Electronic Supporting Information (ESI)

Continuous-Flow Si–H Functionalization of Hydrosilanes via Sequential Organolithium Reactions Catalyzed by Potassium *tert*-Butoxide

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1. General Information

Nuclear magnetic resonance (NMR) spectra were recorded with Bruker Avance III (500 MHz for ¹H NMR, 125 MHz for ¹³C NMR and 99 MHz for ²⁹Si NMR) and Bruker ASCEND 600 (119 MHz for ²⁹Si NMR). ¹H, ¹³C and ²⁹Si chemical shifts are recorded in ppm downfield of tetramethylsilane and referenced to residual solvent peak (CHCl₃ = 7.26) unless otherwise noted. Multiplicities are reported using the following abbreviations: s = singlet, d= doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, sept = septet, m = multiplet, br = broad resonance. GC chromatograph (GC) analysis was performed on an Agilent Technologies 7890A gas chromatograph (Agilent Tech., USA/Germany) using fused silica capillary column (column, 0.25mm x 30m). Mass spectra data were obtained from an Agilent Technologies 5675C VL MSD (EI), the Korea Basic Science Institute (Daegue) on a Jeol JMS 700 high resolution mass spectrometer (EI), and Organic Chemistry Research Center in Seogang university on a Bruker Ultra High Resolution ESI Q-TOF MS/MS Compact System (ESI). Melting points were determined from Stanford Research System OptiMelt MPA 100.

Tetrahydrofuran (THF, anhydrous), diethyl ether (Et₂O, anhydrous), hexane (anhydrous) were purchased from Sigma-Aldrich and used without further purification. *n*-Butyllithium (*n*-BuLi, 2.5 M in hexane), phenyllithium (PhLi, 1.9 M in diethyl ether) and methyllithium (MeLi, 1.6 M in diethyl ether) were purchased from Sigma-Aldrich. Sodium acetate (NaOAc), potassium acetate (KOAc), potassium bis(trimethylsilyl)amide (KHMDS), potassium trimethylsilanolate (KOTMS), lithium *tert*-butoxide (*t*-BuOLi), sodium *tert*-butoxide (*t*-BuONa), potassium *tert*-butoxide (*t*-BuOK) and *t*-BuOK soulution (1.0 M in THF) were purchased from Sigma-Aldrich

and Tokyo Chemical Industry Co. LTD. Dimethylphenylsilane, diphenylsilane, methyldiphenylsilane, triethylsilane, triisopropylsilane and phenylsilane were purchased from Sigma-Aldrich and Tokyo Chemical Industry Co. LTD. Unless otherwise noted, all commercial materials were used without further purification.

Stainless steel (SUS316) tube reactors with inner diameters of 0.25 mm and 1 mm were purchased from GL Science and were cut into appropriate lengths. Stainless steel (SUS304) T-shaped micromixers with inner diameters of 300 and 500 µm were manufactured by YMC Co. and Valco Instruments Co. Inc. The micromixers and tube reactors were connected with stainless steel fittings (GL Science, 1/16" OUW) to construct the flow reaction system. The flow reaction system was dipped in water bath or cooling bath to control the temperature. The reagents were continuously injected to the flow reaction system using a syringe pumps (KD Scientific, Legato 200 and Legato 100), equipped with gas tight syringes (50 mL, inner diameter: 27.6 mm) purchased from SGE Analytical Science. After a steady state was reached (90 s), the product solution was collected for 30 s unless otherwise noted.

2. Direct silvlation using a catalytic amount of additives in a flask

$$\underbrace{ -\text{Li} + \text{H}-\text{SiEt}_3}_{-78 \text{°C}, 10 \text{ min}} \underbrace{ -\text{SiEt}_3}_{12}$$

Triethylsilane (1.2 mmol, 1.2 equiv) was added to a solution of additives in THF (10 mL) in a 50 mL round bottom glass flask with magnetic stirring for 10 min at -78 °C under argon. After being stirred for 10 min, PhLi (0.53 mL, 1.9 M in Et₂O, 1 mmol) was added dropwise to a solution of triethylsilane with additives. The reaction mixture was stirred for specified time and quenched with saturated NH₄Cl aqueous solution (5 mL) and brine (5 mL) and the reaction bath was removed. After addition of 1,3,5-trimethoxybenzene (50 mg) as an internal standard and extracted with Et₂O, an aliquot (2 mL) of the organic phase was concentrated under vacuum and analyzed by ¹H NMR spectroscopy. Based on the relative intensities of peak at 0.96 ppm (9H of triethyl(phenyl)silane (**1a**)) and 6.09 ppm (3H of 1,3,5-trimethoxybenzene), the yield was determined by ¹H NMR spectroscopy.

Entry	Additive	x (mol%)	Yield of 1a (%) ^a
1	-	-	n.d.
2 ^b	-	-	2
3	TMEDA	20	n.d.
4	HMPA	20	n.d.
5	MeCO ₂ Na	20	n.d.
6	EtOK	20	n.d.
7	(Me₃Si)₂NK	20	n.d.
8	Me ₃ SiOK	20	n.d.
9	<i>t</i> -BuOLi	20	2
10	<i>t</i> -BuONa	20	3
11	<i>t-</i> BuOK	20	82
12	t-BuOK	10	40

Table S1. Direct silvlation of PhLi using a catalytic amount of alkali-metal compounds

n.d. = not detected. ^{*a*} Determined by ¹H NMR spectroscopy using 1,3,5-trimethoxy benzene as an internal standard. ^{*b*} The reaction was conducted for 1 h.



3. Si-H mono-functionalizations of hydrosilane by PhLi in a flow microreactor

A microfluidic system consisting of two T-shaped micromixers (M1 and M2), two tube reactors (R1 and R2) and three tube pre-temperature-retaining units (for P1, P2 and P3, inner diameter $\emptyset = 1$ mm and length L = 100 cm) were used. The whole system was immersed in a temperature control bath. A solution of triethylsilane (0.45 M in THF, flow rate: 2.0 mL/min) and a solution of *t*-BuOK (0.12 M in THF, flow rate: 1.0 mL/min) were individually introduced to M1 (\emptyset : 300 µm) by syringe pumps. The resulting solution was passed through R1 ($\emptyset = 250$ or 1000 µm, $L= 4.0 \sim 100$ cm) and was mixed with a solution of PhLi (0.1 M in Et₂O, flow rate 6.0 mL/min) in M2 (\emptyset : 500 µm). The resulting solution was passed through R2 (\emptyset : 1 mm, L: 50~1000 cm). After a steady state was reached, the product solution was collected for 30 s while being quenched with saturated NH₄Cl aqueous solution (2 mL). Then, Et₂O (6 mL), brine (2 mL), and 1,3,5-trimethoxybenzene (50 mg) were added, and then an aliquot (2 mL) of the organic phase was concentrated and analyzed by ¹H NMR spectroscopy (Table S1). Based on the relative intensities of peak at 0.96 ppm (9H of triethyl(phenyl)silane (**1a**)) and 6.09 ppm (3H of 1,3,5trimethoxybenzene), the yield was determined by ¹H NMR spectroscopy.

Entry	<i>t</i> ^{R1} (s)	<i>t</i> ^{R2} (s)	T (°C)	Yield of 1a (%) ^a
1	0.04	2.6	0	14
2	0.63	2.6	0	15
3	7.9	2.6	0	14
4	15.7	2.6	0	12
5	0.04	2.6	25	28
6	0.63	2.6	25	29
7	7.9	2.6	25	27
8	15.7	2.6	25	26
9	15.7	5.2	25	49
10	15.7	10.5	25	78
11	15.7	20.9	25	86
12	15.7	52.3	25	87
13	0.63	5.2	25	65
14	0.63	10.5	25	82

Table S2. The yiel	d of 1 a
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15	0.63	20.9	25	86
16	0.63	52.3	25	93
17	0.04	5.2	25	66
18	0.04	10.5	25	87
19	0.04	20.9	25	89
20	0.04	52.3	25	95

^a Determined by ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.



Figure S1. Gas generation during reaction of *t*-BuOK and hydrosilane in a capillary reactor.

4. Reduction of benzaldehyde by hydrosilane and *t*-BuOK

$$\begin{array}{c} \begin{array}{c} t-BuOK \\ \hline PhMe_2SiH \end{array} \xrightarrow{\ \ \ } PhCHO, THF \\ 25 \ ^{\circ}C \end{array} \begin{array}{c} PhMe_2Si-OtBu + BnOH \\ \hline S1 \\ S2 \end{array}$$

t-BuOK (1.2 equiv) was added to a solution of PhMe₂SiH (1 mmol) in 10 mL of THF in a 50-mL round bottom glass flask at regular pace with magnetic stirring for 10 min at 25 °C under argon. After stirring, benzaldehyde (2 equiv) was added to the solution and stirred for 10 min. The reaction mixture was quenched with saturated NH₄Cl aqueous solution (5 mL) and brine (5 mL) and the reaction bath was removed. After addition of 1,3,5-trimethoxybenzene (50 mg) as an internal standard and extracted with Et₂O (6 mL), an aliquot (2 mL) of the organic phase was concentrated and analyzed by ¹H NMR spectroscopy. We could confirm that product and benzyl alcohol which was reduced from benzaldehyde, were obtained in 50% and 71%, respectively. This result supports the existence of hydride species which can be generated from penta-coordinate silyl intermediate.

5. Si–H mono-functionalizations of various hydrosilanes by organolithiums in a flow microreactor



A microfluidic system consisting of three T-shaped micromixers (M1, M2 and M3), three tube reactors (R1, R2 and R3) and four tube pre-temperature-retaining units (for P1, P2, P3 and P4, $\varphi = 1 \text{ mm}$ and L = 100 cm) were used. The microfluidic system was immersed in a temperature control bath. A solution of aryl bromide (0.1 M in THF, flow rate: 6.0 mL/min) and a solution of alkyllithium (0.42 M in hexane, flow rate: 1.5 mL/min) were introduced to M1 (φ : 300 µm) by syringe pumps. The resulting solution passed through R1 ($\varphi = 250 \text{ or } 1000 \text{ µm}$, $L = 4.0 \sim 10 \text{ cm}$) and was mixed in M3 ($\varphi = 500 \text{ µm}$) with a mixing solution of hydrosilane in THF (flow rate: 2.0 mL/min) and *t*-BuOK in THF (flow rate: 1.0 mL/min) which was reacted in M2 ($\varphi = 300 \text{ µm}$) and R2 ($\varphi = 250 \text{ µm}$, L = 4.0 cm). PhLi or *n*-BuLi (0.1 M, 6.0 mL/min) were directly used, without the use of M1 and R1. The resulting solution was passed through R3 ($\varphi = 1000 \text{ µm}$, L = 1000 cm). After a steady state was reached (90 s), the product solution was collected for 30 s while being quenched with saturated NH4Cl aqueous solution (2 mL). The resulting mixture was extracted with Et₂O (5 mL×3), and washed with brine (5 mL). The organic phase was dried over sodium sulfate. The organic layer was concentrated on a rotary evaporator under reduced pressure. The crude product was purified by column chromatography to give the desired product.

Entry	Substrate	Silane	R1 ($\emptyset \times L$) (μ m × cm)	<i>t</i> ^{R1} (s)	Yield (%)ª
1	Li	H-SiEt₃	b	_	93

Table S3. F	low silylation	with various	hydrosilanes	and organolithiums.
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2	Li	H-SiMe ₂ Ph	b	—	91
3	Li	H-SiMePh ₂	b	_	89
4	Li	H-SiPh ₂	b	_	88
5 ^j	Li	H-Si′Pr₃	b	_	81
6	<i>n</i> -BuLi	H-SiEt₃	e	—	96
7 ^{c,d}	Me Me	H-SiEt₃	250 × 4	0.016	83
8	Me	H-SiEt₃	250 × 4	0.016	81
9	MeBr	H-SiEt₃	250 × 4	0.016	81
10	MeOBr	H-SiEt₃	1000 × 10	0.63	81
11	FBr	H-SiEt₃	250 × 4	0.016	76
12	Cl-Br	H-SiEt₃	250 × 4	0.016	82
13	Br	H-SiMe ₂ Ph	250 × 4	0.016	73
14 ^{d,f,g}	^t BuO ₂ CBr	H-SiMe ₂ Ph	1000 × 4	0.63	55
15 ^{c,d}	Br	H-SiEt₃	250 × 4	0.016	78
16	N_Br	H-SiEt₃	1000 × 4	0.63	64
17	Br	H-SiMe ₂ Ph	250 × 4	0.016	73

^{*a*} Isolation yield. ^{*b*} PhLi (0.1 M in Et₂O) was used. ^{*c*} 0.5 equiv of *t*-BuOK was used. ^{*d*} 3.0 equiv of silane was used. ^{*e*} *n*-BuLi (0.1 M in hexane) was used. ^{*f*} Lithiation was conducted at 0 °C. ^{*g*} For Br-Li exchange, *s*-BuLi was used.



Triethyl(phenyl)silane (1a)

Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.51-7.47 (m, 2H), 7.35-7.34 (m, 3H), 0.96 (t, *J* = 7.5 Hz, 9H), 0.79 (q, *J* = 8.0 Hz, 6H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 137.5, 134.2, 128.7, 127.6, 7.4, 3.3 ppm; ²⁹Si NMR (99 MHz, CDCl₃) δ 1.88 ppm. The spectroscopic data were identical to those reported in the literature.¹



Dimethyldiphenylsilane (1b)

Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.57-7.55 (m, 4H), 7.40-7.38 (m, 6H), 0.59 (s, 6H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 138.2, 134.2, 129.1, 127.8, -2.4 ppm; ²⁹Si NMR (99 MHz, CDCl₃) δ -8.02 ppm. The spectroscopic data were identical to those reported in the literature.²



Methyltriphenylsilane (1c)

White solid; mp 67.1-67.5 °C; 1H NMR (500 MHz, CDCl₃) δ 7.55-7.53 (m, 6H), 7.45-7.42 (m, 3H), 7.40-7.37 (m, 6H), 0.87 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 136.1, 135.3, 129.4, 127.8, -3.4 ppm; ²⁹Si NMR (99 MHz, CDCl₃) δ -11.03 ppm. The melting point was matched with those reported in the literature.³ The spectroscopic data were identical to those reported in the literature.⁴



Triphenylsilane (1d)

Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.61 (dd, J = 7.9, 1.5 Hz, 6H), 7.47-7.39 (m, 9H), 5.50 (s, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 135.8, 133.3, 129.8, 128.1 ppm; ²⁹Si NMR (99 MHz, CDCl₃) δ –18.09 ppm. The spectroscopic data were identical to those reported in the literature.⁵

Si[/]Pr₃

Triisopropyl(phenyl)silane (1e)

Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.53-7.51 (m, 2H), 7.38-7.36 (m, 3H), 1.43 (sept, *J* = 7.6 Hz, 3H), 1.10 (d, *J* = 7.5 Hz, 18H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 135.3, 134.8, 128.5, 127.4, 18.6, 10.7 ppm; ²⁹Si NMR (99 MHz, CDCl₃) δ 1.63 ppm. The spectroscopic data were identical to those reported in the literature.⁶



Triethyl(o-tolyl)silane (1f)

Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.45 (dd, J = 7.7, 1.5 Hz, 1H), 7.29-7.26 (m, 1H), 7.19-7.15 (m, 2H), 2.46 (s, 3H), 0.97 (t, J = 7.9 Hz, 9H), 0.88 (q, J = 7.8 Hz, 6H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 143.9, 135.5, 135.4, 129.8, 128.9, 124.7, 23.0, 7.6, 4.0 ppm; ²⁹Si NMR (99 MHz, CDCl₃) δ 3.09 ppm. The spectroscopic data were identical to those reported in the literature.⁷

Triethyl(m-tolyl)silane (1g)

Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.32-7.31 (m, 2H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.18 (d, *J* = 7.3 Hz, 1H), 2.38 (s, 3H), 0.99 (t, *J* = 8.0 Hz, 9H), 0.80 (q, *J* = 7.9 Hz, 6H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 137.3, 136.9, 134.8, 131.2, 129.5, 127.6, 21.6, 7.4, 3.4 ppm; ²⁹Si NMR (99 MHz, CDCl₃) δ 1.75 ppm. The spectroscopic data were identical to those reported in the literature.⁷

Triethyl(p-tolyl)silane (1h)

Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.42 (d, *J* = 7.9 Hz, 2H), 7.20 (d, *J* = 7.5 Hz, 2H), 2.38 (s, 3H), 0.99 (t, *J* = 8.1 Hz, 9H), 0.80 (q, *J* = 8.0 Hz, 6H) ppm; ¹³C NMR (125 Hz, CDCl₃) δ 138.5, 134.3, 133.7, 128.5, 21.5, 7.4, 3.4 ppm; ²⁹Si NMR (99 MHz, CDCl₃) δ 1.66 ppm. The spectroscopic data were identical to those reported in the literature.⁸

Triethyl(4-methoxyphenyl)silane (1i)

Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.44 (d, *J* = 8.6 Hz, 2H), 6.94 (d, *J* = 8.6 Hz, 2H), 3.84 (s, 3H), 0.98 (t, *J* = 8.1 Hz, 9H), 0.79 (q, *J* = 8.0 Hz, 6H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 160.2, 135.6, 128.2, 113.5, 54.9, 7.4, 3.5 ppm; ²⁹Si NMR (99 MHz, CDCl₃) δ 1.47 ppm. The spectroscopic data were identical to those reported in the literature.⁸

Triethyl(4-fluorophenyl)silane (1j)

Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.50-7.47 (m, 2H), 7.10-7.06 (m, 2H), 0.99 (t, J = 8.2 Hz, 9H), 0.81 (q, J = 8.0 Hz, 6H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 163.6 (d, $J_{C-F} = 245$ Hz), 136.0 (d, $J_{C-F} = 7.5$ Hz), 132.8 (d, $J_{C-F} = 3.8$ Hz), 114.8 (d, $J_{C-F} = 18.8$ Hz), 7.3, 3.4 ppm; ²⁹Si NMR (119 MHz, CDCl₃) δ 2.05 ppm. The

spectroscopic data were identical to those reported in the literature.9

(4-Chlorophenyl)triethylsilane (1k)

Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.2 Hz, 2H), 0.98 (t, *J* = 7.6 Hz, 9H), 0.80 (q, *J* = 7.6 Hz, 6H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 135.7, 135.5, 135.0, 127.9, 7.3, 3.3 ppm; ²⁹Si NMR (99 MHz, CDCl₃) δ 2.35 ppm. The spectroscopic data were identical to those reported in the literature.¹⁰

(4-Bromophenyl)dimethyl(phenyl)silane (11)

White solid; mp 33.0-33.8 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.53-7.50 (m, 4H), 7.41-7.37 (m, 5H), 0.57 (s, 6H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 137.5, 137.1, 135.8, 134.1, 131.0, 129.3, 127.9, 124.0, -2.5 ppm; ²⁹Si NMR (99 MHz, CDCl₃) δ -7.49 ppm; LRMS (EI) cald. For C₁₄H₁₅BrSi: 290.01; found: 290.0.

tert-Butyl 4-(dimethyl(phenyl)silyl)benzoate (1m)

Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.87 (d, *J* = 8.5 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.43-7.41 (m, 2H), 7.31-7.26 (m, 3H), 1.51 (s, 9H), 0.49 (s, 6H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 165.9, 143.9, 137.5, 134.1, 134.0, 132.5, 129.3, 128.4, 127.9, 80.9, 28.2, -2.5 ppm; ²⁹Si NMR (119 MHz, CDCl₃) δ -7.59 ppm; HRMS (ESI) (*m/z*) cald. For C₁₉H₂₄NaO₂Si⁺ [M+Na]⁺: 335.1438; found: C₁₉H₂₄NaO₂Si: 335.1438.



Triethyl(naphthalen-1-yl)silane (1n)

Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 8.12 (d, *J* = 9.0 Hz, 1H), 7.89-7.87 (m, 2H), 7.69 (d, *J* = 7.0 Hz, 1H), 7.53-7.48 (m, 3H), 1.05-0.97 (m, 15H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 137.5, 135.2, 134.5, 133.4, 129.6, 129.1, 127.9, 125.5, 125.2, 125.1, 7.7, 4.5 ppm; ²⁹Si NMR (119 MHz, CDCl₃) δ 3.27 ppm. The spectroscopic data were identical to those reported in the literature.¹¹

3-(Triethylsilyl)pyridine (10)

Yellowish oil. ¹H NMR (500 MHz, CDCl₃) δ 8.68 (s, 1H), 8.60 (dd, J = 5, 1.7 Hz, 1H), 7.82 (dt, J = 7.5, 1.8 Hz, 1H), 7.33-7.30 (m, 1H), 0.99 (t, J = 7.5 Hz, 9H), 0.84 (q, J = 8.0 Hz, 6H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 154.0, 149.3, 142.5, 132.7, 123.4, 7.2, 3.1 ppm; ²⁹Si NMR (99 MHz, CDCl₃) δ 1.90 ppm. The spectroscopic data were identical to those reported in the literature.⁸



(E)-Dimethyl(phenyl)(styryl)silane (1p)

Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.58-7.56 (m, 2H), 7.45 (d, J = 8.1 Hz, 2H), 7.38-7.36 (m, 3H), 7.32 (t, J = 7.6 Hz, 2H), 7.27-7.25 (m, 1H), 6.94 (d, J = 19.2 Hz, 1H), 6.58 (d, J = 19.2 Hz, 1H), 0.43 (s, 6H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 145.3, 138.6, 138.2, 133.9, 129.1, 128.5, 128.2, 127.8, 127.1, 126.5, -2.5 ppm; ²⁹Si NMR (99 MHz, CDCl₃) δ -10.28 ppm. The spectroscopic data were identical to those reported in the literature.¹²

SiMe₂Ph

Butyldimethyl(phenyl)silane (1q)

Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.55-7.53 (m, 2H), 7.39-7.37 (m, 3H), 1.37-1.29 (m, 4H), 0.89 (t, *J* = 6.8 Hz, 3H), 0.79-0.76 (m, 2H), 0.28 (s, 6H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 139.8, 133.6, 128.7, 127.7, 26.6, 26.1, 15.4, 13.8, -3.0 ppm; ²⁹Si NMR (99 MHz, CDCl₃) δ -3.05 ppm. The spectroscopic data were identical to those reported in the literature.²

6. Si-H di-functionalizations of diphenylsilane by organolithiums in a flow



microreactor

A microfluidic system consisting of four T-shaped micromixers (M1, M2, M3 and M4), four tube reactors (R1, R2, R3 and R4) and five tube pre-temperature-retaining units (for P1, P2, P3, P4 and P5, $\emptyset = 1$ mm and L = 100 cm) were used. The microfluidic system was immersed in a temperature control bath. A solution of diphenylsilane

(0.3 M in THF, flow rate: 2.0 mL/min) and a solution of *t*-BuOK (0.12 M in THF, flow rate: 1.0 mL/min) were introduced to M1 (\emptyset : 300 µm) by syringe pumps. The resulting solution flowed through R1 (\emptyset = 250 µm, *L*= 4.0 cm) and was mixed in M3 (\emptyset = 500 µm) with a mixing solution of aryl bromide (0.1 M in THF, flow rate: 6.0 mL/min) and a solution of *n*-BuLi (0.42 M in hexane, flow rate: 1.5 mL/min) which was reacted in M2 (\emptyset = 250 µm, *L* = 4.0 cm). PhLi (0.1 M in Et₂O, flow rate: 6.0 mL/min) was directly used, without the use of M2 and R2. The resulting solution was passed through R3 (\emptyset = 1000 µm, *L* = 1000 cm) and mixed in M4 (\emptyset = 500 µm) with a solution of organolithium (PhLi: 0.48 M in Et₂O, *n*-BuLi: 0.48 M in hexane, flow rate: 3.0 mL/min) and reacted in R4 (\emptyset = 1000 µm, *L* = 1000 cm). After a steady state was reached (90 s), the product solution was extracted with Et₂O (5 mL×3), and washed with brine (5 mL). The organic phase was dried over sodium sulfate. The organic layer was concentrated on a rotary evaporator under reduced pressure. The crude product was purified by column chromatography to give the desired product.



(4-Methoxyphenyl)triphenylsilane (2a)

White solid; mp 155.1-155.8 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.57-7.55 (m, 6H), 7.48 (d, J = 8.7 Hz, 2H), 7.44-7.40 (m, 3H), 7.38-7.35 (m, 6H), 6.93 (d, J = 8.5 Hz, 2H), 3.82 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 160.9, 137.9, 136.4, 134.6, 129.5, 127.9, 124.9, 55.0 ppm; ²⁹Si NMR (119 MHz, CDCl₃) δ –14.42 ppm. The spectroscopic data were identical to those reported in the literature.¹³

Butyl(4-chlorophenyl)diphenylsilane (2b)

Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.50-7.48 (m, 4H), 7.44-7.32 (m, 10H), 1.44-1.33 (m, 6H), 0.87 (t, *J* = 7.1 Hz, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 137.0, 135.8, 135.6, 134.9, 133.9, 129.5, 128.1, 127.9, 26.7, 26.1, 13.7, 12.9 ppm; ²⁹Si NMR (99 MHz, CDCl₃) δ –10.61 ppm; HRMS (ESI) (*m/z*) cald. For C₂₂H₂₃NaClSi⁺ [M+Na]⁺: 373.1150; found: 373.1150.

Butyltriphenylsilane (2c) collecting for 600 s.

Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.53-7.51 (m, 6H), 7.41-7.38 (m, 3H), 7.37-7.34 (m, 6H), 1.48-1.42 (m, 2H), 1.40-1.35 (m, 4H), 0.87 (t, *J* = 7.1 Hz, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 135.7, 135.4, 129.3, 127.8, 26.8, 26.1, 13.7, 13.0 ppm; ²⁹Si NMR (99 MHz, CDCl₃) δ –10.71 ppm. The spectroscopic data were identical to those reported in the literature.¹⁴

7. Si-H tri-functionalizations of phenylsilane by organolithiums in a flow microreactor



7.1. Sequential tri-functionalization of phenylsilane with one organolithium

A microfluidic system consisting of two T-shaped micromixers (M1 and M2), two tube reactors (R1 and R2) and three tube pre-temperature-retaining units (for P1, P2 and P3, $\emptyset = 1$ mm and L = 100 cm) were used. The microfluidic system was immersed in a temperature control bath. A solution of phenylsilane (0.3 M in THF, flow rate: 2.0 mL/min) and a solution of *t*-BuOK (0.12 M in THF, flow rate: 1.0 mL/min) were introduced to M1 (\emptyset : 300 µm) by syringe pumps. The resulting solution flowed through R1 ($\emptyset = 250$ µm, L = 4.0 cm) and was mixed in M2 ($\emptyset = 500$ µm) with a solution of RLi (0.2 M, flow rate: 9.0 mL/min). The resulting solution was passed through R2 ($\emptyset = 1000$ µm, L = 50 cm). After a steady state was reached (90 s), the product solution was collected for 30 s while being quenched with a saturated aqueous NH₄Cl aqueous solution (2 mL). The resulting mixture was extracted with Et₂O (5 mL×3), and washed with brine (5 mL). The organic phase was dried over sodium sulfate. The organic layer was concentrated on a rotary evaporator under reduced pressure. The crude product was purified by column chromatography to give the desired product. The crude product of **3i** was purified by recrystallization with hexane.

Ph Me-Si-Me Me

Trimethyl(phenyl)silane (3a)

A solution of MeLi (0.2 M in Et_2O , flow rate: 9.0 mL/min) was used. The resulting solution was mixed in a flask for 10 min at 25 °C.

Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.53-7.52 (m, 2H), 7.36-7.34 (m, 3H), 0.27 (s, 9H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 140.5, 133.3, 128.8, 127.7, -1.1 ppm; ²⁹Si NMR (119 MHz, CDCl₃) δ -4.10 ppm. The spectroscopic data were identical to those reported in the literature.¹⁵

Ph ⁿBu-Si-Buⁿ ⁿBu

Tributyl(phenyl)silane (3e)

A solution of *n*-BuLi (0.2 M in hexane, flow rate: 9.0 mL/min) was used. The resulting solution was mixed in a flask for 10 min at 50 $^{\circ}$ C.

Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.50-7.47 (m, 2H), 7.34-7.32 (m, 3H), 1.35-1.25 (m, 12H), 0.87 (t, *J* = 6.9 Hz, 9H), 0.79-0.76 (m, 6H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 138.2, 134.1, 128.6, 127.6, 26.8, 26.0, 13.8, 12.2 ppm; ²⁹Si NMR (119 MHz, CDCl₃) δ –2.06 ppm; HRMS (EI) (*m/z*) cald. For C₁₈H₃₂Si: 276.2273; found: C₁₈H₃₂Si: 276.2271

Tetraphenylsilane (3i)

A solution of PhLi (0.2 M in Et₂O, flow rate: 9.0 mL/min) was used. The resulting solution was mixed in a flask for 10 min at 25 °C.

White solid; mp 232.6-233.4 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.58-7.56 (m, 8H), 7.45-7.41 (m, 4H), 7.39-7.35 (m, 8H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 136.4, 134.2, 129.6, 127.9 ppm; ²⁹Si NMR (119 MHz, CDCl₃) δ – 14.51 ppm. The melting point was matched with those reported in the literature.¹⁶ The spectroscopic data were identical to those reported in the literature.¹⁷

7.2. Sequential tri-functionalization of phenylsilane with two different organolithiums



A microfluidic system consisting of three T-shaped micromixers (M1, M2 and M3), three tube reactors (R1, R2 and R3) and four tube pre-temperature-retaining units (for P1, P2, P3 and P4, $\emptyset = 1$ mm and L = 100 cm) were used. The microfluidic system was immersed in a temperature control bath. A solution of phenylsilane (0.3 M in

THF, flow rate: 2.0 mL/min) and a solution of *t*-BuOK (0.12 M in THF, flow rate: 1.0 mL/min) were introduced to M1 (\emptyset : 300 µm) by syringe pumps. The resulting solution flowed through R1 (\emptyset = 250 µm, *L*= 4.0 cm) and was mixed in M2 (\emptyset = 500 µm) with a solution of R¹Li (0.07 M, flow rate: 9.0 mL/min). The resulting solution was passed through R2 (\emptyset = 1000 µm, *L* = 1000 cm) and was mixed in M3 with a solution of R²Li (0.4 M, flow rate: 4.0 mL/min). The resulting solution flowed through R3 (\emptyset = 1000 µm, *L* = 1000 cm). After a steady state was reached (90 s), the product solution was collected for 80 s while being quenched with saturated NH₄Cl aqueous solution (2 mL). The resulting mixture was extracted with Et₂O (5 mL×3), and washed with brine (5 mL). The organic phase was dried over sodium sulfate. The organic layer was concentrated on a rotary evaporator under reduced pressure. The crude product was purified by column chromatography to give the desired product.

Butyldimethyl(phenyl)silane (3b)

A solution of R¹Li (*n*-BuLi: 0.07 M in hexane, 9.0 mL/min) and a solution of R²Li (MeLi: 0.4 M in Et₂O, 4.0 mL/min) were used.

Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.55-7.53 (m, 2H), 7.39-7.37 (m, 3H), 1.37-1.29 (m, 4H), 0.89 (t, *J* = 6.8 Hz, 3H), 0.79-0.76 (m, 2H), 0.28 (s, 6H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 139.8, 133.6, 128.7, 127.7, 26.6, 26.1, 15.4, 13.8, -3.0 ppm; ²⁹Si NMR (99 MHz, CDCl₃) δ -3.05 ppm. The spectroscopic data were identical to those reported in the literature.² The product **3b** is identical to product **1q**.

Dimethyldiphenylsilane (3c)

A solution of R¹Li (PhLi: 0.07 M in Et₂O, 9.0 mL/min) and a solution of R²Li (MeLi: 0.4 M in Et₂O, 4.0 mL/min) were used.

Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.57-7.55 (m, 4H), 7.40-7.38 (m, 6H), 0.59 (s, 6H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 138.2, 134.2, 129.1, 127.8, -2.4 ppm; ²⁹Si NMR (99 MHz, CDCl₃) δ -8.02 ppm. The spectroscopic data were identical to those reported in the literature.² The product **3c** is identical to product **1b**.

Dibutyl(methyl)(phenyl)silane (3d)

A solution of R¹Li (MeLi: 0.07 M in Et₂O, 9.0 mL/min) and a solution of R²Li (*n*-BuLi: 0.4 M in hexane, 4.0 mL/min) were used.

Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.54-7.48 (m, 2H), 7.36-7.33 (m, 3H), 1.34-1.26 (m, 8H), 0.88-0.85 (m, 6H), 0.77-0.74 (m, 4H), 0.24 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 134.3, 133.8, 128.7, 127.6, 26.7, 26.1, 13.9, 13.8 –5.1 ppm; ²⁹Si NMR (119 MHz, CDCl₃) δ –2.28 ppm; HRMS (EI) (*m/z*) cald. For C₁₅H₂₆Si: 234.1804; found: C₁₅H₂₆Si: 273.1801.

Ph ⁿBu-Si-Ph ⁿBu

Dibutyldiphenylsilane (3f)

A solution of R¹Li (PhLi: 0.07 M in Et₂O, 9.0 mL/min) and a solution of R²Li (*n*-BuLi: 0.4 M in hexane, 4.0 mL/min) were used.

Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.50-7.48 (m, 4H), 7.37-7.34 (m, 6H), 1.35-1.32 (m, 8H), 1.09-1.06 (m, 4H), 0.88-0.85 (m, 6H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 136.7, 134.9, 129.0, 127.7, 26.7, 25.9, 13.7, 12.3 ppm; ²⁹Si NMR (99 MHz, CDCl₃) δ –6.69 ppm; HRMS (EI) (*m/z*) cald. For C₂₀H₂₈Si: 296.1960; found: C₁₉H₂₈Si: 296.1961.

Methyltriphenylsilane (3g)

A solution of R¹Li (MeLi: 0.07 M in Et₂O, 9.0 mL/min) and a solution of R²Li (PhLi: 0.4 M in Et₂O, 4.0 mL/min) were used.

White solid; mp 67.1-68.1 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.55-7.53 (m, 6H), 7.45-7.42 (m, 3H), 7.40-7.37 (m, 6H), 0.87 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 136.1, 135.3, 129.4, 127.8, -3.4 ppm; ²⁹Si NMR (99 MHz, CDCl₃) δ -11.03 ppm. The melting point was matched with those reported in the literature.³ The spectroscopic data were identical to those reported in the literature.⁴ The product **3g** is identical to product **1c**.

Butyltriphenylsilane (3h)

A solution of R¹Li (*n*-BuLi: 0.07 M in hexane, 9.0 mL/min) and a solution of R²Li (PhLi: 0.4 M in Et₂O, 4.0 mL/min) were used.

Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.53-7.51 (m, 6H), 7.41-7.38 (m, 3H), 7.37-7.34 (m, 6H), 1.48-1.42 (m, 2H), 1.40-1.35 (m, 4H), 0.87 (t, *J* = 7.1 Hz, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 135.7, 135.4, 129.3, 127.8, 26.8, 26.1, 13.7, 13.0 ppm; ²⁹Si NMR (99 MHz, CDCl₃) δ –10.71 ppm. The spectroscopic data were identical to those reported in the literature.¹⁴ The product **3h** is identical to product **2c**.



7.3. Sequential tri-functionalization of phenylsilane with three different organolithiums

A microfluidic system consisting of four T-shaped micromixers (M1, M2, M3 and M4), four tube reactors (R1, R2, R3 and R4) and five tube pre-temperature-retaining units (for P1, P2, P3, P4 and P5; $\emptyset = 1 \text{ mm}$ and L = 100 cm) were used. The microfluidic system was immersed in a temperature control bath. A solution of phenylsilane (0.3 M in THF, flow rate: 2.0 mL/min) and a solution of *t*-BuOK (0.12 M in THF, flow rate: 1.0 mL/min) were introduced to M1 (\emptyset : 300 µm) by syringe pumps. The resulting solution flowed through R1 ($\emptyset = 250 \text{ µm}$, L = 4.0 cm) and was mixed in M2 ($\emptyset = 500 \text{ µm}$) with a solution of PhLi (0.1 M in Et₂O, flow rate: 6.0 mL/min) and pass through R2 ($\emptyset = 1000 \text{ µm}$, L = 1000 cm). The resulting solution was mixed in M3 with a solution of MeLi (0.2 M in Et₂O, flow rate: 3.0 mL/min) and flowed through R3 ($\emptyset = 1000 \text{ µm}$, L = 1000 cm). After a steady state was reached (90 s), the product solution was extracted for 4 min while being quenched with saturated NH₄Cl aqueous solution (16 mL). The resulting mixture was extracted with Et₂O (40 mL×3), and washed with brine (40 mL). The organic phase was dried over sodium sulfate. The organic layer was concentrated on a rotary evaporator under reduced pressure. The crude product was purified by column chromatography to give the desired product.

Butyl(methyl)diphenylsilane (3j)

Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.52-7.50 (m, 4H), 7.37-7.34 (m, 6H), 1.37-1.34 (m, 4H), 1.08-1.06 (m, 2H), 0.90-0.85 (m, 3H), 0.547 (s, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃) δ 137.6, 134.5, 129.0, 127.8, 26.6, 26.0, 13.9, 13.7 –4.5 ppm; ²⁹Si NMR (99 MHz, CDCl₃) δ –7.09 ppm. The spectroscopic data were identical to those reported in the literature.¹⁸

8. References

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¹H NMR spectra of **triethyl(phenyl)silane (1a)**



S18



¹³C and ²⁹Si NMR spectra of triethyl(phenyl)silane (1a)

²⁹Si NMR spectra of **triethyl(phenyl)silane (1a)**



mdd

<mark>8</mark>9

-70

<mark>9</mark>9

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¹H NMR spectra of dimethyldiphenylsilane (1b)



S21

¹³C NMR spectra of **dimethyldiphenylsilane (1b)**



²⁹Si NMR spectra of **dimethyldiphenylsilane (1b)**



¹H NMR spectra of **methyltriphenylsilane (1c)**









¹H NMR spectra of **triphenylsilane (1d)**







²⁹Si NMR spectra of **triphenylsilane (1d)**



bpm

<mark>-80</mark>

<mark>2</mark>

<mark>0</mark>9

-20

.40

<mark>.</mark>

-20

9

0

2

20

30

40

50

60.81-----

¹H spectra of triisopropyl(phenyl)silane (1e)



¹³C NMR spectra of **triisopropyl(phenyl)silane (1e)**



²⁹Si NMR spectra of **triisopropyl(phenyl)silane (1e)**

−SiⁱPr₃



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¹H, ¹³C and ²⁹Si NMR spectra of triethyl(*o*-tolyl)silane (1f)





¹³C NMR spectra of triethyl(*o*-tolyl)silane (1f)

²⁹Si NMR spectra of **triethyl(***o***-tolyl)silane (1f)**



¹H, ¹³C and ²⁹Si NMR spectra of triethyl(*m*-tolyl)silane (1g)


¹³C NMR spectra of **triethyl**(*m*-tolyl)silane (1g)



²⁹Si NMR spectra of **triethyl(***m***-tolyl)silane (1g)**





-SiEt₃ Me mdd 0 400.1 40 <u>6.24</u> 3 2 3.04)= 878.2-ဗ 4 S G 21,196 7,211 7,412 7,428 <u>2.01</u> ø 6

¹H, ¹³C and ²⁹Si NMR spectra of triethyl(*p*-tolyl)silane (1h)





²⁹Si NMR spectra of **triethyl(***p***-tolyl)silane (1h)**

Me-





-SiEt₃ MeO mdd 0 1.00.1 2.00.920 2.00.810 7.10.0 7.10.0 7.10.0 7.10.0 7.10.0 7.10.0 7.10.0 7.10.0 7.00.0 7. ₹<u>60.9</u> 5 - N ო ≤(20.5 3.842 et 5 ø 9 - 337 876 - 9 2.02 > 154.7 144.7 7454.7 2.00 œ 6

¹H NMR spectra of triethyl(4-methoxyphenyl)silane (1i)



¹³C and ²⁹Si NMR spectra of triethyl(4-methoxyphenyl)silane (1i)



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¹H NMR spectra of triethyl(4-fluorophenyl)silane (1j)





¹³C NMR spectra of triethyl(4-fluorophenyl)silane (1j)



²⁹Si NMR spectra of triethyl(4-fluorophenyl)silane (1j)

20.2—

¹H NMR spectra of (4-chlorophenyl)triethylsilane (1k)





¹³C and ²⁹Si NMR spectra of (4-chlorophenyl)triethylsilane (1k)

²⁹Si NMR spectra of (4-chlorophenyl)triethylsilane (1k)















S53



¹H NMR spectra of *tert*-butyl 4-(dimethyl(phenyl)silyl)benzoate (1m)



¹³C NMR spectra of *tert*-butyl 4-(dimethyl(phenyl)silyl)benzoate (1m)

²⁹Si NMR spectra of *tert*-butyl 4-(dimethyl(phenyl)silyl)benzoate (1m)

^tBuO₂C-

-SiMe₂Ph



65.7-----



S57



S58

²⁹Si NMR spectra of triethyl(naphthalen-1-yl)silane (1n)



mqq <mark>8</mark>9 <mark>2</mark>2 E ဓိ -20 . ဓိ -20 F 2 0 9 20 Ē 8 Ē **4**0 50

72.ε—

¹H NMR spectra of **3-(triethylsilyl)pyridine (10)**







²⁹Si NMR spectra of **3-(triethylsilyl)pyridine (10)**





S63







¹H NMR spectra of **butyldimethyl(phenyl)silane (1q)**



S67





mdd

Ph Si-Ph MeO mdd 0 -2 e <u>⇒(00.E</u> ₽28.6et 5 676'9-926'9-1376 7372 752'L-89£.7 29£.7 9 275.7 275.7 2.04 61.9 <u>3.00</u> 724.7-224.7-86.1 60.9 œ 6 992.7

¹H NMR spectra of (4-methoxyphenyl)triphenylsilane (2a)



¹³C NMR spectra of (4-methoxyphenyl)triphenylsilane (2a)

²⁹Si NMR spectra of (4-methoxyphenyl)triphenylsilane (2a)



mdd

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<mark>9</mark>0

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فميتا كالمطاطع يقداف

بر من منه به ماد والمنه منهماتها والمعادلة، ولمعادلة معادلة والمعادلة وما منه والمعادلة منه معادلة وممانية والم تهدينا منهماتها ومنهماتها معادلها والمعادلة ومنه معادلة معادلة منه منه منهماتها منه منه منه منه منه منه منه منه

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¹H NMR spectra **butyl(4-chlorophenyl)diphenylsilane (2b)**






¹H, ¹³C and ²⁹Si NMR spectra of **butyltriphenylsilane (2c)**



 $^1\mathrm{H},\,^{13}\mathrm{C}$ and $^{29}\mathrm{Si}\,\mathrm{NMR}$ spectra of butyltriphenylsilane (2c)



bpm

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S78



¹³C NMR spectra of **trimethylphenylsilane (3a)**





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¹³C NMR spectra of **butyl(dimethyl)(phenyl)silane (3b)**









S86



¹H NMR spectra of **dibutyl(methyl)(phenyl)silane (3d)**





²⁹Si NMR spectra of **dibutyl(methyl)(phenyl)silane (3d)** Ph ⁿBu-Si-Me

ⁿBu

82.2-



¹H, ¹³C and ²⁹Si NMR spectra of **tributyl(phenyl)silane (3e)**







²⁹Si NMR spectra of **tributyl(phenyl)silane (3e)**



90.2-----



¹H, ¹³C and ²⁹Si NMR spectra of **dibutyldiphenylsilane (3f)**







bpm

40

0

ⁿBu <mark>-80</mark> -70 Ē <mark>0</mark>9 -20 <mark>8</mark> -20 <mark>9</mark>-**9** 20 30 **40** 50

69 . 9 - -----

¹H NMR spectra of **methyltriphenylsilane (3g)**





¹³C and ²⁹Si NMR spectra of **methyltriphenylsilane (3g)**







¹H NMR spectra of **butyltriphenylsilane (3h)**







¹³C and ²⁹Si NMR spectra of **butyltriphenylsilane (3h)**

¹H NMR spectra of tetraphenylsilane (3i)





¹³C NMR spectra of tetraphenylsilane (3i)

²⁹Si NMR spectra of **tetraphenylsilane (3i)**



mqq

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-<mark>8</mark>

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40

50

T2.41-----



¹H NMR spectra of **butyl(methyl)diphenylsilane (3j)**





²⁹Si NMR spectra of **butyl(methyl)diphenylsilane (3j)** Ph Me-Si-Ph

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