EurJOC European Journal of Organic Chemistry

FULL PAPER

DOI: 10.1002/ejoc.201301461

Spiro- and Bicycloannulation of Sulfoximine-Substituted 2-Hydroxy-dihydropyrans: Enantioselective Synthesis of Spiroketals, Spiroethers, and Oxabicycles and Structure of Dihydropyran Oxocarbenium Ions

Michal Lejkowski,[a][‡] Prabal Banerjee,[a][‡‡] Gerhard Raabe,[a] Jan Runsink,[a][†] and Hans-Joachim Gais*[a]

Keywords: Synthetic methods / Spiro compounds / Annulation / Prins cyclization / Sulfoximines / Oxocarbenium ions / Ab initio calculations

A modular enantioselective synthesis of spiroketals, spiroethers, and oxabicycles, each containing a dihydropyran subunit, is described. It is based on the 2,2-spiro- and 2,6-bicycloannulation of sulfoximine-substituted 2-hydroxy-dihydropyrans. Key steps of the spiroannulations are the ring-closing metathesis of the corresponding 2,2-oxadienyl and 2,6-dienyl dihydropyrans and Prins cyclization of 2-alkenyl 2-hydroxy-dihydropyrans. Ring-closing metathesis of the corresponding 2,6-dienyl dihydropyrans gave oxabicycles with oxabicyclo[4.3.1]decane skeletons. These routes were extended to the synthesis of spiroketals and spiroethers incorporating additional annulated six-membered rings. Diastereoselective Prins cyclization of mono- and bicyclic 2-alkenyl-2-hydroxy-dihydropyrans was highly selective and afforded chloro-substituted spirocycles. Substituted 2-hydroxy-dihydropyrans were obtained through cyclization of δ-hydroxy ketones, which were synthesized from enantiomerically pure sulfoximine-substituted homoallylic alcohols through lithiation and trapping of the α-lithioalkenylsulfoximines with unsaturated aldehydes, followed by allylic oxidation. Inter- and intramolecular glycosidations of the 2-hydroxy-dihydropyrans with *O*- and *C*-nucleophiles proceeded with high stereoselectivities and furnished 2,6-*trans*-configured glycosides. Dihydropyran oxocarbenium ions are most likely intermediates in the glycosidations. According to ab initio calculations, sulfoximine- and trimethyl-substituted dihydropyran oxocarbenium ions adopt a half-chair-like conformation. The energy difference between the oxocarbenium ion with pseudoaxial and the one with pseudoequatorial methyl groups is very small. A transition state model for their reactions with nucleophiles is proposed. It features a half-chair-like conformation, a pseudoequatorial C6 substituent, and an *anti*-addition of the nucleophile along an axial trajectory to C2 that produces an *anti*-periplanar lone pair at the O atom. A similar transition state model allows a general explanation for the *trans* stereoselectivity of the reactions between C6-substituted dihydropyran oxocarbenium ions and nucleophiles.

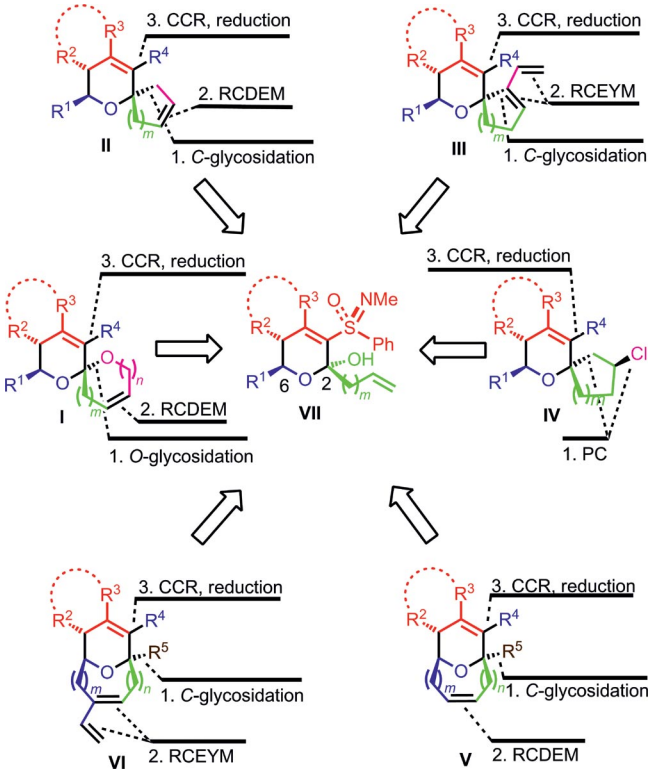
Introduction

The spiroketal,[1] spiroether,[2] and oxabicycle[3] structural motifs are found in a large number of natural and non-natural chiral substances with interesting biological activities and intricate molecular architectures. This has led to much effort being directed towards their enantioselective synthesis and has resulted in the development of several interesting methods for the construction of the spiro and bicyclic frameworks.[1–6]

We became interested in the modular synthesis of the unsaturated sulfoximine-substituted spiroketals **I** (Scheme 1), spiroethers **II**–**IV**, and oxabicycles **V** and **VI** [R^4 = S(O)(NMe)Ph] through 2,2-spiro- and 2,6-bicycloannulation of the 2-hydroxy-dihydropyrans **VII** with the aid of *r*ing-*c*losing *di*ene *m*etathesis (RCDEM[7a–7c]) and *r*ing-*c*losing *e*n*y*ne *m*etathesis (RCEYM[7c–7e]) of the corresponding 2,2-oxadienyl, 2,2-dienyl, and 2,2-enynyl derivatives, respectively,[8–11] and *P*rins *c*yclization (PC) of **VII**. The spiro- and bicyclic sulfoximines **I**–**VI** should be interesting building blocks for the synthesis of unsaturated spiroketals, spiroethers, and oxabicycles containing dihydropyran subunits.[1–5]

The role of the sulfoximine group is in this synthetic scheme is not confined to serving as a chiral auxiliary in the enantioselective synthesis of **VII** (vide infra). The spiroketals **I**, spiroethers **II**–**IV**, and oxabicycles **V** and **VI** having been attained, the sulfoximine group should also allow for a number of synthetically useful transformations, including its replacement through transition-metal-mediated cross-coupling reactions (CCRs) with organometallics or reduction to give the corresponding derivatives **I**–**VI**, R^4 =

[a] Institute of Organic Chemistry, RWTH Aachen University, Landoltweg 1, 52074 Aachen, Germany
E-mail: gais@rwth-aachen.de
http://www.oc.rwth-aachen.de/akgais/akgais_d.html
[‡] Present address: hte Aktiengesellschaft Kurpfalzring 104, 69123 Heidelberg, Germany
[‡‡] Present address: Department of Chemistry, IIT Ropar, Nangal Road, Rupnagar, 140001 Punjab, India
[†] Deceased 2012
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201301461.



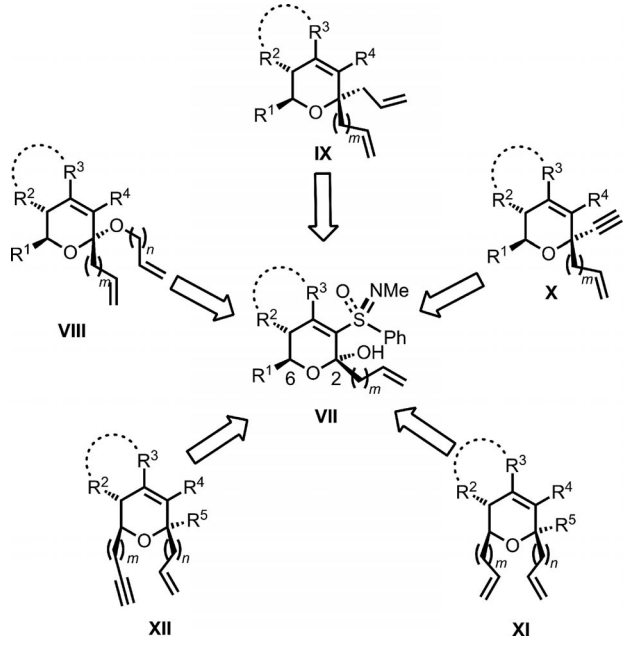
Scheme 1. Spiro- and bicycloannulation of sulfoximine-substituted 2-hydroxy-dihydropyrans **VII** through RCDEM, RCEYM, and PC.

alkyl, aryl, H (Scheme 1).[12] In addition, Michael reactions of the alkenylsulfoximine moieties of **I**–**VI** [R^4 = S(O)(NMe)Ph] with *C*- and heteroatom-nucleophiles should be feasible.[13]

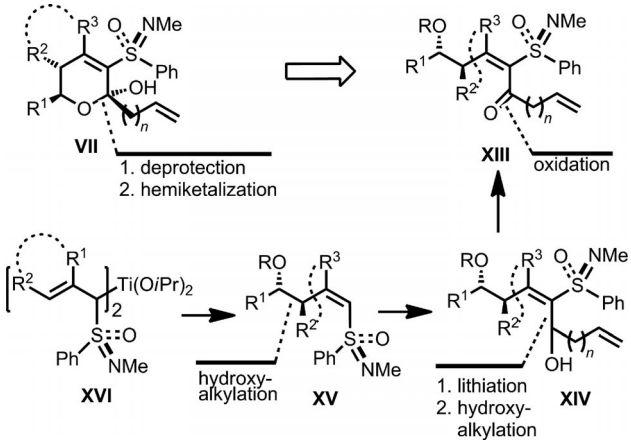
The synthesis of the dienyl, oxadienyl, and enynyl dihydropyrans **VIII**–**XII** (Scheme 2), the starting materials for the RCDEM and RCYEM, was intended to be accomplished through *O*- and *C*-glycosidation, respectively, of the 2-hydroxy-dihydropyrans **VII**. It was hoped that either the stereogenic ring C atoms or the sulfoximine group would provide asymmetric induction in the generation of the anomeric C atom.

It was envisioned that the 2-hydroxy-dihydropyrans **VII** would be obtained from the corresponding enones **XIII**, which can in turn be synthesized from the starting sulfoximine-substituted homoallylic alcohols **XV** via the allylic alcohols **XIV** (Scheme 3).[14] The alkenylsulfoximines **XV**, carrying various alkyl, alkenyl, alkynyl, and aryl groups (R^1), are available through a highly diastereoselective hydroxyalkylation reaction from the corresponding enantiomerically pure sulfoximine-substituted allyltitanium complexes **XVI** and aldehydes.[15] Thanks to the modularity of the planned synthesis of **VII**, a wide range of substituents R^1, R^2, and R^3 can be incorporated. The route outlined in Scheme 3 should also allow the synthesis of bicyclic 2-hydroxy-dihydropyrans **VII** (R^2 and R^3 embedded in a ring), thanks to the accessibility of the corresponding cyclic sulfoximine-substituted homoallylic alcohols **XV**.[15]

As well as being key intermediates in the envisioned synthesis of the spiroketals, spiroethers, and oxabicycles, the



Scheme 2. *O*- and *C*-glycosidation of 2-hydroxy-dihydropyrans **VII**.



Scheme 3. Synthesis of 2-hydroxy-dihydropyrans **VII** starting from sulfoximine-substituted allylic titanium complexes **XVI** via allylic alcohols **XIV**.

dihydropyrans **VII** are themselves of synthetic interest. The synthesis of dihydropyrans containing $\Delta^{3,4}$ double bonds has received considerable attention,[16] because of their occurrence as structural units in a number of naturally occurring substances including spiro- and macrocycles with interesting biological profiles and chemical structures.[1–5,9,11,16] Although several methods for the synthesis of $\Delta^{3,4}$-dihydropyrans have been described, those giving access to substituted derivatives that also possess functional groups at their double bonds are less abundant.[16]

In this article we describe in full detail the modular synthesis of sulfoximine-substituted 2-hydroxy-dihydropyrans by the sulfoximine route, as well as their spiro- and bicycloannulation with the aid of RCDEM and PC, to give spi-

roketals, spiroethers, and oxabicycles.[17] In addition, we report on the synthesis and stereoselective inter- and intramolecular *O*- and *C*-glycosidation of the 2-hydroxy-dihydropyrans. A general transition state model for the *trans*-stereoselective reactions between C6-substituted 5,6-dihydropyran oxocarbenium ions and nucleophiles is proposed. The theoretical structures of sulfoximine- and methyl-substituted dihydropyran oxocarbenium ions are also described.

Results and Discussion

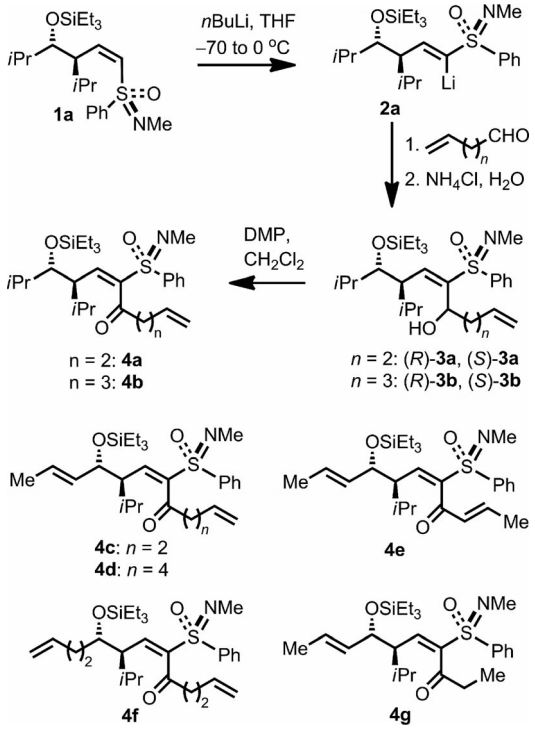
Modular Synthesis of Enones

We had previously studied the RCDEM of trienes of type **XIV** (R^1 = alkenyl, Scheme 3), which gave the corresponding medium-sized carbocycles.[14b] Alkenylsulfoximines **XV** are readily lithiated at the α-position at low temperatures, with formation of the corresponding *Z*-configured α-lithioalkenylsulfoximines.[12e,12g,15b] At 0 °C they undergo isomerization to the corresponding *E*-configured α-lithioalkenylsulfoximines, which can be trapped by unsaturated aldehydes to give the allylic alcohols **XIV** (R^1 = alkenyl).[14b] Their oxidation with Dess–Martin periodinane (DMP) yields ketones **XIII**.

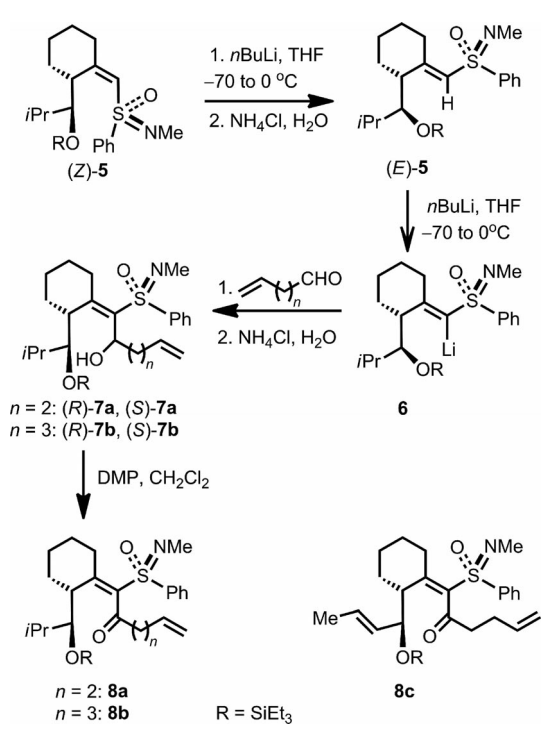
The lithiation of the *Z*-configured alkenylsulfoximine **1a** (Scheme 4), which was obtained enantio- and diastereomerically pure from the corresponding allylic titanium complex and 2-methylpropanal (cf. Scheme 3) on treatment with *n*BuLi at –78 °C to 0 °C, thus gave the corresponding *Z*-configured α-lithioalkenylsulfoximine (not shown). At ambient temperature it underwent isomerization to the *E*-configured isomer **2a**. Treatment of **2a** with pent-4-enal and hex-5-enal furnished the corresponding allylic alcohols **3a** and **3b** as almost 1:1 mixtures of diastereomers in 92% and 91% yields, respectively.

The lack of asymmetric induction in the hydroxyalkylation of **2a** was of no consequence, because of the subsequent oxidation of the alcohols. Treatment of the alcohols **3a** and **3b** (both as mixtures of diastereomers) with DMP afforded the corresponding *E*-configured enones **4a** and **4b** in 89% and 96% yields, respectively. In addition, the enones **4c**–**f** were prepared as starting materials for the synthesis of oxabicycles of type **V** (cf. Scheme 1) from the corresponding alkenylsulfoximines **XV** by the same route.[14b]

The cyclohexanoid enones **8a** and **8b** were synthesized from the *Z*-configured cyclic alkenylsulfoximine (*Z*)-**5** (Scheme 5), itself obtained from the corresponding cyclic allylic titanium complex and 2-methylpropanal (cf. Scheme 3).[14b] Treatment of the enantio- and diastereomerically pure (*Z*)-alkenylsulfoximine (*Z*)-**5** with *n*BuLi at –78 °C to 0 °C, followed by protonation of the intermediate *E*-configured α-lithioalkenylsulfoximine (not shown), gave the *E*-configured alkenylsulfoximine (*E*)-**5** in 98% yield. Lithiation of (*E*)-**5** furnished the *E*-configured α-lithioalkenylsulfoximine **6**, which on treatment with pent-4-enal and hex-5-enal afforded the corresponding allylic alcohols **7a** and **7b**, both as mixtures of diastereomers in 9:1 ratio, in 64% and 75% yields, respectively. The more direct route to the allylic alcohols starting from (*Z*)-**5** and omitting the isolation of (*E*)-**5** gave inferior yields. The DMP oxidation of alcohols **7a** and **7b** (both as the mixtures



Scheme 4. Synthesis of acyclic sulfoximine-substituted δ-hydroxy enones.

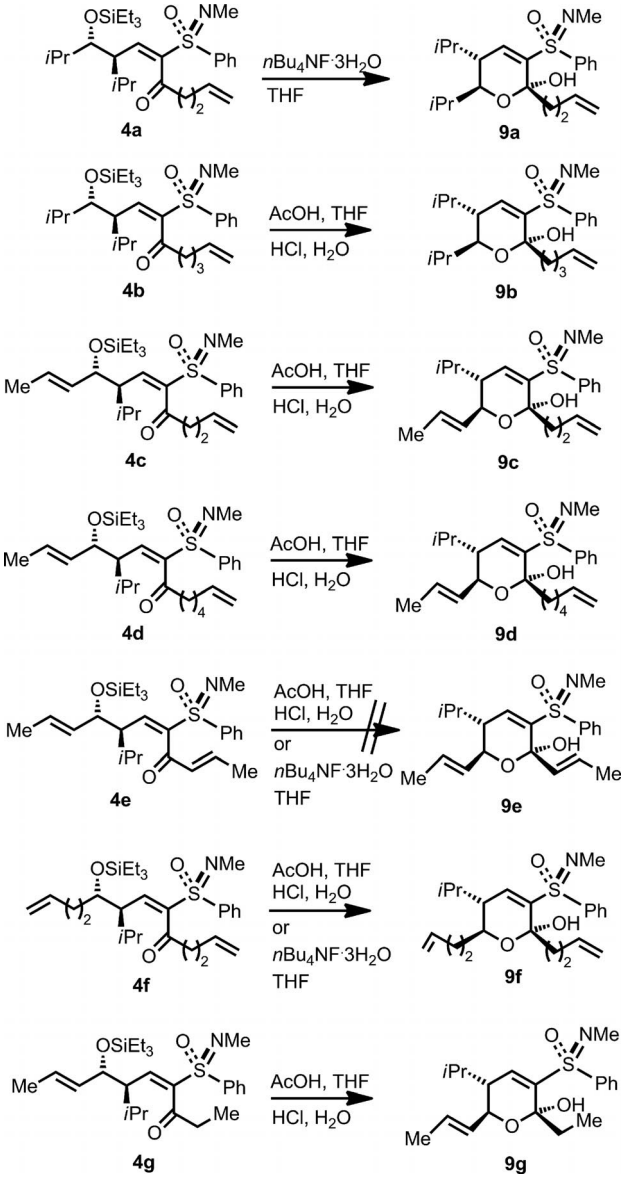


Scheme 5. Synthesis of cyclic sulfoximine-substituted δ-hydroxy enones.

of diastereomers) furnished the corresponding enones **8a** and **8b** in 90% and 98% yields, respectively. Similarly, ketone **8c** was synthesized by this route as described previously.[14b]

Synthesis of 2-Hydroxy Dihydropyrans

As shown in Scheme 2, deprotection and cyclization of the silyloxy-substituted enones **4a**–**g**, **8a**, and **8b** were called for as the next steps. The enone **4f** was subjected to a number of different sets of experimental conditions in order to find the optimum reaction conditions. Treatment of enone **4f** with 1.4 equiv. of nBu$_4$NF·3 H$_2$O in THF gave the 2-hydroxy-dihydropyran **9f** as single diastereomer in 65% yield (Scheme 6). Examination of the crude product by ^{1}H NMR revealed the formation of several unidentified side products together with *N*-methyl-phenyl-sulfinamide. Treatment of **4f** variously with 200 equiv. of AcOH in THF, 2 equiv. of pyridinium *p*-toluenesulfonate (PPTS) in MeOH, or 2 equiv. of *p*TsOH in CH_2Cl_2 did not lead to any noticeable transformation of the enone. Finally, the 2-hydroxy-dihydropyran **9f** was obtained in 90% yield as a single diastereomer upon treatment of enone **4f** with 100 equiv. of AcOH in a mixture of H_2O and THF containing a trace amount of aqueous HCl at room temperature. Similar treatment of the silyl ethers **4b**, **4c**, **4d**, and **4g**[14b] with this mixture of acids in THF and H_2O afforded the corresponding 2-hydroxy-dihydropyrans **9b**, **9c**, **9d**, and **9g** as single diastereomers in 82–90% yields.



Scheme 6. Synthesis of 2-hydroxy-dihydropyrans.

In the case of the cyclization of enone **4a**, the use of nBu$_4$NF·3 H$_2$O gave better results. Treatment of **4a** with 1.4 equiv. of nBu$_4$NF·3 H$_2$O in THF thus furnished the 2-hydroxy-dihydropyran **9a** with a 97% *de* and in 80% yield. Because of the basicity of the sulfoximine group, an excess of acid was used in the cyclization experiments.

The synthesis of the 2-hydroxy-dihydropyran **9e**, containing a penta-1,4-dien-3-ol unit, from enone **4e** could not be achieved under either set of conditions. Only the formation of a number of unidentified compounds was observed.

The α-configuration of the anomeric C atoms of **9a** and **9g** was determined by NOE experiments, which in each case showed diagnostic effects between the hydroxy group and the 6-H atom (Figure 1). On the basis of these results and because of the similarity of the NMR spectroscopic data, the α-configuration was also assigned to the anomeric centers of the 2-hydroxy-dihydropyrans **9b**–**d** and **9f**. Formation of the α-configured 2-hydroxy-dihydropyrans is most likely thermodynamically directed. Because of the anomeric effect,[18] the α-configured diastereomers would be expected to be more stable than the β-configured diastereomers. Presumably the 2-hydroxy-dihydropyrans each have an intramolecular H bond between the hydroxy group and the O or N atom of the sulfoximine group.[13]

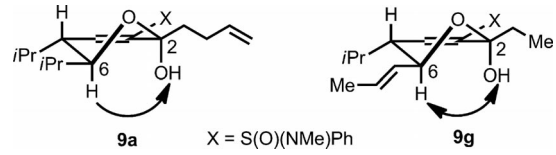
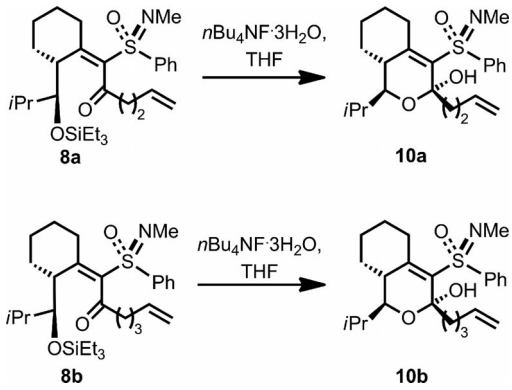


Figure 1. Configuration of the 2-hydroxy-dihydropyrans **9a** and **9g** at C2.

Although H-bond formation could also been taken as a reason for the preference for the α-anomers, modeling experiments showed that H bonds can be formed equally well in the β-anomers. The NMR spectra of the 2-hydroxy-dihydropyrans gave no indication of the presence of the corresponding hydroxy ketones (not shown).

Surprisingly, the cyclization of the cyclic silyloxy-substituted enones **8a** and **8b** under the acidic reaction conditions failed; only decomposition of the enones was observed. Treatment, however, of the enones **8a** and **8b** with 2 (1.5) equiv. of nBu$_4$NF·3 H$_2$O in THF, the method that had generally given less favorable results in the case of the acyclic enones, afforded the corresponding 2-hydroxy-dihydropyr-

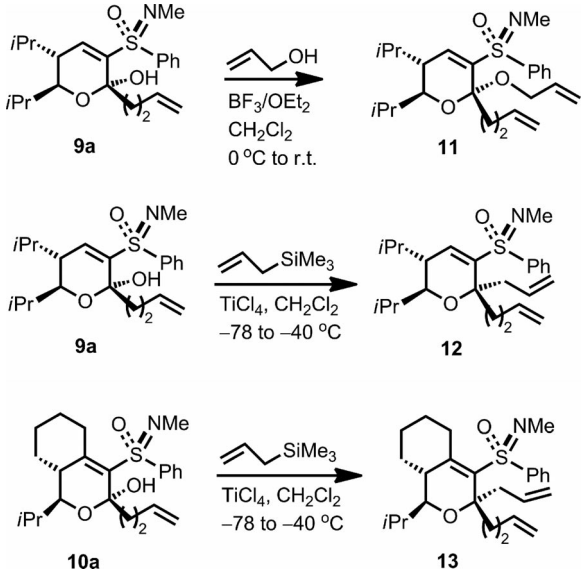
ans **10a** and **10b** as single diastereomers in 79% and 92% yield, respectively (Scheme 7). The α-configuration of the anomeric centers of the bicyclic 2-hydroxy-dihydropyrans was assigned in analogy to those of the monocyclic 2-hydroxy-dihydropyrans.



Scheme 7. Synthesis of bicyclic 2-hydroxy-dihydropyrans.

O- and *C*-Glycosidation of 2-Hydroxy-dihydropyrans

At this stage the synthetic scheme for the spiroketals and spiroethers called for the stereoselective synthesis of 2,2-dienyl and 2,2-oxadienyl dihydropyrans from the mono- and bicyclic 2-hydroxy-dihydropyrans through *O*- and *C*-glycosidations, respectively (Scheme 8).



Scheme 8. Synthesis of 2,2-dienyl and 2,2-oxadienyl dihydropyrans.

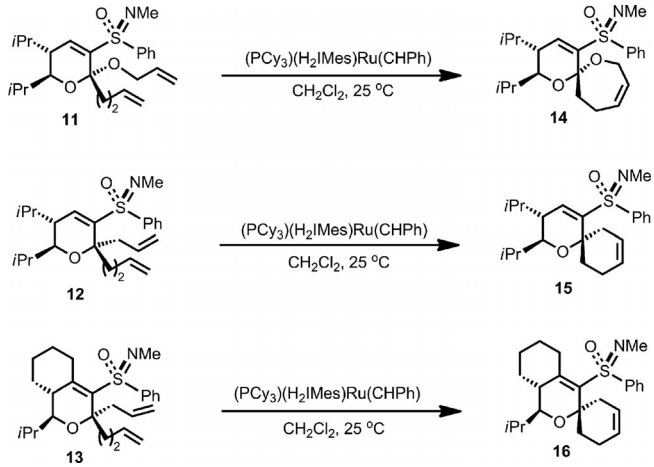
The 2-hydroxy-dihydropyran **9a** was thus treated with allyl alcohol in the presence of 2.6 equiv. of $BF_3{\cdot}Et_2O$, which afforded glycoside **11** with 90% *de* in 80% yield. A Sakurai reaction[19a,19b] between **9a** and allyltrimethylsilane in the presence of 6.1 equiv. of $TiCl_4$ gave glycoside **12** with 90% *de* in 90% yield. Similarly, allylation of the bicyclic 2-hydroxy-dihydropyran **10a** with allyltrimethylsilane in the presence of 6.3 equiv. of $TiCl_4$ afforded the bicyclic glycoside **13** with 90% *de* in 90% yield. Glycosides **11**–**13** were obtained diastereomerically pure through column chromatography. The configuration of the anomeric centers of the glycosides was assigned later, at the stage of the corresponding spiroketals and spiroethers. The minor diastereomers of the *O*- and *C*-glycosides were not isolated. Their structures were interfered from the NMR spectra of the mixtures of diastereomers.

The successful *C*-glycosidation of the 2-hydroxy-dihydropyrans **9a** and **10a** through the Sakurai reaction lends support to the notion of a synthesis of the 2,2-enynyl dihydropyrans **X** through treatment of **VII** with (trimethylsilyl)alkynes[19b,19c] (cf. Scheme 2).

RCDEM of 2,2-Oxadienyl and 2,2-Dienyl Dihydropyrans

In our previous studies of the synthesis of medium-sized carbocycles through RCDEM of sulfoximine-substituted trienes in the presence of ruthenium catalysts, no detrimental effect of the Lewis basic sulfoximine group on the catalyst or intermediates of the catalytic cycle was observed.[14b]

Gratifyingly, RCDEM of oxadiene **11** in the presence of 5 mol-% of the ruthenium catalyst $(PCy_3)(H_2IMes)Ru(CHPh)$[1,20] in CH_2Cl_2 at room temperature gave spiroketal **14** in 85% yield (Scheme 9). Similar RCDEM of diene **12** in the presence of the ruthenium catalyst afforded spiroether **15** in 87% yield. Treatment of the bicyclic diene **13** in the presence of the ruthenium catalyst gave the tricyclic spiroether **16** in 93% yield. The configurations of the spirocenters in spirocycles **14**–**16** are determined by those of the anomeric C atoms in the starting dienyl dihydropyrans. This was confirmed in the case of the spiroketal **14** and spiroether **15** through NOE experiments, which for **14** showed diagnostic effects (Figure 2) between (1) the pseudoaxial 2-H atom and the pseudoaxial 8-H atom, and (2) the pseudoaxial 12-H atom and the *o*-H atom, and for **15** showed effects (Figure 2) between (1) the pseudoequatorial 7-H atom and the pseudoaxial 2-H atom, and (2) the pseudoaxial 11-H atom and the *o*-H atoms. The spirocenters in **14** and **15** thus have the *R* and *S* configurations,



Scheme 9. RCDEM of 2,2-dienyl and 2,2-oxadienyl dihydropyrans.

respectively. Analogously, the *S* configuration was assigned to the spirocenter of **16**. It follows that the dienyl dihydropyrans **11**, **12**, and **13** have the *R*, *S*, and *S* configurations, respectively.

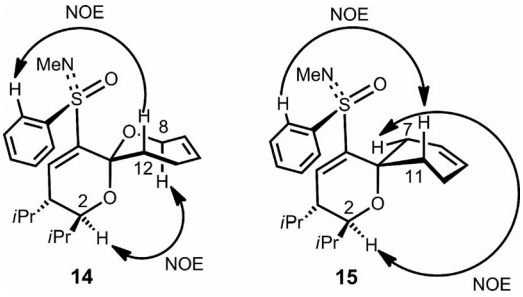
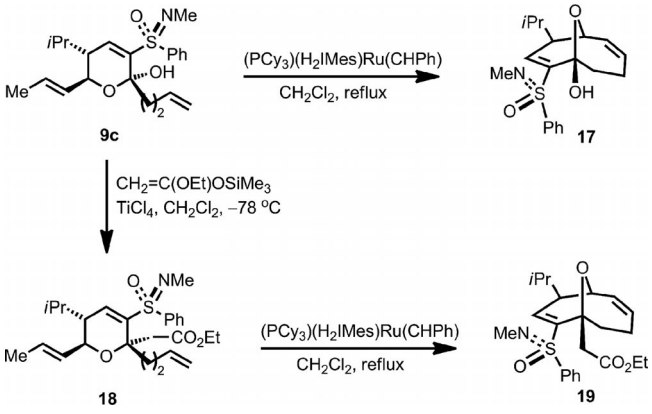


Figure 2. Configurations of the spirocycles **14** and **15** at the spirocenters.

RCDEM of 2,6-Dienyl Dihydropyrans

Thanks to the modular nature of the synthesis of the dihydropyrans **VII**, 2-hydroxy 2,6-dienyl dihydropyrans of type **XI** are also available, and RCDEM of these could offer access to substituted oxabicycles of type **V** (cf. Scheme 1, Scheme 2, and Scheme 3). The 2,6-dienyl dihydropyran **9c** was therefore subjected to treatment with $(PCy_3)(H_2IMes)$-Ru(CHPh) in CH_2Cl_2 at reflux, which afforded oxabicycle **17** in 96% yield (Scheme 10). The NMR spectra of **17** gave no indication of the presence of the corresponding monocyclic hydroxy ketone (not shown).[18b,21]



Scheme 10. Synthesis of oxabicycles by RCDEM of 2,6-dienyl dihydropyrans.

The possibility of obtaining the substituted oxabicycle **19** (Scheme 10) from **17** was also investigated. Not surprisingly, the substitution of the hydroxy group in **17** through a Mukaiyama reaction[19b,22] with $CH_2=C(OSiMe_3)OEt$ in the presence of $TiCl_4$ failed, with the oxabicycle being recovered in high yield. The synthesis of **19** by the opposite sequence of steps was therefore examined. *C*-Glycosidation of the 2-hydroxy-dihydropyran **9c** with $CH_2=C(OSiMe_3)$-OEt in the presence of 1 equiv. of $TiCl_4$ gave glycoside **18** with ≥95% *de* in 63% yield. The *S* configuration at C2 in **18** was determined by NOE experiments, which revealed a diagnostic effect between the pseudoaxial 6-H atom and the methylene H atoms α to the ester group (Figure 3). RCDEM of **18** in the presence of the ruthenium catalyst proceeded cleanly and gave the bridgehead-substituted oxabicycle **19** (Scheme 10) in 90% yield. Surprisingly, RCDEM of the 2,6-dienyl 2-hydroxy-dihydropyrans **9d** and **9f** with formation of the corresponding oxabicycles could not be achieved. Treatment of **9d** and **9f** with $(PCy_3)(H_2IMes)$-Ru(CHPh) in CH_2Cl_2 at reflux for several hours finally led only to the recovery of the dienes in high yields.

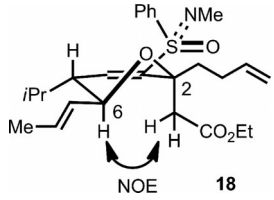
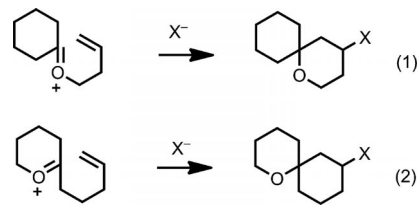


Figure 3. Configuration of the *C*-glycoside **18** at C2.

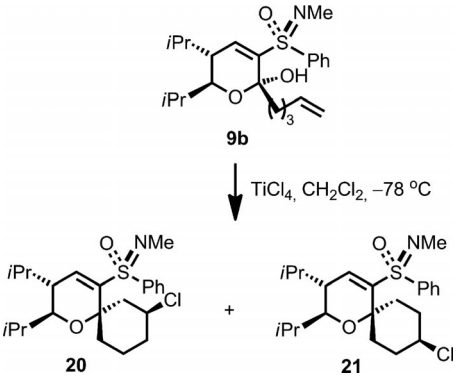
PC of 2-Alkenyl 2-Hydroxy-dihydropyrans

The availability of the 2-hydroxy-dihydropyrans **9b** and **10b**, each bearing a pent-4-enyl group at the C2 atom, provided the possibility to open a route to chloro-substituted spiroethers of type **IV** (cf. Scheme 1) through PC.[23] Formation of spiroethers through PC can in principle occur by two different modes (Scheme 11). Whereas the first mode involves an exocyclic oxocarbenium ion and delivers a spiroether with a substituted tetrahydropyran ring [Equation (1)], the second involves an endocyclic oxocarbenium ion and gives a spiroether with a substituted cyclohexane ring [Equation (2)]. Although the PC of exocyclic oxocarbenium ions had been widely employed in the synthesis of spiroethers,[24] examples of PC of endocyclic oxocarbenium ions have not, to the best of our knowledge, been described.[3,24] However, the synthesis of spiroethers through Sakurai cyclization of endocyclic oxocarbenium ions had been studied.[5a,25,26]



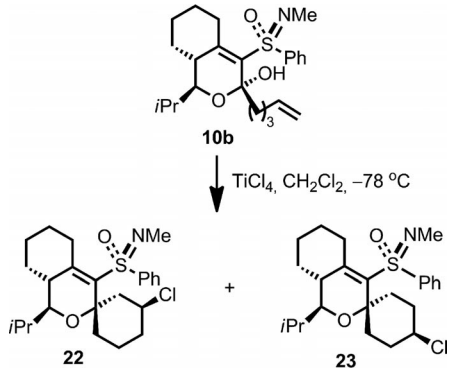
Scheme 11. Principle modes of spiroether formation through PC of exocyclic [Equation (1)] and endocyclic oxocarbenium ions [Equation (2)].

Treatment of **9b** with 3 equiv. of $TiCl_4$ in CH_2Cl_2 at –78 °C highly selectively furnished the chloro-substituted spiroethers **20** (with ≥95% *de*) and **21** (with ≥95% *de*) in a ratio of 8:1 and a combined yield of 80% (Scheme 12). Separation of the isomers by chromatography afforded spiroether **20** in 68% yield and spiroether **21** in 7% yield.



Scheme 12. PC of 2-alkenyl-2-hydroxy-dihydropyrans.

PC of the bicyclic 2-alkenyl-2-hydroxy-dihydropyran **10b** in the presence of 3 equiv. of $TiCl_4$ in CH_2Cl_2 at –78 °C also occurred with high diastereoselectivity to give a mixture of the chloro-substituted spiroethers **22** (≥95% *de*) and **23** (≥95% *de*) in a ratio of 8:1 and a combined yield of 84% (Scheme 13). Separation of the isomers by chromatography afforded spiroether **22** in 69% yield and spiroether **23** in 5% yield.



Scheme 13. PC of bicyclic 2-alkenyl-2-hydroxy-dihydropyrans.

The connectivities and configurations of chloro-substituted spiroethers **20**–**23** were determined by NMR spectroscopy. All signals in the ^{1}H NMR spectra of **20**–**22** and all decisive ones in the ^{1}H NMR spectrum of **23** were identified by standard techniques. The (6*S*,8*S*) configuration was assigned to chlorinated compound **20**, because of the observation of (1) NOE effects between the equatorial 7-H atom and the pseudoaxial 2-H atom, (2) NOE effects between the *o*-H atom of the phenyl ring and the axial 11-H atom, and (3) the magnitude of the coupling constants of 8-H (Figure 4). Similarly, the (6*R*,9*S*) configuration was assigned to chlorinated compound **21** on the basis of the observation of (1) NOE effects between the equatorial 7-H atom and the pseudoaxial 2-H atom, (2) NOE effects between the *o*-H atom of the phenyl ring and the axial 11-H atom, and (3) the magnitude of the coupling constants of 9-H. The (6*S*,8*S*) configuration was assigned to chlorinated compound **22**, because of the observation of (1) NOE effects between the equatorial 7-H atom and the pseudoaxial 2-H atom, (2) NOE effects between the *o*-H atom of the phenyl ring and the axial 11-H atom, and (3) the magnitude of the coupling constants of 8-H. The (6*R*,9*S*) configuration was assigned to chlorinated compound **23** by analogy with **21**.

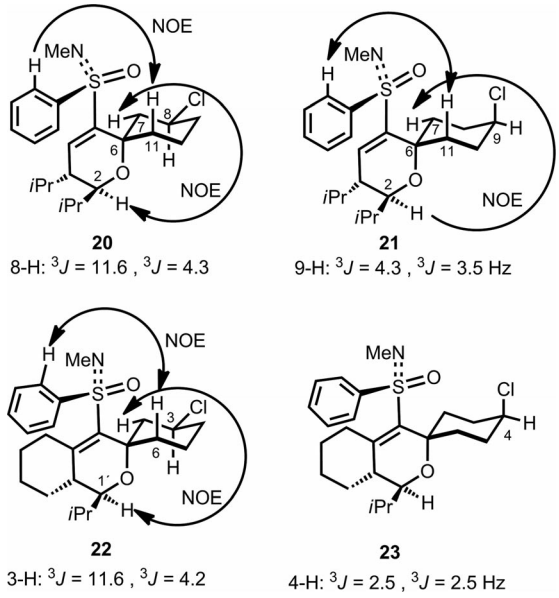


Figure 4. Configurations of the spirocyclic chlorinated compounds **20**–**22** at the spirocenters and at C3 and C4 (numbering of **22** is according to the nomenclature).

The Cl-bearing stereogenic centers of chlorinated compounds **20**–**23** were established in the PC with high stereoselectivites. The formation of the major isomers **20** and **22** presumably involved the carbenium ions **XVII** as intermediates, with these undergoing preferential equatorial intermolecular attack by chloride ion (Figure 5). Axial attack of Cl^- on **XVII** is perhaps hindered as a result of 1,3-diaxial strain with the O atom. The minor chlorinated compounds **21** and **23** might originate from axial attack of Cl^- on the carbenium ions **XVIII**, generated from carbenium ions **XVII** by a competing 1,2-hydride shift.[27] Because of the use of 3 equiv. of $TiCl_4$ in the PC of **9b** and **10b** it would be expected that the sulfoximine groups of the dihydropyrans would be coordinated by $TiCl_4$ and thus that the corresponding $TiCl_4$-coordinated carbenium ions would be formed. This could have also resulted in stereoselective intramolecular equatorial and axial delivery, respectively, of Cl^- onto the electrophilic C atoms of the carbenium ions.

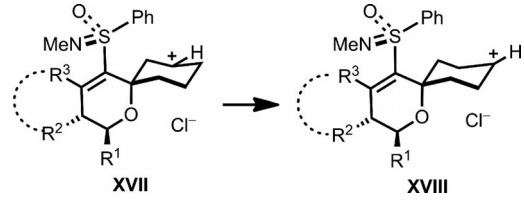


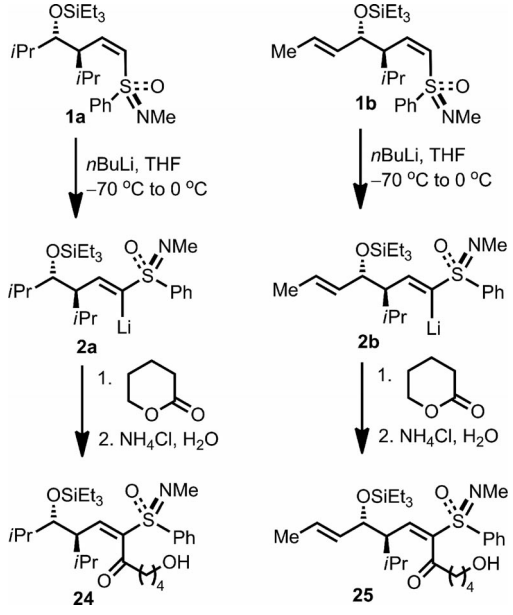
Figure 5. Proposed intermediates in the PC of the alkenyl 2-hydroxy-dihydropyrans **9b** and **10b**.

The Cl atoms in spiroethers **20** and **22** provide opportunities for further functionalization of the cyclohexane ring.

In addition, it is possible to envision PC reactions of **9b** and **10b** in the presence of reagents that should give the corresponding hydroxy-substituted spiroethers.[23b,28]

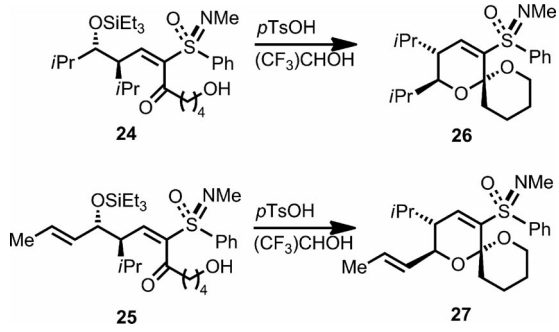
Synthesis and Spiroketalization of Dihydroxy Ketones

Having successfully accomplished the synthesis of spiroketals as shown in Schemes 1, 2, and 3, we became interested in finding out whether it would be possible to open up an additional route to spiroketals based on the conventional internal spiroketalization of sulfoximine-substituted dihydroxy ketones, the synthesis of which should be possible from the alkenylsulfoximines **1a** and **1b** (Scheme 14). Treatment of the α-lithioalkenylsulfoximines **2a** and **2b**, prepared from the corresponding alkenylsulfoximines **1a** and **1b** and *n*BuLi, with δ-valerolactone at –78 °C in THF furnished the corresponding *E*-configured hydroxy ketones **24** and **25** in 94% and 95% yields, respectively.



Scheme 14. Synthesis of sulfoximine-substituted dihydroxy ketones.

Treatment of the silyloxy-substituted hydroxy ketone **24** with 3 equiv. of *p*-toluenesulfonic acid (*p*TsOH) in CH_2Cl_2 caused both desilylation and diastereoselective spiroketalization to give a mixture of the spiroketal **26** and its diastereomer (not shown) with the opposite configuration at the spirocenter, in a ratio of 85:15 and in 80% yield (Scheme 15). The use of pyridinium *p*-toluenesulfonate in CH_2Cl_2 resulted in unselective spiroketalization and afforded a mixture of the diastereomeric spiroketals in a ratio of 1:1 and in 70% yield. Gratifyingly, treatment of **24** with 3 equiv. of *p*TsOH in hexafluoroisopropanol (HFIP) instead of CH_2Cl_2 as solvent furnished spiroketal **26** with ≥95% *de* and in 82% yield.



Scheme 15. Spiroketalization of sulfoximine-substituted dihydroxy ketones.

Similar treatment of the hydroxy ketone **26** (Scheme 15) with 3 equiv. of *p*TsOH in HFIP gave spiroketal **27** with ≥95% *de* and in 86% yield. The selectivity-enhancing effect of HFIP, a solvent with a low nucleophilicity and high H-donor capacity and ionizing power,[29] is noteworthy. However, further experiments directed towards explaining this solvent effect were not carried out.

The configuration of spiroketal **27** was determined by NOE experiments on the basis of the assignment of all signals in the ^{1}H NMR spectrum. Because of the observation of (1) NOE effects between the axial 8-H atom and the pseudoaxial 2-H atom, and (2) NOE effects between the *o*-H atom of the phenyl ring and the axial 11-H atom, the (6*R*) configuration was attributed to the spirocenter of **27** (Figure 6). Accordingly, the (6*R*) configuration was also assigned to the spirocenter of **26**.

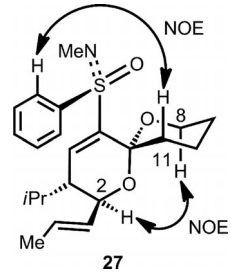


Figure 6. Configuration of spiroketal **27** at the spirocenter (numbering of **27** is according to nomenclature).

Conformations of Dihydropyrans and Spirocycles

According to the magnitudes of $^3J_{5\text{-H},6\text{-H}}$ (9–11 Hz)[30] and NOE experiments the dihydropyran rings in dihyropyrans **9a**–**d**, **9f**, **9g**, **10a**, **10b**, **11**–**13**, and **18** and in spirocycles **14**–**16**, **20**–**23**, **26**–**28**, and **30** (vide infra) each preferentially adopt a half-chair conformation in which the substituents at the neighboring sp^3 C atoms are in a pseudoequatorial relationship. This conformation is devoid of any destabilizing 1,3-diaxial interaction of the substituents in the α- and α′-positions to the O atom. In addition, in the cases of dihydropyrans **9a**–**d**, **9f**, **9g**, **10a**, **10b**, and **11**, each of which has a pseudoaxial substituent containing an O atom at the anomeric C atom, this conformation is stabilized by the an-

omeric effect. The alternative half-chair conformation with the substituents in a pseudoaxial relationship is destabilized by 1,3-diaxial interaction between the substituents at the α- and α′-positions to the O atom. Furthermore, in the cases of **9a**–**d**, **9f**, **9g**, **10a**, **10b**, and **11** it lacks the anomeric stabilization. The second spirocyclic rings of spirocycles **14**–**16**, **20**–**23**, **26**–**28**, and **30** each preferentially adopt a conformation in which the sulfoximine-substituted atom of the dihydropyran ring is in a pseudoequatorial position. This is because of minimization of steric interaction between the second spirocyclic ring and the sulfoximine group. In addition, in spiroketals **26**–**28** and **30** this conformation is stabilized by the anomeric effect, because of the pseudoaxial position of the O atom in the dihydropyran ring in each case. The conformations of the six- and seven-membered rings of spiroketal **14** (Scheme 9) depicted in Figure 7 illustrate the conformational preferences representatively.

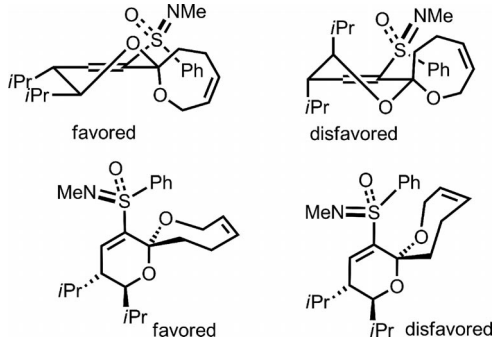
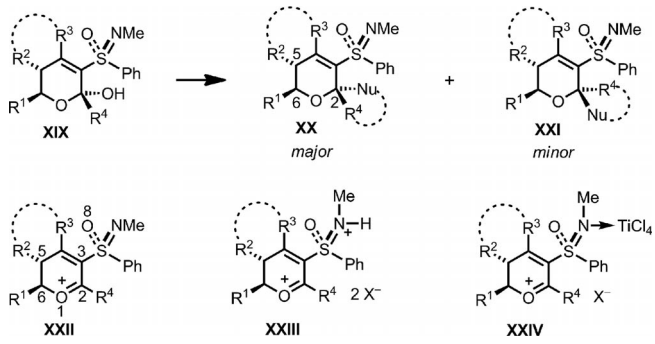


Figure 7. Schematic representation of the conformations of the spirocyclic rings of spiroketal **14**.

Structure and Reactivity of Sulfoximine-Substituted Dihydropyran Oxocarbenium Systems

The inter- and intramolecular glycosidations of 2-hydroxy-dihydropyrans of type **XIX** with both *O*- and *C*-nucleophiles (Nu^-) had uniformly proceeded with high diastereoselectivities, to give the 2,6-*trans*-configured glycosides **XX** (*trans* and *cis* relate to the position of R^1 and Nu) as major diastereomers and the 2,6-*cis*-configured glycosides **XXI** as minor diastereomers (Scheme 16). The glycosidations most likely proceeded through the intermediate formation of sulfoximine-substituted dihydropyran oxocarbenium ions of type **XXII**. The reactions of **XXII** with the *O*-nucleophiles in the presence of the acids might have been reversible, but those with the *C*-nucleophiles are expected to be irreversible. It is thus assumed that the reactions between **XXII** and the *C*-nucleophiles and, because of the similar selectivities, also the *O*-nucleophiles were kinetically directed. Dihydropyran oxocarbenium ions of type **XXII**, in which the double bonds carry no substituents, have found numerous synthetic applications as reactive intermediates (vide infra). Structural information about these oxocarbenium ions is lacking, however, despite their synthetic importance.



Scheme 16. Stereoselective 2,6-*trans O*- and *C*-glycosidations of 2-hydroxy-dihydropyrans **XIX**.

Ab Initio Calculations

In order to obtain information about the structure of **XXII** we carried out ab initio calculations for the diastereomeric trimethyl-substituted dihydropyran oxocarbenium ions **XXV** and **XXVI** (Figure 8). All calculations were performed with the Gaussian09 set of quantum-chemical programs.[31] Both structures were optimized at the MP2 level with employment of the 6-31+G* basis set (Figure 9).

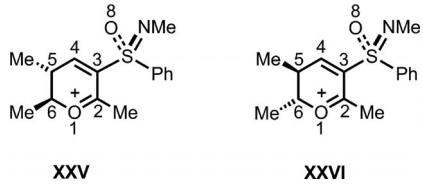


Figure 8. Dihydropyran oxocarbenium ions **XXV** [(R_S,5*R*,6*S*) configuration] and **XXVI** [(R_S,5*S*,6*R*) configuration].

All structures turned out to be relative energy minima. The nature of each fully optimized stationary point was determined by checking the eigenvalues of the corresponding force constant matrix for negative values. To study the nature of bonding in **XXV** and **XXVI**, NBO analyses were performed with the program NBO 3.0[32] as implemented in Gaussian 09 with use of the MP2/6-31+G*-optimized structures.

The Me groups in the oxocarbenium ion **XXV** are in a pseudoequatorial arrangement whereas those in oxocarbenium ion **XXVI** are in a pseudoaxial one. This difference, however, has almost no influence either on the geometric or on the electronic structures of the two carbenium ions. The parent rings of both oxocarbenium ions are nonplanar and have chiral half-chair-like conformations, as shown (Table 1) by the C4–C3–C2–O1 dihedral angles of 22.8° (**XXV**) and 19.0° (**XXVI**) and the C4–C5–C6–O1 dihedral angles of 52.2° (**XXV**) and 49.7° (**XXVI**). The sums of the

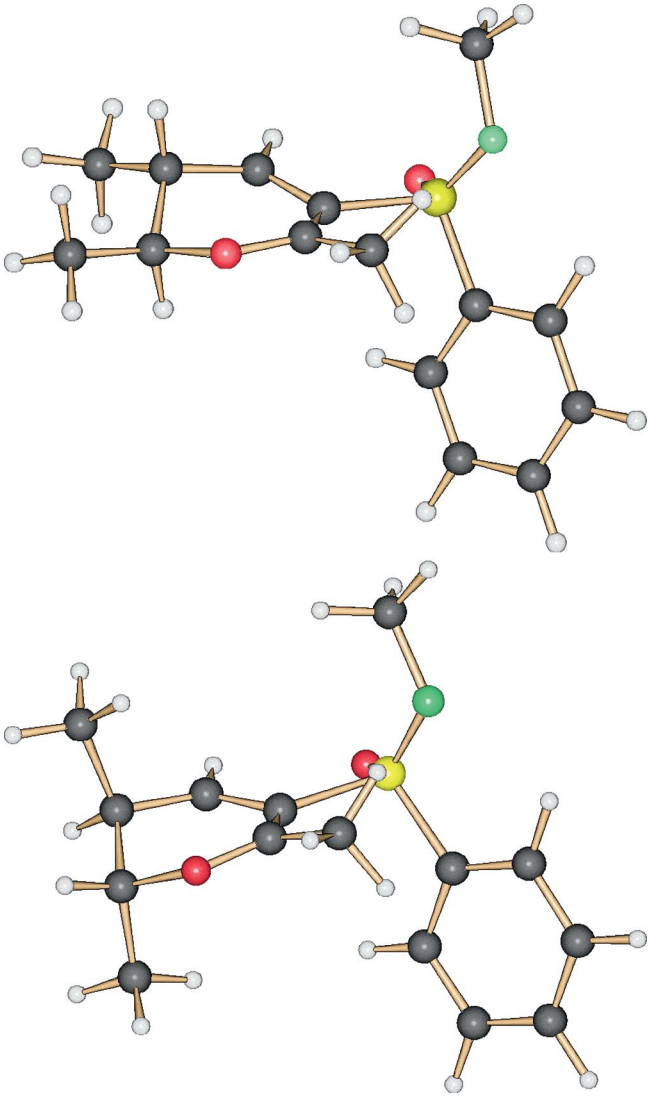


Figure 9. Calculated structures of the dihydropyran oxocarbenium ions: Top: **XXV** (MP2/6-31+G*: –1183.612997 a.u.). Bottom: **XXVI** (MP2/6-31+G*: –1183.613534 a.u.). Numbering: see Figure 7. Color code: C black, S yellow, O red, N green, H white.

bond angles at C4 and C2 are essentially 360.0°, but at C3 values of 358.5° (**XXV**) and 358.8° (**XXVI**) are obtained, showing a slight pyramidalization of the C atom bearing the sulfoximine group. The most striking features are the bond lengths in the C6–O1–C2 segment in each oxocarbenium ion. At 1.291 Å in both oxocarbenium ions the C2–O1 bond is in each case much closer to the length of the C=O double bond in, for example, acetone (1.232 Å), than to the value for a C–O single bond in, for example, dimethyl ether (1.420 Å). Moreover, the lengths of the C6–O1 bonds require comment. With an average value of 1.507 Å they exceed the length of the C_{sp3}–O bonds in dimethyl ether and 3,6-dihydro-2*H*-pyran (1.420 Å) by almost 0.09 Å.[33] The C6–O1–C2 segment therefore appears in each case to be structurally close to the transition state for fragmentation of the C6–O1 bond, resulting in the O=C-Me substituent at C3 and a cationic center at C6.

Table 1. Structural parameters of dihydropyran oxocarbenium ions **XXV** and **XXVI** (MP2/6-31+G* basis set; bond lengths in Å, angles in °).

Parameter	XXV	XXVI
C3–C4	1.359	1.358
C3–C2	1.443	1.444
C2–O1	1.291	1.291
C4–C5	1.498	1.493
C5–C6	1.516	1.519
C6–O1	1.508	1.505
C4–C3–C2–O1	22.8	19.0
C4–C5–C6–O1	52.2	49.7
N–S–C3–C2	–54.3	–53.0
Σ(C4)[a]	360.0	359.9
Σ(C3)[a]	358.5	358.8
Σ(C2)[a]	360.0	360.0

[a] Σ(C*n*): sum of bond angles at carbon atom *n*.

As in the case of the geometric parameters, the NBO analyses gave quite similar results for both carbenium ions (Table 2). At 0.80 e the positive charge of each carbenium ion is mainly localized at carbon atom C2. This carbon atom carries a weakly occupied (0.49–0.50 e) 2*p* orbital, which interacts strongly [$\Delta E(2) \approx -154$ kcal mol^{-1}] [for the definition of $\Delta E(2)$ see ref.[32]] with one of the two lone pairs at oxygen atom O1, resulting in an occupation number of 1.72 e of the donator orbital in both conformers. Another, but somewhat less effective, interaction occurs between the weakly occupied 2*p* orbital at C2 and the π orbital of the C3–C4 double bond [$\Delta E(2) \approx -82$ kcal mol^{-1}], with an occupation number of about 1.81 e. The σ→σ* interaction between the σ(C5–Me) and the σ(C6–Me) orbitals in **XXVI** on the one hand and the σ*(C6–Me) and the σ*(C5–CMe) orbitals on the other hand is weak and does not exceed –3.0 kcal mol^{-1}. In addition, there is a stabilizing hyperconjugative interaction of –6.4 kcal mol^{-1} in **XXVI** between σ(C5–Me) and π*(C3–C4). The NBO analysis of **XXVI** gave no indication of a stabilizing interaction between the pseudoaxial Me group at C6 and the carbenium ion center C2 ($\sigma_{C6-Me} \rightarrow 2p_{C2}$) (vide infra). According to the NBO analyses of **XXV** and **XXVI**, the N and O atoms of

Table 2. Summary of NBO analyses (6-31+G* basis set, energies in kcal mol^{-1}, charges and populations in e) of dihydropyran oxocarbenium ions **XXV** and **XXVI**.

Parameter	XXV	XXVI
Q(C2)	0.8029	0.8023
Q(C3)	–0.5511	–0.5612
Q(C4)	0.0997	0.1007
Q(O1)	–0.5727	–0.5737
Q[S(O8)(NMe)]	0.3709	0.3705
*n**(C2)	0.4949	0.4993
n(O1)	1.7245	1.7227
π(C3–C4)	1.8056	1.8041
$\Delta E_{n(O1)\rightarrow n^*(C2)}$	–154.2	–154.5
$\Delta E_{\pi(C3-C4)\rightarrow n^*(C2)}$	–81.8	–82.7
$\Delta E_{\sigma(C5-Me)\rightarrow \pi^*(C3-C4)}$	–1.9	–6.4
$\Delta E_{\sigma(C5-Me)\rightarrow \sigma^*(C6-Me)}$	–	–2.6
$\Delta E_{\sigma(C6-Me)\rightarrow \sigma^*(C5-Me)}$	–	–2.4

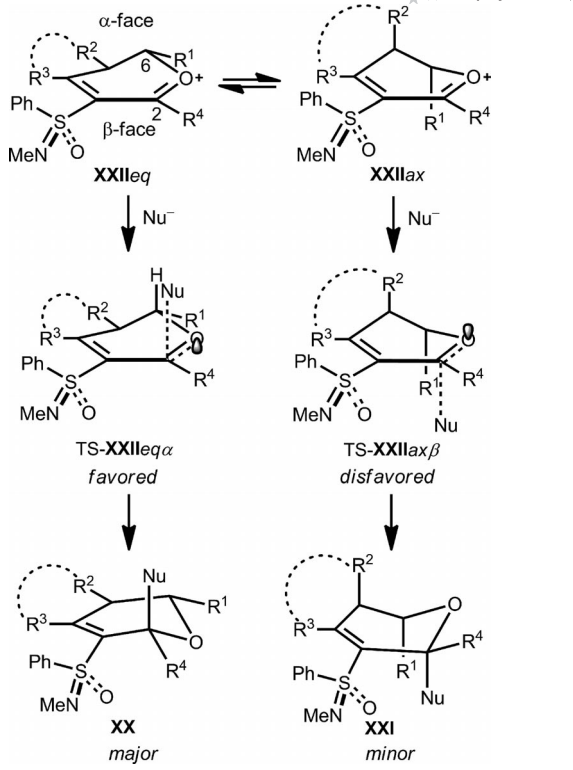
the sulfoximine group, which carries a positive charge of 0.37 e, are also not engaged in a stabilizing interaction with C2.

The difference in energy between **XXV** and **XXVI** is only +0.20 kcal mol^{-1}. To address this small energy difference we estimated the possible influence of the solvent in further geometry optimizations (MP2/6-31+G*) by employing the polarizable continuum model (PCM)[34] and the conductor polarizable continuum model (CPCM)[35] method and using the dielectric constants for CH_2Cl_2 as implemented in Gaussian09. As in the vacuum, the two solvent models give very small energy differences. Isomer **XXVI** remains the more stable, with **XXV** being 0.37 (PCM) and 0.32 kcal mol^{-1} (CPCM) higher in energy. Because these energy differences are quite small, the energetic difference between **XXV** and its conformer also possessing the (R_S,5*R*,6*S*) configuration but pseudoaxial Me groups is most likely also small.

Selectivity Model for Sulfoximine-Substituted Dihydropyran Oxocarbenium Ions XXII

On the basis of the calculations for **XXV** and **XXVI** it is proposed that the dihydropyran oxocarbenium ions **XXII** adopt the two nonplanar conformations **XXII***eq* and **XXII***ax* (Scheme 17), the C5 and C6 substituents of which are in pseudoequatorial and pseudoaxial positions, respectively. Presumably the two conformers have low inversion barriers. The half-chair-like TSs TS-**XXII***eqα* and TS-**XXII***axβ* are envisioned for the reactions of conformers **XXII***eq* and **XXII***ax*, respectively, with Nu$^-$. These TSs, which are expected to be reactant-like,[36] each feature a half-chair-like conformation, an *anti*-addition of Nu$^-$ along a pseudoaxial trajectory to C2 that builds a lone pair at the O atom *anti*-periplanar to the forming C2–Nu bond, and staggering of substituents and lone pairs around the C–O bonds. Generally, the *anti*-addition of Nu$^-$ to cyclic six-membered oxocarbenium ions is kinetically preferred over the *syn*-addition that builds a lone pair at the O atom *syn*-periplanar to the forming C–Nu bond and causes eclipsing around the O–C bonds (*kinetic anomeric effect*).[18,37] Transition state TS-**XXII***eqα*, in which Nu$^-$ adds to C2 from the α-face, affords the major glycoside **XX**, whereas TS TS-**XXII***axβ*, which includes an addition of Nu$^-$ from the β-face, gives the minor glycoside **XXI**. Of the two TSs, TS-**XXII***eqα* should be energetically favored, because of smaller 1,3-diaxial strain.[37f,38] This also implies that conformer **XXII***eq* is the more reactive one.

Although the sulfoximine group of **XXII** is in close proximity to C2, the TS models do not consider an a priori possible influence of this chiral group upon the facial selectivity. This seems to be justified for the following reasons. Firstly, the ab initio calculations for **XXV** and **XXVI** did not reveal any specific stabilizing interaction between C2 and the O or N atom of the sulfoximine group that might lead to a particular C3–S conformation and thus shielding of the β-face in the TS. Secondly, the sulfoximine group of



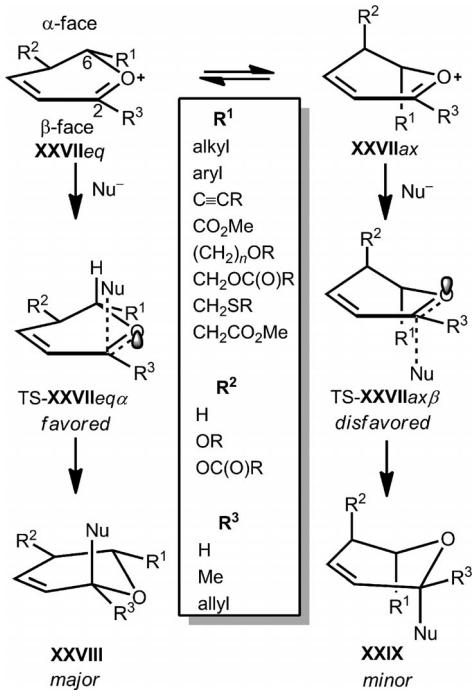
Scheme 17. Stereoselectivity model for the reaction of the sulfoximine-substituted dihydropyran oxocarbenium ions **XXII** with Nu$^-$.

XIX was most likely protonated or Lewis-acid-coordinated,[13,39] because of the use of excess HX and $TiCl_4$. The aminosulfoxonium group in the corresponding oxocarbenium ions **XXIII** and **XXIV** (cf. Scheme 16) should be even less capable of causing a stabilizing interaction with C2 and thus shielding of the β-face.

Selectivity Model for Dihydropyran Oxocarbenium Ions XXVII

Dihydropyran oxocarbenium ions of type **XXVII** (Scheme 18), in which the double bonds carry no substituents, have served as key intermediates in numerous glycosidations of glycal acetates (Ferrier reaction) and 2-hydroxy(alkoxy)-5,6-dihydropyrans.[16i,40,41] With *O*- and *C*-nucleophiles they afford the 2,6-*trans*-configured glycosides **XXVIII** as major diastereomers and 2,6-*cis*-configured glycosides **XXIX** as minor diastereomers, irrespective of the substituent R^1 (*trans* stereoselectivity). Formation of **XXVIII** and **XIX** should, at least with *C*-nucleophiles, be kinetically directed. A selectivity model similar to that proposed for the reactivity of **XXII** can also serve to interpret the preferential production of the 2,6-*trans*-configured glycosides **XXVIII** from the dihydropyran oxocarbenium ions **XXVII** and Nu$^-$. The energetically favored TS TS-**XXVII***eqα* is attained on starting from the 5,6-diequatorial conformer **XXVII***eq*. It features 1) an *anti*-addition of Nu$^-$ along a pseudoaxial trajectory, 2) a half-chair-like conformation,[25,40,41c] and 3) a *syn*-1,3-diaxial arrangement of Nu

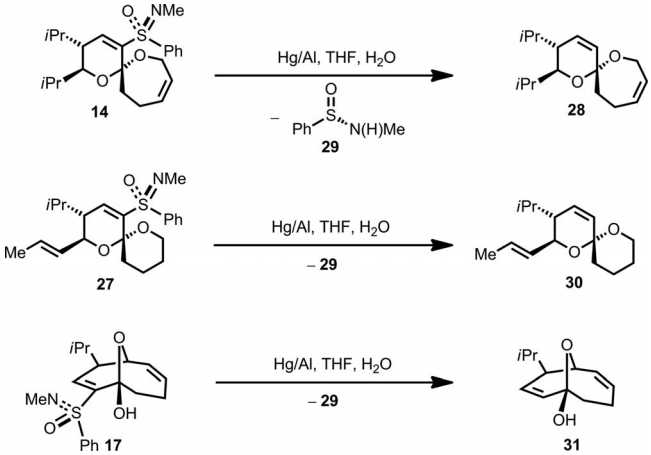
and 6-H, and it yields **XXVIII**. The alternative TS TS-**XXVII***axβ*, which has basic features similar to those of TS-**XXVII***eqα* but has R^1 in a pseudoaxial position, gives the minor diastereomer **XXIX** and is kinetically disfavored because of 1,3-diaxial strain.[37] The stereoselectivity model depicted in Scheme 18 accommodates the large number of different substituents R^1 that have been studied without the necessity to consider their possible interaction with C2 in the ground or transition state.



Scheme 18. Stereoselectivity model for the reactions of dihydropyran oxocarbenium ions of type **XXVII** with Nu^-.

Reduction of Spiro- and Bicyclic Alkenylsulfoximines

Various synthetic transformations of the alkenylsulfoximine moieties of the spirocycles **14**, **15**, **16**, **22**, **26**, and **27**, and also of the oxabicycles **17** and **19**, can be envisioned,



Scheme 19. Reduction of spiro and bicyclic alkenylsulfoximines.

including the reduction of the sulfoximine groups. We have thus far only probed the substitution of the sulfoximine groups in the spirocycles **15** and **27** and the oxabicycle **18** by H atoms. The alkenylsulfoximines **14** and **27** were treated with Al/Hg in THF/H_2O,[42] which afforded the corresponding spiroketals **28** and **30** in 86% and 76% yields, respectively (Scheme 19). A similar reduction of sulfoximine **18** delivered oxabicycle **31** in 75% yield. In addition, the enantiomerically pure sulfinamide **29** was obtained in 59% yield. The conversion of **29** into (*S*)-*N,S*-dimethyl-*S*-phenylsulfoximine, the starting material for the synthesis of **1** and **5**, had already been described.[43]

Conclusions

Mono- and bicyclic 2-hydroxy-dihydropyrans, each containing a sulfoximine group and two stereogenic centers, are accessible from enantio- and diastereomerically pure sulfoximine-substituted homoallylic alcohols in good yields. The spiroannulation of the 2-hydroxy-dihydropyrans through stereoselective glycosidation, RCDEM, and intramolecular Prins cyclization allowed for the synthesis of unsaturated spiroketals and spiroethers containing dihydropyran subunits. The high stereoselectivities of the inter- and intramolecular reactions between the 2-hydroxy-dihydropyrans and *O*- or *C*-nucleophiles are remarkable. The preferential formation of the glycosides with the newly introduced C2 substituent and the C6 substituent in *trans* relative configuration can be explained in terms of a half-chair-like transition state of glycosidation, featuring in each case an *anti*-attack of the nucleophile at C2 of the dihydropyran oxocarbenium ion, a *syn* 1,3-diaxial arrangement of the forming C2–Nu bond and the H atom at C6, and a staggering around the C–O bonds. This transition state model can also be applied to the 2,6-*trans* stereoselective reaction of other dihydropyran oxocarbenium ions. According to ab initio calculations the structure of a dihydropyran oxocarbenium ion is characterized by a half-chair-like conformation and a short C2–O and long C6–O bond. The energy difference between the conformers with pseudoaxial and pseudoequatorial substituents is very small. Spiroketals each containing only one double bond can also be obtained from sulfoximine-substituted homoallylic alcohols by conventional stereoselective internal spiroketalization of the corresponding sulfoximine-substituted dihydroxy ketones with acids in HFIP. Because of the modularity of the synthesis of the dihydropyrans, derivatives with two alkenyl groups at C2 and C6 and either a OH or a CH_2CO_2Et group at C2 are available. Their RCDEM led to oxabicycles with an oxabicyclo[4.3.1]decane skeleton.

Experimental Section

General: All reactions were carried out under argon in oven-dried glassware with use of Schlenk and syringe techniques. Sulfoximine-substituted homoallylic alcohols **1a**, **1b**, and (*Z*)-**5** were synthesized from (*S*)-*S*-methyl-*S*-phenyl-sulfoximine of ≥98% *ee*[39b] and 2-

methylpropanal, but-2-enal, and cyclohexanone, respectively, as described previously.[14,15] CH_2=C(OSiMe_3)OEt was obtained from EtOAc, lithium diisopropylamide, and Me_3SiCl, together with $Me_3SiCH_2CO_2Et$, in a ratio of 1:1 by a procedure described for the synthesis of allegedly pure CH_2=C(OSiMe_3)OEt.[44] Et_2O and THF were distilled from sodium-lead/benzophenone. Toluene was distilled from sodium-lead. CH_2Cl_2 and DMF were distilled from CaH_2. Dess–Martin periodinane, (PCy_3)(H_2IMes)Ru(CHPh), and all other reagents were obtained from commercial sources and used without further purification unless otherwise stated. *n*BuLi was standardized by titration with diphenylacetic acid. Analytical thin-layer chromatography (TLC) was performed on pre-coated TLC plates (E. Merck, silica gel 60 F_{254}, layer thickness 0.2 mm). Flash chromatography was performed with silica gel 60 (E. Merck, 0.063–0.200 mm), and HPLC was performed with a chromasil-100–30 column. ^{1}H and ^{13}C NMR spectra were recorded with Varian VXR 300, Innova 400, or Varian Unity 500 instruments. Chemical shifts are reported relative to TMS (δ 0.00 ppm) as internal standard. Splitting patterns in the ^{1}H NMR spectra are designated as s, singlet; d, doublet; dd, double doublet; t, triplet; q, quartet; quint, quintet; sept, septet; m, multiplet; br., broad and combinations thereof. Peaks in the ^{13}C NMR spectra are denoted as "u" for carbons with zero or two attached protons or as "d" for carbons with one or three attached protons, as determined from the APT pulse sequence. Peaks in the ^{1}H NMR spectra were assigned by GMQCOSY and HETCOR and those in the ^{13}C NMR spectra by DEPT experiments. Low-resolution spectra were recorded with a Varian MAT 212 mass spectrometer, and secondary ion mass spectra were recorded with a Finnigan MAT mass spectrometer. IR spectra were recorded with a Perkin–Elmer FTIR S spectrometer. Absorptions are given in cm^{-1}; only peaks of $\nu \geq 800\ cm^{-1}$ are listed; s = strong, m = medium, and w = weak. Optical rotations were measured with a Perkin–Elmer Model 241 polarimeter at approximately 22 °C.

General Procedure for the Hydroxyalkylation of Alkenylsulfoximines 1a and (*E*)-5 (GP1): *n*BuLi (690 μL of 1.60 M solution in *n*-hexane, 1.1 mmol) was added at –78 °C to a solution of the alkenylsulfoximine (1.0 mmol) in THF (10 mL) and the mixture was stirred at 0 °C for 3 h. A solution of the corresponding aldehyde (2.0 mmol) in THF (3 mL) was then added at –78 °C and the mixture was stirred for 2 h. Subsequently, half-saturated aqueous NaCl (10 mL) was added and the mixture was extracted with EtOAc. The combined organic phases were dried (Na_2SO_4) and concentrated in vacuo. Purification by flash chromatography gave the allylic alcohol as mixture of diastereomers.

General Procedure for the Oxidation of the Allylic Alcohols 3a, 3b, 7a, and 7b (GP2): Dess–Martin periodinane (360 μL of 15 wt.-% solution in CH_2Cl_2, 0.17 mmol) was added to a solution of a mixture of the diasteromeric allylic alcohols (0.10 mmol) in CH_2Cl_2 (5 mL). The mixture was stirred at ambient temperature for 30 min, after which all of the starting material had been consumed as indicated by TLC. The mixture was then treated with aqueous $Na_2S_2O_3$ (10 mL, 10 wt.-%) and saturated $NaHCO_3$ (20 mL). The mixture was stirred for 1 h and then extracted with EtOAc. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Flash chromatography afforded the enone.

General Procedure for the Deprotection and Cyclization of Silyloxy Ketones 4a, 4f, 8a, and 8b (GP3): A solution of (nBu)$_4$NF·3 H_2O (420 mg, 1.30 mmol) in THF (4 mL) was added to a solution of the silyloxy ketone (0.90 mmol) in THF (10 mL). The mixture was stirred at ambient temperature for 1 h, after which all of the starting material had been consumed as indicated by TLC. The mixture was treated with H_2O (5 mL), stirred for 30 min, and then extracted with EtOAc. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Flash chromatography afforded the hemiketal.

General Procedure for the Deprotection and Cyclization of Silyloxy Ketones 4b, 4c, 4d, 4f, and 4g (GP4): A mixture of AcOH, THF, H_2O, and HCl (5 mL) in a ratio of 8:8:1:0.2 was added to a solution of the silyloxy ketone (0.90 mmol) in THF (3 mL). The mixture was stirred at ambient temperature for 3 h, after which time all of the starting material had been consumed as indicated by TLC. The mixture was then treated with a half-saturated aqueous of $NaHCO_3$ (30 mL), stirred for 30 min, and then extracted with EtOAc. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Flash chromatography afforded the hemiketal.

General Procedure for the *C*-Glycosidation of Hemiketals 9a and 10a (GP5): $TiCl_4$ (0.10 mL, 0.90 mmol) and allyltrimethylsilane (150 μL, 0.90 mmol) were added at –78 °C to a solution of the hemiketal (0.15 mmol) in CH_2Cl_2 (5 mL). The mixture was allowed to warm gradually to –40 °C and to stir at this temperature for 4.5 h. Subsequently, saturated aqueous NH_4Cl was added and the mixture was allowed to warm to ambient temperature. Water was added and the mixture was extracted with CH_2Cl_2, dried (Na_2SO_4), and concentrated in vacuo. Purification by flash chromatography on silica gave the 2,2-dienyl dihydropyran.

General Procedure for the RCDEM of 2,2-Dienyl Dihydropyrans 11, 12, and 13 (GP6): A solution of the 2,2-dienyl dihydropyran (0.49 mmol) in CH_2Cl_2 (8 mL) was added to a solution of (PCy_3)(H_2IMes)RuCHPh (0.024 mmol) in CH_2Cl_2 (90 mL). The mixture was stirred at room temperature for 16 h, after which all of the starting material had been consumed as indicated by TLC. The mixture was filtered through a short pad of silica gel, and the solvent was removed in vacuo. Purification by flash chromatography gave the spirocycle.

General Procedure for the RCDEM of 2,6-Dienyl Dihydropyrans 9c and 18 (GP7): A solution of the 2.6-dienyl dihydropyran (0.49 mmol) in CH_2Cl_2 (8 mL) was added to a solution of (PCy_3)(H_2IMes)Ru(CHPh) (0.024 mmol) in CH_2Cl_2 (90 mL). The mixture was stirred at reflux for 16 h, after which all of the starting material had been consumed as indicated by TLC. The mixture was filtered through a short pad of silica gel, and the solvent was removed in vacuo. Purification by flash chromatography gave the oxabicycle.

General Procedure for the PC of Hemiketals 9b and 10b (GP8): A solution of $TiCl_4$ (0.10 mL, 0.90 mmol) in CH_2Cl_2 (5 mL) was added slowly at –78 °C to a solution of the hemiketal (0.30 mmol) in CH_2Cl_2 (5 mL). The mixture was stirred at this temperature for 2 h. Subsequently, saturated aqueous $(NH_4)_2CO_3$ was added and the mixture was allowed to warm to ambient temperature. Water was added, and the mixture was extracted with CH_2Cl_2, dried ($MgSO_4$), and concentrated in vacuo. Purification by flash chromatography on silica gave a mixture of the chlorinated compounds.

General Procedure for the Synthesis of the Hydroxy Ketones 24 and 25 (GP9): *n*BuLi (0.57 mL of 1.60 M solution in *n*-hexane, 0.90 mmol) was added at –78 °C to a solution of alkenylsulfoximine **1** (0.70 mmol) in THF (25 mL), and the mixture was stirred at 0 °C for 3 h. A solution of γ-valerolactone (1.40 mmol) in THF (5 mL) was then added at –78 °C, and the mixture was stirred for 2 h. Subsequently, half-saturated aqueous NaCl (20 mL) was added, and the mixture was extracted with EtOAc. The combined organic

phases were dried ($MgSO_4$) and concentrated in vacuo. Purification by flash chromatography gave the hydroxy ketone.

General Procedure for the Synthesis of Spiroketals 26 and 27 (GP10): A solution of hydroxy ketone (80 mg, 0.15 mmol) in $(CF_3)_2CHOH$ (5 mL) was treated with *p*TsOH (79 mg, 0.45 mmol), and the mixture was stirred at ambient temperature for 3 h. Half-saturated aqueous $NaHCO_3$ (10 mL) was then added and the mixture was extracted with EtOAc. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo. Purification by flash chromatography (EtOAc/cyclohexane 1:5) gave the spiroketal.

General Procedure for the Reduction of Alkenylsulfoximines 15, 18, and 27 (GP11): Small pieces of aluminum amalgam [small pieces of aluminum foil (500 mg) were added to a solution of $HgCl_2$ (500 mg) in 25 mL of water and the mixture was stirred for 30 s; the aluminum foil was then washed with water and THF] were added to a solution of the alkenylsulfoximine (0.10 mmol) in wet THF (2 mL). The mixture was stirred at room temperature for 3 h, after which all of the starting material had been consumed as indicated by TLC. The mixture was filtered through a short pad of celite, and CH_2Cl_2 (20 mL) was then added to the filtrate, which was subsequently washed with water, dried ($MgSO_4$), and concentrated in vacuo. Purification by flash chromatography gave the alkene.

(5*R*,8*R*,9*S*,*E*)-9-(Triethylsilyloxy)-8-isopropyl-10-methyl-6-[(*R*)-*N*-methyl-*S*-phenyl-sulfonimidoyl]-undeca-1,6-dien-5-ol [(*R*)-3a] and (5*S*,8*R*,9*S*,*E*)-9-(Triethylsilyloxy)-8-isopropyl-10-methyl-6-[(*R*)-*N*-methyl-*S*-phenyl-sulfonimidoyl]-undeca-1,6-dien-5-ol [(*S*)-3a]: Treatment of alkenylsulfoximine **1a** (800 mg, 1.90 mmol) and pent-4-enal (300 μL, 2.20 mmoliastereomeric alcohols (*R*)-**3a** and (*S*)-**3a** (890 mg, 92%) as a colorless oil; they were separated by a combination of flash chromatography and HPLC.

Isomer (*R*)-3a or (*S*)-3a: $[\alpha]_D$ = –78.4 (*c* = 1.75, CH_2Cl_2); R_f = 0.38 (*n*-hexane/EtOAc 9:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.40 (q, *J* = 8.2 Hz, 6 H, Si-CH_2CH$_3$), 0.65 (d, *J* = 6.9 Hz, 6 H, two CH_3), 0.70 (d, *J* = 6.9 Hz, 3 H, CH_3), 0.78 (t, *J* = 8.0 Hz, 9 H, Si-CH_2CH_3), 0.85 (d, *J* = 6.9 Hz, 3 H, CH_3), 1.35 [m, 1 H, C*H*(CH_3)$_2$], 1.58 [m, 1 H, C*H*(CH_3)$_2$], 1.65 (m, 1 H, CH*H*-CH=CH_2), 2.10 (m, 2 H, C*H*H-CH_2CH=CH_2, C*H*-CH=C), 2.30 (m, 2 H, CH*H*-CH_2CH=CH_2, C*H*H-CH=CH_2), 2.59 (s, 3 H, N-CH_3), 3.43 (d, *J* = 7.3 Hz, 1 H, CH-OSi), 4.47 (dd, *J* = 9.4, 3.0 Hz, 1 H, C*H*-OH), 4.96 (m, 2 H, CH_2=CHCH_2), 5.64 (br. s, 1 H, OH), 5.76 (m, 1 H, CH_2=C*H*CH_2), 6.26 (d, *J* = 11.3 Hz, 1 H, CH=C-S), 7.45 (m, 3 H, Ph), 7.81 (m, 2 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 5.6 (u), 7.2 (d), 18.4 (d), 19.8 (d), 21.4 (d), 21.9 (d), 29.3 (d), 29.4 (d), 30.6 (u), 33.6 (d), 36.3 (u), 47.5 (d), 69.4 (d), 78.0 (d), 115.2 (u), 128.9 (d), 129.2 (d), 132.4 (d), 138.1 (d), 139.2 (u), 142.9 (u), 144.2 (d) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3888 (w), 3570 (w), 3284 (s), 2957 (m), 1878 (s), 1638 (m), 1463 (s), 1382 (m), 1237 (s), 1145 (s), 1081 (s), 1009 (s), 913 (m), 860 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 508 [M + 1]$^+$ (1), 491 (20), 376 (10), 335 (30), 271 (18), 270 (90), 187 (50), 156 (100). HRMS: calcd. for $C_{28}H_{49}NO_3SSi$: 507.3202; found 507.3204.

Isomer (*S*)-3a or (*R*)-3a: $[\alpha]_D$ = –56.6 (*c* = 1.20, CH_2Cl_2); R_f = 0.39 (*n*-hexane/EtOAc 9:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.53–0.60 (m, 9 H, Si-CH_2CH$_3$, CH_3), 0.65 (d, *J* = 6.6 Hz, 3 H, CH_3), 0.80 (d, *J* = 6.6 Hz, 3 H, CH_3), 087–0.97 (m, 12 H, Si-CH_2CH_3, CH_3), 1.26 [m, 2 H, C*H*(CH_3)$_2$, CH*H*-CH=CH_2], 1.68 [m, 1 H, C*H*(CH_3)$_2$], 1.90–2.01 (m, 2 H, C*H*H-CH_2CH=CH_2, C*H*H-CH=CH_2), 2.15 (br. t, *J* = 9.4 Hz, 1 H, C*H*-CH=C), 2.76 (s, 3 H, N-CH_3), 3.58 (d, *J* = 6.6 Hz, 1 H, CH-OSi), 4.46 (dd, *J* = 9.9, 1.9 Hz, 1 H, C*H*-OH), 4.88 (m, 2 H, CH_2=CHCH_2), 5.67 (m, 2 H, CH_2=C*H*CH_2, OH), 6.92 (d, *J* = 11.0 Hz, 1 H, CH=C-S), 7.43 (m, 3 H, Ph), 7.78 (m, 2 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 5.7 (u), 7.2 (d), 18.7 (d), 19.1 (d), 20.7 (d), 21.5 (d), 29.4 (d), 29.5 (d), 30.7 (u), 33.6 (d), 36.4 (u), 47.6 (d), 69.3 (d), 77.8 (d), 115.1 (u), 128.7 (d), 129.0 (d), 132.2 (d), 137.9 (d), 141.1 (u), 141.9 (u), 145.2 (d) ppm.

(6*R*,9*R*,10*S*,*E*)-9-Isopropyl-11-methyl-7-[(*R*)-*N*-methyl-*S*-phenyl-sulfonimidoyl]-10-(triethylsilyloxy)dodeca-1,7-dien-6-ol [(*R*)-3b] and (6*S*,9*R*,10*S*,*E*)-9-Isopropyl-11-methyl-7-[(*R*)-*N*-methyl-*S*-phenyl-sulfonimidoyl]-10-(triethylsilyloxy)dodeca-1,7-dien-6-ol [(*S*)-3b]: Treatment of sulfoximine **1a** (890 mg, 2.10 mmol) and hex-5-enal (300 mg, 3.15 mmol) as described in **GP1** afforded a 1:1 mixture (^{1}H NMR: NMe) of the diastereomeric alcohols (*R*)-**3b** and (*S*)-**3b** (1.00 g, 91%) as a colorless oil; they were separated by a combination of flash chromatography and HPLC.

Isomer (*S*)-**3b** or (*R*)-**3b:** $[\alpha]_D$ = –61.8 (*c* = 1.00, CH_2Cl_2); R_f = 0.21 (EtOAc/cyclohexane 1:9). ^{1}H NMR (300 MHz, C_6D_6): δ = 0.60 (q, *J* = 7.9 Hz, 6 H, Si-CH_2CH$_3$), 0.68 (d, *J* = 6.8 Hz, 3 H, CH_3), 0.74 (d, *J* = 6.8 Hz, 3 H, CH_3), 0.91 (d, *J* = 6.8 Hz, 3 H, CH_3), 0.99 (d, *J* = 6.8 Hz, 3 H, CH_3), 1.02 (t, *J* = 7.9 Hz, 9 H, Si-CH_2CH_3), 1.31–1.42 [m, 2 H, C=CH-CH-CHOSi-C*H*(CH_3)$_2$, COH-CH_2-C*H*H], 1.51 (ddd, *J* = 13.3, 9.7, 5.9, 3.9 Hz, 1 H, CHOH-CH*H*), 1.80 [m, *J* = 6.9 Hz, 1 H, C=CH-CH-C*H*(CH_3)$_2$], 1.81–1.85 (m, 1 H, COH-CH_2-C*H*H), 2.00 (ddd, *J* = 6.9, 1.3 Hz, 2 H, CH_2-CH=CH), 2.15 (ddd, *J* = 13.4, 9.9, 4.5 Hz, 1 H, CHOH-CH*H*), 2.37 (ddd, *J* = 11.1, 8.2, 2.2 Hz, 1 H, C=CH-C*H*), 2.80 (s, 3 H, N-CH_3), 3.62 (m, *J* = 6.4, 2.0 Hz, 1 H, CH-OSi), 4.80 (m, *J* = 9.9, 3.7 Hz, 1 H, C*H*-OH), 4.94 (dd, *J* = 10.3 Hz, 1 H, CH_2-CH=CH*H*), 4.97 (dd, *J* = 17.1, 1.4 Hz, 1 H, CH_2-CH=CH*H*), 5.72 (ddd, *J* = 17.1, 10.3, 6.7 Hz, 1 H, CH_2-C*H*=CH_2), 6.96–7.08 (m, 3 H, Ph), 7.32 (d, *J* = 11.1 Hz, 1 H, CH=C-S), 7.93–7.97 (m, 2 H, Ph) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 5.5 (u), 7.0 (d), 18.6 (d), 18.7 (d), 20.3 (d), 21.2 (d), 26.1 (u), 29.1 (d), 29.3 (d), 33.3 (d), 33.6 (u), 36.9 (u), 47.6 (d), 69.8 (d), 77.9 (d), 114.4 (u), 128.6 (d), 129.0 (d), 131.6 (d), 138.5 (d), 141.9 (u), 143.3 (u), 143.9 (d) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3279 (m), 2957 (s), 1463 (m), 1416 (w), 1384 (w), 1243 (s), 1149 (m), 1081 (s), 1007 (m), 861 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 524 (4), 523 (10), 522 (26), 521 [M]$^+$ (3), 492 (11), 452 (16), 367 (10), 366 (34), 335 (15), 334 (22), 323 (15), 293 (19), 270 (36), 266 (27), 191 (11), 188 (10), 187 (63), 159 (31), 157 (14), 155 (100), 124 (38), 15 (53), 107 (14), 102 (26). HRMS (EI): calcd. for $C_{29}H_{51}NO_3SSi$: 521.3358; found 521.3358.

Isomer (*R*)-3b or (*S*)-3b: $[\alpha]_D$ = –42.9 (*c* = 1.00, CH_2Cl_2), R_f = 0.28 (EtOAc/cyclohexane 1:9). ^{1}H NMR (300 MHz, C_6D_6): δ = 0.47 (q, *J* = 7.8 Hz, 6 H, Si-CH_2CH$_3$), 0.81 (d, *J* = 6.9 Hz, 3 H, CH_3), 0.82 (d, *J* = 6.9 Hz, 3 H, CH_3), 0.84 (d, *J* = 6.9 Hz, 3 H, CH_3), 0.85 (d, *J* = 6.9 Hz, 3 H, CH_3), 0.87 (t, *J* = 7.8 Hz, 9 H, Si-CH_2CH_3), 1.52 [m, *J* = 6.8 Hz, 1 H, CHOSi-C*H*(CH_3)$_2$], 1.64–1.79 [m, *J* = 6.8, *J* = 6.7 Hz, 2 H, CHOH-CH_2-CH*H*, C=CH-CH-C*H*(CH_3)$_2$], 1.85–2.00 (m, 1 H, CHOH-CH_2-CH*H*), 2.02–2.18 (m, 3 H, COH-C*H*H, CH_2-CH=CH), 2.27 (ddd, *J* = 10.4 Hz, 1 H, C=CH-C*H*), 2.69 (m, 1 H, COH-C*H*H), 3.51 (m, *J* = 7.3, 4.85 Hz, 1 H, CH-OSi), 4.81 (m, *J* = 9.9, 3.8 Hz, 1 H, C*H*-OH), 4.97 (dd, *J* = 10.1 Hz, 1 H, CH_2-CH=CH*H*), 5.04 (dd, *J* = 17.1, 3.3, 1.6 Hz, 1 H, CH_2-CH=CH*H*), 5.81 (ddd, *J* = 17.1, 10.3, 6.7 Hz, 1 H, CH_2-C*H*=CH_2), 6.45 (d, *J* = 11.1 Hz, 1 H, CH=C-S), 7.03–7.06 (m, 3 H, Ph), 7.95–7.98 (m, 2 H, Ph) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 5.4 (u), 7.0 (d), 18.3 (d), 19.5 (d), 21.0 (d), 21.5 (d), 26.1 (u), 28.9 (d), 29.2 (d), 33.4 (d), 36.8 (u), 47.4 (d), 70.2 (d), 78.1 (d), 114.4 (u), 128.7 (d), 129.5 (d), 131.9 (d), 138.7 (d), 142.7 (u), 144.7 (u) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3291 (m), 2957 (s), 2878 (s), 1638 (w), 1464 (m), 1416 (w), 1237 (s), 1144 (s), 1081 (s), 1008 (s), 1008 (m), 910 (w), 862 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 524 (0.5), 523 (5), 522 (14),

521 $[M]^+$ (3), 492 (8), 452 (20), 366 (19), 335 (18), 334 (37), 323 (16), 293 (14), 270 (49), 267 (12), 266 (27), 187 (54), 159 (29), 157 (12), 155 (100), 124 (32), 115 (24), 107 (34), 102 (15). HRMS (EI): calcd. for $C_{29}H_{51}NO_3SSi$: 521.3358; found 521.3360.

(8*R*,9*S*,*E*)-8-Isopropyl-10-methyl-6-[(*R*)-*N*-methyl-*S*-phenyl-sulfonimidoyl]-9-(triethylsilyloxy)-undeca-1,6-dien-5-one (4a): Treatment of a mixture of the allylic alcohols (*R*)-**3a** and (*S*)-**3a** (101 mg, 0.20 mmol) with Dess–Martin periodinane (900 μL, 0.30 mmol) as described in **GP2** afforded ketone **4a** (90 mg, 89%) as a colorless syrup. $[\alpha]_D$ = –116.6 , (*c* = 0.75, CH_2Cl_2); R_f = 0.42 (hexane/EtOAc 9:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.60 (q, *J* = 8.0 Hz, 6 H, Si-CH_2CH$_3$), 0.68 (d, *J* = 6.9 Hz, 3 H, CH$_3$), 0.74 (d, *J* = 6.6 Hz, 3 H, CH$_3$), 0.78 (d, *J* = 6.8 Hz, 3 H, CH$_3$), 0.89 (d, *J* = 6.6 Hz, 3 H, CH$_3$), 0.96 (t, *J* = 8.3 Hz, 9 H, Si-CH$_2$CH_3), 1.50 [m, 1 H, C*H*(CH$_3$)$_2$], 1.74–1.50 [m, 1 H, C*H*(CH$_3$)$_2$], 2.10 (dt, *J* = 8.5, 1.7 Hz, 1 H, C*H*-CH=C), 2.34 (br. q, *J* = 6.4 Hz, 2 H, CH_2-CH=CH$_2$), 2.68 (m, 1 H, CH*H*CO), 2.81 (s, 3 H, N-CH$_3$), 2.92 (m, 1 H, C*H*HCO), 3.58 (dd, *J* = 6.6, 1.4 Hz, 1 H, CH-OSi), 4.98 (m, 2 H, CH_2=CHCH$_2$), 5.78 (m, 1 H, CH$_2$=C*H*CH$_2$), 6.86 (d, *J* = 11.5 Hz, 1 H, CH=C-S), 7.44–7.56 (m, 3 H, Ph), 7.85 (m, 2 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 5.7 (u), 7.2 (d), 18.6 (d), 19.0 (d), 21.1 (d), 21.5 (d), 27.4 (u), 29.5 (d), 29.7 (d), 33.6 (d), 43.8 (u), 48.8 (d) 78.1 (d), 115.3 (u), 128.6 (d), 128.9 (d), 132.6 (d), 136.8 (d), 139.6 (u), 143.3 (u), 148.3 (d), 199.9 (u) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3373 (m), 2955 (s), 1742 (s), 1703 (s), 1634 (w), 1453 (s), 1380 (s), 1248 (s), 1150 (s), 1081 (s), 1003 (m), 917 (m), 854 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 505 $[M]^+$ (8), 433 (10), 350 (5), 320 (7), 319 (22), 318 (100), 307 (30), 278 (11), 269 (20), 265 (35), 248 (11), 239 (13), 194 (20), 187 (81), 167 (70), 159 (48), 125 (37), 115 (83). HRMS: calcd. for $C_{28}H_{47}NO_3SSi$ 505.3045; found 505.3046.

(9*R*,10*S*,*E*)-9-Isopropyl-11-methyl-7-[(*R*)-*N*-methyl-*S*-phenyl-sulfonimidoyl]-10-(triethylsilyloxy)dodeca-1,7-dien-6-one (4b): Treatment of a mixture of the diastereomeric alcohols (*R*)-**3b** and (*S*)-**3b** (312 mg, 0.60 mmol) with Dess–Martin periodinane (1.5 mL of a 15 wt.-% in CH_2Cl_2, 0.90 mmol) as described in **GP2** afforded, after purification by flash chromatography (EtOAc/cyclohexane 1:9), ketone **4b** (299 mg, 96%) as a colorless syrup. $[\alpha]_D$ = –79.2 (*c* = 1.00, CH_2Cl_2); R_f = 0.33 (EtOAc/cyclohexane 1:9). ^{1}H NMR (400 MHz, C_6D_6): δ = 0.59 (q, *J* = 7.6 Hz, 6 H, Si-CH_2CH$_3$), 0.77 (d, *J* = 6.9 Hz, 3 H, CH$_3$), 0.80 (d, *J* = 6.9 Hz, 3 H, CH$_3$), 0.84 (d, *J* = 6.9 Hz, 3 H, CH$_3$), 0.85 (d, *J* = 6.9 Hz, 3 H, CH$_3$), 0.99 (t, *J* = 7.6 Hz, 9 H, Si-CH$_2$CH_3), 1.59 [m, *J* = 6.9 Hz, 1 H, CHOSi-C*H*(CH$_3$)$_2$], 1.79 [m, *J* = 6.9 Hz, 1 H, C=CH-CH-C*H*(CH$_3$)$_2$], 1.85–1.91 (q, *J* = 7.1, 1.8 Hz, 2 H, CO-CH$_2$-CH_2), 2.02 (dddd, *J* = 13.9, 6.6, 3.7, 1.6 Hz, 2 H, CH_2-CH=CH), 2.26 (ddd, *J* = 11.7, 8.7, 1.6 Hz, 1 H, C=CH-C*H*), 2.79 (dt, *J* = 18.3, 7.1, 2.9 Hz, 1 H, CO-C*H*H), 2.93 (s, 3 H, N-CH$_3$), 3.17 (dt, *J* = 18.4, 7.1 Hz, 1 H, CO-C*H*H), 3.58 (m, *J* = 6.6, *J* = 1.7 Hz, 1 H, CH-OSi), 4.95 (dd, *J* = 10.1, 3.3 Hz, 1 H, CH$_2$-CH=CH*H*), 5.00 (dd, *J* = 17.1, 3.6, 1.8 Hz, 1 H, CH$_2$-CH=CH*H*), 5.70 (ddd, *J* = 17.3, 10.1, 6.7 Hz, 1 H, CH$_2$-C*H*=CH$_2$), 6.97–7.05 (m, 3 H, Ph), 7.12 (d, *J* = 12.5 Hz, 1 H, CH=C-S), 8.02–8.05 (m, 2 H, Ph) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 5.9 (u), 7.3 (d), 18.7 (d), 19.0 (d), 21.2 (d), 21.5 (d), 22.9 (u), 29.6 (d), 29.7 (d), 33.2 (u), 33.7 (d), 44.5 (u), 49.1 (d), 78.3 (d), 115.1 (u), 128.8 (d), 129.2 (d), 132.1 (d), 138.2 (d), 140.6 (u), 144.9 (u), 146.6 (d), 200.3 (u) ppm. IR (capillary): $\tilde{\nu}$ = 3072 (w), 2958 (s), 2879 (s), 2807 (m), 1742 (s), 1670 (s), 1639 (w), 1463 (s), 1414 (m), 1373 (m), 1254 (s), 1153 (s), 1081 (s), 1005 (m), 913 (m), 858 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 519 $[M]^+$ (0.5), 491 (3), 490 (3), 478 (13), 476 (10), 365 (14), 364 (39), 335 (14), 333 (26), 332 (100), 322 (11), 321 (38), 308 (10), 293 (10), 292 (20), 279 (33), 270 (25), 237 (11), 188 (11), 187 (64), 178 (22), 167 (13), 163 (11), 159 (44), 156 (33), 135 (34), 124 (34), 116 (10), 115 (72), 107 (17), 103 (23). HRMS (EI): calcd. for $C_{29}H_{49}NO_3SSi$: 519.3202; found 519.3202.

Triethyl ((*R*)-2-Methyl-1-{(*S*,*E*)-2-[(*R*)-*N*-methyl-*S*-phenyl-sulfonimidoyl]}cyclohexyl)propoxysilane [(*E*)-5]: *n*BuLi (1.10 mL of 1.60 M solution in *n*-hexane, 1.77 mmol) was added at –78 °C to a solution of alkenylsulfoximine (*Z*)-**5** (700 mg, 1.61 mmol) in THF (25 mL) and the mixture was stirred at 0 °C for 3 h. Subsequently, half-saturated aqueous NaCl (10 mL) was added, and the mixture was extracted with EtOAc. The combined organic phases were dried ($MgSO_4$) and concentrated in vacuo, which gave alkenylsulfoximine (*E*)-**5** (690 mg, 98%) of 98% purity as a pale yellow oil. $[\alpha]_D$ = –38.1 (*c* = 1.00, CH_2Cl_2); R_f = 0.39 (EtOAc/cyclohexane 1:3). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.40 (q, *J* = 7.9 Hz, 6 H, Si-CH_2CH$_3$), 0.82 (q, *J* = 7.9 Hz, 9 H, Si-CH$_2$CH_3), 0.85 [d, *J* = 6.9 Hz, 3 H, (CH_3)$_2$CH], 0.88 [d, *J* = 6.9 Hz, 3 H, (CH_3)$_2$CH], 1.39–1.75 (m, 6 H, CH=C-CH$_2$-CH_2-CH_2-CH_2, C*H*HCH$_2$CH_2CHCHOSi), 1.94 [m, *J* = 11.5, 6.9, 4.8 Hz, 1 H, (CH$_3$)$_2$C*H*], 2.23 (dd, *J* = 10.8, 5.9 Hz, 1 H, C*H*-C=CH), 2.58 (ddd, *J* = 10.5, 5.8, 4.2 Hz, 1 H, CH*H*-C=CH), 2.68 (s, 3 H, N-CH$_3$), 2.87 (ddd, *J* = 10.5, 5.8, 4.2 Hz, 1 H, CH*H*-C=CH), 3.64 (dd, *J* = 6.1, 4.7 Hz, 1 H, CH-OSi), 6.39 (s, CH=C), 7.48–7.58 (m, 3 H, Ph), 7.88–7.94 (m, 2 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 5.4 (u), 7.1 (d), 17.1 (d), 20.2 (u), 23.4 (u), 28.0 (d), 29.4 (u), 31.0 (d), 32.5 (u), 49.9 (d), 78.1 (d), 124.9 (d), 128.7 (d), 128.8 (d), 131.9 (d), 140.7 (u), 160.3 (u) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2952 (m), 2875 (s), 1453 (s), 1238 (s), 1144 (s), 1106 (s), 1061 (m), 1010 (m), 856 (m), 807 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 435 $[M]^+$ (3), 406 (13), 280 (12), 270 (12), 265 (12), 251 (16), 249 (58), 237 (29), 187 (18), 171 (11), 169 (15), 159 (16), 157 (14), 156 (100), 148 (13), 133 (16), 125 (45), 123 (10), 115 (65), 109 (10), 103 (35). HRMS: calcd. for $C_{24}H_{41}NO_2SSi$: 435.2627; found 435.2639.

(*E*)-1-{(*R*)-2-[(*S*)-2-Methyl-1-(triethylsilyloxy)propyl]cyclohexylidene}-1-[(*R*)-*N*-methyl-*S*-phenyl-sulfonimidoyl]-hex-5-en-2-ol (7a): Treatment of alkenylsulfoximine (*E*)-**5** (1.300 g, 2.99 mmol) and pent-4-enal (350 μmL, 3.50 mmol) as described in **GP1** afforded a 9:1 mixture (^{1}H NMR: NMe) of the diastereomeric alcohols **7a** (1.00 g, 64%) as a colorless syrup. $[\alpha]_D$ = –58.0 (*c* = 1.80, CH_2Cl_2); R_f = 0.39 (*n*-hexane/EtOAc 9:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.35 (q, *J* = 8.2 Hz, 6 H, Si-CH_2CH$_3$), 0.76 (t, *J* = 8.0 Hz, 9 H, Si-CH$_2$CH_3), 0.84 (d, *J* = 7.2 Hz, 3 H, CH$_3$), 0.92 (d, *J* = 7.2 Hz, 3 H, CH$_3$), 1.30–1.87 [m, 9 H, CC*H*HCH_2CH_2CH_2, C*H*HCHOH, C*H*(CH$_3$)$_2$], 2.13 (m, 2 H, CH*H*CHOH, C*H*HCH=CH$_2$), 2.33 (m, 1 H, CH*H*CH=CH$_2$), 2.64 (s, 3 H, N-CH$_3$), 3.22 (br. d, *J* = 9.6 Hz, 1 H, C=CC*H*), 3.40 (br. d, *J* = 13.4 Hz, 1 H, C=CCH*H*), 3.93 (br. d, *J* = 9.9 Hz, 1 H, CH-OSi), 4.86 (dd, *J* = 9.8, 3.0 Hz, 1 H, C*H*-OH), 4.87–5.02 (m, 2 H, CH_2=CH), 5.80 (m, 1 H, C*H*=CH$_2$), 7.40–7.47 (m, 3 H, Ph), 7.92 (m, 2 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 5.5 (u), 7.2 (d), 16.9 (d), 19.1 (d), 20.9 (u), 27.7 (u), 27.8 (u), 29.4 (d), 30.7 (u), 31.3 (u), 32.5 (d), 37.5 (u), 44.2 (d), 70.1 (d), 75.8 (d), 114.6 (u), 128.7 (d), 128.8 (d), 132.0 (d), 138.5 (d), 138.8 (u), 141.5 (u), 158.3 (u) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3401 (w), 3133 (m), 2877 (s), 1728 (m), 1638 (m), 1450 (s), 1385 (m), 1236 (s), 1143 (s), 1107 (s), 1060 (s), 913 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 520 $[M]^+$ (2), 490 (4), 464 (6), 321 (5), 279 (13), 270 (25), 232 (16), 189 (25), 187 (48), 178 (25), 159 (23), 156 (100), 149 (22). HRMS: calcd. for $C_{29}H_{49}NO_3SSi{\cdot}C_4H_7$ 464.2654; found 464.2654.

(2*R*,*E*)-1-{2-[(*S*)-2-Methyl-1-(triethylsilyloxy)propyl]cyclohexylidene}-1-[(*R*)-*N*-methyl-*S*-phenyl-sulfonimidoyl]-hept-6-en-2-ol (7b): Treatment of alkenyl sulfoximine (*E*)-**5** (1.09 g, 2.51 mmol) and hex-5-enal (336 mg, 3.50 mmol) as described in **GP1** afforded

a 9:1 mixture (^{1}H NMR: NMe) of the diastereomeric alcohols **7b** (1.00 g, 75%) as a colorless syrup. $[\alpha]_D$ = –52.1 (c = 1.00, CH_2Cl_2); R_f = 0.18 (EtOAc/cyclohexane 1:9). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.35 (q, J = 7.8 Hz, 6 H, Si-CH_2CH$_3$), 0.78 (t, J = 7.8 Hz, 9 H, Si-CH$_2$CH_3), 0.85 (d, J = 6.9 Hz, 3 H, CH$_3$), 0.92 (d, J = 6.9 Hz, 3 H, CH$_3$), 0.93–1.04 (m, 1 H, C=C-CH$_2$-CH-CH$_2$), 1.30–1.47 (m, 4 H, C=C-CH$_2$-CH-CH$_2$-CH-CH$_2$), 1.60–1.79 (m, 6 H, C=C-CH_2-CH$_2$-CH_2-CH-CH$_2$), 1.83 [m, J = 6.9 Hz, 1 H, C=C-CH-CHOSi-CH(CH$_3$)$_2$], 1.97–2.08 (m, 3 H, COH-CH-CH$_2$-CH_2), 2.64 (s, 3 H, N-CH$_3$), 3.26 (br. d, J = 9.6 Hz, 1 H, C=C-CH-CHOSi), 3.42 (br. d, J = 13.2 Hz, 1 H, C=C-CHH-CH$_2$-CH$_2$-CH$_2$), 3.94 (m, J = 9.9 Hz, 1 H, CH-OSi), 4.82 (d, J = 9.3 Hz, 1 H, CH-OH), 4.88 (dd, J = 10.2 Hz, 1 H, CH$_2$-CH=CHH), 4.96 (dd, J = 17.1 Hz, 1 H, CH$_2$-CH=CHH), 5.78 (ddd, J = 17.1, 10.2, 6.7 Hz, 1 H, CH$_2$-CH=CH$_2$), 7.41–7.48 (m, 3 H, Ph), 7.89–7.96 (m, 2 H, Ph) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 5.3 (u), 7.1 (d), 16.7 (d), 19.0 (d), 20.8 (u), 26.3 (u), 27.6 (u), 29.3 (d), 29.8 (u), 30.5 (u), 32.4 (d), 33.7 (u), 37.8 (u), 44.0 (d), 70.5 (d), 75.7 (d), 114.1 (u), 128.6 (d), 128.7 (d), 131.8 (d), 138.8 (d), 139.0 (d), 141.6 (u), 157.8 (u) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3461 (m), 3070 (w), 2953 (s), 2877 (s), 2802 (w), 1640 (w), 1593 (m), 1459 (s), 1416 (w), 1364 (w), 1236 (s), 1142 (s), 1110 (s), 1073 (s), 1008 (s), 1008 (m), 909 (m), 864 (m), 805 (w) cm^{-1}. MS (EI, 70 eV): m/z (%) = 504 (3), 490 (2), 464 (6), 378 (2), 347 (3), 335 (4), 293 (2), 279 (10), 270 (22), 246 (8), 203 (12), 192 (40), 188 (10), 187 (52), 159 (26), 157 (14), 156 (100), 149 (16), 148 (22), 133 (10), 125 (29), 115 (50), 103 (21), 91 (11), 87 (50), 75 (23). HRMS (EI): calcd. for $C_{30}H_{51}NO_3SSi{\cdot}C_5H_9$ 464.2654; found 464.2654.

(*E*)-1-{(*R*)-2-[(*S*)-2-Methyl-1-(triethylsilyloxy)propyl]cyclohexylidene}-1-[(*R*)-*N*-methyl-*S*-phenyl-sulfonimidoyl]hex-5-en-2-one (8a): Treatment of a mixture of the diastereomeric allylic alcohols **7a** (200 mg, 0.38 mmol) with Dess–Martin periodinane (1.6 mL, 0.58 mmol) as described in **GP2** afforded ketone **8a** (179 mg, 90%) as a colorless oil. $[\alpha]_D$ = +28.0 (c = 1.50, CH_2Cl_2); R_f = 0.41 (*n*-hexane/EtOAc 8:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.45 (q, J = 8.2 Hz, 6 H, Si-CH_2CH$_3$), 0.74 (d, J = 7.2 Hz, 3 H, CH$_3$), 0.80–0.87 (m, 12 H, CH$_3$, Si-CH$_2$CH_3), 1.27–1.35 (m, 3 H, CCH$_2$CH$_2$CH_2CHH), 1.62–1.85 [m, 4 H, CH(CH_3)$_2$, CCHHCH_2CH$_2$], 2.16 (m, 4 H, CH_2CH=CH$_2$, CCHCHOSi, CCH$_2$CH$_2$CH_2CHH), 2.69 (m, 1 H, CHHCH$_2$CH=CH$_2$), 2.77 (s, 3 H, N-CH$_3$), 2.94 (m, 1 H, CHHCH$_2$CH=CH$_2$), 3.40 (br. d, J = 13.2 Hz, 3 H, CCHHCH_2CH$_2$), 3.95 (dd, J = 9.8, 1.6 Hz, 1 H, CH-OSi), 4.80–5.02 (m, 2 H, CH=CH_2), 5.76 (m, 1 H, CH=CH$_2$), 7.41–7.51 (m, 3 H, Ph), 7.97 (m, 2 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 5.7 (u), 7.3 (d), 16.2 (d), 19.4 (d), 20.8 (u), 25.4 (u), 27.6 (u), 28.1 (u), 29.7 (d), 30.9 (u), 31.7 (d), 45.1 (u), 46.0 (d), 75.3 (d), 115.0 (d), 128.8 (d), 128.9 (d), 132.3 (d), 137.2 (u), 141.3 (u), 157.6 (u), 201.5 (u) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3377 (w), 2950 (s), 1753 (s), 1700 (s), 1640 (m), 1611 (m), 1450 (m), 1416 (m), 1248 (s), 1148 (s), 110 (m), 1055 (s), 1001 (m), 914 (s) cm^{-1}. MS (EI, 70 eV): m/z (%) = 518 [M + 1]$^+$ (1), 488 (8), 464 (5), 362 (18), 321 (14), 320 (27), 319 (98), 291 (13), 279 (23), 277 (30), 249 (11), 187 (100), 176 (81), 115 (95). HRMS: calcd. for $C_{29}H_{47}NO_3SSi{-}CH_3N$: 488.2780; found 488.2780.

(*E*)-1-{(*R*)-2-[(*S*)-2-Methyl-1-(triethylsilyloxy)propyl]cyclohexylidene}-1-[(*R*)-*N*-methyl-*S*-phenyl-sulfonimidoyl]hept-6-en-2-one (8b): Treatment of a mixture of the diastereomeric allylic alcohols **7b** (480 mg, 0.90 mmol) with Dess–Martin periodinane (3.28 mL of 15wt.-% in CH_2Cl_2, 1.55 mmol) as described in **GP2** afforded, after purification by flash chromatography (EtOAc/cyclohexane 1:9), ketone **8b** (468 mg, 98%) as a colorless syrup. $[\alpha]_D$ = –17.9 (c = 1.00, CH_2Cl_2); R_f = 0.30 (EtOAc/cyclohexane 1:9). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.51 (q, J = 7.8 Hz, 6 H, Si-CH_2CH$_3$), 0.79 (d, J = 6.9 Hz, 3 H, CH$_3$), 0.91 (d, J = 6.9 Hz, 3 H, CH$_3$), 0.92 (t, J = 7.8 Hz, 9 H, Si-CH$_2$CH_3), 0.93–1.07 (m, 1 H, C=C-CH$_2$-CHH), 1.32–1.48 (m, 3 H, C=C-CHH-CH_2), 1.71–1.94 [m, 7 H, CO-CH$_2$-CH_2, C=C-CHH-CH$_2$-CH_2-CHH, CHOSi-CH(CH$_3$)$_2$], 2.08 (ddd, J = 7.4, 6.7, 1.8 Hz, 2 H, CO-CH$_2$-CH$_2$-CH_2), 2.36 (d, J = 9.8 Hz, 1 H, C=C-CH-CHOSi), 2.66–2.83 (m, 1 H, CO-CHH), 2.83 (s, 3 H, N-CH$_3$), 2.83–2.95 (m, 1 H, CO-CHH), 3.46 (dd, J = 13.2, 3.3 Hz,1 H, CH-OSi-CH-CHH), 4.02 (dd, J = 9.8, 1.7 Hz, 1 H, CH-OSi), 4.95 (dd, J = 10.3, 2.3 Hz, 1 H, CH$_2$-CH=CHH), 5.03 (dd, J = 17.1, 3.6, 1.6 Hz, 1 H, CH$_2$-CH=CHH), 5.80 (ddd, J = 17.1, 10.3, 6.6 Hz, 1 H, CH$_2$-CH=CH$_2$), 7.46–7.55 (m, 3 H, Ph), 8.02–8.06 (m, 2 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 5.5 (u), 7.2 (d), 16.0 (d), 19.3 (d), 20.7 (u), 22.4 (u), 25.3 (u), 27.9 (u), 29.6 (d), 30.9 (u), 31.6 (d), 32.9 (u), 45.1 (u), 45.9 (d), 75.3 (d), 114.8 (u), 128.8 (d), 128.9 (d), 132.4 (d), 137.8 (u), 138.4 (d), 141.5 (u), 157.5 (u), 202.4 (u) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3069 (w), 2951 (s), 2877 (s), 1699 (s), 1611 (w), 1456 (m), 1416 (w), 1362 (w), 1249 (s), 1148 (s), 1109 (s), 1055 (s), 1009 (s), 912 (m), 854 (m) cm^{-1}. MS (EI, 70 eV): m/z (%) = 531 [M]$^+$ (3), 502 (8), 488 (4), 377 (10), 376 (28), 347 (14), 345 (15), 344 (11), 334 (18), 333 (63), 307 (6), 305 (7), 292 (6), 291 (24), 279 (17), 271 (11), 270 (50), 249 (13), 201 (10), 191 (18), 190 (86), 189 (14), 188 (14), 187 (63), 175 (13), 173 (16), 161 (11), 159 (39), 157 (11), 156 (30), 149 (9), 148 (18), 147 (40), 136 (10), 131 (10), 125 (25), 117 (10), 116 (13), 115 (89), 107 (13), 105 (12), 103 (27), 97 (13), 91 (15), 87 (100), 81 (18), 79 (10), 77 (13), 75 (32). HRMS (EI): calcd. for $C_{30}H_{49}NO_3SSi{\cdot}C_2H_5$ 502.2811; found 502.2811.

(2*R*,5*R*,6*S*)-2-(But-3-enyl)-5,6-diisopropyl-3-[(*R*)-*N*-methyl-*S*-phenyl-sulfonimidoyl]-5,6-dihydro-2*H*-pyran-2-ol (9a): Treatment of the silyloxy enone **4a** (440 mg, 0.87 mmol) with (nBu)$_4$NF·3H$_2$O (410 mg, 1.30 mmol) as described in **GP3** afforded a 97:3 mixture (^{1}H NMR: NMe) of the diastereomeric hemiketals **9a** (280 mg, 82%) as a pale yellow oil. $[\alpha]_D$ = –17.5 (c = 1.20, CH_2Cl_2); R_f = 0.39 (hexane/EtOAc 9:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.51 (d, J = 6.9 Hz, 3 H, CH$_3$), 0.75 (d, J = 6.8 Hz, 3 H, CH$_3$), 0.85 (d, J = 6.9 Hz, 3 H, CH$_3$), 1.06 (d, J = 6.8 Hz, 3 H, CH$_3$), 1.82 [m, 1 H, CH(CH$_3$)$_2$], 1.91 [m, 1 H, CH(CH$_3$)$_2$], 1.98 (m, 1 H, CHH-CH=CH$_2$), 2.10 (m, 1 H, CHH-CH=CH$_2$), 2.15–2.25 (m, 3 H, CH_2-COH, CH-CH=C), 2.68 (m, 3 H, N-CH$_3$), 3.68 (dd, J = 9.9, 2.2 Hz, 1 H, CH-O), 4.90 (m, 2 H, CH_2=CHCH$_2$), 5.82 (m, 1 H, CH$_2$=CHCH$_2$), 6.09 (br. s, 1 H, OH), 6.15 (d, J = 1.4 Hz, 1 H, CH=C-S), 7.50–7.67 (m, 3 H, Ph), 7.90 (m, 2 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.6 (d), 16.7 (d), 20.0 (d), 20.6 (d), 25.8 (d), 27.4 (d), 28.2 (u), 29.1 (d), 40.0 (u), 43.2 (d), 72.7 (d), 95.9 (u), 113.7 (u), 129.1 (d), 129.6 (d), 133.0 (d); 137.0 (u), 138.6 (d), 140.1 (d), 142.8 (d) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3945 (w), 3895 (w), 3408 (w), 3165 (m), 2960 (s), 1725 (m), 1638 (m), 1447 (s), 1388 (s), 1241 (s), 1157 (s), 1114 (m), 1075 (m), 915 (m), 851 (s) cm^{-1}. MS (EI, 70 eV): m/z (%) = 392 [M + 1]$^+$ (1), 390 (2), 374 (25), 320 (16), 318 (12), 293 (17), 292 (100), 156 (16). HRMS: calcd. for $C_{22}H_{33}NO_3S{\cdot}H_2O$ 373.2075; found 373.2072.

(2*R*,5*R*,6*S*)-5,6-Diisopropyl-2-(pent-4-enyl)-3-[(*R*)-*N*-methyl-*S*-phenyl-sulfonimidoyl]-5,6-dihydro-2*H*-pyran-2-ol (9b): Treatment of enone **4b** (260 mg, 0.50 mmol) with the mixture of the acids (5 mL) as described in **GP4** afforded, after purification by flash chromatography (EtOAc/cyclohexane 1:9), hemiketal **9b** (162 mg, 80%) as a colorless oil. $[\alpha]_D$ = –11.8 (c = 1.00, CH_2Cl_2); R_f = 0.12 (EtOAc/cyclohexane 1:9). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.51 (d, J = 6.8 Hz, 3 H, CH$_3$), 0.75 (d, J = 6.8 Hz, 3 H, CH$_3$), 0.83 (d, J = 6.8 Hz, 3 H, CH$_3$), 1.06 (d, J = 6.9 Hz, 3 H, CH$_3$), 1.19–1.31 (m, 1 H, CHH-CH=CH$_2$), 1.39–1.52 (m, 1 H, CHH-CH=CH$_2$), 1.80–2.10 [m, 6 H, (CH$_3$)$_2$-CH-CHO-CH-CH(CH$_3$)$_2$, COH-CH_2-CH$_2$-CH_2], 2.14 (ddd, J = 10.0, 2.9, 1.8 Hz, 1 H, CH-CH=C-S),

2.67 (s, 3 H, N-CH_3), 3.67 (dd, J = 10.3, 4.0 Hz, 1 H, CH-O), 4.90 (dd, J = 10.3 Hz, 1 H, CH_2-CH=CHH), 4.96 (dd, J = 17.2 Hz, 1 H, CH_2-CH=CHH), 5.76 (ddd, J = 17.2, 10.3, 6.9 Hz, 1 H, CH_2-CH=CH_2), 6.03 (br. s, 1 H, OH), 6.17 (d, J = 1.6 Hz, 1 H, CH=C-S), 7.55–7.66 (m, 3 H, Ph), 7.88–7.92 (m, 2 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.6 (d), 16.7 (d), 20.0 (d), 20.7 (d), 23.1 (u), 25.8 (d), 27.4 (d), 29.1 (d), 33.7 (d), 40.4 (u), 43.3 (d), 72.7 (d), 96.1 (u), 114.0 (d), 129.1 (d), 129.6 (d), 132.9 (d), 138.9 (u), 140.2 (d), 141.6 (u) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3069 (w), 2962 (s), 2877 (s), 2806 (w), 1731 (w), 1638 (w), 1465 (m), 1387 (w), 1371 (w), 1242 (s), 1159 (m), 1080 (m), 1030 (s), 912 (m), 854 (s) cm^{-1}. MS (EI, 70 eV): m/z (%) = 405 $[M]^+$ (1), 387 (13), 346 (32), 345 (25), 344 (100), 337 (16), 336 (80), 293 (11), 276 (12), 223 (23), 168 (11), 155 (34), 124 (70), 108 (13), 107 (26), 97 (13), 95 (10), 78 (10). HRMS (EI): calcd. for $C_{23}H_{35}NO_3S{\cdot}H_2O$ 387.2232; found 387.2231.

(2*R*,5*R*,6*S*,*E*)-2-(But-3-enyl)-5-isopropyl-3-[(*R*)-*N*-methyl-*S*-phenylsulfonimidoyl]-6-(prop-1-enyl)-5,6-dihydro-2*H*-pyran-2-ol (9c): Treatment of enone **4c** (200 mg, 0.40 mmol) with the mixture of the acids (5 mL) as described in **GP4** afforded, after purification by flash chromatography (EtOAc/cyclohexane 1:9), hemiketal **9c** (129 mg, 90%) as a colorless oil. $[\alpha]_D$ = +0.6 (c = 1.00, CH_2Cl_2); R_f = 0.20 (EtOAc/cyclohexane 1:9). ^{1}H NMR (300 MHz, C_6D_6): δ = 0.41 (d, J = 6.9 Hz, 3 H, CH_3), 0.46 (d, J = 6.8 Hz, 3 H, CH_3), 1.52 (dd, J = 6.6 Hz, 3 H, CH=CH-CH_3), 1.64 [m, J = 6.7, 6.9 Hz, 1 H, CH(CH_3)$_2$], 1.92 (ddd, J = 10.1, 2.9, 1.9 Hz, 1 H, CH-CH=C-S), 2.58 (s, 3 H, N-CH_3), 2.60–2.85 (m, 4 H, CHOH-CH_2-CH_2), 4.52 (dd, J = 9.9, 7.8 Hz, 1 H, CH-O), 4.97 (ddd, J = 10.1, 2.1 Hz, 1 H, CH_2-CH=CHH), 5.17 (ddd, J = 17.1, 3.6 Hz, 1 H, CH_2-CH=CHH), 5.40 (ddd, J = 15.4, 7.9 Hz, 1 H, CH=CH-CH_3), 5.67 (m, J = 15.4, 6.6 Hz, 1 H, CHO-CH=CH), 5.97 (d, J = 1.9 Hz, 1 H, CH=C-S), 6.00 (ddd, J = 17.2, 10.3, 6.3 Hz, 1 H, CH_2-CH=CH_2), 6.99–7.02 (m, 3 H, Ph), 7.77–7.81 (m, 2 H, Ph) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 16.9 (d), 17.9 (d), 20.4 (d), 26.4 (u), 29.0 (d), 29.1 (u), 41.0 (u), 46.4 (d), 71.3 (d), 96.8 (u), 114.3 (u), 129.1 (d), 129.6 (d), 130.1 (d), 130.3 (d), 132.8 (d), 137.3 (d), 137.9 (u), 138.9 (d), 144.5 (u) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3224 (w), 2959 (s), 2876 (s), 2807 (w), 1729 (w), 1638 (w), 1447 (m), 1373 (w), 1241 (s), 1151 (s), 1079 (m), 1037 (w), 968 (w), 912 (w), 852 (m) cm^{-1}. MS (EI, 70 eV): m/z (%) = 389 $[M]^+$ (0.5), 372 (4), 356 (2), 334 (43), 292 (17), 194 (23), 168 (29), 156 (46), 154 (20), 151 (10), 149 (18), 126 (11), 125 (100), 121 (11), 110 (11), 109 (15), 107 (29), 106 (12), 105 (14), 95 (15). HRMS (EI): calcd. for $C_{22}H_{31}NO_3S{\cdot}H_2O$ 372.1997; found 372.1997.

(2*R*,5*R*,6*S*)-2-(Hex-5-enyl)-5-isopropyl-3-[(*S*)-*N*-methyl-*S*-phenylsulfonimidoyl]-6-[(*E*)-prop-1-enyl]-5,6-dihydro-2*H*-pyran-2-ol (9d): Treatment of enone **4d** (250 mg, 0.47 mmol) with the mixture of the acids (5 mL) as described in **GP4** afforded, after purification by flash chromatography (EtOAc/cyclohexane 1:9), hemiacetal **9d** (165 mg, 84%) as a colorless oil. $[\alpha]_D$ = –15.4 (c = 1.00, CH_2Cl_2); R_f = 0.24 (EtOAc/cyclohexane 1:9). ^{1}H NMR (400 MHz, C_6D_6): δ = 0.42 (d, J = 6.9 Hz, 3 H, CH_3), 0.45 (d, J = 6.9 Hz, 3 H, CH_3), 1.32–1.40 (m, 2 H, CO-CH_2-CH_2-CH_2), 1.46–1.56 (m, 2 H, COH-CH_2-CHH-CHH), 1.51 (d, J = 6.4 Hz, 3 H, CH=CH-CH_3), 1.61–1.69 [m, 1 H, CH(CH_3)$_2$], 1.86–1.98 (m, 2 H, CH-CH=C-S, COH-CH_2-CHH), 1.74–1.84 (m, 1 H, COH-CH_2-CH_2-CHH), 1.86–1.98 (m, 2 H, CH-CH=C, COH-CH_2-CHH), 2.09 (dd, J = 14.0, 6.6 Hz, 1 H, COH-CH_2-CH_2-CH_2-CH_2), 2.57 (ddd, J = 13.2, 11.9, 4.8 Hz, 1 H, COH-CHH), 2.62 (s, 3 H, N-CH_3), 2.71 (ddd, J = 13.2, 11.6, 4.7 Hz, 1 H, COH-CHH), 4.57 (dd, J = 8.6 Hz, 1 H, CH-O), 4.96 (ddd, J = 10.2 Hz, 1 H, CH_2-CH=CHH), 5.02 (ddd, J = 17.1, 3.5, 1.7 Hz, 1 H, CH_2-CH=CHH), 5.42 (dq, J = 15.2, 7.8, 1.7 Hz, 1 H, CHO-CH=CH), 5.69 (dq, J = 15.2, 6.4 Hz, 1 H, CHO-CH=CH), 5.81 (ddt, J = 16.9, 10.2, 6.7 Hz, 1 H, CH_2-CH=CH_2), 5.98 (d, J = 1.7 Hz, 1 H, CH=C-S), 6.63 (br. s, 1 H, OH), 6.94–6.98 (m, 3 H, Ph), 7.78–7.82 (m, 2 H, Ph) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 16.9 (d), 17.9 (d), 20.4 (d), 24.1 (d), 26.4 (u), 29.0 (u), 29.6 (u), 34.3 (d), 41.8 (u), 46.4 (d), 71.2 (d), 97.2 (u), 114.2 (u), 129.0 (d), 129.2 (d), 129.7 (d), 130.0 (d), 130.3 (d), 132.7 (d), 137.5 (u), 137.8 (u), 139.2 (d), 144.9 (u) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3381 (w), 3275 (w), 3069 (m), 2958 (s), 2809 (w), 1705 (m), 1637 (m), 1446 (s), 1242 (s), 1149 (s), 1081 (m), 1036 (s), 967 (m), 913 (m), 852 (m) cm^{-1}. MS (EI, 70 eV): m/z (%) = 418 $[M]^+$ (5), 417 (4), 399 (9), 355 (13), 345 (12), 335 (13), 333 (81), 303 (24), 291 (28), 289 (10), 261 (11), 244 (15), 218 (17), 191 (17), 178 (12), 155 (72), 153 (23), 148 (14), 138 (11), 136 (11), 134 (11), 125 (18), 124 (100), 121 (10), 110 (11), 109 (20), 108 (22), 107 (32), 106 (20), 104 (16), 96 (14), 94 (19), 91 (14).

(2*R*,5*R*,6*S*)-2,6-Di(but-3-enyl)-5-isopropyl-3-[(*S*)-*N*-methyl-*S*-phenyl-sulfonimidoyl]-5,6-dihydro-2*H*-pyran-2-ol (9f): Treatment of enone **4f** (80 mg, 0.16 mmol) with $n$$Bu_4NF{\cdot}3H_2O$ (70 mg, 0.22 mmol) at ambient temperature as described in **GP3** afforded, after purification by flash chromatography (EtOAc/cyclohexane 1:9), hemiketal **9f** (40 mg, 65%) as a colorless oil. Treatment of enone **4f** (80 mg, 0.16 mmol) with the mixture of the acids (5 mL) as described in **GP4** afforded, after purification by flash chromatography (EtOAc/cyclohexane 1:9), hemiketal **9f** (49 mg, 80%) as a colorless oil. $[\alpha]_D$ = –11.7 (c = 1.00, CH_2Cl_2); R_f = 0.30 (EtOAc/cyclohexane 1:9). ^{1}H NMR (400 MHz, C_6D_6): δ = 0.35 (d, J = 6.9 Hz, 3 H, CH_3), 0.42 (d, J = 6.9 Hz, 3 H, CH_3), 1.38–1.54 [m, 2 H, CH-O-CHH-CH_2-CH=CH_2, CH(CH_3)$_2$], 1.63 (ddd, J = 14.2, 7.3, 2.5 Hz, 1 H, CHO-CHH-CH_2-CH=CH_2), 1.83 (ddd, J = 9.9, 3.0, 1.9 Hz, 1 H, CH-CH=C-S), 2.33–2.47 (m, 2 H, CHO-CH_2-CH_2-CH=CH_2), 2.57 (s, 3 H, N-CH_3), 2.58–2.83 (m, J = 18.4 Hz, 4 H, COH-CH_2-CH_2), 4.07 (dd, J = 9.5, 2.5 Hz, 1 H, CH-O), 4.98 (dd, J = 10.3, 2.3, 1.2 Hz, 1 H, CH_2-CH=CHH), 5.05 (ddt, J = 10.1, 2.2, 1.3 Hz, 1 H, CH_2-CH=CHH), 5.17 (ddd, J = 17.3, 3.5, 1.7 Hz, 1 H, CH_2-CH=CHH), 5.20 (dd, J = 17.1, 3.5 Hz, 1 H, CH_2-CH=CHH), 5.90 (ddd, J = 17.1, 10.3, 6.7 Hz, 1 H, CH_2-CH=CH_2), 5.92 (d, J = 1.6 Hz, 1 H, CH=C-S), 6.02 (ddd, J = 17.2, 10.1, 6.8 Hz, 1 H, CH_2-CH=CH_2), 6.92–6.97 (m, 3 H, Ph), 7.72–7.77 (m, 2 H, Ph) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 16.8 (u), 20.4 (d), 26.5 (d), 28.9 (d), 29.0 (u), 29.7 (d), 31.6 (u), 41.0 (u), 46.0 (u), 68.7 (d), 96.6 (d), 114.3 (u), 114.9 (u), 129.0 (d), 130.3 (d), 132.7 (d), 137.3 (d), 137.9 (d), 138.5 (u), 139.0 (d), 144.8 (u), 186.8 (u) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3259 (w), 3073 (m), 2960 (s), 2875 (s), 2808 (m), 1725 (s), 1640 (m), 1446 (s), 1242 (s), 1155 (s), 1109 (m), 1078 (s), 996 (w), 913 (s), 853 (s) cm^{-1}. MS (EI, 70 eV): m/z (%) = 386 $[M]^+$ (4), 350 (5), 349 (14), 348 (65), 342 (22), 318 (10), 262 (14), 194 (16), 167 (31), 166 (11), 156 (33), 153 (22), 149 (29), 126 (11), 124 (100), 123 (11), 109 (17), 107 (40), 106 (16), 105 (18), 97 (17), 95 (14), 83 (16), 81 (21), 79 (17), 78 (15), 77 (22), 71 (12). HRMS (EI): calcd. for $C_{23}H_{33}NO_3S{\cdot}C_4H_7$ 348.1633; found 348.1633.

(2*R*,5*R*,6*S*)-2-Ethyl-5-isopropyl-3-[(*S*)-*N*-methyl-*S*-phenyl-sulfonimidoyl]-6-[(*E*)-prop-1-enyl]-5,6-dihydro-2*H*-pyran-2-ol (9g): Treatment of enone **4g** (300 mg, 0.63 mmol) with the mixture of the acids (5 mL) as described in **GP4** afforded, after purification by flash chromatography (EtOAc/cyclohexane 1:9), hemiacetal **9g** (205 mg, 90%) as a colorless oil. $[\alpha]_D$ = –9.6 (c = 1.00, CH_2Cl_2); R_f = 0.28 (EtOAc/cyclohexane 1:9). ^{1}H NMR (400 MHz, C_6D_6): δ = 0.40 (d, J = 6.9 Hz, 3 H, CH_3), 0.44 (d, J = 6.9 Hz, 3 H, CH_3), 1.33 (t, J = 7.2 Hz, 3 H, COH-CH_2-CH_3), 1.51 (d, J = 6.4, J = 1.6 Hz, 3 H, CH=CH-CH_3), 1.63 [m, J = 6.9, J = 3.9 Hz, 1 H, CH(CH_3)$_2$], 1.92 (ddd, J = 9.8, 2.9, 1.8 Hz, 1 H, CH-CH=CH-S), 2.60 (dd, J = 13.7, 7.4 Hz, 1 H, COH-CHH-CH_3), 2.61 (s, 3 H, N-CH_3), 2.76 (dd, J = 13.7, 7.6 Hz, 1 H, COH-CHH-CH_3), 4.54 (dd, J = 9.8, 7.9 Hz, 1 H, CH-O), 5.41 (ddd, J = 15.3, 7.9, 1.6 Hz, 1 H,

CHO-C*H*=CH-CH_3), 5.67 (dq, *J* = 15.3, 6.6 Hz, 1 H, CHO-CH=C*H*-CH_3), 5.96 (d, *J* = 1.8 Hz, 1 H, CH=C-S), 6.96–7.00 (m, 3 H, Ph), 7.82–7.96 (m, 2 H, Ph) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 8.7 (d), 16.9 (d), 17.9 (d), 20.4 (d), 26.5 (d), 29.0 (d), 34.8 (u), 46.5 (d), 71.3 (d), 97.8 (u), 129.2 (d), 129.9 (d), 130.2 (d), 130.6 (d), 132.9 (d), 137.7 (u), 138.2 (d), 145.0 (u) ppm. IR (capillary): $\tilde{\nu}$ = 3251 (w), 3225 (w), 3063 (w), 2961 (s), 2877 (s), 2805 (w), 1730 (w), 1704 (w), 1633 (w), 1447 (m), 1410 (m), 1374 (m), 1241 (s), 1152 (s), 1110 (m), 1082 (s), 1035 (m), 969 (m), 853 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 364 [M + 1]$^+$ (2), 363 (5), 346 (5), 335 (10), 334 (40), 293 (16), 292 (19), 276 (22), 250 (35), 208 (16), 179 (9), 165 (19), 156 (81), 154 (14), 148 (9), 139 (14), 138 (11), 126 (11), 125 (100), 123 (12), 110 (11), 109 (16), 107 (33), 106 (12), 105 (14), 97 (11), 95 (16), 78 (12), 77 (16), 71 (10). HRMS (EI): calcd. for $C_{20}H_{29}NO_3S$ 363.1868; found 363.1869.

(1*S*,3*R*,8*aR*)-3-(But-3-enyl)-1-isopropyl-4-[(*R*)-*N*-methyl-*S*-phenylsulfonimidoyl]-3,5,6,7,8,8a-hexahydro-1*H*-isochromen-3-ol (10a): Treatment of the silyloxy ketone **8a** (150 mg, 0.29 mmol) with $(n\text{Bu})_4$NF·3 H_2O (180 mg, 0.58 mmol) as described in **GP3** afforded a 96:4 mixture (^{1}H NMR: NMe) of the diastereomeric hemiketals **10a** (93 mg, 79%) as a pale yellow oil. $[a]_D$ = +100.4 (*c* = 0.50, CH_2Cl_2); R_f = 0.41 (*n*-hexane/EtOAc 8:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.00 (m, 1 H, CCH_2CH*H*), 0.90 (m, 1 H, CCHCH*H*), 1.10 (d, *J* = 6.9 Hz, 3 H, CH_3), 1.31 (d, *J* = 6.9 Hz, 3 H, CH_3), 1.35–1.50 (m, 2 H, CCH_2CH*H*, CCHCH_2C*H*H), 1.70 (m, 1 H, CCHCH_2CH*H*), 1.90–2.11 [m, 3 H, C*H*(CH_3)$_2$, CH*H*-C=C, CCHC*H*H], 2.31–2.52 (m, 4 H, C*H*-C=C, CH*HCH*$_2$CH=CH_2), 2.68 (s, 3 H, N-CH_3), 2.70–2.74 (m, 1 H, C*H*HCH_2CH=CH_2), 3.33 (br. d, *J* = 15.1 Hz, 1 H, CH*H*-C=C), 3.70 (dd, *J* = 9.6, 2.2 Hz, 1 H, CH-O), 5.10–5.24 (m, 2 H, CH_2=CH), 6.11 (m, 1 H, C*H*=CH_2), 7.24 (br. s, 1 H, OH), 7.62–7.76 (m, 3 H, Ph), 8.06 (m, 2 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.4 (d), 20.2 (d), 23.9 (u), 24.3 (u), 27.6 (d), 28.5 (d), 28.9 (u), 29.4 (u), 31.6 (u), 41.7 (u), 42.0 (d), 75.6 (d), 97.2 (u), 113.6 (u), 128.7 (d), 128.9 (d), 131.9 (d), 136.2 (u), 139.3 (d), 141.6 (u), 155.5 (u) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3390 (m), 2953 (s), 2874 (s), 2253 (m), 1729 (s), 1584 (w), 1449 (m), 1375 (m), 1181 (w), 911 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 403 [M]$^+$ (1), 385 (35), 349 (22), 348 (100), 344 (34), 342 (20), 320 (10), 230 (15), 205 (32), 187 (15), 177 (15), 156 (33), 125 (70). HRMS: calcd. for $C_{23}H_{33}NO_3S·H_2O$ 385.2075; found 385.2075.

(1*S*,3*R*,8a*R*)-1-Isopropyl-3-(pent-4-enyl)-4-[(*R*)-*N*-methyl-*S*-phenylsulfonimidoyl]-3,5,6,7,8,8a-hexahydro-1*H*-isochromen-3-ol (10b): Treatment of enone **8b** (210 mg, 0.39 mmol) with $(n\text{Bu})_4$NF·3 H_2O (190 mg, 0.6 mmol) as described in **GP3** afforded, after purification by flash chromatography (EtOAc/cyclohexane 1:9), hemiketal **10b** (150 mg, 92%) as a pale yellow oil. $[a]_D$ = +80.8 (*c* = 1.00, CH_2Cl_2); R_f = 0.25 (EtOAc/cyclohexane 1:9). ^{1}H NMR (400 MHz, $CDCl_3$): δ = –0.20 (m, *J* = 12.9, *J* = 3.8 Hz, 1 H, C=C-CH_2-CH*H*), 0.74 (dd, *J* = 13.1, 3.7 Hz, 1 H, C=C-CH_2-CH_2-CH_2-C*H*H), 0.92 (d, *J* = 6.9 Hz, 3 H, CH_3), 1.14 (d, *J* = 6.9 Hz, 3 H, CH_3), 1.18–1.37 (m, 2 H, C=C-CH_2-CH*H*-C*H*H), 1.47–1.61 (m, 3 H, COH-CH_2-CH_2, C=C-CH_2-CH_2-C*H*H), 1.67–1.96 [m, 3 H, C=C-C*H*H-CH_2-CH_2-C*H*H, CHO-C*H*(CH_3)$_2$], 2.08–2.24 (m, 4 H, COH-C*H*H-CH_2-CH_2, C=C-C*H*-CHO), 2.44 (ddd, *J* = 9.6, 6.7, 5.2 Hz, 1 H, COH-C*H*H), 2.59 (s, 3 H, N-CH_3), 3.14 (d, *J* = 15.1 Hz, 1 H, C=C-C*H*H), 3.50 (dd, *J* = 9.6, 2.0 Hz, 1 H, CH-O), 4.98 (dd, *J* = 10.3, 2.3 Hz, 1 H, CH_2-CH=CH*H*), 5.07 (ddd, *J* = 17.2, 3.8, 1.6 Hz, 1 H, CH_2-CH=CH*H*), 5.88 (ddd, *J* = 17.2, 10.3, 6.6 Hz, 1 H, CH_2-C*H*=CH_2), 7.00 (br. s, 1 H, OH), 7.54–7.59 (m, 3 H, Ph), 7.88–7.93 (m, 2 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.7 (d), 20.1 (d), 23.5 (u), 23.7 (u), 24.1 (u), 27.4 (d), 28.3 (d), 29.2 (u), 31.4 (d), 33.7 (u), 41.8 (u), 41.9 (u), 75.4 (d), 97.3 (u), 114.0 (u), 128.5 (d), 128.7 (d), 131.7 (d), 136.3 (u), 139.1 (d), 141.5 (u), 155.1 (u) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3063 (w), 2934 (s), 1705 (w), 1604 (m), 1447 (s), 1232 (s), 1147 (s), 1106 (m), 1075 (s), 911 (m), 855 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 417 [M]$^+$ (0.5), 400 (6), 399 (17), 358 (37), 356 (19), 349 (23), 348 (100), 328 (16), 320 (10), 268 (9), 244 (13), 206 (16), 155 (15), 124 (45), 107 (14), 105 (12), 91 (18), 81 (12), 79 (14), 77 (14). HRMS (EI): calcd. for $C_{24}H_{35}NO_3S·H_2O$ 399.2232; found 399.2233.

(2*S*,3*R*,6*R*)-6-(Allyloxy)-6-(but-3-enyl)-2,3-diisopropyl-5-[(*R*)-*N*-methyl-*S*-phenyl-sulfonimidoyl]-3,6-dihydro-2*H*-pyran (11): Treatment of a mixture of the diastereomeric hemiketals **9a** (100 mg, 0.25 mmol) in CH_2Cl_2 (10 mL) with BF_3·OEt_2 (90 mg, 80 µL, 0.64 mmol) and allylic alcohol (150 mg, 180 µL, 2.5 mmol) at 0 °C afforded, after the mixture had warmed to room temperature and been maintained at that temperature for 30 min and evaporation of the volatiles in vacuo, a 95:5 mixture (^{1}H NMR: NMe) of the diastereomeric ketals **11** (88 mg, 80%) as a colorless oil. $[a]_D$ = –15.7 (*c* = 0.60, CH_2Cl_2); R_f = 0.50 (*n*-hexane/EtOAc 9:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.65 (d, *J* = 7.1 Hz, 3 H, CH_3), 0.76 (d, *J* = 6.8 Hz, 3 H, CH_3), 0.91 (d, *J* = 6.9 Hz, 3 H, CH_3), 1.01 (d, *J* = 6.9 Hz, 3 H, CH_3), 1.68–1.94 [m, 5 H, CH_2CH_2CH=CH_2, (CH_3)$_2$C*H*CH, (CH_3)$_2$C*H*CHO, CH_2C*H*HCH=CH_2], 2.16 [dt, *J* = 10.4, *J* = 1.9 Hz, 1 H, (CH_3)$_2$-CHC*H*], 2.50 (m, 1 H, CH_2CH*H*CH=CH_2), 2.74 (s, 3 H, N-CH_3), 3.41 (dd, *J* = 10.4, 2.2 Hz, 1 H, CH-O), 3.92 (m, 2 H, OCH_2CH=CH), 4.75–5.02 (m, 4 H, CH_2=CHCH_2CH_2, CH_2=CHCH_2O), 5.54–5.70 (m, 2 H, CH_2=C*H*CH_2CH_2, CH_2=C*H*CH_2O), 7.12 (d, *J* = 1.9 Hz, 1 H, CH=C-S), 7.34–7.44 (m, 3 H, Ph), 7.8 (m, 2 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.6 (d), 16.9 (d), 20.5 (d), 21.1 (d), 26.4 (d), 27.8 (d), 29.2 (u), 29.9 (d), 33.8 (u), 43.8 (d), 61.6 (d), 71.9 (d), 99.6 (u), 113.9 (u), 114.8 (u), 128.5 (d), 128.8 (d), 131.8 (d), 135.1 (d), 138.6 (d), 141.3 (u), 141.9 (u), 144.5 (d) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3525 (w), 3136 (m), 3071 (s), 2931 (s), 1581 (m), 1446 (s), 1382 (w), 1233 (s), 1144 (s), 1079 (s) cm^{-1}. MS(EI, 70 eV): *m*/*z* (%) = 432 [M + 1]$^+$ (9), 376 (25), 375 (28), 374 (100), 345 (26), 336 (36), 330 (66), 327(22), 277 (25), 248 (24), 218 (16), 167 (25), 149 (26), 124 (74). HRMS: calcd. for $C_{25}H_{37}NO_3S$ 431.2494; found 431.2495.

(2*S*,3*R*,6*S*)-6-Allyl-6-(but-3-enyl)-2,3-diisopropyl-5-[(*R*)-*N*-methyl-*S*-phenyl-sulfonimidoyl]-3,6-dihydro-2*H*-pyran (12): Treatment of hemiketals **9a** (60 mg, 0.15 mmol) with $TiCl_4$ (100 µL, 0.92 mmol) and allyltrimethylsilane (150 µL, 0.92 mmol) as described in **GP5** afforded a 95:5 mixture (^{1}H NMR: NMe) of the diasteromeric dienes **12** (56 mg, 90%) as a colorless oil. $[a]_D$ = –28.0 (*c* = 0.40, CH_2Cl_2); R_f = 0.45 (*n*-hexane/EtOAc 9:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.83 (d, *J* = 6 Hz, 3 H, CH_3), 0.84 (d, *J* = 3.8 Hz, 3 H, CH_3), 0.94 (m, 1 H, CH*H*-C), 1.04 (d, *J* = 6.8 Hz, 3 H, CH_3), 1.09 (d, *J* = 6.9 Hz, 3 H, CH_3), 1.72 (m, 1 H, C*H*H-C), 1.90 [m, 4 H, O-C*H*(CH_3)$_2$, C*H*(CH_3)$_2$, CH_2-C], 2.22 (dt, *J* = 9.9, *J* = 2.7 Hz, 1 H, C*H*-CH=C), 2.78–2.84 (m, 4 H, N-CH_3, C-CH*H*-CH=CH_2), 2.97 (dd, *J* = 15.1, 8.8 Hz, 1 H, C-C*H*H-CH=CH_2), 3.57 (dd, *J* = 9.6, 1.6 Hz, 1 H, CH-O), 4.62 (m, 2 H, CH_2=CHCH_2CH_2), 5.10 (m, 2 H, CH_2=CHCH_2), 5.33 (m, 1 H, CH_2=C*H*CH_2CH_2), 5.94 (m, 1 H, CH_2=C*H*CH_2), 7.05 (d, *J* = 1.9 Hz, 1 H, CH=C-S), 7.40–7.54 (m, 3 H, Ph), 7.90 (m, 2 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.5 (d), 17.4 (d), 21.0 (d), 21.2 (d), 26.5 (d), 27.8 (u), 28.6 (d), 30.1 (d), 35.2 (u), 42.8 (u), 44.1 (d), 71.9 (d), 78.1 (u), 113.6 (u), 117.6 (u), 127.8 (d), 129.0 (d), 132.2 (d), 134.1 (d), 138.7 (d), 141.1 (u), 143.4 (d), 144.7 (u) ppm. MS (EI, 70 eV): *m*/*z* (%) = 415 [M]$^+$ (3), 410 (25), 374 (100), 318 (5), 217 (9), 205 (10), 167 (22), 124 (39), 105 (10), 91 (11). HRMS: calcd. for $C_{25}H_{37}NO_2S·C_3H_5$ 374.2153; found 374.2152.

(1*S*,3*S*,8a*R*)-3-Allyl-3-(but-3-enyl)-1-isopropyl-4-[(*R*)-*N*-methyl-*S*-phenyl-sulfonimidoyl]-3,5,6,7,8,8a-hexahydro-1*H*-isochromene (13):

Treatment of hemiketals **10a** (60 mg, 0.15 mmol) with $TiCl_4$ (10 μL, 0.89 mmol) and allyltrimethylsilane (140 μL, 0.89 mmol) as described in **GP5** afforded a 95:5 mixture (^{1}H NMR: NMe) of the diastereomeric dienes **13** in (57 mg, 90%) as a colorless syrup. $[\alpha]_D$ = +69.8 (*c* = 0.50, CH_2Cl_2); R_f = 0.62 (*n*-hexane/EtOAc 8:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.46 (m, 1 H, CH_2CHH), 0.90 (d, *J* = 6.6 Hz, 3 H, CH_3), 0.92 (m, 1 H, CCHCHH), 1.08 (d, *J* = 6.6 Hz, 3 H, CH_3), 1.30–1.40 (m, 1 H, $CCHCH_2CHH$), 1.49 (m, 1 H, CCH_2CHH), 1.59–1.71 (m, 2 H, CCHH, $CCHCH_2CHH$), 1.80–1.90 [m, 3 H, $CH(CH_3)_2$, $CCHCH_2$], 2.01 (m, 1 H, $CHHCH_2CH=CH_2$), 2.06–2.19 (m, 2 H, $CHHCHHCH=CH_2$), 2.65 (s, 3 H, N-CH_3), 2.74–2.84 (m, 1 H, $CH_2CHHCH=CH_2$), 2.92 (br. dd, *J* = 14.8, 5.8 Hz, 1 H, $CHHCH=CH_2$), 3.33 (dd, *J* = 9.3, 1.9 Hz, 1 H, CH-O), 3.51 (dd, *J* = 14.8, 8.2 Hz, 1 H, $CHHCH=CH_2$), 3.76 (br. d, *J* = 14.3 Hz, 1 H, CCHH), 4.86–4.98 (m, 2 H, $CH_2CH_2CH=CH_2$), 5.74–5.86 (m, 2 H, $CH_2CH=CH_2$), 5.09–5.21 (m, 1 H, $CH_2CH_2CH=CH_2$), 5.94–6.07 (m, 1 H, $CH_2CH=CH_2$), 7.47–7.51 (m, 3 H, Ph), 7.88 (m, 2 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.1 (d), 21.2 (d), 25.1 (u), 25.6 (u), 28.7 (u), 29.5 (d), 29.6 (d), 31.5 (u), 31.9 (u), 36.6 (u), 41.2 (u), 42.5 (d), 74.5 (d), 79.2 (u), 113.4 (u), 117.2 (u), 128.0 (d), 128.6 (d), 131.5 (d), 134.4 (d), 137.8 (u), 139.8 (d), 143.1 (u), 154.6 (u) ppm. IR ($CHCl_3$): ṽ = 3747 (m), 3410 (m), 2947 (w), 1598 (w), 1433 (s), 1215 (s), 1066 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 427 $[M]^+$ (2), 422 (2), 387 (24), 386 (100), 279 (14), 231 (7), 217 (12), 124 (13), 105 (10), 91 (14). HRMS: calcd. for $C_{26}H_{37}NO_2S{\cdot}C_3H_5$: 386.2153; found 386.2152.

(2*S*,3*R*,6*R*,*Z*)-2,3-Diisopropyl-5-[(*R*)-*N*-methyl-*S*-phenyl-sulfonimidoyl]-1,7-dioxaspiro[5.6]dodeca-4,9-diene (14): Treatment of dienes **11** (100 mg, 0.23 mmol) with $(PCy_3)(H_2IMes)Ru(CHPh)$ (10 mg, 0.012 mmol) as described in **GP6** afforded spiroketal **14** (79 mg, 85%) as a pale yellow oil. $[\alpha]_D$ = –33.1 (*c* = 1.35, CH_2Cl_2); R_f = 0.21 (*n*-hexane/EtOAc 9:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.80 (d, *J* = 7.5 Hz, 3 H, CH_3), 0.88 (d, *J* = 6.8 Hz, 3 H, CH_3), 1.06 (d, *J* = 4.4 Hz, 3 H, CH_3), 1.08 (d, *J* = 4.6 Hz, 3 H, CH_3), 1.66 (m, 1 H, CHH-CH_2CH=CH), 1.91 [m, 2 H, $(CH_3)_2CHCH$, $(CH_3)_2CHCHO$], 2.30 [m, 2 H, CHH-CH_2CH=CH, $(CH_3)_2$-CHCH], 2.45 (br. t, *J* = 11.6 Hz, 1 H, CH_2CHHCH=CH), 2.55 (m, 1 H, CH_2CHHCH=CH), 2.81 (s, 3 H, N-CH_3), 3.62 [dd, *J* = 10.2, *J* = 2.2 Hz, 1 H, $(CH_3)_2CHCHO$], 3.83 (dd, *J* = 15.1, 5.8 Hz, 1 H, OCHHCH=CH), 4.32 (dq, *J* = 15.1, 1.6 Hz, 1 H, OCHHCH=CH), 5.59 (m, 1 H, OCH_2CH=CH), 5.83 (m, 1 H, OCH_2CH=CH), 6.99 (d, *J* = 2.2 Hz, 1 H, CH=C-S), 7.44–7.53 (m, 3 H, Ph), 7.88 (m, 2 H, Ph) ppm. ^{1}H NMR (400 MHz, C_6D_6): δ = 0.65 (d, *J* = 6.9 Hz, 3 H, CH_3), 0.83 (d, *J* = 6.9 Hz, 3 H, CH_3), 0.84 (d, *J* = 6.8 Hz, 3 H, CH_3), 1.03 (d, *J* = 6.9 Hz, 3 H, CH_3), 1.56 [dq, *J* = 6.9, 2.9 Hz, 1 H, $(CH_3)_2CHCH$], 1.67 [dq, *J* = 6.9, 2.2 Hz, 1 H, $(CH_3)_2CHCHO$], 1.96 (ddd, *J* = 14.5, 6.6, 2.9 Hz, 1 H, CHH-CH_2CH=CH), 2.15 (dd, *J* = 10.2, 2.4 Hz, 1 H, CHCH=C-S), 2.30 (m, 1 H, CH_2CHHCH=CH), 2.60 (m, 1 H, CH_2CHHCH=CH), 3.00 (s, 3 H, N-CH_3), 3.21 (ddd, *J* = 14.5, 6.4, 2.9 Hz, 1 H, CHH-CH_2CH=CH), 3.64 [dd, *J* = 10.2, 2.2 Hz, 1 H, $(CH_3)_2CHCHO$], 3.96 (dd, *J* = 15.1, 5.4 Hz, 1 H, OCHHCH=CH), 4.26 (dd, *J* = 15.1, 4.5, 1.6 Hz, 1 H, OCHHCH=CH), 5.48 (m, *J* = 10.9, 6.9, 5.4 Hz, 1 H, OCH_2CH=CH), 5.76 (m, *J* = 10.9, 5.2 Hz, 1 H, OCH_2CH=CH), 6.95–7.05 (m, 3 H, Ph), 7.32 (d, *J* = 1.9 Hz, 1 H, CH=C-S), 8.12 (m, 2 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.0 (d), 17.3 (d), 21.1 (d), 21.2 (d), 23.4 (u), 26.8 (d), 28.4 (d), 30.1 (d), 35.6 (u), 59.6 (u), 71.5 (d), 98.6 (u), 128.3 (d), 128.4 (d), 128.5 (d), 131.9 (d), 133.7 (d), 140.9 (u), 142.3 (d), 143.2 (d) ppm. IR ($CHCl_3$): ṽ = 3647 (m), 3589 (m), 2961 (s), 1700 (m), 1649 (m), 1557 (s), 1514 (s), 1387 (m), 1245 (s), 1156 (s), 1107 (w), 1023 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 404 $[M + 1]^+$ (28), 403 (47), 337 (20), 336 (100), 205 (42), 124 (41), 123 (10). HRMS: calcd. for $C_{23}H_{33}NO_3S$: 403.2181; found 403.2181.

(2*S*,3*R*,6*S*)-2,3-Diisopropyl-5-[(*R*)-*N*-methyl-*S*-phenyl-sulfonimidoyl]-1-oxaspiro[5.5]undeca-4,8-diene (15): Treatment of dienes **12** (100 mg, 0.24 mmol) with $(PCy_3)(H_2IMes)Ru(CHPh)$ (10 mg, 0.012 mmol) as described in **GP6** afforded spiroether **15** (81 mg, 87%) as a pale yellow oil. $[\alpha]_D$ = +18.3 (*c* = 1.25, CH_2Cl_2); R_f = 0.25 (*n*-hexane/EtOAc 9:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.82 (d, *J* = 7.0 Hz, 3 H, CH_3), 0.84 (d, *J* = 7.0 Hz, 3 H, CH_3), 0.91 (d, *J* = 6.7 Hz, 3 H, CH_3), 1.09 (d, *J* = 7.0 Hz, 3 H, CH_3), 1.11 (m, 1 H, CH_2CHHCO), 1.82 (m, 1 H, CH_2CHH-CH=CH), 1.86 [dq, *J* = 6.8, *J* = 2.4 Hz, 1 H, $(CH_3)_2CHCHO$], 1.92 [dq, *J* = 7.0, *J* = 4.2 Hz, 1 H, $CH(CH_3)_2$], 2.19 (m, 1 H, CH_2CHHCO), 2.26 (m, 1 H, COCHH-CH=CH), 2.28 [dt, *J* = 9.8, *J* = 2.4 Hz, 1 H, $(CH_3)_2$-CHCH], 2.79 (s, 3 H, N-CH_3), 2.93 (br. d, *J* = 18.2 Hz, 1 H, COCHH-CH=CH), 3.4 (dd, *J* = 9.4, 2.1 Hz, 1 H, CH-O), 5.48 (m, 1 H, CCH_2CH=CH), 5.65 (m, 1 H, CH_2CH_2CH=CH), 6.96 (d, *J* = 2.1 Hz, 1 H, CH=C-S), 7.48–7.55 (m, 3 H, Ph), 7.8 (m, 2 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.8 (d), 17.5 (d), 20.5 (d), 21.2 (d), 21.7 (u), 26.6 (d), 28.3 (d), 29.9 (d), 31.2 (u), 31.7 (u), 71.4 (d), 73.9 (u), 123.3 (d), 126.2 (d), 127.7 (d), 128.9 (d), 132.2 (d), 141.6 (u), 142.2 (d), 145.7 (u) ppm. IR ($CHCl_3$): ṽ = 2962 (m), 2804 (s), 1461 (s), 1381 (w), 1238 (s), 1148 (m), 1085 (m), 1032 (m), 851 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 388 $[M + 1]^+$ (53), 387 $[M]^+$ (70), 344 (10), 257 (14), 214 (23), 189 (100), 125 (73). HRMS: calcd. for $C_{23}H_{33}NO_2S$ 387.2232; found 387.2232.

(1*S*,1′*S*,8*a*′*R*)-1′-Isopropyl-4′-[(*R*)-*N*-methyl-*S*-phenyl-sulfonimidoyl]-1′,5′,6′,7′,8′,8a′-hexahydrospiro[cyclohex[3]ene-1,3′-isochromene] (16): Treatment of dienes **13** (60 mg, 0.14 mmol) with $(PCy_3)(H_2IMes)Ru(CHPh)$ (10 mg, 0.012 mmol) as described in **GP6** afforded spiroether **16** (52 mg, 93%) as a pale yellow oil. $[\alpha]_D$ = +63.7 (*c* = 1.00, CH_2Cl_2); R_f = 0.39 (*n*-hexane/EtOAc 8:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (d, *J* = 6.9 Hz, 3 H, CH_3), 0.95 (d, *J* = 6.7 Hz, 3 H, CH_3), 1.01 (m, 1 H, CCHCHH), 1.22–1.51 (m, 2 H, CCHH, $CCHCH_2CHH$), 1.59–1.72 (m, 4 H, $CCH_2CHHCHCHHCH$, CHHCO), 1.81 [six-lines pattern, *J* = 6.6, 2.5 Hz, 1 H, $CH(CH_3)_2$], 1.88–2.02 (m, 2 H, CH_2CHHCH=CH, $CCHCH_2CHH$), 2.16 (m, 1 H, C=CCH), 2.28–2.50 (m, 2 H, CHHCH=CH, CHHCO), 2.76 (s, 3 H, N-CH_3), 3.00 (six-lines pattern, *J* = 12.1, 6.2 Hz, CH_2CHHCH=CH), 3.14–3.25 (m, 2 H, CH-O, CHHCH=CH), 3.68 (br. d, *J* = 13.9 Hz, C=CCHH), 5.54 (m, 1 H, CH_2CH=CH), 5.72 (m, 1 H, CH_2CH_2CH=CH), 7.44–7.53 (m, 3 H, Ph), 7.92 (m, 2 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 5.2 (d), 20.5 (d), 22.6 (u), 24.5 (u), 26.5 (u), 28.8 (d), 29.8 (d), 31.1 (u), 31.4 (u), 31.8 (u), 32.3 (u), 43.1 (d), 74.3 (d), 75.3 (u), 123.5 (d), 126.4 (d), 126.9 (d), 128.7 (d), 137.3 (u), 143.8 (u), 155.4 (u) ppm. IR ($CHCl_3$): ṽ = 3390 (m), 3359 (m), 2963 (s), 2448 (w), 2393 (w), 1718 (s), 1446 (s), 1378 (m), 1220 (s), 1155 (m), 1022 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 400 $[M + 1]^+$ (89), 398 (10), 369 (16), 368 (32), 352 (14), 351 (54), 345 (12), 341 (11), 328 (16), 322 (11), 321 (43), 320 (76), 310 (11), 302 (23), 297 (20), 288 (20), 276 (10), 269 (64) 235 (16), 218 (44), 201 (49), 173 (34), 144 (31), 124 (66), 105 (55), 91 (100). HRMS: calcd. for $C_{24}H_{33}NO2S$: 399.2230; found 399.2231.

(1*R*,6*S*,7*R*,*Z*)-7-Isopropyl-9-[(*R*)-*N*-methyl-*S*-phenyl-sulfonimidoyl]-10-oxabicyclo-[4.3.1]deca-4,8-dien-1-ol (17): Treatment of diene **9c** (120 mg, 0.30 mmol) with $(PCy_3)(H_2IMes)Ru(CHPh)$ (26 mg, 0.031 mmol) as described in **GP7** afforded, after purification by flash chromatography (EtOAc/cyclohexane 1:5), oxabicycle **17** (100 mg, 96%) as a pale yellow oil. $[\alpha]_D$ = –13.1 (*c* = 1.00, CH_2Cl_2); R_f = 0.10 (EtOAc/cyclohexane 1:5). ^{1}H NMR (400 MHz, C_6D_6): δ = 0.58 (d, *J* = 6.9 Hz, 3 H, CH_3), 0.60 (d, *J* = 6.8 Hz, 3 H, CH_3),

1.45 (dd, *J* = 6.2 Hz, 1 H, C*H*-CH=C-S), 1.59 [m, *J* = 6.9 Hz, 1 H, C*H*(CH_3)$_2$], 2.16 (dd, *J* = 18.0, 6.9, 3.6 Hz, 1 H, COH-CH_2-C*H*H), 2.53 (dd, *J* = 13.0, 4.1 Hz, 1 H, COH-C*H*H), 2.57 (s, 3 H, N-CH_3), 2.61 (dd, *J* = 18.0, 4.7 Hz, 1 H, COH-CH_2-C*H*H), 3.06 (dd, *J* = 13.0, 3.2 Hz, 1 H, COH-C*H*H-CH_2), 4.39 (dd, *J* = 5.3 Hz, 1 H, CH-O), 5.26 (ddd, *J* = 12.5, 2.9 Hz, 1 H, CHO-C*H*=CH), 5.54 (m, *J* = 12.5, 6.9 Hz, 1 H, CHO-CH=C*H*), 6.17 (d, *J* = 5.8 Hz, 1 H, CH=C-S), 6.92–6.96 (m, 3 H, Ph), 7.83–7.86 (m, 2 H, Ph) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 19.8 (d), 20.8 (d), 25.1 (u), 29.0 (d), 32.4 (d), 42.3 (u), 46.2 (d), 72.4 (d), 98.3 (u), 129.0 (d), 129.1 (d), 129.0 (d), 130.0 (d), 132.5 (d), 132.7 (d), 138.4 (u), 140.6 (d), 143.0 (u) ppm. IR (KBr): $\tilde{\nu}$ = 3220 (w), 3062 (w), 3012 (s), 2960 (s), 2926 (s), 2875 (s), 2806 (w), 1732 (w), 1634 (w), 1445 (s), 1370 (m), 1240 (s), 1151 (s), 1085 (m), 933 (w), 857 (s) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 348 (6), 347 [M]$^+$ (10), 321 (3), 305 (9), 304 (50), 276 (11), 192 (28), 177 (9), 163 (7), 156 (58), 149 (14), 147 (10), 138 (13), 131 (10), 125 (100), 121 (12), 109 (13), 108 (10), 107 (37), 106 (12), 105 (21), 97 (12). HRMS (EI): calcd. for $C_{19}H_{25}NO_3S$ 347.1555; found 347.1555.

Ethyl 2-{(2*S*,5*R*,6*S*)-2-(But-3-enyl)-5-isopropyl-3-[(*R*)-*N*-methyl-*S*-phenyl-sulfonimidoyl]}-6-[(*E*)-prop-1-enyl]-5,6-dihydro-2*H*-pyran-2-ylacetate (18): A solution of $TiCl_4$ (60 mg, 0.32 mmol) in CH_2Cl_2 (2 mL) and a solution of a mixture of CH_2=C(OSiMe_3)OEt (0.32 mmol) and $Me_3SiCH_2CO_2Et$ (1:1) in CH_2Cl_2 (5 mL) were added at –78 °C to a solution of hemiketal **9c** (62 mg, 0.16 mmol) in CH_2Cl_2 (6 mL). The mixture was stirred at this temperature for 20 min. $TiCl_4$ (62 mg, 0.32 mmol) and CH_2=C(OSiMe_3)OEt (0.32 mmol) admixed with $Me_3SiCH_2CO_2Et$ were then added. After the mixture had been stirred at this temperature for 20 min, further $TiCl_4$ (62 mg, 0.32 mmol) and CH_2=C(OSiMe_3)OEt (0.32 mmol) admixed with $Me_3SiCH_2CO_2Et$ were added. The mixture was then stirred at –78 °C for 2 h, after which saturated aqueous $(NH_4)_2CO_3$ was added and the mixture was allowed to warm to ambient temperature. Subsequently, water was added, the mixture was extracted with CH_2Cl_2, and the organic phases were dried ($MgSO_4$) and concentrated in vacuo. Purification by flash chromatography (EtOAc/cyclohexane 1:9) gave ester **18** (46 mg, 63%) as a colorless gum. $[\alpha]_D$ = –32.8 (*c* = 1.00, CH_2Cl_2); R_f = 0.12 (EtOAc/cyclohexane 1:9). ^{1}H NMR (400 MHz, C_6D_6): δ = 0.71 (d, *J* = 6.8 Hz, 3 H, CH_3), 0.80 (d, *J* = 6.8 Hz, 3 H, CH_3), 1.01 (t, *J* = 7.3 Hz, CO-CH_2-CH_3), 1.58 (dd, *J* = 6.6, 1.6 Hz, 3 H, CH=CH-CH_3), 1.59–1.62 (m, 1 H, CHOH-CH_2-C*H*H), 1.76 [dq, *J* = 9.7, 6.8, 2.9 Hz, 1 H, C*H*(CH_3)$_2$], 1.98 (ddd, *J* = 9.7, 2.7, 1.9 Hz, 1 H, C*H*-CH=C-S), 2.29–2.39 (m, 1 H, CO-CH_2-C*H*H), 2.48–2.61 (m, *J* = 10.9, 6.2 Hz, 2 H, CO-CH_2-CH_2), 2.90 (s, 3 H, N-CH_3), 3.40 (d, *J* = 14.1 Hz, 1 H, CH*H*-CO), 3.64 (m, *J* = 14.1 Hz, 1 H, CH*H*-CO), 4.00 (dq, *J* = 7.3, 2.5 Hz, 2 H, CO-CH_2-CH_3), 4.30 (dd, *J* = 9.6, 7.8 Hz, 1 H, CH-O), 4.80–4.86 (m, 2 H, CH_2-CH=CH_2), 5.33 (ddd, *J* = 15.2, 7.6, 1.7 Hz, 1 H, C*H*=CH-CH_3), 5.57 (m, *J* = 15.2, 6.6 Hz, 1 H, CHO-CH=C*H*), 5.77 (m, *J* = 17.9, 10.3, 6.5 Hz, 1 H, CH_2-C*H*=CH_2), 6.93–6.99 (m, 3 H, Ph), 7.03 (d, *J* = 1.9 Hz, 1 H, CH=C-S), 7.92–7.95 (m, 2 H, Ph) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 14.3 (d), 17.3 (d), 17.8 (d), 20.8 (d), 26.9 (d), 28.5 (u), 29.9 (d), 36.7 (u), 45.3 (d), 47.2 (d), 60.2 (u), 71.9 (d), 78.3 (u), 114.1 (u), 128.8 (d), 128.9 (d), 129.6 (d), 130.5 (d), 131.9 (d), 138.7 (d), 141.4 (d), 141.5 (d), 145.5 (u), 169.7 (u) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3068 (w), 2960 (s), 2806 (w), 1732 (w), 1636 (w), 1449 (s), 1372 (w), 1249 (s), 1150 (s), 1081 (m), 1039 (m), 967 (w), 914 (w), 851 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 462 (6), 461 (19), 460 (61), 459 [M]$^+$ (11), 416 (15), 415 (13), 414 (49), 409 (24), 404 (10), 372 (24), 368 (19), 363 (22), 362 (100), 348 (3), 335 (10), 334 (32), 316 (19), 273 (12), 264 (28), 263 (15), 262 (10), 261 (38), 250 (13), 235 (12), 217 (15), 209 (17), 207 (12), 189 (12), 179 (14), 175 (14), 173 (17), 168 (28), 163 (18), 162 (11), 160 (26), 159 (11), 157 (13), 156 (68), 147 (32), 145 (19), 139 (12), 135 (13), 133 (19), 131 (15), 126 (13), 125 (93), 121 (13), 120 (11), 119 (30), 117 (14), 109 (14), 107 (34), 106 (18), 105 (40), 97 (15), 95 (22), 93 (13), 91 (38), 81 (14). HRMS (EI): calcd. for $C_{26}H_{37}NO_4S$: 459.2443; found 459.2443.

Ethyl 2-{(1*S*,6*S*,7*R*,*Z*)-7-Isopropyl-9-[(*R*)-*N*-methyl-*S*-phenyl-sulfonimidoyl]}-10-oxabicyclo[4.3.1]deca-4,8-dien-1-ylacetate (19): Treatment of diene **18** (69 mg, 0.15 mmol) with (PCy_3)(H_2IMes)-Ru(CHPh) (13 mg, 0.015 mmol) as described in **GP7** afforded, after purification by flash chromatography (EtOAc/cyclohexane 1:5), oxabicycle **19** (56 mg, 89%) as a pale yellow oil. $[\alpha]_D$ = –26.5 (*c* = 1.00, CH_2Cl_2); R_f = 0.16 (EtOAc/cyclohexane 1:5), ^{1}H NMR (300 MHz, C_6D_6): δ = 0.74 (d, *J* = 6.8 Hz, 3 H, CH_3), 0.75 (d, *J* = 6.8 Hz, 3 H, CH_3), 0.97 (t, *J* = 7.1 Hz, CH_2-CO-CH_2-CH_3), 1.52 (ddd, *J* = 8.4, *J* = 6.3 Hz, 1 H, C*H*-CH=C-S), 1.80–1.92 [m, *J* = 6.7, *J* = 3.4 Hz, 1 H, C*H*(CH_3)$_2$], 1.90–2.02 (m, 1 H, CH*H*-CH=CH), 2.10–2.31 (m, 2 H, C*H*H-CH*H*-CH=CH), 2.70 (ddd, *J* = 13.4, *J* = 4.5 Hz, 1 H, CH*H*-CH_2-CH=CH), 2.93 (s, 3 H, N-CH_3), 3.25 (d, *J* = 14.3 Hz, 1 H, CH*H*-CO), 3.96 (dq, *J* = 7.3, 2.5 Hz, 1 H, CH_2-CO-CH*H*-CH_3), 3.98 (dq, *J* = 7.3, 2.5 Hz, 1 H, CH_2-CO-CH*H*), 4.06 (m, *J* = 14.3 Hz, 1 H, CH*H*-CO), 4.40 (dd, *J* = 5.2 Hz, 1 H, CH-O), 5.20 (ddd, *J* = 12.4, 5.2, 2.7 Hz, 1 H, C*H*=CH-CH_2), 5.39 (ddd, *J* = 12.4, 6.9, 2.7 Hz, 1 H, CH=C*H*-CH_2), 6.95 (d, *J* = 6.3 Hz, 1 H, CH=C-S), 6.93–7.05 (m, 3 H, Ph), 8.04–8.08 (m, 2 H, Ph) ppm. ^{13}C NMR (75 MHz, C_6D_6): δ = 13.9 (d), 20.1 (d), 21.2 (d), 25.9 (u), 29.6 (d), 31.8 (d), 38.8 (u), 45.8 (u), 47.5 (d), 59.4 (u), 72.1 (d), 78.6 (u), 128.4 (d), 128.5 (d), 129.2 (d), 131.6 (d), 132.8 (d), 141.3 (u), 142.5 (d), 143.4 (u), 169.9 (u) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3071 (w), 2960 (s), 2874 (m), 1732 (s), 1639 (w), 1447 (s), 1370 (m), 1248 (s), 1150 (s), 1082 (w), 1037 (m), 967 (w), 912 (m), 851 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 419 (9), 418 (33), 417 [M]$^+$ (50), 375 (24), 374 (100), 373 (11), 372 (52), 328 (32), 302 (29), 263 (12), 262 (22), 244 (17), 219 (31), 215 (11), 214 (49), 175 (24), 174 (19), 173 (15), 159 (12), 156 (48), 148 (22), 147 (26), 145 (19), 138 (11), 133 (31), 132 (26), 131 (38), 124 (58), 117 (16), 107 (20), 106 (11), 105 (26), 97 (12), 91 (26), 81 (12). HRMS (EI): calcd. for $C_{23}H_{31}NO_4S$ 417.1973; found 417.1974.

(2*S*,3*R*,6*S*,8*S*)-8-Chloro-2,3-diisopropyl-5-[(*R*)-*N*-methyl-*S*-phenyl-sulfonimidoyl]-(phenylsulfonyl)-1-oxaspiro[5.5]undec-4-ene (20) and (2*S*,3*R*,6*R*,9*S*)-9-Chloro-2,3-diisopropyl-5-[(*R*)-*N*-methyl-*S*-phenyl-sulfonimidoyl]-1-oxaspiro[5.5]undec-4-ene (21): Treatment of hemiketal **9a** (150 mg, 0.38 mmol) with $TiCl_4$ (210 mg, 1.10 mmol) as described in **GP8** afforded an 8:1 mixture (^{1}H NMR: NMe) of chlorinated compounds **20** and **21** (129 mg, 80%). Separation first by flash chromatography (EtOAc/cyclohexane 1:9) and then by HPLC (EtOAc/cyclohexane 5:95) gave chlorinated compound **20** (110 mg, 68%) and chlorinated compound **21** (11 mg, 7%) as colorless oils.

Chlorinated Compound 20: $[\alpha]_D$ = +9.6 (*c* = 1.00, CH_2Cl_2); R_f = 0.12 (EtOAc/cyclohexane 1:9). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.82 (d, *J* = 6.8 Hz, 3 H, CH_3), 0.84 (d, *J* = 6.8 Hz, 3 H, CH_3), 1.06 (d, *J* = 6.8 Hz, 3 H, CH_3), 1.08 (d, *J* = 6.8 Hz, 3 H, CH_3), 1.09 (m, 1 H, C*H*H-CH_2-CHCl), 1.52 (m, *J* = 12.4, 3.4 Hz, 1 H, C*H*H-CH_2-CH_2-CHCl), 1.60 (m, *J* = 11.4, 3.1 Hz, 1 H, C*H*H-CHCl), 1.71 (ddt, *J* = 12.9, 3.5 Hz, 1 H, C*H*H-CH_2-CH_2-CHCl), 1.93 [m, *J* = 6.9, *J* = 2.4 Hz, 2 H, CHO-C*H*(CH_3)$_2$, C=CH-CH-C*H*(CH_3)$_2$], 2.07 (ddd, *J* = 12.7, *J* = 4.2 Hz, 1 H, C*H*H-CH_2-CHCl), 2.14 (m, *J* = 4.2 Hz, 1 H, C*H*H-CHCl), 2.28 (ddd, *J* = 9.7, 2.6 Hz, 1 H, C=CH-C*H*), 2.43 (m, *J* = 13.8, 4.4, 2.2 Hz, 1 H, CHCl-C*H*H), 2.57 (m, *J* = 13.7, 12.1, 1.7 Hz, 1 H, CHCl-C*H*H), 2.79 (s, 3 H, N-CH_3), 3.45 [dd, *J* = 9.8, 2.3 Hz, 1 H, C*H*O-

CH(CH$_3$)$_2$], 4.08 (tt, J = 11.6, 4.3 Hz, 1 H, CHCl), 6.91 (d, J = 2.4 Hz, 1 H, CH=C-S), 7.47–7.57 (m, 3 H, Ph), 7.83–7.86 (m, 2 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.5 (d), 17.5 (d), 20.9 (u), 21.2 (d), 21.4 (d), 26.7 (d), 28.6 (d), 30.0 (d), 33.5 (u), 35.9 (u), 42.1 (u), 44.2 (d), 55.8 (d), 71.6 (d), 76.5 (u), 127.4 (d), 128.8 (d), 132.1 (d), 141.3 (u), 141.8 (d), 144.5 (u) ppm. IR (in $CHCl_3$): $\tilde{\nu}$ = 2960 (s), 2874 (s), 2803 (w), 1449 (s), 1386 (m), 1370 (m), 1110 (w), 1082 (w), 1037 (s), 952 (m), 852 (s) cm^{-1}. MS (EI, 70 eV): m/z (%) = 426 (2), 425 (4), 424 (5), 423 [M]$^+$ (10), 389 (26), 388 (100), 225 (13), 155 (14), 138 (9), 124 (9). HRMS (EI): calcd. for $C_{23}H_{34}ClNO_2S$ 423.1998; found 423.1998.

Chlorinated Compound 21: $[\alpha]_D$ = –40.5 (c = 1.00, CH_2Cl_2); R_f = 0.10 (EtOAc/cyclohexane 5:95), ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.84 (d, J = 6.9 Hz, 3 H, CH_3), 0.85 (d, J = 6.9 Hz, 3 H, CH_3), 1.04 (d, J = 6.9 Hz, 3 H, CH_3), 1.10 (d, J = 6.9 Hz, 3 H, CH_3), 1.63–1.77 {m, 3 H, CH[C*H*(CH$_3$)$_2$]-COH-C*H*(CH$_3$)$_2$, CH*H*-CHCl}, 1.87–1.96 (m, 2 H, C*H*$_2$-CH$_2$-CHCl-CH*H*), 2.04 (tt, J = 14.1, J = 3.2 Hz, 1 H, CH*H*-CHCl), 2.15 (tt, J = 13.1, J = 3.2 Hz, 1 H, CHCl-CH*H*), 2.30 (m, J = 9.7, 2.6 Hz, 1 H, C=CH-C*H*), 2.60 (m, J = 14.1, 4.0 Hz, 2 H, C*H*H-CH$_2$-CHCl-CH$_2$-C*H*H), 2.81 (s, 3 H, N-CH$_3$), 3.38 (dd, J = 9.7, 2.3 Hz, 1 H, C=CH-CH-C*H*O), 4.42 (quint, J = 2.9 Hz, 1 H, CHCl), 6.96 (d, J = 2.4 Hz, 1 H, CH=C-S), 7.46–7.55 (m, 3 H, Ph), 7.88–7.92 (m, 2 H, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.6 (d), 17.5 (d), 21.3 (d), 21.5 (d), 26.3 (d), 26.9 (d), 28.9 (u), 29.0 (d), 29.1 (d), 30.0 (u), 44.4 (d), 58.8 (d), 71.6 (d), 74.4 (u), 127.8 (d), 128.9 (d), 132.2 (d), 141.4 (u), 141.5 (d), 145.8 (u) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2960 (s), 2877 (s), 2804 (w), 1447 (s), 1384 (w), 1246 (s), 1151 (s), 1110 (w), 1083 (w), 1030 (m), 1003 (m), 950 (w), 921 (w), 852 (m) cm^{-1}. MS (EI, 70 eV): m/z (%) = 426 (4), 425 (12), 424 (11), 423 [M]$^+$ (30), 389 (10), 388 (40), 382 (19), 381 (14), 380 (49), 354 (9), 353 (16), 352 (26), 351 (30), 227 (29), 226 (14), 225 (85), 161 (11), 157 (11), 156 (100), 147 (15), 145 (10), 140 (22), 139 (68), 125 (72), 119 (18), 117 (11), 107 (18), 106 (15), 105 (27), 97 (19), 93 (11), 91 (27), 81 (26), 79 (25), 78 (13), 77 (27). HRMS (EI): calcd. for $C_{23}H_{34}ClNO_2S$ 423.1998; found 423.1996.

(1*S*,1′*S*,3*S*,8a′*R*)-3-Chloro-1′-isopropyl-4′-[(*R*)-*N*-methyl-*S*-phenyl-sulfonimidoyl]-1′,5′,6′,7′,8′,8a′-hexahydro-spiro[cyclohexane-1,3′-isochromene] (22) and (1*R*,1′*S*,4*S*,8a′*R*)-4-Chloro-1′-isopropyl-4′-[(*R*)-*N*-methyl-*S*-phenyl-sulfonimidoyl]-1′,5′,6′,7′,8′,8a′-hexahydro-spiro[cyclohexane-1,3′-isochromene] (23): Treatment of hemiketal **10b** (60 mg, 0.14 mmol) with $TiCl_4$ (82 mg, 0.43 mmol) as described in **GP8** afforded an 8:1 mixture (^{1}H NMR: NMe) of chlorinated compounds **22** and **23** (51 mg, 84%). Separation by flash chromatography (EtOAc/cyclohexane 1:9) gave chlorinated compound **22** (42 mg, 69%) and chlorinated compound **23** (3 mg, 5%) as colorless oils.

Chlorinated Compound 22: $[\alpha]_D$ = +119.6 (c = 1.00, CH_2Cl_2); R_f = 0.20 (EtOAc/cyclohexane 5:95). ^{1}H NMR (400 MHz, C_6D_6): δ = 0.45–0.58 (m, 2 H, C*H*H-CH$_2$-C*H*H-CH$_2$-C=C), 0.90 (dt, J = 14.3, 7.2 Hz, 1 H, C*H*H-CH$_2$-CH$_2$-C=C), 0.89 (d, J = 6.9 Hz, 3 H, CH_3), 0.98 (d, J = 6.9 Hz, 3 H, CH_3), 1.19 (dt, J = 13.0, 4.2 Hz, 1 H, C*H*H-CH$_2$-CH$_2$-C=C), 1.25 (m, 2 H, C*H*H-C*H*H-C=C), 1.41 (d, J = 13.2 Hz, 1 H, C*H*H-CH$_2$-CH$_2$-CH$_2$-C=C), 1.48 (m, 1 H, CClH-CH$_2$-C*H*H), 1.56 [dtd, J = 11.5, 6.9, 2.4 Hz, 1 H, C*H*-(CH$_3$)$_2$], 1.75 (d, J = 12.8 Hz, 1 H, CClH-CH$_2$-CH$_2$-C*H*H), 1.88 (m, 3 H, C*H*-CHO-CH, CClH-C*H*H-C*H*H-CH$_2$), 2.20 (m, 1 H, CClH-C*H*H), 2.82 (s, 3 H, N-CH$_3$), 2.83 (m, 1 H, C*H*H-CClH), 3.03 (dd, J = 9.3, 2.5 Hz, 1 H, CH-O), 3.44 (m, 1 H, CClH-CH$_2$-CH$_2$-C*H*H), 3.52 (dd, J = 13.2, 12.5 Hz, 1 H, C*H*H-CClH), 3.68 (ddd, J = 13.8, 3.5, 2.4 Hz, 1 H, C*H*H-C=C), 4.38 (tt, J = 11.6, 4.2 Hz, 1 H, CHCl), 6.94–6.97 (m, 3 H, Ph), 7.92–7.96 (m, 2 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.3 (d), 21.6 (d), 21.9 (u), 25.1 (u), 26.5 (u), 29.4 (d), 29.9 (d), 31.9 (u), 32.0 (u), 34.5 (u), 36.1 (u), 41.3 (u), 43.1 (d), 56.7 (d), 74.6 (d), 78.0 (u), 126.7 (d), 128.8 (d), 131.8 (d) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3012 (w), 2936 (s), 2868 (s), 2800 (w), 1590 (m), 1449 (s), 1385 (w), 1236 (s), 1146 (s), 1108 (s), 1079 (s), 1049 (s), 963 (w), 860 (s) cm^{-1}. MS (EI, 70 eV): m/z (%) = 438 (3), 437 (7), 436 (9), 435 [M]$^+$ (15), 401 (27), 349 (23), 400 (100), 382 (11), 358 (21), 357 (21), 356 (49), 321 (22), 301 (14), 299 (14), 286 (14), 285 (27), 284 (29), 283 (15), 265 (16), 255 (10), 250 (22), 249 (14), 245 (14), 237 (36), 201 (12), 185 (16), 181 (12), 173 (17), 169 (11), 156 (13), 147 (12), 145 (13), 143 (13), 139 (14), 131 (23), 129 (12), 125 (36), 117 (19), 115 (11), 109 (14), 107 (18), 105 (26), 95 (16), 93 (16), 91 (42), 81 (26). HRMS (EI): calcd. for $C_{24}H_{34}ClNO_2S$ 435.1998; found 435.2001.

Chlorinated Compound 23: R_f = 0.19 (EtOAc/cyclohexane 5:95). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.92 (d, J = 6.9 Hz, 3 H, CH_3), 1.07 (d, J = 6.9 Hz, 3 H, CH_3), 0.97–1.09 (m, 1 H), 1.30–1.57 (m, 4 H), 1.68 (t, J = 13.6 Hz, 2 H), 1.76–1.96 (m, 7 H), 2.04–2.24 (m, 3 H), 2.29 (tt, J = 13.8, J = 3.6 Hz, 1 H), 2.81 (s, 3 H, N-CH$_3$), 3.04 (dd, J = 12.9 Hz, 1 H), 3.19 (dd, J = 9.3, 2.0 Hz, 1 H), 3.42 (t, J = 10.8 Hz, 1 H), 3.62 (d, J = 14.2 Hz, 1 H), 4.48 (quint, J = 2.5 Hz, 1 H, CHCl), 7.47–7.56 (m, 3 H, Ph), 7.89–7.94 (m, 2 H, Ph) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2933 (s), 2870 (s), 2800 (w), 1726 (w), 1590 (w), 1446 (s), 1384 (w), 1266 (m), 1239 (s), 1147 (m), 1106 (m), 1078 (m), 1047 (m), 921 (w), 863 (m) cm^{-1}. MS (EI, 70 eV): m/z (%) = 437 (6), 436 (6), 435 (14), 406 (12), 405 (11), 404 (20), 400 (28), 389 (12), 387 (15), 359 (12), 358 (41), 357 (41), 356 (100), 355 (23), 339 (11), 332 (11), 320 (10), 301 (18), 299 (24), 287 (15), 286 (31), 285 (53), 284 (70), 283 (33), 282 (13), 281 (20), 280 (16), 279 (14), 265 (12), 255 (23), 249 (14), 239 (15), 237 (44), 223 (10), 209 (11), 208 (10), 201 (10), 181 (15), 173 (15), 169 (15), 168 (10), 167 (10), 156 (18), 155 (10), 149 (10), 147 (16), 145 (21), 143 (12), 142 (12), 141 (11), 139 (33), 135 (11), 133 (12), 131 (30), 129 (17), 125 (56), 119 (14), 117 (26), 115 (14), 109 (19), 107 (25), 106 (12), 105 (36), 97 (18), 95 (19). HRMS (EI): calcd. for $C_{24}H_{34}ClNO_2S$ 435.1998; found 435.2019.

(8*R*,9*S*,*E*)-1-Hydroxy-8-isopropyl-10-methyl-6-[(*R*)-*N*-methyl-*S*-phenyl-sulfonimidoyl]-9-(triethylsilyloxy)undec-6-en-5-one (24): Treatment of alkenylsulfoximine **1a** (300 mg, 0.71 mmol) and δ-valerolactone (140 mg, 1.40 mmol) as described in **GP9** afforded, after purification by flash chromatography (EtOAc/*n*-hexane 1:2), hydroxy ketone **24** (350 mg, 94%) as a colorless oil. $[\alpha]_D$ = –72.7 (c = 1.00, CH_2Cl_2); R_f = 0.16 (EtOAc/*n*-hexane 1:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.60 (q, J = 7.9 Hz, 6 H, Si-C*H*$_2$CH$_3$), 0.69 (d, J = 6.8 Hz, 3 H, CH_3), 0.75 (d, J = 6.8 Hz, 3 H, CH_3), 0.78 (d, J = 6.8 Hz, 3 H, CH_3), 0.90 (d, J = 6.8 Hz, 3 H, CH_3), 0.97 (t, J = 7.9 Hz, 9 H, Si-CH$_2$C*H*$_3$), 1.50 [sept, J = 6.8 Hz, 1 H, C=CH-CH-C*H*(CH$_3$)$_2$], 1.55–1.76 [m, 5 H, CO-CH$_2$-C*H*$_2$-C*H*$_2$, CHOSi-C*H*(CH$_3$)$_2$], 2.11 (ddd, J = 11.2, 8.6, 1.4 Hz, 1 H, C=CH-C*H*), 2.65 (td, J = 18.6, 6.8 Hz, 1 H, CO-C*H*H), 2.80 (s, 3 H, N-CH$_3$), 2.90 (td, J = 18.6, 7.0 Hz, 1 H, CO-C*H*H), 3.60 (dd, J = 6.7, 1.4 Hz, 1 H, CH-OSi), 3.64 (t, J = 6.7 Hz, 2 H, C*H*$_2$-OH), 6.86 (d, J = 11.2 Hz, 1 H, CH=C-S), 7.44–7.59 (m, 3 H, Ph), 7.83–7.88 (m, 2 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 5.5 (u), 7.1 (d), 18.4 (d), 18.9 (d), 19.4 (u), 21.1 (d), 21.4 (d), 29.3 (d), 29.6 (d), 31.7 (u), 33.5 (d), 44.1 (u), 48.8 (d), 62.3 (u), 77.9 (d), 128.4 (d), 128.8 (d), 132.5 (d), 139.4 (u), 143.1 (u), 148.1 (d), 200.6 (u) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3408 (m), 2958 (s), 2808 (m), 1698 (s), 1616 (w), 1465 (s), 1411 (w), 1249 (s), 1375 (m), 1253 (s), 1152 (s), 1081 (s), 1011 (m), 858 (w), 800 (w) cm^{-1}. MS (EI, 70 eV): m/z (%) = 524 [M + 1]$^+$ (6), 523 (3), 494 (5), 480 (5), 368 (8), 339 (7), 338 (13), 337 (48), 336 (100), 322 (19), 294 (21), 283 (14), 270 (18), 267 (10), 187 (40), 159 (31), 156 (24), 125 (27), 115 (57), 111 (10), 107 (17), 103 (21), 87

(55). HRMS: calcd. for $C_{28}H_{49}NO_4SSi$ 523.3151; found 523.3151.

(6*E*,8*R*,9*S*,10*E*)-1-Hydroxy-8-isopropyl-6-[(*R*)-*N*-methyl-*S*-phenylsulfonimidoyl]-9-(triethylsilyloxy)dodeca-6,10-dien-5-one (25): Treatment of alkenylsulfoximine **1b** (300 mg, 0.71 mmol) and δ-valerolactone (140 mg, 1.40 mmol) as described in **GP9** afforded, after purification by flash chromatography (EtOAc/*n*-hexane 1:2), hydroxy ketone **25** (350 mg, 95%) as a colorless oil. $[\alpha]_D$ = –64.8 (*c* = 1.00, CH_2Cl_2); R_f = 0.18 (EtOAc/*n*-hexane 1:2). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.57 (q, *J* = 7.9 Hz, 6 H, Si-C*H*$_2$CH$_3$), 0.82 (d, *J* = 6.8 Hz, 3 H, CH$_3$), 0.89 (d, *J* = 6.8 Hz, 3 H, CH$_3$), 0.98 (t, *J* = 7.9 Hz, 9 H, Si-CH$_2$C*H*$_3$), 1.36–1.48 (m, 5 H, CH=CH-CH$_3$, C*H*$_2$-CH$_2$-OH), 1.77 (m, 2 H, CO-CH$_2$-C*H*$_2$), 1.84–2.03 [m, 2 H, C=CH-C*H*-C*H*(CH$_3$)$_2$], 2.83 (td, *J* = 18.4, 7.0 Hz, 1 H, CO-C*H*H), 2.98 (td, *J* = 18.4, 7.1 Hz, 1 H, CO-C*H*H), 3.02 (s, 3 H, N-CH$_3$), 3.39 (t, *J* = 6.3 Hz, 2 H, C*H*$_2$-OH), 4.21 (dd, *J* = 7.0, 3.8 Hz, 1 H, CH-OSi), 5.19–5.34 (m, 2 H, CHOSi-C*H*=C*H*-CH$_3$), 6.95–7.06 (m, 3 H, Ph), 7.02 (d, *J* = 11.2 Hz, 1 H, CH=C-S), 8.08–8.11 (m, 2 H, Ph) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 5.5 (u), 7.1 (d), 17.4 (d), 19.9 (d), 20.4 (u), 21.2 (d), 28.8 (d), 29.7 (d), 32.2 (d), 45.1 (u), 54.2 (d), 62.2 (u), 74.5 (d), 126.6 (d), 127.3 (d), 128.8 (d), 129.0 (u), 132.1 (u), 133.9 (d), 141.1 (u), 144.2 (d), 146.0 (u), 200.5 (u) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3503 (m), 3387 (m), 3213 (w), 3062 (w), 2877 (s), 2807 (m), 1701 (s), 1627 (s), 1450 (m), 1373 (w), 1252 (s), 1153 (m), 1075 (m), 1008 (w), 971 (m), 857 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 492 (2), 408 (2), 336 (14), 207 (11), 186 (16), 185 (100), 115 (28), 87 (23). MS (CI, CH_4): *m*/*z* (%) = 522 $[M]^+$ (100). HMRS: calcd. for $C_{28}H_{47}NO_4SSi{\cdot}CH_3N$ 492.2729; found 492.2728.

(2*S*,3*R*,6*R*)-2,3-Diisopropyl-5-[(*S*)-*N*-methyl-*S*-phenyl-sulfonimidoyl]-1,7-dioxaspiro[5.5]undec-4-ene (26): Treatment of hydroxy ketone **24** (80 mg, 0.15 mmol) with *p*-TsOH (79 mg, 0.45 mmol) as described in **GP10** afforded, after purification by flash chromatography (EtOAc/cyclohexane 1:5), spiroketal **26** (48 mg, 82%) as a colorless oil. $[\alpha]_D$ = –91.6 (*c* = 1.00, CH_2Cl_2); R_f = 0.26 (EtOAc/cyclohexane 1:5). ^{1}H NMR (400 MHz, C_6D_6): δ = 0.68 (d, *J* = 6.8 Hz, 3 H, CH$_3$), 0.85 (d, *J* = 6.8 Hz, 3 H, CH$_3$), 0.87 (d, *J* = 6.8 Hz, 3 H, CH$_3$), 1.03 (d, *J* = 6.8 Hz, 3 H, CH$_3$), 1.05–1.14 (m, 1 H, CO-CH$_2$-C*H*H), 1.38 (ddd, *J* = 13.1, 4.8, 4.0 Hz, 1 H, CO-CH$_2$-C*H*H), 1.42–1.73 [m, 4 H, CO-C*H*$_2$, CHO-C*H*(CH$_3$)$_2$], 1.87 (dt, *J* = 13.0, 3.8 Hz, 1 H, CO-CH$_2$-CH$_2$-C*H*H), 2.11 (ddd, *J* = 7.0, 3.8, 2.4 Hz, 1 H, C=CH-C*H*), 2.93 (s, 3 H, N-CH$_3$), 3.06–3.21 (m, 2 H, CO-C*H*H-CH$_2$-C*H*H), 3.58 (dd, *J* = 10.3, 2.3 Hz, 1 H, CH-O), 3.64 (ddd, *J* = 13.3, 10.8, 2.6 Hz, 1 H, CO-C*H*H), 6.98–7.07 (m, 3 H, Ph), 7.46 (d, *J* = 2.1 Hz, 1 H, CH=C-S), 8.12–8.28 (m, 2 H, Ph) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 15.0 (d), 17.1 (d), 19.0 (u), 20.9 (d), 21.5 (d), 25.0 (u), 26.9 (d), 28.6 (d), 30.0 (d), 32.0 (u), 44.1 (d), 61.4 (u), 71.4 (d), 95.3 (d), 128.4 (d), 129.5 (d), 131.6 (d), 142.2 (u), 143.4 (u), 143.7 (d) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 2959 (s), 2876 (s), 2805 (w), 1734 (w), 1629 (w), 1449 (m), 1373 (m), 1250 (s), 1151 (s), 1109 (w), 1078 (m), 1047 (w), 1006 (s), 907 (w), 858 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 393 $[M]^+$ (3), 392 (8), 391 $[M]^+$ (32), 349 (22), 348 (7), 320 (23), 125 (14). MS (CI, isobutene): *m*/*z* (%) = 392 $[M + 1]^+$ (100). HMRS: calcd. for $C_{22}H_{33}NO_3S$ 391.2181; found 391.2177.

(2*S*,3*R*,6*R*)-3-Isopropyl-5-[(*R*)-*N*-methyl-*S*-phenyl-sulfonimidoyl]-2-[(*E*)-prop-1-enyl]-1,7-dioxaspiro[5.5]undec-4-ene (27): Treatment of hydroxy ketone **25** (90 mg, 0.17 mmol) with *p*TsOH (89 mg, 0.51 mmol) as described in **GP10** afforded, after purification by flash chromatography (EtOAc/*n*-hexane 1:5), spiroketal **27** (57 mg, 86%) as a colorless oil. $[\alpha]_D$ = –115.1 (*c* = 1.00, CH_2Cl_2); R_f = 0.18 (EtOAc/*n*-hexane 1:5). ^{1}H NMR (400 MHz, C_6D_6): δ = 0.73 (d, *J* = 6.8 Hz, 3 H, CH$_3$), 0.85 (d, *J* = 6.8 Hz, 3 H, CH$_3$), 1.04–1.10 (m, 1 H, CO-CH$_2$-C*H*H), 1.35–1.48 (m, 2 H, CO-CH$_2$-C*H*H-C*H*H), 1.51 (d, *J* = 6.4, 1.5 Hz, 3 H, CH=CH-C*H*$_3$), 1.68–1.78 [m, 2 H, CO-CH*H*-CH$_2$, C*H*(CH$_3$)$_2$], 1.95 (dt, *J* = 13.1, 3.8 Hz, 1 H, CO-CH$_2$-CH$_2$-C*H*H), 2.12 (dd, *J* = 10.1, 2.7 Hz, 1 H, C=CH-C*H*), 3.05 (s, 3 H, N-CH$_3$), 3.22 (dt, *J* = 13.3, 4.6 Hz, 1 H, CO-CH$_2$-CH$_2$-CH$_2$-C*H*H), 3.22 (dd, *J* = 10.9, 4.5 Hz, 1 H, CO-C*H*H), 3.64 (ddd, *J* = 13.1, 10.9, 2.5 Hz, 1 H, CO-C*H*H), 4.11 (dd, *J* = 10.1, 7.9 Hz, 1 H, CH-O), 5.45 (dq, *J* = 15.0, 7.8, 1.5 Hz, 1 H, CHO-C*H*=CH-CH$_3$), 5.59 (dq, *J* = 15.0, 6.4 Hz, 1 H, CHO-CH=C*H*-CH$_3$), 6.99–7.07 (m, 3 H, Ph), 7.47 (d, *J* = 2.0 Hz, 1 H, CH=C-S), 8.14–8.18 (m, 2 H, Ph) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 17.3 (d), 17.9 (d), 18.7 (u), 20.8 (d), 24.8 (u), 26.9 (d), 29.9 (d), 31.7 (u), 47.4 (d), 61.2 (u), 69.8 (d), 95.7 (d), 128.6 (d), 129.2 (d), 129.4 (d), 130.5 (d), 131.5 (d), 142.0 (u), 143.0 (d), 143.5 (u) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3063 (w), 2957 (s), 2874 (s), 2806 (m), 1737 (w), 1627 (w), 1447 (s), 1373 (m), 1249 (s), 1152 (s), 1073 (m), 1046 (w), 1004 (s), 965 (m), 911 (m), 888 (w), 855 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 391 (6), 390 (19), 389 $[M]^+$ (34), 375 (10), 374 (39), 347 (15), 346 (66), 319 (17), 318 (16), 305 (27), 304 (14), 292 (14), 256 (11), 243 (10), 235 (54), 234 (61), 225 (20), 219 (18), 206 (35), 205 (46), 192 (17), 191 (66), 177 (18), 167 (11), 165 (12), 164 (20), 163 (32), 156 (39), 151 (58), 150 (73), 149 (74), 148 (17), 147 (12), 139 (32), 137 (16), 136 (12), 135 (31), 133 (11), 131 (22), 126 (12), 125 (100), 123 (14), 122 (12), 121 (24), 119 (15), 111 (11). MS (CI, CH_4): *m*/*z* (%) = 390 $[M + 1]^+$ (100). HMRS: calcd. for $C_{22}H_{31}NO_3S$ 389.2024; found 389.2025.

(2*S*,3*R*,6*R*,*Z*)-2,3-Diisopropyl-1,7-dioxaspiro[5.6]dodeca-4,9-diene (28): Treatment of alkenylsulfoximine **14** (50 mg, 0.13 mmol) with freshly prepared aluminum amalgam (500 mg) as described in **GP11** gave alkene **28** (28 mg, 86%) as a colorless oil. $[\alpha]_D$ = –100.9 (*c* = 0.45, CH_2Cl_2); R_f = 0.80 (*n*-hexane/EtOAc 20:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.68 (d, *J* = 6.9 Hz, 3 H, CH$_3$), 0.84 (d, *J* = 6.9 Hz, 3 H, CH$_3$), 0.93 (d, *J* = 6.9 Hz, 3 H, CH$_3$), 1.01 (d, *J* = 6.9 Hz, 3 H, CH$_3$), 1.68–1.79 [m, 2 H, C*H*HCO, (CH$_3$)$_2$C*H*CHCH], 1.86 [ten-lines pattern, *J* = 9.1, 6.9, 2.2 Hz, 1 H, (CH$_3$)$_2$C*H*CHO], 1.94–2.05 (m, 2 H, CH*H*CO, C*H*CH=CH), 2.15 (dt, *J* = 14.6, 1.1 Hz, 1 H, CH$_2$C*H*HCH=CH), 2.34 (m, 1 H, CH$_2$CH*H*CH=CH), 3.56 (dd, *J* = 10.1, 2.5 Hz, 1 H, CH-O), 3.74 (ddd, *J* = 16.4, 7.4, 1.9 Hz, 1 H, C*H*H-O), 4.54 (d, *J* = 16.7, 2.2 Hz, 1 H, CH*H*-O), 5.52 (m, 1 H, OCH$_2$C*H*=CH), 5.68 (m, 1 H, OCH$_2$CH=C*H*), 5.76 (dd, *J* = 10.2, 1.6 Hz, 1 H, CHC*H*=CH), 5.93 (dd, *J* = 10.2, 2.8 Hz, CHCH=C*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.9 (d), 16.7 (d), 20.8 (d), 21.3 (d), 23.6 (d), 26.3 (d), 27.9 (d), 37.9 (u), 41.8 (d), 59.9 (u), 73.6 (d), 97.8 (u), 128.1 (d), 128.5 (d), 129.1 (d), 131.1 (d) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3024 (m), 2960 (s), 1732 (w), 1657 (w), 1464 (s), 1390 (m), 1279 (m), 1258 (m), 1160 (s), 1110 (s), 1083 (s), 1036 (s), 1012 (s), 899 (m) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 250 $[M]^+$ (6), 232 (12), 219 (8), 207 (18), 189 (6), 181 (10), 180 (15), 179 (16), 178 (100), 163 (45), 137 (40), 135 (13), 124 (44), 123 (15), 95 (65). HRMS: calcd. for $C_{16}H_{26}O_2{\cdot}H_2O$ 232.1827; found 232.1827.

(2*S*,3*R*,6*R*)-3-Isopropyl-2-[(*E*)-prop-1-enyl]-1,7-dioxaspiro[5.5]-undec-4-ene (30): Treatment of alkenylsulfoximine **27** (39 mg, 0.10 mmol) with Al/Hg as described in **GP11** gave, after purification by flash chromatography on silica, the bicyclic spiroketal **30** (18 mg, 76%, EtOAc/cyclohexane 1:40) and sulfinamide **29** (8 mg, 51%, EtOAc/cyclohexane 4:1) as colorless oils. $[\alpha]_D$ = –165.3 (*c* = 1.00, CH_2Cl_2); R_f = 0.12 (EtOAc/cyclohexane 1:40). ^{1}H NMR (400 MHz, C_6D_6): δ = 0.79 (d, *J* = 6.8 Hz, 3 H, CH$_3$), 0.86 (d, *J* = 6.8 Hz, 3 H, CH$_3$), 1.24 (m, 1 H, CO-CH$_2$-CH*H*), 1.39–1.62 [m, 3 H,CO-CH$_2$-CH$_2$-CH$_2$-C*H*$_2$, C*H*(CH$_3$)$_2$], 1.58 (dd, *J* = 6.3, 1.0 Hz, 1 H, CH=CH-C*H*$_3$), 1.77–1.85 [m, 1 H, C*H*(CH$_3$)$_2$, CO-CH$_2$-CH$_2$-C*H*H], 2.06 (dd, *J* = 12.7, 3.4 Hz, 2 H, C*H*-CH=CH, CO-CH$_2$-CH$_2$-C*H*H), 3.63 (ddd, *J* = 10.8, 4.6 Hz, 1 H, CO-C*H*H), 3.99 (ddd,

J = 10.1, 7.6 Hz, 1 H, CO-C*H*H), 4.36 (dd, J = 10.1, 7.7 Hz, 1 H, CH-O), 5.62 (dq, J = 15.3, 7.7, 1.4 Hz, 1 H, CHO-C*H*=CH-CH_3), 5.71 (dd, J = 10.2 Hz, 1 H, CH-CH=C*H*), 5.73 (dq, J = 15.3, 6.4 Hz, 1 H, CHO-CH=C*H*-CH_3), 5.81 (dd, J = 10.2, 2.6 Hz, 1 H, CH-C*H*=CH) ppm. ^{13}C NMR (100 MHz, C_6D_6): δ = 17.3 (d), 16.8 (d), 17.9 (u), 18.9 (d), 21.1 (u), 25.6 (d), 26.6 (d), 35.4 (u), 45.5 (d), 60.7 (u), 71.6 (d), 93.7 (d), 127.9 (d), 128.4 (d), 131.7 (d), 132.2 (u) ppm. IR (capillary): $\tilde{\nu}$ = 3035 (w), 2952 (s), 2872 (s), 1457 (m), 1381 (w), 1269 (w), 1201 (w), 1181 (w), 1120 (w), 1074 (w), 1049 (w), 1002 (s), 968 (w), 898 (w), 808 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 236 $[M]^+$ (0.5), 219 (0.5), 193 (2), 167 (11), 166 (100), 98 (30), 95 (20), 93 (12).

(1*R*,6*S*,7*R*,*Z*)-7-Isopropyl-10-oxabicyclo[4.3.1]deca-4,8-dien-1-ol (31): Treatment of alkenylsulfoximine **18** (38 mg, 0.11 mmol) with freshly prepared aluminum amalgam (500 mg) as described in **GP11** gave, after purification by flash chromatography (first EtOAc/cyclohexane 1:9 and then EtOAc/*n*-hexane 4:1), alkene **31** (16 mg, 75%) and sulfinamide **29** (10 mg, 59%) $[\alpha]_D$ = –139.4 (c = 0.80, acetone) as colorless oils. $[\alpha]_D$ = –6.6 (c = 1.00, CH_2Cl_2); R_f = 0.13 (EtOAc/cyclohexane 1:9). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.99 (d, J = 6.8 Hz, 3 H, CH_3), 1.00 (d, J = 6.8 Hz, 3 H, CH_3), 1.71 (dd, J = 5.7 Hz, 1 H, C*H*-CH=C-S), 1.80 [m, J = 6.8 Hz, 1 H, C*H*$(CH_3)_2$], 2.06 (m, J = 17.3, J = 8.9, J = 3.2 Hz, 2 H, CH=CH-CH_2-CH_2), 2.19 (m, J = 7.6, 3.6 Hz, 2 H, CH=CH-CH_2), 2.37 (m, 3 H, CH=CH-CH_2-CH_2-CO*H*), 4.53 (dd, J = 4.4 Hz, 1 H, C*H*O-CH=CH), 5.57 (m, 2 H, CHO-C*H*=C*H*), 5.77 {dd, J = 10.5, 1.0 Hz, 1 H, CH[CH$(CH_3)_2$]-CH=C*H*}, 5.97 {dd, J = 10.5, 5.7 Hz, 1 H, CH[CH$(CH_3)_2$]-C*H*=CH} ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.1 (d), 20.8 (d), 23.7 (u), 32.1 (d), 38.5 (u), 43.2 (d), 73.8 (d), 96.1 (u), 127.3 (d), 129.6 (d), 130.3 (d), 133.7 (d) ppm. IR ($CHCl_3$): $\tilde{\nu}$ = 3402 (m), 2959 (s), 2873 (s), 1729 (s), 1464 (m), 1373 (w), 1242 (w), 1071 (m), 920 (w), 883 (w) cm^{-1}. MS (EI, 70 eV): *m*/*z* (%) = 195 (5), 194 $[M]^+$ (45), 179 (14), 152 (11), 151 (65), 149 (54), 148 (14), 139 (21), 134 (15), 133 (100), 125 (19), 124 (40), 123 (17), 122 (11), 121 (16), 119 (16), 111 (27), 110 (16), 109 (62), 108 (20), 107 (67), 106 (12), 105 (100), 103 (11), 97 (17), 96 (16), 95 (83), 93 (43), 92 (15), 91 (58). HRMS (EI): calcd. for $C_{19}H_{25}NO_3S$: 194.1306; found 194.1306.

Supporting Information (see footnote on the first page of this article): Copies of the ^{1}H and ^{13}C NMR spectra of all new compounds and NOE data of compounds **9a**, **9g**, **14**, **15**, **18**, **20**, **21**, **22** and **27**.

Acknowledgments

Financial support of this work by the Deutsche Forschungsgemeinschaft (DFG) (GK 440) is gratefully acknowledged.

[1] For reviews, see: a) M. A. Brimble, F. A. Farès, *Tetrahedron* **1999**, *55*, 7661–7706; b) W. Franke, W. Kitching, *Curr. Org. Chem.* **2001**, *5*, 233–251; c) K. T. Mead, B. N. Brewer, *Curr. Org. Chem.* **2003**, *7*, 227–256; d) J. E. Aho, P. M. Pihko, T. K. Rissa, *Chem. Rev.* **2005**, *105*, 4406–4440; e) S. V. Ley, L.-G. Milroy, R. M. Myers, *Sci. Synth.* **2007**, *29*, 613–689; f) B. R. Raju, A. K. Anil, *Molecules* **2008**, *13*, 1942–2038; g) S. Favre, P. Vogel, S. Gerber-Lemaire, *Molecules* **2008**, *13*, 2570–2600; h) E. A. Anderson, B. Gockel, *Sci. Synthesis* **2011**, *3*, 173–228; i) R. G. Carter, D. L. Kuiper, *Sci. Synth.* **2011**, *2*, 863–914; j) R. Rios, *Chem. Soc. Rev.* **2012**, *41*, 1060–1074; k) J. A. Palmes, A. Aponick, *Synthesis* **2012**, *44*, 3699–3721.

[2] For a review, see: S. Rosenberg, R. Leino, *Synthesis* **2009**, 2651–2673.

[3] For reviews, see: a) P. Bernardelli, L. A. Paquette, *Hetereocycles* **1998**, *49*, 531–556; b) I. V. Hartung, H. M. R. Hoffmann, *Angew. Chem.* **2004**, *116*, 1968–1984; *Angew. Chem. Int. Ed.* **2004**, *43*, 1934–1949; c) P. Chiu, M. Lautens, *Top. Curr. Chem.* **1997**, *190*, 1–85; d) K. Takao, K. Tadano, *Heterocycles* **2010**, *81*, 1603–1629.

[4] For recent syntheses of spiroketals, see: a) J. Mandel, N. Dubois, M. Neuburger, N. Blanchard, *Chem. Commun.* **2011**, *47*, 10284–10286; b) M. Commandeur, C. Commandeur, J. Cossy, *Org. Lett.* **2011**, *13*, 6018–6021; c) J. E. Lynch, S. D. Zanatta, J. M. White, M. A. Rizzacasa, *Chem. Eur. J.* **2011**, *17*, 297–304; d) K. Ravindar, M. S. Reddy, P. Deslongchamps, *Org. Lett.* **2011**, *13*, 3178–3181; e) L. Zhu, L. Song, R. Tong, *Org. Lett.* **2012**, *14*, 5892–5895; f) L. Nachbauer, R. Brückner, *Eur. J. Org. Chem.* **2012**, 9604–6923; g) O. Kubo, D. P. Canterbury, G. C. Micalizio, *Org. Lett.* **2012**, *14*, 5748–5751; h) J. Huang, J. R. Yang, J. Zhang, J. Yang, *J. Am. Chem. Soc.* **2012**, *134*, 8806–8809; i) M. Xuan, I. Paterson, S. M. Dalby, *Org. Lett.* **2012**, *14*, 5492–5495.

[5] For recent syntheses of spiroethers, see: a) N. Noguchi, M. Nakada, *Org. Lett.* **2006**, *8*, 2039–2042; b) Q.-W. Zhang, C.-A. Fan, H.-J. Zhang, Y.-Q. Tu, Y.-M. Zhao, P. Gu, Z.-M. Chen, *Angew. Chem.* **2009**, *121*, 8724–8726; *Angew. Chem. Int. Ed.* **2009**, *48*, 8572–8574; c) Z.-W. Jiao, S.-Y. Zhang, C. He, Y.-Q. Tu, S. H. Wang, F.-M. Zhang, Y.-Q. Zhang, H. Li, *Angew. Chem.* **2012**, *124*, 8941–8945; *Angew. Chem. Int. Ed.* **2012**, *51*, 8811–8815; d) P. Sancibrao, D. Gori, C. Kouklovsky, G. Vincent, *Chem. Eur. J.* **2013**, *19*, 5557–5560; e) B.-S. Li, W.-X. Liu, Q.-W. Zhang, S.-H. Wang, F.-M. Zhang, S.-Y. Zhang, Y.-Q. Tu, X.-P. Cao, *Chem. Eur. J.* **2013**, *19*, 5246–5249; f) L. I. Palmer, J. R. De Alaniz, *Org. Lett.* **2013**, *15*, 476–479.

[6] For recent syntheses of oxabicycles, see: a) R. Dhanapal, P. T. Perumal, C. Ramprasath, N. Mathivanan, *Bioorg. Med. Chem. Lett.* **2013**, *23*, 3599–3603; b) X. Gao, M. Harmata, *Tetrahedron* **2013**, *69*, 7675–7682; c) H. Yamada, M. Adachi, M. Isobe, T. Nishikawa, *Chem. Asian J.* **2013**, *8*, 1428–1435.

[7] For reviews, see: a) S. Monfette, D. E. Fogg, *Chem. Rev.* **2009**, *109*, 3783–3816; b) G. C. Vougioukalakis, R. H. Grubbs, *Chem. Rev.* **2010**, *110*, 1746–1787; c) *Metathesis in Natural Product Synthesis* (Eds.: J. Cossy, S. Arseniyadis, C. Meyer), Wiley-VCH, Weinheim, Germany; d) M. Mori, *Materials* **2010**, *3*, 2087–2140; e) C. Fischmeister, C. Bruneau, *Beilstein J. Org. Chem.* **2011**, *7*, 156–166.

[8] For syntheses of carbohydrate spiroketals through spiroannulation with RCDEM and RCEYM, see: a) P. A. V. van Hooft, M. A. Leeuwenburgh, H. S. Overkleeft, G. A. van der Marel, C. A. A. S. Van Boeckel, J. H. van Boom, *Tetrahedron Lett.* **1998**, *39*, 6061–6064; b) M. A. Leeuwenburgh, C. C. M. Appeldoorn, P. A. V. van Hooft, H. S. Overkleeft, G. A. van der Marel, J. H. van Boom, *Eur. J. Org. Chem.* **2000**, 873–877; c) P. A. V. van Hooft, F. E. Qualid, H. S. Overkleeft, G. A. van der Marel, J. H. van Boom, M. A. Leeuwenburgh, *Org. Biomol. Chem.* **2004**, *2*, 1395–1403.

[9] For syntheses of naturally occurring spiroketals through spiroannulation with RCDEM, see: a) J. Liu, R. P. Hsung, *Org. Lett.* **2005**, *7*, 2273–2276; b) S. K. Ghosh, R. P. Hsung, J. Liu, *J. Am. Chem. Soc.* **2005**, *127*, 8260–8261; c) S. K. Ghosh, C. Ko, J. Wang, R. P. Hsung, *Tetrahedron* **2006**, *62*, 10485–10496; d) R. Figueroa, R. P. Hsung, C. C. Guevarra, *Org. Lett.* **2007**, *9*, 4857–4859; e) J.-H. Yang, J. Liu, R. P. Hsung, *Org. Lett.* **2008**, *10*, 2525–2528; f) A. V. Subrahmanyam, K. Palanichamy, K. P. Kalippan, *Chem. Eur. J.* **2010**, *16*, 8545–8556; g) Y. Tang, J.-H. Yang, J. Liu, C.-C. Wang, M.-C. Lv, Y.-B. Wu, X.-L. Yu, C. Ko, R. P. Hsung, *Heterocycles* **2012**, *86*, 565–598.

[10] For syntheses of spiroethers through spiroannulation with RCDEM, see: a) M. J. Bassindale, P. Hamley, A. Leitner, J. P. A. Harrity, *Tetrahedron Lett.* **1999**, *40*, 3247–3250; b) E. Z. Oblak, N. G. Dayanandan, D. L. Wright, *Org. Lett.* **2011**, *13*, 2433–2435.

[11] For syntheses of oxabicycles through bicycloannulation with RCDEM, see: a) P. de Armas, F. García-Tellado, J. J. Marrero-Tellado, *Eur. J. Org. Chem.* **2001**, 4423–4429; b) K. Takao, H.

Yasui, S. Yamamoto, D. Sasaki, S. Kawasaki, G. Watanabe, K. Tadano, *J. Org. Chem.* **2004**, *69*, 8789–8795.

[12] a) I. Erdelmeier, H.-J. Gais, *J. Am. Chem. Soc.* **1989**, *111*, 1125–1126; b) H.-J. Gais, G. Bülow, *Tetrahedron Lett.* **1992**, *33*, 461–464; c) H.-J. Gais, G. Bülow, *Tetrahedron Lett.* **1992**, *33*, 461–464; d) H.-J. Gais, G. Bülow, *Tetrahedron Lett.* **1992**, *33*, 465–468; e) H.-J. Gais, H. Müller, J. Decker, R. Hainz, *Tetrahedron Lett.* **1995**, *30*, 7433–7436; f) M. Schleusner, H.-J. Gais, S. Koep, G. Raabe, *J. Am. Chem. Soc.* **2002**, *124*, 7789–7800; g) H.-J. Gais, C. V. Rao, R. Loo, *Chem. Eur. J.* **2008**, *14*, 6510–6528; h) V. Mahajan, H.-J. Gais, *Chem. Eur. J.* **2011**, *17*, 6187–6195.

[13] a) S. G. Pyne, *Sulfur Rep.* **1992**, *12*, 57–89; b) S. G. Pyne, *Sulfur Rep.* **1999**, *21*, 281–334; c) M. Reggelin, C. Zur, *Synthesis* **2000**, 1–64; d) H.-J. Gais, in: *Asymmetric Synthesis with Chemical and Biological Methods* (Eds.: D. Enders, K.-E. Jaeger), Wiley-VCH, Weinheim, Germany, **2007**, p. 75–115; e) H.-J. Gais, *Heteroat. Chem.* **2007**, *18*, 472–481; f) C. Worch, A. C. Mayer, C. Bolm, in: *Organosulfur Chemistry in Asymmetric Synthesis*, Wiley-VCH, Weinheim, **2008**, pp. 209–229.

[14] a) H.-J. Gais, R. Loo, D. Roder, P. Das, G. Raabe, *Eur. J. Org. Chem.* **2003**, 1500–1526; b) M. Lejkowski, P. Banerjee, S. Schüller, A. Münch, J. Runsink, C. Vermeeren, H.-J. Gais, *Chem. Eur. J.* **2012**, *18*, 3529–3548.

[15] a) H.-J. Gais, R. Hainz, H. Müller, P. R. Bruns, N. Giesen, G. Raabe, J. Runsink, S. Nienstedt, J. Decker, M. Schleusner, J. Hachtel, R. Loo, C.-W. Woo, P. Das, *Eur. J. Org. Chem.* **2000**, 3973–4009; b) L. R. Reddy, H.-J. Gais, C.-W. Woo, G. Raabe, *J. Am. Chem. Soc.* **2002**, *124*, 10427–10434; c) H.-J. Gais, L. R. Reddy, G. Babu, G. Raabe, *J. Am. Chem. Soc.* **2004**, *126*, 4859–4864.

[16] a) R. F. De la Pradilla, M. Tortosa, *Org. Lett.* **2004**, *6*, 2157–2160; b) J. T. Lowe, J. S. Panek, *Org. Lett.* **2005**, *7*, 1529–1532; c) J. A. Marco, M. Carda, J. Murga, E. Falomir, *Tetrahedron* **2007**, *63*, 2929–2958; d) B. M. Trost, D. Amans, W. M. Seganish, C. K. Chung, *J. Am. Chem. Soc.* **2009**, *131*, 17087–17089; e) H. Pellissier, *Tetrahedron* **2009**, *65*, 2839–2877; f) S. Lessard, F. Peng, D. G. Hall, *J. Am. Chem. Soc.* **2009**, *131*, 9612–9613; g) S. Catalán-Muñoz, C. A. Müller, S. V. Ley, *Eur. J. Org. Chem.* **2010**, 183–190; h) W. Chaładaj, R. Kowalczyk, J. Jurczak, *J. Org. Chem.* **2010**, *75*, 1740–1743; i) B. Stenne, J. Timperio, J. Savoie, T. Dudding, S. K. Collins, *Org. Lett.* **2010**, *12*, 2032–2035; j) D. K. Mohapatra, P. P. Das, M. R. Pattanayak, J. S. Yadav, *Chem. Eur. J.* **2010**, *16*, 2072–2078; k) S. Hanessian, T. Focken, X. Mi, R. Oza, B. Chen, D. Ritson, R. Beaudegnies, *J. Org. Chem.* **2010**, *75*, 5601–5618; l) M. Çayir, S. Demirci, S. Sezer, C. Tanyeli, *Tetrahedron: Asymmetry* **2011**, *22*, 1161–1168; m) H. Kobayashi, M. Kanematsu, M. Yoshida, K. Shishido, *Chem. Commun.* **2011**, *47*, 7440–7442; n) M. T. Crimmins, M. W. Haley, E. A. O'Bryan, *Org. Lett.* **2011**, *13*, 4712–4715; o) B. Guo, G. Schwarzwalder, J. T. Njardarson, *Angew. Chem.* **2012**, *124*, 5773–5776; *Angew. Chem. Int. Ed.* **2012**, *51*, 5675–5678.

[17] For a preliminary report of a portion of this work, see: M. Lejkowski, P. Banerjee, J. Runsink, H.-J. Gais, *Org. Lett.* **2008**, *10*, 2713–2726.

[18] a) P. Deslongchamps, *Stereoelectronic Effects in Organic Chemistry*, Wiley, New York, **1983**; b) A. J. Kirby, *The Anomeric Effect and Related Stereoelectronic Effects at Oxygen*, Springer-Verlag, Berlin, **1983**; c) S. Gerber-Lemaire, P. Vogel, *Carbohydr. Chem.* **2009**, *35*, 13–32; d) I. Fleming, *Molecular Orbitals and Organic Chemical Reactions*, Wiley, Chichester **2010**.

[19] a) A. Hosomi, M. Endo, H. Sakurai, *Chem. Lett.* **1976**, 941–942; b) L. Kürti, B. Czakó, *Strategic Applications of Named Reactions in Organic Synthesis*, Elsevier Academic Press, Burlington, **2005**; c) R. Isobe, S. Nishizawa, T. Hosokawa, T. Nishikawa, *Chem. Commun.* **1998**, 2665–2676.

[20] a) P. Schwab, R. H. Grubbs, J. W. Ziller, *J. Am. Chem. Soc.* **1996**, *118*, 100–110; b) M. Scholl, S. Ding, C. W. Lee, R. H. Grubbs, *Org. Lett.* **1999**, *1*, 953–956; c) J. Huang, E. D. Stevens, S. P. Nolan, J. L. Petersen, *J. Am. Chem. Soc.* **1999**, *121*, 2674–2678.

[21] G. Kraemer, A. Oehlhof, H. Meier, *Zeitsch. Naturforsch. B* **2009**, *64*, 847–850.

[22] T. Mukaiyama, K. Matsubara, M. Hora, *Synthesis* **1994**, 1368–1373.

[23] a) I. M. Pastor, M. Yus, *Curr. Org. Chem.* **2007**, *11*, 925–957; b) C. Olier, M. Kaafarani, S. Gastaldi, M. P. Bertrand, *Tetrahedron* **2010**, *66*, 413–445; c) I. M. Pastor, M. Yus, *Curr. Org. Chem.* **2012**, *16*, 1277–1312.

[24] a) A. K. Ghosh, D. Shin, G. Schiltz, *Heterocycles* **2002**, *58*, 659–666; b) G. Sabitha, K. B. Reddy, M. Bhikshapathi, J. S. Yadav, *Tetrahedron Lett.* **2006**, *47*, 2807–2810; c) X.-L. Zhao, L. Liu, Y.-J. Chen, D. Wang, *Tetrahedron* **2006**, *62*, 7113–7120; d) G. Sabitha, K. B. Reddy, M. Bhikshapathi, J. S. Yadav, *Tetrahedron Lett.* **2006**, *47*, 2807–2810; e) J. S. Yadav, B. V. S. Reddy, V. H. Krishna, T. Swamy, G. G. K. S. N. Kumar, *Can. J. Chem.* **2007**, *85*, 412–415; f) M. P. Castaldi, D. M. Troast, J. A. Porco Jr, *Org. Lett.* **2009**, *11*, 3362–3365; g) J. Wang, E. A. Crane, K. A. Scheidt, *Org. Lett.* **2011**, *13*, 3086–3089; h) M. Jacolot, M. Jean, N. Levoin, P. van de Weghe, *Org. Lett.* **2012**, *14*, 58–61.

[25] L. A. Paquette, J. Tae, *J. Org. Chem.* **1996**, *61*, 7860–7866.

[26] a) I. E. Markó, M. Bailey, F. Murphy, J.-P. Declercq, B. Tinant, J. Feneau-Dupont, A. Krief, W. Dumont, *Synlett* **1995**, 123–126; b) I. E. Markó, A. Mekhalfia, F. Murphy, D. J. Bayston, M. Bailey, Z. Janousek, S. Dolan, *Pure Appl. Chem.* **1997**, *69*, 565–570.

[27] L. E. Overman, E. J. Velthuisen, *J. Org. Chem.* **2006**, *71*, 1581–1587.

[28] a) K. Tadpetch, S. D. Rychnovsky, *Org. Lett.* **2008**, *10*, 4839–4842; b) B. V. S. Reddy, A. Venkateswarlu, G. G. K. S. N. Kumar, A. Vinu, *Tetrahedron Lett.* **2010**, *51*, 6511–6515.

[29] a) A. Berkessel, J. A. Adrio, *J. Am. Chem. Soc.* **2006**, *128*, 13412–13420; b) S. P. Panchenko, S. A. Runichina, V. V. Tumanov, *Mendeleev Commun.* **2011**, *21*, 226–228; c) P. Trillo, A. Baeza, C. Najerá, *J. Org. Chem.* **2012**, *77*, 7344–**7354**.

[30] H. Günther, *NMR Spectroscopy*, Wiley, Chichester, UK, **1996**.

[31] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 09*, revision A.02, Gaussian, Inc., Wallingford CT, **2009**.

[32] a) E. D. Glendening, A. E. Reed, J. E. Carpenter, F. Weinhold, *NBO 3.0 Program Manual* (*Natural Bond Orbital*/*Natural Population Analysis*/*Natural Localized Molecular Orbital Programs*), Theoretical Chemistry Institute and Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706; b) F. Weinhold, C. Landis, *Valence and Bonding. A Natural Bond Orbital Donor-Acceptor Perspective*, Cambridge University Press, **2005**.

[33] S. V. Shishkina, O. V. Shishkin, S. M. Desenko, J. Leszcynski, *J. Phys. Chem. A* **2007**, *111*, 2368–2375.

[34] a) M. T. Cancès, B. Mennucci, J. Tomasi, *J. Chem. Phys.* **1997**, *107*, 3032–3041; b) M. Cossi, V. Barone, B. Mennucci, J. Tomasi, *Chem. Phys. Lett.* **1998**, *286*, 253–260; c) B. Mennucci, J. Tomasi, *J. Chem. Phys.* **1997**, *106*, 5151–5158; d) M. Cossi, G.

Scalmani, N. Rega, V. Barone, *J. Chem. Phys.* **2002**, *117*, 43–54.

[35] a) V. Barone, M. Cossi, *J. Phys. Chem. A* **1998**, *102*, 1995–2001; b) M. Cossi, N. Rega, G. Scalmani, V. Barone, *J. Comput. Chem.* **2003**, *24*, 669–681.

[36] a) G. S. Hammond, *J. Am. Chem. Soc.* **1955**, *77*, 334–338; b) J. A. C. Romero, S. A. Tabacco, K. A. Woerpel, *J. Am. Chem. Soc.* **2000**, *122*, 168–169.

[37] a) R. V. Stevens, A. W. M. Lee, *J. Am. Chem. Soc.* **1979**, *101*, 7032–7035; b) R. V. Stevens, A. W. M. Lee, *J. Chem. Soc., Chem. Commun.* **1982**, 102–103; c) M. D. Lewis, J. K. Cha, Y. Kishi, *J. Am. Chem. Soc.* **1982**, *104*, 4976–4978; d) C. L. Perrin, D. B. Young, *J. Am. Chem. Soc.* **2001**, *123*, 4451–4458; e) S. Tamura, H. Abe, A. Matsuda, S. Shuto, *Angew. Chem.* **2003**, *115*, 1051–1053; *Angew. Chem. Int. Ed.* **2003**, *42*, 1021–1023; f) J. M. Um, K. N. Houk, A. J. Philips, *Org. Lett.* **2008**, *10*, 3769–3772.

[38] The TSs involving a β-attack of Nu^- at **XXII***eq* (**XXVII***eq*) and α-attack at **XXII***ax* (**XXVII***ax*) are kinetically disfavored because they each feature a twist-boat-like conformation, *syn*-addition of Nu^-, and partial eclipsing around the C–O bonds.

[39] a) H.-J. Gais, H. Müller, J. Bund, M. Scommoda, J. Brandt, G. Raabe, *J. Am. Chem. Soc.* **1995**, *117*, 2453–2466; b) J. Brandt, H.-J. Gais, *Tetrahedron: Asymmetry* **1997**, *8*, 909–912; c) H.-J. Gais, R. Hainz, H. Müller, P. R. Bruns, N. Giesen, G. Raabe, J. Runsink, S. Nienstedt, J. Decker, M. Schleusner, *Eur. J. Org. Chem.* **2000**, 3973–4009.

[40] a) R. J. Ferrier, O. A. Zubkov, *Org. React.* **2003**, *62*, 569–736; b) A. A. Ansari, R. Lahiri, Y. D. Vankar, *ARKIVOC* **2013**, 316–362.

[41] a) R. D. Dawe, B. Fraser-Reid, *J. Chem. Soc., Chem. Commun.* **1981**, 1180–1181; b) S. Danishefsky, J. F. Kerwin, *J. Org. Chem.* **1982**, *47*, 3803–3806; c) K. C. Nicolaou, C.-K. Hwang, M. E. Duggan, *J. Chem. Soc., Chem. Commun.* **1986**, 925–926; d) K. Maruoka, K. Nonoshita, T. Itoh, H. Yamamoto, *Chem. Lett.* **1987**, 2215–2216; e) S. J. Danishefsky, S. DeNinno, P. Lartey, *J. Am. Chem. Soc.* **1987**, *109*, 2082–2089; f) F. P. J. T. Rutjes, T. M. Kooistra, H. Hiemstra, H. E. Schoemaker, *Synlett* **1998**, 192–194; g) O. Gaertzen, A. M. Misske, P. Wolbers, H. M. R. Hoffmann, *Tetrahedron Lett.* **1999**, *40*, 6359–6363; h) B. Schmidt, H. Wildemann, *Eur. J. Org. Chem.* **2000**, 3145–3163; i) J. S. Yadav, B. V. S. Reddy, A. K. Rajum, C. V. Rao, *Tetrahedron Lett.* **2002**, *43*, 5437–5440; j) R. Saeeng, M. Isobe, *Chem. Lett.* **2006**, *35*, 552–557; k) J. S. Yadav, V. Sunitha, B. V. S. Reddy, P. P. Das, E. Gyanchander, *Tetrahedron Lett.* **2008**, *49*, 855–857; l) A. Gollner, K.-H. Altmann, J. Gertsch, J. Mulzer, *Chem. Eur. J.* **2009**, *15*, 5979–5997; m) R. A. Brawn, J. S. Panek, *Org. Lett.* **2010**, *12*, 4624–4627; n) S. Kusumi, K. Sasaki, S. Wang, T. Watanabe, D. Takahashi, K. Toshima, *Org. Biomol. Chem.* **2010**, *8*, 3164–3178; o) B. Kumar, M. A. Aga, A. Rouf, B. A. Shah, S. C. Taneja, *J. Org. Chem.* **2011**, *76*, 3506–3510; p) J. C. R. Freitas, T. R. Couto, A. A. S. Paulino, J. R. De Reitas Filho, I. Malvestiti, R. A. Oliveira, P. H. Menzes, *Tetrahedron* **2012**, *68*, 10611–10620.

[42] C. W. Schroeck, C. R. Johnson, *J. Am. Chem. Soc.* **1971**, *93*, 5305–5306.

[43] C. R. Johnson, E. U. Jonsson, A. Wambsgans, *J. Org. Chem.* **1979**, *44*, 2061–2065.

[44] M. W. Rathke, D. F. Sullivan, *Synth. Commun.* **1973**, *3*, 67–72.

Received: September 26, 2013
Published Online: November 21, 2013

