Chemistry of Natural Compounds and Bioorganic Chemistry

A novel polyfunctional chiral building block derived from (*S*)-ethyl lactate. Application to the synthesis of the sex pheromone of the southern corn rootworm (*Diabrotica undecimpunctata howardi*)*

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Highly enantiomerically pure (4*S*,5*E*)-4-bromomethylhept-5-enenitrile was prepared from (*S*)-ethyl lactate by a six-step procedure involving a rearrangement of chiral cyclopropylcarbinol. This product was used for the synthesis of the sex pheromone of the southern corn rootworm (*Diabrotica undecimpunctata howardi*), (10*R*)-10-methyltridecan-2-one.

Key words: (*S*)-(−)-ethyl lactate, allylic alcohol, diastereoselective cyclopropanation, Julia—Johnson rearrangement, chiral cyclopropylcarbinol, (4*S*,5*E*)-4-bromomethyl-5-enenitrile, (10*R*)-10-methyltridecan-2-one, sex pheromone, southern corn rootworm (*Diabrotica undecimpunctata howardi*).

Acyclic polyfunctional chiral building blocks (CBB) are widely used in the synthesis of diverse natural products (see, for example, Ref. 2); therefore, extension of the range of these compounds presents certain interest.

In this paper, we discuss an original scheme developed for the transformation of commercially available (*S*)-(−)-ethyl lactate (**1**) (Fluka, *ee* ~99%) in a promising polyfunctional CBB, namely, (4*S*,5*E*)-4-bromomethylhept-5-enenitrile (**2**) having a high enantiomeric purity (Scheme 1). The versatility of this compound as a CBB is due to the obvious possibility of selective modification of any of the functionalized hydrocarbon substituents forming the asymmetric center.

The key step in the synthesis of nitrile **2** is the Julia—Johnson rearrangement of chiral cyclopropylcarbinol **6**, prepared by a stereocontrolled route, on treatment with $ZnBr_2$ in the presence of TMSBr (*cf.* Ref. 3) or 48% HBr.[4] Alcohol **6** was prepared upon a sequence of virtually stereospecific transformations of ester **1**, which was first converted into aldehyde **3** by a known procedure.[5] Olefination of compound **3** by phosphorane **10** under salt-free conditions (*cf.* Ref. 6)

* For preliminary communication, see Ref. 1.

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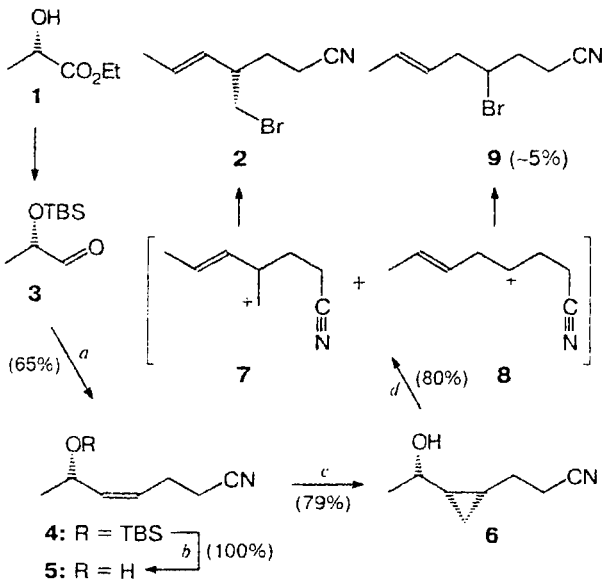
Scheme 1



Reagents and conditions: *a*. $Ph_3P{=}CH(CH_2)_2CN$ (**10**), HMPA—THF, −78→0 °C. *b*. $Bu^n_4N^+F^-$, THF, 20 °C. *c*. CH_2I_2, $ZnEt_2$, CH_2Cl_2, 20 °C. *d*. $ZnBr_2$, TMSBr, CH_2Cl_2, −30→0 °C or HBr (aq.) (48%), 20 °C.

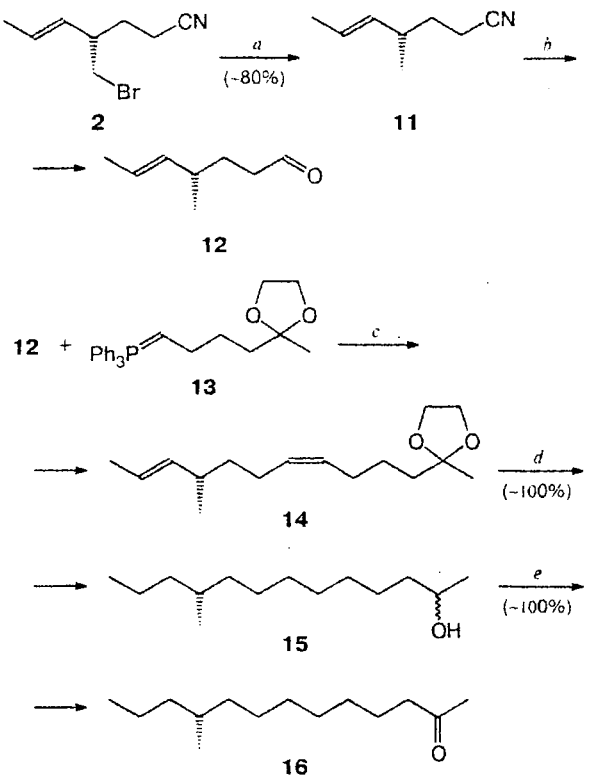
smoothly gave disubstituted olefin **4** (*Z* >99%, data of ^{1}H NMR spectroscopy and GC/MS analysis).* The allylic alcohol **5** corresponding to TBS ether **4** was subsequently cyclopropanated to give substituted cyclopropylcarbinol **6** with high stereoselectivity, as is known for this type of transformations[7] (*de* > 99%, ^{1}H and ^{13}C NMR).

This regioselectivity of the rearrangement of compound **6** into homoallylic bromide **2** has not been observed previously for cyclopropylcarbinols having an additional alkyl substituent in the cyclopropane ring. Normally this process affords a linear product such as **9**; this result has been explained[4,8] by the higher stability of the corresponding secondary carbonium ion, similar to **8**. However, the rearrangement of compound **6** yields only minor amounts (~5%) of secondary bromide **9**, in addition to the major regioisomer, primary bromide **2**. This unusual outcome can be explained by the fact that the molecule of alcohol **6** contains a nitrile group, whose negative inductive effect and/or anchimeric assistance directs the reaction to the route involving the formation of intermediate **7**, in which the cationic center is more remote from this group.

The structures of the previously unknown compounds **2** and **4**—**6** were confirmed by elemental analysis and spectroscopy. As noted above, nitrile **2** contains an admixture (~5%) of linear product **9**, which was identified using GC/MS analysis and also based on the fact that the ^{1}H NMR spectrum of sample **2** contained an additional signal at δ 3.98—4.15 (CHBr) with the corresponding integral intensity.

It appears obvious that the nitrile **2** obtained in this way in an overall yield of ~30% is highly enantiomerically pure, because each of the steps in the sequence **1** → **3** → **4** → **5** → **6** is virtually stereospecific and the rearrangement **6** → **2**, which completes the transformation route, does not involve the chiral center, which finally remains in the molecule of **2**. The high enantiomeric homogeneity of nitrile **2** was confirmed by the synthesis of the sex pheromone of the southern corn rootworm (*Diabrotica undecimpunctata howardi*)[9] starting from this nitrile (Scheme 2, compound **16**).

Scheme 2



Reagents and conditions: *a*. $NaBH_4$, DMSO—H_2O. *b*. DIBAH, *n*-C_6H_{14}, −78→20 °C. *c*. THF—*n*-C_6H_{14}, −78→20 °C. *d*. $CoCl_2$/$LiAlH_4$, −78→20 °C. *e*. PCC, CH_2Cl_2, 20 °C.

For this purpose, compound **2** was first subjected to reductive debromination. Secondary bromide **9**, inert under the reaction conditions, was separated in this step by chromatographic purification of the reaction mixture. The subsequent hydride reduction of the interme-

* It is noteworthy that the Wittig reaction carried out under these conditions is virtually not accompanied by epimerization of the starting aldehyde **3**. This conclusion can be drawn from the final stereochemical outcome of the sequence of transformations considered below.

diate nitrile **11** smoothly gave fairly volatile (4*S*,5*E*)-4-methylhept-5-en-1-al (**12**), which was introduced in the condensation with phosphorane **13** without further purification. The saturation of the multiple bonds in the resulting diene **14** by treatment with [CoH] (*cf.* Refs. 10 and 11) was accompanied by reductive transformation of the ethylene ketal group into the alcoholic function. The final stage of the synthesis consisted in almost quantitative oxidation of the mixture of diastereomeric secondary alcohols **15** into the target ketone **16**.

The newly synthesized compounds **11** and **14** were characterized by sets of spectroscopic and elemental analysis data. The spectral parameters of the previously described[12,13] alcohol mixture **15** and the target ketone **16**[9,12–14] virtually coincided with those reported in the literature. The resulting sample of ketone **16** had $[\alpha]_D^{25}$ −1.52° (*c* 3.6, $CHCl_3$) (*cf.* Ref. 13: $[\alpha]_D^{25}$ −1.65° (*c* 9.39, $CHCl_3$)).

Experimental

IR spectra were recorded on a Specord M-80 instrument. ^1H and ^{13}C NMR spectra for solutions in $CDCl_3$ were recorded on a Bruker AC-200 spectrometer (200.13 and 50.32 MHz, respectively). The ^1H and ^{13}C NMR chemical shifts were measured in the δ scale with respect to the solvent (7.27 for ^1H and 77.0 for ^{13}C). GC/MS analysis was carried out on a Hewlett Packard 5690-II instrument (a 25 m × 0.2 mm capillary column with OV-101, a Hewlett Packard 5972A mass selective detector (EI, 70 eV)). The $[\alpha]_D$ values were measured on a Jasco DIP-360 polarimeter.

(4*Z*,6*S*)-6-(*tert*-Butyldimethylsilyloxy)hept-4-enenitrile (4). At −30 °C, a 1.3 *N* THF solution of $NaN(TMS)_2$ (6.6 mL, 8.6 mmol) was added over a period of 5 min to a vigorously stirred (Ar) suspension of $Ph_3P^+(CH_2)_3CN\ Br^-$[15] (4.8 g, 9.37 mmol) in 50 mL of THF and 8 mL of HMPTA. The yellow-orange slurry formed after keeping the mixture for 15 min at −10 °C was cooled to −78 °C, and a solution of aldehyde **3**[5] (1.47 g, 7.81 mmol) in 5 mL of THF was added over a period of 5 min. The reaction mixture was heated to 20 °C, kept for 1 h, diluted with 70 mL of MeOBu^t, and filtered through a short SiO_2 layer. The filtrate was concentrated *in vacuo* and the residue was chromatographed on 50 g of SiO_2. Elution with a hexane—MeOBu^t mixture (100 : 3 (v/v)) afforded 1.23 g (66%) of TBS ether **4** as a colorless oil. IR (film), ν/cm^{-1}: 675, 745, 785, 820, 845, 890, 945, 1000, 1015, 1045, 1090, 1137, 1190, 1260, 1305, 1335, 1365, 1370, 1390, 1410, 1430, 1448, 1465, 1475, 2260, 2865, 2900, 2940, 2960, 3020. ^1H NMR, δ: 0.05, 0.06 (both s, 6 H, Me_2Si); 0.89 (s, 9 H, Bu^t); 1.22 (d, 3 H, Me, *J* = 6.3 Hz); 2.30—2.55 (m, 4 H, $H_2C(2)$, $H_2C(3)$); 4.58 (dqd, 1 H, HC(6), *J* = 8.1, 6.3, and 1.1 Hz); 5.20—5.35 (m, 1 H, HC(4), $J_{H(4)-H(5)}$ = 11.1 Hz, $J_{H(4)-H(6)}$ = 1.1 Hz); 5.52—5.67 (m, 1 H, HC(5), $J_{H(5)-H(6)}$ = 8.1 Hz). ^{13}C NMR, δ: −4.7, −4.5 (Me_2Si); 17.5 (C(2)); 18.1 ($\underline{C}Me_3$); 23.7 (C(3)); 23.8 (C(7)); 25.8 ($C\underline{Me}_3$); 65.0 (C(6)); 119.0 (CN); 123.3 (C(4)); 138.5 (C(5)). $[\alpha]_D^{18}$ +29.7° (*c* 2.46, $CHCl_3$).

(4*Z*,6*S*)-6-Hydroxyhept-4-enenitrile (5). ***A.*** A solution of TBS ether **4** (0.52 g, 2.17 mmol) and $Bu^n_4N^+F^- \cdot 2H_2O$ (0.82 g, 2.6 mmol) in 17 mL of THF was stirred at 20 °C for 12 h and concentrated *in vacuo*. The residue was chromatographed on 20 g of SiO_2. Elution with MeOBu^t yielded 0.27 g (~100%) of alcohol **5** as a colorless oil. IR (film), ν/cm^{-1}: 760, 840, 875, 935, 1030, 1065, 1105, 1135, 1195, 1225, 1290, 1315, 1370, 1430, 1450, 2655, 2260, 2915, 2975, 3020, 3400. ^1H NMR, δ: 1.24 (d, 3 H, Me, *J* = 6.3 Hz); 2.30—2.63 (m, 4 H, $H_2C(2)$, $H_2C(3)$); 4.57 (dqd, 1 H, HC(6), *J* = 8.1, 6.3, and 1.1 Hz); 5.30—5.50 (m, 1 H, HC(4)); 5.55—5.68 (m, 1 H, HC(5)). ^{13}C NMR, δ: 17.5 (C(2)); 23.4 (C(3), C(7)); 63.3 (C(6)); 119.4 (CN); 125.6 (C(4)); 137.4 (C(5)). Found (%): C, 67.25; H, 8.79; N, 11.37. $C_7H_{11}NO$. Calculated (%): C, 67.17; H, 8.85; N, 11.19. $[\alpha]_D^{24}$ −7.8° (*c* 1.83, $CHCl_3$).

B. A solution of TBS ether **4** (0.9 g, 3.75 mmol) and 0.5 mL of concentrated HCl in 15 mL of EtOH was stirred at 20 °C for 30 min and concentrated *in vacuo* and the residue was chromatographed on 20 g of SiO_2. Elution with MeOBu^t gave 0.47 g (~100%) of alcohol **5**, virtually identical (NMR spectra) to the sample described above.

(1*S*,1″*S*,2*R*)-2-(2′-Cyanoethyl)-1-(1″-hydroxyethyl)cyclopropane (6). Diiodomethane (8.31 g, 31 mmol) was added at −10 °C over a period of 10 min to a stirred (Ar) solution of Et_2Zn (3.80 g, 30.7 mmol) in 70 mL of CH_2Cl_2. The mixture was heated to 0 °C and kept for 30 min; then a solution of alcohol **5** (0.96 g, 7.68 mmol) in 5 mL of CH_2Cl_2 was added to it over a period of 2 min. The reaction mixture was heated to 20 °C, stirred for 48 h, and quenched with a saturated solution of NH_4Cl. The organic layer was washed with a saturated solution of NH_4Cl, diluted by an equal volume of MeOBu^t, washed successively with a saturated solution of Na_2CO_3 and with brine, dried with Na_2SO_4, and concentrated *in vacuo*, and the residue was chromatographed on 20 g of SiO_2. Elution with MeOBu^t yielded 0.84 g (79%) of alcohol **6** as a colorless oil. IR (film), ν/cm^{-1}: 860, 890, 920, 940, 980, 1005, 1025, 1085, 1105, 1138, 1180, 1375, 1425, 1455, 2260, 2930, 2985, 3000, 3170, 3400. ^1H NMR, δ: 0.17—0.26 (m, 1 H, *cis*-HC(3)); 0.76—0.88 (m, 1 H, *trans*-HC(3)); 0.88—1.06 (m, 2 H, HC(1), HC(2)); 1.29 (d, 3 H, MeC(2′), *J* = 6.1 Hz); 1.40, 1.95 (both m, 2 H, $H_2C(1')$); 2.38—2.5 (m, 2 H, $H_2C(2')$); 3.37 (dq, 1 H, HC(1″), *J* = 8.5 and 6.1 Hz). ^{13}C NMR, δ: 9.3 (C(3)); 15.2 (C(2)); 17.5 (C(2′)); 23.8, 24.0 (C(1), C(2″)); 24.9 (C(1′)); 68.2 (C(1″)); 119.6 (C(3′)). Found (%): C, 69.37; H, 9.54; N, 9.84. $C_8H_{13}NO$. Calculated (%): C, 69.03; H, 9.41; N, 10.06. $[\alpha]_D^{16}$ −38.4° (*c* 2.00, MeOH).

(4*S*,5*E*)-4-Bromomethylhept-5-enenitrile (2). ***A.*** Zinc bromide (1.1 g, 4.89 mmol) was added in one portion to a solution of alcohol **6** (0.68 g, 4.89 mmol) in 20 mL of CH_2Cl_2 stirred (Ar) at −30 °C. Then TMSBr (1.87 g, 12.2 mmol) was added over a period of 5 min. The mixture was heated to 0 °C over a period of 20 min, diluted with 30 mL of MeOBu^t, washed successively with a saturated solution of $NaHCO_3$ and with brine, dried with Na_2SO_4, and concentrated *in vacuo*. The residue was chromatographed on 20 g of SiO_2. Gradient elution in the hexane—MeOBu^t system (8 : 1 → 7 : 3 (v/v)) afforded 0.79 g (80%) of nitrile **2** as a colorless oil. IR (film), ν/cm^{-1}: 650, 800, 930, 975, 1225, 1245, 1270, 1305, 1370, 1430, 1450, 1668, 2260, 2860, 2940, 2980, 3030. ^1H NMR, δ: 1.50—1.70 (m, 1 H, HC(3)); 1.72 (dd, 3 H, $H_3C(7)$, *J* = 6.5 and 1.6 Hz); 1.92—2.12 (m, 1 H, HC(3)); 2.22—2.55 (m, 3 H, $H_2C(2)$, HC(4)); 3.28—3.50 (m, 2 H, CH_2Br); 5.19 (ddq, 1 H, HC(5), *J* = 15.3, 8.8, and 1.6 Hz); 5.67 (dq, 1 H, HC(6), *J* = 15.3 and 6.5 Hz). ^{13}C NMR, δ: 15.0 (C(2)); 17.9 (C(7)); 28.6 (C(3)); 37.6 (CH_2Br); 43.5 (C(4)); 119.3 (C(1)); 129.5 (C(6)); 130.2 (C(5)). Found (%): C, 47.66; H, 6.05; Br, 39.29; N, 6.91. $C_8H_{12}BrN$. Calculated (%): C, 47.55; H, 5.98; Br, 39.54; N, 6.93. $[\alpha]_D^{16}$ +45.1° (*c* 1.21, $CHCl_3$).

B. An emulsion of alcohol **6** (0.74 g, 5.30 mmol) and 5 mL of 48% HBr was vigorously stirred at 20 °C for 2 h, and the product was extracted with CH_2Cl_2. The extract was diluted with an equal volume of MeOBu^t, washed successively with a

saturated solution of $NaHCO_3$ and brine, dried with Na_2SO_4, and concentrated *in vacuo*. The residue was chromatographed on 20 g of SiO_2. Elution under conditions described above gave 0.96 g (89%) of nitrile **2**, virtually identical (NMR spectra) to the sample prepared in the previous experiment.

(4*S*,5*E*)-4-Methylhept-5-enenitrile (11). A solution of bromide **2** (0.45 g, 2.23 mmol) and $NaBH_4$ (0.68 g, 17.8 mmol) in 9 mL of DMSO and 2.3 mL of H_2O was stirred at 20 °C for 16 h, diluted with 10 mL of H_2O, and extracted with $MeOBu^t$. The extract was washed successively with H_2O and brine, dried with Na_2SO_4, and concentrated *in vacuo*. The residue was chromatographed on 20 g of SiO_2. Elution with a mixture of pentane—$MeOBu^t$ (37 : 3 (v/v)) afforded 0.22 g (81%) of nitrile **11** as a colorless liquid, b.p. (bath) 75 °C (15 Torr). IR (film), ν/cm^{-1}: 978, 1381, 1427, 1454, 2258, 2875, 2930, 2965, 3015. ^1H NMR, δ: 0.99 (d, 3 H, Me(4), J = 6.7 Hz); 1.38—1.67 (m, 2 H, $H_2C(3)$); 1.64 (dd, 3 H, $H_3C(7)$, J = 6.3 and 1.5 Hz); 2.07—2.43 (m, 3 H, $H_2C(2)$, HC(4)); 5.15 (ddq, 1 H, HC(5), J = 15.3, 8.3 and 1.5 Hz); 5.47 (dq, 1 H, HC(6), J = 15.3 and 6.3 Hz). ^{13}C NMR, δ: 15.2 (C(2)); 17.9, 20.7 (C(7), C(8)); 32.2 (C(3)); 36.3 (C(4)); 119.9 (C(1)); 125.8 (C(6)); 130.6 (C(5)). Found (%): C, 77.93; H, 10.87; N, 11.49. $C_8H_{13}N$. Calculated (%): C, 77.99; H, 10.64; N, 11.36. $[\alpha]_D^{30}$ +61.55° (*c* 2.15, $CHCl_3$).

(4′*Z*,8′*S*,9′*E*)-2-Methyl-(8′-methylundeca-4′,9′-dienyl)-1,3-dioxolane (14). A 0.8 *N* hexane solution of DIBAH (2.41 mL, 1.93 mmol) was added in one portion at −78 °C to a stirred (Ar) solution of nitrile **11** (0.19 g, 1.54 mmol) in 10 mL of hexane. The reaction mixture was stirred for 30 min at −78 °C, heated to 20 °C, stirred for 2 h, and quenched with a saturated solution of NH_4Cl and, 20 min later, with 10 mL of 20% H_2SO_4 over 30 min. The aqueous layer was separated and extracted with hexane. The resulting solution (15 mL) of the fairly volatile aldehyde **12** was dried with Na_2SO_4 and used in the subsequent step without further purification.

An aliquot portion of the solution was analyzed by GC/MS and NMR spectroscopy. The retention time of aldehyde **12** was 4.65 min (evaporator temperature 280 °C, temperature control: 50 °C for 1 min and then temperature programming to 280 °C at a rate of 20 °C min^{-1}). MS, m/z (I_{rel} (%)): 126 $[M]^+$ (1), 112 $[M - Me]^+$ (2), 108 (11), 97 (6), 93 (8), 91 (3), 82 (100), 77 (4), 69 (54), 67 (66). After evaporation of the solvent under atmospheric pressure, the ^1H NMR spectrum of the residue, δ: 0.98 (d, 3 H, MeC(4), J = 7 Hz); 1.4—1.8 (m, 2 H, $H_2C(2)$); 1.64 (dd, 3 H, $H_3C(7)$, J = 6.0 and 1.3 Hz); 2.06 (m, 1 H, HC(4)); 2.40 (m, 1 H, HC(2)); 5.20 (ddq, 1 H, HC(5), J = 15.3, 7.8, and 1.3 Hz); 5.47 (dq, 1 H, HC(6), J = 15.3 and 6.0 Hz); 9.74 (t, 1 H, HCO, J = 1.7 Hz). ^{13}C NMR, δ: 17.8, 20.8, 29.0, 36.5, 41.9, 124.4, 136.1, 202.8.

A 1.3 *N* solution of $NaN(TMS)_2$ (3.2 mL, 4.18 mmol) in THF was added at −30 °C over a period of 5 min to a vigorously stirred (Ar) suspension of $Ph_3P^+(CH_2)_4C(OCH_2)_2Me\ Br^-$ [16] (2.25 g, 4.64 mmol) in 50 mL of THF. The yellow-orange slurry formed after keeping the mixture for 30 min at −10 °C was cooled to −78 °C, and a solution of aldehyde **12** (14.25 mL) prepared previously (see above) was added over a period of 5 min. The reaction mixture was heated to 20 °C, kept for 1 h, diluted with an equal volume of hexane, and filtered through a short layer of SiO_2. The filtrate was evaporated *in vacuo* and the residue was chromatographed on 15 g of SiO_2. Elution with a hexane—$MeOBu^t$ mixture (50 : 1 (v/v)) gave 0.21 g of diene **14** (57%, based on the initial nitrile **11**) as a colorless oil. ^1H NMR, δ: 0.96 (d, 3 H, MeC(8′), J = 6.7 Hz); 1.12—1.38 (m, 2 H, $H_2C(7')$); 1.32 (s, 3 H, MeC(2)); 1.38—1.57 (m, 2 H, $H_2C(2')$); 1.58—1.75 (m, 5 H, $H_2C(1')$, $H_3C(11')$); 1.93—2.17 (m, 5 H, $H_2C(3')$, $H_2C(6')$, $H_2C(8')$); 3.87—4.03 (m, 4 H, H_2CO); 5.20—5.50 (m, 4 H, HC=C). ^{13}C NMR, δ: 17.9 (C(11′)); 20.8 (MeC(8′)); 23.8 (MeC(2)); 24.2, 25.1, 27.3, 37.1, 38.8 (CH_2); 36.3 (C(8′)); 64.6 (CH_2O); 110.1 (C(2)); 123.1 (C(10′)); 120.3, 129.3 (C(4′), C(5′)); 137.3 (C(9)). MS, m/z (I_{rel} (%)): 252 $[M]^+$ (1), 237 $[M - Me]^+$ (2), 190 (1), 175 (1), 161 (1), 150 (5), 141 (2), 135 (7), 121 (4), 109 (7), 108 (4), 107 (4), 103 (3), 102 (2), 99 (8), 95 (5), 87 (100), 82 (7), 81 (8), 69 (12), 67 (13). $[\alpha]_D^{26}$ +15.66° (*c* 1.88, $CHCl_3$).

(2*R*/*S*,10*R*)-10-Methyltridecan-2-ols (15). $LiAlH_4$ (38 mg, 1.0 mmol) was added in one portion to a solution of diene **14** (19.7 mg, 0.078 mmol) and $CoCl_2$ (0.13 g, 1.0 mmol) in 2 mL of THF stirred (Ar) at −78 °C. The resulting green suspension was heated to 20 °C, stirred for 14 h, and treated with H_2O. The aqueous layer was separated and extracted with $MeOBu^t$. The extract was dried with Na_2SO_4 and concentrated *in vacuo*, and the residue was chromatographed on 3 g of SiO_2. Elution with a hexane—$MeOBu^t$ mixture (6 : 1 (v/v)) gave 16.5 mg (99%) of a mixture of approximately equal amounts of epimers **15** as a colorless oil. ^1H NMR, δ: 0.83 (d, 3 H, MeC(10), J = 6.4 Hz); 0.87 (t, 3 H, HC(13), J = 6.9 Hz); 1.10—1.55 (m, 19 H, HC(10), CH_2); 1.18 (d, 3 H, HC(1), J = 6.2 Hz); 3.80 (m, 1 H, HC(2)) (*cf.* Refs. 12 and 13).

(10*R*)-10-Methyltridecan-2-one (16). A solution of a mixture of alcohols **15** (51 mg, 0.24 mmol) in 1 mL of CH_2Cl_2 was added in one portion to a suspension of PCC (20.5 mg, 0.25 mmol) in 3 mL of CH_2Cl_2 stirred at 20 °C. The mixture was stirred for 2 h at 20 °C and diluted with Et_2O; the oily precipitate was triturated until it turned into a powder. The supernatant was filtered through a short layer of SiO_2 and concentrated *in vacuo*, and the residue was chromatographed on 5 g of SiO_2. Elution with a hexane—$MeOBu^t$ mixture (97 : 3 (v/v)) gave 50 mg (99%) of ketone **16** as a colorless oil. ^1H NMR, δ: 0.83 (d, 3 H, MeC(10), J = 6.4 Hz); 0.87 (t, 3 H, HC(13), J = 6.9 Hz); 0.95—1.70 (m, 17 H, HC(10), CH_2); 2.12 (s, 3 H, HC(1)); 2.41 (t, 2 H, HC(3), J = 7.4 Hz) (*cf.* Refs. 9, 12—14). $[\alpha]_D^{25}$ −1.52° (*c* 3.6, $CHCl_3$).

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