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Single and double ring closing metathesis in the formation of dihydropyrans and bisoxacyclic systems with a quaternary centre

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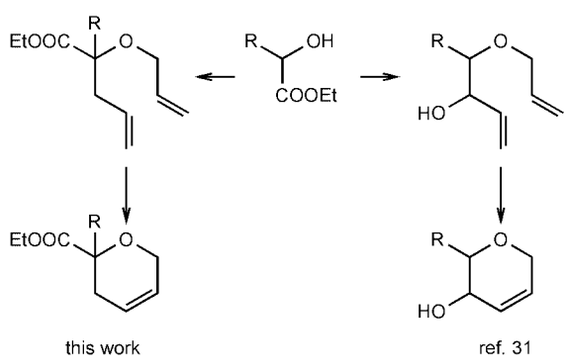
Starting from α-hydroxy carboxylic acid esters, allyl homoallyl ethers with a quaternary centre become available in a one-pot reaction *via* a sequence of *O*-allylation–Wittig-rearrangement–*O*-allylation. Elaboration of the side chain provides various precursors for dihydropyrans and bisoxacyclic systems, which become available by single or double ring closing metathesis. Double ring closing metathesis of the substrates investigated in this study is highly regioselective to give dihydropyrans linked *via* a C–C-bond to a dihydrofuran or an oxepine. The regioisomeric fused products are not formed in the reaction.

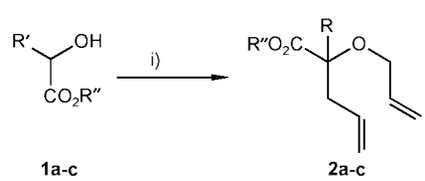
Introduction

The discovery of ruthenium carbene complexes as efficient catalysts for ring closing metathesis by Grubbs and co-workers[1–3] has led to a manifold of different applications of this synthetic method. Thus, over the past few years ring closing metathesis has turned out to be an efficient tool for the preparation of medium-sized and large carba- and heterocycles.[4–6] In the field of heterocyclic chemistry the majority of contributions deal with the synthesis of oxa- and azacycles, and many efforts have been made to develop synthetic methodologies for suitably functionalized precursors. With a view towards *C*-glycosides[7–9] and other functionalized tetrahydropyrans[10,11] we became interested in the synthesis of functionalized α,ω-unsaturated ethers as precursors for dihydropyrans with a quaternary centre in the 2-position.[12,13] While several dihydropyrans are accessible by allylation of a homoallylic alcohol and subsequent ring closing metathesis (RCM),[2,14–17] many substitution patterns require syntheses which are not straightforward. Some of the established solutions over the past few years include Claisen rearrangement–RCM sequences,[18,19] asymmetric aldol addition–RCM strategies,[20,21] and the introduction of olefinic moieties onto carbohydrate scaffolds.[22–27] Elaboration of α-bromo acids or esters into RCM precursors for dihydropyrans has been investigated by us,[12,28] and related strategies have been used for the construction of seven- and eight-membered oxacycles by others.[29,30] In the course of our studies towards hydroxylated dihydropyrans,[31] esters of α-hydroxy carboxylic acids[32] were found to be useful starting materials: *O*-allylation and elaboration of the ester moiety into an allylic alcohol provides appropriately substituted metathesis precursors in two steps. In this contribution, we present an olefin metathesis based synthesis of dihydropyrans with an ester functionality in the side chain using the same starting materials (Scheme 1).

The effect of different functional groups in the side chain on the efficiency of the olefin metathesis reaction was studied. The metathesis precursors investigated here can be elaborated in two steps into tetraenes, which may undergo a double ring closing metathesis reaction leading to bisoxacyclic systems.



Scheme 1



a:R = R′ = Ph; R″ = Me
b:R = R′ = Me; R″ = Et
c:R = allyl; R′ = H; R″ = Bu

Scheme 2 *Reagents and conditions* i) NaH (excess), allyl bromide, THF, 65 °C, (36–44%).

Results and discussion

Synthesis of appropriately functionalized metathesis precursors **2a**–**c** was achieved in a one-pot reaction by treatment of the commercially available and inexpensive starting materials **1a**–**c** with NaH and allyl bromide (Scheme 2). Though yields are moderate, this reaction can be performed on a comparatively large scale and does not require any protecting group chemistry.

Formation of **2a**–**c** may be regarded as a sequential reaction. The first step of the sequence is an *O*-allylation to give **3**, followed by a Wittig-rearrangement (yielding a tertiary alcohol **4**) which is finally allylated to the corresponding allyl homoallyl ethers **2a**–**c**. α-Allylation of hydroxy esters or protected derivatives has also been used for the preparation of tertiary alcohols of type **4**.[33–35] Elucidation of this mechanism was achieved by isolation of the intermediates. Reaction of (*S*)-ethyl lactate with a slight excess of NaH and allyl bromide at elevated temperature yields the *O*-allylated racemic

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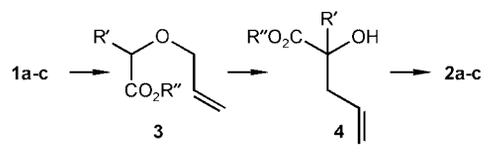
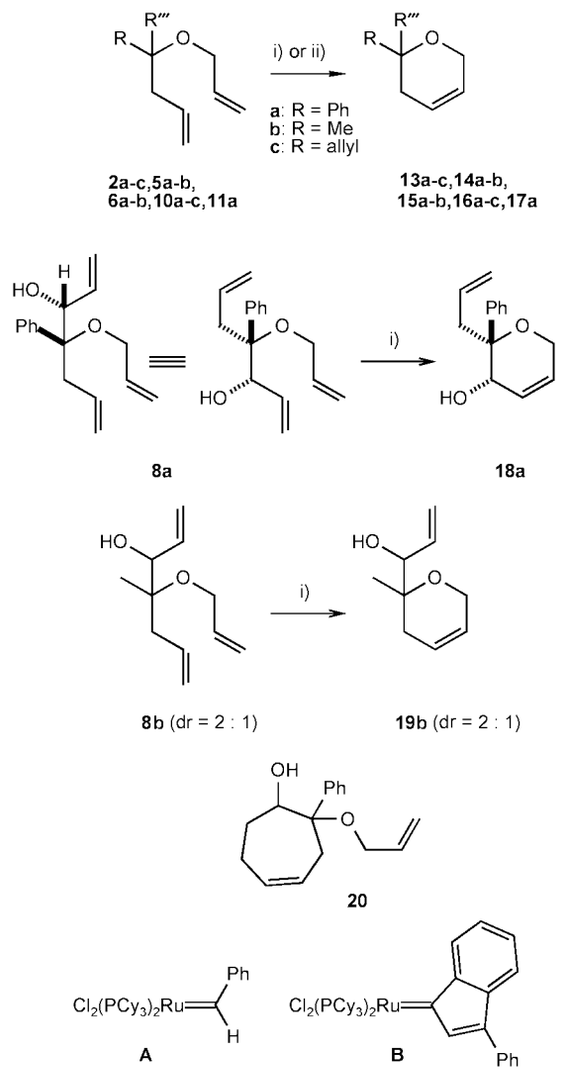
product **3** exclusively.[31] Reaction of methyl mandelate under the same conditions gives a 1:2 mixture of **3** and its Wittig-rearrangement product **4**, along with unreacted starting material. Due to the mechanism, racemisation occurs during this sequence if enantiomerically pure α-hydroxy esters are employed. This has been proven by measurement of the optical rotation ($[\alpha_D] = 0$) of intermediate **3b** and by NMR-shift experiments (Scheme 3).



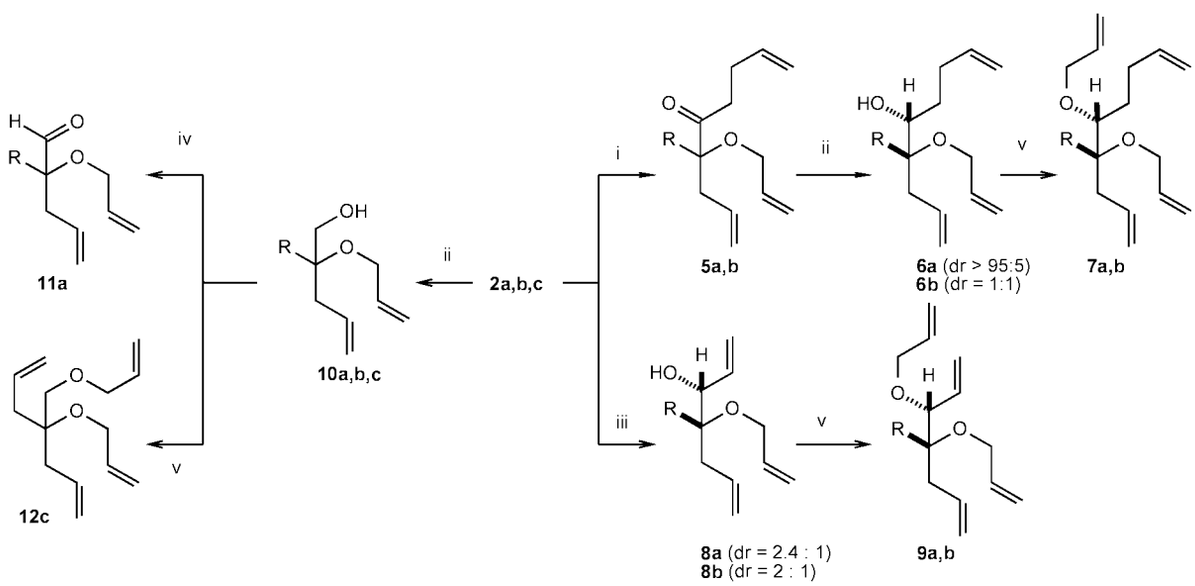
Scheme 3

Synthetic modification of the ester functionality in **2a**,**b**,**c** provides convenient access to other functionalized metathesis precursors (Scheme 4): addition of excess vinylmagnesium chloride gave the product of two consecutive additions: thus, the α,β-unsaturated ketone initially formed reacted further through a 1,4-addition to yield exclusively the 1,4-addition compounds **5a**,**b**. Reduction of esters **2a**,**b**,**c** or ketones **5a**,**b** with DIBAL-H furnishes secondary alcohols **6a**,**b** and primary alcohols **10a**,**b**,**c**, respectively. Reduction of the carbonyl functionality in ketone **5a** proceeds with high diastereoselectivity to give **6a**, whereas **6b** is obtained as a 1:1 mixture under these conditions. The stereochemical result for the formation of **6a** can be explained if chelation control ("Cram's cyclic model") is assumed.[36] Secondary alcohols **8a**,**b** are prepared by reduction of the ester groups in **2a**,**b** to the corresponding aldehydes and addition of vinylmagnesium chloride in a one-pot reaction. The reaction is moderately diastereoselective (2.4:1 for **8a**, 2:1 for **8b**) and the diastereomer shown in Scheme 4 is formed in preference, and is the isomer expected on the basis of the Felkin-Anh model.[37] In the case of **6a** as well as in the case of **8a**,**b**, the relative stereochemistry was tentatively assigned on the basis of the NMR-data. A metathesis precursor with an aldehyde functionality in the side chain is obtained by oxidation of **10a** to the corresponding aldehyde **11a** using PDC. Substrates **7a**,**b**, **9a**,**b** and **12c** suited for the study of double ring closing metathesis reactions become accessible by allylation of alcohols **6a**,**b**, **8a**,**b** and **10c**. The syntheses are summarized in Scheme 4.

With the metathesis precursors **2**,**5**,**6**,**8**,**10**,**11** in hand, efficiency of the ring closing metathesis reaction was examined. Scheme 5 and Table 1 summarize the results. Using Grubbs'



Scheme 5 *Reagents and conditions* i) **A**, DCM, 20 °C; ii) **B**, toluene, 110 °C (see Table 1).



Scheme 4 *Reagents and conditions* i) H_2C=CHMgCl (excess), ether, −70 °C, (64–78%); ii) DIBAL-H, ether, −78 °C, (64–99%); iii) DIBAL-H, H_2C=CHMgCl, ether, −90→20 °C (50–78%); iv) PDC, DCM, 20 °C, (67%); v) NaH, THF, 65 °C, allyl bromide (58–96%).

Table 1 Ring closing metathesis reactions, conditions and yields (see Scheme 4)

Entry	R‴	Starting material	Product	Catalyst loading (%)[a] (Yield) (%)	Catalyst loading (%)[b] (Yield) (%)
1	COOMe	**2a**	**13a**	3 (90)	3 (98)
2	COOEt	**2b**	**13b**	3 (95)	4 (87)
3	COOBu	**2c**	**13c**	3 (72)	4 (96)
4	$-C(O)(CH_2)_2CH=CH_2$	**5a**	**14a**	10 (74)	—
5	$-C(O)(CH_2)_2CH=CH_2$	**5b**	**14b**	3 (0)	6 (—[c])
6	$-CH(OH)(CH_2)_2CH=CH_2$	**6a**	**15a** + **20** (3 : 1)	3 (65)	—
7	$-CH(OH)(CH_2)_2CH=CH_2$	**6b**	**15b**	3 (42)	—
8	$-CH_2OH$	**10a**	**16a**	3 (86)	—
9	$-CH_2OH$	**10b**	**16b**	3 93)	—
10	$-CH_2OH$	**10c**	**16c**	3 (66)	—
11	–CHO	**11a**	**17a**	8 (69)[d]	—
12	$-CH(OH)CH=CH_2$	**8a**	**18a**	3 (40)	—
13	$-CH(OH)CH=CH_2$	**8b**	**19b**	3 (17)	—

[a] Conditions: **A**, DCM, 20 °C. [b] Conditions: **B**, toluene, 100 °C. [c] Conditions: reaction stopped at 50% conversion. [d] Conditions: **A**, toluene, 100 °C.

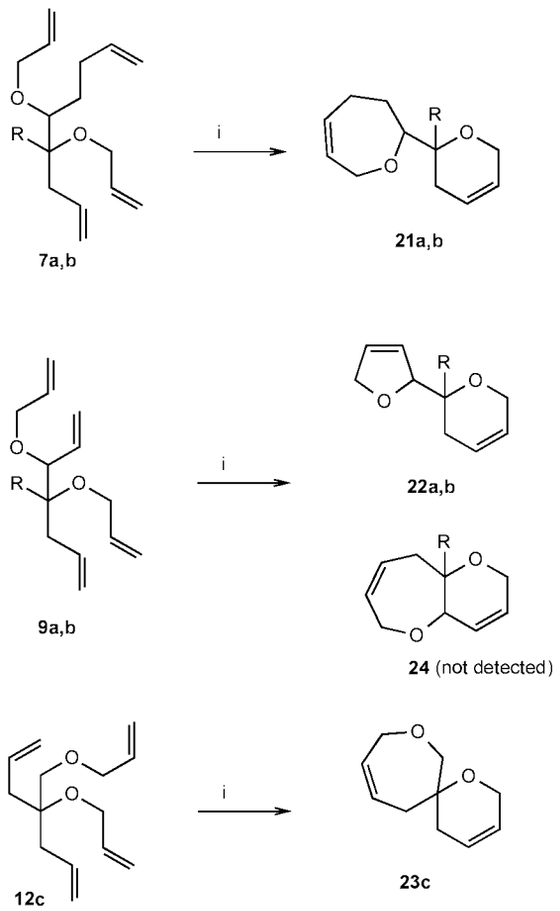
catalyst (**A**), ring closing metathesis is a smooth process for most starting materials. Normally, the reaction is quantitative with a catalyst loading of 3 mol% after 3 hours at ambient temperature. Ketones **5a**,**b** and aldehyde **11a** do not react under these conditions. These results are in accord with observations recently published by Fürstner *et al*. in the course of their studies directed to the synthesis of macrocyclic lactones: in certain cases, the presence of a carbonyl oxygen may inhibit the ring closing metathesis reaction by formation of a stable chelate complex.[38] The authors were able to circumvent this problem by addition of $TiOi\text{-}Pr_4$ as a Lewis-acid, in our case, however, no effect is observed. Ketone **5a** finally undergoes ring closing metathesis when the catalyst loading is increased to 10% and the reaction time to 24 hours. In the case of aldehyde **11a**, rapid conversion to dihydropyran **17a** is achieved with a catalyst loading of 8 mol% in refluxing toluene, whereas virtually no catalysis is observed under the standard conditions. The isolated yield, however, is moderate due to the formation of a variety of unidentified side products. We have also investigated the use of the novel carbene complex **B** for ring closing metathesis.[39] Its preparation is very convenient and avoids the use of hazardous starting materials.[40] Very recently, the correct carbene complex structure, rather than an allenylidene type structure[41] was published for **B**.[42,43] Very rapid conversion is observed for ring closing metathesis of **2a**–**c** with complex **B** in refluxing toluene, whereas virtually no conversion is observed at ambient temperature. Isolated yields are comparable to those obtained with Grubbs' catalyst, and in the case of **13c** significantly better. Ring closing metathesis of ketone **5b** in the presence of 4 mol% of **B** proceeds rapidly in refluxing toluene, however, the reaction stops at approximately 50% conversion. Thus, regardless of the catalyst employed, it appears to be more efficient for preparative purposes to conduct the RCM step with ester or alcohol functionalities in the side chain and modify these subsequently, if required. Ring closing metathesis of trienes **5**, **6** and **8** may in principle yield three different isomers. In the case of ketones **5**, only one isomer was detected as outlined above. In contrast, ring closing metathesis of **6a** yields an inseparable 3 : 1 mixture of dihydropyran **15a** and cycloheptene **20** (Table 1, entry 6). Under the same conditions, the methyl analogue is converted to the dihydropyran **15b**. From ring closing metathesis of triene **8a** (employed as a single diastereomer) the dihydropyran **18a** results as the only isolable product in moderate yield, whereas the analogous methyl compound **18b** (employed as a 2 : 1 mixture of diastereomers) is converted in poor yield (17%) to the dihydropyrans **19b** (2 : 1 mixture of diastereomers). It is quite striking that in nearly all cases where more than two olefinic moieties are available for ring closing metathesis, the yields are moderate (Table 1, entries 4–7) or poor (Table 1, entries 12, 13). We assume that a considerable amount of material is lost by intermolecular metathesis leading to oligomers in these cases, because the mass of crude material obtained from the ring closing metathesis reactions corresponds quite well to the expected amount, thus, it is unlikely that a significant amount of material is lost due to decomposition in volatile low-molecular weight fragments. There is obviously a strong preference for the formation of dihydropyrans over cycloalkenes or larger oxacycles. If two different six membered rings can result from the metathesis reaction (entries 12, 13, formation of **18a** and **19b**) the steric demand of the substituents seems to exert some influence on the regiochemical outcome of the cyclization.

Tetraenes can undergo a double ring closing metathesis leading to bicyclic products. For the tetraenes **7a**,**b** and **9a**,**b** in principle three different regioisomers may result: two annelated bicyclic products, and a product where two oxacycles are linked by a carbon–carbon single bond. Products of this type are the only ones observed for double ring closing metathesis of **7a**,**b** and **9a**,**b**. No carbacycles can be isolated from the reaction mixture, which is in accord with observations recently published by Mioskowski and co-workers for the formation of bisoxacyclic systems linked by methylene or ethylene bridges.[44] It is likely that cycloalkenes are formed as intermediates, however, a ring opening–ring closing metathesis sequence[45–50] may convert these to the final bisoxacyclic products **21** and **22**. Double ring closing metathesis of tetraene **12c** is also highly regioselective, leading to a spirocyclic product **23c** (Scheme 6). A cylcopentene can be assumed as an intermediate, however, it could not be detected from the reaction mixture.[51]

Structural assignment is based on H,H-COSY experiments and on the analysis of geminal and vicinal coupling constants. In the case of tetraenes **9a**,**b**, the alternative cyclization mode (formation of a fused dihydropyran-oxepine system **24**) can be excluded, because the coupling constant ^3J(H2′-H3′) of 6 Hz and the ^{13}C NMR data for the ether carbon atoms of the dihydrofuran fragment are indicative for the structure depicted in Scheme 6. NMR data for fused seven membered–six membered ring systems **24** are significantly different.[52] The relative stereochemistry was determined by NOESY experiments.

Conclusions

In conclusion we have developed a ring closing metathesis based synthesis of dihydropyrans and bisoxacyclic systems with a quaternary centre in the 2-position starting from α-hydroxy esters. Suitable metathesis precursors are available from these inexpensive starting materials in a one-pot-reaction by a sequential *O*-allylation–Wittig-rearrangement–*O*-allylation reaction. Efficiency of the ring closing metathesis reaction



Scheme 6 *Reagents and conditions* i) **A** (6 mol%), DCM, 20 °C, (41–64%).

depends on the substitution pattern of the starting material. While ester- or hydroxy-groups in the side chain give rapid conversions and excellent yields with low catalyst loadings, ketones and aldehydes do not react under the standard conditions, presumably due to chelation of the catalytically active species. If more than two terminal olefinic moities are available for the metathesis reaction, yields drop in most cases due to oligomerization reactions. Nevertheless, formation of six-membered oxacycles seems to be strongly preferred over all other regiochemical options. This becomes even more obvious for double ring closing metathesis reactions, which proceed with high regioselectivity to give exclusively dihydropyrans which are linked to a five- or a seven-membered oxacycle *via* a carbon–carbon bond.

Experimental

General remarks

All experiments were conducted in dry reaction vessels in an atmosphere of dry argon. Solvents were purified by standard procedures. ^{1}H NMR spectra were recorded at 400 MHz in $CDCl_3$ with $CHCl_3$ as internal standard ($\delta = 7.24$). ^{13}C NMR spectra were recorded at 100 MHz in $CDCl_3$ with $CDCl_3$ as internal standard ($\delta = 77.0$). *J* values are given in Hz. The number of coupled protons was analysed by DEPT experiments and is denoted by a number in parentheses following the δ_C value. Signal assignment for cyclic products follows a numbering scheme where the oxygen atom is numbered 1 and the quaternary carbon C2. IR spectra were recorded as films on NaCl plates or as KBr disks. The peak intensities are defined as strong (s), medium (m), and weak (w). Mass spectra were obtained at 70 eV. Melting points are not corrected. The ruthenium catalyst **A** was prepared following Grubbs' procedure.[3] Ruthenium complex **B** was prepared following a procedure by Hill and co-workers.[40]

General procedure for the preparation of allyl homoallyl ethers 2 from α-hydroxy esters

NaH (40.0 g, 60% dispersion in mineral oil, 1.00 mol) was slowly added to a solution of the corresponding α-hydroxy ester (0.87 mol) in THF (300 mL). After the addition was completed, the mixture was heated to reflux for 1 h, cooled to room temperature and allyl bromide (93 mL, 1.08 mol) was added dropwise. The reaction mixture was again heated to reflux for 1 h. Two further portions of NaH (40.0 g, 60% dispersion in mineral oil, 1.00 mol) and allyl bromide (93 mL, 1.08 mol) were added to the refluxing solution, and after each addition heating was continued for 1 h. The reaction mixture was cooled to room temperature, poured onto water (200 mL) and extracted with MTBE. The combined organic layers were dried with $MgSO_4$, filtered and evaporated. The residue was purified by distillation.

***rac*-2-Allyloxy-2-phenylpent-4-enoic acid methyl ester (2a).** Obtained from DL-methyl mandelate (34.7 g, 0.87 mol) as a colourless liquid (26.0 g, 44%), bp 86 °C (0.07 mbar). Found: C, 73.1%; H, 7.4%. $C_{15}H_{18}O_3$ requires C, 73.1%; H, 7.4%. IR (film): ν/cm^{-1} 732 m, 921 m, 1034 m, 1056 s, 1075 m, 1137 m, 1244 m, 1448 m, 1733 s; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.37 (2H, Ph), 7.30–7.17 (3H, Ph), 5.87 (dddd, 1H, $J = 17.3$, 10.5, 5.3, 5.3, *H*C–CH_2–O), 5.61 (dddd, 1H, $J = 17.1$, 10.3, 7.5, 6.3, *H*C–CH_2–C), 5.25 (dddd, 1H, $J = 17.3$, 1.5, 1.5, 1.5, H_2C=CH), 5.08 (dddd, 1H, $J = 10.5$, 1.5, 1.5, 1.5, H_2C=CH), 5.01 (dddd, 1H, $J = 17.1$, 1.5, 1.5, 1.5, H_2C=CH), 4.97 (dm, 1H, $J = 10.3$, H_2C=CH), 3.92 (dddd, 1H, $J = 12.3$, 5.3, 1.5, 1.5, H_2C–O), 3.76 (dddd, 1H, $J = 12.3$, 5.3, 1.5, 1.5, H_2C–O), 3.63 (s, 3H, H_3C–), 2.98 (dddd, 1H, $J = 14.8$, 7.5, 1.5, 1.5, H_2C–C), 2.89 (dddd, 1H, $J = 14.8$, 6.3, 1.5, 1.5, H_2C–C). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7 (0), 139.2 (0), 134.4 (1), 132.1 (1), 128.2 (1), 127.9 (1), 126.1 (1), 118.5 (2), 116.4 (2), 84.0 (0), 65.5 (2), 52.3 (3), 40.1 (2). MS (EI) *m*/*z* (%) 205 ($M^+ - 41$, 16), 189 (90), 157 (32), 145 (35), 129 (25), 105 (100), 71 (20).

***rac*-2-Allyloxy-2-methylpent-4-enoic acid ethyl ester (2b).** Obtained from (*S*)-ethyl lactate (60.0 g, 0.51 mol) as a colourless liquid (35.5 g, 44%), bp 85 °C (40 mbar). Found: C, 66.5%; H, 9.1%. $C_{11}H_{18}O_3$ requires C, 66.6%; H, 9.2%. IR (film) ν/cm^{-1} 920 m, 1110 m, 1157 m, 1252 m, 1733 s, 2983 m. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.95 (dddd, 1H, $J = 17.1$, 10.5, 5.3, 5.3, *H*C–CH_2–O), 5.81 (dddd, 1H, $J = 17.1$, 10.0, 7.3, 7.3, *H*C–CH_2–C), 5.31 (dm, 1H, $J = 17.1$, H_2C=CH), 5.15 (dm, 1H, $J = 17.1$, H_2C=CH), 5.14–5.08 (2H, H_2C=CH), 4.20 (q, 2H, $J = 7.3$, H_2C–O–C=O), 3.98 (d, 2H, $J = 5.3$, H_2C–O–C), 2.57 (dd, 1H, $J = 14.8$, 7.3, H_2C–C), 2.51 (dd, 1H, $J = 14.8$, 7.3, H_2C–C), 1.42 (s, 3H, H_3C–C), 1.30 (t, 3H, $J = 7.3$, H_3C–CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.6 (0), 137.4 (1), 132.4 (1), 118.3 (2), 116.3 (2), 79.8 (0), 65.7 (2), 60.7 (2), 42.7 (2), 21.1 (3), 14.1 (3). MS (EI) *m*/*z* (%) 199 ($M^+ + 1$, 100), 141 (50), 125 (30), 95 (18), 85 (20).

2-Allyl-2-allyloxypent-4-enoic acid butyl ester (2c). Obtained from butyl glycolate (29.4 g, 0.22 mol) as a colourless liquid (20.0 g, 36%), bp 80 °C (0.07 mbar). Deviating from the general procedure, addition of NaH and allyl bromide was repeated three times in this case. Found: C, 71.7%; H, 9.4%. $C_{15}H_{24}O_3$ requires C, 71.4%; H, 9.6%. IR (film) ν/cm^{-1} 918 s, 995 m, 1067 m, 1211 s, 1732 s, 2935 m, 2961 m. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88 (dddd, 1H, $J = 17.3$, 10.5, 5.5, 5.3, *H*C=CH_2), 5.74 (dddd, 1H, $J = 17.3$, 10.3, 7.5, 7.5, *H*C=CH_2), 5.70 (dddd, 1H, $J = 17.3$, 10.3, 7.5, 7.3, *H*C=CH_2), 5.25 (dddd, 1H, $J = 17.3$, 1.5, 1.5, 1.5, H_2C=CH), 5.10 (dddd, 1H, $J = 10.5$, 1.5, 1.5, 1.5, H_2C=CH), 5.09–5.03 (4H, H_2C=CH), 4.08 (t, 2H, $J = 6.8$, H_2C–O–C=O), 3.94 (dm, 2H, $J = 5.5$, H_2C–O–C–CH_2), 2.55 (dd, 2H, $J = 14.8$,

7.5, H_2C–C), 2.50 (dd, 2H, J = 14.8, 7.5, H_2C–C), 1.58 (ddm, 2H, J = 15.0, 7.3, H_2C–), 1.35 (ddm, 2H, J = 15.0, 7.3, H_2C–), 0.89 (t, 3H, J = 7.3, H_3C–). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8 (0), 134.5 (1), 132.2 (1), 118.6 (2), 116.4 (2), 82.1 (0), 65.5 (2), 64.7 (2), 38.8 (2), 30.6 (2), 19.1 (2), 13.5 (3). MS (EI) *m*/*z* (%) 253 (M^+ + 1, 100), 197 (15), 151 (15), 109 (16), 93 (20), 81 (45), 69 (46).

General procedure for the preparation of butenoic ketones (5)

Vinylmagnesium chloride (36 mL, 1.7 M solution in THF, 61 mmol) was added to a solution of the corresponding ester **2** (20 mmol) in Et_2O (100 mL) at −70 °C. The reaction mixture was stirred at this temperature for 1 h and then at 20 °C for 12 h. The reaction mixture was poured into saturated NH_4Cl solution, extracted with MTBE (3 times with 50 mL), dried with $MgSO_4$, filtered and evaporated. The residue was distilled.

***rac*-4-Allyloxy-4-phenylnona-1,8-dien-5-one (5a).** Obtained from **2a** (5.00 g, 20 mmol) as a colourless liquid (3.50 g, 64%), bp 90 °C (0.08 mbar). Found: C, 80.1%; H, 8.3%. $C_{18}H_{22}O_2$ requires C, 80.0%; H, 8.2%. IR (film) ν/cm^{-1} 702 s, 916 s, 996 s, 1072 s, 1447 m, 1642 m, 1716 s, 2924 m, 3078 m. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.27 (5H, Ph), 6.00 (dddd, 1H, J = 17.3, 10.5, 5.0, 4.8, *H*C–CH_2–O), 5.66 (dddd, 1H, J = 17.3, 10.3, 6.5, 6.5, *H*C–CH_2–CH_2), 5.59 (dddd, 1H, J = 17.3, 10.3, 7.3, 6.5, *H*C–CH_2–C–O), 5.45 (dddd, 1H, J = 17.3, 1.5, 1.5, 1.5, H_2C=CH), 5.24 (dddd, 1H, J = 10.5, 1.5, 1.5, 1.5, H_2C=CH), 5.10 (dddd, 1H, J = 17.3, 1.5, 1.5, 1.5, H_2C =CH), 5.04 (dddd, 1H, J = 10.3, 1.5, 1.5, 1.5, H_2C=CH), 4.92 (dddd, 1H, J = 17.3, 1.5, 1.5, 1.5, H_2C=CH), 4.87 (dddd, 1H, J = 10.3, 1.5, 1.5, 1.5, H_2C=CH), 4.05 (dddd, 1H, J = 12.8, 4.8, 1.5, 1.5, H_2C–O), 3.85 (dddd, 1H, J = 12.8, 5.0, 1.5, 1.5, H_2C–O), 3.18 (dddd, 1H, J = 15.5, 7.3, 1.5, 1.5, H_2C–C–O), 2.85 (dddd, 1H, J = 15.5, 6.5, 1.5, 1.5, H_2C–C–O), 2.68 (ddd, 1H, J = 15.1, 8.5, 6.5, H_2C–C=O), 2.58 (ddd, 1H, J = 15.1, 8.5, 6.5, H_2C–C=O), 2.23 (ddddd, 1H, J = 18.1, 8.5, 6.5, 6.5, 1.5, 1.5, H_2C–CH_2–C=O), 2.14 (ddddd, 1H, J = 18.1, 8.5, 6.5, 6.5, 1.5, 1.5, H_2C–CH_2–C=O). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.4 (0), 139.1 (0), 137.2 (1), 134.2 (1), 132.3 (1), 128.5 (1), 127.7 (1), 125.9 (1), 118.3 (2), 116.0 (2), 114.9 (2), 87.7 (0), 64.4 (2), 37.2 (2), 36.0 (2), 27.5 (2). MS (EI) *m*/*z* (%) 213 (M^+ − 57, 42), 195 (30), 187 (60), 171 (15), 145 (18), 129 (15), 105 (100), 69 (20).

***rac*-4-Allyloxy-4-methylnona-1,8-dien-5-one (5b).** Obtained from **2b** (10.00 g, 50 mmol) as a colourless liquid (8.20 g, 78%), bp 100 °C (0.12 mbar). Found: C, 75.0%; H, 9.6%. $C_{13}H_{20}O_2$ requires C, 75.0%; H, 9.7%. IR (film) ν/cm^{-1} 917 m, 996 m, 1071 w, 1716 s, 2934 w, 2981 w. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.94 (dddd, 1H, J = 17.1, 10.3, 5.0, 5.0, *H*C–CH_2–O), 5.83 (dddd, 1H, J = 17.1, 10.3, 6.8, 6.3, *H*C–CH_2–CH_2), 5.72 (dddd, 1H, J = 16.1, 11.3, 7.3, 7.0, *H*C–CH_2–C–O), 5.34 (dddd, 1H, J = 17.3, 1.5, 1.5, 1.5, H_2C=CH), 5.19 (dddd, 1H, J = 10.3, 1.5, 1.5, 1.5, H_2C=CH), 5.10 (dm, 1H, J = 16.1, H_2C=CH), 5.10 (dm, 1H, J = 11.3, H_2C=CH), 5.06 (dm, 1H, J = 17.1, H_2C=CH), 4.98 (dm, 1H, J = 10.5, H_2C=CH), 3.93 (dddd, 1H, J = 12.5, 5.0, 1.5, 1.5, H_2C–O), 3.87 (dddd, 1H, J = 12.5, 5.0, 1.5, 1.5, H_2C–O), 2.74 (dd, 1H, J = 7.5, 4.5, H_2C–C=O), 2.72 (dd, 1H, J = 7.5, 4.5, H_2C–C=O), 2.52 (dd, 1H, J = 14.6, 7.0, H_2C–C–O), 2.43 (dd, 1H, J = 14.6, 7.3, H_2C–C–O), 2.31 (dm, 1H, J = 13.8, H_2C–CH_2–C=O), 2.31 (dm, 1H, J = 13.8, H_2C–CH_2–C=O), 1.31 (s, 3H, H_3C–). ^{13}C NMR (100 MHz, $CDCl_3$) δ 213.4 (0), 137.4 (1), 134.5 (1), 132.4 (1), 118.5 (2), 116.1 (2), 115.1 (2), 84.1 (0) 64.8 (2), 40.9 (2), 36.1 (2), 27.4 (2), 20.3 (3). MS (EI) *m*/*z* (%) 209 (M^+ + 1, <5), 191 (12), 151 (100), 133 (20), 125 (15), 109 (12), 95 (15), 81 (18).

General procedure for the preparation of alcohols 6 and 10

DIBAL-H (19 mL, 107 mmol) was added dropwise to a solution of the corresponding ester (50 mmol) or ketone (90 mmol) in Et_2O (200 mL) at −70 °C. After addition is completed, the mixture was warmed to 20 °C and stirring was continued for 1 h. The reaction was quenched by addition of methanol (15 mL), and the solution was washed with HCl (aq) (1 M). The aqueous layer was extracted with methyl *tert*-butyl ether (MTBE) (3 times 20 mL), and the combined organic extracts were dried with $MgSO_4$, filtered and evaporated.

(4*S,5*R**)-4-Allyloxy-4-phenylnona-1,8-dien-5-ol (6a).** Obtained from **5a** (6.10 g, 22.6 mmol) as a colourless liquid (3.50 g, 64%). Found: C, 79.4%; H, 8.9%. $C_{18}H_{24}O_2$ requires C, 79.4%; H, 8.9%. IR (film) ν/cm^{-1} 705 s, 916 s, 1069 s, 1446 m, 1640 m, 2925 m, 2979 w, 3568 brw. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.15 (5H, Ph), 6.00 (dddd, 1H, J = 17.1, 10.5, 7.5, 6.3, *H*C–CH_2–C), 5.84 (dddd, 1H, J = 17.1, 10.5, 5.3, 5.0, *H*C–CH_2–O), 5.62 (dddd, 1H, J = 17.1, 10.3, 6.5, 6.5, *H*C–CH_2–CH_2), 5.24 (dm, 1H, J = 17.1, H_2C=CH), 5.14 (dddd, 1H, J = 17.1, 1.5, 1.5, 1.5, H_2C=CH), 5.07 (dm, 1H, J = 10.3, H_2C=CH), 5.06 (dm, 1H, J = 10.3, H_2C=CH), 4.85 (dddd, 1H, J = 17.1, 1.5, 1.5, 1.5, H_2C=CH), 4.81 (dddd, 1H, J = 10.3, 1.5, 1.5, 1.5, H_2C=CH), 3.88 (dddd, 1H, J = 12.6, 5.3, 1.5, 1.5, H_2C–O), 3.69 (dm, 1H, J = 12.6, H_2C–O), 3.69 (m, 1H, *H*C–OH), 3.05 (dd, 1H, J = 15.5, 7.5, H_2C–C–O), 2.70 (dd, 1H, J = 15.5, 6.3, H_2C–C–O), 2.14 (m, 1H, H_2C–CH_2–C–OH), 1.94 (m, 1H, H_2C–CH_2–C–OH), 1.94 (brs, 1H, *H*O–), 1.57 (dddd, 1H, J = 15.5, 9.0, 7.0, 1.5, H_2C–C–OH), 1.03 (dddd, 1H, J = 15.5, 9.3, 5.0, 1.5, H_2C–C–OH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.4 (0), 138.5 (1), 134.9 (1), 134.0 (1), 128.1 (1), 127.4 (1), 127.3 (1), 117.6 (2), 115.5 (2), 114.5 (2), 83.0 (0), 76.4 (1), 63.6 (2), 36.2 (2), 30.6 (2), 30.2 (2). MS (EI) *m*/*z* (%) 215 (M^+ − 57, 50), 197 (70), 187 (45), 145 (25), 131 (27), 105 (100), 91 (20), 69 (20), 55 (22).

(4*R,5*R**)- and (4*R**,5*S**)-4-Allyloxy-4-methylnona-1,8-dien-5-ol (6b).** Obtained from **5b** (5.00 g, 24 mmol) as a colourless liquid (5.02 g, 99%). 2:1 mixture of diastereomers. Found: C, 74.1%; H, 10.5%. $C_{13}H_{22}O_2$ requires C, 74.2%; H:,10.5%. IR (film) ν/cm^{-1} 914 s, 997 m, 1066 s, 1380 w, 1641 m, 2927 m, 2979 m, 3476 brw. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.93–5.74 (3H, *H*C=CH_2), 5.24 (dddd, 1H, J = 17.1, 1.5, 1.5, 1.5, H_2C=CH), 5.10 (dddd, 1H, J = 10.3, 1.5, 1.5, 1.5, H_2C=CH), 5.08–4.99 (3H, H_2C=CH), 4.94 (dddd, 1H, J = 10.3, 1.5, 1.5, 1.5, H_2C=CH), 3.95–3.89 (2H, H_2C–O), 3.55 (ddd, 1H, J = 9.8, 3.3, 3.0, *H*C–OH), 2.40 (m, 1H, *H*O–), 2.40–2.03 (4H, H_2C–), 1.60–1.40 (2H, H_2C–), 1.08 (s, 3H, H_3C–). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6 (1), 135.3 (1), 133.3 (1), 117.7 (2), 115.9 (2), 114.7 (2), 79.4 (0), 74.1 (1), 62.5 (2), 38.9 (2), 30.8 (2), 30.2 (2), 17.8 (3). MS (EI) *m*/*z* (%) 153 (M^+ − 57, 100), 135 (60), 111 (8), 95 (15), 81 (5), 70 (5). NMR-data of the minor diastereomer: ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6 (1), 135.5 (1), 134.3 (1), 117.3 (2), 115.6 (2), 114.7 (2), 79.0 (0), 74.8 (1), 62.5 (2), 39.1 (2), 31.0 (2), 30.3 (2), 19.0 (3).

***rac*-2-Allyloxy-2-phenylpent-4-en-1-ol (10a).** Obtained from **2a** (12.0 g, 49 mmol) as a colourless liquid (8.33 g, 78%), bp 90 °C (0.06 mbar). Found: C, 76.8%; H, 8.3%. $C_{14}H_{18}O_2$ requires C, 77.0%; H, 8.3%. IR (film) ν/cm^{-1} 702 s, 770 m, 919 s, 997 s, 1070 s, 1126 s, 1446 m, 1495 m, 1641 m, 2881 m, 2918 m, 2979 m, 3076 m, 3443 brm. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.25 (5H, Ph), 5.93 (dddd, 1H, J = 17.3, 10.5, 5.3, 5.3, *H*C–CH_2–O), 5.73 (dddd, 1H, J = 17.3, 10.3, 7.0, 7.0, *H*C–CH_2–C), 5.32 (dddd, 1H, J = 17.3, 1.5, 1.5, 1.5, H_2C=CH), 5.16 (dddd, 1H, J = 10.5, 1.5, 1.5, 1.5, H_2C=CH), 5.12 (dddd, 1H, J = 17.3, 1.5, 1.5, 1.5, H_2C=CH), 5.07 (dddd, 1H, J = 10.3, 1.5, 1.5, 1.5, H_2C=CH), 3.85 (dddd, 1H, J = 12.3, 5.3, 1.5, 1.5, H_2C–O–C), 3.84 (d, 2H, J = 6.5, H_2C–OH), 3.78 (dddd, 1H, J = 12.3, 5.3, 1.5, 1.5, H_2C–O–C), 2.77 (dddd, 1H, J = 14.6, 7.0, 1.5, 1.5, H_2C–C), 2.71 (dddd, 1H, J = 14.6, 7.0, 1.5, 1.5, H_2C–C), 1.96 (t, 1H, J = 6.5, *H*O–). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1 (0), 134.8 (1), 133.1 (1), 128.3 (1), 127.4 (1), 126.4 (1), 118.2 (2),

116.1 (2), 81.0 (0), 65.6 (2), 63.5 (2), 39.5 (2). MS (EI) *m*/*z* (%) 161 ($M^+ - 57$, 10), 142 (20), 131 (100), 116 (35), 105 (20), 91 (72), 65 (22), 51 (11).

***rac*-2-Allyloxy-2-methylpent-4-en-1-ol (10b).** Obtained from **2b** (3.20 g, 16 mmol) as a colourless liquid (2.50 g, 99%). IR (film) ν/cm^{-1} 917 s, 999 m, 1055 s, 1125 m, 2873 m, 2931 m, 2978 m, 3427 brm. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.82 (dddd, 1H, J = 17.1, 10.3, 5.3, 5.3, *H*C–CH_2–O), 5.71 (dddd, 1H, J = 17.1, 10.3, 7.3, 7.3, *H*C–CH_2–C), 5.19 (dddd, 1H, J = 17.1, 1.5, 1.5, 1.5, H_2C=CH), 5.04 (dddd, 1H, J = 10.3, 1.5, 1.5, 1.5, H_2C=CH), 5.00 (dddd, 1H, J = 17.1, 1.5, 1.5, 1.5, H_2C=CH), 5.00 (dddd, 1H, J = 10.3, 1.5, 1.5, 1.5, H_2C=CH), 3.86 (d, 2H, J = 5.3, H_2C–O), 3.40 (d, 1H, J = 11.5, H_2C–OH), 3.35 (d, 1H, J = 11.5, H_2C–OH), 2.41 (brs, 1H, *H*O–), 2.25 (dddd, 1H, J = 15.8, 7.3, 1.5, 1.5, H_2C–C), 2.21 (dddd, 1H, J = 15.8, 7.3, 1.5, 1.5, H_2C–C), 1.17 (s, 3H, H_3C–). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.3 (1), 133.5 (1), 117.7 (2), 115.8 (2), 77.1 (0), 66.9 (2), 62.6 (2), 39.8 (2), 19.5 (2). MS (EI) *m*/*z* (%) 125 ($M^+ - 31$, 10), 115 (12), 99 (95), 81 (100), 69 (28), 57 (15).

***rac*-2-Allyloxy-2-allylpent-4-en-1-ol (10c).** Obtained from **2c** (1.75 g, 6.9 mmol) as a colourless liquid (1.23 g, 97%). Found: C, 71.9%; H, 9.8%. $C_{11}H_{18}O_2$ requires C, 72.5%; H, 9.9%. IR (film) ν/cm^{-1} 916 s, 1071 s, 1439 m, 1640 s, 2925 m, 3076 m, 3445 s. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84 (ddt, 1H, J = 17.3, 10.3, 5.3, *H*C–CH_2–O), 5.76 (ddt, 2H, J = 17.1, 10.3, 7.3, *H*C–CH_2–C), 5.22 (dddd, 1H, J = 17.1, 1.8, 1.8, 1.8, H_2C=CH), 5.10–5.01 (3H, H_2C=CH), 3.92 (ddd, 1H, J = 5.3, 1.5, 1.5, OCH_2-CH=CH), 3.44 br (d, 2H, J = 4.3, –CH_2OH), 2.31 (dd, 2H, J = 14.3, 7.3, CH*H*CH=CH_2), 2.22 (dd, 1H, J = 14.3, 7.3, CH*H*CH=CH_2), 2.05 br (t, 1H, J = 4.3, H_2C–O*H*). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.0 (1), 133.1 (1), 118.1 (2), 116.0 (2), 78.7 (0), 64.5 (2), 62.4 (2), 37.3 (2). MS (EI) *m*/*z* (%) 125 ($M^+ - 57$, 60), 107 (100), 81 (95).

General procedure for the preparation of alcohols 8

Under an atmosphere of dry argon, DIBAL-H (8.1 mL, 45 mmol) was slowly added to a solution of the ester **2** (41 mmol) in ether at −90 °C. The reaction mixture was stirred at −70 °C for 30 min, and then vinylmagnesium chloride (36 mL 1.7 M solution in THF, 61 mmol) was added. The reaction mixture was allowed to warm to 20 °C, and stirring was continued for 12 h. The mixture was hydrolyzed with diluted hydrochloric acid (1 M), extracted with ether, and then dried with $MgSO_4$. The solvent was evaporated and the crude product purified by column chromatography on silica (using cyclohexane–MTBE mixture (20 : 1) as eluent) or by distillation.

(3*S,4*R**)-4-Allyloxy-4-phenylhepta-1,6-dien-3-ol (8a).** Obtained from **2a** (10.00 g, 41 mmol) as a mixture of two diastereomers (dr = 2.4 : 1). After removal of the minor diastereomer by chromatography (3*S**,4*R**)-**8a** was isolated as a colourless liquid, yield: 5.00 g (50%). Found: C, 78.7%; H, 8.3%. $C_{16}H_{20}O_2$ requires C, 78.7%; H, 8.3%. IR (film) ν/cm^{-1} 706 s, 920 s, 1069 s, 1233 m, 1446 m, 1732 m, 3077 m, 3512 brm. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.26 (5H, Ph), 6.01–5.90 (2H, *H*C=CH_2), 5.39 (ddd, 1H, J = 17.5, 10.3, 7.0, *H*C–CH–OH), 5.32 (dddd, 1H, J = 17.5, 1.5, 1.5, 1.5, H_2C=CH), 5.22 (dddd, 1H, J = 17.1, 1.5, 1.5, 1.5, H_2C=CH), 5.19 (dddd, 1H, J = 17.5, 1.5, 1.5, 1.5, H_2C=CH), 5.18 (dddd, 1H, J = 10.3, 1.5, 1.5, 1.5, H_2C=CH), 5.19 (dddd, 1H, J = 10.3, 1.5, 1.5, 1.5, H_2C=CH), 5.11 (dddd, 1H, J = 10.3, 1.5, 1.5, 1.5, H_2C=CH), 4.41 (dm, 1H, J = 7.0, *H*C–OH), 3.97 (dddd, 1H, J = 12.3, 5.8, 1.5, 1.5, H_2C–O), 3.83 (dddd, 1H, J = 12.3, 5.3, 1.5, 1.5, H_2C–O), 2.94 (ddm, 1H, J = 15.5, 7.0, H_2C–C), 2.83 (dddd, 1H, J = 15.5, 5.5, 1.5, 1.5, H_2C–C), 2.73 (d, 1H, J = 2.5, *H*O–). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.0 (0), 135.7 (1), 134.6 (1), 133.1 (1), 127.7 (1), 127.5 (1), 127.3 (1), 118.3 (2), 118.1 (2), 116.0 (2), 82.1 (0), 77.1 (1), 63.8 (2), 36.7 (2). MS (EI) *m*/*z* (%) 203 ($M^+ - 41$, <5), 187 (100), 169 (33), 145 (22), 117 (23), 105 (95), 69 (28), 55 (15). NMR data for the minor diastereomer (partial overlapping of signals with the major isomer): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.26 (5H, Ph), 6.09 (dddd, 1H, J = 17.1, 10.3, 6.8, 6.5, *H*C=CH_2), 4.00 (dddd, 1H, J = 13.1, 5.3, 1.5, 1.5, H_2C–O), 3.81 (dddd, 1H, J = 13.1, 4.8, 1.5, 1.5, H_2C–O), 3.12 (ddm, 1H, J = 15.3, 7.5, H_2C–C), 2.78 (ddm, 1H, J = 15.3, 6.5, H_2C–C), 2.72 (brs, 1H, *H*O–). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.0 (0), 135.8 (1), 134.8 (1), 133.9 (1), 127.9 (1), 127.5 (1), 127.3 (1), 117.8 (2), 116.3 (2), 115.5 (2), 83.0 (0), 77.6 (1), 63.7 (2), 36.5 (2).

(3*S,4*S**)- and (3*S**,4*R**)-4-Allyloxy-4-methylhepta-1,6-dien-3-ol (8b).** Obtained from **2b** (10.00 g, 50 mmol) as a mixture of two diastereomers (dr = 1.8 : 1). After distillation (bp 90 °C/0.08 mbar) **8b** was isolated as a colourless liquid, yield: 7.20 g (78%). Found: C, 72.4%; H, 10.0%. $C_{11}H_{18}O_2$ requires C, 72.5%; H, 10.0%. IR (film) ν/cm^{-1} 919 s, 996 s, 1065 s, 1129 m, 1378 m, 1423 m, 1458 m, 2981 m, 3464 brm. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.95–5.76 (3H, *H*C=CH_2), 5.32 (dm, 1H, J = 17.5, H_2C=CH), 5.25 (dm, 1H, J = 17.1, H_2C=CH), 5.20 (dm, 1H, J = 10.5, H_2C=CH), 5.12–5.01 (3H, H_2C=CH), 4.07 (d, 1H, J = 5.8, *H*C–OH), 3.96 (d, 2H, J = 5.0, H_2C–O), 2.59, 2.46 (s, 1H, *H*O–), 2.43 (dd, 1H, J = 14.8, 7.0, H_2C–C), 2.36 (dd, 1H, J = 14.8, 7.5, H_2C–C), 2.25 (dd, 1H, J = 14.8, 7.5, H_2C–C), 2.17 (dd, 1H, J = 14.8, 7.0, H_2C–C), 1.13, 1.09 (s, 3H, H_3C–). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.4 (1), 135.8 (1), 135.3 (1), 135.1 (1), 134.1 (1), 133.2 (1), 118.0 (2), 117.7 (2), 117.5 (2), 116.9 (2), 116.0 (2), 155.7 (2), 79.0 (0), 78.8 (0), 76.7 (1), 76.2 (1), 62.7 (2), 62.7 (2), 39.2 (2), 38.9 (2), 19.0 (3), 17.9 (3). MS (EI) *m*/*z* (%) 165 ($M^+ - 17$, <5), 141 (8), 125 (100), 107 (60), 95 (20), 81 (22), 69 (18), 55 (78).

***rac*-2-Allyloxy-2-phenylpent-4-enal (11a).** A solution of alcohol **10a** (5.00 g, 22.9 mmol) in DCM (20 mL) was added dropwise to a suspension of PDC (12.93 g, 34.3 mmol) in DCM (80 mL). The mixture was stirred at 20 °C for 24 hours, filtered and evaporated. The residue was dissolved in ether (100 mL) and filtered through a 10 cm pad of silica. The organic layer was subsequently washed with ice-cold diluted HCl (aq), $NaHCO_3$ (aq) and brine, dried with $MgSO_4$, filtered, evaporated and purified by Kugelrohr distillation at 140 °C (0.13 mbar) to give **11a** as a colourless liquid. Yield: 3.33 g (67%). IR (film) ν/cm^{-1} 706 s, 929 m, 990 s, 1071 m, 1732 s, 2809 w, 3079 w. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.48 (s, 1H, –CHO), 7.35–7.18 (5H, Ph), 5.87 (dddd, 1H, J = 17.3, 10.3, 5.3, 5.3, *H*C–CH_2–O), 5.56 (dddd, 1H, J = 17.3, 10.3, 7.0, 6.8, *H*C–CH_2–C), 5.29 (dddd, 1H, J = 17.3, 1.5, 1.5, 1.5, H_2C=CH), 5.11 (dddd, 1H, J = 10.3, 1.5, 1.5, 1.5, H_2C=CH), 5.03 (dddd, 1H, J = 17.3, 1.5, 1.5, 1.5, H_2C=CH), 4.98 (dddd, 1H, J = 10.3, 1.3, 1.3, 1.3, H_2C=CH), 3.92 (dddd, 1H, J = 12.3, 5.3, 1.5, 1.5, H_2C–O–C), 3.87 (dddd, 1H, J = 12.3, 5.3, 1.5, 1.5, H_2C–O–C), 2.96 (ddm, 1H, J = 15.1, 7.0, H_2C–C), 2.78 (ddm, 1H, J = 15.1, 7.0, H_2C–C). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.1 (0), 136.4 (0), 134.1 (1), 131.5 (1), 128.7 (1), 128.2 (1), 126.7 (1), 118.8 (2), 116.7 (2), 85.9 (0), 64.7 (2), 36.4 (2). MS (EI) *m*/*z* (%) 217 ($M^+ + 1$, 30), 187 (70), 131 (80), 105 (100).

General procedure for the preparation of tetraenes 7, 9, 12

NaH (0.35 g, 60% dispersion in mineral oil, 8.8 mmol) was slowly added to a solution of the corresponding alcohol (7.3 mmol) in THF (50 mL) and heated to reflux for 1 h. Allyl bromide (1.0 mL, 11.0 mmol) was added and the reaction mixture was again refluxed for 1 h. After cooling to ambient temperature water (100 mL) was added and the solution was extracted with MTBE (3 times 50 mL). The combined organic

layers were dried with $MgSO_4$, filtered and evaporated. The residue was purified by flash chromatography on silica to give the corresponding tetraene as a colourless liquid.

[(1*S,2*R**)-1-Allyl-1,2-bis(allyloxy)hex-5-enyl]benzene (7a).** Obtained from alcohol **6a** (2.00 g, 7.3 mmol). Yield: 2.20 g (96%). Found: C, 81.0%; H, 9.1%. $C_{21}H_{28}O_2$ requires C, 80.7%; H, 9.0%. IR (film) ν/cm^{-1} 704 s, 916 s, 994 m, 1070 s, 1096 m, 1132 m, 1446 w, 2860 w, 3076 w. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.38 (2H, Ph), 7.35–7.30 (2H, Ph), 7.28–7.22 (1H, Ph), 6.06–5.89 (3H, *H*C=CH$_2$), 5.71 (dddd, 1H, J = 17.3, 10.3, 7.0, 6.3, *H*C=CH$_2$), 5.35 (dddd, 1H, J = 17.1, 1.5, 1.5, 1.5, H_2C=CH$_2$), 5.28 (dddd, 1H, J = 17.1, 1.5, 1.5, 1.5, H_2C=CH), 5.19 (dddd, 1H, J = 17.3, 1.5, 1.5, 1.5, H_2C=CH), 5.18–5.11 (3H, H_2C=CH), 4.94 (dddd, 1H, J = 17.3, 1.5, 1.5, 1.5, H_2C=CH), 4.90 (dddd, 1H, J = 10.3, 1.5, 1.5, 1.5, H_2C=CH), 4.24 (dddd, 1H, J = 12.8, 5.3, 1.5, 1.5, H_2C–O), 4.16 (dddd, 1H, J = 12.8, 5.3, 1.5, 1.5, H_2C–O), 3.96 (dddd, 1H, J = 12.8, 5.0, 1.5, 1.5, H_2C–O), 3.84 (dddd, 1H, J = 12.8, 4.5, 1.5, 1.5, H_2C–O), 3.57 (dd, 1H, J = 9.3, 2.8, *H*C–O), 3.13 (ddm, 1H, J = 15.6, 7.5, H_2C–C), 2.82 (dd, 1H, J = 15.6, 5.8, H_2C–C), 2.12 (dm, 1H, J = 15.1, H_2C–CH$_2$–CH), 2.02 (dm, 1H, J = 15.1, H_2C–CH$_2$–CH), 1.66 (dddd, 1H, J = 14.1, 9.3, 6.8, 2.8, H_2C–CH–C), 1.16 (dddd, 1H, J = 14.3, 9.3, 9.3, 5.3, H_2C–CH–C). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0 (0), 138.8 (1), 135.3 (1), 135.1 (1), 134.3 (1), 127.6 (1), 127.5 (1), 126.9 (1), 117.5 (2), 115.9 (2), 115.1 (2), 114.5 (2), 83.5 (0), 83.0 (1), 73.7 (2), 63.1 (2), 37.2 (2), 30.9 (2), 30.1 (2). MS (EI) *m*/*z* (%) 255 (M$^+$ − 57, 28), 197 (100), 187 (90).

(4*S,5*S**)- and (4*R**,5*S**)-4,5-Bis(allyloxy)4-methylnona-1,8-diene (7b).** Obtained from **6b** (3.20 g, 15.2 mmol) as a 2:1 mixture of diastereomers after chromatography. Yield: 2.20 g (58%). Found: C, 76.9%; H, 10.5%. $C_{16}H_{26}O_2$ requires C, 76.8%; H, 10.5%. IR (film) ν/cm^{-1} 914 s, 1072 m, 1095 m, 1130 m, 1641 m, 2858 m, 2928 m, 2979 m, 3077 m. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.96–5.74 (4H, *H*C=CH$_2$), 5.24 (dddd, 1H, J = 17.1, 1.5, 1.5, 1.5, H_2C=CH$_2$), 5.13–5.02 (5H, H_2C=CH), 5.01 (dddd, 1H, J = 10.5, 1.5, 1.5, 1.5, H_2C=CH), 4.94 (dm, 1H, J = 10.0, H_2C=CH), 4.17 (dddd, 1H, J = 12.6, 5.5, 1.5, 1.5, H_2C–O), 4.09–3.87 (3H, H_2C–O), 3.26 (dd, 1H, J = 9.8, 2.0, *H*C–O), 2.44 (ddm, 1H, J = 14.8, 7.0, H_2C–), 2.33–2.23 (2H, H_2C–), 2.08 (ddm, 1H, J = 14.8, 7.3, H_2C–), 1.65 (dddm, 1H, J = 13.8, 7.0, 2.3, H_2C–), 1.52 (dddm, 1H, J = 13.8, 9.3, 5.3, H_2C–), 1.15 (s, 3H, H_3C–). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7 (1), 135.9 (1), 135.5 (1), 134.2 (1), 117.2 (2), 115.9 (2), 115.2 (2), 114.7 (2), 84.1 (1), 80.0 (0), 74.0 (1), 63.1 (2), 39.6 (2), 30.9 (2), 30.0 (2), 19.7 (3). MS (EI) *m*/*z* (%) 193 (M$^+$ − 57, 80), 165 (10), 151 (20), 135 (30), 125 (45), 115 (50), 95 (40), 81 (100), 67 (76), 55 (56). NMR-data of the minor diastereomer (obtained from the mixture): ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.33 (ddm, 1H, J = 14.5, 7.0, H_2C–), 1.76 (ddm, 1H, J = 13.8, 6.5, H_2C–). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.9 (1), 135.7 (1), 135.3 (1), 134.4 (1), 117.3 (2), 115.9 (2), 115.3 (2), 114.6 (2), 82.8 (1), 79.4 (0), 73.5 (2), 62.7 (2), 40.1 (2), 31.2 (2), 29.8 (2), 18.7 (3).

(1*S,2*R**)-[1-Allyl-1,2-bis(allyloxy)but-3-enyl]benzene (9a).** Obtained from (3*S**,4*R**)-**8a** (2.70 g, 11.0 mmol). Yield: 2.00 g (64%). Found: C, 80.4%, H: 8.6%. $C_{19}H_{24}O_2$ requires C, 80.2%; H, 8.5%. IR (film) ν/cm^{-1} 712 m, 919 s, 994 m, 1072 s, 1124 m, 1422 w, 1446 w, 2865 w, 2982 w, 3077w. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.22 (5H, Ph), 5.95 (ddm, 1H, J = 17.3, 10.3, *H*C=CH$_2$), 5.94–5.80 (2H, *H*C=CH$_2$), 5.55 (ddd, 1H, J = 17.5, 10.3, 7.3, *H*C=CH$_2$), 5.38 (dddd, 1H, J = 17.3, 1.7, 1.7, 1.7, H_2C=CH), 5.24 (dddd, 1H, J = 10.3, 1.7, 1.7, 1.7, H_2C=CH), 5.22 (dddd, 1H, J = 17.3, 1.7, 1.7, 1.7, H_2C=CH), 5.18 (dddd, 1H, J = 10.0, 1.7, 1.7, 1.7, H_2C=CH), 5.17–5.10 (4H, H_2C=CH), 4.04–3.96 (4H, H_2C–O, *H*C–O), 3.81 (dddd, 1H, J = 13.1, 5.5, 1.7, 1.7, H_2C–O), 3.12 (dd, 1H, J = 14.8, 7.3, H_2C–C), 2.72 (dddd, 1H, J = 14.8, 6.3, 1.7, 1.7, H_2C–C). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.3 (0), 135.2 (1), 135.0 (1), 134.7 (1), 133.7 (1), 127.8 (1), 127.4 (1), 126.8 (1), 119.0 (2), 118.1 (2), 115.9 (2), 115.0 (2), 82.9 (1), 82.5 (0), 69.4 (2), 63.6 (2), 38.8 (2). MS (EI) *m*/*z* (%) 227 (M$^+$ − 57, <5), 187 (30), 169 (15), 157 (15), 145 (20), 129 (15), 117 (20), 105 (100), 91 (18), 81 (18), 69 (30), 55 (20).

(3*R,4*R**)- and (3*R**,4*S**)-3,4-Bis(allyloxy)4-methylhepta-1,6-diene (9b).** Obtained from **8b** (2.40 g, 13.2 mmol) as a mixture of two diastereomers (dr = 1.8:1). Yield: 1.80 g (61%). Found: C, 75.8%, H: 9.9%. $C_{14}H_{22}O_2$ requires C, 75.6%; H, 10.0%. IR (film) ν/cm^{-1} 917 s, 995 m, 1074 s, 1128 m, 1641 w, 2862 w, 2980 m, 3078 w. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92–5.75 (4H, *H*C=CH$_2$), 5.23 (dddd, 1H, J = 17.3, 2.0, 2.0, 2.0, H_2C=CH), 5.23 (dddd, 1H, J = 17.3, 2.0, 2.0, 2.0, H_2C=CH), 5.22 (dddd, 1H, J = 17.3, 1.5, 1.5, 1.5, H_2C=CH), 5.12 (dddd, 1H, J = 10.3, 1.5, 1.5, 1.5, H_2C=CH), 5.08–5.01 (3H, H_2C=CH), 4.97 (dm, 1H, J = 10.3, H_2C=CH), 4.09–3.95 (3H, H_2C–O), 3.77 (dddd, 1H, J = 12.8, 1.5, 1.5, 1.5, H_2C–O), 3.68 (d, 1H, J = 7.0, *H*C–O), 2.48 (dd, 1H, J = 14.5, 7.3, H_2C–C), 2.27 (dd, 1H, J = 14.5, 7.3, H_2C–C), 1.13 (s, 3H, H_3C–). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.8 (1), 135.0 (1), 134.9 (1), 134.2 (1), 118.3 (2), 117.4 (2), 116.8 (2), 115.3 (2), 83.8 (0), 78.4 (0), 69.8 (2), 63.2 (2), 40.2 (2), 18.0 (3). MS (EI) *m*/*z* (%) 165 (M$^+$ − 57, 18), 125 (30), 107 (55), 95 (37), 81 (54), 55 (100). NMR data of the minor diastereomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.65 (dddd, 1H, J = 17.1, 10.0, 7.0, 7.0, *H*C=CH$_2$), 3.62 (d, 1H, J = 7.8, *H*C–O), 2.56 (dd, 1H, J = 14.5, 7.0, H_2C–C), 1.24 (s, 3H, H_3C–). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.1 (1), 136.0 (1), 135.1 (1), 134.8 (1), 117.4 (2), 116.3 (2), 116.2 (2), 115.6 (2), 85.4 (0), 78.5 (0), 69.7 (2), 63.8 (2), 39.8 (2), 20.4 (3).

4,4-Bis(allyloxy)methylhepta-1,6-diene (12c). Obtained from **10c** (1.20 g, 6.6 mmol). Yield: 0.87 g (59%). IR (film) ν/cm^{-1} 811 s, 916 s, 1090 s, 1640 m, 2861 s, 3077 s. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.95–5.75 (4H, –*H*C=CH$_2$), 5.27–5.03 (8H, –HC=C*H*$_2$), 4.01 (ddd, 2H, J = 5.3, 1.5, 1.5, –OC*H*$_2$CH=CH$_2$), 3.94 (ddd, 2H, J = 5.4, 1.5, 1.5, –OC*H*$_2$CH=CH$_2$), 3.33 (s, 2H, H_2COCH$_2$–), 2.33 (d, 4H, J = 7.0, H_2C–CH=CH$_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.6 (1), 134.9 (1), 133.7 (1), 117.8 (2), 116.7 (2), 115.7 (2), 78.2 (0), 72.3 (2), 72.2 (2), 63.0 (2), 38.0 (2). MS (EI) *m*/*z* (%) 223 (M$^+$ + 1, 5), 107 (40), 95 (50), 81 (100).

General procedure for the ring closing metathesis reaction

Method A. Grubbs' catalyst (**A**) (50 mg, 3 mol% except otherwise stated for the individual compounds) was added to a solution of the metathesis precursor (2.0 mmol) in DCM (10 mL) and the mixture was stirred at 20 °C for 12 h. For double ring closing metathesis of tetraenes **7**, **9** and **12**, 8 mol% of catalyst **A** were employed. The solvent was evaporated and the crude dihydropyrans purified by flash chromatography on silica using hexanes–MTBE mixtures as eluent, or by Kugelrohr distillation. *Method B*. Complex **B** (34 mg, 3 mol%) was added to a solution of the metathesis precursor (1.2 mmol) in toluene (10 mL) and the mixture was heated to reflux for 2 hours. The solvent was evaporated and the crude product was purified by flash chromatography or Kugelrohr distillation.

***rac*-2-Phenyl-3,6-dihydro-2*H*-pyran-2-carboxylic acid methyl ester (13a).** Obtained from **2a**, (0.50 g, 2.0 mmol) as a colourless solid (0.40 g, 90%), mp 69 °C. Purification by Kugelrohr distillation at 175 °C (0.11 mbar). Found: C, 71.7%; H, 6.5%. $C_{13}H_{14}O_3$ requires C, 71.5%; H, 6.5%. IR (KBr disk) ν/cm^{-1} 673 s, 699 s, 726 s, 765 s, 1053 s, 1096 s, 1197 s, 1221 s, 1267 s, 1449 s, 1732 s, 2862 m, 2935 m. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59–7.53 (2H, Ph), 7.40–7.27 (3H, Ph), 5.91 (dm, 1H, J = 10.3, *H*4/*H*5), 5.74 (dm, 1H, J = 10.3, *H*4/*H*5), 4.51 (ddddd, 1H, J = 17.0, 2.5, 2.5, 2.5, 2.5, *H*6), 4.29 (ddddd, 1H, J = 17.0, 2.5, 2.5, 2.5, 2.5, *H*6), 3.71 (s, 3H, H_3C–), 3.09 (ddddd, 1H, J = 17.1, 2.5, 2.5, 2.5, 2.5, *H*3), 2.58 (ddddd, 1H, J = 17.1, 2.5, 2.5, 2.5, 2.5, *H*3).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.7 (0), 140.2 (0), 128.4 (1), 127.9 (1), 125.7 (1), 125.1 (1), 122.4 (1), 78.6 (0), 63.3 (2), 52.5 (3), 32.3 (2). MS (EI) *m*/*z* (%) 219 ($M^+ + 1$, <5), 201 (34), 169 (20), 159 (70), 105 (100), 77 (30), 51 (22).

***rac*-2-Methyl-3,6-dihydro-2*H*-pyran-2-carboxylic acid ethyl ester (13b).** Obtained from **2b** (0.60 g, 3.0 mmol) as a colourless liquid (0.49 g, 95%). Purification by Kugelrohr distillation at 130 °C (0.07 mbar). Found: C, 63.6%; H, 8.3%. $C_9H_{14}O_3$ requires C, 63.5%; H, 8.3%. IR (film) ν/cm^{-1} 1015 m, 1092 s, 1192 s, 1287 m, 1448 w, 1736 s, 2901 w, 2936 w, 2983 m. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.77 (dm, 1H, *J* = 10.3, *H*4/*H*5), 5.68 (dm, 1H, *J* = 10.3, *H*4/*H*5), 4.45 (ddddd, 1H, *J* = 17.1, 2.5, 2.5, 2.5, 2.5, *H*6), 4.21 (q, 2H, *J* = 7.0, H_2C–CH_3), 4.21 (ddddd, 1H, *J* = 17.1, 2.5, 2.5, 2.5, 2.5, *H*6), 2.65 (ddddd, 1H, *J* = 17.1, 2.5, 2.5, 2.5, 2.5, *H*3), 2.05 (ddddd, 1H, *J* = 17.1, 2.5, 2.5, 2.5, 2.5, *H*3), 1.45 (s, 3H, H_3C–C), 1.28 (t, 3H, *J* = 7.0, H_3C–CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9 (0), 125.1 (1), 122.3 (1), 74.6 (0), 62.9 (2), 60.9 (2), 32.7 (2), 25.2 (3), 14.1 (3). MS (EI) *m*/*z* (%) 171 ($M^+ + 1$, 30), 153 (10), 141 (12), 97 (100), 81 (8), 53 (6).

***rac*-2-Allyl-3,6-dihydro-2*H*-pyran-2-carboxylic butyl ester (13c).** Obtained from **2c** (0.70 g, 2.8 mmol) as a colourless liquid (0.45 g, 72%). Purification by Kugelrohr distillation at 120 °C (0.07 mbar). Found: C, 69.8%; H, 9.0%. $C_{13}H_{20}O_3$ requires C, 69.6%; H, 9.0%. IR (film) ν/cm^{-1} 919 w, 1093 m, 1183 s, 1740 s, 2911 m, 2934 m, 2960 m. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75 (dddd, 1H, *J* = 16.1, 10.8, 7.3, 7.3, *H*C=CH_2), 5.68 (ddddd, 1H, *J* = 10.5, 2.3, 2.3, 2.3, 2.3, *H*4/*H*5), 5.60 (dm, 1H, *J* = 10.5, *H*4/*H*5), 5.02 (dm, 1H, *J* = 10.8, H_2C=CH), 5.01 (dm, 1H, *J* = 16.1, H_2C=CH), 4.38 (ddddd, 1H, *J* = 17.1, 2.3, 2.3, 2.3, 2.3, *H*6), 4.05 (t, 2H, *J* = 6.8, H_2C–O–C=O), 4.03 (dm, 1H, *J* = 17.1, *H*6), 2.50 (dm, 1H, *J* = 17.1, *H*3), 2.41 (dm, 2H, *J* = 7.3, H_2C–C), 2.13 (ddddd, 1H, *J* = 17.1, 2.3, 2.3, 2.3, 2.3, *H*3), 1.55 (ddm, 2H, *J* = 15.0, 6.8, H_2C), 1.30 (ddm, 2H, *J* = 15.3, 7.3, H_2C), 0.85 (t, 3H, *J* = 7.3, H_3C). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8 (0), 131.9 (1), 125.3 (1), 122.0 (1), 118.4 (2), 77.3 (0), 64.6 (2), 62.9 (2), 43.2 (2), 31.1 (2), 30.5 (2), 19.0 (2), 13.5 (3). MS (EI) *m*/*z* (%) 225 ($M^+ + 1$, 42), 207 (8), 169 (7), 151 (5), 123 (100), 105 (10), 95 (65), 81 (20), 69 (18), 53 (18).

***rac*-1-(2-Phenyl-3,6-dihydro-2*H*-pyran-2-yl)pent-4-en-1-one (14a).** Obtained from **5a** (0.60 g, 2.2 mmol) and **A** (180 mg, 10 mol%) as a colourless liquid (0.40 g, 74%). Found: C, 78.7%; H, 7.4%. $C_{16}H_{18}O_2$ requires C, 79.3%; H, 7.5%. IR (film) ν/cm^{-1} 706 s, 1089 s, 1182 m, 1448 m, 1717 s, 2844 m, 2910 m, 2931 m, 3038 w. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.41 (2H, Ph), 7.38–7.32 (2H, Ph), 7.30–7.25 (1H, Ph), 5.88 (dm, 1H, *J* = 10.0, *H*4/*H*5), 5.67 (ddm, 1H, *J* = 17.1, 10.5, *H*C=CH_2), 5.66 (dm, 1H, *J* = 10.0, *H*4/*H*5), 4.90 (dm, 1, *J* = 17.1, H_2C=CH), 4.86 (dm, 1H, *J* = 10.5, H_2C=CH), 4.30–4.27 (2H, *H*6), 2.94 (dm, 1H, *J* = 17.3, H_2C–CH_2–C=O), 2.48 (dm, 1H, *J* = 17.3, H_2C–CH_2–C=O), 2.62 (ddd, 1H, *J* = 17.8, 6.3, 1.5, *H*3), 2.58 (ddd, 1H, *J* = 17.8, 2.8, 1.5, *H*3), 2.23 (dm, 1H, *J* = 15.3, H_2C–C=O), 2.15 (dm, 1H, *J* = 15.3, H_2C–C=O). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.2 (0), 139.6 (0), 137.0 (1), 128.5 (1), 127.7 (1), 125.3 (1), 125.0 (1), 122.7 (1), 114.9 (2), 83.0 (0), 62.9 (2), 35.1 (2), 30.2 (2), 27.7 (2). MS (EI) *m*/*z* (%) 243 ($M^+ + 1$, <5), 225 (40), 207 (10), 183 (25), 159 (60), 105 (100), 77 (20), 55 (20).

***rac*-1-(2-Methyl-3,6-dihydro-2*H*-pyran-2-yl)pent-4-en-1-one (14b).** Ring closing metathesis of **5b** (0.124 g, 0.6 mmol) in the presence of complex **B** (0.035 g, 6 mol%) in refluxing toluene (10 mL) stopped at 50% conversion. **5b** and **14b** were obtained as an inseparable mixture. NMR-data obtained from the mixture: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.74 (ddm, 1H, *J* = 17.1, 10.3, *H*C=CH_2), 5.73 (dm, 1H, *J* = 10.3, *H*4/*H*5), 5.63 (dm, 1H, *J* = 10.3, *H*4/*H*5), 4.99 (dm, 1H, *J* = 17.1, H_2C=CH), 4.91 (dm, 1H, *J* = 10.3, H_2C=CH), 4.19 (s, 2H, *H*6), 2.70 (dm, 1H, *J* = 18.3, H_2C–C=O), 2.64 (dm, 1H, *J* = 18.3, H_2C–C=O), 2.26 (dm, 1H, *J* = 13.8, H_2C–CH_2–C=O), 2.23 (dm, 1H, *J* = 13.8, H_2C–CH_2–C=O), 1.95 (dm, 1H, *J* = 17.3, *H*3), 1.58 (m, 1H, *H*3), 1.38 (s, 3H, H_3C–). ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.6 (0), 137.3 (1), 124.8 (1), 122.6 (1), 115.0 (2), 78.7 (0), 62.0 (2), 40.8 (2), 35.1 (2), 31.1 (2), 21.7 (3). GC-MS (EI) *m*/*z* (%) 181 ($M^+ + 1$, 20), 163 (18), 145 (10), 127 (15), 97 (100), 81 (20), 55 (15).

(1*R)-1-((*S**)-2-Phenyl-3,6-dihydro-2*H*-pyran-2-yl)pent-4-en-1-ol (15a).** Obtained from **6a** (0.60 g, 2.2 mmol) along with a 20% admixture of cycloheptene **20** as a colourless liquid (0.35 g, 65%). Found: C, 78.7%; H, 8.3%. $C_{16}H_{20}O_2$ requires C, 78.7%; H, 8.3%. IR (film) ν/cm^{-1} 701 s, 915 m, 1015 s, 1093 s, 1262 m, 1449 s, 2844 m, 2924 m, 3476 brm. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.26 (5H, Ph), 5.94 (dm, 1H, *J* = 10.3, *H*4/*H*5), 5.63 (dddd, 1H, *J* = 17.1, 10.3, 6.8, 6.8, *H*C=CH_2), 5.49 (dm, 1H, *J* = 10.3, *H*4/*H*5), 4.88 (dm, 1H, *J* = 17.1, H_2C=CH), 4.85 (dm, 1H, *J* = 10.3, H_2C=CH), 4.10 (ddd, 1H, *J* = 16.8, 5.3, 1.5, *H*6), 3.78 (dm, 1H, *J* = 16.8, *H*6), 3.74 (dd, 1H, *J* = 10.3, 1.5, *H*C–OH), 3.15 (brs, 1H, *H*O–), 2.85 (dm, 1H, *J* = 17.8, *H*3), 2.53 (ddd, 1H, *J* = 17.8, 6.0, 1.5, *H*3), 2.23 (dm, 1H, *J* = 15.8, H_2C–CH_2–CH), 1.92 (dm, 1H, *J* = 15.8, H_2C–CH_2–CH), 1.32 (dddd, 1H, *J* = 13.6, 10.3, 9.3, 5.0, H_2C–CH), 1.08 (dddd, 1H, *J* = 13.6, 9.3, 6.8, 1.5, H_2C–CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.4 (0), 138.2 (1), 128.2 (1), 127.5 (1), 127.4 (1), 125.6 (1), 123.1 (1), 114.5 (2), 79.2 (0), 77.9 (1), 61.6 (2), 30.4 (2), 28.7 (2), 23.2 (2). MS (EI) *m*/*z* (%) 227 ($M^+ - 17$, 40), 209 (22), 173 (57), 159 (100), 145 (35), 105 (58), 77 (18). Selected NMR-data of cycloheptene **20** (obtained from the mixture): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.26 (dddd, 1H, *J* = 17.3, 1.5, 1.5, 1.5, H_2C=CHCHHO), 5.11 (dddd, 1H, *J* = 10.3, 1.5, 1.5, 1.5, H_2C=CHCHHO), 4.03 (dd, 1H, *J* = 7.5, 2.0, *H*COH), 3.63 (dddd, 1H, *J* = 12.5, 5.3, 1.5, 1.5, OCH*H*CH=CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0 (0), 135.0 (1), 133.4 (1), 128.1 (1), 127.5 (1), 127.3 (1), 125.3 (1), 115.6 (2), 81.8 (0), 78.4 (1), 63.5 (2), 31.4 (2), 28.7 (2), 22.1 (2).

(1*R)- and (1*S**)-1-((*R**)-2-Methyl-3,6-dihydro-2*H*-pyran-2-yl)pent-4-en-1-ol (15b).** Obtained from **6b** (0.60 g, 2.9 mmol of a 2:1 mixture of diastereomers) as a colourless liquid. The minor diastereomer was removed by column chromatography. Yield: 0.22 g, (42%). Found: C, 72.6%; H, 10.0%. $C_{11}H_{18}O_2$ requires C, 72.5%; H, 10.0%. IR (film) ν/cm^{-1} 653 m, 912 m, 1018 w, 1092 s, 1192 w, 1377 w, 2836 m, 2934 m, 2977 m, 3476 brm. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83 (dddd, 1H, *J* = 17.3, 10.3, 7.0, 6.2, *H*C=CH_2), 5.74–5.69 (2H, *H*4, *H*5), 5.25 (dd, 1H, *J* = 17.3, 1.5, H_2C=CH), 4.95 (dd, 1H, *J* = 10.3, 1.5, H_2C=CH), 4.16 (dm, 1H, *J* = 16.8, *H*6), 3.99 (m, 1H, *H*6), 3.43 (ddd, 1H, *J* = 7.8, 4.5, 2.8, *H*C–OH), 2.48 (d, 1H, *J* = 2.8, *H*O–), 2.35 (m, 1H, H_2C–), 2.13 (dm, 1H, *J* = 14.8, H_2C–), 2.13 (dm, 1H, *J* = 14.8, H_2C–), 1.77 (dm, 1H, *J* = 18.1, H_2C–), 1.48–1.41 (2H, H_2C–), 1.11 (s, 3H, H_3C–). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6 (1), 125.0 (1), 122.6 (1), 114.8 (2), 76.7 (1), 74.3 (0), 60.5 (2), 31.9 (2), 30.8 (2), 29.9 (2), 15.6 (3). MS (EI) *m*/*z* (%) 183 ($M^+ + 1$, <5), 165 (22), 147 (12), 129 (19), 105 (10), 97 (100), 81 (25), 67 (20), 55 (23).

***rac*-(2-Phenyl-3,6-dihydro-2*H*-pyran-2-yl)methanol (16a).** Obtained from **10a** (0.40 g, 1.8 mmol) as a colourless solid (0.30 g, 86%), mp 110 °C. Found: C, 75.7%; H, 7.4%. $C_{12}H_{14}O_2$ requires C, 75.8%; H, 7.4%. IR (KBr disk) ν/cm^{-1} 670 s, 697 s, 759 m, 1016 m, 1057 s, 1090 s, 1187 m, 1447 m, 2840 m, 2907 m, 3263 brs. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.27 (5H, Ph), 5.91 (dm, 1H, *J* = 10.0, *H*4/*H*5), 5.58 (dm, 1H, *J* = 10.0, *H*4/*H*5), 4.20 (dm, 1H, *J* = 16.8, *H*6), 4.02 (dm, 1H, *J* = 16.8, *H*6), 3.71 (dd, 1H, *J* = 11.3, 4.3, H_2C–OH), 3.55 (dd, 1H, *J* = 11.3, 9.3, H_2C–OH), 2.82 (dm, 1H, *J* = 17.8, *H*3), 2.63 (dm, 1H, *J* = 17.8, *H*3), 2.12 (dd, 1H, *J* = 9.0, 4.3, *H*O–). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.4 (0), 128.4 (1), 127.6 (1), 126.7(1), 125.4 (1),

122.9 (1), 76.7 (0), 70.4 (2), 61.7 (2), 27.5 (2). MS (EI) *m*/*z* (%) 173 ($M^+ - 17$, 38), 159 (80), 155 (50), 105 (100), 91 (42), 77 (25).

***rac*-(2-Methyl-3,6-dihydro-2*H*-pyran-2-yl)methanol (16b).** Obtained from **10b** (0.50 g, 3.2 mmol) as a colourless liquid (0.38 g, 93%). IR (film) ν/cm^{-1} 652 s, 827 m, 1054 s, 1089 s, 1190 m, 1388 m, 1715 m, 2894 m, 2933 s, 2975 m, 3424 brs. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.74 (ddddd, 1H, J = 10.3, 2.5, 2.5, 2.5, 2.5, *H*4/*H*5), 5.66 (ddddd, 1H, J = 10.3, 2.5, 2.5, 2.5, 2.5, *H*4/*H*5), 4.15 (dm, 1H, J = 16.8, *H*6), 4.10 (dm, 1H, J = 16.8, *H*6), 3.46 (d, 1H, J = 11.3, H_2C–OH), 3.39 (d, 1H, J = 11.3, H_2C–OH), 2.27 (ddddd, 1H, J = 17.5, 2.5, 2.5, 2.5, 2.5, *H*3), 2.26 (brs, 1H, *H*O–), 1.72 (ddddd, 1H, J = 17.5, 2.5, 2.5, 2.5, 2.5, *H*3), 1.15 (s, 3H, H_3C–). ^{13}C NMR (100 MHz, $CDCl_3$) δ 124.8 (1), 122.8 (1), 72.0 (0), 69.1 (2), 60.9 (2), 30.6 (2), 19.6 (3). MS (EI) *m*/*z* (%) 129 ($M^+ + 1$, <5), 111 (30), 97 (100), 93 (60), 81 (50), 75 (36), 67 (39), 53 (42).

(2-Allyl-3,6-dihydro-2*H*-pyran-2-yl)methanol (16c). Obtained from **10c** (0.85 g, 4.7 mmol) as a colourless liquid (0.48 g, 66%). Found: C, 69.1%; H, 8.9%. $C_9H_{14}O_2$ requires C, 70.1%; H, 9.1%. IR (KBr disk) ν/cm^{-1} 656 m, 916 s, 1091 s, 1432 m, 1639 w, 2836 s, 2927 s, 3446 s. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.73 (dddd, 1H, J = 17.3, 10.3, 7.8, 7.0, –C*H*=CH_2), 5.69 (dm, 1H, J = 10.3, *H*4/*H*5), 5.63 (dm, 1H, J = 10.3, *H*4/*H*5), 5.02 (dm, 1H, J = 17.3, =CH_2), 5.01 (dm, 1H, J = 10.3, =CH_2), 4.12 (dm, 1H, J = 17.0, *H*6), 4.06 (dm, 1H, J = 17.0, *H*6), 3.46–3.39 (2H, H_2C–OH), 2.58 br (s, 1H, H_2C–O*H*), 2.36 (dd, 1H, J = 14.1, 7.0, –CH*H*CH=CH_2), 2.23 (dd, 1H, J = 14.1, 7.8, –CH*H*CH=CH_2), 2.05 (dm, 1H, J = 17.6, *H*3), 1.84 (dm, 1H, J = 17.6, *H*3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.3 (1), 124.7 (1), 122.4 (1), 118.0 (2), 73.7 (0), 65.8 (2), 60.7 (2), 37.6 (2), 28.3 (2). MS (EI) *m*/*z* (%) 153 ($M^+ - 1$, 2%), 137 ($M^+ -$ OH, 20), 113 ($M^+ -$ allyl, 100).

***rac*-2-Phenyl-3,6-dihydro-2*H*-pyran-2-carbaldehyde (17a).** Obtained from **11a** (0.15 g, 0.7 mmol) and the Grubbs' catalyst **A** (8 mol%) in refluxing toluene. Yield: 0.090 g (69%). IR (film): ν/cm^{-1} 660 m, 699 s, 1087 s, 1449 m, 1735 s, 2844 w, 2931 m, 3053 w. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.50 (s, 1H, –CHO), 7.43-7.28 (5H, Ph), 5.86 (ddddd, 1H, J = 10.3, 2.3, 2.3, 2.3, 2.3, *H*4/*H*5), 5.67 (dddd, 1H, J = 10.3, 2.3, 2.3, 2.3, *H*4/*H*5), 4.44 (ddddd, 1H, J = 17.3, 2.3, 2.3, 2.3, 2.3, *H*6), 4.33 (ddddd, 1H, J = 17.3, 2.3, 2.3, 2.3, 2.3, *H*6), 2.88 (ddddd, 1H, 17.5, 2.3, 2.3, 2.3, 2.3, *H*3), 2.45 (ddddd, 1H, 17.5, 2.3, 2.3, 2.3, 2.3, *H*3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3 (1), 137.1 (0), 128.8 (1), 128.3 (1), 126.0 (1), 125.5 (1), 122.3 (1), 81.5 (0), 63.1 (2), 28.7 (2). MS (EI) *m*/*z* (%) 189 ($M^+ + 1$, 20), 183 (20), 171 (100), 159 (75), 105 (98), 77 (45), 51 (20).

(2*R,3*S**)-2-Allyl-2-phenyl-3,6-dihydro-2*H*-pyran-3-ol (18a).** Obtained from (3*S**, 4*R**)-**8a** (0.56 g, 2.3 mmol) as a colourless liquid. Yield: 0.20 g (40%). IR (film) ν/cm^{-1} 701 s, 919 m, 1025 s, 1092 s, 1182 m, 1272 m, 1448 m, 1757 m, 2841 w, 2932 w, 3035 w, 3443 brm. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53–7.25 (5H, Ph), 6.12 (dddd, 1H, J = 10.0, 5.3, 2.5, 2.5, *H*4), 6.01 (ddd, 1H, J = 10.0, 2.5, 2.5, *H*5), 5.50 (dddd, 1H, J = 17.3, 10.0, 7.5, 6.3, *H*C=CH_2), 5.03 (dddd, 1H, J = 17.1, 1.5, 1.5, 1.5, H_2C=CH), 4.96 (dddd, 1H, J = 10.0, 1.5, 1.5, 1.5, H_2C=CH), 4.38–4.36 (2H, *H*6), 4.12 (d, 1H, J = 5.3, *H*3), 2.86 (dddd, 1H, J = 14.8, 7.5, 1.5, 1.5, H_2C–C), 2.49 (dddd, 1H, J = 14.8, 6.3, 1.5, 1.5, H_2C–), 1.67 (brs, 1H, *H*O–). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6 (0), 133.5 (1), 129.3 (1), 128.1 (1), 127.1 (1), 125.8 (1), 125.2 (1), 117.6 (2), 79.7 (0), 67.3 (1), 61.3 (2), 39.4 (2). MS (EI) *m*/*z* (%) 215 ($M^+ - 1$, <5), 199 (72), 181 (15), 157 (100), 131 (16), 95 (18).

1-(2-Methyl-3,6-dihydro-2*H*-pyran-2-yl)prop-2-en-1-ol (19b). Obtained from **8b** (0.80 g, 3.3 mmol; 2:1 mixture of diastereomers) Yield: 0.14 g (17%) of a 2:1 mixture of diastereomers. IR (film) ν/cm^{-1} 924 m, 997 m, 1091 s, 1374 m, 2836 m, 2974 m, 3457 brm. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80 (dddd, 1H, J = 17.0, 10.5, 6.3, 6.3, *H*C=CH_2), 5.73–5.60 (2H, *H*4, *H*5), 5.29 (dddd, 1H, J = 17.0, 1.5, 1.5, 1.5, H_2C=CH), 5.16 (dddd, 1H, J = 10.5, 1.5, 1.5, 1.5, H_2C=CH), 4.14–4.08 (2H, *H*6), 3.94 (dm, 1H, J = 5.5, *H*C–OH), 2.73 (d, 1H, J = 2.3, *H*O–), 2.18 (dm, 1H, J = 17.3, H_2C–C), 1.71 (dm, 1H, J = 17.3, H_2C–C), 1.08 (s, 3H, H_3C–). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.4 (1), 124.9 (1), 122.4 (1), 117.4 (2), 77.9 (1), 73.9 (0), 60.6 (2), 31.4 (2), 16.6 (3). MS (EI) *m*/*z* (%) 153 ($M^+ - 1$, <5), 137 (45), 119 (15), 109 (20), 97 (100), 93 (25), 79 (10), 55 (40). NMR data of the minor diastereomer (obtained from the mixture): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.32 (dddd, 1H, J = 17.3, 1.5, 1.5, 1.5, H_2C=CH), 5.18 (dddd, 1H, J = 10.5, 1.5, 1.5, 1.5, H_2C=CH), 2.87 (brs, 1H, *H*O–), 2.43 (dm, 1H, J = 17.3, H_2C–C), 1.54 (dm, 1H, J = 17.3, H_2C–C), 1.11 (s, 3H, H_3C–). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.3 (1), 124.4 (1), 123.0 (1), 117.8 (2), 78.5 (1), 73.6 (0), 60.9 (2), 28.2 (2), 18.5 (3).

(*R)-2-((*S**)-2-Phenyl-3,6-dihydro-2*H*-pyran-2-yl)-2,3,4,7-tetrahydrooxepine (21a).** Obtained from **7a** (0.60 g, 1.9 mmol) and catalyst **A** (0.10 g, 6 mol%) as a colourless liquid. Purification by chromatography on silica (cyclohexane–MTBE = 5:1). Yield: 0.20 g (41%). Found: C, 79.7%; H, 7.8%. $C_{17}H_{20}O_2$ requires C, 79.7%; H, 7.9%. IR (film) ν/cm^{-1} 656 m, 701 s, 1014 s, 1137 s, 1448 m, 2831 m, 2927 m, 3033 w. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47–7.41 (2H, Ph), 7.36–7.30 (2H, Ph), 7.29–7.24 (1H, Ph), 5.88 (ddd, 1H, J = 10.0, 5.3, 2.5, *H*4), 5.71 (dm, 1H, J = 10.0, *H*C–CH_2–CH_2), 5.60 (dm, 1H, J = 10.0, *H*C–CH_2–O–CH), 5.53 (dm, 1H, J = 10.0, *H*5), 4.44 (dd, 1H, J = 16.1, 4.5, H_2C–O–CH), 4.17 (dm, 1H, J = 16.8, *H*6), 4.10 (ddd, 1H, J = 16.1, 2.3, 2.3, H_2C–O–CH), 3.89 (dm, 1H, J = 16.8, *H*6), 3.69 (dd, 1H, J = 9.3, 2.8, *H*C–O), 2.85 (ddddd, 1H, J = 17.6, 2.8, 2.8, 2.8, 2.8, *H*3), 2.65 (dm, 1H, J = 17.6, *H*3), 2.24 (dddm, 1H, J = 16.6, 5.8, 4.3, H_2C–CH_2–CH), 1.90 (ddm, 1H, J = 16.6, 6.7, H_2C–CH_2–CH), 1.62 (ddddm, 1H, J = 14.0, 6.7, 4.3, 2.8, H_2C–CH–C), 1.36 (ddddd, 1H, J = 14.0, 9.5, 9.3, 4.3, 1.5, H_2C–CH–C). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.2 (0, Ph), 130.6 ((1), *C*H–CH_2–CH_2), 129.4 ((1), *C*H–CH_2–O–CH), 127.8, 127.4, 127.1 ((1), Ph), 125.7 ((1), *C*5), 122.9 ((1), *C*4), 86.9 ((1), *C*H–O), 78.5 ((0), *C*2), 69.8 ((2), *C*H_2–O–CH), 61.8 ((2), *C*6), 28.8 ((2), *C*H_2–CH–C), 26.7 ((2), *C*3), 26.4 ((2), *C*H_2–CH_2–CH). MS (EI) *m*/*z* (%) 257 ($M^+ + 1$, 15), 239 (58), 221 (25), 185 (10), 159 (100), 143 (12), 105 (75), 77 (12), 67 (12).

2-(2-Methyl-3,6-dihydro-2*H*-pyran-2-yl)-2,3,4,7-tetrahydrooxepine (21b). Obtained from **7b** (0.20 g, 0.80 mmol, 2:1 mixture of diastereomers) and catalyst **B** (8 mol%) in refluxing toluene as a colourless liquid. After chromatography a single diastereomer of **18b** (0.10 g, 64%) was obtained. IR (film) ν/cm^{-1} 799 m, 1018 s, 1092 s, 1261 m, 2934 m, 2963 m. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81–5.64 (3H, H4/5 + *H*C–CH_2–CH_2), 5.58 (dm, 1H, J = 11.3, H4/5), 4.46 (dd, 1H, J = 16.2, 4.5, H_2C–O–CH), 4.20–4.08 (2H, H6), 4.02 (dm, 1H, J = 16.2, H_2C–O–CH), 3.31 (dd, 1H, J = 9.3, 3.3, *H*C–O), 2.47 (m, 1H, CH*H*), 2.30 (m, 1H, CH*H*), 2.05 (m, 1H, CH*H*), 1.92 (m, 1H, CH*H*), 1.71 (m, 1H, CH*H*), 1.69 (m, 1H, CH*H*), 1.19 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 130.5 (1), 129.5 (1), 125.2 (1), 122.9 (1), 86.5 (1), 74.1 (0), 70.3 (2), 61.0 (2), 30.6 (2), 28.5 (2), 26.3 (2), 18.4 (3). MS (EI) *m*/*z* (%) 195 ($M^+ + 1$, 12), 177 (52), 165 (45), 159 (20), 147 (20), 141 (20), 107 (25), 97 (100), 81 (25), 53 (20).

(2*S)-2-((*R**)-2,3–Dihydrofuran-2-yl)-2-phenyl-3,6-dihydro-2*H*-pyran (22a).** Obtained from (1*S**,2*R**)-**9a** (0.60 g, 2.1 mmol). Yield: 0.15 g (45%). IR (film) ν/cm^{-1} 656 m, 701 s, 728 m, 1057 m, 1086 s, 1179 m, 1448 m, 2848 s, 2924 m, 3035 m. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, 2H, J = 8.0, *o*-H, Ph), 7.27 (dd, 2H, J = 8.0, 7.0, *m*-H, Ph), 7.21 (t, 1H, J = 7.0, *p*-H, Ph),

5.79 (dm, 1H, J = 10.3, *H*4), 5.77 (dm, 1H, J = 6.0, *H*C–CH–C), 5.44 (dm, 1H, J = 10.3, *H*5), 5.26 (dm, 1H, J = 6.0, *H*C=CH–CH), 4.94 (m, 1H, *H*C–O), 4.57 (dm, 1H, J = 13.1, H_2C–O–CH), 4.47 (dddm, 1H, J = 13.1, 6.5, 2.0, H_2C–O–CH), 4.12 (dm, 1H, J = 16.8, *H*6), 3.82 (dm, 1H, J = 16.8, *H*6), 2.59 (dm, 1H, J = 17.8, *H*3), 2.48 (dm, 1H, J = 17.8, *H*3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.4 ((0), Ph), 128.5 ((1), *C*H–CH–C), 128.0 ((1), Ph), 127.4 ((1), Ph), 127.4 ((1), Ph), 125.9 ((1), *C*H=CH–CH), 125.8 ((1), *C*5), 122.6 ((1), *C*4), 92.8 ((1), *C*H–O), 79.0 ((0), *C*2), 76.6 ((2), *C*H_2–O–CH), 61.8 ((2), *C*6), 25.5 ((2), *C*3). MS (EI) *m*/*z* (%) 227 ($M^+ - 1$, <5), 211 (50), 193 (20), 159 (100), 105 (80), 77 (15), 69 (20).

(2*R)- and (2*S**)-2-((*R**)-2,3-Dihydrofuran-2-yl)-2-methyl-3,6-dihydro-2*H*-pyran (22b).** Obtained from **9b** (0.17 g, 0.8 mmol 2 : 1 mixture of diastereomers) and catalyst **B** (7.5 mol%) in refluxing toluene as a mixture of two diastereomers (dr = 2 : 1). Yield: 0.06 g (47%). IR (film) ν/cm^{-1} 654 m, 827 m, 920 m, 1094 s, 1133 m, 1759 s, 2844 m, 2934 m, 2978 m. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.97 (dm, 1H, J = 6.3, –OCH-HCH=C*H*–), 5.73 (dm, 1H, J = 6.3, –OCHHC*H*=CH–), 5.69 (m, 1H, H4), 5.66 (dm, 1H, J = 10.3, H5), 4.71 (m, 1H, *H*C–O), 4.63–4.60 (2H, H_2C–O), 4.14–4.10 (2H, H6), 2.13 (ddm, 1H, J = 17.3, 2.3, H3), 1.70 (ddm, 1H, J = 17.3, 2.3, H3), 1.13 (s, 3H, H_3C). ^{13}C NMR (100 MHz, $CDCl_3$) δ 128.6 (1), 126.2 (1), 125.4 (1), 122,4 (1), 91.6 (1), 75.9 (2), 74.3 (0), 60.7 (2), 30.2 (2), 17.9 (3). MS (EI) *m*/*z* (%) 167 ($M^+ + 1$, <5), 149 (30), 131 (34), 113 (70), 97 (100), 69 (50). NMR data of the minor diastereomer (obtained from the mixture): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80 (dm, 1H, J = 6.3, *H*C=CH), 2.24 (dm, 1H, J = 17.3, H3), 1.81 (dm, 1H, J = 17.3, H3), 1.05 (s, 3H, H_3C). ^{13}C NMR (100 MHz, $CDCl_3$) δ 128.1 (1), 126.5 (1), 125.0 (1), 122.8 (1), 91.2 (1), 75.9 (2), 73.9 (0), 61.0 (2), 31.4 (2), 17.9 (3).

1,8-Dioxaspiro[5.6]dodeca-3,10-diene (23c). Obtained from **12c** (0.56 g, 2.5 mmol). Yield: 0.21 g (50%). IR (film) ν/cm^{-1} 655 s, 1093 s, 1123, s, 1459 s, 1656 m, 2827 s, 2931 s, 3032 s. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.72–5.55 (4H, H4/5, *H*C=CH), 4.26 (dm, 1H, J = 16.3, OCH*H*CH=), 4.16 (dm, 1H, J = 16.3, OCH-*H*CH=), 4.08 (dm, 1H, J = 17.3, OCH*H*CH=), 4.02 (dm, 1H, J = 17.3, OCH*H*CH=), 3.70 (d, 1H, J = 12.8, OCH*H*C), 3.57 (d, 1H, J = 12.8, OCH*H*C), 2.47 (dm, 1H, J = 13.8, CCH*H*), 2.41 (dm, 1H, J = 13.8, CCH*H*), 1.97 (dm, 1H, J = 13.8, H3), 1.85 (dm, 1H, J = 13.8, H3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 130.1 (1), 125.6 (1), 125.3 (1), 122.4 (1), 78.6 (2), 75.5 (0), 70.8 (2), 61.3 (2), 33.1 (2), 31.4 (2). MS (EI) *m*/*z* (%) 167 ($M^+ + 1$, 30), 134 (85), 113 (100).

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