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Alkoxy group facilitated ring closing metathesis (RCM) of acyclic 1,6-dienes Facile synthesis of non-racemic highly substituted cyclopentenols

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Available online 2 May 2006

Abstract

Alkoxymethyl groups at the C-5 allylic position of 1,6-dienols have been found to accelerate RCM reaction significantly with the Grubbs' catalyst $PhCH=Ru(PCy_3)_2Cl_2$ over those of 1,6-dienols containing alkyl or hydroxymethyl groups. This phenomenon has been used for direct access to 4-silyloxymethyl and 4,6-bis(silyloxymethyl) cyclopentenols, potential intermediates to the synthesis of carbasugars and the carbocyclic nucleosides carbovir, abacavir and BCA.
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Keywords: Asymmetric synthesis; Cyclopentenes; Metathesis; Nucleosides

1. Introduction

Ring closing metathesis [1] of acyclic dienes in the presence of a metal alkylidene complex as catalyst has emerged as an efficient method for the construction of cyclic alkenes. The success of RCM is influenced to a great extent by the efficiency of the catalyst, substituents present on the tether between the alkene units and the nature and size of the rings to be formed. As part of our continued interest [2] in the application of RCM reaction for the synthesis of highly functionalised carbo- and heterocyclic compounds, we required rapid access to the substituted cyclopentenols **2**. We envisioned that RCM of 1,6-dienes **1** with Grubbs' catalyst $PhCH=Ru(PCy_3)_2Cl_2$ **3** would be the most straight forward way for achieving this goal. The RCM of acyclic 1,7-dienols [3] generally proceeds without any complication to form cyclohexene derivatives. However, the success of RCM of acyclic 1,6-dienols with the catalyst **3** is influenced to a great extent by the substituents. The 1,6-dienes investigated so far either have a ring or geminal or vicinal sub-stitutents. In these cases the alkene units are conformationally predisposed for ring closure either by the pre-existing ring [4] or by Thorpe–Ingold effect [5] of the geminal substituents or by Gauche interaction [5–7] of the vicinal substituents and RCM proceeds smoothly to form cyclopentenols. However

there is no systematic investigation on the RCM of 1,6-dienes **1** where the above conformational preferences are absent. Hoye and Zhao [8] has recently demonstrated that an alkyl or alkoxy substituent at the allylic position that increases steric crowding retards RCM while a tertiary hydroxyl group at the allylic position accelerates RCM significantly. However, a secondary hydroxyl group at the allylic position adversely affects [3b,8,9] metathesis reducing the yields of RCM products through reductive elimination of the enolyl ruthenium hydride arising from tautomerization of the initially formed Ru-carbene. It has also been reported [9,10] that secondary allylic alcohols when treated with catalytic quantity of Ru catalyst undergo another non-metathetic [11] redox isomerization to form ethyl ketones. We now report [12] that the RCM of the acyclic 1,6-dienes of the general structure **1** having a secondary OH at one allylic center and a bulky alkoxy group at the other allylic center both of which deter RCM can be made to undergo smooth ring closure with the catalyst **3** leading to the facile synthesis of the cyclopentenols.

The cyclopentenol **2a** represent the carbocyclic moiety of the carbocylic nucleosides [13] carbovir **4** [14] and abacavir **5** [6], while the cyclopentenol **2b** has the carbocyclic moiety present in bis(hydroxymethyl)cyclopentenyl adenine (BCA) **6** [15]. (−)-Abacavir has recently been introduced as a drug to combat AIDS while (−)-carbovir and (−)-BCA are potential inhibitors of HIV reverse transcriptase, the causative agent of AIDS. In addition the cyclopentenol **2a** may be considered as an intermediate to carbasugars, e.g. **7** [16] incorporation of which

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in oligosaccharides makes them metabolically stable glycosyl transferase substrates without loss of activity of the parent oligosaccharides.

2. Results and discussion

The optically pure diene **1a** was prepared from the unsaturated ester **10** which in turn was obtained along with the diastereoisomeric ester **9** from 1,2:5,6-di-*O*-cyclohexylidine D-mannitol **8** (Scheme 1) following the literature procedure [2d]. The ester **10** was converted to the aldehyde **11** through LiAlH₄ reduction followed by Swern oxidation of the resulting alcohol. Addition of vinyl magnesium bromide to the aldehyde **11** produced a 1:1 diastereomeric mixture of the dienols **12**. Regeneration of the vicinal diol from the ketal **12** followed by its periodate cleavage afforded the lactol **13**. LiAlH₄ reduction of the lactol **13** provided the dienol **1a**. The results of the RCM reactions are summarized in Table 1 (Scheme 2).

Treatment of the dienol **1a** with 6 mol% of the catalyst **3** either in CH₂Cl₂ at rt for 24 h or in refluxing benzene produced an intractable mixture in which none of the cyclized product **2a**
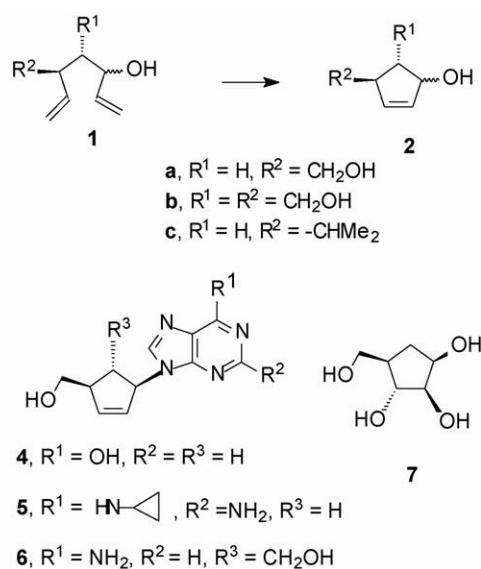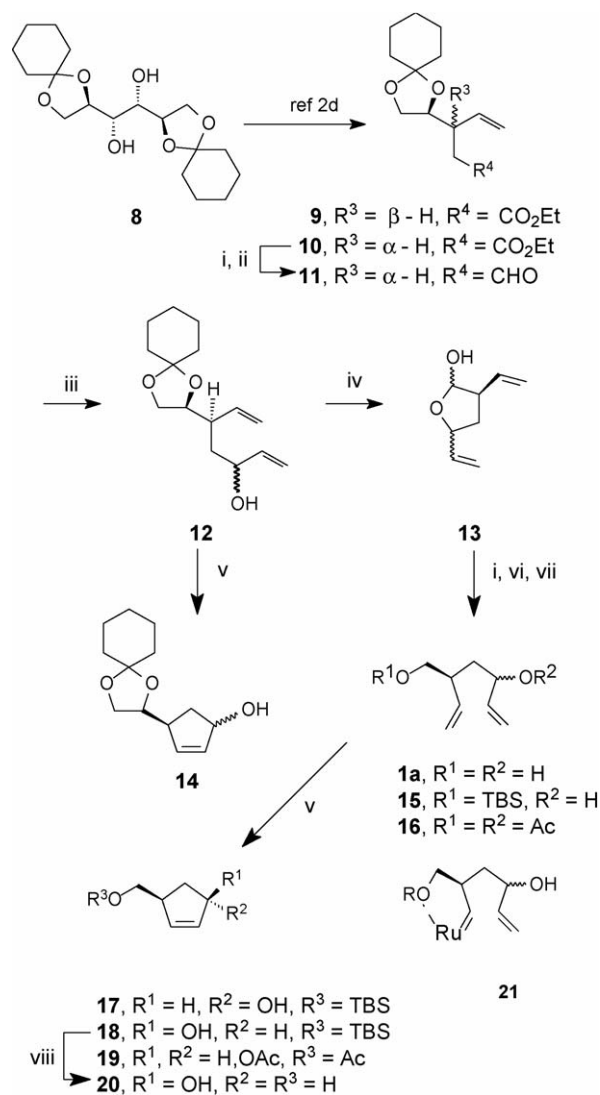

Scheme 1.

Table 1
RCM of dienols

Entry	Diene	Reaction time (h)[a]	Cyclopentenol (%)
1	**1a**	24	[b]
2	**12**	24	**14** (83)
3	**15**	24	**17** and **18** (93)
4	**16**	2	**19** (91)
5	**1c**	24	**2c**[c]

[a] All reactions were carried out at rt with 6 mol% of the catalyst **3**.
[b] An intractable mixture was obtained.
[c] A complex mixture of products were obtained in which **1c** and **2c** (7:3) along with a methyl ketone were detected by ¹H NMR.

Scheme 2. Reagents and conditions: (i) LiAlH₄, Et₂O, rt, 92%; (ii) oxalylchloride, DMSO, Et₃N, 82%; (iii) CH₂=CHMgBr, THF, 70 °C, 1 h, 74%; (iv) (a) 6 M HCl, THF, 1 h, (b) NaIO₄, MeCN/H₂O (3:2), 1 h (76% overall); (v) (PCy₃)₂Cl₂RuCHPh, DCM, rt, 24 h 93% for **14**, **17** and **18**; 2 h, 90% for **19**; (vi) TBSCl, DMAP, Imidazole, Et₃N, DCM, rt, 36 h, 87%; (vii) Ac₂O, Et₃N, pyridine, DCM, rt, 2 h, 43%; (viii) TBAF, THF, rt, 1 h, 83%.

could be detected (entry 1). Amazingly, RCM of the dienols **12** (entry 2) having a bulky ketal moiety proceeded smoothly to produce a diastereoisomeric mixture of the cyclopentenols **14** in 83% yield. Even the dienol **15** having the much bulkier silyl group, prepared from silylation of the dienols **1a**, under identical condition underwent smooth ring closure to produce a mixture of the cyclopentenols **17** and **18** in 93% yield (entry 3). RCM of the diacetate **16**, prepared from acetylation of the dienol **1a**, was even faster and took only 2 h for completion to produce the cyclopentene derivative **19** (entry 4) in 91% yield [17]. The inertness of the dienol **1a** towards RCM is possibly due to strong complexation of OH to Ru which retards RCM. Consequently protection of OH diminishes chelation in the dienes and promote RCM. However certain amount of chelation of Ru by the alkoxy oxygen [18] of the dienes **12**, **15** and **16** as shown in the
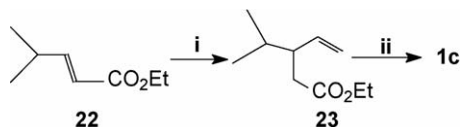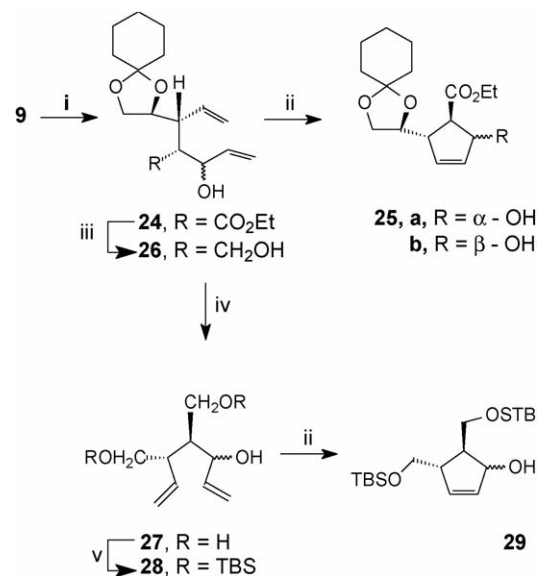
Scheme 3. Reagents and conditions: (i) (a) LiAlH$_4$, Et$_2$O, rt, 71%, (b) CH$_3$C(OEt)$_3$, propionic acid, 140 °C, 6 h, 64%; (ii) (a) LiAlH$_4$, Et$_2$O, rt, 77%, (b) oxalylchloride, DMSO, Et$_3$N, (c) CH$_2$=CHMgBr, THF, 70 °C, 1 h (82% overall).

Scheme 4. Reagents and conditions: (i) LDA, acrolein, 74%; (ii) (PCy$_3$)$_2$Cl$_2$RuCHPh, C$_6$H$_6$, rt, 5 h, 85% for **25** and 83% for **29**; (iii) LiAlH$_4$, Et$_2$O, rt, 73%, (iv) (a) AcOH/H$_2$O (4:1), 4 h, (b) NaIO$_4$, (c) LiAlH$_4$, Et$_2$O, 1 h (68% overall); (v) TBSCl, DMAP, imidazole, Et$_3$N, DCM, rt, 4 h, 50%.

structure **21** is obviously benificial. It may direct metathesis initiation at the alkene nearest to the alkoxy group and thus overrides the competitive non-metathetic fragmentation processes due to allylic secondary OH group. The bulkier alkoxy groups in the dienols **12** and **15** also facilitate dissociation of the oxygen atom from the stabilized Ru-carbene **21** required for subsequent reaction with the second alkene unit. Thus acetate being a better leaving group than silyloxy dissociated at a faster rate from the stabilzed complex **21** and the ring closure was complete in only 2 h (entry 4).

To understand the role of alkoxy groups in facilitating RCM, the dienol **1c** was chosen. The C$_5$-substituent in the dienol **1c** lacks oxygen and imposes steric effect comparable to the ketal unit in **12** or the silyloxy group in **15**. The dienol **1c** was prepared from isbutyraldehyde as depicted in Scheme 3. Wittig–Horner reaction of isobutyraldehyde afforded the unsaturated ester **22** in 91% yield. The unsaturated ester **22** was converted to the ester **23** in 64% yield through *ortho*-ester Claisen rearrangement of the allyl alcohol derived from reduction of the ester moiety. The dienol **1c** was obtained from the ester **23** through a three-step sequence involving reduction of the ester, Swern oxidation of the resulting alcohol and reaction of the aldehyde thus obtained with vinyl magnesium bromide. Reaction of the dienol **1c** in CH$_2$Cl$_2$ at rt for 24 h with 6 mol% of the catalyst **3** produced a complex mixture (entry 5). ^{1}H NMR spectrum of this mixture showed a broad singlet at δ 4.85 in addition to a multiplet at δ 4.08 attributed to the C$_3$–H of the starting dienol **1c**. The broad singlet at δ 4.85 is assigned to the C$_1$–H of the RCM product **2c** on comparison with the chemical shifts (δ 4.86 and 4.83) of the C$_1$–H of the cyclopentenols **14** and **17**. The integration of these two proton signals in the reaction mixture revealed that the ratio of the unreacted dienol **1c** and the RCM product **2c** is 7:3. In addition a carbonyl absorption at ν_{max} 1712 cm^{-1} and a COMe resonance at δ 2.10 ppm in the reaction mixture suggests a competitive β-elimination process during RCM in accord with the observation of Hoye and Zhao [8]. Thus facile RCM of the dienols **12**, **15** and **16** having bulky alkoxy/acetoxy groups compared to the sluggish reactivity of the dienol **1c** lacking alkoxy group establishes that the alkoxy groups have a definitive role in facilitating RCM reaction with the Ru-catalyst **3**.

The cyclopentenols **17** and **18** were separated by column chromatography to produce the pure cyclopentenol **17**, [α]$_D^{25}$ −153 (c 0.1, CHCl$_3$) [13c], [α]$_D^{20}$ −134.8 (c 2.02, CHCl$_3$) and **18**, [α]$_D^{25}$ −69 (c 0.1, CHCl$_3$) in 42 and 38% yields, respectively. The cyclopentenol **17** has already been converted [13c] to (−)-carbovir **4**. Desilylation of the cyclopentenol **18** provided

the cyclopentenol **20**, [α]$_D^{25}$ −45 (c 0.1, CH$_2$Cl$_2$) [13d], [α]$_D^{25}$ −44.3 (c 1.5, CH$_2$Cl$_2$) in 83% yield. The cyclopentenol **20** has also been converted [13d] to (−)-carbovir **4**.

The scope of this alkoxy facilitated RCM was extended for the facile construction of the carbocyclic moiety present in BCA (Scheme 4). Condensation of the lithium enolate of the ester **9** with acrolein afforded a 1:1 diastereoisomeric mixture of the dienol **24**. The assignment of anti relationship of the COOEt group with the substituent bearing the ketal unit in the dienols **24** is based on Houk's model [19] for electrophilic addition to alkenes having an α chiral centre. RCM of the dienol **24** in benzene at rt with 6 mol% of the catalyst **3** was complete within 5 h to produce the cyclopentenols **25** as a diastereoisomeric mixture (ca. 1:1) in quantitative yield. Similarly the RCM of the dienol **27**, obtained from the ketal **24** as shown in Scheme 2, was complete in less than 5 h with the catalyst **3** to produce the cyclopentenol **29** in 79% yield. It is noteworthy that ring closure of the dienols **24** and **28** was faster compared to that of the dienols **12** and **15**. This is possibly due to a synergy of alkoxy facilitation and gauche effect of the vicinally placed ketal and carboethoxy groups. The dienols **29** with the anti disposition of the silyloxymethyl groups represent the carbocyclic moiety of BCA.

3. Conclusion

In conclusion, we have demonstrated the role of neighboring alkoxy groups in facilitating RCM reaction of acyclic 1,6-dienes with the catalyst **3** leading to the synthesis of enantiomerically pure carbocyclic cores present in carbovir, abacavir and BCA. This investigation has also accomplished a formal synthesis of (−)-carbovir.

4. Experimental section

4.1. General

All reactions were carried out under an atmosphere of N_2. A usual work up involves extraction of the reaction mixture with diethyl ether unless otherwise stated, washing of organic extracts with brine, drying over anhydrous Na_2SO_4 and removal of solvent at reduced pressure. Column chromatography was performed on silica gel (60–120 mesh). Petrol refers to the fraction of petroleum ether b.p. 60–80 °C. IR spectra were recorded in thin film. ^{1}H and ^{13}C NMR spectra were recorded in CDCl$_3$ solution at 300 and 75 MHz, respectively. Elemental analyses were carried out at the microanalytical laboratory of this department.

4.2. Procedures for synthesis

4.2.1. 3R-(1,4-dioxa-spiro[4.5]dec-2S-yl)-pent-4-enal (11)

To a cooled (0 °C) magnetically stirred suspension of LiAlH$_4$ (0.2 g, 5.34 mol) in diethyl ether (8 mL) was added drop-wise a solution of the unsaturated ester 10 (1.3 g, 4.85 mmol) in diethyl ether (8 mL). The reaction mixture was allowed to warm to rt and stirred for additional 1 h. It was again cooled to 0 °C and quenched by sequential addition of water (0.2 mL), 15% aqueous NaOH (0.2 mL) and water (0.6 mL) and stirred for 15 min. The white granular precipitate formed was filtered off. The ether layer was dried and the solvent was evaporated to give the corresponding alcohol (1 g, 92%); IR: ν_{max} (neat) 3416, 2935, 2862, 1638, 1450, 1365 cm^{-1}; ^{1}H NMR: δ 1.37 (2H, br s), 1.51–1.80 (8H, m), 2.33–2.42 (1H, m), 3.59–3.78 (2H, m), 3.99 (1H, dd, $J = 6.4$, 8.0 Hz), 4.08–4.14 (1H, m), 5.08–5.19 (2H, m), 5.67–5.80 (1H, m); ^{13}C NMR: δ 24.2 (CH$_2$), 24.3 (CH$_2$), 25.6 (CH$_2$), 34.5 (CH$_2$), 35.3 (CH$_2$), 36.3 (CH$_2$), 44.1 (CH), 60.9 (OCH$_2$), 67.1 (OCH$_2$), 78.1 (OCH), 109.9 (C), 118.0 (CH$_2$), 137.9 (CH). Anal. calcd. for C$_{13}$H$_{22}$O$_3$: C, 68.99; H, 9.80. Found: C, 68.67; H, 9.72. This alcohol was oxidised as follows.

To a magnetically stirred cooled (−78 °C) solution of oxalyl chloride (0.3 mL, 3.82 mmol) in dichloromethane (3 mL), a solution of DMSO (0.6 mL, 7.8 mmol) in dichloromethane (3 mL) was added drop-wise. After stirring the reaction mixture at −78 °C for 15 min a solution of the alcohol (720 mg, 3.19 mmol) in dichloromethane (4 mL) was added and stirred for 45 min. Triethylamine (1.8 mL) was added and the reaction mixture was allowed to attain rt and stirred for 1 h. The reaction mixture was quenched by addition of water (1 mL). The organic phase was separated and washed with water (2 × 2 mL), brine (2 × 3 mL), dried and concentrated to provide the aldehyde 11 (580 mg, 82%) as a colourless liquid; IR: ν_{max} (neat) 2936, 2862, 1724, 1448, 1365 cm^{-1}; ^{1}H NMR: δ 1.38 (2H, br s), 1.38–1.66 (8H, m), 2.61 (1H, dd, $J = 1.7$, 5.6 Hz), 2.67 (1H, dd, $J = 1.9$, 5.8 Hz), 2.90–2.98 (1H, m), 3.63 (1H, dd, $J = 7.3$, 8.2 Hz), 3.96 (1H, dd, $J = 9.2$, 10.8 Hz), 4.15–4.21 (1H, m), 5.09–5.18 (2H, m), 5.68–5.80 (1H, m), 9.73 (1H, t, $J = 1.9$ Hz); ^{13}C NMR: δ 24.2 (CH$_3$), 24.3 (CH$_2$), 25.5 (CH$_2$), 35.0 (CH$_2$), 36.2 (CH$_2$), 40.7 (CH), 44.5 (CH$_2$), 66.2 (OCH$_2$), 77.0 (OCH), 110.2 (C), 118.4 (CH$_2$), 136.3 (CH), 201.8 (CO). Anal. calcd. for C$_{13}$H$_{20}$O$_3$: C, 69.61; H, 8.99. Found: C, 69.47; H, 8.76.

4.2.2. 5R-(1,4-dioxa-spiro[4.5]dec-2S-yl)-hepta-1, 6-dien-3-ol (12)

To a stirred solution of vinylmagnesium bromide [prepared from vinyl bromide (2.9 g, 27 mmol) in THF (40 mL) and magnesium (320 mg, 13.5 mmol)] the aldehyde 11 (600 mg, 2.7 mmol) in THF (5 mL) was added and refluxed gently for 1 h. The reaction mixture was allowed to attain rt and cooled to 0 °C and quenched by water (4 mL) and filtered. Organic phase was washed with brine (3 × 4 mL), dried. Evaporation of the solvent followed by column chromatography (18% diethyl ether–petrol) furnished the alcohol 12 as a diastereoisomeric mixture (530 mg, 74%); IR: ν_{max} (neat) 3427, 2935, 2862, 1643, 1448, 1365 cm^{-1}; ^{1}H NMR: δ 1.31 (2H, br s), 1.40–1.64 (8H, m), 2.19–2.28 (1H, m), 2.39–2.50 (2H, m), 2.82 (1H, br s), 3.52–3.60 (1H, m), 3.88 (1H, t, $J = 7.6$ Hz), 3.96–4.13 (2H, m), 4.96–5.17 (4H, m), 5.58–5.86 (2H, m); ^{13}C NMR: δ 24.1 (CH$_2$), 24.3 (CH$_3$), 25.5 (CH$_2$), 35.2 (CH$_2$), 35.2 (CH$_2$), 36.2 (CH$_2$), 38.7 (CH$_2$), 43.6 (CH), 67.0 (OCH$_2$), 70.3 (OCH), 78.4 (OCH), 109.7 (C), 114.2 (CH$_2$), 118.2 (CH$_2$), 137.8 (CH), 142.0 (CH); ^{13}C NMR: δ 24.1 (CH$_2$), 24.3 (CH$_3$), 25.5 (CH$_2$), 35.2 (CH$_2$), 36.2 (CH$_2$), 38.8 (CH$_2$), 43.6 (CH), 66.9 (OCH$_2$), 71.2 (OCH), 77.8 (OCH), 109.8 (C), 114.2 (CH$_2$), 117.8 (CH$_2$), 138.1 (CH), 141.0 (CH). Anal. calcd. for C$_{15}$H$_{24}$O$_3$: C, 71.39; H, 9.59. Found: C, 71.16; H, 9.38.

4.2.3. 1R,4S- and 1S,4S-(1,4-dioxa-spiro[4.5]dec-2S-yl)-cyclopent-2-enols (14)

A solution of the alcohol mixture 12 (200 mg, 0.8 mmol) in benzene (16 mL) was treated with Grubbs' catalyst 3 (40 mg) under argon atmosphere and stirred at rt for 24 h. The residual mass obtained after removal of solvent was chromatographed to afford the pure cyclopentenol 1R,4S-14 (72 mg, 40%); $R_f = 0.49$ (EtOAc/hexane 1:1); $[\alpha]_D^{22} = -161.75$ (c, 2.85, CHCl$_3$); ^{1}H NMR: δ 1.36 (2H, br s), 1.49–1.59 (8H, m), 1.72–1.88 (2H, m), 2.06 (1H, br s), 3.02 (1H, m), 3.54 (1H, dd, $J = 6.4$, 7.9 Hz), 3.82 (1H, dd, $J = 6.4$, 12.6 Hz), 3.96 (1H, dd, $J = 6.2$, 7.9 Hz), 4.84 (1H, m), 5.87–5.90 (1H, m), 6.02 (1H, dd, $J = 2.0$, 5.8 Hz); ^{13}C NMR: δ 23.7 (CH$_2$), 23.9 (CH$_2$), 25.0 (CH$_2$), 34.8 (CH$_2$), 35.9 (CH$_2$), 36.3 (CH$_2$), 48.2 (CH), 67.4 (OCH$_2$), 76.7 (OCH), 78.8 (OCH), 109.6 (C), 134.6 (CH), 136.2 (CH) and the cyclopentenol 1S,4S-14 (77 mg, 43%); $R_f = 0.54$ (EtOAc/hexane 1:1); $[\alpha]_D^{22} = -90.5$ (c, 5.05, CHCl$_3$); ^{1}H NMR: δ 1.34 (2H, br s), 1.52 (8H, m), 2.23–2.33 (2H, m), 2.27 (2H, dt, $J = 7.6$, 14.6 Hz), 2.69–2.73 (1H, m), 3.66 (1H, t, $J = 7$ Hz), 4.60 (1H, d, $J = 7$ Hz), 5.85 (1H, dd, $J = 1.9$, 5.5 Hz), 5.95–5.98 (1H, m); ^{13}C NMR: δ 23.6 (CH$_2$), 23.8 (CH$_2$), 24.9 (CH$_2$), 34.6 (CH$_2$), 35.7 (CH$_2$), 36.9 (CH$_2$), 46.6 (CH), 66.9 (OCH$_2$), 75.4 (OCH), 77.4 (OCH), 109.7 (C), 132.7 (CH), 136.2 (CH). Anal. calcd. for C$_{13}$H$_{20}$O$_3$: C, 69.61; H, 8.99. Found: C, 69.42; H, 9.01.

4.2.4. 3S,5-divinyl-tetrahydro-furan-2-ol (13)

To a solution of the alcohol 12 (400 mg, 1.6 mmol) in THF (3 mL), HCl (2 mL, 6N) was added drop-wise and stirred for 1 h. The reaction mixture was diluted with ether (5 mL) and washed with water (2 × 3 mL). The combined aqueous

part was then stirred with NaIO$_4$ (0.75 g) for 1 h. Usual work up of the reaction mixture followed by column chromatography provided the lactol **13** (98 mg, 76%) (based on recovered starting alchol **12**) as a diastereomeric mixture; IR: ν_{max} (neat) 3398, 3080, 2982, 2937, 1716, 1643, 1450, 1425, 1348 cm^{-1}; ^{1}H NMR: (of the mixture) δ 1.52–2.37 (2H, m), 2.80–2.86 (1H, m), 3.10 (1H, br s), 4.40–4.89 (1H, m), 5.06-5.35 (4H, m), 5.74–5.98 (2H, m); ^{13}C NMR: (of the mixture) δ 34.2 (CH$_2$), 35.0 (CH$_2$), 35.5 (CH$_2$), 37.7 (CH$_2$), 47.1 (CH), 49.5 (CH), 49.8 (CH), 51.3 (CH), 78.6 (OCH), 79.3 (OCH), 80.5 (OCH), 81.3 (OCH), 98.7 (OCH), 99.0 (OCH), 102.3 (OCH), 102.7 (OCH), 114.8 (CH$_2$), 115.8 (CH$_2$), 115.9 (CH$_2$), 115.9 (CH$_2$), 116.1 (CH$_2$), 116.3 (CH$_2$), 116.9 (CH$_2$), 116.9 (CH$_2$), 135.0 (CH), 135.2 (CH), 136.7 (CH), 137.6 (CH), 137.8 (CH), 138.7 (CH), 139.8 (CH), 139.9 (CH). Anal. calcd. for C$_8$H$_{12}$O$_2$: C, 68.55; H, 8.63. Found: C, 68.39; H, 8.48.

4.2.5. Synthesis of the diene (1a)

To a cooled (0 °C) magnetically stirred suspension of LiAlH$_4$ (34 mg, 0.9 mmol) in diethyl ether (1.5 mL) was added drop-wise a solution of the lactol **13** (80 mg, 0.6 mmol) in diethyl ether (1 mL). The reaction mixture was allowed to attain rt and stirred for additional 1 h. It was again cooled to 0 °C and quenched by sequential addition of water (0.05 mL), 15% aqueous NaOH (0.05 mL) and water (0.15 mL). The organic phase was separated and dried. Solvent was removed to afford the diol **1a** (52 mg, 84%) as a 1:1 diastereoisomeric mixture; IR: ν_{max} (neat) 3348, 3078, 2926, 2854, 1641, 1454, 1421, 1379 cm^{-1}; ^{1}H NMR: (of the mixture) δ 1.37–1.55 (2H, m), 2.23–2.37 (1H, m), 3.32–3.45 (2H, m), 3.69 (2H, br s), 3.99–4.12 (1H, m), 4.92–5.11 (4H, m), 5.45–5.80 (2H, m); ^{13}C NMR: (of the mixture) δ 38.4 (CH$_2$), 38.9 (CH$_2$), 42.5 (CH), 43.6 (CH), 65.3 (OCH$_2$), 65.7 (OCH$_2$), 70.7 (OCH), 70.7 (OCH), 113.9 (CH$_2$), 115.0 (CH$_2$), 116.4 (CH$_2$), 116.6 (CH$_2$), 139.1 (CH), 139.3 (CH), 140.4 (CH), 141.2 (CH). Anal. calcd. for C$_8$H$_{14}$O$_2$: C, 67.57; H, 9.22. Found: C, 67.40; H, 8.97.

4.2.6. 5R-(tert-butyl dimethyl silanyloxy)-hepta-1, 6-dien-3-ol (15)

To a solution of the diol **1a** (70 mg, 0.5 mmol) in dichloromethane (2 mL) was added TBSCl (80 mg, 0.5 mmol), triethyl amine (0.1 mL, 0.74 mmol), DMAP (5 mg) and imidazole (catalytic amount). The mixture was stirred under nitrogen for 36 h at rt. Usual work up of the reaction mixture followed by column chromatography (8% diethyl ether–petrol) afforded the silyl ether **15** (110 mg, 87%) as a diastereoisomeric mixture; IR: ν_{max} (neat) 3331, 2928, 1715 cm^{-1}; ^{1}H NMR: (of the mixture) δ 0.0 (6H, s), 0.84 (9H, s), 1.48–1.74 (2H, m), 2.26–2.46 (1H, m), 3.45 (1H, dd, $J = 7.0$, 9.7 Hz), 3.56 (1H, dd, $J = 4.9$, 9.9 Hz), 4.07–4.20 (1H, m), 4.98-5.21 (4H, m), 5.57–5.89 (2H, m); ^{13}C NMR: (of the mixture) δ −5.6 (CH$_3$), −5.5 (CH$_3$), −5.5 (CH$_3$), 18.2 (C), 25.7 (CH$_3$), 25.8 (CH$_3$), 39.1 (CH$_2$), 39.6 (CH$_2$), 42.8 (CH), 43.7 (CH), 66.7 (OCH$_2$), 67.0 (OCH$_2$), 71.0 (OCH), 113.7 (CH$_2$), 114.6 (CH$_2$), 115.7 (CH$_2$), 115.8 (CH$_2$), 139.5 (CH), 139.6 (CH), 140.8 (CH), 141.5 (CH). Anal. calcd. for C$_{14}$H$_{28}$O$_2$Si: C, 65.57; H, 11.00. Found: C, 65.38; H, 10.89.

4.2.7. 1R,4R-(tert-butyl dimethyl silanyloxy)-cyclopent-2-enol (17) and 1S,4R-(tert-butyl dimethyl silanyloxy)-cyclopent-2-enol (18)

To a solution of the alcohol **1a** (100 mg, 0.4 mmol) in dichloromethane (7 mL), Grubbs' catalyst **3** (20 mg) was added and stirred under argon atmosphere for 24 h at rt. Solvent was removed and the residual mass was chromatographed (10% diethyl ether–petrol) to afford the cyclopentenols **17** (37 mg, 42%); $[\alpha]_D^{25}$ = − 153 (c 0.1, CHCl$_3$) [12c], $[\alpha]_D^{20}$ = − 134.8 (c 2.02, CHCl$_3$); IR: ν_{max} (neat) 3334, 2957, 1713 cm^{-1}; ^{1}H NMR: δ 0.01 (6H, s), 0.86 (9H, s), 1.77 (1H, ddd, $J = 14.1$, 7.8, 3.3 Hz), 1.91 (1H, ddd, $J = 14.1$, 7.3, 4.6 Hz), 2.29 (1H, br s), 2.85–3.10 (1H, m), 3.46 (2H, ddd, $J = 24.3$, 9.6, 6.5 Hz), 4.78–4.92 (1H, m), 5.85 (1H, dt, $J = 5.6$, 2.0 Hz), 5.94 (1H, dd, $J = 5.6$, 1.6 Hz); ^{13}C NMR: δ −5.4 (CH$_3$), 18.2 (C), 25.8 (CH$_3$), 36.8 (CH$_2$), 47.3 (CH), 66.7 (OCH$_2$), 76.9 (OCH), 134.2 (CH), 136.9 (CH) the cyclopentenol **18** (34 mg, 38%); $[\alpha]_D^{25}$ = − 69 (c 0.1, CHCl$_3$); IR: ν_{max} (neat) 3331, 2957, 1715 cm^{-1}; ^{1}H NMR: δ 0.01 (6H, s), 0.84 (9H, s), 1.48 (2H, d, $J = 15.3$ Hz), 2.10–2.35 (1H, m), 2.60–2.85 (1H, m), 3.40–3.70 (1H, m), 4.40–4.65 (1H, m), 5.65–5.75 (1H, m), 5.85–5.95 (1H, m); ^{13}C NMR: δ −5.6 (CH$_3$), 18.4 (C), 25.9 (CH$_3$), 36.9 (CH$_2$), 46.2 (CH), 64.3 (OCH$_2$), 75.4 (OCH), 134.8 (CH), 135.2 (CH) and a fraction containing a mixture of **17** and **18** (12 mg, 13%).

4.2.8. 1R,4S-hydroxymethyl-cyclopent-2-enol (20)

A solution of the silyl ether **18** (20 mg, 0.09 mmol) in THF (0.5 mL) was treated with TBAF (0.2 mL, 1 M solution in THF) and stirred for 1 h at rt. Solvent was removed and the residue was chromatographed (20% diethyl ether–petrol) to furnish the known diol **20** (7 mg, 70%); IR: ν_{max} (neat) 3410, 2932 cm^{-1}; $[\alpha]_D^{25}$ −45 (c 0.1, CH$_2$Cl$_2$) [12d], $[\alpha]_D^{25}$ −44.3 (c 1.5, CH$_2$Cl$_2$); ^{1}H NMR: δ 1.70–1.88 (2H, m), 2.30–2.40 (2H, m), 2.84–2.88 (1H, m), 3.59–3.77 (2H, m), 4.68 (1H, d, $J = 7.2$ Hz), 5.82–5.85 (1H, m), 5.98–6.01 (1H, m); ^{13}C NMR: δ 37.3 (CH$_2$), 46.5 (CH), 63.7 (OCH$_2$), 75.9 (OCH), 135.2 (CH), 135.9 (CH).

4.2.9. Synthesis of the diacetate (16)

To a cooled (0 °C) magnetically stirred solution of the diol **1a** (55 mg, 0.4 mmol) in dichloromethane (2 mL) was added drop-wise acetic anhydride (0.09 mL, 1 mmol), triethylamine (0.07 mL, 0.5 mmol) and pyridine (0.04 mL, 0.5 mmol) successively. The reaction mixture was then allowed to stir under argon atmosphere for 2 h at rt. Solvent was evaporated and the residual mass was extracted with ether. The ether layer was then washed with 10% hydrochloric acid (1 mL) followed by brine (1 mL) and dried. The residual mass obtained after solvent removal was chromatographed (10% diethyl ether–petrol) to afford a diastereoisomeric mixture of the diacetates **16** (37 mg, 43%) as a colourless liquid; ^{1}H NMR: (of the mixture) δ 2.04, 2.06 and 2.07 (all siglets accounting for 6H), 2.45–2.50 (1H, m), 3.97–4.06 (3H, m), 5.05–5.29 (4H, m), 5.62–5.78 (2H, m); ^{13}C NMR: (of the mixture) δ 20.67 (CH$_3$), 20.69 (CH$_3$), 20.9 (CH$_3$), 21.0 (CH$_3$), 35.2 (CH$_2$), 35.5 (CH$_2$), 39.46 (CH), 39.56 (CH), 66.79 (OCH$_2$), 66.82 (OCH$_2$), 72.0 (OCH), 72.9 (OCH), 116.4 (CH$_2$), 116.9 (CH$_2$), 117.51 (CH$_2$), 117.56 (CH$_2$), 135.6 (CH), 136.3 (CH), 137.2 (CH), 137.6 (CH), 169.8 (CO), 169.9 (CO),

170.75 (CO), 170.78 (CO); HRMS: 249.1130 (M^+ + Na) (calcd. for $C_{12}H_{18}O_4Na$ 249.1103).

4.2.10. RCM of the diacetates (16)

A solution of the diacetates **16** (25 mg, 0.1106 mmol) in dichloromethane (1.8 mL) was treated with Grubbs' catalyst (5 mg, 0.0061 mmol) for 2 h at rt. Solvent was removed and the residual mass was chromatographed (9% diethyl ether–petrol) to afford 6 mg of unreacted diacetate **16** and a 3:2 diastereoisomeric mixture of the cyclopentenes **19** (15 mg, 91% based on recovered starting material); ^1H NMR: (of the mixture) δ 1.96–2.14 (8H, m, having three singlets at δ 2.04, 2.06, 2.07 for $OCOCH_3$), 2.44–2.54 (1H, m), 3.93–4.09 (3H, m), 5.63–6.04 (2H, m); ^{13}C NMR: δ (for the major isomer from the mixture) 20.9 (CH_3), 21.2 (CH_3), 33.9 (CH_2), 44.04 (CH), 66.9 (OCH_2), 79.6 (OCH), 131.3 (CH), 137.9 (CH), 170.9 (CO), 171.02 (CO); δ (for the minor isomer from the mixture) 21.23 (CH_3), 21.26 (CH_3), 33.5(CH_2), 43.7 (CH), 67.4 (OCH_2), 79.2 (OCH), 131.4 (CH), 136.9 (CH), 170.7 (CO), 170.9 (CO); HRMS: 221.0847 (M^+ + Na) (calcd. for $C_{10}H_{14}O_4Na$ 221.0790). The ^{13}C chemical shifts observed for the minor diacetate was closely comparable to those of the corresponding syn diacetate reported in literature [12e].

4.2.11. 4-Methyl-pent-2-enoic acid ethyl ester (22)

Triethyl phosphonoacetate (21.8 g, 97.2 mmol) was added drop-wise at rt to a magnetically stirred suspension of sodium hydride (4 g, 83.3 mmol, 50% suspension in mineral oil) in THF (20 mL). The resulting solution was stirred for 45 min. A solution of isobutyraldehyde (5 g, 69.4 mmol) in THF (20 mL) was added to it. After stirring for 14 h at rt, the reaction mixture was quenched by adding saturated aqueous NH_4Cl (4 mL). Usual work up of the reaction mixture followed by distillation afforded a mixture of the E- and Z-isomer of the ester **22** (9 g, 91%); b.p. 146–148 °C; IR: ν_{max} (neat) 2964, 2937, 2904, 2872, 1720, 1653, 1466, 1367, 1300, 1267 cm^{-1}; ^1H NMR: (of the mixture) δ 0.86–1.03 (6H, m), 1.07–1.26 (3H, m), 2.31–2.36 (1H, m), 4.02–4.11 (2H, m), 5.65 (1H, dd, J = 2.2, 15.7 Hz), 6.78–6.87 (1H, m); ^{13}C NMR: (of the major isomer from the mixture) δ 14.0 (CH_3), 20.9 (CH_3), 30.6 (CH), 59.8 (OCH_2), 118.4 (CH), 155.0 (CH), 166.6 (CO).

4.2.12. Synthesis of 3-isopropyl-pent-4-enoic acid ethyl ester (23)

The unsaturated ester **22** (6.1 g, 48 mmol) in diethyl ether (150 mL) was reduced with $LiAlH_4$ (1.8 g, 47.2 mmol) to afford the corresponding allyl alcohol (3.05 g, 71%). This alcohol without characterisation was subjected to ortho ester Claisen rearrangement by heating with triethyl orthoacetate (20 mL, 108.5 mmol) and propionic acid (cat) to provide the ester **23** (3.7 g, 64%); b.p. 140–142 °C, IR: ν_{max} (neat) 2959, 2935, 2906, 2872, 1736, 1468, 1387, 1369 cm^{-1}; ^1H NMR: δ 0.76–1.00 (6H, m), 1.09–1.20 (3H, m), 1.43–1.56 (2H, m), 2.19–2.36 (2H, m), 3.94–4.12 (2H, m), 4.91–4.97 (2H, m), 5.52–5.61 (1H, m); ^{13}C NMR: δ 14.0 (CH_3), 22.2 (CH_3), 27.5

(CH_3), 31.1 (CH), 34.8 (CH_2), 46.5 (CH), 59.8 (OCH_2), 115.8 (CH_2), 138.5 (CH), 172.7 (CO).

4.2.13. 5-Isopropyl-hepta-1,6-dien-3-ol (1c)

The unsaturated ester **23** (0.4 g, 2.35 mmol) in diethyl ether (7 mL) was reduced with $LiAlH_4$ (110 mg, 2.82 mmol) as described above for reduction of the ester **10** to afford the corresponding alcohol (230 mg, 77%); ^1H NMR: δ 0.67–0.98 (6H, m), 1.16–1.23 (2H, m), 1.47–1.67 (2H, m), 2.28 (1H, brs), 3.47–3.71 (2H, m), 4.93–5.07 (2H, m), 5.51–5.63 (1H, m). ^{13}C NMR: δ 22.9 (CH_3), 28.2 (CH_3), 30.9 (CH), 35.1 (CH_2), 47.8 (CH), 61.8 (OCH_2), 116.2 (CH_2), 140.8 (CH). The aldehyde obtained by Swern oxidation of this alcohol (180 mg, 1.41 mmol), following the procedure described for preparation of the aldehyde **11**, was allowed to react with vinyl magnesium bromide following the procedure described earlier to yield the dienol **1c** (180 mg, 82%); IR: ν_{max} (neat) 3384, 3311, 3076, 2957, 2932, 2872, 1686, 1637, 1466, 1421, 1385, 1367 cm^{-1}. ^1H NMR: δ 0.81–0.99 (6H, m), 1.07–2.23 (4H, m), 4.04–4.11 (1H, m), 4.93–5.22 (4H, m), 5.51–5.93 (2H, m), ^{13}C NMR: δ 19.0 (CH_3), 19.3 (CH_3), 20.7 (CH_3), 20.8 (CH_3), 32.2 (CH), 32.3(CH), 39.7 (CH_2), 39.7 (CH_2), 46.9 (CH), 47.8 (CH), 72.6 (OCH), 73.7 (OCH), 114.0 (CH_2), 114.9 (OCH_2), 115.6 (OCH_2), 116.7 (OCH_2), 140.6 (CH), 141 (CH), 141.7 (CH), 142.2 (CH).

4.2.14. Ethyl-(3S)-3-[(4S)-1,4-dioxaspiro[4.5]dec-2-yl]-2-[(1R)-1-hydroxyprop-2-enyl]-pent-4-enoate (24)

A solution of the ester **9** (1.00 g, 3.73 mmol) in THF (4 mL) was added drop-wise to a magnetically stirred solution of LDA [prepared from diisopropylamine (0.77 mL, 5.52 mmol) in anhydrous THF (2 mL) and nBuLi (3.05 mL, 4.88 mmol, 1.6 M in hexane)] at −78 °C under Ar atmosphere. The temperature was then slowly raised to −30 °C and sttirred at that temperature for 1 h. The reaction mixture was again cooled to −78 °C and to it HMPA (1 mL) followed by acrolein (0.33 mL, 4.85 mmol) was added drop-wise and stirred at −78 °C for another 2 h. After quenching with saturated aqueous ammonium chloride solution (1 mL), the reaction mixture was worked up in the usual way to afford after chromatography (10% diethyl ether–petrol) a 1:1 diastereomeric mixture of the alcohols **24** (900 mg, 74%); IR: ν_{max} 1732.0, 3444.6 cm^{-1}; ^1H NMR: (300 MHz) δ (of the mixture) 1.21 (6H, t, J = 7.14 Hz), 1.33 (4H, br s), 1.48–1.53 (16H, m), 2.44–2.70 (3H, m), 2.83–2.97 (3H, m), 3.57–3.63 (4H, dd, J = 16.9, 7.8 Hz), 3.89–4.16 (6H, m), 4.31 (2H, m), 5.07–5.26 (8H, m), 5.80–5.87 (4H, m); ^{13}C NMR: 14.5 (CH_3), 14.6 (CH_3), 24.07 (CH_2), 24.13 (CH_2), 24.21 (CH_2), 25.46 (CH_2), 25.5 (CH_2), 34.9 (CH_2), 35.2 (CH_2), 35.9 (CH_2), 36.1 (CH_2),.45.9 (CH), 46.1 (CH), 53.4 (CH), 54.0 (CH), 60.8 (OCH_2), 60.9 (OCH_2), 66.8 (OCH_2), 67.3 (OCH_2), 72.0 (OCH), 72.3 (OCH), 75.9 (OCH), 76.0 (OCH), 109.9 (C), 110.1 (C), 117.0 (CH_2), 117.3 (CH_2), 119.6 (CH_2), 120.3 (CH_2), 134.6 (CH), 134.7 (CH), 136.9 (CH), 138.5 (CH), 172.4 (CO), 172.8 (CO). Anal. calcd. for $C_{18}H_{28}O_5$: C, 66.64; H,8.70. Found: C, 66.84; H, 8.65. HRMS: 347.1811 (M^+ + Na) (calcd. for $C_{18}H_{28}O_5Na$ 347.1836).

4.2.15. Ethyl (1R,2S,5S)-2-[(4S)-1,4-dioxaspiro[4.5]dec-2-yl]-6-hydroxycyclopent-3-ene-1-carboxylate (25a) and ethyl (1R,2S,5S)-2-[(4S)-1,4-dioxaspiro[4.5]dec-2-yl]-6-hydroxycyclopent-3-ene-1-carboxylate (25b)

The diene **24** (2 g, 6.17 mmol) in anhydrous benzene (100 mL) was treated with Grubbs' catalyst (101 mg, 0.12 mmol) for 5 h at rt to afford after chromatgraphy (15% diethyl ether–petrol) cyclopentenols **25a** and **25b** as a diastereomeric mixture (ca. 1:1) (1.56 g, 85%); IR: ν_{max} (of the mixture) 1732.0, 3446.6 cm^{-1}; HRMS: 319.1508 ($M^+ +$ Na) (calcd. for $C_{16}H_{24}O_5Na$ 319.1521). The pure cyclopentenols **25a**, $[\alpha]_D^{25}$ +5.7 (c 0.1, CHCl$_3$); ^{1}H NMR: δ 1.29 (3H, t, $J = 7.1$ Hz), 1.38 (2H, m), 1.54–1.65 (8H, m), 3.00 (1H, t, $J = 6.9$ Hz), 3.44 (1H, m), 3.67 (1H, dd, $J = 6.8$ Hz), 4.01 (1H, dd, $J = 6.3$, 8 Hz), 4.10 (1H, dd, $J = 6.0$, 12.0 Hz), 4.20 (2H, q, $J = 6.9$ Hz), 4.97 (1H, m), 5.90 (1H, m), 6.03 (1H, dd, $J = 1.6$, 5.7 Hz); ^{13}C NMR: δ 14.1 (CH$_3$), 23.7 (CH$_2$), 23.9 (CH$_2$), 25.1 (CH$_2$), 34.6 (CH$_2$), 36.0 (CH$_2$), 50.1 (CH), 50.4 (CH), 60.9 (OCH), 66.9 (OCH$_2$), 76.6 (OCH), 76.9 (OCH), 109.7 (C), 132.5 (CH), 135.7 (CH), 172.0 (CO) and **25b**, $[\alpha]_D^{25}$ +19.5 (c 0.1, CHCl$_3$); ^{1}H NMR: δ 1.28 (3H, t, $J = 7.1$ Hz), 1.36 (2H, m), 1.48–1.62 (8H, m), 1.61 (1H, br s), 3.03 (1H, t, $J = 7.8$ Hz), 3.42 (1H, m), 3.55 (1H, dd, $J = 6.5$, 8.0 Hz), 3.94 (1H, dd, $J = 6.4$, 8.1 Hz), 4.04 (1H, dd, $J = 6.1$, 12.1 Hz), 4.15 (2H, q, $J = 7.1$ Hz), 4.93 (1H, m), 5.79 (1H, dd, $J = 1.7$, 5.7 Hz), 5.83 (1H, m); ^{13}C NMR: δ 14.1 (CH$_3$), 23.7 (CH$_2$), 23.8 (CH$_2$), 25.0 (CH$_2$), 34.7 (CH$_2$), 36.0 (CH$_2$), 50.1 (CH), 50.3 (CH), 60.8 (OCH$_2$), 66.7 (OCH$_2$), 76.8 (OCH), 77.3 (OCH), 109.7 (C), 133.3 (CH), 135.0 (CH), 172.3 (CO) were obtained through preparative TLC of a portion of the above product mixture. *syn*-Orientation of the 1,3-substituents in the cyclopentenol **25a** was determined from NOE (2.65%).

4.2.16. (2S)-2-[(1R)-1-[(4S)-1,4-dioxaspiro[4.5]dec-2-yl]-prop-2-enyl]pent-4-ene-1,3-diol (26)

A solution of the ester **24** (630 mg, 1.94 mol) in ether (4 mL) was reduced with LiAlH$_4$ (74 mg, 1.94 mmol) according to the procedure described above to afford a 1:1 diastereomeric mixture of the diols **26** (400 mg, 73%) as a colourless viscous liquid after chromatography (25% diethyl ether–petrol); ^{1}H NMR: (of the mixture) δ 1.34 (4H, br s), 1.55 (16H, m), 1.83 (2H, m), 2.50 (2H, m), 3.64 (6H, m), 3.76 (2H, br s), 3.83 (2H, br s), 3.94 (4H, m), 4.31 (1H, m), 4.36 (1H, m), 5.01–5.29 (8H, m), 5.80–5.90 (4H, m); ^{13}C NMR: δ 24.0 (CH$_2$), 24.0 (CH$_2$), 25.1 (CH$_2$), 25.2 (CH$_2$), 34.0 (CH$_2$), 34.6 (CH$_2$), 34.9 (CH$_2$), 35.7 (CH$_2$), 36.0 (CH$_2$), 43.7 (CH), 43.9 (CH), 45.4 (CH), 49.2 (CH), 60.3 (OCH$_2$), 61.1 (OCH$_2$), 66.8 (OCH$_2$), 66.9 (OCH$_2$), 73.0 (OCH), 73.8 (OCH), 74.2 (OCH), 74.8 (OCH), 109.8 (C), 114.8 (CH$_2$), 116.4 (CH$_2$), 117.7 (CH$_2$), 119.2 (CH$_2$), 135.3 (CH), 136.0 (CH), 137.5 (CH), 138.9 (CH); HRMS: 305.1688 ($M^+ +$ Na) (calcd. for $C_{16}H_{26}O_4Na$ 305.1729).

4.2.17. (4S,5S)-4,5-bis(tert-butyl-dimethylsilanyloxymethyl)hepta-1,6-dien-3-ol (28)

A solution of the diol **26** (400 mg, 1.42 mmol) in aqueous acetic acid (80%, 4 mL) was stirred at 80 °C for 4 h. On cooling to 0 °C, NaIO$_4$ (304 mg, 1.42 mmol) was added to it and stirred for another 1 h. The reaction mixture was diluted with EtOAC (20 mL) and washed repeatedly with 5% aqueous NaOH solution till it is alkaline. The organic layer was separated and dried over Na$_2$SO$_4$. Evaporation of the solvent under vacuum afforded a liquid (190 mg, 79%). A solution of this liquid in ether (2 mL) was added to a magnetically stirred suspension of LiAlH$_4$ (43 mg, 1.12 mmol) in ether (1 mL) at 0 °C and stirring was continued for 1 h. After quenching with 15% NaOH solution (0.5 mL), the reaction mixture was extracted with ether (3 × 20 mL) and dried over Na$_2$SO$_4$ and concentrated to afford the triol **27** as a colourless viscous liquid (130 mg, 68%); ^{1}H NMR: (of the mixture) δ 1.25 (2H, br s), 1.67 (2H, br s), 1.92–2.08 (2H, m), 2.47–2.54 (2H, m), 2.62 (2H, br s), 3.42–3.89 (8H, m), 4.32 (1H, m), 4.40 (1H, m), 5.09–5.36 (8H, m), 5.77–5.95 (4H, m); ^{13}C NMR: δ 44.9 (CH), 45.7 (CH), 46.9 (CH), 47.9 (CH), 61.5 (OCH$_2$), 63.7 (OCH$_2$), 64.7 (OCH$_2$), 66.1 (OCH$_2$), 73.1 (OCH), 74.4 (OCH), 116.2 (CH$_2$), 116.4 (CH$_2$), 117.9 (CH$_2$), 118.2 (CH$_2$), 138.4 (CH), 138.9 (CH), 138.5 (CH), 138.6 (CH).

A mixture of the triol **27** (138 mg, 0.76 mmol), as obtained above, dichloromethane (2 mL), triethylamine (0.42 mL, 3.024 mmol), DMAP (5 mg), imidazole (5 mg), *t*-butyldimethylsilyl chloride (249 mg, 1.66 mmol) was stirred for 4 h at room temperature. After evaporation of the solvent the residual mass was chromatographed (5% diethyl ether–petrol) to afford the silylether **28** (150 mg, 50%); ^{1}H NMR: (of the mixture) δ −0.90 (36H, s), 0.07 (24H, s), 1.54 (2H, br s), 2.05–2.10 (2H, m), 2.31–2.36 (2H, m), 3.57–3.82 (8H, m), 4.24 (2H, m), 5.10–5.37 (8H, m), 5.74–5.97 (4H, m); ^{13}C NMR: δ −5.31 (CH$_3$), −5.28 (CH$_3$), −5.25 (CH$_3$), −5.22 (CH$_3$), −5.19 (CH$_3$), −5.12 (CH$_3$), −5.05 (CH$_3$), 18.5 (C), 18.6 (C), 25.99 (CH$_3$), 26.13 (CH$_3$), 26.21 (CH$_3$), 26.23 (CH$_3$), 45.0 (CH), 45.5 (CH), 47.5 (CH), 63.0 (OCH$_2$), 63.8 (OCH$_2$), 65.3 (OCH$_2$), 65.5 (OCH$_2$), 73.1 (OCH), 74.3 (OCH), 115.5 (CH$_2$), 115.7 (CH$_2$), 116.6 (CH$_2$), 116.8 (CH$_2$), 139.3 (CH), 139.4 (CH) 139.5 (CH), 139.7 (CH). Anal. calcd. for $C_{21}H_{44}O_3Si_2$: C, 62.94; H, 11.07; Found: C, 63.40; H, 11.31; HRMS: 423.2710 ($M^+ +$ Na) (calcd. for $C_{21}H_{44}O_3Si_2Na$ 423.2727).

4.2.18. (4S,5S)-4,5-bis(tert-butyl-dimethylsilanyloxymethyl)cyclopent-2-en-1-ol (29)

The diene **28** (130 mg, 0.325) in anhydrous benzene (2 mL) was treated with Grubbs' catalyst (6 mg, 0.0073 mmol) for 5 h at rt afforded after chromatagraphy (15% diethyl ether–petrol) cyclopentenol **29** (100 mg, 83%); $[\alpha]_D^{25}$ −15 °C (c 0.1, CHCl$_3$); ^{1}H NMR: (of the mixture) δ −0.07 (12H, s), −0.04 (12H, s), 0.85 (9H, s), 0.86 (9H, s), 0.884 (9H, s), 2.05–2.13 (1H, m), 2.20 (1H, m), 2.65–2.69 (1H, m), 2.96–3.00 (1H, m), 3.05 (1H, d, $J = 5.3$ Hz), 3.41–3.47 (1H, m), 4.39–4.43 (1H, m), 3.46–3.65 (2H, m), 3.52–3.60 (1H, m), 3.73–3.85 (3H, m), 3.79 (1H, dd, $J = 7.0$, 10.0 Hz), 3.91–3.97 (1H, m), 3.92 (1H, dd, $J = 4.8$ Hz), 4.39–4.43 (1H, m), 4.86 (1H, m), 5.79–5.82 (1H, m), 5.83 (2H, br s), 6.04–6.06 (1H, m); ^{13}C NMR: δ −5.2 (CH$_3$), −5.0 (CH$_3$), 18.4 (C), 18.6 (C), 25.90 (CH$_3$), 25.98 (CH$_3$), 26.16 (CH$_3$), 26.24 (CH$_3$), 46.6 (CH), 47.2 (CH), 49.5 (CH), 50.3 (CH), 61.2 (OCH$_2$), 64.9 (OCH$_2$), 66.6 (OCH$_2$), 66.8 (OCH$_2$), 78.2 (OCH), 79.2 (OCH), 133.9 (CH), 134.2

(CH), 135.5 (CH), 135.9 (CH); HRMS: 395.2390 ($M^+ +$ Na) (calcd. for $C_{19}H_{40}Si_2O_3Na$ 395.2414).

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