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Synthesis of conjugated γ- and δ-lactones from aldehydes and ketones via a vinylation(allylation)-ring closing metathesis–oxidation sequence

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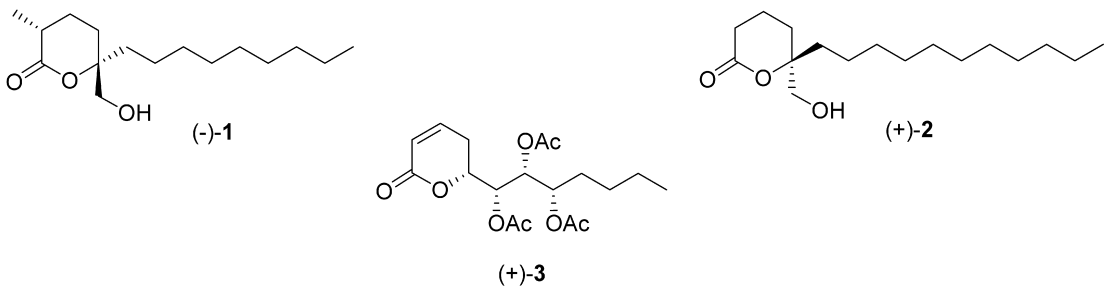
Abstract—Nucleophilic *C*-vinylation and *C*-allylation of aldehydes and ketones followed by O-allylation of the obtained carbinols gave the corresponding allyl or homoallyl ethers, respectively. Ring-closing metathesis of these compounds afforded in many cases cyclic ethers (dihydrofurans and dihydropyrans, respectively) bearing disubstituted and trisubstituted C=C bonds. These were then subjected to allylic oxidation to yield conjugated γ- and δ-lactones. Reasons for the observed failures are presented and discussed.

1. Introduction

For some time, we have been interested in the synthesis of pharmacologically active, chiral natural products using easily available chirons, most particularly erythrulose,[1] as starting materials. Among the different types of structures that have attracted our attention are (−)-malyngolide **1**, (+)-tanikolide **2**, (+)-boronolide **3** and other saturated and unsaturated, naturally occurring lactones (Scheme 1).[2]

As a general method to construct δ-lactone rings, we envisaged ring closing metatheses (RCM)[3] in esters **6** of allyl carbinols of structure **5** (n=1) with an acrylic-type acid (Scheme 2).[4] Carbinols **5** were in turn to be prepared from carbonyl compounds **4**. Ruthenium catalysts **A** and **B**,[3d] as well as molybdenum catalyst **C**,[3b] should efficiently catalyze RCM processes in esters **6** and lead to conjugated δ-lactones of general structure **7** (n=1).[5] The use of vinyl carbinols **5** (n=0) as the starting materials should similarly lead to conjugated γ-lactones **7** (n=0). If desired, conjugated lactones **7** should further provide saturated γ- and δ-lactones by subsequent hydrogenation, Michael addition or similar functional manipulations at the C=C bond. The overall reaction sequence would represent a synthetic equivalent of the general d^3 and d^4 synthons depicted below, the former being an example of synthon with



Scheme 1.

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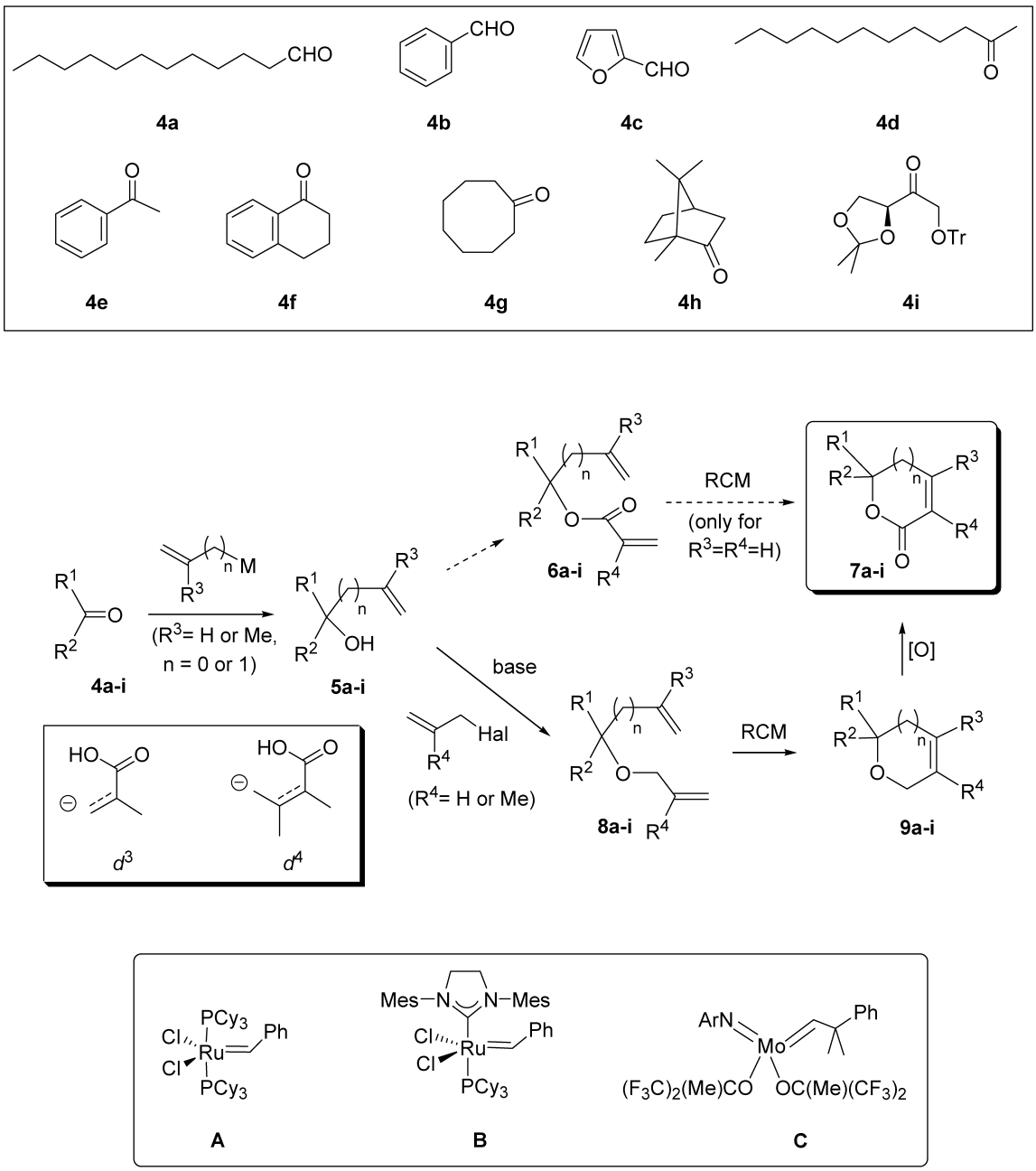


Scheme 2. Vinylation/allylation–RCM–oxidation sequence.

inverted polarity (Umpolung).[6] The feasibility of this methodology has been established for conjugated γ- and δ-lactones bearing a disubstituted C=C bond, which were prepared by means of RCM of allyl and homoallyl acrylates, respectively.[7] In relation to our ongoing synthetic projects mentioned above, our aim was to test the applicability of this procedure to the preparation of conjugated γ- and δ-lactones with a higher degree of substitution at the C=C bond.

2. Results and discussion

To start with, carbonyl compounds **4a–i** were subjected to *C*-allylation[8,9] to allyl carbinols **5a–i** (Scheme 2, R^3=H or Me, *n*=1), which were obtained in all cases with good yields.[10] We then acylated the alcohol group of the allylation products **5** with acryloyl or methacryloyl chloride to yield the corresponding esters **6**. In contrast with that observed previously with unsubstituted acrylates **6** (R^3, R^4=H),[7] compounds **6** (R^3 or R^4=Me) did not undergo RCM with catalyst **A**, neither after a prolonged reaction time nor after addition of Lewis acids.[11] The use of the second-generation ruthenium catalyst **B**, found useful in other cases for the preparation of even tetrasubstituted olefins,[12] was equally unsuccessful here. In view of the failure to obtain lactones with a trisubstituted C=C bond by this procedure,[13] we considered an alternative method based on *O*-allylation of allyl carbinols **5** and RCM of the resulting ethers **8** to dihydropyrans **9**,[14] followed by allylic oxidation of the latter compounds.

Table 1. Chemical yields (%) of the metathesis (**8→9**) and allylic oxidation steps (**9→7**) in the synthesis of conjugated δ-lactones **7** (catalyst A was used)

n=1	R_3=R_4=H		R_3=H, R_4=CH_3		R_3=CH_3, R_4=H	
Carbonyl substrate	**8→9**	**9→7**	**8→9**	**9→7**	**8→9**	**9→7**
4a	89	80	–[a]	–	88	80
4b	98	70	–[a]	–	85	73
4c	90	75	–[a]	–	90	78
4d	81	82	94	70	87	70
4e	82	73	83	71	93	70
4f	82	71	97	82	92	75
4g	87	77	78	67	82	70
4h	94	86	80	77	–[b]	–
4i	87	65	–[b]	–	–[b]	–

[a] Recovered starting material with variable amounts of dimer (cross metathesis product).
[b] In this case, acyclic ether **8** was not prepared.

As a matter of fact, *O*-allylation of carbinols **5** to allyl ethers **8** proceeded uneventfully. RCM of the latter compounds using **A** afforded cyclic ethers **9** in good yields (Table 1).[10] Trisubstituted C=C bonds (**9**, R^3 or R^4=Me) were also formed under these conditions.[15,16] Unfortunately, tetrasubstituted olefins (**9**, R^3=R^4=Me) were not obtained,[17] even when using the much more reactive Schrock molybdenum catalyst **C**.[3b] Finally, oxidation of the allylic methylene next to the oxygen atom in cyclic ethers **9** was achieved using the complexes of chromium trioxide with pyridine[18] or with 3,5-dimethylpyrazole.[19] While both reagents gave similar yields, CrO_3/3,5-dimethylpyrazole was reactive at lower temperatures, a feature of interest in the case of sensitive substrates (see yields in Table 1).

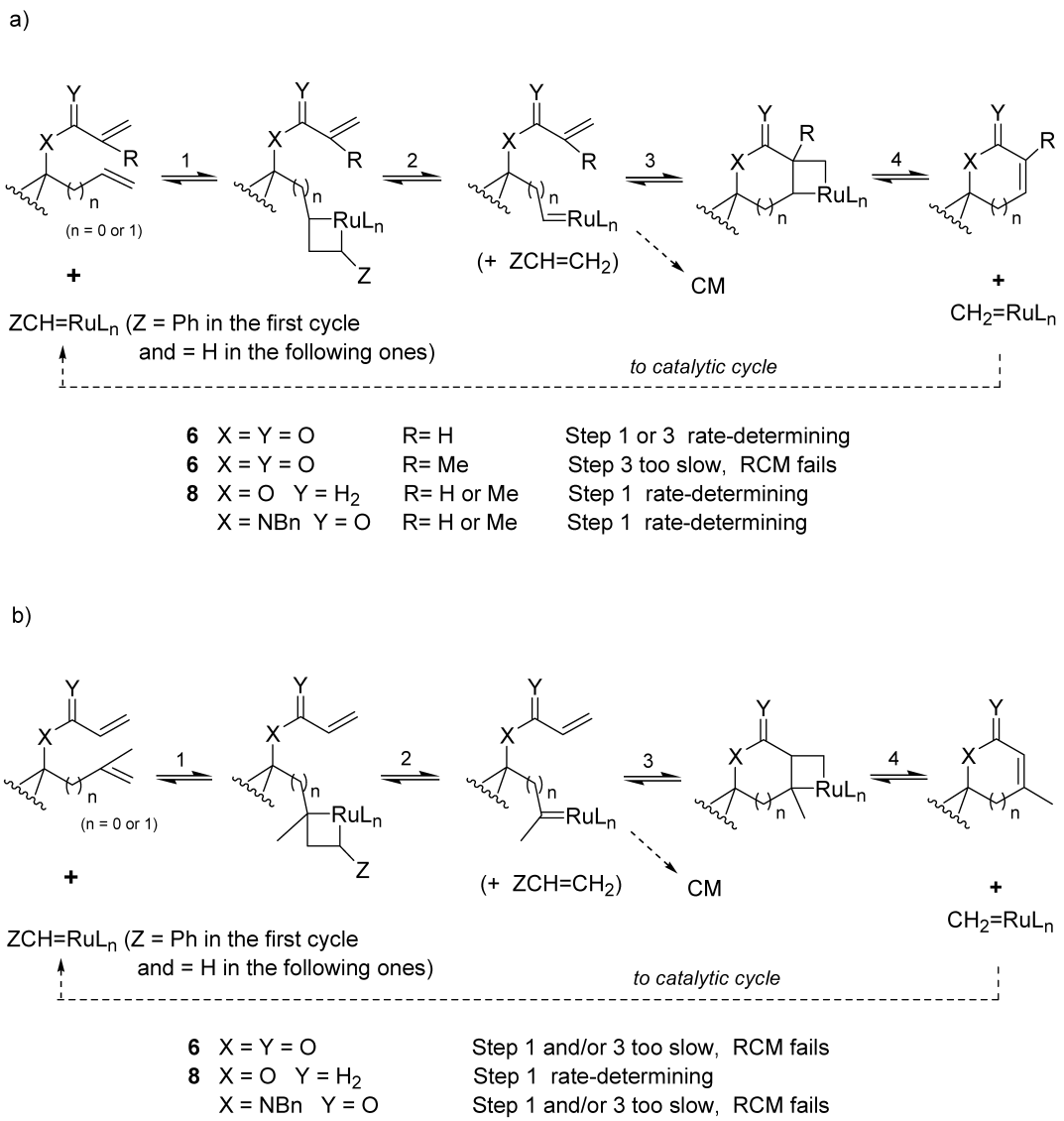
We further tested the feasibility of the preparation of conjugated five-membered lactones with the same methodology. *C*-alkenylation of carbonyl compounds **4** with either vinyl or isopropenyl magnesium bromide afforded allyl alcohols **5** (Scheme 2, R^3=H or Me, *n*=0)[10] which were then subjected to the same *O*-allylation/metathesis/oxidation sequence. Here again, the yields of the metathesis steps (Table 2) were high in all cases where the reaction worked. Catalyst **A** was able to promote RCM in bisallyl ethers **8a–i** (R^3=R^4=H) to yield the expected dihydrofurans **9a–i**, then converted by allylic oxidation into conjugated γ-lactones **7a–i** (R^3=R^4=H).[20] However, the same catalyst was much less effective with ethers **8a–i** when either R^3 or R^4≠H: the metathesis step took place only for aldehydes **4a** and **4b** (**4c** was not tested here) and with R^3=H and R^4=Me (see Table 2). Molybdenum catalyst **C** gave rise to RCM on ether **8d** (R^3=Me, R^4=H) to yield the trisubstituted olefin **9d** (R^3=Me, R^4=H), precursor in turn of β-methyl-γ-lactone **7d** (R^3=Me, R^4=H). In contrast, **C** failed to promote the formation of the trisubstituted olefin **9d** (R^3=H, R^4=Me).

The results described above deserve some comment. A relevant question is why RCM of methacrylates of allyl carbinols do not work whereas those of the corresponding methacrylamides do.[5] Furthermore, RCM of acrylate esters of methallyl carbinols does not work here and did not work with the corresponding acrylamides, either. The reasons for the failures observed here are likely to be the same in both situations. RCM processes are reversible and usually characterized by small changes in enthalpy ($\Delta H \sim 0$). Their advance is driven mainly by the favourable entropic factor ($\Delta S > 0$) related to the extrusion of a small volatile molecule (ethylene in most cases). RCM rates have been shown to depend on steric *and* electronic factors (the metal atom has Lewis acidic character in complexes A–C, thus electron-poor olefins react sluggishly).[3] For instance, polar functional groups at the C=C bond may in some cases block the catalytic cycle.[21] Particularly marked is the retarding effect of an increasing degree of substitution, not only at the C=C bond itself, but also in allylic position.[22] Within Chauvin's mechanistic view,[23] it may be assumed that the first intermolecular metal carbene-olefin (2+2) cycloaddition step of the catalytic cycle (step 1, Scheme 3) is rate-determining and takes place on the electronically least deactivated and/or sterically least encumbered C=C bond. The second, and faster, (2+2) cycloaddition is intramolecular and therefore less sensitive to steric hindrance. For derivatives of alcohols and amines unsubstituted at the C=C bond (Scheme 3a), the obvious target for the catalyst in step 1 is the nonconjugated double bond of the vinyl or allyl moiety.

Table 2. Chemical yields (%) of the metathesis (**8→9**) and allylic oxidation steps (**9→7**) in the synthesis of conjugated γ-lactones **7** (catalyst A was used unless otherwise indicated)

n=0	R_3=R_4=H		R_3=H, R_4=CH_3		R_3=CH_3, R_4=H	
Carbonyl substrate	**8→9**	**9→7**	**8→9**	**9→7**	**8→9**	**9→7**
4a	87	81	89	–[a]	–[b]	–
4b	89	77	91	–[a]	–[b]	–
4d	87	72	–[c]	–	87[d]	75
4e	92	71	–[c]	–	–[b]	–
4f	83	73	–[c]	–	–[b]	–

[a] See Ref. 20.
[b] Recovered starting material with variable amounts of dimer (cross metathesis product).
[c] No reaction with catalysts A, B or C.
[d] With catalyst C.



Scheme 3. Chauvin's catalytic cycles with precursors **6** and **8** (amide analogues of **6** are included for comparison) in relation with the degree and type of substitution at the C=C bonds: (a) unsubstituted bond at the alcohol (amine) part. (b) unsubstituted bond at the acid part (CM=cross metathesis).

The second, intramolecular cycloaddition (step 3) is comparatively fast for amides (X=NBn, Y=O), even when the conjugated C=C bond is disubstituted (R=Me).[5] For acrylate esters **6**, however, the presence or absence of substituents at Cα of the acrylate moiety is a decisive feature: unsubstituted acrylates (X=Y=O, R=H) undergo RCM to yield conjugated lactones with no substituent at C_α, whereas methacrylates (X=Y=O, R=Me) fail to give the reaction. In the last case, it seems likely that step 3 is now very slow on both steric and electronic grounds. The fact that the process still works for methacrylamides is in all likelihood due to the fact that the conjugated double bond is less deactivated in amides than in esters (N more electron-donating than O, thus ester CO more electron-withdrawing than amide CO). For ethers **8** (X=O, $Y=H_2$) step 3 is fast (C=C bond not electronically deactivated), and the RCM process takes place uneventfully to yield both disubstituted and trisubstituted olefins (R=H or Me). It is worth noting, however, that ethers **8** prepared by *C*-allylation and *O*-methallylation of aldehydes **4a–c** (Table 1) did not give RCM but rather dimeric products resulting from cross metathesis (CM). Apparently, carbene complex formed after step 2 reacts intermolecularly with another olefin molecule faster than intramolecularly to give the metallacyclobutane. Again, steric hindrance to the intramolecular step 3 is the only reasonable explanation for this behaviour. However, the same ethers *prepared from ketones* **4d–h** do give RCM products, this fact being likely attributable to the *gem*-dialkyl (Thorpe–Ingold) effect.[24] Needless to say, when both C=C bonds are disubstituted (Scheme 2, $R^3=R^4=Me$), steps 1 and 3 are exceedingly slow and RCM does not take place at all.[17]

When substituents are present at the alcohol part of the acrylates or at the amide part of acrylamides,[5] both the conjugated and the unconjugated C=C bond are unreactive for electronic and steric reasons, respectively (Scheme 3b). Step 1 therefore becomes very slow (and step 3 as well) no matter which C=C bond is attacked first (the unconjugated in Scheme 3b) with the result that RCM does not take place at all. In analogously substituted ethers **8** (X=O, $Y=H_2$), where at least one C=C bond is not electronically

deactivated, RCM takes place and gives the expected trisubstituted olefins (see Tables 1 and 2). Failures were observed, however, in some specific cases. In RCM of methallyl ethers prepared from ketones via vinyl carbinols (Scheme 3a, n=0), step 1 is expected to be slow because of the double allylic substitution near the first-reacting vinyl C=C bond.[22] As a matter of fact, RCM did not take place for these compounds (Table 2, columns 4 and 5). For allyl ethers prepared from both aldehydes and ketones via isopropenyl carbinols (Scheme 3b, n=0), step 3 is likely very slow so that CM becomes competitive (Table 2, columns 6 and 7). The highly reactive catalyst C seems to be required for these RCM reactions to occur but the difficult use and preparation of this molybdenum complex (no longer commercially available) makes this possibility much less attractive.

In summary, the synthetic sequence described above constitutes a useful procedure for the preparation of conjugated γ- and δ-lactones of various structural types, which may then be converted into other types of lactones by suitable functional manipulation. It is also worth noting that this goal can be achieved in many cases with the aid of ruthenium catalyst A, which is both affordable and easy to use. Other catalysts like B, C or recently developed variants thereof are more active in specific cases but are also highly expensive, not commercially available or difficult to prepare and/or use.[3] We are currently investigating the synthesis of naturally occurring lactones with the aid of this reaction sequence. Some results have already been published[2b,c] and others will be reported in due course.

3. Experimental

NMR spectra (Varian Unity 300, 400 and 500 NMR spectrometers) were measured in $CDCl_3$ solution at 25°C. ^{13}C NMR signal multiplicities were determined with the DEPT pulse sequence. Mass spectra were run by the electron impact (EIMS, 70 eV) on a VG AutoSpec mass spectrometer. IR spectra were recorded as films on NaCl Plate (oils) or as KBr pellets (solids). For optically active compounds, rotatory powers were measured at 25°C. Reactions which required an inert atmosphere were carried out under argon with flame-dried glassware. Commercial reagents (Aldrich or Fluka) were used as received. THF was freshly distilled from sodium-benzophenone ketyl. Dichloromethane was freshly distilled from CaH_2. Unless detailed otherwise, 'work-up' means pouring the reaction mixture into satd. aqueous NH_4Cl, extraction with the solvent indicated in parenthesis, additional washing with 5% aq $NaHCO_3$, (if acids had been utilized in the reaction) or with 5% aq HCl (if bases had been utilized), drying over anhydrous Na_2SO_4 or $MgSO_4$ and solvent removal in vacuo. Where solutions were filtered through a Celite pad, the pad was additionally washed twice with the same solvent used, and the washings incorporated to the main organic layer. Column chromatography was performed on silica gel (Süd-Chemie AG, 60–200 μ) with the eluent indicated in each case.

Some of the compounds mentioned in this paper have previously been reported in the literature.[10] Compounds **5b** (R^3=H, n=0,1) are commercially available. The other carbinols of general formula **5** were prepared from carbonyl compounds **4** either by the literature procedures[10] or by one of the procedures described below. Some cyclic ethers **9** have been previously prepared via RCM. Complete analytical data are given below for all new compounds. IR data are given only when relevant functions (OH, CO) are present. High-resolution NMR data ($^1H/^{13}C$) are given not only for new compounds but also for known compounds where low-resolution or incomplete NMR data were reported. Except for products derived from carbonyl compounds **4h** and **4i**, all chiral compounds described here were obtained as racemic mixtures.

3.1. General procedure for vinyl and isopropenyl addition to carbonyl compounds 4

Carbonyl compound **4** (1 mmol) was dissolved under Ar in dry THF (10 mL), cooled to 0°C and treated with vinylmagnesium bromide (commercial 1M solution in THF, 2 mL, 2 mmol) or isopropenylmagnesium bromide (commercial 0.5M solution in THF, 4 mL, 2 mmol). The mixture was stirred for 2 h at 0°C and worked up (CH_2Cl_2). After removal of all volatiles in vacuo, the residue was chromatographed on silica gel (hexanes–EtOAc mixtures) to yield carbinols **5** (n=0, R^3=H or Me). Chemical yields: 80–95%.

3.2. General procedure for allyl and methallyl addition to carbonyl compounds 4

Method (A) Carbonyl compound **4** (1 mmol) was dissolved in THF (2 mL). After addition of saturated aqueous ammonium chloride (8 mL), the solution was treated with zinc powder (458 mg, ca. 7 mmol) and allyl bromide (780 μL, ca. 9 mmol) or methallyl chloride (890 μL, ca. 9 mmol). The mixture was stirred for 18–24 h at room temperature (TLC monitoring) and worked up (EtOAc). Column chromatography on silica gel (hexanes–EtOAc mixtures) yielded carbinols **5** (n=1, R^3=H or Me). Chemical yields: 80–85%.

Method (B) Carbonyl compound **4** (1 mmol) was dissolved under Ar in dry THF (10 mL), cooled to 0°C and treated with allylmagnesium bromide (commercial 1 M solution in THF, 2 mL, 2 mmol). The mixture was stirred for 2 h at 0°C and worked up (CH_2Cl_2). Column chromatography of the residue on silica gel (hexanes–EtOAc mixtures) afforded allyl carbinols **5** (n=1, R^3=H). For the preparation of methallyl carbinols **5** (n=1, R^3=Me), a solution of methallylmagnesium chloride was generated from methallyl chloride by means of the standard procedure[9b] and used as above. Chemical yields: 75–90%.

3.2.1. 2-Methyltetradec-1-en-3-ol, 5a (R^3=Me, n=0). Oil; IR ν_{max} cm^{-1}: 3370 (br); ^1H NMR (500 MHz) δ 4.90 (1H, br s), 4.79 (1H, br s), 4.00 (1H, t, J=6.6 Hz), 3.70 (1H, br s, OH), 1.70 (3H, br s), 1.55–1.45 (2H, m), 1.40–1.20 (18H, br m), 0.86 (3H, t, J=7 Hz); ^{13}C NMR (125 MHz) δ 147.7 (C), 75.9 (CH), 110.8, 34.9, 31.9, 29.7, 29.6 (×2), 29.5 (×2), 29.4, 25.6, 22.7 (CH_2), 17.4, 14.1 (CH_3). Anal. Calcd for $C_{15}H_{30}O$: C, 79.58; H, 13.36. Found: C, 79.34; H, 13.50.

3.2.2. Pentadec-1-en-4-ol, 5a (R^3=H, n=1). ^{1}H NMR (500 MHz) δ 5.83 (1H, dddd, J=17, 10, 7, 5 Hz), 5.15–5.10 (2H, m), 3.65 (1H, m), 2.30 (1H, dt, J=14, 5 Hz), 2.15 (1H, dt, J=14, 7 Hz), 1.60–1.40 (3H, m), 1.40–1.20 (18H, br m), 0.88 (3H, t, J=7 Hz); ^{13}C NMR (125 MHz) δ 135.0, 70.8 (CH), 118.1, 42.0, 36.9, 31.9, 29.7 (×3), 29.6 (×2), 29.4, 25.7, 22.7 (CH_2), 14.1 (CH_3).

3.2.3. 2-Methylpentadec-1-en-4-ol, 5a (R^3=Me, n=1). Oil; IR ν_{max} cm^{-1}: 3400 (br); ^{1}H NMR (500 MHz) δ 4.90 (1H, br s), 4.82 (1H, br s), 3.73 (1H, m), 2.22 (1H, br dd, J=14, 3.3 Hz), 2.10 (1H, dd, J=14, 9.3 Hz), 1.77 (3H, s), 1.70 (1H, br s, OH), 1.50 (2H, m), 1.40–1.20 (18H, br m), 0.89 (3H, t, J=7 Hz); ^{13}C NMR (125 MHz) δ 143.0 (C), 69.0 (CH), 113.6, 46.5, 37.4, 32.1, 30.0, 29.8 (×3), 29.6 (×2), 26.0, 22.7 (CH_2), 22.9, 14.1 (CH_3). Anal. Calcd for $C_{16}H_{32}O$: C, 79.93; H, 13.42. Found: C, 80.00; H, 13.47.

3.2.4. 2-Methyl-1-phenyl-2-propen-1-ol, 5b (R^3=Me, n=0). ^{1}H NMR (500 MHz) δ 7.40–7.25 (5H, br m), 5.20 (1H, quint, J=1 Hz), 5.12 (1H, br s), 4.94 (1H, m), 2.30 (1H, br s, OH), 1.62 (3H, s); ^{13}C NMR (125 MHz) δ 146.8, 142.0 (C), 128.3, 127.6, 126.5, 77.8 (CH), 111.1 (CH_2), 18.2 (CH_3).

3.2.5. 3-Methyl-1-phenyl-3-buten-1-ol, 5b (R^3=Me, n=1). ^{1}H NMR (500 MHz) δ 7.40–7.25 (5H, br m), 4.95 (1H, br s), 4.87 (1H, br s), 4.80 (1H, m), 2.80 (1H, br s, OH), 2.50–2.40 (2H, m), 1.82 (3H, s); ^{13}C NMR (125 MHz) δ 144.0, 142.0 (C), 128.1, 127.1, 125.6, 71.4 (CH), 113.5, 47.9 (CH_2), 22.1 (CH_3).

3.2.6. 1-(2-Furyl)-3-methyl-3-buten-1-ol, 5c (R^3=Me, n=1). ^{1}H NMR (500 MHz) δ 7.35 (1H, s), 6.30 (1H, br s), 6.22 (1H, br s), 4.87 (1H, br s), 4.81 (2H, br s), 2.55 (2H, d, J=7 Hz), 2.30 (1H, br s, OH), 1.72 (3H, s); ^{13}C NMR (125 MHz) δ 156.1, 141.8 (C), 141.6, 110.1, 105.9, 65.5 (CH), 114.0, 44.1 (CH_2), 22.2 (CH_3).

3.2.7. 3-Methyltridec-1-en-3-ol, 5d (R^3=H, n=0). Oil; IR ν_{max} cm^{-1}: 3450 (br); ^{1}H NMR (500 MHz) δ 5.92 (1H, dd, J=17.5, 10.8 Hz), 5.20 (1H, d, J=17.5 Hz), 5.04 (1H, d, J=10.8 Hz), 1.55–1.40 (2H, m), 1.40–1.20 (20H, br m), 0.88 (3H, t, J=7 Hz); ^{13}C NMR (125 MHz) δ 73.3 (C), 145.4 (CH), 111.5, 42.4, 32.0, 30.1, 29.6 (×3), 29.3, 23.9, 22.7 (CH_2), 27.7, 14.1 (CH_3). Anal. Calcd for $C_{14}H_{28}O$: C, 79.18; H, 13.29. Found: C, 79.00; H, 13.44.

3.2.8. 2,3-Dimethyltridec-1-en-3-ol, 5d (R^3=Me, n=0). Oil; IR ν_{max} cm^{-1}: 3460 (br); ^{1}H NMR (500 MHz) δ 4.95 (1H, br s), 4.79 (1H, br s), 1.72 (3H, s), 1.55 (2H, m), 1.35–1.20 (17H, br m), 1.27 (3H, s), 0.87 (3H, t, J=7 Hz); ^{13}C NMR (125 MHz) δ 150.6, 75.4 (C), 109.4, 40.3, 32.0, 30.1, 29.6 (×3), 29.3, 23.7, 22.7 (CH_2), 27.5, 19.4, 14.1 (CH_3). Anal. Calcd for $C_{15}H_{30}O$: C, 79.58; H, 13.36. Found: C, 79.53; H, 13.50.

3.2.9. 4-Methyltetradec-1-en-4-ol, 5d (R^3=H, n=1). Oil; IR ν_{max} cm^{-1}: 3400 (br); ^{1}H NMR (500 MHz) δ 5.80 (1H, ddt, J=17, 10, 7 Hz), 5.08 (1H, br d, J=10 Hz), 5.05 (1H, br d, J=17 Hz), 2.16 (2H, d, J=7 Hz), 1.55 (1H, br s, OH), 1.40 (2H, m), 1.35–1.15 (16H, br m), 1.11 (3H, s), 0.83 (3H, t, J=7 Hz); ^{13}C NMR (125 MHz) δ 72.2 (C), 134.1 (CH), 118.3, 46.4, 41.4, 32.0, 30.21, 29.7 (×3), 29.4, 23.9, 22.7 (CH_2), 26.7, 14.1 (CH_3). Anal. Calcd for $C_{15}H_{30}O$: C, 79.58; H, 13.36. Found: C, 79.33; H, 13.41.

3.2.10. 2,4-Dimethyltetradec-1-en-4-ol, 5d (R^3=Me, n=1). Oil; IR ν_{max} cm^{-1}: 3420 (br); ^{1}H NMR (500 MHz) δ 4.91 (1H, m), 4.75 (1H, m), 2.21 (1H, d, J=13.5 Hz), 2.17 (1H, d, J=13.5 Hz), 1.83 (3H, s), 1.60 (1H, br s, OH), 1.50–1.20 (18H, br m), 1.16 (3H, s), 0.88 (3H, t, J=7 Hz); ^{13}C NMR (125 MHz) δ 143.0, 72.4 (C), 114.8, 49.4, 42.7, 32.0, 30.3, 29.7, 29.6 (×2), 29.4, 24.2, 22.7 (CH_2), 27.0, 25.0, 14.1 (CH_3). Anal. Calcd for $C_{16}H_{32}O$: C, 79.93; H, 13.42. Found: C, 80.00; H, 13.49.

3.2.11. 3-Methyl-2-phenylbut-3-en-2-ol, 5e (R^3=Me, n=0). ^{1}H NMR (500 MHz) δ 7.45 (2H, m), 7.33 (2H, m), 7.24 (1H, m), 5.20 (1H, br s), 4.96 (1H, quint, J=1.2 Hz), 1.90 (1H, br s, OH), 1.70 (3H, s), 1.63 (3H, s); ^{13}C NMR (125 MHz) δ 150.2, 146.0, ~77.0 (overlapped by chloroform signal) (C), 128.2, 127.0, 125.3 (CH), 110.7 (CH_2), 28.7, 19.2 (CH_3).

3.2.12. 1,2,3,4-Tetrahydro-1-isopropenyl-1-naphtol, 5f (R^3=Me, n=0). Oil; IR ν_{max} cm^{-1}: 3450 (br); ^{1}H NMR (500 MHz) δ 7.33 (1H, m), 7.20 (2H, m), 7.14 (1H, m), 5.20 (1H, d, J=2 Hz), 5.07 (1H, quint, J=1.5 Hz), 2.80 (2H, m), 2.15–1.80 (5H, br m), 1.67 (3H, s); ^{13}C NMR (125 MHz) δ 150.0, 139.8, 137.4, 75.7 (C), 128.9, 127.4, 127.3, 126.3 (CH), 112.1, 35.6, 29.8, 19.2 (CH_2), 19.7 (CH_3). Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 83.00; H, 8.49.

3.2.13. 1,2,3,4-Tetrahydro-1-(2-methyl-2-propenyl)-1-naphtol, 5f (R^3=Me, n=1). Oil; IR ν_{max} cm^{-1}: 3480 (br); ^{1}H NMR (500 MHz) δ 7.58 (1H, d, J=7.8 Hz), 7.20–7.15 (2H, m), 7.10 (1H, d, J=7.6 Hz), 4.92 (1H, br s), 4.77 (1H, br s), 2.85–2.75 (2H, m), 2.60 (1H, d, J=14 Hz), 2.53 (1H, d, J=14 Hz), 2.10 (1H, m), 2.00 (1H, br s), 1.90–1.70 (3H, br m), 1.72 (3H, s); ^{13}C NMR (125 MHz) δ 142.8, 142.7, 136.5, 72.4 (C), 128.9, 127.1, 126.8, 126.3 (CH), 115.2, 50.2, 36.0, 29.8, 24.7 (CH_2), 20.0 (CH_3). Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.10; H, 8.89.

3.2.14. 1-(2-Methyl-2-propenyl)cyclooctanol, 5g (R^3=Me, n=1). Oil; IR ν_{max} cm^{-1}: 3460 (br); ^{1}H NMR (500 MHz) δ 4.83 (1H, m), 4.65 (1H, br s), 2.10 (2H, s), 1.76 (3H, s), 1.80–1.30 (15H, br m); ^{13}C NMR (125 MHz) δ 142.7, 74.5 (C), 114.5, 48.7, 36.0 (×2), 28.1 (×2), 24.7, 22.1 (×2) (CH_2), 25.0 (CH_3). Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 79.00; H, 12.22.

3.3. General procedure for *O*-allylation and *O*-methallylation of carbinols 5 to acyclic ethers 8

A 35% suspension of KH in mineral oil (0.23 g, equivalent to ca. 2 mmol of active hydride) was washed three times under Ar with dry hexane. Dry THF (5 mL) was then added, followed by a solution of carbinol **5** (1 mmol) in dry THF (5 mL). The solution was stirred at room temperature for 30 min. Allyl bromide or methallyl chloride (2 mmol) was then added dropwise, followed by tetrabutylammonium iodide (37 mg, 0.1 mmol). The reaction mixture was then heated overnight at reflux. Work-up (CH_2Cl_2) and column

chromatography on silica gel (hexanes–EtOAc mixtures) furnished the expected ethers **8**. Chemical yields: 65–90%.

3.3.1. 3-(2-Propenyloxy)tetradec-1-ene, 8a (R^3=H, R^4=H, *n*=0). Oil; ^{1}H NMR (500 MHz) δ 5.93 (1H, ddt, *J*=17, 10.5, 5.2 Hz), 5.70 (1H, ddd, *J*=17, 10.5, 7.5 Hz), 5.26 (1H, dq, *J*=17, 1.5 Hz), 5.20–5.15 (3H, m), 4.07 (1H, br dd, *J*=13, 5.2 Hz), 3.85 (1H, br dd, *J*=13, 5.2 Hz), 3.70 (1H, q, *J*=7.5 Hz), 1.65 (1H, m), 1.50 (1H, m), 1.40–1.20 (18H, br m), 0.89 (3H, t, *J*=7 Hz); ^{13}C NMR (125 MHz) δ 139.3, 135.3, 80.8 (CH), 116.7, 116.5, 69.2, 35.5, 32.0, 29.7, 29.6, 29.5 (×3), 29.4, 25.4, 22.7 (CH_2), 14.1 (CH_3). Anal. Calcd for $C_{17}H_{32}O$: C, 80.88; H, 12.78. Found: C, 81.00; H, 12.67.

3.3.2. 3-(2-Propenyloxy)-2-methyltetradec-1-ene, 8a (R^3=Me, R^4=H, *n*=0). Oil; ^{1}H NMR (500 MHz) δ 5.90 (1H, ddd, *J*=17, 10.5, 1.5 Hz), 5.24 (1H, dq, *J*=17, 1.5 Hz), 5.13 (1H, dq, *J*=10.5, 1.5 Hz), 4.90 (1H, br s), 4.86 (1H, br s), 3.95 (1H, ddt, *J*=13, 5.3, 1.5 Hz), 3.74 (1H, ddt, *J*=13, 6, 1.5 Hz), 3.65 (1H, t, *J*=7 Hz), 1.64 (3H, s), 1.60 (1H, m), 1.48 (1H, m), 1.40–1.20 (18H, br m), 0.88 (3H, t, *J*=7 Hz); ^{13}C NMR (125 MHz) δ 144.9 (C), 135.3, 83.5 (CH), 116.4, 113.3, 68.9, 33.6, 32.0, 29.7, 29.6, 29.5 (×2), 29.4, 29.3, 25.8, 22.7 (CH_2), 16.5, 14.1 (CH_3). Anal. Calcd for $C_{18}H_{34}O$: C, 81.13; H, 12.86. Found: C, 81.07; H, 12.78.

3.3.3. 3-(2-Methyl-2-propenyloxy)tetradec-1-ene, 8a (R^3=H, R^4=Me, *n*=0). Oil; ^{1}H NMR (500 MHz) δ 5.68 (1H, ddd, *J*=18, 10, 7 Hz), 5.17 (1H, br d, *J*=10 Hz), 5.15 (1H, br d, *J*=18 Hz), 4.95 (1H, br s), 4.87 (1H, br s), 3.93 (1H, d, *J*=12.5 Hz), 3.75 (1H, d, *J*=12.5 Hz), 3.66 (1H, q, *J*=7 Hz), 1.75 (3H, s), 1.70–1.20 (20H, br m), 0.90 (3H, d, *J*=7 Hz); ^{13}C NMR (125 MHz) δ 142.6 (C), 139.3, 80.5 (CH), 116.6, 111.8, 72.0, 35.6, 32.0, 29.7, 29.6 (×2), 29.5 (×2), 29.4, 25.5, 22.7 (CH_2), 19.7, 14.1 (CH_3). Anal. Calcd for $C_{18}H_{34}O$: C, 81.13; H, 12.86. Found: C, 81.30; H, 12.95.

3.3.4. 4-(2-Propenyloxy)pentadec-1-ene, 8a (R^3=H, R^4=H, *n*=1). Oil; ^{1}H NMR (500 MHz) δ 5.95–5.80 (2H, br m), 5.25 (1H, br d, *J*=17 Hz), 5.13 (1H, br d, *J*=10.3 Hz), 5.05 (1H, br d, *J*=17 Hz), 5.03 (1H, br d, *J*=10.5 Hz), 4.02 (1H, br dd, *J*=12.5, 5.5 Hz), 3.96 (1H, br dd, *J*=12.5, 5.5 Hz), 3.34 (1H, quint, *J*=5.8 Hz), 2.25 (2H, m), 1.50–1.20 (20H, br m), 0.88 (3H, t, *J*=7 Hz); ^{13}C NMR (125 MHz) δ 135.5, 135.2, 78.6 (CH), 116.6, 116.3, 70.0, 38.5, 33.9, 32.0, 29.8, 29.7 (×2), 29.6 (×2), 29.4, 25.4, 22.7 (CH_2), 14.1 (CH_3). Anal. Calcd for $C_{18}H_{34}O$: C, 81.13; H, 12.86. Found: C, 81.24; H, 12.99.

3.3.5. 4-(2-Methyl-2-propenyloxy)pentadec-1-ene, 8a (R^3=H, R^4=Me, *n*=1). Oil; ^{1}H NMR (500 MHz) δ 5.86 (1H, ddt, *J*=17.5, 10.5, 7 Hz), 5.10 (1H, br d, *J*=17.5 Hz), 5.06 (1H, br d, *J*=10.5 Hz), 5.00 (1H, br s), 4.88 (1H, br s), 3.94 (1H, br d, *J*=12.5 Hz), 3.89 (1H, br d, *J*=12.5 Hz), 3.36 (1H, quint, *J*=5.8 Hz), 2.30 (2H, m), 1.78 (3H, s), 1.55–1.20 (20H, br m), 0.90 (3H, t, *J*=7 Hz); ^{13}C NMR (125 MHz) δ 142.9 (C), 135.2, 78.6 (CH), 116.7, 111.9, 73.0, 38.3, 33.8, 32.0, 29.8, 29.7 (×4), 29.4, 25.4, 22.7 (CH_2), 19.8, 14.1 (CH_3). Anal. Calcd for $C_{19}H_{36}O$: C, 81.36; H, 12.94. Found: C, 81.34; H, 12.82.

3.3.6. 2-Methyl-4-(2-propenyloxy)pentadec-1-ene, 8a (R^3=Me, R^4=H, *n*=1). Oil; ^{1}H NMR (500 MHz) δ 5.90 (1H, ddt, *J*=17, 10.5, 5.7 Hz), 5.27 (1H, br d, *J*=17 Hz), 5.14 (1H, br d, *J*=10.5 Hz), 4.79 (1H, br s), 4.74 (1H, br s), 4.00 (2H, m), 3.46 (1H, quint, *J*=6 Hz), 2.30 (1H, br dd, *J*=14, 6 Hz), 2.13 (1H, br dd, *J*=14, 6 Hz), 1.77 (3H, s), 1.55–1.20 (20H, br m), 0.89 (3H, t, *J*=7 Hz); ^{13}C NMR (125 MHz) δ 143.1 (C), 136.2, 77.6 (CH), 116.5, 112.5, 70.0, 42.7, 34.1, 32.0, 29.8, 29.6 (×4), 29.4, 25.4, 22.7 (CH_2), 23.0, 14.1 (CH_3). Anal. Calcd for $C_{19}H_{36}O$: C, 81.36; H, 12.94. Found: C, 81.45; H, 13.00.

3.3.7. [1-(2-propenyloxy)-2-propenyl]benzene, 8b (R^3=H, R^4=H, *n*=0). ^{1}H NMR (400 MHz) δ 7.40–7.25 (5H, br m), 6.00–5.90 (2H, m), 5.35–5.15 (4H, br m), 4.82 (1H, d, *J*=6.8 Hz), 4.05–3.95 (2H, m); ^{13}C NMR (100 MHz) δ 141.0 (C), 138.9, 134.8, 128.3, 127.6, 126.8, 82.0 (CH), 116.8, 116.2, 69.2 (CH_2).

3.3.8. [3-Methyl-1-(2-propenyloxy)-3-butenyl]benzene, 8b (R^3=Me, R^4=H, *n*=1). Oil; ^{1}H NMR (500 MHz) δ 7.40–7.25 (5H, br m), 5.94 (1H, ddt, *J*=17, 10.5, 5.5 Hz), 5.27 (1H, ddt, *J*=17, 1.5, 1.5 Hz), 5.16 (1H, ddt, *J*=10.5, 1.5, 1.5 Hz), 4.83 (1H, br s), 4.74 (1H, br s), 4.50 (1H, dd, *J*=8, 5.5 Hz), 3.96 (1H, br dd, *J*=12, 5.5 Hz), 3.77 (1H, br dd, *J*=12, 6 Hz), 2.62 (1H, dd, *J*=14, 8 Hz), 2.37 (1H, dd, *J*=14, 5.5 Hz), 1.78 (3H, s); ^{13}C NMR (125 MHz) δ 142.3, 142.2 (C), 135.0, 128.3, 127.6, 126.7, 80.2 (CH), 116.7, 112.7, 69.5, 46.6 (CH_2), 22.9 (CH_3). Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.33; H, 8.86.

3.3.9. [1-(2-Methyl-2-propenyloxy)-3-butenyl]benzene, 8b (R^3=H, R^4=Me, *n*=1). Oil; ^{1}H NMR (300 MHz) δ 7.35–7.25 (5H, br m), 5.73 (1H, ddt, *J*=17.3, 10.2, 7 Hz), 4.97 (1H, br d, *J*=17.3 Hz), 4.92 (1H, br d, *J*=10.2 Hz), 4.86 (1H, br s), 4.78 (1H, br s), 4.22 (1H, dd, *J*=7.5, 6 Hz), 3.74 (1H, d, *J*=12.5 Hz), 3.57 (1H, d, *J*=12.5 Hz), 2.52 (1H, dt, *J*=14, 7.5 Hz), 2.33 (1H, dt, *J*=14, 6 Hz), 1.64 (3H, s); ^{13}C NMR (75 MHz) δ 142.0, 141.7 (C), 134.6, 128.0, 127.3, 126.5, 80.7 (CH), 116.6, 111.8, 72.1, 42.7 (CH_2), 19.6 (CH_3). Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.03; H, 9.08.

3.3.10. 2-[1-(2-Propenyloxy)but-3-enyl]furan, 8c (R^3=H, R^4=H, *n*=1). ^{1}H NMR (500 MHz) δ 7.37 (1H, d, *J*=1.7 Hz), 6.27 (1H, dd, *J*=3.2, 1.7 Hz), 6.19 (1H, d, *J*=3.2 Hz), 5.80 (1H, ddt, *J*=17.5, 10.5, 5.5 Hz), 5.70 (1H, ddt, *J*=17, 10, 7 Hz), 5.18 (1H, dq, *J*=17.5, 11 Hz), 5.09 (1H, dq, *J*=17.5, 1.5 Hz), 5.02 (1H, dq, *J*=17, 1.5 Hz), 4.96 (1H, dq, *J*=10, 1.5 Hz), 4.32 (1H, t, *J*=7 Hz), 3.92 (1H, ddt, *J*=13, 5.5, 1.5 Hz), 3.80 (1H, ddt, *J*=13, 5.5, 1.5 Hz), 2.60 (1H, dtt, *J*=14, 7, 1.5 Hz), 2.53 (1H, dtt, *J*=14, 7, 1.5 Hz); ^{13}C NMR (125 MHz) δ 154.2 (C), 142.2, 134.7, 134.2, 110.0, 108.1, 73.9 (CH), 117.2, 117.1, 69.5, 38.7 (CH_2).

3.3.11. 2-[3-Methyl-1-(2-propenyloxy)but-3-enyl]furan, 8c (R^3=Me, R^4=H, *n*=1). Oil; ^{1}H NMR (500 MHz) δ 7.36 (1H, s), 6.30 (1H, br s), 6.25 (1H, br d, *J*=3 Hz), 5.85 (1H, ddt, *J*=17.2, 10.5, 5.7 Hz), 5.22 (1H, br d, *J*=17.2 Hz), 5.13 (1H, br d, *J*=10.5 Hz), 4.75 (1H, br s), 4.71 (1H, br s), 4.49 (1H, t, *J*=7 Hz), 3.95 (1H, br dd, *J*=12.5, 5 Hz), 3.80 (1H, br dd, *J*=12.5, 6 Hz), 2.65 (1H, br dd, *J*=14, 7 Hz), 2.53 (1H, br dd, *J*=14, 7 Hz), 1.70 (3H, s); ^{13}C NMR (125 MHz) δ 154.3, 141.8 (C), 142.2, 134.7, 110.0, 108.0, 73.0 (CH), 117.1, 112.9, 69.5, 42.5 (CH_2), 22.7 (CH_3). Anal.

Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 75.00; H, 8.48.

3.3.12. 2-[1-(2-Methyl-2-propenyloxy)but-3-enyl]furan, 8c (R^3=H, R^4=Me, n=1). Oil; ^{1}H NMR (500 MHz) δ 7.36 (1H, d, J=1 Hz), 6.30 (1H, dd, J=3.5, 1 Hz), 6.25 (1H, d, J=3.5 Hz), 5.75 (1H, ddt, J=17.1, 10.3, 7 Hz), 5.06 (1H, ddt, J=17.1, 1.5, 1.5 Hz), 5.00 (1H, ddt, J=10.3, 1.5, 1.5 Hz), 4.94 (1H, br s), 4.85 (1H, br s), 4.33 (1H, t, J= 7 Hz), 3.85 (1H, br d, J=12.5 Hz), 3.74 (1H, br d, J= 12.5 Hz), 2.66 (1H, dtt, J=14, 7, 1.5 Hz), 2.57 (1H, dtt, J=14, 7, 1.5 Hz), 1.70 (3H, s); ^{13}C NMR (125 MHz) δ 154.3, 142.1 (C), 142.2, 134.3, 110.0, 108.0, 73.6 (CH), 117.1, 112.4, 72.4, 38.8 (CH_2), 19.6 (CH_3). Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.88; H, 8.28.

3.3.13. 3-Methyl-3-(2-propenyloxy)tridec-1-ene, 8d (R^3=H, R^4=H, n=0). Oil; ^{1}H NMR (500 MHz) δ 5.90 (1H, m), 5.77 (1H, dd, J=17.7, 11 Hz), 5.27 (1H, br d, J=17.5 Hz), 5.15–5.00 (3H, br m), 3.82 (2H, m), 1.40–1.20 (21H, br m), 0.87 (3H, t, J=7 Hz); ^{13}C NMR (125 MHz) δ 77.6 (C), 143.4, 136.2 (CH), 115.5, 114.4, 63.6, 40.2, 32.0, 30.2, 29.7 (×3), 29.4, 23.7, 22.7 (CH_2), 22.1, 14.1 (CH_3). Anal. Calcd for $C_{17}H_{32}O$: C, 80.88; H, 12.78. Found: C, 81.00; H, 12.88.

3.3.14. 3-Methyl-3-(2-methyl-2-propenyloxy)tridec-1-ene, 8d (R^3=H, R^4=Me, n=0). Oil; ^{1}H NMR (500 MHz) δ 5.79 (1H, dd, J=17.5, 10.5 Hz), 5.14 (1H, d, J=10.5 Hz), 5.12 (1H, d, J=17.5 Hz), 5.00 (1H, br s), 4.82 (1H, br s), 3.72 (2H, br s), 1.73 (3H, s), 1.55 (2H, m), 1.40–1.20 (16H, br m), 1.24 (3H, s), 0.87 (3H, t, J=7 Hz); ^{13}C NMR (125 MHz) δ 142.5, 77.6 (C), 143.4 (CH), 114.3, 110.6, 66.2, 40.4, 32.0, 30.2, 29.7, 29.6, 29.5, 29.4, 23.7, 22.7 (CH_2), 22.1, 19.8, 14.1 (CH_3). Anal. Calcd for $C_{18}H_{34}O$: C, 81.13; H, 12.86. Found: C, 81.31; H, 12.98.

3.3.15. 2,3-Dimethyl-3-(2-propenyloxy)tridec-1-ene, 8d (R^3=Me, R^4=H, n=0). Oil; ^{1}H NMR (500 MHz) δ 5.90 (1H, ddt, J=17.2, 10.7, 5.5 Hz), 5.26 (1H, ddq, J=17.2, 1.6, 1.6 Hz), 5.10 (1H, ddq, J=10.7, 1.5, 1.5 Hz), 4.96 (1H, br s), 4.86 (1H, br s), 3.78 (1H, br dd, J=12.5, 5.5 Hz), 3.69 (1H, br dd, J=12.5, 5.5 Hz), 1.69 (3H, s), 1.60 (2H, m), 1.40–1.20 (19H, br m), 0.87 (3H, t, J=7 Hz); ^{13}C NMR (125 MHz) δ 147.8, 79.9 (C), 136.0 (CH), 115.7, 113.2, 63.4, 38.8, 32.0, 30.2, 29.7 (×2), 29.6, 29.4, 24.0, 22.7 (CH_2), 21.5, 18.6, 14.1 (CH_3). Anal. Calcd for $C_{18}H_{34}O$: C, 81.13; H, 12.86. Found: C, 81.25; H, 12.90.

3.3.16. 4-Methyl-4-(2-propenyloxy)tetradec-1-ene, 8d (R^3=H, R^4=H, n=1). Oil; ^{1}H NMR (500 MHz) δ 5.90 (1H, ddt, J=17.5, 10.5, 5 Hz), 5.80 (1H, ddt, J=17, 10, 7 Hz), 5.26 (1H, ddt, J=17, 1.5, 1.5 Hz), 5.08 (1H, ddt, J= 10.5, 1.5, 1.5 Hz), 5.05–5.00 (2H, m), 3.87 (2H, br d, J= 5 Hz), 2.24 (2H, m), 1.50–1.40 (2H, m), 1.35–1.20 (16H, br m), 1.12 (3H, s), 0.88 (3H, t, J=7 Hz); ^{13}C NMR (125 MHz) δ 76.6 (C), 136.0, 134.6 (CH), 117.1, 115.6, 62.3, 42.8, 37.9, 32.0, 30.2, 29.7 (×3), 29.4, 23.3, 22.7 (CH_2), 23.2, 14.1 (CH_3). Anal. Calcd for $C_{18}H_{34}O$: C, 81.13; H, 12.86. Found: C, 81.20; H, 12.90.

3.3.17. 4-(2-Propenyloxy)-2,4-dimethyltetradec-1-ene, 8d (R^3=Me, R^4=H, n=1). Oil; ^{1}H NMR (500 MHz) δ 5.90 (1H, ddt, J=17.2, 10.5, 5.2 Hz), 5.27 (1H, dq, J=17.2, 1.5 Hz), 5.10 (1H, dq, J=10.5, 1.5 Hz), 4.84 (1H, m), 4.70 (1H, m), 3.88 (2H, m), 2.26 (1H, d, J=14 Hz), 2.18 (1H, d, J=14 Hz), 1.81 (3H, s), 1.50–1.20 (18H, br m), 1.14 (3H, s), 0.88 (3H, t, J=7 Hz); ^{13}C NMR (125 MHz) δ 143.2, 77.2 (C), 136.1 (CH), 115.5, 114.1, 62.3, 45.8, 38.6, 32.0, 30.3, 29.7 (×2), 29.6, 29.4, 23.4, 22.7 (CH_2), 24.4, 23.7, 14.1 (CH_3). Anal. Calcd for $C_{19}H_{36}O$: C, 81.36; H, 12.94. Found: C, 81.50; H, 12.84.

3.3.18. 4-(2-Methyl-2-propenyloxy)-4-methyltetradec-1-ene, 8d (R^3=H, R^4=Me, n=1). Oil; ^{1}H NMR (500 MHz) δ 5.85 (1H, ddt, J=17.2, 10.6, 7 Hz), 5.10–5.05 (2H, m), 5.00 (1H, br s), 4.83 (1H, br s), 3.76 (2H, br s), 2.27 (2H, m), 1.74 (3H, s), 1.48 (2H, m), 1.40–1.20 (16H, br m), 1.13 (3H, s), 0.89 (3H, t, J=7 Hz); ^{13}C NMR (125 MHz) δ 143.4, 76.6 (C), 134.8 (CH), 117.1, 110.8, 65.1, 43.0, 38.1, 32.0, 30.3, 29.7 (×3), 29.4, 23.4, 22.7 (CH_2), 23.1, 19.9, 14.1 (CH_3). Anal. Calcd for $C_{19}H_{36}O$: C, 81.36; H, 12.94. Found: C, 81.46; H, 12.80.

3.3.19. [1-(2-Propenyloxy)-1-methyl-2-propenyl]benzene, 8e (R^3=H, R^4=H, n=0). Oil; ^{1}H NMR (500 MHz) δ 7.49 (2H, m), 7.36 (2H, m), 7.27 (1H, m), 6.10 (1H, dd, J=17.4, 10.8 Hz), 6.00 (1H, ddt, J=17.3, 10.5, 5 Hz), 5.37 (1H, br d, J=17.3 Hz), 5.31 (1H, br d, J=10.5 Hz), 5.20–5.10 (2H, m), 3.90 (2H, m), 1.66 (3H, s); ^{13}C NMR (125 MHz) δ 144.8, 79.5 (C), 143.0, 135.7, 128.2, 127.1, 126.3 (CH), 115.5, 114.4, 64.2 (CH_2), 24.8 (CH_3). Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 83.00; H, 8.69.

3.3.20. [1-(2-Propenyloxy)-1,2-dimethyl-2-propenyl]benzene, 8e (R^3=Me, R^4=H, n=0). Oil; ^{1}H NMR (500 MHz) δ 7.49 (2H, m), 7.33 (2H, m), 7.24 (1H, m), 6.00 (1H, ddt, J=17.3, 10.4, 5 Hz), 5.37 (1H, dq, J=17.3, 1.8 Hz), 5.20 (1H, br s), 5.15 (1H, dq, J=10.4, 1.8 Hz), 5.10 (1H, quint, J=1.4 Hz), 3.90 (1H, ddt, J=13, 5, 1.8 Hz), 3.84 (1H, ddt, J=13, 5, 1.8 Hz), 1.62 (3H, s), 1.53 (3H, s); ^{13}C NMR (125 MHz) δ 148.5, 145.5, 81.5 (C), 135.9, 127.9, 126.6, 125.8 (CH), 115.2, 113.2, 63.5 (CH_2), 24.3, 19.0 (CH_3). Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.06; H, 8.99.

3.3.21. [1-Methyl-1-(2-methyl-2-propenyloxy)-2-propenyl]benzene, 8e (R^3=H, R^4=Me, n=0). Oil; ^{1}H NMR (500 MHz) δ 7.49 (2H, m), 7.37 (2H, m), 7.28 (1H, m), 6.06 (1H, dd, J=17.3, 10.8 Hz), 5.34 (1H, d, J=17.3 Hz), 5.26 (1H, d, J=10.8 Hz), 5.11 (1H, s), 4.90 (1H, s), 3.81 (1H, d, J=12.5 Hz), 3.76 (1H, d, J=12.5 Hz), 1.78 (3H, s), 1.67 (3H, s); ^{13}C NMR (125 MHz) δ 145.0, 143.2, 79.3 (C), 143.1, 128.1, 127.0, 126.2 (CH), 114.3, 110.6, 66.7 (CH_2), 24.4, 19.8 (CH_3). Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.22; H, 8.90.

3.3.22. [1-Methyl-1-(2-propenyloxy)-3-butenyl]benzene, 8e (R^3=H, R^4=H, n=1). Oil; ^{1}H NMR (500 MHz) δ 7.40 (2H, m), 7.35 (2H, m), 7.25 (1H, m), 5.92 (1H, ddt, J=17.3, 10.5, 5.3 Hz), 5.68 (1H, ddt, J=17.3, 9, 7 Hz), 5.30 (1H, ddt, J=17.3, 1.8, 1.8 Hz), 5.14 (1H, ddt, J=9, 1.6, 1.6 Hz), 5.05–5.00 (2H, m), 3.80 (1H, ddt, J=12.5, 5.3, 1.6 Hz), 3.69 (1H, ddt, J=12.5, 5.3, 1.8 Hz), 2.60 (1H, br dd, J=14, 7 Hz), 2.55 (1H, br dd, J=14, 7 Hz), 1.56 (3H, s); ^{13}C NMR

(125 MHz) δ 145.1, 78.9 (C), 135.6, 134.2, 128.2, 127.0, 126.2 (CH), 117.7, 115.7, 63.8, 47.7 (CH_2), 23.4 (CH_3). Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.03; H, 9.02.

3.3.23. [1-Methyl-1-(2-methyl-2-propenyloxy)-3-butenyl]-benzene, 8e (R^3=H, R^4=Me, n=1). Oil; ^{1}H NMR (400 MHz) δ 7.38 (2H, m), 7.33 (2H, m), 7.25 (1H, m), 5.68 (1H, m), 5.05–4.95 (3H, m), 4.84 (1H, br s), 3.66 (1H, br d, J=12.5 Hz), 3.56 (1H, br d, J=12.5 Hz), 2.60 (1H, br dd, J=14, 7 Hz), 2.54 (1H, br br d, J=14, 7 Hz), 1.70 (3H, s), 1.55 (3H, s); ^{13}C NMR (100 MHz) δ 145.0, 143.0, 78.7 (C), 134.2, 128.1, 126.9, 126.2 (CH), 117.5, 110.5, 66.3, 47.8 (CH_2), 23.2, 19.9 (CH_3). Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.34; H, 9.25.

3.3.24. [1,3-Dimethyl-1-(2-propenyloxy)-3-butenyl]benzene, 8e (R^3=Me, R^4=H, n=1). Oil; ^{1}H NMR (500 MHz) δ 7.40 (2H, m), 7.33 (2H, m), 7.25 (1H, m), 5.92 (1H, ddt, J=17.3, 10.5, 5.3 Hz), 5.31 (1H, ddt, J=17.3, 1.8, 1.8 Hz), 5.12 (1H, ddt, J=9, 1.6, 1.6 Hz), 4.80 (1H, br s), 4.60 (1H, br s), 3.82 (1H, ddt, J=13, 5.3, 1.6 Hz), 3.65 (1H, ddt, J=13, 5.3, 1.8 Hz), 2.55 (1H, br d, J=14 Hz), 2.45 (1H, br d, J=14 Hz), 1.60 (3H, s), 1.55 (3H, s); ^{13}C NMR (125 MHz) δ 145.4, 142.6, 79.4 (C), 135.8, 128.1, 127.0, 126.3 (CH), 115.3, 114.9, 63.7, 52.3 (CH_2), 24.3, 22.4 (CH_3). Anal. Calcd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 83.23; H, 9.43.

3.3.25. [1,3-Dimethyl-1-(2-methyl-2-propenyloxy)-3-butenyl]benzene, 8e (R^3=Me, R^4=Me, n=1). Oil; ^{1}H NMR (500 MHz) δ 7.45 (2H, m), 7.36 (2H, m), 7.28 (1H, m), 5.14 (1H, br s), 4.92 (1H, br s), 4.87 (1H, br s), 4.68 (1H, br s), 3.78 (1H, br d, J=12.5 Hz), 3.60 (1H, br d, J=12.5 Hz), 2.62 (1H, br d, J=13.5 Hz), 2.52 (1H, br d, J=13.5 Hz), 1.78 (3H, s), 1.68 (3H, s), 1.66 (3H, s); ^{13}C NMR (125 MHz) δ 145.5, 142.9, 142.5, 79.1 (C), 128.0, 126.9, 126.3 (CH), 114.8, 110.3, 66.4, 52.5 (CH_2), 24.3, 22.2, 19.9 (CH_3). Anal. Calcd for $C_{16}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.53; H, 9.74.

3.3.26. 1,2,3,4-Tetrahydro-1-(2-propenyloxy)-1-vinylnaphthalene, 8f (R^3=H, R^4=H, n=0). Oil; ^{1}H NMR (500 MHz) δ 7.43 (1H, m), 7.19 (2H, m), 7.11 (1H, m), 6.10 (1H, dd, J=17.3, 10.8 Hz), 5.90 (1H, ddt, J=17.3, 10.5, 5 Hz), 5.29 (1H, br d, J=17.3 Hz), 5.19 (1H, d, J=10.8 Hz), 5.09 (1H, br d, J=10.5 Hz), 5.00 (1H, d, J=17.3 Hz), 3.83 (1H, br dd, J=12.5, 5.3 Hz), 3.77 (1H, d, J=12.5, 5.3 Hz), 2.85–2.75 (2H, br m), 2.52 (1H, br dd, J=14, 7 Hz), 2.30 (1H, br dd, J=14, 7 Hz), 2.10–1.80 (2H, br m); ^{13}C NMR (125 MHz) δ 138.5, 137.5, 79.1 (C), 143.7, 135.9, 128.8, 128.7, 127.3, 125.7 (CH), 115.5, 114.5, 64.0, 32.6, 29.6, 19.9 (CH_2). Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 84.24; H, 8.38.

3.3.27. 1,2,3,4-Tetrahydro-1-(2-methyl-2-propenyloxy)-1-vinylnaphthalene, 8f (R^3=H, R^4=Me, n=0). Oil; ^{1}H NMR (500 MHz) δ 7.43 (1H, m), 7.18 (2H, m), 7.10 (1H, m), 6.10 (1H, dd, J=17.3, 10.7 Hz), 5.16 (1H, d, J=10.7 Hz), 5.05 (1H, br s), 5.03 (1H, d, J=17.3 Hz), 4.85 (1H, br s), 3.71 (1H, d, J=12.5 Hz), 3.66 (1H, d, J=12.5 Hz), 2.80 (2H, br m), 2.20–1.80 (4H, br m), 1.72 (3H, s); ^{13}C NMR (125 MHz) δ 143.2, 138.5, 137.6, 79.0 (C), 143.9, 128.8, 128.7, 127.2, 125.7 (CH), 114.3, 110.7, 66.6, 32.6, 29.7, 20.0 (CH_2), 19.9 (CH_3). Anal. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 84.34; H, 8.98.

3.3.28. 1,2,3,4-Tetrahydro-1-isopropenyl-1-(2-propenyloxy)naphthalene, 8f (R^3=Me, R^4=H, n=0). Oil; ^{1}H NMR (500 MHz) δ 7.33 (1H, dd, J=7.5, 1.5 Hz), 7.15 (2H, m), 7.10 (1H, dd, J=7.5, 1.5 Hz), 5.88 (1H, ddt, J=17.2, 10.4, 5 Hz), 5.27 (1H, dq, J=17.2, 1.5 Hz), 5.07 (1H, dq, J=10.4, 1.5 Hz), 4.97 (1H, br s), 4.60 (1H, br s), 3.74 (2H, m), 2.80 (2H, m), 2.10–1.80 (4H, br m), 1.77 (3H, m); ^{13}C NMR (125 MHz) δ 149.4, 138.5, 137.5, 81.7 (C), 139.1, 128.9, 128.7, 127.3, 125.5 (CH), 115.1, 114.1, 64.2, 31.4, 29.7, 19.9 (CH_2), 19.3 (CH_3). Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 84.24; H, 8.77.

3.3.29. 1,2,3,4-Tetrahydro-1-(2-propenyl)-1-(2-propenyloxy)naphthalene, 8f (R^3=H, R^4=H, n=1). Oil; ^{1}H NMR (500 MHz) δ 7.50 (1H, dd, J=7.5, 1.5 Hz), 7.25–7.15 (2H, m), 7.10 (1H, dd, J=7.5, 1.5 Hz), 5.90 (2H, m), 5.30 (1H, ddt, J=17.3, 1.8, 1.8 Hz), 5.10 (1H, ddt, J=10.5, 1.7, 1.7 Hz), 5.06 (1H, br d, J=10.3 Hz), 5.03 (1H, br d, J=17 Hz), 3.80 (1H, ddt, J=13, 5.2, 1.7 Hz), 3.65 (1H, ddt, J=13, 4.8, 1.8 Hz), 2.75 (2H, m), 2.60 (2H, m), 2.00 (2H, m), 1.87 (2H, m); ^{13}C NMR (125 MHz) δ 139.6, 138.5, 78.0 (C), 136.1, 134.7, 128.7, 127.1, 126.3, 126.0 (CH), 117.4, 115.2, 63.7, 47.8, 30.5, 29.7, 20.6 (CH_2). Anal. Calcd for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 84.25; H, 8.90.

3.3.30. 1,2,3,4-Tetrahydro-1-(2-methyl-2-propenyloxy)-1-(2-propenyl)naphthalene, 8f (R^3=H, R^4=Me, n=1). Oil; ^{1}H NMR (500 MHz) δ 7.50 (1H, dd, J=7.5, 1.5 Hz), 7.25–7.15 (2H, m), 7.10 (1H, dd, J=7.5, 1.5 Hz), 5.90 (1H, m), 5.10–5.00 (3H, m), 4.85 (1H, br s), 3.70 (1H, br d, J=13 Hz), 3.55 (1H, br d, J=13 Hz), 2.90–2.60 (4H, m), 2.00–1.80 (4H, m), 1.71 (3H, s); ^{13}C NMR (125 MHz) δ 143.4, 139.7, 138.4, 77.8 (C), 134.8, 128.7 (×2), 127.0, 126.0 (CH), 117.4, 110.2, 66.3, 47.8, 30.5, 29.7, 20.6 (CH_2), 19.8 (CH_3). Anal. Calcd for $C_{17}H_{22}O$: C, 84.25; H, 9.15. Found: C, 84.27; H, 9.01.

3.3.31. 1,2,3,4-Tetrahydro-1-(2-methyl-2-propenyl)-1-(2-propenyloxy)naphthalene, 8f (R^3=Me, R^4=H, n=1). Oil; ^{1}H NMR (500 MHz) δ 7.48 (1H, dd, J=7.5, 1.5 Hz), 7.20–7.10 (2H, m), 7.05 (1H, dd, J=7.5, 1.5 Hz), 5.85 (1H, m), 5.28 (1H, ddt, J=17.2, 1.8, 1.8 Hz), 5.07 (1H, ddt, J=10.4, 1.8, 1.8 Hz), 4.86 (1H, br s), 4.68 (1H, br s), 3.78 (1H, ddt, J=13, 5, 1.8 Hz), 3.57 (1H, ddt, J=13, 5, 1.8 Hz), 2.80–2.70 (2H, m), 2.55 (1H, br d, J=14 Hz), 2.52 (1H, br d, J=14 Hz), 2.10–1.80 (4H, m), 1.78 (3H, s); ^{13}C NMR (125 MHz) δ 143.4, 140.3, 139.2, 78.7 (C), 136.2, 128.7, 127.0 (×2), 126.0 (CH), 114.9, 114.8, 63.7, 51.2, 29.8, 29.6, 21.0 (CH_2), 24.5 (CH_3). Anal. Calcd for $C_{17}H_{22}O$: C, 84.25; H, 9.15. Found: C, 84.36; H, 9.24.

3.3.32. 1-(2-Propenyl)-1-(2-propenyloxy)cyclooctane, 8g (R^3=H, R^4=H, n=1). Oil; ^{1}H NMR (500 MHz) δ 5.90 (1H, m), 5.82 (1H, m), 5.27 (1H, br dd, J=17.3, 1.8 Hz), 5.10–5.00 (3H, m), 3.86 (2H, d, J=5.5 Hz), 2.25 (2H, d, J=7 Hz), 1.80 (2H, m), 1.70–1.40 (12H, br m); ^{13}C NMR (125 MHz) δ 78.9 (C), 135.9, 134.5 (CH), 117.1, 115.7, 62.0, 41.2, 32.6 (×2), 28.4 (×2), 24.8, 21.7 (×2) (CH_2).

Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.76; H, 11.79.

3.3.33. 1-(2-Methyl-2-propenyl)-1-(2-propenyloxy)cyclooctane, 8g (R^3=Me, R^4=H, n=1). Oil; ^{1}H NMR (300 MHz) δ 5.90 (1H, m), 5.25 (1H, m), 5.10 (1H, m), 4.82 (1H, br s), 4.67 (1H, br s), 3.87 (2H, m), 2.18 (2H, s), 1.79 (3H, s), 1.80–1.40 (14H, br m); ^{13}C NMR (75 MHz) δ 143.1, 79.5 (C), 135.8 (CH), 115.5, 114.0, 62.0, 43.5, 32.8 (×2), 28.4 (×2), 24.8, 21.7 (×2) (CH_2), 24.2 (CH_3). Anal. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 80.96; H, 11.70.

3.3.34. 1-(2-Methyl-2-propenyloxy)-1-(2-propenyl)cyclooctane, 8g (R^3=H, R^4=Me, n=1). Oil; ^{1}H NMR (500 MHz) δ 5.85 (1H, ddt, J=17.2, 10.5, 7 Hz), 5.10–5.00 (3H, m), 4.85 (1H, br s), 3.76 (2H, s), 2.25 (2H, d, J=7 Hz), 1.74 (3H, s), 1.85–1.40 (14H, br m); ^{13}C NMR (125 MHz) δ 143.4, 78.7 (C), 134.7 (CH), 117.0, 110.9, 64.7, 41.6, 32.8 (×2), 28.4 (×2), 24.9, 21.7 (×2) (CH_2), 20.0 (CH_3). Anal. Calcd for $C_{15}H_{26}O$: C, 81.02; H, 11.79. Found: C, 81.10; H, 11.90.

3.3.35. (1*R*,2*R*,4*R*)-1,7,7-Trimethyl-2-(2-propenyl)-2-(2-propenyloxy)bicyclo(2.2.1(heptane, 8h (R^3=H, R^4=H, n=1). Oil, $[\alpha]_D$=−4.5 (*c* 9.6; $CHCl_3$); ^{1}H NMR (500 MHz) δ 6.00–5.90 (2H, m), 5.28 (1H, ddt, J=17.2, 1.8, 1.8 Hz), 5.10–5.00 (3H, m), 3.88 (2H, m), 2.69 (1H, ddt, J=16, 5, 2.5 Hz), 2.20 (2H, m), 1.80–1.70 (2H, m), 1.50–1.20 (4H, br m), 1.01 (3H, s), 0.93 (3H, s), 0.84 (3H, s); ^{13}C NMR (125 MHz) δ 85.2, 53.2, 50.2 (C), 136.3, 136.1, 45.1 (CH), 115.5, 114.6, 61.2, 41.7, 40.6, 30.5, 27.1 (CH_2), 21.2, 21.0, 12.1 (CH_3). Anal. Calcd for $C_{16}H_{26}O$: C, 81.99; H, 11.18. Found: C, 81.96; H, 11.28.

3.3.36. (1*R*,2*R*,4*R*)-1,7,7-Trimethyl-2-(2-methyl-2-propenyloxy)-2-(2-propenyl)bicyclo(2.2.1(heptane, 8h (R^3=H, R^4=Me, n=1). Oil, $[\alpha]_D$=+8.5 (*c* 6.9; $CHCl_3$); ^{1}H NMR (500 MHz) δ 5.95 (1H, m), 5.05–4.95 (3H, m), 4.78 (1H, br s), 3.74 (2H, br s), 2.71 (1H, ddt, J=15.5, 4.5, 2.2 Hz), 2.20 (2H, m), 1.73 (3H, s), 1.75–1.65 (2H, m), 1.60–1.50 (2H, m), 1.40 (1H, m), 1.07 (1H, m), 1.00 (3H, s), 0.93 (3H, s), 0.83 (3H, s); ^{13}C NMR (125 MHz) δ 143.2, 85.0, 53.2, 50.2 (C), 136.2, 45.1 (CH), 115.4, 110.0, 63.8, 41.5, 40.4, 30.4, 27.1 (CH_2), 21.2, 21.0, 20.0, 12.0 (CH_3). Anal. Calcd for $C_{17}H_{28}O$: C, 82.20; H, 11.36. Found: C, 82.01; H, 11.49.

3.3.37. (4*S*,1′*S*)-4-(1-Allyloxy-1-trityloxymethylbut-3-enyl)-2,2-dimethyl-1,3-dioxolane, 8i (R^3=H, R^4=H, n=1). Oil, $[\alpha]_D$=−7.7 (*c* 1.6; $CHCl_3$); ^{1}H NMR (300 MHz) δ 7.50–7.20 (15H, m), 5.80 (1H, m), 5.60 (1H, m), 5.20 (1H, br dd, J=17.2, 1.8 Hz), 5.05 (1H, br dd, J=10.5, 1.8 Hz), 4.90 (2H, m), 4.30 (1H, t, J=7.5 Hz), 4.14 (1H, dd, J=13, 5 Hz), 4.05 (1H, dd, J=13, 5 Hz), 3.90 (1H, dd, J=8, 7.5 Hz), 3.79 (1H, dd, J=8, 7.5 Hz), 3.42 (1H, d, J=9.5 Hz), 3.12 (1H, d, J=9.5 Hz), 2.45 (2H, m), 1.30 (6H, s); ^{13}C NMR (75 MHz) δ 143.7, 108.6, 86.9, 78.3 (C), 135.8, 133.2, 128.8, 127.7, 126.9, 78.7 (CH), 117.9, 115.0, 65.0, 64.7, 64.4, 36.1 (CH_2), 26.2, 24.9 (CH_3). Anal. Calcd for $C_{32}H_{36}O_4$: C, 79.31; H, 7.49. Found: C, 79.46; H, 7.59.

3.3.38. General procedure for ring-closing metathesis of ethers 8 to dihydrofurans/dihydropyrans 9. (i) With catalysts **A** or **B**: the substrate (1 mmol) and catalyst A or B (25 mg, ca. 0.03 mmol) were dissolved in dry, degassed CH_2Cl_2 (10 mL) and heated at reflux under Ar for 18–24 h (TLC monitoring). The volatiles were then removed in vacuo and the residue was chromatographed on silica gel (elution with hexanes–EtOAc mixtures). (ii) With catalyst **C**: 23 mg of the catalyst (ca. 0.03 mmol) was weighed in a dry box and placed in a flame-dried flask under argon. The substrate (0.5 mmol) was dissolved in dry, degassed benzene (5 ml) and added via syringe to the flask containing the catalyst. After stirring for 24 h at reflux, the volatiles were removed in vacuo and the residue was chromatographed on silica gel (elution with hexanes–EtOAc mixtures). For chemical yields, see Tables 1 and 2.

3.3.39. 2-Undecyl-2,5-dihydrofuran, 9a (R^3=H, R^4=H, n=0). Oil; ^{1}H NMR (300 MHz) δ 5.85 (1H, dq, J=6, 2 Hz), 5.77 (1H, dq, J=6, 2 Hz), 4.80 (1H, m), 4.60 (2H, m), 1.50 (2H, m), 1.40–1.20 (18H, br m), 0.86 (3H, t, J=7 Hz); ^{13}C NMR (75 MHz) δ 130.0, 126.3, 86.1 (CH), 74.9, 36.1, 32.0, 29.8, 29.7, 29.6 (×3), 29.4, 25.3, 22.7 (CH_2), 14.1 (CH_3). Anal. Calcd for $C_{15}H_{28}O$: C, 80.29; H, 12.58. Found: C, 80.40; H, 12.66.

3.3.40. 4-Methyl-2-undecyl-2,5-dihydrofuran, 9a (R^3=H, R^4=Me, n=0). Oil; ^{1}H NMR (500 MHz) δ 5.35 (1H, sept, J=2 Hz), 4.72 (1H, m), 4.49 (1H, ddq, J=12, 2, 2 Hz), 4.44 (1H, ddq, J=12, 2, 2 Hz), 1.68 (3H, s), 1.45 (2H, m), 1.40–1.20 (18H, br m), 0.81 (3H, t, J=7 Hz); ^{13}C NMR (125 MHz) δ 135.9 (C), 124.0, 86.9 (CH), 77.7, 36.5, 32.0, 29.8, 29.7 (×2), 29.6 (×2), 29.4, 25.4, 22.7 (CH_2), 14.1, 12.3 (CH_3). Anal. Calcd for $C_{16}H_{30}O$: C, 80.61; H, 12.68. Found: C, 80.69; H, 12.60.

3.3.41. 2-Undecyl-3,6-dihydro-2*H*-pyran, 9a (R^3=H, R^4=H, n=1). Oil; ^{1}H NMR (300 MHz) δ 5.80 (2H, m), 4.20 (2H, m), 3.50 (1H, m), 2.00 (2H, m), 1.50–1.20 (20H, br m), 0.88 (3H, t, J=7 Hz); ^{13}C NMR (75 MHz) δ 126.2, 124.3, 73.6 (CH), 65.9, 36.0, 31.9, 31.1, 29.7 (×4), 29.4 (×2), 25.5, 22.7 (CH_2), 14.1 (CH_3). Anal. Calcd for $C_{16}H_{30}O$: C, 80.61; H, 12.68. Found: C, 80.73; H, 12.50.

3.3.42. 4-Methyl-2-undecyl-3,6-dihydro-2*H*-pyran, 9a (R^3=Me, R^4=H, n=1). Oil; ^{1}H NMR (500 MHz) δ 5.39 (1H, br s), 4.14 (2H, m), 3.40 (1H, m), 2.00–1.80 (2H, br m), 1.68 (3H, br s), 1.60–1.40 (2H, br m), 1.40–1.20 (18H, br m), 0.86 (3H, t, J=7 Hz); ^{13}C NMR (125 MHz) δ 131.9 (C), 119.8, 73.9 (CH), 65.9, 36.1, 36.0, 31.9, 29.7 (×4), 29.6, 29.4, 25.5, 22.7 (CH_2), 23.0, 14.1 (CH_3). Anal. Calcd for $C_{17}H_{32}O$: C, 80.88; H, 12.78. Found: C, 80.78; H, 12.61.

3.3.43. 2-(2-Furyl)-3,6-dihydro-2*H*-pyran, 9c (R^3=H, R^4=H, n=1). Oil; ^{1}H NMR (500 MHz) δ 7.40 (1H, d, J=2 Hz), 6.33 (1H, dd, J=3.2, 2 Hz), 6.29 (1H, d, J=3.2 Hz), 5.88 (1H, dtt, J=10, 5, 2.5 Hz), 5.76 (1H, dtt, J=10, 5, 1.5 Hz), 4.64 (1H, dd, J=10, 3.6 Hz), 4.33 (1H, ddq, J=16.5, 5, 2.5 Hz), 4.24 (1H, ddq, J=16.5, 5, 1.5 Hz), 2.60 (1H, m), 2.28 (1H, m); ^{13}C NMR (125 MHz) δ 154.2 (C), 142.1, 126.0, 123.4, 109.9, 106.6, 68.7 (CH), 65.7, 28.6 (CH_2). Anal. Calcd for $C_9H_{10}O_2$: C, 71.98; H, 6.71. Found: C, 71.77; H, 6.61.

3.3.44. 2-(2-Furyl)-4-methyl-3,6-dihydro-2*H*-pyran, 9c (R^3=Me, R^4=H, n=1). Oil; ^{1}H NMR (500 MHz) δ 7.39

(1H, d, *J*=1.5 Hz), 6.33 (1H, dd, *J*=3.3, 1.5 Hz), 6.29 (1H, d, *J*=3.3 Hz), 5.45 (1H, br s), 4.60 (1H, dd, *J*=10, 3.6 Hz), 4.27 (1H, br d, *J*=16 Hz), 4.21 (1H, br d, *J*=16 Hz), 2.53 (1H, m), 2.12 (1H, br d, *J*=17 Hz), 1.75 (3H, s); ^{13}C NMR (125 MHz) δ 154.5, 131.2 (C), 142.3, 119.7, 110.1, 106.9, 69.0 (CH), 65.8, 33.4 (CH_2), 23.0 (CH_3). Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 73.27; H, 7.51.

3.3.45. 2-Decyl-2-methyl-2,5-dihydrofuran, 9d (R^3=H, R^4=H, *n*=0). Oil; ^{1}H NMR (300 MHz) δ 5.80 (1H, m), 5.70 (1H, m), 4.64 (2H, m), 1.40–1.10 (21H, br m), 0.88 (3H, t, *J*=7 Hz); ^{13}C NMR (75 MHz) δ 90.2 (C), 133.7, 125.1 (CH), 74.6, 41.2, 32.0, 30.2, 29.7 (×3), 29.4, 24.5, 22.8 (CH_2), 26.6, 14.1 (CH_3). Anal. Calcd for $C_{15}H_{28}O$: C, 80.29; H, 12.58. Found: C, 80.41; H, 12.69.

3.3.46. 2-Decyl-2,3-dimethyl-2,5-dihydrofuran, 9d (R^3=Me, R^4=H, *n*=0). Oil; ^{1}H NMR (300 MHz) δ 5.40 (1H, m), 4.45 (2H, m), 1.60 (3H, br s), 1.50 (2H, m), 1.40–1.10 (19H, br m), 0.88 (3H, t, *J*=7 Hz); ^{13}C NMR (75 MHz) δ 140.8, 90.6 (C), 119.7 (CH), 73.0, 39.2, 32.0, 30.2, 29.7 (×3), 29.5, 23.8, 22.8 (CH_2), 25.5, 14.2, 12.2 (CH_3). Anal. Calcd for $C_{16}H_{30}O$: C, 80.61; H, 12.68. Found: C, 80.72; H, 12.79.

3.3.47. 2-Decyl-2-methyl-3,6-dihydro-2*H*-pyran, 9d (R^3=H, R^4=H, *n*=1). Oil; ^{1}H NMR (500 MHz) δ 5.75–5.65 (2H, m), 4.10 (2H, m), 2.04 (1H, br d, *J*=17.5 Hz), 1.89 (1H, br d, *J*=17.5 Hz), 1.55 (1H, m), 1.40–1.20 (17H, br m), 1.15 (3H, s), 0.86 (3H, t, *J*=7 Hz); ^{13}C NMR (125 MHz) δ 71.7 (C), 125.3, 123.1 (CH), 60.9, 40.1, 35.0, 32.0, 30.3, 29.7 (×3), 29.4, 23.5, 22.7 (CH_2), 22.9, 14.1 (CH_3). Anal. Calcd for $C_{16}H_{30}O$: C, 80.61; H, 12.68. Found: C, 80.51; H, 12.77.

3.3.48. 2-Decyl-2,4-dimethyl-3,6-dihydro-2*H*-pyran, 9d (R^3=Me, R^4=H, *n*=1). Oil; ^{1}H NMR (500 MHz) δ 5.31 (1H, m), 4.00 (2H, m), 1.85 (1H, m), 1.70 (1H, m), 1.60 (3H, br s), 1.50–1.10 (18H, br m), 1.07 (3H, s), 0.80 (3H, t, *J*=7 Hz); ^{13}C NMR (125 MHz) δ 130.4, 72.0 (C), 118.6 (CH), 61.0, 40.1, 40.0, 31.9, 30.3, 29.7 (×2), 29.6, 29.3, 23.5, 22.7 (CH_2), 23.3, 23.0, 14.1 (CH_3). Anal. Calcd for $C_{17}H_{32}O$: C, 80.88; H, 12.78. Found: C, 80.70; H, 12.60.

3.3.49. 2-Decyl-2,5-dimethyl-3,6-dihydro-2*H*-pyran, 9d (R^3=H, R^4=Me, *n*=1). Oil; ^{1}H NMR (500 MHz) δ 5.42 (1H, m), 3.95 (2H, m), 2.00 (1H, br d, *J*=17 Hz), 1.86 (1H, br ddq, *J*=17, 2, 2 Hz), 1.60 (3H, br s), 1.50–1.20 (18H, br m), 1.15 (3H, s), 0.88 (3H, t, *J*=7 Hz); ^{13}C NMR (125 MHz) δ 131.7, 71.6 (C), 117.6 (CH), 64.3, 40.0, 35.1, 32.0, 30.4, 29.7, 29.6 (×2), 29.3, 23.6, 22.7 (CH_2), 22.9, 18.5, 14.1 (CH_3). Anal. Calcd for $C_{17}H_{32}O$: C, 80.88; H, 12.78. Found: C, 80.79; H, 12.89.

3.3.50. 2-Methyl-2-phenyl-2,5-dihydrofuran, 9e (R^3=H, R^4=H, *n*=0). Oil; ^{1}H NMR (500 MHz) δ 7.36 (2H, m), 7.27 (2H, m), 7.18 (1H, m), 5.95 (1H, dt, *J*=6, 2 Hz), 5.80 (1H, dt, *J*=6, 2 Hz), 4.75 (1H, dt, *J*=13, 2 Hz), 4.68 (1H, dt, *J*=13, 2 Hz), 1.59 (3H, s); ^{13}C NMR (125 MHz) δ 146.4, 90.7 (C), 134.3, 128.3, 126.8, 125.0, 124.7 (CH), 74.7 (CH_2), 28.1 (CH_3). Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.69; H, 7.60.

3.3.51. 2,4-Dimethyl-2-phenyl-3,6-dihydro-2*H*-pyran, 9e (R^3=Me, R^4=H, *n*=1). Oil; ^{1}H NMR (500 MHz) δ 7.43 (2H, m), 7.36 (2H, m), 7.26 (1H, m), 5.33 (1H, br s), 4.18 (1H, br d, *J*=16.5 Hz), 3.96 (1H, dq, *J*=16.5, 2 Hz), 2.55 (1H, br d, *J*=17 Hz), 2.33 (1H, br d, *J*=17 Hz), 1.80 (3H, s), 1.53 (3H, s); ^{13}C NMR (125 MHz) δ 145.4, 130.4, 74.0 (C), 128.1, 126.8, 125.4, 119.3 (CH), 61.8, 39.0 (CH_2), 29.4, 23.2 (CH_3). Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 82.79; H, 8.61.

3.3.52. 2,5-Dimethyl-2-phenyl-3,6-dihydro-2*H*-pyran, 9e (R^3=H, R^4=Me, *n*=1). Oil; ^{1}H NMR (300 MHz) δ 7.45 (2H, m), 7.38 (2H, m), 7.27 (1H, m), 5.58 (1H, m), 4.02 (1H, br d, *J*=17 Hz), 3.82 (1H, br d, *J*=17 Hz), 2.65 (1H, br d, *J*=17 Hz), 2.38 (1H, br d, *J*=17 Hz), 1.54 (3H, br s), 1.50 (3H, s); ^{13}C NMR (75 MHz) δ 145.3, 132.3, 73.6 (C), 128.0, 126.7, 125.5, 117.3 (CH), 65.0, 34.2 (CH_2), 29.4, 18.6 (CH_3). Anal. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57. Found: C, 83.01; H, 8.67.

3.3.53. Spiro[1,2,3,4-tetrahydronaphthalene-1,2′-(2,5-dihydrofuran)], 9f (R^3=H, R^4=H, *n*=0). Oil; ^{1}H NMR (500 MHz) δ 7.40–7.15 (4H, br m), 6.08 (1H, br d, *J*=6 Hz), 5.90 (1H, m), 4.86 (1H, br d, *J*=13 Hz), 4.80 (1H, br d, *J*=13 Hz), 2.92 (1H, dt, *J*=16.5, 5.5 Hz), 2.82 (1H, dt, *J*=16.5, 5.5 Hz), 2.10 (2H, m), 1.90 (2H, m); ^{13}C NMR (125 MHz) δ 139.1, 137.0, 89.0 (C), 134.5, 128.8, 128.1, 127.5, 126.2, 125.7 (CH), 74.5, 35.9, 29.6, 20.1 (CH_2). Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.70; H, 7.69.

3.3.54. Spiro[1,2,3,4-tetrahydronaphthalene-1,2′-(3,6-dihydro-2*H*-pyran)], 9f (R^3=H, R^4=H, *n*=1). Oil; ^{1}H NMR (500 MHz) δ 7.60 (1H, dd, *J*=8, 1.5 Hz), 7.22 (2H, m), 7.12 (1H, dd, *J*=8, 1.5 Hz), 5.92 (1H, m), 5.86 (1H, br d, *J*=10 Hz), 4.32 (1H, br d, *J*=17 Hz), 4.20 (1H, br d, *J*=17 Hz), 2.90 (1H, dt, *J*=16.5, 7 Hz), 2.80 (1H, dt, *J*=16.5, 5 Hz), 2.55 (1H, d quint, *J*=18, 2.5 Hz), 2.26 (1H, br d, *J*=18 Hz), 2.16 (1H, m), 2.05–1.90 (2H, m), 1.77 (1H, m); ^{13}C NMR (125 MHz) δ 141.1, 137.0, 72.0 (C), 128.5, 127.2, 127.0, 126.2, 125.6, 123.8 (CH), 61.4, 35.9, 31.3, 29.7, 19.8 (CH_2). Anal. Calcd for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.90; H, 7.99.

3.3.55. 4′-Methylspiro[1,2,3,4-tetrahydronaphthalene-1,2′-(3,6-dihydro-2*H*-pyran)], 9f (R^3=Me, R^4=H, *n*=1). Oil; ^{1}H NMR (300 MHz) δ 7.55 (1H, m), 7.25–7.10 (3H, m), 5.55 (1H, br s), 4.25 (1H, br d, *J*=16.5 Hz), 4.15 (1H, br d, *J*=16.5 Hz), 2.95–2.75 (2H, m), 2.45 (1H, br d, *J*=18 Hz), 2.10–1.70 (5H, m), 1.79 (3H, s); ^{13}C NMR (75 MHz) δ 140.9, 137.1, 131.2, 72.2 (C), 128.5, 127.1, 127.0, 126.0, 119.1 (CH), 61.4, 40.8, 31.8, 29.7, 19.8 (CH_2), 23.2 (CH_3). Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 84.09; H, 8.45.

3.3.56. 5′-Methylspiro[1,2,3,4-tetrahydronaphthalene-1,2′-(3,6-dihydro-2*H*-pyran)], 9f (R^3=H, R^4=Me, *n*=1). Oil; ^{1}H NMR (300 MHz) δ 7.60 (1H, m), 7.32 (2H, m), 7.15 (1H, m), 5.60 (1H, m), 4.20 (1H, br d, *J*=17 Hz), 4.05 (1H, br d, *J*=17 Hz), 2.90–2.70 (2H, m), 2.50 (1H, m), 2.20–1.70 (5H, m), 1.71 (3H, s); ^{13}C NMR (75 MHz) δ 140.9, 137.0, 132.0, 72.0 (C), 128.5, 127.1, 126.9, 126.0, 118.2 (CH), 64.8, 36.1, 31.5, 29.8, 19.9 (CH_2), 18.7 (CH_3). Anal.

Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 83.99; H, 8.35.

3.3.57. 1-Oxaspiro[5.7]tridec-3-ene, 9g (R^3=H, R^4=H, *n*=1). Oil; ^{1}H NMR (500 MHz) δ 5.70 (2H, m), 4.07 (2H, br s), 1.95 (2H, br s), 1.85 (2H, m), 1.70-1.40 (12H, br m), 1.68 (3H, br s); ^{13}C NMR (125 MHz) δ 74.0 (C), 125.4, 123.1 (CH), 60.6, 35.3, 33.0 (×2), 28.4 (×2), 24.8, 21.4 (×2) (CH_2). Anal. Calcd for $C_{12}H_{20}O$: C, 79.94; H, 11.18. Found: C, 80.02; H, 11.30.

3.3.58. 3-Methyl-1-oxaspiro[5.7]tridec-3-ene, 9g (R^3=H, R^4=Me, *n*=1). Oil; ^{1}H NMR (300 MHz) δ 5.38 (1H, m), 3.90 (2H, m), 2.45 (1H, br d, *J*=15 Hz), 2.30 (1H, br d, *J*=15 Hz), 1.90–1.30 (14H, br m), 1.69 (3H, br s); ^{13}C NMR (75 MHz) δ 131.6, 73.9 (C), 117.4 (CH), 64.0, 35.4, 33.01 (×2), 28.5 (×2), 24.9, 21.6 (×2) (CH_2), 18.7 (CH_3). Anal. Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.27; H, 11.30.

3.3.59. 4-Methyl-1-oxaspiro[5.7]tridec-3-ene, 9g (R^3=Me, R^4=H, *n*=1). Oil; ^{1}H NMR (300 MHz) δ 5.37 (1H, br s), 4.04 (2H, m), 2.00–1.40 (16H, br m), 1.68 (3H, br s); ^{13}C NMR (75 MHz) δ 130.3, 74.3 (C), 118.6 (CH), 60.7, 40.4, 33.1 (×2), 28.5 (×2), 24.9, 21.6 (×2) (CH_2), 23.2 (CH_3). Anal. Calcd for $C_{13}H_{22}O$: C, 80.35; H, 11.41. Found: C, 80.50; H, 11.50.

3.3.60. (1*R*,2*R*,4*R*)-1,7,7-Trimethylspiro[bicyclo[2.2.1]-heptane-2,2′-(3,6-dihydro-2*H*-pyran)], 9h (R^3=H, R^4=H, *n*=1). Oil, $[\alpha]_D$=−40.8 (*c* 2; $CHCl_3$); ^{1}H NMR (500 MHz) δ 5.77 (1H, m), 5.70 (1H, br d, *J*=10 Hz), 4.20 (1H, br d, *J*=17.5 Hz), 4.00 (1H, br d, *J*=17.5 Hz), 2.34 (1H, br d, *J*=15 Hz), 2.22 (1H, br dt, *J*=15, 3.5 Hz), 1.70 (3H, m), 1.50–1.30 (4H, m), 1.01 (3H, s), 0.87 (3H, s), 0.84 (3H, s); ^{13}C NMR (125 MHz) δ 80.8, 52.4, 49.0 (C), 126.4, 124.3, 45.5 (CH), 59.4, 39.3, 32.9, 30.1, 27.3 (CH_2), 21.2, 20.9, 10.3 (CH_3). Anal. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75. Found: C, 81.55; H, 10.89.

3.3.61. (1*R*,2*R*,4*R*)-1,7,7,5′-Tetramethylspiro[bicyclo-[2.2.1]heptane-2,2′-(3,6-dihydro-2*H*-pyran)], 9h (R^3=H, R^4=Me, *n*=1). Oil, $[\alpha]_D$=−56.2 (*c* 6.6; $CHCl_3$); ^{1}H NMR (500 MHz) δ 5.46 (1H, m), 4.06 (1H, br d, *J*=16.5 Hz), 3.80 (1H, br d, *J*=16.5 Hz), 2.30 (1H, br d, *J*=15 Hz), 2.18 (1H, br dt, *J*=15, 3.5 Hz), 1.70 (3H, m), 1.60 (3H, s), 1.50–1.30 (4H, m), 1.02 (3H, s), 0.87 (3H, s), 0.84 (3H, s); ^{13}C NMR (125 MHz) δ 132.8, 80.8, 52.3, 49.0 (C), 118.6, 45.5 (CH), 62.6, 39.3, 32.8, 30.2, 27.3 (CH_2), 21.1, 20.9, 18.3, 10.3 (CH_3). Anal. Calcd for $C_{15}H_{24}O$: C, 81.76; H, 10.98. Found: C, 81.80; H, 11.00.

3.3.62. (2*S*,4′*S*)-2-(2,2-Dimethyl-1,3-dioxolan-4-yl)-2-trityloxymethyl-3,6-dihydro-2*H*-pyran, 9i (R^3=H, R^4=H, *n*=1). Oil, $[\alpha]_D$=+8.5 (*c* 4; $CHCl_3$); ^{1}H NMR (500 MHz) δ 7.44 (2H, m), 7.30 (2H, m), 7.24 (1H, m), 5.70 (1H, m), 5.57 (1H, br d, *J*=10 Hz), 4.41 (1H, dd, *J*=8, 7 Hz), 4.15 (1H, br d, *J*=16.5 Hz), 3.98 (1H, br d, *J*=16.5 Hz), 3.88 (1H, dd, *J*=8.5, 7 Hz), 3.72 (1H, dd, *J*=8.5, 8 Hz), 3.27 (1H, d, *J*=9.6 Hz), 3.16 (1H, d, *J*=9.6 Hz), 2.40 (1H, dt, *J*=17, 3 Hz), 2.00 (1H, br d, *J*=17 Hz), 1.41 (3H, s), 1.38 (3H, s); ^{13}C NMR (125 MHz) δ 125.0, 122.1, 109.1, 86.8, 74.1 (C), 143.6, 128.7, 127.8, 127.1, 79.3 (CH), 64.9, 62.0, 61.7, 24.7 (CH_2), 26.2, 25.3 (CH_3). Anal. Calcd for $C_{30}H_{32}O_4$: C, 78.92; H, 7.06. Found: C, 78.80; H, 7.00.

3.4. General procedure for allylic oxidation of compounds 9 to conjugated lactones 7

Powdered chromium trioxide (1.2 g, 12 mmol) was dried in vacuo in a dessicator containing P_2O_5. Then it was suspended under Ar in dry CH_2Cl_2 (10 mL), cooled to −20°C and treated rapidly at this temperature with 3,5-dimethylpyrazole (1.16 g, 12 mmol). After stirring the mixture for 15 min., the substrate (1 mmol) dissolved in dry CH_2Cl_2 (1 mL) was added. The reaction mixture was then stirred for 1 h at the same temperature, treated with 5M aqueous NaOH (5 mL) and further stirred at 0°C for 1 h. The reaction mixture was then poured into diluted HCl and the organic layer was washed with brine, dried on anhydrous Na_2SO_4, filtered through Celite, concentrated in a rotary evaporator and chromatographed on silica gel (elution with hexanes–EtOAc, 9:1). Chemical yields: see Tables 1 and 2.

3.4.1. 5-Undecyl-2(5*H*)-furanone, 7a (R^3=H, R^4=H, *n*=0). ^{1}H NMR (300 MHz) δ 7.44 (1H, dd, *J*=5.7, 2 Hz), 6.08 (1H, dd, *J*=5.7, 2 Hz), 5.01 (1H, ddt, *J*=7.5, 5.7, 2 Hz), 1.80–1.60 (2H, br m), 1.50–1.20 (18H, br m), 0.86 (3H, t, *J*=7 Hz); ^{13}C NMR (75 MHz) δ 173.1 (C), 156.3, 121.5, 83.5 (CH), 33.2, 31.9, 29.6 (×2), 29.5, 29.4, 29.3 (×2), 25.0, 22.7 (CH_2), 14.1 (CH_3).

3.4.2. 4-Methyl-6-undecyl-5,6-dihydropyran-2-one, 7a (R^3=Me, R^4=H, *n*=1). Oil; IR ν_{max} cm^{-1}: 1722; ^{1}H NMR (500 MHz) δ 5.78 (1H, br s), 4.35 (1H, tt, *J*=4.5, 4.5 Hz), 2.35–2.25 (2H, m), 2.18 (1H, dd, *J*=18, 3.8 Hz), 1.96 (3H, br s), 1.80–1.40 (4H, br m), 1.40–1.20 (15H, br m), 0.87 (3H, t, *J*=7 Hz); ^{13}C NMR (125 MHz) δ 165.4, 157.0 (C), 116.5, 77.0 (overlapped by solvent signal) (CH), 34.8, 34.7, 31.9, 29.6 (×3), 29.5, 29.4, 29.3, 24.9, 22.7 (CH_2), 23.0, 14.1 (CH_3). EIMS, *m/z* (% rel. int.) 266.2244 [M^+] (15), 111 (100), 82 (23). Calcd for $C_{17}H_{30}O_2$, *M*= 266.2246. Anal. Calcd for $C_{17}H_{30}O_2$: C, 76.64; H, 11.35. Found: C, 76.76; H, 11.11.

3.4.3. 5-Phenyl-2(5*H*)-furanone, 7b (R^3=H, R^4=H, *n*=0). ^{1}H NMR (400 MHz) δ 7.53 (1H, dd, *J*=5.5, 1.6 Hz), 7.40–7.35 (3H, br m), 7.30–7.25 (2H, br m), 6.23 (1H, dd, *J*=5.5, 2 Hz), 6.01 (1H, dd, *J*=2, 1.6 Hz); ^{13}C NMR (100 MHz) δ 173.1, 134.2 (C), 155.8, 129.3, 129.0, 126.5, 121.0, 84.4 (CH).

3.4.4. 4-Methyl-6-phenyl-5,6-dihydropyran-2-one, 7b (R^3=Me, R^4=H, *n*=1). ^{1}H NMR (500 MHz) δ 7.40–7.25 (5H, br m), 5.92 (1H, tq, *J*=1.5 Hz), 5.40 (1H, ddd, *J*=12, 3.8, 1.5 Hz), 2.65 (1H, dddq, *J*=18, 12, 1.5, 1.5 Hz), 2.45 (1H, dd, *J*=18, 3.8 Hz), 2.02 (3H, d, *J*=1.5 Hz); ^{13}C NMR (125 MHz) δ 164.8, 157.0, 138.7 (C), 128.6, 128.5, 126.1, 116.9, 78.7 (CH), 37.0 (CH_2), 23.0 (CH_3).

3.4.5. 6-(2-Furyl)-5,6-dihydropyran-2-one, 7c (R^3=H, R^4=H, *n*=1). Oil; IR ν_{max} cm^{-1}: 1729; ^{1}H NMR (500 MHz) δ 7.39 (1H, dd, *J*=2, 1 Hz), 6.92 (1H, ddd, *J*=9.9, 5.7, 2.5 Hz), 6.40 (1H, dd, *J*=3.3, 1 Hz), 6.35 (1H, dd, *J*=3.3, 2 Hz), 6.06 (1H, ddd, *J*=9.9, 2.5, 1.2 Hz), 5.46 (1H, dd, *J*=11, 4 Hz), 2.89 (1H, ddt, *J*=18.5, 11, 2.5 Hz),

2.59 (1H, dddd, J=18.5, 5.7, 4, 1.2 Hz); ^{13}C NMR (125 MHz) δ 163.3, 150.5 (C), 144.6, 143.1, 121.4, 110.5, 109.0, 72.4 (CH), 27.7 (CH_2). EIMS, m/z (% rel. int.) 164.0476 [M^+] (100), 94 (33), 68 (71). Calcd for $C_9H_8O_3$, M=164.0473. Anal. Calcd for $C_9H_8O_3$: C, 65.85; H, 4.91. Found: C, 66.00; H, 4.80.

3.4.6. 6-(2-Furyl)-4-methyl-5,6-dihydropyran-2-one, 7c (R^3=Me, R^4=H, n=1). Oil; IR ν_{max} cm^{-1}: 1725; ^{1}H NMR (300 MHz) δ 7.39 (1H, dd, J=2, 1 Hz), 6.41 (1H, dd, J=3, 1 Hz), 6.35 (1H, dd, J=3, 2 Hz), 5.88 (1H, sext, J=1 Hz), 5.45 (1H, dd, J=11, 4 Hz), 2.90 (1H, ddt, J=18, 11, 1.5 Hz), 2.50 (1H, br dd, J=18, 4 Hz), 2.02 (3H, d, J=1 Hz); ^{13}C NMR (75 MHz) δ 164.1, 156.6, 150.8 (C), 143.0, 116.7, 110.5, 108.8, 71.8 (CH), 32.8 (CH_2), 23.0 (CH_3). EIMS, m/z (% rel. int.) 178.0628 [M^+] (58), 133 (22), 94 (38), 82 (100). Calcd for $C_{10}H_{10}O_3$, M=178.0630. Anal. Calcd for $C_{10}H_{10}O_3$: C, 67.41; H, 5.66. Found: C, 67.30; H, 5.80.

3.4.7. 5-Decyl-4,5-dimethyl-2(5*H*)-furanone, 7d (R^3=Me, R^4=H, n=0). Oil; IR ν_{max} cm^{-1}: 1752; ^{1}H NMR (400 MHz) δ 5.69 (1H, q, J=1.5 Hz), 1.95 (3H, d, J=1.5 Hz), 1.80 (1H, m), 1.55 (1H, m), 1.38 (3H, s), 1.30–1.15 (15H, br m), 1.00 (1H, m), 0.84 (3H, t, J=7 Hz); ^{13}C NMR (100 MHz) δ 172.4, 172.0, 89.5 (C), 116.5 (CH), 36.8, 31.8, 29.6, 29.5, 29.4, 29.3, 29.2, 22.9, 22.7 (CH_2), 23.7, 14.1, 13.1 (CH_3). EIMS, m/z (% rel. int.) 252.2096 [M^+] (3), 237 (7), 209 (100), 125 (28), 112 (93), 111 (88). Calcd for $C_{16}H_{28}O_2$, M=252.2089. Anal. Calcd for $C_{16}H_{28}O_2$: C, 76.14; H, 11.18. Found: C, 76.19; H, 11.30.

3.4.8. 5-Decyl-5-methyl-2(5*H*)-furanone, 7d (R^3=H, R^4=H, n=0). Colourless solid, mp 37–39°C; IR ν_{max} cm^{-1}: 1757; ^{1}H NMR (500 MHz) δ 7.33 (1H, d, J=5.5 Hz), 6.00 (1H, d, J=5.5 Hz), 1.80–1.60 (2H, m), 1.45 (3H, s), 1.30–1.15 (16H, br m), 0.87 (3H, t, J=7 Hz); ^{13}C NMR (125 MHz) δ 172.6, 89.1 (C), 160.5, 120.5 (CH), 38.4, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 23.8, 22.7 (CH_2), 24.0, 14.1 (CH_3). EIMS, m/z (% rel. int.) 238.1935 [M^+] (2), 195 (100), 140 (26), 111 (23), 98 (92), 97 (92). Calcd for $C_{15}H_{26}O_2$, M=238.1933. Anal. Calcd for $C_{15}H_{26}O_2$: C, 75.58; H, 10.99. Found: C, 75.44; H, 11.04.

3.4.9. 6-Decyl-6-methyl-5,6-dihydropyran-2-one, 7d (R^3=H, R^4=H, n=1). Colourless solid, mp 28–30°C; IR ν_{max} cm^{-1}: 1721; ^{1}H NMR (500 MHz) δ 6.76 (1H, dt, J=10, 5 Hz), 6.00 (1H, dd, J=10, 1.8 Hz), 2.50 (1H, dt, J=18, 1.8 Hz), 2.30 (1H, ddd, J=18, 5, 1.8 Hz), 1.80–1.60 (2H, m), 1.39 (3H, s), 1.40–1.15 (16H, br m), 0.87 (3H, t, J=7 Hz); ^{13}C NMR (125 MHz) δ 164.5, 82.4 (C), 143.5, 121.0 (CH), 40.9, 33.8, 31.9, 29.8, 29.6 (×3), 29.3, 23.7, 22.7 (CH_2), 25.2, 14.1 (CH_3). EIMS, m/z (% rel. int.) 252.2101 [M^+] (2), 237 (14), 111 (100), 68 (64). Calcd for $C_{16}H_{28}O_2$, M=252.2090. Anal. Calcd for $C_{16}H_{28}O_2$: C, 76.14; H, 11.18. Found: C, 76.29; H, 11.14.

3.4.10. 6-Decyl-4,6-dimethyl-5,6-dihydropyran-2-one, 7d (R^3=Me, R^4=H, n=1). Colourless solid, mp 48–50°C; IR ν_{max} cm^{-1}: 1713; ^{1}H NMR (500 MHz) δ 5.77 (1H, sext, J=1.5 Hz), 2.40 (1H, d, J=18 Hz), 2.18 (1H, d, J=18 Hz), 1.93 (3H, d, J=1.5 Hz), 1.70–1.60 (2H, m), 1.35 (3H, s), 1.30–1.15 (16H, br m), 0.85 (3H, t, J=7 Hz); ^{13}C NMR (125 MHz) δ 164.7, 155.2, 81.5 (C), 115.9 (CH), 40.8, 39.1, 31.8, 29.7, 29.4, 29.3, 29.2, 29.1, 23.7, 22.6 (CH_2), 25.1, 23.2, 14.1 (CH_3). EIMS, m/z (% rel. int.) 266.2242 [M^+] (6), 251 (14), 221 (8), 125 (100), 82 (44). Calcd for $C_{17}H_{30}O_2$, M=266.2246. Anal. Calcd for $C_{17}H_{30}O_2$: C, 76.64; H, 11.35. Found: C, 76.59; H, 11.44.

3.4.11. 6-Decyl-3,6-dimethyl-5,6-dihydropyran-2-one, 7d (R^3=H, R^4=Me, n=1). Oil; IR ν_{max} cm^{-1}: 1718; ^{1}H NMR (500 MHz) δ 6.42 (1H, m), 2.45 (1H, ddq, J=18, 5, 1.5 Hz), 2.25 (1H, ddq, J=18, 4, 2 Hz), 1.89 (3H, q, J=1.5 Hz), 1.70–1.60 (2H, m), 1.36 (3H, s), 1.40–1.20 (16H, br m), 0.86 (3H, t, J=7 Hz); ^{13}C NMR (125 MHz) δ 165.4, 127.8, 82.3 (C), 137.3 (CH), 40.8, 34.2, 31.9, 29.8, 29.6 (×2), 29.5, 29.3, 23.8, 22.7 (CH_2), 25.2, 17.0, 14.1 (CH_3). EIMS, m/z (% rel. int.) 266.2245 [M^+] (4), 251 (10), 221 (28), 185 (19), 125 (100), 96 (38), 82 (64). Calcd for $C_{17}H_{30}O_2$, M=266.2246. Anal. Calcd for $C_{17}H_{30}O_2$: C, 76.64; H, 11.35. Found: C, 76.70; H, 11.24.

3.4.12. 5-Methyl-5-phenyl-2(5*H*)-furanone, 7e (R^3=H, R^4=H, n=0). ^{1}H NMR (500 MHz) δ 7.63 (1H, d, J=5.5 Hz), 7.35–7.30 (5H, m), 6.05 (1H, d, J=5.5 Hz), 1.83 (3H, s); ^{13}C NMR (125 MHz) δ 172.3, 139.3, 89.0 (C), 160.4, 128.9, 128.4, 124.8, 119.4 (CH), 26.4 (CH_3).

3.4.13. 6-Methyl-6-phenyl-5,6-dihydropyran-2-one, 7e (R^3=H, R^4=H, n=1). Colourless solid, mp 53–54°C; IR ν_{max} cm^{-1}: 1713; ^{1}H NMR (500 MHz) δ 7.40–7.20 (5H, m), 6.72 (1H, dt, J=9.6, 3.8 Hz), 5.95 (1H, br d, J=9.6 Hz), 2.93 (1H, br dd, J=18.2, 5 Hz), 2.76 (1H, br dt, J=18.2, 2 Hz), 1.67 (3H, s); ^{13}C NMR (125 MHz) δ 163.7, 82.9 (remaining C peak overlapped by another signal) (C), 143.6, 128.2, 127.3, 124.2, 121.3 (CH), 35.0 (CH_2), 29.8 (CH_3). EIMS, m/z (% rel. int.) 188.0838 [M^+] (32), 173 (40), 105 (71), 77 (32), 68 (100). Calcd for $C_{12}H_{12}O_2$, M=188.0837. Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.44; H, 6.60.

3.4.14. 3,6-Dimethyl-6-phenyl-5,6-dihydropyran-2-one, 7e (R^3=H, R^4=Me, n=1). Oil; IR ν_{max} cm^{-1}: 1715; ^{1}H NMR (400 MHz) δ 7.35–7.25 (5H, m), 6.41 (1H, ddq, J=5.3, 5, 1.5 Hz), 2.90 (1H, ddq, J=18, 5.3, 1.5 Hz), 2.77 (1H, ddq, J=18, 5, 1.5 Hz), 1.83 (3H, dt, J=1.5, 1.5 Hz), 1.68 (3H, s); ^{13}C NMR (100 MHz) δ 165.6, 144.3, 128.8, 83.2 (C), 137.3, 128.5, 127.5, 124.5 (CH), 35.7 (CH_2), 30.2, 16.9 (CH_3). EIMS, m/z (% rel. int.) 202.0998 [M^+] (10), 187 (14), 105 (33), 82 (100). Calcd for $C_{13}H_{14}O_2$, M=202.0994. Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.17; H, 7.01.

3.4.15. 4,6-Dimethyl-6-phenyl-5,6-dihydropyran-2-one, 7e (R^3=Me, R^4=H, n=1). Colourless solid, mp 85–87°C; IR ν_{max} cm^{-1}: 1713; ^{1}H NMR (500 MHz) δ 7.40–7.20 (5H, m), 5.74 (1H, br s), 2.82 (1H, br d, J=18 Hz), 2.73 (1H, br d, J=18 Hz), 1.89 (3H, s), 1.67 (3H, s); ^{13}C NMR (125 MHz) δ 164.3, 155.3, 143.6, 82.1 (C), 128.1, 127.1, 123.8, 116.2 (CH), 40.1 (CH_2), 29.8, 23.0 (CH_3). EIMS, m/z (% rel. int.) 202.0995 [M^+] (17), 187 (54), 105 (66), 82 (100). Calcd for $C_{13}H_{14}O_2$, M=202.0994. Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.28; H, 7.07.

3.4.16. Spiro[1,2,3,4-tetrahydronaphthalene-1,5′-2(5*H*)-furanone], 7f (R^3=H, R^4=H, n=0). Colourless solid, mp 78–80°C; IR ν_{max} cm^{-1}: 1753; ^{1}H NMR (500 MHz) δ 7.47

(1H, d, J=5.5 Hz), 7.25 (1H, m), 7.15 (2H, m), 7.04 (1H, m), 6.20 (1H, d, J=5.5 Hz), 3.00–2.80 (2H, br m), 2.20–1.90 (4H, br m); ^{13}C NMR (125 MHz) δ 172.8, 137.8, 131.3, 87.7 (C), 160.2, 129.7, 129.0, 126.9, 126.5, 120.3 (CH), 34.3, 29.3, 19.8 (CH_2). EIMS, m/z (% rel. int.) 200.0833 [M^+] (100), 172 (16), 144 (54), 128 (60), 115 (47). Calcd for $C_{13}H_{12}O_2$, M=200.0837. Anal. Calcd for $C_{13}H_{12}O_2$: C, 77.98; H, 6.04. Found: C, 78.08; H, 6.09.

3.4.17. Spiro[1,2,3,4-tetrahydronaphthalene-1,2′-[2*H*]-pyran]-6′ (3′H)-one, 7f (R^3=H, R^4=H, n=1). Oil; IR ν_{max} cm^{-1}: 1715; ^{1}H NMR (500 MHz) δ 7.55 (1H, m), 7.20 (2H, m), 7.07 (1H, m), 6.80 (1H, ddd, J=10, 6, 2.5 Hz), 6.10 (1H, ddd, J=10, 3, 1 Hz), 2.90–2.60 (4H, br m), 2.30 (1H, m), 2.15 (1H, m), 2.00 (1H, m), 1.72 (1H, m); ^{13}C NMR (125 MHz) δ 163.5, 138.3, 137.0, 82.3 (C), 143.3, 128.9, 128.2, 127.5, 126.5, 121.3 (CH), 35.8, 33.4, 29.2, 20.0 (CH_2). EIMS, m/z (% rel. int.) 214.1000 [M^+] (35), 129 (40), 68 (100). Calcd for $C_{14}H_{14}O_2$, M=214.0993. Anal. Calcd for $C_{14}H_{14}O_2$: C, 78.48; H, 6.59. Found: C, 78.68; H, 6.49.

3.4.18. 4′-Methylspiro[1,2,3,4-tetrahydronaphthalene-1,2′-[2*H*]pyran]-6′ (3′H)-one, 7f (R^3=Me, R^4=H, n=1). Colourless solid, mp 90–92°C; IR ν_{max} cm^{-1}: 1716; ^{1}H NMR (400 MHz) δ 7.50 (1H, m), 7.20 (2H, m), 7.08 (1H, m), 5.90 (1H, br s), 2.90–2.70 (3H, m), 2.49 (1H, d, J=18.5 Hz), 2.20 (1H, ddd, J=13, 6.5, 3 Hz), 2.10 (1H, ddd, J=13, 10, 3 Hz), 1.98 (1H, m), 1.97 (3H, s), 1.70 (1H, m); ^{13}C NMR (100 MHz) δ 164.3, 155.0, 138.3, 137.0, 81.5 (C), 128.8, 128.1, 127.3, 126.4, 116.1 (CH), 41.0, 33.4, 29.2, 20.0 (CH_2), 23.2 (CH_3). EIMS, m/z (% rel. int.) 228.1145 [M^+] (25), 129 (30), 82 (100). Calcd for $C_{15}H_{16}O_2$, M=228.1150. Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.99; H, 7.00.

3.4.19. 5′-Methylspiro[1,2,3,4-tetrahydronaphthalene-1,2′-[2*H*]pyran]-6′ (3′H)-one, 7f (R^3=H, R^4=Me, n=1). Oil; IR ν_{max} cm^{-1}: 1711; ^{1}H NMR (500 MHz) δ 7.54 (1H, m), 7.20 (2H, m), 7.08 (1H, m), 6.48 (1H, ddq, J=6, 3, 1.5 Hz), 2.90–2.75 (3H, m), 2.60 (1H, ddq, J=18.5, 6, 1.2 Hz), 2.30 (1H, br ddd, J=13.5, 6, 2.5 Hz), 2.10 (1H, dddd, J=13.5, 11.5, 3.3, 1 Hz), 1.99 (3H, dt, J=1.5, 1.5 Hz), 1.98 (1H, m), 1.75 (1H, m); ^{13}C NMR (125 MHz) δ 165.0, 138.5, 136.9, 128.2, 82.3 (C), 137.1, 128.8, 128.0, 127.5, 126.4 (CH), 36.2, 33.3, 29.2, 20.0 (CH_2), 17.0 (CH_3). EIMS, m/z (% rel. int.) 228.1153 [M^+] (21), 213 (8), 199 (14), 144 (14), 129 (20), 82 (100). Calcd for $C_{15}H_{16}O_2$, M=228.1150. Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 79.00; H, 6.97.

3.4.20. 1-Oxaspiro[5.7]tridec-3-en-2-one, 7g (R^3=H, R^4=H, n=1). Oil; IR ν_{max} cm^{-1}: 1718; ^{1}H NMR (500 MHz) δ 6.70 (1H, dt, J=10, 4.8 Hz), 5.96 (1H, br d, J=10 Hz), 2.38 (2H, m), 2.10–2.00 (2H, m), 1.80–1.40 (12H, br m); ^{13}C NMR (125 MHz) δ 163.8, 85.3 (C), 143.2, 121.0 (CH), 34.4 (×2), 33.6, 27.9 (×2), 24.9, 21.7 (×2) (CH_2); EIMS, m/z (% rel. int.) 194.1308 [M^+] (3), 166 (11), 123 (36), 109 (53), 109 (37), 68 (100). Calcd for $C_{12}H_{18}O_2$, M=194.1307. Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 74.29; H, 9.47.

3.4.21. 3-Methyl-1-oxaspiro[5.7]tridec-3-en-2-one, 7g (R^3=H, R^4=Me, n=1). Oil; IR ν_{max} cm^{-1}: 1709; ^{1}H NMR (500 MHz) δ 6.39 (1H, m), 2.37 (2H, m), 2.10–2.05 (2H, m), 1.89 (3H, d, J=1.5 Hz), 1.80–1.60 (7H, br m), 1.50–1.30 (5H, br m); ^{13}C NMR (125 MHz) δ 165.3, 128.1, 85.3 (C), 137.0 (CH), 34.6 (×2), 34.1, 28.0 (×2), 25.0, 21.8 (×2) (CH_2), 17.0 (CH_3); EIMS, m/z (% rel. int.) 194.1308 (M^+((3), 166 (11), 123 (36), 109 (53), 109 (37), 68 (100). Calcd for $C_{12}H_{18}O_2$, M=194.1307. Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 75.03; H, 9.80.

3.4.22. 4-Methyl-1-oxaspiro[5.7]tridec-3-en-2-one, 7g (R^3=Me, R^4=H, n=1). Colourless solid, mp 46–48°C; IR ν_{max} cm^{-1}: 1710; ^{1}H NMR (500 MHz) δ 5.76 (1H, br s), 2.30 (2H, s), 2.10–2.00 (2H, m), 1.92 (3H, s), 1.80–1.40 (12H, br m); ^{13}C NMR (125 MHz) δ 164.6, 154.7, 84.5 (C), 116.2 (CH), 39.1, 34.6 (×2), 28.0 (×2), 25.0, 21.8 (×2) (CH_2), 23.2 (CH_3); EIMS, m/z (% rel. int.) 208.1461 [M^+] (13), 180 (10), 137 (41), 124 (43), 109 (37), 82 (100). Calcd for $C_{13}H_{20}O_2$, M=208.1463. Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found: C, 74.99; H, 9.60.

3.4.23. (1*R*,2*R*,4*R*)-1,7,7-Trimethylspiro[bicyclo[2.2.1]-heptane-2,2′-[2*H*]pyran]-6′ (3′H)-one, 7h (R^3=H, R^4=H, n=1) and (1*R*,2*R*,4*R*)-1,7,7,5′-tetramethylspiro[bicyclo-[2.2.1]heptane-2,2′-[2*H*]pyran]-6′ (3′H)-one, 7h (R^3=H, R^4=Me, n=1). The physical and spectral properties of these two lactones were reported in our previous communication.[4a]

3.4.24. (6*S*,4′*S*)-6-(2,2-Dimethyl-1,3-dioxolan-4-yl)-6-trityl-oxymethyl-5,6-dihydropyran-2-one, 7i (R^3=H, R^4=H, n=1). Colourless solid,[25] mp 86–87°C; $[\alpha]_D$=+6.2 (c 1; $CHCl_3$); IR ν_{max} cm^{-1}: 1727; ^{1}H NMR (500 MHz) δ 7.40 (2H, m), 7.30 (2H, m), 7.24 (1H, m), 5.70 (1H, m), 6.67 (1H, dt, J=10, 4.5 Hz), 5.95 (1H, br d, J=10 Hz), 4.35 (1H, dd, J=7, 6.5 Hz), 3.95 (1H, dd, J=8.8, 7 Hz), 3.88 (1H, dd, J=8.8, 6.5 Hz), 3.33 (1H, d, J=10 Hz), 3.23 (1H, d, J=10 Hz), 2.67 (1H, br dd, J=19, 4.5 Hz), 2.55 (1H, br d, J=19 Hz), 1.0 (3H, s), 1.26 (3H, s); ^{13}C NMR (125 MHz) δ 162.5, 128.6, 109.8, 87.5, 83.1 (C), 143.3, 128.7, 128.0, 127.3, 120.3, 77.9 (CH), 64.7, 64.0, 25.8 (CH_2), 26.0, 25.0 (CH_3). EIMS, m/z (% rel. int.) 470.2098 [M^+] (1), 455 (2), 412 (10), 393 (11), 243 (100), 165 (38), 101 (14). Calcd for $C_{30}H_{30}O_5$, M=470.2093. Anal. Calcd for $C_{30}H_{30}O_5$: C, 76.57; H, 6.43. Found: C, 76.70; H, 6.21.

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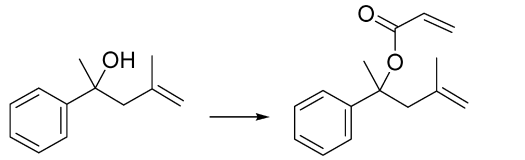
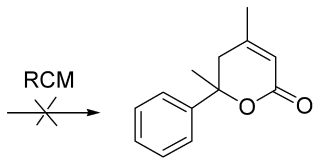


5e (R^3=Me, n=1) **6e** (R^3=Me, R^4=H, n=1)



7e (R^3=Me, R^4=H, n=1)

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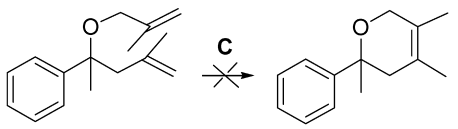
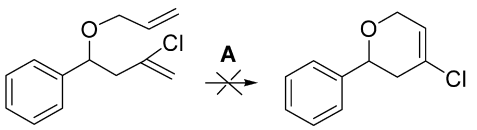
15. (a) Kirkland, T. A.; Grubbs, R. H. *J. Org. Chem.* **1997**, *62*, 7310–7318. (b) Chang, S.; Grubbs, R. H. *J. Org. Chem.* **1998**, *63*, 864–866, It is worth mentioning here that we have had good results working at substrate concentrations of up to 0.1 M in some cases.
16. As indicated in Table 1, RCM of some diolefins **8** were unsuccessful. Only starting material was recovered together with variable amounts of products identified as dimers resulting from a intermolecular cross metathesis through the monosubstituted double bond (see comments in the text). There is ample precedent for this type of behaviour.[3]
17. This was tested in the case of cyclic ether **8e** (R^3=Me, R^4=Me, *n*=1), which was recovered unchanged from the RCM reaction mixture with catalyst C (the high price and instability of the meanwhile noncommercial catalyst C, which had to be consumed up just after opening the vial, only permitted us to carry a few experiments with it). Another failure was observed in the case of chloroether **8b** (R^3=Cl, R^4=H, *n*=1), prepared in two steps from benzaldehyde,[4b] which only gave dimerization products in the presence of A.



8e (R^3=R^4=Me, n=1)



8b (R^3=Cl, R^4=H, n=1)

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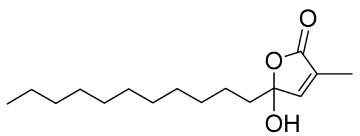
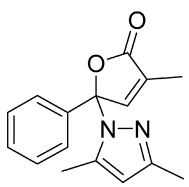


i



ii

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