# Chiral synthons from carvone. Part 50.† Enantiospecific approaches to both enantiomers of bicyclo[4.3.0]nonane-3,8-dione derivatives

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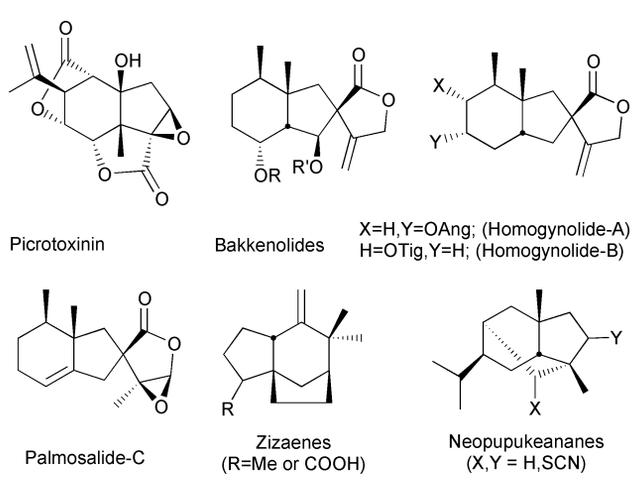
Enantiospecific synthesis of both enantiomeric forms of bicyclo[4.3.0]nonane-3,8-dione derivatives has been described starting from (*R*)-carvone employing two different cyclopentannulation methodologies. Thus, in the first methodology, carveol (**5**) was converted into tricyclic ketone **4** employing a Claisen rearrangement and intramolecular diazo ketone cyclopropanation reactions. Degradation of the isopropenyl group followed by cyclopropane cleavage and cuprate addition generated the dione (−)-**12a**. Whereas, a Wacker mediated cyclopentannulation of (*R*)-carvone *via* the dione **15** furnished the enone **17**. Functional group manipulation including the degradation of isopropenyl group transformed the enone **17** into the dione (+)-**12a**, which on regioselective ketalisation generated the ketoketal (+)-**2**.

The creativity of Nature in devising varied molecular architectures is revealed through the isolation of a wide range of natural products with remarkable skeletal build-up and multifarious functionality.[1] Development of methodologies for the total synthesis of natural products with diverse architecture and varying degrees of complexity is an area that has inspired and attracted several generations of organic chemists.[2] Particularly in the last three decades, dramatic advances were made in the development of new synthetic methodologies with high regio-, stereo- and enantiocontrol. Monoterpenes are being widely used as chiral auxiliaries but their potential as chiral synthons has not been properly exploited.[3] The overwhelming emphasis on carbohydrates as chirons[4] in natural product synthesis has somewhat marginalised the importance of the abundantly available monoterpenes as chiral building blocks for the synthesis of natural products in their optically active form. This has come about despite the fact that monoterpenes are cheap, readily available (in several cases, in both enantiomeric forms unlike carbohydrates and amino acids) and are endowed with only one or two chiral centres with modest functionality, which means that it does not require recourse to wasteful manoeuvres to dispense with excess chirality or functionality as in carbohydrate based approaches. More interestingly, terpenes can be readily restructured into cyclic and acyclic fragments that can be directly incorporated into carbocyclic frameworks of complex target molecules.

Functionalised bicyclo[4.3.0]nonanes (hydrindane systems), in particular with a substituent at one of the ring junction positions, or as part structures are present in many biologically important natural products, *e.g.* picrotoxinin, bakkenolides, homogynolides, palmosalide, zizaenes, neopupukenanes, *etc*. Our interest in the synthesis of sesquiterpene natural products containing a hydrindane framework led us to investigate new approaches for the construction of bicyclo[4.3.0]nonanes in optically active form. The readily available monoterpene carvone (**1**) is an excellent chiral starting material in the synthesis of natural products.[3] (*S*)-Carvone has been exploited by de Groot and coworkers for the construction of several functionalised decalin systems[5] and their conversion to a variety of natural products. We have employed (*R*)-carvone as the chiral starting material for the synthesis of a variety of bridged systems and sesquiterpenoids.[6,7] In continuation of our interest in the development of enantiospecific methodologies for the generation of both enantiomers of a particular carbon framework, starting from a single enantiomer of carvone,[6c,e,7] herein we describe details of our investigation on the synthesis of both enantiomers of the bicyclo[4.3.0]nonane based ketoketal **2** employing two different cyclopentannulation methodologies.[8]




The isopropenyl group in carvone **1** was readily recognised as a masked hydroxy group. To begin with, for the enantiospecific synthesis of the (−)-ketoketal **2** an orthoester Claisen rearrangement–intramolecular diazo ketone cyclopropanation based approach was chosen starting from (*R*)-carvone **1**. The retrosynthetic pathway for the (−)-ketoketal **2** is depicted in Scheme 1. It was anticipated that conjugate addition of a methyl group followed by regio-selective ketalisation could transform the enedione **3** into the ketoketal **2**, and degradation of the isopropenyl group followed by acid catalysed ring opening of cyclopropane could transform the tricyclic ketone **4** into the

† For parts 49 and 48, see: references 6*a* and 6*b*, respectively.

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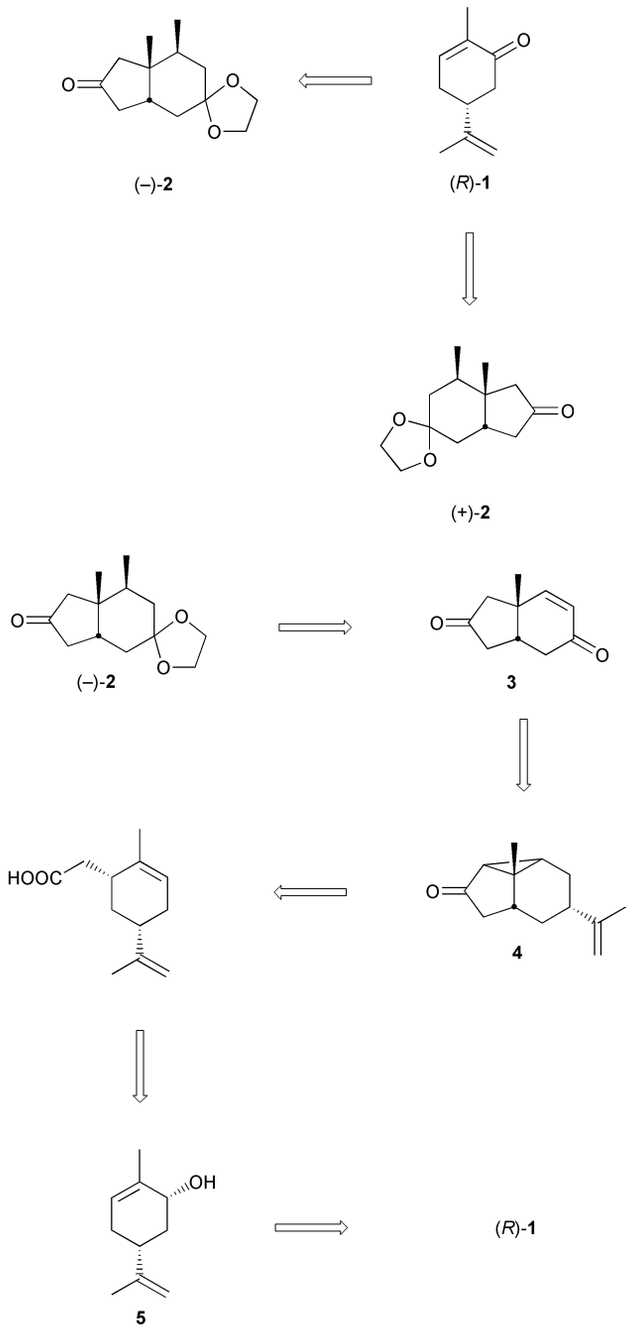
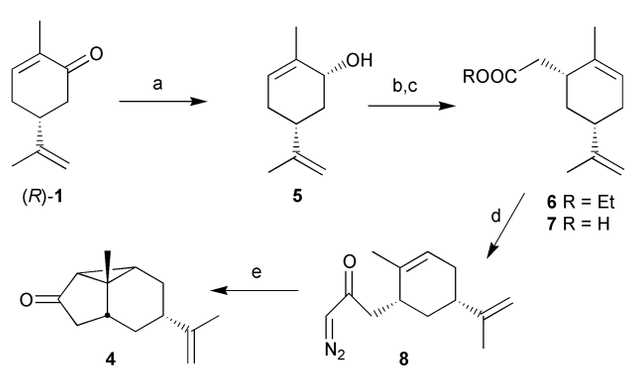



**Scheme 1**

enedione **3**. A stereospecific Claisen rearrangement and intramolecular diazo ketone cyclopropanation could be exploited for the conversion of carveol (**5**) into the tricyclic ketone **4**.

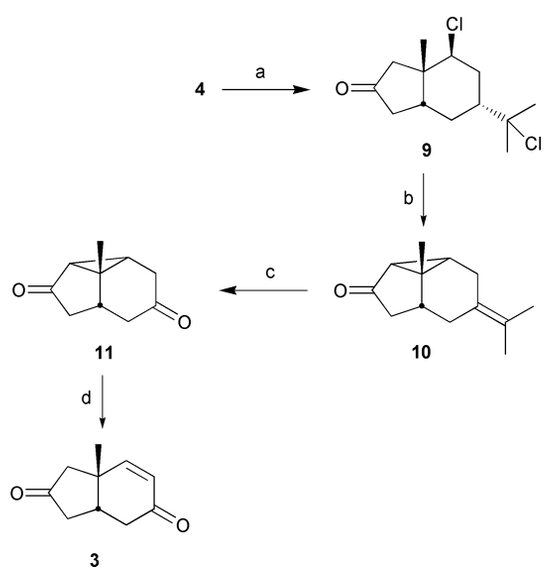
Synthesis of the tricyclic ketone **4** is depicted in Scheme 2.




**Scheme 2** (a) LAH; (b) $MeC(OEt)_3$, $Hg(OAc)_2$, Δ; (c) NaOH; (d) $(COCl)_2$, $CH_2N_2$; (e) $CuSO_4$.

Lithium aluminium hydride (LAH) reduction of (*R*)-carvone (**1**) in ether at −90 °C furnished carveol (**5**), the precursor for the projected Claisen rearrangement, in quantitative yield with a very high degree of stereoselectivity. The *syn* relationship between the hydroxy and isopropenyl groups in carveol was well established.[9] An orthoester variant of the Claisen rearrangement, developed[10] by Johnson *et al.* was used for the stereospecific introduction of the acetate side chain. Thus, thermal activation (180 °C) of a solution of carveol (**5**), triethyl orthoacetate and a catalytic amount of mercuric acetate in a sealed tube furnished the γ,δ-unsaturated ester **6** in 70% yield, whose structure was established from its spectral data. The stereochemistry of the ester side chain was assigned based on the well-established stereospecificity of the Claisen rearrangement. The ester **6** was transformed into the tricyclic ketone **4** *via* an intramolecular diazo ketone cyclopropanation[11] strategy. Thus, hydrolysis of the ester **6** using 15% aqueous sodium hydroxide and methanol furnished the acid **7**. Treatment of the acid **7** with oxalyl chloride in benzene furnished the acid chloride, which on addition to an excess of ethereal diazomethane furnished the diazo ketone **8**. Anhydrous copper sulfate catalyzed decomposition of the diazo ketone **8** in refluxing cyclohexane using a tungsten lamp led to the intramolecular insertion of the intermediate ketocarbenoid into the ring olefin in a regio- and stereospecific manner, resulting in the formation of the cyclopropyl ketone **4** in 50% yield (from the acid **7**). The *cis* stereochemistry of the ring junction was a consequence of the insertion of the intermediate ketocarbenoid from the preferred *syn* face of the olefin.

With the successful synthesis of the cyclopropyl ketone **4**, attention was turned towards the degradation of the isopropenyl side chain into oxygen functionality, Scheme 3. Since

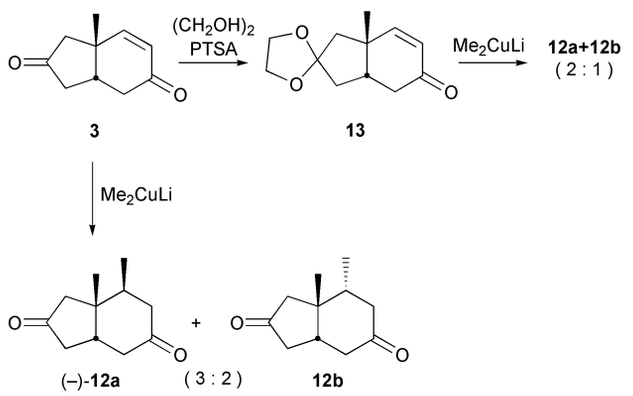



**Scheme 3** (a) HCl; (b) DBU; (c) $O_3$, $Me_2S$; (d) *p*TSA.

a one-pot conversion of isopropenyl group into an acetoxy group employing a Criegee rearrangement[12] was found to be inefficient, an alternative route was envisaged. Isomerisation of the isopropenyl to the isopropylidene group by an addition–elimination sequence and oxidative cleavage to generate the ketone functionality was contemplated. Thus, treatment of the cyclopropyl ketone **4** with an excess of freshly prepared saturated solution of hydrogen chloride gas in ether generated the dichloride **9** *via* addition of hydrogen chloride to both olefinic and cyclopropane moieties. Reaction of the dichloride **9** with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in benzene at 160 °C in a sealed tube led to double dehydrochlorination to furnish the cyclopropyl ketone **10**. Ozonolysis of the tricyclic ketone **10** in methanol–methylene chloride followed

by reductive work up of the ozonide with dimethyl sulfide furnished the dione **11**, which was found to undergo partial isomerisation to enedione **3** on a silica gel column. Treatment of the dione **11** with a catalytic amount of toluene-*p*-sulfonic acid (*p*TSA) in methylene chloride brought about the complete isomerisation *via* the cleavage of the cyclopropane ring furnishing the enedione **3**, whose structure rests secured from its spectral data.

Addition of lithium dimethylcopper to the enedione **3**, furnished a 3 : 2 epimeric mixture of hydrindanediones **12a**,**b** in 71% yield (Scheme 4). The structures of the diones **12a**,**b**

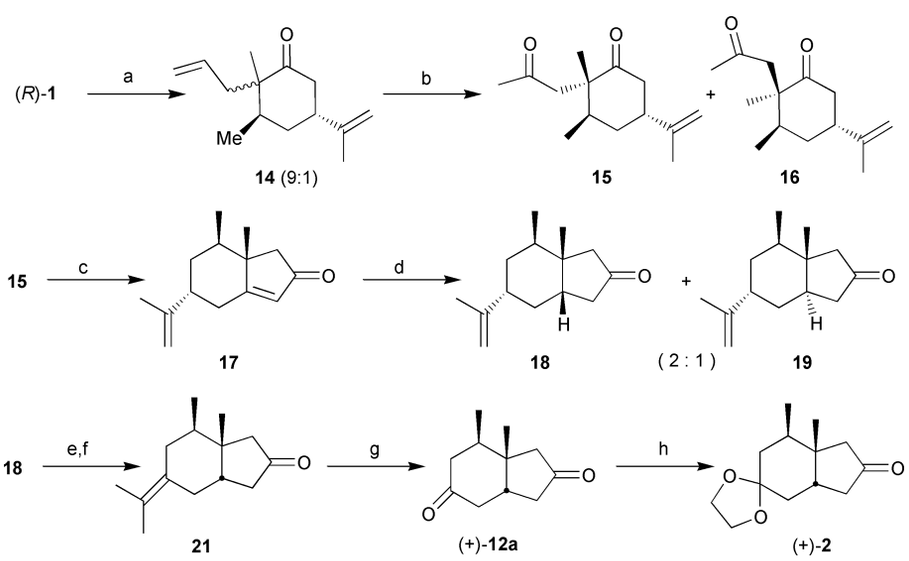



**Scheme 4**

were established from the spectral data. It was anticipated that protection of the 5-membered ring ketone in enedione **3** as its cyclic ketal might increase the stereoselectivity in the cuprate reaction. Accordingly, regioselective protection of the five membered ketone in the enedione **3** with ethylene glycol in the presence of a catalytic amount of *p*TSA using a Dean–Stark water separator furnished the ketal **13** in 69% yield in a highly regioselective manner. However, reaction of the ketoketal **13** with lithium dimethylcopper followed by hydrolysis of the ketal moiety in the product generated a 2 : 1 mixture of the diones **12a**,**b** with only marginal increase in stereoselectivity.

In the second approach, for the generation of enantiomeric compounds, initial introduction of the secondary methyl group and construction of a hydrindane by Wacker mediated cyclopentannulation methodology was envisaged, as depicted in Scheme 5. For the addition of methyl and allyl groups to the enone at the β and α positions, respectively, in a *trans* manner, a cuprate mediated 1,4-addition followed by allylation of the intermediate enolate was chosen. Thus, addition of lithium dimethylcopper to (*R*)-carvone **1** followed by quenching of the resultant enolate with allyl bromide in the presence of HMPT provided a 9 : 1 epimeric mixture of the ketone **14**. The stereochemistry of the secondary methyl group in **14** was assigned based on the preferred addition of the nucleophile *trans* to the isopropenyl group, which has enough precedence in the literature.[13] Similarly, stereoselective alkylation of the intermediate enolate generates the quaternary carbon as both the secondary methyl at C-3 and the isopropenyl group at C-5 directs the approach of the electrophile *trans* to the secondary methyl group. The regiospecificity of the Wacker reaction[14] for the oxidation of monosubstituted olefins was exploited for the conversion of the allyl into an acetonyl group for the generation of the 1,4-diketone necessary for cyclopentannulation. Thus, reaction of the allyl compound **14** with palladium chloride and cuprous chloride in a mixture of *N*,*N*-dimethylformamide and water in an oxygen atmosphere furnished a 9 : 1 mixture of the 1,4-diketones **15** and **16**, which were separated on a silica gel column. Intramolecular aldol condensation of the major dione **15** using 10% aqueous potassium hydroxide in methanol cleanly furnished the enone **17**, whose structure was established from its spectral data. The $^{13}$C NMR spectrum of the enone **17** exhibited a singlet at $\delta$ 207.6 ppm due to the carbonyl carbon, two olefinic carbon resonances at 187.3 and 127.4 typical for a β-substituted cyclopentenone moiety,[15] two olefinic signals at 146.0 and 111.7 ppm due to $C{=}CH_2$ carbons in addition to aliphatic carbon resonances, confirming the structure of the enone **17**.

For further elaboration, regiospecific reduction of the *endo* cyclic olefin was addressed first, employing electron transfer methodology. Thus, regiospecific reduction of the enone **17** with lithium in liquid ammonia in the presence of *tert*-butanol (2-methylpropan-2-ol) furnished a ≈2 : 1 mixture of the *cis* and *trans* hydrindanones **18** and **19**, which were separated by column chromatography on silver nitrate impregnated silica gel. For the conversion of the isopropenyl moiety into ketone functionality, as in the first approach, the three step sequence was used. Thus, addition of hydrogen bromide followed by DBU mediated dehydrobromination of the resultant tertiary bromide **20** transformed the hydrindanone **18** into the isomerised compound **21** in near quantitative yield. Ozonolysis of the isopropylidene group in **21** followed by reductive work up with triphenylphosphine furnished the dione **12a** in 88% yield, whose structure was established from its spectral data. Regioselective protection of the 6-membered ring ketone with 1.0 equivalent of ethylene glycol and *p*TSA using a Dean–Stark




**Scheme 5** (a) $Me_2CuLi$, $CH_2CH{=}CH_2Br$; (b) $PdCl_2$, CuCl, DMF–$H_2O$, $O_2$; (c) KOH; (d) Li, liq. $NH_3$; (e) HBr, (f) DBU; (g) $O_3$, $Me_2S$; (h) $(CH_2OH)_2$, *p*TSA.

water separator in refluxing benzene transformed the dione **12a** into the (+)-ketoketal **2** in 68% yield, whose structure was established from its spectral data.

In conclusion, employing two different cyclopentannulation methodologies, (*R*)-carvone has been transformed, *via* several useful chiral synthons, into both enantiomeric forms of bicyclo[4.3.0]nonane-3,8-dione derivatives, potential precursors in sesquiterpene synthesis.

## Experimental

Melting points are recorded using a Tempo melting point apparatus in capillary tubes and are uncorrected. IR spectra were recorded on a Perkin-Elmer 781 spectrophotometer. $^1$H (90, 200 and 270 MHz) and $^{13}$C NMR (22.5, 50 and 100 MHz) spectra were recorded on JEOL FX-90Q, Bruker ACF-200, WH-270 and AMX-400 spectrometers. The chemical shifts ($\delta$ ppm) and the coupling constants (Hz) are reported in the standard fashion with reference to either internal tetramethylsilane (for $^1$H) or the central line (77.1 ppm) of $CDCl_3$ (for $^{13}$C). In the $^{13}$C NMR spectra off-resonance multiplicities, when recorded are given in parentheses. Low and high resolution mass measurements were carried out using a JEOL JMS-DX 303 GC-MS instrument using a direct inlet mode. Relative intensities of the ions are given in parentheses. Elemental analyses were carried out using a Carlo Erba 1106 CHN analyser. Optical rotations were measured using a Jasco DIP-370 digital polarimeter and $[\alpha]_D$ values are given in the units of $10^{-1}$ deg cm$^2$ g$^{-1}$. Ozonolysis was carried out using a Penwalt Wallace and Tierman ozonator. Acme's silica gel (100–200 mesh), approximately 15–20 g per 1 g of the crude product, was used for column chromatography. All small-scale dry reactions were carried out using a standard syringe-septum technique. Dry THF was obtained by distillation over sodium–benzophenone ketyl. HBr in ether was prepared by bromination of tetralin with bromine according to the Vogel procedure.

### (+)-(1*R*,5*R*)-5-Isopropenyl-2-methylcyclohex-2-enylacetic acid (7)

A solution of carveol **5** (4.0 g, 26.3 mmol), triethyl orthoacetate (25 ml, 136.6 mmol) and mercuric acetate (25 mg) was placed in a sealed tube and heated to 180 °C for 6 days in an oil bath. The reaction mixture was cooled, diluted with ether (90 ml), washed with 1 M HCl, saturated aq. $NaHCO_3$ and brine, and dried ($Na_2SO_4$). Evaporation of the solvent and purification of the product on a silica gel column using ethyl acetate–hexane (1 : 40) as eluent furnished the ester **6** (4.1 g, 70%): $\nu_{max}$ (neat) 1735, 1640, 885 cm$^{-1}$. $\delta_H$ (90 MHz, $CDCl_3$) 5.28 (1 H, m, H-3), 4.55 (2 H, br s, C=C$H_2$), 3.96 (2 H, q, *J* 7.2 Hz, OC$H_2$CH$_3$), 1.40–2.70 (8 H, m), 1.66 (3 H, s) and 1.58 (3 H, s) (2 × olefinic $CH_3$), 1.20 (3 H, t, *J* 7.2 Hz, OCH$_2$C$H_3$). To a solution of the ester **6** (4.0 g, 18 mmol) in 20 ml methanol was added 15% aq. NaOH (30 ml). The reaction mixture was refluxed for 8 h, cooled to RT and acidified with 3 M HCl. It was then extracted with ether (3 × 25 ml). The ether extract was washed with brine and dried ($Na_2SO_4$). Evaporation of the solvent furnished the acid **7** (3.3 g, 95%) as a yellow oil. $[\alpha]_D^{24}$: +21.3 (*c* 4.0, $CHCl_3$). $\nu_{max}$ (neat) 3000, 1707, 1644, 885 cm$^{-1}$. $\delta_H$ (90 MHz, $CDCl_3$) 11.6 (1 H, br s, COO*H*), 5.50 (1 H, br s, H-3), 4.64 (2 H, s, C=C$H_2$), 2.50–2.80 (2 H, m, H-α), 1.00–2.30 (6 H, m), 1.67 (3 H, s) and 1.63 (3 H, s) (2 × olefinic $CH_3$). $\delta_C$ (100 MHz, $CDCl_3$) 179.9 (C=O), 149.6 (*C*=CH$_2$), 134.3 (C-2), 123.9 (C-3), 108.8 (C=*C*H$_2$), 41.3, 38.8, 37.1, 35.1, 31.1, 21.0, 20.7. Mass: *m*/*z* 194 (M$^+$, 25%), 151 (15), 134 (55), 126 (37), 119 (60), 105 (67), 93 (70), 84 (45), 81 (100). HRMS: *m*/*z* Calcd. for $C_{12}H_{18}O_2$: *M* 194.1307. Found: M$^+$, 194.1299.

### (−)-(1*S*,2*S*,4*R*,6*R*,9*R*)-4-Isopropenyl-1-methyltricyclo-[4.3.0.0$^{2,9}$]nonan-8-one (4)

To a magnetically stirred solution of the acid **7** (3.0 g, 15.46 mmol) in dry benzene (6 ml) was slowly added oxalyl chloride (3.0 ml, 34.9 mmol) and the reaction mixture was stirred for 2 h at RT. Evaporation of benzene and excess oxalyl chloride under reduced pressure furnished the acid chloride, which was taken in dry ether (10 ml) and added dropwise to a cold magnetically stirred ethereal solution of diazomethane (250 ml, prepared from 30 g of *N*-nitroso-*N*-methylurea and 260 ml of 60% aq. KOH solution). The reaction mixture was slowly warmed up to RT, stirred for 2 h and the excess diazomethane and ether were carefully evaporated on a water bath. Rapid purification by filtration of the crude product through a silica gel column using ethyl acetate–hexane (1 : 5) as eluent furnished the diazo ketone **8** (3.0 g) as a yellow oil. $\nu_{max}$ (neat) 2080, 1640, 890 cm$^{-1}$. $\delta_H$ (90 MHz, $CDCl_3$) 6.50 (1 H, br s, olefinic H), 6.21 (1 H, s, C*H*N$_2$), 4.65 (2 H, s, C=C$H_2$), 2.50–2.80 (2 H, m, H-α), 1.80–2.30 (6 H, m), 1.68 (6 H, s, 2 × olefinic C$H_3$). To a magnetically stirred, refluxing (by keeping two 100 W tungsten lamps near the flask) suspension of anhydrous copper sulfate (14 g) in 400 ml dry cyclohexane was added, dropwise, a solution of the diazo ketone **8** (3.0 g) in cyclohexane (70 ml) over a period of 2 h and refluxed for 4 h. The reaction mixture was then cooled and copper sulfate was filtered off using a sintered funnel. Evaporation of the solvent and purification of the product on a silica gel column using ethyl acetate–hexane (1 : 20 to 1 : 5) as eluent furnished the tricyclic ketone **4** (1.46 g, 50% from the acid **7**) as a yellow oil. $[\alpha]_D^{24}$: −100.5 (*c* 1.9, $CHCl_3$). $\nu_{max}$ (neat) 1720, 1640, 890 cm$^{-1}$. $\delta_H$ (200 MHz, $CDCl_3$) 4.70 (2 H, br s, C=C$H_2$), 2.73 (1 H, dd, *J* 19.5 and 12 Hz), 2.50–2.70 (1 H, m), 2.30 (1 H, m), 1.90–2.20 (2 H, m), 1.50–1.80 (3 H, m), 1.68 (3 H, s, olefinic $CH_3$), 1.35 (3 H, s, *tert*-$CH_3$), 1.25 (1 H, dd, *J* 14.2 and 8.8 Hz), 1.04 (1 H, d of t, *J* 14.2 and 6.6 Hz). $\delta_C$ (100 MHz, $CDCl_3$) 213.2 (s, C=O), 148.6 (s, *C*=CH$_2$), 108.6 (t, C=*C*H$_2$), 47.6 (t, *C*H$_2$C=O), 40.4 (d), 39.3 (d), 32.8 (d), 30.7 (s, C-1), 28.5 (t), 26.8 (t), 20.1 (d), 22.9 (q), 19.8 (q). Mass: *m*/*z* 190 (M$^+$, 5%), 162 (10), 147 (20), 133 (25), 107 (60), 93 (60), 79 (100). HRMS: *m*/*z* Calcd. for $C_{13}H_{18}O$: *M*, 190.1358. Found: M$^+$, 190.1353.

### (+)-(1*S*,2*S*,4*R*,6*R*)-2-Chloro-4-(2-chloro-2-propyl)-1-methyl-bicyclo[4.3.0]nonan-8-one (9)

A saturated solution of HCl gas in ether (150 ml) was added to the tricyclic ketone **4** (658 mg, 3.46 mmol) and the reaction mixture was stirred for 36 h under a closed system at RT. It was then diluted with ether (20 ml), washed with water, saturated $NaHCO_3$ solution and brine, and dried ($Na_2SO_4$). Evaporation of the solvent and purification of the residue on a silica gel column using ethyl acetate–hexane (1 : 10 to 1 : 5) as eluent furnished the dichloride **9** (760 mg, 84%), which was recrystallised from a mixture of hexane and $CH_2Cl_2$. Mp: 93–95 °C. $[\alpha]_D^{24}$: +173 (*c* 1.2, $CHCl_3$). $\nu_{max}$ (Nujol) 1740 cm$^{-1}$. $\delta_H$ (200 MHz, $CDCl_3$) 4.39 (1 H, t, *J* 2.9 Hz, C*H*Cl), 2.63 (1 H, dd, *J* 18.7 and 7.1 Hz, H-7a), 2.43 (1 H, d, *J* 17.8 Hz, H-9a), 2.10–2.35 (3 H, m), 1.85–2.05 (4 H, m), 1.58 (6 H, s, ClC(C$H_3$)$_2$), 1.24 (3 H, d, *J* 1 Hz, C$^1$-$CH_3$), 1.03 (1 H, q, *J* 12 Hz). $\delta_C$ (50 MHz, $CDCl_3$) 216.7 (C=O), 73.2 (*C*-Cl), 66.6 (*C*H-Cl), 46.6 (*C*H$_2$C=O), 44.9 (*C*H$_2$C=O), 42.7 (C-1), 42.1 (CH), 37.8 (CH), 31.9 ($CH_2$), 31.2 ($CH_2$), 30.9 ($CH_3$), 30.8 ($CH_3$), 27.1 ($CH_3$). Mass: *m*/*z* 262 (M$^+$, 25%), 264 (M$^+$ + 2, 15%), 227 (15), 191 (100), 183 (32), 149 (28), 121 (25), 109 (50), 107 (48). Anal. Calcd. for $C_{13}H_{20}Cl_2O$: C, 59.32; H, 7.66. Found: C, 59.06; H, 7.69%.

### (−)-(1*S*,2*S*,6*R*,9*R*)-4-Isopropylidene-1-methyltricyclo-[4.3.0.0$^{2,9}$]nonan-8-one (10)

A solution of the dichloride **9** (208 mg, 0.79 mmol) and DBU (240 mg, 0.236 ml, 1.58 mmol) in dry benzene (2 ml) was heated in a sealed tube at 160 °C for 30 min. The reaction mixture was

then cooled to RT, diluted with ether (10 ml), washed with water, 3 M HCl (5 ml), saturated aq. $NaHCO_3$ solution and brine, and dried ($Na_2SO_4$). Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate–hexane (1 : 20 to 1 : 5) as eluent furnished the tricyclic compound **10** (116 mg, 77.3%). $[\alpha]_D^{23}$: −150 (*c* 0.2, $CHCl_3$). $\nu_{max}$ (neat) 1720 $cm^{-1}$. $\delta_H$ (90 MHz, $CDCl_3$) 1.50–2.60 (9 H, m), 1.60 (6 H, br s, 2 × olefinic $CH_3$), 1.35 (3 H, s, *tert*-$CH_3$). $\delta_C$ (100 MHz, $CDCl_3$) 215.1 (C, C=O), 126.7 (C) and 123.6 (C) (olefinic C), 44.8 ($CH_2$, C-7), 41.4 (CH), 35.1 (C, C-1), 34.8 (CH), 29.6 ($CH_2$), 28.7 (CH), 24.1 ($CH_2$), 20.6 ($CH_3$), 20.2 ($CH_3$), 20.0 ($CH_3$). Mass: *m*/*z* 190 ($M^+$, 4%), 149 (15), 133 (25), 109 (85), 105 (60), 43 (100). HRMS: *m*/*z* Calcd. for $C_{13}H_{18}O$: *M*, 190.1358. Found: $M^+$, 190.1357.

### (−)-(1*S*,6*S*)-6-Methylbicyclo[4.3.0]non-4-ene-3,8-dione (3)

Through a cold (−70 °C) solution of the compound **10** (400 mg, 2.1 mmol) in methanol (0.1 ml) and $NaHCO_3$ (catalytic) in 12 ml of $CH_2Cl_2$ was passed a stream of pre-cooled ozone in oxygen gas until the reaction mixture turned to blue in colour. Excess ozone was flushed off by passing oxygen gas. Dimethyl sulfide (1.1 g, 1.3 ml, 17.8 mmol) was added to the reaction mixture, allowed to warm up to RT and stirred for 10 h. It was then diluted with $CH_2Cl_2$, washed with brine and dried ($Na_2SO_4$). Evaporation of the solvent furnished the dione **11**, which was taken in 5 ml $CH_2Cl_2$ and a catalytic amount *p*TSA was added and stirred at RT for 8 h. Evaporation of the solvent and purification of the product on a silica gel column using ethyl acetate–hexane (1 : 5 to 2 : 5) as eluent furnished the enedione **3** (307 mg, 89%) as an oil. $[\alpha]_D^{25}$: −55 (*c* 2.5, MeOH). $\nu_{max}$ (neat) 1745, 1675 $cm^{-1}$. $\delta_H$ (90 MHz, $CDCl_3$) 6.61 (1 H, d, *J* 10.2 Hz, H-5), 6.00 (1 H, d, *J* 10.2 Hz, H-4), 2.00–2.80 (7 H, m), 1.40 (3 H, s, *tert*-$CH_3$). $\delta_C$ (22.5 MHz, $CDCl_3$) 214.4 (s, C-8), 196.9 (s, C-3), 154.2 (d, C-5), 128.0 (d, C-4), 51.9 (t), 42.8 (t), 40.7 (d, C-1), 40.4 (s, C-6), 37.4 (t), 25.0 (q). Mass: *m*/*z* 164 ($M^+$, 48%), 122 (20), 95 (100), 79 (35), 67 (50), 41 (60). HRMS: *m*/*z* Calcd. for $C_{10}H_{12}O_2$: *M*, 164.0837. Found: $M^+$, 164.0818.

### (1*R*,5*S*,6*R*) and (1*R*,5*R*,6*R*)-5,6-Dimethylbicyclo[4.3.0]nonan-3,8-diones (12a and b)

To a cold (−5 °C) magnetically stirred solution of lithium dimethylcopper (0.92 mmol) in ether [prepared from CuI (174 mg, 0.913 mmol) and MeLi (1.97 ml of a 0.93 M solution in ether, 1.83 mmol)] was slowly added a solution of the enedione **3** (50 mg, 0.305 mmol) in 1 ml of dry ether. The reaction mixture was slowly warmed up to RT and stirred for 3 h. It was then quenched with 5% aq. ammonia solution and extracted with ether (3 × 5 ml). The ether extract was washed with brine and dried ($Na_2SO_4$). Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate–hexane (1 : 5 to 2 : 5) as eluent furnished a 3 : 2 mixture of epimers of the diketone **12a**,**b** (39 mg, 71%) as an oil. $\nu_{max}$ (neat) 1740, 1710 $cm^{-1}$. $\delta_H$ (270 MHz, $CDCl_3$, 3 : 2 diastereomeric mixture) 1.80–2.80 (10 H, m), 1.27 and 1.18 (3 H, s, *tert*-$CH_3$), 0.97 and 1.02 (3 H, d, *J* 6.6 Hz, *sec*-$CH_3$). $\delta_C$ (100 MHz, $CDCl_3$): *For the major isomer* **12a**: 215.8 (C, C-8), 210.3 (C, C-3), 51.9 ($CH_2$), 45.5 (CH), 44.9 ($CH_2$), 42.0 ($CH_2$), 40.7 (2 C, C and $CH_2$), 35.7 (CH), 18.7 ($CH_3$), 16.6 ($CH_3$). *For the minor isomer* **12b**: 217.0 (C, C-8), 209.6 (C, C-3), 45.2 ($CH_2$), 45.1 ($CH_2$), 44.6 (CH), 42.3 ($CH_2$), 40.8 (C), 26.2, 17.8. Mass: *m*/*z* 180 ($M^+$, 27 %), 137 (12), 111 (20), 109 (18), 96 (26), 69 (100). HRMS: *m*/*z* Calcd. for $C_{11}H_{16}O_2$: *M*, 180.1150. Found: $M^+$, 180.1140.

### (−)-(1*R*,6*S*)-8,8-Ethylenedioxy-6-methylbicyclo[4.3.0]non-4-en-3-one (13)

A magnetically stirred solution of the enedione **3** (180 mg, 1.1 mmol), ethylene glycol (72 µl, 1.3 mmol) and a catalytic amount of *p*TSA in 35 ml of dry benzene was refluxed using a Dean–Stark water separator for 3.5 h. It was cooled, washed with saturated aq. $NaHCO_3$ and brine, and dried ($Na_2SO_4$). Evaporation of the solvent under reduced pressure and purification of the product on a silica gel column using ethyl acetate–hexane (1 : 5 to 2 : 5) as eluent furnished the ketoketal **13** (124 mg, 54%, 63% based on consumed starting material). $[\alpha]_D^{25}$: −26.3 (*c* 3.8, $CHCl_3$). $\nu_{max}$ (neat) 1675 $cm^{-1}$. $\delta_H$ (270 MHz, $CDCl_3$) 6.60 (1 H, d, *J* 9.9 Hz, H-5), 5.92 (1 H, d, *J* 9.9 Hz, H-4), 3.86 (4 H, s, $OCH_2CH_2O$), 2.62 (1 H, dd, *J* 17.9 and 6.0 Hz), 1.90–2.45 (5 H, m), 1.83 (1 H, dd, *J* 13.6 and 10.7 Hz), 1.29 (3 H, s, *tert*-$CH_3$). $\delta_C$ (22.5 MHz, $CDCl_3$) 197.7 (s, C=O), 156.3 (d, C-5), 126.5 (d, C-4), 115.1 (s, O-C-O), 64.0 (t) and 63.7 (t) [$OCH_2CH_2O$], 50.8 (t), 42.4 (d, C-1), 41.7 (2 C, s and t), 37.2 (t), 24.9 (q, $CH_3$). Mass: *m*/*z* 208 ($M^+$, 5%), 164 (17), 112 (28), 99 (17), 95 (35), 86 (100). Further elution of the column furnished the unreacted starting material **3** (25 mg, 14%).

### (1*R*,5*S*,6*R*) and (1*R*,5*R*,6*R*)-5,6-Dimethylbicyclo[4.3.0]nonan-3,8-diones (12a,b)

Reaction of the ketal **13** (50 mg, 0.24 mmol) in 1 ml of ether with lithium dimethylcopper [prepared from CuI (136 mg, 0.72 mmol) and MeLi (2 ml of a 0.7 M solution in ether, 1.4 mmol)], as described earlier, for 3 h furnished 50 mg of the product, which was taken up in 1.5 ml of THF and 3 M aq. HCl (1.0 ml) and stirred for 5 h at RT. It was then extracted with ether (3 × 5 ml), washed with water, saturated $NaHCO_3$ solution and brine, and dried ($Na_2SO_4$). Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate–hexane (1 : 5 to 2 : 5) as eluent furnished a 2 : 1 epimeric mixture of the diketones **12a**,**b** (31 mg, 70%).

### (2*S*,3*R*,5*R*) and (2*R*,3*R*,5*R*)-2-Allyl-5-isopropenyl-2,3-dimethylcyclohexanones (14)

To a cold (−10 °C), magnetically stirred solution of lithium dimethylcopper [prepared from cuprous iodide (1.9 g, 10 mmol) and methyllithium in ether (20 mmol, 26 ml of a 0.765 M solution in ether)] was added a solution of (*R*)-carvone (**1**, 1.0 g, 6.66 mmol) in dry ether (15 ml) over a period of 15 min. The reaction mixture was stirred for 30 min at RT, and a mixture of allyl bromide (8.0 g, 5.6 ml, 66.1 mmol) and HMPT (1.43 g, 1.4 ml, 8 mmol) was added over 5 min. It was stirred for 24 h at RT, quenched with 25% aq. $NH_4Cl$ solution and extracted with ether (3 × 15 ml). The ether extract was washed with brine and dried ($Na_2SO_4$). Evaporation of the solvent and purification of the residue on a silica gel column, using ethyl acetate–hexane (1 : 48) as eluent, furnished a 9 : 1 epimeric mixture of the product **14** (1.22 g, 89%) as pale yellow oil. Partial purification on a long silica gel column furnished a small amount of major epimer of the product **14**. $[\alpha]_D^{24}$: +37 (*c* 1.2, $CHCl_3$). $\nu_{max}$ (neat) 1705, 1640, 910, 890 $cm^{-1}$. $\delta_H$ (200 MHz, $CDCl_3$) 5.63 (1 H, t of dd, *J* 17.5, 9.5 and 7.3 Hz, H-2′), 5.08 (1 H, d, *J* 17.5 Hz) and 5.07 (1 H, d, *J* 9.5 Hz) [H-3′], 4.79 (1 H, s) and 4.72 (1 H, s) [$C=CH_2$], 2.30–2.70 (5 H, m), 1.90–2.20 (2 H, m), 1.60–1.70 (1 H, m), 1.75 (3 H, s, olefinic $CH_3$), 1.00 (3 H, s, *tert*-$CH_3$), 0.91 (3 H, d, *J* 7.2 Hz, *sec*-$CH_3$). $\delta_C$ (22.5 MHz, $CDCl_3$) 213.4 (s, C=O), 146.8 (s, *C*=$CH_2$), 133.2 (d, *C*H=$CH_2$), 117.0 (t, CH=*C*$H_2$), 109.7 (t, C=*C*$H_2$), 51.1 (s, C-2), 42.2, 41.3, 39.9, 36.0 (d), 32.2 (t), 20.4 (q), 18.3 (q), 15.3 (q). Mass: *m*/*z* 206 ($M^+$, 10%), 191 (20), 163 (30), 123 (25), 109 (40), 95 (95), 41 (100). HRMS: *m*/*z* Calcd. for $C_{14}H_{22}O$: *M*, 206.1671. Found: $M^+$, 206.1679.

### (2*S*,3*R*,5*R*) and (2*R*,3*R*,5*R*)-5-Isopropenyl-2,3-dimethyl-2-(2-oxopropyl)cyclohexanones (15) and (16)

A suspension of palladium chloride (61 mg, 0.34 mmol) and cuprous chloride (500 mg, 5 mmol) in DMF (2.5 ml) and water (0.5 ml, 27.8 mmol) was magnetically stirred in an oxygen atmosphere, created *via* evacuative displacement of air using an

oxygen balloon, for 1 h at RT. A solution of the 9 : 1 mixture of the allyl compound **14** (1.03 g, 5 mmol) in 1 ml of DMF was then added, and the reaction mixture was stirred for 24 h at RT in the oxygen atmosphere. 3 M HCl (5 ml) was added to the reaction mixture and extracted with ether (3 × 10 ml). The ether layer was washed with saturated aq. $NaHCO_3$ solution followed by brine and dried ($Na_2SO_4$). Evaporation of the solvent and careful chromatography of the residue on a silica gel column using ethyl acetate–hexane (1 : 20 to 1 : 10) as eluent, furnished the diketone **16** (86 mg, 7.7%) as oil and **15** (775 mg, 70%) as a white solid, which was recrystallised from hexane. *For the minor diketone* **16**: $\nu_{max}$ (neat) 1700, 1640, 885 $cm^{-1}$. $\delta_H$ (90 MHz, $CDCl_3$) 4.77 (2 H, br s, C=$CH_2$), 2.10–2.90 (5 H, m), 2.17 (3 H, s, $CH_3$C=O), 1.74 (3 H, s, olefinic $CH_3$), 1.60–1.85 (3 H, m), 1.41 (3 H, s, *tert*-$CH_3$), 0.86 (3 H, d, *J* 7.0 Hz, *sec*-$CH_3$). $\delta_C$ (22.5 MHz, $CDCl_3$) 212.1 (s, ring C=O), 205.7 (s, Me*C*=O), 146.6 (s, *C*=$CH_2$), 109.2 (t, C=*C*$H_2$), 49.9 (s, C-2), 45.1 (t, *C*$H_2$C=O), 41.1 (t, C-6), 40.2 (d), 37.3 (d), 32.1 (t), 30.7 (q), 21.7 (q), 19.9 (q), 15.5 (q). *For the major diketone* **15**: mp: 53–54 °C. $[\alpha]_D^{23}$: +6.1 (*c* 1.14, $CHCl_3$). $\nu_{max}$ (neat) 1710, 1700, 1650, 895 $cm^{-1}$. $\delta_H$ (90 MHz, $CDCl_3$) 4.83 (1 H, s) and 4.75 (1 H, s) (C=$CH_2$), 2.78 (2 H, br s), 2.56 (2 H, br s), 2.20–2.50 (1 H, m), 2.12 (3 H, s, COC*H*$_3$), 1.65–1.85 (3 H, m), 1.72 (3 H, s, olefinic $CH_3$), 1.02 (3 H, s, *tert*-$CH_3$), 0.88 (3 H, d, *J* 7.2 Hz, *sec*-$CH_3$). $\delta_C$ (22.5 MHz, $CDCl_3$) 211.8 (s, ring C=O), 205.5 (s, Me*C*=O), 146.3 (s, *C*=$CH_2$), 109.6 (t, C=*C*$H_2$), 49.4 (s, C-2), 49.1 (t, *C*$H_2$COC$H_3$), 41.1 (t, C-6), 39.5 (d, C-5), 34.4 (d, C-3), 31.7 (t, C-4), 30.2 (q, CO*C*$H_3$), 20.0 (q), 17.8 (q), 14.4 (q). Mass: *m*/*z* 222 ($M^+$, 5%), 165 (90), 109 (22), 95 (25), 43 (100). Anal. Calcd. for $C_{14}H_{22}O_2$: C, 75.63; H 9.97. Found: C, 75.74; H 10.19%.

### (+)-(1*S*,2*R*,4*R*)-4-Isopropenyl-1,2-dimethylbicyclo[4.3.0]non-6-en-8-one (17)

To a solution of the diketone **15** (686 mg, 3.09 mmol) in 1 ml of methanol was added 10% aq. KOH (1.73 ml, 3.71 mmol), and the reaction mixture was refluxed for 3 h. It was cooled and extracted with ether (3 × 10 ml). The ether extract was washed with water followed by brine and dried ($Na_2SO_4$). Evaporation of the solvent and purification of the residue on a silica gel column, using ethyl acetate–hexane (1 : 6) as eluent furnished the enone **17** (600 mg, 95%) as an oil. $[\alpha]_D^{25}$: +44.2 (*c* 1.0, $CHCl_3$). $\nu_{max}$ (neat) 1700, 1620, 888 $cm^{-1}$. $\delta_H$ (200 MHz, $CDCl_3$) 5.80 (1 H, s, H-7), 4.73 (1 H, s) and 4.84 (1 H, s) [C=$CH_2$], 2.50–3.10 (3 H, m), 2.20 (2 H, s, H-9), 1.50–1.80 (3 H, m), 1.70 (3 H, s, olefinic $CH_3$), 1.12 (3 H, s, *tert*-$CH_3$), 0.91 (3 H, d, *J* 6.1 Hz, *sec*-$CH_3$). $\delta_C$ (50 MHz, $CDCl_3$) 207.6 (C=O), 187.3 (C-6), 146.0 (*C*=$CH_2$), 127.4 (C-7), 111.7 (C=*C*$H_2$), 50.6 (C-9), 46.7 (C-1), 40.5, 36.4, 31.4, 30.0, 22.5, 18.5, 16.6. Mass: *m*/*z* 204 ($M^+$, 28%), 189 (20), 162 (100), 147 (31), 134 (62), 119 (40), 105 (33), 95 (29). HRMS: *m*/*z* Calcd. for $C_{14}H_{20}O$: *M*, 204.1514. Found: $M^+$, 204.1514.

### (−)-(1*S*,2*R*,4*R*,6*S*) and (−)-(1*S*,2*R*,4*R*,6*R*)-4-Isopropenyl-1,2-dimethylbicyclo[4.3.0]nonan-8-ones (18) and (19)

To a dark blue coloured solution of lithium (190 mg, 27.3 mmol) in 400 ml of freshly distilled ammonia was added, dropwise, a solution of the enone **17** (1.5 g, 7.35 mmol) and *tert*-butanol (0.6 ml, 6.4 mmol) in 20 ml of dry THF over a period of 15 min. The reaction mixture was stirred for 50 min and then quenched with ammonium chloride. Ammonia was evaporated, it was diluted with water and extracted with ether (3 × 25 ml). The ether extract was washed with brine and dried ($Na_2SO_4$). Evaporation of the solvent and purification of the residue over a silver nitrate impregnated silica gel column using ethyl acetate–hexane (1 : 50 to 1 : 10) as eluent furnished the *trans*-hydrindanone **19** (305 mg, 20%), *cis*-hydrindanone **18** (650 mg, 43%) and the unreacted starting material **17** (300 mg, 20%). For the *trans* isomer **19**: $[\alpha]_D^{24}$: −186 (*c* 2.7, $CHCl_3$). $\nu_{max}$ (neat) 1745, 1640, 888 $cm^{-1}$. $\delta_H$ (200 MHz, $CDCl_3$) 4.93 (1 H, s) and 4.84 (1 H, s) [C=$CH_2$], 2.43 (1 H, m, H-4), 1.50–2.20 (10 H, m), 1.76 (3 H, s, olefinic $CH_3$), 0.83 (3 H, d, *J* 6.3 Hz, *sec*-$CH_3$), 0.79 (3 H, s, *tert*-$CH_3$). $\delta_C$ (22.5 MHz, $CDCl_3$) 215.6 (s, C=O), 146.6 (s, *C*=$CH_2$), 110.0 (t, C=*C*$H_2$), 53.3 (t, *C*$H_2$C=O), 42.1 (s, C-1), 40.6 (d, C-4), 40.0 (d), 38.7 (d), 37.4 (t), 31.7 (t), 25.5 (t), 22.2 (q), 16.6 (q), 10.6 (q). Mass: *m*/*z* 206 ($M^+$, 15%), 178 (11), 163 (35), 149 (11), 135 (15), 123 (40), 121 (50), 109 (30), 107 (35), 96 (100). HRMS: *m*/*z* Calcd. for $C_{14}H_{22}O$: *M*, 206.1671. Found: $M^+$, 206.1658. *For the cis isomer* **18**: $[\alpha]_D^{26}$: −100.4 (*c* 2.5, $CHCl_3$). $\nu_{max}$ (neat) 1740, 1640, 890 $cm^{-1}$. $\delta_H$ (270 MHz, $CDCl_3$) 4.69 (1 H, s) and 4.72 (1 H, s) [C=$CH_2$], 2.54 (1 H, dd, *J* 18.7 and 8.5 Hz, H-7a), 1.95 and 2.52 (2 H, 2 × d, *J* 18.5 Hz, H-9), 1.40–2.30 (8 H, m), 1.72 (3 H, s, olefinic $CH_3$), 1.06 (3 H, d, *J* 7.1 Hz, *sec*-$CH_3$), 1.03 (3 H, s, *tert*-$CH_3$). $\delta_C$ (22.5 MHz, $CDCl_3$) 219.2 (s, C=O), 149.4 (s, *C*=$CH_2$), 108.5 (t, C=*C*$H_2$), 48.1 (t, C-9), 44.8 (t, C-7), 40.5 (s, C-1), 38.6 (d), 37.1 (d), 34.6 (t), 33.8 (2 C, d & t), 25.4 (q), 21.0 (q), 16.0 (q). Mass: *m*/*z* 206 ($M^+$, 22%), 163 (35), 149 (25), 109 (55), 95 (55), 40 (100). HRMS: *m*/*z* Calcd. for $C_{14}H_{22}O$: *M*, 206.1671. Found: $M^+$, 206.1688.

### (−)-(1*S*,2*R*,6*S*)-4-Isopropylidene-1,2-dimethylbicyclo[4.3.0]nonan-8-one (21)

To an ice cold magnetically stirred saturated solution of HBr in dry ether (50 ml) [by dissolving HBr gas, generated by bromination of tetralin, in ether] was added the hydrindanone **18** (400 mg, 1.94 mmol) in 2 ml of dry ether. The reaction mixture was stirred at the same temp for 6 h, diluted with ether (30 ml), washed with water, aq. $NaHCO_3$ and brine, and dried ($Na_2SO_4$). Evaporation of the solvent furnished the tertiary bromide **20**. A solution of the bromide **20** and DBU (0.347 ml, 2.3 mmol) in 5 ml of benzene was taken up in a sealed tube and heated at 130 °C for 30 min. The reaction mixture was then cooled to RT, diluted with water and extracted with ether (3 × 10 ml). The ether extract was washed with 3 M HCl, saturated $NaHCO_3$ solution and brine, and dried ($Na_2SO_4$). Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate–hexane (1 : 20) as eluent furnished the isopropylidene compound **21** containing a trace amount of the starting material **18** (390 mg, 97.5% in two steps). $[\alpha]_D^{26}$: +79.1 (*c* 2.73, $CHCl_3$). $\nu_{max}$ (neat) 1740 $cm^{-1}$. $\delta_H$ (90 MHz, $CDCl_3$) 2.35 (1 H, d, *J* 18 Hz), 2.16 (2 H, s, C*H*$_2$C=O), 1.93 (1 H, d, *J* 18 Hz), 1.60–2.60 (6 H, m), 1.68 (3 H, s), 1.63 (3 H, s), 1.10 (3 H, s, *tert*-$CH_3$), 0.85 (3 H, d, *J* 6.3 Hz, *sec*-$CH_3$). $\delta_C$ (22.5 MHz, $CDCl_3$) 218.7 (s, C=O), 127.1 (s) and 123.9 (s) [olefinic C], 52.4 (t, *C*$H_2$C=O), 45.0 (d), 40.8 (s, C-1), 40.4 (t), 35.3 (d), 33.8 (t), 28.3 (t), 19.7 (2 C, q), 18.7 (q), 16.1 (q). Mass: *m*/*z* 206 ($M^+$, 80%), 163 (40), 149 (45), 121 (75), 110 (40), 109 (100), 107 (50). HRMS: *m*/*z* Calcd. for $C_{14}H_{22}O$: *M*, 206.1671. Found: $M^+$, 206.1668.

### (+)-(1*S*,5*R*,6*S*)-5,6-Dimethylbicyclo[4.3.0]nonan-3,8-dione (12a)

Ozonolysis of the enone **21** (390 mg, 1.89 mmol), in $CH_2Cl_2$ (10 ml) and methanol (0.4 ml), as described for the compound **10**, followed by reductive work up with triphenylphosphine (500 mg, 1.9 mmol) for 4 h at RT and purification of the product over a silica gel column using ethyl acetate–hexane (1 : 5 to 2 : 5) as eluent furnished the dione **12a** (300 mg, 88%). $[\alpha]_D^{24}$: +88.4 (*c* 1.9, $CHCl_3$). $\nu_{max}$ (neat) 1740, 1710 $cm^{-1}$. $\delta_H$ (200 MHz, $CDCl_3$) 1.70–2.80 (10 H, m), 1.21 (3 H, s, *tert*-$CH_3$), 0.90 (3 H, d, *J* 6.6 Hz, *sec*-$CH_3$). $\delta_C$ (100 MHz, $CDCl_3$) 215.9 (C), 210.4 (C), 51.9 ($CH_2$), 45.5 (CH), 45.0 ($CH_2$), 42.0 ($CH_2$), 40.7 (2 C, C & $CH_2$), 35.7 (CH), 18.7 ($CH_3$), 16.6 ($CH_3$). Mass: *m*/*z* 180 ($M^+$, 25 %), 111 (10), 69 (100). HRMS: *m*/*z* Calcd. for $C_{11}H_{16}O_2$: *M*, 180.1150. Found: $M^+$, 180.1143.

### (+)-(1*S*,2*R*,6*R*)-4,4-Ethylenedioxy-1,2-dimethylbicyclo[4.3.0]nonan-8-one (2)

Regioselective protection of the dione **12a** (320 mg, 1.77 mmol)

in 2 ml of dry benzene using ethylene glycol (98 µl, 108 mg, 1.75 mmol) and *p*TSA (catalytic) in 70 ml of dry benzene for 3 h, as described for the ketoketal **13**, and purification of the product over a silica gel column using ethyl acetate–hexane (1 : 5) as eluent furnished the ketoketal **2** (256 mg, 64.5%) as an oil. $[\alpha]_D^{25}$: +69.8 (*c* 1.64, $CHCl_3$). $\nu_{max}$ (neat) 1730 $cm^{-1}$. $\delta_H$ (270 MHz, $CDCl_3$) 3.85–4.00 (4 H, m, $OCH_2CH_2O$), 2.93 (1 H, d of t, *J* 16.0 and 7.0 Hz), 1.40–2.50 (9 H, m), 1.06 (3 H, s, *tert*-$CH_3$), 0.85 (3 H, d, *J* 6.7 Hz, *sec*-$CH_3$). $\delta_C$ (50 MHz, $CHCl_3$ + $CDCl_3$) 219 (C=O), 109 (O-*C*-O), 64.4 and 63.5 ($OCH_2CH_2O$), 58.3, 52.2, 43.5, 41.5, 38.5, 31.8, 31.4, 18.4, 16.0. Mass: *m*/*z* 224 ($M^+$, 5%), 154 (35), 139 (10), 113 (100). HRMS: *m*/*z* Calcd. for $C_{13}H_{20}O_3$: *M*, 224.1412. Found: $M^+$, 224.1416.

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