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Enantiospecific synthesis of angular triquinanes

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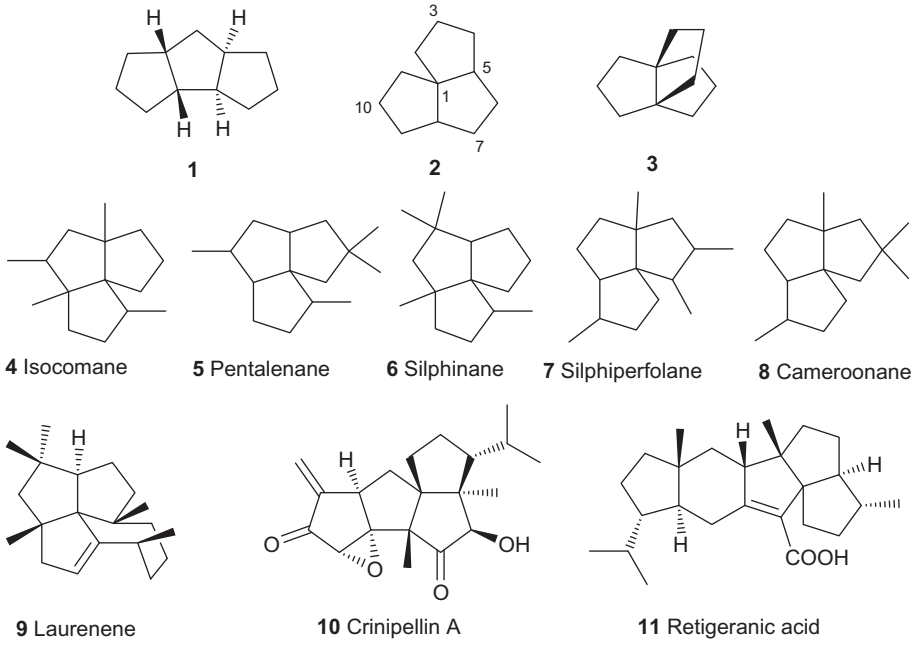
Dedicated to Professor R.V. Venkateswaran on the occasion of his 65th birthday

ABSTRACT

The enantiospecific synthesis of angular triquinanes has been developed starting from the readily available (*S*)-campholenaldehyde. Two alternate strategies have been used, one employing a Johnson's ortho-ester Claisen rearrangement followed by an intramolecular cyclopropanation and regioselective cyclopropane ring cleavage, and a second one based on a RCM reaction.

1. Introduction

The polycyclopentanoid natural products, commonly referred as polyquinanes, have aroused a great deal of interest among synthetic chemists in the last three decades.[1] Although the first polyquinane natural product was revealed to chemists only in the second half of the 20th century, a number of polyquinanes have been encountered since then among plant, marine, and microbial sources. So far, natural products containing up to four fused cyclopentanes have been revealed. Among the polyquinanes, triquinanes are the most commonly encountered in sesquiterpenes and are classified, according to ring fusion, as linear **1**, angular **2** or propellane **3**. The linear triquinanes bearing the thermodynamically favored *cis*, *anti*, *cis*-tricyclo[6.3.0.0^{2,6}]undecane **1** framework, and the angular triquinane **2** are the most abundant among natural polyquinanes. The sesquiterpene natural products containing an angular triquinane moiety, isolated so far fall into five different skeletal types **4**–**8** on the basis of the location of the four carbon substituents on the tricyclo[6.3.0.0^{1,5}]undecane **2**, and based on the biogenesis it is expected to discover new angular triquinane frameworks in the future. In addition, di- and sesterterpene natural products,[2] such as laurenene **9**, crinipellin **10,** and retigeranic acid



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11, also incorporate an angular triquinane unit in their core structures.

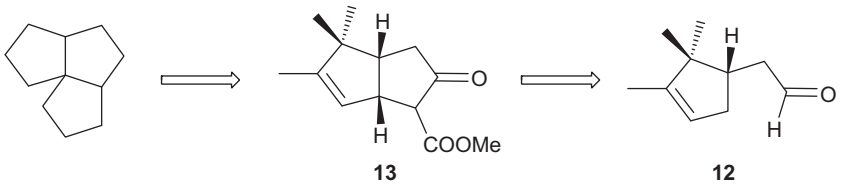
Among the readily available monoterpenes, pinenes are relatively less exploited as chirons in total synthesis.[3] As α-pinene is one of the most abundantly available monoterpenes, its conversion to a variety of enantiopure bi-and tricyclic compounds enhances the repertoire of synthetic chemists. Conversion of α-pinene into α-campholenaldehyde **12** via Lewis acid mediated rearrangement of the corresponding epoxide has been well established.[4] Although, it has been employed in the synthesis of a variety of industrially (fragrance) important monocyclic compounds, the utility of campholenaldehyde **12** in the synthesis of polycyclic compounds has not been explored to its full potential.[5] In this context, in our laboratory readily available α-campholenaldehyde **12** has been employed as the chiral starting material in the enantiospecific synthesis of a variety of functionalized bi- and tricyclic frameworks suitable for further elaboration into natural products and their analogues.[6] In a continuation of our interest in the synthesis of enantiopure compounds by employing a chiral pool approach,[6,7] we herein describe two strategies for the enantiospecific generation of angular triquinanes starting from the readily available (*S*)-campholenaldehyde **12**.

2. Results and discussion

Recently, we have reported[6a] the enantiospecific synthesis of the diquinane ester **13** starting from campholenadehyde **12** employing an intramolecular rhodium carbenoid CH insertion reaction.[8] It was contemplated that the diquinane ester **13** could be further elaborated into functionalised angular triquinanes (Scheme 1), and two alternate strategies have been conceived. One was based on a Johnson's orthoester Claisen rearrangement and intramolecular cyclopropanation-cyclopropane ring cleavage sequence, and the other one employing a ring-closing metathesis (RCM) reaction.

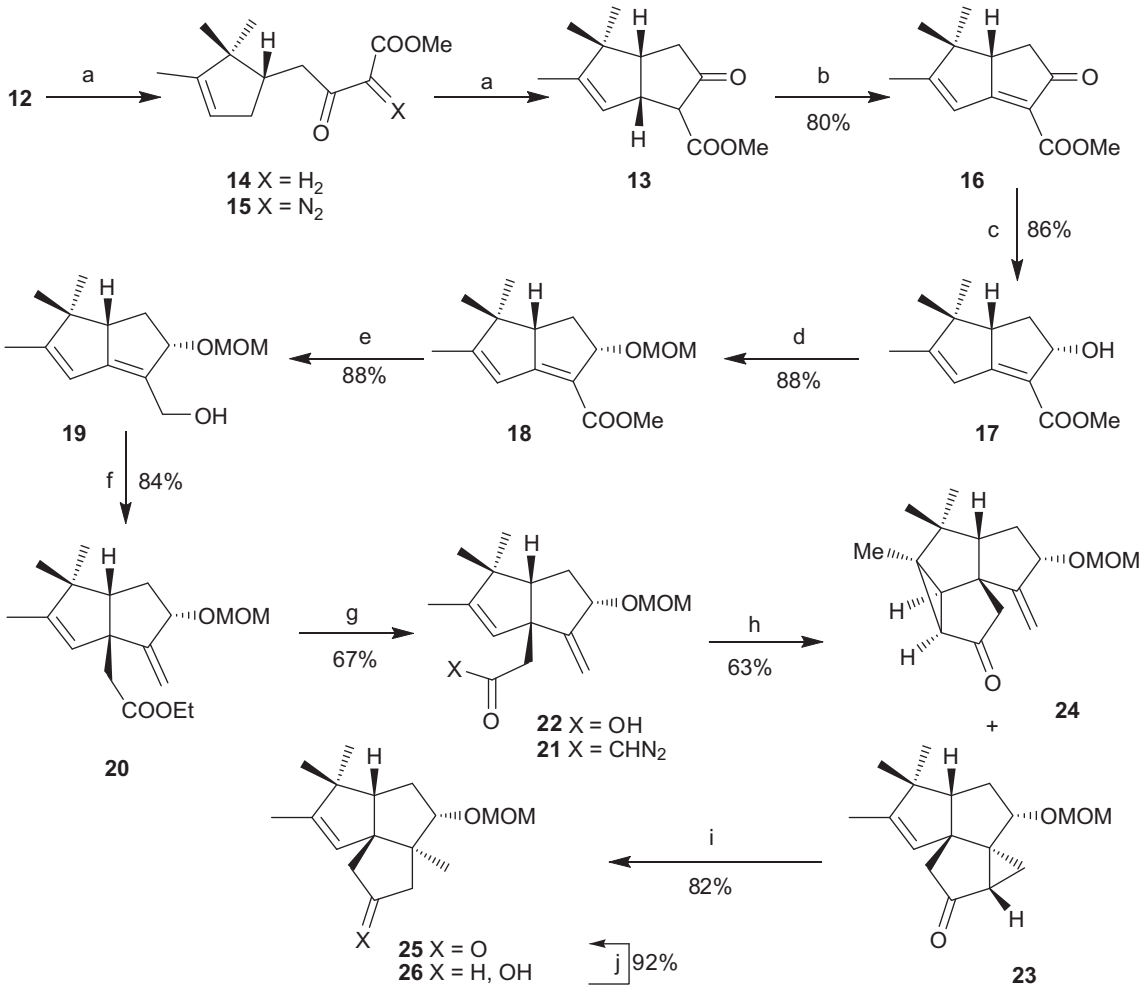
The synthetic sequences are depicted in Schemes 2 and 3. To begin with, the synthesis of the key intermediate of the sequence, the diquinane β-ketoester **13**, has been carried out by employing the earlier developed method.[6a] Thus, campholenaldehyde **12** was converted into the α-diazo-β-ketoester **15**, via stannous chloride mediated coupling with methyl diazoacetate, followed by a diazo transfer reaction on the β-keto ester **14**. Treatment of the diazo ester **15** with a catalytic amount of rhodium acetate furnished the diquinane **13** via insertion of the rhodium carbenoid into the allylic C–H bond in a highly regio- and stereoselective manner, which on selenation and deselenation generated the dienone ester **16**. Prior to the conversion of the ester in the diquinane **16** into a primary alcohol (a precursor for Claisen rearrangement), the ketone in **16** was masked. Thus, regio- and stereoselective Luche reduction of the dienone ester **16** with sodium borohydride and cerium trichloride heptahydrate furnished the secondary alcohol **17** in 86% yield. Treatment of alcohol **17** in methylene chloride with methoxymethyl chloride and ethyldiisopropylamine (DIPEA) in the presence of a catalytic amount of 4-*N*,*N*-dimethylaminopyridine (DMAP) furnished the MOM ether **18** in 88% yield. Low temperature reduction of the ester in **18** with lithium aluminum hydride (LAH) in ether generated the primary allyl alcohol **19** in 88% yield. The requisite quaternary carbon atom (C-1) required for the angular triquiane was created by a Claisen rearrangement. Thus, Johnson's orthoester Claisen rearrangement[9] of the allyl alcohol **19** with triethyl orthoacetate in the presence of a catalytic amount of propionic acid in a sealed tube at 180 °C furnished the diene ester **20** in 84% yield, whose structure was assigned based on the spectroscopic data. The stereochemistry of the newly created quaternary carbon atom was assigned on the basis of the thermodynamically preferred *cis* ring junction of two five membered rings. It is well established that γ,δ-unsaturated acids can be converted into bicyclo[3.1.0]hexanes via an intramolecular cyclopropanation of the corresponding diazoketone.[10] It is worth noting that the ester **20** has two olefins at the γ-position, a trisubstituted one in the ring, and an *exo* methylene group, for the possible cyclopropanation to take place via the diazoketone **21**, and that both would lead to angular triquinanes. Base mediated hydrolysis of the ester **20** generated the acid **22**, which was transformed into the diazoketone **21** via the corresponding acid chloride. Anhydrous copper sulfate–copper catalyzed decomposition of the diazoketone **21** in refluxing cyclohexane and insertion of the resultant carbenoid in either of the two olefins furnished a ~5:1 mixture of the tetracyclic ketones **23** and **24** in 63% yield, which were separated by column chromatography on silica gel impregnated with 10% silver nitrate. It is interesting to note that the intermediate carbenoid exhibited a preference to insert into the disubstituted olefin rather than the electron rich trisubstituted ring olefin, probably due to steric crowding in the transition state. The structures of the tetracyclic ketones **23** and **24** were established from their spectroscopic data, in particular, ^{1}H and ^{13}C NMR spectroscopy. The cyclopropane ring in the tetracyclic ketone **23** was cleaved in a regioselective manner by employing a solvated electron strategy, which is known to cleave the cyclopropane bond which has better overlap with the π system of the carbonyl group.[11] Thus, treatment of the compound **23** with lithium in liquid ammonia furnished a mixture of the triquinane ketone **25** and the alcohol **26**, in a highly regioselective manner. Subsequent oxidation with pyridinium dichromate (PDC) in methylene chloride transformed the alcohol **26** into the triquinane **25**.

Subsequently, an alternative strategy based on a RCM reaction was conceived *via* introduction of the vinyl and allyl groups at the C-1 and C-2 carbons, respectively, of the diquinane **13** (Scheme 3). Thus, reaction of the diquinane **16** with vinylmagnesium bromide in the presence of copper iodide furnished the β-ketoester **27** in 62% yield, which was found to exist as a mixture of keto and enol forms. Alkylation of the β-ketoester **27** with potassium carbonate and allyl bromide in refluxing acetone furnished mainly the O-allylated compound **28** in 90% yield, which on thermal activation underwent a Claisen rearrangement[12] to furnish a 2:1 mixture of the C-allylated β-ketoesters **29n** and **29x** in 98% yield, which were separated by column chromatography on silica gel. Structures of the *endo* and *exo* esters **29n** and **29x** were established from their spectroscopic data, and the stereochemistry at the newly created quaternary carbon was tentatively assigned on the basis of the preferred transition state in the Claisen rearrangement, which was confirmed by the facile RCM reaction[13] of the

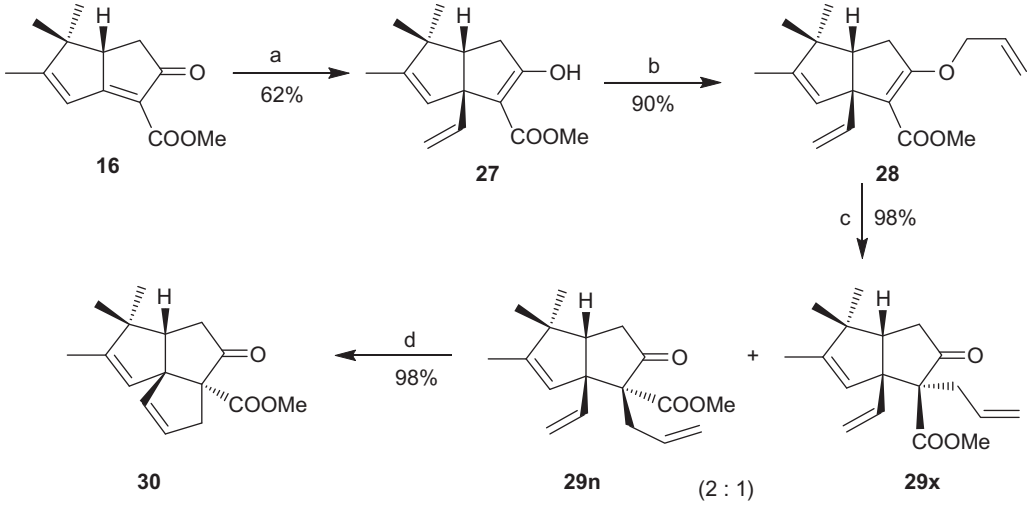


13 12

Scheme 1.



Scheme 2. Reagents and conditions: (a) Ref. 6a; (b) (i) PhSeCl, py, CH_2Cl_2, (ii) 30% aq H_2O_2, CH_2Cl_2; (c) $NaBH_4$, $CeCl_3{\cdot}7H_2O$, MeOH; (d) MOMCl, $^iPr_2NEt$, DMAP, CH_2Cl_2; (e) LAH, Et_2O; (f) $MeC(OEt)_3$, EtCOOH, Δ; (g) (i) NaOH, MeOH, H_2O, (ii) $(COCl)_2$, C_6H_6, (iii) CH_2N_2, Et_2O; (h) $CuSO_4$, Cu, *c*-C_6H_{12}; **23**/**24** 5:1; (i) Li, liq. NH_3, THF, ^{t}BuOH; (j) PDC, CH_2Cl_2.



Scheme 3. Reagents: (a) $CH_2{=}CHMgBr$, CuI, THF; (b) K_2CO_3, $CH_2{=}CHCH_2Br$, acetone; (c) C_6H_6, Δ; (d) $Cl_2Ru(Pcy_3)_2{=}CHPh$, CH_2Cl_2.

major isomer **29n**. Finally, treatment of the major isomer **29n** with 10 mol % of Grubbs first generation catalyst ($Cl_2Ru(Pcy_3)_2{=}CHPh$) in methylene chloride at room temperature for 0.5 h furnished the triquinane ester **30** in near quantitative yield, whose structure was established from its spectroscopic data. Expectedly, the minor β-ketoester **29x** failed to undergo the RCM reaction, even under strong conditions, as the vinyl and allyl groups are oriented *trans* to one other.

3. Conclusions

The enantioselective synthesis of angular triquinanes starting from readily available (*S*)-campholenaldehyde **12** has been developed by employing two different strategies. The first one is based on a Johnson's *ortho*-ester Claisen rearrangement followed by a regioselective intramolecular diazoketone cyclopropanation and cyclopropane ring cleavage. The second strategy, which is much simpler, is based on a RCM reaction.

4. Experimental

4.1. General

IR spectra were recorded on Jasco FTIR 410 and Perkin Elmer FTIR spectrum BX and GX spectrophotometers. ^{1}H (300 and 400 MHz) and ^{13}C (75 and 100 MHz) NMR spectra were recorded on Jeol λ-300 and Brucker Avance 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 1H) 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 ionization mode. Optical rotations were measured using a Jasco DIP-370 and Jasco P-1020 polarimeters 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–hexane and methylene chloride–hexane were used as an eluent. Visualization of the spots was accomplished by exposure to iodine vapor. Acme's silica gel (100–200 mesh) was used for column chromatography.

4.2. Methyl (3*S*,5*R*)-3-hydroxy-6,6,7-trimethylbicyclo[3.3.0]-octa-1,7-diene-2-carboxylate 17

To a magnetically stirred solution of the keto ester[6c] **16** (160 mg, 0.73 mmol) in methanol (1.5 mL) at 0 °C were added $CeCl_3{\cdot}7H_2O$ (271 mg, 0.73 mmol) and $NaBH_4$ (55 mg, 1.45 mmol) and stirred for 10 min at the same temperature. Methanol was evaporated under reduced pressure, water (4 mL) was added to the residue and extracted with ether (3 × 10 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 on a silica gel column using ethyl acetate–hexane (1:4) as eluent furnished the secondary alcohol **17** (138 mg, 86%) as an oil. $[\alpha]_D^{23} = -27.4$ (*c* 3.5, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3513 (OH), 1706 (OC=O), 1648, 1586, 1377, 1361, 1272, 1213, 1192, 1146, 1115, 1017, 859, 795; ^{1}H NMR (300 MHz): δ 6.21 (1H, s, H-8), 5.19 (1H, t, *J* 6.9 Hz, H-3), 3.72 (3H, s, OCH_3), 3.67 (1H, br s, OH), 2.74 (1H, ddd, *J* 10.8, 7.2, and 1.5 Hz), 2.29 (1H, dt, *J* 11.7, and 6.9 Hz), 1.86 (3H, s, olefinic-CH_3), 1.48 (1H, td, *J* 11.7, and 8.1 Hz), 1.11 (3H, s), and 0.91 (3H, s) [2 × *tert*-CH_3]; ^{13}C NMR (75 MHz): δ 171.3 (C), 166.1 (C), 165.7 (C), 121.6 (CH, C-8), 117.5 (C, C-2), 79.8 (CH, C-3), 58.8 (CH, C-5), 50.8 (CH_3, OCH_3), 46.0 (C, C-6), 34.2 (CH_2, C-4), 25.6 (CH_3), and 22.1 (CH_3) [2 × *tert*-CH_3], 14.3 (CH_3, olefinic-CH_3); HRMS: *m/z* Calcd. for $C_{13}H_{18}O_3Na$ (M+Na): 245.1154; Found: 245.1146.

4.3. Methyl (3*S*,5*R*)-3-(methoxymethoxy)-6,6,7-trimethylbicyclo[3.3.0]octa-1,7-diene-2-carboxylate 18

To a magnetically stirred cold (0–5 °C) solution of the secondary alcohol **17** (123 mg, 0.55 mmol) in CH_2Cl_2 (1 mL) were added DMAP (14 mg, 0.11 mmol), DIPEA (0.2 mL, 1.15 mmol), and methoxymethyl chloride (0.1 mL, 1.30 mmol) and stirred for 4 h at rt. Water (4 mL) was added to the reaction mixture and extracted with CH_2Cl_2 (3 × 8 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 on a silica gel column using ethyl acetate–hexane (3:17) as eluent furnished the MOM ether **18** (129 mg, 88%) as an oil. $[\alpha]_D^{21} = -43.7$ (*c* 2.5, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 1707 (OC=O), 1647, 1587, 1355, 1273, 1214, 1190, 1148, 1114, 1040, 917, 858; ^{1}H NMR (300 MHz): δ 6.27 (1H, s, H-8), 5.11 (1H, t, *J* 6.6 Hz, H-3), 4.92, and 4.64 (2H, 2 × d, *J* 6.9 Hz, OCH_2O), 3.71 (3H, s, CO_2CH_3), 3.38 (3H, s, OCH_3), 2.72 (1H, t, *J* 9.0 Hz), 2.38 (1H, dt, *J* 12.3, and 6.6 Hz), 1.87 (3H, s, olefinic-CH_3), 1.63–1.48 (1H, m), 1.11 (3H, s), and 0.92 (3H, s) [2 × *tert*-CH_3]; ^{13}C NMR (75 MHz): δ 170.7 (C, C-1), 166.6 (C), 164.9 (C), 122.0 (CH, C-8), 117.0 (C, C-2), 96.6 (CH_2, OCH_2O), 85.9 (CH, C-3), 59.3 (CH, C-5), 55.2 (CH_3, OCH_3), 50.7 (CH_3, CO_2CH_3), 46.1 (C, C-6), 34.0 (CH_2, C-4), 25.6 (CH_3), and 22.1 (CH_3) [2 × *tert*-CH_3], 14.3 (CH_3, olefinic-CH_3); HRMS: *m/z* calcd for $C_{15}H_{22}O_4Na$ (M+Na): 289.1417; found: 289.1405.

4.4. (3*S*,5*R*)-3-(Methoxymethoxy)-6,6,7-trimethylbicyclo[3.3.0]-octa-1,7-diene-2-methanol 19

To a cold (−70 °C), magnetically stirred solution of the ester **18** (123 mg, 0.46 mmol) in dry ether (2 mL) was added LAH (53 mg, 1.39 mmol) and the reaction mixture was stirred at the same temperature for 0.5 h. Ethyl acetate (0.5 mL) was carefully added to the reaction mixture to consume the excess reagent. The reaction was then quenched with water (4 mL) and extracted with ether (3 × 8 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 on a silica gel column using ethyl acetate–hexane (3:7) as eluent furnished the primary allyl alcohol **19** (97 mg, 88%) as an oil. $[\alpha]_D^{22} = -40.0$ (*c* 0.6, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3418 (OH), 1360, 1216, 1149, 1127, 1103, 1038, 918; ^{1}H NMR (400 MHz): δ 5.85 (1H, s, H-8), 4.95 (1H, t, *J* 6.6 Hz, H-3), 4.67 (2H, s, OCH_2O), 4.16, and 4.13 (2H, 2 × d, *J* 13.2 Hz, C*H*$_2$OH), 3.35 (3H, s, OCH_3), 2.75 (1H, br s, OH), 2.63 (1H, t, *J* 8.3 Hz, H-5), 2.27 (1H, dt, *J* 11.4, and 6.3 Hz), 1.73 (3H, s, olefinic-CH_3), 1.44 (1H, td, *J* 10.8, and 8.1 Hz,), 1.04 (3H, s), and 0.81 (3H, s) [2 × *tert*-CH_3]; ^{13}C NMR (100 MHz): δ 162.6 (C), 149.9 (C), 124.7 (C), 118.9 (CH, C-8), 96.2 (CH_2, OCH_2O), 89.4 (CH, C-3), 58.6 (CH, C-5), 58.0 (CH_2, CH_2OH), 55.4 (CH_3, OCH_3), 45.1 (C, C-6), 34.5 (CH_2, C-4), 26.1 (CH_3), and 21.2 (CH_3) [2 × *tert*-CH_3], 13.8 (CH_3, olefinic-CH_3); HRMS: *m/z* calcd for $C_{14}H_{22}O_3Na$ (M+Na): 261.1465; found: 261.1464.

4.5. Ethyl 2-[(1*R*,5*S*,7*S*)-7-(methoxymethoxy)-3,4,4-trimethyl-8-methylenebicyclo[3.3.0]oct-2-en-1-yl]acetate 20

A solution of the allyl alcohol **19** (90 mg, 0.38 mmol), triethyl orthoacetate (0.7 mL, 3.85 mmol) and a catalytic amount of propionic acid was placed in a Carius tube and heated to 180 °C for 3 days. The reaction mixture was cooled to RT, diluted with ether (10 mL), washed with 3 *N* HCl (3 mL) followed by saturated aq $NaHCO_3$ solution (2 mL) and 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 the γ,δ-unsaturated ester **20** (98 mg, 84%) as an oil. $[\alpha]_D^{23} = -17.6$

(*c* 7.0, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 1736 (OC=O), 1661, 1368, 1338, 1174, 1150, 1120, 1097, 1050, 999, 918, 894; ^1H NMR (300 MHz): δ 5.15 (1H, s, H-2′), 5.06, and 4.88 (2H, 2 × d, *J* 2.4 Hz, C=CH_2), 4.71 and 4.68 (2H, 2 × d, *J* 6.6 Hz, OCH_2O), 4.50–4.35 (1H, m, H-7′), 4.07 (2H, q, *J* 7.2 Hz, OCH_2CH_3), 3.36 (3H, s, OCH_3), 2.64, and 2.44 (2H, 2 × d, *J* 15.3 Hz, H-2), 2.35 (1H, dd, *J* 8.1, and 7.5 Hz), 2.15 (1H, dt, *J* 11.7, and 6.9 Hz), 1.56 (3H, s, olefinic-CH_3), 1.39 (1H, q, *J* 11.1 Hz), 1.24 (3H, t, *J* 6.9 Hz, OCH_2CH_3), 1.11 (3H, s), and 0.96 (3H, s) [2 × *tert*-CH_3]; ^{13}C NMR (75 MHz): δ 171.0 (C, OC=O), 156.6 (C, C=CH_2), 144.3 (C, C-3), 129.3 (CH, C-2′), 105.3 (CH_2, C=CH_2), 95.9 (CH_2, OCH_2O), 79.6 (CH, C-7′), 59.7 (CH_2, OCH_2CH_3), 55.9 (C, C-1′), 55.1 (CH_3, OCH_3), 52.8 (CH, C-5′), 47.4 (C, C-4′), 45.2 (CH_2, C-2), 34.6 (CH_2, C-6′), 29.6 (CH_3), and 21.8 (CH_3) [2 × *tert*-CH_3], 14.2 (CH_3, OCH_2CH_3), 12.1 (CH_3, olefinic-CH_3); HRMS: *m/z* calcd for $C_{18}H_{28}O_4Na$ (M+Na): 331.1886; found: 331.1897.

4.6. (1*S*,2*S*,4*S*,8*R*,11*S*)-2-(Methoxymethoxy)-5,5,6-trimethyltetracyclo[6.4.0.0^{1,11}.0^{4,8}]dodec-6-en-10-one 23 and (1*S*,4*R*,5*S*,6*R*,8*S*,10*S*)-10-(methoxymethoxy)-6,7,7-trimethyl-11-methylenetetracyclo[6.3.0.0^{1,5}.0^{4,6}]undecan-3-one 24

To a magnetically stirred solution of the ester **20** (98 mg, 0.32 mmol) in methanol (2 mL) was added 10% aq. NaOH (2 mL) and then refluxed for 5 h. The reaction mixture was cooled to rt and washed with CH_2Cl_2 (1 mL). The aqueous layer was then acidified with 3 M HCl (3 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The organic extract was washed with brine (5 mL) and dried (Na_2SO_4). Evaporation of the solvent furnished the acid **22** (90 mg, 100%) as an oil. IR (neat): ν_{max}/cm^{-1} 3081 (br, OH), 3029, 1709 (C=O), 1662, 1150, 1120, 1049, 999, 918, 896, 849, 828.

To a magnetically stirred solution of the acid **22** (66 mg, 0.24 mmol) in dry benzene (2 mL) was added oxalyl chloride (0.1 mL, 1.16 mmol) and then stirred for 3 h at rt. Evaporation of the excess oxalyl chloride and solvent under reduced pressure gave the acid chloride, which was taken in dry ether (2 mL), added to a cold (0–5 °C), magnetically stirred ethereal solution of diazomethane [excess, prepared from *N*-nitroso-*N*-methylurea (700 mg, 6.80 mmol), 5 mL of 60% aqueous KOH solution and 6 mL of ether] and the reaction mixture was stirred at 0 °C for 30 min and at rt for 2.5 h. Careful evaporation of the excess diazomethane and solvent on a hot water bath and purification of the residue on a silica gel column using ethyl acetate–hexane (1:9) as eluent furnished the diazoketone **21** (48 mg, 67%) as a yellow oil. IR (neat): ν_{max}/cm^{-1} 3086, 2101 (N=N), 1635 (C=O), 1362, 1314, 1215, 1149, 1119, 1048, 998, 917, 893, 846, 831.

To a magnetically stirred, refluxing (by placing two 100 W tungsten lamps near the reaction flask) suspension of copper powder (107 mg, 1.68 mmol) and anhydrous copper sulfate (80 mg, 0.50 mmol) in dry cyclohexane (7 mL) was added drop wise, a solution of the diazoketone **21** (48 mg, 0.16 mmol) in dry cyclohexane (4 mL) over a period of 20 min and the reaction mixture was refluxed for 3.5 h. It was then cooled to rt, copper and copper sulfate were filtered off using a sintered funnel. Evaporation of the solvent under reduced pressure and purification of the residue on a silver nitrate impregnated silica gel column using ethyl acetate–hexane (1:19) as eluent first furnished the major tetracyclic ketone **23** (23 mg, 52%) as an oil. $[\alpha]_D^{22} = +80.0$ (*c* 1.4, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3027, 1725 (C=O), 1359, 1249, 1220, 1197, 1147, 1101, 1048, 916, 778; ^1H NMR (300 MHz): δ 5.12 (1H, s, H-7), 4.60 and 4.50 (2H, 2 × d, *J* 6.9 Hz, OCH_2O), 3.80–3.75 (1H, m, H-2), 3.29 (3H, s, OCH_3), 2.30–2.00 (5H, m), 1.70 (1H, dd, *J* 9.1, and 5.4 Hz), 1.62–1.58 (1H, m), 1.60 (3H, s, olefinic-CH_3), 1.46 (1H, dd, *J* 4.7 and 3.3 Hz), 1.08 (3H, s) and 1.04 (3H, s) [2 × *tert*-CH_3]; ^{13}C NMR (75 MHz): δ 211.4 (C, C=O), 147.3 (C, C-6), 126.3 (CH, C-7), 94.6 (CH_2, OCH_2O), 81.1 (CH, C-2), 59.6 (C, C-8), 59.2 (CH, C-11), 55.1 (CH_3, OCH_3), 49.0 (C), 47.3 (C), 46.9 (CH_2, C-9), 35.3 (CH_2, C-3), 34.8 (CH, C-4), 31.1 (CH_3), and 23.0 (CH_3) [2 × *tert*-CH_3], 16.5 (CH_2, C-2), 12.6 (CH_3, olefinic-CH_3); HRMS: *m/z* calcd for $C_{17}H_{24}O_3Na$ (M+Na): 299.1624; found: 299.1631.

Further elution of the column with ethyl acetate–hexane (1:9) furnished the minor tetracyclic ketone **24** (5 mg, 11%) as an oil. $[\alpha]_D^{22} = -8.6$ (*c* 0.7, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3032, 1719 (C=O), 1370, 1212, 1151, 1118, 1044, 1012, 917, 899, 885; ^1H NMR (300 MHz): δ 5.25 (1H, d, *J* 2.4 Hz) and 5.15 (1H, d, *J* 3.0 Hz) [C=CH_2], 4.77 and 4.71 (2H, 2 × d, *J* 6.6 Hz, OCH_2O), 4.40–4.25 (1H, m, H-10), 3.41 (3H, s, OCH_3), 2.71 (1H, dd, *J* 18.0, and 1.5 Hz, H-2A), 2.57 (1H, d, *J* 5.1 Hz, H-4), 2.27 (1H, d, *J* 18.0 Hz, H-2B), 2.17 (1H, quintet, *J* 5.7 Hz), 1.85–1.55 (3H, m), 1.10 (6H, s), and 1.07 (3H, s) [3 × *tert*-CH_3]; ^{13}C NMR (100 MHz): δ 213.5 (C, C=O), 156.2 (C, C-11), 107.7 (CH_2, C=CH_2), 96.1 (CH_2, OCH_2O), 79.6 (CH, C-10), 63.2 (CH), 56.3 (C, C-1), 55.4 (CH_3, OCH_3), 55.2 (CH_2, C-2), 54.5 (CH), 50.4 (C, C-6), 47.9 (CH), 44.7 (C, C-7), 35.5 (CH_2, C-9), 29.2 (CH_3), 25.4 (CH_3), and 19.5 (CH_3) [3 × *tert*-CH_3]; HRMS: *m/z* calcd for $C_{17}H_{24}O_3Na$ (M+Na): 299.1624; found: 299.1612.

4.7. (1*R*,5*S*,6*S*,8*S*)-6-(Methoxymethoxy)-5,9,9,10-tetramethyltricyclo[6.3.0.0^{1,5}]undec-10-en-3-one 25 and (1*R*,3*R*,5*S*,6*S*,8*S*)-6-(methoxymethoxy)-5,9,9,10-tetramethyltricyclo[6.3.0.0^{1,5}]-undec-10-en-3-ol 26

To magnetically stirred, freshly distilled (over sodium and ferric chloride) ammonia (50 mL) in a two-necked RB flask equipped with a Dewar condenser was added a solution of the tetracyclic ketone **23** (23 mg, 0.08 mmol) in THF (2 mL) and anhydrous ^{t}BuOH (0.3 mL) followed by the addition of freshly cut lithium (33 mg, 4.71 mmol). The resulting blue colored solution was stirred for 15 min at −30 °C and then the reaction was quenched carefully with solid NH_4Cl. After evaporation of ammonia, the residue was taken in water (5 mL) and extracted with ether (3 × 4 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 (1:9) as eluent first furnished the triquinane ketone **25** (10 mg, 43%) as an oil. $[\alpha]_D^{22} = -5.0$ (*c* 1.2, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 1742 (C=O), 1377, 1361, 1221, 1180, 1146, 1119, 1096, 1042, 995, 918, 848; ^1H NMR (300 MHz): δ 5.13 (1H, s, H-11), 4.65, and 4.56 (2H, 2 × d, *J* 6.6 Hz OCH_2O), 3.60 (1H, dd, *J* 8.7, and 5.1 Hz, H-6), 3.34 (3H, s, OCH_3), 2.44 and 2.35 (2H, 2 × dd, *J* 19.2, and 1.5 Hz), 2.35 and 2.15 (2H, 2 × dd, *J* 18.3, and 1.2 Hz), 2.07–1.91 (2H, m, H-7), 1.70–1.50 (1H, m, H-8), 1.62 (3H, d, *J* 1.5 Hz, olefinic-CH_3), 1.05 (3H, s), 1.02 (3H, s), and 0.98 (3H, s) [3 × *tert*-CH_3]; ^{13}C NMR (75 MHz): δ 217.3 (C, C=O), 146.8 (C, C-10), 126.5 (CH, C-11), 95.7 (CH_2, OCH_2O), 84.7 (CH, C-6), 61.1 (C, C-1), 58.4 (CH, C-8), 55.3 (CH_3, OCH_3), 52.4 (CH_2), and 51.2 (CH_2) [C-2 and C-4], 50.3 (C, C-5), 47.4 (C, C-9), 32.2 (CH_2, C-7), 30.5 (CH_3), 22.3 (CH_3), and 18.7 (CH_3) [3 × *tert*-CH_3], 12.4 (CH_3, olefinic CH_3); HRMS: *m/z* calcd for $C_{17}H_{26}O_3Na$ (M+Na): 301.1781; found: 301.1784.

Further elution of the column with ethyl acetate–hexane (1:4) furnished the alcohol **26** (9 mg, 39%) as an oil. $[\alpha]_D^{23} = -6.7$ (*c* 0.9, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3397 (OH), 3029, 1376, 1361, 1229, 1217, 1146, 1109, 1042, 998, 918, 851; ^1H NMR (300 MHz): δ 5.07 (1H, s, H-11), 4.61, and 4.56 (2H, 2 × d, *J* 6.6 Hz, OCH_2O), 4.13 (1H, tt, *J* 9.9, and 6.0 Hz, H-3), 3.51 (1H, dd, *J* 11.7, and 5.0 Hz, H-6), 3.32 (3H, s, OCH_3), 2.03 (1H, dd, *J* 11.3, and 6.0 Hz), 1.93 (1H, dd, *J* 12.0, and 6.0 Hz), 1.85–1.67 (2H, m), 1.64 (1H, br s, OH), 1.55 (3H, s, olefinic-CH_3), 1.50–1.15 (3H, m), 1.02 (3H, s), 0.90 (3H, s), and 0.88 (3H, s) [3 × *tert*-CH_3]; ^{13}C NMR (75 MHz): δ 144.8 (C, C-10), 128.2 (CH, C-11), 95.7 (CH_2, OCH_2O), 84.8 (CH, C-6), 71.5 (CH, C-3), 62.5 (C, C-1), 56.4 (CH, C-8), 55.1 (CH_3, OCH_3), 50.3 (C, C-5), 48.5 (CH_2), 48.4 (CH_2), 46.8 (C, C-9), 32.8 (CH_2), 30.0 (CH_3), 21.8 (CH_3), and 19.3 (CH_3) [3 × *tert*-CH_3], 12.4

(CH_3, olefinic-CH_3); HRMS: *m/z* calcd for $C_{17}H_{28}O_3Na$ (M+Na): 303.1937; found: 303.1925.

4.8. Oxidation of the alcohol 26

To a magnetically stirred solution of the alcohol **26** (9 mg, 0.03 mmol) in CH_2Cl_2 (0.5 mL) was added PDC (95 mg, 0.34 mmol) and stirred for 1 h at RT. The reaction mixture was then filtered through a small silica gel column with an excess of CH_2Cl_2. Evaporation of the solvent and purification of the residue on a silica gel column using ethyl acetate–hexane (1:9) as eluent furnished the ketone **25** (8 mg, 92%) as oil.

4.9. Methyl (1*R*,5*R*)-6,6,7-trimethyl-3-oxo-1-vinylbicyclo[3.3.0]-oct-7-ene-2-carboxylate 27

To a cold (−30 °C), magnetically stirred suspension of CuI (22 mg, 0.11 mmol) in dry THF (2 mL) was added a solution of vinylmagnesium bromide (2.5 mL, 1 M solution in THF, 2.5 mmol) over a period of 20 min. After stirring the reaction mixture for 30 min at −30 °C, a solution of the keto ester **16** (250 mg, 1.14 mmol) in dry THF (3 mL) was added and stirred for 1 h at the same temperature. It was then quenched with saturated aq. NH_4Cl (10 mL) and extracted with ether (3 × 10 mL). The ether 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 (1:20) as eluent furnished the keto ester **27** (174 mg, 62%) as a colorless oil, which was found to exist in the enol form. R_f (1:19 EtOAc/hexane) 0.4; $[\alpha]_D^{25} = +2.0$ (*c* 8.1, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3261, 3081, 3046, 2956, 2866, 1760, 1732, 1651, 1615, 1446, 1354, 1281, 1218, 1167, 1042, 993, 912, 845, 804; ^1H NMR (300 MHz, $CDCl_3$): δ 10.55 (1H, s, OH), 5.87 (1H, dd, *J* 18.0, and 9.9 Hz, *H*C=CH_2), 5.41 (1H, s, H-8), 4.88 (1H, d, *J* 9.9 Hz), and 4.87 (1H, d, *J* 18.0 Hz) [HC=C*H*$_2$]. 3.72 (3H, s, OCH_3), 2.64 (1H, dd, *J* 18.3, and 8.7 Hz), 2.51–2.42 (1H, m), 2.21 (1H, dd, *J* 9.3, and 3.0 Hz), 1.64 (3H, s, olefinic CH_3), 1.05 (3H, s, *tert*-CH_3), 0.93 (3H, s, *tert*-CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.1 (C, CO_2CH_3), 170.0 (C, C-3), 147.6 (C, C-7), 144.7 (CH, HC=CH_2), 126.6 (CH, C-8), 111.3 (CH_2, HC=CH_2), 104.6 (C, C-2), 62.5 (C), 55.2 (CH_3, OCH_3), 50.8 (CH, C-5), 47.8 (C), 32.2 (CH_2, C-4), 29.2 (CH_3), 22.8 (CH_3), 12.7 (CH_3); HRMS: *m/z* Calcd. for $C_{15}H_{20}O_3Na$ (M+Na): 271.1310. Found: 271.1302.

4.10. Methyl (1*R*,2*S*,5*S*) and (1*R*,2*R*,5*S*)-2-allyl-6,6,7-trimethyl-3-oxo-1-vinylbicyclo[3.3.0]oct-7-ene-2-carboxylates 29x and 29n

To a solution of the β-keto ester **27** (70 mg, 0.28 mmol) in acetone (2 mL) were added K_2CO_3 (195 mg, 1.41 mmol) and allyl bromide (0.12 mL, 1.39 mmol) and refluxed for 2 h. The reaction mixture was cooled to rt, diluted with water (3 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 on a silica gel column using ethyl acetate–hexane (1:9) as eluent furnished the O-allylated ester **28** (73 mg, 90%). $[\alpha]_D^{23} = +3.0$ (*c* 2.3, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 2925, 2860, 1738 (OC=O), 1696, 1617, 1437, 1380, 1270, 1213, 1058, 917, 849, 788; ^1H NMR (400 MHz): δ 6.00–5.87 (2H, m) [2 × C*H*=CH_2], 5.55 (1H, s, H-8), 5.41 (1H, d, *J* 17.2 Hz), 5.25 (1H, d, *J* 10.6 Hz), 4.94 (1H, d, *J* 17.7 Hz), and 4.90 (1H, d, *J* 11.8 Hz) [2 × CH=CH_2], 4.61–4.56 (2H, m, OCH_2), 3.67 (3H, s, CO_2CH_3), 2.66 (1H, dd, *J* 17.5, and 8.4 Hz), and 2.58 (1H, dd, *J* 17.5, and 3.1 Hz) [H-4], 2.19 (1H, dd, *J* 8.8, and 3.1 Hz), 1.63 (3H, s, olefinic-CH_3), 1.03 (3H, s), and 0.94 (3H, s) [2 × *tert*-CH_3]; ^{13}C NMR (100 MHz): δ 167.2 (C, OC=O), 164.7 (C, C-3), 147.2 (C, C-7), 145.1 (CH, vinylic *C*H=CH_2), 133.2 (CH, allylic *C*H=CH_2), 127.6 (CH, C-8), 117.4 (CH_2), and 111.4 (CH_2) [2 × CH=*C*H_2], 70.4 (CH_2, OCH_2), 63.6 (C, C-1), 54.6 (CH_3, OCH_3), 50.5 (CH, C-5), 48.0 (C, C-6), 30.7 (CH_2, C-4), 29.1 (CH_3), and 22.8 (CH_3) [2 × *tert*-CH_3], 12.6 (CH_3, olefinic-CH_3); HRMS: *m/z* calcd for $C_{18}H_{24}O_3Na$ (M+Na): 311.1623; found: 311.1610.

A solution of the O-allylated ester **28** (73 mg, 0.25 mmol) in benzene (2 mL) was placed in a Carius tube and heated to 110 °C for 30 min. The reaction mixture was cooled to RT. 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 (2*S*)-keto ester **29x** (23 mg, 32%) as an oil. $[\alpha]_D^{23} = -13.8$ (*c* 2.1, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3081, 1752 (OC=O), 1735 (C=O), 1637, 1363, 1274, 1239, 1225, 1168, 1120, 1077, 997, 915, 852; ^1H NMR (300 MHz): δ 6.15–5.85 (1H, m, CH_2CH=CH_2), 5.95 (1H, dd, *J* 17.4, and 10.5 Hz, *H*C=CH_2 on C-1), 5.40 (1H, s, H-8), 5.20–5.00 (4H, m) [2 × CH=CH_2], 3.67 (3H, s, OCH_3), 2.85–2.60 (3H, m), 2.40–2.25 (2H, m, H-4), 1.65 (3H, d, *J* 1.5 Hz, olefinic-CH_3), 1.08 (3H, s), and 1.01 (3H, s) [2 × *tert*-CH_3]; ^{13}C NMR (75 MHz): δ 213.3 (C, C=O), 170.1 (C, OC=O), 149.1 (C, C-7), 142.4 (CH, H*C*=CH_2 on C-1), 135.0 (CH, CH_2*C*H=CH_2), 123.1 (CH, C-8), 117.2 (CH_2), and 115.7 (CH_2) [2 × CH=CH_2], 66.8 (C), 64.7 (C), 52.8 (CH, C-5), 51.9 (CH_3, OCH_3), 48.1 (C, C-6), 40.7 (CH_2), 35.5 (CH_2), 27.5 (CH_3), and 23.3 (CH_3) [2 × *tert*-CH_3], 12.9 (CH_3, olefinic-CH_3); HRMS: *m/z* calcd for $C_{18}H_{24}O_3Na$ (M+Na): 311.1624; found: 311.1618.

Further elution of the column with ethyl acetate–hexane (1:9) furnished the (2*R*)-keto ester **29n** (48 mg, 66%) as an oil. $[\alpha]_D^{22} = -28.5$ (*c* 3.5, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3081, 1747 (OC=O), 1730 (C=O), 1638, 1363, 1310, 1307, 1235, 1166, 1127, 998, 917, 854; ^1H NMR (300 MHz): δ 6.11 (1H, dd, *J* 17.4, and 10.5 Hz, *H*C=CH_2 on C-1), 5.70 (1H, ddt, *J* 17.4, 9.3, and 7.2 Hz, CH_2C*H*=CH_2), 5.18 (1H, dd, *J* 10.8, and 1.0 Hz), 5.09 (1H, s, H-8), 5.15–4.95 (3H, m), 3.71 (3H, s, OCH_3), 2.67 (1H, dd, *J* 13.8, and 7.2 Hz), 2.54–2.39 (3H, m), 2.32 (1H, dd, *J* 13.8, and 7.2 Hz), 1.63 (3H, d, *J* 1.5 Hz, olefinic-CH_3), 1.09 (3H, s), and 1.00 (3H, s) [2 × *tert*-CH_3]; ^{13}C NMR (75 MHz): δ 211.9 (C, C=O), 170.4 (C, OC=O), 147.6 (C, C-7), 141.1 (CH, HC=CH_2 on C-1), 133.0 (CH, CH_2C*H*=CH_2), 125.1 (CH, C-8), 118.9 (CH_2), and 115.7 (CH_2) [2 × CH=CH_2], 66.9 (C), 63.0 (C), 52.2 (CH, C-5), 51.7 (CH_3, OCH_3), 48.3 (C, C-6), 40.5 (CH_2), 37.5 (CH_2), 27.4 (CH_3), and 23.1 (CH_3) [2 × *tert*-CH_3], 12.7 (CH_3, olefinic-CH_3); HRMS: *m/z* calcd for $C_{18}H_{24}O_3Na$ (M+Na): 311.1624; found: 311.1631.

4.11. Methyl (1*R*,5*R*,8*S*)-9,9,10-trimethyl-6-oxotricyclo-[6.3.0.0^{1,5}]undeca-2,10-diene-5-carboxylate 30

To a magnetically stirred solution of the (2*R*)-keto ester **29n** (23 mg, 0.08 mmol) in dry CH_2Cl_2 (8 mL, 0.01 M) was added Grubbs' catalyst $Cl_2Ru(Pcy_3)_2$=CHPh (7 mg, 10 mol%) 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 (1:4) as eluent furnished the angular triquinane **30** (20 mg, 98%) as an oil. $[\alpha]_D^{24} = +21.9$ (*c* 1.6, $CHCl_3$); IR (neat): ν_{max}/cm^{-1} 3051, 1748 (OC=O), 1732 (C=O), 1656, 1620, 1363, 1297, 1255, 1228, 1186, 1157, 1129, 1068, 963, 843, 773, 729, 716, 611; ^1H NMR (300 MHz): δ 5.53 (1H, dt, *J* 5.4, and 2.4 Hz) and 5.36 (1H, dt, *J* 5.4, and 2.4 Hz) [H-2 and 3], 4.98 (1H, d, *J* 0.9 Hz, H-11), 3.61 (3H, s, OCH_3), 3.12 (1H, dt, *J* 17.4, and 2.1 Hz, H-4A), 2.77 (1H, dd, *J* 17.1, and 8.4 Hz, H-7A), 2.69 (1H, dt, *J* 17.4, and 2.1 Hz, H-4B), 2.39 (1H, dd, *J* 17.1, and 8.7 Hz, H-7B), 2.26 (1H, t, *J* 9.0 Hz, H-8), 1.63 (3H, d, *J* 1.2 Hz, olefinic-CH_3), 1.11 (3H, s), and 0.97 (3H, s) [2 × *tert*-CH_3]; ^{13}C NMR (75 MHz): δ 214.5 (C, C=O), 171.2 (C, OC=O), 150.2 (C, C-10), 135.7 (CH, C-2), 127.8 (CH, C-3), 124.0 (CH, C-11), 75.0 (C, C-5), 67.5 (C, C-1), 55.2 (CH, C-8), 51.9 (CH_3, OCH_3), 48.0 (C, C-9), 41.7 (CH_2), 39.8 (CH_2), 30.1 (CH_3), and 22.7 (CH_3) [2 × *tert*-CH_3], 12.6 (CH_3, olefinic-CH_3); HRMS: *m/z* calcd for $C_{16}H_{21}O_3$ (M+H): 261.1491; found: 261.1490.

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