Supporting Information for

Synthesis of Hydrosilanes via Lewis-Base-Catalyzed Reduction of Alkoxydilsane by NaBH₄

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Experimental details and compound characterization data

General considerations

All manipulations were performed under a nitrogen atmosphere using Schlenk techniques or a glove box. Hexane, C\textsubscript{6}H\textsubscript{6}, toluene, THF and CH\textsubscript{2}Cl\textsubscript{2} were purified by a solvent purification system (MBraun SPS-800 or Glass Contour Ultimate Solvent System). C\textsubscript{6}D\textsubscript{6} was dried over sodium benzophenone ketyl and distilled. Me\textsubscript{2}PhSiOiPr (1c-iPr)\textsuperscript{1}, Me\textsubscript{2}PhSiOPh (1c-Ph)\textsuperscript{2}, MePh\textsubscript{2}SiOMe (1d)\textsuperscript{1}, Me\textsubscript{2}(tBu)SiOMe (1g)\textsuperscript{3} and iPr\textsubscript{3}SiOMe (1h)\textsuperscript{4} were prepared according to the literature procedures. NaBH\textsubscript{4} granular (99.99% trace metals basis) was purchased from Sigma-Aldrich Co. LLC. and used without purification. All other reagents were purchased from commercial suppliers and used without further purification unless otherwise noted. \textsuperscript{1}H, \textsuperscript{13}C\{\textsuperscript{1}H\}, \textsuperscript{11}B\{\textsuperscript{1}H\} and \textsuperscript{29}Si\{\textsuperscript{1}H\} NMR spectra (\textsuperscript{1}H, 600 MHz; \textsuperscript{11}B, 193 MHz; \textsuperscript{13}C, 151 MHz; \textsuperscript{29}Si, 119 MHz) were recorded using a Bruker AVANCE 600 spectrometer. Chemical shifts are reported in \(\delta\) (ppm) and are referenced to the residual solvent signals for \(\textsuperscript{1}H\) and \(\textsuperscript{13}C\), and to boron trifluoride diethyl ether complex (0.0 ppm) for \(\textsuperscript{11}B\) and to trimethyl(phenyl)silane (–4.7 ppm) for \(\textsuperscript{29}Si\).

Synthesis of Me\textsubscript{2}PhSiOiBu (1-tBu)

To a hexane solution (10 mL) of tBuOH (0.87 g, 12 mmol), was added Me\textsubscript{2}PhSiCl (2.0 g, 12 mmol) and NEt\textsubscript{3} (1.2 g, 12 mmol). The reaction mixture was stirred at room temperature for 24 h. The solution was filtered, and the resulting solid was washed with hexane (20 mL). The filtrate and washings were combined. Fractional distillation was performed to give Me\textsubscript{2}PhSiOiBu (1-tBu) (0.79 g, 3.8 mmol, 32%).

Catalytic reduction of alkoxyisilane with BH\textsubscript{3}·thf

A typical procedure (Table 1, entry 11) is as follows. A vial was charged with a THF solution (0.3 mL) of Me\textsubscript{2}(nOct)SiOMe (1a) (41 mg, 0.20 mmol), HMPA (1.8 mg, 0.010 mmol) and mesitylene (6.0 mg, 0.050 mmol) as an internal standard. To the solution was added 1 M BH\textsubscript{3}·thf THF solution (0.20 mL, 0.20 mmol) at room temperature, and then the solution was stirred for 24 h. The reaction mixture was analyzed by \textsuperscript{1}H NMR to determine the conversion of 1a (0.18 mmol, 91%) and the NMR yield of Me\textsubscript{2}(nOct)SiH (2a) (0.18 mmol, 91%).

Catalytic reduction of alkoxyisilane with NaBH\textsubscript{4}

Determination of NMR yield

Typical procedure 1 (Table 2, entry 8) is as follows. A micro tube (diameter: φ8, length: 50 mm, volume: 1 mL) was charged with a C\textsubscript{6}D\textsubscript{6} suspension (0.05 mL) of NaBH\textsubscript{4} (7.6 mg, 0.20 mmol),
which is pre-grinded in a mortar, nOctNBr (5.6 mg, 0.010 mmol), Me₂(nOct)SiOMe (1a) (41 mg, 0.20 mmol), HMPA (1.8 mg, 0.010 mmol) and mesitylene (6.0 mg, 0.050 mmol) as an internal standard. After EtBr (22 mg, 0.20 mmol) was added, the solution was stirred at room temperature for 24 h (a magnetic stirrer bar: φ1.5 x 8 mm, rotating speed: 1,500 rpm). The resulting solution was analyzed by ¹H NMR to determine the conversion of 1a (0.19 mmol, 93%) and the NMR yield of Me₂(nOct)SiH (2a) (0.19 mmol, 93%).

**Determination of isolated yield**

Typical procedure 2 (Table 2, entry 8) is as follows. A 3 mL conical vial was charged with a C₆H₆ suspension (0.5 mL) of NaBH₄ (76 mg, 2.0 mmol), which is pre-grinded in a mortar, (nOct)₂NBr (56 mg, 0.10 mmol), Me₂(nOct)SiOMe (1a) (410 mg, 2.0 mmol) and HMPA (18 mg, 0.10 mmol). EtBr (220 mg, 2.0 mmol) was added at room temperature, and then the solution was stirred at room temperature for 24 h (a magnetic stirrer bar: φ1.5 x 8 mm, rotating speed: 1,500 rpm). The solution was diluted with hexane (20 mL) and filtered through a silica gel pad (eluent: hexane (100 mL)). The volatiles were removed in vacuo to give Me₂(nOct)SiH (2a) as a colourless liquid (319 mg, 1.9 mmol, 93%).

**Gram scale synthesis of Ph₂SiH₂ (2k)**

A 10 mL pear shaped flask was charged with a C₆H₆ suspension (2.5 mL) of NaBH₄ (0.76 g, 20 mmol), which is pre-grinded in a mortar, nOctNBr (280 mg, 0.50 mmol), Ph₂Si(OMe)₂ (1k) (2.4 g, 10 mmol) and HMPA (360 mg, 2.0 mmol) and sealed with a septum equipped with a needle. EtBr (2.2 g, 20 mmol) was added at room temperature, and then the solution was stirred at room temperature for 24 h (a magnetic stirrer bar of φ3 x 10 mm, 1,500 rpm). The solution was diluted with hexane (20 mL) and filtered through a silica gel pad (eluent: hexane (100 mL)). The volatiles were removed in vacuo to give Ph₂SiH₂ (2k) as a colorless liquid (1.3 g, 7.3 mmol, 73%).

**Compound characterization data**

The products in Table 1 and Table 2, Me₂(nOct)SiH (2a)⁵, Et₃SiH (2b)⁶, Me₃PhSiH (2c)⁶, Me₂(C₂F₅)SiH (2f)⁶, MeCySiH₂ (3i)⁷, MePhSiH(OMe) (2j)⁷, MePhSiH₂ (3j)⁷, Ph₂SiH(OH)₂ (2k)⁵, Ph₂SiH₂ (3k)⁸, Me{Cl(CH₂)₃}SiH₂ (3m)⁸, Me{CF₃(CH₂)₂}SiH₂ (3n)⁹, nC₁₂H₂₅SiH₃ (4p)¹⁰, CySiH₃ (4q)⁹, and Ph₃SiH (4r)⁹ were identified by comparing their ¹H NMR data with those previously reported. MeCySiH(OMe) (2i) and Cy₂SiH(OMe) (2l) were identified by comparing their ¹H NMR data with those alternatively synthesized by following the reported procedure.¹¹
MePh₂SiH (2d), Ph₃SiH (2e), Me₂(tBu)SiH (2g), iPr₃SiH (2h) and nHexSiH₃ (2o) were identified by comparing their ¹H NMR data with commercial sources.

dimethyl(octyl)silane (2a)

Reduction with BH₃·thf

The general procedure was followed with Me₂(nOct)SiOMe (1a) (41 mg, 0.20 mmol), HMPA (1.8 mg, 0.010 mmol) and 1 M BH₃·thf THF solution (0.20 mL, 0.20 mmol). The resulting solution was analyzed by ¹H NMR to determine the conversion of 1a (0.18 mmol, 91%) and the NMR yield of Me₂(nOct)SiH (2a) (0.18 mmol, 91%).

Reduction with NaBH₄

The general procedure was followed with NaBH₄ (76 mg, 2.0 mmol), nOct₂NBr (56 mg, 0.10 mmol), Me₂(nOct)SiOMe (1a) (410 mg, 2.0 mmol), HMPA (18 mg, 0.10 mmol) and EtBr (220 mg, 2.0 mmol). The residue was filtered with a silica gel pad (eluent: hexane (100 mL)) to provide 2a as a colorless liquid in 93% (319 mg).

¹H NMR (C₆D₆, RT, ppm): δ 0.06 (d, 6H, ³J_HH = 3.6 Hz, SiMe₂), 0.57 (m 2H, SiC₃H₂(CH₂)₆CH₃), 0.92 (t, 3H, ³J_HH = 7.0 Hz, Si(CH₂)₇CH₃), 1.22-1.42 (m, 12H, SiCH₂(CH₂)₆CH₃), 4.15 (sep, 1H, ³J_HH = 3.6 Hz, SiH).

¹³C NMR (C₆D₆, RT, ppm): δ –4.3 (s, SiMe), 14.3 (s, SiOct), 14.4 (s, SiOct), 23.1 (s, SiOct), 24.8 (s, SiOct), 29.7 (s, SiOct), 29.7 (s, SiOct), 32.3 (s, SiOct), 33.6 (s, SiOct).

²⁹Si NMR (C₆D₆, RT, ppm): δ –12.8 (s).

triethylsilane (2b)

Reduction with BH₃·thf

The general procedure was followed with Et₃SiOMe (1b) (23 mg, 0.20 mmol), HMPA (1.8 mg, 0.010 mmol) and 1 M BH₃·thf THF solution (0.20 mL, 0.20 mmol). The resulting solution was analyzed by ¹H NMR to determine the conversion of 1b (0.16 mmol, 80%) and the NMR yield of Et₃SiH (2b) (0.15 mmol, 75%).
Reduction with NaBH₄

The general procedure 1 was followed with NaBH₄ (7.6 mg, 0.20 mmol), nOct₂NBr (5.6 mg, 0.010 mmol), Et₃SiOMe (1b) (23 mg, 0.20 mmol), HMPA (1.8 mg, 0.010 mmol) and EtBr (22 mg, 0.20 mmol). The resulting solution was analyzed by ¹H NMR to determine the conversion of 1b (0.20 mmol, 96%) and the NMR yield of Et₃SiH (2b) (0.20 mmol, 96%).

¹H NMR (C₆D₆, RT, ppm): δ 0.53 (dq, 6H, ³J_HH = 3.2 Hz, ³J_HH = 7.9 Hz, SiCH₂CH₃), 0.90 (s, 9H, SiBu), 3.88 (sep, 1H, ³J_HH = 3.2 Hz, SiH).

Reduction with BH₃·thf

The general procedure was followed with Me₂PhSiOMe (1c) (33 mg, 0.20 mmol), HMPA (1.8 mg, 0.010 mmol) and 1 M BH₃·thf THF solution (0.20 mL, 0.20 mmol). The resulting solution was analyzed by ¹H NMR to determine the conversion of 1c (0.18 mmol, 91%) and the NMR yield of Me₂PhSiH (2c) (0.18 mmol, 88%).

Reduction with NaBH₄

The residue was filtered with a silica gel pad (eluent: pentane (100 mL)) to provide 2c as a colorless liquid in 83% (226 mg).

¹H NMR (C₆D₆, RT, ppm): δ 0.21 (d, 6H, ³J_HH = 3.8 Hz, SiMe₂), 4.63 (sept, 1H, ³J_HH = 3.8 Hz, SiH), 7.19 (m, 3H, m-p-CH), 7.47 (m, 2H, o-CH).

¹³C NMR (C₆D₆, RT, ppm): δ –3.8 (s, SiMe), 128.3 (s, SiPh), 129.5 (s, SiPh), 134.3 (s, SiPh), 137.4 (s, SiPh).

²⁹Si NMR (C₆D₆, RT, ppm): δ –16.7 (s).

dimethyl(phenyl)silane (2c)

Reduction with BH₃·thf

methylidiphenylsilane (2d)
Reduction with BH₃·thf

The general procedure was followed with MePh₂SiOMe (1d) (46 mg, 0.20 mmol), HMPA (1.8 mg, 0.010 mmol) and 1 M BH₃·thf THF solution (0.20 mL, 0.20 mmol). The resulting solution was analyzed by ¹H NMR to determine the conversion of 1d (0.15 mmol, 78%) and the NMR yield of MePh₂SiH (2d) (0.15 mmol, 78%),

Reduction with NaBH₄

The general procedure 1 was followed with NaBH₄ (7.6 mg, 0.2 mmol), nOct₄NBr (5.6 mg, 0.010 mmol), MePh₂SiOMe (1d) (46 mg, 0.20 mmol), HMPA (1.8 mg, 0.010 mmol) and EtBr (22 mg, 0.2 mmol). The resulting solution was analyzed by ¹H NMR to determine the conversion of 1d (0.18 mmol, 92%) and the NMR yield of MePh₂SiH (2d) (0.18 mmol, 92%).

¹H NMR (C₆D₆, RT, ppm): δ 0.46 (d, 3H, ³JHH = 3.8 Hz, SiMe), 5.14 (q, 2H, ³JHH = 3.8 Hz, SiH₂), 7.12-7.20 (m, 3H, m,p-CH), 7.50 (m, 2H, o-CH).

¹³C NMR (C₆D₆, RT, ppm): δ –5.0 (s, SiMe), 128.3 (s, SiPh), 129.6 (s, SiPh), 135.2 (s, SiPh), 135.5 (s, SiPh).

²⁹Si NMR (C₆D₆, RT, ppm): δ –17.1 (s).

Triphenylsilane (2e)

The general procedure 2 was followed with CH₂Cl₂ (0.5 mL), NaBH₄ (76 mg, 2.0 mmol), nOct₄NBr (56 mg, 0.10 mmol), Ph₃SiOMe (1e) (580 mg, 2.0 mmol), HMPA (72 mg, 0.40 mmol) and EtBr (220 mg, 2.0 mmol). The residue was filtered with a silica gel pad (eluent: toluene (100 mL)) to provide the title compound 2e as a white solid in 91% (474 mg).

¹H NMR (C₆D₆, RT, ppm): δ 5.71 (s, 1H, SiH), 7.09-7.19 (m, 9H, m,p-CH), 7.59 (m, 6H, o-CH).

¹³C NMR (C₆D₆, RT, ppm): δ 128.4 (s, SiPh), 130.0 (s, SiPh), 133.7 (s, SiPh), 136.2 (s, SiPh).

²⁹Si NMR (C₆D₆, RT, ppm): δ –17.5 (s).
dimethyl(pentafluorophenyl)silane (2f)

![Structure](image)

The general procedure 1 was followed with NaBH₄ (7.6 mg, 0.20 mmol), nOct₄NBr (5.6 mg, 0.010 mmol), Me₂(C₆F₅)SiOEt (1f-Et) (54 mg, 0.20 mmol), HMPA (7.2 mg, 0.040 mmol) and EtBr (22 mg, 0.20 mmol). The resulting solution was analyzed by ¹H NMR to determine the conversion of 1f-Et (0.19 mmol, 95%) and the NMR yield of Me₂(C₆F₅)SiH (2f) (0.14 mmol, 69%).

¹H NMR (C₆D₆, RT, ppm): δ 0.15 (dt, 6H, JHH = 3.9 Hz, JC = 0.8 Hz, SiMe₂), 4.57 (ep, 1H, JHH = 3.9 Hz, SiH).

tert-butyldimethylsilane (2g)

![Structure](image)

The general procedure 1 was followed with NaBH₄ (15.2 mg, 0.40 mmol), nOct₄NBr (5.6 mg, 0.010 mmol), Me₂(tBu)SiOMe (1g) (29 mg, 0.20 mmol), HMPA (36 mg, 0.20 mmol) and EtBr (44 mg, 0.40 mmol). The resulting solution was analyzed by ¹H NMR to determine the conversion of 1g (0.17 mmol, 85%) and the NMR yield of Me₂(tBu)SiH (2g) (0.13 mmol, 64%).

¹H NMR (C₆D₆, RT, ppm): δ –0.02 (d, 6H, JHH = 3.7 Hz, SiMe₂), 0.96 (t, 9H, JHH = 7.9 Hz, SiCH₂CH₃), 3.87 (sep, 1H, JHH = 3.7 Hz, SiH).

triisopropylsilane (2h)

![Structure](image)

The general procedure 1 was followed with NaBH₄ (15.2 mg, 0.40 mmol), nOct₄NBr (5.6 mg, 0.010 mmol), Pr₃SiOMe (1h) (38 mg, 0.20 mmol), HMPA (36 mg, 0.20 mmol) and EtBr (44 mg, 0.40 mmol). The resulting solution was analyzed by ¹H NMR to determine the conversion of 1h (0.12 mmol, 58%) and the NMR yield of Pr₃SiH (2h) (0.064 mmol, 32%).

¹H NMR (C₆D₆, RT, ppm): δ 0.95-1.05 (m, 3H, JHH = 3.7 Hz, SiCH(CH₃)₂), 1.07 (d, 18H, JHH = 6.5 Hz, SiCH(CH₃)₂), 3.59 (q, 1H, JHH = 2.2 Hz, SiH).
cyclohexyl(methoxy)methylsilane (2i)

The general procedure 1 was followed with NaBH$_4$ (15.2 mg, 0.40 mmol), nOct$_4$NBr (5.6 mg, 0.010 mmol), MeCySi(OMe)$_2$ (1i) (38 mg, 0.20 mmol), HMPA (1.8 mg, 0.010 mmol) and EtBr (44 mg, 0.40 mmol). The resulting solution was analyzed by $^1$H NMR to determine the conversion of 1i (0.16 mmol, 81%) and the NMR yield of MeCySiH(OMe) (2i) (0.010 mmol, 5%) and MeCySiH$_2$ (3i) (0.15 mmol, 76%).

$^1$H NMR (C$_6$D$_6$, RT, ppm): $\delta$ 0.10 (d, 3H, $^3$J$_{HH}$ = 2.9 Hz, SiMe), 0.76 (m, 1H, SiC$_5$H($CH_2$)$_5$), 1.14-1.30 (m, 6H, SiC$_5$H($CH_2$)$_5$), 1.62-1.82 (m, 6H, SiC(CH$_2$)$_5$), 3.33 (s, 3H, OMe) 4.61 (qd, 1H, $^3$J$_{HH}$ = 3.0, 2.9 Hz, SiH).

13C NMR (C$_6$D$_6$, RT, ppm): $\delta$ 14.2 (s, SiMe), 22.0 (s, SiCy), 27.0 (s, SiCy), 27.9 (s, SiCy), 29.1 (2, SiCy).

$^{29}$Si NMR (C$_6$D$_6$, RT, ppm): $\delta$ −27.1 (s).

cyclohexyl(methy)lsilane (3i)

The general procedure 2 was followed with NaBH$_4$ (152 mg, 4.0 mmol), nOct$_4$NBr (56 mg, 0.10 mmol), MeCySi(OMe)$_2$ (1i) (380 mg, 2.0 mmol), HMPA (18 mg, 0.10 mmol) and EtBr (440 mg, 4.0 mmol). The residue was filtered with a silica gel pad (eluent: cold pentane (100 mL)) to provide 3i as a colorless liquid in 73% (187 mg).

$^1$H NMR (C$_6$D$_6$, RT, ppm): $\delta$ 0.00 (t, 3H, $^3$J$_{HH}$ = 4.2 Hz, SiMe), 0.69 (m, 1H, SiC(CH$_2$)$_5$), 1.07-1.24 (m, 6H, SiC(CH$_2$)$_5$), 1.57-1.73 (m, 6H, SiC(CH$_2$)$_5$), 3.82 (qd, 2H, $^3$J$_{HH}$ = 2.9, 4.2 Hz, SiH).

$^{13}$C NMR (C$_6$D$_6$, RT, ppm): $\delta$ 14.2 (s, SiMe), 22.0 (s, SiCy), 27.0 (s, SiCy), 27.9 (s, SiCy), 29.1 (2, SiCy).

methoxy(methyl)phenylsilane (2j)

The general procedure 1 was followed with NaBH$_4$ (15.2 mg, 0.40 mmol), nOct$_4$NBr (5.6 mg, 0.010 mmol), MePhSi(OMe)$_2$ (1j) (36 mg, 0.20 mmol), HMPA (1.8 mg, 0.010 mmol) and EtBr
(44 mg, 0.40 mmol). The resulting solution was analyzed by $^1$H NMR to determine the conversion of $1j$ (0.15 mmol, 75%) and the NMR yield of MePhSiH(OMe) ($2j$) (0.010 mmol, 5%) and MePhSiH$_2$ ($3j$) (0.14 mmol, 71%).

$^1$H NMR (C$_6$D$_6$, RT, ppm): $\delta$ 0.32 (t, 3H, $^3$J$_{HH}$ = 2.9 Hz, SiMe), 3.30 (s, 3H, OMe), 5.18 (q, 1H, $^3$J$_{HH}$ = 2.9 Hz, SiH), 7.20 (m, 3H, m, p-C$_6$H), 7.56 (m, 2H, o-C$_6$H).

$methyl$(phenyl)silane ($3j$)

The general procedure 2 was followed with NaBH$_4$ (152 mg, 4.0 mmol), nOct$_4$NBr (56 mg, 0.10 mmol), MePhSi(OMe)$_2$ ($1j$) (360 mg, 2.0 mmol), HMPA (18 mg, 0.10 mmol) and EtBr (440 mg, 4.0 mmol). The residue was filtered with a silica gel pad (eluent: cold pentane (100 mL)) to provide $3j$ as a colorless liquid in 66% (161 mg).

$^1$H NMR (C$_6$D$_6$, RT, ppm): $\delta$ 0.18 (t, 3H, $^3$J$_{HH}$ = 4.3 Hz, SiMe), 4.49 (q, 2H, $^3$J$_{HH}$ = 4.3 Hz, SiH$_2$), 7.11-7.19 (m, 3H, m, p-C$_6$H), 7.45 (m, 2H, o-C$_6$H).

$^{13}$C NMR (C$_6$D$_6$, RT, ppm): $\delta$ –7.7 (s, SiMe), 128.3 (s, SiPh), 129.8 (s, SiPh), 133.4 (s, SiPh), 135.1 (s, SiPh).

$^{29}$Si NMR (C$_6$D$_6$, RT, ppm): $\delta$ –35.5 (s).

$\text{methoxydiphenylsilane}$ ($2k$)

The general procedure 1 was followed with NaBH$_4$ (15.2 mg, 0.40 mmol), nOct$_4$NBr (5.6 mg, 0.010 mmol), Ph$_2$Si(OMe)$_2$ ($1k$) (49 mg, 0.20 mmol), HMPA (7.2 mg, 0.040 mmol) and EtBr (44 mg, 0.40 mmol). The resulting solution was analyzed by $^1$H NMR to determine the conversion of $1k$ (0.15 mmol, 73%) and the NMR yield of Ph$_2$SiH(OMe) ($2k$) (0.0060 mmol, 3%) and Ph$_2$SiH$_2$ ($3k$) (0.14 mmol, 72%).

$^1$H NMR (C$_6$D$_6$, RT, ppm): $\delta$ 3.40 (s, 3H, OMe), 5.61 (s, 1H, SiH), 7.09-7.19 (m, 6H, m, p-C$_6$H), 7.65 (m, 4H, o-C$_6$H).
diphenylsilane (3k)

![Structure of diphenylsilane](image)

The general procedure 2 was followed with NaBH₄ (152 mg, 4.0 mmol), nOct₄NBr (56 mg, 0.10 mmol), Ph₂Si(OMe)₂ (1k) (490 mg, 2.0 mmol), HMPA (18 mg, 0.10 mmol) and EtBr (440 mg, 4.0 mmol). The residue was filtered with a silica gel pad (eluent: cold pentane (100 mL)) to 3k as a colorless liquid in 72% (265 mg).

¹H NMR (C₆D₆, RT, ppm): δ 5.08 (s, 2H, Si-H), 7.09-7.19 (m, 6H, m, p-C₆H₆), 7.51 (m, 4H, o-C₆H₆).

¹³C NMR (C₆D₆, RT, ppm): δ 128.4 (s, SiPh), 130.1 (s, SiPh), 131.7 (s, SiPh), 136.0 (s, SiPh).

²⁹Si NMR (C₆D₆, RT, ppm): δ -33.2 (s).

dicyclopentyl(methoxy)silane (2l)

![Structure of dicyclopentyl(methoxy)silane](image)

The general procedure 1 was followed with NaBH₄ (15.2 mg, 0.40 mmol), nOct₄NBr (5.6 mg, 0.010 mmol), Cyp₂Si(OMe)₂ (1l) (38 mg, 0.20 mmol), HMPA (36 mg, 0.20 mmol) and EtBr (44 mg, 0.40 mmol). The resulting solution was analyzed by ¹H NMR to determine the conversion of 1l (0.17 mmol, 86%) and the NMR yield of Cyp₂SiH(OMe) (2l) (0.010 mmol, 5%) and Cyp₂SiH₂ (3l) (0.15 mmol, 77%).

¹H NMR (C₆D₆, RT, ppm): δ 1.04 (m, 1H, SiCH(CH₂)₄), 1.36 (m, 2H, SiCH(CH₂)₄), 1.46 (m, 2H, SiCH(CH₂)₄), 1.58 (m, 2H, SiCH(CH₂)₄), 1.80 (m, 2H, SiCH(CH₂)₄), 3.43 (s, 3H, OMe), 4.57 (t, 2H, JHH = 2.3 Hz, SiH).

dicyclopentylsilane (3l)

![Structure of dicyclopentylsilane](image)

The general procedure 2 was followed with NaBH₄ (152 mg, 4.0 mmol), nOct₄NBr (56 mg, 0.10 mmol), Cyp₂Si(OMe)₂ (1l) (460 mg, 2.0 mmol), HMPA (360 mg, 2.0 mmol) and EtBr (440 mg,
4.0 mmol). The residue was filtered with a silica gel pad (eluent: cold pentane (100 mL)) to provide 3l as a colorless liquid in 72% (242 mg).

$^1$H NMR (C$_6$D$_6$, RT, ppm): δ 0.99 (m, 1H, SiCH(CH$_2$)$_3$), 1.36 (m, 2H, SiCH(CH$_2$)$_3$), 1.46 (m, 2H, SiCH(CH$_2$)$_3$), 1.58 (m, 2H, SiCH(CH$_2$)$_3$), 1.80 (m, 2H, SiCH(CH$_2$)$_3$), 3.92 (t, 2H, $^3$J$_{HH}$ = 3.2 Hz, SiH).

$^{13}$C NMR (C$_6$D$_6$, RT, ppm): δ 20.8 (s, SiC$_{py}$), 27.2 (s, SiC$_{py}$), 30.4 (s, SiC$_{py}$).

$^{29}$Si NMR (C$_6$D$_6$, RT, ppm): δ -16.7 (s).

3-chloropropylmethysilane (3m)

\[
\begin{array}{c}
\text{Cl} \\
\text{Me} \ \text{Si} \\
\text{H}
\end{array}
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The general procedure 1 was followed with NaBH$_4$ (15.2 mg, 0.40 mmol), nOct$_4$NBr (5.6 mg, 0.010 mmol), Me[Cl(CH$_2$)$_3$]Si(OMe)$_2$ (1m) (37 mg, 0.20 mmol), HMPA (1.8 mg, 0.010 mmol) and EtBr (44 mg, 0.40 mmol). The resulting solution was analyzed by $^1$H NMR to determine the conversion of 1m (0.16 mmol, 78%) and the NMR yield of Me[Cl(CH$_2$)$_3$]SiH (3m) (0.14 mmol, 70%).

$^1$H NMR (C$_6$D$_6$, RT, ppm): δ 0.11 (t, 3H, $^3$J$_{HH}$ = 4.2 Hz, SiMe$_2$), 0.40 (m, 2H, SiCH$_2$CH$_2$CH$_2$Cl), 1.46 (m, 2H, SiCH$_2$CH$_2$CH$_2$Cl), 3.05 (t, 2H, $^3$J$_{HH}$ = 6.8 Hz, SiCH$_2$CH$_2$CH$_2$Cl), 3.77 (sept, 2H, $^3$J$_{HH}$ = 4.2 Hz, SiH$_2$).

3,3,3-trifluoropropylmethysilane (3n)

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\begin{array}{c}
\text{F} \\
\text{F} \\
\text{Me} \ \text{Si} \\
\text{H}
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The general procedure 1 was followed with NaBH$_4$ (15.2 mg, 0.40 mmol), nOct$_4$NBr (5.6 mg, 0.010 mmol), Me{F$_3$C(CH$_2$)$_2$}Si(OMe)$_2$ (1n) (37 mg, 0.20 mmol), HMPA (7.2 mg, 0.040 mmol) and EtBr (44 mg, 0.40 mmol). The resulting solution was analyzed by $^1$H NMR to determine the conversion of 1n (0.16 mmol, 78%) and the NMR yield of Me{F$_3$C(CH$_2$)$_2$}SiH (3n) (0.13 mmol, 64%).

$^1$H NMR (C$_6$D$_6$, RT, ppm): δ 0.21 (t, 3H, $^3$J$_{HH}$ = 4.1 Hz, SiMe$_2$), 0.52 (m, 2H, SiCH$_2$CH$_2$CF$_3$), 1.66 (m, 2H, SiCH$_2$CH$_2$CF$_3$), 3.63 (sept, 2H, $^3$J$_{HH}$ = 4.1 Hz, SiH$_2$).
hexylsilane (4o)

The general procedure 1 was followed with NaBH$_4$ (22.8 mg, 0.60 mmol), nOct$_4$NBr (5.6 mg, 0.010 mmol), nHexSiOMe (1o) (23 mg, 0.20 mmol), HMPA (7.2 mg, 0.040 mmol) and EtBr (65 mg, 6.0 mmol). The resulting solution was analyzed by $^1$H NMR to determine the NMR yield of nHexSiH$_3$ (4o) (0.13 mmol, 67%).

$^1$H NMR (C$_6$D$_6$, RT, ppm): $\delta$ 0.51-0.56 (m, 2H, SiCH$_2$(CH$_2$)$_4$CH$_3$), 0.86 (t, 3H, $^3$J$_{HH}$ = 7.2 Hz, SiCH$_2$(CH$_2$)$_4$CCH$_3$), 1.12-1.35 (m, 8H, SiCH$_2$(CH$_2$)$_4$CH$_3$), 3.61 (t, 3H, $^3$J$_{HH}$ = 3.9 Hz, SiH$_3$).

dodecylsilane (4p)

The general procedure 2 was followed with NaBH$_4$ (228 mg, 6.0 mmol), nOct$_4$NBr (56 mg, 0.10 mmol), nC$_{12}$H$_{25}$Si(OMe)$_3$ (1p) (580 mg, 2.0 mmol), HMPA (72 mg, 0.40 mmol) and EtBr (650 mg, 6.0 mmol). The residue was filtered with a silica gel pad (eluent: cold pentane (100 mL)) to provide 4p as a colorless liquid in 76% (305 mg).

$^1$H NMR (C$_6$D$_6$, RT, ppm): $\delta$ 0.55 (m, 2H, SiCH$_2$(CH$_2$)$_{10}$CH$_3$), 0.92 (t, 3H, $^3$J$_{HH}$ = 7.1, SiCH$_2$(CH$_2$)$_{10}$CH$_3$), 1.18-1.38 (m, 20H, SiCH$_2$(CH$_2$)$_{10}$CH$_3$).

$^{13}$C NMR (C$_6$D$_6$, RT, ppm): $\delta$ 6.1 (s, SiC$_{12}$H$_{25}$), 14.3 (s, SiC$_{12}$H$_{25}$), 23.1 (s, SiC$_{12}$H$_{25}$), 26.7 (s, SiC$_{12}$H$_{25}$), 29.6 (s, SiC$_{12}$H$_{25}$), 29.8 (s, SiC$_{12}$H$_{25}$), 29.9 (s, SiC$_{12}$H$_{25}$), 30.1 (s, SiC$_{12}$H$_{25}$), 30.1 (s, SiC$_{12}$H$_{25}$), 30.1 (s, SiC$_{12}$H$_{25}$), 32.3(s, SiC$_{12}$H$_{25}$), 32.9 (s, SiC$_{12}$H$_{25}$).

$^{29}$Si NMR (C$_6$D$_6$, RT, ppm): $\delta$ –59.4 (s).

dodecylsilane-d$_3$ (4p-d$_3$)

The general procedure 2 was followed with NaBD$_4$ (99 atom% D, 250 mg, 6.0 mmol), nOct$_4$NBr (56 mg, 0.10 mmol), nC$_{12}$H$_{25}$Si(OMe)$_3$ (1p) (580 mg, 2.0 mmol), HMPA (72 mg, 0.40 mmol) and EtBr (650 mg, 6.0 mmol). The residue was filtered with a silica gel pad (eluent: cold pentane (100 mL)) to provide 4p as a colorless liquid in 70% (286 mg, 1.4 mmol, 98 atom% D).
$^1$H NMR (C$_6$D$_6$, RT, ppm): $\delta$ 0.54 (t, 2H, $^3J_{HH} = 7.9$ Hz, SiCH$_2$(CH$_2$)$_3$CH$_3$), 0.92 (t, 3H, $^3J_{HH} = 7.5$, SiC(CH$_2$)$_{10}$CH$_3$), 1.18-1.38 (m, 20H, SiCH$_2$(CH$_2$)$_{10}$CH$_3$).

$^{13}$C NMR (C$_6$D$_6$, RT, ppm): $\delta$ 5.9 (s, SiC$_{12}$H$_{25}$), 14.3 (s, SiC$_{12}$H$_{25}$), 23.1 (s, SiC$_{12}$H$_{25}$), 26.6 (s, SiC$_{12}$H$_{25}$), 29.6 (s, SiC$_{12}$H$_{25}$), 29.8 (s, SiC$_{12}$H$_{25}$), 30.0 (s, SiC$_{12}$H$_{25}$), 30.1 (s, SiC$_{12}$H$_{25}$), 30.1 (s, SiC$_{12}$H$_{25}$), 32.3 (s, SiC$_{12}$H$_{25}$), 32.8 (s, SiC$_{12}$H$_{25}$).

$^{29}$Si NMR (C$_6$D$_6$, RT, ppm): $\delta$ –60.2 (sept, $^1J_{SiD} = 29.3$ Hz).

cyclohexylsilane ($4q$)

The general procedure 1 was followed with NaBH$_4$ (22.8 mg, 0.60 mmol), nOct$_4$NBr (5.6 mg, 0.010 mmol), CySi(OMe)$_3$ ($1q$) (23 mg, 0.20 mmol), HMPA (7.2 mg, 0.040 mmol) and EtBr (65 mg, 6.0 mmol). The resulting solution was analyzed by $^1$H NMR to determine the NMR yield of CySiH$_3$ ($4q$) (0.13 mmol, 67%).

$^1$H NMR (C$_6$D$_6$, RT, ppm): $\delta$ 0.75 (m, 1H, SiC(HCH)$_2$H), 1.05-1.18 (m, 5H, ax-CH), 1.50-1.66 (m, 5H, eq-CH), 3.58 (d, 3H, $^3J_{HH} = 3.1$ Hz, SiH$_3$).

phenylsilane ($4r$)

The general procedure 1 was followed with NaBH$_4$ (22.8 mg, 0.60 mmol), nOct$_4$NBr (5.6 mg, 0.010 mmol), PhSi(OMe)$_3$ ($1r$) (22 mg, 0.20 mmol), HMPA (7.2 mg, 0.040 mmol) and EtBr (65 mg, 6.0 mmol). The resulting solution was analyzed by $^1$H NMR to determine the NMR yield of PhSiH$_3$ ($4r$) (0.10 mmol, 49%).

$^1$H NMR (C$_6$D$_6$, RT, ppm): $\delta$ 4.23 (s, 3H, SiH), 7.07 (m, 2H, $m$-CH), 7.11 (m, 1H, $p$-CH), 7.39 (m, 2H, $o$-CH).

References


