



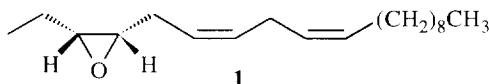
Access to Unsaturated Chiral Epoxides. Part. III¹: Synthesis of a Component of the Sex Pheromone of *Boarmia selenaria*

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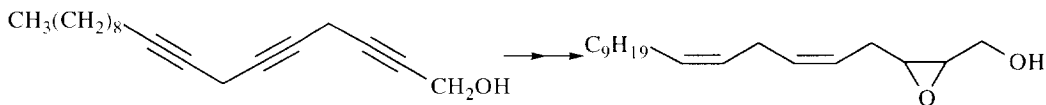
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Abstract : A general method for the synthesis of chiral *cis* epoxides, which we have previously described, is used to synthesize the active enantiomer **1** of the sex pheromone of *Boarmia selenaria*.

As part of an ongoing program on the preparation of Lepidopteran sexual pheromones, the synthesis of sex pheromone component of the giant Looper : *Boarmia selenaria* was easily achieved using a previously described strategy¹ developed in our laboratory in the preparation of chiral epoxides. The crude pheromone extract of *Boarmia selenaria* contains two components (3*Z*,6*Z*,9*Z*)-3,6,9-nonadecatriene and the epoxidien **1**.

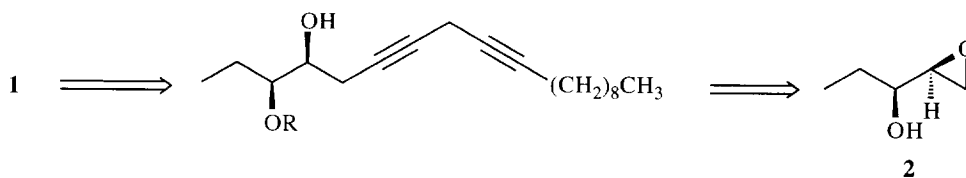


It has been shown that the active isomer was the (3*S*,4*R*) isomer³. The synthesis of compound **1** in optically active form has been already described by Millar and coll.² and by Becker and coll.³. Both used a strategy derived from Mori's method⁴, which involves a triynol obtained from alkynyl coupling reactions. Reduction of the corresponding triynol is achieved by hydroboration or catalytic semi-hydrogenation and the terminal epoxide is obtained by Sharpless epoxidation. The compound **1** is then prepared by action of lithiumcuprate derivatives on the corresponding tosylate.

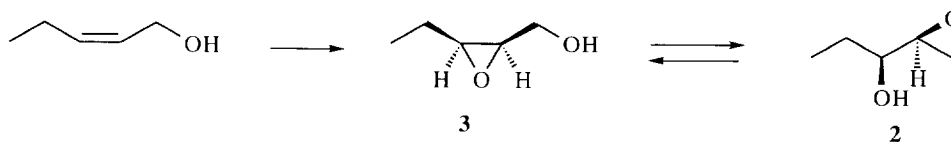


Preliminary results concerning this work were presented at 4th Belgian Organic Synthesis Symposium, Leuven, 25-29 May 1992.

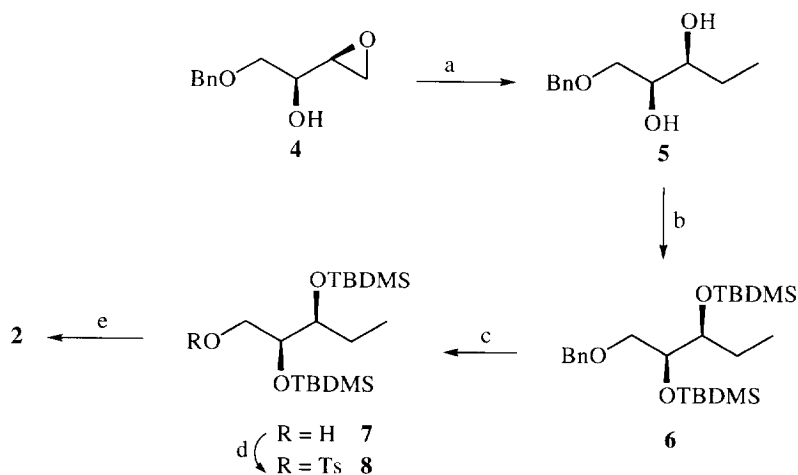
We present here another approach based on the following retrosynthetic scheme:



Starting from (2Z)-pent-2-en-1-ol the epoxyalcohol **3** was easily prepared in optically active form by Sharpless epoxidation⁶. When submitted to Payne's rearrangement⁵ it leads to **2** in poor yield¹, the equilibrium being in favour of compound **3**.



To circumvent this problem, we found it more convenient to start from compound **4** which can be opened by addition of organometallic compounds. This compound has been already described^{7,8} surprisingly with opposite specific rotations for the same enantiomer. The method previously described¹ can be applied to the case of the compound **2**. The result is depicted in the scheme 1 :



a : $(\text{CH}_3)_2\text{LiCu}$, -70°C , $\text{BF}_3 \cdot (\text{C}_2\text{H}_5)_2\text{O}$; b : TBDMStriflate, 2,6-lutidine, CH_2Cl_2 ; c : H_2 , Pd/C ; d : TsCl, NC_5H_5 , $+5^\circ\text{C}$; e : $(\text{C}_4\text{H}_9)_4\text{N}^+$, F⁻, THF

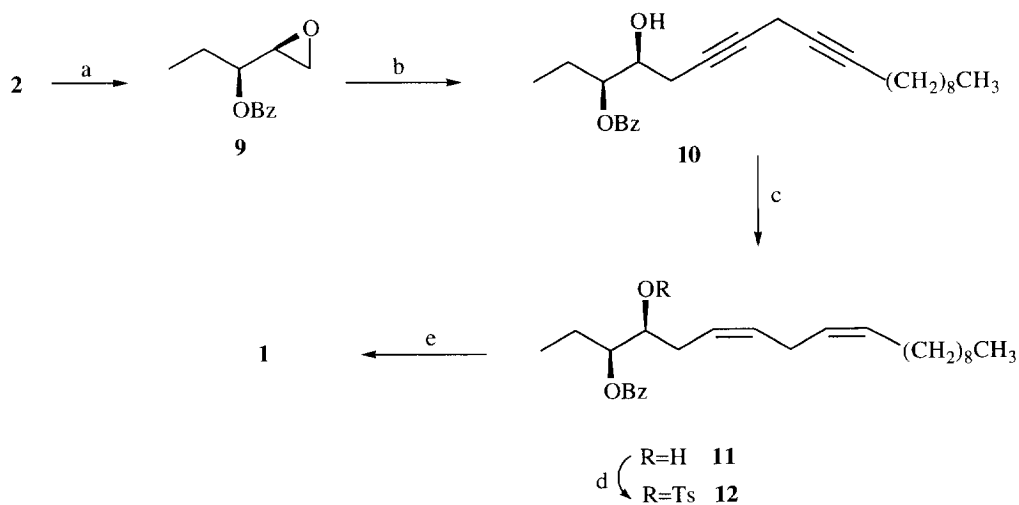
Scheme 1

The lithiumdimethylcuprate reacts with **4** in presence of a Lewis acid and gives **5** in high yield. The complete bissilylation was found difficult and could be only performed by the use of TBDMS triflate. The results of various attempts are reported in Table 1.

Conditions	MONOSILYLATED	DISYLATED
TBDMSCl DMAP, (C ₂ H ₅) ₃ N, CH ₂ Cl ₂	100% 24h	30% 5 days
TBDMS-N-methyltrifluoroacetamide, (C ₂ H ₅) ₃ N, CH ₃ CN	100% 48h	30% 6 days
TBDMS triflate (C ₂ H ₅) ₃ N, CH ₂ Cl ₂	–	Quantitative 1h
TBDMS triflate 2,6-lutidine, CH ₂ Cl ₂	–	Quantitative 1h

TABLE 1

We have previously shown that alkynyllithium reacts easily, at low temperature, on epoxyalcohols themselves or on their derivatives^{10,1} in presence of an excess of Lewis acid. The synthesis of **1** is depicted on scheme 2 :



a : BzCl, NC₅H₅ ; b : C₉H₁₉C≡C-CH₂-C≡CLi, BF₃·(C₂H₅)₂O, -70°C ; c : H₂ /Lindlar catalyst ; d : TsCl, NC₅H₅, +20°C ; e : K₂CO₃, CH₃OH

Scheme 2

Desilylation of **8** and spontaneous epoxide ring formation was performed by treatment with fluoride tetrabutylammonium leading to **2** in a good yield. The benzoate **9** was prepared according to standard method and its enantiomeric purity was determined to be higher than > 95 % by HPLC on chiral pak of (+) column⁹.

The tetradeca-1,4-diyne was prepared according to the method previously described for the (10Z,13Z,16Z)-nonadeca-10,13,16,18-tetraen-1-ol with slight modifications¹¹. The compound **10** was obtained according to Yamaguchi's method¹² with a good yield (88 %).

The enantiomer (3R,4S) can be prepared in the same way from the tosylate of compound **2**.

Experimental Section

NMR spectra were recorded on Bruker WP 200 and WM 400 spectrometers in CDCl₃. The chemical shifts of ¹H NMR signals : δ are reported in ppm (TMS as internal standard, $\delta = 0$). Coupling constants : J are reported in Hertz. The abbreviations : s, d, t, q, p, m and br signify : singlet, doublet, triplet, quartet, quintet, multiplet and broad respectively. IR spectra were recorded on a Perkin-Elmer using 1600 FT IR neat films on NaCl plates. Melting points were determined on a Büchi 510 apparatus and are uncorrected.

Low resolution mass spectra were recorded on a Ribermag R 10-10 B spectrometer under chemical ionization (NH₃) conditions, high resolution mass spectra were recorded on ZAB.HFQ.VG apparatus. Optical rotations were measured on a Perkin-Elmer 241 polarimeter in a 1-dm cell, in dichloromethane solutions.

All reactions were carried out under an inert atmosphere. Dry solvents were freshly distilled before used. Tetrahydrofuran (THF) was distilled from sodium-benzophenone. Dichloromethane was distilled from P₂O₅.

All reactions were monitored by thin layer chromatography carried out on Merck silicagel plates (Ref. 5549) using 5 % ethanolic phosphomolybdic acid/heat as developing agent. Merck silicagel (Ref. 9384) was used for flash chromatography.

The synthesis of (2S,3S)-1,2-epoxy-3-hydroxy-4-benzyloxybutane **4** and trimethylsilyl-1-bromo-3-prop-1-yne are described in¹⁰. 1-Undecyne and (2Z)-pent-2-en-1-ol were purchased from Lancaster and distilled prior to use.

Tetradeca-1,4-diyne

a/ 1-Trimethylsilyltetradeca-1,4-diyne

To a solution of 1-undecyne (7.6 g, 50 mmoles) in anhydrous tetrahydrofuran (100 ml), was added slowly a solution of ethylmagnesium bromide (41 ml of 1.2M in tetrahydrofuran, 50 mmoles) at room temperature. After 20 min of refluxing, catalytic amount of CuCl is added at room temperature. After 15 min of stirring, pure trimethylsilyl-1-bromo-3-prop-1-yne (9.5 g, 50 mmoles) is added. A strong thermic effect (+ 10°C) is observed, after the end of introduction, the mixture is refluxed during 30 min. Then the mixture is worked up by dropwise addition of aqueous saturated ammonium chloride with a catalytic amount of potassium cyanide. The aqueous layer was extracted with ether (3 x 100 ml). The combined organic layers were washed with water, dried (MgSO₄) and concentrated, the crude diyne was purified by flash chromatography (ethylacetate/cyclohexane : 5/95) (11.7 g, 90 % yield). ¹H NMR (200 MHz) : H₃ : 3.19 (t, J = 2.5 Hz) ; H₆ : 2.16 (tt, J = 7.5 Hz and J = 2.5 Hz) ; H₁₄ : 0.89 (t, J = 7.4 Hz) ; H₇₋₁₃ : 1.25 (s) ; CH₃-Si : 0.19 (s). ¹³C NMR (50.28 MHz) : C₁ : 84.7 ; C₂ : 101 ; C₄, C₅ : 81.2, 73.4 ; C₆ : 18.5 ; C₇₋₁₁ : 29 ; C₁₂ : 32 ; C₁₃ : 22.8 ; C₁₄ : 14.2. IR ν_{\max} : 2182 ; 1249 ; 842.

b/ Tetradeca-1,4-diyne

To a solution of trimethylsilyl-1-tetradeca-1,4-diyne (13.4g, 51.7 mmoles) in ethylalcohol (125 ml) was added dropwise a solution of silver nitrate (27g, 160 mmoles) in a mixture water/ethylalcohol (60ml/180ml). After stirring 1 hour, an aqueous solution of potassium cyanide is added (50g, 75 ml). The aqueous layer is extracted with pentane (3 x 150 ml), dried (MgSO_4) and concentrated. The crude product is purified by distillation, b.p. = 95°C (0.3 mmHg) (8.7 g, 88 % yield). $^1\text{H NMR}$ (200 MHz): H_1 : 2.02 (t, $J = 2.5$ Hz); H_3 : 3.12 (td, $J = 2.5$ Hz); H_6 : 2.12 (tt, $J = 7.5$ Hz and $J = 2.5$ Hz); H_{14} : 0.85 (t, $J = 7.5$ Hz); H_{7-13} : 1.2 (s). $^{13}\text{C NMR}$ (50.28 MHz): C_1 : 68.3; C_2 : 81.2; C_4, C_5 : 70.73, 79; C_3 : 9.5; C_6 : 18.8; C_{14} : 14.1; C_{13} : 23; C_{12} : 32; C_{7-11} : 29. IR ν_{max} : 3313; 639.

(2S,3R)-2,3-epoxypentan-1-ol 3

Dry methylene chloride (400 ml) was cooled to -30°C, titanium isopropoxide (12 ml, 40 mmoles) and L-(+)-dimethyltartrate (8.2 g, 40 mmoles) was added sequentially. The mixture was stirred 5 min at -30°C and (2Z)-pent-2-en-1-ol (3.4 g, 40 mmoles) was added dropwise. Stirring was continued for 10 min and t-butylhydroperoxyde (21 ml of 3.6M in toluene, 80 mmoles) was added dropwise. The resulting mixture was maintained at -30°C for 2 days and then saturated aqueous sodium sulfate was added at -30°C. The mixture was stirred vigorously for 2 hours at room temperature, filtered through a Celite pad, after addition of ether (300 ml). The filtrate was dried (Na_2SO_4), evaporated and the residue is purified by flash chromatography (ethylacetate/cyclohexane: 50/50). A mixture of compound **3** and dimethyltartrate is isolated. Finally **3** is isolated by distillation, b.p. = 81°C (15 mmHg); (2.1 g, 51 % yield, 59 % yield⁸, 42 % yield⁷). $[\alpha]_{\text{D}}^{22} = -13.4$ (c: 2.3) [Litt. $[\alpha]_{\text{D}} = -11.8$ (c: 1.7, CH_2Cl_2)⁸; $[\alpha]_{\text{D}} = +3$ (c: 0.2 ether)⁷]. $^1\text{H NMR}$ (200 MHz): H_1 : 3.8-3.6 (ddd); H_2, H_3 : 3.16 (m), 3.02 (m); H_4 : 1.55 (qd, $J = 7$ Hz); H_5 : 1.01 (t, $J = 7$ Hz); OH: 3 (br s). $^{13}\text{C NMR}$ (50.28 MHz): C_1 : 60.6; C_2, C_3 : 57.3, 58.4; C_4 : 21.3; C_5 : 10.6. IR ν_{max} : 3470.

The compound (2R,3S) **3** (50 % yield, $[\alpha]_{\text{D}}^{22} = +12.8$ (c: 1.8). [Litt. $[\alpha]_{\text{D}} = -3.1$ (c: 0.4, ether)] was synthesized by the same procedure and on the same scale.

(2S,3S)-1-benzyloxy-2,3-dihydroxypentane 5

To a suspension of cuprous iodide (5.6 g, 30 mmoles) in anhydrous ether (40 ml), at -60°C, methylolithium (33 ml, 1.6M in ether) was added dropwise under vigorous stirring. After 1 h at -20°C, a solution of (2S,3S)-1,2-epoxy-3-hydroxy-4-benzyloxybutane **4** (1.3 g, 6.7 mmoles) in anhydrous tetrahydrofuran (10 ml) was added at -60°C, immediately after borontrifluoride etherate (4.5 ml) is introduced. After 15 min, the mixture is worked up by dropwise addition of aqueous saturated ammonium chloride solution and ammonium hydroxyde (5 ml) under vigorous stirring, keeping the temperature at -60°C. The mixture was allowed to warm to room temperature and the aqueous layer was extracted with ether (3 x 50 ml). The combined organic layers were washed with water, dried (Na_2SO_4), concentrated, flash chromatographed (ethylacetate/cyclohexane: 40/60), giving **5** (1.1 g, 76 % yield). m.p. = 47°C; $[\alpha]_{\text{D}}^{22} = -9$ (c: 1.3). $^1\text{H NMR}$ (200 MHz): $\text{H}_1, \text{H}_2, \text{H}_3$: 3.6 (m); H_4 : 1.53 (q, $J = 7.5$ Hz); H_5 : 0.96 (t, $J = 7.5$ Hz); OH: 2.7 (br s); CH_2 : 4.5 (AB). $^{13}\text{C NMR}$ (50.28 MHz): $\text{C}_1, \text{C}_2, \text{C}_3, \text{CH}_2$: 72, 72.9, 73.7; C_4 : 26.5; C_5 : 10.1. IR ν_{max} : 3567; 3055; 1096. MS m/z : $\text{MH} + \text{NH}_4^+$: 228 (50 %); MH^+ : 211 (90 %). Anal. Calcd $\text{C}_{12}\text{H}_{18}\text{O}_3$: C: 68.54; H: 8.63; Found: C: 68.45; H: 8.84.

(2S,3S)-1-benzyloxy-2,3-di(t-butylidimethylsilyloxy)-pentane 6

At 0°C to a molar solution of **5** (1.6 g, 8 mmoles) in anhydrous dichloromethane (8 ml) is added 2,6-lutidine (4.1 ml, 33.9 mmoles), t-butylidimethylsilyltrifluoromethanesulfonate (6.1 ml, 25.4 mmoles). The

resulting mixture was worked up by dropwise addition of aqueous saturated ammonium chloride (100 ml) at room temperature. The aqueous layer was extracted with dichloromethane (3 x 100 ml). The combined organic layers were washed by 1N hydrochloric acid, then 1N sodium hydroxide, and finally by water until neutrality, dried (Na₂SO₄) and concentrated. Flash chromatography (ethylacetate/cyclohexane : 5/95) gave pure **6** (3.4 g, 99 % yield). $[\alpha]_D^{22} = -23$ (c : 1.82). ¹H NMR (200 MHz) : H_{1a} : 3.22 (dd, J = 8 Hz, J = 10 Hz) ; H_{1b} : 3.36 (dd, J = 2 Hz, J = 10 Hz) ; H₂ : 3.61 (m) ; H₃ : 3.36 (dt, J = 4 Hz, J = 8 Hz) ; H₅, t-C₄H₉ : 0.76 (br s) ; H_{4a} : 1.03 (qd, J = 2 Hz, J = 7 Hz) ; H_{4b} : 1.56 (qd, J = 4 Hz, J = 7 Hz) ; CH₂ : 4.36 ; CH₃-Si : 0,03 (s). ¹³C NMR (50.28 MHz) : C₁, C₂, C₃, CH₂ : 71.7, 73.3, 74.9, 76 ; C₄ : 24.1 ; C₅ : 11.5 ; CH₃-Si : - 4.4 ; $\underline{\text{C}}\text{H}_3\text{-C}$: 25.9 ; $\underline{\text{C}}\text{H}_3\text{-C}$: 18.2. IR ν_{max} : 1109 ; 1255 ; 835 ; 700 ; 735. MS m/z = MH⁺ : 439 (100 %).

(2S,3S)-1-hydroxy-2,3-di(t-butyl dimethylsilyloxy)-pentane 7

A solution of **6** (3.5 g, 8 mmoles) in methanol (150 ml) with palladium on charcoal (10 %) was stirred under a hydrogen atmosphere for 3 hours. After filtration of the catalyst and concentration, the crude product **7** was purified by flash chromatography (ethylacetate/cyclohexane: 20/80) (2.3 g, 85 % yield). $[\alpha]_D^{22} = -19.3$ (c : 1.6). ¹H NMR (200 MHz) : H₁ : 3.54 (m) ; H₂, H₃ : 3.75 (m) ; H_{4a} : 1.29 (qd, J = 2.5 Hz, J = 7 Hz) ; H_{4b} : 1.67 (qd, J = 4 Hz, J = 7 Hz) ; H₅ : t-C₄H₉ : 0.86 (br s) ; HO : 2.3 ; CH₃-Si : 0.04 (s). ¹³C NMR (50.28 MHz) : C₁ : 63.3 ; C₂ : 77.3 ; C₃ : 74 ; C₄ : 23.6 ; C₅ : 11.5 ; $\underline{\text{C}}\text{H}_3\text{-C}$: 25.9 ; CH₃- $\underline{\text{C}}$: 18 ; CH₃-Si : - 4. IR ν_{max} : 3466 ; 1361 ; 1098 ; 1260 ; 836. MS m/z : M + H⁺ : 349 (100 %) ; M + NH₄⁺ : 366 (10 %).

(2S,3S)-1-tosyloxy-2,3-di(t-butyl dimethylsilyloxy)-pentane 8

To a solution of **7** (0.8 g, 2.3 mmoles) in dry pyridine (5 ml) at 0°C was added p-toluenesulfonylchloride (0.9 g, 4.6 mmoles). The reaction mixture was kept at + 6°C for 5 hours and then poured onto ice. The mixture was extracted with ether (3 x 50 ml) and the combined extracts were washed with 1N hydrochloric acid until neutrality, dried (Na₂SO₄, K₂CO₃) and concentrated. The crude product was then purified by flash chromatography (ethylacetate/cyclohexane : 10/90) to give **8** (1.1 g, 95 % yield). $[\alpha]_D^{22} = -40$ (c : 1.75). ¹H NMR (200 MHz) : H₁ : 4.1-3.9 (m) ; H₂, H₃ : 3.42 (m), 3.82 (m) ; H_{4a} : 1.09 (qd, J = 3.7 Hz, J = 7 Hz) ; H_{4b} : 1.65 (qd, J = 4 Hz, J = 7 Hz) ; H₅, t-C₄H₉ : 0.81 (br s) ; CH₃-Si : 0.05 (s) ; $\underline{\text{C}}\text{H}_3\text{-C}_6\text{H}_4$: 2.40 (s). ¹³C NMR (50.28 MHz) : C₁, C₂, C₃ : 71.7, 73.6 , 75.5 ; C₄ : 23.7 ; C₅ : 11.4 ; CH₃- $\underline{\text{C}}$: 18 ; $\underline{\text{C}}\text{H}_3\text{-C}$: 25.8 ; CH₃-Si : - 4.4 ; $\underline{\text{C}}\text{H}_3\text{-C}_6\text{H}_4$: 21.7). IR ν_{max} : 1599 ; 1473 ; 1178 ; 1258 ; 837. MS m/z : M + NH₄⁺ : 520 (40 %) ; MH⁺ : 503 (90 %).

(2S,3S)-1,2-epoxy-3-hydroxypentane 2

To a solution of **8** (1 g, 2 mmoles) in anhydrous tetrahydrofuran (8 ml), at room temperature, was added dropwise a solution of tetra n-butylammonium fluoride (6.2 ml of 1M THF). After 2 hours, the reaction mixture was diluted with a saturated aqueous ammonium chloride solution (25 ml) and extracted continuously with ether (100 ml). The combined extracts were dried (Na₂SO₄), filtered and concentrated to give **2**. Flash chromatography (ether/pentane : 70/30) gave pure **2** (0.15 g, 72 % yield). $[\alpha]_D^{22} = +11.3$ (c : 1.56). ¹H NMR (200 MHz) : H_{1a} : 2.71 (dd) ; H_{1b} : 2.22 (dd) ; H₂ : 2.97 (m) ; H₃ : 3.34 (m) ; H₄ : 1.63 (qt, J = 7.4 Hz) ; H₅ : 0.99 (t, J = 7.4 Hz) ; H₆ : 2.5 (br s). ¹³C NMR (50.28 MHz) : C₁ : 45.1 ; C₂ : 55.3 ; C₃ : 73.1 ; C₄ : 27.4 ; C₅ : 9.8. IR ν_{max} : 3426 ; 3050 ; 1255 .

(2S,3S)-1,2-epoxy-3-benzoyloxypentane 9

To a solution of **2** (0.4 g, 4 mmoles) in dry pyridine (10 ml), at room temperature, was added benzoyl chloride (0.5 ml, 4.4 mmoles). After 30 min the reaction mixture was diluted with water (20 ml) and extracted with methylene chloride (3 x 40 ml). The combined organic extracts were washed with 1N hydrochloric acid

untill neutrality and dried (Na_2SO_4). After filtration and concentration, the crude product **9** was then purified by flash chromatography (ethyl acetate/cyclohexane : 30/70) (0.6 g, 72 % yield). $[\alpha]_D^{22} = + 8.5$ (c : 1.7). The enantiomeric excess is > 95 % determined by HPLC on chiral pak OT(+)column⁹. $^1\text{H NMR}$ (200 MHz) : $\text{H}_{1\text{a}}$: 2.71 (dd) ; $\text{H}_{1\text{b}}$: 2.86 (t) ; H_2 : 3.21 (m) ; H_4 : 1.86 (q, J = 7.3 Hz) ; H_5 : 1.03 (t, J = 7.3 Hz) ; H_3 : 4.93 (q, J = 7.3 Hz). $^{13}\text{C NMR}$ (50.28 MHz) : C_2 : 52.9 ; C_1 : 44.8 ; C_3 : 75.5 ; C_4 : 24.7 ; C_5 : 9.7, $\text{C}=\text{O}$: 166. IR ν_{max} : 3062 ; 1720 ; 1600 ; 1272 ; 1112 ; 712. HRMS Calc. for $\text{C}_{12}\text{H}_{14}\text{O}_3$: 206.0942 ; Found : 206.0947.

(3S,4S)-3-benzoyloxy-4-hydroxynonadeca-6,9-diyne 10

To a solution of tetradeca-1,4-diyne (1.5 g, 7.8 mmoles) in anhydrous tetrahydrofuran (40 ml) was added slowly a solution of butyllithium (4.9 ml of 1.6N in hexane), at - 60°C. After 15 min, a solution of **9** (0.7 g, 3.5 mmoles) in tetrahydrofuran (5 ml) was added, followed by borontrifluoride etherate (1.3 ml, 10.5 mmoles). The resulting mixture was maintained at - 70°C for 30 min, and then was worked up by dropwise addition of aqueous saturated ammonium chloride solution. After warming to room temperature, the aqueous layer was extracted with ether (3 x 50 ml) and the combined organic layers were washed with water, dried (MgSO_4) and concentrated. Purification by flash chromatography (ethyl acetate/cyclohexane : 20/80) giving **10** (1.2 g, 88 % yield). $[\alpha]_D^{22} = + 2.8$ (c : 1.56). $^1\text{H NMR}$ (200 MHz) : H_1 : 0.96 (t, J = 9 Hz) ; H_{19} : 0.85 (t, J = 7.4 Hz) ; H_8 : 3 (t, J = 2.5Hz) ; H_5 : 2.45 (tt) ; H_4 : 3.9 (m) ; H_3 : 5.12 (m) ; H_{11} : 2.09 (tt) ; H_2 : 1.80 (q, J = 9 Hz) ; H_{12-18} : 1.2. $^{13}\text{C NMR}$ (50.28 MHz) : C_1 , C_8 : 10.5, 10.4 ; C_{19} : 14.8 ; C_4 : 71.3 ; C_3 : 78.1 ; C_6 , C_7 , C_9 , C_{10} : 78.4, 74.5, 76.4, 81.5 ; C_{17} : 32.6 ; C_{11} : 19.4 ; C_{18} : 23.3 ; $\text{C}=\text{O}$: 167.1 ; H_{12-16} : 29. IR ν_{max} : 3446 ; 1719 ; 1601 ; 1273 ; 1114 ; 712.

(3S,4S,6Z,9Z)-3-benzoyloxy-4-hydroxynonadeca-6,9-diene 11

A solution of **10** (1.2 g, 3 mmoles) in methanol (100 ml) with Lindlar catalyst was stirred under hydrogen atmosphere for 1 hour. After filtration of the catalyst and concentration the residue was purified by flash chromatography (ethyl acetate/cyclohexane : 10/90) to give pure **11** (0.75 g, 62 % yield). $[\alpha]_D^{22} = + 3.4$ (c : 1.16). $^1\text{H NMR}$ (200 MHz) : H_1 : 0.96 (t, J = 9 Hz) ; H_{19} : 0.85 (t, J = 7.4 Hz) ; H_2 : 1.84 (q, J = 9 Hz) ; H_3 : 5.07 (m) ; H_4 : 3.8 (m) ; H_5 : 2.32 (t, J = 6.3 Hz) ; H_8 : 2.74 (t, J = 6.1 Hz) ; H_{11} : 1.91 (m) ; H_{12-18} : 1.2 ; H_6 , H_7 , H_9 , H_{19} : 5.29, - 5.47 (m). $^{13}\text{C NMR}$ (50.28 MHz) : C_1 : 9.9 ; C_2 : 22.8 ; C_3 : 78 ; C_4 : 72 ; C_6 , C_7 , C_9 , C_{10} : 131.7, 130.7, 124.7, 127.6 ; C_8 : 22.8 ; C_{19} : 14.2 ; $\text{C}=\text{O}$: 166.5 ; C_{11-16} : 29-31 ; C_{17} : 32 ; C_{18} : 23.7. IR ν_{max} : 3422 ; 1718 ; 3040 ; 1273 ; 711.

(3S,4S,6Z,9Z)-3-benzoyloxy-4-tosyloxynonadeca-6,9-diene 12

To a solution of **11** (0.43 g, 1 mmole) in dry pyridine (2 ml) was added p-toluenesulfonylchloride (0.4 g, 2 mmoles) at 0°C. The reaction mixture was kept at 0°C for 1 day and then poured onto ice. The mixture was extracted with ether (3 x 20 ml) and the combined extracts were washed with 1N hydrochloric acid, dried (Na_2SO_4 , K_2CO_3) and concentrated. The crude product was then purified by flash chromatography (ethyl acetate/cyclohexane : 30/70) to give **12** (0.44 g, 73 % yield). $[\alpha]_D^{22} = + 18.8$ (c : 1.1). $^1\text{H NMR}$ (200 MHz) : H_1 , H_{19} : 0.86 (t, J = 7.5 Hz) ; H_2 : 1.68 (m) ; H_3 : 4.75 (m) ; H_4 , H_6 , H_7 , H_9 , H_{10} : 5.36-5.15 ; H_5 : 2.43 (t, J = 6.7 Hz) ; H_8 : 2.57 (t, J = 6.7 Hz) ; H_{11} : 1.9 (m) ; H_{13-18} : 1.23 (s). $^{13}\text{C NMR}$ (50.28 MHz) : C_1 : 9.6 ; C_2 : 22.7 ; C_3 : 74.3 ; C_4 : 81.9 ; C_6 , C_7 , C_9 , C_{10} : 132.4, 130.8, 126.8, 122.3 ; $\text{C}=\text{O}$: 165.7 ; C_{19} : 14.1 ; C_5 : 23.6 ; $\text{C}_\text{H}_3\text{-C}_6\text{H}_4$: 21.6 ; C_{11-16} : 29 ; C_{17} : 32 ; C_{18} : 23.6. IR ν_{max} : 1719.

(3S,4R,6Z,9Z)-3,4-epoxynonadeca-6,9-diene 1

To a solution of **12** (0.44 g, 0.8 mmoles) in dry methanol (20 ml) at room temperature, was added in small portions, anhydrous potassium carbonate (4 equivalents) under vigorous stirring. After 2 hours, the

solvent is removed and the mixture was directly purified by flash chromatography (ethyl acetate/cyclohexane : 10/90) to give pure **1** (0.21 g, 92 % yield). $[\alpha]_D^{22} = + 0.77$ (c : 1.1). [Lit. $[\alpha]_D = + 2.5$ (c : 2.7)²]. ¹H NMR (400 MHz) : H₁ : 1.05 (t, J = 7.4 Hz) ; H₁₉ : 0.88 (t, J = 6.7 Hz) ; H₃, H₄ : 2.95, 2.89 (m) ; H₅ : 2.4-2.2 (m) ; H₆, H₇, H₉, H₁₀ : 5.49-5.33 (m) ; H₂ : 1.57 (m) ; H₈ : 2.8 (t, J = 6.7 Hz) ; H₁₂₋₁₈ : 1.3 ; H₁₁ : 2.04 (q, J = 6.8 Hz). ¹³C NMR (50.28 MHz) : C₁ : 10.7 ; C₂ : 21.2 ; C₃, C₄ : 58.5-56.7 ; C₅ : 26.3 ; C₆, C₇, C₉, C₁₀ : 124.3, 127.3, 131, 130.9 ; C₁₉ : 14.2 ; C₁₈ : 32 ; C₁₇ : 22.8 ; C₈ : 26 ; C₁₁ : 27.4 ; C₁₂₋₁₆ : 29.

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