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Acetylenic silyl ketone as polysynthetic equivalent of useful building blocks in organic synthesis

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Abstract—Ethynyl silyl ketone **1** proved to be a very efficient Michael acceptor in carbocupration and metallocupration reactions. In particular, when using carbocuprates, a smooth entry to polyenals can be obtained, while, when using metallocuprates, silyl- and stannyl-propenoyl silanes may be obtained, very powerful intermediates in organic synthesis. © 2001 Elsevier Science Ltd. All rights reserved.

Organosilicon compounds have recently gained a predominant role in the development of novel synthetic methodologies for the preparation of various biologically active compounds, and for their potential in selective organic synthesis.[1] In this context, for instance, allyl,[2] vinyl,[3] and dienylsilanes[4] have received much attention and their synthetic utility has been outlined in numerous new carbon-carbon bond forming reactions.

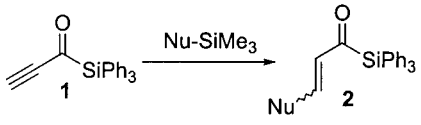
Our interest in organosilicon chemistry has been mainly focused on the synthesis and reactivity of acylsilanes.[5] In recent years these molecules have been shown to be particularly versatile compounds, participating in a number of interesting chemical transformations, some of them particular of the acylsilane moiety, such as Brook rearrangements, oxidation to carboxylic acids and fluoride promoted conversion to ketones and aldehydes.[6] More recently, they have been shown to be particularly useful in the preparation of regio- and stereoisomerically defined enol silyl ethers.[7] Furthermore the presence of a double bond together with the acylsilane moiety provides an expansion of acylsilane synthetic potentialities, and opens the way to the possible construction of novel and more versatile synthons.[8] In this context, unsaturated acylsilanes[9] have recently emerged as useful intermediates, due to the high reactivity of their vinyl moiety.[10] Our interest in this chemistry led us to evaluate the potential of these compounds as effective building blocks for the construction of more complex molecules.

Our recent findings that propenoylsilanes[11] and stannanes[12] undergo very efficient uncatalyzed Michael type reactions with several silylated nucleophiles under rather mild and neutral conditions, prompted us to investigate more closely the reactions of unsaturated acylsilanes toward different Michael donors. The aim being to open a new route to polyfunctionalized molecules, capable of further transformations toward the synthesis of more complex frameworks, i.e. useful intermediates in the construction of biologically active compounds. In particular our attention has been focused on the reactivity of a particular acylsilane, acetylenic silyl ketone **1**, which in our opinion could have disclosed an even higher degree of reactivity of the parent ethylenic derivative.

In this paper we report on our recent results on the reactivity and the synthetic potentialities of acetylenic silyl ketone **1** as a useful synthetic equivalent. Preliminary accounts of this reactivity have appeared.[13]

1. Carbocupration reactions

Recently we disclosed the spontaneous reactivity between acetylenic silyl ketone **1** with different silylated nucleophiles to afford, in mild conditions, a variety of β-functionalized propenoylsilanes (Scheme 1).[14] Beside offering a new methodology for the synthesis of various heterofunctionalized propenoylsilanes, silyl ketone **1** acts as a very



Nu = R_2N, RS, Hal, N_3

Scheme 1.

Keywords: acylsilanes; cuprates; Michael reactions; polyenes; polyenals.
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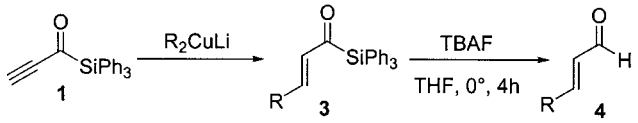
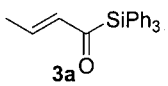
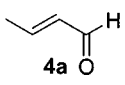
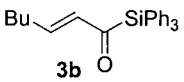
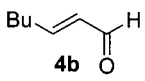
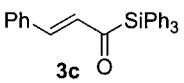
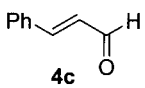
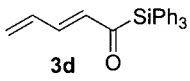
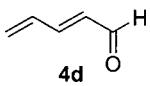
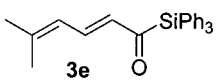
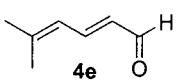
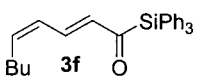
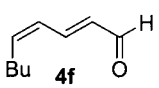
PII: S0040-4020(01)00578-6

Table 1. Synthesis of β-functionalized α,β-unsaturated acylsilanes and aldehydes



R	Product	Conditions	Yield (%)[a]	Aldehyde	Yield (%)[a]
Me	 **3a**	Et_2O, -78°C 40 min	93	 **4a**	78
Bu	 **3b**	Et_2O, -78°C 40 min	89	 **4b**	84
Ph	 **3c**	Et_2O, -78°C 40 min	89	 **4c**	79
	 **3d**	Et_2O, -78°C 1 h	73	 **4d**	68[b]
	 **3e**	Et_2O, -78°C 1h	70	 **4e**	81[c]
	 **3f**	Et_2O, -78°C, 1h -30°C 30 min	63	 **4f**	86[d]

[a] Yield are of chromatographically pure compounds.
[b] Ref. 25.
[c] Ref. 26.
[d] Ref. 27.

good Michael acceptor, underlining the very different chemical behaviour between such compounds and propargyl aldehyde, a compound which is structurally related, and which can be easily obtained from ketone **1** by simple fluoride ion induced desilylation.[15]

These concepts prompted us to investigate deeper the chemical behaviour of compound **1** toward nucleophiles of a different nature such as carbocuprates. Carbocupration of acetylenic esters has in fact found a wide range of synthetic applications, although in some cases it is difficult to avoid some isomerized product.[16] The reaction of acetylenic ketones and aldehydes is even more sensitive to this isomerization, although the $RCu–BR'_3$ reagent[17] seems somewhat more efficient in this respect. In this context, Normant and Alexakis have presented the carbocupration of acetylenic acetals as an alternative methodology to the carbocupration of acetylenic esters, ketones and aldehydes.[18]

Although some carbocupration reactions on ethylenic derivatives have been reported,[9] no such detailed study on the acetylenic series has yet been presented in the literature.

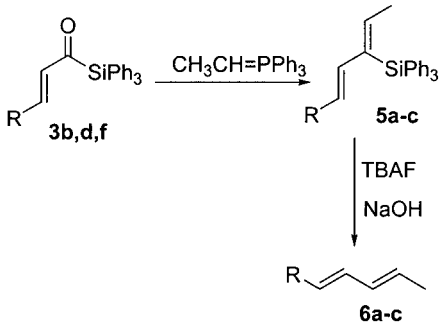
Thus, acetylenic silyl ketone **1** reacts smoothly when treated with different carbocuprates, leading to the isolation in good to excellent yield, of the corresponding Michael adducts **3a–f** (Table 1).

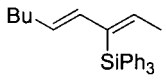
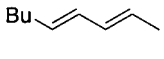
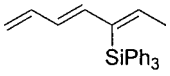
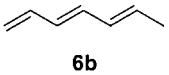
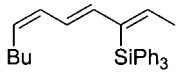
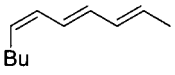
Both aliphatic, aromatic and unsaturated cuprates react disclosing a novel access to the class of mono- and polyunsaturated acylsilanes.[19] All the carbocupration reactions proved to be completely stereoselective, the *E* isomers being the only isolated products. Examples of this reactivity are summarized in Table 1.

In this context, of particular synthetic interest it appears the synthesis of polyunsaturated acylsilanes **3d–f**. It is in fact well established that acylsilanes can be easily converted into the corresponding aldehydes by simple treatment with TBAF in THF at room temperature. This chemical behaviour can be well applied to the newly synthesized acylsilanes, affording the corresponding aldehydes **4a–c**. Particularly interesting is the desilylation of acylsilanes **3d–f** to obtain polyenals **4d–f** in good yield (Table 1).

This methodology then discloses a novel access to stereochemically pure polyenals,[20] useful intermediates in the

Table 2. Wittig reaction and desilylation

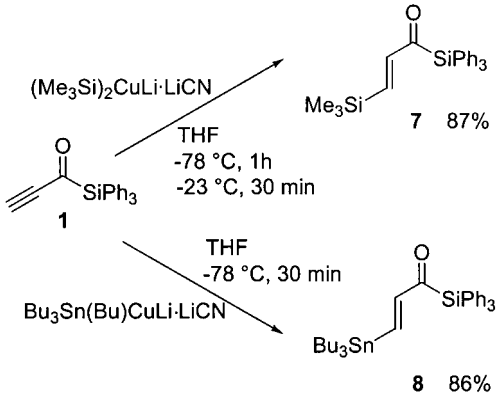


Compound **5**	Yield (%)[a,b]	Compound **6**	Yield (%)[a,c]
 **5a**	83	 **6a**	91
 **5b**	78	 **6b**	82
 **5c**	74	 **6c**	89

[a] Yields are of chromatographically pure compounds.
[b] Reactions run in ether at room temperature for 24 h.
[c] Reactions run in refluxing NaOH/TBAF for 12 h.

stereoselective synthesis of conjugated polyenes, a class of compounds which includes natural products such as arachidonic acid metabolites and insect pheromones. Results are summarized in Table 1.

The importance of this general access to dienoylsilanes is not limited to the synthesis of polyenals. This is best demonstrated in their use as intermediates in synthetic organic chemistry by further transformations. While in fact, *Z*-alkenes may be conveniently obtained by reactions of different aldehydes in the Wittig conditions, the same cannot be said for *E*-alkenes when non-stabilized ylides are used. On the contrary, the use of acylsilanes may offer



Scheme 2.

an easy access to this class of compounds.[21] Upon reaction of α,β-unsaturated acylsilanes **3b**, **d**, **f** with ethylidenetriphenylphosporane, the corresponding *Z*-silylated derivatives **5a–c** are obtained in satisfactory yield. Again simple desilylation, with retention of geometry, of compounds **5a–c** affords a stereoselective access to polyenes **6a–c** with *E* geometry of the newly formed terminal double bond (Table 2).

Moreover, the presence of a vinylsilane moiety in compounds **5a–c**, may provide a further functionalization site, thus leading to richly functionalized molecules. Then, in conclusion, dienoylsilanes may afford an easy access both to *Z* or *E* terminal polyenes, in strict relation to the particular synthetic needs (Table 2).

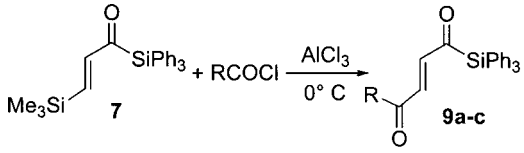
2. Metallocupration reactions

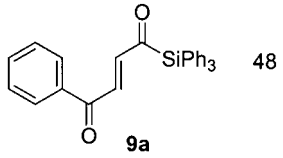
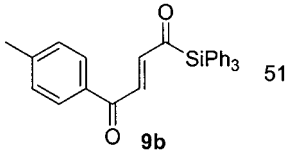
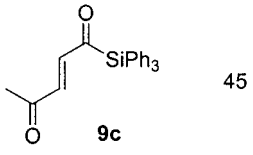
The clean and high yielding reactivity demonstrated by carbocuprates prompted us to investigate different Michael donors, whose intrinsic structure could give the starting molecule a further degree of reactivity.

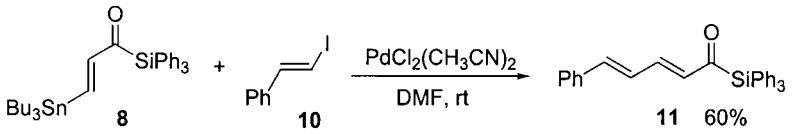
Metallocupration reactions[22] have only recently emerged as powerful tools in organic synthesis, and they appear to be the reactions of choice.

Thus, upon reacting silyl ketone **1** with both silyl and stannyl cuprates, a clean reaction occurred, and the corresponding adducts could be isolated in excellent yields allowing an easy access to polymetalated molecules, whose reactivity could possibly be tuned in strict relation to the nature of both the C–Si and the C–Sn bonds (Scheme 2), for instance, compound **7** may be easily reacted with acyl

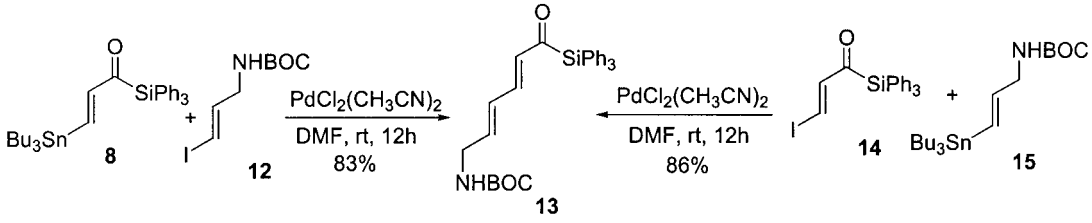
Table 3. Synthesis of polyfunctionalized propenoylsilanes



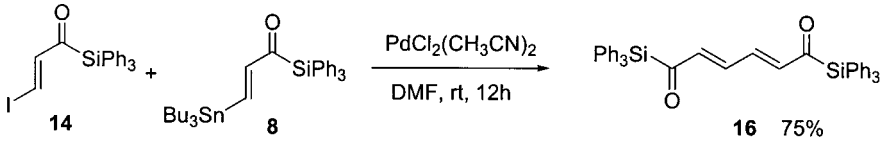
Electrophile	Product	Yield (%)
PhCOCl	 **9a**	48
4-TolylCOCl	 **9b**	51
CH_3COCl	 **9c**	45



Scheme 3.



Scheme 4.



Scheme 5.

chlorides in the presence of $AlCl_3$ to afford the still unreported conjugated enediones **9a–c**. Examples of this reactivity are summarized in Table 3.

The stannyl derivative **8** proved even more interesting from the synthetic point of view. Upon reaction with different vinyl iodides under palladium catalyzed conditions, a clean reaction occurred, opening an alternative and general synthetic pathway to dienoylsilanes, as reported in Scheme 3.

This reactivity, as shown in Scheme 4, is not restricted to simple vinyl iodides, but may be conveniently extended to more functionalized molecules, such as the NH–BOC protected derivative **12**, thus envisaging a general behaviour of this class of compounds, that can be easily reacted with **8** to afford compound **13**, which can be considered a building block for more complex biologically active molecules, such as oxazolomycin.

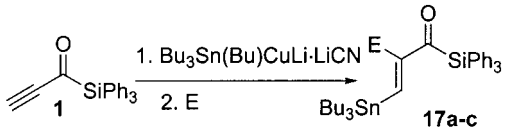
Furthermore the same compound **13** can be obtained by reacting **14** with **15**, in similar yields by the use of the classical reactivity of an enonic framework toward stannylated nucleophiles (Scheme 4).[23]

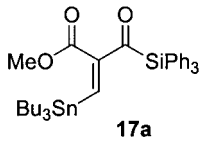
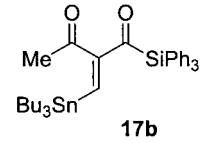
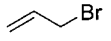
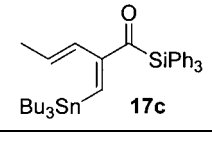
This shows that by using stannylcupration reactions, a fine tuning of the reactional polarity of the C-3 carbon of the enonic framework can be achieved in a nucleophilic fashion.

A further probe of this peculiar behaviour is the synthesis of the dienoylbisacylsilane **16**[24] that can be conveniently obtained from the same starting compound, namely acetylenic silyl ketone **1**, in which again the reactional polarity of the C-3 carbon atom may be selected both toward a nucleophilic or an electrophilic behaviour in strict relation to the synthetic needs (Scheme 5).

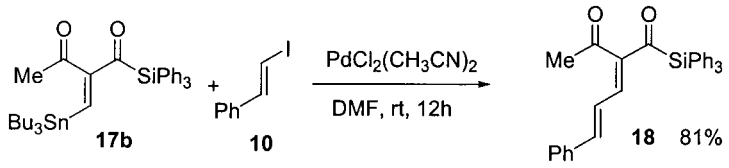
The versatility of the 'stannylcupration' technique is not limited to the β-functionalization of the ethynyl silyl ketone **1**, but the vinylcuprate intermediate may be easily further functionalized by 'in situ' quench with different electrophiles, thus leading to richly functionalized molecules. Results are reported in Table 4.

Table 4. Double functionalization of **1**



Electrophile	Product	Yield (%)
CO_2 Me_2SO_4	 **17a**	83[a]
CH_3COCl	 **17b**	68[b]
	 **17c**	51[b]

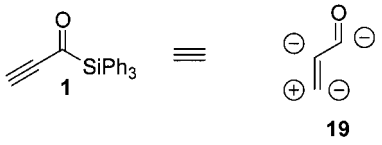
[a] −78°C to −10°C, 1.5 h, rt.
[b] −78°C, 30 min; 20°C, 30 min.



Scheme 6.

Finally, the polyfunctionalized vinylstannanes thus obtained may be further reacted under Pd catalysis to afford, as in the case of compound **17b**, extremely richly functionalized molecules, whose interest as building blocks for the synthesis of much more complex molecules is evident (Scheme 6).

Thus, in conclusion, acetylenic silyl ketone may effectively be considered a much more versatile synthetic equivalent than simply a masked propargyl aldehyde, and propose compound **1** as real building block for the construction of polyfunctionalized molecules. Moreover, the chemistry reported definitely shows that compound **1** could be considered as the real synthetic equivalent of the synthon **19**.



3. Experimental

3.1. General

NMR spectra were recorded at 200 and 300 MHz on Varian Gemini 200 and Varian VXR 300 spectrometers, and were measured as $CDCl_3$ solutions. All solvents were dried with standard techniques, and distilled before use or stored over molecular sieves. Column chromatography was carried out with the flash chromatography technique on silica gel. Preparative TLC was performed by using silica gel plates. All the reactions were run under a dry nitrogen or argon atmosphere. Organic solutions were dried over Na_2SO_4. Unless otherwise mentioned, starting materials were obtained from commercial sources and used without further purification.

3.1.1. General procedure (compounds 3a–f). A solution of the appropriate carbocuprate (1 mmol), prepared according to the literature, is cooled to −78°C and treated dropwise with a solution of **1** (1 mmol) in anhydrous diethyl ether (3 mL) and stirred at this temperature. After quenching with a saturated ammonium chloride solution (5 mL), the mixture is warmed to room temperature and diluted with diethyl ether (3 mL). The organic layer is separated, washed with ammonia buffer (5 mL), water (3×5 mL) and dried over Na_2SO_4. Evaporation of the solvent affords the crude product, which can be purified on silica gel (petroleum ether/diethyl ether).

3.1.2. (2*E*)-Butenoyltriphenylsilane (3a). Following the general procedure, a mixture of CuBr·Me_2S (0.345 g, 1.68 mmol) and freshly distilled Me_2S (2 mL) in anhydrous diethyl ether (2 mL) is cooled to 0°C under argon atmosphere, and slowly treated under vigorous stirring with 1.6 M ethereal solution of MeLi (2.1 mL, 3.36 mmol),[28] warmed to room temperature for 10 min, then cooled to −78°C and treated dropwise with **1** (0.524 g, 1.68 mmol) in anhydrous diethyl ether (5 mL) over a period of 10 min. After 40 min stirring at −78°C the reaction mixture was quenched with saturated ammonium chloride solution (10 mL), allowed to reach room temperature and diluted with diethyl ether (5 mL). The organic layer was separated, washed with ammonia buffer (10 mL), water (3×10 mL), dried over Na_2SO_4 and filtered. Concentration of the filtrate followed by chromatographic purification (SiO_2, petroleum ether/diethyl ether) provided 0.51 g (yield 93%) of **3a** as a bright yellow oil, which is stable for several months if stored in the cold. IR (CCl_4, cm^{-1}): 3040, 2970, 1605, 1475, 1375, 1300, 1250, 970, 750, 690. ^1H NMR (δ, $CDCl_3$, 300 MHz): 7.71–7.32 (m, 15H), 6.68 (dq, 1H, J=17.1, 6.6 Hz), 6.5 (dq, 1H, J=17.1, 1.3 Hz), 1.8 (dd, 3H, J=6.6, 1.3 Hz). ^{13}C NMR (δ, $CDCl_3$, 75 MHz): 231.3, 145.2, 138.5, 136.7, 135.4, 130.3, 128.3, 18.7. MS (*m/z* %): 328 (M^+, 3), 313 (7), 312 (3), 287 (83), 259 (61), 182 (100), 105 (30), 77 (93), 53 (12). HRMS: $C_{22}H_{20}OSi$, calcd 328.1283; found 328.1273.

3.1.3. (2*E*)-Heptenoyltriphenylsilane (3b). A mixture of CuBr·Me_2S (0.065 g, 0.32 mmol) and freshly distilled Me_2S (0.38 mL) in anhydrous ether (1 mL) is cooled to −78°C under argon atmosphere, and slowly treated with 1.6 M solution of *n*-BuLi (0.4 mL, 0.64 mmol)[29], then warmed to −50°C for 10 min, then cooled again to −78°C and treated with a solution of **1** (100 mg, 0.32 mmol) in anhydrous diethyl ether (1 mL). After 40 min stirring at −78°C the reaction is worked up as before, to afford, after chromatographic purification (SiO_2, petroleum ether/diethyl ether) 100 mg of **3b** as a yellow oil (89%). IR (CCl_4, cm^{-1}): 3025, 2950, 1615, 1476, 1370, 1307, 1251, 980, 763, 694. ^1H NMR (δ, $CDCl_3$, 300 MHz): 7.68–7.33 (m, 15H), 6.67 (dt, 1H, J=16.0, 6.8 Hz), 6.43 (dt, 1H, J=16.0, 1.0 Hz), 2.11–1.96 (m, 2H), 1.42–1.15 (m, 4H), 0.94 (t, 3H J=5.5 Hz). ^{13}C NMR (δ, $CDCl_3$, 50 MHz): 230.8, 151.0, 138.5, 136.8, 135.4, 130.3, 128.3, 28.0, 25.0, 21.0, 17.1. MS (*m/z*, %): 370 (M^+, 2), 327 (31), 313 (70), 287 (56), 259 (73), 182 (100), 105 (38), 77 (89), 53 (18). Anal. calcd for $C_{25}H_{26}OSi$: C, 81.03; H, 7.07. Found: C, 80.79; H, 7.21.

3.1.4. (2*E*)-3-Phenyl-propenoyltriphenylsilane (3c). CuBr·Me_2S (0.250 g, 1.22 mmol) and freshly distilled Me_2S (1.5 mL) in anhydrous diethyl ether (1.5 mL) are cooled to 0°C and slowly treated under inert atmosphere with a 2 M solution of PhLi in cyclohexane/ether (1.2 mL, 2.44 mmol), then allowed to react for 15 min. The mixture is cooled to −78°C and treated dropwise with a solution of **1**

(0.381 g, 1.22 mmol) in anhydrous diethyl ether (3.5 mL). After 40 min at −78°C the mixture is worked-up as described before to afford, after purification on silica gel (hexanes/diethyl ether), 433 mg of **3c** as a yellow thick oil (89%). IR (CCl_4, cm^{-1}): 3039, 1607, 1580, 1470, 1255, 894. ^1H NMR (δ, $CDCl_3$, 200 MHz): 7.85–7.36 (m, 21H), 6.56 (d, 1H, J=15.8 Hz). ^{13}C NMR (δ, $CDCl_3$, 50 MHz): 226.6, 151.4, 135.4, 134.6, 132.7, 129.3, 128.9, 128.5, 127.8, 127.4, 125.7. MS (*m/z*, %): 390 (M^+, 2), 313 (73), 287 (51), 259 (63), 182 (100), 105 (27), 77 (78). Anal. calcd for $C_{27}H_{22}OSi$: C, 83.03; H, 5.68. Found: C, 82.81; H, 5.42.

3.1.5. (2*E*)-2,4-Pentadienoyltriphenylsilane (3d). A mixture of $CuBr{\cdot}Me_2S$ (40 mg, 0.19 mmol) and freshly distilled Me_2S (0.2 mL) in anhydrous ether (0.5 mL) is cooled to −78°C under argon atmosphere, and treated with a 2.0 M ethereal solution of vinyllithium (0.2 mL, 0.40 mmol),[28] warmed to −60°C for 20 min, then cooled again to −78°C and treated dropwise with a solution of **1** (50 mg, 0.16 mmol) in anhydrous diethyl ether (1.5 mL). After 1 h stirring at −78°C the reaction is worked up as before, to afford, after chromatographic purification (SiO_2, petroleum ether/diethyl ether) 39 mg of **3d** (73%) as a pale brown oil. IR (CCl_4): 3031, 1600, 1475, 1255, 751, 693. ^1H NMR (δ, $CDCl_3$, 300 MHz): 7.70–7.29 (m, 15H), 6.89 (dd, 1H, J=15.6, 10.8 Hz), 6.52 (bd, 1H, J=15.6 Hz), 6.35 (apparent dt, 1H, J=16.8, 10.8, 9.9 Hz), 5.47 (dd, 1H, J=9.9, 0.6 Hz), 5.42 (dd, 1H, J=16.8, 0.6 Hz), ^{13}C NMR (δ, $CDCl_3$, 50 MHz): 231.2, 149.8, 138.8, 136.8, 136.0, 135.4, 130.3, 128.2, 118.4, MS (*m/z*, %): 340 (M^+, 26), 313 (3), 259 (100), 182 (95), 155 (45), 105 (71), 53 (65). HRMS: $C_{23}H_{20}OSi$ calcd 340.1283, found 340.1298.

3.1.6. (2*E*)-5-Methyl-2,4-hexadienoyltriphenylsilane (3e). 2-Methyl-1-propenyllithium is prepared under argon atmosphere from a suspension of lithium pieces (0.157 g, 22.6 mmol) in anhydrous diethyl ether (20 mL) by adding 1 mL of a solution of 2-methyl-1-bromo-propene (2.7 g, 20.0 mmol) in anhydrous diethyl ether (5 mL).[30] An exotermic reaction is observed, and after 30 min the remaining 4 mL of the ethereal solution of the bromine derivative are added. The mixture is reacted for 3 h and filtered to remove unreacted lithium and lithium bromide. 0.46 mL (0.37 mmol) of this solution are then added to a −78°C cooled solution of $CuBr{\cdot}Me_2S$ (0.038 g, 0.18 mmol) in anhydrous ether (0.25 mL) and Me_2S (0.2 mL). After 40 min stirring at −78°C the temperature is raised to −50°C for 1 h and cooled again to −78°C, then treated with **1** (50 mg, 0.16 mmol) in anhydrous diethyl ether (1 mL). After 1 h stirring at −78°C the reaction is warmed to −50°C for 40 min, then recooled to −78°C and worked up as before, to afford, after chromatographic purification (SiO_2, petroleum ether/diethyl ether) 41 mg of **3e** (70%, dark yellow oil). IR (CCl_4, cm^{-1}): 3030, 1604, 1375, 1250, 969, 843, 760. ^1H NMR (δ, $CDCl_3$, 300 MHz): 7.71–7.30 (m, 15H), 6.65–6.61 (m, 1H, J=17.1, 10.4, 1.3 Hz determined through spin–spin decoupling experiments), 6.54–6.41 (m, 1H), 6.31 (dd, 1H, J=17.1, 0.8 Hz), 1.88 (d, 3H, J=1.4 Hz), 1.81 (d, 3H, J=1.1 Hz). ^{13}C NMR (δ, $CDCl_3$): 235.4, 148.0, 138.6, 136.9, 135.4, 130.3, 128.5, 128.3, 125.1, 18.9, 18.7. MS (*m/z*, %): 368 (M^+,1), 353 (27), 313 (1), 287 (80), 259 (80), 182 (100), 105 (31), 77 (78), 53 (8), 51 (9). Anal. calcd for $C_{25}H_{24}OSi$: C, 81.47; H, 6.56. Found: C, 81.00; H, 6.79.

3.1.7. (2*E*,4*Z*)-Nona-2,4-dienoyltriphenylsilane (3f). A solution of (*Z*-hexenyl)cuprate, prepared according the reported procedure[31] from $CuBr{\cdot}Me_2S$ (130 mg, 0.64 mmol), 1.6 M solution of *n*-BuLi (0.8 mL, 1.28 mmol) and acetylene, is cooled to −78°C and treated dropwise with a solution of **1** (0.156 g, 0.5 mmol) in anhydrous diethyl ether (2 mL). The orange solution is stirred 1 h at −78°C, then 30 min at −30°C, the reaction mixture was quenched and worked up in the usual way. Chromatographic purification (SiO_2, petroleum ether/diethyl ether) provided 125 mg (63%) of **3f** (dark yellow oil). IR (CCl_4, cm^{-1}): 3030, 2961, 1590, 1475, 1376, 889, 757, 698. ^1H NMR (δ, $CDCl_3$, 300 MHz): 7.69–7.36 (m, 15H), 6.97–6.80 (m, 1H, J_{trans}=16.9 Hz, determined through spin–spin decoupling experiments), 6.76–6.58 (apt, 1H, J_{cis}=9.0 Hz, determined through spin–spin decoupling experiments), 6.54–6.41 (m, 1H, J_{cis}=9 Hz), 6.31 (dd, 1H, J_{trans}=16.9 Hz), 2.20–2.01 (m, 2H), 1.67–1.50 (m, 4H), 1.01–0.88 (m, 3H). ^{13}C NMR (δ, $CDCl_3$, 75 MHz): 235.4, 148.5, 138.1, 136.9, 135.4, 130.3, 128.4, 128.3, 126.3, 30.7, 25.1, 19.4, 17.4. MS (*m/z*, %): 339 (M^+−57, 28), 313 (6), 312 (9), 287 (80), 259 (50), 182 (100), 105 (18), 77 (93), 53 (8). HRMS: $C_{27}H_{28}OSi$ calcd 396.1902, found 396.1910.

3.1.8. General procedure (compounds 4a–f). A solution of triphenylsilylacylsilane **3a–f** (0.5 mmol) in THF (0.5 mL) is cooled to 0°C and treated with a solution of TBAF (0.5 mmol) in THF (1 mL). After stirring 4 h at this temperature, the mixture is diluted with diethyl ether, quenched with a saturated solution of $NaHCO_3$ and allowed to reach room temperature. The organic layer is separated, washed with water (2×3 mL) and dried over Na_2SO_4. Evaporation of the solvent affords the aldehydes **4a–f** as yellow oils, which can be purified on silica gel (petroleum ether/diethyl ether).

Spectroscopical data for aldehydes **4a–c** are consistent with an autentic specimen. Data for compounds **4d–f** are identical to those reported in the literature.[25–27]

3.1.9. (2*Z*,4*E*)-3-Triphenylsilyl-2,4-nonadiene (5a). *Typical procedure*. A solution of ethylidenetriphenylphosphorane, prepared from ethyltriphenylphosphonium bromide (102 mg, 0.27 mmol) in dry dietyl ether (1.5 mL) and 2 M solution of phenyllithium in cyclohexane/ether (1.3 mL, 0.27 mmol), was treated with a solution of 2(*E*)-heptenoyltriphenylsilane **3b** (100 mg, 0.27 mmol) in anhydrous ether (1 mL). After 24 h stirring at room temperature, the reaction mixture is diluted with diethyl ether (5 mL), and poured into 10% HCl solution (10 mL). The organic layer is separated, washed with 10% HCl (5 mL) and water (3×10 mL), and dried over Na_2SO_4. Removal of the solvent and chromatographic purification (SiO_2, petroleum ether/diethyl ether) affords 85 mg (83%) of **5a** as a pale yellow oil. IR (CCl_4, cm^{-1}): 3071, 3028, 2975, 2938, 1591, 1475, 1378, 1309, 1260, 751, 718, 695. ^1H NMR (δ, $CDCl_3$, 300 MHz): 7.76–7.30 (m, 15H), 6.28 (dd, 1H, J=16.8, 0.7 Hz), 5.10 (dt, 1H J=16.8, 5.8 Hz), 4.91 (dq, 1H, J=6.6, 0.7 Hz), 2.11–2.01 (m, 2H), 1.71–1.40 (m, 5H),

1.22–0.80 (m, 5H). ^{13}C NMR (δ, $CDCl_3$, 75 MHz): 138.7, 136.1, 135.2, 133.4, 130.3, 129.3, 128.2, 127.1, 36.8, 22.4, 18.7, 15.9, 13.7. MS (*m/z*, %): 382 (M^+, 28), 367 (12), 325 (88), 287 (100), 259 (83), 182 (100), 53 (12). Anal. calcd for $C_{27}H_{30}Si$: C, 84.76; H, 7.90. Found: C, 84.68; H, 8.03.

3.1.10. (3*E*,5*Z*)-5-Triphenylsilyl-1,3,5-heptatriene (5b). Yield: 78% (yellow oil). IR (CCl_4, cm^{-1}): 3090, 3035, 2960, 2930, 2860, 1640, 1620, 1465, 1440, 975, 945, 900. ^{1}H NMR (δ, $CDCl_3$, 300 MHz): 7.70–7.30 (m, 15H), 6.55–6.52 (m, 1H, *J*=15.0, 11.0 Hz, determined through spin–spin decoupling experiments), 6.50–6.37 (m, 2H), 5.76 (q, 1H, *J*=6.9 Hz), 5.48 (m, 1H), 5.31 (m, 1H), 1.82 (d, 3H, *J*=6.9 Hz). ^{13}C NMR (δ, $CDCl_3$, 75 MHz): 138.8, 136.8, 133.0, 132.3, 130.3, 129.8, 128.0, 127.7, 125.5, 117.0, 18.7. MS (*m/z*, %): 352 (M^+, 33), 337 (81), 325 (80), 287 (100), 259 (80), 180 (99), 53 (12). Anal. calcd for $C_{25}H_{24}Si$: C, 85.17; H, 6.86. Found: C, 85.00; H, 7.12.

3.1.11. (2*Z*,4*E*,6*Z*)-3-Triphenylsilyl-2,4,6-undecatriene (5c). Yield: 74% (orange–yellow oil). IR (CCl_4, cm^{-1}): 3073, 3027, 2978, 2936, 1589, 1473, 1377, 1308, 1261, 753, 723, 695. ^{1}H NMR (δ, $CDCl_3$, 300 MHz): 7.70–7.30 (m, 15H), 6.12–5.85 (m, 2H), 5.81 (dt, 1H, *J*=9.0, 7.2 Hz), 5.21 (dd, 1H, *J*=16.9, 0.8 Hz), 4.97 (bq 1H, *J*=6.7 Hz), 2.10–2.02 (m, 2H), 1.70–1.41 (m, 5H), 1.21–0.85 (m, 5H). ^{13}C NMR (δ, $CDCl_3$, 50 MHz): 137.7, 136.5, 136.1, 135.1, 133.3, 131.2, 129.3, 128.7, 128.1, 127.1, 37.0, 22.5, 18.7, 15.0, 13.2. MS (*m/z*, %): 408 (M^+, 3), 393 (21), 351 (93), 287 (100), 182 (93), 77 (91), 53 (18). Anal. calcd for $C_{29}H_{32}Si$: C, 70.49; H, 15.71. Found: C, 70.55; H, 15.68.

3.1.12. (2*E*,4*E*)-2,4-Nonadiene (6a). *Typical procedure*. A solution of (2*Z*,4*E*)-3-triphenylsilyl-2,4-nonadiene **5a** (60 mg, 0.16 mmol) in THF (2 mL) is treated with a NaOH/TBAF solution (10 mg of NaOH and 76 mg of TBAF in THF/H_2O, 0.24 mmol) and refluxed for 12 h. The resulting mixture is diluted with Et_2O (5 mL), washed with a saturated solution of NH_4Cl and water. After drying over Na_2SO_4 and removing of the solvent, the crude product is purified on silica gel to afford 18 mg of pure diene **6a** (91%) as a yellow oil. IR (CCl_4, cm^{-1}): 3020, 1640, 1625, 1465, 990, 965. ^{1}H NMR (δ, $CDCl_3$, 200 MHz): 6.30–6.11 (m, 1H), 5.91–5.62 (m, 3H), 2.21–2.09 (m, 2H), 1.68 (bd, 3H, *J*=6.7 Hz), 1.42–1.30 (m, 4H), 0.91 (t, 3H, *J*=6.9 Hz). ^{13}C NMR (δ, $CDCl_3$, 50 MHz): 136.9, 133.2, 129.8, 129.1, 33.3, 30.2, 22.9, 17.8, 14.0. MS (*m/z*, %): 124 (M^+, 10), 109 (13), 82 (87), 81 (100), 95 (13), 67 (21). HRMS: C_9H_{16} calcd 124.1252, found 124.1266.

3.1.13. (3*E*,5*E*)-1,3,5-Heptatriene (6b). Yield: 82% (dark yellow oil). IR (CCl_4, cm^{-1}): 3010, 1628, 1610, 1458, 1430, 1010, 975, 935, 890. ^{1}H NMR (δ, $CDCl_3$, 200 MHz): 6.61–6.57 (m, 3H), 6.19 (bdd, 1H, *J*=15.8, 10.3 Hz), 5.79 (dq, 1H, *J*=15.8, 6.9 Hz), 5.25–5.14 (m, 2H), 1.69 (bq, 3H, *J*=6.9 Hz). ^{13}C NMR (δ, $CDCl_3$, 50 MHz): 136.4, 132.0, 130.1, 127.8, 125.3, 116.7, 17.5. MS (*m/z*, %): 94 (M^+, 12), 67 (31), 41 (100). HRMS: C_7H_{10} calcd 94.0782, found 94.0775.

3.1.14. (2*E*,4*E*,6*Z*)-2,4,6-Undecatriene (6c). Yield: 89% (orange oil). IR (CCl_4, cm^{-1}): 3051, 1630, 1620, 1461, 1005, 970, 960, 940, 880, 835. ^{1}H NMR (δ, $CDCl_3$, 200 MHz): 6.35–5.98 (m, 4H), 5.80 (dq, 1H, *J*=16.2, 7.0 Hz), 5.46 (dt, 1H, *J*=10.8, 6.9 Hz), 2.16–1.97 (m, 2H), 1.70 (bd, 3H, *J*=6.9 Hz), 1.37–1.28 (m, 4H), 0.90 (t, 3H, *J*=7.1 Hz). ^{13}C NMR (δ, $CDCl_3$, 50 MHz): 135.8, 129.6, 126.3, 125.7, 124.9, 123.7, 32.9, 31.8, 22.7, 17.7, 13.2. MS (*m/z*, %): 150 (M^+, 28), 107 (10), 93 (51), 79 (100), 41 (39). HRMS: $C_{11}H_{18}$ calcd 150.1409, found 150.1415.

3.1.15. (*E*)-3-Trimethylsilyl-propenoyltriphenylsilane (7). A solution of bis(trimethylsilyl)cuprate, prepared following standard procedure[5a] from Me_3SiLi and CuCN (0.5 mmol), is cooled to −78°C and treated with **1** (125 mg, 0.4 mmol). After 1 h stirring, the solution is warmed to −23°C and reacted for 30 min. After quenching with saturated ammonium chloride solution (10 mL), the solution is allowed to reach room temperature. The reaction mixture is diluted with ether (10 mL) and the organic layer is washed with ammonia buffer (2×10 mL) and water (2×10 mL) of and dried over Na_2SO_4. Removal of the solvent affords the title compound (134 mg) as a bright yellow oil (87%). IR (CCl_4, cm^{-1}): 3064, 3030, 2973, 2931, 1608, 1591, 1475, 1371, 1307, 1255, 1244, 843. ^{1}H NMR (δ, $CDCl_3$, 300 MHz): 7.70–7.30 (m, 15H), 6.68 (d, 1H, *J*=16.5 Hz), 6.38 (d, 1H, *J*=16.5 Hz), 0.10 (s, 9H). ^{13}C NMR (δ, $CDCl_3$, 75 MHz): 231.63, 141.38, 136.73, 135.45, 130.31, 128.46, 128.31, 2.18. MS (*m/z*, %): 386 (M^+, 3), 371 (23), 313 (17), 312 (6), 287 (81), 182 (100), 105 (80), 53 (12). HRMS: $C_{24}H_{26}OSi_2$ calcd 386.1522, found 386.1531.

3.1.16. (*E*)-3-Tributylstannyl-propenoyltriphenylsilane (8). To a solution of the stannylcuprate, prepared from CuCN (0.067 g, 0.75 mmol), 1.6 M solution of *n*-BuLi in hexane (0.63 mL, 1.5 mmol) and Bu_3SnH (0.4 mL) in anhydrous THF (2 mL), cooled to −78°C, propinoyltriphenylsilane **1** (234 mg, 0.75 mmol) is added dropwise. After 30 min stirring at −78°C the reaction mixture is quenched with saturated NH_4Cl solution (5 mL). Usual workup procedure affords a bright yellow oil purified by flash chromatography: hexabutyldistannane is eluted with petroleum ether and the pure product is recovered by elution with diethyl ether/petroleum ether 1:1. The product must be stored in the cold and protected from light. Yield: 86% (389 mg). IR (CCl_4, cm^{-1}): 3036, 1598, 1310, 969, 753, 697. ^{1}H NMR (δ, $CDCl_3$, 300 MHz): 7.70–7.33 (m, 15H), 6.88 (d, 1H, *J*=16.8 Hz), 6.56 (d, 1H, *J*=16.8 Hz), 1.58–1.26 (m, 12H), 1.00–0.81 (m, 15H). ^{13}C NMR (δ, $CDCl_3$, 50 MHz): 233.4, 141.2, 140.5, 136.9, 135.4, 130.3, 128.4, 25.1, 24.2, 13.0, 9.88. MS(*m/z*, %): 604 (M^+, 3), 589 (21), 547 (78), 490 (23), 313 (2), 291 (17), 287 (81), 182 (100), 57 (23). HRMS: $C_{33}H_{44}OSiSn$ calcd 602.2183, found 602.2193.

3.1.17. (*E*)-3-Benzoyl-propenoyltriphenylsilane (9a). *Typical procedure*. A solution of PhCOCl (78 mg, 0.61 mmol) in dry CH_2Cl_2 (1 mL) is added under inert atmosphere to a dispersion of dry $AlCl_3$ (160 mg, 1.2 mmol) in anhydrous CH_2Cl_2 (1 mL) at 0°C. After 10 min stirring the clear obtained solution is transferred via a syringe in a flask containing a solution of **7** (134 mg, 0.35 mmol) in dry CH_2Cl_2 (1.5 mL). After 3 h stirring at 0°C, usual quench with NH_4Cl and workup with ether follow. Filtration on florisil affords the title compound (70 mg, 48%) as a yellow oil. IR (CCl_4, cm^{-1}): 3077, 3028, 2974, 2935, 1635, 1590, 1472, 1371, 1258, 972,

777, 699. ^{1}H NMR (δ, $CDCl_3$, 300 MHz): 7.81 (d, 1H, J=16.9 Hz), 7.77–7.31 (m, 20H), 6.87 (d, 1H, J=16.9 Hz). ^{13}C NMR (δ, $CDCl_3$, 50 MHz): 236.7, 200.1, 148.7, 141.9, 140.7, 135.7, 134.6, 130.2, 129.7, 129.2, 128.8, 121.2. MS (*m/z*, %): 418 (1), 406 (17), 403 (12), 390 (22), 341 (6), 287 (63), 259 (70), 182 (100), 159 (71), 77 (88), 53 (8). Anal. calcd for $C_{28}H_{22}O_2Si$: C, 80.35; H, 5.30. Found: C, 80.06; H, 5.54.

3.1.18. (*E*)-3-(*p*-Toluoyl)-propenoyltriphenylsilane (9b). Yield: 51% (yellow oil). IR (CCl_4, cm^{-1}): 3053, 2991, 1646, 1640, 1633, 1595, 1460, 1352, 1251, 851. ^{1}H NMR (δ, $CDCl_3$, 200 MHz): 7.88 (d, 1H, J=16.3 Hz), 7.70–7.39 (m, 19H), 7.02 (d, 1H, J=16.3 Hz), 2.25 (s, 3H). ^{13}C NMR (δ, $CDCl_3$, 50 MHz): 235.9, 193.5, 149.1, 143.0, 141.5, 135.8, 135.1, 134.9, 129.3, 129.0, 128.8, 127.6, 21.4. MS (*m/z*, %): 432 (5), 416 (11), 341 (28), 287 (59), 259 (78), 119 (100), 91 (85), 65 (8). Anal. calcd for $C_{29}H_{24}O_2Si$: C, 80.52; H, 5.59. Found: C, 80.37; H, 5.71.

3.1.19. (*E*)-3-Acetyl-propenoyltriphenylsilane (9c). Yield: 45% (yellow oil). IR (CCl_4, cm^{-1}): 3022, 2987, 1661, 1650, 1637, 1596, 1467, 1348, 1250, 852. ^{1}H NMR (δ, $CDCl_3$, 300 MHz): 7.73–7.32 (m, 15H), 7.21 (d, 1H, J=16.4 Hz), 6.87 (d, 1H, J=16.4 Hz), 2.31 (bs, 3H). ^{13}C NMR (δ, $CDCl_3$, 50 MHz): 231.8, 193.3, 149.8, 144.5, 136.1, 134.4, 130.1, 128.9, 25.6. MS (*m/z*, %): 356 (18), 341 (51), 313 (59), 259 (19), 97 (55), 43 (100). Anal. calcd for $C_{23}H_{20}O_2Si$: C, 77.49; H, 5.65. Found: C, 77.18; H, 6.00.

3.1.20. (2*E*,4*E*)-5-Phenyl-2,4-pentadienoyltriphenylsilane (11). Compound **8** (121 mg, 0.2 mmol) and 1-(*E*)-iodo-2-phenylethylene **10** (46 mg, 0.2 mmol),[32] are mixed under an inert atmosphere and then dissolved in anhydrous DMF (0.5 mL). Then $PdCl_2(CH_3CN)_2$ (2 mg, 7.7×10^{-3} mmol) are added and the mixture is stirred 24 h in the dark at room temperature, then diluted with diethyl ether (10 mL) and washed with water (2×10 mL). The organic layer is dried over Na_2SO_4 and, after removal of the solvent, 50 mg (0.12 mmol, yield 60%) of the pure product are obtained by flash chromatography (diethyl ether/petroleum ether) as a yellow thick oil. IR (CCl_4, cm^{-1}): 3095, 3038, 1607, 1475, 1311, 1255, 968, 751, 730, 710, 693. ^{1}H NMR (δ, $CDCl_3$, 300 MHz): 7.76–7.30 (m, 20H), 6.87 (ddd, 1H, J=16.9, 10.3, 0.8 Hz), 6.76 (ddd, 1H, J=15.3, 10.3, 0.9 Hz), 6.58 (bdd, 1H, J=15.3, 0.8 Hz), 6.31 (bdd, 1H, J=16.9, 0.9 Hz). ^{13}C NMR (δ, $CDCl_3$, 50 MHz): 230.7, 141.3, 140.5, 136.7, 135.4, 130.3, 129.3, 128.4, 128.2, 125.8, 125.1, 120.1, 119.7, 118.6. MS (*m/z*, %): 416 (M^+, 8), 339 (71), 313 (7), 287 (80), 182 (100), 77 (91), 53 (1). Anal. calcd for $C_{29}H_{24}OSi$: C, 83.61; H, 5.81. Found: C, 83.40; H, 6.03.

3.1.21. (2*E*,4*E*)-6-*t*-Butoxycarbonylamino-2,4-hexadienoyltriphenylsilane (13). *Procedure 1*. Preparation of(*E*)-*N*-Boc-3-iodo-2-propen-1-amine (**12**). A solution of I_2 (101 mg, 0.40 mmol) in CH_2Cl_2 (2 mL) is added to (*E*)-*N*-Boc-3-tributylstannyl-2-propen-1-amine **15** (171 mg, 0.38 mmol)[33] and the mixture is allowed to react for 8 h at room temperature. Removal of the solvent, followed by filtration on florisil with hexane and then with ether, affords 105 mg (yield 98%) of **12** as a colorless liquid to be stored in the dark. IR (CCl_4, cm^{-1}): 3352, 3040, 2957, 2926, 1702, 1608, 1463, 1310, 970. ^{1}H NMR (δ, $CDCl_3$, 200 MHz): 6.57 (dt, 1H, J=16.5, 5.8 Hz), 6.23 (dt, 1H, J=16.5, 1.0 Hz), 4.68 (bs, 1H), 3.66 (bdd, 2H, J=5.8, 1.0 Hz), 1.40 (s, 9H). ^{13}C NMR (δ, $CDCl_3$): 155.4, 144.2, 80.0, 77.7, 43.3, 28.3. MS (*m/z*, %): 283 (M^+, 3), 157 (10), 156 (8), 127 (34), 101 (100), 85 (43), 73 (88), 57 (98). HRMS: $C_8H_{14}INO_2$ calcd 283.0069, found 283.0050.

(*E*)-*N*-Boc-3-iodo-2-propene-1-amine **12** (45 mg, 0.16 mmol) and acylsilane **8** (96 mg, 0.16 mmol) are dissolved in anhydrous DMF (1.5 mL), together with $PdCl_2(CH_3CN)_2$ (2 mg, 7.7×10^{-3} mmol) and allowed to react in the dark for 12 h at room temperature. The reaction mixture is then diluted with ether (10 mL) and washed with water (5×10 mL). The organic layer is dried over Na_2SO_4 and, after removal of the solvent, 62 mg (yield 83%) of pure **13** (yellow thick oil) are recovered by filtration on florisil with ether, after elution of the stannylated by-products with hexane. IR (neat, cm^{-1}): 3363, 3040, 2981, 1702, 1610, 1510, 1460, 1360, 990. ^{1}H NMR (δ, $CDCl_3$, 300 MHz): 7.71–7.30 (m, 15H), 6.55 (dd, 1H, J=14.3, 10.0 Hz), 6.51 (d, 1H, J=14.1 Hz), 6.38 (ddt, 1H, J=15.2, 10.0, 5.0 Hz), 5.86 (dt, 1H, J=15.1, 6.5 Hz), 5.21 (bs, 1H), 3.90 (apt, 2H, J=5.0 Hz), 1.45 (s, 9H). ^{13}C NMR (δ, $CDCl_3$): 231.4, 155.4, 148.5, 136.7, 134.5, 132.3, 129.6, 128.5, 128.3, 127.4, 77.6, 42.3, 28.8. MS (*m/z*, %): 412 (M^+-57, 4), 368 (21), 313 (7), 182 (100), 77 (91). Anal. calcd for $C_{29}H_{31}NO_3Si$: C, 74.16; H, 5.92; N, 2.98. Found: C, 74.32; H, 6.27; N, 2.80.

Procedure 2. Preparation of (*E*)-3-iodopropenoyltriphenylsilane (**14**). Propynoylsilane **1** (31 mg, 0.1 mmol) is dissolved in $CHCl_3$ (1 mL) and iodotrimethylsilane (22 mg, 0.11 mmol) is added. After 30 min stirring at room temperature the solvent is evaporated and the usual purification by filtration with hexane and ether follows, to afford 40 mg of **14** (yield 92%) as an orange oil to be stored in the dark. IR (CCl_4, cm^{-1}): 3079, 3031, 1599, 1475, 1309, 1254, 968, 751, 693. ^{1}H NMR (δ, $CDCl_3$, 200 MHz): 7.70–7.36 (m, 16H), 7.21 (d, 1H, J=18 Hz). ^{13}C NMR (δ, $CDCl_3$): 231.0, 140.5, 136.7, 135.4, 132.4, 130.3, 89.4. MS (*m/z*, %): 440 (M^+,18), 313 (6), 312 (7), 311 (18), 254 (9), 182 (100), 77 (91). Anal. calcd for $C_{21}H_{17}IOSi$: C, 57.28; H, 3.89. Found: C, 57.00; H, 4.07.

(*E*)-3-Iodopropenoyltriphenylsilane **14** (40 mg, 0.10 mmol) and **15** (45 mg, 0.10 mmol)[33] are dissolved in dry DMF (1.5 mL), together with $PdCl_2(CH_3CN)_2$ (2 mg, 7.7×10^{-3} mmol). The procedure is the same as Procedure 1 and affords 41 mg of **13** (yield 86%).

3.1.22. 1,6-Bis-(triphenylsilyl)-(2*E*, 4*E*)-hexadien-1,6-dione (16). Following the previous procedure, (*E*)-3-iodopropenoyltriphenylsilane **14** (40 mg, 0.1 mmol) and (*E*)-3-tributylstannylpropenoyltriphenylsilane **8** (55 mg, 0.1 mmol) afford the title compound **16** in 75% yield (47 mg) as an orange thick oil. IR (CCl_4, cm^{-1}): 3072, 3032, 1583, 751, 691. ^{1}H NMR (δ, $CDCl_3$, 200 MHz): 7.69–7.28 (m, 30H), 6.89 (d, 2H, J=16.1 Hz), 6.44 (d, 2H, J=16.1 Hz). ^{13}C NMR (δ, $CDCl_3$, 50 MHz): 234.7, 142.9, 135.5, 133.3, 130.3, 129.0, 128.8. MS (*m/z*, %): 626 (M^+, 5), 549 (3), 368 (85), 312 (12), 287 (85), 259 (63), 182 (100), 105 (32), 77 (91). Anal. calcd for $C_{42}H_{34}O_2Si_2$: C, 80.47; H, 5.47. Found: C, 80.19; H, 5.61.

3.1.23. (*E*)-2-Carbethoxymethyl-3-tributylstannylpropenoyltriphenylsilane (17a). To a solution of the stannyl derivative **8**, prepared with the usual procedure from **1** (69 mg, 0.22 mmol), a large excess of solid CO_2 is added at −78°C. The reaction mixture is allowed to reach very slowly (about 2 h) −10°C, then is quenched with dimethylsulfate (28 mg, 0.22 mmol) and allowed to react for 1.5 h at room temperature. The reaction mixture is diluted with ether (10 mL) and then poured into ammonia buffer (10 mL). The organic layer is washed with ammonia buffer (3×10 mL), saturated NH_4Cl solution (2×10 mL) and water (3×10 mL). The organic layer is dried and, after removal of the solvent, the crude product is purified by filtration with hexane on florisil, recovering the pure product **17a** with ether in 83% yield (121 mg) as an orange–yellow oil. IR (CCl_4, cm^{-1}): 3078, 3033, 2972, 2936, 1717, 1601, 1473, 1378, 1310, 1255, 969, 752, 695. ^1H NMR (δ, $CDCl_3$, 200 MHz): 7.70–7.30 (m, 15H), 6.83 (s, 1H), 4.01 (s, 3H), 1.59–1.24 (m, 12H), 1.20–0.80 (m, 15H). ^{13}C NMR (δ, $CDCl_3$): 227.9, 166.5, 144.3, 142.0, 137.0, 135.4, 130.3, 128.4, 51.5, 25.1, 24.2, 13.0, 9.9. MS (*m*/*z*, %): 631 (M^+−OMe, 13), 605 (71), 548 (12), 291 (31), 182 (100), 77 (91), 57 (81). Anal. calcd for $C_{35}H_{46}O_3SiSn$: C, 63.55; H, 7.01. Found: C, 63.19; H, 7.30.

3.1.24. (*E*)-2-Acetyl-3-tributylstannylpropenoyltriphenylsilane (17b). To a solution of the stannyl derivative **8**, prepared from **1** (69 mg, 0.22 mmol), acetyl chloride (17 mg, 0.22 mmol) is added at −78°C and stirred for 30 min. The reaction mixture is allowed to reach slowly (about 2 h) room temperature and, after 30 min stirring at 20°C, usual workup procedure follows. 96.4 mg of **17b** (68%) are obtained as a yellow oil. IR (CCl_4, cm^{-1}): 3079, 3031, 2972, 2936, 1630, 1597, 1475, 1375, 1309, 1253, 968, 751, 693. ^1H NMR (δ, $CDCl_3$, 200 MHz): 7.70–7.34 (m, 15H), 6.95 (s, 1H), 2.31 (s, 3H), 1.60–1.25 (m, 12H), 1.20–0.86 (m, 15H). ^{13}C NMR (δ, $CDCl_3$): 228.7, 197.5, 147.1, 141.9, 137.6, 135.1, 128.6, 128.3, 25.7, 25.1, 24.2, 13.2, 9.8. MS (*m*/*z*, %): 646 (M^+, 2), 603 (13), 589 (91), 532 (11), 291 (18), 276 (61), 182 (100). Anal. calcd for $C_{35}H_{46}O_2SiSn$: C, 65.12; H, 7.18. Found: C, 64.90; H, 7.25.

3.1.25. (*E*)-[2-(1-Propenyl)]-3-tributylstannylpropenoyltriphenylsilane (17c). A solution of the stannylderivative **8**, prepared from **1** (69 mg, 0.22 mmol), is treated at −78°C with allylbromide (26 mg, 0.22 mmol) and stirred for 30 min. The solution is allowed to reach slowly room temperature and after 30 min the usual work-up procedure affords the crude product, which isomerizes to the conjugated diene **17c** upon standing at room temperature (24 h). Usual purification gives 72 mg of pure **17c** (51%) as a yellow oil. IR (CCl_4, cm^{-1}): 3049, 3026, 2985, 2930, 1645, 1611, 1473, 1371, 1255, 970, 853. ^1H NMR (δ, $CDCl_3$, 200 MHz): 7.69–7.31 (m, 15H), 6.41 (bd, 1H, *J*=15.9 Hz), 6.20 (s, 1H), 5.68 (dq, 1H, *J*=15.9, 7.2 Hz), 1.70 (bd, 3H, *J*=7.2 Hz), 1.51–1.28 (m, 12H), 1.25–0.82 (m, 15H). ^{13}C NMR (δ, $CDCl_3$): 228.0, 148.2, 139.0, 136.9, 135.2, 130.3, 129.1, 128.2, 126.4, 25.9, 25.3, 17.4, 13.1, 9.7. MS (*m*/*z*, %): 629 (M^+−15, 11), 603 (51), 385 (100) 353 (35). Anal. calcd for $C_{36}H_{48}OSiSn$: C, 67.19; H, 7.52. Found: C, 66.85; H, 7.72.

3.1.26. 2-Acetyl-5-phenyl-(2*E*,4*E*)-pentadienoyltriphenylsilane (18). Following the previous procedure, (*E*)-2-acetyltributylstannylpropenoyltriphenylsilane **17b** (95 mg, 0.15 mmol) and 1-(*E*)-iodo-2-phenylethylene 10 (34 mg, 0.15 mmol) afford the title compound (56 mg, 0.12 mmol) as a pale yellow oil in 81% yield. IR (neat, cm^{-1}): 3071, 3030, 2971, 2939, 1630, 1591, 1473, 1371, 1251, 968, 751, 693. ^1H NMR (δ, $CDCl_3$, 300 MHz): 7.72–7.33 (m, 21H), 6.85 (dd, 1H, *J*=16.9, 12.1 Hz), 6.76 (d, 1H, *J*=16.9 Hz), 2.31 (s, 3H). ^{13}C NMR (δ, $CDCl_3$): 232.8, 196.9, 147.2, 142.3, 137.0, 135.7, 131.4, 130.2, 129.1, 128.8, 128.2, 127.5, 126.0, 25.6. MS (*m*/*z*, %): 415 (M^+−43, 21), 381 (81), 342 (12), 287 (71), 259 (71), 199 (71), 182 (100), 105 (30), 77 (92), 53 (10). Anal. calcd for $C_{31}H_{26}O_2Si$: C, 81.18; H, 5.71. Found: C, 81.00; H, 5.83.

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