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Synthesis of naturally occurring diene and trienes by Te/Li exchange on (1*Z*,3*Z*)-butyltelluro-4-methoxy-1,3-butadiene

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ABSTRACT

(1*Z*,3*Z*)-Butyltelluro-4-methoxy-1,3-butadiene **2** was obtained by the hydrotelluration of (*Z*)-1-methoxy-but-1-en-3-ynes **1**. The butadienyllithium **3** obtained by the Te/Li exchange reaction in the (1*Z*,3*Z*)-1-butyltelluro-4-methoxy-1,3-butadiene **2** reacted with aldehydes to form the corresponding alcohols **4a–d** with total retention of configuration. The alcohols formed undergo hydrolysis, resulting in the $\alpha,\beta,\gamma,\delta$-unsaturated aldehydes of (*E*,*E*) configuration, which are precursors of trienes obtained from natural sources. The products of this reaction were employed in the synthesis of methyl-(2*E*,4*E*)-decadienoate **7**, which is a component of the flavor principles of ripe Bartlett pears. Performing the Wittig reaction of the methyl triphenylphosphorane with the deca-(2*E*,4*E*)-dienal **5a**, we were able to synthesize the undeca-(1,3*E*,5*E*)-triene **6a**. This compound is a sex-pheromone component of the marine brown algae *Fucus serratus*, *Dictyopteris plagiograma*, and *Dictyopteris australis*. Performing the Wittig reaction of methyl triphenylphosphorane with the octa-(2*E*,4*E*)-dienal **5c**, the nona-(1,3*E*,5*E*)-triene **6b** was synthesized. The compound obtained is a sex-pheromone component of the marine brown alga *Sargassum horneri*. The octa-(*1*,3*E*,5*E*)-triene **6c** was easily obtained from hepta-(2*E*,4*E*)-dienal **5d** by the Wittig reaction with methyl triphenylphophorane. This compound is a sex-pheromone component of the marine brown alga *Fucus serratus*.

Conjugated polyene system construction has received considerable attention by chemists, since it constitutes a fundamental structural feature of many insect pheromones,[1] components of the female sex attractant and alarm system[1b] of seaweeds, and other biologically active compounds.[1c]

Undeca-(1,3*E*,5*E*)-triene **6a** is a sex-pheromone component of the marine brown algae *Fucus serratus*, *Dictyopteris plagiograma*, and *Dictyopteris australis*[2] and is present in the essential oil of galbanum (*Ferula gabaniflua*).[3]

The analogous nona-(1,3*E*,5*E*)-triene **6b** is a sex-pheromone component of the marine brown alga *Sargassum horneri*, and octa-(*1*,3*E*,5*E*)-triene **6c** is a sex-pheromone component of the marine brown alga *Fucus serratus*.[4] Methyl-(2*E*,4*E*)-decadienoate **7** is a component of the flavor principles of ripe Bartlett pears (Fig. 1).[1c,5,21]

The essential synthetic problem has been to prepare the functionalized diene system in a highly stereoselective manner, and a wide variety of synthetic approaches has been used.[1c,6–21]

Vinyl tellurium compounds can be used in the preparation of diene and triene systems. We and other investigators have developed procedures for the preparation of (1*Z*,3*Z*)-butyltelluro-l,3-butadienes that could be used as building-blocks in the synthesis of these systems.[22–25,32,33]

Here, we report our results on the application of a highly functionalized (1*Z*,3*Z*)-1-butyltelluro-4-methoxy-1,3-butadiene[22] **2** bearing a butyltelluro moiety at the 1-position of the butadienylic system as an intermediate in the synthesis of **6a**, **6b**, **6c**, and **7** (Scheme 1).

The stereospecific hydrotelluration of methoxy-1-buten-3-yne **1** with sodium butyltellurolate anion, which was obtained in situ using dibutyl ditelluride and sodium borohydride in ethanol under nitrogen and reflux, produces the corresponding (1*Z*,3*Z*)-1-butyltelluro-4-methoxy-1,3-butadiene **2** (Eq. 1).[22]

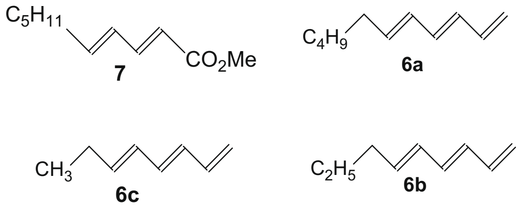

Figure 1.

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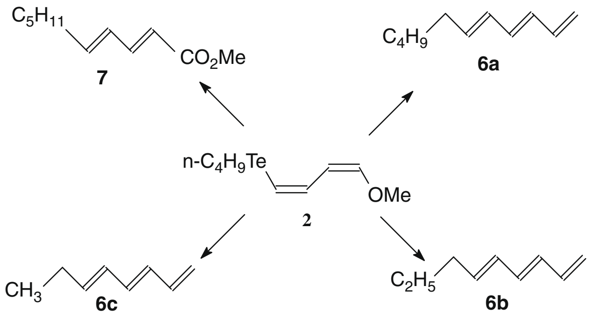
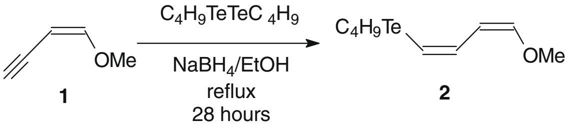


Scheme 1.

Stereochemical assignments of the double bonds bearing the tellurium moiety were made on the basis of chemical shifts and coupling constants, since the *J*-values of a wide range of (*E*)-and (*Z*)-vinylic tellurides are known.[24b]



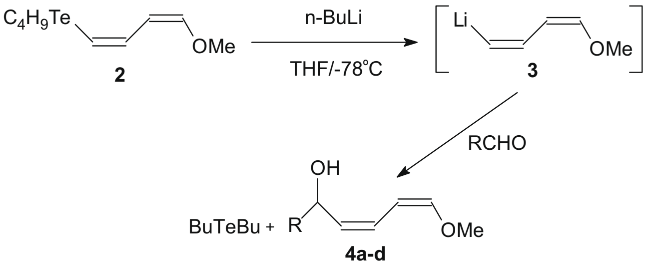
(1)

The ^{1}H NMR spectrum of (1*Z*,3*Z*)-1-butyltelluro-4-methoxy-1,3-butadiene **2** showed the coupling constants $J_{1,2}$ = 10.5 Hz and $J_{2,3}$ = 10.4 Hz of olefinic protons of a tellurium double bond that resonate at 6.91 ppm (2-H) and 6.45 ppm (1-H), while olefinic protons of oxygen bearing a double bond resonate at 5.92 ppm (4-H) and 4.96 ppm (3-H) with the coupling constants $J_{3,2}$ = 10.4 Hz, and $J_{3,4}$ = 6.6 Hz. These data clearly indicate the *Z*,*Z* configuration of compound **2**. No other isomers were detected by either GC/MS or ^{13}C NMR, which showed only four olefinic signals (101.1, 108.1, 131.6, and 148.8).

The Te/Li exchange reaction on compound **2** with 2.0 equiv of butyllithium in THF at −78 °C resulted in formation of the corresponding (1*Z*,3*Z*)-butadienyllithium **3**[34], which by sequential reaction with aldehydes afforded the corresponding alcohols **4a**–**d** (Scheme 2).

Treatment of compound **3** with hexanaldehyde afforded the corresponding alcohol (1*Z*,3*Z*)-1-methoxy-5-hydroxy-5-pentyl-1,3-pentadiene **4a** at a 70% yield, and treatment with pentanaldehyde afforded the alcohol (1*Z*,3*Z*)-1-methoxy-5-hydroxy-5-butyl-1,3-pentadiene **4b** at a 75% yield.[35]

However, compound (1*Z*,3*Z*)-1-methoxy-5-hydroxy-5-propyl-1,3-pentadiene **4c** obtained from treatment of **3** with butanaldehyde and (1*Z*,3*Z*)-1-methoxy-5-hydroxy-5-ethyl-1,3-pentadiene **4d** obtained from treatment of **3** with propanaldehyde were spontaneously and quantitatively transformed after some time (~24 h) into the octa-(2*E*,4*E*)-dienal **5c**, with an isomeric purity of 100%, and into the hepta-(2*E*,4*E*)-dienal **5d,** also with an isomeric purity of 100%, as confirmed by the analytical methods employed (^{1}H NMR, ^{13}C NMR, CG/MS, IR, and elemental analysis).[37a,b]



a: R = C_5H_{11}, **b**: R = C_4H_9, **c**: R = C_3H_7, **d**: R = C_2H_5

Scheme 2.

The conversions of **4a** to deca-(2*E*,4*E*)-dienal **5a** and of **4b** to nona-(2*E*,4*E*)-dienal **5b** were performed with H_2SO_4 (25% aqueous sol), SiO_2 and dichloromethane as solvent at 92% and 93% yield, respectively.[36a,b]

Scheme 3 illustrates the proposed mechanism for the formation of the unsaturated aldehydes **5a**–**b** of *E*,*E* configuration, from their derived alcohols **4a**–**b** of *Z*,*Z* configuration, containing the methoxyl grouping.

In the first stage of this proposed mechanism, the hydroxyl group of substrate **4** is protonated forming structure **8**. At this point, Scheme 3 divides, because the mechanism is likely to follow two different paths. On path a, a water molecule can simultaneously attack the carbon to which the methoxyl grouping is attached (structure **8**) followed by transposition of the double bond and elimination of the water molecule, resulting in structure **13**, which is in equilibrium with structure **14**. In structure **14**, the displacement of a pair of electrons from oxygen leads to the aldehyde carbonyl, and consequently the expulsion of the methoxyl grouping, in the form of methanol **16**, results in structure **15**. Subsequently, structure **15** by the loss of a proton, gives the aldehyde α,β,γ,δ-unsaturated **5** of *E*,*E* configuration. Another alternative is represented in path b of Scheme 3. Structure **8**, which has the protonated hydroxyl, can lose a molecule of water, forming a carbocation, which is illustrated by structure **9**. In this intermediate **9**, the double bond is transposed, with formation of another carbocation **10**. In intermediate **10**, the double bond will be rapidly transposed, forming the more stable carbocation located in the carbon bearing the methoxyl grouping, resulting in structure **11**, which is in resonance with structure **12**. Then, the carbocation in **11** is attacked by the electron pair of the oxygen of a water molecule, becoming structure **13**. As previously mentioned, structure **13** is in equilibrium with structure **14**. The pair of electrons of the oxygen in intermediate **14** is displaced, forming the carbonyl, with subsequent expulsion of methanol **16**, supplying structure **15**. The loss of a proton in **15** provides α,β,γ,δ-unsaturated aldehydes **5** of configuration *E*,*E*.

The analysis of coupling constants in ^{1}H NMR spectra[36] clearly confirms the inversion of configuration of the acid hydrolysis of alcohols **4a**–**b**, which validates our proposed mechanism.

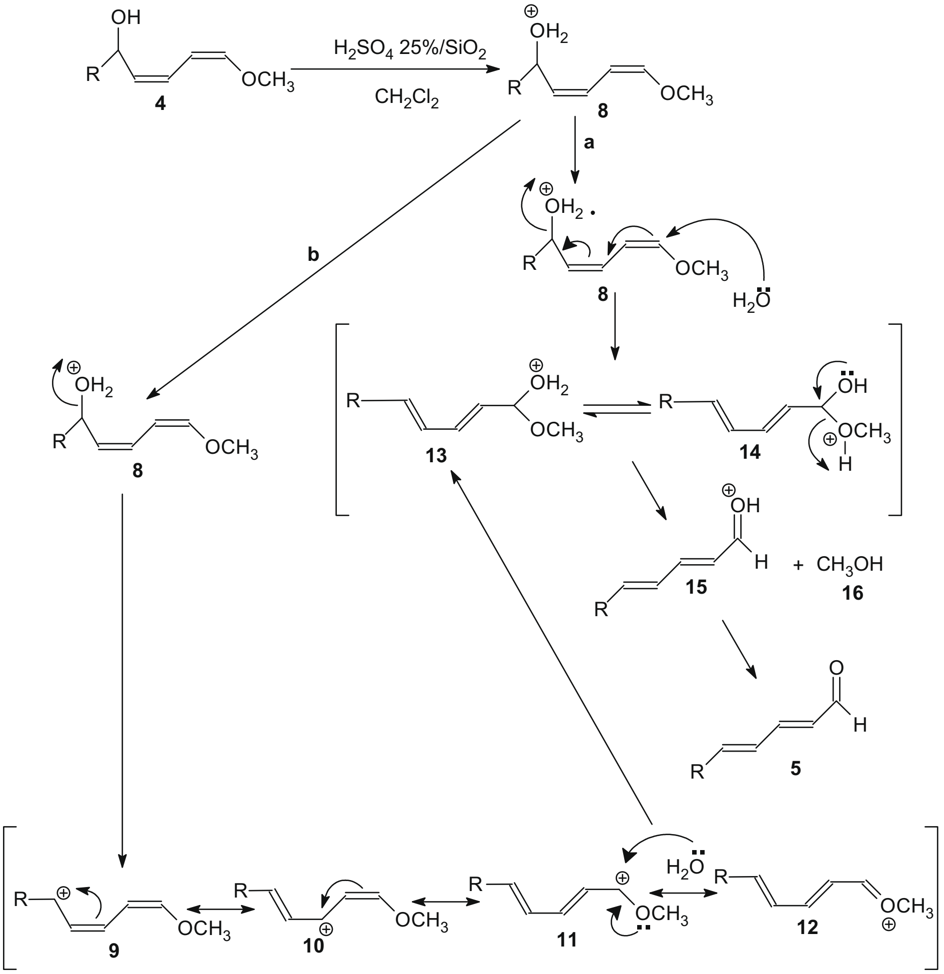
It is noteworthy that pentadienals are important building-blocks in the synthesis of a range of polyunsaturated natural products.[20,26–31]

The product deca-(2*E*,4*E*)-dienal **5a** was employed in the synthesis of the methyl-(2*E*,4*E*)-decadienoate **7**. Treatment of compound **5a** with MnO_2, NaCN, and MeOH afforded the corresponding ester **7** in 100% isomeric purity, as confirmed by the analytical methods employed (^{1}H NMR, ^{13}C NMR, CG/MS, IR, and elemental analysis),[38] at 88% yield after purification in a chromatography column using a mixture of petroleum ether and CH_2Cl_2 (3:1) as eluents (Scheme 4).

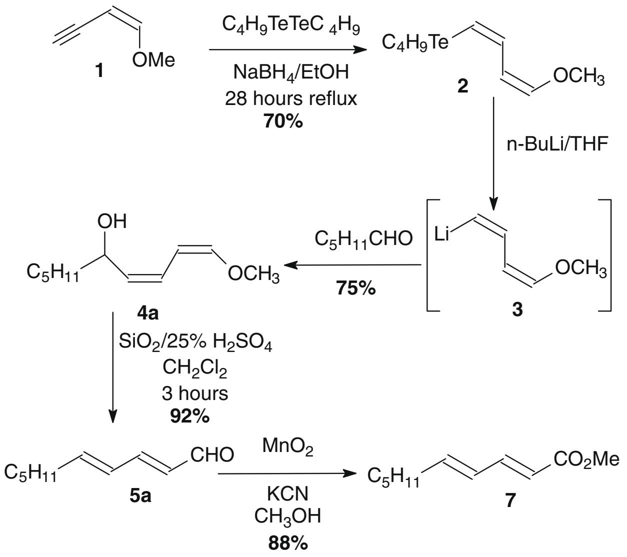
This product was synthesized in four stages from methoxy-1-buten-3-yne 1, which is a product available commercially at low cost. All the stages involved in the synthetic strategy that we employed occurred with yields of 70% or higher.

Among the advantages of this synthetic route that we developed are: fewer stages, high yields, and total stereo chemical control of the double bonds formed, in all stages of the process.

Performing the Wittig reaction of methyl triphenylphosphorane[39] with the deca-(2*E*,4*E*)-dienal **5a**, using *n*-BuLi as the base, we synthesized the undeca-(3*E*,5*E*)-triene **6a**[40] at 90% yield after purification in a chromatography column using pentane as eluent. This compound **6a** is a sex-pheromone component of the marine brown algae *Fucus serratus*,[21] *Dictyopteris plagiograma*,[2,21] and *Dictyopteris australis*.[2,21]



Scheme 3.



Scheme 4.

The nona-(1,3*E*,5*E*)-triene **6b**[41] purified in a chromatography column using pentane as eluent was easily obtained at 90% yield from octa-(2*E*,4*E*)-dienal **5c**, by the Wittig reaction with methyl triphenylphosphorane.[39] The obtained compound **6b** is a sex-pheromone component of the marine brown alga *Sargassum horneri*.[4]

Performing the Wittig reaction of methyl triphenylphosphorane[39] with the hepta-(2*E*,4*E*)-dienal **5d**, the octa-(1,3*E*,5*E*)-triene **6c**[42] was synthesized at 88% yield after purification in a chromatography column using pentane as eluent. This compound **6c** is a sex-pheromone component of the marine brown alga *Fucus serratus*.[2]

In conclusion, we describe the application of (1*Z*,3*Z*)-1-butyltelluro-4-methoxy-1,3-butadiene **2** as intermediary in the synthesis of natural products **7**, **6a**, **6b**, and **6c**. For this, we employed the Te/Li exchange reaction in this compound **2**, which occurred with total retention of configuration. Another important feature was the systematic obtaining of (*E*,*E*)-pentadienals by hydrolysis of butadienyl alcohols **4** of (*Z*,*Z*) configuration using H_2SO_4 adsorbed in silica and CH_2Cl_2 as solvent of the reaction, and the natural compounds were obtained by classical reactions including the Wittig reaction and oxidation of dienal **5a** to ester **7** using MnO_2/NaCN/CH_3OH.[21,38–42]

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32. *Experimental section:* General remarks. ^{1}H and ^{13}C NMR spectra were recorded on a 300 MHz or a 400 MHz spectrometer as noted. GC/MS (using a HP-1 fused silica capillary column) and direct insertion spectra (EI) were measured at 70 eV. Elemental analyses were performed at the Instrumental Analysis Center of the Chemistry Department, Chemistry Institute of the University of São Paulo. Reaction flasks and syringes were oven-dried (120 °C) before use. Melting points (uncorrected) were determined on a Kofler hot plate. All reactions were carried out under an atmosphere of dry nitrogen and monitored by TLC using prepared plates (Silica Gel 60 F254 on aluminum). The chromatograms were observed by the use of UV or the developing agent ethanolic vanillin. Merck silica gel (230–400 mesh) was used for flash chromatography. THF was distilled over sodium/benzophenone immediately before use. Dibutyl ditelluride was prepared by the method reported in the literature.[43]
33. *Typical procedure for (1Z,3Z)-1-butyltelluro-4-methoxy-1,3-butadiene* **2**.[22] To a solution of 1-methoxy-but-1-en-3-yne **1** (sol 50% water/methanol 1:4; 0.640 g, 1.0 ml, 8.0 mmol) and dibutyl ditelluride (0.738 g, 2.0 mmol) in ethanol (80 ml) at room temperature under nitrogen, sodium borohydride (0.22 g, 6.0 mmol) was added. After the end of the addition, the yellow mixture was heated at reflux for 28 h. Then it was cooled to room temperatue, diluted with ethyl acetate (60 ml), and washed with NH_4Cl saturated solution (3 × 25 ml). After the organic phase was dried over anhydrous $MgSO_4$, the solvent was removed under reduced pressure and the residue purified by flash chromatography on silica gel with hexane/ethyl acetate (9:1) as the mobile phase. After evaporation of hexane, compound **2**, which is very stable, was obtained as a yellow–orange oil. Yield: 0.7574 g (70%). MS *m/z* 270 (56.05) $C_9H_{16}OTe$, 213 (40.18) ($-C_4H_9$), 84 (100.00) ($-C_4H_9Te$); ^{1}H NMR (300 MHz) (δ in $CDCl_3$) 0.91 (3H, t, J = 7 Hz, 4-H_3), 1.48 (2H, sext, J = 7 Hz, 3-H_2), 1.78 (2H, quint, J = 7 Hz, 2-H_2), 2.64 (2H, t, J = 7 Hz, 1-H_2), 3.64 (3H, s), 4.96 (1H, ddd, $J_{3,4}$ = 10.4 Hz, $J_{2,3}$ = 6.6 Hz, $J_{1,3}$ ~0.7 Hz, 3-H), 5.92 (1H, dq, $J_{3,4}$ = 6.6 Hz, J ~1.0 Hz, J ~0.7 Hz, 4-H), 6.45 (1H, ddd, $J_{1,2}$ = 10.5 Hz, $J_{1,3}$ ~1.0, $J_{1,4}$ ~0.7 Hz, 1-H), 6.91 (1H, dd, $J_{1,2}$ = 10.5 Hz, $J_{2,3}$ = 10.4 Hz, 2-H). ^{13}C NMR 6.4, 13.4, 24.9, 34.1, 60.1, 101.1, 108.1, 131.6, 148.8. Anal. Calcd for $C_9H_{16}OTe$: C, 40.36; H, 6.02. Found: C, 40.73; H, 5.99.
34. *Te/Li exchange reaction on (1Z,3Z)-1-butyltelluro-4-methoxy-1,3-butadiene* **2**.[22] To a solution of **2** (0.267 g, 1.0 mmol) in THF (8.0 ml), cooled to −78 °C under N_2, BuLi (0.76 ml, 1.1 mmol, 1.43 M) was added in one portion. The reaction mixture was stirred at this temperature and after 1.0 min, the butadienyl lithium **3** formed can be used in situ. The observations of the reactions of this intermediate (total disappearance of **9** followed by TLC and formation of only one product) indicated that it is formed in high yield.
35. *Typical procedure for (1Z,3Z)-1-methoxy-5-hydroxy-butyl-1,3-pentadiene* **4b**. To a solution of butadienyl lithium **10** formed as above, freshly distilled pentanaldehyde (0.101 ml; 1.0 mmol) was added at −78 °C and stirred for 30 min at this temperature, then allowed to reach room temperature and stirred for an additional 30 min. The solution was treated with a saturated solution of NH_4Cl, diluted with ether (30 ml) and washed with saturated NH_4Cl solution (3 × 15 ml). After the organic phase was dried over anhydrous $MgSO_4$, the solvent was removed under reduced pressure, resulting in a pale-yellow liquid. Yield: 0.10 g (75% yield). Compound **4b** can be further purified by flash chromatography using a mixture of ethyl acetate/hexane (8:2) as eluent. However, prolonged contact with SiO_2 must be avoided since it causes hydrolysis of **4b** to form compound **5b**. MS *m/z* 170 (16.14), 128 (6.89), 113 (100.00) $[M-C_4H_9]^+$, 85 (36.26), 55 (19.23), 45 (30.67); ν_{max} 3383, 2931–2857, 1649, 1606, 1456, 1420, 1263, 1108, 1018, 929, and 753 cm^{-1}; ^{1}H NMR (300 MHz) (δ in $CDCl_3$) 0.85 (3H, t, J = 7.5 Hz, 9-H_3), 1.30 (2H, sext, J = 7 Hz, 8-H_2), 1.45 (2H, quint, J = 7 Hz, 7-H_2), 1.54 (2H, quart, J = 7 Hz, 6-H_2), 2.30 (1H, br s, OH), 3.60 (3H, s, OCH_3), 4.05 (1H, dt, $J_{5,6}$ = 7, $J_{5,4}$ = 7 Hz, 7-H_2), 4.45 (1H, dd, $J_{4,5}$ = 1.4, $J_{3,4}$ = 10 Hz, 4-H), 5.25 (1H, m), 5.95 (1H, d, $J_{1,2}$ = 6.9 Hz, 1-H), 6.35

(1H, t, $J = 11.5$ Hz, 2-H); ^{13}C NMR (75 MHz, δ in CDCl$_3$): 13.78, 22.41, 27.40, 36.88, 59.80, 67.53, 101.73, 121.84, 130.70, 148.23.

36. *(a) Typical procedure for nona-(2E,4E)-dienal* **5b.** To a solution of (1*Z*,3*Z*)-1-methoxy-5-hydroxy-5-butyl-1,3-pentadiene **4b** (0.1702 g, 1.0 mmol) in CH_2Cl_2 (10 ml) was added SiO_2 (2.0 g) at room temperature under atmospheric pressure. After 5 min, 25% H_2SO_4 (2.0 ml) was added dropwise. The reaction medium was agitated for 3 h and then washed with NH_4Cl saturated solution (3 × 25 ml). The organic phase was dried over anhydrous $MgSO_4$, the solvent removed under reduced pressure, and the residue purified by flash chromatography on silica gel with hexane: ethyl acetate (8:2) as the mobile phase. After evaporation of hexane, the compound **5b** was obtained as a yellow–orange oil. Yield: 0.1286 g (93%).ν_{max} 2963–2850, 1687, 1660, 1643, 1626, 1585, 1462, 1416, 1366, 1261, 1095, 1006, 973, and 801 cm^{-1}; δ (300 MHz) 0.99 (3H, t, $J = 7.5$ Hz, 8-H$_3$), 2.11 (2H, dq, $J_{6,7} = 7.5$, $J_{7.8} = 7.5$ Hz, 7-H$_2$), 5.02 (1H, dd, $J_{1,1} = 1.4$, $J_{1,2} = 10$ Hz, $\acute{1}$-H), 5.15 (1H, dd, $J_{1,1} = 1.4$, $J_{1.2} = 16.5$ Hz, 1-H), 5.75 (1H, dt, $J_{6,7} = 7.5$, $J_{5,6} = 15$ Hz, 6-H), 6.0–6.2 (3H, m, 3-H, 4-H and 5-H), 6.33 (1H, ddd, $J_{1,2} = 10$, $J_{2,3} = 10$, $J_{1,2} = 16{,}5$ Hz, 2-H; λ_{max} (hexane) 252, 262, 272 nm; *(b) deca-(2E,4E)-dienal* **5a.** The procedure described above for the preparation of nona-(2*E*,4*E*)-dienal **5b** was repeated using (1*Z*,3*Z*)-1-methoxy-5-hydroxy-5-pentyl-1,3-pentadiene **4a** (0.1843 g; 1.0 mmol) and gave compound **5a** as a yellow–orange oil. Yield: 0.1401 g (92%). ν_{max} 2958, 2929, 2857, 1613, 1514, 1467, 1454, 1163, 1112, 1013, and 988 cm^{-1}; ^{1}H NMR (300 MHz) (δ in CDCl$_3$) 0.87 (3H, t, $J = 7$ Hz, 10-H$_3$), 1.16–1.59 (6 H, m, 7-H$_2$, 8-H$_2$ and 9-H$_2$), 2.19 (2H, dt, $J_{5,6} = 7$, $J_{6,7} = 7$ Hz, 6-H$_2$), 6.05 (1H, $J_{1,2} = 8$, $J_{2,3} = 15$ Hz, 2-H), 6.25–6.30 (2H, m, 4-H and 5-H), 7.06 (1H, dd, $J_{3,4} = 10$, $J_{2,3} = 15$ Hz, 3-H), 9.51 (1H, d, $J = 8$ Hz, 1-H); *m*/*z* 170 (M+NH$_4$, 100%), 153 (M+H, 12); R_f (pentene–dichloromethane 1:1) 0.48, UV active.

37. (a) *Octa-(2E,4E)-dienal* **5c**. ν_{max} 2965–2874, 1640, 1619, 1462, 1439, 1322, 1217, 974, 943 and 903 cm^{-1}; ^{1}H NMR (300 MHz) (δ in CDCl$_3$) 1.01 (3H, t, $J = 7.5$ Hz, 8-H$_3$), 2.11 (2H, dq, $J_{6,7}$ 7.5, $J_{7.8}$ 7.5 Hz, 7-H2), 5.02 (1H, dd, $J_{1,1}$ 1.4, $J_{1,2}$ 10 Hz, $\acute{1}$-H), 5.15 (1H, dd, $J_{1,1}$ 1.4, $J_{1.2}$ 16.5 Hz, 1-H), 5.75 (1H, dt, $J_{6,7}$ 7.5, $J_{5,6}$ 15 Hz, 6-H), 6.0–6.2 (3H, m, 3-H, 4-H and 5-H), 6.33 (1H, ddd, $J_{1,2}$ 10 Hz, $J_{2,3}$ 10 Hz, $J_{1,2}$ 16.5 Hz, 2-H; λ_{max} (hexane) 252, 262, 272 nm. (b) *Hepta-(2E,4E)-dienal* **5d**. GC/MS *m*/*z* 236 (M$^+$), 110, 95, 82, 81 (100%), 67, 53, 39; ν_{max} 2965–2874, 1640, 1619, 1462, 1439, 1322, 1217, 974, 943, and 903 cm^{-1}; ^{1}H NMR (300 MHz) (δ in CDCl$_3$) 1.01 (3H, t, $J = 7.5$ Hz, 8-H$_3$), 2.14 (2H, ddq, $J_{5,7} = 1.5$, $J_{6.7} = 6.5$, $J_{7,8} = 7.5$ Hz, 7-H$_2$), 5.09 (1H, br d, $J = 10.5$ Hz, $\acute{1}$-H), 5.18 (1H, dd, $J_{1,\acute{1}} = 1.9$, $J_{1,2} = 16.7$ Hz, 1-H), 5.77 (1H, dt, $J_{6,7} = 6.5$, $J_{5,6} = 15$ Hz, 6-H), 5.87 and 5.96 (each 1H, dd, J 10.5 and 10.5 Hz, 3-H and 4-H), 6.48 (1H, ddt, $J_{5,7} = 1.5$, $J_{4,5} = 10.5$, $J_{5,6} = 15$ Hz, 5-H) 6.79 (1H, overlapping ddd, $J_{\acute{1},2} = 10.5$, $J_{1,2} = 16.7$ Hz, 2-H); ^{13}C NMR (75 MHz, δ in CDCl$_3$): 13.14, 25.89, 117.06, 124.53, 127.75.64, 130.24, 132.18, 138.11; λ_{max} (hexane) 252, 262, 272 nm.

38. *Typical procedure for methyl-(2E,4E)-decadienoate* **7**.[5,21] To a stirred solution of aldehyde **5a** (76 mg, 0.5 mmol) and methanol (10 ml) manganese dioxide (795 mg, 10 mmol) was added, and then sodium cyanide (100 mg, 2 mmol) followed by glacial acetic acid (0.03 ml). The resulting suspension was stirred at room temperature for 3 h, filtered, and the filtrate evaporated. The residue was redissolved in water (10 ml) and extracted with ether (3 × 10 ml). The combined organic extracts were washed with water (2 × 10 ml), brine (10 ml), dried, and evaporated. Flash chromatography of the residue (elution with petroleum–dichloromethane 3:1) gave the title compound **7** (78 mg, 86%) as a pale-yellow oil. ν_{max} 2955, 2929, 2858, 1721, 1645, 1617, 1435, 1312, 1265, 1246, 1202, 1175, 1142, 1000, 914, and 876 cm^{-1}; ^{1}H NMR (300 MHz) (δ in CDCl$_3$) 0.87 (3H, t, $J = 7$ Hz, 10-H$_3$), 1.21–1.45 (6 H, m, 7-H$_2$, 8-H$_2$ and 9-H$_2$), 2.13 (2H, dt, $J_{5,6} = 7$, $J_{6,7} = 7$ Hz, 6-H$_2$), 3.72 (3H, s, CO$_2$Me), 5.76 (1H, d, $J = 15.5$ Hz, 2-H), 6.10–6.15 (2H, m, 4-H and 5-H), 7.24 (1H, dd, $J_{3,4} = 10$ Hz, $J_{2,3} = 15.5$ Hz, 3-H); ^{13}C NMR (75 MHz, δ in CDCl$_3$): 13.97, 22.44, 28.33, 31.34, 32.93, 51.42, 118.59, 128.24, 145.03, 145.41, 167.76, 188.56; GC/MS *m*/*z* 200 (M+NH$_4$, 100%), 183 (M+H, 25).

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40. *Typical procedure for undeca-(1,3E,5E)-triene* **6a.**[2,3,21] To stirred methylene triphenylphosphorane [prepared from methyltriphenylphosphonium bromide (357 mg, 1.0 mmol) and *n*-butyllithium (2.5 M in hexane, 0.4 ml, 1.0 mmol) in THF (3 ml) at 0 °C] under N$_2$ the aldehyde **5a** (76 mg, 0.5 mmol) was added in THF (1 ml). After 1 h the solution was allowed to warm to room temperature, and after a further 1 h water (5 ml) was added and the mixture extracted with pentane (3 × 5 ml). The combined organic solution was washed with water (3 × 5 ml), brine (10 ml), dried, and the solvent removed at atmospheric pressure. The residue was applied to a plug of silica, eluted with pentane, and the eluate carefully distilled off at atmospheric pressure to obtain the title compound **6a** (68 mg, 90%) as a volatile colorless liquid; ν_{max} 3021, 2958, 2921, 2857, 1642, 1627, 1585, 1467, 1005, 909, and 735 cm^{-1}; ^{1}H NMR (300 MHz) (δ in CDCl$_3$) 0.87 (3H, t, $J = 7$ Hz, 11-H$_3$), 1.19–1.42 (6 H, m, 8-H$_2$, 9-H$_2$, 10-H$_2$), 2.07 (2H, dt, $J_{6,7} = 7$, $J_{7,8} = 7$ Hz, 7-H$_2$), 5.02 (1H, dd, $J_{1,\acute{1}} = 1.4$, $J_{\acute{1},2} = 10$ Hz, $\acute{1}$-H), 5.15 (1H, dd, $J_{1,\acute{1}} = 1.4$, $J_{1.2} = 16.7$ Hz, 1-H), 5.71 (1H, dt, $J_{6,7} = 7$, $J_{5,6} = 14.5$ Hz, 6-H), 6.00–6.24 (3H, m, 3-H, 4-H and 5-H), 6.34 (1H, ddd, $J_{\acute{1},2} = 10$ Hz, $J_{2,3} = 10$ Hz, $J_{1,2} = 16.7$ Hz, 2-H).

41. *Typical procedure for nona (1,3E,5E)- triene* **6b.** To stirred methylene triphenylphosphorane [prepared from methyltriphenylphosphonium bromide (357 mg, 1.0 mmol) and *n*-butyllithium (2.5 M in hexane, 0.4 ml, 1.0 mmol) in THF (3 ml) at 0 °C] under N$_2$ the aldehyde **5c** (55 mg, 0.5 mmol) was added in THF (1 ml). After 1 h the solution was allowed to warm to room temperature, and after a further 1 h water (5 ml) was added and the mixture extracted with pentane (3 × 5 ml). The combined organic solution was washed with water (3 × 5 ml), brine (10 ml), dried, and the solvent removed at atmospheric pressure. The residue was applied to a plug of silica, eluted with pentane, and the eluate carefully distilled off at atmospheric pressure to obtain the title compound **6b** (48 mg, 88%) as a volatile colorless liquid; ν_{max} 2963–2850, 1687, 1660, 1643, 1626, 1585, 1462, 1416, 1366, 1261, 1095, 1006, 973, and 801 cm^{-1}; δ (300 MHz) 0.99 (3H, t, J 7.5 Hz, 8-H$_3$), 2.11 (2H, dq, $J_{6,7}$ 7.5 Hz, $J_{7.8}$ 7.5 Hz, 7-H2), 5.02 (1H, dd, $J_{1,1}$ 1.4 Hz, $J_{1,2}$ 10 Hz, 1-H), 5.15 (1H, dd, $J_{1,1}$ 1.4 Hz, $J_{1.2}$ 16.5 Hz, 1-H), 5.75 (1H, dt, $J_{6,7}$ 7.5 Hz, $J_{5,6}$ 15 Hz, 6-H), 6.0–6.2 (3H, m, 3-H, 4-H and 5-H), 6.33 (1H, ddd, $J_{1,2}$ 10 Hz, $J_{2,3}$ 10 Hz, $J_{1,2}$ 16.5 Hz, 2-H; λ_{max} (hexane) 252, 262, 272 nm.

42. *Typical procedure for octa-(1,3E,5E)-triene* **6c.**[21] To stirred methylene triphenylphosphorane [prepared from methyltriphenylphosphonium bromide (357 mg, 1.0 mmol) and *n*-butyllithium (2.5 M in hexane, 0.4 ml, 1.0 mmol) in THF (3 ml) at 0 °C] under N$_2$ the aldehyde **5d** (55 mg, 0.5 mmol) was added in THF (1 ml). After 1 h the solution was allowed to warm to room temperature, and after a further 1 h water (5 ml) was added and the mixture extracted with pentane (3 × 5 ml). The combined organic solution was washed with water (3 × 5 ml), brine (10 ml), dried, and the solvent removed at atmospheric pressure. The residue was applied to a plug of silica, eluted with pentane, and the eluate carefully distilled off at atmospheric pressure to obtain the title compound **6c** (48 mg, 88%) as a volatile colorless liquid; ν_{max} 2963–2850, 1687, 1660, 1643, 1626, 1585, 1462, 1416, 1366, 1261, 1095, 1006, 973, and 801 cm^{-1}; ^{1}H NMR (300 MHz) (δ in CDCl$_3$) 0.99 (3H, t, $J = 7.5$ Hz, 8-H$_3$), 2.11 (2H, dq, $J_{6,7} = 7.5$, $J_{7.8} = 7.5$ Hz, 7-H$_2$), 5.02 (1H, dd, $J_{1,\acute{1}} = 1.4$, $J_{\acute{1},2} = 10$ Hz, $\acute{1}$-H), 5.15 (1H, dd, $J_{1,\acute{1}} = 1.4$, $J_{1.2} = 16.5$ Hz, 1-H), 5.75 (1H, dt, $J_{6,7} = 7.5$ Hz, $= J_{5,6} = 15$ Hz, 6-H), 6.0–6.2 (3H, m, 3-H, 4-H and 5-H), 6.33 (1H, ddd, $J_{\acute{1},2} = 10$, $J_{2,3} = 10$, $J_{1,2} = 16.5$ Hz, 2-H); ^{13}C NMR (75 MHz, δ in CDCl$_3$): 14.13, 25.65, 127.75, 129.83, 148.64, 153.61, 193.91; GC/MS *m*/*z* 108 (M$^+$), 110, 95, 77 (100%), 51; λ_{max} (hexane) 252, 262, 272 nm.

43. Cava, M. P.; Engman, L. *Synth. Commun.* **1982**, *12*, 163.