSi⁺[M+H]⁺ 296.1829, found 296.1840.



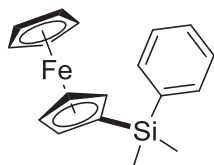
6-(Dimethyl(phenyl)silyl)-1-methyl-1H-indole **4l**

The general procedure B was followed, but reaction was carried out at 120 °C for 36 h and 0.75 mmol PhMe₂SiH₂ was used in the presence of B(C₆F₅)₃ (10 mol%). Purification via column chromatography on silica gel (Hexane/CH₂Cl₂ = 4/1, v/v) afforded **4l** as colorless oil (38.4 mg, 58% yield). ¹H NMR (500 MHz, CDCl₃): δ = 0.60 (s, 6H), 3.77 (s, 3H), 6.46 (d, *J* = 2.5 Hz, 1H), 7.04 (d, *J* = 3.0 Hz, 1H), 7.24 (d, *J* = 6.5 Hz, 1H), 7.33-7.34 (m, 3H), 7.47 (s, 1H), 7.54-7.56 (m, 2H), 7.63 (d, *J* = 7.5 Hz, 1H) ppm. ¹³C NMR (126 MHz, CDCl₃): δ = -1.7, 32.9, 101.0, 115.2, 120.6, 124.8, 127.9, 129.0, 129.4, 129.5, 129.8, 134.4, 136.8, 139.4 ppm. HRMS (EI⁺): calcd for C₁₇H₁₉NSi⁺[M]⁺ 265.1281, found 265.1279.



2-(Dimethyl(phenyl)silyl)-1-methyl-1*H*-indole **4m**

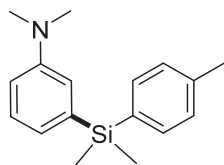
The general procedure was followed, but B(C₆F₅)₃ (10 mol%) was used. Purification via column chromatography on silica gel (Hexane/CH₂Cl₂ = 5/1, v/v) afforded **4m** as colorless oil (42.5 mg, 64% yield). ¹H NMR (500 MHz, CDCl₃): δ = 0.64 (s, 6H), 3.62 (s, 3H), 6.79 (s, 1H), 7.08 (t, *J* = 7.0 Hz, 1H), 7.20-7.23 (m, 1H), 7.28 (d, *J* = 8.5 Hz, 1H), 7.33-7.39 (m, 3H), 7.52 (d, *J* = 6.0 Hz, 2H), 7.63 (d, *J* = 8.0 Hz, 1H) ppm. ¹³C NMR (126 MHz, CDCl₃): δ = -1.7, 33.1, 109.2, 113.2, 119.3, 120.9, 122.3, 128.2, 128.5, 129.5, 134.2, 137.7, 139.0, 140.5 ppm. HRMS (EI⁺): calcd for C₁₇H₁₉NSi⁺[M]⁺ 265.1281, found 265.1281.



(Dimethyl(phenyl)silyl)ferrocene **4n**

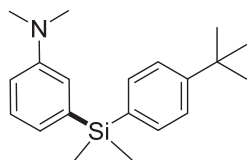
The general procedure was followed. Purification via column chromatography on silica gel (Hexane/CH₂Cl₂ = 10/1, v/v) afforded **4n** as a yellow solid (57.5 mg, 72% yield). ¹H NMR (500 MHz, CDCl₃): δ = 0.52 (s, 6H), 4.09 (s, 5H), 4.14 (t, *J* = 1.5 Hz,

2H), 4.36 (t, $J = 1.5$ Hz, 2H), 7.32-7.33 (m, 3H), 7.52-7.53 (m, 2H) ppm. ^{13}C NMR (126 MHz, CDCl_3): $\delta = -1.6, 68.4, 69.9, 71.1, 73.5, 127.8, 128.9, 133.8, 139.9$ ppm. HRMS (ESI^+): calcd for $\text{C}_{18}\text{H}_{20}\text{FeSi}^+[\text{M}]^+$ 320.0678, found 320.0674.



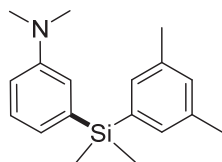
3-(Dimethyl(p-tolyl)silyl)-*N,N*-dimethylaniline **5a**

The general procedure B was followed. Purification via column chromatography on silica gel (Hexane/ $\text{CH}_2\text{Cl}_2 = 4/1$, v/v) afforded **5a** as colorless oil (56.3 mg, 84% yield). ^1H NMR (500 MHz, CDCl_3): $\delta = 0.52$ (s, 6H), 2.34 (s, 3H), 2.91 (s, 6H), 6.76 (dd, $J = 8.0$ Hz, 2.0 Hz, 1H), 6.87-6.90 (m, 2H), 7.16 (d, $J = 7.5$ Hz, 2H), 7.22-7.25 (m, 1H), 7.43 (d, $J = 7.5$ Hz, 2H) ppm. ^{13}C NMR (126 MHz, CDCl_3): $\delta = -2.0, 21.6, 40.8, 113.7, 118.4, 122.8, 128.67, 128.72, 134.4, 135.1, 138.93, 138.98, 150.1$ ppm. HRMS (ESI^+): calcd for $\text{C}_{17}\text{H}_{24}\text{NSi}^+[\text{M}+\text{H}]^+$ 270.1673, found 270.1676.



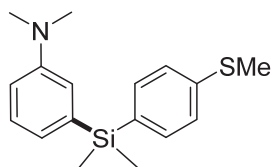
3-((4-*tert*-Butylphenyl)dimethylsilyl)-*N,N*-dimethylaniline **5b**

The general procedure B was followed. Purification via column chromatography on silica gel (Hexane/ $\text{CH}_2\text{Cl}_2 = 4/1$, v/v) afforded **5b** as colorless oil (56.8 mg, 73% yield). ^1H NMR (500 MHz, CDCl_3): $\delta = 0.53$ (s, 6H), 1.31 (s, 9H), 2.92 (s, 6H), 6.76 (d, $J = 8.0$ Hz, 1H), 6.89-6.91 (m, 2H), 7.22-7.23 (m, 1H), 7.36 (d, $J = 8.0$ Hz, 2H), 7.48 (d, $J = 7.5$ Hz, 2H) ppm. ^{13}C NMR (126 MHz, CDCl_3): $\delta = -2.1, 31.4, 34.8, 40.8, 113.7, 118.4, 122.8, 124.8, 128.7, 134.2, 135.2, 139.0, 150.1, 152.0$ ppm. HRMS (ESI^+): calcd for $\text{C}_{20}\text{H}_{30}\text{NSi}^+[\text{M}+\text{H}]^+$ 312.2142, found 312.2142.



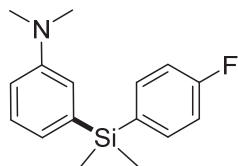
3-((3,5-Dimethylphenyl)dimethylsilyl)-*N,N*-dimethylaniline **5c**

The general procedure B was followed. Purification via column chromatography on silica gel (Hexane/CH₂Cl₂ = 3/1, v/v) afforded **5c** as colorless oil (55.8 mg, 79% yield). ¹H NMR (500 MHz, CDCl₃): δ = 0.52 (s, 6H), 2.29 (s, 6H), 2.92 (s, 6H), 6.76 (d, *J* = 8.0 Hz, 1H), 6.88-6.91 (m, 2H), 6.99 (s, 1H), 7.15 (s, 2H), 7.21-7.25 (m, 1H) ppm. ¹³C NMR (126 MHz, CDCl₃): δ = -2.0, 21.5, 40.8, 113.7, 118.4, 122.8, 128.7, 130.9, 132.0, 137.1, 138.4, 139.0, 150.1 ppm. HRMS (ESI⁺): calcd for C₁₈H₂₆NSi⁺[M+H]⁺ 284.1829, found 284.1830.



3-((4-Methylthiophenyl)dimethylsilyl)-*N,N*-dimethylaniline **5d**

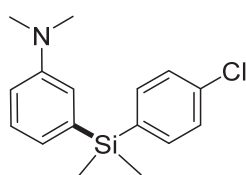
The general procedure B was followed. Purification via column chromatography on silica gel (Hexane/CH₂Cl₂ = 1.5/1, v/v) afforded **5d** as colorless oil (61.6 mg, 82% yield). ¹H NMR (500 MHz, CDCl₃): δ = 0.52 (s, 6H), 2.46 (s, 3H), 2.92 (s, 6H), 6.75-6.77 (m, 1H), 6.86-6.88 (m, 2H), 7.21-7.24 (m, 3H), 7.43-7.45 (m, 2H) ppm. ¹³C NMR (126 MHz, CDCl₃): δ = -2.1, 15.5, 40.7, 113.7, 118.3, 122.7, 125.7, 128.7, 134.7, 138.6, 139.8, 150.1 ppm. HRMS (ESI⁺): calcd for C₁₇H₂₄NSSi⁺[M+H]⁺ 302.1393, found 302.1399.



3-((4-Fluorophenyl)dimethylsilyl)-*N,N*-dimethylaniline **5e**

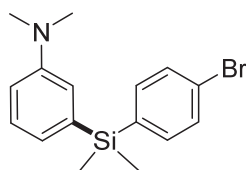
The general procedure B was followed. Purification via column chromatography on

silica gel (Hexane/CH₂Cl₂ = 3/1, v/v) afforded **5e** as colorless oil (45.6 mg, 67% yield). ¹H NMR (500 MHz, CDCl₃): δ = 0.53 (s, 6H), 2.92 (s, 6H), 6.76-6.78 (m, 1H), 6.86-6.87 (m, 2H), 7.03 (t, *J* = 9.0 Hz, 2H), 7.24 (t, *J* = 4.0 Hz, 1H), 7.48-7.51 (m, 2H) ppm. ¹³C NMR (126 MHz, CDCl₃): δ = -2.0, 40.7, 113.8, 115.0 (d, *J* = 19.5 Hz, 1C), 118.2, 122.6, 128.8, 134.3 (d, *J* = 3.8 Hz, 1C), 136.3 (d, *J* = 7.3 Hz, 1C), 138.5, 150.1, 163.9 (d, *J* = 248.2 Hz, 1C) ppm. HRMS (ESI⁺): calcd for C₁₆H₂₁FNSi⁺[M+H]⁺ 274.1422, found 274.1423.



3-((4-Chlorophenyl)dimethylsilyl)-*N,N*-dimethylaniline **5f**

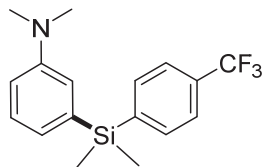
The general procedure B was followed. Purification via column chromatography on silica gel (Hexane/CH₂Cl₂ = 4/1, v/v) afforded **5f** as colorless oil (50.6 mg, 70% yield). ¹H NMR (500 MHz, CDCl₃): δ = 0.52 (s, 6H), 2.92 (s, 6H), 6.76-6.78 (m, 1H), 6.85-6.86 (m, 2H), 7.23-7.24 (m, 1H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H) ppm. ¹³C NMR (126 MHz, CDCl₃): δ = -2.2, 40.7, 113.9, 118.2, 122.6, 128.1, 128.8, 135.4, 135.7, 137.2, 138.1, 150.1 ppm. HRMS (ESI⁺): calcd for C₁₆H₂₁ClNSi⁺[M+H]⁺ 290.1126, found 290.1125.



3-((4-Bromophenyl)dimethylsilyl)-*N,N*-dimethylaniline **5g**

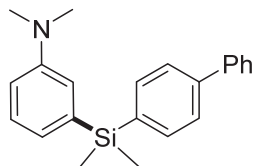
The general procedure B was followed. Purification via column chromatography on silica gel (Hexane/CH₂Cl₂ = 4/1, v/v) afforded **5g** as colorless oil (54.3 mg, 65% yield). ¹H NMR (500 MHz, CDCl₃): δ = 0.52 (s, 6H), 2.92 (s, 6H), 6.77 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 6.84-6.86 (m, 2H), 7.23-7.24 (m, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H) ppm. ¹³C NMR (126 MHz, CDCl₃): δ = -2.2, 40.7, 113.9, 118.1,

122.6, 124.0, 128.8, 131.0, 136.0, 137.7, 138.0, 150.1 ppm. HRMS (ESI⁺): calcd for C₁₆H₂₁BrNSi⁺[M+H]⁺ 334.0621, found 334.0634.



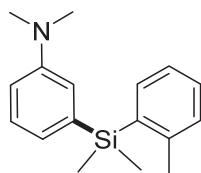
3-(Dimethyl(4-(trifluoromethyl)phenyl)silyl)-*N,N*-dimethylaniline **5h**

The general procedure B was followed. Purification via column chromatography on silica gel (Hexane/CH₂Cl₂ = 4/1, v/v) afforded **5h** as colorless oil (58.2 mg, 72% yield). ¹H NMR (500 MHz, CDCl₃): δ = 0.56 (s, 6H), 2.93 (s, 6H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.86 (m, 2H), 7.24-7.26 (m, 1H), 7.56 (d, *J* = 7.5 Hz, 2H), 7.64 (d, *J* = 7.5 Hz, 2H) ppm. ¹³C NMR (126 MHz, CDCl₃): δ = -2.4, 40.7, 114.0, 118.1, 122.6, 124.36 (q, *J* = 3.8 Hz, 1C), 124.42 (q, *J* = 272.7 Hz, 1C), 128.9, 131.0 (q, *J* = 32.1 Hz, 1C), 134.6, 137.6, 144.0, 150.2 ppm. HRMS (ESI⁺): calcd for C₁₇H₂₁F₃NSi⁺[M+H]⁺ 324.1390, found 324.1392.



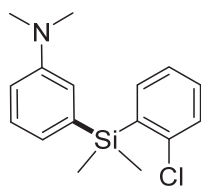
3-(Biphenyl-4-yl)dimethylsilyl)-*N,N*-dimethylaniline **5i**

The general procedure B was followed. Purification via column chromatography on silica gel (Hexane/CH₂Cl₂ = 3/1, v/v) afforded **5i** as a white solid (60.6 mg, 73% yield). ¹H NMR (500 MHz, CDCl₃): δ = 0.57 (s, 6H), 2.92 (s, 6H), 6.77 (d, *J* = 7.5 Hz, 1H), 6.92-6.93 (m, 2H), 7.26 (t, *J* = 8.0 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.56-7.62 (m, 6H) ppm. ¹³C NMR (126 MHz, CDCl₃): δ = -2.1, 40.8, 113.8, 118.3, 122.8, 126.6, 127.3, 127.5, 128.8, 128.9, 134.8, 137.6, 138.6, 141.3, 141.8, 150.1 ppm. HRMS (ESI⁺): calcd for C₂₂H₂₆NSi⁺[M+H]⁺ 332.1829, found 332.1836.



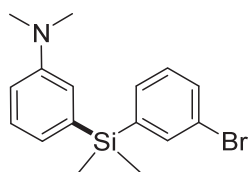
3-((Dimethyl(o-tolyl)silyl)-N,N-dimethylaniline **5j**

The general procedure B was followed. Purification via column chromatography on silica gel (Hexane/CH₂Cl₂ = 3/1, v/v) afforded **5j** as colorless oil (38.6 mg, 57% yield). ¹H NMR (500 MHz, CDCl₃): δ = 0.57 (s, 6H), 2.31 (s, 3H), 2.90 (s, 6H), 6.75 (d, *J* = 8.5 Hz, 1H), 6.84-6.87 (m, 2H), 7.13-7.18 (m, 2H), 7.20-7.24 (m, 1H), 7.26-7.29 (m, 1H), 7.48 (d, *J* = 7.0 Hz, 1H) ppm. ¹³C NMR (126 MHz, CDCl₃): δ = -1.2, 23.4, 40.8, 113.6, 118.2, 122.7, 125.0, 128.7, 129.6, 129.9, 135.6, 136.7, 139.5, 144.3, 150.1 ppm. HRMS (ESI⁺): calcd for C₁₇H₂₄NSi⁺[M+H]⁺ 270.1673, found 270.1671.



3-((2-Chlorophenyl)dimethylsilyl)-N,N-dimethylaniline **5k**

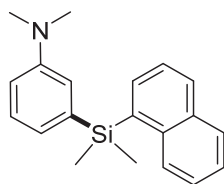
The general procedure B was followed. Purification via column chromatography on silica gel (Hexane/CH₂Cl₂ = 3/1, v/v) afforded **5k** as colorless oil (32.6 mg, 45% yield). ¹H NMR (500 MHz, CDCl₃): δ = 0.65 (s, 6H), 2.93 (s, 6H), 6.79 (dd, *J* = 8.5 Hz, 2.5 Hz, 1H), 6.90 (d, *J* = 7.0 Hz, 1H), 6.93 (d, *J* = 2.5 Hz, 1H), 7.15-7.18 (m, 1H), 7.24-7.27 (m, 2H), 7.31-7.33 (m, 2H) ppm. ¹³C NMR (126 MHz, CDCl₃): δ = -1.7, 40.8, 113.8, 118.5, 122.8, 126.0, 128.7, 129.4, 130.9, 137.2, 137.6, 138.1, 141.4, 150.1 ppm. HRMS (ESI⁺): calcd for C₁₆H₂₁ClNSi⁺[M+H]⁺ 290.1126, found 290.1127.



3-((3-Bromophenyl)dimethylsilyl)-N,N-dimethylaniline **5l**

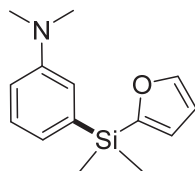
The general procedure B was followed. Purification via column chromatography on

silica gel (Hexane/CH₂Cl₂ = 3/1, v/v) afforded **5l** as colorless oil (62.5 mg, 75% yield). ¹H NMR (500 MHz, CDCl₃): δ = 0.53 (s, 6H), 2.92 (s, 6H), 6.77 (d, *J* = 7.5 Hz, 1H), 6.85 (m, 2H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.42 (d, *J* = 7.0 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 1H), 7.64 (s, 1H) ppm. ¹³C NMR (126 MHz, CDCl₃): δ = -2.3, 40.7, 113.9, 118.1, 122.6, 123.0, 128.9, 129.7, 132.1, 132.7, 136.8, 137.8, 142.2, 150.1 ppm. HRMS (ESI⁺): calcd for C₁₆H₂₁BrNSi⁺[M+H]⁺ 334.0621, found 334.0612.



3-(Dimethyl(naphthalen-1-yl)silyl)-*N,N*-dimethylaniline **5m**

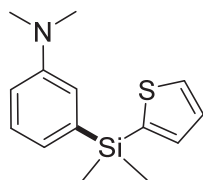
The general procedure B was followed. Purification via column chromatography on silica gel (Hexane/CH₂Cl₂ = 4/1, v/v) afforded **5m** as colorless oil (30.8 mg, 40% yield). ¹H NMR (500 MHz, CDCl₃): δ = 0.70 (s, 6H), 2.87 (s, 6H), 6.75 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 6.89-6.93 (m, 2H), 7.20-7.23 (m, 1H), 7.35-7.38 (m, 1H), 7.42-7.46 (m, 2H), 7.71 (d, *J* = 6.0 Hz, 1H), 7.83-7.88 (m, 2H), 8.01 (d, *J* = 8.5 Hz, 1H) ppm. ¹³C NMR (126 MHz, CDCl₃): δ = -0.7, 40.7, 113.7, 118.4, 122.8, 125.2, 125.4, 125.7, 128.8, 128.9, 129.0, 130.2, 133.5, 134.8, 136.3, 137.2, 139.4, 150.1 ppm. HRMS (ESI⁺): calcd for C₂₀H₂₄NSi⁺[M+H]⁺ 306.1673, found 306.1684.



3-(Furan-2-yl)dimethylsilyl)-*N,N*-dimethylaniline **5n**

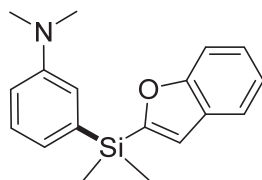
The general procedure B was followed. Purification via column chromatography on silica gel (Hexane/CH₂Cl₂ = 3/1, v/v) afforded **5n** as colorless oil (40.7 mg, 66% yield). ¹H NMR (500 MHz, CDCl₃): δ = 0.53 (s, 6H), 2.93 (s, 6H), 6.38 (s, 1H), 6.67 (d, *J* = 3.0 Hz, 1H), 6.76-6.78 (m, 1H), 6.91-6.92 (m, 2H), 7.23-7.25 (m, 1H), 7.67 (s,

1H) ppm. ^{13}C NMR (126 MHz, CDCl_3): δ = -2.7, 40.7, 109.5, 114.0, 118.1, 121.0, 122.4, 128.8, 137.6, 147.1, 150.2, 158.7 ppm. HRMS (EI^+): calcd for $\text{C}_{14}\text{H}_{19}\text{NOSi}^+[\text{M}]^+$ 245.1230, found 245.1220.



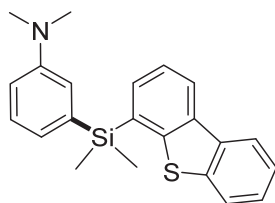
3-(Dimethyl(thiophen-2-yl)silyl)-*N,N*-dimethylaniline **5o**

The general procedure B was followed. Purification via column chromatography on silica gel (Hexane/ CH_2Cl_2 = 3/1, v/v) afforded **5o** as colorless oil (37.2 mg, 57% yield). ^1H NMR (500 MHz, CDCl_3): δ = 0.58 (s, 6H), 2.93 (s, 6H), 6.77 (d, J = 8.0 Hz, 1H), 6.91-6.93 (m, 2H), 7.18-7.29 (m, 3H), 7.61 (d, J = 4.5 Hz, 1H) ppm. ^{13}C NMR (126 MHz, CDCl_3): δ = -1.0, 40.7, 114.0, 118.1, 122.4, 128.3, 128.8, 131.1, 135.4, 138.3, 138.4, 150.1 ppm. HRMS (ESI^+): calcd for $\text{C}_{14}\text{H}_{20}\text{NSSi}^+[\text{M}+\text{H}]^+$ 262.1080, found 262.1080.



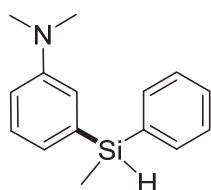
3-(Benzofuran-2-yl)dimethylsilyl)-*N,N*-dimethylaniline **5p**

The general procedure B was followed. Purification via column chromatography on silica gel (Hexane/ CH_2Cl_2 = 3/1, v/v) afforded **5p** as colorless oil (48.5 mg, 66% yield). ^1H NMR (500 MHz, CDCl_3): δ = 0.61 (s, 6H), 2.94 (s, 6H), 6.79 (dd, J = 8.0 Hz, 2.0 Hz, 1H), 6.96-6.99 (m, 3H), 7.18 (t, J = 7.0 Hz, 1H), 7.24-7.28 (m, 2H), 7.49 (d, J = 8.0 Hz, 1H), 7.55 (d, J = 7.5 Hz, 1H) ppm. ^{13}C NMR (126 MHz, CDCl_3): δ = -2.8, 40.7, 111.5, 114.2, 117.6, 118.1, 121.2, 122.4, 122.5, 124.5, 128.1, 128.9, 136.7, 150.2, 158.5, 162.2 ppm. HRMS (ESI^+): calcd for $\text{C}_{18}\text{H}_{22}\text{NOSi}^+[\text{M}+\text{H}]^+$ 296.1465, found 296.1466.



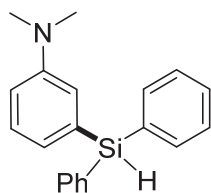
3-(Dibenzo[*b,d*]thiophen-4-yl)dimethylsilyl)-*N,N*-dimethylaniline **5q**

The general procedure B was followed. Purification via column chromatography on silica gel (Hexane/CH₂Cl₂ = 3/1, v/v) afforded **5q** as colorless oil (68.3 mg, 76% yield). ¹H NMR (500 MHz, CDCl₃): δ = 0.74 (s, 6H), 2.91 (s, 6H), 6.78-6.80 (m, 1H), 6.96 (d, *J* = 7.0 Hz, 1H), 6.99 (s, 1H), 7.24-7.26 (m, 1H), 7.41-7.44 (m, 3H), 7.56-7.58 (m, 1H), 7.78-7.80 (m, 1H), 8.13-8.17 (m, 2H) ppm. ¹³C NMR (126 MHz, CDCl₃): δ = -2.2, 40.8, 114.0, 118.6, 121.5, 122.7, 123.0, 123.9, 124.2, 126.6, 128.8, 132.7, 133.9, 134.9, 135.4, 137.5, 139.7, 145.8, 150.1 ppm. HRMS (EI⁺): calcd for C₂₂H₂₃NSSi⁺[M]⁺ 361.1315, found 361.1296.



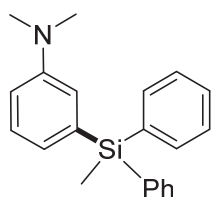
N,N-dimethyl-3-(methyl(phenyl)silyl)aniline **5r**

The general procedure B was followed. Purification via column chromatography on silica gel (Hexane/CH₂Cl₂ = 4/1, v/v) afforded **5r** as colorless oil (41.3 mg, 69% yield). ¹H NMR (500 MHz, CDCl₃): δ = 0.61 (d, *J* = 4.0 Hz, 3H), 2.93 (s, 6H), 4.91 (q, *J* = 4.0 Hz, 1H), 6.78 (dd, *J* = 8.0 Hz, 2.0 Hz, 1H), 6.91 (d, *J* = 7.0 Hz, 1H), 6.93 (d, *J* = 2.5 Hz, 1H), 7.23-7.25 (m, 1H), 7.33-7.37 (m, 3H), 7.56-7.58 (m, 2H) ppm. ¹³C NMR (126 MHz, CDCl₃): δ = -4.7, 40.7, 114.1, 118.9, 123.2, 128.0, 128.9, 129.5, 135.0, 135.8, 135.9, 150.2 ppm. HRMS (ESI⁺): calcd for C₁₅H₂₀NSi⁺[M+H]⁺ 242.1360, found 242.1361.



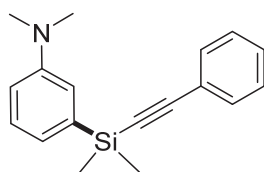
3-(Diphenylsilyl)-*N,N*-dimethylaniline **5s**

The general procedure B was followed. Purification via column chromatography on silica gel (Hexane/CH₂Cl₂ = 4/1, v/v) afforded **5s** as colorless oil (46.5 mg, 61% yield). ¹H NMR (500 MHz, CDCl₃): δ = 2.90 (s, 6H), 5.44 (s, 1H), 6.80 (dd, J = 8.0 Hz, 2.0 Hz, 1H), 6.91 (d, J = 7.0 Hz, 1H), 6.96 (d, J = 2.5 Hz, 1H), 7.24-7.25 (m, 1H), 7.34-7.40 (m, 6H), 7.58-7.60 (m, 4H) ppm. ¹³C NMR (126 MHz, CDCl₃): δ = 40.7, 114.3, 119.8, 124.2, 128.1, 128.9, 129.8, 133.8, 133.9, 136.0, 150.2 ppm. HRMS (ESI⁺): calcd for C₂₀H₂₂NSi⁺[M+H]⁺ 304.1516, found 304.1516.



N,N-Dimethyl-3-(methyldiphenylsilyl)aniline **5t**

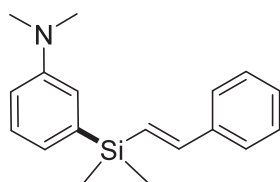
The general procedure B was followed. Purification via column chromatography on silica gel (Hexane/CH₂Cl₂ = 4/1, v/v) afforded **5t** as colorless oil (44.5 mg, 56% yield). ¹H NMR (500 MHz, CDCl₃): δ = 0.82 (s, 3H), 2.88 (s, 6H), 6.79 (d, J = 8.5 Hz, 1H), 6.85-6.88 (m, 2H), 7.23 (d, J = 8.0 Hz, 1H), 7.32-7.39 (m, 6H), 7.53 (d, J = 6.5 Hz, 4H) ppm. ¹³C NMR (126 MHz, CDCl₃): δ = -3.1, 40.7, 113.9, 119.5, 123.9, 127.9, 128.7, 129.4, 135.5, 136.6, 136.7, 150.1 ppm. HRMS (ESI⁺): calcd for C₂₁H₂₄NSi⁺[M+H]⁺ 318.1673, found 318.1679.



3-(Dimethyl(phenylethynyl)silyl)-*N,N*-dimethylaniline **5u**

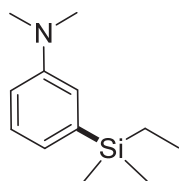
The general procedure B was followed. Purification via column chromatography on

silica gel (Hexane/CH₂Cl₂ = 4/1, v/v) afforded **5u** as colorless oil (32.5 mg, 47% yield). ¹H NMR (500 MHz, CDCl₃): δ = 0.48 (s, 6H), 2.97 (s, 6H), 6.79 (d, *J* = 8.0 Hz, 1H), 7.03 (d, *J* = 7.0 Hz, 1H), 7.10 (s, 1H), 7.26-7.31 (m, 4H), 7.49 (d, *J* = 6.5 Hz, 2H) ppm. ¹³C NMR (126 MHz, CDCl₃): δ = -0.6, 40.8, 92.6, 106.7, 114.1, 117.9, 122.1, 123.3, 128.3, 128.7, 128.8, 132.2, 137.6, 150.2 ppm. HRMS (ESI⁺): calcd for C₁₈H₂₂NSi⁺[M+H]⁺ 280.1516, found 280.1515.



(*E*)-3-(Dimethyl(styryl)silyl)-*N,N*-dimethylaniline 5u

The general procedure B was followed. Purification via column chromatography on silica gel (Hexane/CH₂Cl₂ = 4/1, v/v) afforded **5v** as colorless oil (57.8 mg, 82% yield). ¹H NMR (500 MHz, CDCl₃): δ = 0.42 (s, 6H), 2.94 (s, 6H), 6.59 (d, *J* = 19.5 Hz, 1H), 6.76-6.78 (m, 1H), 6.93-6.97 (m, 3H), 7.23-7.26 (m, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.44 (d, *J* = 7.5 Hz, 2H) ppm. ¹³C NMR (126 MHz, CDCl₃): δ = -2.3, 40.8, 113.8, 118.0, 122.5, 126.6, 127.7, 128.2, 128.6, 128.7, 138.5, 139.1, 145.2, 150.2 ppm. HRMS (ESI⁺): calcd for C₁₈H₂₄NSi⁺[M+H]⁺ 282.1673, found 282.1676.



3-(Ethyldimethylsilyl)-*N,N*-dimethylaniline 5w

The general procedure B was followed, but EtMe₂SiH (1.25 mmol) was used. Purification via column chromatography on silica gel (Hexane/CH₂Cl₂ = 4/1, v/v) afforded **5w** as colorless oil (41.8 mg, 81% yield). ¹H NMR (500 MHz, CDCl₃): δ = 0.24 (s, 6H), 0.73 (q, *J* = 8.0 Hz, 2H), 0.97 (t, *J* = 8.0 Hz, 3H), 2.95 (s, 6H), 6.75 (d, *J* = 7.5 Hz, 1H), 6.87-6.89 (m, 2H), 7.22-7.25 (m, 1H) ppm. ¹³C NMR (126 MHz, CDCl₃): δ = -3.3, 7.61, 7.64, 40.8, 113.5, 117.8, 122.2, 128.6, 140.1, 150.1 ppm.

HRMS (ESI⁺): calcd for C₁₂H₂₂NSi⁺[M+H]⁺ 208.1516, found 208.1518.

7. X-ray Crystallographic Study of compound **4a**•HCl

Under air atmosphere, to a stirred solution of **4a** (100 mg, 0.39 mmol) in Et₂O (3 mL) was added hydrogen chloride solution in ethyl ether (1.5 mL, 1.0 mol/L). The reaction was stirred for 10 min at r.t. The mixture was concentrated in vacuo to afford **4a**•HCl as white solid. The crude product was washed with hexane (5 mL). Then, in a glove box, obtained white solid was dissolved in a mixture of CH₂Cl₂ and hexane. Single crystals suitable for X-ray crystallography were grown by slow evaporation of the prepared solution in a refrigerator (−30 °C).

X-ray diffraction data collections were performed on a Bruker D8 QUEST diffractometer equipped with a CMOS area detector, using a I μ S (Incoatec Microfocus Source) microfocus sealed tube with Mo K α radiation (λ = 0.71073 Å) at 173 K. The Bravais lattice and the unit cell parameters were determined by the Bruker APEX2 software package.¹² The raw frame data were processed, and absorption corrections were done using SAINT and SADABS embedded in Bruker APEX2 to yield the reflection data (hkl) file.¹² All of the structures were solved using SHELXS-2013.¹³ Structural refinement was performed using the WINGX-Version 2014.1 system,¹⁴ on F² anisotropically for all of the non-hydrogen atoms by the fullmatrix least-squares method. Analytical scattering factors for neutral atoms were used throughout the analysis. The hydrogen atoms were placed at calculated positions, which were then refined using a riding model. The residual electron densities in all of the structures were of no chemical significance. The crystallographic figure was drawn by using ORTEP-III software.¹⁵ CCDC number 1565171 (for **4a**•HCl) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

X-ray structure of compound **4a**•HCl

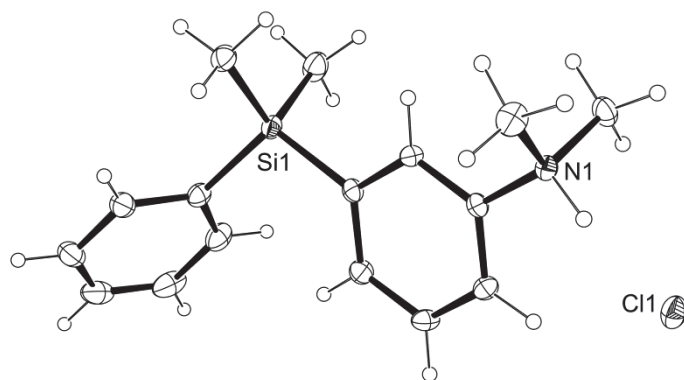


Figure S1. Crystal structure of compound **4a·HCl**.

Crystal data and structure refinement for compound 4a·HCl.

Identification code	shelx	
Empirical formula	C ₁₆ H ₂₂ Cl N Si	
Formula weight	291.88	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	<i>P</i> 2 ₁ /c	
Unit cell dimensions	<i>a</i> = 12.7816(11) Å	α = 90°.
	<i>b</i> = 11.3525(9) Å	β = 106.203(3)°.
	<i>c</i> = 11.9115(11) Å	γ = 90°.
Volume	1659.7(2) Å ³	
<i>Z</i>	4	
Density (calculated)	1.168 Mg/m ³	
Absorption coefficient	0.290 mm ⁻¹	
<i>F</i> (000)	624	
Crystal size	0.300 x 0.200 x 0.200 mm ³	
Theta range for data collection	2.444 to 25.141°.	
Index ranges	-15 ≤ <i>h</i> ≤ 15, -13 ≤ <i>k</i> ≤ 13, -14 ≤ <i>l</i> ≤ 14	
Reflections collected	20206	
Independent reflections	2958 [<i>R</i> (int) = 0.1084]	
Completeness to theta = 25.141°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.745 and 0.543	
Refinement method	Full-matrix least-squares on <i>F</i> ²	
Data / restraints / parameters	2958 / 0 / 176	
Goodness-of-fit on <i>F</i> ²	1.061	
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0447, <i>wR</i> 2 = 0.1060	

R indices (all data)

R1 = 0.0715, wR2 = 0.1232

Extinction coefficient

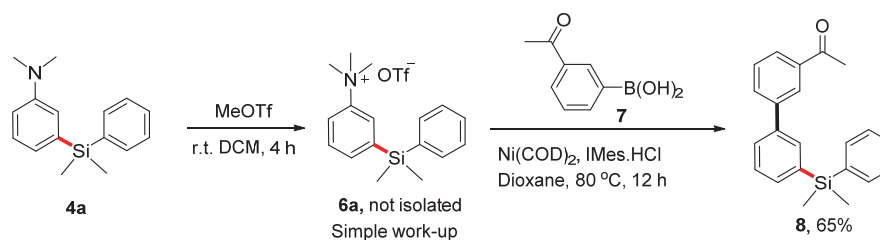
n/a

Largest diff. peak and hole

0.325 and -0.359 e.Å⁻³

8. Chemical Transformations of Products 4a and 5i

8.1 Suzuki-type cross-coupling starting from product 4a with arylboronic acids 7

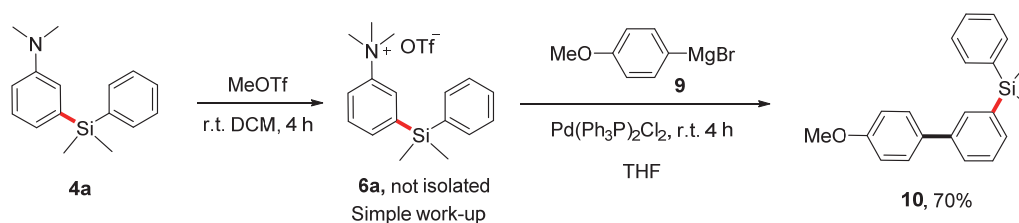


1-(3'-(Dimethyl(phenyl)silyl)biphenyl-3-yl)ethanone 8 According to the literature procedures,^{7,8} to a dry 20-mL Schlenk tube equipped with a magnetic stir bar was charged product **4a** (63.8 mg, 0.25 mmol) and CH₂Cl₂ (2 mL). To the resultant stirring solution was added dropwise methyl trifluoromethanesulfonate (49.5 mg, 1.2 equiv) at r.t. The solution was stirred at r.t. for 4 h, at which time TLC analysis indicated complete consumption of **4a**. The reaction mixture was concentrated to remove CH₂Cl₂ and the residue was washed with MTBE and hexanes, and dried under vacuum to give product **6** as thick oil, which was used directly for the next step.

In a glovebox, obtained product **6a**, Ni(COD)₂ (6.9 mg, 0.025 mmol), IMes·HCl (8.5 mg, 0.025 mmol), arylboronic acid **7** (83.3 mg, 0.50 mmol, 2 equiv), CsF (116.5 mg, 0.75 mmol, 3 equiv) and dioxane (2.0 mL) were combined in a 20-mL Schlenk tube equipped with a magnetic stir bar. The Schlenk tube was taken out of the glovebox and was heated to 80 °C and stirred for 12 h. Upon cooling to r.t., the mixture was filtered through a plug of silica, washing with ethyl acetate. The solvent was removed in vacuo and the residue was purified by silica gel chromatography (hexanes/EtOAc = 10/1) to afford the desired products **8** (53.5 mg, 65% yield). ¹H NMR (500 MHz, CDCl₃): δ = 0.60 (s, 6H), 2.64 (s, 3H), 7.35-7.37 (m, 3H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.51-7.56 (m, 4H), 7.61 (d, *J* = 7.5 Hz, 1H), 7.73-7.76 (m, 2H), 7.92 (d, *J* = 8.0 Hz, 1H), 8.13 (s, 1H) ppm. ¹³C NMR (126 MHz, CDCl₃): δ = -2.2, 26.9, 127.2, 127.3,

128.0, 128.2, 128.5, 129.2, 129.4, 132.0, 133.0, 133.9, 134.3, 137.8, 138.1, 139.4, 139.8, 142.2, 198.2 ppm. HRMS (ESI⁺): calcd for C₂₂H₂₂NaOSi⁺ [M+Na]⁺ 353.1332, found 353.1331.

8.2 Kumada-type cross-coupling starting from product **4a** with aryl Grignard reagents **9**

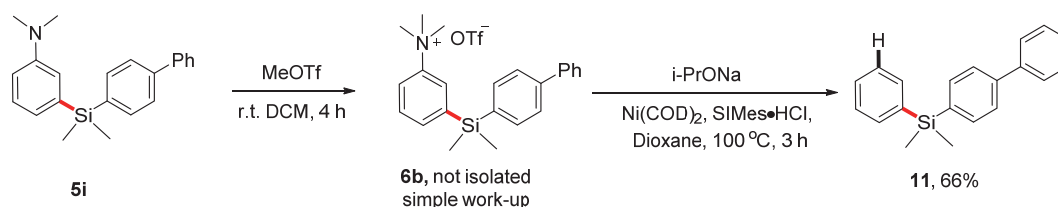


(4'-Methoxybiphenyl-3-yl)dimethyl(phenyl)silane 10 According to the literature procedures,⁷ to a dry 20-mL Schlenk tube equipped with a magnetic stir bar was charged product **4a** (63.8 mg, 0.25 mmol) and CH₂Cl₂ (2 mL). To the resultant stirring solution was added dropwise methyl trifluoromethanesulfonate (49.5 mg, 1.2 equiv) at r.t. The solution was stirred at r.t. for 4 h, at which time TLC analysis indicated complete consumption of **4a**. The reaction mixture was concentrated to remove CH₂Cl₂ and the residue was washed with MTBE and hexanes, and dried under vacuum to give product **8** as thick oil, which was used directly for the next step.

In a glovebox, to a dry 20-mL Schlenk tube equipped with a magnetic stir bar was charged obtained product **6a**, PdCl₂(PPh₃)₂ (3.5 mg, 0.005 mmol) and THF (1.5 mL), and the resultant slurry was stirred for 5 minutes. Then 4-methoxyphenylmagnesium bromide (0.5M solution in THF, 0.55 mL, 0.275 mmol, 1.1 equiv) was added dropwise at r.t. The solution was stirred at r.t. for 4 h. The reaction mixture was quenched by the addition of water (5 mL) and 2N HCl (1 mL), and extracted with MTBE. The organic extract was dried (MgSO₄), filtered, and concentrated, and the crude product was purified by silica gel chromatography (hexanes/CH₂Cl₂ = 2/1) to afford the desired products **10** (55.6 mg, 70% yield). ¹H NMR (500 MHz, CDCl₃): δ = 0.58 (s, 6H), 3.82 (s, 3H), 6.96 (d, *J* = 9.0 Hz, 2H), 7.34-7.36 (m, 3H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.46 (d, *J* = 7.5 Hz, 1H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.53-7.56 (m, 3H),

7.69 (s, 1H) ppm. ^{13}C NMR (126 MHz, CDCl_3): δ = -2.2, 55.5, 114.3, 127.8, 128.0, 128.3, 128.4, 129.3, 132.66, 132.73, 134.2, 134.3, 138.3, 138.8, 140.3, 159.3 ppm. HRMS (EI^+): calcd for $\text{C}_{21}\text{H}_{22}\text{OSi}^+$ $[\text{M}]^+$ 318.1434, found 318.1435.

8.3 Removal of dialkyl amino group in product **5i**

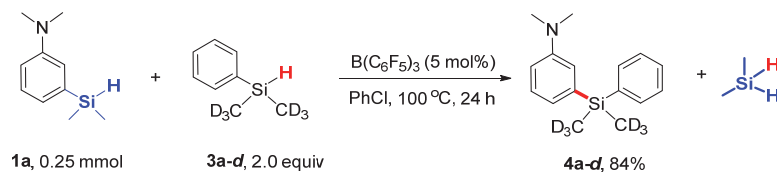


Biphenyl-4-yltrimethylsilane 11 According to the literature procedures,^{7,9} to a dry 20-mL Schlenk tube equipped with a magnetic stir bar was charged product **5i** (167 mg, 0.50 mmol) and CH_2Cl_2 (4 mL). To the resultant stirring solution was added dropwise methyl trifluoromethanesulfonate (100 mg, 1.2 equiv) at r.t. The solution was stirred at r.t. for 4 h, at which time TLC analysis indicated complete consumption of **5i**. The reaction mixture was concentrated to remove CH_2Cl_2 and the residue was washed with MTBE and hexanes, and dried under vacuum to give product **6b** as thick oil, which was used directly for the next step.

In a glovebox, a dry 20-mL Schlenk tube equipped with a magnetic stir bar was charged with obtained product **11**, $\text{Ni}(\text{COD})_2$ (13.8 mg, 0.05 mmol, 10 mol%), $\text{SiMes}\cdot\text{HCl}$ (18.4 mg, 0.05 mmol, 10 mol%), *i*-PrONa (125 mg, 1.5 mmol, 3 equiv) and dioxane (2 mL). The Schlenk tube was taken out of the glovebox and was heated to 100 °C and stirred for 3 h. The solvent was removed in vacuo and the residue was purified by silica gel chromatography (hexanes) to afford the desired products **11** (95.2 mg, 66% yield). ^1H NMR (500 MHz, CDCl_3): δ = 0.58 (s, 6H), 7.31-7.36 (m, 4H), 7.42 (t, J = 7.5 Hz, 2H), 7.54-7.59 (m, 8H) ppm. ^{13}C NMR (126 MHz, CDCl_3): δ = -2.2, 126.7, 127.3, 127.5, 128.0, 128.9, 129.3, 134.3, 134.8, 137.1, 138.3, 141.2, 142.0 ppm. Spectroscopic data for **11** match those previously reported in the literature.¹⁰

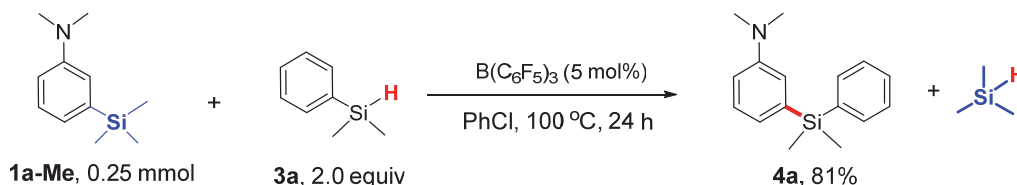
9. Control Experiments for Mechanism Study

9.1 Reaction of hydrosilane **1a** with Ph(CD₃)₂SiH (**3a-d**)



In a glovebox, hydrosilane **1a** (45 mg, 0.25 mmol) was added to a solution of B(C₆F₅)₃ (6.4 mg, 5.0 mol%) in chlorobenzene (0.5 mL) in a 20-mL Schlenk tube with a magnetic stir bar. Ph(CD₃)₂SiH (**3a-d**) (71 mg, 0.5 mmol), which was prepared from reaction of phenyldichlorosilane with methyl-D₃-magnesium iodide solution,¹¹ was then added. The Schlenk tube was taken out of the glovebox and the reaction mixture was stirred at 100 °C (oil bath) for 24 h. After completion of the reaction, the mixture was cooled to room temperature. The mixture was diluted with 10 mL of CH₂Cl₂ and analyzed by TLC. The combined organic phases were concentrated and the resulting residue was purified by column chromatography on silica gel to provide the product **4a-d** in 84% yield (54.8 mg). ¹H NMR (500 MHz, CDCl₃): δ = 2.91 (s, 6H), 6.75-6.77 (m, 1H), 6.88-6.89 (m, 2H), 7.21-7.25 (m, 1H), 7.33-7.34 (m, 3H), 7.53-7.54 (m, 2H) ppm. ¹³C NMR (126 MHz, CDCl₃): δ = 40.7, 113.7, 118.4, 122.8, 127.9, 128.7, 129.1, 134.4, 138.7, 138.8, 150.1 ppm. HRMS (ESI⁺): calcd for C₁₆H₁₆D₆NSi⁺ [M+H]⁺ 262.1893, found 262.1895.

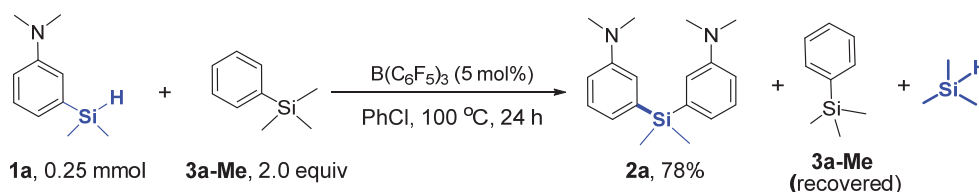
9.2 Reaction of (*m*-Me₂NC₆H₄)Me₃Si (**1a-Me**) with PhMe₂SiH **3a**



In a glovebox, hydrosilane **1a-Me** (48.3 mg, 0.25 mmol) was added to a solution of B(C₆F₅)₃ (6.4 mg, 5.0 mol%) in chlorobenzene (0.5 mL) in a 20-mL Schlenk tube with a magnetic stir bar. Hydrosilane **3a** (68 mg, 0.5 mmol) was then added. The Schlenk tube was taken out of the glovebox and the reaction mixture was stirred at

100 °C (oil bath) for 24 h. After completion of the reaction, the mixture was cooled to room temperature. The mixture was diluted with 10 mL of CH₂Cl₂ and analyzed by TLC. The combined organic phases were concentrated and the resulting residue was purified by column chromatography on silica gel to provide the product **4a** in 81% yield (51.5 mg).

9.3 Reaction of hydrosilane **1a** with PhMe₃Si (**3a-Me**)



In a glovebox, hydrosilane **1a** (45 mg, 0.25 mmol) was added to a solution of B(C₆F₅)₃ (6.4 mg, 5.0 mol%) in chlorobenzene (0.5 mL) in a 20-mL Schlenk tube with a magnetic stir bar. PhMe₃Si (**3a-Me**) (75 mg, 0.5 mmol) was then added. The Schlenk tube was taken out of the glovebox and the reaction mixture was stirred at 100 °C (oil bath) for 24 h. After completion of the reaction, the mixture was cooled to room temperature. The mixture was diluted with 10 mL of CH₂Cl₂ and analyzed by TLC. The combined organic phases were concentrated and the resulting residue was purified by column chromatography on silica gel to provide the product **2a** in 78% yield (29.1 mg).

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11. Copies of ^1H and ^{13}C NMR spectra

