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Effect of ring fusion stereochemistry on double bond geometry. Unexpected formation of nine-membered cyclic ether with *E*-configurated double bond through RCM

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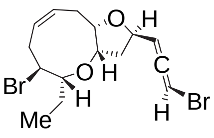
ABSTRACT

Formation of a nine-membered cyclic ether with *E*-configurated double bond was observed during construction of 5-9-5 tricycles through RCM of dienes. Ring fusion stereochemistry in the products oxonenes was found to have profound influence on the olefin geometry. *cis-anti-cis* 5-9-5 tricycle was obtained with *Z*-configurated olefin while *cis-syn-cis* 5-9-5 system was obtained with *E*- as well as *Z*-configurated double bond with the former predominating.

1. Introduction

Nine-membered cyclic ethers are present in a variety of marine natural products. The bicyclic ethers isolaurallene **1**,[1] neolaurallene **2**,[2] polycyclic ethers[3] brevetoxin-A, and ciguatoxins are representative examples. All of these compounds contain at least one nine-membered ring with *Z*-configurated double bond within the ring. Many of these compounds exhibit interesting biological activities. Thus synthesis of medium-sized cyclic ethers has received considerable attention.[4] Construction of medium-sized rings (8–10) through ring closure of the corresponding linear precursors is extremely difficult[5] because of transannular interactions in the transition state. A number of indirect but efficient methodologies[6] have thus been developed for their synthesis.



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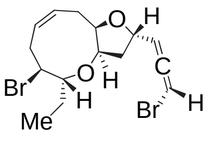

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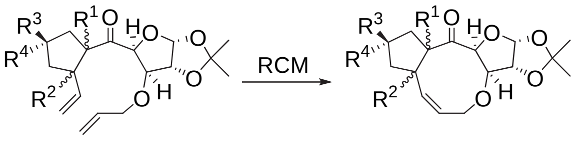
Ring closing metathesis (RCM)[7] of acyclic precursors with terminal alkene units has emerged as a powerful tool for direct synthesis of cycloalkenes of different ring sizes. Generally in RCM eight- and nine-membered carbo-, and hetero-cyclic rings are obtained in high yields with *Z*-configurated olefin. To date there is only one example reported[8] in literature for the formation of *trans*-cyclooctene through RCM. Although there are a number of reports on the synthesis of nine-membered carbocycles[9] and cyclic ethers[10] through RCM, all of them produce carba-and oxa-cycles with *Z*-configurated olefin.



4

3, a $R^1 = R^2 = R^3 = \beta$-H, R^4= vinyl
b $R^1 = R^2 = \alpha$-H, R^3= vinyl, R^4= H

In continuation to our interest in the application of RCM reaction in organic synthesis,[11] we became interested in RCM of dienes **3**. RCM of dienes **3** is expected to produce the tricycles **4** with nine-membered cyclic ether having *Z*-olefinic geometry. We herein present[12] the results of RCM of the dienes **3** demonstrating that the relative stereochemistry at the ring fusion at both ends of the

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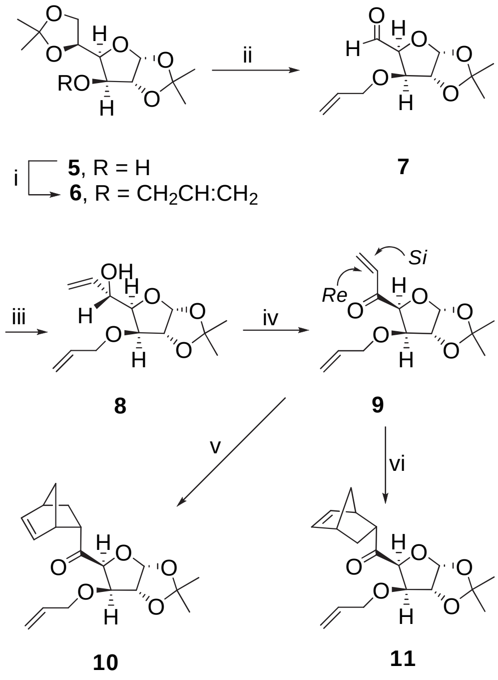
central ring to be formed influences the olefin geometry significantly resulting in the synthesis of nine-membered cyclic ether with *E*-configurated double bond. To the best of our knowledge this is the first example of the formation of oxonene with an *E*-olefinic geometry through RCM.[13]

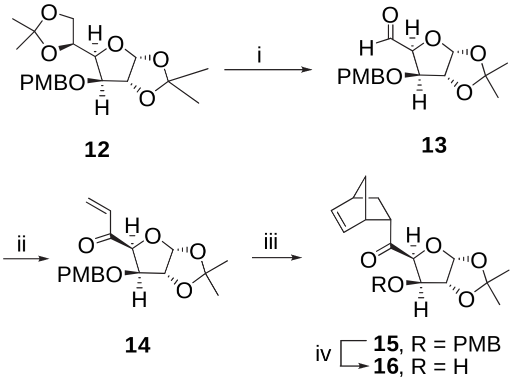
2. Results and discussion

For the synthesis of the dienes **3a** and **3b**, we planned to employ ring opening metathesis of the appropriate norbornene derivatives prepared from the dienophile **9**. The dienophile **9** was prepared as follows (Scheme 1). The hydroxyl group in diacetone glucose **5** was transformed to the allyl ether **6**[10f] on reaction of its sodium salt with allyl bromide. Selective removal of the 5,6-acetonide moiety and periodate cleavage of the vicinal diol resulted in the known aldehyde **7**.[10f] Reaction of this aldehyde with vinyl magnesium bromide afforded the carbinol **8** as a single diastereomer in 70% yield. Assignment of stereochemistry to the newly created stereocentre in **8** was based on addition of vinyl magnesium bromide on the face opposite to the allyloxy group as the other face of the aldehyde unit is blocked by the allyloxy group. Dess–Martin periodinane oxidation of the carbinol **8** produced the enone **9** in excellent yield.



Scheme 1. Reagents and conditions: (i) NaH, HMPA, THF, $CH_2{=}CHCH_2Br$, rt, 83%; (ii) (a) 75% aq HOAc, 12 h, 78%, (b) $NaIO_4$, CH_3CN/H_2O (3:1), 2 h, 70%; (iii) $CH_2{=}CHMgBr$, THF, −78 °C to rt, 5 h, 70%, (iv) DMP, CH_2Cl_2, 1 h, 90%; (v) cyclopentadiene, $ZnCl_2$, CH_2Cl_2, −78 °C, 5 h, 95%; (vi) cyclopentadiene, CH_2Cl_2, 0 °C→rt, 5h, 81%.

Diels–Alder reaction of the enone **9** with cyclopentadiene may proceed from the *Re*-face as well as from the *Si*-face to produce either the adduct **10** or **11**. When the enone **9** was treated with cyclopentadiene in the presence of anhydrous $ZnCl_2$ as catalyst, the reaction was found to be highly diastereoselective producing exclusively the adduct **10** in 95% isolated yield as an oil. The overall structure of the product could be discerned from NMR spectral data. However, it was difficult to distinguish the structure **10** from **11** based on only NMR spectral data. At this stage we decided to prepare an analogue of **10** as a crystalline solid so that the structure could be solved by X-ray crystallography. Indeed a solid analogue **15** was prepared as follows (Scheme 2). Acid induced deprotection of the 5,6-acetonide moiety of the known glucofuranose derivative **12**[14] followed by periodate cleavage of the resulting vicinal diol afforded the aldehyde **13**. Addition of vinyl magnesium bromide to the aldehyde **13** and subsequent oxidation of the carbinol afforded the required enone **14**. Diels–Alder reaction of the enone **14** with cyclopentadiene in the presence of anhydrous $ZnCl_2$ as catalyst was found to be highly diastereoselective producing exclusively the adduct **15** in 92% isolated yield. Removal of PMB protecting group afforded the hydroxy compound **16** as a crystalline solid, mp 112–114 °C. The structure of the adduct **16** was established by determination of X-ray crystal structure (Fig. 1).[15] The crystal structure of **16** clearly reveals that diene added to the *Re*-face of the enone **14**. With establishment of the structure of the adduct **15**, the structure of the Diels–Alder adduct of the enone **9** was assigned the structure as depicted in **10**.



Scheme 2. Reagents and conditions: (i) (a) 75% aq HOAc, 12 h, 80%, (b) $NaIO_4$, CH_3CN/H_2O (3:1), 2 h, 73%; (ii) (a) $CH_2{=}CHMgBr$, THF, −78 °C to rt, 5h, 68%; (b) DMP, CH_2Cl_2, 1 h, 95%; (iii) cyclopentadiene, $ZnCl_2$, CH_2Cl_2, −78 °C, 5 h, 92%; (iv) DDQ, CH_2Cl_2/H_2O (18:1), 4 h, 87%.

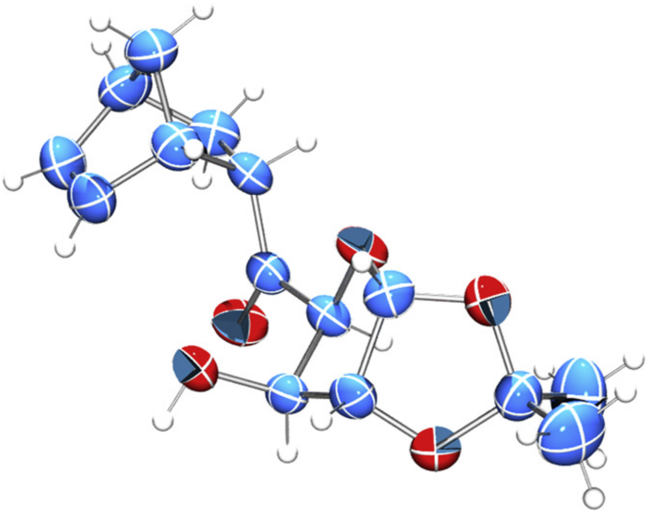
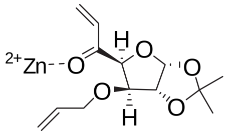


Fig. 1. ORTEP diagram of compound **16**.

It may be noted that the *Re*-face of the dienophile **9** is blocked by the alkoxy group and Diels–Alder reaction was expected to take place by addition on the unhindered *Si*-face of the enone **9** to give the adduct **11**. It appeared that the catalyst played an important role in dictating the facial selectivity. So we decided to carry out Diels–Alder reaction of the enone **9** with cyclopentadiene without using any catalyst. To our delight a Diels–Alder Adduct was obtained as a liquid in 81% yield. This adduct was found to be different than the adduct **10** as revealed from NMR spectral data. This adduct was assigned the structure **11** arising out of the addition of the diene on the unhindered *Si*-face. The change in facial selectivity in presence of Lewis acid as catalyst may be attributed as follows. Initially the enone **9** forms a metal co-ordinated species **17**. Rotation along the C_4–C_5 bond in the complex **17** forms a tight five-membered metal chelate **18**. Chelate formation is probably the driving force for this rotation. During this process the *Re*-face of the diene is no longer blocked and addition took place through chelate **18** leading to the product **10**.



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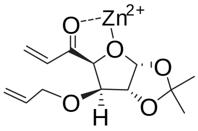

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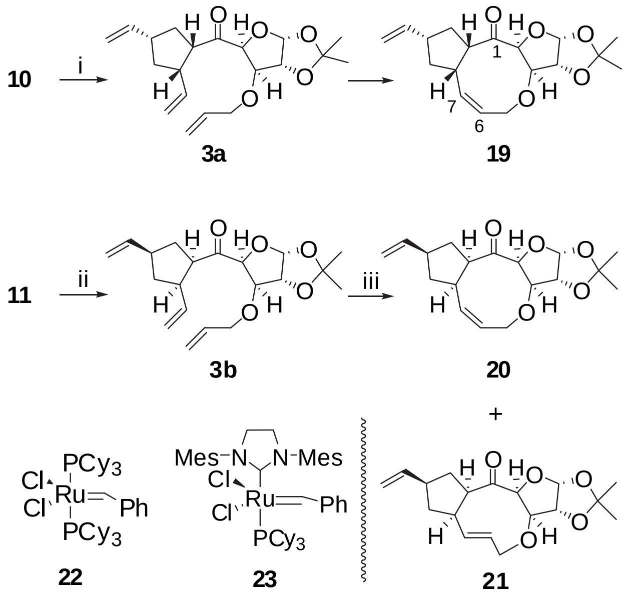
With the norbornene derivatives **10** and **11** ready in hand, we focused on their ring opening metathesis (Scheme 3). The adduct **10** was first subjected to metathesis. Exposure of a dichloromethane solution of **10** with Grubbs' first generation catalyst **22** in the presence of ethylene at rt led complete consumption of the starting material within 15 min and afforded, after purification through column chromatography, mainly the triene **3a** in 81% yield. That the compound **3a** is the ring opened product was easily ascertained from the appearance of three olefinic methines at δ 133.3, 139.0, 141.9, and three methylenes at 113.6, 115.7, and 118.6 in its ^{13}C NMR spectrum. Similarly treatment of the adduct **11** in dichloromethane solution with Grubbs' first generation catalyst at rt in the presence of ethylene underwent smooth ring opening to afford the triene **3b** in 96% yield.



Scheme 3. Reagents and conditions: (i) catalyst **22** (5 mol %), CH_2Cl_2, C_2H_4, rt, 6 h, 78%; (ii) catalyst **22** (10 mol %), CH_2Cl_2, C_2H_4, rt, 1 h, 96%; (iii) catalyst **23** (6 mol %), CH_2Cl_2, C_2H_4, rt, 12 h, 29% (for **21**) and 21% (for **20**).

The triene **3a** on treatment with the catalyst **22** for 6 h at rt afforded the tricycle **19** in 78% yield. Assignment of *Z*-olefinic geometry in the nine-membered ring in **19** could be easily made from the coupling constant (J=10.5 Hz) of the C_6 and C_7 olefinic protons at δ 5.51 (dt, J=4, 10.5 Hz) and 5.57 (dt, J=2, 10.5 Hz). The triene **3b** failed to undergo ring closure with the catalyst **22** even after prolonged heating in toluene. However, the triene **3b** could be cyclized on treating a dichloromethane solution with the Grubbs' second generation catalyst **23** at rt for 12 h. Careful chromatography of the product led to isolation of the tricycles **20** (21%) and **21** (29%) along with a dimeric compound (14%, not characterized). *cis*-Olefinic geometry in **20** was confirmed by the coupling constant (J=11 Hz) between C_6 and C_7 H's, which appeared at δ 5.45 (J=0.6, 3.4, and 11.4 Hz) and 5.80 (J=2.4, 9, and 11 Hz). The *cis*-olefinic geometry in **20** was further confirmed by analysis of its 2D NMR (HSQC, COSY, and NOESY) spectra (Fig. 2). Analysis of ^1H NMR spectra of **21** revealed that both the C_6 and C_7 olefinic protons appeared as an overlapping multiplet at δ 5.63–5.71. It was difficult to determine the coupling constant values for the ring olefinic protons from this complex pattern. Thus we had to take resort to 2D NMR spectra. While the COSY and NOESY (Fig. 2) spectra of **20** showed a strong correlation between C_6 and C_7 protons, no such correlation was observed between the ring alkene protons in its COSY and NOESY spectra (Supplementary data). This confirmed that the nine-membered cyclic ether in **21** contains an *E*-configurated olefin.

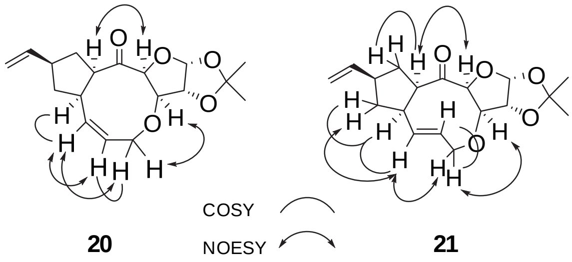


Fig. 2. COSY and NOESY analysis of **20** and **21**.

The diene **3a** differs from **3b** in the stereochemistry of the five-membered ring fused to the nine-membered ring to be formed during RCM. Remarkably this subtle difference in structures of the diene precursors leads to the formation of thermodynamically less stable *E*-alkene in the oxonene. Indeed DFT calculation[16] of energy associated with the *cis*-oxonene **19** formed from RCM of **3a** shows it be energetically much more stable by 5.62 Kcal/mol than its trans-analogue. Thus as expected *cis*-oxonene **19** was formed. On the other hand the *trans*-oxonene **21** is energetically more stable by 3.40 Kcal/mol over the *cis*-oxonene **20** both of which are obtained by RCM of the diene **3b**. In this case the energy difference between **20 and 21** is less compared to that between **19** and its *trans*-analogue. Thus formation of *trans*-oxonene **21** competes favorably and leads to a mixture of *cis*- and *trans*-oxonene **20** and **21**, respectively.

3. Conclusion

We have demonstrated that nine-membered cyclic ether with thermodynamically less stable *E*-configurated geometry[13] can be formed through RCM reaction of diene. It is not the strain energy associated with incorporation of *trans*-alkene in the ring but probably the overall stability of the resulting ring system that dictates the olefin geometry. In the present example, *cis-syn-cis* stereochemistry of the ring junction at both ends of the nine-membered ring made *E*-configurated oxonene more stable than the corresponding *Z*-analogue.

4. Experimental section

4.1. General

Melting points were taken in open capillaries in sulfuric acid bath and are uncorrected. Petroleum ether refers to the fraction having bp 60–80 °C. A usual work up of the reaction mixture consists of extraction with diethyl ether, washing with brine, drying over Na_2SO_4, and removal of the solvent in vacuo. Column chromatography was carried out with silica gel (60–120 mesh). Peak positions in ^1H and ^{13}C NMR spectra are indicated in parts per million downfield from internal TMS in δ units. NMR spectra were recorded in $CDCl_3$ solution at 300, 500, and 600 MHz for ^1H and 75, 125 MHz for ^{13}C on Bruker-Avance DPX_{300}, DPX_{500}, DPX_{600} instruments. ^{13}C Peaks assignment is based on DEPT experiment. IR spectra were recorded as liquid film for liquids and in KBr plate for solids on Shimadzu FTIR-8300 instrument. Optical rotations were measured using Jasco P-1020 digital polarimeter and $[\alpha]_D$ values are given in units of 10^{-1} deg cm^2 g^{-1}. Mass spectra were measured in a QTOF I (quadrupole-hexapole-TOF) mass spectrometer with an orthogonal *Z*-spray-electrospray interface on Micro (YA-263) mass spectrometer (Manchester, UK). Unless otherwise indicated, all reactions were carried out under a blanket of Ar.

4.1.1. 1-((3aR,5R,6S,6aR)-6-(Allyloxy)-tetrahydro-2,2-dimethylfuro[2,3-d][1,3]dioxol-5-yl)prop-2-en-1-ol ***8***. To a magnetically stirred solution of the known aldehyde **7** (900 mg, 3.95 mmol) in dry THF (10 mL) at −78 °C was added vinyl magnesium bromide (1.0 M solution in THF, 5.9 mmol, 5.9 mL) dropwise. The reaction mixture was stirred at that temperature for 1 h. The temperature of the reaction mixture was slowly raised to rt. After stirring for 4 h at rt it was quenched with saturated NH_4Cl solution (1.0 mL). Usual work up of the reaction mixture and purification of the crude residue by column chromatography (25% Et_2O/petroleum ether) afforded the alcohol **8** (785 mg, 70%) as colorless oil; R_f (30% EtOAc/petroleum ether) 0.7; $[\alpha]_D^{24}$ −41.96 (*c* 5.95, $CHCl_3$); IR ν_{max} (liquid film) 3477, 2987, 2935, 1737, 1643, 1454, 1427, 1375 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 6.00–5.95 (1H, m, =CH), 5.91 (1H, d, *J* 2.8 Hz, O–CH–O), 5.88–5.77 (1H, m, =CH), 5.35 (1H, d, *J* 17.4 Hz, =CH_2), 5.25 (1H, d, *J* 17.4 Hz, =CH_2), 5.17 (2H, d, *J* 10.5 Hz, =CH_2), 4.49 (1H, d, *J* 3.5 Hz, CH), 4.43 (1H, d, *J* 5.1 Hz, CH), 4.11 (1H, dd, *J* 11.8, 5.21 Hz), 3.92–4.01 (3H, m), 2.99 (1H, br s, OH), 1.41 (3H, s, CH_3), 1.25 (3H, s, CH_3); δ_C (75 MHz, $CDCl_3$) 137.8, 133.5, 118.3, 115.9, 111.6, 105.1, 82.6, 81.9, 81.5, 71.1, 70.5, 26.7, 26.3; HRMS (ESI) (*m*/*z*): $[M+Na]^+$, found 279.1209. $C_{13}H_{20}O_5Na$ requires 279.1208.

4.1.2. 1-((3aR,5S,6R,6aR)-6-(Allyloxy)-tetrahydro-2,2-dimethylfuro[2,3-d][1,3]dioxol-5-yl)prop-2-en-1-one ***9***. A solution of the hydroxy compound **8** (100 mg, 0.391 mmol) in anhydrous dichloromethane (10 mL) was degassed by bubbling Ar and DMP (329 mg, 0.781 mmol) was added to it. The reaction mixture was stirred for 1 h and quenched by adding dropwise (1:1 mixture of saturated aqueous sodium thiosulfate and saturated sodium bicarbonate) till a transparent solution is obtained. The compound was extracted with ether and concentrated under vacuum and purified by column chromatography (15% Et_2O/petroleum ether) to afford the enone **9** (89 mg, 90%) as colorless oil; R_f (20% EtOAc/petroleum ether) 0.8; $[\alpha]_D^{25}$ −50.5 (*c* 1.36, $CHCl_3$); IR ν_{max} (liquid film) 2991, 2939, 1710, 1610, 1446, 1377 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 6.76 (1H, dd, *J* 17.4, 10.6 Hz, =CH), 6.29 (1H, d, *J* 17.3 Hz, =CH_2), 6.04 (1H, d, *J* 3.5 Hz, O–CH–O), 5.68 (1H, dd, *J* 10.4, 1.4 Hz, =CH_2), 5.73–5.63 (1H, m, =CH), 5.18–5.08 (2H, m, =CH_2), 4.74 (1H, d, *J* 3.5 Hz, O–CH–CO), 4.53 (1H, d, *J* 3.5 Hz, O–CH), 4.21 (1H, d, *J* 3.5 Hz, C*H*–O–CH_2), 3.98 (1H, dd, *J* 12.8, 5.3 Hz, OCH_2), 3.86 (1H, dd, *J* 12.9, 5.5 Hz, OCH_2), 1.43 (3H, s, CH_3), 1.28 (3H, s, CH_3); δ_C (75 MHz, $CDCl_3$) 196.0, 133.2, 132.2, 128.7, 117.8, 112.3, 105.8, 84.8, 83.4, 82.1, 71.3, 26.9, 26.3; HRMS (ESI) (*m*/*z*): $[M+Na]^+$, found 277.1050. $C_{13}H_{18}O_5Na$ requires 277.1052.

4.1.3. ((3aR,5S,6R,6aR)-6-(Allyloxy)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)((1S,2S,4S)-bicyclo[2.2.1]hept-5-en-2-yl)methanone ***10***. To a magnetically stirred solution of the dienophile **9** (100 mg, 0.393 mmol) in DCM (5 mL) at −78 °C, $ZnCl_2$ (106 mg, 0.779 mmol) was added and stirred for 30 min followed by addition of freshly distilled cyclopentadiene (78 mg, 1.18 mmol). After stirring for 5 h, the reaction mixture was quenched with brine (0.2 mL) and worked up in the usual way to afford, after column chromatography (10% Et_2O/petroleum ether), the adduct **10** (120 mg, 95%); R_f (15% EtOAc/petroleum ether) 0.8; $[\alpha]_D^{26}$ −112 (*c* 0.28, $CHCl_3$); IR ν_{max} (liquid film) 2976, 2937, 1708, 1381 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 6.12 (1H, dd, *J* 5.3, 3.1 Hz, =CH), 6.05 (1H, d, *J* 3.6 Hz, O–CH–O), 5.83 (1H, dd, *J* 5.4, 2.2 Hz, =CH), 5.79–5.74 (1H, m, =CH), 5.27–5.16 (2H, m, =CH_2), 4.65 (1H, d, *J* 3.6 Hz, O–CH–CO), 4.54 (1H, d, *J* 3.8 Hz, OCH), 4.19 (1H, d, *J* 3.6 Hz, C*H*–O–CH_2), 4.03 (1H, dd, *J* 12.7, 5.3 Hz, OCH_2), 3.94 (1H, dd, *J* 12.8, 5.8 Hz, OCH_2), 3.39–3.33 (1H, m, CH), 3.23 (1H, br s, CH), 2.85 (1H, br s, CH), 1.82–1.74 (1H, ddd, *J* 11.9, 8.9, 3.6 Hz), 1.45 (3H, s, CH_3), 1.42–1.37 (2H, m), 1.31 (3H, s, CH_3), 1.28 (1H, m); δ_C (75 MHz, $CDCl_3$) 208.1, 137.1, 133.7, 132.3, 118.2, 112.2, 105.7, 85.6, 83.1, 82.0, 71.4, 50.1, 48.7, 46.2, 42.8, 28.8, 26.9, 26.4; HRMS (ESI) (*m*/*z*): $[M+Na]^+$, found 343.1525. $C_{18}H_{24}O_5Na$ requires 343.1521.

4.1.4. ((3aR,5S,6R,6aR)-6-(Allyloxy)-tetrahydro-2,2-dimethylfuro[2,3-d][1,3]dioxol-5-yl)(bicyclo[2.2.1]hept-5-en-2-yl)methanone ***11***. To a stirred solution of the dienophile **9** (200 mg, 0.787 mmol) in dry THF (5 mL) at 0 °C, freshly distilled cyclopentadiene (156 mg, 2.36 mmol) was added dropwise. Stirring was continued for 1 h at 0 °C and 6 h at rt. Solvent was removed in vacuo and the residue was purified by column chromatography (12% Et_2O/petroleum ether) to afford the cycloadduct **11** (204 mg, 81%); R_f (20% EtOAc/petroleum ether) 0.85; δ_H (300 MHz, $CDCl_3$) 6.16 (1H, dd, *J* 5.5, 3.1 Hz, =CH), 6.08 (1H, d, *J* 3.6 Hz, O–CH–O), 5.80–5.77 (1H, m, =CH), 5.75–5.68 (1H, m, =CH), 5.22–5.14 (2H, m, =CH_2), 4.56 (1H, d, *J* 3.5 Hz, O–CH–CO), 4.54 (1H, d, *J* 3.4 Hz, OCH), 4.15 (1H, d, *J* 3.5 Hz, C*H*–OCH_2), 4.00 (1H, dd, *J* 12.9, 5.1 Hz, OCH_2), 3.89 (1H, dd, *J* 12.7, 5.4 Hz, OCH_2), 3.46–3.42 (1H, m, CH–CO), 3.41 (1H, br s, CH), 2.89 (1H, br s, CH), 1.72–1.64 (1H, m), 1.48 (3H, s, CH_3), 1.42–1.37 (2H, m), 1.33 (3H, s, CH_3), 1.27–1.22 (1H, m); δ_C (75 MHz, $CDCl_3$) 209.2, 137.6, 133.7, 131.5, 117.8, 112.3, 106.1, 85.7, 84.0, 82.2, 71.7, 50.3, 48.9, 46.3, 43.0, 27.7, 27.0, 26.4; HRMS (ESI) (*m*/*z*): $[M+Na]^+$, found 343.1524. $C_{18}H_{24}O_5Na$ requires 343.1521.

4.1.5. (3aR,5S,6S,6aR)-6-(4-Methoxybenzyloxy)-tetrahydro-2,2-dimethylfuro[2,3-d][1,3]dioxole-5-carbaldehyde ***13***. A solution of the acetonide **12** (2.0 g, 2.63 mmol) and aqueous acetic acid (75%, 10 mL) was stirred at rt for 12 h. The resulting solution was concentrated under reduced pressure and the residual mass was purified by column chromatography (40% EtOAc/petroleum ether) to afford the corresponding diol (1.43 g, 80%) as colorless oil; R_f (50% EtOAc/petroleum ether) 0.5; $[\alpha]_D^{26}$ −32.7 (*c* 6.4, $CHCl_3$); IR ν_{max} (liquid film) 3439, 2987, 2937, 1612, 1514, 1416, 1379 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.24 (2H, d, *J* 8.3 Hz, Ar–H), 6.85 (2H, d, *J* 8.4 Hz, Ar–H), 5.88 (1H, d, *J* 3.5 Hz, O–CH–O), 4.62–4.55 (2H, m, CH_2), 4.47 (1H, d, *J* 11.3 Hz, CH), 4.09–4.06 (2H, m), 3.98–3.97 (1H, m), 3.75 (4H, br s, OCH_3), 3.64 (1H, dd, *J* 11.4, 5.2 Hz, CH), 3.08 (2H br s, OH), 1.45 (3H, s, CH_3), 1.28 (3H, s, CH_3); δ_C (75 MHz, $CDCl_3$) 159.5, 129.5 (2C), 129.3, 114.0 (2C), 111.7, 105.1, 82.2, 81.5, 79.9, 71.8, 69.1, 64.2, 55.2, 26.7, 26.2; HRMS (ESI) (*m*/*z*): $[M+Na]^+$, found 363.1422. $C_{17}H_{24}O_7Na$ requires 363.1420.

To a magnetically stirred ice-cold solution of the diol (2.5 g, 7.35 mmol) obtained as above in acetonitrile/water (3:1, 24 mL) was added $NaIO_4$ (2.36 g, 11.03 mmol) in several portions. The reaction mixture was allowed to stir at 0 °C for 2 h. The precipitated white solid was filtered off after washing it thoroughly with diethyl ether. Usual work up of the filtrate afforded the title aldehyde **13** (1.60 g, 73%) as colorless liquid; IR ν_{max} (liquid film) 2978, 2928, 1737, 1610, 1587, 1514, 1373 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 9.56 (1H, s, CHO), 7.10 (2H, d, *J* 8.5 Hz, Ar–H), 6.79 (2H, d, *J* 8.5 Hz, Ar–H), 6.03 (1H, d, *J* 3.4 Hz, O–CH–O), 4.55 (1H, d, *J* 3.4 Hz, CH), 4.48 (1H, br s, CH), 4.46

(1H, d, *J* 11.6 Hz, CH_2Ph), 4.33 (1H, d, *J* 11.6 Hz, CH_2Ph), 4.24 (1H, d, *J* 3.7 Hz, CH–OPMB), 3.72 (3H, s, OMe), 1.39 (3H, s, CH_3), 1.25 (3H, s, CH_3); δ_C (75 MHz, $CDCl_3$) 200.1, 159.7, 129.6 (2C), 128.7, 114.0 (2C), 112.6, 106.3, 84.7, 83.3, 82.3, 72.2, 55.4, 27.1, 26.4; HRMS (ESI) (*m*/*z*): $[M+Na]^+$, found 331.1156. $C_{16}H_{20}O_6Na$ requires 331.1158.

4.1.6. 1-((3aR,5S,6R,6aR)-6-(4-Methoxybenzyloxy)-tetrahydro-2,2-dimethylfuro[2,3-d][1,3]dioxol-5-yl)prop-2-en-1-one ***14***. Following the procedure described for **8**, the aldehyde **13** (2.23 g, 7.2 mmol) in dry THF (15 mL) was reacted with vinyl magnesium bromide (15 mL, 15 mmol, 1.0 M in THF) to afford the corresponding carbinol (1.63 g, 68%) as colorless oil; R_f (30% EtOAc/petroleum ether) 0.5; $[\alpha]_D^{26}$ −42.6 (*c* 5.1, $CHCl_3$); IR ν_{max} (liquid film) 3498, 2987, 2935, 1612, 1585, 1514, 1463, 1375 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.22 (2H, d, *J* 7.6 Hz, Ar–H), 6.86 (2H, d, *J* 7.1 Hz, Ar–H), 5.96 (1H, d, *J* 2.6 Hz, CH), 5.84–5.73 (1H, m), 5.39 (1H, d, *J* 17.1 Hz), 5.17 (1H, d, *J* 10.6 Hz), 4.61–4.57 (2H, m), 4.47 (1H, t, *J* 5.9 Hz), 4.37 (1H, d, *J* 11.3 Hz), 4.03–4.01 (1H, m), 3.90 (1H, br s), 3.77 (3H, s), 2.52 (1H, br s, OH), 1.46 (3H, s), 1.30 (3H, s); δ_C (75 MHz, $CDCl_3$) 159.5, 135.8, 129.6 (2C), 129.0, 116.9, 113.9 (2C), 111.8, 105.0, 83.1, 82.2, 82.1, 71.6, 70.9, 55.2, 26.8, 26.3; HRMS (ESI) (*m*/*z*): $[M+Na]^+$, found 359.1475. $C_{18}H_{24}O_6Na$ requires 359.1471.

Following the procedure described for **9**, the hydroxy compound obtained as above (1.7 g, 5.06 mmol) in dry DCM (25 mL) was oxidized with DMP (2.6 g, 6.07 mmol) to afford the enone **14** (1.61 g, 95%) as colorless liquid; R_f (20% EtOAc/petroleum ether) 0.7; $[\alpha]_D^{25}$ −52.8 (*c* 2.6, $CHCl_3$); IR ν_{max} (liquid film) 2988, 2936, 1698, 1612, 1514, 1403, 1383 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.1 (2H, d, *J* 8.5 Hz, Ar–H), 6.82 (2H, d, *J* 8.7 Hz, Ar–H), 6.76–6.71 (1H, m, =CH), 6.33 (1H, d, *J* 17.4 Hz, =CH_2), 6.07 (1H, d, *J* 3.5 Hz, O–CH–O), 5.68 (1H, d, *J* 10.1 Hz, =CH_2), 4.78 (1H, d, *J* 3.6 Hz, O–CH–CO), 4.57 (1H, d, *J* 3.5 Hz, OCH), 4.47 (1H, d, *J* 11.6 Hz, OCH_2Ar), 4.37 (1H, d, *J* 11.5 Hz, OCH_2Ar), 4.28 (1H, d, *J* 3.5 Hz, C*H*–OCH_2Ar), 3.76 (3H, s, OMe), 1.45 (3H, s, CH_3), 1.30 (3H, s, CH_3); δ_C (75 MHz, $CDCl_3$) 195.1, 159.5, 132.4, 129.5 (2C), 128.9, 128.6, 113.8 (2C), 112.3, 105.9, 84.9, 83.2, 82.2, 72.1, 55.3, 27.0, 26.4; HRMS (ESI) (*m*/*z*): $[M+Na]^+$, found 357.1314. $C_{18}H_{22}O_6Na$ requires 357.1314.

4.1.7. ((1S,2S,4S)-Bicyclo[2.2.1]hept-5-en-2-yl(3aR,5S,6R,6aR)-6-(4-methoxybenzyloxy)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)methanone ***15***. The enone **14** (270 mg, 0.81 mmol) was allowed to react with cyclopentadiene (267 mg, 4.04 mmol) in presence of $ZnCl_2$ (120 mg, 0.882 mmol) to afford after column chromatography the adduct **15** (297 mg, 92%); R_f (20% EtOAc/petroleum ether) 0.8; $[\alpha]_D^{25}$ −88.4 (*c* 3.0, $CHCl_3$); IR ν_{max} (liquid film) 2972, 2938, 1705, 1612, 1585, 1514, 1456, 1375 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 7.12 (2H, d, *J* 8.5 Hz, Ar–H), 6.80 (2H, d, *J* 8.5 Hz, Ar–H), 6.04 (1H, dd, *J* 5.2, 3.1 Hz, =CH), 6.00 (1H, d, *J* 3.6 Hz, O–CH–O), 5.70 (1H, dd, *J* 5.4, 2.4 Hz, =CH), 4.62 (1H, d, *J* 3.6 Hz, O–CH–CO), 4.51 (1H, d, *J* 3.6 Hz, OCH), 4.47 (1H, d, *J* 11.6 Hz, OCH_2Ar), 4.34 (1H, d, *J* 11.6 Hz, OCH_2Ar), 4.20 (1H, d, *J* 3.60 Hz, C*H*–O–CH_2Ar), 3.71 (3H, s, OMe), 3.16–3.12 (1H, m, CH–CO), 3.10 (1H, br s, CH), 2.77 (1H, br s, CH), 1.72–1.64 (1H, m), 1.39 (3H, s, CH_3), 1.37–1.27 (1H, m), 1.25 (3H, s, CH_3), 1.18–1.13 (2H, m); δ_C (75 MHz, $CDCl_3$) 207.5, 159.6, 137.1, 132.2, 129.7 (2C), 129.0, 113.9 (2C), 112.1, 105.6, 85.4, 82.8, 81.8, 72.0, 55.3, 50.0, 48.8, 46.2, 42.6, 28.6, 27.0, 26.4; HRMS (ESI) (*m*/*z*): $[M+Na]^+$, found 423.1788. $C_{23}H_{28}O_6Na$ requires 423.1783.

4.1.8. (Bicyclo[2.2.1]hept-5-en-2-yl)((3aR,6R,6aR)-tetrahydro-6-hydroxy-2,2-dimethylfuro[2,3-d][1,3]dioxol-5-yl)methanone ***16***. To a stirred solution of **15** (320 mg, 0.8 mmol) in DCM (8.1 mL) and water (0.5 mL) was added DDQ (272 mg, 1.2 mmol) at rt. After 3 h precipitated solid was removed by decantation and washed with CH_2Cl_2 (5 mL). The combined CH_2Cl_2 solution was then washed with saturated $NaHCO_3$, water and saturated NaCl, and dried over Na_2SO_4. Evaporation of the solvent in vacuo gave an oil, which was chromatographed on silica gel to give a white solid **16** (195 mg, 87%), mp 112–114 °C; R_f (30% EtOAc/petroleum ether) 0.5; $[\alpha]_D^{26}$ −146.21 (*c* 2.0, $CHCl_3$); IR ν_{max} (KBr plate) 3442, 2985, 2965, 1710, 1384, 1374 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 6.15 (1H, dd, *J* 5.4, 3.0 Hz, =CH), 6.07 (1H, d, *J* 3.5 Hz, O–CH–O), 5.84 (1H, dd, *J* 5.4, 2.6 Hz, =CH), 4.69 (1H, d, *J* 3.0 Hz, O–CH–CO), 4.56 (1H, d, *J* 3.4 Hz, OCH), 4.52 (1H, br s, C*H*–OH), 3.41–3.35 (1H, m), 3.33 (1H, br s, CH), 3.10 (1H, br s, CH), 2.90 (1H, br s, CH), 2.10 (1H, br s, OH), 1.86–1.78 (1H, m), 1.49 (3H, s, CH_3), 1.47–1.43 (2H, m), 1.33 (3H, s, CH_3); δ_C (75 MHz, $CDCl_3$)209.8; 137.6, 131.9, 112.1, 105.4, 86.0, 84.6, 76.1, 50.1, 49.6, 46.4, 42.8, 28.4, 27.0, 26.3; HRMS (ESI) (*m*/*z*): $[M+Na]^+$, found 303.1205. $C_{15}H_{20}O_5Na$ requires 303.1208.

4.1.9. Synthesis of the tricycle ***19***. Grubbs' first generation catalyst (15 mg, 0.018 mmol) was dissolved in degassed CH_2Cl_2 (2 mL) and was added through a syringe to a solution of the norbornene derivative **10** (200 mg, 0.62 mmol) in degassed CH_2Cl_2 (50 mL). This solution was then purged with ethylene and stirred at rt for 15 min under an ethylene atmosphere. The solvent was then removed by rotary evaporation and purified by column chromatography (10% Et_2O/petroleum ether) to afford the compound **3a** (176 mg, 81%) as colorless oil; R_f (20% EtOAc/petroleum ether) 0.6; IR ν_{max} (liquid film) 2983, 2937, 1707, 1373 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 6.03 (1H, d, *J* 3.5 Hz, O–CH–O), 5.88–5.66 (3H, m, =CH), 5.26–5.17 (3H, m, =CH_2), 5.05–4.89 (3H, m, =CH_2), 4.73 (1H, d, *J* 3.8 Hz, O–CH–CO), 4.50 (1H, d, *J* 3.6 Hz, –O–CH–), 4.25 (1H, d, *J* 3.8 Hz, –O–CH–), 4.06 (1H, dd, *J* 12.6, 5.3 Hz, OCH_2), 3.88 (1H, dd, *J* 12.7, 6.1 Hz, OCH_2), 3.22 (1H, q, *J* 8.1 Hz), 2.91–2.80 (1H, m), 2.60–2.46 (1H, m), 1.98–1.79 (3H, m), 1.61–1.49 (1H, m), 1.44 (3H, s, CH_3), 1.31 (3H, s, CH_3); δ_C (75 MHz, $CDCl_3$) 205.9, 141.9, 139.0, 133.3, 118.6, 115.7, 113.6, 112.3, 105.7, 86.1, 82.8, 81.9, 71.1, 51.4, 48.0, 44.0, 39.6, 34.9, 27.1, 26.5.

A solution of the triene **3a** (100 mg, 0.28 mmol) in dichloromethane (40 mL) was treated with Grubbs' first generation catalyst **22** (12 mg, 0.014 mmol) under Ar atmosphere and stirred at rt for 6 h. The residual mass obtained after removal of solvent was chromatographed (12% Et_2O/petroleum ether) to afford **19** (71 mg, 78%) as colorless liquid; R_f (15% EtOAc/petroleum ether) 0.85; $[\alpha]_D^{25}$ −77.6 (*c* 2.4, $CHCl_3$); IR ν_{max} (liquid film) 2983, 2937, 1707, 1373 cm^{-1}; δ_H (500 MHz, $CDCl_3$) 6.09 (1H, d, *J* 3.2 Hz, O–CH–O), 5.85 (1H, tdd, *J* 18.0, 10.0, 7.2 Hz, =CH), 5.57 (1H, dt, *J* 10.5, 2.0 Hz, =CH), 5.51 (1H, dt, *J* 10.5, 4.0 Hz, =CH), 5.06 (1H, d, *J* 17.1 Hz, =CH_2), 4.96 (1H, d, *J* 10.3 Hz, =CH_2), 4.53 (1H, d, *J* 3.1 Hz, O–CH–CO), 4.40 (1H, d, *J* 15.0 Hz,), 4.33 (1H, d, *J* 2.3 Hz), 4.04 (1H, d, *J* 1.7 Hz), 4.00 (1H, q, *J* 9.6 Hz), 3.82 (1H, dd, *J* 15.0, 10.6 Hz), 3.42 (1H, quintet, *J* 8.7 Hz), 2.56 (1H, sextet, *J* 8.6 Hz), 2.19 (1H, td, *J* 7.6, 6.4 Hz), 1.82 (2H, t, *J* 10.0 Hz), 1.48 (3H, s, CH_3), 1.40–1.36 (1H, m), 1.33 (3H, s, CH_3); δ_C (75 MHz, $CDCl_3$) 211.8, 141.7, 141.6, 125.2, 113.7, 112.8, 105.9, 86.3, 85.5, 84.3, 68.6, 51.1, 44.4, 41.2, 40.3, 35.8, 26.9, 26.5; HRMS (ESI) (*m*/*z*): $[M+Na]^+$, found 343.1524. $C_{18}H_{24}O_5Na$ requires 343.1521.

4.1.10. ((3aR,5S,6R,6aR)-6-(Allyloxy)-2,2-dimethyltetrahydrofuro[2,3-d][1,3]dioxol-5-yl)((1R,2R,4R)-2,4-divinylcyclopentyl)methanone ***3b***. To a solution of **11** (60 mg, 0.19 mmol) in dry CH_2Cl_2 (30 mL) under ethylene atmosphere at rt was added a solution of the catalyst **22** (15 mg, 0.018 mmol) in CH_2Cl_2 (2 mL). After stirring for 1 h, the reaction mixture was concentrated. Column chromatography of the residue (10% Et_2O/petroleum ether) gave the ring opened product **3b** (59 mg, 96%) as colorless oil; R_f (20% EtOAc/petroleum ether) 0.7; ν_{max} (liquid film) 2971, 1709, 1442 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 6.04 (1H, d, *J* 3.5 Hz, O–CH–O), 5.88–5.61 (3H, m), 5.21–5.13 (2H, m), 5.04–4.98 (2H, m), 4.92–4.87 (2H, m), 4.50 (1H, d, *J* 3.5 Hz, O–CH–CO), 4.41 (1H, d, *J* 3.4 Hz, OCH), 4.14 (1H, d, *J* 3.4 Hz, CH–O–CH_2), 4.02–3.86 (2H, m), 3.71–3.62 (1H, m), 3.10 (1H, quintet, *J* 8.5 Hz, CH), 2.55–2.46 (1H, m), 2.06–1.97 (1H, m), 1.91–1.62 (3H, m), 1.42 (3H, s, CH_3), 1.31 (3H, s, CH_3); δ_C (75 MHz, $CDCl_3$) 210.8, 142.2, 139.8, 133.8, 117.8, 114.9, 113.4, 112.3, 106.1, 85.9, 84.0, 82.1, 71.7, 52.6, 45.6, 43.5, 39.0, 33.6, 27.1, 26.6; HRMS (ESI) (m/z): $[M+Na]^+$, found 371.1839. $C_{20}H_{28}O_5Na$ requires 371.1834.

*4.1.11. Synthesis of tricycles **20** and **21**.* Following the metathesis procedure described above, the ring opened product **3b** (42 mg, 0.12 mmol) in CH_2Cl_2 (20 mL) was treated with the catalyst **23** (6 mg, 6 mol %) in argon atmosphere (12 h) to afford, after column chromatography (35% Et_2O/petroleum ether), the tricycles **20** (8 mg, 21%) and **21** (11 mg, 29%) as colorless oil. Compound **20**; R_f (30% EtOAc/petroleum ether) 0.35; $[\alpha]_D^{27}$ −5.4 (c 1.2, $CHCl_3$); IR ν_{max} (liquid film) 3076, 2986, 2935, 1726, 1641 cm^{-1}; δ_H (600 MHz, $CDCl_3$) 6.09 (1H, d, J 3.6 Hz, O–CH–O), 5.80 (1H, ddd, J 11, 9, 2.4 Hz, =CH–), 5.82–5.74 (1H, m, =CH–), 5.45 (1H, ddd, J 11.4, 3.4, 0.6 Hz, =CH–), 5.06 (1H, td, J 17.1, 1.8 Hz, $=CH_2$), 4.95 (1H, td, J 10.3, 1.2 Hz, $=CH_2$), 4.88 (1H, d, J 3.7 Hz, OCH), 4.58 (1H, d, J 3.7 Hz, OCH), 4.53 (1H, d, J 3.5 Hz, OCH), 4.38 (1H, td, J 15.5, 3.0 Hz, OCH_2), 3.94 (1H, dd, J 15.4, 5.3 Hz, OCH_2), 3.08–3.03 (1H, m), 2.89–2.80 (2H, m), 2.12–2.05 (2H, m), 1.53 (1H, dd, J 11.4, 10.8 Hz), 1.47 (3H, s), 1.32 (3H, s), 1.28–1.22 (1H, m); δ_C (125 MHz, $CDCl_3$) 207.3, 140.9, 140.8, 124.6, 114.1, 112.4, 106.3, 87.7, 82.6, 78.4, 65.7, 50.6, 45.5, 45.4, 42.9, 36.8, 27.2, 26.5; HRMS (ESI) (m/z): $[M+Na]^+$, found 343.1523. $C_{18}H_{24}O_5Na$ requires 343.1521. Compound **21**; R_f (30% EtOAc/petroleum ether) 0.40; $[\alpha]_D^{26}$ −21.4 (c 1.1, $CHCl_3$); IR ν_{max} (liquid film) 3077, 2984, 2938, 1724, 1641 cm^{-1}; δ_H (600 MHz, $CDCl_3$) 6.00 (1H, d, J 3.6 Hz, O–CH–O), 5.82 (1H, ddd, J 17.4, 10.2, 7.2 Hz, =CH–), 5.72–5.63 (2H, m, CH=CH), 5.06 (1H, td, J 17.4, 1.2 Hz, $=CH_2$), 4.97 (1H, ddd, J 10.3, 1.5, 0.6 Hz, $=CH_2$), 4.73 (1H, d, J 2.4 Hz, OCH), 4.65 (1H, d, J 2.4 Hz, OCH), 4.52 (1H, d, J 3.0 Hz, OCH), 4.24 (1H, dd, J 12.6, 6.0 Hz, OCH_2), 3.86 (1H, dd, J 12.5, 9.5 Hz, OCH_2), 3.52–3.42 (2H, m, $CH–CH_2$), 2.62–2.53 (1H, m), 2.23–2.16 (1H, m), 2.04–1.97 (1H, m), 1.93–1.83 (1H, m), 1.60–1.52 (1H, m), 1.54 (3H, s, CH_3), 1.31 (3H, s, CH_3); δ_C (125 MHz, $CDCl_3$) 205.9, 141.0, 140.6, 128.0, 114.2, 112.2, 104.8, 89.6, 87.3, 85.1, 68.9, 53.4, 44.1, 40.8, 39.7, 37.2, 27.0, 26.4; HRMS (ESI) (m/z): $[M+Na]^+$, found 343.1525. $C_{18}H_{24}O_5Na$ requires 343.1521.

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Supplementary data

Supplementary data associated with this article can be found online at doi:10.1016/j.tet.2010.09.084. These data include MOL files and InChIKeys of the most important compounds described in this article.

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