Pergamon

Tetrahedron 55 (1999) 4353–4368

TETRAHEDRON

Stereoselective Approaches to (*E,E,E*) and (*Z,E,E*)-α-Chloro-ω-Substituted Hexatrienes: Synthesis of *all E* Polyenes

Benoit Crousse,[a] Margarita Mladenova,[b] Pascal Ducept,[a] Mouâd Alami*#[a] and Gérard Linstrumelle[a]

a: Département de Chimie associé au CNRS, Ecole Normale Supérieure, 24 rue Lhomond 75231 Paris Cedex 05, France

b: Institute of Organic Chemistry, Bulgarian Academy of Sciences, BG-1113 Sofia, Bulgaria

Received 29 October 1998; accepted 4 February 1999

Abstract: Two stereocontrolled synthetic approaches to (*E,E,E*) and (*Z,E,E*)-α-chloro-ω-substituted hexatrienes **1-3** are described starting from unsaturated compounds **4-6**. The key step of the first approach is based on the palladium-catalyzed rearrangement of *bis*-allylic acetates **4** and **5** and the second one is based on the stereoselective reduction of homopropargylic alcohols **6** followed by an elimination reaction. These stable chlorotrienes **1-3** are suitable synthetic intermediates for the construction of navenone B and *all E* polyenes (trienes, tetraenes, hexaenes and heptaenes).

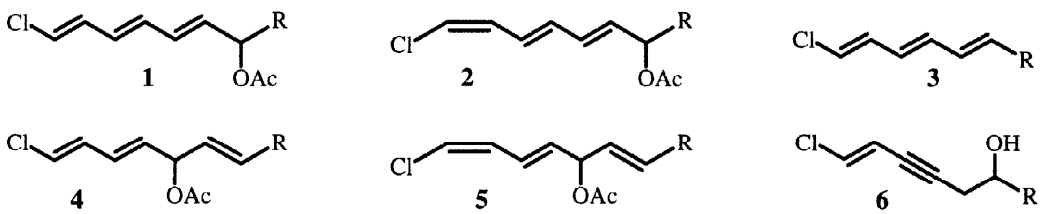
Stereodefined halogenopolyenes are an important class of compounds extensively used in organic synthesis mainly for the formation of C-C bonds via transition metal catalyzed coupling reactions.[1] Many methods are now available for the stereocontrolled preparation of halogenodienes from acetylenic precursors[2] or carbonyl compounds.[3] In contrast, few routes for the synthesis of halogenotrienes (mostly bromides) have been developed and most of them display low stereoselectivity. Typically, they were prepared by stereoselective hydrogenolysis of conjugated 1,1-dibromo-1-alkenes,[4] substitution of (*E*)-metalloalkenes with halogen-groups[5] or by haloalkenylation of aldehydes using Wittig type reagents.[6] This last procedure was recently used in efficient syntheses of *all E*-polyene compounds.[6g,6h]

Motivated by our interest in the synthesis of stereodefined polyenes based on a stereospecific coupling reaction of unsaturated vinyl chlorides with alkynes via palladium catalysis,[7] we required a versatile and stereoselective route to functionalized chlorotrienes **1-3**. The use of these compounds would be of interest since they are non photosensitive and should be more stable than the corresponding bromides[4] or iodides. Furthermore, preliminary results[8] have showed that vinyl chlorides, which are generally considered to be poor

* Fax: (+33) 1 01 30 75 60 21

0040-4020/99/$ - see front matter
PII: S0040-4020(99)00123-4

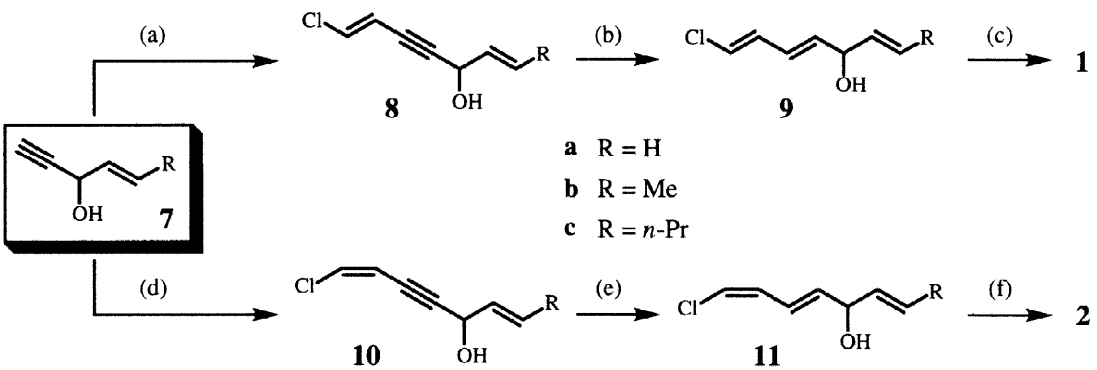
reactants, undergo rapid coupling with organometallic reagents under appropriate conditions allowing access to highly unsaturated compounds. We wish to detail herein our results, previously reported,[9] towards the stereocontrolled synthesis of functionalized (*E,E,E*) and (*Z,E,E*)-ω-substituted chlorotrienes **1-3** suitable for the rapid construction of conjugated *all E*-polyenes compounds. Two different synthetic approaches were devised. The first one, which leads to functionalized chlorotrienes **1** and **2**, is based on palladium mediated rearrangement of *bis*-allylic acetates **4** and **5** and the second one, is based on the stereoselective reduction of homopropargylic alcohols **6** into (*E*)-homoallylic alcohols followed by an elimination reaction.



RESULTS AND DISCUSSION

Synthesis of chlorotrienes from *bis*-allylic acetates 4 and 5

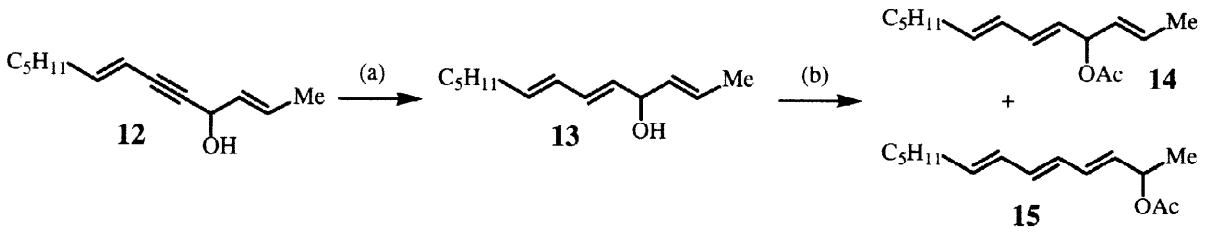
The required chloroenynes **8** were readily obtained by coupling of (*E*)-1,2-dichloroethylene with the enynols **7** in ether in the presence of $PdCl_2(PPh_3)_2$-CuI as catalyst and piperidine[10] (Scheme 1). The stereoselective reduction of the propargylic alcohols **8** by means of sodium bis-(2-methoxyethoxy) aluminium hydride (Red-Al®) led to the corresponding pure (*E,E,E*)-ω-chlorotrienols **9** in good yields (80-93%, Scheme 1). Further reaction of **9** with Ac_2O in Et_3N-CH_2Cl_2 followed by rearrangement of the corresponding acetoxy derivatives **4** under palladium catalysis[11] afforded in good overall yields the desired pure (*E,E,E*)-ω-chloroacetates **1a-c**.



Scheme 1: **(a)** (*E*)-ClCH=CHCl (3 eq.), piperidine (2 eq.), 1% $PdCl_2(PPh_3)_2$, 10% CuI, Et_2O (**8a**: 77%, **8b**: 84%, **8c**: 81%); **(b)** Red-Al, THF, -30° to 20°C (**9a**: 93%, **9b**: 90%, **9c**: 97%); **(c)** (*i*) Ac_2O, Et_3N, CH_2Cl_2; (*ii*) 5% $PdCl_2(MeCN)_2$, THF, 20°C (**1a**: 95%, **1b**: 52%, **1c**: 84%); **(d)** (*Z*)-ClCH=CHCl (2 eq.), $BuNH_2$ (2 eq.), 1% $Pd(PPh_3)_4$, 10%, CuI, Et_2O (**10a**: 82%, **10b**: 80%, **10c**: 76%); **(e)** Red-Al, THF, -30° to 20°C (**11a**: 80%, **11b**: 90%, **11c**: 91%); **(f)** (*i*) Ac_2O, Et_3N, CH_2Cl_2; (*ii*) 5% $PdCl_2(MeCN)_2$, THF, 20°C (**2a**: 96%, **2b**: 91%, **2c**: 93%).

Under the same strategy, stereodefined (*Z,E,E*)-ω-chloroacetates **2a-c** were also readily prepared in good yields starting from (*Z*)-1,2-dichloroethylene[10] instead of the (*E*)-isomer (Scheme 1).

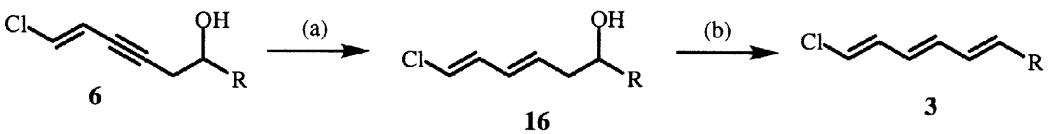
It may be pointed out that in the rearrangement step, the presence of a chlorine atom in **9** and **11** has a significant influence on the formation of the conjugated triene compounds **1** and **2**. Thus, when treating **13** bearing an alkyl group instead of chlorine atom, with Ac_2O in CH_2Cl_2-Et_3N followed by $PdCl_2(MeCN)_2$ (5%) a mixture of acetates **14** and **15** were obtained in a 75:25 ratio (Scheme 2).



Scheme 2: (a) Red-Al, THF, -30° to 20°C (78%); (b) (*i*) Ac_2O, Et_3N, CH_2Cl_2; (*ii*) 5% $PdCl_2(MeCN)_2$, THF, 20°C (48%).

Synthesis of chlorotrienes from ω-chloro-homopropargylic alcohols 6

We were also interested in developing a stereoselective approach to α-chloro-ω-arylhexatrienes which could be suitable intermediates for the construction of *all E* α,ω-diaryl polyenes.[12] Our synthetic approach to chlorotrienes **3** starts from readily available chloroenynes[10] **6**. Thus stereoselective reduction of the homopropargylic alcohol function[13] in **6a-c** using Red-Al® produced exclusively the (*E,E*)-chlorodienes**16a-c** in good yields (62-93%, Table I). Further reaction of **16a-c** with MsCl in CH_2Cl_2 followed by treatment of the corresponding mesylates with DBU afforded in good yields the (*E,E,E*)-chlorotrienes **3a-c** containing less than 3% of the (*E,E,Z*)-isomers. The pure *all-E* α-chloro-ω-arylhexatrienes **3a-c** were easily obtained by recrystallisation.



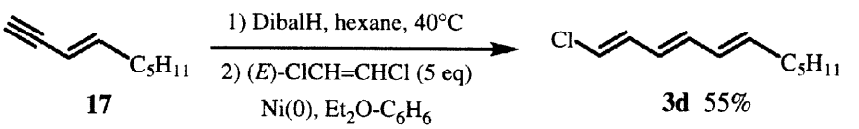
Scheme 3: (a) Red-Al (1.3 equiv), Et_2O, -20° to 36°C, 2 to 5h; (b) (*i*) MsCl (1.2 equiv), Et_3N (1.5 equiv), CH_2Cl_2, 0° to rt; (*ii*) DBU (1.5 equiv), CH_2Cl_2, 0° to rt.

Table I: Synthesis of Various Homoallylic Alcohols **16** and Chlorotrienes **3**.

Entry	R	Isolated Yield of **16** (%)	Isolated Yield of **3** (%)	Product
1	C_6H_5	79	74	**a**
2	*p*-*i*-Pr-C_6H_4	93	61	**b**
3	*p*-MeO-C_6H_4	62	72	**c**
4	C_5H_{11}	82	45	**d**
5	H	90	-[a]	**e**

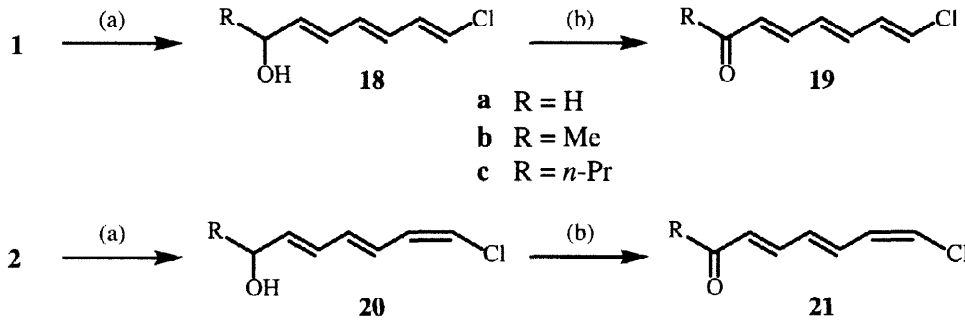
a/ The chlorotriene **3e** could not be detected by NMR in the crude reaction mixture.[14]

In a similar way, α-chloro-ω-alkylhexatriene **3d** was obtained from **6d** in a moderate overall yield (37%, entry 4, Table I). It should be noted that **3d** may also be prepared from terminal enyne **17** *via* hydroalumination followed by selective nickel-catalyzed cross coupling reaction with (*E*)-1,2-dichloroethylene.[10b,15]



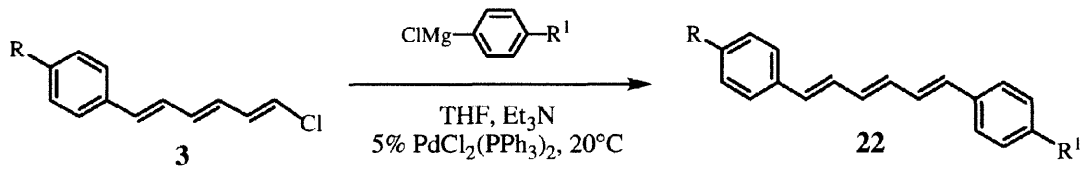
Having established easily procedures for the synthesis of stereodefined chlorotrienes **1-3**, we investigated the synthetic utility of these compounds as intermediates in organic synthesis particularly their elaboration *via* further reactions into stereodefined polyenes compounds.

ω-Chloroacetates **1** and **2** previously prepared were used for the synthesis of ω-chlorotrienals and ω-chlorotrienones (Scheme 4). Thus, the acetoxy group can smoothly and quantitatively be removed by treatment with K_2CO_3 in dry methanol yielding the corresponding chloroalcohols **18** and **20** which, without purification, upon oxidation with manganese oxide[16] afforded in good overall yields stereochemically pure (*E,E,E*) and (*Z,E,E*)-ω-chlorotrienals and ω-chlorotrienones **19** and **21**. Such unsaturated compounds, owing to the presence of two reactive terminal functions, have recently attracted attention as useful building blocks for the synthesis of polyenes.[6d-h]



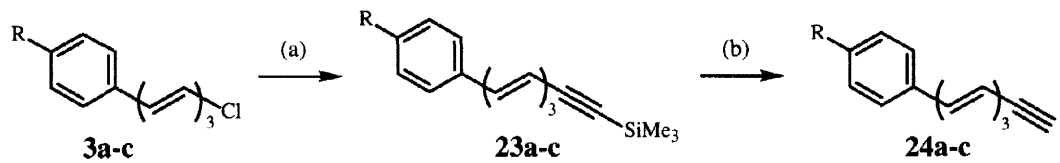
Scheme 4: (**a**) K_2CO_3, MeOH; (**b**) MnO_2, CH_2Cl_2, 20°C (**19a**: 79%, **19b**: 67%, **19c**: 53%, **21a**: 95%, **21b**: 73%, **21c**: 51%).

The chlorine atom is not inert to further coupling reactions. Thus, chlorotrienes **3** were subjected to coupling with aryl Grignard reagents in the presence of $PdCl_2(PPh_3)_2$ in Et_3N-THF,[17] thus providing an efficient route to isomerically pure (*E,E,E*)-diaryl hexatrienes **22** in good yield.



R = H	R^1 = OMe	78%
R = OMe	R^1 = H	82%

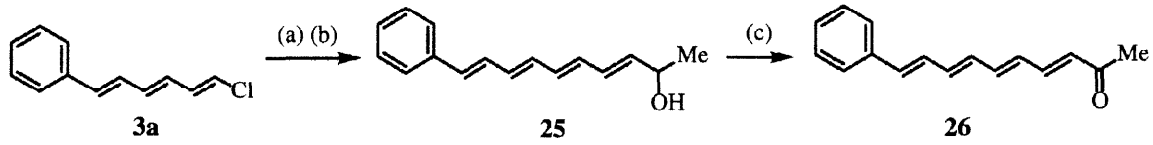
In a similar way, chlorotrienes **3a-c** were also subjected to palladium-copper coupling with trimethylsilyl acetylene[8] followed by desilylation using K_2CO_3 in MeOH providing an efficient access to pure terminal (*E,E,E*)-trienyne **24** in good overall yields (Scheme 5).



a R = H **b** R = *i*-Pr **c** R = OMe

Scheme 5: (**a**) $Me_3SiC{\equiv}CH$ (1.2 equiv), $PdCl_2(PhCN)_2$ 5%, CuI 10%, piperidine (R = H: 91%, R = *i*-Pr: 93%, R = OMe: 72%); (**b**) K_2CO_3, MeOH, 0° to 20°C, 1h (R = H: 90%, R = *i*-Pr: 98%, R = OMe: 94%).

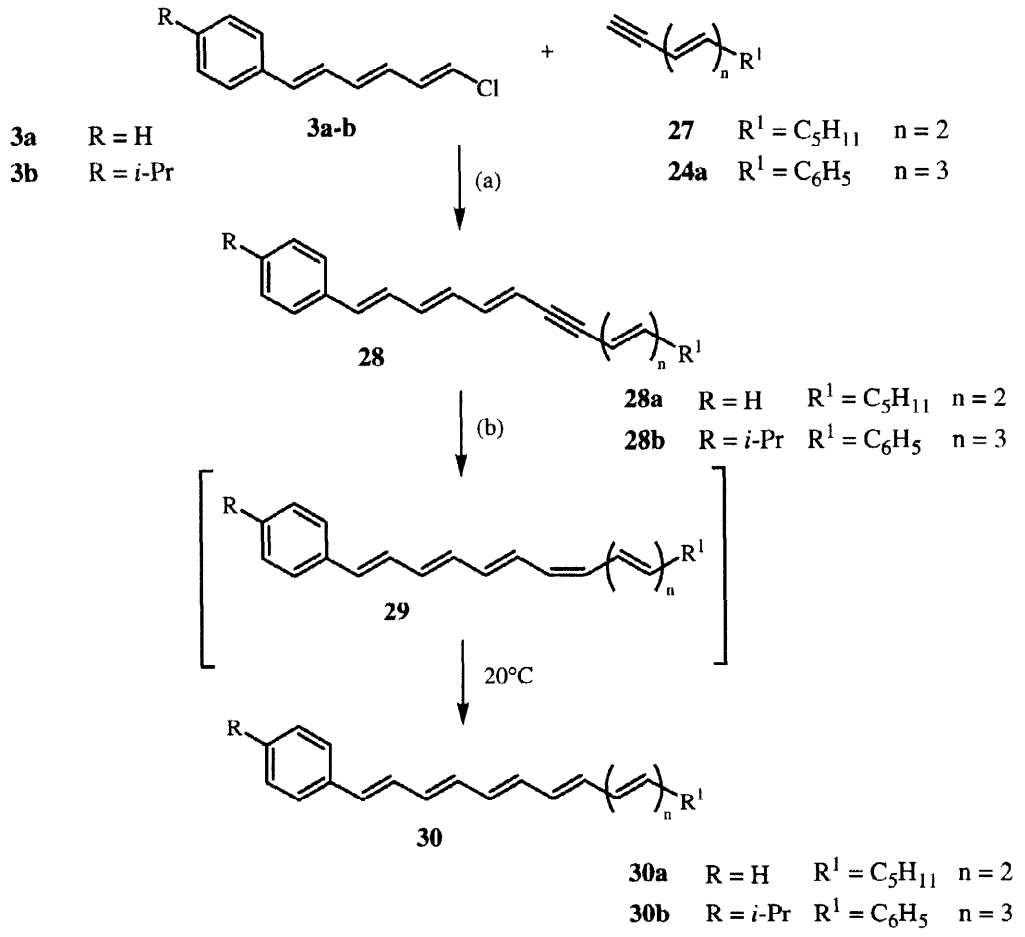
If the acetylenic partner is 1-butyn-3-ol (Scheme 6), selective reduction with Red-Al® of the propargylic alcohol function leads to the tetraene **25** in 79% overall yield. Subsequent oxydation of the allylic alcohol **25** with manganese oxide[16] in CH_2Cl_2 afforded in 80% yield navenone B **26** which is an alarm pheromone of the mollusc *Navamax inermis*.[18]



Scheme 6: (a) HC ≡CCH(OH)Me, piperidine, 5% $PdCl_2(PhCN)_2$, 10% CuI, 20°C; (b) Red-Al, Et_2O, -30° to 20°C (79% from **3a**); (c) MnO_2, CH_2Cl_2, 20°C (80%).

Chlorotrienes **3** are also suitable synthetic intermediates for the synthesis of molecules having long polyenic chains. Thus the coupling of **3a-b** with polyenynes **24a** or **27** under Pd-Cu catalysis[8] followed by selective reduction of the triple bond with activated zinc[19] lead to polyenes **29**. These latter having one *Z*-double bond were not stable at room temperature and isomerized readily to pure *all E* polyenes **30** (Scheme 7).

In conclusion, we have succeeded in developing two efficient synthetic approaches for the synthesis of conjugated α-Chloro-ω-Substituted Hexatrienes **1-3** starting from readily available precursors. The use of these chlorotrienes as intermediates for the elaboration of polyunsaturated compounds is of great interest since they are less photosensitive and more stable than the corresponding bromides or iodides. Furthermore, they react easily and rapidly with organometallic species under appropriate conditions allowing access to conjugated *all E* polyenes.



Scheme 7: (a) 5% $PdCl_2(PhCN)_2$, 10%CuI, piperidine, 20°C (**28a**: 60%, **28b**: 53%); (b) Zn (Cu/Ag), $MeOH/H_2O$ 1/1, 30°C (**30a**: 70%, **30b**: 50%).

EXPERIMENTAL

NMR spectra were recorded on a Bruker AC 200 MHz, VM 250 or AM 400 instrument. $CDCl_3$ was used as solvent with TMS as internal standard. Mass spectra were recorded on a Nermag R 10-10 (fitted with a GC-mass coupling; column: CP Sil 5, Chrompack, 40 m). IR spectra were recorded on a Perkin-Elmer 599 spectrophotometer (neat, cm^{-1}). Gaz chromatographic analyses were performed on a model Girdel equipped with capillary column (SGE 50 QC 2 / BP5 0.25). Satisfactory microanalyses were obtained for all new compounds. Analytical TLC was performed on 0.25 mm precoated silica gel plates (Merck). All reactions were carried out in anhydrous conditions under inert atmosphere. Products were purified by distillation or by silica gel column chromatography (Kieselgel 60 Merck: 230-400 Mesh). Melting points are uncorrected. Ether and THF were distilled from sodium and benzophenone. Catalysts ($PdCl_2(PPh_3)_2$[20], $PdCl_2(PhCN)_2$[21] and $NiCl_2(PPh_3)_2$[22]) and 1-alkynes **7**[23] were prepared following literature procedures. Sodium *bis*(2-methoxyethoxy)aluminium hydride (Red-Al®), 3.4 M solution in toluene was purchased from Aldrich. Zn powder was purchased from E. Merck (zinc powder for analysis > 230 mesh ASTM, 60 μm).

Procedure for the Pd-Cu Catalyzed Coupling Reaction of (*E*) -1,2-Dichloroethylene with 1-Alkynes: To a solution of $PdCl_2(PPh_3)_2$ (0.01 equiv.), (*E*)-1,2-dichloroethylene (3 equiv.), piperidine (2 equiv.) and alkyne **7** in ether was added CuI (0.1 equiv.). The reaction was slightly exothermic and the temperature was maintained between 15-20 °C by using a water bath. The stirred reaction was kept at room temperature for 4 h and treated with saturated solution of NH_4Cl. The aqueous layer was extracted with ether (3 x 20 mL), the combined organic layers were washed successively with aqueous HCl (0.2M, 15 mL), $NaHCO_3$ (10 mL) and H_2O (2 x 30 mL), dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by silica gel column chromatography to give pure (*E*)-chloroenyne **6** or **8** (stereoisomeric purity ≥ 99% determined by GC).

(5E)-6-Chloro-1-phenyl-hex-5-en-3-yn-1-ol **6a**: 8.43 g (82%, yellow solid) obtained from 1-phenyl-but-3-yn-1-ol (50 mmol, 7.31 g); mp: 54-55°C (*i*-Pr_2O); IR (KBr) cm^{-1} 3280, 3070, 3010, 2830, 2800, 2220, 1590, 1050, 920; ^1H NMR (250 MHz, $CDCl_3$) δ 7.39 to 7.28 (m, 5H), 6.44 (d, 1H, J = 13.6Hz), 5.88 (dt, 1H, J = 13.6 and 2.3Hz), 4.86 (dt, 1H, J = 6.3 and 2.3Hz), 2.74 (dd, 2H, J = 6.3 and 2.3Hz), 2.31 (d, 1H, J = 3.5Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 142.45, 129.85, 128.40, 127.90, 125.65, 113.65, 89.05, 77.95, 72.35, 30.20; CIMS (NH_3) m/e (relative intensity) 226 ($(M+18)^+$, ^{37}Cl, 31), 224 ($(M+18)^+$, ^{35}Cl, 100), 208 (M^+, ^{37}Cl, 20), 206 (M^+, ^{35}Cl, 25), 189 (14), 174 (12), 157 (14), 105 (38); Anal. calcd for $C_{12}H_{11}ClO$: C, 69.74; H, 5.36 Found: C, 69.89; H, 5.48.

(5E)-6-Chloro-1-(p-isopropylphenyl)-hex-5-en-3-yn-1-ol **6b**: 5.80 g (83%, yellow solid) obtained from 1-(*p*-isopropylphenyl)-but-3-yn-1-ol (28.2 mmol, 5.30 g); mp: 44-45°C (petroleum ether/ether); IR (KBr) cm^{-1} 3350, 3070, 2860, 2230, 1620, 1065; ^1H NMR (250 MHz, $CDCl_3$) δ 7.29 (d, 2H, J = 8.2Hz), 7.20 (d, 2H, J = 8.2Hz), 6.45 (d, 1H, J = 13.6Hz), 5.89 (dt, 1H, J = 13.6 and 2.3Hz), 4.83 (dt, 1H, J = 6.3 and 2.5Hz), 2.89 (sept, 1H, J = 6.9Hz), 2.73 (dd, 2H, J = 6.5 and 2.3Hz), 2.32 (d, 1H, J = 3.0Hz), 1.23 (d, 6H, J = 6.9Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 148.80, 139.95, 129.85, 126.55, 125.70, 113.80, 89.30, 77.95, 72.35, 33.80, 30.30, 23.95; Anal. calcd for $C_{15}H_{17}ClO$: C, 72.43; H, 6.89 Found: C, 72.29; H, 6.98.

(5E)-6-Chloro-1-(p-methoxyphenyl)-hex-5-en-3-yn-1-ol **6c**: 7.16 g (89%, yellow oil) obtained from 1-(*p*-methoxyphenyl)-but-3-yn-1-ol (34 mmol, 5.98 g); IR (neat) cm^{-1} 3415, 3075, 2910, 2225, 1615, 1060; ^1H NMR (250 MHz, $CDCl_3$) δ 7.27 (d, 2H, J = 8.6Hz), 6.86 (d, 2H, J = 8.7Hz), 6.43 (d, 1H, J = 13.6Hz), 5.87 (dt, 1H, J = 13.6 and 2.3Hz), 4.78 (t, 1H, J = 6.3Hz), 3.78 (s, 3H), 2.70 (dd, 2H, J = 6.3 and 2.3Hz), 2.41 (s, 1H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 159.25, 134.70, 129.80, 126.95, 113.80, 113.75, 89.20, 77.90, 72.05, 55.20, 30.25; Anal. calcd for $C_{13}H_{13}ClO_2$: C, 65.97; H, 5.54 Found: C, 66.10; H, 5.68.

(1E)-1-Chloro-undec-1-en-3-yn-6-ol **6d**: 4.20 g (75%, colourless oil) obtained from non-1-yn-4-ol (29 mmol, 4.0 g); IR (neat) cm^{-1} 3375, 3080, 2950, 2855, 2225, 1595; ^1H NMR (250 MHz, $CDCl_3$) δ 6.46 (d, 1H, J = 13.7Hz), 5.89 (dt, 1H, J = 13.7 and 2.4Hz), 3.74 (m, 1H), 2.52 (ddd, 1H, J = 17.1, 5.5 and 2.2Hz), 2.40 (ddd, 1H, J = 17.1, 5.5 and 2.2Hz), 1.85 (s, 1H), 1.50 (quint, 2H, J = 6.5Hz), 1.45 to 1.20 (m, 6H), 0.87 (t, 3H, J = 6.5Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 129.70, 113.80, 89.30, 77.90, 70.05, 36.35, 31.70, 28.30, 25.25, 22.55, 14.00; Anal. calcd for $C_{11}H_{17}ClO$: C, 65.83; H, 8.54 Found: C, 65.91; H, 8.61.

(5E)-6-Chloro-hex-5-en-3-yn-1-ol **6e**: 5.46 g (93%, yellow oil) obtained from but-3-yn-1-ol (36.9 mmol, 3.76 g); IR (neat) cm^{-1} 3360, 3080, 2960, 2800, 2230, 1590, 1050; ^1H NMR (250 MHz, $CDCl_3$) δ 6.42 (d, 1H, J = 13.6Hz), 5.84 (dt, 1H, J = 13.6 and 2.3Hz), 3.64 (t, 2H, J = 6.5Hz), 3.57 (s, 1H), 2.48 (td, 2H, J = 6.5 and 2.3Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 129.60, 113.65, 89.55, 77.00, 60.55, 23.55; Anal. calcd for C_6H_7ClO: C, 55.19; H, 5.40 Found: C, 55.29; H, 5.51.

(1E)-1-Chloro-hepta-1,6-dien-3-yn-5-ol **8a**: 1.64 g (77%, yellow oil) obtained from **7a** (15 mmol, 1.23 g); R_f = 0.53 (petroleum ether/ether 2:1); IR (neat) cm^{-1} 3360, 1650, 1580, 1150, 950; ^1H NMR (250 MHz, $CDCl_3$) δ 6.59 (d, 1H, J = 13.7Hz), 5.99 (ddd, 1H, J = 17.0, 10.1 and 6.0Hz), 5.98 (dd, 1H, J = 13.7 and 1.4Hz), 5.47 (dt,

1H, J = 17.0 and 1.2Hz), 5.27 (dt, 1H, J = 10.1 and 1.2Hz), 5.00 (dt, 1H, J = 6.0 and 1.4Hz), 2.00 (d, 1H, J = 6.4Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 136.35, 131.20, 116.75, 112.95, 90.30, 81.15, 63.40; Anal. calcd for C_7H_7ClO: C, 58.97; H, 4.95 Found: C, 59.19; H, 5.02.

(1E,6E)-1-Chloro-octa-1,6-dien-3-yn-5-ol **8b**: 1.97 g (84%, yellow oil) obtained from **7b** (15 mmol, 1.44 g); R_f = 0.53 (petroleum ether/ether 2:1); IR (neat) cm^{-1} 3340, 2220, 1670, 1580, 1230, 1170, 960; ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.54 (d, 1H, J = 13.7Hz), 5.95 (dd, 1H, J = 13.7 and 2.0Hz), 5.83 (qdd, 1H, J = 14.0, 6.5 and 1.0Hz), 5.55 (ddq, 1H, J = 14.0, 6.5 and 1.5Hz), 4.90 (br.d, 1H, J = 5.8Hz), 2.24 (br.s, 1H), 1.79 (d, 3H, J = 6.5Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 130.90, 129.70, 129.15, 113.10, 91.10, 80.75, 63.20, 17.40; Anal. calcd for C_8H_9ClO: C, 61.35; H, 5.79 Found: C, 61.28; H, 5.85.

(1E,6E)-1-Chloro-deca-1,6-dien-3-yn-5-ol **8c**: 2.25 g (81%, yellow oil) obtained from **7c** (15 mmol, 1.86 g); R_f = 0.56 (petroleum ether/ether 2:1); IR (neat) cm^{-1} 3340, 2218, 1670, 1586, 1230, 1165, 975, 919, 858; ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.56 (d, 1H, J = 13.7Hz), 5.98 (dd, 1H, J = 13.7 and 1.8Hz), 5.80 (dt, 1H, J = 15.3 and 6.7Hz), 5.61 (dd, 1H, J = 15.3 and 6.3Hz), 4.94 (br t, 1H, J = 5.7Hz), 2.19 (d, 1H, J = 5.7Hz), 2.05 (q, 2H, J = 7.0Hz), 1.43 (sext., 2H, J = 7.4Hz), 0.91 (t, 3H, J = 7.3Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 134.40, 130.10, 128.70, 113.35, 91.35, 80.95, 63.50, 34.15, 22.15, 13.80; CIMS (NH_3) m/e (relative intensity) 205 (7), 186 (M^+, ^{37}Cl, 9), 184 (M^+, ^{35}Cl, 14), 169 (34), 167 (100), 131 (31), 125 (16), 91 (30), 79 (21) ; Anal. calcd for $C_{10}H_{13}ClO$: C, 65.04; H, 7.10 Found: C, 65.19; H, 7.18.

Procedure for the Pd-Cu Catalyzed Coupling Reaction of (Z)-1,2-Dichloroethylene with 1-Alkynes: To a solution of $Pd(PPh_3)_4$ (0.225 mmol, 260 mg), (*Z*)-1,2-dichloroethylene (30 mmol, 2.91 g), butylamine (30 mmol, 2.19 g) and alkyne **7** (15 mmol) in ether (30 mL) was added CuI (1.5 mmol, 0.286 g) at 15-20 °C (exothermic reaction). The stirred reaction was kept at room temperature for 4 h and treated with saturated solution of NH_4Cl. The aqueous layer was extracted with ether (3 x 20 mL), the combined organic layers were washed successively with aqueous HCl (0.2M, 15 mL), $NaHCO_3$ (10 mL) and H_2O (2 x 30 mL), dried over $MgSO_4$ and concentrated under vacuum. The residue was purified by silica gel column chromatography to give pure (*Z*)-chloroenyne **10** (stereoisomeric purity ≥ 99% determined by GC).

(1Z)-1-Chloro-hepta-1,6-dien-3-yn-5-ol **10a**: 1.75 g (82%, yellow oil); IR (neat) cm^{-1} 3360, 1646, 1590, 1143, 1021, 944, 736; ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.40 (d, 1H, J = 7.4Hz), 5.98 (ddd, 1H, J = 17.1, 10.1 and 5.2Hz), 5.89 (dd, 1H, J = 7.4 and 1.8Hz), 5.51 (dt, 1H, J = 17.1 and 1.3Hz), 5.24 (dt, 1H, J = 10.1 and 1.2Hz), 5.05 (dd, 1H J = 5.2 and 1.4Hz), 2.48 (brs, 1H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 136.30, 129.15, 116.90, 111.40, 95.65, 80.00, 63.50; CIMS (NH_3) m/e (relative intensity) 161 (3), 159 (9), 144 M^+, ^{37}Cl, 39), 142 (M^+, ^{35}Cl, 100), 127 (14), 125 (44), 107 (15); Anal. calcd for C_7H_7ClO: C, 58.97; H, 4.95 Found: C, 59.15; H, 5.08.

(1Z,6E)-1-Chloro-octa-1,6-dien-3-yn-5-ol **10b**: 1.88 g (80%, yellow oil); R_f = 0.42 (petroleum ether/ether 2:1); IR (neat) cm^{-1} 3405, 1690, 1632, 1576, 1454, 1337, 996, 762, 721; ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.36 (d, 1H, J = 7.5Hz), 5.95 (qdd, 1H, J = 13.8, 6.4 and 1.0Hz), 5.90 (dd, 1H, J = 7.5 and 1.6Hz), 5.65 (ddq, 1H, J = 13.8, 5.7 and 1.5Hz), 4.94 (t, 1H, J = 5.7Hz), 2.28 (d, 1H, J = 5.7Hz), 1.68 (d, 3H, J = 6.4Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 129.60, 129.25, 128.85, 111.50, 96.70, 79.60, 63.25, 17.45; Anal. calcd for C_8H_9ClO: C, 61.35; H, 5.79 Found: C, 61.29; H, 5.82.

(1Z,6E)-1-Chloro-deca-1,6-dien-3-yn-5-ol **10c**: 2.10 g (76%, yellow oil); R_f = 0.41 (petroleum ether/ether 2:1); IR (neat) cm^{-1} 3390, 1675, 1615, 1570, 980; ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.45 (d, 1H, J = 7.5Hz), 6.03 (m, 1H), 5.96 (dd, 1H, J = 7.5 and 1.6Hz), 5.65 (ddt, 1H, J = 15.0, 6.0 and 1.4Hz), 5.03 (br.t., 1H, J = 6.0Hz), 2.07 (q, 1H, J = 7.2Hz), 1.98 (d, 1H, J = 6.2Hz), 1.44 (sext, 2H, J = 7.4Hz), 0.92 (t, 3H, 7.4Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 134.30, 128.90, 128.45, 111.55, 96.75, 79.65, 63.35, 33.95, 21.95, 13.60; Anal. calcd for $C_{10}H_{13}ClO$: C, 65.04; H, 7.10 Found: C, 65.15; H, 7.18.

(2E,7E)-Trideca-2,7-dien-5-yn-4-ol **12**: To a stirred solution of (*E*)-1-iodo-1-heptene (5.75 mmol, 1.29 g), $PdCl_2(PPh_3)_2$ (0.06 mmol, 41 mg) and CuI (0.58 mmol, 110.5 mg) in piperidine (9 mL) was slowly added (addition time 10 min) **7b** (6.33 mmol, 608 mg) in 3 mL of piperidine while maintaining the temperature between 15 and 20°C. The stirred reaction was kept at room temperature for 2h and treated with saturated solution of NH_4Cl. The aqueous layer was extracted with ether (3 x 20 mL), the combined organic layers were washed successively with aqueous HCl (0.2M, 15 mL), $NaHCO_3$ (10 mL) and H_2O (2 x 30 mL), dried over $MgSO_4$ and concentrated under vacuum. Purification by flash chromatography (petroleum ether / AcOEt 2:1) afforded the pure (*E,E*)-dienyne **12** as a yellow oil (stereoisomeric purity ≥ 98% determined by GC) in 95% yield (1.05 g). IR (neat) cm^{-1} 3345, 2220, 1665, 1580, 1165; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.15 (dt, 1H, J = 15.8 and 7.1Hz), 5.86 (ddq, 1H, J = 15.2, 6.3 and 1.0Hz), 5.60 (ddq, 1H, J = 15.2, 6.3 and 1.5Hz), 5.47 (dq, 1H, J = 15.8 and 1.7Hz), 4.90 (t, 1H, J = 5.7Hz), 2.11 (dq, 2H, J = 7.3 and 1.2Hz), 1.90 (d, 1H, J = 5.8Hz), 1.75 (dt, 3H, J = 6.2 and 1.0Hz), 1.21 to 1.31 (m, 6H), 0.89 (t, 3H, J = 6.7Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 145.65, 130.35, 128.55, 108.70, 86.80, 84.65, 63.30, 32.95, 31.20, 28.25, 22.35, 17.340, 13.90; Anal. calcd for $C_{13}H_{20}O$: C, 81.20; H, 10.48 Found: C, 81.34; H, 10.55.

General Procedure for the Reduction of Propargyl Alcohol Function with Red-Al®: To a stirred solution of Red-Al® (1.5 equiv., 3.4N in toluene) in anhydrous THF, under an argon atmosphere, was added dropwise, at -20°C, propargylic alcohol **8** or **10** in solution in THF. The reaction was stirred at room temperature and monitored by TLC analysis until complete consumption of the starting material (30 min to 4 h). The reaction was hydrolyzed, at -20°C, with aqueous hydrochloric acid (1M, 10 mL) and extracted with Et_2O (2 x 20 mL). The organic extract was dried over $MgSO_4$ and the solvent was removed in vacuo. The residue was purified by silica gel column chromatography to give pure product (stereoisomeric purity ≥ 98% determined by GC).

(1E,3E)-1-Chloro-hepta-1,3,6-trien-5-ol **9a**: 1.61 g (93%, yellow oil) obtained from **8a** (12 mmol, 1.71 g); IR (neat) cm^{-1} 3368, 1655, 1590 1423, 1286, 985, 929, 840; ^1H NMR (200 MHz, $CDCl_3$) δ 6.48 (dd, 1H, J = 13.4 and 10.7Hz), 6.23 (d, 1H, J = 13.4Hz), 6.18 (ddd, 1H, J = 15.4, 10.6 and 1.2Hz), 5.89 (ddd, 1H, J = 17.2, 10.3 and 6.0Hz), 5.75 (dd, 1H, J = 15.4 and 6.0Hz), 5.29 (dt, 1H, J = 17.2 and 1.3Hz), 5.18 (dt, 1H, J = 10.3 and 1.3Hz), 4.68 (dt, 1H, J = 6.0 and 3.6Hz), 1.83 (d, 1H, J = 3.6Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 138.75, 134.75, 132.80, 126.50, 121.45, 115.60, 73.05; CIMS (NH_3) m/e (relative intensity) 144 (M^+, ^{35}Cl, 6), 129 (35), 127 (100), 109 (18), 86 (17); Anal. calcd for C_7H_9ClO: C, 58.14; H, 6.27 Found: C, 58.23; H, 6.35.

(1E,3E,6E)-1-Chloro-octa-1,3,6-trien-5-ol **9b**: 1.71 g (90%, yellow oil) obtained from **8b** (12 mmol, 1.88 g); R_f = 0.36 (petroleum ether/ether 2:1); IR (neat) cm^{-1} 3415, 1640, 1570, 1375, 1295, 1070, 995, 835, 670; ^1H NMR (250 MHz, $CDCl_3$) δ 6.45 (dd, 1H, J = 13.3 and 10.5Hz), 6.20 (d, 1H, J = 13.3Hz), 6.08 (m, 1H), 5.73 (dd, 1H, J = 15.8 and 6.0Hz), 5.69 (qd, 1H, J = 15.3 and 6.0Hz), 5.49 (ddq, 1H, J = 15.3, 6.5 and 1.4Hz), 4.60 (t, 1H, J = 6.3Hz), 1.98 (br s, 1H), 1.71 (d, 3H, J = 6.7Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 135.60, 132.90, 131.90, 127.90, 125.95, 121.10, 72.85, 17.65; CIMS (NH_3) m/e (relative intensity) 174 (6), 157 ($(M-1)^+$, ^{35}Cl, 11), 151 (50), 141 (100), 109 (7), 105 (12); Anal. calcd for $C_8H_{11}ClO$: C, 60.57; H, 6.99 Found: C, 60.63; H, 7.08.

(1E,3E,6E)-1-Chloro-deca-1,3,6-trien-5-ol **9c**: 2.17 g (97%, yellow oil) obtained from **8c** (12 mmol, 2.22 g); R_f = 0.46 (petroleum ether/ether 2:1); IR (neat) cm^{-1} 3410, 1630, 1565, 1360, 1060, 990; ^1H NMR (250 MHz, $CDCl_3$) δ 6.45 (dd, 1H, J = 13.4 and 10.4Hz), 6.20 (d, 1H, J = 13.4Hz), 6.15 (m, 1H), 5.70 (m, 2H), 5.47 (dd, 1H, J = 15.3 and 6.7Hz), 4.61 (t, 1H, J = 6.1Hz), 2.02 (q, 2H, J = 7.1Hz), 1.88 (br s, 1H), 1.43 (sext, 2H, J = 7.3Hz), 0.90 (t, 3H, J = 7.3Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 135.65, 133.05, 132.90, 130.75, 125.95, 121.05, 72.90, 34.20, 22.10, 13.60; Anal. calcd for $C_{10}H_{15}ClO$: C, 64.34; H, 8.10 Found: C, 64.59; H, 8.28.

(1Z,3E)-1-Chloro-hepta-1,3,6-trien-5-ol **11a**: 1.16 g (80%, yellow oil) obtained from **10a** (10 mmol, 1.43 g); R_f = 0.41 (petroleum ether / ether 2:1); IR (neat) cm^{-1} 3390, 1640, 1580, 1350, 1060, 970; ^1H NMR (250 MHz, $CDCl_3$) δ 6.68 (ddt, 1H, J = 15.4, 10.4 and 1.1Hz), 6.32 (dd, 1H, J = 10.4 and 7.1Hz), 6.04 (d, 1H, J = 7.1Hz), 5.94 (ddd, 1H, J = 17.2, 10.3 and 5.9Hz), 5.89 (dd, 1H, J = 15.4, and 5.9Hz), 5.31 (dt, 1H, J = 17.2 and 1.4Hz), 5.20 (dt, 1H, J = 10.3 and 1.3Hz), 4.75 (m, 1H), 1.85 (d, 1H, 4.0Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 138.65, 137.25, 128.90, 123.95, 119.10, 115.70, 73.30; CIMS (NH_3) m/e (relative intensity) 144 (M^+, ^{35}Cl, 7), 129 (32), 127 (100), 109 (21), 86 (15); Anal. calcd for C_7H_9ClO: C, 58.14; H, 6.27 Found: C, 58.29; H, 6.42.

(1Z,3E,6E)-1-Chloro-octa-1,3,6-trien-5-ol **11b**: 1.43 g (90%, yellow oil) obtained from **10b** (10 mmol, 1.59 g); R_f = 0.38 (petroleum ether / ether 2:1); IR (neat) cm^{-1} 3384, 1650, 1595, 1455, 1347, 1067, 975, 766; ^1H NMR (250 MHz, $CDCl_3$) δ 6.63 (dd, 1H, J = 15.4 and 10.4Hz), 6.30 (dd, 1H, J = 10.4 and 7.1Hz), 6.00 (d, 1H, J = 7.1Hz), 5.91 (dd, 1H, J = 15.4 and 6.4Hz), 5.74 (qd, 1H, J = 15.3 and 6.5Hz), 5.45 (ddq, 1H, J = 15.3, 6.5 and 1.5Hz), 4.67 (t, 1H, J = 6.4Hz), 1.94 (s, 1H), 1.72 (d, 3H, J = 6.4Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 138.25, 132.00, 129.20, 128.20, 123.60, 118.95, 73.35, 17.85; CIMS (NH_3) m/e (relative intensity) 174 (5), 157 ($(M-1)^+$, ^{35}Cl, 13), 151 (48), 141 (100), 105 (12); Anal. calcd for $C_8H_{11}ClO$: C, 60.57; H, 6.99 Found: C, 60.69; H, 7.12.

(1Z,3E,6E)-1-Chloro-deca-1,3,6-trien-5-ol **11c**: 1.70 g (91%, yellow oil) obtained **10c** (10 mmol, 1.85 g); R_f = 0.42 (petroleum ether/ether 2:1); IR (neat) cm^{-1} 3405, 1645, 1560, 1360, 980; ^1H NMR (250 MHz, $CDCl_3$) δ 6.65 (dd, 1H, J = 10.5 and 15.4Hz), 6.30 (dd, 1H, J = 10.5 and 7.1Hz), 6.01 (d, 1H, J = 7.1Hz), 5.98 (dd, 1H, J = 15.4 and 6.3Hz), 5.72 (td, 1H, J = 15.4 and 6.4Hz), 5.51 (ddt, 1H, J = 15.4, 6.7 and 1.3Hz), 4.69 (br t, 1H), 2.03 (q, 2H, J = 6.9Hz), 1.83 (br s, 1H), 1.41 (sext, 2H, J = 7.4Hz), 0.91 (t, 3H, J = 7.4Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 138.15, 133.20, 130.65, 129.05, 123.45, 118.80, 73.20, 34.25, 22.15, 13.60; Anal. calcd for $C_{10}H_{15}ClO$: C, 64.34; H, 8.10 Found: C, 64.52; H, 8.18.

(2E,5E,7E)-Trideca-2,5,7-trien-4-ol **13**: 760 mg (78%, yellow oil) obtained from **12** (5 mmol, 962 mg); IR (neat) cm^{-1} 3365, 1665, 1637, 1590, 1454, 1080, 990; ^1H NMR (250 MHz, $CDCl_3$) δ 6.19 (ddd, 1H, J = 14.9, 10.3 and 0.9Hz), 6.04 (ddt, 1H, J = 14.7, 10.3 and 1.1 Hz), 5.78 to 5.47 (m, 4H), 4.59 (br t, 1H, J = 6.5Hz), 2.07 (q, 2H, J = 6.7Hz), 1.82 (s, 1H), 1.71 (d, 3H, J = 6.3Hz), 1.41 to 1.28 (m, 6H), 0.89 (t, 3H, J = 6.7Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 135.80, 132.50, 131.95, 130.95, 129.35, 127.15, 73.40, 32.55, 31.30, 28.85, 22.45, 17.65, 13.95; CIMS (NH_3) m/e (relative intensity) 193 ($(M-1)^+$, 33), 177 (80), 144 (45), 127 (43), 109 (72), 81 (100); Anal. calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41 Found: C, 80.50; H, 11.47.

General Procedure for bis(acetonitrile)Palladium Chloride Rearrangements

(2E,4E,6E)-1-Acetoxy-7-chloro-hepta-2,4,6-triene **1a**: To a stirred solution of alcohol **9a** (10 mmol, 1.45 g) and triethylamine (12 mmol, 1.7 mL) in CH_2Cl_2 (15 mL) was added at -30°C Ac_2O (12 mmol, 1.2 mL). The reaction was stirred at room temperature and monitored by TLC analysis until complete consumption of the starting material (1 to 3h). The mixture reaction was then treated with water (30 mL). The aqueous layer was extracted with ether (3 x 20 mL), dried over $MgSO_4$ and concentrated under *vacuum*. Rapid filtration (R_f = 0.63) through a short pad of silica gel (packed with petroleum ether/ether 1:3 containing 0.5 vol.% of Et_3N) lead to the acetate **4a** (crude product): ^1H NMR (250 MHz, $CDCl_3$) δ 6.50 to 6.13 (m, 3H), 5.91 to 5.61 (m, 3H), 5.33 (m, 2H), 2.08 (s, 3H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 169.75, 134.75, 132.45, 130.50, 128.85, 122.40, 117.60, 74.20, 21.15.

The acetate **4a** previously prepared in THF (15 mL) was treated with $PdCl_2(MeCN)_2$ (0.4 mmol, 100 mg). The reaction was stirred at room temperature and monitored by TLC analysis until complete consumption of the starting material (2 to 5h). After evaporation of the solvent *in vacuo* and rapid filtration through a short pad of silica gel (packed with petroleum ether/ether 3:1 containing 0.5 vol.% of Et_3N) the pure chlorotriene **1a** (*E,E,E* stereoisomeric purity ≥ 95%) was isolated as a yellow oil in a 95% overall yield (1.77 g). IR (neat) cm^{-1} 3466, 1736, 1690, 1240, 1000, 835; ^1H NMR (250 MHz, $CDCl_3$) δ 6.54 to 6.43 (m, 1H), 6.31 to 6.14 (m, 4H), 5.78 (dt, 1H, J = 14.4 and 6.5Hz), 4.61 (d, 2H, J = 6.6Hz), 2.08 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 170.65, 133.45, 133.30, 132.05, 129.40, 127.95, 121.55, 64.45, 20.90; CIMS (NH_3) m/e (relative intensity) 205 (7), 203 (24), 186 (M^+, ^{35}Cl, 2), 129 (38), 127 (100), 107 (15); UV (EtOH) λ = 271 nm (ε_{max} = 30500) and 282 nm (ε = 24700).

(1E,3E,5E)-7-Acetoxy-1-chloro-octa-1,3,5-triene **1b**: Following the procedure described for **1a**, the acetylation of alcohol **9b** (8 mmol, 1.27 g) lead to a mixture of acetates **4b** and **1b**. After rearrangement of this mixture in the presence of $PdCl_2(MeCN)_2$ (0.32 mmol, 83 mg), **1b** (*E,E,E* stereoisomeric purity ≥ 95%) was isolated as a yellow oil in a 52% overall yield (830 mg). R_f (petroleum ether/ether 3:1) = 0.62; IR (neat) cm^{-1} 3455, 1736, 1646, 1242, 1050, 997, 836; ^1H NMR (250 MHz, $CDCl_3$) δ 6.49 to 6.42 (m, 1H), 6.23 to 6.14 (m, 4H), 5.72 (dd, 1H, J = 14.4 and 6.7Hz), 5.39 (quint, 1H, J = 6.5Hz), 2.04 (s, 3H), 1.32 (d, 3H, J = 6.5Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 170.20, 133.75, 133.40, 132.30, 130.95, 129.20, 121.30, 70.45, 21.25, 20.10; CIMS (NH_3) m/e (relative intensity) 200 (M^+, ^{35}Cl, 3), 143 (33), 141 (100), 105 (10); UV (EtOH) λ = 271 nm (ε_{max} = 32700), λ = 282 nm (ε = 28800).

(1E,3E,5E)-7-Acetoxy-1-chloro-deca-1,3,5-triene **1c**: Following the procedure described for **1a**, the acetylation of alcohol **9c** (8 mmol, 1.49 g) lead to a mixture of acetates **4c** and **1c**. After rearrangement of this mixture in the presence of $PdCl_2(MeCN)_2$ (0.32 mmol, 83 mg), **1c** (*E,E,E* stereoisomeric purity ≥ 95%) was isolated as a yellow oil in a 84% overall yield (1.54 g). R_f (petroleum ether/ether 3:1) = 0.62; IR (neat) cm^{-1} 1737, 1689, 1379, 1245, 833; ^1H NMR (250 MHz, $CDCl_3$) δ 6.48 to 6.42 (m, 1H), 6.27 to 6.13 (m, 4H), 5.66 (dd, 1H, J = 14.5 and 7.0Hz), 5.29 (q, 1H, J = 6.8Hz), 2.06 (s, 3H), 1.68 to 1.50 (m, 2H), 1.39 to 1.28 (m, 4H), 0.92 (t, 3H, J = 7.2Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 170.35, 133.40, 132.85, 132.35, 131.75, 129.15, 121.25, 74.10, 36.45, 21.20, 16.35, 13.75; Anal. calcd for $C_{12}H_{17}ClO_2$: C, 63.02; H, 7.49 Found: C, 63.34; H, 7.55; UV (EtOH) λ = 272 nm (ε_{max} = 33000).

(2E,4E,6Z)-1-Acetoxy-7-chloro-hepta-2,4,6-triene **2a**: The same procedure was used as described for **1a** starting from alcohol **11a** (6 mmol, 877 mg). **5a** (crude product): ^1H NMR (250 MHz, $CDCl_3$) δ 6.75 (ddd, 1H, J = 14.1, 10.4 and 0.9Hz), 6.30 (dd, 1H, J = 10.3 and 7.1Hz), 5.99 (d, 1H, J = 7.1Hz), 5.92 to 5.78 (m, 3H), 5.34 to 5.22 (m, 2H), 2.09 (s, 3H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 169.75, 134.65, 133.00, 128.60, 125.85, 119.90, 117.75, 74.30, 21.10.

After rearrangement of **5a** in the presence of $PdCl_2(MeCN)_2$ (0.24 mmol, 62 mg), **2a** (*E,E,Z* stereoisomeric purity ≥ 95%) was isolated as a yellow oil in a 96% yield (833 mg). R_f (petroleum ether/ether 3:1) = 0.62; IR (neat) cm^{-1} 1741, 1684, 1238, 990, 767; ^1H NMR (200 MHz, $CDCl_3$) δ 6.68 (dd, 1H, J = 14.4 and 10.3Hz), 6.26 to 6.45 (m, 3H), 6.07 (d, 1H, J = 7.5Hz), 5.88 (dt, 1H, J = 14.4 and 6.4Hz), 4.65 (d, 2H, J = 6.4Hz), 2.1 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 170.60, 134.15, 133.55, 129.35, 128.65, 126.80, 119.20, 64.35, 20.85; CIMS (NH_3) m/e (relative intensity) 205 (14), 203 (45), 186 (M^+, ^{35}Cl, 11), 129 (32), 127 (100), 109 (22), 107 (67); UV (EtOH) λ = 273 nm (ε_{max} = 30400).

(1Z,3E,5E)-7-Acetoxy-1-chloro-octa-1,3,5-triene **2b**: Following the procedure described for **1a**, the acetylation of alcohol **11b** (6 mmol, 952 mg) lead to a mixture of acetates **5b** and **2b** (**5b/2b** ≈ 1/2). After rearrangement of this mixture in the presence of $PdCl_2(MeCN)_2$ (0.24 mmol, 62 mg), **2b** (*Z,E,E* stereoisomeric purity ≥ 95%) was isolated as a yellow oil in a 91% overall yield (1.1 g). R_f (petroleum ether/ether 3:1) = 0.62; IR (neat) cm^{-1} 3450, 1744, 1650, 1245, 1060, 985; ^1H NMR (200 MHz, $CDCl_3$) δ 6.65 to 6.58 (m, 1H), 6.38 to 6.28 (m, 3H), 6.02 (d, 1H, J = 7.0Hz), 5.77 (dd, 1H, J = 6.3 and 14.0Hz), 5.42 (quint, 1H, J = 6.3Hz), 2.06 (s, 3H), 1.34 (d, 3H, J = 6.4Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 170.20, 134.40 (2C), 131.05, 129.40, 126.65, 118.95, 70.30,

21.25, 20.05; CIMS (NH_3) m/e (relative intensity) 200 (M^+, ^{35}Cl, 2), 143 (31), 141 (100), 105 (8); UV (EtOH) λ = 273 nm (ε_{max} = 30500).

(1Z,3E,5E)-7-Acetoxy-1-chloro-deca-1,3,5-triene **2c**: Following the procedure described for **1a**, the acetylation of alcohol **11c** (5 mmol, 934 mg) lead to a mixture of acetates **5c** and **2c** (**5c/2c** ≈ 1/2). After rearrangement of this mixture in the presence of $PdCl_2(MeCN)_2$ (0.20 mmol, 52 mg), **2c** (*Z,E,E* stereoisomeric purity ≥ 95%) was isolated as a yellow oil in a 93% overall yield (1.06 g). R_f (petroleum ether/ether 3:1) = 0.63; IR (neat) cm^{-1} 1729, 1683, 1630, 1240, 751; ^1H NMR (400 MHz) δ 6.69 to 6.63 (m, 1H), 6.40 to 6.33 (m, 3H), 6.06 (d, 1H, J = 7.0Hz), 5.68 (dd, 1H, J = 13.9 and 6.7Hz), 5.33 (q, 1H, J = 6.7Hz), 2.09 (s, 3H), 1.74 to 1.56 (m, 2H), 1.42 to 1.32 (m, 2H), 0.95 (t, 3H, J = 7.4Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 170.50, 134.70, 133.75, 132.05, 129.60, 126.80, 119.15, 73.70, 32.60, 21.40, 18.55, 13.95; Anal. calcd for $C_{12}H_{17}ClO_2$: C, 63.02; H, 7.49 Found: C, 63.39; H, 7.57; UV (EtOH) λ = 274 nm (ε_{max} = 30100).

General Procedure for the Synthesis of ω-Chloro-trienal and -trienones (19 and 21): To a solution of **1** or **2** (2 mmol) in MeOH (3 mL) was added at 0°C K_2CO_3 (2.2 mmol, 304 mg). The reaction mixture was stirred at room temperature and monitored by TLC analysis until complete consumption of the starting material (1 to 3h) before to be concentrated. Ether was added (20 mL) and the organic layer washed with water (2 x 10 mL), dried over $MgSO_4$ and the solvent was removed *in vacuo*. Owing to their low stability during the purification step, compounds **18** or **20** (crude products) were used for the synthesis of **19** or **21** without purification.

MnO_2 (40 mmol, 3.50 g) was added at room temperature to a solution of **18** or **20** in methylene chloride (10 mL). After stirring for 1 to 3h (TLC monitoring), the mixture was filtered through a pad of celite, the solvent was removed *in vacuo* and the residue was first purified by silica gel column chromatography then by recrystallization to give pure product.

(2E,4E,6E)-7-Chloro-hepta-2,4,6-trienal **19a**: 225 mg (79% from **1a**, yellow solid); R_f = 0.45 (ether/petroleum ether 1:1.5); mp: 85-86°C (CH_2Cl_2/pentane). IR (KBr) cm^{-1} 2750, 1678, 1608, 1555, 1163, 1118, 1013, 829, 624; ^1H NMR (250 MHz, $CDCl_3$) δ 9.56 (d, 1H, J = 7.9Hz), 7.17 (dd, 1H, 15.3 and 10.3Hz), 6.48 to 6.68 (m, 4H), 6.23 (dd, 1H, J = 7.9 and 15.3Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 193.20, 150.50, 137.40, 132.80, 132.20, 130.40, 126.75; CIMS (NH_3) m/e (relative intensity) 162 (6), 160 (20), 145 ($(M+1)^+$, ^{37}Cl, 52), 143 ($(M+1)^+$, ^{35}Cl, 100), 107 (38), 79 (16); UV (EtOH) λ = 311 nm (ε_{max} = 38700); Anal. calcd for C_7H_7ClO: C, 58.97; H, 4.95 Found: C, 59.11; H, 4.99.

(3E,5E,7E)-8-Chloro-octa-3,5,7-trien-2-one **19b**: 210 mg (67% from **1b**, yellow solid); R_f = 0.40 (ether/petroleum ether 1:1.5); mp: 80-81°C (CH_2Cl_2/petroleum ether); IR (KBr) cm^{-1} 3415, 1680, 1597, 1566, 1000, 965, 832, 624; ^1H NMR (250 MHz, $CDCl_3$) δ 7.13 (dd, 1H, J = 15.5 and 10.8Hz), 6.28 to 6.62 (m, 4H), 6.21 (d, 1H, J = 15.5Hz), 2.29 (s, 3H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 198.00, 142.05, 136.45, 133.00, 131.10, 131.00, 125.50, 27.45; CIMS (NH_3) m/e (relative intensity) 174 (3), 159 ($(M+1)^+$, ^{37}Cl, 31), 157 ($(M+1)^+$, ^{35}Cl, 100), 141 (5), 121 (22), 94 (9), 77 (8); UV (EtOH) λ = 310 nm (ε_{max} = 36500); Anal. calcd for C_8H_9ClO: C, 61.35; H, 5.79 Found: C, 61.47; H, 5.83.

(5E,7E,9E)-10-Chloro-deca-5,7,9-trien-4-one **19c**: 196 mg (53% from **1c**, yellow solid); R_f = 0.43 (ether/petroleum ether 1:1.5); mp: 67-68°C (CH_2Cl_2/petroleum ether); IR (Nujol) cm^{-1} 1684, 1598, 1555, 1004, 838, 726; ^1H NMR (250 MHz, $CDCl_3$) δ 7.14 (dd, 1H, J = 15.4 and 10.9Hz), 6.61 to 6.24 (m, 4H), 6.21 (d, 1H, J = 15.4Hz), 2.54 (t, 2H, J = 7.4Hz), 1.65 (sext, 2H, J = 7.4Hz), 0.94 (t, 3H, J = 7.4Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 200.35, 141.10, 136.30, 133.10, 131.10, 130.30, 125.25, 42.80, 17.70, 13.75; CIMS (NH_3) m/e (relative intensity) 202 (7), 187 ($(M+1)^+$, ^{37}Cl, 36), 185 ($(M+1)^+$, ^{35}Cl, 100), 149 (22), 141 (35), 113 (11); UV (EtOH) λ = 311 nm (ε_{max} = 33200); Anal. calcd for $C_{10}H_{13}ClO$: C, 65.04; H, 7.10 Found: C, 65.17; H, 7.14.

(2E,4E,6Z)-7-Chloro-hepta-2,4,6-trienal **21a**: 270 mg (95% from **2a**, yellow oil); R_f = 0.45 (ether/petroleum ether 1:1.5); IR (neat) cm^{-1} 1683, 1615,1090, 990, 759; ^1H NMR (200 MHz, $CDCl_3$) δ 9.62 (d, 1H, J = 7.9Hz), 7.20 (dd, 1H, J = 15.1 and 10.9Hz), 7.08 (dd, 1H, J = 15.0 and 10.6Hz), 6.57 (dd, 1H, J = 15.0 and 11.1Hz), 6.46 (dd, 1H, J = 10.6 and 7.1Hz), 6.30 (d, 1H, J = 7.1Hz), 6.23 (dd, 1H, J = 15.2 and 7.9Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 193.45, 150.85, 134.70, 132.85, 132.60, 128.95, 124.15; CIMS (NH_3) m/e (relative intensity) 162 (14), 160 (48), 145 ($(M+1)^+$, ^{37}Cl, 42), 143 ($(M+1)^+$, ^{35}Cl, 100), 109 (63); UV (EtOH) λ = 310 nm (ε_{max} = 36200); Anal. calcd for C_7H_7ClO: C, 58.97; H, 4.95 Found: C, 59.09; H, 5.03.

(3E,5E,7Z)-8-Chloro-octa-3,5,7-trien-2-one **21b**: 228 mg (73% from **2b**, yellow solid); R_f = 0.40 (ether/petroleum ether 1:1.5); mp: 32-33°C (CH_2Cl_2/pentane); IR (nujol) cm^{-1} 1672, 1603, 1566, 1362, 1260, 999, 766; ^1H NMR (200 MHz, $CDCl_3$) δ 7.20 (dd, 1H, J = 15.7 and 11.1Hz), 6.98 (dd, 1H, J = 10.8 and 15.2Hz), 6.52 to 6.39 (m, 2H), 6.25 to 6.17 (m, 2H), 2.31 (s, 3H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 198.40, 142.60, 133.75, 133.05, 131.90, 129.15, 122.95, 27.40; CIMS (NH_3) m/e (relative intensity) 174 (5), 159 ($(M+1)^+$, ^{37}Cl, 33), 157 ($(M+1)^+$, ^{35}Cl, 100), 141 (7), 121 (19); UV (EtOH) λ = 309 nm (ε_{max} = 34600); Anal. calcd for C_8H_9ClO: C, 61.35; H, 5.79 Found: C, 61.42; H, 5.82.

(5E,7E,9Z)-10-Chloro-deca-5,7,9-trien-4-one **21c**: 188 mg (51% from **2c**, yellow solid); R_f = 0.43 (ether/petroleum ether 1:1.5); mp: 49-49.5°C (CH_2Cl_2/pentane); IR (nujol) cm^{-1} 1678, 1602, 1465, 1370, 1000, 730; ^1H NMR (250 MHz, $CDCl_3$) δ 7.16 (dd, 1H, J = 15.5 and 11.1Hz), 6.92 (dd, 1H, J = 10.7 and 15.0Hz), 6.43 to 6.32 (m, 2H), 6.18 to 6.12 (m, 2H), 2.49 (t, 2H, J = 7.3Hz), 1.60 (sext, 2H, J = 7.4Hz), 0.88 (t, 3H, J = 7.4Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 200.50, 141.35, 133.45, 133.20, 131.00, 129.00, 122.55, 42.45, 17.75, 13.80; CIMS (NH_3) m/e (relative intensity) 202 (6), 187 ($(M+1)^+$, ^{37}Cl, 35), 185 ($(M+1)^+$, ^{35}Cl, 100), 151 (8), 141 (12); UV (EtOH) λ = 309 nm (ε_{max} = 32400); Anal. calcd for $C_{10}H_{13}ClO$: C, 65.04; H, 7.10 Found: C, 65.15; H, 7.12.

General Procedure for the Reduction of Homopropargylic Alcohols 6a-e: To a stirred solution of Red-Al® (26 mmol, 3.4N in toluene) in anhydrous ether (20 mL), was added dropwise, at –20°C, a solution of homopropargylic alcohol 6 (20 mmol) in 3 mL of ether. After complete addition, the cold bath was removed and the reaction was heated on a steam bath for 5h before treatment at –30°C with aq. HCl (1M, 20 mL). After extraction with ether (3 x 20 mL), the organic extract was dried over $MgSO_4$, the solvent was removed *in vacuo* and the residue was purified by silica gel column chromatography (petroleum ether/AcOEt 70:30) to give pure product (stereoisomeric purity ≥ 99% determined by GC).

(3E,5E)-6-Chloro-1-phenyl-hexa-3,5-dien-1-ol **16a**: 3.30 g (79%, yellow oil); IR (neat) cm^{-1} 3385, 3065, 2930, 1585, 1460, 1290, 1045, 980; ^1H NMR (250 MHz, $CDCl_3$) δ 7.35 to 7.26 (m, 5H), 6.40 (dd, 1H, J = 13.1 and 10.5Hz), 6.10 (d, 1H, J = 13.1Hz), 6.05 (ddt, 1H, J = 15.0, 10.5 and 1.2Hz), 5.66 (dt, 1H, J = 15.0 and 7.4Hz), 4.71 (t, 1H, J = 6.8Hz), 2.51 (t, 2H, J = 7.0Hz), 2.04 (brs, 1H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 143.65, 133.25, 130.85, 129.10, 128.35, 127.55, 125.70, 119.60, 73.50, 42.30; Anal. calcd for $C_{12}H_{13}ClO$: C, 69.07; H, 6.28 Found: C, 68.91; H, 6.14.

(3E,5E)-6-Chloro-1-(p-isopropylphenyl)-hexa-3,5-dien-1-ol **16b**: 4.66 g (93%, yellow oil); IR (neat) cm^{-1} 3380, 3085, 2960, 1610, 1510, 1465, 1420, 1055, 970; ^1H NMR (250 MHz, $CDCl_3$) δ 7.29 (d, 2H, J = 8.2Hz), 7.20 (d, 2H, J = 8.2Hz), 6.33 (dd, 1H, J = 13.1 and 10.7Hz), 6.04 (d, 1H, J = 13.1Hz), 5.97 (dd, 1H, J = 15.2 and 10.7Hz), 5.58 (dt, 1H, J = 15.2 and 7.2Hz), 4.59 (t, 1H, 6.4Hz), 2.89 (sept, 1H, J = 6.9Hz), 2.73 (dd, 2H, J = 6.4 and 2.3Hz), 2.32 (d, 1H, J = 3.0Hz), 1.23 (d, 6H, J = 6.9Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 148.80, 139.95, 133.80, 130.80, 128.45, 127.70, 125.70, 73.80, 42.50, 33.90, 23.95; Anal. calcd for $C_{15}H_{19}ClO$: C, 71.85; H, 7.64 Found: C, 71.52; H, 7.52.

(3E,5E)-6-Chloro-1-(p-methoxyphenyl)-hexa-3,5-dien-1-ol **16c**: 2.96 g (62%, yellow oil); IR (neat) cm^{-1} 3385, 3070, 2960, 2890, 2835, 1610, 1585, 1465, 1305, 1035, 990; ^1H NMR (250 MHz, $CDCl_3$) δ 7.27 (m, 2H), 6.80 (m, 2H), 6.33 (dd, 1H, J = 13.1 and 10.8Hz), 6.04 (d, 1H, J = 13.1Hz), 5.97 (dd, 1H, J = 15.2 and 10.6Hz), 5.58 (dt, 1H, J = 15.2 and 7.2Hz), 4.59 (t, 1H, J = 6.8Hz), 3.72 (s, 3H), 2.43 (t, 2H, J = 7.0Hz), 2.30 (d, 1H, J = 3.1Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 159.10, 135.85, 133.35, 131.05, 129.15, 127.00, 119.65, 113.80, 73.25, 55.25, 42.40; Anal. calcd for $C_{13}H_{15}ClO_2$: C, 65.41; H, 6.33 Found: C, 65.34; H, 6.22.

(1E,3E)-1-Chloro-undeca-1,3-dien-6-ol **16d**: 3.32 g (82%, yellow oil); IR (neat) cm^{-1} 3340, 2910, 2840, 1570, 970; ^1H NMR (250 MHz, $CDCl_3$) δ 6.42 (dd, 1H, J = 13.1 and 10.8Hz), 6.11 (d, 1H, J = 13.1Hz), 6.05 (dd, 1H, J = 15.1 and 10.8Hz), 5.70 (dt, 1H, J = 15.1 and 7.4Hz), 3.63 (m, 1H), 2.21 (m, 2H), 1.47 to 1.21 (m, 9H), 0.87 (t, 3H, J = 6.5Hz); ^{13}C NMR (63 MHz, $CDCl_3$) δ 133.40, 131.45, 129.10, 119.55, 71.05, 40.70, 36.90, 31.80, 25.30, 22.60, 14.00; Anal. calcd for $C_{11}H_{19}ClO$: C, 65.17; H, 9.45 Found: C, 65.08; H, 9.49.

(3E,5E)-6-Chloro-hexa-3,5-dien-1-ol **16e**: 2.39 g (90%, yellow oil); IR (neat) cm^{-1} 3370, 3088, 2960, 2840, 1650, 1590, 1100; ^1H NMR (250 MHz, $CDCl_3$) δ 6.40 (dd, 1H, J = 13.0 and 10.6Hz), 6.10 (d, 1H, J = 13.0Hz), 6.05 (dd, 1H, J = 15.0 and10.6Hz), 5.66 (dt, 1H, J = 15.0 and 7.2Hz), 3.65 (t, 2H, J = 6.3Hz), 2.31 (q, 2H, J = 6.3Hz), 1.71 (s, 1H); ^{13}C NMR (63 MHz, $CDCl_3$) δ 133.25, 131.30, 128.70, 119.50, 61.60, 35.85; Anal. calcd for C_6H_9ClO: C, 54.35; H, 6.84 Found: C, 54.49; H, 6.96.

General Procedure for the Synthesis of Chlorotrienes 3: To a stirred solution of chlorodiene 16 (10 mmol) and triethylamine (15 mmol, 2.1 mL) in CH_2Cl_2 (15 mL) was added at 0°C, methanesulfonyl chloride (12 mmol, 0.93 mL). After stirring at room temperature for 30 min, the mixture was hydrolyzed with a saturated aqueous solution of ammonium chloride (10 mL) and extracted with ether (3 x 20 mL). The combined organic layers were washed with water until pH = 7, dried over $MgSO_4$ and the solvent was removed *in vacuo*. The crude product thus obtained was dissolved in CH_2Cl_2 (20 mL) and DBU (15 mmol, 2.3 mL) was added at 0°C. The reaction mixture was stirred at room temperature overnight before to be hydrolyzed with a saturated aqueous solution of ammonium chloride (20 mL) and extracted with ether (3 x 20 mL). The organic extract was dried over $MgSO_4$ and the solvent was removed *in vacuo*. The residue was first purified by silica gel column chromatography (petroleum ether/CH_2Cl_2 80:20) then by recrystallization (**3a-c**) to give pure product.

(1E,3E,5E)-1-Chloro-6-phenyl-1,3,5-hexatriene **3a**: 1.41 g (74% from **16a**, yellow solid); mp: 99-101°C (*i*-Pr_2O); IR (KBr) cm^{-1} 3550, 3410, 3015, 2925, 1635, 1620, 1595, 1125, 1005, 960; ^1H NMR (400 MHz) δ 7.44 (d, 2H, J = 7.0Hz), 7.36 (t, 2H, J = 7.0Hz), 7.27 (t, 1H, J = 7.0Hz), 6.83 (dd, 1H, J = 16.0 and 10.5Hz), 6.64 (d, 1H, J = 16.0Hz), 6.58 (dd, 1H, J = 13.0 and 10.5Hz), 6.43 (dd, 1H, J = 15.0 and 10.5Hz), 6.31 (dd,

1H, J = 15.0 and 10.5Hz), 6.28 (d, 1H, J = 13.0Hz); ^{13}C NMR (100 MHz) δ 136.95, 133.75, 133.74 (for 2 C), 128.80, 128.55, 128.40, 128.25, 127.75, 120.75; CIMS (relative intensity) 208 ((M+18)$^+$, ^{35}Cl, 30%), 191 ((M+1)$^+$, ^{35}Cl, 100%); UV (CH_2Cl_2) λ = 322 nm (ε_{max} = 40000), λ = 337 nm (ε = 29500); Anal. calcd for $C_{12}H_{11}Cl$: C, 75.59; H, 5.81 Found: C, 75.55; H, 5.79.

(1E,3E,5E)-1-Chloro-6-(p-isopropylphenyl)-1,3,5-hexatriene **3b**: 1.42 g (61% from **16b**, yellow solid); R_f (petroleum ether/CH_2Cl_2 9:1) = 0.59; mp: 95-97°C (*i*-Pr_2O); IR (KBr) cm^{-1} 3075, 3000, 2870, 1645, 1615, 1470, 1390; ^{1}H NMR (400 MHz) δ 7.32 (d, 2H, J = 8.2Hz), 7.17 (d, 2H, J = 8.2Hz), 6.73 (dd, 1H, J = 15.5 and 9.9Hz), 6.56 (d, 1H, J = 15.5Hz), 6.52 (dd, 1H, J = 13.0 and 10.7Hz), 6.37 (dd, 1H, J = 15.1 and 9.9Hz), 6.22 (dd, 1H, J = 15.1 and 10.7Hz), 6.20 (d, 1H, J = 13.0Hz), 2.88 (sept, 1H, J = 6.9Hz), 1.23 (d, 6H, J = 6.9Hz); ^{13}C NMR (63 MHz) δ 148.80, 134.70, 134.00, 133.85, 133.80, 128.05, 127.50, 126.75, 126.45, 120.40, 33.90, 23.85; CIMS (relative intensity) 235 ((M+1)$^+$, ^{37}Cl, 37), 234 (M$^+$, ^{37}Cl, 29), 233 ((M+1)$^+$, ^{35}Cl, 91), 232 (M$^+$, ^{35}Cl, 8), 200 (22), 199 (100), 197 (43), 189 (10); UV (CH_2Cl_2) λ = 326 nm (ε_{max} = 45000), λ = 341 nm (ε = 33000); Anal. calcd for $C_{15}H_{17}Cl$: C, 77.41; H, 7.36 Found: C, 77.03; H, 7.30.

(1E,3E,5E)-1-Chloro-6-(p-methoxyphenyl)-1,3,5-hexatriene **3c**: 1.59 g (72% from **16c**, yellow solid); mp: 100-102°C (*i*-Pr_2O); IR (KBr) cm^{-1} 3060, 3010, 2965, 2935, 2840, 1640, 1620, 1595, 1570, 1260, 995; ^{1}H NMR (400 MHz) δ 7.33 (m, 2H), 6.83 (m, 2H), 6.65 (dd, 1H, J = 15.3 and 9.3Hz), 6.52 (d, 1H, J = 15.3Hz), 6.51 (dd, 1H, J = 13.0 and 10.3Hz), 6.35 (dd, 1H, J = 14.5 and 9.3Hz), 6.19 (dd, 1H, J = 14.5 and 10.3Hz), 6.18 (d, 1H, J = 13.0Hz), 3.80 (s, 3H); ^{13}C NMR (63 MHz) δ 159.45, 134.10, 133.95, 133.40, 129.90, 127.70, 127.50, 126.35, 120.10, 114.15, 55.30; CIMS (relative intensity) 223 ((M+1)$^+$, ^{37}Cl, 30), 222 (M$^+$, ^{37}Cl, 16), 221 ((M+1)$^+$, ^{35}Cl, 100), 220 (M$^+$, ^{35}Cl, 7), 219 (24), 188 (13), 187 (82), 185 (30); UV (CH_2Cl_2) λ = 332 nm (ε_{max} = 38000); Anal. calcd for $C_{13}H_{13}ClO$: C, 70.75; H, 5.94 Found: C, 70.62; H, 5.90.

(1E,3E,5E)-1-Chloro-1,3,5-undecatriene **3d**: 830 mg (45% from **16d**, yellow oil); IR (neat) cm^{-1} 3420, 3010, 2970, 2850, 1650, 1060; ^{1}H NMR (400 MHz) δ 6.33 (dd, 1H, J = 13.1 and 10.5Hz), 6.18 (dd, 1H, J = 14.6 and 9.6Hz), 6.11 (d, 1H, J = 13.1Hz), 6.01 (m, 2H), 5.74 (dt, 1H, J = 15.1 and 6.9Hz), 2.05 (q, 2H, J = 6.9Hz), 1.50 to 1.20 (m, 6H), 0.85 (t, 3H, J = 7.0Hz); ^{13}C NMR (63 MHz) δ 137.10, 134.00, 133.85, 129.70, 125.80, 119.40, 32.80, 31.35, 28.80, 22.45, 13.95; Anal. calcd for $C_{11}H_{17}Cl$: C, 71.53; H, 9.28 Found: C, 71.73; H, 9.40. **3d** was also prepared in 55% yield (1.00 g) from enyne **17** according to the literature procedure.[10b]

(1E,3E,5E)-1-(p-Methoxyphenyl)-1-phenyl-1,3,5-hexatriene **22**: To a solution of $PdCl_2(PPh_3)_2$ (0.05 mmol, 35 mg), chlorotriene **3** (1 mmol), triethylamine (8 mmol, 1.1 mL) in 3 mL of anhydrous THF was added dropwise at 20°C a solution of Grignard reagents (2 mmol, 1.0N in THF). After stirring at room temperature for 2 to 4h, the reaction was hydrolyzed at 0°C with aqueous hydrochloric acid (1M, 10 mL) and extracted with Et_2O (3 x 10 mL). The organic extract was dried over $MgSO_4$ and the solvent was removed *in vacuo*. Filtration through silica gel (eluent: CH_2Cl_2) gave pure triene **22** as a yellow solid in 78 to 82% yield; mp: 210-212°C (CH_2Cl_2/Et_2O); IR (KBr) cm^{-1} 3560, 3470, 3415, 1617, 1508, 1300, 1245, 1180, 995; ^{1}H NMR (250 MHz) δ 7.48 to 7.18 (m, 7H), 6.98 to 6.68 (m, 4H), 6.68 to 6.38 (m, 4H), 3.82 (s, 3H); ^{13}C NMR (63 MHz) δ 159.55, 137.65, 134.15, 132.60, 132.45, 132.10, 130.30, 129.45, 128.80, 127.75, 127.55, 127.20, 126.40, 114.25, 55.40; Anal. calcd for $C_{19}H_{18}O$: C, 86.99; H, 6.92 Found: C, 87.03; H, 6.95.

General Procedure for the Synthesis of Trienynes 23: To a suspension of $PdCl_2(PhCN)_2$ (0.25 mmol, 100 mg), CuI (0.5 mmol, 95 mg) and chlorotriene **3** (5 mmol) in piperidine (10 mL) was slowly added, at room temperature, *via* a syringe pump (addition time 1h) trimethylsilyl acetylene (6 mmol, 583 mg) in 2 mL of piperidine. The reaction was stirred at room temperature and monitored by TLC analysis until complete consumption of the chlorotriene **3** (3 to 4h) before to be treated by a similar procedure as described for **8a**. The crude product was first purified by silica gel column chromatography (petroleum ether/CH_2Cl_2 9:1) then by recrystallization to give pure trienyne **23**.

(3E,5E,7E)-8-Phenyl-1-trimethylsilyl-octa-3,5,7-trien-1-yne **23a**: 1.15 g (91%, orange solid); mp: 86-87°C (petroleum ether); IR (KBr) cm^{-1} 2960, 2850, 1620, 1590, 1515, 1460, 1305, 1180, 1075; ^{1}H NMR (400 MHz) δ 7.38 (d, 2H, J = 7.1Hz), 7.30 (t, 2H, J = 7.1Hz), 7.21 (t, 1H, J = 7.1Hz), 6.80 (dd, 1H, J = 15.1 and 10.7Hz), 6.67 (dd, 1H, J = 15.1 and 10.7Hz), 6.61 (d, 1H, J = 15.1Hz), 6.46 (dd, 1H, J = 15.1 and 10.7Hz), 6.35 (dd, 1H, J = 15.1 and 10.7Hz), 5.64 (d, 1H, J = 15.1Hz), 0.19 (s, 9H); ^{13}C NMR (63 MHz) δ 142.70, 137.00, 135.70, 134.50, 132.10, 128.70, 128.50, 127.90, 126.50, 110.95, 104.90, 98.40, -0.05; UV (CH_2Cl_2) λ = 364 nm (ε = 41000), λ = 347 nm (ε_{max} = 52000); Anal. calcd for $C_{17}H_{20}Si$: C, 80.89; H, 7.99 Found: C, 80.60; H, 8.04.

(3E,5E,7E)-8-(p-Isopropylphenyl)-1-trimethylsilyl-octa-3,5,7-trien-1-yne **23b**: 1.37 g (93%, orange solid); mp: 86-88°C (ether/petroleum ether); IR (KBr) cm^{-1} 2960, 2380, 1640, 1615, 1390, 1275, 1100; ^{1}H NMR (400 MHz) δ 7.32 (d, 2H, J = 8.2Hz), 7.17 (d, 2H, J = 8.2Hz), 6.76 (dd, 1H, J = 15.4 and 10.0Hz), 6.70 (dd, 1H, J = 15.5 and 10.5Hz), 6.59 (d, 1H, J = 15.4Hz), 6.44 (dd, 1H, J = 14.7 and 10.0Hz), 6.32 (dd, 1H, J = 14.7 and 10.5Hz), 5.62 (d, 1H, J = 15.5Hz), 2.88 (sept, 1H, J = 6.9Hz), 1.23 (d, 6H, J = 6.9Hz), 0.19 (s, 9H); ^{13}C

NMR (63 MHz) δ 148.95, 142.85, 135.95, 134.70, 134.55, 131.55, 127.70, 126.80, 126.55, 110.55, 105.00, 98.20, 33.90, 23.85, -0.05; Anal. calcd for $C_{20}H_{26}Si$: C, 81.57; H, 8.90 Found: C, 81.53; H, 8.86.

(3E,5E,7E)-8-(p-Methoxyphenyl)-1-trimethylsilyl-octa-3,5,7-trien-1-yne **23c**: 1.02 g (72%, orange solid); mp: 142-143°C (ether/petroleum ether); IR (KBr) cm^{-1} 3545, 3415, 3010, 2955, 2895, 2840, 2155, 2115, 1615, 1590, 1510, 1255, 1010, 850; ^1H NMR (250 MHz) δ 7.32 (d, 2H, J = 8.8Hz), 6.84 (d, 2H, J = 8.8Hz), 6.70 (dd, 1H, J = 15.5 and 10.5Hz), 6.67 (dd, 1H, J = 15.4 and 9.6Hz), 6.55 (d, 1H, J = 15.3Hz), 6.43 (dd, 1H, J = 14.6 and 9.6Hz), 6.29 (dd, 1H, J = 14.6 and 10.5Hz), 5.60 (d, 1H, J = 15.5Hz), 3.79 (s, 3H), 0.18 (s, 9H); ^{13}C NMR (63 MHz) δ 159.55, 142.95, 136.05, 134.20, 131.00, 129.90, 127.80, 126.50, 114.15, 110.20, 105.05, 98.00, 55.30, -0.05; CIMS (relative intensity) 284 (23), 283 ($(M+1)^+$, 100), 282 (M^+, 33); UV (CH_2Cl_2) λ = 358 nm (ε_{max} = 55500); Anal. calcd for $C_{18}H_{22}OSi$: C, 76.54; H, 7.85 Found: C, 76.60; H, 7.89.

General Procedure for the Synthesis of Terminal Trienynes 24: A mixture of trienyne **23** (3 mmol), MeOH (5 mL) and K_2CO_3 (3.3 mmol, 460 mg) was stirred at room temperature for 1 to 2h before to be concentrated. CH_2Cl_2 was added (20 mL) and the organic layer washed with water (2 x 10 mL), dried over $MgSO_4$ and the solvent was removed *in vacuo*. The crude product was purified by silica gel column chromatography (petroleum ether/CH_2Cl_2 9:1) to give pure terminal trienyne **24**.

(3E,5E,7E)-8-Phenyl-octa-3,5,7-trien-1-yne **24a**: 568 mg (90%, orange solid); mp: 76-77°C (ether); IR (KBr) cm^{-1} 3480, 3410, 3280, 3025, 2095, 1645, 1625, 1005; ^1H NMR (400 MHz) δ 7.44 (d, 2H, J = 7.1Hz), 7.36 (t, 2H, J = 7.1Hz), 7.27 (t, 1H, J = 7.1Hz), 6.79 (dd, 1H, J = 15.7 and 10.7Hz), 6.68 (d, 1H, J = 15.7Hz), 6.53 (dd, 1H, J = 15.0 and 10.5Hz), 6.41 (dd, 1H, J = 15.0 and 10.7Hz), 5.67 (dd, 1H, J = 15.7 and 2.3Hz), 3.16 (d, 1H, J = 2.3Hz); ^{13}C NMR (63 MHz) δ 142.70, 137.00, 135.70, 134.50, 132.10, 128.70, 128.50, 127.90, 126.50, 110.95, 104.90, 98.40; CIMS (relative intensity) 181 ($(M+1)^+$, 100), 180 (M^+, 62), 179 ($(M-1)^+$, 45), 178 (22), 165 (46); UV (CH_2Cl_2) λ = 338 nm (ε_{max} = 45000), λ = 355 nm (ε = 36500); Anal. calcd for $C_{14}H_{12}$: C, 93.29; H, 6.71 Found: C, 93.40; H, 6.74.

(3E,5E,7E)-8-(p-Isopropylphenyl)-octa-3,5,7-trien-1-yne **24b**: 653 mg (98%, orange solid); mp: 60-62°C (ether/petroleum ether) ; IR (KBr) cm^{-1} 3480, 3415, 3240, 2960, 2085, 1645, 1615, 1005; ^1H NMR (400 MHz) δ 7.32 (d, 2H, J = 8.2Hz), 7.17 (d, 2H, J = 8.2Hz), 6.76 (dd, 1H, J = 15.4 and 9.9Hz), 6.73 (dd, 1H, J = 15.5 and 10.5Hz), 6.60 (d, 1H, J = 15.4Hz), 6.46 (dd, 1H, J = 14.7 and 9.9Hz), 6.33 (dd, 1H, J = 14.7 and 10.5Hz), 5.58 (dd, 1H, J = 15.5 and 2.4Hz), 3.09 (d, 1H, J = 2.4Hz), 2.88 (sept, 1H, J = 6.9Hz), 1.23 (d, 6H, J = 6.9Hz); ^{13}C NMR (100 MHz) δ 149.00, 143.50, 136.20, 134.80, 134.60, 131.15, 127.55, 126.80, 126.60, 109.40, 83.45, 83.35, 33.90, 23.85; CIMS (relative intensity) 224 ($(M+2)^+$, 31), 223 ($(M+1)^+$, 100), 222 (M^+, 14), 179 (10); Anal. calcd for $C_{17}H_{18}$: C, 91.84; H, 8.16 Found: C, 91.98; H, 8.12.

(3E,5E,7E)-8-(p-Methoxyphenyl)-octa-3,5,7-trien-1-yne **24c**: 593 mg (94%, orange solid); R_f (petroleum ether/CH_2Cl_2) = 0.37; mp: 127-128°C (ether) ; IR (KBr) cm^{-1} 3475, 3415, 3270, 2955, 2935, 1640, 1615, 1590, 1515, 1180, 1150, 1000; ^1H NMR (400 MHz) δ 7.33 (d, 2H, J = 8.8Hz), 6.84 (d, 2H, J = 8.8Hz), 6.73 (dd, 1H, J = 15.5 and 10.6Hz), 6.67 (dd, 1H, J = 15.3 and 9.8Hz), 6.56 (d, 1H, J = 15.3Hz), 6.45 (dd, 1H, J = 14.5 and 9.8Hz), 6.30 (dd, 1H, J = 14.5 and 10.6Hz), 5.56 (dd, 1H, J = 15.5 and 2.4Hz), 3.80 (s, 3H), 3.09 (d, 1H, J = 2.4Hz); ^{13}C NMR (63 MHz) δ 159.60, 143.60, 136.30, 134.40, 130.60, 129.80, 127.85, 126.35, 114.15, 109.05, 114.15, 109.05, 83.50, 80.20, 55.30; CIMS (relative intensity) 212 ($(M+2)^+$, 27), 211 ($(M+1)^+$, 100), 210 (M^+, 19); UV (CH_2Cl_2) λ = 350 nm (ε_{max} = 51000), λ = 367 nm (ε = 44000); Anal. calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71 Found: C, 85.52; H, 6.80.

Synthesis of Navenone B

(3E,5E,7E,9E)-10-Phenyl-deca-3,5,7,9-tetraen -2-ol **25**[18]: To a suspension of $PdCl_2(PhCN)_2$ (0.15 mmol, 60 mg), CuI (0.3 mmol, 57 mg) and chlorotriene **3a** (3 mmol, 572 mg) in piperidine (7 mL) was slowly added, at room temperature, *via* a syringe pump (addition time 1h) 3-btyn-2-ol (4.5 mmol, 315 mg) in 2 mL of piperidine. The reaction was stirred at room temperature and monitored by TLC analysis until complete consumption of the chlorotriene **3a** (3h) before to be treated by a similar procedure as described for **8a**. The crude product obtained was enough pure and was used for the synthesis of **25** without purification; ^1H NMR (250 MHz) δ 7.35 (m, 5H), 6.80 (dd, 1H, J = 15.4 and 9.6Hz), 6.64 (dd, 1H, J = 15.1 and 10.5Hz), 6.59 (d, 1H, J = 15.1Hz), 6.45 (dd, 1H, J = 14.4 and 9.6Hz), 6.33 (dd, 1H, J = 14.4 and 10.5Hz), 5.63 (dd, 1H, J = 15.4 and 1.8Hz), 4.65 (qd, 1H, J = 6.7 and 1.8Hz), 1.85 (s, 1H), 1.55 (d, 3H, J = 6.5Hz); ^{13}C NMR (63 MHz) δ 142.05, 135.45, 134.45, 131.80, 128.65, 128.45, 127.90, 126.95, 126.50, 110.35, 94.50, 83.70, 59.00, 24.35.

The propargylic alcohol function of this crude material was reduced by Red-Al® according to the procedure described for **9a**. The residue obtained was first purified by silica gel column chromatography (AcOEt/CH_2Cl_2 1:4) then by recrystallization to give pure tetraene **25** as a yellow solid: 488 mg (79% from **3a**); mp: 124-126°C; IR (KBr) cm^{-1} 3550, 3410, 3015, 1640, 1615, 1595, 1120, 1005; ^1H NMR (400 MHz) δ 7.45 (d, 2H, J = 7.5Hz), 7.36 (t, 2H, J = 7.5Hz), 7.28 (d, 1H, J = 7.5Hz), 6.88 (dd, 1H, J = 15.0 and 6.9Hz), 6.61 (d, 1H, J = 15.0Hz), 6.50 to 6.25 (m, 5H), 5.82 (dd, 1H, J = 15.0 and 7.0Hz), 4.42 (quint, 1H, J = 7.9Hz), 1.60 (s, 1H), 1.35 (d, 3H, J = 7.9Hz); ^{13}C NMR (63 MHz) δ 137.50, 137.30, 133.50, 133.30, 133.15, 132.65,

132.30, 129.80, 129.00, 128.60, 127.50, 126.30, 68.60, 23.30; CIMS (relative intensity) 244 ($(M+18)^+$, 20), 227 ($(M+1)^+$, 15), 209 (100); Anal. calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02 Found: C, 85.07; H, 8.09.

(3E,5E,7E,9E)-10-Phenyl-deca-3,5,7,9-tetraen -2-one **26**[18]: To a suspension of MnO_2 (40 mmol, 3.50 g) in CH_2Cl_2 (10 mL) was added tetraenol **25** (2 mmol, 452 mg). After 1h, the mixture was filtered on a pad of celite. Evaporation of the solvent gave the crude product, which was chromatographed over silica gel (petroleum ether/ether); 358 mg (80%, orange solid); mp: 137-138°C; ^{1}H NMR (400 MHz) δ 7.46 (d, 2H, J = 7.5Hz), 7.37 (t, 2H, J = 7.4Hz), 7.31 (d, 1H, J = 7.5Hz), 7.23 (dd, 1H, J = 15.0 and 11.0Hz), 6.91 (dd, 1H, J = 15.0 and 10.4Hz), 6.74 (dd, 1H, J = 14.0 and 11.0Hz), 6.72 (d, 1H, J = 15.0Hz), 6.64 (dd, 1H, J = 14.0 and 10.5Hz), 6.48 (dd, 1H, J = 14.0 and 11.0Hz), 6.42 (dd, 1H, J = 14.0 and 11.0Hz), 6.20 (d, 1H, J = 15.5Hz), 2.32 (s, 3H); ^{13}C NMR (100 MHz) δ 198.30, 143.20, 141.55, 137.70, 136.85, 135.30, 132.15, 130.50, 129.85, 128.70, 128.45, 128.15, 126.65, 27.35.

(1E,3E,5E,9E,11E)-1-Phenyl-heptadeca-1,3,5,9,11-pentaen-7-yne **28a**: The same procedure was used as described for **23**, from chlorotriene **3a** (1 mmol, 191 mg) and terminal dienyne[10b] **27** (1.2 mmol, 178 mg). Purification by silica gel chromatography (petroleum ether/CH_2Cl_2 8:2) afforded the polyenyne **28a** as an orange solid in 60% yield (181 mg); mp: 95-97°C; IR (KBr) cm^{-1} 3020, 2965, 2920, 2855, 2075, 1635, 1615, 1595, 1260, 1000, 990; ^{1}H NMR (400 MHz) δ 7.45 (d, 2H, J = 7.0Hz), 7.37 (t, 2H, J = 7.0Hz), 7.29 (d, 1H, J = 7.0Hz), 6.87 (dd, 1H, J = 15.0 and 10.0Hz), 6.69 (dd, 1H, J = 15.0 and 10.0Hz), 6.66 (d, 1H, 15.0Hz), 6.61 (dd, 1H, J = 15.0 and 10.0Hz), 6.51 (dd, 1H, J = 15.0 and 10.0Hz), 6.43 (dd, 1H, J = 15.0 and 10.0Hz), 6.16 (dd, 1H, J = 15.0 and 10.0Hz), 5.87 (dt, 1H, J = 15.0 and 7.0Hz), 5.83 (dd, 1H, J = 15.0 and 2.0Hz), 5.70 (dd, 1H, J = 15.0 and 2.0Hz), 2.16 (q, 2H, J = 7.0Hz), 1.55 (quint, 2H, J = 7.0Hz), 1.40 to 1.25 (m, 4H), 0.94 (t, 3H, J = 7.0Hz); ^{13}C NMR (63 MHz) δ 142.05, 141.05, 138.50, 137.15, 134.95, 134.10, 132.55, 129.85, 128.65, 127.80, 126.50, 111.55, 108.90, 93.70, 91.80, 32.85, 31.40, 28.70, 22.50, 14.00; UV (CH_2Cl_2) λ = 348 nm (ε_{max} = 43600); Anal. calcd for $C_{23}H_{26}$: C, 91.34; H, 8.66 Found: C, 91.57; H, 8.71.

(1E,3E,5E,9E,11E,13E)-1-(p-Isopropylphenyl)-14-phenyl-tetradeca-1,3,5,9,11,13-hexatrien-7-yne **28b**: The same procedure was used as described for **23**, from chlorotriene **3b** (2 mmol, 466 mg) and terminal trienyne **24a** (1 mmol, 180 mg). Purification by recrystallization (CH_2Cl_2) afforded the polyenyne **28b** as an orange solid in 53% yield (200 mg); mp: 210-211°C (CH_2Cl_2); IR (KBr) cm^{-1} 3550, 3475, 3415, 3015, 2955, 2870, 1885, 1815, 1735, 1620, 1595, 1450, 1285, 1000, 865; ^{1}H NMR (400 MHz) δ 7.50 to 7.20 (m, 9H), 6.87 (dd, 1H, J = 15.5 and 10.0Hz), 6.83 (dd, 1H, J = 15.5 and 10.0Hz), 6.69 (m, 4H), 6.47 (m, 4H), 5.86 (dd, 1H, 13.0 and 2.5Hz), 5.83 (dd, 1H, J = 13.0 and 2.5Hz), 2.93 (sept, 1H, J = 7.0Hz), 1.29 (d, 6H, J = 7.0Hz); ^{13}C NMR (63 MHz) δ 148.90, 141.60, 141.35, 137.10, 135.60, 135.25, 134.75, 134.35, 134.25, 132.55, 132.00, 128.70, 127.85, 126.80, 126.55, 126.50, 111.45, 111.00, 94.35, 94.10, 33.90, 23.85; CIMS (relative intensity) 394 ($(M+18)^+$, 3), 378 ($(M+2)^+$, 32), 377 ($(M+1)^+$, 100) 376 (M^+, 19); UV (CH_2Cl_2) λ = 280 nm (ε = 17500), λ = 339 nm (ε = 27000), λ = 423 nm (ε_{max} = 78000), λ = 449 nm (ε = 64000); Anal. calcd for C29H28: C, 92.50; H, 7.50 Found: C, 92.46; H, 7.54.

(1E,3E,5E,7E,9E,11E)-1-Phenyl-1,3,5,7,9,11-heptadecahexaene 30a: A solution of polyenyne 28a (0.33 mmol, 100 mg) in MeOH (5 mL) was added to a suspension of activated zinc19 (1 g) in 1/1 MeOH/H2O (8 mL). After stirring for 3h at 30°C, the suspension was filtered on a pad of celite and the solid washed with MeOH. The combined solutions were evaporated under reduced pressure and the residue was dissolved in ether (20 mL) dried over MgSO4 and evaporated under reduced pressure to give 70 mg (70%, crude product) of the hexaene 30a as an orange-brown solid which is unstable during the purification step (95% isomeric purity); mp: 173-175°C; IR (nujol) cm-1 3060, 3010, 2950, 2920, 2845, 1635, 1605, 1010, 975; 1H NMR (400 MHz) _ 7.45 (d, 2H, J = 7.0Hz), 7.35 (t, 2H, J = 7.0Hz), 7.25 (d, 1H, J = 7.0Hz), 6.89 (m, 1H), 6.59 (d, 1H, J = 15.0Hz), 6.47 to 6.29 (m, 8H), 6.14 (dd, 1H, J = 15.0 and 10.0Hz), 5.88 (dt, 1H, J = 15.0 and 7.0Hz), 2.25 (q, 2H, J = 7.0Hz), 1.45 (quint, 2H, J = 7.0Hz), 1.37 to 1.25 (m, 4H), 0.92 (t, 3H, J = 7.0Hz); ^{13}C NMR (63 MHz) δ 137.50, 136.30, 133.85, 133.75, 133.05, 132.65, 132.35, 130.80, 130.60, 129.30, 127.45, 128.65, 126.35, 32.95, 31.45, 29.00, 22.55, 14.05; CIMS (relative intensity) 305 ($(M+1)^+$, 100); UV (CH_2Cl_2) λ = 381 nm (ε_{max} = 35000).

(1E,3E,5E,7E,9E,11E,13E)-1-(p-Isopropylphenyl)-14-phenyl-1,3,5,7,9,11,13-tetradecaheptaene **30b**: The same procedure was used as described for **30a**, from polyenyne **28b** (0.14 mmol, 53 mg). The heptaene **30b** was obtained as a highly insoluble red solid. UV, CIMS and microanalyses were consistent with the assigned structure. 26 mg (50%); mp: 279-280°C; CIMS (relative intensity) 379 ($(M+1)^+$, 100); UV (CH_2Cl_2) λ = 342 nm (ε = 15000), λ = 417 nm (ε = 61500), λ = 439 nm (ε_{max} = 76500), λ = 468 nm (ε = 59000)); Anal. calcd for $C_{29}H_{30}$: C, 92.01; H, 7.99 Found: C, 91.78; H, 7.94.

ACKNOWLEDGEMENTS

The authors are grateful to the CNRS for their financial support of this work.

REFERENCES AND NOTES

Present adress: Ecole Supérieure de Chimie Organique et Minérale, Département de Chimie associé au CNRS, 13 Bd de l'Hautil, 95092 Cergy-Pontoise Cedex, France.

1. For reviews see: a) Heck, R.F.; *Palladium Reagents in Organic Syntheses*; Academic Press: London, **1985**. b) Knight, D.W. In *Comprehensive Organic Synthesis*; Trost, B.M. and Fleming, I., Eds.: Pergamon Press: New York, **1991**, *3*, 481-520. c) Tsuji, J. *Palladium Reagents and Catalysts*; John Wiley & Sons Ltd.: Chichester, **1995**. d) Cousins, R.P.C. *Contemporary Org. Synth.* **1995**, 441-461.
2. For a review see: a) Marsden, S.P. *Contemporary Org. Synth.* **1997**, 118-135. For some representative examples see: b) Tohdo, K.; Hamada, Y.; Shioiri, T. *Tetrahedron Lett.* **1992**, *33*, 2031-2034. c) Babudri, F.; Fiandanese, V.; Mazzone, L.; Naso, F. *Tetrahedron Lett.* **1994**, *35*, 8847-8850. d) Stewart, S.K.; Whiting, A. *Tetrahedron Lett.* **1995**, *36*, 3929-3932. e) Wong, T.; Tjepkema, M.W.; Audrain, H.; Wilson, P.D.; Fallis, A.G. *Tetrahedron Lett.* **1996**, *37*, 755-758. f) Nishiyama, T.; Esumi, T.; Iwabuchi, Y.; Irie, H.; Hatakeyama, S. *Tetrahedron Lett.* **1998**, *39*, 43-46. g) Bujard, M.; Ferri, F.; Alami, M. *Tetrahedron Lett.* **1998**, *39*, 4243-4246.
3. a) Duhamel, L.; Plé, G.; Ramondenc, Y. *Tetrahedron Lett.* **1989**, *30*, 7377-7380. b) Vicart, N.; Castet-Caillabet, D.; Ramondenc, Y.; Plé, G.; Duhamel, L. *Synlett.* **1998**, 411-412. For other methods see: c) Ronald, R.C.; Lansinger, J.M.; Lillie, T.S.; Wheeler, C.J. *J. Org. Chem.* **1982**, *47*, 2541-2549. d) Corey, E.J.; Ruden, R.A. *Tetrahedron Lett.* **1973**, 1495-1499. e) Matsumoto, M.; Kuroda, K. *Tetrahedron Lett.* **1980**, *21*, 4021-4024. f) Ratovelomanana, V.; Linstrumelle, G.; *Tetrahedron Lett.* **1984**, *25*, 6001-6004. g) Hayashi, T.; Konishi, M.; Okamoto, Y.; Kabeta, K.; Kumada, M. *J. Org. Chem.* **1986**, *51*, 3772-3781. h) Avignon-Tropis, M.; Pougny, J.R.; Frechard-Ortuno, I.; Linstrumelle, G. *Tetrahedron* **1991**, *47*, 7279-7286. i) Chemin, D.; Linstrumelle, G. *Tetrahedron* **1992**, *48*, 1943-1952. j) Yokokawa, F.; Hamada, Y.; Shioiri, T. *Tetrahedron Lett.* **1993**, *34*, 6559-6562. k) Lipshutz, B.H.; Alami, M.; Susfalk, R.B. *Synlett* **1993**, 693-695. l) Babudri, F.; Fiandanese, V.; Naso, F.; Punzi, A. *Tetrahedron Lett.* **1994**, *35*, 2067-2070. m) Chowdhury, S.; Roy, S. *J. Org. Chem.* **1997**, *62*, 199-200.
4. Uenishi, J.; Kawahama, R.; Yonemitsu, O.; Tsuji, J. *J. Org. Chem.* **1996**, *61*, 5716-5717.
5. Kiehl, A.; Eberhardt, A.; Müllen, K. *Liebigs Ann.* **1995**, 223-230.
6. a) Spangler, C.W.; Woods, G.F. *J. Org. Chem.* **1963**, *30*, 2218-2222. b) Williams, D.R.; Nishitani, K.; Bennett, W.; Sit, S.Y. *Tetrahedron Lett.* **1981**, *22*, 3745-3748. c) Soullez, D.; Plé, G.; Duhamel, L.; Duhamel, P. *J. Chem. Soc. Chem. Commun.* **1995**, 563-564. d) Charoenying, P.; Davies, D.H.; McKerrecher, D.; Taylor, R.J.K. *Tetrahedron Lett.* **1996**, *37*, 1913-1916. e) Macdonald, G.; Lewis, N.J.; Taylor, R.J.K. *J. Chem. Soc. Chem. Commun.* **1996**, 2647-2648. f) Soullez, D.; Plé, G.; Duhamel, L; *J. Chem. Soc. Perkin Trans. 1*, **1997**, 1639-1645. g) Lipshutz, B.H.; Lindsley, C. *J. Am. Chem. Soc.* **1997**, *119*, 4555-4556. h) Lipshutz, B.H.; Ullman, B.; Lindsley, C.; Pecchi, S.; Buzard, D.J.; Dickson, D. *J. Org. Chem.* **1998**, *63*, 6092-6093.
7. For a review see: a) Linstrumelle, G.; Alami, M. *(E) and (Z)-dichloroethylene* in *Encyclopedia of Reagents for Organic Synthesis*, Paquette, L.; Ed., Wiley, Chichester **1995**, *3*, 1710-1712. b) Crousse, B.; Alami, M.; Linstrumelle, G. *Tetrahedron Lett.* **1995**, *36*, 4245-4248.
8. Alami, M.; Linstrumelle, G. *Tetrahedron Lett.* **1991**, *32*, 6109-6112.
9. a) Mladenova, M.; Alami, M.; Linstrumelle, G. *Tetrahedron Lett.* **1996**, *37*, 6547-6550. b) Crousse, B.; Alami, M.; Linstrumelle, G. *Tetrahedron Lett.* **1997**, *38*, 5297-5300.
10. a) Chemin, D.; Linstrumelle, G. *Tetrahedron* **1994**, *50*, 5335-5344. b) Alami, M.; Gueugnot, S.; Domingues, E.; Linstrumelle, G. *Tetrahedron* **1995**, *51*, 1209-1220.
11. a) Overman, L.E.; Knoll, F.M. *Tetrahedron Lett.* **1979**, 321-324. b) Oehlschlager, A.C.; Mishra, P.; Dhami, S. *Can. J. Chem.* **1984**, *62*, 791-797.
12. Blanchard-Desce, M.; Alain, V.; Bedworth, P.V.; Marder, S.R.; Fort, A.; Runser, C.; Barzoukas, M. *Chem. Eur. J.* **1997**, *3*, 1091-1104.
13. Crousse, B.; Alami, M.; Linstrumelle, G. *Synlett* **1997**, 992-994.
14. Reaction of **16e** with MsCl followed by treatment of the corresponding mesylate with DBU leads to a mixture of materials (no starting material was left). Chlorotriene **3e** was probably formed but it is not stable under these conditions and decomposed rapidly. This observation has also been noticed in a previous study, see: Spangler, C.W.; Woods, G.F. *J. Org. Chem.* **1965**, *28*, 2218-2222.
15. Ratovelomanana, V.; Linstrumelle, *G. Bull. Soc. Chim. Fr.* **1986**, 174-176.
16. Cahiez, G.; Alami, M. Manganese dioxide, in *Encyclopedia of Reagents for Organic Synthesis*, Paquette, L.; Ed. Wiley, Chichester **1995**, *5*, 3229-3235.
17. Ramiandrasoa, P.; Brehon, B.; Thivet, A.; Alami, M.; Cahiez, G. *Tetrahedron Lett.* **1997**, *38*, 2447-2450.

18. a) Sleeper, H.L.; Fenical, W. *J. Am. Chem. Soc.* **1977**, *99*, 2367-2368. b) Hemming, K.; Taylor, R.J.K. *J. Chem. Soc. Chem. Comm.* **1993**, 1409-1410. c) Soullez, D.; Ramondenc, Y.; Ple, G.; Duhamel, L. *Nat. Prod. Lett.* **1994**, *4*, 203-208; *CA* **1994**, *121*, 179296. d) Solladié, G.; Colobert, F.; Stone, G.B. *Synlett.* **1995**, 1135-1137.
19. Boland, W.; Schroer, N.; Sieler, C.; Feigel, M. *Helv. Chim. Acta* **1987**, *70*, 1025-1040.
20. Itatani, H.; Bailer, J.C. *J. Am. Oil. Chem. Soc.* **1967**, *44*, 147-149.
21. Doyle, J. R.; Slade, P. E.; Jonassen, H. B. *Inorg. Synth.* **1960**, *6*, 216-219.
22. Cotton, F. A.; Faut, O. D.; Goodgame, D. M. L. *J. Am. Chem. Soc.* **1961**, *83*, 344-351.
23. Schmidt, B.; Kocienski, P.; Reid, G. *Tetrahedron* **1996**, *52*, 1617-1630.