Regioselective preparation of tetrasubstituted alkenes from ketones using Krief's methodology as a key step for a straightforward synthesis of dienynes

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Dedicated to Professor Alain Krief on the occasion of his 65th birthday and retirement

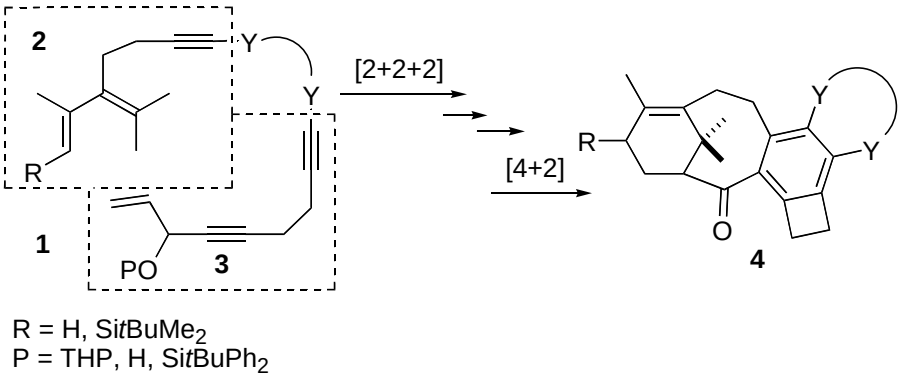
Abstract
Dienynes **2a-c** bearing a silylated substituent (Si*t*BuMe$_2$, SiMe$_2$Ph, Si(*i*Pr)$_3$) at the terminal position of the 1,3-butadiene moiety are highly valuable compounds as they constitute the north part of polyunsaturated precursors to the taxane framework that we have reached through [2+2+2]/[4+2] cyclization strategies. They have been efficiently prepared over ten steps from the corresponding trialkylsilylchlorosilanes, the crucial step of these syntheses being the olefination of a ketone that was eventually successful *via* selenoacetals.

Keywords: Dienyne, selenoacetal, olefination, taxoid, [2+2+2] cyclizations

Introduction

In the past ten years, taxane diterpenoids have been one of the most challenging synthetic targets due to the unique tetracyclic structure which includes an eight-membered ring and a bridgehead double bond. They also display a high therapeutic potential.[1] As a consequence, an impressive range of synthetic designs was proposed toward syntheses of taxol and its analogues; to date, six total syntheses have been reported.[2]

In this context and as part of our ongoing research program directed toward metal-catalyzed reactions and cascades for the elaboration of basic skeletons of natural products,[3] we have recently described an approach to the taxane framework.[4] Indeed, a combination of a cobalt(I)-mediated [2+2+2] cyclization and a [4+2] cycloaddition allows the formation of the tetracyclic skeleton of taxoids starting from highly functionalized polyunsaturated partners as depicted in Scheme 1.

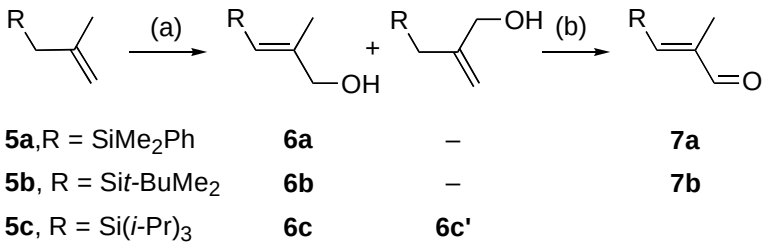


Scheme 1

The link between the two unsaturated moieties **2** and **3** can be either an alkylated (–$(CH_2)_4$–) or a silylated tether (–O–Si(*i*Pr)$_2$–O–) which ensures the chemo- and the regioselectivity of the [2+2+2] cyclizations between the three alkyne units. The success of these cycloaddition reactions was related to the presence of a sterically demanding substituent such as trialkylsilyl group at the terminal position of the 1,3-butadiene moiety which prevents some competitive cyclizations.
If the preparation of dienyne moiety **2** with R = Si*t*BuMe$_2$ of the precursor **1** is now quite efficient through the use of selenoacetals described by Krief,[5] it requires to adapt the reported procedures to the requisite substrates. In this paper, we report in details our efforts toward the preparation of a series of dienynes **2**.

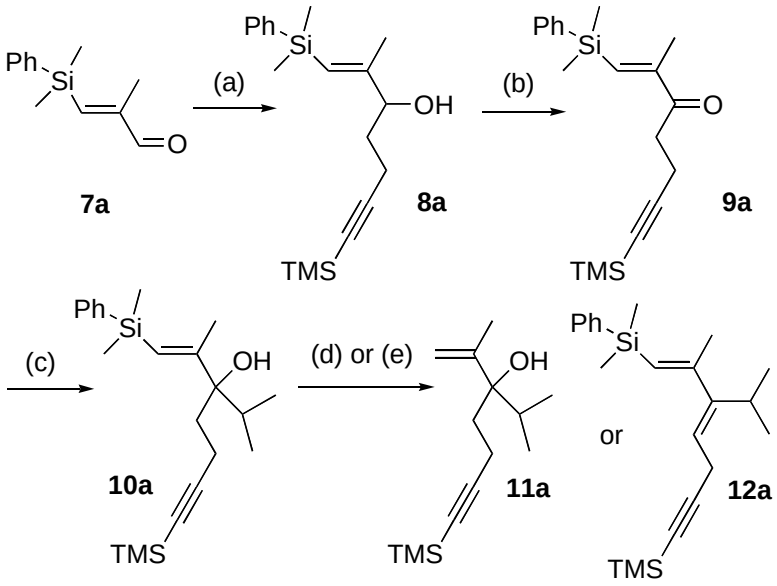
Results and Discussion

In order to evaluate the influence of the sterical demand of the silylated substituent at the terminal position of the 1,3 butadiene moiety on the course of the cyclizations, we envisioned to prepare the dienynes **2a-c** with R = Si*t*BuMe$_2$, SiMe$_2$Ph, Si(*i*Pr)$_3$ starting from the corresponding *E*-3-trialkylsilyl-2-methyl-2-propen-1-ol **6a-c**. Those were prepared following a procedure reported by our laboratory[6] which consists in the sequence - generation of the silyl allyl carbanion[7] from 2-methyl-3-trialkylsilyl-prop-1-ene **5a-c** prepared quantitatively from 3-chloro-2-methylprop-1-ene and trialkylchlorosilane under Barbier's conditions, alkylation with dimethylchlorosilane and then chemoselective Tamao oxidation. Consecutive Swern oxidation[8] furnished the aldehydes **7a-c** in high overall yield. The high steric hindrance brought by Si(*i*Pr)$_3$ did not allow a regioselective deprotonation of **5c** with Schlosser's base and two inseparable allylic alcohols **6c** and **6c'** were obtained as a 60:40 mixture in 50% yield (Scheme 2).



Scheme 2. (a) 1. (1/1) *t*-BuOK/*n*-BuLi (1.1 equiv), hexane, 0 °C; **5a-c**, Et_2O, –78 °C to rt; $ClSiMe_2H$ (1.1 equiv), Et_2O, – 78 °C. 2. $KHCO_3$ (3 equiv), 30% H_2O_2 in water (12 equiv), MeOH, Δ, **6c**/**6c'** : 50% (60:40). (b) $(COCl)_2$, DMSO, NEt_3, CH_2Cl_2, – 78 °C to rt, **7a**: 72%; **7b**: 75% over the two steps.

In a first set of experiments carried out with aldehyde **7a**, we envisioned to introduce in a straightforward manner the triple bond and the double bond according to Scheme 3.

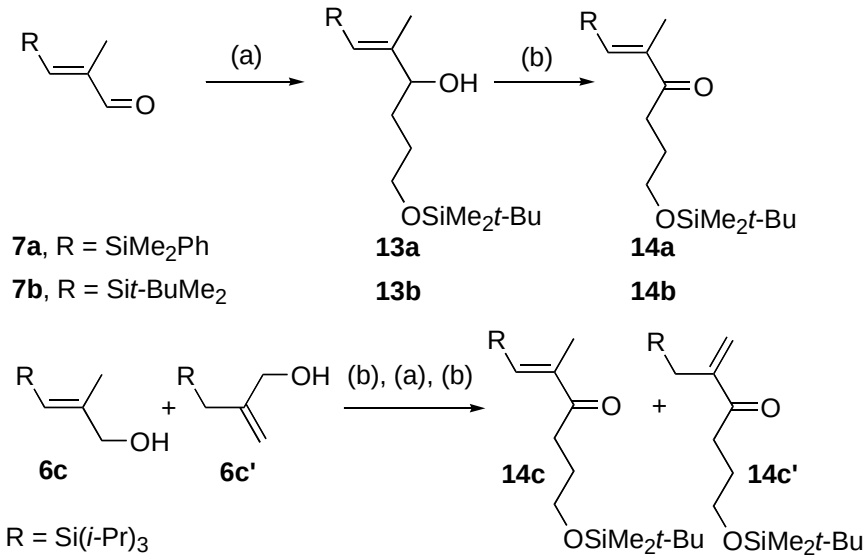


Scheme 3. (a) 1. $ZnCl_2$ (3.3 equiv), Mg (4.5 equiv), $Me_3SiC{\equiv}C(CH_2)_2Cl$ (3 equiv), THF, Δ then CuCN (6 equiv), LiCl (12 equiv), THF, –20 °C. 2. **7a**, $Et_2O{\bullet}BF_3$ (6 equiv), –78 to –30 °C, **8a**: 54%. (b) $(COCl)_2$, DMSO, NEt_3, CH_2Cl_2, –78 °C to rt, **9a**: 90%. (c) *i*-PrMgCl (1.2 equiv), HMPA (2 equiv), Et_2O, 0 °C to rt, **10a**: 50%. (d) PTSA (0.2 equiv), benzene, Δ, **11a**: 70%. (e) P_2O_5, xylenes, Δ.

Indeed, the alkylation of **7a** with copper(I) reagent[9] derived from (4-chlorobut-1-ynyl)trimethylsilane prepared from the corresponding zinc derivative[10] furnished in presence of $Et_2O{\bullet}BF_3$, alcohol **8a** in 54% yield; it is worthy of note that this reaction is not reproducible. Subsequent oxidation led to enone **9a** in 90% yield which was alkylated with isopropylmagnesium chloride in presence of 2 equivalents of HMPA to give tertiary alcohol **10a**

in 50% yield beside starting material. In the absence of HMPA, the reduction of the enone occured and the secondary alcohol was obtained admixed with **10a** in a 1:1 mixture. Several attempts aiming at the elimination of tertiary alcohol **10a** were unsuccessful and whatever the conditions we used, we were unable to get the desired diene. Two transformations were only observed in acidic media. Indeed, in presence of PTSA in refluxing benzene or $Et_2O•BF_3$ in refluxing ether, **10a** underwent a protodesilylation affording compound **11a**. On the contrary, phosphorous pentoxide allowed dehydration of **10a** leading to diene **12a**.

Considering the above results, two issues had to be addressed : (i) the introduction of the homopropargylic chain, (ii) the olefination of the ketone. To answer to the first item, we envisaged to alkylate the aldehydes **7a-c** with an alkyl chain bearing a silylated ether which could be further transformed in a simple manner into an alkyne. Thus, addition of the aldehydes **7a-b** to the lithio derivative of 3-(*tert*-butyldimethylsilyloxy)-1-iodo propane furnished the corresponding alcohols **13a-b** in 90% and 70% respectively (Scheme 4). Swern oxidation led to the enones **14a-b** in very high yields. The sequence - Swern oxidation, alkylation, Swern oxidation- from the 60:40 mixture of alcohols **6c** and **6c'** led to the corresponding enones **14c** and **14c'** in 75% overall yield with the same ratio.



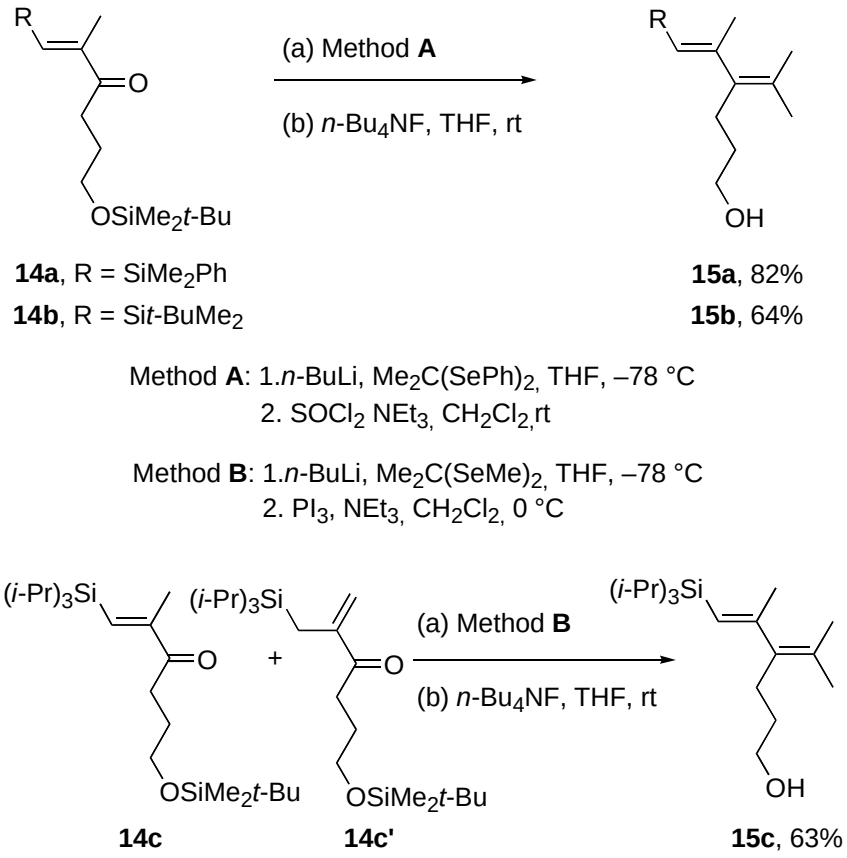
Scheme 4. (a) *t*-BuLi, *t*-$BuMe_2SiO(CH_2)_3I$, –78 °C, THF, **13a**: 70%; **13b**: 90%. (b) $(COCl)_2$, DMSO, NEt_3, CH_2Cl_2, –78 °C to rt, **14a**: 66%; **14b:** 92%; **14c**/**14c'**: 75% over three steps.

In order to produce efficiently the tetrasubstituted double bond, we next turned our attention to 2,2-bis(methylseleno)propane.[5,11] Indeed, Krief *et al.* has reported that such reagents can be quantitatively reduced with *n*-BuLi to the α-selenoalkylithiums. Those are highly reactive toward aldehydes and ketones, leading to the hydroxyselenides which can be eliminated to highly substituted olefins. The use of such a reagent or its homologue 2,2-bis(phenylseleno)propane has been already described by Williams[12] and Jenkins[13] in their

approach to taxane model system. However, as far as we were aware, they had never been employed for the generation of a 1,3-butadiene moiety bearing a silylated group at the terminal position. Depending on the nature of the substituent on selenium, methyl *versus* phenyl, two procedures for the elimination of the hydroxyselenides are available. They consist in employing PI_3[14] or thionyl chloride respectively in presence of triethylamine in dichloromethane.

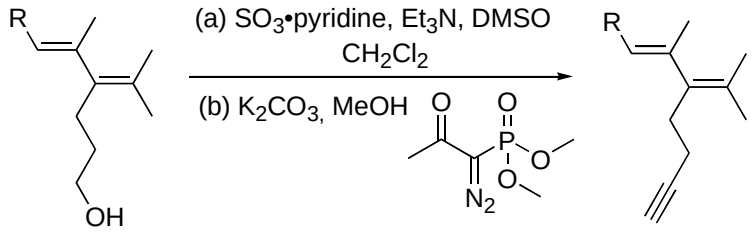
At the time we started this study, 2,2-bis(methylseleno)propane was commercially available but unfortunately its marketing disappeared and in spite of a generous gift from Krief's laboratory we were unable to run the whole study. Therefore, we decided to employ 2,2-bis(phenylseleno)propane which was prepared according to the work of Krief with phenylselenol and acetone in presence of a Lewis acid.[5] However, we slightly modified the procedure by using $Et_2O{\bullet}BF_3$ in chloroform instead of $TiCl_4$ or $ZnCl_2$. In that case, treatment with aqueous NaOH and evaporation of the solvent furnished 2,2-bis(phenylseleno)propane in 81% yield.

Whatever the reagent that we used, the olefination of the enones **14a-c** were very successful and after subsequent deprotection of the silylated ethers, the dienols **15a-c** were obtained in 63% to 87% yield over three steps according to Scheme 5. It is noteworthy that the mixture of enones **14c** and **14c'** was converted only into the most stable dienol **15c**.



Scheme 5

After oxidation[15] of **15a-c**, chain extension was achieved through Ohira-Bestman procedure[16] and led to the dienynes **2a-c** in 60-80% yield (Scheme 6).



15a,R = $SiMe_2Ph$ **2a**, 60%

15b, R = Si*t*-$BuMe_2$ **2b**, 63%

15c, R = Si(*i*-$Pr)_3$ **2c**, 80%

Scheme 6

Conclusions

In summary, we have developed an efficient preparation of dienynes **2a-c**. They were obtained in ten steps from the corresponding commercially available chorosilanes in 27% overall yield (**2b**). This required the optimization of each step especially the olefination of the ketone which was particularly successful through the use of selenoacetals and Krief' methodology. The dienynes **2a-c** are highly valuable compounds as they constitute the north part of functionalized polyunsaturated precursors to the taxane framework that we have reached through the [2+2+2]/[4+2] cyclizations strategy.

Experimental Section

General Procedures. Reactions were carried out under argon in flame-dried glassware, with magnetic stirring and degassed anhydrous solvents. All commercially available reagents were used without further purification unless otherwise noted. All solvents were reagent grade and distilled under positive pressure of dry nitrogen before use. THF was distilled from sodium/benzophenone. Solid reagents were dried *in vacuo* (0.5 to 0.1 mmHg). Thin layer chromatography (TLC) was performed on Merck 60 F_{254} silica gel. Merck Geduran SI 60 Å silica gel (35-70 μm) was used for column chromatography according to Still's method.[17] PE and EE refer to petroleum ether and Et_2O. Chemical shifts are given in ppm, referenced to the residual proton resonances of the solvents (δ = 7.26 for $CDCl_3$; δ = 7.16 for C_6D_6). Coupling constants (*J*) are given in Hertz (Hz). The terms m, s, d, t, q, quint refer to multiplet, singlet, doublet, triplet, quartet, quintet; br means that the signal is broad. We use (I), (II), (III) and (IV)

to characterize primary, secondary, tertiary and quaternary carbons. Elemental analysis were performed by the Service Régional de Microanalyse de l'Université Pierre et Marie Curie. Low-resolution mass spectra (MS) and high resolution mass spectra (HRMS) were measured by Service de spectrométrie de masse de l'ICSN-CNRS, Gif-sur-Yvette. Infrared spectra (IR) were recorded on a Bruker Tensor 27 spectrometer. Absorbance frequencies are given at maximum of intensity in cm^{-1}.

Dimethylphenyl-(2-methyl-allyl)-silane (5a) To a suspension of 4.81 g of magnesium ring (148.9 mmol, 1.0 equiv) in 10 mL of THF was added dropwise, at room temperature, a solution of 25 mL of chlorodimethylphenylsilane (198.1 mmol, 1.3 equiv) and 19.3 mL of methyl-chloropropene (198.1 mmol,1.3 equiv) in 100 mL of THF. After the addition, the reaction mixture was heated at reflux for 12h. The solution was then diluted with Et_2O and washed successively with a saturated solution of NH_4Cl and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude oil was purified by flash chromatography on silica gel (PE) and gave **5a** as a colorless oil (28 g, quantitative). IR (neat) 3080, 2980, 1630, 1420, 1245, 1110, 725, 695 cm^{-1} – ^1H NMR (200 MHz, $CDCl_3$) δ 7.64-7.54 (m, 2H), 7.48-7.64 (m, 3H), 4.70 (s, 1H), 4.58 (s, 1H), 1.87 (s, 2H), 1.71 (s, 3H), 0.40 (s, 6H). – ^{13}C NMR (50 MHz, $CDCl_3$) δ 143.4 (IV), 139.3 (IV), 133.8 (2C, III), 129.2 (III), 128.0 (2C, III), 109.0 (II), 27.9 (II), 25.5 (I), -2.7 (2C, I). – EIMS (m/z, %) 152 (100), 102 (78). Anal. Calcd. for $C_{12}H_{18}Si$: C, 75.71; H, 9.53. Found: C, 75.39; H, 9.60.

***tert*-Butyl-dimethyl-(2-methyl-allyl)-silane (5b)** was previously described according to reference 6

Triisopropyl-(2-methyl-allyl)-silane (5c) was prepared following the procedure described for **5a**. (29.5 g, 92%) IR (neat) 3070, 2950, 2920, 2850, 1670, 1460, 1250, 1360 cm^{-1} – ^1H NMR (400 MHz, $CDCl_3$) δ 4.63 (s, 2H), 1.82 (s, 3H), 1.67 (s, 2H), 1.15-1.05 (m, 21H). – ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.4 (IV), 109.0 (II), 25.6 (I), 20.7 (II), 18.7 (6C, I), 11.8 (3C, III).

3-(Dimethylphenylsilyl)-2-methyl-propenal (7a)

1. 3-(dimethylphenylsilyl)-2-methyl-prop-2-en-1-ol (6a). To a cooled (0°C) suspension of 9.19 g of *t*-BuOK (81.9 mmol, 1.1 equiv) in 85 mL of hexane were added dropwise 39 mL of *n*-BuLi (solution 2.1 M in hexane, 81.9 mmol, 1.1 equiv). The solution was stirred for 10 min at this temperature and then cooled to –78 °C. After dilution of the reaction mixture with 57 mL of Et_2O, a solution of 14.2 g of **5a** (74.5 mmol, 1.0 equiv) in 57 mL of Et_2O was added. Then, the mixture was warmed to room temperature and stirred for 4h. After being cooled to –78 °C, 9.1 mL of the chlorodimethyl-silane (81.9 mmol, 1.1 equiv) were added. After 1h, the solution was diluted with Et_2O and washed successively with a saturated solution of NH_4Cl and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The resulting compound was used directly in the oxidation procedure without further purification.

To a solution of the preceding compound (74.5 mmol, 1.0 equiv) in 310 mL of THF and 310 mL of MeOH were added 22.4 g of $KHCO_3$ (223.5 mmol, 3.0 equiv) and 22.8 mL of H_2O_2 (30% in

water, 894.0 mmol, 12.0 equiv). After being stirred at reflux for 15 min, 22.8 mL of H_2O_2 were added. This last procedure was repeated twice. The mixture was filtered on a celite pad and diluted with Et_2O. The organic layer was successively washed with water, a saturated solution of sodium thiosulfate and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The resulting alcohol (**6a**) was used directly in the next step without further purification.

2. A solution of 11.5 mL of dimethylsulfoxide (162.2 mmol, 2.6 equiv) in 112 mL of CH_2Cl_2 was added dropwise at –78 °C to a solution of 7.1 mL of oxalyl chloride (81.1 mmol, 1.3 equiv) in 292 mL of CH_2Cl_2. After 15 min, a solution of the preceding compound (62.4 mmol, 1.0 equiv) in 160 mL of CH_2Cl_2 was added slowly. After the solution was stirred at –78 °C for 15 min, 45.1 mL of triethylamine (326.2 mmol, 5.2 equiv) were added. The reaction mixture was immediately warmed to room temperature, diluted with Et_2O, washed successively with a saturated solution of NH_4Cl and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by flash chromatography (PE) furnished aldehyde **7a** (11.4 g, 72% over 3 steps). IR (neat) 3060, 2950, 2680, 1680, 1590, 1420, 725, 700 cm^{-1} – ^1H NMR (200 MHz, $CDCl_3$) δ 9.48 (s, 1H), 7.57-7.54 (m, 2H), 7.42-7.39 (m, 3H), 6.86 (d, *J* = 1.0 Hz, 1H), 1.84 (d, *J* = 1.2 Hz, 3H), 0.53 (s, 6H). – ^{13}C NMR (50 MHz, $CDCl_3$) δ 193.3 (III), 153.4 (IV), 150.9 (III), 136.9 (IV), 133.7 (2C, III), 129.5 (III), 128.1 (2C, III), 13.6 (I), -2.0 (2C, I). – CIMS 222 (MNH_4^+, 100), 336 (65), 152 (45), 110 (35), 204 (M, 30).152 (100), 102 (78). – Anal. Calcd. for $C_{12}H_{16}OSi$: C, 70.53; H, 7.89. Found: C, 70.41; H, 8.04.

3-(*tert*-Butyldimethylsilyl)-2-methyl-propenal (7b). The procedure used was the same as for **7a**; (**7b**) was previously described.[6]

2-Methyl-3-(triisopropylsilyl)-prop-2-en-1-ol (6c) and 2-[triisopropylsilyl)-methyl]-prop-2-en-1-ol (6c') were prepared following the procedure described for (**6a**). (5.38 g, 50%, inseparable 60:40 mixture of **6c**:**6c'**). (**6c)** IR (neat) 3370, 2940, 2850, 1660, 1460, 1370, 1240, 830, 775 cm^{-1} – ^1H NMR (400 MHz, $CDCl_3$) δ 4.95 (d, *J* = 1.5 Hz, 1H), 4.80 (d, *J* = 1.3 Hz, 1H), 4.06 (s, 2H), 1.63 (s, 2H), 1.21 (m, 3H), 1.09 (s, 18H). – ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3 (IV), 116.2, (III), 69.5 (II), 18.9 (6C, I), 18.7 (I), 12.3 (3C, III). (**6c'**) IR (neat) 3370, 2940, 2850, 1660, 1460, 1370, 1240, 830, 775 cm^{-1} – ^1H NMR (400 MHz, $CDCl_3$) δ 5.44 (s, 1H), 4.06 (s , 2H), 1.79 (s, 3H), 1.21 (m, 3H), 1.09 (s, 18H). – ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.3 (IV), 107.8 (IV), 67.3 (II), 19.7 (II), 18.9 (6C, I), 11.5 (3C, III).

1-(Dimethylphenylsilyl)-2-methyl-7-(trimethylsilyl)-hept-1-en-6-yn-3-ol (8a). A 1M THF solution of $ZnCl_2$ (56.1 mL, 56.1 mmol, 3.3 equiv) was added to magnesium turnings (1.83 g, 76.5 mmol, 4.5 equiv). Some drops of 1,2-dibromoethane were added followed by a slow addition of (4-chloro-but-1-ynyl)-trimethylsilane (8 g, 51 mmol, 3 equiv). After being heated at reflux for 4 h and then cooled to –20 °C, a solution of CuCN (8.95 g, 100 mmol, 6 equiv) and LiCl (8.46 g, 200 mmol, 12 equiv) in THF (200 mL) was added to the reaction mixture. After being stirred for 15 min, the temperature was cooled down to –78 °C and successively, a solution of **7a** (3.46 g, 17 mmol, 1 equiv) in THF (50 mL) and $Et_2O{\bullet}BF_3$ (6.3 mL, 51 mmol, 6 equiv) were added. After being stirred for 2h at –30 °C, the temperature was cooled to –78 °C and the reaction mixture was hydrolyzed with a solution of NH_4Cl/NH_4OH (2/1), diluted with Et_2O. The

organic layer was washed successively with a saturated solution of NH_4Cl and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by flash chromatography (PE/EE 8/2) furnished **8a** (3.0 g, 54%). IR (neat) 3400, 3100, 2950, 2150, 1610, 1420, 1250, 845, 735, 720 cm^{-1} – ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (m, 2H), 7.33 (m, 3H), 5.68 (s, 1H), 4.15 (m, 1H), 2.31 (m, 2H), 1.78 (m, 2H), 1.68 (s, 3H), 0.37 (s, 6H), 0.15 (s, 9H). – ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0 (IV), 139.6 (IV), 133.6 (2C, III), 128.7 (III), 127.7 (2C, III), 120.9 (III), 106.8 (IV), 85.4 (IV), 76.9 (III), 33.9 (II), 17.6 (I), 16.4 (II), 0.0 (3C, I), -1.2 (2C, I).

1-(Dimethylphenylsilyl)-2-methyl-7-(trimethylsilyl)-hept-1-en-6-yn-3-one (9a) was prepared following Swern procedure described for (**7a**). Purification by flash chromatography (PE/EE 9/1) gave **9a** (0.278 g, 90%). IR (neat) 3070, 2950, 2200, 1660, 1610, 1410 cm^{-1} – ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (m, 2H), 7.37 (m, 3H), 6.78 (s, 1H), 2.97 (m, 2H), 2.50 (m, 2H), 1.84 (s, 3H), 0.45 (s, 6H), 0.13 (s, 9H). – ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.8 (IV), 156.0 (IV), 138.6 (IV), 133.7 (2C, III), 128.8 (III), 127.5 (2C, III), 120.6 (III), 106.1 (IV), 84.7 (IV), 36.2 (II), 17.1 (I), 16.8 (II), 0.0 (3C, I), -1.1 (2C, I) .

1-(Dimethylphenylsilyl)-3-isopropyl-2-methyl-7-(trimethylsilyl)-hept-1-en-6-yn-3-ol (10a). To a cooled (0 °C) solution of **9a** (0.22 g, 0.67 mmol, 1 equiv) and HMPA (0.24 mL, 1.34 mmol, 2 equiv) in THF (2 mL) was added dropwise a solution of isopropylmagnesium chloride (0.4 mL, 0.8 mmol, 1.2 equiv) in THF. After being stirred at room temperature until TLC had indicated completion, the reaction mixture was diluted with ether, washed successively with a saturated solution of NH_4Cl and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by flash chromatography (PE/EE 9/1) furnished **10a** (0.125 g, 50%). IR (neat) 3400, 2930, 2870, 2180,1640, 1430, 1240, 910 cm^{-1} – ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (m, 2H), 7.33 (m, 3H), 5.75 (s, 1H), 2.16 (m, 1H), 2.03 (m, 1H), 1.92 (m, 1H), 1.79 (m, 1H), 1.69 (m, 1H),1.58 (s, 3H), 0.98 (m, 3H), 0.75 (m, 3H), 0.36 (s, 6H), 0.13 (s, 9H). – ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.4, (IV), 139.7 (IV), 133.6 (2C, III),128.7 (III), 127.7 (2C, III), 121.2 (III), 107.7 (IV), 85.3 (IV), 79.1 (IV), 35.4 (II), 18.9 (I), 16.9 (I), 16.1 (I), 15.1 (III), 14.9 (II), 0.0 (3C, I), -1.1 (2C, I).

3-Isopropyl-2-methyl-7-(trimethylsilyl)-hept-1-en-6-yn-3-ol (11a). A solution of **10a** (0.113 g, 0.3 mmol, 1 equiv) in benzene (1 mL) was heated at reflux for 2h in presence of *para*-toluenesulfonic acid (PTSA, 1 mg, 0.2 equiv) with a Dean-Stark apparatus. After being cooled at room temperature, the reaction mixture was diluted with ether, washed successively with a saturated solution of $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by flash chromatography (PE/EE 9/1) gave **11a** (0.05 g, 70%). IR (neat) 3400, 2930, 2870, 2150,1640, 1430, 910 cm^{-1} – ^1H NMR (400 MHz, $CDCl_3$) δ 5.02 (br s, 1H), 4.97 (br s, 1H), 2.24-2.12 (m, 4H), 1.68 (s, 3H), 1.03 (d, J = 6.6 Hz, 3H), 0.90 (m, 1H), 0.81 (d, J = 6.6 Hz, 3H), 0.16 (s, 9H). – ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.1 (IV), 127.8 (II), 112.0 (IV), 85.1 (IV), 79.7 (IV), 35.3 (II), 34.0 (II), 19.9 (I), 16.9 (I), 16.1 (I), 14.9 (III), -0.2 (3C, I).

6-(*tert*-Butyldimethylsilyloxy)-1-(dimethylphenylsilyl)-2-methyl-hex-1-en-3-ol (13a). To a cooled (–78 °C) solution of 37 mL of THF were slowly added 100 mL of *tert*-butyllithium (solution 1.5 M in pentane, 150.0 mmol, 3.4 equiv) and a solution of 26.2 g of 1-iodo-3-(*tert*-butyldimethylsilyloxy)-propane (87.2 mmol, 2.0 equiv) in 300 mL of THF. After being stirred 15

min at this temperature, a solution of 8.91 g of compound **7a** (43.6 mmol, 1.0 equiv) in 190 mL of THF was added. The solution was then diluted with Et_2O and the organic layer was successively washed with saturated solutions of sodium thiosulfate, NH_4Cl and then brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude oil was purified by flash chromatography on silica gel (PE/EE 9/1) affording **13a** as a colorless oil (11.6 g, 70%). IR (neat) 3300, 3030, 2950, 1600, 810, 750 cm^{-1} – ^1H NMR (200 MHz, $CDCl_3$) δ 7.56-7.52 (m, 2H), 7.37-7.33 (m, 3H), 5.68 (s, 1H), 4.06 (t, *J* = 4.3 Hz, 1H), 3.67 (t, *J* = 5.4 Hz, 2H), 1.69 (s, 3H), 1.64-1.59 (m, 2H), 0.92 (s, 9H), 0.89-0.84 (m, 2H), 0.38 (s, 6H), 0.08 (s, 6H). – ^{13}C NMR (50 MHz, $CDCl_3$) δ 158.2 (IV), 139.8 (IV), 133.8 (2C, III), 128.8 (III), 127.8 (2C, III), 120.4 (III), 78.0 (III), 63.5 (III), 32.6 (III), 28.9 (III), 26.0 (3C, I), 18.4 (IV), 17.9 (I), -0.9 (2C, I), -5.2 (2C, I). – Anal. Calcd. for $C_{21}H_{38}O_2Si_2$: C, 66.6; H, 10.11. Found: C, 66.5; H, 10.16.

1-(*tert*-Butyldimethylsilyl)-6-(*tert*-butyldimethylsilyloxy)-2-methyl-hex-1-en-3-ol (13b) was prepared following the procedure described for **13a** (3.32 g, 90%). IR (neat) 3320, 3030, 2950, 1600, 1230, 810, 750 cm^{-1} – ^1H NMR (400 MHz, $CDCl_3$) δ 5.55 (s, 1H), 4.03 (t, *J* = 5.2 Hz, 1H), 3.66 (t, *J* = 5.6 Hz, 2H), 1.77 (s, 3H), 1.69-1.56 (m, 4H), 0.91 (s, 9H), 0.87 (s, 9H), 0.10 (s, 6H), 0.07 (s, 6H). – ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0 (IV), 120.3 (III), 78.6 (III), 63.4 (II), 32.4 (II), 28.9 (II), 26.5 (3C, I), 26.0 (3C, I), 18.4 (IV), 17.5 (I), 17.3 (IV), -4.2 (2C, I), -5.3 (2C, I). – Anal. Calcd. for $C_{19}H_{42}O_2Si_2$: C, 63.62; H, 11.80. Found: C, 63.60; H, 11.78.

6-(*tert*-butyldimethylsilyloxy)-1-(dimethylphenylsilyl)-2-methyl-hex-1-en-3-one (14a) was prepared following Swern procedure described above for **7a**; (5.06 g, 66%). IR (neat) 3030, 2980,1690,1670, 1250, 1100, 835, 715 cm^{-1} – ^1H NMR (200 MHz, $CDCl_3$) δ 7.54-7.53 (m, 2H), 7.39-7.36 (m, 3H), 6.82 (s, 1H), 3.65 (t, *J* = 5.9 Hz, 2H), 2.83 (t, *J* = 7.4 Hz, 2H), 1.87-1.86 (m, 5H), 0.90 (s, 9H), 0.47 (s, 6H), 0.05 (s, 6H). – ^{13}C NMR (50 MHz, $CDCl_3$) δ 202.3 (IV), 152.8 (IV), 137.8 (IV), 137.4 (III), 133.8 (2C, III), 129.4 (III), 128.1 (2C, III), 62.3 (II), 33.4 (II), 27.7 (II), 26.0 (3C, I), 18.4 (IV), 17.1 (I), -1.5 (2C, I), -5.2 (2C, I). – EIMS (m/z, %) 377 (MH^+, 100), 245 (25), 152 (15). – Anal. Calcd. for $C_{21}H_{36}O_2Si_2$: C, 66.96; H, 9.63. Found: C, 66.84; H, 10.00.

1-(*tert*-Butyldimethylsilyl)-6-(*tert*-butyldimethylsilyloxy)-2-methyl-hex-1-en-3-one (14b) was prepared following Swern procedure described above for **7a**; (1.85 g, 92%). IR (neat) 3030, 2980, 1685, 1665, 1250, 1100, 835, 715 cm^{-1} – ^1H NMR (400 MHz, $CDCl_3$) δ 6.70 (s, 1H), 3.63 (t, *J* = 6.0 Hz, 2H), 2.79 (t, *J* = 7.6 Hz, 2H), 1.92 (s, 3H), 1.81 (qt, *J* = 6.0, 7.2 Hz, 2H), 0.92 (s, 9H), 0.88 (s, 9H), 0.35 (s, 6H), 0.16 (s, 6H). – ^{13}C NMR (50 MHz, $CDCl_3$) δ 202.3 (IV), 152.3 (IV), 137.2 (III), 62.3 (II), 33.5 (II), 27.8 (II), 26.5 (3C, I), 26.0 (3C, I), 18.4 (IV), 17.2 (IV), 17.0 (I), -4.7 (2C, I), -5.3 (2C, I).

6-(*tert*-Butyldimethylsilyloxy)-2-methyl-1-(triisopropylsilyl)-hex-1-en-3-one (14c) and **6-(*tert*-Butyldimethylsilyloxy)-2-[(triisopropylsilyl)-methyl]-hex-1-en-3-one (14c')** were prepared from the 60:40 mixture of **6c**/**6c'** following the sequence – Swern oxidation, alkylation, Swern oxidation– and the procedures described above for **7a** and **13a**. (1.60 g, 75% over three steps). **(14c)** IR (neat) 3030, 2980, 1685, 1665, 1250, 1100, 835, 715 cm^{-1} – ^1H NMR (400 MHz, $CDCl_3$) δ 6.68 (s, 1H), 3.66 (t, *J* = 5.9 Hz, 2H), 2.84 (t, *J* = 7.3 Hz, 2H), 1.95 (s, 3H), 1.83 (m, 2H), 1.26-1.22 (m, 3H), 1.09 (d, *J* = 7.2 Hz, 18H), 0.89 (s, 9H), 0.04 (s, 6H). – ^{13}C NMR (100

MHz, $CDCl_3$) δ 202.2 (IV), 152.9 (IV), 136.0 (III), 62.3 (II), 33.7 (II), 27.8 (II), 26.0 (3C, I), 18.9 (6C, I), 18.4 (IV), 18.1 (3C, III), 12.1 (I), -5.3 (2C, I). **(14c')** IR (neat) 3030, 2980, 1685, 1650, 1250, 1100, 835, 715 cm^{-1} – ^1H NMR (400 MHz, $CDCl_3$) δ 5.91 (s, 1H), 5.67 (s, 1H), 3.63 (t, *J* = 4.4 Hz, 2H), 2.79 (t, *J* = 7.4 Hz, 2H), 1.91 (s, 2H), 1.83 (m, 2H), 1.26-1.22 (m, 3H), 1.04 (br s, 18H), 0.89 (s, 9H), 0.49 (s, 6H). – ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 201.7 (IV), 148.1 (IV), 121.7 (II), 62.3 (II), 33.7 (II), 27.8 (II), 26.0 (3C, I), 18.7 (6C, I), 18.4 (IV), 18.1 (3C, III), 12.9 (II), -5.3 (2C, I).

Preparation of 2,2-bis(phenylseleno)propane. At room temperature, to a solution of phenylselenol (10 g, 63.7 mmol, 2 equiv) in $CHCl_3$ (32 mL) was added to acetone (2.4 mL, 31.8 mmol, 1 equiv). After being cooled at 0 °C, $Et_2O•BF_3$ (12.6 mL, 47.8 mmol, 1.5 equiv) was added to the reaction mixture. The temperature was warmed to room temperature, the mixture was stirred until TLC had indicated completion and diluted with Et_2O, washed successively with a 5% solution of aqueous NaOH and brine, dried over magnesium sulfate, filtered and concentrated *in vacuo.* 2,2-bis(phenylseleno)propane[5] (9.23 g, 81%) crystallized and was used without any further purification.

4-[2-(Dimethylphenyl-silyl)-1-methyl-vinyl]-5-methyl-hex-4-en-1-ol (15a)

1. To a cooled (-78°C) solution of 5.19 g of 2,2-bis(phenylseleno)propane (14.5 mmol, 1.15 equiv) in 53 mL of THF were added dropwise 6.6 mL of *n*-butyllithium (solution 2.1 M in pentane, 13.9 mmol, 1.1 equiv). After being stirred 15 min at this temperature, a solution of 4.76 g of compound **14a** (12.6 mmol, 1.0 equiv) in 25 mL of THF was added. The mixture was warmed to room temperature. After being stirred for 1 h, the solution was diluted with Et_2O and the organic layer was washed successively with a saturated solution of NH_4Cl and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude oil was used directly in the elimination reaction without further purification.

2. Method A. To a solution of the preceding compound in 75 mL of CH_2Cl_2 were added 11.7 mL of triethylamine (84.4 mmol, 7.0 equiv). The mixture was cooled to 0°C and 1.8 mL of thionyle chloride (24.1 mmol, 2.0 equiv) were added. The solution was warmed to room temperature. After being stirred for 2 h, the solution was then diluted with Et_2O and the organic layer was washed with a saturated solution of NH_4Cl and then, brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude oil was used directly in the elimination reaction without further purification.

3. To a cooled (0°C) solution of the preceding compound in 170 mL of THF were added dropwise 13.9 mL of *tetra*-butylammonium fluoride (1M in THF, 13.9 mmol, 1.2 equiv). The solution was warmed to room temperature and stirred until completion of the reaction by TLC. The reaction mixture was extracted with Et_2O, washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flash chromatography (PE/EE 9/1) and furnished **15a** (2.89 g, 82% from **14a**). IR (neat) 3540, 3030, 2920, 1560, 1230, 1090, 725 cm^{-1} – ^1H NMR (200 MHz, $CDCl_3$) δ 7.55-7.54 (m, 2H), 7.36-7.32 (m, 3H), 5.26 (s, 1H), 3.63 (t, *J* = 6.4 Hz, 2H), 2.19 (t, *J* = 7.4 Hz, 2H), 1.73 (s, 3H), 1.63-1.55 (m, 8H), 0.37 (s, 6H). – ^{13}C NMR

(50 MHz, $CDCl_3$) δ 158.0 (IV), 140.2 (IV), 139.8 (IV), 133.8 (2C, III), 128.8 (III), 127.84 (2C, III), 124.81 (III), 124.3 (IV), 62.9, (II) 31.5 (II), 27.2 (II), 22.3 (I), 21.9 (I), 19.7 (I), -0.8 (2C, I). – Anal. Calcd. for $C_{18}H_{28}OSi$: C, 74.94; H, 9.78. Found: C, 74.93; H, 9.82.

4-[2-(*tert*-Butyldimethylsilyl)-1-methyl-vinyl]-5-methyl-hex-4-en-1-ol (15b) was prepared following the procedure described for **15a**. (1.66 g, 64% from **14b**). IR (neat) 3550, 3030, 2900, 1570, 1230, 1080, 810, 750 cm^{-1} – ^1H NMR (400 MHz, $CDCl_3$) δ 5.09 (s, 1H), 3.64 (t, *J* = 6.4 Hz, 2H), 2.18 (t, *J* = 7.4 Hz, 2H), 1.83 (s, 3H), 1.70-1.55 (m, 8H), 0.93 (s, 9H), 0.11 (s, 6H). – ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.5 (IV), 140.3 (IV), 135.6 (IV), 124.7 (III), 63.0 (II), 31.5 (II), 27.1 (II), 26.6 (3C, I), 25.7 (I), 21.9 (I), 19.6 (I), 17.4 (IV), -4.3 (2C, I). – Anal. Calcd. for $C_{16}H_{32}OSi$: C, 71.57; H, 12.01. Found: C, 71.42; H, 11.91.

5-Methyl-4-[1-methyl-2-triisopropylsilyl)-vinyl]-hex-4-en-1-ol (15c)

1. To a cooled (-78°C) solution of 2,2-bis(methylseleno)propane (0.825 g, 3.76 mmol, 1 equiv) in THF (16 mL) were added dropwise 1.8 mL of *n*-butyllithium (solution 2.2 M in hexane, 3.95 mmol, 1.05 equiv). After being stirred 1h at this temperature, a solution of 1.5 g of **14c/14c'** (3.76 mmol, 1.0 equiv) in 11 mL of THF was added. The mixture was warmed to room temperature and then diluted with Et_2O. The organic layer was washed successively with a saturated solution of NH_4Cl and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude oil was used directly in the next step without further purification.

2. Method B. To a solution of the preceding compound in 20 mL of CH_2Cl_2 were added 3.83 mL of NEt_3 (27.3 mmol, 7.25 equiv). The mixture was cooled to 0°C and a solution of 3.22 g of PI_3 (9.26 mmol, 2.5 equiv) in CH_2Cl_2 (66 mL) was added. After being stirred at 0 °C, the solution was diluted with Et_2O, washed with a saturated solution of NH_4Cl and then brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude oil was used directly in the next step without further purification.

3. The deprotection of the silylated ether followed the procedure described for **15a** and furnished **15c** (0.74 g, 63%). IR (neat) 3550, 3030, 2900, 1580, 1250, 1080, 810 cm^{-1} – ^1H NMR (400 MHz, $CDCl_3$) δ 5.31 (s, 1H), 3.64 (t, *J* = 6.4 Hz, 2H), 2.20 (t, *J* = 7.3 Hz, 2H), 1.82 (s, 3H), 1.69 (s, 6H), 1.65-1.61 (m, 2H), 1.16 (m, 3H), 1.08 (d, *J* = 6.4 Hz, 18H) – ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1 (IV), 140.5 (IV), 123.9 (IV), 122.6, (III), 62.9, (II) 31.5 (II), 26.9 (II), 22.8 (I), 22.0 (I), 19.0 (6C, I),18.9 (I), 12.3 (3C, III), -0.8 (2C, I).

4-[2-(dimethylphenylsilyl)-1-methyl-vinyl]-6-methyl-hept-1-yn-5-ene (2a)

1. To a cooled (0°C) solution of 2.83 g of **15a** (9.8 mmol, 1 equiv) in 17 mL of CH_2Cl_2 were added 13.9 mL of DMSO (196.3 mmol, 20 equiv), 13.6 mL of triethylamine (98.2 mmol, 10 equiv) and 8.19 g of SO_3•pyridine (58.9 mmol, 6 equiv). The mixture was stirred at room temperature until the reaction was completed by TLC. The solution was diluted with Et_2O, washed successively with a saturated solution of NH_4Cl and brine, dried over $MgSO_4$, filtered on a celite pad and concentrated. The crude oil was used in the next step without further purification.

2. To a solution of the preceding compound (7.8 mmol, 1 equiv) in 80 mL of MeOH were added 2.14 g of K_2CO_3 (15.5 mmol, 2 equiv) and a solution of 1.79 g of dimethyl-1-diazo-2-oxopropylphosphonate (9.3 mmol, 1.2 equiv) in 40 mL of MeOH. The mixture was stirred for 12h at room temperature. The solution was diluted with Et_2O, washed with a saturated solution of NH_4Cl and then brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude oil was purified by flash chromatography (pentane) and gave **2a** (1.66 g, 60% from **15a**). IR (neat) 3380, 3020, 2980, 1590, 1420, 840, 730, 700 cm^{-1} – ^1H NMR (200 MHz, $CDCl_3$) δ 7.62-7.59 (m, 2H), 7.41-7.38 (m, 3H), 5.34 (d, *J* = 1.0 Hz, 1H), 2.43 (t, *J* = 7.9 Hz, 2H), 2.30-2.20 (m, 2H), 1.98 (t, *J* = 2.5 Hz, 1H),1.78 (d, *J* = 1.0 Hz, 3H), 1.75 (s, 3H), 1.73 (s, 3H), 0.43 (s, 6H). – ^{13}C NMR (50 MHz, $CDCl_3$) δ 157.1 (IV), 140.1 (IV), 138.6 (IV), 133.7 (2C, III), 128.8 (III), 127.8 (2C, III), 125.5 (III), 125.4 (IV), 84.8 (IV), 68.2 (II), 30.2, (II), 22.2 (I), 21.9 (I), 19.7 (I), 17.7 (II), -0.8 (2C, I) – HRMS Calcd for $C_{19}H_{26}Si$: (MH^+) 283.180. Found 283.188.

***tert*-Butyl-(3-isopropylidene-2-methyl-hept-1-en-6-ynyl)-dimethyl-silane (2b)** was prepared following the procedure for **2a**. (0.775 g, 64% from **15b**). IR (neat) 2980, 2950, 2100, 1660, 1610, 1440, 1250, 930 cm^{-1} – ^1H NMR (200 MHz, $CDCl_3$) δ 5.12 (s, 1H), 2.37 (t, *J* = 7.6 Hz, 2H), 2.19 (td, *J* = 7.6 , 2.7 Hz, 2H), 1.94 (t, *J* = 2.8 Hz, 1H), 1.82 (s, 3H), 1.70 (s, 3H), 1.66 (s, 3H), 0.91 (s, 9H), 0.12 (s, 6H). – ^{13}C NMR (50 MHz, $CDCl_3$) δ 155.6 (IV), 139.2 (IV), 125.3 (III), 125.0 (IV), 84.8 (IV), 68.0 (III), 30.1 (II), 26.6 (3C, I), 21.9 (2C, I), 19.7 (I), 17.7 (II), 17.4 (IV), -4.1 (2C, I). – Anal. Calcd. for $C_{17}H_{30}Si$: C, 77.98; H, 11.52. Found: C, 77.95; H, 11.33.

Triisopropyl-(3-isopropylidene-2-methyl-hept-1-en-6-ynyl)-silane (2c) same procedure as for **2a**. (0.550 g, 80% from **15c**). IR (neat) 3310, 2980, 2950, 2100, 1660, 1610, 1440, 1260, 930 cm^{-1} – ^1H NMR (400 MHz, $CDCl_3$) δ 5.05 (s, 1H), 2.40-2.37 (m, 2H), 2.24-2.20 (m, 2H), 1.94 (t, *J* = 2.5 Hz, 1H), 1.83 (s, 3H), 1.72 (s, 3H), 1.70 (s, 3H), 1.19-1.07 (m, 21H). – ^{13}C NMR (50 MHz, $CDCl_3$) δ 156.3 (IV), 139.4 (IV), 125.0 (IV), 123.3 (III), 84.8 (IV), 68.0 (III), 30.1 (II), 22.7 (I), 21.9 (I), 19.7 (I), 19.1 (6C, I), 17.7 (II), 12.3 (3C, III).

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