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Supporting Information

Chiral Chalcogenyl-Substituted Naphthyl- and Acenaphthyl-Silanes and Their Cations

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Supporting Information

for

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1. Experimental part
1.1 General remarks

All experiments were carried out under argon or nitrogen atmosphere using Schlenk techniques. The glass equipment was stored in an oven at 120°C and evacuated prior to use. The solvents n-pentane, n-hexane, benzene, tetrahydrofuran and diethyl ether were dried over sodium-potassium alloy and distilled under nitrogen atmosphere. The deuterated solvents were first dried over NaK and then either condensed before use or stored over molecular sieve (4 Å). Commercially available solid materials were stored and weighted in a glove box or dried at high vacuum before use. The n-butyl lithium was used as a 1.6 M solution in n-hexane. 1,8-Dibromonaphthalene, 5,6-dibromoacenaphtene, 1-Bromo-8-dimethylsilylnaphthalene, trityl borate [Ph₃C][B(C₆F₅)₄] were synthesized according to literature procedures.[S1-S4] Thin-layer chromatography was performed using commercial available aluminium foil (Fluka) coated with silica gel 60 and fluorescent indicator F254. For the column chromatography silica gel of the mesh size 60 from Merck was used. For preparative TLC, the pre-coated TLC plates SIL G-200 from MACHEREY-NAGEL were used.

GC/MS spectra were performed on a Thermo Focus DSQ (stationary phase: DB5 column, length 25 m, diameter 0.2 mm, film thickness 0.33 µm; temperature program: $T_{\text{initial}} = 60^\circ\text{C}$ for 5 min, then heating with $10^\circ\text{C}/\text{min}$ to $T_{\text{end}} = 280^\circ\text{C}$, staying at this temp. for 10 min; detector: EI with 70 eV) or on a Shimadzu GCMS-QP2020 equipped with a Macherey-Nagel Optima 5 HT column (30 m, 0.25 mm ID, 0.25 µm film thickness) and a Shimadzu GC/MS-QP2020 mass selective detector. High resolution mass spectra were measured on a Finnigan-LCQ or a Finnigan-MAT95 spectrometer using ESI, CI or EI.

GC spectra were performed on a Shimadzu GC-2010 Plus equipped with a Macherey-Nagel Optima 5 MS column (15 m, 0.25 mm ID, 0.25 µm film thickness) and a flame ionization detector.

Chiral GC spectra were measured on a GC-2010 Plus from Shimadzu. The column used, is a FS-Lipodex E [Octakis-(2,3-di-O-pentyl-3-butyryl)-γ-cyclodextrin, 25 m, 0.25 mm, constant flow, carrier gas hydrogen: 1.5 cm³min⁻¹] from Macherey-Nagel.

Chiral HPLC was performed on a Thermo Scientific Dionex Ultimate 3000 with a Lux 5µm Cellulose-3, 250 x 4.6 mm column and a flow rate of the eluent of 1mL/min at 25°C.

The determination of the optical rotation was performed using the Polartronic M from Schmidt+Haensch with Na-D-line (589 nm) at 20°C (cell lengths: 1 dm).

Infrared spectra were performed on a Bruker Tensor 27 spectrometer with a MKII Reflection Golden Gate Single Diamond ATR system.

NMR spectra were recorded on Bruker Avance 500, Bruker Avance III 500 spectrometer. $^1$H NMR spectra were referenced to the residual solvent resonance as internal standard (benzene-d₆: δ$^1$H(C₆D₆H) = 7.20, toluene-d₈: δ$^1$H(C₆D₅CD₂H) = 2.08, chloroform-d₃: δ$^1$H(C₆D₅CH₂H) = 7.26).
\( \delta^1H(\text{CHCl}_3) = 7.24 \), chlorobenzene-\( d_5 \): \( \delta^1H(\text{C}_6\text{D}_4\text{HCl}) = 7.14 \) and \( ^{13}C \) NMR spectra by using the central line of the solvent signal (benzene-\( d_6 \): \( \delta ^{13}C(\text{C}_6\text{D}_6) = 128.0 \), toluene-\( d_8 \): \( \delta ^{13}C(\text{C}_6\text{D}_5\text{CD}_3) = 20.4 \), chloroform-\( d_1 \): \( \delta ^{13}C(\text{CDCl}_3) = 77.0 \), chlorobenzene-\( d_5 \): \( \delta ^{13}C(\text{C}_6\text{D}_5\text{Cl}) = 134.2 \)). \( ^{29}\text{Si}(^1\text{H}) \) NMR spectra were referenced to an external standard \( ^{29}\text{Si}(\text{Me}_2\text{SiHCl}) = 11.1 \) versus tetramethylsilane (TMS)). \( ^{77}\text{Se} \) NMR spectra against external \( \text{Me}_2\text{Se} (\delta ^{77}\text{Se}(\text{Me}_2\text{Se}) = 0.0) \), \( ^{125}\text{Te} \) NMR spectra against external \( \text{Ph}_2\text{Te}_2 (\delta ^{125}\text{Te}(\text{Ph}_2\text{Te}_2) = 422.0) \), \( ^{19}\text{F} \) NMR spectra against external \( \text{CFCl}_3 (\delta ^{19}\text{F}(\text{CFCl}_3) = 0.0) \), and \( ^{11}\text{B} \) NMR spectra against \( \text{BF}_3\cdot\text{OEt}_2 (\delta ^{11}\text{B}(\text{BF}_3\cdot\text{OEt}_2) = 0.0) \). The \( ^{29}\text{Si}(^1\text{H}) \) NMR inverse gated spectra were recorded with a relaxation delay \( D_1 = 10 \) s. The \( ^{29}\text{Si}(^1\text{H}) \) INEPT spectra were recorded with delays \( D_3 = D_4 = 0.001 \) (for silanes) \( D_3 = 0.0122 \) s and \( D_4 = 0.0313 \) s (for silyl borates), if not given otherwise. For silanes, combustion analysis values for carbon show often too low values, which we attribute to the formation and incomplete combustion of silicon carbide, although vanadium pentoxide as combustion aid was used. Satisfactory combustion analyses could not be obtained from all silyl borates due to their high reactivity.
1.2 Synthesis and characterization of silanes

**General procedure A:** The starting material was dissolved in THF and cooled to -80 °C. Then \( n \)-butyl lithium was added dropwise. The reaction mixture was stirred for 60 min at that temperature. After the dropwise addition of the corresponding chlorosilane, the mixture was stirred for another 60 min at -80 °C and was then allowed to warm to room temperature over night. Thereafter, an aqueous \( \text{NH}_4\text{Cl} \) solution (ca. 20 mL) was added to the reaction mixture and the product was extracted with \( \text{Et}_2\text{O} \) (3 x 20 mL). The combined organic layer was dried over \( \text{Na}_2\text{SO}_4 \) and the solvent was removed under reduced pressure. The product was purified by column chromatography or crystallization.

**General procedure B:** The starting material was dissolved in THF and cooled to -80°C. Then \( n \)-butyl lithium was added dropwise and the reaction mixture was stirred for 70 minutes. During this time, the reaction mixture was allowed to warm to -30°C. Subsequently, the reaction mixture was cooled to -70°C and chlorodimethylsilane was added. The mixture was stirred for additional 30 minutes at -70°C and then warmed to r.t. over night. After completion of the reaction, \( \text{NH}_4\text{Cl} \) solution (10 mL) was added to the reaction mixture and the product was extracted with \( \text{Et}_2\text{O} \) (3 x 10 mL). The organic layer was dried over \( \text{Na}_2\text{SO}_4 \) and the solvent was removed under low pressure. The product was purified by column chromatography or crystallization.

**General Procedure C:** The starting material was dissolved in THF and cooled to -80 °C. Then \( n \)-butyl lithium was added dropwise. The reaction mixture was stirred for 60 min at that temperature. A solution of diphenyl disulfide or diphenyl diselenide in THF was added dropwise and the mixture was stirred for another 60 min at -80 °C. Then the mixture was allowed to warm to room temperature over night. An aqueous \( \text{NH}_4\text{Cl} \) solution (ca. 20 mL) was added to the reaction mixture and the product was extracted with \( \text{Et}_2\text{O} \) (3 x 20 mL). The combined organic layer was dried over \( \text{Na}_2\text{SO}_4 \) and the solvent was removed under reduced pressure. The product was purified by column chromatography or crystallization.
1.2.1 Synthesis and characterization of bromo-substituted silanes

8-Phenylmethylsilyl-1-bromonaphthalene 8a
The title silane was synthesized according to General Procedure A using 1.0 equiv. of 1,8-dibromonaphthalene (10.00 mmol, 2.86 g), 1.0 equiv. of n-butyllithium (10.00 mmol, 6.25 mL) and 1.0 equiv. of phenylmethylchlorosilane (10.00 mmol, 1.57 g). The product was purified by column chromatography using petroleum ether as eluent (R_f = 0.18). 8-Phenylmethylsilyl-1-bromonaphthalene was obtained as a yellow oil. Yield 3.00 g (9.10 mmol; 91%).

\[
\begin{align*}
\text{MePhSi} & \quad \text{H} \\
\text{Br} &
\end{align*}
\]

^1H NMR (500.13 MHz, 297.4 K, C_6D_6) δ = 0.87 (d, \(^3J_{H,H} = 3.6\) Hz, 3 H, SiCH_3), 6.01 (q, \(^3J_{H,H} = 3.6\) Hz, \(^1J_{H,Si} = 203.5\) Hz, 1 H, SiH), 6.82 (t, \(^3J_{H,H} = 7.8\) Hz, 1 H, 3-H), 7.08 (t, \(^3J_{H,H} = 7.6\) Hz, 1 H, 6-H), 7.19-7.22 (m, 3 H, o-Ph-H, 2-H), 7.42 (dd, \(^3J_{H,H} = 8.1\) Hz, \(^4J_{H,H} = 1.0\) Hz, 1 H, 4-H), 7.51 (dd, \(^3J_{H,H} = 8.2\) Hz, \(^4J_{H,H} = 1.0\) Hz, 1 H, 5-H), 7.58-7.61 (m, 3 H, m-Ph-H, p-Ph-H), 8.01 (dd, \(^3J_{H,H} = 7.0\) Hz, \(^4J_{H,H} = 1.2\) Hz, 1 H, 7-H).

^13C\(^{1H}\) NMR (125.77 MHz, 297.6 K, C_6D_6) δ = -0.1 (SiCH_3), 123.8 (C-1), 125.7 (C-6), 126.1 (C-3), 128.2 (m-PhCH), 129.2 (p-PhCH), 129.6 (C-4), 131.9 (C-5), 132.6 (C-2), 134.6 (C-8), 134.9 (o-PhCH), 136.5 (C-9), 137.3 (C-10), 139.3 (SiC(CH_3)), 141.0 (C-7).

^29Si\(^{1H}\) INEPT NMR (99.31 MHz, 673.2 K, C_6D_6, \(D_3 = 0.0013, D_4 = 0.0013\)) δ = -13.9. GC/MS \(t_R: 23.7\) min, m/z (%) 329 [M+2] (1), 327 [M+] (2), 325 (2), 313 (7), 311 (8), 250 (65), 248 (67), 231 (46), 215 (17), 202 (38), 179 (10), 168 (100), 154 (28), 141 (52), 126 (15), 123 (18), 115 (23), 109 (22), 107 (19), 105 (35), 103 (13), 91 (10), 77 (26), 63 (6), 53 (29).

IR (ATR, 298 K, neat): ν = 2103, 2152 cm\(^{-1}\). HR/MS (LIFDI) C_{17}H_{15}BrSi, calc.: 326.0121, found: 326.0122. EA C_{17}H_{15}BrSi, calculated: C 62.39, H 4.62, found: C 62.69, H 4.95.
Figure S 1 – $^1$H NMR spectrum (500.13 MHz, 297.4 K, C$_6$D$_6$) of 8-phenylmethylsilyl-1-bromonaphthalene 8a (# impurities).

Figure S 2 – $^{13}$C($^1$H) NMR spectrum (125.77 MHz, 297.6 K, C$_6$D$_6$) of 8-phenylmethylsilyl-1-bromonaphthalene 8a (*C$_6$D$_6$).
8-tert-Butylmethylsilyl-1-bromonaphthalene, 8b
The title compound was synthesized according to general procedure A using 0.40 g (1.40 mmol) 1,8-Dibromonaphthalene, 0.74 mL (1.40 mmol) tert-butyl lithium and 0.19 g (1.40 mmol) chloro(tert-butyl)methylsilane. The by-product 1-bromonaphthalene was removed by bulb to bulb distillation (78°C, 0.13 mbar). The 8-tert-butylmethylsilyl-1-bromonaphthalene 8b was obtained as a yellow oil. Yield 0.20 g (0.64 mmol; 46 %).

\[
\begin{array}{c}
\text{(t-Bu)MeSi} \\
\text{H}
\end{array}
\]

\[\begin{array}{c}
1^\text{H} \text{NMR} \ (500.13 \text{ MHz, 298.4 K, C}_{6}\text{D}_{6}) \ \delta = 0.60 \ (d, \ ^3J_{HH} = 3.7 \text{ Hz, } 3 \text{ H, SiCH}_3), \ 1.08 \ (s, 9 \text{ H, C(CH}_3)_3), \ 5.56 \ (q, \ ^3J_{HH} = 3.7 \text{ Hz, } ^1J_{SH} = 201.2 \text{ Hz, } 1 \text{ H, SiH}), \ 6.86 \ (t, \ ^3J_{HH} = 7.7 \text{ Hz, } 1 \text{ H, 3-H}), \ 7.17 \ (t, \ ^3J_{HH} = 7.5 \text{ Hz, } 1 \text{ H, 6-H}), \ 7.44 \ (dd, \ ^3J_{HH} = 8.1 \text{ Hz, } ^4J_{HH} = 1.1 \text{ Hz, } 1 \text{ H, 4-H}), \ 7.52 \ (dd, \ ^3J_{HH} = 8.1 \text{ Hz, } ^4J_{HH} = 1.1 \text{ Hz, } 1 \text{ H, 5-H}), \ 7.70 \ (dd, \ ^3J_{HH} = 8.0 \text{ Hz, } ^4J_{HH} = 1.4 \text{ Hz, } 1 \text{ H, 2-H}), \ 7.97 \ (dd, \ ^3J_{HH} = 7.0 \text{ Hz, } ^4J_{HH} = 1.2 \text{ Hz, } 1 \text{ H, 7-H}). \end{array}
\]

\[\begin{array}{c}
13^\text{C} \{^1\text{H}\} \text{ NMR} \ (125.77 \text{ MHz, 298.6 K, C}_{6}\text{D}_{6}) \ \delta = -2.5 \ (\text{SiCH}_3), \ 18.2 \ (\text{SiC(CH}_3)_3), \ 28.9 \ (\text{SiC(CH}_3)_3), \ 123.6 \ (\text{C-1}), \ 125.1 \ (\text{C-6}), \ 125.9 \ (\text{C-3}), \ 129.7 \ (\text{C-4}), \ 131.5 \ (\text{C-5}), \ 133.0 \ (\text{C-2}), \ 135.7 \ (\text{C-8}), \ 136.5 \ (\text{C}^{10}), \ 137.2 \ (\text{C}^9), \ 139.0 \ (\text{C-7}). \end{array}
\]

\[\begin{array}{c}
29^\text{Si} \{^1\text{H}\} \text{ NMR} \ (99.31 \text{ MHz, 305.0 K, C}_{6}\text{D}_{6}); \ \delta = -0.7. \end{array}
\]

\[\begin{array}{c}
29^\text{Si} \text{ INEPT NMR} \ (99.31 \text{ MHz, 305.0 K, C}_{6}\text{D}_{6}, \text{D}_3 = \text{D}_4 = 0.0013 \text{ s}) \ \delta = -0.7 \ (\text{d, } 1J_{SH} = 201.9 \text{ Hz}). \end{array}
\]

\[\begin{array}{c}
\text{GC/MS} \ t_{R}: \ 20.1 \ \text{min, m/z (}) \ % \ 307 \ [\text{M}^+\text{-H, 37Cl}] (0.3), \end{array}
\]
305 [M-H, 35Cl] (0.3), 291 (0.8), 249 (56), 235 (3), 183 (3), 169 (100), 167 (49), 155 (16), 141 (15), 129.1 (7), 115 (14), 107 (7), 77 (4), 57 (6). IR (ATR, 298 K, neat): ν = 2100, 2170 cm⁻¹

HR/MS (LIFDI) C₁₅H₁₉₇₉Br²₈Si, calculated: 306.0434, found: 306.0442. EA C₁₅H₁₉BrSi, calc.: C 58.63, H 6.23, found: C 58.72, H 6.49.

Figure S 4 – ¹H NMR spectrum (500.13 MHz, 298.4 K, C₆D₆) of 8-tert-butyldimethylsilyl-1-bromonaphthalene 8b.

Figure S 5 – ¹³C(¹H) NMR spectrum (125.77 MHz, 298.6 K, C₆D₆) of 8-tert-butyldimethylsilyl-1-bromonaphthalene 8b (C₆D₆).
6-Phenylmethylsilyl-5-bromoacenaphthene 5

The title compound was synthesized according to general procedure A using 1.87 g (6.00 mmol) 5,6-dibromoacenaphthene, 3.8 mL (6.00 mmol) n-butyl lithium and 0.89 mL (6.00 mmol) chloro(methyl)phenylsilane. The product was purified by crystallization from hexanes at r.t. and was obtained as a yellow solid. Yield 1.88 g (5.32 mmol, 89%).

\[\text{1}^1\text{H NMR} \ (499.87 \text{ MHz, 305.1 K, C}_6\text{D}_6): \delta = 0.93 (d, 3 H, \text{J}_{H,H} = 3.7 \text{ Hz, SiCH}_3), 2.77-2.82 (m, 2 H, 2-H), 2.85-2.90 (m, 2 H, 1-H), 6.07 (q, 1 H, \text{J}_{H,H} = 3.7 \text{ Hz, J}_{H,\text{Si}} = 202.2 \text{ Hz, SiH}), 6.71 (d, 1 H, \text{J}_{H,H} = 7.4 \text{ Hz, 3-H}), 6.97 (d, 1 H, \text{J}_{H,H} = 7.0 \text{ Hz, 8-H}), 7.22-7.26 (m, 3 H, 15-H, 15′-H, 16-H), 7.61 (d, 1 H, \text{J}_{H,H} = 7.4 \text{ Hz, 4-H}), 7.64-7.70 (m, 2 H, 14-H, 14′-H), 7.99 (d, 1 H, \text{J}_{H,H} = 7.0 \text{ Hz, 7-H}). \]

\[\text{13C}^{1^1\text{H}} \text{ NMR} \ (125.71 \text{ MHz, 305.0 K, CDCl}_3): \delta = -0.6 (\text{CH}_3), 29.8 (\text{CH}_2), 30.4 (\text{CH}_2), 118.1 (\text{C}), 119.9 (\text{CH}), 120.6 (\text{CH}), 128.0 (\text{CH}), 128.7 (\text{C}), 129.0 (\text{CH}), 133.4 (\text{CH}), 134.9 (\text{CH}), 135.7 (\text{C}), 138.9 (\text{C}), 141.2 (\text{C}), 141.7 (\text{CH}), 146.9 (\text{C}), 149.7 (\text{C}). \]

\[\text{29Si}^{1^1\text{H}} \text{ NMR} \ (99.31 \text{ MHz, } \text{C}_6\text{D}_6): \delta = -0.7. \]
305.0 K, CDCl$_3$): $\delta = -15.2$. $^{29}$Si($^1$H) NMR (99.36 MHz, 299.6 K, C$_6$D$_6$): $\delta = -15.0$. IR (ATR, 298 K, neat): $\tilde{\nu} = 2146$ cm$^{-1}$. HR/MS (El) C$_{19}$H$_{17}$BrSi, calc.: 352.0277, found: 352.0287. EA C$_{19}$H$_{17}$BrSi calc.: C 64.59, H 4.85, found: C 64.80, H 5.17.

Figure S 7 – $^1$H NMR spectrum (499.87 MHz, 305.1 K, C$_6$D$_6$) of 5-bromo-6-(methylphenylsilyl)acenaphthene 5 (#C$_6$D$_6$).
Figure S 8 – $^{29}\text{Si}(^1\text{H})$ INEPT NMR spectrum (99.31 MHz, 305.0 K, C$_6$D$_6$) of 5-bromo-6-(methylphenylsilyl)acenaphthene 5.
1.2.2 Synthesis and characterization of chalcogenyl-substituted silanes

5-Methylphenylsilyl-6-phenoxyacenaphthene 3a
The title compound 3a was synthesized according to general procedure B using 1.0 equiv. (2.00 mmol, 0.65 g) 5-Bromo-6-phenoxyacenaphthene 1, 1.0 equiv. (2.00 mmol, 1.26 mL) n-butyl lithium and 1.2 equiv. (2.40 mmol, 376 mg) chloro(methyl)phenylsilane. In addition, 1.1 equiv. (2.20 mmol, 256 mg) TMEDA was added to the starting material before adding n-butyl lithium. The raw product was purified by column chromatography using n-pentane as eluent (R_F = 0.20). The product 3a was obtained as a colorless oil. Yield 0.40 mg (1.11 mmol; 55 %).

\[ \text{PhMeSi} \]  \[ \text{OPh} \]  
\[ \begin{array}{c} 3 \\
10 \\
1 \\
4 \\
5 \\
8 \\
7 \\
12 \\
9 \\
6 \\
2 \\
11 \\
13 \\
14 \end{array} \]

\[ ^1H \text{ NMR} \] (499.9 MHz, 298.1 K, C_6D_6) \[ \delta = 0.84 \text{ (d, } ^3J_{H,H} = 3.7 \text{ Hz, 3 H, SiCH}_3, 2.98-3.02 \text{ (m, 2 H, 1-H), 3.05-3.08 \text{ (m, 2 H, 2-H), 5.63 \text{ (q, } ^3J_{H,H} = 3.7 \text{ Hz, } ^1J_{H,Si} = 196.2 \text{ Hz, 1 H, Si-H), 6.75 \text{ (d, } ^3J_{H,H} = 6.6 \text{ Hz, 1 H, 7-H), 6.81-6.83 \text{ (m, 2 H, O-\text{o-Ph), 6.87-6.92 \text{ (m, 2 H, 8-H, O-\text{p-Ph), 7.04-7.09 \text{ (m, 2 H, O-\text{m-Ph), 7.13-7.19 \text{ (m, 4 H, Si-\text{m/p-Ph, 3-H), 7.58-7.61 \text{ (m, 2 H, Si-\text{o-Ph), 7.99 \text{ (d, } ^3J_{H,H} = 6.9 \text{ Hz, 1 H, 4-H) ppm.} \text{ ^{13}C{^1H} NMR} \] (125.7 MHz, 297.8 K, C_6D_6) \[ \delta = -2.9 \text{ (SiCH}_3, \\
29.7 \text{ (CH}_2, \text{ C-2), 31.0 \text{ (CH}_2, \text{ C-1), 113.8 \text{ (C-7), 119.4 \text{ (C-8), 120.2 \text{ (C-3), 120.7 \text{ (CH, OPh), 123.8 \text{ (CH, OPh), 125.7 \text{ (C, C-5), 127.9 \text{ (CH), 128.9 \text{ (CH), 129.2 \text{ (C), 129.9 \text{ (CH), 135.0 \text{ (CH, SiPh), 138.2 \text{ (C, Si-ipso-Ph), 139.3 \text{ (CH, C-4), 140.5 \text{ (C), 141.4 \text{ (C), 148.6 \text{ (C), 153.3 \text{ (C, C-6), 156.8 \text{ (C, O- ipso-Ph).} \text{ ^{29}Si{^1H} INEPT NMR} \] (99.3 MHz, 297.9 K, C_6D_6) \[ \delta = -14.7 \text{. IR (ATR, fest): } \tilde{\nu}\text{(Si-H) [cm}^{-1}] = 2096, 2136. \text{ GC-MS } t_R = 32.8 \text{ min, m/z } (M^+) = 366. \text{ HR/MS calculated: m/z = 366.1440; found (EI): m/z = 366.1442.} \]
Figure S 9 – $^1$H NMR spectrum (499.9 MHz, 298.1 K, C$_6$D$_6$) of 5-(methylphenylsilyl)-6-phenoxyacenaphthene 3a (*C$_6$D$_5$H, # impurities).

Figure S 10 – $^{13}$C($^1$H) NMR spectrum (125.7 MHz, 297.8 K, C$_6$D$_6$) of 5-(methylphenylsilyl)-6-phenoxyacenaphthene 3a (*C$_6$D$_5$, # impurities).
5-Methyl-\textit{tert}-butylsilyl-6-phenoxyacenaphthene 3b

The title compound 3b was synthesized according to general procedure B using 1.0 equiv. (1.00 mmol, 325 mg) 5-bromo-6-phenoxyacenaphene 1, 1.1 equiv. (1.10 mmol, 0.70 mL) \textit{n}-butyl lithium and 1.5 equiv. (1.50 mmol, 205 mg) chloro(\textit{tert}-butyl)methylsilane. The chlorosilane was added at -50 °C and the reaction mixture was stirred for further 60 min at this temperature. The raw product was purified by column chromatography using \textit{n}-pentane as eluent (R$_F$ = 0.26). The product 3b was obtained as a colorless oil. Yield 134 mg (0.39 mmol; 39 %).

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{figure.png}
\caption{Figure S 11 – $^{29}$Si($^1$H) INEPT NMR spectrum (99.3 MHz, 297.9 K, \textit{C$_6$D$_6$}) of 5-(methylphenylsilyl)-6-phenoxyacenaphthene 3a.}
\end{figure}

$^1$H NMR (499.9 MHz, 298.1 K, \textit{C$_6$D$_6$}) $\delta$ = 0.56 (d, $^3$J$_{H,H}$ = 3.8 Hz, 3 H, SiMe), 1.19 (s, 9 H, Si(t-Bu)), 2.98-3.02 (m, 2 H, 1-H), 3.05-3.09 (m, 2 H, 2-H), 4.95 (q, $^3$J$_{H,H}$ = 3.8 Hz, $^1$J$_{H,\text{Si}}$ = 192.9 Hz, 1 H, Si-H), 6.85 (d, $^3$J$_{H,H}$ = 7.5 Hz, 1 H, 7-H), 6.91-6.96 (m, 2 H, 3-H, p-Ph), 7.07-7.10 (m, 2 H, o-Ph), 7.12-7.16 (m, 2 H, m-Ph), 7.21-7.22 (m, 1 H, 3-H), 7.98 (d, $^3$J$_{H,H}$ = 6.9 Hz, 1 H, 4-H).

$^{13}$C($^1$H) NMR (125.7 MHz, 297.8 K, \textit{C$_6$D$_6$}) $\delta$ = -4.8 (SiCH3), 18.1 (C, t-Bu), 28.5 (CH3, t-Bu), 29.6 (CH2, C-2), 30.9 (CH2, C-1), 114.9 (CH, C-7), 119.3 (CH, C-8), 119.9 (CH, C-3), 120.8 (CH, Ph), 123.7 (CH, Ph), 125.9 (C, C-5), 129.5 (C), 130.1 (CH, Ph), 139.0 (CH, C-4), 141.0 (C), 141.4 (C), 148.2 (C), 153.2 (C, C-6), 157.6 (C, i-Ph).

$^{29}$Si($^1$H) NMR (99.3 MHz, 297.9 K,
C_6D_6) δ = 3.1. **GC-MS** t_r = 26.5 min, m/z (M^+) = 346. **HR/MS** calculated: m/z = 346.1747; found (EI): m/z = 346.1757. **IR** (ATR, solid): ν(Si-H) [cm^{-1}] = 2090, 2151. **EA** C_{23}H_{26}SiO, calculated: C 79.72, H 7.56, solid: C 80.00, H 7.66.

Figure S 12 – ^1H NMR spectrum (499.9 MHz, 298.1 K, C_6D_6) of 5-(tert-butylmethylsilyl)-6-phenoxyacenaphthene 3b.

Figure S 13 – ^13C[^1H] NMR spectrum (125.7 MHz, 297.8 K, C_6D_6) of 5-(tert-butylmethylsilyl)-6-phenoxyacenaphthene 3b (*C_6D_6).
1-Phenylsulfanyl-8-(phenylmethylsilyl)naphthalene 9

The title compound was synthesized according to general procedure C using 1.0 equiv. (3.06 mmol, 1.00 g) 8-phenylmethylsilyl-1-bromonaphthalene, 1.0 equiv. (3.06 mmol, 1.91 mL) n-butyl lithium and 1.0 equiv. (3.06 mmol, 0.67 g) diphenyl disulfide. The raw-product was purified by column chromatography using petroleum ether/ethyl acetate (99:1) as eluent (RF = 0.26). Silane 9 was obtained as a colorless solid after crystallization from n-pentane at -18 °C. Yield 0.96 g (2.70 mmol; 88 %).

\[
\begin{align*}
\text{PhMeSi} & \quad (\text{Ph}) \\
\text{H} & \quad \text{Ph}
\end{align*}
\]

\(^1\text{H} \text{NMR} \ (500.13 \text{ MHz}, \ 298.4 \text{ K}, \ C_6D_6) \ \delta = 0.85 \ (d, \ 3J_{H,H} = 3.5 \text{ Hz}, \ 3 \text{ H, SiCH}_3), \ 5.87 \ (q, \ 3J_{H,H} = 3.5 \text{ Hz}, \ 1J_{H,\text{Si}} = 203.0 \text{ Hz, 1 H, SiH}), \ 6.77-6.84 \ (m, 5 \text{ H, SPh}), \ 7.07 \ (t, \ 3J_{H,H} = 7.6 \text{ Hz, 1 H, 3-H}), \ 7.11-7.15 \ (m, 3 \text{ H, Si-}m-\text{Ph, Si-p-Ph}), \ 7.21-7.24 \ (m, 1 \text{ H, 6-H}), \ 7.53-7.55 \ (m, 2 \text{ H, Si-o-Ph}), \ 7.60 \ (dd, \ 3J_{H,H} = 8.1 \text{ Hz, 4J}_{H,\text{Si}} = 1.2 \text{ Hz, 1 H, 4-H}), \ 7.66 \ (dd, \ 3J_{H,H} = 8.1 \text{ Hz, 4J}_{H,\text{Si}} = 1.1 \text{ Hz, 1 H, 5-H}), \ 7.75 \ (dd, \ 3J_{H,H} = 7.2 \text{ Hz, 4J}_{H,\text{Si}} = 1.3 \text{ Hz, 1 H, 2-H}), \ 8.08 \ (dd, \ 3J_{H,H} = 6.9 \text{ Hz, 4J}_{H,\text{Si}} = 1.0 \text{ Hz, 1 H, 7-H}). \ \ ^{13}\text{C}(^1\text{H}) \text{NMR} \ (125.77 \text{ MHz}, \ 298.3 \text{ K}, \ C_6D_6) \ \delta = -0.5 \ (\text{SiCH}_3), \ 125.4 \ (\text{CH}), \ 126.0 \ (\text{CH}), \ 126.2 \ (\text{CH}), \ 127.2 \ (\text{C}), \ 128.5 \ (\text{CH}), \ 128.7 \ (\text{CH}), \ 129.0 \ (\text{CH}), \ 131.5 \ (\text{CH}), \ 131.9 \ (\text{C}), \ 132.1 \ (\text{CH}), \ 134.2 \ (\text{CH}), \ 134.7 \ (\text{CH}), \ 135.6 \ (\text{C}), \ 137.6 \ (\text{C}), \ 139.6 \ (\text{C}), \ 140.6 \ (\text{CH}), \ 140.6 \ (\text{C}), \ 140.9 \ (\text{CH}). \ \ ^{29}\text{Si}^1\text{H} \text{NMR} \ (99.31 \text{ MHz}, \ 673.2 \text{ K}, \ C_6D_6) \ \delta = -16.9. \ \text{IR} \ (\text{ATR, solid}):
$\tilde{v}(\text{Si-H}) \ [\text{cm}^{-1}] = 2144$. **HR/MS** calculated: $m/z = 356.1055$; found (ESI): $m/z = 355.0595$. **EA**

$C_{23}H_{20}SSi$, calculated: C 77.48, H 5.65; S 8.99, found: C 76.41, H 5.98, S 8.60.

Figure S 15 – $^1$H NMR spectrum (499.87 MHz, 305.1 K, $C_6D_6$, $^*C_6D_5H$) of 1-phenylsulfanyl-8-phenylmethylsilyl-naphthalene 9 ($^*C_6D_5H$, # silicon grease and water).

Figure S 16 – $^{29}$Si{$^1$H} INEPT NMR spectrum (99.3 MHz, 297.9 K, $C_6D_6$, $D_3 = D_4 = 0.0013$) of 1-phenylsulfanyl-8-phenylmethylsilylnaphthene 9.
5-Phenylsulfanyl-6-phenylmethylsilylacenaphthene 4a
The title compound was synthesized according to general procedure A using 1.0 equiv. (4.31 mmol, 1.47 g) 5-bromo-6-phenylsulfanylacenaphene 2, 1.0 equiv. (4.31 mmol, 2.69 mL) n-butyl lithium and 1.0 equiv. (4.31 mmol, 0.65 mL) chloro(methyl)phenylsilane. The product was purified by crystallization from n-pentane and obtained as a colorless solid. Yield 1.07 g (2.80 mmol; 65 %).

$^1$H NMR (499.87 MHz, 305.1 K, C$_6$D$_6$) $\delta$ = 0.88 (d, $^3$J = 3.6 Hz, 3 H, SiCH$_3$), 2.91-3.95 (m, 2 H, CH$_2$), 2.96-3.00 (m, 2 H, CH$_2$), 5.89 (q, $^3$J = 3.4 Hz, $^1$J$_{H, Si}$ = 202.8 Hz, 1 H, SiH), 6.80-6.83 (m, 1 H, CH, S-p-Ph), 6.87-6.92 (m, 4 H, CH, S-m/o-Ph), 6.96 (d, $^3$J = 7.3 Hz, 1 H, CH, 3-H), 7.10 (d, $^3$J = 7.0 Hz, 1 H, CH, 8-H), 7.14-7.17 (m, 3 H, CH, Si-m/p-Ph), 7.60-7.64 (m, 2 H, CH, Si-o-Ph), 7.79 (d, $^3$J = 7.1 Hz, 1 H, CH, 4-H), 8.05 (d, $^3$J = 7.0 Hz, 1 H, CH, 7-H).

$^{13}$C($^1$H) NMR (125.71 MHz, 305.0 K, C$_6$D$_6$) $\delta$ = -1.0 (SiCH$_3$), 30.1 (CH$_2$, C-2), 30.3 (CH$_2$, C-1), 120.2 (CH, C-8), 120.7 (CH, C-3), 125.1 (CH, S-p-Ph), 126.7 (C, C-5), 126.9 (CH, S-m-Ph), 128.1 (CH, Si-m-Ph), 128.8 (CH, S-p-Ph), 128.9 (C, C-6), 129.0 (CH, S-o-Ph), 134.9 (CH, Si-o-Ph), 139.3 (C, Si-ips-o-Ph), 139.5 (C, C-12), 139.7 (CH, C-4), 140.9 (C, C-11), 141.5 (C, S-ips-o-Ph), 141.9 (CH, C-7), 149.5 (C, C-10), 149.7 (C, C-9).

$^{29}$Si($^1$H) NMR (99.31 MHz, 305.0 K, C$_6$D$_6$) $\delta$ = -17.2.

GC/MS $t_R = 30.8$ min, m/z (%): 51 (16), 77 (38), 152 (71), 227 (64), 289 (100), 305 (24), 367 (41), 382 (23) [M$^+$. HR/MS calculated: m/z = 382.1206; found (EI): m/z = 382.1196. IR (ATR, solid): $\tilde{v}$(Si-H) [cm$^{-1}$] = 2091. EA C$_{25}$H$_{22}$SSi, calculated: C 78.48, H 5.80, S 8.38; found: C 78.57, H 6.63, S 8.08.
Figure S 17 – $^1$H NMR spectrum (499.87 MHz, 305.1 K, C$_6$D$_6$) of 5-phenylsulfanyl-6-phenylmethylsilylnaphthene 4a (*C$_6$D$_5$H).

Figure S 18 – $^{13}$C($^1$H) NMR spectrum (125.71 MHz, 305.0 K, C$_6$D$_6$) of 5-phenylsulfanyl-6-phenylmethylsilylnaphthene 4a (*C$_6$D$_6$).
5-Phenylsulfanyl-6-methyl-tert-butyldimethylsilylacenaphthene 4b

The title compound was synthesized according to general procedure B using 1.0 equiv. (990.43 µmol, 338 mg) 5-bromo-6-phenylsulfanylacenaphene 2, 1.0 equiv. (990.43 µmol, 0.63 mL) n-butyl lithium and 1.0 equiv. (990.43 µmol, 94 mg) chloro(tert-butyl)methyl silane. The product 4b was purified by crystallization from n-pentane and obtained as an orange solid. Yield 107 mg (297.13 µmol, 30 %).

\[ ^1H\text{ NMR} \ (500.13 \text{ MHz}, 298.9 \text{ K}, C_6D_6) \delta = 0.54 \ (d, ^3J_{H,H} = 3.4 \text{ Hz}, 3 \text{ H}, \text{SiCH}_3), 1.19 \ (s, 9 \text{ H}, \text{Si}(t-Bu)), 2.91-2.95 \ (m, 2 \text{ H}, \text{CH}_2), 2.98-3.02 \ (m, 2 \text{ H}, \text{CH}_2), 5.41 \ (q, ^3J_{H,H} = 3.3 \text{ Hz}, ^1J_{H,\text{Si}} = 199.8 \text{ Hz}, 1 \text{ H}, \text{SiH}), 6.82-6.85 \ (m, 1 \text{ H}, p-\text{Ph}), 6.92-6.95 \ (m, 2 \text{ H}, m-\text{Ph}), 6.98 \ (d, ^3J_{H,H} = 7.1 \text{ Hz}, 1 \text{ H}, 3-\text{H}), 7.05-7.06 \ (m, 2 \text{ H}, o-\text{Ph}), 7.16 \ (d, ^3J_{H,H} = 7.0 \text{ Hz}, 1 \text{ H}, 8-\text{H}), 7.88 \ (d, ^3J_{H,H} = 7.1 \text{ Hz}, 1 \text{ H}, 4-\text{H}), 8.01 \ (d, ^3J_{H,H} = 7.0 \text{ Hz}, 1 \text{ H}, 7-\text{H}) \]

\[ ^13C\{^1H\text{ NMR} \ (125.71 \text{ MHz}, 305.0 \text{ K}, C_6D_6) \delta = -3.2 \ (\text{SiCH}_3), 18.5 \ (C, t\text{Bu}), 30.0 \ (\text{CH}_2, C-2), 30.3 \ (\text{CH}_2, C-1), 119.8 \ (\text{CH}, C-8), 120.5 \ (\text{CH}, C-3), 125.2 \ (\text{CH}, p-\text{Ph}), 126.9 \ (C, ipso-\text{Ph}), 127.2 \ (\text{CH}, o-\text{Ph}), 129.1 \ (\text{CH}, m-\text{Ph}), 129.6 \ (C, C-6), 139.4 \ (C, C-12), 139.8 \ (\text{CH}, C-4), 140.2 \ (\text{CH}, C-7), 141.0 \ (C, C-5), 141.3 \ (C, C-11), 149.2 \ (C, C-9), 149.5 \ (C, C-10). \]

\[ ^29Si\{^1H\text{ NMR} \ (99.36 \text{ MHz}, 299.1 \text{ K}, C_6D_6) \delta = -3.3. \]

HR/MS calculated: m/z = 362.1519; found (EI): m/z = 362.1508. IR (ATR, solid): \(\tilde{\nu}(\text{Si-H}) [\text{cm}^{-1}] = 2175.\)
Figure S 20 – $^1$H NMR spectrum (500.13 MHz, 298.9 K, C$_6$D$_6$) of 5-phenylsulfanyl-6-(tert-butyl)methylsilylacenaphthene 4b (*C$_6$D$_5$H, # silicon grease).

Figure S 21 – $^{13}$C($^1$H) NMR spectrum (125.71 MHz, 305.0 K, C$_6$D$_6$) of 5-phenylsulfanyl-6-(tert-butyl)methylsilylacenaphthene 4b (*C$_6$D$_6$, # silicon grease).
1-Phenylselanyl-8-phenylmethylsilylnaphthalene 10a
The title compound was synthesized according to general procedure C in diethylether using 1.00 g (3.06 mmol) 8-phenylmethylsilyl-1-bromonaphthalene 8a, 1.91 mL (3.06 mmol) n-butyl lithium and 0.95 g (3.06 mmol) diphenyl diselenide. The raw-product was purified by column chromatography using n-hexane as eluent (R_F = 0.11). Silane 10a was obtained as a colorless oil. Yield 1.10 g (2.76 mmol; 91%).

\[
\text{H NMR (499.87 MHz, 305.0 K, C}_6\text{D}_6\text{): } \delta = 0.87 (d, 3H, }^3J_{H,H} = 3.6 \text{ Hz), 5.98 (q, 1H, }^3J_{H,H} = 3.6 \text{ Hz, }^1J_{H,Si} = 202.4 \text{ Hz), 6.77 - 6.83 (m, 3H), 6.91 - 6.93 (m, 2H), 7.02-7.05 (m, 1H), 7.12 - 7.15 (m, 3H), 7.19 - 7.22 (m, 1H), 7.54 - 7.56 (m, 2H), 7.60 (dd, 1H, }^3J_{H,H} = 8.1 \text{ Hz, }^4J_{H,H} = 1.4 \text{ Hz), 7.65 (dd, 1H, }^3J_{H,H} = 8.1 \text{ Hz, }^4J_{H,H} = 1.4 \text{ Hz), 7.95 (dd, 1H, }^3J_{H,H} = 7.1 \text{ Hz, }^4J_{H,H} = 1.5 \text{ Hz), 8.09 (dd, 1H, }^3J_{H,H} = 6.9 \text{ Hz, }^4J_{H,H} = 1.4 \text{ Hz). 13C{'}^1H NMR (125.71 MHz, 305.0 K, C}_6\text{D}_6\text{): } \delta = -0.0 \text{ (CH}_3\text{), 125.7 (CH), 126.21 (CH), 126.24 (CH), 128.8 (CH), 129.3 (CH), 129.8 (CH), 130.4 (C), 131.5 (CH), 132.0 (CH), 134.7 (CH), 135.6 (C), 135.7 (C), 136.4 (C), 139.4 (C), 139.6 (C), 140.9 (CH). Two C missing, due to overlap with the solvent signal. 29Si{'}^1H NMR (99.31 MHz, 305.0 K, C}_6\text{D}_6\text{): } \delta = -18.0. 29Si INEPT NMR (99.31 MHz, 305.0 K, C}_6\text{D}_6\text{, D}3 = D4 = 0.0013): \delta
\]
= -18.0 (dm, ¹J_{Si,H} = 202.1 Hz). †⁷⁷Se{¹H} NMR (95.36 MHz, 305.0 K, C₆D₆): δ = 393.0. †⁷⁷Se NMR (95.36 MHz, 305.0 K, C₆D₆): δ = 393.0 (d, †TS_{Se,H} = 13.9 Hz). GC/MS tr: 31.3 min, m/z (%): 403 [M+] (16), 389 (31), 387 (18), 326 (23), 311 (63), 309 (34), 249 (36), 231 (32), 215 (14), 202 (72), 179 (8), 169 (19), 167 (30), 141 (46), 127 (44), 115 (24), 105 (27), 77 (100), 51 (60). IR (ATR, 298 K, neat): ν = 2083, 2141 cm⁻¹. HR/MS (LIFDI) C₂₃H₂₀SeSi, calc.: 404.0494, found: 404.0482. EA C₂₃H₂₀SeSi, calc.: C 68.47, H 5.00, found: C 68.39, H 5.65.

Figure S 23 – ¹H NMR spectrum (499.87 MHz, 305.0 K, C₆D₆) of 1-phenylselanyl-8-phenylmethylsilylnaphthalene 10a.
Figure S 24 – $^{13}$C($^1$H) NMR spectrum (125.71 MHz, 305.0 K, C$_6$D$_6$) of 1-phenylselany-8-phenylmethylsilylnaphthalene 10a.

Figure S 25 – $^{29}$Si($^1$H) INEPT NMR spectrum (99.31 MHz, 305.0 K, C$_6$D$_6$) of 1-phenylselany-8-phenylmethylsilylnaphthalene 10a.
Figure S 26 – $^{77}$Se($^1$H) NMR spectrum (95.36 MHz, 305.0 K, C$_6$D$_6$) of 1-phenylselanyl-8-phenylmethylsilylnaphthalene 10a.

1-Phenyldiseleno-8-tert-buthylmethylsilylnaphthalene 10b
The title compound was synthesized according to general procedure C in diethyl ether using 500 mg (1.63 mmol) 8-tert-buthylmethylsilyl-1-bromonaphthalene 8b, 1.02 mL (1.63 mmol) n-butyl lithium and 508 mg (1.63 mmol) diphenyl diselenid. The raw-product was purified by column chromatography using n-hexane as eluent (R$_f$ = 0.28). Silane 10b was obtained as a colorless oil. Yield 0.40 g (0.75 mmol; 46%).

$^1$H NMR (499.87 MHz, 305.0 K, C$_6$D$_6$): $\delta$ = 0.61 (d, 3H, $^3$J$_{H,H}$ = 3.6 Hz, Si-CH$_3$), 1.09 (s, 9H, Si-C(CH$_3$)$_3$), 5.45 (q, 1H, $^1$J$_{H,Si}$ = 196.3 Hz, 3J = 3.6 Hz, $^TS$J$_{H,Se}$ = 28.1 Hz, Si-H), 6.85 - 6.88 (m, 3H, 12-H, 14-H), 7.00 (dd, 1H, $^3$J$_{H,H}$ = 7.3 Hz, $^3$J$_{H,H}$ = 8.0 Hz, 3-H), 7.15 - 7.17 (m, 2H, 13-H), 7.25 - 7.28 (m, 1H, 6-H), 7.53 (dd, 1H, $^3$J$_{H,H}$ = 8.1 Hz), 7.63 (dd, 1H, $^3$J$_{H,H}$ = 1.4 Hz, 4-H), 7.65 - 7.68 (m, 2H, 13-H), 7.91 (dd, 1H, $^3$J$_{H,H}$ = 7.2 Hz, $^4$J$_{H,H}$ = 1.3 Hz, 2-H), 7.95 (dd, 1H, $^3$J$_{H,H}$ = 6.9 Hz, $^4$J$_{H,H}$ = 1.2 Hz, 7-H). $^{13}$C($^1$H) NMR (125.71 MHz, 305.0 K, C$_6$D$_6$): $\delta$ = -3.6 (CH$_3$, Si-CH$_3$), 18.7 (C, Si-C(CH$_3$)$_3$), 28.8 (CH$_3$, Si-C(CH$_3$)$_3$), 124.9 (CH, C-6), 126.1 (CH, C-3), 126.8 (CH, C-14), 129.4 (CH, C-12), 130.5 (CH, C-4), 131.3 (CH, C-5), 131.7 (CH, C-13), 132.1 (C,
C-1), 135.3 (C, C-10), 136.4 (C, C-8), 136.6 (C, C-11), 137.4 (CH, C-7), 137.6 (CH, C-2), 140.7 (C, C-9). $^{29}$Si($^1$H) NMR (99.31 MHz, 305.0 K, C$_6$D$_6$): δ = -4.9. $^{29}$Si INEPT NMR (99.31 MHz, 305.0 K, C$_6$D$_6$, D3 = D4 = 0.0013 s): δ = -4.8 (dm, $^1$J$_{Si,H}$ = 196.3 Hz). $^{77}$Se($^1$H) NMR (95.36 MHz, 305.0 K, C$_6$D$_6$): δ = 416.2. $^{77}$Se NMR (95.36 MHz, 305.0 K, C$_6$D$_6$): δ = 416.3 (d, $^{TS}$J$_{Se,H}$ = 26.6 Hz), 448.7 (s), 461.6 (s). GC/MS: tR: 25.5 min, m/z (%) 383 [M+H, 37Cl] (0.6), 381 [M+H, 35Cl] (0.6), 381 [M+-H, 37Cl] (0.3), 369 (1), 327 (100), 249 (50), 235 (24), 202 (12), 167 (18), 154 (8), 141 (37), 127 (62), 101 (4), 77 (25), 57 (21). IR (ATR, 298 K, neat): ν = 2131 cm$^{-1}$. HR/MS (LIFDI) C$_{21}$H$_{24}$Se$_2$Si, calc.: 384.0807, found: 384.0808.

Figure S 27 – $^1$H NMR spectrum (499.87 MHz, 305.0 K, C$_6$D$_6$) of 1-phenylselanyl-8-tert-butylmethyisilylnaphthalene 10b.
Figure S28 – $^{13}$C($^1$H) NMR spectrum (125.71 MHz, 305.0 K, C$_6$D$_6$) of 1-phenylselanyl-8-tert-butylmethylsilylnaphthalene 10b.

Figure S29 – $^{29}$Si($^1$H) NMR spectrum (99.31 MHz, 305.0 K, C$_6$D$_6$) of 1-phenylselanyl-8-tert-butylmethylsilylnaphthalene 10b.
Figure S 30 – $^{77}$Se($^1$H) NMR spectrum (95.36 MHz, 305.0 K, C$_6$D$_6$) of 1-phenylseleno-8-tert-butylmethylsilylnaphthalene 10b.

5-Phenylselanyl-6-phenylmethysilylacacenaphthene 6
The title compound was synthesized according to general procedure B using 1.06 g (3.00 mmol) 5-bromo-6-(methylphenylsilyl)acenaphthene 5, 1.9 mL (3.00 mmol) n-butyl lithium and 0.94 g (3.00 mmol) diphenyl diselenid. The reaction was carried out at -30 °C. The product was purified by crystallization from n-pentane at -28 °C and was obtained as a white solid. Yield 0.8 g (1.86 mmol, 62%).

$^1$H NMR (499.87 MHz, 305.0 K, CDCl$_3$): $\delta$ = 0.73 (d, 3 H, $^3$J$_{H,H}$ = 3.6 Hz), 3.34-3.38 (m, 4 H), 5.55 (q, 1 H, $^3$J$_{H,H}$ = 3.6 Hz, $^1$J$_{H,Si}$ = 202.2 Hz), 6.91 - 6.93 (m, 2 H), 7.01 - 7.02 (m, 3 H), 7.19 - 7.27 (m, 5 H), 7.43 - 7.44 (m, 2 H), 7.85 - 7.87 (m, 2 H). $^{13}$C($^1$H) NMR (125.55 MHz, 305.0 K, CDCl$_3$): $\delta$ = -0.70 (CH$_3$), 30.1 (CH$_2$), 30.3 (CH$_2$), 119.8 (CH), 120.7 (CH), 124.2 (C), 125.8 (CH), 127.8 (CH), 128.6 (CH), 129.0 (CH), 129.5 (CH), 129.6 (C), 134.6 (CH), 136.4 (C), 139.3 (C), 139.3 (C), 140.6 (C), 140.9 (CH), 141.6 (CH), 149.2 (C), 149.8 (C). $^{29}$Si($^1$H) NMR (99.31
MHz, 305.0 K, CDCl$_3$): $\delta = -18.1$. $^{77}$Se{$^1$H} NMR (95.36 MHz, 305.0 K, CDCl$_3$): $\delta = 374.1$. IR (ATR, 298 K, neat): $\tilde{\nu} = 2094$ cm$^{-1}$. HR/MS (El) C$_{25}$H$_{22}$SiSe, calc.: 430.0651, found: 430.0639.

EA C$_{25}$H$_{22}$SiSe, calc.: C 69.91, H 5.16, found: C 70.05, H 5.55.

Figure S 31 – $^1$H NMR spectrum (499.87 MHz, 305.0 K, CDCl$_3$) of 5-phenylselanyl-6-phenylmethylsilylacenaphthene 6.
Figure S 32 – $^{13}\text{C}^1\text{H}$ NMR spectrum (125.55 MHz, 305.0 K, CDCl$_3$) of 5-phenylselanyl-6-phenylmethylsilacenaphthene 6.

Figure S 33 – $^{29}\text{Si}^1\text{H}$ NMR spectrum (99.31 MHz, 305.0 K, CDCl$_3$) of 5-phenylselanyl-6-phenylmethylsilacenaphthene 6.
5-Mesityltellanyl-6-phenylmethylsilylacenaphthene 7
A solution of 1.77 g (5.00 mmol) 5-bromo-6-(methylphenylsilyl)acenaphthene 5 in diethyl ether (45 mL) was cooled to -10 °C. 3.1 mL (5.00 mmol) n-butyl lithium were added dropwise to the solution via syringe and the reaction mixture was stirred for four hours. In a round-bottom flask 2.47 mg (5.00 mmol) dimesityl ditelluride were suspended in diethyl ether (150 mL) and added to the reaction mixture at -80 °C via Teflon tube. The reaction mixture was allowed to warm to room temperature overnight. Then saturated ammonium chloride solution (200 mL) was added, the phases were separated and the aqueous phase was extracted with diethyl ether (3 × 200 mL). The combined organic layers were dried over magnesium sulphate, and the solvent was removed under reduced pressure. After column chromatography (PE/EA, 60:1, Rf = 0.25) only a crude product was obtained. Recrystallization from ethyl acetate yielded the pure product as a slightly beige solid. Yield 441 mg (0.85 mmol, 17 %).
$^1$H NMR (499.87 MHz, 305.1 K, C$_6$D$_6$): $\delta$ = 0.99 (d, 3 H, $^3$J$_{H,H} = 3.5$ Hz, $^T$S$^H$J$_{H,Te}$ = 9.0 Hz, SiCH$_3$), 2.10 (s, 3 H, p-CH$_3$), 2.45 (s, 6 H, o-CH$_3$), 2.86-2.88 (m, 2 H, H-2), 2.92-2.95 (m, 2 H, H-1), 6.29 (q, 1 H, $^3$J$_{H,H} = 3.5$ Hz, $^1$J$_{H,Si} = 193$ Hz, $^T$S$^H$J$_{H,Te}$ = 66 Hz, SiH), 6.70 (d, 1 H, $^3$J$_{H,H} = 7.2$ Hz, H-3), 6.81 (s, 2 H, H-19, H-19'), 7.06 (d, 1 H, $^3$J$_{H,H} = 7.0$ Hz, H-8), 7.23-7.24 (m, 3 H, H-15, H-15', H-16), 7.69-7.71 (m, 2 H, H-14, H-14'), 7.78 (d, 1 H, $^3$J$_{H,H} = 7.2$ Hz, H-4), 7.92 (d, 1 H, $^3$J$_{H,H} = 7.0$ Hz, H-7).

$^{13}$C{$^1$H} NMR (125.71 MHz, 305.0 K, C$_6$D$_6$): $\delta$ = 0.0 (CH$_3$, SiCH$_3$), 21.0 (CH$_3$, p-CH$_3$), 29.1 (2 × CH$_3$, o-CH$_3$), 29.6 (CH$_2$, C-2), 30.2 (CH$_2$, C-1), 114.2 (C, C-5), 119.5 (CH, C-8), 121.4 (CH, C-3), 125.8 (C, C-17), (128.1 (2 × CH, C-19, C-19'), 128.0, 128.2; overlap with solvent signal), 129.4 (3 × CH, C15, C15', C16), 130.6 (C, C-6), 135.5 (CH, C-14, C-14'), 138.5 (C, C-13), C138.8 (C, C-20), 138.8 (CH, C-4), 140.4 (CH, C-7), 140.5, 141.3 (2 × C, C-11, C-12), 144.9 (2 × C, C-18, C-18'), 146.8 (C, C-10), 150.0 (C, C-9).

$^{29}$Si{$^1$H} INEPT NMR (99.31 MHz, 305.0 K, C$_6$D$_6$): $\delta$ = -21.3.

$^{125}$Te{$^1$H} NMR (157.74 MHz, 305.0 K, C$_6$D$_6$): $\delta$ = 432.4 ($^T$S$^H$J$_{Te,H} = 91$ Hz).

IR (ATR, 305 K, neat): $\tilde{\nu}$SiH = 2108 cm$^{-1}$.

HR/MS (El): [C$_{28}$H$_{28}$SiTe], calculated: m/z = 522.1017, found: m/z = 522.1000. m.p.: 146-148 °C

Figure S 35 – $^1$H NMR spectrum (499.87 MHz, 305.1 K, C$_6$D$_6$) of 5-mesityltellanyl-6-phenylmethylsilylacenaphthene 7.
Figure S 36 – $^{13}\text{C}({}^1\text{H})$ NMR spectrum (125.71 MHz, 305.0 K, C$_6$D$_6$) of 5-mesityltellanyl-6-phenylmethylysilylacenaphthene 7.

Figure S 37 – $^{13}\text{C}({}^1\text{H})$ DEPT NMR spectrum (125.71 MHz, 305.0 K, C$_6$D$_6$) of 5-mesityltellanyl-6-phenylmethylysilylacenaphthene 7.
Figure S 38 – $^{29}$Si($^1$H) NMR spectrum (99.31 MHz, 305.0 K, C$_6$D$_6$) of 5-mesityltellanyl-6-phenylmethylsilylacenaphthene 7.

Figure S 39 – $^{125}$Te($^1$H) NMR spectrum (157.74 MHz, 305.0 K, C$_6$D$_6$) of 5-mesityltellanyl-6-phenylmethylsilylacenaphthene 7.
1.3 Synthesis and characterization of chalcogenyl-stabilized silyl borates

**General Procedure D:** The silane and trityl borate \([\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]\) were dissolved in benzene. Then the solution of the trityl borate was added to the silane at r.t. and the biphasic reaction mixture was stirred for 30 min. Subsequently, the phases were separated, the upper, nonpolar phase was removed and the polar phase was washed with benzene three times. After removing the solvent under low pressure, the residue was dissolved in a deuterated solvent and analyzed by NMR spectroscopy.

**Phenoxy-Stabilized Methylphenylsilyl borate 13a[B(C_6F_5)_4]**

The title compound 13a[B(C_6F_5)_4] was synthesized according to general procedure D using 1.1 equiv. (410 µmol, 151 mg) of 5-methylphenylsilyl-6-phenoxyacenaphthene 3a and 1.0 equiv. (380 µmol, 346 mg) of trityl borate.

![Diagram](image)

**¹H NMR** (499.9 MHz, 305.0 K, C_6D_6) \(\delta = 0.63\) (s, 3 H, SiCH₃), 3.07-3.12 (m, 2 H, CH₂), 3.19-3.24 (m, 2 H, CH₂), 6.15 (d, \(^3\)J\(_{HH}\) = 7.8 Hz, 1 H, 7-H), 6.82-6.84 (m, 1 H, 8-H), 6.98-7.02 (m, 2 H, SiPh), 7.08-7.13 (m, 3 H, SiPh), 7.28-7.33 (m, 1 H, OPh), 7.35-7.38 (m, 1 H, 3-H), 7.61 (d, \(^3\)J\(_{HH}\) = 7.0 Hz, 1 H, 4-H), the signals of m- and o-OPh were not found. **¹³C{¹H} NMR** (125.7 MHz, 305.0 K, C_6D_6) \(\delta = -3.9\) (SiCH₃), 30.6 (CH₂), 32.4 (CH₂), 108.7 (CH, C-7), 112.1 (C, C-5), 119.7 (CH, C-8), 121.6 (CH, SiPh), 124.2 (CH, C-3), 125.0 (C, ipso-SiPh), 125.5 (C, C-12), 129.4 (CH, SiPh), 131.3 (CH, SiPh), 135.2 (CH), 135.5 (CH, SiPh), 135.9 (CH, C-4), 138.9 (C, C-11), 149.8 (C), 147.9 (C), 151.5 (C), 151.9 (C, C-6). **²⁹Si{¹H} NMR** (99.3 MHz, 305.0 K, C_6D_6) \(\delta = 60.8\) ppm. **¹¹B{¹H} NMR** (160.46 MHz, 305.0 K, C_6D_6) \(\delta = -16.0\). **¹⁹F{¹H} NMR** (470.30 MHz, 305.0 K, C_6D_6) \(\delta = -166.7(-166.4)\) (m, 8 F, [B(C_6F_5)_4]), -162.6 (t, \(^3\)J\(_{FF}\) = 20.6 Hz, 4 F, [B(C_6F_5)_4]), -132.1(-131.8) (m, 8 F, [B(C_6F_5)_4]).
Figure S 40 – $^1$H NMR spectrum (500 MHz, 305 K, C$_6$D$_6$) of phenylmethylsilyl borate 13a[B(C$_6$F$_5$)$_4$] (*C$_6$D$_5$H).

Figure S 41 – $^{13}$C($^1$H) NMR spectrum (125.7 MHz, 305.0 K, C$_6$D$_6$) of phenylmethylsilyl borate 13a[B(C$_6$F$_5$)$_4$].
Phenoxy-Stabilized tert-Butylmethylsilyl Borate 13b[B(C₆F₅)₄]

The title compound 13b[B(C₆F₅)₄] was synthesized according to general procedure D using 1.0 equiv. (380 µmol, 130 mg) of 5-methylphenylsilyl-6-phenoxyacenaphthene 3b and 1.0 equiv. (380 µmol, 346 mg) of trityl borate.

**1H NMR** (499.9 MHz, 305.1 K, C₆D₆) δ = 0.37 (s, 3 H, CH₃), 0.69 (s, 9 H, t-Bu), 2.99-3.03 (m, 2 H, CH₂), 3.11-3.15 (m, 2 H, CH₂), 6.18 (d, J_H,H = 7.8 Hz, 1 H, 7-H), 6.78-6.81 (m, 1 H, 8-H), 7.13-7.24 (m, 4 H, overlap with C₆D₅H), 7.28-7.31 (m, 1 H, 3-H), 7.50 (d, J_H,H = 7.1 Hz, 1 H, 4-H), OPh signals broad and not listed. **13C{1H} NMR** (125.7 MHz, 305.1 K, C₆D₆) δ = -4.9 (SiCH₃), 20.8 (C, t-Bu), 23.8 (CH₃, t-Bu), 30.5 (CH₂), 32.3 (CH₂), 108.7 (CH, C-7), 113.3 (C, C-5), 119.5 (CH, C-8), 121.4 (CH, OPh), 124.0 (CH, C-3), 125.0 (C, C-12), 131.6 (CH, OPh), 132.1 (CH, OPh), 135.1 (CH, C-4), 138.8 (C, C-11), 146.0 (C, C-9), 149.5 (C, ipso-OPh), 151.3 (C, C-10), 153.0 (C, C-6). **29Si{1H} NMR** (99.3 MHz, 305.1 K, C₆D₆) δ = 72.2. **19F{1H} NMR** (470.30 MHz, 305.0 K, C₆D₆) δ = -166.7(-166.4) (m, 8 F, [B(C₆F₅)₄]), -162.6 (t, 3 J_F,F = 20.6 Hz, 4 F, [B(C₆F₅)₄]), -132.1(-131.8) (m, 8 F, [B(C₆F₅)₄]).
Figure S43 – $^1$H NMR spectrum (499.9 MHz, 305.1 K, C$_6$D$_6$) of phenoxy-stabilized tert-butyldimethylsilyl borate 13b[B(C$_6$F$_5$)$_4$].

Figure S44 – $^{13}$C($^1$H) NMR spectrum (125.7 MHz, 305.1 K, C$_6$D$_6$) of phenoxy-stabilized tert-butyldimethylsilyl borate 13b[B(C$_6$F$_5$)$_4$].
Figure S 45 – $^{29}\text{Si}^1\text{H}$ NMR spectrum (99.31 MHz, 305.0 K, C$_6$D$_6$) of phenoxy-stabilized tert-butylmethylsilyl borate 13b[B(C$_6$F$_5$)$_4$].

Phenylsulfanyl-Stabilized Methylphenylsilyl Borate 13c[B(C$_6$F$_5$)$_4$]

The title compound 13c[B(C$_6$F$_5$)$_4$] was synthesized according to general procedure D using 1.0 equiv. (347 µmol, 133 mg) of 6-methylphenylsilyl-5-phenylsulfanylacenaphthene 4a and 1.0 equiv. (347 µmol, 312 mg) of trityl borate.

$^1\text{H}$ NMR (499.9 MHz, 305.1 K, C$_7$D$_8$) $\delta$ = 0.33 (s, 2 H, SiCH$_3$, trans-13c), 0.79 (s, 3 H), SiCH$_3$, cis-13c), 3.03-3.17 (m, 7 H, CH$_2$), 6.15 (dm, $^3$$J_{\text{H,H}}$ = 7.9 Hz, 2 H, S-o-Ph, cis-13c), 6.54-6.59 (m, 3 H, SPh), 6.70-6.75 (m, 1 H, S-p-Ph, cis-13c), 6.79-6.87 (m, 4 H), 6.92-6.99 (m, 3 H, SPh), 7.02-7.20 (m, 9 H), 7.22-7.27 (m, 2 H), 7.40 (d, $^3$$J_{\text{H,H}}$ = 7.0 Hz, 1 H, 7-H, cis-13c), 7.43 (d, $^3$$J_{\text{H,H}}$ = 7.0 Hz, 0.6 H, 7-H, trans-13c). $^{13}\text{C}^1\text{H}$ NMR (125.7 MHz, 305.1 K, C$_7$D$_8$) $\delta$ = -4.4 (SiCH$_3$, trans-13c), -2.8 (SiCH$_3$, cis-13c), 31.0 (CH$_2$), 31.4 (CH$_2$), 116.1 (C), 117.3 (C), 119.0 (C-6), 122.7 (CH), 122.8 (CH), 123.4 (CH), 123.5 (CH), 123.6 (C), 125.5 (CH), 126.5 (C), 127.8 (CH, SPh), 128.3 (CH), 128.6 (CH), 129.0 (CH), 129.3 (CH), 129.7 (CH), 130.5 (CH), 131.5 (CH, SPh), 131.6 (CH), 132.8 (CH, SPh), 133.9 (CH), 134.2 (CH), 134.4 (CH), 134.9 (CH), 135.8 (CH), 137.0 (dm, $^1$$J_{\text{C,F}}$ = 246.3 Hz, [B(C$_6$F$_5$)$_4$]), 138.3 (CH, C-7), 138.4 (CH, C-7), 138.9 (dm, $^1$$J_{\text{C,F}}$ = 244.1 Hz, [B(C$_6$F$_5$)$_4$]), 139.4 (C), 139.6 (C), 139.7 (C), 139.9 (C), 149.2 (dm, $^1$$J_{\text{C,F}}$
= 240.0 Hz, [B(C₆F₅)₄]), 153.0 (C), 154.4 (C), 154.5 (C). $^{29}$Si($^1$H) NMR (99.3 MHz, 305.1 K, C₇D₈) δ = 53.9 (cis-13c), 51.2 (trans-13c). $^{11}$B($^1$H) NMR (160.38 MHz, 305.1 K, C₇D₈) δ = -16.0.

$^{19}$F($^1$H) NMR (470.30 MHz, 305.1 K, C₇D₈) δ = -166.6 (-166.4) (m, 8 F, [B(C₆F₅)₄]), -162.7 (t, $^3$J$_{F,F}$ = 20.6 Hz, 4 F, [B(C₆F₅)₄]), -131.8 (-131.6) (m, 8 F, [B(C₆F₅)₄]).

Figure S 46 – $^1$H NMR spectrum (499.9 MHz, 305.1 K, C₇D₈) of phenylsulfanyl-stabilized methylphenylsilyl borate 13c[B(C₆F₅)₄].

Figure S 47 – $^{13}$C($^1$H) NMR spectrum (125.7 MHz, 305.1 K, C₇D₈) of phenylsulfanyl-stabilized methylphenylsilyl borate 13c[B(C₆F₅)₄].
Naphthyl-Substituted Phenylsulfanyl-Stabilized Methylphenylsilyl Borate 14a[B(C₆F₅)₄]

The title compound 37b[B(C₆F₅)₄] was synthesized according to general procedure D using 1.0 equiv. (433 μmol, 154 mg) of 8-methylphenylsilyl-1-phenylsulfanyl-naphthalene 9 and 1.0 equiv. (433 μmol, 400 mg) of trityl borate.

\[ \text{[B(C}_6\text{F}_5)_4]^- \]

\(^1\)H NMR (499.87 MHz, 304.9 K, C\(_7\)D\(_8\)) \(\delta = 0.33\) (s, 2 H, SiCH\(_3\), \text{trans-14a}), 0.73 (s, 3 H, SiCH\(_3\), \text{cis-14a}), 6.10 (d, \(^3J_{HH} = 7.9\) Hz, 2 H, S-o-Ph, \text{cis-14a}), 6.48 (d, \(^3J_{HH} = 7.9\) Hz, 1 H, S-o-Ph, \text{trans-14a}), 6.56 (t, \(^3J_{HH} = 7.7\) Hz, 2 H), 6.72-6.77 (m, 3 H), 6.82-6.85 (m, 2 H), 6.87-6.88 (m, 1 H), 6.91-6.94 (m, 2 H), 6.97-6.98 (m, 1 H), 7.03-7.08 (m, 4 H), 7.11-7.22 (m, 4 H), 7.24-7.28 (m, 2 H), 7.34-7.36 (m, 2 H), 7.41-7.44 (m, 2 H), 7.50-7.53 (m, 0.5 H), 7.75-7.81 (m, 3.5 H).

\(^{13}\)C\(^{1}\)H NMR (75.48 MHz, 294.3 K, C\(_7\)D\(_8\)) \(\delta = -6.1\) (SiCH\(_3\), \text{trans-14a}), -3.4 (CH\(_3\), \text{cis-14a}), 122.4 (C), 122.7 (C), 124.5 (C), 124.6 (C), 125.1 (C), 127.9 (CH), 128.7 (CH), 128.7 (CH), 129.1 (CH), 129.3 (CH), 129.7 (C), 127.8 (CH), 130.3 (CH), 130.7 (CH), 131.6 (CH), 131.8 (CH), 132.9 (C), 133.0 (CH), 133.3 (CH), 133.9 (C), 134.0 (C), 134.2 (CH), 134.3 (CH), 134.3 (C), 134.5 (C), 137.0 (dm, \(J = 246.6\) Hz, [B(C\(_6\)F\(_5\))\(_4\)])}, 135.0 (CH), 135.8 (CH), 136.7

Figure S 48 – \(^{29}\)Si\(^{[1}\)H] NMR spectrum (99.3 MHz, 305.1 K, C\(_7\)D\(_8\)) of phenylsulfanyl-stabilized methylphenylsilyl borate 13c[B(C\(_6\)F\(_5\))\(_4\)].
(C), 136.8 (CH), 138.9 (dm, J = 245.4 Hz, [B(C_6F_5)_4])], 139.7 (C), 139.9 (C), 142.3 (CH), 143.2 (CH), 149.2 (dm, J = 241.6 Hz, [B(C_6F_5)_4]), signal of i-C of [B(C_6F_5)_4]^+ overlaps with solvent signal. $^{29}$Si{$^1$H} NMR (99.31 MHz, 305.0 K, C_7D_8) δ = 42.9 (trans-14a), 45.5 (cis-14a).

Figure S 49 – $^1$H NMR spectrum (499.87 MHz, 304.9 K, C_7D_8) of phenylsulfanyl-stabilized methylphenylsilyl borate 14a[B(C_6F_5)_4].
Figure S 50 – $^{13}$C($^1$H) NMR spectrum (75.48 MHz, 294.3 K, C$_7$D$_8$) of phenylsulfanyl-stabilized methylphenylsilyl borate 14a[B(C$_6$F$_5$)$_4$].
Figure S 51 – $^{13}$C(1H) DEPT NMR spectrum (75.48 MHz, 294.3 K, C$_7$D$_8$) of phenylsulfanyl-stabilized methylphenylsilyl borate 14a[B(C$_6$F$_5$)$_4$].
Figure S 52 – $^{29}\text{Si}(^1\text{H})$ NMR spectrum (99.3 MHz, 305.1 K, C$_7$D$_8$) of phenylsulfanyl-stabilized methylphenylsilyl borate 14a[B(C$_6$F$_5$)$_4$].
Figure S 53 – $^1$H VT NMR spectra (500 MHz, C$_7$D$_8$) of phenylsulfanyl-stabilized methylphenylsilyl borate 14a[B(C$_6$F$_5$)$_4$].

Phenylsulfanyl-Stabilized tert-Butylmethylsilyl Borate 13d[B(C$_6$F$_5$)$_4$]

The title compound 35c[B(C$_6$F$_5$)$_4$] was synthesized according to general procedure D using 1.0 equiv. (389 µmol, 141 mg) of 6-tert-butylmethylsilyl-5-phenylsulfanylacenaphthene 4b and 1.0 equiv. (389 µmol, 359 mg) of trityl borate.

$^1$H NMR (499.9 MHz, 305.1 K, C$_6$D$_8$) $\delta$ = 0.12 (s, 3H, CH$_3$), 0.89 (s, 9 H, t-Bu), 3.05-3.25 (m, 4 H, CH$_2$), 6.67 (dm, $J_{H,H}$ = 7.9 Hz, 2 H, o-Ph), 7.03-7.07 (m, 2 H, m-Ph), 7.11-7.12 (m, 1 H, 3-H), 7.13-7.16 (m, 1 H, p-Ph), 7.27-7.29 (m, 1 H, 8-H), 7.34 (dm, $J_{H,H}$ = 7.0 Hz, 1 H, 8-H), 7.56 (d, $J_{H,H}$ = 7.0 Hz, 1 H, 7-H).

$^{13}$C($^1$H) NMR (125.7 MHz, 305.0 K, C$_6$D$_8$) $\delta$ = -7.3 (SiCH$_3$), 20.7 (C, t-Bu), 24.3 (CH$_3$, t-Bu), 30.9 (CH$_2$), 31.3 (CH$_2$), 116.7 (C), 119.6 (C-6), 122.6 (CH, C-3), 123.1 (CH, C-8), 124.4 (C), 124.4-126.1 (brm, [B(C$_6$F$_5$)$_4$]), 128.4 (CH, o-Ph), 131.4 (CH, m-Ph), 132.6 (CH, p-Ph), 133.5 (CH, C-4), 137.0 (dm, $^1J_{C,F}$ = 240.1 Hz, [B(C$_6$F$_5$)$_4$]), 137.4 (CH,
C-7), 138.9 (dm, $^1J_{C,F} = 238.5$ Hz, [B(C$_6$F$_5$)$_4$]), 139.3 (C), 139.3 (C), 149.1 (dm, $^1J_{C,F} = 244.1$ Hz, [B(C$_6$F$_5$)$_4$]), 152.5 (C), 154.4 (C). $^{29}$Si($^1$H) NMR (99.3 MHz, 305.0 K, C$_6$D$_6$) $\delta = 70.0$. $^{29}$Si($^1$H) NMR (99.3 MHz, 297.9 K, CD$_2$Cl$_2$) $\delta = 70.5$. $^{11}$B($^1$H) NMR (160.38 MHz, 305.0 K, C$_6$D$_6$) $\delta = -16.0$. $^{19}$F($^1$H) NMR (470.30 MHz, 305.1 K, C$_6$D$_6$) $\delta = -166.6$ (-166.4) (m, 8 F, [B(C$_6$F$_5$)$_4$]), -162.7 (t, $^3J_{F,F} = 20.7$ Hz, 4 F, [B(C$_6$F$_5$)$_4$]), -132.0 (-131.7) (m, 8 F, [B(C$_6$F$_5$)$_4$]).

Figure S 54 – $^1$H NMR spectrum (499.9 MHz, 305.1 K, C$_6$D$_6$) of phenylsulfanyl-stabilized methyl(tert-butyldisilyl)borate 13d[B(C$_6$F$_5$)$_4$].
Figure S 55 – $^{13}$C($^1$H) NMR spectrum (125.7 MHz, 305.0 K, C$_6$D$_6$) of phenylsulfanyl-stabilized methyl(tert-butyl)lsilyl borate $^{13}$d[B(C$_{6}$F$_5$)$_4$].
Selanyl-Stabilized Methylphenylsilyl Borate 13e[B(C₆F₅)₄]

The title compound 13e[B(C₆F₅)₄] was synthesized according to general procedure D using 1.0 equiv. (406 µmol, 174 mg) of 5-phenylselanyl-6-phenylmethyldenaphthene 6 and 0.8 equiv. (325 µmol, 300 mg) of trityl borate.

\[
\begin{align*}
\text{PhMeSi} & \quad \text{SePh} \\
\end{align*}
\]

\(^1\text{H} \text{NMR}\) (499.87 MHz, 305.0 K, C₆D₆): \(\delta = 0.40\) (s, 1.8 H, trans-Me-H), 0.83 (s, 3 H, cis-Me-H), 3.05-3.14 (m, 7 H), 6.07 (d, 2 H, cis-o-Ph-H, \(^3\)J = 7.3 Hz), 6.52-6.55 (m, 3 H), 6.71-6.74 (m, 1 H), 6.79-6.80 (m, 2 H), 6.82-6.85 (m, 2 H), 6.90-6.93 (m, 1 H), 6.96-7.08 (m, 4 H), 7.12-7.15 (m, 4 H), 7.18-7.20 (m, 2 H), 7.24-7.28 (m, 2 H), 7.31-7.36 (m, 2 H).

\(^13\text{C} \left(\text{^1}\text{H}\right) \text{NMR}\) (125.71 MHz, 305.0 K, C₆D₆): \(\delta = -4.8\) (CH₃, trans), -2.5 (CH₃, cis), 30.9 (CH₂), 31.3 (CH₂), 118.4 (C), 119.6 (C), 121.8 (C), 121.9 (C), 122.7 (CH), 122.8 (CH), 123.2 (CH), 123.2 (CH), 124.4 (C), 126.6 (CH), 126.9 (C), 128.6 (CH), 129.2 (CH), 129.7 (CH), 129.9 (CH), 130.8 (CH), 130.9 (CH), 131.7 (CH), 132.1 (CH), 134.0 (CH), 134.3 (CH), 134.9 (CH), 135.0 (CH), 135.2 (CH), 135.2 (CH), 135.2 (CH), 135.2 (CH), 135.2 (CH).
135.6 (CH), 137.0 (dm, $^1J(C,F) = 236.8$ Hz, [B(C$_6$F$_5$)$_4$]), 138.5 (CH), 138.7 (CH), 139.1 (dm, $^1J(C,F) = 235.4$ Hz, [B(C$_6$F$_5$)$_4$]), 140.2 (C), 140.5 (C), 140.6 (C), 144.5 (C), 149.2 (dm, $^1J(C,F) = 242.7$ Hz, [B(C$_6$F$_5$)$_4$]) 153.0 (C), 154.0 (C), 154.2 (C). (ipsp-C of [B(C$_6$F$_5$)$_4$] overlaps with the solvent signal). $^{29}$Si{$^1$H} NMR (99.31 MHz, 305.0 K, C$_7$D$_8$): $\delta = 49.7$ ($J_{Si,Se} = 59.5$ Hz, trans), 52.3 ($J_{Si,Se} = 59.1$ Hz, cis). $^{77}$Se{$^1$H} NMR (95.36 MHz, 305.0 K, C$_7$D$_8$): $\delta = 260.3$ (cis), 262.6 (trans). $^{11}$B{$^1$H} NMR (160.38 MHz, 305.0 K, C$_7$D$_8$): $\delta = -16.0$. $^{19}$F{$^1$H} NMR (470.30 MHz, 305.0 K, C$_7$D$_8$): $\delta = -166.6$(-166.4) (m, 8F), -162.7 (t, $J = 20.1$, 4F), 131.8(-131.5) (m, 8F).

Figure S 57 – $^1$H NMR spectrum (499.9 MHz, 305.1 K, C$_7$D$_8$) of phenylselanyl-stabilized methylphenylsilyl borate 13e[B(C$_6$F$_5$)$_4$] (*C$_6$D$_5$CHD$_2$, #C$_6$H$_{12}$).
Figure S 58 – $^{13}$C($^1$H) NMR spectrum (125.7 MHz, 305.0 K, C$_7$D$_8$) of phenylselanyl-stabilized methylphenylsilyl borate 13e[B(C$_6$F$_5$)$_4$] (*C$_7$D$_8$, #C$_6$H$_{12}$).
Figure S 59 – $^{29}$Si($^1$H) NMR spectrum (99.31 MHz, 305.0 K, C$_7$D$_8$) of phenylselanyl-stabilized methylphenylsilyl borate 13e[B(C$_6$F$_5$)$_4$].
Figure S 60 – $^{77}$Se($^1$H) NMR spectrum (95.36 MHz, 305.0 K, C$_7$D$_8$) of phenylselanyl-stabilized methylphenylsilyl borate $^{13e}$[B(C$_6$F$_5$)$_4$].

Selanyl-Stabilized Methylphenylsilyl Borate $^{14b}$[B(C$_6$F$_5$)$_4$]

The title compound $^{14b}$[B(C$_6$F$_5$)$_4$] was synthesized according to general procedure D using 1.0 equiv. (446 µmol, 180 mg) of 1-phenylselanyl-8-phenylmethylsilylnaphthalene $^{10a}$ and 0.8 equiv. (357 µmol, 329 mg) of trityl borate.

$^1$H NMR (499.87 MHz, 305.0 K, C$_6$D$_6$): $\delta$ = 0.37 (s, 2H, Si-CH$_3$, trans), 0.77 (s, 3H, Si-CH$_3$, cis), 6.03 (d, 2H, $^3$J = 7.9 Hz, Se-Ph- o-H, cis), 6.44 (d, 1.4H, $^3$J = 7.9 Hz, Se-Ph- o-H, trans), 6.56 (t, 2H, $^3$J = 7.4 Hz, Se-Ph- m-H, cis), 6.72-6.80 (m, 3H, cis), 6.85-6.93 (m, 4H), 7.03 - 7.14 (m, 5H), 7.25 - 7.33 (m, 5H), 7.40 (t, $^3$J = 7.5 Hz, 2H), 7.80-7.85 (m, 4H). $^{13}$C($^1$H) NMR (125.71 MHz, 305.0 K, C$_6$D$_6$): $\delta$ = -5.6 (CH$_3$, trans), -3.1 (CH$_3$, cis), 123.4 (C), 124.1-126.1 (brm, [B(C$_6$F$_5$)$_4$]), 124.3 (C), 124.7 (C), 125.9 (C), 126.5 (CH), 127.9 (CH), 128.3 (CH), 128.4 (CH), 128.7 (CH), 128.9 (CH), 129.6 (CH), 129.8 (CH), 130.8 (CH), 130.9 (CH), 131.6 (CH), 132.0 (C), 132.1 (CH), 132.8 (CH), 132.9 (CH), 133.8 (CH), 134.0 (CH), 134.3 (CH), 134.7 (C), 134.9 (CH), 135.5 (CH), 136.9 (CH), 136.9 (dm, $^1$J$_{C,F}$ = 234.6 Hz, [B(C$_6$F$_5$)$_4$]), 137.0 (CH),
138.9 (dm, $^{1}J_{C,F} = 136.4$ Hz, [B(C₆F₅)₄]), 139.9 (C), 140.2 (C), 149.1 (d, $^{1}J_{C,F} = 239.8$ Hz, [B(C₆F₅)₄]). ²⁹Si{¹H} NMR (99.31 MHz, 305.0 K, C₆D₆): δ = 41.4 (trans), 43.7 (cis). ²⁹Si{¹H} INEPT NMR (99.31 MHz, 305.0 K, C₆D₆, D₃ = 0.0112 s, D₄ = 0.0313 s): δ = 41.4, 43.7 ($J_{Si,Se} = 61$ Hz). ⁷⁷Se{¹H} NMR (95.36 MHz, 305.0 K C₆D₆): δ = 254.7 (cis), 256.1 (trans).

Figure S 61 – ¹H NMR spectrum (499.87 MHz, 305.0 K, C₆D₆) of phenylselanyl-stabilized methylphenylsilyl borate 1₄b[B(C₆F₅)₄].
Figure S 62 – $^{13}$C($^1$H) NMR spectrum (125.71 MHz, 305.0 K, C$_6$D$_6$) of phenylselanyl-stabilized methylphenylsilyl borate $14b$[B(C$_6$F$_5$)$_4$].
Figure S 63 – $^{29}\text{Si}(^{1}\text{H})$ INEPT NMR spectrum (99.31 MHz, 305.0 K, C$_6$D$_6$, $D_3 = 0.0112$ s, $D_4 = 0.0313$ s) of phenylselanyl-stabilized methylphenylsilyl borate 14b[B(C$_6$F$_5$)$_4$].
Figure S 64 – $^{77}\text{Se}^{1}\text{H}$ NMR spectrum (95.36 MHz, 305.0 K C$_6$D$_6$) of phenylselanyl-stabilized methylphenylsilyl borate 14b[B(C$_6$F$_5$)$_4$].

Selanyl-Stabilized tert-butylphenylsilyl Borate 14c[B(C$_6$F$_5$)$_4$]

The title compound 14c[B(C$_6$F$_5$)$_4$] was synthesized according to general procedure D using 1.0 equiv. (443 µmol, 170 mg) of 1-phenylselanyl-8-tert-butylmethylsilylnaphthalene 10b and 0.8 equiv. (355 µmol, 327 mg) of trityl borate.

$^1$H NMR (499.87 MHz, 304.9 K, C$_6$D$_6$): $\delta$ = 0.06 (s, 3H, Si-CH$_3$, trans), 0.37 (s, Si-CH$_3$, cis), 0.59 (s, Si-C(CH$_3$)$_3$, cis), 0.73 (s, 9H, Si-C(CH$_3$)$_3$, trans), 6.40 - 6.42 (m, 2H, 2'-H), 6.87 (t, 2H, $^3$J = 7.9 Hz, 3'-H), 6.98 - 7.01 (m, 1H, 4'-H), 7.19 - 7.22 (m, 1H, 3-H), 7.24-7.26 (m, 1H), 7.33 - 7.39 (m, 2H), 7.71-7.74 (m, 2H, 4-H, 6-H).

$^{13}$C($^1$H) NMR (125.71 MHz, 305.0 K C$_6$D$_6$): $\delta$ = -7.6 (CH$_3$, Si-CH$_3$), 20.8 (C, Si-C(CH$_3$)$_3$), 24.7 (CH$_3$, Si-C(CH$_3$)$_3$), 123.1 (C, C-1'), 124.3-125.9 (brm, [B(C$_6$F$_5$)$_4$]), 125.1 (C), 128.3 (CH, C-3), 128.5 (CH, C-2'), 128.7 (CH), 131.7 (CH, C-3'), 132.1 (CH, C-4'), 132.6 (CH, C-6), 133.7 (CH), 133.9 (CH, C-4), 134.7 (C, C-10), 136.2 (CH, C-7), 137.0 (dm, $^1$J$_{C,F}$ = 240.2 Hz, [B(C$_6$F$_5$)$_4$]), 138.9 (dm, $^1$J$_{C,F}$ = 241.0 Hz, [B(C$_6$F$_5$)$_4$]). One C missing due to overlap. $^{29}$Si($^1$H)
NMR (99.31 MHz, 305.0 K, C₆D₆): δ = 54.3 (cis), 62.9 (trans). ²⁹Si¹H INEPT NMR (99.31 MHz, 305.0 K, C₆D₆, D₃ = 0.0112 s, D₄ = 0.0313 s) δ = 62.9 (J₆₇,Se = 67.6 Hz). ⁷⁷Se¹H NMR (95.36 MHz, 305.0 K, C₆D₆): δ = 232.0 (J₆₇,Se = 67.6 Hz, trans), 251.7 (cis).

Figure S 65 – ¹H NMR spectrum (499.87 MHz, 304.9 K, C₆D₆) of phenylselanyl-stabilized tert-butylmethylsilyl borate 14c[B(C₆F₅)₄].
Figure S 66 – $^{13}$C($^1$H) NMR spectrum (125.71 MHz, 305.0 K C$_6$D$_6$) of phenylselanyl-stabilized tert-butylmethylsilyl borate 14c[B(C$_6$F$_5$)$_4$].

Figure S 67 – $^{13}$C($^1$H) DEPT NMR spectrum (125.71 MHz, 305.0 K C$_6$D$_6$) of phenylselanyl-stabilized tert-butylmethylsilyl borate 14c[B(C$_6$F$_5$)$_4$].
Figure S 68 – $^{29}\text{Si}({}^1\text{H})$ NMR spectrum (99.31 MHz, 305.0 K, C$_6$D$_6$) of phenylselanyl-stabilized tert-butylmethylsilyl borate 14c[B(C$_6$F$_5$)$_4$].
Figure S 69 – $^1\text{H}/^{29}\text{Si}$ HMBC NMR spectrum (499.87 MHz, 304.9 K, C$_6$D$_6$) of phenylselanyl-stabilized tert-butylmethylsilyl borate $14\text{c}[$B(C$_6$F$_5$)$_4$].
Figure S 70 – $^{77}$Se($^1$H) NMR spectrum (95.36 MHz, 305.0 K C$_6$D$_6$) of phenylselanyl-stabilized tert-butylmethylsilyl borate 14c[B(C$_6$F$_5$)$_4$].

Tellanyl-Stabilized Methylphenylsilyl Borate 13f[B(C$_6$F$_5$)$_4$]

The title compound 13f[B(C$_6$F$_5$)$_4$] was synthesized according to general procedure D using 1.2 equiv. (442 µmol, 230 mg) of 5-mesityltellanyl-6-phenylmethylacenaphthene 7 and 1.0 equiv. (363 µmol, 335 mg) of trityl borate.

$^1$H NMR (499.87 MHz, 305.0 K, C$_6$D$_6$): $\delta$ = 0.62 (s, 3 H, SiCH$_3$, trans), 0.88 (s, 3 H, SiCH$_3$, $^3$J$_{H,Te}$ = 17.8 Hz, cis), 1.50 (s, 5 H, o-CH$_3$, cis), 1.70 (s, 6 H, o-CH$_3$, trans), 1.88 (s, 3 H, p-CH$_3$, cis), 2.06 (s, 3 H, p-CH$_3$, trans), 3.05–3.10 (m, 8 H, 4 × CH$_2$, H–1, H–2, cis/trans), 6.19 (s, 2 H, H–19, H–19′, cis), 6.60 (s, 2 H, H–19, H–19′, trans), 6.83–6.86 (m, 2 H, H–14, H–14′, cis), 7.02–7.05 (m, 1 H), 7.09–7.16 (m, 6 H, H–14, H–14′, trans), 7.21–7.25 (m, 3 H), 7.26–7.32 (m, 4 H), 7.36 (d, 1 H, $^3$J$_{H,H}$ = 7.0 Hz, H–7, trans), 7.45 (d, 1 H, $^3$J$_{H,H}$ = 7.3 Hz, H–4, cis). $^{13}$C($^1$H) NMR (125.71 MHz, 305.0 K, C$_6$D$_6$): $\delta$ = -2.7 (CH$_3$, SiCH$_3$, trans), -1.4 (CH$_3$, SiCH$_3$, cis), 19.9, 20.3 (2 × CH$_3$, p-CH$_3$), 23.8 (2 × CH$_3$, o-CH$_3$, cis), 24.4 (2 × CH$_3$, o-CH$_3$, trans), 30.5, 30.6,
30.7, 30.7 (4 × CH₂, C–1, C–2, cis/trans), 113.5, 113.9 (C), 114.6 (C, 2 × C, C–17, cis/trans), 122.1 (C), 122.3 (CH), 122.6 (CH), 122.6 (CH), 124.1–126.1 (m, Cₚ₋₀, [B(C₆F₅)₄]), 127.3 (C), 127.9 (C), 128.1 (C), 128.3 (CH), 128.4 (CH), 128.5 (CH), 128.6, 129.0 (CH), 129.6 (CH), 129.8, 131.4 (CH, C–19, C–19′, trans), 131.8 (CH, C–19, C–19′, cis), 133.0 (CH), 133.6 (CH), 134.9 (CH), 134.9 (CH), 135.4 (CH), 137.9 (tm, CF, [B(C₆F₅)₄]), 138.5 (CH), 138.6 (CH), 139.3 (CH, C–7, trans), 139.8 (CH, C–4, cis), 140.7 (C), 140.7 (C), 141.7, 141.9 (2 × C, C–20, cis/trans), 142.9, 143.2, 143.3, 143.4 (4 × C, C–18, C–18′, cis/trans), 149.2 (d, CF, J_C,F = 241 Hz, [B(C₆F₅)₄]), 152.9, 153.1 (2 × C, C–9, cis/trans), 153.7, 153.9 (2 × C, C–10, cis/trans).

²⁹Si{¹H} NMR (99.31 MHz, 305.0 K, C₆D₆): δ = 36.4 (trans), 40.7 (cis). ²⁸Si{¹H} INEPT NMR (99.31 MHz, 305.0 K, C₆D₆): δ = 36.4 (J_Si,Te = 171 Hz, trans), 40.7 (J_Si,Te = 163 Hz, cis).

¹²⁵Te{¹H} NMR (157.74 MHz, 305.0 K, C₆D₆): δ = 234.4 (J_Te,SI = 171 Hz, trans), 239.7 (J_Te,SI = 163 Hz, cis). ¹¹B{¹H} NMR (160.38 MHz, 305.0 K, C₆D₆): δ = -15.9 ([B(C₆F₅)₄]). ¹⁹F{¹H} NMR (470.30 MHz, 305.0 K, C₆D₆): δ = -166.90 (16 F, [B(C₆F₅)₄]), -162.87 (8 F, [B(C₆F₅)₄]), -162.23 (8 F, [B(C₆F₅)₄]), -131.68 (brs, 16 F, [B(C₆F₅)₄]).

Figure S 71 – ¹H NMR spectrum (499.87 MHz, 305.0 K, C₆D₆) of mesitylteyllanyl-stabilized phenylmethyisilyl borate 13f[B(C₆F₅)₄].
Figure S 72 – $^{13}$C($^1$H) NMR spectrum (125.71 MHz, 305.0 K, C$_6$D$_6$) of mesityltellanyl-stabilized phenylmethylsilyl borate 13f[B(C$_6$F$_5$)$_4$].
Figure S 73 – $^{29}$Si(1'H) INEPT NMR spectrum (99.31 MHz, 305.0 K, C$_6$D$_6$) of mesityltellanyl-stabilized phenylmethyldisilyl borate 13f[B(C$_6$F$_5$)$_4$].
Figure S 74 – $^{125}$Te($^1$H) NMR spectrum (157.74 MHz, 305.0 K, C$_6$D$_6$) of mesityltellanyl-stabilized phenylmethysilyl borate $13f[B(C_6F_5)_4]$. 
1.4 Chiral Resolution and Chiral Memory Experiments

General Procedure F: A Schlenk flask was charged with copper(I) chloride and triphenylphosphane in a ratio of 1:2. Toluene was added and the mixture was stirred until triphenylphosphane was dissolved. Subsequently sodium tert-butoxide (equimolar to CuCl) was added at r.t. and the mixture was stirred until the color turned yellow (5 – 10 min). The pyridyl alcohol (\(R\))-E was dissolved in toluene and added at r.t. to the catalyst mixture. The mixture turned orange. Subsequently the silane was added either as a solid in one portion or dissolved in toluene whereupon the mixture turned brown-red. After stirring for approximately 16 h, the reaction mixture was filtrated through a thin layer of silica gel to remove the Cu(I) species, the solvent was removed and the crude product was purified by a two-step column chromatography if not mentioned otherwise in the details. The first column chromatography (eluent petroleum ether/ethyl acetate 100:0 \(\rightarrow\) 50:50) with a short column resulted in two fraction: 1. (+)-Silane + Ph\(_3\)P, 2. Siloxanes + impurities. Both fractions needed further purification which is specified for each compound in detail below.

6-Phenoxy-5-methylphenylsilylacenaphthene 3a

The kinetic resolution of the title compound 3a was performed according to General Procedure F using 305.6 \(\mu\)mol copper(I) chloride, 1.61 mmol of the pyridyl alcohol and 3.06 mmol of silane 3a. The catalyst was prepared as usual at r.t., then the mixture was cooled with an ice bath, first the alcohol/toluene and subsequently the silane/toluene mixture was added dropwise, the mixture was warmed slowly to r.t. over night. The crude product was purified by a short column chromatography (eluent petroleum ether/ethyl acetate 100:0 \(\rightarrow\) 0:100) resulting in two fractions. Fraction 1 ((+)-silane 3a + Ph\(_3\)P) was further purified by oxidation of the phosphane with \(\text{H}_2\text{O}_2\). Therefore, the solid were dissolved in petroleum ether and 0.6 mL \(\text{H}_2\text{O}_2\) (30w% in \(\text{H}_2\text{O}\)) was added at r.t.. After stirring the mixture for 16 h the solid which precipitated was filtered off and the phases were separated. The solvent of the organic layer was removed and the residue was purified via recrystallization from hexanes. (+)-Silane 3a was obtained with a yield of 52 % and an ee of 56 % ([\(\alpha\]) = +12° (0.01 mol L\(^{-1}\))). Fraction 2 (siloxanes 12a) was not further purified (yield 61 %). The crude fraction 2 was used for the reduction of siloxane to obtain (-)-silane 3a.

![PhMeSi-O-OPh](image-url)
$^1$H NMR (499.87 MHz, 305.0 K, C$_6$D$_6$) $\delta = 0.99$ (s, 3 H, SiCH$_3$), 1.21 (s, 9 H, t-Bu), 2.99-3.04 (m, 2 H, CH$_2$), 3.12-3.17 (m, 2 H, CH$_2$), 5.02 (s, 1 H, OCH), 6.47 (dm, $^3$$J_{HH} = 7.7$ Hz, 2 H, OPh), 6.50-6.53 (m, 1 H, Py), 6.56 (d, $^3$$J_{HH} = 7.5$ Hz, 1 H, 7-H), 6.78-6.81 (m, 2 H, Si-m-Ph), 6.82-6.85 (m, 2 H, 8-H, O-ipsoph), 6.89-6.97 (m, 4 H, Py, OPh, Si-p-Ph), 7.16-7.18 (m, 2 H, Si-σ-Ph), 7.26 (dm, $^3$$J_{HH} = 7.9$ Hz, 1 H, Py), 7.46 (dm, $^3$$J_{HH} = 6.9$ Hz, 1 H, 3-H), 8.27-8.31 (m, 1 H, Py), 8.96 (d, $^3$$J_{HH} = 6.9$ Hz, 1 H, 4-H). Additional signals for second diastereomer: 0.57 (s, SiCH$_3$), 1.06 (s, t-Bu), 4.94 (s, OCH), 7.51 (d, $^3$$J_{HH} = 7.0$ Hz, 3-H), 8.47-8.49 (m, Py), 8.96 (d, $^3$$J_{HH} = 7.0$ Hz, 4-H). $^{13}$C($^1$H) NMR (125.71 MHz, 305.0 K, C$_6$D$_6$) $\delta = -2.0$ (SiCH$_3$), 26.8 (CH$_3$, t-Bu), 29.6 (CH$_2$), 31.0 (CH$_2$), 36.8 (C, t-Bu), 84.5 (CH, OC), 112.0 (CH, C-7), 119.1, 120.3 (CH, C-3), 121.3 (CH), 121.3 (CH, Py), 123.1 (CH, Py), 124.0 (CH), 126.1 (C), 127.1 (CH), 128.2 (CH, Py), 128.7 (C), 129.6 (CH), 133.6 (CH), 134.5 (CH, Py), 138.5 (CH, C-4), 139.0 (C), 140.0 (C, ace), 141.4 (C, ace), 147.5 (CH, Py), 148.5 (C, ace), 153.4 (C, C-6), 155.4 (C, O-ipsoph), 162.3 (C, Py). $^{29}$Si($^1$H) NMR (99.31 MHz, 305.0 K, C$_6$D$_6$) $\delta = -5.0$ (main), -4.6. $^1$H/$^15$N HMBC NMR (499.87 MHz, 305.0 K, C$_6$D$_6$) $\delta = 316.5$ (main), 317.5.

Figure S 75 – $^1$H NMR spectrum (499.87 MHz, 305.0 K, C$_6$D$_6$) of siloxanes 12(Ch=O).
Figure S 76 – $^{13}$C($^1$H) NMR spectrum (125.71 MHz, 305.0 K, C$_6$D$_6$) of siloxanes 12(Ch=O).

Figure S 77 – $^{29}$Si($^1$H) INEPT NMR spectrum ((99.31 MHz, 305.0 K, D$_3$ = 0.0122 s, D$_4$ = 0.0313 s, C$_6$D$_6$) of siloxanes 12(Ch=O) (# silicon grease).
6-Methylphenylsilyl-5-phenylsulfanylacenaphthene 4a

For the chiral resolution of 1.0 equiv. (1.05 mmol, 401.0 mg) of the title compound 4a 0.2 equiv. (213.14 µmol, 21.1 mg) copper(I)chloride, 0.4 equiv. (242.34 µmol, 111.3 mg) triphenylphosphane, 0.2 equiv. (208.11 µmol, 20.0 mg) sodium tert-butoxide and 0.55 equiv. (576.75 µmol, 95.3 mg in 3.5 mL toluene) of the pyridyl alcohol (R)-11 were used. The catalyst was prepared in 2.0 mL toluene and the silane 4a was added as a solid in one portion. The crude product was an oil which was adsorbed on silica for a solid deposition at the column. Eluent for column chromatography petroleum ether/ethyl acetate 98:2 → 90:10. Two fractions collected: the first fraction was the (+)-silane 4a and Ph_3P, which was further purified via preparative TLC (eluent petroleum ether/ethyl acetate 99:1, TLC was three times eluted). The yield of (+)-silane 43b ([(α]D = 11, c = 0.06 mol L⁻¹ in Et_2O; ee = 66 %) was 113.0 mg (295.35 µmol, 56 %). The second fraction contained the siloxanes 12b and impurities. Siloxanes 12(Ch=S) were obtained purely by adding a pentane/ethyl acetate 9:1 mixture to the oil. Siloxanes 12(Ch=S) were dissolved and the impurities precipitated. After removal of the solvent, siloxanes 12(Ch=S) were obtained as a colorless viscous oil. The yield of siloxanes 12(Ch=S) was 171.0 mg (313.29 µmol, 60 %).

\[ ^1H \text{ NMR} \] (499.87 MHz, 305.0 K, C_6D_6) δ = 1.09 (s, 3 H, SiCH_3), 1.19 (s, 9 H, t-Bu), 2.94-2.97 (m, 2 H, CH_2), 3.06-3.08 (m, 2 H, CH_2), 5.00 (s, 1 H, OCH), 6.49-6.52 (m, 1 H, Py), 6.56-6.58 (m, 2 H), 6.70-6.74 (m, 3 H), 6.77-6.80 (m, 2 H, SiPh), 6.84-6.90 (m, 2 H, Py), 6.93 (dm, 3J_H_H = 7.2, 1 H, 3-H), 7.18-7.21 (m, 2 H, Py, overlap with C_6D_5H), 7.23-7.24 (m, 2 H, SiPh), 7.43 (dm, 3J_H_H = 7.1, 1 H, 8-H), 7.66 (d, 3J_H_H = 7.1 Hz, 1 H, 4-H), 8.29-8.30 (m, 1 H, Py), 9.19 (d, 3J_H_H = 7.1 Hz, 7-H). Additional signals for second diasteromer: 0.66 (s, SiCH_3), 1.03 (s, t-Bu), 4.96 (s, OCH), 6.64-6.68 (m), 7.03-7.07 (m), 7.10-7.14 (m), 7.49 (dm, 3J_H_H = 7.0 Hz), 7.53-7.56 (m), 7.59 (dm, 3J_H_H = 7.9 Hz), 7.69 (d, 3J_H_H = 7.2 Hz), 8.46-8.49 (m), 8.62 (d, 3J_H_H = 7.0), 9.32 (d, 3J_H_H = 7.1 Hz). \[ ^{13}C\{^1H\} \text{ NMR} \] (125.71 MHz, 305.0 K, C_6D_6) δ = -0.6 (SiCH_3), 26.8 (CH_3, t-Bu), 30.1 (CH_2), 30.3 (CH_2), 36.8 (C, t-Bu), 84.5 (CH, OC), 120.2 (CH, C-8), 120.6 (CH, C-3), 121.2 (CH, Py), 123.2 (CH, Py), 124.8 (CH), 126.3 (C), 126.8 (CH), 127.3 (CH), 127.9 (CH), 128.6 (CH), 129.0 (C, C-6), 133.1 (CH, SiPh), 134.4 (CH), 139.4(CH, C-4), 139.4 (C), 140.0 (C), 140.9 (C, ace), 141.3 (CH, C-7), 141.4 (C), 147.5 (CH, Py), 149.3 (C, ace), 149.6 (C, ace), 181.1 (C, ace), 182.6 (C, ace).
162.2 (C, Py). Additional signals for the second diastereomer: -0.2 (SiCH₃), 26.7 (CH₃, t-Bu), 36.7 (C, t-Bu), 83.9 (CH, OC), 120.3 (CH), 120.6 (CH), 121.7 (CH), 122.9 (CH), 124.7 (CH), 126.2 (C), 126.5 (CH), 127.1, (CH), 127.9 (CH), 128.3 (CH), 129.0 (C), 135.1 (CH), 139.5 (CH), 139.6 (C), 140.1 (CH), 141.2 (C), 141.3 (CH), 141.7 (C), 148.0 (CH), 163.7 (C). $^{29}$Si$^{1}$$^{1}$$^{H}$ NMR (99.31 MHz, 305.0 K, C₆D₆) $\delta$ = -7.7 (main), -7.5. $^{1}$$^{H}$$^{15}$N HMBC NMR (499.87 MHz, 305.0 K, C₆D₆) $\delta$ = 310.6, 307.8 (main).

Figure S 78 – $^{1}$$^{H}$ NMR spectrum (499.87 MHz, 305.0 K, C₆D₆) of siloxanes 12(Ch=S) (° second diastereomer, # impurities or residual solvent).
Figure S 79 – $^{13}\text{C}(^{1}\text{H})$ NMR spectrum (125.71 MHz, 305.0 K, C$_6$D$_6$) of siloxanes 12(Ch=S).

Figure S 80 – $^{29}\text{Si}(^{1}\text{H})$ INEPT NMR spectrum ((99.31 MHz, 305.0 K, C$_6$D$_6$) of siloxanes 12(Ch=S) (° second diastereomer, # silicon grease/impurities).
Figure S 81 – $^1$H/$^29$Si HMBC NMR spectrum (499.87 MHz, 304.9 K, C$_6$D$_6$) of siloxanes 12(Ch=S) (# impurities).

8-Methylphenylsilyl-1-phenylsulfanyl-naphthalene 9

For the chiral resolution of 1.0 equiv. (818.94 µmol, 292.0 mg) of the title compound 9 0.1 equiv. (163.78 µmol, 16.0 mg) copper(I)chloride, 0.2 equiv. (327.58 µmol, 86.0 mg) triphenylphosphane, 0.1 equiv. (163.78 µmol, 16.0 mg) sodium tert-butoxide and 0.6 equiv. (491.36 µmol, 81.0 mg in 2 mL toluene) of pyridyl alcohol (R)-11 were used. The catalyst was prepared in 2 mL toluene and the silane was added as a solid. The first column chromatography resulted in two fractions: 1. (+)-silane 9 + Ph$_3$P (209 mg), 2. Siloxanes 12(naph,Ch=O) + impurities (217 mg). Preparative TLC of the first fraction (eluent petroleum ether, eluted three times) gave 86.0 mg (241.19 µmol, 59 %) of (+)-silane 9 ([α]$_D$ = 17, c = 0.04 molL$^{-1}$ in Et$_2$O; ee = 84 %). Preparative TLC of the second fraction (eluent petroleum ether/ethyl acetate 9:1) gave 159.0 mg (305.90 µmol, 75 %) of siloxanes 12(naph,Ch=O).
$^1$H NMR (499.87 MHz, 305.1 K, C$_6$D$_6$) δ = 1.07 (s, 3 H, SiCH$_3$), 1.15 (s, 9 H, t-Bu), 4.91 (s, 1 H, OCH), 6.40-6.43 (m, 2 H, SPh), 6.48-6.52 (m, 1 H, Py), 6.65-6.71 (m, 3 H, SPh), 6.74-6.78 (m, 2 H), 6.83-6.88 (m, 2H, Py), 7.04-7.10 (m, 3 H, naph, Py), 7.13-7.17 (m, 2 H, SiPh), 7.56-7.61 (m, 1 H, 6-H), 7.62-7.67 (m, 2 H, SPh), 7.76-7.79 (m, 1 H), 8.26-8.29 (m, 1 H, Py), 9.24-9.28 (m, 7-H), the sum of the integrals in the aromatic region is by 1 H too high, most likely due to overlap with the second diastereomer. Additional signals for second diastereomer: 0.63 (s, SiCH$_3$), 0.99 (s, t-Bu), 4.90 (s, OCH), 6.36-6.39 (m), 6.57-6.59 (m), 7.43-7.48 (m), 7.49-7.52 (m), 8.44-8.47 (m, Py), 9.33-9.36 (m, 7-H). $^{13}$C($^1$H) NMR (125.71 MHz, 305.0 K, C$_6$D$_6$) δ = -0.6 (SiCH$_3$), 26.7 (CH$_3$, t-Bu), 36.6 (C, t-Bu), 84.4 (CH, OC), 120.9 (CH, Py), 122.9 (CH, Py), 125.0 (CH), 125.8 (CH, naph), 125.8 (CH), 126.7 (CH, SPh), 127.1 (CH), 127.6 (CH), 128.5 (CH), 131.2 (C), 131.3 (CH), 131.5 (CH), 132.6 (CH), 134.1 (C, C-8/Si-ipso-Ph), 134.2 (CH), 135.4 (C), 137.0 (CH), 139.2 (C, C-8/Si-ipo-Ph), 140.1 (CH, C-7), 140.1 (C), 140.9 (C), 147.3 (CH, Py), 161.9 (C, Py). Additional signals for the second diastereomer: -0.1 (SiCH$_3$), 26.6 (CH$_3$, t-Bu), 36.5 (C, t-Bu), 83.3 (CH, OC), 121.5 (CH), 122.7 (CH), 124.9 (CH), 135.6 (C), 140.6 (C), 141.7 (C), 147.9 (CH), 163.4 (C). $^{29}$Si($^1$H) NMR (99.31 MHz, 305.0 K, C$_6$D$_6$) δ = -11.2 (main), -10.9. $^1$H/$^{15}$N HMBC NMR (499.87 MHz, 305.0 K, C$_6$D$_6$) δ = 316.6. HRMS protonated at N atom C$_{33}$H$_{34}$NOSSi, found: 520.2128, calculated 520.2130.

Figure S 82 – $^1$H NMR spectrum (499.87 MHz, 305.0 K, C$_6$D$_6$) of siloxanes 12 (naph, Ch=O) (*) second diastereomer, # impurities or residual solvent).
Figure S 83 — $^{13}$C($^1$H) NMR spectrum (125.71 MHz, 305.0 K, C$_6$D$_6$) of siloxanes 12(naph,CH=O).

Figure S 84 — $^{29}$Si($^1$H) NMR spectrum (99.31 MHz, 305.0 K, C$_6$D$_6$) of siloxanes 12(naph,CH=O) (second diastereomer, # impurities).
Figure S 85 – $^1$H/$^{29}$Si HMBC NMR spectrum (499.87 MHz, 304.9 K, C$_6$D$_6$) of siloxanes 12 (# impurities).
Reduction of siloxanes 12

The siloxanes 12 were dissolved in 2-20 mL diethylether and di-iso-butylaluminiumhydride (1 M in n-hexane) was added at r.t. The mixture was stirred for 16 h and afterwards quenched by addition of 1-20 mL 1 M hydrochloric acid. The two phasic mixture was stirred for 20-60 min, the phases were separated and the product was extracted from the aqueous layer (3 x 5-20 mL Et₂O). After removal of the solvent, the product was purified via column chromatography or preparative TLC (eluent PE). Details see Table S1. 

**Entry 1**: Reaction in 20 mL Et₂O, work up with 20 mL 1 M hydrochloric acid. **Entry 2**: Reaction in 4 mL Et₂O, work up with 3 mL 1 M hydrochloric acid. **Entry 3**: Reaction in 2 mL Et₂O, work up with 1 mL 1 M hydrochloric acid.

Table S1 – Batches of the reduction of siloxanes 12 to the corresponding (-)-silanes 3a, 4a and 9 ([α]D measured in Et₂O).

| Entry | Comp. | 1.0 equiv. siloxane | 2.0-2.5 equiv. DIBAL-H | Yield | [α]D (-)-silane | ee (-)-silane |
|-------|-------|---------------------|------------------------|-------|----------------|--------------|
| 1     | 12(Ch=O) | 993 mg (1.87 mmol) | 4.70 ml (4.69 mmol) | 561 mg (82 %) | -11° (0.02 mol L⁻¹) | 64 %         |
| 2     | 12(Ch=S) | 174 mg (318.79 µmol) | 0.64 mL (637.58 µmol) | 97 mg (80 %) | -11° (0.05 mol L⁻¹) | 64 %         |
| 3     | 12(naph,Ch=O) | 158 mg (303.98 µmol) | 0.76 mL (759.94 µmol) | 75 mg (69 %) | -15° (0.04 mol L⁻¹) | 54 %         |

Chiral Memory

A Schlenk tube was charged with 1.0 equiv. of silane (-)-3a, (-)-4a or (+)-9 and a second Schlenk tube was charged with 1.0 equiv. of trityl borate [Ph₃C][B(C₆F₅)₄]. The solids were dissolved in DCM or chlorobenzene, respectively. The silane was cooled to the temperature indicated in Table S2 and trityl borate was added. The mixture was stirred for the time indicated in Table S2. Then, sodium triethyl borohydride in toluene was added and the mixture was stirred overnight. The solvent was removed and the residue was suspended in petroleum ether. The mixture was filtrated through a thin layer of silica, the solvent was removed and the crude product was purified via preparative TLC (eluent petroleum ether). After the purification, the formation of silanes was confirmed by NMR spectroscopy and then their optical rotation was measured and their ee was determined via chiral HPLC (Table S3)
Table S2 – Batches, reaction conditions and yields of the chiral memory experiments.

| Comp. | Silane | Trityl borate | Et₂B-H (1 M in toluene) | Conditions | Yield |
|-------|--------|---------------|--------------------------|------------|-------|
| (+)-9 | 106.6 µmol, 38 mg | 106.6 µmol, 98 mg | 159.9 µmol, 0.15 mL | Cl-Ph, r.t., 30 min | 24 % |
| (-)-3a | 177.3 µmol, 65 mg | 173.5 µmol, 160 mg | 266.0 µmol, 0.27 mL | Cl-Ph, -40 °C, 30 min | 14 % |
| (-)-3a | 180.1 µmol, 66 mg | 180.1 µmol, 166 mg | 270.1 µmol, 0.27 mL | DCM, -80 °C, 20 min | 0 % |
| (-)-4a | 252.5 µmol, 97 mg | 252.5 µmol, 233 mg | 328.2 µmol, 0.33 mL | Cl-Ph, -40 °C, 15 min | 14 % |

Table S3 – Results of the optical rotation measured in Et₂O and the chiral HPLC analysis of the chiral memory experiments.

| Silane | $[\alpha]_D$ start | ee start | $[\alpha]_D$ end | ee end |
|--------|------------------|---------|----------------|-------|
| (+)-9  | $+17^\circ$ (0.04 molL⁻¹) | 84 % | $0^\circ$ (0.004 molL⁻¹) | - |
| (-)-3a | $-11^\circ$ (0.02 molL⁻¹) | 54 % | $-4^\circ$ (0.005 molL⁻¹) | 32 % |
| (-)-3a | $-11^\circ$ (0.02 molL⁻¹) | 54 % | Decomposition | decomposition |
| (-)-4a | $-10^\circ$ (0.05 molL⁻¹) | 64 % | $-9^\circ$ (0.006 molL⁻¹) | 64 % |
1.5 Data from X-ray diffraction analysis of compounds 3a, 4a and 4b

Data were recorded on a Bruker CCD area detector. Structures were refined anisotropically using the program SHELXL-97. Pertinent data are summarized in Tables S4-6. CCDC-2011380, CCDC-2011381, CCDC-2011382 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre. The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table S4.

| Property                        | Value                      |
|---------------------------------|----------------------------|
| Empirical formula               | C25 H22 O Si               |
| Formula weight                  | 366.51                     |
| Temperature                     | 130(2) K                   |
| Wavelength                      | 0.71073 Å                  |
| Crystal system                  | Triclinic                  |
| Space group                     | P-1                        |
| Unit cell dimensions            | a = 8.5366(3) Å, b = 9.6243(3) Å, c = 12.6333(4) Å, g = 91.6942(16)° |
| Volume                          | 982.63(6) Å³               |
| Z                               | 2                          |
| Density (calculated)            | 1.239 Mg/m³                |
| Absorption coefficient          | 0.131 mm⁻¹                 |
| F(000)                          | 388                        |
| Crystal size                    | 0.400 x 0.300 x 0.080 mm³  |
| Theta range for data collection | 1.702 to 32.029°           |
| Index ranges                    | -12<=h<=12, -14<=k<=14, -18<=l<=18 |
| Reflections collected           | 29138                      |
| Independent reflections         | 6839 (R(int) = 0.0263)      |
| Observed reflections (I > 2(I)) | 5592                       |
| Completeness to theta           | 100.0 %                    |
| Absorption correction           | Semi-empirical from equivalents |
| Max. and min. transmission      | 1.0000 and 0.9178          |
| Refinement method               | Full-matrix least-squares on F² |
| Data / restraints / parameters  | 6839 / 0 / 270             |
| Goodness-of-fit on F²           | 1.015                      |
| Final R indices (>2sigma(I))    | R1 = 0.0454, wR2 = 0.1168   |
| R indices (all data)            | R1 = 0.0583, wR2 = 0.1249   |
| Extinction coefficient          | n/a                        |
| Largest diff. peak and hole     | 0.450 and -0.255 e.Å⁻³     |
### Table S5

| Property                          | Value                                      |
|----------------------------------|--------------------------------------------|
| Empirical formula                | C25 H22 S Si                               |
| Formula weight                   | 382.57                                     |
| Temperature                      | 130(2) K                                   |
| Wavelength                       | 0.71073 Å                                  |
| Crystal system                   | Monoclinic                                 |
| Space group                      | Cc                                         |
| Unit cell dimensions             | a = 10.0944(6) Å                           |
|                                  | b = 12.9115(8) Å                           |
|                                  | c = 30.6744(17) Å                          |
|                                  | a = 90°.                                   |
|                                  | b = 91.183(3)°.                            |
|                                  | g = 90°.                                   |
| Volume                           | 3997.1(4) Å                                |
| Z                                | 8                                          |
| Density (calculated)             | 1.271 Mg/m³                                 |
| Absorption coefficient           | 0.229 mm⁻¹                                 |
| F(000)                           | 1616                                       |
| Crystal size                     | 0.220 x 0.220 x 0.180 mm³                  |
| Theta range for data collection  | 1.328 to 30.034°                           |
| Index ranges                     | -14<=h<=14, -18<=k<=18, -43<l<=43           |
| Reflections collected            | 38800                                      |
| Independent reflections          | 11514 (R(int) = 0.0468)                    |
| Observed reflections (I > 2(I))  | 8195                                       |
| Completeness to theta = 30.034°  | 100.0 %                                    |
| Absorption correction            | Semi-empirical from equivalents            |
| Max. and min. transmission       | 1.0000 and 0.8984                          |
| Refinement method                | Full-matrix least-squares on F²            |
| Data / restraints / parameters   | 11514 / 2 / 517                            |
| Goodness-of-fit on F²            | 1.028                                      |
| Final R indices (>2sigma(I))     | R1 = 0.0594, wR2 = 0.1169                  |
| R indices (all data)             | R1 = 0.0932, wR2 = 0.1295                  |
| Absolute structure parameter     | 0.25(12)                                   |
| Extinction coefficient           | n/a                                        |
| Largest diff. peak and hole      | 0.437 and -0.573 eÅ⁻³                      |
Table S6

| Property                      | Value                   |
|-------------------------------|-------------------------|
| Empirical formula             | C23 H26 S Si            |
| Formula weight                | 362.59                  |
| Temperature                   | 100(2) K                |
| Wavelength                    | 0.71073 Å               |
| Crystal system                | Triclinic               |
| Space group                   | P-1                     |
| Unit cell dimensions          |                         |
| a                             | 9.3083(4) Å             |
| b                             | 9.9308(4) Å             |
| c                             | 11.2694(5) Å            |
| a = 83.2067(14)°             |                         |
| b = 72.0268(13)°             |                         |
| g = 82.5637(13)°             |                         |
| Volume                        | 979.17(7) Å³            |
| Z                             | 2                       |
| Density (calculated)          | 1.230 Mg/m³             |
| Absorption coefficient        | 0.229 mm⁻¹              |
| F(000)                        | 388                     |
| Crystal size                  | 0.400 x 0.350 x 0.300 mm³ |
| Theta range for data collection| 1.906 to 40.249°        |
| Index ranges                  | -16<=h<=16, -18<=k<=18, -20<=l<=20 |
| Reflections collected         | 83778                   |
| Independent reflections       | 12317 (R(int) = 0.0170) |
| Observed reflections (I > 2(I))| 10986                  |
| Completeness to theta = 40.249° | 100.0 %               |
| Absorption correction         | Semi-empirical from equivalents |
| Max. and min. transmission    | 1.0000 and 0.9688       |
| Refinement method             | Full-matrix least-squares on F² |
| Data / restraints / parameters| 12317 / 0 / 234         |
| Goodness-of-fit on F²         | 1.013                   |
| Final R indices (I>2sigma(I)) | R1 = 0.0291, wR2 = 0.0843 |
| R indices (all data)          | R1 = 0.0338, wR2 = 0.0891 |
| Extinction coefficient        | n/a                     |
| Largest diff. peak and hole   | 0.892 and -0.539 e.Å⁻³  |
2. Computational Details

All quantum chemical calculations were carried out using the Gaussian09 package.\textsuperscript{57} The molecular structure optimizations were performed using the M06-2X functional\textsuperscript{58} along with the def2-TZVP basis set for the elements Te, Se, S, Si, O, C, H and using the corresponding pseudopotential for Te.\textsuperscript{59} Every stationary point was identified by a subsequent frequency calculation either as minimum (Number of imaginary frequencies (NIMAG): 0) or transition state (NIMAG: 1). The SCF energies (E(SCF)) and the absolute computed Gibbs free energies at $T = 298.15 \text{ K}$ and $p = 0.101 \text{ MPa (1 atm)}$ in the gas phase (G298) are given in Table S7 for all optimized molecular structures. The optimized molecular structures of all compounds of interest are given as cartesian coordinates in the structure file (Computed_Molecular_structures.xyz).
Table S7. Calculated absolute energies, $E$(SCF), and free enthalpies at 298 K, $G^{298}$ for the compounds of interest (at M06-2X/def2-TZVP). "Cation isodes" and "silane isodes" are silyl cations and silanes used for the calculation of the isodesmic reactions given in Scheme 5.

| Compound | $E$(SCF) [a.u.] | ZPVE [kJ mol$^{-1}$] | $G$(298) [a.u.] |
|----------|----------------|---------------------|-----------------|
| Ace-OPh-SiMePh cation 13a | -1329.77950 | 1023 | -1329.44362 |
| Ace-OPh-SiMePh cation isodes | -1329.74123 | 1021 | -1329.40743 |
| Ace-OPh-SiMePh silane isodes | -1330.58763 | 1040 | -1330.24734 |
| Ace-OPh-SiMePh silane 3a | -1330.58994 | 1044 | -1330.24496 |
| Ace-OPh-SiMe(tBu) cation 13b | -1255.96866 | 1101 | -1255.60243 |
| Ace-OPh-SiMe(tBu) cation isodes | -1255.92539 | 1101 | -1255.56205 |
| Ace-OPh-SiMe(tBu) silane 3b | -1256.77680 | 1125 | -1256.40153 |
| Ace-OPh-SiMe(tBu) silane isodes | -1256.77925 | 1122 | -1256.40580 |
| Ace-SPh-SiMePh cation cis cis-13c | -1652.75595 | 1015 | -1652.42261 |
| Ace-SPh-SiMePh cation trans trans-13c | -1652.75408 | 1016 | -1652.42098 |
| Ace-SPh-SiMePh cation TS (cis/trans) | -1652.72635 | 1014 | -1652.39463 |
| Ace-SPh-SiMePh cation isodes | -1652.70682 | 1013 | -1652.37807 |
| Ace-SPh-SiMePh silane anti trans 4a | -1633.54956 | 1035 | -1633.21101 |
| Ace-SPh-SiMePh silane syn trans 4a | -1635.55002 | 1034 | -1635.21193 |
| Ace-SPh-SiMePh silane isodes | -1635.55383 | 1033 | -1635.21756 |
| Ace-SPh-SiMePh silane TS cis-18a | -2076.51162 | 1262 | -2076.09706 |
| Ace-SPh-SiMePh silane cis 18a | -2076.50867 | 1261 | -2076.09805 |
| Ace-SPh-SiMePh silane TS 18a | -2076.49394 | 1259 | -2076.08296 |
| Ace-SPh-SiMePh cation cis cis-13d | -1578.94321 | 1097 | -1578.57823 |
| Ace-SPh-SiMePh cation trans trans-13d | -1578.94676 | 1096 | -1578.58323 |
| Ace-SPh-SiMePh cation TS (cis/trans) | -1578.91799 | 1091 | -1578.55267 |
| Ace-SPh-SiMePh cation isodes | -1578.89082 | 1092 | -1578.53221 |
| Ace-SPh-SiMePh silane anti trans 4b | -1579.73833 | 1116 | -1579.36799 |
| Ace-SPh-SiMePh silane syn trans 4b | -1579.73856 | 1117 | -1579.36797 |
| Ace-SPh-SiMePh silane isodes | -1579.74524 | 1115 | -1579.37627 |
| Ace-SPh-SiMePh silane TS 18b | -2002.69516 | 1345 | -2002.24919 |
| Ace-SePh-SiMePh cation cis 13e | -3656.14276 | 1011 | -3655.81108 |
| Ace-SePh-SiMePh cation trans 13e | -3656.14078 | 1011 | -3655.81172 |
| Ace-SePh-SiMePh cation TS (cis/trans) | -3656.10479 | 1009 | -3655.77569 |
| Ace-SePh-SiMePh cation isodes | -3656.09273 | 1009 | -3655.76821 |
| Ace-SePh-SiMePh silane cis 6 | -3656.93769 | 1031 | -3656.59975 |
| Ace-SePh-SiMePh silane isodes | -3656.94023 | 1030 | -3656.60664 |
| Ace-TeMes-SiMePh cation cis 13f | -1640.43108 | 1227 | -1640.02345 |
| Ace-TeMes-SiMePh cation trans 13f | -1640.42899 | 1228 | -1640.02396 |
| Ace-TeMes-SiMePh cation TS (cis/trans) | -1640.38931 | 1225 | -1639.98506 |
| Ace-TeMes-SiMePh cation isodes | -1640.38199 | 1226 | -1639.98074 |
| Ace-TeMes-SiMePh silane syn cis 7 | -1641.22026 | 1249 | -1640.80474 |
| Ace-TeMes-SiMePh silane isodes | -1641.22896 | 1245 | -1640.81978 |
| Naph-SPh-SiMePh cation cis cis-14a | -1575.33717 | 923 | -1575.03619 |
| Naph-SPh-SiMePh cation trans trans-14a | -1575.33548 | 922 | -1575.03658 |
| Naph-SPh-SiMePh cation TS (cis/trans) | -1575.30856 | 921 | -1575.00973 |
| Naph-SPh-SiMePh cation isodes | -1575.27879 | 920 | -1574.98213 |
| Naph-SPh-SiMePh silane 9a | -1576.12915 | 942 | -1575.82367 |
| Naph-SPh-SiMePh silane isodes | -1576.13507 | 942 | -1575.83113 |
| Naph-SePhSiMe(Ph) cation cis 14b | -3578.72361 | 920 | -3578.42464 |
| Naph-SePhSiMe(Ph) cation trans 14b | -3578.72140 | 920 | -3578.42414 |
| Naph-SePhSiMe(Ph) cation TS (cis/trans) | -3578.68612 | 917 | -3578.39036 |
| Naph-SePhSiMe(Ph) silane 10a | -3579.51389 | 938 | -3579.21043 |
| Naph-SePhSiMe(Ph) cation isodes | -3578.66720 | 918 | -3578.37233 |
| Naph-SePhSiMe(Ph) silane isodes | -3579.52069 | 939 | -3579.21792 |
| Naph-SePhSiMe(tBu) cation cis 14c | -3504.91025 | 998 | -3504.58197 |
| Naph-SePhSiMe(tBu) cation trans 14c | -3504.91346 | 997 | -3504.58691 |
For the assignment of the IR bands of the syn- and anti-structures of silanes x-x (SPh, R = Me, t-Bu, Ph), their molecular structures were calculated at the M06-2X/Def2-TZVP level of theory at T = 298.15 K and p = 0.101 MPa (1 atm) in the gas phase with a subsequent frequency analysis. To account for anharmonicity effects, a scaling factor for the Si – H vibration was determined from the correlation of the computed data and the experimental results for a representative collection of silanes (Figure S86). The scaling factor is given by the scope of the line of best fit which is 0.9619 ± 0.0030.

Figure S 86 – Correlation of the calculated wavenumber obtained at M06-2X/Def2-TZVP of the $\nu$(Si – H) vibration and the experimental value for silanes 4a,b, 5-bromo-6-dimethylsilyl acenaphthene, 5-dimethylsilyl acenaphthene, 5-phenylsulfanyl-6-dimethylsilylacenaphthene and triethylsilane.
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