The Simultaneous In-Situ Generation of Aldehydes and Phosphorus Ylides: A Convenient Multi-Step One-Pot Olefination Protocol

Qian Wang,[a] Heng-xu Wei,[a] and Manfred Schlosser*[a]

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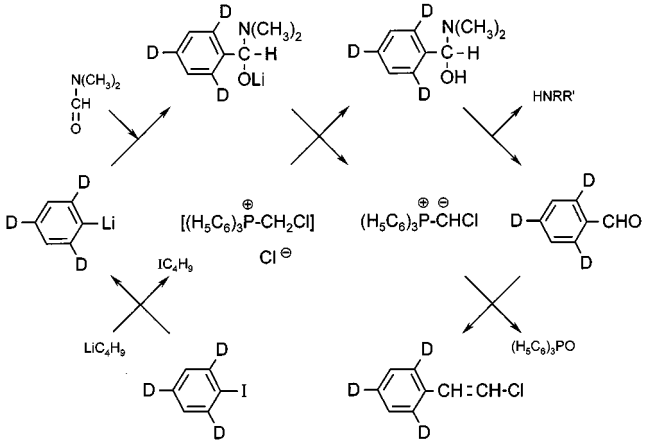
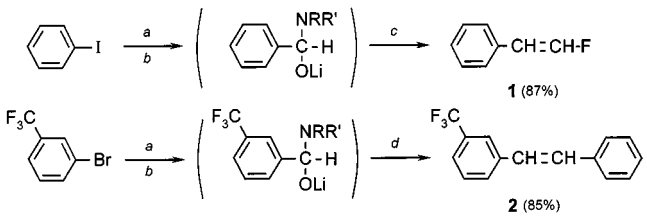
The lithium α-(dimethylamino)alkoxides resulting from the nucleophilic addition of an organolithium reagent to *N,N*-dimethylformamide are basic enough to deprotonate alkyltriphenylphosphonium salts suspended in tetrahydrofuran. The aldehydes liberated by the spontaneous decomposition of the resulting α-amino alcohols (hemiaminals) undergo a Wittig reaction with the simultaneously generated phosphorus ylides to afford olefins in excellent overall yields. This in situ method offers the unique advantage in its applicability to labile aldehydes which otherwise would become prey to (*Z*/*E*)-isomerization or self-condensation processes.

The acylation of organolithium reagents using carboxamides is one of the most proficient methods for the preparation of aldehydes and ketones.[1][2] The key intermediate in the reaction sequence is a lithium α-(*N,N*-dialkylamino)alkoxide or lithium α-(*N*-alkyl-*N*-arylamino)alkoxide. Upon neutralization, the corresponding α-amino alcohol (hemiaminal) is formed. It instantaneously decomposes to give an aldehyde or ketone, along with a secondary amine. As we found decades ago,[3] the mineral acid usually employed at the neutralization stage can be replaced by a phosphonium salt. Thus one can simultaneously produce a phosphorus ylide and a carbonyl compound which, of course, will combine with each other to undergo a Wittig olefination reaction. In this way, [2,4,6-$^2H_3$]phenyllithium, generated from [2,4,6-$^2H_3$]iodobenzene by halogen−metal exchange with butyllithium, has been directly converted into [2,4,6-$^2H_3$]-ω-chlorostyrene upon consecutive treatment with *N*-methylformanilide and (chloromethyl)triphenylphosphonium chloride.[3]



Unless applied in protic media,[4] lithium alkoxides are virtually inert towards ordinary phosphonium salts. For example, lithium 2-methyl-1-phenylbutanoate reacts slowly with a slurry of benzyltriphenylphosphonium bromide in tetrahydrofuran and not at all with butyltriphenylphosphonium bromide. Therefore, one may suspect the scope of the multi-stage one-pot sequence described above to be limited to relatively acidic phosphonium salts. Fortunately this is not true. As a systematic study has revealed, the method is generally applicable, convenient, and offers other distinct advantages.

First we tested (fluoromethyl)triphenylphosphonium bromide. The corresponding ylide being rather labile, the standard procedure[5] is known to provide only moderate yields. In contrast, the route leading from iodobenzene through phenyllithium and its adduct with *N,N*-dimethylformamide afforded ω-fluorostyrene (**1**, *Z*/*E* 50:50) in excellent yield (87%). The same holds for the preparation of 3-(trifluoromethyl)stilbene (**2**, 85%; *Z*/*E* 41:59) starting with 3-bromobenzotrifluoride and benzyltriphenylphosphonium bromide.



(*a*) LiC_4H_9; (*b*) O=CH-NRR'; (*c*) $[(H_5C_6)_3P\text{-}CH_2F]Br$; (*d*) $[(H_5C_6)_3P\text{-}CH_2C_6H_5]Br$.

The halogen−metal exchange can, of course, also be applied to 1-alkenyl type substrates such as (*Z*)-1-propenyl bromide, (*E*)-ω-styryl bromide and (*Z*)-ω-styryl iodide. In such cases, we used only nonactivated alkyltriphenylphosphonium salts as the phosphorus component. The latter being comparably weak *CH*-acids, their deprotonation by the formamide−adduct required extended exposure times, typically 6−12 h rather than 1−2 h as in the previous examples. It was, however, possible to accelerate the reaction by either replacing *N,N*-dimethylformamide by *N*-methylformanilide or, most efficiently, by adding one equivalent of potassium

[a] Institut de Chimie organique de l'Université, Bâtiment de Chimie (BCh),
CH-1015 Lausanne-Dorigny, Switzerland
Fax: (internat.) +41-21/692-3965

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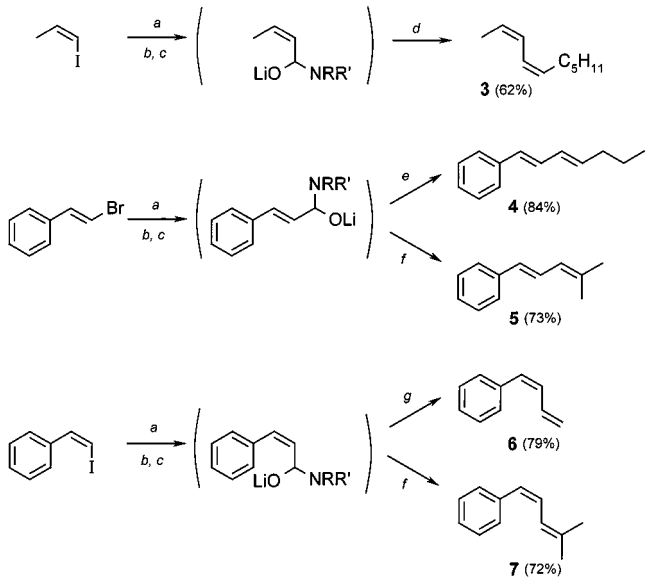
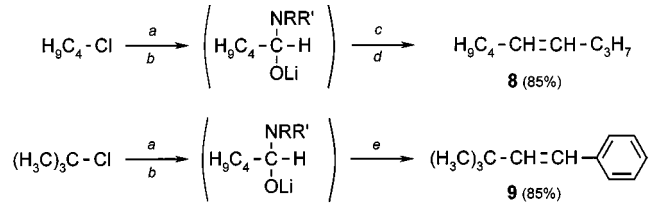
tert-butoxide. Under these conditions, 2,4-decadiene (**3**, 62%; *Z,Z*/*Z,E* = 90:10), 1-phenyl-1,3-heptadiene (**4**, 84%; *E,Z*/*E,E* 80:20), (*E*)-4-methyl-1-phenyl-1,3-pentadiene (**5**, 73%), (*Z*)-1-phenyl-1,3-butadiene (**6**, 79%) and (*Z*)-4-methyl-1-phenyl-1,3-pentadiene (**7**, 72%) were obtained in acceptable yields.



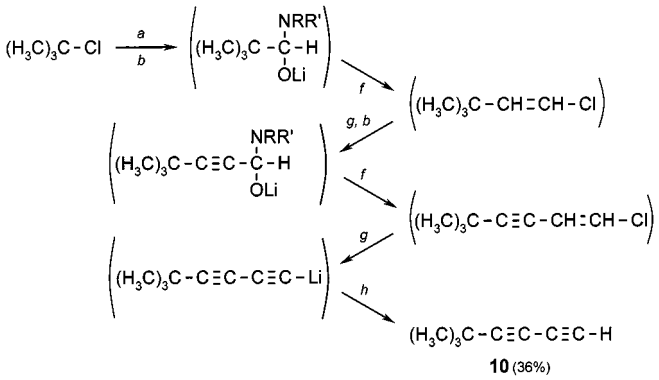
(*a*) $LiC(CH_3)_3$ [2.0 equiv.]; (*b*) O=CH-NRR'; (*c*) $KOC(CH_3)_3$; (*d*) $[(H_5C_6)_3\overset{\oplus}{P}\text{-}C_6H_{13}]\overset{\ominus}{Br}$; (*e*) $[(H_5C_6)_3\overset{\oplus}{P}\text{-}C_4H_9]\overset{\ominus}{Br}$; (*f*) $[(H_5C_6)_3\overset{\oplus}{P}\text{-}CH(CH_3)_2]\overset{\ominus}{Br}$; (*g*) $[(H_5C_6)_3\overset{\oplus}{P}\text{-}CH_3]\overset{\ominus}{Br}$.

The permutational halogen−metal exchange is a particularly reliable, though by no means unique method for the generation of the required organolithium species. Whenever possible, one may use commercial reagents such as butyllithium or *tert*-butyllithium, both of which are manufactured by the reductive insertion of the metal into the carbon−halogen bond of the corresponding chloride. The consecutive treatment of *N*,*N*-dimethylformamide with butyllithium and butyltriphenylphosphonium bromide gave 4-nonene (**8**; 85%; *Z*/*E* 93:7), with *tert*-butyllithium and benzyltriphenylphosphonium bromide 3,3-dimethyl-1-phenyl-1-butene (**9**; 85%; *Z*/*E* 82:18).



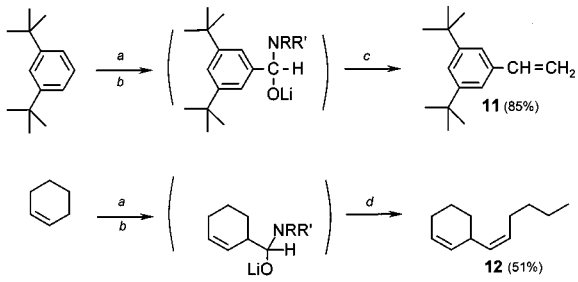
(*a*) Li [2.0 equiv.]; (*b*) O=CH-NRR'; (*c*) $KOC(CH_3)_3$; (*d*) $[(H_5C_6)_3\overset{\oplus}{P}\text{-}C_4H_9]\overset{\ominus}{Br}$; (*e*) $[(H_5C_6)_3\overset{\oplus}{P}\text{-}CH_2C_6H_5]\overset{\ominus}{Br}$.

In a strictly analogous manner, 1-chloro-3,3-dimethyl-1-butene was made, though not isolated. Butyllithium-promoted E2cb-elimination[6] converted it immediately into 3,3-dimehtyl-1-butynyllithium. Nucleophilic addition of the latter acetylide onto *N*,*N*-dimethylformamide was followed by chloromethylenation of the 4,4-dimethyl-3-pentynal afforded 1-chloro-5,5-dimethyl-1-hexen-3-yne generated in situ. Dehydrochlorination gave 5,5-dimethyl-1,3-hexadiyne (**10**; 36% overall).



(*a*) Li [2.0 equiv.]; (*b*) O=CH-N$(CH_3)_2$; (*c*) $KOC(CH_3)_3$; (*d*) $[(H_5C_6)_3\overset{\oplus}{P}\text{-}C_5H_{11}]\overset{\ominus}{Br}$; (*e*) $[H_5C_6)_3\overset{\oplus}{P}\text{-}CH_2C_6H_5]\overset{\ominus}{Br}$; (*f*) $[(H_5C_6)_3\overset{\oplus}{P}\text{-}CH_2Cl]\overset{\ominus}{Cl}$; (*g*) LiC_4H_9 [2.0 equiv.]; (*h*) H_2O

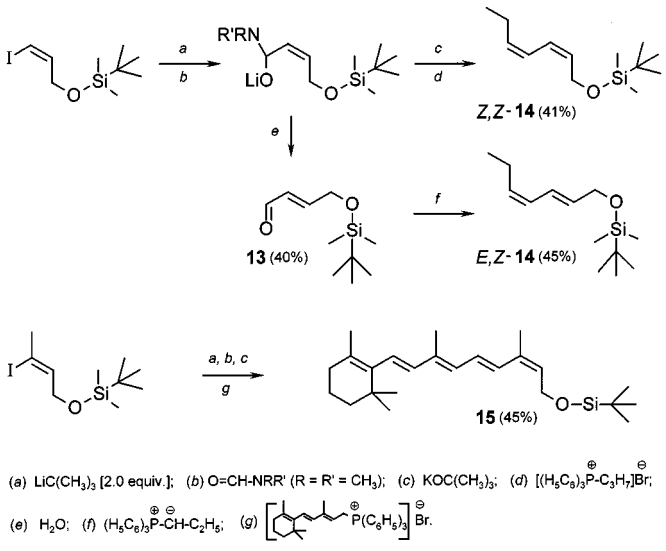
Superbase chemistry[7−9] offers another versatile access to organometallic intermediates. Metalation[10] of 1,3-di-*tert*-butylbenzene with the butyllithium/potassium *tert*-butoxide mixture, followed by the addition of *N*,*N*-dimethylformamide and methyltriphenylphosphonium bromide gave 3,5-di-*tert*-butylstyrene (**11**; 85%). (*Z*)-3-(1-Hexenyl)cyclohexene (**12**; 51%, *Z*/*E* 97:3) was obtained in a similar reaction sequence employing cyclohexene and hexyltriphenylphosphonium bromide as main components.



(*a*) LiC_4H_9 + $KOC(CH_3)_3$; (*b*) O=CH-NRR' (R = R' = CH_3); (*c*) $[(H_5C_6)_3\overset{\oplus}{P}\text{-}CH_3]\overset{\ominus}{Br}$; (*d*) $[(H_5C_6)_3\overset{\oplus}{P}\text{-}C_5H_{11}]\overset{\ominus}{Br}$.

Compared with Wittig reactions carried out under salt-free conditions,[11,12] the in-situ technique described here cannot avoid the presence of lithium salts and other polar compounds, all known to ruin optimal *cis*-selectivities. The (*Z*/*E*) ratios observed are indeed far below of what could be achieved under ideal conditions (e.g., in the case of **8** 93:7 rather than 99:1). On the other hand, the in-situ protocol will often be the method of choice when one has to olefinate a base-sensitive or otherwise structurally vulnerable aldehyde. An attempt to prepare (*Z*)-4-(*tert*-butyldimethylsilyloxy)-2-butenal by generating (*Z*)-3-(*tert*-butyldimethylsilyloxy)-1-propenyllithium from the corresponding iodide, allowing it to react with *N*,*N*-dimethylformamide and neutralizing the adduct thus formed, failed. Extensive (*Z*/*E*) isomerization took place during the workup process and (*E*)-4-(*tert*-butyldimethylsilyloxy)-2-butenal (*E*-**13**; 40%) was isolated as the main product. Condensation of

this aldehyde afforded the *O*-(*tert*-butyldimethylsilyl)-protected (2*E*,4*Z*)-2,4-heptadien-1-ol (*E,Z*-**14**; 45%). The (2*Z*,4*Z*)-isomer (*Z,Z*-**14**; 41%; *Z*,*Z*/*Z*,*E* 83:17) was predominantly formed when the 3-(*tert*-butyldimethylsilyloxy)-1-propenyllithium/*N*,*N*-dimethylformamide adduct was added to a vigorously stirred suspension of propyltriphenylphosphonium bromide in tetrahydrofuran. In the same way, the branched homolog 3-(*tert*-butyldimethylsilyloxy)-11-methyl-1-propenyllithium was generated from *tert*-butyldimethylsilyl (*Z*)-3-iodo-2-butenyl ether, and was consecutively treated with *N,N*-dimethylformamide and 2-(β-ionylidene)ethyltriphenylphosphonium bromide. After hydrolysis under acidic conditions, the *O*-(*tert*-butyldimethylsilyl)-protected Δ^{13}-(*Z*)-retinol (vitamin A) was obtained as a 2:3 Δ^{11}-(*Z*/*E*) mixture (**15**; 45%).



(*a*) $LiC(CH_3)_3$ [2.0 equiv.]; (*b*) O=CH-NRR' (R = R' = CH_3); (*c*) $KOC(CH_3)_3$; (*d*) $[(H_5C_6)_3\overset{\oplus}{P}\text{-}C_3H_7]\overset{\ominus}{Br}$; (*e*) H_2O; (*f*) $(H_5C_6)_3\overset{\oplus}{P}\overset{\ominus}{C}H\text{-}C_2H_5$; (*g*) $\left[\text{allyl-}\overset{\oplus}{P}(C_6H_5)_3\right]\overset{\ominus}{Br}$.

Experimental Section

Starting materials were purchased from Fluka (CH-9479 Buchs), Aldrich (D-89552 Steinheim), and Merck-Schweiz (CH-8953 Dietikon), unless literature sources or details of the preparation are given. Solutions of butyllithium in hexanes (1.5 M and "11.5 M", i.e. containing the organometallic reagent to the extent of 90%) were supplied by CheMetall (D-60271 Frankfurt), and potassium *tert*-butoxide by Callery (Pittsburgh, PA 15230). − All commercial reagents were used without further purification. Air- and moisture-sensitive compounds were stored in Schlenk tubes or Schlenk burettes. They were protected by and handled under an atmosphere of 99.995% pure N_2 (glassware: Glasgerätebau Pfeifer, D-98711 Frauenwald). Anhydrous pentanes were obtained by treatment for 2 h with finely-powdered CaH_2, and stirring at reflux before distillation: other paraffinic or aromatic hydrocarbons (e.g., hexanes, benzene, and toluene) were dried by azeotropic distillation. Diethyl ether, tetrahydropyran, and THF were dried by distillation from Na wire after the characteristic blue color of sodium diphenyl ketyl generated in situ was found to persist.[13,14] Ethereal extracts were dried with Na_2SO_4. Before distillation of compounds prone to radical polymerization or sensitive to acids, a spatula tip of hydroquinone or K_2CO_3, respectively, was added. The temperature of dry ice/methanol baths is consistently indicated at −75°C and "room temperature" (22−26°C) as 25°C. − Melting ranges (mp) are reproducible after resolidification, unless otherwise stated ("dec."), and are corrected by using a calibration curve which was established with authentic standards. If no melting points are given, it means that all attempts to crystallize the liquid product have failed even at temperatures as low as −75°C. − If reduced pressure is not specified, boiling ranges were determined under ordinary atmospheric conditions (725 ± 25 Torr). − Silica gel (Merck Kieselgel 60) or 70−230 mesh (0.06−0.20 mm) particle size was used for column chromatography. The solid support was suspended in hexane and, when all air bubbles had escaped, was washed into the column. When the level of the liquid was still 3−5 cm above the silica layer, the dry powder (obtained by adsorption of the crude product mixture onto 15−20 g silica gel and subsequent evaporation of the solvent) was poured on top of the column. − Whenever reaction products were not isolated, their yields were determined by gas chromatography, comparing their peak areas with that of an internal standard, and correcting the ratios by calibration factors. Product ratios were determined and the purity of distilled compounds was checked on at least two columns loaded with stationary phases of different polarity. Chromosorb G-AW of 80 −100 and 60−80 mesh particle size was used as the support for packed analytical or preparative columns (2 or 3 m long, 2 mm inner diameter and 3 or 6 m long, 1 cm inner diameter, respectively). Packed columns were made of glass, while quartz was the material for coated, Grob-type capillary columns (≥ 10 m long). In the case of programmed temperature increase, a rate of 10°C min^{-1} was maintained. The stationary phases employed are encoded as DB-1 and DB-1701 (both silicone type), APL (Apiezon-L hydrocarbon) and C-20M, DB-Wax, or DB-FFAP (all belonging to the polyethylene glycol type). − Nuclear magnetic resonance spectra of ^1H nuclei in $CDCl_3$ solution were recorded at 400 MHz. Chemical shifts δ refer to the signal of tetramethylsilane. Coupling constants (*J*) are measured in Hz. − Mass spectra were obtained at 70 eV ionization potential, maintaining a source temperature of 200°C. Whenever no molecular peak was observed under standard conditions, chemical ionization ("c.i.") in an ammonia atmosphere at 100°C source temperature was applied. Elementary analyses were executed by the laboratory of I. Beetz, D-96301 Kronach. The expected numbers are calculated on the basis of atomic weights according to the 1986 IUPAC recommendations.

ω-Fluorostyrene (1): Butyllithium (25 mmol), from which the commercial solvent (hexanes) had been stripped off, was dissolved in precooled (−75°C) tetrahydrofuran (50 mL). Still at −75°C, iodobenzene (2.8 mL, 5.1 g, 25 mmol) and, in 10-min intervals, *N*,*N*-dimethylformamide (2.0 mL, 1.9 g, 25 mmol) and (fluoromethyl)triphenylphosphonium tetrafluoroborate[5] (9.6 g, 25 mmol) were added. The mixture was vigorously stirred for 2 h at 25°C and, after addition of potassium *tert*-butoxide (2.8 g, 25 mmol), for another 2 h. A sample was withdrawn to determine the yield and isomeric composition by gas chromatography (30 m, DB−1, 50°C; 30 m, DB−WAX, 50°C; styrene as an "internal standard"): 87%; (*Z*/*E*) = 51:49. The reaction mixture was poured into water (50 mL) and extracted with hexanes (2 × 25 mL). The combined organic layers were washed with brine (25 mL), dried, and concentrated. Upon distillation the product was collected as a colorless liquid; bp 75−76°C/70 Torr (ref.[15] bp 70−74°C/65 Torr); n_D^{20} = 1.5279 (ref.[16] n_D^{20} = 1.5284). − ^1H NMR: δ = 7.4 (m, 5 H), 7.20 (dd, *J* = 83.1, 11.2 Hz, 0.5 H), 6.68 (dd, *J* = 82.4, 5.5 Hz, 0.5 H), 6.42 (dd, *J* = 19.5, 11.2 Hz, 0.5 H), 5.63 (dd, *J* = 44.9, 5.5 Hz, 0.5 H).

3-(Trifluoromethyl)stilbene (2): At −75°C, a solution of 3-bromobenzotrifluoride (5.6 g, 25 mmol) in tetrahydrofuran (100 mL) was treated first with *tert*-butyllithium (1.5 M in pentanes, 34 mL, 50 mmol) and, 10 min later, with *N*,*N*-dimethylformamide (2.0 mL, 1.9 g, 25 mmol). After addition of benzyltriphenylphosphonium bromide (10.9 g, 25 mmol), the mixture was vigorously stirred for 6 h at 25°C. It was then adsorbed onto silica gel (25 mL) and evaporated to dryness. The powder was poured on top of a column filled with more silica gel (100 mL) and eluted with a 1:20 (v/v) mixture of ethyl acetate and hexanes. The (*Z*)-isomer (*Z*-**2**) was eluted first; 2.2 g (35%). − ^{1}H NMR: δ = 7.50 (s, 1 H), 7.4 (m, 2 H), 7.3 (m, 6 H), 6.73 (d, *J* = 12.2 Hz, 1 H), 6.60 (d, *J* = 12.2 Hz, 1 H). − ^{19}F NMR: δ = −63.4. The (*E*)-isomer (*E*-**2**) followed afterwards; mp 65−67°C (ref.[17] mp 66.6−67.0°C); 3.1 g (50%). − ^{1}H NMR: δ = 7.59 (s, 1 H), 7.3 (m, 3 H), 7.2 (m, 1 H), 7.1 (m, 3 H), 6.90 (t, *J* = 7.9 Hz, 1 H), 6.83 (d, *J* = 16.5 Hz, 1 H), 6.71 (d, *J* = 16.5 Hz, 1 H). − ^{19}F NMR: δ = −63.2.

(2*Z*)-2,4-Decadiene (3): At −75°C, (*Z*)-1-bromopropene (2.1 mL, 3.0 g, 25 mmol) and, 5 min later, *N*,*N*-dimethylformamide (2.0 mL, 1.9 g, 25 mmol) were added to a solution of *tert*-butyllithium (50 mmol) in neat tetrahydrofuran (50 mL). Hexyltriphenylphosphonium bromide (11.0 g, 25 mmol) was added. After 6 h of stirring at 25°C, the reaction mixture was poured into water (50 mL) and extracted with hexanes (2 × 25 mL). The combined organic layers were washed with brine (25 mL), dried, and concentrated. Upon distillation, the product was collected as a colorless liquid (2.1 g, 62%). − Bp 65−68°C/60 Torr (ref.[18] bp 45−47°C/38 Torr). − n_D^{20} = 1.4588 (ref.[19] n_D^{20} = 1.4581). − According to gas chromatography (30 m, DB−1, 60°C; 30 m, DB−WAX, 60°C), the (2*Z*,4*Z*)- and (2*Z*,4*E*)-isomers were present in the ratio of 90:10. − ^{1}H NMR: δ = 6.32 (ddq, *J* = 15.1, 10.9, 1.2 Hz, 0.1 H), 6.2 (m, 1.8 H), 5.97 (tq, *J* = 10.9, 1.5 Hz, 0.1 H), 5.66 (dt, *J* = 15.1, 7.1 Hz, 0.1 H), 5.5 (m, 1.8 H), 5.36 (dq, *J* = 10.9, 7.0 Hz, 0.1 H), 2.16 (q, *J* = 7.2 Hz, 1.8 H), 2.09 (q, *J* = 7.1 Hz, 0.2 H), 1.75 (d, *J* = 6.8 Hz, 2.7 H), 1.73 (dd, *J* = 7.0, 1.7 Hz, 0.3 H), 1.3 (m, 6 H), 0.88 (t, *J* = 6.6 Hz, 2.7 H), 0.86 (t, *J* = 6.8 Hz, 0.3 H).

(1*E*)-1-Phenyl-1,3-heptadiene (4): At −75°C and in 10-min intervals, *tert*-butyllithium (1.5 M in pentanes, 33 mL, 50 mmol), *N*,*N*-dimethylformamide (2.0 mL, 1.9 g, 25 mmol), and butyltriphenylphosphonium bromide (10 g, 25 mmol) were added to a solution of (*E*)-β-bromostyrene[20] (3.2 mL, 4.6 g, 25 mmol) in tetrahydrofuran (0.10 L). The mixture was vigorously stirred for 2 h at 25°C and, after addition of potassium *tert*-butoxide (2.8 g, 25 mmol), again for 2 h at 25°C, before being poured into water (50 mL) and extracted with hexanes (2 × 25 mL). The combined organic layers were washed with brine (25 mL), dried, and concentrated. Upon distillation, the product was collected as a colorless liquid (3.6 g, 84%). − Bp 135−137°C/10 Torr (ref.[21] bp 129−133°C/5.0 Torr) − n_D^{20} = 1.5780 (ref.[21] n_D^{20} = 1.5902). − According to gas chromatography (3 m, 5% APL, 160°C; 3 m, 5% C−20M, 160°C), the (1*E*,3*Z*)- and (1*E*,3*E*)-isomers were present in the ratio of 80:20. − ^{1}H NMR: δ = 7.3 (m, 5 H), 7.06 (dd, *J* = 15.7, 11.2 Hz, 0.8 H), 6.74 (dd, *J* = 15.5, 10.1 Hz, 0.2 H), 6.53 (d, *J* = 15.7 Hz, 0.8 H), 6.44 (d, *J* = 15.5 Hz, 0.2 H), 6.21 (dd, *J* = 15.5, 10.1 Hz, 0.2 H), 6.17 (t, *J* = 11.1 Hz, 0.8 H), 5.84 (dt, *J* = 15.5, 7.2 Hz, 0.2 H), 5.54 (dt, *J* = 11.1, 7.7 Hz, 0.8 H), 2.27 (dtm, *J* = 7.5, 7.5 Hz, 1.6 H), 2.13 (q, *J* = 7.2 Hz, 0.4 H), 1.5 (m, 2 H), 0.96 (t, *J* = 7.2 Hz, 2.4 H), 0.93 (t, *J* = 7.2 Hz, 0.6 H).

(*E*)-4-Methyl-1-phenyl-1,3-pentadiene (5): Analogously using isopropyltriphenylphosphonium bromide as the phosphorus component (2.9 g, 73%). − Bp 75−77°C/1 Torr (ref.[22] bp 78−80°C/1.2 Torr). − n_D^{20} = 1.6051 (ref.[23] n_D^{20} = 1.6045). − ^{1}H NMR: δ = 7.40 (dt, *J* = 7.6, 1.3 Hz, 2 H), 7.31 (tt, *J* = 7.6, 1.3 Hz, 2 H), 7.20 (tt, *J* = 7.6, 1.3 Hz, 1 H), 6.98 (dd, *J* = 15.5, 11.0 Hz, 1 H), 6.43 (d, *J* = 15.5 Hz, 1 H), 6.01 (dm, *J* = 11.0 Hz, 1 H), 1.91 (d, *J* = 0.9 Hz, 3 H), 1.89 (s, 3 H).

(*Z*)-1-Phenyl-1,3-butadiene (6): At −75°C and in 10-min intervals, *tert*-butyllithium (1.5 M in pentanes, 33 mL, 50 mmol), *N*,*N*-dimethylformamide (2.0 mL, 1.9 g, 25 mmol), and methyltriphenylphosphonium bromide (9.0 g, 25 mmol) were added to a solution of (*Z*)-ω-iodostyrene[24] (5.8 g, 25 mmol) in tetrahydrofuran (0.10 L). The mixture was vigorously stirred for 2 h at 25°C and, after addition of potassium *tert*-butoxide (2.8 g, 25 mmol), again for another 2 h at 25°C, before being poured into water (50 mL) and extracted with hexanes (2 × 25 mL). The combined organic layers were washed with brine (25 mL), dried, and concentrated. Upon distillation, the product was collected as a colorless liquid (2.6 g, 79%). − Bp 80−81°C/10 Torr (ref.[25] bp 86°C/11 Torr). − n_D^{20} = 1.6104 (ref.[25] n_D^{25} = 1.6088). − ^{1}H NMR: δ = 7.3 (m, 5 H), 6.88 (dtd, *J* = 16.9, 10.2, 1.1 Hz, 1 H), 6.44 (d, *J* = 11.6 Hz, 1 H), 6.25 (dt, *J* = 11.6, 0.6 Hz, 1 H), 5.36 (dm, *J* = 16.9 Hz, 1 H), 5.21 (dm, *J* = 10.3 Hz, 1 H).

(*Z*)-1-Phenyl-4-methyl-1,3-pentadiene (7): Analogously using isopropyltriphenylphosphonium bromide as the phosphorus component (2.9 g, 73%). − Bp 123−127°C/10 Torr (ref.[26] bp 125−130°C/11 Torr). − n_D^{20} = 1.6013 (ref.[26] n_D^{25} = 1.5985). − ^{1}H NMR: δ = 7.33 (dd, *J* = 3.9, 1.0 Hz, 4 H), 7.2 (m, 1 H), 6.42 (t, *J* = 10.9 Hz, 1 H), 6.4 (m, 1 H), 6.30 (d, *J* = 10.9 Hz, 1 H), 1.85 (s, 3 H), 1.83 (s, 3 H).

4-Nonene (8): At −75°C, butyllithium (1.5 M in hexanes, 17 mL, 25 mmol) and, 5 min later, butyltriphenylphosphonium bromide (10 g, 25 mmol) were added to a solution of *N*,*N*-dimethylformamide (2.0 mL, 1.9 g, 25 mmol) in tetrahydrofuran (50 mL). Upon stirring for 2 h at 25°C, potassium *tert*-butoxide (2.8 g, 25 mmol) was added. After another 2 h at 25°C, the reaction mixture was poured into water (50 mL) and extracted with hexanes (2 × 25 mL). The combined organic layers were washed with brine (25 mL), dried, and concentrated. Upon distillation, the product was collected as a colorless liquid (2.7 g, 85%). − Bp 144−146°C (ref.[27] bp 145−146°C). − n_D^{20} = 1.4190 (ref.[27] n_D^{18} = 1.4224). − A (*Z*/*E*) ratio of 93:7 was determined by gas chromatography (30 m, DB−1701, 50°C; 30 m, DB−FFAP, 50°C). − ^{1}H NMR: δ = 5.4 (m, 2 H), 2.0 (m, 4 H), 1.4 (m, 6 H), 0.9 (m, 6 H).

3,3-Dimethyl-1-phenyl-1-butene (9): At −75°C, *tert*-butyllithium (1.5 M in pentanes, 17 mL, 25 mmol) and, 5 min later, benzyltriphenylphosphonium bromide (10 g, 25 mmol) were added to a solution of *N*,*N*-dimethylformamide (2.0 mL, 1.9 g, 25 mmol) in tetrahydrofuran (50 mL). Upon stirring for 6 h at 25°C, the reaction mixture was poured into water (50 mL) and extracted with hexanes (2 × 25 mL). The combined organic layers were washed with brine (25 mL), dried, and concentrated. Upon distillation, the product was collected as a colorless liquid (3.4 g, 85%). − Bp 84−85°C/10 Torr (ref.[28] bp 78°C/13 Torr). − n_D^{20} = 1.5075 (ref.[28] n_D^{20} = 1.502). − A (*Z*/*E*) ratio of 82:18 was obtained according to gas chromatography (5 m, 5% C−20M, 150°C; 3 m, 5% APL, 150°C). − ^{1}H NMR: δ = 7.3 (m, 5 H), 6.41 (d, *J* = 12.8 Hz, 0.8 H), 6.32 (d, *J* = 16.1 Hz, 0.2 H), 6.25 (d, *J* = 16.1 Hz, 0.2 H), 5.60 (d, *J* = 12.8 Hz, 0.8 H), 1.12 (s, 1.8 H), 0.97 (s, 7.2 H).

5,5-Dimethyl-1,3-hexadiyne (10): *N*-Methylformanilide (6.2 mL, 6.8 g, 50 mmol) and, 5 min later, (chloromethyl)triphenylphosphonium chloride (17.0 g, 50 mmol) were added to a solution of *tert*-butyllithium (50 mmol) in tetrahydrofuran (0.10 L) at −75°C. After 24 h of stirring at 0°C, pentanes (0.20 L) was added to the reaction mixture. Upon filtration and distillation, 1-chloro-3,3-dimethyl-1-butene was obtained as a colorless liquid (4.4 g, 74%). −

Bp 109−110°C (ref.[29] bp 105°C/730 Torr); n_D^{20} = 1.4273 (ref.[29] n_D^{20} = 1.4276). − A (*Z*/*E*) ratio of 51:49 was determined by gas chromatography (30 m, DB−1701, 40°C; 30 m, DB−FFAP, 25°C). − ^{1}H NMR: δ = 5.93 (d, *J* = 13.4 Hz, 0.5 H), 5.87 (d, *J* = 8.0 Hz, 0.5 H), 5.84 (d, *J* = 13.4 Hz, 0.5 H), 5.66 (d, *J* = 8.0 Hz, 0.5 H), 1.20 (s, 4.5 H), 1.04 (s, 4.5 H). Solutions of butyllithium (50 mmol) in hexanes (33 mL) and 1-chloro-3,3-dimethyl-1-butene (3.0 g, 25 mmol) in tetrahydrofuran (0.15 L) were combined and kept at 25°C for 2 h before being treated with *N*-methylformanilide (6.2 mL, 6.8 g, 50 mmol) and 15 min later, (chloromethyl)triphenylphosphonium chloride (9.5 g, 25 mmol). After stirring for 24 h at 0°C, a solution of butyllithium (50 mmol) in hexanes (33 mL) was added. After 2 h of stirring at 25°C, the mixture was poured into a saturated aqueous solution of ammonium chloride (0.10 L) and extracted with diethyl ether (3 × 20 mL). The combined organic layers were dried with anhydrous sodium sulfate. Distillation afforded a colorless liquid (0.95 g, 36%). − Bp 65−68°C/110 Torr (ref.[30] bp 50−55°C/100 Torr). − n_D^{20} = 1.4584 (ref.[30] n_D^{20} = 1.4581). − ^{1}H NMR: δ = 2.03 (s, 1 H), 1.25 (s, 9 H). − ^{13}C NMR: δ = 85.79 (1 C), 68.28 (1 C), 67.94 (1 C), 63.31 (1 C), 30.29 (3 C), 27.82 (1 C).

3,5-Di-*tert*-butylstyrene (11): A dark-brown mixture resulted when a suspension of 1,3-di-*tert*-butylbenzene (5.6 mL, 4.8 g, 25 mmol), butyllithium (25 mmol), and potassium *tert*-butoxide (2.8 g, 25 mmol) in hexanes (12.5 mL) was stirred for 24 h at 25°C. At 0°C, *N*,*N*-dimethylformamide (2.0 mL, 1.9 g, 25 mmol) in tetrahydrofuran (0.10 L) and methyltriphenylphosphonium bromide (9.0 g, 25 mmol) were added consecutively. After 6 h of stirring at 25°C, the reaction mixture was poured into water (50 mL) and extracted with hexanes (3 × 25 mL). The combined organic layers were washed with brine (25 mL), dried, and concentrated. Upon distillation, the product was collected as a colorless liquid (4.6 g, 85%). − Bp 132−135°C/4 Torr. − ^{1}H NMR: δ = 7.36 (t, *J* = 2.0 Hz, 1 H), 7.28 (d, *J* = 2.0 Hz, 2 H), 6.77 (dd, *J* = 17.5, 11.0 Hz, 1 H), 5.76 (dd, *J* = 17.5, 1.0 Hz, 1 H), 5.24 (dd, *J* = 11.0, 1.0 Hz, 1 H), 1.35 (s, 18 H). − $C_{16}H_{24}$ (216.37): calcd. C 88.82, H 11.18; found C 89.01, H 11.14.

(*Z*)-1-(3-Cyclohexenyl)-1-hexene (12): A solution of cyclohexene (2.6 mL, 2.1 g, 25 mmol), butyllithium (25 mmol) and potassium *tert*-butoxide (2.8 g, 25 mmol) in neat tetrahydrofuran (12.5 mL) was stirred for 1 h at −50°C. Upon treatment with *N*,*N*-dimethylformamide (2.3 mL, 2.2 g, 30 mmol) in tetrahydrofuran (50 mL) at −75°C, the orange-yellow mixture immediately decolorized. Pentyltriphenylphosphonium bromide (10.4 g, 25 mmol) was added. After 6 h of stirring at −75°C, the reaction mixture was poured into water (50 mL) and extracted with hexanes (3 × 25 mL). The combined organic layers were washed with brine (25 mL), dried, and concentrated. Distillation gave a colorless liquid (2.3 g, 51%). − Bp 88−92°C/10 Torr (ref.[32] bp 77°C/4 Torr). − n_D^{20} = 1.4750 (ref.[32] n_D^{25} = 1.4742). − A (*Z*/*E*) ratio of 97:3 was determined by gas chromatography (30 m, DB−1, 80°C; 30 m, DB−FFAP, 60°C). − ^{1}H NMR: δ = 5.7 (dm, *J* = 10.2 Hz, 1 H), 5.45 (dq, *J* = 10.2, 2.2 Hz, 1 H), 5.34 (dt, *J* = 10.6, 7.1 Hz, 1 H), 5.22 (ddt, *J* = 10.6, 9.2, 1.2 Hz, 1 H), 3.1 (m, 1 H), 2.1 (m, 2 H), 2.0 (m, 2 H), 1.8 (m, 2 H), 1.6 (m, 1 H), 1.3 (m, 5 H), 0.90 (t, *J* = 7.0 Hz, 3 H).

(*Z*)-3-(*tert*-Butyldimethylsilyl)oxy-1-iodo-1-propene: (*Z*)-3-Iodo-2-propen-1-ol[32] (2.6 mL, 4.6 g, 25 mmol), *tert*-butylchlorodimethylsilane (6.0 mL, 5.3 g, 35 mmol), and imidazole (2.4 g, 35 mmol) were dissolved in *N*,*N*-dimethylformamide (25 mL) and kept overnight (15 h) at 25°C. Water (0.10 L) was added, and the mixture was extracted with diethyl ether (5 × 50 mL). The combined organic layers were washed with brine (2 × 50 mL). Upon distillation, the product was collected as a colorless liquid (6.2, 83%). − Bp 64−66°C/1 Torr. − n_D^{20} = 1.4858. − ^{1}H NMR: δ = 6.42 (dt, *J* = 7.6, 5.3 Hz, 1 H), 6.24 (dt, *J* = 7.6, 1.8 Hz, 1 H), 4.25 (dd, *J* = 5.3, 1.8 Hz, 2 H), 0.94 (s, 9 H), 0.10 (s, 6 H). − ^{13}C NMR: δ 156.0, 130.7, 62.3, 25.8 (3 C), 18.3, −5.5 (2 C). − MS: *m*/*z* (%): 299 (19) [M^+ + 1], 298 (1) [M^+], 258 (22), 241 (100). − $C_9H_{19}IOSi$ (298.23): calcd. C 36.25, H 6.42; found C 36.36, H 6.29.

(*Z*)-4-(*tert*-Butyldimethylsilyl)oxy-2-iodo-2-butene: Analogously from (*Z*)-3-iodo-2-buten-1-ol[33] (2.7 mL, 5.0 g, 25 mmol) (6.4 g, 82%). − Bp 72−73°C/0.5 Torr. − n_D^{20} = 1.4754. − ^{1}H NMR: δ 5.69 (tq, *J* = 5.5, 1.5 Hz, 1 H), 4.18 (dq, *J* = 5.5, 1.5 Hz, 2 H), 2.50 (q, *J* = 1.5 Hz, 3 H), 0.91 (s, 9 H), 0.09 (s, 6 H). − ^{13}C NMR: δ 135.3, 99.1, 68.6, 35.5, 25.9 (3 C), 18.3, −5.1 (2 C). − MS (c.i.): *m*/*z* (%): 330 (36) [$M^+ + NH_4$,], 313 (40) [M^+ + 1], 312 (3) [M^+], 272 (64), 74 (100). − $C_{10}H_{21}IOSi$ (312.26): calcd. C 38.46, H 6.78; found C 38.42, H 7.14.

(*E*)-4-(*tert*-Butyldimethylsilyl)oxy-2-butenal (*E*-13): At −75°C, *tert*-butyllithium (50 mL) in pentanes (35 mL) and, 5 min later, *N*,*N*-dimethylformamide (1.9 mL, 1.8 g, 25 mmol) were added to a solution of (*Z*)-3-(*tert*-butyldimethylsilyl)oxy-1-iodo-1-propene (5.7 mL, 7.5 g, 25 mmol) in diethyl ether (50 mL). The mixture was allowed to reach 25°C before being poured into water (50 mL). Extraction with diethyl ether (3 × 50 mL), washing with brine (10 mL) and distillation afforded a colorless liquid (2.0 g, 40%). − Bp 64−66°C/0.5 Torr. − n_D^{20} = 1.4566. − ^{1}H NMR: δ 9.61 (d, *J* = 8.1 Hz, 1 H), 6.86 (dt, *J* = 15.6, 3.5 Hz, 1 H), 6.39 (ddt, *J* = 15.6, 8.1, 2.1 Hz, 1 H), 4.44 (ddm, *J* = 3.5, 2.1 Hz, 2 H), 0.91 (s, 9 H), 0.09 (s, 6 H). − ^{13}C NMR: δ 193.2, 156.0, 130.7, 62.3, 25.8 (3 C), 18.3, −5.3 (2 C). − MS: *m*/*z* (%): 201 (4) [M^+ + 1], 200 (1) [M^+], 75 (100). − $C_{10}H_{20}O_2Si$ (200.35): calcd. C 59.95, H 10.06; found C 59.86, H 9.97.

(2*Z*,4*Z*)-1-(*tert*-Butyldimethylsilyl)oxy-2,4-heptadiene (*Z*,*Z*-14): At −75°C and in intervals of 5 min, *tert*-butyllithium (50 mmol) in pentanes (35 mL), *N*,*N*-dimethylformamide (1.9 mL, 1.8 g, 25 mmol), potassium *tert*-butoxide (2.8 g, 25 mmol), and propyltriphenylphosphonium bromide (9.6 g, 25 mmol) were added consecutively to a solution of (*Z*)-3-(*tert*-butyldimethylsilyl)oxy-1-iodo-1-propene (5.7 mL, 7.5 g, 25 mmol) in diethyl ether (50 mL). After 6 h of vigorous stirring at 25°C, the mixture was cooled to 0°C and poured into ice-cold hexanes (0.20 L). Filtration, evaporation, and distillation of the organic solution gave a colorless oil (2.3 g, 41%) which, according to NMR and gas chromatography (30 m, DB−1, 150°C; 30 m, DB−WAX, 120°C), contained (2*Z*,4*Z*)-**14** and (2*Z*,4*E*)-**14** in a ratio of 5:1. − Bp 59−60°C/0.4 Torr. − n_D^{20} = 1.4558. − ^{1}H NMR: δ = 6.28 (tm, *J* = 11.2 Hz, 1 H), 6.15 (tm, *J* = 11.2 Hz, 1 H), 5.5 (m, 2 H), 4.36 (dd, *J* = 6.2, 1.5 Hz, 1.66 H), 4.35 (dd, *J* = 6.2, 1.4 Hz, 0.34 H), 2.2 (m, 2 H), 1.10 (t, *J* = 7.5 Hz, 3 H), 0.90 (s, 9 H), 0.08 (s, 6 H). − ^{13}C NMR: δ = 135.2, 130.6, 12.7, 122.5, 59.6, 26.0 (3 C), 20.7, 18.4, 14.1, −5.1 (2 C). − MS: *m*/*z* (%): 227 (3) [M^+ + 1], 169 (30), 95 (100). − $C_{13}H_{26}OSi$ (226.43): calcd. C 68.96, H 11.57; found C 68.62, H 11.97.

(2*E*,4*Z*)-1-(*tert*-Butyldimethylsilyl)oxy-2,4-heptadiene (*E*,*Z*-14): At −75°C and with stirring, aldehyde **13** (5.2 mL, 5.0 g, 25 mmol) was added dropwise to an ylide solution[34] prepared from propyltriphenylphosphonium bromide (9.6 g, 25 mmol) and sodium amide (1.1 g, 28 mmol) in diethyl ether (50 mmol). The reaction mixture was allowed to reach 25°C and was worked up as described in the preceding paragraph. According to NMR and gas chromatography (see above), the distilled product (2.5 g, 45%) contained (2*E*,4*Z*)-**14** and (2*E*,4*E*)-**14** in a ratio of 24:1. − Bp 60−61°C/0.4 Torr. −

n_D^{20} = 1.4565. – ^{1}H NMR: δ = 6.53 (ddm, *J* = 15.0, 11.2 Hz, 1 H), 5.97 (dd, *J* = 11.2, 11.0 Hz, 1 H), 5.73 (dt, *J* = 15.0, 5.2 Hz, 1 H), 5.41 (dt, *J* = 11.0, 7.5 Hz, 1 H), 4.24 (dd, *J* = 5.2, 1.6 Hz, 2 H), 2.19 (t, *J* = 7.5, 1.5 Hz, 2 H), 1.00 (t, *J* = 7.5 Hz, 3 H), 0.92 (s, 9 H), 0.08 (s, 6 H). – ^{13}C NMR: δ 133.6, 132.2, 127.3, 125.1, 63.7, 26.0 (3 C), 21.0, 18.4, 14.3, –5.2 (2 C). – MS: *m*/*z*(%): 227 (2) [M^+ + 1], 226 (7) [M^+], 89 (22), 73 (100). – $C_{13}H_{26}OSi$ (226.42): calcd. C 68.96, H 11.57; found C 68.66, H 11.91.

(2*Z*)-1-(*tert*-Butyldimethylsilyl)oxy-3,7-dimethyl-9-(2,6,6-trimethyl-1-cyclohexenyl)-2,4,6,8-nonatetraene [*tert*-Butyldimethylsilyl Δ^{13}-(*Z*)-Retinyl Ether, 15]: At –75°C and with stirring, *tert*-butyllithium (50 mmol) in pentanes (35 mL), *N*,*N*-dimethylformamide (1.9 mL, 1.8 g, 25 mmol), potassium *tert*-butoxide (2.8 g, 25 mmol), and [2-(β-ionylidene)ethyl]triphenylphosphonium bromide[35] (13.6 g, 25 mmol) were added in this order and in intervals of 5 min to a solution of (*Z*)-4-(*tert*-butyldimethylsilyl)oxy-2-iodo-2-butene (6.0 mL, 7.8 g, 25 mmol) in diethyl ether (50 mL). The mixture was vigorously stirred at 25°C for 6 h before being cooled to 0°C, and poured into ice-cold hexanes (0.20 L). The filtered organic solution was adsorbed on silica gel (25 mL) and purified by column chromatography silica [(100 mL), eluent 1:40 (v/v) mixture of ethyl acetate and hexanes]. After evaporation of the solvents, a pale yellow oil (4.5 g, 45%) was collected which according to NMR was composed of Δ^{13}-(*Z*) and of Δ^{11}-(*E*) isomers in the ratio of 2:3. – n_D^{20} = 1.5749. – ^{1}H NMR: δ = 6.6 (m, 1 H), 6.4 (m, 0.6 H), 6.28 (d, *J* = 15.1 Hz, 0.4 H), 6.1 (m, 3 H), 5.46 (t, broad, *J* = 6.5 Hz, 1 H), 4.4 (m, 2 H), 2.0 (m, 2 H), 1.92 (s, 1.8 H), 1.90 (s, 1.2 H), 1.71 (s, 3 H), 1.6 (m, 2 H), 1.5 (m, 2 H), 1.18 (s, 3 H), 1.0 (m, 6 H), 0.91 (s, 9 H), 0.11 (s, 6 H). – MS: *m*/*z* (%): 401 (1) [M^+ + 1], 379 (3), 92 (92), 73 (100). – $C_{26}H_{44}OSi$ (400.72): calcd. C 77.93, H 11.07; found C 77.96, H 11.10.

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