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An Improved Catalyst System for the Iron-Catalyzed Intermolecular Ring-Expansion Reactions of Epoxides

Gerhard Hilt,* Patrick Bolze, and Klaus Harms[a]

Abstract: A considerable improvement is reported in the iron-catalyzed ring-expansion reactions of epoxides generating tetrahydrofuran derivatives by formal insertion of an alkene. Optimization of the catalyst system revealed that a preformed [Fe(salen)] complex minimizes the formation of polymerization side-products so that increased yields of intermolecular reactions were obtained. However, more importantly, the scope of the reaction could also be enlarged considerably. The iron-catalyzed ring-expansion reaction can now be applied to some styrene oxide derivatives, acting as radical donors, as well as to a wide variety of acceptor-substituted acyclic alkenes and cyclic dienes that act as radical acceptors. The use of unsymmetrical radical acceptors led to interesting questions concerning the regiochemistry of the reactions. The conservation of the stereochemistry of the starting materials in the products was investigated through a study of the reactions of *E*- and *Z*-configured acceptor-substituted double bonds. The reactions of fumaric and maleic esters were performed and the ratios of diastereomeric and regioisomeric products were determined.

Keywords: cyclization · epoxides · iron · salen · tetrahydrofuran

Introduction

Cycloaddition processes and other intermolecular reactions that lead to the formation of cyclic products are amongst the most powerful tools in organic synthetic chemistry. Such processes can be used for the synthesis of either carbo- or heterocyclic products, for example, the Diels–Alder or 1,3-dipolar cycloaddition reaction. The potential of these reactions increases dramatically if the chemo-, regio-, and stereoselectivities of such intermolecular processes can be efficiently controlled. Several of the intra- and intermolecular approaches to the synthesis of tetrahydrofurans recently reported involve transition-metal-catalyzed reactions.[1] As a result of numerous structural investigations and the economic and ecologic advantages associated with iron-catalyzed reactions, iron-catalyzed reactions have attracted much attention over the last decade.[2] Therefore, it is not surprising that many innovative applications of iron catalysts have been described in recent years. A very recent addition to the arsenal of synthetic organic chemistry was the iron-catalyzed ring-expansion reaction of an epoxide generating tetrahydrofuran derivatives by formal regioselective insertion of an acceptor-substituted alkene.[3] Optimization of this new iron-catalyzed reaction for intermolecular ring expansion and the desired increase in reactivity of the catalyst system led us to a catalyst with a salen-type ligand design that allowed a considerable increase in the scope of the reaction.[4]

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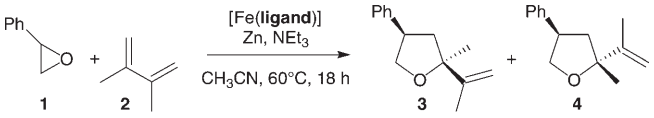
Results and Discussion

The previously investigated iron-catalyzed ring-expansion reaction of epoxides to tetrahydrofurans proceeds by formal insertion of an alkene. Screening of different ligand systems led to an improved catalyst system consisting of an iron(II) salt and a salen ligand.[3] The catalyst was generated in situ and gave satisfactory results compared with the initially used phosphine or NHC ligand systems. Further improvements were made when a preformed formal [Fe(salen)] complex was used.[5] Characterization of this species led us to the conclusion that the precatalyst does not consist of a square-planar iron(II) complex, but rather of an oxygen-bridged dimeric species corresponding to an [Fe^{III}(salen)] complex that could be crystallized and characterized by X-ray analysis.[6] Nevertheless, when the crude product was investigated by cyclic voltammetry only a relatively small wave assigned to the reduction of the [Fe^{III}(salen)] complex to the corresponding [Fe^{II}(salen)] complex was observed at

$E^{\ominus} = +87$ mV (vs. Ag/AgCl), whereas the main peak of the cyclic voltammogram at $E^{\ominus} = -265$ mV (vs. Ag/AgCl) was assigned to the further reduction of the proposed [Fe^{II}(salen)] complex, generated from $Fe(OAc)_2$ and the salen ligand, to a reduced [Fe^{I}(salen)] species (reduction peak potential: $E^{p}_{red} = -320$ mV).[7] Therefore, we propose that the preformed [Fe(salen)] complex, either in its crystallized iron(III) form or as a coordinative saturated iron(II) complex, is reduced by zinc powder under the conditions of the ring-expansion reaction in acetonitrile. Further electroanalytical investigations of the reduction process revealed that the original reduction peak assigned to the Fe^{II}/Fe^{I} reduction was shifted from its original value ($E^{p}_{red} = -320$ mV vs. Ag/AgCl) after the addition of base (NEt_3) by more than 300 mV to more negative potentials (to $E^{p}_{red} = -680$ mV) with the formation of a largely insoluble precipitate. Accordingly, the reduction potentials of the iron complexes are enhanced after complexation with the Lewis base triethylamine which allows electron transfer to the epoxide to proceed more efficiently. Note that, based on investigations of similar iron complexes, it is more likely that electron transfer into the LUMO of the [Fe^{II}(salen)] complex leads to an octahedral iron species in which the electron is largely delocalized in the ligand rather than to the formal formation of an iron(I) species.[8] In this scenario the free coordination site of the octahedral iron ligand sphere can be occupied by the epoxide and will lead to electron transfer from the salen ligand via the iron center to the epoxide.[9]

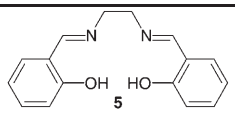
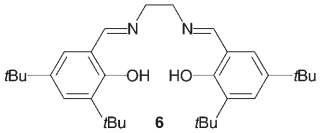
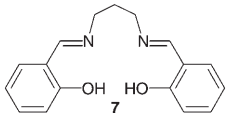
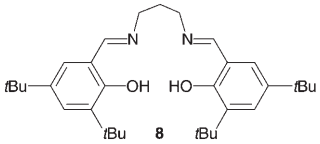
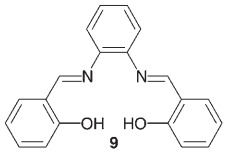
The reactivity and selectivity of the very promising salen-type ligand family were explored through the reaction of styrene oxide (**1**) (radical donor) with 2,3-dimethyl-1,3-butadiene (**2**) (as radical acceptor), which leads in a one-step reaction to a mixture of diastereomers of the tetrahydrofuran derivatives **3** and **4** (Scheme 1).[3]



Scheme 1. Prototype of the iron-catalyzed ring-expansion reaction of epoxides.

For this and subsequent investigations we adopted reaction conditions in which high reactivity was combined with relatively low catalyst loading, minimizing polymerization side reactions. Therefore, 20 mol% of the iron precatalyst was used together with 140 mol% zinc powder and 30 mol% NEt_3 in acetonitrile (1.0 mL) at 60 °C over night. The ratio of the starting materials was varied taking into account the relative reactivity of the starting materials in the iron-catalyzed process.[10] In an earlier report the nature of the salen-type ligand had a profound influence on the diastereoselectivity of an intramolecular ring-expansion reaction.[3] When preformed iron catalysts with five selected salen-type ligands (**5**–**9**) were tested in the intermolecular reaction shown in Scheme 1, we found to our surprise that variation in the salen ligand motif had only a very limited effect on the diastereoselectivity and yield of the ring-expansion reaction (Table 1).

Table 1. Results obtained for the ring-expansion reaction of styrene oxide with different salen-type ligands.

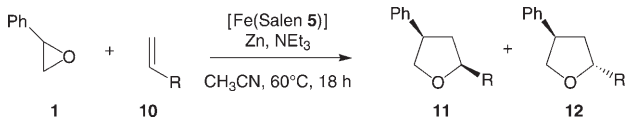
Entry[a]	salen-type ligand	d.r. (**3**:**4**)[b]	Yield [%]
1	 **5**	80:20	83
2	 **6**	79:21	84
3	 **7**	77:23	44
4	 **8**	78:22	83
5	 **9**	–	traces

[a] Reagents and conditions: Styrene oxide (1.0 mmol), 2,3-dimethyl-1,3-butadiene (0.5 mL), Fe complex (0.2 mmol), triethylamine (0.3 mmol), zinc powder (1.4 mmol), acetonitrile (1.0 mL), 60 °C, 15–16 h. [b] The diastereoselectivity was determined by ^{1}H NMR spectroscopy of the crude product.

As can be seen from Table 1the diastereoselectivity changes marginally when either the backbone of the salen ligand was altered or the ligand possessed bulky substituents. Although in the case of the *tert*-butyl-substituted Jacobsen-type ligand **6** the diastereoselectivity of the intramolecular ring-expansion reaction was enhanced, in the intermolecular reaction of **1** and **2** essentially no change was observed. For the salen ligand **5** (Table 1, entry 1) and the *tert*-butyl derivative **6** (Table 1, entry 2) the good yields were reproduced in contrast to the intramolecular case in which a better diastereoselectivity was obtained with the *tert*-butyl-salen ligand **6** accompanied by a reduced yield. When the backbone of the salen ligand was altered as in **7** and **8** again both the diastereoselectivities and the chemical yield of **8** (but not **7**) were almost identical to the results obtained with salen ligand **5**. The considerably inferior result obtained with the propyl-modified salen derivative **7** (Table 1, entry 3) seems to be inconsistent. These differences arise from problems encountered during the generation and isolation of the preformed iron complex which could not be solved by altering the reaction conditions according to the literature.[11] In contrast, when the propyl-modified ligand

with *tert*-butyl substituents **8** (Table 1, entry 4) was used both the diastereoselectivity and the chemical yield were restored. Extension of the π system realized by inclusion of benzene in the backbone, as in the salen-type ligand **9** (Table 1, entry 5), led to considerably reduced reactivity and only to traces of the desired product. The future strategy for increasing the diastereoselectivity will involve the installation of more bulky substituents pointing out of the equatorial plane of the salen-type ligand. Accordingly, the following investigations were conducted with the originally introduced preformed [Fe(salen)] complex using ligand **5**. These investigations were performed in acetonitrile at moderate temperatures (60 °C) utilizing NEt_3 as a Lewis base additive. A very limiting factor of the previously described iron phosphine and NHC ligand catalyst systems was the rather large amounts of polymerization side products formed with these catalyst systems. Under intermolecular reaction conditions the yields seldom exceeded 50% isolated yield with various substrates, whereas a single product was formed in >95% purity, as judged from a GCMS analysis. The products were isolated by simple filtration through silica gel. Herein, we report a significant improvement of the iron catalyst systems in terms of the yields compared with all the previously reported ring-expansion reactions. In addition, the scope of the ring-expansion reaction could be extended considerably by utilization of the preformed [Fe(salen)] complex.

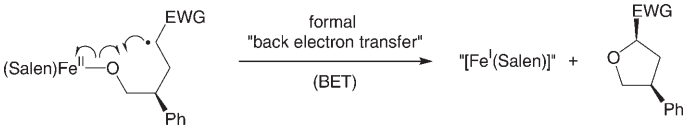
In a second series of experiments styrene oxide **1** was converted under [Fe(salen)] catalysis with various 1,3-dienes and acceptor-substituted alkene derivatives **10** to regiochemically pure polysubstituted tetrahydrofuran derivatives **11** and **12** (Scheme 2).



Scheme 2. The intermolecular iron-catalyzed ring-expansion reaction.

Simple terminal, di-, or trisubstituted alkenes could not be used as radical acceptors because the secondary alkyl-substituted radical intermediate is not sufficiently stable for completion of the radical cycle. On the other hand, the high chemoselectivity for attack on a functionalized alkene moiety proved to be of particular interest as even trisubstituted alkenes also present in the starting material do not react under the reaction conditions. In addition, it should be very clear that much more interesting products are formed when functionalized alkenes are used as starting materials **10** rather than simple unfunctionalized alkenes. In the case of the functionalized alkenes **10**, the synthetic potential of the resulting tetrahydrofuran derivatives **11** and **12** clearly compensates for the fact that simple alkenes cannot be used as radical acceptors. The very appealing chemistry of functionalized tetrahydrofurans **11** and **12** inspired us to investigate the use of a wide variety of functionalized starting materials **10** rather than the problem associated with the incorporation of simple alkenes. In fact, the very profound chemoselectivity of the iron-catalyzed reaction allows alkenes with various functionalities to be used as starting materials providing a synthetic route to polyfunctionalized and unsaturated tetrahydrofuran derivatives. Accordingly, attempts were made to carry out the iron-catalyzed ring-expansion reaction with a broad range of α,β-unsaturated starting materials **10** in which the intermediate radical is stabilized by an electron-accepting functionality. The results are summarized in Table 2.

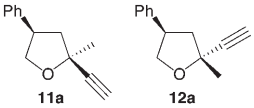
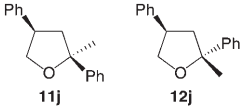
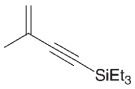
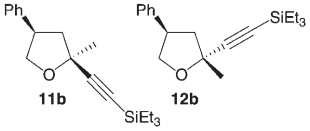
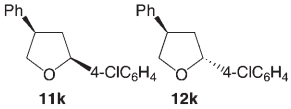
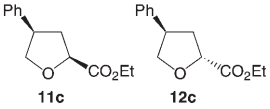
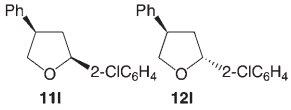
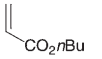
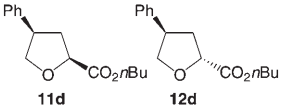
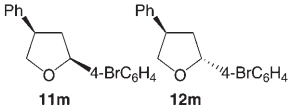
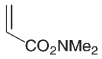
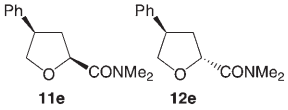
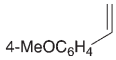
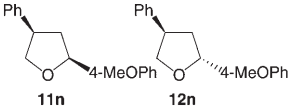
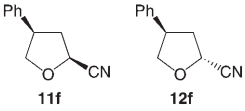
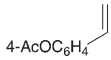
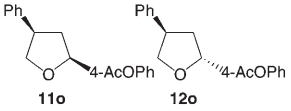
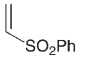
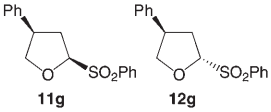
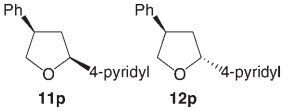
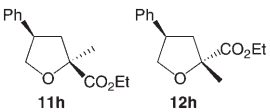
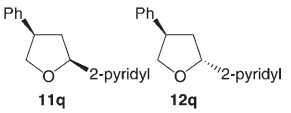
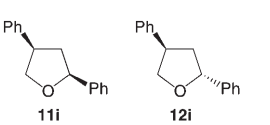
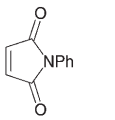
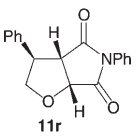
Based on the proposed radical-type mechanism for the ring-expansion reaction,[12] the diastereoselectivity can be controlled during the attack of the stabilized radical (e.g., by an electron-withdrawing group (EWG), Scheme 3) on



Scheme 3. Proposed mechanism for the cyclization reaction.

the iron-bound oxygen atom resulting in a net back-electron transfer reaction (BET) to the iron center. Therefore, the steric situation of the substituents on the radical acceptor alkene functionality must play an important role in determining the diastereoselectivity of the ring closure outlined in Scheme 3. Accordingly, the transformation of styrene oxide with enyne derivatives gave the products **11a** and **12a** in good yields and with exclusive regiochemistry and chemoselectivity leaving the alkyne functionality untouched (Table 2, entry 1). However, the diastereoselectivity of the reaction was very low reflecting the steric demand of a methyl substituent compared with an alkyne subunit. Introduction of the $SiEt_3$ group (Table 2, entry 2) did not reduce the reactivity of the reaction and reflected the stability of silylalkynyl groups in the starting material under the reaction conditions. Nevertheless, the diastereoselectivity for **11b**/**12b** was not improved and attempts to use sterically more bulky silyl protecting groups were dismissed based on the very limited effect of the $SiEt_3$ group. The next few transformations with simple acceptor-substituted double bonds (Table 2, entries 3–8) show that the diastereoselectivity (**11c–h**:**12c–h**) of the reaction reflects the steric bulkiness of the acceptor functionality. Fortunately, many types of radical acceptors are viable as functional groups. Among them are nitriles, sulfones, and amides, which could give rise to compounds with interesting chemistry leading to the generation of complex target molecules through the improved ring-expansion approach presented herein. The iron-catalyzed ring-expansion reaction with styrene as radical acceptor (Table 2, entry 9) led regioselectively to the natural products calyxolan B (**11i**, *cis* product) and calyxolan A (**12i**, *trans* product) in a good chemical yield of 79%.[13] For comparison, the identical transformation catalyzed by the iron dihalide/phos-

Table 2. Results of the intermolecular iron-catalyzed ring-expansion reactions of styrene oxide with alkenes **10**.

Entry	Alkene[a]	Products (**11** and **12**)	Yield [%] (d.r. **11**:**12**[b])	Entry	Alkene[a]	Products (**11** and **12**)	Yield [%] (d.r. **11**:**12**[b])
1		 **11a** **12a**	72 (52:48)	10		 **11j** **12j**	71 (70:30)
2		 **11b** **12b**	80 (51:49)	11		 **11k** **12k**	62 (69:31)
3		 **11c** **12c**	65 (69:31)	12		 **11l** **12l**	53 (71:29)
4		 **11d** **12d**	50 (70:30)	13		 **11m** **12m**	48 (70:30)
5		 **11e** **12e**	51 (68:32)	14		 **11n** **12n**	57 (69:31)
6		 **11f** **12f**	73 (56:44)	15		 **11o** **12o**	54 (73:27)
7[c]		 **11g** **12g**	62 (78:22)	16		 **11p** **12p**	83 (69:31)
8		 **11h** **12h**	81 (71:29)	17		 **11q** **12q**	80 (66:34)
9		 **11i** **12i**	79 (70:30)	18[c]		 **11r**	69 (>99:1)

[a] Reagents and conditions: Styrene oxide (1.0 mmol), alkene (0.5 mL), Fe complex (0.2 mmol), triethylamine (0.3 mmol), zinc powder (1.4 mmol), acetonitrile (1.0 mL), 60 °C, 15–16 h. [b] The diastereoselectivity was determined by ^{1}H NMR spectroscopy of the crude product. [c] Reagents and conditions: Styrene oxide (3.0 mmol), alkene (1.0 mmol), Fe complex (0.2 mmol), triethylamine (0.3 mmol), zinc powder (1.4 mmol), acetonitrile (1.0 mL), 60 °C, 15–16 h.

phine/NHC catalyst system gave a combined yield of up to 55 % of an **11i**/**12i** mixture after a tedious optimization procedure to reduce the formation of polymerization side-products. An alternative reaction sequence that gives the same products was described recently and acts as a benchmark for the synthesis of these relatively simple natural products. In this investigation Piras and co-workers described the synthesis of calyxolan B in a three-step synthesis.[14] Compared with this benchmark reaction our approach with a single-step reaction from commercially available starting materials seems competitive.

Variation of the styrene derivative with functional groups on the arene ring revealed the excellent chemoselectivity of the ring-expansion reaction with a wide range of functional groups proving viable. Under the reaction conditions, chloro-, bromo-, alkoxy-, acetoxyphenyl, and pyridyl substituents were found to be reactive and the products **11k–q**/**12k–q** were obtained in acceptable-to-good yields. Although reductive and presumably radical reaction conditions were applied, no traces of a debromination reaction were observed which would have led to the calyxolans **11i** and **12i** (see Table 2, entry 9). These latter examples of functionalized radical acceptors extend the scope of the reaction significantly. In addition, the conversion of α-methylstyrene (Table 2, entry 10), which gives the tetrahydrofuran derivatives **11j** and **12j** in good yields with acceptable diastereoselectivity, also extends the scope of the reaction to 1,1-disubstituted radical acceptors. A polyfunctionalized bicyclic

product **11r** was generated when *N*-phenylmaleimide was used as the starting material (Table 2, entry 18). This transformation led to a single diastereomer **11r** with *cis* fusion of the two five-membered rings in good chemical yield which could not be realized with the previously investigated catalyst systems. The latter two examples were the first iron-catalyzed reactions in which a 1,1-disubstituted as well as a 1,2-disubstituted double bond system underwent reaction. The relative stereochemistries of the products were confirmed by NOESY and other two-dimensional NMR techniques. Nevertheless, when possible the NMR assignments were verified by X-ray analysis of crystalline ring-expansion products. The X-ray structures of compounds **11g** and **11r** shown in Figure 1 confirm the relative stereochemistries of the products formed in the ring-expansion process.[15]

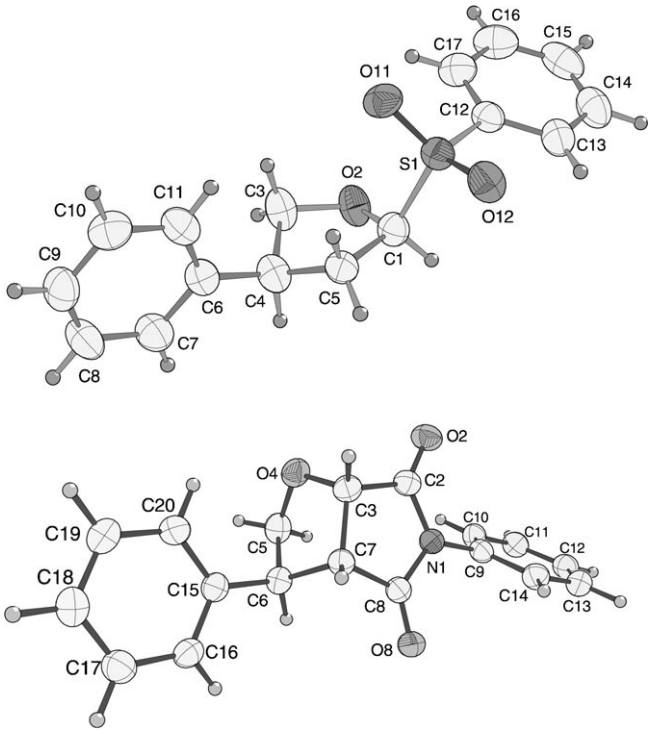
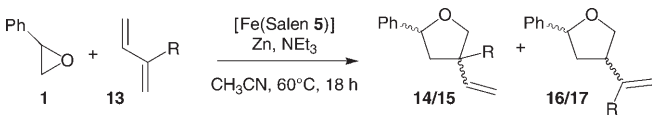


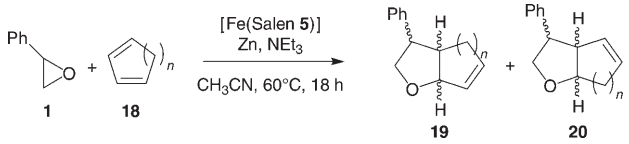
Figure 1. X-ray structures of **11g** (top) and **11r** (bottom).

In a third set of experiments we investigated the use of unsymmetrical 1,3-dienes such as isoprene and myrcene as starting materials (Scheme 4). Besides the formation of diastereomers **14** and **15**, diastereomers of the regioisomeric products **16** and **17** were also expected upon attack of the two differently substituted double bonds.



Scheme 4. Iron-catalyzed ring expansion with acyclic unsymmetrical radical acceptors.

A similar problem was encountered when the ring-expansion reaction was applied to cyclic non-acceptor-substituted 1,3-dienes as starting materials. This transformation led to a mixture of regioisomeric diastereomers **19** and **20** (Scheme 5). The results for the two sets of experiments with acyclic and cyclic 1,3-dienes are summarized in Table 3.

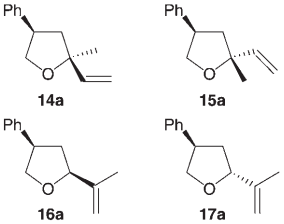
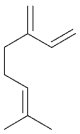
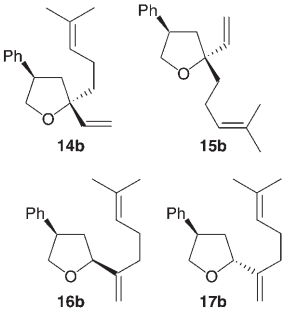
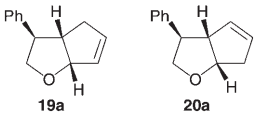
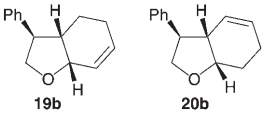
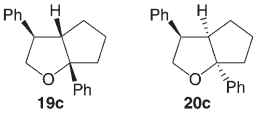
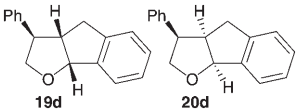


Scheme 5. Iron-catalyzed ring expansion with cyclic unsymmetrical radical acceptors.

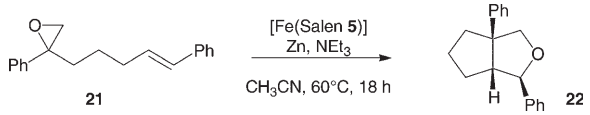
The reaction with isoprene (Table 3, entry 1) led to an inseparable mixture of regio- and diastereomers. In some cases (almost) pure fractions or enrichments of one diastereomer were obtained by repeated column chromatography which simplified the assignment of the two-dimensional NMR data of the crude complex mixture of products. Of these products a preference for attack of the radical donor on the more substituted double bond of the 1,3-diene (**14**, **15**) over attack on the less substituted double bond (**16**, **17**) could be detected. This behavior can be rationalized in terms of the better stabilization of the intermediate radical by hyperconjugation with the alkyl substituent. This behavior was also reflected in the reaction with myrcene (Table 3, entry 2). In this case the regioisomeric products could be separated. The exclusive attack on the 1,3-diene allows the incorporation of a monosubstituted as well as a trisubstituted olefin moiety into the product without any trace of attack on these functionalities or the formation of a bicyclic ring-closure reaction product. The use of cyclic 1,3-dienes, 1-phenylcyclopentene, and indene led to bicyclic and tricyclic products (Table 3, entries 3–6) that are predominantly *cis*,*cis* fused. As expected the use of cyclopentadiene gave a rather low yield of **19a** and **20a** even though an excess of the monomer was used. On the other hand, the use of 1,3-cyclohexadiene led exclusively to the *cis*-fused products **19b** and **20b** which could be separated in a good overall yield. The possibilities inherent in the use of cyclic dienes and in particular of indene derivatives open the way to new bi- and tricyclic ring-expansion products **19** and **20**. Of particular interest was the reaction of 1-phenylcyclopentene, the first example of the use of a trisubstituted radical acceptor. In addition, the products **19c** and **20c** are regioisomers of compound **22** generated in the intramolecular reaction of 2-phenyl-2-(5-phenylpent-4-enyl)oxirane (**21**) through the same iron-catalyzed ring-expansion reaction (Scheme 6).[3] The NMR assignment for **19c** was also verified by X-ray analysis of a crystalline sample (Figure 2) which confirmed the *cis* relationship between the two phenyl substituents as well as the *cis* fusion of the bicyclic ring system.[16]

In the reaction, *N*-phenylmaleimide, with a *Z*-configured double bond, was converted into the bicyclic product **11r**

Table 3. Results obtained in the iron-catalyzed ring-expansion reactions of cyclic and acyclic unsymmetrical radical acceptors.

Entry	Alkene[a]	Product	Yield [%] (d.r.[b])
1		 **14a** **15a** **16a** **17a**	64 (58:23:11:8)
2		 **14b** **15b** **16b** **17b**	59 (65:35)
3		 **19a** **20a**	18 (90:10) **19a**: 9 **20a**: 10
4		 **19b** **20b**	**19b**: 37 **20b**: 29
5[c]		 **19c** **20c**	51 (65:35)
6[c]		 **19d** **20d**	20 (50:50)

[a] Reagents and conditions: Styrene oxide (1.0 mmol), alkene (0.5 mL), Fe complex (0.2 mmol), triethylamine (0.3 mmol), zinc powder (1.4 mmol), acetonitrile (1.0 mL), 60 °C, 15–16 h. [b] The diastereoselectivity was determined by ^{1}H NMR spectroscopy of the crude product. [c] Reagents and conditions: Styrene oxide (3.0 mmol), alkene (1.0 mmol), Fe complex (0.2 mmol), triethylamine (0.3 mmol), zinc powder (1.4 mmol), acetonitrile (1.0 mL), 60 °C, 15–16 h.



Scheme 6. Intramolecular iron-catalyzed ring-expansion reaction of epoxide **21**.

with perfect *cis* fusion. The formation of a *trans* product was unlikely and was not detected. In this respect, the use of acyclic 1,2-bis-acceptor-substituted double-bond radical acceptors could give rise to an inversion of the stereochemistry in the intermediate radical. For this purpose the reactions of some fumaric and maleic esters were investigated to determine whether the stereochemistry of the double bond in the starting materials **23** was conserved to give a *cis*,*trans* configuration in the products **24**–**27** (Scheme 7). The results of these investigations are summarized in Table 4.

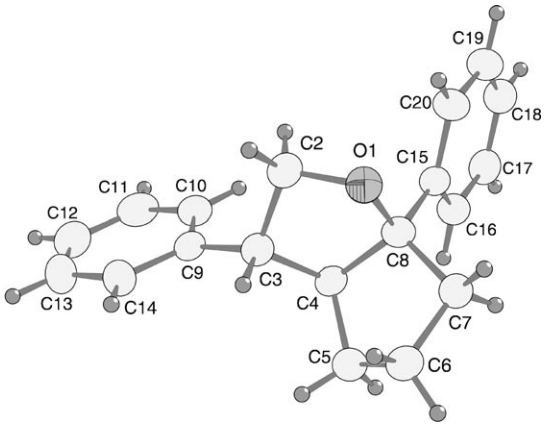
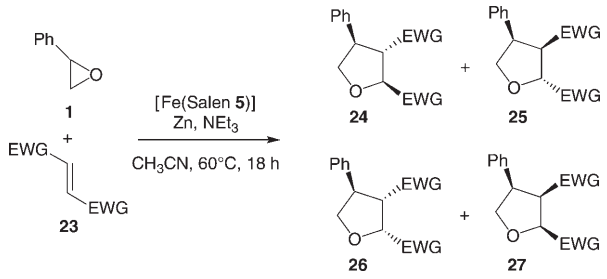


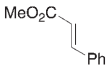
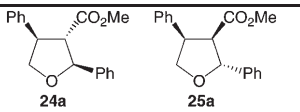
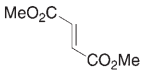
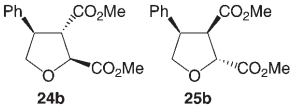
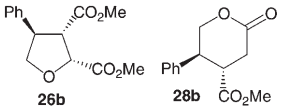
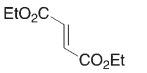
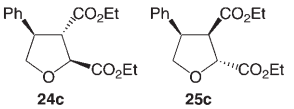
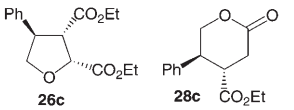
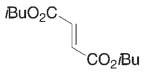
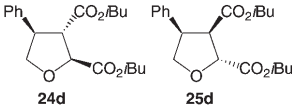
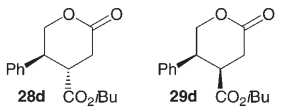
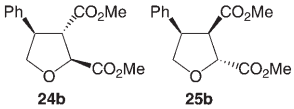
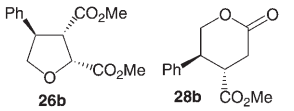
Figure 2. X-ray structure of **19c**.



Scheme 7. Iron-catalyzed reactions of bis-acceptor-substituted radical acceptors.

The use of a cinnamic ester (Table 4, entry 1) led to a single regioisomer as a 1:1 mixture of the diastereomers **24a** and **25a** in an acceptable chemical yield, indicating that the steric demand of an ester moiety is similar to that of a phenyl substituent. Of particular interest were the investigations concerning the fumaric and maleic esters. It can be seen that the reaction leads to a complex mixture of diastereomers consisting of up to three tetrahydrofuran derivatives detected in reasonable amounts. In some cases it was possible to enrich one diastereomer by column chromatography on silica gel which simplified the assignment of the two-dimensional NMR signals to the proposed diastereomers. The assignments and the comparison between the methyl esters of fumaric and maleic acid (Table 4, entries 2 and 5) revealed that an *E* double bond is mostly conserved in a *trans* configuration, as observed in the products **24b** and **25b** (Table 4, entry 2). On the other hand, a *Z*-configured double bond in the starting material is mostly converted into a *trans* configuration in the tetrahydrofuran products

Table 4. Results obtained in the iron-catalyzed ring-expansion reactions with bis-acceptor-substituted radical acceptors.

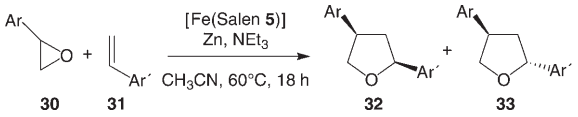
Entry	Alkene **23**[a]	Products	Yield [%] (d.r.[b])
1		 **24a** **25a**	54 (50:50)
2		 **24b** **25b**  **26b** **28b**	55 (42:33:25) **28b**: 10
3		 **24c** **25c**  **26c** **28c**	46 (40:51:9) **28c**: 31 (only *trans*)
4		 **24d** **25d**  **28d** **29d**	33 (47:53) 9 (85:15)
5		 **24b** **25b**  **26b** **28b**	29 (44:36:20) **28b**: 6 (only *trans*)

[a] Reagents and conditions: Styrene oxide (1.0 mmol), 2,3-dimethyl-1,3-butadiene (0.5 mL), Fe complex (0.2 mmol), triethylamine (0.3 mmol), zinc powder (1.4 mmol), acetonitrile (1.0 mL), 60 °C, 15–16 h. [b] The diastereoselectivity was determined by ^{1}H NMR spectroscopy of the crude product.

24b and **25b** (Table 4, entry 5). Similar ratios were obtained for the diastereomers **24b**, **25b**, and **26b** starting with either dimethyl fumarate (**24b**/**25b**/**26b** = 42:33:25) or dimethyl maleate (**24b**/**25b**/**26b** = 44:36:20). This indicates that the lifetime of the intermediate radical is long enough for an isomerization process to occur so that the geometry of the double bond is irrelevant in this type of ring-expansion process. Because the yield and reactivity were higher in the reaction of methyl fumarate it is advantageous to use *E*-configured double bond systems. On the other hand these experiments exclude mechanistic possibilities such as a concerted addition of carbonyl ylides possibly generated through alternative ring-opening of the epoxide.[17]

The diastereomeric ratios are influenced marginally by the steric bulkiness of the alcohol component of the ester (Table 4, entries 3 and 4), but excellent diastereoselectivities could not be obtained by this modification. When the steric bulk was increased, the two isomers **25c** and **25d** were predominantly formed. In the case of the isobutyl ester the corresponding isomer **26d** could not be detected at all. In addition, lactone derivatives of type **28** were isolated in varying yields which were presumably formed by a further reduction of the acceptor-substituted radical intermediate to the anion, its protonation, and transesterification to the corresponding lactones. A strong preference for the *trans*-configured products was observed and only in the case of the isobutyl ester was a *cis*-**29d** isolated and characterized as a minor isomer.

Next we focussed our attention on the use of radical donor component **30** bearing functional groups (Scheme 8). In combination with functionalized styrenes **31** a rapid approach to tetrahydrofuran products of difunctionalized calyxolan derivatives (**32** and **33**) and higher substituted derivatives was envisaged.

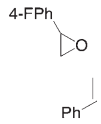
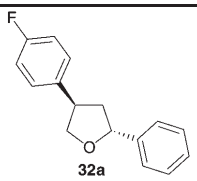
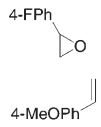
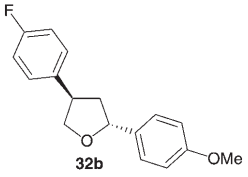
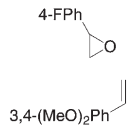
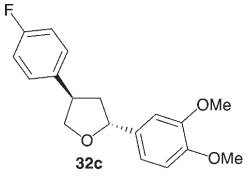
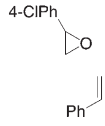
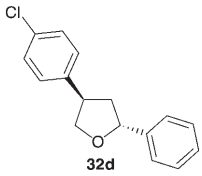
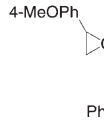
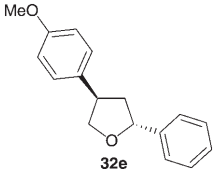
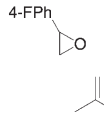
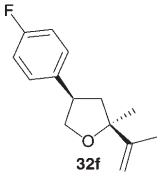
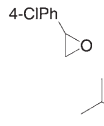
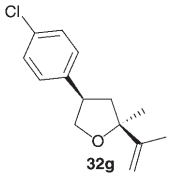
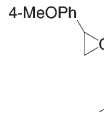
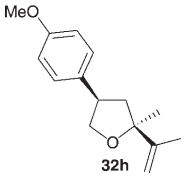
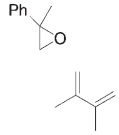
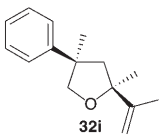


Scheme 8. Iron-catalyzed synthesis of diaryltetrahydrofurans.

Variation of the functional groups attached to styrene oxide **30** was initiated to investigate the effect of substituents upon the reactivity of the radical donor. After coordination of the epoxide to the iron catalyst we propose an electron transfer from the iron complex to the LUMO of the starting material which is most likely located in the aromatic ring of the epoxide. Accordingly, reduced reactivity should be encountered if the electron density within the aromatic ring or the steric bulkiness was increased by electron-donating substituents, whereas electron-abstracting substituents should increase the rate of electron transfer. However, the electron-transfer reaction generates a radical functionality that is located next to a strained three-membered ring system which leads to a fast ring-opening reaction resulting in iron–oxygen bond formation and an arene-stabilized radical intermediate. The results of these investigations are summarized in Table 5.

This last set of experiments revealed that several halide- and alkoxy-functionalized radical donors and acceptors can be used in the iron-catalyzed process. In the cases of fluoro- and chloro-substituted epoxides higher yields were obtained than with the methoxy-functionalized styrene oxide. As was anticipated, the rate of reaction with the electron-abstracting substituents was higher than with the alkoxy-substituted styrene oxide (Table 5, entries 5 and 8) indicating that electron transfer from the reduced iron species to the epoxide **30** depends on the redox potential of the styrene oxide and that the electron is transferred to the phenyl ring of the styrene oxide. Nevertheless, when the electron density is also

Table 5. Results obtained for the iron-catalyzed synthesis of calyxolan derivatives.

Entry	Epoxide **30** Alkene **31**	*cis*-product **32**	Yield [%] (d.r.)
1		 **32a**	72 (69:31)
2		 **32b**	70 (70:30)
3		 **32c**	75 (70:30)
4		 **32d**	72 (69:31)
5		 **32e**	57 (70:30)
6		 **32f**	75 (80:20)
7		 **32g**	77 (79:21)
8		 **32h**	59 (81:19)
9		 **32i**	46 (62:38)

enhanced in the radical donor, the styrene oxide, an acceptable yield of **32e** could be obtained. On the other hand, if the electron density is enhanced in the radical acceptor component (Table 5, entries 2 and 3) no negative effect on the reactivity was observed and good yields of the corresponding products were obtained. Thereby an interesting range of calyxolan derivatives could be generated that have potential activity in biological tests.[18] Transformations with 2,3-dimethyl-1,3-butadiene also led to ring-expansion products in acceptable-to-good yields. With this substrate, the scope of the reaction could be broadened by the use of a 1,1-disubstituted epoxide to generate a 2,2,4,4-tetrasubstituted tetrahydrofuran derivative. Hence, for the first time the ring-expansion methodology has been applied to the regioselective formation of two quaternary centers in a single synthetic step.

Conclusion

An improved iron catalyst system for intermolecular ring-expansion reactions has proved effective with di- and trisubstituted radical acceptors, several styrene oxide derivatives as radical donors, as well as with several functional groups within both components. The presence of these functional groups within the starting materials has extended the scope of this simple approach to polysubstituted and polyfunctionalized tetrahydrofurans and thereby the chemistry of tetrahydrofuran derivatives. Worth mentioning is the high chemoselectivity of the iron-catalyzed reaction, with only acceptor- (and aryl-) substituted double bonds being attacked while other double and triple bonds are untouched. The salen-type iron catalysts led to regioselectively pure and in some cases diastereomerically enriched products in acceptable-to-good yields thereby extending the scope of the

reaction considerably. The steric bulkiness of the substituents in the starting materials plays an important role in determining the relative stereochemistry of the products. The use of cyclic dienes led to interesting bi- and tricyclic products and the iron-catalyzed reaction could also be used to generate a wide range of simple calyxolan derivatives. The reactions with maleic and fumaric esters revealed that the reactions could not take place by concerted additions via carbonyl ylides thereby allowing the reaction mechanism to be elucidated. Nevertheless, the use of *E* double bond systems in combination with the [Fe(salen)] catalyst system seems to be advantageous in terms of reactivity.

Experimental Section

NMR spectra were recorded with a Bruker Avance 300, DRX 400, DRX 500, or Avance 600 spectrometer (^{1}H: 300, 400, 500, or 600 MHz; ^{13}C: 75, 100, 125, or 150 MHz; ^{19}F: 282 MHz) using TMS as the internal standard ($\delta = 0$ ppm) unless otherwise noted. IR spectra were recorded with a Bruker Physics IFS 200 Interferometer or a Nicolet Magna-IR 750 instrument. Mass and GC–MS spectra were recorded with a Hewlett-Packard 6890 GC-System equipped with a Hewlett-Packard 5973 Mass Selective Detector. To record (high-resolution) mass spectra a Finnigan MAT 95S and a Finnigan LTQ (ESI, HRMS) spectrometer were used. Analytical thin-layer chromatography was performed on Merck silica gel 60 F254. For column chromatography Merck silica gel 60 (230–400 mesh ASTM) was used. All reactions were carried out under an inert atmosphere (nitrogen or argon) using standard Schlenk techniques. Acetonitrile from Acros chemicals was used. The ligands were prepared according to or by adapting literature methods.[19] The [Fe^{II}(salen)] complex was synthesized by an adapted method.[5] The data were collected on a STOE IPDS diffractometer at 173 K using $Mo_{K\alpha}$ radiation. The structures were solved by using direct methods and refined by using the full-matrix least-squares procedure in SHELX-97 (G. M. Sheldrick, University of Göttingen, **1997**).

General procedure A (GPA): [Fe^{II}(salen)] (0.2 mmol) and zinc powder (1.4 mmol) were suspended in acetonitrile (1.0 mL). Then triethylamine (0.3 mmol) was added and the mixture was heated until boiling. After 5 min the alkene (0.5 mL) and epoxide (1.0 mmol) were added. After stirring for 15–18 h at 60 °C the mixture was filtered through a pad of silica (eluent: Et_2O) and concentrated under reduced pressure. The crude product was purified by column chromatography. The following products were synthesized by GPA: **3** and **4**, **11** and **12** (Table 2, entries 1–6 and 8–17), **14**–**17**, **19**, and **20** (Table 3, entries 1–4), and **32** (Table 5, entries 1—9).

General procedure B (GPB): [Fe(II)(salen)] (0.2 mmol) and zinc powder (1.4 mmol) were suspended in acetonitrile (1.0 mL). Then triethylamine (0.3 mmol) was added and the mixture was heated until boiling. After 5 min the alkene (1.0 mmol) and the epoxide (3.0 mmol) were added. After stirring for 15–18 h at 60 °C the mixture was filtered through a pad of silica (eluent: Et_2O) and concentrated under reduced pressure. The crude product was purified by column chromatography. The following products were synthesized by GPB: **11** and **12** (Table 2, entries 7 and 18), **19** and **20** (Table 3, entries 5 and 6), and **24**–**26**, **28**, and **29** (Table 4, entries 1–5).

2-Isopropenyl-2-methyl-4-phenyltetrahydrofuran (3/4): Yield: 83 %, **3**:**4** = 80:20, $R_f = 0.39$ (CH_2Cl_2/pentane = 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): *cis* isomer, **3**: $\delta = 7.60$–7.42 (m, 5H), 5.32 (brs, 1H), 5.02 (brs, 1H), 4.52 (t, $J = 7.8$ Hz, 1H), 4.00 (dd, $J = 10.0$, 8.3 Hz, 1H), 3.88–3.74 (m, 1H), 2.50 (dd, $J = 12.3$, 8.0 Hz, 1H), 2.33 (t, $J = 11.6$ Hz, 1H), 1.65 (s, 3H), 2.06 ppm (s, 2H); further signals for the *trans* isomer, **4**: $\delta = 5.32$ (brs, 1H), 5.10 (brs, 1H), 4.52 (t, $J = 8.3$ Hz, 1H), 4.09 (t, $J = 8.6$ Hz, 1H), 3.72–3.59 (m, 1H), 2.73 (dd, $J = 12.3$, 7.3, Hz, 1H), 2.03 (s, 2H), 1.70 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): *cis* isomer, **3**: $\delta = 150.0$, 140.9, 128.4, 127.3, 126.5, 108.1, 85.6, 74.1, 45.2, 44.6, 26.7, 19.2 ppm; further signals for the *trans* isomer, **4**: $\delta = 148.8$, 141.7, 128.4, 127.2, 126.4, 109.5, 86.0, 73.6, 45.3, 44.7, 26.4, 19.2 ppm; IR (film): $\tilde{\nu} = 2971$, 2865, 1645, 1603, 1495, 1450, 1368, 1118, 1049, 901, 760, 699 cm^{-1}; HRMS: *m*/*z* calcd for $[C_{14}H_{18}O]^+$: 202.1358; found: 202.1362.

2-(1-Ethynyl)-2-methyl-4-phenyltetrahydrofuran (11a/12a): Yield: 72 %, **11a**/**12a** = 52:48, $R_f = 0.36$ (CH_2Cl_2/pentane = 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): *cis* isomer, **11a**: $\delta = 7.20$–7.12 (m, 5H), 4.18 (dd, $J = 9.0$, 7.7 Hz, 1H), 3.80 (d, $J = 8.6$ Hz, 1H), 3.77–3.64 (m, 1H), 2.56 (dd, $J = 12.1$, 7.5 Hz, 1H), 2.39 (s, 1H), 1.86 (dd, $J = 12.3$, 10.3 Hz, 1H), 1.58 ppm (s, 3H); further signals for the *trans* isomer, **12a**: $\delta = 4.28$ (t, $J = 8.3$ Hz, 1H), 3.85–3.80 (m, 1H), 3.47–3.32 (m, 1H), 2.45 (s, 1H), 2.32 (dd, $J = 10.0$, 8.6 Hz, 2H), 1.54 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): *cis* isomer, **11a**: $\delta = 140.4$, 128.5, 127.1, 126.6, 86.7, 76.8, 74.2, 71.1, 49.0, 45.1, 27.5 ppm; further signals for the *trans* isomer, **12a**: $\delta = 142.0$, 128.5, 127.5, 126.7, 87.6, 76.2, 74.6, 71.3, 48.0, 45.1, 28.5 ppm; IR (film): $\tilde{\nu} = 2980$, 2933, 2866, 2108, 1603, 1494, 1453, 1245, 1111, 1034, 760, 700, 649 cm^{-1}; HRMS: *m*/*z* calcd for $[C_{13}H_{14}O]^+$: 186.1045; found: 186.1049.

Triethyl[2-(2-methyl-4-phenyltetrahydro-2-furanyl)-1-ethynyl]silane (11b/12b): Yield: 80 %, **11b**/**12b** = 51:49, $R_f = 0.49$ (CH_2Cl_2/pentane = 1:2). ^{1}H NMR (300 MHz, $CDCl_3$): *cis* isomer, **11b**: $\delta = 7.32$–7.08 (m, 5H), 4.29 (t, $J = 8.3$ Hz, 1H), 3.80 (t, $J = 8.1$ Hz, 1H), 3.75–3.62 (m, 1H), 2.54 (dd, $J = 12.1$, 7.5 Hz, 1H), 1.84 (dd, $J = 12.1$, 10.2 Hz, 1H), 1.57 (s, 3H), 0.93 (t, $J = 7.9$ Hz, 9H), 0.55 ppm (q, $J = 8.0$ Hz, 6H); further signals for the *trans* isomer, **12b**: $\delta = 4.17$ (t, $J = 8.4$ Hz, 1H), 3.82 (t, $J = 9.2$ Hz, 1H), 3.45–3.31 (m, 1H), 2.35–2.27 (m, 2H), 1.54 (s, 3H), 0.53 ppm (q, $J = 8.0$ Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): *cis* isomer, **11b**: $\delta = 141.3$, 128.5, 127.1, 126.52, 110.8, 85.0, 77.3, 74.1, 49.5, 45.2, 27.5, 7.44, 4.37 ppm; further signals for the *trans* isomer, **12b**: $\delta = 142.6$, 128.4, 127.7, 126.58, 109.9, 84.5, 76.8, 74.8, 48.6, 45.3, 28.4, 7.41, 4.35 ppm; IR (film): $\tilde{\nu} = 2954$, 2874, 2161, 1456, 1245, 1032, 1017, 737, 700 cm^{-1}; HRMS: *m*/*z* calcd for $[C_{19}H_{28}OSi]^+$: 300.1909; found: 300.1900.

Ethyl 4-phenyltetrahydro-2-furancarboxylate (11c/12c): Yield: 65 %, **11c**/**12c** = 69:31, $R_f = 0.25$ (CH_2Cl_2/pentane = 10:1). ^{1}H NMR (300 MHz, $CDCl_3$): *cis* isomer, **11c**: $\delta = 7.39$–7.21 (m, 5H), 4.62 (t, $J = 8.2$ Hz, 1H), 4.30 (t, $J = 8.0$ Hz, 1H), 4.25 (q, $J = 7.0$ Hz, 2H), 3.95 (t, $J = 9.1$ Hz, 1H), 3.60–3.40 (m, 1H), 2.84–2.71 (m, 1H), 2.23–2.08 (m, 1H), 1.31 ppm (t, $J = 7.2$ Hz, 3H); further signals for the *trans* isomer, **12c**: $\delta = 4.71$ (dd, $J = 8.6$, 4.3 Hz, 1H), 4.43 (t, $J = 8.0$ Hz, 1H), 4.24 (q, $J = 7.4$ Hz, 2H), 3.90 (t, $J = 8.0$ Hz, 1H), 2.58–2.46 (m, 1H), 2.45–2.32 ppm (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): *cis* isomer, **11c**: $\delta = 172.9$, 139.8, 128.64, 127.3, 126.9, 77.3, 75.2, 61.0, 45.1, 38.2, 14.1 ppm; further signals for the *trans* isomer, **12c**: $\delta = 173.0$, 141.1, 128.66, 127.1, 126.7, 77.2, 75.4, 43.7 ppm; IR (film): $\tilde{\nu} = 2980$, 1749, 1271, 1202, 1102, 1030, 858, 757, 701 cm^{-1}; HRMS: *m*/*z* calcd for $[C_{17}H_{18}O_3]^+$: 220.1099; found: 220.1099.

***n*-Butyl 4-phenyltetrahydro-2-furancarboxylate (11d/12d)**: Yield: 50 %, **11d**/**12d** = 70:30, $R_f = 0.60$ (EtOAc/CH_2Cl_2/pentane = 1:5:10). ^{1}H NMR (300 MHz, $CDCl_3$): *cis* isomer, **11d**: $\delta = 7.28$–7.11 (m, 5H), 4.52 (dd, $J = 8.2$, 7.8 Hz, 1H), 4.19 (t, $J = 8.0$ Hz, 1H), 4.10 (t, $J = 6.7$ Hz, 2H), 3.85 (dd, $J = 9.6$, 8.5 Hz, 1H), 3.50–3.30 (m, 1H), 2.67 (dt, $J = 12.7$, 7.8 Hz, 1H), 2.04 (ddd, $J = 12.7$, 10.2, 8.5 Hz, 1H), 1.63–1.51 (m, 2H), 1.39–1.23 (m, 2H), 0.852 ppm (t, $J = 7.4$ Hz, 3H); further signals for the *trans* isomer, **12d**: $\delta = 4.61$ (dd, $J = 8.7$, 4.3 Hz, 1H), 4.32 (dd, $J = 8.2$, 7.6 Hz, 1H), 4.09 (t, $J = 6.7$ Hz, 2H), 3.80 (t, $J = 8.0$ Hz, 1H), 2.40 (ddd, $J = 12.2$, 7.8, 4.3 Hz, 1H), 2.28 (dt, $J = 12.9$, 8.6 Hz, 1H), 0.859 ppm (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): *cis* isomer, **11d**: $\delta = 172.9$, 139.8, 128.54, 127.2, 126.7, 77.2, 75.1, 64.7, 45.0, 38.2, 30.5, 18.9, 13.5 ppm; further signals for the *trans* isomer, **12d**: $\delta = 173.0$, 141.1, 128.56, 127.0, 126.6, 77.1, 75.3, 43.7 ppm; IR (film): $\tilde{\nu} = 2959$, 1735 1454, 1201, 1103, 757, 701 cm^{-1}; HRMS: *m*/*z* calcd for $[C_{15}H_{20}O_3+Na]^+$: 271.1311; found: 271.1305.

***N*,*N*-Dimethyl-4-phenyltetrahydro-2-furancarboxamide (11e/12e)**: Yield: 51 %, **11e**/**12e** = 68:32, $R_f = 0.20$ (EtOAc/pentane = 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): *cis* isomer, **11e**: $\delta = 7.27$–7.11 (m, 5H), 4.75 (dd, $J = 8.2$, 7.3 Hz, 1H), 4.15 (t, $J = 7.9$ Hz, 1H), 3.79 (dd, $J = 8.0$, 5.6 Hz, 1H), 3.37 (tt, $J = 10.1$, 7.9 Hz, 1H), 3.03 (s, 3H), 2.92 (s, 3H), 2.54–2.33 ppm (m, 2H); further signals for the *trans* isomer, **12e**: $\delta = 4.84$ (dd, $J = 8.2$, 3.9 Hz, 1H), 4.26 (t, $J = 7.9$ Hz, 1H), 3.76 (dd, $J = 8.1$, 3.6 Hz, 1H), 3.37

(quin, $J=7.8$ Hz, 1H), 2.90 (s, 3H), 2.66 (ddd, $J=12.1$, 8.0, 3.9 Hz, 1H), 2.10 ppm (dt, $J=12.5$, 8.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): *cis* isomer, **11e**: $\delta=171.0$, 140.1, 128.52, 127.5, 126.7, 76.3, 75.0, 45.4, 36.8, 36.75, 35.72 ppm; further signals for the *trans* isomer, **12e**: $\delta=171.1$, 141.8, 128.55, 127.1, 126.5, 76.1, 75.1, 44.4, 36.78, 35.71 ppm; IR (film): $\tilde{\nu}=2939$, 1650, 1495 (m), 1090, 702 cm^{-1}; HRMS: *m/z* calcd for $[C_{13}H_{17}NO+Na]^+$: 242.1157; found: 242.1152.

4-Phenyltetrahydro-2-furancarbonitrile (11f/12f): Yield: 73%, **11f/12f** = 56:44, $R_f=0.23$ (CH_2Cl_2/pentane = 1:1). ^{1}H NMR (500 MHz, $CDCl_3$): *cis* isomer, **11f**: $\delta=7.36$–7.17 (m, 5H), 4.80 (dd, $J=7.8$, 6.9 Hz, 1H), 4.28 (dd, $J=8.0$, 8.6 Hz, 1H), 3.87 (t, $J=9.2$ Hz, 1H), 3.45 (quin, $J=8.8$ Hz, 1H), 2.41–2.34 (m, 1H), 2.81 ppm (dt, $J=13.0$, 8.4 Hz, 1H); further signals for the *trans* isomer, **12f**: $\delta=4.91$ (dd, $J=8.2$, 2.8 Hz, 1H), 4.36 (t, $J=8.2$ Hz, 1H), 3.94 (t, $J=8.1$ Hz, 1H), 3.70 (quin, $J=8.0$ Hz, 1H), 2.65 ppm (ddd, $J=13.0$, 7.6, 2.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): *cis* isomer, **11f**: $\delta=138.7$, 128.9, 127.3, 127.0, 119.3, 75.1, 66.9, 44.8, 39.4 ppm; further signals for the *trans* isomer, **12f**: $\delta=139.9$, 127.4, 127.3, 119.1, 66.9, 43.9, 39.9 ppm; IR (film): $\tilde{\nu}=3062$, 2954, 2878, 2240, 1603, 1495, 1455, 1068, 1040, 918, 759, 700 cm^{-1}; HRMS: *m/z* calcd for $[C_{11}H_{11}NO]^+$: 173.0841; found: 173.0845.

4-Phenyl-2-phenylsulfonyltetrahydrofuran (11g/12g): Yield: 62%, **11g/12g** = 78:22, $R_f=0.37$ (CH_2Cl_2/pentane = 2:1), m.p. 104–106 °C. ^{1}H NMR (500 MHz, $CDCl_3$): *cis* isomer, **11g**: $\delta=7.92$ (d, $J=7.3$ Hz, 2H), 7.62 (t, $J=7.5$ Hz, 1H), 7.52 (t, $J=7.8$ Hz, 2H), 7.30–7.11 (m, 5H), 4.97 (t, $J=7.5$ Hz, 1H), 4.18 (t, $J=7.9$ Hz, 1H), 4.00 (dd, $J=11.2$, 8.2 Hz, 1H), 3.47–3.35 (m, 1H), 2.81–2.66 ppm (m, 2H); further signals for the *trans* isomer, **12g**: $\delta=7.90$ (d, $J=7.0$ Hz, 2H), 5.02 (dd, $J=8.2$, 3.4 Hz, 1H), 4.46 (t, $J=7.9$ Hz, 1H), 3.91 (dd, $J=11.2$, 8.2 Hz, 1H), 3.72 (quin, $J=7.5$ Hz, 1H), 3.06 (ddd, $J=14.4$, 8.1, 3.1 Hz, 1H), 2.36 ppm (dt, $J=14.3$, 8.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): *cis* isomer, **11g**: $\delta=138.8$, 137.7, 136.9, 129.18, 129.0, 128.7, 127.5, 126.8, 93.7, 75.8, 45.0, 33.3 ppm; further signals for the *trans* isomer, **12g**: $\delta=140.8$, 136.7, 129.16, 127.3, 126.9, 94.4, 76.7, 43.4, 34.3 ppm; IR (KBr): $\tilde{\nu}=2951$, 1303, 1281, 1146, 690, 585, 548 cm^{-1}; HRMS: *m/z* calcd for $[C_{16}H_{16}O_3S+Na]^+$: 311.0718; found: 311.0712.

Ethyl 2-methyl-4-phenyltetrahydro-2-furancarboxylate (11h/12h): Yield: 81%, **11h/12h** = 71:29, $R_f=0.16$ (Et_2O/pentane = 1:5). ^{1}H NMR (300 MHz, $CDCl_3$): *cis* isomer, **11h**: $\delta=7.56$–7.38 (m, 5H), 4.51 (t, $J=7.8$ Hz, 1H), 4.07 (dd, $J=10.3$, 8.6 Hz, 1H), 3.97 (s, 3H), 3.80–3.64 (m, 1H), 2.66 (dd, $J=12.9$, 10.0 Hz, 1H), 2.55 (dd, $J=12.3$, 8.6 Hz, 1H), 1.75 ppm (s, 3H); further signals for the *trans* isomer, **12h**: $\delta=4.56$ (t, $J=8.3$ Hz, 1H), 4.12 (t, $J=8.5$ Hz, 1H), 3.03 (dd, $J=12.8$, 7.5 Hz, 1H), 2.16 (dd, $J=12.8$,10.8 Hz, 1H), 1.79 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): *cis* isomer, **11h**: $\delta=175.4$, 139.5, 128.5, 127.2, 126.7, 83.5, 75.2, 52.25, 44.5, 44.0, 25.2 ppm; further signals for the *trans* isomer, **12h**: $\delta=175.2$, 141.0, 127.0, 126.6, 84.4, 75.2, 52.29, 45.1, 44.6, 24.3 ppm; IR (film): $\tilde{\nu}=2951$, 1735, 1454, 1287, 1121, 1042, 755, 700 cm^{-1}; HRMS: *m/z* calcd for $[C_{13}H_{14}O_3]^+$: 220.1099; found: 220.1094.

2,4-Diphenyltetrahydrofuran (11i/12i): Yield: 79%, **11i/12i** = 70:30, $R_f=0.41$ (CH_2Cl_2/pentane = 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): *cis* isomer, **11i** (Calyxolan B): $\delta=7.47$–7.20 (m, 10H), 5.08 (dd, $J=10.2$, 5.8 Hz, 1H), 4.37 (t, $J=8.2$ Hz, 1H), 4.02 (t, $J=8.5$ Hz, 1H), 3.96–3.84 (m, 1H), 2.84–2.70 (m, 1H), 2.03 (q, $J=10.5$ Hz, 1H); further signals for the *trans* isomer, **12i** (Calyxolan A): $\delta=5.24$ (dd, $J=7.0$, 6.0 Hz, 1H), 4.47 (t, $J=8.0$ Hz, 1H), 3.95 (t, $J=8.3$ Hz, 1H), 3.59–3.47 (m, 1H), 2.48 (ddd, $J=12.6$, 7.6, 7.6 Hz, 1H), 2.33 ppm (ddd, $J=12.6$, 8.3, 6.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): *cis* isomer, **11i** (Calyxolan B): $\delta=142.6$, 141.6, 128.6, 128.4, 127.3, 127.20, 126.6, 125.6, 81.8, 75.0, 46.0, 43.7 ppm; further signals for the *trans* isomer, **12i** (Calyxolan A): $\delta=143.5$, 142.0, 128.6, 128.3, 127.28, 127.1, 126.6, 125.4, 80.5, 75.1, 44.3, 42.6 ppm; IR (film): $\tilde{\nu}=2935$, 1779, 1495, 1451, 1063, 753, 699 cm^{-1}; HRMS: *m/z* calcd for $[C_{16}H_{16}O]^+$: 224.1201; found: 224.1204. The NMR data is in accord with literature data.[13]

2-Methyl-2,4-diphenyltetrahydrofuran (11j/12j): Yield: 71%, **11j/12j** = 70:30, $R_f=0.36$ (CH_2Cl_2/pentane = 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): *cis* isomer, **11j**: $\delta=7.30$–7.65 (m, 10H), 4.52 (t, $J=7.8$ Hz, 1H), 3.82 (dd, $J=10.0$, 8.3 Hz, 1H), 3.89–3.72 (m, 1H), 2.76 (dd, $J=12.3$, 8.0 Hz, 1H), 2.43 (dd, $J=12.3$, 10.6 Hz, 1H), 1.73 ppm (s, 3H); further signals for the *trans* isomer, **12j**: $\delta=4.46$ (t, $J=8.3$ Hz, 1H), 4.10 (t, $J=8.8$ Hz, 1H), 3.50–3.34 (m, 1H), 2.84 (dd, $J=12.2$, 7.2 Hz, 1H), 2.32 (t, $J=11.8$ Hz, 1H), 1.78 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): *cis* isomer, **11j**: $\delta=148.9$, 140.8, 128.4, 128.2, 127.3, 126.6, 126.4, 124.4, 74.4, 47.9, 45.7, 30.5 ppm; further signals for the *trans* isomer, **12j**: $\delta=147.6$, 141.6, 128.5, 128.1, 127.2, 126.5, 126.5, 124.6, 73.9, 48.2, 44.5, 30.1 ppm; IR (film): $\tilde{\nu}=2970$, 1494, 1445, 1370, 1046, 763, 700 cm^{-1}; HRMS: *m/z* calcd for $[C_{17}H_{18}O]^+$: 238.1358; found: 238.1360.

2-(4-Chlorophenyl)-4-phenyltetrahydrofuran (11k/12k): Yield: 62%, **11k/12k** = 69:31, $R_f=0.42$ (CH_2Cl_2/pentane = 1:2). ^{1}H NMR (300 MHz, $CDCl_3$): *cis* isomer, **11k**: $\delta=7.30$–7.11 (m, 9H), 4.96 (dd, $J=10.1$, 5.8 Hz, 1H), 4.27 (t, $J=8.2$ Hz, 1H), 3.92 (t, $J=8.5$ Hz, 1H), 3.63–3.50 (m, 1H), 2.67 (ddd, $J=12.8$, 7.2, 5.8 Hz, 1H), 1.90 (dt, $J=12.4$, 10.4 Hz, 1H); further signals for the *trans* isomer, **12k**: $\delta=5.11$ (dd, $J=7.7$, 5.8 Hz, 1H), 4.37 (dd, $J=8.5$, 7.4 Hz, 1H), 3.92 (t, $J=8.3$ Hz, 1H), 3.50–3.38 (m, 1H), 2.39 (dt, $J=12.6$, 7.7 Hz, 1H), 2.19 (ddd, $J=12.6$, 8.3, 5.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): *cis* isomer, **11k**: $\delta=141.4$, 141.2, 133.0, 128.6, 128.5, 127.1, 127.0, 126.7, 81.0, 75.03, 49.9, 43.7 ppm; further signals for the *trans* isomer, **12k**: $\delta=142.1$, 141.7, 132.8, 128.4, 127.2, 126.8, 79.8, 75.07, 44.3, 42.6 ppm; IR (film): $\tilde{\nu}=2929$, 2863, 1491, 1090, 1069, 1013, 825, 757, 699 cm^{-1}. HRMS: *m/z* calcd for $[C_{16}H_{15}ClO]^+$: 258.0811; found: 258.0807.

2-(2-Chlorophenyl)-4-phenyltetrahydrofuran (11l/12l): Yield: 53%, **11l/12l** = 71:29, $R_f=0.30$ (CH_2Cl_2/pentane = 1:4). ^{1}H NMR (300 MHz, $CDCl_3$): *cis* isomer, **11l**: $\delta=7.58$ (dd, $J=7.7$, 1.6 Hz, 1H), 7.28–7.05 (m, 8H), 5.28 (dd, $J=9.8$, 6.0 Hz, 1H), 4.28 (t, $J=8.1$ Hz, 1H), 3.93 (t, $J=8.5$ Hz, 1H), 3.65–3.47 (m, 1H), 2.93 (ddd, $J=13.1$, 7.3, 6.1 Hz, 1H), 1.80–1.65 ppm (m, 1H); further signals for the *trans* isomer, **12l**: $\delta=7.51$ (dd, $J=7.7$, 1.6 Hz, 1H), 5.40 (dd, $J=8.2$, 4.9 Hz, 1H), 4.41 (t, $J=7.9$ Hz, 1H), 3.85 (t, $J=8.6$ Hz, 1H), 3.43–3.28 (m, 1H), 2.55 (dt, $J=12.7$, 8.5 Hz, 1H), 2.15 ppm (ddd, $J=12.8$, 8.1, 4.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): *cis* isomer, **11l**: $\delta=141.3$, 140.8, 131.5, 129.3, 128.55, 128.16, 127.1, 127.0, 126.6, 126.1, 78.8, 74.8, 45.9, 41.9 ppm; further signals for the *trans* isomer, **12l**: $\delta=141.5$, 141.2, 131.3, 129.3, 128.59, 128.10, 127.2, 126.7, 126.3, 78.0, 75.2, 43.9, 41.1 ppm; IR (film): $\tilde{\nu}=2974$, 1472, 1073, 1047, 1032, 754, 699 cm^{-1}; HRMS: *m/z* calcd for $[C_{16}H_{15}ClO]^+$: 258.0811; found: 258.0805.

2-(4-Bromophenyl)-4-phenyltetrahydrofuran (11m/12m): Yield: 48%, **11m/12m** = 70:30, $R_f=0.30$ (CH_2Cl_2/pentane = 1:3). ^{1}H NMR (300 MHz, $CDCl_3$): *cis* isomer, **11m**: $\delta=7.38$ (d, $J=8.5$ Hz, 2H), 7.27–7.10 (m, 7H), 4.92 (dd, $J=10.1$, 5.8 Hz, 1H), 4.25 (t, $J=8.2$ Hz, 1H), 3.91 (t, $J=8.5$ Hz, 1H), 3.61–3.47 (m, 1H), 2.65 (ddd, $J=12.8$, 7.2, 5.8 Hz, 1H), 1.85 ppm (dt, $J=12.4$, 10.4 Hz, 1H); further signals for the *trans* isomer, **12m**: $\delta=5.08$ (dd, $J=7.6$, 5.9 Hz, 1H), 4.35 (dd, $J=8.5$, 7.4 Hz, 1H), 3.85 (t, $J=8.3$ Hz, 1H), 3.47–3.94 (m, 1H), 2.37 (dt, $J=12.5$, 7.7 Hz, 1H), 2.17 ppm (ddd, $J=12.6$, 8.3, 5.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): *cis* isomer, **11m**: $\delta=141.7$, 141.4, 131.4, 128.6, 127.3, 127.14, 126.69, 121.0, 81.0, 75.00, 45.9, 43.6 ppm; further signals for the *trans* isomer, **12m**: $\delta=142.6$, 141.6, 131.3, 127.2, 127.16, 126.66, 120.8, 79.8, 75.03, 44.2, 42.5 ppm; IR (film): $\tilde{\nu}=2969$, 1486, 1069, 1010, 821, 757, 699 cm^{-1}; HRMS): $[C_{16}H_{15}BrO]^+$: 302.0306; found: 302.0296.

2-(4-Methoxyphenyl)-4-phenyltetrahydrofuran (11n/12n): Yield: 57%, **11n/12n** = 69:31, $R_f=0.31$ (EtOAc/pentane = 1:15). ^{1}H NMR (300 MHz, $CDCl_3$): *cis* isomer, **11n**: $\delta=7.25$–7.04 (m, 7H), 6.77 (d, $J=8.7$ Hz, 2H), 4.88 (dd, $J=10.2$, 5.6 Hz, 1H), 4.20 (t, $J=8.3$ Hz, 1H), 3.88 (t, $J=8.4$ Hz, 1H), 3.67 (s, 3H), 3.56–3.45 (m, 1H), 2.57 (ddd, $J=12.6$, 7.2 5.6 Hz, 1H), 1.87 ppm (dt, $J=12.3$, 10.5 Hz, 1H); further signals for the *trans* isomer, **12n**: $\delta=5.05$ (t, $J=6.8$ Hz, 1H), 4.31 (dd, $J=8.4$, 7.5 Hz, 1H), 3.79 (t, $J=8.2$ Hz, 1H), 3.45–3.36 (m, 1H), 2.36–2.13 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): *cis* isomer, **11n**: $\delta=159.0$, 141.9, 134.4, 128.5, 127.1, 127.0, 126.55, 113.8, 81.5, 74.8, 55.2, 45.9, 43.6 ppm; further signals for the *trans* isomer, **12n**: $\delta=158.8$, 142.1, 135.4, 127.2, 126.7, 126.52, 113.7, 80.3, 74.9, 44.5, 42.5 ppm; IR (film): $\tilde{\nu}=2934$, 1612, 1513, 1455, 1302, 1247, 1173, 1036, 830, 759, 700 cm^{-1}; HRMS: *m/z* calcd for $[C_{17}H_{18}O_2]^+$: 254.1307; found: 254.1308.

2-(4-Acetoxyphenyl)-4-phenyltetrahydrofuran (11o/12o): Yield: 54%, **11o/12o** = 73:27, $R_f=0.24$ (EtOAc/pentane = 1:10). ^{1}H NMR (300 MHz, $CDCl_3$): *cis* isomer, **11o**: $\delta=7.38$–7.10 (m, 7H), 7.09 (d, $J=8.5$ Hz, 2H),

4.98 (dd, $J=10.1$, 5.7 Hz, 1H), 4.26 (t, $J=8.2$ Hz, 1H), 3.92 (t, $J=8.5$ Hz, 1H), 3.62–3.50 (m, 1H), 2.66 (ddd, $J=12.7$, 7.2, 5.8 Hz, 1H), 2.20 (s, 3H), 1.90 ppm (dt, $J=12.4$, 10.5 Hz, 1H); further signals for the *trans* isomer, **12o**: $\delta=5.14$ (dd, $J=7.6$, 5.9 Hz, 1H), 4.36 (dd, $J=8.4$, 7.5 Hz, 1H), 3.85 (t, $J=8.2$ Hz, 1H), 3.50–3.37 (m, 1H), 2.37 (dt, $J=12.6$, 7.7 Hz, 1H), 2.29–2.18 ppm (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): *cis* isomer, **11o**: $\delta=$ 169.44, 149.8, 141.5, 140.2, 128.5, 127.1, 126.69, 126.63, 121.4, 81.2, 75.0, 45.9, 43.6, 21.0 ppm; further signals for the *trans* isomer, **12o**: $\delta=169.40$, 149.6, 141.8, 141.1, 127.2, 126.5, 126.4, 121.3, 80.0, 74.9, 44.2, 42.6 ppm; IR (film): $\tilde{\nu}=2937$, 1755, 1507, 1369, 1217, 1195, 1048, 911, 846, 759, 701 cm^{-1}; HRMS: *m/z* calcd for $[C_{18}H_{18}O_3+Na]^+$: 305.1154; found: 305.1148.

4-(4-Phenyltetrahydro-2-furanyl)pyridine (11p/12p): Yield: 83%, **11p/12p** = 69:31, $R_f=0.36$ (EtOAc/CH_2Cl_2/pentane = 2:1:1). ^{1}H NMR (300 MHz, $CDCl_3$): *cis* isomer, **11p**: $\delta=8.50$ (d, $J=5.9$ Hz, 2H), 7.27–7.11 (m, 7H), 5.00 (dd, $J=9.9$, 6.1 Hz, 1H), 4.30 (t, $J=8.2$ Hz, 1H), 3.91 (t, $J=8.6$ Hz, 1H), 3.66–3.50 (m, 1H), 2.82–2.68 (m, 1H), 1.85 ppm (dt, $J=$ 12.3, 10.4 Hz, 1H); further signals for the *trans* isomer, **12p**: $\delta=5.14$ (dd, $J=7.9$, 5.5 Hz, 1H), 4.37 (t, $J=7.9$ Hz, 1H), 3.90 (t, $J=8.2$ Hz, 1H), 3.47–3.32 (m, 1H), 2.45 (dt, $J=12.5$, 8.0 Hz, 2H), 2.26–2.10 ppm (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): *cis* isomer, **11p**: $\delta=151.8$, 149.8, 140.8, 128.64, 127.11, 126.8, 120.37, 80.0, 75.1, 45.8, 43.0 ppm; further signals for the *trans* isomer, **12p**: $\delta=152.6$, 149.7, 141.2, 128.67, 127.18, 120.33, 78.9, 44.0, 42.1 ppm; IR (film): $\tilde{\nu}=2971$, 1602, 1495, 1411, 1064, 992, 822, 759, 701 cm^{-1}; HRMS: *m/z* calcd for $[C_{15}H_{15}NO_3+H]^+$: 226.1230; found: 226.1226.

2-(4-Phenyltetrahydro-2-furanyl)pyridine (11q/12q): Yield: 80%, **11q/12q** = 66:34, $R_f=0.25$ (EtOAc/CH_2Cl_2/pentane = 2:2:5). ^{1}H NMR (300 MHz, $CDCl_3$): *cis* isomer, **11q**: $\delta=8.57$–8.43 (m, 1H), 7.58 (dt, $J=$ 7.7, 1.7 Hz, 1H), 7.42 (t, $J=7.6$ Hz, 1H), 7.27–7.02 (m, 6H), 5.10 (dd, $J=$ 9.6, 6.4 Hz, 1H), 4.28 (t, $J=8.1$ Hz, 1H), 3.90 (t, $J=8.6$ Hz, 1H), 3.68–3.46 (m, 1H), 2.88–2.73 (m, 1H), 2.12–1.97 ppm (m, 1H); further signals for the *trans* isomer, **12q**: $\delta=5.22$ (t, $J=6.5$ Hz, 1H), 4.37 (t, $J=7.8$ Hz, 1H), 3.86 (t, $J=8.3$ Hz, 1H), 3.77 (quin, $J=8.1$ Hz, 1H), 2.46 ppm (dd, $J=8.2$, 6.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): *cis* isomer, **11q**: $\delta=$ 162.2, 148.9, 141.0, 136.5, 128.41, 127.1, 126.5, 122.0, 119.5, 82.1, 75.0, 45.7, 41.5 ppm; further signals for the *trans* isomer, **12q**: $\delta=162.6$, 149.0, 141.4, 136.4, 128.46, 126.4, 121.9, 119.8, 81.3, 75.1, 43.8, 40.6 ppm; IR (film): $\tilde{\nu}=2867$, 1590, 1472, 1435, 1079, 1048, 993, 757, 700 cm^{-1}; HRMS: *m/z* calcd for $[C_{15}H_{15}NO_3+H]^+$: 226.1230; found: 226.1226.

3,5-Diphenylperhydrofuro[2,3-*c*]pyrrole-4,6-dione (11r): Yield: 69%, $R_f=0.34$ (EtOAc/pentane = 1:4), m.p. 166–168 °C. ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=7.53$–7.48 (m, 2H), 7.43–7.29 (m, 8H), 5.08 (d, $J=7.4$ Hz, 1H), 4.23–4.18 (m, 2H), 3.88–3.84 (m, 1H), 3.60 ppm (dd, $J=3.0$, 7.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=175.0$, 173.1, 140.9, 131.3, 129.2, 129.1, 128.9, 127.5, 126.8, 126.2, 77.9, 74.5, 49.0, 53.2 ppm; IR (KBr): $\tilde{\nu}=$ 3059, 2878, 1710, 1492, 1382, 1200, 1086, 840, 731 cm^{-1}; HRMS: *m/z* calcd for $[C_{18}H_{15}NO_3+Na]^+$: 316.0950; found: 316.0944.

2-Methyl-4-phenyl-2-vinyltetrahydrofuran (main product) (14a+15a) and 2-Isopropenyl-4-phenyltetrahydrofuran (minor product) (16a+17a): Yield: 64%, **14a/15a/16a/17a** = 58:23:11:8, $R_f=0.36$, (CH_2Cl_2/pentane = 1:2). ^{1}H NMR (600 MHz, $CDCl_3$): *cis* isomer, **14a**: $\delta=7.26$–7.10 (m, 5H), 5.96 (dd, $J=17.3$, 10.7 Hz, 1H), 5.18 (dd, $J=17.4$, 1.2 Hz, 1H), 4.96 (dd, $J=10.7$, 1.2 Hz, 1H), 4.17 (t, $J=8.0$ Hz, 1H), 3.52–3.44 (m, 1H), 2.16 (dd, $J=12.5$, 8.3 Hz, 1H), 1.96 (dd, $J=12.2$, 10.7 Hz, 1H), 1.30 ppm (s, 3H); further signals for the *trans* isomer, **15a**: $\delta=5.83$ (dd, $J=17.2$, 10.6 Hz, 1H), 5.20 (dd, $J=17.2$, 1.3 Hz, 1H), 4.99 (dd, $J=10.6$, 1.4 Hz, 1H), 3.77 (t, $J=8.6$ Hz, 1H), 3.44–3.33 (m, 1H), 2.24 (dd, $J=12.2$, 7.3 Hz, 1H), 1.82 (t, $J=11.7$ Hz, 1H), 1.34 ppm (s, 3H); further signals for the *cis* isomer, **16a**: $\delta=4.99$ (brs, 1H), 4.76 (brs, 1H), 4.38 (dd, $J=$ 10.0, 6.8 Hz, 1H), 4.15 (dd, $J=11.9$, 8.3 Hz, 1H), 3.75–3.71 (m, 1H), 2.42–2.36 (m, 1H), 1.80–1.73 (m, 1H), 1.69 ppm (s, 3H); further signals for the *trans* isomer, **17a**: $\delta=4.47$ (t, $J=6.9$ Hz, 1H), 4.21 (dd, $J=8.4$, 7.3 Hz, 1H), 2.11–2.06 (m, 2H), 1.66 ppm (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): *cis* isomer, **14a**: $\delta=144.1$, 141.1, 128.4, 127.3, 126.5, 111.2, 83.13, 74.04, 45.7, 45.4, 26.7 ppm; further signals for the *trans* isomer, **15a**: $\delta=$ 143.4, 141.5, 127.2, 126.4, 111.8, 83.5, 74.02, 45.8, 44.5, 26.9 ppm; further signals for the *cis* isomer, **16a**: $\delta=145.2$, 141.6, 128.5, 127.1, 110.17, 83.10, 74.6, 45.6, 39.9, 18.0 ppm; further signals for the *trans* isomer, **17a**: $\delta=$ 145.6, 142.1, 110.10, 81.1, 74.7, 44.4, 38.8, 18.2 ppm; IR (film): $\tilde{\nu}=2970$, 2864, 1495, 1452, 1047, 993, 921, 756, 699, 528 cm^{-1}; HRMS: *m/z* calcd for $[C_{13}H_{16}O]^+$: 188.1201; found: 188.1197.

2-(4-Methyl-3-pentenyl)-4-phenyl-2-vinyltetrahydrofuran (main product, 14b/15b): Yield: 59%, **14b/15b** = 65:35, $R_f=0.22$ (CH_2Cl_2/pentane = 1:4). ^{1}H NMR (500 MHz, $CDCl_3$): *cis* isomer, **14b**: $\delta=7.24$–7.17 (m, 2H), 7.16–7.09 (m, 3H), 5.85 (dd, $J=17.3$, 10.8 Hz, 1H), 5.20 (dd, $J=17.3$, 1.6 Hz, 1H), 5.07–5.03 (m, 1H), 5.01 (dd, $J=10.8$, 1.6 Hz, 1H), 4.14 (t, $J=7.9$ Hz, 1H), 3.65 (dd, $J=9.8$, 8.6 Hz, 1H), 3.45–3.37 (m, 1H), 2.22 (dd, $J=12.6$, 8.7 Hz, 1H), 2.05–1.93 (m, 2H), 1.93 (dd, $J=12.6$, 10.2 Hz, 1H), 1.66–1.56 (m, 5H), 1.53 ppm (s, 3H); further signals for the *trans* isomer, **15b**: $\delta=5.75$ (dd, $J=17.2$, 10.6 Hz, 1H), 5.22 (dd, $J=17.2$, 1.8 Hz, 1H), 5.06 (dd, $J=10.7$, 1.8 Hz, 1H), 4.17 (t, $J=8.1$ Hz, 1H), 3.74 (t, $J=8.8$ Hz, 1H), 3.37–3.31 (m, 1H), 2.17 (dd, $J=12.6$, 7.2 Hz, 1H), 1.84 (t, $J=11.7$ Hz, 1H), 1.55–1.48 ppm (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): *cis* isomer, **14b**: $\delta=142.8$, 141.2, 131.43, 128.46, 127.4, 126.5, 124.3, 111.7, 85.6, 73.9, 45.6, 44.5, 40.5, 25.6, 22.8, 17.6 ppm; further signals for the *trans* isomer, **15b**: $\delta=142.3$, 141.5, 131.40, 128.48, 127.2, 112.9, 86.1, 74.0, 44.2, 44.0, 40.4, 23.1 ppm; IR (film): $\tilde{\nu}=2925$, 1451, 1048, 922, 756, 699 cm^{-1}; HRMS: *m/z* calcd for $[C_{18}H_{24}O]^+$: 256.1827; found: 256.1829.

2-(5-Methyl-1-methylene-4-hexenyl)-4-phenyltetrahydrofuran (minor product, 16b/17b): Yield: 18%, **16b/17b** = 90:10, $R_f=0.13$ (CH_2Cl_2/pentane = 1:4). ^{1}H NMR (500 MHz, $CDCl_3$): *cis* isomer, **16b**: $\delta=7.36$–7.31 (m, 2H), 7.30–7.22 (m, 3H), 5.21–5.15 (m, 2H), 4.89 (brs, 1H), 4.51 (dd, $J=10.1$, 5.9 Hz, 1H), 4.25 (t, $J=8.1$ Hz, 1H), 3.86 (t, $J=8.6$ Hz, 1H), 3.57–3.50 (m, 1H), 2.56–2.50 (m, 1H), 2.27–2.02 (m, 4H), 1.88 (dt, $J=$ 12.6, 10.2 Hz, 1H), 1.71 (s, 3H), 1.64 ppm (s, 3H); further signals for the *trans* isomer, **17b**: $\delta=5.14$ (brs, 1H), 4.61 (t, $J=6.9$ Hz, 1H), 4.33 (dd, $J=8.4$, 7.3 Hz, 1H), 3.83 (t, $J=8.2$ Hz, 1H), 3.50–3.43 (m, 1H), 1.62 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): *cis* isomer, **16b**: $\delta=149.3$, 141.7, 131.76, 128.5, 127.24, 126.57, 124.07, 108.66, 82.7, 74.5, 45.7, 40.5, 31.9, 26.5, 25.6, 17.7 ppm; further signals for the *trans* isomer, **17b**: $\delta=149.7$, 142.1, 131.79, 127.28, 126.51, 124.04, 108.61, 81.5, 74.7, 44.3, 39.2, 32.0, 26.4 ppm; IR (film): $\tilde{\nu}=2926$, 1452, 1070, 900, 805, 757, 699 cm^{-1}; HRMS: *m/z* calcd for $[C_{18}H_{24}O]^+$: 256.1827; found: 256.1821.

3-Phenyl-3,3a,4,6a-tetrahydro-2*H*-cyclopenta[*b*]furan (19a): Yield: 9%, $R_f=0.30$ (CH_2Cl_2/pentane = 1:1). ^{1}H NMR (500 MHz, $CDCl_3$): $\delta=7.33$–7.28 (m, 2H), 7.24–7.19 (m, 1H), 7.15–7.09 (m, 2H), 5.89 (dt, $J=5.3$, 2.6 Hz, 1H), 5.71 (dq, $J=5.8$, 2.2 Hz, 1H), 5.27 (dt, $J=7.0$, 2.1 Hz, 1H), 4.12 (dd, $J=8.3$, 6.5 Hz, 1H), 3.70 (dd, $J=10.7$, 8.3 Hz, 1H), 3.62–3.52 (m, 1H), 3.27–3.18 (m, 1H), 2.19 (ddt, $J=17.9$, 9.1, 2.2 Hz, 1H), 1.98–1.88 ppm (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta=139.5$, 136.0, 129.4, 128.3, 126.3, 89.0, 67.8, 48.4, 43.3, 34.0 ppm; IR (film): $\tilde{\nu}=2930$, 1496, 1449, 1357, 1062, 1033, 753, 700 cm^{-1}. HRMS: *m/z* calcd for $[C_{13}H_{14}O]^+$: 186.1045; found: 186.1046.

3-Phenyl-3,3a,6,6a-tetrahydro-2*H*-cyclopenta[*b*]furan (20a): Yield: 10%, $R_f=0.40$ (CH_2Cl_2/pentane = 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.30$–7.10 (m, 4H), 7.04 (d, $J=7.5$ Hz, 1H), 5.87–5.80 (m, 1H), 5.73 (dq, $J=$ 5.8, 2.1 Hz, 1H), 5.26–5.17 (m, 1H), 3.96 (dd, $J=8.7$, 6.0 Hz, 1H), 3.67 (dd, $J=8.3$, 6.8 Hz, 1H), 3.92–2.80 (m, 2H), 2.62–2.50 (m, 1H), 2.32–2.20 ppm (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=142.5$, 133.5, 130.8, 128.5, 127.3, 126.5, 89.4, 73.1, 53.9, 48.1, 38.4 ppm; IR (film): $\tilde{\nu}=2926$, 1494, 1356, 1061, 1040, 753, 700 cm^{-1}; HRMS: *m/z* calcd for $[C_{13}H_{14}O]^+$: 186.1045; found: 186.1043.

3-Phenyl-2,3,3a,4,5,7a-hexahydrobenzo[*b*]furan (19b): Yield: 37%, $R_f=$ 0.24 (CH_2Cl_2/pentane = 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.57$–7.38 (m, 5H), 6.18–6.09 (m, 1H), 6.07–5.98 (m, 1H), 4.72–4.65 (m, 1H), 4.48 (t, $J=8.3$ Hz, 1H), 3.99 (t, $J=8.3$ Hz, 1H), 3.36 (q, $J=7.6$ Hz, 1H), 2.64–2.51 (m, 1H), 2.39–2.25 (m, 1H), 2.11–2.07 (m, 1H), 2.06–1.94 (m, 1H), 1.79–1.65 ppm (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=142.3$, 130.3, 128.6, 127.5, 126.8, 126.5, 75.2, 73.9, 49.5, 45.3, 23.3, 22.4 ppm; IR (film): $\tilde{\nu}=2926$, 1494, 1029, 757, 701, 663 cm^{-1}; HRMS: *m/z* calcd for $[C_{14}H_{16}O]^+$: 200.1201; found: 200.1199.

3-Phenyl-2,3,3a,6,7,7a-hexahydrobenzo[*b*]furan (20b): Yield: 29%, $R_f=$ 0.14 (CH_2Cl_2/pentane = 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.52$–7.33 (m, 5H), 6.23–6.15 (m, 1H), 6.14–6.06 (m, 1H), 4.54–4.46 (m, 1H), 4.44–

4.31 (m, 2H), 4.03–3.90 (m, 1H), 2.58–2.44 (m, 1H), 2.25–2.12 (m, 1H), 2.07–1.89 (m, 1H), 1.38–1.25 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.1, 132.2, 128.3, 128.2, 126.4, 125.5, 75.3, 69.2, 48.6, 41.8, 24.5, 20.0 ppm; IR (film): $\tilde{\nu}$ = 2926, 1494, 1060, 1027, 764, 700 cm^{-1}; HRMS: *m*/*z* calcd for $[C_{14}H_{16}O]^+$: 200.1201; found: 200.1204.

3,6a-Diphenylperhydrocyclopenta[*b*]furan (19c/20c): Yield: 51%, **19c**/**20c** = 65:35, R_f = 0.30 (CH_2Cl_2/pentane = 1:2). The products could be enriched by column chromatography. Analytical data for the main diastereomer, **19c**: m.p. 70–73 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.43 (d, *J* = 7.9 Hz, 2H), 7.34 (t, *J* = 7.8 Hz, 2H), 7.26–7.19 (m, 3H), 7.16 (t, *J* = 7.3 Hz, 1H), 7.07 (d, *J* = 7.02 Hz, 2H), 4.22 (t, *J* = 8.1 Hz, 1H), 3.61 (dd, *J* = 10.8, 7.5 Hz, 1H), 3.09 (dt, *J* = 10.8, 7.5 Hz, 1H), 2.85 (t, *J* = 7.4 Hz, 1H), 2.24–2.16 (m, 1H), 2.05–1.91 (m, 2H), 1.90–1.80 (m, 2H), 1.74–1.64 ppm (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 147.2, 140.9, 128.5, 128.3, 127.6, 126.5, 126.3, 124.6, 96.1, 73.7, 60.6, 55.4, 44.8, 34.2, 25.0 ppm; IR (film): $\tilde{\nu}$ = 2951, 1600, 1490, 1444, 1043, 756, 701 cm^{-1}; HRMS: *m*/*z* calcd for $[C_{19}H_{20}O]^+$: 264.1514; found: 264.1517. Analytical data for the minor diastereomer, **20c**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.50 (d, *J* = 7.5 Hz, 2H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.32–7.17 (m, 4H), 7.13 (d, *J* = 7.5 Hz, 2H), 4.40 (t, *J* = 7.9 Hz, 1H), 4.23 (dd, *J* = 10.1, 8.2 Hz, 1H), 3.65–3.57 (m, 1H), 3.05–2.95 (m, 1H), 2.23–2.16 (m, 1H), 2.14–2.06 (m, 1H), 1.90–1.67 (m, 3H), 1.55–1.47 ppm (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 146.6, 139.5, 128.2, 128.07, 128.06, 126.4, 126.2, 124.9, 96.4, 71.0, 55.9, 46.7, 43.6, 27.5, 26.6 ppm; IR (film): $\tilde{\nu}$ = 2955, 2868, 1600, 1494, 1446, 1047, 758, 700 cm^{-1}; HRMS: *m*/*z* calcd for $[C_{19}H_{20}O]^+$: 264.1514; found: 264.1518.

3-Phenyl-3,3a,4,8b-tetrahydro-2*H*-indeno[1,2-*b*]furan (19d/20d): Yield: 20%, **19d**/**20d** = 50:50, R_f = 0.31 (CH_2Cl_2/pentane = 1:1). ^{1}H NMR (500 MHz, $CDCl_3$): diastereomer **19d**: δ = 7.42–7.36 (m, 1H), 7.30–7.12 (m, 6H), 7.04–6.97 (m, 2H), 5.58 (d, *J* = 6.8 Hz, 1H), 4.17–4.09 (m, 1H), 3.70–3.61 (m, 2H), 3.46–3.37 (m, 1H), 2.72 (dd, *J* = 17.4, 9.4 Hz, 1H), 2.50 ppm (dd, *J* = 17.3, 4.7 Hz, 1H); further signals for **20d**: δ = 5.61 (d, *J* = 7.2 Hz, 1H), 4.02 (dd, *J* = 8.6, 6.8 Hz, 1H), 3.82 (dd, *J* = 8.3, 7.8 Hz, 1H), 3.16–3.06 (m, 2H), 3.00–2.93 (m, 1H), 2.90–2.81 ppm (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): diastereomer **19d**: δ = 143.9, 141.8, 139.0, 128.7, 128.36, 128.32, 126.9, 126.4, 125.51, 124.3, 87.9, 69.4, 48.5, 45.5, 33.2 ppm; further signals for **20d**: δ = 142.4, 141.9, 141.7, 128.6, 127.4, 127.1, 126.7, 125.54, 87.7, 74.5, 53.3, 50.0, 36.5 ppm; IR (film): $\tilde{\nu}$ = 2943, 1060, 1036, 751, 699 cm^{-1}; HRMS: *m*/*z* calcd for $[C_{17}H_{16}O]^+$: 236.1201; found: 236.1204.

Methyl 2,4-diphenyltetrahydro-3-furancarboxylate (24a/25a): Yield: 54%, **24a**/**25a** = 50:50, R_f = 0.70 (EtOAc/CH_2Cl_2/pentane = 1:2:10). ^{1}H NMR (500 MHz, $CDCl_3$): *trans*:*trans* isomer, **24a**: δ = 7.37–7.12 (m, 10H), 5.11 (d, *J* = 8.8 Hz, 1H), 4.34 (t, *J* = 8.5 Hz, 1H), 4.09 (dd, *J* = 8.7, 7.4 Hz, 1H), 3.75–3.69 (m, 4H), 3.88–3.81 (m, 1H), 3.55 (s, 3H), 3.07 ppm (dd, *J* = 11.0, 6.8 Hz, 1H); further signals for the *trans*:*cis* isomer, **25a**: δ = 5.38 (d, *J* = 7.8 Hz, 1H), 4.44 (dd, *J* = 8.8, 6.6 Hz, 1H), 4.26 (dd, *J* = 8.8, 6.1 Hz, 1H), 3.81–3.77 (m, 1H), 3.07 (dd, *J* = 9.1, 7.9 Hz, 1H), 3.23 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): *trans*:*trans* isomer, **24a**: δ = 172.8, 140.5, 140.4, 128.7, 128.5, 127.9, 127.2, 127.1, 125.8, 84.6, 75.0, 60.9, 52.0, 50.7 ppm; further signals for the *trans*:*cis* isomer, **25a**: δ = 172.8, 141.6, 138.4, 128.4, 128.3, 128.1, 127.6, 125.7, 81.7, 73.8, 58.6, 51.3, 48.8 ppm; IR (film): $\tilde{\nu}$ = 2950, 1733, 1494, 1454, 1435, 1063, 756, 699 cm^{-1}; HRMS: *m*/*z* calcd for $[C_{18}H_{18}O_3+H]^+$: 283.1333; found: 283.1329.

Dimethyl 4-phenyltetrahydro-2,3-furandicarboxylate (24b/25b/26b): Yield: 55%, **24b**/**25b**/**26b** = 42:33:25. The products could be enriched by column chromatography. Analytical data for the *trans*:*trans* isomer, **24b**: R_f = 0.32 (EtOAc/CH_2Cl_2/pentane = 1:2:10). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.28–7.15 (m, 5H), 4.76 (d, *J* = 7.1 Hz, 1H), 4.27 (t, *J* = 8.3 Hz, 1H), 3.96 (t, *J* = 9.1 Hz, 1H), 3.73 (s, 3H), 3.70–3.63 (m, 1H), 3.62 (s, 3H), 3.32 ppm (dd, *J* = 9.1, 7.2 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ = 172.1, 171.1, 138.1, 128.8, 127.46, 127.42, 80.1, 75.6, 55.6, 52.4, 50.0 ppm; IR (film): $\tilde{\nu}$ = 2954, 1738, 1437, 1223, 1105, 759, 701 cm^{-1}; HRMS: *m*/*z* calcd for $[C_{14}H_{16}O_5+Na]^+$: 287.0896; found: 287.0890. Analytical data for the *trans*:*cis*, **25b**, and *cis*:*trans*, **26b**, isomers: R_f = 0.23 (EtOAc/CH_2Cl_2/pentane = 1:2:10). ^{1}H NMR (600 MHz, $CDCl_3$): *trans*:*cis* isomer, **25b**: δ = 7.32–7.12 (m, 5H), 4.96 (d, *J* = 6.3 Hz, 1H), 4.28 (dd, *J* = 8.6, 6.4 Hz, 1H), 4.20 (dd, *J* = 8.7, 5.1 Hz, 1H), 3.75–3.69 (m, 4H), 3.62–3.57 (m, 1H), 3.25 ppm (s, 3H); further signals for the *cis*:*trans* isomer, **26b**: δ = 4.81 (d, *J* = 8.5 Hz, 1H), 4.51 (t, *J* = 8.2 Hz, 1H), 3.90 (t, *J* = 8.2 Hz, 1H), 3.83 (dd, *J* = 16.7, 8.3 Hz, 1H), 3.67 (s, 3H), 3.57 (s, 3H), 3.45 ppm (dd, *J* = 11.7, 5.7 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): *trans*:*cis* isomer, **25b**: δ = 172.0, 170.3, 137.7, 128.3, 127.8, 127.38, 78.1, 74.2, 53.8, 52.4, 51.7, 48.2 ppm; further signals for the *cis*:*trans* isomer, **26b**: δ = 170.7, 170.6, 139.0, 128.8, 127.31, 127.2, 79.0, 75.5, 55.3, 52.2, 52.1, 47.4 ppm; IR (film): $\tilde{\nu}$ = 2953, 1738, 1437, 1213, 1106, 759, 701 cm^{-1}; HRMS: *m*/*z* calcd for $[C_{14}H_{16}O_5+Na]^+$: 287.0896; found: 287.0890.

Methyl 2-oxo-5-phenyltetrahydro-2*H*-4-pyrancarboxylate (28b): Yield: 10%, R_f = 0.14 (EtOAc/CH_2Cl_2/pentane = 1:2:10). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.34–7.30 (m, 2H), 7.28–7.24 (m, 1H), 7.22–7.19 (m, 2H), 4.54 (t, *J* = 8.8 Hz, 1H), 4.14 (dd, *J* = 9.2, 10.4 Hz, 1H), 3.59–3.51 (m, 1H), 3.49 (s, 3H), 3.11–3.05 (m, 1H), 2.67 (dd, *J* = 16.7, 5.3 Hz, 1H), 2.59 ppm (dd, *J* = 16.7, 6.3 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 176.6, 171.0, 136.9, 129.1, 128.0, 127.4, 72.1, 51.8, 47.1, 43.4, 32.5 ppm; IR (film): $\tilde{\nu}$ = 2952, 1775, 1737, 1207, 1177, 1017, 761, 702 cm^{-1}; HRMS: *m*/*z* calcd for $[C_{13}H_{14}O_4+Na]^+$: 287.0790; found: 287.0784.

Diethyl 4-phenyltetrahydro-2,3-furandicarboxylate (24c/25c/26c): Yield: 46%, **24b**/**25b**/**26b** = 40:51:9, R_f = 0.28 (EtOAc/pentane = 1:15). ^{1}H NMR (500 MHz, $CDCl_3$): *trans*:*cis* isomer, **25c**: δ = 7.30–7.12 (m, 5H), 4.95 (d, *J* = 6.3 Hz, 1H), 4.32–4.26 (m, 1H), 4.25–4.15 (m, 3H), 3.78–3.69 (m, 3H), 3.57 (dd, *J* = 8.9, 6.3 Hz, 1H), 1.23 (t, *J* = 7.1 Hz, 3H), 0.81 ppm (t, *J* = 7.1 Hz, 3H); further signals for the *trans*:*trans* isomer, **24c**: δ = 4.74 (d, *J* = 7.4 Hz, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.98 (t, *J* = 9.1 Hz, 1H), 3.69–3.62 (m, 3H), 3.27 (dd, *J* = 9.0, 7.5 Hz, 1H), 1.12 ppm (t, *J* = 7.1 Hz, 3H); further signals for the *cis*:*trans* isomer, **26c**: δ = 4.79 (d, *J* = 6.3 Hz, 1H), 4.52 (t, *J* = 8.2 Hz, 1H), 3.91 (t, *J* = 8.1 Hz, 1H), 3.88–3.82 (m, 1H), 3.42 ppm (t, *J* = 8.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): *trans*:*cis* isomer, **25c**: δ = 171.7, 169.9, 137.9, 128.4, 128.3, 127.35, 78.4, 74.2, 61.4, 60.8, 53.8, 48.1, 14.1, 13.6 ppm; further signals for the *trans*:*trans* isomer, **24c**: δ = 171.6, 171.3, 138.2, 128.7, 127.4, 127.39, 80.2, 75.5, 61.3, 55.9, 50.0, 14.0 ppm; further signals for the *cis*:*trans* isomer, **26c**: δ = 174.3, 79.1, 75.3, 55.4, 47.5 ppm; IR (film): $\tilde{\nu}$ = 2981, 1734, 1373, 1213, 1103, 1029, 758, 701 cm^{-1}; HRMS: *m*/*z* calcd for $[C_{16}H_{20}O_5+Na]^+$: 315.1208; found: 315.1203.

Ethyl 2-oxo-5-phenyltetrahydro-2*H*-4-pyrancarboxylate (28c): Yield: 31%, R_f = 0.21 (EtOAc/pentane = 1:15). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.33–7.10 (m, 5H), 4.52 (t, *J* = 8.7 Hz, 1H), 4.11 (t, *J* = 9.8 Hz, 1H), 3.98–3.86 (m, 2H), 3.56–3.50 (m, 1H), 3.09–3.03 (m, 1H), 2.65 (dd, *J* = 16.7, 5.2 Hz, 1H), 2.56 (dd, *J* = 16.7, 6.3 Hz, 1H), 1.08 ppm (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 176.7, 170.5, 137.0, 129.1, 128.0, 127.3, 72.0, 60.8, 47.1, 43.4, 32.8, 13.9 ppm; IR (film): $\tilde{\nu}$ = 2978, 1776, 1733, 1375, 1183, 1106, 1021, 760, 701 cm^{-1}; HRMS: *m*/*z* calcd for $[C_{14}H_{16}O_4+Na]^+$: 271.0946; found: 271.0941.

Diisobutyl 4-phenyltetrahydro-2,3-furandicarboxylate (24d/25d): Yield: 33%, **24d**/**25d** = 47:53, R_f = 0.41 (EtOAc/CH_2Cl_2/pentane = 1:1:15). ^{1}H NMR (500 MHz, $CDCl_3$): *trans*:*cis* isomer, **25d**: δ = 7.27–7.12 (m, 5H), 4.96 (d, *J* = 6.6 Hz, 1H), 4.29 (dd, *J* = 9.0, 5.9 Hz, 1H), 4.20 (dd, *J* = 8.7, 5.2 Hz, 1H), 3.75–3.69 (m, 4H), 3.95–3.87 (m, 2H), 3.76–3.70 (m, 1H), 3.58 (dd, *J* = 8.8, 6.6 Hz, 1H), 3.51 (dd, *J* = 10.6, 6.6 Hz, 1H), 3.32 (dd, *J* = 10.6, 6.5 Hz, 1H), 1.89 (hept, *J* = 6.7 Hz, 1H), 1.52 (hept, *J* = 6.7 Hz, 1H), 0.87 (d, *J* = 6.7 Hz, 6H), 0.66 (d, *J* = 6.8 Hz, 3H), 0.64 ppm (d, *J* = 7.0 Hz, 3H); further signals for the *trans*:*trans* isomer, **24d**: δ = 4.78 (d, *J* = 7.5 Hz, 1H), 4.28 (t, *J* = 8.2 Hz, 1H), 3.98 (t, *J* = 9.13 Hz, 1H), 3.85 (dd, *J* = 10.6, 6.6 Hz, 1H), 3.76 (dd, *J* = 10.6, 6.5 Hz, 1H), 3.69–3.62 (m, 1H), 3.58 (dd, *J* = 8.9, 7.1 Hz, 1H), 1.76 (hept, *J* = 6.7 Hz, 1H), 0.85 (d, 6H, *J* = 6.7 Hz, 6H), 0.74 (d, *J* = 6.7 Hz, 3H), 0.73 ppm (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): *trans*:*cis* isomer, **25d**: δ = 171.64, 169.9, 137.8, 128.4, 127.9, 127.34, 78.4, 74.3, 71.33, 71.0, 54.0, 48.2, 27.64, 27.2, 18.88, 18.82 ppm; further signals for the *trans*:*trans* isomer, **24d**: δ = 171.69, 171.3, 138.0, 128.7, 127.4, 127.37, 80.0, 75.6, 71.31, 71.2, 56.0, 50.2, 27.62, 27.5, 18.78, 18.72 ppm; IR (film): $\tilde{\nu}$ = 2962, 1736, 1470, 1270, 1213, 1105, 1009, 758, 700 cm^{-1}; HRMS: *m*/*z* calcd for $[C_{20}H_{28}O_5+H]^+$: 349.2017; found: 349.2010.

Isobutyl 2-oxo-5-phenyltetrahydro-2*H*-4-pyrancarboxylate (28d/29d): Yield: 9%, **28d**/**29d** = 85:15, R_f = 0.12 (EtOAc/CH_2Cl_2/pentane = 1:1:15).

^{1}H NMR (500 MHz, $CDCl_3$): *trans* isomer, **28d**: δ = 7.30 (t, J = 7.4 Hz, 2H), 7.24 (t, J = 7.1 Hz, 1H), 7.19 (d, J = 7.1 Hz, 2H), 4.53 (t, J = 8.7 Hz, 1H), 4.12 (dd, J = 10.0, 9.5 Hz, 1H), 3.70 (dd, J = 10.6, 6.7 Hz, 1H), 3.66 (dd, J = 10.6, 6.7 Hz, 1H), 3.59–3.51 (m, 1H), 3.05 (dt, J = 11.5, 5.6 Hz, 1H), 2.67 (dd, J = 16.7, 5.2 Hz, 1H), 2.60 (dd, J = 16.7, 6.1 Hz, 1H), 1.76 (hept, J = 6.7 Hz, 1H), 0.81 ppm (d, 6H, J = 6.7 Hz); further signals for the *cis* isomer, **29d**: δ = 4.60 (dd, J = 9.5, 6.1 Hz, 1H), 3.82 (dd, J = 8.1, 6.3 Hz, 1H), 3.80–3.72 (m, 2H), 3.37 ppm (ddd, J = 10.4, 8.7, 3.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): *trans* isomer, **28d**: δ = 176.7, 170.6, 137.0, 129.1, 128.0, 127.4, 72.1, 71.0, 47.1, 43.4, 32.7, 27.5, 18.9 ppm; IR (film): $\tilde{\nu}$ = 2962, 1774, 1728, 1470, 761, 702 cm^{-1}; HRMS: m/z calcd for $[C_{16}H_{20}O_4+Na]^+$: 299.1252; found: 299.1254.

4-(4-Fluorophenyl)-2-phenyltetrahydrofuran (32a/33a): Yield: 72%, **32a/33a** = 69:31, R_f = 0.24 (CH_2Cl_2/pentane = 1:2). ^{1}H NMR (300 MHz, $CDCl_3$): *cis* isomer, **32a**: δ = 7.31–7.19 (m, 4H), 7.18–7.03 (m, 3H), 6.92–6.80 (m, 2H), 4.92 (dd, J = 10.1, 5.8 Hz, 1H), 4.19 (t, J = 8.2 Hz, 1H), 3.83 (t, J = 8.4 Hz, 1H), 3.55–3.41 (m, 1H), 2.60 (ddd, J = 12.8, 7.2, 5.9 Hz, 1H), 1.81 ppm (dt, J = 12.4, 10.4 Hz, 1H); further signals for the *trans* isomer, **33a**: δ = 5.08 (dd, J = 7.7, 5.9 Hz, 1H), 4.30 (dd, J = 8.4, 7.4 Hz, 1H), 3.76 (t, J = 8.2 Hz, 1H), 3.41–3.30 (m, 1H), 2.35–2.12 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): *cis* isomer, **32a**: δ = 161.6 (d, J = 242.8 Hz), 142.4, 137.4 (d, J = 3.3 Hz), 128.5 (d, J = 7.8 Hz), 128.39, 127.3, 125.5, 115.3 (d, J = 21.3 Hz), 81.6, 74.9, 45.1, 43.7 ppm; further signals for the *trans* isomer, **33a**: δ = 143.4, 137.6 (d, J = 3.3 Hz), 128.7 (d, J = 7.8 Hz), 128.33, 127.1, 125.4, 80.4, 43.6, 42.6 ppm; ^{19}F NMR (282 MHz, $CDCl_3$): *cis* isomer, **32a**: δ = −116.2 ppm; further signal for the *trans* isomer, **33a**: δ = −116.3 ppm; IR (film): $\tilde{\nu}$ = 2938, 1604, 1511, 1224, 1050, 832, 757, 699 cm^{-1}; HRMS: m/z calcd for $[C_{16}H_{15}FO]^+$: 242.1107; found: 242.1105.

4-(4-Fluorophenyl)-2-(4-methoxyphenyl)tetrahydrofuran (32b/33b): Yield: 70%, **32b/33b** = 70:30, R_f = 0.31 (CH_2Cl_2/pentane = 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): *cis* isomer, **32b**: δ = 7.14 (d, J = 8.8 Hz, 2H), 7.09–7.00 (m, 2H), 6.87–6.76 (m, 2H), 6.71 (d, J = 8.7 Hz, 2H), 4.81 (dd, J = 10.1, 5.6 Hz, 1H), 4.11 (t, J = 8.2 Hz, 1H), 3.77 (t, J = 8.3 Hz, 1H), 3.48–3.36 (m, 1H), 2.50 (ddd, J = 12.7, 7.3, 5.7 Hz, 1H), 1.74 ppm (dt, J = 12.4, 10.4 Hz, 1H); further signals for the *trans* isomer, **33b**: δ = 7.11 (d, J = 8.8 Hz, 2H), 4.97 (t, J = 6.9 Hz, 1H), 4.23 (dd, J = 8.2, 7.4 Hz, 1H), 3.67 (t, J = 8.1 Hz, 1H), 3.36–3.26 (m, 1H), 2.26–2.05 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): *cis* isomer, **32b**: δ = 161.5 (d, J = 243.3 Hz), 159.0, 137.7 (d, J = 2.7 Hz), 134.3, 128.5 (d, J = 7.3 Hz), 127.0, 115.3 (d, J = 21.3 Hz), 113.8, 81.4, 74.8, 55.1, 45.1, 43.71 ppm; further signals for the *trans* isomer, **33b**: δ = 158.8, 137.8 (d, J = 3.3 Hz), 135.3, 128.6 (d, J = 7.7 Hz), 126.7, 113.7, 80.2, 74.9, 43.79, 42.6 ppm; ^{19}F NMR (282 MHz, $CDCl_3$): *cis* isomer, **32b**: δ = −116.3 ppm; further signal for the *trans* isomer, **33b**: δ = −116.4 ppm. IR (film): $\tilde{\nu}$ = 2936, 1612, 1511, 1302, 1247, 1174, 1036, 830, 534 cm^{-1}; HRMS: m/z calcd for $[C_{17}H_{17}FO_2]^+$: 272.1213; found: 272.1215.

2-(3,4-Dimethoxyphenyl)-4-(4-fluorophenyl)tetrahydrofuran (32c/33c): Yield: 75%, **32c/33c** = 70:30, R_f = 0.27 (EtOAc/pentane = 1:5). ^{1}H NMR (300 MHz, $CDCl_3$): *cis* isomer, **32c**: δ = 7.22–7.12 (m, 2H), 6.99–6.75 (m, 5H), 4.94 (dd, J = 10.0, 5.7 Hz, 1H), 4.25 (t, J = 8.2 Hz, 1H), 3.90 (t, J = 8.3 Hz, 1H), 3.830 (s, 3H), 3.81 (s, 3H), 3.61–3.50 (m, 1H), 2.65 (ddd, J = 12.8, 7.3, 5.7 Hz, 1H), 1.88 ppm (dt, J = 12.4, 10.3 Hz, 1H); further signals for the *trans* isomer, **33c**: δ = 5.08 (t, J = 6.8 Hz, 1H), 4.36 (dd, J = 8.6, 7.3 Hz, 1H), 3.837 (s, 3H), 3.50–3.38 (m, 1H), 2.40–2.20 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): *cis* isomer, **32c**: δ = 161.6 (d, J = 243.0 Hz), 149.09, 148.4, 137.6 (d, J = 3.5 Hz), 134.9, 128.6 (d, J = 7.5 Hz), 117.9, 115.3 (d, J = 21.2 Hz), 111.1, 109.0, 81.6, 74.8, 55.9, 55.8, 45.1, 43.6 ppm; further signals for the *trans* isomer, **33c**: δ = 149.06, 148.3, 137.8 (d, J = 2.9 Hz), 135.8, 128.7 (d, J = 7.5 Hz), 117.6, 108.9, 80.3, 75.0, 43.8, 42.7 ppm; ^{19}F NMR (282 MHz, $CDCl_3$): *cis* isomer, **32c**: δ = −116.4 ppm; further signal for the *trans* isomer, **33c**: δ = −116.3 ppm; IR (film): $\tilde{\nu}$ = 2936, 1604, 1512, 1464, 1263, 1235, 1159, 1137, 1028, 834, 763, 536 cm^{-1}; HRMS: m/z calcd for $[C_{18}H_{19}FO_3]^+$: 302.1318; found: 302.1318.

4-(4-Chlorophenyl)-2-phenyltetrahydrofuran (32d/33d): Yield: 72%, **32d/33d** = 69:31, R_f = 0.47 (CH_2Cl_2/pentane = 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): *cis* isomer, **32d**: δ = 7.32–7.04 (m, 9H), 4.94 (dd, J = 10.1, 5.8 Hz, 1H), 4.21 (t, J = 8.2 Hz, 1H), 3.86 (t, J = 8.3 Hz, 1H), 3.55–3.44 (m, 1H), 2.63 (ddd, J = 12.9, 7.4, 5.9 Hz, 1H), 1.84 ppm (dt, J = 12.4, 10.3 Hz, 1H); further signals for the *trans* isomer, **33d**: δ = 5.11 (dd, J = 7.6, 6.0 Hz, 1H), 4.33 (dd, J = 8.5, 7.3 Hz, 1H), 3.79 (t, J = 8.1 Hz, 1H), 3.44–3.33 (m, 1H), 2.37–2.15 ppm (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): *cis* isomer, **32d**: δ = 142.3, 140.4, 132.2, 128.6, 128.50, 128.39, 127.4, 125.5, 81.6, 74.8, 45.2, 43.6 ppm; further signals for the *trans* isomer, **33d**: δ = 143.3, 140.5, 128.58, 128.33, 127.1, 125.3, 80.4, 43.8, 42.5 ppm; IR (film): $\tilde{\nu}$ = 2969, 1493, 1091, 1051, 823, 757, 699 cm^{-1}; HRMS: m/z calcd for $[C_{16}H_{15}ClO]^+$: 258.0811; found: 258.0809.

4-(4-Methoxyphenyl)-2-phenyltetrahydrofuran (32e/33e): Yield: 57%, **32e/33e** = 70:30, R_f = 0.39 (EtOAc/pentane = 1:20). ^{1}H NMR (300 MHz, $CDCl_3$): *cis* isomer, **32e**: δ = 7.36–7.24 (m, 4H), 7.23–7.15 (m, 1H), 7.15–7.06 (m, 2H), 6.82–6.73 (m, 2H), 4.98 (dd, J = 10.2, 5.7 Hz, 1H), 4.24 (t, J = 8.2 Hz, 1H), 3.87 (t, J = 8.5 Hz, 1H), 3.69 (s, 3H), 3.58–3.45 (m, 1H), 2.63 (ddd, J = 12.7, 7.1, 5.8 Hz, 1H), 1.90 ppm (dt, J = 12.3, 10.6 Hz, 1H); further signals for the *trans* isomer, **33e**: δ = 5.13 (dd, J = 7.7, 5.8 Hz, 1H), 4.35 (dd, J = 8.3, 7.5 Hz, 1H), 3.81 (t, J = 8.2 Hz, 1H), 3.70 (s, 3H), 3.45–3.34 (m, 1H), 2.34 (dt, J = 12.5, 7.8 Hz, 1H), 2.21 ppm (ddd, J = 12.5, 8.2, 5.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): *cis* isomer, **32e**: δ = 158.34, 142.7, 133.5, 128.37, 128.1, 127.3, 125.6, 114.0, 81.7, 75.16, 55.2, 45.2, 43.7 ppm; further signals for the *trans* isomer, **33e**: δ = 158.31, 143.6, 133.9, 128.31, 128.2, 127.1, 125.4, 80.4, 75.19, 43.5, 42.7 ppm; IR (film): $\tilde{\nu}$ = 2934, 1611, 1514, 1249, 1179, 1037, 828, 757, 700 cm^{-1}; HRMS: m/z calcd for $[C_{17}H_{18}O_2]^+$: 254.1307; found: 254.1317.

4-(4-Fluorophenyl)-2-isopropenyl-2-methyltetrahydrofuran (32f/33f): Yield: 75%, **32f/33f** = 80:20, R_f = 0.34 (CH_2Cl_2/pentane = 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): *cis* isomer, **32f**: δ = 7.23–7.15 (m, 2H), 7.02–6.95 (m, 2H), 5.07 (dd, J = 1.9, 0.8 Hz, 1H), 4.78 (quin, J = 1.6 Hz, 1H), 4.26 (t, J = 7.8 Hz, 1H), 3.70 (dd, J = 10.0, 8.3 Hz, 1H), 3.61–3.48 (m, 1H), 2.26 (dd, J = 12.4, 7.8 Hz, 1H), 2.03 (dd, J = 12.5, 10.6 Hz, 1H), 1.81 (dd, J = 1.3, 0.8 Hz, 1H), 1.39 ppm (s, 3H); further signals for the *trans* isomer, **33f**: δ = 4.85 (quin, J = 1.7 Hz, 1H), 4.21 (t, J = 8.3 Hz, 1H), 3.79 (t, J = 8.6 Hz, 1H), 3.47–3.34 (m, 1H), 2.48 (dd, J = 12.4, 7.3 Hz, 1H), 1.78 (dd, J = 1.4, 0.7 Hz, 1H), 1.45 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): *cis* isomer, **32f**: δ = 161.6 (d, J = 243.7 Hz), 149.9, 136.7 (d, J = 3.6 Hz), 128.7 (d, J = 8.0 Hz), 115.3 (d, J = 21.2 Hz), 108.2, 85.6, 74.1, 45.4, 44.6, 26.7, 19.2 ppm; further signals for the *trans* isomer, **33f**: δ = 161.4 (d, J = 243.6 Hz), 137.4 (d, J = 2.9 Hz), 128.6 (d, J = 8.0 Hz), 109.6, 86.0, 73.6, 44.7, 44.0, 26.4, 19.1 ppm; ^{19}F NMR (282 MHz, $CDCl_3$): *cis* isomer, **32f**: δ = −116.8 ppm; IR (film): $\tilde{\nu}$ = 2972, 1512, 1226, 1160, 1051, 902, 832 cm^{-1}; HRMS: m/z calcd for $[C_{14}H_{17}FO]^+$: 220.1263; found: 220.1259.

4-(4-Chlorophenyl)-2-isopropenyl-2-methyltetrahydrofuran (32g/33g): Yield: 77%, **32g/33g** = 79:21, R_f = 0.35 (CH_2Cl_2/pentane = 1:2). ^{1}H NMR (300 MHz, $CDCl_3$): *cis* isomer, **32g**: δ = 7.17 (d, J = 8.5 Hz, 2H), 7.06 (d, J = 8.4 Hz, 2H), 5.02–4.96 (m, 1H), 4.73–4.66 (m, 1H), 4.17 (t, J = 7.9 Hz, 1H), 3.62 (dd, J = 9.8, 8.4 Hz, 1H), 3.51–3.37 (m, 1H), 2.17 (dd, J = 12.4, 7.9 Hz, 1H), 1.94 (dd, J = 12.3, 10.6 Hz, 1H), 1.77–1.72 (m, 3H), 1.31 ppm (s, 3H); further signals for the *trans* isomer, **33g**: δ = 4.80–4.85 (m, 1H), 4.12 (t, J = 8.2 Hz, 1H), 3.71 (t, J = 8.6 Hz, 1H), 3.37–3.24 (m, 1H), 2.40 (dd, J = 12.3, 7.2 Hz, 1H), 1.72–1.67 (m, 3H), 1.36 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): *cis* isomer, **32g**: δ = 149.8, 139.6, 132.2, 128.6, 128.5, 108.2, 85.6, 73.9, 45.2, 44.7, 26.7, 19.2 ppm; further signals for the *trans* isomer, **33g**: δ = 148.6, 140.3, 132.1, 109.6, 86.4, 73.4, 44.6, 44.1, 26.4, 19.1 ppm; IR (film): $\tilde{\nu}$ = 2927, 1493, 1092, 1050, 1014, 902, 824, 530 cm^{-1}; HRMS: m/z calcd for $[C_{14}H_{17}ClO]^+$: 236.0968; found: 236.0961.

2-Isopropenyl-4-(4-methoxyphenyl)-2-methyltetrahydrofuran (32h/33h): Yield: 59%, **32h/33h** = 81:19, R_f = 0.34 (EtOAc/pentane = 1:20). ^{1}H NMR (300 MHz, $CDCl_3$): *cis* isomer, **32h**: δ = 7.16 (d, J = 8.7 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 5.12–5.08 (m, 1H), 4.83–4.78 (m, 1H), 4.26 (t, J = 7.9 Hz, 1H), 3.79 (s, 3H), 3.72 (dd, J = 10.2, 8.3 Hz, 1H), 3.62–3.46 (m, 1H), 2.25 (dd, J = 12.3, 7.8 Hz, 1H), 2.06 (dd, J = 12.2, 10.9 Hz, 1H), 1.87–1.82 (m, 3H), 1.41 ppm (s, 3H); further signals for the *trans* isomer, **33h**: δ = 4.90–4.85 (m, 1H), 4.22 (t, J = 8.2 Hz, 1H), 3.46–3.33 (m, 1H), 2.47 (dd, J = 12.3, 7.2 Hz, 1H), 1.82–1.79 (m, 3H), 1.47 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): *cis* isomer, **32h**: δ = 158.26, 150.0, 132.8, 128.1, 113.8, 108.0, 85.4, 74.2, 55.1, 45.3, 44.4, 26.7, 19.1 ppm; further signals for the *trans* isomer, **33h**: δ = 158.21, 148.9, 133.5, 128.0, 109.4, 85.8, 73.7, 44.6, 43.8, 26.4 ppm; IR (film): $\tilde{\nu}$ = 2970, 1514, 1443, 1249, 1038, 900, 826 cm^{-1}; HRMS: m/z calcd for $[C_{15}H_{20}O_2]^+$: 232.1463; found: 232.1461.

2-Isopropenyl-2,4-dimethyl-4-phenyltetrahydrofuran (32i/33i): Yield: 46%, **32i/33i** = 62:38, R_f = 0.38 (CH_2Cl_2/pentane = 1:1). ^{1}H NMR (300 MHz, $CDCl_3$): *cis* isomer, **32i**: δ = 7.30–7.08 (m, 5H), 5.10–5.04 (m, 1H), 4.77–4.68 (m, 1H), 4.09 (d, J = 8.5 Hz, 1H), 3.87 (d, J = 8.5 Hz, 1H), 2.24 (d, J = 12.7 Hz, 1H), 2.09 (d, J = 12.5 Hz, 1H), 1.79–1.73 (m, 3H), 1.29 (s, 3H), 1.19 ppm (s, 3H); further signals for the *trans* isomer, **33i**: δ = 4.97–4.93 (m, 1H), 4.64–4.59 (m, 1H), 2.35 (d, J = 12.7 Hz, 1H), 1.94 (d, J = 12.7 Hz, 1H), 1.67–1.63 (m, 3H), 1.43 (s, 3H), 1.41 ppm (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = *cis* isomer, **32i**: δ = 150.3, 148.3, 128.36, 125.97, 125.8, 108.3, 85.3, 77.8, 50.6, 48.0, 28.6, 27.4, 19.6 ppm; further signals for the *trans* isomer, **33i**: δ = 149.6, 148.0, 128.32, 125.94, 107.7, 50.4, 48.3, 29.7, 28.2, 19.0 ppm; IR (film): $\tilde{\nu}$ = 2969, 2869, 1445, 1061, 902, 762, 700 cm^{-1}; HRMS: m/z calcd for $[C_{15}H_{20}O]^+$: 216.1514; found: 216.1513.

[1] For recent references, see: M. B. Hay, A. R. Hardin, J. P. Wolfe, *J. Org. Chem.* **2005**, *70*, 3099; G. Liang, I. B. Seiple, D. Trauner, *Org. Lett.* **2005**, *7*, 2837; C.-G. Yang, N. W. Reich, Z. Shi, C. He, *Org. Lett.* **2005**, *7*, 4553; E. Mertz, J. M. Tinsley, W. R. Roush, *J. Org. Chem.* **2005**, *70*, 8035; C. Shin, S. N. Chavre, A. N. Pae, J. H. Cha, H. Y. Koh, M. H. Chang, J. H. Choi, Y. S. Cho, *Org. Lett.* **2005**, *7*, 3283; C. Huo, X. Jia, W. Zhang, L. Yang, J. Lü, Z. Liu, *Synlett* **2004**, 251; B. M. Trost, H. C. Shen, J.-P. Surivet, *J. Am. Chem. Soc.* **2004**, *126*, 12565; B. Banerjee, S. C. Roy, *Synthesis* **2005**, 2913; J. M. Cuerva, J. Justicia, J. L. Oller-López, J. E. Oltra, *Top. Curr. Chem.* **2006**, *264*, 63; M. Bottex, M. Cavicchioli, B. Hartmann, N. Monteiro, G. Balme, *J. Org. Chem.* **2001**, *66*, 175; M. A. Evans, J. P. Morken, *Org. Lett.* **2005**, *7*, 3371; C. J. Kressierer, T. J. J. Müller, *Org. Lett.* **2005**, *7*, 2237; L. Zhao, X. Lu, W. Xu, *J. Org. Chem.* **2005**, *70*, 4059; H.-Y. Jang, F. W. Hughes, H. Gong, J. Zhang, J. S. Brodbelt, M. J. Krische, *J. Am. Chem. Soc.* **2005**, *127*, 6174; P. A. Evans, K. W. Lai, J. R. Swayer, *J. Am. Chem. Soc.* **2005**, *127*, 12644; V. Nair, S. Mathai, R. L. Varma, *J. Org. Chem.* **2004**, *69*, 1413; G. Zuo, J. Louie, *J. Am. Chem. Soc.* **2005**, *127*, 5798.

[2] For an excellent review on the application of iron catalysts in organic synthesis, see: C. Bolm, J. Legros, J. Le Paih, L. Zotti, *Chem. Rev.* **2004**, *104*, 6217.

[3] G. Hilt, P. Bolze, I. Kieltsch, *Chem. Commun.* **2005**, 1996; G. Hilt, C. Walter, P. Bolze, *Adv. Synth. Catal.* **2006**, *348*, 1241.

[4] For leading references on iron-catalysed polymerization reactions, see: G. A. Luinstra, G. R. Haas, F. Molnar, V. Bernhart, R. Eberhardt, B. Rieger, *Chem. Eur. J.* **2005**, *11*, 6298; M. W. Bouwkamp, E. Lobkovsky, P. J. Chirik, *J. Am. Chem. Soc.* **2005**, *127*, 9660.

[5] C. S. Marvel, S. A. Aspey, E. A. Dudley, *J. Am. Chem. Soc.* **1956**, *78*, 4905.

[6] J. R. Dorfman, J. J. Girerd, E. D. Simhon, T. D. P. Stack, R. H. Holm, *Inorg. Chem.* **1984**, *23*, 4407.

[7] Reagents and conditions: 0.1 M $LiClO_4$ in CH_3CN, glassy carbon working electrode ($\varnothing$ = 3 mm), Pt wire counter-electrode, Ag/AgCl reference electrode, 100 mV s^{-1}.

[8] P. Ghosh, E. Bill, F. Neese, T. Weyhermüller, K. Wieghardt, *J. Am. Chem. Soc.* **2003**, *125*, 1293; S. Ciurli, E. M. Meyer, C. Floriani, A. Chiesi-Villa, C. Guastini, *J. Chem. Soc., Chem. Commun.* **1987**, 281; P. S. Braterman, J. I. Song, R. D. Peacock, *Inorg. Chem.* **1992**, *31*, 555.

[9] The π orbitals of the ligand-centered LUMO overlaps with the free electron pair of the axially bonded epoxide through two of the three d_π orbitals (d_{xz} and d_{yz}) of the iron center. Electron transfer takes place in this way.

[10] The alkene/epoxide ratio was 3–4:1 for most of the starting materials. Only in the case of cyclopentadiene was a fivefold excess used.

[11] J. L. K. F. de Vries, J. M. Trooster, E. de Boer, *J. Chem. Soc., Dalton Trans.* **1974**, 1771.

[12] Instead of the initially proposed back-electron transfer leading to a benzylic cation (see ref. [3]), which would proceed under reductive conditions, we favor a homolytic iron–oxygen bond cleavage initiated by an attack of the benzylic radical onto the oxygen atom.

[13] A. D. Rodríguez, O. M. Cóbar, O. L. Padilla, *J. Nat. Prod.* **1997**, *60*, 915.

[14] A. M. Bernard, A. Frongia, P. P. Piras, F. Secci, M. Spiga, *Org. Lett.* **2005**, *7*, 4565.

[15] CCDC-629505 and CCDC-629506 contain the supplementary crystallographic data for **11g** and **11r**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[16] CCDC-629507 contains the supplementary crystallographic data for **19c**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[17] V. Nair, S. Mathai, R. L. Varma, *J. Org. Chem.* **2004**, *69*, 1413.

[18] D. M. Skytte, S. F. Nielsen, M. Chen, L. Zhai, C. E. Olsen, S. B. Christensen, *J. Med. Chem.* **2006**, *49*, 436, and unpublished results.

[19] A. Simion, C. Simion, T. Kanda, S. Nagashima, Y. Mitoma, T. Yamada, K. Mimura, M. Tashiro, *J. Chem. Soc. Perkin Trans. 1* **2001**, 2071.

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