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Enantiospecific synthesis of ABC-ring system of A-nor and abeo 4(3→2) tetra and pentacyclic triterpenes

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ABSTRACT

Enantiospecific synthesis of ABC-ring systems of A-nor and abeo 4(3→2) tetra and pentacyclic triterpenes has been accomplished starting from the readily available monoterpene (*R*)-carvone. (*R*)-Carvone was used as the B-ring of the target molecules. A lithium-liquid ammonia mediated cyclisation of δ,ε-unsaturated ester was employed for the cyclopentannulation at the C-5 and C-6 carbons of carvone and an RCM reaction was employed for the cyclohexannulation to generate the ABC-ring system of A-nor tetra and pentacyclic triterpenes. The strategy has been extended for the synthesis of the ABC-ring system of abeo 4(3→2) tetra and pentacyclic triterpenes.

1. Introduction

Triterpenes comprising six isoprene units contain a number of arrangements ranging from acyclic to heptacyclic systems. However, majority of triterpenes isolated so far from a variety of natural sources contain either tetra or pentacyclic carbon frameworks, e.g. dammarane, lanostane, betulin, oleane, ursane, lupane, hopane.[1] Among these tetra and pentacyclic triterpene groups, except for lanostanes all share a common ABC-ring system. In addition to these groups, a number of A-ring modified siblings were also isolated from natural sources. For example, a number of A-nor tetra and pentacyclic triterpenoids were reported during the last seven decades.[2] Similarly, a number of abeo 4(3→2) and abeo 3(2→1) tetra and pentacyclic triterpenes have also been isolated from a number of natural sources.[2] Some representative examples are depicted in Chart 1.

A number of triterpenes are known to exhibit important biological properties and have been used in folk medicines.[3] In addition, there have been a number of studies reported in the literature on the multifarious pharmacological activities of A-ring modified triterpene derivatives obtained by ring contraction and transformation of A-ring of naturally available pentacyclic triterpenes.[4]

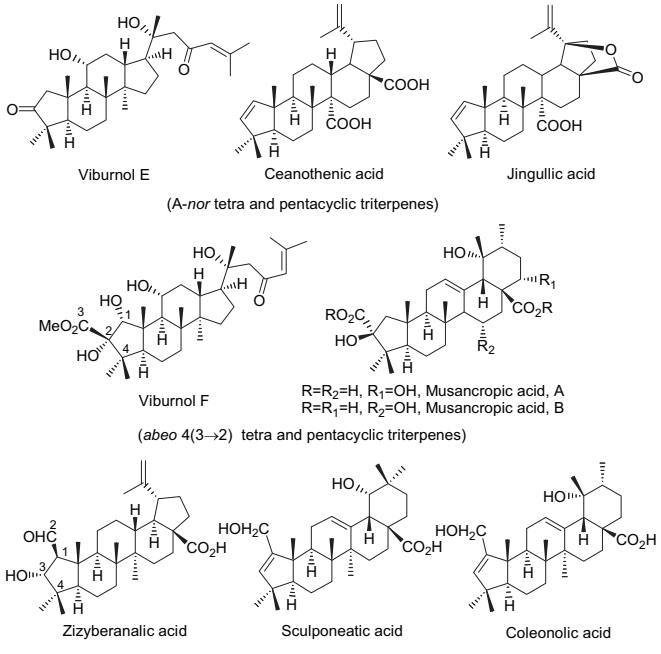

Chart 1.

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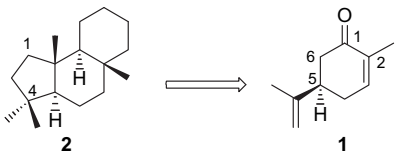
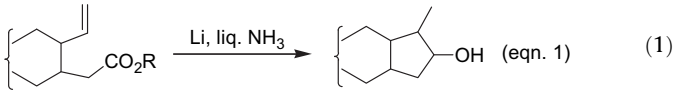
Some of the A-ring modified derivatives were proved to exhibit significant inhibitory activity against HIV virus, produce nitric oxide (NO) induced by interferin-γ (IFN-γ) in mouse macrophages, cellular proliferation of human leukaemia and breast cancer cell lines, etc. Presence of electron withdrawing substituents on the A-ring proven to be more biological active against monocytic differentiation of human myeloid leukaemia cells and adipogenic differentiation of mouse. Recently, the research group of Subba Rao reported[5] the A-ring modified oleananes, 2-cyano-3,12-dioxooleanane-1,19(11)-dien-28-oic acid (CDDO) analogues, which were found to exhibit cytotoxic activities against human leukaemia and breast cancer cell lines.

In all the A-nor and abeo-tetra and pentacyclic triterpenes known so far, ABC-ring system is common, including the location of the carbon substituents and stereochemistry at the ring junction carbons, cf. Chart 1. In continuation of our interest[6] in the synthesis of a variety of bi- and tricyclic carbon frameworks, enroute to natural products, starting from the readily available monoterpene carvone **1**, herein we report an enantiospecific approach for the construction of ABC-ring system of A-nor and abeo-tetra and pentacyclic triterpenes.

2. Results and discussion

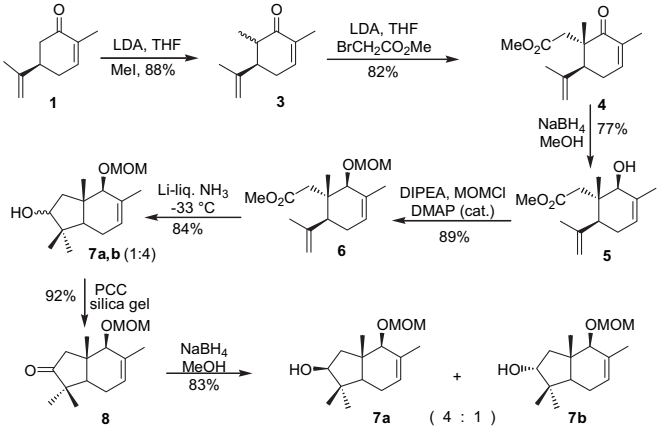
Initially, synthesis of the ABC-ring system **2** of A-nor tetra and pentacyclic triterpenes has been investigated. It was readily visualised that (*R*)-carvone **1** can serve as the B-ring of **2**, as the absolute configuration at the C-5 position of the target correlates to the stereo centre of carvone **1**, and the isopropenyl group can serve as the C-4 carbon of the target along with the gem dimethyl groups. Stereocontrolled cyclopentannulation at the C-5 and C-6 carbons, and cyclohexannulation at the C-1 and C-2 carbons of carvone **1** would lead to the ABC-ring system **2** of A-nor tetra and pentacyclic triterpenes.





(1)

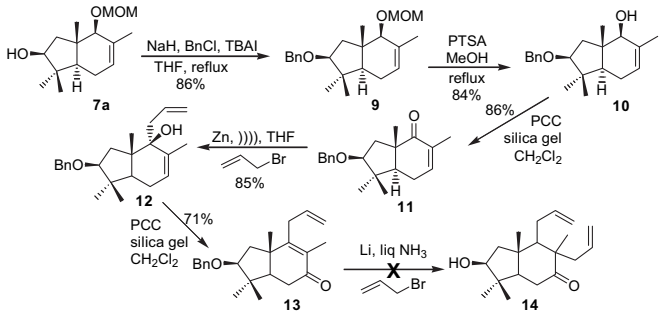
For the cyclopentannulation at the C-5 and C-6 carbons of carvone **1**, lithium-liquid ammonia mediated cyclisation of δ,ε-unsaturated esters (Eq. 1), a methodology[7] developed earlier in our laboratory, was investigated involving the isopropenyl group of carvone. Since the AB-ring system of **2** required *trans* ring junction, first methyl group followed by an acetate group were introduced at the C-6 position of the carvone **1** exploiting the well established preference of kinetic alkylation on carvone derivatives.[8] Thus, generation of the kinetic dienolate of carvone **1** employing LDA in dry THF and alkylation with methyl iodide generated a 2:3 diastereomeric mixture of 6-methylcarvone[8] **3**, Scheme 1. Repeating the alkylation one more time on 6-methylcarvone **3** using LDA and methyl bromoacetate furnished the *trans*-keto ester **4** in 72% yield (for 2 steps). The stereochemistry of the acetate side chain in the keto ester **4** was assigned in analogy to the well established alkylation of (*R*)-carvone, i.e., approach of the electrophile from the opposite side of the isopropenyl group.[8] To overcome the practical problems at later stages, the ketone group in the keto ester **4** was masked. Chemo- and stereoselective reduction of the keto ester **4** with sodium borohydride in methanol at −20 °C furnished exclusively the hydroxy ester **5** in 77% yield. The stereochemistry of the hydroxy group in the ester **5** was assigned as *trans* to the acetate side chain, in analogy with the reduction of 5-alkylcyclohexenones.[9] The hydroxy group in the hydroxy ester **5** was protected as its methoxymethyl (MOM) ether by treatment with ethyldiisopropylamine (DIPEA), methoxymethyl chloride and a catalytic amount of DMAP in anhydrous methylene chloride at RT for six hours to furnish the MOM ether **6** in 89% yield, whose structure was established from its spectral data.



Scheme 1.

Next, construction of the five membered ring by employing lithium in liquid ammonia mediated cyclisation of the δ,ε-unsaturated ester in the ester **6** was explored. Thus, reaction of the ester **6** in THF with lithium in freshly distilled liquid ammonia furnished a 1:4 epimeric mixture of the bicyclic alcohols **7a** and **7b** in 84% yield. The stereochemistry of the secondary hydroxy group was assigned on the basis of thermodynamic considerations. Mechanistically the alcohol **7** was formed by the reduction of the initially formed cyclic ketone **8** under the reaction conditions (lithium in liquid ammonia), which is expected to generate thermodynamic product. For further confirmation, the 1:4 epimeric mixture of the alcohols **7a** and **7b** was oxidised to the ketone **8** and carried out the reduction to generate the epimeric alcohols under kinetic conditions. Thus, oxidation of the epimeric mixture of the alcohol **7** with PCC and silica gel in anhydrous methylene chloride at RT for two hours furnished the ketone **8** in 92% yield. Reduction of the ketone **8** with sodium borohydride in methanol at room temperature for 30 min furnished, as expected, a 4:1 mixture of the epimeric alcohols **7a** and **7b**, in 83% yield, which was separated by column chromatography on silver nitrate impregnated silica gel. The minor alcohol **7b** obtained in the reduction was identified (IR, ^{1}H and ^{13}C NMR) as the major isomer that was obtained during the lithium-liquid ammonia mediated cyclisation of the ester **6**. Based on the approach of the hydride from the less hindered face in the hydrindanone (i.e. opposite to the tertiary methyl group at the ring junction), the major alcohol **7a** was assigned as the 8*S* isomer. For proceeding further, the hydroxy group in **7a** was protected by treating with sodium hydride, benzyl chloride and a catalytic amount of TBAI in refluxing THF to furnish the benzyl ether **9** in 86% yield. For the construction of the C-ring, the C-2 ketone was regenerated. Hydrolysis of the MOM ether **9** using a catalytic

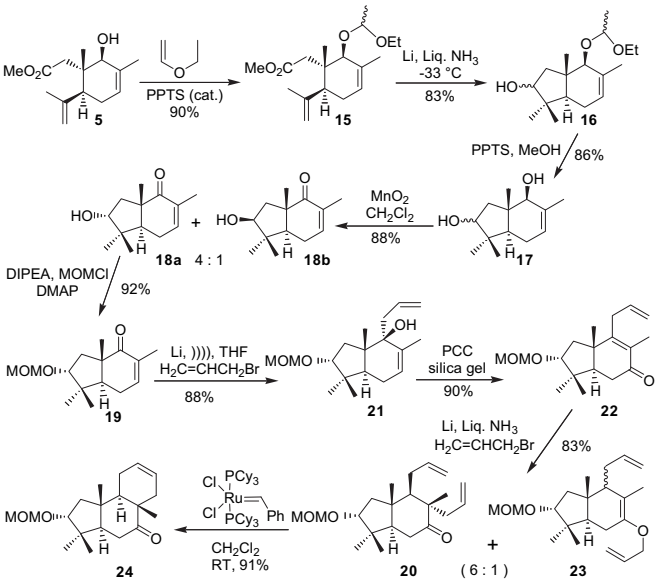
amount of PTSA in refluxing methanol furnished the alcohol **10** in 84% yield, which on oxidation with PCC and silica gel in anhydrous methylene chloride at RT furnished the enone **11** in 86% yield. For the construction of the C-ring, introduction of two allyl units at C-2 and C-3 carbons of the hydrindane **11**, followed by an RCM reaction was conceived, Scheme 2.



Scheme 2.

For the introduction of an allyl moiety at the C-2 carbon, an alkylative 1,3-enone transposition methodology[10] was chosen. Sonochemically accelerated Barbier reaction of the enone **11** with zinc and allyl bromide in THF generated the tertiary alcohol **12** in 85% yield, which on oxidation with PCC and silica gel in anhydrous methylene chloride furnished the transposed enone **13**. A reductive allylation reaction was explored for the introduction of the second allyl group at the α-position of the enone **13**, which will also cleave the benzyl ether. However, reaction of the enone **13** with lithium in liquid ammonia, both in the presence as well as in the absence of a proton source, followed by quenching with allyl bromide did not furnish the *bis*allyl product **14**.

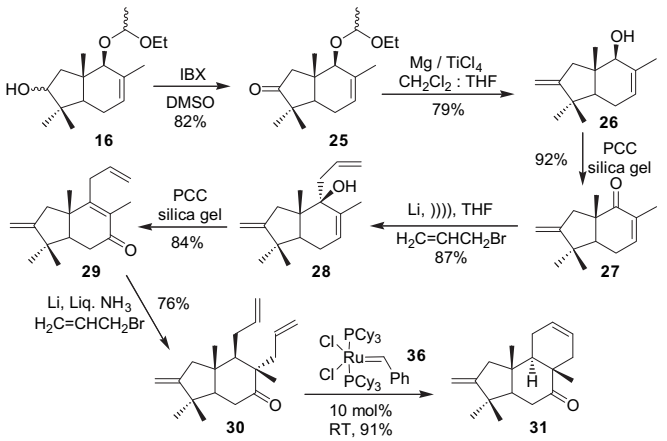
Since the reductive allylation reaction was unsuccessful with the enone **13**, partly may be due to the competing side reactions due to the benzyl ether, change of the protecting group was considered. A methoxymethyl group was chosen as it will be stable to standard reductive allylation conditions. In order to avoid the regiochemical complications in deprotecting MOM ether of the allyl alcohol (at the C-2 position) in the presence of MOM ether at the C-8 position, a more labile α-ethoxyethyl group was opted for protecting the allyl alcohol. With this reasoning, sequence was modified starting from the hydroxy ester **5**, Scheme 3. Treatment of the hydroxy ester **5** with ethyl vinyl ether and a catalytic amount of pyridinium *p*-toluenesulfonate (PPTS) in methylene chloride at room temperature furnished a 2:3 epimeric mixture (at the ethoxy group) of the acetal **15** in 90% yield. Reaction of the ester **15** in THF with lithium in freshly distilled liquid ammonia furnished a mixture of the bicyclic alcohol **16** in 83% yield. Hydrolysis of the acetal **16** using a catalytic amount of PPTS in methanol furnished a 4:1 epimeric mixture of the diol **17** in 86% yield. Selective allylic oxidation of the diol **17** with manganese dioxide in methylene chloride furnished a 4:1 epimeric mixture of the hydroxy ketones **18a** and **18b** in 88% yield, which was separated by column chromatography on silica gel. The sequence was then continued with the major hydroxy ketone **18a**. Treatment of the alcohol **18a** with DIPEA, methoxymethyl chloride and a catalytic amount of DMAP at room temperature gave the MOM ether **19** in 92% yield. Attention was then focused on the construction of the C-ring via the *bis*allyl ketone **20**. Sonochemically accelerated Barbier reaction of the enone **19** with lithium and allyl bromide in THF generated the tertiary allyl alcohol **21** in 88% yield, which on oxidation with a mixture of PCC and silica gel in methylene chloride furnished the enone **22** in 90% yield. Reaction of the enone **22** with lithium in liquid ammonia followed by alkylation of the resultant enolate with allyl bromide furnished a 1:6 mixture of *O*-allyl and *C*-allyl ethers **23** and **20**, respectively, in 83% yield, which was separated by column chromatography on silica gel. The stereochemistry at the two newly created chiral centers in *bis*allyl ketone **20** was assigned on the basis of the thermodynamic considerations, which was supported by literature precedent.[6k,11] Finally, RCM reaction of the *bis*allyl ketone **20** with 10 mol % of Grubbs' first generation catalyst in methylene chloride at room temperature furnished the tricyclic ketone **24** in 91% yield, whose structure was deduced from its spectral data.



Scheme 3.

The tricyclic system **24** represents the ABC-ring system of A-nor tetra and pentacyclic triterpenes. The oxygen functionality present in the A-ring of **24**, as it is a masked ketone, could be used for the introduction of the requisite carbon in the A-ring to modify **24** into ABC-ring system of both abeo 4(3→2) or abeo 3(2→1) tetra and pentacyclic triterpenes. However, it was contemplated to introduce the requisite carbon in the early part of the sequence to generate the ABC-ring system of abeo 4(3→2) tetra and pentacyclic triterpenes, starting from the hydroxy acetal **16**, Scheme 4. Oxidation of the bicyclic alcohol **16** with IBX[12] in dimethyl sulfoxide for 1 h at room temperature furnished a 1:1 diastereomeric mixture of the ketone **25** in 82% yield. Introduction of the C-3 carbon of abeo 4(3→2) triterpenes via a Wittig olefination was then investigated. Since, the conventional Wittig reaction with methylenetriphenylphosphorane was unsuccessful, methylenation was carried out by employing the conditions developed by Yan and co-workers,[13] which also resulted in the hydrolysis of the ethoxyethyl moiety. Treatment of the ketone **25** with methylene chloride, magnesium and titanium chloride in THF furnished the hydroxyolefin **26** in 79% yield, whose structure was assigned from its spectral data. Oxidation of the allyl alcohol **26** with PCC and silica gel in anhydrous methylene chloride furnished the enone **27** in 92% yield. A sonochemically accelerated Barbier reaction of the enone **27** with lithium and allyl bromide generated the allylic tertiary alcohol **28** in 87% yield, which on oxidation with a mixture of PCC and silica gel in methylene chloride furnished the transposed enone **29**. Reaction of the enone **29** with lithium in liquid ammonia followed by alkylation with allyl bromide generated the *bis*allyl ketone **30** in 76% yield, in a highly regio- and stereoselective manner. Finally, RCM reaction of the *bis*allyl ketone **30** with Grubbs' first generation catalyst in 0.005 M anhydrous methylene chloride solution at room temperature furnished the tricyclic ketone **31** in 91% yield, whose structure was established from its spectral data. The tricyclic ketone **31** represents the ABC-

ring system of abeo 4(3→2) tetra and pentacyclic triterpenes, containing the requisite *trans*, *anti*, *trans*-ring fusion and functionalities in all the rings for further elaboration.



Scheme 4.

3. Conclusions and summary

Enantiospecific synthesis of ABC-ring systems of A-nor tetra and pentacyclic triterpenes and abeo 4(3→2) tetra and pentacyclic triterpenes has been accomplished starting from the readily available monoterpene (*R*)-carvone **1**. It was readily visualised (*R*)-carvone **1** as the B-ring of the target molecules, as the absolute configuration at the C-5 position of the target correlates to the stereo centre of (*R*)-carvone **1**, and the isopropenyl group can serve as the C-4 carbon of the target molecules along with the gem dimethyl groups. Cyclopentannulation at the C-5 and C-6 carbons of carvone **1** was accomplished by employing a lithium-liquid ammonia mediated cyclisation of δ,ε-unsaturated ester, which was obtained by sequential kinetic alkylations of carvone **1**. Reductive allylation of the bicyclic enone **22**, followed by RCM reaction of the *bis*allyl hydrindane **20** generated the ABC-ring system **24**, which also contained the BC-*trans* ring junction as in A-nor tetra and pentacyclic triterpenes. The strategy has been further extended for the synthesis of the ABC-ring system **31** of abeo 4(3→2) tetra and pentacyclic triterpenes.

4. Experimental section

4.1. General

IR spectra were recorded on Jasco FTIR 410 and Perkin Elmer FTIR spectrophotometer. ^{1}H (300 and 400 MHz) and ^{13}C (75 and 100 MHz) NMR spectra were recorded on JNM λ-300 and Brucker AMX 400 spectrometers using a 1:1 mixture of $CDCl_3$ and CCl_4 as solvent. The chemical shifts (δ ppm) and coupling constants (Hz) are reported in the standard fashion with reference to either internal tetramethylsilane (for ^{1}H) or the central line (77.0 ppm) of $CDCl_3$ (for ^{13}C). In the ^{13}C NMR spectra, the nature of the carbons (C, CH, CH_2, or CH_3) was determined by recording the DEPT-135 spectra, and is given in parentheses. High resolution mass spectra were recorded on a Micromass Q-TOF micro mass spectrometer using electron spray ionisation mode. Optical rotations were measured using a Jasco DIP-370 digital polarimeter and Jasco P-1020 polarimeter and $[\alpha]_D$ values are given in units of 10^{-1} deg cm^2 g^{-1}. Analytical thin-layer chromatography (TLC) were performed on glass plates (7.5×2.5 and 7.5×5.0 cm) coated with Acme's silica gel G containing 13% calcium sulfate as binder and various combinations of ethyl acetate and hexane were used as eluent. Visualisation of spots was accomplished by exposure to iodine vapour. Acme's silica gel (100–200 mesh) was used for column chromatography (approximately 15–20 g per 1 g of the crude product). All small-scale dry reactions were carried out using standard syringe-septum technique. Low temperature reactions were carried out using a bath made of sodium chloride and ice, or alcohol and liquid nitrogen.

*4.1.1. Methyl 2-[(1S,6S)-6-isopropenyl-1,3-dimethyl-2-oxocyclohex-3-enyl]acetate (**4**).* To a cold (0 °C), magnetically stirred solution of diisopropylamine (1.2 mL, 8.54 mmol) in anhydrous THF (2 mL) was added a solution of ^{n}BuLi (2.4 M in hexane, 3 mL, 7.20 mmol) and stirred for 10 min. To LDA thus formed was added drop wise a solution of 6-methylcarvone[8] **3** (700 mg, 4.27 mmol) in anhydrous THF (6 mL) over a period of 5 min and stirred for 45 min at the same temperature. To the enolate thus formed was added a solution of methyl bromoacetate (980 mg, 6.40 mmol) in THF (1 mL) at the same temperature and stirred for 8 h at rt. The reaction mixture was then diluted with water (4 mL) and extracted with ether (3×5 mL). The combined organic extract was washed with brine (5 mL) and dried (Na_2SO_4). Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate–hexane (1:9) as eluent furnished the keto ester **4** (831 mg, 82%) as oil. R_f (1:9 EtOAc:hexane) 0.5; $[\alpha]_D^{26}$ +22.4 (*c* 3.2, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3077, 2973, 2925, 1740, 1670, 1641, 1436, 1406, 1377, 1356, 1198, 1170, 1078, 1019, 902, 842; ^{1}H NMR (400 MHz): δ 6.63 (1H, br s, H-4′), 4.91 (1H, s) and 4.72 (1H, s) [C=CH_2], 3.59 (3H, s, OCH_3), 3.27 (1H, dd, *J* 11.1 and 4.8 Hz), 2.86 and 2.29 (2H, 2×d, *J* 16.9 Hz, H-2), 2.54–2.42 (1H, m), 2.30–2.20 (1H, m), 1.76 (3H, s) and 1.70 (3H, s) [2×olefinic-CH_3], 1.01 [3H, s, *tert*-CH_3]; ^{13}C NMR (100 MHz): δ 201.8 (C, C=O), 171.7 (C, OC=O), 144.5 (C, *C*=CH_2), 142.5 (CH, C-4′), 133.9 (C, C-3′), 115.2 (CH_2, C=*C*H_2), 51.1 (CH_3, OCH_3), 47.0 (C, C-1′), 46.1 (CH, C-6′), 39.7 (CH_2, C-2), 28.4 (CH_2, C-5′), 23.3 (CH_3), 19.0 (CH_3), 16.5 (CH_3); HRMS: *m*/*z* Calcd for $C_{14}H_{20}O_3Na$ (M+Na): 259.1310; Found 259.1315.

*4.1.2. Methyl 2-[(1S,2S,6S)-2-hydroxy-6-isopropenyl-1,3-dimethylcyclohex-3-enyl]acetate (**5**).* To a cold (−20 °C), magnetically stirred solution of the keto ester **4** (610 mg, 2.58 mmol) in dry methanol was added $NaBH_4$ (150 mg, 3.87 mmol) in three portions over a period of 15 min and stirred for 15 min at the same temperature. Water (5 mL) was added to the reaction mixture and extracted with ether (2×5 mL). The combined ether extract was washed with brine (5 mL) and dried (Na_2SO_4). Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate–hexane (1:9) as eluent furnished the hydroxy ester **5** (475 mg, 77%) as colourless oil. R_f (1:9 EtOAc:hexane) 0.4; $[\alpha]_D^{25}$ +68.5 (*c* 1.5, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3489, 3074, 2951, 2918, 1736, 1640, 1439, 1378, 1215, 1165, 1064, 1043, 1015, 896; ^{1}H NMR (400 MHz): δ 5.42 (1H, br s, H-4′), 4.87 (1H, s) and 4.80 (1H, s) [C=CH_2], 4.22 (1H, br s, H-2′), 3.66 (3H, s, OCH_3), 2.79 (1H, br s, OH), 2.48 and 2.18 (2H, 2×d, *J* 14.5 Hz, H-2), 2.37 (1H, dd, *J* 11.5 and 4.9 Hz), 2.30–2.10 (1H, m), 2.00–1.80 (1H, m), 1.77 (3H, s) and 1.71 (3H, s) [2×olefinic-CH_3], 1.00 (3H, s, *tert*-CH_3). ^{13}C NMR (100 MHz): δ 174.3 (C, OC=O), 146.1 (C, *C*=CH_2), 135.4 (C, C-3′), 122.2 (CH, C-4′), 114.7 (CH_2, C=*C*H_2), 76.8 (CH, C-2), 51.5 (CH_3, OCH_3), 48.8 (CH, C-6′), 43.4 (CH_2, C-2), 40.9 (C, C-1′), 28.9 (CH_2, C-5′), 23.2 (CH_3), 19.6 (CH_3), 12.7 (CH_3); HRMS: *m*/*z* Calcd for $C_{14}H_{22}O_3Na$ (M+Na): 261.1467; Found 261.1465.

*4.1.3. Methyl [(1S,2S,6S)-2-(2-methoxymethoxy)-1,3-dimethyl-6-isopropenylcyclohex-3-enyl]acetate (**6**).* To an ice cold solution of the alcohol **5** (386 mg, 1.62 mmol) in dry CH_2Cl_2 (1 mL) were added DIPEA (0.6 mL, 3.24 mmol), DMAP (20 mg, 10 mol %), and MOMCl (0.2 mL, 3.24 mmol) and stirred for 30 min at the same temperature. The reaction mixture was stirred at RT for 6 h and then poured into water (4 mL) and extracted with CH_2Cl_2 (2×5 mL). Combined

CH_2Cl_2 extract was washed with brine (4 mL) and dried (Na_2SO_4). Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate–hexane (1:19) as eluent furnished the MOM ether **6** (410 mg, 89%) as colourless oil. R_f (1:19 EtOAc:hexane) 0.55; $[\alpha]_D^{27}$ +98.7 (*c* 9.1, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3077, 2950, 2919, 2848, 1738, 1637, 1437, 1366, 1216, 1190, 1162, 1093, 1032, 966, 920, 898; ^1H NMR (400 MHz): δ 5.40 (1H, br s, H-4′), 4.79 (1H, s) and 4.72 (1H, s) [C=CH_2], 4.65 (2H, s, OCH_2O), 4.56 (1H, s, H-2′), 3.58 (3H, s, $COOCH_3$), 3.36 (3H, s, OCH_2OCH_3), 2.88 (1H, dd, *J* 11.6 and 5.1 Hz), 2.53 and 2.20 (2H, 2×d, *J* 17.5 Hz, H-2), 2.30–2.10 (1H, m), 1.86 (1H, d, *J* 17.8 Hz), 1.71 (3H, s) and 1.68 (3H, s) [2×olefinic-CH_3], 0.91 (3H, s, *tert*-CH_3); ^{13}C NMR (100 MHz): δ 172.3 (C, OC=O), 146.0 (C, C=CH_2), 135.0 (C, C-3′), 122.7 (CH, C-4′), 114.5 (CH_2, C=CH_2), 99.1 (CH_2, OCH_2O), 83.0 (CH, C-2′), 56.0 (CH_3) and 50.6 (CH_3) [2×OCH_3], 45.7 (CH, C-6′), 39.6 (C, C-1′), 38.9 (CH_2, C-2), 28.8 (CH_2, C-5′), 22.5 (CH_3), 20.3 (CH_3), 15.6 (CH_3); HRMS: *m*/*z* Calcd for $C_{16}H_{26}O_4Na$ (M+Na): 305.1729; Found: 305.1726.

*4.1.4. (1S,2S,6R)-2-(Methoxymethoxy)-1,3,7,7-tetramethylbicyclo[4.3.0]non-3-en-8-one (**8**).* To a magnetically stirred, freshly distilled (over sodium and ferric chloride) ammonia (20 mL) in a two-necked round bottom flask equipped with Dewar condenser was added a solution of the ester **6** (428 mg, 1.51 mmol) in dry THF (4 mL) followed by freshly cut lithium (52 mg, 7.55 mmol). The resulting blue coloured solution was stirred at −33 °C for 45 min and then the reaction was carefully quenched with solid NH_4Cl. After evaporation of ammonia, the residue was taken in water (6 mL) and extracted with ether (2×5 mL). The combined organic extract was washed with brine (4 mL) and dried (Na_2SO_4). Evaporation of the solvent and purification of the residue on a silica gel column using ethyl acetate–hexane (1:9) as eluent furnished a 1:4 epimeric mixture of the bicyclic alcohols **7a** and **7b** (320 mg, 84%) as oil.

To a magnetically stirred solution of the alcohols **7a** and **7b** (320 mg, 1.26 mmol) in anhydrous CH_2Cl_2 (2 mL) was added a homogeneous mixture of PCC (670 mg, 3.12 mmol) and silica gel (670 mg), and stirred at RT for 2 h. The reaction mixture was filtered through a small pad of silica gel using CH_2Cl_2 (10 mL) as eluent. Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate–hexane (1:19) as eluent furnished the ketone **8** (291 mg, 92%) as colourless oil. R_f (1:9 EtOAc:hexane) 0.6; $[\alpha]_D^{27}$ 64.3 (*c* 20, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3023, 2971, 2951, 2897, 2850, 2824, 1739, 1467, 1454, 1411, 1383, 1246, 1214, 1193, 1152, 1099, 1044, 1032, 980, 919; ^1H NMR (400 MHz): δ 5.51 (1H, s, H-4), 4.64 (2H, s, OCH_2O), 3.92 (1H, s, H-2), 3.36 (3H, s, OCH_3), 2.30 (2H, s, H-9), 2.15–1.80 (3H, m), 1.69 (3H, s, olefinic-CH_3), 1.00 (6H, s) and 0.90 (3H, s) [3×*tert*-CH_3]; ^{13}C NMR (100 MHz): δ 222.1 (C, C=O), 136.0 (C, C-3), 123.4 (CH, C-4), 97.2 (CH_2, OCH_2O), 86.1 (CH, C-2), 55.8 (CH_3, OCH_3), 52.1 (CH_2, C-9), 51.5 (CH, C-6), 44.9 (C, C-7), 40.8 (C, C-1), 27.7 (CH_3), 22.9 (CH_2), 21.5 (CH_3), 20.0 (CH_3), 14.1 (CH_3); HRMS: *m*/*z* Calcd for $C_{15}H_{24}O_3Na$ (M+Na): 275.1623; Found: 275.1615.

*4.1.5. (1S,2S,6S,8S) and (1S,2S,6S,8R)-2-(Methoxymethoxy)-1,3,7,7-tetramethylbicyclo[4.3.0]non-3-en-8-ols (**7a** and **7b**).* To a magnetically stirred solution of the ketone **8** (291 mg, 1.15 mmol) in dry methanol (2 mL) was added $NaBH_4$ (65 mg, 1.73 mmol) in two portions and stirred at RT for a period of 30 min. The solvent was evaporated under reduced pressure, water (3 mL) was added to the reaction mixture and extracted with ether (2×5 mL). The combined ether layer was washed with brine (3 mL) and dried (Na_2SO_4). Evaporation of the solvent and purification of the residue over a silver nitrate (15%) impregnated silica gel column using ethyl acetate–hexane (1:9) as eluent first furnished the (1*S*,2*S*,6*S*,8*S*) isomer **7a** (212 mg, 66%) as colourless oil. R_f (1:4 EtOAc:hexane) 0.5 on silver nitrate (15%) impregnated silica gel; $[\alpha]_D^{23}$ −14.6 (*c* 3.5, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3437, 2948, 2894, 2858, 1465, 1439, 1381, 1214, 1151, 1098, 1045, 1032, 1004, 982, 918, 902; ^1H NMR (400 MHz): δ 5.42 (1H, br s, H-4), 4.65 and 4.60 (2H, 2×d, *J* 6.8 Hz, OCH_2O), 3.83 (1H, dd, *J* 7.9 and 1.9 Hz, H-8), 3.69 (1H, br s, H-2), 3.34 (3H, s, OCH_3), 1.96 (1H, dd, *J* 13.8 and 7.9 Hz) and 1.66 (1H, dd, *J* 13.8 and 2.4 Hz) [H-9], 1.95–1.50 (2H, m), 1.61 (3H, s, olefinic-CH_3), 1.45 (1H, br s, OH), 1.29 (1H, dd, *J* 12.0 and 4.8 Hz), 0.96 (3H, s), 0.92 (3H, s) and 0.89 (3H, s) [3×*tert*-CH_3]; ^{13}C NMR (100 MHz): δ 136.0 (C, C-3), 124.4 (CH, C-4), 97.0 (CH_2, OCH_2O), 87.5 (CH, C-2), 82.2 (CH, C-8), 55.8 (CH_3, OCH_3), 54.3 (CH, C-6), 47.5 (CH_2, C-9), 44.5 (C), 42.5 (C), 31.0 (CH_3), 23.2 (CH_2, C-5), 20.0 (CH_3), 19.4 (CH_3), 15.1 (CH_3); HRMS: *m*/*z* Calcd for $C_{15}H_{26}O_3Na$ (M+Na): 277.1780; Found277.1781.

Further elution of the column with ethyl acetate–hexane (1:9) as eluent furnished the (1*S*,2*S*,6*S*,8*R*) isomer **7b** (53 mg, 17%) as colourless oil. R_f (1:4 EtOAc:hexane) 0.45 on silver nitrate (15%) impregnated silica gel; $[\alpha]_D^{24}$ −38.8 (*c* 3.6, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3437, 2948, 2894, 2858, 1465, 1439, 1381, 1213, 1151, 1098, 1045, 1032, 1004, 918, 902; ^1H NMR (400 MHz): δ 5.39 (1H, br s, H-4), 4.63 and 4.58 (2H, 2×d, *J* 6.8 Hz, OCH_2O), 3.96 (1H, dd, *J* 9.9 and 6.8 Hz, H-8), 3.74 (1H, br s, H-2), 3.33 (3H, s, OCH_3), 2.13 (1H, dd, *J* 11.6 and 6.8 Hz, H-9A), 2.00–1.60 (3H, m), 1.60 (3H, s, olefinic-CH_3), 1.49 (1H, dd, *J* 11.6 and 5.6 Hz, H-9B), 1.30 (1H, t, *J* 10.7 Hz), 0.91 (3H, s), 0.81 (3H, s) and 0.79 (3H, s) [3×*tert*-CH_3]; ^{13}C NMR (100 MHz): δ 135.5 (C, C-3), 123.9 (CH, C-4), 97.2 (CH_2, OCH_2O), 87.1 (CH, C-2), 81.3 (CH, C-8), 55.9 (CH_3, OCH_3), 53.9 (CH, C-6), 47.9 (CH_2, C-9), 41.9 (C), 39.8 (C), 26.2 (CH_3), 25.4 (CH_3), 23.6 (CH_2, C-5), 20.0 (CH_3), 14.1 (CH_3); HRMS: *m*/*z* Calcd for $C_{15}H_{26}O_3Na$ (M+Na): 277.1780; Found: 277.1779.

*4.1.6. (1S,2S,6S,8S)-8-Benzyloxy-2-(methoxymethoxy)-1,3,7,7-tetramethylbicyclo[4.3.0]non-3-ene (**9**).* To a magnetically stirred suspension of NaH (36 mg, 0.9 mmol) and a catalytic amount of TBAI (4 mg) in THF (2 mL) was added a solution of the alcohol **7a** (92 mg, 0.36 mmol) in THF (1 mL) and benzyl chloride (0.1 mL, 1.08 mmol) and refluxed for 16 h. It was then quenched with water (3 mL) and extracted with ether (2×5 mL). The combined ether extract was washed with brine (3 mL) and dried (Na_2SO_4). Evaporation of the solvent and purification of the residue on a silica gel column using ethyl acetate–hexane (1:19) as eluent furnished the benzyl ether **9** (106 mg, 86%) as oil. R_f (1:19 EtOAc:hexane) 0.6; IR (neat): ν_{max}/cm^{-1} 3063, 3028, 2947, 2894, 2858, 1496, 1454, 1381, 1351, 1212, 1151, 1122, 1097, 1068, 1045, 1031, 964, 918, 735, 698; ^1H NMR (300 MHz): δ 7.50–6.75 (5H, m, Ar-H), 5.58 (1H, br s, H-4), 4.81 and 4.75 (2H, 2×d, *J* 6.6 Hz, OCH_2O), 4.66 and 4.52 (2H, 2×d, *J* 12.0 Hz, OCH_2Ph), 3.84 (1H, br s, H-2), 3.67 (1H, dd, *J* 8.1 and 2.4 Hz, H-8), 3.49 (3H, s, OCH_3), 2.25–1.50 (4H, m), 1.77 (3H, s, olefinic-CH_3), 1.42 (1H, dd, *J* 11.7 and 4.8 Hz), 1.11 (6H, s) and 1.09 (3H, s) [3×*tert*-CH_3]; ^{13}C NMR (75 MHz): δ 139.4, 135.9, 130.9, 128.4 (2C), 127.0 (2C), 124.5, 97.0 (OCH_2O), 89.3 (C-2), 87.4 (C-8), 72.0 (OCH_2Ph), 55.8 (OCH_3), 54.3, 44.7, 44.1, 42.7, 31.8, 23.2, 20.0, 14.5; HRMS: *m*/*z* Calcd for $C_{22}H_{32}O_3Na$ (M+Na): 367.2249; Found: 277.1781.

*4.1.7. (1S,2S,6R,8S)-8-Benzyloxy-1,3,7,7-tetramethylbicyclo[4.3.0]non-3-en-2-ol (**10**).* To a magnetically stirred solution of the MOM ether **9** (30 mg, 0.09 mmol) in methanol (2 mL) was added a catalytic amount of PTSA (3 mg, 20 mol %) and the reaction mixture was refluxed for 3 h. The solvent was evaporated under reduced pressure, $NaHCO_3$ solution (3 mL) was added to the reaction mixture and extracted with ether (2×5 mL). The combined ether layer was washed with brine (3 mL) and dried (Na_2SO_4). Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate–hexane (1:19) as eluent furnished the allyl alcohol **10** (23 mg, 84%) as colourless oil. R_f (1:19 EtOAc:hexane) 0.4; $[\alpha]_D^{26}$ +12.8 (*c* 2.0, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3448, 3088, 3064, 3027, 2947, 2896, 2860, 1497, 1454, 1438, 1380, 1364, 1350, 1169, 1120, 1087, 1067, 1037, 992, 880, 734, 697; ^1H NMR (400 MHz): δ 7.40–7.10 (5H, m, Ar-H), 5.43 (1H, br s, H-4), 4.53 and 4.37 (2H, 2×d, *J* 12.0 Hz, OCH_2Ph), 3.77 (1H, s, H-2), 3.53 (1H, dd, *J* 7.6 and 2.6 Hz), 2.00–1.20 (4H, m), 1.65 (3H, s, olefinic-CH_3), 1.28 (1H, dd, *J* 12.0 and 3.2 Hz),

0.98 (3H, s), 0.96 (3H, s) and 0.95 (3H, s) [3×*tert*-CH_3]; ^{13}C NMR (100 MHz): δ 139.3 (C), 136.4 (C), 128.2 (2C, CH), 127.2 (2C, CH), 127.1 (CH), 124.3 (CH), 89.1 (CH, C-8), 81.7 (CH, C-2), 71.8 (CH_2, O*C*H_2Ph), 54.1 (CH, C-6), 44.7 (C), 43.2 (C), 43.1 (CH_2, C-9), 31.5 (CH_3), 23.3 (CH_2, C-5), 20.0 (CH_3), 19.2 (CH_3), 13.7 (CH_3); HRMS: *m*/*z* Calcd for $C_{20}H_{28}O_2Na$ (M+Na): 323.1987; Found: 323.1980.

*4.1.8. (1S,6S,8S)-8-Benzyloxy-1,3,7,7-tetramethylbicyclo[4.3.0]non-3-en-2-one (**11**).* To a magnetically stirred solution of the alcohol **10** (20 mg, 0.07 mmol) in anhydrous CH_2Cl_2 (0.5 mL) was added a homogeneous mixture of PCC (45 mg, 0.21 mmol) and silica gel (45 mg), and stirred at RT for 2.5 h. The reaction mixture was filtered through a small pad of silica gel using CH_2Cl_2 (10 mL) as eluent. Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate–hexane (1:19) as eluent furnished the enone **11** (19 mg, 86%) as colourless oil. R_f (1:19 EtOAc:hexane) 0.55; $[\alpha]_D^{26}$ −28.1 (*c* 2.7, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3065, 2951, 2926, 2868, 1681, 1454, 1375, 1355, 1199, 1157, 1142, 1112, 1088, 1067, 1050, 1028, 1010, 841, 735, 697; ^{1}H NMR (400 MHz): δ 7.40–7.10 (5H, m, Ar-H), 6.57 (1H, br s, H-4), 4.55 and 4.36 (2H, 2×d, *J* 12.4 Hz, OC*H*$_2$Ph), 3.51 (1H, dd, *J* 7.8 and 2.4 Hz, H-8), 2.40–2.00 (3H, m), 1.78 (1H, dd, *J* 14.0 and 2.4 Hz), 1.71 (3H, s, olefinic-CH_3), 1.65 (1H, dd, *J* 11.5 and 4.2 Hz), 1.14 (3H, s), 1.04 (3H, s) and 0.98 (3H, s) [3×*tert*-CH_3]; ^{13}C NMR (100 MHz): δ 204.6 (C, C=O), 143.1 (CH, C-4), 139.1 (C), 134.4 (C), 128.3 (2C, CH), 127.3 (CH), 127.1 (2C, CH), 87.9 (CH, C-8), 71.9 (CH_2, O*C*H_2Ph), 54.7 (CH, C-6), 51.4 (C, C-1), 43.6 (C, C-7), 37.7 (CH_2, C-9), 31.0 (CH_3), 24.7 (CH_2, C-5), 20.3 (CH_3), 18.3 (CH_3), 16.4 (CH_3); HRMS: *m*/*z* Calcd for $C_{20}H_{26}O_2Na$ (M+Na): 321.1830; Found: 321.1817.

*4.1.9. (1S,2S,6S,8S)-2-Allyl-8-benzyloxy-1,3,7,7-tetramethylbicyclo[4.3.0]non-3-en-2-ol (**12**).* To a sonochemically irradiated suspension of zinc (52 mg, 0.8 mmol) in dry THF (2 mL) in a round bottom flask placed in an ultrasonic clean bath, was added a mixture of the enone **11** (30 mg, 0.1 mmol) and allyl bromide (0.1 mL, 1.0 mmol) in THF (1 mL) at 15–20 °C over a period of 1 min. The reaction mixture was sonochemically irradiated for 1 h. The reaction mixture was then decanted from excess lithium, quenched with saturated aqueous NH_4Cl solution (2 mL) and extracted with ether (2×5 mL). The combined ether extract was washed with brine (3 mL) and dried (Na_2SO_4). Evaporation of the solvent and purification of the residue on a silica gel column using ethyl acetate–hexane (1:19) as eluent, furnished the tertiary alcohol **12** (29 mg, 85%) as oil. R_f (1:14 EtOAc:hexane) 0.5; $[\alpha]_D^{26}$ −26.4 (*c* 2.0, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3490, 3068, 2948, 2863, 1637, 1497, 1453, 1378, 1364, 1352, 1159, 1088, 1068, 1028, 1002, 908, 811, 734, 697; ^{1}H NMR (400 MHz): δ 7.30–7.10 (5H, m, Ar-H), 5.81 (1H, ddt, *J* 16.9, 9.8 and 6.7 Hz, C*H*=CH_2), 5.47 (1H, br s, H-4), 4.98 (1H, d, *J* 16.9) and 4.96 (1H, d, *J* 9.8 Hz) [CH=C*H*$_2$], 4.53 and 4.36 (2H, 2×d, *J* 12.2 Hz, OC*H*$_2$Ph), 3.47 (1H, dd, *J* 7.4 and 3.6 Hz, H-8), 2.55–2.25 (2H, m), 2.06 (1H, dd, *J* 13.8 and 7.4 Hz), 2.00–1.25 (5H, m), 1.65 (3H, s, olefinic-CH_3), 1.05 (3H, s), 0.97 (3H, s) and 0.93 (3H, s) [3×*tert*-CH_3]; HRMS: *m*/*z* Calcd for $C_{23}H_{32}O_2Na$ (M+Na): 363.2292; Found: 363.2274.

*4.1.10. (1R,6S,8S)-5-Allyl-8-benzyloxy-4,6,9,9-tetramethylbicyclo[4.3.0]non-4-en-3-one (**13**).* To a magnetically stirred solution of the alcohol **12** (23 mg, 0.07 mmol) in anhydrous CH_2Cl_2 (0.5 mL) was added a homogeneous mixture of PCC (60 mg, 0.27 mmol) and silica gel (60 mg), and stirred at RT for 8 h. The reaction mixture was then filtered through a small pad of silica gel using CH_2Cl_2 (10 mL) as eluent. Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate–hexane (1:19) as eluent furnished the enone **13** (18 mg, 71%) as colourless oil. R_f (1:19 EtOAc:hexane) 0.5; $[\alpha]_D^{25}$ +49.0 (*c* 2.0, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3065, 3030, 2948, 2866, 1663, 1607, 1454, 1376, 1352, 1322, 1280, 1158, 1096, 1066, 1028, 993, 913, 735, 697; ^{1}H NMR (400 MHz): δ 7.35–7.10 (5H, m, Ar-H), 5.71 (1H, ddt, *J* 17.0, 10.6 and 6.0 Hz, C*H*=CH_2), 5.01 (1H, dd, *J* 10.6 and 1.5 Hz) and 4.96 (1H, dd, *J* 17.1 and 1.6 Hz) [CH=C*H*$_2$], 4.52 and 4.40 (2H, 2×d, *J* 12.2 Hz, OC*H*$_2$Ph), 3.60 (1H, dd, *J* 5.9 and 2.2 Hz), 3.02 (1H, dd, *J* 15.0 and 5.7 Hz), 2.90 (1H, dd, *J* 15.0 and 5.7 Hz), 2.50–2.25 (2H, m), 2.00–1.50 (3H, m), 1.64 (3H, s, olefinic-CH_3), 1.17 (3H, s), 1.01 (3H, s) and 0.99 (3H, s) [3×*tert*-CH_3]; ^{13}C NMR (100 MHz): δ 200.3 (C, C=O), 163.3 (C, C-5), 139.0 (C, C-4), 134.0 (CH, *C*H=CH_2), 131.3 (C), 128.3 (2C, CH), 127.3 (CH), 127.0 (2C, CH), 116.5 (CH_2, CH=*C*H_2), 87.9 (CH, C-8), 72.3 (CH_2, O*C*H_2Ph), 55.0 (CH, C-1), 47.8 (C), 43.2 (C), 41.2 (CH_2), 35.3 (CH_2), 35.2 (CH_2), 32.1 (CH_3), 20.5 (CH_3), 19.9 (CH_3), 11.5 (CH_3); HRMS: *m*/*z* Calcd for $C_{23}H_{30}O_2Na$ (M+Na): 361.2144; Found: 361.2141.

*4.1.11. Methyl 2-[(1S,2R,6S)-2-(1-ethoxyethoxy)-6-isopropenyl-1,3-dimethylcyclohex-3-enyl]acetate (**15**).* To a magnetically stirred solution of the alcohol **5** (480 mg, 2.01 mmol) in dry CH_2Cl_2 (2 mL) was added ethyl vinyl ether (0.3 mL, 6.03 mmol) and PPTS (25 mg, 5 mol %) and stirred the reaction mixture at RT for 6 h. Solid $NaHCO_3$ (15 mg) was added to the reaction mixture and the solvent was removed under reduced pressure at rt. The residue was purified on a silica gel column using ethyl acetate–hexane (1:19) as eluent to furnish a 2:3 epimeric mixture of the acetal **15** (562 mg, 92%) as oil. R_f (1:19 EtOAc:hexane) 0.6; $[\alpha]_D^{21}$ +49.4 (*c* 10.8, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3076, 2981, 2951, 2922, 1738, 1636, 1436, 1378, 1326, 1217, 1162, 1127, 1096, 1058, 1039, 953, 898; ^{1}H NMR (400 MHz, 2:3 mixture of diastereomers): δ 5.39 (1H, br s, H-4′), 4.77 (1H, s), 4.69 (2H, s), 4.59 (1H, q, *J* 5.0 Hz, OC*H*(CH_3)O), 3.60 and 3.57 (3H, s, OCH_3), 3.52 and 3.40 (2H, q, *J* 7.0 Hz, OC*H*$_2$$CH_3$), 2.92 (1H, d, *J* 17.8 Hz), 2.81 (1H, dd, *J* 10.9 and 4.9 Hz), 2.50–2.00 (2H, m), 1.84 (1H, t, *J* 18.4 Hz), 1.75 and 1.72 (3H, s, olefinic-CH_3), 1.71 and 1.67 (3H, s, olefinic-CH_3), 1.29 (3H, d, *J* 5.0 Hz, OCH(C*H*$_3$)O), 1.19 and 1.10 (3H, t, *J* 7.0 Hz, OCH_2CH_3), 0.92 and 0.89 (3H, s) [*tert*-CH_3]; ^{13}C NMR (100 MHz): δ 172.4 and 172.8 (C, OC=O), 146.2 and 146.1 (C, *C*=CH_2), 135.8 and 135.3 (C, C-3′), 122.0 and 123.0 (CH, C-4′), 114.5 (CH_2, C=*C*H_2), 102.0 and 102.1 (CH, O*C*H(CH_3)O), 79.1 and 80.2 (CH, C-2′), 62.5 and 61.8 (CH_2, O*C*$H_2$$CH_3$), 50.8 and 50.4 ($CH_3$, OCH_3), 46.2 and 45.5 (CH, C-6′), 40.4 and 39.4 (C, C-1′), 39.3 and 38.6 (CH_2, C-2), 28.9 and 28.7 (CH_2, C-5′), 22.1 and 22.3 (CH_3), 21.1 and 20.4 (CH_3), 20.7 and 20.2 (CH_3), 15.9 and 15.6 (CH_3), 15.5 and 15.1 (CH_3); HRMS: *m*/*z* Calcd for $C_{18}H_{30}O_4Na$ (M+Na): 333.2042; Found: 333.2036.

*4.1.12. (1S,2R,6S)-2-(1-Ethoxyethoxy)-1,3,7,7-tetramethylbicyclo[4.3.0]non-3-en-8-ol (**16**).* To a magnetically stirred, freshly distilled (over sodium and ferric chloride) ammonia (20 mL) in a two-necked round bottom flask equipped with Dewar condenser was added a solution of the ester **15** (400 mg, 1.29 mmol) in dry THF (1 mL) followed by freshly cut lithium (45 mg, 6.45 mmol). The resulting blue coloured solution was stirred at −33 °C for 45 min and then the reaction was carefully quenched with solid NH_4Cl. After evaporation of ammonia, the residue was taken in water (5 mL) and extracted with ether (3×5 mL). The combined organic extract was washed with brine (10 mL) and dried (Na_2SO_4). Evaporation of the solvent and purification of the residue on a silica gel column using ethyl acetate–hexane (1:9) as eluent furnished a diastereomeric mixture of the bicyclic alcohol **16** (302 mg, 83%) as oil. R_f (1:9 EtOAc:hexane) 0.5; $[\alpha]_D^{21}$ −28.9 (*c* 19.0, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3402, 2973, 2895, 1448, 1378, 1342, 1328, 1147, 1125, 1095, 1035, 998, 935, 892, 807; ^{1}H NMR (400 MHz, mixture of isomers): δ 5.42 (1H, br s, H-4), 4.90–4.60 (1H, m, *J* 5.3 Hz, OC*H*(CH_3)O), 4.20–3.30 (4H, m), 2.30–1.50 (5H, m), 1.68 and 1.63 (3H, s, olefinic-CH_3), 1.30 (3H, d, *J* 5.2 Hz), 1.25–1.00 (4H, m), 0.96 (3H, s), 0.88 (3H, s), 0.87 and 0.81 (3H, s); ^{13}C NMR (100 MHz, signals due to two major isomers): δ 136.1 and 135.9 (C, C-3), 123.6 and 123.4 (CH, C-4), 101.2 and 99.2 (CH, O*C*H(CH_3)O), 85.7 and 85.1 (CH, C-2), 81.4 and 81.2 (CH, C-8), 59.9 and 59.5 (CH_2, O*C*$H_2$$CH_3$), 54.0 (CH, C-6), 48.3 and 48.0 (CH), 42.2 (C), 40.0 and 39.4 (C), 26.3

and 26.2 (CH_3), 25.5 (CH_3), 23.6 and 23.5 (CH_2), 20.3 and 20.2 (CH_3), 20.1 and 19.9 (CH_3), 15.5 and 15.4 (CH_3), 14.2 and 14.1 (CH_3); HRMS: *m*/*z* Calcd for $C_{17}H_{30}O_3Na$ (M+Na): 305.2085; Found: 305.2085.

*4.1.13. (1S,2S,6S)-1,3,7,7-Tetramethylbicyclo[4.3.0]non-3-ene-2,8-diol (**17**).* To a magnetically stirred solution of the alcohol **16** (372 mg, 1.33 mmol) in methanol (2 mL) was added PPTS (35 mg, 10 mol %) and the reaction mixture was stirred at RT for 6 h. Solid $NaHCO_3$ (20 mg) was added to the reaction mixture. Solvent was then removed under reduced pressure at RT and the residue was purified on a silica gel column using ethyl acetate–hexane (1:3) as eluent to furnish a 1:4 epimeric mixture of the alcohol **17** (239 mg, 86%) as oil. R_f (1:3 EtOAc:hexane) 0.4; $[\alpha]_D^{25}$ −45.5 (*c* 7.2, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3376, 2955, 2925, 2893, 2864, 1450, 1381, 1346, 1256, 1149, 1121, 1048, 1036, 995, 877; ^1H NMR (400 MHz, 1:4 epimeric mixture): δ 5.45 (1H, br s, H-4), 4.04 (1H, dd, *J* 9.6 and 7.0 Hz, H-8), 3.89 and 3.82 (1H, br s, H-2), 2.22 (1H, dd, *J* 11.9 and 6.6 Hz), 2.00–1.20 (8H, m), 1.70 (3H, s, olefinic-CH_3), 1.00 (3H, s), 0.96 and 0.90 (3H, s), 0.85 (3H, s); ^{13}C NMR (100 MHz): δ 136.5 and 136.0 (C, C-3), 124.1 and 123.5 (CH, C-4), 82.2 and 81.4 (CH, C-2), 81.5 and 81.0 (CH, C-8), 54.1 and 53.7 (CH, C-6), 46.6 and 47.1 (CH_2, C-9), 42.9 and 42.2 (C, C-1), 40.4 (C, C-7), 26.2 (CH_3), 30.6 and 25.5 (CH_3), 23.3 and 23.7 (CH_2), 19.2 (CH_3), 14.3 and 13.4 (CH_3); HRMS: *m*/*z* Calcd for $C_{13}H_{21}O$ (M−OH): 193.1587; Found: 193.1592.

*4.1.14. (1S,6S,8S) and (1S,6S,8R)-8-Hydroxy-1,3,7,7-tetramethylbicyclo[4.3.0]non-3-en-2-ones (**18a** and **18b**).* To a magnetically stirred solution of the diol **28** (208 mg, 0.99 mmol) in dry CH_2Cl_2 (2 mL) was added MnO_2 (258 mg, 2.97 mmol) and stirred at RT for 8 h. The reaction mixture was filtered through a small pad of silica gel column using CH_2Cl_2 (15 mL) as eluent. Evaporation of the solvent and purification of the residue on a silica gel column using ethyl acetate–hexane (1:19) as eluent first furnished the 1*S*,6*S*,8*S*-isomer **18b** (36 mg, 17%) as oil. R_f (1:4 EtOAc:hexane) 0.45; $[\alpha]_D^{26}$ −56.1 (*c* 0.7, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3466, 2954, 2926, 2899, 1672, 1450, 1433, 1375, 1195, 1158, 1107, 1089, 1046, 1023, 842, 830; ^1H NMR (300 MHz): δ 6.63 (1H, br s, H-4), 3.91 (1H, dd, *J* 7.8 and 3.0 Hz, H-8), 2.36 (1H, dd, *J* 14.4 and 8.1 Hz), 2.40–2.10 (2H, m), 1.77 (3H, s, olefinic-CH_3), 1.73 (1H, dd, *J* 11.4 and 4.5 Hz), 1.62 (1H, dd, *J* 14.4 and 2.4 Hz), 1.55 (1H, br s, OH), 1.21 (3H, s) and 1.03 (6H, s) [3×*tert*-CH_3]; ^{13}C NMR (75 MHz): δ 204.1 (C=O), 142.6 (C-4), 134.5 (C-3), 81.3 (C-8), 54.9 (C-1), 51.2 (C-7), 43.5, 41.4, 30.3, 24.8, 19.6, 18.7, 16.4.

Further elution of the column with ethyl acetate–hexane (1:9) as eluent furnished the 1*S*,6*S*,8*R*-isomer **18a** (146 mg, 71%) as oil. R_f (1:4 EtOAc:hexane) 0.4; $[\alpha]_D^{21}$ −130.7 (*c* 1.3, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3250, 2962, 2949, 2889, 2859, 1671, 1466, 1449, 1376, 1259, 1196, 1182, 1122, 1066, 1046, 1034, 1000, 962, 851, 742; ^1H NMR (400 MHz): δ 6.62 (1H, br s, H-4), 4.07 (1H, dd, *J* 8.9 and 7.2 Hz, H-8), 2.30–2.10 (3H, m), 1.98 (1H, dd, *J* 10.8 and 4.9 Hz), 1.75 (3H, s, olefinic-CH_3), 1.90–1.50 (1H, m), 1.64 (1H, dd, *J* 12.7 and 9.4 Hz), 1.06 (3H, s), 1.05 (3H, s) and 0.94 (3H, s) [3×*tert*-CH_3]; ^{13}C NMR (100 MHz): δ 204.2 (C, C=O), 143.1 (CH, C-4), 134.2 (C, C-3), 80.5 (CH, C-8), 54.6 (CH, C-6), 49.0 (C, C-1), 41.9 (CH_2, C-9), 41.0 (C, C-7), 26.4 (CH_3), 25.0 (CH_3), 24.9 (CH_2, C-5), 17.7 (CH_3), 16.3 (CH_3); HRMS: *m*/*z* Calcd for $C_{13}H_{20}O_2Na$ (M+Na): 231.1361; Found: 231.1358.

*4.1.15. (1S,6S,8R)-8-Methoxymethoxy-1,3,7,7-tetramethylbicyclo[4.3.0]non-3-en-2-one (**19**).* To an ice cold solution of the alcohol **18a** (144 mg, 0.69 mmol) in dry CH_2Cl_2 (1.5 mL) were added DIPEA (0.3 mL, 1.72 mmol), DMAP (8 mg, 10 mol %) and MOMCl (0.2 mL, 2.41 mmol), and stirred for 30 min at the same temperature. The reaction mixture was stirred at RT for 5 h and then poured into water (3 mL) and extracted with CH_2Cl_2 (2×5 mL). Combined CH_2Cl_2 extract was washed with brine (4 mL) and dried (Na_2SO_4). Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate–hexane (1:19) as eluent furnished the MOM ether **19** (161 mg, 92%) as colourless oil. R_f (1:19 EtOAc:hexane) 0.5; $[\alpha]_D^{26}$ −98.0 (*c* 2.4, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 2961, 2929, 2889, 1682, 1466, 1450, 1375, 1147, 1103, 1047, 999, 917, 843; ^1H NMR (400 MHz): δ 6.54 (1H, br s, H-4), 4.56 and 4.52 (2H, 2×d, *J* 6.7 Hz, O*CH*$_2$O), 3.86 (1H, dd, *J* 9.5 and 6.8 Hz, H-8), 3.28 (3H, s, OCH_3), 2.30–2.00 (3H, m), 1.90 (1H, dd, *J* 10.3 and 5.6 Hz), 1.69 (3H, s, olefinic-CH_3), 1.60 (1H, dd, *J* 12.3 and 10.0 Hz), 1.01 (3H, s), 0.99 (3H, s) and 0.88 (3H, s) [3×*tert*-CH_3]; ^{13}C NMR (100 MHz): δ 203.7 (C, C=O), 142.6 (CH, C-4), 134.3 (C, C-3), 95.9 (CH_2, OCH_2O), 84.9 (CH, C-8), 55.1 (CH_3, OCH_3), 54.6 (CH, C-6), 49.1 (C, C-1), 40.8 (C, C-7), 39.3 (CH_2), 27.2 (CH_3), 25.8 (CH_3), 24.8 (CH_2), 17.5 (CH_3) and 16.3 (CH_3); HRMS: *m*/*z* Calcd for $C_{15}H_{24}O_3Na$ (M+Na): 275.1617; Found: 275.1608.

*4.1.16. (1S,2S,6S,8R)-2-Allyl-8-(methoxymethoxy)-1,3,7,7-tetramethylbicyclo[4.3.0]non-3-en-2-ol (**21**).* To a sonochemically irradiated suspension of lithium (44 mg, 6.34 mmol) in dry THF (2 mL) in a round bottom flask placed in an ultrasonic cleaning bath, was added a solution of the enone **19** (160 mg, 0.63 mmol) and allyl bromide (0.4 mL, 5.07 mmol) in THF (1 mL) at 15–20 °C over a period of 2 min. The reaction mixture was sonochemically irradiated for 1 h. The reaction mixture was then decanted from the excess lithium, quenched with saturated aqueous NH_4Cl solution (4 mL) and extracted with ether (2×5 mL). The combined ether extract was washed with brine (4 mL) and dried (Na_2SO_4). Evaporation of the solvent and purification of the residue on a silica gel column using ethyl acetate–hexane (1:19) as eluent furnished the tertiary alcohol **21** (165 mg, 88%) as oil. R_f (1:19 EtOAc:hexane) 0.45; $[\alpha]_D^{26}$ −99.1 (*c* 1.1, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3502, 3076, 2956, 2891, 2845, 1637, 1465, 1448, 1376, 1215, 1147, 1121, 1104, 1047, 998, 908, 816; ^1H NMR (400 MHz): δ 5.85 (1H, ddt, *J* 17.1, 10.0 and 6.1 Hz, *CH*=CH_2), 5.50 (1H, br s, H-4), 5.11 (1H, d, *J* 17.1 Hz) and 5.06 (1H, d, *J* 10.1 Hz) [CH=*CH*$_2$], 4.65 and 4.62 (2H, 2×d, *J* 6.6 Hz, OCH_2O), 3.89 (1H, dd, *J* 10.2 and 6.4 Hz, H—8), 3.36 (3H, s, OCH_3), 2.51 (1H, dd, *J* 14.4 and 6.0 Hz), 2.44 (1H, dd, *J* 14.4 and 8.8 Hz), 2.00–1.60 (5H, m), 1.69 (3H, s, olefinic-CH_3), 1.55 (1H, br s, OH), 1.01 (3H, s), 0.93 (3H, s) and 0.88 (3H, s) [3×*tert*-CH_3]; ^{13}C NMR (100 MHz): δ 137.7 (C, C-3), 135.6 (CH, *C*H=CH_2), 124.7 (CH, C-4), 117.6 (CH_2, CH=*CH*$_2$), 96.2 (CH_2, OCH_2O), 85.9 (CH, C-8), 78.2 (C, C-2), 55.1 (CH_3, OCH_3), 50.1 (CH, C-6), 45.6 (C), 41.2 (CH_2), 39.6 (C), 39.3 (CH_2), 26.8 (CH_3), 26.5 (CH_3), 23.8 (CH_2), 18.4 (CH_3), 16.8 (CH_3); HRMS: *m*/*z* Calcd for $C_{18}H_{30}O_3Na$ (M+Na): 317.2093; Found: 317.2101.

*4.1.17. (1R,6S,8R)-5-Allyl-8-(methoxymethoxy)-4,6,9,9-tetramethylbicyclo[4.3.0]non-4-en-3-one (**22**).* To a magnetically stirred solution of the tertiary alcohol **21** (165 mg, 0.56 mmol) in anhydrous CH_2Cl_2 (1 mL) was added a homogeneous mixture of PCC (240 mg, 1.12 mmol) and silica gel (240 mg) and stirred at RT for 8 h. The reaction mixture was filtered through a small pad of silica gel column using CH_2Cl_2 (10 mL) as eluent. Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate–hexane (1:19) as eluent furnished the enone **22** (148 mg, 90%) as oil. R_f (1:19 EtOAc:hexane) 0.5; $[\alpha]_D^{25}$ −8.3 (*c* 4.0, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3080, 2958, 2935, 2889, 2822, 1666, 1607, 1465, 1377, 1324, 1276, 1215, 1200, 1146, 1105, 1080, 1046, 995, 916; ^1H NMR (400 MHz): δ 5.75 (1H, ddt, *J* 16.9, 10.7 and 6.1 Hz, *CH*=CH_2), 5.06 (1H, dd, *J* 10.7 and 1.5 Hz) and 5.03 (1H, dd, *J* 16.9 and 1.6 Hz) [CH=*CH*$_2$], 4.63 and 4.61 (2H, 2×d, *J* 6.7 Hz, OCH_2O), 3.96 (1H, dd, *J* 9.7 and 6.9 Hz), 3.34 (3H, s, OCH_2OCH_3), 3.05 (1H, dd, *J* 14.8 and 6.0 Hz), 2.97 (1H, dd, *J* 14.8 and 6.1 Hz), 2.50–2.20 (2H, m), 2.17 (1H, dd, *J* 11.6 and 6.6 Hz), 2.06 (1H, dd, *J* 13.2 and 5.9 Hz), 1.69 (3H, s, olefinic-CH_3), 1.64 (1H, t, *J* 10.6 Hz), 1.05 (3H, s), 1.03 (3H, s) and 0.93 (3H, s) [3×*tert*-CH_3]; ^{13}C NMR (100 MHz): δ 199.9 (C, C=O), 162.6 (C, C-5), 133.7 (CH, *C*H=CH_2), 131.4 (C, C-4), 116.7 (CH_2,

CH=CH_2), 96.3 (CH_2, OCH_2O), 84.7 (CH, C-8), 55.2 (CH, C-1), 54.5 (CH_3, OCH_3), 44.8 (C, C-6), 42.2 (CH_2, C-2), 40.0 (C, C-9), 35.4 (CH_2), 35.1 (CH_2), 26.2 (CH_3), 25.7 (CH_3), 20.8 (CH_3), 11.4 (CH_3); HRMS: *m/z* Calcd for $C_{18}H_{28}O_3Na$ (M+Na): 315.1936; Found: 315.1935.

*4.1.18. (1R,6R,8R)-5-Allyl-8-(methoxymethoxy)-4,6,9,9-tetramethylbicyclo[4.3.0]non-3-en-3-yl allyl ether (**23**) and (1R,4S,5R,6S,8R)-4,5-bisallyl-8-methoxymethoxy-4,6,9,9-tetramethylbicyclo[4.3.0]-nonan-3-one (**20**).* To a magnetically stirred, freshly distilled (over sodium and ferric chloride) ammonia (15 mL) in a two-necked round bottom flask equipped with Dewar condenser was added a solution of the enone **22** (150 mg, 0.51 mmol) and ^{t}BuOH (0.1 mL) in dry THF (3 mL) followed by freshly cut lithium (22 mg, 3.05 mmol). The resulting blue coloured solution was stirred at −33 °C for 10 min and it was then carefully treated with allyl bromide (0.4 mL, 5.13 mmol) and stirred the reaction mixture for 40 min. After evaporation of ammonia, NH_4Cl solution (5 mL) was added to the residue and extracted with ether (2×5 mL). The combined organic extract was washed with brine (4 mL) and dried (Na_2SO_4). Evaporation of the solvent and purification of the residue on a silica gel column using ethyl acetate–hexane (1:19) as eluent furnished an epimeric mixture of the *O*-allylated compound **23** (21 mg, 12%) as oil. R_f (1:19 EtOAc:hexane) 0.5; $[\alpha]_D^{25}$ −25.6 (*c* 1.6, $CHCl_3$). IR (neat): ν_{max}/cm^{-1} 3077, 2958, 2928, 1667, 1639, 1465, 1376, 1330, 1298, 1214, 1148, 1101, 1048, 996, 917; ^{1}H NMR (400 MHz, mixture of diastereomers): δ 6.10–5.70 (2H, m, 2×C*H*=CH_2), 5.31 (1H, d, *J* 17.1 Hz), 5.18 (1H, d, *J* 10.4 Hz), 5.07–4.90 (2H, m), 4.75–4.50 (2H, m, OCH_2O), 4.30–4.15 (2H, m, OCH_2), 3.90–3.75 (1H, m), 3.37 and 3.36 (3H, s, OCH_3), 2.50–1.20 (7H, m), 1.67 and 1.62 (3H, s), 1.02 (3H, s), 0.92 (3H, s), 0.87 and 0.75 (3H, s); ^{13}C NMR (100 MHz, mixture of diastereomers): δ 147.6 and 147.0 (C, C-3), 140.0 and 139.2 (CH), 134.9 (CH), 117.3 and 117.1 (C, C-4), 116.6 (CH_2), 114.7 and 114.6 (CH_2), 96.2 and 96.1 (CH_2, OCH_2O), 86.3 and 86.2 (CH, C-8), 69.3 and 69.1 (CH_2, OCH_2), 55.6 and 55.1 (CH_3, OCH_3), 51.8 and 50.3 (CH, C-5), 48.3 (CH, C-1), 45.6 and 41.5 (CH_2), 41.0 and 40.3 (C), 39.2 and 39.0 (C), 34.1 and 33.8 (CH_2), 26.7 and 26.6 (CH_3), 26.5 and 26.3 (CH_3), 24.1 and 23.7 (CH_2), 22.0 and 15.8 (CH_3), 14.4 and 13.4 (CH_3).

Further elution of the column with ethyl acetate–hexane (1:19) furnished the C—allylated ketone **20** (120 mg, 70%) as oil. R_f (1:9 EtOAc:hexane) 0.5; $[\alpha]_D^{26}$ −27.9 (*c* 4.0, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3076, 2957, 2935, 2888, 2823, 1699, 1639, 1466, 1442, 1416, 1376, 1214, 1146, 1120, 1102, 1046, 995, 916; ^{1}H NMR (400 MHz): δ 5.77 (1H, ddt, *J* 17.2, 10.0 and 6.6 Hz), 5.60–5.40 (1H, m), 5.10–4.85 (4H, m, 2×CH=C*H*$_2$), 4.59 and 4.56 (2H, 2×d, *J* 6.7 Hz, OCH_2O), 3.88 (1H, dd, *J* 9.9 and 6.8 Hz), 3.33 (3H, s, OCH_3), 2.49 (1H, dd, *J* 13.7 and 5.5 Hz), 2.40–2.10 (5H, m), 2.05 (1H, dd, *J* 13.7 and 9.1 Hz), 1.81 (1H, t, *J* 6.7 Hz), 1.61 (1H, dd, *J* 14.6 and 5.4 Hz), 1.23 (1H, t, *J* 10.8 Hz), 1.07 (3H, s), 0.96 (3H, s), 0.92 (3H, s) and 0.90 (3H, s) [4×*tert*-CH_3]; ^{13}C NMR (100 MHz): δ 215.0 (C, C=O), 139.4 (CH) and 134.9 (CH) [2×*C*H=CH_2], 118.5 (CH_2) and 115.5 (CH_2) [2×CH=*C*H$_2$], 96.1 (CH_2, OCH_2O), 85.6 (CH, C-8), 55.1 (CH_3, OCH_3), 54.9 (CH, C-5), 52.2 (C, C-4), 52.0 (CH, C-1), 47.3 (CH_2), 44.9 (CH_2), 42.6 (C), 39.9 (C), 37.0 (CH_2), 32.7 (CH_2), 26.2 (CH_3), 26.1 (CH_3), 23.1 (CH_3), 15.9 (CH_3); HRMS: *m/z* Calcd for $C_{21}H_{34}O_3Na$ (M+Na): 357.2406; Found: 357.2392.

*4.1.19. (1R,2S,4R,6R,9S)-4-(Methoxymethoxy)-2,5,5,9-tetramethyltricyclo[7.4.0.0^{2,6}]tridec-11-en-8-one (**24**).* To a magnetically stirred solution of the *bis*allyl ketone **20** (30 mg, 0.09 mmol) in anhydrous CH_2Cl_2 (3 mL) was added a solution of Grubbs first generation catalyst (6 mg, 10 mol %) in anhydrous CH_2Cl_2 (6 mL) and the reaction mixture was stirred at RT for 4 h. Evaporation of the solvent and purification of the residue on a silica gel column using ethyl acetate–hexane (1:19) as eluent furnished the tricyclic ketone **24** (25 mg, 91%) as oil. R_f (1:19 EtOAc:hexane) 0.5; $[\alpha]_D^{26}$ −38.0 (*c* 2.0, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3023, 2951, 2897, 1704, 1651, 1467, 1450, 1376, 1305, 1258, 1216, 1186, 1158, 1144, 1120, 1104, 1086, 1072, 1049, 993, 917, 694, 662, 609; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.80–5.40 (2H, m, olefinic H), 4.63 and 4.60 (2H, 2×d, *J* 6.6 Hz, OCH_2O), 4.02 (1H, dd, *J* 9.8 and 7.0 Hz, H-4), 3.35 (3H, s, O*CH*$_3$), 2.56 (1H, t, *J* 14.8 Hz), 2.40–1.80 (6H, m), 1.75–1.50 (2H, m), 1.08 (1H, t, *J* 6.8 Hz), 1.06 (6H, s), 1.00 (3H, s) and 0.91 (3H, s) [4×*tert*-CH_3]; ^{13}C NMR (100 MHz, $CDCl_3$): δ 215.2 (C, C=O), 125.5 (CH), 125.1 (CH), 96.2 (CH_2, O*CH*$_2$O), 85.9 (CH, C-4), 58.8 (CH), 55.2 (CH_3, O*CH*$_3$), 52.1 (CH, C-1), 46.9 (C, C-9), 46.7 (CH_2), 41.1 (C), 40.5 (C), 38.0 (CH_2), 36.7 (CH_2), 25.9 (CH_3), 25.7 (CH_3), 24.7 (CH_2), 19.3 (CH_3) and 15.8 (CH_3); HRMS: *m/z* Calcd for $C_{19}H_{30}O_3Na$ (M+Na): 329.2093; Found: 329.2079.

*4.1.20. (1S,2R,6S)-2-(1-Ethoxyethoxy)-1,3,7,7-tetramethylbicyclo[4.3.0]non-3-en-8-one (**25**).* To a magnetically stirred solution of the diastereomeric mixture of the alcohol **16** (150 mg, 0.53 mmol) in DMSO (2 mL) was added IBX (300 mg, 1.06 mmol), and the reaction mixture was stirred at RT for 1 h. Water (5 mL) and saturated $NaHCO_3$ solution (4 mL) were added to the reaction mixture and extracted with ether (2×5 mL). The combined ether layer was washed with brine (4 mL) and dried (Na_2SO_4). Evaporation of the solvent and purification of the residue on a silica gel column using ethyl acetate–hexane (1:19) as eluent furnished a 1:1 diastereomeric mixture of the ketone **25** (122 mg, 82%) as oil. R_f (1:19 EtOAc:hexane) 0.5; $[\alpha]_D^{21}$ +63.1 (*c* 5.0, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 2975, 2934, 2898, 1740, 1455, 1384, 1246, 1127, 1095, 1055, 1038, 935, 892; ^{1}H NMR (400 MHz, mixture of isomers): δ 5.52 and 5.50 (1H, br s, H-4), 4.72 and 4.70 (1H, q, *J* 5.2 Hz), 4.12 and 3.90 (1H, s, H-2), 3.75–3.25 (2H, m), 2.50–2.20 (2H, m), 2.10–1.75 (3H, m), 1.73 and 1.68 (3H, s, olefinic-CH_3), 1.32 and 1.31 (3H, d, *J* 5.4 Hz, OCH(*CH*$_3$)O), 1.18 (3H, t, *J* 6.5 Hz, OCH_2*CH*$_3$), 1.00 (3H, s), 0.91 and 0.87 (3H, s); ^{13}C NMR (100 MHz, mixture of isomers): δ 223.1 and 222.4 (C, C=O), 136.5 and 136.2 (C, C-3), 123.4 and 123.3 (CH, C-4), 101.4 and 98.8 (CH, O*CH*(CH_3)O), 85.6 and 83.3 (CH, C-2), 59.5 and 59.4 (CH_2, O*CH*$_2$CH$_3$), 52.5 and 52.4 (CH_2, C-9), 51.6 and 51.5 (CH, C-6), 45.3 and 44.4 (C, C-7), 41.0 (C, C-1), 27.8 (CH_3), 23.0 and 22.9 (CH_2), 21.6 (CH_3), 20.3 and 20.2 (CH_3), 20.0 and 19.7 (CH_3), 15.5 and 15.4 (CH_3), 14.2 and 14.1 (CH_3); HRMS: *m/z* Calcd for $C_{17}H_{28}O_3Na$ (M+Na): 303.1936; Found: 303.1927.

*4.1.21. (1S,2S,6S)-1,3,7,7-Tetramethyl-8-methylenebicyclo[4.3.0]non-3-en-2-ol (**26**).* To an ice cold suspension of Mg (820 mg, 34.24 mmol) and $TiCl_4$ (0.9 mL, 8.56 mmol) in CH_2Cl_2 (5 mL) was added drop wise a solution of the ketone **25** (300 mg, 1.07 mmol) in CH_2Cl_2 (2 mL) and THF (2 mL), and stirred for 30 min at 0 °C, and then stirred at RT for 5 h. The reaction mixture was recooled to 0 °C and saturated K_2CO_3 solution (3 mL) was added followed by 3 N HCl (10 mL) and stirred for 15 min and extracted with ether (2×10 mL). The combined ether layer was washed with brine (5 mL) and dried (Na_2SO_4). Evaporation of the solvent and purification of the residue on a silica gel column using ethyl acetate–hexane (1:19) as eluent furnished the alcohol **26** (174 mg, 79%) as oil. R_f (1:19 EtOAc:hexane) 0.5; $[\alpha]_D^{26}$ +8.1 (*c* 1.8, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3402, 3068, 3019, 2975, 2956, 2920, 2894, 2859, 1652, 1462, 1438, 1378, 1362, 1060, 1035, 995, 880; ^{1}H NMR (400 MHz): δ 5.47 (1H, br s, H-4), 4.91 (1H, d, *J* 2.4 Hz) and 4.82 (1H, d, *J* 2.4 Hz) [C=CH_2], 3.94 (1H, br s, H-2), 2.42 and 2.22 (2H, 2×d, *J* 14.7 Hz, H-9), 2.00–1.50 (2H, m), 1.72 (3H, s, olefinic-CH_3), 1.62 (1H, t, *J* 8.6 Hz), 1.36 (1H, br s, OH), 1.06 (3H, s), 1.04 (3H, s) and 0.80 (3H, s) [3×*tert*-CH_3]; ^{13}C NMR (100 MHz): δ 161.6 (C, C-8), 136.5 (C, C-3), 123.7 (CH, C—4), 105.5 (CH_2, C=*C*H$_2$), 80.6 (CH, C-2), 54.2 (CH, C-6), 46.9 (CH_2, C-9), 43.9 (C), 41.3 (C), 32.5 (CH_3), 26.3 (CH_3), 23.7 (CH_2, C-5), 19.2 (CH_3), 12.0 (CH_3); HRMS: *m/z* Calcd for $C_{14}H_{21}$ (M−OH): 189.1643; Found: 189.1643.

*4.1.22. (1S,6S)-1,3,7,7-Tetramethyl-8-methylenebicyclo[4.3.0]non-3-en-2-one (**27**).* To a magnetically stirred solution of the alcohol **26** (130 mg, 0.63 mmol) in anhydrous CH_2Cl_2 (1 mL) was added a homogeneous mixture of PCC (340 mg, 1.57 mmol) and silica gel

(340 mg), and stirred at RT for 2 h. The reaction mixture was filtered through a small pad of silica gel using CH_2Cl_2 (10 mL) as eluent. Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate–hexane (1:19) as eluent furnished the enone **27** (118 mg, 92%) as colourless oil. R_f (1:19 EtOAc:hexane) 0.55; $[\alpha]_D^{21}$ −49.3 (*c* 1.5, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3070, 2959, 2924, 2863, 1682, 1655, 1462, 1448, 1434, 1371, 1354, 1195, 1047, 1009, 883, 841; ^1H NMR (400 MHz): δ 6.64 (1H, s, H-4), 4.99 (1H, d, *J* 2.3 Hz) and 4.88 (1H, d, *J* 2.3 Hz) [C=CH_2], 2.56 and 2.33 (2H, 2×d, *J* 15.5 Hz, H-9), 2.30–2.20 (2H, m), 2.00 (1H, dd, *J* 9.7 and 6.0 Hz), 1.77 (3H, s, olefinic-CH_3), 1.10 (3H, s), 1.08 (3H, s) and 1.00 (3H, s) [3×*tert*-CH_3]; ^{13}C NMR (100 MHz): δ 204.0 (C, C=O), 159.6 (C, C-8), 142.9 (CH, C-4), 134.9 (C, C-3), 106.9 (CH_2, C=*C*H_2), 55.0 (CH, C-6), 50.2 (C, C-1), 41.7 (C, C-7), 41.3 (CH_2, C-9), 31.9 (CH_3), 26.6 (CH_3), 24.9 (CH_2), 16.9 (CH_3), 16.3 (CH_3); HRMS: *m*/*z* Calcd for $C_{14}H_{21}O$ (M+H): 205.1592; Found: 205.1593.

*4.1.23. (1S,2S,6S)-2-Allyl-1,3,7,7-tetramethyl-8-methylenebicyclo[4.3.0]non-3-en-2-ol (**28**).* To a sonochemically irradiated suspension of lithium (32 mg, 4.62 mmol) in dry THF (2 mL) in a round bottom flask placed in an ultrasonic cleaning bath, was added a mixture of the enone **27** (118 mg, 0.58 mmol) and allyl bromide (0.3 mL, 3.46 mmol) in THF (1 mL) at 15–20 °C over a period of 2 min. The reaction mixture was sonochemically irradiated for 1 h. The reaction mixture was then decanted from the excess lithium, quenched with saturated aqueous NH_4Cl solution (4 mL) and extracted with ether (2×5 mL). The combined ether extract was washed with brine (4 mL) and dried (Na_2SO_4). Evaporation of the solvent and purification of the residue on a silica gel column using ethyl acetate–hexane (1:19) as eluent furnished the tertiary alcohol **28** (124 mg, 87%) as oil. R_f (1:19 EtOAc:hexane) 0.5; $[\alpha]_D^{21}$ −30.0 (*c* 2.1, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3500, 3072, 2977, 2955, 2923, 2853, 1653, 1638, 1446, 1376, 1362, 1025, 987, 910, 879, 816; ^1H NMR (400 MHz): δ 5.87 (1H, ddt, *J* 18.4, 10.8 and 6.1 Hz, C*H*=CH_2), 5.53 (1H, br s, H-4), 5.10 (1H, d, *J* 18.3 Hz) and 5.07 (1H, d, *J* 10.8 Hz) [CH=C*H*$_2$], 4.89 (1H, d, *J* 2.1 Hz) and 4.79 (1H d *J* 2.4 Hz) [C=CH_2], 2.62 (1H, d, *J* 14.2 Hz), 2.54 (1H, dd, *J* 14.4 and 6.1 Hz), 2.47 (1H, dd, *J* 14.4 and 8.6 Hz), 2.10 (1H, d, *J* 14.2 Hz), 2.03 (1H, dd, *J* 11.8 and 6.0 Hz), 1.90–1.60 (2H, m), 1.72 (3H, s, olefinic-CH_3), 1.51 (1H, br s, OH), 1.05 (3H, s), 1.03 (3H, s) and 0.86 (3H, s) [3×*tert*-CH_3]; ^{13}C NMR (100 MHz): δ 161.7 (C, C-8), 138.2 (C, C-3), 135.8 (CH, *C*H=CH_2), 124.8 (CH, C-4), 117.3 (CH_2, CH=*C*H_2), 104.7 (CH_2, C=*C*H_2), 77.8 (C, C-2), 50.4 (CH, C-6), 47.5 (C), 41.5 (CH_2), 41.4 (CH_2), 40.7 (C), 33.0 (CH_3), 26.0 (CH_3), 24.1 (CH_2), 18.4 (CH_3) and 15.5 (CH_3); HRMS: *m*/*z* Calcd for $C_{17}H_{25}$ (M−OH): 229.1950; Found: 229.1954.

*4.1.24. (1S,6S)-5-Allyl-4,6,9,9-tetramethyl-8-methylenebicyclo[4.3.0]non-4-en-3-one (**29**).* To a magnetically stirred solution of the tertiary alcohol **28** (124 mg, 0.50 mmol) in anhydrous CH_2Cl_2 (1 mL) was added a homogeneous mixture of PCC (270 mg, 1.25 mmol) and silica gel (270 mg), and stirred at RT for 8 h. The reaction mixture was filtered through a small pad of silica gel using CH_2Cl_2 (10 mL) as eluent. Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate–hexane (1:19) as eluent furnished the enone **29** (102 mg, 84%) as colourless oil. R_f (1:19 EtOAc:hexane) 0.6; $[\alpha]_D^{21}$ +64.1 (*c* 1.4, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3073, 2958, 2930, 2863, 1666, 1609, 1456, 1374, 1319, 1277, 1195, 1080, 1020, 912, 883, 744; ^1H NMR (400 MHz): δ 5.78 (1H, ddt, *J* 16.8, 10.4 and 6.2 Hz, C*H*=CH_2), 5.10 (1H, d, *J* 10.4 Hz) and 5.04 (1H, d, *J* 16.8 Hz) [CH=C*H*$_2$], 5.01 (1H, d, *J* 2.5 Hz) and 4.92 (1H, d, *J* 2.5 Hz) [C=CH_2], 3.08 (1H, dd, *J* 14.9 and 5.9 Hz), 2.97 (1H, dd, *J* 14.8 and 6.0 Hz), 2.80–2.20 (4H, m), 2.12 (1H, dd, *J* 13.5 and 5.5 Hz), 1.73 (3H, s, olefinic-CH_3), 1.08 (3H, s), 1.07 (3H, s) and 1.01 (3H, s) [3×*tert*-CH_3]; ^{13}C NMR (100 MHz): δ 199.8 (C, C=O), 161.9 (C, C-8), 159.4 (C, C-5), 133.8 (CH, *C*H=CH_2), 132.0 (C, C-4), 116.7 (CH_2, CH=*C*H_2), 107.3 (CH_2, C=*C*H_2), 54.8 (CH, C-1), 46.1 (C), 44.1 (CH_2, C-2), 41.2 (C), 35.3 (CH_2), 35.2 (CH_2), 32.0 (CH_3), 25.4 (CH_3), 19.9 (CH_3), 11.5 (CH_3); HRMS: *m*/*z* Calcd for $C_{17}H_{25}O$ (M+H): 245.1905; Found: 245.1911.

*4.1.25. (1R,4S,5R,6S)-4,5-bisallyl-4,6,9,9-tetramethyl-8-methylenebicyclo[4.3.0]nonan-3-one (**30**).* To a magnetically stirred, freshly distilled (over sodium and ferric chloride) ammonia (15 mL) in a two-necked round bottom flask equipped with Dewar condenser was added a solution of the enone **29** (100 mg, 0.41 mmol) and ^{t}BuOH (0.1 mL) in dry THF (2 mL) followed by freshly cut lithium (14 mg, 2 mmol). The resulting blue coloured solution was stirred at −33 °C for 10 min and then the enolate was carefully quenched with allyl bromide (0.4 mL, 4.10 mmol) and stirred the reaction mixture at −33 °C to RT for 40 min. After evaporation of ammonia, NH_4Cl solution (5 mL) was added to the residue and extracted with ether (2×5 mL). The combined organic extract was washed with brine (4 mL) and dried (Na_2SO_4). Evaporation of the solvent and purification of the residue on a silica gel column using CH_2Cl_2–hexane (1:9) as eluent furnished the *bis*allyl ketone **30** (89 mg, 76%) as oil. R_f (1:6 CH_2Cl_2:hexane) 0.6; $[\alpha]_D^{21}$ +20.7 (*c* 3.5, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3075, 2976, 2959, 2886, 1703, 1654, 1639, 1462, 1442, 1416, 1375, 998, 912, 882; ^1H NMR (400 MHz): δ 5.95–5.70 (1H, m) and 5.70–5.50 (1H, m) [2×C*H*=CH_2], 5.15–4.89 (4H, m, 2×CH=C*H*$_2$), 4.90 (1H, s) and 4.85 (1H, s) [C=CH_2], 2.75–2.00 (8H, m), 1.87 (1H, t, *J* 6.4 Hz), 1.65 (1H, dd, *J* 15.0 and 4.7 Hz), 1.09 (3H, s), 1.04 (3H, s), 0.99 (3H, s) and 0.92 (3H, s) [4×*tert*-CH_3]; ^{13}C NMR (100 MHz): δ 214.9 (C, C=O), 160.7 (C, C-8), 138.9 (CH, *C*H=CH_2), 134.7 (CH, *C*H=CH_2), 117.8 (CH_2, CH=*C*H_2), 115.0 (CH_2, CH=*C*H_2), 105.8 (CH_2, C=*C*H_2), 55.5 (CH, C-1), 52.1 (C), 50.4 (CH, C-5), 49.3 (CH_2, C-2), 43.6 (C), 43.4 (CH_2), 40.4 (C), 36.6 (CH_2), 31.9 (CH_2), 31.8 (CH_3), 24.8 (CH_3), 22.4 (CH_3) and 14.4 (CH_3); HRMS: *m*/*z* Calcd for $C_{20}H_{30}O$ (M+Na): 309.2194; Found: 309.2202.

*4.1.26. (1R,2S,6R,9S)-2,5,5,9-Tetramethyl-4-methylenetricyclo[7.4.0.0^{2,6}]tridec-11-en-8-one (**31**).* To a magnetically stirred solution of the ketone **30** (23 mg, 0.08 mmol) in anhydrous CH_2Cl_2 (2 mL) was added a solution of Grubbs first generation catalyst (6 mg, 10 mol %) in anhydrous CH_2Cl_2 (5 mL) and the reaction mixture was stirred at RT for 4 h. Evaporation of the solvent under reduced pressure and purification of the residue on a $AgNO_3$ (15%) impregnated on silica gel column using ethyl acetate–hexane (1:19) as eluent furnished the tricyclic ketone **31** (19 mg, 91%) as oil. R_f (1:19 EtOAc:hexane) 0.5; $[\alpha]_D^{21}$ +15.4 (*c* 1.0, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3067, 3022, 2955, 2935, 2904, 2861, 1703 (C=O), 1652, 1452, 1436, 1373, 883, 648; ^1H NMR (400 MHz, $CDCl_3$): δ 5.70–5.50 (2H, m, CH=CH), 4.98 (1H, d, *J* 2.5 Hz) and 4.91 (1H, d, *J* 2.5 Hz) [C=CH_2], 2.62 (1H, t, *J* 15.0 Hz), 2.40–1.85 (6H, m), 1.80–1.50 (3H, m), 1.09 (3H, s), 1.05 (3H, s) and 1.03 (6H, s) [4×*tert*-CH_3]; ^{13}C NMR (100 MHz, $CDCl_3$): δ 215.4 (C, C=O), 161.2 (C, C-4), 125.5 (CH), 125.1 (CH), 106.9 (CH_2, C=*C*H_2), 59.3 (CH, C-6), 51.2 (CH, C-1), 48.5 (CH_2, C-7), 47.0 (C, C-9), 42.3 (C), 41.4 (C), 37.7 (CH_2), 36.5 (CH_2), 31.8 (CH_3), 25.0 (CH_3), 24.5 (CH_2), 18.9 (CH_3), 14.9 (CH_3); HRMS: *m*/*z* Calcd for $C_{18}H_{26}ONa$ (M+Na): 281.1881; Found: 281.1875.

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References and notes

1. (a) Xiao, W.-L.; Li, R.-T.; Huang, S.-X.; Pu, J.-X.; Sun, H.-D. *Nat. Prod. Rep.* **2008**, *25*, 871; (b) Connolly, J. D.; Hill, R. A. *Nat. Prod. Rep.* **2008**, *25*, 794 earlier reviews in the series.
2. (a) Machida, K.; Kikuchi, M. *Tetrahedron Lett.* **1996**, *37*, 4157; (b) Eade, R. A.; Ellis, J.; Harper, P.; Simes, J. J. H. *Aust. J. Chem.* **1973**, *26*, 831; (c) De Mayo, P.; Starratt,

A. N. *Can. J. Chem.* **1962**, *40*, 1632; (d) Eade, R. A.; Ellis, J.; Simes, J. J. H. *Aust. J. Chem.* **1967**, *20*, 2737; (e) Machida, K.; Kikuchi, M. *Tetrahedron Lett.* **1997**, *38*, 571; (f) Machida, K.; Kikuchi, M. *Chem. Pharm. Bull.* **1997**, *45*, 1928; (g) Lontsi, D.; Sondengam, B. L.; Martin, M. T.; Bodo, B. *Phytochemistry* **1991**, *30*, 2361; (h) Julian, P. L.; Pikl, J.; Dawson, R. *J. Am. Chem. Soc.* **1938**, *60*, 77; (i) Boyer, J. P.; Eade, R. A.; Locksley, H.; Simes, J. J. H. *Aust. J. Chem.* **1958**, *11*, 236; (j) Guise, G. B.; Ritchie, E.; Taylor, W. *Aust. J. Chem.* **1958**, *11*, 236; (k) De Mayo, P.; Starratt, A. N. *Tetrahedron Lett.* **1961**, 259; (l) De Mayo, P.; Starratt, A. N. *Can. J. Chem.* **1962**, *40*, 788; (m) Guise, G. B.; Ritchie, E.; Taylor, W. C. *Aust. J. Chem.* **1962**, *15*, 314; (n) Mechoulam, R. *J. Am. Chem. Soc.* **1962**, *27*, 4070; (o) Eade, R. A.; Kornis, G.; Simes, J. J. H. *Aust. J. Chem.* **1964**, *17*, 141; (p) Eade, R. A.; Ellis, J.; Harper, P.; Simes, J. J. H. *J. Chem. Soc., Chem. Commun.* **1969**, 579; (q) Merkuza, V. M.; Mascaretti, O. A.; Crohare, R.; Ruveda, E. A. *Phytochemistry* **1971**, *10*, 908; (r) Ritchie, E. *Taylor. Aust. J. Chem.* **1972**, *25*, 2209; (s) Roitman, J.; Jurd, L. *Phytochemistry* **1978**, *17*, 491; (t) Kundu, A. B.; Barik, B. R.; Mondal, D. N.; Dey, A. K.; Banerji, A. *Phytochemistry* **1989**, *28*, 3155; (u) Roy, R.; Vishwakarma, R. A.; Varma, N.; Tandon, J. S. *Tetrahedron Lett.* **1990**, *31*, 3467; (v) Lee, S.-S.; Su, W.-C.; Liu, K. C. *J. Nat. Prod.* **1991**, *54*, 615; (w) Lee, S.-S.; Lin, C.-J.; Liu, K. C. *J. Nat. Prod.* **1992**, *55*, 602; (x) Lee, S.-S.; Lin, B.-F.; Liu, K. C. *Phytochemistry* **1996**, *43*, 847; (y) Li, X.-C.; Cai, L.; Wu, C. D. *Phytochemistry* **1997**, *46*, 97; (z) Yoshikawa, K.; Kondo, Y.; Kimura, E.; Arihara, S. *Phytochemistry* **1998**, *49*, 2057; (aa) Wang, F.; Li, X.-M.; Liu, J.-K. *Chem. Pharm. Bull.* **2009**, 525; (bb) Wu, X.-H.; Ruan, J.-L.; Cai, Y.-L. *Biochem. Syst. Ecol.* **2009**, *37*, 509.

3. (a) Wei, Y.; Maa, C.-M.; Hattori, M. *Bioorg. Med. Chem.* **2009**, *17*, 3003; (b) Shah, B. A.; Qazi, G. N.; Taneja, S. C. *Nat. Prod. Rep.* **2009**, *26*, 72; (c) Chopra, R.N.; Nayar, S.L.; Chopra, I.C. 'Glossary of Indian Medicinal Plants', 1956, pp 261. (d) Kim, J. G. *Illustrated Natural Drugs Encyclopedia*; Namsandang: Seoul, 1984; Vol. 1; pp. 424; (e) Grieve, M. *A Modern Herbal*; Dovelications: New York, NY, 1971; pp. 673; (f) Banno, N.; Akihisa, T.; Tokuda, H.; Yasukawa, K.; Higashihara, H.; Ukiya, M.; Watanabe, K.; Kimura, Y.; Hasegawa, J.-I.; Nishino, H. *Biosci. Biotechnol. Biochem.* **2004**, *68*, 85.
4. (a) Kuo, R.-Y.; Qian, K.; Morris-Natschke, S. L.; Lee, K.-H. *Nat. Prod. Rep.* **2009**, *26*, 1321; (b) Wei, Y.; Ma, C.-M.; Hattori, M. *Bioorg. Med. Chem.* **2009**, 3003; (c) Anand, K. K.; Singh, B.; Chand, D.; Chandan, B. K.; Gupta, V. N. *J. Ethnopharmacol.* **1989**, *27*, 121; (d) Pandy, V. B.; Devi, S. *Planta Med.* **1990**, *56*, 649; (e) Chuakul, W.; Jaikaew, C.; Thai, J. *Phytopharmacy* **1998**, *5*, 28; (f) Suksamrarn, S.; Panseeta, P.; Kunchanawatta, S.; Distaporn, T.; Ruktasing, S.; Suksamrarn, A. *Chem. Pharm. Bull.* **2006**, *54*, 535; (g) Nakagawa-Goto, K.; Yamada, K.; Taniguchi, M.; Tokuda, H.; Lee, K. H. *Bioorg. Med. Chem.* **2009**, 3378; (h) Lee, S.-M.; Park, J.-G.; Lee, Y.-H.; Lee, C.-G.; Min, B.-S.; Kim, J.-H.; Lee, H.-K. *Biol. Pharm. Bull.* **2004**, *27*, 1883.
5. Rao, G. S. R. S.; Kondaiah, P.; Singh, S. K.; Ravanan, P.; Sporn, M. B. *Tetrahedron* **2008**, *64*, 11541.
6. For some recent examples, see: (a) Srikrishna, A.; Gharpure, S. J. *J. Chem. Soc., Perkin Trans. 1* **2000**, 3191; (b) Srikrishna, A.; Gharpure, S. J. *J. Org. Chem.* **2001**, *65*, 4379; (c) Srikrishna, A.; Anebouselvy, K. *J. Org. Chem.* **2001**, *65*, 7102; (d) Srikrishna, A.; Kumar, P. R. *Tetrahedron Lett.* **2002**, *43*, 1109; (e) Srikrishna, A.; Dethe, D. H.; Kumar, P. R. *Tetrahedron Lett.* **2004**, *45*, 2939; (f) Srikrishna, A.; Dethe, D. H. *Org.Lett.* **2004**, *6*, 165; (g) Srikrishna, A.; Dinesh, C. *Tetrahedron: Asymmetry* **2005**, *16*, 2203; (h) Srikrishna, A.; Kumar, P. P.; Reddy, T. J. *Indian J. Chem.* **2005**, *44B*, 1430; (i) Srikrishna, A.; Satyanarayana, G. *Tetrahedron: Asymmetry* **2005**, *16*, 3992; (j) Srikrishna, A.; Ravi, G.; Satyanarayana, G. *Tetrahedron Lett.* **2007**, *48*, 73; (k) Srikrishna, A.; Pardeshi, V. H.; Satyanarayana, G. *Tetrahedron: Asymmetry* **2008**, *19*, 1984; (l) Srikrishna, A.; Pardeshi, V. H.; Triveni, P. *Tetrahedron: Asymmetry* **2008**, *19*, 1392; (m) Srikrishna, A.; Anebouselvy, K. *Indian J. Chem.* **2008**, *47B*, 449; (n) Srikrishna, A.; Ravi, G. *Tetrahedron* **2008**, *64*, 2565; (o) Srikrishna, A.; Ravi, G.; Venkatasubbaiah, D. R. C. *Synlett* **2009**, 32.
7. (a) Srikrishna, A.; Ramasastry, S. S. V. *Tetrahedron Lett.* **2004**, *45*, 379; (b) Srikrishna, A.; Kumar, P. R.; Ramasastry, S. S. V. *Tetrahedron Lett.* **2004**, *45*, 383; (c) Cossy, J.; Gille, B.; Bellosta, V. *J. Org. Chem.* **1998**, *63*, 3141.
8. Gesson, J.-P.; Jacquesy, J.-C.; Renoux, B. *Tetrahedron Lett.* **1986**, *27*, 4461.
9. Garver, L.; van Eikeren, P.; Byrd, J. E. *J. Org. Chem.* **1976**, *41*, 2773.
10. (a) Buchi, G.; Egger, B. *J. Org. Chem.* **1971**, *36*, 2021; (b) Srikrishna, A.; Hemamalini, P. *Indian J. Chem.* **1990**, *29B*, 201.
11. (a) Srikrishna, A.; Reddy, T. J. *Indian J. Chem.* **1995**, *34B*, 844; (b) Srikrishna, A.; Reddy, T. J. *Arkivoc* **2001**, 9.
12. (a) Nicolaou, K. C.; Zhong, Y.-L.; Baran, P. S. *J. Am. Chem. Soc.* **2000**, *122*, 7596; (b) Wirth, T. *Angew. Chem. Int. Ed.* **2001**, *40*, 2812.
13. Yan, T.-H.; Tsai, C.-C.; Chien, C.-T.; Cho, C.-C.; Huang, P.-C. *Org. Lett.* **2004**, *6*, 4961.