Efficient Synthesis of Branched Propargyl- and Allylsilanes

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Dedicated to Prof. Dr. Manfred Regitz with best wishes on the occasion of his 60 th birthday.

The transformation of α-silylated aldehydes **3a** - **h** into the propargylsilanes **5a** - **k** and the (*Z*)-allylsilane **6** is described. The readily available *tert*-butylimine **1** of acetaldehyde is silylated and alkylated in a one-pot procedure to obtain the α-silylated aldehydes **3a** - **h** after hydrolysis of the imine moiety in 77 - 96% yield. C-1 homologation by the Corey–Fuchs method gave 1,1 - dibromoallylsilanes **4a** - **h** in 70 - 96% yield which can be transformed into the mono- and disubstituted propargylsilanes **5a** - **k** in 33 - 95% yield. Hydrogenation of the propargylsilanes e.g. **5e** with $Ni(OAc)_2$ / $NaBH_4$ gives the (*Z*)-allylsilane **6a** in 80% yield.

Allyl- and propargylsilanes are valuable building blocks in organic synthesis and many procedures are known for the preparation of these compounds with a terminal silane moiety[1,2]. However, only a few methods are available which allow the synthesis of more complex branched propargyl- and allylsilanes[3] such as the Wittig Reaction of α-silyl aldehydes[4]. A disadvantage of the latter procedure is the low diastereoselectivity in the formation of the double bond. This can be of disadvantage as we have recently shown for the enantioselective silicon terminated Heck Reaction[5].

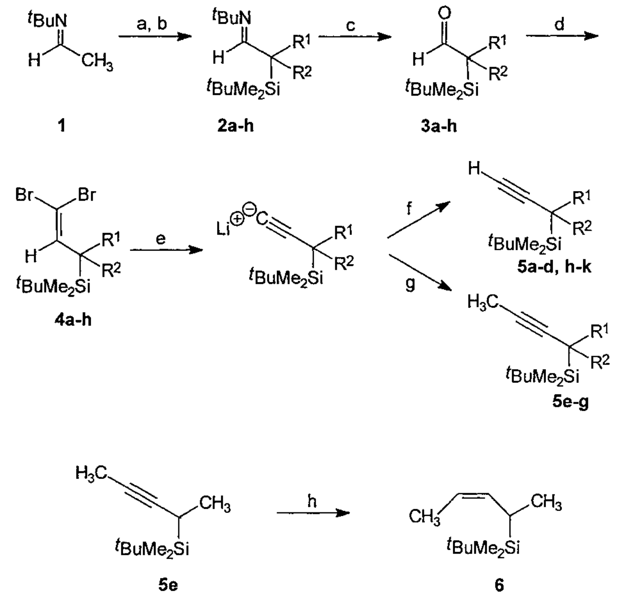
In this paper we describe a new procedure for the synthesis of branched propargylsilanes from which the corresponding (*Z*)-allylsilanes can be obtained by hydrogenation, starting from α-*tert*-butyl-dimethylsilylaldehydes[6,7,8] using the Corey–Fuchs protocol[9].

Acetaldehyde was transformed into the *tert*-butylimine **1** [10], which was deprotonated with LDA and then treated with *tert*-butyldimethylsilyl chloride to give the α-silylimine **2a**. Repeated deprotonation with BuLi in THF and mono- or bisalkylation of **2a** using haloalkanes yield the mono- or bisalkylated α-silylimines **2a** - **h** which were hydrolysed without purification to afford the corresponding α-silylaldehydes **3a** [6], **3b** [4], **3c** [7], **3d** - **e**, **3f** [6] and **3g** - **h** in 77-90% yield based on the imine **1** (table 1, scheme 1).

2a and **2b** are quite unstable and are cleaved already on silica gel with 90% yield. The hydrolysis of **2c** and **2e** - **h** was performed in a two phase system with 1M acetic acid and dichloromethane in 81-86% yield. For the cleavage of the most stable imine **2d** to give the aldehyde **3d** the hydrolysis was performed under ultrasound for 3 h at 60 °C.

The α-silylaldehydes **3a** - **d** were transformed into the 1,1 - dibromoalkenes **4a** - **h** in 70-94% yield using 5.7 equiv. of triphenylphosphane and 2.8 equiv. of tetrabromomethane in dichloromethane for 2-22 h at 0 °C or room temperature. The purified 1,1 - dibromoalkenes **4a** - **h** were treated with 2.14 equiv. of MeLi or BuLi in diethyl ether or THF at -78 °C for 30 min to give the acetylide which can be quenched either with water or haloalkane such as iodomethane. In the former process one obtains propargylsilanes **5a**, **5b** [11], **5c** - **d**, and **h** - **k** with a monosubstituted triple bond, whereas in the latter process any type of double substituted propargylsilanes **5e** [11] and **5f** - **g** can be formed (table 2, scheme 1). It should be noted that the propargylsilanes **5a** and **5b** are highly volatile.

Propargylsilanes can easily be hydrogenated to give (*Z*)-allylsilanes. As an example, **5e** was treated with $Ni(OAc)_2 \cdot 4\ H_2O$ in the presence of 1 equiv. of $NaBH_4$, H_2 and ethylenediamine in ethanol for 3 h at room temperature [12]. After workup **6** was obtained in 80% yield. The ^{13}C NMR spectrum of the product shows that **6** is not contaminated by the other possible isomer.



a) 1 equiv. LDA, TBDMSCl, THF, b) 1 equiv. BuLi, R^1I and optionally BuLi, R^2I, c) H_3O^+ method II - IV (see experimental part), d) 2.8 equiv. CBr_4, 5.7 equiv. Ph_3P, CH_2Cl_2, e) 2.14 equiv. BuLi or MeLi, THF or ether - method VI-VIII (see experimental part), f) H_2O, g) MeI, h) $Ni(OAc)_2$ * 4 H_2O, $NaBH_4$, H_2, ethylenediamine (yield: 80%)

Scheme 1

Table 1. Synthesis of the α-silylaldehydes **3a** - **h** and of the 1,1 - dibromo compounds **4a** - **h**

R^1	R^2	**3**[1)]	Hydrolysis of **2**[3)]	Yield	**4**[1)]	Yield
H	H	**a** [2)]	method II	90%	**a**	94%
H	Me	**b** [2)]	method II	90%	**b**	96%
Me	Me	**c** [2)]	method III	83%	**c**	70%
H	*i*-Pr	**d**	method IV	77%	**d**	72%
H	$Me(CH_2)_3$	**e**	method III	81%	**e**	80%
H	$Me(CH_2)_5$	**f** [2)]	method III	83%	**f**	85%
H	$PhCH_2$	**g**	method III	86%	**g**	88%
H	$Ph(CH_2)_2$	**h**	method III	81%	**h**	90%

1) compounds are racemic

2) compound is known: ref. 4, 6, 7

3) for the description of the methods see experimental part

The structures of the new compounds were mainly determined by ^1H and ^{13}C NMR spectroscopy (Tables 3 - 5). For the aldehyde proton of the α-silylaldehydes **3a** - **h** characteristic signals are found at $\delta = 9.64$-9.76 as a singlet for **3c**, a triplet for **3a** and as doublets for **3b**, **3d-h** with $J = 2.5$-5.2 Hz. The alkyne proton of the monosubstituted alkynes **5a** - **d** and **5h** - **k** resonates at $\delta = 1.82$-2.04. In the ^1H NMR

Table 2. Synthesis of the propargylsilanes **5a - k**

5[1]	R^1	R^2	R^3	base / electrophile / method[3]	Yield
a	H	H	H	MeLi / H$^+$ / VIII	33%[4]
b[2]	H	Me	H	MeLi / H$^+$ / VIII	74%
c	Me	Me	H	*n*-BuLi / H$^+$ / VI	80%
d	H	*i*-Pr	H	*n*-BuLi / H$^+$ / VI	62%
e[2]	H	Me	Me	*n*-BuLi / MeI / VII	87%
f	Me	Me	Me	*n*-BuLi / MeI / VII	66%
g	H	*i*-Pr	Me	*n*-BuLi / MeI / VII	88%
h	H	$Me(CH_2)_3$	H	*n*-BuLi / H$^+$ / VI	94%
i	H	$Me(CH_2)_5$	H	*n*-BuLi / H$^+$ / VI	84%
j	H	$PhCH_2$	H	*n*-BuLi / H$^+$ / VI	95%
k	H	$Ph(CH_2)_2$	H	*n*-BuLi / H$^+$ / VI	83%

1) compounds are racemic

2) compound is known: ref. 11

3) for the description of the methods see experimental part

4) not optimized, **5a** is very volatile

spectrum of the double substituted propargylsilanes **5e - g** such a signal is missing. Characteristic resonances for the allylsilane **6** are found at δ = 2.05 as doublet of a quartet with J = 7.3 and 10.5 Hz and at δ = 5.20-5.32 as a multiplet.

In summary, a highly diversitive and efficient synthesis of substituted propargylsilanes has been described from which the corresponding (*Z*)-allylsilanes can easily and stereoselectivly be obtained by hydrogenation.

^{1}H and ^{13}C NMR: Varian XL-200, VXR-200, Bruker AMX-300. IR: Bruker IFS-25. MS: MAT 311 A. HRMS: MAT 731. Elemental analyses: analytical laboratory of the University of Göttingen. Column chromatography: Macherey, Nagel & Co Kieselgel 60 (0.063-0.200nm). Analytical TLC: Macherey, Nagel & Co (Sil G/UV$_{254}$). Solvents (distilled from): Et_2O (KOH), petroleum ether, bp 40-80 °C (KOH), pentane (KOH), EtOAc (CaH_2), CH_2Cl_2 (CaH_2), THF ($LiAlH_4$). Solvents used for chromatography: *A*, petroleum ether/EtOAc (7:1); *B*, pentane; *C*, petroleum ether/EtOAc (9:1); *D*, petroleum ether/EtOAc (30:1); *E*, petroleum ether.

TBDMSCl and CBr_4 were purchased from Fluka; imine **1** was prepared by a known method[10].

General Procedures for the Preparation of the α-Silylated Imines 2a - h (I) and Their Hydrolysis to Aldehydes 3a - h (II-IV):

(I): To an aprox. 1 M solution of LDA in THF, prepared from freshly distilled diisopropylamine (1.03 equiv.) and BuLi in hexane (1.00 equiv., 2.36 M) by stirring at 0 °C for 30 min, was added imine **1** in THF at 0 °C and the mixture was stirred for 30 min at this temperature. The red coloured solution was treated with 1.00 equiv. of a 2 M solution of TBDMSCl in THF and Bu_4NI (0.05 equiv.) at 0 °C and then stirred at r. t. for 3 h to give **2a**. For the synthesis of the imines **2b - d** BuLi in hexane (1.00 equiv., 2.36 M) was added to the mixture at 0 °C. For the synthesis of the imines **2e - h** imine **2a** was first isolated and then deprotonated using LDA (1.00 equiv.) at -78 °C. The mixtures were stirred for 1 h at the same temperature, treated with the alkyl halide (1.00 equiv. of the alkyl iodides for the imines **2b - d**, **h** and 1.00 equiv. of the alkyl bromides for the imines **2e - g**) and then allowed to warm up to r. t. over 12 h. For the second alkylation the solution was cooled down to 0 °C and 1.20 equiv. of BuLi in hexane and 1.20 equiv. MeI were used at the same conditions as described for the first alkylation step.

The mixtures were diluted with diethyl ether or petroleum ether (2 mL / mmol **1**), poured onto ice-water and the organic layer was separated. The aqueous layer was extracted with diethyl ether or petroleum ether (2 x 2 mL / mmol **1**). The combined organic layers were washed with brine, dried over $MgSO_4$ and evaporated in vacuo.

The following three methods were used to hydrolyse the imines **2a - h**:

(II): The imines **2a - b** were dissolved in eluent *A* (aprox. 5 M) and filtered through a column of silica gel (ratio imine: silica gel = 1:10) with eluent *A*.

(III): A solution of the imines **2c - h** in dichloromethane (ca. 0.5 M) was stirred vigorously with 1.00 equiv. of 1 M aqueous acetic acid. The phases were separated after 1 h and the aqueous layer was extracted with dichloromethane (2 mL / mmol **1**). The combined organic layers were diluted with diethyl ether (1 v/v), washed with water (2 x 1 mL / mmol **1**), saturated sodium bicarbonate (2 x 1 mL / mmol **1**), dried over $MgSO_4$ and evaporated in vacuo. The residue was purified by column chromatography (eluent *A* for **3c - d** and eluent *C* for **3e - h**).

(IV): As described for III, but under ultrasound for 3 h at 40 °C.

The yields and the NMR data are shown in the table 1 and table 3, respectively.

1,1-Dibromoallylsilanes 4a - h; General Procedure V :

To a stirred solution of tetrabromomethane (2.80 equiv.) in freshly distilled dichloromethane (1 M) was added a solution of triphenylphosphane (5.70 equiv.) in dichloromethane (2 M) at 0 °C, and after 30 min a solution of the aldehydes **3a - h** in dichloromethane (0.5 M). Stirring was continued for 2 - 22 h (**3a - b**: 2 h at 0 °C, **3c - d**: 22 h at 0 °C, **3e - h**: 2 h at room temperature; TLC, eluent *B* or *C*).

Table 3. NMR data of compounds **3a - h**

	^{1}H NMR ($CDCl_3$, TMS) δ, J(Hz)	^{13}C NMR ($CDCl_3$, TMS) δ	Molecular Formula[1]
3a	0.11 (s, 6 H, $Si(\underline{CH}_3)_2$), 0.93 (s, 9 H, $C(\underline{CH}_3)_3$), 2.28 (d, J=4.4, 2 H, CH_2), 9.70 (t, J=4.4, 1 H, CHO)	-5.66 ($Si(\underline{CH}_3)_2$), 16.82 ($Si\underline{C}(CH_3)_3$), 26.01 ($SiC(\underline{CH}_3)_3$), 36.38 ($OHC\underline{CH}_2$), 200.78 (CHO)	$C_8H_{18}SiO$ (158.30)
3b	0.06, 0.08 (each s, 6 H, $Si(\underline{CH}_3)_2$), 0.96 (s, 9 H, $C(\underline{CH}_3)_3$, 1.21 (d, J=6.8, 3 H, $OHCCH(\underline{CH}_3)$), 2.55 (dq, J=6.8, 2.5, 1 H, $OHC\underline{CH}$), 9.76 (d, J=2.5, 1 H, CHO)	-6.92, -6.83 ($Si(\underline{CH}_3)_2$), 9.01 ($OHCCH(\underline{CH}_3)$), 17.55 ($Si\underline{C}(CH_3)$), 26.75 ($SiC(\underline{CH}_3)_3$), 40.98 ($OHC\underline{CH}$), 203.22 (CHO)	$C_9H_{20}SiO$ (172.32)
3c	0.07 (s, 6 H, $Si(\underline{CH}_3)_2$), 0.94 (s, 9 H, $C(\underline{CH}_3)_3$), 1.26 (s, 6 H, $OHCC(\underline{CH}_3)_2$), 9.68 (s, 1 H, CHO)	-7.51 ($Si(\underline{CH}_3)_2$), 18.90 ($Si\underline{C}(CH_3)_3$), 19.06 ($OHCC(\underline{CH}_3)_2$), 27.74 ($SiC(\underline{CH}_3)_3$), 43.33 ($OHC\underline{C}$), 206.14 (CHO)	$C_{10}H_{22}SiO$ (186.35)
3d	0.10, 0.15 (each s, 6 H, $Si(\underline{CH}_3)_2$), 0.94 (s, 9 H, $C(\underline{CH}_3)_3$), 1.06 (d, J=6.5, 3 H, $CH(CH_3)_2$), 1.16 (d, J=6.9, 3 H, $CH(CH_3)_2$), 2.21-2.27 (m, 2 H, $OHC\underline{CH}$, $\underline{CH}(CH_3)_2$), 9.74 (d, J=5.2, 1 H, CHO)	-5.08 ($Si(\underline{CH}_3)_2$), 17.85 ($Si\underline{C}(CH_3)_3$), 22.13, 24.49 ($CH(\underline{CH}_3)_2$), 26.83 ($SiC(\underline{CH}_3)_3$), 27.25 ($\underline{CH}(CH_3)_2$), 53.81 ($OHC\underline{CH}$), 204.37 (CHO)	$C_{11}H_{24}OSi$ (200.20)
3e	0.01, 0.04 (each s, 6 H, $Si(\underline{CH}_3)_2$), 0.84 (t, J=4.8, 3 H, $(CH_2)_3\underline{CH}_3$), 0.90 (s, 9 H, $C(\underline{CH}_3)_3$), 1.06-1.48 (m, 6 H, $(\underline{CH}_2)_3CH_3$), 2.38 (m, 1 H, $OHC\underline{CH}$), 9.64 (d, J=3.6, 1 H, CHO)	-6.53, -6.41 ($Si(\underline{CH}_3)_2$), 13.83 ($(CH_2)_3\underline{CH}_3$), 17.75 ($Si\underline{C}(CH_3)_3$), 22.46, 24.80, 33.23 ($(\underline{CH}_2)_3CH_3$), 26.86 ($SiC(\underline{CH}_3)_3$), 48. 25 ($OHC\underline{CH}$), 203.56 (CHO)	$C_{12}H_{26}OSi$ (214.43)
3f	0.01, 0.04 (each s, 6 H, $Si(\underline{CH}_3)_2$), 0.84 (t, 3 H, J=4.8, $(CH_2)_5\underline{CH}_3$), 0.91 (s, 9 H, $C(\underline{CH}_3)_3$), 1.08-1.47 (m, 10 H, $(\underline{CH}_2)_5CH_3$), 2.38 (ddd, J=2.0, 3.6, 11.2, 1 H, $OHC\underline{CH}$), 9.64 (d, J=3.6 , 1 H, CHO)	-6.52, -6.40 ($Si(\underline{CH}_3)_2$), 14.00 ($(CH_2)_5\underline{CH}_3$), 17.75 ($Si\underline{C}(CH_3)_3$), 22.56, 25.15, 29.11, 31.06, 31.61 ($(\underline{CH}_2)_5CH_3$), 26.87 ($SiC(\underline{CH}_3)_3$), 48.31 ($OHC\underline{CH}$), 203.57 (CHO)	$C_{14}H_{30}OSi$ (242.48)
3g	0.14, 0.20 (each s, 6 H, $Si(\underline{CH}_3)_2$),1.02 (s, 9 H, $C(\underline{CH}_3)_3$), 2.75 (dd, J=14.4, 2.0, 1 H, $PhCH_2$), 2.87 (dt, J=10.8, 2.8, 1 H, $OHC\underline{CH}$), 3.42 (dd, J=14.4, 10.8, 1 H, $PhCH_2$), 7.12-7.33 (m, 5 H, ArH), 9.73 (d, J=2.8, 1 H, CHO)	-6.38, -6.26 ($Si(\underline{CH}_3)_2$), 17.91 ($Si\underline{C}(CH_3)_3$), 26.95 ($SiC(\underline{CH}_3)_3$), 30.60 ($Ph\underline{CH}_2$), 50.08 ($OHC\underline{CH}$), 126.03 (C_{ar}), 128.18 (C_{ar}), 128.43 (C_{ar}), 142.18 (C_{ar}), 202.11 (CHO)	$C_{15}H_{24}OSi$ (248.44)
3h	0.02,0.05 (each s, 6 H, $Si(\underline{CH}_3)_2$), 0.90 (s, 9 H, $C(\underline{CH}_3)_3$), 2.26-2.52 (m, 4 H, $OHC\underline{CH}$ and $PhCH_2CH_2$), 2.61-2.78 (m, 1 H, $PhCH_2CH_2$), 7.11-7.32 (m, 5 H, ArH), 9.69 (d, J=3.2, 1 H, CHO)	-6.43, -6.39 ($Si(\underline{CH}_3)_2$), 17.77 ($Si\underline{C}(CH_3)_3$), 26.85 ($SiC(\underline{CH}_3)_3$), 27.07 ($PhCH_2\underline{CH}_2$), 36.69 ($Ph\underline{CH}_2CH_2$), 47.64 ($OHC\underline{CH}$), 125.99 (C_{ar}), 128.38 (C_{ar}), 128.49 (C_{ar}), 141.46 (C_{ar}), 202.88 (CHO)	$C_{16}H_{26}OSi$ (262.47)

1) Satisfactory microanalysis obtained for compounds **3a**, **c - h**: ± 0.30.

Table 4. NMR data of compounds **4a - h**

	^{1}H NMR ($CDCl_3$, TMS) δ, *J*(Hz)	^{13}C NMR ($CDCl_3$, TMS) δ	Molecular Formula 1), 2)
4a	0.03 (s, 6 H, $Si(\underline{CH}_3)_2$), 0.92 (s, 9 H, $C(\underline{CH}_3)_3$), 1.60 (d, *J*=8.8, 2 H, $\underline{CH}_2$), 6.40 (t, *J*=8.8, 1 H, $Br_2C{=}\underline{CH}$)	-5.97 ($Si(\underline{CH}_3)_2$), 16.73 ($Si\underline{C}(CH_3)_3$), 20.87 ($\underline{CH}_2Si$), 25.35 ($SiC(\underline{CH}_3)_3$), 84.78 ($Br_2\underline{C}{=}CH$), 136.20 ($Br_2C{=}\underline{CH}$)	$C_9H_{18}SiBr_2$ (314.12)
4b	0.00, 0.01 (each s, 6 H, $Si(\underline{CH}_3)_2$), 0.94 (s, 9 H, $C(\underline{CH}_3)_3$), 1.10 (d, *J*=7.4, 3 H, $CH(\underline{CH}_3)$), 2.08 (dq, *J*=11.5, 7.4, 1 H, $\underline{CH}(CH_3)$), 6.25 (d, *J*=11.5, 1 H, $Br_2C{=}\underline{CH}$)	-7.35, -7.29 ($Si(\underline{CH}_3)_2$), 14.81 ($CH(\underline{CH}_3)$), 17.37 ($Si\underline{C}(CH_3)_3$), 26.50 ($\underline{CH}(CH_3)$), 27.04 ($SiC(\underline{CH}_3)_3$), 84.34 ($Br_2\underline{C}{=}CH$), 142.84 ($Br_2C{=}\underline{CH}$)	$C_{10}H_{20}SiBr_2$ (328.11)
4c	0.06 (s, 6 H, $Si(\underline{CH}_3)_2$), 0.98 (s, 9 H, $C(\underline{CH}_3)_3$), 1.29 (s, 6 H, $Br_2C{=}CHC(\underline{CH}_3)_2$), 6.56 (s, 1 H, $Br_2C{=}\underline{CH}$)	-7.08 ($Si(\underline{CH}_3)_2$), 18.84 ($Si\underline{C}(CH_3)_3$), 24.66 ($C(\underline{CH}_3)_2$) 28.05 ($SiC(\underline{CH}_3)_3$), 31.77 ($\underline{C}(CH_3)_2$), 80.39 ($Br_2\underline{C}{=}CH$), 145.62 ($Br_2C{=}\underline{CH}$)	$C_{11}H_{22}SiBr_2$ (342.17)
4d	0.03, 0.06 (each s, 6 H, $Si(\underline{CH}_3)_2$), 0.93 (s, 9 H, $C(\underline{CH}_3)_3$), 0.92 (d, *J*=4.7, 3 H, $CH(\underline{CH}_3)_2$), 0.98 (d, *J*=6.6, 3 H, $CH(\underline{CH}_3)_2$), 2.01-2.10 (m, 2 H, $\underline{HC}Si$, $\underline{CH}(CH_3)_2$), 6.34 (d, *J*=11.7, 1 H, $Br_2C{=}\underline{CH}$)	-5.99, -5.68 ($Si(\underline{CH}_3)_2$), 17.51 ($Si\underline{C}(CH_3)_3$), 20.01, 24.14 ($CH(\underline{CH}_3)_2$), 26.96 ($SiC(\underline{CH}_3)_3$), 29.42, 38.93 ($\underline{CH}(CH_3)_2$, $\underline{HC}Si$), 86.54 ($Br_2\underline{C}{=}C$), 138.76 ($Br_2C{=}\underline{CH}$)	$C_{12}H_{24}SiBr_2$ (356.19)
4e	-0.04, -0.03 (each s, 6 H, $Si(\underline{CH}_3)_2$), 0.87 (t, *J*=4.8, 3 H, $(CH_2)_3\underline{CH}_3$), 0.90 (s, 9 H, $C(\underline{CH}_3)_3$), 1.11-1.58 (m, 6 H, $(\underline{CH}_2)_3CH_3$), 1.99 (dt, *J*=8.0, 2.4, 1 H, $Si\underline{CH}$), 6.16 (d, *J*=8.0, 1 H, $Br_2C{=}\underline{CH}$)	-6.96 ($Si(\underline{CH}_3)_2$), 14.00 ($(CH_2)_3\underline{CH}_3$), 17.44 ($Si\underline{C}(CH_3)_3$), 27.11 ($SiC(\underline{CH}_3)_3$), 22.44, 29.51, 31.86 ($(\underline{CH}_2)_3CH_3$), 33.16 ($\underline{HC}Si$), 84.91 ($Br_2\underline{C}{=}C$), 142.05 ($Br_2C{=}\underline{CH}$)	$C_{13}H_{26}SiBr_2$ (370.24)
4f	-0.04, -0.03 (each s, 6 H, $Si(\underline{CH}_3)_2$), 0.87 (t, *J*=4.8, 3 H, $(CH_2)_5\underline{CH}_3$), 0.90 (s, 9 H, $C(\underline{CH}_3)_3$), 1.11-1.58 (m, 10 H, $(\underline{CH}_2)_5CH_3$), 1.99 (dt, *J*=7.2, 2.0, 1 H, $Si\underline{CH}$), 6.14 (d, *J*=7.2, 1 H, $Br_2C{=}\underline{CH}$)	-6.94 ($Si(\underline{CH}_3)_2$), 14.11 ($(CH_2)_5\underline{CH}_3$), 17.46 ($Si\underline{C}(CH_3)_3$), 27.13 ($(SiC(\underline{CH}_3)_3$), 22.69, 29.07, 29.67, 29.82, 31.79 ($(\underline{CH}_2)_5CH_3$), 33.19 ($\underline{HC}Si$), 84.89 ($Br_2\underline{C}{=}C$), 142.02 ($Br_2C{=}\underline{CH}$)	$C_{15}H_{30}SiBr_2$ (398.30)
4g	0.02, 0.06 (each s, 6 H, $Si(\underline{CH}_3)_2$), 0.95 (s, 9 H, $C(\underline{CH}_3)_3$), 2.32 (dt, *J*=11.6, 2.8, 1 H, $Si\underline{CH}$), 2.51 (t, *J*=14.0, 1 H, $PhCH_2$), 2.93 (dd, *J*=14.0, 2.8, 1 H, $PhCH_2$), 6.19 (d, *J*=11.6, 1 H, $Br_2C{=}\underline{CH}$), 7.06-7.27 (m, 5 H, ArH)	-6.88, -6.83 ($Si(\underline{CH}_3)_2$), 17.52 ($Si\underline{C}(CH_3)_3$), 27.14 ($SiC(\underline{CH}_3)_3$), 34.99 ($\underline{HC}Si$), 36.00 ($Ph\underline{CH}_2$), 86.04 ($Br_2\underline{C}{=}C$), 125.97 (C_{ar}), 128.21 (C_{ar}), 128.28 (C_{ar}), 140.69 ($Br_2C{=}\underline{CH}$), 141.05 (C_{ar})	$C_{16}H_{24}SiBr_2$ (404.26)
4h	0.00, 0.02 (each s, 6 H, $Si(\underline{CH}_3)_2$), 0.92 (s, 9 H, $C(\underline{CH}_3)_3$), 1.60-1.99 (m, 2 H, $Ph\underline{CH}_2CH_2^*$), 2.08 (dt, *J*=11.2, 2.4, 1 H, $Si\underline{CH}$), 2.40-2.83 (m, 2 H, $PhCH_2\underline{CH}_2^*$), 6.28 (d, *J*=11.2, 1 H, $Br_2C{=}\underline{CH}$), 7.16-7.36 (m, 5 H, ArH)	-6.86,-6.80 ($Si(\underline{CH}_3)_2$), 17.43 ($Si\underline{C}(CH_3)_3$), 27.07 ($SiC(\underline{CH}_3)_3$), 32.12 ($PhCH_2\underline{CH}_2^*$), 33.12 ($\underline{HC}Si$), 36.12 ($Ph\underline{CH}_2CH_2^*$), 85.56 ($Br_2\underline{C}{=}C$), 125.84 (C_{ar}), 128.33 (C_{ar}), 128.53 (C_{ar}), 141.58 ($Br_2C{=}\underline{CH}$), 141.87 (C_{ar})	$C_{17}H_{26}SiBr_2$ (418.29)

1) Satisfactory microanalysis obtained for compounds **4a**, **b**, **g**, **h**: C, H ±0.30; **4c**: C, H ±0.46. High resolution mass spectra with the correct molecular mass are obtained for compounds **4d - f**.

2) The mass - spectra of the compounds **4a - h** show the characteristic 1:2:1 distribution for the correct molecular mass.

- Note: the assignment of signals marked with an asterisk (*) may be interchanged.

Ether (4 mL / mmol aldehyde **3**) was added, the precipitate was filtered off and washed with ether (3 x 2 mL / mmol **3**). The combined filtrates were washed with water (3 mL / mmol **3**), saturated sodium bicarbonate (3 mL / mmol **3**), saturated ammonium chloride (3 mL / mmol **3**), saturated brine (3 mL / mmol **3**), dried over $MgSO_4$ and evaporated in vacuo. The residue was purified by column chromatography on silica gel (eluent *B* or *D*).

The yields and the NMR data are shown in tables 1 and 4, respectively.

Mono- and Bisubstituted Alkynes 5a - g; General Procedures VI - VIII :

(VI): Monosubstituted Alkynes 5c, d, h - k

To a solution of the 1,1 - dibromoallylsilanes **4a - h** (1.00 equiv., 0.25 M) in THF at - 78 °C BuLi (2.14 equiv., 2.36 M) was added. After stirring for 30 min at -78 °C, the mixture was quenched with diethyl ether / water (1 : 1 v/v; 10 mL / mmol **4**) at -78 °C and the aqueous layer washed with ether (3 x 20 mL / mmol **4**). The combined organic layers were then washed with saturated brine (20 mL / mmol **4**), dried over $MgSO_4$, evaporated in vacuo and the residue purified by column chromatography on silica gel (solvent *B* or *E*).

(VII): Disubstituted Alkynes 5e - g

After addition of BuLi, as described in the general procedure VI, the reaction was quenched with MeI (1.20 equiv.) and the mixture heated for 2 h at 40 °C and afterwards stirred for 18 h at r. t. Work up was performed as in general procedure VI.

(VIII): Volatile Monosubstituted Alkynes 5a, 5b

The reaction was performed as described in general procdure VI. However instead of THF, diethyl ether was used as solvent and MeLi (2.14 equiv., 1.6 M) in diethyl ether as base.

The yields and the NMR data are shown in tables 2 and 5, respectively.

Synthesis of the allylsilane (2*RS*, 3*Z*)-(2-*tert*-Butyldimethylsilyl)pent-3-ene (6):
To a solution of $Ni(OAc)_2 \cdot 4\,H_2O$ (18 mg, 0.07 mmol) in ethanol (1 mL) under H_2 - atmosphere a solution of $NaBH_4$ (3 mg, 0.07 mmol) dissolved in ethanol (1 mL) and ethylenediamine (0.01 mL, 0.14 mmol) was added. The propargylsilane **5e** (102 mg, 0.56 mmol) was then added and the suspension stirred for 3 h, filtered through silica gel and the solvent evaporated in vacuo. The residue was purified by column chromatography on silica gel (solvent *B*) to give **6** (81mg, 80 %) as a colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = -0.07, -0.05 (each s, 6 H, $Si(\underline{CH}_3)_2$), 0.92 (s, 9 H, $SiC(\underline{CH}_3)_3$), 1.05 (d, *J* = 7.3Hz, 3 H, 1-H_3), 1.59 (d, *J* = 5.1Hz, 3 H, 5-H_3), 2.05 (dq, *J* = 7.3, 10.5Hz, 1 H, 2-H), 5.20-5.32 (m, 2 H, 3-H, 4-H). Satisfactory microanalysis (± 0.30) was obtained.

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Table 5. NMR data for compounds **5a - k**

	^1H NMR ($CDCl_3$, TMS) δ, *J*(Hz)	^{13}C NMR ($CDCl_3$, TMS) δ	Molecular Formula$^{1)}$
5a	0.09 (s, 6 H, $Si(\underline{CH}_3)_2$), 0.93 (s, 9 H, $C(\underline{CH}_3)_3$), 1.50 (d, *J*=3.1, 2 H, CH_2), 1.82 (t, *J*=3.1, 1 H, $\underline{HC}\equiv C$)	-6.59 ($Si(\underline{CH}_3)_2$), 2.85 ($\underline{CH}_2Si$), 16.80 ($Si\underline{C}(CH_3)_3$), 26.39 ($SiC(\underline{CH}_3)_3$), 66.87 ($\underline{HC}\equiv C$), 82.98 ($HC\equiv\underline{C}$)	$C_9H_{18}Si$ (154.31)
5b	0.00, 0.07 (each s, 6 H, $Si(\underline{CH}_3)_2$), 0.95 (s, 9 H, $C(\underline{CH}_3)_3$), 1.21 (d, *J*=7.3, 3 H, $CH(\underline{CH}_3)$), 1.81 (dq, *J*=7.3, 2.7, 1 H, $\underline{CH}(CH_3)$), 1.96 (d, *J*=2.7,1 H, $\underline{HC}\equiv C$)	-7.80, -7.53 ($Si(\underline{CH}_3)_2$), 10.10 ($CH(\underline{CH}_3)$), 16.03 ($\underline{CH}(CH_3)$), 17.57 ($Si\underline{C}(CH_3)_3$), 27.12 ($SiC(\underline{CH}_3)_3$), 67.78 ($\underline{HC}\equiv C$), 89.16 ($HC\equiv\underline{C}$)	$C_{10}H_{20}Si$ (168.34)
5c	0.40 (s, 6 H, $Si(\underline{CH}_3)_2$), 0.99 (s, 9 H, $C(\underline{CH}_3)_3$), 1.22 (s, 6 H, $C(\underline{CH}_3)_2$), 2.04 (s, 1 H, $\underline{HC}\equiv C$)	-7.68 ($Si(\underline{CH}_3)_2$), 17.81 ($Si\underline{C}(CH_3)_3$), 19.02 ($Si\underline{C}(CH_3)_2$), 26.02 ($SiC(\underline{CH}_3)_2$*) 28.07 ($SiC(\underline{CH}_3)_3$*), 68.05 ($HC\equiv\underline{C}$), 93.27 ($\underline{HC}\equiv C$)	$C_{11}H_{22}Si$ (182.36)
5d	0.02, 0.11 (each s, 6 H, $Si(\underline{CH}_3)_2$), 0.92 (s, 9 H, $C(\underline{CH}_3)_3$), 0.93 (d, *J*=3.0, 3 H, $CH(\underline{CH}_3)_2$), 1.05 (d, *J*=6.5, 3 H, $CH(\underline{CH}_3)_2$), 1.82-1.95 (m, 2 H, $HC\equiv C\underline{CH}$, $\underline{CH}(CH_3)_2$), 1.99 (d, *J*=2.8, 1 H, $\underline{HC}\equiv C$)	-6.78, -6.12 ($Si(\underline{CH}_3)_2$), 17.53 ($Si\underline{C}(CH_3)_3$), 19.48 ($HC\equiv C\underline{CH}$), 24.05, 24.11 ($CH(\underline{CH}_3)_2$), 26.95 ($SiC(\underline{CH}_3)_3$), 27.68 ($\underline{CH}(CH_3)_2$), 77.64 ($\underline{HC}\equiv C$), 84.74 ($HC\equiv\underline{C}$)	$C_{12}H_{24}Si$ (196.39)
5e	0.00, 0.06 (each s, 6 H, $Si(\underline{CH}_3)_2$), 0.96 (s, 9 H, $C(\underline{CH}_3)_3$), 1.18 (d, *J*=7.1, 3 H, $CH(\underline{CH}_3)$), 1.75-1.81 (m, 1 H, $\underline{CH}(CH_3)$), 1.80 (s, 3 H, $\underline{H_3C}C\equiv C$)	-7.82, -7.41 ($Si(\underline{CH}_3)_2$), 3.62 ($\underline{H_3C}C\equiv C$), 10.28 ($CH(\underline{CH}_3)$), 16.29 ($\underline{CH}(CH_3)$), 17.41 ($Si\underline{C}(CH_3)_3$), 27.12 ($SiC(\underline{CH}_3)_3$), 74.90, 83.21 ($H_3C\underline{C}\equiv\underline{C}$)	$C_{11}H_{22}Si$(182.36)
5f	0.00 (s, 6 H, $Si(\underline{CH}_3)_2$), 0.96 (s, 9 H, $C(\underline{CH}_3)_3$), 1.26 (s, 6 H, $C(\underline{CH}_3)_2$), 1.76 (s, 3 H, $\underline{H_3C}C\equiv C$)	-7.69 ($Si(\underline{CH}_3)_2$), 11.30 ($\underline{H_3C}C\equiv C$), 25.33, 26.39 ($Si\underline{C}(CH_3)_3$), ($Si\underline{C}(CH_3)_2$), 33.90 ($SiC(\underline{CH}_3)_2$), 35.63 ($SiC(\underline{CH}_3)_3$), 82.82, 95.05 ($H_3C\underline{C}\equiv\underline{C}$)	$C_{13}H_{30}Si$ (214.44)
5g	0.00, 0.08 (each s, 6 H, $Si(\underline{CH}_3)_2$), 0.92 (s, 9 H, $C(\underline{CH}_3)_3$), 0.93 (d, *J*=6.3, 3 H, $CH(\underline{CH}_3)_2$), 1.03 (d, *J*=6.6, 3 H, $CH(\underline{CH}_3)_2$), 1.74-1.88 (m, 2 H, $H_3CC\equiv C\underline{CH}$, $\underline{CH}(CH_3)_2$), 1.80 (s, 3 H, $\underline{H_3C}C\equiv C$)	-6.59, -6.00 ($Si(\underline{CH}_3)_2$), 3.63 ($\underline{H_3C}C\equiv C$), 17.39 ($Si\underline{C}(CH_3)_3$), 19.75, 24.25 ($CH(\underline{CH}_3)_2$), 24.42 ($H_3CC\equiv C\underline{CH}$), 26.99 ($SiC(\underline{CH}_3)_3$), 28.02 ($\underline{CH}(CH_3)_2$), 77.88, 78.64 ($H_3C\underline{C}\equiv\underline{C}$)	$C_{12}H_{24}Si$ (196.39)
5h	0.02, 0.08 (each s, 6 H, $Si(\underline{CH}_3)_2$), 0.91 (t, *J*=6.0, 3 H, $(CH_2)_3\underline{CH}_3$), 0.96 (s, 9 H, $C(\underline{CH}_3)_3$), 1.20-1.78 (m, 7 H, $Si\underline{CH}$, $(\underline{CH}_2)_3CH_3$), 1.97 (d, *J*=2.8, 1 H, $\underline{HC}\equiv C$)	-7.50 ($Si(\underline{CH}_3)_2$), 14.01 $(CH_2)_3\underline{CH}_3)$, 16.83 ($HC\equiv C\underline{CH}$), 17.64 ($Si\underline{C}(CH_3)_3$), 27.19 ($SiC(\underline{CH}_3)_3$), 22.32, 29.54, 31.61 $(\underline{CH}_2)_3CH_3)$, 68.89, 87.49 ($\underline{HC}\equiv\underline{C}$),	$C_{13}H_{26}Si$ (210.44)
5i	0.01, 0.06 (each s, 6 H, $Si(\underline{CH}_3)_2$), 0.86 (t, *J*=6.0, 3 H, $(CH_2)_5\underline{CH}_3$), 0.92 (s, 9 H, $C(\underline{CH}_3)_3$), 1.14-1.48 (m, 10 H, $(\underline{CH}_2)_5CH_3$), 1.67-1.74 (m, 1 H, $Si\underline{CH}$), 1.95 (d, *J*=2.5, 1 H, $\underline{HC}\equiv C$)	-7.30 ($Si(\underline{CH}_3)_2$), 14.12 $(CH_2)_5\underline{CH}_3)$, 16.88 ($HC\equiv C\underline{CH}$), 17.65 ($Si\underline{C}(CH_3)_3$), 27.21 ($SiC(\underline{CH}_3)_3$), 22.71, 28.97, 29.40, 29.87, 31.82 $(\underline{CH}_2)_5CH_3)$, 68.90, 87.51 ($\underline{HC}\equiv\underline{C}$)	$C_{15}H_{30}Si$ (238.49)
5j	0.07, 0.11 (each s, 6 H, $Si(\underline{CH}_3)_2$), 0.97 (s, 9 H, $C(\underline{CH}_3)_3$), 1.91 (d, *J*=2.4, 1 H, $\underline{HC}\equiv C$), 2.00 (m, 1 H, $Si\underline{CH}$), 2.58 (t, *J*=13.6, 1 H, $PhCH_2$), 2.83 (dd, *J*=13.6, 3.2, 1 H, $PhCH_2$), 7.10-7.31 (m, 5 H, ArH)	-7.70, -6.98 ($Si(\underline{CH}_3)_2$), 17.75 ($Si\underline{C}(CH_3)_3$), 19.73 ($HC\equiv C\underline{CH}$), 27.25 ($SiC(\underline{CH}_3)_3$), 36.13 ($Ph\underline{CH}_2$), 70.20, 86.57 ($\underline{HC}\equiv\underline{C}$), 126.09 ($C_{ar}$), 128.11 ($C_{ar}$), 128.56 ($C_{ar}$), 141.58 ($C_{ar}$)	$C_{16}H_{24}Si$ (244.45)
5k	0.00, 0.08 (each s, 6 H, $Si(\underline{CH}_3)_2$), 0.93 (s, 9 H, $C(\underline{CH}_3)_3$), 1.74 (t, *J*=5.6, 2 H, $Ph\underline{CH}_2CH_2$), 1.68-1.80 (m, 1 H, $Si\underline{CH}$), 2.06 (d, *J*=2.4, 1 H, $\underline{HC}\equiv C$), 2.57-2.74 and 2.95-3.10 (m, 2 H, $PhCH_2\underline{CH}_2$), 7.13-7.34 (m, 5 H, ArH)	-7.27, -7.15 ($Si(\underline{CH}_3)_2$), 16.53 ($HC\equiv C\underline{CH}$), 17.62 ($Si\underline{C}(CH_3)_3$), 27.16 ($SiC(\underline{CH}_3)_3$), 32.00, 35.48 $Ph\underline{CH}_2\underline{CH}_2)$, 69.63, 86.98 ($\underline{HC}\equiv\underline{C}$), 125.77 ($C_{ar}$), 128.30 ($C_{ar}$), 128.58 ($C_{ar}$), 142.04 ($C_{ar}$)	$C_{17}H_{26}Si$ (258.48)

1) Satisfactory microanalysis obtained for compounds **5a**, **c**, **d**, **f**, **g**, **j**, **k**: C, H ± 0.25. High resolution mass spectra with the correct molecular mass are obtained for compounds **5f**, **g**, **h**, **i**

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