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Note

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Pt-catalyzed hydrosilylation of 1,3-diynes with triorganosilanes – regio- and stereoselective synthesis of mono- or bissilylated adducts

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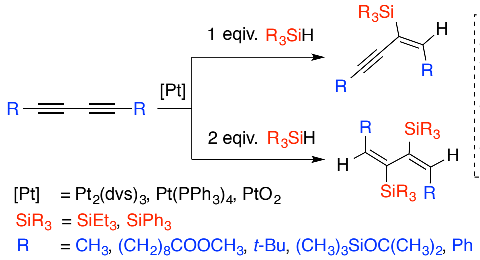


- The first mono- or bishydrosilylation of 1,3-diynes with equimolar reagents ratio,
- Commercially available reagents and Pt catalysts,
- High products yields and processes selectivities.

ABSTRACT: An efficient method has been successfully developed for the functionalization of various 1,3-diynes by the hydrosilylation reaction with triethyl- or triphenylsilane catalyzed by Pt catalysts ($Pt_2(dvs)_3$, PtO_2 or $Pt(PPh_3)_4$). Comprehensive optimization studies were performed for the first time to find suitable process conditions for the stereo- and regioselective formation of mono- or bissilylated adducts from commercially available substrates and catalysts. Silylsubstituted 1,3-enynes or bissilyl-functionalized buta-1,3-dienes were obtained with excellent yields and fully characterized.

Conjugated 1,3-diynes constitute useful and versatile building blocks in the synthesis of natural compounds, pharmaceuticals, π−conjugated polymers and optoelectronic materials.[1-11] Their functionalization occurs mostly *via* the addition reaction to the unsaturated C-C bonds and can lead to multisubstituted products.[3,12,13] The regio- and stereoselectivity of such processes depends on the structure of 1,3-diyne, the second reagent, the catalyst, and the process conditions.

Straightforward and 100% atom efficient hydrosilylation of alkynes,[12-21] which occurs *via* the addition of the Si-H bond to the C≡C bond, facilitates the modification of 1,3-diynes to silylfunctionalized 1,3-enyes or disilylsubstituted 1,3-butadienes or allenes.[22-26]The ability to form nine different isomers shows the process complexity. The reactivity of silyl groups in desilylation or coupling processes leads to such products representing useful (enyne and diene) synthons in advanced organic synthesis.[27-36] The high tolerance of the hydrosilylation process to various functional groups, its simplicity and diversity of the selectivity makes this method the first choice when the incorporation of a silyl group into the molecule is required. A number of scientific articles discuss the modification of monoynes with organosilicon compounds,[13-16,33,37,38] but the functionalization of conjugated 1,3-diynes, due to their much more complex structure, is far more difficult to control according to the regio- and stereoselectivity, and is limited to just a few examples.[23-26] In the reported works, the hydrosilylation of conjugated diynes has been catalyzed by homogeneous or heterogeneous catalysts containing Ru, Rh, Ni, Pd, Pt.[23-26] Depending on the type of the catalyst, reagents and reaction conditions, substituted but-3-en-1-ynes, buta-1,3-dienes, allenes or polymeric systems, cross-linked with silyl moieties have been obtained. Several molecular catalysts (e.g. commercially used Pt Karstedt's complex – $Pt_2(dvs)_3$ (Platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex)), as well as nanoparticles, have been examined in the hydrosilylation of conjugated diynes but, unfortunately the previously published articles do not contain detailed studies on the process conditions (reagents molar ratio, temperature, reaction time) or their efficiency. The results showed that it is possible to form different silylated enynes or bissilylated dienes in a more or less predictable manner, but the utility of the method is limited only to several diynes, which did not exhaust the subject of their Si-functionalization.[39]

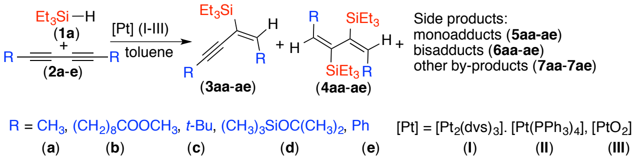
In light of this research, we have noticed that there is still a lack of comprehensive studies on the formation of mono- and bisadducts in the hydrosilylation of 1,3-diynes using a stoichiometric quantity of reagents and commercially available catalysts. Moreover, the aim of our study was to develop straightforward and efficient protocols for the preparation of such compounds which can be further used as building blocks in organic synthesis.

Therefore, we examined mono- and bishydrosilylation of structurally and electronically different 1,3-diynes, i.e.: hexa-2,4-diyne (**2a**), 10,12-docosadiyndioic acid dimethyl ester (**2b**) 2,2,7,7-tetramethyl-3,5-octadiyne (**2c**), 1,4-(1,1-dimethyloxy-trimethylsilyl)buta-1,3-diyne (**2d**) and 1,4-diphenylbuta-1,3-diyne (**2e**) with Et_3SiH (**1a**) or Ph_3SiH (**1b**), using stoichiometric quantities of reagents in the presence of commercially available catalysts: $Pt_2(dvs)_3$ (**I**), $Pt(PPh_3)_4$ (**II**) or PtO_2 (**III**). In the previously reported studies, the best selectivities were achieved in the reactions with using the silanes or 1,3-diynes in excess. Moreover, no optimization concerning the reagent ratio or concentration was discussed. Due to the high atom efficiency of the hydrosilylation reaction, the equimolar ratio of reagents has a positive impact on the process economy and the post-reaction mixture separation.

At the beginning of our research, we used free of steric hindrance Et_3SiH (**1a**) as a reagent and $Pt_2(dvs)_3$ (**I**), which is the first choice in the hydrosilylation reaction, and in the industrial scale. The initial catalytic tests were carried out with $4x10^{-4}$ mol of Pt/1 mol Si-H ratio at 100 °C. The monohydrosilylation of linear diynes **2a** and **2b** in the presence of **I**, due to the easy access of silane to unsaturated bonds was nonselective (Table 1, entry 1, 8). The application of the equimolar amount of reagents under standard reaction conditions led to the mixture of mono- and bisadduct. Lowering the reaction temperature to r.t. and a 10-fold excess of diyne over silane led to the obtaining of monoadduct in the vast majority of cases (Table 1, entry 2). The application of more sterically crowded and less reactive 1 mol% of [$Pt(PPh_3)_4$] (**II**) revealed the formation of a single product **3ac** under the same process conditions for the first time (Table 1, entry 4). The total conversion of reagents used in 1:1 molar ratio was achieved after 24 h. The same Pt-complex selectively catalyzed the monohydrosilylation of **2b** (Table 1, entry 6). Raising the temperature to 40°C immediately affected the reaction selectivity by increasing the amount of bisadduct formation, for the processes catalyzed by **II** and **III**. Typical reaction conditions were sufficient for bishydrosilylation of **2a** with 2 equiv. of **1a** in 6 hours (Table 1, entry 3). However, doubling the $Pt_2(dvs)_3$ (**I**) concentration and extending the reaction time to 24 h was required for the quantitative synthesis of product **4ab** (Table 1, entry 10).

The Pt Karstedt's catalytic system worked well in the monohydrosilylation of bulky 2,2,7,7-tetramethyl-3,5-octadiyne (**2c**) and electron rich 1,4-bistrimethylsiloxy-1,3-butadiyne (**2d**). The reaction occurred quantitatively with the *syn*-addition of silane and formation of internal alkenyl silanes **3ac** and **3ad** (Table 1, entries 11, 13).

Table 1. Hydrosilylation of 1,3-diynes (2a-e) with triethylsilane (1a) in the presence of Pt catalysts (I-III).[a]

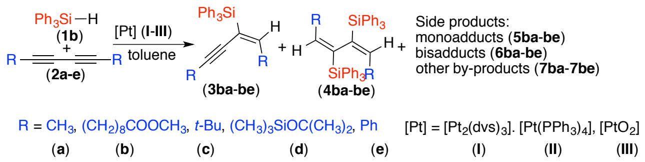


Ent.	2	[Pt]/[1a]/[2]	Cat.	T [°C]	t [h]	Conv. of 1a [%]	Selectivity 3/4/5/6/7 [%]
1	**2a**	4x10^{-4}/1/1	I	100	24	99	31/64/0/5/0
2		4x10^{-3}/1/10	I	r.t.	6	99	94/1/4/0/0
3		4x10^{-4}/2/1	I	100	6	99	0/99/0/0/0
4		10^{-2}/1/1	II	r.t.	24	99	99/0/0/0/0
5	**2b**	10^{-2}/1/1	II	40	24	99	89/10/0/0/0
6		10^{-2}/1/1.1	II	r.t.	24	99	99/0/0/0/0
7		10^{-2}/1/1	II	r.t.	48	99	89/10/0/0/0
8		4x10^{-3}/1/1	I	100	24	64	56/0/3/0/5
9		4x10^{-2}/1/1	III	40	70	80	45/0/35/0/0
10		8x10^{-4}/2/1	I	140[b]	24	99	0/99/0/0/0
11	**2c**	4x10^{-4}/1/1	I	100	24	99	99/0/0/0/0
12		8x10^{-4}/2/1	I	140[b]	48	75	42/52/5/0/0
13	**2d**	4x10^{-4}/1/1	I	100	24	99	99/0/0/0/0
14		8x10^{-4}/2/1	I	100	24	50	99/0/0/0/0
15	**2e**	2x10^{-1}/1/1	III	40	24	99	99/0/0/0/0
16		9.7x10^{-2}/1/1	III	40	24	95	95/0/0/0/0
17		9.7x10^{-2}/1/1	III	60	24	98	95/1/1/1/0
18		6x10^{-2}/1/1	II	40	72	98	91/7/0/0/0
19		6x10^{-2}/1/1	II	60	24	99	89/10/0/0
20		4x10^{-4}/1/1	I	100	48	91	64/23/2/2/0
21		4x10^{-3}/1.1/1	I	60	48	98	96/1/1/0/0
22		8x10^{-4}/2/1	I	140[b]	24	99	0/93/0/6/0

[a] Reaction conditions: toluene (2 mL). Conversions of reagents were determined by GC and GC-MS analysis; process selectivity was confirmed by ^{1}H, ^{29}Si NMR, GC-MS; [b] reaction carried out in xylene.

The synthesis of bisadduct was not successful for the hydrosilylation of **2d**, while the employment of silane to **2c** led to a mixture of mono- (**3ac**) and bisadduct (**4ac**), even when a two-fold excess of **1a,** 8x10^{-4} mol of $Pt_2(dvs)_3$ (**I**) and a higher temperature of 140°C were applied (Table 1, entry 12). Nevertheless, the formation of bisadduct with this bulky reagent **2c** was not detected in any previously published works when a higher excess of silane was used. The selective hydrosilylation of electronically different 1,4-diphenylbuta-1,3-diyne (**2e**) to form defined silylated product is difficult to implement. The equimolar hydrosilylation in the presence of **I** under various concentrations and temperatures occurred with a poor selectivity (Table 1, entry 20-22). Similar results were obtained when pre-catalyst (**II**) was used at 60°C and 40°C (Table 1, entry 18, 19). The incomplete conversion of reagents and the recurring presence of bisadduct in the post-reaction mixture were observed. The exclusive synthesis of monosilylated product **3ae** was possible when 2x10^{-1} mol of **III** was used and the reaction was carried out at 40°C for 24 h (Table 1, entry 15). However, in order to obtain bissilylated product, the reagents and catalyst **I** were used in the ratio [**I**]:[**1a**]:[**2e**] = 8x10^{-4}:1:2. After 24 h at 140°C, the complete conversion of substrates was achieved and two isomeric products were formed (**4ae**/**6ae** = 93/6) – Table 1, entry 22. The synthesis of bisadducts with different silanes has already been described in the literature but in all cases, an excess of silane or diyne were used. No equimolar quantity of reagents was used, which is reported for the first time in this document.

Table 2. Hydrosilylation of 1,3-diynes (2a-e) with triphenylsilane (1b) in the presence of Pt catalysts (I-III).[a]



Ent.	2	[Pt]/[1b]/[2]	Cat.	T [°C]	t [h]	Conv. of 1b [%]	Selectivity 3/4/5/6/7 [%]
1	**2a**	4x10^{-4}/1/1	I	100	24	99	92/8/0/0/0
2		4x10^{-4}/1/1	I	60	24	99	95/5/0/0/0
3		8x10^{-3}/1/1	I	r.t.	48	99	99/0/0/0/0
4		4x10^{-3}/2/1	I	100	48	99	90/0/10/0/0
5		4x10^{-4}/2/1	I	100	24	83	19/57/0/0/0
6	**2b**	4x10^{-2}/1/1	II	r.t.	120	99[b]	93/0/7/0/0
7		9.7x10^{-2}/1/1	III	100	24	99	47/0/53/0
8		4x10^{-3}/1/1	I	r.t.	48	99	93/0/7/0/0
9		4x10^{-4}/2/1	I	100	24	90[b]	10/80/0/10/0
10	**2c**	4x10^{-3}/1/1	I	100	24	99	99/0/0/0/0
11		4x10^{-4}/2/1	I	100	48	77	50/0/0/0/27
12	**2d**	4x10^{-4}/1/1	I	100	72	99	99/0/0/0/0
13	**2e**	4x10^{-3}/1/1	I	100	24	99	99/0/0/0/0
14		8x10^{-4}/2/1	I	100	24	77	50/0/0/0/27

[a] Reaction conditions: toluene (2 mL). Conversions of reagents were determined by GC and GC-MS analysis; process selectivity was confirmed by ^{1}H, ^{29}Si NMR, GC-MS; [b] reaction carried out in xylene.

The same optimization was carried out for mono- and bisaddition of more hindered Ph$_3$SiH (**1b**) to 1,3-diynes (**2a**-**e**). The hydrosilylation of hexa-1,3-diyne (**2a**) under standard reaction conditions led to the formation of monoadduct **3ba** in high excess to the bisilylated hexa-1,3-diene (**4ba**) (Table 2, entry 1). Lowering the process temperature to r.t., as well as increasing that of the Pt$_2$(dvs)$_3$ catalyst (**I**) concentration by an order of magnitude, and doubling the reaction time, exclusively yielded product **3ba** with a complete conversion of reagents used in the 1:1 ratio (Table 2, entry 3). The product **3ba** was easily crystallized from the *n*-hexane, by its slow evaporation and the X-ray structure was measured. The analysis of the crystal structure clearly showed that the process occurred regioselectively with the *syn*-addition of the Si-H bond into the C-C triple bond and the formation of β-*E*-product (for details see SI). The selective synthesis of bissilylated buta-1,3-diene was not possible. A mixture of mono- and bissilylated products were obtained irrespective of the process conditions (Table 2, entry 4, 5). The bulkier silane **1b** did not affect the selectivity of the hydrosilylation of **2b**. In that case, again the application of $Pt_2(dvs)_3$ (**I**), $[Pt(PPh_3)_4]$ (**II**) and r.t. were necessary to obtain isomer **3bb** with a 93% yield (Table 2, entry 6, 8). When a higher temperature and catalysts **I** or **III** were used, both isomers were obtained in different ratios.

Moreover, 4x10^{-2} mol of Pt had to be used to provide the total conversion of **1b**. Because of the steric hindrance of silane **1b** and 2,2,7,7-tetramethyl-3,5-octadiyne (**2c**) in the hydrosilylation reaction the only monoadduct **3bc** was formed, even when the ratio **2c**/**1b** = 1:2 was used. The crystal structure of compound **3bc** was measured, showing that the β-*E*-isomer was obtained in the *syn*-addition of **1b** to the C≡C bond of **2c** **(**the molueclar structure of **3bc** is presented in SI**)**. Hydrosilylation of another bulky diyne **2d** required an extension of the reaction time to 72 h for more steric **1b**, compared to an analog reaction with **1a**. In this particular case, the synthesis of bisadduct was not achieved.

Hydrosilylation of **2e** with **1b** occurred selectively with the application of **I**. In order to reach total conversion during the monohydrosilylation reaction, reagents and a catalyst were used with the following ratio: **I**:**1b**:**2e** = 4x10^{-3}:1:1 (Table 2, entry 13). A lower concentration of the catalyst was insufficient for obtaining a high yield of the desired product. The formation of bisadduct **4be** with a 2-fold excess of **1b** did not occur (Table 2, entry 14). Compound **3be** was the only product.

The isolated yields of the mono- and bishydrosilylation products obtained under optimized reaction conditions (Tables 1 and 2) are presented in Figure 1.

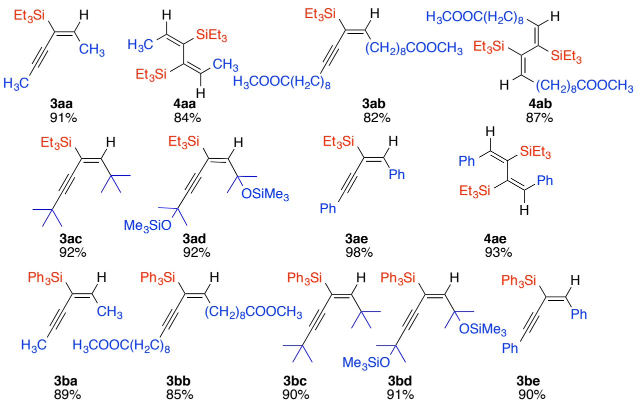


Figure 1. The isolated yields of mono- and bishydrosilylation products.

We have clearly demonstrated that the application of commercially available catalysts and the appropriate choice of reaction conditions and reagents made it possible to obtain the desired mono- or bisilylated products in the hydrosilylation of 1,3-diynes with high yields and selectivities. The reactions occurred *via syn*-addition of tertiary silane to the C-C triple bond with the formation of the internal alkenyl silane. Pt-Karstedt's catalyst was used for the synthesis of bisadducts, while PtO_2 and $Pt(PPh_3)_4$ because of their lower activity were more sufficient for the selective formation of monosilylated enynes. For the first time, applying optimized reaction conditions, it was possible to obtain the desired product using equimolar quantities of reagents, which due to the atom-economy reaction simplifies the separation procedure and reduces the cost of the process.

Experimental Section

General information.

Fourier Transform-Infrared (FT-IR) spectra were recorded on a Bruker Tensor 27 Fourier transform spectrophotometer equipped with a SPECAC Golden Gate, diamond ATR unit, with ensuring a resolution of $2cm^{-1}$.

NMR spectra were recorded at 25°C on a Bruker Ultra Shield 300 MHz or Bruker Ascend 400 MHz NANOBAY spectrometers. $CDCl_3$ was used as a solvent and for internal deuterium lock. Chemical shifts were reported in ppm with reference to the residual solvent peaks for ^{1}H and ^{13}C NMR and to TMS for ^{29}Si NMR. The multiplicities were reported as follows: singlet (s), doublet (d), a doublet of triplets (dt), multiplet (m), triplet (t) and broad resonances (br).

GC-MS analyses were performed on a Bruker 450-GC with a 30 m Varian DB-5 0.25 mm capillary column and a Scion SQ-MS detector. Two temperature programs were used a) 80°C (3 min), 10°C/min, 250 °C (30 min), b) 150°C (3 min), 10°C/min, 280°C (44.5 min).

GC analyses were performed on a Bruker Scion 435-GC equipped with a 30 m Varian DB-5 0.25 mm capillary column. Two temperature programs were used a) 80°C (3 min), 10°C/min, 250°C (30 min), b) 150°C (3 min), 10°C/min, 280 °C (44.5 min).

Elemental analyses were carried out on Vario EL III Analyser. The content of hydrogen and carbon was obtained as data in percentage.

Diffraction data were collected by the ω-scan technique at room temperature (**1**) or at 100(1) K (**2**) on Rigaku XCalibur four-circle diffractometer with EOS CCD detector and graphite-monochromated MoK_α radiation (λ=0.71073 Å). The data were corrected for Lorentz-polarization as well as for absorption effects.[40] Precise unit-cell parameters were determined by a least-squares fit of 5900 (**1**) and 5637 (**3**) reflections of the highest intensity, chosen from the whole experiment. The structures were solved with SHELXT-2013[41] and refined with the full-matrix least-squares procedure on F^2 by SHELXL-2013.[42] All non-hydrogen atoms were refined anisotropically, hydrogen atoms were placed in idealized positions and refined as 'riding model' with isotropic displacement parameters set at 1.2 (1.5 for CH_3) times U_{eq} of appropriate carrier atoms.

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, Nos. CCDC-1873913 (**3ba**) and CCDC-1873914 (**3bc**). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK; e-mail: deposit@ccdc.cam.ac.uk, or www: www.ccdc.cam.ac.uk.

To prove the regioselectivity of the process, *cis*-addition of silane (**1a**) to diyne (**2a** or **2c**), and formation of products **4aa** and **3ac**, for which we did not obtain any crystal structures, we have carried out additional ^{1}H-^{13}C HSQC and NOESY 2D NMR experiments. Theses analysis clearly showed the assumed process selectivity (for details see SI).

Melting Point analyses were carried out using Melting Point M-565 Buchi apparatus equipped with a CD Demo MeltingPoint Monitor. The compound was placed in the capillary and heated with the temperature gradients 2.5°C/min, 5°C/min and 10°C/min. The melting point was detected automatically and by the visual inspections through the lens. Each analysis was repeated three times.

General procedure for hydrosilylation of 1,3-diynes (2a–e) with triethylsilane (1a) and triphenylsilane (1b) – a synthesis of monosilylsubsituted 1,3-enyes (3).

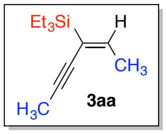
To a solution of silane (**1a-b**) (1.0 mmol) and an appropriate 1,3-diyne (**2a-e**) (1.0 mmol) in 2mL of toluene or xylene Pt catalyst was added in the [**Pt**]:[**1b**] of [4x10^{-4}–10^{-2}]:[1] ratio depending on the experiment and the catalyst (for detailed ratio please see Tables 1 and 2 in the manuscript). Subsequently, the reaction mixture was heated to 40-140°C (oil bath) or kept at room temperature and stirred until the full conversion of Si–H was detected. The reaction time for hydrosilylation of each 1,3-diyne was determined by GC-MS, ^{1}H NMR and for products with a mass above 600 g/mol was determined only by ^{1}H NMR. Then the solvent was evaporated under vacuum. The crude product was dissolved in *n*-hexane and filtered through silica gel. After evaporation products were characterized by NMR, GC-MS, IR and elemental analysis. Reactions, which were carried out at 140°C were performed in a Schlenk flask with a Rotaflo® stopcock.

General procedure for hydrosilylation of 1,3-diynes (2a–e) with triethylsilane (1a) and triphenylsilane (1b) – a synthesis of bisilylsubsituted 1,3-dienes (4).

To a solution of silane (**1a-b**) (2.0 mmol) and an appropriate 1,3-diyne (**2a-e**) (1.0 mmol) in 2mL of toluene or xylene Pt catalyst was added in the [Pt]:[1b] of [$4x10^{-4}$–10^{-2}]:[1] ratio depending on the experiment and the catalyst (for detailed information concerning reagents ratios please see Tables 1 and 2 in the manuscript). Subsequently, the reaction mixture was heated to 40-140 °C (oil bath) or kept at room temperature and stirred until the full conversion of Si–H was detected. The reaction time for hydrosilylation of each 1,3-diyne was determined by GC-MS, ^{1}H NMR and for products with a mass above 600 g/mol was determined only by ^{1}H NMR. Then the solvent was evaporated under vacuum. The crude product was dissolved in *n*-hexane and filtered through silica gel. After evaporation products were characterized by NMR, GC-MS, IR and elemental analysis. Reactions, which were carried out at 140°C were performed in a Schlenk flask with a Rotaflo® stopcock.

Analytical data for obtained products.

(2*E*)-3-Triethylsilyl-hex-2-en-4-yne (3aa).

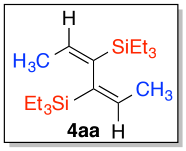


3aa

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 0.63 (m, 6H, $C\underline{H}_2CH_3$, $J_{H,H}$= 7.6 Hz), 0.94 (t, 9H, $CH_2C\underline{H}_3$, $J_{H,H}$= 7.8 Hz), 1.94 (d, 3H, $=C(H)C\underline{H}_3$), 2.02 (s, 3H, $\equiv CC\underline{H}_3$), 6.09 (m, 1H, $=C\underline{H}$, $J_{H,H}$= 6.4 Hz). ^{13}C {^{1}H}NMR (75 MHz, $CDCl_3$, δ, ppm): 3.0 ($C\equiv C\underline{C}H_3$), 4.8 ($\underline{C}H_2CH_3$), 7.4 ($CH_2\underline{C}H_3$), 18.2 ($=C(H)\underline{C}H_3$), 79.0 ($\underline{C}\equiv CCH_3$), 93.4 ($C\equiv \underline{C}CH_3$), 123.0 ($=\underline{C}(Si(CH_2CH_3)_3)$), 145.6

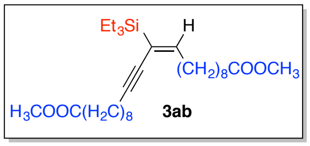
(=$\underline{C}$(H)CH$_3$). ^{29}Si NMR (79 MHz, CDCl$_3$, δ, ppm): 2.2 ($\underline{Si}$CH$_2$CH$_3$). GC-MS (EI, 70 eV) m/z (rel. int., %): 194.2 (M$^+$, 20), 166.3 (23), 165.3 (60), 125.1 (100). FT-IR (ATR, cm^{-1}): 3054, 2957, 2924, 2872, 1705, 1590, 1435, 1376, 1312, 1260, 1189, 1164, 1119, 1095, 1072, 1026, 801, 750, 720, 693, 537. Elemental Anal. Calc. for $C_{12}H_{22}Si$: C, 74,14; H, 11.41; found: C, 74.03; H, 11.38. Isolated yield = 179 mg (91 %) from 197 mg (1 mmol), transparent liquid.

(2*E*, 4*E*)- 2,4-Bis(triethylsilyl)hexa-2,4-diene (4aa).



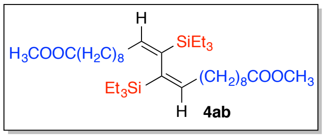
^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 0.59 (m, 12H, SiC$\underline{H}_2$CH$_3$), 0.94 (t, 18H, SiCH$_2$C$\underline{H}_3$, $J_{H,H}$= 7.9 Hz), 1.54 (d, 6H, =CHC$\underline{H}_3$) 5.77 (m, 2H, =C$\underline{H}$CH$_3$, $J_{H,H}$= 6.4 Hz).^{13}C {^{1}H} NMR (75 MHz, CDCl$_3$, δ, ppm): 4.1 ($\underline{C}$H$_2$CH$_3$), 7.7 (CH$_2\underline{C}$H$_3$), 16.3 (=CH$\underline{C}$H$_3$), 133.5 (=$\underline{C}$HCH$_3$), 141.9 ($\underline{C}$=CHCH$_3$). ^{29}Si NMR (79 MHz, CDCl$_3$, δ, ppm): -1.29 ($\underline{Si}$CH$_2$CH$_3$). GC-MS (EI, 70 eV) m/z (rel. int., %): 310.3 (M$^+$, 10), 253.3 (25), 166.2 (13), 115.1 (100). FT-IR (ATR, cm^{-1}): 2952, 2909, 2874, 1716, 1458, 1416, 1376, 1236, 1005, 969, 799, 714, 586, 529. Elemental Anal. Calc. for $C_{18}H_{38}Si_2$: C, 69.59; H, 12.33; found: C, 69.38; H, 12.21 Isolated yield = 264 mg (84 %) from 314 mg (1 mmol), pale yellow liquid.

Dimethyl (*E*)-11-(triethylsilyl)docos-10-en-12-ynedioate (3ab).



^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 0.62 (m, 6H, SiC$\underline{H}_2$CH$_3$, $J_{H,H}$= 7.8 Hz), 0.93 (t, 9H, SiCH$_2$C$\underline{H}_3$, $J_{H,H}$= 7.9 Hz), 1.29-2.37 (m, 32H, CH$_3$OOC(C$\underline{H}_2$)$_8$), 3.66 (s, 6H, C$\underline{H}_3$OOC), 5.97 (t, 1H, C$\underline{H}$=C, $J_{H,H}$= 6.9 Hz). ^{13}C {^{1}H} NMR (75 MHz, CDCl$_3$, δ, ppm): 2.6 (SiCH$_2\underline{C}$H$_3$), 7.7 (Si$\underline{C}$H$_2$CH$_3$), 19.3-34.2 (CH$_3$OOC($\underline{C}$H$_2$)$_8$), 51.5 ($\underline{C}$H$_3$OOC), 65.4 (C≡$\underline{C}$-$\underline{C}$≡C), 80.1 (C≡$\underline{C}$-CSi), 97.5 ($\underline{C}$≡C-CSi), 122.0 ($\underline{C}$H=CSi), 151.2 (CH=$\underline{C}$Si), 174.4 (CH$_3$OO$\underline{C}$). ^{29}Si NMR (79 MHz, CDCl$_3$, δ, ppm): -2.16 ($\underline{Si}$CH$_2$CH$_3$). GC-MS (EI, 70 eV) m/z (rel. int., %): 506.6 (M$^+$, 19), 117.0 (95), 115.1 (49), 87.2 (100). FT-IR (ATR, cm^{-1}): 2955, 2936, 2912, 2876, 1376, 1358, 1249, 1158, 1034, 850, 751. Elemental Anal. Calc. for $C_{30}H_{54}O_4Si$: C, 71.09; H, 10.74; found: C, 71.16; H, 10.82. Isolated yield = 427 mg (82 %) from 529 mg (1 mmol), yellow oil

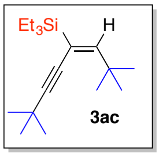
Methyl (10*E*,12*E*)-21-(methylperoxy)-11,12-bis(triethylsilyl)docosa-10,12,21-trienoate (4ab).



4ab

^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 0.56 (m, 12H, $SiC\underline{H}_2CH_3$, $J_{H,H}$= 7.9 Hz), 0.93 (t, 18H, $SiCH_2C\underline{H}_3$, $J_{H,H}$= 7.8 Hz), 1.26 (m, 20H, $CH_3OOCCH_2CH_2(C\underline{H}_2)_5CH_2$), 1.60 (m, 4H, $CH_3OOCCH_2C\underline{H}_2(CH_2)_5CH_2$), 1.90 (m, 4H, $CH_3OOCCH_2CH_2(CH_2)_5C\underline{H}_2$), 2.29 (t, 4H, $CH_3OOCC\underline{H}_2CH_2(CH_2)_5CH_2$, $J_{H,H}$= 7.5 Hz), 3.65 (s, 6H, $C\underline{H}_3OOC$), 5.58 (t, 2H, $C\underline{H}$=C, $J_{H,H}$= 6.5 Hz). ^{13}C {^{1}H} NMR (75 MHz, CDCl$_3$, δ, ppm): 4.1 ($SiCH_2\underline{C}H_3$), 7.7 ($Si\underline{C}H_2CH_3$), 25.1, 29.3, 29.4, 29.6, 29.8, 31.0. 34.2 ($CH_3OOC(\underline{C}H_2)_8$), 51.6 ($\underline{C}H_3OOC$), 139.7 ($\underline{C}H$=CSi), 140.4 (CH=$\underline{C}$Si), 174.7 ($CH_3OO\underline{C}$). ^{29}Si NMR (79 MHz, CDCl$_3$, δ, ppm): -1.54 ($\underline{Si}CH_2CH_3$). GC MS (EI, 70 eV) m/z (rel. int., %): 622.8 (M+, 44), 117.0 (27), 115.1 (46), 87.2 (100). FT-IR (ATR, cm^{-1}): 2948, 2921, 2873, 2853, 1750, 1458, 1236, 1169, 1012, 716. Elemental Anal. Calc. for $C_{36}H_{70}O_4Si_2$: C, 69.49; H, 11.32; found: C, 69.19; H, 11.44. Isolated yield = 555mg (87 %) from 638 mg (1 mmol), transparent liquid.

(*E*)-4-Triethylsilyl-2,2,7,7-tetramethyloct-3-en-5-yn (3ac).

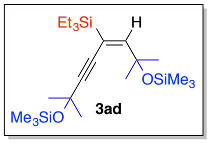


3ac

^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 0.62 (m, 6H, $C\underline{H}_2CH_3$, $J_{H,H}$= 7.8 Hz), 0.95 (t, 9H, $CH_2C\underline{H}_3$, $J_{H,H}$= 7.8 Hz), 1.19 (s, 9H, $(C\underline{H}_3)_3$), 1.24 (s, 9H, $(C\underline{H}_3)_3$), 5.85 (s, 1H, $=C\underline{H}(C(CH_3)_3)$. ^{13}C {^{1}H} NMR (75 MHz, CDCl$_3$, δ, ppm): 3.1 ($Si\underline{C}H_2CH_3$), 7.5($SiCH_2\underline{C}H_3$), 28.6 ($\equiv C\text{-}\underline{C}(CH_3)_3$), 29.9 ($=C\text{-}C(\underline{C}H_3)_3$), 31.0 ($\equiv C\text{-}C(\underline{C}H_3)_3$), 35.8 ($=C\text{-}\underline{C}(CH_3)_3$), 79.0 ($\equiv\underline{C}\text{-}C(CH_3)_3$), 108.4 ($\underline{C}\equiv C\text{-}C(CH_3)_3$), 118.9 ($=\underline{C}\text{-}C(CH_3)_3$), 158.9 ($\underline{C}=C\text{-}C(CH_3)_3$). ^{29}Si NMR (79 MHz, CDCl$_3$, δ, ppm): 3.16 ($\underline{Si}CH_2CH_3$). GC MS (EI, 70 eV) m/z (rel. int., %): 278.3 (M+, 17), 139.1 (56), 115.0 (61), 87.1 (100). FT-IR (ATR, cm^{-1}): 2990, 2909, 2874, 1578, 1476, 1306, 1246, 1004, 718, 696. Elemental Anal. Calc. for $C_{18}H_{34}Si$: C, 77,61; H, 12.30; found: C, 77.54; H, 12.33. Isolated yield = 260 mg (92%) from 283 mg (1 mmol), transparent liquid.

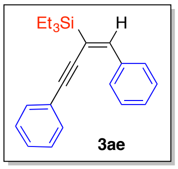
Product **3ac** has been previously obtained.[41]

(*E*)-4-Triethylsilyl-2,7-dimethyl-2,7-trimethylsiloxy-octa-3-en-5-yne (3ad).



^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 0.13 (s, 9H, $OSi(C\underline{H}_3)_3$), 0.17 (s, 9H, $OSi(C\underline{H}_3)_3$), 0.68 (m, 6H, $C\underline{H}_2CH_3$), 0.95 (t, 9H, $CH_2C\underline{H}_3$, $J_{H,H}$= 7.8 Hz), 1.51 (s, 6H, $=CHC(C\underline{H}_3)_2$-$OSi(CH_3)_3$), 1.54 (s, 6H, $C\equiv CC(C\underline{H}_3)_2OSi(CH_3)_3$), 6.24 (s, 1H, $=C\underline{H}C(CH_3)_2OSi(CH_3)_3$). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, δ, ppm): 2.1 ($C\equiv CC(CH_3)_2OSi(\underline{C}H_3)_3$), 2.7 ($=CHC(CH_3)_2OSi(\underline{C}H_3)_3$), 2.9 ($CH_2\underline{C}H_3$), 7.4 ($\underline{C}H_2CH_3$), 30.0 ($=CH$-$C(\underline{C}H_3)_2OSi(CH_3)_3$), 33.2 ($C\equiv CC(\underline{C}H_3)_2OSi(CH_3)_3$), 67.6 ($C\equiv C\underline{C}(CH_3)_2OSi(CH_3)_3$), 76.8 ($=CH\underline{C}(CH_3)_2OSi(CH_3)_3$), 81.8 (-$\underline{C}\equiv CCCH_3)_2OSi(CH_3)_3$), 104.8 ($C\equiv \underline{C}C(CH_3)_2OSi(CH_3)_3$), 117.4 ($\underline{C}=CHC(CH_3)_2OSi(CH_3)_3$), 160.6 ($=\underline{C}HC(CH_3)_2OSi(CH_3)_3$). ^{29}Si NMR (79 MHz, $CDCl_3$, δ, ppm): 4.94 ($\underline{Si}CH_2CH_3$), 9.34 ($C=CH$-$C(CH_3)_2O\underline{Si}(CH_3)_3$), 12.44 ($C\equiv C$-$C(CH_3)_2O\underline{Si}(CH_3)_3$). GC MS (EI, 70 eV) m/z (rel. int., %): 426.4 (M+, 20), 131.1 (100), 73.1 (34), 87.1 (18). FT-IR (ATR, cm^{-1}): 3424, 2954, 2912, 2875, 1742, 1459, 1416, 1360, 1282, 1239, 1168, 1050, 1003, 961, 842, 720, 700, 587. Elemental Anal. Calc. for $C_{22}H_{46}O_2Si_3$: C, 61.90; H, 10.86; found: C, 61.79; H, 10.82. Isolated yield = 394 mg (92%) from 428 mg (1 mmol), transparent oil.

(*E*)-2-Triethylsilyl-1,4-diphenylbuta-1-en-3-yne (3ae)

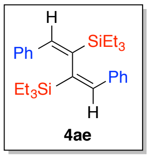


^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 0.86 (m, 6H, $C\underline{H}_2CH_{3,}$ $J_{H,H}$= 7.7 Hz), 1.09 (t, 9H, $CH_2C\underline{H}_{3,}$ $J_{H,H}$= 7.8 Hz), 6.87 (s, 1H, $=C\underline{H}$), 7.32 - 8.06 (m, 10H, $C_6\underline{H}_5$). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, δ, ppm): 3.2 ($CH_2\underline{C}H_3$), 7.5 ($\underline{C}H_2CH_3$), 91.0 ($\underline{C}\equiv CC_6H_5$), 100.6 ($\equiv\underline{C}C_6H_5$), 121.0 ($=\underline{C}(H)C_6H_5$), 124.6, 128.0, 128.4, 128.5, 128.6, 129.0 ($\underline{C}_6H_5$), 131.4

$(=\underline{C}Si(CH_2CH_3)_3)$, 132.7, 138.0 $(\underline{C}_6H_5)$, 145.0 $(=\underline{C}H)$. ^{29}Si NMR (79 MHz, $CDCl_3$, δ, ppm): 5.38 $(\underline{Si}CH_2CH_3)$. GC MS (EI, 70 eV) m/z (rel. int., %): 318.3 (M^+, 99), 131.0 (100), 87.1 (50), 59.1 (60). FT-IR (ATR, cm^{-1}): 3085, 2967, 2925, 2863, 1567, 1462, 1428, 1360, 1109, 746, 707, 507. Elemental Anal. Calc. for $C_{22}H_{26}Si$: C, 82.96; H, 8.23; found: C, 83.03; H, 8.30 Isolated yield = 317 mg (98%) from 323 mg (1 mmol), yellow oil.

Product **3ae** has been previously obtained.[23]

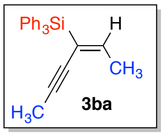
(1*E*, 3*E*)-2,3-Bis(triethylsilyl)-1,4-diphenylbuta-1,3-diene (4ae).



4ae

^{1}H NMR (300 MHz, CDCl3, δ, ppm): 0.60 (m, 12H, $-C\underline{H}_2CH_3$), 0.99 (t, 18H, $-CH_2C\underline{H}_3$, $J_{H,H}$= 7.9 Hz), 6.83 (s, 2H, $C=C\underline{H}$) 7.28-7.65 (m, 10H, $C_6\underline{H}_5$). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, δ, ppm): 4.4 $(CH_2\underline{C}H_3)$, 7.8 $(\underline{C}H_2CH_3)$, 127.2 $(C=CHCH=\underline{C}H-)$, 128.3 $(C=\underline{C}HCH=CH-)$, 129.0 $(C=CH\underline{C}H=CH-)$, 136.8 $(\underline{C}=CHCH=CH-)$, 139.8 $(\underline{C}H=CSi)$, 145.7 $(CH=\underline{C}Si)$. ^{29}Si NMR (79 MHz, $CDCl_3$, δ, ppm): 1.73 $(\underline{Si}CH_2CH_3)$. GC MS (EI, 70 eV) m/z (rel. int., %): 434.5 (M^+, 34), 180.2 (48), 115.2 (100), 87.2 (97). FT-IR (ATR, cm^{-1}): 3058, 3022, 2952, 2909, 2873, 1598, 1491, 1457, 1414, 1376, 1237, 1074, 1005, 972, 919, 798, 751, 719, 690, 594. Elemental Anal. Calcd for $C_{28}H_{42}Si_2$: C, 77.35; H, 9.74; found: C, 77.41; H, 9.67. Isolated yield = 410 mg (93%) from 441 mg (1 mmol), yellow oil.

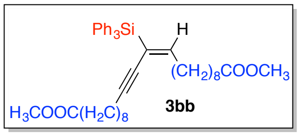
(2*E*)-3-Triphenylsilyl-hex-2-en-4-yne (3ba).



3ba

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.96 (s, 3H, $\equiv CC\underline{H}_3$), 2.01 (d, 3H, $=CC\underline{H}_3$), 6.22 (m, 1H, $=C\underline{H}$, $J_{H,H}$= 6.5 Hz), 7.34 - 7.62 (m, 15H, $C_6\underline{H}_5$). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, δ, ppm): 4.9 $(\equiv C\underline{C}H_3)$, 18.4 $(=C\underline{C}H_3)$, 79.3 $(\underline{C}\equiv CCH_3)$, 95.6 $(\equiv\underline{C}CH_3)$, 120.7 $(=\underline{C}Si(C_6H_5)_3)$, 127.8, 129.7, 134.0, 136.5 $(\underline{C}_6H_5)$, 151.3 $(=\underline{C}H)$. ^{29}Si NMR (79 MHz, $CDCl_3$, δ, ppm): -15.96 $(\underline{Si}C_6H_5)$. GC MS (EI, 70 eV) m/z (rel. int., %): 388.2 (M^+, 30), 260.2 (45), 259.2 (100), 181.1 (57). FT-IR (ATR, cm^{-1}): 3100, 2912, 2846, 1578, 1483, 1425, 1257, 1107, 737, 694, 504, 483.

Elemental Anal. Calc. for $C_{24}H_{22}Si$: C, 85.15; H, 6.55; found: C, 85.24; H, 6.52. Isolated yield = 310 mg (89%) from 348 mg (1 mmol), white solid, mp = 116-122°C. Crystal data: $C_{24}H_{22}Si$, M_r = 338.50, triclinic, P-1, a = 7.1974(5) Å, b = 8.1606(7) Å, c = 16.5692(10) Å, α = 82.517(6)°, β = 83.519(5)°, γ = 77.911(7)°, V = 939.82(12) Å^3, Z = 2, F(000) = 360, d_x = 1.196 g·cm^{-3}, μ = 0.128 mm^{-1}. 14413 reflections collected up to 2Θ = 27.0°, of which 3834 independent (R_{int} = 0.023), 3290 with I>2σ(I). Final R(F) [I>2σ(I)] = 0.039, wR(F^2) [I>2σ(I)] = 0.093, R(F) [all data] = 0.048, wR(F^2) [all data] = 0.099, S = 1.05, max/min Δρ = 0.36/–0.24 e·Å^{-3}.

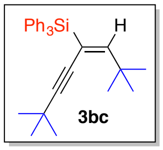


3bb

Dimethyl (*E*)-11-(triphenylsilyl)docos-10-en-12-ynedioate (3bb).

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.10-2.37 (m, 32H, $CH_3OOC(C\underline{H}_2)_8$), 3.57 (s, 6H, $C\underline{H}_3OOC$), 6.04 (t, 1H, $C\underline{H}$=C, $J_{H,H}$= 7.0 Hz), 7.13-7.52 (m, 15H, $C_6\underline{H}_5$). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, δ, ppm): 19.9, 25.0, 28.7, 28.9, 29.0, 29.2, 32.5, 34.1 ($CH_3OOC(\underline{C}H_2)_8$), 51.5 ($\underline{C}H_3OOC$), 80.4 (C≡$\underline{C}$-CSi), 99.7 ($\underline{C}$≡C-CSi), 119.5 ($\underline{C}$H=CSi), 127.7-136.4 ($\underline{C}_6H_5$), 156.5 (CH=$\underline{C}$Si), 174.3 ($CH_3OO\underline{C}$). ^{29}Si NMR (79 MHz, $CDCl_3$, δ, ppm): -15.99 ($\underline{Si}C_6H_5$). FT-IR (ATR, cm^{-1}): 3069, 2928, 2855, 1736, 1429, 1363, 1171, 1109, 1028, 998, 866, 741, 698, 541, 507. Elemental Anal. Calc. for $C_{42}H_{54}O_4Si$: C, 77.49; H, 8.36; found: C, 77.42; H, 8.40. Isolated yield = 570 mg (85%) from 671mg (1 mmol), white solid, mp = 116-122°C.

2,2,7,7-Tetramethyl-4-triphenylsilyl-oct-3-en-5-yne (3bc).

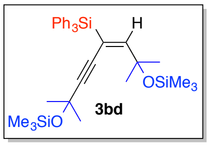


3bc

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 1.13 (s, 9H, $(C\underline{H}_3)_3$), 1.29 (s, 9H, $(C\underline{H}_3)_3$), 6.15 (s, 1H, =$C\underline{H}(C(CH_3)_3)$), 7.26-7.70 (m, 15H, $C_6\underline{H}_5$). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, δ, ppm): 28.5 (=$C(H)C(\underline{C}H_3)_3$), 29.7 (≡$C\underline{C}(CH_3)_3$), 30.6 (=$C(H)\underline{C}(CH_3)_3$), 36.1 (≡$CC(\underline{C}H_3)_3$), 79.7 ($\underline{C}$≡$CC(CH_3)_3$), 110.7 (≡$\underline{C}C(CH_3)_3$), 117.2 (=$\underline{C}Si(C_6H_5)_3$), 127.7, 129.5, 134.3, 136.6 ($\underline{C}_6H_5$), 164.2 (=$\underline{C}$H). ^{29}Si NMR (79 MHz, $CDCl_3$, δ, ppm): -14.99 ($\underline{Si}(C_6H_5)_3$). GC MS (EI, 70 eV) m/z (rel. int., %): 422.4 (M+, 16), 260.3 (27), 259.2 (100), 181.1 (17). FT-IR (ATR, cm^{-1}): 3068, 2973, 2956, 2864, 1567, 1475, 1462, 1428, 1360, 1264, 1246, 1203, 1187, 1109, 1028, 997, 746, 707, 698, 620, 545, 525, 508, 497, 425. Elemental Anal. Calcd for $C_{30}H_{34}Si$: C, 85.25; H, 8.11; found: C, 85.21; H, 8.14. Isolated yield = 391 mg (90%) from 434 mg (1 mmol), white solid, mp = 99-102°C. Crystal data: $C_{30}H_{34}Si$, M_r = 422.66, orthorhombic, $P2_12_12_1$, a = 8.4109(4) Å, b = 10.9387(4) Å, c = 28.7518(13) Å, V = 2645.3(2) Å^3, Z = 4, F(000) = 912, d_x = 1.061 g·cm^{-3}, μ = 0.102 mm^{-1}. 14123 reflections collected up to 2Θ = 27.1°, of which 5233 independent (R_{int} = 0.021), 4608 with I>2σ(I). Final R(F) [I>2σ(I)] = 0.040, wR(F^2) [I>2σ(I)] = 0.103, R(F) [all data] = 0.049, wR(F^2) [all data] = 0.1107, S = 1.05, max/min Δρ = 0.22/–0.14 e·Å^{-3}.

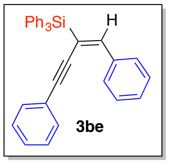
Product **3bc** has been previously obtained.[17]

2,7-Dimethyl-2,7-bis(trimethylsiloxy)-4-triphenylsilyl-oct-3-en-5-yne (3bd).



^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): -0.04 (s, 9H, $OSi(C\underline{H}_3)_3$), -0.02 (s, 9H, $OSi(C\underline{H}_3)_3$), 1.32 (s, 6H, $=C(H)C(C\underline{H}_3)_2OSi(CH_3)_3$), 1.61 (s, 6H, $C\equiv C\text{-}C(C\underline{H}_3)_2OSi(CH_3)_3$), 6.39 (s, 1H, $=C(\underline{H})C(CH_3)_2OSi(CH_3)_3$, 7.26-7.63 (m, 15H, $C_6\underline{H}_5$). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, δ, ppm): 1.8 ($\equiv CC(CH_3)_2OSi(\underline{C}H_3)_3$), 2.4 ($=C(H)C(CH_3)_2OSi(\underline{C}H_3)_3$), 29.9 ($=C(H)C(\underline{C}H_3)_2OSi(CH_3)_3$), 32.8 ($\equiv CC(\underline{C}H_3)_2OSi(CH_3)_3$), 67.4 ($\equiv C\underline{C}(CH_3)_2OSi(CH_3)_3$), 77.0 ($=C(H)\underline{C}(CH_3)_2OSi(CH_3)_3$), 82.2 ($\underline{C}\equiv CC(CH_3)_2OSi(CH_3)_3$), 106.8 ($\equiv\underline{C}C(CH_3)_2OSi(CH_3)_3$), 115.9 ($=\underline{C}SiC_6H_5$), 127.9, 129.8, 133.4, 136.6 ($\underline{C}_6H_5$), 165.9 ($=\underline{C}(H)C(CH_3)_2OSi(CH_3)_3$). ^{29}Si NMR (79 MHz, $CDCl_3$, δ, ppm): -14.21 ($\underline{Si}(C_6H_5)_3$), 9.70 ($C=CH\text{-}C(CH_3)2O\underline{Si}(CH_3)_3$), 12.76 ($C\equiv C\text{-}C(CH_3)_2O\underline{Si}(CH_3)_3$. GC MS (EI, 70 eV) m/z (rel. int., %): 570.4 (M+, 21), 259.2 (90), 131.1 (100), 73.1 (73). FT-IR (ATR, cm^{-1}): 3070, 2978, 2955, 2930, 1428, 1376, 1250, 1159, 1110,1035, 804, 707, 509. Elemental Anal. Calcd for $C_{34}H_{46}O_2Si_3$: C, 71.52; H, 8.12; found: C, 71.47; H, 8.05. Isolated yield = 526 mg (91 %) from 578 mg (1 mmol), light yellow liquid.

(*1E*)-1,4-Diphenyl-2-triphenylsilyl-but-1-3-yne (3be).



3be

^{1}H NMR (300 MHz, CDCl$_3$, δ, ppm): 7.10 (s, 1H, $=C\underline{H}$), 7.33-8.12 (m, 25H, $C_6\underline{H}_5$). ^{13}C {^{1}H} NMR (75 MHz, CDCl$_3$, δ, ppm): 91.5 ($\equiv\underline{C}C_6H_5$), 102.2 ($\underline{C}\equiv CC_6H_5$), 118.2 ($=\underline{C}Si(C_6H_5)_3$), 124.2, 128.0, 128.2, 128.2, 128.4, 129.1, 129.3, 129.9, 131.3, 133.4, 136.6, 137.6 ($\underline{C}_6H_5$), 149.7 ($=\underline{C}H$). ^{29}Si NMR (79 MHz, CDCl$_3$, δ, ppm): -13.49 ($\underline{Si}C_6H_5$). GC MS (EI, 70 eV) m/z (rel. int., %): 462.3 (M$^+$, 66), 259.2 (100), 181.1 (57), 105.1 (32). FT-IR (ATR, cm^{-1}): 3066, 308, 1487, 1426, 1108, 1016, 774, 690, 508, 488, 472. Elemental Anal. Calcd for $C_{34}H_{26}Si$: C, 88.27; H, 5.66; found: C, 88.36; H, 5.71. Isolated yield = 427 mg (90%) from 474 mg (1 mmol), yellow solid, mp =114-120°C.

Product **3be** has been previously obtained. [23]

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Supporting Information

Description of spectroscopic data for all new compounds, X-ray analysis and literature description on previous methods on hydrosilylation of 1,3-diynes. (PDF)

Author Contributions

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

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