Supplementary Material (ESI) for Chemical Communications

Aminosilylation of arynes with aminosilanes: synthesis of 2-silylaniline derivatives

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Supplementary Information

General Remarks. All manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under a purified argon atmosphere. Nuclear magnetic resonance spectra were taken on a JEOL EX-270 (^{1}H, 270 MHz; ^{13}C, 67.8 MHz) spectrometer or a JEOL Lambda-400 (^{1}H, 400 MHz; ^{13}C, 99.5 MHz; ^{29}Si, 78.5 MHz) spectrometer using residual chloroform (^{1}H) or $CDCl_3$ (^{13}C) as an internal standard and tetramethylsilane (^{29}Si) as an external standard. The preparative recycling gel permeation chromatography was performed with GL Science PU 614 equipped with Shodex GPC H-2001L and -2002L columns (benzene or chloroform as an eluent). Unless otherwise noted, commercially available reagents were used without purification. 18-Crown-6 was recrystallized from distilled MeCN. KF (spray-dried) was vacuum dried at 100 °C for 12 h. THF was distilled from sodium/benzophenone ketyl. MeCN was distilled from phosphorus pentoxide.

Aryne Precursors. 2-(Trimethylsilyl)phenyl triflate (**1a**), [1] 4,5-dimethyl-2-(trimethylsilyl)phenyl triflate (**1b**), [2] 3-(trimethylsilyl)-2-naphthyl triflate (**1c**), [3] 6-(trimethylsilyl)-5-indanyl triflate (**1d**),[2] 3-(trimethylsilyl)-5,6,7,8-tetrahydro-2-naphthyl triflate (**1e**),[3] 3,6-dimethoxy-2-(trimethylsilyl)phenyl triflate (**1f**),[2] 3-methoxy-2-(trimethylsilyl)phenyl triflate (**1g**), [4] 6-methyl-2-(trimethylsilyl)phenyl triflate (**1h**), [5] 1-(trimethylsilyl)-2-naphthyl triflate (**1i**),[6] 4-methyl-2-(trimethylsilyl)phenyl triflate (**1j**),[7] and 4-fluoro-2-(trimethylsilyl)phenyl triflate (**1k**)[3] were prepared according to literature procedures.

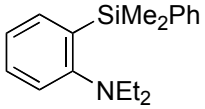
Aminosilanes. All aminosilanes were prepared from corresponding amines and chlorosilanes according to procedure A or B as follows.

Procedure A (for **2a**–**2j** and **2l**–**2n**): To a CH_2Cl_2 (15 mL) solution of an amine (0.014 mol) and triethylamine (0.024 mol) was added a chlorosilane (0.012 mol) at 0 °C, and the resulting mixture was stirred at r.t. overnight. After the solvent was distilled away (15 mmHg), dry n-hexane (20 mL) was added to the residue, and the insoluble materials were filtered through a

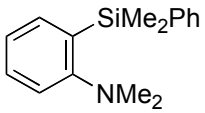
Celite plug. Concentration of the solution gave an aminosilane, which can be used for the aminosilylation without further purification.

Procedure B (for **2k**): To a THF solution (6 mL) of 1,2,3,4-tetrahydroisoquinoline (0.79 g, 6.0 mmol) was added *n*-BuLi (1.54 M solution in *n*-hexane, 3.9 mL, 6.0 mmol) at 0 °C, and the mixture was stirred at 0 °C for 0.5 h. To this mixture was added chlorodimethylphenylsilane (1.0 g, 6.0 mmol), and the resulting mixture was stirred at r.t. overnight before the removal of the solvent in vacuo. The residue was treated with dry *n*-hexane (20 mL), and the insoluble materials were filtered through a Celite pad. Evaporation of the solvent gave **2k** of sufficient purity.

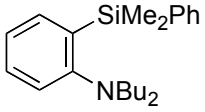
Aminosilylation of arynes. ***A general procedure.*** To a THF solution (1.0 mL) of an aryne precursor (0.30 mmol), an aminosilane (0.20 □mol) and 18-crown-6 (0.159 g, 0.60 mmol) was added KF (0.035 g, 0.60 mmol), and the resulting mixture was stirred at 0 °C. After the time specified in Table 1, Scheme 1 or Scheme 2, the mixture was diluted with ethyl acetate, filtered through a Celite plug, and washed twice with brine. Evaporation of the solvent followed by gel permeation chromatography (benzene or chloroform as an eluent) gave the corresponding product.



***N,N*-Diethyl-2-(dimethylphenylsilyl)aniline (3aa).** Isolated in 65% yield as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.59 (s, 6 H), 0.83 (t, *J* = 6.93 Hz, 6 H), 2.79 (q, *J* = 6.93 Hz, 4 H), 7.12-7.18 (m, 2 H), 7.31-7.36 (m, 4 H), 7.44-7.54 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ -0.86, 11.68, 48.38, 123.58, 124.24, 127.46, 128.41, 129.96, 134.12, 136.68, 137.04, 140.43, 158.65; ^{29}Si NMR ($CDCl_3$) δ -9.86; Anal. Calcd for $C_{18}H_{25}NSi$: C, 76.26; H, 8.89; N, 4.94. Found: C, 76.26; H, 8.83; N, 5.24.

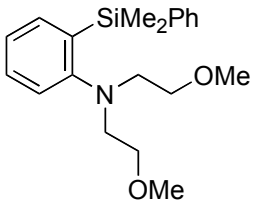


***N,N*-Dimethyl-2-(dimethylphenylsilyl)aniline (3ab).** Isolated in 54% yield as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.58 (s, 6 H), 2.41 (s, 6 H), 7.14 (td, *J* = 7.37, 0.97 Hz, 1 H), 7.24-7.25 (m, 1 H), 7.31-7.34 (m, 3 H), 7.36-7.43 (m, 2 H), 7.52-7.55 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ -1.63, 46.58, 121.78, 124.96, 127.40, 128.34, 130.64, 134.11, 136.06, 136.71, 140.20, 161.26; ^{29}Si NMR ($CDCl_3$) δ -10.97; Anal. Calcd for $C_{16}H_{21}NSi$: C, 75.23; H, 8.29; N, 5.48. Found: C, 75.12; H, 8.18; N, 5.78.

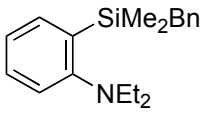


***N,N*-Dibutyl-2-(dimethylphenylsilyl)aniline (3ac).** Isolated in 42% yield as a pale yellow oil: ^{1}H NMR ($CDCl_3$) δ 0.59 (s, 6 H), 0.78 (t, *J* = 7.26 Hz, 6 H), 1.04 (sext, *J* = 7.58 Hz, 4 H), 1.18-1.27 (m, 4 H), 2.67-2.72 (m, 4 H), 7.11-7.18 (m, 2 H), 7.29-7.35 (m, 4 H), 7.47-7.53 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ -0.82, 13.96, 20.70, 28.79, 55.31, 123.13, 123.81, 127.44, 128.41, 129.96, 134.03, 136.12,

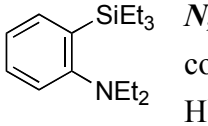
136.73, 140.45, 159.21; ^{29}Si NMR ($CDCl_3$) δ -9.80; Anal. Calcd for $C_{22}H_{33}NSi$: C, 77.81; H, 9.79; N, 4.12. Found: C, 77.67; H, 9.88; N, 4.21.



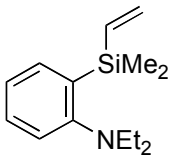
***N,N*-Bis(2-methoxyethyl)-2-(dimethylphenylsilyl)aniline (3ad).** Isolated in 33% yield as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.59 (s, 6 H), 3.00-3.05 (m, 4 H), 3.15-3.20 (m, 10 H), 7.15 (t, *J* = 7.25 Hz 1 H), 7.28-7.41 (m, 5 H), 7.47-7.52 (m, 3 H); ^{13}C NMR ($CDCl_3$) -0.86, 55.01, 58.45, 70.53, 123.88, 124.48, 127.61, 128.60, 130.26, 134.05, 136.11, 136.86, 140.25, 158.11; ^{29}Si NMR ($CDCl_3$) δ -9.59; Anal. Calcd for $C_{20}H_{29}NO_2Si$: C, 69.92; H, 8.51; N, 4.08. Found: C, 69.70; H, 8.45; N, 4.05.



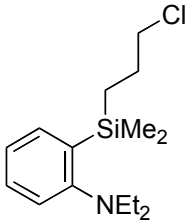
***N,N*-Diethyl-2-(benzyldimethylsilyl)aniline (3ae).** Isolated in 49% yield as a white solid: ^{1}H NMR ($CDCl_3$) δ 0.23 (s, 6 H), 1.04 (t, *J* = 6.93 Hz, 6 H), 2.43 (s, 2 H), 2.97 (q, *J* = 6.93 Hz, 4 H), 6.97-7.22 (m, 7 H), 7.34-7.48 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ -1.74, 12.04, 26.52, 48.70, 123.54, 123.82, 124.33, 127.99, 128.45, 129.81, 135.97, 137.36, 140.70, 158.53; ^{29}Si NMR ($CDCl_3$) δ -5.53; HRMS Calcd for $C_{19}H_{27}NSi$: M^+, 297.1913. Found: *m/z* 297.1900.



***N,N*-Diethyl-2-(triethylsilyl)aniline (3af).** Isolated in 43% yield as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.83-0.96 (m, 15 H), 1.01 (t, *J* = 6.93 Hz, 6 H), 2.94 (q, *J* = 6.93 Hz, 4 H), 7.07-7.18 (m, 2 H), 7.31 (td, *J* = 6.42, 1.65 Hz, 1 H), 7.45 (dd, *J* = 7.41, 1.65 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 4.01, 7.64, 11.83, 48.48, 123.34, 123.88, 129.29, 135.71, 136.77, 158.90; ^{29}Si NMR ($CDCl_3$) δ 1.85; Anal. Calcd for $C_{16}H_{29}NSi$: C, 72.93; H, 11.09; N, 5.32. Found: C, 72.95; H, 11.09; N, 5.21.

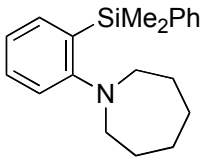


***N,N*-Diethyl-2-(dimethylvinylsilyl)aniline (3ag).** Isolated in 52% yield as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.39 (s, 6 H), 1.01 (t, *J* = 6.93 Hz, 6 H), 2.94 (q, *J* = 6.93 Hz, 4 H), 5.72 (dd, *J* = 20.30, 3.96 Hz, 1 H), 5.98 (dd, *J* = 14.69, 3.96 Hz, 1 H), 6.43 (dd, *J* = 20.30, 14.69 Hz, 1 H), 7.10-7.20 (m, 2 H), 7.35 (t, *J* = 7.26 Hz, 1 H), 7.52 (d, *J* = 7.59 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ -1.42, 11.95, 48.52, 123.34, 124.21, 129.76, 130.71, 136.12, 137.41, 140.38, 158.36; ^{29}Si NMR ($CDCl_3$) δ -13.13; HRMS Calcd for $C_{13}H_{20}NSi$: M^+-Me, 218.1365. Found: *m/z* 218.1368.

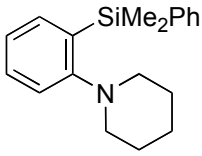


***N,N*-Diethyl-2-[(3-chloropropyl)dimethylsilyl]aniline (3ah).** Isolated in 40% yield as a yellow oil: ^{1}H NMR ($CDCl_3$) 0.31 (s, 6 H), 0.89-0.96 (m, 2 H), 1.01 (t, *J* = 6.93 Hz, 6 H), 1.69-1.81 (m, 2 H), 2.93 (q, *J* = 6.93 Hz, 4 H), 3.50 (t, *J* = 6.93 Hz, 2 H), 7.13-7.20 (m, 2 H), 7.34 (t, *J* = 7.26 Hz, 1 H), 7.46 (d, *J* = 6.60 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ -1.35, 11.99, 14.16, 28.00,

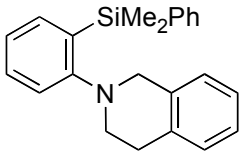
48.18, 48.61, 123.49, 124.35, 129.79, 135.87, 137.14, 158.58; ^{29}Si NMR ($CDCl_3$) δ -4.45; Anal. Calcd for $C_{15}H_{26}ClNSi$: C, 63.46; H, 9.23; N, 4.93. Found: C, 63.32; H, 9.28; N, 5.01.



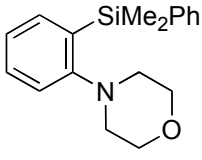
***N*-[2-(Dimethylphenylsilyl)phenyl]hexamethyleneimine (3ai).** Isolated in 51% yield as a white solid: ^{1}H NMR ($CDCl_3$) δ 0.60 (s, 6 H), 1.41-1.52 (m, 4 H), 1.55-1.62 (m, 4 H), 2.83 (t, *J* = 5.61 Hz, 4 H), 7.14 (t, *J* = 7.25 Hz, 1 H), 7.25 (d, *J* = 7.59 Hz, 1 H), 7.31-7.43 (m, 5 H), 7.49-7.53 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ -1.15, 26.85, 28.00, 59.09, 123.74, 124.53, 127.48, 128.34, 130.80, 133.91, 135.47, 136.26, 140.45, 163.52; ^{29}Si NMR ($CDCl_3$) δ -9.94; Anal. Calcd for $C_{20}H_{27}NSi$: C, 77.61; H, 8.79; N, 4.53. Found: C, 77.38; H, 8.71; N, 4.55.



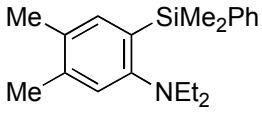
***N*-[2-(Dimethylphenylsilyl)phenyl]piperidine (3aj).** Isolated in 49% yield as a white solid: ^{1}H NMR ($CDCl_3$) δ 0.61 (s, 6 H), 1.40-1.59 (m, 6 H), 2.58-2.65 (m, 4 H), 7.17-7.21 (m, 1 H), 7.32-7.44 (m, 6 H), 7.54-7.57 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ -1.56, 24.03, 25.84, 55.26, 122.68, 125.09, 127.39, 128.34, 130.55, 133.96, 136.26, 136.80,140.32, 161.28; ^{29}Si NMR ($CDCl_3$) δ -10.33; Anal. Calcd for $C_{19}H_{25}NSi$: C, 77.23; H, 8.53; N, 4.74. Found: C, 77.14; H, 8.56; N, 4.71.



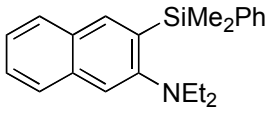
***N*-[2-(Dimethylphenylsilyl)phenyl]-1,2,3,4,-tetrahydroisoquinoline (3ak).** Isolated in 40% yield as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 0.52 (s ,6 H), 2.77 (t, *J* = 5.60 Hz, 2 H), 3.04 (t, *J* = 5.60 Hz, 2 H), 3.74 (s, 2 H), 6.78 (d, *J* = 7.59 Hz, 1 H), 7.09-7.32 (m, 8 H), 7.40-7.52 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ -1.54, 29.29, 50.98, 57.65, 122.59, 125.28, 125.48, 125.89, 126.36, 127.39, 128.34, 128.59, 130.84, 133.93, 134.14, 135.31, 136.17, 137.22, 139.89, 159.98; ^{29}Si NMR ($CDCl_3$) δ -10.48; HRMS Calcd for $C_{23}H_{25}NSi$: M^+, 343.1756. Found: *m/z* 343.1753.



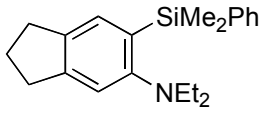
***N*-[2-(Dimethylphenylsilyl)phenyl]morpholine (3al).** Isolated in 31% yield as a white solid: ^{1}H NMR ($CDCl_3$) δ 0.57 (s, 6 H), 2.62 (t, *J* = 4.62 Hz, 4 H), 3.54 (t, *J* = 4.62 Hz, 4 H), 7.22 (td, *J* = 7.26, 0.99 Hz, 1 H), 7.29-7.32 (m, 4 H) 7.39-7.52 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ -1.43, 54.04, 66.88, 122.86, 125.71, 127.48, 128.52, 130.84, 133.85, 136.30, 137.02, 140.13, 159.35; ^{29}Si NMR ($CDCl_3$) δ -10.43; Anal. Calcd for $C_{18}H_{23}NOSi$: C, 72.68; H, 7.79; N, 4.71. Found: C, 72.51; H, 7.74; N, 4.75.



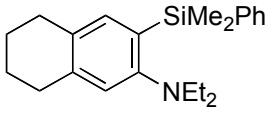
***N,N*-Diethyl-4,5-dimethyl-2-(dimethylphenylsilyl)aniline (3ba).** Isolated in 64% yield as a white solid: ^{1}H NMR ($CDCl_3$) δ 0.57 (s, 6 H), 0.80 (t, *J* = 7.26 Hz, 6 H), 2.22 (s, 3 H), 2.24 (s, 3 H), 2.73 (q, *J* = 7.26 Hz, 4 H), 6.93 (s, 1 H), 7.20 (s, 1 H), 7.28-7.31 (m, 3 H), 7.50-7.54 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ -0.84, 11.82, 19.34, 20.02, 48.40, 124.73, 124.77, 127.36, 128.28, 132.32, 133.74, 134.10, 137.58, 138.50, 140.64, 156.59; ^{29}Si NMR ($CDCl_3$) δ -10.58; Anal. Calcd for $C_{20}H_{29}NSi$: C, 77.11; H, 9.38; N, 4.50. Found: C, 76.81; H, 9.27; N, 4.37.



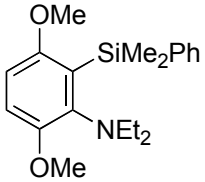
2-Diethylamino-3-(dimethylphenylsilyl)naphthalene (3ca). Isolated in 45% yield as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 0.67 (s, 6 H), 0.85 (t, *J* = 7.26 Hz, 6 H), 2.88 (q, *J* = 7.26 Hz, 4 H), 7.31-7.57 (m, 8 H), 7.71-7.79 (m, 2 H), 8.00 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ -0.70, 11.29, 48.09, 120.52, 124.69, 126.36, 126.81, 127.49, 127.91, 128.50, 130.69, 134.12, 134.68, 137.27, 137.93, 140.23, 155.11; ^{29}Si NMR ($CDCl_3$) δ -9.41; HRMS Calcd for $C_{22}H_{27}NSi$: M^+, 333.1913. Found: *m/z* 333.1920.



5-Diethylamino-6-(dimethylphenylsilyl)indan (3da). Isolated in 38% yield as a white solid: ^{1}H NMR ($CDCl_3$) δ 0.58 (s, 6 H), 0.83 (t, *J* = 7.26 Hz, 6 H), 2.08 (quint, *J* = 7.26 Hz, 2 H), 2.75 (q, *J* = 7.26 Hz, 4 H), 2.87 (t, *J* = 7.26 Hz, 2 H), 2.90 (t, *J* = 7.26 Hz, 2 H), 7.02 (s, 1 H), 7.30-7.33 (m, 4 H), 7.53-7.57 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ -0.70, 11.75, 25.52, 32.35, 33.03, 48.48, 119.71, 127.39, 128.25, 132.00, 134.14, 134.32, 140.18, 140.86, 146.65, 157.36; ^{29}Si NMR ($CDCl_3$) δ -10.37; Anal. Calcd for $C_{21}H_{29}NSi$: C, 77.96; H, 9.03; N, 4.33. Found: C, 77.70; H, 9.07; N, 4.39.

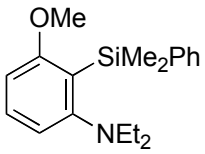


2-Diethylamino-3-(dimethylphenylsilyl)-5,6,7,8-tetrahydronaphthalene (3ea). Isolated in 33% yield as a white solid: ^{1}H NMR ($CDCl_3$) δ 0.56 (s, 6 H), 0.81 (t, *J* = 6.93 Hz, 6 H), 1.78 (m, 4 H), 2.68-2.76 (m, 8 H), 6.84 (s, 1 H), 7.14 (s, 1 H), 7.29-7.31 (m, 3 H), 7.51-7.55 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ -0.82, 11.74, 23.13, 23.42, 28.99, 29.54, 48.27, 124.01, 127.35, 128.27, 132.90, 133.66, 134.12, 137.32, 139.03, 140.67, 156.05; ^{29}Si NMR ($CDCl_3$) δ -10.57; HRMS Calcd for $C_{22}H_{31}NSi$: M^+, 337.2226. Found: *m/z* 337.2234.

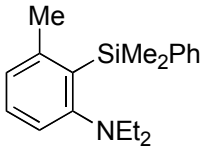


***N,N*-Diethyl-3,6-dimethoxy-2-(dimethylphenylsilyl)aniline (3fa).** Isolated in 46% yield as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 0.59 (s, 6 H), 0.88 (t, *J* = 7.26 Hz, 6 H), 2.90-3.10 (m, 4 H), 3.47 (s, 3 H), 3.75 (s, 3 H), 6.63 (d, *J* = 8.58 Hz, 1 H), 6.82 (d, *J* = 8.58 Hz, 1 H), 7.27-7.29 (m, 3 H), 7.48-7.52 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 1.55, 13.19, 47.76, 55.33, 108.07,

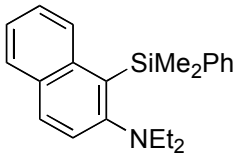
113.10, 127.06, 127.64, 129.02, 133.48, 142.50, 144.53, 154.52, 158.71; ^{29}Si NMR ($CDCl_3$) δ -10.44; HRMS Calcd for $C_{20}H_{29}NO_2Si$: M^+, 343.1968. Found: *m/z* 343.1974.



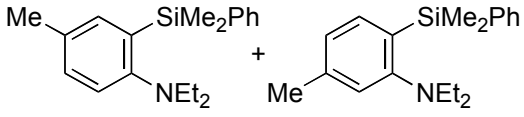
***N,N*-Diethyl-3-methoxy-2-(dimethylphenylsilyl)aniline (3ga).** Isolated in 57% yield as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.59 (s, 6 H), 0.89 (t, *J* = 7.26 Hz, 6 H), 2.93 (q, *J* = 7.26 Hz, 4 H), 3.57 (s, 3 H), 6.58 (d, *J* = 8.25 Hz, 1 H), 6.77 (d, *J* = 7.92 Hz, 1 H), 7.25-7.28 (m, 4 H), 7.50-7.52 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ1.10, 11,27, 48.30, 54.90, 105.84, 115.85, 122.97, 127.13, 127.82, 130.57, 133.55, 142.17, 159.07, 165.82; ^{29}Si NMR ($CDCl_3$) δ -10.60; HRMS Calcd for $C_{19}H_{27}NOSi$: M^+, 313.1862. Found: *m/z* 313.1869.



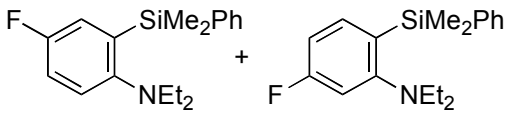
***N,N*-Diethyl-3-methyl-2-(dimethylphenylsilyl)aniline (3ha).** Isolated in 45% yield as a yellow oil: ^{1}H NMR ($CDCl_3$) δ0.62 (s, 6 H), 0.91 (t, *J* = 7.26 Hz, 6 H), 2.18 (s, 3 H), 2.92 (q, *J* = 7.26 Hz, 4 H), 6.91 (d, *J* = 7.26 Hz, 1 H), 7.03 (d, *J* = 7.92 Hz, 1 H), 7.25-7.30 (m, 4 H), 7.43-7.47 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 2.75, 11.38, 24.40, 48.77, 120.94, 126.81, 127.60, 128.09, 129.40, 133.39, 134.61, 142.53, 146.11, 158.47; ^{29}Si NMR ($CDCl_3$) δ -10.15; Anal. Calcd for $C_{19}H_{27}NSi$: C, 76.70; H, 9.15; N, 4.71. Found: C, 76.45; H, 9.04; N, 4.92.



2-Diethylamino-1-(dimethylphenylsilyl)naphthalene (3ia). Isolated in 52% yield as a yellow oil: ^{1}H NMR ($CDCl_3$) δ 0.73 (s, 6 H), 0.96 (t, *J* = 7.26 Hz, 6 H), 3.08 (q, *J* = 7.26 Hz, 4 H), 7.18-7.35 (m, 5 H), 7.43 (d, *J* = 8.58 Hz, 1 H), 7.48-7.52 (m, 2 H), 7.79 (d, *J* = 7.92 Hz, 1 H), 7.85-7.91 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 2.99, 11.86, 49.26, 122.44, 123.97, 124.92, 127.67, 128.27, 128.36, 129.13, 130.35, 130.89, 131.27, 133.80, 138.56, 142.10, 156.84; ^{29}Si NMR ($CDCl_3$) δ -9.48; HRMS Calcd for $C_{22}H_{27}NSi$: M^+, 333.1913. Found: *m/z* 333.1926.

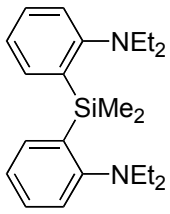


A mixture of *N,N*-diethyl-4-methyl-2-(dimethylphenylsilyl)aniline (3ja) and *N,N*-diethyl-5-methyl-2-(dimethylphenylsilyl)aniline (3'ja). Isolated in 72% yield as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.57 (m, 12 H), 0.77-0.84 (m, 12 H), 2.31-2.32 (m, 6 H), 2.68-2.80 (m, 8 H), 6.94 (d, *J* = 8.58 Hz, 2 H), 7.06 (d, *J* = 7.92 Hz, 1 H), 7.16 (d, *J* = 7.92 Hz , 1 H), 7.30-7.34 (m, 8 H), 7.50-7.53 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ -0.84, 11.72, 11.75, 21.04, 21.40, 48.30, 48.43, 123.38, 124.26, 125.14, 127.40, 128.34, 130.75, 133.24, 133.46, 134.11, 136.59, 136.82, 137.05, 139.95, 140.47, 140.61, 156.10, 158.78; ^{29}Si NMR ($CDCl_3$) δ -10.24, -10.18; Anal. Calcd for $C_{19}H_{27}NSi$: C, 76.70; H, 9.15; N, 4.71. Found: C, 76.43; H, 9.20; N, 4.71.

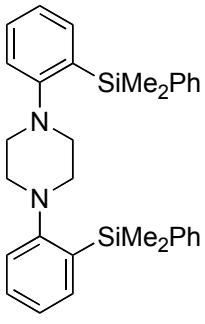


A mixture of *N,N*-diethyl-4-fluoro-2-(dimethylphenylsilyl)aniline (3ka) and *N,N*-diethyl-5-fluoro-2-(dimethylphenylsilyl)aniline (3'ka). Isolated in 68% yield as a colorless oil: ^{1}H NMR ($CDCl_3$) δ 0.57-0.59 (m, 6 H), 0.77-0.85 (m, 6 H), 2.67-2.80 (m, 4 H), 6.79-6.87 (m, 1 H), 6.97-7.14 (m, 2 H), 7.27-7.41 (m, 3 H), 7.47-7.53 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ -1.14, -0.94, 11.52, 11.67, 48.31, 48.67, 110.54 (d, J_{C-F}= 18.9 Hz), 111.20 (d, J_{C-F} = 19.7 Hz), 116.54 (d, J_{C-F} = 22.2 Hz), 122.25 (d, J_{C-F} = 19.7 Hz), 124.96 (d, J_{C-F} = 7.38 Hz), 127.55, 128.56, 128.66, 131,99, 134,02, 134.08, 137.96 (d, J_{C-F} = 9.02 Hz), 139.47, 140.01, 140.17 (d, J_{C-F} = 3.28 Hz), 154.23 (d, J_{C-F} = 3.28 Hz), 159.70 (d, J_{C-F} = 245 Hz), 160.77 (d, J_{C-F} = 6.56 Hz), 164.53 (d, J_{C-F} = 249 Hz); ^{29}Si NMR ($CDCl_3$) δ -9.83, -9.74 (d, J_{Si-F} = 1.92 Hz); Anal. Calcd for $C_{18}H_{24}FNSi$: C, 71.71; H, 8.02; N, 6.30. Found: C, 71.49; H, 7.90; N, 6.28.

Aminosilylation using 2m or 2n. To a THF solution (2.0 mL) of **1a** (0.179 g, 0.60 mmol), an aminosilane (0.20 □mol) and 18-crown-6 (0.322 g, 1.2 mmol) was added KF (0.070 g, 1.2 mmol), and the resulting mixture was stirred at 0 °C. After the time specified in Scheme 4, the mixture was diluted with ethyl acetate, filtered through a Celite plug, and washed twice with brine. Evaporation of the solvent followed by gel permeation chromatography (eluent: benzene for **3am**, chloroform for **3an**) gave the corresponding product.



Bis[2-(diethylamino)phenyl]dimethylsilane (3am). Isolated in 35% yield as a white solid: ^{1}H NMR ($CDCl_3$) δ 0.61 (s, 6 H), 0.81 (t, J = 7.26 Hz, 12 H), 2.79 (q, J = 7.26 Hz, 8 H), 7.06-7.12 (m, 3 H), 7.25-7.33 (m, 3 H), 7.53-7.56 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 0.65, 11.43, 47.84, 123.27, 123.65, 129.24, 136.82, 138.19, 157.95; ^{29}Si NMR ($CDCl_3$) δ -11.05; HRMS Calcd for $C_{22}H_{34}N_2Si$: M^+, 354.2491. Found: *m/z* 354.2502.



***N,N'*-Bis[2-(dimethylphenylsilyl)phenyl]piperazine (3an).** Isolated in 25% yield as a white solid: ^{1}H NMR ($CDCl_3$) δ 0.57 (s, 12 H), 2.50 (m, 8 H), 7.19 (t, J = 7.26 Hz, 2 H), 7.22-7.31 (m, 8 H), 7.41-7.46 (m, 4 H), 7.51-7.54 (m, 4 H); ^{13}C NMR ($CDCl_3$) δ -1.35, 53.73, 122.79, 125.43, 127.44, 128.46, 130.66, 133.93, 136.28, 136.91, 140.27, 160.11; ^{29}Si NMR ($CDCl_3$) δ -10.42; Anal. Calcd for $C_{32}H_{38}N_2Si_2$: C, 75.83; H, 7.56; N, 5.53. Found: C, 76.05; H, 7.46; N, 5.67.

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