A Synthesis of Densely Functionalized 2,3-Dihydropyrans Using Ring-Closing Metathesis and Base-Induced Rearrangements of Dihydropyran Oxides

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The preparation of dihydropyran and dihydrofuran oxides and their rearrangement in the presence of lithium dialkylamides to functionalized 2,3-dihydropyrans or 2,3-dihydrofurans, respectively, is described. The regiochemical outcome of the reaction can be influenced by the relative configuration of the starting epoxides and the steric demand of the base. The 2,3-dihydropyrans obtained were converted stereoselectively to difunctionalized 3,4-dihydropyrans by the carbon-Ferrier reaction, or to fused acetals by addition of dimedone, mediated by ceric ammonium nitrate. The stereochemical results are rationalized by mechanistic proposals.

Introduction

Densely functionalized tetrahydropyrans and -furans are important targets in organic synthesis, as these structures are found in a large variety of biologically active natural products.[1−11] The variation and structural diversity of the target molecules in question had a strong impact on the development of synthetic methods.[13−16] Many syntheses employ carbohydrates as readily available starting materials. In particular, 1,2-unsaturated derivatives − the so-called glycals − are starting materials in a variety of transformations.[17,18] More recently, metal-mediated approaches to these cyclic enolethers have been developed. The cyclization of acetylenic alcohols at a metal template yields 2,3-dihydrofurans or 2,3-dihydropyrans, either directly[19] or via a carbene complex intermediate, which is subsequently cleaved by action of a base.[20] Alternatively, ring-closing metathesis of appropriately substituted enol ethers gives cyclic enol ethers related to glycals; however, use of the conveniently accessible Grubbs′ catalyst is rather limited in these cases.[21−23]

In the course of our studies directed towards the cleavage of conformationally rigid dihydropyran oxides by nucleophiles,[24] we investigated the base-promoted rearrangement of these substrates with a view towards the synthesis of 2,3-dihydropyrans and -furans.[25,26] The base-promoted rearrangement of epoxides to allylic alcohols in the presence of lithium dialkylamides has been used in organic synthesis for a long time.[27−29] From early investigations into the mechanism it became clear that the rearrangement proceeds via a *syn*-selective β-elimination, with the lithium ion coordinating to the epoxide oxygen and the nitrogen of the base, thereby directing the amide to the *syn*-β-hydrogen.[30,31] To the best of our knowledge, this reaction has not been systematically investigated for the corresponding oxygen heterocycles. A recent report by Brimble et al. describes a single example of a base-promoted rearrangement of a spiroacetal-derived dihydropyran oxide, leading to a 3,4-dihydropyran derivative as the major product.[32] A two-step synthesis of glycals from carbohydrate-derived epoxides by subsequent epoxide opening with iodide and elimination of lithium methoxide was described by Thiem et al.[33] More recently, the epoxides of glycosyl phosphonates were shown to be very sensitive towards base (due to the acidifying phosphonate group) and to undergo rearrangement to phosphonated glycals even in the presence of sodium acetate.[34] In this contribution, we present a novel approach to functionalized 2,3-dihydropyrans, which uses the base-induced rearrangement of dihydropyran oxides as a key step. Some dihydrofuran oxides were also investigated as substrates for base-induced rearrangements. Furthermore, we present some examples for the utilization of the dihydropyrans obtained in this way for the stereoselective synthesis of difunctionalized dihydropyrans and fused acetals.

Results and Discussion

Preparation of the Dihydropyran Oxides

The dihydropyran oxides required for this study were obtained by epoxidation of 3,4-dihydropyrans, which are available from homoallylic alcohols by *O*-allylation and subsequent ring-closing metathesis (Scheme 1 and Table 1). An influence of the relative configuration of the epoxides on the regiochemical course of the rearrangement reaction is to be expected; thus we attempted to make both diastereomeric dihydropyran oxides available. Diastereomeric dihydropyran oxides can easily be separated by column chromatography. In most cases, epoxidation was achieved using MCPBA. If the 2-position of the dihydropyran is a quaternary centre (**3f**,**g**), action of MCPBA leads to decomposition, probably due to cleavage of the dihydropyran ring. In these cases, MMPP (magnesium monoperoxophthalate) was used. The diphenyl derivative **3j** was epoxidized with

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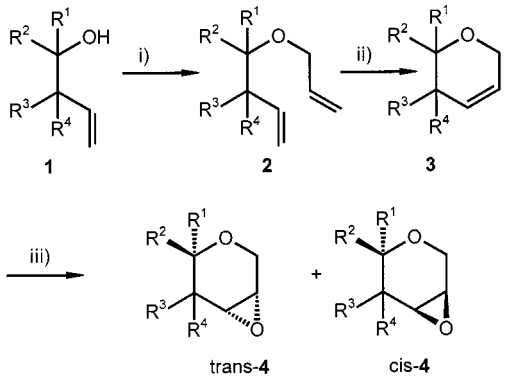
DMDO (dimethyldioxirane) in acetone; all other agents lead to complete and rapid decomposition of the material. Figure 1 shows the different dihydropyran oxides **4** employed in this study. Throughout this manuscript we will refer to a numbering scheme for the tetrahydropyran ring system which may well deviate from systematic nomenclature in some cases. The numbering is demonstrated for **4a** in Figure 1.

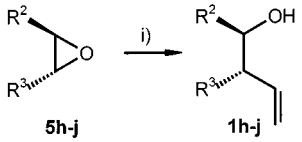


Scheme 1. Synthesis of dihydropyran oxides
Reagents and conditions: i) NaH, allyl bromide, THF, 65 °C (77−91%); ii) Grubbs′ catalyst (2 mol-%), DCM, 20 °C (85−95%); iii) MCPBA or MMPP or DMDO, 20 °C, then separate (65−80%).

Table 1. Designation used for the dihydropyran oxides **1**−**4**

1−**4**	R^1	R^2	R^3	R^4
a	H	Ph	H	H
b	H	4-$MeOC_6H_4$−	H	H
c	H	*c*-C_6H_{11}−	H	H
d	H	−(*S**,*S**)-CH(Me)Ph	H	H
e	H	−(*R**,*S**)-CH(Me)Ph	H	H
f	Me	Ph	H	H
g	−$(CH_2)_6$−		H	H
h	H	−$CH_2OCMe_2OCH_2$−		H
i	H	−$(CH_2)_4$−		H
j	H	Ph	Ph	H
k	Me	H	OH	−CH=CH_2
l	Ph	H	OH	H

The homoallylic alcohols **1a**−**g** were prepared by Grignard addition of allylmagnesium bromide to the corresponding aldehydes or ketones. Alcohol (*S*)-**1b** was obtained in enantiomerically enriched form (90% *ee*) by an enzymatic resolution of racemic **1b**, using lipase PS in vinyl acetate.[35] Alcohols **1h**−**j** were obtained by cleavage of epoxides **5h**−**j** with vinylmagnesium chloride in the presence of CuI or $CuBrSMe_2$ (Scheme 2).[36]



Scheme 2. Preparation of *trans*-disubstituted homoallylic alcohols
Reagents and conditions: i) CuI, vinylmagnesium chloride, THF, −30 °C (40−55%)

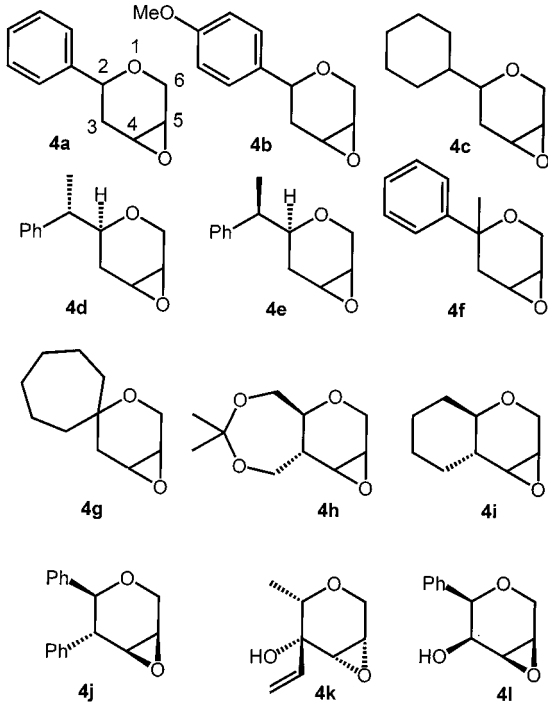
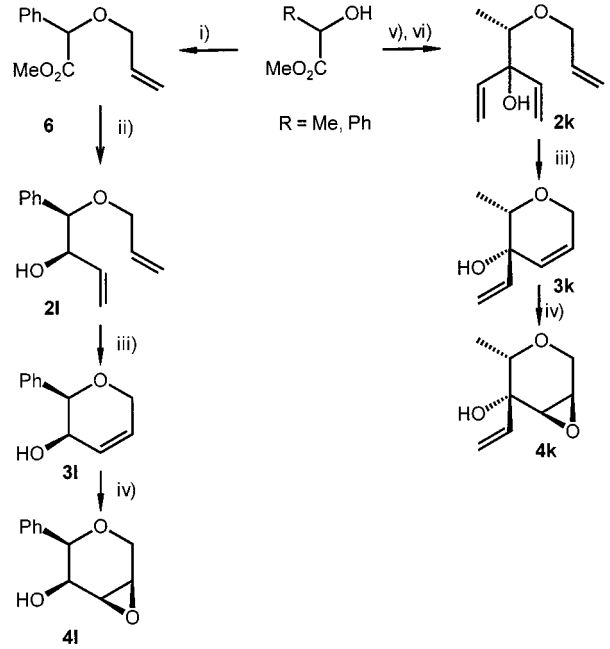


Figure 1. Numbering scheme for dihydropyran oxides **4a**−**l**

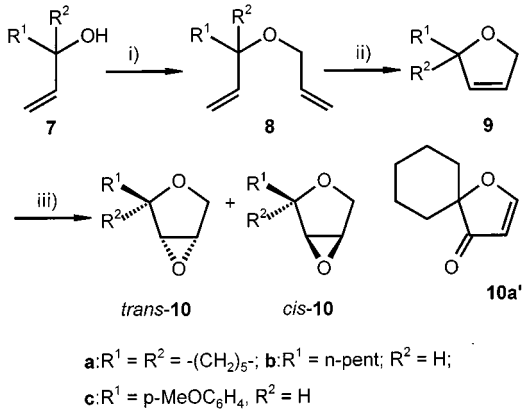
Addition of vinylmagnesium chloride to ethyl lactate gives the homoallylic alcohol (*S*)-**1k**.[37a] The subsequent *O*-allylation has to be carried out at 0 °C to avoid allylation of the tertiary hydroxy functionality. Allyl homoallyl ether **2l** was obtained in a slightly different manner, by allylating methyl mandelate with allyl bromide and silver oxide to give allyloxy ester **6** (action of sodium hydride leads to par-



Scheme 3. Preparation of dihydropyran oxides **4k,l**
Reagents and conditions: i) Ag_2O, allyl bromide, Et_2O, 20 °C (99% of **6**); ii) DIBAL, Et_2O, −90 °C, vinylmagnesium chloride, −90 °C to 20 °C (97% of **2l**); iii) Grubbs′ catalyst (5 mol-%), DCM, 20 °C (66−69%); iv) $VO(acac)_2$, *t*BuOOH, toluene, 110 °C; v) vinylmagnesium chloride (3 equiv.), Et_2O, −70 °C (86%); vi) NaH, THF, 0 °C, then allyl bromide, 0 °C (51%).

tial Wittig rearrangement), following a literature procedure.[37b] Subsequent reduction of the ester functionality and addition of vinylmagnesium chloride in a one-pot reaction furnishes **2l**. Ring-closing metathesis yields **3k** and **l** with a hydroxy functionality in the allylic position, allowing the use of substrate-directed epoxidations. We used *tert*-butyl hydroperoxide and $VO(acac)_2$ as a catalyst to achieve diastereoselective epoxidation. In the case of **3k**, epoxidation is also highly regioselective, as only the endocyclic double bond is attacked. (Scheme 3).

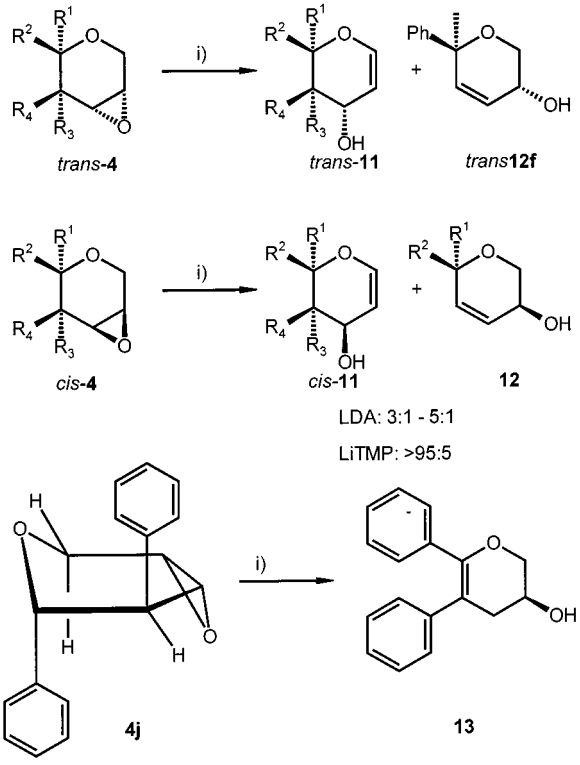
Three dihydrofuran oxides **10a−c** were synthesized, in similar manner to dihydropyran oxides **4a−g**. Starting from diallyl ethers **8a−c** (obtained from allylic alcohols **7a−c** by allylation with allyl bromide/NaH), dihydrofurans **9a−c** were obtained by ring-closing metathesis. Epoxidation with MCPBA gave dihydrofuran oxides **10a−c**. In the case of **10a**, varying amounts of a dihydrofuranone **10a′** were obtained (Scheme 4).



Scheme 4. Preparation of dihydrofuran oxides
Reagents and conditions: i) NaH, allyl bromide, THF (52−76%); ii) Grubbs′ catalyst (2 mol-%), DCM, 20 °C (66−90%); iii) MCPBA, DCM, 20 °C, then separate (54−81%).

Base-Induced Rearrangement of Dihydropyran Oxides

Reaction of diastereomerically pure dihydropyran oxides *trans*-**4a−i** with one equivalent of LDA or LiTMP in THF at ambient temperature gave a clean rearrangement to the corresponding 2,3-dihydropyrans. Only dihydropyran oxide *trans*-**4f**, with a quaternary centre in the 2-position, did not give satisfactory selectivity with LDA, as 30% of regioisomer *trans*-**12f** resulted. This problem was circumvented by using LiTMP instead of LDA. If the *cis* isomers were treated with LDA, inseparable mixtures of regioisomers of varying composition resulted in the cases of **4a−c**. Typical ratios were 3:1 to 5:1 in favour of the cyclic enol ether. The ratio of regioisomers improved to >95:5 if LiTMP was used as a base. Rearrangement of dihydropyran oxide **4j** was a very special case, as reaction with lithium dialkyl amides yielded the unexpected rearrangement product **13** exclusively. This product obviously results from initial deprotonation of H3 and subsequent isomerization of the double bond into conjugation with both phenyl substituents. The geometry of **4j** (deduced from its ^1H NMR spectroscopic data: ^3J(H2-H3) = 2.8 Hz) differs significantly from the geometries of all other dihydropyran oxides studied in this work, as the phenyl groups adopt pseudoaxial configurations here in order to minimize steric interactions which would otherwise occur. This may result in significant distortion of the oxacycle, making abstraction of $H6_{ax}$ unfavourable. Additionally, H3 is a benzylic hydrogen and will therefore be more acidic than H3 protons in the other dihydropyran oxides (Scheme 5).



Scheme 5. Base-promoted rearrangement of dihydropyran oxides
Reagents and conditions: i) LDA or LiTMP, THF, 20 °C (38−89%)

Consideration of the mechanism postulated for base-promoted rearrangements with lithium amides may rationalize the different selectivities observed for *cis*- and *trans*-dihydropyran oxides (Figure 2). In the transition state, the lithium ion coordinates to the epoxide oxygen and directs the amide to the *syn*-hydrogen. Fragmentation of this transition state is assumed to proceed in a concerted manner, because there is no hint that a carbanionic intermediate (i.e. a β-lithiated epoxide with the lithium located at the β-carbon centre) plays a significant role during the rearrangement process.[27] In the case of the dihydropyran oxides **4a−f**, the substituent in the 2-position is a molecular anchor group and adopts a pseudoequatorial position, indicated by the *trans*-diaxial coupling constants ^3J(H2-$H3_{ax}$) of approximately 11 Hz. In the case of **4f**, a NOESY experiment was used to show that the methyl group adopts a pseudoaxial and the phenyl group a pseudoequatorial position. If the generally accepted mechanism for the rearrangement of epoxides to allylic alcohols is operating here, the *syn*-hydrogens in the 3- or the 6-position are required for abstraction. In the case of the *trans*-dihydropyran oxides, the *syn*-hydrogens are pseudoequatorially oriented in the 3- and pseudo-

axially oriented in the 6-position. For the *cis*-dihydropyran oxides the situation is reversed: the *syn*-proton in the 3-position is pseudoaxially oriented and the *syn*-proton in the 6-position adopts a pseudoequatorial position. For the *trans*- as well as for the *cis*-dihydropyran oxide, abstraction of a pseudoaxially oriented hydrogen may proceed via a transition state where a nearly synclinal conformation is attained (transition states **A** and **D**). Thus, in the case of *cis*-dihydropyran oxides, the products *cis*-**12** resulting from transition state **D** should be preferred. However, this rationale does not take into account steric interactions between the dialkylamide and the substituent in the 2-position, and obviously these outweigh the benefits resulting from synclinal arrangement in transition state **D** and so make transition state **C** (leading to the desired 2,3-dihydropyrans *cis*-**11**) more favourable overall. Thus, improvement of the regioselectivity when LDA is substituted by LiTMP may be rationalized by greater steric hindrance between the base and the substituent in the 2-position. The exceptional behaviour of *trans*-**4f** may result from distortion of the molecule by steric interactions of the axially oriented methyl group. For 2-phenylethyl-substituted dihydropyran oxides **4d** and **e**, comparatively good selectivities were obtained even with LDA, which is probably due to better shielding of the 3-position of the dihydropyran ring. For spirocyclic derivative **4g**, the ratio of regioisomers **11** and **12** was very good (50:1) even when LDA was used as a base, which may probably be explained by steric interactions between the base and the cycloheptane ring. For dihydropyran oxides **4h**, **i**, **k** and **l**, with a substituent in the 3-position, no regioisomeric rearrangement products **12** were detected at all (Figure 2).

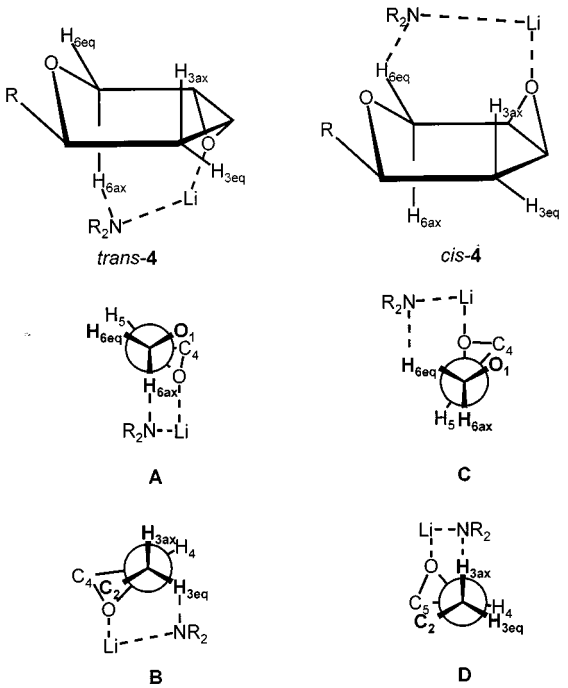
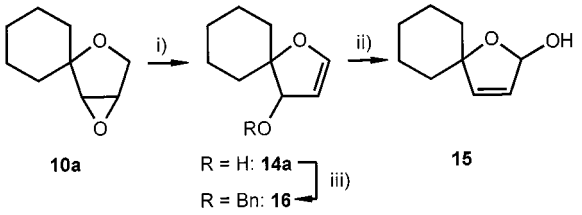


Figure 2. Transition states for the deprotonation step of base-promoted rearrangements of dihydropyran oxides.

One may argue that it is not primarily the stereochemistry of the dihydropyran oxide starting materials that influences the regioselectivity of the rearrangement (see discussion above) but the relative stereochemistry of the transition states depicted in Figure 2. Thus, it may well be that the lithium chelate transition state for the *cis*-dihydropyran oxides undergoes a conformational change prior to the rearrangement.

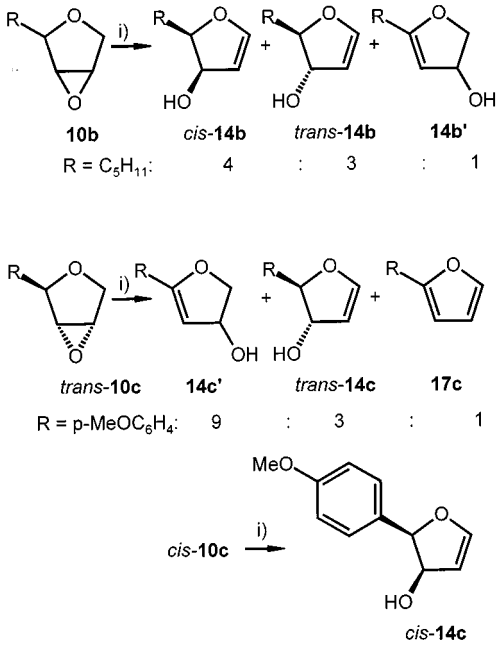
It would be an interesting extension, both from the synthetic and from the mechanistic point of view, to employ dihydrofuran oxides in base-induced rearrangement reactions. The expected products, 2,3-dihydrofurans with a hydroxy function in the allylic position, are normally prepared from carbohydrate-derived starting materials, using elimination reactions,[38] or from nucleosides.[39] These compounds are useful building blocks in the synthesis of polyether antibiotics[40,41] or *C*-nucleosides.[42] From a mechanistic point of view, it is interesting to see whether good regiocontrol can also be achieved for five-membered oxacycles, in which both β-positions are adjacent to the ring oxygen. For substrate **10a**, with a quaternary centre in the 2-position, no regioisomers are to be expected. Only the rearrangement product **14a** is observed in NMR spectra of the crude product. Column chromatography on silica induces a partial rearrangement to hemiacetal **15**; this is suppressed if the hydroxy group in **14a** is protected as a benzyl ether **16** (Scheme 6).



Scheme 6. Base induced rearrangement of **10a** and subsequent double bond migration
Reagents and conditions: i) LDA, THF, 20 °C (95%); ii) SiO_2; iii) NaH, benzyl bromide, THF, 65 °C (78%).

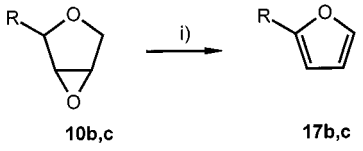
Dihydrofuran oxide **10b** was obtained as an inseparable mixture of diastereomers and used directly in the rearrangement reaction. A 4:3:1 mixture of isomers resulted, and was characterized by NMR spectroscopy of the crude reaction mixture. The two major products resulted from deprotonation at C5 and were diastereomers; *trans*-**14b** slightly preferred. Assignment of relative configuration is based on the value for ^3J(H2-H3), which is approximately 2.5 Hz for the major diastereomer and 7.0 Hz for the minor isomer. These values are in good agreement with those reported in the literature for similarly substituted glycals.[39] The third isomer − **14b′** − was formed by abstraction of H2. The corresponding isomers were obtained for 2-methoxyphenyl derivatives *trans*- and *cis*-**10c**. Treatment of *trans*-**10c** with LiTMP gave three products in a ratio of 9:3:1; these were identified as **14c′**, *trans*-**14c** and the elimination product, furan **17c**. Compound **14c′** was identified by the characteristic AB coupling pattern for hydrogens H5 and H5′. Base-

induced rearrangement of *cis*-**10c** yielded only one rearrangement product, which was identified as *cis*-**14c**. It may be concluded that (at least for **10c**) the *syn* elimination mechanism is also operating for dihydrofuran oxides, as product **14c′** is only observed for the *trans* isomer. The preference for **14c′** in this case may be attributed to higher acidity in the benzylic position and a more rigid conformation of **10c** compared to **10b** (Scheme 7).



Scheme 7. Product distribution for base-promoted rearrangements of dihydrofuran oxides **10b,c**
Reagents and conditions: i) LDA or LiTMP, THF, 20 °C

Attempts to separate individual compounds from the mixtures were not successful, due at least in part to decomposition upon chromatography. Therefore, the mixtures of stereoisomeric dihydrofuran oxides **10b** and **c** were treated with LDA followed by tosyl chloride, inducing an elimination to the corresponding furans **17b** and **c**. Isolated yields of **17** were approximately 75% based on the starting epoxide (Scheme 8).

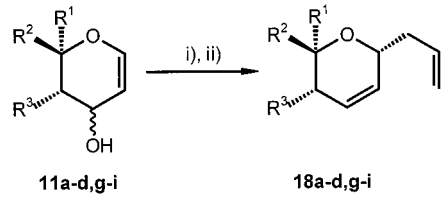


Scheme 8. One-pot procedure for the preparation of furans from dihydrofuran oxides
Reagents and conditions: i) LDA, THF, then TosCl (75%).

Stereoselective Transformations of Dihydropyrans 11

The dihydropyrans obtained by base-promoted rearrangement are structurally related to glycals, which have proven to be valuable starting materials for a large variety of target molecules in carbohydrate chemistry.[43] Glycals also serve as building blocks in the synthesis of marine natural products with 2,6-difunctionalized dihydropyrans embedded in a macrocycle.[44] A reaction commonly used in this field is the so called carbon−Ferrier rearrangement:[45,46] the nucleophilic displacement of a leaving group by a carbon electrophile, such as allyltrimethylsilane,[47] mediated by Lewis acid. More recently, this transformation has been applied to a variety of syntheses.[48−52] These reactions proceed via an oxocarbenium ion and normally yield the kinetic substitution product − the *trans* or α anomer − in good yields and with high diastereoselectivities, explained by a kinetic anomeric effect.[53−55] Related investigations have also been made for nucleophilic displacement reactions in tetrahydrofuran derivatives.[56]

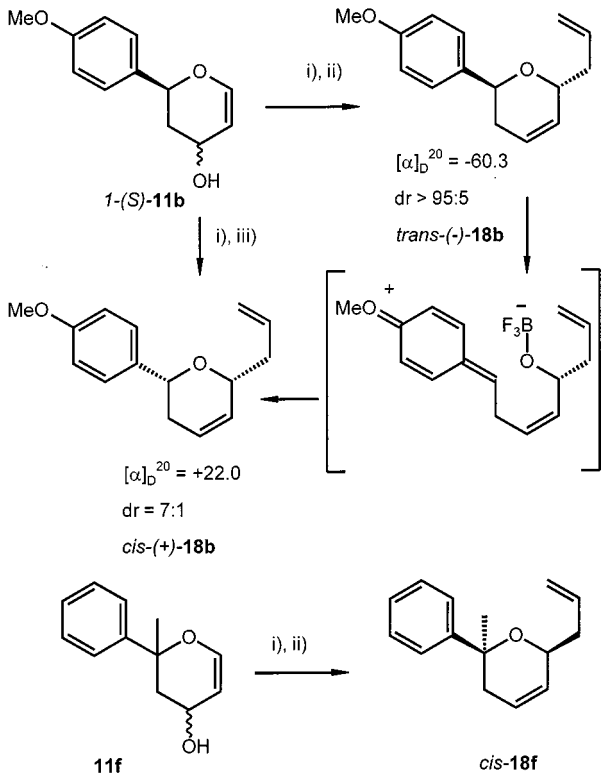
We have studied the reaction of cyclic enol ethers **11a−d**, **f-i** (diastereomerically pure or as mixtures of *trans* and *cis* isomers) with allyltrimethylsilane and $BF_3{\cdot}OEt_2$. For **11a**, **c**, **d**, **h** and **i**, formation of the *trans*-dihydropyrans **18** proceeded with good diastereoselectivity (>95:5, determined by ^1H NMR spectroscopy). The acetal structure in **11h** was cleaved under the reaction conditions and it was not possible to obtain the resulting diol in analytically pure form and in good yield (Scheme 9). The stereochemical results obtained are in agreement with those predicted on the basis of the kinetic anomeric effect.



Scheme 9. Stereoselective allylation of 2,3-dihydropyrans
Reagents and conditions: i) Ac_2O, NEt_3, DMAP (cat.), DCM, 0 °C; ii) allyltrimethylsilane, $BF_3{\cdot}OEt_2$, DCM, −78 °C (49−87% over two steps).

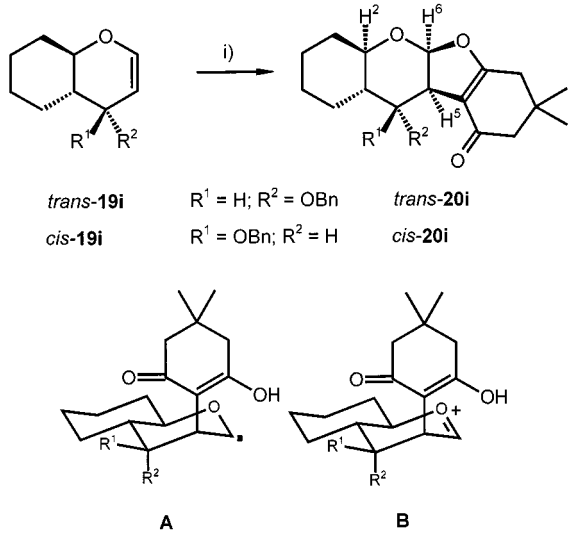
Allylation of the 4-methoxyphenyl derivative **11b** under the same conditions gave the expected kinetic product *trans*-**18b** if the reaction was carried out at −80 °C and quenched at this temperature after consumption of the starting material was complete (Scheme 10). If the reaction mixture was warmed to −10 °C and stirring was continued for 3 hours, a rearrangement to the thermodynamically more stable *cis* isomer occurred (*cis*/*trans* = 7:1). We propose that this anomerization proceeds via a cleavage, mediated by Lewis acid, of the C2−O-bond, followed by isomerization and recyclization, a mechanism originally proposed by Suzuki et al. for anomerization reactions of *C*-aryl glycosides.[57] Thus, *cis*-**18b** is the product of a sequential allylation reaction/anomerization mediated by Lewis acid. The fact that the first step of the sequence is fast at very low temperatures compared to the second step allowed us to control the stereochemical outcome just by controlling the temperature and reaction time. We used enantiomerically enriched (*ee* = 90%) homoallylic alcohol (*S*)-(−)-**1b** as a starting material for this sequence. No significant deviation from the ratio of enantiomers in (+)-*cis*-**18b** could be detected by NMR shift experiments ($Eu(hfc)_3$, 500 MHz), compared to (−)-**1b**. Electronic stabilization of the intermediate seems to play an important role, because no noticeable anomerization to the *cis* isomer was observed for the phenyl derivative *trans*-**18a**. Allylation of **11f** preferentially yields the dihydropyran *cis*-

18f, with a quaternary centre at C2 (*cis*/*trans* = 17:1) (Scheme 10). The *cis* arrangement of the phenyl and the allyl substituent was unambiguously determined by NOESY experiments: NOE interactions between H6 and the methyl group show that both substituents adopt a pseudoaxial position; thus, phenyl and allyl substituent must be oriented pseudoequatorially. It is difficult to decide what the origin of this stereochemical outcome is. The reason may be a shielding of one face of the cyclic oxycarbenium ion in the transition state by the pseudoaxially oriented methyl group, making an attack of the nucleophile from the opposite side energetically more favourable. Alternatively, an anomerization of the intermediate substitution product *trans*-**18f** may occur, analogously to **18b**. However, *trans*-**18f** could not be detected in significant amounts when the reaction was conducted and quenched at −80 °C (Scheme 10).



Scheme 10. *cis*-Stereoselective allylation reactions
Reagents and conditions: i) Ac_2O, NEt_3, DMAP (cat.), DCM, 0 °C; ii) allyltrimethylsilane, $BF_3{\cdot}OEt_2$, DCM, −78 °C (87% over two steps for **18b**, 78% for **18f**); iii) allyltrimethylsilane, $BF_3{\cdot}OEt_2$, DCM, −78 °C to −10 °C, 3 h (75% over two steps).

Our synthetic route to dihydropyrans **11** makes accessible individual diastereomers with different relative configurations of substituents R^{1-4}. This advantage can be exploited for investigations into the diastereoselectivity of addition reactions across the endocyclic enol ether double bond. Over the past few years, addition of 1,3-dicarbonyl radicals (generated by oxidation of 1,3-dicarbonyl compounds with Mn^{III} or Ce^{IV} salts)[58] to enol ethers has been investigated for C−C bond-forming reactions.[59-60] The reaction has also been applied to the synthesis of fused acetals from dihydropyrans and dihydrofurans;[61,62] however, to the best of our knowledge, only conformationally mobile dihydropyran substrates without stereogenic centres have so far been investigated. We have chosen the conformationally rigid *trans*-decalin analogues **11i** (both diastereomers were investigated separately) to study the stereochemical outcome of the reaction with dimedone in the presence of CAN. Subjecting unprotected **11i** to the reaction conditions led to rapid and complete decomposition of the starting material. We repeated the reaction with the benzyl-protected derivatives *trans*- and *cis*-**19i** (Scheme 11). In both cases, formation of one diastereomer of the tetracyclic derivative **20i** was strongly preferred, with diastereomeric ratios of approximately 20:1. Related compounds have been prepared from glycals by rhodium-catalysed carbenoid insertion[63] and by radical cascades of *O*-glycosides with acetylene functionality in their side chains.[64,65]



Scheme 11. CAN-mediated annellation of dimedone to dihydropyrans
Reagents and conditions: i) CAN, $NaHCO_3$, acetonitrile, water, 20 °C (60%).

Elucidation of the relative configuration was achieved both for *cis*- and *trans*-**20i** by analysis of the coupling constants and by COSY and NOESY experiments. Orientation of the benzyloxy group does not seem to exert any significant influence on the stereochemical outcome of the addition; the five-membered oxacycle is anellated in such a way that relative orientation of hydrogens H2, H5 and H6 is *cis*, regardless of the relative configuration of the starting material. Formation of products *cis*- and *trans*-**20i** may be rationalized on the basis of a mechanism recently proposed by Linker et al. for the CAN-mediated addition of malonates to glycals;[60] in the first step of the mechanism the dimedone radical will attack at the carbon atom C5, leading to anomeric radical intermediate **A**. The rigid decalin-like structure of the molecule is probably the reason for the preferred axial attack of the dimedone radical. In the next step of the mechanism, oxidation of the anomeric radical will occur, leading to an oxo carbeniumion intermediate **B**, which is attacked by one of the carbonyl oxygens, thereby

creating the acetal bond. Elimination of H^+ completes the mechanism.

Conclusion

In conclusion, we have shown that dihydropyran oxides can be converted into synthetically useful dihydropyrans in good yields and selectivities, starting from easily accessible homoallylic alcohols. Dihydrofurans with one quaternary centre can be prepared analogously, while for other derivatives regioselectivity is poor. However, in these cases a clean elimination reaction leads to functionalized furans in preparatively useful yields. The regiochemical results of the base-induced rearrangement reactions are in agreement with a *syn*-deprotonation mechanism. Utilization of the dihydropyrans obtained in this study is possible either by converting the newly generated alcohol functionality into a leaving group (stereoselective synthesis of difunctionalized *cis*- or *trans*-dihydropyrans, depending on the reaction conditions) or by addition reactions across the enol ether bond.

Application of the methodology described in this contribution is currently under investigation in our laboratory.

Experimental Section

General Remarks: All experiments were conducted in dry reaction vessels under an atmosphere of dry argon. Solvents were purified by standard procedures. − Unless otherwise stated, ^{1}H NMR spectra were recorded at 400 MHz in $CDCl_3$ with $CHCl_3$ as internal standard (δ = 7.24). Signal assignment for tetrahydropyran derivatives refers to the numbering scheme denoted in Figure 1 and does not necessarily correlate to systematic nomenclature. − ^{13}C NMR spectra were recorded at 100 MHz in $CDCl_3$ with $CDCl_3$ as internal standard (δ = 77.0). In some cases, NMR spectra were recorded in C_6D_6 (^{1}H NMR: C_6D_5H as internal standard, δ = 7.18; ^{13}C NMR: C_6D_6 as internal standard, δ = 128.0). *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. − IR spectra were recorded as films on NaCl plates or as KBr disks. The peak intensities are defined as very strong (vs), strong (s), medium (m), and weak (w). − Mass spectra were obtained at 70 eV. − Melting points are not corrected. − Alcohols **1a−g** were prepared by addition of allylmagnesium bromide to the appropriate aldehyde or ketone.[66] 4,4-Dimethyl-3,5,8-trioxabicyclo[5.1.0]octane (**5h**)[67] and 2-vinyl-1-cyclohexanol (**1i**)[36] have been described in the literature. Experimental and analytical details for compounds **2a,b** and **c**, **3a, b** and **c** and **4a, b** and **c** have been described by us previously.[24] The ruthenium catalyst $Cl_2(PCy_3)_2Ru{=}CHPh$ was prepared following Grubbs' procedure.[68]

General Procedure for the Preparation of Alcohols 1h−j by Cleavage of Epoxides: CuI (5.70 g, 30.0 mmol) was suspended in dry ether (80 mL) and the mixture cooled to −60 °C. A solution of vinylmagnesium chloride (70.0 mmol, 41.0 mL) in THF was added, and the mixture was stirred at −60 °C for 30 min. A solution of the epoxide (30.0 mmol) in ether (25 mL) was slowly added and the reaction mixture was warmed to −30 °C. Stirring was continued until the starting material had been fully consumed as indicated by TLC. The reaction mixture was poured onto aqueous NH_4Cl solution and filtered to remove any precipitates. The organic layer was separated, and the aqueous layer was extracted with ether. The combined organic extracts were dried with $MgSO_4$, and the crude product was purified by flash chromatography.

(5*S,6*R**)-2,2-Dimethyl-6-vinyl-1,3-dioxepan-5-ol (1h):** Obtained from **5h** (7.20 g, 50.0 mmol) as a colourless liquid. Yield: 5.90 g (55%). − LRMS (EI); *m*/*z*: [M^+] not found, 115 (23), 59 (100). − ^{1}H NMR: δ = 5.71 (ddd, 1 H, *J* = 17.3, 10.5, 8.3, −C*H*=CH_2), 5.20 (d, 1 H, *J* = 17.3, =CH_2), 5.17 (d, 1 H, *J* = 10.5, =CH_2), 3.72 (dd, 1 H, *J* = 12.3, 2.3, OC*H*H), 3.65 (dd, 1 H, *J* = 12.3, 3.0, OC*H*H), 3.62−3.47 (3 H, OCH*H*, C*H*OH), 2.36 (d, 1 H, *J* = 5.3, O*H*), 2.23 (m, 1 H, C*H*−CH=), 1.31 (s, 3 H, Me), 1.28 (s, 3 H, Me). − ^{13}C NMR: δ = 136.5 (1), 118.1 (2), 101.2 (0), 72.2 (1), 63.2 (2), 60.9 (2), 51.2 (1), 24.6 (3), 24.5 (3). − IR (NaCl, neat): $\tilde{\nu}$ = 3454 (s), 2989 (s), 1640 (m), 1372 (s), 1220 (s), 1047 (s), 919 (s), 846 (s).

(1*S,2*R**)-1,2-Diphenylbut-3-en-1-ol (1j):** Obtained from **5j** (7.90 g, 40.0 mmol) as a colourless solid, m.p. 70 °C. Yield: 3.60 g (40%). − $C_{16}H_{16}O$ (224.3): calcd. C 85.6, H 7.2; found C 85.0, H 7.2. − ^{1}H NMR: δ = 7.37−7.21 (10 OH, Ph), 5.89 (ddd, 1 H, *J* = 17.1, 10.3, 8.0 Hz, −C*H*=), 4.99 (ddd, 1 H, *J* = 10.3, 1.3, 1.0, =C*H*$_2$), 4.89 (d, 1 H, *J* = 8.0, C*H*OH), 4.85 (ddd, 1 H, *J* = 17.1, 1.5, 1.3, =C*H*$_2$), 3.63 (dd, 1 H, *J* = 8.0, 8.0, C*H*−CH=), 2.00 (s(br.), 1 H, O*H*). − ^{13}C NMR: δ = 141.8 (0), 140.2 (0), 137.6 (1), 128.7 (1), 128.6 (1), 128.0 (1), 127.7 (1), 127.0 (1), 127.0 (1), 117.2 (2), 77.4 (1), 58.4 (1). − IR (NaCl, neat): $\tilde{\nu}$ = 3386 (s), 3029 (m), 1495 (m), 1454 (s), 1051 (m), 1010 (m), 754 (s), 698 (s). −

Methyl 2-Allyloxy-2-phenylacetate (6): To a solution of methyl mandelate (3.00 g, 18.0 mmol) in ether (100 mL) was added allyl bromide (2.3 mL, 27.0 mmol) and silver oxide (8.40 g, 36.0 mmol) under an atmosphere of argon. The mixture was refluxed for 2 hours in the dark, and then stirring was continued for 48 hours at room temperature. The silver salts were removed by filtration, washed with ether (100 mL) and the solvent was removed in vacuo to give analytically pure **6** (3.70 g, 99%). − $C_{12}H_{14}O_3$ (206.2): calcd. C 69.9, H 6.8; found C 69.4, H 6.8. LRMS (EI); *m*/*z*: 207 (M^+ + 1, <5), 147 (95), 129 (10), 121 (36), 105 (100), 91 (12), 77 (8), 51 (10). − ^{1}H NMR δ = 7.48−7.43 (2 H, Ph), 7.37−7.30 (3 H, Ph), 5.93 (dddd, 1 H, *J* = 17.3, 10.3, 6.0, 5.5, C*H*=CH_2), 5.28 (dddd, 1 H, *J* = 17.3, 1.5, 1.5, 1.5, C*H*$_2$=CH), 5.21 (ddm, 1 H, *J* = 10.3, 1.3, C*H*$_2$=CH), 4.94 (s, 1 H, C*H*−O), 4.06−4.03 (2 H, C*H*$_2$−O), 3.80 (s, 3 H, C*H*$_3$). − ^{13}C NMR: δ = 171.0 (0), 136.1 (0), 133.6 (1), 128.5 (1), 128.4 (1), 127.1 (1), 118.0 (2), 79.5 (1), 70.2 (2), 52.0 (3). − IR (NaCl, neat): $\tilde{\nu}$ = 3032 (w), 2953 (m), 2865 (w), 1755 (s), 1554 (m), 1209 (s), 1173 (s), 1101 (s), 699 s.

(*S*)-3-Vinylpent-4-en-2-ol (1k):[37a] To a solution of methyllactate (6.00 g, 51.0 mmol) in ether (200 mL) was added vinylmagnesium chloride (1.7 M solution in THF, 120 mL, 203 mmol) at −70 °C. The mixture was allowed to warm to room temperature and stirring was continued for 12 hours. The reaction was poured onto saturated NH_4Cl solution, extracted with ether and the organic layer was dried with $MgSO_4$. Filtration and removal of the solvent under reduced pressure gave crude **1l** (5.60 g, 86%), which was sufficiently pure for preparative purposes. − $C_7H_{12}O_2$ (128.2): calcd. C 65.6, H 9.4; found C 65.6, H 9.4. − $[\alpha]_D^{23}$ = +5.1 (*c* = 1.66, DCM). − LRMS (EI); *m*/*z*: 111 (M^+ − OH, 10%), 83 (20), 55 (100). − ^{1}H NMR: δ = 5.95 (dd, 1 H, *J* = 17.3, 10.8, C*H*=CH_2), 5.93 (dd, 1 H, *J* = 17.3, 10.8, C*H*=CH_2), 5.38 (dd, 1 H, *J* = 17.3, 1.3, C*H*$_2$=CH), 5.35 (dd, 1 H, *J* = 17.3, 1.3, C*H*$_2$=CH), 5.23 (dd, 1 H, *J* = 10.8, 1.3, C*H*$_2$=CH), 5.22 (dd, 1 H, *J* = 10.8, 1.3, C*H*$_2$=CH), 3.67 (dq, 1 H, *J* = 6.5, 4.3, C*H*−CH_3), 2.45 (br. s, 1 H, *H*O), 2.24 (br.

s, 1 H, *H*O), 1.12 (d, 3 H, *J* = 6.5, C*H*$_3$−CH). − ^{13}C NMR: δ = 140.0 (1), 138.0 (1), 115.7 (2), 115.3 (2), 78.4 (0), 72.7 (1), 16.8 (3). − IR (NaCl, neat): ṽ = 3430 (s), 2987 (m), 1424 (m), 1087 (m), 1001 (s), 930 (s).

General Procedure for the Preparation of Allyl Ethers 2a−j and 8a−c: NaH (2.10 g 60% dispersion in mineral oil, 53.0 mmol) was suspended in dry THF (100 mL). A solution of the corresponding homoallylic or allylic alcohol **1** or **7**, respectively, (34.0 mmol) in THF (35 mL) was added dropwise with stirring at ambient temperature. After the addition was complete, the mixture was heated to reflux for 30 min and then cooled to ambient temperature. Allyl bromide (4.4 mL, 51.0 mmol) was added slowly, causing an exothermic reaction and formation of a white precipitate. The mixture was stirred for one hour, after which time the starting material had been consumed completely, as monitored by TLC. Water (50 mL) was carefully added with stirring and the mixture was diluted with MTBE (150 mL). The organic layer was washed with saturated NH_4Cl solution and dried with $MgSO_4$. The solvent was evaporated and the residue distilled or chromatographed on silica.

1-((*S*)-1-Allyloxybut-3-enyl)-4-methoxybenzene (2b): Obtained from (*S*)-**1b** (2.30 g, 12.8 mmol) as a colourless liquid, b.p. 120 °C (0.1 mbar), yield: 2.86 g (100%). − $[\alpha]_D^{20}$ = −38.2 (*c* = 2.44, $CHCl_3$).

((1*S,2*S**)-2-Allyloxy-1-methylpent-4-enyl)benzene (2d):** Obtained from **1d** (3.70 g, 21.0 mmol) as a colourless liquid, b.p. 120 °C (0.5 mbar), yield: 4.10 g (90%). − $C_{15}H_{20}O$ (216.3): calcd. C 83.2, H 9.3; found C 82.6, H 9.4. − LRMS (EI); *m*/*z*: 175 (M^+ − 41, 49), 111 (100), 41 (64). − ^{1}H NMR: δ = 7.30−7.15 (5 H, Ph), 5.88 (dddd, 1 H, *J* = 17.3, 10.5, 5.6, 5.6, OCH$_2$C*H*=), 5.82 (dddd, 1 H, *J* = 17.3, 10.3, 7.3, 7.0, CHCH$_2$C*H*=), 5.24 (ddd, 1 H, *J* = 17.3, 3.3, 1.8, =C*H*$_2$), 5.12 (ddd, 1 H, *J* = 10.5, 3.0, 1.3, =C*H*$_2$), 5.02 (dm, 1 H, *J* = 10.3, =C*H*$_2$), 4.99 (ddd, 1 H, *J* = 17.3, 3.3, 1.3, =C*H*$_2$), 4.03 (dddd, 1 H, *J* = 12.6, 5.6, 1.5, 1.5, OC*H*$_2$), 3.89 (dddd, 1 H, *J* = 12.6, 5.6, 1.5, 1.5, OC*H*$_2$), 3.44 (ddd, 1 H, *J* = 6.8, 6.5, 5.0, C*H*O−), 2.87 (qd, 1 H, *J* = 7.0, 6.8, C*H*CH$_3$), 2.22 (ddd, 1 H, *J* = 14.5, 7.0, 5.0, CHC*H*HCH=), 2.07 (ddd, 1 H, *J* = 14.5, 7.3, 6.5, CHC*H*HCH=), 1.33 (d, 3 H, *J* = 7.0, CH$_3$). − ^{13}C NMR: δ = 144.7 (0), 135.1 (1), 134.9 (1), 128.2 (1), 127.8 (1), 126.1 (1), 116.8 (2), 116.4 (2), 83.3 (1), 71.3 (2), 43.4 (1), 36.4 (2), 17.0 (3). − IR (NaCl, neat): ṽ = 3078 (m), 2930 (m), 2858 (m), 1641 (m), 1453 (m), 1085 (s), 916 (s), 701 (s).

((1*R,2*S**)-2-Allyloxy-1-methylpent-4-enyl)benzene (2e):** Obtained from **1e** (2.30 g, 13.0 mmol) as a colourless liquid, b.p. 120 °C (0.5 mbar), yield: 2.30 g (81%). − LRMS (EI); *m*/*z*: 175 (M^+ − 41, 47), 111 (100), 41 (51). − ^{1}H NMR: δ = 7.33−7.17 (5 H, Ph), 5.85 (dddd, 1 H, *J* = 17.0, 10.5, 7.0, 7.0, CH$_2$C*H*=CH$_2$), 5.73 (dddd, 1 H, *J* = 17.0, 10.2, 5.8, 5.3, OCHCH$_2$C*H*=CH$_2$), 5.17 (dm, 1 H, *J* = 17.0, =C*H*$_2$), 5.09 (dm, 1 H, *J* = 10.5, =C*H*$_2$), 5.07 (dm, 1 H, *J* = 10.1, =C*H*$_2$), 5.06 (dm, 1 H, *J* = 17.0, =C*H*$_2$), 3.97 (dddd, 1 H, *J* = 12.6, 5.8, 1.5, 1.5, OC*H*$_2$), 3.83 (dddd, 1 H, *J* = 12.6, 5.3, 1.5, 1.5, OC*H*$_2$), 3.45 (ddd, 1 H, *J* = 6.8, 6.8, 5.8, C*H*O−), 2.98 (qd, 1 H, *J* = 6.8, 6.8, C*H*CH$_3$), 2.28−2.15 (2, CHC*HH*CH=), 1.33 (d, 3 H, *J* = 6.8, CH$_3$). − ^{13}C NMR: δ = 143.9 (0), 135.4 (1), 135.3 (1), 128.3 (1), 128.0 (1), 126.2 (1), 116.7 (2), 116.3 (2), 83.4 (1), 71.4 (2), 42.9 (1), 35.8 (2), 16.7 (3). − IR (NaCl, neat): ṽ = 3078 (m), 2976 (s), 2858 (m), 1641 (m), 1453 (m), 1073 (s), 916 (s), 701 (s).

(1-Allyloxy-1-methylbut-3-enyl)benzene (2f): Obtained from **1f** (3.00 g, 18.0 mmol) as a colourless liquid. Yield: 3.60 g (89%). − $C_{14}H_{18}O$ (202.3): calcd. C 83.1, H 8.9; found C 82.9, H 9.2. − LRMS (EI); *m*/*z*: 161 (M^+ − 41,), 145 (100). − ^{1}H NMR: δ = 7.42−7.22 (5 H, Ph), 5.92 (dddd, 1 H, *J* = 17.1, 10.3, 5.3, 5.3, OCH$_2$C*H*=CH$_2$), 5.69 (dddd, 1 H, *J* = 17.1, 10.8, 7.0, 7.0, CH$_2$C*H*=CH$_2$), 5.30 (dddd, 1 H, *J* = 17.1, 1.8, 1.5, 1.5, =CH$_2$), 5.13 (dddd, 1 H, *J* = 10.3, 1.5, 1.5, 1.5, =CH$_2$), 5.02 (dm, 1 H, *J* = 10.8, =CH$_2$), 5.01 (dm, 1, *J* = 17.1, =CH$_2$), 3.79 (dddd, 1 H, *J* = 12.6, 5.3, 1.5, 1.5, OCH*H*), 3.68 (dddd, 1 H, *J* = 12.6, 5.3, 1.8, 1.5, OCH*H*), 2.61 (dd, 1 H, *J* = 14.1, 7.0, CH*H*), 2.54 (dd, 1 H, *J* = 14.1, 7.0, CH*H*), 1.56 (s, 3 H, C*H*$_3$). − ^{13}C NMR: δ = 144.9 (0), 135.5 (1), 134.1 (1), 128.1 (1), 126.9 (1), 126.1 (1), 117.6 (2), 115.6 (2), 78.8 (0), 63.8 (2), 47.6 (2), 23.3 (3). − IR (NaCl, neat): ṽ = 3076 (m), 2980 (s), 2859 (m), 1641 (m), 1446 (s), 1069 (s), 916 (s), 701 (s).

1-Allyl-1-allyloxycycloheptane (2g): Obtained from **1g** (2.30 g, 15.0 mmol) as a colourless liquid. Yield: 2.80 g (96%). − LRMS (EI); *m*/*z*: 153 (M^+ − CH$_2$CH=CH$_2$, 100%), 41 (88). − ^{1}H NMR: δ = 5.89 (ddt, 1 H, *J* = 17.3, 10.3, 5.3, OCH$_2$C*H*=CH$_2$), 5.81 (ddt, 1 H, *J* = 17.3, 10.5, 7.0, CH$_2$C*H*=CH$_2$), 5.26 (ddt, 1 H, *J* = 17.3, 1.8, 1.8, =CH$_2$), 5.08 (ddt, 1 H, *J* = 10.3, 1.8, 1.5, =CH$_2$), 5.03 (dm, 1 H, *J* = 10.5, =CH$_2$), 5.01 (dm, 1 H, *J* = 17.3, =CH$_2$), 3.86 (ddd, 1 H, *J* = 5.3, 1.5, 1.5, OC*H*$_2$), 2.23 (ddd, 1 H, *J* = 7.0, 1.3, 1.3, OC*H*H), 1.77 (dd, 1 H, *J* = 14.1, 8.5, C*H*H(cycloheptane), 1.65−1.30 (10 H, cycloheptane). − ^{13}C NMR: δ = 136.0 (1), 134.5 (1), 117.1 (2), 115.5 (2), 79.4 (0), 62.0 (2), 43.1 (2), 37.7 (2), 29.7 (2), 22.1 (2). − IR (NaCl, neat): ṽ = 3075 (m), 2978 (s), 2924 (vs), 2857 (vs), 1461 (s), 1127 (m), 1065 (s), 995 (s).

(5*S,6*R**)-5-Allyloxy-2,2-dimethyl-6-vinyl-1,3-dioxepane (2h):** Obtained from **1h** (5.90 g, 34.0 mmol) as a colourless liquid. Yield: 5.60 g (77%). − $C_{12}H_{20}O_3$ (212.29): C 67.9, H 9.5; found C 67.9, H, 9.5. − LRMS (EI); *m*/*z*: 212 (M^+, 1%), 124 (23), 101 (70), 55 (100). − ^{1}H NMR: δ = 5.85 (dddd, 1 H, *J* = 17.3, 10.3, 5.8, 5.8, OCH$_2$C*H*=CH$_2$), 5.70 (ddd, 1 H, *J* = 17.3, 10.5, 7.8, CHC*H*=CH$_2$), 5.23 (dddd, 1 H, *J* = 17.3, 1.5, 1.5, 1.5, =CH$_2$), 5.13 (dm, 1 H, *J* = 17.3, =CH$_2$), 5.11 (dm, 1 H, *J* = 10.5, =CH$_2$), 4.05 (dddd, 1 H, *J* = 12.8, 5.8, 1.5, 1.5, OCH*H*CH=CH$_2$), 3.98 (dddd, 1 H, *J* = 12.8, 5.8, 1.3, 1.3, OCH*H*C*H*=CH$_2$), 3.67 (dd, 1 H, *J* = 12.3. 4.3, OCH*H*), 3.64 (dd, 1 H, *J* = 12.3, 7.0, OCH*H*), 3.60 (dd, 1 H, *J* = 12.6, 3.6, OCH*H*), 3.53 (dd, 1 H, *J* = 12.6, 8.5, OCH*H*), 3.21 (ddd, 1 H, *J* = 7.3, 7.3, 4.3), 2.34 (ddd, 1 H, *J* = 8.5, 7.3, 3.6), 1.31 (s, 3 H), 1.28 (s, 3 H). − ^{13}C NMR: δ = 136.9 (1), 135.0 (1), 117.0 (2), 117.0 (2), 101.0 (0), 80.1 (1), 70.9 (2), 61.7 (2), 61.6 (2), 49.1 (1), 24.7 (3), 24.4 (3). − IR (NaCl, neat): ṽ = 2990 (s), 2941 (s), 1380 (s), 1372 (s), 1220 (s), 1161 (s), 1085 (s), 919 (s).

(1*R,2*S**)-1-Allyloxy-2-vinylcyclohexane (2i):** Obtained from **1i** (1.30 g, 10.0 mmol) as a colourless liquid. Yield: 1.40 g (85%). − LRMS (EI); *m*/*z*: 167 (M^+ + 1, 5%), 109 (100). − ^{1}H NMR: δ = 5.93−5.81 (2 H, −C*H*=CH$_2$), 5.23 (dddd, 1 H, *J* = 17.3, 1.8, 1.8, 1.8, =C*H*$_2$), 5.09 (dddd, 1 H, *J* = 10.3, 1.8, 1.3, 1.3, =C*H*$_2$), 5.03 (ddd, 1 H, *J* = 17.6, 1.8, 1.3, =C*H*$_2$), 4.97 (ddd, 1 H, *J* = 10.3, 1.8, 1.0, =C*H*$_2$), 4.05 (dddd, 1 H, *J* = 12.8, 5.5, 1.5, 1.5, OCH*H*), 3.91 (dddd, 1 H, *J* = 12.8, 5.5, 1.5, 1.5, OCH*H*), 2.98 (ddd, 1 H, *J* = 9.5, 9.5, 4.4, CHC*H*OCH$_2$), 2.10−1.95 (2 H, CH, CH$_2$), 1.80−1.68 (2 H, CH, CH$_2$), 1.60 (m, 1 H, CH, CH$_2$), 1.26−1.10 (4 H, CH, CH$_2$). − ^{13}C NMR: δ = 141.6 (1), 135.6 (1), 116.2 (2), 113.9 (2), 81.0 (1), 69.8 (2), 47.6 (1), 31.3 (2), 31.0 (2), 25.0 (2), 24.6 (2). − IR (NaCl, neat): ṽ = 3079 (m), 2926 (vs), 2856 (vs), 1640 (m), 1449 (m), 1093 (s), 912 (s), 805 (m).

(1*S,2*R**)-1-Allyloxy-1,2-diphenylbut-3-ene (2j):** Obtained from **1j** (1.00 g, 5.0 mmol) as a colourless liquid. Yield: 1.00 g (84%). − LRMS (EI); *m*/*z*: 207 (M^+ − OCH$_2$CH=CH$_2$, 40%), 147 (100), 105 (90). − ^{1}H NMR: δ = 7.45−7.05 (5 H, Ph), 5.95 [ddd, 1 H, *J* = 17.1, 10.0, 8.3, CH(Ph)C*H*=CH$_2$], 5.72 (dddd, 1 H, *J* = 16.8,

10.5, 5.9, 4.8, $OCH_2CH{=}CH_2$), 5.07 (dm, 1 H, J = 16.8, $=CH_2$), 5.06 (dm, 1 H, J = 10.0, $=CH_2$), 4.95 (dm, 1 H, J = 10.5, $=CH_2$), 4.86 (dm, 1 H, J = 17.1, $=CH_2$), 4.58 [d, 1 H, J = 7.5, OC*H*(Ph)], 3.89 (dddd, 1 H, J = 13.3, 4.8, 1.8, 1.5, OC*H*H), 3.66 (dddd, 1 H, J = 13.3, 5.9, 1.3, 1.3, OC*H*H), 3.65 (dd, 1 H, J = 8.3, 7.5, C*H*Ph). − ^{13}C NMR: δ = 141.1 (0), 140.2 (0), 138.4 (1), 134.8 (1), 129.0−127.0 (1), 126.3 (1), 125.4 (1), 116.5 (2), 116.4 (2), 84.1 (1), 69.4 (2), 57.3 (1). − IR (NaCl, neat): ṽ = 3083 (m), 3028 (m), 2859 (m), 1494 (m), 1452 (m), 1088 (s), 1069 (s), 919 (s), 699 (s).

1-Allyloxy-1-vinylcyclohexane (8a):[69] Obtained from **7a** (3.50 g, 28.0 mmol) as a colourless liquid. Yield: 2.40 g (52%). − ^{1}H NMR: δ = 5.87 (ddt, 1 H, J = 17.1, 10.5, 5.5, $OCH_2CH{=}CH_2$), 5.69 (dd, 1 H, J = 17.6, 11.1, $CHHCH{=}CH_2$), 5.23 (ddt, 1 H, J = 17.1, 1.8, 1.8, $OCH_2CH{=}CH_2$), 5.11 (dd, 1 H, J = 11.1, 1.3, $CH{=}CH_2$), 5.09 (dd, 1 H, J = 17.6, 1.5, $CH{=}CH_2$), 5.05 (ddt, 1 H, J = 10.6, 1.8, 1.5, $OCH_2CH{=}CH_2$), 3.74 (ddd, 1 H, J = 10.6, 1.8, 1.5, $OCHHCH{=}CH_2$), 1.77−1.15 (10 H, CH_2). − ^{13}C NMR: δ = 143.1 (1), 135.9 (1), 115.3 (2), 114.4 (2), 75.8 (0), 62.6 (2), 34.3 (2), 25.7 (2), 21.7 (2).

3-Allyloxyoct-1-ene (8b):[70] Obtained from **7b** (6.50 g, 51.0 mmol) as a colourless liquid, b.p. 100 °C (7 mbar). Yield: 6.50 g (76%). − ^{1}H NMR: δ = 5.88 (dddd, 1 H, J = 17.3, 10.3, 6.0, 5.0, $OCH_2CH{=}CH_2$), 5.64 (ddd, 1 H, J = 16.6, 10.8, 7.8, $CHCH{=}CH_2$), 5.23 (dddd, 1 H, J = 17.3, 1.8, 1.8, 1.8, $OCH_2CH{=}CH_2$), 5.17−5.10 (3 H, $CHHCH{=}CH_2$ + $CHCH{=}CH_2$), 4.01 (dddd, 1 H, J = 12.8, 5.0, 1.5, 1.5, OCHH), 3.80 (dddd, 1 H, J = 12.8, 6.0, 1.5, 1.3, OCHH), 3.64 (ddd, 1 H, J = 7.8, 6.4, 6.4, OC*H*CH=), 1.66−1.20 (8 H, CH_2), 0.85 (t, 3 H, J = 7.0, CH_3). − ^{13}C NMR: δ = 139.2 (1), 135.2 (1), 116.7 (2), 116.5 (2), 80.7 (1), 69.1 (2), 35.4 (2), 31.8 (2), 25.0 (2), 22.6 (2), 14.0 (3).

1-(1-Allyloxyallyl)-4-methoxybenzene (8c): Obtained from **7c** (4.50 g, 27.0 mmol) as a colourless liquid, b.p. 175 °C (0.3 mbar). Yield: 3.50 g (63%). − LRMS (EI) *m*/*z*: 204 (M^+, 25%), 163 (77), 147 (73), 135 (100). − ^{1}H NMR: δ = 7.16 (d, 2 H, J = 8.3, Ar), 6.78 (d, 2 H, J = 8.3, Ar), 5.89−5.77 (2 H, CH=), 5.17 (dddd, 1 H, J = 17.3, 1.8, 1.8, 1.8, $OCH_2CH{=}CH_2$), 5.15 (ddd, 1 H, J = 17.1, 1.5, 1.5, $CHCH{=}CH_2$), 5.07 (ddd, 1 H, J = 10.3, 1.5, 1.0, $CHCH{=}CH_2$), 5.06 (dddd, 1 H, J = 10.5, 1.8, 1.5, 1.5, OCH2CHCH2), 4.65 (d, 1 H, J = 6.5, CHO), 3.87 (dddd, 1 H, J = 12.8, 5.5, 1.5, 1.3, OCHH), 3.83 (dddd, 1 H, J = 12.8, 7.0, 1.5, 1.5, OCHH), 3.67 (s, 3 H, OCH_3). − ^{13}C NMR: δ = 159.0 (0), 139.0 (1), 134.8 (1), 133.0 (1), 128.1 (1), 116.6 (2), 115.8 (2), 113.7 (1), 81.5 (1), 68.9 (2), 55.1 (3). − IR (KBr, neat): ṽ = 2836 (m), 1611 (s), 1512 (s), 1247 (s), 1071 (m), 1036 (m), 924 (m), 829 (m).

(*S*)-3-(1-Allyloxyethyl)-penta-1,4-dien-3-ol (2k): A solution of diol **1k** (1.00 g, 8.0 mmol) was cooled to 0 °C. NaH (60% dispersion in mineral oil, 0.31 g, 8.0 mmol) was added, followed by allyl bromide (1.0 mL, 12.0 mmol). The mixture was stirred at 0 °C for 12 hours, after which time the reaction was complete as indicated by TLC. The reaction was diluted with MTBE, hydrolysed with saturated NH_4Cl solution, dried with $MgSO_4$, filtered and the solvent was removed in vacuo. The residue was purified by flash chromatography (hexanes/MTBE, 2:1). Yield: 0.67 g (51%). − $C_{10}H_{16}O_2$ (168.23): C 71.4, H 9.6; found C 71.4, H 9.6. − $[\alpha]_D^{26}$ = +19.6 (c = 1.40, $CHCl_3$). − LRMS (EI); *m*/*z*: 163 (M^+ + 1, < 5), 151 (10), 133 (10), 107 (14), 95 (90), 85 (26), 73 (16), 67 (16), 55 (100). − ^{1}H NMR: δ = 5.92 (dd, 1 H, J = 17.3, 10.3, C−C*H*=CH_2), 5.91 (dd, 1 H, J = 17.3, 10.8, C−C*H*=CH_2), 5.82 (dddd, 1 H, J = 17.3, 10.3, 6.0, 5.5, CH_2−C*H*=CH_2), 5.31 (dd, 1 H, J = 17.3, 1.5 CH_2=CH−C), 5.29 (dd, 1 H, J = 17.3, 1.5, CH_2=CH−C), 5.19 (dddd, 1 H, J = 17.3, 3.0, 1.5, 1.5, CH_2=CH−CH_2), 5.13 (dd, 1 H, J = 10.8, 1.5, CH_2=CH−C), 5.13 (dd, 1 H, J = 10.8, 1.5, CH_2=CH−C), 5.09 (dddd, 1 H, J = 10.3, 3.0, 1.5, 1.5, CH_2=CH−CH_2), 4.05 (dddd, 1 H, J = 12.8, 5.5, 1.5, 1.5, CH_2−CH), 3.87 (dddd, 1 H, J = 12.8, 6.0, 1.5, 1.5, CH_2−CH), 3.35 (q, 1 H, J = 6.3, C*H*−CH_3), 2.53 (br. s, 1 H, *H*O), 1.07 (d, 3 H, J = 6.3, CH_3−CH). − ^{13}C NMR: δ = 139.9 (1), 138.8 (1), 134.8 (1), 116.8 (2), 114.7 (2), 114.6 (2), 80.1 (1), 77.7 (0), 70.6 (2), 14.1 (3). − IR (NaCl, neat): ṽ = 3464 (s), 2983 (m), 2871 (m), 1411 (m), 1374 (m), 1091 (s), 995 (s), 924 (s).

(1*S,2*S**)-1-Allyloxy-1-phenyl-but-3-en-2-ol (2l):** To a solution of ester **6** (2.50 g, 12.0 mmol) in ether (100 mL) was added at −90 °C DIBAL (2.6 mL, 15 mmol). After complete consumption of the ester (TLC control), vinylmagnesium chloride (1.7 M solution in THF, 10.7 mL, 18 mmol) was added and the mixture was slowly warmed to room temperature. After stirring for 12 hours, the reaction was poured into water, the precipitate was dissolved with the minimum amount possible of 2 N HCl (aq), and the mixture was extracted with ether. The organic extracts were dried and evaporated, and the residue was purified by column chromatography on silica (hexanes/MTBE, 3:1) to give **2k** (2.40 g, 97%) as an inseparable mixture of diastereomers (1*S**,2*S**):(1*S**,2*R**) = 5:1. − LRMS (EI); *m*/*z*: 187 (M^+ − OH, 29), 169 (18), 147 (100), 129 (65), 117 (25), 105 (100), 91 (28), 57 (10), 51 (10). − ^{1}H NMR: δ = 7.28−7.19 (5 H, Ph), 5.81 (dddd, 1 H, J = 17.3, 10.5, 6.3, 5.0, CH_2−C*H*), 5.52 (ddd, 1 H, J = 17.3, 10.5, 5.5, CH−C*H*=CH_2), 5.16 (dddd, 1 H, J = 17.3, 1.5, 1.5, 1.5, CH_2=CH−CH_2), 5.12 (ddd, 1 H, J = 17.3, 1.5, 1.3, CH_2=CH−CH), 5.09 (dddd, 1 H, J = 10.5, 1.5, 1.3, 1.3, CH_2=CH−CH_2), 4.99 (ddd, 1 H, J = 10.5, 1.5, 1.5, CH_2=CH−CH), 4.15 (dddd, 1 H, J = 8.0, 5.5, 1.5, 1.3, C*H*−OH), 4.06 (d, 1 H, J = 8.0, C*H*−Ph), 3.89 (dddd, 1 H, J = 12.6, 5.0, 1.5, 1.5, CH_2−CH), 3.73 (dddd, 1 H, J = 12.6, 6.3, 1.5, 1.3, CH_2−CH), 3.07 (br. s, 1 H, *H*O). − ^{13}C NMR: δ = 137.8 (0), 135.4 (1), 134.3 (1), 128.3 (1), 128.2 (1), 127.8 (1) 117.3 (2), 116.9 (2), 85.1 (1), 76.1 (1), 69.5 (2). − IR (NaCl, neat): ṽ = 3464 (s), 3083 (m), 2866 (m), 1647 (w), 1453 (m), 1256 (m), 1083 (s), 995 (s), 926 (s), 702 s. − NMR spectroscopical data of the minor diastereomer (partially overlapped by the signals for the major isomer): ^{1}H NMR: δ = 4.34 (d, 1 H, J = 5.0, C*H*−Ph), 3.95 (dddd, 1 H, J = 12.8, 5.0, 1.5, 1.5, CH_2−CH). − ^{13}C NMR: δ = 137.8 (0), 136.3 (1), 134.4 (1), 128.3 (1), 127.9 (1), 127.6 (1), 117.1 (2), 116.5 (2), 83.9 (1), 75.7 (1), 69.9 (2).

General Procedure for the Preparation of Dihydropyrans 3 and Dihydrofurans 9: The ruthenium catalyst (138 mg, 2 mol-%) was added in one portion to a solution of the corresponding ether **2** or **8** (8.4 mmol) in DCM (40 mL). The mixture was stirred at room temperature until complete conversion was indicated by TLC (approximately 0.5 h). The solvent was evaporated and the residue was purified by kugelrohr distillation or by flash chromatography as indicated for the individual compounds.

(*S*)-2-(4-Methoxyphenyl)-3,6-dihydro-2*H*-pyran (3b): Obtained from (*S*)-**2b** (1.10 g, 5.0 mmol) as a colourless liqid, b.p. 150 °C (0.09 mbar), yield: 0.87 g (91%). − $[\alpha]_D^{20}$ = −73.7 (c = 2.78, $CHCl_3$).

(*S)-2-[(*S**)-1-Phenylethyl)]-3,6-dihydro-2*H*-pyran (3d):** Obtained from **2d** (2.10 g, 10.0 mmol) as a colourless liquid. TLC: cyclohexane/ether 40:1. Purification by kugelrohr distillation, b.p. 130 °C (0.3 mbar). Yield: 1.70 g (90%). − LRMS (EI); *m*/*z*: 188 (M^+, 4), 105 (85), 83 (100), 55 (81). − ^{1}H NMR: δ = 7.32−7.25 (2, Ph), 7.23−7.18 (3 H, Ph), 5.75−5.65 (2 H, H3,4), 4.30−4.18 (2 H, $H5_{ax/eq}$), 3.54 (ddd, 1 H, J = 10.3, 8.5, 3.3, H2), 2.74 (dq, 1 H, J = 8.5, 6.8, C*H*CH_3), 1.92 (dddd, 1 H, J = 17.1, 10.3, 3.5, 3.5, $H3_{ax}$), 1.63

(dm, 1 H, J = 17.1, $H3_{eq}$), 1.38 (d, 3 H, J = 6.8, CH_3). − ^{13}C NMR: δ = 144.2 (0), 128.3 (1), 127.8 (1), 126.3 (1), 126.0 (1), 124.4 (1), 78.3 (1), 66.3 (2), 45.6 (1), 29.5 (2), 18.4 (3). − IR (NaCl, neat): ṽ = 3061 (m), 3030 (m), 2929 (s), 2829 (s), 1494 (m), 1452 (m), 1180 (m), 1091 (s), 701 (s).

(*S)-2-[(*R**)-1-Phenylethyl]-3,6-dihydro-2*H*-pyran (3e):** Obtained from **2e** (1.10 g, 5.0 mmol) as a colourless liquid. TLC: cyclohexane/ether 40:1. Purification by kugelrohr distillation, b.p. 130 °C (0.3 mbar). Yield: 0.80 g (85%). − ^{1}H NMR: δ = 7.26−7.10 (5 H,' Ph), 5.73 (dm, 1 H, J = 10.0, H3), 5.62 (dm, 1 H, J = 10.0, H4), 4.08 (dm, 1 H, J = 16.5, H5), 4.01 (dm, 1 H, J = 16.5, H5), 3.58 (ddd, 1 H, J = 10.0, 7.3, 3.5, H2), 2.80 (dq, 1 H, J = 7.3, 7.0, C*H*CH_3), 2.03 (ddm, 1 H, J = 17.1, 10.0, $H3_{ax}$), 1.92 (dm, 1 H, J = 17.1, $H3_{eq}$), 7.0, 6.8, $H3_{eq}$), 1.20 (d, 3 H, J = 7.0, CH_3). − ^{13}C NMR: δ = 144.5 (0), 128.1 (1), 127.8 (1), 126.3 (1), 126.1 (1), 124.2 (1), 77.7 (1), 66.4 (2), 44.8 (1), 28.3 (2), 17.2 (3). − IR (NaCl, neat): ṽ = 3061 (m), 3030 (m), 2929 (s), 2831 (s), 1494 (m), 1452 (m), 1180 (m), 1089 (s), 700 (s).

2-Methyl-2-phenyl-3,6-dihydro-2*H*-pyran (3f): Obtained from **2f** (3.40 g, 17.0 mmol) as a colourless liquid. TLC: cyclohexane/ether 40:1. Purification by kugelrohr distillation, b.p. 150 °C (0.3 mbar). Yield: 2.80 g (95%). − $C_{12}H_{14}O$ (174.2): calcd.C 82.7, H 8.1; found C 82.6, H 8.4. − LRMS (EI); *m*/*z*: 174 (M^+, 15%), 157 (100). − ^{1}H NMR: δ = 7.45 (d, 2 H, J = 8.0, Ph, *ortho*-H), 7.35 (dd, 2 H, J = 8.0, 7.3, Ph, *meta*-H), 7.25 (t, 1 H, J = 7.3, Ph, *para*-H), 5.87 (dm, 1 H, J = 10.3, H3,4), 5.62 (dm, 1 H, J = 10.3, H3,4), 4.18 (dm, 1 H, J = 16.8, H5), 3.96 (dm, 1 H, J = 16.8, H5), 2.68 (dm, 1 H, J = 17.6, H3), 2.39 (dm, 1 H, J = 17.6, H3), 1.50 (s, 3 H, CH_3). − ^{13}C NMR: δ = 145.2 (0), 128.1 (1), 126.8 (1), 125.9 (1), 125.5 (1), 123.0 (1), 73.6 (0), 61.7 (2), 34.0 (2), 29.4 (3). − IR (NaCl, neat): ṽ = 3034 (m), 2975 (s), 2927 (s), 2833 (s), 1494 (m), 1445 (s), 1088 (m), 763 (s), 700 (s).

1-Oxaspiro[5,6]dodec-3-ene (3g):[71] Obtained from **2g** (1.46 g, 7.5 mmol) as a colourless liquid. TLC: cyclohexane/ether 20:1. Purification by kugelrohr distillation, b.p. 150 °C (7 mbar). Yield: 1.12 g (90%). − ^{1}H NMR: δ = 5.71−5.63 (2 H, H4,5), 4.06 (m, 2 H, H6), 1.92 (m, 2 H, H3), 1.80−1.30 (12 H, CH_2). − ^{13}C NMR: δ = 125.7 (1), 123.2 (1), 74.5 (0), 60.6 (2), 38.2 (2), 35.7 (2), 29.9 (2), 21.8 (2).

(5*R,11*S**)-8,8-Dimethyl-1,7,9-trioxabicyclo[5.4.0]undec-3-ene (3h):** Obtained from **2h** (5.50 g, 26.0 mmol) as a colourless liquid. TLC: cyclohexane/ether, 3:1. Purification by kugelrohr distillation, b.p. 160 °C (3 mbar). Yield: 4.40 g (92%). − $C_{10}H_{16}O_3$ (184.2): calcd. C 65.2, H 8.8; found C 65.5, H 8.7. − LRMS (EI); *m*/*z*: 183 (M^+ − 1, 48%), 125 (58), 95 (60), 43 (100). − ^{1}H NMR: δ = 5.36 (dm, 1 H, J = 10.3, H5), 5.31 (dm, 1 H, J = 10.3, H4), 4.07 (dm, 1 H, J = 16.8, H6), 3.99 (dddd, 1 H, J = 16.8, 4.5, 1.5, 1.5, H6), 3.86 (dd, 1 H, J = 11.5, 4.5, C-2CH*H*O), 3.81 (dd, 1 H, J = 11.5, 8.8, C-2CH*H*O), 3.38 (dd, 1 H, J = 12.1, 4.8, C-3CH*H*O), 3.33 (dd, 1 H, J = 12.1, 10.0, C-3CH*H*O), 3.27 (ddd, 1 H, J = 8.8, 8.8, 4.5, H2), 2.47 (m, 1 H, H3), 1.28 (s, 3 H, CH_3), 1.27 (s, 3 H, CH_3). − ^{13}C NMR: δ = 127.7 (1), 125.4 (1), 101.3 (0), 78.6 (1), 67.0 (2), 64.8 (2), 62.3 (2), 43.2 (1), 25.1 (3), 25.0 (3). − IR (NaCl, neat): ṽ = 3028 (m), 2940 (m), 1220 (s), 1094 (s), 1076 (s), 838 (m).

(5*S,10*R**)-1-Oxabicyclo[4.4.0]dec-3-ene (3i):** Obtained from **2i** (1.60 g, 10.0 mmol) as a colourless liquid. TLC: cyclohexane/ether, 40:1. Purification by kugelrohr distillation, b.p. 130 °C (7 mbar). Yield: 1.30 g (95%). − LRMS (EI); *m*/*z*: 139 (M^+ + 1, 100%), 121 (60). − ^{1}H NMR: δ = 5.60 (dm, 1 H, J = 10.0, H3,4), 5.55 (dm, 1 H, J = 10.0, H3,4), 4.21 (dm, 1 H, J = 16.6, H6), 4.15 (dm, 1 H, J = 16.6, H6), 3.01 (ddd, 1 H, J = 10.8, 9.0, 3.8, H2), 1.96−1.60 (4 H, CH_2), 1.35−1.20 (3 H, CH_2), 1.00 (m, 1 H, CH, CH_2), 0.81 (m, 1 H, CH, CH_2). − ^{13}C NMR: δ = 129.6 (1), 125.6 (1), 78.7 (1), 66.3 (2), 40.8 (1), 32.0 (2), 30.5 (2), 25.9 (2), 25.1 (2). − IR (NaCl, neat): ṽ = 3076 (m), 2924 (s), 2852 (s), 1641 (m), 1449 (m), 1081 (s), 912 (m), 708 (m).

(2*S,3*R**)-2,3-Diphenyl-3,6-dihydro-2*H*-pyran (3j):** Obtained from **2j** (1.00 g, 3.8 mmol) as a colourless liquid. TLC: cyclohexane/ether 20:1. Purification by flash chromatography. Yield: 0.81 g (89%). − LRMS (EI); *m*/*z*: 235 (M^+ − 1, 5%), 219 (40), 130 (100). − ^{1}H NMR: δ = 7.14−7.05 (6 H, Ph), 6.96−6.90 (4 H, Ph), 6.13−6.02 (2 H,H3,4), 4.97 (d, 1 H, J = 3.3, H2), 4.60 (d, 1 H, J = 17.0, H6), 4.51 (d, 1 H, J = 17.0, H6), 3.48 (m, 1 H, H3). − ^{13}C NMR: δ = 140.4 (0), 138.5 (0), 129.9 (1), 128.1 (1), 127.5 (1), 127.3 (1), 126.7 (1), 126.4 (1), 126.3 (1), 125.8 (1), 79.2 (1), 67.2 (2), 47.7 (1). − IR (NaCl, neat): ṽ = 3030 (m), 1452 (s), 1093 (s), 741 (s), 699 (s).

(2*S*,3*S*)- and (2*S*,3*R*)-2-Methyl-3-vinyl-3,6-dihydro-2*H*-pyran-3-ol (3k): Obtained from triene **2k** (1.46 g, 6.0 mmol) as a 2.5:1 mixture of diastereomers. TLC: hexanes/MTBE, 2:1. Purification by flash chromatography on silica. Yield: 0.55 g (66%). − $[\alpha]_D^{26}$ = +150.2 (c = 1.64, $CHCl_3$). − LRMS (EI); *m*/*z*: 123 (M^+ − OH, 84), 95 (75), 81 (100), 78 (12), 69 (18), 67 (50), 55 (36). − IR (NaCl, neat): ṽ = 3442 (s), 2985 (m), 1376 (m), 1065 (s), 993 (s), 972 (s), 925 (m). − **(2*S*, 3*S*)-3k:** ^{1}H NMR: δ = 5.92 (ddd, 1 H, J = 10.0, 4.0, 3.5, C*H*=CH), 5.80 (ddd, 1 H, J = 10.0, 1.5, 1.5, C*H*=CH), 5.78 (dd, 1 H, J = 17.6, 10.8, C*H*=CH_2), 5.36 (dd, 1 H, J = 17.6, 1.5, CH_2=CH), 5.20 (dd, 1 H, J = 10.8, 1.5, CH_2=CH), 4.22 (ddd, 1 H, J = 16.8, 3.5, 1.8, CH_2−CH), 4.16 (ddd, 1 H, J = 16.8, 4.0, 1.5, CH_2−CH), 3.50 (q, 1 H, J = 6.3, C*H*−CH_3), 2.58 (br. s, 1 H, *H*O−), 1.21 (d, 3 H, J = 6.3, CH_3−CH). − ^{13}C NMR: δ = 139.5 (1), 130.7 (1),128.2 (1), 115.0 (2), 77.7 (1), 70.0 (0), 65.7 (2), 14.1 (3). − **(2*S*, 3*R*)-3k:** ^{1}H NMR: δ = 5.98 (dd, 1 H, J = 17.6, 10.8, C*H*=CH_2), 5.27 (dd, 1 H, J = 17.3, 1.5, CH_2=CH), 5.22 (dd, 1 H, J = 10.8, 1.5, CH_2=CH), 3.57 (q, 1 H, J = 6.3, C*H*−CH_3), 2.46 (br. s, 1 H, *H*O−), 1.17 (d, 3 H, J = 6.3, CH_3−CH). − ^{13}C NMR: δ = 138.3 (1), 131.0 (1), 126.2 (1), 114.4 (2), 77.0 (1), 71.9 (0), 65.2 (2), 14.8 (3).

(2*S,3*S**)-2-Phenyl-3,6-dihydro-2*H*-pyran-3-ol (3l):** Obtained from **2l** (2.10 g, 10.0 mmol) as a colourless liquid; 5:1 mixture of diastereomers. TLC: hexanes/MTBE 2:1. Purification by flash chromatography on silica. Yield: 1.25 g (69%). − LRMS (EI); *m*/*z*: 177 (M^+ + 1, 56), 161 (10), 149 (12), 135 (100), 121 (80), 91 (50), 77 (58), 65 (20), 51 (30). − ^{1}H NMR: δ = 7.31−7.27 (5 H, Ph), 6.03 (dddd, 1 H, J = 10.0, 5.3, 3.3, 3.0, C*H*=CH−CH_2), 5.94 (ddd, 1 H, J = 10.0, 3.5, 1.5, C*H*−CH_2), 4.53 (d, 1 H, J = 1.7, C*H*−C), 4.34 (ddd, 1 H, J = 17.1, 3.5, 1.8, CH_2), 4.21 (dm, 1 H, J = 16.9, CH_2), 3.96 (m, 1 H, C*H*−OH), 1.63 (d (br.), 1 H, J = 7.3, *H*O). − ^{13}C NMR: δ = 138.5 (0), 130.2 (1), 128.2 (1), 127.4 (1), 126.5 (1), 126.0 (1), 79.2 (1), 66.6 (2), 64.9 (1). − IR (NaCl, neat): ṽ = 3443 (s), 3034 (m), 2823 (m), 1452 (m), 1182 (m), 1092 (s), 1022 (s), 733 (s), 700 s. Spectroscopical data of the minor diastereomer (2*S**, 3*R**)-3l (partially overlapped by the signals of the major isomer): ^{1}H NMR: δ = 7.35−7.20 (5 H, Ph), 1.92 (br. s, 1 H, *H*O). − ^{13}C NMR: δ = 139.4 (0), 128.4 (1), 128.2 (1), 128.0 (1), 127.7 (1), 127.1 (1), 81.0 (1), 68.7 (2), 65.9 (1).

1-Oxaspiro[4,5]dec-3-ene (9a):[71] Obtained from **8a** (1.20 g, 7.2 mmol) as a colourless liquid. TLC: cyclohexane/ether 30:1. Purification by kugelrohr distillation at 125 °C (7 mbar). Yield: 0.90 g (90%). − ^{1}H NMR: δ = 5.84 (dt, 1 H, J = 6.3, 2.3, H4), 5.78 (dt, 1 H, J = 6.3, 1.0, H3), 4.59 (dd, 1 H, J = 2.3, 1.0, H5), 1.71−1.30 (10 H, CH_2). − ^{13}C NMR: δ = 133.8 (1), 125.1 (1), 89.4 (0), 73.6 (2), 37.0 (2), 25.4 (2), 23.4 (2).

2-Pentyl-2,5-dihydrofuran (9b):[72] Obtained from **8b** (2.00 g, 11.9 mmol) as a colourless liquid. TLC: cyclohexane/ether 50:1.

Purification by kugelrohr distillation at 125 °C (7 mbar). Yield: 1.10 g (66%). − ^{1}H NMR: δ = 5.82 (dddd, 1 H, *J* = 6.3, 2.0, 1.8, 1.8, H3,4), 5.74 (dm, 1 H, *J* = 6.3, H3,4), 4.77 (m, 1 H, H2), 4.61 (dddd, 1 H, *J* = 12.6, 5.8, 2.3, 1.5, H5), 4.55 (dddd, 1 H, *J* = 12.6, 4.3, 2.3, 1.5, H5), 1.52−1.47 (2 H, CH_2) 1.40−1.20 (6 H, CH2), 0.88−0.80 (3 H, CH_3). − ^{13}C NMR: δ = 129.8 (1), 126.2 (1), 86.1 (1), 74.9 (2), 36.0 (2), 31.9 (2), 24.9 (2), 22.6 (2), 14.0 (3).

2-(4-Methoxyphenyl)-2,5-dihydrofuran (9c): Obtained from **8c** (1.24 g, 6.1 mmol) as a colourless liquid. TLC: cyclohexane/ether 10:1. Purification by kugelrohr distillation at 125 °C (0.15 mbar). Yield: 0.94 g (87%). − $C_{11}H_{12}O_2$ (176.2): calcd. C 74.9, H 6.9; found C 74.2, H, 7.1. − LRMS (EI); *m*/*z*: 176 (M^+, 87%), 145 (49), 135 (100). − ^{1}H NMR: δ = 7.19 (d, 2 H, *J* = 8.8, *ortho*-H, Ar), 6.85 (d, 2 H, *J* = 8.8, *meta*-H, Ar), 6.00 (dddd, 1 H, *J* = 6.3, 2.3, 1.8, 1.8, H3,4), 5.82 (dm, 1 H, *J* = 6.3, H3,4), 5.71 (m, 1 H, H2), 4.81 (dddd, 1 H, *J* = 12.8, 5.8, 2.0, 1.8, H5), 4.69 (dddd, 1 H, *J* = 12.8, 4.3, 2.5, 1.8, H5), 3.76 (s, 3 H, OMe). − ^{13}C NMR: δ = 159.3 (0), 134.0 (0), 129.9 (1), 127.8 (1), 126.6 (1), 113.8 (1), 87.4 (1), 75.4 (2), 55.2 (3). − IR (NaCl, neat): ṽ = 2838 (m), 1611 (m), 1512 (s), 1245 (s), 1062 (s), 1035 (m), 829 (m).

General Procedure for the Preparation of Dihydropyran Oxides 4 and Dihydrofuran Oxides 10. − Method A: MCPBA (70% w/w, 1.90 g, 7.5 mmol) was added in one portion to a solution of the corresponding dihydropyran (6.0 mmol) in DCM (40 mL). The mixture was stirred until the starting material had been completely consumed (TLC). The reaction mixture was diluted with MTBE (50 mL), and washed twice with saturated Na_2SO_3 solution and saturated Na_2CO_3 solution. The organic layer was separated, dried and evaporated. The residue was chromatographed on silica using cyclohexane/MTBE mixtures.

Method B: The corresponding dihydropyran (6.0 mmol) was dissolved in ethanol (30 mL) and water (19 mL). MMPP (7.0 g, 14.2 mmol) was added in three portions and the homogeneous solution was stirred until the starting material had been completely consumed (TLC). Most of the solvent was evaporated, and the residue was dissolved in water (20 mL) and extracted with MTBE. The organic layer was washed twice with saturated Na_2SO_3 solution and saturated Na_2CO_3 solution, dried and evaporated. The residue was chromatographed on silica using cyclohexane/MTBE mixtures.

Method C: A solution of dimethyldioxirane in acetone (0.1 M, 3.7 mmol, 37 mL) was added to a solution of the corresponding dihydropyran (3.4 mmol) at 0 °C. The solution was warmed to room temperature and stirred until the starting material had been completely consumed. The reaction mixture was washed with Na_2SO_3 solution and the organic layer was separated, dried and evaporated. The residue was purified by column chromatography on silica using cyclohexane/MTBE mixtures.

Method D: To a solution of the dihydropyran (12.0 mmol) in toluene (50 mL) was added $VO(acac)_2$ (2 mol-%). After addition of *tert*-butyl hydroperoxide (5.5 M solution in decane, 2.8 mL, 16 mmol) the solution was refluxed for 2 hours, washed with saturated Na_2SO_3 solution and water. The organic layer was dried with $MgSO_4$, filtered and evaporated, and the residue was purified by flash chromatography.

(1*S,4*S**,6*R**)-4-(4-Methoxyphenyl)-3,7-dioxabicyclo[4.1.0]heptane (*trans*-4b) and (1*R**,*S**,6*S**)-4-(4-Methoxyphenyl)-3,7-dioxabicyclo[4.1.0]heptane (*cis*-4b):** Obtained from (*S*)-**3b** (0.87 g, 4.6 mmol). Method A. TLC: cyclohexane/ether, 5:1. Purification and separation of diastereomers by column chromatography on silica. − **Diastereomer *trans*-4b:** Colourless liquid. Yield: 0.31 g (33%). − $[\alpha]_D^{20}$ = −41.7 (*c* = 0.60, $CHCl_3$). − **Diastereomer *cis*-4b:** Colourless liquid. Yield: 0.30 g (32%). − $[\alpha]_D^{20}$ = −47.0 (*c* = 0.67, $CHCl_3$).

(1*S,4*S**)-4-[(*S**)-1-Phenylethyl]-3,7-dioxabicyclo[4.1.0]heptane (*trans*-4d) and (1*R**,4*S**)-4-[(*S**)-1-Phenylethyl]-3,7-dioxabicyclo[4.1.0]heptane (*cis*-4d):** Obtained from **3d** (1.00 g, 5.3 mmol). Method A. TLC: cyclohexane/ether 20:1. Purification and separation of diastereomers by column chromatography on silica. − **Diastereomer *trans*-4d:** Colourless crystals, m.p. 48 °C. Yield: 0.45 g (42%). − $C_{13}H_{16}O_2$ (204.3): calcd. C 76.4, H 7.9; found C 76.3, H 7.9. − LRMS (EI); *m*/*z*: 204 (M^+, 35%), 99 (100), 71 (71), 45 (26). − ^{1}H NMR: δ = 7.32−7.13 (5 H, Ph), 4.27 (dd, 1 H, *J* = 13.7, 4.0, $H6_{eq}$), 3.95 (d, 1 H, *J* = 13.8, $H6_{ax}$), 3.40 (ddd, 1 H, *J* = 11.0, 8.3, 2.5, H2), 3.28 (m, 1 H, H4), 3.24 (dd, 1 H, *J* = 4.3, 4.0, H5), 2.61 (dq, 1 H, *J* = 8.3, 6.8, C*H*CH_3), 1.74 (ddd, 1 H, *J* = 14.6, 2.5, 2.0, $H3_{eq}$), 1.56 (ddd, 1 H, *J* = 14.6, 11.0, 1.8, $H3_{ax}$), 1.30 (d, 3 H, *J* = 6.8, CH_3). − ^{13}C NMR: δ = 143.4 (0), 128.4 (1), 127.9 (1), 126.5 (1), 74.5 (1), 66.1 (2), 51.2 (1), 51.1 (1), 45.3 (1), 29.7 (2), 18.5 (3). − IR (KBr, neat): ṽ = 2964 (s), 2854 (s), 1490 (m), 1454 (s), 1112 (s), 1011 (s), 814 (s), 758 (s). − **Diastereomer *cis*-4d:** Colourless oil. Yield: 0.58 g (53%). − LRMS (EI); *m*/*z*: 204 (M^+, 19%), 99 (100), 71 (66), 45 (23). − ^{1}H NMR: δ = 7.33−7.14 (5 H, Ph), 4.27 (d, 1 H, *J* = 13.3, H6), 3.84 (d, 1 H, *J* = 13.3, H6), 3.23 (dd, 1 H, *J* = 5.8, 4.3, H4), 3.20 (ddd, 1 H, *J* = 11.3, 8.5, 4.0, H2), 3.04 (d, 1 H, *J* = 4.3, H5), 2.63 (dq, 1 H, *J* = 8.5, 6.8, C*H*CH_3), 1.70 (dd, 1 H, *J* = 15.6, 11.3, $H3_{ax}$), 1.54 (ddd, 1 H, *J* = 15.6, 5.8, 4.0, $H3_{eq}$), 1.32 (d, 3 H, *J* = 6.8, CH_3). − ^{13}C NMR: δ = 143.7 (0), 128.4 (1), 127.8 (1), 126.5 (1), 77.7 (1), 65.0 (2), 49.9 (1), 49.1 (1), 45.5 (1), 28.3 (2), 18.2 (3). − IR (NaCl, neat): ṽ = 2962 (s), 2843 (s), 1493 (m), 1453 (s), 1127 (s), 1007 (s), 807 (s), 703 (s).

(1*S,4*S**)-4-[(*R**)-1-Phenylethyl]-3,7-dioxabicyclo[4.1.0]heptane (*trans*-4e) and (1*R**,4*S**)-4-[(*R**)-1-Phenylethyl]-3,7-dioxabicyclo[4.1.0]heptane (*cis*-4e):** Obtained from **3e** (0.75 g, 4.0 mmol). Method A: TLC: cyclohexane/ether, 20:1. Purification and separation of diastereomers by column chromatography on silica. − **Diastereomer *trans*-4e:** Colourless oil. Yield: 0.40 g (49%). − ^{1}H NMR: δ = 7.32−7.25 (2 H, Ph), 7.23−7.14 (3 H, Ph), 4.16 (dd, 1 H, *J* = 13.7, 4.3, $H6_{eq}$), 3.81 (d, 1 H, *J* = 13.7, $H6_{ax}$), 3.51 (ddd, 1 H, *J* = 11.2, 6.8, 2.3, H2), 3.36 (m, 1 H, H4), 3.21 (dd, 1 H, *J* = 4.3, 4.3, H5), 2.73 (dq, 1 H, *J* = 7.3, 6.8, C*H*CH_3), 2.08 (ddd, 1 H, *J* = 14.6, 2.3, 2.0, $H3_{eq}$), 1.68 (ddd, 1 H, *J* = 14.6, 11.2, 1.8, $H3_{ax}$), 1.24 (d, 3 H, *J* = 7.3, CH_3). − ^{13}C NMR: δ = 143.8 (0), 128.1 (1), 127.9 (1), 126.2 (1), 73.8 (1), 66.0 (2), 51.3 (1), 51.2 (1), 44.4 (1), 28.8 (2), 17.4 (3). − IR (KBr, neat): ṽ = 2966 (s), 2940 (s), 2906 (s), 1603 (m), 1494 (s), 1452 (s), 1380 (s), 1112 (s), 1094 (s), 815 (s), 767 (s). − **Diastereomer *cis*-4e:** Colourless oil. Yield: 0.25 g (31%). − ^{1}H NMR: δ = 7.33−7.26 (2 H, Ph), 7.24−7.18 (3 H, Ph), 4.15 (d, 1 H, *J* = 13.5, H6), 3.70 (dd, 1 H, *J* = 13.5, 0.8, H6), 3.35 (dd, 1 H, *J* = 5.5, 4.0, H4), 3.31 (ddd, 1 H, *J* = 11.1, 7.3, 4.3, H2), 3.03 (d, 1 H, *J* = 4.0, H5), 2.81 (qd, 1 H, *J* = 7.3, 7.0, C*H*CH_3), 1.93 (ddd, 1 H, *J* = 15.5, 5.5, 4.3, $H3_{eq}$), 1.85 (dd, 1 H, *J* = 15.5, 11.1, $H3_{ax}$), 1.23 (d, 3 H, *J* = 7.0, CH_3). − ^{13}C NMR: δ = 143.8 (0), 128.2 (1), 127.7 (1), 126.2 (1), 77.1 (1), 65.0 (2), 49.8 (1), 49.0 (1), 44.5 (1), 26.8 (2), 16.6 (3). − IR (KBr, neat): ṽ = 2966 (s), 2940 (s), 1603 (m), 1494 (s), 1452 (s), 1112 (s), 1007 (s), 815 (s), 768 (s), 701 (s).

(1*S,4*S**)-4-Methyl-4-phenyl-3,7-dioxabicyclo[4.1.0]heptane (*trans*-4f) and (1*R**,4*S**)-4-Methyl-4-phenyl-3,7-dioxabicyclo[4.1.0]heptane (*cis*-4f):** Obtained from 3f (1.04 g, 6.0 mmol). Method B. TLC: cyclohexane/ether, 3:1. Purification and separation of diastereomers by column chromatography on silica. − **Diastereomer *trans*-4f:** Colourless solid, m.p. 54 °C. Yield: 0.63 g (52%). − $C_{12}H_{14}O_2$

(190.2): calcd. C 75.8, H 7.4; found C 75.8, H 7.4. − LRMS (EI); *m*/*z*: 190 (M^+, 1%), 175 (86), 105 (100). − ^{1}H NMR: δ = 7.45−7.25 (5 H, Ph), 3.98 (d, 1 H, *J* = 13.8, H6), 3.56 (d, 1 H, *J* = 13.8, H6), 3.45 (dd, 1 H, *J* = 5.5, 4.4, H4), 2.86 (d, 1 H, *J* = 4.0, H5), 2.74 (dd, 1 H, *J* = 15.8, 5.5, H3), 2.13 (d, 1 H, *J* = 15.8, H3), 1.24 (s, 3 H, CH_3). − ^{13}C NMR: δ = 142.8 (0), 128.6 (1), 127.4 (1), 126.5 (1), 73.0 (1), 59.8 (2), 49.3 (1), 48.6 (1), 32.5 (2), 31.8 (3). − IR (KBr, disk): ṽ = 3058 (m), 3018 (m), 2986 (m), 2927 (s), 1444 (s), 1280 (s), 1120 (s), 1051 (s), 808 (s)704 (s). − **Diastereomer *cis*-4f:** Colourless oil. Yield: 0.18 g (15%). − ^{1}H NMR: δ = 7.41 (d, 2 H, *J* = 8.0, *ortho*-Ph), 7.33 (dd, 2 H, *J* = 8.0, 7.3, *meta*-Ph), 7.24 (t, 1 H, *J* = 7.3, *para*-Ph), 4.19 (d, 1 H, *J* = 13.8, H6), 4.14 (dd, 1 H, *J* = 13.8, 1.8, H6), 3.44 (dd, 1 H, *J* = 5.0, 4.5, H4), 3.20 (d, 1 H, *J* = 4.5, H2), 2.36 (d, 1 H, *J* = 15.3, H3), 2.20 (dd, 1 H, *J* = 15.3, 5.0, H3), 1.50 (s, 3 H, CH_3). − ^{13}C NMR: δ = 146.6 (0), 128.1 (1), 126.7 (1), 124.7 (1), 71.9 (0), 59.5 (2), 48.8 (1), 48.7 (1), 34.7 (2), 27.2 (3). − IR (NaCl, neat): ṽ = 2975 (m), 1494 (m), 1446 (s), 1114 (s), 800 (m), 764 (s), 701 (s).

1-Oxaspiro[5,6]dodec-3-ene Oxide (4g): Obtained from **3g** (0.70 g, 4.2 mmol). Method B. TLC: cyclohexane/ether 3:1. Purification by column chromatography on silica. Colourless oil. Yield: 0.48 g (63%). − $C_{11}H_{18}O_2$ (182.3): calcd. C 72.5, H 10.0; found C 72.4, H 10.3. − LRMS (EI); *m*/*z*: 182 (M^+, 10%), 125 (83), 112 (46), 55 (100). − ^{1}H NMR: δ = 3.96 (d, 1 H, *J* = 13.8, H6), 3.87 (dd, 1 H, *J* = 13.8, 1.6, H6), 3.23 (ddd, 1 H, *J* = 4.3, 4.3, 1.6, H4), 3.05 (d, 1 H, *J* = 4.3, H5), 1.75−1.18 (14 H, H3 + CH_2). − ^{13}C NMR: δ = 72.9 (0), 58.8 (2), 49.0 (1), 48.9 (1), 42.1 (2), 35.5 (2), 34.3 (2), 29.5 (2), 29.5 (2), 21.6 (2), 21.5 (2). − IR (NaCl, neat): ṽ = 2924 (s), 2856 (s), 1456 (m), 1112 (s).

(3*S,6*R**,12*S**)-9,9-Dimethyl-1,4,8,10-tetraoxatricyclo-[5.4.0.0^{3,6}]dodecane (*trans*-4h) and (3*R**,6*R**,12*S**)-9,9-Dimethyl-1,4,8,10-tetraoxatricyclo[5.4.0.0^{3,6}]dodecane (*cis*-4h):** Obtained from **3h** (1.05 g, 5.7 mmol). Method A. TLC: cyclohexane/ether, 3:1. Purification and separation of diastereomers by column chromatography on silica. Diastereomer *trans*-**4h**: Colourless crystals, m.p. 35 °C. Yield: 0.68 g (60%). $C_{10}H_{16}O_4$ (200.2): calcd. C 60.0, H 8.0; found C 59.9, H 7.8. − LRMS (EI); *m*/*z*: 200 (M^+, 1%), 185 (35), 142 (42), 112 (49), 82 (73), 43 (100). − ^{1}H NMR: δ = 4.12 (dd, 1 H, *J* = 13.6, 3.3, $H6_{eq}$), 3.93 (d, 1 H, *J* = 13.6, $H6_{ax}$), 3.67 (d, 1 H, *J* = 7.0, OCH*H*CH3), 3.67 (d, 1 H, *J* = 7.0, OCH*H*CH3), 3.56 (dd, 1 H, *J* = 11.5, 4.6, OCH*H*CH2), 3.52 (dd, 1 H, *J* = 11.5, 9.0, OCH*H*CH2), 3.30 (ddd, 1 H, *J* = 9.8, 9.0, 4.6, H2), 3.23−3.19 (2 H, H4,5), 2.05 (ddd, 1 H, *J* = 9.8, 7.0, 7.0, H3), 1.30 (s, 3 H, CH_3), 1.26 (s, 3 H, CH_3). − ^{13}C NMR: δ = 101.1 (0, $C(CH_3)_2$), 73.2 (1, C2), 65.4 (2, C6), 64.1 (2, OCH_2C2), 61.1 (2, OCH_2C3), 51.9, 50.5 (1, C4,5), 44.2 (1, C3), 24.9, 24.8 (3, CH_3). − IR (KBr, disk): ṽ = 2989 (s), 2976 (s), 1466 (m), 1381 (s), 1372 (s), 1208 (s), 1092 (s), 1072 (s), 1043 (s), 850 (s), 735 (s). − **Diastereomer *cis*-4h:** Colourless solid, m.p. 69 °C. Yield: 0.17 g (15%). − ^{1}H NMR: δ = 4.18 (d, 1 H, *J* = 13.3, H6), 3.82 (d, 1 H, *J* = 13.3, H6), 3.75 (dd, 1 H, *J* = 12.0, 4.6, OCH*H*CH3), 3.65 (dd, 1 H, *J* = 11.8, 4.3, OC*H*HCH2), 3.52 (dd, 1 H, *J* = 12.0, 9.8, OCH*H*CH3), 3.49 (dd, 1 H, *J* = 11.8, 7.0, OCH*H*CH2), 3.03 (d, 1 H, *J* = 4.0, H4,5), 3.00 (m, 1 H, H2), 2.97 (d, 1 H, *J* = 4.0, H4,5), 2.02 (ddd, 1 H, *J* = 11.0, 9.8, 4.6, H3), 1.31 (s, 3 H, CH_3), 1.27 (s, 3 H, CH_3). − ^{13}C NMR: δ = 101.2 (0, $C(CH_3)_2$), 76.5 (1, C2), 65.4 (2, C6), 63.9 (2, OCH_2C2), 60.8 (2, OCH_2C3), 52.0, 49.1 (1, C4,5), 41.2 (1, C3), 24.6, 24.5 (3, CH_3). − IR (KBr, disk): ṽ = 2991 (m), 2947 (s), 1375 (s), 1260 (s), 1214 (s), 1109 (s), 1074 (s), 1031 (s), 819 (s).

(3*S,5*R**,10*R**)-Dioxatricyclo[4.4.0.0^{3,5}]undecane (*trans*-4i) and (3*R**,5*R**,10*R**)-Dioxatricyclo[4.4.0.0^{3,5}]undecane (*cis*-4i):** Obtained from **3i** (1.30 g, 9.4 mmol). Method A. TLC: cyclohexane/ether 5:1. Purification and separation of diastereomers by column chromatography on silica. − **Diastereomer *trans*-4i:** Colourless oil. Yield: 0.48 g (33%). − $C_9H_{14}O_2$ (154.2): calcd. C 70.1, H 9.2; found C 70.0, H 9.5. − LRMS (EI); *m*/*z*: 155 (M^+ + 1, 50%), 137 (100). − ^{1}H NMR: δ = 4.12 (dd, 1 H, *J* = 13.6, 4.0, $H6_{eq}$), 3.94 (d, 1 H, *J* = 13.6, $H6_{ax}$), 3.22 (dd, 1 H, *J* = 4.0, 4.0, H5), 3.12 (d, 1 H, *J* = 4.0, H4), 3.07 (ddd, 1 H, *J* = 10.8, 9.8, 4.3, H2), 1.85−1.57 (5 H, CH_2 + H3), 1.36−1.13 (4 H, CH_2). − ^{13}C NMR: δ = 73.2 (1), 65.3 (2), 54.2 (1), 52.1 (1), 41.9 (1), 31.8 (2), 27.7 (2), 25.9 (2), 24.7 (2). − IR (NaCl, neat): ṽ = 2931 (s), 2858 (s), 1446 (m), 1146 (m), 1105 (s), 872 (m), 829 (m). − **Diastereomer *cis*-4i:** Colourless oil. Yield: 0.43 g (30%). − LRMS (EI); *m*/*z*: 155 (M^+ + 1, 50%), 137 (100), 119 (50), 95 (60). − ^{1}H NMR: δ = 4.17 (d, 1 H, *J* = 13.3, H6), 3.81 (dd, 1 H, *J* = 13.3, 1.0, H6), 3.03 (d, 1 H, *J* = 4.0, H4,5), 2.95 (d, 1 H, *J* = 4.0, H4,5), 2.66 (ddd, 1 H, *J* = 10.3, 10.3, 3.8, H2), 1.88−1.65 (4 H, CH_2, H3), 1.53 (ddd, 1 H, *J* = 12.8, 10.0, 3.5, CH_2, H3), 1.31−1.10 (4 H, CH_2, H3). − ^{13}C NMR: δ = 78.1 (1), 65.1 (2), 54.6 (1), 49.9 (1), 40.6 (1), 31.9 (2), 29.0 (2), 25.8 (2), 24.9 (2). − IR (NaCl, neat): ṽ = 2933 (s), 2857 (s), 1448 (m), 1122 (s), 1041 (m), 830 (m), 792 (m).

(1*R,4*S**,5*R**,6*S**)-4,5-Diphenyl-3,7-dioxabicyclo[4.1.0]heptane (4j):** Obtained from **3j** (0.81 g, 3.4 mmol). Method C. TLC: cyclohexane/ether, 20:1. Purification by column chromatography on silica. Colourless oil. Yield: 0.40 g (47%). − ^{1}H NMR: δ = 7.21−6.85 (10 H, Ph), 4.92 (d, 1 H, *J* = 2.8, H2), 4.56 (dd, 1 H, *J* = 13.8, 3.8, $H6_{eq}$), 4.31 (d, 1 H, *J* = 13.8, $H6_{ax}$), 3.50 (m, 1 H, H4), 3.45 (dd, 1 H, *J* = 4.3, 3.8, H5), 3.33 (m, 1 H, H3). − ^{13}C NMR: δ = 139.7 (0), 136.4 (0), 129.9 (1), 127.7 (1), 127.6 (1), 127.0 (1), 126.8 (1), 125.6 (1), 74.2 (1), 65.7 (2), 54.9 (1), 51.1 (1), 46.8 (1).

(1*S*,4*S*,5*R*,6*S*)-4-Methyl-5-vinyl-3,7-dioxabicyclo[4.1.0]heptan-5-ol (4k): Obtained from **3k** (0.70 g, 5 mmol). Method D. Yield of crude product: 0.75 g (96%). Purification by flash chromatography was impossible because of rapid decomposition of the material on silica. Purification by kugelrohr distillation (0.2 mbar, 140 °C) leads to significant decrease in the yield and did not give analytically pure **3k**. For preparative purposes crude **3k** may be used. − ^{1}H NMR: δ = 5.75 (dd, 1 H, *J* = 17.6, 11.1, C*H*=CH_2), 5.39 (dd, 1 H, *J* = 17.6, 1.3, CH_2=CH), 5.22 (dd, 1 H, *J* = 11.1, 1.3, CH_2=CH), 4.09 (d, 1 H, *J* = 13.3, O−CH_2), 3.73 (d, 1 H, *J* = 13.6, O−CH_2), 3.23 (s, 2 H, C*H*−O−C*H*, isochron), 3.07 (q, 1 H, *J* = 6.5, C*H*−CH_3), 2.70 (br. s, 1 H, *H*O), 1.00 (d, 3 H, *J* = 6.5, CH_3−CH). − ^{13}C NMR: δ = 138.3 (1), 116.2 (2), 78.0 (1), 68.7 (0), 64.6 (2), 57.0 (1), 52.0 (1), 13.4 (3).

(1*S,4*S**,5*R**,6*R**)-4-Phenyl-3,7-dioxabicyclo[4.1.0]heptan-5-ol (4l):** Obtained from **3l** (2.12 g, 12 mmol). Method D. Yield of crude product: 1.8 g (95%). Purification by flash chromatography was impossible because of rapid decomposition of the material on silica. Purification by kugelrohr distillation (0.2 mbar, 160 °C) leads to significant decrease of the yield and did not give analytically pure **4l**. For preparative purposes crude **4l** may be used. − ^{1}H NMR: δ = 7.31−7.16 (5 H, Ph), 4.29 (d, 1 H, *J* = 13.6, O−CH_2), 4.18 (d, 1 H, *J* = 2.0, C*H*−Ph), 3.99 (ddd, 1 H, *J* = 10.8, 5.5, 2.0, C*H*−OH), 3.86 (d, 1 H, *J* = 13.6, O−CH_2), 3.59 (dd, 1 H, *J* = 5.5, 4.0, CH−C*H*−O−CH), 3.26 (d, 1 H, *J* = 4.0, CH_2−C*H*−O), 2.33 (d, 1 H, *J* = 10.8, CH−O*H*). − ^{13}C NMR: δ = 137.2 (0), 128.1 (1), 127.5 (1), 126.0 (1), 79.7 (1), 65.2 (2), 64.1 (1), 52.4 (1), 51.5 (1).

1-Oxaspiro[4,5]dec-3-ene Oxide (10a): Obtained from **9a** (0.46 g, 3.4 mmol) as a colourless liquid along with varying amounts of ketone **10a′**. Method A. TLC: cyclohexane/ether 5:1. Purification by column chromatography on silica. Yield: 0.30 g (54%). − LRMS

(EI); *m/z*: 155 (M^+ + 1, 100%), 137 (60), 111 (40). − ^{1}H NMR: δ = 3.94 (d, 1 H, *J* = 10.8, H5), 3.66 (d, 1 H, *J* = 3.0, H3,4), 3.65 (d, 1 H, *J* = 10.8, H5), 3.49 (d, 1 H, *J* = 3.0, H5), 1.67−1.35 (10, CH_2). − ^{13}C NMR: δ = 79.5 (0), 65.3 (2), 59.9 (1), 55.3 (1), 31.3 (2), 31.0 (2), 25.3 (2), 22.9 (2), 22.1 (2). − IR (KBr, neat): ṽ = 2934 (s), 2856 (s), 1448 (m), 1079 (s), 1059 (s), 1031 (s).

1-Oxaspiro[4,5]dec-2-en-4-one (10a′): Obtained from **9a** (0.46 g, 3.4 mmol) as a colourless liquid along with **10a**. Yield 0.15 g (29%). − LRMS (EI); *m/z*: 153 (M^+ + 1, 100%), 135 (10), 81 (20). − ^{1}H NMR: δ = 7.41 (d, 1 H, *J* = 5.6, H5), 5.94 (d, 1 H, *J* = 5.6, H4), 1.80−1.22 (10 H, CH_2). − ^{13}C NMR: δ = 172.5 (0), 160.6 (1), 120.0 (1), 88.5 (0), 34.5 (2), 24.5 (2), 22.3 (2). − IR (KBr, neat): ṽ = 2937 (s), 2862 (m), 1749 (s), 1449 (m), 1210 (m), 1138 (m), 971 (m), 818 (m).

2-Pentyl-3,6-dioxabicyclo[3.1.0]hexane (10b): Obtained from **9b** (1.80 g, 13.1 mmol) as an inseparable mixture of diastereomers. Method A. Colourless liquid. TLC: cyclohexane/ether 10:1. Purification by flash chromatography. Yield: 1.60 g (76%). − $C_9H_{16}O_2$ (156.2): calcd. C 69.1, H 10.2; found C 68.4, H, 9.9. − LRMS (EI); *m/z*: 157 (M^+ + 1, 60%), 139 (100). − ^{1}H NMR: δ = 4.01−3.86 (2 H, CHHO, CHO), 3.72−3.49 (3 H, CHHO, CHO), 1.64−1.55 (1 H), 1.42−1.18 (7 H, CHH), 0.88−0.75 (3 H, CH_3). − ^{13}C NMR: δ = 77.5 (1), 77.5 (1), 67.3 (2), 65.8 (2), 58.8 (1), 57.3 (1), 55.7 (1), 55.7 (1), 31.7 (2), 31.6 (2), 30.8 (2), 29.9 (2), 25.7 (2), 25.0 (2), 22.4 (2), 22.4 (2), 13.9 (3), 13.9 (3). − IR (NaCl, neat) 2956 (s), 2931 (s), 2858 (s), 1073 (s), 863 (s).

(2*R,5*S**)-2-(4-Methoxyphenyl)-3,6-dioxabicyclo[3.1.0]hexane (*trans*-10c) and (2*R**,5*R**)-2-(4-Methoxyphenyl)-3,6-dioxabicyclo[3.1.0]hexane (*cis*-10c):** Obtained from **9c** (0.90 g, 5.1 mmol) as a 4:1 mixture of diastereomers. Method A. TLC: cyclohexane/ether 5:1. Separation of diastereomers was achieved by column chromatography. **Diastereomer *trans*-10c:** Colourless solid, m.p. 58 °C. Yield: 0.60 g (61%). − $C_{11}H_{12}O_3$ (192.2): calcd. C 68.7, H 6.3; found C 68.4, H, 6.3. − LRMS (EI); *m/z*: 192 (M^+, 100%), 175 (38), 135 (38), 121 (35). − ^{1}H NMR: δ = 7.14 (d, 2 H, *J* = 8.8, Ar), 6.85 (d, 2 H, *J* = 8.8, Ar), 5.02 (s, 1 H, H2), 4.08 (d, 1 H, *J* = 10.5, H5), 3.91 (d, 1 H, *J* = 10.5, Ar), 3.85, (d, 1 H, *J* = 3.0, H3,4), 3.74 (s, 3 H, OMe), 3.73 (d, 1 H, *J* = 3.0, H3,4). − ^{13}C NMR: δ = 159.3 (0), 130.3 (0), 127.1 (1), 114.0 (1), 78.7 (1), 67.0 (2), 59.7 (1), 56.6 (1), 55.1 (3). − IR (KBr, disk): ṽ = 2935 (w), 2870 (m), 1610 (m), 1513 (s), 1248 (s), 1064 (m), 1052 (m), 1028 (s), 856 (s), 830 (s), 820 (s). − **Diastereomer *cis*-10c:** Colourless liquid. Yield 0.20 g (20%). − ^{1}H NMR: δ = 7.37 (d, 2 H, *J* = 8.8, Ar), 6.86 (d, 2 H, *J* = 8.8, Ar), 4.71 (s, 1 H, H2), 4.22 (d, 1 H, *J* = 10.8, H5), 3.81−3.76 (6 H, H3,4,5, OMe). − ^{13}C NMR: δ = 159.7 (0), 128.8 (0), 128.7 (1), 113.8 (1), 78.6 (1), 68.0 (2), 58.9 (1), 56.0 (1), 55.3 (3). − IR (KBr, neat): ṽ = 2957 (m), 2857 (m), 1613 (s), 1514 (s), 1248 (s), 1230 (s), 1175 (s), 1069 (s), 1032 (s), 868 (s).

General Procedure for the Preparation of 2,3-Dihydropyrans 11: To a solution of LDA or LiTMP (1.7 mmol) in THF (6 mL) was added a solution of the epoxide (1.1 mmol) in THF (3 mL). The red solution was stirred at room temperature until conversion was completed (TLC). The mixture was diluted with MTBE (30 mL) and washed with aqueous NH_4Cl solution. The organic layer was separated, dried, filtered and evaporated. The oily residue was purified by flash chromatography on silica with hexane/MTBE mixtures as eluents.

(2*S,4*R**)-2-Phenyl-3,4-dihydro-2*H*-pyran-4-ol (*trans*-11a):** Obtained from *trans*-**4a** (0.25 g, 1.6 mmol). TLC: cyclohexane/ether, 3:1. Purification by flash chromatography on silica. Colourless oil. Yield: 0.18 g (72%). − LRMS (EI); *m/z*: 159 (M^+ − OH, 100%). − ^{1}H NMR (C_6D_6): δ = 7.32 (d, 2 H, *J* = 7.5, *ortho*-H, Ph), 7.16 (dd, 2 H, *J* = 7.5, 7.3, *meta*-H, Ph), 7.09 (d, 1 H, *J* = 7.3, *para*-H, Ph), 6.48 (d, 1 H, *J* = 6.0, H6), 4.97 (dd, 1 H, *J* = 12.3, 1.8, H2), 4.83 (ddd, 1 H, *J* = 6.0, 6.0, 1.5, H5), 3.90 (m, 1 H, H4), 1.94 (dd, 1 H, *J* = 14.3, 1.8, $H3_{eq}$), 1.89 (s br., 1 H, OH), 1.71 (ddd, 1 H, *J* = 14.3, 12.3, 3.8, $H3_{ax}$). − ^{13}C NMR (C_6D_6): δ = 146.9 (1), 141.7 (0), 128.6 (1), 127.9 (1), 126.4 (1), 103.5 (1), 73.3 (1), 59.8 (1), 39.9 (2). − IR (NaCl, neat): ṽ = 3363 (vs, br.), 1642 (s), 1241 (s), 1056 (s).

(2*S,4*S**)-2-Phenyl-3,4-dihydro-2*H*-pyran-4-ol (*cis*-11a):** Obtained from *cis*-**4a** (0.25 g, 1.6 mmol). TLC: cyclohexane/ether 3:1. Purification by flash chromatography on silica. Colourless oil. Yield: 0.19 g (76%). − LRMS (EI); *m/z*: 177 (M^+ + 1, 65%), 159 (100). − ^{1}H NMR (C_6D_6): δ = 7.23 (d, 2 H, *J* = 8.5, *ortho*-H, Ph), 7.16 (dd, 2 H, *J* = 8.5, 7.0, *meta*-H, Ph), 7.09 (tt, 1 H, *J* = 7.0, 1.3, *para*-H, Ph), 6.37 (dd, 1 H, *J* = 6.3, 0.8, H6), 4.74 (ddd, 1 H, *J* = 6.3, 2.0, 1.8, H5), 4.70 (dd, 1 H, *J* = 12.0, 1.8, H2), 4.32 (dd, 1 H, *J* = 9.5, 6.5, H4), 2.05 (dddd, 1 H, *J* = 13.1, 6.5, 1.8, 1.8, $H3_{eq}$), 1.84 (ddd, 1 H, *J* = 13.1, 12.0, 9.5, $H3_{ax}$), 1.64 (s br., 1 H, OH). − ^{13}C NMR (C_6D_6): δ = 145.0 (1), 141.2 (0), 128.6 (1), 128.0 (1), 126.2 (1), 106.5 (1), 77.0 (1), 63.4 (1), 40.6 (2). − IR (NaCl, neat): ṽ = 3363 (vs, br.), 1644 (s), 1234 (s), 1038 (s), 759 (s).

(2*S,4*R**)-2-(4-Methoxyphenyl)-3,4-dihydro-2*H*-pyran-4-ol (*trans*-11b):** Obtained from *trans*-**4b** (0.57 g, 2.8 mmol). TLC: cyclohexane/ether, 2:1. Purification by flash chromatography on silica. Colourless oil. Yield: 0.43 g (75%). − $C_{12}H_{14}O_3$ (206.2): calcd. C 69.9; H 6.8; found C 69.5, H 6.8. − $[\alpha]_D^{20}$ = +86.0 (*c* = 0.38, $CHCl_3$). − LRMS (EI); *m/z*: 206 (M^+, 11%), 134 (100). − ^{1}H NMR: δ = 7.29 (d, 2 H, *J* = 8.8, Ar), 6.89 (d, 2 H, *J* = 8.8, Ar), 6.62 (d, 1 H, *J* = 6.3, H6), 5.04 (ddd, 1 H, *J* = 6.3, 6.0, 1.8, H5), 4.86 (dd, 1 H, *J* = 12.3, 2.0, H2), 4.19 (m, 1 H, H4), 3.70 (s, 3 H, OMe), 2.04 (ddd, 1 H, *J* = 14.3, 4.0, 2.0, $H3_{eq}$), 1.93 (ddd, 1 H, *J* = 14.3, 12.3, 3.8, $H3_{ax}$), 1.92 (s br., 1 H, OH). − ^{13}C NMR: δ = 159.3 (0), 147.4 (1), 132.9 (0), 127.5 (1), 113.8 (1), 102.6 (1), 72.7 (1), 60.0 (1), 55.3 (3), 38.9 (2). − IR (NaCl, neat): ṽ = 3387 (vs, br.), 1641 (m), 1614 (m), 1518 (s), 1252 (s), 1239 (s), 1061 (s), 1040 (s), 826 (s).

(2*S,4*S**)-2-(4-Methoxyphenyl)-3,4-dihydro-2*H*-pyran-4-ol (*cis*-11b):** Obtained from *cis*-**4b** (0.22 g, 1.1 mmol). TLC: cyclohexane/ether, 2:1. Purification by flash chromatography on silica. Colourless oil. Yield: 0.15 g (68%). $[\alpha]_D^{20}$ = −11.0 (*c* = 0.78, $CHCl_3$). − LRMS (EI); *m/z*: 206 (M^+, 5%), 134 (100). − ^{1}H NMR (C_6D_6): δ = 7.19 (d, 2 H, *J* = 8.5, Ar), 6.79 (d, 2 H, *J* = 8.5, Ar), 6.42 (d, 1 H, *J* = 6.3, H6), 4.83 (d, 1 H, *J* = 6.3, H5), 4.73 (d, 1 H, *J* = 12.0, H2), 4.45 (ddm, 1 H, *J* = 9.8, 6.6, H4), 3.33 (s, 3 H, OMe), 2.44 (s, br., 1 H, OH), 2.14 (dd, 1 H, *J* = 12.8, 6.6, $H3_{eq}$), 1.97 (ddd, 1 H, *J* = 12.8, 12.0, 9.8, $H3_{ax}$). − ^{13}C NMR (C_6D_6): δ = 160.3 (0), 145.7 (1), 133.8 (0), 128.2 (1), 114.6 (1), 107.0 (1), 77.4 (1), 64.2 (1), 55.3 (3), 40.9 (2). − IR (NaCl, neat): ṽ = 3302 (vs, br.), 3232 (vs, br.), 1642 (m), 1613 (m), 1516 (s), 1461 (m), 1254 (s), 1234 (s), 1031 (s), 824 (s).

(2*S,4*R**)-2-Cyclohexyl-3,4-dihydro-2*H*-pyran-4-ol (*trans*-11c):** Obtained from *trans*-**4c** (0.80 g, 4.4 mmol). TLC: cyclohexane/ether 2:1. Purification by flash chromatography on silica. Colourless oil. Yield: 0.64 g (80%). − $C_{11}H_{18}O_2$ (182.3): calcd. C 72.4, H 10.0; found C 71.9, H 10.0. − LRMS (EI); *m/z*: 182 (M^+, 40%), 110 (34), 81 (100). − ^{1}H NMR: δ = 6.62 (d, 1 H, *J* = 6.0, H6), 4.90 (ddd, 1 H, *J* = 6.0, 5.8, 1.8, H5), 4.09 (m, 1 H, H4), 3.62 (ddd, 1 H, *J* = 12.3, 5.5, 1.8, H2), 1.87−1.40 (8 H, C_6H_{11}), 1.28−0.97 (5 H, C_6H_{11}). − ^{13}C NMR: δ = 147.5 (1), 102.3 (1), 75.1 (1), 69.9 (1), 41.7 (1), 33.7 (2), 28.6 (2), 28.2 (2), 26.4 (2), 26.2 (2), 26.1 (2). − IR (NaCl, neat): ṽ = 3346 (vs, br.), 2925 (s), 2853 (s), 1641 (m), 1450 (m), 1243 (s), 1048 (s).

(2*S,4*S**)-2-Cyclohexyl-3,4-dihydro-2*H*-pyran-4-ol (*cis*-11c):** Obtained from *cis*-**4c** (0.27 g, 1.5 mmol) using LiTMP instead of LDA. TLC: cyclohexane/ether 1:1. Purification by flash chromatography on silica. Colourless oil. Yield: 0.17 g (63%). − LRMS (EI); *m*/*z*: 182 (M^+, 2%), 151 (14), 99 (100), 71 (58). − ^{1}H NMR: δ = 6.31 (d, 1 H, *J* = 6.0, H6), 4.67 (ddd, 1 H, *J* = 6.0, 1.8, 1.8, H5), 4.28 (dd, 1 H, *J* = 9.5, 6.5, H4), 3.50 (ddd, 1 H, *J* = 11.8, 5.5, 1.0, H2), 1.85 (ddm, 1 H, *J* = 12.8, 6.5, $H3_{eq}$), 1.80 (m, 1 H, C_6H_{11}), 1.73−1.62 (2 H, C_6H_{11}), 1.62−1.55 (3 H, C_6H_{11}), 1.53 (ddd, 1 H, *J* = 12.8, 11.8, 9.5, $H3_{ax}$), 1.35 (m, 1 H, C_6H_{11}), 1.21−0.95 (5 H, C_6H_{11}). − ^{13}C NMR: δ = 145.1 (1), 106.2 (1), 79.2 (1), 63.8 (1), 42.1 (1), 35.5 (2), 28.8 (2), 28.3 (2), 26.8 (2), 26.5 (2), 26.4 (2). − IR (NaCl, neat): ṽ = 3347 (vs, br.), 2926 (s), 2853 (s), 1642 (s), 1450 (m), 1233 (s), 1035 (s), 787 (s), 757 (m). If LDA was used as a base, *cis*-**11c** and *cis*-**12c** were isolated as an inseparable 2.5:1 mixture of regioisomers. − Selected NMR spectroscopic data of the by-product: **(3*S**,6*S**)-6-cyclohexyl-3,6-dihydro-2*H*-pyran-3-ol (*cis*-12c):** ^{1}H NMR (C_6D_6): δ = 5.86 (dm, 1 H, *J* = 10.0, H3,4), 5.50 (dm, 1 H, *J* = 10.0, H3,4), 3.89 (d, 1 H, *J* = 11.8, H6), 3.72−3.56 (2 H, H2, 5), 3.34 (dd, 1 H, *J* = 11.8, 2.0, H6). − ^{13}C NMR (C_6D_6): δ = 132.7 (1), 127.7 (1), 78.5 (1), 72.5 (2), 62.8 (1).

(2*S,4*R**)-2-[(*S**-1-Phenylethyl]-3,4-dihydro-2*H*-pyran-4-ol (*trans*-11d):** Obtained from *trans*-**4d** (0.28 g, 1.4 mmol). TLC: cyclohexane/ether, 2:1. Purification by flash chromatography on silica. Colourless oil. Yield: 0.21 g (75%). − LRMS (EI); *m*/*z*: 204 (M^+, 20%), 99 (100), 91 (23), 71 (44). − ^{1}H NMR: δ = 7.31−7.25 (2 H, Ph), 7.22−7.16 (3 H, Ph), 6.49 (d, 1 H, *J* = 6.3, H6), 4.87 (ddd, 1 H, *J* = 6.3, 5.0, 1.8, H5), 3.98 (m, 1 H, H4), 3.93 (ddd, 1 H, *J* = 12.1, 7.3, 2.0, H2), 2.88 (dq, 1 H, *J* = 7.3, 7.0, C*H*CH_3), 2.19 (s br., 1 H, OH), 1.61 (ddd, 1 H, *J* = 14.3, 4.0, 2.0, $H3_{eq}$), 1.43 (ddd, 1 H, *J* = 14.3, 12.1, 4.0, $H2_{ax}$), 1.38 (d, 3 H, *J* = 7.0, CH_3). − ^{13}C NMR: δ = 147.0 (1), 143.3 (0), 128.3 (1), 127.8 (1), 126.4 (1), 102.5 (1), 75.0 (1), 59.5 (1), 44.2 (1), 34.7 (1), 17.3 (3). − IR (NaCl, neat): ṽ = 3363 (vs, br.), 2926 (m), 1640 (s), 1452 (m), 1241 (s), 701 (s).

(2*S,4*S**)-2-[(*S**-1-Phenylethyl]-3,4-dihydro-2*H*-pyran-4-ol (*cis*-11d):** Obtained from *cis*-**4d** (0.45 g, 2.2 mmol). TLC: cyclohexane/ether, 2:1. Purification by flash chromatography on silica. Colourless oil. Yield: 0.40 g (89%). − LRMS (EI); *m*/*z*: 204 (M^+, 22%), 186 (22), 117 (55), 99 (100), 71 (60). − ^{1}H NMR (C_6D_6): δ = 7.30−7.15 (5 H, Ph), 6.39 (dd, 1 H, *J* = 6.3, 1.0, H6), 4.75 (ddd, 1 H, *J* = 6.3, 1.8, 1.8, H5), 4.19 (dd, 1 H, *J* = 9.5, 6.7, H4), 3.86 (ddd, 1 H, *J* = 11.6, 8.0, 1.8, H2), 2.86 (dq, 1 H, *J* = 8.0, 7.0, C*H*CH_3), 1.85 (dddd, 1 H, *J* = 12.8, 6.7, 1.8, 1.5, $H3_{eq}$), 1.75 (s, br., 1 H, OH), 1.51 (ddd, 1 H, *J* = 12.8, 11.6, 9.5, $H3_{ax}$), 1.41 (d, 3 H, *J* = 7.0, CH_3). − ^{13}C NMR (C_6D_6): δ = 145.3 (1), 144.4 (0), 129.2 (1), 128.7 (1), 127.3 (1), 107.0 (1), 79.7 (1), 63.7 (1), 45.3 (1), 36.8 (2), 18.3 (3). − IR (NaCl, neat): ṽ = 3384 (vs, br.), 2965 (m), 1643 (s), 1452 (m), 1232 (s), 701 (s).

(2*S,4*R**)-2-[(*R**-1-Phenylethyl]-3,4-dihydro-2*H*-pyran-4-ol (*trans*-11e):** Obtained from *trans*-**4e** (0.15 g, 0.7 mmol). TLC: cyclohexane/ether, 2:1. Purification by flash chromatography on silica. Colourless oil. Yield: 0.13 g (86%). − LRMS (EI); *m*/*z*: 204 (M^+, 14%), 117 (31), 105 (63), 99 (100), 91 (32), 71 (62). − ^{1}H NMR (C_6D_6): δ = 7.20−7.05 (5 H, Ph), 6.32 (dd, 1 H, *J* = 6.0, H6), 4.70 (ddd, 1 H, *J* = 6.0, 6.0, 1.8, H5), 4.07 (ddd, 1 H, *J* = 12.6, 5.5, 1.8, H2), 3.84 (m, 1 H, H4), 2.76 (qd, 1 H, *J* = 7.0, 5.5, C*H*CH_3), 2.15 (s, br., 1 H, OH), 1.65 (dm, 1 H, *J* = 14.1, $H3_{eq}$), 1.27 (m, 1 H, H_{3ax}), 1.26 (d, 3 H, *J* = 7.0, CH_3). − ^{13}C NMR: δ = 147.0 (1), 143.4 (0), 128.7 (1), 128.4 (1), 126.6 (1), 103.1 (1), 75.0 (1), 59.7 (1), 44.2 (1), 34.8 (2), 17.5 (3). − IR (KBr, neat): ṽ = 3370 (s, br.), 2967 (m), 1641 (s), 1241 (s), 1075 (m), 1049 (m), 701 (s).

(2*S,4*S**)-2-((*R**-1-Phenylethyl)-3,4-dihydro-2*H*-pyran-4-ol (*cis*-11e):** Obtained from *cis*-**4e** (0.27 g, 1.3 mmol). TLC: cyclohexane/ether, 2:1. Purification by flash chromatography on silica. Colourless oil. Yield: 0.19 g (71%). − ^{1}H NMR: δ = 7.34−7.18 (5 H, Ph), 6.33 (dd, 1 H, *J* = 6.3, 1.0, H6), 4.67 (ddd, 1 H, *J* = 6.3, 2.0, 1.8, H5), 4.38 (dddd, 1 H, *J* = 9.5, 6.5, 1.8, 1.5, H4), 4.05 (ddd, 1 H, *J* = 11.8, 6.0, 1.8, H2), 2.99 (qd, 1 H, *J* = 7.3, 6.0, C*H*CH_3), 2.10 (dddd, 1 H, *J* = 12.8, 6.5, 1.8, 1.5, $H3_{eq}$), 1.89 (s, br., 1 H, OH), 1.47 (dddd, 1 H, *J* = 12.8, 11.8, 9.5, $H3_{ax}$), 1.34 (d, 3 H, *J* = 7.3, CH_3). − ^{13}C NMR: δ = 145.1 (1), 142.6 (0), 128.1 (1), 128.1 (1), 126.5 (1), 105.4 (1), 78.6 (1), 63.4 (1), 43.6 (1), 34.8 (1), 16.5 (3).

(2*S,4*R**)-2-Methyl-2-phenyl-3,4-dihydro-2*H*-pyran-4-ol (*trans*-11f):** Obtained from *trans*-**4f** (0.20 g, 1.0 mmol) using LiTMP instead of LDA. TLC: cyclohexane/ether, 3:1. Purification by flash chromatography on silica. Colourless oil, contaminated with 5% of the regioisomer *trans*-**12f**. Yield: 0.14 g (70%). − $C_{12}H_{14}O_2$ (190.2): calcd. C 75.8, H 7.4; found C 75.7, H 7.3. − LRMS (EI); *m*/*z*: 190 (M^+, 3%), 172 (10), 118 (100). − ^{1}H NMR (C_6D_6): δ = 7.28 (dm, 2 H, *J* = 8.0, *ortho*-H, Ph), 7.16 (dd, 2 H, *J* = 8.0, 7.3, *meta*-H, Ph), 7.07 (tt, 1 H, *J* = 7.3, 1.3, *para*-H, Ph), 6.34 (dd, 1 H, *J* = 6.3, 1.5, H6), 4.68 (ddd, 1 H, *J* = 6.3, 2.0, 1.8, H5), 3.86 (ddm, 1 H, *J* = 9.0, 6.0, H4), 2.44 (ddd, 1 H, *J* = 13.3, 6.0, 1.3, $H3_{eq}$), 2.40 (s, br., 1 H, OH), 1.92 (dd, 1 H, *J* = 13.3, 9.0, $H3_{ax}$), 1.47 (s, 3 H, CH_3). − ^{13}C NMR: δ = 145.4 (0), 143.3 (1), 128.6 (1), 127.0 (1), 124.8 (1), 105.8 (1), 79.3 (0), 61.2 (1), 42.8 (2), 30.8 (3). − IR (KBr, neat): ṽ = 3364 (s, br.), 2977 (m), 2929 (m), 1645 (s), 1446 (m), 1238 (s), 1078 (s), 1033 (s), 761 (m), 700 (s). If LDA was used as a base, *trans*-**11f** and *trans*-**12f** were isolated as an inseparable 3:1 mixture of regioisomers. − Selected NMR spectroscopic data of the by-product: **(3*R**,6*S**)-6-methyl-6-phenyl-3,6-dihydro-2*H*-pyran-3-ol (*trans*-12f):** ^{1}H NMR (C_6D_6): δ = 5.94 (d, 1 H, *J* = 10.2, H3), 5.85 (dd, 1 H, *J* = 10.2, 4.5, H4), 3.72 (d, 1 H, *J* = 12.1, H6), 3.55 (m, 1 H, H5), 3.45 (dd, 1 H, *J* = 12.1, 2.8, H6), 1.46 (s, 3 H, CH_3). − ^{13}C NMR (C_6D_6): δ = 145.0 (0), 135.9 (1), 128.5 (1), 127.3 (1), 126.6 (1), 126.3 (1), 75.6 (0), 67.2 (1), 62.0 (2), 30.6 (3).

(2*S,4*S**)-2-Methyl-2-phenyl-3,4-dihydro-2*H*-pyran-4-ol (*cis*-11f):** Obtained from *cis*-**4f** (0.18 g, 0.9 mmol). TLC: cyclohexane/ether, 3:1. Purification by flash chromatography on silica. Colourless oil. Yield: 0.12 g (67%). − ^{1}H NMR (C_6D_6): δ = 7.33 (dd, 2 H, *J* = 8.3, 1.3, *ortho*-H, Ph), 7.14 (dd, 2 H, *J* = 8.3, 7.0, *meta*-H, Ph), 7.03 (tt, 1 H, *J* = 7.0, 1.3, *para*-H, Ph), 6.33 (dd, 1 H, *J* = 6.3, 1.3, H6), 4.78 (dd, 1 H, *J* = 6.3, 3.3, H5), 4.08 (m, 1 H, H4), 2.08 (dd, 1 H, *J* = 14.1, 6.0, H3), 1.96 (ddd, 1 H, *J* = 14.1, 5.8, 0.8, H3), 1.34 (s, 3 H, CH_3). − ^{13}C NMR: δ = 145.4 (0), 143.6 (1), 128.5 (1), 127.1 (1), 125.2 (1), 105.0 (1), 78.1 (0), 61.1 (1), 43.3 (2), 27.8 (3). − IR (KBr, neat): ṽ = 3374 (s, br.), 2978 (m), 2928 (m), 1643 (s), 1446 (m), 1243 (s), 1080 (s), 1028 (s), 763 (s), 700 (s).

1-Oxaspiro[5,6]dodec-2-en-4-ol (11g): Obtained from **4g** (0.48 g, 2.6 mmol). TLC: cyclohexane/ether 3:1. Purification by flash chromatography on silica. Colourless oil. Yield: 0.40 g (83%). − $C_{11}H_{18}O_2$ (182.3): calcd. C 72.4, H 10.0; found C 72.4, H 10.0. − LRMS (EI); *m*/*z*: 182 (M^+, 39), 110, (85), 95 (73), 82 (100), 73 (84). − ^{1}H NMR (C_6D_6): δ = 6.24 (dd, 1 H, *J* = 6.3, 1.5, H6), 4.75 (ddd, 1 H, *J* = 6.3, 2.5, 1.3, H5), 4.15 (m, 1 H, H4), 2.02−1.84 (3 H, H3 + OH), 1.75 (s br., 1 H, OH), 1.71−1.50 (6, CH_2), 1.46−1.39 (2 H, CH_2), 1.35−1.16 (3 H, CH_2). − ^{13}C NMR: δ = 143.3 (1), 105.3 (1), 80.4 (0), 61.1 (1), 43.3 (2), 40.1 (2), 37.0 (2), 30.1 (2), 30.0 (2), 22.5 (2), 22.2 (2). − IR (KBr, film): ṽ = 3346 (s), 2925 (s), 1640 (s), 1241 (s), 1028 (s), 788 (m), 762 (m), 739 (m).

(4*R,5*S**,11*S**)-8,8-Dimethyl-1,7,9-trioxabicyclo[5.4.0]dodec-2-en-4-ol (*trans*-11h):** Obtained from *trans*-**4h** (0.20 g, 1.0 mmol). TLC: cyclohexane/ether, 1:1. Purification by flash chromatography on silica. Colourless solid, m.p. 98 °C. Yield: 0.17 g (85%). − $C_{13}H_{16}O_4$ (236.3): calcd. C 60.0, H 8.1; found C 60.0, H 8.1. − LRMS (EI); *m*/*z*: 200 (M^+, 42%), 112 (54), 83 (100), 43 (82). − ^{1}H NMR: δ = 6.46 (d, 1 H, *J* = 6.0, H6), 5.01 (dd, 1 H, *J* = 6.0, 5.6, H5), 4.06 (dd, 1 H, *J* = 5.6, 3.5, H4), 3.90−3.65 (5 H, CH_2O + H2), 1.69 (dddd, 1 H, *J* = 10.8, 10.8, 3.5, 3.5, H3), 1.32 (s, 3 H, CH_3), 1.32 (s, 3 H, CH_3). − ^{13}C NMR: δ = 146.9 (1), 103.6 (1), 101.2 (0), 72.1 (1), 62.7 (2), 61.7 (1), 60.1 (2), 45.7 (1), 24.7 (3), 24.6 (3). − IR (KBr, disk): ṽ = 3364 (vs, br.), 2950 (m), 1633 (s), 1384 (m), 1370 (m), 1261 (s), 816 (m).

(4*S,5*S**,11*S**)-8,8-Dimethyl-1,7,9-trioxabicyclo[5.4.0]dodec-2-en-4-ol(*cis*-11h):** Obtained from *cis*-**4h** (0.14 g, 0.7 mmol). TLC: cyclohexane/ether, 1:1. Purification by flash chromatography on silica. Colourless oil. Yield: 0.10 g (71%). − LRMS (EI); *m*/*z*: 200 (M^+, 5%), 83 (29), 55 (35), 43 (100). − ^{1}H NMR (C_6D_6): δ = 6.22 (dd, 1 H, *J* = 6.0, 1.3, H6), 4.65 (dd, 1 H, *J* = 6.0, 1.9, H5), 4.00 (dd, 1 H, *J* = 12.3, 3.5, CHHO), 3.83 (dd, 1 H, *J* = 11.6, 10.0, CHHO), 3.79−3.74 (2 H, CHHO + H4), 3.50 (ddd, 1 H, *J* = 10.6, 10.0, 4.3, H2), 3.35 (dd, 1 H, *J* = 12.3, 10.8, CHHO), 2.50 (s, br., 1 H, OH), 1.78 (dddd, 1 H, *J* = 10.8, 10.8, 10.6, 3.5, H3), 1.26 (s, 3 H, CH_3), 1.24 (s, 3 H, CH_3). − ^{13}C NMR: δ = 144.9 (1), 106.8 (1), 101.4 (0), 77.0 (1), 64.6 (2), 63.2 (1), 60.0 (2), 48.5 (1), 24.8 (3), 24.8 (3). − IR (KBr, neat): ṽ = 3429 (s, br.), 2989 (m), 2944 (m), 1643 (s), 1375 (s), 1220 (s), 1098 (s), 1078 (s), 1041 (s), 836 (m).

(4*R,5*S**,10*S**)-1-Oxabicyclo[4.4.0]dec-2-en-4-ol (*trans*-11i):** Obtained from *trans*-**4i** (0.48 g, 3.1 mmol). TLC: cyclohexane/ether, 5:1. Purification by flash chromatography on silica. Colourless solid, m.p. 38 °C. Yield: 0.42 g (87%). − LRMS (EI); *m*/*z*: 154 (M^+, 55), 110 (67), 73 (98), 67 (100). − ^{1}H NMR (C_6D_6): δ = 6.38 (d, 1 H, *J* = 6.0, H6), 4.85 (dd, 1 H, *J* = 6.0, 5.8, 2.2, H5), 3.70−3.60 (2 H, H2 + H4), 2.09 (m, 1 H, H3), 1.75−0.80 (8 H, CH_2). − ^{13}C NMR (C_6D_6): δ = 146.8 (1), 104.2 (1), 73.5 (1), 62.5 (2), 44.4 (1), 32.9 (2), 26.6 (2), 26.4 (2), 25.1 (2). − IR (NaCl, neat): ṽ = 3406 (vs, br.), 2934 (s), 2862 (s), 1642 (s), 1237 (s), 1108 (s), 1064 (s).

(4*S,5*S**,10*S**)-1-Oxabicyclo[4.4.0]dec-2-en-4-ol (*cis*-11i):** Obtained from *cis*-**4i** (0.43 g, 2.8 mmol). TLC: cyclohexane/ether, 5:1. Purification by flash chromatography on silica. Colourless solid, m.p. 115 °C. Yield: 0.35 g (81%). − LRMS (EI); *m*/*z*: 154 (M^+, 53), 110 (46), 73 (100), 67 (71). − ^{1}H NMR: δ = 6.29 (dd, 1 H, *J* = 6.3, 1.5, H6), 4.65 (dd, 1 H, *J* = 6.3, 2.0, H5), 3.85 (d, 1 H, *J* = 8.8, H4), 3.53 (ddd, 1 H, *J* = 10.8, 10.5, 4.5, H2), 2.16 (dm, 1 H, *J* = 13.1, CH*H*), 1.96 (dm, 1 H, *J* = 12.3, CH*H*), 1.75 (dm, 1 H, *J* = 12.0, CH*H*), 1.67 (dm, 1 H, *J* = 12.0, CH*H*), 1.47 (s br., 1 H, O*H*), 1.41−1.12 (4 H, CH*H*), 0.90 (dddd, 1 H, *J* = 13.0, 13.0, 13.0, 3.8, CH*H*). − ^{13}C NMR: δ = 144.7 (1), 105.4 (1), 77.2 (1), 68.2 (1), 46.1 (1), 31.7 (2), 28.8 (2), 25.0 (2), 24.4 (2). − IR (KBr, disk): ṽ = 3406 (vs, br.), 2933 (s), 1645 (s), 1231 (s), 1043 (s), 1036 (s).

5,6-Diphenyl-3,4-dihydro-2*H*-pyran-3-ol (13): Obtained from **4j** (0.40 g, 1.6 mmol). TLC: cyclohexane/ether, 5:1. Purification by flash chromatography on silica. Colourless oil. Yield: 0.27 g (68%). − LRMS (EI); *m*/*z*: 252 (M^+, 100%), 209 (57), 117 (64), 105 (99). − ^{1}H NMR: δ = 7.23−6.68 (10 H, Ph), 3.85 (dddd, 1 H, *J* = 6.3, 5.5, 5.3, 2.5, H5), 3.77 (dm, 1 H, *J* = 10.3, H6), 3.72 (ddd, 1 H, *J* = 10.3, 6.3, 1.2, H6), 2.90 (s br., 1 H, OH), 2.47 (ddd, 1 H, *J* = 17.3, 5.5, 1.2, H4), 2.33 (dd, 1 H, *J* = 17.3, 5.3, H4). − ^{13}C NMR: δ = 149.5 (0), 141.8 (0), 136.6 (0), 130.0 (1), 129.8 (1), 128.4 (1), 127.9 (1), 127.8 (1), 126.3 (1), 110.2 (0), 69.9 (2), 63.9 (1), 36.8 (2). − IR (KBr, neat): ṽ = 3403 (s, br.), 3057 (m), 2925 (m), 1639 (m), 1446 (m), 1237 (m), 1140 (m), 788 (s), 762 (s), 698 (s).

(2*S*,3*S*,4*S*)-2-Methyl-3-vinyl-3,4-dihydro-2*H*-pyran-3,4-diol (11k): Obtained from **4k** (1.60 g, 10.0 mmol). TLC: hexanes/MTBE 1:2. Purification by kugelrohr distillation (0.2 mbar, 200 °C). Yield: 0.60 g (38%). Analytically pure samples can be obtained with significant loss of material by subsequent column chromatography on silica. − $C_8H_{12}O_3$ (156.2): calcd. C 61.5, H 7.7; found C 61.2, H 7.9. − $[\alpha]_D^{20}$ = +32.9 (*c* = 2.55, DCM). − LRMS (EI); *m*/*z*: 157 (M^+ + 1, <5), 139 (40), 121 (10), 111 (30), 93 (15), 83 (70), 73 (15), 55 (100). − ^{1}H NMR (C_6D_6): δ = 6.35 (dd, 1 H, *J* = 6.3, 1.5, O−C*H*=CH), 5.59 (dd, 1 H, *J* = 17.3, 10.8, C*H*=CH_2), 5.45 (dd, 1 H, *J* = 17.3, 1.5, CH_2=CH), 5.30 (dd, 1 H, *J* = 10.8, 1.5, CH_2=CH), 4.71 (dd, 1 H, *J* = 6.3, 2.0, C*H*=CH−O), 4.17 (br. s, 1 H, HO−C*H*), 3.85 (q, 1 H, *J* = 6.5, C*H*−CH_3), 2.24 (br. s, 1 H, *H*O), 2.12 (br. s, 1 H, *H*O), 1.17 (d, 3 H, *J* = 6.5, CH_3−CH). − ^{13}C NMR (C_6D_6): δ = 144.5 (1), 137.6 (1), 116.8 (2), 103.3 (1), 75.6 (1), 71.6 (1), 67.6 (1), 14.2 (3). − IR (NaCl, neat): ṽ = 3455 (s), 2988 (m), 1652 (s), 1237 (s), 1095 (s), 1023 (s), 980 (s).

(2*S,3*S**,4*S**)-2-Phenyl-3,4-dihydro-2*H*-pyran-3,4-diol (11l):** Obtained from **4l** (1.90 g, 10.0 mmol). TLC: hexanes/MTBE, 1:2. Purification by kugelrohr distillation (0.2 mbar, 160 °C). Yield: 0.85 g (45%). Analytically pure samples can be obtained with significant loss of material by subsequent kugelrohr distillation and column chromatography. − $C_{11}H_{12}O_3$ (192.2): calcd. C 68.7, H 6.3; found C 68.1, H 6.3. − LRMS (EI); *m*/*z*: 175 (M^+ − OH, 10), 159 (100), 131 (22), 105 (43), 91 (30), 79 (20), 70 (61), 55 (13). − ^{1}H NMR (C_6D_6): δ = 7.26−6.98 (5 H, Ph), 6.20 (dm, 1 H, *J* = 6.0, O−C*H*=CH), 4.54 (ddd, 1 H, *J* = 6.3, 1.8, 1.5, HC−C*H*=CH), 4.47 (s, 1 H, C*H*−Ph), 4.18 (m, 1 H, HO−C*H*−CH=CH), 3.62 (d, 1 H, *J* = 4.0, OH−C*H*−CH−Ph), 3.30 (br. s, 2 H, −O*H*). − ^{13}C NMR (C_6D_6): δ = 144.8 (1), 138.6 (0), 128.4 (1), 127.9 (1), 127.0 (1), 103.4 (1), 78.7 (1), 68.6 (1), 65.3 (1). − IR (NaCl, neat): ṽ = 3396 (s), 1647 (s), 1233 (s), 1142 (s), 1065 (s), 709 s.

1-Oxaspiro[4,5]dec-2-en-4-ol (14a): Obtained from **10a** (0.21 g, 1.4 mmol). TLC: cyclohexane/ether 3:1. Colourless oil. Yield: 0.20 g (95%). − LRMS (EI); *m*/*z*: 153 (M^+ − 1, 10), 137 (100). − ^{1}H NMR (C_6D_6): δ = 6.27 (d, 1 H, *J* = 2.5, H5), 4.88 (dd, 1 H, *J* = 2.5, 2.5, H4), 4.27 (d, 1 H, *J* = 2.5, H3), 1.85−1.10 (11 H, CH_2 + OH). − ^{13}C NMR (C_6D_6): δ = 149.0 (1), 103.0 (1), 88.4 (0), 78.7 (1), 34.9 (2), 30.0 (2), 25.7 (2), 23.5 (2), 23.1 (2). − IR (KBr, film): ṽ = 3376 (s), 2934 (s), 2860 (m), 1613 (m), 1068 (s). − Selected NMR spectroscopic data for the rearrangement product **1-Oxaspiro[4,5]dec-3-en-2-ol (15):** ^{1}H NMR (C_6D_6): δ = 6.03 (d, 1 H, *J* = 6.1), 5.74 (d, 1 H, *J* = 6.0), 5.57 (d, 1 H, *J* = 6.1), 3.48 (d, 1 H, *J* = 6.0, OH). − ^{13}C NMR (C_6D_6): δ = 139.0 (1), 127.1 (1), 102.2 (1), 89.1 (0), 39.0 (2), 27.5 (2), 25.6 (2), 23.4 (2), 23.1 (2).

4-Benzyloxy-1-oxaspiro[4,5]dec-3-ene (16): Dihydrofuran **14a** (0.17 g, 1.1 mmol) was dissolved in THF (10 mL) and NaH (80 mg, 60% dispersion in mineral oil, 2.0 mmol) was added. The mixture was heated to reflux for 30 min., and benzyl bromide (0.24 mL, 2.0 mmol) was added. The mixture was again heated to reflux for 30 min, cooled to room temperature, diluted with MTBE and hydrolysed. The organic layer is separated, dried, and evaporated. The residue is purified by flash chromatography on silica to give **16** (0.21 g, 78%). − LRMS (EI); *m*/*z*: 243 (M^+ − 1, 2%), 137 (100), 91 (20). − ^{1}H NMR (C_6D_6): δ = 7.32 (d, 2 H, *J* = 7.3, Ph), 7.21 (dd, 2 H, *J* = 7.3, Ph), 7.12 (t, 1 H, *J* = 7.3, Ph), 6.36 (d, 1 H, *J* = 2.8, H5), 4.99 (dd, 1 H, *J* = 2.8, 2.3, H4), 4.42 (d, 1 H, *J* = 12.0, OCH*H*Ph), 4.25 (d, 1 H, *J* = 12.0, OCH*H*Ph), 4.08 (d, 1 H, *J* =

2.3, H3), 2.15−1.18 (10 H, CH_2). − ^{13}C NMR (C_6D_6): δ = 149.5 (1), 139.6 (0), 128.5 (1), 127.5 (1), 127.5 (1), 99.9 (1), 88.2 (2), 85.7 (1), 70.2 (2), 35.6 (2), 30.4 (2), 25.8 (2), 23.4 (2), 23.2 (2). − IR (NaCl, neat): ṽ = 2934 (s), 2860 (m), 1612 (m), 1453 (m), 1088 (s), 1075 (s), 733 (m), 696 (m).

Base-Induced Rearrangement of Dihydrofuran Oxide 10b: Following the general procedure for base-induced rearrangements, **10b** (1:1 mixture of diastereomers, 0.56 g, 3.6 mmol) was treated with LDA. An inseparable 4:3:1 mixture of three compounds was obtained (NMR spectroscopic data obtained from the mixture; only characteristic data are listed). − **(2*R**,3*R**)-2-Pentyl-2,3-dihydrofuran-3-ol (*cis*-14b):** ^{1}H NMR (C_6D_6): δ = 6.32 (d, 1 H, *J* = 2.5, H5), 4.97 (dd, 1 H, *J* = 2.5, 2.5, H4), 4.50 (m, 1 H, H3), 4.31 (m, 1 H, H2). − ^{13}C NMR (C_6D_6): δ = 149.5 (1), 103.2 (1), 89.8 (1), 78.6 (1). − **(2*R**,3*S**)-2-Pentyl-2,3-dihydrofuran-3-ol (*trans*-14b):** ^{1}H NMR (C_6D_6): δ = 6.39 (d, 1 H, *J* = 2.5, H5), 5.07 (dd, 1 H, *J* = 2.5, 2.5, H4), 4.49 (m, 1 H, H3), 3.93 (ddd, 1 H, *J* = 7.0, 7.0, 7.0, H2). − ^{13}C NMR (C_6D_6): δ = 150.3 (1), 104.6 (1), 86.1 (1), 73.1 (1). − **5-Pentyl-2,3-dihydrofuran-3-ol (14b′):** ^{1}H NMR (C_6D_6): δ = 4.82 (br. s, 1 H, H3), 4.74 (d (br.), 1 H, *J* = 7.0, H4), 4.18 (dd, 1 H, *J* = 10.5, 2.0, H5), 4.05 (dd, 1 H, *J* = 10.5, 7.0, H5′). − ^{13}C NMR (C_6D_6): δ = 164.2 (0), 98.7 (1), 78.3 (1), 74.3 (2).

Base-Induced Rearrangement of Dihydrofuran Oxides *trans*- and *cis*-10c: Following the general procedure for base-induced rearrangements, **10c** (1:1 mixture of diastereomers, 0.56 g, 3.6 mmol) was treated with LiTMP. In the case of *trans*-**10c** an inseparable 9:3:1 mixture of dihydrofurans **14c′**, *trans*-**14c** and the elimination product **17c** was obtained. − **5-(4-Methoxyphenyl)-2,3-dihydrofuran-3-ol (14c′):** ^{1}H NMR (C_6D_6): δ = 7.50 (d, 2 H, *J* = 8.5, Ar), 6.70 (d, 2 H, *J* = 8.5, Ar), 5.28 (d, 1 H, *J* = 2.6, H3), 4.76 (ddd, 1 H, *J* = 7.0, 2.6, 2.2, H4), 4.20 (dd, 1 H, *J* = 10.6, 2.2, H5), 4.11 (dd, 1 H, *J* = 10.6, 7.0, H5′), 3.38 (s, 3 H, OMe). − ^{13}C NMR (C_6D_6): δ = 160.8 (0), 160.0 (0), 127.6 (1), 123.4 (0), 114.0 (1), 96.6 (1), 78.4 (2), 74.5 (1), 55.0 (3). − **(2*R**,3*S**)-2-(4-Methoxyphenyl)-2,3-dihydrofuran-3-ol (*trans*-14c):** ^{1}H NMR (C_6D_6): δ = 7.11 (d, 2 H, *J* = 8.8, Ar), 6.70 (d, 2 H, *J* = 8.8, Ar), 6.45 (d, 1 H, *J* = 2.5, H5), 5.16 (d, 1 H, *J* = 2.5, H2), 4.92 (dd, 1 H, *J* = 2.5, 2.5, H4), 4.64 (dd, 1 H, *J* = 2.5, 2.5, H3), 3.38 (s, 3 H, OMe). − ^{13}C NMR (C_6D_6): δ = 159.7 (0), 150.3 (1), 126.7 (1), 114.2 (1), 103.0 (1), 90.6 (1), 81.6 (1), 55.0 (3), signal for *ipso*-C overlapped by solvent signal. In the case of *cis*-**10c** an inseparable mixture of unchanged starting material and dihydrofuran *cis*-**14c** was obtained: **(2*R**,3*R**)-2-(4-Methoxyphenyl)-2,3-dihydrofuran-3-ol (*cis*-14c):** ^{1}H NMR (C_6D_6): δ = 7.45 (d, 2 H, *J* = 8.5, Ar), 6.83 (d, 2 H, *J* = 8.8, Ar), 6.48 (d, 1 H, *J* = 2.5, H5), 5.12 (dd, 1 H, *J* = 2.5, 2.5, H4), 5.01 (d, 1 H, *J* = 6.8, H2), 4.53 (dd, 1 H, *J* = 6.8, 2.5, H3), 3.32 (s, 3 H, OMe). − ^{13}C NMR (C_6D_6): δ = 160.2 (0), 150.3 (1), 129.2 (1), 127.3 (0), 114.0 (1), 104.7 (1), 87.2 (1), 74.0 (1), 54.7 (3),

Procedure for the Preparation of Furans from Dihydrofuran Oxides: To a solution of LDA (12.0 mmol) in THF (10 mL) was added a solution of the corresponding dihydrofuran oxide **10b** or **c** (6.0 mmol) in THF (10 mL). The mixture was stirred until the epoxide was completely consumed, and then TosCl was added. The mixture was stirred for 30 min., poured into water (20 mL) and extracted with MTBE. The organic layer was dried and evaporated; the residue was purified by kugelrohr distillation or by column chromatography.

2-Pentylfuran (17b):[73] Obtained from dihydrofuran oxide **10b** (0.90 g, 5.8 mmol). Purification by kugelrohr distillation at 15 mbar, 100 °C. Yield: 0.60 g (75%). − ^{1}H NMR: δ = 7.27 (m, 1 H, H5), 6.52 (dd, 1 H, *J* = 3.0, 1.8, H4), 5.95 (m, 1 H, H3), 2.58 (t, 2 H, *J* = 7.5, Fu−C*H*$_2$-), 1.60 (m, 2 H, CH_2), 1.35−1.25 (4 H, −CH_2CH_2-), 0.88 (t, 3 H, *J* = 7.0, −CH_3). − ^{13}C NMR: δ = 156.6 (0), 140.6 (1), 110.0 (1), 104.5 (1), 31.4 (2), 27.9 (2), 27.7 (2), 22.4 (2), 14.0 (3).

2-(4-Methoxyphenyl)furan (17c):[74] Obtained from dihydrofuran oxide **10c** (0.32 g, 1.7 mmol). Purification by column chromatography on silica, hexanes/MTBE, 10:1. Yield: 0.25 g (76%). − ^{1}H NMR: δ = 7.60 (d, 1 H, *J* = 9.0, Ar), 7.42 (dd, 1 H, *J* = 1.8, 0.8, H5), 6.92 (d, 1 H, *J* = 9.0, Ar), 6.51 (dd, 1 H, *J* = 3.3, 0.8, H3), 6.44 (dd, 1 H, *J* = 3.3, 1.8, H4), 3.83 (s, 3 H, OMe). − ^{13}C NMR: δ = 159.0 (0), 154.0 (0), 141.3 (1), 125.2 (1), 124.0 (0), 114.1 (1), 111.5 (1), 103.3 (1), 55.2 (3).

General Procedure for the Preparation of 6-Allylated 3,4-Dihydropyrans 18: To a solution of the corresponding dihydropyran (2.2 mmol) in DCM (10 mL) was added NEt_3 (0.7 mL, 5.0 mmol) and acetyl chloride (0.28 mL, 4.0 mmol) at 0 °C. The mixture was stirred at 0 °C until conversion was complete and then the reaction was quenched by addition of saturated aqueous NH_4Cl solution. The organic layer was separated, dried and evaporated. The residue was redissolved in dry DCM under an atmosphere of dry argon, cooled to −78 °C, and allyltrimethylsilane (0.5 mL, 3.0 mmol) was added, followed by BF_3OEt_2. The mixture was stirred at this temperature until conversion was complete (TLC), warmed to room temperature, diluted with MTBE (20 mL) and washed with saturated aqueous Na_2CO_3 solution. The organic layer is dried with $MgSO_4$, evaporated and the residue was purified by flash chromatography on silica with hexane/MTBE mixtures.

(2*S,6*R**)-6-Allyl-2-phenyl-3,6-dihydro-2*H*-pyran (18a):** Obtained from **11a** (0.25 g, 1.4 mmol). TLC: cyclohexane/ether 25:1. Purification by flash chromatography on silica. Colourless oil. Yield: 0.20 g (71%). − $C_{14}H_{16}O$ (200.3): calcd. C 83.9, H 8.1; found C 83.9, H 8.1. − LRMS (EI); *m*/*z*: 200 (M^+, 1%), 159 ($M^+ - C_3H_5$, 100), 91 ($C_7H_7^+$, 75). − ^{1}H NMR: δ = 7.41−7.32 (4 H, Ph), 7.27 (tt, 1 H, *J* = 7.3, 1.5, *para*-H, Ph), 5.96 (dm, 1 H, *J* = 10.3, H4,5), 5.89 (dddd, 1 H, *J* = 17.1, 10.3, 7.3, 6.8, CHHC*H*=CH_2), 5.81 (dm, 1 H, *J* = 10.3, H4,5), 5.12 (dddd, 1 H, *J* = 17.1, 2.0, 1.5, 1.5, =CH_2), 5.07 (dm, 1 H, *J* = 10.3, =CH_2), 4.75 (dd, 1 H, *J* = 8.4, 4.6, H2), 4.32 (m, 1 H, H6), 2.52 (ddddd, 1 H, *J* = 14.1, 7.8, 6.8, 1.5, 1.5, CH*H*CH=CH_2), 2.41−2.29 (3 H, H3 + CH*H*CHCH$_2$). − ^{13}C NMR: δ = 142.2 (0), 134.9 (1), 129.3 (1), 128.3 (1), 127.4 (1), 126.3 (1), 124.4 (1), 117.0 (2), 72.9 (1), 69.8 (1), 39.0 (2), 31.4 (2). − IR (NaCl, neat): ṽ = 3032 (m), 2922 (m), 2897 (m), 1641 (m), 1390 (m), 1080 (s), 1055 (s), 913 (m).

(2*S*,6*R*)-6-Allyl-2-(4-methoxyphenyl)-3,6-dihydro-2*H*-pyran (*trans*-18b): Obtained from **11b** (0.17 g, 0.8 mmol). It is essential in this case to quench the reaction at −80 °C by addition of Na_2CO_3 solution. TLC: cyclohexane/ether 20:1. Purification by flash chromatography on silica. Colourless oil. Yield: 0.16 g (87%). − $[\alpha]_D^{20}$ = −60.3 (*c* = 1.16, $CHCl_3$). − LRMS (EI); *m*/*z*: 230 (M^+, 10%), 189 (44), 121 (100). − ^{1}H NMR: δ = 7.32 (d, 2 H, *J* = 8.4, Ar), 6.88 (d, 2 H, *J* = 8.4, Ar), 5.95 (dm, 1 H, *J* = 10.3, H4,5), 5.89 (dddd, 1 H, *J* = 17.2, 10.3, 7.3, 7.0, CHHC*H*=CH_2), 5.80 (dm, 1 H, *J* = 10.3, H4,5), 5.12 (dddd, 1 H, *J* = 17.2, 1.8, 1.5, 1.5, =CH_2), 5.07 (dm, 1 H, *J* = 10.3, =CH_2), 4.72 (dd, 1 H, *J* = 8.5, 4.0, H2), 4.28 (m, 1 H, H6), 3.79 (s, 3 H, OMe), 2.51 (ddd, 1 H, *J* = 14.0, 7.3, 6.5, CH*H*CH=CH_2), 2.41−2.27 (3 H, H3 + CH*H*CHCH$_2$). − ^{13}C NMR: δ = 158.9 (0), 134.9 (1), 134.3 (0), 129.3 (1), 127.6 (1), 124.4 (1), 116.9 (2), 113.6 (1), 72.7 (1), 69.4 (1), 55.2 (3), 39.0 (2), 31.2 (2). − IR (KBr, neat): ṽ = 3033 (w), 2930 (m), 2902 (m), 1613 (m), 1515 (s), 1248 (s), 1175 (s), 1037 (s), 827 (s).

(2*R*,6*R*)-6-Allyl-2-(4-methoxyphenyl)-3,6-dihydro-2*H*-pyran (*cis*-18b): Obtained from **11b** (0.14 g, 0.7 mmol). After addition of

BF_3OEt_2 the reaction mixture was allowed to warm to −10 °C and stirring was continued at this temperature for 3 hours. Progress of the reaction was monitored by TLC: cyclohexane/ether 20:1. Ratio of diastereomers: *cis*/*trans* = 7:1. Purification by chromatography on silica. Colourless oil. Yield: 0.11 g (70%) of *cis*-**18b** and 0.01 g (5%) of *trans*-**18b**. − $[\alpha]_D^{20}$ = +22.0 (*c* = 0.80, $CHCl_3$). − LRMS (EI); *m*/*z*: 230 (M^+, 9%), 189 ($M^+ - C_3H_5$, 45%), 121 (100). − ^{1}H NMR (500 MHz): δ = 7.30 (d, 2 H, *J* = 8.8, Ar), 6.87 (d, 2 H, *J* = 8.8, Ar), 5.91 (dddd, 1 H, *J* = 17.0, 10.2, 7.0, 7.0, −C*H*=), 5.90 (m, 1 H, H5), 5.73 (dm, 1 H, *J* = 10.2, H4), 5.12 (dm, 1 H, *J* = 17.0, $=CH_2$), 5.08 (dm, 1 H, *J* = 10.2, $=CH_2$), 4.55 (dd, 1 H, *J* = 10.3, 3.5, H2), 4.36 (m, 1 H, H6), 3.79 (s, 3 H, OMe), 2.42 (ddd, 1 H, *J* = 14.0, 7.0, 6.5, −CH*H*CH=), 2.35 (ddd, 1 H, *J* = 14.0, 7.5, 7.0, −CH*H*CH=), 2.27 (ddm, 1 H, *J* = 17.0, 10.5, $H3_{ax}$), 2.18 (dm, 1 H, *J* = 17.0, $H3_{eq}$). − ^{13}C NMR: δ = 158.9 (0), 135.1 (0), 134.5 (1), 129.6 (1), 127.0 (1), 125.0 (1), 117.0 (2), 113.7 (1), 75.3 (1), 74.9 (1), 55.2 (3), 39.9 (2), 33.1 (2). − IR (NaCl, neat): ṽ = 2954 (m), 2836 (m), 1613 (s), 1514 (s), 1248 (s), 1175 (m), 1034 (s), 829 (m).

(2*S,6*R**)-6-Allyl-2-cyclohexyl-3,6-dihydro-2*H*-pyran (18c):** Obtained from **11c** (0.16 g, 0.9 mmol). TLC: cyclohexane/ether, 40:1. Purification by flash chromatography on silica. Colourless oil. Yield: 0.12 g (67%). − $C_{14}H_{22}O$ (206.3): calcd. C 81.5, H 10.7; found C 81.5, H 10.8. − LRMS (EI); *m*/*z*: M^+ not observed, 165 ($M^+ - C_3H_5$, 100%), 147 (34). − ^{1}H NMR: δ = 5.85 (dddd, 1 H, *J* = 17.1, 10.3, 7.3, 6.8, −C*H*=), 5.81 (dm, 1 H, *J* = 10.3, H4,5), 5.68 (dm, 1 H, *J* = 10.3, H4,5), 5.06 (dddd, 1 H, *J* = 17.1, $=CH_2$), 5.03 (dm, 1 H, *J* = 10.3, $=CH_2$), 4.18 (m, 1 H, H6), 3.33 (ddd, 1 H, *J* = 7.3, 7.3, 5.3, H2), 2.39 (ddddd, 1 H, *J* = 14.1, 8.3, 6.8, 1.5, 1.3, CH*H*CH=CH_2), 2.20 (ddddd, 1 H, *J* = 14.1, 7.3, 5.5, 1.3, 1.0, CH*H*CH=CH_2), 2.03−1.90 (3 H, C_6H_{11} + H3), 1.75−1.58 (4 H, C_6H_{11} + H3), 1.35 (m, 1 H, C_6H_{11} + H3), 1.28−1.10 (2 H, C_6H_{11} + H3), 1.03−0.80 (3 H, C_6H_{11} + H3). − ^{13}C NMR: δ = 135.3 (1), 129.2 (1), 124.6 (1), 116.6 (2), 72.9 (1), 71.6 (1), 42.3 (1), 38.6 (2), 29.4 (2), 28.7 (2), 28.1 (2), 26.6 (2), 26.2 (2), 26.0 (2). − IR (NaCl, neat): ṽ = 3078 (w), 2923 (s), 2852 (s), 1641 (w), 1450 (w), 1081 (s), 707 (m).

(2*S,6*R**)-6-Allyl-2-[(*S**-1-phenylethyl]-3,6-dihydro-2*H*-pyran (18d):** Obtained from **11d** (0.45 g, 2.2 mmol). TLC: cyclohexane/ether, 20:1. Purification by flash chromatography on silica. Colourless oil. Yield: 0.40 g (80%). − LRMS (EI); *m*/*z*: M^+ not observed, 187 ($M^+ - C_3H_5$, 47%), 105 (100, $C_7H_7^+$). − ^{1}H NMR: δ = 7.32−7.17 (5 H, Ph), 5.91 (dddd, 1 H, *J* = 17.1, 10.3, 7.0, 7.0, −C*H*=), 5.76−5.66 (2 H, H4,5), 5.13 (dddd, 1 H, *J* = 17.1, 2.0, 1.5, 1.5, $=CH_2$), 5.09 (dm, 1 H, *J* = 10.3, $=CH_2$), 4.30 (m, 1 H, H6), 3.71 (ddd, 1 H, *J* = 9.0, 8.8, 3.5, H2), 2.75 (dq, 1 H, *J* = 8.8, 6.8, C*H*CH_3), 2.47 (ddd, 1 H, *J* = 14.5, 7.0, 6.8, CH*H*CH=CH_2), 2.28 (ddd, 1 H, *J* = 14.5, 7.0, 5.3, CH*H*CH=CH_2), 1.83 (ddm, 1 H, *J* = 17.2, 9.0, $H3_{ax}$), 1.64 (ddd, 1 H, *J* = 17.2, $H3_{eq}$), 1.38 (ddd, 1 H, *J* = 6.8, CH_3). − ^{13}C NMR: δ = 144.4 (0), 135.2 (1), 128.9 (1), 128.3 (1), 127.8 (1), 126.3 (1), 124.5 (1), 116.7 (2), 72.7 (1), 72.6 (1), 45.0 (1), 38.7 (2), 29.0 (2), 18.6 (3). − IR (NaCl, neat) 3029 (w), 2963 (m), 1493 (m), 1452 (m), 1083 (m), 1019 (m), 701 (s).

(2*S,6*S**)-6-Allyl-2-methyl-2-phenyl-3,6-dihydro-2*H*-pyran (18f):** Obtained from **11f** (0.13 g, 0.7 mmol). TLC: cyclohexane/ether 20:1. Purification by flash chromatography on silica. Colourless oil. Yield: 0.11 g (78%). − LRMS (EI); *m*/*z*: 214 (M^+, 1%), 173 ($M^+ - C_3H_5$, 100%), 121 (47), 105 (90), 79 (74). − ^{1}H NMR (C_6D_6): δ = 7.55 (dd, 2 H, *J* = 8.0, 1.3, *ortho*-H, Ph), 7.26 (dd, 2 H, *J* = 8.0, 7.3, *meta*-H, Ph), 7.13 (t, 1 H, *J* = 7.3, *para*-H, Ph), 6.01 (dddd, 1 H, *J* = 17.1, 10.0, 7.0, 6.8, −C*H*=), 5.64 (dddd, 1 H, *J* = 10.3, 5.5, 2.0, 1.8, H4), 5.57 (dm, 1 H, *J* = 10.3, H5), 5.13 (dm, 1 H, *J* = 17.1, $=CH_2$), 5.10 (dm, 1 H, *J* = 10.0, $=CH_2$), 4.23 (m, 1 H, H6), 2.44 (ddd, 1 H, *J* = 14.1, 7.0, 6.8, CH*H*CH=CH_2), 2.35 (ddd, 1 H, *J* = 14.1, 7.3, 6.8, CH*H*CH=CH_2), 2.31 (dm, 1 H, *J* = 17.1, H3), 1.99 (ddd, 1 H, *J* = 17.1, 5.5, 2.8, H3), 1.42 (s, 3 H, CH_3). − ^{13}C NMR (C_6D_6): δ = 149.7 (0), 135.3 (1, −CH=), 128.8 (1, C4), 128.3 (1, *meta*-C, Ph), 126.7 (1, *para*-C, Ph), 124.5 (1, *ortho*-C, Ph), 123.8 (1, C4), 116.9 (2, $=CH_2$), 73.6 (0, C2), 69.4 (1, C6), 40.3 (2, −CHHCH=), 36.8 (2, C3), 24.5 (3, CH_3). − IR (NaCl, neat): nu(tuilde) = 3074 (m), 3031 (s), 2976 (s), 2930 (s), 1641 (m), 1494 (s), 1446 (s), 1087 (s), 1073 (s), 913 (s), 762 (s), 699 (s).

2-Allyl-1-oxaspiro[5,6]dodec-3-ene (18g): Obtained from **11g** (0.45 g, 1.6 mmol). TLC: cyclohexane/ether 25:1. Purification by flash chromatography on silica. Colourless oil. Yield: 0.38 g (74%). − $C_{14}H_{22}O$ (206.3): calcd. C 81.5, H 10.7; found C 81.4, H 10.7. − LRMS (EI); *m*/*z*: 206 (M^+, 1%), 165 ($M^+ - C_3H_5$, 100%). − ^{1}H NMR: δ = 5.86 (dddd, 1 H, *J* = 17.1, 10.3, 7.3, 6.3, −C*H*=), 5.69 (dddd, 1 H, *J* = 10.3, 5.3, 2.0, 2.0, H4,5), 5.63 (dddd, 1 H, *J* = 10.3, 2.5, 1.3, 1.3, H4,5), 5.08 (dddd, 1 H, *J* = 17.1, 2.0, 1.5, 1.5, $=CH_2$), 5.03 (dddd, 1 H, *J* = 10.3, 2.0, 1.3, 1.3, $=CH_2$), 4.04 (m, 1 H, H6), 2.30 (ddddd, 1 H, *J* = 14.1, 6.5, 6.5, 1.5, 1.5, C*H*H), 2.19 (ddddd, 1 H, *J* = 14.1, 7.5, 6.8, 1.3, 1.3, CH*H*), 2.00−1.21 (14 H, CHH + H3). − ^{13}C NMR: δ = 135.1 (1), 128.9 (1), 123.7 (1), 116.5 (2), 75.1 (0), 68.2 (1), 43.3 (2), 40.0 (2), 36.0 (2), 33.9 (2), 29.8 (2), 29.6 (2), 21.9 (2), 21.7 (2). − IR (NaCl, neat): ṽ = 2926 (s), 2857 (m), 1641 (w)m 1460 (w), 1038 (m).

[(2*S,3*R**,6*S**)-6-Allyl-3-hydroxymethyl-3,6-dihydro-2*H*-pyran-2-yl]methanol (18h):** Obtained from **11h** (0.20 g, 1.0 mmol). TLC: cyclohexane/ethyl acetate 1:1. Purification by flash chromatography on silica. Colourless oil. Yield: 0.09 g (49%). Attempts to obtain analytically pure samples were not successful. A significant loss of material occurred during workup. − ^{1}H NMR: δ = 5.80 (dddd, 1 H, *J* = 17.1, 10.3, 7.0, 7.0, −C*H*=), 5.79 (d, 1 H, *J* = 10.3, H4,5), 5.66 (ddd, 1 H, *J* = 10.3, 2.5, 2.5, H4,5), 5.07 (d, 1 H, *J* = 17.1, $=CH_2$), 5.04 (d, 1 H, *J* = 10.3, $=CH_2$), 4.18 (m, 1 H, H6), 3.80−3.50 (5 H, CHHO, H2), 2.90 (s br., 2 H, OH), 2.40−2.15 (3 H, CHH, H3). − ^{13}C NMR: δ = 134.4 (1), 130.6 (1), 125.1 (1), 117.3 (2), 72.0 (1), 70.7 (1), 64.0 (2), 63.6 (2), 38.7 (2), 38.7 (1).

(2*R,5*S**,10*R**)-2-Allyl-1-oxabicyclo[4.4.0]dec-3-ene (18i):** Obtained from **11i** (0.25 g, 1.6 mmol). TLC: cyclohexane/ether, 20:1. Purification by flash chromatography on silica. Colourless oil. Yield: 0.23 g (80%). − LRMS (EI); *m*/*z*: M^+ not observed, 137 ($M^+ - C_3H_5$, 100%), 119 (19), 69 (40). − ^{1}H NMR: δ = 5.85 (dddd, 1 H, *J* = 17.1, 10.2, 7.3, 6.8, −C*H*=), 5.63 (dd, 1 H, *J* = 10.0, 2.3, H4,5), 5.59 (d, 1 H, *J* = 10.0, H4,5), 5.07 (dm, 1 H, *J* = 17.1, $=CH_2$), 5.03 (dm, 1 H, *J* = 10.2, $=CH_2$), 4.20 (m, 1 H, H6), 3.10 (ddd, 1 H, *J* = 10.5, 9.3, 4.0, H2), 2.40 (ddd, 1 H, *J* = 13.8, 8.3, 6.8, CH*H*CH=CH_2), 2.24 (ddd, 1 H, *J* = 13.8, 7.3, 6.3, CH*H*CH=CH_2), 1.88−1.61 (5 H, C*H*H), 1.35−1.17 (3 H, C*H*H), 1.00 (m, 1 H, C*H*H). − ^{13}C NMR: δ = 135.1 (1, −CH=), 130.2 (1, C4,5), 128.5 (1, C4,5), 116.8 (2, $=CH_2$), 73.4 (0, C6), 72.9 (1, C2), 40.6 (1, C3), 39.2 (2, −CHHCH=), 32.0, 30.4, 25.8, 25.2 (2, CHH). − IR (NaCl, neat): ṽ = 2930 (s), 2856 (m), 1640 (m), 1449 (m), 1102 (s), 712 (m).

Procedure for the Preparation of Benzyl Ethers *trans*- and *cis*-19i: To a solution of the alcohols *trans*- or *cis*-**11i** (0.23 g, 1.5 mmol) was added NaH (60% dispersion in mineral oil, 120 mg, 3.0 mmol). The mixture was heated to reflux for 30 min., and then benzyl bromide (0.23 mL, 2.0 mmol) was added. The mixture was again refluxed until the reaction was complete as indicated by TLC (hexanes/MTBE, 10:1). After aqueous workup the residue was purified by flash chromatography on silica.

(4*S,4a*S**,8a*R**)-4-Benzyloxy-4a,5,6,7,8,8a-hexahydro-4*H*-chromene (*trans*-19i):** Obtained from *trans*-**11i** (0.23 g, 1.5 mmol). Yield: 0.31 g (85%). − LRMS (EI); *m*/*z*: 243 (M^+ − 1, 5%), 137 (M^+ − OBn, 100%), 91 ($C_7H_7^+$, 30%). − ^{1}H NMR: δ = 7.34 (d, 2 H, *J* = 7.5, *o*-H, Ph), 7.22 (dd, 2 H, *J* = 7.5, 7.5, *m*-H, Ph), 7.13 (t, 1 H, *J* = 7.5, *p*-H, Ph), 6.50 (d, 1 H, *J* = 6.3, H6), 4.92 (dd, 1 H, *J* = 6.3, 5.3, H5), 4.61 (d, 1 H, *J* = 12.0, OCH*H*Ph), 4.27 (d, 1 H, *J* = 12.0, OC*H*HPh), 4.00 (ddd, 1 H, *J* = 11.1, 11.1, 4.8, H2), 3.43 (dd, 1 H, *J* = 5.3, 3.8, H4), 2.11 (dm, 1 H, *J* = 12.5, CHH), 1.70 (ddd, 1 H, *J* = 13.0, 13.0, 3.3, CHH), 1.56−1.30 (5 H, CHH + H3), 1.14−0.95 (2 H, CHH). − ^{13}C NMR: δ = 146.7 (1), 139.9 (0), 128.5 (1), 127.7 (1), 127.5 (1), 100.3 (1), 73.7 (1), 69.7 (2), 68.5 (1), 43.3 (1), 32.7 (2), 26.4 (2), 26.0 (2), 24.5 (2). − IR (NaCl, neat): ṽ = 3060 (m), 2936 (s), 2862 (s), 1640 (s), 1453 (s), 1254 (s), 1109 (s), 1058 (s), 735 (s), 697 (s).

(4*R,4a*S**,8a*R**)-4-Benzyloxy-4a,5,6,7,8,8a-hexahydro-4*H*-chromene (*cis*-19i):** Obtained from *cis*-**11i** (0.11 g, 0.7 mmol). Yield: 0.15 g (90%). − LRMS (EI); *m*/*z*: 243 (M^+ − 1, 5%), 137 (M^+ − OBn, 100%), 91 ($C_7H_7^+$, 30%). − ^{1}H NMR: δ = 7.35 (d, 2 H, *J* = 7.5, *o*-H, Ph), 7.23 (dd, 2 H, *J* = 7.5, 7.5, *m*-H, Ph), 7.13 (t, 1 H, *J* = 7.5, *p*-H, Ph), 6.42 (dd, 1 H, *J* = 6.3, 1.5, H6), 4.86 (dd, 1 H, *J* = 6.3, 1.5, H5), 4.53 (d, 1 H, *J* = 12.0, OCH*H*Ph), 4.29 (d, 1 H, *J* = 12.0, OC*H*HPh), 3.69 (ddd, 1 H, *J* = 9.0, 1.5, 1.5, H4), 3.41 (ddd, 1 H, *J* = 11.1, 11.1, 4.5, H2), 2.24 (dm, 1 H, *J* = 13.8, CHH), 1.98 (dm, 1 H, *J* = 12.3, CHH), 1.79 (dddd, 1 H, *J* = 12.0, 11.1, 9.0, 3.7, H3), 1.55−1.30 (3 H, CHH), 1.05−0.93 (2 H, CHH), 0.65 (dddd, 1 H, *J* = 13.0, 13.0, 13.0, 3.8, CHH). − ^{13}C NMR: δ = 145.3 (1), 139.6 (0), 128.5 (1), 127.8 (1), 127.5 (1), 102.1 (1), 77.5 (1), 75.2 (1), 69.7 (2), 43.4 (1), 32.2 82), 29.1 (2), 25.3 (2), 24.5 (2). − IR (NaCl, neat): ṽ = 3062 (m), 2935 (s), 2858 (s), 1642 (s), 1452 (m), 1233 (m), 1113 (s), 1060 (s), 735 (s), 697 (s).

Procedure for the Preparation of Tetracycles *trans*- and *cis*-20i: To a solution of dihydropyran *trans*- or *cis*-**19i** (0.24 g, 1.0 mmol) in acetonitrile (10 mL) was added dimedone (0.21 g, 1.5 mmol), $NaHCO_3$ (0.34 g, 4.0 mmol) and CAN (1.10 g, 2.0 mmol). The mixture was stirred until the starting material had been completely consumed (TLC hexanes/MTBE, 1:1), diluted with MTBE (40 mL), filtered through a thin pad of Celite, and the solvent removed in vacuo. The residue was purified by flash chromatography on silica using hexanes/MTBE mixtures as eluent.

Tetracycle *trans*-20i: Obtained from (4*S**,4a*S**,8a*R**)-**19i** (0.24 g, 1.0 mmol). Yield 0.23 g (60%). − LRMS (EI); *m*/*z*: 382 (M^+, 1%), 291 (M^+ − C_7H_7, 54), 181 (41), 91 (100). − ^{1}H NMR: δ = 7.42 (d, 2 H, *J* = 7.5, *o*-H, Ph), 7.23 (dd, 2 H, *J* = 7.5, 7.5, *m*-H, Ph), 7.13 (t, 1 H, *J* = 7.5, *p*-H, Ph), 5.93 (d, 1 H, *J* = 6.3, OC*H*O), 4.71 (d, 1 H, *J* = 12.1, OCH*H*Ph), 4.51 (d, 1 H, *J* = 12.1, OC*H*HPh), 4.41 (s, 1 H, C*H*OBn), 3.88 (ddd, 1 H, *J* = 10.8, 10.8, 4.3, CH_2CHO), 3.34 (dm, 1 H, *J* = 6.3, C*H*C=C), 2.10 (d, 1 H, *J* = 15.8, CH*H*CMe_2), 2.04 (d, 1 H, *J* = 15.8, CH*H*CMe_2), 1.96 (dd, 1 H, *J* = 17.8, 2.3, CH*H*CMe_2), 1.84 (dd, 1 H, *J* = 17.8, 2.4, CH*H*CMe_2), 1.60−0.85 (9 H, CHH), 0.73 (s, 3 H, Me), 0.73 (s, 3 H, Me). − ^{13}C NMR: δ = 193.6 (0), 175.8 (0), 139.4 (0), 128.5 (1), 128.1 (1), 127.7 (1), 111.6 (0), 105.0 (1), 74.0 (1), 72.0 (2), 71.3 (1), 51.4 (2), 43.8 (1), 43.0 (2), 41.7 (1), 37.7 (2), 33.8 (2), 28.4 (2), 28.1 (2), 27.4 (0), 26.0 (3), 24.7 (3). − IR (NaCl, neat): ṽ = 2934 (s), 2864 (s), 1633 (s), 1399 (m), 1109 (s), 1090 (s), 699 (s).

Tetracycle *cis*-20i: Obtained from (4*R**,4a*S**,8a*R**)-**19i** (0.10 g, 0.4 mmol). Yield 0.09 g (59%). − $C_{24}H_{30}O_4$ (382.5): calcd. C 75.4, H 7.9; found C 75.3, H 8.6. − LRMS (EI); *m*/*z*: 382 (M^+, 1%), 291 (25), 108 (54), 91 (100), 81 (61), 56 (82). − ^{1}H NMR: δ = 7.64 (d, 2 H, *J* = 7.5, *o*-H, Ph), 7.25 (dd, 2 H, *J* = 7.5, 7.5, *m*-H, Ph), 7.13 (t, 1 H, *J* = 7.5, *p*-H, Ph), 5.88 (d, 1 H, *J* = 7.5, OC*H*O), 5.03 (d, 1 H, *J* = 11.0, OCH*H*Ph), 4.65 (d, 1 H, *J* = 11.0, OC*H*HPh), 3.55 (dd, 1 H, *J* = 8.5, 5.0, C*H*OBn), 3.41 (ddd, 1 H, *J* = 10.8, 10.8, 4.5, CH_2CHO), 3.14 (dd, 1 H, *J* = 7.5, 5.0, C*H*C=C), 2.11 (d, 1 H, *J* = 15.8, CH*H*CMe_2), 2.05 (d, 1 H, *J* = 15.8, CH*H*CMe_2), 2.05−1.95 (2 H, CHH), 1.96 (d, 1 H, *J* = 17.6, CH*H*CMe_2), 1.87 (dd, 1 H, *J* = 17.6, 2.0, CH*H*CMe_2), 1.60−1.25 (4 H, CHH), 1.07−0.60 (3 H, CHH), 0.82 (s, 3 H, Me), 0.75 (s, 3 H, Me). − ^{13}C NMR: δ = 102.1 (0), 174.8 (0), 139.7 (0), 128.7 (1), 128.4 (1), 127.6 (1), 116.0 (0), 108.5 (1), 81.7 (1), 72.8 (1), 72.7 (2), 51.3 (2), 45.2 (1), 41.8 (1), 37.7 (2), 33.0 (2), 32.5 (0), 29.7 (2), 29.0 (3), 27.6 (3), 25.6 (2), 24.7 (2). − IR (NaCl, neat): ṽ = 2934 (s), 2865 (s), 1654 (s), 1631 (s), 1401 (m), 1388 (s), 1189 (s), 1161 (s), 1113 (m).

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