

Electronic Supplementary Information (ESI)

Palladium(0)-Catalyzed C(sp³)-Si Bond Formation via Formal Carbene Insertion into Si-H Bond

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1) General.

All the reactions were performed under a nitrogen atmosphere in a flame-dried reaction flask. All solvents were distilled under a nitrogen atmosphere prior to use. Dioxane was dried over Na with benzophenone-ketyl intermediate as indicator. For chromatography, 200-300 mesh silica gel (Qingdao, China) was employed. ^1H and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz with Bruker ARX 400 spectrometer. Chemical shifts are reported in *ppm* using tetramethylsilane as internal standard and CDCl_3 as solvent. Mass spectra were obtained on an Agilent 5975C inert 350 EI mass spectrometer. HRMS were obtained on a Bruker Apex IV FTMS or Waters GCT Premier. The aldehydes and ketones were purchased from J&K, Adamas and Alfa. *N*-tosylhydrazones were prepared according to the literature procedure.^[1] The palladium catalysts and ligands were purchased from Acros and TCI.

2) General procedure for Pd(0)-catalyzed Si-H bond insertions

a) General procedure for Si-H bond insertion

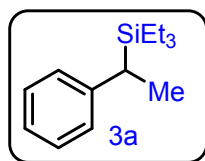
Under a nitrogen atmosphere, a solution of *N*-tosylhydrazone (0.3 mmol), Et_3SiH (0.45 mmol), $\text{Pd}(\text{P}^t\text{Bu}_3)_2$ (0.006 mmol, 2 mol%), LiO^tBu (0.9 mmol, 3.0 equiv) in dioxane (4.0 mL) was heated at 120 °C for 2 h. Upon completion of the reaction, the solvent was removed in *vacuo* to provide a crude mixture, which was purified by silica gel column chromatography to afford the pure product.

b) General procedure for sequential Si-H bond insertion with Et_2SiH_2

Under a nitrogen atmosphere, a solution of *N*-tosylhydrazone **1d** (0.3 mmol), Et_2SiH_2 (0.45 mmol), $\text{Pd}(\text{P}^t\text{Bu}_3)_2$ (0.006 mmol, 2 mol%), LiO^tBu (0.9 mmol, 3.0 equiv) in dioxane (4.0 mL) was heated at 120 °C for 2 h. The reaction vessel was then taken out of the oil bath and cooled to room temperature. Under a nitrogen atmosphere, $\text{Pd}(\text{P}^t\text{Bu}_3)_2$ (0.006 mmol, 2 mol%), *N*-tosylhydrazone **1a** or **4a** (0.45 mmol), LiO^tBu (0.9 mmol, 3.0 equiv) were sequentially added to the same vessel. The vessel was put into the 120 °C oil bath again and heated for another 2 h. Upon completion of the reaction, the solvent was removed in *vacuo* to provide a crude mixture, which was purified by silica gel column chromatography to afford the pure product.

3) Spectral data of the Si-H insertion products

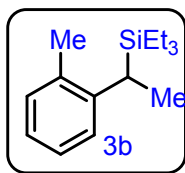
Triethyl(1-phenylethyl)silane²



Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.24-7.20 (m, 2H), 7.08-7.06 (m, 3H), 2.30 (q, J = 7.6 Hz, 1H), 1.37 (d, J = 7.6 Hz, 3H), 0.88 (t, J = 7.9 Hz, 9H), 0.51 (q, J = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.24, 127.97, 127.08, 124.15, 26.78, 15.37, 7.47,

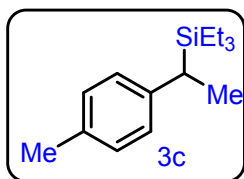
2.02.

Triethyl(1-(*o*-tolyl)ethyl)silane³



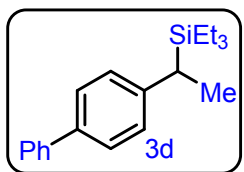
Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.12-7.08 (m, 3H), 7.00-6.96 (m, 1H), 2.52 (q, *J* = 7.5 Hz, 1H), 2.28 (s, 3H), 1.35 (d, *J* = 7.5 Hz, 3H), 0.87 (t, *J* = 7.9 Hz, 9H), 0.54 (q, *J* = 8.0 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 145.01, 134.46, 130.02, 126.81, 125.81, 123.97, 21.61, 20.42, 16.60, 7.48, 2.42.

Triethyl(1-(*p*-tolyl)ethyl)silane³



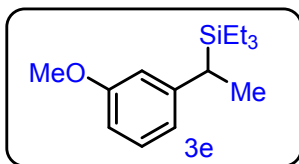
Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.09 (d, *J* = 7.9 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 2.34-2.28 (m, 4H), 1.40 (d, *J* = 7.6 Hz, 3H), 0.94 (t, *J* = 7.9 Hz, 9H), 0.56 (q, *J* = 7.9 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 140.05, 130.42, 125.69, 123.98, 23.22, 17.87, 12.54, 4.51, -0.94.

(1-([1,1'-Biphenyl]-4-yl)ethyl)triethylsilane

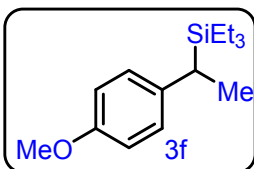


Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.58 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.47 (dd, *J* = 6.5, 1.8 Hz, 2H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.30-7.26 (m, 1H), 7.14-7.12 (m, 2H), 2.35 (q, *J* = 7.6 Hz, 1H), 1.40 (d, *J* = 7.6 Hz, 3H), 0.91 (t, *J* = 7.9 Hz, 9H), 0.54 (q, *J* = 7.9 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 145.50, 141.14, 136.97, 128.63, 127.46, 126.76, 126.71, 126.63, 26.54, 15.38, 7.51, 2.06; HRMS (ESI, *m/z*): calcd for C₂₀H₂₉Si [M+H]⁺ 297.2033, found 297.2032.

Triethyl(1-(3-methoxyphenyl)ethyl)silane



Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.16-7.12 (m, 1H), 6.68-6.61 (m, 3H), 3.78 (s, 3H), 2.28 (q, *J* = 7.6 Hz, 1H), 1.36 (d, *J* = 7.6 Hz, 3H), 0.89 (t, *J* = 7.9 Hz, 9H), 0.52 (q, *J* = 7.9 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 159.40, 148.04, 128.80, 119.79, 113.07, 109.19, 55.02, 26.94, 15.36, 7.47, 2.08; LRMS (EI, *m/z*): 250 (M⁺, 63), 221 (13), 115 (98), 87 (100), 59 (29).

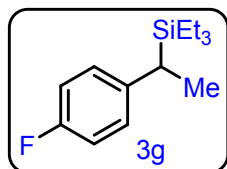


Triethyl(1-(4-methoxyphenyl)ethyl)silane³

Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 6.98 (d, *J* = 8.6 Hz, 2H), 6.79 (d, *J* = 8.7 Hz, 2H), 3.76 (s, 3H), 2.24 (q, *J* = 7.6 Hz,

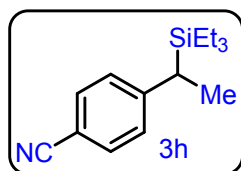
1H), 1.34 (d, $J = 7.6$ Hz, 3H), 0.89 (t, $J = 7.9$ Hz, 9H), 0.50 (q, $J = 7.9$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 156.59, 138.18, 127.80, 113.43, 55.13, 25.60, 15.69, 7.49, 2.03.

Triethyl(1-(4-fluorophenyl)ethyl)silane



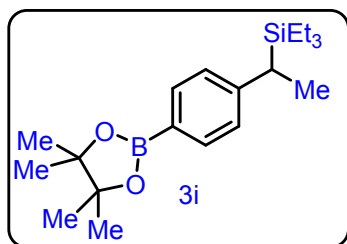
Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.02-6.98 (m, 2H), 6.94-6.89 (m, 2H), 2.28 (q, $J = 7.6$ Hz, 1H), 1.35 (d, $J = 7.6$ Hz, 3H), 0.88 (t, $J = 7.9$ Hz, 9H), 0.50 (q, $J = 7.9$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.28 (d, $J = 241.6$ Hz), 141.78 (d, $J = 241.6$ Hz), 128.08 (d, $J = 7.4$ Hz), 114.67 (d, $J = 21.0$ Hz), 26.00, 15.63, 7.44, 1.97; HRMS (EI, m/z): calcd for $\text{C}_{14}\text{H}_{23}\text{FSi}$ $[\text{M}]^+$ 238.1553, found 238.1561.

4-(1-(Triethylsilyl)ethyl)benzonitrile



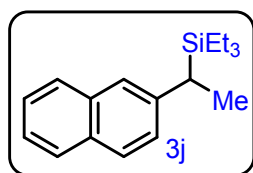
Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.51 (d, $J = 8.4$ Hz, 2H), 7.15 (d, $J = 8.2$ Hz, 2H), 2.40 (q, $J = 7.4$ Hz, 1H), 1.38 (d, $J = 7.5$ Hz, 3H), 0.89 (t, $J = 7.9$ Hz, 9H), 0.50 (q, $J = 8.0$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 152.65, 131.75, 127.53, 119.38, 107.59, 27.97, 14.79, 7.31, 1.81; HRMS (ESI, m/z): calcd for $\text{C}_{15}\text{H}_{24}\text{NSi}$ $[\text{M}+\text{H}]^+$ 246.1672, found 246.1671.

Pinacol 4-((1-Triethylsilyl)ethyl)phenylborinate



Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.68 (d, $J = 8.1$ Hz, 2H), 7.08 (d, $J = 7.9$ Hz, 2H), 2.33 (q, $J = 7.5$ Hz, 1H), 1.37 (d, $J = 7.5$ Hz, 3H), 1.33 (s, 12H), 0.88 (t, $J = 7.9$ Hz, 9H), 0.50 (q, $J = 7.9$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 150.05, 134.55, 128.31, 126.58, 83.47, 27.39, 24.85, 15.17, 7.47, 2.02; HRMS (EI, m/z): calcd for $\text{C}_{20}\text{H}_{35}\text{O}_2\text{BSi}$ $[\text{M}]^+$ 346.2494, found 346.2494.

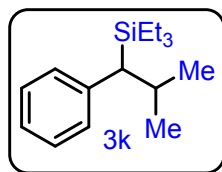
Triethyl(1-(naphthalen-2-yl)ethyl)silane²



Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.78-7.69 (m, 3H), 7.48 (s, 1H), 7.44-7.34 (m, 2H), 7.25-7.23 (m, 1H), 2.47 (q, $J = 7.5$ Hz, 1H), 1.47 (d, $J = 7.6$ Hz, 3H), 0.90 (t, $J = 7.9$ Hz, 9H), 0.54 (q, $J = 7.9$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.08,

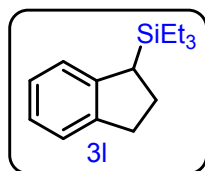
133.72, 131.22, 127.49, 127.22, 127.17, 127.05, 125.67, 124.39, 124.25, 27.08, 15.50, 7.53, 2.12.

Triethyl(2-methyl-1-phenylpropyl)silane⁴



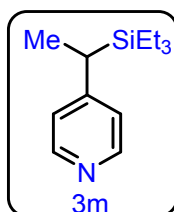
Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.20 (t, J = 7.5 Hz, 2H), 7.08 (t, J = 7.3 Hz, 1H), 7.02 (d, J = 7.3 Hz, 2H), 2.23-2.14 (m, 1H), 1.86 (d, J = 9.9 Hz, 1H), 1.07 (d, J = 6.6 Hz, 3H), 0.87 (t, J = 7.9 Hz, 9H), 0.77 (d, J = 6.5 Hz, 3H), 0.51 (q, J = 7.9 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 144.54, 128.92, 127.88, 124.27, 42.75, 30.55, 23.61, 7.67, 3.94.

(2,3-Dihydro-1*H*-inden-1-yl)triethylsilane



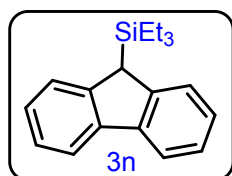
Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.16 (d, J = 6.9 Hz, 1H), 7.10-7.00 (m, 3H), 2.92-2.88 (m, 2H), 2.66 (dd, J = 4.2, 9.7 Hz, 1H), 2.34-2.24 (m, 1H), 2.10-2.03 (m, 1H), 0.91 (t, J = 7.9 Hz, 9H), 0.59 (q, J = 7.9 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 146.72, 143.43, 125.82, 124.61, 124.24, 123.56, 32.99, 31.20, 27.42, 7.55, 2.74; HRMS (EI, m/z): calcd for C₁₅H₂₄Si [M]⁺ 232.1647, found 232.1644.

4-((Triethylsilyl)methyl)pyridine



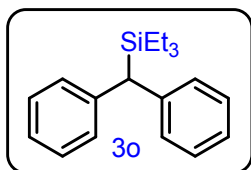
Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 8.41-8.39 (m, 2H), 6.99-6.97 (m, 2H), 2.33 (q, J = 7.4 Hz, 1H), 1.38 (d, J = 7.4 Hz, 3H), 0.90 (t, J = 7.9 Hz, 9H), 0.52 (q, J = 7.8 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 155.78, 149.19, 122.54, 27.04, 14.33, 7.39, 1.85; HRMS (ESI, m/z): calcd for C₁₃H₂₄NSi [M+H]⁺ 222.1672, found 222.1670.

Triethyl(9*H*-fluoren-9-yl)silane



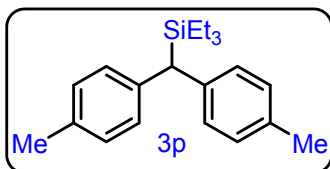
Yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.85 (d, J = 7.5 Hz, 2H), 7.49 (d, J = 7.4 Hz, 2H), 7.33 (t, J = 7.3 Hz, 2H), 7.27 (t, J = 7.4 Hz, 2H), 4.01 (s, 1H), 0.81 (t, J = 7.9 Hz, 9H), 0.48 (q, J = 7.8 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 145.79, 140.48, 125.89, 125.09, 124.01, 119.85, 39.22, 7.30, 2.21; HRMS (ESI, m/z): calcd for C₁₉H₂₅Si [M+H]⁺ 281.1720, found 281.1719.

Benzhydryltriethylsilane²



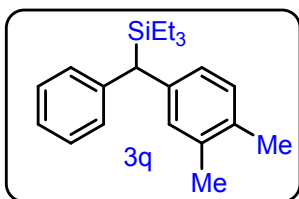
Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.27-7.21 (m, 8H), 7.13-7.09 (m, 2H), 3.65 (s, 1H), 0.84 (t, *J* = 7.9 Hz, 9H), 0.60 (q, *J* = 7.8 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 142.85, 128.74, 128.23, 124.99, 42.96, 7.45, 3.36.

(Di-*p*-tolylmethyl)triethylsilane



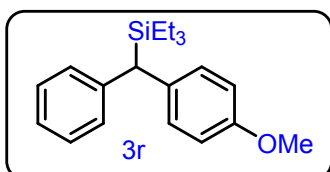
Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.12 (d, *J* = 8.1 Hz, 4H), 7.03 (d, *J* = 8.0 Hz, 4H), 3.56 (s, 1H), 2.27 (s, 6H), 0.85 (t, *J* = 7.9 Hz, 9H), 0.59 (q, *J* = 7.9 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 140.08, 134.21, 128.90, 128.61, 41.82, 20.87, 7.52, 3.40; HRMS (EI, *m/z*): calcd for C₂₁H₃₀Si [M]⁺ 310.2111, found 310.2111.

((3,4-Dimethylphenyl)(phenyl)methyl)triethylsilane

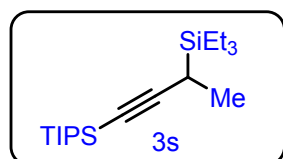


Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.22 (dd, *J* = 1.7, 8.2 Hz, 4H), 7.10-7.06 (m, 1H), 7.01-7.00 (m, 3H), 3.57 (s, 1H), 2.20 (s, 3H), 2.19 (s, 3H), 0.85 (t, *J* = 7.9 Hz, 9H), 0.60 (q, *J* = 7.9 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 143.34, 140.17, 136.19, 133.04, 130.37, 129.44, 128.57, 128.17, 126.25, 124.79, 42.40, 19.90, 19.19, 7.51, 3.41; HRMS (EI, *m/z*): calcd for C₂₁H₃₀Si [M]⁺ 310.2111, found 310.2110.

Triethyl((4-methoxyphenyl)(phenyl)methyl)silane



Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.24-7.22 (m, 4H), 7.19-7.16 (m, 2H), 7.12-7.08 (m, 1H), 6.81-6.79 (m, 2H), 3.76 (s, 3H), 3.59 (s, 1H), 0.85 (t, *J* = 7.8 Hz, 9H), 0.59 (q, *J* = 7.8 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 157.20, 143.39, 134.96, 129.80, 128.50, 128.20, 124.83, 113.66, 55.15, 41.75, 7.48, 3.38; HRMS (EI, *m/z*): calcd for C₂₀H₂₈OSi [M]⁺ 312.1904, found 312.1905.

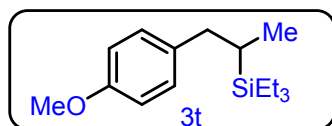


Triethyl(4-(triisopropylsilyl)but-3-yn-2-yl)silane

Pale yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 1.89 (q, *J* = 7.3 Hz, 1H), 1.21 (d, *J* = 7.3 Hz, 3H), 1.08-1.03 (m, 21H),

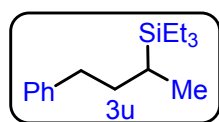
0.99 (t, $J = 7.9$ Hz, 9H), 0.69-0.62 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 112.95, 78.69, 18.64, 15.39, 11.46, 11.18, 7.49, 2.24; MS (EI, m/z): 324 (M^+ , 2), 281 (100), 157 (58), 115 (60), 87 (49), 59 (33).

Triethyl(1-(4-methoxyphenyl)propan-2-yl)silane



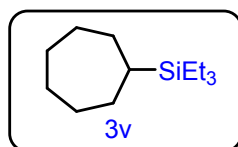
Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.06 (d, $J = 8.5$ Hz, 2H), 6.82 (d, $J = 8.6$ Hz, 2H), 3.78 (s, 3H), 2.83 (dd, $J = 3.4, 13.8$ Hz, 1H), 2.20 (dd, $J = 11.9, 13.7$ Hz, 1H), 1.09-1.02 (m, 1H), 0.98 (t, $J = 7.9$ Hz, 9H), 0.83 (d, $J = 7.4$ Hz, 3H), 0.59 (q, $J = 7.9$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.57, 134.90, 129.58, 113.47, 55.19, 37.24, 19.38, 13.75, 7.69, 2.15; MS (EI, m/z): 264 (M^+ , 25), 235 (100), 193 (50), 115 (58), 87 (78), 59 (29).

Triethyl(4-phenylbutan-2-yl)silane⁵



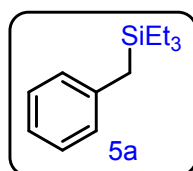
Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.28-7.24 (m, 2H), 7.20-7.14 (m, 3H), 2.87-2.79 (m, 1H), 2.51-2.43 (m, 1H), 1.83-1.75 (m, 1H), 1.49-1.39 (m, 1H), 1.03 (d, $J = 7.4$ Hz, 3H), 0.92 (t, $J = 7.9$ Hz, 9H), 0.85-0.77 (m, 1H), 0.53 (q, $J = 7.9$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.04, 128.41, 128.23, 125.52, 35.15, 34.15, 16.43, 14.11, 7.67, 2.14.

Cycloheptyltriethylsilane



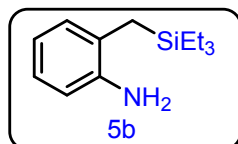
Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 1.77-1.68 (m, 4H), 1.61-1.56 (m, 2H), 1.51-1.37 (m, 4H), 1.30-1.22 (m, 2H), 0.94 (t, $J = 7.9$ Hz, 9H), 0.77 (tt, $J = 3.1, 11.1$ Hz, 1H), 0.52 (q, $J = 7.9$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 30.38, 29.13, 28.25, 23.71, 7.77, 2.27; HRMS (EI, m/z): calcd for $\text{C}_{13}\text{H}_{28}\text{Si}$ [M] $^+$ 212.1955, found 212.1955.

Benzyltriethylsilane²



Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.19 (t, $J = 7.6$ Hz, 2H), 7.07-7.00 (m, 3H), 2.09 (s, 2H), 0.91 (t, $J = 7.9$ Hz, 9H), 0.50 (q, $J = 5.9$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.65, 128.12, 128.08, 123.65, 21.60, 7.27, 2.95.

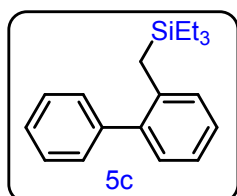
2-((Triethylsilyl)methyl)aniline



Yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 6.94-6.90 (m, 2H),

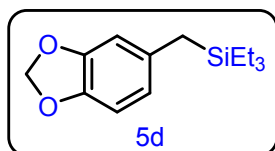
6.69-6.62 (m, 2H), 3.47 (s, 2H), 1.94 (s, 2H), 0.92 (t, $J = 7.9$ Hz, 9H), 0.57 (q, $J = 7.9$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.13, 129.57, 125.17, 125.07, 118.77, 115.47, 16.31, 7.29, 3.54; HRMS (EI, m/z): calcd for $\text{C}_{13}\text{H}_{23}\text{NSi}$ $[\text{M}]^+$ 221.1594, found 221.1594.

([1,1'-Biphenyl]-2-ylmethyl)triethylsilane



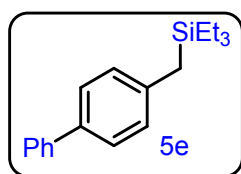
Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.40-7.28 (m, 5H), 7.21-7.08 (m, 4H), 2.23 (s, 2H), 0.69 (t, $J = 7.9$ Hz, 9H), 0.32 (q, $J = 7.9$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 142.46, 140.68, 138.27, 130.28, 129.66, 129.34, 128.05, 126.99, 126.52, 123.96, 18.18, 7.02, 3.32; HRMS (EI, m/z): calcd for $\text{C}_{19}\text{H}_{26}\text{Si}$ $[\text{M}]^+$ 282.1798, found 282.1794.

(Benzo[d][1,3]dioxol-5-ylmethyl)triethylsilane

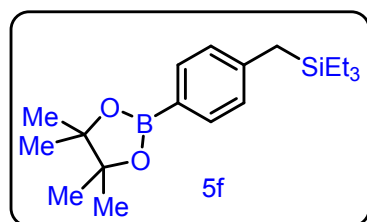


Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 6.66 (d, $J = 7.9$ Hz, 1H), 6.51 (d, $J = 1.6$ Hz, 1H), 6.45 (dd, $J = 1.7, 7.9$ Hz, 1H), 5.88 (s, 2H), 2.01 (s, 2H), 0.92 (t, $J = 7.9$ Hz, 9H), 0.50 (q, $J = 7.9$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.37, 144.13, 134.23, 120.36, 108.67, 108.05, 100.50, 21.10, 7.28, 2.92; HRMS (EI, m/z): calcd for $\text{C}_{14}\text{H}_{22}\text{O}_2\text{Si}$ $[\text{M}]^+$ 250.1384, found 250.1380.

([1,1'-Biphenyl]-4-ylmethyl)triethylsilane²



Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.58 (d, $J = 7.4$ Hz, 2H), 7.46-7.39 (m, 4H), 7.29 (t, $J = 7.3$ Hz, 1H), 7.08 (d, $J = 8.1$ Hz, 2H), 2.14 (s, 2H), 0.94 (t, $J = 7.9$ Hz, 9H), 0.54 (q, $J = 7.9$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 141.17, 139.92, 136.61, 128.75, 128.64, 128.47, 126.80, 126.74, 126.70, 21.28, 7.31, 2.96.

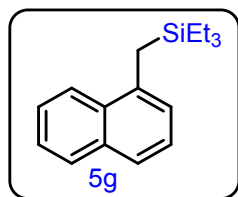


Pinacol 4-((Triethylsilyl)methyl)phenylborinate

Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.64 (d, $J = 8.0$ Hz, 2H), 7.02 (d, $J = 8.0$ Hz, 2H), 2.12 (s, 2H), 1.33 (s, 12H), 0.91 (t, $J = 7.9$ Hz, 9H), 0.49 (q, $J = 7.9$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.53, 134.71, 127.56, 83.48, 24.86, 22.28, 7.26, 2.94; HRMS (EI, m/z): calcd for $\text{C}_{19}\text{H}_{33}\text{O}_2\text{BSi}$ $[\text{M}]^+$

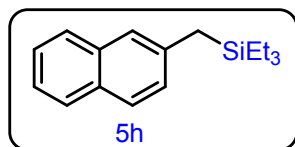
332.2337, found 332.2337.

Triethyl(naphthalen-1-ylmethyl)silane⁶



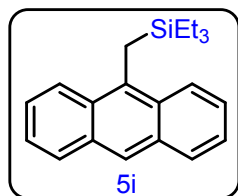
Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, *J* = 7.9 Hz, 1H), 7.80 (d, *J* = 7.7 Hz, 1H), 7.58 (d, *J* = 8.1 Hz, 1H), 7.47-7.41 (m, 2H), 7.35-7.31 (m, 1H), 7.18 (d, *J* = 7.1 Hz, 1H), 2.56 (s, 2H), 0.87 (dt, *J* = 1.3, 7.9 Hz, 9H), 0.51 (dq, *J* = 1.3, 7.9 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 142.46, 140.68, 138.27, 130.28, 129.66, 129.34, 128.05, 126.99, 126.52, 123.96, 18.18, 7.02, 3.32.

Triethyl(naphthalen-2-ylmethyl)silane⁶



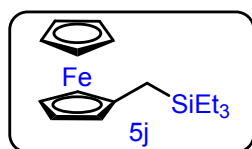
Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, *J* = 8.1 Hz, 1H), 7.69 (t, *J* = 8.0 Hz, 2H), 7.43-7.38 (m, 2H), 7.34 (t, *J* = 7.9 Hz, 1H), 7.175 (d, *J* = 8.4 Hz, 1H), 2.26 (s, 2H), 0.93 (t, *J* = 7.9 Hz, 9H), 0.53 (q, *J* = 7.9 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 138.41, 133.83, 130.91, 127.90, 127.54, 127.49, 126.92, 125.71, 125.20, 124.26, 21.94, 7.32, 3.04.

(Anthracen-9-ylmethyl)triethylsilane



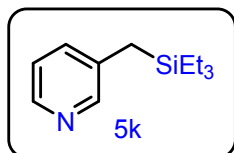
Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 8.21-8.19 (m, 3H), 7.96 (d, *J* = 8.7 Hz, 2H), 7.47-7.41 (m, 4H), 3.15 (s, 2H), 0.79 (t, *J* = 7.8 Hz, 9H), 0.51 (q, *J* = 7.8 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 134.46, 131.61, 129.10, 129.04, 125.22, 124.71, 124.45, 123.57, 14.66, 7.25, 4.24; HRMS (EI, *m/z*): calcd for C₂₁H₂₆Si [M]⁺ 306.1798, found 306.1795.

((Triethylsilyl)methyl)ferrocene



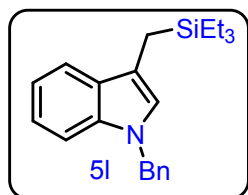
Orange oil; ¹H NMR (400 MHz, CDCl₃) δ 4.05 (s, 5H), 3.96 (t, *J* = 1.7 Hz, 2H), 3.94 (d, *J* = 1.7 Hz, 2H), 1.73 (s, 2H), 0.88 (t, *J* = 7.9 Hz, 9H), 0.43 (q, *J* = 7.9 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 87.29, 68.67, 67.99, 66.51, 14.18, 7.32, 3.06; HRMS (EI, *m/z*): calcd for C₁₇H₂₆FeSi [M]⁺ 314.1148, found 314.1146.

3-((Triethylsilyl)methyl)pyridine



Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 8.31 (s, 2H), 7.33-7.31 (m, 1H), 7.12 (dd, $J = 4.8, 7.7$ Hz, 1H), 2.07 (s, 2H), 0.92 (t, $J = 7.9$ Hz, 9H), 0.52 (q, $J = 7.9$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.27, 145.36, 136.34, 135.08, 123.03, 18.54, 7.17, 2.82; HRMS (EI, m/z): calcd for $\text{C}_{12}\text{H}_{21}\text{NSi}$ $[\text{M}]^+$ 207.1438, found 207.1437.

1-Benzyl-3-((triethylsilyl)methyl)-1H-indole



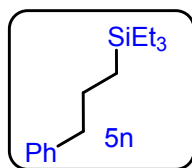
Pale yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.54 (d, $J = 7.8$ Hz, 1H), 7.25-7.19 (m, 4H), 7.13-7.05 (m, 4H), 6.77 (s, 1H), 5.26 (s, 2H), 2.13 (s, 2H), 0.92 (t, $J = 7.9$ Hz, 9H), 0.53 (q, $J = 7.9$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.10, 136.38, 128.84, 128.61, 127.33, 126.52, 124.45, 121.31, 119.25, 118.35, 112.64, 109.28, 77.31, 49.67, 8.19, 7.44, 3.41; HRMS (ESI, m/z): calcd for $\text{C}_{22}\text{H}_{30}\text{NSi}$ $[\text{M}+\text{H}]^+$ 336.2142, found 336.2146.

Triethyl(3-(triisopropylsilyl)prop-2-yn-1-yl)silane²



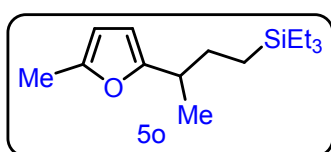
Orange oil; ^1H NMR (400 MHz, CDCl_3) δ 1.60 (s, 2H), 1.09-1.02 (m, 21H), 0.97 (t, $J = 7.9$ Hz, 9H), 0.64 (q, $J = 7.9$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 106.64, 78.40, 18.64, 11.49, 7.24, 3.40, 3.16.

Triethyl(3-phenylpropyl)silane⁷



Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.29-7.22 (m, 2H), 7.18-7.16 (m, 3H), 2.61 (t, $J = 7.7$ Hz, 2H), 1.65-1.57 (m, 2H), 0.91 (t, $J = 7.9$ Hz, 9H), 0.58-0.54 (m, 2H), 0.49 (q, $J = 7.9$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 142.74, 128.43, 128.19, 125.57, 40.24, 26.07, 11.32, 7.44, 3.28.

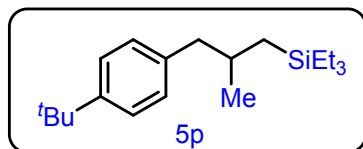
Triethyl(3-(5-methylfuran-2-yl)butyl)silane



Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 5.82 (s, 2H), 2.66 (h, $J = 6.8$ Hz, 1H), 2.24 (s, 3H), 1.69-1.60 (m, 1H), 1.52-1.41 (m, 1H), 1.20 (d, $J = 7.0$ Hz, 3H), 0.90 (t, $J = 7.9$ Hz, 9H), 0.52-0.44 (m, 8H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.94, 149.88, 105.47, 104.13, 36.19, 29.84, 18.51, 13.48, 8.22, 7.38, 3.21; HRMS (EI, m/z): calcd

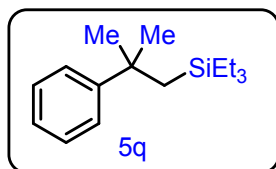
for C₁₅H₂₈OSi [M]⁺ 252.1904, found 252.1902.

(3-(4-(*tert*-Butyl)phenyl)-2-methylpropyl)triethylsilane



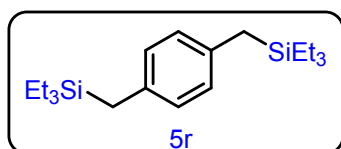
Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.28 (d, *J* = 8.3 Hz, 2H), 7.06 (d, *J* = 8.1 Hz, 2H), 2.59 (dd, *J* = 5.8, 13.2 Hz, 1H), 2.35 (dd, *J* = 8.4, 13.2 Hz, 1H), 1.92-1.80 (m, 1H), 1.30 (s, 9H), 0.92-0.88 (m, 12H), 0.55-0.43 (m, 8H); ¹³C NMR (100 MHz, CDCl₃) δ 148.37, 138.72, 128.84, 124.95, 47.03, 34.35, 31.62, 31.46, 22.84, 19.68, 7.50, 4.05; HRMS (EI, *m/z*): calcd for C₁₈H₃₁Si [M-C₂H₅]⁺ 275.2190, found 275.2188.

Triethyl(2-methyl-2-phenylpropyl)silane



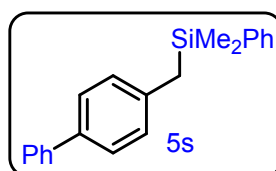
Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.38 (d, *J* = 8.3 Hz, 2H), 7.27 (t, *J* = 7.6 Hz, 2H), 7.14 (t, *J* = 6.9 Hz, 1H), 1.38 (s, 6H), 1.12 (s, 2H), 0.80 (t, *J* = 7.9 Hz, 9H), 0.31 (q, *J* = 7.9 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 151.51, 127.88, 125.41, 125.32, 37.09, 32.43, 29.41, 7.38, 4.51; HRMS (EI, *m/z*): calcd for C₁₄H₂₃Si [M-C₂H₅]⁺ 219.1564, found 219.1564.

1,4-Bis((triethylsilyl)methyl)benzene



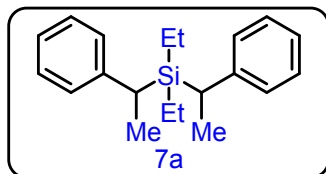
Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 6.85 (s, 4H), 2.02 (s, 4H), 0.89 (t, *J* = 7.9 Hz, 18H), 0.49 (q, *J* = 7.9 Hz, 12H); ¹³C NMR (100 MHz, CDCl₃) δ 135.58, 127.91, 20.79, 7.28, 3.00; HRMS (EI, *m/z*): calcd for C₂₀H₃₈Si₂ [M]⁺ 334.2507, found 334.2506.

([1,1'-Biphenyl]-4-ylmethyl)dimethyl(phenyl)silane



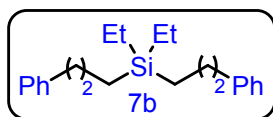
Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.58-7.56 (m, 2H), 7.49-7.47 (m, 2H), 7.43-7.27 (m, 8H), 6.99 (d, *J* = 7.6 Hz, 2H), 2.34 (s, 2H), 0.28 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 141.12, 138.88, 138.38, 136.91, 133.71, 129.06, 128.68, 128.65, 127.73, 126.76, 25.87, -3.43; HRMS (ESI, *m/z*): calcd for C₂₁H₂₂NaSi [M+Na]⁺ 325.1383, found 325.1384.

Diethylbis(1-phenylethyl)silane (mixture of racemate and mesomer)



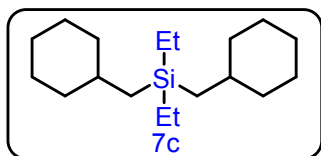
Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.25-7.20 (m, 4H), 7.10-7.03 (m, 6H), 2.35 (q, $J = 7.6$ Hz, 1H), 2.30 (q, $J = 7.6$ Hz, 1H), 1.35 (d, $J = 7.6$ Hz, 3H), 1.29 (d, $J = 7.6$ Hz, 3H), 1.01 (t, $J = 7.9$ Hz, 1.5H), 0.78 (t, $J = 7.8$ Hz, 3H), 0.69 (q, $J = 8.0$ Hz, 1H), 0.61 (t, $J = 7.8$ Hz, 1.5H), 0.52 (q, $J = 7.7$ Hz, 2H), 0.40 (q, $J = 7.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.09, 146.04, 128.08, 127.42, 127.40, 124.39, 26.73, 26.29, 16.12, 15.95, 7.88, 7.42, 7.16, 2.46, 1.56, 1.02; MS (EI, m/z): 296 (M^+ , 3), 191 (100), 149 (61), 121 (40), 73 (32).

Diethylbis(3-phenylpropyl)silane



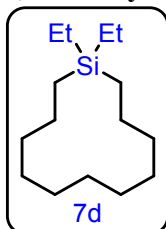
Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.32-7.28 (m, 4H), 7.22-7.18 (m, 6H), 2.63 (t, $J = 7.6$ Hz, 4H), 1.65-1.57 (m, 4H), 0.91 (t, $J = 7.9$ Hz, 6H), 0.60-0.56 (m, 4H), 0.54-0.48 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 142.66, 128.43, 128.19, 125.59, 40.16, 26.03, 11.57, 7.46, 3.59; HRMS (EI, m/z): calcd for $\text{C}_{20}\text{H}_{27}\text{Si}$ [$\text{M}-\text{C}_2\text{H}_5$] $^+$ 295.1876, found 295.1873.

Bis(cyclohexylmethyl)diethylsilane



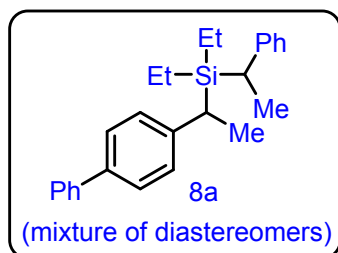
Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 1.69-1.64 (m, 10H), 1.39-1.31 (m, 2H), 1.26-1.09 (m, 8H), 0.97-0.87 (m, 8H), 0.55-0.47 (m, 8H); ^{13}C NMR (100 MHz, CDCl_3) δ 37.13, 34.20, 26.70, 26.28, 21.35, 7.65, 5.35; HRMS (EI, m/z): calcd for $\text{C}_{16}\text{H}_{31}\text{Si}$ [$\text{M}-\text{C}_2\text{H}_5$] $^+$ 251.2190, found 251.2189.

1,1-Diethylsilacyclododecane



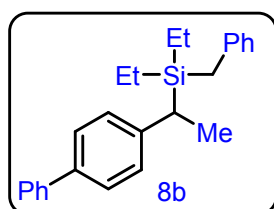
Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 1.36-1.26 (m, 18H), 0.92 (t, $J = 7.9$ Hz, 6H), 0.55-0.46 (m, 8H); ^{13}C NMR (100 MHz, CDCl_3) δ 30.97, 26.29, 25.55, 25.45, 21.56, 10.54, 7.46, 4.00.

(1-([1,1'-Biphenyl]-4-yl)ethyl)diethyl(1-phenylethyl)silane



Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.60 (dd, $J = 2.0, 7.7$ Hz, 2H), 7.50-7.46 (m, 2H), 7.42 (t, $J = 7.6$ Hz, 2H), 7.31 (t, $J = 7.3$ Hz, 1H), 7.24-7.21 (m, 2H), 7.15-7.05 (m, 5H), 2.44-2.31 (m, 2H), 1.39 (dd, $J = 2.7, 7.6$ Hz, 3H), 1.33 (dd, $J = 1.8, 7.6$ Hz, 3H), 1.04 (t, $J = 7.9$ Hz, 1.5H), 0.84-0.79 (m, 3H), 0.73 (q, $J = 7.9$ Hz, 1H), 0.66 (t, $J = 7.8$ Hz, 1.5H), 0.56 (q, $J = 7.6$ Hz, 2H), 0.47-0.41 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.03, 145.97, 145.32, 145.27, 141.07, 141.06, 137.17, 128.66, 128.10, 127.78, 127.75, 127.42, 127.40, 126.78, 126.70, 124.41, 26.70, 26.42, 26.29, 26.00, 16.16, 16.11, 16.02, 15.93, 7.91, 7.50, 7.48, 7.23, 2.46, 1.61, 1.59, 1.06; HRMS (EI, m/z): calcd for $\text{C}_{26}\text{H}_{32}\text{Si}$ $[\text{M}]^+$ 372.2268, found 372.2270.

(1-([1,1'-Biphenyl]-4-yl)ethyl)(benzyl)diethylsilane



Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.60 (dd, $J = 1.3, 8.4$ Hz, 2H), 7.51-7.48 (m, 2H), 7.42 (t, $J = 7.6$ Hz, 2H), 7.34-7.29 (m, 1H), 7.18 (t, $J = 7.6$ Hz, 2H), 7.14-7.11 (m, 2H), 7.06 (t, $J = 7.9$ Hz, 1H), 7.06 (d, $J = 7.4$ Hz, 2H), 2.38 (q, $J = 7.6$ Hz, 1H), 2.12 (s, 2H), 1.41 (d, $J = 7.6$ Hz, 3H), 0.89 (t, $J = 7.9$ Hz, 3H), 0.82 (t, $J = 7.9$ Hz, 3H), 0.59-0.48 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 144.94, 141.08, 140.12, 137.24, 128.67, 128.30, 128.18, 127.68, 126.79, 126.75, 126.49, 123.96, 26.51, 20.43, 15.51, 7.38, 7.31, 2.54, 2.04; HRMS (EI, m/z): calcd for $\text{C}_{25}\text{H}_{30}\text{Si}$ $[\text{M}]^+$ 358.2111, found 358.2114.

4) References

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5) ^1H and ^{13}C NMR Spectra

