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An alternative synthesis of (8*E*,10*Z*)-tetradeca-8,10-dienal, sex pheromone of horse-chestnut leafminer (*Cameraria ohridella*)

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ABSTRACT

The stereoselective synthesis of the sex pheromone of horse-chestnut leafminer was efficiently carried out using methodology based on the Pd(0)-catalyzed cross-coupling of 1-pentynylmagnesium bromide with the corresponding vinyl iodides as the key step.

1. Introduction

(8*E*,10*Z*)-Tetradeca-8,10-dienal (**1**) was identified by Svatos et al.[1] as the female sex pheromone of the horse-chestnut leafminer, *Cameraria ohridella* (Lepidoptera, Gracillariidae). This insect is an economically important defoliating pest of horse-chestnuts (*Aesculus hippocastanum* L.) and it is found throughout Europe.

The reported synthetic routes to **1**[2,4,5] are based on the C–C bond forming strategy with different carbon chain units. The first synthesis of (8*E*,10*Z*)-tetradeca-8,10-dienal was achieved by Svatos et al.[2] by employing the C7+C2+C5 strategy. The key intermediate for the synthesis, the (*E*)-14-(*tert*-butoxy)tetradec-6-en-4-yne, was prepared by Sonogashira cross-coupling[3] of (*E*)-9-(*tert*-butoxy)-1-iodonon-1-ene (prepared in five steps from heptane-1,7-diol) with 1-pentyne. A Sonogashira protocol,[2] involving the reaction of a terminal alkyne with an organic halide in the presence of a catalytic amount of Pd–phosphine complex and CuI as well as amine base and benzene as the solvent, generally offered acceptable results at a relatively small scale. The use of the toxic solvent makes this process much less attractive for large-scale preparation.

The improved procedures for the synthesis of the pheromone *C. ohridella*, reported both by Francke et al.[4] (C7+C3+C4 strategy) and Szocs et al.[5] (C8+C2+C4 strategy), employ the Wittig reaction as the key step. However, such a process does not afford a product of high enough chemical or isomeric purity. Another important drawback of the Wittig reaction-based process is the high cost of removal of triphenylphosphine oxide (the main by-product of the Wittig reaction), especially on the industrial process scale.

In 2007 Christmann et al.[6] reported a short synthesis of aldehyde **1** (over four steps) using a combination of two Wittig reactions. The shortcoming of the Wittig reaction, especially a relatively low isomeric purity of the product (ca. 90%), makes this method a less desirable alternative, considering the potential commercial application. It should be noted that in all published up-to-date synthetic routes toward pheromone **1** that expensive chromatographic purification is necessary for most of the isolated compounds. Thus, the development of an expeditious, cost-effective, and operationally simple synthetic approach is necessary. A particular incentive for this work is that this pheromone is increasingly used for large-scale field tests.

We report herein a new stereoselective synthesis for (8*E*,10*Z*)-tetradeca-8,10-dienal (**1**, C5+C5+C4 strategy), which successfully overcomes the major limitations of the strategies published previously and which can be scaled up easily. The stereospecific introduction of double bonds in this synthesis was achieved by the methodology based on the Pd(0)-catalyzed cross-coupling between suitable haloalkene and the known[7] 1-pentynylmagnesium bromide. This type of cross-coupling[8] was also used for the preparation of a key compound in Svatos's strategy,[2] (*E*)-14-(*tert*-butoxy)tetradec-6-en-4-yne (**13**). In addition, we synthesized the (8*E*,10*Z*)-tetradeca-8,10-dien-1-ol (precursor of the title pheromone, **18**), by a simple methodology based on the stereoselective dehydration of α-alkynediols with potassium hydrogen sulfate.[9]

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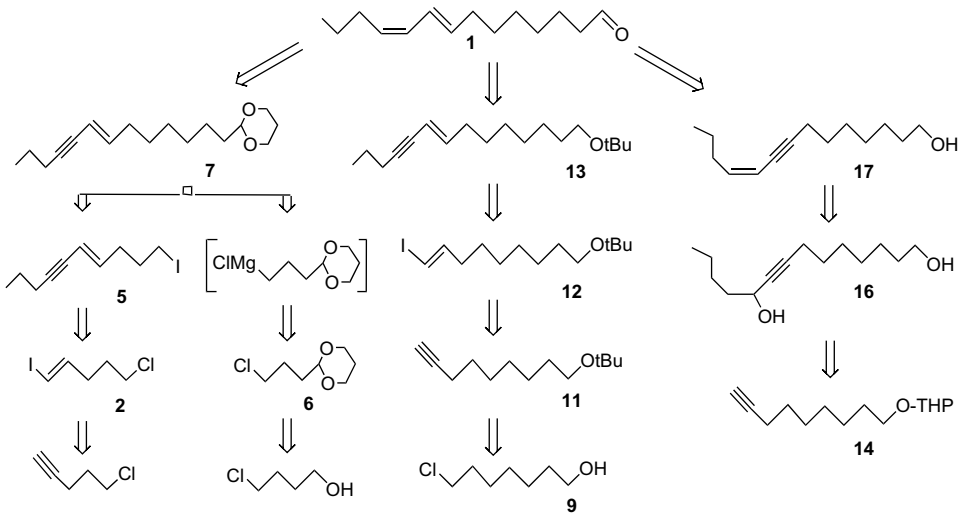


Scheme 1. Retrosynthetic analysis of aldehyde **1** of the female-produced contact sex pheromone of the horse-chestnut leafminer, *C. ohridella*.

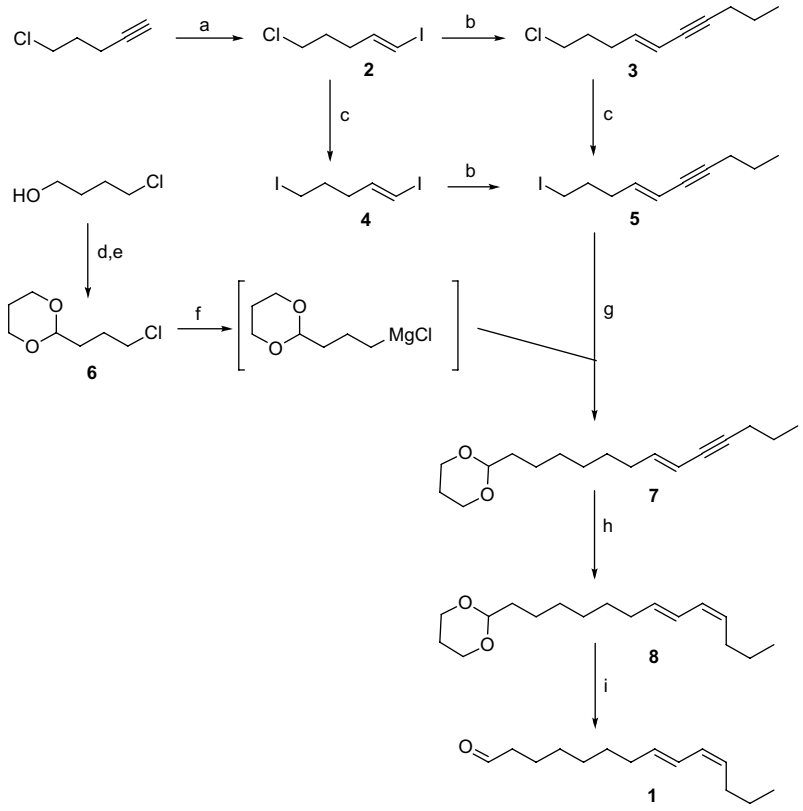
The retrosynthetic analysis of pheromone **1** (with part of the different disconnection strategies realized in this paper) is shown in Scheme 1.

2. Results and discussion

2.1. Synthesis of pheromone 1 employing the C5+C5+C4 strategy

Scheme 2 summarizes the coupling of individual building blocks to construct intermediate with the carbon skeleton of target pheromone and its further conversion to the final aldehyde **1**.

Thus, starting with commercial 5-chloro-1-pentyne and diisobutyl aluminum hydride (DIBAH) in hexane we prepared the corresponding alkenyl diisobutylalane,[10] which without isolation was iodinated to give (*E*)-vinyl iodide **2** in a high stereoisomeric purity (>99%, GC). Iodide **2** reacts efficiently with 1-pentynylmagnesium bromide (generated in situ from magnesium, ethyl bromide, and 1-pentyne) and 3% $Pd(PPh_3)_4$ in THF below 15 °C for 1 h, to give chloro-enyne **3** in 89% yield. Chloro-enyne **3** showed a high stereoisomeric purity (>99%) established by ^1H NMR spectroscopy and GC analysis. Iodination of chloride **3** in methyl ethyl ketone with NaI gave crude compound **5**, which was used without further purification in the next step.



Scheme 2. Synthesis of **1** employing the C5+C5+C4 strategy; (a) 1. DIBAH, hexane, 50 °C; 2. I_2, THF, −40 °C (63%, two steps); (b) *n*-PrC≡CMgBr, 3 mol % $Pd(PPh_3)_4$, THF (89% for **3**; 99% for **5**); (c) NaI, $CH_3COC_2H_5$ (90% for **4**; 95% for **5**); (d) PCC, CH_2Cl_2; (e) $HOCH_2CH_2CH_2OH$, TsOH, toluene (47%, two steps); (f) Mg, C_2H_5I, THF; (g) CuBr, THF, −20 °C→10 °C (80%); (h) 1. dicyclohexylborane, THF, 2. glacial AcOH, 3. 6 N NaOH, 4. 30% H_2O_2 (83%); (i) HCO_2H–CCl_3CH_3 (72%).

In an alternative approach, enyne **5** was prepared by iodination of chloride **2**, followed by the reported cross-coupling reaction.[8] The coupling reaction between di-iodide **4** and 1-pentynylmagnesium bromide proceeded quantitatively with an exclusive attack at the alkenyl iodide.[11] The overall yield for the two-step sequence was ca. 90%. The crude iodide **5** was coupled with the Grignard reagent, prepared from 2-(3-chloropropyl)-1,3-dioxane (**6**) in THF, under copper(I) catalysis to afford enyne **7** in 80% yield and stereoisomeric purity of >99%. Chloride **6** was prepared by the oxidation of 4-chloro-1-butanol with pyridinium chlorochromate (PCC), followed by the protection of crude intermediate aldehyde as 1,3-dioxane derivative using 1,3-propanediol–*p*-toluenesulfonic acid, under conditions of continuous removal of the water–toluene azeotrope.[12] The yield of **6** was 47% (over two steps). The selective hydroboration of acetylene group in enyne **7** with dicyclohexylborane and successive protonolysis of the vinyl–boron intermediate with acetic acid and treatment with alkaline H_2O_2 gave diene **8** in 83% yield. The stereoisomeric purity of **8** was ca. 98%. Compound **8** was directly converted to the final aldehyde **1** (in 72% yield) by treatment with anhydrous formic acid and 1,1,1-trichloroethane (1:1) at 45 °C (using a method reported by Normant et al.[13]). Pheromone **1** partially isomerized (~2%) under these vigorous conditions. Spectroscopic data of aldehyde **1** were in full accordance with those in the literature.[2,4,6] This aldehyde had similar stereoisomeric purity (ca. 95%) with the title pheromone prepared by Svatos et al.[2] Aldehyde **1** and propheromone **8** were tested successfully in a separate biological investigation.[14]

2.2. Synthesis of the key intermediate 13 according to C7+C2+C5 strategy

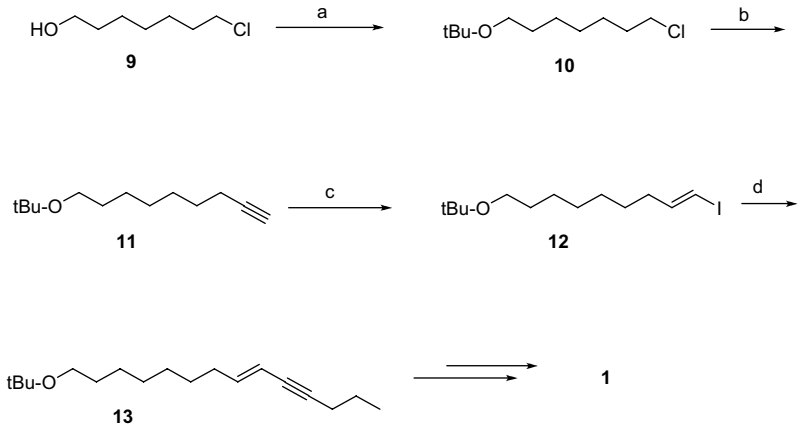
Vinyl iodide **12**, which finally was converted to the key synthon **13** by mentioned earlier cross-coupling reaction with 1-pentynylmagnesium bromide, was synthesized in a simple three-step reaction sequence from 7-chloroheptan-1-ol[15] (Scheme 3). Protection of the hydroxyl group in chlorohydrin **9** as the *tert*-butyl ether followed by the ethynylation of chloride **10** using a procedure previously developed in our laboratory[16] gave terminal alkyne **11** in ca. 70% yield (over two steps). Alkyne **11** was readily converted to vinyl iodide **12** by treatment with diisobutyl aluminum hydride (DIBAH) in hexane, followed by the iodination.[17] The stereoisomeric purity of vinyl iodide **12** was ca. 94%. The Pd(0)-catalyzed cross-coupling of iodide **12** with 1-pentynylmagnesium bromide gave key intermediate **13** in 94% yield. The small increase (ca. 4%) of the stereoisomeric purity of product was noted, in comparison to the starting iodide **12**. It may be explained by the higher reactivity of the *E*-iodo-alkenes compared to their *Z*-counterparts.[18] Enyne **13** was successfully used by Svatos et al.[2] during the synthesis of pheromone **1** (over four steps).

2.3. Precursor of the target pheromone ((8*E*,10*Z*)-tetradeca-8,10-dien-1-ol, 18)

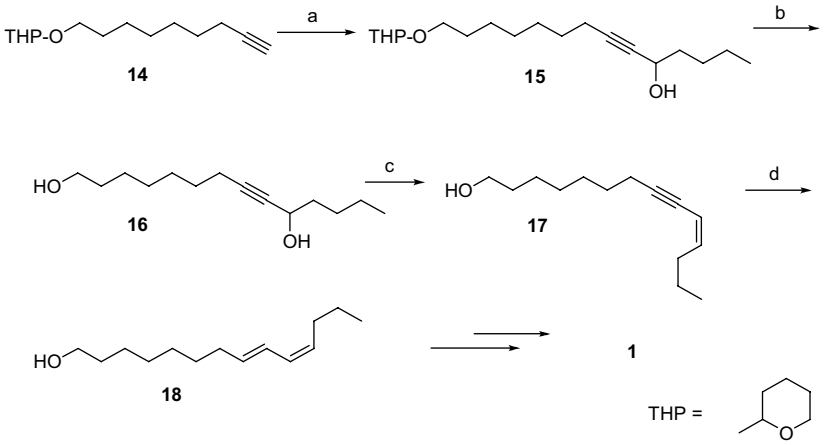
The synthesis of (8*E*,10*Z*)-tetradeca-8,10-dien-1-ol (**18**), the precursor of pheromone **1**,[2] was accomplished starting from the readily available alkyne **14**[16] (Scheme 4). Thus, the transmetallation of alkyne **14** with *n*-butyllithium, followed by the treatment with pentanal led to the corresponding alcohol **15** in 84% yield. Alcohol **15** was converted into the free diol **16** by treatment with *p*-toluenesulfonic acid in methanol. α-Alkynediol **16** was dehydrated with potassium hydrogen sulfate[9] by distillation under reduced pressure (vacuum oven, 155–165 °C/0.2 mmHg). Enynol **17** was obtained in 40% yield and its analysis (by GC) indicated that it exists as mixture of 10*Z* and 10*E* isomers in a ratio of 81:19, which was also confirmed by the ^{1}H NMR spectrum. Dienol **18** was obtained in 71% yield by the reduction of enyne **17** with an excess of lithium tetrahydroaluminate (LAH) in a mixture of diglyme and THF[19] at 117–121 °C for 29 h. The GC and ^{1}H NMR analyses of alcohol **18** indicated a 67:33 ratio of isomers (i.e., 10*Z*-isomer and the respective 10*E*-isomer). The latter can be removed as a THP ether derivative by Diels–Alder reaction with tetracyanoethylene.[4]

3. Conclusion

The work described herein establishes a different/improved approach to the synthesis of sex pheromone of *C. ohridella* and its precursors using the Pd(0)-catalyzed cross-coupling of 1-pentynylmagnesium bromide with suitable vinyl iodides. The high yield and stereoselectivity in addition to the mild reaction conditions make the present process [both variants—the (C5+C5+C4) approach as well as Svatos's strategy] useful for the synthesis of the title pheromone. Moreover, the variant of the synthesis using the (C5+C5+C4) strategy is arguably more straightforward than other reported methods (minimal number of steps using less expensive raw materials). Furthermore, this strategy could serve as a general methodology for the synthesis of the *E*–*Z* dienic pheromones with an aldehyde function. The protected aldehyde (acetal **8**, propheromone) obtained by applying this methodology could be a useful tool for the study of a controlled release of the pheromone into the environment.[12]



Scheme 3. Synthesis of the key intermediate **13** according to C7+C2+C5 strategy; (a) isobutylene, Amberlyst H-15, hexane (84%); (b) LiC≡CH·EDA, DMA, −5 °C→ rt, (82%); (c) 1. DIBAH, hexane, 53 °C, 2. I_2, THF, −47 °C (61%, two steps); (d) *n*-PrC≡CMgBr, 3 mol % $Pd(PPh_3)_4$, THF (94%).



Scheme 4. Synthesis of precursor **18**; (a) 1. *n*-BuLi, THF, −30 °C→0 °C, 2. pentanal, THF, −25 °C (84%, two steps); (b) TsOH, MeOH (85%); (c) $KHSO_4$, Büchi B-580 vacuum oven 155–165 °C/0.2 mmHg (40%); (d) LAH, diglyme–THF, 117–121 °C for 29 h (71%).

4. Experimental

4.1. General

All anhydrous solvents and reagents were prepared from reagent grade materials using conventional methods.[20] The reactions of air- and moisture-sensitive materials were carried out in a flame-dried glassware under an argon atmosphere. The transfer of air- and water-sensitive solutions was done using hypodermic syringes. Column chromatography was performed using Merck Silica gel 60 (0.04–0.063 mm). Thin-layer chromatography was performed on Alufolien with Merck Silica gel 60 F_{254}. IR spectra were measured using FT/IR-420 'Jasco' instrument (neat, cm^{-1}). ^1H NMR spectra were recorded using Varian 200 MHz spectrometer for solutions in $CDCl_3$ (internal TMS). ^{13}C NMR spectra were obtained on a Varian 200 MHz spectrometer operating at 50.2 MHz, unless otherwise noted. Chemical shifts (δ) are reported in parts per million and coupling constants in hertz. Mass spectra were measured on an API 365 or AMD M-40W spectrometer. The purity of the synthesized compounds was estimated by GC method, using a Varian STAR 3400 CX chromatograph equipped with a flame ionization detector (250 °C), injector 'on column' (230 °C), and a capillary column: DB1 (30 m, 0.53 mm i.d., 0.25 μm), the inert carrier gas was nitrogen. The oven temperature was programmed from 90 °C (held for 3 min) to 180 °C at 20 °C min^{-1} (held for 0 min) and then temperature was ramped to 230 °C at 5 °C min^{-1} (held for 10 min). 7-Chloroheptan-1-ol (**10**) and 9-(2-tetrahydropyranyloxy)-1-nonyne (**15**) were prepared according to Ref. 16.

4.2. (*E*)-1-Iodo-5-chloro-1-pentene (2)[10]

A solution of diisobutyl aluminum hydride (1 M in hexane, 100 mL, 100 mmol) was added to a solution of 1-chloro-4-pentyne (10 g, 97.5 mmol) in hexane (50 mL) at room temperature. The mixture was heated at 50 °C for 2 h, cooled to −40 °C, and THF (50 mL) was added, followed by a dropwise addition of a solution of iodine (25.4 g, 100 mmol) in THF (90 mL). The mixture was warmed to −10 °C and quenched with 5% sulfuric acid (90 mL). The organic layer was separated, washed with saturated aqueous sodium thiosulfate, brine, and dried over anhydrous magnesium sulfate. The solution was filtered, the filtrate was evaporated, and the residue was distilled under reduced pressure using a Büchi B-580 vacuum oven (125–140 °C/2 mmHg) to afford vinyl iodide **2** (14.2 g; 63%) as a colorless oil (GC purity 96%). IR: 947 (CH=CH trans); ^1H NMR: 1.72–2.04 (m, 2H, CH_2CH_2Cl), 2.24 (dq, 2H, J=1.2, 7.2, CH_2CH=C), 3.54 (t, 2H, J=6.5, CH_2Cl), 6.10 (dt, H, J=1.2, 14.2, CH=C*H*), 6.49 (dt, H, J=7.0, 14.4, C*H*=CH); HRMS (EI): $[M]^{+\bullet}$ m/z 229.93557, calcd for $C_5H_8^{35}ClI$ 229.93593.

4.3. (*E*)-10-Chlorodec-6-en-4-yne (3)

A solution of pentynylmagnesium bromide in THF (100 mL) was prepared[7] from magnesium (1.37 g, 0.056 g-atoms), ethyl bromide (4.6 mL, 6.7 g, 61 mmol), and 1-pentyne (5 mL, 3.5 g, 52 mmol), which was added over 15 min to a stirred mixture of vinyl iodide **2** (9.2 g, 40 mmol) and tetrakis(triphenylphosphine)palladium (1.4 g, 1.2 mmol, 3 mol % catalyst) in THF (60 mL) at 5 °C. The mixture was stirred for 1 h at 14 °C, quenched with 20% aqueous ammonium chloride (100 mL), and organic layer was separated. The aqueous layer was extracted with petroleum ether (3×120 mL). The combined organic extracts were washed with 20% aqueous ammonium chloride (2×120 mL), brine (2×120 mL), and dried over anhydrous magnesium sulfate. The solution was filtered, the filtrate was concentrated in vacuo, and the residue was purified by distillation under reduced pressure (Büchi B-580 vacuum oven, 95–110 °C/0.4 mmHg) to give enyne **3** (6.1 g; 89%) as a colorless oil (GC purity 95%). IR: 2220 (C≡C), 956 (CH=CH trans); ^1H NMR: 1.02 (t, 3H, J=7.4, CH_3), 1.48–1.70 (m, 2H, CH_3CH_2), 1.76–2.06 (m, 2H, CH_2CH_2Cl), 2.22–2.40 (m, 4H, $CH_2C{\equiv}CCH{=}CHCH_2$), 3.57 (t, 2H, J=6.5, CH_2Cl), 5.55 (m, H, J=15.8, CH=C*H*), 6.03 (dt, H, J=7.1, 15.8, C*H*=CH); HRMS (EI): $[M]^{+\bullet}$ m/z 170.08632, calcd for $C_{10}H_{15}^{35}Cl$ 170.08623.

4.4. (*E*)-1,5-Diiodo-1-pentene (4)

To a solution of compound **2** (13.9 g, 60.3 mmol) in 2-butanone (180 mL), the anhydrous sodium iodide (24 g, 160 mmol) was added at room temperature. The reaction mixture was heated under gentle reflux for 7 h and then stirred at room temperature overnight. The mixture was cooled (0 °C) and hexane (350 mL) was added to precipitate the inorganic salts, which were filtered off using a sintered glass funnel. The filtrate was concentrated in vacuo and pentane (200 mL) was added to precipitate the residual inorganic salts. The solution was filtered, the filtrate was concentrated in vacuo to afford the iodide **4** (17.5 g; 90%) as a colorless oil, which was used without further purification. IR: 941 (CH=CH trans); ^1H NMR: 1.80–2.02 (m, 2H, CH_2CH_2I), 2.08–2.30 (m, 2H, CH=CHC*H*$_2$), 3.18 (t, 2H, J=6.7, CH_2I), 6.11 (dt, H, J=1.3, 14.4, CH=C*H*), 6.47 (dt, H, J=7.2, 14.4, C*H*=CH); HRMS (EI): $[M]^{+\bullet}$ m/z 321.87081, calcd for $C_5H_8I_2$ 321.87155.

4.5. (*E*)-10-Iododec-6-en-4-yne (5) from chlorodecenyne (3)

To a solution of compound **3** (5.8 g, 34 mmol) in 2-butanone (90 mL), the anhydrous sodium iodide (10.4 g, 69 mmol) was added at room temperature. The reaction mixture was heated under gentle reflux for 9 h and then stirred at room temperature overnight. Hexane (150 mL) was added to the cooled mixture (0 °C) to precipitate inorganic salts, which were filtered off using sintered glass funnel. The filtrate was concentrated in vacuo and additional pentane (150 mL) was added to precipitate the residual inorganic salts. The solution was filtered again and the filtrate was concentrated in vacuo to afford iodide **5** (8.5 g; 95%) as a colorless oil, which was used without purification in the next step. IR: 2220 (C≡C), 952 (CH=CH trans); ^{1}H NMR: 0.99 (t, 3H, *J*=7.3, CH_3), 1.44–1.66 (m, 2H, CH_3CH_2), 1.80–1.98 (m, 2H, CH_2CH_2I), 2.12–2.34 (m, 4H, $CH_2C{\equiv}CCH{=}CHCH_2$), 3.18 (t, 2H, *J*=6.8, CH_2I), 5.46–5.62 (m, H, CH=CH), 5.97 (dt, H, *J*=7.2, 15.7, CH=CH); HRMS (EI): $[M]^{+\bullet}$ *m*/*z* 262.02161, calcd for $C_{10}H_{15}I$ 262.02185.

4.6. (*E*)-10-Iododec-6-en-4-yne (5) from diiodopentene (4)

A solution of pentynylmagnesium bromide in THF (150 mL), prepared[7] from magnesium (2.03 g, 0.083 g-atoms), ethyl bromide (6.6 mL, 9.6 g, 88 mmol), and 1-pentyne (7.4 mL, 5.1 g, 75 mmol), was added over 20 min to a stirred mixture of vinyl iodide **4** (17.48 g, 54.3 mmol) and tetrakis(triphenylphosphine)palladium (1.75 g, 1.5 mmol, 3 mol% catalyst) in THF (75 mL) at 5 °C. The mixture was stirred for 1 h at 10 °C, then quenched with 20% aqueous ammonium chloride (140 mL), and the organic layer was separated. The aqueous layer was extracted with petroleum ether (3×150 mL). The combined organic solutions were washed with 20% aqueous ammonium chloride (2×200 mL) and brine (200 mL). The organic layer was concentrated and 300 mL of pentane was added to the residue. The mixture was washed with 20% aqueous ammonia (2×100 mL), 20% aqueous ammonium chloride (2×150 mL), water (150 mL), and dried with magnesium sulfate. Finally, the mixture was filtered through a charcoal plug and concentrated under reduced pressure. The crude enyne **5** (14.1 g, 99%) was used in the next step without further purification.

4.7. 2-(3-Chloropropyl)-1,3-dioxane (6)

A solution of freshly distilled 90% 4-chloro-1-butanol (25 g, 207 mmol) in dichloromethane (200 mL) was added slowly (over 1.5 h) to a suspension of pyridinium chlorochromate (93 g, 431 mmol) in dichloromethane (200 mL). The mixture was stirred for 3.5 h at room temperature and diluted with anhydrous ether (500 mL), filtered through a pad of Celite™ and neutral alumina. The residue (black gum) was triturated with ether (3×100 mL, anhydrous). The combined etheral solutions were concentrated to give crude aldehyde (17.8 g) as a pale yellow, fragrant liquid.

To a solution of the crude aldehyde (17.7 g, 166 mmol) dissolved in toluene (600 mL), the trimethylene glycol (15 mL) was added, followed by *p*-toluenesulfonic acid (0.2 g). The resulting mixture was stirred under gentle reflux with a water-separator for 16 h and then cooled to room temperature. The reaction mixture was washed with saturated aqueous sodium bicarbonate (350 mL), water (3×350 mL), dried with magnesium sulfate, filtered, and the filtrate evaporated in vacuo. The residue was distilled under reduced pressure (Büchi B-580 vacuum oven, 125–140 °C/5 mmHg) to give acetal **6** (16 g, 47%) as a colorless oil (GC purity 95%). IR: 1146 (C–O); ^{1}H NMR: 1.27–1.42 (m, H, OCH_2CHHCH_2O), 1.67–2.21 (m, 5H, $2CH_2$ and OCH_2CHHCH_2O), 3.56 (t, 2H, *J*=6.5, CH_2Cl), 3.67–3.84 (m, 2H, OCH_2), 4.02–4.18 (m, 2H, OCH_2), 4.56 (t, H, *J*=4.9, $CH_2OCHOCH_2$); HRMS (EI): $[M-H]^+$ *m*/*z* 163.05185, calcd for $C_7H_{12}O_2^{35}Cl$ 163.05258.

4.8. 2-(7*E*-Tridecen-9-ynyl)-1,3-dioxane (7)

To a solution of magnesium (1.35 g, 0.056 g-atoms) in THF (12 mL), were added freshly distilled 2-(3-chloropropyl)-1,3-dioxane **6** (0.35 mL) and ethyl iodide (0.17 mL, 0.33 g, 2.1 mmol) under argon. The mixture was gently refluxed until the reaction started. The additional portions of freshly distilled 2-(3-chloropropyl)-1,3-dioxane **6** (7.1 mL, 8.25 g, 50.5 mmol) were added at a rate sufficient to maintain a gentle reflux (the mixture was heated to reflux if needed). After complete addition, the mixture was stirred at 60 °C until all magnesium was consumed, and then cooled to room temperature to give a Grignard reagent solution.

The Grignard reagent solution was diluted with THF (25 mL) and the solution was added dropwise over 35 min to a stirred mixture of (*E*)-10-iododec-6-en-4-yne **5** (8.4 g, 32 mmol) and cuprous(I) bromide (0.64 g) in THF (135 mL) at −20 °C. The mixture was stirred at −15 °C for 15 min and was allowed to warm up gradually to 10 °C and stirred for 30 min. Subsequently, the reaction mixture was cooled to −5 °C and quenched with saturated aqueous ammonium chloride (80 mL). The organic layer was separated and the aqueous layer was extracted with ether (150 mL). The combined organic solutions were washed with saturated aqueous ammonium chloride (2×150 mL), brine (2×100 mL), and dried over anhydrous magnesium sulfate. The solution was filtered, and the filtrate was concentrated in vacuo. The residue was partially purified by distilling off the volatile impurities (Büchi B-580 vacuum oven, 60–70 °C/0.05 mmHg). The crude product was purified by column chromatography on silica-gel (9:1 hexane–ether) to give enyne **7** (6.75 g, 80%) as a colorless oil (GC purity 98%). IR: 2210 (C≡C), 1146 (C–O), 958 (CH=CH trans); ^{1}H NMR: 0.99 (t, 3H, *J*=7.3, CH_3), 1.16–1.68 (m, 13H, $6CH_2$ and OCH_2CHHCH_2O), 1.94–2.20 (m, 3H, $CH_2CH{=}C$ and OCH_2CHHCH_2O), 2.26 (dt, 2H, *J*=1.9, 7.2, $CH_2C{\equiv}C$), 3.66–3.86 (m, 2H, OCH_2), 4.02–4.18 (m, 2H, OCH_2), 4.50 (t, H, *J*=5.1, $CH_2OCHOCH_2$), 5.45 (dt, 1H, *J*=1.7, 15.8, CH=CH), 6.04 (dt, 1H, *J*=6.9, 15.6, CH=CH); ^{13}C NMR: 13.72 (CH_3), 21.51 (CH_2), 22.44 (CH_2), 24.04 (CH_2), 26.03 (CH_2), 28.87 (CH_2), 29.13 (CH_2), 29.42 (CH_2), 33.08 (CH_2), 35.36 (CH_2), 67.07 ($2CH_2O$), 79.50 (C≡C), 88.69 (C≡C), 102.57 (CH=CH), 110.00 (HC=CH), 143.46 (CHO_2); HRMS (EI): $[M]^{+\bullet}$ *m*/*z* 264.20953, calcd for $C_{17}H_{28}O_2$ 264.20893.

4.9. 2-((7*E*,9*Z*)-trideca-7,9-dienyl)-1,3-dioxane (8)

To a stirred and cooled suspension of dicyclohexylborane in THF (70 mL), freshly prepared from boron–dimethyl sulfide complex (2 mol L^{-1}, 16.2 mL) and cyclohexene (6.8 mL, 5.52 g, 67.2 mmol), the solution of enyne **7** (6.67 g, 25.3 mmol) in THF (84 mL) was added dropwise at 0 °C (ice bath). The reaction mixture was kept at room temperature for 4 h, diluted with glacial acetic acid (8.4 mL), and then heated at 60 °C for 5 h. The oxidation of the resulting dicyclohexylborinate was achieved by treatment with aqueous 6 N sodium hydroxide (33.6 mL), followed by the dropwise addition of 30% hydrogen peroxide (8.4 mL) at 30 °C. The mixture was stirred for additional 30 min and product was extracted with hexane (4×120 mL). The combined extracts were washed with brine and dried over anhydrous magnesium sulfate. The solution was filtered, the filtrate evaporated, and the volatile impurities were distilled off (Büchi B-580 vacuum oven, 70–76 °C/0.05 mmHg). The residue was purified by column chromatography on silica-gel (hexane–ether, 9:1) to yield diene **8** (5.6 g; 83%) as a colorless oil (GC purity 95%). IR: 1146 (C–O), 984, 947 (cis,trans-conjugated diene); ^{1}H NMR: 0.92 (t, 3H, *J*=7.5, CH_3), 1.20–1.68 (m, 13H, $6CH_2$ and OCH_2CHHCH_2O), 1.96–2.24 (m, 5H, $2CH_2CH{=}C$ and OCH_2CHHCH_2O), 3.66–3.86 (m, 2H, OCH_2), 4.00–4.20 (m, 2H, OCH_2), 4.50 (t, H, *J*=5.2, $CH_2OCHOCH_2$), 5.30 (dt, H, *J*=7.5, 10.8, CH=C), 5.64 (dt, 1H, *J*=7.1, 14.8, CH=C), 5.95 (br t, 1H, *J*=10.8, CH=C), 6.29 (ddq, 1H, *J*=1.2, 11.0, 15.0, CH=C); ^{13}C NMR: 13.94 (CH_3), 23.06 (CH_2), 24.07 (CH_2), 26.02

(CH_2), 29.25 (CH_2), 29.43 (CH_2), 29.49 (CH_2), 29.90 (CH_2), 33.00 (CH_2), 35.38 (CH_2), 67.05 ($2CH_2O$), 102.58 (CHO_2), 125.84 (CH=CH), 128.94 (CH=CH), 129.99 (HC=CH), 134.74 (CH=CH); HRMS (EI): $[M]^{+\bullet}$ m/z 266.22507, calcd for $C_{17}H_{30}O_2$ 266.22458.

4.10. (8*E*,10*Z*)-Tetradeca-8,10-dienal (1)

Anhydrous formic acid (6 mL) was added dropwise (under argon atmosphere) to a stirred and cooled solution of acetal **8** (1.78 g, 6.7 mmol) in dry 1,1,1-trichloroethane (6 mL) at 0 °C (ice bath). The emulsion was stirred at 45 °C (oil bath) for 5 h, and the reaction mixture was cooled and poured into cold water (120 mL). Subsequent standard work-up and purification by column chromatography on silica-gel (0.3% triethylamine in benzene–hexane, 1:1) afforded dienal **1** (1 g, 72%) as a colorless oil (GC purity 94%). IR: 1727 (C=O), 984, 949 (cis,trans-conjugated diene); ^{1}H NMR: 0.92 (t, 3H, J=7.3, CH_3), 1.20–1.74 (m, 10H, $5CH_2$), 2.00–2.22 (m, 4H, $2CH_2CH$=C), 2.42 (dt, 2H, J=1.9, 7.4, CH_2CHO), 5.31 (dt, H, J=7.6, 10.8, C*H*=C), 5.64 (dt, H, J=7.2, 14.9, C*H*=C), 5.96 (t, H, J=10.8, C*H*=C), 6.30 (ddq, H, J=1.0, 10.8, 14.9, C*H*=C), 9.77 (t, H, J=1.9, CHO); ^{13}C NMR: 13.95 (CH_3), 22.18 (CH_2), 23.06 (CH_2), 29.06 (CH_2), 29.16 (CH_2), 29.32 (CH_2), 29.92 (CH_2), 32.91 (CH_2), 44.05 (CH_2), 126.00 (CH=CH), 128.87 (CH=CH), 130.19 (CH=CH), 134.48 (HC=CH), 203.07 (CHO); HRMS (EI): $[M]^{+\bullet}$ m/z 208.32507, calcd for $C_{14}H_{24}O$ 208.32458.

4.11. 1-Chloro-7-(*tert*-butoxy)heptane (10)

Compound **10** was prepared from chloroheptanol **9** (11.3 g, 75 mmol), 2-methylpropene, and Amberlyst H-15 (2.0 g) using a reported procedure.[21] The yield was 84% (13.0 g); bp 62–64 °C/0.05 mmHg (lit.[17] bp 65 °C/0.03 mmHg). IR: 1083 (C–O), 726, 650 (C–Cl); ^{1}H NMR: 1.18 (s, 9H, ^{t}Bu), 1.06–1.90 (m, 10H, $5CH_2$), 3.33 (t, 2H, J=6.4, CH_2OR), 3.53 (t, 2H, J=6.9, CH_2Cl).

4.12. 9-(*tert*-Butoxy)non-1-yne (11)

To a cooled (−5 °C) suspension of lithium acetylide–ethylenediamine complex (4.7 g, 52 mmol) in dry DMA (40 mL) under argon 1-chloro-7-(*tert*-butoxy)heptane **10** (4.1 g, 19.8 mmol) was added dropwise over 75 min. The mixture was stirred for 18 h at room temperature, poured into iced water, and extracted with petroleum ether. The combined organic extracts were washed with brine, dried over anhydrous magnesium sulfate, filtered, and the filtrate concentrated in vacuo. The residue was purified by column chromatography on silica-gel (25:1 hexane–ether) to give the known alkyne **11** (3.2 g; 82%)[17] as a colorless oil (GC purity 95%). IR: 2120 (C≡CH), 1085 (C–O); ^{1}H NMR (200 MHz): 1.18 (s, 9H, ^{t}Bu), 1.22–1.64 (m, 10H, $5CH_2$), 1.93 (t, 1H, J=2.6, C≡C*H*), 2.18 (dt, 2H, J=2.6, 7.0, CH_2C≡C), 3.32 (t, 2H, J=6.6, CH_2O).

4.13. (*E*)-9-(*tert*-Butoxy)-1-iodonon-1-ene (12)

To a solution of alkyne **11** (5.12 g, 26.1 mmol) in hexane (5 mL), was added the diisobutyl aluminum hydride (1 M in hexane, 27 mL, 27 mmol) at room temperature. The mixture was heated to 53 °C for 2 h, then cooled to −47 °C, and THF (12.5 mL) was added, followed by a dropwise addition of solution of iodine (6.6 g, 26 mmol) in THF (12.5 mL). The mixture was slowly warmed to room temperature (30 min) and hydrolyzed with 5% sulfuric acid (25 mL). The organic layer was separated and the aqueous layer was extracted with ether (25 mL). The combined extracts were washed with saturated aqueous sodium bicarbonate (35 mL), saturated aqueous sodium thiosulfate (35 mL), brine (35 mL), and dried over anhydrous magnesium sulfate. The solution was filtered, the filtrate evaporated, and the volatile impurities removed (Büchi B-580 vacuum oven, 70–86 °C/0.05 mmHg). The residue was purified by column chromatography on silica-gel (hexane–ethyl acetate, 80:1) to give vinyl iodide **12** (5.15 g; 61%) as a colorless oil (GC purity 90%). ^{1}H NMR: 1.18 (s, 9H, ^{t}Bu), 1.24–1.62 (m, 10H, $5CH_2$), 2.04 (br q, 2H, J=6.8, CH_2CH=C), 3.32 (t, 2H, J=6.6, CH_2OR), 5.96 (dt, H, J=1.4, 14.2, CH=C*H*), 6.51 (dt, H, J=7.2, 14.2, C*H*=CH); HRMS (EI): $[M]^{+\bullet}$ m/z 324.09448, calcd for $C_{13}H_{25}OI$ 324.09502.

4.14. (*E*)-14-(*tert*-Butoxy)tetradec-6-en-4-yne (13)

A solution of 1-pentynylmagnesium bromide in THF (45 mL), prepared[7] from magnesium (0.59 g, 0.025 g-atoms), ethyl bromide (1.95 mL, 2.83 g, 26 mmol), and 1-pentyne (2.15 mL, 1.49 g, 22 mmol), was added over 15 min to a stirred mixture of vinyl iodide **12** (5.1 g, 15.7 mmol) and tetrakis(triphenylphosphine)palladium (533 mg, 0.46 mmol, 3 mol % catalyst) in THF (20 mL) at 5 °C. The mixture was stirred for 1 h at 14 °C, then quenched with 20% aqueous ammonium chloride (50 mL), and organic layer was separated. The aqueous layer was extracted with petroleum ether (3×60 mL). The combined extracts were washed with 20% aqueous ammonium chloride (2×100 mL), brine (2×100 mL), and dried over anhydrous magnesium sulfate. The solution was filtered and the filtrate was evaporated in vacuo. The purification of the residue by column chromatography on silica-gel (40:1 hexane–ether) gave the corresponding enyne **13** (3.9 g, 94%) as a colorless oil (GC purity 94%). IR: 2220 (C≡C), 1083 (C–O), 955 (CH=CH trans); ^{1}H NMR: 0.99 (t, 3H, J=7.3, CH_3), 1.18 (s, 9H, ^{t}Bu), 1.24–1.66 (m, 12H, $6CH_2$), 2.07 (br q, 2H, J=6.6, CH_2CH=C), 2.26 (dt, 2H, J=2.0, 7.0, CH_2C≡C), 3.32 (t, 2H, J=6.6, CH_2OR), 5.44 (dt, H, J=1.6, 15.8, CH=C*H*), 6.05 (dt, H, J=7.2, 15.6, C*H*=CH); ^{13}C NMR: 13.73 (CH_3), 21.53 (CH_2), 22.46 (CH_2), 26.36 (CH_2), 27.76 ($3CH_3$), 28.98 (CH_2), 29.25 (CH_2), 29.50 (CH_2), 30.85 (CH_2), 33.13 (CH_2), 61.79 (CH_2O), 72.60 ($OC(CH_3)_3$), 79.52 (C≡C), 88.69 (C≡C), 109.97 (CH=CH), 143.56 (HC=CH); HRMS (ESI): $[M+Na]^+$ m/z 287.2349, calcd for $C_{18}H_{32}ONa$ 287.2345.

4.15. 1-(2-Tetrahydropyranyloxy)-10-hydroxytetradec-8-yne (15)

To a stirred solution of *n*-BuLi (1.4 M in hexane, 14 mL, 19.6 mmol) was added dropwise the solution of 9-(2-tetrahydropyranyloxy)-1-nonyne **14** (3.6 g, 16 mmol) in dry THF (32 mL) over 15 min at −30 °C. The mixture was warmed to 0 °C, stirred for 15 min, cooled to −30 °C and the solution of pentanal (2.2 mL, 1.8 g, 20.9 mmol) in dry THF (7 mL) was added and stirring continued for 60 min at −25 °C. The reaction mixture allowed to warm up to room temperature, stirred for 2 h, then poured into cold water (50 mL), and extracted with hexane (3×70 mL). The combined extracts were washed with brine (2×100 mL), dried over anhydrous magnesium sulfate, filtered, and the filtrate was concentrated under reduced pressure. The residue was purified by column chromatography on silica-gel (hexane–ether, 2:1) to give tetradecynol **15** (4.2 g, 84%) as a colorless oil (GC purity 94%). IR: 3436 (OH), 2213 (C≡C); ^{1}H NMR: 0.92 (t, 3H, J=7.0, CH_3), 1.20–1.96 (m, 22H, $11CH_2$), 2.14–2.26-(m, 2H, CH_2C≡C), 3.28–3.96 (m, 4H, 2 °CH_2), 4.26–4.40 (m, 1H, C*H*OH), 4.58 (dd, 1H, J=2.7, 4.1, OC*H*O); ^{13}C NMR: 14.21 (CH_3), 18.82 (CH_2), 19.85 (CH_2), 22.56 (CH_2), 25.67 (CH_2), 26.26 (CH_2), 27.57 (CH_2), 28.73 (CH_2), 28.88 (CH_2), 29.07 (CH_2), 29.83 (CH_2), 30.94 (CH_2), 38.10 (CH_2), 62.52 (CHOH), 62.90 (CH_2O), 67.79 (CH_2O), 81.61 (C≡C), 85.56 (C≡C), 99.02 (CHO_2); HRMS (ESI): $[M+Na]^+$ m/z 333.2414, calcd for $C_{19}H_{34}O_3Na$ 333.2400.

4.16. 10-Hydroxytetradec-8-yn-1-ol (16)

A solution of compound **15** (4 g, 13 mmol) in methanol (30 mL) was treated with *p*-toluenesulphonic acid (92 mg) and stirred at room temperature for 5 h. The saturated aqueous sodium

bicarbonate (1.3 mL) was added and stirring continued for 15 min at room temperature. Methanol was removed under reduced pressure and the residue was treated with ether (80 mL). The precipitated solids were filtered off and the organic layer was separated. The aqueous layer was extracted with ether (3×10 mL). The combined extracts were washed with brine, dried over anhydrous magnesium sulfate, filtered, and the filtrate was concentrated in vacuo. The crude product was purified by column chromatography on silica-gel (hexane–ethyl acetate, 2:1) to give diol **16** (2.5 g; 85%) as a colorless oil (GC purity 96%). IR: 3348 (OH), 2229 (C≡C); ^{1}H NMR: 0.92 (t, 3H, J=7.1, CH_3), 1.20–1.80 (m, 16H, 8CH_2), 2.20 (dt, 2H, J=2.0, 6.8, CH_2C≡C), 3.64 (t, 2H, J=6.5, CH_2OH), 4.34 (tt, 1H, J=2.0, 6.5, CHOH); ^{13}C NMR: 14.03 (CH_3), 18.63 (CH_2), 22.39 (CH_2), 25.57 (CH_2), 27.39 (CH_2), 28.50 (CH_2), 28.67 (CH_2), 28.80 (CH_2), 32.64 (CH_2), 37.93 (CH_2), 62.72 (CHOH), 62.95 (CH_2OH), 81.50 (C≡C), 85.34 (C≡C); HRMS (ESI): $[M+Na]^+$ m/z 249.1832, calcd for $C_{14}H_{26}O_2Na$ 249.1825.

4.17. 10(*Z*)-Tetradecen-8-yn-1-ol (17)

A mixture of diol **16** (0.45 g, 2 mmol) and potassium hydrogen sulfate (100 mg) was distilled using Büchi B-580 vacuum oven (temperature 155–165 °C, pressure 0.2 mmHg, time 40 min). The distillate was diluted with ether (20 mL), washed with saturated aqueous sodium bicarbonate (10 mL), and dried over anhydrous magnesium sulfate. The solution was filtered and the filtrate was evaporated to give enynol **17** (165 mg, 40%) as a colorless oil. The GC analysis indicates that compound **17** has 81% stereoisomeric purity.[22] IR: 3341 (OH), 2215 (C≡C), 730 (CH=CH cis); ^{1}H NMR: 0.93 (t, 3H, J=7.3, CH_3), 1.20–1.76 (m, 12H, 6CH_2), 2.24–2.37 (m, 4H, CH_2C≡CCH=CHCH_2), 3.64 (t, 2H, J=6.3, CH_2OH), 5.42–5.48 (m, 1H, CH=CH), 5.82 (dt, 1H, J=7.4, 10.8, CH=CH); ^{13}C NMR: 13.77 (CH_3), 19.49 (CH_2), 22.18 (CH_2), 25.66 (CH_2), 28.79 (2CH_2), 28.94 (CH_2), 32.09 (CH_2), 32.73 (CH_2), 63.02 (CH_2OH), 77.48 (C≡C), 94.31 (C≡C), 109.92 (CH=CH), 143.19 (HC=CH); HRMS (ESI): $[M+Na]^+$ m/z 231.1718, calcd for $C_{14}H_{24}ONa$ 231.1725.

4.18. (8*E*,10*Z*)-Tetradeca-8,10-dien-1-ol (18)

Lithium tetrahydroaluminate (100 mg, 2.6 mmol) was added in portions to an ice-cooled mixture of dry diglyme (1.2 mL) and THF (0.15 mL) under argon atmosphere. When the vigorous foaming had subsided the solution of enynol **17** (104 mg, 0.5 mmol) in diglyme (0.3 mL) was added to the thick slurry. Following the initial foaming, the mixture was heated at 117–121 °C (oil bath) for 29 h. The mixture was cooled to 0 °C and the hexane (8 mL) was added, followed by a cautious dropwise addition of water (0.2 mL), followed by 20% sodium hydroxide (0.16 mL), and water (0.75 mL). The mixture was stirred for 15 min to allow the precipitate to granulate, then the hexane layer was decanted, and the solid residue was rinsed several times with of hexane (4×5 mL). The combined hexane solutions were washed with water (3×5 mL), brine (10 mL), and dried over anhydrous magnesium sulfate. The solution was filtered and the filtrate was concentrated in vacuo. Residue was purified by column chromatography on silica-gel (hexane–ethyl acetate, 2:1) to give dienol **18** (74 mg, 71%) as a colorless oil. GC analysis indicated that compound **18** has 67% stereoisomeric purity.[23] IR: 3330 (C–O), 982, 947 (cis,trans-conjugated diene); ^{1}H NMR: 0.92 (t, 3H, J=7.2, CH_3), 1.20–1.70 (m, 12H, 6CH_2), 1.92–2.24 (m, 4H, 2CH_2CH=C), 3.64 (t, 2H, J=6.5, CH_2OH), 5.32 (dt, H, J=7.4, 10.6, CH=C), 5.66 (dt, H, J=7.2, 15.1, CH=C), 5.97 (br t, H, J=10.7, CH=C), 6.30 (ddq, H, J=1.2, 10.9, 15.1, CH=C); ^{13}C NMR: 13.79 (CH_3), 22.90 (CH_2), 25.69 (CH_2), 29.17 (CH_2), 29.28 (CH_2), 29.33 (CH_2), 29.75 (CH_2), 32.77 (CH_2), 32.84 (CH_2), 63.06 (CH_2OH), 125.71 (CH=CH), 128.76 (CH=CH), 129.92 (CH=CH), 134.57 (HC=CH); HRMS (ESI): $[M+Na]^+$ m/z 233.1875, calcd for $C_{14}H_{26}ONa$ 233.1881.

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22. ^{1}H NMR spectra for enynol **17** contain additional signals of its *E*-counterpart (in ratio 1:4): 0.90 (t, 3H, J=7.5, CH_3), 2.03–2.09 (m, 2H, CH_2CH=C), 2.19–2.23 (m, 2H, CH_2C≡C), 5.45–5.48 (m, H, CH=CH), 6.05 (dt, H, J=7.0, 15.5, CH=CH).
23. ^{1}H NMR spectra for dienol **18** contain additional signals of its *E*-counterpart: 0.90 (t, 3H, J=7.2, CH_3), 1.92–2.24 (m, 4H, 2CH_2CH=CH), 5.34–5.76 (m, 2H, CH=CH), 5.86–6.08 (m, 2H, CH=CH).