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Reaction of hydrosilanes with alkynes catalyzed by gold nanoparticles supported on TiO_2

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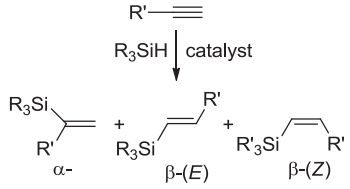
ABSTRACT

Gold nanoparticles supported on TiO_2 (0.8–1.4 mol %) catalyze the β-(*E*) regioselective hydrosilylation of a variety of functionalized terminal alkynes with alkylhydrosilanes in 1,2-dichloroethane (70 °C). The product yields are excellent, and the reaction times relatively short, while almost equimolar amounts of alkynes and hydrosilanes can be used. Minor side-products in up to 35% relative yield of *cis*-oxidative (dehydrogenative) disilylation, an unprecedented reaction pathway, are formed in the cases of the less hindered hydrosilanes and alkynes. Triethoxysilane reacts faster and affords apart from β-(*E*) addition products, minor α-hydrosilylation regio-isomers in upto 15% relative yield. Internal alkynes are generally less reactive or even unreactive. It is proposed that cationic Au(I) species stabilized by the support are the reactive catalytic sites, forming in the presence of hydrosilanes either silyl–Au(III)–H (hydrosilylation pathway) or Au(III)–disilyl species (dehydrogenative disilylation pathway). Regarding the mechanism of hydrosilylation, kinetic experiments are in agreement with silyl carbometallation of the triple bond in the rate determining step of the reaction.

1. Introduction

The selective synthesis of vinyl silanes via hydrosilylation of alkynes plays a crucial role in organic synthesis due to the significance of such key-intermediates in a wide range of synthetic applications. Alkyne hydrosilylation is catalyzed by a variety of cationic metals, including Pt, Pd, Rh, Ru, Ti, Co, Y, Ir, Ni as well as organo–lanthanide, and actinide complexes.[1] Furthermore, alkyne hydrosilylation can be promoted via free radicals.[2] Generally, terminal alkynes are more reactive substrates as compared to their internal counterparts, although a remarkable progress has been recently achieved.[3] Terminal alkynes may provide three possible regioisomeric adducts (Scheme 1) depending on the topology of addition, the α-silyl, and the two diastereomeric β-(*Z*) and β-(*E*) products. The observed selectivity depends on the nature of the catalyst, the substitution of the alkyne and/or hydrosilane, the solvent, and the reaction conditions. To account for the differences in product selectivity, two main mechanisms have been proposed, the Chalk–Harrod,[4] mainly for the cases of Pt, Co, Ni, and Pd-catalyzed additions, which lead to β-(*E*) isomers, and the Crabtree–Ojima[5] for Rh, Ru, Ir, Y, and Ti, that provide selectively or unselectively the thermodynamically unfavorable β-(*Z*) adducts.



Scheme 1. Possible regio-isomeric products from the hydrosilylation of terminal alkynes.

Although numerous metal-catalyzed hydrosilylation methodologies exist, surprisingly, no homogeneous Au(I)-catalyzed protocol is known. Based on a typical transition metal-catalyzed hydrosilylation mechanism that involves oxidative insertion of the metal into the σ Si–H bond, gold in the oxidation state of +1 could reasonably be expected as an active catalyst, operating through a Au(I)/Au(III) catalytic cycle. On the other hand, gold nanoparticles have recently been recognized as active heterogeneous hydrosilylation catalysts, however, few reports appear in the literature and the scope and limitations of this reaction has not been studied. Caporusso and co-workers[6] reported in 2005 the solvent-free hydrosilylation of a single substrate (1-hexyne) using as catalysts acetone-solvated gold nanoparticles supported on carbon and γ-alumina, at 70 °C. Moderate to excellent yields were found, while the selectivity was close to 100% in favor of the β-(*E*) isomers. The same group extended their studies focusing again on

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the hydrosilylation of 1-hexyne.[7] A screening of the size of gold nanoparticles obtained from gold vapor and acetone via the metal vapor synthesis technique, and deposited on a variety of different supports (C, Al_2O_3, Fe_3O_4, CeO_2, TiO_2, and ZrO_2), was achieved. The best results were obtained in the presence of Au/γ-Al_2O_3. In all experiments, a 4/1 ratio of alkyne/silane was used. Corma and co-workers reported[8] that Au nanoparticles supported on CeO_2 (5% mol) catalyze the hydrosilylation of phenylacetylene in high yield and β-(*E*) selectivity (70 °C). The molar ratio of phenylacetylene to the hydrosilanes was 3/1. Unfortunately, these studies were limited to a single substrate (phenylacetylene). Surprisingly, a homogeneous Au(III)-based catalyst used in the same studies was active, and afforded unselectively a mixture of β-(*E*) and β-(*Z*) adducts. Organ and Shore[9] reported that thin gold film on the surface of glass (boronsilicate) capillaries are active catalysts for the fast hydrosilylation of terminal alkynes in a continuous-flow reactor while being heated under microwave irradiation. In all experiments, the molar ratio of alkyne to silane was 2/1. Regarding product selectivity, the β-(*E*) products were always predominating, with β-(*Z*) and α-isomers being formed as side-products. The temperature reached on the gold film inside the microwave apparatus during the continuous-flow experiments was ~185–195 °C.

Following our interest in the use of the readily available gold nanoparticles supported on titania (Au/TiO_2)[10] as a powerful catalyst for the selective isomerization of epoxides into allyl alcohols,[11] cycloisomerization/oxidative dimerization of aryl propargyl ethers,[12] cycloisomerization of 1,6-enynes,[13] and in the oxidative cycloaddition of 1,1,3,3-tetramethyldisiloxane to alkynes,[14] we focus in this manuscript on a detailed examination (scope and limitations) of the Au/TiO_2-catalyzed alkyne hydrosilylation. As it has been noted above, so far the few alkyne hydrosilylation studies involving catalysis by supported gold nanoparticles have been limited to two specific substrates (1-hexyne and phenylacetylene), with rather poor molecular economy as alkynes have been used in 3–4 M excess relative to the silanes.

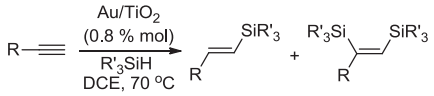
2. Results and discussion

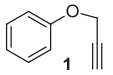
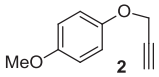
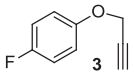
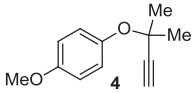
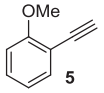
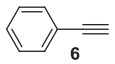
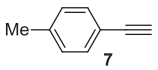
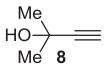
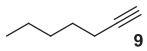
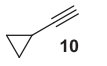
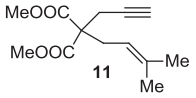
We were pleased to find that by using almost equimolar amounts of terminal alkynes and hydrosilanes and around 0.5–1.0 mol % catalyst loading, the hydrosilylation reactions go to completion within 2–4 h at reflux in 1,2-dichloethane (DCE) as solvent, under an inert atmosphere and strictly dry conditions. The gold nanoparticles can be easily recovered at the end of the reaction and reused with little deterioration of their activity. Since any moisture present into the reaction system hydrolyzes the hydrosilanes into the corresponding silanols and eventually their dehydration products 1,3-disiloxanes, we finally used 1.5–2 equivalents of silanes in all experiments to compensate their partial competitive hydrolysis, as for simplicity the reactions were carried out under open air conditions and the solvent was not exhaustively dried prior to use. The hydrolytic dehydrogenative oxidation of hydrosilanes into silanols/1,3-disiloxanes was independently found in our hands to be catalyzed by Au/TiO_2 under ambient conditions. Several analogous heterogeneous catalytic examples have recently appeared in the literature using hydroxyapatite-supported gold nanoparticles,[15] a nanoporous gold material,[16] and a carbon nanotube–gold nanohybrid.[17] Additionally, the reaction is purely heterogeneous in nature. ICP analysis revealed that the gold content in the supernatant reaction solution was below parts per million level, as shown in previous work from our group.[12]

The examples from the hydrosilylation of a series of terminal alkynes using a variety of alkyl-substituted hydrosilanes (triethylsilane, dimethylphenylsilane, triphenylsilane) are presented in Table 1. Our findings in brief reveal that Au/TiO_2 is an excellent catalyst for the regioselective *cis*-hydrosilylation of functionalized terminal alkynes forming β-(*E*) isomers. α-Isomers were formed in some cases, however, always in <4% relative yield, while β-(*Z*) isomers were not detected at all. The less hindered triethylsilane and dimethylphenylsilane react faster (2–4 h) compared to the bulky triphenylsilane, which requires up 12 h to drive the reactions to completion. Worth mentioning are the reactions of propargyl aryl ethers **1**–**4** in the presence of hydrosilanes that solely provide hydrosilylation products, relative to their cyclization pathway into 2*H*-chromenes[12] in the absence of silanes. Furthermore, no competitive hydrosilylation was seen on the double bond of 1,6-enyne **11**. To establish the selective reactivity of a triple bond relative to a double C–C bond, we tested the hydrosilylation of styrene with Et_3SiH. Under prolonged heating at reflux (8 h), however, traces of hydrosilylation products were seen.[18]

To our surprise, in the reactions of triethylsilane and more profoundly for dimethylphenylsilane, minor products resulting from a *syn*-oxidative disilylation pathway were detected in up to 35% relative yield. Their amount depends on the steric

Table 1
Hydrosilylation/oxidative *cis*-disilylation of terminal alkynes catalyzed by Au/TiO_2

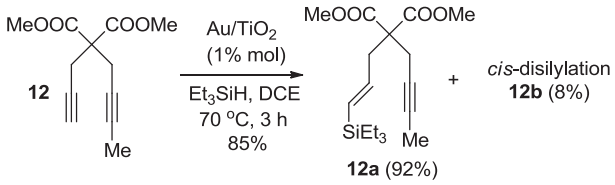


	β-(*E*)	Disilylation	Silane	Time/Yield[a]
	**1a** (89%) **1c** (90%)	**1b** (11%) **1d** (10%)	Et_3SiH $PhMe_2SiH$	3 h/83% 3 h/86%
	**2a** (90%)	**2b** (10%)	Et_3SiH	3 h/84%
	**3a** (92%)	**3b** (8%)	Et_3SiH	2 h/82%
	**4a**	—	Et_3SiH	3 h/95%
	**5a** (95%)	**5b** (4%)	Et_3SiH	3 h/74%
	**6a** (95%) **6c** (88%)	**6b** (5%) **6d** (12%)	Et_3SiH $PhMe_2SiH$	2 h/91% 3 h/86%
	**7a**	—	Ph_3SiH[b]	12 h/85%
	**8a**	—	Ph_3SiH[b]	6 h/84%
	**9a** (65%) **9c**	**9b** (35%) —	$PhMe_2SiH$ Ph_3SiH[b]	2 h/81% 12 h/78%
	**10a** (82%)	**10b** (82%)	$PhMe_2SiH$	3 h/83%
	**11a** (87%)	**11b** (13%)	Et_3SiH	3 h/84%

[a] Isolated overall yields after column chromatography.
[b] 1.4 mol % of catalyst was used.

requirements of silane and alkyne. We were able to isolate in two cases such di-adducts (**9b**, **10b**) in pure form by very careful column chromatography and elucidate their stereochemistry by means of NOE experiments. The relative yield of *cis*-disilanes is nearly independent of the concentration of the reacting silane (0.5–4 equivalents). In addition, di-adducts do not derive from an oxidative silylation of mono-hydrosilylated products, but rather oxidative *cis*-disilylation is competing with the hydrosilylation pathway. Thus, pure alkenylsilanes are unreactive against hydrosilanes when heating at reflux in the presence of Au/TiO_2. For all other di-adducts, being formed in minor amounts, purification was extremely difficult, however, were cleanly seen in the ^1H NMR spectrum of the crude mixtures having a characteristic singlet olefinic absorption in the region of 6.0–7.0 ppm, and by GC–MS. Triphenylsilane did not provide any di-silylation products, apparently due to steric reasons. To the best of our knowledge, this is the first example in the literature that *cis*-disilyl products are formed via double a oxidative addition of mono-hydrosilanes into an alkyne, and is relevant to the Au/TiO_2-catalyzed oxidative cycloaddition of 1,1,3,3-tetramethyldisiloxane to alkynes recently reported[14] by our group. Alternatively, *cis*-disilylation is known[19] via the Pt or Pd-catalyzed addition of 1,2-disilanes to alkynes, while to the best of our knowledge there is one relevant example in the diethyl(bipyridyl)nickel(II)-catalyzed addition of hydrosilanes to internal alkynes, which provides competing pathways of hydrosilylation and dehydrogenative *cis*-disilylation.[20] This example is limited, however, to activated hydrosilanes bearing at least two chlorine substituents.

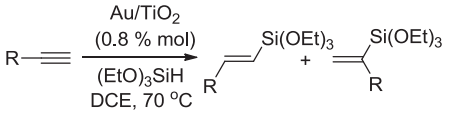
Internal alkynes (diphenylacetylene, 3-hexyne or 1-phenyl-1-propyne) are unreactive even after prolonged heating at reflux. The selective reactivity of terminal versus internal alkynes was clearly shown in the hydrosilylation of diyne **12**, which provides in the presence of triethylsilane the addition product **12a** (accompanied by minor *cis*-disilylated **12b)** in high yield without the internal triple bond being affected (Scheme 2).

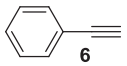
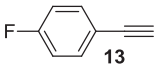
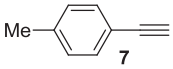
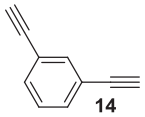
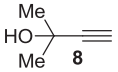


Scheme 2. Selective hydrosilylation of the terminal versus an internal triple bond in diyne **12**.

We next focused on the use of triethoxysilane as a hydrosilylation reagent (Table 2). The vinyl silyloxy hydrosilylation products from alkynes and this specific silane are very useful intermediates for Pd-catalyzed cross coupling reactions[21] with aryl or vinyl halides. It was found that $(EtO)_3SiH$ (1.5–2 equiv) reacts smoothly at 70 °C with a variety of terminal alkynes affording primarily products of the β-(*E*) hydrosilylation pathway. However, in contrast to trialkylsilanes, $(EtO)_3SiH$ additionally provides α-isomers as side-products in up to 15% relative yield. Generally, $(EtO)_3SiH$ reacts faster as compared to Et_3SiH, and the reactions go to completion within 0.5–2 h at reflux in DCE. While symmetrical internal alkynes are either completely unreactive (3-hexyne), or react extremely extremely slowly (diphenylacetylene yields a hydrosilylation product in merely 8% relative yield after heating at reflux for 72 h based on GC–MS analysis), hex-1-yn-1-ylbenzene (**15**) and ethyl but-2-ynoate (**16**) were smoothly hydrosilylated, with **15** forming the single regioisomer **15a** (proof of structure by NOE experiments) in 77% isolated yield (10 h, 70 °C), while **16** provided after 30 min an equimolar mixture of **16a** and **16b**

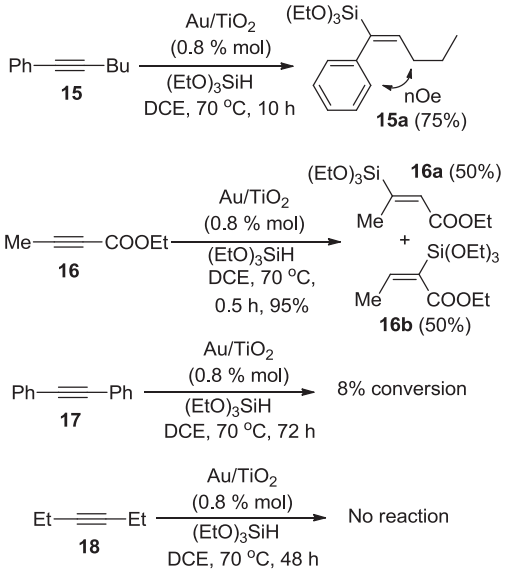
Table 2
Hydrosilylation of terminal alkynes catalyzed by Au/TiO_2 in the presence of $(EtO)_3SiH$



	β-(*E*)	α-	Time/Yield[a]
 6	**6e** (90%)	**6f** (10%)	2 h/91%
 13	**13a** (85%)	**13b** (15%)	1 h/92%
 7	**7b** (90%)	**7c** (10%)	2 h/92%
 14	**14a** (86%)	**14b** (14%)	1.5 h/75%
 8	**8b** (100%)	—	2 h/94%

[a] Isolated yields of combined β-(*E*)+α-hydrosilylation products.

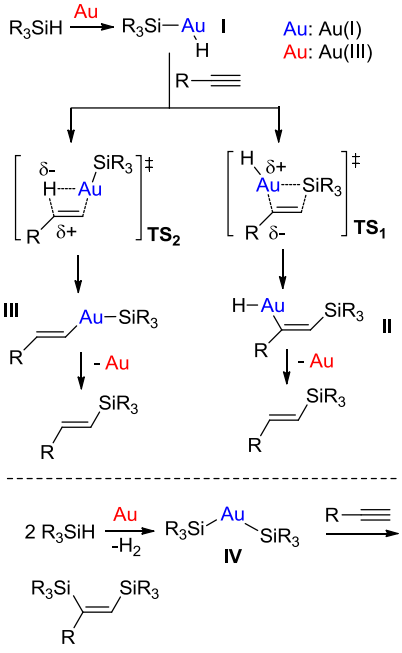
(stereochemistry of adducts proved by NOE experiments) in 95% isolated yield (Scheme 3). Commenting on the case of **15**, analogous selectivity was reported in the homogeneous Pt(II)-catalyzed hydrosilylation of internal aryl alkynes.[22] The high reactivity of internal alkyne **16** could be attributed to the highly polar nature of its triple bond. Alami and co-workers[23] have invoked triple bond polarization arguments to rationalize the regiochemistry in the Pd-catalyzed hydrostannylation of diaryl alkynes. On the other hand, the absence of regioselectivity in the hydrosilylation of **16** is surprising, taken into account the highly polar nature of its triple bond. An explanation is provided in the mechanistic analysis below. For comparison, the Ru and Pd-catalyzed hydrosilylation of **16**[24] and structurally similar compounds yield selectively one regioisomer, analogous to **16a**.



Scheme 3. Hydrosilylation of some internal alkynes with $(EtO)_3SiH$.

To draw mechanistic conclusions, a kinetic study in the competitive hydrosilylation of some aryl acetylenes with triethylsilane was performed. It was found that electron withdrawing substituents on the aryl ring accelerate the reaction rate relative to electron donating substituents. The competitions were carried out upon reacting an equimolar mixture of the competing acetylenes with a limited amount of hydrosilane, at approximately 10–20% conversion. Then the crude reaction mixture was analyzed by GC and ^{1}H NMR spectroscopy. For example, *p*-fluorophenylacetylene (**13**) reacts 2.5 faster as compared to the parent phenylacetylene (**6**). Furthermore, phenylacetylene reacts two times faster upon competing with *p*-tolylacetylene (**7**), and **13** six times faster than the methoxy-substituted **5**. These results indicate the development of a partial negative charge on the benzylic position of aryl acetylenes in the transition state of the rate determining step of the reaction. An analogous kinetic profile had been observed in the $RuCl_2(PPh_3)_3$ catalyzed hydrosilylation of aryl acetylenes with $HSiCl_2Me$.[25]

As supported gold nanoparticles on metal oxide surfaces contain apart from Au^0 oxidized Au species,[26] we chose, based on the preceding discussion in the introduction section of this article, Au^I as the most reasonable active catalytic sites of Au/TiO_2 for hydrosilylation.[27] The Au^I–Au^{III} redox catalytic cycles required for our proposed mechanism shown in Scheme 4 are well documented in the literature.[28] Thus, oxidative insertion of Au^I into the σ Si–H bond[29] of the hydrosilane will generate an Au^{III}–hydride[30] intermediate species **I**. Subsequently, **I** adds to the triple bond through a silylmetallation path forming intermediate **II** via transition state $\mathbf{TS_1}$. The hydrometallation pathway (classical Chalk–Harrod mechanism) to form **III** via $\mathbf{TS_2}$ is unlike. The reason is that in $\mathbf{TS_1}$ a negative charge is developing on the more substituted carbon of the alkyne, in agreement with the kinetic profile of the hydrosilylation of aryl acetylenes presented above. On the other hand, in $\mathbf{TS_2}$ a partial positive charge should develop at the same position. The unselective reaction of **16**, more likely implies the participation of the two competing mechanisms (hydrometallation and silylmetallation). Formation of the oxidative disilylation side-products might involve a gold(III)–disilyl species **IV**, formed either by the dehydrogenative reaction among metal-hydride intermediate **I** and a molecule of hydrosilane (Scheme 4), or by the dehydrogenative direct coupling of two hydrosilane molecules with Au(I). Since there is no significant dependence on the ratio of hydrosilylation/oxidative disilylation with the variation of hydrosilane concentration (alkyne/hydrosilane ratio ranging from 2/1 to 1/3), we tend to propose that the second option (dehydrogenative direct coupling of two hydrosilane molecules with Au) is more likely to occur. The first option (dehydrogenative reaction among metal-hydride **I** and a molecule of hydrosilane) should lead to an increase in the relative ratio of disilylation with increasing hydrosilane concentration. The existence of metal disilyl species of type **IV** is well documented by the reaction of 1,2-disilanes[19] with Pd or Pt, and hydrosilanes with Pt,[31] while recently a relevant specific example was presented[32] in the intermolecular oxidative insertion of a Au(I) salt into a Si–Si bond. Additionally, Kumada has proposed[20] in the Ni(II)-catalyzed dehydrogenative disilylation of alkynes, an analogous disilylnickel intermediate. The possibility that gold(0), as proposed in the catalytic diboration of alkenes,[33] are the catalytic sites cannot be excluded, however, it is rather unlikely in our opinion, as a stepwise disilylation should not be expected to provide one geometrical disilyl isomer.



Scheme 4. Proposed mechanism for the Au/TiO_2-catalyzed terminal alkyne hydrosilylation.

3. Conclusions

In conclusion, we have shown that Au/TiO_2 (0.8–1.4 mol %) is a highly efficient catalyst for the hydrosilylation of a wide variety of functionalized alkynes forming primarily β-(*E*) addition products. Terminal alkynes are significantly more reactive when compared to internal alkynes. An unprecedented dehydrogenative minor *cis*-oxidative disilylation pathway was uncovered for the cases of the less hindered hydrosilanes and alkynes. In the Au/TiO_2-catalyzed hydrosilylation protocol there is no need to add the alkyne into excess relative to the hydrosilane, since over-reaction with the addition products (alkenylsilanes) is not observed. Our proposed hydrosilylation mechanism requires a Au(I)–Au(III) redox catalytic cycle, with a silylmetallation pathway predominating. The current work extends the utility of a readily available catalyst (Au/TiO_2) toward new applications in organic chemistry.

4. Experimental section

4.1. General

The reactions were monitored by thin-layer chromatography (TLC) carried out on silica gel plates (60F-254) with UV light as the visualizing method and an acidic mixture of phosphomolybdic acid/cerium(IV) sulfate accompanied by heating of the plate as a developing system. Flash column chromatography was carried out on SiO_2 (silica gel 60, particle size 0.040–0.063 mm) with the specified eluent. NMR spectra were recorded on a Bruker DPX-300 instrument. Electrospray ionization (ESI) mass spectrometry (MS) experiments were performed with a GC–MS QP 5050 Shimadzu single-quadrupole mass spectrometer. GC analyses and kinetics were performed by using a Shimadzu GC-17A model equipped with a 60 m HP-5 capillary column.

4.2. Synthesis of substrates

Alkynes **5**–**10**, and **13**–**18** are commercially available. Aryl propargyl ethers **1**–**4** were prepared in yields ranging from 89 to 95% by alkylation of the corresponding phenols as described in a previous publication from our group.[12] Enyne **11**[13] and diyne **12**[34] were prepared in 74% and 72% overall yield, respectively, by double alkylation of dimethyl malonate (prenyl bromide, and propargyl

bromide for **11**, and 1-bromo-2-butyne, and propargyl bromide for **12**), as described in the literature.

4.3. Typical procedure for the Au/TiO_2-catalyzed hydrosilylation reaction

To a vial containing phenylacetylene, **6** (67 μL, 0.6 mmol), dimethylphenylsilane (0.155 mL, 1.0 mmol), and 1,2-dichloroethane (2 mL) were added Au/TiO_2 (95 mg, 1 wt % in Au, ~0.005 mmol). The reaction was heated to 70 °C for 2 h, and then the slurry was filtered with the aid of dichloromethane (3 mL) through a short pad of silica gel. The filtrate was evaporated under vacuum and the residue was chromatographed with hexane as eluent to afford a mixture containing **6c** and **6d** (135 mg, 86% yield) in a relative ratio of 88/12.

4.4. Spectroscopic data of hydrosilylation products

4.4.1. (E)-Triethyl(3-phenoxyprop-1-enyl)silane[35] ***(1a)***. Colorless oil. R_f (hexane/ethyl acetate=4/1) 0.71; ^{1}H NMR (300 MHz, $CDCl_3$): 7.30–7.25 (m, 2H), 6.97–6.90 (m, 3H), 6.24 (dt, J_1=19.0 Hz, J_2=4.5 Hz, 1H), 5.98 (dt, J_1=19.0 Hz, J_2=1.5 Hz, 1H), 4.58 (dd, J_1=4.5 Hz, J_2=1.5 Hz, 2H), 0.94 (t, J=8.0 Hz, 9H), 0.68 (q, J=8.0 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 158.6, 142.0, 129.4, 129.0, 120.7, 114.8, 70.8, 7.3, 3.3; MS (EI): 248 (9%), 219 (M^+–Et, 56%), 179 (38%), 151 (100%), 123 (61%), 87 (58%), 69 (34%), 59 (67%); HRMS: M+H^+, found 249.1671. $C_{15}H_{24}OSi$+H, requires 249.1674.

4.4.2. (Z)-(3-Phenoxyprop-1-ene-1,2-diyl)bis(triethylsilane) ***(1b)***. This compound was formed as a side-product to **1a** in 11% relative yield, and could not be separated from **1a** as they have similar R_f values. ^{1}H NMR (300 MHz, $CDCl_3$) characteristic absoprtions: 7.27–7.22 (m, 2H), 6.86–6.70 (m, 3H), 6.67 (s, 1H), 4.62 (br s, 2H), 0.90–0.97 (m, 18H), 0.65–0.71 (m, 12H); MS (EI): 333 (M^+–Et, 17%), 179 (33%), 151 (29%), 115 (100%), 87 (91%), 59 (86%).

4.4.3. (E)-Dimethyl(3-phenoxyprop-1-enyl)(phenyl)silane ***(1c)***. Colorless oil. R_f (hexane/ethyl acetate=10/1) 0.62; IR (neat, cm^{-1}): 2954, 2358, 1598, 1494, 1426, 1367, 1301, 1240, 1153, 1111, 1030, 1015, 986, 784, 751, 729, 690; ^{1}H NMR (300 MHz, $CDCl_3$): 7.53–7.50 (m, 2H), 7.35–7.25 (m, 5H), 6.95–6.89 (m, 3H), 6.29 (dt, J_1=19.0 Hz, J_2=4.0 Hz, 1H), 6.19 (dt, J_1=19.0 Hz, J_2=1.0 Hz, 1H), 4.59 (dd, J_1=4.0 Hz, J_2=1.0 Hz, 2H), 0.37 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 158.6, 142.4, 138.2, 133.8, 130.3, 129.4, 129.0, 127.8, 120.8, 114.8, 70.4, −2.7; MS (EI): 268 (6%), 253 (M^+–Me, 13%), 213 (12%), 190 (6%), 175 (17%), 159 (14%), 151 (100%), 135 (68%), 121 (25%), 105 (17%), 91 (11%), 77(8%), 59 (67%); HRMS: M+H^+, found 269.1354. $C_{17}H_{20}OSi$+H, requires 269.1361.

4.4.4. (Z)-(3-Phenoxyprop-1-ene-1,2-diyl)bis(dimethyl(phenyl)silane) ***(1d)***. This compound was formed as a side-product to **1c** in 10% relative yield, and could not be separated from **1c** as they have similar R_f values. ^{1}H NMR (300 MHz, $CDCl_3$) characteristic absoprtions: 6.99 (s, 1H), 4.56 (d, J=1.5 Hz, 2H), 0.33 (s, 6H), 0.21 (s, 6H); MS (EI): 402 (M^+, 1%), 387 (M^+–Me, 3%), 309 (9%), 213 (18%), 159 (15%), 135 (100%).

4.4.5. (E)-Triethyl(3-(4-methoxyphenoxy)prop-1-enyl)silane ***(2a)***. Colorless oil. R_f (hexane/ethyl acetate=10/1) 0.60; IR (neat, cm^{-1}): 2951, 2908, 2873, 2359, 1505, 1456, 1225, 1106, 1072, 1039, 1015, 822, 794, 717; ^{1}H NMR (300 MHz, $CDCl_3$): 6.85 (d, J=7.0 Hz, 2H), 6.82 (d, J=7.0 Hz, 2H), 6.22 (dt, J_1=19.0 Hz, J_2=4.5 Hz, 1H), 5.98 (dt, J_1=19.0 Hz, J_2=1.5 Hz, 1H), 4.52 (dd, J_1=4.5 Hz, J_2=1.5 Hz, 2H), 3.77 (s, 3H), 0.94 (t, J=8.0 Hz, 9H), 0.59 (q, J=8.0 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 153.8, 152.9, 142.3, 128.8, 115.8, 114.5, 71.6, 55.7, 7.3, 3.3; MS (EI): 278 (33%), 249 (M^+–Et, 33%), 209 (37%), 181 (100%), 153 (98%), 147 (53%), 123 (55%), 115 (57%), 97 (35%), 87 (98%), 77 (18%), 69 (47%), 59 (88%); %); HRMS: M+H^+, found 279.1778. $C_{16}H_{26}O_2Si$+H, requires 279.1780.

4.4.6. (Z)-(3-(4-Methoxyphenoxy)prop-1-ene-1,2-diyl)bis(triethylsilane) ***(2b)***. This compound was formed as a side-product to **2a** in 10% relative yield, and could not be separated from **2a** as they have similar R_f values. ^{1}H NMR (300 MHz, $CDCl_3$) characteristic absoprtions: 6.77 (s, 1H), 4.50 (d, J=1.5 Hz, 2H), 2.75 (s, 3H); MS (EI): 392 (M^+, 2%), 363 (M^+–Et, 4%), 238 (34%), 209 (27%), 181 (23%), 153 (24%), 115 (83%), 87 (100%), 59 (88%).

4.4.7. (E)-Triethyl(3-(4-fluorophenoxy)prop-1-enyl)silane ***(3a)***. Colorless oil. R_f (hexane/ethyl acetate=10/1) 0.69; IR (neat, cm^{-1}): 2952, 2909, 2874, 2359, 1504, 1456, 1369, 1294, 1198, 1096, 1070, 1015, 825, 804, 742, 717; ^{1}H NMR (300 MHz, $CDCl_3$): 6.98–6.92 (m, 2H), 6.88–6.82 (m, 2H), 6.21 (dt, J_1=19.0 Hz, J_2=4.5 Hz, 1H), 5.98 (dt, J_1=19.0 Hz, J_2=1.5 Hz, 1H), 4.53 (dd, J_1=4.5 Hz, J_2=1.5 Hz, 2H), 0.94 (t, J=8.0 Hz, 9H), 0.60 (q, J=8.0 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 156.9 (d, J_{C-F}=237.0 Hz), 154.8, 141.7, 129.3, 115.8 (d, J_{C-F}=2.0 Hz), 115.6 (d, J_{C-F}=17.0 Hz), 71.4, 7.3, 3.3; MS (EI): 266 (8%), 237 (M^+–Et, 36%), 197 (46%), 169 (68%), 141 (46%), 115 (42%), 97 (35%), 87 (67%), 69 (44%), 59 (100%); HRMS: M+H^+, found 267.1575. $C_{15}H_{23}FOSi$+H, requires 267.1580.

4.4.8. (Z)-(3-(4-Fluorophenoxy)prop-1-ene-1,2-diyl)bis(triethylsilane) ***(3b)***. This compound was formed as a side-product to **3a** in 8% relative yield, and could not be separated from **3a** as they have similar R_f values. ^{1}H NMR (300 MHz, $CDCl_3$) characteristic absoprtions: 6.89 (s, 1H), 4.52 (br s, 2H); MS (EI): 351 (M^+–Et, 17%), 269 (13%), 226 (16%), 169 (25%), 125 (27%), 115 (100%), 87 (96%), 59 (90%).

4.4.9. (E)-Triethyl(3-(4-methoxyphenoxy)-3-methylbut-1-enyl)silane ***(4a)***. Colorless oil. R_f (hexane/ethyl acetate=6/1) 0.48; IR (neat, cm^{-1}): 2951, 2909, 2873, 1503, 1463, 1378, 1231, 1211, 1173, 1122, 1039, 996, 892, 842, 791, 773, 717; ^{1}H NMR (300 MHz, $CDCl_3$): 6.89 (d, J=9.0 Hz, 2H), 6.74 (d, J=9.0 Hz, 2H), 6.29 (d, J=19.0 Hz, 1H), 5.67 (d, J=19.0 Hz, 1H), 3.76 (s, 3H), 1.38 (s, 6H), 0.92 (t, J=8.0 Hz, 9H), 0.59 (q, J=8.0 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 155.1, 152.9, 149.4, 124.3, 123.5, 113.7, 80.5, 55.5, 26.7, 7.3, 3.4; MS (EI): 306 (M^+, 1%), 182 (5%), 153 (62%), 140 (20%), 125 (100%), 109 (47%), 97 (62%), 81 (33%), 59 (46%); HRMS: M+H^+, found 307.2104. $C_{18}H_{30}O_2Si$+H, requires 307.2093.

4.4.10. (E)-Triethyl(2-methoxystyryl)silane[36] ***(5a)***. Colorless oil. R_f (hexane) 0.31; ^{1}H NMR (300 MHz, $CDCl_3$): 7.55 (d, J=7.5 Hz, 1H), 7.30 (d, J=19.5 Hz, 1H), 7.23 (t, J=7.5 Hz, 1H), 6.94 (t, J=7.5 Hz, 1H), 6.87 (d, J=7.5 Hz, 1H), 6.39 (d, J=19.5 Hz, 1H), 3.85 (s, 3H), 0.99 (t, J=8.0 Hz, 9H), 0.68 (q, J=8.0 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 156.4, 139.0, 128.9, 126.2, 126.0, 120.6, 120.0, 111.0, 55.5, 7.4, 3.6; MS (EI): 248 (7%), 219 (M^+–Et, 78%), 175 (100%), 147 (42%), 135 (8%), 59 (27%); HRMS: M+H^+, found 249.1687. $C_{15}H_{24}OSi$+H, requires, 249.1685.

4.4.11. (Z)-(1-(2-Methoxyphenyl)ethene-1,2-diyl)bis(triethylsilane) ***(5b)***. This compound was formed as a side-product to **5a** in ~4% relative yield, and was identified by GC–MS. MS (EI): 333 (M^+–Et, 100%), 289 (9%), 233 (16%), 204 (22%), 176 (16%), 115 (42%), 87 (74%), 59 (65%).

4.4.12. (E)-Triethyl(styryl)silane[9] ***(6a)***. Colorless oil. R_f (hexane/ethyl acetate=10/1) 0.72; ^{1}H NMR (300 MHz, $CDCl_3$): 7.48 (d, J=7.0 Hz, 2H), 7.36 (t, J=7.0 Hz, 2H), 7.27 (t, J=7.0 Hz, 1H), 6.95 (d,

J=19.0 Hz, 1H), 6.46 (d, J=19.0 Hz, 1H), 1.03 (t, J=8.0 Hz, 9H), 0.70 (q, J=8.0 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 144.8, 138.2, 128.5, 127.9, 126.3, 125.9, 7.4, 3.5; MS (EI): 218 (18%), 189 (M^+−Et, 100%), 161 (89%), 131 (68%), 105 (38%), 59 (88%); HRMS: M+H$^+$, found 219.1564. $C_{14}H_{22}Si$+H, requires, 219.1569.

*4.4.13. (Z)-(1-Phenylethene-1,2-diyl)bis(triethylsilane) (**6b**).* This compound was formed as a side-product to **6a** in 5% relative yield, and was identified by GC–MS, and by a characteristic absorption of the olefinic hydrogen atom in the ^{1}H NMR spectrum of the crude reaction mixture at 7.01 ppm. MS (EI): 332 (1%), 303 (M^+−Et, 36%), 163 (61%), 115 (53%), 87 (83%), 59 (100%).

*4.4.14. (E)-Dimethyl(phenyl)(styryl)silane[9] (**6c**).* Colorless oil. R_f (hexane/ethyl acetate=10/1) 0.68; ^{1}H NMR (300 MHz, $CDCl_3$): 7.73–7.69 (m, 2H), 7.55 (d, J=7.5 Hz, 2H), 7.48–7.32 (m, 6H), 7.06 (d, J=19.0 Hz, 1H), 6.70 (d, J=19.0 Hz, 1H), 0.55 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 145.4, 134.5, 134.0, 133.1, 129.1, 128.6, 128.3, 128.0, 127.2, 126.6, -2.4. MS (EI): 238 (33%), 223 (M^+−Me, 55%), 145 (49%), 105 (38%), 91 (54%), 77 (58%), 58 (100%).

*4.4.15. (Z)-(1-Phenylethene-1,2-diyl)bis(triethylsilane) (**6d**).* This compound was formed as a side-product to **6c** in 12% relative yield, and could not be separated from **6c** as they have identical R_f values. ^{1}H NMR (300 MHz, $CDCl_3$) characteristic absorptions: 6.91 (s, 1H), 0.35 (s, 6H), 0.33 (s, 6H); MS (EI): 357 (M^+−Me, 8%), 294 (4%), 236 (21%), 135 (100%).

*4.4.16. (E)-(4-Methylstyryl)triphenylsilane[37] (**7a**).* White solid. R_f (hexane/ethyl acetate=10/1) 0.64; ^{1}H NMR (300 MHz, $CDCl_3$): 7.65 (d, J=7.0 Hz, 6H), 7.52–7.40 (m, 9H), 7.23 (d, J=8.0 Hz, 1H), 7.18 (d, J=8.0 Hz, 1H), 7.06 (d, J=19.0 Hz, 1H), 6.97 (d, J=19.0 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 148.9, 138.6, 136.1, 135.7, 134.7, 129.6, 129.3, 128.0, 126.8, 121.5, 21.3; MS (EI): 376 (27%), 298 (58%), 284 (29%), 221 (38%), 207 (15%), 196 (57%), 181 (100%), 155 (15%), 105 (52%), 77 (10%); HRMS: M+H$^+$, found 377.1721. $C_{27}H_{24}Si$+H, requires, 377.1725.

*4.4.17. (E)-2-Methyl-4-(triphenylsilyl)but-3-en-2-ol[38] (**8a**).* Colorless oil. R_f (hexane/ethyl acetate=10/1) 0.22; ^{1}H NMR (300 MHz, $CDCl_3$): 7.53–7.49 (m, 6H), 7.43–7.34 (m, 9H), 6.39 (d, J=19.0 Hz, 1H), 6.29 (d, J=19.0 Hz, 1H), 1.34 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 159.0, 135.9, 134.5, 129.5, 127.9, 118.6, 72.4, 29.4; MS (EI): 326 (M^+−H_2O, 28%), 248 (100%), 199 (92%), 181 (84%), 155 (19%), 129 (17%), 105 (74%), 79 (10%), 53 (16%); HRMS: M+H$^+$, found 345.1682. $C_{23}H_{24}OSi$+H, requires, 345.1675.

*4.4.18. (E)-Hept-1-enyl(dimethyl)phenylsilane[39] (**9a**).* Colorless oil. R_f (hexane/ethyl acetate=10/1) 0.58; ^{1}H NMR (300 MHz, $CDCl_3$): 7.57–7.53 (m, 2H), 7.39–7.35 (m, 3H), 6.15 (dt, J_1=6.0 Hz, J_2=18.5 Hz, 1H), 5.78 (dd, J_1=18.5 Hz, J_2=1.5 Hz, 1H), 2.20–2.13 (m, 2H), 1.46–1.37 (m, 2H), 1.33–1.26 (m, 4H), 0.92 (t, J=6.5 Hz, 3H), 0.34 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 149.5, 139.4, 133.8, 128.8, 127.7, 127.1, 36.8, 31.5, 28.3, 22.5, 14.1, −2.4; MS (EI): 232 (7%), 217 (M^+−Me, 75%), 175 (8%), 161 (58%), 135 (49%), 121 (100%), 105 (27%), 59 (36%).

*4.4.19. (Z)-Hept-1-ene-1,2-diylbis(dimethylphenylsilane) (**9b**).* Colorless oil. R_f (hexane/ethyl acetate=10/1) 0.52; IR (neat, cm^{-1}): 2956, 2925, 2856, 2359, 2341, 1616, 1427, 1246, 1112, 990, 817, 782, 727, 696; ^{1}H NMR (300 MHz, $CDCl_3$): 7.49–7.45 (m, 4H), 7.41–7.28 (m, 6H), 6.63 (s, 1H), 2.28 (t, J=7.5 Hz, 2H), 1.43–1.38 (m, 2H), 1.32–1.22 (m, 4H), 0.89 (t, J=7.5 Hz, 3H), 0.29 (s, 6H), 0.20 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 162.1, 143.2, 140.4, 139.6, 134.2, 133.9, 128.8, 128.6, 127.6 (2C), 44.1, 31.7, 30.0, 22.5, 14.1, −0.2, −0.4; MS (EI): 366 (M^+, 1%), 351 (M^+−Me, 6%), 310 (22%), 231 (28%), 197 (32%), 160 (22%), 135 (100%); HRMS: M+H$^+$, found 367.2281. $C_{23}H_{34}Si_2$+H, requires, 367.2277.

*4.4.20. (E)-Hept-1-enyltriphenylsilane[39] (**9c**).* Colorless oil. R_f (hexane/ethyl acetate=4/1) 0.58; ^{1}H NMR (300 MHz, $CDCl_3$): 7.66 (dd, J_1=1.5 Hz, J_2=7.5 Hz, 6H), 7.53–7.44 (m, 9H), 6.36–6.27 (m, 2H), 2.37–2.33 (m, 2H), 1.59–1.54 (m, 2H), 1.45–1.40 (m, 4H), 1.01 (t, J=6.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 153.8, 136.1, 135.6, 130.2, 128.0, 123.3, 37.1, 31.6, 28.3, 22.6, 14.2; MS (EI): 356 (10%), 285 (94%), 207 (45%), 183 (100%), 146 (20%), 105 (78%), 78 (50%); HRMS: M+H$^+$, found 357.2033. $C_{25}H_{28}Si$+H, requires, 357.2038.

*4.4.21. (E)-(2-Cyclopropylvinyl)dimethyl(phenyl)silane[40] (**10a**).* Colorless oil. R_f (hexane/ethyl acetate=10/1) 0.71; ^{1}H NMR (300 MHz, $CDCl_3$): 7.57–7.52 (m, 2H), 7.38–7.33 (m, 3H), 5.84 (d, J=18.5 Hz, 1H), 5.57 (dd, J_1=18.5 Hz, J_2=8.5 Hz, 1H), 1.56–1.49 (m, 1H), 0.81–0.76 (m, 2H), 0.51–0.46 (m, 2H), 0.33 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 152.7, 139.3, 133.8, 128.8, 127.7, 124.1, 17.6, 7.4, −2.4; MS (EI): 187 (M^+−Me, 55%), 174 (90%), 159 (94%), 145 (59%), 135 (78%); HRMS: M+H$^+$, found 203.1252. $C_{13}H_{18}Si$+H, requires, 203.1256.

*4.4.22. (Z)-(1-Cyclopropylethene-1,2-diyl)bis(dimethyl(phenyl)silane) (**10b**).* Colorless oil. R_f (hexane/ethyl acetate=10/1) 0.66; IR (neat, cm^{-1}): 3067, 2998, 2954, 2897, 2359, 2342, 1427, 1247, 1109, 1047, 1018, 807, 767, 726, 696; ^{1}H NMR (300 MHz, $CDCl_3$): 7.44–7.41 (m, 4H), 7.36–7.26 (m, 6H), 6.36 (s, 1H), 1.62–1.57 (m, 1H), 0.66–0.61 (m, 2H), 0.54–0.51 (m, 2H), 0.32 (s, 6H), 0.19 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 162.1, 143.2, 140.4, 136.8, 134.2, 133.9, 128.8, 128.7, 127.6, 127.6, 22.0, 7.6, −0.1, −0.5; MS (EI): 336 (M^+, 1%), 321 (M^+−Me, 1%), 197 (6%), 186 (18%), 158 (9%), 135 (100%); HRMS: M+H$^+$, found 337.1807. $C_{21}H_{28}Si_2$+H, requires, 337.1803.

*4.4.23. (E)-Dimethyl 2-(3-methylbut-2-enyl)-2-(3-(triethylsilyl)allyl) malonate (**11a**).* Colorless oil. R_f (hexane/ethyl acetate=4/1) 0.59; IR (neat, cm^{-1}): 2952, 2912, 2874, 2359, 2342, 1735, 1456, 1435, 1288, 1231, 1194, 1169, 1071, 1013, 770, 719, 669; ^{1}H NMR (300 MHz, $CDCl_3$): 5.85 (dt, J_1=19.0 Hz, J_2=7.0 Hz, 1H), 5.65 (d, J=19.0 Hz, 1H), 4.95 (t, J=7.5 Hz, 1H), 3.69 (s, 6H), 2.68 (d, J=7.5 Hz, 2H), 2.60 (d, J=7.5 Hz, 2H), 1.70 (s, 3H), 1.60 (s, 3H), 0.91 (t, J=8.0 Hz, 9H), 0.53 (q, J=8.0 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 171.6, 141.6, 135.6, 131.8, 117.6, 58.0, 52.2, 40.1, 31.2, 26.0, 17.9, 7.3, 3.4; MS (EI): 354 (M^+, 1%), 325 (M^+−Et, 28%), 257 (12%), 225 (79%), 199 (18%), 167 (20%), 135 (14%), 117 (58%), 89 (57%), 69 (100%), 59 (48%); HRMS: M+H$^+$, found 355.2301. $C_{19}H_{34}O_4Si$+H, requires, 355.2304.

*4.4.24. (Z)-Dimethyl 2-(2,3-bis(triethylsilyl)allyl)-2-(3-methylbut-2-en-1-yl)malonate (**11b**).* This compound was formed as a side-product to **11a** in 13% relative yield, and could not be separated from **11a** as they have identical R_f values. Yet, it was clearly identified by GC–MS, and in the ^{1}H NMR spectrum of the crude reaction mixture. ^{1}H NMR (300 MHz, $CDCl_3$) characteristic absoprtions: 6.16 (s, 1H), 4.93 (t, J=7.5 Hz, 1H), 3.67 (s, 3H), 2.87 (s, 2H), 2.73 (m, 2H), 2.68 (d, J=7.5 Hz, 2H), 1.66 (s, 3H), 1.55 (s, 3H), 0.77–0.60 (m, 12H); MS (EI): 468 (M^+, 1%), 439 (M^+−Et, 36%), 225 (49%), 115 (45%), 87 (100%), 59 (88%).

*4.4.25. (E)-Dimethyl 2-(but-2-ynyl)-2-(3-(triethylsilyl)allyl)malonate (**12a**).* Colorless oil. R_f (hexane/ethyl acetate=4/1) 0.58; IR (neat, cm^{-1}): 2951, 2908, 2873, 2341, 1608, 1509, 1457, 1415, 1236, 1196, 1178, 1010, 986, 825, 790, 778, 753, 714; ^{1}H NMR (300 MHz, $CDCl_3$): 5.85 (dt, J_1=19.0 Hz, J_2=6.5 Hz, 1H), 5.73 (d, J=19.0 Hz, 1H), 3.72 (s, 6H) 2.84 (d, J=6.5 Hz, 2H), 2.74 (q, J=2.5 Hz, 2H), 1.76 (t, J=2.5 Hz, 3H), 0.92 (t, J=7.5 Hz, 9H), 0.53 (q, J=7.5 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 170.5, 141.0, 132.6, 78.8, 73.4, 57.4, 52.5, 39.9, 23.2, 7.3, 3.5, 3.4; MS (EI): 338 (M^+, 1%), 309 (M^+−Et, 40%), 249 (45%),

221 (7%), 161 (10%), 133, (44%), 117 (74%), 105 (35%), 89 (100%), 75 (26%), 59 (96%); HRMS: M+H$^+$, found 339.1988. $C_{18}H_{30}O_4Si$+H, requires, 339.1991.

*4.4.26. (Z)-Dimethyl 2-(2,3-bis(triethylsilyl)allyl)-2-(but-2-yn-1-yl) malonate (**12b**).* This compound was formed as a side-product to **12a** in 8% relative yield, and could not be separated from **12a** as they have almost identical R_f values. Yet, it was clearly identified by GC–MS, and in the ^{1}H NMR spectrum of the crude reaction mixture. ^{1}H NMR (300 MHz, $CDCl_3$) characteristic absoprtions: 6.19 (s, 1H), 3.71 (s, 3H), 3.00 (s, 2H), 2.82 (q, J=2.5 Hz, 2H), 1.75 (t, J=2.5 Hz), 0.72–0.58 (m, 12H); MS (EI): 423 (M$^+$–Et, 18%), 393 (6%), 247 (13%), 117 (36%), 87 (100%), 59 (89%).

*4.4.27. (E)-Triethoxy(styryl)silane[36] (**6e**).* Colorless oil. R_f (hexane/ethyl acetate=4/1) 0.63; ^{1}H NMR (300 MHz, $CDCl_3$): 7.48 (d, J=7.5 Hz, 2H), 7.38–7.29 (m, 3H), 7.23 (d, J=19.0 Hz, 1H), 6.19 (d, J=19.0 Hz, 1H), 3.90 (q, J=7.0 Hz, 6H), 1.28 (t, J=7.0 Hz, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): 149.1, 137.6, 128.7, 128.5, 126.8, 117.7, 58.6, 18.3; MS (EI): 266 (M$^+$, 6%), 251 (M$^+$–Me, 24%), 222 (29%), 193 (27%), 176 (55%), 149 (68%), 147 (100%).

*4.4.28. Triethoxy(1-phenylvinyl)silane[36] (**6f**).* This known compound was formed as a side-product to **6e** in 10% relative yield, and could not be separated from **12a** as they have almost identical R_f values. ^{1}H NMR (300 MHz, $CDCl_3$) characteristic absoprtions in the crude reaction mixture: 6.15 (d, J=2.5 Hz, 1H), 5.97 (d, J=2.5 Hz, 1H), 3.90 (q, J=7.0 Hz, 6H), 1.27 (t, J=7.0 Hz, 9H); MS (EI): 266 (M$^+$, 3%), 251 (25%), 222 (49%), 207 (8%), 193 (46%), 176 (62%), 149 (81%), 147 (100%), 131 (51%), 119 (32%), 103 (40%), 91 (41%), 79 (74%), 63 (69%).

*4.4.29. (E)-Triethoxy(4-fluorostyryl)silane (**13a**).* Colorless oil. R_f (hexane/ethyl acetate=4/1) 0.56; IR (neat, cm^{-1}): 2974, 2927, 2886, 2359, 2340, 1601, 1507, 1411, 1390, 1294, 1228, 1157, 1070, 992, 954, 830, 795; ^{1}H NMR (300 MHz, $CDCl_3$): 7.47–7.42 (m, 2H), 7.17 (d, J=19.0 Hz, 1H), 7.05–6.99 (m, 2H), 6.08 (d, J=19.0 Hz, 1H), 3.88 (q, J=7.0 Hz, 6H), 1.27 (t, J=7.0 Hz, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): 163.0 (d, J_{C-F}=247.0 Hz), 147.7, 133.9 (d, J_{C-F}=3.0 Hz), 128.4 (d, J_{C-F}=8.0 Hz), 117.5 (d, J_{C-F}=2.0 Hz), 115.4 (d, J_{C-F}=21.5 Hz), 58.6, 18.2; MS (EI): 284 (M$^+$, 18%), 169 (M$^+$–Me, 73%), 240 (75%), 211 (71%), 165 (86%), 147 (73%), 91 (100%); HRMS: M+H$^+$, found 285.1314. $C_{14}H_{21}FO_3Si$+H, requires, 285.1322.

*4.4.30. Triethoxy(1-(4-fluorophenyl)vinyl)silane (**13b**).* This known compound was formed as a side-product to **13a** in 15% relative yield, and could not be separated from **13a** as they have almost identical R_f values. ^{1}H NMR (300 MHz, $CDCl_3$) characteristic absoprtions: 6.10 (d, J=2.5 Hz, 1H), 5.94 (d, J=2.5 Hz, 1H), 3.86 (m, 6H), 1.20 (t, J=7.0 Hz, 9H); MS (EI): 284 (M$^+$, 15%), 269 (73%), 240 (74%), 211 (68%), 194 (35%), 165 (87%), 147 (73%), 118 (67%), 91 (100%), 79 (65%), 63 (58%).

*4.4.31. (E)-Triethoxy(4-methylstyryl)silane[36] (**7b**).* Colorless oil. R_f (hexane/ethyl acetate=4/1) 0.63; ^{1}H NMR (300 MHz, $CDCl_3$): 7.37 (d, J=8.0 Hz, 2H), 7.19 (d, J=19.0 Hz, 1H), 7.15 (d, J=8.0 Hz, 2H), 6.11 (d, J=19.0 Hz, 1H), 3.89 (q, J=7.0 Hz, 6H), 2.35 (s, 3H), 1.27 (t, J=7.0 Hz, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): 149.0, 138.7, 135.0, 129.2, 126.7, 116.3, 53.6, 21.2, 18.2; MS (EI): 280 (M$^+$, 30%), 265 (M$^+$–Me, 84%), 236 (100%), 190 (76%), 118 (98%).

*4.4.32. (E)-Triethoxy(2-methoxystyryl)silane[36] (**7c**).* This known compound was formed as a side-product to **7b** in 10% relative yield, and could not be separated from **7b** as they have almost identical R_f values. ^{1}H NMR (300 MHz, $CDCl_3$) characteristic absorptions: 6.13 (d, J=2.5 Hz, 1H), 5.93 (d, J=2.5 Hz, 1H), 2.33 (s, 3H); MS (EI): 280 (M$^+$, 13%), 265 (77%), 236 (98%), 207 (37%), 190 (70%), 163 (80%), 145 (43%), 118 (100%), 89 (84%), 79 (37%), 63 (37%).

*4.4.33. (E)-Triethoxy(3-ethynylstyryl)silane (**14a**).* Colorless oil. R_f (hexane/ethyl acetate=4/1) 0.61; IR (neat, cm^{-1}): 3294, 2973, 2925, 2885, 1608, 1589, 1571, 1390, 1203, 1165, 1069, 992, 954, 829, 778; ^{1}H NMR (300 MHz, $CDCl_3$): 7.61 (s, 1H), 7.47–7.40 (m, 2H), 7.29 (d, J=7.5 Hz, 1H), 7.16 (d, J=19.0 Hz, 1H), 6.20 (d, J=19.0 Hz, 1H), 3.89 (q, J=7.0 Hz, 6H), 3.08 (s, 1H), 1.27 (t, J=7.0 Hz, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): 147.9, 137.8, 132.1, 130.4, 128.5, 127.1, 122.4, 119.2, 83.3, 77.3, 58.6, 18.3; MS (EI): 290 (M$^+$, 8%), 276 (7%), 244 (23%), 202 (29%), 126 (60%), 79 (57%), 45 (100%); HRMS: M+H$^+$, found 291.1412. $C_{16}H_{22}O_3Si$+H, requires, 291.1416.

*4.4.34. Triethoxy(1-(3-ethynylphenyl)vinyl)silane (**14b**).* This compound was formed as a side-product to **14a** in 14% relative yield, and could not be separated from **14a** as they have almost identical R_f values. ^{1}H NMR (300 MHz, $CDCl_3$) characteristic absoprtions: 6.13 (d, J=2.5 Hz, 1H), 5.98 (d, J=2.5 Hz, 1H), 3.85 (q, J=7.0 Hz, 6H), 3.06 (s, 1H), 1.21 (t, J=7.0 Hz, 9H); MS (EI): 290 (M$^+$, 7%), 244 (23%), 202 (32%), 156 (30%), 135 (28%), 102 (31%), 79 (57%), 63 (58%).

*4.4.35. (E)-2-Methyl-4-(triethoxysilyl)but-3-en-2-ol (**8b**).* Colorless oil. R_f (hexane/ethyl acetate=4/1) 0.50; IR (neat, cm^{-1}): 3341, 2973, 2930, 2359, 2341, 1621, 1426, 1362, 1221, 1021, 960, 905, 835, 806, 785, 761, 714; ^{1}H NMR (300 MHz, $CDCl_3$): 6.53 (d, J=19.0 Hz, 1H), 5.61 (d, J=19.0 Hz, 1H), 3.82 (q, J=7.0 Hz, 6H), 1.30 (s, 6H), 1.23 (t, J=7.0 Hz, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): 159.4, 114.1, 72.0, 58.5, 29.2, 18.2; HRMS: M+H$^+$, found 249.1522. $C_{11}H_{24}O_4Si$+H, requires, 249.1522. M$^+$–H_2O, found 231.1410. $C_{11}H_{22}O_3Si$+H, requires, 231.1416.

*4.4.36. (E)-Triethoxy(1-phenylhex-1-enyl)silane (**15a**).* Colorless oil. R_f (hexane/ethyl acetate=6/1) 0.55; IR (neat, cm^{-1}): 2972, 2925, 2360, 2341, 1490, 1441, 1389, 1166, 1100, 1073, 954, 777, 719, 699; ^{1}H NMR (300 MHz, $CDCl_3$): 7.32–7.26 (m, 2H), 7.21–7.13 (m, 3H), 6.37 (t, J=7.0 Hz, 1H), 3.78 (q, J=7.0 Hz, 6H), 2.08 (q, J=7.0 Hz, 2H), 1.42–1.30 (m, 2H), 1.32–1.20 (m, 2H), 1.17 (t, J=7.0 Hz, 9H), 0.83 (t, J=7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): 147.6, 140.5, 135.2, 128.5, 127.8, 125.7, 58.6, 31.5, 29.5, 22.3, 18.1, 13.9; MS (EI): 322 (M$^+$, 19%), 278 (25%), 221 (14%), 163 (100%), 135 (60%), 119 (85%), 79 (42%), 63 (26%); HRMS: M+H$^+$, found 323.2035. $C_{18}H_{30}O_3Si$+H, requires, 323.2042.

*4.4.37. (E)-Ethyl 3-(triethoxysilyl)but-2-enoate[41] (**16a**).* Colorless oil. R_f (hexane/ethyl acetate=4/1) 0.41; ^{1}H NMR (300 MHz, $CDCl_3$): 6.31 (q, J=2.0 Hz, 1H), 4.17 (q, J=7.0 Hz, 2H), 3.83 (q, J=7.0 Hz, 6H), 2.21 (d, J=2.0 Hz, 3H), 1.29 (t, J=7.0 Hz, 3H), 1.24 (t, J=7.0 Hz, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): 165.7, 151.2, 130.5, 59.8, 58.8, 18.2, 16.8, 14.3; MS (EI): 231 (M$^+$–OEt, 68%), 202 (63%), 187 (100%), 163 (38%), 135 (44%), 79 (83%); HRMS: M+H$^+$, found 277.1463. $C_{12}H_{24}O_5Si$+H, requires, 277.1471.

*4.4.38. (E)-Ethyl 2-(triethoxysilyl)but-2-enoate[41] (**16b**).* Colorless oil. R_f (hexane/ethyl acetate=4/1) 0.35; ^{1}H NMR (300 MHz, $CDCl_3$): 6.80 (q, J=7.0 Hz, 1H), 4.21 (q, J=7.0 Hz, 2H), 3.84 (q, J=7.0 Hz, 6H), 2.05 (d, J=7.0 Hz, 3H), 1.31 (t, J=7.0 Hz, 3H), 1.22 (t, J=7.0 Hz, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): 168.9, 154.4, 128.7, 60.1, 58.8, 18.1, 17.6, 14.3; MS (EI): 231 (M$^+$–OEt, 100%), 202 (31%), 187 (15%), 158 (44%), 119 (24%), 79 (47%); HRMS: M+H$^+$, found 277.1463. $C_{12}H_{24}O_5Si$+H, requires, 277.1471.

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Supplementary data

Copies of ^{1}H and ^{13}C NMR spectra of all compounds, as well as, copies of MS spectra of key compounds. Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2012.08.021.

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