Supplementary Data for:

Catalytic metal-free Si-N cross-dehydrocoupling

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General Information

Synthesis and techniques

All preparations were done in oven dried (140 °C) glassware under an atmosphere of dry, O_2 -free Ar employing both Schlenk line techniques and a *MBraun* inert atmosphere glove box. Experiments on NMR scale were carried out in Teflon cap sealed J Young NMR tubes. Solvents were purified with a Grubbs-type column system manufactured by *MBraun* and dispensed into thick-walled glass Schlenk bombs equipped with Young type Teflon valve stop-cocks. All solvents were stored over 4 Å molecular sieves in the glove box. Molecular sieves (4 Å) were dried at 140 °C under vacuum for 24 h prior to use. Deuterated solvents were vacuum transferred from sodium/benzophenone (C₆D₆) or CaH₂ (CD₂Cl₂), degassed by 3 freeze-pump-thaw cycles and stored over 4 Å molecular sieves for usage in a glove box. Technical grade solvents for extraction were distilled prior to use.

Reagents and materials

All commercially available silanes and amines were used as received (*Sigma Aldrich, ABCR*) without further purification unless noted otherwise. Liquid substrates were stored over molecular sieves in the glovebox. Tris(pentafluorophenyl)borane (2) was purchased from Sigma Aldrich and used as received.

Characterization

NMR spectra were recorded on a *Bruker* AC 300 (300 MHz) or *Bruker* DRX 600 (600 MHz) spectrometer as solutions. Chemical shifts are expressed in parts per million (ppm, δ) downfield from tetramethylsilane (TMS) and are referenced to the residual proton signals of C₆D₆ (7.16 ppm, 128.06 ppm) or CD₂Cl₂ (5.32 ppm, 53.84 ppm) as internal standard. All coupling constants are absolute values and are expressed in Hertz (Hz). The description of ¹H NMR signals include: s = singlet, br. s = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, etc. The description of ¹³C NMR signals include C = quartenery carbon atom, CH = tertiary carbon atom, CH₂ = secondary carbon atom, CH₃ = primary carbon atom. The spectra were analyzed according to first order. High resolution mass spectrometry (HRMS) analysis were obtained from the Analytical Facility in the Institute of Organic Chemistry, KIT.

Experimental Details

General procedure for the catalytic dehydro coupling in 0.2 mmol scale (GP1)

In a glove box a Schlenk flask with J Young Teflon tap was charged with $B(C_6F_5)_3$ (10.2 mg, 0.02 mmol, 1.00 mol%) and the corresponding amine (2.00 mmol, 1 equiv.) or diamine (1.00 mmol, 0.50 equiv.) and dissolved in CH_2Cl_2 (5 ml). The hydrosilane (2.00 mmol, 1.00 equiv.) was dissolved in CH_2Cl_2 (5 ml) and added dropwise to the solution. The reaction mixture was stirred for the time and at the temperature indicated in *Table 1*. The Reaction was monitored by NMR and stopped after 99% conversion by addition of pentane/ Et_2O 9:1 containing 4% NEt₃ (10 ml). The mixture was filtered over a pad of Celite layered with a small amount of silica gel and eluted with pentane/ Et_2O 9:1 containing 4% NEt₃ (10 ml). All volatiles were removed under reduced pressure and the compounds were obtained in analytical purity.

Analytical data for compounds in Table 1



Entry 3

Diphenylmethyl-N,N-di-p-tolylsilylamine (**6a**) (GP1, 1 h, room temperature, 73% isolated yield, white powder): ¹H NMR (300 MHz, C₆D₆): δ = 7.81 – 7.74 (m, 4H, H_{Ar}), 7.21 – 7.14 (m, 6H, H_{Ar}), 7.02 (d, *J* = 8.3 Hz, 4H, H_{tol}), 6.84 (d, *J* = 8.3 Hz, 4H, H_{tol}), 2.03 (s, 6H, ArC*H*₃), 0.50 (s, 3H, SiC*H*₃); ¹³C NMR (75 MHz, C₆D₆): δ = 146.3 (C), 136.8 (C), 135.4 (CH), 131.8 (C), 130.0 (CH), 129.8 (CH), 128.3 (CH), 125.3 (CH), 20.7 (CH₃), 0.8 (CH₃); MS (EI, 70 mV) *m/z*: 393 (100) [M]⁺, 198 (15), 197 (80), 196 (17), 181 (19); HRMS (EI) exact mass for [M]⁺ (C₂₇H₂₇NSi): calc *m/z* 393.1913, found 393.1910.

Entry 5



Diphenylmethyl-N,N-diphenylsilylamine (**6b**) (GP1, 1 h, room temperature, 91% isolated yield, white powder): ¹H NMR (300 MHz, C₆D₆): δ = 7.75 – 7.67 (m, 4H, H_{Ar}), 7.20 – 7.11 (m, 6H, H_{Ar}), 7.06 – 6.94 (m, 8H, H_{Ar}), 6.84 – 6.75 (m, 2H, H_{Ar}), 0.46 (s, 3H, SiC*H*₃); ¹³C NMR (75 MHz, C₆D₆): δ = 148.4 (C), 136.4 (C), 135.3 (CH), 129.9 (CH), 129.4 (CH), 127.9 (CH), 125.3 (CH), 122.8 (CH), 0.7 (CH₃); MS (EI, 70 mV) *m/z*: 366 (27), 365 (84) [M]⁺, 198 (21), 197 (100); HRMS (EI) exact mass for [M]⁺ (C₂₅H₂₃NSi): calc *m/z* 365.1600, found 365.1601.

S3

Entry 6



9-diphenylmethylsilylcarbazole (6c) (GP1, 1 h, room temperature, 97% isolated yield, white powder): ¹H NMR (300 MHz, C₆D₆): $\delta = 8.06 - 7.97$ (m, 2H, H_{Ar}), 7.49 - 7.39 (m, 4H, H_{Ar}), 7.20 - 7.00 (m, 12H, H_{Ar}), 0.89 (s, 3H, SiCH₃); ¹³C NMR (75 MHz, C₆D₆): $\delta = 145.1$ (C), 135.4 (CH), 134.8 (C), 130.7 (CH), 128.7 (CH), 127.2 (C), 125.8 (CH), 120.5 (CH), 120.4 (CH), 114.6 (CH), 1.4 (CH₃); MS (EI, 70 mV) *m/z*: 363 (100) [M]⁺, 317 (36), 197 (89), 195 (21), 167 (28); HRMS (EI) exact mass for [M]⁺ (C₂₅H₂₁NSi): calc *m/z* 363.1443, found 363.1442.

Entry 7



4-Ethyl-9-diphenylsilylcarbazole (**6d**) (GP1, 1 h, room temperature, 83% isolated yield, white powder): ¹H NMR (300 MHz, C₆D₆): $\delta = 8.08$ (d, J = 7.3 Hz, 1H, H_{Ar}), 7.93 (s, 1H, H_{Ar}), 7.51 – 7.45 (m, 4H, H_{Ar}), 7.22 – 7.03 (m, 10H, H_{Ar}), 6.94 (d, J = 8.7 Hz, 1H, H_{Ar}), 2.66 (q, J = 7.2 Hz, 2H, CH₂CH₃), 1.21 (t, J = 7.2 Hz, 3H, CH₂CH₃), 0.91 (s, 3H, SiCH₃); ¹³C NMR (75 MHz, C₆D₆): $\delta = 145.5$ (C), 143.6 (C), 136.2 (C), 135.4 (CH), 134.9 (C), 134.9 (C), 130.7 (CH), 128.7 (CH), 127.4 (C), 127.3 (C), 126.1 (CH), 125.6 (CH), 120.4 (CH), 120.3 (CH), 119.2 (CH), 114.6 (CH), 114.5 (CH), 29.2 (CH₂), 16.7 (CH₃), -1.3 (CH₃); **MS** (EI, 70 mV) *m/z*: 391 (100) [M]⁺, 197 (80), 195 (37), 180 (47); **HRMS** (EI) exact mass for [M]⁺ (C₂₇H₂₅NSi): calc *m/z* 391.1756, found 391.1755.

Entry 8



Preparation of 2,7-dibromo-9-diphenylmethylsilylcarbazole (6e)

In a glove box a sealable NMR tube with J Young Teflon tap was charged with 2,7dibromocarbazole (32.5 mg, 0.10 mmol, 1.00 equiv.), methyl(diphenyl)silane (19.8 mg, 0.10 mmol, 1.00 equiv.) and B(C₆F₅)₃ (5.12 mg, 0.01 mmol, 10 mol%) and dissolved in CD₂Cl₂ (0.6 ml). After 24 h at room temperature approximately >95% conversion to product was observed by NMR spectroscopy. ¹H NMR (300 MHz, CD₂Cl₂): $\delta = 7.89$ (d, J = 8.3 Hz, 2H, H_{Ar}), 7.64 – 7.53 (m, 6H, H_{Ar}), 7.48 (t, J = 7.1 Hz, 4H, H_{Ar}), 7.31 (d, J = 8.3 Hz, 2H, H_{Ar}), 7.00 (s, 2H, H_{Ar}), 1.19 (s, 3H, SiCH₃).

Entry 9





In a glove box a sealable NMR tube with J Young Teflon tap was charged with carbazole (16.7 mg, 0.10 mmol, 1.00 equiv.), triethylsilane (11.6 mg, 0.10 mmol, 1.00 equiv.) and $B(C_6F_5)_3$ (5.12 mg, 0.01 mmol, 10 mol%) and dissolved in CD_2Cl_2 (0.6 ml). After 1 h at room temperature approximately >95% conversion to product was observed by NMR spectroscopy.

¹**H NMR** (300 MHz, CD₂Cl₂): $\delta = 8.10$ (d, J = 7.6 Hz, 2H, H_{Ar}), 7.68 (d, J = 8.3 Hz, 2H, H_{Ar}), 7.41 (t, J = 7.5 Hz, 2H, H_{Ar}), 7.26 (t, J = 7.4 Hz, 2H, H_{Ar}), 1.29 (dd, J = 15.5, 7.7 Hz, 6H, CH₂CH₃), 1.02 (t, J = 7.8 Hz, 9H, CH₂CH₃).

Entry 10



1,1,3,3-Tetramethyl-N,N,N',N'-tetra-p-tolyldisiloxane-1,3-diamine (**6g**) (GP1, 1 h, room temperature, 97% isolated yield, colorless oil): ¹H NMR (300 MHz, C₆D₆): δ = 7.06 (d, *J* = 8.2 Hz, 8H), 6.95 (d, *J* = 8.2 Hz, 8H), 2.11 (s, 12H), 0.32 (s, 12H); ¹³C NMR (75 MHz, C₆D₆): δ = 146.3 (C), 132.1 (C), 130.1 (CH), 125.5 (CH), 20.8 (CH₃), 1.39 (CH₃); MS (EI, 70 mV) *m/z*: 524, 197 (100), 196 (29); HRMS (EI) exact mass for [M]⁺ (C₃₂H₄₀N₂OSi₂): calc *m/z* 524.2674, found 524.2673.

Entry 11



N-Diphenylmethylsilylaniline (**6h**) (GP1, 72 h, 70 °C, 5 mol% of B(C₆F₅)₃, 90% isolated yield, white solid): ¹**H** NMR (300 MHz, C₆D₆): δ = 7.67 – 7.53 (m, 4H, H_{Ar}), 7.21 – 7.10 (m, 6H, H_{Ar}), 6.99 (t, *J* = 7.7 Hz, 2H, H_{Ar}), 6.68 (t, *J* = 7.7 Hz, 1H, H_{Ar}), 6.57 (d, *J* = 7.7 Hz, 2H, H_{Ar}), 3.51 (bs, 1H, N*H*), 0.65 (s, 3H, SiC*H*₃); ¹³C NMR (75 MHz, C₆D₆): δ = 147.1 (C), 136.4 (C), 135.0 (CH), 130.1 (CH), 129.5 (CH), 128.4 (CH), 118.7 (CH), 117.30 (CH), -2.78 (CH₃); **MS** (EI, 70 mV) *m/z*: 289 (25) [M]⁺, 274 (20), 200 (17), 199 (100), 120 (24), 93 (30); **HRMS** (EI) exact mass for [M]⁺ (C₁₉H₁₉NSi): calc *m/z* 289.1287, found 289.1285.

Entry 12



N-Diphenylmethylsilyl-2,6-dimethylanilin (**6i**) (GP1, 48 h, 70 °C, 90% isolated yield, yellowish solid): ¹H NMR (600 MHz, C₆D₆): $\delta = 7.62 - 7.56$ (m, 4H, H_{Ar}), 7.20 - 7.14 (m, 6H, H_{Ar}), 6.94 (d, J = 7.3 Hz, 2H, H_{Ar}), 6.83 (t, J = 7.4 Hz, 1H, H_{Ar}), 2.92 (bs, 1H, NH), 2.08 (bs, 6H, CH₃), 0.57 (s, 3H, CH₃); ¹³C NMR (151 MHz, C₆D₆): $\delta = 143.43$, 138.43, 135.24, 134.70, 134.41, 130.84, 129.92, 129.82, 128.97, 128.65, 128.35, 121.98, 118.16, 20.42, -2.13; MS (EI, 70 mV) *m/z*: 317 (2), 198 (59), 183 (36), 120 (100), 105 (46); HRMS (EI) exact mass for [M]⁺ (C₂₁H₂₃NSi): calc *m/z* 317.1594, found 317.1595.

Entry 13



N-Diphenylmethylsilyl-2-tertbutylanilin (**6j**) (GP1, 48 h, 70 °C, 93% isolated yield, yellowish solid): ¹**H NMR** (600 MHz, C₆D₆): $\delta = 7.72 - 7.66$ (m, 4H, H_{Ar}), 7.26 (d, J = 7.9 Hz, 1H, H_{Ar}), 7.20 - 7.13 (m, 6H, H_{Ar}), 6.95 (d, J = 8.0 Hz, 1H, H_{Ar}), 6.85 (t, J = 7.6 Hz, 1H, H_{Ar}), 6.74 (t, J = 7.5 Hz, 1H, H_{Ar}), 4.26 (s, 1H, N*H*), 1.35 (s, 9H, C(C*H*₃)₃), 0.78 (s, 3H, C*H*₃); ¹³C NMR (151 MHz, C₆D₆): $\delta = 145.28$, 136.73, 135.38, 134.87, 130.15, 128.52, 128.35, 127.98, 127.28, 127.00, 119.04, 119.01, 34.12, 30.13, -2.60. MS (EI, 70 mV) *m/z*: 345 (5), 199 (46), 198 (72), 183 (50), 134 (55), 120 (100), 105 (60); **HRMS** (EI) exact mass for [M]⁺(C₂₃H₂₇NSi): calc *m/z* 345.1907, found 345.1908.

S5

Entry 14



N-Diphenylmethylsilyl-2-methyl-4-chloroanilin (6k) (GP1, 36 h, 60 °C, 97% isolated yield, purple powder): ¹H NMR (300 MHz, C₆D₆): $\delta = 7.63 - 7.57$ (m, 4H, H_{Ar}), 7.22 - 7.16 (m, 6H, H_{Ar}), 6.96 (d, J = 2.4 Hz, 1H, H_{Ar}), 6.74 (dd, J = 8.6, 2.4 Hz, 1H, H_{Ar}), 6.60 (d, J = 8.6 Hz, 1H, H_{Ar}), 3.51 (s, 1H, N*H*), 1.66 (s, 3H, C*H*₃), 0.66 (s, 3H, C*H*₃); ¹³C NMR (75 MHz, C₆D₆): $\delta = 143.8$ (C), 136.1 (C), 134.8 (CH), 130.5 (CH), 130.4 (CH), 128.5 (CH), 127.0 (CH), 126.1 (C), 123.5 (C), 117.3 (CH), 17.2 (CH₃), -2.8 (CH₃); MS (EI, 70 mV) *m/z*: 339 (33) [M+2]⁺, 338 (22) [M+1]⁺, 337 (100) [M], 197 (73); HRMS (EI) exact mass for [M]⁺ (C₂₀H₂₀ClNSi): calc *m/z* 337.1048, found 337.1050.

Entry 15



N-Diphenylmethylsilyl-2-chloroanilin (**6I**) (GP1, 24 h, 60 °C, 91% isolated yield, white solid): ¹**H NMR** (300 MHz, C₆D₆): δ = 7.60 – 7.54 (m, 4H, H_{Ar}), 7.19 – 7.10 (m, 5H, H_{Ar}), 6.78 (dd, *J* = 8.1, 1.4 Hz, 1H, H_{Ar}), 6.61 (td, *J* = 8.1, 1.4 Hz, 1H, H_{Ar}), 6.61 (td, *J* = 8.1, 1.4 Hz, 1H, H_{Ar}), 6.37 (td, *J* = 8.1, 1.4 Hz, 1H, H_{Ar}), 4.75 (bs, 1H, N*H*), 0.60 (s, 3H, SiC*H*₃); ¹³**C NMR** (75 MHz, C₆D₆): δ = 143.7 (C), 135.6 (C), 134.8 (CH), 130.3 (CH), 129.7 (CH), 128.5 (CH), 127.8 (CH), 122.2 (C), 119.2 (CH), 117.2 (CH), -2.9 (CH₃); **MS** (EI, 70 mV) *m/z*: 325 (33), 324 (22), 323 (100) [M], 230 (31), 197 (56), 131 (40), 69 (100); **HRMS** (EI) exact mass for [M]⁺ (C₁₉H₁₈CINSi): calc *m/z* 323.0892, found 323.0894.

Entry 16



N-Diphenylmethylsilyl-2,6-dichloroanilin (**6m**) (GP1, 36 h, room temperature, 88% isolated yield, white powder): ¹H NMR (300 MHz, C₆D₆): δ = 7.68 – 7.61 (m, 4H, H_{Ar}), 7.20 – 7.13 (m, 6H, H_{Ar}), 6.86 (d, *J* = 8.0 Hz, 2H, H_{Ar}), 6.15 (t, *J* = 8.0 Hz, 1H, H_{Ar}), 4.68 (bs, 1H, N*H*), 0.82 (s, 3H, SiC*H*₃); ¹³C NMR (75 MHz, C₆D₆): δ = 142.0 (C), 137.9 (C), 134.6 (CH), 129.9 (CH), 128.7 (CH), 128.3 (CH), 124.6 (C), 120.1 (CH), -0.4 (CH₃); MS (EI, 70 mV) *m/z*: 359 (46) [M]⁺, 357 (58) [M]⁺, 344 (50), 342 (51), 199 (100), 197 (42); HRMS (EI) exact mass for [M]⁺ (C₁₉H₁₇NSiCl₂): calc *m/z* 357.0507, found 357.0509.

Entry 17



N-Diphenylmethylsilyl-3,5-trichloromethylanilin (**6n**) (GP1, 24 h, room temperature, 97% isolated yield, white powder): ¹H NMR (300 MHz, C₆D₆): $\delta = 7.49 - 7.43$ (m, 4H, H_{Ar}), 7.19 - 7.12 (m, 7H, H_{Ar}), 6.69 (s, 2H, H_{Ar}), 3.47 (s, 1H, N*H*), 0.53 (s, 3H, SiC*H*₃); ¹³C NMR (75 MHz, C₆D₆): $\delta = 148.5$ (C), 134.8 (CH), 132.4 (q, *J* = 33 Hz, CF₃), 137.4 (CH), 128.6 (CH), 125.9 (C), 122.3 (C), 116.7 (CH), 111.4 (CH), -3.3 (CH₃); MS (EI, 70 mV) *m/z*: 426 (22) [M+1]⁺, 425 (96) [M]⁺, 411 (29), 410 (100), 197 (48); HRMS (EI) exact mass for [M]⁺(C₂₁H₁₇NSiF₆): calc *m/z* 425.1034, found 425.1036.

N,N[•]-*bis(diphenylmethylsilyl)-N,N*[•]-*diphenylbenzene-1,4-diamine* (**60**) (GP1, 24 h, 2 mol% B(C₆F₅)₃, room temperature, 26% isolated yield, grey powder): ¹H NMR (300 MHz, C₆D₆): δ = 7.69 – 7.61 (m, 8H, H_{Ar}), 7.24 – 7.09 (m, 12H, H_{Ar}), 7.02 – 6.89 (m, 8H, H_{Ar}), 6.85 (s, 4H, H_{Ar}), 6.80 – 6.70 (m, 2H, H_{Ar}), 0.51 (s, 6H, SiC*H*₃); ¹³C NMR (75 MHz, C₆D₆): δ = 149.5 (C), 143.3 (C), 136.5 (C), 135.4 (CH), 129.8 (CH), 129.2 (CH), 128.8 (CH), 128.3 (CH), 122.4 (CH), 121.2 (CH), 0.0 (CH₃); MS (EI, 70 mV) *m/z*: 653 (56), 652 (100) [M+], 199.1 (24), 197 (58), 69 (14); HRMS (EI) exact mass for [M]⁺ (C₄₄H₄₄N₂Si₂): calc *m/z* 652.2725, found 652.2726.

Entry 19

Entry 18

N,N'-Bis[(diphenylmethylsilyl)phenyl]ethylendiamin (**6p**) (GP1, 24 h, 70 °C, 92% isolated yield, colorless oil): ¹**H NMR** (300 MHz, C₆D₆): $\delta = 7.64 - 7.55$ (m, 2H, H_{Ar}), 7.54 - 7.47 (m, 8H, H_{Ar}), 7.20 - 7.11 (m, 10H, H_{Ar}), 6.98 - 6.90 (m, 4H, H_{Ar}), 6.90 - 6.84 (m, 4H, H_{Ar}), 6.85 - 6.70 (m, 2H, H_{Ar}), 3.61 (s, 4H, CH₂CH₂), 0.54 (s, 6H, SiCH₃); ¹³**C NMR** (75 MHz, C₆D₆): $\delta = 148.4$ (C), 136.9 (C), 135.3 (CH), 129.8 (CH), 129.0 (CH), 128.3 (CH), 122.3 (CH), 121.0 (CH), 48.3 (CH₂), -1.3 (CH₃); **MS** (EI, 70 mV) *m/z*: 605 (2) [M+1]⁺, 604 (3) [M]⁺, 303 (25), 302 (93), 197 (100); **HRMS** (EI) exact mass for [M]⁺ (C₄₀H₄₀N₂Si₂): calc *m/z* 604.2730, found 604.2732.

Entry 20

1,2,3-Triphenyl-1,3,2-diazasilolidine (**6q**) (GP1, 24 h, 60 °C, Product was purified by filtration over a pad of celite, eluation with pentane and subsequent removal of all volatiles under reduced pressure, 83% yield, yellow solid): ¹H NMR (300 MHz, C₆D₆): δ = 7.68 – 7.58 (m, 2H, H_{Ar}), 7.22 – 7.00 (m, 8H, H_{Ar}), 6.80 – 6.69 (m, 5H, H_{Ar}), 5.90 (s, 1H, Si*H*), 3.37 – 3.27 (m, 2H, CH₂), 3.23 – 3.14 (m, 2H, CH₂); ¹³C NMR (75 MHz, C₆D₆): δ = 147.54 (C), 134.74 (CH), 131.41 (CH), 129.59 (CH), 128.75 (CH), 128.35 (C), 119.02 (CH), 115.37 (CH), 45.27 (CH₂). MS (EI, 70 mV) *m/z*: 316 (18) [M], 212 (34), 107 (74), 106 (100); HRMS (EI) exact mass for [M]⁺(C₂₀H₂₀N₂Si): calc *m/z* 316.1390, found 316.1393.

Entry 21



l-(Diphenylmethylsilyl)indoline (**6r**) In a glove box a sealable NMR tube with J Young Teflon tap was charged with indole (5.7 mg, 0.05 mmol, 1.0 equiv.), diphenylmethylsilane (10.0 mg, 0.05 mmol, 1.0 equiv.) and $B(C_6F_5)_3$ (2.5 mg, 0.005 mmol, 10 mol%) and dissolved in CD_2Cl_2 (0.6 ml). After 3 days at 60 °C approximately 47% conversion to product was observed by NMR spectroscopy. The compound was not isolated. The yield was determined from crude product by NMR spectroscopy.





Entry 22



5-*Chloro-1-(diphenylmethylsilyl)indoline* (**6s**) (GP1, 24 h, 70 °C, 81% isolated yield, yellow solid): ¹H NMR (300 MHz, C₆D₆): δ = 7.56 – 7.47 (m, 4H, H_{Ar}), 7.21 – 7.12 (m, 6H, H_{Ar}), 6.93 (s, 1H, H_{Ar}), 6.71 (d, *J* = 7.8 Hz, 1H, H_{Ar}), 6.21 (d, *J* = 7.8 Hz, 1H, H_{Ar}), 3.27 (t, *J* = 8.8 Hz, 2H, CH₂), 2.50 (t, *J* = 8.8 Hz, 2H, CH₂), 0.59 (s, 3H, SCH₃); ¹³C NMR (75 MHz, C₆D₆): δ = 150.7, 135.4, 135.2, 135.1, 134.2, 130.3, 129.8, 128.5, 128.3, 127.2, 125.1, 122.9, 111.5, 50.8, 30.0, - 2.8; MS (EI, 70 mV) *m/z*: 351 (37), 350 (30), 349 (100), 198 (20), 197 (91); HRMS (EI) exact mass for [M]⁺ (C₂₁H₂₀NCISi): calc 349.1048, found 349.1050.

Entry 23



l-(*Diphenylmethylsilyl*)-2-*methylindoline* (**6t**) (GP1, 24 h, 70 °C, 96% isolated yield, brown solid): ¹**H NMR** (600 MHz, C₆D₆): δ = 7.67 – 7.55 (m, 4H, H_{Ar}), 7.17 (m, 6H, H_{Ar}), 7.09 (d, *J* = 7.2 Hz, 1H, H_{Ar}), 6.84 (t, *J* = 7.6 Hz, 1H, H_{Ar}), 6.71 (t, *J* = 6.9 Hz, 1H, H_{Ar}), 6.56 (d, 7.8 Hz, 1H, H_{Ar}), 3.86 – 3.72 (m, 1H, CHCH₃), 3.13 (dd, *J* = 15.4, 9.3 Hz, 1H, CH_AH_B), 2.32 (d, *J* = 15.4 Hz, 1H, CH_AH_B), 0.93 (d, *J* = 6.3 Hz, 3H, CHCH₃), 0.69 (s, 3H, SiCH₃).; ¹³C **NMR** (151 MHz, C₆D₆): δ = 135.38 (CH), 135.32 (CH), 130.04 (CH), 129.99 (CH), 128.33(CH), 127.55 (CH), 125.28 (CH), 118.56 (CH), 111.77 (CH), 56.88 (CH), 38.14 (CH₂), 24.03 (CH₃), -2.28 (CH₃); **MS** (EI, 70 mV) *m/z*: 330 (25) [M+1], 329 (100) [M], 314 (60), 199 (33), 197 (42), 118 (41); **HRMS** (EI) exact mass for [M]⁺(C₂₂H₂₃NSi): calc 328.9940, found 328.9938.

Entry 24



l-(Diphenylmethylsilyl)-2-phenylindoline (**6u**) (GP1, 24 h, 70 °C, 97% isolated yield, white solid): ¹**H NMR** (300 MHz, C₆D₆): δ = 7.59 – 7.54 (m, 2H, H_{Ar}), 7.50 – 7.45 (m, 2H, H_{Ar}), 7.20 – 7.09 (m, 7H, H_{Ar}), 7.03 – 6.95 (m, 5H, H_{Ar}), 6.92 – 6.84 (m, 1H, H_{Ar}) 6.76 – 6.63 (m, 2H, H_{Ar}), 4.77 (dd, *J* = 10.5, 2.6 Hz, 1H, C*H*), 3.49 (dd, *J* = 15.8, 10.5 Hz, 1H, C*H*_AH_B), 2.77 (dd, *J* = 15.9, 2.3 Hz, 1H, , CH_AH_B), 0.59 (s, 3H, SiCH₃); ¹³C NMR (75 MHz, C₆D₆): δ = 152.2 (C), 147.5 (C), 135.9 (C), 135.7 (C), 135.5 (CH), 135.4 (CH), 130.0 (CH), 130.0 (C), 129.9, (CH), 128.7 (CH), 128.3 (CH), 128.2 (CH), 127.7 (CH), 127.2 (CH), 126.1 (CH), 125.4 (CH), 118.9 (CH), 110.9 (CH), 65.1 (CH), 40.4 (CH₂), -2.35 (CH₃); **MS** (EI, 70 mV) *m/z*: 391 (2) [M]⁺, 199 (100), 195 (63), 118 (60); **HRMS** (EI) exact mass for [M]⁺ (C₂₇H₂₅NSi): calc 391.1751, found 391.1750.

Entry 25



I-(Diphenylmethylsilyl)-2,3-dimethylindoline (**6v**) (GP1, 24 h, 70 °C, 92% isolated yield, white solid): ¹H NMR (600 MHz, C₆D₆): δ = 7.68 – 7.59 (m, 4H, H_{Ar}), 7.22 – 7.12 (m, 6H. H_{Ar}), 6.98 (d, *J* = 7.2 Hz, 1H, H_{Ar}), 6.84 (t, *J* = 7.6 Hz, 1H, H_{Ar}), 6.74 (t, *J* = 7.3 Hz, 1H, H_{Ar}), 6.54 (d, *J* = 7.9 Hz, 1H, H_{Ar}), 3.76 (dq, *J* = 13.1, 6.5 Hz, 1H, CHCH₃), 3.42 – 3.34 (m, 1H, CHCH₃), 1.02 (d, *J* = 7.1 Hz, 3H, CH₃), 0.87 – 0.79 (m, 3H, CH₃), 0.70 (s, *J* = 6.5 Hz, 3H, SiCH₃).; ¹³C NMR (75 MHz, C₆D₆): δ = 150.42 (C), 136.47 (C), 136.30 (C), 135.82 (C), 135.40 (CH), 135.33 (CH), 130.05 (CH), 129.99 (CH), 128.55 (C), 128.35 (CH), 128.33 (CH), 127.55 (CH), 123.44 (CH), 118.74 (CH), 111.78 (C), 61.67 (CH), 40.67 (CH), 17.19 (CH₃), 11.92 (CH₃), -2.15 (CH₃). MS (EI, 70 mV) *m/z*: 343 (3), 241 (80), 199 (100), 145 (52) 144 (52) 130 (32); HRMS (EI) exact mass for [M]⁺ (C₂₂H₂₃NSi): calc 343.1751, found 343.1752.

Preparation of cis-2,3-Dimethylindoline



A vial was charged with 1-(Methyl(diphenyl)silyl)-2,3-dimethylindoline (**6v**) (100 mg, 0.29 mmol, 1.00 equiv.) and dissolved in 2 ml diethylether. 1 M TBAF solution in THF (0.32 ml, 0.32 mmol, 1.10 equiv.) was added dropwise. After stirring the reaction mixture for 3 h at room temperature a saturated NaHCO₃ solution was added (2 ml) and the aqueos phase was extracted with diethylether. The combined organic layer was dried over anhydrous sodium sulfate. Filtration and removal of all volatiles in vacuo followed by column chromatography (cyclohexane:ethylacetate 50:1 to 10:1) yielded the title compound as a yellow oil (26%). ¹**H NMR** (300 MHz, CDCl₃): $\delta = 7.11 - 6.97$ (m, 2H, H_{Ar}), 6.73 (t, J = 7.3 Hz, 1H, H_{Ar}), 6.61 (d, J = 7.6 Hz, 1H, H_{Ar}), 4.02 - 3.87 (m, 1H, CHCH₃), 3.65 (bs, 1H, NH), 3.34 - 3.19 (m, 1H, CHCH₃), 1.18 (d, J = 7.2 Hz, 3H, CHCH₃), 1.13 (d, J = 6.5 Hz, 3H, CHCH₃).

NMR data is in agreement with literature reported chemical shifts and signal pattern:^[1] ¹**H** NMR (500 MHz, C₆D₆): δ 7.09 – 7.01 (m, 2H, H_{Ar}), 6.76 – 6.72 (m, 1H, H_{Ar}), 6.63 – 6.62 (m, 1H, H_{Ar}), 3.99 – 3.93 (m, 1H, CHCH₃), 3.65 (bs, 1H, NH), 3.31 – 3.25 (m, 1H, CHCH₃), 1.19 (d, *J* = 7.2 Hz, 3H, CHCH₃), 1.15 (d, *J* = 6.5 Hz, 3H, CHCH₃).

^[1] F. O. Arp, G. C. Fu, J. Am. Chem. Soc. 2006, 128, 14264-14265.

Mechanistic experiments

Preparation of 1-D-2,3-dimethylindole (1-D-5v)



A solution of 2,3-Dimethyl-1*H*-indole (250 mg, 1.72 mmol) in CD₃OD (1 ml, 21.9 mmol) was stirred over night at room temperature. The solvent was evaporated and the residue was once again dissolved in CD₃OD (1 ml, 21.9 mmol). Removal of the solvent under reduced pressure yielded the deuterated indole in 95% yield. ¹**H NMR** (300 MHz, CD₂Cl₂): δ = 7.43 (d, *J* = 6.8 Hz, 1H, H_{Ar}), 7.24 (d, *J* = 7.0 Hz, 1H, H_{Ar}), 7.11 – 6.98 (m, 2H, H_{Ar}), 2.36 (s, 3H, CH₃), 2.21 (s, 3H, CH₃).

Prepapation of D-methyldiphenylsilane



In a glove box a sealable NMR tube with J Young Teflon tap was charged with methyl(diphenyl)silane (10 mg, 0.05 mmol, 1.0 equiv.) and $B(C_6F_5)_3$ (2.6 mg, 0.005 mmol, 10 mol%) and dissolved in C_6D_6 (0.6 ml). The solution was freeze-pump thawed for 2 cycles and charged with D_2 at 77 K. After heating for 17 h at 70 °C approximately 90% of hydrogen in the silane was replaced by deuterium. ¹H NMR (300 MHz, C_6D_6): $\delta = 7.55 - 7.44$ (m, 4H, H_{Ar}), 7.26 – 7.07 (m, 6H, H_{Ar}), 0.45 (s, 3H, CH_3).

Preparation of 3-D-2,3-dimethyl-1-(diphenylmethylsilyl)indoline (3-D-6r)



In a glove box a sealable NMR tube with J Young Teflon tap was charged with 2,3dimethylindol-1-D (10 mg, 0.07 mmol, 1.0 equiv.), methyl(diphenyl)silane (13.6 mg, 0.068 mmol, 1.0 equiv.) and B(C₆F₅)₃ (3.5 mg, 0.007 mmol, 10 mol%) and dissolved in C₆D₆ (1 ml). After heating the solution to 70 °C for 24 h approximately 90% of conversion to 3-deuterated product was observed. ¹H NMR (300 MHz, C₆D₆): δ = 7.78 – 7.68 (m, 4H, H_{Ar}), 7.34 – 7.21 (m, 6H, H_{Ar}), 7.10 (d, *J* = 7.1 Hz, 1H, H_{Ar}), 6.95 (t, *J* = 7.6 Hz, 1H, H_{Ar}), 6.85 (t, *J* = 7.2 Hz, 1H, H_{Ar}), 6.65 (d, *J* = 7.7 Hz, 1H, H_{Ar}), 3.94 – 3.77 (m, 1H, CHCH₃), 1.13 (s, 3H, CDCH₃), 0.94 (s, *J* = 5.7 Hz, 3H, CHCH₃), 0.82 (s, 3H, SiCH₃).

Preparation of 2-D-2,3-dimethyl-1-(diphenylmethylsilyl)indoline (2-D-6r)



In a glove box a sealable NMR tube with J Young Teflon tap was charged with 2,3-dimethyl-1*H*-indole (7.3 mg, 0.05 mg, 1.0 equiv.), methyl(diphenyl)silane-*d* (10 mg, 0.05 mmol, 1.0 eq) and B(C₆F₅)₃ (2.6 mg, 0.005 mmol, 10 mol%) and dissolved in C₆D₆ (1 ml). After heating the solution to 70 °C for 24 h approximately 83% of conversion to 2-deuterated product was observed. . ¹H NMR (300 MHz, C₆D₆): δ = 7.80 – 7.68 (m, 4H, H_{Ar}), 7.32 – 7.21 (m, 6H, H_{Ar}), 7.10 (d, *J* = 7.0 Hz, 1H, H_{Ar}), 6.95 (t, *J* = 7.5 Hz, 1H, H_{Ar}), 6.85 (t, *J* = 7.2 Hz, 1H, H_{Ar}), 6.65 (d, *J* = 7.7 Hz, 1H, H_{Ar}), 3.49 (q, *J* = 6.8 Hz, 1H, CHCH₃), 1.14 (d, *J* = 7.1 Hz, 3H, CDCH₃), 0.93 (s, 3H, CDCH₃), 0.82 (s, 3H, SiCH₃).

Preparation of 1-(methyldiphenylsilyl)-2,3-dimethylindole (8)



The title compound was prepared according to a literature reported procedure.^[2] A 10 ml Schlenk flask was charged with 10.9 mg Zn(OTf)₂ (0.03 mmol, 0.05 equiv.) and heated to 80 °C under vacuum for 20 minutes. The white solid was dissolved in 0.5 ml of propionitrile and subsequently 87.1 mg 2,3-dimethylindole (0.6 mmol, 1.0 equiv.), 0.05 ml pyridine (0.6 mmol, 1.0 equiv.) and 0.14 ml methyl(diphenyl)silane (142 mg, 0.72 mmol, 1.20 equiv.) were added. After heating the solution to 90 °C for 48 h a saturated NaHCO₃ solution was added and the aqueous phase was extracted with ethylacetate. The combined organic layer was washed with brine and dried over anhydrous sodium sulfate. Filtration and removal of all volatiles *in vacuo* followed by column chromatography (cyclohexane:ethylacetate 80:1) yielded the title compound as a white solid (35%).

¹**H NMR** (300 MHz, C_6D_6): $\delta = 7.64 - 7.57$ (m, 1H, H_{Ar}), 7.48 - 7.38 (m, 4H, H_{Ar}), 7.23 - 7.03 (m, 8H, H_{Ar}), 7.03 - 6.94 (m, 1H, H_{Ar}), 2.18 (s, 3H, CH_3), 1.97 (s, 3H, CH_3), 0.85 (s, 3H, SiCH₃); ¹³**C NMR** (75 MHz, C_6D_6): $\delta = 142.09$, 136.80, 135.92, 135.18, 133.15, 133.06, 130.40, 128.55, 121.40, 120.22, 118.34, 114.32, 112.31, 14.32, 9.11, 0.70.

Cross experiments

In a glove box a sealable NMR tube with J Young Teflon tap was charged with 10 mg 1-(diphenyl(methyl)silyl)-2,3dimethylindole (0.03 mmol, 1.0 equiv.), 5.6 mg 2-phenylindole (0.03 mmol, 1.0 equiv.), 5.8 mg methyl(diphenyl)silane (0.03 mmol, 1.0 equiv.) and 1.5 mg B(C₆F₅)₃ (0.003 mmol, 10 mol%) and dissolved in CD₂Cl₂ (0.6 ml). After 24 h at 70 °C approximately 95% conversion of diphenylmethylsilane was observed by NMR spectroscopy with **6u** as the main product (**6u**:**6v** > 95:5).

In a glove box a sealable NMR tube with J Young Teflon tap was charged with 10 mg 1-(diphenyl(methyl)silyl)-2,3dimethylindole (0.03 mmol, 1.0 equiv.), 3.9 mg 2-methylindole (0.03 mmol, 1.0 equiv.), 5.8 mg methyl(diphenyl)silane (0.03 mmol, 1.0 equiv.) and 1.5 mg B(C₆F₅)₃ (0.003 mmol, 10 mol%) and dissolved in CD₂Cl₂ (0.6 ml). After 24 h at 70 °C approximately 80% conversion of diphenylmethylsilane was observed by NMR spectroscopy with **6t** as the main product (**6t**:**6v** > 90:10).

^[2] T. Tsuchimoto, Y. Iketani, M. Sekine, Chem. Eur. J. 2012, 18, 9500-9504.



































S42

