

The reactivity of α - and β -iodo propenoylsilanes: an alternative access to polyunsaturated acylsilanes

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Abstract

Reaction of 2- and 3-iodopropenoyltriphenylsilanes with unsaturated tin derivatives affords a mild and general entry to variously functionalized dienoylsilanes. The β -iodo derivative affords, under palladium catalyzed conditions, good yields of the expected compounds, while α -iodo propenoylsilane proved somewhat less reactive under these conditions. The α -iodo derivative could be anyway efficiently reacted with organozinc species to generate several α -branched propenoylsilanes.

Keywords: Iodo propenoylsilanes, dienoylsilanes, organozinc compounds.

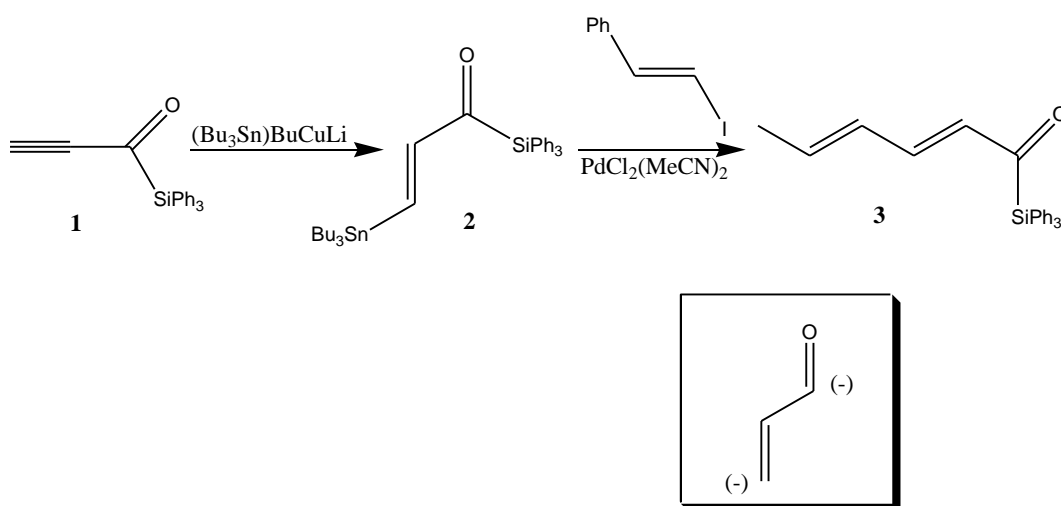
Introduction

Since their first discovery by A.G.Brook, acylsilanes¹ have attracted a reasonable deal of attention, due to the striking differences of their reactional behaviour with respect to ordinary carbonyl compounds. Acylsilanes may in fact undergo specific transformations of the $-\text{COSiMe}_3$ moiety such as Brook rearrangement,² oxidation to carboxylic acids,³ fluoride promoted conversion to aldehydes,³ and catalyzed nucleophilic acylations.⁴ Subsequent exploitation of their reactivity has led to a constant and growing use of acylsilanes in devising new synthetic methodologies, affording such compounds a relevant position in the development of novel and more versatile synthons for organic chemistry.⁵

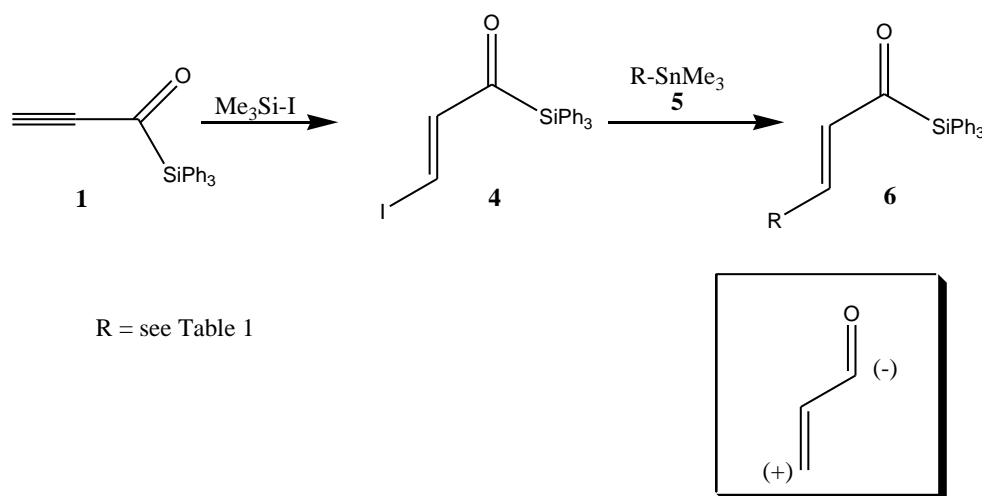
The presence of a double bond together with the acylsilane moiety provides an expansion of acylsilane synthetic potentialities, and opens the way to the possible construction of novel and more versatile synthons.

In this context, ethylenic and acetylenic acylsilanes^{2,6} have recently emerged as versatile intermediates, due to the high reactivity of the unsaturated moiety: such compounds may in fact participate in TiCl_4 promoted allylations,⁷ 1,4-additions with silylated nucleophiles⁸ or act as dienophiles in Diels-Alder reactions,² and [1,3]-dipolar cycloadditions.⁹ [3+2] Annulations with allenylsilanes⁹ and with ketone enolate¹⁰ have also been reported, together with [3+4] annulations with α,β -unsaturated methyl ketone enolates.¹¹

On the other hand, despite their synthetic interest, little attention has been devoted until recently to polyunsaturated acylsilanes. Few examples are reported of syntheses of dienoylsilanes, like the reaction of (α -phosphonoacyl)silane^{6d} or (trimethylsilyl)acetyltrimethylsilane³ with α,β -unsaturated aldehydes and the rearrangement of α -methylene β -hydroxy acylsilanes,¹² thus evidencing the still present need for alternative procedures.



Scheme 1



Scheme 2

We have been interested in acylsilane chemistry since several years,^{4, 13} and more recently our attention has been focused on the unsaturated series,⁸ like ethylenic and acetylenic derivatives. Such compounds, beside undergoing smooth uncatalyzed Michael additions with several silylated nucleophiles⁸, proved also very efficient tools in the stereopredetermined synthesis of polyenals and polyenes through carbocupration¹⁴ and stannylcupration¹⁵ reactions. In particular, while carbocupration reactions afforded a direct general synthesis of dienoylsilanes, stannylcupration of propynoylsilane 1 led to (*E*)-3-tributylstannyl propenoylsilane 2, a molecule with a further functionalization site, nucleophilic in character, (Scheme 1). In fact reaction of 2 with vinyl iodides, in the presence of $\text{PdCl}_2(\text{CH}_3\text{CN})_2$ leads to a clean functionalization of position 3 of the enonic framework.

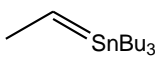
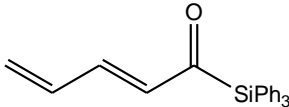
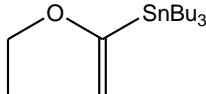
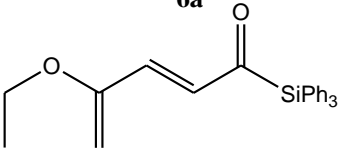
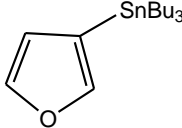
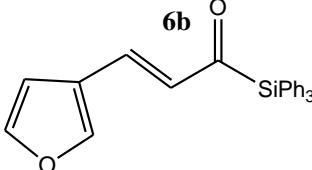
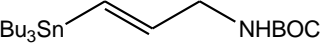
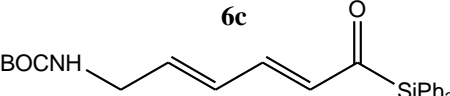
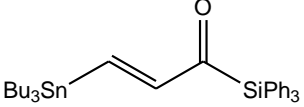
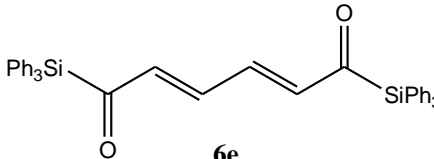
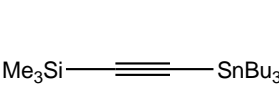
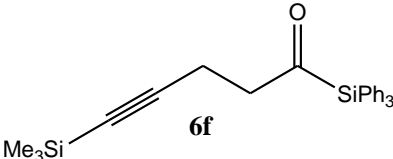
These results led us to undertake a more detailed study on the chemical behaviour of related molecules, with the aim to develop new and possibly more versatile synthons, and in this connection, the reactivity of 2- and 3-iodo propenoylsilanes has been evaluated.

(*E*)-3-Iodo propenoylsilane 4 can be easily obtained in good yields through the Michael reaction of Me_3SiI with acetylenic ketone 1 at room temperature in CH_2Cl_2 (Scheme 2).

Compound 4 proved an extremely useful intermediate, undergoing clean palladium catalyzed¹⁶ couplings with functionalized tin compounds, to afford a variety of novel 3-functionalized ethylenic silyl ketones 6a-f (Scheme 2), thus opening a different synthetic pathway for the construction of polyunsaturated acylsilanes,¹⁷ as compared to carbo- and stannylcupration reactions.

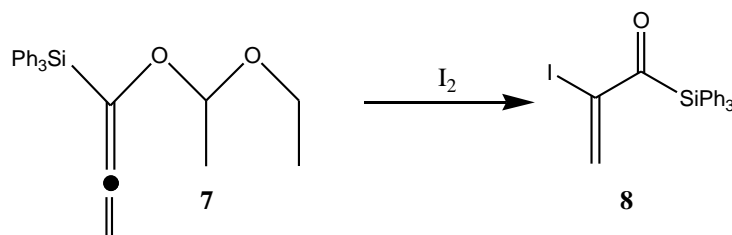
The generality of the reaction is evidenced by the use of nucleophiles containing both nitrogen or oxygen based functionalities (Table 1, entries 2-4). Reactions proved to be stereoselective, only the corresponding *E* isomers being isolated from the reaction mixtures. The only exception to this behaviour proved to be compound 6c which was obtained as an equimolar mixture of *E* and *Z* isomers.

Table 1. Functionalization of 3-iodopropenylsilane

Entry	Nucleophile	Product	Time (h)	Yield (%)
1	 5a	 6a	1	70
2	 5b	 6b	1	75
3	 5c	 6c	1	73
4	 5d	 6d	12	86
5	 5e	 6e	8	84
6	 5f	 6f	9	64

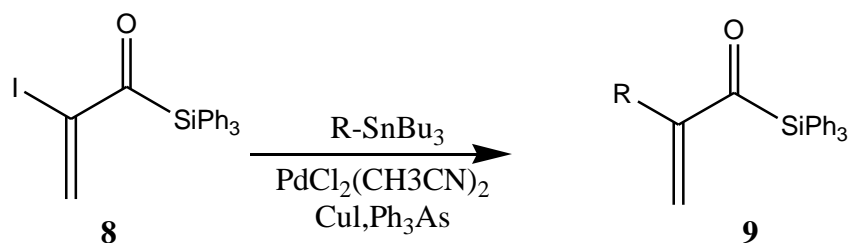
Interestingly, when the nucleophile is the 3-stannylpropenylsilane **5e**, the dienyl bis-acylsilane **6e** could be obtained. Furthermore, by reacting the bis(metallic)acetylene **5f** (Entry 6, Table 1), the acetylenic propenylsilane **6f** could be isolated, evidencing a simple entry to the barely known class of acetylenic propenylsilanes.¹⁸

It is interesting to note the inversion of the reaction polarity of position 3 of the enonic framework, with respect to the 3-tributylstannyl derivative **2**, this time reacting in an electrophilic fashion. This finally establishes the possibility of fine tuning of the reaction polarity of this position in the enonic framework, so that can react either in a nucleophilic or electrophilic fashion.



Scheme 3

For the complete development of the behaviour of the acylsilane skeleton, the possibility of α -functionalization was also taken into consideration, with the aim to uncover a possible general pathway to the isomeric 2-vinylpropenoilsilanes. The synthesis of the α -iodo derivative could be accomplished by reacting the allene 7 with iodine at $-78\text{ }^{\circ}\text{C}$ (Scheme 3).

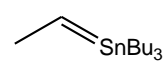
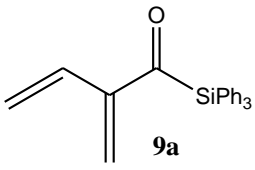
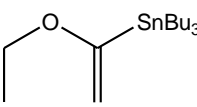
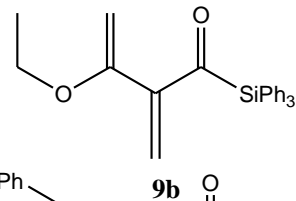
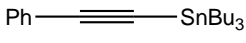
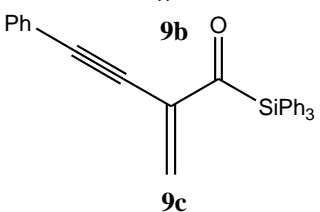


R = see Table 2

Scheme 4

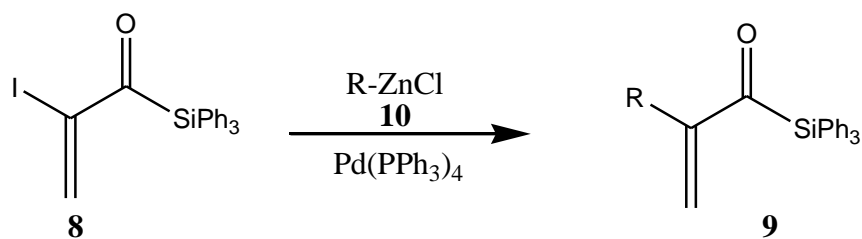
α -Iodopropenoilsilane 8 was then reacted with several stannylated nucleophiles. PdCl₂(CH₃CN)₂ alone proved unable, in this case, to induce the reaction, and the concomitant action of CuI and Ph₃As was required to obtain reasonable yields of the wanted compounds (Scheme 4). Under these conditions, vinyl stannane 5a reacted to afford 9a in reasonable yield, while the reaction of 5b and 5g was more sluggish, leading to 9b and 9c in somewhat lower yield (Table 2). Unfortunately aromatic and heteroaromatic stannanes failed to afford even traces of the functionalized propenoilsilane. Furthermore, also the bis-metallic alkyne 5f proved quite unreactive toward compound 8 as did tributyl(ethynyl)tin.

Table 2. Functionalization of 2-iodopropenylsilane

Entry	Nucleophile	Product	Yield (%)
1	 5a	 9a	56
2	 5b	 9b	39
3	 5g	 9c	20

These shortcomings, together with the fact that an ongoing project in our laboratories required a reasonable access to an unsubstituted 2-alkynyl silyl ketone, led us to search for a different functionalization methodology.

The last decades have witnessed a very rapid expansion of the types of organometallic reagents in organic synthesis. Such compounds have in fact expanded from the classical organoalkali or Grignard reagents, to organometallics containing more electropositive metals such as Si, Sn, Cu, B, Al, Zn. The utility of such organometallic reagents relies mainly in the fact that they are virtually "non basic organometallics" and therefore compatible with polar functional groups.



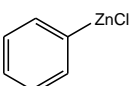
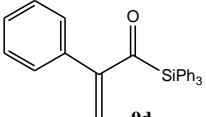
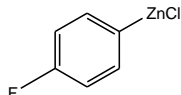
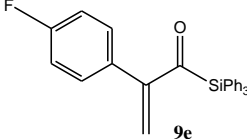
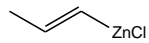
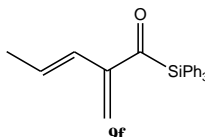
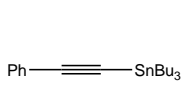
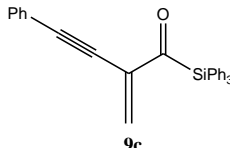
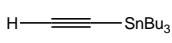
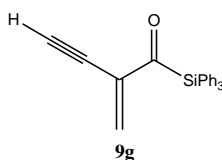
R = see Table 3

Scheme 5

Attempts to react different lithium carbocuprates with 2-iodo propenylsilane **8**, did not afford even traces of 2-functionalized propenylsilanes, but generally resulted in complex mixtures, not containing the wanted compounds. This behaviour was not unexpected, being in agreement with previous observations by other authors on similar compounds.¹⁹

The functionalization via organocuprates being then unsuccessful, we moved toward different organometallic compounds. Zinc derivatives have been recently shown to be very reactive toward similar derivatives, leading to the synthesis of functionalized molecules, not easily accessible through the common synthetic procedures.²⁰ In particular, such organometallics can afford, under palladium catalysis, the synthesis of alkynyl systems, avoiding disproportionation reactions which are inevitably found with lithium or cuprate derivatives. They have also been successfully used in the functionalization of α -iodo carboxylates.²¹

Table 3. Organozinc functionalization of 2-iodopropenoylsilane

Entry	Nucleophile	Product	Yield (%)
1	 10a	 9d	61
2	 10b	 9e	53
3	 10c	 9f	46
4	 10d	 9c	44
5	 10e	 9g	35

Thus, the reaction of 2-iodopropenoylsilane **8** with several zinc derivatives **10a-e**, obtained by treatment of the corresponding Grignard reagent with ZnCl_2 , proceeds smoothly, in the presence of $\text{Pd}(\text{PPh}_3)_4$ to afford a clean functionalization of position 2 of the unsaturated acylsilane **8** (Scheme 5). Different zinc compounds can be successfully reacted, leading to the first general synthesis to the class of these isomeric dienoylsilanes (Table 3).

Aromatic as well as vinylic and acetylenic derivatives can be reacted, leading to variously functionalized propenoylsilanes in reasonable yields, thus showing a broader generality than tin compounds. Noteworthy, this methodology allows even a smooth access to the alkynyl derivative **9g**.

This reactivity then offers the first general method for the synthesis of 2-substituted propenoylsilanes 9, the study of whose chemical behaviour should prove extremely interesting due to the potentialities of the acylsilane moiety.

Then, in conclusion, the palladium catalyzed reactivity of β -iodo propenoylsilane with ethylenic and acetylenic stannanes affords a general entry into the class of dienoylsilanes. α -Iodo propenoylsilane, on the other hand, proved less reactive in these conditions, but could nevertheless be efficiently functionalized through the action of several organozinc derivatives.

Experimental Section

General Procedures. All reactions were performed in oven-dried glassware equipped with a magnetic stirring bar under a positive pressure of dry argon using standard syringe techniques. THF was distilled from Na/benzophenone prior to use. TLC was performed on precoated silica gel 60 F₂₅₄ plates.

NMR spectra were recorded on spectrometers operating at 200 and 300 MHz (¹H) and at 50 and 75 MHz (¹³C) in deuteriochloroform (CDCl₃), with chloroform as an internal reference (7.26 ppm ¹H, 77.0 ppm ¹³C).

(E)-3-Iodopropenoylsilane (4). Propynoyltriphenylsilane 1 (58 mg 0.185 mmol) of was dissolved in 0.5 mL of CH₂Cl₂ and treated with 40.7 mg (28.9 mL, 0.203 mmol) of iodotrimethylsilane at room temperature and stirred for 4 h. The mixture was then diluted with ether, and poured into a separatory funnel containing a 1/1 ether: pentane mixture and 10% aqueous NaHSO₃. Separation of the organic layer and evaporation afforded the crude product which was purified by elution on florisil first with hexane and then with ether to obtain 75 mg of 4 (92%).

IR (CCl₄) 3079, 3031, 1599, 1475, 1309, 1254, 968, 751, 693 cm⁻¹. ¹H NMR (CDCl₃, 200 MHz) δ (ppm) 7.21 (d, 1H, J = 18 Hz), 7.27-7.70 (m, 16H). ¹³C NMR (CDCl₃, 75 MHz) δ (ppm) 100.9, 128.3, 130.5, 130.7, 136.2, 149.0, 228.0. MS (m/z) 440 (M⁺, 18), 313 (6), 312 (7), 311 (18), 254 (9), 182 (100), 77 (91).

General procedure for (E)-3-iodopropenoylsilane functionalization

(E)-3-iodopropenoylsilane 4 (0.1 mmol) was dissolved in 0.8 mL of CH₂Cl₂ and treated with an equimolar amount of nucleophile. The mixture was stirred 15 min, then treated with PdCl₂(CH₃CN)₂ (0.01 mmol). The progress of the reaction is monitored by tlc, and at the end the mixture was diluted with ether, washed with water, the organic layer separated and the solvent evaporated to afford the crude product as an oil, purified by chromatography (oil).

2(E),4(E)-Pentadienoyltriphenylsilane (6a)

^1H NMR (CDCl_3 , 300 MHz) δ (ppm) 5.42 (dd, 1H, $J = 16.8, 0.6$ Hz), 5.47 (dd, 1H, $J = 9.9, 0.6$ Hz), 6.35 (dt, 1H, $J = 16.8, 10.8, 9.9$ Hz), 6.52 (bd, 1H, $J = 15.6$ Hz), 6.89 (dd, 1H, $J = 15.6, 10.8$ Hz), 7.2-7.7 (m, 15H). ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm) 114.3, 118.2, 128.1, 130.2, 131.8, 135.6, 136.2, 142.9, 231.2. MS (m/z) 340 (M^+ , 26), 313 (3), 259 (100), 236 (11), 199 (30), 181 (95), 155 (48), 105 (80), 53 (68). Anal. Calcd. for $\text{C}_{23}\text{H}_{20}\text{OSi}$: C, 81.13; H, 5.92. Found: C, 80.92; H, 6.12.

(E)-4-Ethoxy-2,4-pentadienyltriphenylsilane (6b). ^1H NMR (CDCl_3 , 200 MHz) δ (ppm) 1.25 (t, 3H, $J = 5.0$ Hz), 3.75 (q, 2H, $J = 5.0$ Hz), 4.18 (d, 1H, $J = 1.96$ Hz), 4.4 (d, 1H, $J = 1.96$ Hz), 6.62 (d, 1H, $J = 15.8$ Hz), 6.85 (d, 1H, $J = 15.8$ Hz), 7.3-7.7 (m, 15H). MS (m/z) 384 (M^+ , 21), 355 (20), 276 (10), 259 (100), 227 (29), 199 (33), 181 (92), 155 (37), 149 (84), 105 (60), 80 (21), 53 (32), 41 (37).

3-(3-Furyl)propenyltriphenylsilane (6c). *Cis-trans* isomers have been obtained as a 60/40 mixture, and separated by tlc (hexanes/ether 5/1). ^1H NMR (CDCl_3 , 200 MHz) Trans isomer: δ (ppm) 6.45-6.48 (m, 1H), 6.81 (d, 1H, $J = 16.1$ Hz), 7.22 (d, 1H, $J = 16$ Hz), 7.35-7.7 (m, 17H). Cis isomer: δ 6.29 (d, 1H, $J = 12.0$ Hz), 6.75 (d, 1H, $J = 12.0$ Hz), 6.89 (bd, 1H), 7.35-7.7 (m, 17 H). MS (m/z) Trans isomer: 380 (M^+ , 3), 259 (29), 121 (3), 84 (100). Cis isomer: 380 (M^+ , 8), 259 (100), 199 (6), 181 (27), 105 (26), 77 (9), 65 (18), 57 (10).

6-(N-*t*-(Butoxycarbonyl)amino)-2(E),4(E)-esadienyltriphenylsilane (6d). IR (CCl_4) 3363, 3040, 2981, 1702, 1610, 1510, 1460, 1360, 990 cm^{-1} . ^1H NMR (CDCl_3 , 200 MHz) δ (ppm) 1.45 (s, 9H), 3.90 (t, 2H, $J = 5.0$ Hz), 5.86 (dt, 1H, $J = 15.1, 6.5$ Hz), 6.38 (ddt, 1H, $J = 15.1, 10.0, 5.0$ Hz), 6.51 (d, 1H, $J = 14.3$), 6.53 (dd, 1H, $J = 14.3, 10.0$ Hz), 7.3-7.7 (m, 15H). ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm) 28.4, 42.4, 77.7, 118.9, 121.4, 128.3, 128.4, 131.3, 136.1, 136.7, 138.5, 155.4, 231.4. MS (m/z) 412 (M^+ -57, 4), 368 (21), 313 (7), 182 (100), 77 (91). Anal. Calcd. for $\text{C}_{29}\text{H}_{31}\text{NO}_3\text{Si}$: C, 74.16; H, 5.92; N, 2.98. Found: C, 74.32; H, 6.82; N, 2.80.

2(E),4(E)-Esadienyl-1,6-dione-1,6-bis-triphenylsilane (6e). IR: 3072, 3032, 1583, 751, 691 cm^{-1} . ^1H NMR (CDCl_3 , 200 MHz) δ (ppm) 6.5 (d, 2H, $J = 16.3$), 7.3-7.6 (m, 30H), 7.7 (d, 2H, $J = 16.3$ Hz). ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm) 114.9, 128.8, 130.3, 135.6, 140.7, 142.8, 234.8. 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 $\text{C}_{42}\text{H}_{34}\text{O}_2\text{Si}_2$: C, 80.47; H, 5.47. Found: C, 80.19; H, 5.61.

(E)-1-Triphenylsilyl-5-trimethylsilyl-2-en-4-pentyn-1-one (6f). ^1H NMR (CDCl_3 , 200 MHz) δ (ppm) 0.4 (s, 9H), 6.43 (d, 1H, $J = 16.0$ Hz), 6.88 (d, 1H, $J = 16.0$ Hz), 7.3-7.7 (m, 15H). ^{13}C NMR (CDCl_3 , 50 MHz) δ (ppm) 235.6, 152.1, 135.7, 134.9, 130.2, 129.3, 128.3, 101.2, 85.4, 0.04. MS (m/z) 410 (M^+ , 0.1), 313 (0.8), 276 (65), 259 (13), 199 (100), 152 (9), 122 (32), 77 (48), 51 (14).

2-Iodopropenyltriphenylsilane (8). 1-(1-Ethoxyethoxy)-1-trimethylsilyl-1,2-propadiene (50 mg, 0.25 mmol) was dissolved in 1 mL of CH_2Cl_2 , cooled to -78°C and slowly treated with a solution of 63.4 mg (0.25 mmol) of I_2 in 1 mL of CH_2Cl_2 . The mixture was stirred 5 min, then

poured into a 1:1 ether/pentane mixture and 10% aqueous NaHSO₃. The crude product was purified by elution on florisil with hexanes/ether 30/1. (77%).

¹H NMR (CDCl₃, 200 MHz) δ (ppm) 7.10 (d, 1H, J = 2.93 Hz), 7.25 (d, 1H, J = 2.93 Hz), 7.3-7.7 (m, 15H). ¹³C NMR (CDCl₃, 75 MHz) δ (ppm) 124.3, 128.3, 130.5, 131.1, 136.2, 143.8, 222.6. MS (m/z) 440 (M⁺, 1), 371 (3), 313 (46), 259 (100), 180 (100), 105 (77), 53(23).

General procedure for 2-iodopropenoylsilane functionalization

A solution of PdCl₂(PhCN)₂ (0.005 mmol), CuI (0.01 mmol) and Ph₃As (0.01 mmol) in 0.5 mL of N-methyl pyrrolidinone was stirred 5 min at room temperature, under inert atmosphere, then added with a solution of 2-iodopropenoylsilane (0.1 mmol) in 1 mL of N-methylpyrrolidinone, followed by the addition of the nucleophile (0.12 mmol).

The mixture was stirred at room temperature and progress of the reaction was monitored by tlc (eluant: hexanes/diethyl ether 9/1). After 2-iodopropenoylsilane disappearance (12-24 h), the solution was diluted with diethyl ether, washed with water, and the organic layer separated. Evaporation of the solvent afforded the crude product as an oil, which was purified by chromatography (oil).

2-Methylene-3-butenoyltriphenylsilane (9a). ¹H NMR (CDCl₃, 200 MHz) δ (ppm) 5.77 (dd, 1H, J = 10.9 Hz), 5.99 (dd, 1H, J = 17.8 Hz), 6.17 (d, 1H, J = 2.67 Hz), 6.38 (d, 1H, J = 2.67 Hz), 6.67 (dd, 1H, J = 17.8, J = 10.9 Hz), 7.2-7.7 (m, 15H). MS (m/z) 340 (M⁺, 27), 276 (19), 259 (100), 227 (37), 199 (69), 183 (58), 150 (39), 135 (25), 105 (34), 77 (37).

2-Methylene-3-ethoxy-3-butenoyltriphenylsilane (9b). ¹H NMR (CDCl₃, 200 MHz) δ (ppm) 1.2 (t, 3H), 3.5 (q, 2H), 4.05 (m, 1H), 4.4 (m, 1H), 5.54 (bs, 1H), 5.94 (bs, 1H), 7.3-7.7 (m, 15H). MS (m/z) 384 (M⁺, 2), 355 (6), 340 (4), 313 (3), 276 (8), 259 (100), 199 (33), 181 (35), 155 (15), 105 (28), 77 (10).

2-Methylen-4-phenyl-3-butynoyltriphenylsilane (9c). ¹H NMR (CDCl₃, 200 MHz) δ (ppm) 6.58 (d, 1H, J = 1.93 Hz), 6.61 (d, 1H, J = 1.93 Hz), 7.0-7.7 (m, 20H). ¹³C NMR (CDCl₃, 50 MHz) δ (ppm) 89.3, 93.5, 122.3, 123.1, 127.8, 128.4, 130.5, 132.4, 135.6, 141.4, 145.2, 231.9. MS (m/z) 414 (M⁺, 3), 386 (4), 259 (100), 181 (19), 155 (8), 105 (12), 77 (7). Anal. Calcd. for C₂₉H₂₂OSi: C, 84.02; H, 5.35. Found: C, 84.29; H, 5.46.

Typical procedure for zinc functionalization of 2-iodopropenoylsilane. 2-Phenyl-propenoyltriphenylsilane (9d)

A round bottom flask was charged, under nitrogen atmosphere, with 0.24 mL (0.12 mmol) of a THF solution of ZnCl₂, cooled to -23 °C and treated with 0.18 mL (0.15 mmol) of a THF solution of phenylmagnesium bromide. After a few minutes, the mixture was treated with 45 mg (0.1 mmol) of 2-iodopropenoylsilane and 9.3 mg (0.01 mmol) of Pd(PPh₃)₄. The obtained mixture was stirred 4 h at -23 °C, then warmed to room temperature and stirred overnight. The mixture was quenched with satd. NH₄Cl, the organic layer separated, dried and the solvent evaporated. Tlc (hexanes/ether 20/1) afforded the pure compound.

^1H NMR (CDCl_3 , 200 MHz) δ (ppm) 5.98 (bs, 1H), 6.16 (bs, 1H), 7.0-7.7 (m, 20H). ^{13}C NMR (CDCl_3 , 50 MHz) δ (ppm) 126.2, 126.8, 127.7, 128.3, 128.4, 131.2, 132.8, 134.9, 136.2, 153.1, 227.9. MS (m/z) 390 (M^+ , 15), 313 (7), 285 (70), 259 (88), 131 (76), 77 (91). Anal. Calcd. for $\text{C}_{27}\text{H}_{22}\text{OSi}$: C, 83.03; H, 5.68. Found: C, 82.87; H, 5.81.

2-(4-Fluorophenyl)-propenoyltriphenylsilane (9e). ^1H NMR (CDCl_3 , 200 MHz) δ (ppm) 6.01 (bs, 1H), 6.15 (bs, 1H), 6.9-7.1 (m, 2H), 7.2-7.3 (m, 2H), 7.3-7.7 (m, 15H). ^{13}C NMR (CDCl_3 , 50 MHz) δ (ppm) 114.7, 115.4, 127.8, 128.1, 129.1, 129.8, 130.5, 133.0, 135.8, 136.1, 153.1, 161.3, 167.6, 232.2. MS (m/z) 408 (M^+ , 16), 317 (10), 287 (17), 259 (100), 181 (31), 155 (16), 105 (23), 77 (3), 53 (10).

2-Methylene-3-pentenoyltriphenylsilane (9f). ^1H NMR (CDCl_3 , 200 MHz) δ (ppm) 1.6-1.8 (dd, 3H), 5.7-5.9 (dq, 1H), 6.02 (s, 1H), 6.08 (s, 1H), 6.15 (bd, 1H), 7.2-7.7 (m, 15H). ^{13}C NMR (CDCl_3 , 50 MHz) δ (ppm) 17.1, 125.7, 128.0, 129.5, 129.8, 130.8, 133.2, 136.3, 154.2, 232.4. MS (m/z) 354 (M^+ , 20), 313 (60), 277 (100), 259 (92), 95 (70), 77 (56), 67 (41).

2-Methylene-3-butynoyltriphenylsilane (9g). ^1H NMR (CDCl_3 , 200 MHz) δ (ppm) 2.5 (s, 1H), 5.4 (bd, 2H), 7.2-7.7 (m, 15H). ^{13}C NMR (CDCl_3 , 75 MHz) δ (ppm) 81.2, 83.7, 128.1, 129.8, 133.2, 135.8, 139.2, 143.3, 232.5. MS (m/z) 338 (M^+ , 35), 312 (61), 300 (53), 261 (84), 259 (100), 79 (75), 77 (79).

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