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Enantioselective syntheses of *cis*, *syn*, *cis*- and *cis*, *anti*, *cis*-linear triquinanes

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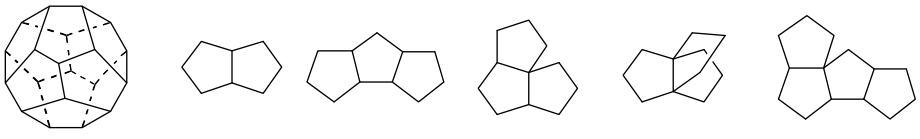
Abstract—Enantioselective syntheses of both *cis*, *syn*, *cis*- and *cis*, *anti*, *cis*-linear triquinanes, starting from the readily available (*S*)-campholenaldehyde, employing an RCM reaction-based cyclopentannulation strategy, are described.

1. Introduction

Over the last three decades, a rapid growth has been witnessed in the development of synthetic methodologies for generating polycondensed cyclopentane rings, commonly known as polyquinanes, in the context of natural product synthesis[1] as well as aesthetically appealing molecules such as dodecahedrane **1**.[2] While polyquinanes have been known to Nature since time immemorial, they were revealed to humans only in the second half of 20th century. For example, the structure determination of the first 'authentic' polyquinane natural product, hirsutic acid-C[3] was accomplished in 1966. Despite this belated discovery, polyquinane natural products have rapidly proliferated and have been encountered among plant, marine, and microbial sources. Polyquinane skeleta have been found among sesqui- and diterpenes and even in bioactive steroids. So far, natural products containing up to four fused cyclopentanes, **2**–**6**, have been unravelled. Whereas the aesthetically appealing, synthetically accomplished dodecahedrane **1** has 12 cyclopentanes.



1 **2** **3** **4** **5** **6**

The polyquinane natural products have aroused a great deal of interest among synthetic chemists in recent years. Indeed, polyquinanes have spearheaded the drive and provided the impetus for the development of new strategies for cyclopentannulations.[1] Among the polyquinanes, triquinanes are the most commonly encountered in sesquiterpenes and are classified according to ring fusion as linear **3**, angular **4**, or propellane **5**. The linear triquinanes, bearing a thermodynamically favored *cis*, *anti*, *cis*-tricyclo-[6.3.0.0^{2,6}]undecane ***3cac*** moiety as the fundamental ring system are the most abundant among natural polyquinanes. On the other hand, the corresponding *cis*, *syn*, *cis*-tricyclo[6.3.0.0^{2,6}]undecane ***3csc*** is an integral part of the aesthetically appealing polyquinanes such as dodecahedrane **1** and its analogues.

(*S*)-Campholenaldehyde **7** is a readily available cyclopentane-based chiral starting material. It has been employed in the synthesis of a variety of industrially (fragrance) important monocyclic compounds.[4] However, it has been under utilized in the synthesis of polycyclic compounds in organic synthesis.[5] Recently, we have reported an efficient route for the enantiospecific conversion of (*S*)-campholenaldehyde **7** into diquinanes employing an intramolecular rhodium carbenoid CH insertion reaction.[6] In continuation of our interest in the enantiospecific synthesis of polycyclic compounds starting from (*S*)-campholenaldehyde **7**, we herein report enantioselective syntheses of both *cis*, *anti*,

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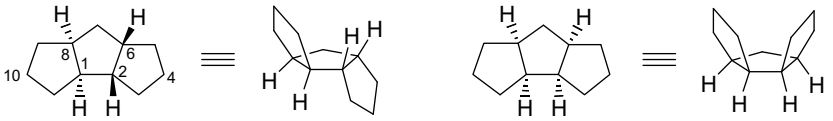


3cac **3csc**

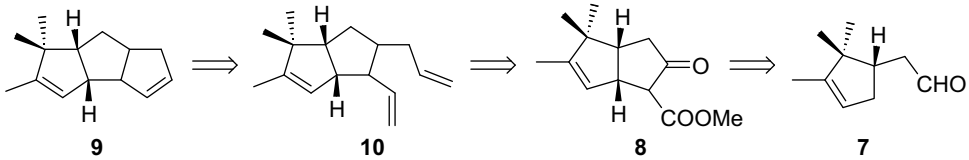
cis- and *cis*, *syn*, *cis*-tricyclo[6.3.0.0^{2,6}]undecanes. Since the diquinane ester **8** could be obtained readily from campholenaldehyde **7**, it was thought to annulate a third cyclopentane ring at C_2–C_3 positions for the generation of a linear triquinane **9** and the RCM reaction was chosen as the key step. It was conceived that the conversion of the ester group into a vinyl group, and introduction of an allyl group at the C-3 position would generate a suitable precursor, for example, **10**, for cyclopentannulation via a RCM reaction, Scheme 1.

2. Results and discussion

To begin with, the synthesis of a *cis*, *syn*, *cis*-triquinane **3*csc*** was addressed (Scheme 2) starting from the β-keto ester **11**, which was prepared[6] from campholenaldehyde **7** in four steps employing an intramolecular rhodium carbenoid CH insertion[7] of the α-diazo-β-keto ester **12** and stereoselective methylation of the β-keto ester **8**. The ester group in **11** was transformed into a vinyl group, employing a three-step protocol. Thus, reduction of the β-keto ester **11** with lithium aluminum hydride (LAH) in anhydrous ether at ice temperature gave a 1:1 epimeric mixture of diol **13** in 98% yield, which on oxidation with pyridinium chlorochromate (PCC) and silica gel in methylene chloride furnished the keto aldehyde **14** in 95% yield. A regioselective Wittig reaction of keto aldehyde **14** with methylenetriphenylphosphorane (generated from potassium tertiary amyl oxide and methyltriphenylphosphonium iodide)[8] in dry benzene at ice temperature for one minute gave ketone **15** in 90% yield, whose structure was established from its spectral data. Sonochemically accelerated Barbier reaction of ketone **15** with zinc and allyl bromide in THF gave a 3:2 epimeric mixture of the tertiary alcohols **16a** and **16b** in 93% yield, which were separated by column chromatography on silica gel and their structures established from spectral data. Based on the preferential approach of the nucleophile from the *exo*-face of the molecule, the stereochemistry at the newly created quaternary center was assigned (major isomer as *endo* and minor isomer as *exo*), which was further confirmed by the cyclization of the *exo* isomer **16b** into a triquinane.

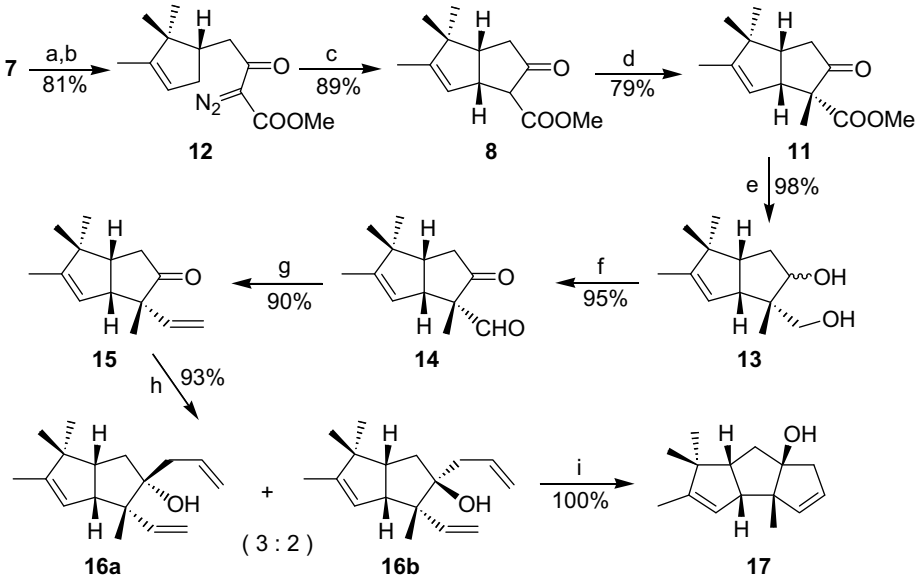
For the annulation of the cyclopentane ring, an RCM reaction[9] was conceived. The reaction of dienol **16b** with 5 mol % of Grubbs' first generation catalyst [$Cl_2(PCy_3)_2$-Ru=CHPh] in methylene chloride (0.1 M) for 30 min at room temperature furnished the *cis*, *syn*, *cis*-triquinane **17** in quantitative yield. The structure of triquinane **17** was determined from its spectral data. The presence of the protonated molecular ion peak at 219.1744 ($C_{15}H_{23}O$) in the high-resolution mass spectrum, and in the IR spectrum the presence of a broad absorption band at 3419 cm^{-1} due to a hydroxy group and the absence of absorption bands corresponding to terminal olefins suggested the formation of triquinane **17**. The presence of two multiplets at δ 5.63–5.60 and 5.40–5.38 corresponding to H-3 and H-4 protons, a broad singlet at 5.11 due to H-11 proton, a multiplet at 2.85-2.72 due to H-1 proton, a doublet of a triplet at 2.54 due to H-8 proton, a doublet of a multiplet at 2.43 and a doublet at 2.21 corresponding to H-5 protons, a triplet at 1.54 due to an olefinic methyl, a broad singlet at 1.35–1.25 due to the hydroxy proton, and three singlets at 1.03, 0.97, and 0.91 ppm corresponding to three tertiary methyl groups in the ^{1}H NMR spectrum established the structure of triquinane **17**. The 15 line ^{13}C NMR spectrum with characteristic carbon resonances, a quaternary carbon at δ 145.6 (C-10) and three methine resonances at 139.2 (C-3), 125.7, and 123.6 (C-4 and C-11) due to the carbons of the two olefinic groups, a quaternary carbon signal at 90.7 due to the hydroxy bearing carbon, two quaternary carbons at 59.3 (C-2) and 46.5 (C-9), two methine resonances at 57.0 (C-1) and 54.0 (C-8), two methylenes at 43.9 and 41.7, and four methyl signals at 28.1, 22.3, 21.4 and 12.8 ppm confirmed the structure of triquinane **17**.

After successfully accomplishing the synthesis of a *cis*, *syn*, *cis*-triquinane **17**, the synthesis of a *cis*, *anti*, *cis*-triquinane **6*cac*** was investigated. It was obvious that the presence of the vinyl and allyl groups on the *exo*-face of the diquinane moiety would lead to *cis*, *anti*, *cis*-triquinane, Scheme 3. Accordingly, the route was modified and an allyl group was introduced at the C-2 position of the diquinane ester, as the alkylation of the β-keto ester **8** results in preferential *exo* substitution. Thus, the treatment of β-keto ester **8** with potassium carbonate and allyl bromide in refluxing acetone furnished allylated compound **18** in a highly stereoselective manner. A three step protocol was employed for the protection of the ester moiety in **18** as the MOM ether of the corresponding primary alcohol. The reduction of keto ester **18** with an excess of LAH furnished a 2:1 diastereomeric mixture of diol **19**. The primary alcohol in diol **19** was regioselectively protected as its MOM ether by reaction

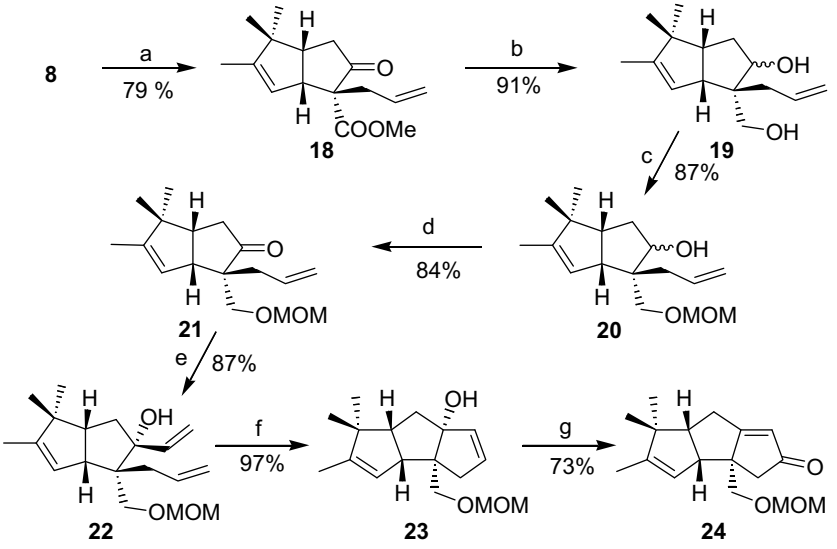


9 **10** **8** **7**

Scheme 1.



Scheme 2. Reagents: (a) $SnCl_2{\cdot}2H_2O$, N_2CHCO_2Me, CH_2Cl_2; (b) TsN_3, NEt_3, CH_3CN; (c) $Rh_2(OAc)_4$, CH_2Cl_2; (d) K_2CO_3, acetone, MeI; (e) LAH, Et_2O; (f) PCC, silica gel, CH_2Cl_2; (g) $Ph_3P{=}CH_2$, C_6H_6; (h) Zn, $BrCH_2CH{=}CH_2$, THF,))); (i) $Cl_2(PCy_3)_2Ru{=}CHPh$ (5 mol %), CH_2Cl_2.



Scheme 3. Reagents: (a) K_2CO_3, acetone, $BrCH_2CH{=}CH_2$; (b) LAH, Et_2O; (c) MOMCl, $^{i}Pr_2NEt$, DMAP; (d) PDC, CH_2Cl_2; (e) $CH_2{=}CHMgBr$, $CeCl_3$, THF; (f) $Cl_2(PCy_3)_2Ru{=}CHPh$ (5 mol %), CH_2Cl_2; (g) PCC, silica gel, CH_2Cl_2.

with methoxymethyl chloride, ethyldiisopropylamine, and 4-*N*,*N*-dimethylaminopyridine (DMAP) in methylene chloride to furnish an epimeric mixture of the MOM ether **20**. Oxidation of the secondary alcohol with pyridinium dichromate (PDC) in methylene chloride transformed the epimeric mixture of the MOM ether **20** into the keto ether **21**. Reaction of the bicyclic ketone **21** with vinylmagnesium bromide in the presence of anhydrous cerium chloride furnished the RCM precursor, hydroxydiene **22** in a highly stereoselective manner (>95%). Finally, the reaction of hydroxydiene **22** was carried out with 5 mol% of Grubbs' first generation catalyst in methylene chloride (0.05 M) for 5 h at room temperature to furnish the *cis*, *anti*, *cis*-triquinane **23** in quantitative yield. The sterically crowded polyfunctional triquinane **23** containing a tertiary allyl alcohol moiety was found to be very stable, and underwent a 1,3-transposition[10] on oxidation with PCC and silica gel in methylene chloride for eleven hours at room temperature to furnish triquinane enone **24**. The structures of triquinanes **23** and **24** were established from their spectral data.

3. Conclusion

In conclusion, we have accomplished efficient enantioselective syntheses of both *cis*, *syn*, *cis*- and *cis*, *anti*, *cis*-triquinanes **17** and **23**, starting from (*S*)-campholenaldehyde **7**, employing an RCM-based cyclopentannulation of diquinane **8**. Triquinanes **17** and **23** were obtained in six steps each, in overall yields of 25% and 44%, respectively, from

the keto ester **8** (obtained from campholenaldehyde in three steps in 72% yield). Extension of the methodology for the enantioselective synthesis of triquinane-based natural products is currently under investigation.

4. Experimental

IR spectra were recorded on a Jasco FTIR 410 spectrophotometer. ^{1}H (300 and 400 MHz) and ^{13}C (75 and 100 MHz) NMR spectra were recorded on JEOL JNM λ-300 and Brucker Avance 400 spectrometers. The chemical shifts (δ ppm) and coupling constants (Hertz) 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, the nature of carbons (C, CH, CH_2, CH_3) was determined by recording the DEPT-135 spectra, and is given in parentheses. High-resolution mass spectra were recorded using Micromass Q-TOF micro mass spectrometer using electron spray ionization mode. Optical rotations were measured using a Jasco DIP-370 digital polarimeter and $[\alpha]_D$ values are given in units of 10^{-1} deg cm^2 g^{-1}.

4.1. (1*R*,4*S*,5*R*)-4-Hydroxymethyl-4,7,8,8-tetramethylbicyclo[3.3.0]oct-6-en-3-ol 13

To a cold (0 °C) magnetically stirred solution of the keto ester[6] **11** (170 mg, 0.72 mmol) in dry ether (5 mL) was added LAH (82 mg, 2.16 mmol) and the reaction mixture was stirred at the same temperature for 2 h. Ethyl acetate (1 mL) was carefully added to the reaction mixture to consume the excess reagent and the reaction was quenched with ice cold water (0.3 mL). The suspension was filtered through a sintered funnel and the residue was thoroughly washed with ether (3 × 5 mL). The ether layer was washed with brine and dried over Na_2SO_4. Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate–hexane (1:3) as an eluent furnished the minor diol **13a** (70 mg, 46%) as an oil. $[\alpha]_D^{25} = -20.0$ (*c* 1.5, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3366, 3034, 1459, 1374, 1360, 1253, 1214, 1147, 1100, 1043, 1014, 871, 839; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.20 (1H, br s, H-6), 3.81 and 3.43 (2H, 2 × d, *J* 11.4 Hz, C*H*$_2$OH), 3.73 (1H, t, *J* 6.3 Hz, H-3), 2.90–2.70 (2H, m, 2 × OH), 2.70 (1H, dt, *J* 7.8 and 2.1 Hz), 2.29 (1H, q, *J* 8.4 Hz), 2.05–1.80 (1H, m), 1.69 (1H, dt, *J* 13.2 and 7.5 Hz), 1.56 (3H, t, *J* 1.5 Hz, olefinic CH_3), 1.04 (3H, s), 0.97 (3H, s) and 0.95 (3H, s) [3 × *tert*-CH_3]; ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.4 (C, C-7), 122.7 (CH, C-6), 82.2 (CH, C-3), 66.6 (CH_2, CH_2OH), 56.0 (CH), 49.9 (CH), 47.3 (C), 47.0 (C), 35.9 (CH_2, C-2), 28.8 (CH_3), 24.3 (CH_3), 22.2 (CH_3), 12.6 (CH_3); HRMS: *m*/*z*: (M+Na) calcd for $C_{13}H_{22}O_2Na$, 233.1517; found, 233.1523.

Further elution of the column with ethyl acetate–hexane (2:5) furnished the major diol **13b** (78 mg, 52%) as a solid, which was recrystallized from methanol. Mp: 82–83 °C; $[\alpha]_D^{24} = -11.2$ (*c* 3.3, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3367, 3035, 1460, 1375, 1360, 1261, 1221, 1167, 1099, 1078, 1043, 1014, 872, 841, 792; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.04 (1H, br s, H-6), 3.92 (1H, dd, *J* 9.3 and 7.5 Hz, H-3), 3.73 and 3.66 (2H, 2 × d, *J* 10.2 Hz, C*H*$_2$OH), 2.81 (1H, dt, *J* 7.8 and 2.7 Hz), 2.46 (1H, ddd, *J* 10.5, 7.5 and 3.0 Hz), 2.20–1.90 (3H, m), 1.70–1.55 (1H, m), 1.57 (3H, s, olefinic CH_3), 1.04 (3H, s), 0.99 (3H, s) and 0.96 (3H, s) [3 × *tert*-CH_3]; ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.0 (C, C-7), 121.5 (CH, C-6), 78.2 (CH, C-3), 70.5 (CH_2, CH_2OH), 55.8 (CH), 48.7 (CH), 47.2 (2C, C, C-4 and C-8), 33.7 (CH_2, C-2), 29.3 (CH_3), 22.7 (CH_3), 17.3 (CH_3), 12.7 (CH_3); HRMS *m*/*z*: (M+Na) calcd for $C_{13}H_{22}O_2Na$, 233.1517; found, 233.1521; Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 73.92; H, 10.32.

4.2. (1*R*,2*S*,5*R*)-3-Oxo-2,6,6,7-tetramethylbicyclo[3.3.0]oct-7-ene-2-carboxaldehyde 14

To a magnetically stirred solution of a mixture of diols **13** (148 mg, 0.70 mmol) in anhydrous CH_2Cl_2 (3 mL) were added a homogeneous mixture of PCC (760 mg, 3.52 mmol) and silica gel (760 mg) in one portion and stirred for 4 h at rt. The reaction mixture was filtered through a small silica gel column using more CH_2Cl_2. Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate–hexane (1:4) as eluent furnished keto aldehyde **14** (138 mg, 95%) as an oil; $[\alpha]_D^{25} = -51.5$ (*c* 1.3, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3037, 2729, 1741, 1716, 1454, 1387, 1365, 1302, 1263, 1227, 1173, 1113, 1074; ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.63 (1H, s, H–C=O), 5.27 (1H, br s, H-8), 3.25–3.15 (1H, m, H-1), 2.63–2.55 (1H, m, H-5), 2.50–2.30 (2H, m, H-4), 1.63 (3H, s, olefinic CH_3), 1.25 (3H, s), 1.06 (3H, s) and 1.03 (3H, s) [3 × *tert*-CH_3]; ^{13}C NMR (75 MHz, $CDCl_3$): δ 215.4 (C, C=O), 200.3 (CH, HC=O), 149.4 (C, C-7), 120.7 (CH, C-8), 64.0 (C, C-2), 54.6 (CH, C-1), 48.0 (CH, C-5), 47.3 (C, C-6), 39.5 (CH_2, C-4), 26.4 (CH_3), 21.7 (CH_3), 19.6 (CH_3), 12.7 (CH_3).

4.3. (1*R*,4*R*,5*R*)-4,7,8,8-Tetramethyl-4-vinylbicyclo-[3.3.0]oct-6-en-3-one 15

To a freshly prepared ^{t}AmO$^-$K$^+$ [prepared from potassium (60 mg, 1.5 mmol) and *t*-amyl alcohol (3 mL) followed by the evaporation of the excess *t*-amyl alcohol under reduced pressure] in dry benzene (5 mL) was added methyltriphenylphosphonium iodide (706 mg, 1.75 mmol) and the reaction mixture was stirred at rt for 30 min. The resultant yellow color solution was allowed to settle. The solution of methylenetriphenylphosphorane was added to a magnetically stirred solution of the keto aldehyde **14** (120 mg, 0.60 mmol) in dry benzene (1 mL) at 0 °C and stirred for 1 min. The reaction was quenched with aq NH_4Cl solution and extracted with ether (3 × 5 mL). The combined organic layer was washed with brine and dried over Na_2SO_4. Evaporation of the solvent and purification of the residue over a silica gel column using CH_2Cl_2–hexane (1:4) as eluent furnished ketone **15** (107 mg, 90%) as an oil; $[\alpha]_D^{27} = -30.0$ (*c* 0.6, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 1740, 1647, 1456, 1375, 1363, 1167, 1113, 1080, 1022, 995, 910; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.87 (1H, dd, *J* 17.7 and 11.1 Hz, *H*C=CH$_2$), 5.21 (1H, dd, *J* 10.8 and 1.2 Hz, HC=C*H*$_2$, *cis*), 5.19 (1H, br s, H-6), 5.13 (1H, dd, *J* 17.7 and 1.2 Hz, HC=C*H*$_2$, *trans*), 3.10–3.00 (1H, m, H-5), 2.53 (1H, td, *J* 9.3 and 6.0 Hz, H-1), 2.35 and 2.23 (2H,

2 × dd, *J* 18.9 and 9.3 Hz, H-2), 1.60 (3H, t, *J* 1.5 Hz, olefinic CH_3), 1.16 (3H, s), 1.06 (3H, s) and 1.01 (3H, s) [3 × *tert*-CH_3]; ^{13}C NMR (75 MHz, $CDCl_3$): δ 219.0 (C, C=O), 148.1 (C, C-7), 138.8 (CH, H*C*=CH_2), 122.8 (CH, C-6), 115.4 (CH_2, *C*H_2=CH), 56.9 (CH, C-5), 55.2 (C, C-4), 47.8 (CH, C-1), 47.7 (C, C-8), 38.6 (CH_2, C-2), 26.4 (CH_3), 23.2 (CH_3), 21.8 (CH_3), 12.8 (CH_3); HRMS *m*/*z*: (M+Na) calcd for $C_{14}H_{20}ONa$, 227.1412; found, 227.1409.

4.4. (1*R*,3*S*,4*R*,5*R*) and (1*R*,3*R*,4*R*,5*R*)-4,7,8,8-Tetramethyl-3-(2-propenyl)-4-vinylbicyclo[3.3.0]oct-6-en-3-ols 16a and 16b

To a suspension of zinc (105 mg, 1.6 mmol) in anhydrous THF (1 mL) in a round bottom flask, placed in an ultrasonic cleaning bath, was added a solution of ketone **15** (65 mg, 0.32 mmol) and allyl bromide (0.11 mL, 1.6 mmol) in dry THF (4 mL) and the reaction mixture was sonochemically irradiated for 30 min. The reaction was quenched with saturated aqueous NH_4Cl and extracted with ether (3 × 5 mL). The combined organic layer was washed with brine and dried over 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 first furnished the *endo*-tertiary alcohol **16a** (43 mg, 56%) as an oil. $[\alpha]_D^{23} = -19.2$ (*c* 1.2, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3532, 3077, 3033, 1638, 1439, 1414, 1373, 1361, 1266, 1251, 1218, 1197, 1156, 1091, 1037, 1000, 911, 884, 843, 740; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.31 (1H, dd, *J* 17.7 and 11.1 Hz, *H*C=CH_2), 6.00–5.80 (1H, m, H-2′), 5.43 (1H, s, H-6), 5.25–4.95 (4H, m, 2 × HC=C*H*$_2$), 2.88 (1H, dt, *J* 7.2 and 2.7 Hz), 2.45 (1H, ddd, *J* 11.1. 6.9 and 3.9 Hz), 2.40–1.80 (5H, m), 1.61 (3H, s, olefinic CH_3), 1.06 (3H, s), 1.03 (3H, s) and 1.01 (3H, s) [3 × *tert*-CH_3]; ^{13}C NMR (75 MHz, $CDCl_3$): δ 149.6 (C, C-7), 141.7 (CH, H*C*=CH_2), 135.4 (CH, C-2′), 126.1 (CH, C-6), 116.6 (CH_2), 114.3 (CH_2), 84.9 (C, C-3), 61.4 (CH, C-5), 54.0 (C, C-4), 50.3 (CH, C-1), 48.0 (C, C-8), 40.3 (CH_2), 39.8 (CH_2), 29.4 (CH_3), 23.2 (CH_3), 22.4 (CH_3), 12.7 (CH_3); HRMS *m*/*z*: (M+Na) calcd for $C_{17}H_{26}ONa$, 269.1881; found, 269.1873.

Further elution of the column with ethyl acetate–hexane (1:19) furnished the *exo*-tertiary alcohol **16b** (30 mg, 38%) as an oil. $[\alpha]_D^{22} = -31.4$ (*c* 0.7, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3492, 3080, 3033, 1636, 1465, 1439, 1413, 1372, 1360, 1253, 1097, 1003, 911, 882, 843; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.83 (1H, ddt, *J* 17.4, 9.9 and 7.2 Hz, H-2′), 5.63 (1H, dd, *J* 17.7 and 10.8 Hz, *H*C=CH_2), 5.15–4.90 (5H, m), 2.99 (1H, dt, *J* 5.7 and 2.1 Hz, H-5), 2.66 (1H, q, *J* 9.1 Hz, H-1), 2.08 (2H, d, *J* 7.2 Hz, H-1′), 1.66 (1H, s), 1.70–1.50 (2H, m, H-2), 1.57 (3H, t, *J* 1.8 Hz, olefinic CH_3), 1.14 (3H, s), 1.02 (3H, s) and 0.95 (3H, s) [3 × *tert*-CH_3]; ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.7 (C, C-7), 144.0 (CH, H*C*=CH_2), 134.6 (CH, C-2′), 124.1 (CH, C-6), 118.8 (CH_2, C-3′), 111.2 (CH_2, HC=*C*H_2), 84.3 (C, C-3), 59.4 (CH, C-5), 52.5 (C, C-4), 51.5 (CH, C-1), 46.2 (C, C-8), 41.3 (CH_2), 39.4 (CH_2), 29.9 (CH_3), 22.1 (CH_3), 17.9 (CH_3), 12.5 (CH_3); HRMS *m*/*z*: (M+Na) calcd for $C_{17}H_{26}ONa$, 269.1881; found, 269.1889.

4.5. (1*R*,2*R*,6*R*,8*R*)-2,9,9,10-Tetramethyltricyclo-[6.3.0.0^{2,6}]undeca-3,10-dien-6-ol 17

To a magnetically stirred solution of tertiary alcohol **16b** (35 mg, 0.14 mmol) in anhydrous CH_2Cl_2 (1.5 mL, 0.1 M) was added Grubbs' first generation catalyst (6 mg, 5 mol %, 0.007 mmol) and the reaction mixture was stirred at rt for 30 min. Evaporation of the solvent under reduced pressure and purification of the residue over a silica gel column using ethyl acetate–hexane (1:9) as eluent furnished triquinane **17** (31 mg, 100%) as an oil. $[\alpha]_D^{23} = -24.0$ (*c* 0.5, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3419, 3047, 1448, 1374, 1360, 1295, 1271, 1203, 1154, 1112, 1072, 1051, 1020, 962, 934, 916, 890, 851, 822, 759, 741, 713; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.63–5.60 (1H, m) and 5.40–5.38 (1H, m) [H-3 and H-4], 5.11 (1H, br s, H-11), 2.85–2.72 (1H, m, H-1), 2.54 (1H, dt, *J* 12.0 and 7.5 Hz, H-8), 2.43 (1H, dm, *J* 16.2 Hz) and 2.21 (1H, d, *J* 16.2 Hz) [H-5], 1.70–1.50 (2H, m, H-7), 1.54 (3H, t, *J* 1.5 Hz, olefinic CH_3), 1.35–1.25 (1H, br s), 1.03 (3H, s), 0.97 (3H, s) and 0.91 (3H, s) [3 × *tert*-CH_3]; ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.6 (C, C-10), 139.2 (CH, C-3), 125.7 (CH, C-4), 123.6 (CH, C-11), 90.7 (C, C-6), 59.3 (C, C-2), 57.0 (CH, C-1), 54.0 (CH, C-8), 46.5 (C, C-9), 43.9 (CH_2), 41.7 (CH_2), 28.1 (CH_3), 22.3 (CH_3), 21.4 (CH_3), 12.8 (CH_3); HRMS *m*/*z*: (M+H) calcd for $C_{15}H_{23}O$, 219.1749; found, 219.1744.

4.6. Methyl (1*R*,2*R*,5*R*)-2-(prop-2-enyl)-6,6,7-trimethylbicyclo[3.3.0]oct-7-ene-2-carboxylate 18

To a solution of β-keto ester **8** (210 mg, 0.89 mmol) in acetone (3 mL) were added K_2CO_3 (1.23 g, 8.9 mmol) and allyl bromide (0.76 mL, 8.9 mmol) and refluxed for 5 h. It was cooled to rt, diluted with water (5 mL) and extracted with ether (3 × 5 mL). The combined organic layer was washed with brine (5 mL), and dried over 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 α-allyl-β-keto ester **18** (198 mg, 79%) as an oil. $[\alpha]_D^{24} = +186.1$ (*c* 6.1, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3079, 3037, 1748, 1732, 1640, 1436, 1231, 920; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.67 (1H, ddt, *J* 19.2, 10.4 and 7.2 Hz, *H*C=CH_2), 5.09 (1H, d, *J* 10.4 Hz) and 5.08 (1H, d, *J* 19.4 Hz) [HC=C*H*$_2$], 4.92 (1H, br s, H-8), 3.66 (3H, s, OCH_3), 3.32 (1H, br s, H-1), 2.60–2.15 (5H, m), 1.59 (3H, s, olefinic CH_3), 1.02 (3H, s) and 0.97 (3H, s) [2 × *tert*-CH_3]; ^{13}C NMR (100 MHz, $CDCl_3$): δ 213.1 (C, C=O), 171.2 (C, OC=O), 147.9 (C, C-7), 132.8 (CH, H*C*=CH_2), 122.3 (CH, C-8), 119.3 (CH_2, HC=*C*H_2), 62.1 (C, C-2), 53.2 (CH_3, OCH_3), 51.7 (CH), 48.2 (CH), 47.7 (C, C-6), 41.0 (CH_2), 39.4 (CH_2), 26.6 (CH_3), 21.6 (CH_3), 12.6 (CH_3); HRMS *m*/*z*: (M+Na) calcd for $C_{16}H_{22}O_3Na$, 285.1467; found, 285.1476.

4.7. (1*R*,4*S*,5*R*)-7,7,8-Trimethyl-4-hydroxymethyl-4-(prop-2-enyl)bicyclo[3.3.0]oct-6-en-3-ol 19

To a cold (0 °C) magnetically stirred solution of β-keto ester **18** (150 mg, 0.57 mmol) in dry ether (4 mL) was added LAH (109 mg, 2.86 mmol) and the reaction mixture was stirred at the same temperature for 2 h. Ethyl acetate

(0.3 mL) was carefully added to the reaction mixture to consume the excess reagent and the reaction was quenched with 3 M HCl (5 mL) and extracted with ether (3 × 5 mL). The ether layer was washed with brine (5 mL) and dried over Na_2SO_4. Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate–hexane (1:3) as eluent furnished a 1:2 mixture of diol **19** (123 mg, 91%) as an oil. Less polar diol **19a**: $[\alpha]_D^{22} = +60.3$ (*c* 2.1, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3354, 3075, 3034, 1639, 1460, 1438, 1361, 1225, 1094, 1065, 1052, 1027, 913; ^1H NMR (400 MHz, $CDCl_3$): δ 5.89 (1H, ddt, *J* 16.8, 10.0 and 7.2 Hz, *H*C=CH_2), 5.13–5.02 (3H, m), 3.85–3.81 (1H, m, H-3), 3.76 and 3.51 (2H, 2 × d, *J* 11.4 Hz, C*H*$_2$OH), 2.85–2.80 (1H, m), 2.46 (1H, dd, *J* 13.4 and 7.2 Hz), 2.19 (1H, q, *J* 7.9 Hz), 1.98 (1H, dd, *J* 13.4 and 7.4 Hz), 1.95–1.85 (1H, m), 1.72–1.64 (1H, m), 1.56 (3H, s, olefinic CH_3), 0.98 (3H, s) and 0.97 (3H, s) [2 × *tert*-CH_3]; ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.0 (C), 135.1 (CH), 122.2 (CH), 117.7 (CH_2), 81.6 (CH, C-3), 64.4 (CH_2, CH_2OH), 52.9 (CH), 49.2 (CH), 48.8 (C), 46.8 (C), 41.4 (CH_2, C-1′), 35.7 (CH_2, C-2), 28.6 (CH_3), 21.9 (CH_3), 12.5 (CH_3); HRMS *m*/*z*: (M+Na) calcd for $C_{15}H_{24}O_2Na$, 259.1674; found, 259.1676. More polar diol **19b**: $[\alpha]_D^{23} = -25.5$ (*c* 2.2, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3335, 3073, 3028, 1637, 1466, 1435, 1376, 1179, 1111, 1031, 1021, 998, 913, 894, 837; ^1H NMR (300 MHz, $CDCl_3$): δ 5.94 (1H, ddt, *J* 16.8, 9.9 and 7.8 Hz, C*H*=CH_2), 5.14 (1H, *J* 16.8 Hz) and 5.10 (1H, d, *J* 9.6 Hz) [HC=C*H*$_2$], 4.95 (1H, s, H-6), 4.00 (1H, t, *J* 7.8 Hz), 3.72 and 3.52 (2H, 2 × d, *J* 10.5 Hz, C*H*$_2$OH), 3.00–2.94 (1H, m), 2.70–2.40 (3H, m), 2.05–1.85 (2H, m), 1.68–1.57 (1H, m), 1.57 (3H, s, olefinic CH_3), 1.00 (3H, s) and 0.98 (3H, s) [2 × *tert*-CH_3]; ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.6 (C, C-7), 135.9 (CH), 121.6 (CH, C-6), 117.7 (CH_2, C-3′), 79.3 (CH, C-3), 67.4 (CH_2, CH_2OH), 52.4 (CH), 50.3 (C), 49.6 (CH), 47.1 (C), 34.0 (CH_2, C-2), 33.9 (CH_2), 29.4 (CH_3), 22.7 (CH_3), 12.8 (CH_3); HRMS *m*/*z*: (M+Na) calcd for $C_{15}H_{24}O_2Na$, 259.1674; found, 259.1675.

4.8. (1*R*,4*S*,5*R*)-6,6,7-Trimethyl-2-(methoxymethoxymethyl)-2-(prop-2-enyl)bicyclo[3.3.0]oct-7-en-3-one 21

To a magnetically stirred ice cold solution of diol **19** (110 mg, 0.47 mmol) in CH_2Cl_2 (1 mL) were added DIPEA (0.82 mL, 4.70 mmol), DMAP (10 mg), and methoxymethyl chloride (0.1 mL, 0.94 mmol) sequentially and the reaction mixture was stirred for 1 h at the same temperature. Water (3 mL) was added to the reaction mixture and extracted with CH_2Cl_2 (2 × 5 mL). The combined CH_2Cl_2 layer was washed with brine (5 mL) and dried over Na_2SO_4. Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate–hexane (1:6) as eluent furnished a 1:2 mixture of the mono methoxymethyl ether **20** (117 mg, 87%) as an oil. To a magnetically stirred solution of the alcohol **20** (60 mg, 0.232 mmol) in anhydrous CH_2Cl_2 (2 mL) was added PDC (872 mg, 2.32 mmol) and stirred vigorously for 8.5 h at rt. The reaction mixture was then filtered through a small silica gel column and the column was eluted with more CH_2Cl_2. Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate–hexane (1:19) as eluent furnished ketone **21** (51 mg, 84%) as an oil. $[\alpha]_D^{22} = +133.0$ (*c* 3.6, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3078, 3047, 1734, 1640, 1466, 1440, 1217, 1172, 1150, 1109, 1045, 997, 918; ^1H NMR (400 MHz, $CDCl_3$): δ 5.74–5.64 (1H, m, *H*C=CH_2), 5.18 (1H, s, H-6), 5.03 (1H, d, *J* 11.0 Hz) and 5.02 (1H, d, *J* 15.7 Hz) [HC=C*H*$_2$], 4.54 (2H, s, OCH_2O), 3.54 and 3.42 (2H, 2 × d, *J* 9.8 Hz, OCH_2), 3.32 (3H, s, OCH_3), 3.20–3.14 (1H, m), 2.50–2.17 (5H, m), 1.59 (3H, s, olefinic CH_3), 1.03 (3H, s) and 0.97 (3H, s) [2 × *tert*-CH_3]; ^{13}C NMR (100 MHz, $CDCl_3$): δ 218.3 (C=O), 147.5 (C-7), 133.5 (H*C*=CH_2), 122.6 (C-6), 118.3 (HC=*C*H_2), 96.8 (OCH_2O), 69.2 (OCH_2), 56.2, 55.3, 52.8, 47.8, 47.5, 39.6 (2 C), 26.6, 21.8, 12.7; HRMS *m*/*z*: (M+Na) calcd for $C_{17}H_{26}O_3Na$, 301.1780; found, 301.1776.

4.9. (1*R*,3*S*,4*S*,5*R*)-7,8,8-Trimethyl-4-(methoxymethoxymethyl)-4-(prop-2-enyl)-3-vinylbicyclo[3.3.0]oct-6-en-3-ol 22

Cerium chloride heptahydrate (536 mg, 1.44 mmol) was dried at 150–160 °C and 0.05 Torr for 3.5 h and blanketed with nitrogen while being cooled. Dry THF (1 mL) was introduced and the slurry was stirred for 10 min at rt. A solution of ketone **21** (40 mg, 0.144 mmol) in dry THF (1.5 mL) was added to the reaction mixture and stirred for 25 min at 0 °C. To a solution of vinylmagnesium bromide in dry THF [freshly prepared from vinyl bromide (0.1 mL, 1.44 mmol), and magnesium (35 mg, 1.44 mmol) in dry THF (4 mL)] was added the above reaction mixture and stirred for 1 h at rt. The reaction mixture was then quenched with satd aq NH_4Cl (5 mL) and extracted with ether (3 × 5 mL). The combined organic layer was washed with brine (5 mL) and dried over 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 tertiary alcohol **22** (37 mg, 87%) as an oil. $[\alpha]_D^{23} = +87.6$ ($CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3518, 3076, 1638, 1440, 1418, 1361, 1154, 1108, 1046, 1000, 917; ^1H NMR (400 MHz, $CDCl_3$): δ 5.95 (1H, dd, *J* 17.1 and 10.8 Hz), 5.91–5.80 (1H, m), 5.27 (1H, dd, *J* 17.1 and 1.6 Hz), 5.18 (1H, s, H-6), 5.10-4.98 (3H, m), 4.60 and 4.54 (2H, 2 × d, *J* 6.5 Hz, OCH_2O), 3.69 and 3.50 (2H, 2 × d, *J* 10.0 Hz, OCH_2), 3.35 (3H, s, OCH_3), 3.19 (1H, br s, OH), 3.07 (1H, dm, *J* 8.2 Hz), 2.50–2.35 (2H, m), 2.04 (1H, dd, *J* 14.1 and 10.2 Hz), 1.91 (1H, dd, *J* 14.2 and 6.9 Hz) 1.87 (1H, dd, *J* 13.7 and 8.0 Hz), 1.59 (3H, s, olefinic CH_3), 1.02 (3H, s) and 1.01 (3H, s) [2 × *tert*-CH_3]; ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.3 (C, C-7), 140.2 (CH), 135.8 (CH), 123.8 (CH, C-6), 117.3 (CH_2), 112.9 (CH), 96.9 (CH_2, OCH_2O), 85.6 (C, C-3), 68.7 (CH_2, OCH_2), 55.5 (CH_3, OCH_3), 54.5 (CH), 53.2 (C), 49.6 (CH), 47.3 (C), 40.4 (CH_2), 38.7 (CH_2), 29.9 (CH_3), 22.8 (CH_3), 12.6 (CH_3); HRMS *m*/*z*: (M+Na) calcd for $C_{19}H_{30}O_3Na$, 329.2093; found, 329.2080.

4.10. (1*R*,2*S*,6*R*,8*R*)-9,9,10-Trimethyl-2-(methoxymethoxymethyl)tricyclo[6.3.0.0^{2,6}]undeca-4,10-dien-6-ol 23

To a magnetically stirred solution of tertiary alcohol **22** (17 mg, 0.07 mmol) in anhydrous CH_2Cl_2 (7 mL, 0.05 M) was added Grubbs' first generation catalyst (4 mg, 5 mol %) and the reaction mixture was stirred at rt for

5 h. Catalyst was filtered-off through a small silica gel column using excess CH_2Cl_2 (15 mL). Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate–hexane (1:9) as eluent furnished triquinane **23** (16 mg, 97%) as an oil. $[\alpha]_D^{23} = +108.9$ (*c* 1.4, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3446, 3048, 1469, 1441, 1375, 1362, 1145, 1108, 1070, 1046, 919, 736; ^1H NMR (400 MHz, $CDCl_3$): δ 5.80 (1H, dt, *J* 5.6 and 2.8 Hz, H-5), 5.46 (1H, dt, *J* 5.6 and 2.8 Hz, H-4), 5.22 (1H, s, H-11), 4.63 and 4.59 (2H, 2 × d, *J* 6.5 Hz, OCH_2O), 3.71 and 3.58 (2H, 2 × d, *J* 9.3 Hz, OCH_2), 3.36 (3H, s, OCH_3), 2.89 (1H, td, *J* 17.3 and 2.3 Hz), 2.82–2.78 (1H, m), 2.16 (1H, d, *J* 17.2 Hz), 2.10–2.00 (1H, m), 1.87 (1H, t, *J* 11.8 Hz), 1.79 (1H, dd, *J* 12.2 and 7.0 Hz), 1.56 (3H, s, olefinic CH_3), 0.94 (3H, s) and 0.92 (3H, s) [2 × *tert*-CH_3]; ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.1 (C, C-10), 136.4 (CH, C-5), 132.2 (CH, C-4), 123.1 (CH, C-11), 96.9 (CH_2, OCH_2O), 94.6 (C, C-6), 70.9 (CH_2, OCH_2), 60.0 (CH_3, OCH_3), 55.5 (CH), 52.44 (CH), 52.4 (C, C-2), 46.9 (C, C-9), 46.1 (CH_2), 39.3 (CH_2), 26.6 (CH_3), 21.1 (CH_3), 12.6 (CH_3); HRMS *m*/*z*: (M+Na) calcd for $C_{17}H_{26}O_3Na$, 301.1780; found, 301.1780.

4.11. (1*R*,2*R*,8*R*)-9,9,10-Trimethyl-2-(methoxymethoxymethyl)tricyclo[6.3.0.0^{2,6}]undeca-5,10-dien-4-one 24

To a magnetically stirred solution of a mixture of the tertiary alcohol **23** (11 mg, 0.04 mmol) in anhydrous CH_2Cl_2 (1 mL) were added a homogeneous mixture of PCC (128 mg, 0.6 mmol) and silica gel (128 mg) in one portion and stirred for 11 h at rt. The reaction mixture was filtered through a small silica gel column using more CH_2Cl_2. Evaporation of the solvent and purification of the residue over a silica gel column using ethyl acetate–hexane (1:4) as eluent furnished keto aldehyde **24** (8 mg, 73%) as an oil. $[\alpha]_D^{23} = +52.6$ (*c* 0.7, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 1713, 1637, 1440, 1151, 1109, 1044, 917, 856; ^1H NMR (400 MHz, $CDCl_3$): δ 5.80 (1H, d, *J* 1.7 Hz), 5.26 (1H, s, H-11), 4.56 and 4.97 (2H, 2 × d, *J* 6.7 Hz, OCH_2O), 3.45 and 3.24 (2H, 2 × d, *J* 9.5 Hz, OCH_2), 3.30 (3H, s, OCH_3), 3.05–2.95 (1H, m, H-1), 2.69 and 2.19 (2H, 2 × d, *J* 17 Hz, H-3), 2.65–2.35 (3H, m), 1.65 (3H, s, olefinic CH_3), 0.84 (3H, s) and 0.68 (3H, s) [2 × *tert*-CH_3]; ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.5 (C, C=O), 187.0 (C, C-6), 148.8 (C, C-10), 124.8 (CH, C-11), 120.9 (CH, C-5), 96.4 (CH_2, OCH_2O), 70.0 (CH_2, OCH_2), 55.4 (2C, CH), 53.9 (CH_3, OMe), 53.8 (C, C-2), 49.5 (CH_2, C-3), 46.4 (C, C-9), 29.5 (CH_3), 29.3 (CH_2, C-7), 22.4 (CH_3), 12.6 (CH_3); HRMS *m*/*z*: (M+Na) calcd for $C_{17}H_{24}O_3Na$, 299.1623; found, 299.1636.

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