Stereoselective Construction of *cis-transoid-cis*-Tricyclo[7.3.0.0^{2,7}]dodecanes by an Intramolecular Diels–Alder Reaction: a Formal Total Synthesis of (±)-$\Delta^{9(12)}$-Capnellene

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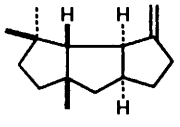
(1*R**,2*S**)-2-(2-Oxobut-3-enyl)-1-(1-oxoprop-2-enyl)-1,3,3-trimethylcyclopentane **5** was prepared stereoselectively from 4,4-dimethylcyclopent-2-en-1-one **6** and then converted into the conjugated silyl enol ether **17**. Intramolecular cycloaddition of **17**, followed by base-catalysed equilibration, provided (1*S**,2*R**,7*R**,9*R**)-3-*tert*-butyldimethylsiloxy-9,12,12-trimethyltricyclo[7.3.0.0^{2,7}]dodec-3-en-8-one **18a**, which was transformed, after contraction of the cyclohexene ring, into the synthetic intermediate **32** for (±)-$\Delta^{9(12)}$-capnellene **1**.

$\Delta^{9(12)}$-Capnellene **1**,[1a] isolated from the soft coral *Capnella imbricata*, is believed to be the biogenetic precursor to the capnellene family of linear triquinane-type sesquiterpenes **2a–f**. These compounds show biological activities similar to those of the hilstane family, which possesses antibacterial and antitumour properties.[1b] The capnellane family seems to act as



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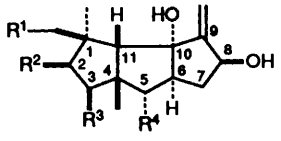
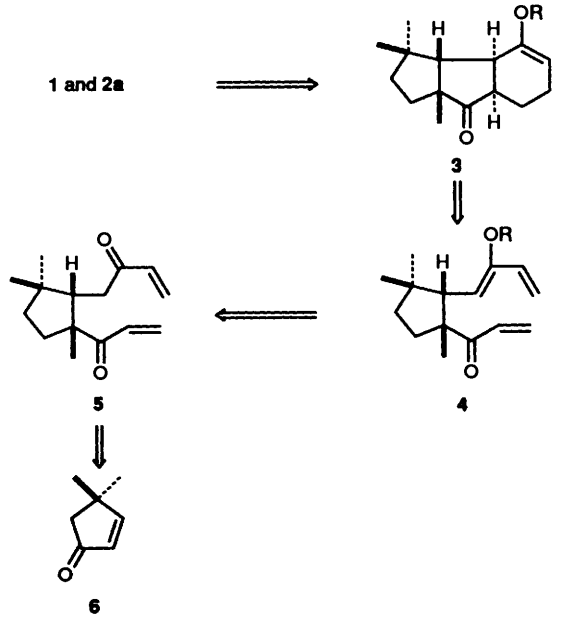


2

2a $R^1 = R^2 = R^3 = H$, $R^4 = OH$
2b $R^1 = R^3 = H$, $R^2 = R^4 = OH$
2c $R^1 = R^2 = R^3 = R^4 = H$
2d $R^1 = R^2 = R^4 = H$, $R^3 = OH$
2e $R^1 = R^3 = R^4 = H$, $R^2 = OH$
2f $R^2 = R^4 = H$, $R^1 = R^3 = OH$

chemical defence agents in the coral reef biomass to inhibit the growth of microorganisms and the settlement of larvae.[2] Thus, synthesis of the *cis-transoid-cis*-tricyclo[6.3.0.0^{2,6}]undecane skeleton has presented a challenge which has attracted the attention of synthetic chemists.[3,4] We have planned a new synthetic approach aiming at $\Delta^{9(12)}$-capnellene **1** and $\Delta^{9(12)}$-capnellene-5α,8β,10α-triol **2a**[5] *via* the *cis-transoid-cis*-tricyclo[7.3.0.0^{2,7}]dodecane derivative **3**, which would be created by an intramolecular Diels–Alder reaction of the triene **4**. It was further expected that the triene **4** could be provided from the bis-enone **5** derived from the known cyclopentenone **6**[6] (Scheme 1). We describe here in full a formal total synthesis of (±)-$\Delta^{9(12)}$-capnellene **1** according to this strategy.[7]

Concurrent introduction of two kinds of carbon units at the C-2 and C-3 positions of the cyclopent-2-enone **6**[6] was successfully carried out by conjugate addition of vinylmagnesium bromide in the presence of copper(I) iodide and *N,N,N′,N′*-tetramethylethylenediamine (TMEDA),† followed by trapping of the resulting enolate with Mander's reagent[8] in

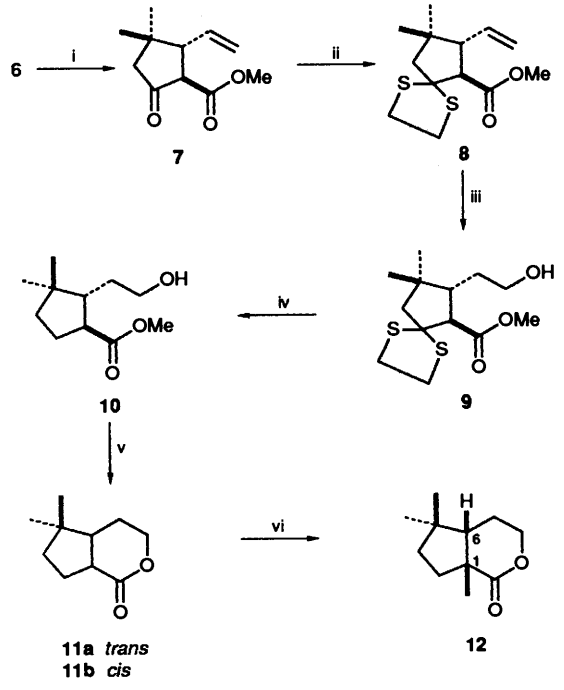


Scheme 1

the presence of hexamethylphosphoric triamide (HMPA) (Scheme 2). In order to remove the carbonyl group of the keto ester **7**, obtained in 89% yield as a single stereoisomer, **7** was converted, using ethane-1,2-dithiol in the presence of boron trifluoride–diethyl ether, into the thioacetal **8** in 93% yield. Since dethioacetalization of **8** utilizing Raney nickel accompanied hydrogenation of the vinyl group, the olefin **8** was subjected to hydroboration–oxidation prior to the dethioacetalization. Selective transformation into the primary alcohol **9** was achieved by the action of dicyclohexylborane,[9] followed by oxidation with hydrogen peroxide in the presence of sodium hydroxide. The thioacetal group of **9**, formed in 88% yield, was reduced on heating together with W-2 Raney nickel in hot methanol. On the treatment of the ester **10**, quantitatively produced, with a catalytic amount of (+)-camphor-10-sulfonic acid (CSA) in hot benzene provided the lactones **11a** and **11b** as a mixture of *trans* and *cis* compounds in a 1.6:1 ratio. Two isomers **11a** and **11b** were separated by high performance liquid chromatography (HPLC). In its 500 MHz ^{1}H NMR spectrum, the angular hydrogen at the C-1 position of the *trans*-isomer **11a** resonated at 2.51 ppm as a double double doublet (*J* 7.8, 9.8 and 13.2 Hz), while the hydrogen of the *cis*-isomer was observed at 2.96 ppm as double triplet (*J* 6.8 and 10.5 Hz). Deprotonation of

† The following abbreviations have been used throughout for reagents: *N,N,N′,N′*-tetramethylethylenediamine (TMEDA), hexamethylphosphoric triamide (HMPA), camphorsulfonic acid (CSA), lithium diisopropylamide (LDA), diisobutylaluminium hydride (DIBAL), tetrahydrofuran (THF), triacetoxyperiodinane (TAPI), *tert*-butyldimethylsilyl chloride (TBDMSCl), *tert*-butyldimethylsilyl trifluoromethanesulfonate (TBDMSOTf) and 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU).

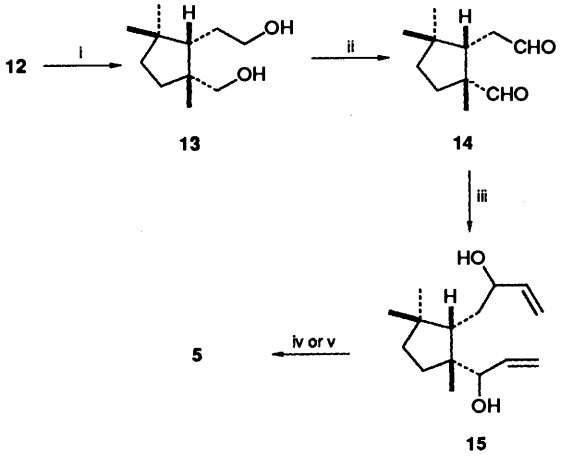
the mixture **11a** and **11b** with lithium di-isopropylamide (LDA), followed by the reaction of the lithium enolate with methyl iodide at −78 °C to room temperature, gave the methylated compound **12** in 74% yield as a single stereoisomer. The *cis* structure of **12** was determined by the 8.2% nuclear Overhauser effect (NOE) between the methyl group at the C-1 position and the angular hydrogen at the C-6 position (Scheme 2). Thus, the



Scheme 2 *Reagents:* i, CH_2=$CHMgBr$, CuI, TMEDA then $NCCO_2Me$, HMPA; ii, $HSCH_2CH_2SH$, BF_3·Et_2O; iii, dicyclohexylborane then H_2O_2, NaOH; iv, Raney Ni; v, CSA; vi, LDA; MeI

requisite stereochemistry on the *A* ring was stereoselectively constructed by the above methylation step.

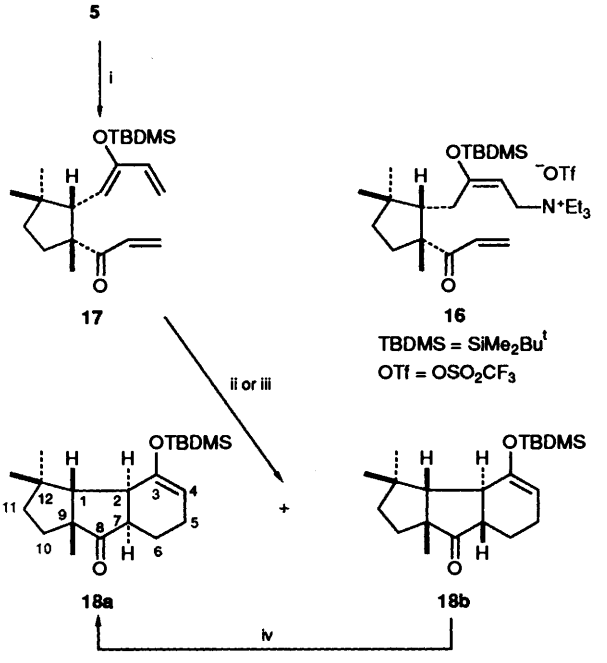
For the purpose of the conversion of the *cis* fused lactone **12** into the bis-enone **5** (Scheme 3), **12** was first reduced with an



Scheme 3 *Reagents:* i, DIBAL; ii, DMSO, $(COCl)_2$ then Et_3N; iii, CH_2=$CHMgBr$; iv, TAPI; v, Ph_3BiCO_3

excess of diisobutylaluminium hydride (DIBAL) in tetrahydrofuran (THF) at 0 °C to afford quantitatively the diol **13**, m.p. 64–66 °C. Swern oxidation of **13**, followed by the reaction of the resulting dial **14** with vinylmagnesium bromide, produced the bis-allyl alcohols **15** in 96% overall yield as a stereoisomeric mixture. Oxidation of **15** using manganese dioxide, pyridinium dichromate, tetrapropylammonium perruthenate or Swern oxidation gave complex mixtures. Transformation of **15** to the bis-enone **5** was accomplished by the use of the Dess–Martin triacetoxyperiodinane (TAPI)[10] or triphenylbismuth carbonate.[11] Thus, **5** was prepared in 75% yield by the former reagent and in 62% yield by the latter respectively.

In order to transform the bis-enone **5** into the corresponding conjugated silyl enol ether **17** (Scheme 4), **5** was treated



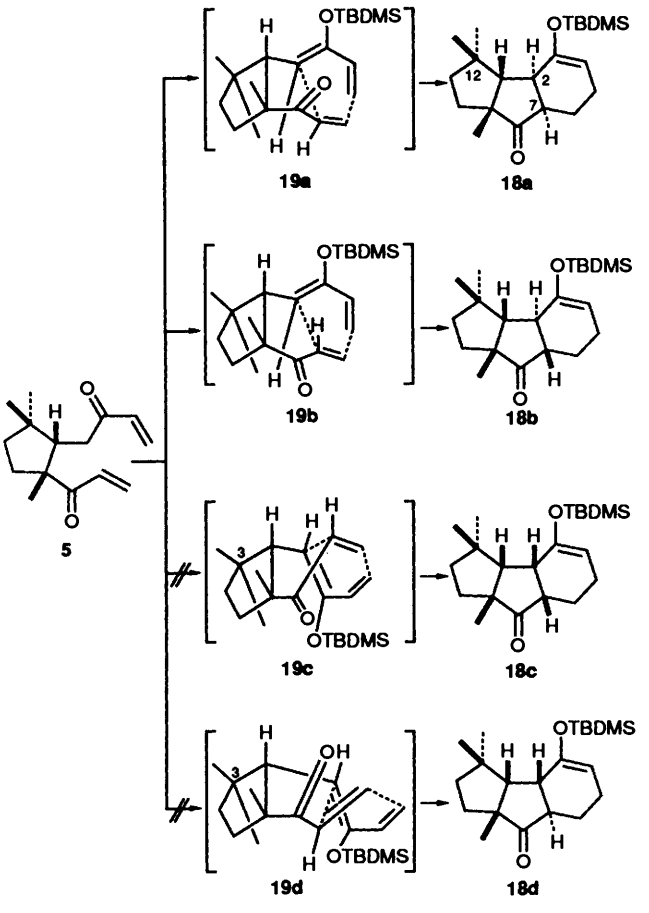
Scheme 4 *Reagents:* i, TBDMSCl, $KOBu^t$; ii, Al_2O_3; iii, heat; iv, DBU

with lithium hexamethyldisilazide and *tert*-butyldimethylsilyl chloride (TBDMSCl) but intractable polar products formed. Reaction of **5** with trimethylsilyl chloride, zinc chloride and triethylamine[12] was carried out at various temperatures, but none of the required product was obtained. Treatment of **6** with *tert*-butyldimethylsilyl trifluoromethanesulfonate (TBDMSOTf) in the presence of triethylamine[13] gave only a polar product, the structure of which was tentatively assigned to the salt **16**.

After a number of trials, the production of the desired triene **17** was achieved by a modification of Lévy's procedure.[14] Thus, a solution of potassium *tert*-butoxide in THF was slowly added to a stirred mixture of **5** and TBDMSCl in THF at −78 °C. The silyl enol ether **17** formed was isolated after treatment with silica gel. Reverse addition of the mixture of **5** and TBDMSCl to the solution of potassium *tert*-butoxide in THF resulted in a rather low yield. The triene **17**, thus obtained, was subjected to the intramolecular Diels–Alder reaction without further purification. Two stereoisomers **18a** and **18b** were obtained in 55% overall yield from **5** in 1:2 ratio on heating **17** in refluxing benzene for 2 h. The cycloaddition of **17** carried out in the presence of neutral alumina as Lewis acid[15] at room temperature for 20 h produced two isomers **18a** and **18b** in 26% yield in 10:1 ratio. Treatment of the mixture of **18a** and **18b** with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in hot benzene caused epimerization of **18b** into **18a** so that after 4 h, **18a** was quantitatively obtained as the sole stereoisomer from the mixture (Scheme 4). Thus, **18a** was stereoselectively synthesized in 55% overall yield from **5** by the following successive processes; triene formation, intramolecular cycloaddition, performed by heating **17** in hot benzene, and base treatment.

It is considered that the *cis-transoid-cis* isomer **18a** must be more stable than the *cis-transoid-trans* isomer **18b**, the former arising *via* the *endo* form **19a**, and the latter *via* the *exo* form **19b**. It is also expected that, in the conformations **19c** and **19d**

leading to the *cisoid* isomers **18c** and **18d**, there is considerable repulsion between one of the methyl groups at the C-3 position and the oxygen of the siloxy group (Scheme 5). It is, therefore,

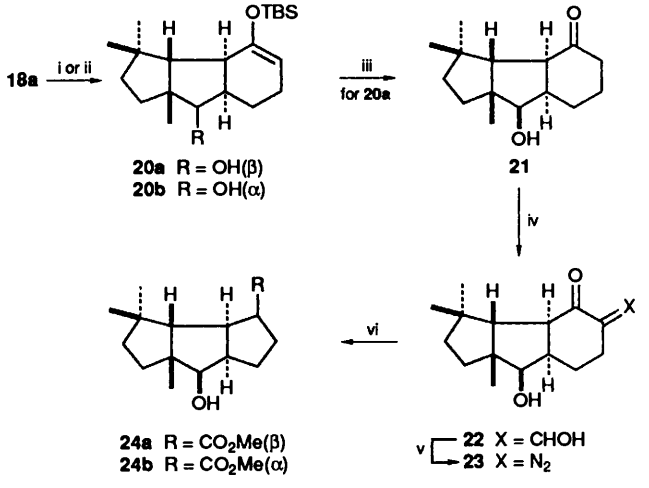


Scheme 5

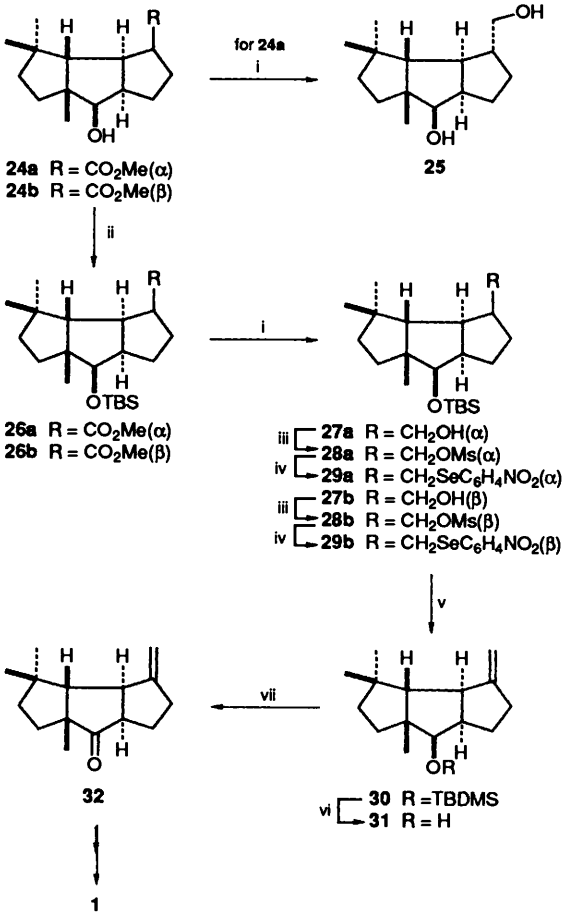
deduced that the product **18a**, obtained by the above treatment, would be the desired *cis-transoid-cis*-isomer. The structure was supported by the 13.3% NOE between one of the methyl groups at the C-12 position and the hydrogen at the C-2 position as well as the 8.4% NOE between the same methyl group and the hydrogen at the C-7 position.

Reduction of the carbonyl group of **18a** with sodium borohydride gave the single stereoisomer **20a** in 92% yield, while the other stereoisomer **20b** was exclusively obtained in 90% yield by reduction with metallic lithium in the presence of methanol in liquid ammonia (Scheme 6). The former compound, **20a**, is, therefore, a kinetically controlled product, while the latter, **20b**, is a thermodynamically controlled product. The TBDMS group of **20a** was removed by the action of tetrabutylammonium fluoride to afford the ketone **21** in 100% yield. The contraction of the *C* ring was achieved by Wolff rearrangement.[12a,16] Thus, **21** was transformed into the diazo ketone **23** in two steps: hydroxymethylenation (84% yield) followed by diazo exchange reaction of the resulting **22** with toluene-*p*-sulfonyl azide in the presence of triethylamine (80% yield). Irradiation of **23** in methanol furnished a 3:1 mixture of the rearranged products **24a** and **24b** in 71% yield. Both stereoisomers **24a**, m.p. 101–102 °C and **24b**, m.p. 90–93 °C, were readily separated by silica gel chromatography. The stereochemistry of the methoxycarbonyl group of the major isomer **24a** was tentatively assigned as α, since the *C*-methyl groups of **24a** were observed at lower fields (δ 0.95, 1.02 and 1.23) in the ^{1}H NMR spectrum compared with those of the minor one **24b** (δ 0.89, 0.91 and 1.15 ppm).

Transformation of the diol **25**, obtained by reduction of **24a** with DIBAL, into the corresponding methylene compound utilizing several methods failed. Therefore, the hydroxy group of **24a** was first protected. Treatment of **24a** with TBDMSOTf in the presence of 2,6-dimethylpyridine and 4-*N*,*N*-dimethylaminopyridine (DMAP) afforded the TBDMS ether **26a** in 98% yield. Reduction of **26a** with DIBAL at 0 °C formed the primary alcohol **27a** in 95% yield. Attempted transformation of **27a** into the 2-nitrophenylseleno compound **29a** using 2-nitrophenyl



Scheme 6 *Reagents:* i, $NaBH_4$; ii, Li, liq. NH_3, MeOH; iii, Bu_4NF; iv, HCO_2Et, NaOMe; v, TsN_3, Et_3N; vi, hv, MeOH



Scheme 7 *Reagents:* i, DIBAL; ii, TBDMSOTf, 2,6-dimethylpyridine, DMAP; iii, MsCl, Et_3N; iv, 2-$NO_2C_6H_4SeCN$, $NaBH_4$; v, H_2O_2; vi, Bu_4NF; vii, TAPI

selenocyanate and triphenylphosphine[17] failed. Therefore, by the Sharpless procedure,[18] the alcohol **27a** was converted quantitatively into the mesylate **28a**, which was then treated with 2-nitrophenyl selenide anion, prepared by the reaction of 2-nitrophenyl selenocyanate with sodium borohydride. Oxidation of the seleno compound **29a**, obtained in 98% yield, with 30% hydrogen peroxide, followed by the spontaneous elimination of the selenoxide, produced the olefin **30** in 70% yield. The same olefin **30** was further synthesized from the isomer **24b** possessing the β-orientated methoxycarbonyl group *via* **26b**–**29b**, according to the same procedures as above. Substitution of the mesylate **28b** with 2-nitrophenyl selenocyanate proceeded more slowly due to the sterically hindered functionality.

The TBDMS group of **30** was cleaved with tetrabutylammonium fluoride to give, in 90% yield, the secondary alcohol **31**, which was oxidized using TAPI[10] to the ketone **32** in 91% yield. The IR (neat), ^1H and ^{13}C NMR and MS spectra of the product **32** were consistent with those of the authentic compound.[3o] Since **32** had been converted into (±)-$\Delta^{9(12)}$-capnellene **1**,[3h,o] the formal total synthesis was accomplished (Scheme 7).

Experimental

General Methods.—M.p.s were determined on a Yanako micromelting point apparatus and are uncorrected. IR spectra were recorded on a JASCO IR-Report-100 spectrophotometer. NMR spectra were measured on a JEOL-FX-90A or a JNM-GX-500 spectrometer. Chemical shifts are reported relative to internal $SiMe_4$, and *J* values are given in Hz. Mass spectra were measured on a JEOL-JMS-01SG-2, JEOL-DX-300 or JEOL-DX-303 spectrometer. All reactions except hydrogenation were run under dry N_2 or Ar. Solvents were freshly distilled prior to use: THF and Et_2O were distilled from Na–benzophenone; CH_2Cl_2 was distilled from P_2O_5. Unless otherwise noted, all reaction mixtures were dried, after work-up, over anhydrous Na_2SO_4. Silica gel column chromatography was carried out with Merck Kieselgel 60 (70–230 mesh). TLC was carried out on Merck Kieselgel 60 F_{254} (0.25 mm). HPLC was performed with a Gilson HPLC system Model 302/303 and monitored by UV absorption and refractive-index measurements.

(2R*,3R*)-2-*Methoxycarbonyl*-4,4-*dimethyl*-3-*vinylcyclopentanone* **7**.—To a suspension of copper(I) iodide (360 mg, 1.9 mmol) in dry THF (30 cm^3) was added at ambient temperature TMEDA (4.9 cm^3, 32.5 mmol) and the mixture was stirred for 5 min at the same temperature. To the resulting mixture was slowly added at −78 °C a solution of vinylmagnesium bromide in dry THF (1 mol dm^{-3}; 35 cm^3, 35 mmol). After the mixture had been stirred for 1 h at −78 °C, a solution of the enone **6**[6] (2.00 g, 18.2 mmol) in dry THF (13 cm^3) was added dropwise to it during 1.5 h; the whole was then stirred for 4 h at −78 °C. To the stirred solution were added at −78 °C, HMPA (3.1 cm^3, 17.8 mmol) and methyl cyanoformate[8] (4.2 cm^3, 52.9 mmol), and stirring was continued for 8 h. The mixture was then allowed to warm slowly to ambient temperature. After addition of saturated aqueous NH_4Cl, the resulting mixture was extracted with hexane (×2) and Et_2O. The combined extracts were washed with brine, dried and evaporated under reduced pressure to give a residue, which was subjected to chromatography on silica gel. Elution with hexane–AcOEt (19:1 v/v) afforded the *title compound* **7** (3.16 g, 89%) as an oil (Found: C, 67.05; H, 8.3. $C_{11}H_{16}O_3$ requires C, 67.3; H, 8.2%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1755 (C=O), 1728 (C=O), 1640 (C=C) and 1152 (C–O); δ_H(90 MHz; $CDCl_3$) 0.92 (3 H, s, Me), 1.20 (3 H, s, Me), 2.30 (2 H, s, 5-H_2), 2.97 (1 H, dd, *J* 7.2 and 11.9, 3-H), 3.30 (1 H, d, *J* 11.9, 2-H), 3.76 (3 H, s, OMe), 5.00–5.30 (2 H, m, CH=CH_2) and 5.83 (1 H, ddd, *J* 7.2, 10.8 and 18.6, CH=CH_2); *m/z* 196 (M^+).

(2S*,3R*)-1,1-(1,2-*Ethylenedithio*)-2-*methoxycarbonyl*-4,4-*dimethyl*-3-*vinylcyclopentane* **8**.—To a stirred solution of the keto ester **7** (5.20 g, 26.5 mmol) in CH_2Cl_2 (32 cm^3) were added at ambient temperature ethane-1,2-dithiol (3.36 cm^3, 40.0 mmol) and boron trifluoride–diethyl ether (3.36 cm^3, 27.3 mmol), and the mixture was stirred for 36 h at the same temperature. After addition of water, the mixture was thoroughly extracted with Et_2O. The extract was washed with saturated aqueous $NaHCO_3$ and brine, dried and evaporated under reduced pressure to afford a residue, which was chromatographed on silica gel eluting with hexane–AcOEt (9:1 v/v) to give the *title compound* **8** (6.74 g, 93%) as an oil (Found: C, 57.25; H, 7.5; S, 23.35. $C_{13}H_{20}O_2S_2$ requires C, 57.3; H, 7.4; S, 23.55%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1740 (C=O), 1640 (C=C) and 1160 (C–O); δ_H(90 MHz; $CDCl_3$) 0.98 (3 H, s, Me), 1.04 (3 H, s, Me), 2.34 (2 H, s, 5-H_2), 2.73 (1 H, dd, *J* 7.6 and 12.3, 3-H), 2.80–3.50 (5 H, m), 3.71 (3 H, s, OMe), 4.90–5.20 (2 H, m, CH=CH_2) and 5.74 (1 H, ddd, *J* 7.6, 9.2 and 17.7, C*H*=CH_2); *m/z* 272 (M^+).

(2S*,3R*)-1,1-(1,2-*Ethylenedithio*)-3-(2-*hydroxyethyl*)-2-*methoxycarbonyl*-4,4-*dimethylcyclopentane* **9**.—Dicyclohexylborane[9] was prepared by reaction of cyclohexene (7.08 cm^3) with borane–dimethyl sulfide complex (10 mol dm^{-3}, 3.33 cm^3) in dry THF (33.3 cm^3). To a stirred solution of the olefin **8** (3.0 g, 11.1 mmol) in dry THF (5.0 cm^3) was slowly added, with ice cooling, the above mixture of dicyclohexylborane in THF (20.1 cm^3). The mixture was stirred for 1 h with ice cooling after which MeOH (5.0 cm^3), aqueous NaOH (3 mol dm^{-3}, 3.7 cm^3) and 30% hydrogen peroxide (1.26 cm^3) were added to it. The resulting mixture was stirred for 30 min and then neutralized with 10% hydrochloric acid with ice cooling. After concentration under reduced pressure, the resulting residue was taken up in Et_2O. The extract was washed with saturated aqueous $NaHCO_3$ and brine, dried and evaporated under reduced pressure. The residue was chromatographed on silica gel with hexane–AcOEt (3:2 v/v) as eluent to give the *title compound* **9** (2.8 g, 88%) as plates, m.p. 76–77 °C (Et_2O–hexane) (Found: C, 54.1; H, 7.6; S, 21.95. $C_{13}H_{22}O_3S_2$ requires C, 53.75; H, 7.65; S, 22.1%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3550 (OH), 1730 (C=O) and 1163 (C–O); δ_H(90 MHz; $CDCl_3$) 0.96 (3 H, s, Me), 1.06 (3 H, s, Me), 1.60–1.85 (1 H, m, 3-H), 2.10 (1 H, br s, OH), 2.00–2.40 (2 H, m, C$H_2$$CH_2$OH), 2.30 (2 H, s, 5-$H_2$), 2.90–3.68 (7 H, m) and 3.75 (3 H, s, OMe); *m/z* 290 (M^+).

(1S*,2R*)-2-(2-*Hydroxyethyl*)-1-*methoxycarbonyl*-3,3-*dimethylcyclopentane* **10**.—A mixture of the thioketal **9** (483 mg, 1.67 mmol) and Raney Ni (W-2) (10.0 g) in MeOH (18 cm^3) was heated for 24 h under reflux and a H_2 (1 atm) atmosphere. After having been cooled, the mixture was filtered through Celite and washed with MeOH and $CHCl_3$. Evaporation of the combined filtrate and washings under reduced pressure gave a residue, which was acidified by addition of 10% hydrochloric acid with ice cooling after addition of Et_2O. The aqueous layer was extracted thoroughly with Et_2O and the extract was washed with brine, dried and evaporated under reduced pressure. Chromatography of the residue on silica gel with hexane–AcOEt (3:2 v/v) as eluent afforded the title compound **10** (333 mg, 100%) as an oil; $\nu_{max}(CHCl_3)/cm^{-1}$ 3600 (OH) and 1730 (C=O); δ_H(500 MHz; $CDCl_3$) 0.79 (3 H, s, Me), 1.04 (3 H, s, Me), 1.25–2.08 (7 H, m), 2.21 (1 H, br s, OH), 2.57 (1 H, dt, *J* 5.3 and 10.1, 1-H), 3.51 (1 H, ddd, *J* 5.3, 8.0 and 10.7, C*H*HOH), 3.64 (1 H, ddd, *J* 4.8, 5.9 and 10.7, CH*H*OH) and 3.72 (3 H, s, OMe); *m/z* 200 (M^+).

7,7-*Dimethyl*-3-*oxabicyclo*[4.3.0]*nonan*-2-*ones* **11a** *and* **11b**.—A stirred solution of the hydroxy ester **10** (403 mg, 2.01 mmol) and CSA (36.0 mg, 0.16 mmol) in dry benzene (14 cm^3) was heated for 24 h at 80 °C. After dilution with benzene, the

resulting mixture was washed with saturated aqueous $NaHCO_3$ and brine, dried and evaporated under reduced pressure. The residue was purified by silica gel column chromatography eluting with hexane–AcOEt (4:1 v/v) to afford a mixture of two lactones (329.8 mg, 97%) as an oil in a ratio of 1.6:1. Separation of two isomers was carried out by HPLC on Si 80–199-C5 with hexane–AcOEt (17:3 v/v) as eluent to give the trans-*lactone* **11a** (203 mg, 60%) as an oil; $\nu_{max}(CHCl_3)/cm^{-1}$ 1740 (C=O); δ_H(500 MHz; $CDCl_3$) 0.88 (3 H, s, Me), 1.06 (3 H, s, Me), 1.50–1.75 (4 H, m), 1.84–1.95 (3 H, m), 2.51 (1 H, ddd, *J* 7.8, 9.8 and 13.2, 1-H), 4.33 (1 H, dd, *J* 7.8 and 11.9, 4-H) and 4.38 (1 H, dd, *J* 7.8 and 11.9, 4-H); *m/z* 168 (M^+) (Found: M^+, 168.1142. $C_{10}H_{16}O_2$ requires *M*, 168.1150).

The second eluate gave the cis-*lactone* **11b** (126 mg, 37%) as an oil; $\nu_{max}(CHCl_3)/cm^{-1}$ 1730 (C=O); δ_H(500 MHz; $CDCl_3$) 0.81 (3 H, s, Me), 1.02 (3 H, s, Me), 1.41 (1 H, ddd, *J* 8.5, 9.8 and 12.6), 1.50–1.59 (2 H, m), 1.82–1.88 (1 H, m), 2.04–2.20 (3 H, m), 2.96 (1 H, dt, *J* 6.8 and 10.5, 1-H), 4.14 (1 H, ddd, *J* 1.9, 10.9 and 12.5, 4-H) and 4.38 (1 H, ddd, *J* 2.4, 4.0 and 10.9, 4-H); *m/z* 168 (M^+) (Found: M^+, 168.1139).

(1R*,6S*)-1,7,7-*Trimethyl*-3-*oxabicyclo*[4.3.0]*nonan*-2-*one* **12**.—To a stirred solution of LDA, prepared from butyllithium–hexane (1.54 mol dm^{-3}; 5.2 cm^3, 8.01 mmol) and di-isopropylamine (1.35 cm^3, 9.63 mmol) in dry THF (10 cm^3), was added dropwise at −78 °C a solution of the mixture of lactones **11a** and **11b** (193 mg, 1.15 mmol) in dry THF (1.0 cm^3). After having been stirred for 1 h at −78 to −20 °C, to the stirred mixture was added at −78 °C methyl iodide (1.29 cm^3, 20.7 mmol); the mixture was then stirred for 1.5 h at −78 °C–ambient temperature. After addition of saturated aqueous NH_4Cl, the mixture was thoroughly extracted with Et_2O. The extract was washed with aqueous $Na_2S_2O_3$ (0.1 mol dm^{-3}) and brine, dried and evaporated under reduced pressure to afford a residue, which was chromatographed on silica gel. Elution with hexane–AcOEt (9:1 v/v) gave the title compound **12** (154.9 mg, 74%) as a pale yellowish oil; $\nu_{max}(CHCl_3)/cm^{-1}$ 1730 (C=O); δ_H(500 MHz; $CDCl_3$) 0.82 (3 H, s, 7-Me), 1.07 (3 H, s, 7-Me), 1.40 (3 H, s, 1-Me), 1.44–1.49 (2 H, m), 1.60 (1 H, ddt, *J* 4.0, 12.0 and 13.9, 5-H), 1.66 (1 H, ddd, *J* 3.8, 6.1 and 13.8, 9-H), 1.71 (1 H, dd, *J* 6.8 and 12.0, 6-H), 1.88 (1 H, dddd, *J* 1.4, 2.5, 6.8 and 13.9, 5-H), 2.35 (1 H, ddd, *J* 7.6, 10.3 and 13.8, 9-H), 4.24 (1 H, ddd, *J* 1.4, 11.1 and 13.9, 4-H) and 4.38 (1 H, ddd, *J* 2.5, 4.0 and 11.1, 4-H); *m/z* 182 (M^+).

(1R*,2S*)-2-(2-*Hydroxyethyl*)-1-*hydroxymethyl*-1,3,3-*trimethylcyclopentane* **13**.—To a stirred solution of the trimethyl lactone **12** (240 mg, 1.10 mmol) in dry THF (20 cm^3) was slowly added at 0 °C a solution of DIBAL in hexane (1 mol dm^{-3}; 6.6 cm^3, 6.6 mmol), and the mixture was stirred for 30 min at 0 °C and for 1 h at ambient temperature. After addition of water (2.5 cm^3), the mixture was stirred for 30 min at ambient temperature and then filtered through Celite. The filtrate and washings with Et_2O were dried and evaporated under reduced pressure to give a residue, which was subjected to chromatography on silica gel. Elution with hexane–AcOEt (1:1 v/v) afforded the *title compound* **13** (244 mg, 100%) as plates, m.p. 64–66 °C (Et_2O–hexane) (Found: C, 70.6; H, 11.9. $C_{11}H_{22}O_2$ requires C, 70.9; H, 11.9%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3630 (OH) and 3435 (OH); δ_H(90 MHz; $CDCl_3$) 0.83 (3 H, s, Me), 0.98 (3 H, s, Me), 1.09 (3 H, s, Me), 1.10–1.80 (7 H, m), 2.50 (2 H, br s, 2 × OH), 3.42 (1 H, d, *J* 10.5, C*H*HOH), 3.55–3.86 (2 H, m, CH_2OH) and 3.56 (1 H, d, *J* 10.5, CH*H*OH); *m/z* 168 ($M^+ - H_2O$) (Found: $M^+ - H_2O$, 168.1471. $C_{11}H_{20}O$ requires *m/z*, 168.1513).

(1R*,2R*)-2-(2-*Hydroxybut*-3-*enyl*)-1-(1-*hydroxyprop*-2-*enyl*)-1,3,3-*trimethylcyclopentane* **15**.—To a stirred solution of oxalyl chloride (1.9 cm^3, 21.5 mmol) in dry CH_2Cl_2 (5.0 cm^3) was slowly added at −78 °C a solution of dimethyl sulfoxide (DMSO) (3.1 cm^3, 43.0 mmol) in dry CH_2Cl_2 (5.0 cm^3). After having been stirred for 5 min at −78 °C, to the mixture was added at −78 °C a solution of the diol **13** (0.966 g, 5.2 mmol) in dry CH_2Cl_2 (10 cm^3). After having been stirred for 10 min, followed by addition of Et_3N (9.0 cm^3, 64.5 mmol), the mixture was stirred for 15 min at −78 °C and for 30 min at ambient temperature. After addition of water, the mixture was thoroughly extracted with hexane. The extract was washed with brine, dried and evaporated under reduced pressure to give the dial **14** as an oil, which was used for the next reaction without purification.

A solution of the above dial **14** in dry THF (23.6 cm^3) was slowly added into a stirred solution of vinylmagnesium bromide in dry THF (1 mol dm^{-3}; 50.0 cm^3, 50.0 mmol), and the mixture was stirred for 12 h at ambient temperature. After addition of saturated aqueous NH_4Cl with ice cooling, the resulting mixture was thoroughly extracted with Et_2O. The extract was washed with brine, dried and evaporated under reduced pressure. The residue was chromatographed on silica gel with hexane–AcOEt (7:3 v/v) as eluent to give the *title compounds* **15** (1.19 g, 96% from **13**) as a stereoisomeric mixture (Found: C, 75.75; H, 11.1. $C_{15}H_{26}O_2$ requires C, 75.6; H, 11.0%); $\nu_{max}(CHCl_3)/cm^{-1}$ 3600 (OH) and 3400 (OH); δ_H(90 MHz; $CDCl_3$) 0.77 (3 H, s, 2 × Me), 0.91 (3/2 H, s, Me), 0.96 (3/2 H, s, Me), 1.07 (3/2 H, s, Me), 1.10 (3/2 H, s, Me), 1.15–2.30 (7 H, m), 2.70–3.20 (2 H, br s, 2 × OH), 5.03–5.44 (4 H, m, olefinic H) and 5.67–5.68 (2 H, m, olefinic H); *m/z* 205 ($M^+ - Me - H_2O$).

(1R*,2S*)-2-(2-*Oxobut*-3-*enyl*)-1-(1-*oxoprop*-2-*enyl*)-1,3,3-*trimethylcyclopentane* **5**.—*Method A*. To a stirred solution of TAPI[10] (179 mg, 0.423 mmol) in dry CH_2Cl_2 (2.0 cm^3) was added at ambient temperature a solution of the bisallyl alcohols **15** (15.2 mg, 0.064 mmol) in dry CH_2Cl_2 (2.0 cm^3), and the mixture was stirred for 2 h at the same temperature. After addition of Et_2O and saturated aqueous $NaHCO_3$ containing $Na_2S_2O_3$ (10 mg) with ice cooling, the mixture was stirred for 10 min at ambient temperature. The mixture was thoroughly extracted with Et_2O. The extract was washed with saturated aqueous $NaHCO_3$ and water, dried and evaporated under reduced pressure. Chromatography of the residue on silica gel with hexane–AcOEt (19:1 v/v) as eluent gave the *title compound* **5** (11.2 mg, 75%) as an oil (Found: C, 76.8; H, 9.3. $C_{15}H_{22}O_2$ requires C, 76.9; H, 9.45%); $\nu_{max}(CHCl_3)/cm^{-1}$ 1690 (C=O); δ_H(500 MHz; $CDCl_3$) 0.87 (3 H, s, Me), 0.97 (3 H, s, Me), 1.22–1.62 (3 H, m), 1.41 (3 H, s, Me), 2.13 (1 H, dd, *J* 6.0 and 8.0, 2-H), 2.23–2.32 (1 H, m), 2.66 (1 H, dd, *J* 6.0 and 17.5, C*H*HCO), 2.71 (1 H, dd, *J* 8.0 and 17.5, CH*H*CO), 5.56 (1 H, dd, *J* 2.0 and 10.0, C=C*H*H), 5.77 (1 H, dd, *J* 1.6 and 10.5, C=C*H*H), 6.22 (1 H, dd, *J* 1.6 and 17.8, C=CH*H*), 6.23 (1 H, dd, *J* 2.0 and 16.5, C=CH*H*), 6.35 (1 H, dd, *J* 10.5 and 17.8, C*H*=CH_2) and 6.72 (1 H, dd, *J* 10.0 and 16.5, C*H*=CH_2); *m/z* 234 (M^+) (Found: M^+, 234.1613. $C_{15}H_{22}O_2$ requires *M*, 234.1619).

Method B. A solution of the bisallyl alcohols **15** (24.9 mg, 0.105 mmol) and triphenylbismuth carbonate[11] (160 mg, 0.32 mmol) in dry CH_2Cl_2 (4.0 cm^3) was stirred for 24 h at 40 °C and then filtered through Celite. The filtrate was evaporated under reduced pressure to give a residue, which was subjected to chromatography on silica gel. Elution with hexane–AcOEt (19:1 v/v) afforded the bis-enone **5** (15.2 mg, 62%) as an oil, whose IR, ^1H NMR and MS spectra were identical with those of compound **5**, prepared by the Method A.

(1S*,2R*,7R*,9R*)-**18a***and*(1S*,2R*,7S*,9R*)-3-tert-*Butyldimethylsiloxy*-9,12,12-*trimethyltricyclo*[7.3.0.$0^{2,7}$]*dodec*-3-*en*-8-*one* **18b**.—To a stirred solution of the bis-enone **5** (46.0 mg, 0.154 mmol) and TBDMSCl (27.8 mg, 0.185 mmol) in dry THF (2.0 cm^3) was slowly added during 2 h at −78 °C a solution of

freshly prepared potassium *tert*-butoxide (19.0 mg, 0.169 mmol) in dry THF (17 cm^3), and the mixture was stirred for 1 h at −78 °C. The mixture was poured onto silica gel (*ca.* 5.0 g) under ice cooling. The resulting mixture was filtered through glass filter using AcOEt as eluent. The combined filtrate and washings were evaporated under reduced pressure to give a residue, which was chromatographed on silica gel with hexane–AcOEt (1:1 v/v) to afford the siloxy diene **17** as an oil, which was immediately subjected to the intramolecular Diels–Alder reaction.

Method A. A solution of the above product **17** in dry benzene (5.0 cm^3) was heated for 2 h under reflux. Evaporation of the resulting mixture under reduced pressure provided a residue, which was purified by column chromatography on silica gel. Elution with hexane–AcOEt (19:1 v/v) gave the mixture (1:2) of the *title compounds* **18a** and **18b** (37.4 mg, 55%) as an oil; $\nu_{max}(CHCl_3)/cm^{-1}$ 1730 (C=O); δ_H(500 MHz; $CDCl_3$) 0.12, 0.14, 0.18 and 0.19 [6 H (1:1:2:2), each s, $SiMe_2$], 0.92 and 0.95 [9 H (1:2), each s, Bu^t], 0.94, 1.05, 1.06, 1.11 and 1.26 [9 H (1:4:1:1:2), each s, 3 × Me], 1.25–1.31 (1/3 H, m), 1.38–1.62 (3 H, m), 1.80–1.87 (1 H, m), 1.88–1.92 (2/3 H, m), 1.96–2.19 (13/3 H, m), 2.20 (1/3 H, br s), 2.51 (2/3 H, ddd, *J* 6.0, 11.5 and 14.0, 7-H), 2.56 (1/3 H, ddd, *J* 3.5, 5.0 and 8.5, 7-H), 2.64 (1/3, br d, *J* 8.5, 2-H), 4.62–4.64 (2/3 H, m, 4-H) and 4.74–4.77 (1/3 H, m, 4-H); *m/z* 348 (M^+) (Found: M^+, 348.2490. $C_{21}H_{36}O_2Si$ requires *M*, 348.2483).

Method B. A mixture of the above siloxy diene **17** and neutral alumina (2.0 g) in hexane–AcOEt (7:3 v/v; 7.0 cm^3) was stirred for 20 h at room temperature. The mixture was filtered through Celite. The combined filtrate and washings with Et_2O were dried and evaporated under reduced pressure. Silica gel chromatography of the residue eluating with hexane–AcOEt (49:1 v/v) gave the mixture (10:1) of tricyclic compounds **18a** and **18b** (12.1 mg, 26%) as an oil; $\nu_{max}(CHCl_3)/cm^{-1}$ 1730 (C=O); δ_H(500 MHz; $CDCl_3$) 0.12, 0.14, 0.18 and 0.19 [6 H (10:10:1:1), each s, $SiMe_2$], 0.92 and 0.95 [9 H (10:1), each s, Bu^t], 0.94, 1.05, 1.06, 1.11 and 1.26 [9 H (10:2:10:10:1), each s, 3 × Me], 1.25–1.31 (10/11 H, m), 1.38–1.62 (3/11 H, m), 1.80–1.87 (30/11 H, m), 1.88–1.92 (1/11 H, m), 1.96–2.19 (16/11 H, m), 2.20 (10/11 H, br s), 2.51 (3/11 H, ddd, *J* 6.0, 11.5 and 14.0, 7-H), 2.56 (10/11 H, ddd, *J* 3.5, 5.0 and 8.5, 7-H), 2.64 (10/11 H, br d, *J* 8.5, 2-H), 4.62–4.64 (1/11 H, m, 4-H) and 4.74–4.77 (10/11 H, m, 4-H); *m/z* 348 (M^+) (Found: M^+, 348.2493).

(1S*,2R*,7R*,9R*)-3-tert-*Butyldimethylsiloxy*-9,12,12-*trimethyltricyclo*[7.3.0.0^{2,7}]*dodec*-3-*en*-8-*one* **18a**.—A solution of the above mixture of tricyclic compounds **18a** and **18b** (4.0 mg, 0.0115 mmol) and DBU (0.17 cm^3, 0.115 mmol) in dry benzene (3.0 cm^3) was heated for 4 h under reflux. After dilution with hexane, the mixture was washed with 5% aqueous $KHSO_4$ and brine, and dried. Evaporation of the mixture, followed by chromatography of the residue on silica gel with hexane–AcOEt (19:1 v/v), gave the *cis-transoid-cis*-isomer **18a** (4.0 mg, 100%) as a powder, m.p. 52–56 °C; $\nu_{max}(CHCl_3)/cm^{-1}$ 1730 (C=O); δ_H(500 MHz; $CDCl_3$) 0.12 (3 H, s, SiMe), 0.14 (3 H, s, SiMe), 0.92 (9 H, s, Bu^t), 0.94 (3 H, s, Me), 1.06 (3 H, s, Me), 1.11 (3 H, s, Me), 1.25–1.31 (1 H, m), 1.41–1.52 (2 H, m), 1.56–1.62 (2 H, m), 1.80–1.87 (3 H, m), 2.01–2.07 (1 H, m, 6β-H), 2.20 (1 H, br s), 2.56 (1 H, ddd, *J* 3.5, 5.0 and 8.5, 7-H), 2.64 (1 H, br d, *J* 8.5, 2-H) and 4.74–4.77 (1 H, m, 4-H); δ_C(125 MHz; $CDCl_3$) −4.485 (q), −4.376 (q), 18.101 (s), 20.325 (t), 20.574 (t), 24.976 (q), 25.349 (q), 25.847 (q), 30.840 (q), 37.435 (t), 39.582 (d), 41.386 (t), 43.066 (s), 49.117 (d), 56.661 (s), 58.870 (d), 103.823 (d), 151.716 (s) and 227.173 (s).

(1S*,2R*,7R*,8R*,9R*)-3-tert-*Butyldimethylsiloxy*-8-*hydroxy*-9,12,12-*trimethyltricyclo*[7.3.0.0^{2,7}]*dodec*-3-*ene* **20a**.—To a stirred solution of the siloxy ketone **18a** (40.5 mg, 0.116 mmol) in anhydrous MeOH (3.0 cm^3) was added portionwise at 0 °C sodium borohydride (17.7 mg, 0.466 mmol), and the mixture was stirred for 12 h at 0 °C. Removal of the solvent under reduced pressure provided a residue, which was partitioned between Et_2O and brine. The combined ethereal extracts were dried and evaporated under reduced pressure to give a residue, which was chromatographed on silica gel. Elution with hexane–AcOEt (9:1 v/v) afforded the *title compound* **20a** (37.3 mg, 92%) as an oil; ν_{max}(neat)/cm^{-1} 3470 (OH); δ_H(500 MHz; $CDCl_3$) 0.49 (3 H, s, SiMe), 0.53 (3 H, s, SiMe), 0.93 (9 H, s, Bu^t), 1.02 (3 H, s, Me), 1.04 (3 H, s, Me), 1.18 (3 H, s, Me), 1.22–1.59 (5 H, m), 1.63–1.75 (1 H, m), 1.85–1.89 (1 H, m), 1.91–2.02 (2 H, m), 2.15–2.24 (1 H, m), 2.26–2.34 (2 H, m), 3.77 (1 H, br s, 8-H) and 4.78 (1 H, m, 4-H); *m/z* 350 (M^+) (Found: M^+, 350.2626. $C_{21}H_{38}O_2Si$ requires *M*, 350.2639).

(1S*,2R*,7R*,8R*,9R*)-8-*Hydroxy*-9,12,12-*trimethyltricyclo*[7.3.0.0^{2,7}]*dodecan*-3-*one* **21**.—To a stirred solution of the siloxy alcohol **20** (99.0 mg, 0.257 mmol) in THF (4.5 cm^3) was slowly added at 0 °C a solution of tetrabutylammonium fluoride in THF (1 mol dm^{-3}; 0.8 cm^3, 0.8 mmol) containing water (5 w/v%), and the mixture was stirred for 30 min at ambient temperature. After evaporation under reduced pressure, the residue was taken up into Et_2O. The extract was washed with brine, dried and evaporated under reduced pressure to give a residue, which was subjected to chromatography on silica gel. Elution with hexane–AcOEt (9:1 v/v) provided the *title compound* **21** (60.6 mg, 100%) as an oil; ν_{max}(neat)/cm^{-1} 3460 (OH) and 1700 (C=O); δ_H(500 MHz; $CDCl_3$) 0.95 (3 H, s, Me), 1.06 (3 H, s, Me), 1.26 (3 H, s, Me), 1.42–1.58 (5 H, m), 1.72–1.83 (2 H, m), 1.87–1.94 (1 H, m), 2.10–2.19 (1 H, m), 2.27–2.34 (2 H, m), 2.41 (1 H, ddd, *J* 5.0, 9.8 and 15.0, 4-H), 2.49 (1 H, dd, *J* 6.0 and 8.3, 2-H), 2.55 (1 H, ddd, *J* 5.0, 7.0 and 15.0, 4-H) and 3.65 (1 H, d, *J* 4.3, 8-H); *m/z* 236 (M^+) (Found: M^+, 236.1788. $C_{15}H_{24}O_2$ requires *M*, 236.1775).

(1S*,2R*,7R*,8R*,9R*)-8-*Hydroxy*-4-*hydroxymethylene*-9,12,12-*trimethyltricyclo*[7.3.0.0^{2,7}]*dodecan*-3-*one* **22**.—After addition of anhydrous MeOH (0.11 cm^3, 2.79 mmol) to a mixture of NaH (60% oily suspension; 90.0 mg, 2.34 mmol) in dry Et_2O (2.0 cm^3) with ice cooling, to the resulting mixture were added a solution of the hydroxy ketone **21** (82.1 mg, 0.390 mmol) in dry Et_2O (1.0 cm^3) and ethy formate (0.63 cm^3, 7.81 mmol). After having been stirred for 4 h at ambient temperature, followed by dilution with saturated aqueous NH_4Cl, the mixture was thoroughly extracted with Et_2O. The extract was washed with water and brine, dried and evaporated under reduced pressure to give a residue, which was chromatographed on silica gel. Elution with hexane–AcOEt (4:1 v/v) afforded the *title compound* **22** (77.4 mg, 84%) as an oil; ν_{max}(neat)/cm^{-1} 3440 (OH) and 1690 (C=C); δ_H(500 MHz; $CDCl_3$) 1.10 (6 H, s, 2 × Me), 1.22 (3 H, s, Me), 1.27–1.55 (5 H, m), 1.93–1.99 (1 H, m), 2.10 (1 H, d, *J* 7.4, 1-H), 2.22 (1 H, ddd, *J* 4.6, 12.8 and 14.7, 5-H), 2.40 (1 H, dt, *J* 3.7 and 14.7, 5-H), 2.42–2.46 (1 H, m, 7-H), 2.58 (1 H, t, *J* 7.4, 2-H), 3.80 (1 H, d, *J* 5.5, 8-H), 8.59 (1 H, br d, *J* 4.0, =CH) and 14.35 (1 H, br d, *J* 4.0, =CHO*H*); *m/z* 264 (M^+) (Found: M^+, 264.1700. $C_{16}H_{24}O_3$ requires *M*, 264.1724).

(1S*,2R*,3R*,6R*,7R*,8R*)-**24a** *and* (1S*,2R*,3S*,6R*,7R*,-8R*)-7-*Hydroxy*-3-*methoxycarbonyl*-8,11,11-*trimethyltricyclo*-[6.3.0.0^{2,6}]*undecane* **24b**.—To a stirred solution of the hydroxymethylene derivative **22** (41.0 mg, 0.155 mmol) in dry CH_2Cl_2 (2.0 cm^3) were added under ice cooling Et_3N (0.10 cm^3, 0.758 mmol) and a solution of toluene-*p*-sulfonyl azide (112.0 mg, 0.568 mmol) in dry CH_2Cl_2 (0.5 cm^3), and the mixture was stirred for 3 h at ambient temperature. After evaporation of the solvent under reduced pressure, the residue was chromatographed on silica gel with hexane–AcOEt (3:2 v/v) to afford the

diazo ketone **23** (32.5 mg, 80%) as an oil; ν_{max}(neat)/cm^{-1} 2080 (C=N$^+$=N$^-$) and 1710 (C=O); δ_H(500 MHz; $CDCl_3$) 1.08 (3 H, s, Me), 1.12 (3 H, s, Me), 1.21 (3 H, s, Me), 1.40–1.48 (1 H, m), 1.50–1.58 (2 H, m), 1.63–1.77 (2 H, m), 2.01–2.10 (2 H, m), 2.40–2.49 (2 H, m), 2.57 (1 H, t, *J* 7.4, 2-H), 2.67 (1 H, ddd, *J* 4.6, 11.0 and 14.3, 5-H), 2.81 (1 H, dt, *J* 5.0 and 14.3, 5-H) and 3.79 (1 H, d, *J* 5.5, 8-H).

An ice-cooled solution of the above diazo ketone **23** in anhydrous MeOH (20 cm^3) was irradiated for 2 h through a Pyrex filter with a 400-W high-pressure mercury lamp. Evaporation of the solvent under reduced pressure afforded a residue which was purified by chromatography on silica gel. Elution with hexane–AcOEt (4:1 v/v) provided the *title compound* **24a** (17.6 mg, 53%) as plates, m.p. 101–102 °C; ν_{max}($CHCl_3$)/cm^{-1} 1734 (C=O), 1145 (C–O) and 1041 (C–O–C); δ_H(500 MHz; $CDCl_3$) 0.95 (3 H, s, Me), 1.02 (3 H, s, Me), 1.23 (3 H, s, Me), 1.41–1.48 (2 H, m), 1.49–1.62 (3 H, m), 1.75–1.90 (3 H, m), 2.04–2.12 (1 H, m), 2.40–2.46 (1 H, m), 2.63–2.73 (2 H, m), 3.66 (3 H, s, OMe) and 3.80 (1 H, d, *J* 6.8, 7-H); *m/z* 266 (M^+) (Found: M^+, 266.1864. $C_{16}H_{26}O_3$ requires *M*, 266.1881).

Elution with hexane–AcOEt (4:1 v/v) gave the isomer **24b** (5.9 mg, 18%) as plates, m.p. 90–93 °C; ν_{max}($CHCl_3$)/cm^{-1} 1730 (C=O), 1150 (C–O) and 1041 (C–O–C); δ_H(500 MHz; $CDCl_3$) 0.89 (3 H, s, Me), 0.91 (3 H, s, Me), 1.15 (3 H, s, Me), 1.21–1.32 (2 H, m), 1.38–1.51 (3 H, m), 1.66–1.73 (1 H, m), 1.80–1.87 (1 H, m), 1.88–1.95 (1 H, m), 1.97–2.07 (1 H, m), 2.56–2.62 (1 H, m), 2.70–2.78 (1 H, m), 2.82–2.88 (1 H, m), 3.66 (3 H, s, OMe) and 3.83–3.89 (1 H, m, 7-H); *m/z* 266 (M^+) (Found: M^+, 266.1858).

(1S*,2R*,3R*,6R*,7R*,8R*)-7-*Hydroxy*-3-*hydroxymethyl*-8,11,11-*trimethyltricyclo*[6.3.0.0^{2,6}]*undecane* **25**.—To a stirred solution of the hydroxy ester **24a** (2.0 mg, 0.091 mmol) in dry THF (0.4 cm^3) was added at 0 °C a solution of DIBAL in hexane (1 mol dm^{-3}; 0.06 cm^3, 0.06 mmol), and the mixture was stirred for 30 min at the same temperature and for 1 h at ambient temperature. After addition of water (0.1 cm^3), followed by stirring for 30 min at ambient temperature, the resulting mixture was filtered through Celite using Et_2O. The combined filtrate and washings were dried and evaporated under reduced pressure to give a residue, which was subjected to silica gel chromatography. Elution with hexane–AcOEt (3:2 v/v) afforded the *title compound* **25** (1.8 mg, 100%) as plates, m.p. 101–102 °C; ν_{max}($CHCl_3$)/cm^{-1} 3360 (OH); δ_H(500 MHz; $CDCl_3$) 0.96 (3 H, s, Me), 1.11 (3 H, s, Me), 1.21 (3 H, s, Me), 1.28–1.64 (4 H, m), 1.65–1.78 (2 H, m), 1.91–2.02 (2 H, m), 2.61 (1 H, quint., *J* 7.8, 6-H), 3.44 (1 H, dd, *J* 6.0 and 11.5, C*H*HOH), 3.62 (1 H, dd, *J* 5.5 and 11.5, CH*H*OH) and 3.86 (1 H, d, *J* 7.0, 7-H); *m/z* 238 (M^+) (Found: M^+, 238.1938. $C_{15}H_{26}O_2$ requires *M*, 238.1931).

(1S*,2R*,3R*,6R*,7R*,8R*)-7-tert-*Butyldimethylsiloxy*-3-*methoxycarbonyl*-8,11,11-*trimethyltricyclo*[6.3.0.0^{2,6}]*undecane* **26a**.—To a stirred solution of the hydroxy ester **24a** (51.8 mg, 0.195 mmol), DMAP (12.0 mg, 0.098 mmol) and 2,6-dimethylpyridine (0.18 cm^3, 1.52 mmol) in CH_2Cl_2 (1.5 cm^3) was added at 0 °C TBDMSOTf (0.23 cm^3, 1.02 mmol) and the mixture was stirred for 4 h at ambient temperature. After dilution with CH_2Cl_2, the mixture was washed with saturated aqueous NH_4Cl and brine, and dried. Evaporation of the solvent under reduced pressure gave a residue, which was chromatographed on silica gel. Elution with hexane–AcOEt (17:3 v/v) afforded the *title compound* **26a** (72.4 mg, 98%) as an oil; ν_{max}(neat)/cm^{-1} 1730 (C=O); δ_H(500 MHz; $CDCl_3$) 0.01 (6 H, s, $SiMe_2$), 0.86 (9 H, s, Bu^t), 0.92 (3 H, s, Me), 0.97 (3 H, s, Me), 1.12 (3 H, s, Me), 1.34–1.55 (5 H, m), 1.63–1.70 (1 H, m), 1.75–1.85 (2 H, m), 2.00–2.07 (1 H, m), 2.35 (1 H, dt, *J* 5.0 and 8.5), 2.56–2.65 (2 H, m), 3.65 (3 H, s, OMe) and 3.85 (1 H, d, *J* 8.0, 7-H); *m/z* 323 (M^+ – Bu^t) (Found: M^+ – Bu^t, 323.2031. $C_{18}H_{31}O_3Si$ requires *m/z*, 323.2041).

(1S*,2S*,3R*,6R*,7R*,8R*)-7-tert-*Butyldimethylsiloxy*-3-*hydroxymethyl*-8,11,11-*trimethyltricyclo*[6.3.0.0^{2,6}]*undecane* **27a**.—To a stirred solution of the siloxy ester **26a** (72 mg, 0.189 mmol) in dry THF (3 cm^3) was added at 0 °C a solution of DIBAL in hexane (0.95 mol dm^{-3}; 2.0 cm^3, 1.9 mmol), and the mixture was stirred for 30 min at 0 °C and for 1 h at ambient temperature. After addition of water (2.0 cm^3), the mixture was stirred for 30 min and filtered through Celite using Et_2O. The combined filtrate and washings were dried and evaporated under reduced pressure to give a residue, which was chromatographed on silica gel with hexane–AcOEt (9:1 v/v) as eluent to afford the *title compound* **27a** (63.4 mg, 95%) as an oil; ν_{max}(neat)/cm^{-1} 3340 (OH) and 1092 (OSi); δ_H(500 MHz; $CDCl_3$) 0.020 and 0.024 (each 3 H, each s, $SiMe_2$), 0.89 (9 H, s, Bu^t), 0.94 (3 H, s, Me), 0.97 (3 H, s, Me), 1.11 (3 H, s, Me), 1.24–1.46 (5 H, m), 1.47–1.60 (3 H, m), 1.76–1.97 (4 H, m), 2.48 (1 H, quint., *J* 8.2, 6-H), 3.42 (1 H, dd, *J* 7.4 and 10.8, C*H*HOH), 3.57 (1 H, dd, *J* 6.0 and 10.8, CH*H*OH) and 3.86 (1 H, d, *J* 7.6, 7-H); *m/z* 352 (M^+) and 295 (M^+ – Bu^t) (Found: M^+ – Bu^t, 295.2088. $C_{17}H_{31}O_2Si$ requires *m/z*, 295.2093).

(1S*,2S*,3R*,6R*,7R*,8R*)-7-tert-*Butyldimethylsiloxy*-3-(2-*nitrophenylseleno*)*methyl*-8,11,11-*trimethyltricyclo*[6.3.0.0^{2,6}]-*undecane* **29a**.—To a solution of the siloxy alcohol **27a** (45.1 mg, 0.128 mmol) in dry CH_2Cl_2 (1.0 cm^3) was added Et_3N (0.096 cm^3, 0.641 mmol). After the mixture had been stirred for 5 min, methanesulfonyl chloride (0.044 cm^3, 0.384 mmol) was added to it at 0 °C. The mixture was then stirred for 30 min at 0 °C, diluted with benzene, washed with 5% aqueous $KHSO_4$ and water, dried and evaporated under reduced pressure. Chromatography of the residue on silica gel with hexane–AcOEt (17:3 v/v) as eluent gave the mesylate **28a** (50.5 mg, 100%) as an oil; ν_{max}(neat)/cm^{-1} 1354 and 1174 (SO_2) and 1091 (OSi); δ_H(90 MHz; $CDCl_3$) 0.03 (6 H, s, $SiMe_2$), 0.90 (9 H, s, Bu^t), 0.94 (3 H, s, Me), 0.99 (3 H, s, Me), 1.12 (3 H, s, Me), 1.25–2.60 (12 H, m), 3.00 (3 H, s, SO_2Me) and 3.85 (1 H, d, *J* 7.4, 7-H); *m/z* 415 (M^+ – Me) (Found: M^+ – Me, 415.2322. $C_{21}H_{39}O_4SSi$ requires *m/z*, 415.2336).

To a stirred solution of the mesylate **28a** (55.8 mg, 0.128 mmol) in dry THF (1.0 cm^3) was added at ambient temperature during 3 days the freshly prepared reagent; this was in the form of six batches separately prepared by the reaction of 2-nitrophenyl selenocyanate (37 mg, 0.187 mmol) with sodium borohydride (7.5 mg, 0.195 mmol) in anhydrous EtOH (0.5 cm^3) at 0 °C. After the reaction, the mixture was diluted with saturated aqueous NH_4Cl and thoroughly extracted with CH_2Cl_2. The extract was washed with brine, dried and evaporated under reduced pressure to give a residue, which was subjected to chromatography on silica gel. Elution with hexane–AcOEt (9:1 v/v) afforded the *title compound* **29a** (66.8 mg, 98%) as a pale yellowish oil; ν_{max}(neat)/cm^{-1} 1525 and 1350 (NO_2), 1093 (OSi) and 870 (C–N); δ_H(500 MHz; $CDCl_3$) 0.024 and 0.026 (each 3 H, each s, $SiMe_2$), 0.88 (9 H, s, Bu^t), 0.95 (3 H, s, Me), 0.99 (3 H, s, Me), 1.09 (3 H, s, Me), 1.24–1.47 (4 H, m), 1.48–1.65 (3 H, m), 1.87 (1 H, dt, *J* 7.8 and 22.1), 1.92–2.13 (3 H, m), 2.56–2.65 (1 H, m, 6-H), 2.77 (1 H, dd, *J* 8.4 and 10.8, C*H*HSe), 3.01 (1 H, dd, *J* 6.0 and 10.8, CH*H*Se), 3.84 (1 H, d, *J* 7.2, 7-H), 7.30 (1 H, ddd, *J* 1.8, 6.2 and 8.2, ArH), 7.46–7.55 (2 H, m, 2 × ArH) and 8.28 (1 H, dd, *J* 1.8 and 8.2, ArH); *m/z* 480 (M^+ – Bu^t) (Found: M^+ – Bu^t, 480.1460. $C_{23}H_{34}NO_3SeSi$ requires *m/z*, 480.1471).

(1S*,2R*,6R*,7R*,8R*)-7-tert-*Butyldimethylsiloxy*-3-*methylene*-8,11,11-*trimethyltricyclo*[6.3.0.0^{2,6}]*undecane* **30**.—

Method A. To a stirred solution of the seleno compound **29a** (4.0 mg, 0.0077 mmol) in dry THF (0.5 cm^3) was added at 0 °C 30% H_2O_2 (0.01 cm^3, 0.077 mmol), and the mixture was stirred for 2.5 h at ambient temperature. After addition of saturated aqueous $NaHCO_3$, the resulting mixture was thoroughly extracted with mixtures of benzene and hexane (1:1 v/v). The organic layer was washed with saturated aqueous $NaHCO_3$ and brine, dried and evaporated under reduced pressure to afford a residue which was chromatographed on silica gel with hexane–AcOEt (19:1 v/v) as eluent to provide the *title compound* **30** (1.8 mg, 70%) as an oil; ν_{max}(neat)/cm^{-1} 1640 (C=C); δ_H(500 MHz; $CDCl_3$) 0.03 (6 H, s, $SiMe_2$), 0.90 (9 H, s, Bu^t), 1.00 (3 H, s, Me), 1.01 (3 H, s, Me), 1.10 (3 H, s, Me), 1.37–1.45 (3 H, m), 1.48–1.63 (3 H, m), 1.83 (1 H, ddd, *J* 8.7, 13.2 and 16.6), 2.23 (1 H, dtt, *J* 2.0, 9.0 and 16.2), 2.41–2.49 (1 H, m), 2.54–2.62 (2 H, m), 3.90 (1 H, d, *J* 6.7, 7-H) and 4.73 and 4.78 (each 1 H, each br s, $=CH_2$); *m/z* 319 (M^+ – Me) (Found: M^+ – Me, 319.2463. $C_{20}H_{35}OSi$ requires *m/z*, 319.2457).

Method B. According to the above procedure, the isomer **29b** (3.9 mg, 0.0075 mmol) was converted into the olefin **30** (1.6 mg, 64%) as an oil, which was identical in all respects with the above sample, prepared by Method A.

(1S*,2S*,3S*,6R*,7R*,8R*)-7-tert-*Butyldimethylsiloxy*-3-*methoxycarbonyl*-8,11,11-*trimethyltricyclo*[6.3.0.$0^{2,6}$]*undecane* **26b**.—According to the same procedure for the production of **26a**, the hydroxy ester **24b** (5.8 mg, 0.02 mmol) was converted, using TBDMSOTf (0.02 cm^3, 0.08 mmol), DMAP (1.0 mg, 0.008 mmol) and 2,6-dimethylpyridine (0.02 cm^3, 0.12 mmol) in CH_2Cl_2 (1.0 cm^3), into the *title compound* **26b** (7.7 mg, 93%) as an oil; ν_{max}(neat)/cm^{-1} 1740 (C=O); δ_H(500 MHz; $CDCl_3$) 0.01 and 0.02 (each 3 H, each s, $SiMe_2$), 0.86 (6 H, s, 2 × Me), 0.89 (9 H, s, Bu^t), 1.07 (3 H, s, Me), 1.20–1.61 (5 H, m), 1.62–2.09 (4 H, m), 2.35–2.94 (3 H, m), 3.65 (3 H, s, OMe) and 3.81 (1 H, d, *J* 6.8, 7-H); *m/z* 380 (M^+) (Found: M^+, 380.2705. $C_{22}H_{40}O_3Si$ requires *M*, 380.2746).

(1S*,2S*,3S*,6R*,7R*,8R*)-7-tert-*Butyldimethylsiloxy*-3-*hydroxymethyl*-8,11,11-*trimethyltricyclo*[6.3.0.$0^{2,6}$]*undecane* **27b**.—According to the same procedure for the production of **27a**, the ester **26b** (7.7 mg, 0.019 mmol) was reduced with DIBAL–hexane (1.0 mmol dm^{-3}; 0.2 cm^3, 0.2 mmol) in dry THF (0.5 cm^3) to give the *title compound* **27b** (6.0 mg, 84%) as an oil; ν_{max}(neat)/cm^{-1} 3340 (OH); δ_H(500 MHz; $CDCl_3$) 0.01 and 0.02 (each 3 H, each s, $SiMe_2$), 0.89 (9 H, s, Bu^t), 0.94 (3 H, s, Me), 0.95 (3 H, s, Me), 1.03 (3 H, s, Me), 1.23–1.52 (7 H, m), 1.59 (1 H, br s, OH), 1.72 (1 H, dt, *J* 7.2 and 12.8), 1.94 (1 H, ddd, *J* 4.0, 9.2 and 13.9), 2.11 (1 H, ddd, *J* 6.2, 12.0 and 18.3), 2.26 (1 H, dd, *J* 6.6 and 12.8), 2.53–2.61 (1 H, m), 3.56 (1 H, dd, *J* 7.2 and 10.2, C*H*HOH), 3.70 (1 H, dd, *J* 7.1 and 10.2, CH*H*OH) and 3.80 (1 H, d, *J* 7.2, 7-H); *m/z* 295 (M^+ – Bu^t) (Found: M^+ – Bu^t, 295.2115).

(1S*,2S*,3S*,6R*,7R*,8R*)-7-tert-*Butyldimethylsiloxy*-3-*methylsulfonyloxymethyl*-8,11,11-*trimethyltricyclo*[6.3.0.$0^{2,6}$]-*undecane* **29b**.—According to the same procedure for the production of **28a**, the alcohol **27b** (4.0 mg, 0.011 mmol) was transformed, using methanesulfonyl chloride (0.003 cm^3, 0.035 mmol) and Et_3N (0.008 cm^3, 0.057 mmol) in dry CH_2Cl_2 (1.0 cm^3), into the mesylate **28b** (4.0 mg, 82%) as an oil; ν_{max}(neat)/cm^{-1} 1360 and 1181 (SO_2); δ_H(90 MHz; $CDCl_3$) 0.03 (6 H, s, $SiMe_2$), 0.89 (9 H, s, Bu^t), 0.94 (6 H, s, 2 × Me), 1.04 (3 H, s, Me), 3.00 (3 H, s, SO_2Me), 3.81 (1 H, d, *J* 7.1, 7-H) and 4.10–4.30 (2 H, m, CH_2OMs); *m/z* 415 (M^+ – Me) (Found: M^+ – Me, 415.2330).

According to the same procedure for the production of **29b**, the mesylate **28b** (4.0 mg, 0.0093 mmol) was converted, using 2-nitrophenyl selenocyanate (53 mg, 0.23 mmol) and sodium borohydride (10.5 mg, 0.28 mmol), into the *title compound* **29b** (3.9 mg, 80%) as an oil; ν_{max}(neat)/cm^{-1} 1514 and 1332 (NO_2), 1099 (OSi) and 839 (C–N); δ_H(500 MHz; $CDCl_3$) 0.01 and 0.03 (each 3 H, each s, $SiMe_2$), 0.89 (9 H, s, Bu^t), 1.02 (6 H, s, 2 × Me), 1.05 (3 H, s, Me), 1.20–1.45 (6 H, m), 1.68 (1 H, dt, *J* 6.2 and 12.1), 1.85–2.05 (2 H, m), 2.20–2.30 (1 H, m), 2.35 (1 H, dd, *J* 6.0 and 13.5), 2.57–2.63 (1 H, m), 2.85 (1 H, t, *J* 10.6, C*H*HSe), 3.01 (1 H, dd, *J* 5.4 and 10.6, CH*H*Se), 3.83 (1 H, d, *J* 7.8, 7-H), 7.30 (1 H, ddd, *J* 1.4, 7.2 and 8.4, ArH), 7.46–7.55 (2 H, m, 2 × ArH) and 8.26 (1 H, dd, *J* 1.4 and 8.1, ArH); *m/z* 522 (M^+ – Me) and 480 (M^+ – Bu^t) (Found: M^+ – Bu^t, 480.1491).

(1S*,2R*,6R*,7R*,8R*)-7-*Hydroxy*-3-*methylene*-8,11,11-*trimethyltricyclo*[6.3.0.$0^{2,6}$]*undecane* **31**.—To a stirred solution of the siloxymethylene derivative **30** (10.0 mg, 0.0299 mmol) in THF (0.5 cm^3) was added at 0 °C a solution of tetrabutylammonium fluoride in THF (1 mol dm^{-3}; 0.12 cm^3, 0.12 mmol) containing water (5 w/v%), and the mixture was heated for 4 h at 60 °. After evaporation of the solvent, the residue was chromatographed on silica gel eluting with hexane–AcOEt (9:1 v/v) to afford the *title compound* **31** (5.9 mg, 90%) as an oil; ν_{max}(neat)/cm^{-1} 3430 (OH) and 1651 (C=C); δ_H(500 MHz; $CDCl_3$) 1.03 (3 H, s, Me), 1.06 (3 H, s, Me), 1.20 (3 H, s, Me), 1.25–1.30 (1 H, m), 1.41–1.52 (4 H, m), 1.66–1.69 (1 H, m), 1.71–1.79 (1 H, m), 1.80–1.87 (1 H, m), 2.33–2.41 (1 H, m), 2.46–2.54 (1 H, m), 2.62–2.70 (2 H, m), 3.78 (1 H, br t, *J* 6.4, 7-H) and 4.78 and 4.84 (each 1 H, each s, $=CH_2$); *m/z* 220 (M^+) (Found: M^+, 220.1839. $C_{15}H_{24}O$ requires *M*, 220.1854).

(1S*,2R*,6R*,8R*)-3-*Methylene*-8,11,11-*trimethyltricyclo*-[6.3.0.$0^{2,6}$]*undecan*-7-*one* **32**.—To a stirred solution of TAPI[10] (33.5 mg, 0.079 mmol) in dry CH_2Cl_2 (1.0 cm^3) was added a solution of the alcohol **31** (5.8 mg, 0.0264 mmol) in dry CH_2Cl_2 (1.0 cm^3), and the mixture was stirred for 30 min at ambient temperature. After addition of Et_2O and saturated aqueous $NaHCO_3$ containing $Na_2S_2O_3$ (5 mg) with ice cooling, the mixture was stirred for 10 min at ambient temperature. The resulting mixture was thoroughly extracted with Et_2O and the extract was washed with saturated aqueous $NaHCO_3$ and water, dried and evaporated under reduced pressure. Chromatography of the residue on silica gel with hexane–AcOEt (19:1 v/v) as eluent gave the ketone **32** (5.2 mg, 91%) as an oil, whose IR, ^1H NMR (100 MHz; $CDCl_3$), ^{13}C NMR (50 MHz; $CDCl_3$) and MS spectra agreed well with those reported for the authentic compound.[30]

(1S*,2R*,7R*,8S*,9R*)-3-tert-*Butyldimethylsiloxy*-8-*hydroxy*-9,12,12-*trimethyltricyclo*[7.3.0.$0^{2,7}$]*dodec*-3-*ene* **20b**.—To a mixture of liquid NH_3 (4.0 cm^3) and anhydrous MeOH (0.5 cm^3) were added at −33 °C a solution of the ketone **18a** (2.0 mg, 0.0057 mmol) in dry THF (2.0 cm^3), followed by metallic Li (90.0 mg, 13.0 mmol), and the resulting mixture was stirred for 1 h at the same temperature. After addition of saturated aqueous NH_4Cl, followed by evaporation of NH_3, the residue was acidified with 5% aqueous $KHSO_4$. The mixture was extracted with CH_2Cl_2 and the extract was washed with brine, dried and evaporated under reduced pressure to give a residue, which was subjected to chromatography on silica gel. Elution with hexane–AcOEt (19:1 v/v) afforded the *title compound* **20b** (1.8 mg, 90%) as an oil; ν_{max}(neat)/cm^{-1} 3370 (OH), 1660 (C=C) and 1061 (OSi); δ_H(500 MHz; $CDCl_3$) 0.10 (3 H, s, SiMe), 0.12 (3 H, s, SiMe), 0.91 (9 H, s, Bu^t), 0.97 (3 H, s, Me), 1.06 (3 H, s, Me), 1.18 (3 H, s, Me), 1.20–1.27 (2 H, m), 1.34–1.40 (1 H, m), 1.47–1.55 (3 H, m), 1.68–1.74 (1 H, m), 1.83–1.90 (2 H, m), 1.94–1.99 (1 H, m), 2.30–2.34 (1 H, m), 3.63 (1 H, s, *J* 11.0, 8-H) and 4.62–4.64 (1 H, m, 4-H); *m/z* 350 (M^+) (Found: M^+, 350.2648. $C_{21}H_{38}O_2Si$ requires *M*, 350.2639).

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