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First syntheses of model long-chain trichloro[ω-(trimethylsilyl)alkynyl]silanes suitable for self-assembled monolayers on silicon surfaces

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ABSTRACT

The preparation of the title compounds involves the introduction of the required $Me_3SiC{\equiv}C$ and trichlorosilyl groups at the termini of the alkyl chain via derivatization of easily accessible and inexpensive materials/reagents. Trichloro[ω-(trimethylsilyl)alkynyl]silanes are useful for the linkage to a hydroxylated silicon surface for multilayer formation and for further chemical modification of the tail group of the monolayer.

1. Introduction

During the past 20 years, self-assembled monolayers (SAMs) of alkylsilanes or alkanethiolates on silica or gold surfaces have intensively been studied in interfacial reactions of important areas such as chemical and biosensor technology, corrosion prevention, lubrication, adhesion, nonlinear optical films, electronics, and other areas.[1,2] Significant effort has been devoted to the introduction of various organic functionalities to SAMs by either separated synthesis of a desired molecule and subsequent formation of SAMs or direct chemical modification of the tail group of the monolayer.[1]

The formation of SAMs on silica by using a functionalized silane furnishes a useful and direct opportunity to introduce any functional group on the surface.[3,4] We have recently reported an easy entry to long-chain alkenyltrichloro and triethoxysilane substructures **1**,[5] which are important substrates for the introduction of terminal groups on the surface such as –OH, $–NH_2$ or CO_2H.[3,6] The key step of the synthesis involves Li_2CuCl_4-catalyzed coupling reaction of ω-unsaturated Grignard reagents with alkyl α,ω-disulfonates.

$H_2C{=}CH(CH_2)_nSiR_3$ — **1** (R = Cl, OEt)

$TMS{-}{\equiv}{-}(CH_2)_nSiCl_3$ — **2a-e** (n = 8, 10, 11, 14, 16)

The first preparation of nonadecenyltrichlorosilane, abbreviated as NTS in the literature, was described.[5] NTS is of major interest, since it forms spontaneously, highly ordered, 2D-crystalline SAMs on silicon.[3a]

Here we report on the synthesis of trichloro[ω-(trimethylsilyl)-alkynyl]silanes **2a–e** with chain lengths suitable for the formation of self-assembled monolayers. In these compounds, one end is substituted with an $SiCl_3$ group for the reaction with the hydroxylated silicon surface, whereas the other end has an $Me_3SiC{\equiv}C$ group suitable for further functionalization (azide–alkyne Huisgen 1,3-dipolar cycloaddition,[7] Sonogashira coupling,[8,9] etc.) and multilayer formation.

From this series, only trichloro[19-(trimethylsilyl)-18-nonadecynyl]silane (SA-NTS, n=17) is known.[10] Monolayers of polyacetylene type, which consists entirely of conjugated double bonds, were prepared from SA-NTS adsorbed monomolecularly on a silicon substrate by a chemical adsorption followed by polymerization initiated either by catalysts or by high-energy electron beam irradiation. To the best of our knowledge, the process used for the preparation of SA-NTS has neither been patented nor published.

2. Results and discussion

The method devised for the preparation of the C10, C12, C13, C16, and C18 analogs trichloro[ω-(trimethylsilyl)alkynyl]silanes **2a–e** via derivatization of easily accessible and inexpensive materials/reagents is summarized in Scheme 1 and Table 1.[11] 1-Bromoalkanols **5a**,**b**,**d**,**e** were prepared in good yields (63–92%) by simply

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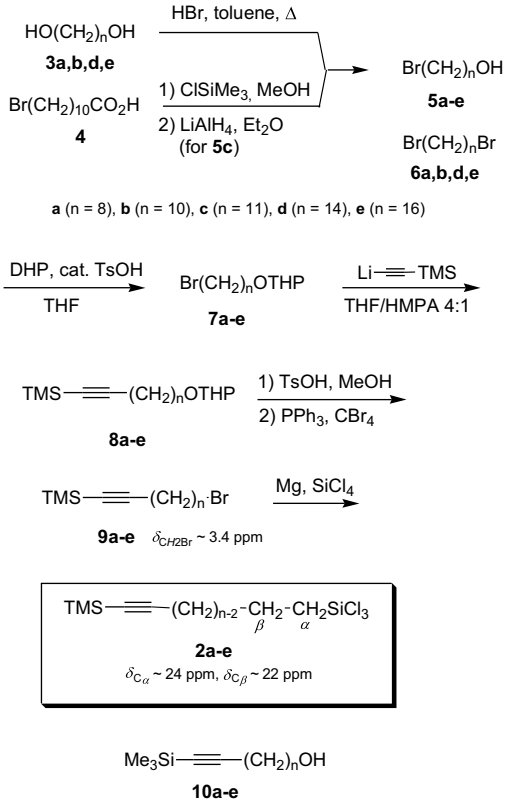
refluxing the corresponding alkanediols **3** in a mixture of aqueous hydrogen bromide (48%) and toluene without a Dean–Stark trap.[12] Under these conditions, bromoalkanols **5** were contaminated with less than 2% of dibromoalkanes **6**. The product distribution deviates significantly from the statistical 25:50:25 mixture of alkanediol/bromoalkanol/dibromide that one might expect presumably because bromoalkanols are less reactive compared to diols due to the formation of aggregates such as reverse micelles or water/oil microemulsions. Such aggregates may be expected to shield the polar hydroxyl groups from reagents in the bulk solvent.[12]



Scheme 1. Syntheses of trichloro[ω-(trimethylsilyl)alkynyl]silanes **2a–e**.

11-Bromoundecan-1-ol (**5c**) was prepared by esterification of 11-bromoundecanoic acid (**4**) (Me_3SiCl, MeOH)[13] followed by reduction[14] with lithium aluminum hydride in ether (92%). After protection with 2,3-dihydro-4-pyran,[15] (ω-bromoalkoxy)tetrahydro-2*H*-pyrans **7a–e** were coupled with lithium trimethylsilylacetylide, in the presence of HMPA in THF,[16] to yield alkynyl derivatives **8a–e** (65–85%). For **8d** and **8e**, 3 equiv of lithium trimethylsilylacetylide was required to drive the reaction to completion. Conversion decreased to less than 10–15% in the absence of HMPA. Unexpectedly, **8e** lost its protection during hydrolytic workup (pH 6) to give the alcohol **10e** (65%). Unreacted **8a–d** were

Table 1
Preparation of long-chain trichloro[ω-(trimethylsilyl)alkynyl] silanes **2a–e**[a]

n	Compounds	**5**	**7**	**8**	**9**	**2**
8	**a**	90	98	71	71	52
10	**b**	87	92	70	92	57
11	**c**	92	98	85	85	61
14	**d**	72	91	68[b]	78	53
16	**e**	63	92	65[b,c]	95	58

[a] Purified yields (chromatography) except otherwise noted.
[b] Lithium trimethylsilylacetylide (3 equiv) was used.
[c] Crude yield of **10e**.

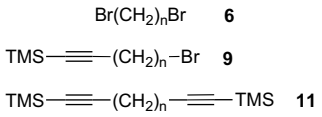


Figure 1.

easily eliminated by column chromatography. After deprotection of **8a–d** (*p*-toluenesulfonic acid, MeOH), the free alcohols **10a–e** were easily converted to **9a–e** (PPh_3, CBr_4, −30 °C, dichloromethane).[17]

The synthesis of (ω-bromoalk-1-ynyl)silanes **9** with different chain lengths by coupling terminal alkyl α,ω-dibromides **6** with lithium trimethylsilylacetylide is known in principle (Fig. 1). With substrates disposing twice of the required functionality, crude yields generally do not exceed 35–40%.[18] Alkyl α,ω-dihalides also lead to cyclic products by radical cyclization that reduces dramatically the yield of the coupling reaction.[19] It has been shown recently by Luh that one of the two carbon–bromine bonds in **6** can be selectively replaced if 0.75 equiv of the Grignard reagent TMS–≡–MgI is employed in the presence of $Pd_2(dba)_3$–Ph_3P (10–40 mol %).[20] Nevertheless, in this procedure, separation by chromatography of the monocoupled (ω-bromoalk-1-ynyl)silanes **9** from the dibromides **6** and the dicoupled products **11** (5–20% of the crude material) causes difficulties due to their very close polarity.[21] In this work, (ω-bromoalk-1-ynyl)silanes **9a–e** were easily separated from their precursors **8a–e** (see Experimental section).

Platinum-catalyzed addition of trichlorosilane ($HSiCl_3$) to a double bond provides a practical route to saturated alkyltrichlorosilanes.[22] A convenient and general method involves reaction of a Grignard reagent with $SiCl_4$.[3b,5] The conversion into the Grignard reagent was carried out by reacting (ω-bromoalk-1-ynyl)trimethylsilanes **9a–e** with finely shredded turnings of metallic magnesium in THF at rt. The Grignard was transferred into a flask containing $SiCl_4$ in THF. After standard workup (see Experimental section) and purification by bulb-to-bulb distillation, the reaction afforded trichloro[ω-(trimethylsilyl)alkynyl]silanes **2a–e** in 52–61% yield. Examination of the ^1H NMR spectra of **2a–e** revealed the disappearance of the triplet at ~3.4 ppm (CH_2Br) (Scheme 1). ^{13}C NMR spectra displayed two new peaks at ~24 and ~22 ppm, which can be attributed to the carbons C_α and C_β, respectively. NMR spectroscopy also suggests that the purities of these compounds are greater than 97% and that the impurities, which we could detect did not contain the $SiCl_3$ group. In the IR spectrum, strong absorptions were observed at 2930 (CH_2, ν_{as}) and 2170 (C≡C) cm^{-1}.

3. Conclusion

We have devised convenient preparations of terminal long-chain alkynyl trichlorosilanes **2a–e** that heretofore have been inaccessible. Their high solubility in most organic solvents and easy hydrolysis should also render them useful for sol–gel and other hydrolysis processes. Compounds **2** can be hydrolyzed and then cross-linked so as to obtain new materials, or serve as comonomers for synthesizing new polymers in order to modify the chemical and mechanical properties by the functionalities introduced on the pending chains. The application of compounds **2a–e** for the formation of self-assembled monolayers will be published separately.

4. Experimental

4.1. General methods and starting materials

NMR spectra were recorded on a 200- or 400-MHz spectrometer. ^{13}C NMR spectra were obtained with broadband proton

decoupling. For spectra recorded in $CDCl_3$, chemical shifts were recorded relative to the internal TMS (tetramethylsilane) reference signal. IR spectra were recorded on an FTIR spectrophotometer. Commercial reagents were used without further purification. Flash column chromatography was performed over silica gel (100–200 mesh). Thin layer chromatography was performed using Silica Gel F_{254} TLC plates and visualized with Stain-CAM (Cerium Ammonium Molybdate) solution. Tetrahydrofuran was dried from sodium benzophenone ketyl. *n*-BuLi (1.6 M in hexanes) was titrated periodically against 2,5-dimethoxybenzyl alcohol.

1-Bromoalkanols **5a**,**b**,**d**,**e** were prepared according to a procedure published elsewhere[12] (63–72%, see Table 1) and **5c** was prepared by a procedure adapted from Rodriguez et al.[13] TMSCl (2 mL, 0.016 mol) was added slowly to 11-bromoundecanoic acid (**4**) (8 g, 30 mmol) dissolved in 2,2-dimethoxypropane/MeOH (50 mL, 4:1 v/v) and stirred for 18 h at rt. After concentration in vacuo, the residue was purified by flash chromatography (cyclohexane/ethylacetate 20:1, R_f=0.40) to give methyl 11-bromoundecanoate as a yellow oil (8.37 g, 99%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.67 (s, 3H, C*H*$_3$), 3.41 (t, 2H, *J*=6.9 Hz, C*H*$_2$Br), 2.30 (t, 2H, *J*=7.3 Hz, C*H*$_2$CO), 1.85 (m, 2H), 1.29–1.63 (m, 14H). This ester (13 g, 46.4 mmol) was then added dropwise to a cold suspension of $LiAlH_4$ (2 g, 50 mmol) in dry ether (100 mL) at 0 °C over a period of 30 min. After being stirred at this temperature for 2 h, the mixture was quenched successively with methanol (1 mL) and 2 M HCl (200 mL) at 0 °C. The aqueous layer was extracted with ether, the combined organic layers were washed successively with 2 M HCl and saturated bicarbonate, and dried over $MgSO_4$. Concentration in vacuo and flash chromatography (cyclohexane/ethylacetate 5:1, R_f=0.25) gave **5c** (10.8 g, 92%) as a white solid, mp 45–48 °C (lit.[23] 43–44 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.64 (t, 2H, *J*=6.5 Hz, C*H*$_2$O), 3.41 (t, 2H, *J*=6.8 Hz, C*H*$_2$Br), 1.86 (m, 2H), 1.29–1.60 (m, 18H).

4.2. Preparation of (ω-bromoalkoxy)tetrahydro-2*H*-pyrans 7a–e: general procedure

3,4-Dihydro-2*H*-pyran (1.5 equiv) and *p*-toluenesulfonic acid monohydrate (0.6 mol %) were added successively to **5a**–**e** dissolved in THF.[15] After being stirred for 4 h at rt, the solution was concentrated in vacuo and the residue was purified by column chromatography on silica gel (cyclohexane/ethylacetate 95:5) to give **7a**–**e**.

*4.2.1. 2-(8-Bromooctyloxy)-tetrahydro-2H-pyran (**7a**)*

According to the general procedure, 3,4-dihydro-2*H*-pyran (7.8 mL, 86 mmol) and *p*-toluenesulfonic acid monohydrate (70 mg, 0.35 mmol) were added successively to 8-bromooctan-1-ol **5a** (11.9 g, 57 mmol) in THF (100 mL). Workup in the usual manner followed by chromatography afforded **7a** (16.40 g, 98%) as a colorless oil (cyclohexane/ethylacetate 20:1, R_f=0.35).[24] ^{1}H NMR (200 MHz, $CDCl_3$) δ: 4.57 (t, 1H, *J*=2.7 Hz, OC*H*O), 3.93–3.68 (m, 2H, C*H*$_2$), 3.56–3.33 (m, 2H), 3.41 (t, 2H, *J*=6.8 Hz, C*H*$_2$Br), 1.92–1.35 (m, 18H, C*H*$_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 98.9, 67.6, 62.4, 34.0, 32.8, 30.8, 29.7, 29.3, 28.7, 28.1, 26.2, 25.5, 19.7.

*4.2.2. 2-(10-Bromodecyloxy)-tetrahydro-2H-pyran (**7b**)*

According to the general procedure, 3,4-dihydro-2*H*-pyran (1.1 mL, 12.6 mmol) and *p*-toluenesulfonic acid monohydrate (10 mg, 0.05 mmol) were added successively to 10-bromodecan-1-ol **5b** (2 g, 8.4 mmol) in THF (12 mL). Workup in the usual manner followed by chromatography afforded **7b** (2.48 g, 92%) as a colorless oil (cyclohexane/ethylacetate 7:3, R_f=0.62).[18b] ^{1}H NMR (200 MHz, $CDCl_3$) δ: 4.59 (s, 1H, C*H*), 3.95–3.88 (m, 2H, C*H*$_2$O$_{THP}$), 3.85 (dt, 2H, *J*=9.6, 6.5 Hz, C*H*$_2$O), 3.75–3.67 (m, 2H, C*H*$_2$Br), 1.89–1.28 (m, 22H, C*H*$_2$, C*H*$_{2THP}$). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 98.9, 67.6, 62.4, 34.3, 32.9, 30.8, 29.7, 29.3, 28.7, 28.1, 26.2, 25.8, 25.5, 19.4.

*4.2.3. 2-(11-Bromoundecyloxy)-tetrahydro-2H-pyran (**7c**)*

According to the general procedure, 3,4-dihydro-2*H*-pyran (5.4 mL, 62.1 mol) and *p*-toluenesulfonic acid monohydrate (50 mg, 0.25 mmol) were added successively to 11-bromoundecan-1-ol **5c** (10 g, 41.4 mol) in THF (100 mL). Workup in the usual manner followed by chromatography afforded **7c** (13.70 g, 98%) as a colorless oil (cyclohexane/ethylacetate 20:1, R_f=0.40).[25] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.58 (s, 1H, C*H*), 3.53–3.35 (m, 2H, C*H*$_2$), 3.90–3.70 (m, 2H, C*H*$_2$), 3.41 (t, 2H, *J*=7.1 Hz, C*H*$_2$Br), 1.89–1.28 (m, 24H, C*H*$_2$, C*H*$_{2THP}$). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 98.9, 67.7, 62.4, 34.0, 32.9, 30.8, 29.8, 29.5, 29.5, 29.4, 29.2, 28.8, 28.2, 26.2, 25.5, 19.5.

*4.2.4. 2-(14-Bromotetradecyloxy)-tetrahydro-2H-pyran (**7d**)*

According to the general procedure, 3,4-dihydro-2*H*-pyran (0.9 mL, 10.2 mmol) and *p*-toluenesulfonic acid monohydrate (7.7 mg, 0.04 mmol) were added successively to 14-bromotetradecan-1-ol **5d** (2.0 g, 6.81 mmol) in THF (10 mL). Workup in the usual manner followed by chromatography afforded **7d** (2.34 g, 91%) as a colorless oil (cyclohexane/ethylacetate 7:3, R_f=0.57).[15,26] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.58 (s, 1H, C*H*), 3.79–3.74 (m, 2H, C*H*$_2$O$_{THP}$), 3.72 (dt, 2H, *J*=9.6 Hz, *J*=6.5 Hz, C*H*$_2$O), 3.44–3.37 (m, 2H, C*H*$_2$Br), 1.86–1.26 (m, 30H, C*H*$_2$, C*H*$_{2THP}$). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 99.0, 67.8, 62.4, 34.0, 32.9, 30.8, 29.8, 29.8, 29.5, 29.5, 29.4, 29.2, 28.8, 28.2, 26.2, 25.5, 19.7.

*4.2.5. 2-(16-Bromohexadecyloxy)-tetrahydro-2H-pyran (**7e**)*

According to the general procedure, 3,4-dihydro-2*H*-pyran (1.2 mL, 13 mmol) and *p*-toluenesulfonic acid monohydrate (10 mg, 0.05 mmol) were added successively to 16-bromohexadecan-1-ol **5e** (2.78 g, 8.7 mmol) in THF (10 mL). Workup in the usual manner followed by chromatography afforded **7e** (3.23 g, 92%) as a colorless oil (cyclohexane/ethylacetate 7:3, R_f=0.33).[12] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.55 (s, 1H, C*H*), 3.82–3.78 (m, 2H, C*H*$_2$O$_{THP}$), 3.76 (dt, 2H, *J*=9.6, 6.5 Hz, C*H*$_2$O), 3.44–3.36 (m, 2H, C*H*$_2$Br), 1.87–1.20 (m, 34H, C*H*$_2$, C*H*$_{2THP}$). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 98.8, 66.7, 62.4, 34.0, 32.9, 30.8, 29.8, 29.5, 29.5, 29.4, 29.2, 29.1, 28.9, 28.8, 28.2, 26.2, 25.5, 19.7.

4.3. Preparation of trimethyl[ω-(tetrahydro-2*H*-pyran-2-yloxy)alk-1-ynyl]silanes 8a–e: general procedure

Trimethylsilylacetylene in a dry 4:1 (v/v) THF/HMPA solution was cooled to −50 °C under an argon atmosphere. *n*-BuLi (1.6 M in hexanes) was added over a period of 30 min. The mixture was allowed to warm up to 0 °C and stirred for 30 min. After being maintained at rt for 1 h, the mixture was cooled to −20 °C and 2-(ω-bromoalkoxy)tetrahydro-2*H*-pyran **7a**–**e** in dry THF was added. Stirring was continued for 5 h at 0 °C and then overnight at rt. Saturated NH_4Cl was added, the aqueous layer was extracted with ether, dried over $MgSO_4$, and purified by column chromatography to give **8a**–**e**.

*4.3.1. Trimethyl-[10-(tetrahydro-2H-pyran-2-yloxy)-dec-1-ynyl]silane (**8a**)*

According to the general procedure, with trimethylsilylacetylene (1.7 mL, 12 mmol) in dry THF/HMPA (25 mL, 4:1 v/v), *n*-BuLi (1.6 M in hexanes, 7.5 mL, 12 mmol), and 2-(8-bromooctyloxy)tetrahydro-2*H*-pyran (**7a**, 3.5 g, 12 mmol) in dry THF (5 mL). Workup in the usual manner followed by chromatography afforded **8a** (2.60 g, 71%) as a colorless oil (cyclohexane/ethylacetate 25:1, R_f=0.30).[27] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.58 (s, 1H, C*H*), 3.93–3.67 (m, 2H, C*H*$_2$), 3.65–3.32 (m, 2H, C*H*$_2$), 2.21 (t, 2H, *J*=7.0 Hz, C*H*$_2$–CC), 1.64–1.32 (m, 18H, C*H*$_2$), 0.15 (s, 9H, TMS). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 108.1, 99.2, 84.6, 67.1, 62.1, 31.2, 30.1, 29.7, 29.4, 29.0, 28.6, 26.6, 26.9, 20.2, 20.1, 0.06.

4.3.2. Trimethyl-[12-(tetrahydro-2H-pyran-2-yloxy)-dodec-1-ynyl]silane (**8b**)

According to the general procedure, with trimethylsilylacetylene (0.9 mL, 6.22 mmol) in dry THF/HMPA (12 mL, 4:1 v/v), *n*-BuLi (1.6 M in hexanes, 3.9 mL, 6.22 mmol) and 2-(10-bromodecyloxy)-tetrahydro-2*H*-pyran (**7b**, 2 g, 6.22 mmol) in dry THF (5 mL). Workup in the usual manner followed by chromatography afforded **8b** (1.48 g, 70%) as a colorless oil (cyclohexane/ethylacetate 9:1, R_f=0.53). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.57 (s, 1H, CH), 3.84 (m, 1H, CH_2O_{THP}), 3.70 (dt, 1H, J=6.9 Hz, J=4.1 Hz, CH_2O), 3.49 (m, 1H, CH_2O_{THP}), 3.36 (dt, 1H, J=6.9 Hz, J=4.1 Hz, CH_2O), 2.20 (t, 2H, J=6.9 Hz, CH_2C), 1.60–1.28 (m, 22H, CH_2, CH_{2THP}), 0.14 (s, 9H, TMS). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 107.6, 98.7, 84.0, 67.5, 62.1, 30.6, 29.6, 29.3, 28.9, 28.6, 28.5, 26.8, 26.1, 25.7, 25.4, 19.7, 19.5, 0.02. HRMS (ESI), calcd: 338.264. Found: 338.2648. IR (neat): 2929, 2855, 2174, 1465, 1248 cm^{-1}. Anal. Calcd for $C_{20}H_{38}O_2Si$: C, 70.94; H, 11.31. Found: C, 71.01; H, 11.02.

4.3.3. Trimethyl-[13-(tetrahydro-2H-pyran-2-yloxy)-tridec-1-ynyl]silane (**8c**)

According to the general procedure, with trimethylsilylacetylene (5.1 mL, 36.6 mmol) in dry THF/HMPA (70 mL, 4:1 v/v), *n*-BuLi (1.6 M in hexanes, 22.9 mL, 36.6 mmol), and 2-(11-bromoundecyloxy)tetrahydro-2*H*-pyran (**7c**, 12.30 g, 36.6 mmol) in dry THF (10 mL). Workup in the usual manner followed by chromatography afforded **8c** (11.0 g, 85%) as a colorless oil (cyclohexane/ethylacetate 20:1, R_f=0.35).[28] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.58 (s, 1H, C*H*), 3.93–3.67 (m, 2H, CH_2), 3.65–3.32 (m, 2H, CH_2), 2.21 (t, 2H, J=6.9 Hz, CH_2–CC), 1.66–1.28 (m, 24H, CH_2), 0.15 (s, 9H, TMS). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 107.8, 98.8, 84.2, 67.5, 62.1, 30.6, 29.6, 29.4, 28.6, 28.5, 28.5, 28.3, 26.8, 26.1, 25.7, 25.3, 19.7, 19.5, 0.02.

4.3.4. Trimethyl-[16-(tetrahydro-2H-pyran-2-yloxy)-hexadec-1-ynyl]silane (**8d**)

According to the general procedure, with trimethylsilylacetylene (2.7 mL, 18.6 mmol) in dry THF/HMPA (19 mL, 4:1 v/v), *n*-BuLi (1.6 M in hexanes, 12.0 mL, 18.6 mmol), and 2-(14-bromotetradecyloxy)-tetrahydro-2*H*-pyran (**7d**, 2.36 g, 6.2 mmol) in dry THF (10 mL). Workup in the usual manner followed by chromatography afforded **8d** (1.67 g, 68%) as a colorless oil (cyclohexane/ethylacetate 20:1, R_f=0.30). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 4.60 (s, 1H, CH), 3.84 (m, 1H, CH_2O_{THP}), 3.70 (dt, 1H, J=6.9, 4.4 Hz, CH_2O), 3.49 (m, 1H, CH_2O_{THP}), 3.35 (dt, 1H, J=6.9, 4.4 Hz, CH_2O), 2.17 (t, 2H, J=6.9 Hz, CH_2C), 1.63–1.22 (m, 30H, CH_2, CH_{2THP}), 0.15 (s, 9H, TMS). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 107.7, 98.8, 84.1, 67.6, 62.3, 30.8, 29.7, 29.6, 29.6, 29.5, 29.0, 28.8, 28.6, 26.2, 25.5, 19.8, 19.7, 0.1. HRMS (ESI), calcd: 394.3267. Found: 394.3268. IR (neat): 2925, 2853, 2175, 1452, 1248 cm^{-1}.

4.3.5. 18-(Trimethylsilyl)octadec-17-yn-1-ol (**10e**)

According to the general procedure used for the preparation of **8a–d**, with trimethylsilylacetylene (2.1 mL, 14.8 mmol) in dry THF/HMPA (19 mL, 4:1 v/v), *n*-BuLi (1.6 M in hexanes, 9.3 mL, 14.8 mmol), and 2-(16-bromohexadecyloxy)tetrahydro-2*H*-pyran (**7e**, 2.0 g, 4.95 mmol) in dry THF (5 mL). Workup in the usual manner afforded **10e** (1.09 g, 65%) as a colorless oil, which was used as such in the next step (cyclohexane/ethylacetate 5:1, R_f=0.25). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 3.35 (t, 2H, J=6.5 Hz, CH_2O), 2.17 (t, 2H, J=6.9 Hz, CH_2C), 1.56–1.22 (m, 28H, CH_2), 0.11 (s, 9H, TMS). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 107.4, 84.1, 62.3, 32.6, 28.7, 28.6, 28,6, 28.4, 28.3, 27.9, 19.6, 0.15. HRMS (ESI), calcd: 338.3005. Found: 338.3008.

4.4. Deprotection of 8a–d. Preparation of (ω-bromoalk-1-ynyl)trimethylsilanes 9a–e: general procedure

Trimethyl-[ω-(tetrahydro-2*H*-pyran-2-yloxy)-alk-1-ynyl]-silanes **8a–d** and *p*-toluenesulfonic acid monohydrate (5 mol %) in methanol were allowed to stir for 2 days at rt. After evaporation of the solvent, the residue was dissolved in dichloromethane (DCM) and cooled to −30 °C under argon. PPh_3 in DCM and CBr_4 in DCM were successively added. After being stirred at this temperature for 3 h, the solution was concentrated in vacuo and the residue was purified by column chromatography to give **9a–d**. 18-(Trimethylsilyl)octadec-17-yn-1-ol (**10e**) was directly treated with PPh_3/CBr_4 to afford **9e** (see below).

4.4.1. (10-Bromodec-1-ynyl)trimethylsilane (**9a**)

According to the general procedure, trimethyl-[10-(tetrahydro-2*H*-pyran-2-yloxy)-dec-1-ynyl]silane (**8a**, 1.16 g, 3.73 mmol) was deprotected by *p*-toluenesulfonic acid monohydrate (36 mg, 0.19 mmol) in methanol (24 mL). The residue was dissolved in DCM (20 mL) and treated successively with PPh_3 (1.47 g, 5.6 mmol) in DCM (5 mL) and CBr_4 (1.86 g, 5.6 mmol) in DCM (5 mL). After evaporation of the solvent and chromatography (hexane/ethylacetate 20:1), **9a** was isolated as a colorless oil (0.765 g, 71%) (cyclohexane/ethylacetate 5:1, R_f=0.20). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 3.41 (t, 2H, J=6.8 Hz, CH_2Br), 2.21 (t, 2H, J=6.9 Hz, CH_2C), 1.86 (m, 2H, CH_2), 1.57–1.32 (m, 10H, CH_2), 0.15 (s, 9H, TMS). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 107.4, 84.1, 33.8, 32.6, 28.7, 28.6, 28.4, 28.3, 27.9, 19.6, 0.15. IR (neat): 2929, 2855, 2174, 1462, 1247, 1027, 838, 758, 639 cm^{-1}. HRMS (CI), calcd: 289.0987. Found: 289.0984. Anal. Calcd for $C_{13}H_{25}BrSi$: C, 53.97; H, 8.71. Found: C, 53.77; H, 8.58.

4.4.2. (12-Bromododec-1-ynyl)trimethylsilane (**9b**)

According to the general procedure, trimethyl-[10-(tetrahydro-2*H*-pyran-2-yloxy)-dodec-1-ynyl]silane (**8b**, 0.844 g, 2.49 mmol) was deprotected by *p*-toluenesulfonic acid monohydrate (25 mg, 0.13 mmol) in methanol (12 mL). The residue was dissolved in DCM (15 mL) and treated successively with PPh_3 (980 mg, 3.73 mmol) in DCM (5 mL) and CBr_4 (1.24 g, 3.73 mmol) in DCM (5 mL). After evaporation of the solvent and chromatography (hexane/ethylacetate 20:1), **9b** was isolated as a colorless oil (0.72 g, 92%) (cyclohexane/ethylacetate 9:1, R_f=0.66).[18] ^{1}H NMR (200 MHz, $CDCl_3$) δ: 3.40 (t, 2H, J=6.8 Hz, CH_2Br), 2.17 (t, 2H, J=6.9 Hz, CH_2C), 1.91 (q, 2H, J=6.8 Hz, CH_2CH_2Br), 1.28–1.55 (m, 14H, CH_2), 0.14 (s, 9H, TMS). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 107.4, 84.1, 33.8, 32.6, 28.7, 28.6, 28.4, 28.3, 28.3, 27.9, 19.6, 0.15.

4.4.3. (13-Bromotridec-1-ynyl)trimethylsilane (**9c**)

According to the general procedure, trimethyl-[10-(tetrahydro-2*H*-pyran-2-yloxy)-tridec-1-ynyl]silane (**8c**, 1.31 g, 3.73 mmol) was deprotected by *p*-toluenesulfonic acid monohydrate (36 mg, 0.19 mmol) in methanol (12 mL). The residue was dissolved in DCM (20 mL) and treated successively with PPh_3 (1.47 mg, 5.6 mmol) in DCM (5 mL) and CBr_4 (1.86 g, 5.6 mmol) in DCM (5 mL). After evaporation of the solvent and chromatography (hexane/ethylacetate 20:1), **9c** was isolated as a colorless oil (1.05 g, 85%) (cyclohexane/ethylacetate 20:1, R_f=0.20). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 3.41 (t, 2H, J=6.9 Hz, CH_2Br), 2.21 (t, 2H, J=7.0 Hz, CH_2C), 1.82 (m, 2H, CH_2), 1.57–1.30 (m, 16H, CH_2), 0.15 (s, 9H, TMS). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 107.6, 84.0, 33.8, 32.6, 29.3, 29.2, 28.9, 28.6, 28.4, 28.0, 26.7, 19.7, 0.17. IR (neat): 2924, 2853, 2172, 1463, 1247, 839, 759, 639 cm^{-1}. HRMS (ESI), calcd: 330.1378. Found: 330.1383.

4.4.4. (16-Bromohexadec-1-ynyl)trimethylsilane (**9d**)

According to the general procedure, trimethyl-[10-(tetrahydro-2*H*-pyran-2-yloxy)hexadec-1-ynyl]silane (**8d**, 1.47 g, 3.73 mmol) was deprotected by *p*-toluenesulfonic acid monohydrate (36 mg, 0.19 mmol) in methanol (24 mL). The residue was dissolved in DCM (20 mL) and treated successively with PPh_3 (1.47 mg, 5.6 mmol) in DCM (5 mL) and CBr_4 (1.86 g, 5.6 mmol) in DCM (5 mL). After evaporation of the solvent and chromatography (hexane/ethylacetate 20:1), **9d** was isolated as a colorless oil (1.08 g, 78%)

(cyclohexane/ethylacetate 9:1, R_f=0.66). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 3.40 (t, 2H, J=7.0 Hz, CH_2Br), 2.17 (t, 2H, J=7.0 Hz, CH_2C), 1.91 (q, 2H, J=7.0 Hz, CH_2CH$_2$Br), 1.55–1.26 (m, 22H, CH_2), 0.14 (s, 9H, TMS). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 107.7, 84.1, 33.9, 32.8, 29.56, 29.52, 29.47, 29.42, 29.0, 28.9, 28.7, 28.6, 28.4, 28.1, 19.8, 0.17. HRMS (ESI), calcd: 372.1848. Found: 372.1849. IR (neat): 2925, 2852, 2174, 1464, 1248 cm^{-1}. Anal. Calcd for $C_{19}H_{37}BrSi$: C, 61.10; H, 9.99. Found: C, 60.95; H, 10.01.

4.4.5. *(18-Bromooctadec-1-ynyl)trimethylsilane (**9e**)*

(Trimethylsilyl)octadec-17-yn-1-ol (**10e**, 1.10 g, 3.25 mmol) was dissolved in DCM (20 mL) and treated successively with PPh_3 (1.28 mg, 4.87 mmol) in DCM (5 mL) and CBr_4 (1.62 g, 4.87 mmol) in DCM (5 mL). After evaporation of the solvent and chromatography (hexane/ethylacetate 25:1), **9e** was isolated as a pale yellow oil (1.23 g, 95%) (cyclohexane/ethylacetate 9:1, R_f=0.71). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 3.40 (t, 2H, J=6.9 Hz, CH_2Br), 2.20 (t, 2H, J=6.9 Hz, CH_2C), 1.85 (q, 2H, J=6.9 Hz, CH_2CH$_2$Br), 1.56–1.25 (m, 26H, CH_2), 0.14 (s, 9H, TMS). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 107.7, 84.1, 33.9, 32.8, 29.6, 29.5, 29.5, 29.4, 29.0, 28.7, 28.7, 28.6, 28.4, 28.1, 19.8, 0.18. MS (EI): 328 [M−SiMe$_3$]$^+$. IR (neat): 2925, 2852, 2174, 1464, 1248 cm^{-1}.

4.5. Preparation of trichloro[(trimethylsilyl)alkynyl]-silanes (2a–e)

The glassware was dried with a heat gun at ~500 °C for 3 h under vacuum prior to use, and the Mg was dried in an oven overnight. In a flask flushed with argon were combined the (ω-bromoalk-1-ynyl)trimethylsilanes **9a–e** (2.3 mmol), metallic magnesium (223 mg, 9.25 mmol of finely shredded turnings), and 10 mL of THF. The mixture was allowed to react at rt for 3–4 h during which the color of the solution changed from light yellow to clear black. The Grignard was transferred into a flask containing $SiCl_4$ (1.1 mL, 9.2 mmol) in dry THF (5 mL) under argon. The resulting mixture was stirred overnight at rt. The solvent and residual $SiCl_4$ were removed by a trap-to-trap distillation and the residue was triturated under argon with anhydrous cyclohexane. The supernatant solution was transferred via cannula into a dry flask connected to a cold trap. Concentration in vacuo followed by bulb-to-bulb distillation afforded **2a–e**.

4.5.1. *Trichloro[10-(trimethylsilyl)dec-9-ynyl]silane (**2a**)*

According to the general procedure, (10-bromodec-1-ynyl)-trimethylsilane (**9a**, 662 mg, 2.3 mmol) afforded **2a** (0.41 g, 52%) as a yellow oil: bp 110–125 °C (0.08 mbar). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 2.21 (t, 2H, J=7.0 Hz, CH_2C), 1.64–1.32 (m, 14H, CH_2), 0.15 (s, 9H, TMS). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 107.4, 84.2, 31.6, 28.7, 28.6, 28.5, 28.4, 24.1, 22.1, 19.6, 0.15. IR (neat): 2932, 2854, 2174, 1464, 1093 cm^{-1}.

4.5.2. *Trichloro[12-(trimethylsilyl)dodec-11-ynyl]silane (**2b**)*

According to the general procedure, (12-bromododec-1-ynyl)-trimethylsilane (**9b**, 0.72 g, 2.30 mmol) afforded **2b** (0.49 g, 57%) as a colorless oil: bp 175–190 °C (0.4 mbar). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.21 (t, 2H, J=6.9 Hz, CH_2C), 1.52 (q, 2H, J=6.9 Hz, CH_2CH$_2$C), 1.47–1.28 (m, 16H, CH_2), 0.14 (s, 9H, TMS). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 107.7, 84.2, 31.9, 28.7, 28.6, 28.5, 28.4, 24.1, 22.1, 19.8, 0.16. IR (neat): 2925, 2852, 2174, 1464, 1048 cm^{-1}.

4.5.3. *Trichloro[13-(trimethylsilyl)tridec-12-ynyl]silane (**2c**)*

According to the general procedure, (13-bromotridec-1-ynyl)-trimethylsilane (**9c**, 0.76 g, 2.30 mmol) afforded **2c** (0.54 g, 61%) as a colorless oil: bp 160–180 °C (0.08 mbar). ^{1}H NMR (200 MHz, $CDCl_3$) δ: 2.21 (t, 2H, J=6.9 Hz, CH_2C), 1.63–1.28 (m, 20H, CH_2), 0.14 (s, 9H, TMS). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 107.6, 84.1, 31.6, 29.3, 29.2, 29.1, 28.9, 28.7, 28.6, 28.4, 24.1, 22.1, 19.8, 0.16. IR (neat): 2931, 2855, 2174, 1464, 1101 cm^{-1}.

4.5.4. *Trichloro[16-(trimethylsilyl)hexadec-15-ynyl]silane (**2d**)*

According to the general procedure, (16-bromohexadec-1-ynyl)-trimethylsilane (**9d**, 0.86 g, 2.30 mmol) afforded **2d** (0.52 g, 53%) as a colorless oil: bp 175–185 °C (0.4 mbar). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.21 (t, 2H, J=6.9 Hz, CH_2C), 1.52 (q, 2H, J=6.9 Hz, CH_2CH$_2$C), 1.47–1.28 (m, 24H, CH_2), 0.14 (s, 9H, TMS). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 107.5, 84.0, 31.9, 30.3, 29.2, 29.1, 28.9, 28.8, 28.7, 28.6, 28.4, 24.1, 22.1, 19.3, 0.3. IR (neat): 2936, 2852, 2175, 1466, 1080 cm^{-1}.

4.5.5. *Trichloro[18-(trimethylsilyl)octadec-17-ynyl]silane (**2e**)*

According to the general procedure, (18-bromooctadec-1-ynyl)-trimethylsilane (**9e**, 0.924 g, 2.30 mmol) afforded **2e** (0.61 g, 58%) as a yellow oil: bp 190–200 °C (0.08 mbar). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.21 (t, 2H, J=6.9 Hz, CH_2C), 1.52 (q, 2H, J=6.9 Hz, CH_2CH$_2$C), 1.47–1.28 (m, 28H, CH_2), 0.14 (s, 9H, TMS). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 107.6, 84.0, 33.8, 33.7, 31.9, 30.3, 29.2, 29.1, 28.9, 28.8, 28.7, 28.6, 28.4, 24.1, 22.1, 19.3, 0.3. IR (neat): 2933, 2854, 2175, 1464, 1093 cm^{-1}.

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