Supporting Information
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Titanium-Catalyzed Hydroaminoalkylation of Vinylsilanes and a One-Pot Procedure for the Synthesis of 1,4-Benzooazasilines

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SUPPORTING INFORMATION
General Remarks

Unless otherwise noted, all reactions were performed under an inert atmosphere of nitrogen in oven-dried Schlenk tubes (Duran glassware, 100 mL, ø = 30 mm) equipped with Teflon® stopcocks and magnetic stirring bars (12 × 2.5 mm). Toluene was purified by distillation from sodium wire and degassed. Catalyst III,[1] catalyst II,[2] and the N-methylanilines[3] were synthesized according to literature procedures. Prior to use, all substrates were distilled or recrystallized and degassed. Catalysts III and II, the vinylsilanes, the N-methylanilines, and toluene were stored in a nitrogen-filled glove box (M. Braun, Unilab). All other chemicals were purchased from commercial sources and were used without further purification. For flash chromatography, silica gel from GRACE Davison (particle size 0.037-0.063 mm) was used. Light petroleum ether (b.p. 40-60 °C, PE), tert-butyl methyl ether (MTBE), CH₂Cl₂ and EtOAc used for flash chromatography were distilled prior to use. For thin layer chromatography, silica gel on TLC aluminum foils with fluorescent indicator 254 nm from Fluka were used. The substances were detected with UV light or iodine. All products that have already been reported in the literature were identified by comparison of the obtained ¹H NMR and ¹³C NMR spectra with those reported in the literature. New compounds were additionally characterized by infrared (IR) spectroscopy, GC-MS, high resolution mass spectrometry (HRMS), ²⁹Si NMR and ¹⁹F NMR spectroscopy. NMR spectra were recorded on the following spectrometers: Bruker Fourier 300, Bruker Avance DRX 500 or Bruker Avance III, 500 MHz. All ¹H NMR spectra are reported in δ units (ppm) relative to the signal of CDCl₃ at 7.26 ppm. J values are given in Hz. All ¹³C NMR spectra are reported in δ units (ppm) relative to the central line of the triplet for CDCl₃ at 77.0 ppm. ²⁹Si NMR spectra are reported in δ units (ppm) relative to the external standard Me₂SiHCl (δ = 11.1 ppm) in relation to SiMe₄ (δ = 0.0 ppm). ¹⁹F NMR spectra are reported in δ units (ppm) relative to trichlorofluoromethane (δ = 0.0 ppm). Infrared spectra were recorded on a Bruker Vector 22 spectrometer or a Bruker Tensor 27 spectrometer (ATR). GC-MS analyses were performed on a Thermo Finnigan Focus gas chromatograph equipped with a DSQ mass detector and Agilent DB-5 column (length: 30 m, inner diameter: 0.32 mm, film thickness: 0.25 μm, (94%-Methyl)-(5%-phenyl)-(1%-vinyl)polysiloxan). GC analyses were performed on a Shimadzu GC-2010 gas chromatograph equipped with a flame ionization detector. High resolution mass spectra (HRMS) and mass spectra (MS) were recorded on a Waters Q-TOF Premier spectrometer in EI or ESI mode (ESI⁺, TOF).

Dimethylphenylvinylsilane (1)[4]

![Dimethylphenylvinylsilane](image)

Under an atmosphere of argon, an oven-dried Schlenk flask equipped with a reflux condenser and a dropping funnel was charged with magnesium turnings (3.16 g, 130.04 mmol) and dry THF (10 mL). After the addition of some drops of a solution of bromobenzene (20.42 g, 130.06 mmol) in THF (70 mL), the reaction mixture was gently heated with a heat gun until the reaction started. Then the remaining solution of bromobenzene was added slowly and afterwards, the reaction mixture was refluxed for 1 h. After cooling the mixture to 25 °C, chlorodimethylvinylsilane (12.06 g, 99.96 mmol) in THF (10 mL) was added dropwise and the resulting mixture was refluxed again for further 16 h. The
reaction was hydrolyzed with ice water (100 mL), the layers were separated and the aqueous layer was extracted with Et₂O (90 mL). Afterwards, the combined organic layers were dried with MgSO₄ and the solvent was evaporated under reduced pressure. The product 1 (13.61 g, 83.85 mmol, 84 %) was obtained from the residue by vacuum distillation (26 mbar, b.p. 62 ºC). ¹H NMR (500 MHz, CDCl₃): δ = 7.56-7.50 (m, 2 H), 7.39-7.34 (m, 3 H), 6.30 (dd, J = 20.3, 14.6 Hz, 1 H), 6.06 (dd, J = 14.6, 3.7 Hz, 1 H), 5.76 (dd, J = 20.3, 3.7 Hz, 1 H), 0.36 (s, 6 H) ppm. ¹³C(¹H) NMR (125 MHz, DEPT, CDCl₃): δ = 138.4 (C), 138.0 (CH), 133.8 (CH₂), 132.8 (CH), 129.0 (CH), 127.8 (CH), −3.0 (CH₃) ppm.

**General Procedure A for the hydroaminoalkylation of vinylsilanes with N-methylanilines:** An oven-dried Schlenk tube equipped with a Teflon stopcock and a magnetic stirring bar was transferred into a nitrogen-filled glovebox and charged with catalyst III (154 mg, 0.20 mmol, 10 mol%) and toluene (0.5 mL). Afterwards, the N-methylaniline (2.00 mmol), the vinylsilane (2.20 mmol) and toluene (0.5 mL) were added and the mixture was heated to 160 ºC for 24 h. After the reaction mixture had been cooled to room temperature, the crude product was purified by flash chromatography (SiO₂).

**N-(2-(Dimethyl(phenyl)silyl)propyl)aniline (4a)**

![Structure of 4a](image)

General procedure A was used to synthesize compound 4a from dimethylphenylvinylsilane (1) and N-methylaniline (3). After purification by flash chromatography (PE/EtOAc, 60:1), 4a (390 mg, 1.45 mmol, 72 %) was isolated as a colorless oil. In addition, a second fraction that contained a mixture of 4a and 4b (30 mg, 0.11 mmol, 4a/4b = 43:57) was also isolated. Rₗ = 0.16 (SiO₂, PE/EtOAc, 60:1). ¹H NMR (500 MHz, CDCl₃): δ = 7.56-7.48 (m, 2 H), 7.41-7.32 (m, 3 H), 7.12 (t, J = 7.7 Hz, 2 H), 6.65 (t, J = 7.0 Hz, 1 H), 6.44 (d, J = 8.2 Hz, 2 H), 3.49 (br. s, 1 H), 3.24 (dd, J = 12.1, 5.1 Hz, 1 H), 3.01-2.91 (m, 1 H), 1.33-1.22 (m, 1 H), 1.05 (d, J = 7.3 Hz, 3 H), 0.33 (s, 6 H) ppm. ¹³C(¹H) NMR (125 MHz, DEPT, CDCl₃): δ = 148.3 (C), 137.8 (C), 133.9 (CH), 129.1 (CH), 127.8 (CH), 116.9 (CH), 112.6 (CH), 46.6 (CH₂), 20.2 (CH), 13.1 (CH₃), −4.5 (CH₃), −5.3 (CH₃) ppm.

**N-(2-(Dimethyl(phenyl)silyl)propyl)-2-methylaniline (19a)**

![Structure of 19a](image)

General procedure A was used to synthesize compound 19a from dimethylphenylvinylsilane (1) and 2,N-dimethylaniline (5). After purification by flash chromatography (PE/EtOAc, 60:1), 19a (80 mg, 0.28 mmol, 14 %) was isolated as a colorless oil. Rₗ = 0.21 (SiO₂, PE/EtOAc, 60:1). ¹H NMR (500 MHz, CDCl₃): δ = 7.58-7.50 (m, 2 H), 7.41-7.35 (m, 3 H), 7.11-7.06 (m, 1 H), 7.00 (d, J = 7.0 Hz, 1 H), 6.62 (t, J = 7.3 Hz, 1 H), 6.50 (d, J = 8.0 Hz, 1 H), 3.42 (br. s, 1 H), 3.29 (dd, J = 12.0, 5.4 Hz, 1 H), 3.02 (dd, J = 11.9, 8.8 Hz, 1 H), 1.94 (s, 3 H), 1.41-1.31 (m, 1 H), 1.10 (d, J = 7.4 Hz, 3 H), 0.35 (s, 3 H),
0.35 (s, 3 H) ppm. $^{13}$C($^1$H) NMR (125 MHz, DEPT, CDCl$_3$): $\delta =$ 146.2 (C), 137.9 (C), 133.9 (CH), 129.9 (CH), 129.1 (CH), 127.9 (CH), 127.0 (CH), 121.8 (C), 116.5 (CH), 109.5 (CH), 46.7 (CH$_2$), 20.1 (CH), 17.1 (CH$_3$), 13.3 (CH$_3$), $-$4.3 (CH$_3$), $-$5.2 (CH$_3$) ppm. $^{29}$Si($^1$H) NMR (99.4 MHz, CDCl$_3$): $\delta =$ $-$0.8 ppm.

GC/MS (El, 70 eV): $m/z$ (%) = 283 (3) [M$^+$], 148 (6), 135 (58) [C$_8$H$_{11}$Si]$^+$, 120 (100) [C$_8$H$_{10}$N]$^+$, 91 (24) [C$_4$H$_7$]$^+$, 77 (12) [C$_6$H$_8$]$^+$.

HRMS (ESI, +): calcd. (C$_{18}$H$_{28}$NNaSi) 306.1654, found 306.1648 [M+Na]$^+$. IR (ATR, neat): $\lambda$ = 3419, 3069, 2955, 2866, 1606, 1586, 1511, 1472, 1445, 1427, 1377, 1314, 1249, 1190, 1111, 1051, 985, 831, 812, 771, 743, 699 cm$^{-1}$.

$N$-(2-(Dimethyl(phenyl)silyl)propyl)-3-methylaniline (20a)

![Structure of 20a]

General procedure A was used to synthesize compound 20a from dimethylphenylvinylsilane (1) and 3,N-dimethylaniline (6). After purification by flash chromatography (PE/EtOAc, 60:1), 20a (400 mg, 1.41 mmol, 71 %) was isolated as a colorless oil. In addition, a second fraction that contained a mixture of 20a and 20b (80 mg, 0.28 mmol, 20a:20b = 64:36) was also isolated. $R_f$ = 0.17 (SiO$_2$, PE/EtOAc, 60:1). $^1$H NMR (500 MHz, CDCl$_3$): $\delta =$ 7.54-7.53 (m, 2 H), 7.41-7.36 (m, 3 H), 7.05-6.99 (m, 1 H), 6.49 (d, $J =$ 7.4 Hz, 1 H), 6.28-6.27 (m, 2 H), 3.51 (br. s, 1 H), 3.24 (dd, $J =$ 12.2, 5.0 Hz, 1 H), 2.94 (dd, $J =$ 12.1, 9.1 Hz, 1 H), 2.25 (s, 3 H), 1.25-1.31 (m, 1 H), 1.06 (d, $J =$ 7.4 Hz, 3 H), 0.33 (s, 6 H) ppm. $^{13}$C($^1$H) NMR (125 MHz, DEPT, CDCl$_3$): $\delta =$ 148.3 (C), 138.9 (C), 137.9 (C), 133.9 (CH), 129.1 (CH), 129.0 (CH), 127.9 (CH), 117.9 (CH), 113.5 (CH), 109.9 (CH), 46.7 (CH$_2$), 21.6 (CH$_2$), 20.2 (CH), 13.1 (CH$_3$), $-$4.4 (CH$_3$), $-$5.3 (CH$_3$) ppm. $^{29}$Si($^1$H) NMR (99.4 MHz, INEPT, CDCl$_3$): $\delta =$ $-$0.8 ppm.

GC/MS (El, 70 eV): $m/z$ (%) = 283 (4) [M$^+$], 135 (14) [C$_8$H$_{11}$Si]$^+$, 120 (100) [C$_8$H$_{10}$N]$^+$, 91 (18) [C$_7$H$_7$]$^+$.

HRMS (ESI, +): calcd. (C$_{18}$H$_{28}$NNaSi) 306.1654, found 306.1652 [M+Na]$^+$. IR (ATR, neat): $\lambda$ = 3416, 3046, 2954, 2865, 2357, 1742, 1604, 1589, 1509, 1489, 1427, 1376, 1326, 1304, 1249, 1178, 1111, 991, 831, 812, 767, 734, 691 cm$^{-1}$.

$N$-(2-(Dimethyl(phenyl)silyl)propyl)-4-methylaniline (21a)

![Structure of 21a]

General procedure A was used to synthesize compound 21a from dimethylphenylvinylsilane (1) and 4,N-dimethylaniline (7). After purification by flash chromatography (PE/EtOAc, 60:1), 21a (400 mg, 1.41 mmol, 71 %) was isolated as a colorless oil. In addition, a second fraction that contained a mixture of 21a and 21b (30 mg, 0.11 mmol, 21a:21b = 35:65) was also isolated. $R_f$ = 0.11 (SiO$_2$, PE/EtOAc, 60:1). $^1$H NMR (500 MHz, CDCl$_3$): $\delta =$ 7.59-7.52 (m, 2 H), 7.42-7.41 (m, 3 H), 6.98 (d, $J =$ 7.6 Hz, 3 H), 6.42 (dd, $J =$ 8.0, 1.7 Hz, 2 H), 3.45 (br. s, 1 H), 3.27 (dd, $J =$ 11.7, 4.7 Hz, 2 H), 2.97 (dd, $J =$ 12.0, 9.1 Hz, 1 H), 2.26 (s, 3 H), 1.38-1.25 (m, 1 H), 1.09 (d, $J =$ 7.3 Hz, 3 H), 0.36 (s, 6 H) ppm. $^{13}$C($^1$H) NMR (125 MHz, DEPT, CDCl$_3$): $\delta =$ 146.1 (C), 137.9 (C), 133.9 (CH), 129.6 (CH), 129.1 (CH),
127.8 (CH), 126.2 (C), 113.0 (CH), 47.1 (CH$_2$), 20.3 (CH), 20.3 (CH$_3$) 13.1 (CH$_3$), –4.5 (CH$_3$), –5.2 (CH$_3$) ppm. $^{29}$Si[$^1$H] NMR (99.4 MHz, INEPT, CDCl$_3$): $\delta$ = –0.8 ppm. GC/MS (El, 70 eV): $m/z$ (%) = 283 (3) [M$^+$], 148 (4), 135 (62) [C$_9$H$_{13}$Si$^+$], 120 (100) [C$_9$H$_{15}$N$^+$], 91 (18) [C$_7$H$_7$]$^+$, 77 (12) [C$_6$H$_3$]$^+$. HRMS (El): calcd. (C$_{18}$H$_{26}$NSi) 283.1751, found 283.1751 [M$^+$]. IR (ATR, neat): $\lambda^{-1}$ = 3414, 3068, 3048, 3019, 2953, 2921, 2866, 1617, 1519, 1472, 1427, 1316, 1301, 1248, 1182, 1111, 986, 831, 806, 771, 734, 700 cm$^{-1}$.

**N-(2-(Dimethyl(phenyl)silyl)propyl)-3-fluoroaniline (22a)**

![Structure](image)

General procedure A was used to synthesize compound 22a from dimethylphenylvinylsilane (1) and N-methyl-3-fluoroaniline (8). After purification by flash chromatography (PE/EtOAc, 60:1), 22a (298 mg, 1.04 mmol, 52 %) was isolated as a yellow oil. In addition, a second fraction that contained a mixture of 22a and 22b (93 mg, 0.32 mmol, 22a:22b = 81:19) was also isolated. $R_t$ = 0.19 (SiO$_2$, PE/EtOAc, 60:1). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 7.54-7.50 (m, 2 H), 7.44-7.34 (m, 3 H), 7.04 (td, $J = 8.1, 6.7$ Hz, 1 H), 6.35 (td, $J = 8.3, 2.3$ Hz, 1 H), 6.21 (dd, $J = 8.1, 2.2$ Hz, 1 H), 6.14 (dt, $J = 11.6, 2.4$ Hz, 1 H), 3.20 (dd, $J = 12.2, 5.2$ Hz, 1 H), 2.95 (dd, $J = 12.2, 9.1$ Hz, 1 H), 1.34-1.23 (m, 1 H), 1.07 (d, $J = 7.4$ Hz, 3 H), 0.34 (s, 6 H) ppm. $^{13}$C[$^1$H] NMR (125 MHz, DEPT, CDCl$_3$): $\delta$ = 164.1 (d, $^1$J$_{C,F}$ = 242 Hz, C), 150.0 (d, $^2$J$_{C,F} = 10$ Hz, C), 137.7 (C), 133.9 (CH), 130.10 (d, $^3$J$_{C,F}$ = 10 Hz, CH), 129.2 (CH), 128.0 (CH), 108.5 (CH), 103.2 (d, $^2$J$_{C,F} = 22$ Hz, CH), 99.1 (d, $^2$J$_{C,F} = 25$ Hz, CH), 46.6 (CH$_2$), 20.2 (CH), 13.1 (CH$_3$), –4.5 (CH$_3$), –5.4 (CH$_3$) ppm. $^{19}$F[$^1$H] NMR (470 MHz, CDCl$_3$): $\delta$ = –113.0 ppm. $^{29}$Si[$^1$H] NMR (99.4 MHz, INEPT, CDCl$_3$): $\delta$ = –0.8 ppm. GC/MS (El, 70 eV): $m/z$ (%) = 287 (5) [M$^+$], 135 (100) [C$_9$H$_{13}$Si$^+$], 124 (92) [C$_7$H$_6$F$^+$], 105 (17), 77 (9) [C$_6$H$_3$]$^+$). HRMS (El, 70 eV): calcd. (C$_{17}$H$_{28}$FNSi) 287.1500, found 287.1508 [M$^+$]. IR (ATR, neat): $\lambda^{-1}$ = 3427, 3069, 2955, 2900, 2867, 1620, 1588, 1509, 1496, 1427, 1335, 1249, 1175, 1149, 1112, 997, 830, 814, 773, 759, 735, 702, 683, 632 cm$^{-1}$.

**N-(2-(Dimethyl(phenyl)silyl)propyl)-4-fluoroaniline (23a)**

![Structure](image)

General procedure A was used to synthesize compound 23a from dimethylphenylvinylsilane (1) and N-methyl-4-fluoroaniline (9). After purification by flash chromatography (PE/EtOAc, 60:1), 23a (480 mg, 1.67 mmol, 83 %) was isolated as a colorless oil. In addition, a second fraction that contained a mixture of 23a and 23b (38 mg, 0.13 mmol, 23a:23b = 25:75) was also isolated. $R_t$ = 0.14 (SiO$_2$, PE/EtOAc, 60:1). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 7.56-7.50 (m, 2 H), 7.42-7.36 (m, 3 H), 6.88-6.80 (m, 2 H), 6.40-6.33 (m, 2 H), 3.45 (br. s, 1 H), 3.19 (dd, $J = 12.0, 5.2$ Hz, 1 H), 2.93 (dd, $J = 12.0, 9.1$ Hz, 1 H), 1.34-1.21 (m, 1 H), 1.07 (d, $J = 7.4$ Hz, 3 H), 0.34 (s, 6 H) ppm. $^{13}$C[$^1$H] NMR (125 MHz, DEPT,
CDCl₃): δ = 155.6 (d, J CF = 234 Hz, C), 144.6 (C), 137.8 (C), 133.9 (CH), 129.2 (CH), 127.9 (CH),
115.5 (d, J CF = 22 Hz, CH), 113.4 (d, J CF = 7 Hz, CH), 47.4 (CH₂), 20.2 (CH), 13.1 (CH₃), −4.4 (CH₃),
−5.3 (CH₃) ppm. ¹H NMR (470 MHz, CDCl₃): δ = −128.5 ppm. ²⁹Si(¹H) NMR (99.4 MHz, CDCl₃): δ =
−0.8 ppm. GC/MS (EI, 70 eV): m/z (%) = 287 [M⁺] (8), 135 [C₆H₁₁Si⁺] (25), 124 [C₂H₆FN⁺] (100), 105
[C₂H₃N/C₂H₅Si⁺] (7). HRMS (ESI): calcd. (C₁₇H₃₂FNNaSi) 310.1403, found 310.1405 [M+Na⁺]. IR
(ATR, neat): λ⁻¹ = 3068, 2954, 2901, 2868, 1509, 1474, 1427, 1314, 1250, 1218, 1111, 986, 813, 770,
734, 700 cm⁻¹.

N-(2-(Dimethyl(phenyl)silyl)propyl)-3-chloroaniline (24a)

General procedure A was used to synthesize compound 24a from dimethylphenylvinylsilane (1) and
N-methyl-3-chloroaniline (10). After purification by flash chromatography (PE/EtOAc, 60:1), 24a (360
mg, 1.18 mmol, 59 %) was isolated as a yellow oil. In addition, a second fraction that contained a
mixture of 24a and 24b (180 mg, 0.59 mmol, 24a/24b = 87:13) was also isolated. Rₖ = 0.22 (SiO₂,
PE/EtOAc, 60:1). ¹H NMR (500 MHz, CDCl₃): δ = 7.58-7.51 (m, 2 H), 7.45-7.37 (m, 3 H), 7.03 (t, J =
8.0 Hz, 1 H), 6.63 (dd, J = 7.8, 1.3 Hz, 1 H), 6.42 (t, J = 2.2 Hz, 1 H), 6.30 (dd, J = 8.2, 2.0 Hz, 1 H),
3.69 (br. s, 1 H), 3.21 (dd, J = 12.2, 5.3 Hz, 1 H), 2.96 (dd, J = 12.2, 9.0 Hz, 1 H), 1.29 (ddq, J = 8.7,
7.3, 5.2 Hz, 1 H), 1.08 (d, J = 7.3 Hz, 3 H), 0.36 (s, 6 H) ppm. ¹³C(¹H) NMR (125 MHz, DEPT, CDCl₃):
δ = 149.3 (C), 137.7 (C), 134.9 (C), 133.8 (CH), 130.0 (CH), 129.2 (CH), 128.0 (CH), 116.8 (CH),
112.2 (CH), 111.1 (CH), 46.7 (CH₂), 20.3 (CH), 13.1 (CH₃), −4.4 (CH₃), −5.4 (CH₃) ppm. ²⁹Si(¹H) NMR
(99.4 MHz, INEPT, CDCl₃): δ = −0.8 ppm. GC/MS (EI, 70 eV): m/z (%) = 303 (8) [M⁺], 168 (5), 140
(64) [C₂H₅CN⁺], 135 (100) [C₆H₁₁Si⁺], 105 (18), 77 (7) [C₆H₅⁺]. HRMS (EI): calcd. (C₁₇H₃₂FNNaSi)
303.1205, found 303.1202 [M⁺]. IR (ATR, neat): λ⁻¹ = 3069, 2954, 2904, 2867, 1597, 1574, 1501,
1486, 1471, 1427, 1324, 1249, 1111, 1091, 1076, 987, 831, 812, 764, 734, 699, 680 cm⁻¹.

N-(2-(Dimethyl(phenyl)silyl)propyl)-4-chloroaniline (25a)

General procedure A was used to synthesize compound 25a from dimethylphenylvinylsilane (1) and
N-methyl-4-chloroaniline (11). After purification by flash chromatography (PE/EtOAc, 60:1), 25a (440
mg, 1.45 mmol, 72 %) was isolated as a yellow oil. In addition, a second fraction that contained a
mixture of 25a and 25b (50 mg, 0.16 mmol, 25a/25b = 32:68) was also isolated. Rₖ = 0.16 (SiO₂,
PE/EtOAc, 60:1). ¹H NMR (500 MHz, CDCl₃): δ = 7.56-7.48 (m, 2 H), 7.45-7.32 (m, 3 H), 7.11-7.01 (m,
2 H), 6.41-6.31 (m, 2 H), 3.54 (br. s, 1 H) 3.22 (dd, J = 12.2, 5.2 Hz, 1 H), 2.96 (br. t, J = 10.6, 1 H),
1.39-1.23 (m, 1 H), 1.12-1.04 (m, 3 H), 0.37 (s, 6 H) ppm. ¹³C(¹H) NMR (125 MHz, DEPT, CDCl₃): δ =
146.8 (C), 137.7 (C), 133.8 (CH), 129.2 (CH), 128.9 (CH), 127.9 (CH), 121.4 (C), 113.6 (CH), 46.8
(CH₂), 20.2 (CH), 13.1 (CH₃), −4.4 (CH₃), −5.4 (CH₃) ppm. ²⁹Si(¹H) NMR (99.4 MHz, CDCl₃): δ = −0.8 ppm. GC/MS (EI, 70 eV): m/z (%) = 303 (6) [M⁺], 135 (100) [C₆H₄Si⁺], 105 (16). HRMS (ESI, +): calcd. (C₁₇H₂₃ClSi) 304.1288, found 304.1283 [M⁺H⁺]. IR (ATR, neat): ν = 3069, 2955, 2902, 2868, 1600, 1498, 1427, 1315, 1249, 1176, 1110, 831, 810, 771, 734, 699 cm⁻¹.

**N-(2-(Dimethyl(phenyl)silyl)propyl)-3-bromoaniline (26a)**

![Structure of N-(2-(Dimethyl(phenyl)silyl)propyl)-3-bromoaniline (26a)](image)

General procedure A was used to synthesize compound 26a from dimethylphenylvinylsilane (1) and N-methyl-3-bromoaniline (12). After purification by flash chromatography (PE/EtOAc, 60:1), 26a (115 mg, 0.33 mmol, 17%) was isolated as a yellow oil. In addition, a second fraction that contained a mixture of 26a and 26b (420 mg, 1.21 mmol, 26a/26b = 94:6) was also isolated. Rf = 0.17 (SiO₂, PE/EtOAc, 60:1). ¹H NMR (500 MHz, CDCl₃): δ = 7.59-7.51 (m, 2 H), 7.45-7.37 (m, 3 H), 6.97 (t, J = 8.0 Hz, 1 H), 6.78 (d, J = 7.9 Hz, 1 H), 6.57 (t, J = 2.0 Hz, 1 H), 6.33 (dd, J = 8.4, 2.2 Hz, 1 H), 3.65 (br. s, 1 H), 3.20 (dd, J = 12.1, 5.1 Hz, 1 H), 2.95 (dd, J = 12.2, 8.9 Hz, 1 H), 1.34-1.22 (m, 1 H), 1.07 (d, J = 7.4 Hz, 3 H), 0.35 (s, 6 H) ppm. ¹³C(¹H) NMR (125 MHz, DEPT, CDCl₃): δ = 149.4 (C), 137.6 (C), 133.8 (CH), 129.2 (CH), 128.0 (CH), 123.2 (C), 119.6 (CH), 115.0 (CH), 111.4 (CH), 46.6 (CH₂), 20.2 (CH), 13.1 (CH₃), −4.4 (CH₃), −5.4 (CH₃) ppm. ²⁹Si(¹H) NMR (99.4 MHz, INEPT, CDCl₃): δ = −0.8 ppm. GC/MS (EI, 70 eV): m/z (%) = 347 (3) [M⁺], 184 (22) [C₇H₄BrN⁺], 135 (100) [C₆H₄Si⁺], 105 (35), 77 (6) [C₆H₃⁺]. HRMS (EI, 70 eV): calcd. (C₁₇H₂₂BrNSi) 347.0699, found 347.0706 [M⁺]. IR (ATR, neat): ν = 3069, 3023, 2953, 2897, 2868, 1594, 1571, 1497, 1481, 1427, 1414, 1321, 1249, 1111, 1066, 984, 830, 811, 770, 734, 699, 680 cm⁻¹.

**N-(2-(Dimethyl(phenyl)silyl)propyl)-4-bromoaniline (27a)**

![Structure of N-(2-(Dimethyl(phenyl)silyl)propyl)-4-bromoaniline (27a)](image)

General procedure A was used to synthesize compound 27a from dimethylphenylvinylsilane (1) and N-methyl-4-bromoaniline (13). After purification by flash chromatography (PE/EtOAc, 60:1), 27a (453 mg, 1.30 mmol, 65%) was isolated as a yellow oil. In addition, a second fraction that contained a mixture of 27a and 27b (81 mg, 0.23 mmol, 27a/27b = 66:33) was also isolated. Rf = 0.29 (SiO₂, PE/EtOAc, 60:1). ¹H NMR (500 MHz, CDCl₃): δ = 7.54-7.49 (m, 2 H), 7.41-7.36 (m, 3 H), 7.19 (d, J = 8.9 Hz, 2 H), 6.29 (d, J = 8.8 Hz, 2 H), 3.62 (br. s, 1 H), 3.18 (dd, J = 12.2, 5.3 Hz, 1 H), 2.92 (dd, J = 12.2, 9.0 Hz, 1 H), 1.32-1.21 (m, 1 H), 1.05 (d, J = 7.4 Hz, 3 H), 0.33 (s, 6 H) ppm. ¹³C(¹H) NMR (125 MHz, DEPT, CDCl₃): δ = 147.1 (C), 137.7 (C), 133.9 (CH), 131.8 (CH), 129.2 (CH), 127.9 (CH), 114.2 (CH), 108.5 (C), 46.8 (CH₂), 20.1 (CH), 13.1 (CH₃), −4.4 (CH₃), −5.4 (CH₃) ppm. ²⁹Si(¹H) NMR (99.4 MHz, CDCl₃): δ = −0.8 ppm. GC/MS (EI, 70 eV): m/z (%) = 347 (2) [M⁺], 184 (30) [C₇H₄BrN⁺], 135 (100) [C₆H₄Si⁺], 105 (23), 91 (12) [C₆H₃⁺]. HRMS (ESI, +): calcd. (C₁₇H₂₂BrNSi) 348.0783, found
348.0787 [M+H]+. IR (ATR, neat): λ−1 = 3422, 3072, 3050, 2957, 2932, 2903, 2871, 1596, 1497, 1429, 1399, 1316, 1295, 1251, 1179, 1113, 1074, 1000, 833, 811, 773, 737, 702, 650, 614 cm−1.

**N-(2-(Dimethyl(phenyl)silyl)propyl)-4-methoxyaniline (28a)**

![Structure of 28a](image)

General procedure A was used to synthesize compound 28a from dimethylphenylvinylsilane (1) and N-methyl-4-methoxyaniline (14). After purification by flash chromatography (PE/MTBE, 20:1), 28a (435 mg, 1.45 mmol, 73 %) was isolated as a yellow oil. In addition, a second fraction that contained a mixture of 28a and 28b (55 mg, 0.18 mmol, 28a:28b = 32:68) was also isolated. Rf = 0.10 (SiO2, PE/MTBE, 20:1). 1H NMR (500 MHz, CDCl3): δ = 7.53-7.51 (m, 2 H), 7.39-7.35 (m, 3 H), 6.74 (d, J = 8.9 Hz, 2 H), 6.43 (d, J = 8.9 Hz, 2 H), 3.73 (s, 3 H), 3.20 (dd, J = 12.1, 5.0 Hz, 1 H), 2.91 (dd, J = 11.9, 9.2 Hz, 1 H), 1.26 (ddq, J = 9.1, 7.2, 5.0 Hz, 1 H), 1.05 (d, J = 7.4 Hz, 3 H), 0.32 (s, 6 H) ppm. 13C(H) NMR (125 MHz, DEPT, CDCl3): δ = 151.9 (C), 142.6 (C), 138.0 (C), 133.9 (CH), 129.1 (CH), 127.9 (CH), 114.9 (CH), 55.9 (CH3), 47.7 (CH2), 20.2 (CH). 13C (CH3, −4.4 (CH2), −5.2 (CH3) ppm. 29Si(1H) NMR (99.4 MHz, INEPT, CDCl3): δ = −0.8 ppm. GC/MS (EI, 70 eV): m/z (%) = 299 (4) [M]+, 135 (100) [C6H11Si]++, 107 (12) [C8H5O]+, 77 (7) [C8H5]+. HRMS (ESI, +): calcd. (C18H23NOSi) 300.1783 [M+H]+, found 300.1784. IR (ATR, neat): λ−1 = 3395, 3070, 2955, 2902, 2869, 2833, 1590, 1512, 1466, 1429, 1408, 1309, 1234, 1181, 1113, 1040, 988, 814, 774, 736, 702 cm−1.

**N-(2-(Dimethyl(phenyl)silyl)propyl)-4-trifluoromethoxyaniline (29a)**

![Structure of 29a](image)

General procedure A was used to synthesize compound 29a from dimethylphenylvinylsilane (1) and N-methyl-4-trifluoromethoxyaniline (15). After purification by flash chromatography (PE/EtOAc, 60:1), 29a (486 mg, 1.37 mmol, 69 %) was isolated as a colorless oil. In addition, a second fraction that contained a mixture of 29a and 29b (65 mg, 0.18 mmol, 29a:29b = 51:49) was also isolated. Rf = 0.16 (SiO2, PE/EtOAc, 60:1). 1H NMR (500 MHz, CDCl3): δ = 7.56-7.52 (m, 2 H), 7.43-7.37 (m, 3 H), 6.99 (d, J = 8.5 Hz, 2 H), 6.37 (d, J = 8.9 Hz, 2 H), 3.61 (br. s, 1 H), 3.21 (dd, J = 12.1, 5.3 Hz, 1 H), 2.95 (dd, J = 12.1, 9.0 Hz, 1 H), 1.33-1.24 (m, 1 H), 1.08 (d, J = 7.4 Hz, 3 H), 0.35 (s, 6 H) ppm. 13C(H) NMR (125 MHz, DEPT, CDCl3): δ = 147.0 (C), 140.1 (C), 137.7 (C), 133.9 (CH), 129.2 (CH), 127.9 (CH), 122.3 (CH), 120.7 (q, 1JC,F = 255 Hz, C), 112.7 (CH), 46.9 (CH2), 20.2 (CH), 13.1 (CH3), −4.4 (CH3), −5.4 (CH3) ppm. 19F(1H) NMR (470 MHz, CDCl3): δ = −58.5 ppm. 29Si(1H) NMR (99.4 MHz, CDCl3): δ = −0.8 ppm. GC/MS (EI, 70 eV): m/z (%) = 353 (6) [M]+, 296 (6), 190 (48) [C8H7F3NO]+, 135 (100) [C8H11Si]++, 105 (2). HRMS (ESI, +): calcd. (C18H23F3NOSi) 354.1501, found 354.1493 [M+H]+.
IR (ATR, neat): $\lambda^{-1} = 3423, 3070, 2957, 2872, 1613, 1514, 1428, 1248, 1220, 1199, 1153, 1110, 916, 829, 812, 772, 735, 700, 670 \text{ cm}^{-1}$.

$N$-(2-(Dimethyl(phenyl)silyl)propyl)-4-(methylthio)aniline (30a)

![Structure of 30a](image)

General procedure A was used to synthesize compound 30a from dimethylphenylvinylsilane (1) and N-methyl-4-(methylthio)aniline (16). After purification by flash chromatography (PE/MTBE, 40:1), 30a (366 mg, 1.16 mmol, 58 %) was isolated as a yellow oil. In addition, a second fraction that contained a mixture of 30a and 30b (33 mg, 0.10 mmol, 30a:30b = 54:46) was also isolated. $R_f = 0.11$ (SiO$_2$, PE/MTBE, 40:1). $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 7.59-7.54$ (m, 2 H), 7.46-7.38 (m, 3 H), 7.21 (d, $J = 8.6$ Hz, 2 H), 6.42 (d, $J = 8.6$ Hz, 2 H), 3.66 (br. s, 1 H), 2.36 (dd, $J = 12.2$, 5.2 Hz, 1 H), 2.98 (dd, $J = 12.2$, 9.1 Hz, 1 H), 2.43 (s, 3 H), 1.36 (m, 1 H), 1.09 (d, $J = 7.4$ Hz, 3 H), 0.37 (s, 6 H) ppm. $^{13}$C($^1$H) NMR (125 MHz, DEPT, CDCl$_3$): $\delta = 147.1$ (C), 137.7 (C), 133.8 (CH), 131.6 (CH), 129.1 (CH), 127.9 (CH), 123.7 (C), 113.2 (CH), 46.8 (CH$_2$), 20.2 (CH), 19.3 (CH$_3$), 13.1 (CH$_3$), $-4.5$ (CH$_3$), $-5.3$ (CH$_3$) ppm. $^{26}$Si($^1$H) NMR (99.4 MHz, INEPT, CDCl$_3$): $\delta = -0.8$ ppm. GC/MS (EI, 70 eV): $m/z$ (%): 315 (9) [M]$^+$, 152 (50) [C$_9$H$_9$NS]$^+$, 135 (100) [C$_6$H$_5$Si]$^+$, 105 (10), 91 (5). HRMS (EI, 70 eV): calcd. (C$_{18}$H$_{25}$NSSi) 315.1471, found 315.1477 [M]$^+$. IR (ATR, neat): $\lambda^{-1} = 3407, 3068, 2952, 2918, 2864, 1598, 1500, 1471, 1427, 1312, 1288, 1248, 1182, 1110, 967, 831, 810, 771, 734, 700 \text{ cm}^{-1}$.

$N$-(2-(Dimethyl(phenyl)silyl)propyl)-N-cyclohexylamine (31a)

![Structure of 31a](image)

General procedure A with complex II (109 mg, 0.20 mmol, 10 mol%) as the catalyst and a reaction temperature of 140 °C was used to synthesize compound 31a from dimethylphenylvinylsilane (1) and N-methylcyclohexylamine (17). After purification by flash chromatography (PE/MTBE, 30:1 with 2 % NEt$_3$) and subsequent Kugelrohr distillation (5 × 10$^{-1}$ mbar, b.p. 170 °C), 31a (303 mg, 1.10 mmol, 55 %) was isolated as a colorless oil. $R_f = 0.20$ (PE/MTBE, 30:1 with 2 % NEt$_3$). $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 7.54-7.48$ (m, 2 H), 7.37-7.32 (m, 3 H), 2.76 (dd, $J = 11.5$, 4.7 Hz, 1 H), 2.46 (dd, $J = 11.5$, 9.5 Hz, 1 H), 2.31 (t, $J = 10.4$, 3.7 Hz, 1 H), 1.82-1.72 (m, 2 H), 1.71-1.65 (m, 2 H), 1.63-1.55 (m, 1 H), 1.17-0.95 (m, 6 H), 0.98 (d, $J = 7.3$ Hz, 3 H), 0.28 (s, 6 H) ppm. $^{13}$C($^1$H) NMR (125 MHz, DEPT, CDCl$_3$): $\delta = 138.4$ (C), 133.9 (CH), 128.8 (CH), 127.7 (CH), 56.6 (CH), 49.4 (CH$_2$), 33.8 (CH$_3$), 33.4 (CH$_2$), 26.3 (CH$_2$), 25.1 (CH$_2$), 25.0 (CH$_2$), 20.6 (CH), 13.1 (CH$_3$), $-4.5$ (CH$_3$), $-4.8$ (CH$_3$) ppm. $^{26}$Si($^1$H) NMR (99.4 MHz, INEPT, CDCl$_3$): $\delta = -0.9$ ppm. GC/MS (EI, 70 eV): $m/z$ (%): 275 (1) [M]$^+$, 190 (5), 135 (55) [C$_9$H$_5$Si]$^+$, 112 (100) [C$_7$H$_4$N]$^+$. HRMS (EI): calcd. (C$_{17}$H$_{29}$NSi) 275.2064, found 275.2066 [M]$^+$. IR (ATR, neat): $\lambda^{-1} = 2926, 2852, 1449, 1427, 1247, 1111, 831, 812, 770, 732, 698 \text{ cm}^{-1}$. 

9
**N-(1-Phenyl-3-(dimethyl(phenyl)silyl)propyl)-N-methylamine (32b)**

![Chemical Structure of 32b](image)

General procedure A with complex II (109 mg, 0.20 mmol, 10 mol%) as the catalyst and a reaction temperature of 140 °C was used to synthesize compound 32b from dimethylphenylvinylsilane (1) and N-methylbenzylamine (18). After purification by flash chromatography (PE/MTBE, 30:1 with 2 % NEt₃), 32b 305 mg, 1.08 mmol, 54 %) was isolated as a colorless oil. \( R_f = 0.22 \) (PE/MTBE, 30:1 with 2 % NEt₃).

1H NMR (500 MHz, CDCl₃): \( \delta = 7.44-7.39 \) (m, 2 H), 7.29 (dd, \( J = 9.8, 4.4 \) Hz, 5 H), 7.22-7.18 (m, 3 H), 3.33 (t, \( J = 6.8 \) Hz, 1 H), 2.21 (s, 3 H), 1.74-1.65 (m, 1 H), 1.65-1.56 (m, 1 H), 0.76-0.66 (m, 1 H), 0.58-0.49 (m, 1 H), 0.19 (s, 3 H), 0.19 ppm. 13C{1H} NMR (125 MHz, DEPT, CDCl₃): \( \delta = 143.8 \) (C), 139.1 (C), 133.5 (CH), 128.8 (CH), 128.3 (CH), 127.7 (CH), 127.4 (CH), 126.9 (CH), 68.1 (CH), 34.5 (CH₃), 31.9 (CH₂), 12.1 (CH₂), -3.2 (CH₃), -3.3 (CH₃) ppm. 29Si{1H} NMR (99.4 MHz, CDCl₃): \( \delta = -2.6 \) ppm. GC/MS (EI, 70 eV): m/z (%) = 135 (10) [C₈H₁₁Si]+, 120 (100) [C₂H₅N]⁺. HRMS (ESI, +): calcd. (C₈H₂₆N) 284.1835, found 284.1835 [M+H⁺]. IR (ATR, neat): \( \lambda⁻¹ = 2952, 2786, 1452, 1427, 1248, 1113, 814, 775, 759, 728, 698 \) cm⁻¹.

**Triphenylvinylsilane (33)[8]**

![Chemical Structure of 33](image)

Under an atmosphere of argon, an oven-dried Schlenk flask equipped with a rubber septum was charged with triphenylchlorosilane (25.21 g, 85.50 mmol) and dry THF (50 mL). At ambient temperature, vinylmagnesiumchloride (94 mL, 94.01 mmol, 1.0 M solution in THF) was added dropwise. The reaction mixture was stirred at ambient temperature for 16 h and afterwards, saturated NH₄Cl solution (100 mL) was slowly added. The layers were separated and the organic layer was washed with H₂O (120 mL) and brine (120 mL). Afterwards, the organic layer was dried with MgSO₄ and the solvent was evaporated under reduced pressure. After purification by flash chromatography (PE/MTBE, 80:1), 33 (16.87 g, 58.89 mmol, 69 %) was isolated as a colorless solid. \( R_f = 0.33 \) (SiO₂, PE/MTBE, 80:1). 1H NMR (500 MHz, CDCl₃): \( \delta = 7.62 \) (dd, \( J = 7.9, 1.4 \) Hz, 6 H), 7.50-7.47 (m, 3 H), 7.46-7.39 (m, 6 H), 6.78 (dd, \( J = 20.2, 14.6 \) Hz, 1 H), 6.40 (dd, \( J = 14.6, 3.6 \) Hz, 1 H), 5.89 (dd, \( J = 20.2, 3.6 \) Hz, 1 H) ppm. 13C{1H} NMR (125 MHz, DEPT, CDCl₃): \( \delta = 136.8 \) (CH₂), 135.9 (CH), 134.2 (C), 133.9 (CH), 129.5 (CH), 127.9 (CH) ppm.
(4-Methoxyphenyl)dimethylvinylsilane (34)[7]

Under an atmosphere of argon, an oven-dried Schlenk flask equipped with a dropping funnel was charged with iso-propyl-Mg-Cl (1.9 mL, 3.90 mmol, 2 M in THF) and dry THF (20 mL) and cooled to 0 °C. At this temperature n-BuLi (3.1 mL, 7.75 mmol, 2.5 M in hexane) was added dropwise and the reaction mixture was stirred for 5 minutes. 4-Methoxybromobenzene (1.44 g, 7.70 mmol) was added and stirring was continued for 1 h. Chlorodimethylvinylsilane (2.78 g, 23.14 mmol) was added dropwise and the reaction mixture was stirred for 2 h at ambient temperature. The reaction was hydrolyzed with saturated NH₄Cl solution (5 mL) and after separation of the layers the aqueous layer was washed with EtOAc (2 × 50 mL). The combined organic layers were dried with MgSO₄ and the solvent was removed in a rotary evaporator. Kugelrohr distillation (30 mbar, b.p. 134 °C) afforded 34 (1.42 g, 7.38 mmol, 96 %) as a colorless liquid.

\[
\begin{align*}
\text{MeO} & \quad \text{Si} \\
\text{MeO} & \quad \text{Si}
\end{align*}
\]

\[
\delta = 7.49 (d, J = 8.5 \text{ Hz}, 2 \text{H}), 6.95 (d, J = 8.5 \text{ Hz}, 2 \text{H}), 6.31 (dd, J = 20.3, 14.6 \text{ Hz}, 1 \text{H}), 6.07 (dd, J = 14.6, 3.7 \text{ Hz}, 1 \text{H}), 5.77 (dd, J = 20.3, 3.8 \text{ Hz}, 1 \text{H}), 3.84 (s, 3 \text{H}), 0.36 (s, 6 \text{H}) \text{ ppm.}
\]

\[
\begin{align*}
1^H \text{ and } 13C \{^1H\} \text{ NMR (125 MHz, CDCl}_3\}: \delta = 160.4 (C), 138.4 (CH), 135.3 (CH), 132.5 (CH_2), 129.1 (C), 113.6 (CH), 55.0 (CH_3), -2.8 (CH_3) \text{ ppm.}
\end{align*}
\]

GC/MS (EI, 70 eV): m/z (%) = 222 (2) [M]+, 207 (100) [C_{11}H_{15}O_2Si]⁺, 177 (28), 147 (75), 145 (62), 91 (19). HRMS (EI): calcd. (C_{12}H_{18}O_2Si) 222.1071, found 222.1075 [M]+. IR (ATR, neat): \lamda^{-1} = 2941, 2834, 1582, 1459, 1426, 1236, 1171, 1101, 1007, 945, 820, 780, 715, 695 cm^{-1}.

(2,6-Dimethoxyphenyl)dimethylvinylsilane (35)[8]

Under an atmosphere of argon, an oven-dried Schlenk flask equipped with a dropping funnel was charged with a mixture of 1,3-dimethoxybenzene (7.27 g, 52.65 mmol), TMEDA (6.42 g, 55.23 mmol) and n-pentane (60 mL). n-BuLi (21.1 mL, 52.75 mmol, 2.5 M in hexane) was added dropwise within 1 h and the resulting suspension was stirred at ambient temperature for 16 h. Chlorodimethylvinylsilane (8.23 g, 68.21 mmol) in diethyl ether (80 mL) was added within 1 h and the reaction mixture was stirred again for 16 h. The resulting precipitate was filtered off and washed with diethyl ether (3 × 100 mL). The combined organic layers were concentrated in a rotary evaporator and the residue was purified by Kugelrohr distillation (8 × 10^{-3} mbar, b.p. 105 °C) to afford 35 (5.03 g, 22.65 mmol, 45 %) as a colorless liquid. \[H \text{ NMR (500 MHz, CDCl}_3\): \delta = 7.34-7.25 (m, 1 \text{H}), 6.57-6.43 (m, 3 \text{H}), 5.92 (d, J = 14.3 \text{ Hz}, 1 \text{H}), 5.70 (d, J = 20.4 \text{ Hz}, 1 \text{H}), 3.81-3.73 (m, 6 \text{H}), 0.44-0.36 (m, 6 \text{H}) \text{ ppm.} \]

\[1^{13}C \{^1H\} \text{ NMR (125 MHz, DEPT, CDCl}_3\}: \delta = 165.4 (C), 141.1 (CH), 131.6 (CH), 129.2 (CH_2), 113.0 (C), 103.8 (CH), 55.3 (CH_3), -0.5 (CH_3) \text{ ppm.} \]

\[^{29}Si \text{ HMBC NMR (500 MHz, 99.4 MHz, CDCl}_3\}: \delta = -14.4 \text{ ppm. GC/MS (EI, 70 eV): m/z (%) = 222 (2) [M]^+, 207 (100) [C_{11}H_{15}O_2Si]^+, 177 (28), 147 (75), 145 (62), 91 (19). HRMS (EI): calcd. (C_{12}H_{18}O_2Si) 222.1071, found 222.1075 [M]^+. IR (ATR, neat): \lamda^{-1} = 2941, 2834, 1582, 1459, 1426, 1236, 1171, 1101, 1007, 945, 820, 780, 715, 695 cm^{-1}.\]
(2,4,6-Trimethoxyphenyl)dimethylvinylsilane (36)[8]

![Chemical Structure](image)

Under an atmosphere of argon, an oven-dried Schlenk flask equipped with a dropping funnel was charged with a mixture of 1,3,5-trimethoxybenzene (8.86 g, 52.71 mmol), TMEDA (6.42 g, 55.23 mmol) and n-pentane (60 mL). n-BuLi (21.1 mL, 52.75 mmol, 2.5 M in hexane) was added dropwise within 1 h and the resulting suspension was stirred at ambient temperature for 16 h. Chlorodimethylvinylsilane (8.23 g, 68.21 mmol) in diethyl ether (80 mL) was added within 1 h and the reaction mixture was stirred again for 16 h. The resulting precipitate was filtered off and washed with diethyl ether (3 × 100 mL). The combined organic layers were concentrated in a rotary evaporator and the residue was purified by Kugelrohr distillation (6.5 × 10⁻² mbar, b.p. 140 °C) and subsequent flash chromatography (SiO₂, PE/EtOAc, 30:1) to afford 36 (6.65 g, 26.38 mmol, 53 %) as a colorless liquid. Rf: 0.09 (PE/EtOAc, 30:1). ¹H NMR (500 MHz, CDCl₃): δ = 6.44 (dd, J = 20.4, 14.5 Hz, 1 H), 6.08 (s, 2 H), 5.88 (dd, J = 14.5, 3.9 Hz, 1 H), 5.65 (dd, J = 20.4, 3.9 Hz, 1 H), 3.82 (s, 3 H), 3.74 (s, 6 H), 0.34 (s, 6 H) ppm. ¹³C{¹H} NMR (125 MHz, DEPT, CDCl₃): δ = 166.3 (C), 163.3 (C), 141.3 (CH), 129.1 (CH₂), 104.3 (C), 90.5 (CH), 55.2 (CH₃), −0.5 (CH₃) ppm. ²⁹Si{¹H}²⁹Si HMBC NMR (500 MHz, 99.4 MHz, CDCl₃): δ = −15.1 ppm. GC/MS (EI, 70 eV): m/z (%): 252 (17) [M]+, 237 (100) [C₁₂H₁₇O₃Si]+, 177 (47), 175 (37), 165 (37), 151 (17). HRMS (EI): calcld. (C₁₃H₂₀O₃Si) 252.1176, found 252.1182 [M]+.

IR (ATR, neat): λ⁻¹: 3004, 2956, 2836, 1574, 1454, 1398, 1325, 1218, 1204, 1155, 1118, 1090, 1041, 1009, 947, 809, 777, 698 cm⁻¹.

(ortho-Bromophenyl)dimethylvinylsilane (37)[9]

Under an atmosphere of argon, an oven-dried Schlenk flask equipped with a rubber septum was charged with o-dibromobenzene (7.20 g, 30.00 mmol) and a mixture of dry THF and dry Et₂O (1/1, 100 mL). After the mixture had been cooled to −110 °C (cool bath: THF/Et₂O, 1:1 + liquid nitrogen), n-BuLi (2.5 mol/L in n-hexane, 12.8 mL, 32.00 mmol) was added dropwise within 0.5 h and the resulting mixture was stirred at −110 °C for 1 h. At the same temperature, chlorodimethylvinylsilane (5.43 g, 15.00 mmol) was added within 0.5 h and after stirring for 1 h at −110 °C, the reaction mixture was stirred over night at ambient temperature. The reaction was hydrolyzed with saturated NH₄Cl solution (100 mL), the layers were separated and the aqueous layer was extracted with Et₂O (3 × 100 mL). Afterwards, the combined organic layers were washed with brine (100 mL), dried with MgSO₄ and the solvent was evaporated under reduced pressure. The residue was purified by flash chromatography (SiO₂, PE) to afford 37 (5.26 g, 21.81 mmol, 73 %) as a colorless liquid. Rf = 0.41 (SiO₂, PE). ¹H NMR (500 MHz, CDCl₃): δ = 7.53 (d, J = 7.9 Hz, 1 H), 7.45 (d, J = 7.3 Hz, 1 H), 7.27 (t, J = 7.3 Hz, 1 H), 7.20 (t, J = 7.6 Hz, 1 H), 6.45 (dd, J = 20.4, 14.7 Hz, 1 H), 6.09 (dd, J = 14.7, 3.5 Hz, 1 H), 5.80 (dd, J
\[ 13^1\text{H} \text{NMR (125 MHz, DEPT, CDCl}_3\]): \delta = 139.8 (C), 137.6 (CH), 136.7 (CH), 132.9 (CH), 132.8 (CH\textsubscript{2}), 130.9 (CH), 130.6 (C), 126.4 (CH), \sim 2.3 (\text{CH}_3) \text{ ppm.} \]

**N-(2-(Trimethylsilyl)propyl)aniline (38a)**

General procedure A was used to synthesize compounds 38a and 38b from trimethylvinylsilane (2) and N-methylaniline (3). After purification by flash chromatography (PE/MTBE, 80:1), a mixture of 38a and 38b (240 mg, 1.16 mmol, 58 %, 38a/38b = 97:3) was isolated as a colorless oil. \( R_f = 0.14 \) (SiO\textsubscript{2}, PE/MTBE, 80:1). Major regioisomer 28a: \( ^1\text{H} \text{NMR (500 MHz, CDCl}_3\): \delta = 7.20-7.15 (m, 2 H), 6.69 (t, \( J = 7.3 \text{ Hz}, 1 \text{ H}), 6.60 \text{ (d, } J = 7.5 \text{ Hz, 2 H}), 3.70 \text{ (br. s, 1 H), 3.33-3.26 (m, 1 H), 2.98-2.90 (m, 1 H), 1.07-1.02 \text{ (m, 4 H), 0.04 (s, 9 H) ppm.} \)

\[ ^{13}\text{C}^1\text{H} \text{ NMR (125 MHz, DEPT, CDCl}_3\): \delta = 148.6 (C), 129.2 (CH), 117.1 (CH), 112.8 (CH), 46.7 (CH\textsubscript{2}), 12.8 (CH\textsubscript{3}), \sim 3.1 (\text{CH}_3) \text{ ppm.} \]

**N-(2-(Triphenylsilyl)propyl)aniline (39a)**

General procedure A with complex II (109 mg, 0.20 mmol, 10 mol%) as the catalyst and a reaction temperature of 140 °C was used to synthesize compound 39a from triphenylvinylsilane (33) and N-methylaniline (3). After purification by flash chromatography (PE/MTBE, 40:1), 39a (530 mg, 1.35 mmol, 67 %) was isolated as a colorless solid. In addition, a second fraction that contained a mixture of 39a and 39b (66 mg, 0.17 mmol, 39a/39b = 29:71) was also isolated. \( R_f = 0.15 \) (SiO\textsubscript{2}, PE/MTBE, 40:1). \( ^1\text{H} \text{ NMR (500 MHz, CDCl}_3\): \delta = 7.61 (dd, \( J = 7.9, 1.5 \text{ Hz}, 6 \text{ H}), 7.47-7.42 (m, 3 \text{ H}), 7.40 \text{ (t, } J = 7.1 \text{ Hz, 6 H}), 7.13 \text{ (t, } J = 7.8 \text{ Hz, 2 H}), 6.67 \text{ (t, } J = 7.3 \text{ Hz, 1 H}), 6.43 \text{ (d, } J = 7.6 \text{ Hz, 2 H}), 3.67 \text{ (br. s, 1 H), 3.52 (dd, } J = 12.3, 4.2 \text{ Hz, 1 H}), 3.15 \text{ (dd, } J = 12.3, 9.3 \text{ Hz, 1 H}), 2.09 \text{ (ddq, } J = 13.4, 7.4, 4.3 \text{ Hz, 1 H}), 1.27 \text{ (d, } J = 7.4 \text{ Hz, 3 H) ppm.} \)

\[ ^{13}\text{C}^1\text{H} \text{ NMR (125 MHz, DEPT, CDCl}_3\): \delta = 148.1 (C), 136.0 (CH), 133.8 (C), 129.6 (CH), 129.1 (CH), 128.0 (CH), 117.0 (CH), 112.8 (CH), 46.8 (CH\textsubscript{2}), 18.4 (CH), 14.0 (CH\textsubscript{3}) \text{ ppm.} \)

\[ ^1\text{H}^{29}\text{Si HMBC NMR (500 MHz, 99.4 MHz, CDCl}_3\): \delta = \sim 9.9 \text{ ppm. GC/MS (El, 70 eV): m/z (\% = 393 (2) [M]+, 315 (2), 259 (17) [C}_{18}H_{13}Si]+, 181 (10), 106 (100) [C}_{7}H_{8}N]+. HRMS (El, 70 eV): calcd. (C_{27}H_{27}NSi) 393.1907, found 393.1916 [M]+. IR (ATR, neat): \lambda^{-1} = 3412, 3069, 3044, 2928, 2874, 1600, 1500, 1462, 1426, 1380, 1302, 1258, 1190, 1181, 1131, 1107, 1078, 1054, 997, 973, 867, 750, 744, 727, 699 \text{ cm}^{-1.} \]
**N-(2-((4-Methoxyphenyl)dimethylsilyl)propyl)aniline (40a)**

![Chemical Structure](attachment:image.png)

General procedure A was used to synthesize compound 40a from (4-methoxyphenyl)dimethylvinylsilane (34) and N-methylaniline (3). After purification by flash chromatography (PE/MTBE, 40:1), 40a (497 mg, 1.66 mmol, 83 %) was isolated as a light yellow oil. In addition, a second fraction that contained a mixture of 40a and 40b (41 mg, 0.14 mmol, 40a/40b = 37:63) was also isolated. Rf = 0.13 (SiO2, PE/MTBE, 40:1). 1H NMR (500 MHz, CDCl3): δ = 7.49 (d, J = 8.1 Hz, 2 H), 7.16 (t, J = 7.7 Hz, 2 H), 6.97 (d, J = 8.2 Hz, 2 H), 6.69 (t, J = 7.2 Hz, 1 H), 6.49 (d, J = 8.2 Hz, 2 H), 3.85 (s, 3 H), 3.58 (br. s, 1 H), 3.27 (dd, J = 12.1, 5.0 Hz, 1 H), 2.98 (dd, J = 11.9, 9.3 Hz, 1 H), 1.34-1.22 (m, 1 H), 1.08 (d, J = 7.4 Hz, 3 H), 0.34 (s, 6 H) ppm. 13C{1H} NMR (125 MHz, DEPT, CDCl3): δ = 160.5 (C), 148.3 (C), 135.3 (CH), 129.1 (CH), 128.5 (C), 116.9 (CH), 113.6 (CH), 112.6 (CH), 55.0 (CH3), 46.7 (CH2), 20.4 (CH), 13.1 (CH3), −4.3 (CH3), −5.1 (CH3) ppm. 29Si{1H} NMR (99.4 MHz, INEPT, CDCl3): δ = −1.2 ppm. MS (El, 70 eV): m/z (%) = 299 (14) [M]+, 242 (25), 191 (14), 165 (85) [C29H31OSi]−, 106 (100) [C29H29N]+, 77 (7). HRMS (El, 70 eV): calcd. (C31H31BrSiO) 299.1700, found 299.1701 [M]+. IR (ATR, neat): λ = 3410, 3049, 3018, 2952, 2903, 2864, 2835, 1594, 1564, 1502, 1463, 1313, 1276, 1245, 1181, 1110, 1030, 990, 867, 808, 769, 747, 691 cm−1.

**N-(2-((2-Bromophenyl)dimethylsilyl)propyl)aniline (43a)**

![Chemical Structure](attachment:image.png)

General procedure A was used to synthesize compound 43a from (ortho-bromophenyl)dimethylvinylsilane (37) and N-methylaniline (3). After purification by flash chromatography (PE/MTBE, 60:1), 43a (410 mg, 1.18 mmol, 58 %) was isolated as a colorless oil. In addition, a second fraction that contained a mixture of 43a and 43b (60 mg, 0.17 mmol, 43a/43b = 50:50) was also isolated. Rf = 0.27 (PE/MTBE, 60:1). 1H NMR (500 MHz, CDCl3): δ = 7.55 (dd, J = 7.9, 0.9 Hz, 1 H), 7.41 (dd, J = 7.3, 1.8 Hz, 1 H), 7.29 (td, J = 7.3, 1.1 Hz, 1 H), 7.23 (td, J = 7.6, 1.8 Hz, 1 H), 7.13 (dd, J = 8.4, 7.4 Hz, 2 H), 6.66 (t, J = 7.3 Hz, 1 H), 6.48 (d, J = 7.9 Hz, 2 H), 3.20 (dd, J = 12.1, 5.6 Hz, 1 H), 2.98 (dd, J = 12.1, 9.5 Hz, 1 H), 1.88-1.78 (m, 1 H), 1.05 (d, J = 7.4 Hz, 3 H), 0.42 (s, 3 H), 0.42 (s, 3 H) ppm. 13C{1H} NMR (125 MHz, DEPT, CDCl3): δ = 148.3 (C), 139.3 (C), 136.8 (CH), 133.0 (CH), 131.0 (CH), 130.4 (C), 129.1 (CH), 126.5 (CH), 117.0 (CH), 112.8 (CH), 46.9 (CH3), 19.0 (CH), 13.1 (CH3), −3.7 (CH3), −4.1 (CH3) ppm. 29Si{1H} NMR (99.4 MHz, INEPT, CDCl3): δ = 3.1 ppm. GC/MS (El, 70 eV): m/z (%) = 349 (4) [M(81Br)]+, 347 (4) [M(79Br)]+, 212 (10) [C9H1081BrSi]+, 210 (11) [C9H1079BrSi]+, 133 (11), 106 [C7H7N]+, 91 (20), 77 (10) [C6H8]+. HRMS (El): calcd. (C17H22BrNSi) 347.0699, found 347.0707 [M]+. IR (ATR, neat): λ = 3054, 2949, 1601, 1504, 1410, 1316, 1250, 1120, 1103, 1017, 835, 811, 771, 744, 690 cm−1.
General Procedure B for the one-pot procedure for the formation of 1,4-benzoazasilines: An oven-dried Schlenk tube equipped with a Teflon stopcock and a magnetic stirring bar was transferred into a nitrogen-filled glovebox and charged with catalyst III (154 mg, 0.20 mmol, 10 mol%) and toluene (0.5 mL). Afterwards, the N-methylaniline (2.00 mmol), (ortho-bromophenyl)dimethylvinylsilane (37, 2.20 mmol) and toluene (0.5 mL) were added. After the mixture had been heated to 160 °C for 24 h, the Schlenk tube was cooled to room temperature and transferred back into a nitrogen-filled glovebox. Then Pd$_2$(dba)$_3$ (46 mg, 0.05 mmol, 2.5 mol%), RuPhos (66 mg, 0.1 mmol, 7 mol%), NaO'Bu (288 mg, 3.0 mmol) and toluene (5 mL) were added. After heating the mixture to 110 °C for additional 24 h, the crude product was purified by flash chromatography (SiO$_2$).

3,4,4-Trimethyl-1-phenyl-1,2,3,4-tetrahydrobenzo[b][1,4]azasiline (44a)

General procedure B was used to synthesize compound 44a from (ortho-bromophenyl)dimethylvinylsilane (37) and N-methylaniline (3). After purification by flash chromatography (PE), 44a (420 mg, 1.57 mmol, 79 %) was isolated as a colorless oil. R$_f$ = 0.20 (SiO$_2$, PE). $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ = 7.39 (dd, $J$ = 7.2, 1.5 Hz, 1 H), 7.32 (t, $J$ = 7.9 Hz, 2 H), 7.16 (d, $J$ = 7.5 Hz, 2 H), 7.10-7.03 (m, 2 H), 6.83 (td, $J$ = 7.2, 0.6 Hz, 1 H), 6.66 (d, $J$ = 8.4 Hz, 1 H), 3.85 (dd, $J$ = 13.1, 3.6 Hz, 1 H), 3.55 (dd, $J$ = 13.1, 9.6 Hz, 1 H), 1.30-1.23 (m, 1 H), 1.04 (d, $J$ = 7.5 Hz, 3 H), 0.28 (s, 3 H), 0.26 (s, 3 H) ppm. $^{13}$C($^1$H) NMR (125 MHz, DEPT, CDCl$_3$): $\delta$ = 154.1 (C), 149.6 (C), 135.1 (CH), 129.5 (CH), 129.4 (CH), 124.7 (CH), 123.6 (C), 123.1 (CH), 119.2 (CH), 117.8 (CH), 57.5 (CH$_3$), 17.9 (CH), 13.0 (CH$_3$), −1.7 (CH$_3$), −4.4 (CH$_3$) ppm. $^{29}$Si($^1$H) NMR (99.4 MHz, INEPT, CDCl$_3$): $\delta$ = −8.1 ppm. GC/MS (EI, 70 eV): m/z (%) = 267 (40) [M]$^+$, 225 (100) [C$_{14}$H$_{15}$NSi]$^+$, 210 (40), 180 (8), 105 (11) [C$_7$H$_7$N]$^+$, 91 (5) [C$_8$H$_5$N]$^+$. HRMS (EI): calcd. (C$_{17}$H$_{21}$NSi) 267.1438, found 267.1440 [M]$^+$.

IR (ATR, neat): $\lambda$ nm $^{-1}$ = 2948, 2864, 1585, 1557, 1494, 1472, 1431, 1340, 1248, 1175, 1129, 1088, 835, 808, 722, 750, 696, 610.

3,4,4-Trimethyl-1-(3-methylphenyl)-1,2,3,4-tetrahydrobenzo[b][1,4]azasiline (45a)

General procedure B was used to synthesize compound 45a from (ortho-bromophenyl)dimethylvinylsilane (37) and 3,N-dimethylaniline (6). After purification by flash
chromatography (PE), 45a (290 mg, 1.03 mmol, 52 %) was isolated as a colorless oil. Rf = 0.13 (SiO2, PE). 1H NMR (500 MHz, CDCl3): δ = 7.37 (dd, J = 7.2, 1.6 Hz, 1 H), 7.21 (t, J = 7.7 Hz, 1 H), 7.09-7.03 (m, 1 H), 6.99 (s, 1 H), 6.96 (d, J = 7.8 Hz, 1 H), 6.89 (d, J = 7.5 Hz, 1 H), 6.81 (td, J = 7.1, 0.6 Hz, 1 H), 6.63 (d, J = 8.4 Hz, 1 H), 3.81 (dd, J = 13.1, 3.6 Hz, 1 H), 3.53 (dd, J = 13.1, 9.6 Hz, 1 H), 2.32 (s, 3 H), 1.33-1.19 (m, 1 H), 1.03 (d, J = 7.5 Hz, 3 H), 0.27 (s, 3 H), 0.25 (s, 3 H) ppm. 13C[1H] NMR (125 MHz, DEPT, CDCl3): δ = 154.2 (C), 149.5 (C), 139.2 (C), 135.0 (CH), 129.5 (CH), 129.2 (CH), 125.6 (CH), 124.1 (CH), 123.3 (C), 121.9 (CH), 118.9 (CH), 117.6 (CH), 57.5 (CH2), 21.4 (CH), 17.9 (CH3), 13.0 (CH3), –1.7 (CH3), –4.4 (CH3) ppm. 29Si[1H] NMR (99.4 MHz, INEPT, CDCl3): δ = –8.4 ppm. GC/MS (El, 70 eV): m/z (%) = 281 (26) [M]+, 239 (100) [C15H17NSi]+, 223 (30) [C16H17N]+, 180 (14), 105 (24) [C7H7N]+. HRMS (El, 70 eV): calcld. (C18H23NSi) 281.1594, found 281.1602 [M]+. IR (ATR, neat): λ1 = 3055, 2951, 2865, 1602, 1583, 1557, 1487, 1472, 1433, 1341, 1295, 1277, 1264, 1248, 1165, 1129, 1085, 837, 808, 773, 753, 744, 720, 701, 650, 637, 617 cm−1.

3,4,4-Trimethyl-1-(4-methylphenyl)-1,2,3,4-tetrahydrobenzo[b][1,4]azasiline (46a)

General procedure B was used to synthesize compound 46a from (ortho-bromophenyl)dimethylvinylsilane (37) and 4,N-dimethylaniline (7). After purification by flash chromatography (PE), 46a (270 mg, 0.96 mmol, 48 %) was isolated as a colorless oil. Rf = 0.12 (SiO2, PE). 1H NMR (500 MHz, CDCl3): δ = 7.37 (dd, J = 7.2, 1.8 Hz, 1 H), 7.17-7.14 (m, 2 H), 7.09-7.03 (m, 3 H), 6.78 (dt, J = 7.2, 0.9 Hz, 1 H), 6.57 (d, J = 8.4 Hz, 1 H), 3.79 (dd, J = 13.0, 3.5 Hz, 1 H), 3.54 (dd, J = 13.0, 9.4 Hz, 1 H), 2.35 (s, 3 H), 1.27-1.20 (m, 1 H), 1.04 (d, J = 7.5 Hz, 3 H), 0.29 (s, 3 H), 0.25 (s, 3 H) ppm. 13C[1H] NMR (125 MHz, DEPT, CDCl3): δ = 154.4 (C), 147.1 (C), 135.0 (CH), 133.2 (C), 130.1 (CH), 129.5 (CH), 125.4 (CH), 122.5 (C), 118.4 (CH), 116.9 (CH), 57.8 (CH3), 20.9 (CH), 17.8 (CH3), 13.0 (CH3), –1.7 (CH3), –4.4 (CH3) ppm. 29Si[1H] NMR (99.4 MHz, INEPT, CDCl3): δ = –8.6 ppm. GC/MS (El, 70 eV): m/z (%) = 281 (27) [M]+, 239 (100) [C15H17NSi]+, 223 (26) [C16H17N]+, 180 (12), 119 (24) [C9H9N]+, 105 (19) [C7H7N]+, 91 (19) [C7H7]+. HRMS (El, 70 eV): calcld. (C18H23NSi) 281.1594, found 281.1592 [M]+. IR (ATR, neat): λ1 = 3064, 3022, 2939, 2920, 2897, 2865, 2826, 1583, 1556, 1471, 1430, 1364, 1335, 1313, 1293, 1277, 1254, 1175, 1128, 1114, 1084, 1033, 988, 973, 886, 840, 806, 776, 756, 744, 724, 718, 702, 691, 666, 628, 608 cm−1.
3,4,4-Trimethyl-1-(3-fluorophenyl)-1,2,3,4-tetrahydrobenzo[b][1,4]azasiline (47a)

General procedure B was used to synthesize compound 47a from (ortho-bromophenyl)dimethylvinylsilane (37) and N-methyl-3-fluoroaniline (8). After purification by flash chromatography (PE), 47a (278 mg, 0.97 mmol, 49 %) was isolated as a slightly beige oil. \( R_f = 0.15 \) (SiO\(_2\), PE). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 7.40 \) (dd, \( J = 7.3, 1.5 \) Hz, 1 H), 7.23-7.06 (m, 2 H), 6.91 (td, \( J = 7.1, 2.9 \) Hz, 1 H), 6.88-6.82 (m, 2 H), 6.79 (td, \( J = 8.2, 2.6 \) Hz, 1 H), 3.86 (dd, \( J = 13.4, 3.7 \) Hz, 1 H), 3.47 (dd, \( J = 13.2, 10.0 \) Hz, 1 H), 1.32-1.21 (m, 1 H), 1.00 (d, \( J = 7.7 \) Hz, 3 H), 0.22 (s, 6 H) ppm.

\(^13\)C\{\(^1\)H\} NMR (125 MHz, DEPT, CDCl\(_3\)): \( \delta = 163.7 \) (d, \( ^1J_{C,F} = 245 \) Hz, C), 153.1 (C), 151.2 (d, \( ^3J_{C,F} = 10 \) Hz, C), 135.1 (CH), 130.2 (d, \( ^3J_{C,F} = 10 \) Hz, CH), 129.6 (CH), 126.1 (C), 120.9 (CH), 119.9 (CH), 117.9 (CH), 109.3 (d, \( ^2J_{C,F} = 23 \) Hz, CH), 108.4 (d, \( ^2J_{C,F} = 21 \) Hz, CH), 56.8 (CH\(_2\)), 18.1 (CH), 13.1 (CH\(_3\)), \(-1.7 \) (CH\(_3\)), \(-4.7 \) (CH\(_3\)) ppm. \(^19\)F\{\(^1\)H\} NMR (470 MHz, CDCl\(_3\)): \( \delta = \) \(-112.2 \) ppm. MS (EI, 70 eV): \( m/z \) (%) = 285 (82) [M]+, 244 (64), 243 (100) [C\(_{14}\)H\(_{14}\)FNSi]+, 228 (37) [C\(_{13}\)H\(_{11}\)FNSi]+, 166 (29), 77 (17) [C\(_6\)H\(_5\)]+. HRMS (EI, 70 eV): calcd. (C\(_{17}\)H\(_{20}\)FNSi) 285.1344, found 285.1348 [M]+.

IR (ATR, neat): \( \lambda \) = 3057, 2997, 2952, 2901, 2866, 1608, 1585, 1558, 1486, 1472, 1431, 1346, 1296, 1278, 1260, 1248, 1191, 1147, 1129, 1087, 927, 837, 808, 773, 757, 744, 725, 693 cm\(^{-1}\).

3,4,4-Trimethyl-1-(4-fluorophenyl)-1,2,3,4-tetrahydrobenzo[b][1,4]azasiline (48a)

General procedure B was used to synthesize compound 48a from (ortho-bromophenyl)dimethylvinylsilane (37) and N-methyl-4-fluoroaniline (9). After purification by flash chromatography (PE), 48a (322 mg, 1.13 mmol, 56 %) was isolated as a slightly beige oil. \( R_f = 0.18 \) (SiO\(_2\), PE). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \( \delta = 7.40 \) (dd, \( J = 7.2, 1.5 \) Hz, 1 H), 7.17-7.13 (m, 2 H), 7.10-7.04 (m, 3 H), 6.83 (t, \( J = 7.0 \) Hz, 1 H), 6.52 (d, \( J = 8.4 \) Hz, 1 H), 3.78 (dd, \( J = 13.0, 3.4 \) Hz, 1 H), 3.55 (dd, \( J = 12.9, 9.3 \) Hz, 1 H), 1.33-1.19 (m, 1 H), 1.08 (d, \( J = 7.4 \) Hz, 3 H), 0.32 (s, 3 H), 0.28 (s, 3 H) ppm. \(^13\)C\{\(^1\)H\} NMR (125 MHz, DEPT, CDCl\(_3\)): \( \delta = 159.4 \) (d, \( ^1J_{C,F} = 242 \) Hz, C), 154.3 (C), 145.7 (C), 135.1 (CH), 129.6 (CH), 127.2 (d, \( ^3J_{C,F} = 8 \) Hz, CH), 122.6 (C), 118.7 (CH), 116.6 (CH), 116.2 (d, \( ^2J_{C,F} = 22 \) Hz, CH), 58.1 (CH\(_2\)), 17.8 (CH), 13.0 (CH\(_3\)), \(-1.7 \) (CH\(_3\)), \(-4.4 \) (CH\(_3\)) ppm. \(^19\)F\{\(^1\)H\} NMR (470 MHz, CDCl\(_3\)):
CDCl$_3$): $\delta = -119.0$ ppm. $^{29}$Si($^1$H) NMR (99.4 MHz, INEPT, CDCl$_3$): $\delta = -8.3$ ppm. GC/MS (EI, 70 eV): $m/z$ (%) = 285 (26) [M$^+$], 243 (100) [C$_{14}$H$_{14}$FNSi]$^+$, 228 (20) [C$_{13}$H$_{11}$FNSi]$^+$, 198 (6), 121 (8). HRMS (EI, 70 eV): calcd. (C$_{17}$H$_{20}$FNSi) 285.1344, found 285.1351 [M$^+$].

IR (ATR, neat): $\lambda$ = 3047, 2993, 2952, 2872, 2834, 1584, 1557, 1504, 1473, 1433, 1366, 1336, 1304, 1278, 1253, 1243, 1229, 1214, 1180, 1151, 1131, 1085, 1068, 1017, 973, 881, 868, 832, 805, 772, 755, 740, 725, 717, 692, 669, 626 cm$^{-1}$.

3,4,4-Trimethyl-1-(3-chlorophenyl)-1,2,3,4-tetrahydrobenzo[b][1,4]azasiline (49a)

General procedure B was used to synthesize compound 49a from (ortho-bromophenyl)dimethylvinylsilane (37) and N-methyl-3-chloroaniline (10). After purification by flash chromatography (PE), 49a (250 mg, 0.83 mmol, 41 %) was isolated as a slightly beige oil. $R_f = 0.22$ (SiO$_2$, PE). $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 7.41$ (dd, $J = 7.2, 1.6$ Hz, 1 H), 7.18 (t, $J = 8.1$ Hz, 1 H), 7.16–7.08 (m, 2 H), 7.00 (dd, $J = 8.2, 2.2$ Hz, 1 H), 6.97–6.88 (m, 2 H), 6.79 (d, $J = 8.3$ Hz, 1 H), 3.86 (dd, $J = 13.3, 3.9$ Hz, 1 H), 3.50 (dd, $J = 13.3, 9.8$ Hz, 1 H), 1.27 (ddq, $J = 3.9, 7.6, 10.0$ Hz, 1 H), 1.02 (d, $J = 7.5$ Hz, 3 H), 0.25 (s, 3 H), 0.24 (s, 3 H) ppm. $^{13}$C($^1$H) NMR (125 MHz, DEPT, CDCl$_3$): $\delta = 153.1$ (C), 150.7 (C), 135.1 (CH), 134.8 (C), 130.2 (CH), 129.7 (CH), 125.7 (C), 122.9 (CH), 122.0 (CH), 121.0 (CH), 120.7 (CH), 119.4 (CH), 57.0 (CH$_2$), 18.1 (CH), 13.1 (CH$_3$), $-1.7$ (CH$_3$), $-4.6$ (CH$_3$) ppm.

IR (ATR, neat): $\lambda$ = 3059, 2951, 2896, 2866, 1593, 1584, 1557, 1474, 1434, 1295, 1276, 1249, 1084, 837, 809, 775, 700, 632 cm$^{-1}$.

3,4,4-Trimethyl-1-(4-chlorophenyl)-1,2,3,4-tetrahydrobenzo[b][1,4]azasiline (50a)

General procedure B was used to synthesize compound 50a from (ortho-bromophenyl)dimethylvinylsilane (37) and N-methyl-4-chloroaniline (11). After purification by flash chromatography (PE), 50a (180 mg, 0.60 mmol, 30 %) was isolated as a colorless solid. $R_f = 0.21$ (SiO$_2$, PE). $^1$H NMR (500 MHz, CDCl$_3$): $\delta = 7.39$ (dd, $J = 7.4, 1.7$ Hz, 1 H), 7.26-7.23 (m, 2 H), 7.11-
7.06 (m, 3 H), 6.86 (t, J = 7.2 Hz, 1 H), 6.68 (d, J = 8.3 Hz, 1 H), 3.81 (dd, J = 13.2, 3.7 Hz, 1 H), 3.51 (dd, J = 13.2, 9.5 Hz, 1 H), 1.29-1.21 (m, 1 H), 1.02 (d, J = 7.4 Hz, 3 H), 0.26 (s, 3 H), 0.24 (s, 3 H) ppm. \(^{13}\)C\(^{1}\)H NMR (125 MHz, DEPT, CDCl\(_3\)): \(\delta = 153.5\) (C), 148.2 (C), 135.1 (CH), 129.6 (CH), 129.4 (CH), 127.6 (C), 125.2 (CH), 124.6 (C), 119.9 (CH), 118.4 (CH), 57.4 (CH\(_2\)), 18.0 (CH), 13.1 (CH\(_3\)), –1.7 (CH\(_3\)), –4.5 (CH\(_3\)) ppm. \(^{29}\)Si\(^{1}\)H NMR (99.4 MHz, INEPT, CDCl\(_3\)): \(\delta = –8.0\) ppm. GC/MS (EI, 70 eV): \(m/z\) (%) = 301 (27) [M]\(^+\), 259 (100) [C\(_{14}\)H\(_{14}\)ClNSi]\(^+\), 209 (8), 166 (18) [C\(_{12}\)H\(_{8}\)N]\(^+\), 93 (32) [C\(_6\)H\(_7\)N]\(^+\).

HRMS (EI, 70 eV): calcd. (C\(_{17}\)H\(_{20}\)ClNSi) 301.1048, found 301.1054 [M]\(^+\).

IR (ATR, neat): \(\lambda = 3066, 2951, 2920, 2897, 2866, 2830, 1581, 1555, 1487, 1471, 1427, 1365, 1336, 1304, 1275, 1254, 1175, 1128, 1109, 1082, 990, 973, 836, 805, 758, 723, 702, 621, 610 \text{ cm}^{-1}.

3,4,4-Trimethyl-1-(4-methoxyphenyl)-1,2,3,4-tetrahydrobenzo[b][1,4]azasiline (51a)

General procedure B was used to synthesize compound 51a from (ortho-bromophenyl)dimethylvinylsilane (37) and N-methyl-4-methoxyaniline (14). After purification by flash chromatography (PE/MTBE, 80:1), 51a (289 mg, 0.97 mmol, 49%) was isolated as a colorless solid. \(R_f = 0.10\) (SiO\(_2\), PE/MTBE, 80:1). \(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta = 7.37\) (dd, J = 7.2, 1.7 Hz, 1 H), 7.15-7.11 (m, 2 H), 7.04 (ddd, J = 8.6, 7.1, 1.7 Hz, 1 H), 6.76 (td, J = 7.2, 0.9 Hz, 1 H), 6.44 (d, J = 8.3 Hz, 1 H), 3.84 (s, 3 H), 3.74 (dd, J = 12.9, 3.4 Hz, 1 H), 3.53 (dd, J = 12.9, 9.2 Hz, 1 H), 1.30-1.19 (m, 1 H), 1.08 (d, J = 7.4 Hz, 3 H), 0.31 (s, 3 H), 0.28 (s, 3 H) ppm. \(^{13}\)C\(^{1}\)H NMR (125 MHz, DEPT, CDCl\(_3\)): \(\delta = 156.6\) (C), 154.8 (C), 142.7 (C), 135.1 (CH), 129.6 (CH), 127.7 (CH), 121.3 (C), 117.8 (CH), 115.8 (CH), 114.9 (CH), 58.3 (CH\(_2\)), 55.5 (CH\(_3\)), 17.7 (CH), 12.9 (CH\(_3\)), –1.7 (CH\(_3\)), –4.3 (CH\(_3\)) ppm. \(^{29}\)Si\(^{1}\)H NMR (99.4 MHz, INEPT, CDCl\(_3\)): \(\delta = –8.6\) ppm. MS (EI, 70 eV): \(m/z\) (%) = 297 (89) [M]\(^+\), 255 (100) [C\(_{15}\)H\(_{13}\)NOSi]\(^+\), 240 (100) [C\(_{14}\)H\(_{12}\)NOSi]\(^+\), 212 (18), 197 (12) [C\(_{13}\)H\(_{11}\)NO]\(^+\), 166 (12). 127 (26). HRMS (EI, 70 eV): calcd. (C\(_{18}\)H\(_{20}\)NSiO) 297.1543, found 297.1543 [M]\(^+\). IR (ATR, neat): \(\lambda = 3059, 3037, 2995, 2960, 2902, 2868, 2836, 1584, 1555, 1505, 1473, 1431, 1328, 1296, 1276, 1235, 1180, 1127, 1108, 1085, 1015, 989, 971, 836, 807, 793, 775, 750, 719, 699, 668, 626, 610 \text{ cm}^{-1}.\)
3,4,4-Trimethyl-1-(4-(trifluoromethoxy)phenyl)-1,2,3,4-tetrahydrobenzo[b][1,4]azasiline (52a)

General procedure B was used to synthesize compound 52a from (ortho-bromophenyl)dimethylvinylsilane (37) and N-methyl-4-(trifluoromethoxy)aniline (15). After purification by flash chromatography (PE/MTBE, 80:1), 52a (231 mg, 0.66 mmol, 33 %) was isolated as a light yellow oil. Rf = 0.27 (SiO2, PE/MTBE, 80:1). 1H NMR (500 MHz, CDCl3): δ = 7.47 (dd, J = 7.3, 1.6 Hz, 1 H), 7.20 (s, 4 H), 7.16 (dd, J = 8.8, 7.2, 1.7 Hz, 1 H), 6.94 (t, J = 7.2 Hz, 1 H), 6.76 (d, J = 8.2 Hz, 1 H), 3.91 (dd, J = 13.1, 3.8 Hz, 1 H), 3.59 (dd, J = 13.2, 9.7 Hz, 1 H), 1.40-1.30 (m, 1 H), 1.10 (d, J = 7.5 Hz, 3 H), 0.34 (s, 3 H), 0.33 (s, 3 H) ppm.

13C{1H} NMR (125 MHz, DEPT, CDCl3): δ = 153.6 (C), 148.3 (C), 144.2 (C), 135.2 (CH), 129.7 (CH), 124.9 (CH), 124.7 (C), 122.1 (CH), 120.6 (q, 1JCF = 256 Hz) 120.1 (CH), 118.4 (CH), 57.4 (CH2), 18.0 (CH), 13.0 (CH3), −1.8 (CH3), −4.6 (CH3) ppm.

19F{1H} NMR (470 MHz, CDCl3): δ = −58.1 ppm.

29Si{1H} NMR (99.4 MHz, INEPT, CDCl3): δ = −7.9 ppm.

GC/MS (EI, 70 eV): m/z (%) = 351 (47) [M]+, 309 (100) [C15H14F3NOSi]+, 240 (16), 212 (6), 166 (6), 69 (10). HRMS (EI, 70 eV): calcd. (C18H20F3NOSi) 351.1261, found 351.1264 [M]+.

IR (ATR, neat): λmax = 3049, 3000, 2955, 2901, 2868, 1587, 1504, 1473, 1434, 1434, 1247, 1220, 1203, 1158, 1084, 835, 805, 774, 744, 694, 612 cm⁻¹.

3,4,4-Trimethyl-1-(4-(methylthio)phenyl)-1,2,3,4-tetrahydrobenzo[b][1,4]azasiline (53a)

General procedure B was used to synthesize compound 53a from (ortho-bromophenyl)dimethylvinylsilane (37) and N-methyl-4-(methylthio)aniline (16). After purification by flash chromatography (PE/MTBE, 30:1), 53a (293 mg, 0.93 mmol, 47 %) was isolated as a light yellow oil. Rf = 0.32 (SiO2, PE/MTBE, 30:1). 1H NMR (500 MHz, CDCl3): δ = 7.42 (dd, J = 7.2, 1.8 Hz, 1 H), 7.28 (d, J = 8.5 Hz, 2 H), 7.13 (d, J = 8.5 Hz, 2 H), 7.10 (dd, J = 8.5, 1.5 Hz, 1 H), 6.87 (t, J = 7.4 Hz, 1 H), 6.70 (d, J = 8.4 Hz, 1 H), 3.85 (dd, J = 13.1, 3.6 Hz, 1 H), 3.56 (dd, J = 13.1, 9.5 Hz, 1 H), 2.51 (s, 3 H), 1.33-1.25 (m, 1 H), 1.07 (d, J = 7.5 Hz, 3 H), 0.31 (s, 3 H), 0.29 (s, 3 H) ppm. 13C{1H} NMR (125 MHz, DEPT, CDCl3): δ = 153.8 (C), 147.3 (C), 135.1 (CH), 131.8 (C), 129.6 (CH), 128.8 (CH), 125.0 (CH), 123.8 (C), 119.3 (CH), 117.9 (CH), 57.4 (CH2), 17.9 (CH), 17.0 (CH3), 13.0 (CH3), −1.7 (CH3), −
4.5 (CH$_3$) ppm. $^{29}$Si($^1$H) NMR (99.4 MHz, INEPT, CDCl$_3$): $\delta = -8.1$ ppm. MS (EI, 70 eV): $m/z$ (%) = 313 (98) [M]$^+$, 271 (100) [C$_{15}$H$_7$NSSi]$^+$, 256 (99) [C$_{14}$H$_{14}$NSSi]$^+$, 244 (39), 229 (14), 214 (14), 166 (26), 135 (24). HRMS (EI, 70 eV): calcd. (C$_{18}$H$_{23}$NSSi) 313.1315, found 313.1323 [M]$^+$. IR (ATR, neat): $\lambda$ cm$^{-1}$ = 3059, 2954, 2921, 2901, 2866, 1586, 1556, 1493, 1474, 1434, 1344, 1275, 1251, 1177, 1131, 1085, 970, 836, 808, 775, 755, 745, 729, 699, 623, 613.

References:
Dimethylphenylvinylsilane (1)

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C)

$^{13}$C($^1$H) NMR (125 MHz, CDCl$_3$, 25 °C)
$N$-(2-(Dimethyl(phenyl)silyl)propyl)aniline (4a)

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C)

$^{13}$C($^1$H) NMR (125 MHz, CDCl$_3$, 25 °C)
\textbf{N-(2-(Dimethyl(phenyl)silyl)propyl)-2-methylaniline (19a)}

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C)

$^{13}$C($^1$H) NMR (125 MHz, CDCl$_3$, 25 °C)
$^{29}$Si($^1$H) NMR (99.4 MHz, CDCl$_3$, 25 °C)
**N-(2-(Dimethyl(phenyl)silyl)propyl)-3-methylaniline (20a)**

\[
\begin{align*}
\text{H NMR (500 MHz, CDCl}_3\text{, 25 °C)}
\end{align*}
\]

\[
\begin{align*}
\text{C}\{\text{H}\} \text{ NMR (125 MHz, CDCl}_3\text{, 25 °C)}
\end{align*}
\]

\[\text{\textsuperscript{13}C(\text{\textsuperscript{1}H}) NMR (125 MHz, CDCl}_3\text{, 25 °C)}\]
$^{29}\text{Si}^1\text{H}}$ NMR (99.4 MHz, INEPT, CDCl$_3$, 25 °C)
N-(2-(Dimethyl(phenyl)silyl)propyl)-4-methylaniline (21a)

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C)

$^{13}$C($^1$H) NMR (125 MHz, CDCl$_3$, 25 °C)
$^{29}$Si($^1$H) NMR (99.4 MHz, INEPT, CDCl$_3$, 25 °C)
$N$-(2-(Dimethyl(phenyl)silyl)propyl)-3-fluoroaniline (22a)

$^{1}H$ NMR (500 MHz, CDCl$_3$, 25 °C)

$^{13}C(^1H)$ NMR (125 MHz, CDCl$_3$, 25 °C)
$^{19}\text{F} (^1\text{H}) \text{ NMR (470 MHz, CDCl}_3, 25 \, ^\circ\text{C})$ 

$^{29}\text{Si} (^1\text{H}) \text{ NMR (99.4 MHz, INEPT, CDCl}_3, 25 \, ^\circ\text{C})$
$N$-(2-(Dimethyl(phenyl)silyl)propyl)-4-fluoroaniline (23a)

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C)

$^{13}$C($^1$H) NMR (125 MHz, CDCl$_3$, 25 °C)
$^{19}\text{F}(^1\text{H})$ NMR (470 MHz, CDCl$_3$, 25 °C)

$^{29}\text{Si}(^1\text{H})$ NMR (99.4 MHz, CDCl$_3$, 25 °C)
$N$-(2-(Dimethyl(phenyl)silyl)propyl)-3-chloroaniline (24a)

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C)

$^{13}$C($^1$H) NMR (125 MHz, CDCl$_3$, 25 °C)

34
$^{29}$Si($^1$H) NMR (99.4 MHz, INEPT, CDCl$_3$, 25 °C)
$N$-(2-(Dimethyl(phenyl)silyl)propyl)-4-chloroaniline (25a)

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C)

$^{13}$C($^1$H) NMR (125 MHz, CDCl$_3$, 25 °C)
$^{29}\text{Si}^{[1\text{H}]} \text{NMR (99.4 MHz, CDCl}_3, 25 \, ^\circ\text{C)}$
$N$-(2-(Dimethyl(phenyl)silyl)propyl)-3-bromoaniline (26a)

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C)

$^{13}$C($^1$H) NMR (125 MHz, CDCl$_3$, 25 °C)
$^{29}\text{Si}^{[1]}\text{H} \text{ NMR (99.4 MHz, INEPT, CDCl}_3\text{, 25 °C)}$
N-(2-(Dimethyl(phenyl)silyl)propyl)-4-bromoaniline (27a)

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C)

$^{13}$C($^1$H) NMR (125 MHz, CDCl$_3$, 25 °C)
$^{29}\text{Si}[^1\text{H}]$ NMR (99.4 MHz, CDCl$_3$, 25 °C)
$N$-(2-(Dimethyl(phenyl)silyl)propyl)-4-methoxyaniline (28a)

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C)

$^{13}$C($^1$H) NMR (125 MHz, CDCl$_3$, 25 °C)
$^{29}\text{Si}^{(1)\text{H}}} \text{NMR (99.4 MHz, INEPT, CDCl}_3, 25 \, ^\circ\text{C}}$
$N$-(2-(Dimethyl(phenyl)silyl)propyl)-4-trifluoromethoxyaniline (29a)

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C)

$^{13}$C($^1$H) NMR (125 MHz, CDCl$_3$, 25 °C)
$^{19}$F($^1$H) NMR (470 MHz, CDCl$_3$, 25 °C)

$^{29}$Si($^1$H) NMR (99.4 MHz, CDCl$_3$, 25 °C)
$N$-(2-(Dimethyl(phenyl)silyl)propyl)-4-(methylthio)aniline (30a)

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C)

$^{13}$C($^1$H) NMR (125 MHz, CDCl$_3$, 25 °C)
$^{29}\text{Si}^1\text{H}}$ NMR (99.4 MHz, INEPT, CDCl$_3$, 25 °C)
$N$-(2-(Dimethyl(phenyl)silyl)propyl)$-N$-cyclohexylamine (31a)

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C)

$^{13}$C($^1$H) NMR (125 MHz, CDCl$_3$, 25 °C)
$^{29}\text{Si}[^1\text{H}]$ NMR (99.4 MHz, INEPT, CDCl$_3$, 25 °C)
N-(1-Phenyl-3-(dimethyl(phenyl)silyl)propyl)-N-methylamine (32b)

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C)

$^{13}$C($^1$H) NMR (125 MHz, CDCl$_3$, 25 °C)
$^{29}$Si($^1$H) NMR (99.4 MHz, CDCl$_3$, 25 °C)
Triphenylvinylsilane (33)

\[ \text{Ph} \quad \text{Ph} \]

\[ \text{Ph} \quad \text{Si} \quad \text{Ph} \]

\(^1\text{H} \text{NMR} \ (500 \text{ MHz, CDCl}_3, 25 \text{ °C})\)

\(^{13}\text{C}(^1\text{H}) \text{NMR} \ (125 \text{ MHz, CDCl}_3, 25 \text{ °C})\)
(4-Methoxyphenyl)dimethylvinylsilane (34)

\[ \text{MeO} \]

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C)

\[ \text{C}^{13}{^1}\text{H} \] NMR (125 MHz, CDCl$_3$, 25 °C)

$^{13}$C($^1$H) NMR (125 MHz, CDCl$_3$, 25 °C)
(2,6-Dimethoxyphenyl)dimethyldimethylvinylsilane (35)

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C)

$^{13}$C($^1$H) NMR (125 MHz, CDCl$_3$, 25 °C)
$^{1}H^{29}Si$ HMBC NMR (500 MHz, 99.4 MHz, CDCl$_3$, 25 °C)
(2,4,6-Trimethoxyphenyl)dimethylvinylsilane (36)

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C)

$^{13}$C($^1$H) NMR (125 MHz, CDCl$_3$, 25 °C)
$\text{H}^{29}\text{Si} \text{ HMBC NMR (500 MHz, 99.4 MHz, CDCl}_3, 25 \, ^\circ\text{C}}$
(ortho-Bromophenyl)dimethylvinylsilane (37)

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C)

$^{13}$C($^1$H) NMR (125 MHz, CDCl$_3$, 25 °C)
$N$-(2-((Trimethylsilyl)propyl)aniline (38a)

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C)

$^{13}$C($^1$H) NMR (125 MHz, CDCl$_3$, 25 °C)
$N$-(2-(Triphenylsilyl)propyl)aniline (39a)

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C)

$^{13}$C($^1$H) NMR (125 MHz, CDCl$_3$, 25 °C)
$\text{H-Si}$ HMBC NMR (500 MHz, 99.4 MHz, CDCl$_3$, 25 °C)
N-(2-((4-Methoxyphenyl)dimethylsilyl)propyl)aniline (40a)

\[ \text{MeO} \]

\[ \text{Si} \]

\[ \text{H} \]

$^1H$ NMR (500 MHz, CDCl$_3$, 25 °C)

$^{13}C(^1H)$ NMR (125 MHz, CDCl$_3$, 25 °C)
$^{29}\text{Si}[^1\text{H}]$ NMR (99.4 MHz, INEPT, CDCl$_3$, 25 °C)
N-(2-((2-Bromophenyl)dimethylsilyl)propyl)aniline (43a)

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C)

$^{13}$C($^1$H) NMR (125 MHz, CDCl$_3$, 25 °C)
$^{29}$Si($^1$H) NMR (99.4 MHz, INEPT, CDCl$_3$, 25 °C)
3,4,4-Trimethyl-1-phenyl-1,2,3,4-tetrahydrobenzo[b][1,4]azasiline (44a)

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C)

$^{13}$C($^1$H) NMR (125 MHz, CDCl$_3$, 25 °C)
$^{29}\text{Si}[^1\text{H}]$ NMR (99.4 MHz, INEPT, CDCl$_3$, 25 °C)
3,4,4-Trimethyl-1-(3-methylphenyl)-1,2,3,4-tetrahydrobenzo[\(\beta\)][1,4]azasiline (45a)

\[ \text{\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}, 25 °C)} \]

\[ \text{\textsuperscript{13}C(\textsuperscript{1}H) NMR (125 MHz, CDCl\textsubscript{3}, 25 °C)} \]
$^{29}$Si($^1$H) NMR (99.4 MHz, INEPT, CDCl$_3$, 25 °C)
3,4,4-Trimethyl-1-(4-methylphenyl)-1,2,3,4-tetrahydrobenzo[b][1,4]azasiline (46a)

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C)

$^{13}$C($^1$H) NMR (125 MHz, CDCl$_3$, 25 °C)
$^{29}$Si($^1$H) NMR (99.4 MHz, INEPT, CDCl₃, 25 °C)
3,4,4-Trimethyl-1-(3-fluorophenyl)-1,2,3,4-tetrahydrobenzo[b][1,4]azasiline (47a)

\[ \begin{align*}
\text{Si} & \quad \text{N} \\
\text{F} & \\
\end{align*} \]

\(^1\)H NMR (500 MHz, CDCl\(_3\), 25 °C)

\(^{13}\)C\(^{1}\)H NMR (125 MHz, CDCl\(_3\), 25 °C)
$^{19}\text{F}(^1\text{H})$ NMR (470 MHz, CDCl$_3$, 25 °C)

$^{29}\text{Si}(^1\text{H})$ NMR (99.4 MHz, INEPT, CDCl$_3$, 25 °C)
3,4,4-Trimethyl-1-(4-fluorophenyl)-1,2,3,4-tetrahydrobenzo[b][1,4]azasiline (48a)

$\text{H NMR (500 MHz, CDCl}_3$, 25 °C)$

$\text{C}^{13}(\text{H})$ NMR (125 MHz, CDCl$_3$, 25 °C)
$^{19}$F($^1$H) NMR (470 MHz, CDCl$_3$, 25 °C)

$^{29}$Si($^1$H) NMR (99.4 MHz, INEPT, CDCl$_3$, 25 °C)
3,4,4-Trimethyl-1-(3-chlorophenyl)-1,2,3,4-tetrahydrobenzo[b][1,4]azasiline (49a)

\[ \text{\( \text{Si} \)} \]

\[ \text{\( \text{Cl} \)} \]

\( ^1H \) NMR (500 MHz, CDCl\(_3\), 25 °C)

\( ^{13}C(\text{\( H \))} \) NMR (125 MHz, CDCl\(_3\), 25 °C)
$^{29}$Si($^1$H) NMR (99.4 MHz, INEPT, CDCl$_3$, 25 °C)
3,4,4-Trimethyl-1-(4-chlorophenyl)-1,2,3,4-tetrahydrobenzo[b][1,4]azasiline (50a)

$^{1}H$ NMR (500 MHz, CDCl$_3$, 25 °C)

$^{13}C(^1H)$ NMR (125 MHz, CDCl$_3$, 25 °C)
$^{29}\text{Si}^1\text{H}$ NMR (99.4 MHz, INEPT, CDCl$_3$, 25 °C)
3,4,4-Trimethyl-1-(4-methoxyphenyl)-1,2,3,4-tetrahydrobenzo[\b][1,4]azasiline (51a)

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C)

$^{13}$C($^1$H) NMR (125 MHz, CDCl$_3$, 25 °C)
$^29\text{Si}[^1\text{H}] \text{ NMR (99.4 MHz, INEPT, CDCl}_3\text{, 25 °C)}$
3,4,4-Trimethyl-1-(4-(trifluoromethoxy)phenyl)-1,2,3,4-tetrahydrobenzo[b][1,4]azasiline (52a)

$^1$H NMR (500 MHz, CDCl$_3$, 25 °C)

$^{13}$C($^1$H) NMR (125 MHz, CDCl$_3$, 25 °C)
$^{19}$F($^1$H) NMR (470 MHz, CDCl$_3$, 25 °C)

$^{29}$Si($^1$H) NMR (99.4 MHz, INEPT, CDCl$_3$, 25 °C)
$3,4,4'$-Trimethyl-$1'-(4'-(methylthio)phenyl)-1,2,3,4$-tetrahydrobenzo$[b][1,4]$azasiline (53a)

$\text{Si} \quad \text{N}
\quad \text{SMe}

^1H NMR (500 MHz, CDCl$_3$, 25 °C)

$\text{C}^\text{13}$(^1H) NMR (125 MHz, CDCl$_3$, 25 °C)
$^{29}$Si($^1$H) NMR (99.4 MHz, INEPT, CDCl$_3$, 25 °C)