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Synthesis and Reactions of Monosilylated 1,3,5-Hexatriyne and 1,3,5,7-Octatetrayne. Total Synthesis of Caryoynencins

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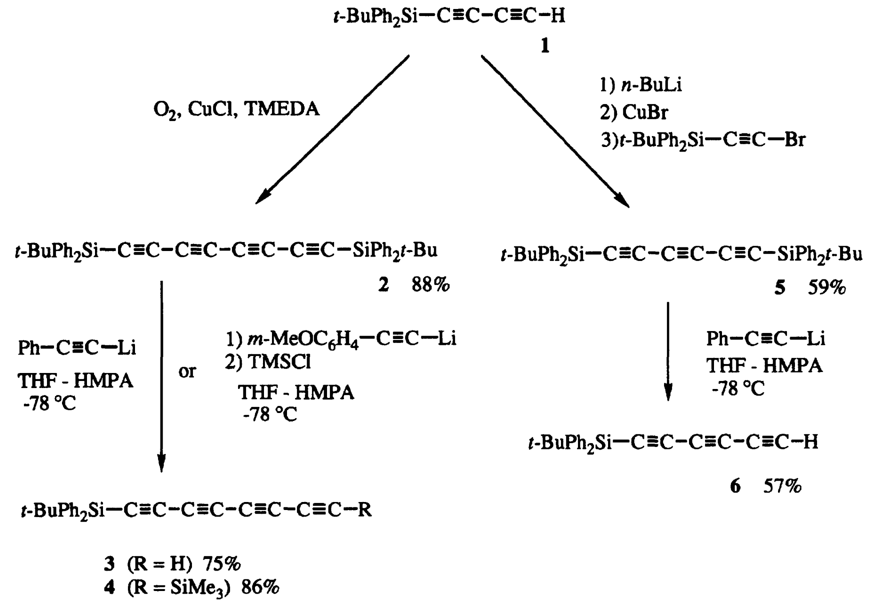
Selective monodesilylation of 1,8-bis(*t*-butyldiphenylsilyl)-1,3,5,7-octatetrayne and 1,6-bis(*t*-butyldiphenylsilyl)-1,3,5-hexatriyne with lithiated phenylacetylene gave unstable 1-(*t*-butyldiphenylsilyl)-1,3,5,7-octatetrayne and 1-(*t*-butyldiphenylsilyl)-1,3,5-hexatriyne, respectively. The terminal acetylenes on lithiation added to aldehydes and a ketone giving polyynols in high yields. The reaction was applied to the synthesis of polyyne antibiotics, caryoynencins. Polymerization of the terminal octatetrayne on an ITO-coated glass plate gave a film, which showed conductivity of 10^{-4} S cm^{-1} when doped with SO_3.

Natural products with terminal 1,3,5-hexatriyne and 1,3,5,7-octatetrayne structure show potent antibacterial and antifungal activities.[1,2] The conjugated polyynes, however, are extremely unstable, and polymerize spontaneously when concentrated. From the standpoint of material sciences the polymerizing ability is intriguing, since the polyyne polymers possessing highly conjugated π-system can exhibit interesting electrical or optical properties.[3,4] Thus, the development of synthetic methods of the terminal polyynes is an attractive field in organic synthesis. Monosilyl protected polyynes obviously are useful building blocks for this purpose. Although 1-triethylsilyl-1,3,5-hexatriyne and 1-triethylsilyl-1,3,5,7-octatetrayne were reported by Walton,[5] the yields were too low to be used in organic synthesis. Selective removal of a trimethylsilyl group from 1,4-bis(trimethylsilyl)-1,3-butadiyne with methyllithium was reported by Holmes,[6] and the methodology was applied to 1,6-bis(trimethylsilyl)-1,3,5-hexatriyne by Lewis.[1c] Problems, however, were later noted for the latter reaction.[7] The present report describes synthesis and reactions of 1-(*t*-butyldiphenylsilyl)-1,3,5,7-octatetrayne (**3**)[8] and 1-(*t*-butyldiphenylsilyl)-1,3,5-hexatriyne (**6**). The bulky silyl group was employed with expectations to stabilize **3** and **6** and to avoid use of volatile substances. The first synthesis of polyyne antibiotics, caryoynencins **13**,[1a] was also achieved.

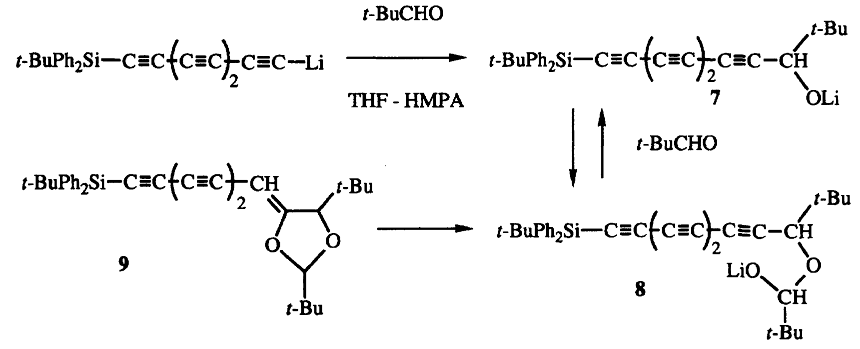
The synthetic studies started from 1-(*t*-butyldiphenylsilyl)-1,3-butadiyne (**1**), which was conveniently prepared according to the method of Zweifel[9] from commercially available 1-methoxyl-1-buten-3-yne and *t*-butyldiphenylsilyl chloride. Dimerization of **1** with the Hay catalyst[10] gave bis-silylated 1,3,5,7-octatetrayne **2** (Scheme 1). Protected 1,3,5-hexatriyne **5** was synthesized by copper-mediated coupling of lithiated **1** with bromo(*t*-butyldiphenylsilyl)acetylene in pyridine.[11] Use of bromo(trimethylsilyl)acetylene was unsatisfactory because of desilylation and decomposition of the product during the reaction. The classical Cadiot–Chodkiewicz coupling in DMF gave very low yield of **5**. Although the triyne **5** was first synthesized by Diederich,[7] the present coupling reaction turned out to be convenient to us.

Selective removal of a silyl group was studied with the tetrayne **2**. Since alkaline treatment of 1,8-bis(triethylsilyl)-1,3,5,7-octatetrayne was reported by Walton[5] to give a mixture of the starting material, monodeprotected, and bis-deprotected product, Holmes' procedure[6] was reexamined. Although treating **2** with methyllithium, butyllithium, or *t*-butyllithium under several reaction conditions resulted in decomposition, the less nucleophilic lithiated phenylacetylene gave the desired mono-protected **3** in THF–HMPA at −78 °C. HMPA was essential, and no reaction took place in the absence of the polar co-solvent. The tetrayne **3** polymerized instantaneously by concentration, and all the purification procedures were carried out in solutions. Yield of purified **3** was estimated by concentrating a part of the solution, and weighing the polymer. The selective desilylation of **3** with *m*-methoxyphenylacetylene followed by quenching with trimethylsilyl chloride gave 1-(*t*-butyldiphenylsilyl)-8-(trimethylsilyl)-1,3,5,7-octatetrayne (**4**) in 86% yield. The substituted phenylacetylene was used to facilitate chromatographic separation of **4** from by-products such as silylated phenylacetylenes. The tetrayne **4** possessing two acetylenic terminals with differentiated protecting groups can be another useful building block for polyyne synthesis, although **4**, being less stable than **2**, slowly decomposed at concentrated state. Selective deprotection of 1,3,5-hexatriyne **5** was similarly conducted with the lithiated phenylacetylene in THF–HMPA. The triyne **6** also polymerized by concentration. Contrary to the expectation, use of the bulky *t*-butyldiphenylsilyl group did not stabilize **3** and **6** sufficient enough for isolation.

When the intermediate lithiated polyyne in the above THF–HMPA mixture was reacted with 2,2-dimethylpropanal, a dioxolane **9** was formed (Scheme 2). Since



Scheme 1.



Scheme 2.

simple adducts were obtained with lithiated **3** in THF as will be described later, the dioxolane formation was attributable to the presence of HMPA. It may be interesting to note that an equilibrium between alkoxylithium **7** and hemiacetal **8** exists in solution. Trials to activate **2** with CsF[12] or Bu_4NF[13] in the presence of 2,2-dimethylpropanal also gave related 1,3-dioxolane derivatives.

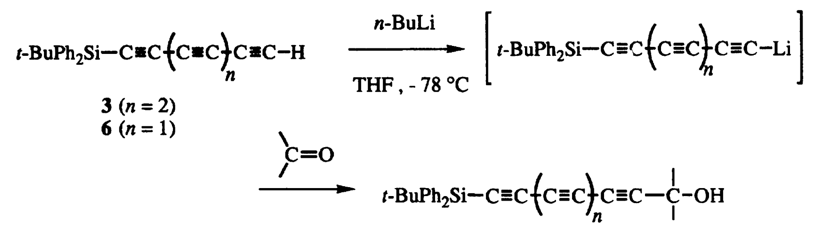
Polyynes **3** and **6** were smoothly lithiated with butyllithium in THF at −78 °C without any sign of organometallic addition to the polyyne moiety. The lithium acetylides added to aldehydes and a ketone in high yields (Scheme 3, Table 1). Oxiranes were cleaved in the presence of $BF_3 \cdot OEt_2$ (Scheme 4).[14] These polyynols were relatively stable, and were isolated at concentrated state. Formation of lithiated triynes and tetraynes via silicon-lithium exchange[1c] or via halogen–lithium exchange was reported.[15] It is now shown that the proton-lithium exchange proceeds effectively.

Removal of *t*-butyldiphenylsilyl group from the polyynols was carried out by alkaline treatments in THF–water (Scheme 5). Use of methanol, ethanol, or 2-propanol solvent gave adducts of the alcohols at the terminal triple bonds. ^1H NMR spectra of the desilylated polyynols were obtained by careful silica-gel chromatography with hexane–ethyl acetate and solvent exchange to $CDCl_3$–CCl_4.

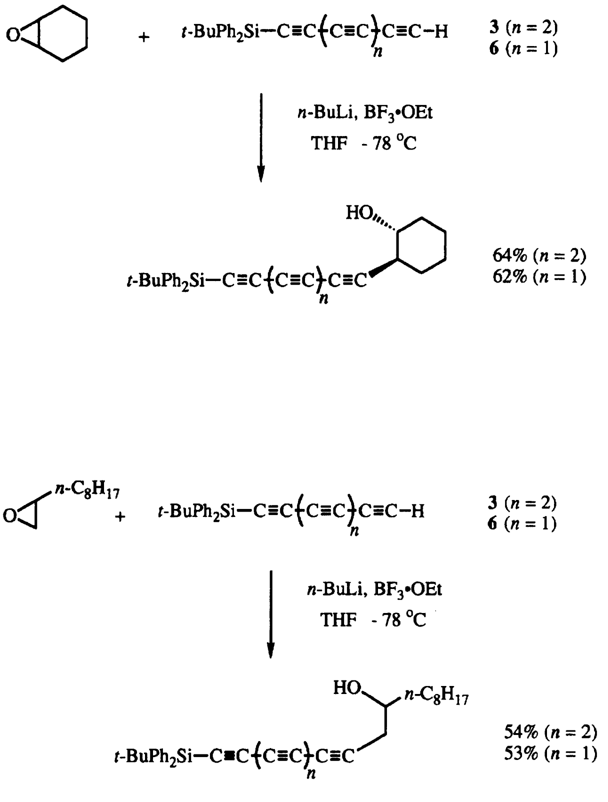
Table 1. Addition Reactions of Lithiated **3** and **6** to Aldehydes and a Ketone

Polyyne	Carbonyl compound	Yield (%)
3	*t*-BuCHO	83
	n-C_4H_9CHO	80
	n-$C_6H_{13}CHO$	86
	n-C_3H_7CH=CHCHO	88
	PhCHO	75
	Cyclohexanone	87
6	*t*-BuCHO	98
	n-$C_6H_{13}CHO$	95
	n-C_3H_7CH=CHCHO	86
	Cyclohexanone	92

Properties of polymerized **3** were briefly studied. Concentrating a hexane solution of **3** by evaporater gave poly-**3** as black shiny powder, which was insoluble even in DMSO and DMF. FTIR spectra indicated the ab-



Scheme 3.



Scheme 4.

sence of acetylenic C–H and the presence of C≡C moiety. We tentatively assigned a structure shown in Scheme 6 for poly-**3**, which assumed the polymerization at the terminal carbon–carbon triple bond. The reaction took place in the dark, and is not the photoinitiated.

Since the insolubility prevented the processing of the poly-**3**, concomitant polymerization with film-formation was studied. Thus, a hexane solution of **3** was concentrated on an ITO-coated glass plate in vacuo. The black film formed was peeled off, FTIR spectra of which was essentially the same with the polymer powder. An Au-coated glass could also be used for the film synthesis. The conductivity of a film was 10^{-10} to 10^{-11} $\mathrm{S\,cm^{-1}}$, which was enhanced to 10^{-4} $\mathrm{S\,cm^{-1}}$ when doped with SO_3 (Fig. 1). I_2-doping was not effective. This is a novel synthesis of conductive polyacetylene at ambient temperature which does not employ catalyst or photoirradiation.[16)]

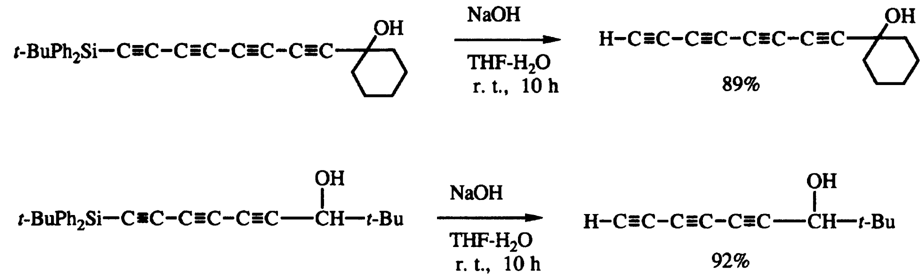
Reactive aryl halides were coupled with **3** in the presence of palladium catalysts under solid–liquid phase-transfer conditions (Scheme 7).[17)] Use of amine bases, even of extremely hindered 2,2,6,6-tetramethylpiperidine, promoted the decomposition of **3**.[18)]

Caryoynencins **13** are antibiotics isolated from liquid cultures of a plant pathogen *Pseudomonas caryophylli*, and show potent antibacterial activities.[1a)] They possess conjugated dientetrayne structure. As an application of the polyyne reactions, the first synthesis of **13** was conducted (Scheme 8). The strategies are as follows; i) addition of lithiated **3** to methyl (6*E*,8*E*)-10-oxo-6,8-decadienoate (**10**), ii) allylic rearrangement of the hydroxyl group, and iii) deprotection. The dienal **10** was synthesized from methyl 6-oxohexanoate[19)] and 4-lithio-1-methoxy-1,3-butadiene,[20)] and was reacted with lithiated **3** in THF at −78 to −40 °C (61% yield). The adduct **11** was rearranged with 45% HF giving **12** as a 2 : 1 mixture of (7*E*,9*E*)- and (7*E*,9*Z*)-isomers. Removal of the protecting groups in a mixture of 3 M NaOH (1 M=1 $\mathrm{mol\,dm^{-3}}$) and THF at 0 °C under phase-transfer conditions accomplished the first synthesis of **13**. The addition of Bu_4NBr considerably promoted the deprotection. The desilylation of **12** took place in 15 min at 0 °C, and the ester hydrolysis required about 14 h. UV and NMR spectra of the synthetic **13** coincided with the natural caryoynencins.[1a)] According to the literature,[1a)] **13** was reacted with diazomethane in ethyl acetate at 0 °C, and a pyrazole **14** was obtained. The 1,3-dipolar addition was quite sensitive to the solvent employed, and very low yield of **14** was formed in ether or methanol. While formation of *N*-methylpyrazole **15** was reported by Kakisawa,[1a)] we obtained N–H derivative **14**. The reason of this differences is unclear. IR and UV spectra of **14** agreed with those of **15**. ^{1}H NMR and ^{13}C NMR also coincided except for the peaks of N–Me. Studies on the synthesis and the biological activities of caryoynencins analogs are now under way.

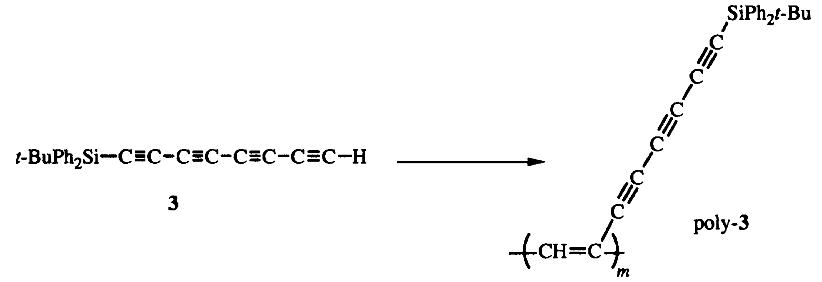
In summary, monosilylated polyynes **3** and **6** were prepared by selective monodesilylation of **2** and **5**. Reactions of **3** and **6**, including lithiation, Pd-coupling, and polymerization were studied. The first synthesis of caryoynencins **13** was achieved.

Experimental

Terminal polyyne compounds polymerize instantaneously by concentration, and were handled in solution throughout the purification procedures. Although disubstituted polyynes are relatively stable, most of them gradually decomposed. Therefore, satisfactory elemental analysis could not be obtained, and high-resolution MS (HRMS) data are



Scheme 5.



Scheme 6.

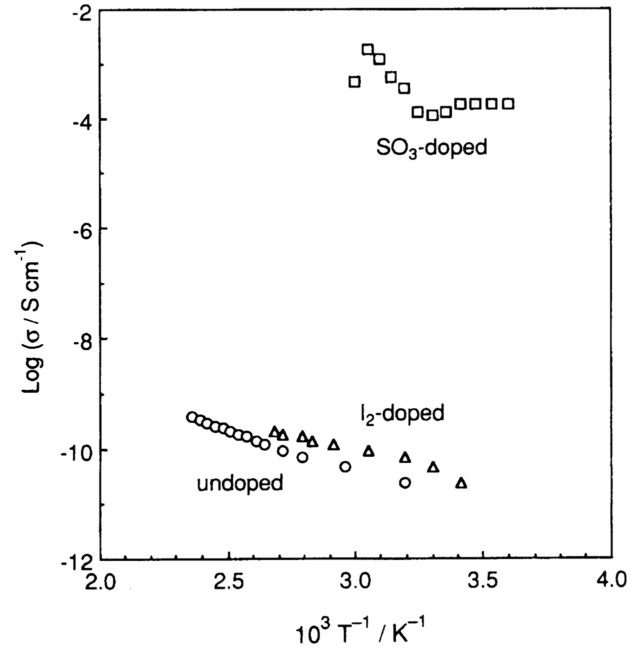
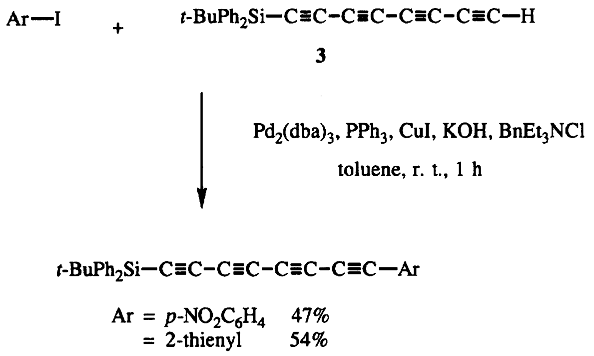


Fig. 1. Conductivities of undoped and doped poly-**3**.



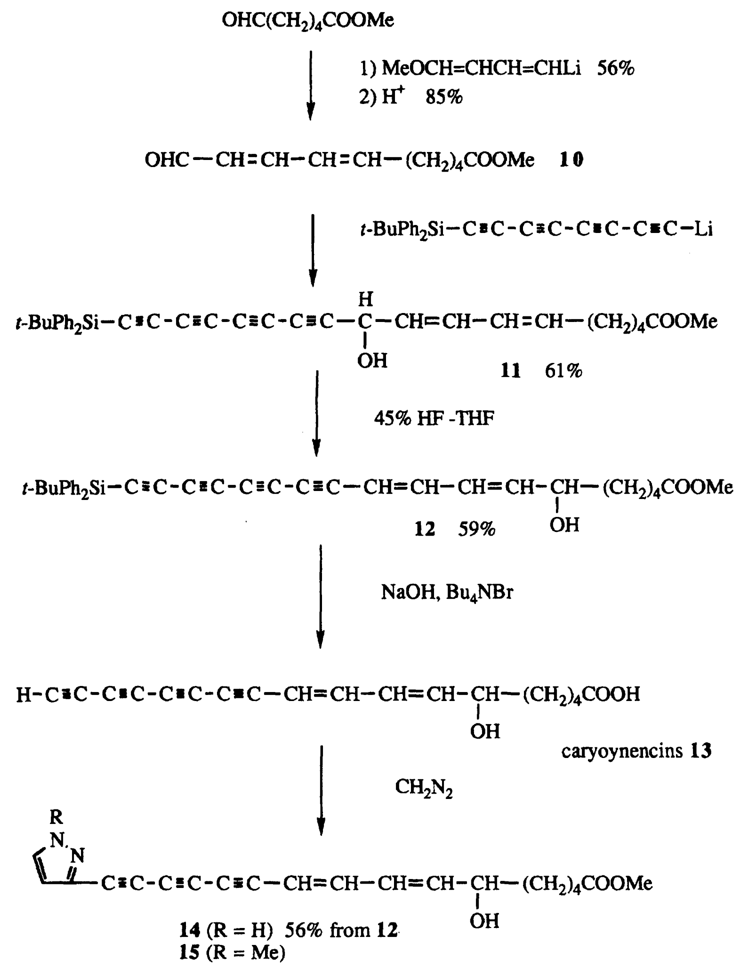
Scheme 7.

shown. ^{1}H NMR and ^{13}C NMR spectra were obtained on a JEOL JNM-FX-60 (60 MHz), Varian Gemini 200 (200 MHz), or Brucker AM-600 (600 MHz). Chemical shift values were given in ppm relative to internal Me_4Si or $CHCl_3$ (δ=7.24). IR spectra were recorded on a Shimadzu IR-408 or JASCO FT/IR-7000. MS spectra were taken with JEOL JMS-DX-300, HITACHI M-52, or JEOL HX-110. UV spectra were obtained on a Shimadzu UV-160A or JASCO Ubest-30. THF was distilled from sodium, and redistilled from benzophenone ketyl just prior to use. HMPA was distilled from CaH_2, and stored over molecular sieves 4 Å.

1-(*t*-Butyldiphenylsilyl)-1,3-butadiyne (1). Prepared from comercially available 1-methoxy-1-buten-3-yne and *t*-butyldiphenylsilyl chloride according to the method of Zweifel.[9] ^{1}H NMR (60 MHz, $CDCl_3$) δ=1.10 (9H, s), 2.17 (1H, s), 7.3—7.5 (6H, m), 7.7—7.9 (4H, m). IR (neat) 3260, 2220, 2060 cm^{-1}.

1,8-Bis(*t*-butyldiphenylsilyl)-1,3,5,7-octatetrayne (2). Hay catalyst[10] was prepared by mixing acetone (4 ml), TMEDA (0.1 mL), and CuCl (0.2 g) under a nitrogen atmosphere, and by stirring for 10 min. A part of the solution (2 mL) was added to an acetone (10 mL) solution of **1** (1.90 g, 6.6 mmol), and oxygen was bubbled for 1 h with vigorous stirring. 2 M (1 M=1 mol dm^{-3}) HCl was added and the organic materials were extracted twice with ether. The combined extracts were washed with water and brine, dried over Na_2SO_4, and concentrated. Tetrayne **2** (1.66 g, 88%) was isolated by silica-gel chromatography with hexane–benzene eluent. Mp 156—158 °C (hexane). ^{1}H NMR (200 MHz, $CDCl_3$) δ=1.12 (18H, s), 7.3—7.5 (12H, m), 7.6—7.8 (8H, m). IR (neat) 2050 cm^{-1}. ^{13}C NMR (50 MHz, $CDCl_3$) δ=19.9, 27.2, 62.8, 62.8, 84.4, 91.4, 128.1, 130.1, 131.9, 135.7. UV (hexane) λ_{max} (log ε) 264 (5.2), 251 (5.1), 240 (4.9) nm. HRMS. Found: m/z 574.2522. Calcd for $C_{40}H_{38}Si_2$: M, 574.2512.

1-(*t*-Butyldiphenylsilyl)-1,3,5,7-octatetrayne (3).



Scheme 8.

Under a nitrogen atmosphere, a THF–hexane solution (10 and 4.3 mL) of lithium phenylacetylide was prepared from phenylacetylene (780 mg, 7.7 mmol) and butyllithium (6.6 mmol) at −78 °C. HMPA (2 mL) and a THF (10 mL) solution of **2** (2.0 g, 3.5 mmol) were added, and the mixture was stirred at the temperature for 1 h. The reaction was quenched by adding water, and organic materials were extracted twice with ether. The combined extracts were washed with water and brine, and dried over Na_2SO_4. After most of the solvents were removed under a reduced pressure, the residue was flash chromatographed (hexane). Fractions containing **3** were collected and concentrated to a small volume. The volume of the solution was adjusted to 8 ml by adding THF, and the solution was stored at −30 °C over molecular sieves 4 Å. Yield of **3** (75%) was estimated by concentrating a part of the solution and weighing the polymer. ^{1}H NMR (200 MHz, $CDCl_3$–CCl_4) δ=2.18 (1H, s), 7.3—7.5 (6H, m), 7.7—7.8 (4H, m). UV (hexane) λ_{max} (relative intensity) 242 (1.0), 234 (0.83) nm. In the preliminary communication,[8] we described a wrong UV data for **3**. They should be replaced with the present data.

1-(*t*-Butyldiphenylsilyl)-8-trimethylsilyl-1,3,5,7-octatetrayne (4). This compound was obtained in 86% yield by carrying out the above reaction using *m*-methoxyphenylacetylene and quenching the reaction with trimethylsilyl chloride. ^{1}H NMR (200 MHz, $CDCl_3$) δ=0.30 (9H, s), 1.15 (9H, s), 7.3—7.5 (6H, m), 7.7—7.9 (4H, m). ^{13}C NMR (50 MHz, $CDCl_3$) δ=0.0, 19.6, 27.6, 62.6, 62.8, 63.1, 63.3, 84.3, 88.4, 88.9, 91.9, 128.5, 130.5, 132.3, 136.1.

Poly[1-(*t*-butyldiphenylsilyl)-1,3,5,7-octatetrayne] (poly-3). Concentration of a hexane solution (ca. 0.3 M) of **3** by a vaccum pump gave poly-**3** as black powder. Anal. Found: C; 83.53, H; 6.74%. Calcd for $C_{24}H_{20}Si$: C; 85.66, H; 5.99%. IR (KBr) 2154, 2090, 2067 cm^{-1}. A film of poly-**3** was synthesized as follows. A hexane solution (ca. 0.1 mL) of **1a** (ca. 0.3 M) was dropped on an ITO-coated glass plate (10×10 mm) and concentrated in a vessel (400 cm^3) using oil rotary vaccum pump at pumping speed 100 L min^{-1} with slight heating on a hot plate. The resulted black film of **2a** was removed from the plate. FTIR spectra was essentially the same with the polymer powder. Conductivity was measured by four-point probe method.

2,5-Bis(*t*-butyl)-4-[7-(*t*-butyldiphenylsilyl)-2,4,6-heptatriynylidene]-1,3-dioxolane (9): When an excess 2,2-dimethylpropanal was added to the THF–HMPA solution of lithiated **3** at −78 °C, **9** was obtained in 30% yield. ^{1}H NMR (60 MHz, $CDCl_3$) δ=1.00 (9H, s), 1.01 (9H, s), 1.09 (9H, s), 4.24 (1H, dd, J=1, 2 Hz), 4.67 (1H, d, J=2 Hz), 4.86 (1H, d, J=1 Hz), 7.2—7.5 (6H, m), 7.5—7.8 (4H, m). IR (neat) 2170, 2060, 1640 cm^{-1}. UV (hexane) λ_{max} (log ε) 355 (4.5), 331 (4.6), 311 (4.5), 293 (4.2), 270 (5.0), 254 (4.9) nm. HRMS. Found: m/z 508.2793. Calcd for $C_{34}H_{40}O_2Si$: M, 508.2796.

Bromo(*t*-butyldiphenylsilyl)acetylene. The compound was prepared from 1-(*t*-butyldiphenylsilyl)-2-(trimethylsilyl)acetylene in 79% yield employing the method of Zweifel.[12] ^{1}H NMR (200 MHz, CDCl$_3$) δ=1.09 (9H, s), 7.3—7.4 (6H, m), 7.7—7.8 (4H, m). ^{13}C NMR (50 MHz, CDCl$_3$) δ=18.7, 27.0, 65.3, 82.6, 127.8, 129.7, 132.6, 135.4. IR (neat) 2126 cm^{-1}.

1,9-Bis(*t*-butyldiphenylsilyl)-1,3,5-hexatriyne (5). Under a nitrogen atmosphere, a hexane solution (0.24 mL) of butyllithium (0.37 mmol) was added to a stirred THF (2 mL) solution of **1** (107 mg, 0.37 mmol) at −78 °C. After 15 min, the mixture was allowed to warm to 0 °C, and CuBr (53 mg, 0.37 mmol) was added. Stirring was continued for 30 min at r.t. The solvents were then removed under a reduced pressure, and the residue was suspended in pyridine (2 mL). Bromo(*t*-butyldiphenylsilyl)acetylene (128 mg, 0.37 mmol) was added, and the mixture was stirred at 50 °C for 1 h.[10] The reaction was quenched by adding ice cold 2 M HCl, and the organic materials were extracted twice with hexane. The combined extracts were washed with 2 M HCl, saturated aqueous NaHCO$_3$, and brine. After dried on Na$_2$SO$_4$, the solvents were removed under a reduced pressure. Flash chromatography on silica gel gave **5** (116 mg, 56%). ^{1}H NMR, IR, and ^{13}C NMR spectra coincided with the reported values.[7]

1-(*t*-Butyldiphenylsilyl)-1,3,5-hexatriyne (6). Desilylation of **5** was carried out as described in the synthesis of **3**. ^{1}H NMR (200 MHz, CDCl$_3$–CCl$_4$) δ=1.10 (9H, s), 2.14 (1H, s), 7.4—7.5 (6H, m), 7.7—7.8 (4H, m).

Addition Reaction of Lithiated 3 and 6 to Aldehydes and a Ketone: 11-(*t*-Butyldiphenylsilyl)-2,2-dimethyl-4,6,8,10-undecatetrayn-3-ol. Under a nitrogen atmosphere, a hexane solution (0.17 mL) of butyllithium (0.27 mmol) was added to a THF–hexane solution (5 mL and 0.5 mL) of **3** (0.8 mmol) at −78 °C. After 30 min at the temperature, a THF (1 mL) solution of 2,2-dimethylpropanal (15 mg, 0.18 mmol) was added. Stirring was continued for 1 h, and the reaction was quenched by adding water. The organic materials were extracted twice with ether, and the combined extracts were washed with water and brine, dried over Na$_2$SO$_4$, and concentrated. The adduct (60 mg, 80%) was obtained by silica-gel flash chromatography. ^{1}H NMR (60 MHz, CDCl$_3$) δ=1.01 (9H, s), 1.10 (9H, s), 1.8 (1H, brs), 4.09 (1H, s), 7.2—7.5 (6H, m), 7.5—7.9 (4H, m). ^{13}C NMR (15 MHz, CDCl$_3$) δ=19.1, 25.4, 27.1, 36.6, 62.0, 62.6 (overlapped), 63.6, 70.6, 71.9, 79.0, 84.0, 91.4, 128.0, 130.0, 131.8, 135.6. IR (neat) 3350, 2230, 2160, 2080 cm^{-1}. UV (hexane) $\lambda_{\max}$ (log ε) 253 (5.1), 241 (5.1) nm. HRMS. Found: m/z 422.2076. Calcd for $\mathrm{C_{29}H_{30}OSi}$: M, 422.2065.

13-(*t*-Butyldiphenylsilyl)-6,8,10,12-tridecatetrayn-5-ol. ^{1}H NMR (60 MHz, CDCl$_3$) δ=0.7—1.0 (3H, m), 1.10 (9H, s), 1.0—2.0 (7H, m), 4.2—4.4 (1H, m), 7.2—7.5 (6H, m), 7.5—7.8 (4H, m). ^{13}C NMR (15 MHz, CDCl$_3$) δ=14.0, 19.1, 22.4, 27.1, 37.2, 61.8, 62.6, 62.8, 63.0, 64.0, 69.8, 79.9, 84.0, 91.3, 128.0, 130.0, 131.8, 135.6. IR (neat) 3350, 2210, 2150, 2060 cm^{-1}. UV (hexane) $\lambda_{\max}$ (log ε) 252 (5.1), 240 (5.1) nm. HRMS. Found: w/z 365.1333 (M−*t*-Bu). Calcd for $\mathrm{C_{25}H_{21}OSi}$: M−*t*-Bu, 365.1360.

15-(*t*-Butyldiphenylsilyl)-8,10,12,14-pentadecatetrayn-7-ol. ^{1}H NMR (60 MHz, CDCl$_3$) δ=0.7—1.0 (3H, m), 1.10 (9H, s), 1.0—2.0 (10H, m), 2.1 (1H, brs), 4.42 (1H, t, J=6 Hz), 7.2—7.5 (6H, m), 7.5—7.9 (4H, m). ^{13}C NMR (15 MHz, CDCl$_3$) δ=14.2, 19.1, 22.6, 25.0, 27.1, 28.9, 31.7, 37.4, 61.8, 62.6, 62.8, 63.0, 63.3, 69.8, 79.8, 84.0, 91.3, 128.0, 130.0, 131.8, 135.6. IR (neat) 3350, 2220, 2160, 2070 cm^{-1}. UV (hexane) $\lambda_{\max}$ (log ε) 252 (5.1), 240 (5.1) nm. HRMS. Found: m/z 451.2477 (M+H). Calcd for $\mathrm{C_{31}H_{35}OSi}$: M+H, 451.2457.

15-(*t*-Butyldiphenylsilyl)-5-pentadecen-8,10,12,14-tetrayn-7-ol. ^{1}H NMR (60 MHz, CDCl$_3$) δ=0.91 (3H, t, J=7 Hz), 1.10 (9H, s), 1.0—1.8 (2H, m), 1.7—2.3 (3H, m), 4.88 (1H, d, J=5 Hz), 5.52 (1H, dd, J=5, 15 Hz), 5.91 (1H, dt, J=15, 6 Hz), 7.2—7.5 (6H, m), 7.5—7.9 (4H, m). ^{13}C NMR (15 MHz, CDCl$_3$) δ=13.8, 19.1, 22.0, 27.1, 34.1, 61.8, 62.6, 63.0, 63.4, 64.5, 70.7, 77.9, 84.2, 91.3, 127.4, 128.0, 130.0, 131.8, 135.6. IR (neat) 3350, 2220, 2150, 2070 cm^{-1}. UV (hexane) $\lambda_{\max}$ (log ε) 255 (5.2), 242 (5.2) nm. HRMS. Found: m/z 377.1370 (M−*t*-Bu). Calcd for $\mathrm{C_{26}H_{21}OSi}$: M−*t*-Bu, 377.1362.

9-(*t*-Butyldiphenylsilyl)-1-phenyl-2,4,6,8-nonatetrayn-1-ol. ^{1}H NMR (60 MHz, CDCl$_3$) δ=1.10 (9H, s), 2.40 (1H, brs), 5.49 (1H, s), 7.2—7.5 (11H, m), 7.5—7.9 (4H, m). ^{13}C NMR (15 MHz, CDCl$_3$) δ=19.9, 27.0, 61.6, 62.5, 63.1, 64.8, 65.0, 71.3, 77.8, 84.4, 91.3, 126.7, 128.0, 128.9, 130.0, 131.7, 135.5, 138.9. IR (neat) 3400, 2200, 2130, 2050 cm^{-1}. UV (hexane) $\lambda_{\max}$ (log ε) 256 (5.2), 244 (5.1) nm. HRMS. Found: m/z 385.1066 (M−*t*-Bu). Calcd for $\mathrm{C_{27}H_{17}OSi}$: M−*t*-Bu, 385.1049.

1-[8-(*t*-Butyldiphenylsilyl)-1,3,5,7-octatetraynyl]cyclohexanol. ^{1}H NMR (60 MHz, CDCl$_3$) δ=1.10 (9H, s), 1.2—2.3 (11H, m), 7.2—7.5 (6H, m), 7.5—7.9 (4H, m). ^{13}C NMR (15 MHz, CDCl$_3$) δ=19.1, 23.1, 25.0, 27.1, 39.6, 62.0, 62.6, 62.7, 63.8, 69.1, 69.3, 82.5, 83.8, 91.4, 127.9, 130.0, 131.8, 135.5. IR (neat) 3350, 2220, 2170, 2070 cm^{-1}. UV (hexane) $\lambda_{\max}$ (log ε) 254 (5.1), 242 (5.0), 231 (4.7) nm. HRMS. Found: m/z 377.1328 (M−*t*-Bu). Calcd for $\mathrm{C_{26}H_{21}OSi}$: M−*t*-Bu, 377.1361.

9-(*t*-Butyldiphenylsilyl)-2,2-dimethyl-4,6,8-nonatriyn-3-ol. ^{1}H NMR (60 MHz, CDCl$_3$) δ=1.01 (9H, s), 1.09 (9H, s), 1.95 (1H, d, J=7 Hz), 4.08 (1H, d, J=7 Hz), 7.2—7.5 (6H, m), 7.5—7.8 (4H, m). ^{13}C NMR (15 MHz, CDCl$_3$) δ=19.1, 25.4, 27.1, 36.6, 61.8, 63.7, 70.5, 71.8, 79.2, 83.3, 91.6, 128.0, 130.0, 132.1, 135.6. IR (neat) 3350, 2230, 2170, 2070 cm^{-1}. UV (hexane) $\lambda_{\max}$ (log ε) 226 (5.2) nm. HRMS. Found: m/z 398.2061. Calcd for $\mathrm{C_{27}H_{30}OSi}$: M, 398.2064.

13-(*t*-Butyldiphenylsilyl)-8,10,12-tridecatriyn-7-ol. ^{1}H NMR (60 MHz, CDCl$_3$) δ=0.7—1.0 (3H, m), 1.09 (9H, s), 1.0—2.0 (11H, m), 4.2—4.6 (1H, m), 7.2—7.5 (6H, m), 7.5—7.8 (4H, m). ^{13}C NMR (15 MHz, CDCl$_3$) δ=14.2, 19.0, 22.6, 25.1, 27.1, 28.9, 31.8, 37.5, 61.7, 63.0, 64.0, 69.8, 79.9, 83.4, 91.4, 127.9, 129.9, 132.0, 135.6. IR (neat) 3300, 2210, 2180, 2080 cm^{-1}. UV (hexane) $\lambda_{\max}$ (log ε) 253 (4.3), 226 (5.2) nm. HRMS. Found: m/z 369.1625 (M−*t*-Bu). Calcd for $\mathrm{C_{25}H_{25}OSi}$: M−*t*-Bu, 369.1674.

13-(*t*-Butyldiphenylsilyl)-5-tridecen-8,10,12-triyn-7-ol. ^{1}H NMR (60 MHz, CDCl$_3$) δ=0.7—1.0 (3H, m), 1.09 (9H, s), 1.0—1.7 (4H, m), 1.7—2.3 (2H, m), 2.6 (1H, brs), 4.86 (1H, d, J=5 Hz), 5.50 (1H, dd, J=5, 15 Hz), 5.91 (1H, dt, J=15, 5 Hz), 7.2—7.5 (6H, m), 7.5—7.8 (4H, m). ^{13}C NMR (15 MHz, CDCl$_3$) δ=13.7, 19.0, 22.0, 27.1, 34.1, 61.7, 63.3, 64.4, 70.6, 78.0, 83.7, 91.4, 127.6, 127.9, 129.9, 132.0, 135.2, 135.5. IR (neat) 3300, 2220, 2110 cm^{-1}. UV (hexane) $\lambda_{\max}$ (log ε) 255 (4.1), 228 (5.0) nm. HRMS.

Found: *m/z* 353.1346 (M − *t*-Bu). Calcd for $C_{24}H_{21}OSi$: M − *t*-Bu, 353.1360.

1-[6-(*t*-Butyldiphenylsilyl)-1,3,5-hexatriynyl]cyclohexanol. ^{1}H NMR (60 MHz, $CDCl_3$) δ=1.09 (9H, s), 1.0—2.0 (10H, m), 2.1 (1H, brs), 7.2—7.5 (6H, m), 7.5—7.8 (4H, m). ^{13}C NMR (15 MHz, $CDCl_3$) δ=19.0, 23.1, 25.0, 27.1, 39.7, 61.8, 64.0, 69.2, 69.4, 82.6, 83.3, 91.6, 127.9, 129.9, 132.0, 135.6. IR (neat) 3300, 2200, 2160, 2060 cm^{-1}. UV (hexane) λ_{max} (log ε) 301 (2.7), 277 (3.4), 254 (4.3), 228 (5.1) nm. HRMS. Found: *m/z* 353.1346 (M − *t*-Bu). Calcd for $C_{24}H_{21}OSi$: M − *t*-Bu, 353.1360.

Desilylation Reaction: 1-(1,3,5,7-Octatetraynyl)cyclohexanol. A mixture of 1-[8-(*t*-butyldiphenylsilyl)-1,3,5,7-octatetraynyl]cyclohexanol (42 mg, 0.10 mmol), 3 M NaOH aq (3 mL), and THF (3 mL) was stirred at r.t. for 3 h, and then diluted with water. The organic materials were extracted twice with ether, and the combined organic layers were washed with water and brine, dried over Na_2SO_4, and concentrated to a small volume. A solution of the pure product was obtained by silica-gel chromatography with ethyl acetate : hexane (1 : 5) eluent. ^{1}H NMR spectra was obtained by carefully exchanging the solvents to CCl_4 by repeating the concentration to a small volume and adding $CDCl_3$. ^{1}H NMR (60 MHz, $CDCl_3$–CCl_4) δ=1.0—2.0 (11H, m), 2.12 (1H, s). UV (hexane) λ_{max} (log ε) 236 (4.8), 224 (4.7) nm. Removal of the solvents gave insoluble polymer (17 mg, 90%).

2,2-Dimethyl-4,6,8-nonatriyn-3-ol. ^{1}H NMR (60 MHz, $CDCl_3$) δ=0.99 (9H, s), 1.79 (1H, d, *J*=6 Hz), 2.11 (1H, s), 4.05 (1H, d, *J*=6 Hz).

Reaction with Epoxides: 2-[8-(*t*-Butyldiphenylsilyl)-1,3,5,7-octatetraynyl]cyclohexanol. Under a nitrogen atmosphere, a hexane solution (0.11 mL) of butyllithium (0.17 mmol) was added to a THF–hexane (5 and 0.5 mL) solution of **3** (0.47 mmol) at −78 °C, and the resulted mixture was stirred for 30 min at the temperature. Then, $BF_3 \cdot OEt_2$ (24 mg, 0.17 mmol) was added, which was followed by a THF (1 mL) solution of cyclohexene oxide (11 mg, 0.11 mmol). After 1 h at the temperature, the reaction was quenched by adding water, and the organic materials were extracted twice with ether. The combined extracts were washed with water and brine, dried over Na_2SO_4, and concentrated. The residue was chromatographed on silica gel giving the product (31 mg, 64%). ^{1}H NMR (60 MHz, $CDCl_3$) δ=1.10 (9H, s), 1.0—2.6 (10H, m), 3.3—3.8 (1H, m), 7.2—7.5 (6H, m), 7.5—7.9 (4H, m). IR (neat) 3350, 2250, 2180, 2080 cm^{-1}. UV (hexane) λ_{max} (log ε) 254 (5.3), 242 (5.3), 231 (5.0) nm. HRMS. Found: *m/z* 434.2026. Calcd for $C_{30}H_{30}OSi$: M, 434.2065.

18-(*t*-Butyldiphenylsilyl)-11,13,15,17-octadecatetrayn-9-ol. ^{1}H NMR (60 MHz, $CDCl_3$) δ=0.7—1.0 (3H, m), 1.0—1.8 (14H, m), 1.10 (9H, s), 2.0 (1H, brs), 2.50 (2H, d, *J*=5 Hz), 3.7—4.0 (1H, m), 7.2—7.5 (6H, m), 7.5—7.9 (4H, m). IR (neat) 3350, 2250, 2170, 2080 cm^{-1}. UV (hexane) λ_{max} (log ε) 253 (5.1), 241 (5.0), 230 (4.8) nm. HRMS. Found: *m/z* 492.2881. Calcd for $C_{34}H_{40}OSi$: M, 492.2848.

2-[6-(*t*-Butyldiphenylsilyl)-1,3,5-hexatriynyl]cyclohexanol. ^{1}H NMR (60 MHz, $CDCl_3$) δ=1.09 (9H, s), 1.0—2.6 (10H, m), 3.3—3.8 (1H, m), 7.2—7.5 (6H, m), 7.5—7.8 (4H, m). IR (neat) 3350, 2220, 2180, 2110 cm^{-1}. UV (hexane) λ_{max} (log ε) 255 (3.9), 229 (5.1) nm. HRMS. Found: *m/z* 410.2083. Calcd for $C_{28}H_{30}OSi$: M, 410.2066.

16-(*t*-Butyldiphenylsilyl)-11,13,15-hexadecatriyn-9-ol. ^{1}H NMR (60 MHz, $CDCl_3$) δ=0.7—1.0 (3H, m), 1.09 (9H, s), 1.0—2.0 (15H, m), 2.50 (2H, d, *J*=5 Hz), 3.5—4.0 (1H, m), 7.2—7.5 (6H, m), 7.5—7.9 (4H, m). IR (neat) 3350, 2220, 2180, 2110 cm^{-1}. UV (hexane) λ_{max} (log ε) 253 (3.8), 227 (5.0) nm. HRMS. Found: *m/z* 468.2807. Calcd for $C_{32}H_{40}OSi$: M, 468.2847.

Reaction with Aryl Halides: 8-(*t*-Butyldiphenylsilyl)-1-(2-thienyl)-1,3,5,7-octatetrayne. Under a nitrogen atmosphere, a mixture of $Pd_2(dba)_3 \cdot CHCl_3$ (dba= dibenzylideneacetone) (18 mg, 0.02 mmol), PPh_3 (20 mg, 0.08 mmol), CuI (7.6 mg, 0.04 mmol), 2-thienyl iodide (21 mg, 0.1 mmol), **3** (0.12 mmol), $BnEt_3N^+Cl^-$ (19 mg, 0.1 mmol), and powdered KOH (225 mg, 5.6 mmol) in toluene (7 mL) was stirred at r.t. for 1 h. Water was added, and organic materials were extracted twice with ethyl acetate, and dried over Na_2SO_4. The residue was chromatographed on silica gel giving the product (24 mg, 54%). ^{1}H NMR (60 MHz, $CDCl_3$–CCl_4) δ=1.11 (9H, s), 6.96 (1H, dd, *J*=3, 5 Hz), 7.1—7.5 (8H, m), 7.5—7.8 (4H, m). IR (neat) 2180, 2120, 2060, 1430, 700 cm^{-1}. UV (EtOH) λ_{max} (log ε) 402 (3.6), 373 (3.8), 347 (3.7), 326 (3.6), 303 (4.4), 286 (4.2) nm. HRMS. Found: *m/z* 418.1230. Calcd for $C_{28}H_{22}SSi$: M, 418.1211.

8-(*t*-Butyldiphenylsilyl)-1-*p*-nitrophenyl-1,3,5,7-octatetrayne. ^{1}H NMR (60 MHz, $CDCl_3$–CCl_4) δ=1.11 (9H, s), 7.1—7.5 (6H, m), 7.5—7.9 (6H, m), 8.18 (2H, d, *J*=9 Hz). IR (neat) 2060, 1590, 1520, 1340 cm^{-1}. UV (EtOH) λ_{max} (log ε) 393 (3.8), 364 (3.9), 340 (3.9), 311 (4.1), 299 (4.2), 286 (4.1), 245 (4.4) nm. HRMS. Found: *m/z* 457.1492. Calcd for $C_{30}H_{23}NO_2Si$: M, 457.1497.

Synthesis of Caryoynencins 13. Methyl 10-Oxo-6,8-decadienoate (10). Under an argon atmosphere, a hexane solution (3.3 mL) of butyllithium (5.4 mmol) was added to 3-tributylstannyl-1-methoxy-1,3-butadiene (2.24 g, 6.0 mmol)[20] in THF (24 mL) at −78 °C. After stirring for 30 min, methyl 6-oxohexanoate (865 mg, 6.0 mmol)[19] in THF (12 mL) was added, and the mixture was stirred at −60 °C for 1.5 h. Water was added, and the organic materials were extracted twice with ethyl acetate, washed with brine, and dried over Na_2SO_4. Solvents were removed in vacuo, and the residue was chromatographed on silica gel giving an isomeric mixture of methyl 6-hydroxy-10-methoxy-7,9-decadienoate (689 mg, 56%). To a THF (36 mL) solution of the adduct (678 mg, 2.9 mmol) was added water (10 mL) and *d*-camphorsulfonic acid (2.40 g, 10.3 mmol), and the mixture was stirred for 20 min. Saturated aqueous $NaHCO_3$ was added, and organic materials were extracted twice with ethyl acetate. The combined extracts were washed with brine, dried over Na_2SO_4, concentrated, and flash chromatographed over silica gel giving **10** (494 mg, 85%). ^{1}H NMR (200 MHz, $CDCl_3$) δ=1.4—1.7 (4H, m), 2.23 (2H, t, *J*=7.0 Hz), 2.34 (2H, t, *J*=7.2 Hz), 3.68 (3H, s), 6.08 (1H, dd, *J*=8.0, 15.3 Hz), 6.2—6.4 (2H, m), 7.08 (1H, dd, *J*=9.7, 15.4 Hz), 9.53 (1H, d, *J*=7.0 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ=24.7, 28.3, 33.1, 34.1, 51.9, 129.3, 130.6, 146.6, 152.9, 174.2, 194.2. IR (neat) 1738, 1684, 1640 cm^{-1}. UV (hexane) λ_{max} (log ε) 273 (4.4). MS *m/z* (rel intensity) 196 (M, 12), 178 (M − H_2O, 4), 165 (M − CH_3O, 26), 146 (20), 136 (23), 122 (29), 104 (30), 81 (100). HRMS. Found: *m/z* 196.1080. Calcd for $C_{11}H_{16}O_3$: M, 196.1099.

Methyl 18-(*t*-Butyldiphenylsilyl)-10-hydroxy-6,8-octadecadien-11,13,15,17-tetraynoate (11). Under an argon atmosphere at −78 °C, butyllithium (1.27 mmol) in hexane (0.79 mL) was added to a hexane–THF (30 and 30 mL) solution of **3** prepared from **2** (1.39 g, 2.42 mmol). Ater stirring for 30 min at the temperature, **10** (248 mg, 1.26 mmol) in THF (6 mL) was added. The mixture was warmed to −40 °C for 30 min, and was stirred for 1.5 h at the temperature. The reaction was quenched by adding water, and organic meterials were extrated twice with ether, washed with brine, dried over Na_2SO_4. Solvents were removed in vacuo, and flash silica-gel chromatography gave **11** (411 mg, 61%). ^{1}H NMR (200 MHz, $CDCl_3$) $\delta=1.10$ (9H, s), 1.3—1.6 (2H, m), 1.6—1.8 (2H, m), 2.15 (2H, t, $J=7.2$ Hz), 2.32 (2H, t, $J=7.0$ Hz), 4.98 (1H, t, $J=5.4$ Hz), 5.63 (1H, dd, $J=6.0$, 15.0 Hz), 5.80 (1H, dt, $J=15.2$, 6.6 Hz), 6.05 (1H, dd, $J=10.2$, 15.0 Hz), 6.37 (1H, ddd, $J=15.0$, 10.0, 1.0 Hz), 7.4—7.5 (6H, m), 7.6—7.8 (4H, m). ^{13}C NMR (50 MHz, $CDCl_3$) $\delta=18.9$, 24.3, 26.9, 28.4, 32.2, 33.8, 51.5, 61.6, 62.4, 62.8, 62.9, 64.3, 70.6, 77.4, 84.0, 91.2, 127.2, 127.9, 128.9, 129.9, 131.7, 133.5, 135.4, 137.3, 174.1. IR (neat) 3430, 2144, 2062, 1740, 789, 700 cm^{-1}.

Methyl 18-(*t*-Butyldiphenylsilyl)-6-hydroxy-7,9-octadecadien-11,13,15,17-tetraynoate (12). A mixture of **11** (211 mg, 0.40 mmol), THF (2 mL), and 45% aqueous HF (5 mL) was stirred at room temperature for 5 h, and quenched by adding saturated aqueous $NaHCO_3$. Organic materials were extrated twice with ethyl acetate, washed with brine, and dried over Na_2SO_4. Solvents were removed in vacuo, and flash silica-gel chromatography gave **12** (103 mg, 49%) as a 2 : 1 mixture of (7*E*,9*E*)- and (7*E*,9*Z*)-isomers. ^{1}H NMR (600 MHz, $CDCl_3$) $\delta=1.100$ and 1.106 (9H, s), 1.34—1.51 (2H, m), 1.54—1.70 (4H, m), 2.33 (2H, t, $J=7.5$ Hz), 2.34 (2H, t, $J=7.4$ Hz), 3.66 and 3.68 (3H, s), 4.22 (0.6H, q, $J=5.9$ Hz, $H_6(EE)$), 4.28 (0.3H, q, $J=6.6$ Hz, $H_6(EZ)$), 5.49 (0.3H, d, $J=10.7$ Hz, $H_{10}(EZ)$), 5.64 (0.6H, d, $J=15.5$ Hz, $H_{10}(EE)$), 5.98 (0.6H, dd, $J=6.0$, 15.2 Hz, $H_7(EE)$), 6.01 (0.3H, dd, $J=6.5$, 15.1 Hz, $H_7(EZ)$), 6.32 (0.6H, ddq, $J=15.3$, 11.0, 0.6 Hz, $H_8(EE)$), 6.64 (0.3H, t, $J=10.7$ Hz, $H_9(EZ)$), 6.75 (0.3H, ddt, $J=15.1$, 11.2, 1.1 Hz, $H_8(EZ)$), 6.88 (0.6H, dd, $J=11.0$, 15.5 Hz, $H_9(EE)$), 7.36—7.43 (6H, m), 7.72—7.75 (4H, m). ^{13}C NMR (150 MHz, $CDCl_3$) $\delta=19.03$, 24.64 and 24.71, 24.79 and 24.84, 27.01, 33.85 and 33.90, 36.61 and 36.64, 51.53, 62.08 and 62.33, 62.68 and 62.78, 64.72 and 65.07, 68.06 and 68.78, 71.73 (C_6/EE), 71.92 (C_6/EZ), 74.50 and 80.38, 84.73 and 84.93, 91.41 and 91.45, 96.11, 106.68 (C_{10}/EZ), 108.67 (C_{10}/EZ), 127.08 (C_8/EZ), 127.92, 128.68 (C_{10}/EE), 129.92, 131.85, 135.54, 141.89 (C_7/EE), 142.74 (C_7/EZ), 146.17 (C_8/EZ), 147.06 (C_9/EE), 174.03 and 174.06. IR (neat) 3430, 2186, 2118, 2058, 1738, 986, 700 cm^{-1}. UV (MeOH) λ_{max} ($\log\varepsilon$) 397 (4.0), 369 (4.2), 344, (4.1) 322 (4.0), 305 (4.8), 289 (4.6), 276 (4.3), 261 (4.2), 241 (4.6), 231 (4.6) nm.

Caryoynencins 13. A mixture of **12** (80 mg, 0.15 mmol), Bu_4NBr (211 mg, 0.60 mmol), 3 M NaOH aq (13 mL), and THF (40 mL) was stirred at 0 °C. Desilylation was completed within 10 min as monitored by UV spectra of aliquot samples, and ester hydrolysis required about 14 h. Then, the reaction was quenched by adding 2 M HCl. Organic materials were extracted twice with ether, and the combined organic layers were washed with water and brine, dried over Na_2SO_4, and concentrated to a small volume. Silica-gel chromatography with ethyl acetate: methanol (20 : 1) eluent and concentration to a small volume gave a solution of **13**. The solution was divided into two equal volumes, and one of them was converted to ethyl acetate solution by repeated addition of ethyl acetate and evaporation. Excess diazomethane in ether was added at 0 °C, and the mixture was settled for 30 min. After removing excess diazomethane by bubbling nitrogen, the solvents were removed in vacuo. Silica-gel flash chromatography gave pyrazole **14** (15 mg, 59% from **12**). ^{1}H NMR (600 MHz, $CDCl_3$) $\delta=1.32$—1.52 (2H, m), 1.53—1.71 (4H, m), 2.31 (1H, t, $J=7.8$ Hz), 2.34 (1H, t, $J=7.8$ Hz), 3.67 (1H, s), 3.67 (2H, s), 4.23 (0.6H, q, $J=6.2$ Hz), 4.29 (0.3H, q, $J=6.6$ Hz), 5.50 (0.3H, d, $J=10.7$ Hz), 5.68 (0.6H, d, $J=15.5$ Hz), 5.93 (0.6H, dd, $J=15.2$, 6.2 Hz), 6.00 (0.3H, dd, $J=15.2$, 6.4 Hz), 6.33 (0.6H, dd, $J=15.2$, 11.0 Hz), 6.57 (1H, d, $J=2.2$ Hz), 6.61 (0.3H, t, $J=6.7$ Hz), 6.76 (0.3H, dd, $J=15.2$, 11.2 Hz), 6.82 (0.6H, dd, $J=15.4$, 11.1 Hz), 7.59 (1H, brs). ^{13}C NMR (150 MHz, $CDCl_3$) $\delta=24.6$, 24.7, 24.8, 24.9, 33.9, 33.9, 36.6, 36.6, 51.6, 51.6, 66.8, 67.2, 67.6, 67.7, 70.2, 70.7, 71.7, 71.9, 76.5, 76.8, 78.8, 80.2, 107.0, 109.1, 111.4, 111.4, 127.1, 128.8, 132.1, 141.4, 142.3, 145.2, 146.2, 174.2, 174.3. IR (neat) 3198, 2202, 2166, 1717, 986, 770 cm^{-1}. UV (MeOH) λ_{max} ($\log\varepsilon$) 365 (4.5), 354 (4.3), 344, (4.6) 331 (4.5), 321 (4.5), 311 (4.4), 292 (4.8), 276 (4.9) nm. ^{1}H NMR and ^{13}C NMR data agreed with the authentic data[1a)] except that the peaks of N–Me were missing. UV and IR spectra also coincided. The other solution of the purified **13** was used for characterization. ^{1}H NMR and ^{13}C NMR spectra were obtained by carefully exchanging the solvents to $CDCl_3$ by repeating the concentration to a small volume and adding $CDCl_3$. Trials to prepare CCl_4 solution gave polymer presumably because of the low solubility of **13** in CCl_4. ^{1}H NMR (600 MHz, $CDCl_3$) $\delta=1.38$—1.55 (2H, m), 1.55—1.63 (2H, m), 1.63—1.71 (2H, m), 2.22 (0.6H, s), 2.24 (0.3H, s), 2.37 (1H, t, $J=7.6$ Hz), 2.38 (1H, t, $J=7.5$ Hz), 4.22 (0.6H, q, $J=6.3$ Hz), 4.28 (0.3H, q, $J=5.9$ Hz), 5.47 (0.3H, d, $J=10.6$ Hz), 5.62 (0.6H, d, $J=15.5$ Hz), 5.93 (0.6H, dd, $J=15.2$, 6.2 Hz), 6.01 (0.3H, dd, $J=15.2$, 6.4 Hz), 6.31 (0.6H, dd, $J=15.3$, 11.0 Hz), 6.64 (0.3H, t, $J=10.7$ Hz), 6.74 (0.3H, ddt, $J=15.2$, 11.2, 1.0 Hz), 6.83 (0.6H, dd, $J=15.5$, 10.9 Hz). ^{13}C NMR (150 MHz, $CDCl_3$) $\delta=24.4$, 24.5, 24.7, 24.8, 33.5, 33.5, 36.6, 61.0, 61.0, 61.1, 61.2, 64.2, 64.6, 67.8, 68.4, 68.5, 68.6, 68.6, 68.8, 71.7, 71.9, 74.0, 76.3, 77.8, 80.2, 106.7, 108.6, 127.1, 128.7, 141.8, 142.7, 146.2, 147.1, 178.0. UV (MeOH) λ_{max} 384, 357, 334, 313, 295, 281 nm. MS (API) m/z 279 (M−H). CD_3OD solution of **13** was prepared by subjecting the crude extracts to silica-gel thin-layer chromatography (ethyl acetate as the develping solvent) followed by elution with CD_3OD. ^{1}H NMR and UV spectra of the synthetic **13** in CD_3OD agreed with the authentic data.[1a)]

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