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# Enantiospecific synthesis of (+)-*trans*-α-himachalene *via* an intramolecular type II carbonyl ene reaction[†]

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Enantiospecific synthesis of (+)-*trans*-α-himachalene starting from (*R*)-carvone is described. An intramolecular type II carbonyl ene reaction has been employed as the key step for the construction of the bicyclo[5.4.0]undecane ring system.

**Keywords**: Enantiospecific synthesis, himachalenes, sesquiterpenes, (*R*)-carvone, intramolecular ene-reaction

Flea beetles constitute the largest subfamily of the leaf beetle family Chrysomelidae[1]. Adult flea beetles feed on host plant foliage and the larvae typically feed on the roots of the same plant[2]. The group includes both agricultural pests and beneficial species. For example, *Phyllotreta cruciferae* Goeze is a significant pest of canola and rapeseed in the northern prairie areas of the United States and Canada and it also attacks cabbage, horseradish and other crucifers in many regions[3]. On the other hand *Aphthona flava* Guillebeau, *A. czwalinae*, and *A. cyparissiae* are effective biocontrol agents[4] of the leafy spurge (*Euphorbia esula* L.). In an attempt to discover the possible pheromone components of the flea beetles, the research group of Bartelt[5] has investigated on the volatile constituents from the four species *Phyllotreta cruciferae*, *A. flava*, *A. czwalinae* and *A. cyparissiae.* These investigations led to the isolation[5] of eight male specific compounds, *trans*-α-himachalene **1**, himachala-7,9(12)-diene **2**, 9β-hydroxyhimachal-7-ene **3**, 9α-hydroxyhimachal-7-ene **4**, 12-*nor*himachal-7-en-9-one **5**, himachala-7,9-diene **6**, γ-cadinene **7** and *ar*-himachalene **8**, from these four beetle species in various ratios, whose structures were established by spectroscopic (NMR and mass) methods and chemical conversions, **Figure 1**. Structure of *trans*-α-himachalene (+)-**1** was further confirmed by comparison of the $^1$H NMR spectral data with that of the optical antipode reported by Sukh Dev and Joseph[6]. The sesquiterpenes himachalenes from plant sources were known for nearly five decades[7]. During 1952-68 Dev and co-workers reported the isolation of α-himachalene **9**, β-himachalene **10**, γ-himachalene **11**, *ar*-himachalene **8**, himachalol **12** and allohimachalene **13** from the Himalayan deodar *Cedrus deodara*. During the course of structure elucidation, Dev and Joseph[6] have transformed *cis*-α-himachalene **9** into *trans*-α-himachalene (-)-**1**.

A few total and formal syntheses of *cis*-α-himachalene **9** were known in the literature[8]. In continuation of the interest in the enantiospecific synthesis of natural products[9] starting from the readily and abundantly available monoterpene (*R*)-carvone **14**, herein is presented the details of the enantiospecific first total synthesis[10] of *trans*-α-himachalene (+)-**1** employing an intramolecular type II carbonyl ene reaction as the key step.

Retrosynthetic analysis of *trans*-α-himachalene **1** is depicted in **Scheme I**. It was anticipated that presence of the propanaldehyde and isopropenyl side chains at C-3 and C-4 positions of methylcyclohexene, *e.g.* **15**, would be ideal for generating hydroxyhimachalene **16** *via* a carbonyl ene reaction[11]. It was contemplated that the aldehyde **15** or its equivalent could be obtained from carvone **14** *via* the keto ester **17**.

The synthetic sequence is depicted in **Schemes II-IV**. Generation of the kinetic dienolate of (*R*)-carvone **14** employing LDA in THF at 0°C and alkylation with methyl bromoacetate at –70°C generated exclusively the *trans*-keto ester **18** in 75% yield in a highly stereoselective manner (>95% by

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† Respectfully dedicated to Professor Sukh Dev on his 85th Birthday.

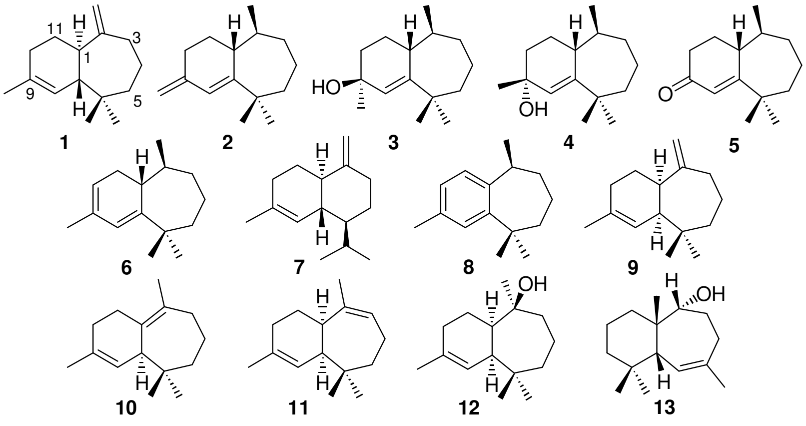
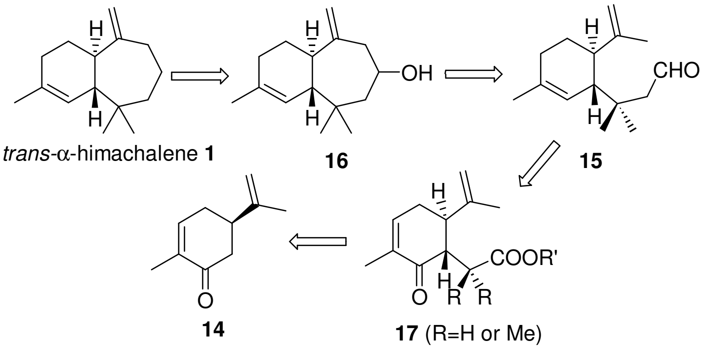


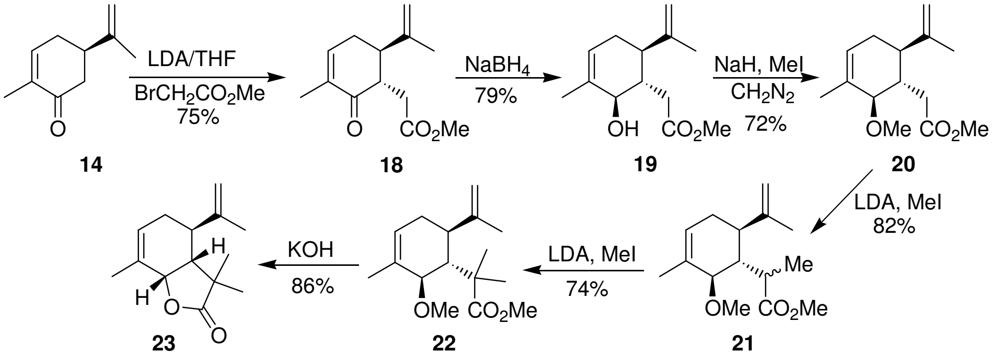
Figure 1

NMR). Attention was then focused on the creation of the *gem*-dimethyl group. To overcome regiochemical problem, it was decided to mask the ketone group in the keto ester **18**. Chemo- and stereoselective reduction of the ketoester **18** with sodium borohydride in methanol at –30°C furnished exclusively the hydroxy ester **19** in 79% yield. Stereochemistry of the hydroxy group in the hydroxy ester **19** was assigned in analogy with the reduction of carvone[12] (a γ-lactone would have formed if the other stereoisomer is formed in the reduction). Williamson's etherification of the hydroxy ester **19** with sodium hydride and methyl iodide in the presence of a catalytic amount of tetrabutylammonium iodide (TBAI) in refluxing THF furnished a 5:2 mixture of the methyl ether **20** and the corresponding carboxylic acid in 72% yield, which on esterification with an excess of ethereal diazomethane transformed into the ester **20**. Alkylation of the ester **20** using LDA and methyl iodide in THF at ice temperature furnished a 4:1 epimeric mixture of the α-methyl ester **21**. In a similar manner, second alkylation of the epimeric mixture of the ester **21** with LDA and methyl iodide in THF-HMPA at ice temperature furnished α,α-dimethyl ester **22** in 60% yield (for two steps). Subsequently, construction of the seven-membered ring was addressed *via* homologation of the ester side chain in **22**. Hydrolysis of the ester **22** with 4 *M* ethanolic potassium hydroxide at reflux temperature, however, furnished the *cis*-lactone **23** in 86% yield, whose structure was established from its spectral data.

Since, hydrolysis of the ester **22** resulted in the lactone **23**, an alternate Wittig reaction based strategy for the homologation of the ester was investigated. Accordingly, reduction of the ester **22** with LAH in ether at 0°C furnished the primary alcohol **24** in 86% yield, which on oxidation with PCC and sodium acetate in methylene chloride furnished the aldehyde **25** in 72% yield. Wittig reaction of the aldehyde **25** with methoxymethylenetriphenylphosphorane, generated from methoxymethyltriphenylphosphonium chloride and potassium *tert*-amylate in THF, at RT furnished a 1:1 *E*/*Z* mixture of the enol ether **26** in 71% yield. Acid catalyzed hydrolysis of the enol ether **26** in 0.02 *M* THF solution using 3*N* aqueous hydrochloric acid at RT furnished, instead of the aldehyde **27**, a 5:1 mixture of the bicyclic alcohol **28** and the diol **29**, in 66% yield, which were separated by column chromatography over silica gel. The structures of the alcohols **28** and **29** were deduced from their spectral data. It is worth mentioning that the reaction proceeded in a highly stereoselective manner, and only one stereoisomer was obtained. No attempt was made to assign the stereochemistry of the alcohol in **28** as it was to be deoxygenated at a later stage of the sequence. Structure of the diol **29** was assigned on the basis of $^{13}$C NMR resonances of the ring olefinic carbons which are comparable to those of the methoxy alcohol **28**. Formation of the bicyclic alcohol **28** could be readily explained *via* the acid catalysed hydrolysis of the enol ether moiety in **26** followed by intramolecular ene reaction of the aldehyde **27**. Acid catalyzed hydrolytic cleavage of the allyl ether moiety in **28** generates the diol **29**. In order to unambiguously establish the structure of the alcohol **28**, it was converted into the enone **31** *via* the ketone **30**. Thus, oxidation of the alcohol **28** with PCC and sodium acetate in methylene chloride at RT furnished the β,γ-unsaturated ketone **30** in 80% yield, which on isomerisation with 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) in methylene chloride at RT furnished the enone **31** in 90% yield.



**Scheme I**



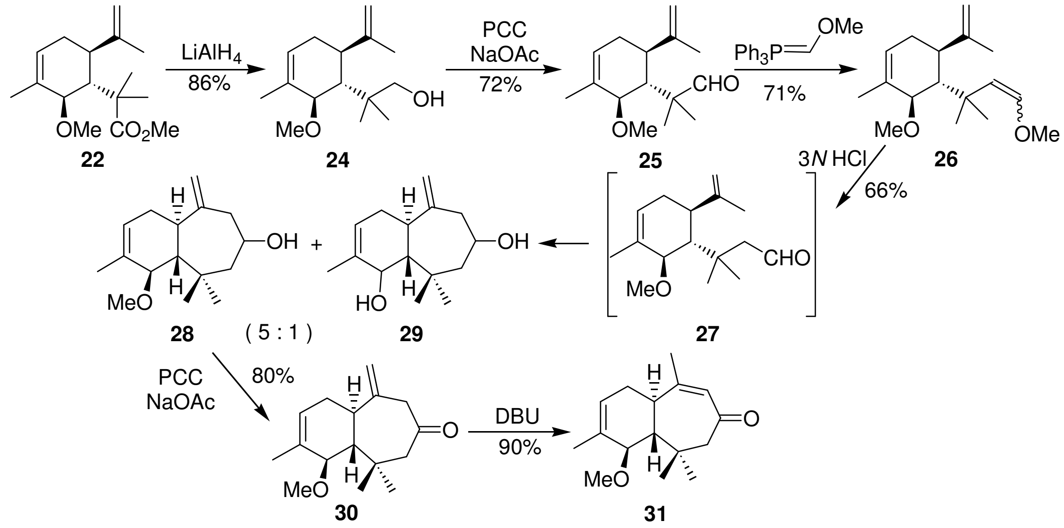
**Scheme II**

Thereafter, attention was turned to the conversion of the bicyclic alcohol **28** into *trans*-α-himachalene **1** *via* reductive deoxygenation of the C-4 hydroxy group and reductive cleavage of the allylic methoxy group. Since typical Barton's deoxygenation protocol *via* the corresponding dithiocarbonate was unsuccessful, it was decided to carry out the deoxygenation[13] of the hydroxy group in the alcohol **28** *via* the methanesulphonate **32**. Thus, reaction of the alcohol **28** with methanesulfonyl chloride, pyridine and a catalytic amount of DMAP in methylene chloride at RT furnished the mesylate **32** in 71% yield. Reaction of the mesylate **32** with lithium in liquid ammonia and THF at –33°C furnished directly *trans*-α-himachalene **1**, instead of the methyl ether **33**, *via* simultaneous reductive demesylation and allylic demethoxylation reactions. The structure of the synthetic (+)-*trans*-α-himachalene **1** was confirmed by comparing the $^1$H NMR spectral data with that of the natural sample isolated[5] from the flea beetle, and the $^{13}$C NMR spectral data reported by Bernardini and co-workers[7f].

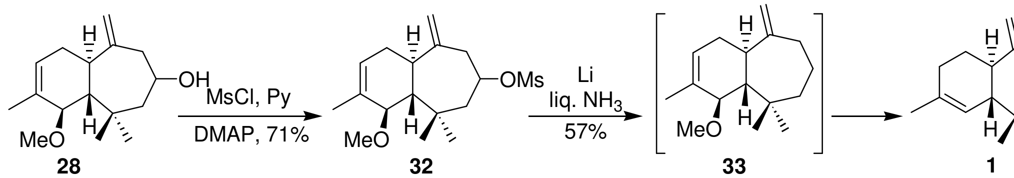
In conclusion, enantiospecific first total synthesis of the sesquiterpene (+)-*trans*-α-himachalene **1** has been accomplished in 11 steps, employing an intramolecular carbonyl ene reaction as the key step. The present synthesis also confirmed the absolute configuration of the natural *trans*-α-himachalene **1** obtained from flea beetles.

## Experimental Section

Melting points were recorded using a Mettler FP1 melting point apparatus in capillary tubes and are uncorrected. IR spectra were recorded on a Jasco FTIR 410 spectrophotometer. $^1$H (300 MHz) and $^{13}$C (75 MHz) NMR spectra were recorded on a JNM λ-300 spectrometer. The chemical shifts (δ ppm) and coupling constants (Hz) are reported in the standard fashion with reference to either internal tetramethylsilane (for $^1$H) or the central line (77.0 ppm) of $CDCl_3$ (for $^{13}$C). In the $^{13}$C NMR spectra, the nature of the carbons (C, CH, $CH_2$ or $CH_3$) was determined by recording the DEPT-135 spectra, and is given in parentheses. Low-resolution mass spectra were recorded using a Shimadzu QP-5050A GCMS instrument using direct inlet mode. Relative intensities are given in parentheses. Elemental analyses were carried out using Carlo Erba 1106 CHN analyser. High-resolution mass spectra were recorded



Scheme III



Scheme IV

using Micromass Q-TOF micro mass spectrometer using electro-spray ionization mode. Optical rotations were measured using a Jasco DIP-370 digital polarimeter and $[\alpha]_D$ values are given in units of $10^{-1}$ deg cm$^2$ g$^{-1}$.

**Methyl 2-[(1*S*,6*R*)-6-isopropenyl-3-methyl-2-oxo-cyclohex-3-enyl]acetate 18**. To a cold (- 15°C), magnetically stirred solution of diisopropylamine (4.21 mL, 30.0 mmoles) in anhydrous THF (20 mL) was added a solution of $^n$BuLi (2.5 *M* in hexane, 10.4 mL, 26 mmoles) over a period of 5 min and stirred for 10 min. To LDA thus formed was added drop-wise a solution of (*R*)-carvone **14** (3 g, 20.0 mmoles) in anhydrous THF (20 mL) over a period of 10 min and stirred for 1 hr at the same temperature. The enolate thus formed was cooled to –70°C and treated with methyl bromoacetate (2.04 mL, 22.0 mmoles) and stirred for 3 hr at –70°C and for 6 hr at RT. It was then diluted with water and extracted with ether (2 × 20 mL). The combined organic extract was washed with 3 *N* HCl followed by brine and dried (anhyd. Na$_2$SO$_4$). Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate-hexane (1:10) as eluent furnished the ketoester **18** (3.33 g, 75%) as colourless oil. $[\alpha]^{25}_D$: +16.1° (*c* 9.7, CHCl$_3$); IR (neat): 2951, 2923, 1739, 1672, 1646, 1437, 1361, 1227, 1213, 1175, 1156, 1094, 998, 899, 853 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$ + CCl$_4$): δ 6.66 (1 H, br s, H-4'), 4.82 (2 H, s, C=CH$_2$), 3.67 (3 H, s, OCH$_3$), 2.90-2.65 (2 H, m), 2.60-2.10 (4 H, m), 1.76 (3 H, s) and 1.72 (3 H, s) [2 × olefinic CH$_3$]; $^{13}$C NMR (75 MHz, CDCl$_3$ + CCl$_4$): δ 198.8 (C, C=O), 172.7 (C, O-C=O), 144.9 (C, *C*=CH$_2$), 142.8 (CH, C-4'), 135.0 (C, C-3'), 114.3 (CH$_2$, C=*C*H$_2$), 51.4 (CH$_3$, OCH$_3$), 48.2 (CH, C-1'), 46.4 (CH, C-6'), 31.9 (CH$_2$), 31.3 (CH$_2$), 18.2 (CH$_3$), 16.1 (CH$_3$); MS: *m/z* (%) 190 (M-MeOH, 25), 149 (50), 148 (45), 121 (20), 105 (20), 82 (100); HRMS: *m/z* Calcd. for C$_{13}$H$_{18}$O$_3$Na (M+Na): 245.1154. Found: 245.1124.

**Methyl [(1*S*,2*R*,6*R*)-2-hydroxy-6-isopropenyl-3-methylcyclohex-3-enyl]acetate 19**. To a cold (–30°C), magnetically stirred solution of the keto ester **18** (500 mg, 2.25 mmoles) in dry methanol (5 mL) was added NaBH$_4$ (94 mg, 2.48 mmoles) in small portions over a period of 15 min and stirred for 30 min at the same temperature. The reaction was then quenched with water (5 mL) and extracted with ether (3 × 5 mL). The combined ether extract was washed with brine and dried (anhyd. Na$_2$SO$_4$). Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate-hexane (1:5) as eluent furnished the hydroxyester **19** (398 mg, 79%) as colourless oil. $[\alpha]^{25}_{D}$: +42.1° (*c* 7.7, $CHCl_3$); IR (neat): 3438, 2940, 2917, 1736, 1721, 1643, 1437, 1375, 1248, 1196, 1157, 1017, 1000, 894 $cm^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$ + $CCl_4$): δ 5.42 (1 H, br s, H-4'), 4.77 (2 H, s, $C{=}CH_2$), 3.95-3.80 (1 H, m, C*H*-OH), 3.65 (3 H, s, $OCH_3$), 2.60-2.30 (2 H, m), 2.30-1.75 (5 H, m), 1.72 (3 H, s) and 1.67 (3 H, s) [2 × olefinic $CH_3$]; $^{13}$C NMR (75 MHz, $CDCl_3$ + $CCl_4$): δ 174.6 (C, O-C=O), 146.6 (C, *C*=$CH_2$), 136.0 (C, C-3'), 122.7 (CH, C-4'), 113.6 ($CH_2$, C=*C*$H_2$), 75.8 (CH, CH-OH), 51.6 ($CH_3$, $OCH_3$), 46.5 (CH, C-6'), 42.0 (CH, C-1'), 36.7 ($CH_2$), 30.7 ($CH_2$), 19.4 ($CH_3$), 18.4 ($CH_3$); MS: *m/z* (%) 192 (M-MeOH, 25), 149 (70), 135 (60), 133 (50), 121 (70), 109 (85), 105 (60), 91 (70), 81 (100); HRMS: *m/z* Calcd. for $C_{13}H_{20}O_3Na$ (M+Na): 247.1310. Found: 247.1323.

**Methyl 2-[(1*S*,2*R*,6*R*)-6-isopropenyl-2-methoxy-3-methylcyclohex-3-en-1-yl]acetate 20**. To a magnetically stirred, ice cold suspension of NaH (355 mg, 60% dispersion in oil, 8.9 mmoles, washed with dry hexane) and tetrabutylammonium iodide (10 mg) in THF (6 mL) was added a solution of the alcohol **19** (398 mg, 1.78 mmoles) in THF (6 mL) and stirred for 30 min at RT. To the alkoxide thus formed, was added methyl iodide (0.67 mL, 10.7 mmoles) and the reaction mixture was gently refluxed for 6 hr. It was then quenched with water (5 mL) and extracted with ether (2 × 5 mL). The combined ether extract was washed with brine and dried (anhyd. $Na_2SO_4$). Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate-hexane (1:30 to 1:20) as eluent furnished the methyl ether **20** (215 mg, 50%) as oil. The aqueous layer was acidified with 3 *N* HCl, extracted with $CH_2Cl_2$ (3 × 5 mL) and the organic extract was washed with brine and dried (anhyd. $Na_2SO_4$). Evaporation of the solvent furnished an acid (90 mg, 22%), which was taken in ether (3 mL) and added dropwise to an ice cold, magnetically stirred ethereal solution of diazomethane (excess, prepared from 1 g of *N*-nitroso-*N*-methylurea and 20 mL of 60% aqueous KOH solution and 20 mL of ether) and the reaction mixture was stirred at RT for 1 hr. Careful evaporation of the excess diazomethane and solvent on water bath and purification of the residue over a silica gel column using ethyl acetate-hexane (1:20) as eluent furnished a further amount of the methoxy ester **20** (80 mg) as yellow oil. $[\alpha]^{22}_{D}$: +66.6° (*c* 3.5, $CHCl_3$); IR (neat): 2923, 1739, 1640, 1435, 1366, 1185, 1162, 1098, 1070, 887 $cm^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$ + $CCl_4$): δ 5.51 (1 H, br s, H-4'), 4.74 (2 H, s, $C{=}CH_2$), 3.82-3.72 (1 H, m, C*H*-OMe), 3.61 (3 H, s, $CO_2CH_3$), 3.17 (3 H, s, $OCH_3$), 2.39 (1 H, d, *J* = 14.1 Hz), 2.30-1.80 (5 H, m), 1.66 (6 H, s, 2 × olefinic $CH_3$); $^{13}$C NMR (75 MHz, $CDCl_3$ + $CCl_4$): δ 173.1 (C, O-C=O), 146.3 (C, *C*=$CH_2$), 134.6 (C, C-3'), 125.4 (CH, C-4'), 113.5 ($CH_2$, C=*C*$H_2$), 83.2 (CH, *C*H-OMe), 54.0 ($CH_3$, $OCH_3$), 51.2 ($CH_3$, $CO_2$*C*$H_3$), 46.7 (CH, C-6'), 37.5 (CH, C-1'), 36.1 ($CH_2$), 30.8 ($CH_2$), 19.5 ($CH_3$), 18.3 ($CH_3$); MS: *m/z* (%) 238 ($M^+$, 12), 164 (33), 149 (35), 133 (50), 123 (25), 105 (47), 98 (100), 91 (35); HRMS: *m/z* Calcd. for $C_{14}H_{22}O_3Na$ (M+Na): 261.1467. Found: 261.1450.

**Methyl 2-[(1*R*,2*R*,6*R*)-6-isopropenyl-2-methoxy-3-methylcyclohex-3-enyl]propionate 21**. To a cold (0°C), magnetically stirred solution of diisopropylamine (0.88 mL, 6.3 mmoles) in anhydrous THF (3 mL) was slowly added a solution of $^n$BuLi (2.5 *M* in hexane, 2.10 mL, 5.25 mmoles) over a period of 5 min and stirred for 10 min. To LDA thus formed was added dropwise a solution of the ester **20** (500 mg, 2.1 mmoles) in anhydrous THF (2 mL) over a period of 5 min and stirred for 1 hr at the same temperature. The enolate thus formed was treated with methyl iodide (0.78 mL, 12.6 mmoles) and stirred for 6 hr at RT. The reaction mixture was diluted with water and extracted with ether (2 × 5 mL). The combined organic extract was washed with brine and dried (anhyd. $Na_2SO_4$). Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate-hexane (1:20) as eluent gave a 4:1 epimeric mixture of the propionate **21** (433 mg, 82%) as colourless oil. $[\alpha]^{24}_{D}$: +59.1° (*c* 3.2, $CHCl_3$); IR (neat): 3072, 2946, 1737, 1643, 1437, 1381, 1251, 1197, 1142, 1087, 894, 834 $cm^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$ + $CCl_4$, signals due to the major isomer): δ 5.47 (1 H, br s, H-4'), 4.77 (2 H, s, $C{=}CH_2$), 3.78 (1 H, d, *J* = 9.0 Hz, H-2'), 3.62 (3 H, s, $CO_2CH_3$), 3.16 (3 H, s, $OCH_3$), 2.60-1.70 (5 H, m), 1.73 (3 H, s) and 1.69 (3 H, s) [2 × olefinic $CH_3$], 1.02 (3 H, d, *J* = 6.9 Hz, *sec*-$CH_3$); $^{13}$C NMR (75 MHz, $CDCl_3$ + $CCl_4$, signals due to the major isomer): δ 176.2 (C, OC=O), 146.2 (C, *C*=$CH_2$), 134.9 (C, C-3'), 125.0 (CH, C-4'), 113.6 ($CH_2$, C=*C*$H_2$), 78.2 (CH, C-2'), 55.5 ($CH_3$, $OCH_3$), 51.4 ($CH_3$, $CO_2$*C*$H_3$), 45.2 (CH), 42.7 (CH), 37.6 (CH), 30.8 ($CH_2$, C-5'), 19.9 ($CH_3$), 17.6 ($CH_3$), 9.1 ($CH_3$, *sec*-$CH_3$]; MS: *m/z* (%) 252 ($M^+$, 3), 237

(5), 177 (15), 165 (15), 149 (23), 133 (50), 123 (18), 105 (20), 98 (80), 49 (100); HRMS: *m/z* Calcd. for $C_{15}H_{24}O_3Na$ (M+Na): 275.1623. Found: 275.1618.

**Methyl 2-[(1*R*,2*R*,6*R*)-6-isopropenyl-2-methoxy-3-methylcyclohex-3-enyl]-2-methyl-propionate 22**. To a cold (0°C), magnetically stirred solution of diisopropylamine (0.72 mL, 5.15 mmoles) in anhydrous THF (3 mL) was slowly added a solution of $^n$BuLi (2.5 *M* in hexane, 1.87 mL, 4.3 mmoles) over a period of 5 min and stirred for 10 min. To LDA thus formed was added HMPA (0.90 mL, 5.25 mmoles) followed by a solution of the propionate **21** (433 mg, 1.72 mmoles) in anhydrous THF (2 mL) over a period of 5 min and stirred for 1 hr at the same temperature. Methyl iodide (0.64 mL, 10.3 mmoles) was added to the reaction mixture and stirred for 6 hr at RT. It was then diluted with water and extracted with ether (2 × 5 mL). The ether extract was washed with brine and dried (anhyd. $Na_2SO_4$). Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate-hexane (1:20) as eluent furnished the ester **22** (338 mg, 74%) as colourless oil. $[\alpha]^{25}_{D}$: +94.2° (*c* 6.4, $CHCl_3$); IR (neat): 2936, 1732, 1437, 1381, 1252, 1190, 1128, 1089, 887 $cm^{-1}$; $^1$H NMR (300 MHz, $CDCl_3 + CCl_4$): δ 5.73 (1 H, br s, H-4'), 4.70 (2 H, br s, $C{=}CH_2$), 3.60 (3 H, s, $CO_2CH_3$), 3.52 (1 H, s, C*H*-OMe), 3.20 (3 H, s, $OCH_3$), 2.45 (1 H, dd, *J* = 6.9 and 2.7 Hz), 2.40-2.00 (2 H, m), 2.00-1.85 (1 H, m), 1.74 (3 H, s) and 1.72 (3 H, s) [2 × olefinic $CH_3$], 1.18 (3 H, s) and 1.11 (3 H, s) [2 × *tert*-$CH_3$]; $^{13}$C NMR (75 MHz, $CDCl_3 + CCl_4$): δ 177.7 (C, OC=O), 148.8 (C, *C*=$CH_2$) 134.5 (C, C-3'), 126.6 (CH, C-4'), 111.7 ($CH_2$, C=*C*$H_2$), 78.6 (CH, C-2'), 54.5 ($CH_3$, $OCH_3$), 51.3 ($CH_3$, $CO_2$*C*$H_3$), 46.1 (CH), 45.4 (C, C-2), 42.7 (CH), 29.5 ($CH_2$, C-5'), 23.4 ($CH_3$), 23.0 ($CH_3$), 21.7 ($CH_3$), 19.9 ($CH_3$); MS: *m/z* (%) 207 (M-$CO_2CH_3$, 8), 165 (30), 149 (45), 133 (90), 123 (50), 114 (45), 109 (50), 102 (100), 98 (90), 93 (40), 91 (40); HRMS: *m/z* Calcd. for $C_{16}H_{26}O_3Na$ (M+Na): 289.1780. Found: 289.1797.

**(1*S*,5*R*,6*R*)-5-Isopropenyl-2,7,7-trimethyl-9-oxa-bicyclo[4.3.0]non-2-en-8-one 23**. A solution of the ester **22** (50 mg, 1.89 mmoles) in 4 *M* ethanolic KOH (1.4 mL, 5.64 mmoles) was refluxed for 10 hr in an oil bath. The reaction mixture was cooled, neutralized with 3 *N* aqueous HCl and extracted with $CH_2Cl_2$ (3 × 5 mL). The combined organic layer was washed with brine and dried (anhyd. $Na_2SO_4$). Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate-hexane (1:10) as eluent furnished the lactone **23** (41 mg, 86%) as oil. $[\alpha]^{22}_{D}$ : –18.3° (*c* 1.2, $CHCl_3$); IR (neat): 2971, 1767, 1640, 1454, 1389, 1260, 1208, 1152, 916, 806 $cm^{-1}$; $^1$H NMR (300 MHz, $CDCl_3 + CCl_4$): δ 5.72 (1 H, d, *J* = 4.5 Hz, H-3), 4.82 (1 H, s) and 4.76 (1 H, s) [$C{=}CH_2$], 4.69 (1 H, d, *J* = 6.0 Hz, H-1), 2.38 (1 H, dd, *J* = 11.4 and 3.6 Hz), 2.25-2.00 (2 H, m), 1.87 (3 H, s) and 1.77 (3 H, s) [2 × olefinic $CH_3$], 2.00-1.70 (1 H, m), 1.34 (3 H, s) and 1.19 (3 H, s) [2 × *tert*-$CH_3$]; $^{13}$C NMR (75 MHz, $CDCl_3 + CCl_4$): δ 181.1 (C, OC=O), 148.8 (C, *C*=$CH_2$), 130.6 (C, C-2), 127.1 (CH, C-3), 111.9 ($CH_2$, C=*C*$H_2$), 76.6 (CH, C-1), 47.7 (CH), 45.1 (C, C-7), 40.0 (CH), 33.1 ($CH_2$, C-4), 26.6 ($CH_3$), 21.9 ($CH_3$), 21.7 ($CH_3$), 21.0 ($CH_3$); MS: *m/z* (%) 220 ($M^+$, 5), 177 (10), 167 (10), 161 (15), 135 (30), 133 (55), 119 (35), 109 (100), 105 (40), 93 (45), 91 (40); HRMS: *m/z* Calcd. for $C_{14}H_{20}O_2Na$ (M+Na): 243.1361. Found: 243.1366.

**2-[(1*R*,2*R*,6*R*)-6-Isopropenyl-2-methoxy-3-methylcyclohex-3-enyl]-2-methylpropanol 24**. To a cold (0°C), magnetically stirred solution of the ester **22** (388 mg, 1.46 mmoles) in dry ether (3 mL) was added $LiAlH_4$ (111 mg, 2.92 mmoles) and stirred for 2 hr. The reaction mixture was then diluted with ether (10 mL) and carefully quenched with water (5 mL). The organic layer was separated and the aqueous phase was extracted with ether (3 × 5 mL). The combined organic phase was washed with brine and dried (anhyd. $Na_2SO_4$). Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate-hexane (1:10) as eluent furnished the alcohol **24** (298 mg, 86%) as oil. $[\alpha]^{25}_{D}$: +111.3° (*c* 4.8, $CHCl_3$); IR (neat): 3434, 2964, 2926, 1642, 1446, 1378, 1189, 1090, 1073, 886 $cm^{-1}$; $^1$H NMR (300 MHz, $CDCl_3 + CCl_4$): δ 5.79 (1 H, br s, H-4'), 4.83 (1 H, s) and 4.76 (1 H, s) [$C{=}CH_2$], 3.71 (1 H, s, H-2'), 3.28 (2 H, s, C*H*$_2$OH), 3.23 (3 H, s, $OCH_3$), 2.35-2.00 (4 H, m), 2.00-1.70 (1 H, m), 1.78 (6 H, s, 2 × olefinic $CH_3$), 0.92 (3 H, s) and 0.83 (3 H, s) [2 × *tert*-$CH_3$]; $^{13}$C NMR (75 MHz, $CDCl_3 + CCl_4$): δ 151.0 (C, *C*=$CH_2$), 134.8 (C, C-3'), 127.4 (CH, C-4'), 111.3 ($CH_2$, C=*C*$H_2$), 78.9 (CH, C-2'), 71.3 ($CH_2$, $CH_2OH$), 54.1 ($CH_3$, $OCH_3$), 44.7 (CH), 43.0 (CH), 38.7 (C, C-2), 30.1 ($CH_2$, C-5'), 22.9 ($CH_3$), 22.6 ($CH_3$), 22.0 ($CH_3$), 20.2 ($CH_3$); MS: *m/z* (%) 238 ($M^+$, 3), 175 (12), 165 (20), 133 (30), 123 (22), 119 (23), 109 (25), 105 (25), 98 ($C_6H_9O$, 100), 91 (30); HRMS: *m/z* Calcd. for $C_{15}H_{26}O_2Na$ (M+Na): 261.1830. Found: 261.1841.

**2-[(1*R*,2*R*,6*R*)-6-Isopropenyl-2-methoxy-3-methylcyclohex-3-enyl]-2-methylpropanal 25**. To a magnetically stirred solution of the primary alcohol **24** (298 mg, 1.25 mmoles) in 1 mL of dry $CH_2Cl_2$ was added a homogeneous mixture of PCC (538 mg, 2.5 mmoles) and sodium acetate (512 mg, 6.25 mmoles) and stirred vigorously for 1 hr at RT. The reaction mixture was then filtered through a small celite pad and eluted with an excess of ether. Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate-hexane (1:20) as eluent furnished the aldehyde **25** (213 mg, 72%) as oil. $[\alpha]^{24}_{D}$: +88.0° (*c* 7.0, $CHCl_3$); IR (neat): 2971, 2933, 2711, 1722, 1643, 1444, 1398, 1377, 1188, 1091, 1070, 890 $cm^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$ + $CCl_4$): δ 9.27 (1 H, s, O=C-H), 5.63 (1 H, s, H-4'), 4.78 (1 H, s) and 4.73 (1 H, s) [C=$CH_2$], 3.55 (1 H, d, *J* = 5.1 Hz, H-2'), 3.14 (3 H, s, $OCH_3$), 2.40-2.00 (3 H, m), 1.90-1.60 (1 H, m), 1.71 (3 H, s) and 1.68 (3 H, s) [2 × olefinic $CH_3$], 1.02 (6 H, s) [2 × *tert*-$CH_3$]; $^{13}$C NMR (75 MHz, $CDCl_3$ + $CCl_4$): δ 202.4 (CH, C=O), 148.6 (C, *C*=$CH_2$), 134.9 (C, C-3'), 125.9 (CH, C-4'), 113.1 ($CH_2$, C=*C*$H_2$), 79.2 (CH, C-2'), 54.7 ($CH_3$, $OCH_3$), 49.0 (C, C-2), 46.0 (CH), 43.3 (CH), 30.3 ($CH_2$, C-5'), 20.7 ($CH_3$), 20.3 ($CH_3$), 20.2 ($CH_3$), 18.2 ($CH_3$); MS: *m/z* (%) 236 ($M^+$, 10), 195 (20), 187 (20), 165 (20), 149 (70), 135 (90), 123 (55), 119 (65), 109 (45), 99 (70), 98 (100), 91 (50); HRMS: *m/z* Calcd. for $C_{15}H_{24}O_2Na$ (M+Na): 259.1674. Found: 259.1696.

**(1*R*,5*R*,6*R*)-5-Isopropenyl-6-(4-methoxy-2-methylbut-3-en-2-yl)-2-methylcyclohex-2-enyl methyl ether 26**. To a magnetically stirred solution of freshly prepared $^t$AmOK [prepared from potassium (175 mg, 4.5 mmoles) and $^t$AmOH (4 mL) followed by evaporation of the excess $^t$AmOH under vacuum] in dry THF (4 mL) was added methoxymethyltriphenylphosphonium chloride (1.85 g, 5.4 mmoles) and the resulting wine red coloured solution was stirred for 15 min at RT. To the dark red coloured solution of methoxymethylenetriphenylphosphorane was added a solution of the aldehyde **25** (213 mg, 0.9 mmole) in dry THF (2 mL) and stirred for 3 hr at RT. Saturated aqueous $NH_4Cl$ solution (5 mL) was added to the reaction mixture and extracted with ether (2 × 10 mL). The combined ether extract was washed with brine and dried (anhyd. $Na_2SO_4$). Evaporation of the solvent and purification of the residue over a neutral alumina column using hexane as eluent furnished a 1:1 *E,Z* mixture of the enol ether **26** (169 mg, 71%) as oil. $[\alpha]^{26}_{D}$: +52.3° (*c* 7.0, $CHCl_3$); IR (neat): 2964, 2930, 1651, 1651, 1454, 1379, 1208, 1090, 938, 884, 743 $cm^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$ + $CCl_4$, mixture of *E,Z* isomers): δ 6.20 (d, *J* = 12.6 Hz) and 5.67 (d, *J* = 6.9 Hz) [1 H, C=C*H*-OMe], 5.68 (1 H, s, H-3), 4.69 (2 H, br s, C=$CH_2$), 4.67 (d, *J* = 12.6 Hz) and 4.15 (d, *J* = 6.9) [1 H, C*H*=CH-OMe], 3.55 and 3.44 (3 H, s, =C-$OCH_3$), 3.48 (1 H, s, C*H*-OMe), 3.25 (3 H, s, $OCH_3$), 2.45-1.80 (4 H, m), 1.76 (3 H, s) and 1.74 (3 H, s) [2 × olefinic $CH_3$], 1.09 and 1.04 (3 H, s) and 1.01 and 0.98 (3 H, s) [2 × *tert*-$CH_3$]; $^{13}$C NMR (75 MHz, $CDCl_3$ + $CCl_4$, mixture of *E,Z* isomers): δ 150.4 (C, *C*=$CH_2$), 145.4 and 145.2 (CH, HC=*C*H-OMe), 135.4 and 135.3 (C, C-2), 126.4 and 126.0 (CH, C-3), 115.6 and 112.7 (CH, *C*H=CHOMe), 110.8 and 110.4 ($CH_2$, C=*C*$H_2$), 79.5 and 79.1 (CH, C-1), 59.6 ($CH_3$), 55.9 and 55.4 ($CH_3$), 50.4 and 48.7 (CH), 41.7 and 41.1 (CH), 38.4 and 37.2 (C, *C*$Me_2$), 29.3 and 29.1 ($CH_2$, C-4), 27.6 and 27.4 ($CH_3$), 26.7 and 26.6 ($CH_3$), 22.6 and 22.4 ($CH_3$), 21.3 and 21.2 ($CH_3$); HRMS: *m/z* Calcd. for $C_{17}H_{28}O_2$ Na (M+Na): 287.1987. Found: 287.2003.

**(1*R*,7*R*,8*R*)-8-Methoxy-6,6,9-trimethyl-2-methylenebicyclo[5.4.0]undec-9-en-4-ol 28**. A solution of the enol ether **26** (176 mg, 0.67 mmole) in THF (33 mL) and 3 *N* HCl (3 mL) was magnetically stirred for 1.5 hr at RT. The reaction mixture was diluted with water (5 mL) and extracted with ether (3 × 10 mL). The combined ether extract was washed with aqueous $NaHCO_3$ solution and brine, and dried (anhyd. $Na_2SO_4$). Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate-hexane (1:10 to 1:5) as eluent furnished the bicyclic alcohol **28** (91 mg, 55%) as oil; $[\alpha]^{24}_{D}$: +64.3° (*c* 3.0, $CHCl_3$); IR (neat): 3393, 2926, 1637, 1466, 1444, 1389, 1368, 1188, 1089, 1068, 1032, 931, 889 $cm^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$ + $CCl_4$): δ 5.77 (1 H, d, *J* = 6.6 Hz, H-10), 4.90 (1 H, s) and 4.80 (1 H, s) [C=$CH_2$], 3.96 (1 H, br s, H-4), 3.87 (1 H, d, *J* = 6.3 Hz, H-8), 3.09 (3 H, s, $OCH_3$), 2.68 (1 H, dd, *J* = 13.2 and 3.9 Hz), 2.35-2.00 (3 H, m), 1.90-1.70 (3 H, m), 1.70 (3 H, s, olefinic $CH_3$), 1.70-1.40 (2 H, m), 1.16 (3 H, s) and 0.89 (3 H, s) [2 × *tert*-$CH_3$]; $^{13}$C NMR (75 MHz, $CDCl_3$ + $CCl_4$): δ 150.5 (C, C-2), 134.8 (C, C-9), 127.9 (CH, C-10), 113.0 ($CH_2$, C=*C*$H_2$), 78.8 (CH, C-8), 66.7 (CH, C-4), 52.4 ($CH_2$), 51.0 ($CH_3$, $OCH_3$), 47.3 (CH), 43.4 (CH), 42.8 ($CH_2$), 35.8 (C, C-6), 33.2 ($CH_2$), 31.0 ($CH_3$), 24.5 ($CH_3$), 21.0 ($CH_3$); MS: *m/z* (%) 250 ($M^+$, 12), 218 (10), 147 (18), 133 (20), 119 (32), 105 (30), 99 (20), 91 (35), 49 (100); HRMS: *m/z* Calcd. for $C_{16}H_{26}O_2Na$ (M+Na): 273.1830. Found: 273.1841.

Further elution of the column with ethyl acetate-hexane (1:3) furnished (1*R*,7*R*)-6,6,9-trimethyl-2-methylenebicyclo[5.4.0]undec-9-ene-4,8-diol **29** (17 mg, 11%) as oil. $[\alpha]^{23}_{D}$: +25.5° (*c* 2.0, $CHCl_3$); IR (neat): 3353 (OH), 2928, 1636, 1541, 1458, 1367, 1280, 1183, 1020, 1013, 890 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3 + CCl_4$): δ 5.39 (1 H, s, H-10), 4.93 (1 H, s) and 4.84 (1 H, s) [C=$CH_2$], 4.00-3.85 (1 H, m, H-4), 3.83 (1 H, s, H-8), 2.79 (1 H, dd, *J* = 14.1 and 6.6 Hz), 2.41 (1 H, br t, *J* = 11.8 Hz), 2.17 (1 H, d, *J* = 14.4 Hz), 1.91 (1 H, d, *J* = 11.7 Hz), 1.79 (3 H, s, olefinic $CH_3$), 1.80-1.60 (3 H, m), 1.50-1.05 (3 H, m), 1.08 (3 H, s) and 0.76 (3 H, s) [2 × *tert*-$CH_3$]; $^{13}C$ NMR (75 MHz, $CDCl_3 + CCl_4$): δ 149.9 (C, C-2) and 134.7 (C, C-9), 126.9 (CH, C-10), 112.6 ($CH_2$, C=*C*$H_2$), 67.7 (CH) and 66.2 (CH) [C-4 and 8], 49.5 ($CH_2$), 46.6 (CH), 42.8 ($CH_2$), 41.5 ($CH_2$), 34.5 (CH), 34.2 (C, C-6), 28.1 ($CH_3$), 25.3 ($CH_3$), 21.3 ($CH_3$); MS: *m/z* (%) 236 ($M^+$, 15), 185 (20), 175 (20), 161 (30), 147 (75), 135 (43), 133 (45), 121 (46), 119 (75), 109 (80), 105 (70), 91 (100), 73 (75), 69 (70), 49 (90); HRMS: *m/z* Calcd. for $C_{15}H_{24}O_2Na$ (M+Na): 259.1674. Found: 259.1696.

**(1*R*,7*R*,8*R*)-8-Methoxy-6,6,9-trimethyl-2-methylenebicyclo[5.4.0]undec-9-en-4-one 30**. To a magnetically stirred solution of the alcohol **28** (50 mg, 0.2 mmole) in $CH_2Cl_2$ (0.3 mL) was added PCC (86 mg, 0.4 mmole) and sodium acetate (82 mg, 1.0 mmole) and stirred vigorously for 1 hr at RT. The reaction mixture was then filtered through a small celite column and eluted the column with an excess of ether. Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate-hexane (1:20) as eluent furnished the ketone **30** (40 mg, 80%) as oil. $[\alpha]^{25}_{D}$: +108.0° (*c* 2.0, $CHCl_3$); IR (neat): 2950, 2927, 1711, 1642, 1470, 1440, 1372, 1309, 1209, 1065, 897 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3 + CCl_4$): δ 5.81 (1 H, d, *J* = 6.4 Hz, H-10), 5.09 (1 H, s) and 4.95 (1 H, s) [C=C*H*$_2$], 4.06 (1 H, d, *J* = 6.4 Hz, H-8), 3.12 and 2.96 (2 H, 2 × d, *J* = 18.0 Hz, H-3), 3.06 (3 H, s, $OCH_3$), 2.86 and 2.18 (2 H, 2 × d, *J* = 11.6 Hz, H-5), 2.43 (1 H, d of t, *J* = 12.0 and 4.0 Hz, H-1), 2.20-2.10 (1 H, m), 1.95-1.85 (1 H, m), 1.83 (1 H, dd, *J* = 12.0 and 6.8 Hz, H-7), 1.71 (3 H, s, olefinic $CH_3$), 1.19 (3 H, s) and 1.03 (3 H, s) [2 × *tert*-$CH_3$]; $^{13}C$ NMR (75 MHz, $CDCl_3 + CCl_4$): δ 210.1 (C, C=O), 148.5 (C, C-2), 133.9 (C, C-9), 127.8 (CH, C-10), 114.8 ($CH_2$, C=*C*$H_2$), 78.0 (CH, C-8), 56.7 ($CH_2$, C-3), 49.7 ($CH_3$, $OCH_3$), 49.0 ($CH_2$, C-5), 47.3 (CH, C-7), 44.2 (CH, C-1), 37.7 (C, C-6), 33.5 ($CH_2$, C-11), 30.7 ($CH_3$), 23.1 ($CH_3$), 20.7 ($CH_3$); MS: *m/z* (%) 216 (M-MeOH, 3), 149 (10), 132 (10), 119 (10), 111 (10), 105 (10), 98 (100), 91 (15), 84 (15); HRMS: *m/z* Calcd. for $C_{16}H_{24}O_2Na$ (M+Na): 271.1674. Found: 271.1672.

**(1*R*,7*R*,8*R*)-8-Methoxy-2,6,6,9-tetramethylbicyclo[5.4.0]undeca-2,9-dien-4-one 31**. To a magnetically stirred solution of the β,γ-unsaturated ketone **30** (20 mg, 0.08 mmole) in $CH_2Cl_2$ (0.3 mL) was added DBU (2 drops) and the reaction mixture was stirred for 2 hr at RT. It was then diluted with ether (5 mL) and washed with 3 *N* HCl, water and brine, and dried (anhyd. $Na_2SO_4$). Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate-hexanes (1:10) as eluent furnished the enone **31** (18 mg, 90%) as oil. $[\alpha]^{23}_{D}$: +296° (*c* 1.8, $CHCl_3$); IR (neat): 2954, 2923, 2894, 2871, 1656, 1614, 1466, 1442, 1390, 1371, 1348, 1328, 1297, 1232, 1092, 1081, 1018, 936, 884, 836, 794 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3 + CCl_4$): δ 5.97 (1 H, s, H-3), 5.91 (1 H, d, *J* = 6.6 Hz, H-10), 3.47 (1 H, s, H-8), 3.20 (3 H, s, $OCH_3$), 2.65-2.50 (1 H, m), 2.55 and 2.20 (2 H, 2 × d, *J* = 11.7 Hz, H-5), 2.36 (1 H, t of t, *J* = 13.8 and 2.7 Hz), 2.35-2.15 (1 H, m), 2.02 (3 H, s, $C_2$-$CH_3$), 1.84 (3 H, s, $C_9$-$CH_3$), 1.90-1.75 (1 H, m), 1.13 (3 H, s) and 0.77 (3 H, s) [2 × *tert*-$CH_3$]; $^{13}C$ NMR (75 MHz, $CDCl_3 + CCl_4$): δ 199.9 (C, C=O), 165.8 (C, C-2), 137.9 (C, C-9), 131.7 (CH, C-3), 127.6 (CH, C-10), 79.6 (CH, C-8), 58.9 ($CH_3$, $OCH_3$), 57.2 ($CH_2$, C-5), 55.9 (CH), 39.9 (CH), 34.4 (C, C-6), 27.3 ($CH_3$), 25.7 ($CH_2$, C-8), 24.2 ($CH_3$), 23.6 ($CH_3$), 22.6 ($CH_3$); HRMS: *m/z* Calcd. for $C_{16}H_{25}O_2$ (M+1): 249.1854. Found: 249.1857.

**(1*R*,7*R*,8*R*)-8-Methoxy-6,6,9-trimethyl-2-methylenebicyclo[5.4.0]undec-9-en-4-yl methanesulfonate 32**. To a magnetically stirred solution of the bicyclic alcohol **28** (30 mg, 0.12 mmole) in $CH_2Cl_2$ (0.2 mL) was added pyridine (0.03 mL, 0.36 mmole), MsCl (0.018 mL, 0.24 mmole) and a catalytic amount of DMAP. The reaction mixture was stirred at RT for 2 hr. It was then diluted with water (5 mL) and extracted with ether (3 × 5 mL). The organic phase was washed with 3 *N* HCl, saturated aqueous $NaHCO_3$ solution and brine, and dried (anhyd. $Na_2SO_4$). Evaporation of the solvent under reduced pressure and purification of the residue over a silica gel column using ethyl acetate-hexane (1:10) as eluent furnished the mesylate **32** (27 mg, 71%) as oil; $[\alpha]^{22}_{D}$: +26.7° (*c* 1.2, $CHCl_3$); IR (neat): 2933, 1641, 1466, 1442, 1354, 1335, 1172, 1068, 907 $cm^{-1}$; $^1H$ NMR

(300 MHz, $CDCl_3 + CCl_4$): δ 5.76 (1 H, d, *J* = 6.6 Hz, H-10), 4.93 (1 H, s) and 4.87 (1 H, s) [$C=CH_2$], 3.85 (1 H, d, *J* = 5.4 Hz, H-8), 3.30-2.95 (1 H, m, H-4), 3.09 (3 H, s, $OCH_3$), 2.97 (3 H, s, $OSO_2CH_3$), 2.82 (1 H, dd, *J* = 14.1 and 5.4 Hz), 2.50 (1 H, dd, *J* = 14.4 and 6.0 Hz), 2.40-1.90 (3 H, m), 1.90-1.60 (3 H, m), 1.70 (3 H, s, olefinic $CH_3$), 1.19 (3 H, s) and 0.90 (3 H, s) [2 × *tert*-$CH_3$]; $^{13}$C NMR (75 MHz, $CDCl_3$ + $CCl_4$): δ 148.2 (C, C-2), 134.8 (C, C-9), 127.8 (CH, C-10), 114.1 ($CH_2$, C=$CH_2$), 78.8 (CH), 77.7 (CH), 51.5 ($CH_3$, $OCH_3$), 49.0 ($CH_2$), 47.8 (CH), 42.4 (CH), 41.5 ($CH_2$), 38.7 ($CH_3$, $OSO_2CH_3$), 35.5 (C, C-6), 32.3 ($CH_2$), 30.1 ($CH_3$), 24.4 ($CH_3$), 21.1 ($CH_3$); MS: *m/z* (%) 328 ($M^+$, 1), 157 (10), 145 (10), 119 (10), 111 (20), 98 (100); HRMS: *m/z* Calcd. for $C_{17}H_{28}O_4SNa$ (M+Na): 351.1606. Found: 351.1630.

**(1*R*,7*R*)-6,6,9-Trimethyl-2-methylenebicyclo-[5.4.0]undec-8-ene (*trans*-α-Himachalene 1)**. To magnetically stirred, freshly distilled (over sodamide) ammonia (30 mL) in a two necked flask, equipped with Dewar condenser, was added freshly cut lithium (6 mg, 0.85 mmole) followed by a solution of the mesylate **32** (27 mg, 0.08 mmole) in anhydrous THF (3 mL). The resulting blue coloured solution was stirred for 30 min at –33°C and then the reaction was quenched with solid $NH_4Cl$. After evaporation of ammonia, the residue was taken in water (5 mL) and extracted with $CH_2Cl_2$ (3 × 3 mL). The combined $CH_2Cl_2$ extracts were washed with brine and dried (anhyd. $Na_2SO_4$). Evaporation of the solvent and purification of the residue over a 10% $AgNO_3$ impregnated silica gel column using hexane as eluent furnished *trans*-α-himachalene **1** (9.6 mg, 57%) as volatile oil.[5] $[\alpha]^{25}_D$: +67.1° (*c* 1.4, hexane). {Lit.[5] $[\alpha]_D$: +50.0° (*c* 0.008, hexane), Lit.[6] for (–)-**1** $[\alpha]_D$: –39.5°}; IR (neat): 2924, 1636, 1458, 1364, 1018, 884 $cm^{-1}$. $^1$H NMR (500 MHz, $CDCl_3$): δ 5.28 (1 H, br s, H-8), 4.76 (1 H, s) and 4.68 (1 H, s) [$C=CH_2$], 2.35-2.20 (2 H, m), 2.10-1.95 (2 H, m), 1.90-1.75 (2 H, m), 1.67 (3 H, s, olefinic $CH_3$), 1.75-1.50 (3 H, m), 1.50-1.40 (1 H, m), 1.37-1.20 (2 H, m), 0.96 (3 H, s) and 0.70 (3 H, s) [2 × *tert*-$CH_3$]; $^{13}$C NMR (75 MHz, $CDCl_3$ + $CCl_4$): δ 155.5 (C, C-2), 133.7 (C, C-9), 123.6 (CH, C-8), 109.5 ($CH_2$, C=$CH_2$), 50.3 (CH, C-7), 40.43 (CH, C-1), 40.37 ($CH_2$), 36.2 (C, C-6), 34.5 ($CH_2$), 31.5 ($CH_2$), 30.7 ($CH_2$), 29.5 ($CH_3$), 23.9 ($CH_3$), 22.9 ($CH_3$), 20.1 ($CH_2$, C-4); MS: *m/z* (%) ($C_{15}H_{24}$) 204 ($M^+$, 5), 203 (25), 189 (12), 175 (10), 161 (15), 149 (30), 135 (40), 133 (35), 121 (45), 119 (40), 109 (70), 105 (60), 91 (60), 69 (100).

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