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A direct route to angularly substituted hydrindanes. Formal synthesis of bakkenolide-A and synthesis of an advanced intermediate to umbellactal

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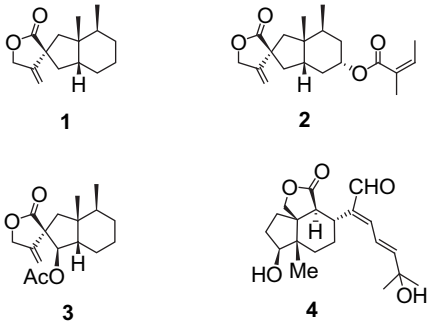
ABSTRACT

A direct route for the synthesis of highly functionalized angularly substituted hydrindanes has been developed. The key step involves RO–RCM of an appropriately functionalized norbornene derivative. The hydrindane derivative obtained in this way has been used to accomplish a formal synthesis of bakkenolide-A. This protocol has also been extended for the synthesis of an advanced intermediate to the synthesis of the diterpene umbellactal.

1. Introduction

Hydrindane ring system with an angular substituent is frequently encountered in terpenoids. Representative examples include sesquiterpenes of the bakkanes family such as bakkenolide-A (**1**),[1] homogynolide-A (**2**),[2] 9-acetoxyfukinanolide (**3**),[3] etc. Most of the bakkanes also contain a spiro-fused β-methylene γ-butyrolactone moiety. The recently isolated diterpene umbellactal (**4**)[4] is also a *cis*-hydrindane derivative with an angularly fused γ-lactone. Bakkenolide-A and umbellactal exhibit cytotoxicity toward several carcinoma cell lines.[5] The former also acts as an effective insect antifeedant.[6] The novel molecular architecture along with interesting biological activities elicited considerable interest for the synthesis of these compounds culminating in a number of elegant approaches for the total synthesis of bakkanes.[7] These approaches include construction of hydrindanes by (i) annulation of a five-membered ring onto a properly constructed cyclohexane derivative,[7b–j] (ii) ring contraction of decalin derivatives,[7k,n] and (iii) intramolecular Diels–Alder reaction[7l–m] in appropriately designed substrates. Among these approaches, only intramolecular Diels–Alder route provides direct access to *cis*-hydrindane derivatives.

We thought of developing a route that not only allows direct construction of *cis*-hydrindane derivatives with an angular substituent but at the same time introduces functionality at both the rings of the resulting hydrindane system for elaboration to the



highly functionalized bakkanes as well as umbellactal. Our retrosynthetic plan is delineated in Scheme 1. The hydrindane derivative **5** was envisaged as the key intermediate for entry into bakkanes as well as umbellactal. The vicinal ester units in **5** can be transformed to methyl groups for bakkanes while they can be employed to construct the angularly fused γ-lactone present in umbellactal. Domino metathesis of norbornene derivatives and other strained cycloalkenes involving ring opening–ring closing metathesis (RO–RCM) has recently emerged as a powerful tool[8] for the construction of fused bicyclic rings including *cis*-hydrindanes.[9] This protocol has been employed successfully in the synthesis of natural products.[10] Very recently, we have demonstrated that a sequence of RO–RCM of norbornenes with multiple alkene chains leads to densely functionalized bridged[11] and linearly arrayed tricycles.[12] Intrigued by these observations, we visualized that a direct synthesis of the *cis*-hydrindane derivative **5** could be achieved through RO–RCM of the

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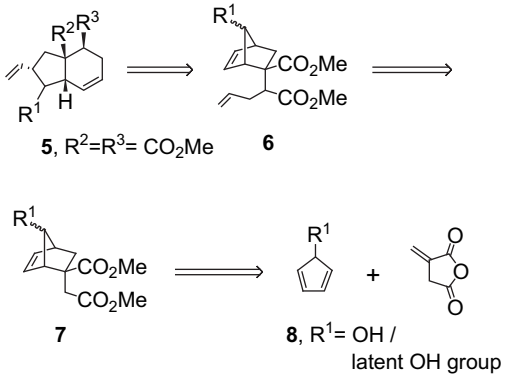
norbornene derivative **6**. The latter can be obtained from allylation of the diester **7**, available from Diels–Alder adduct of itaconic anhydride with the cyclopentadiene derivative **8**. Herein, we report[13] results of the investigation toward the synthesis of bakkanes and umbellactal based on the concept delineated in Scheme 1.



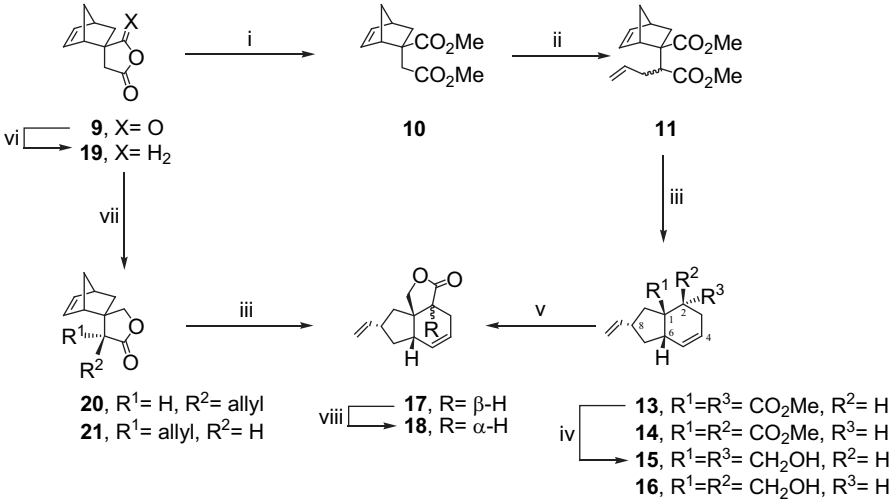
Scheme 1.

2. Results and discussion

We initially chose the norbornene derivative **10** to establish the efficacy of the concept. The dimethyl ester **10** was prepared[14] from the anhydride **9**[15] obtained by Diels–Alder reaction of the itaconic anhydride with the cyclopentadiene (Scheme 2). Alkylation of the lithium enolate of the ester **10** with the allyl bromide afforded diester **11** as a 2:1 chromatographically inseparable mixture in 90% yield.

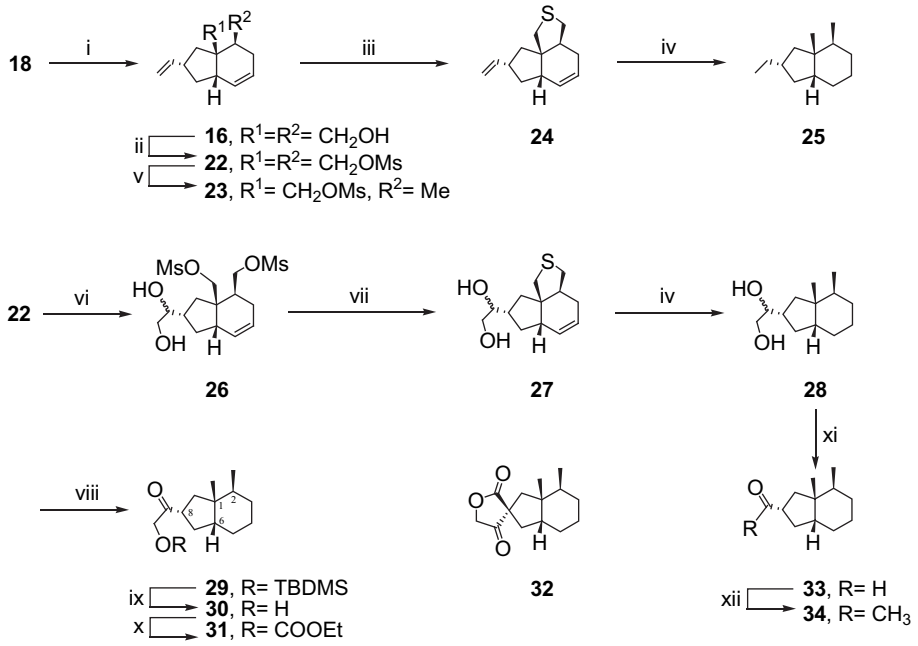
Treatment of the mixture of the diesters **11** with Grubbs' catalyst $Cl_2(PCy_3)_2Ru{=}CHPh$ **12**,[16] produced a mixture of hydrindanes **13** and **14** in near quantitative yield. The structures of **13** and **14** could be easily ascertained from analysis of ^1H and ^{13}C NMR spectra. Synthesis of bakkanes requires the hydrindane **14** in which C-1 and C-2 esters are *syn* to each other. We thought that the C-2 carbomethoxy group in the diastereoisomer **13** in the mixture of **13** and **14** could be epimerized to produce the desired diester **14**. However, the C-2 ester in the mixture of **13** and **14** as obtained above when treated with NaOMe in MeOH failed to undergo epimerization and the ratio of **13** and **14** in the mixture remained unchanged. In order to make the *cis*-hydrindane derivative with C-1, C-2 substituents *syn* to each other, the following protocol was adopted. The mixture of **13** and **14** was reduced with lithium aluminum hydride to produce a mixture of the diols **15** and **16**. The mixture of these diols was next transformed to a mixture of the *trans*-lactone **17** and *cis*-lactone **18** in 70% yield by two consecutive oxidation steps using IBX and followed by Jones reagent. The angularly fused *trans*-lactone **17** appears to be highly strained and hence energetically less stable. Thus, it should be isomerizable to the *cis*-lactone **18**. Indeed, a quantum mechanical calculation[17] revealed that *cis*-lactone **18** is more stable than the *trans*-lactone **17** by 3.9 kcal/mol. Thus, the mixture of the *cis*- and *trans*-lactones, when treated with DBU in benzene under reflux afforded exclusively the *cis*-lactone **18** in 80% yield.

An alternative route to the *cis*-lactone **18** was also developed. Reduction of the anhydride **9** with $NaBH_4$ afforded known lactone **19**[18] in excellent yield. Alkylation of the lithium enolate of the lactone **19** with the allyl bromide led to an inseparable mixture of the lactones **20** and **21** in 4:1 ratio in 85% yield. Construction of a Dreiding model of the lactone **19** revealed that allylation would proceed preferentially from the face away from the ethylene bridge, as the other face is blocked to some extent by the ethylene bridge to produce lactone **20** as the major product. This structural assignment to the lactones **20** and **21** was confirmed by their transformation to the tricyclic lactones **17** and **18**, respectively, as follows: Treatment of the mixture of lactones **20** and **21** with the catalyst **12** afforded a mixture of the hydrindane derivatives **17** and **18** prepared already in a different route as described above in 4:1 ratio in 70% yield. Comparison of ^{13}C NMR spectral data of the minor component of this mixture was found to be identical with that of the *cis*-lactone **18**. This confirmed the structure of the major and minor allylated products as **20** and **21**, respectively. The lactone **18** represents the core structure of umbellactal.



Scheme 2. Reagents and conditions: (i) (a) TFA, THF/H_2O (2:1), 60 °C, (b) CH_2N_2, Et_2O, 95%; (ii) LDA, allyl bromide, THF, −78 °C, 90%; (iii) catalyst **12** (2 mol %), DCM, C_2H_4, rt, 5 h, 95%; (iv) $LiAlH_4$, Et_2O, 0 °C, 90%; (v) (a) IBX, DMSO/acetone (1:4), rt, 1 h, (b) Jones reagent, acetone, 0 °C, 80%; (vi) $NaBH_4$, DMF, 0 °C, 70%; (vii) LDA, allyl bromide, THF, −78 °C, 85%; (viii) DBU, C_6H_6, reflux, 2 h, 82%.

We next focused on the transformation of the lactone unit to dimethyl groups. The lactone **17** was reduced with $LiAlH_4$ to afford the diol **16** in 90% yield (Scheme 3). The diol **16** was transformed to the dimesylate **22**. Reduction of the dimesylate with $LiAlH_4$ led to monodeoxygenation leading to the formation of **23**. Attempts for deoxygenation of **22** with Zn/NaI or $LiEt_3BH$ afforded the same product **23**. The dimesylate **22** was next converted to the sulfide **24** on treatment with Na_2S. The cyclic sulfide **24** was subjected to reduction with Raney Ni W-4. In this way deoxygenation of both the mesyl groups in **22** could be achieved. But the reaction was accompanied with reduction of the double bonds also to afford the



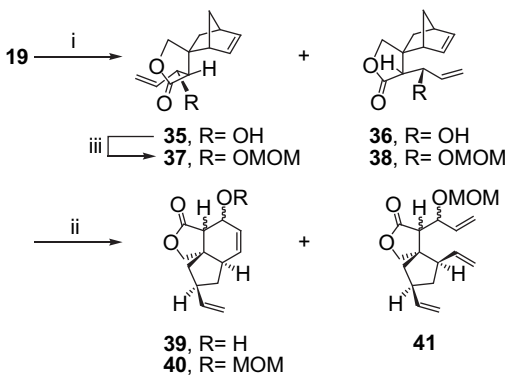
Scheme 3. Reagents and conditions: (i) $LiAlH_4$, Et_2O, 0 °C, 92%; (ii) MsCl, Et_3N, DCM, 0 °C, 1 h, 90%; (iii) Na_2S/DMF, 50 °C, 3 h, 90%; (iv) Raney Ni W-4, THF, rt, 80%; (v) $LiEt_3BH$, THF, 80%; (vi) OsO_4, NMO, THF/H_2O (4:1), rt, 12 h, 80%; (vii) Na_2S/DMF, 50 °C, 6 h, 85%; (viii) (a) TBDMSCl, DMAP, Et_3N, DCM, rt, 95%, (b) DMP, DCM, rt, 90%; (ix) TBAF, THF, rt, 80%; (x) $ClCO_2Et$, DMAP, Py, DCM, 96%; (xi) $NaIO_4$, THF/H_2O (2:1), 0 °C; (xii) (a) MeMgI, Et_2O, 0 °C, 90%, (b) DMP, DCM, rt, 96%.

hydrindane derivative **25** with the desired vicinal dimethyl groups. Since the vinyl unit will be required for annulation of the spiro lactone unit for bakkanes, we modified the above sequence as follows: selective dihydroxylation of the dimesylate **22** with OsO_4 produced the diol **26** in 80% yield. The dimesylate **26** was transformed to cyclic sulfide **27**. Reduction of cyclic sulfide **27** was achieved with Raney Ni W-4 to afford the dimethyl derivative **28** in 85% yield. For construction of the spiro lactone unit, the compound **28** was converted to the hydroxy-ketone **30** through a three-step sequence involving silylation of the primary hydroxy group with TBDMSCl followed by oxidation of the secondary hydroxy group with Dess–Martin periodinane (DMP) and desilylation. The hydroxy-ketone **30** was treated with ethylchloroformate to afford the carbonate **31**. It was anticipated that a carbanion generated at C-8 would trigger an intramolecular nucleophilic reaction resulting in the synthesis of the spiro lactone **32**. However, attempted spirolactonization of **31** with a variety of bases to afford **32** was unsuccessful. The diol **28** was, thus, transformed to the ketone **34** in the following way. Periodate cleavage of the diol unit in **28** afforded aldehyde **33**. Addition of MeMgI to the aldehyde **33** followed by DMP oxidation gave ketone **34**. The ketone **34** has already been converted[19] to bakkenolide-A in three steps. With the synthesis of the ketone **34**, a formal synthesis of bakkenolide-A is, thus, achieved.

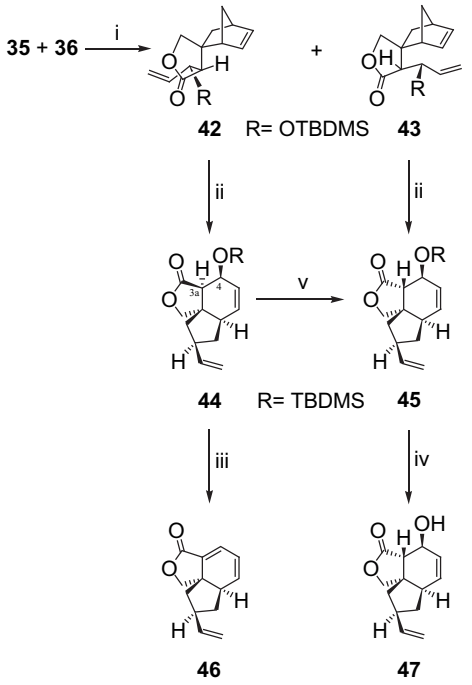
We next focused on synthesis of umbellactal. This required introduction of an alkyl chain in the six-membered ring of the hydrindane derivative **18**. We thought that a hydrindane system with a hydroxy group in the six-membered ring will enable introduction of alkyl chain. Toward this end the enolate of the lactone **19** was allowed to react with acrolein (Scheme 4). A mixture of adducts **35** and **36** along with their corresponding hydroxy epimers was obtained in 83% yield, the ratio of the four isomers being about 5:2:2:1. Stereochemical assignment at the newly generated carbon centers in **35** and **36** was based on analogy to the formation of **20** and **21** from **19**. The stereochemistry at the centers bearing the hydroxy groups in **35** and **36** was based on their transformation to **44** and **45** (Scheme 5), respectively. Metathesis of this mixture of adducts with Grubbs' catalyst **12** produced a mixture of tricycles **39** in poor yield (20%) along with 50% of unreacted norbornene derivatives.

RCM of dienes bearing free hydroxy groups with Grubbs' I catalyst has occasionally been reported[20] to proceed with low yields possibly due to decomposition of the active ruthenium/methylene catalyst generated after the first catalytic cycle. Protection of the hydroxy groups generally improves the yield of metathesis product. The hydroxy group in the above mixture of the adducts **35** and **36** was protected with $CH_2(OMe)_2$ to afford the corresponding MOM protected ethers **37** and **38** along with the other two epimers at the MOM bearing stereocenters. Metathesis of the MOM protected derivatives **37** and **38** gave the tricycles **40** in significantly improved yield (50%). However a substantial amount of the ring-opened product **41** (25%) remained uncyclized under the above reaction condition.

To enhance further the efficiency of the metathesis, the hydroxy group in the above mixture of aldol adducts **35** and **36** was protected with TBDMSCl to give the silyl ethers **42** and **43**, respectively. Column chromatography of the silylated mixture afforded pure silyl



Scheme 4. Reagents and conditions: (i) LDA, acrolein, THF, −78 °C, 83%; (ii) Grubbs' I (5 mol %), DCM, C_2H_4, rt, 23 h, 20% (for **39**), 50% (for **40**); (iii) $CH_2(OMe)_2$, $BF_3{\cdot}OEt_2$, DCM, 0 °C, 75%.



Scheme 5. Reagents and conditions: (i) TBDMSCl, DMAP, Im, Et_3N, DCM, rt, 50% (for **42**), 19% (for **43**); (ii) Grubbs' I (5 mol %), DCM, C_2H_4, rt, 12 h, 72% (for **44**), 70% (for **45**); (iii) TBAF, THF, rt, 12 h, 85%; (iv) TBAF, THF, rt, 6 h, 75%; (v) DBU, C_6H_6, Δ, 1 h, 43% (**45**) and 35% (**46**).

ethers **42** and **43** in 50% and 19% yields, respectively. Metathesis of the silyl ether **42** under the above condition afforded, after chromatography, the tricyclic compound **44** in 72% yield. Similarly, metathesis of the silyl ether **43** provided the tricycle **45** in 70% yield. The stereochemical assignment of the *trans*-lactone **44** (except the C-4 center) is based on analogy to the formation of **17** from **20**. To determine the stereochemistry of the C-4 substituent, the lactone **44** was subjected to desilylation. The product isolated in 85% yield was found to be exclusively **46** presumably arising from facile dehydration of the in situ generated corresponding hydroxy group. This indicated that C-3a H and the C-4 silyloxy group in **44** were *anti* to each other. In contrast, desilylation of **45** produced exclusively the hydroxy-compound **47** (75%), which failed to undergo dehydration under a variety of conditions indicating that C-3a H and C-4 OH in **47** were *syn* to each other. This also confirmed the stereochemical assignment of lactone **45**. The stereochemical assignment of **44** was further confirmed when the latter was found to isomerize to the *cis*-lactone **45** (43%) on treatment with DBU in benzene under reflux. During isomerization of **44**, the diene **46** was also isolated in ca. 35% yield. The IR absorption of the lactone carbonyl was observed at an unusually higher frequency (ν_{max} 1787 cm^{-1}) in **44** than that (ν_{max} 1762 cm^{-1}) of **45** also indicated the presence of a highly strained *trans*-lactone ring in **44**. The silyl ether **45** represents the highly functionalized tricyclic skeleton present in umbellactal.

3. Conclusion

We have demonstrated that RO–RCM of norbornene derivatives can be employed efficiently to construct directly highly functionalized angularly substituted hydrindane derivatives. This protocol has been employed to accomplish a formal synthesis of bakkenolide-A. The potential of this protocol toward the synthesis of the biologically active diterpene umbellactal has also been explored leading to the construction of an advanced intermediate.

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 workup 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 MHz for ^1H and 75 MHz for ^{13}C on Bruker-Avance DPX_{300} instrument. ^{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. 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. Methyl 2-(1-(methoxycarbonyl)but-3-enyl)bicyclo[2.2.1]hept-5-ene-2-carboxylate **11**.* A solution of the ester **10** (2.0 g, 9.14 mmol) in THF (20 mL) was added drop wise to a magnetically stirred solution of LDA [prepared from diisopropyl amine (2.56 mL, 18.3 mmol) in anhydrous THF (20 mL) and ^nBuLi (10.3 mL, 16.5 mmol, 1.6 M in hexane)] at −78 °C and the reaction mixture was stirred at that temperature for 1 h. Freshly distilled allyl bromide (1.6 mL, 18.2 mmol) was added drop wise to the reaction mixture at the same temperature and was allowed to attain rt for 2 h. After quenching with saturated aqueous NH_4Cl solution, the reaction mixture was worked up in the usual way to afford, after column chromatography (10% Et_2O/petroleum ether), the ester **11** (2.2 g, 90%) as 2:1 diastereomeric mixture as colorless oil; R_f (20% EtOAc/petroleum ether) 0.8; ν_{max} (liquid film) 2976, 2950, 1732, 1435, 1334 cm^{-1}; δ_H (300 MHz, $CDCl_3$) (for major isomer from the mixture) 6.18 (2H, br s, =CH), 5.52–5.61 (1H, m, =CH), 4.83–4.92 (2H, m, $=CH_2$), 3.62 (3H, s, OCH_3), 3.61 (3H, s, OCH_3), 2.73 (1H, s), 3.13 (1H, s), 2.36 (1H, dd, *J* 12.7, 3.8 Hz), 2.25–2.31 (1H, m), 2.07–2.12 (2H, m), 1.42 (1H, d, *J* 8.7 Hz), 1.18 (1H, d, *J* 8.8 Hz), 0.96 (1H, dd, *J* 12.4, 2.4 Hz); δ_C (75 MHz, $CDCl_3$) (for major isomer) 175.6, 172.9, 139.1, 136.1, 134.5, 116.2, 57.5, 52.8, 51.9, 51.4, 49.7, 48.5, 41.8, 36.3, 32.8; (for minor isomer) 175.6, 173.8, 140.4, 135.9, 132.0, 116.5, 56.8, 54.0, 52.0, 51.5, 49.5, 47.9, 42.3, 35.0, 33.5; HRMS (ESI) (*m*/*z*): $[M+Na]^+$, found 287.1256. $C_{15}H_{20}O_4Na$ requires 287.1259.

4.1.2. (2S,3aR*,7aS*)-Dimethyl 2,3,3a,4,5,7a-hexahydro-2-vinyl-1H-indene-3a,4-dicarboxylates **13** and **14**.* To a solution of **11** (1.0 g, 3.8 mmol) in dry CH_2Cl_2 (100 mL) under ethylene atmosphere at rt was added a solution of catalyst **12** (62 mg, 2 mol %) in CH_2Cl_2 (5 mL). After stirring for 5 h, the reaction mixture was concentrated. Column chromatography of the residue (10% Et_2O/petroleum ether) gave a mixture of **13** and **14** (950 mg, 95%) as colorless oil; R_f (20% EtOAc/petroleum ether) 0.7; ν_{max} (liquid film) 2972, 2875, 1734, 1448, 1420 cm^{-1}; δ_H (300 MHz, $CDCl_3$) (for the mixture of **13** and **14**) 5.71–5.55 (3H, m, =CH), 5.02–4.79 (2H, m, $=CH_2$), 3.69, 3.66, 3.64, 3.62 (total 6H, all s, OMe), 2.85–2.53 (3H, m), 2.39–2.14 (4H, m), 1.44–1.38 (1H, m), 1.24–1.17 (1H, m); δ_C (75 MHz, $CDCl_3$) (for major isomer) 177.2, 174.0, 143.8, 131.7, 122.5, 112.7, 55.1, 52.3, 51.8, 44.2, 43.8, 40.9, 37.5, 34.3, 23.6; (for minor isomer) 176.7, 174.3, 141.6, 129.0, 123.4, 113.7, 52.0, 51.7, 51.1, 45.8, 44.1, 43.7, 42.5, 40.1, 26.0; HRMS (ESI) (*m*/*z*): $[M+Na]^+$, found 287.1256. $C_{15}H_{20}O_4Na$ requires 287.1259.

4.1.3. (2S,3aR*,7aS*)-2,3,3a,4,5,7a-Hexahydro-3a,4-dihydroxymethyl-2-vinyl-1H-indenes **15** and **16**.* To a suspension of $LiAlH_4$

(72 mg, 1.9 mmol) in dry ether (5 mL) at 0 °C was added a solution of the diesters **13** and **14** (250 mg, 0.95 mmol) in dry ether (5 mL). The reaction mixture was allowed to stir at that temperature for 1 h and then quenched by sequential addition of water (0.08 mL), aqueous NaOH solution (0.08 mL, 15%), and water (0.24 mL), and allowed to attain rt. The resulting suspension was filtered and the filtrate was dried and concentrated and the residual mass was purified by column chromatography (30% Et_2O/petroleum ether) to give a mixture of diols **15** and **16** (176 mg, 90%) as a colorless liquid; R_f (40% EtOAc/petroleum ether) 0.5; ν_{max} (liquid film) 3273, 3018, 2900, 1640, 1446 cm^{-1}; δ_H (300 MHz, $CDCl_3$) (for the mixture of **15** and **16**) 5.74–5.61 (2H, m, =CH), 5.52–5.49 (1H, m, =CH), 4.99–4.79 (2H, m, $=CH_2$), 3.81 (1H, dd, *J* 11.2, 2.1 Hz, OCH_2), 3.62–3.34 (2H, m, OCH_2), 3.15 (1H, d, *J* 11.3 Hz, OCH_2), 2.63–2.42 (1H, m), 2.24–2.15 (2H, m), 1.98–1.75 (3H, m), 1.73–1.51 (2H, m), 1.26–1.12 (3H, m); δ_C (75 MHz, $CDCl_3$) (for major isomer) 144.0, 133.0, 123.0, 112.4, 68.3, 65.2, 49.4, 42.0, 41.9, 40.1, 38.1, 32.4, 25.3; (for minor isomer) 142.5, 128.5, 125.9, 113.0, 65.8, 62.4, 47.0, 45.6, 42.8, 42.4, 40.7, 39.6, 25.5; HRMS (ESI) (*m*/*z*): $[M+Na]^+$, found 231.1365. $C_{13}H_{20}O_2Na$ requires 231.1361.

4.1.4. (6aS,8S*,9aR*)-3a,4,6a,7,8,9-Hexahydro-8-vinylindeno[3a,4-c]-furan-3(1H)-ones **17** and **18**.* A mixture of dimethyl sulfoxide (3 mL), acetone (12 mL), and *o*-iodoxybenzoic acid (1.27 g, 4.53 mmol) was stirred for 1 h, and the resulting solution was added to the mixture of diols **15** and **16** (787 mg, 3.78 mmol). After 1 h at rt, the reaction mixture was quenched with water (10 mL) and filtered through Celite. The filtrate was extracted with dichloromethane (3×10 mL), washed with water, dried (Na_2SO_4), concentrated, and used for the next step without further purification. The crude lactols (100 mg, 0.48 mmol) in acetone (2 mL) was immediately treated with Jones reagent at 0 °C until the color of the reagent persisted. Work up of the reaction mixture with diethyl ether followed by purification of the residue by column chromatography (10% Et_2O/petroleum ether) afforded an inseparable mixture of lactones **17** and **18** (79 mg, 80%) as a liquid; R_f (30% EtOAc/petroleum ether) 0.7; ν_{max} (liquid film) 3020, 2935, 2869, 1780, 1639, 1446 cm^{-1}; δ_H (300 MHz, $CDCl_3$) (for major isomer) 5.76–5.57 (2H, m, =CH), 5.45 (1H, dd, *J* 9.9, 1.3 Hz, =CH), 5.02–4.83 (2H, m, $=CH_2$), 4.19 (1H, d, *J* 8.3 Hz, OCH_2), 3.99–3.92 (1H, m, OCH_2), 2.78–2.61 (1H, m), 2.55–2.43 (1H, m), 2.40–1.97 (2H, m), 1.87–1.79 (1H, m), 1.63–1.55 (1H, m), 1.45–1.37 (1H, m), 1.29–1.08 (2H, m); δ_C (75 MHz, $CDCl_3$) (for major isomer) 176.4, 142.5, 133.5, 123.1, 113.4, 77.3, 50.8, 43.2, 41.8, 40.5, 36.1, 33.5, 20.5; (for minor isomer) 178.5, 140.9, 131.4, 121.9, 114.0, 79.1, 47.9, 42.2, 42.1, 41.7, 40.6, 40.2, 20.9; HRMS (ESI) (*m*/*z*): $[M+Na]^+$, found 227.1045. $C_{13}H_{16}O_2Na$ requires 227.1048.

4.1.5. (3aS,6aS*,8S*,9aR*)-3a,4,6a,7,8,9-Hexahydro-8-vinyl-indeno[3a,4-c]furan-3(1H)-one **18**.* A mixture of the lactones **17** and **18** (250 mg, 1.2 mmol) and DBU (0.9 mL) in PhH (5 mL) was refluxed for 2 h. The resulting slurry was worked up by washing with 1 M HCl. Purification of the crude mixture by column chromatography (10% Et_2O/petroleum ether) gave *cis*-lactone **18** (205 mg, 82%) as a colorless liquid; R_f (30% EtOAc/petroleum ether) 0.7; ν_{max} (liquid film) 2927, 2858, 1778, 1639, 1458, 1370 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 5.74–5.68 (1H, m, =CH), 5.66 (2H, br s, =CH), 4.99 (1H, d, *J* 17.1 Hz, =CH), 4.93 (1H, d, *J* 10.2 Hz, =CH), 4.13 (1H, d, *J* 8.5 Hz, OCH_2), 3.99 (1H, d, *J* 8.5 Hz, OCH_2), 2.53–2.45 (2H, m), 2.41–2.39 (1H, m), 2.34–2.21 (2H, m), 1.85 (1H, dd, *J* 12.7, 6.0 Hz), 1.65–1.57 (1H, t, *J* 12.4 Hz), 1.22–1.08 (2H, m); δ_C (75 MHz, $CDCl_3$) 178.5, 140.9, 131.4, 121.9, 114.0, 79.1, 47.9, 42.2, 42.1, 41.7, 40.6, 40.2, 20.9; HRMS (ESI) (*m*/*z*): $[M+Na]^+$, found 227.1047. $C_{13}H_{16}O_2Na$ requires 227.1048.

*4.1.6. Synthesis of spiro lactones **20** and **21**.* Following the above described protocol a solution of the lactone **19** (1.0 g, 6.09 mmol) in THF (10 mL) was allylated with allyl bromide (1.1 mL, 12.2 mmol) to afford, after column chromatography (10% Et_2O/petroleum ether), the lactones **20** and **21** (1.05 g, 85%) as colorless oil; R_f (30% EtOAc/petroleum ether) 0.8; ν_{max} (liquid film) 2968, 2873, 1774, 1639, 1448 cm^{-1}; δ_H (300 MHz, $CDCl_3$) (for the mixture of **20** and **21**) 6.31–6.25 (1H, m, =CH), 6.06–6.03 (1H, m, =CH), 5.83–5.69 (1H, m, =CH), 5.14–5.02 (2H, m, $=CH_2$), 4.27–4.19 (1H, m, OCH_2), 4.11–4.08 (1H, m, OCH_2), 2.84 (1H, br s), 2.68 (1H, br s), 2.38–2.26 (2H, m), 2.23–2.17 (1H, m), 1.58–1.34 (3H, m), 1.22–1.15 (1H, m); δ_C (75 MHz, $CDCl_3$) (for major isomer) 179.4, 139.9, 134.4, 133.8, 117.9, 78.0, 50.5, 50.3, 48.1, 47.6, 41.8, 34.2, 33.4; (for minor isomer) 178.3, 139.4, 134.3, 133.4, 117.7, 78.5, 50.4, 50.3, 47.5, 46.2, 44.2, 42.4, 32.4; HRMS (ESI) (*m*/*z*): $[M+Na]^+$, found 227.1046. $C_{13}H_{16}O_2Na$ requires 227.1048.

4.1.7. (2S,3aR*,4S*,7aS*)-2,3,3a,4,5,7a-Hexahydro-3a,4-bis(hydroxy-methyl)-2-vinyl-1H-indene **16**.* Following the above described protocol a solution of the tricyclic lactone **18** (350 mg, 1.72 mmol) in diethyl ether (5 mL) was reduced with $LiAlH_4$ (78 mg, 2.06 mmol) to afford, after column chromatography (30% Et_2O/petroleum ether), the diol **16** (328 mg, 92%) as viscous liquid; R_f (40% EtOAc/petroleum ether) 0.5; ν_{max} (liquid film) 3271, 2937, 2869, 1640, 1458 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 5.79–5.57 (3H, m, =CH), 4.95 (1H, d, *J* 17.1 Hz, =CH), 4.86 (1H, d, *J* 10.2 Hz, =CH), 3.76 (1H, dd, *J* 11.2, 1.8 Hz, OCH_2), 3.61–3.56 (2H, m, OCH_2), 3.14 (1H, d, *J* 11.2 Hz, OCH_2), 2.51–2.49 (1H, m), 2.19–2.12 (2H, m), 1.99–1.86 (4H, m), 1.56–1.51 (1H, m), 1.29–1.16 (3H, m); δ_C (75 MHz, $CDCl_3$) 142.5, 128.5, 125.9, 113.0, 65.7, 62.3, 46.9, 45.6, 42.8, 42.3, 40.7, 39.5, 25.5; HRMS (ESI) (*m*/*z*): $[M+Na]^+$, found 231.1365. $C_{13}H_{20}O_2Na$ requires 231.1361.

4.1.8. (2S,3aR*,4S*,7aS*)-2,3,3a,4,5,7a-Hexahydro-3a,4-bis(methyl-sulfonyloxymethyl)-2-vinyl-1H-indene **22**.* To a solution of the diol **16** (150 mg, 0.72 mmol) in CH_2Cl_2 (3 mL) were added triethylamine (0.40 mL, 2.88 mmol) and mesylchloride (0.16 mL, 2.16 mmol) at 0 °C. The resulting solution was stirred at that temperature for 1 h. The reaction mixture was concentrated and the residue was purified by column chromatography (50% Et_2O/petroleum ether) to give the dimesylate **22** (236 mg, 90%) as a white crystalline solid; R_f (50% EtOAc/petroleum ether) 0.6; mp 105–107 °C; ν_{max} (KBr plate) 3026, 2939, 1641, 1329, 1174 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 5.76–5.70 (3H, m, =CH), 5.01 (1H, d, *J* 17.1 Hz, $=CH_2$), 4.93 (1H, d, *J* 10.1 Hz, $=CH_2$), 4.39 (1H, dd, *J* 9.8, 2.1 Hz, CH_2OMs), 4.19 (1H, d, *J* 7.7 Hz, CH_2OMs), 4.12 (1H, d, *J* 9.8 Hz, CH_2OMs), 3.97 (1H, d, *J* 9.7 Hz, CH_2OMs), 3.01 (6H, s, OMs), 2.59–2.57 (1H, m), 2.31–2.22 (2H, m), 2.13–2.04 (2H, m), 2.02–1.95 (2H, m), 1.51–1.42 (1H, m), 1.33–1.21 (1H, m); δ_C (75 MHz, $CDCl_3$) 141.2, 128.2, 124.5, 114.0, 71.9, 71.2, 44.6, 44.1, 42.6, 41.4, 40.9, 39.5, 37.5 (2C), 26.0; HRMS (ESI) (*m*/*z*): $[M+Na]^+$, found 387.0911. $C_{15}H_{24}O_6S_2Na$ requires 387.0912.

4.1.9. (2S,3aR*,4S*,7aR*)-2-Ethyl-octahydro-3a,4-dimethyl-1H-indene **25**.* Na_2S (43 mg, 0.54 mmol) was added to a solution of the dimesylate **22** (100 mg, 0.27 mmol) in DMF (3 mL) and stirred at 50 °C for 3 h. After addition of H_2O, the resulting slurry was partitioned between EtOAc/hexane and H_2O. The combined organic layers were washed thoroughly with brine, dried, and concentrated in vacuo. Purification of the residual mass by column chromatography (10% EtOAc/petroleum ether) gave **24** (51 mg, 90%) as a colorless oil; R_f (40% EtOAc/petroleum ether) 0.5; ν_{max} (liquid film) 2926, 1639 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 5.82–5.70 (1H, m, =CH), 5.68 (2H, br s, =CH), 4.99 (1H, d, *J* 17.1 Hz, $=CH_2$), 4.90 (1H, d, *J* 10.2 Hz, $=CH_2$), 3.01 (1H, dd, *J* 10.3, 5.1 Hz, SCH_2), 2.81 (1H, d, *J* 10.1 Hz, SCH_2), 2.67–2.61 (2H, m, SCH_2), 2.42–2.38 (1H, m), 2.16–2.12 (1H, m), 2.04–1.88 (3H, m), 1.33–1.13 (4H, m); δ_C (75 MHz, $CDCl_3$) 142.3, 129.6, 123.7, 113.2, 53.6, 45.4, 43.9, 42.8, 42.7, 41.9, 40.7, 35.8, 27.1. Without further characterization **24** was used directly for the next step.

A mixture of the thioether **24** (50 mg, 0.24 mmol) and Raney Ni W-4 (ca. 100 mg) in THF (2 mL) was stirred at rt for 2 h. The reaction

mixture was filtered through Celite and washed with EtOAc. The filtrate was concentrated in vacuo. Purification of the residual mass by column chromatography (4% Et_2O/petroleum ether) gave **25** (35 mg, 80%) as a colorless oil; ν_{max} (liquid film) 2956, 1483 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 1.65–1.58 (3H, m), 1.55–1.45 (4H, m), 1.42–1.25 (9H, m), 0.88–0.86 (2 H, m), 0.85 (3H, s, CH_3), 0.76 (3H, d, *J* 6.6 Hz, CH_3); δ_C (75 MHz, $CDCl_3$) 47.6, 45.5, 42.7, 38.9, 36.5, 35.9, 31.1, 29.8, 25.1, 21.7, 20.8, 16.6, 13.4; HRMS (ESI) (*m*/*z*): $[M+Na]^+$, found 203.1767. $C_{13}H_{24}Na$ requires 203.1776.

4.1.10. ((2S,3aS*,4S*,7aS*)-2,3,3a,4,5,7a-Hexahydro-4-methyl-2-vinyl-1H-inden-3a-yl)methyl methanesulfonate* ***23***. $LiEt_3BH$ (1.5 mL, 1.5 mmol, 1.0 M solution in THF) was added drop wise to the dimesylate **22** (140 mg, 0.38 mmol) in THF (3 mL) at 0 °C and the mixture was stirred at rt for 3 h. After the addition of 1.0 M HCl, the resulting slurry was partitioned between EtOAc and H_2O. The combined organic layers were washed with saturated aqueous $NaHCO_3$, brine, dried (Na_2SO_4), and concentrated in vacuo. Purification of the residue by column chromatography (10% Et_2O/petroleum ether) gave **23** (83 mg, 80%) as a colorless oil; R_f (20% EtOAc/petroleum ether) 0.6; ν_{max} (liquid film) 3020, 2956, 1639, 1458 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 5.73–5.61 (3H, m, =CH), 4.92 (1H, d, *J* 17.1 Hz, $=CH_2$), 4.83 (1H, d, *J* 10.2 Hz, $=CH_2$), 4.09 (1H, d, *J* 9.2 Hz, CH_2OMs), 4.02 (1H, d, *J* 9.3 Hz, CH_2OMs), 2.93 (3H, s, OMs), 2.50–2.45 (1H, m), 2.37–2.31 (1H, m), 1.99–1.89 (3H, m), 1.77–1.65 (2H, m), 1.36 (1H, d, *J* 10.6 Hz), 1.31 (1H, d, *J* 10.7 Hz), 0.92 (3H, d, *J* 6.5 Hz, CH_3); δ_C (75 MHz, $CDCl_3$) 142.1, 128.3, 125.7, 113.3, 72.2, 45.2, 43.0, 42.9, 41.5, 40.0, 37.2, 34.7, 31.2, 15.5; HRMS (ESI) (*m*/*z*): $[M+Na]^+$, found 293.1183. $C_{14}H_{22}O_3SNa$ requires 293.1187.

4.1.11. 1-((2S,3aR*,4S*,7aS*)-2,3,3a,4,5,7a-Hexahydro-3a,4-dimethyl methanesulfonate-1H-inden-2-yl)ethane-1,2-diol* ***26***. To a solution of the hydrindane derivative **22** (50 mg, 0.14 mmol) and NMO (18 mg, 0.15 mmol) in THF (1 mL) and H_2O (0.25 mL) was added OsO_4 (0.04 mL, 0.0034 mmol, 2.5 wt % in ^tBuOH) at 0 °C. The mixture was stirred at rt for 12 h and the resulting slurry was partitioned between EtOAc and H_2O. The combined organic layer was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. Purification of the crude mixture by column chromatography (90% EtOAc/petroleum ether) gave **26** (43 mg, 80%) as colorless oil; ν_{max} (liquid film) 3519, 3417, 2940, 1640 cm^{-1}; δ_H (300 MHz, $CDCl_3$) (for the mixture) 5.68 (2H, br s, =CH), 4.47–4.41 (1H, m, CH_2OH), 4.15 (2H, d, *J* 7.8 Hz, OCH_2), 3.94 (1H, d, *J* 9.8 Hz, OCH_2), 3.63 (1H, d, *J* 10.7 Hz, OCH_2), 3.52–3.47 (1H, m, CH_2OH), 3.50–3.41 (1H, m, CHOH), 3.02 (3H, s, OMs), 3.01 (3H, s, OMs), 2.32–2.18 (3H, m), 2.10–1.91 (6H, m), 1.67–1.50 (1H, m), 1.23–1.18 (1H, m); δ_C (75 MHz, $CDCl_3$) (for the mixture) 128.3, 128.1, 124.6, 124.4, 75.8, 75.2, 72.2, 72.1, 71.5 (2C), 65.8 (2C), 44.6, 44.4, 43.8, 43.7, 40.8, 40.7, 40.1, 39.8, 37.5, 37.4 (2C), 37.3, 37.2, 36.9, 35.9, 35.3, 26.1 (2C); HRMS (ESI) (*m*/*z*): $[M+Na]^+$, found 421.0965. $C_{15}H_{26}O_8S_2Na$ requires 421.0967.

4.1.12. 1-((3aS,6aS*,8S*,9aR*)-1,3,3a,4,6a,7,8,9-Octahydroindeno[3-a,4-c]thiophen-8-yl)ethane-1,2-diol* ***27***. Following the above described protocol a solution of the dimesylate **26** (500 mg, 1.25 mmol) in DMF (10 mL) was treated with Na_2S (196 mg, 2.50 mmol) to afford, after column chromatography (40% EtOAc/petroleum ether), the cyclic thioether **27** (256 mg, 85%) as a colorless oil; R_f (50% EtOAc/petroleum ether) 0.2; ν_{max} (liquid film) 3390, 3016, 2931, 1666, 1454 cm^{-1}; δ_H (300 MHz, $CDCl_3$) (for the mixture) 5.58 (2H, br s, =CH), 3.64–3.60 (1H, m, CHOH), 3.49–3.36 (2H, m, CH_2OH), 3.25 (2H, br s, OH), 3.01–2.94 (1H, m, SCH_2), 2.79–2.76 (1H, m, SCH_2), 2.64–2.55 (2H, m, SCH_2), 2.35 (1H, br s), 2.07–1.99 (4H, br s), 1.73–1.66 (1H, m), 1.43–1.35 (1H, m), 1.26–1.08 (2H, m); δ_C (75 MHz, $CDCl_3$) (for the mixture) 129.5, 129.4, 123.7, 123.6, 76.5, 76.4, 65.9 (2C), 53.5, 53.2, 43.3 (2C), 42.0, 41.9 (2C), 41.8, 41.3, 41.1, 41.0 (2C), 37.1, 36.7, 35.7 (2C), 27.0, 26.9; HRMS (ESI) (*m*/*z*): $[M+Na]^+$, found 263.1082. $C_{13}H_{20}O_2SNa$ requires 263.1082.

4.1.13. 1-((2S,3aR*,4S*,7aR*)-Octahydro-3a,4-dimethyl-1H-inden-2-yl)ethane-1,2-diol* ***28***. Following the above described protocol a solution of the cyclic thioether **27** (100 mg, 0.41 mmol) was reduced with Raney Ni W-4 (ca. 500 mg) to afford, after column chromatography (40% Et_2O/petroleum ether), the compound **28** (75 mg, 85%) as a colorless oil; R_f (50% EtOAc/petroleum ether) 0.3; ν_{max} (liquid film) 3385, 2860, 1641, 1386 cm^{-1}; δ_H (300 MHz, $CDCl_3$) (for the mixture) 3.67 (1H, d, *J* 10.4 Hz, CH_2OH), 3.50–3.45 (1H, m, CH_2OH), 3.42–3.36 (1H, m, CHOH), 2.79 (2H, br s, OH), 2.01–1.99 (2H, m), 1.73–1.67 (3H, m), 1.55–1.36 (7H, m), 1.14–1.01 (1H, m), 0.86 (3H, s, CH_3), 0.78, 0.75 (total 3H, two d, *J* 6.7 and 7.1 Hz, respectively, CH_3); δ_C (75 MHz, $CDCl_3$) (for the mixture) 77.9 (2C), 66.2, 66.0, 47.4, 47.2, 43.5, 43.4, 41.7, 41.6, 39.7, 39.6, 35.8, 35.7, 33.0, 32.6, 31.1, 31.0, 24.8, 24.6, 21.6, 21.5, 20.6, 20.5, 16.6, 16.5; HRMS (ESI) (*m*/*z*): $[M+Na]^+$, found 235.1675. $C_{13}H_{24}O_2Na$ requires 235.1674.

4.1.14. 1-((2S,3aR*,4S*,7aS*)-Octahydro-3a,4-dimethyl-1H-inden-2-yl)-2-(tert-butyl)dimethylsilyloxy ethanone* ***29***. To a cooled (0 °C) solution of **28** (280 mg, 1.32 mmol) in CH_2Cl_2 (20 mL) were added Et_3N (0.2 mL), TBDMSCl (297 mg, 1.98 mmol), and DMAP (cat). The mixture was stirred for 3 h and diluted with saturated brine. This was extracted with CH_2Cl_2 (3×5 mL). The combined organic layers were dried and concentrated in vacuo. The residue was purified by column chromatography (5% Et_2O/petroleum ether) to provide the corresponding silyl ether (409 mg, 95%) as colorless oil; R_f (10% EtOAc/petroleum ether) 0.8; ν_{max} (liquid film) 3579, 3481, 2954, 1463, 1377 cm^{-1}; δ_H (300 MHz, $CDCl_3$) (for the mixture) 3.66–3.62 (1H, m, CHOH), 3.44–3.31 (2H, m, CH_2OH), 2.50 (1H, t, *J* 3.5 Hz), 2.01–1.92 (1H, m), 0.06 (6H, br s, Me_2Si), 1.81–1.75 (1H, m), 1.71–1.59 (2H, m), 1.55–1.35 (9H, m), 0.89 (9H, br s, ^tBuSi), 0.87, 0.86 (total 3H, two s, CH_3), 0.78, 0.75 (total 3H, two d, *J* 7.4 and 7.3 Hz, respectively, CH_3); δ_C (75 MHz, $CDCl_3$) (for the mixture) 77.1, 77.0, 66.7, 66.5, 47.4, 47.2, 42.6, 42.5, 41.6, 41.5, 39.4, 39.3, 35.6, 35.5, 33.0, 32.5, 31.0 (2C), 26.0 (6C), 24.9, 24.7, 21.6, 21.5, 20.6, 20.5, 18.4 (2C), 16.6, 16.5, −5.2, −5.3 (3C); HRMS (ESI) (*m*/*z*): $[M+Na]^+$, found 349.2537. $C_{19}H_{38}O_2SiNa$ requires 349.2539.

To a magnetically stirred suspension of DMP (550 mg, 1.3 mmol) in CH_2Cl_2 (10 mL) at 0 °C, the silyl ether obtained as above (354 mg, 1.08 mmol) in CH_2Cl_2 (5 mL) was added drop wise. The reaction mixture was stirred for 30 min and was quenched with 10% $Na_2S_2O_3$ solution (3 mL) doped with $NaHCO_3$. The organic layer was separated and the aqueous part extracted with diethyl ether (2×10 mL). The combined organic layer was dried, concentrated, and purified by column chromatography (3% Et_2O/petroleum ether) to afford **29** (316 mg, 90%) as colorless liquid; ν_{max} (liquid film) 2954, 2858, 1730, 1462, 1381, 1253 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 4.23 (2H, s, $CH_2OTBDMS$), 3.20–3.08 (1H, m, CHCO), 2.12–1.96 (2H, m), 1.76–1.65 (3H, m), 1.52–1.48 (3H, m), 1.45–1.34 (4H, m), 0.91 (9H, s, ^tBuSi), 0.87 (3H, s, CH_3), 0.75 (3H, d, *J* 6.5 Hz, CH_3), 0.07 (6H, s, Me_2Si); δ_C (75 MHz, $CDCl_3$) 212.8, 68.9, 47.5, 44.2, 43.2, 40.4, 33.4, 31.6, 30.8, 25.9 (3C), 24.4, 21.2, 20.1, 18.5, 16.6, −5.4 (2C); HRMS (ESI) (*m*/*z*): $[M+Na]^+$, found 347.2386. $C_{19}H_{36}O_2SiNa$ requires 347.2382.

4.1.15. 1-((2S,3aR*,4S*,7aR*)-Octahydro-3a,4-dimethyl-1H-inden-2-yl)-2-hydroxyethanone* ***30***. Desilylation of the hydrindane derivative **29** (285 mg, 0.88 mmol) in THF (5 mL) was accomplished with tetrabutylammonium fluoride (277 mg, 0.88 mmol) at rt for 4 h. After addition of water, the resulting slurry was partitioned between ether and water. The combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. Purification of the residue by column chromatography (10% Et_2O/petroleum ether) afforded the hydroxy-ketone **30** (147 mg, 80%) as colorless liquid; R_f (10% EtOAc/petroleum ether) 0.4; ν_{max} (liquid

film) 3417, 2924, 2860, 1712, 1656, 1462, 1381 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 4.24 (2H, s, CH_2OH), 3.19 (1H, br s, OH), 2.99–2.89 (1H, m, C*H*CO), 2.06–1.97 (2H, m), 1.80–1.70 (2H, m), 1.56–1.54 (3H, m), 1.50–1.35 (4H, m), 1.09–1.04 (1H, m), 0.87 (3H, s, CH_3), 0.75 (3H, d, *J* 6.4 Hz, CH_3); δ_C (75 MHz, $CDCl_3$) 212.4, 67.4, 47.5, 44.8, 43.2, 40.3, 33.6, 32.1, 30.7, 24.2, 21.1, 20.0, 16.5; HRMS (ESI) (*m*/*z*): $[M+Na]^+$, found 233.1513. $C_{13}H_{22}O_2Na$ requires 233.1517.

4.1.16. Ethyl 2-((2S,3aR*,4S*,7aR*)-Octahydro-3a,4-dimethyl-1H-inden-2-yl)-2-oxoethyl carbonate* ***31****.* To a solution of the hydroxy-ketone **30** (184 mg, 0.87 mmol) in CH_2Cl_2 (7 mL) at 0 °C were added DMAP (ca. 5 mg), pyridine (1.63 mL), and ethylchloroformate (1.0 mL, 10.4 mmol), and the resulting mixture was quenched with 2 N aqueous HCl and extracted with EtOAc (2×10 mL). Combined extracts were dried (Na_2SO_4), filtered, and concentrated in vacuo. Purification of the residual mass by column chromatography (5% Et_2O/petroleum ether) gave the carbonate **31** (237 mg, 96%) as colorless liquid; R_f (10% EtOAc/petroleum ether) 0.6; ν_{max} (liquid film) 2929, 2873, 1755, 1732, 1463, 1373, 1263 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 4.68 (2H, s, OCH_2CO), 4.20 (2H, q, *J* 6.9 Hz, OCH_2), 3.02–2.90 (1H, m, C*H*CO), 2.10–2.04 (2H, m), 1.77–1.72 (2H, m), 1.51–1.47 (3H, m), 1.42–1.37 (3H, m), 1.32–1.27 (4H, m), 1.08–1.02 (1H, m), 0.86 (3H, s, CH_3), 0.74 (3H, d, *J* 6.5 Hz, CH_3); δ_C (75 MHz, $CDCl_3$) 205.8, 154.8, 69.8, 64.6, 47.5, 44.8, 43.2, 39.7, 33.3, 31.6, 30.7, 24.2, 21.0, 19.9, 16.5, 14.3; HRMS (ESI) (*m*/*z*): $[M+Na]^+$, found 305.1725. $C_{16}H_{26}O_4Na$ requires 305.1729.

4.1.17. 1-((2S,3aR*,4S*,7aR*)-Octahydro-3a,4-dimethyl-1H-inden-2-yl)ethanone* ***34****.* To a magnetically stirred ice-cold solution of the diol **28** (100 mg, 0.47 mmol) in THF/water (4.5 mL, 2:1) was added $NaIO_4$ (201.6 mg, 0.94 mmol) in portions. The reaction mixture was allowed to stir at 0 °C for 30 min. The precipitated white solid was filtered off after washing it thoroughly with diethyl ether. Usual workup of the filtrate afforded the aldehyde **33**, which was immediately used for the next step without purification.

To a solution of the crude aldehyde **33** in dry ether (5 mL) was added methylmagnesium iodide (3.0 M in Et_2O, 0.37 mL, 1.1 mmol) at 0 °C. The mixture was stirred at that temperature for 1 h, and to this was added saturated aqueous NH_4Cl solution. After stirring it for 15 min at rt, the mixture was extracted with ether (2×5 mL). The combined organic layer was dried, concentrated in vacuo. The resulting crude product was chromatographed (10% Et_2O/petroleum ether) affording the corresponding methyl addition product (83 mg, 90%) as colorless liquid; R_f (20% EtOAc/petroleum ether) 0.6; ν_{max} (liquid film) 3364, 2928, 2870, 1460, 1375 cm^{-1}; δ_H (300 MHz, $CDCl_3$) (for the mixture) 3.56–3.50 (1H, m), 1.95–1.87 (1H, m), 1.72–1.32 (13H, m), 1.14, 1.13 (total 3H, two d, *J* 6.2 and 6.1 Hz, respectively, CH_3COH), 0.86 (3H, s, CH_3), 0.76, 0.74 (total 3H, two d, *J* 6.3 and 6.1 Hz, respectively, CH_3); δ_C (75 MHz, $CDCl_3$) (for both diastereoisomers) 73.6, 73.4, 47.4 (2C), 45.4, 45.3, 42.7, 42.6, 42.0, 41.7, 35.7, 35.6, 33.1, 32.9, 31.0 (2C), 24.9, 24.7, 22.4 (2C), 21.6 (2C), 20.6 (2C), 16.5 (2C); HRMS (ESI) (*m*/*z*): $[M+Na]^+$, found 219.1725. $C_{13}H_{24}ONa$ requires 219.1725.

To a solution of the hydroxy-compound thus obtained (56 mg, 0.28 mmol) in CH_2Cl_2 (3 mL) at rt was added DMP (144.6 mg, 0.34 mmol) portion wise and the reaction mixture was allowed to stir for 1 h. The reaction mixture was quenched with 10% $Na_2S_2O_3$ solution (2 mL) doped with $NaHCO_3$ at ice-cold condition and stirred vigorously until the organic layer became transparent. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated in vacuo. Purification of the residue by column chromatography (5% Et_2O/petroleum ether) gave **34** (53 mg, 96%) as colorless oil; R_f (10% EtOAc/petroleum ether) 0.7; ν_{max} (liquid film) 2957, 2872, 1711, 1462 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 2.95–2.90 (1H, m), 2.13 (3H, s, $COCH_3$), 2.09–2.00 (2H, m), 1.82–1.72 (3H, m), 1.53–1.32 (7H, m), 0.87 (3H, s, CH_3), 0.76 (3H, d, *J* 6.6 Hz, CH_3); δ_C (75 MHz, $CDCl_3$) 211.2, 49.6, 47.4, 43.0, 39.9, 33.6, 31.6, 30.8, 28.9, 24.4, 21.2, 20.0, 16.5; HRMS (ESI) (*m*/*z*): $[M+Na]^+$, found 217.1569. $C_{13}H_{22}ONa$ requires 217.1568.

4.1.18. Synthesis of hydroxy-lactones ***35*** *and* ***36****.* A solution of the lactone **19** (990 mg, 6.04 mmol) in THF (12 mL) was added drop wise to a magnetically stirred solution of LDA (prepared from diisopropyl amine (1.6 mL, 12.1 mmol) in anhydrous THF (12 mL) and ^nBuLi (6.8 mL, 10.8 mmol, 1.6 M in hexane)) at −78 °C and the reaction mixture was stirred at that temperature for 1 h. Freshly distilled acrolein (0.8 mL, 12.1 mmol) was added drop wise to the reaction mixture at the same temperature and was allowed to stir for 1 h. After quenching with saturated aqueous NH_4Cl solution, the reaction mixture was worked up in the usual way to afford, after column chromatography (40% Et_2O/petroleum ether), hydroxy-lactones **35** and **36** and their corresponding hydroxy epimers (1.1 g, 83%) as colorless oil; R_f (30% EtOAc/petroleum ether) 0.5; ν_{max} (liquid film) 3273, 2870, 1775, 1638, 1462 cm^{-1}; δ_H (300 MHz, $CDCl_3$) (for major isomer) 6.33 (1H, dd, *J* 5.5, 3.1 Hz, =CH), 6.08 (1H, dd, *J* 5.3, 2.7 Hz, =CH), 5.81–5.70 (1H, m, =CH), 5.30 (1H, d, *J* 17.2 Hz, $=CH_2$), 5.20 (1H, d, *J* 10.4 Hz, $=CH_2$), 4.33 (1H, br s, OH), 4.26 (1H, d, *J* 8.9 Hz, OCH_2), 4.10 (1H, d, *J* 8.9 Hz, OCH_2), 3.11 (1H, d, *J* 7.8 Hz, C*H*OH), 2.83 (1H, br s), 2.69 (1H, br s), 2.44 (1H, d, *J* 4.1 Hz, CHCO), 1.80 (1H, dd, *J* 12.6, 2.5 Hz), 1.54 (1H, d, *J* 8.8 Hz), 1.38 (1H, dd, *J* 12.6, 3.4 Hz), 1.29 (1H, d, *J* 8.9 Hz); δ_C (75 MHz, $CDCl_3$) (for major isomer) 179.5, 140.4, 137.2, 133.7, 117.4, 79.2, 72.5, 53.4, 51.2, 48.7, 47.6, 41.9, 34.6; HRMS (ESI) (*m*/*z*): $[M+Na]^+$, found 243.0994. $C_{13}H_{16}O_3Na$ requires 243.0997.

4.1.19. Synthesis of the compounds ***37*** *and* ***38****.* To a magnetically stirred solution of the mixture of alcohols **35** and **36** and their epimers (440 mg, 1.99 mmol) in CH_2Cl_2 (3 mL), dimethoxy methane (0.53 mL, 6.0 mmol) and $BF_3 \cdot Et_2O$ (0.3 mL, 2.4 mmol) were added drop wise at 0 °C. After complete addition, the reaction mixture was stirred for 1 h at 0 °C. After quenching with saturated aqueous $NaHCO_3$ solution, the reaction mixture was worked up in the usual way to afford, after column chromatography (10% Et_2O/petroleum ether), the MOM ether derivatives **37** and **38** and their epimers (422 mg, 80%) as colorless liquid; R_f (30% EtOAc/petroleum ether) 0.6; ν_{max} (liquid film) 1774, 1642 cm^{-1}; δ_H (300 MHz, $CDCl_3$) (for major isomer) 6.32 (1H, dd, *J* 5.5, 3.06 Hz, =CH), 6.22 (1H, dd, *J* 5.5, 2.5 Hz, =CH), 5.79–5.70 (1H, m, =CH), 5.47 (1H, d, *J* 17.3 Hz, $=CH_2$), 5.42 (1H, d, *J* 10.5 Hz, $=CH_2$), 4.65 (1H, d, *J* 6.8 Hz, OCH_2), 4.52 (1H, d, *J* 6.8 Hz, OCH_2), 4.35 (1H, dd, *J* 8.6, 3.0 Hz, CHOMOM), 4.30 (1H, d, *J* 5.5 Hz, OCH_2), 4.04 (1H, d, *J* 8.3 Hz, OCH_2), 3.34 (3H, s, OCH_3), 2.90 (1H, br s), 2.87 (1H, br s), 2.31 (1H, d, *J* 3.0 Hz, CHCO), 1.94 (1H, dd, *J* 11.8, 3.7 Hz), 1.52 (1H, d, *J* 8.7 Hz), 1.39 (1H, d, *J* 9.0 Hz), 1.25–1.21 (1H, m); δ_C (75 MHz, $CDCl_3$) (for major isomer) 177.0, 139.7, 134.6, 134.0, 121.4, 93.0, 79.2, 75.0, 55.7 (2C), 49.2, 47.5, 46.4, 46.0, 42.0; HRMS (ESI) (*m*/*z*): $[M+Na]^+$, found 287.1255. $C_{15}H_{20}O_4Na$ requires 287.1259.

4.1.20. (6aR,8R*,9aS*)-3a,4,6a,7,8,9-Hexahydro-4-hydroxy-8-vinyl-indeno[3a,4-c]furan-3(1H)-one* ***39****.* To a solution of the mixture of hydroxy-lactones **35** and **36** and their hydroxy epimers (80 mg, 0.36 mmol) in dry CH_2Cl_2 (30 mL) under ethylene atmosphere at rt was added a solution of Grubbs' catalyst **12** (17 mg, 5 mol %) in CH_2Cl_2 (1 mL). After stirring for 30 h, the reaction mixture was concentrated. Purification of the residue by column chromatography (10% Et_2O/petroleum ether) gave the tricyclic lactone **39** as a diastereoisomeric mixture (16 mg, 20%) as colorless oil; R_f (40% EtOAc/petroleum ether) 0.5; ν_{max} (liquid film) 3470, 1760, 1645, 1469 cm^{-1}; δ_H (300 MHz, $CDCl_3$) (for major diastereoisomer) 5.86–5.79 (3H, m, =CH), 5.07–4.96 (2H, m, $=CH_2$), 4.45–4.41 (1H, m, C*H*OH), 4.24 (1H, d, *J* 8.4 Hz, OCH_2), 4.10–4.07 (1H, m, OCH_2), 2.82 (1H, d, *J* 5.6 Hz), 2.53–2.39 (2H, m), 2.35–2.21 (1H, m), 2.03–1.91

(1H, m), 1.83–1.56 (2H, m), 1.14–1.02 (1H, m); δ_C (75 MHz, $CDCl_3$) (for major isomer of the mixture) 177.1, 139.8, 132.4, 128.7, 114.7, 80.6, 63.6, 48.9, 48.8, 42.4, 42.0, 41.9, 41.1; (for minor isomer of the mixture) 178.5, 140.3, 133.0, 126.3, 114.5, 79.1, 64.5, 50.4, 47.3, 43.9, 43.2, 40.9, 39.9; HRMS (ESI) (m/z): $[M+Na]^+$, found 243.0995. $C_{13}H_{16}O_3Na$ requires 243.0997.

4.1.21. (6aR,8R*,9aS*)-3a,4,6a,7,8,9-Hexahydro-4-(methoxymethoxy)-8-vinylindeno[3a,4-c]furan-3(1H)-one* ***40****.* Following the metathesis procedure described above, the mixture of lactones **37** and **38** and their epimers (90 mg, 0.34 mmol) in CH_2Cl_2 (35 mL) was treated with the catalyst **12** (14 mg, 5 mol %) in ethylene atmosphere (17 h) to afford, after column chromatography (10% Et_2O/petroleum ether), the cyclized tricyclic lactone **40** as a diastereoisomeric mixture (45 mg, 50%) as colorless liquid; R_f (30% EtOAc/petroleum ether) 0.5; ν_{max} (liquid film) 1772, 1641, 1469 cm^{-1}; δ_H (300 MHz, $CDCl_3$) (for major isomer) 5.82 (2H, br s, =CH), 5.74–5.66 (1H, m, =CH), 5.00 (1H, d, *J* 17.7 Hz, $=CH_2$), 4.93 (1H, d, *J* 10.2 Hz, $=CH_2$), 4.74 (1H, d, *J* 6.7 Hz, OCH_2), 4.70 (1H, d, *J* 6.8 Hz, OCH_2), 4.44 (1H, br s, CHOMOM), 4.11 (1H, d, *J* 8.5 Hz, OCH_2), 4.00 (1H, d, *J* 8.5 Hz, OCH_2), 3.37 (3H, s, OCH_3), 2.88 (1H, d, *J* 2.2 Hz), 2.54–2.44 (2H, m), 2.38–2.29 (1H, m), 2.05 (1H, t, *J* 12.5 Hz), 1.83 (1H, dd, *J* 12.7, 6.0 Hz), 1.34–1.24 (1H, m); δ_C (75 MHz, $CDCl_3$) (for major isomer) 176.0, 140.8, 134.5, 123.1, 114.2, 96.1, 79.2, 68.9, 55.7, 47.3, 47.1, 43.0, 41.6, 41.1, 40.0; HRMS (ESI) (m/z): $[M+Na]^+$, found 287.1256. $C_{15}H_{20}O_4Na$ requires 287.1259.

4.1.22. Synthesis of silyl ether compounds ***42*** *and* ***43****.* To a cooled (0 °C) solution of mixture of **35**, **36** and its hydroxy epimers (511 mg, 2.32 mmol) as obtained above in CH_2Cl_2 (20 mL) were added Et_3N (0.64 mL, 4.64 mmol), TBDMSCl (696 mg, 4.64 mmol), and DMAP (cat). The mixture was stirred for 36 h and diluted with saturated brine. This was extracted with CH_2Cl_2 (3×10 mL). The combined organic layers were dried and concentrated in vacuo. The residue was purified by column chromatography (5% Et_2O/petroleum ether) to provide **42** (388 mg, 50%) and **43** (147 mg, 19%) as the major hydroxy-lactones. Compound **42** as a colorless oil; ν_{max} (liquid film) 2940, 1778, 1643, 1462 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 6.27–6.24 (1H, m, =CH), 5.99–5.96 (1H, m, =CH), 5.75–5.64 (1H, m, =CH), 5.14 (1H, d, *J* 17.4 Hz, $=CH_2$), 5.07 (1H, d, *J* 10.5 Hz, $=CH_2$), 4.69 (1H, d, *J* 2.1 Hz, CHOSi), 4.33 (1H, d, *J* 8.4 Hz, OCH_2), 4.05 (1H, d, *J* 8.4 Hz, OCH_2), 2.76 (1H, s), 2.64 (1H, s), 2.20 (1H, s, *CH*CO), 2.17 (1H, dd, *J* 11.5, 2.7 Hz), 1.49 (1H, d, *J* 8.4 Hz), 1.34 (1H, dd, *J* 13.0, 3.4 Hz), 1.27 (1H, d, *J* 9.0 Hz), 0.86 (9H, s, 3×CH_3), 0.00 (3H, s, CH_3), −0.03 (3H, s, CH_3); δ_C (75 MHz, $CDCl_3$) 180.0, 140.0, 139.9, 133.7, 115.4, 79.5, 74.8, 54.3, 50.9, 49.3, 47.5, 41.9, 34.6, 25.9 (3C), 17.9, −4.8, −5.0; HRMS (ESI) (m/z): $[M+Na]^+$, found 357.1863. $C_{19}H_{30}O_3SiNa$ requires 357.1862. Compound **43** as a colorless oil; ν_{max} (liquid film) 2877, 1776, 1645, 1460 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 6.29–6.26 (1H, m), 6.18–6.15 (1H, m), 5.97–5.86 (1H, m, =CH), 5.34 (1H, d, *J* 17.3 Hz, $=CH_2$), 5.22 (1H, d, *J* 10.2 Hz, $=CH_2$), 4.57 (1H, d, *J* 4.7 Hz, CHOSi), 4.45 (1H, d, *J* 7.7 Hz, OCH_2), 4.01 (1H, d, *J* 7.7 Hz, OCH_2), 2.95 (1H, s), 2.85 (1H, s), 2.13 (1H, d, *J* 2.3 Hz, CHCO), 1.90 (1H, dd, *J* 11.7, 3.8 Hz), 1.50 (1H, d, *J* 8.34 Hz), 1.42 (1H, d, *J* 8.8 Hz), 1.13 (1H, d, *J* 12.1 Hz), 0.91 (9H, s, 3×CH_3), 0.05 (3H, s, CH_3), 0.03 (3H, s, CH_3); δ_C (75 MHz, $CDCl_3$) 178.3, 139.9, 139.3, 135.4, 116.4, 80.2, 74.8, 57.7, 48.9, 47.8 (2C), 46.2, 41.6, 26.0 (3C), 18.2, −4.4, −4.9; HRMS (ESI) (m/z): $[M+Na]^+$, found 357.1860. $C_{19}H_{30}O_3SiNa$ requires 357.1862.

4.1.23. (3aR,4S*,6aR*,8R*,9aS*)-3a,4,6a,7,8,9-Hexahydro-4-(tert-butyl)dimethylsilyloxy-8-vinylindeno[3a,4-c]furan-3(1H)-one* ***44****.* The catalyst **12** (10 mg, 5 mol %) was dissolved in CH_2Cl_2 (4 mL) and was added via syringe to a solution of the lactone **42** (80 mg, 0.24 mmol) in degassed CH_2Cl_2 (40 mL). This solution was then purged with ethylene and stirred at rt for 12 h under an ethylene atmosphere. The solvent was then removed by rotary evaporator and the residue was purified by column chromatography (10% Et_2O/petroleum ether) to give **44** (58 mg, 72%) as a colorless oil; R_f (5% EtOAc/petroleum ether) 0.5; ν_{max} (liquid film) 2952, 2885, 1787, 1641, 1469, 1373 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 5.80–5.66 (2H, m, =CH), 5.59 (1H, dd, *J* 9.8, 1.9 Hz, =CH), 4.95 (1H, d, *J* 16.8 Hz, $=CH_2$), 4.87 (1H, d, *J* 10.0 Hz, $=CH_2$), 4.53 (1H, br s, CHOSi), 4.21 (1H, d, *J* 8.2 Hz, OCH_2), 3.89 (1H, dd, *J* 8.2, 1.9 Hz, OCH_2), 2.59–2.55 (1H, m), 2.54 (1H, d, *J* 3.6 Hz), 2.53–2.51 (1H, m), 2.45 (1H, t, *J* 12.3 Hz), 2.26–2.21 (1H, m), 1.65 (1H, dd, *J* 13.1, 6.6 Hz), 1.40–1.35 (1H, m), 0.85 (9H, s, 3×CH_3), 0.16 (3H, s, CH_3), 0.11 (3H, s, CH_3); δ_C (75 MHz, $CDCl_3$) 173.5, 142.5, 135.5, 126.5, 113.1, 77.4, 61.4, 49.7, 47.2, 44.1, 42.0, 37.0, 35.9, 25.7 (3C), 18.0, −4.4, −5.1; HRMS (ESI) (m/z): $[M+Na]^+$, found 357.1857. $C_{19}H_{30}O_3SiNa$ requires 357.1862.

4.1.24. (3aS,4S*,6aR*,8R*,9aS*)-3a,4,6a,7,8,9-Hexahydro-4-(tert-butyl)dimethylsilyloxy-8-vinylindeno[3a,4-c]furan-3(1H)-one* ***45****.* Following the metathesis procedure described above, the lactone **43** (70 mg, 0.21 mmol) in DCM (35 mL) was treated with the catalyst **12** (8.6 mg, 5 mol %) for 12 h to afford, after column chromatography (10% Et_2O/petroleum ether), the tricyclic lactone **45** (49 mg, 70%) as a colorless liquid; R_f (5% EtOAc/petroleum ether) 0.6; ν_{max} (liquid film) 1762, 1645, 1469 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 5.96–5.91 (1H, m, =CH), 5.86 (1H, dd, *J* 9.9, 1.7 Hz, =CH), 5.75–5.70 (1H, m, =CH), 5.04 (1H, d, *J* 17.1 Hz, $=CH_2$), 4.96 (1H, d, *J* 10.3 Hz, $=CH_2$), 4.52 (1H, t, *J* 5.0 Hz, CHOSi), 4.17 (1H, d, *J* 7.1 Hz, OCH_2), 4.09 (1H, d, *J* 7.7 Hz, OCH_2), 2.49–2.45 (1H, m), 2.42–2.36 (1H, m), 2.22 (1H, d, *J* 4.6 Hz), 2.26–2.20 (1H, m), 2.09 (1H, dd, *J* 5.0, 1.2 Hz), 1.24–1.15 (2H, m), 0.83 (9H, s, 3×CH_3), 0.06 (3H, s, CH_3), 0.02 (3H, s, CH_3); δ_C (75 MHz, $CDCl_3$) 177.7, 140.0, 134.3, 126.0, 114.5, 80.3, 63.4, 51.9, 48.4, 46.7, 41.8, 40.2, 40.0, 25.7 (3C), 17.9, −3.9, −5.2; HRMS (ESI) (m/z): $[M+Na]^+$, found 357.1864. $C_{19}H_{30}O_3SiNa$ requires 357.1862.

4.1.25. (6aR,8R*,9aS*)-6a,7,8,9-Tetrahydro-8-vinylindeno[3a,4-c]furan-3(1H)-one* ***46****.* To a magnetically stirred solution of **44** (23 mg, 0.07 mmol) in THF (1 mL) was added TBAF (0.07 mL, 0.07 mmol, 1 M solution in THF) at 0 °C. The mixture was stirred at rt for 3 h. After addition of water, the resulting slurry was partitioned between diethyl ether and water. The combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. Purification of the crude mass by column chromatography (10% Et_2O/petroleum ether) gave **46** (12 mg, 85%) as colorless oil; R_f (30% EtOAc/petroleum ether) 0.5; ν_{max} (liquid film) 1759, 1747, 1642, 1458 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 6.85 (1H, d, *J* 5.1 Hz, =CH), 6.08–6.02 (1H, m, =CH), 5.82 (1H, dd, *J* 9.4, 2.5 Hz, =CH), 5.76–5.65 (1H, m, =CH), 5.04 (1H, d, *J* 17.1 Hz, $=CH_2$), 4.95 (1H, d, *J* 10.1 Hz, $=CH_2$), 4.29 (1H, d, *J* 8.3 Hz, OCH_2), 3.85 (1H, dd, *J* 8.2, 1.3 Hz, OCH_2), 2.83 (1H, s), 2.58–2.38 (2H, m), 1.98 (1H, dd, *J* 12.4, 6.2 Hz), 1.65–1.57 (2H, m); δ_C (75 MHz, $CDCl_3$) 170.2, 140.5, 138.0, 129.7, 127.4, 120.3, 114.5, 78.4, 47.7, 43.2, 42.2, 38.2, 37.7; HRMS (ESI) (m/z): $[M+Na]^+$, found 225.0895. $C_{13}H_{14}O_2Na$ requires 225.0892.

4.1.26. (3aS,4S*,6aR*,8R*,9aS*)-3a,4,6a,7,8,9-Hexahydro-4-hydroxy-8-vinylindeno[3a,4-c]furan-3(1H)-one* ***47****.* Following the procedure described for desilylation of the tricycle **44**, the silyl protected tricycle **45** (20 mg, 0.06 mmol) in THF (1 mL) at 0 °C was deprotected using TBAF (0.06 mL, 0.06 mmol) to afford, after column chromatography (30% Et_2O/petroleum ether), the hydroxy-lactone **47** (10 mg, 75%) as a colorless liquid; R_f (30% EtOAc/petroleum ether) 0.4; ν_{max} (liquid film) 3485, 3018, 2900, 1759, 1643, 1373, 1217 cm^{-1}; δ_H (300 MHz, $CDCl_3$) 5.90–5.79 (2H, m, =CH), 5.76–5.65 (1H, m, =CH), 5.04 (1H, d, *J* 17.2 Hz, $=CH_2$), 4.98 (1H, d, *J* 10.3 Hz, $=CH_2$), 4.45–4.42 (1H, m, *CH*OH), 4.24 (1H, d, *J* 8.4 Hz, OCH_2), 4.09 (1H, d, *J* 8.4 Hz, OCH_2), 3.91 (1H, d, *J* 9.9 Hz, OH), 2.82 (1H, d, *J* 5.6 Hz, CHCO), 2.55–2.43 (2H, m), 2.35–2.26 (2H, m), 1.93 (1H, dd, *J* 12.8, 5.5 Hz), 1.14–1.02 (1H, m); δ_C (75 MHz, $CDCl_3$) 178.4, 139.9, 132.4,

128.7, 114.8, 80.7, 63.7, 48.9, 48.8, 42.5, 41.9, 41.8, 41.2; HRMS (ESI) (m/z): $[M+Na]^+$, found 243.0992. $C_{13}H_{16}O_3Na$ requires 243.0997.

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Supplementary data

Supplementary data associated with this article can be found in online version, at doi:10.1016/j.tet.2009.09.029.

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