Synthesis of α-hydroxy and α-oxospiranes through ruthenium(II)-catalyzed ring-closing metathesis

Pompiliu S. Aburel, Christian Rømming, Kuangbiao Ma and Kjell Undheim *

Department of Chemistry, University of Oslo, N-0315, Oslo, Norway

Received (in Cambridge, UK) 14th February 2001, Accepted 10th May 2001
First published as an Advance Article on the web 30th May 2001

Efficient methodology for the construction of functionalized spiranes using Ru(II)-catalyzed ring-closing metathesis reactions is described. The substrates were appropriately substituted five-, six- and seven-membered cycloalkanes which were spiroannulated by five-, six- and seven-membered rings, respectively. The relative stereochemistry of selected substituted spiranes has been determined by single crystal X-ray analyses. The X-ray structures formed the basis for NMR correlations of the relative stereochemistry in the groups of compounds prepared. Relative rates in oxidation reactions could also be used for stereochemical correlations.

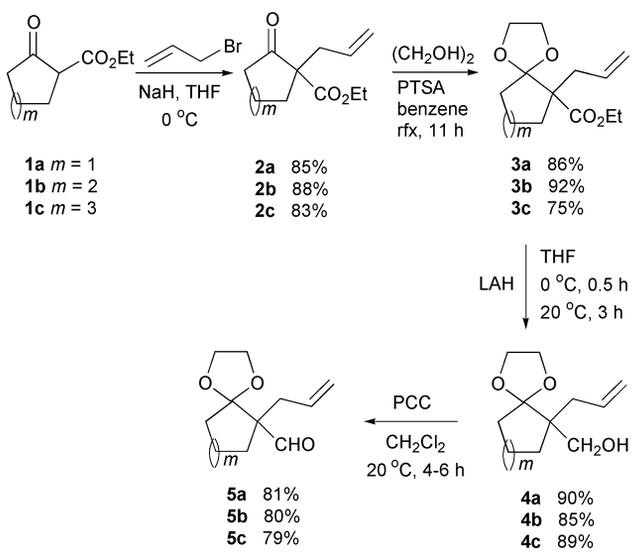
Introduction

In spiranes there is no rotation around the quaternary spiro-center. As a consequence, spiranes are rather rigid structures and potentially useful as rigid frameworks for attachment of functional groups, pharmacophoric groups or coordinating functions for metal complexation. We have for some time been engaged in developing methodologies for ready access to functionalized spiranes and have reported on the preparation of β,β′-dioxospiranes and on α,β′-dioxospiranes.[1,2] For additional modifications, we have also reported on carbosubstitutions in α,α′-dioxospiro[4.4]nonanes.[3] Several methods for the preparation of spiranes have been described which include palladium promoted spiroannulations onto carbo- or heterocyclic substrates,[4] cascade reactions,[4,5] nickel mediated reactions of alkynes,[6] radical promoted spiroannulations,[7] spiroannulation of ketals,[8] rearrangement reactions,[9] rhodium-catalyzed hydroacylations,[10] copper or samarium mediated spiroannulations,[11,12] aldol condensations and alkylations,[13,14] our Rh(II)-carbenoid insertion reactions,[1,2] Ru(II)-effected spirocycle assembly,[15] Ru(II)-catalyzed spiroannulations of dihydropyrazines to form heterocyclic spiranes,[16] and in construction of silaspiranes.[17] Considerable efforts recently have been directed towards stereoselective syntheses.[14,18,19]

Our previous constructions of β,β′-dioxo- and α,β′-dioxospiranes were based on rhodium(II)-carbenoid C–H insertion reactions for spiroannulation.[1,2] The ring sizes in the substrates could be varied but the spiroannulation was limited to the addition of five-membered carbocycles. In this work we report on the spiroannulation of five- to seven-membered rings using bis(tricyclohexylphosphine)(benzylidene)ruthenium dichloride [Ru(II)] catalyzed ring-closing metathesis (RCM) reactions. The Grubbs Ru(II)-catalyst systems have become very important tools in synthetic organic chemistry.[20,21] We have on several occasions applied these tools to the construction of heterocyclic rings and heterocyclic spiranes.[16] In this work the substrates used for the formation of α,α′-dioxospiranes were appropriately functionalized five- to seven-membered carbocyclic 1,1-dienes. Five- to seven-membered rings were formed in the spiroannulation reactions.

Results and discussion

The five-, six- and seven-membered ring substrates for the RCM effected spirane constructions shown in Schemes 4 and 5 were prepared from 2-oxocycloalkane-1-carboxylates **1** (Scheme 1). These were metalated and allylated to the quaternary carbon derivatives **2**. The keto group was protected as an ethylene acetal in structures **3** before LAH reduction of the ester function to furnish the alcohols **4**. These were oxidized in high yields by pyridinium chlorochromate (PCC) in methylene dichloride at ambient temperature to the corresponding carbaldehydes **5** which were converted into alcohols by Grignard reagents (Scheme 2).



1a *m* = 1 **1b** *m* = 2 **1c** *m* = 3

2a 85% **2b** 88% **2c** 83%

3a 86% **3b** 92% **3c** 75%

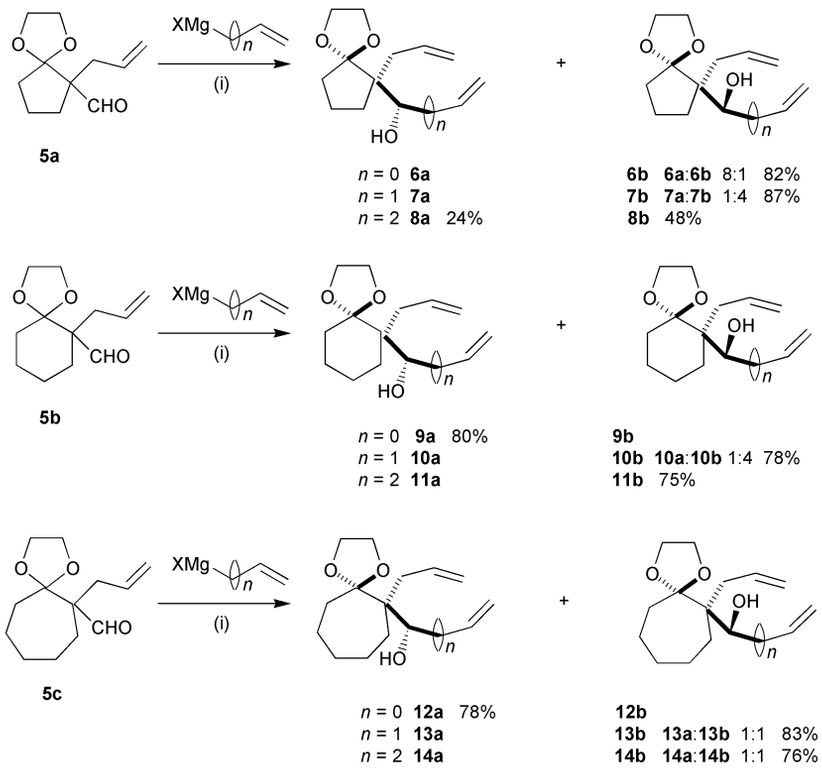
4a 90% **4b** 85% **4c** 89%

5a 81% **5b** 80% **5c** 79%

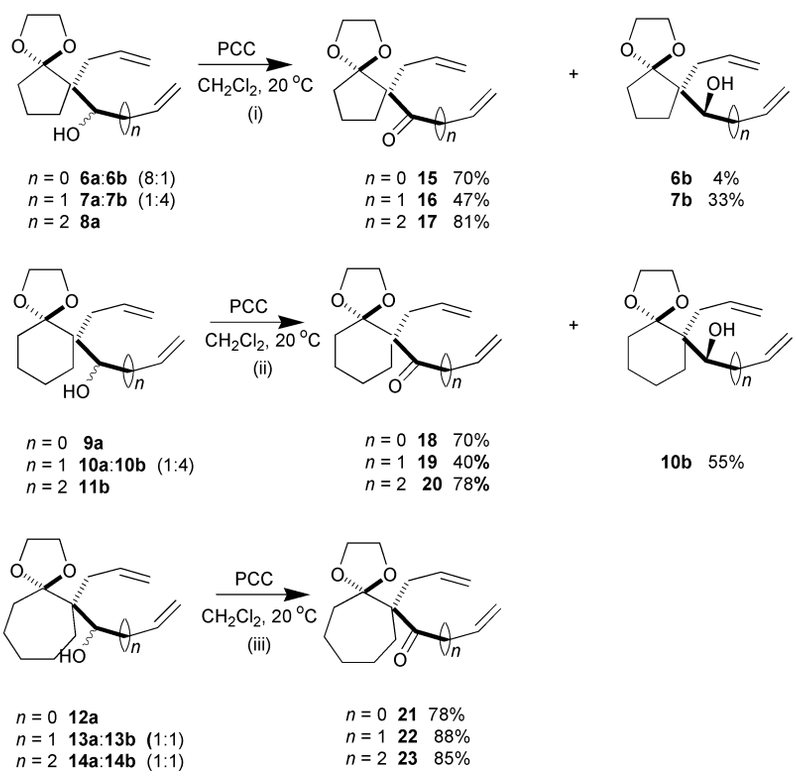
Scheme 1

The stereochemistry of the adducts formed from the Grignard reagents and the carbonyl group was strongly affected by the ring size of the substrates **5** and by the nature of the Grignard reagent (Scheme 2). With the cyclopentane derivative **5a** and vinylmagnesium chloride, rapid adduct formation at 0 °C gave the alcohol epimers **6a** and **6b** in the ratio 8 : 1, whereas the isomer ratios with the larger allyl bromide and butenyl bromide Grignard reagents were 1 : 4 and 1 : 2, respectively. The isomers in the pair **8a**–**8b** were separated by flash chromatography. The other isomer pairs were not separated. The stereochemical preferences were different in the cyclohexane **5b** substrate series. With the vinyl Grignard reagent only the **9a** isomer was isolated. With the cycloheptane substrates the same preferred stereochemical course gave the isomer **12a**. With the allyl

 DOI: 10.1039/b101462p



Scheme 2 *Reagents and conditions*: (i) (a) $n = 0$, X = Cl, THF, 0 °C, 10 min; (b) $n = 1$, X = Br, Et_2O, 0 °C, 2 h; (c) $n = 2$, X = Br, THF, 0 °C, 6 h.



Scheme 3 *Reaction conditions*: (i) **15** (2.5 h), **16** (3 h), **17** (9 h); (ii) **18** (6 h), **19** (4 h), **20** (10 h); (iii) **21** (5 h), **22** (7 h), **23** (9 h).

Grignard reagent formation of the isomer pair **10a**–**10b** corresponds to the finding in the five-membered ring series **7a**–**7b** (1 : 4). From the cycloheptane substrate **5c**, the ratio was 1 : 1 in the epimer pair **13a**–**13b**. With the butenyl Grignard reagent only the alcohol isomer **11b** was isolated from the cyclohexane substrate **5b**. On the other hand, the cycloheptane isomer gave the alcohol epimers **14a**–**14b** in the ratio 1 : 1. The favoured stereochemical course is likely to result from the conformational preferences of the substrates and the accessibility of the carbonyl group in such conformers. In addition, there will be interactions with the ether oxygen in the acetal function. But the great variation in product formation within each ring size also points to steric interactions with the organic moiety in the Grignard reagent.

The alcohols from the Grignard reactions were oxidized by PCC at ambient temperature (Scheme 3). In the cycloheptane series, the isomer **12a** and the epimer pairs **13a**–**13b** and **14a**–**14b** were all oxidized to the corresponding ketones **21**–**23** in high yields. In the cyclohexane series, the isomers **9a** and **11b** were converted to the ketones **18** and **20**, respectively,

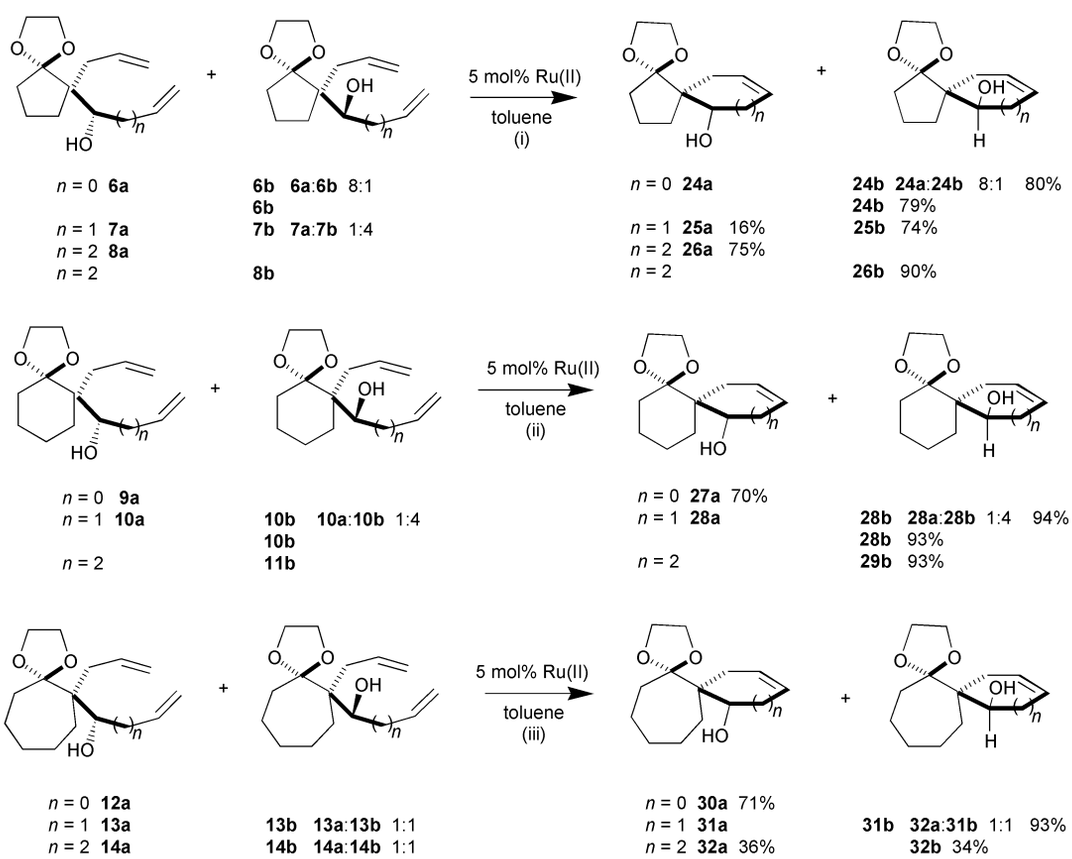
whereas oxidation of the epimer pair **10a**–**10b** resulted in selective oxidation of only the **10a** isomer. The major part of the other alcohol isomer **10b** was recovered. Similar results were seen in the cyclopentane series in that the isomer pairs **6a**–**6b** and **7a**–**7b** reacted by selective oxidation of the **6a** and **7a** isomers, respectively, whereas the alcohol epimers **6b** and **7b** were slowly oxidized and **7b** was largely recovered from the product mixture after the reaction. In accordance with these findings the alcohol isomer **8a** was converted to the corresponding ketone **17** in high yield. In the suggested conformational illustrations in Scheme 2, the hydroxy group can be regarded as having a *cis* or a *trans* relationship to the acetal function. The structures **6a**–**14a**, in this respect, have a *trans* relationship and structures **6b**–**14b** a *cis* relationship. The relative structure assignments correspond to the relative configurations in the hydroxylated spiranes **24**–**32** in Scheme 4. In the oxidations it is the hydroxy group with the *cis* relationship to the acetal group which is the more difficult to oxidize (Scheme 3). ^{1}H NMR spectra show strong H-bonding to the acetal oxygen which, when taken together with steric interactions, can be used to rationalize the relative rates of the isomer reactions. High selectivity in the oxidations can be achieved, but with longer reaction times or more vigorous reaction conditions both isomers are oxidized to the ketone. Some simple oxidation experiments with the hydroxylated spiranes **24**–**32** are shown in Scheme 6 (*vide infra*).

The RCM reactions of the hydroxy series **6**–**14** were run in toluene solution at slightly elevated temperatures (Scheme 4) using 5 mol% of the ruthenium(II)-catalyst. The catalyst was added in two portions, one half at a time, to maintain an active concentration of the catalyst throughout the reaction. All substrates, irrespective of the relative configuration at the alcoholic carbon, gave high yields of the corresponding spiranes **24**–**32**, *i.e.* the alcohol epimer ratios were the same in the substrates and the products. The progress of the reaction was monitored by GLC or TLC.

The five- and seven-membered ring structures **24**, **26**, **27**, **29**, **30** and **32** were formed at 60–75 °C in 68–93% yield. The reaction time was 4 h. The six-membered ring structures **25**, **28** and **31** were formed at 30 °C over the course of 30 min in 90–94% yield. The easier formation of the six-membered ring compared with the five- and seven-membered rings in RCM reactions with the Ru(II)-catalyst was also observed for the reaction of ketones in Scheme 5.

In Scheme 5 RCM reactions of the corresponding ketones **15**–**23** are shown. Toluene was used as solvent with 5 mol% Ru(II)-catalyst. Invariably the RCM reaction gave high yields of the ketospiranes **33**–**41** from the acyclic ketones **15**–**23**. The reaction conditions, the temperature and the reaction time, showed that six-membered ring formation took place more easily than the formation of other ring sizes.

Besides X-ray analyses (*vide infra*), ^{1}H NMR spectroscopy was used in the assignment of structures to the epimeric alcohols. In the ^{1}H NMR spectra the proton signal from the hydroxy group in the *trans* configuration in the spiroannulated cyclopentyl derivative **24a** was located at 3.20 ppm, in the *cis* configuration in **24b** at 4.74 ppm. In the corresponding cyclohexane series the proton in the *trans*-structure **27a** is located at 3.10 ppm and in the cycloheptane derivative **30a** at 3.09 ppm. The corresponding values in the spiroannulated cyclohexene derivatives for the *trans* series were for **25a** at 3.39 ppm, **28a** at 4.01 ppm, and for **31a** 3.64 ppm, and in the *cis* series **25b**, **28b**, **31b** the figures were 3.96, 4.20, and 4.54 ppm, respectively. Similarly the shift values in the spiroannulated cycloheptane derivatives assigned *trans* configurations **26a**, **32a** were 3.75 and 3.80 ppm and in the *cis* series **26b**, **29b**, and **32b**, the values were 4.17, 4.32 and 4.32 ppm, respectively. The patterns in either series, when taken together with the X-ray data, allow assignment of relative configurations for all the spirane alcohols. Since the RCM reaction does not involve the epimeric alcohol, carbon assignment of the relative structure to the

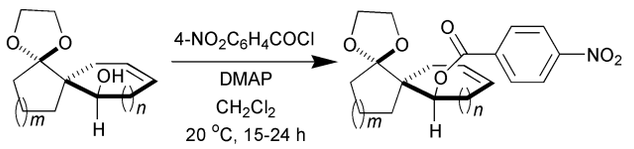


Scheme 4 *Reaction conditions*: (i) **24** (70 °C, 4 h), **25** (30 °C, 0.5 h), **26a** (60 °C, 4 h), **26b** (60 °C, 4 h); (ii) **27a** (60 °C, 4 h), **28** (30 °C, 0.5 h), **29b** (80 °C, 4 h); (iii) **30a** (70 °C, 2 h), **31** (30 °C, 0.5 h), **32** (60 °C, 2 h).

acyclic alcohols **6**–**14** follows from the structures of the spirane alcohols.

Hydrogen bonding and its influence on the oxidation rates of epimeric alcohol pairs is shown in Scheme 6. The relative rates of oxidation were monitored by ^{1}H NMR or by TLC. The results showed clearly that the *cis* structures were oxidized significantly slower than the *trans* structures.

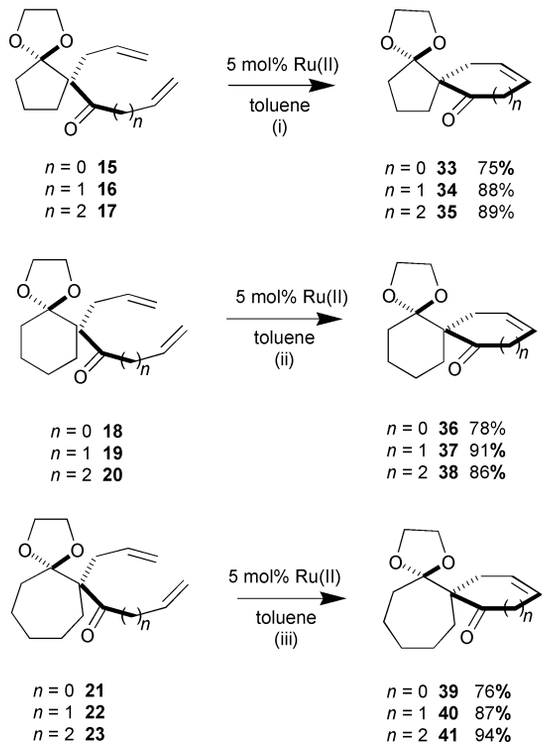
The relative stereochemistry in the spiroannulated six-membered ring systems **25** and **28** was established by a single crystal X-ray analysis of the crystalline *p*-nitrobenzoates **42** and **44** (Scheme 7, Figs. 1 and 2). The alcohols were originally



25b *m* = 1, *n* = 1 — **42** 89%
26b *m* = 1, *n* = 2 — **43** 75%
28b *m* = 2, *n* = 1 — **44** 84%
29b *m* = 2, *n* = 2 — **45** 75%

Scheme 7

obtained in a non-crystalline state and were therefore converted to the respective crystalline *p*-nitrobenzoate esters by simple acylation. The X-ray data are consistent with the products assigned the *cis* configurations **25b** and **28b**. In the same manner, for X-ray analysis the spiroannulated non-crystalline cycloheptane alcohols **26b** and **29b** were converted into the crystalline *p*-nitrobenzoates **43** and **45** (Figs. 3 and 4). These assignments in the spirane alcohols also confirm the relative configurational assignments in the coresponding acyclic alcohols before the ring-closing reactions as shown in Scheme 4.



n = 0 **15** — *n* = 0 **33** 75%
n = 1 **16** — *n* = 1 **34** 88%
n = 2 **17** — *n* = 2 **35** 89%

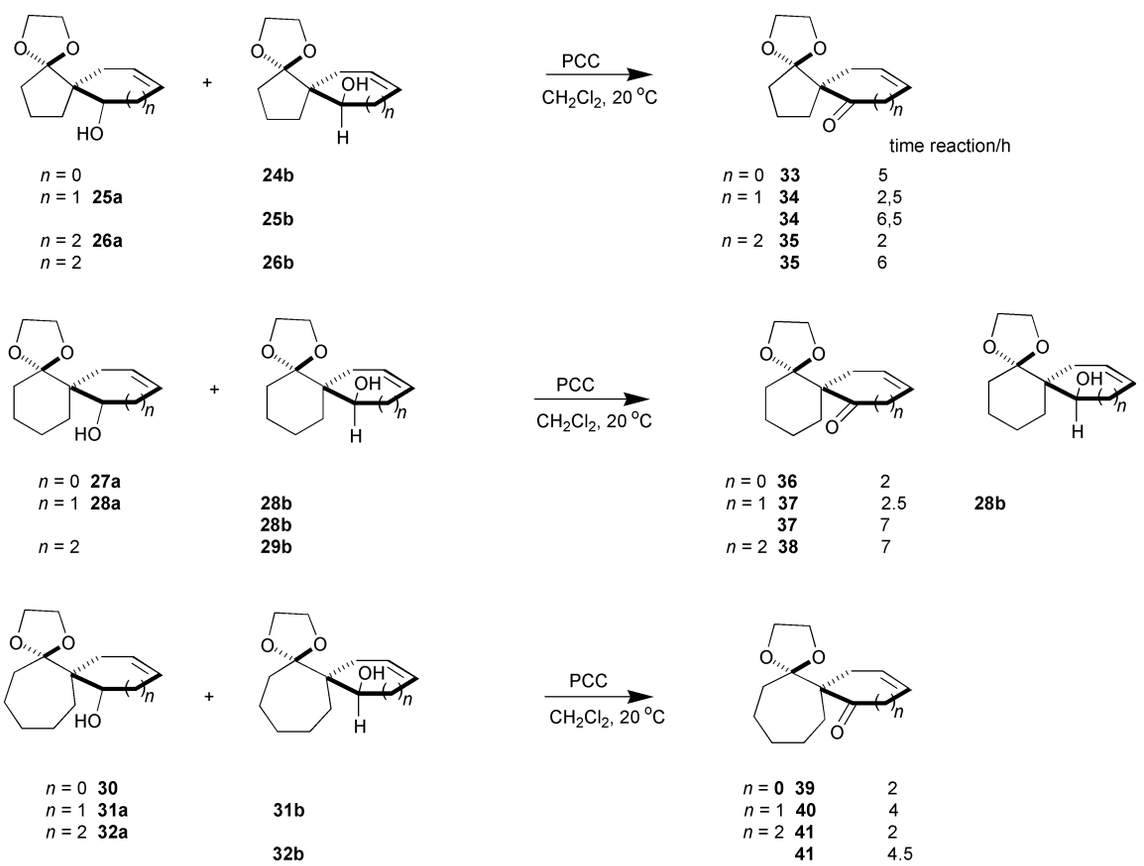
n = 0 **18** — *n* = 0 **36** 78%
n = 1 **19** — *n* = 1 **37** 91%
n = 2 **20** — *n* = 2 **38** 86%

n = 0 **21** — *n* = 0 **39** 76%
n = 1 **22** — *n* = 1 **40** 87%
n = 2 **23** — *n* = 2 **41** 94%

Scheme 5 *Reaction conditions*: (i) **33** (70 °C, 4 h), **34** (30 °C, 0.5 h), **35** (60 °C, 4 h); (ii) **36** (75 °C, 2 h), **37** (30 °C, 0.5 h), **38** (60 °C, 4 h); (iii) **39** (75 °C, 4 h), **40** (30 °C, 0.5 h), **41** (75 °C, 2 h).

Experimental

The ^{1}H NMR spectra were recorded at 200 or 300 MHz and the ^{13}C NMR spectra at 50 or 75 MHz unless otherwise specified. *J* values are given in Hz. The mass spectra were recorded at 70 eV under electron impact conditions (EI) and are presented



n = 0 — **24b**
n = 1 **25a** — **25b**
n = 2 **26a** — **26b**

n = 0 **33** 5
n = 1 **34** 2,5
34 6,5
n = 2 **35** 2
35 6

n = 0 **27a** — **28b**
n = 1 **28a** — **28b**
n = 2 — **29b**

n = 0 **36** 2
n = 1 **37** 2.5
37 7
n = 2 **38** 7

28b

n = 0 **30** — **31b**
n = 1 **31a** — **32b**
n = 2 **32a**

n = 0 **39** 2
n = 1 **40** 4
n = 2 **41** 2
41 4.5

Scheme 6 **24**–**32** (0.023 mmol) in 1 ml CH_2Cl_2 was added rapidly at ambient temperature to a suspension of pyridinium chlorochromate (0.035 mmol) in 1 ml CH_2Cl_2. The relative rates of oxidation were monitored by TLC.

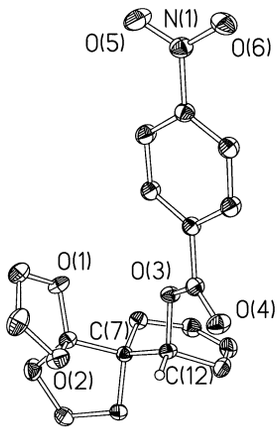


Fig. 1 The ORTEP plot of compound **42**. Ellipsoids are shown at 50% probability. For clarity only the hydrogen at C(12) is shown.

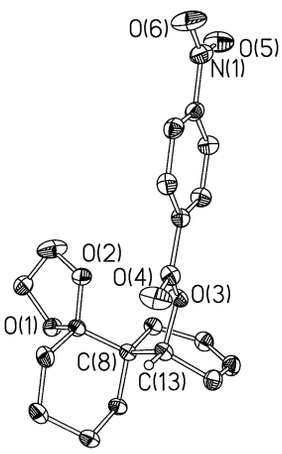


Fig. 2 The ORTEP plot of compound **43**. Ellipsoids are shown at 50% probability. For clarity only the hydrogen at C(13) is shown.

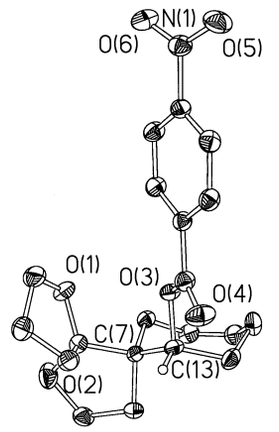


Fig. 3 The ORTEP plot of compound **44**. Ellipsoids are shown at 50% probability. For clarity only the hydrogen at C(13) is shown.

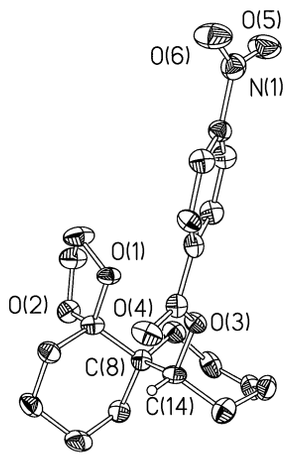


Fig. 4 The ORTEP plot of compound **45**. Ellipsoids are shown at 50% probability. For clarity only the hydrogen at C(14) is shown.

as *m*/*z* (% rel. int.). Dry THF was distilled over sodium and benzophenone. Dry dichloromethane was distilled from calcium hydride under argon. Diethyl ether was dried over sodium. Toluene was distilled from calcium hydride and degassed by bubbling argon through. Bis(tricyclohexylphosphine)(benzylidene)ruthenium(II) dichloride was purchased from Strem Chemicals Inc.

X-Ray crystallographic analysis for compounds 42, 43, 44 and 45 †

X-Ray data were collected on a Siemens SMART CCD diffractometer[22] using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Data collection method: ω-scan, range 0.6°, crystal to detector distance 5 cm. Data reduction and cell determination were carried out with the SAINT and XPREP programs.[22] Absorption corrections were applied by the use of the SADABS program.[23] The structures were determined and refined using the SHELXTL program package.[24] The non-hydrogen atoms were refined with anisotropic thermal parameters; hydrogen positions were found from difference Fourier maps and refined with isotropic thermal parameters.

The crystals of compound **45** were in the form of very thin plates (thickness 0.01 mm and less). The data were thus of poor quality but sufficed for the determination of the relative configuration. Crystal data for $C_{19}H_{21}NO_6$ (**42**): M = 359.37, monoclinic, $P2_1/c$, a = 18.811(1), b = 6.993(1), c = 13.717(1) Å, β = 109.12(1)°, V = 1704.7(2) Å^3, Z = 4, D_x = 1.400 Mg m^{-3}, μ = 0.105 mm^{-1}, T = 150(2) K, 31408 reflections were measured in the 2θ range 6.9–66.3°, R_{int} = 0.039. 332 Parameters were refined against 6482F^2, $R1$ = 0.048, R_w2 = 0.127 for $I_o > 2\sigma(I_o)$ and $R1$ = 0.064, R_w2 = 0.143 for all data.

Crystal data for $C_{20}H_{23}NO_6$ (**43**): M = 373.39, monoclinic, $P2_1/c$, a = 19.205(2), b = 6.591(1), c = 15.014(2) Å, β = 109.51(1)°, V = 1791.3(3) Å^3, Z = 4, D_x = 1.385 Mg m^{-3}, μ = 0.102 mm^{-1}, T = 150(2) K, 26933 reflections were measured in the 2θ range 4.5–56.6°, R_{int} = 0.057. 336 Parameters were refined against 4444F^2, $R1$ = 0.044, R_w2 = 0.098 for $I_o > 2\sigma(I_o)$ and $R1$ = 0.069, R_w2 = 0.108 for all data.

Crystal data for $C_{20}H_{23}NO_6$ (**44**): M = 373.39, monoclinic, $P2_1/n$, a = 6.856(1), b = 12.836(1), c = 20.535(2) Å, β = 96.06(1)°, V = 1797.1(3) Å^3, Z = 4, D_x = 1.380 Mg m^{-3}, μ = 0.102 mm^{-1}, T = 150(2) K, 38813 reflections were measured in the 2θ range 3.7–71.7°, R_{int} = 0.022. 336 Parameters were refined against 8006F^2, $R1$ = 0.047, R_w2 = 0.124 for $I_o > 2\sigma(I_o)$ and $R1$ = 0.064, R_w2 = 0.136 for all data.

Crystal data for $C_{21}H_{25}NO_6$ (**45**): M = 387.42, triclinic, $P\bar{1}$, a = 8.321(1), b = 12.541(1), c = 18.952(2) Å, α = 99.02(1), β = 98.99(1), γ = 102.45(1)°, V = 1869.8(3) Å^3, Z = 4, D_x = 1.376 Mg m^{-3}, μ = 0.101 mm^{-1}, T = 150(2) K, 14769 reflections were measured in the 2θ range 3.4–46.5°, R_{int} = 0.089. 706 Parameters were refined against 5348F^2, $R1$ = 0.098, R_w2 = 0.287 for $I_o > 2\sigma(I_o)$ and $R1$ = 0.130, R_w2 = 0.310 for all data.

Ethyl 2-oxocycloheptane-1-carboxylate 1c

Compound **1c** was synthesized as described previously.[25]

Ethyl 1-allyl-2-oxocyclopentane-1-carboxylate 2a

A solution of ethyl 2-oxocyclopentane-1-carboxylate (5.5 g, 35.25 mmol) in THF (60 ml) was added dropwise to a solution of sodium hydride (1.69 g, 38.7 mmol, 55–65% moistened with

† CCDC reference numbers 161066–161069. See http://www.rsc.org/suppdata/p1/b1/b101462p/ for crystallographic files in .cif or other electronic format.

oil) in THF (60 ml). The mixture was stirred at ambient temperature for 1 h before a solution of allyl bromide (4.69 g, 38.77 mmol) in THF (60 ml) was added dropwise over 30 min. The mixture was left at ambient temperature overnight, the solvent distilled off, the residual material redissolved in ethyl acetate (250 ml) and the solution washed with brine (2 × 50 ml), dried ($MgSO_4$) and the product isolated after flash chromatography using hexane–EtOAc 10 : 1, R_f 0.30. The product was a colourless oil (5.80 g, 85%). HRMS: M 196.1092. $C_{11}H_{16}O_3$ requires 196.1099. ν_{max}(film)/cm^{-1} 3050, 2960, 2890 (C–H), 1740 (C=O, ketone), 1710 (CO, ester), 1630 (C=C); δ_H($CDCl_3$) 1.14–1.19 (3 H, t, *J* 7, CH_3CH$_2$O), 1.80–1.95 (3 H, m, CH$_2$, 1 H from CH$_2$), 2.09–2.40 (4 H, m, 1 H from CH_2CH=CH$_2$, 1 H from CH$_2$, CH$_2$), 2.54–2.59 (1 H, m, CH_2CH=CH$_2$), 4.03–4.12 (2 H, q, *J* 7, CH$_3$CH_2O), 4.99–5.05 (2 H, m, CH$_2$CH=CH_2), 5.54–5.68 (1 H, m, CH$_2$C*H*=CH$_2$); δ_C($CDCl_3$) 13.9 (*C*H$_3$CH$_2$O), 19.3 (CH$_2$), 31.9 (CH$_2$), 37.6 (CH$_2$), 37.9 (CH$_2$), 59.7 (1-C), 61.3 (CH$_3$*C*H$_2$O), 118.8 (CH=*C*H$_2$), 132.9 (*C*H=CH$_2$), 170.7 (*C*O$_2$Et), 214.3 (2-C=O); *m*/*z* (EI) 109 (M$^+$, 3%), 168 (35), 151 (16), 123 (70), 113 (51), 105 (32), 95 (100), 80 (53).

Ethyl 1-allyl-2-oxocyclohexane-1-carboxylate 2b

Compound **2b** was obtained following the procedure described above as a colourless oil (89%), R_f 0.37. HRMS: M 210.1248. $C_{12}H_{18}O_3$ requires 210.1255. ν_{max}(film)/cm^{-1} 2910, 2840 (C–H), 1727 (C=O, ketone), 1708 (CO, ester), 1625 (C=C); δ_H($CDCl_3$) 1.15–1.19 (3 H, t, *J* 7, CH_3CH$_2$O), 1.39–1.93 (5 H, m, 3 × CH$_2$), 2.21–2.29 (1 H, dd, *J* 14, 8, CH_2CH=CH$_2$), 2.34–238 (3 H, m, 1 H from CH$_2$, CH$_2$), 2.42–2.56 (1 H, dd, *J* 14, 7, CH_2CH=CH$_2$), 4.07–4.14 (2 H, q, *J* 7, CH$_3$CH_2O), 4.92–4.98 (2 H, m, CH$_2$CH=CH_2), 5.59–5.71 (1 H, m, CH$_2$C*H*=CH$_2$); δ_C($CDCl_3$) 14.0 (*C*H$_3$CH$_2$O), 22.3 (CH$_2$), 27.4 (CH$_2$), 35.6 (CH$_2$), 39.1 (CH$_2$), 40.9 (CH$_2$), 60.7 (1-C), 61.0 (CH$_3$*C*H$_2$O), 118.0 (CH=*C*H$_2$), 133.2 (*C*H=CH$_2$), 171.3 (*C*O$_2$Et), 207.3 (2-C=O); *m*/*z* (EI) 210 (M$^+$, 49%), 192 (17), 165 (35), 137 (100), 119 (41), 67 (37).

Ethyl 1-allyl-2-oxocycloheptane-1-carboxylate 2c

Compound **2c** was obtained following the procedure described above as a colourless oil (83%), R_f 0.28. HRMS: M 224.1404. $C_{13}H_{20}O_3$ requires 224.1412. ν_{max}(film)/cm^{-1} 3045, 2920, 2860 (C–H), 1740 (C=O, ketone), 1700 (CO, ester); 1638 (C=C); δ_H($CDCl_3$) 1.15–1.23 (3 H, t, *J* 7, CH_3CH$_2$O), 1.28–1.80 (7 H, m, 3 × CH$_2$, 1 H from CH$_2$), 1.96–2.11 (1 H, m, from CH$_2$), 2.24–2.36 (1 H, dd, *J* 14, 7, CH_2CH=CH$_2$), 2.40–2.43 (1 H, m, from CH$_2$), 2.57–2.61 (1 H, m, from CH$_2$), 2.65–2.72 (1 H, dd, *J* 14, 7, CH_2CH=CH$_2$), 4.06–4.17 (2 H, q, *J* 7, CH$_3$CH_2O), 4.95–5.06 (2 H, m, CH$_2$CH=CH_2), 5.57–5.74 (1 H, m, CH$_2$C*H*=CH$_2$); δ_C($CDCl_3$) 14.0 (*C*H$_3$CH$_2$O), 24.5 (CH$_2$), 25.4 (CH$_2$), 29.8 (CH$_2$), 31.9 (CH$_2$), 39.5 (CH$_2$), 42.0 (CH$_2$), 61.1 (CH$_3$*C*H$_2$O), 62.7 (1-C), 118.5 (CH=*C*H$_2$), 133.5 (*C*H=CH$_2$), 171.9 (*C*O$_2$Et), 209.0 (2-C=O); *m*/*z* (EI) 224 (M$^+$, 51%), 195 (5), 151 (89), 150 (100), 137 (37), 81 (69), 67 (90).

Ethyl 1-allyl-2,2-ethylenedioxycyclopentane-1-carboxylate 3a

A solution of the cyclopentanone **2a** (6.0 g, 30.6 mmol), ethylene glycol (5.7 ml), and toluene-*p*-sulfonic acid (0.3 g) in benzene (200 ml) was heated under reflux for 11 h using a Dean–Stark trap. Most of the solvent was then distilled off, the residual material poured into 10% NH_4OH (50 ml) and the mixture extracted with diethyl ether (3 × 50 ml). The combined ethereal extracts were dried ($MgSO_4$), the ether distilled off and the residual material subjected to flash chromatography using hexane–EtOAc 8 : 1, R_f 0.29. The product (11.5 g, 86%) was a colourless oil. HRMS: M 240.1363. $C_{13}H_{20}O_4$ requires 240.1361. ν_{max}(film)/cm^{-1} 3050, 2965, 2875 (C–H), 1720 (CO$_2$Et), 1630 (C=C); δ_H($CDCl_3$) 1.18–1.23 (3 H, t, *J* 7, CH_3-CH$_2$O), 1.52–1.81 (5 H, m, 4 × CH$_2$, 1H from CH$_2$), 2.02–2.09 (1 H, dd, *J* 14, 8, CH_2CH=CH$_2$), 2.28–2.38 (1 H, m, from CH$_2$), 2.74–2.81 (1 H, dd, *J* 14, 7, CH_2CH=CH$_2$), 3.76–3.97 (4 H, m, OCH$_2$CH$_2$O), 4.06–4.13 (2 H, q, *J* 7, CH$_3$CH_2O), 4.96–5.06 (2 H, m, CH$_2$CH=CH_2), 5.51–5.63 (1 H, m, CH$_2$C*H*=CH$_2$); δ_C($CDCl_3$) 14.2 (*C*H$_3$CH$_2$O), 19.2 (CH$_2$), 30.6 (CH$_2$), 36.0 (CH$_2$), 37.9 (CH$_2$), 58.2 (1-C), 60.3 (CH$_3$*C*H$_2$O), 64.6 and 65.4 (OCH$_2$CH$_2$O), 117.7 (CH=*C*H$_2$), 118.7 (2-C), 134.2 (*C*H=CH$_2$), 173.4 (*C*O$_2$Et); *m*/*z* (EI) 240 (M$^+$, 4%), 195 (32), 167 (56), 99 (100), 86 (82), 79 (259), 67 (32), 55 (51).

Ethyl 1-allyl-2,2-ethylenedioxycyclohexane-1-carboxylate 3b

Compound **3b** was obtained from the ketone **2b** following the procedure described above as a colourless oil (92%), R_f 0.28. HRMS: M 245.1514. $C_{14}H_{22}O_4$ requires 245.1518. ν_{max}(film)/cm^{-1} 2910, 2860 (C–H), 1720 (CO$_2$Et); δ_H($CDCl_3$) 1.15–1.22 (3 H, t, *J* 7, CH_3CH$_2$O), 1.35–1.94 (8 H, m, 4 × CH$_2$), 2.21–2.32 (1 H, dd, *J* 14, 8, CH_2CH=CH$_2$), 2.68–2.80 (1 H, dd, *J* 14, 6.5, CH_2CH=CH$_2$), 3.80–3.89 (4 H, m, OCH$_2$CH$_2$O), 4.02–4.13 (2 H, q, *J* 7, CH$_3$CH_2O), 4.90–5.02 (2 H, m, CH$_2$CH=CH_2), 5.48–5.70 (1 H, m, CH$_2$C*H*=CH$_2$); δ_C($CDCl_3$) 14.1 (*C*H$_3$CH$_2$O), 20.6 (CH$_2$), 23.0 (CH$_2$), 29.9 (CH$_2$), 32.0 (CH$_2$), 35.9 (CH$_2$), 54.3 (1-C), 60.2 (CH$_3$*C*H$_2$O), 64.5 and 64.7 (OCH$_2$CH$_2$O), 110.6 (2-C), 117.4 (CH=*C*H$_2$), 134.0 (*C*H=CH$_2$), 173.4 (*C*O$_2$Et); *m*/*z* (EI) 254 (M$^+$, 12%), 213 (7), 181 (17), 125 (11), 99 (100), 86 (28), 55 (12).

Ethyl 1-allyl-2,2-ethylenedioxycycloheptane-1-carboxylate 3c

Compound **3c** was obtained from the ketone **2c** following the procedure described above as a colourless oil (89%), R_f 0.28. HRMS: M 268.1670. $C_{15}H_{24}O_4$ requires 245.1674. ν_{max}(film)/cm^{-1} 3030, 2910, 2880 (C–H), 1720 (CO$_2$Et), 1637 (C=C); δ_H($CDCl_3$) 1.17–1.25 (3 H, t, *J* 7, CH_3CH$_2$O), 1.38–1.78 (8 H, m, 4 × CH$_2$), 1.76–1.84 (1 H, m, from CH$_2$), 1.98–2.12 (1 H, m, from CH$_2$), 2.16–2.27 (1 H, dd, *J* 14, 6, CH_2CH=CH$_2$), 2.76–2.88 (1 H, dd, *J* 14, 7, CH_2CH=CH$_2$), 3.81–3.93 (4 H, m, OCH$_2$CH$_2$O), 4.05–4.18 (2 H, q, *J* 7, CH$_3$CH_2O), 4.92–5.05 (2 H, m, CH$_2$CH=CH_2), 5.56–5.73 (1 H, m, CH$_2$C*H*=CH$_2$); δ_C($CDCl_3$) 14.2 (*C*H$_3$CH$_2$O), 22.2 (CH$_2$), 23.0 (CH$_2$), 28.9 (CH$_2$), 32.5 (CH$_2$), 34.5 (CH$_2$), 38.9 (CH$_2$), 57.5 (1-C), 60.1 (CH$_3$*C*H$_2$O), 63.9 and 64.6 (OCH$_2$CH$_2$O), 112.9 (2-C), 117.3 (CH=*C*H$_2$), 134.9 (*C*H=CH$_2$), 173.9 (*C*O$_2$Et); *m*/*z* (EI) 268 (M$^+$, 14%), 227 (39), 195 (37), 171 (14), 99 (100), 86 (11), 55 (34).

1-Allyl-2,2-ethylenedioxycyclopentane-1-methanol 4a

LAH (0.646 g, 17 mmol) was added in five portions to a solution of the carboxylic ester **3a** (2.4 g, 10 mmol) in dry THF (40 ml) at 0 °C and the mixture stirred at this temperature for 0.5 h and at ambient temperature for 6 h. Excess LAH was destroyed with saturated NH_4Cl, the mixture extracted with ethyl acetate (3 × 25 ml), the combined organic extracts dried ($MgSO_4$) and evaporated and the residual material subjected to flash chromatography using hexane–EtOAc 5 : 1, R_f 0.15. The product (3.71 g, 90%) was a colourless oil. HRMS: M 198.1254. $C_{11}H_{18}O_3$ requires 198.1255. ν_{max}(film)/cm^{-1} 3506 (OH), 3020, 2940, 2860 (C–H), 1625 (C=C); δ_H($CDCl_3$) 1.47–1.61 (4 H, m, 2 × CH$_2$), 1.67–1.85 (2 H, m, CH$_2$), 2.04–2.11 (1 H, dd, *J* 14, 7, CH_2CH=CH$_2$), 2.24–2.31 (1 H, dd, *J* 14, 7, CH_2CH=CH$_2$), 2.81–2.86 (1 H, dd, *J* 8, 5, CH$_2$O*H*), 3.36–3.43 (1 H, dd, *J* 12, 8, CH_2OH), 3.53–3.58 (1 H, dd, *J* 12, 8, CH_2OH), 3.82–3.93 (4 H, m, OCH$_2$CH$_2$O), 4.96–5.07 (2 H, m, CH$_2$CH=CH_2), 5.70–5.84 (1 H, m, CH$_2$C*H*=CH$_2$); δ_C($CDCl_3$) 18.8 (CH$_2$), 30.2 (CH$_2$), 34.4 (CH$_2$), 35.3 (CH$_2$), 49.6 (1-C), 64.2 and 64.5 (OCH$_2$CH$_2$O), 65.6 (CH$_2$OH), 117.2 (CH=*C*H$_2$), 120.2 (2-C), 135.3 (*C*H=CH$_2$); *m*/*z* (EI) 198 (M$^+$, 2%), 167 (20), 157 (7), 139 (5), 125 (8), 113 (6), 99 (100), 86 (23), 79 (8).

1-Allyl-2,2-ethylenedioxycyclohexane-1-methanol 4b

Compound **4b** was obtained from the carboxylic ester **3b** following the procedure described above as a colourless oil (86%), R_f 0.22. HRMS: M 212.1403. $C_{12}H_{20}O_3$ requires 212.1412. ν_{max}(film)/cm^{-1} 3500 (OH), 2910, 2880 (C–H), 1630 (C=C); δ_H($CDCl_3$) 1.31–1.56 (8 H, m, 4 × CH_2), 2.07–2.14 (1 H, dd, *J* 14, 8, C*H*$_2$CH=CH_2), 2.29–2.36 (1 H, dd, *J* 14, 8, C*H*$_2$CH=CH_2), 2.80–2.84 (1 H, dd, *J* 7, 4, CH_2O*H*), 3.27–3.43 (1 H, dd, *J* 12, 7, C*H*$_2$OH), 3.66–3.71 (1 H, dd, *J* 12, 3, C*H*$_2$OH), 3.71–3.90 (4 H, m, OCH_2CH_2O), 4.94–5.02 (2 H, m, CH_2CH=C*H*$_2$), 5.70–5.79 (1 H, m, CH_2C*H*=CH_2); δ_C($CDCl_3$) 20.0 (CH_2), 23.1 (CH_2), 29.4 (CH_2), 30.0 (CH_2), 34.1 (CH_2), 44.3 (1-C), 63.9 and 64.3 (OCH_2CH_2O), 64.9 (CHOH), 113.4 (2-C), 117.4 (CH=*C*H$_2$), 134.3 (*C*H=CH_2); *m*/*z* (EI) 212 (M^+, 8%), 181 (12), 171 (9), 125 (14), 99 (100), 86 (29), 55 (19).

1-Allyl-2,2-ethylenedioxycycloheptane-1-methanol 4c

Compound **4c** was obtained from the carboxylic ester **3c** following the procedure described above as a colourless oil (89%), R_f 0.22. HRMS: M 226.1569. $C_{13}H_{22}O_3$ requires 226.1570. ν_{max}(film)/cm^{-1} 3520 (OH), 3060, 2920, 2865 (C–H), 1632 (C=C); δ_H($CDCl_3$) 1.39–1.79 (10 H, m, 5 × CH_2), 2.12–2.19 (1 H, dd, *J* 14, 8, C*H*$_2$CH=CH_2), 2.26–2.33 (1 H, dd, *J* 14, 6, C*H*$_2$CH=CH_2), 3.16–3.20 (1 H, dd, *J* 9, 3, CH_2O*H*), 3.23–3.30 (1 H, dd, *J* 11, 9, C*H*$_2$OH), 3.59–3.64 (1 H, dd, *J* 11, 3, C*H*$_2$OH), 3.86–3.96 (4 H, m, OCH_2CH_2O), 5.01–5.08 (2 H, m, CH_2CH=C*H*$_2$), 5.79–5.92 (1 H, m, CH_2C*H*=CH_2); δ_C($CDCl_3$) 21.3 (CH_2), 21.4 (CH_2), 28.5 (CH_2), 30.8 (CH_2), 32.4 (CH_2), 35.2 (CH_2), 47.5 (1-C), 63.7 and 63.9 (OCH_2CH_2O), 66.6 (CHOH), 116.2 (2-C), 118.2 (CH=*C*H$_2$), 135.5 (*C*H=CH_2); *m*/*z* (EI) 226 (M^+, 8%), 209 (7), 195 (43), 185 (60), 167 (11), 129 (9), 99 (100), 86 (10), 53 (5).

1-Allyl-2,2-ethylenedioxycyclopentane-1-carbaldehyde 5a

A solution of the alcohol **4a** (1.26 g, 6.3 mmol) in dichloromethane (6 ml) was added rapidly to a suspension of pyridinium chlorochromate (2.04 g, 9.5 mmol) in dichloromethane (10 ml) at ambient temperature. The reaction mixture became a clear solution before a precipitate appeared. TLC monitoring showed that the reaction had gone to completion after 6 h. The black reaction mixture was diluted with 5 volumes of anhydrous diethyl ether, the solvent decanted, the black solid washed twice with ether, the combined ether solutions filtered through Florisil, the filtrate evaporated and the residual material subjected to flash chromatography using hexane–EtOAc 7 : 1, R_f 0.29. The product was a colourless oil (1.02 g, 81%). HRMS: M 196.1098. $C_{11}H_{16}O_3$ requires 196.1099. ν_{max}(film)/cm^{-1} 3020, 2940, 2860 (C–H), 1720 (CH=O), 1625 (C=C); δ_H($CDCl_3$) 1.53–1.79 (5 H, m, 4 × CH_2, 1 H from CH_2), 2.13–2.23 (2 H, m, 1 H from CH_2, 1 H from C*H*$_2$CH=CH_2), 2.58–2.65 (1 H, dd, *J* 14, 7, C*H*$_2$CH=CH_2), 3.80–3.95 (4 H, m, OCH_2CH_2O), 4.95–5.04 (2 H, m, CH_2CH=C*H*$_2$), 5.47–5.60 (1 H, m, CH_2C*H*=CH_2), 9.52 (1 H, s, CH=O); δ_C($CDCl_3$) 19.3 (CH_2), 27.9 (CH_2), 34.7 (CH_2), 35.5 (CH_2), 60.5 (1-C), 64.7 and 64.9 (OCH_2CH_2O), 117.9 (CH=*C*H$_2$), 118.9 (2-C), 133.6 (*C*H=CH_2), 203.6 (CH=O); *m*/*z* (EI) 196 (M^+, 2%), 167 (10), 139 (42), 125 (22), 108 (16), 99 (100), 86 (30), 79 (27), 67 (55), 55 (81).

1-Allyl-2,2-ethylenedioxycyclohexane-1-carbaldehyde 5b

Compound **5b** was obtained from the alcohol **4b** following the procedure described above as a colourless oil (89%), R_f 0.47. HRMS: M 210.1263. $C_{12}H_{18}O_3$ requires 210.1255. ν_{max}(film)/cm^{-1} 2915, 2862 (C–H), 1715 (CH=O), 1637 (C=C); δ_H($CDCl_3$) 1.35–1.50 (6 H, m, 3 × CH_2), 1.59–1.87 (2 H, m, CH_2), 2.20–2.28 (1 H, dd, *J* 14, 6, C*H*$_2$CH=CH_2), 2.57–2.64 (1 H, dd, *J* 14, 8, C*H*$_2$CH=CH_2), 3.82–3.93 (4 H, m, OCH_2CH_2O), 4.92–4.98 (2 H, m, CH_2CH=C*H*$_2$), 5.42–5.48 (1 H, m, CH_2C*H*=CH_2), 9.62 (1 H, s, CH=O); δ_C($CDCl_3$) 20.3 (CH_2), 22.9 (CH_2), 27.2 (CH_2), 32.4 (CH_2), 33.5 (CH_2), 56.7 (1-C), 64.5 and 64.7 (OCH_2CH_2O), 110.5 (2-C), 118.0 (CH=*C*H$_2$), 132.6 (*C*H=CH_2), 204.9 (CH=O); *m*/*z* (EI) 210 (M^+, 2%), 182 (24), 139 (25), 125 (16), 99 (100), 86 (53), 67 (15), 55 (22).

1-Allyl-2,2-ethylenedioxycycloheptane-1-carbaldehyde 5c

Compound **5c** was obtained from the alcohol **4c** following the procedure described above as a colourless oil (79%), R_f 0.34. HRMS: M 224.1411. $C_{13}H_{20}O_3$ requires 224.1412. ν_{max}(film)/cm^{-1} 3020, 2915, 2862 (C–H), 1715 (CH=O), 1663 (C=C); δ_H($CDCl_3$) 1.35–1.75 (9 H, m, 4 × CH_2, 1 H from CH_2), 1.92–1.97 (1 H, m, 1 H from CH_2), 2.28–2.35 (1 H, dd, *J* 14, 7, C*H*$_2$CH=CH_2), 2.61–2.68 (1 H, dd, *J* 14, 7, C*H*$_2$CH=CH_2), 3.85–3.92 (4 H, m, OCH_2CH_2O), 4.97–5.04 (2 H, m, CH_2-CH=C*H*$_2$), 5.50–5.64 (1 H, m, CH_2C*H*=CH_2), 9.57 (1 H, s, CH=O); δ_C($CDCl_3$) 21.5 (CH_2), 21.8 (CH_2), 28.1 (CH_2), 28.3 (CH_2), 33.8 (CH_2), 35.6 (CH_2), 59.0 (1-C), 64.0 and 64.3 (OCH_2CH_2O), 113.5 (2-C), 118.1 (CH=*C*H$_2$), 133.4 (*C*H=CH_2), 204.0 (CH=O); *m*/*z* (EI) 224 (M^+, 3%), 195 (43), 155 (23), 139 (42), 99 (100), 86 (11), 67 (10), 55 (14).

1-(1-Allyl-2,2-ethylenedioxycyclopentan-1-yl)prop-2-en-1-ol 6a and 6b

Vinylmagnesium chloride (3.54 ml, 6.02 mmol, 1.7 M in THF) was added dropwise to a solution of the carbaldehyde **5a** (0.84 g, 4.3 mmol) in THF (10 ml) under argon at 0 °C. The reaction was stopped after 10 min by the addition of saturated NH_4Cl solution. The aqueous layer was extracted with CH_2Cl_2 (3 × 30 ml), the combined organic layers dried ($MgSO_4$) and evaporated. The residual material was subjected to flash chromatography using hexane–EtOAc 7 : 1 as eluent, R_f 0.26. The product (**6a** and **6b** 8 : 1; 0.78 g, 81%) was a colourless oil. HRMS: M 224.1408. $C_{13}H_{20}O_3$ requires 224.1412. ν_{max}(film)/cm^{-1} 3490 (OH), 3020, 2960, 2880 (C–H) 1630 (C=C); δ_H($CDCl_3$) 1.41–1.93 (6 H, m, 3 × CH_2), 2.08–22.25 (1 H, dd, *J* 14.5, 7, C*H*$_2$CH=CH_2), 2.28–2.39 (1 H, dd, *J* 14.5, 8, C*H*$_2$CH=CH_2), 3.30–3.44 (1 H, d, *J* 5, CHO*H* (**6b**), d, *J* 7, CHO*H* (**6a**)), 3.79–3.96 (4 H, m, OCH_2CH_2O), 4.08–4.16 (1 H, m, C*H*OH), 4.95–5.29 (4 H, m, 2 × CH=C*H*$_2$), 5.74–6.06 (2 H, m, 2 × C*H*=CH_2); δ_C($CDCl_3$) (**6a**): 18.8 (CH_2), 30.5 (CH_2), 34.6 (CH_2), 35.8 (CH_2), 51.8 (CH_2), 63.8 and 63.84 (OCH_2CH_2O), 75.7 (CHOH), 115.3 (CH=*C*H$_2$), 117.12 (HC(OH)CH=*C*H$_2$), 120.6 (2-C), 135.5 (*C*H=CH_2), 137.8 (HC(OH)*C*H=CH_2); (**6b**): 19.8 (CH_2), 29.7 (CH_2), 36.5 (CH_2), 38.6 (CH_2), 52.3 (1-C), 64.0 and 64.1 (OCH_2CH_2O), 75.3 (CHOH), 116.2 (CH=*C*H$_2$), 117.16 (HC(OH)CH=*C*H$_2$), 120.2 (2-C), 136.1 (*C*H=CH_2), 137.7 (HC(OH)*C*H=CH_2); *m*/*z* (EI) 224 (M^+, 0.5%), 183 (16), 167 (32), 139 (16), 124 (11), 112 819), 99 (100), 55 (64).

(1*R,1′*S**)-1-(1-Allyl-2,2-ethylenedioxycyclopentan-1-yl)prop-2-en-1-ol 6b**

Compound **6b** was isolated as the non-reacted part of the epimeric alcohol substrate **6a**–**6b** (8 : 1) in an oxidation reaction for the preparation of the ketone **15** (*vide infra*). The product was a colourless oil (4%), R_f 0.24. HRMS: M 224.1415. $C_{13}H_{20}O_3$ requires 224.1412. ν_{max}(film)/cm^{-1} 3495 (OH), 3020, 2970, 2860 (C–H) 1635 (C=C); δ_H($CDCl_3$) 1.57–1.94 (6 H, m, 3 × C*H*$_2$), 2.13–2.21 (1 H, m, C*H*$_2$CH=CH_2), 2.30–2.39 (1 H, dd, *J* 14.5, 8, C*H*$_2$CH=CH_2), 3.43–3.45 (1 H, d, *J* 5, CHO*H*), 3.83–3.97 (4 H, m, OCH_2CH_2O), 4.12–4.17 (1 H, m, C*H*OH), 4.99–5.23 (4 H, m, 2 × CH=C*H*$_2$), 5.79–6.09 (2 H, m, 2 × C*H*=CH_2); δ_C($CDCl_3$) 19.7 (CH_2), 29.6 (CH_2), 36.5 (CH_2), 38.8 (CH_2), 52.2 (1-C), 64.0 and 64.1 (OCH_2CH_2O), 75.4 (CHOH), 116.5 (CH=*C*H$_2$), 117.2 (HC(OH)CH=*C*H$_2$), 120.2 (2-C), 136.3 (*C*H=CH_2), 137.7 (HC(OH)*C*H=CH_2); *m*/*z* (EI) (M^+, 1%), 206 (7), 183 (22), 168 (46), 139 (16), 124 (17), 99 (100), 86 (14), 55 (27).

1-(1-Allyl-2,2-ethylenedioxycyclopentan-1-yl)but-3-en-1-ol 7a and 7b

Mg powder (0.35 g, 14.3 mmol) in diethyl ether was stirred under argon overnight, the ether decanted, diethyl ether (20 ml) added followed by two small crystals of I_2. The mixture was stirred for 5 min before a solution of allyl bromide (1.61 g, 12.8 mmol) in diethyl ether (20 ml) was added dropwise at a sufficient rate to maintain slight reflux. The mixture was stirred for 3 h before the Grignard reagent was added to a solution of the carbaldehyde **5a** (1.40 g, 7.14 mmol) in diethyl ether (5 ml) at 0 °C under argon. The reaction was stopped after 3 h by the addition of a saturated NH_4Cl solution. The layers were separated and the aqueous layer extracted with diethyl ether (3 × 30 ml), the combined organic layers dried ($MgSO_4$), evaporated and the product isolated from the residual material by flash chromatography using hexane–EtOAc 7 : 1 as eluent, R_f 0.20. The product mixture (**7a**–**7b** 1 : 4; 1.47 g, 87%) was a colourless oil. HRMS: M 238.1565. $C_{14}H_{22}O_3$ requires 238.1568. ν_{max}(film)/cm^{-1} 3500 (O–H), 3050, 2965, 2870 (C–H), 1625 (C=C); δ_H($CDCl_3$) 1.22–1.84 (6 H, m, 3 × CH_2), 2.00–2.42 (4 H, m, 2 H from CH_2CH=CH_2, 2 H from OHCH_2CH=CH_2), 3.11–3.17 (1 H, d, *J* 3, CHO*H* (**7a**), d, *J* 6, CHO*H* (**7b**)), 3.66–3.73 (1 H, m, C*H*OH), 3.83–4.07 (4 H, m, OCH_2CH_2O), 4.97–5.07 (4 H, m, CH_2CH=CH_2, CH(OH)CH_2CH=CH_2), 5.80–5.96 (2 H, m, CH_2CH=CH_2 CH(OH)CH_2CH=CH_2); δ_C($CDCl_3$) (**7a**): 19.8 (CH_2), 30.3 (CH_2), 36.3 (CH_2), 36.5 (CH_2), 38.8 (CH_2), 52.4 (1-C), 63.9 and 64.2 (OCH_2CH_2O), 73.1 (CHOH), 116.0 (CH=*C*H_2), 116.7 (CH(OH)CH_2CH=*C*H_2), 120.4 (2-C), 136.4 (*C*H=CH_2), 136.9 (CH(OH)CH_2CH=CH_2); (**7b**): 18.8 (CH_2), 30.9 (CH_2), 34.4 (CH_2), 35.6 (CH_2), 37.0 (CH_2), 51.6 (1-C), 63.8 and 63.7 (OCH_2CH_2O), 74.7 (CHOH), 115.8 (CH=*C*H_2), 117.0 (CH(OH)CH_2CH=*C*H_2), 120.7 (2-C), 135.7 (*C*H=CH_2), 137.3 (CH(OH)CH_2CH=CH_2); *m*/*z* (EI) 238 (M^+, 1.37%), 220 (12), 197 (98), 168 (49), 155 (6), 135 (20), 107 (24), 99 (100), 86 (18), 67 (15), 55 (23).

(1*R**,1′*S**)-1-(1-Allyl-2,2-ethylenedioxycyclopentan-1-yl)but-3-en-1-ol 7b

Compound **7b** was isolated as the non-reacted part of the epimeric alcohol substrate **7a**–**7b** (1 : 4) in an oxidation reaction for the preparation of the ketone **16** (*vide infra*). The product was a colourless oil (33%), R_f 0.25. HRMS: M 238.1570. $C_{14}H_{22}O_3$ requires 238.1568. ν_{max}(film)/cm^{-1} 3500 (O–H), 3040, 2954, 2894 (C–H), 1635 (C=C); δ_H($CDCl_3$) 1.55–1.84 (6 H, m, 3 × CH_2), 2.15–2.42 (4 H, m, 2 × CH_2), 3.15–3.17 (1 H, d, *J* 6, CHO*H*), 3.66–3.72 (1 H, ddd, *J* 10, 6, 2, C*H*OH), 3.83–3.99 (4 H, m, OCH_2CH_2O), 4.98–5.09 (4 H, m, 2 × CH=CH_2), 5.80–5.96 (2 H, m, 2 × C*H*=CH_2); δ_C($CDCl_3$) 18.8 (CH_2), 30.9 (CH_2), 34.4 (CH_2), 35.7 (CH_2), 37.0 (CH_2), 51.6 (1-C), 63.6 and 63.8 (OCH_2CH_2O), 74.7 (CHOH), 115.8 (CH=*C*H_2), 117.0 (CH(OH)CH_2CH=*C*H_2), 120.7 (2-C), 135.7 (*C*H=CH_2), 137.3 (CH(OH)CH_2CH=*C*H_2); *m*/*z* (EI) 238 (M^+, 0.90%), 197 (49), 167 (25), 135 (13), 99 (100), 79 (14), 67 (17), 55 (26).

1-(1-Allyl-2,2-ethylenedioxycyclopentan-1-yl)pent-4-en-1-ol 8a and 8b

The Grignard reagent was prepared following the procedure described above from Mg (0.29 g, 12.2 mmol) and 4-bromobut-1-ene (1.21 g, 8.98 mmol) in THF (12 ml) and added to a solution of the carbaldehyde **5a** (0.8 g, 4 mmol) in THF (5 ml) under argon at 0 °C. The reaction mixture was worked up as above and the product isolated after flash chromatography using hexane–EtOAc 7 : 1. The first eluted product was **8a** followed by **8b**

(1*S,1′*S**)-1-(1-Allyl-2,2-ethylenedioxycyclopentan-1-yl)-pent-4-en-1-ol 8a.** The product was a colourless oil (24%), R_f 0.33. HRMS: M 252.1728. $C_{15}H_{24}O_3$ requires 252.1725. ν_{max}(film)/cm^{-1} 3500 (O–H), 3040, 2955, 2875 (C–H), 1638 (C=C); δ_H($CDCl_3$) 1.38–1.78 (8 H, m, 4 × CH_2), 2.00–2.06 (2 H, m, CH_2), 2.30–2.41 (2 H, m, CH_2), 3.09–3.11 (1 H, dd, *J* 4, 1.5, CHO*H*), 3.63–3.68 (1 H, ddd, *J* 10.5, 4, 2, C*H*OH), 3.83–3.97 (4 H, m, OCH_2CH_2O), 4.88–5.03 (4 H, m, 2 × CH=CH_2), 5.76–5.89 (2 H, m, 2 × C*H*=CH_2); δ_C($CDCl_3$) 19.9 (CH_2), 30.4 (CH_2), 30.8 (CH_2), 30.9 (CH_2), 36.7 (CH_2), 38.9 (CH_2), 52.5 (1-C), 63.9 and 64.1 (OCH_2CH_2O), 72.9 (CHOH), 114.3 (CH=*C*H_2), 116.7 (CH(OH)$(CH_2)_2$CH=*C*H_2), 120.4 (2-C), 136.5 (*C*H=CH_2), 139.1 (CH(OH)$(CH_2)_2$*C*H=CH_2); *m*/*z* (EI) 252 (M^+, 0.7%), 221 (10), 193 (7), 168 (41), 139 (14), 124 (25), 99 (100), 86 (17), 55 (27).

(1*R,1′*S**)-1-(1-Allyl-2,2-ethylenedioxycyclopentan-1-yl)-pent-4-en-1-ol 8b.** A colourless oil (48%), R_f 0.30. HRMS: M 252.1729. $C_{15}H_{24}O_3$ requires 252.1725. ν_{max}(film)/cm^{-1} 3504 (O–H), 3040, 2940, 2885 (C–H), 1630 (C=C); δ_H($CDCl_3$) 1.37–1.83 (8 H, m, 4 × CH_2), 1.95–2.08 (1 H, m, from CH_2CH_2CH=CH_2), 2.12–2.19 (1 H, dd, *J* 14, 7, CH_2CH=CH_2), 2.28–2.39 (2 H, m, 1 H from CH_2CH=CH_2, 1 H from CH_2CH_2CH=CH_2), 3.14–3.16 (1 H, d, *J* 6, CHO*H*), 3.55–3.61 (1 H, ddd, *J* 10, 6, 3, C*H*OH), 3.82–3.99 (4 H, m, OCH_2CH_2O), 4.89–5.04 (4 H, m, 2 × CH=CH_2), 5.73–5.91 (2 H, m, 2 × C*H*=CH_2); δ_C($CDCl_3$) 18.8 (CH_2), 30.9 (CH_2), 31.4 (CH_2), 31.5 (CH_2), 34.4 (CH_2), 35.7 (CH_2), 51.7 (1-C), 63.5 and 63.7 (OCH_2CH_2O), 74.4 (CHOH), 114.4 (CH=*C*H_2), 116.9 (CH(OH)$(CH_2)_2$CH=*C*H_2), 120.8 (2-C), 135.8 (*C*H=CH_2), 138.8 (CH(OH)$(CH_2)_2$-*C*H=CH_2); *m*/*z* (EI) 252 (M^+, 0.3%), 211 (7), 168 (33), 124 (22), 99 (100), 79 (20), 67 (26), 55 (46).

(1*S,1′*S**)-1-(1-Allyl-2,2-ethylenedioxycyclohexan-1-yl)-prop-2-en-1-ol 9a.** Compound **9a** was obtained following the procedure described above from the carbaldehyde **5b** and vinylmagnesium chloride as a colourless oil (80%), R_f 0.39. HRMS: M 238.1577. $C_{14}H_{22}O_3$ requires 238.1568. ν_{max}(film)/cm^{-1} 3598 (O–H), 3050, 2935, 2860 (C–H), 1625 (C=C); δ_H($CDCl_3$) 1.38–1.65 (8 H, m, 4 × CH_2), 2.23–2.31 (1 H, dd, *J* 15, 7, CH_2-CH=CH_2), 2.36–2.43 (1 H, dd, *J* 15, 7, CH_2CH=CH_2), 3.77–3.79 (1 H, d, *J* 3, CHO*H*), 3.85–3.99 (4 H, m, OCH_2CH_2O), 4.36–4.39 (1 H, m, C*H*OH), 4.90–5.26 (4 H, m, 2 × CH=CH_2), 5.82–6.02 (2 H, m, 2 × C*H*=CH_2); δ_C($CDCl_3$) 20.1 (CH_2), 23.1 (CH_2), 30.3 (CH_2), 30.6 (CH_2), 33.5 (CH_2), 46.8 (1-C), 63.2 and 64.8 (OCH_2CH_2O), 75.7 (CHOH), 114.3 (2-C), 115.36 (CH=*C*H_2), 116.2 (HC(OH)CH=*C*H_2), 135.8 (*C*H=CH_2), 137.2 (HC(OH)*C*H=CH_2); *m*/*z* (EI) 238 (M^+, 2%), 197 (17), 182 (51), 139 (20), 99 (100), 67 (29), 55 (48).

1-(1-Allyl-2,2-ethylenedioxycyclohexan-1-yl)but-3-en-1-ol 10a and 10b

Compounds **10a** and **10b** were obtained from the carbaldehyde **5b** and allyl bromide following the procedure described above as a colourless oil (1 : 4 mixture) (78%), R_f 0.19. HRMS: M 252.1735. $C_{15}H_{24}O_3$ requires 252.1725. ν_{max}(film)/cm^{-1} 3490 (O–H), 3050, 2920, 2890 (C–H), 1630 (C=C); δ_H($CDCl_3$) 1.18–1.70 (8 H, m, 4 × CH_2), 2.14–2.50 (4 H, m, 2 H from CH_2CH=CH_2, 2 H from OHCH_2CH=CH_2), 3.58–3.63 (1 H, s, CHO*H* (**10a**), m, CHO*H* (**10b**)), 3.86–3.98 (5 H, m, 1 from C*H*OH, 4 from OCH_2CH_2O), 4.90–5.03 (4 H, m, CH_2CH=CH_2, CH(OH)CH_2CH=CH_2), 5.81–5.93 (2 H, m, CH_2CH=CH_2, CH(OH)CH_2CH=CH_2); δ_C($CDCl_3$) (**10b**): 20.2 (CH_2), 23.0 (CH_2), 30.0 (CH_2), 30.5 (CH_2), 33.4 (CH_2), 36.0 (CH_2), 46.5 (1-C), 63.2 and 64.3 (OCH_2CH_2O), 74.3 (CHOH), 114.3 (2-C), 115.5 (CH=*C*H_2), 116.1 (CH(OH)CH=*C*H_2), 136.0 (*C*H=CH_2), 137.3 (CH(OH)*C*H=CH_2); (**10a**): 19.9 (CH_2), 23.03 (CH_2), 27.8 (CH_2), 30.2 (CH_2), 36.2 (CH_2), 36.9 (CH_2), 46.2 (1-C), 63.3 and 64.1 (OCH_2CH_2O), 72.9 (CHOH), 114.4 (2-C), 115.7 (CH=*C*H_2), 116.4 (CH(OH)CH_2CH=*C*H_2), 135.7 (*C*H=CH_2), 137.4 (CH(OH)CH_2*C*H=CH_2); *m*/*z* (EI) 252 (M^+, 1.3%), 211 (42), 182 (55), 139 (36), 121 (30), 113 (57), 99 (100), 86 (62), 79 (55), 67 (57), 55 (66).

(1*R,1′*S**)-1-(1-Allyl-2,2-ethylenedioxycyclohexan-1-yl)but-3-en-1-ol 10b**

Only alcohol isomer **10b** was isolated as the non-reacted part of the epimeric alcohol substrate **10a** and **10b** (1 : 4) in an oxidation reaction for the preparation of the ketone **19** (*vide infra*). The product was a colourless oil (55%), R_f 0.17. HRMS: M 252.1720. $C_{15}H_{24}O_3$ requires 252.1725. ν_{max}(film)/cm^{-1} 3500 (O–H), 2935, 2860 (C–H), 1635 (C=C); δ_H($CDCl_3$) 1.21–1.71 (8 H, m, 4 × CH_2), 2.20–2.46 (4 H, m, 2 × CH_2), 3.66–3.90 (1 H, m, CHO*H*), 3.86–4.01 (5 H, m, 1 H from C*H*OH, 4 H from OCH_2CH_2O), 4.92–5.09 (4 H, m, 2 × CH=CH_2), 5.81–5.97 (2 H, m, 2 × C*H*=CH_2); δ_C($CDCl_3$) 20.2 (CH_2), 23.1 (CH_2), 30.1 (CH_2), 30.7 (CH_2), 33.5 (CH_2), 36.1 (CH_2), 46.6 (1-C), 63.3 and 64.4 (OCH_2CH_2O), 74.4 (CHOH), 114.4 (2-C), 115.6 (CH=*C*H_2), 116.2 (CH(OH)CH_2CH=*C*H_2), 136.1 (*C*H=CH_2), 137.5 (CH(OH)CH_2*C*H=CH_2); *m*/*z* (EI) 252 (M^+, 12%), 211 (10), 168 (36), 124 (22), 99 (100), 86 (25), 55 (29).

(1*R,1′*S**)-1-(1-Allyl-2,2-ethylenedioxycyclohexan-1-yl)pent-4-en-1-ol 11b**

Compound **11b** was obtained following the procedure described above from the carbaldehyde **5b** and 4-bromobut-1-ene as a colourless oil (75%), R_f 0.41. HRMS: M 266.1880. $C_{16}H_{26}O_3$ requires 266.1881. ν_{max}(film)/cm^{-1} 3500 (O–H), 3050, 2910, 2860 (C–H), 1603 (C=C); δ_H($CDCl_3$) 1.34–1.71 (10 H, m, 5 × CH_2), 2.02–2.07 (1 H, m, C*H*CH=CH_2), 2.29–2.36 (3 H, m, C*H*CH=CH_2, CH_2CH=CH_2), 3.63–3.65 (1 H, m, CHO*H*), 3.88–3.99 (5 H, m, 4 from OCH_2CH_2O, 1 from C*H*OH), 4.90–5.05 (4 H, m, 2 × CH=CH_2), 5.76–5.98 (2 H, m, 2 × C*H*=CH_2); δ_C($CDCl_3$) 20.3 (CH_2), 23.2 (CH_2), 30.3 (CH_2), 30.7 (CH_2), 30.8 (CH_2), 31.4 (CH_2), 33.6 (CH_2), 46.7 (1-C), 63.3 and 64.5 (OCH_2CH_2O), 73.9 (CHOH), 114.4 (CH=*C*H_2), 114.6 (2-C), 116.0 (HC(OH)$(CH_2)_2$CH=*C*H_2), 136.4 (*C*H=CH_2), 139.1 (HC(OH)$(CH_2)_2$*C*H=CH_2); *m*/*z* (EI) 266 (M^+, 13%), 225 (26), 182 (91), 163 (11), 139 (23), 127 (31), 99 (100), 86 (27), 67 (16), 55 (22).

(1*S,1′*S**)-1-(1-Allyl-2,2-ethylenedioxycycloheptan-1-yl)prop-2-en-1-ol 12a**

Compound **12a** was obtained following the procedure described above from the carbaldehyde **5c** and vinylmagnesium chloride as a colourless oil (78%), R_f 0.22. HRMS: M 252.1276. $C_{15}H_{24}O_3$ requires 252.1725. ν_{max}(film)/cm^{-1} 3500 (O–H), 3038, 2960, 2875 (C–H), 1635 (C=C); δ_H($CDCl_3$) 1.47–1.72 (10 H, m, 5 × CH_2), 2.26–2.29 (2 H, d, *J* 8, CH_2CH=CH_2), 3.80–3.82 (1 H, d, *J* 6, CHO*H*), 3.85–3.94 (4 H, m, OCH_2CH_2O), 4.20–4.24 (1H, m, C*H*OH), 4.93–5.25 (4H, m, 2 × CH=CH_2), 5.85–6.06 (2 H, m, 2 × C*H*=CH_2); δ_C($CDCl_3$) 21.8 (CH_2), 22.5 (CH_2), 28.6 (CH_2), 32.5 (CH_2), 33.2 (CH_2), 36.3 (CH_2), 50.1 (1-C), 62.7 and 63.6 (OCH_2CH_2O), 77.4 (CHOH), 114.8 (CH=*C*H_2), 116.4 (2-C), 116.6 (HC(OH)CH=*C*H_2), 136.8 (*C*H=CH_2), 138.1 (HC(OH)*C*H=CH_2); *m*/*z* (EI) 256 (M^+, 1%), 211 (15), 197 (11), 168 (43), 139 (45), 99 (100), 55 (37).

1-(1-Allyl-2,2-ethylenedioxycycloheptan-1-yl)but-3-en-1-ol 13a and 13b

The isomer mixture of **13a** and **13b** (1 : 1) was obtained following the procedure described above from the carbaldehyde **5c** and allyl bromide. The product was a colourless oil (83%), R_f 0.32. HRMS: M 266.1881. $C_{16}H_{26}O_3$ requires 266.1882. ν_{max}(film)/cm^{-1} 3505 (O–H), 3070, 2910, 2895 (C–H), 1640 (C=C); δ_H($CDCl_3$) 1.39–1.62 (10 H, m, 5 × CH_2), 2.08–2.42 (4 H, m, 2 × CH_2), 3.12–3.82 (2 H, d, *J* 5, CHO*H* (**13a**), d, *J* 4, CHO*H* (**13b**), dd, *J* 10, 4, *CH*OH (**13a**), dd, *J* 10, 5, *CH*OH (**13b**)), 3.83–3.99 (4H, m, OCH_2CH_2O), 4.92–5.07 (4 H, m, CH_2CH=CH_2, CH(OH)CH_2CH=CH_2), 5.83–6.02 (2 H, m, CH_2C*H*=CH_2, CH(OH)CH_2C*H*=CH_2); δ_C($CDCl_3$) 21.6 (CH_2), 22.4 (CH_2), 22.73 (CH_2), 22.76 (CH_2), 28.3 (CH_2), 29.6 (CH_2), 30.8 (CH_2), 32.6 (CH_2), 32.8 (CH_2), 33.9 (CH_2), 36.3 (CH_2), 36.6 (CH_2), 37.0 (CH_2), 39.9 (CH_2), 46.8 and 50.2 (2 × 1-C), 62.76, 62.77, 63.5 and 63.7 (2 × OCH_2CH_2O), 75.0 and 76.2 (2 × CHOH), 115.6, 115.9, 116.03 and 116.7 (2 × CH=*C*H_2, 2 × HC(OH)CH_2CH=*C*H_2), 116.09 and 116.5 (2 × 1-C), 136.5, 136.8, 137.6 and 137.7 (2 × *C*H=CH_2, 2 × HC(OH)CH_2-*C*H=CH_2); *m*/*z* (EI) 266 (M^+, 3%), 225 (100), 196 (75), 155 (29), 139 (45), 99 (93), 55 (23).

1-(1-Allyl-2,2-ethylenedioxycycloheptan-1-yl)pent-4-en-1-ol 14a and 14b

The isomer mixture of **14a** and **14b** (1 : 1) was obtained following the procedure described above from the carbaldehyde **5c** and 4-bromobut-1-ene. The product was a colourless oil (76%), R_f 0.31. HRMS: M. 280.2035. $C_{17}H_{28}O_3$ requires 280.2038. ν_{max}(film)/cm^{-1} 3502 (O–H), 3045, 2910, 2847 (C–H), 1634 (C=C); δ_H($CDCl_3$) 1.44–1.75 (12 H, m, 6 × CH_2), 1.98–2.39 (4 H, m, 2 × CH_2), 3.13–3.70 (2 H, d, *J* 6, CHO*H* (**14a**), dd, *J* 10, 6, C*H*OH (**14a**), d, *J* 2, CHO*H* (**14b**), dd, *J* 4, 2, C*H*OH (**14b**)), 3.85–3.97 (4 H, m, OCH_2CH_2O), 4.89–5.03 (4 H, 2 × CH=CH_2), 5.78–5.95 (2 H, m, 2 × C*H*=CH_2); δ_C($CDCl_3$) 21.6 (CH_2), 22.4 (CH_2), 22.7 (CH_2), 22.8 (CH_2), 28.4 (CH_2), 29.6 (CH_2), 29.8 (CH_2), 31.0 (CH_2), 31.3 (CH_2), 31.5 (2 × CH_2), 32.7 (CH_2), 33.0 (CH_2), 34.1 (CH_2), 36.4 (CH_2), 37.8 (CH_2), 49.9 and 50.4 (2 × 1-C), 62.7, 62.73, 63.6 and 63.7 (2 × OCH_2-CH_2O), 75.1 and 75.9 (2 × CHOH), 114.2, 114.4, 115.9 and 116.7 (2 × CH=*C*H_2, 2 × HC(OH)$(CH_2)_2$CH=*C*H_2), 116.1 and 116.2 (2 × 2-C), 136.6, 136.9, 139.1 and 139.2 (2 × *C*H=CH2, 2 × HC(OH)$(CH_2)_2$*C*H=CH_2d); *m*/*z* (EI) 280 (M^+, 7%), 239 (25), 196 (100), 153 (15), 99 (51), 55 (14).

1-(1-Allyl-2,2-ethylenedioxycyclopentan-1-yl)prop-2-en-1-one 15 and recovered alcohol 6b

The mixture of the alcohols **6a** and **6b** (8 : 1; 0.448 g, 2 mmol) in dichloromethane (3 ml) was added rapidly at ambient temperature to a suspension of pyridinium chlorochromate (0.648 g, 3 mmol) in dichloromethane (4 ml). The mixture became briefly homogeneous before a black precipitate was formed. TLC monitoring showed that the reaction had gone to completion after 6 h. The reaction mixture was diluted with 5 volumes of anhydrous diethyl ether, the solvent decanted, the black solid washed twice with diethyl ether and the combined ethereal solution filtered through Florisil. Evaporation of filtrate and flash chromatography of the residual material using hexane–EtOAc 10 : 1, R_f 0.33, led to separation of the ketone **15** and the alcohol **6b**. The ketone was first eluted and was obtained as a colourless oil (0.328 g, 70%). HRMS: M 222.1247. $C_{13}H_{18}O_3$ requires 222.1255. ν_{max}(film)/cm^{-1} 3020, 2960, 2880 (C–H), 1680 (C=O),1600 (C=C); δ_H($CDCl_3$) 1.54–1.82 (5 H, m, 2 × CH_2, 1 H from CH_2), 2.17–2.24 (1 H, dd, *J* 14.5, 8, CH_2CH=CH_2), 2.30–2.40 (1 H, m, CH_2), 2.74–2.82 (1 H, dd, *J* 14.5, 6.5, CH_2CH=CH_2), 3.75–3.92 (4 H, m, OCH_2-CH_2O), 4.93–5.01 (2 H, m, CH_2CH=CH_2), 5.38–5.48 (1 H, m, CH_2C*H*=CH_2), 5.49–5.51 (1 H, dd, *J* 10, 2, COCH=CH_2), 6.17–6.23 (1 H, dd, *J* 17, 2, COCH=CH_2), 6.74–6.83 (1 H, dd, *J* 17, 10, COC*H*=CH_2); δ_C($CDCl_3$) 18.5 (CH_2), 28.6 (CH_2), 34.9 (CH_2), 36.8 (CH_2), 61.1 (1-C), 64.1 and 64.8 (OCH_2CH_2O), 118.0 (CH=*C*H_2), 118.6 (2-C), 126.4 (COCH=*C*H_2), 133.1 (*C*H=CH_2), 133.5 (CO*C*H=CH_2), 199.7 (C=O); *m*/*z* (EI) 222 (M^+, 2%), 167 (5), 139 (7), 112 (8), 99 (100), 79 (4), 67 (6), 55 (24).

The second product was the epimer pure alcohol **6b** that was obtained as an oil in 4% yield. The physical data are given above.

1-(1-Allyl-2,2-ethylenedioxycyclopentan-1-yl)but-3-en-1-one 16 and recovered alcohol 7b

The oxidation was carried out following the procedure described above with a mixture of the alcohols **7a** and **7b** (1 : 4)

and pyridinium chlorochromate in dichloromethane for 3 h. The products were separated by flash chromatography. The ketone was first eluted and was obtained as a colourless oil (47%), R_f 0.36. HRMS: M 236.1420. $C_{14}H_{20}O_3$ requires 236.1412. ν_{max}(film)/cm^{-1} 3060, 2975, 2890 (C–H), 1700 (C=O), 1645 (C=C); δ_H($CDCl_3$) 1.57–1.79 (5 H, m, 2 × CH_2, 1 H from CH_2), 2.13–2.20 (1 H, dd, *J* 14.5, 7, CH_2CH=CH_2), 2.28–2.48 (1 H, m, CH_2), 2.76–2.83 (1 H, dd, *J* 14.5, 7, CH_2CH=CH_2), 3.20–3.25 (2 H, m, COCH_2CH=CH_2), 3.76–3.99 (4 H, m, OCH_2CH_2O), 4.96–5.09 (4 H, m, 2 × =CH_2), 5.41–5.55 (1 H, m, CH_2C*H*=CH_2), 5.82–5.95 (1 H, m, $COCH_2$C*H*=CH_2); δ_C($CDCl_3$) 18.8 (CH_2), 29.0 (CH_2), 34.8 (CH_2), 37.1 (CH_2), 44.4 (CH_2), 62.1 (1-C), 63.9 and 64.7 (OCH_2CH_2O), 117.4 (CH=*C*H_2), 118.1 ($COCH_2$CH=*C*H_2), 118.6 (2-C), 131.9 (*C*H=CH_2), 133.6 ($COCH_2$*C*H=CH_2), 208.9 (C=O); *m*/*z* (EI) 236 (M^+, 5%), 195 (35), 167 (30), 99 (100), 55 (6).

The second product was the pure alcohol isomer **7b** that was obtained as an oil in 33% yield. The physical data are given above.

1-(1-Allyl-2,2-ethylenedioxycyclopentan-1-yl)pent-4-en-1-one 17

Compound **17** was obtained from the alcohol **8a** by oxidation with pyridinium chlorochromate in CH_2Cl_2 for 9 h following the procedure described above as a colourless oil (81%), R_f 0.34. HRMS: M 250.1567. $C_{15}H_{22}O_3$ requires 250.1568. ν_{max}(film)/cm^{-1} 3070, 2981, 2890 (C–H), 1698 (C=O), 1643 (C=C); δ_H($CDCl_3$) 1.57–1.76 (5 H, m, 1 H from CH_2, 2 × CH_2), 2.10–2.39 (4 H, m, 2 × CH_2), 2.49–2.56 (2 H, m, 1 H from CH_2, 1 H from CH_2CH=CH_2), 2.75–2-86 (1 H, dd, *J* 14.5, 7, CH_2-CH=CH_2), 3.79–3.93 (4 H, m, OCH_2CH_2O), 4.87–5.07 (4 H, m, 2 × CH_2=), 5.38–5.59 (1 H, m, CH_2C*H*=CH_2), 5.67–5.88 (1 H, m, $CO(CH_2)_2$C*H*=CH_2); δ_C($CDCl_3$) 18.8 (CH_2), 27.8 (CH_2), 29.2 (CH_2), 34.9 (CH_2), 37.3 (CH_2), 39.2 (CH_2), 62.0 (1-C), 63.9 and 64.7 (OCH_2CH_2O), 114.6 (CH=*C*H_2), 117.9 ($CO(CH_2)_2$-CH=*C*H_2), 118.7 (2-C), 133.8 (*C*H=CH_2), 138.0 ($CO(CH_2)_2$-*C*H=CH_2), 210.2 (C=O); *m*/*z* (EI) 250 (M^+, 0.4%), 167 (16), 139 (6), 123 (5), 112 (11), 99 (100), 67 (12), 55 (46).

1-(1-Allyl-2,2-ethylenedioxycyclohexan-1-yl)prop-2-en-1-one 18

Compound **18** was obtained following the procedure described above from the oxidation of the alcohol **9a** using pyridinium chlorochromate in dichloromethane for 6 h. The ketone was obtained as a colourless oil (70%), R_f 0.38. HRMS: M 236.1416. $C_{14}H_{20}O_3$ requires 236.1412. ν_{max}(film)/cm^{-1} 2950, 2880 (C–H), 1680 (C=O), 1600 (C=C); δ_H($CDCl_3$) 1.20–1.67 (7 H, m, 1 H from CH_2, 6 H from 3 × CH_2), 2.01–2.06 (1 H, m, CH_2), 2-38–2.46 (1 H, dd, *J* 15, 8, CH_2CH=CH_2), 2.78–2.85 (1 H, dd, *J* 15, 6, CH_2CH=CH_2), 3.78–3.91 (4 H, m, OCH_2-CH_2O), 4.93–5.01 (2 H, m, CH=CH_2), 5.36–5.42 (1 H, m, CH_2C*H*=CH_2), 5.44–5.50 (1 H, dd, *J* 10, 2, COCH=CH_2), 6.15–6.21 (1 H, dd, *J* 17, 2, COCH=CH_2), 7.00–7.09 (1 H, dd, *J* 17, 10, COC*H*=CH_2); δ_C($CDCl_3$) 20.4 (CH_2), 23.0 (CH_2), 28.5 (CH_2), 32.0 (CH_2), 34.6 (CH_2), 57.5 (1-C), 64.1 and 64.6 (OCH_2CH_2O), 111.3 (2-C), 118.0 (COCH=*C*H_2), 123.3 (CH=*C*H_2), 132.9 (*C*H=CH_2), 134.2 (CO*C*H=CH_2), 200.9 (C=O); *m*/*z* (EI) 236 (M^+, 24%), 208 (10), 195 (46), 181 (92), 139 (26), 125 (28), 112 (32), 99 (100), 86 (61), 55 (44).

1-(1-Allyl-2,2-ethylenedioxycyclohexan-1-yl)but-3-en-1-one 19 and recovered alcohol 10b

The oxidation was carried out following the procedure described above with a mixture of the alcohols **10a** and **10b** (1 : 4) and pyridinium chlorochromate in dichloromethane for 4 h. The products were separated by flash chromatography. The ketone was a colourless oil (40%), R_f 0.24. HRMS: 250.1567. $C_{15}H_{22}O_3$ requires 250.1568. ν_{max}(film)/cm^{-1} 2920, 2865 (C–H), 1690 (C=O), 1630 (C=C); δ_H($CDCl_3$) 1.40–2.10 (8 H, m, 4 × CH_2), 2.26–2.37 (1 H, dd, *J* 15, 8, CH_2CH=CH_2), 2.72–2.82 (1 H, dd, *J* 15, 7, CH_2CH=CH_2), 3.21–3.44 (2 H, m, COCH_2-CH=CH_2), 3.79–3.94 (4 H, m, OCH_2CH_2O), 4.90–5.05 (4 H, m, 2 × =CH_2), 5.32–5.53 (1 H, m, CH_2C*H*=CH_2), 5.78–5.99 (1 H, m, $COCH_2$C*H*=CH_2); δ_C($CDCl_3$) 20.5 (CH_2), 22.9 (CH_2), 28.9 (CH_2), 31.7 (CH_2), 35.1 (CH_2), 45.2 (CH_2), 58.6 (1-C), 63.9 and 64.4 (OCH_2CH_2O), 110.8 (2-C), 117.1 (CH=*C*H_2), 117.9 ($COCH_2$CH=*C*H_2), 132.2 (*C*H=CH_2), 133.2 ($COCH_2$*C*H=CH_2), 209.9 (C=O); *m*/*z* (EI) 264 (M^+, 12%), 223 (6), 181 (82), 139 (169), 112 (17), 99 (100), 86 (50), 55 (75).

The second product was the pure alcohol isomer **10b** that was a colourless oil in 55% yield. The physical data are given above.

1-(1-Allyl-2,2-ethylenedioxycyclohexan-1-yl)pent-4-en-1-one 20

Compound **20** was obtained following the procedure described above by oxidation of the alcohol **11b** using pyridinium chlorochromate in dichloromethane for 10 h. The ketone was a colourless oil (78%), R_f 0.27. HRMS: M 264.1722. $C_{16}H_{24}O_3$ requires 264.1725. ν_{max}(film)/cm^{-1} 2910, 2840 (C–H), 1680 (C=O), 1625 (C=C); δ_H($CDCl_3$) 1.46–1.63 (7 H, m, 3 × CH_2, 1 H from CH_2), 2.01–2.16 (2 H, m, CH_2), 2.18–2.28 (1 H, m, CH_2), 2.20–2.39 (1 H, dd, *J* 14, 8, CH_2CH=CH_2), 2.60–2.70 (2 H, m, CH_2), 2.72–2.80 (1 H, dd, *J* 14, 8, CH_2CH=CH_2), 3.85–3.94 (4 H, m, OCH_2CH_2O), 4.93–5.03 (4 H, m, 2 × CH_2=), 5.41–5.53 (1 H, m, CH_2C*H*=CH_2), 5.72–5.85 (1 H, m, $CO(CH_2)_2$-C*H*=CH_2); δ_C($CDCl_3$) 20.6 (CH_2), 23.0 (CH_2), 27.9 (CH_2), 29.2 (CH_2), 31.8 (CH_2), 35.5 (CH_2), 40.0 (CH_2), 58.5 (1-C), 64.0 and 64.4 (OCH_2CH_2O), 111.1 (2-C), 114.7 (CH=*C*H_2), 127.8 (CO-$(CH_2)_2$CH=*C*H_2), 133.5 (*C*H=CH_2), 138.1 ($CO(CH_2)_2$-*C*H=CH_2), 211.2 (C=O); *m*/*z* (EI) 264 (M^+, 18%), 223 (6), 181 (82), 112 (17), 99 (100), 86 (49), 55 (75).

1-(1-Allyl-2,2-ethylenedioxycycloheptan-1-yl)prop-2-en-1-one 21

Compound **21** was obtained following the procedure described above by oxidation of the alcohol **12a** using pyridinium chlorochromate in dichloromethane for 5 h The ketone was a colourless oil (82%), R_f 0.31. HRMS: M 250.1566. $C_{15}H_{22}O_3$ requires 250.1568. ν_{max}(film)/cm^{-1} 2910, 2840 (C–H), 1685 (C=O), 1630 (C=C); δ_H($CDCl_3$) 1.21–1.79 (9 H, m, 4 × CH_2, 1 H from CH_2), 2.16–2.24 (1 H, m, CH_2), 2.26–2.33 (1 H, dd, *J* 14, 8, CH_2CH=CH_2), 2.80–2.88 (1 H, dd, *J* 14, 7, CH_2CH=CH_2), 3.79–3.92 (4 H, m, OCH_2CH_2O), 4.91–5.00 (2 H, m, 2 × CH_2=), 5.44–5.50 (1 H, dd, *J* 10, 2, COCH=CH_2), 5.52–5.55 (1 H, m, CH_2C*H*=CH_2), 6.14–6.20 (1 H, dd, *J* 17, 2, COCH=CH_2), 6.89–6.98 (1 H, dd, *J* 17, 10, COC*H*=CH_2); δ_C($CDCl_3$) 22.1 (CH_2), 22.9 (CH_2), 28.8 (CH_2), 31.2 (CH_2), 33.9 (CH_2), 38.0 (CH_2), 60.1 (1-C), 63.1 and 64.2 (OCH_2CH_2O), 113.5 (2-C), 117.8 (CH=*C*H_2), 125.9 (COCH=*C*H_2), 133.6 (*C*H=CH_2), 134.0 (CO*C*H=CH_2), 200.3 (C=O); *m*/*z* (EI) 252 (M^+, 3%), 209 (25), 195 (68), 139 (23), 99 (100), 55 (26).

1-(1-Allyl-2,2-ethylenedioxycycloheptan-1-yl)but-3-en-1-one 22

The oxidation was carried out following the procedure described above with a mixture of the alcohols **13a** and **13b** (1 : 1) and pyridinium chlorochromate in dichloromethane for 7 h. The ketone was obtained as a colourless oil (88%) after flash chromatography, R_f 0.29. HRMS: M 264.1733. $C_{16}H_{24}O_3$ requires 264.1725. ν_{max}(film)/cm^{-1} 2915, 2856 (C–H), 1690 (C=O), 1636 (C=C); δ_H($CDCl_3$) 1.43–1.80 (9 H, m, 4 × CH_2, 1 H from CH_2), 2.14–2.23 (1 H, m, from CH_2), 2.24–2.31 (1 H, dd, *J* 15, 8, CH_2CH=CH_2), 2.80–2.88 (1 H, m, CH_2CH=CH_2), 3.21–3.41 (2 H, m, COCH_2CH=CH_2), 3.82–3.94 (4 H, m, OCH_2CH_2O), 4.95–5.07 (4 H, m, 2 × =CH_2), 5.44–5.58 (1 H, m, CH_2C*H*=CH_2), 5.85–5.98 (1 H, m, $COCH_2$C*H*=CH_2); δ_H($CDCl_3$) 22.1 (CH_2), 23.0 (CH_2), 29.1 (CH_2), 31.7 (CH_2), 33.5 (CH_2), 38.4 (CH_2), 44.5 (CH_2), 61.4 (1-C), 62.9 and 64.0 (OCH_2CH_2O), 113.4 (2-C), 117.0 (CH=*C*H_2), 117.9 ($COCH_2$-CH=*C*H_2), 132.7 (*C*H=CH_2), 133.9 ($COCH_2$*C*H=CH_2), 209.4

(C=O); *m*/*z* (EI) 264 (M^+, 3%), 223 (100), 195 (57), 153 (7), 139 (11), 99 (63), 67 (12), 55 (6).

1-(1-Allyl-2,2-ethylenedioxycycloheptan-1-yl)pent-4-en-1-one 23

The oxidation was carried out following the procedure described above with a mixture of the alcohols **14a** and **14b** (1 : 1) and pyridinium chlorochromate in dichloromethane for 7 h. The ketone was obtained as a colourless oil (85%) after flash chromatography, R_f 0.42. HRMS: M 278.1878. $C_{17}H_{26}O_3$ requires 278.1882. ν_{max}(film)/cm^{-1} 2915, 2856 (C–H), 1700 (C=O), 1639 (C=C); δ_H($CDCl_3$) 1.29–1.80 (9 H, m, 1 H from CH_2, 4 × CH_2), 2.15–2.67 (6 H, m, 1 H from CH_2, 1 H from C*H*$_2$CH=CH_2, 2 × CH_2), 2.81–2.88 (1H, dd, *J* 14, 7, C*H*$_2$-CH=CH_2), 3.82–3.88 (4 H, m, OCH_2CH_2O), 4.88–5.04 (4 H, m, 2 × CH=C*H*$_2$), 5.44–5.58 (1 H, m, C*H*$_2$CH=CH_2), 5.69–5.85 (1 H, m, $CO(CH_2)_2CH$=CH_2); δ_C($CDCl_3$) 22.1 (CH_2), 23.1 (CH_2), 28.3 (CH_2), 29.2 (CH_2), 32.0 (CH_2), 33.5 (CH_2), 38.7 (CH_2), 39.2 (CH_2), 61.1 (1-C), 62.3 and 64.0 (OCH_2CH_2O), 113.4 (2-C), 114.5 (CH=*C*H_2), 117.7 ($CO(CH_2)_2CH$=*C*H_2), 134.1 (*C*H=CH_2), 138.2 ($CO(CH_2)_2$*C*H=CH_2), 210.8 (C=O); *m*/*z* (EI) 278 (M^+, 13%), 237 (25), 195 (98), 139 (17), 127 (59), 99 (100), 55 (15).

trans- and *cis*-6,6-Ethylenedioxyspiro[4.4]non-2-en-1-ol 24a and 24b

Bis(tricyclohexylphosphine)(benzylidene)ruthenium dichloride (20.5 mg, 0.025 mmol) in dry toluene (1 ml), was added to a solution of the epimeric alcohols **6a** and **6b** (8 : 1) (0.224 g, 1 mmol) in dry toluene (20 ml) under argon. The mixture was stirred and heated under argon at 70 °C for 2 h when another portion of bis(tricyclohexylphosphine)(benzylidene)ruthenium dichloride (20.5 mg, 0.025 mmol) in dry toluene (1 ml) was added. The heating was continued at 70 °C for 4 h. The cold reaction mixture was filtered, the filtrate evaporated and the residual material subjected to flash chromatography using CH_2Cl_2–EtOAc 8 : 1, R_f 0.21. The yield of the alcohols **24a** and **24b** (8 : 1) was 0.156 g (80%) as a colourless oil (Found: C, 67.60; H, 8.37. $C_{11}H_{16}O_3$ requires C, 67.34; H, 8.16%). HRMS: M 196.1098. $C_{11}H_{16}O_3$ requires 196.1099. ν_{max}(film)/cm^{-1} 3505, 3480 (C–OH), 3010, 2945, 2870 (C–H), 1610 (C=C); δ_H($CDCl_3$) 1.62–2.14 (7 H, m, 3 × CH_2, 1 H from CH_2), 2.51–2.75 (1H, dq, *J* 17, 5, 2, 1 H from CH_2), 3.19–3.80 (1 H, 3.20, d, *J* 7, CHO*H*-(*trans*), 3.80–3.85 (1 H, m, C*H*OH (*cis*)), 3.85–3.98 (4 H, m, OCH_2CH_2O), 4.37–4.74 (1 H, 4.39, dt, *J* 7, 2, C*H*OH(*trans*)), 4.73 (1 H, d, *J* 5, CHO*H*(*cis*)), 5.67–5.76 (1 H, m, CH=), 5.86–5.90 (1 H, m, CH=); δ_C($CDCl_3$) (*trans*): 18.0 (CH_2), 33.4 (CH_2), 37.0 (CH_2), 38.6 (CH_2), 54.9 (5-C), 63.4 and 65.1 (OCH_2CH_2O), 83.1 (CHOH), 118.8 (6-C), 132.7 (3-CH=), 133.6 (2-CH=); (*cis*): 17.9 (CH_2), 29.5 (CH_2), 33.4 (CH_2), 40.1 (CH_2), 57.9 (5-C), 64.3 and 64.9 (OCH_2CH_2O), 78.2 (CHOH), 118.9 (6-C), 131.2 (3-CH=), 132.6 (2-CH=); *m*/*z* (EI) 196 (M^+, 8%), 178 (11), 153 (12), 134 (17), 106 (14), 99 (100), 92 (64), 79 (15), 55 (30).

cis-6,6-Ethylenedioxyspiro[4.4]non-2-en-1-ol 24b

When the RCM reaction was repeated following the procedure described above with epimerically pure alcohol **6b** the corresponding *cis* product **24b** was obtained as a colourless oil (79%), R_f 0.21. HRMS: M 196.1097. $C_{11}H_{16}O_3$ requires 196.1099. ν_{max}(film)/cm^{-1} 3489, (C–OH), 3020, 2940, 2880 (C–H), 1624 (C=C); δ_H($CDCl_3$) 1.67–1.96 (6 H, m, 3 × CH_2), 1.98–2.05 (1 H, dt, *J* 17, 2, from CH_2), 2.69–2.77 (1 H, dq, *J* 17, 4, 2, from CH_2), 3.77–3.80 (1 H, m, C*H*OH), 3.87–4.00 (4 H, m, OCH_2CH_2O), 4.74 (1 H, d, *J* 5, CHO*H*), 5.75–5.78 (1 H, m, CH=), 5.88–5.92 (1H, m, CH=); δ_C($CDCl_3$) 17.8 (CH_2), 29.6 (CH_2), 33.4 (CH_2), 40.1 (CH_2), 57.8 (5-C), 64.4 and 64.9 (OCH_2CH_2O), 78.2 (CHOH), 118.9 (6-C), 131.2 (3-CH=), 132.6 (2-CH=); *m*/*z* (EI) 196 (M^+, 2%), 178 (6), 152 (44), 134 (35), 106 (35), 92 (100), 79 (68), 55 (30).

trans- and *cis*-1,1-Ethylenedioxyspiro[4.5]dec-8-en-6-ol 25a and 25b

The RCM reaction was carried out following the procedure described above with a mixture of the alcohols **7a** and **7b** (1 : 4) and 5 mol% Ru(II)-catalyst at 30 °C for 0.5 h. The epimeric alcohols were separated by flash chromatography using CH_2Cl_2–EtOAc 8 : 1. Compound **25b** was eluted first.

***cis*-1,1-Ethylenedioxyspiro[4.5]dec-8-en-6-ol 25b.** A colourless oil (74%), R_f 0.54 (Found: C, 68.40; H, 8.87. $C_{12}H_{18}O_3$ requires C, 68.57; H, 8.57%). HRMS: M 210.1259. $C_{12}H_{18}O_3$ requires 210.1255. ν_{max}(film)/cm^{-1} 3480, (C–OH), 3004, 2900, 2890 (C–H), 1650 (C=C); δ_H($CDCl_3$) 1.46–2.00 (8 H, m, 4 × CH_2), 2.16–2.34 (2 H, m, CH_2), 3.87–3.96 (6 H, m, 1 H from C*H*OH, 1 H from CHO*H*, 4 H from OCH_2CH_2O), 5.45–5.62 (2 H, m, 2 × CH=); δ_C($CDCl_3$) 19.1 (CH_2), 26.8 (CH_2), 31.8 (CH_2), 33.2 (CH_2), 36.1 (CH_2), 49.1 (6-C), 64.0 and 64.4 (OCH_2CH_2O), 68.8 (CHOH), 120.5 (7-C), 124.6 (4-CH=), 124.9 (3-CH=); *m*/*z* (EI) 210 (M^+, 3%), 191 (26), 167 (10), 148 (30), 130 (26), 104 (34), 99 (100), 86 (22), 55 (13).

***trans*-1,1-Ethylenedioxyspiro[4.5]dec-8-en-6-ol 25a.** A colourless oil (16%), R_f 0.42 (Found: C, 68.80; H, 8.59. $C_{12}H_{18}O_3$ requires C, 68.57; H, 8.57%). HRMS: M 210.1249. $C_{12}H_{18}O_3$ requires 210.1255. ν_{max}(film)/cm^{-1} 3496, (C–OH), 3010, 2910, 2870 (C–H), 1640 (C=C); δ_H($CDCl_3$) 1.46–1.62 (4 H, m, 2 × CH_2), 1.73–1.80 (3 H, m, CH_2, 1 H from CH_2), 2.05–2.18 (2 H, m, CH_2), 2.34–2.42 (1 H, m, from CH_2), 3.39 (1 H, s, CHO*H*), 3.83–3.98 (4 H, m, OCH_2CH_2O), 4.01 (1 H, s, C*H*OH), 5.50–5.54 (1 H, m, CH=), 5.60–5.65 (1 H, m, CH=); δ_C($CDCl_3$) 17.8 (CH_2), 27.0 (CH_2), 30.8 (CH_2), 32.0 (CH_2), 32.8 (CH_2), 47.0 (6-C), 64.1 and 64.4 (OCH_2CH_2O), 68.2 (CHOH), 119.5 (7-C), 123.0 (4-CH=), 125.0 (3-CH=); (EI) 210 (M^+, 2%), 191 (25), 148 (35), 104 (33), 99 (100), 86 (22), 55 (16).

trans-1,1-Ethylenedioxyspiro[4.6]undec-9-en-6-ol 26a

The RCM reaction was carried out following the procedure described above with the alcohol epimer **8a** and 5 mol% Ru(II)-catalyst at 60 °C for 4 h. The product after flash chromatography was a colourless oil (75%), R_f 0.48 (Found: C, 69.39; H, 9.1. $C_{13}H_{20}O_3$ requires C, 69.64; H, 8.92%). HRMS: M 224.1405. $C_{13}H_{20}O_3$ requires 224.1412. ν_{max}(film)/cm^{-1} 3501, (C–OH), 3000, 2930, 2878 (C–H), 1645 (C=C); δ_H($CDCl_3$) 1.48–2.18 (12 H, m, 6 × CH_2), 3.75 (1 H, dd, *J* 9, 4, CHO*H*), 3.80–3.96 (4 H, m, OCH_2CH_2O), 4.23 (1 H, s, C*H*OH), 5.49–5.57 (1 H, m, CH=), 5.75–5.83 (1 H, m, CH=); δ_C($CDCl_3$) 18.7 (CH_2), 23.5 (CH_2), 25.4 (CH_2), 30.3 (CH_2), 31.5 (CH_2), 34.1 (CH_2), 52.0 (7-C), 63.5 and 64.7 (OCH_2CH_2O), 74.6 (CHOH), 121.8 (8-C), 127.5 (5-CH=), 133.1 (4-CH=); *m*/*z* (EI) 224 (M^+, 8%), 206 (7), 180 (9), 162 (15), 120 (24), 99 (100), 86 (27), 55 (20).

cis-1,1-Ethylenedioxyspiro[4.6]undec-9-en-6-ol 26b

When the RCM reaction was repeated following the procedure described above with epimerically pure alcohol **8b** the corresponding *cis* product **26b** was obtained as a colourless oil (90%), R_f 0.42 (Found: C, 69.81; H, 9.21. $C_{13}H_{20}O_3$ requires C, 69.64; H, 8.92%). HRMS: M 224.1412. $C_{13}H_{20}O_3$ requires 224.1412. ν_{max}(film)/cm^{-1} 3485, (C–OH), 3000, 2910, 2860 (C–H), 1640 (C=C); δ_H($CDCl_3$) 1.41–1.92 (10 H, m, 5 × CH_2), 2.51–2.81 (2 H, m, CH_2), 3.19 (1 H, t, *J* 2 C*H*OH), 3.79–3.99 (4 H, m, OCH_2CH_2O), 4.17 (1 H, t, *J* 2, CHO*H*), 5.53–5.66 (1 H, m, CH=), 5.77–5.89 (1 H, m, CH=); δ_C($CDCl_3$) 17.6 (CH_2), 20.6 (CH_2), 25.5 (CH_2), 29.0 (CH_2), 30.7 (CH_2), 32.8 (CH_2), 49.8 (7-C), 63.8 and 64.1 (OCH_2CH_2O), 72.7 (CHOH), 120.2 (8-C), 128.5 (5-CH=), 133.5 (4-CH=); *m*/*z* (EI) 224 (M^+, 4%), 206 (5), 180 (10), 162 (11), 120 (22), 99 (100), 86 (24), 55 (17).

trans-6,6-Ethylenedioxyspiro[4.5]dec-2-en-1-ol 27a

Compound **27a** was obtained following the procedure described above from the alcohol epimer **9a** and 5 mol% of the Ru(II)-catalyst at 60 °C for 4 h. The product was a colourless oil (68%), R_f 0.53 (Found: C, 68.35; H, 8.77. $C_{12}H_{18}O_3$ requires C, 68.57; H, 8.57%). HRMS: M 210.1262. $C_{12}H_{18}O_3$ requires 210.1256. ν_{max}(film)/cm^{-1} 3505 (C–OH), 2910, 2815 (C–H), 1590 (C=C); δ_H($CDCl_3$) 1.45–1.61 (7 H, m, 1 H from CH_2, 6 H from 3 × CH_2), 1.73–1.83 (2 H, m, CH_2), 2.60–2.69 (1 H, dq, *J* 17, 5, 2, 1 H from CH_2), 3.10 (1 H, d, *J* 10, CHO*H*), 3.82–4.03 (4 H, m, OCH_2CH_2O), 4.37–4.42 (1 H, dt, *J* 10, 2, C*H*OH), 5.67–5.70 (1 H, m, CH=), 5.76–5.80 (1 H, m, CH=); δ_C($CDCl_3$) 21.4 (CH_2), 23.4 (CH_2), 31.6 (CH_2), 36.3 (CH_2), 40.5 (CH_2), 51.3 (5-C), 63.1 and 65.2 (OCH_2CH_2O), 80.9 (CHOH), 112.4 (s), 132.5 (3-CH=), 132.6 (2-CH=); *m*/*z* (EI) 210 (M^+, 18%), 193 (7), 153 (19), 148 (59), 137 (19), 122 (30), 99 (100), 95 (29), 86 (26), 55 (36).

trans- and *cis*-7,7-Ethylenedioxyspiro[5.5]undec-3-en-1-ol 28a and 28b

The RCM reaction was carried out following the procedure described above with a mixture of the alcohols **10a** and **10b** (1 : 4) and 5 mol% Ru(II)-catalyst at 28 °C for 0.5 h. The isomer ratio of **28a** and **28b** was 1 : 4 after flash chromatography. The product was a colourless oil (94%), R_f 0.32 (Found: C, 69.95; H, 8.67. $C_{13}H_{20}O_3$ requires C, 69.64; H, 8.92%). HRMS: M 224.1403. $C_{13}H_{20}O_3$ requires 224.1412. ν_{max}(film)/cm^{-1} 3480 (C–OH), 2920, 2860 (C–H), 1610 (C=C); δ_H($CDCl_3$) 1.30–2.34 (12 H, m, 6 × CH_2), 3.89–3.98 (4 H, m, OCH_2CH_2O), 4.00–4.20 (2 H, 4.01, s, CHO*H*(*trans*), 4.04, d, *J* 3, C*H*OH(*cis*), 4.13, s, C*H*OH(*trans*), 4.20, s, CHO*H*(*cis*)), 5.42–5.49 (1 H, m, CH=), 5.57–5.62 (1 H, m, CH=); δ_C($CDCl_3$) (*trans*): 19.5 (CH_2), 22.4 (CH_2), 22.9 (CH_2), 29.5 (CH_2), 29.7 (CH_2), 30.8 (CH_2), 45.5 (7-C), 63.4 and 64.3 (OCH_2CH_2O), 68.5 (CHOH), 114.8 (7-C), 123.7 (4-CH=), 124.0 (3-CH=); (*cis*): 20.0 (CH_2), 23.2 (CH_2), 25.8 (CH_2), 29.8 (CH_2), 30.0 (CH_2), 30.7 (CH_2), 42.4 (6-C), 63.5 and 65.0 (OCH_2CH_2O), 76.9 (CHOH), 113.6 (7-C), 122.3 (4-CH=), 124.6 (3-CH=); *m*/*z* (EI) 224 (M^+, 8%), 224 (5), 205 (22), 162 (70), 144 (39), 134 (30), 99 (100), 86 (53), 73 (50), 55 (61).

cis-7,7-Ethylenedioxyspiro[5.5]undec-3-en-1-ol 28b

When the RCM reaction was repeated following the procedure described above with epimerically pure alcohol **10b** the corresponding *cis* product **28b** was obtained as a colourless oil (93%), R_f 0.32. HRMS: M 224.1417. $C_{13}H_{20}O_3$ requires 224.1412. ν_{max}(film)/cm^{-1} 3495 (C–OH), 2940, 2890 (C–H), 1620 (C=C); δ_H($CDCl_3$) 1.31–2.37 (12 H, m, 6 × CH_2), 3.83–4.01 (4 H, m, OCH_2CH_2O), 4.07 (1 H, d, *J* 3, C*H*OH), 4.20 (1 H, s, CHO*H*), 5.44–5.51 (1 H, m, CH=), 5.56–5.64 (1 H, m, CH=); δ_C($CDCl_3$) 20.0 (CH_2), 23.2 (CH_2), 25.8 (CH_2), 29.8 (CH_2), 30.0 (CH_2), 30.7 (CH_2), 42.4 (6-C), 63.5 and 65.0 (OCH_2CH_2O), 67.9 (CHOH), 113.6 (7-C), 122.3 (4-CH=), 124.6 (3-CH=); *m*/*z* (EI) 224 (M^+, 4%), 205 (10), 162 (20), 144 (10), 134 (13), 99 (100), 86 (21), 73 (14), 55 (17).

cis-1,1-Ethylenedioxyspiro[5.6]dodec-10-en-7-ol 29b

Compound **29b** was obtained following the procedure described above from the alcohol epimer **11b** using 5 mol% Ru(II)-catalyst at 80 °C for 4 h. The product was a white crystalline solid (93%), mp 46 °C (Et_2O), R_f 0.40 (Found: C, 70.29; H, 9.21. $C_{14}H_{22}O_3$ requires C, 70.58; H, 9.24%). HRMS: M 238.1575. $C_{14}H_{22}O_3$ requires 238.1568. ν_{max}(film)/cm^{-1} 3480 (O–H), 3000, 2910, 2860 (C–H), 1510 (C=C); δ_H($CDCl_3$) 1.98–1.87 (11 H, m, 1 H from CH_2, 5 × CH_2), 1.98–2.06 (1 H, dd, *J* 15, 9, from CH_2), 2.61–2.68 (1 H, m, CH_2), 2.73–2.81 (1 H, m, from CH_2), 3.88–4.02 (4 H, m, OCH_2CH_2O), 4.12 (1H, s, C*H*OH), 4.32 (1 H, s, CHO*H*), 5.49–5.56 (1 H, m, CH=), 5.76–5.83 (1 H, m, CH=); δ_C($CDCl_3$) 20.0 (CH_2), 20.5 (CH_2), 23.3 (CH_2), 25.2 (CH_2), 26.8 (CH_2), 29.6 (CH_2), 30.0 (CH_2), 44.4 (7-C), 63.5 and 64.7 (OCH_2CH_2O), 72.5 (CHOH), 114.5 (8-C), 127.5 (5-CH=), 133.2 (4-CH=); *m*/*z* (EI) 238 (M^+, 5%), 176 (17), 148 (7), 134 (23), 125 (34), 112 (15), 99 (100), 91 (20), 86 (30), 79 (22), 67 (20), 55 (28).

trans-6,6-Ethylenedioxyspiro[4.6]undec-2-en-1-ol 30a

Compound **30a** was obtained from the alcohol epimer **12a** using 5 mol% of Ru(II)-catalyst at 70 °C for 2 h. The product was a colourless oil (71%), R_f 0.51 (Found: C, 69.55; H, 8.77. $C_{13}H_{20}O_3$ requires C, 69.64; H, 8.92%). HRMS: M 224.1408. $C_{13}H_{20}O_3$ requires 224.1412. ν_{max}(film)/cm^{-1} 3506 (C–OH), 3010, 2935, 2880 (C–H), 1625 (C=C); δ_H($CDCl_3$) 1.44–1.81 (10 H, m, 5 × CH_2), 2.10–2.20 (1 H, m, CH_2), 2.63–2.71 (1 H, dq, *J* 17, 4, 2, from CH_2), 3.09 (1H, d, *J* 10, CHO*H*), 3.83–4.00 (4 H, m, OCH_2CH_2O), 4.36–4.43 (1 H, dt, *J* 10, 2, C*H*OH), 5.68–5.72 (1 H, m, CH=), 5.78–5.82 (1 H, m, CH=); δ_C($CDCl_3$) 19.8 (CH_2), 21.9 (CH_2), 26.1 (CH_2), 33.5 (CH_2), 36.9 (CH_2), 45.0 (CH_2), 54.8 (5-C), 63.5 and 64.7 (OCH_2CH_2O), 80.4 (CHOH), 114.3 (6-C), 132.4 (3-CH=), 132.9 (2-CH=); *m*/*z* (EI) 224 (M^+, 15%), 206 (17), 162 (26), 120 (31), 99 (100), 86 (25), 55 (11).

trans- and *cis*-7,7-Ethylenedioxyspiro[5.6]dodec-3-en-1-ol 31a and 31b

The RCM reaction was carried out following the procedure described above with a mixture of the alcohols **13a** and **13b** (1 : 1) and 5 mol% Ru(II)-catalyst at 60 °C for 2 h. The product after flash chromatography was a mixture of the alcohol epimers **31a** and **31b** in the ratio 1 : 1. The product was a colourless oil (93%), R_f 0.45. HRMS: M 238.1564. $C_{14}H_{22}O_3$ requires 238.1568. ν_{max}(film)/cm^{-1} 3480 (C–OH), 3001, 2920, 2845 (C–H), 1650 (C=C); δ_H($CDCl_3$) 1.47–2.39 (14 H, m, 7 × CH_2), 3.63–4.54 (6 H, 3.63, d, *J* 2, CHO*H*(*trans*), 3.88–4.00, m, OCH_2CH_2O, 4.00–4.07, m, C*H*OH(*cis*), 4.20–4.24, m, C*H*OH(*trans*), 4.54, d, *J* 2, CHO*H*(*cis*)), 5.47–5.61 (2 H, m 2 × CH=); δ_C($CDCl_3$) *(cis/trans)* 21.1 (CH_2), 21.2 (CH_2), 21.8 (CH_2), 21.9 (CH_2), 25.3 (CH_2), 26.8 (CH_2), 27.7 (CH_2), 20.2 (CH_2), 30.8 (CH_2), 31.0 (CH_2), 31.3 (CH_2), 31.4 (CH_2), 32.8 (CH_2), 32.9 (CH_2), 45.8 and 45.9 (2 × 6-C), 63.5, 63.7, 64.0 and 64.4 (2 × OCH_2CH_2O), 68.6 and 70.4 (2 × CHOH), 115.9 and 116.2 (2 × 7-C), 122.7, 124.1, 124.8 and 125.3 (2 × 3-CH=, 2 × 2-CH=); *m*/*z* (EI) 238 (M^+, 60%), 219 (17), 181 (14), 167 (12), 99 (100), 86 (13), 55 (12).

trans- and *cis*-8,8-Ethylenedioxyspiro[6.6]tridec-4-en-1-ol 32a and 32b

The RCM reaction was carried out following the procedure described above with a mixture of the alcohols **14a** and **14b** (1 : 1) and 5 mol% Ru(II)-catalyst at 30 °C for 0.5 h. The product on flash chromatography was separated into the two epimeric alcohols **32a** and **32b**. Compound **32b** was eluted first.

***cis*-8,8-Ethylenedioxyspiro[6.6]tridec-4-en-1-ol 32b.** A colourless oil (36%), R_f 0.44. HRMS: M 252.1724. $C_{15}H_{24}O_3$ requires 252.1725. ν_{max}(film)/cm^{-1} 3490 (C–OH), 3001, 2930 (C–H), 1650 (C=C); δ_H($CDCl_3$) 1.35–1.99 (14 H, m, 7 × CH_2), 2.60–2.69 (2 H, m, CH_2), 3.89–3.99 (4 H, m, OCH_2CH_2O), 4.26 (1 H, d, *J* 3, C*H*OH), 4.32 (1 H, d, *J* 3, CHO*H*), 5.51–5.55 (1 H, m, CH=), 5.77–5.79 (1 H, m, CH=); δ_C($CDCl_3$) 21.0 (CH_2), 21.2 (CH_2), 21.6 (CH_2), 26.5 (CH_2), 26.9 (CH_2), 28.1 (CH_2), 29.9 (CH_2), 32.5 (CH_2), 48.5 (7-C), 63.5 and 64.5 (OCH_2CH_2O), 72.6 (CHOH), 116.5 (8-C), 128.4 (5-CH=), 132.7 (4-CH=); *m*/*z* (EI) 252 (M^+, 29%), 209 (51), 155 (30), 113 (21), 99 (100), 55 (14).

***trans*-8,8-Ethylenedioxyspiro[6.6]tridec-4-en-1-ol 32a.** A colourless oil (34%), R_f 0.31. HRMS: M 252.1732. $C_{15}H_{24}O_3$ requires 252.1725. ν_{max}(film)/cm^{-1} 3500 (C–OH), 3008, 2930, 2840 (C–H), 1645 (C=C); δ_H($CDCl_3$) 1.51–1.73 (12 H, 6 × CH_2), 2.08–2.13 (4 H, m, 2 × CH_2), 3.84–4.05 (5 H, m, 1 H from CHO*H*, 4 H from OCH_2CH_2O), 4.24 (1 H, s, C*H*OH), 5.55–5.61 (1 H, m CH=), 5.74–5.79 (1 H, m, CH=); δ_C($CDCl_3$) 20.9 (CH_2), 21.9 (CH_2), 23.9 (CH_2), 26.3 (CH_2), 27.8 (CH_2), 30.2 (CH_2), 30.4 (CH_2), 31.7 (CH_2), 49.3 (7-C), 63.6 and 63.9 (OCH_2CH_2O), 76.2 (CHOH), 117.8 (8-C), 127.5 (5-CH=), 132.3 (4-CH=); *m*/*z* (EI) 252 (M^+, 35%), 209 (55), 155 (30), 113 (26), 99 (100), 55 (7).

6,6-Ethylenedioxyspiro[4.4]non-2-en-1-one 33

Bis(tricyclohexylphosphine)(benzylidene)ruthenium dichloride (13 mg, 0.016 mmol) in dry toluene (1 ml), was added to a solution of the ketone **15** (0.150 g, 0.67 mmol) in dry toluene (20 ml) under argon. The mixture was stirred and heated at 70 °C for 2 h when another portion of bis(tricyclohexylphosphine)(benzylidene)ruthenium dichloride (13 mg, 0.016 mmol) in dry toluene (1 ml) was added. The heating under argon was continued at 70 °C for 2 h. The cold reaction mixture was filtered, the filtrate evaporated and the residual material subjected to flash chromatography using CH_2Cl_2–EtOAc 8 : 1. The product was a colourless oil (91%), R_f 0.37 (Found: C, 68.23; H, 7.49. $C_{11}H_{14}O_3$ requires C, 68.04; H, 7.21%). HRMS: M 194.0948. $C_{11}H_{14}O_3$ requires 194.0942. ν_{max}(film)/cm^{-1} 3005, 2965, 2885 (C–H), 1705 (C=O), 1634 (C=C); δ_H($CDCl_3$) 1.62–1.94 (4 H, m, 2 CH_2), 2.01–2.13 (2 H, m, CH_2), 2.29–2.40 (1 H, dt, *J* 19, 2, CH_2CH=CH), 2.95–3.03 (1 H, dt, *J* 19, 2, CH_2CH=CH), 3.77–3.90 (4 H, m, OCH_2CH_2O), 6.03–6.06 (1 H, dt, *J* 6, 2, CH=), 7.59–7.63 (1 H, m, CH=); δ_C($CDCl_3$) 19.0 (CH_2), 33.4 (CH_2), 34.2 (CH_2), 39.1 (CH_2), 57.9 (5-C), 64.5 and 65.3 (OCH_2CH_2O), 118.8 (6-C), 133.1 (3-CH=), 162.7 (2-CH=), 210.1 (1-C=O); *m*/*z* (EI) 194 (M^+, 9%), 137 (7), 99 (100), 79 (8), 66 (7), 55 (14).

1,1-Ethylenedioxyspiro[4.5]dec-8-en-6-one 34

Compound **34** was prepared following the procedure described above from ketone **16** (0.42 mmol) using 5 mol% Ru(II)-catalyst at 30 °C for 4 h. The product was a colourless oil (89%), R_f 0.53 (Found: C, 69.47; H, 7.89. $C_{12}H_{16}O_3$ requires C, 69.23; H, 7.69%). HRMS: M 208.1106. $C_{12}H_{16}O_3$ requires 208.1099. ν_{max}(film)/cm^{-1} 3009, 2910, 2870 (C–H), 1700 (C=O), 1655 (C=C); δ_H($CDCl_3$) 1.19–1.31 (1 H, m, from CH_2), 1.48–1.82 (4 H, m, 2 × CH_2), 2.10–2.18 (1 H, m, from CH_2), 2.37–2.44 (1 H, m, from CH_2), 2.62–2.69 (1 H, dd, *J* 18, 5, CH_2), 2.71–2.79 (1 H, m, from CH_2), 2.95–3.03 (1 H, m, from CH_2), 3.75–3.90 (4 H, m, OCH_2CH_2O), 5.57–5.64 (1 H, m, CH=), 5.69–5.76 (1 H, m, CH=); δ_C($CDCl_3$) 19.6 (CH_2), 33.4 (CH_2), 33.5 (CH_2), 36.1 (CH_2), 40.3 (CH_2), 58.1 (6-C), 64.7 and 65.0 (OCH_2CH_2O), 117.8 (7-C), 123.7 (4-CH=), 126.0 (3-CH=), 210.1 (1-C=O); *m*/*z* (EI) 208 (M^+, 29%), 137 (6), 99 (100), 79 (15), 55 (14).

1,1-Ethylenedioxyspiro[4.6]undec-9-en-6-one 35

Compound **35** was obtained from ketone **17** (0.80 mmol) using 5 mol% Ru(II)-catalyst at 60 °C for 4 h. The product was a colourless oil (89%), R_f 0.57 (Found: C, 70.49; H, 8.41. $C_{13}H_{18}O_3$ requires C, 70.27; H, 8.10%). HRMS: M 222.1257. $C_{13}H_{18}O_3$ requires 222.1255. ν_{max}(film)/cm^{-1} 3000, 2940, 2885 (C–H), 1695 (C=O), 1645 (C=C); δ_H($CDCl_3$) 1.37–1.83 (5 H, m, 1 H from CH_2, 2 × CH_2), 1.98–2.10 (1 H, dd, *J* 15, 8.5, from CH_2), 2.23–2.48 (4 H, m, 2 × CH_2), 2.82–2.95 (1 H, m, from CH_2), 3.20–3.35 (1 H, m, from CH_2), 3.78–3.91 (4 H, m, OCH_2CH_2O), 5.38–5.46 (1 H, m, CH=), 5.57–5.72 (1 H, m, CH=); δ_C($CDCl_3$) 19.4 (CH_2), 28.4 (CH_2), 29.0 (CH_2), 32.1 (CH_2), 34.5 (CH_2), 38.8 (CH_2), 64.5 and 65.0 (OCH_2CH_2O), 65.7 (7-C), 118.4 (8-C), 126.3 (5-CH=), 129.4 (4-CH=), 213.7 (1-C=O); *m*/*z* (EI) 222 (M^+, 3%), 194 (3), 112 (22), 99 (100), 79 (9), 55 (14).

6,6-Ethylenedioxyspiro[4.5]dec-2-en-1-one 36

Compound **36** was obtained from ketone **18** (0.78 mmol) using 5 mol% Ru(II)-catalyst at 75 °C for 2 h. The product was a white crystalline solid (78%), R_f 0.52, mp 95–95.3 °C (sublimation at 70 °C/0.5 mmHg) (Found: C, 69.56; H, 7.79. $C_{12}H_{16}O_3$ requires C, 69.23; H, 7.69%). HRMS: M 208.1090. $C_{12}H_{16}O_3$ requires 208.1099. ν_{max}(KBr)/cm^{-1} 2920, 2860 (C–H), 1680 (C=O), 1600 (C=C); δ_H($CDCl_3$) 1.20–1.98 (8 H, m, 4 × CH_2), 2.23–2.35 (1 H, dt, *J* 19, 2, CH_2CH=CH), 2.81–2.93 (1 H, dt, *J* 19, 2, CH_2CH=CH), 3.72–3.92 (4 H, m, OCH_2CH_2O), 5.99–6.03 (1 H, dt, *J* 6, 2, CH=), 7.54–7.60 (1 H, m, CH=); δ_C($CDCl_3$) 20.7 (CH_2), 23.1 (CH_2), 31.9 (CH_2), 33.7 (CH_2), 40.4 (CH_2), 53.7 (5-C), 64.4 and 65.2 (OCH_2CH_2O), 110.7 (6-C), 133.1 (3-CH=), 162.2 (2-CH=), 210.1 (1-C=O); *m*/*z* (EI) 208 (M^+, 24%), 163 (14), 125 (35), 111 (32), 99 (100), 83 (36), 71 (47), 57 (100).

7,7-Ethylenedioxyspiro[5.5]undec-3-en-1-one 37

Compound **37** was obtained from ketone **19** (0.60 mmol) and 5 mol% Ru(II)-catalyst at 30 °C for 0.5 h. The product was a colourless oil (91%), R_f 0.53 (Found: C, 70.54; H, 8.33. $C_{13}H_{18}O_3$ requires C, 70.27; H, 8.10%). HRMS: M 222.1250. $C_{13}H_{18}O_3$ requires 222.1255. ν_{max}(film)/cm^{-1} 3005, 2908, 2860 (C–H), 1700 (C=O), 1460 (C=C); δ_H($CDCl_3$) 1.04–1.09 (1 H, m, from CH_2), 1.38–1.63 (5 H, m, 2 × CH_2, 1 H from CH_2), 2.01–2.11 (1 H, m, from CH_2), 2.15–2.28 (2 H, m, CH_2), 2.52–2.60 (1 H, m, from CH_2), 2.70–2.95 (2 H, m, CH_2), 3.75–4.00 (4 H, m, OCH_2CH_2O), 5.52–5.58 (1 H, m, CH=), 5.64–5.68 (1 H, m, CH=); δ_C($CDCl_3$) 21.7 (CH_2), 23.3 (CH_2), 31.6 (CH_2), 33.0 (CH_2), 33.3 (CH_2), 40.3 (CH_2), 55.9 (6-C), 63.9 and 65.4 (OCH_2CH_2O), 110.3 (7-C), 122.8 (4-CH=), 125.3 (3-CH=), 210.0 (1-C=O); *m*/*z* (EI) 222 (M^+, 14%), 177 (25), 160 (80), 133 (32), 112 (32), 99 (100), 86 (27), 55 (37).

1,1-Ethylenedioxyspiro[5.6]dodec-10-en-7-one 38

Compound **38** was obtained from ketone **20** (0.60 mmol) using 5 mol% Ru(II)-catalyst at 60 °C for 4 h. The product was a colourless oil (86%), R_f 0.55 (Found: C, 70.94; H, 8.76. $C_{14}H_{20}O_3$ requires C, 71.18; H, 8.47%). HRMS: M 236.1409. $C_{14}H_{20}O_3$ requires 236.1412. ν_{max}(film)/cm^{-1} 3005, 2920, 2840 (C–H), 1690 (C=O), 1590 (C=C); δ_H($CDCl_3$) 1.36–2.31 (12 H, m, 6 × CH_2), 2.50–2.60 (2 H, m, CH_2), 3.77–3.90 (4 H, m, OCH_2CH_2O), 5.43–5.48 (1 H, m, CH=), 5.56–5.60 (1 H, m, CH=); δ_C($CDCl_3$) 20.8 (CH_2), 22.9 (CH_2), 27.1 (CH_2), 28.6 (CH_2), 29.4 (CH_2), 31.4 (CH_2), 39.2 (CH_2), 61.7 (7-C), 64.3 and 64.7 (OCH_2CH_2O), 111.0 (8-C), 125.7 (5-CH=), 129.8 (4-CH=), 214.4 (1-C=O); *m*/*z* (EI) 236 (M^+, 40%), 191 (14), 125 (17), 112 (16), 99 (100), 86 (43), 79 (24), 55 (29).

6,6-Ethylenedioxyspiro[4.6]undec-2-en-1-one 39

Compound **39** was obtained following the procedure described above from ketone **21** (40 mmol) using 5 mol% Ru(II)-catalyst at 75 °C for 4 h. The product was a colourless oil (86%), R_f 0.46 (Found: C, 70.49; H, 8.38. $C_{13}H_{18}O_3$ requires C, 70.27; H, 8.10%). HRMS: M 222.1256. $C_{13}H_{18}O_3$ requires 222.1255. ν_{max}(film)/cm^{-1} 3003, 2910, 2880 (C–H), 1700 (C=O), 1610 (C=C); δ_H($CDCl_3$) 1.47–1.84 (9 H, m, 4 × CH_2, 1 H from CH_2), 2.13–2.18 (1 H, m, from CH_2), 2.34–2.42 (1 H, dt, *J* 19, 2, CH_2CH=CH), 2.86–2.93 (1 H, dt, *J* 19, 2, CH_2CH=CH), 3.77–3.90 (4 H, m, OCH_2CH_2O), 5.98–6.01 (1 H, m, CH=), 7.54–7.58 (1 H, m, CH=); δ_C($CDCl_3$) 21.4 (CH_2), 22.8 (CH_2), 27.6 (CH_2), 33.5 (CH_2), 35.2 (CH_2), 40.5 (CH_2), 56.8 (5-C), 64.2 and 64.3 (OCH_2CH_2O), 113.3 (6-C), 132.6 (3-CH=), 162.2 (2-CH=), 210.8 (1-C=O); *m*/*z* (EI) 222 (M^+, 12%), 113 (27), 99 (100), 86 (7), 55 (11).

7,7-Ethylenedioxyspiro[5.6]dodec-3-en-1-one 40

Compound **40** was obtained following the procedure described above from ketone **22** (0.38 mmol) and 5 mol% Ru(II)-catalyst. The product was a colourless oil (87%), R_f 0.43 (Found: C, 71.41; H, 8.20. $C_{14}H_{20}O_3$ requires C, 71.18; H, 8.47%). HRMS: M 236.1421. $C_{14}H_{20}O_3$ requires 236.1412. ν_{max}(film)/cm^{-1} 3003, 2945, 2860 (C–H), 1700 (C=O), 1610 (C=C); δ_H($CDCl_3$) 1.38–1.72 (8 H, m, 4 × CH_2), 1.94–1.98 (1 H, m, from CH_2), 2.18–2.30 (2 H, m, CH_2), 2.48–2.57 (1 H, m, from CH_2), 2.82–2.85 (2 H, m, CH_2), 3.79–3.93 (4 H, m, OCH_2CH_2O), 5.58–5.64 (1 H, m, CH=), 5.68–5.75 (1 H, m, CH=); δ_C($CDCl_3$) 20.6 (CH_2), 22.0 (CH_2), 27.0 (CH_2), 32.1 (CH_2), 33.3 (CH_2), 33.7 (CH_2), 40.8 (CH_2), 58.2 (6-C), 64.1 and 64.3 (OCH_2CH_2O), 113.2 (7-C), 123.0 (4-CH=), 126.4 (3-CH=), 210.7 (1-C=O); *m*/*z* (EI) 236 (M^+, 29%), 208 (7), 191 (10), 174 (46), 151 (35), 137 (20), 99 (100), 79 (15), 55 (12).

8,8-Ethylenedioxyspiro[6.6]tridec-3-en-1-one 41

Compound **41** was obtained from ketone **23** (0.45 mmol) using 5 mol% Ru(II)-catalyst at 75 °C for 2 h. The product was a colourless oil (94%), R_f 0.51 (Found: C, 72.26; H, 8.61. $C_{15}H_{22}O_3$ requires C, 72; H, 8.80%). HRMS: M 250.1561. $C_{15}H_{22}O_3$ requires 250.1569. ν_{max}(film)/cm^{-1} 3003, 2960, 2840 (C–H), 1705 (C=O), 1631 (C=C); δ_H($CDCl_3$) 1.41–1.67 (8 H, m, 4 × CH_2), 1.98–2.06 (2 H, m, CH_2), 2.21–2.44 (4 H, m, 2 × CH_2), 2.84–2.85 (1 H, m, from CH_2), 3.41–3.51 (1 H, m, from CH_2), 3.79–3.90 (4 H, m, OCH_2CH_2O), 5.47–5.52 (1 H, m, CH=), 5.58–5.62 (1 H, m, CH=); δ_C($CDCl_3$) 22.5 (CH_2), 22.6 (CH_2), 27.30 (CH_2), 29.0 (CH_2), 29.7 (CH_2), 31.0 (CH_2), 33.3 (CH_2), 39.9 (CH_2), 63.5 (O*C*H_2CH_2O), 64.5 (7-C), 64.6 (OCH_2CH_2O), 113.4 (8-C), 126.2 (5-CH=), 129.6 (4-CH=), 215.0 (1-C=O); *m*/*z* (EI) 250 (M^+, 65%), 165 (12), 141 (15), 125 (5), 99 (100), 86 (13), 55 (12).

***cis*-1,1-Ethylenedioxyspiro[4.5]dec-8-en-6-yl *p*-nitrobenzoate 42**

A mixture of *p*-nitrobenzoyl chloride (0.256 g, 1.42 mmol), the alcohol **25b** (0.100 g, 0.47 mmol) and DMAP (0.175 g, 1.42 mmol) in dry CH_2Cl_2 (7 ml) was stirred at ambient temperature for 15 h when TLC monitoring showed that the reaction had gone to completion. The solvent was distilled off and the crude product purified by flash chromatography using hexane–EtOAc 5 : 1, R_f 0.36. The product was a pale yellow crystalline material (0.152 g, 89%), mp 131 °C (Et_2O). HRMS: M 359.1368. $C_{19}H_{21}NO_6$ requires 359.1368. ν_{max}(KBr)/cm^{-1} 2960, 2840 (C–H), 1710 (C=O), 1450 (NO_2); δ_H($CDCl_3$) 1.56–2.01 (7 H, m, 3 × CH_2, 1 H from CH_2), 2.32 (2 H, s, CH_2), 2.75–2.81 (1 H, d, *J* 18, from CH_2), 3.38–3.42 (1 H, m, from O*C*H_2CH_2O), 3.67–3.80 (3 H, m, OCH_2CH_2O), 5.48 (1 H, s, *H*COOCPhNO_2), 5.53–5.57 (1 H, m, CH=), 5.72–5.78 (1 H, m, CH=), 8.16–8.28 (4 H, m, 4 × CH_{Ar}); δ_C($CDCl_3$) 17.3 (CH_2), 28.0 (CH_2), 29.4 (CH_2), 31.6 (CH_2), 34.0 (CH_2), 46.7 (6-C), 63.9 and 64.6 (OCH_2CH_2O), 71.7 (1-H *C*OOCPh), 118.0 (7-C), 122.4 (4-CH=), 123.45 (CH_{Ar}), 123.52 (CH_{Ar}), 125.3 (3-CH=), 130.6 (CH_{Ar}), 130.7 (CH_{Ar}), 136.4 (CNO_2), 150.4 (CH=$C_{Ar}CO_2$), 165.2 (C=O, ester); *m*/*z* (EI) 359 (M^+, 5%), 209 (5), 193 (55), 150 (50), 131 (100), 104 (57), 99 (100), 91 (36), 55 (60).

The structure has been confirmed by a single crystal X-ray analysis (Fig. 1).

***cis*-1,1-Ethylenedioxyspiro[4.6]undec-9-en-6-yl *p*-nitrobenzoate 43**

Compound **43** was obtained following the procedure described above from the alcohol **26b** as a crystalline solid (75%), R_f 0.41, mp 165.5–166 °C (Et_2O). HRMS: M 373.1526. $C_{20}H_{23}NO_6$ requires 373.1525. ν_{max}(KBr)/cm^{-1} 2960, 2840 (C–H), 1710 (C=O), 1450 (NO_2); δ_H($CDCl_3$) 1.39–1.65 (4 H, m, 2 × CH_2), 1.80–1.92 (4 H, m, 2 × CH_2), 2.02–2.10 (2 H, m, CH_2), 2.31–2.36 (1 H, m, from CH_2), 3.00–3.06 (1 H, m, from CH_2), 3.31–3.95 (4 H, m, OCH_2CH_2O), 5.62–5.64 (1 H, d, *J* 5, *H*COOCPhNO2), 5.69–5.76 (1 H, m, CH=), 5.88–5.94 (1 H, m, CH=), 8.19–8.27 (4 H, m, 4 × CH_{Ar}); δ_C($CDCl_3$) 17.8 (CH_2), 21.3 (CH_2), 27.1 (CH_2), 27.6 (CH_2), 31.3 (CH_2), 34.3 (CH_2), 49.7 (7-C), 63.5 and 64.2 (OCH_2CH_2O), 76.7 (1-H*C*OOCPh), 119.1 (8-C), 123.6 (2 × CH_{Ar}), 128.6 (5-CH=), 130.6 (2 × CH_{Ar}), 132.8 (4-CH=), 136.4 (CNO_2), 150.4 (CH=$C_{Ar}CO_2$), 163.4 (C=O, ester); *m*/*z* (EI) 373 (M^+, 56%), 330 (5), 290 (11), 223 (24), 207 (54), 150 (14), 99 (100), 55 (6).

The structure has been confirmed by a single crystal X-ray analysis (Fig. 2).

***cis*-7,7-Ethylenedioxyspiro[5.5]undec-3-en-1-yl *p*-nitrobenzoate 44**

Compound **44** was obtained following the procedure described above from the alcohol **28b** as a crystalline solid (84%), R_f 0.46, mp 142–142.5 °C (Et_2O). HRMS: M 373.1516. $C_{20}H_{23}NO_6$ requires 373.1525. ν_{max}(KBr)/cm^{-1} 2920, 2890 (C–H), 1705 (C=O), 1510, 1350 (NO_2, CH=CH_{Ar}); δ_H($CDCl_3$) 1.38–1.75 (8 H, m, 4 × CH_2), 2.06–2.20 (2 H, m, CH_2), 2.39–2.46 (1 H, m, from CH_2), 2.59–2.67 (1 H, m, from CH_2), 3.45–3.54 (1 H, m, O*C*H_2CH_2O), 3.71–3.81 (3 H, m, O*C*H_2*C*H_2O), 5.49–5.52 (1 H, m, CH=), 5.69 (1 H, s, *H*COOCPhNO_2), 5.73–5.78 (1 H, m, CH=), 8.14–8.24 (4 H, m, 4 × CH_{Ar}); δ_C($CDCl_3$) 20.2 (CH_2), 23.1 (CH_2), 26.3 (CH_2), 29.0 (CH_2), 30.2 (CH_2), 30.7 (CH_2), 42.8 (6-C), 63.6 and 64.7 (OCH_2CH_2O), 71.4 (1-H*C*OOCPh), 111.7 (7-C), 121.5 (4-CH=), 123.4 (2 × CH_{Ar}), 125.7 (3-CH=), 130.7 (2 × CH_{Ar}), 136.9 (CNO_2), 150.3 (CH=$C_{Ar}CO_2$), 164.2 (C=O, ester); *m*/*z* (EI) 373 (M^+, 15%), 223 (10), 207 (77), 144 (65), 117 (30), 104 (37), 99 (100), 91 (79), 73 (43), 55 (27).

The structure has been confirmed by a single crystal X-ray analysis (Fig. 3).

***cis*-1,1-Ethylenedioxyspiro[5.6]dodec-10-en-7-yl *p*-nitrobenzoate 45**

Compound **45** was obtained following the procedure described above from the alcohol **29b** as a crystalline solid (75%), R_f 0.37, mp 114.2–114.5 °C (Et_2O). HRMS: M 387.1674. $C_{21}H_{25}NO_6$ requires 387.1681. ν_{max}(KBr)/cm^{-1} 2940, 2890 (C–H), 1713 (C=O), 1530, 1355 (NO_2, CH=CH_{Ar}); δ_H($CDCl_3$) 1.44–1.92 (11 H, m, 5 × CH_2, 1 H from CH_2), 2.26–2.34 (2 H, m, CH_2), 2.95–3.02 (1 H, m, from CH_2), 3.41–3.48 (1 H, m, 1 H from O*C*H_2CH_2O), 3.71–3.81 (3 H, m, 3 H from OCH_2CH_2O), 5.66–6.00 (3 H, m, 2 H from CH=, 1 H from *H*COOCPhNO_2), 8.16–8.33 (4 H, m, 4 × CH_{Ar}); δ_C($CDCl_3$) 20.1 (CH_2), 21.6 (CH_2), 23.2 (CH_2), 25.2 (CH_2), 26.7 (CH_2), 29.9 (CH_2), 30.3 (CH_2), 45.1 (7-C), 63.5 and 64.3 (OCH_2CH_2O), 76.1 (H*C*OOCPh), 112.6 (8-C), 123.5 (2 × CH_{Ar}), 128.0 (5-CH=), 130.7 (2 × CH_{Ar}), 131.9 (4-C), 136.8 (CNO_2), 150.4 (CH=$C_{Ar}CO_2$), 163.7 (C=O, ester); *m*/*z* (EI) 387 (M^+, 63%), 237 (42), 221 (100), 192 (25), 150 (34), 125 (52), 99 (86), 55 (16).

The structure has been confirmed by a single crystal X-ray analysis (Fig. 4).

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