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An Efficient Synthesis of 1,3(E),5(Z), 1,3(E),5(E) and 1,3(Z),5(Z)-Trienes: Application to the Synthesis of Galbanolenes and (9Z,11E)-9,11,13-Tetradecatrien-1-yl Acetate.

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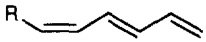
Abstract: The (Pd-Cu)-catalyzed reactions of trimethylsilyl acetylene with (E) or (Z)-chloroenynes, or 1-chloro-(1E,3E)-dienes, followed by desilylation and zinc-reduction of the triple bonds led respectively to (3E,5Z), (3Z,5Z) and (3E,5E)-trienes. Application to the syntheses of galbanolenes and (9Z,11E)-9,11,13-tetradecatrien-1-yl acetate has been realized.

Stereodefined conjugated trienes having terminal vinyl units are found in natural products:

- (3E,5Z) and (3E,5E)-1,3,5-undecatrienes **1a** and **3a** (galbanolenes) have been isolated from essential oils of galbanum[1] and seaweed.[2] The isomer **1a** is known to exhibit interesting olfactive properties and is widely used in the perfume industry.

- (9Z,11E)-9,11,13-tetradecatrienyl acetate **1b** and the corresponding aldehyde have been isolated as main components of the sex pheromone of two Lepidoptera species[3]: *Ectomyelois ceratoniae (pyralidae)* which is a widespread pyralid moth of nuts and fruits and *Stenoma cecropia (Stenomidae)* which is a serious defoliator of oil palm trees in South America.

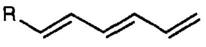


1

2

a R = C_5H_{11}

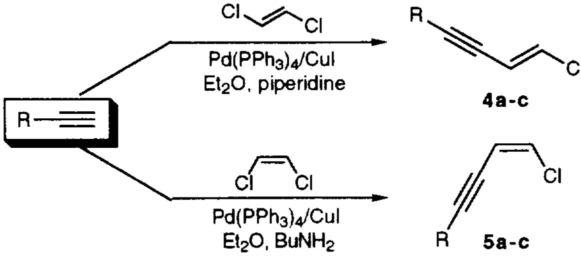
b R = $(CH_2)_8$-OAc



3

Among the various methods available for the stereoselective synthesis of conjugated trienes having a defined geometry,[4] the Wittig reaction has often been utilized. However, this reaction is not totally stereoselective and isolation of pure isomers by chromatography is required.[3a, 5] A new approach based on the sequential stereospecific substitution of (E) and (Z)-dichloroethylenes by terminal alkynes followed by stereoselective reduction of the triple bonds appears to be a promising alternative.[6, 7] Furthermore, vinyl chlorides have recently been shown to react very rapidly with 1-alkynes to give high yields of enynes[8] (71-97%) in the presence of a catalytic amount of $PdCl_2(PhCN)_2$ and CuI in piperidine.[9] We report herein a short and chemoselective synthesis of the trienes **1**, **2a** and **3a** which is based on the stereospecific palladium-copper catalyzed reaction of trimethylsilyl acetylene with respectively (E)-chloroenyne **4a**, (Z)-chloroenyne **5a**, and 1-chloro-(1E,3E)-diene **10** followed by desilylation and zinc reduction of the triple bonds.

The pure (E) and (Z)-chloroenynes **4** and **5** were easily obtainable in high stereoisomeric purity ($\geq$ 99.9%) by reaction of 1-alkynes with (E) and (Z)-1,2-dichloroethylenes[6] in the presence of $Pd(PPh_3)_4$ and CuI in ether (scheme 1)[10].

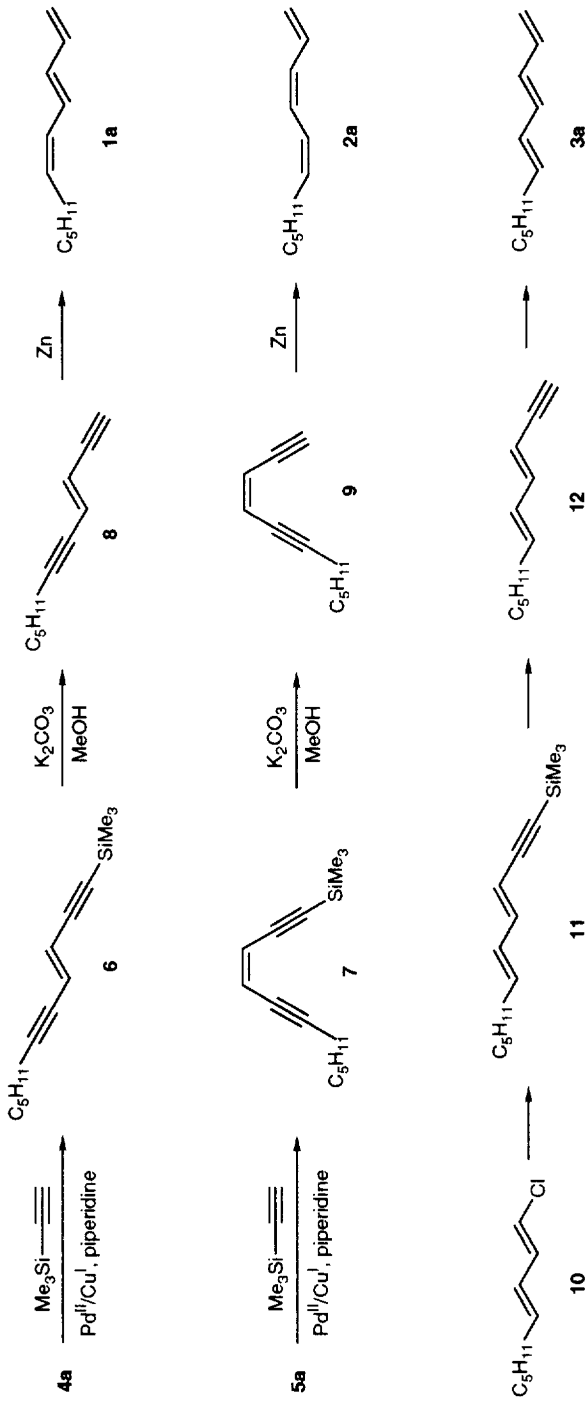


a R = C_5H_{11}
b R = $C_5H_{11}CH(OH)$
c R = Me_3Si

Scheme 1

Treatment of the chloroenynes **4a** and **5a** with trimethylsilyl acetylene in the presence of CuI and $PdCl_2(PhCN)_2$ (which was more efficient than $Pd(PPh_3)_4$)[8] in piperidine led to the enediynes **6** and **7** in 95 and 93% yield respectively (stereoisomeric purity $\geq$ 99.9%) (scheme 2). The enediynes **6** and **7** can also be prepared from (Z) or (E)-1,2-dichloroethylene and 1-alkynes by an experimentally straightforward one-pot procedure involving two sequential Pd-catalyzed coupling reactions.[6c]

Desilylation of **6** with K_2CO_3 in MeOH afforded (3E)-3-undecene-1,5-diyne **8** (85% yield, stereoisomeric purity $\geq$ 99.9%) which was stereoselectively reduced by activated zinc[7, 11] into (3E,5Z)-1,3,5-undecatriene **1a**


4a
Me3Si—≡
PdII/CuI, piperidine
C5H11
SiMe3
6
K2CO3
MeOH
C5H11
8
Zn
C5H11
1a
5a
Me3Si—≡
PdII/CuI, piperidine
C5H11
SiMe3
7
K2CO3
MeOH
C5H11
9
Zn
C5H11
2a
C5H11
Cl
10
C5H11
SiMe3
11
C5H11
12
C5H11
3a

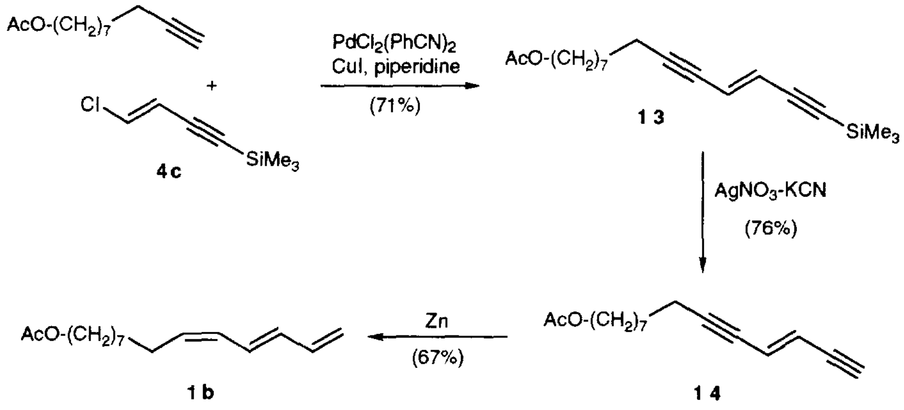
Scheme 2

in 50% yield (95% isomeric purity: 2% of **3a** and two by-products (2 x 1.5%) were detected). It is noticeable that the experimentally simple zinc reduction of alkynes leads efficiently to (Z)-olefins, the presence of a small amount (~2%) of the corresponding (E)-isomer has not yet been reported.

Under the same conditions, the (Z,Z) conjugated triene **2a** was obtained (~95% isomeric purity determined by NMR[12]) from the enediyne **7** in a 58% overall yield.

(3E,5E)-1,3,5-undecatriene **3a** was prepared similarly from (1E,3E)-1-chloro-1,3-nonadiene **10** which was obtained in 98% stereoisomeric purity by the reaction of a vinyl alane with (E)-dichloroethylene.[6b, 13] Treatment of chlorodiene **10** with trimethylsilyl acetylene under Pd-Cu catalysis gave the dienyne **11** in 88% yield (98% stereoisomeric purity). Desilylation (86%) and reduction (68%) gave (3E,5E)-1,3,5-undecatriene **3a** in 95% purity.

The pheromone **1b** was prepared by a chemoselective three-step synthesis in 36% overall yield according to the following sequence: the chloroenyne **4c** was coupled with 9-decyn-1-yl acetate in the presence of PdCl$_2$(PhCN)$_2$, CuI[8] to give the acetate **13** (stereoisomeric purity ≥ 99.9%) in 71% yield. Desilylation with AgNO$_3$-KCN[14] (76%) followed by stereoselective reduction with zinc[7,11] (67%) furnished the pheromone **1b** (95% isomeric purity).



Scheme 3

In conclusion, we have described a practical and chemoselective access to conjugated enediynes and 1,3,5-trienes from (E) and (Z)-dichloroethylenes. The efficiency of the procedure was illustrated by short syntheses of galbanolenes and (9Z,11E)-9,11,13-tetradecatrien-1-yl acetate.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were recorded on a Bruker AC 200, VM 250 or AM 400 instrument ($CDCl_3$, δ (ppm), J (Hz)). Mass spectra were determined on a Nermag R 10/10 instrument in the NH_3 chemical ionisation mode. IR spectra were measured on a Perkin Elmer 599 spectrophotometer (neat, cm^{-1}). Stereoisomeric purity of all products was determined by gas chromatographic analyses performed on a model Girdel equipped with capillary column (SGE 50 QC 2 / BP5 0.25). Analytical TLC was performed on 0.25 mm precoated silica gel plates (Merck). Products were purified by distillation or by column chromatography (silica gel 60 230-400 mesh ASTM, 0.040-0.063 mm) purchased from E. Merck. All glassware was oven-dried at 140 °C and all reactions were conducted under argon atmosphere. Boiling points are uncorrected. Ether was distilled from sodium and benzophenone. $Pd(PPh_3)_4$[15], $PdCl_2(PhCN)_2$[16] and $NiCl_2(PPh_3)_2$[17] were prepared following literature procedures. Zn powder was purchased from E. Merck (zinc powder for analysis >230 mesh ASTM, 60 µm).

General Procedure for the Pd^0/Cu^I Catalyzed Cross Coupling Reaction of (E)-1,2-Dichloroethylene with 1-Alkynes.

(1E)-1-Chloro-1-nonen-3-yne (4a): To a solution of $Pd(PPh_3)_4$ (0.9 mmol, 1.04 g), (E)-1,2-dichloroethylene (0.45 mol, 43.62 g), piperidine (0.18 mol, 15.33 g) and 1-heptyne (0.09 mol, 8.66 g) in ether (180 mL) was added CuI (9 mmol, 1.71 g). 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 (30 mL). 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. In order to remove palladium catalyst and PPh_3, the crude product was filtered on a pad of celite (pentane). Purification by distillation afforded the coupling product **4a** (E stereoisomeric purity ≥ 99.9%) in 82% yield (11.56 g); bp 50 °C (0.1 mmHg); IR (neat) cm^{-1} 3070, 2960, 2850, 2210, 1590, 920; ^1H NMR (200 MHz, $CDCl_3$) δ 6.41 (1H, d, J = 13.6 Hz), 5.89 (1H, dt, J = 13.6, 2.3 Hz), 2.27 (2H, td, J = 6.9, 2.3 Hz), 1.56 to 1.20 (6H, m), 0.88 (3H, t, J = 6.9 Hz); ^{13}C NMR (250 MHz, $CDCl_3$) δ 128.65, 114.30, 93.45, 75.65, 31.05, 28.15, 22.15, 19.35, 13.95; CIMS (NH_3) m/e (relative intensity) 174 ($(M+NH_4)^+$, 5), 156 (M^+, 16), 141 (22), 127 (50), 121 (100), 114 (73); Anal. calcd. for $C_9H_{13}Cl$: C, 69.20; H, 8.39 Found: C, 69.41; H, 8.19.

(1E)-1-Chloro-1-decen-3-yn-5-ol (4b): yield 85% (159 mg); E stereoisomeric purity ≥ 99.9%; TLC R_f (10% AcOEt/petroleum ether) 0.50; IR (neat) cm^{-1} 3340, 3060, 1580, 1120, 920; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.54 (1H, dd, J = 13.7, 0.3 Hz), 5.96 (1H, dd, J = 13.6, 1.9 Hz), 4.45 (1H, m), 1.85 (1H, d, J = 5.4 Hz), 1.79 to 1.56 (2H, m), 1.50 to 1.20 (6H, m), 0.88 (3H, t, J = 6.6 Hz); ^{13}C NMR (250 MHz, $CDCl_3$) δ 130.60, 113.20, 92.90, 79.75, 62.80, 37.55, 31.35, 24.75, 22.50, 13.95; CIMS (NH_3) m/e (relative intensity) 204 ($(M+NH_4)^+$, 41), 188 (M^+, ^{37}Cl, 33), 186 (M^+, ^{35}Cl, 100); Anal. calcd. for $C_{10}H_{15}ClO$: C, 64.49; H, 8.12 Found: C, 64.17; H, 8.05.

(1E)-1-Chloro-4-trimethylsilyl-1-buten-3-yne (4c): The reaction was carried out in benzene instead of ether*; distillation yield 76% (3.29 g); E stereoisomeric purity ≥ 99.9%; bp 85 °C (40 mmHg); IR (neat) cm^{-1} 3090, 2985, 2910, 2180, 2130, 2080, 1590, 1250, 1230, 1080, 925, 850, 770; ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.56 (1H, d, J = 13.5 Hz), 5.92 (1H, d, J = 13.5 Hz), 0.17 (9H, s); ^{13}C NMR (250 MHz, $CDCl_3$) δ 131.55, 113.90, 99.60, 97.70, -0.30; CIMS (NH_3) m/e (relative intensity) 160 (M^+, ^{37}Cl, 38), 158 (M^+, ^{35}Cl, 100), 143 (37), 108 (84), 94 (47), 80 (20); Anal. calcd. for $C_7H_{11}ClSi$: C, 53.15; H, 7.02 Found: C, 52.89; H, 7.08.

* a 35% yield was obtained in ether.

General Procedure for the Pd^0/Cu^I Catalyzed Cross Coupling Reaction of (Z)-1,2-Dichloroethylene with 1-Alkynes.

(1Z)-1-Chloro-1-decen-3-yn-5-ol (5b): To a solution of $Pd(PPh_3)_4$ (0.3 mmol, 0.35 g), (Z)-1,2-dichloroethylene (0.06 mol, 5.82 g), butylamine (0.06 mol, 4.38 g) and 1-octyn-3-ol (0.03 mol, 3.79 g) in ether (60 mL) was added CuI (3 mmol, 0.57 g) at 15-20 °C (exothermic reaction). The stirred reaction was kept at room temperature for 4 h and treated by a similar procedure as described for **4a**; yield 84% (4.7 g); Z stereoisomeric purity ≥ 99.9%; bp 95-98 °C (0.1 mmHg); IR (neat) cm^{-1} 3350, 3050, 2900, 2870, 2150, 1580, 700; ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.36 (1H, d, J = 7.5 Hz), 5.87 (1H, dd, J = 7.5, 2.0 Hz), 4.83 (1H, td, J = 6.6, 2.0 Hz), 2.11 (1H, s), 1.81 to 1.62 (2H, m), 1.58 to 1.20 (6H, m), 0.89 (3H, t, J = 6.7 Hz); ^{13}C NMR (250 MHz, $CDCl_3$) δ 128.50, 111.55, 98.65, 78.50, 62.85, 37.50, 31.35, 24.70, 22.45, 13.90; CIMS (NH_3) m/e (relative intensity) 204 ($(M+NH_4)^+$, 38), 188 (M^+,^{37}Cl, 35), 186 (M^+, ^{35}Cl, 100). Anal. calcd. for $C_{10}H_{15}ClO$: C, 64.49; H, 8.12 Found: C, 64.23; H, 8.21.

(1Z)-1-Chloro-1-nonen-3-yne (5a): yield 85% (668 mg); Z stereoisomeric purity ≥ 99.9%; TLC R_f (petroleum ether) 0.75; ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.27 (1H, d, J = 7.4 Hz), 5.83 (1H, dt, J = 7.4, 2.2 Hz), 2.37 (2H, td, J = 6.9, 2.2 Hz), 1.56 (2H, quint, J = 6.7 Hz), 1.43 to 1.18 (4H, m), 0.89 (3H, t, J = 6.9 Hz); ^{13}C NMR (400 MHz, $CDCl_3$) δ 126.60, 112.45, 99.30, 74.55, 30.95, 28.15, 22.10, 19.55, 13.85; CIMS (NH_3) m/e (relative intensity) 174 ($(M+NH_4)^+$, 2), 156 (M^+, 5), 141 (22), 127 (60), 121 (100), 91 (81). The spectral properties of **5a** were in good agreement with those reported in the literature.[6a,18]

(1Z)-1-Chloro-4-trimethylsilyl-1-buten-3-yne (5c): yield 64% (203 mg); Z stereoisomeric purity ≥ 99.9%; TLC R_f (pentane) 0.70; IR (neat) cm^{-1} 3020, 2950, 2895, 2150, 1595, 1570, 1250, 1010, 850, 760, 730, 670; ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.38 (1H, d, J = 7.4 Hz), 5.87 (1H, d, J = 7.4 Hz), 0.20 (9H, s); ^{13}C NMR (250 MHz, $CDCl_3$) δ 129.20, 112.05, 103.75, 98.15, -0.30; CIMS (NH_3) m/e (relative intensity) 160 (M^+, ^{37}Cl, 33), 158 (M^+, ^{35}Cl, 100), 143 (40), 108 (70), 94 (31); Anal. calcd. for $C_7H_{11}ClSi$: C, 53.15; H, 7.02 Found: C, 52.90; H, 6.91.

(1E,3E)-1-Chloro-1,3-nonadiene (10): The catalyst $Ni(PPh_3)_4$ was prepared following literature procedure.[19] Ethyl magnesium bromide (2 mmol) in ether was added, at 0 °C, to a suspension of $NiCl_2(PPh_3)_2$ (1 mmol, 600 mg) and triphenyl phosphine (2 mmol, 525 mg) in anhydrous ether (10 mL). Effervescence occured and the red-dark mixture of $Ni(PPh_3)_4$ was stirred further for 15 min. at 0 °C. After 10 min. at room temperature, a solution of (E)-1,2-dichloroethylene (0.5 mol, 48.5 g) in ether (300 mL) and benzene (100 mL) was added dropwise at 20 °C. Then, a solution of (E)-diisobutyl-1-heptenyl alane (0.1 mol) in hexane (prepared[20] from 1-heptyne (0.1 mol, 9.6 g) and diisobutyl aluminium hydride (0.1 mol, 100 mL) in hexane (10 mL)) was added dropwise at 20 °C over a 20-30 min. period. The reaction mixture was kept for an additional 3 h at room temperature before being poured slowly into a precooled aqueous H_2SO_4 4N (20 mL). The aqueous layer was extracted with ether (2 x 30 mL) and the combined organic layers were washed successively with aqueous $NaHCO_3$ (20 mL) and H_2O (2 x 10 mL), dried over $MgSO_4$ and the solvent was removed *in vacuo*. Filtration through silica gel (R_f (petroleum ether) 0.85) afforded the chlorodiene **10** (98% stereoisomeric purity) in 80% yield (12.7 g); IR (neat) cm^{-1} 3050, 3010, 1570, 970, 925, 830, 810, 745; ^{1}H NMR (200 MHz, $CDCl_3$) δ 6.40 (1H, dd, J = 13.1, 10.5 Hz), 6.05 (1H, d, J = 13.1 Hz), 5.95 (1H, dd, J = 15.1, 10.5 Hz), 5.68 (1H, dt, J = 15.1, 6.9 Hz), 2.05 (2H, q, J = 6.9 Hz), 1.54 to 1.15 (6H, m), 0.86 (3H, t, J = 6.7 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 136.25, 133.85, 126.00, 118.15, 32.60, 31.35, 28.70, 22.50, 13.95; m/e (relative intensity) 158 (M^+, 21), 90 (64), 88 (100); Anal. calcd. for $C_9H_{15}Cl$: C, 68.32; H, 9.56 Found: C, 68.05; H, 9.62.

General Procedure for the Pd^{II}/Cu^{I} Catalyzed Cross Coupling Reaction of Vinyl Chlorides with 1-Alkynes.

(3E)-1-Trimethylsilyl-3-undecene-1,5-diyne (6): To a suspension of $PdCl_2(PhCN)_2$ (0.05 mmol, 19 mg) in piperidine (3 mL) was added successively vinyl chloride **4a** (1 mmol, 156.7 mg), trimethylsilyl acetylene (2 mmol, 197 mg) and CuI (0.1 mmol, 19 mg). The reaction was stirred at room temperature and monitored by TLC analysis until complete consumption of the vinyl chloride (2-3 h) before to be treated by a similar procedure as described for **4a**; yield 95% (207 mg); E stereoisomeric purity ≥ 99.9%; TLC R_f (petroleum ether) 0.26; IR (neat) cm^{-1} 3030, 2960-2860, 2205, 2180, 2110, 975; ^1H NMR (250 MHz, $CDCl_3$) δ 6.00 (1H, dt, J = 16.0, 2.0 Hz), 5.85 (1H, d, J = 16.0 Hz), 2.30 (2H, td, J = 7.0 Hz, 2.0 Hz), 1.60 to 1.44 (2H, m), 1.42 to 1.30 (4H, m), 0.88 (3H, t, J = 7.0 Hz), 0.16 (9H, s); ^{13}C NMR (250 MHz, $CDCl_3$) δ 122.85, 119.30, 103.40, 98.80, 96.80, 79.00, 31.05, 28.20, 22.15, 19.65, 13.95, -0.20; CIMS (NH_3) m/e (relative intensity) 236 ($(M+NH_4)^+$, 26), 221 (23), 220 (43), 219 ($(M+H)^+$, 100), 218 (M^+, 13); Anal. calcd. for $C_{14}H_{22}Si$: C, 77.01; H, 10.16 Found: C, 77.18; H, 10.01.

(3Z)-1-Trimethylsilyl-3-undecene-1,5-diyne (7): The same procedure was used as described for **6**; yield 93% (203 mg); Z stereoisomeric purity ≥ 99.9%; TLC R_f (petroleum ether) 0.45; IR (neat) cm^{-1} 3020, 2960-2860, 2220, 2140, 1600, 1250, 1145, 1020, 845, 765, 750; ^1H NMR (250 MHz, $CDCl_3$) δ 5.81 (1H, dt, J = 11.0, 2.0 Hz), 5.72 (1H, d, J = 11.0 Hz), 2.38 (2H, td, J = 7.0, 2.0 Hz), 1.60 to 1.47 (2H, m), 1.42 to 1.22 (4H, m), 0.89 (3H, t, J = 7.0 Hz), 0.19 (9H, s); ^{13}C NMR (250 MHz, $CDCl_3$) δ 121.55, 118.10, 102.30, 101.70, 99.60, 78.10, 31.00, 28.35, 22.15, 19.75, 13.90, -0.10; CIMS (NH_3) m/e (relative intensity) 236 ($(M+NH_4)^+$, 100), 221 (40), 220 (20), 219 ($(M+H)^+$, 41), 218 (M^+, 17), 203 (13), 107 (10); Anal. calcd. for $C_{14}H_{22}Si$: C, 77.01; H, 10.16 Found: C, 77.15; H, 10.05.

(3E,5E)-1-Trimethylsilyl-3,5-undecadien-1-yne (11): The same procedure was used as described for **6**; yield 88% (388 mg); 98% stereoisomeric purity; TLC R_f(petroleum ether) 0.51; IR (neat) cm^{-1} 2160, 2130, 1690, 1640, 1470, 1250, 1080, 990, 850, 765; ^1H NMR (200 MHz, $CDCl_3$) δ 6.59 (1H, dd, J = 15.6, 10.5 Hz), 6.04 (1H, dd, J = 15.1, 10.5 Hz), 5.78 (1H, dt, J = 15.1, 6.9 Hz), 5.47 (1H, d, J = 15.6 Hz), 2.07 (2H, q, J = 6.9 Hz), 1.50 to 1.15 (6H, m), 0.86 (3H, t, J = 6.7 Hz), 0.15 (9H, s); ^{13}C NMR (200 MHz, $CDCl_3$) δ 143.30, 138.75, 129.55, 108.55, 104.80, 95.95, 32.75, 31.35, 28.65, 22.45, 13.95, -0.05; CIMS (NH_3) m/e (relative intensity) 238 ($(M+NH_4)^+$, 4), 222 (24), 221 ($(M+H)^+$, 100), 220 (M^+, 7), 110 (14); Anal. calcd. for $C_{14}H_{24}Si$: C, 76.31; H, 10.99 Found: C, 76.09; H, 11.05.

(11E)-14-Trimethylsilyl-11-tetradecene-9,13-diyn-1-yl acetate (13): The same procedure was used as described for the synthesis of **6**, from chloroenyne **4c** (1.5 equiv) and 9-decyn-1-yl acetate (1 equiv); yield 71% (450 mg); E stereoisomeric purity ≥ 99.9%; TLC R_f (5% AcOEt/petroleum ether) 0.43; IR (neat) cm^{-1} 3040, 2940-2860, 2220, 2170, 2120, 1740, 1250, 945, 850, 770; ^1H NMR (250 MHz, $CDCl_3$) δ 5.98 (1H, dt, J = 16.0, 2.0 Hz), 5.85 (1H, d, J = 16.0 Hz), 4.02 (2H, t, J = 6.7 Hz), 2.29 (2H, td, J = 6.8, 2.0 Hz), 2.01 (3H, s), 1.57 to 1.27 (12H, m), 0.15 (9H, s); ^{13}C NMR (250 MHz, $CDCl_3$) δ 171.15, 122.75, 119.30, 103.30, 98.85, 96.60, 79.00, 64.55, 29.05, 28.90, 28.70, 28.55, 28.40, 25.80, 21.00, 19.60, -0.20; CIMS (NH_3) m/e (relative intensity) 336 ($(M+NH_4)^+$, 86), 319 ($(M+H)^+$, 100), 318 (M^+, 5); Anal. calcd. for $C_{19}H_{30}O_2Si$: C, 71.65; H, 9.50 Found: C, 71.77; H, 9.55.

(3E)-3-Undecene-1,5-diyne (8): A mixture of enediyne **6** (0.915 mmol, 200 mg), MeOH (3 mL) and K_2CO_3 (1.01 mmol, 140 mg) was stirred at room temperature for 4 h before to be concentrated. Ether was added (20 mL) and the organic layer washed with H_2O (2 x 10 mL), dried over $MgSO_4$ and the solvent was removed *in vacuo*. Purification by flash chromatography (R_f (petroleum ether) 0.65) afforded the enediyne **8** (E stereoisomeric purity ≥ 99.9%) in 85% yield (114 mg); IR (neat) cm^{-1} 3300, 3020, 2950-2850, 2200, 1585, 940; ^1H NMR (250 MHz, $CDCl_3$) δ 6.10 (1H, dt, J = 16.1, 2.1 Hz), 5.84 (1H, dd, J = 16.1, 2.3 Hz), 3.07 (2H, d, J = 2.3 Hz), 2.31 (2H, td, J = 7.0, 2.1 Hz), 1.57 to 1.27 (6H, m), 0.88 (3H, t, J = 6.9 Hz); ^{13}C NMR (250 MHz, $CDCl_3$) δ 123.75, 118.30, 96.90, 82.00, 81.00, 78.60, 31.05, 28.15, 22.15, 19.55, 13.95; CIMS (NH_3) m/e (relative intensity) 165 ($(M+H)^+$, 10), 164 (M^+, 100), 117 (12); Anal. calcd. for $C_{11}H_{14}$: C, 90.34; H, 9.66 Found: C, 90.67; H, 9.60.

(3Z)-3-Undecene-1,5-diyne (9): The same procedure was used as described for **8**; yield 84% (259 mg); Z stereoisomeric purity ≥ 99.9%; TLC R_f (petroleum ether) 0.56; IR (neat) cm^{-1} 3300, 2970-2880, 2220, 1580, 755; ^1H NMR (250 MHz, $CDCl_3$) δ 5.87 (1H, dt, J = 11.0, 2.4 Hz), 5.69 (1H, dd, J = 11.0, 2.3 Hz), 3.27 (1H, d, J = 2.3 Hz), 2.37 (2H, td, J = 7.0, 2.4 Hz), 1.57 to 1.17 (6H, m), 0.88 (3H, t, J = 7.0 Hz); ^{13}C

NMR (250 MHz, $CDCl_3$) δ 122.45, 116.90, 99.65, 80.90, 83.65, 77.80, 30.95, 28.20, 22.15, 19.70, 13.95; CIMS (NH_3) m/e (relative intensity) 165 ($(M+H)^+$, 15), 164 (M^+, 100), 131 (28), 117 (29), 115 (17), 108 (16), 104 (22); Anal. calcd. for $C_{11}H_{14}$: C, 90.34; H, 9.66 Found: C, 90.62; H, 9.76.

(3E,5E)-3,5-Undecadien-1-yne (12): The same procedure was used as described for **8**; yield 86% (127 mg); 98% stereoisomeric purity; TLC R_f (petroleum ether) 0.45; IR (neat) cm^{-1} 3400, 2100, 1640, 1470, 990; ^1H NMR (200 MHz, $CDCl_3$) δ 6.62 (1H, dd, J = 15.7, 10.5 Hz), 6.06 (1H, dd, J = 10.5, 15.2 Hz), 5.81 (1H, dt, J = 15.2, 6.9 Hz), 5.44 (1H, dd, J = 15.7, 2.3 Hz), 2.95 (1H, d, J = 2.3 Hz), 2.08 (2H, q, J = 6.7 Hz), 1.55 to 1.15 (6H, m), 0.87 (3H, t, J = 6.6 Hz); ^{13}C NMR (200 MHz, $CDCl_3$) δ 143.85, 138.95, 129.30, 107.45, 83.10, 78.55, 32.70, 31.35, 28.60, 22.45, 13.95; CIMS (NH_3) m/e (relative intensity) 166 ($(M+NH_4)^+$, 100), 149 ($(M+H)^+$, 58), 148 (M^+, 3); Anal. calcd. for $C_{11}H_{16}$: C, 89.11; H, 10.89 Found: C, 89.45; H, 10.93.

(11E)-11-Tetradecene-9,13-diyn-1-yl acetate (14): To a silylated (E)-enediyne **13** (0.32 mmol, 103 mg) dissolved in 0.65 mL of ethanol was added, in 5 min. at room temperature, silver nitrate (0.83 mmol, 142 mg) dissolved in 1.2 mL of water and 0.3 mL of ethanol. The temperature rose to 30 °C and a precipitate of the silver acetylide was formed. After 15 min., the stirred reaction was treated with a solution of potassium cyanide (3.91 mmol, 258 mg) in 0.4 mL of water. Stirring was continued until the precipitate had dissolved and the reaction mixture was then worked up and purified by a similar procedure as described for **8** to give the enediyne **14** (E stereoisomeric purity ≥ 99.9%) in 76% yield (60 mg); R_f (5% AcOEt/petroleum ether) 0.40; IR (neat) cm^{-1} 3300, 3040, 2940-2860, 2220, 2110, 1740, 1595, 950; ^1H NMR (250 MHz, $CDCl_3$) δ 6.04 (1H, dt, J = 16.0, 2.2 Hz), 5.82 (1H, dd, J = 16.0, 2.3 Hz), 4.02 (2H, t, J = 6.7 Hz), 3.07 (1H, d, J = 2.3 Hz), 2.30 (2H, td, J = 7.0, 2.2 Hz), 2.02 (3H, s), 1.67 to 1.25 (12H, m); ^{13}C NMR (250 MHz, $CDCl_3$) δ 171.20, 123.70, 118.30, 96.70, 81.95, 81.05, 78.65, 64.55, 29.05, 28.90, 28.70, 28.55, 28.40, 25.80, 20.95, 19.55; CIMS (NH_3) m/e (relative intensity) 264 ($(M+NH_4)^+$, 100), 247 ($(M+H)^+$, 5); Anal. calcd. for $C_{16}H_{22}O_2$: C, 78.00; H, 9.01 Found: C, 78.34; H, 9.11.

General Procedure for the Reduction of 8, 9, 12 and 14 with Activated Zinc

(3E,5Z)-1,3,5-Undecatriene (1a): Activated zinc dust was prepared as previously described.[7,11] A solution of compound **8** (3.57 mmol, 522 mg) in 10 mL H_2O-MeOH (1/1) was added to the suspension of activated Zn (2 g) and stirred at 35 °C. After 2 h, the mixture was filtered on a pad of celite and concentrated. Ether was added (20 mL) and the organic layer washed with H_2O (2 x 15 mL), dried over $MgSO_4$ and the solvent was removed *in vacuo*. Examination of the crude product by TLC showed one spot (R_f (pentane) 0.60) corresponding to the triene **1a.** Purification by flash chromatography and carefull distillation of the solvents afforded the undecatriene **1a** (95% isomeric purity) in 50% yield (268 mg); IR (neat) cm^{-1} 3080, 3020, 2960-2860, 1620, 1575, 1005, 940, 900, 760; ^1H NMR (250 MHz, $CDCl_3$) δ 6.49 (1H, dd, J = 14.9, 11.0 Hz), 6.42 (1H, ddd, J = 16.8, 11.0, 10.6 Hz), 6.21 (1H, dd, J = 14.9, 10.6 Hz), 6.03 (1H, dd, 11.0 Hz), 5.50 (1H, dt, J = 11.0, 7.0 Hz), 5.20 (1H, d, J = 16.8 Hz), 5.09 (1H, d, J = 11.0 Hz), 2.20 (2H, q, J = 7.0 Hz), 1.45 to 1.20 (6H, m), 0.90 (3H, t, J = 6.7 Hz); ^{13}C NMR (250 MHz, $CDCl_3$) δ 137.25, 133.60, 132.90, 128.70, 128.25, 116.80, 31.45, 29.30, 27.85, 22.55, 14.05; CIMS (NH_3) m/e (relative intensity) 151 ($(M+H)^+$, 100), 150 (M^+, 23), 92 (19), 93 (34), 80 (83), 79 (33).

The spectral properties of **1a** were in good agreement with those reported in the literature.[13]

(9Z,11E)-9,11,13-Tetradecatrien-1-yl acetate (1b): The same procedure was used as described previously for **1a**; yield (crude product) 67% (95% isomeric purity); IR (neat) cm^{-1} 3090, 3020, 2930-2860, 1740, 1620, 1250, 1010, 940, 900; ^1H NMR (250 MHz, $CDCl_3$) δ 6.50 (1H, dd, J = 14.8, 11.0 Hz), 6.40 (1H, ddd, J = 17.0, 10.2, 10.5 Hz), 6.19 (1H, dd, J = 14.8, 10.5 Hz), 6.01 (1H, dd, J = 11.0 Hz), 5.47 (1H, dt, J = 11.0, 7.7 Hz), 5.2 (1H, d, J = 17.0 Hz), 5.07 (1H, d, J = 10.2 Hz), 4.05 (2H, t, J = 6.7 Hz), 2.20 (2H, q, J = 7.0 Hz), 2.05 (3H, s); ^{13}C NMR (250 MHz, $CDCl_3$) δ 171.20, 137.20, 133.45, 132.90, 128.60, 128.30, 116.85, 64.60, 29.55, 29.30, 29.15, 29.10, 28.55, 27.80, 25.85, 21.00; CIMS (NH_3) m/e (relative intensity) 268 ($(M+NH_4)^+$, 15), 252 (23), 251 ($(M+H)^+$, 100), 250 (M^+, 6).

The spectral properties of **1b** were in good agreement with those reported in the literature.[3a]

(3Z,5Z)-1,3,5-Undecatriene (2a): The same procedure was used as described for **1a**; yield (crude product) 72%; ~95% isomeric purity determined by NMR;[12] IR (neat) cm^{-1} 3095, 3020, 2960, 2860, 1620, 1570, 1010, 905, 750; ^1H NMR (250 MHz, $CDCl_3$) δ 6.85 (1H, ddd, J = 16.5, 10.6 Hz), 6.47 (1H, dd, J = 11.0 Hz), 6.29 (1H, dd, J = 11.0 Hz), 6.02 (1H, dd, J = 11.0 Hz), 5.53 (1H, dt, J = 9.5, 7.6 Hz), 5.26 (1H, d, J = 16.3 Hz), 5.17 (1H, d, J = 10.6 Hz), 2.20 (2H, q, J = 7.4 Hz), 1.6 to 1.2 (6H, m), 0.90 (3H, t, J = 7.0 Hz); ^{13}C NMR (250 MHz, $CDCl_3$) δ 134.05, 132.05, 129.35, 124.95, 123.30, 117.90, 31.40, 29.20, 27.45, 22.50, 14.00.

The spectral properties of **2a** were in good agreement with those reported in the literature.[5, 22]

(3E,5E)-1,3,5-Undecatriene (3a): The same procedure was used as described for **1a**; yield 68% (48 mg); 95% purity; TLC R_f(petroleum ether) 0.58; IR (neat) cm^{-1} 3100, 1630, 1585, 1470, 1380, 1005, 975, 895; ^{1}H NMR (250 MHz, CDCl$_3$) δ 6.33 (1H, dt, J = 16.6, 9.8 Hz), 6.24 to 6.05 (3H, m), 5.71 (1H, dt, J = 14.9, 7.0 Hz), 5.15 (1H, dd, J = 16.6, 1.5 Hz), 5.02 (1H, dd, J = 10.0, 1.5 Hz), 2.08 (2H, q, J = 7.0 Hz), 1.60 to 1.25 (6H, m), 0.87 (3H, t, J = 6.7 Hz); ^{13}C NMR (250 MHz, CDCl$_3$) δ 137.20, 136.20, 133.65, 130.95, 130.10, 116.15, 32.80, 31.40, 28.95, 22.50, 14.00; CIMS (NH$_3$) m/e (relative intensity) 151 ((M+H)$^+$, 100), 150 (M$^+$, 5), 110 (12).

The spectral properties of **3a** were in good agreement with those reported in the literature.[4]

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