Regioselective Samarium Diiodide Induced Couplings of Carbonyl Compounds with 1,3-Diphenylallene and Alkoxyallenes: A New Route to 4-Hydroxy-1-enol Ethers

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Abstract: Since its introduction into synthetic organic chemistry, samarium diiodide has found broad application in a variety of synthetically important transformations. Herein, we describe the first successful intermolecular additions of samarium ketyls to typical allenes such as 1,3-diphenylallene (**7**), methoxyallene (**12**) and benzyloxyallene (**25**). Reaction of different samarium ketyls with 1,3-diphenylallene (**7**) occurred exclusively at the central carbon atom of the allene to afford products **9** in moderate to good yields. In contrast, reductive coupling of cyclic ketones to methoxyallene (**12**) regioselectively provided 4-hydroxy-1-enol ethers **13**, which derive from addition to the terminal allene carbon atom of **12**, in moderate to good yields. Whereas the *E*/*Z* selectivity with respect to the enol ether double bond is low, excellent diastereoselectivity has been observed in certain cases with regard to the ring configuration (e.g. compound **13b**). Studies with deuterated tetrahydrofuran and alcohol were performed to gain information about the reaction mechanism of this coupling process, which involves alkenyl radicals. The couplings of samarium ketyls derived from acyclic ketones and aldehydes gave lower yields, and in several cases cyclopentanols **20** are formed as byproducts. Branched acyclic ketones and conformationally more flexible cyclic ketones such as cycloheptanone led to a relatively high amount of cyclopentanol derivatives **20**, whose formation involves an intramolecular hydrogen atom transfer through a geometrically favoured six-membered transition state followed by a cyclization step. The samarium diiodide mediated addition of **8b** to benzyloxyallene (**25**) afforded the expected enol ethers **26**, albeit in only low yield. Additionally, spirocyclic compounds **27** and **28** were obtained, which are formed by a cascade reaction involving an addition/cyclization sequence. In the novel coupling process described here methoxyallene (**12**) serves as an equivalent of acrolein. The 1,4-dioxygenated products obtained contain a masked aldehyde functionality and are therefore valuable building blocks in organic synthesis.

Keywords: allenes · cyclopentanols · enol ethers · radical reactions · samarium diiodide

Introduction

Since the pioneering studies of Kagan and his co-workers in the late 1970s,[1] samarium diiodide has attracted considerable attention. It has rapidly been established as an exceptionally useful and versatile one-electron-transfer reductant in organic synthesis, which promotes a variety of synthetically important transformations including sequential reactions. The outstanding properties of this reagent, which include its easy preparation, its applicability under mild and selective conditions, and the possibility of tuning its reactivity and selectivity by assistance of catalysts and additives, and its usefulness in organic synthesis have been outlined in several reviews.[2] One important class of samarium diiodide induced reactions is the intermolecular or intramolecular coupling of carbonyl compounds with carbon–carbon multiple bonds (Scheme 1). Many reactions of different ketyls with alkenes have been intensively studied by Molander and his group.[3] In recent years, our group[4] has reported different cyclizations of samarium ketyls with alkenyl,[5] alkynyl,[6,7] aryl[8] and heteroaryl[9] units leading to highly functionalized carbocycles and heterocycles, often in good yields and with excellent diastereoselectivities.

However, reactions of samarium ketyls with α,β-unsaturated aldehydes, in particular with acrolein, have rarely

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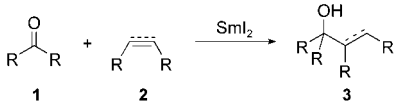

Scheme 1. Samarium diiodide promoted ketyl–olefin coupling reactions.

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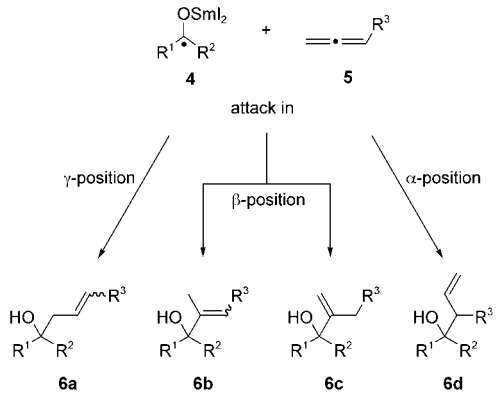
been studied. α,β-Unsaturated aldehydes have mainly been used in samarium diiodide induced iodomethylations[10] and Mukaiyama aldol reactions.[11] A few cyclizations of α,β-unsaturated aldehydes to double and triple bonds have recently been reported.[12]

Intermolecular and intramolecular coupling reactions of samarium ketyls with cumulated double bonds are also very rare. Whereas intermolecular couplings with allenes have not been studied at all, only a few examples of cyclizations involving electron-deficient allenyl aldehydes leading to substituted cycloalkanols have been described by Gillmann.[13]

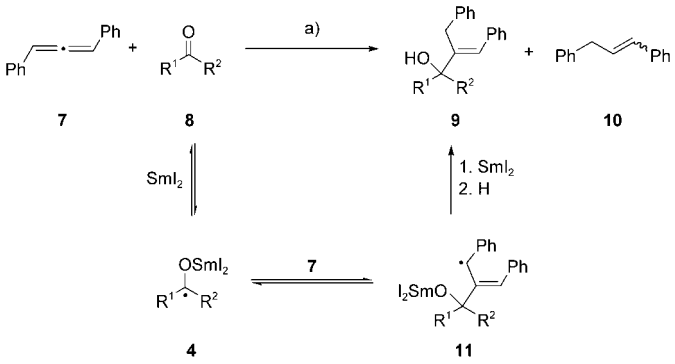
As part of our interest in samarium diiodide mediated ketyl–olefin coupling reactions,[4–9] we therefore focussed our attention[7] on intermolecular additions of ketyls to substituted allenes and recently published our preliminary results.[14] In principle, three electronically different carbon atoms are available for the coupling process of a substituted allene with the ketyl radical anion. Scheme 2 illustrates the possible reaction pathways and the resulting addition products **6a–d** which might be obtained by samarium diiodide mediated coupling of ketyls **4** with monosubstituted allenes **5**. The attack of the ketyl to the allene can occur at the α- (**6d**), β- (**6b**,**c**) and γ-positions (**6a**) to the substituent. To investigate the regiochemical and stereochemical features of samarium ketyl additions we used 1,3-diphenylallene and methoxyallene as typical model substrates.



Scheme 2. Possible pathways of ketyl couplings with monosubstituted allenes.

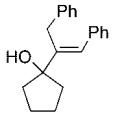
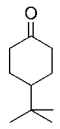
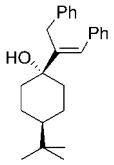
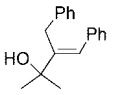
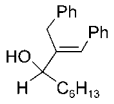
Results and Discussion

Reactions of samarium ketyls with 1,3-diphenylallene: Experiments with different samarium ketyls were first performed with 1,3-diphenylallene (**7**) which has only two different allene carbon atoms. In the presence of samarium diiodide, HMPA (hexamethylphosphoramide) and *tert*-butanol, allene **7** (1.1–1.2 equiv) was coupled with different carbonyl compounds **8** (Scheme 3, Table 1) to yield products **9**, which displayed characteristic ^{1}H NMR signals at $\delta \approx$ 7.0 ppm. As expected, addition of the ketyl occurred exclusively to the central allene carbon atom of **7**, since the resulting intermediate **11** is a highly stabilized allylic and benzylic radical. A mixture of *E* and *Z* isomers of 1,3-diphenylpropene (**10**) was isolated as a byproduct (in ≈28% in the case of **9a**, >70% purity according to ^{1}H NMR spectroscopy), which is the result of simple reduction of the allene moiety.



Scheme 3. a) SmI_2 (2.2 equiv), HMPA (18 equiv), *t*BuOH (2.0 equiv), THF, RT, overnight.

Table 1. Samarium diiodide induced coupling of 1,3-diphenylallene (**7**) with carbonyl compounds **8**.[a]

Entry	Carbonyl compound **8**	Coupling product **9**	Yield [%] (*E*/*Z*)[b]
1	 **8a**	 **9a**	69 (>97:3)
2	 **8b**	 **9b**	45[c] (>97:3), (*dr*>97:3)[d]
3	 **8c**	 **9c**	31 (>97:3)
4	 **8d**	 **9d**	21[e] (80:20)

[a] Conditions: **8** (1.0 equiv), **7** (1.1–1.2 equiv), SmI_2 (2.2 equiv), HMPA (18 equiv), *t*BuOH (2.0 equiv), THF, RT, overnight. [b] Yields for isolated products after chromatography. *E*/*Z* ratios (according to ^{1}H NMR spectroscopy) are given in parentheses. [c] *trans*-4-*tert*-Butylcyclohexanol (19%) was obtained as byproduct. [d] Diastereoselectivity with respect to the cyclohexane ring. [e] Purity >90% according to ^{1}H NMR spectroscopy.

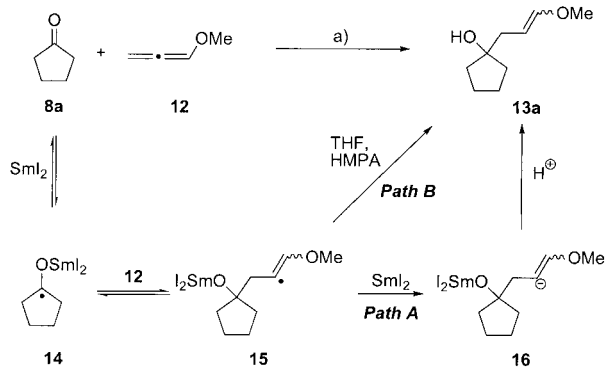
Cyclic ketones such as cyclopentanone (**8a**, Table 1, entry 1) and 4-*tert*-butylcyclohexanone (**8b**, entry 2) underwent smooth coupling with **7** to afford products **9a** and **9b** as single diastereomers (*dr*>97:3) with respect to the double bond in 69 and 45% yield, respectively. In the case of **8b**, 4-*tert*-butylcyclohexanol was isolated in 19% as a byproduct. The configuration of the double bond was established by NOESY spectroscopy. Only the *E* isomer was selectively formed during this coupling process. In terms of the relative stereochemistry at the cyclohexane ring, product

9b was isolated as a single diastereomer. Although the configuration of **9b** has not been determined, it is highly likely to be the *trans* isomer.[15]

Acyclic ketones such as acetone (**8c**, Table 1, entry 3) and aldehydes such as heptanal (**8d**, entry 4) can also be used for this coupling reaction; however, only low yields of **9c** and **9d** could be obtained after chromatography. Further products (e.g. pinacolic coupling products) could not be isolated. As with the cyclic ketones, coupling product **9c** was obtained as the pure *E* isomer. In the case of heptanal, the *E*/*Z* selectivity was lower, and an 80:20 mixture of the *E* and *Z* isomers was isolated. The diastereoselectivity is apparently controlled by the size of the added fragment derived from the carbonyl compound.

Reactions of samarium ketyls derived from cyclic ketones with methoxyallene: Methoxyallene (**12**) (Scheme 4) is a versatile C3 building block.[16] Reactions of this allene or other alkoxyallenes in the presence of samarium diiodide have generally not been reported. Methoxyallene itself has only been applied to a samarium(II)-induced [3+2] cycloaddition with carbonyl ylides.[17]

As a model reaction, coupling of **12** with cyclopentanone (**8a**) was studied under different conditions (Scheme 4, Table 2). The samarium(II)-induced reaction of **12** with **8a** was performed as above, and a single product **13a** (Scheme 4) was isolated in 65% yield after chromatography (entry 1). By using an excess of methoxyallene (**12**) (2.0 equiv, entry 2) the yield of **13a** could be increased to 85%. No reaction occurred in the absence of the additive HMPA (entry 3). According to previous reports,[18,19] HMPA is required for successful couplings, since this cosolvent significantly increases the reduction power of samarium(II). Coupling of **12** with **8a** in the presence of one equivalent of samarium diiodide was also successful (entry 4); however, only 38%[20] of **13a** could be isolated showing that at least two equivalents of samarium diiodide are necessary for an efficient coupling process.[21]



Scheme 4. a) SmI_2, HMPA, *t*BuOH, THF, RT, overnight.

In a control experiment, methoxyallene (**12**) was treated with samarium diiodide and HMPA in the absence of ketone **8a**. The colour of the reaction solution gradually changed from deep violet (complex of SmI_2 and HMPA) to green indicating that **12** itself slowly reacts with samarium diiodide. Decomposition or oligomerisation of methoxyallene (**12**) takes place, probably induced by the Lewis acidic samarium(II) or samarium(III) species present or by an electron-transfer process.

Table 2. Samarium diiodide induced coupling of methoxyallene (**12**) with cyclopentanone (**8a**).[a]

Entry	Equiv **12**[b]	Equiv SmI_2[b]	Equiv HMPA[b]	Yield of **13a** [%] (*E*/*Z*)[c]
1	1.0	2.2	18	65[d] (60:40)
2	2.0	2.2	18	85 (60:40)
3	2.0	2.2	–	–
4	2.0	1.0	18	38[e] (55:45)

[a] Conditions: **8a** (1.0 equiv), **12**, SmI_2, HMPA, *t*BuOH (2.0 equiv), THF, RT, overnight. [b] With respect to cyclopentanone (**8a**). [c] Yields for isolated products after chromatography. *E*/*Z* ratios (according to ^{1}H NMR spectroscopy) are given in parentheses. [d] Purity >90% according to ^{1}H NMR spectroscopy. [e] As a mixture with HMPA. Yield was calculated according to the ratio determined by ^{1}H NMR spectroscopy.

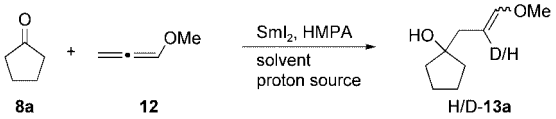
In contrast to allene **7**, coupling of **8a** with **12** selectively occurred at the terminal carbon atom of methoxyallene to afford 4-hydroxy-1-enol ether **13a** as an *E*/*Z* mixture (Scheme 4). Formation of the samarium ketyls from the carbonyl functionality generates a nucleophilic radical which selectively adds to the γ-position with respect to the methoxy group. Although alkoxyallenes appear to be nucleophilic components at first glance, their terminal double bond has significant electrophilic character and can therefore smoothly react with a nucleophilic radical such as the samarium ketyl.[22] In this novel coupling process methoxyallene (**12**) serves as an equivalent of acrolein (which is probably too reactive for this kind of coupling) and it provides 4-hydroxy-1-enol ethers as products which bear a synthetically useful masked aldehyde functionality. In principle, the overall process involves a formal umpolung[23] of reactivity (electrophilic carbonyl compound→nucleophilic ketyl) which allows for the construction of 1,4-dioxygenated compounds.

We propose the mechanism shown in Scheme 4. In accordance with literature reports,[3–9] ketyl radical anion **14** is reversibly generated by electron transfer from samarium diiodide to the carbonyl group. Subsequent addition of **14** to **12** affords alkenyl radical **15** which can be reduced by a second equivalent of samarium diiodide to the corresponding vinyl anion **16** (pathway A). Protonation by the additive *tert*-butanol finally furnishes **13a**. Since alkenyl radicals such as **15** are highly reactive intermediates, the direct conversion of **15** to **13a** by abstraction of hydrogen from the solvent THF (or the additive HMPA) has to be considered as mechanistic alternative (pathway B).[24]

To investigate the mechanistic details of the ketyl–methoxyallene coupling, experiments were carried out with deuterated THF as solvent and deuterated methanol as proton source (Table 3). The percentage of deuterium in **13a** was estimated from the ratio of the alkenyl protons determined by ^{1}H NMR spectroscopy.[25] In the presence of [D_8]THF and with *tert*-butanol as proton source (entry 1) crude **13a** was obtained with approximately 20–30% deuterium incorporation. However, using [D_4]MeOH as proton

source in normal THF (entry 2) only small amounts (ca. 5%) of deuterium were incorporated in **13a**. Combination of [D_8]THF and [D_4]MeOH (entry 3) resulted in the incorporation of approximately 20% deuterium.

Table 3. Mechanistic studies with **8a** and **12** in the presence of deuterated THF and/or proton source.[a]



8a **12** H/D-**13a**

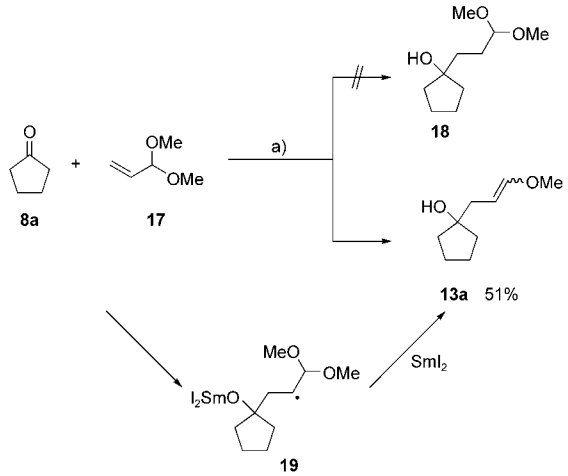
Entry	Solvent	Proton source	Yield [%] H/D-**13a**	Content of deuterium [%] in **13a**[b]
1	[D_8]THF	*t*BuOH	50	*E* isomer: 20 *Z* isomer: 30
2	THF	[D_4]MeOH	58	*E* isomer: 5 *Z* isomer: 5
3	[D_8]THF	[D_4]MeOH	67	*E* isomer: 20 *Z* isomer: 20

[a] Conditions: **8a** (1.0 equiv), **12** (2.0 equiv), SmI_2 (2.2 equiv), HMPA (18 equiv), proton source (2.0 equiv), solvent, RT, overnight. [b] Estimated according to the ratio of alkenyl protons determined by ^{1}H NMR spectroscopy of the crude mixture. The content of deuterium significantly decreases to 4–15% during chromatography on aluminium oxide (activity III) probably as a result of proton exchange by protonation/deprotonation.

These results indicate that the solvent, but not the proton source, has an important influence on the incorporation of deuterium in **13a**. As expected, alkenyl radicals such as **15** are highly reactive intermediates and only a fairly small fraction is reduced to anion **16** by a second equivalent of samarium diiodide (pathway A, Scheme 4) to give the protonated or deuterated product. In accordance with Inanaga's[26] and Curran's[24,27] results, the direct conversion of alkenyl radical **15** to **13a** by abstraction of hydrogen or deuterium from the solvent and/or the additive HMPA (pathway B) is more favourable. Although available in high concentration, only 20–30% of **13a** is obtained by abstraction of deuterium from the solvent [D_8]THF (entry 1). We therefore assume that **13a** is most probably formed by abstraction of hydrogen from the methyl groups of the additive HMPA which is a far better hydrogen donor leading to a well-stabilized radical.[28]

We envisaged that ketyl–alkene coupling of acrolein dimethylacetal (**17**) with **8a** in the presence of samarium diiodide and HMPA (Scheme 5) would also lead to a protected aldehyde derivative. However, under standard conditions, the expected coupling product **18** was not obtained, and **13a** was isolated in 51% yield as single product. Intermolecular addition of ketyl **14** to the double bond of **17** affords radical **19**, which is transformed into **13a** by a second electron transfer of samarium diiodide and subsequent β-elimination of methanolate. Coupling of **8a** with methoxyallene (**12**) is therefore a more efficient reaction.

The first successful coupling of **8a** and **12** and the versatility of building blocks **13** for further synthetic transformations, which has actually been demonstrated,[29] encouraged us to investigate the scope and limitations of the new coupling reaction in more detail. Reductive couplings were generally performed by adding a THF solution of carbonyl compound **8**, methoxyallene (**12**) and *tert*-butanol to a solution of freshly prepared samarium diiodide and HMPA in THF at room temperature. Several cyclic ketones were combined with **12**, and the results of these reactions are summarized in Table 4. In general, products **13** were obtained as mixtures of *E* and *Z* isomers in ratios of 50:50 to 65:35 (according to ^{1}H NMR spectroscopy). In almost all cases, the *E* isomer was slightly preferred.

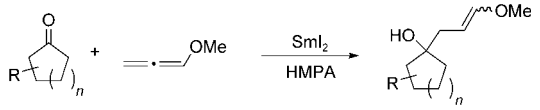


Scheme 5. a) SmI_2 (2.2 equiv), HMPA (18 equiv), *t*BuOH (2.0 equiv), THF, RT, overnight.

As with cyclopentanone (**8a**), similar cyclic ketones such as cyclobutanone (**8e**, Table 4, entry 1) and cyclohexanone (**8f**, entry 2) afforded the addition products **13e** and **13f** as the only isolated products in good yields. In contrast, coupling of **12** with cycloheptanone (**8g**, entry 3) under standard conditions unexpectedly furnished two constitutional isomers. Separation by chromatography gave the expected coupling product **13g** in 29% yield and bicyclic compound **20g** in 34% yield as a single diastereomer whose configuration has not yet been determined. The latter product arises as a result of the higher conformational flexibility of the cycloheptane ring which leads, in a sequential reaction, to a second carbon–carbon coupling step. Formation of bicyclic derivatives **20** can thus be explained by an intramolecular hydrogen atom transfer[30] to alkenyl radical **15** to afford alkyl radical **21**. The six-membered transition state involved is geometrically very favoured (Scheme 6). Radical **21** subsequently attacks the enol ether double bond in a 5-*exo-trig* cyclization leading to stabilized radical **22**. A second electron transfer of samarium diiodide followed by protonation finally yields **20**.

Substituted cycloalkanones (Table 4, entries 4–7) and a piperidinone derivative (entry 8) can also be used in this novel coupling reaction to give moderate to good yields of the expected enol ethers. With 2-methylcyclohexanone (**8h**, entry 4) as precursor the enol ether **13h** was obtained in low overall yield (35%). The decreased efficacy of this transformation is probably caused by the α-methyl substituent, which sterically disfavours the attack of the ketyl to the

Table 4. Samarium diiodide induced coupling of methoxyallene (**12**) with cyclic ketones **8**.[a]



8 **12** **13**

Entry	Ketone **8**	Addition product **13** [%][b]	Cyclization product **20**[b]
1	**8e** ($n=0$)	**13e** 65 (65:35)[c]	–
2	**8f** ($n=2$)	**13f** 79 (60:40)	–[d]
3	**8g** ($n=4$)	**13g** 29 (60:40)	**20g** 34 ($dr>97:3$)
4	**8h**	*cis*-**13h** 14 (50:50), *trans*-**13h** 21 (55:45)	–
5	**8i**	**13i** 29 (60:40)	**20i** 43 (*dr* 60:40)
6	**8b**	**13b** 58 (60:40),[e] $dr>97:3$[f]	–
7	**8j**	**13j** 54 (55:45)	–
8	**8k**	**13k** 51 (50:50)[g]	–[h]

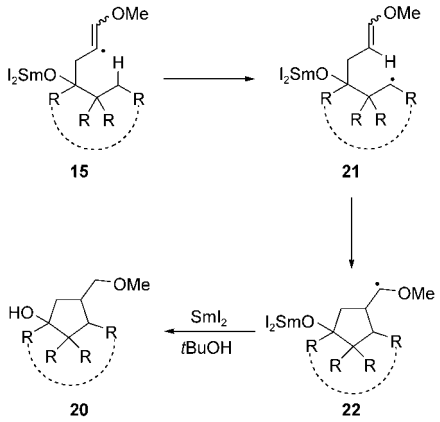
[a] Conditions: **8** (1.0 equiv), **12** (2.0–3.0 equiv), SmI_2 (2.2–2.5 equiv), HMPA (18 equiv), *t*BuOH (2.0 equiv), THF, RT, overnight. [b] Yield for isolated products after chromatography. *E*/*Z* ratios (according to ^{1}H NMR spectroscopy) are given in parentheses. [c] Purity >95% according to ^{1}H NMR spectroscopy. [d] Traces of a bicyclic compound related to **20g** were detected in the crude mixture. [e] Starting material **8b** was recovered in 41%. [f] Only *trans* isomer was detected. [g] Isolation of 11% of secondary alcohol. [h] Small amounts of a bicyclic compound related to **20g** were obtained after chromatography.

allene. A low diastereoselectivity (60:40) in favour of the *trans* isomer was recorded.[31]

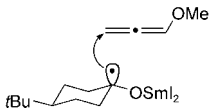
Coupling of methoxyallene (**12**) with 3-*tert*-butylcyclohexanone (**8i**, Table 4, entry 5) also gave the desired coupling product **13i** in only low yield (29%), but as a single diastereomer in this case. The bicyclic compound **20i** was obtained as the main product in 43% yield and as a 60:40 mixture of diastereomers. Although the six-membered ring is conformationally less flexible than the seven-membered ring (entry 3), the intramolecular hydrogen atom transfer through the six-membered transition state (Scheme 6) can compete because a more stabilized tertiary radical is involved in this case.

The reaction of **12** with 4-*tert*-butylcyclohexanone (**8b**, Table 4, entry 6) was more efficient, and the expected coupling product **13b** was obtained in 58% yield. In addition, starting material **8b** was recovered in 41% yield after chromatography. Apparently, conversion of this ketone was incomplete, which may also have occurred in other experiments in which unconsumed starting material was not isolated owing to its volatility. The reaction of **8b** and **12** was therefore carried out with 4.2 equivalents of samarium diiodide. Only traces of starting material **8b** were detected in the crude mixture; however, the yield of **13b** was not dramatically increased (62%). Addition of samarium diiodide to a solution of **8b** and **12** (i.e., reverse addition mode) slightly improved the yield of **13b**, albeit 16% of the starting material was recovered. In all experiments, **13b** was obtained as a single diastereomer ($dr>$ 97:3) with respect to the cyclohexane ring. The relative configuration was determined by transforming **13b** into the corresponding γ-lactone as described previously.[14,29] By comparing the data of this lactone with the data of the *cis* and *trans* isomers reported in the literature,[32] **13b** was unambiguously assigned as the *trans* isomer. This selectivity can nicely be explained by assuming that the sterically demanding samarium alkoxy and *tert*-butyl groups of the intermediate ketyl prefer equatorial positions (Scheme 7). As a consequence the attack of **12** takes place in the axial position leading to the *trans* product.

Other substituents and even heteroatoms are tolerated in the 4-position (Table 4, entries 7 and 8). Reaction of **8j** with **12** under standard conditions afforded coupling product **13j** as the only isolated product in 54% yield. Coupling of Boc-protected piperidinone **8k** with methoxyallene (**12**) furnish-



Scheme 6. Proposed mechanism for the formation of cyclopentanols **20**.



Scheme 7. Intermediate ketyl radical anion in the addition of **8b** to **12**.

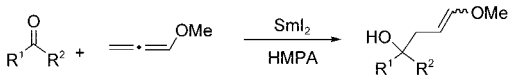
major product was the expected coupling product **13m**, whereas the minor component was identified as cyclopentanol derivative **20m**. Branched ketones such as isopropylmethylketone (**8n**) and pinacolone **8o** (entries 4 and 5) gave the desired products **13** in even lower yields probably for steric reasons; on the other hand they facilitated the formation of cyclopentanol derivatives **20** through intramolecular hydrogen atom transfer according to Scheme 6. Starting with **8n** an 85:15 mixture of coupling product **13n** and cyclopentanol **20n** was obtained in 24% yield. In the case of pinacolone **8o**, only traces of the desired product **13o** were isolated, and the cyclization product **20o** was isolated as the major component of this reaction in 21% yield. All cyclopentanol derivatives were obtained as single diastereomers with as yet unknown configurations. The Houk–Beckwith[33] transition state model presented in Scheme 8 should be assumed for the addition of the radical **21** to the enol ether double bond, in which the sterically demanding samarium group is located in an equatorial position. Cyclization should then produce cyclopentanol derivatives **20** with *cis*-orientated hydroxyl and CH_2OMe groups.

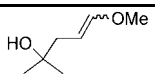
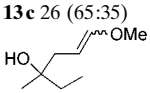
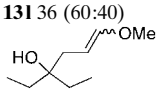
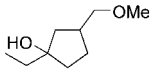
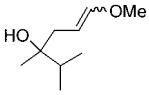
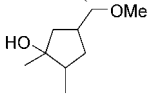
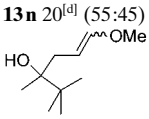
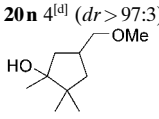
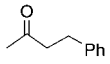
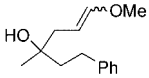
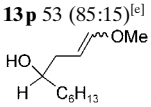
ed the desired product **13k** in moderate yield (51%); however, a bicyclic compound analogous to **20g** could be detected in a mixture along with other components.

Reactions of samarium ketyls derived from acyclic ketones and aldehydes with methoxyallene: The successful results with cyclic ketones motivated us to study the reactions of methoxyallene (**12**) with acyclic ketones and aldehydes. This variation significantly diminished the yields of coupling products **13** (Table 5) and cyclopentanol derivatives **20** were formed to a higher degree.

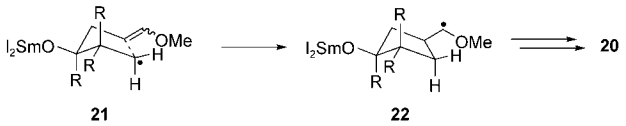
Reaction of **12** with acetone (**8c**, Table 5, entry 1) and butan-2-one (**8l**, entry 2) afforded the corresponding adducts **13c** and **13l** in 26% and 36% yield, respectively. The low efficacies of these transformations may be due to the volatility of the products (and by-products). Performing the coupling process with pentan-3-one (**8m**, entry 3) significantly improved the mass balance to give 52% overall yield; however, an 85:15 mixture of two isomeric compounds was obtained. The

Table 5. Samarium diiodide induced coupling of methoxyallene (**12**) with acyclic ketones and aldehydes **8**.[a]



Entry	Ketone **8**	Addition product **13** [%][b,c]	Cyclization product **20**[b]
1			–
	8c	**13c** 26 (65:35)	
2			–
	8l	**13l** 36 (60:40)	
3			
	8m	**13m** 44[d] (55:45)	**20m** 8[d] ($dr > 97:3$)
4			
	8n	**13n** 20[d] (55:45)	**20n** 4[d] ($dr > 97:3$)
5			
	8o	**13o** 5[d] (60:40)	**20o** 21[d] ($dr > 97:3$)
6			–
	8p	**13p** 53 (85:15)[e]	
7			–
	8d	**13d** 43 (55:45)	

[a] Conditions: **8** (1.0 equiv), **12** (2.0–3.0 equiv), SmI_2 (2.2–2.5 equiv), HMPA (18 equiv), *t*BuOH (2.0 equiv), THF, RT, overnight. [b] Yield for isolated products after chromatography. [c] *E*/*Z* ratios (according to ^{1}H NMR spectroscopy) are given in parentheses. [d] **13** and **20** were obtained as a mixture. Yield was calculated according to the ratio determined by ^{1}H NMR spectroscopy. [e] As a mixture with 14% 4-phenylbutan-2-ol. Yield was calculated according to the ratio determined by ^{1}H NMR spectroscopy.

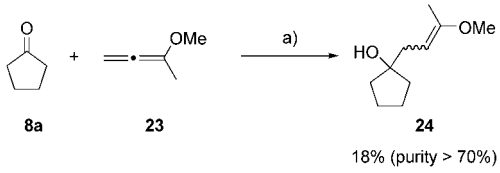


Scheme 8. Transition state and intermediate according to the Houk–Beckwith model for cyclizations leading to **20**.

Aryl-substituted carbonyl compounds such as acetophenone and benzaldehyde are unsuitable precursors for the samarium diiodide induced coupling reactions with methoxyallene (**12**). The resulting ketyl radicals are considerably better stabilized by the aryl group and are therefore less reactive. In addition, the increased bulk introduced with the phenyl substituent may also hamper the reaction with **12**. Coupling of phenylacetone with **12** was also unsuccessful resulting in the formation of a very complex mixture of products. In contrast, 4-phenylbutan-2-one (**8p**, Table 5, entry 6) can successfully be coupled with methoxyallene (**12**) to afford the desired coupling product **13p** as an inseparable mixture (85:15) with 4-phenylbutan-2-ol.

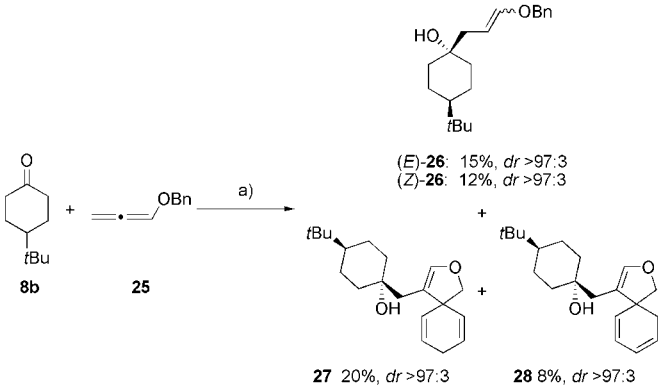
Samarium ketyls derived from aldehydes also undergo the coupling process with methoxyallene (**12**). Reaction of heptanal (**8d**) with **12** furnished the corresponding adduct **13d** in moderate yield (Table 5, entry 7). Ketyl radical anions from aldehydes are less stabilized than those from ketones and are therefore generally more prone to simple reduction and/or to the pinacol coupling process, which apparently reduces the efficacy of the desired carbon–carbon bond-forming process with the allene.

Reactions of samarium ketyls with substituted methoxyallene derivatives and other alkoxyallenes: We also studied the reaction of carbonyl compounds with substituted methoxyallene derivatives and other alkoxyallenes. When cyclopentanone (**8a**) was combined with 1-methoxydodeca-1,2-diene[34] in the presence of samarium diiodide and HMPA no reaction took place, and only starting material was recovered after chromatography. Coupling of **8a** with different 1-substituted methoxyallene derivatives in most cases led to the formation of rather complex product mixtures. However, the most simple compound of this series, 3-methoxybuta-1,2-diene (**23**),[35] and **8a** (Scheme 9) gave the expected coupling product **24**, albeit in disappointing yield (18%) and low purity according to ^{1}H NMR spectroscopy. As in the reaction of different samarium ketyls with methoxyallene (**12**), the attack of the ketyl radical occurs selectively in γ-position to the methoxy group.



Scheme 9. a) SmI_2 (2.2 equiv), HMPA (18 equiv), *t*BuOH (2.0 equiv), THF, RT, overnight.

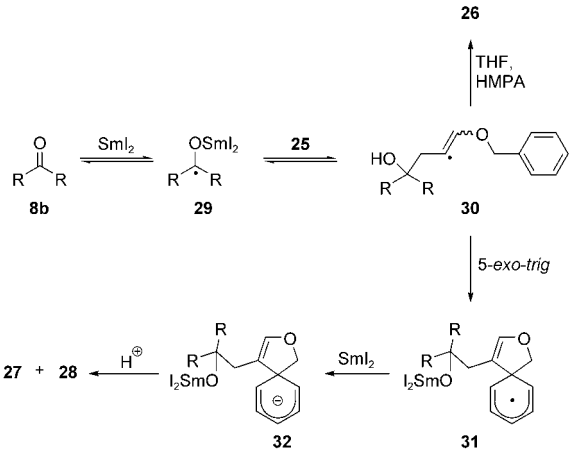
Other 1-alkoxy-1,2-propadienes can also be applied to this coupling reaction. When the reaction was performed with benzyloxyallene (**25**) and 4-*tert*-butylcyclohexanone (**8b**) the expected enol ether **26** was isolated in a mixture together with two other components in 67% overall yield after chromatography. Separation by HPLC yielded (*E*)-**26** (15%), (*Z*)-**26** (12%) and two spirocyclic derivatives **27** (20%) and **28** (8%), respectively (Scheme 10). The structures of these compounds were unambiguously identified by NMR spectroscopy. Compounds **26**–**28** were obtained in diastereomerically pure form; however, the relative configuration of the hydroxyl and *tert*-butyl groups at the cyclohexyl ring could not be determined. Again, the configurations depicted in Scheme 10 are highly likely by analogy with the results obtained in the coupling of **8b** with **12**.



Scheme 10. a) SmI_2 (2.2 equiv), HMPA (18 equiv), *t*BuOH (2.0 equiv), THF, RT, overnight.

The formation of spirocyclic compounds **27** and **28** probably occurs in a similar manner to the ketyl–aryl cyclizations previously reported by us and others.[8,9] These reactions feature dearomatization of the aryl ring leading to products with cyclohexadienyl subunits. Similar samarium diiodide promoted cyclizations of γ-aryl-substituted ketyls to give spirocyclic compounds have recently been described by Berndt[36] and Tanaka.[37] However, in the case of **27** and **28** the precursor for the cyclization is an alkenyl radical which is formed in situ by samarium diiodide induced coupling of **25** and **8b**. The proposed mechanism for this cascade reaction is presented in Scheme 11. Analogous to the coupling with methoxyallene, ketyl radical **29** adds in γ-position to the alkoxy substituent to afford alkenyl radical **30**. This intermediate is either converted into enol ether **26** by hydrogen abstraction or into pentadienyl radical **31** by 5-*exo*-*trig* cyclization onto the *ipso*-position of the aromatic ring. The conceivable 6-*trig* cyclization was not observed. Subsequently, radical **31** is reduced by a second equivalent of samarium diiodide to the corresponding anion **32**, which is finally protonated regioselectively to yield **27** and **28**. By analogy with the Birch reduction,[38] the 1,4-diene **27** is obtained as the major product, whereas the thermodynamically more stable conjugated 1,3-diene **28** represents only the byproduct.

Although this reaction produced compounds in only moderate yield, it nevertheless delivers products with a complex



Scheme 11. Proposed mechanism of the coupling of **8b** and **25**.

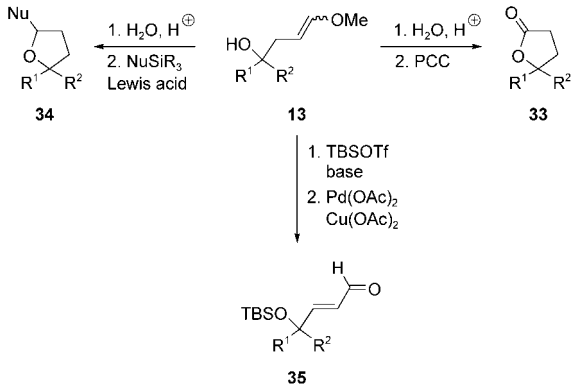
functionality pattern. This transformation therefore deserves further investigation and optimisation.

Conclusion

We have successfully studied the first intermolecular addition of samarium ketyls to allenes. The reactions were applied to different ketyls and typical allenes such as 1,3-diphenylallene (**7**), methoxyallene (**12**) and benzyloxyallene (**25**). The reductive coupling of different samarium ketyls with 1,3-diphenylallene (**7**) afforded the expected *E*-configured addition products **9** in moderate to good yields. The attack of the ketyl radical exclusively occurred at the central carbon atom of the allene owing to the formation of a stabilized radical intermediate. In contrast, the reactions with methoxyallene (**12**) regioselectively provide products **13** derived from ketyl additions to the terminal position of the allene. Several four-, five- and six-membered cycloalkanones smoothly undergo this transformation to afford **13** in moderate to good yields as *E*/*Z* mixtures. Samarium ketyls derived from acyclic ketones and aldehydes are less suitable for this kind of coupling reaction and give lower yields. A competing reaction leading to the formation of cyclopentanol derivatives **20** occurs in certain cases, which reduces the efficacy of the coupling process. Branched acyclic ketones and conformationally more flexible ketyl precursor such as cycloheptanone led to the formation of compound **20**, since the intramolecular hydrogen atom transfer is possible through a geometrically favoured six-membered transition state.

Aryl-substituted carbonyl compounds and α-phenyl carbonyl compounds provide only complex product mixtures. Employment of 1- or 3-substituted methoxyallene derivatives either led to recovery of starting material or to complex mixtures. The samarium diiodide induced coupling of **8b** with benzyloxyallene (**25**) afforded the expected enol ethers **26** in only low yields, and a competing intermolecular addition/spirocyclization sequence leads to the formation of spirocyclic compounds **27** and **28**.

In this novel coupling reaction methoxyallene serves as an equivalent of acrolein, and the resulting 1,4-dioxygenated products are obtained by umpolung of reactivity (electrophilic carbonyl compound→nucleophilic ketyl). The 4-hydroxy-1-enol ethers **13** contain a masked aldehyde functionality and are valuable building blocks which have been converted into γ-lactones **33** or (via γ-lactols) into highly substituted tetrahydrofuran derivatives **34** (Scheme 12).[29] Alternatively, aldehydes such as **35** are available after protection of the hydroxyl group. Further synthetic applications of compounds **13** are conceivable.



Scheme 12. Synthetic applications of 4-hydroxy-1-enol ethers **13**.

Experimental Section

General methods: Reactions were generally performed under argon in flame-dried flasks, and the components were added by means of syringe. Unless otherwise stated, materials were obtained from commercial suppliers and were used without further purification. Hexamethylphosphoramide (HMPA, Fluka) was distilled and kept under argon over 4 Å molecular sieves. **Warning: HMPA has been identified as a carcinogenic reagent. Use of gloves is required during handling. Reactions and chromatography should be performed in a well-vented hood**. Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone under argon for each of the SmI_2 reactions. 1,2-Diiodoethane (Acros) was dried in vacuo, sublimated before use and kept under argon at 0 °C. Samarium (≈40 mesh) was obtained from Acros and used as supplied. Products were purified by flash chromatography on silica gel (230–400 Mesh, Merck) or neutral alumina (activity III, Fluka). Unless otherwise stated, yields refer to analytically pure samples. Isomer ratios were derived from suitable ^{1}H NMR integrals.

^{1}H NMR [$CDCl_3$ (7.25 ppm) or TMS (0.00 ppm) as internal standard] and ^{13}C NMR spectra [$CDCl_3$ (77.0 ppm) as internal standard] were recorded on a Bruker AC250, AM270 or AC500 and Joel Eclipse 500 in $CDCl_3$ solution at 25 °C. Missing signals are hidden by signals of the second compound or they could not be unambiguously identified as a result of low intensity. Integrals are in accordance with assignments; coupling constants are given in Hz. The assignments refer to IUPAC nomenclature; primed numbers belong to the side chain. IR spectra were measured with an FTIR spectrophotometer Nicolet 5SXC (Perkin–Elmer). MS and HRMS analyses were performed on Finnigan MAT711 (EI, 8 kV), MAT CH7A (EI, 3 kV) and CH5DF (FAB, 3 kV) at 80 eV. The peak of the molecular ion (M^+, if possible, otherwise a characteristic fragment was chosen) and the peak with the highest intensity are given. The complete set of peaks was collected elsewhere.[7] Elemental analysis were recorded on a Perkin–Elmer elemental analyzer. Melting points were measured on a Reichert apparatus and are uncorrected.

General procedure for SmI_2 induced couplings of carbonyl compounds with allenes: Samarium powder (2.4–2.5 equiv) and 1,2-diiodoethane (2.2 equiv) were suspended in freshly distilled anhydrous THF (10 mL

per g-atom samarium) under an argon atmosphere and stirred for 2 h at room temperature. HMPA (18 equiv) was added to the resulting dark blue solution. Carbonyl compound **8** (1.0 equiv), allene **7**, **12** or **25** (1.1–3.0 equiv) and *tert*-butanol (2.0 equiv) were dissolved in anhydrous THF (15 mL per mmol **8**) and then added to the deep violet solution. After 16–18 h the mixture was quenched with saturated aqueous sodium bicarbonate and water, the organic layer was separated, and the aqueous layer was extracted three times with diethyl ether. The combined organic layers were washed once with water and twice with brine, dried with anhydrous magnesium sulfate, filtered and evaporated. The resulting crude oil was purified by column chromatography on silica gel or neutral aluminium oxide (activity III) using *n*-hexane/ethyl acetate.

1-[(*E*)-1-Benzyl-2-phenylethenyl]cyclopentan-1-ol (9a): The reaction was performed according to the general procedure by using 1,3-diphenylallene (**7**) (0.192 g, 1.00 mmol) and cyclopentanone (**8a**) (0.076 g, 0.90 mmol). Chromatography on silica gel with *n*-hexane/ethyl acetate (95:5) gave a mixture of (*E*)- and (*Z*)-1,3-diphenylpropene **10** (0.054 g, 28%, purity >70%) as a yellow oil and **9a** (0.173 g, 69%, *E*:*Z* > 97:3) as a colourless oil. ^{1}H NMR data of **10** are in accordance with literature data.[39] **9a**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.29–7.23, 7.20–7.16 (2 m, 8H, 2H; Ph), 7.02 (s, 1H; 2′-H), 3.79 (s, 2H; CH_2Ph), 1.88–1.78, 1.70–1.64 (2m, 2×4H; 2-H, 3-H, 4-H, 5-H), 1.30 ppm (brs, 1H; OH); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 144.0, 140.3, 137.5 (3s, Ph, C-1′), 128.5, 128.4, 128.3, 126.7, 126.0 (5d, Ph), 127.1 (d, C-2′), 85.6 (s, C-1), 39.9, 23.4 (2t, C-2, C-3, C-4, C-5), 34.6 ppm (t, CH_2Ph); IR (film): $\tilde{\nu}$ = 3420 (O–H), 3080–3025 (=C–H), 2960–2870 (C–H), 1600–1495 cm^{-1} (C=C); MS (EI, 40°C): *m*/*z* (%): 278 (1) [M^+], 169 (100) [$M^+ - CH_2C_6H_5 - H_2O$]; elemental analysis calcd (%) for $C_{20}H_{22}O$ (278.4): C 86.29, H 7.97; found: C 86.51, H 7.81.

1-[(*E*)-1-Benzyl-2-phenylethenyl]-4-*tert*-butylcyclohexan-1-ol (9b): Compound **7** (0.190 g, 0.988 mmol) and 4-*tert*-butylcyclohexanone (**8b**) (0.139 g, 0.901 mmol) were treated with SmI_2 and HMPA according to the general procedure. Chromatography on silica gel with *n*-hexane/ethyl acetate (90:10 to 70:30) yielded **9b** (0.140 g, 45%, *E*:*Z* > 97:3, *dr* > 97:3) as a pale yellow oil and *trans*-4-*tert*-butylcyclohexanol (0.027 g, 19%, *dr* > 97:3) as a colourless oil. ^{1}H NMR data of *trans*-4-*tert*-butylcyclohexanol are in accordance with literature data.[40] **9b**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.39–7.18 (m, 10H; Ph), 7.01 (s, 1H; 2′-H), 3.85 (s, 2H; CH_2Ph), 2.36–2.33, 1.67–1.65, 1.55–1.50, 1.20–1.13 (4m, 2H, 2H, 3H, 3H; 2-H, 3-H, 4-H, 5-H, 6-H, OH), 0.87 ppm (s, 9H; C(CH_3)$_3$); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 141.2, 140.1, 137.7 (3s, Ph, C-1′), 130.2, 128.6, 128.6, 128.4, 128.3, 126.8 (6d, Ph), 126.0 (d, C-2′), 75.7 (s, C-1), 47.4 (d, C-4), 37.5, 24.7 (2t, C-2, C-3, C-4, C-5), 33.5 (t, CH_2Ph), 32.2, 27.5 ppm (s, q, C(CH_3)$_3$); IR (film): $\tilde{\nu}$ = 3385 (O–H), 3080–3025 (=C–H), 2950–2865 (C–H), 1600–1495 cm^{-1} (C=C); MS (EI, 40°C): *m*/*z* (%): 348 (4) [M^+], 257 (100) [$M^+ - C_7H_7$]; HRMS: *m*/*z*: calcd for $C_{25}H_{32}O$: 348.2453; found: 348.2462.

(3*E*)-3-Benzyl-2-methyl-4-phenylbut-3-en-2-ol (9c): Acetone **8c** (0.026 g, 0.45 mmol) and **7** (0.110 g, 0.572 mmol) were treated with SmI_2 and HMPA under the described conditions. Chromatography on silica gel with *n*-hexane/ethyl acetate (95:5) afforded **9c** (0.035 g, 31%, *E*:*Z* > 97:3) as a colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.31–7.18 (m, 10H; Ph), 6.98 (s, 1H; 4-H), 3.81 (s, 2H; CH_2Ph), 1.39 ppm (s, 6H; 1-H, 2-CH_3); OH signal not observed; ^{13}C NMR (126 MHz, $CDCl_3$): δ = 146.4, 140.6, 137.8 (3s, C-3, Ph), 128.8, 128.7, 128.5, 128.5, 126.9, 126.2 (6d, Ph), 126.8 (d, C-4), 74.8 (s, C-2), 34.4 (t, CH_2Ph), 30.8 ppm (q, C-1, 2-CH_3); IR (film): $\tilde{\nu}$ = 3400 (O–H), 3080–3025 (=C–H), 2975–2855 (C–H), 1600–1495 cm^{-1} (C=C); MS (EI, 40°C): *m*/*z* (%): 252 (54) [M^+], 161 (100) [$M^+ - C_7H_7$]; HRMS: *m*/*z*: calcd for $C_{18}H_{20}O$: 252.1514; found: 252.1533.

(1*E*)- and (1*Z*)-2-Benzyl-1-phenylnon-1-en-3-ol (9d): The reaction was carried out according to the general procedure by using **7** (0.104 g, 0.541 mmol) and heptanal (**8d**) (0.055 g, 0.48 mmol). Chromatography on silica gel with *n*-hexane/ethyl acetate (100:0 to 95:5) afforded **9d** (0.031 g, 21%, *E*:*Z* 80:20) as a colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$): *E* isomer: δ = 7.38–7.16 (m, 10H; Ph), 6.84 (s, 1H; 1-H), 4.15 (dd, ^3J = 4.5, 7.4 Hz, 1H; 3-H), 3.86 (d, ^2J = 15.5 Hz, 1H; CH_2Ph), 3.57 (d, ^2J = 15.7 Hz, 1H; CH_2Ph), 1.70–1.20 (m, 11H; 4-H, 5-H, 6-H, 7-H, 8-H, OH), 0.88 ppm (t, ^3J = 6.9 Hz, 3H; 9-H); *Z* isomer: δ = 7.38–7.16 (m, 10H; Ph), 6.24 (s, 1H; 1-H), 4.72 (dd, ^3J = 5.6, 8.2 Hz, 1H; 3-H), AB part of ABX system (δ_A = 3.65, δ_B = 3.53, $^2J_{AB}$ = 15.7, $^4J_{AX}$ = 1.1 Hz, each 1H; CH_2Ph), 1.70–1.20 (m, 11H; 4-H, 5-H, 6-H, 7-H, 8-H, OH), 0.88 ppm (t, ^3J = 6.9 Hz, 3H; 9-H); ^{13}C NMR (126 MHz, $CDCl_3$): *E* isomer: δ = 127.2 (d, C-1), 75.4 (d, C-3), 34.4 (t, CH_2Ph), 36.3, 31.9, 29.3, 25.8, 22.7 (5t, C-4, C-5, C-6, C-7, C-8), 14.1 ppm (q, C-9); *Z* isomer: δ = 129.7 (d, C-1), 70.4 (d, C-3), 37.3 (t, CH_2Ph), 35.6, 31.8, 29.3, 26.0, 22.7 (5t, C-4, C-5, C-6, C-7, C-8), 14.1 ppm (q, C-9); the following signals could not be unambiguously assigned to one of the isomers: δ = 144.0, 142.9, 140.3, 139.7, 137.4, 134.9 [6s, (*E*)/(*Z*)-C-2, (*E*)/(*Z*)-Ph], 129.7, 129.6, 128.8, 128.7, 128.6, 128.6, 128.5, 128.2, 126.8, 126.7, 126.3, 126.2 ppm [12d, (*E*)/(*Z*)-Ph]; IR (film): $\tilde{\nu}$ = 3385 (O–H), 3080–3025 (=C–H), 2955–2855 (C–H), 1600–1495 cm^{-1} (C=C); MS (EI, 100°C): *m*/*z* (%): 308 (5) [M^+], 217 (100) [$M^+ - C_7H_7$]; HRMS: *m*/*z*: calcd for $C_{22}H_{28}O$: 308.2140; found: 308.2152.

^{1}H NMR and ^{13}C NMR data of compounds **13** are presented in Tables 6 and 7, respectively.

1-[(*E*)/(*Z*)-3-Methoxyprop-2-enyl]cyclopentan-1-ol (13a): Cyclopentanone (**8a**) (0.084 g, 1.00 mmol) and methoxyallene (**12**) (0.140 g, 2.00 mmol) were treated with SmI_2 and HMPA according to the general procedure. Chromatography on aluminium oxide (activity III) using *n*-hexane/ethyl acetate (90:10 to 80:20) yielded a mixture of (*E*)-**13a** and (*Z*)-**13a** (0.133 g, 85%, *E*:*Z* 60:40) as a colourless oil. IR (film): $\tilde{\nu}$ = 3425 (O–H), 3060–3040 (=C–H), 2955–2830 (C–H), 1665–1655 cm^{-1} (C=C); MS (EI, 30°C): *m*/*z* (%): 156 (2) [M^+], 72 (100) [$C_4H_8O^+$]; HRMS: *m*/*z*: calcd for $C_9H_{16}O_2$: 156.1150; found: 156.1163.

SmI_2-induced coupling of cyclopentanone (8a) with 3,3-dimethoxyprop-1-ene (17): Cyclopentanone (**8a**) (0.084 g, 1.00 mmol) and 3,3-dimethoxyprop-1-ene (**17**) (0.204 g, 2.00 mmol) were treated with SmI_2 and HMPA under the described conditions. Chromatography on aluminium oxide (activity III) using *n*-hexane/ethyl acetate (90:10 to 75:25) gave a mixture of (*E*)-**13a** and (*Z*)-**13a** (0.080 g, 51%, *E*:*Z* 60:40) as a colourless oil.

1-[(*E*)/(*Z*)-3-Methoxyprop-2-enyl]cyclobutan-1-ol (13e): The reaction was performed according to the general procedure using cyclobutanone (**8e**) (0.068 g, 0.97 mmol) and **12** (0.140 g, 2.00 mmol). Chromatography on aluminium oxide (activity III) using *n*-hexane/ethyl acetate (90:10 to 75:25) yielded a mixture of (*E*)-**13e** and (*Z*)-**13e** (0.090 g, 65%, purity according to ^{1}H NMR spectroscopy >95%, *E*:*Z* 65:35) as a colourless oil. IR (film): $\tilde{\nu}$ = 3400 (O–H), 3060–2835 (=C–H, C–H), 1670–1655 cm^{-1} (C=C); MS (EI, 40°C): *m*/*z* (%): 142 (17) [M^+], 71 (100) [$C_4H_7O^+$]; HRMS: *m*/*z*: calcd for $C_8H_{14}O_2$: 142.0994; found: 142.0984.

1-[(*E*)/(*Z*)-3-Methoxyprop-2-enyl]cyclohexan-1-ol (13f): Cyclohexanone (**8f**) (0.098 g, 1.00 mmol) and **12** (0.140 g, 2.00 mmol) were treated with SmI_2 and HMPA under the described conditions. Chromatography on aluminium oxide (activity III) using *n*-hexane/ethyl acetate (90:10 to 75:25) afforded a mixture of (*E*)-**13f** and (*Z*)-**13f**[41] (0.134 g, 79%, *E*:*Z* 60:40) as a colourless oil. IR (film): $\tilde{\nu}$ = 3435 (O–H), 3060–3040 (=C–H), 3000–2855 (C–H), 1665–1655 cm^{-1} (C=C); MS (EI, 30°C): *m*/*z* (%): 170 (2) [M^+], 72 (100) [$C_4H_8O^+$]; HRMS: *m*/*z*: calcd for $C_{10}H_{18}O_2$: 170.1307; found: 170.1315.

1-[(*E*)/(*Z*)-3-Methoxyprop-2-enyl]cycloheptan-1-ol (13g) and 7-(methoxymethyl)bicyclo[4.2.1]nonan-1-ol (20g): Cycloheptanone (**8g**) (0.112 g, 1.00 mmol) and **12** (0.140 g, 2.00 mmol) were treated with SmI_2 and HMPA according to the general procedure. Chromatography on aluminium oxide (activity III) using *n*-hexane/ethyl acetate (90:10 to 75:25 to 50:50) resulted in a mixture of (*E*)-**13g** and (*Z*)-**13g** (0.054 g, 29%, *E*:*Z* 60:40) and **20g** (0.062 g, 34%, *dr* > 97:3) as colourless oils. **13g**: IR (film): $\tilde{\nu}$ = 3435 (O–H), 3060–3040 (=C–H), 2995–2855 (C–H), 1655 cm^{-1} (C=C); MS (EI, 30°C): *m*/*z* (%): 184 (1) [M^+], 72 (100) [$C_4H_8O^+$]; HRMS: *m*/*z*: calcd for $C_{11}H_{20}O_2$: 184.1463; found 184.1483; elemental analysis calcd (%) for $C_{11}H_{20}O_2$ (184.3): C 71.70, H 10.94; found C 71.37, H 10.48. **20g**: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.30 (s, 3H; OCH_3), AB part of ABX system (δ_A = 3.24, δ_B = 3.19, $^2J_{AB}$ = 8.9, $^3J_{AX}$ = 7.5, $^3J_{BX}$ = 6.5 Hz, each 1H; 7-CH_2O), 2.07–2.04, 1.96–1.86, 1.83–1.75, 1.73–1.52, 1.48–1.32 ppm (5m, 1H, 2H, 3H, 5H, 4H; 2-H, 3-H, 4-H, 5-H, 6-H, 7-H, 8-H, 9-H, OH); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 82.3 (s, C-1), 78.4 (t, 7-CH_2O), 58.6 (q, OCH_3), 46.5 (d, C-6), 37.6 (d, C-7), 43.8, 43.6, 41.2, 34.2, 24.9, 23.0 ppm (6t, C-2, C-3, C-4, C-5, C-8, C-9); IR (film): $\tilde{\nu}$ = 3395 (O–H), 2920–2735 cm^{-1} (C–H); MS (EI, 60–80°C): *m*/*z* (%): 184 (3) [M^+], 111 (100); HRMS: *m*/*z*: calcd for $C_{11}H_{20}O_2$: 184.1463; found 184.1473.

***cis*- and *trans*-1-[(*E*)/(*Z*)-3-Methoxyprop-2-enyl]-2-methylcyclohexan-1-ol (*cis*- and *trans*-13h)**: Allene **12** (0.210 g, 3.00 mmol) and 2-methylcyclohexanone (**8h**) (0.112 g, 1.00 mmol) were treated with SmI_2 and HMPA

Table 6. ^{1}H NMR data (500 MHz, $CDCl_3$) of enol ethers **13**.

Enol ether	$-CH_2CH{=}CHOMe$ δ [ppm] (td, J [Hz])	$-CH_2CH{=}CHOMe$ δ [ppm] (td, J [Hz])	$-OMe$ δ [ppm] (s)	$CH_2CH{=}CHOMe$ δ [ppm] (dd, J [Hz])	Other signals δ [ppm] (J [Hz])
(*E*)-**13a**	6.38 (^4J=1.1, ^3J=12.6)	4.78 (^3J=7.8, 12.6)	3.55	2.19 (^4J=1.1, ^3J=7.8)	1.85–1.76, 1.67–1.53 (2m, 3H, 6H; 2-H, 3-H, 4-H, 5-H, OH)
(*Z*)-**13a**	6.06 (^4J=1.3, ^3J=6.3)	4.48 (^3J=7.7, 6.3)	3.60	2.36 (^4J=1.3, ^3J=7.7)	1.85–1.76, 1.67–1.53 (2m, 3H, 6H; 2-H, 3-H, 4-H, 5-H, OH)
(*E*)-**13e**	6.38[a] (^3J=12.6)	4.72 (^3J=7.6, 12.6)	3.52	2.19 (^3J=7.6)[a]	2.05–1.96, 1.74–1.64, 1.53–1.42 (3m, 2H, 2H, 2H; 2-H, 3-H, 4-H)[b]
(*Z*)-**13e**	6.06 (^4J=1.2, ^3J=6.3)	4.44 (^3J=7.6, 6.3)	3.57	2.37 (^4J=1.2, ^3J=7.6)	2.05–1.96, 1.74–1.64, 1.53–1.42 (3m, 2H, 2H, 2H; 2-H, 3-H, 4-H)[b]
(*E*)-**13f**	6.32 (^4J=1.2, ^3J=12.6)	4.76 (^3J=7.9, 12.6)	3.54	2.05 (^4J=1.2, ^3J=7.8)	1.65 (brs, 1H; OH), 1.61–1.33, 1.28–1.20 (2m, 9H, 1H; 2-H, 3-H, 4-H, 5-H, 6-H)
(*Z*)-**13f**	6.06 (^4J=1.3, ^3J=6.3)	4.45 (^3J=7.9, 6.3)	3.59	2.23 (^4J=1.3, ^3J=7.9)	1.69 (brs, 1H; OH), 1.61–1.33, 1.28–1.20 (2m, 9H, 1H; 2-H, 3-H, 4-H, 5-H, 6-H)
(*E*)-**13g**	6.33 (^4J=1.2, ^3J=12.6)	4.76 (^3J=7.9, 12.6)	3.55	2.07 (^4J=1.2, ^3J=7.9)	1.69–1.35 (m, 13H; 2-H, 3-H, 4-H, 5-H, 6-H, 7-H, OH)
(*Z*)-**13g**	6.06 (^4J=1.3, ^3J=6.3)	4.46 (^3J=7.8, 6.3)	3.59	2.24 (^4J=1.3, ^3J=7.8)	1.69–1.35 (m, 13H; 2-H, 3-H, 4-H, 5-H, 6-H, 7-H, OH)
cis-(*E*)-**13h**	6.30 (^4J=1.2, ^3J=12.6)	4.71 (^3J=7.9, 12.6)	3.54	2.11, 2.08[c,d] ($^2J_{AB}$=13.8, $^3J_{AX}$/J_{BX}=7.9, $^4J_{AY}$/J_{BY}=1.2)	1.68–1.16 (m, 10H; 2-H, 3-H, 4-H, 5-H, 6-H, OH), 0.89 (d, ^3J=6.5, 3H; 2-CH_3)
cis-(*Z*)-**13h**	6.01 (^4J=1.3, ^3J=6.3)	4.39[d] (^3J=6.3, 7.6, 8.1)	3.59	2.37[d] (^4J=1.3, ^3J=7.6, ^2J=14.1) 2.17[d] (^4J=1.3, ^3J=8.1, ^2J=14.1)	1.68–1.16 (m, 10H; 2-H, 3-H, 4-H, 5-H, 6-H, OH), 0.91 (d, ^3J=6.6, 3H; 2-CH_3)
trans-(*E*)-**13h**	6.34 (^4J=1.2, ^3J=12.6)	4.74 (^3J=7.9, 12.6)	3.55	2.10, 2.01[c,d] ($^2J_{AB}$=14.3, $^3J_{AX}$/J_{BX}=7.9, $^4J_{AY}$=1.2)	1.78–1.16 (m, 10H; 2-H, 3-H, 4-H, 5-H, 6-H, OH), 0.93 (d, ^3J=7.0, 3H, 2-CH_3)
trans-(*Z*)-**13h**	6.07 (^4J=1.4, ^3J=6.3)	4.45 (^3J=7.8, 6.3)	3.59	2.26, 2.18[c,d] ($^2J_{AB}$=14.5, $^3J_{AX}$/J_{BX}=7.8, $^4J_{AY}$=1.4)	1.78–1.16 (m, 10H; 2-H, 3-H, 4-H, 5-H, 6-H, OH), 0.94 (d, ^3J=7.0, 3H, 2-CH_3)
(*E*)-**13i**	6.31[a] (^3J=12.6)	4.70 (^3J=7.8, 12.6)	3.53	2.16, 2.09[c,d] ($^2J_{AB}$=14.4, $^3J_{AX}$/J_{BX}=7.9, $^4J_{AY}$=0.9)	1.80–0.99 (m, 10H; 2-H, 3-H, 4-H, 5-H, 6-H, OH), 0.82 (s, 9H; $C(CH_3)_3$)
(*Z*)-**13i**	6.05 (^4J=1.2, ^3J=6.3)	4.41 (^3J=7.9, 6.3)	3.57	2.32, 2.26[c,d] ($^2J_{AB}$=14.5, $^3J_{AX}$/J_{BX}=7.9, $^4J_{AY}$=0.9)	1.80–0.99 (m, 10H; 2-H, 3-H, 4-H, 5-H, 6-H, OH), 0.81 (s, 9H; $C(CH_3)_3$)
(*E*)-**13b**	6.34 (^4J=1.1, ^3J=12.6)	4.74 (^3J=7.9, 12.6)	3.55	2.14 (^4J=1.1, ^3J=7.9)	1.61 (brs, 1H; OH), 1.81–1.75, 1.70–1.66, 1.42–1.34, 1.13–1.02 (4m, 2H, 2H, 2H, 3H; 2-H, 3-H, 4-H, 5-H, 6-H), 0.86 (s, 9H; $C(CH_3)_3$)
(*Z*)-**13b**	6.08 (^4J=1.3, ^3J=6.3)	4.45 (^3J=7.9, 6.3)	3.59	2.31 (^4J=1.3, ^3J=7.9)	1.91 (brs, 1H; OH), 1.81–1.75, 1.70–1.66, 1.42–1.34, 1.13–1.02 (4m, 2H, 2H, 2H, 3H; 2-H, 3-H, 4-H, 5-H, 6-H), 0.86 (s, 9H; $C(CH_3)_3$)
(*E*)-**13j**	6.31[a] (^3J=12.6)	4.72 (^3J=7.9, 12.6)	3.52	2.05 (^4J=1.1, ^3J=7.9)	3.92 (m, 4H; 2-H, 3-H), 1.91–1.84, 1.64–1.55 (2m, 2H, 6H; 6-H, 7-H, 9-H, 10-H), 1.41 (brs, 1H; OH)
(*Z*)-**13j**	6.05 (^4J=1.2, ^3J=6.3)	4.42 (^3J=8.0, 6.3)	3.56	2.23 (^4J=1.2, ^3J=8.0)	3.92 (m, 4H; 2-H, 3-H), 1.91–1.84, 1.64–1.55 (2m, 2H, 6H; 6-H, 7-H, 9-H, 10-H), 1.69 (brs, 1H; OH)
(*E*)-**13k**	6.34[a] (^3J=12.6)	4.73 (^3J=7.9, 12.6)	3.55	2.07 (^4J=1.1, ^3J=7.9)	3.79, 3.18 (m, 4H; 4H, 2-H, 6-H), 1.81, 1.78 (2brs, 1H, 1H; OH), 1.59–1.48 (m, 8H; 3-H, 5-H), 1.46, 1.45 (2s, 9H, 9H; $C(CH_3)_3$)[e]
(*Z*)-**13k**	6.08 (^4J=1.2, ^3J=6.2)	4.43 (^3J=8.0, 6.2)	3.60	2.24 (^4J=1.2, ^3J=8.0)	
(*E*)-**13c**	6.32 (^4J=1.2, ^3J=12.6)	4.77 (^3J=7.9, 12.6)	3.55	2.07 (^4J=1.2, ^3J=7.9)	1.53 (brs, 1H; OH), 1.20 (s, 6H; 1-H, 2-CH_3)
(*Z*)-**13c**	6.04 (^4J=1.3, ^3J=6.3)	4.45 (^3J=7.9, 6.3)	3.59	2.25 (^4J=1.3, ^3J=7.9)	1.75 (brs, 1H; OH), 1.21 (s, 6H; 1-H, 2-CH_3)
(*E*)-**13l**	6.33 (^4J=1.2, ^3J=12.6)	4.75 (^3J=7.9, 12.6)	3.55	2.07, 2.05[c,d] ($^2J_{AB}$=14.0, $^3J_{AX}$/$^3J_{BX}$=7.9, $^4J_{AY}$/J_{BY}=1.2)	1.69 (brs, 1H; OH), 1.53–1.44 (m, 2H; 2-H), 1.13 (s, 3H; 3-CH_3), 0.91 (t, ^3J=7.5, 3H; 1-H)
(*Z*)-**13l**	6.04 (^4J=1.3, ^3J=6.3)	4.43 (^3J=7.8, 6.3)	3.59	2.25, 2.22[c,d] ($^2J_{AB}$=14.2, $^3J_{AX}$/$^3J_{BX}$=7.8, $^4J_{AY}$/J_{BY}=1.3)	1.75 (brs, 1H; OH), 1.53–1.44 (m, 2H; 2-H), 1.14 (s, 3H; 3-CH_3), 0.91 (t, ^3J=7.5, 3H; 1-H)
(*E*)-**13m**	6.30 (^4J=1.0, ^3J=12.6)	4.69 (^3J=7.9, 12.6)	3.52	2.02 (^4J=1.0, ^3J=7.9)	1.48–1.41 (m, 4H; CH_2), 1.31 (brs, 1H; OH), 0.85 (t, ^3J=7.5, 6H; CH_3)

Table 6. (Continued)

Enol ether	$-CH_2CH=CHOMe$ δ [ppm] (td, J [Hz])	$-CH_2CH=CHOMe$ δ [ppm] (td, J [Hz])	$-OMe$ δ [ppm] (s)	$CH_2CH=CHOMe$ δ [ppm] (dd, J [Hz])	Other signals δ [ppm] (J [Hz])
(*Z*)-**13m**	6.01 (^4J = 1.3, ^3J = 6.3)	4.38 (^3J = 7.8, 6.3)	3.57	2.19 (^4J = 1.3, ^3J = 7.8)	1.60 (br s, 1H; OH), 1.48–1.41 (m, 4H; CH_2), 0.85 (t, ^3J = 7.5, 6H; CH_3)
(*E*)-**13n**	6.33 (^4J = 1.1, ^3J = 12.6)	4.76 (^3J = 7.8, 12.6)	3.55	2.11, 2.05[c,d] ($^2J_{AB}$ = 14.1, $^3J_{AX}$/ $^3J_{BX}$ = 7.8, $^4J_{BY}$ = 1.1)	1.75 (br s, 1H; OH), 1.76–1.60 (m, 1H; 2-H), 1.06 (s, 3H; 3-CH_3), 0.90, 0.90 (2d, ^3J = 6.8, each 3H; 1-H, 2-CH_3)
(*Z*)-**13n**	6.05 (^4J = 1.3, ^3J = 6.3)	4.46 (^3J = 7.8, 6.3)	3.59	2.28, 2.23[c,d] ($^2J_{AB}$ = 14.3, $^3J_{AX}$/ $^3J_{BX}$ = 7.8, $^4J_{BY}$ = 1.3)	1.76–1.60 (m, 1H; 2-H), 1.50 (br s, 1H; OH), 1.07 (s, 3H; 3-CH_3), 0.94, 0.94 (2d, ^3J = 6.9, each 3H; 1-H, 2-CH_3)
(*E*)-**13o**[f]	6.27[a] (^3J = 12.4)	4.76 (^3J = 7.9, 12.4)	3.52	–[g]	1.06, 1.05 (2s, each 3H; 3-CH_3), 0.92, 0.91 (2s, each 9H; $C(CH_3)_3$)[e,b]
(*Z*)-**13o**[f]	6.03[a] (^3J = 6.4)	4.46 (^3J = 7.6, 6.4)	3.55	–[g]	
(*E*)-**13p**	6.37[a] (^3J = 12.6)	4.78 (^3J = 7.8, 12.6)	3.56	2.19–2.11[h]	7.31–7.28, 7.22–7.18 (2m, 2H, 3H; Ph), 2.80–2.65 (m, 2H; 1-H), 1.81–1.73 (m, 3H; 2-H, OH), 1.24 (s, 3H; 3-CH_3)
(*Z*)-**13p**	6.07 (^4J = 1.2, ^3J = 6.3)	4.49 (^3J = 7.9, 6.3)	3.60	2.33, 2.29[c,d] ($^2J_{AB}$ = 14.1, $^3J_{AX}$/ $^3J_{BX}$ = 7.9, $^4J_{AY}$/$^4J_{BY}$ = 1.2)	7.29–7.25, 7.21–7.15 (2m, 2H, 3H; Ph), 2.75–2.65 (m, 2H; 1-H), 1.82–1.73 (m, 2H; 2-H), 1.62 (br s, 1H; OH), 1.24 (s, 3H; 3-CH_3)
(*E*)-**13d**	6.33[a] (^3J = 12.6)	4.68[d] (^3J = 7.0, 8.2, 12.6)	3.51	2.14[i] (^4J = 1.2, ^3J = 4.2, 7.0, ^2J = 14.0), 1.95[i] (^4J = 0.7, ^3J = 7.7, 8.2, ^2J = 14.0)	3.52–3.47 (m, 1H; 4-H), 1.69 (d, ^3J = 3.7, 1H; OH), 1.45–1.23 (m, 10H; 5-H, 6-H, 7-H, 8-H, 9-H), 0.86 (t, ^3J = 6.9, 3H; 10-H)
(*Z*)-**13d**	6.00 (^4J = 1.3, ^3J = 6.3)	4.39 (^3J = 7.5, 6.3)	3.57	2.22–2.18[h]	3.61–3.56 (m, 1H; 4-H), 1.84 (d, ^3J = 4.0, 1H; OH), 1.45–1.23 (m, 10H; 5-H, 6-H, 7-H, 8-H, 9-H), 0.86 (t, ^3J = 6.9, 3H; 10-H)

[a] Allylic coupling could not be detected. [b] The signal of the hydroxyl group was not observed. [c] AB part of ABXY system. [d] ddd. [e] The signals could not be assigned to one of the isomers. [f] Mixture with **20o**. These signals in the ^{1}H NMR spectrum of the mixture can be assigned to compound **13o**. [g] Signals are not observed. [h] Multiplet. [i] dddd.

according to the general procedure. Chromatography on aluminium oxide (activity III) with *n*-hexane/ethyl acetate (100:0 to 75:25) yielded *cis*-**13h** (0.026 g, 14%, purity according to ^{1}H NMR spectroscopy >90%, *E*:*Z* 50:50) as a colourless oil and *trans*-**13h** (0.038 g, 21%, purity according to ^{1}H NMR spectroscopy >90%, *E*:*Z* 55:45) as a colourless oil.

3-*tert*-Butyl-1-[(*E*)/(*Z*)-3-methoxyprop-2-enyl]cyclohexan-1-ol (13i) and 5-*tert*-butyl-6-(methoxymethyl)bicyclo[3.2.1]octan-1-ol (20i): 3-*tert*-Butylcyclohexanone (**8i**) (0.154 g, 1.00 mmol) and **12** (0.140 g, 2.00 mmol) were treated with SmI_2 and HMPA under the described conditions. Chromatography on silica gel using *n*-hexane/ethyl acetate (90:10 to 75:25, +1% triethylamine) afforded a mixture of (*E*)-**13i** and (*Z*)-**13i** (0.066 g, 29%, purity according to ^{1}H NMR spectroscopy >70% *E*:*Z* 60:40) and **20i** (0.097 g, 43%, purity according to ^{1}H NMR spectroscopy >80%, *dr* 60:40) as colourless oils. **13i**: IR (film): $\tilde{\nu}$ = 3405 (O–H), 3060–3040 (=C–H), 2940–2865 (C–H), 1665–1655 cm^{-1} (C=C); MS (EI, 40°C): *m*/*z* (%): 226 (1) [M^+], 72 (100) [$C_4H_8O^+$]; HRMS: *m*/*z*: calcd for $C_{14}H_{26}O_2$: 226.1933; found: 226.1953. **20i**: ^{1}H NMR (500 MHz, $CDCl_3$): isomer A: δ = 3.72 (dd, ^3J = 3.8, ^2J = 8.0 Hz, 1H; 6-CH_2O), 3.32 (s, 3H; OCH_3), 3.23 (dd, ^2J = 8.0, ^3J = 10.4 Hz, 1H; 6-CH_2O), 2.05–1.16 (m, 11H; 2-H, 3-H, 4-H, 6-H, 7-H, 8-H, OH), 0.89 ppm (s, 9H; $C(CH_3)_3$); isomer B: δ = 3.53 (dd, ^3J = 4.1, ^2J = 9.1 Hz, 1H; 6-CH_2O), 3.35 (dd, ^2J = 9.1, ^3J = 11.6 Hz, 1H; 6-CH_2O), 3.29 (s, 3H; OCH_3), 2.05–1.16 (m, 12H; 2-H, 3-H, 4-H, 6-H, 7-H, 8-H, OH), 0.92 ppm (s, 9H; $C(CH_3)_3$); ^{13}C NMR (126 MHz, $CDCl_3$): isomer A: δ = 86.2 (t, 6-CH_2O), 58.8 ppm (s, OCH_3); isomer B: δ = 74.8 (t, 6-CH_2O), 58.7 ppm (s, OCH_3); because of the impurities the missing signals could not be assigned; IR (film): $\tilde{\nu}$ = 3380 (O–H), 2955–2810 cm^{-1} (C–H); MS (EI, 40°C): *m*/*z* (%): 226 (1) [M^+], 153 (100) [$M^+ - C_4H_9O$]; HRMS: *m*/*z*: calcd for $C_{14}H_{24}O$ [$M^+ - H_2O$]: 208.1827; found: 208.1834.

***trans*-4-(*tert*-Butyl)-1-[(*E*)/(*Z*)-3-methoxyprop-2-enyl]cyclohexan-1-ol (13b)**: 4-*tert*-Butylcyclohexanone (**8b**) (0.463 g, 3.00 mmol) and **12** (0.630 g, 8.99 mmol) were treated with SmI_2 and HMPA according to the general procedure. The resulting crude oil was purified by column chromatography on aluminium oxide (activity III) using *n*-hexane/ethyl acetate (90:10 to 70:30) to furnish **8b** (0.188 g, 41%) and a mixture of (*E*)-**13b** and (*Z*)-**13b** (0.397 g, 58%, *E*:*Z* 60:40, *dr* >97:3) as a colourless solid. M.p. 49–50°C; IR (KBr): $\tilde{\nu}$ = 3410 (O–H), 3060–3040 (=C–H), 2940–2865 (C–H), 1655 cm^{-1} (C=C); MS (EI, 30°C): *m*/*z* (%): 226 (1) [M^+], 72 (100) [$C_4H_8O^+$]; HRMS: *m*/*z*: calcd for $C_{14}H_{26}O_2$: 226.1933; found 226.1956; elemental analysis calcd (%) for $C_{14}H_{26}O_2$ (226.4): C 74.29, H 11.58; found C 74.04, H 11.12.

8-[(*E*)/(*Z*)-3-Methoxyprop-2-enyl]-1,4-dioxaspiro[4.5]decan-8-ol (13j): The reaction was performed using 1,4-dioxaspiro[4.5]decan-8-one (**8j**) (0.156 g, 1.00 mmol) and **12** (0.140 g, 2.00 mmol) according to the general procedure. Chromatography on aluminium oxide (activity III) using *n*-hexane/ethyl acetate (85:15 to 70:30 to 50:50) yielded a mixture of (*E*)-**13j** and (*Z*)-**13j** (0.124 g, 54%, *E*:*Z* 55:45) as a colourless oil. IR (film): $\tilde{\nu}$ = 3480 (O–H), 3040–3020 (=C–H), 2935–2885 (C–H), 1655 cm^{-1} (C=C); MS (EI, 30°C): *m*/*z* (%): 228 (3) [M^+], 129 (100) [$M^+ - C_5H_7O_2$]; HRMS: *m*/*z*: calcd for $C_{12}H_{20}O_4$: 228.1362; found 228.1383; elemental analysis calcd (%) for $C_{12}H_{20}O_4$ (228.3): C 63.14, H 8.83; found C 62.65, H 8.56.

***N*-(*tert*-Butoxycarbonyl)-4-[(*E*)/(*Z*)-3-methoxyprop-2-enyl]piperidin-4-ol (13k)**: Boc-protected piperidinone **8k** (0.199 g, 1.00 mmol) and **12** (0.140 g, 2.00 mmol) were treated with SmI_2 and HMPA under the described conditions. Chromatography on aluminium oxide (activity III) using *n*-hexane/ethyl acetate (70:30 to 50:50) gave *N*-*tert*-butoxycarbonylpiperidin-4-ol (0.023 g, 11%), a mixture of (*E*)-**13k** and (*Z*)-**13k** (0.137 g, 51%,

Table 7. ^{13}C NMR data (500 MHz, $CDCl_3$) of enol ethers **13**.

Enol ether	$-CH_2CH=CHOMe$ δ [ppm] (d)	$-CH_2CH=CHOMe$ δ [ppm] (d)	$HO-CR_3$ δ [ppm] (s)	$-OMe$ δ [ppm] (q)	$-CH_2CH=CHOMe$ δ [ppm] (t)	Other signals δ [ppm]
(*E*)-**13a**	149.8	97.8	81.5	56.0	39.5	39.2, 39.1, 23.9 (3t, CH_2)[a]
(*Z*)-**13a**	148.3	101.9	82.0	59.5	35.6	
(*E*)-**13e**	149.9	96.7	73.9	55.9	37.8	35.3, 35.0, 11.8 (3t, CH_2)[a]
(*Z*)-**13e**	148.7	101.0	74.8	59.5	33.9	
(*E*)-**13f**	149.7	96.8	70.8	56.0	40.4	37.4, 37.2, 25.8, 25.8, 22.4, 22.2 (6t, CH_2)[a]
(*Z*)-**13f**	148.4	101.1	71.7	59.5	36.3	
(*E*)-**13g**	149.8	97.2	74.8	56.0	41.5	40.9, 40.8, 29.8, 29.8, 22.4, 22.4 (6t, CH_2)[a]
(*Z*)-**13g**	148.4	101.4	75.7	59.5	37.5	
cis-(*E*)-**13h**	149.3	97.5	72.6	56.0	38.8	38.4, 37.9 (2d, C-2), 36.2, 36.2, 30.7, 30.6, 25.6, 25.6, 21.9, 21.7 (8t, CH_2), 15.0, 14.9 (2q, 2-CH_3)[a]
cis-(*Z*)-**13h**	147.9	101.6	73.4	59.5	35.1	
trans-(*E*)-**13h**	149.5	96.5	73.3	56.0	32.4	40.9, 40.4 (2d, C-2), 36.2, 35.9, 31.0, 30.8, 24.1, 23.8, 23.2, 23.0 (8t, CH_2), 15.2, 15.1 (2q, 2-CH_3)[a]
trans-(*Z*)-**13h**	148.4	101.0	74.3	59.5	28.6	
(*E*)-**13i**	149.7	96.6	73.7	56.1	35.5	[b]
(*Z*)-**13i**	148.6	101.1	71.7	59.6	32.3	[b]
(*E*)-**13b**	149.8	96.7	71.4	56.0	34.8	47.5 (d, C-4), 38.5, 38.2, 24.5, 24.3 (4t, C-2, C-3, C-5, C-6), 32.2, 27.6 (s, q, $C(CH_3)_3$)
(*Z*)-**13b**	148.6	101.1	72.5	59.5	31.1	47.6 (d, C-4), 38.5, 38.2, 24.5, 24.3 (4t, C-2, C-3, C-5, C-6), 36.1, 27.6 (s, q, $C(CH_3)_3$)
(*E*)-**13j**	105.1	96.5	69.7	56.1	40.6	108.9 (s, C-5), 64.2, 64.1 (2t, C-2, C-3)[c]
(*Z*)-**13j**	148.7	100.7	70.8	59.5	36.5	108.9 (s, C-5), 64.2, 64.1 (2t, C-2, C-3)[c]
(*E*)-**13k**	150.2	95.8	–[d]	56.9	41.0	154.8 (s, CO)[e]
(*Z*)-**13k**	148.8	99.9	–[d]	59.5	36.8	154.8 (s, CO)[e]
(*E*)-**13c**	149.8	97.7	70.2	56.1	41.9	28.8 (q, C-1, 2-CH_3)
(*Z*)-**13c**	149.3	101.8	71.0	59.5	38.1	28.9 (q, C-1, 2-CH_3)
(*E*)-**13l**	149.7	97.4	72.2	56.0	39.5	33.9 (t, C-2), 25.8 (q, 3-CH_3), 8.1 (q, C-1)
(*Z*)-**13l**	148.3	101.5	73.1	59.5	35.7	34.2 (t, C-2), 25.9 (q, 3-CH_3), 8.3 (q, C-1)
(*E*)-**13m**	149.6	97.2	74.0	56.1	36.7	30.8, 30.6 (2 t, CH_2), 7.9, 7.8 (2q, CH_3)[a]
(*Z*)-**13m**	148.2	101.4	75.0	59.5	33.0	
(*E*)-**13n**	149.6	97.2	74.0	56.0	37.9	36.4 (d, C-2), 22.4 (q, 3-CH_3), 17.7, 17.6 (2q, C-1, 2-CH_3)
(*Z*)-**13n**	148.3	101.4	75.0	59.5	34.2	36.8 (d, C-2), 22.5 (q, 3-CH_3), 17.0, 16.9 (2q, C-1, 2-CH_3)
(*E*)-**13p**	149.8	97.1	71.9	56.0	40.3	142.5 (s, Ph), 128.3,[f] 125.7 (2d, Ph), 43.3 (t, C-2), 30.2 (t,C-1), 26.3 (q, 3-CH_3)
(*Z*)-**13p**	148.5	101.2	72.9	59.6	36.3	142.8 (s, Ph), 128.3,[f] 125.6 (2d, Ph), 43.7 (t, C-2), 30.5 (t, C-1), 26.6 (q, 3-CH_3)
(*E*)-**13d**	149.4	98.2	71.4	56.0	35.7	14.0 (q, C-10)[g]
(*Z*)-**13d**	148.2	102.1	71.7	60.0	31.8	14.0 (q, C-10)[g]

[a] The signals could not be assigned to one of the isomers. [b] Because of the impurities the missing signals could not be assigned. [c] The following signals could not be assigned to one of the isomers: $\delta = 34.6$, 34.5, 30.6, 30.5 (4t, CH_2). [d] The signals could not be assigned to one of the isomers: $\delta = 69.9$, 68.9 (2s, C-4). [e] The following signals could not be assigned to one of the isomers: $\delta = 79.2$, 79.1, 28.4, 28.4 (2s, 2q, $C(CH_3)_3$), 39.8 (brt, C-2, C-6), 36.5, 36.3 (2t, C-3, C-5). [f] Signal shows doubled intensity. [g] The following signals could not be assigned to one of the isomers: $\delta = 36.9$, 36.5, 32.0, 31.8, 29.3, 29.3, 25.7, 25.6, 22.6 (9t, C-5, C-6, C-7, C-8, C-9).

E:*Z* 50:50) as a colourless oil and a mixture (0.053 g), which probably contains a bicyclic compound like **20g. 13k**: IR (film): $\tilde{\nu} = 3445$ (O–H), 3040–2830 (=C–H, C–H), 1695, 1670 cm^{-1} (C=O, C=C); MS (EI, 80 °C): *m*/*z* (%): 271 (4) [M^+], 57 (100) [$C_4H_9^+$]; HRMS: *m*/*z*: calcd for $C_{14}H_{25}NO_4$: 271.1784; found 271.1765; elemental analysis calcd (%) for $C_{14}H_{25}NO_4$ (271.4): C 61.97, H 9.29, N 5.16; found C 61.59, H 8.95, N 5.05.

(*E*)- and (*Z*)-5-Methoxy-2-methylpent-4-en-2-ol (13c): Acetone **8c** (0.058 g, 1.00 mmol) and **12** (0.140 g, 2.00 mmol) were treated with SmI_2 and HMPA according to the general procedure. Chromatography on aluminium oxide (activity III) using *n*-hexane/ethyl acetate (90:10 to 70:30) yielded a mixture of (*E*)-**13c** and (*Z*)-**13c** (0.034 g, 26%, *E*:*Z* 65:35) as a yellow oil. IR (film): $\tilde{\nu} = 3430$ (O–H), 2995–2915 (=C–H, C–H), 1655 cm^{-1} (C=C); MS (EI, 30 °C): *m*/*z* (%): 130 (2) [M^+], 59 (100) [$C_3H_7O^+$]; HRMS: *m*/*z*: calcd for $C_7H_{14}O_2$: 130.0994; found 130.0986. An elemental analysis could not be recorded due to the high volatility of the compound.

(*E*)- and (*Z*)-6-Methoxy-3-methylhex-5-en-3-ol (13l): The reaction was carried out using **12** (0.140 g, 2.00 mmol) and butan-2-one (**8l**) (0.072 g, 1.00 mmol) according to the general procedure. Chromatography on aluminium oxide (activity III) with *n*-hexane/ethyl acetate (80:20 to 70:30) afforded **13l** (0.052 g, 36%, *E*:*Z* = 60:40) as a colourless oil. IR (film): $\tilde{\nu} = 3425$ (O–H), 3060–3040 (=C–H), 2955–2835 (C–H), 1655 cm^{-1} (C=C); MS (EI, 30 °C): *m*/*z* (%): 144 (3) [M^+], 72 (100) [$C_4H_8O^+$]; HRMS: *m*/*z*: calcd for $C_8H_{16}O_2$: 144.1150; found 144.1173.

(*E*)- and (*Z*)-3-Ethyl-6-methoxyhex-5-en-3-ol (13m): Diethylketone (**8m**) (0.086 g, 1.00 mmol) and **12** (0.140 g, 2.00 mmol) were treated with SmI_2 and HMPA under the described conditions. Chromatography on aluminium oxide (activity III) using *n*-hexane/ethyl acetate (100:0 to 80:20) afforded a mixture of **13m** (*E*:*Z* 55:45) and 1-ethyl-3-methoxymethylcyclopentan-1-ol (**20m**) (*dr* > 97:3) in a ratio of 85:15 (0.082 g, 52%, purity > 90%) as a colourless oil. **13m**: IR (film): $\tilde{\nu} = 3460$ (O–H), 3060–3040 (=C–H), 2965–2830 (C–H), 1665–1655 cm^{-1} (C=C); MS (EI, 40 °C): *m*/*z* (%): 158 (1) [M^+], 72 (100) [$C_4H_8O^+$]; HRMS: *m*/*z*: calcd for $C_9H_{18}O_2$: 158.1307; found 158.1318. **20m**: The following signals in the ^1H NMR of the mixture can be assigned to **20m**: ^1H NMR (500 MHz, $CDCl_3$): $\delta =$ 3.40 (s, 3H; OCH_3), 3.39 (m, 2H; CH_2OCH_3), 3.07 (brs, 1H; OH), 0.99 ppm (t, $^3J = 7.5$ Hz, 3H; CH_3).

(*E*)- and (*Z*)-6-Methoxy-2,3-dimethylhex-5-en-3-ol (13n) and 4-methoxymethyl-1,2-dimethylcyclopentan-1-ol (20n): The reaction was performed according to the general procedure using **12** (0.140 g, 2.00 mmol) and 3-methylbutan-2-one (**8n**) (0.086 g, 1.00 mmol). Chromatography on alumi-

nium oxide (activity III) with *n*-hexane/ethyl acetate (95:5 to 60:40) afforded a mixture of **13n** (*E*:*Z* 55:45) and **20n** (0.038 g, 24%, **13n**:**20n** 85:15) as a colourless oil. **13n**: IR (film): $\tilde{\nu}$ = 3470 (O–H), 3060–3040 (=C–H), 2960–2830 (C–H), 1655 cm^{-1} (C=C); MS (EI, 30 °C): *m*/*z* (%): 158 (1) [M^+], 72 (100) [$C_4H_8O^+$]; HRMS: *m*/*z*: calcd for $C_9H_{18}O_2$: 158.1307; found 158.1322. The following signals in the ^1H and ^{13}C NMR spectra of the mixture can be assigned to compound **20n**: ^1H NMR (500 MHz, $CDCl_3$): δ = 3.37 (s, 3H; OCH_3), 3.32 (m, 2H; CH_2OCH_3), 3.11 (br s, 1H; OH), 1.19 ppm (s, 3H; 1-CH_3); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 78.1 (s, C-1), 76.3 (t, CH_2OCH_3), 58.9 (q, OCH_3), 44.8, 35.0, 35.0 (2t, d, CH, CH_2), 24.4 (q, 1-CH_3), 11.9 ppm (q, 2-CH_3).

4-Methoxymethyl-1,2,2-trimethylcyclopentan-1-ol (20o) and (*E*)/(*Z*)-6-methoxy-2,2,3-trimethylhex-5-en-3-ol (13o): Pinacolone (**8o**) (0.088 g, 1.00 mmol) and **12** (0.140 g, 2.00 mmol) were treated with SmI_2 and HMPA according to the general procedure. Chromatography on aluminium oxide (activity III) using *n*-hexane/ethyl acetate (90:10 to 70:30) gave a mixture of **13o** (*E*:*Z* 60:40) and 4-methoxymethyl-1,2,2-trimethylcyclopentan-1-ol (**20o**) (*dr* > 97:3) in a ratio of 20:80 (0.039 g, 26%) as a colourless oil. **20o**: ^1H NMR (500 MHz, $CDCl_3$): δ = 3.33 (s, 3H; OCH_3), AB part of ABX system (δ_A = 3.29, δ_B = 3.27, $^2J_{AB}$ = 8.6, $^3J_{AX}$ = 3.9, $^3J_{BX}$ = 3.7 Hz, each 1H; 4-CH_2), 3.05 (br s, 1H; OH), 2.31–2.23 (m, 1H; 4-H), 2.11 (dd, ^3J = 11.4, ^2J = 14.2 Hz, 1H; 5-H), 1.65 (dd, ^3J = 8.8, ^2J = 12.8 Hz, 1H; 3-H), 1.53 (dd, ^3J = 3.2, ^2J = 14.2 Hz, 1H; 5-H), 1.48 (dd, ^3J = 9.0, ^2J = 12.8 Hz, 1H; 3-H), 1.08, 0.94, 0.83 ppm (3s, each 3H; 1-CH_3, 2-CH_3, 2-CH_3); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 81.0 (s, C-1), 76.1 (t, 4-CH_2), 58.9 (q, OCH_3), 46.2 (s, C-2), 42.6 (t, C-5), 41.2 (t, C-3), 33.7 (d, C-4), 25.9, 21.1, 20.4 ppm (3q, 1-CH_3, 2-CH_3, 2-CH_3); IR (film): $\tilde{\nu}$ = 3475 (O–H), 2940–2870 cm^{-1} (C–H); MS (EI, 60 °C): *m*/*z* (%): 172 (6) [M^+], 43 (100) [$C_2H_3O^+$]; HRMS: *m*/*z*: calcd for $C_{10}H_{20}O_2$: 172.1463; found 172.1482.

(5*E*)- and (5*Z*)-6-Methoxy-3-methyl-1-phenylhex-5-en-3-ol (13p): 4-Phenylbutan-2-one (**8p**) (0.148 g, 1.00 mmol) and **12** (0.140 g, 2.00 mmol) were treated with SmI_2 and HMPA under the described conditions. Chromatography on aluminium oxide (activity III) with *n*-hexane/ethyl acetate (95:5 to 80:20) afforded an 85:15 mixture (0.137 g) of **13p** (*E*:*Z* 85:15) and 4-phenylbutan-2-ol as a colourless oil. Separation using HPLC [nucleosil 50-5, *n*-hexane/ethyl acetate (85:15), 128 mL min^{-1}, 112 bar] yielded (*Z*)-**13p** (0.013 g, 6%) as a colourless oil and a mixture (0.094 g) of (*E*)-**13p** and 4-phenylbutan-2-ol in a ratio of 85:15. (*Z*)-**13p**: IR (film): $\tilde{\nu}$ = 3450 (O–H), 3085–2825 (=C–H, C–H), 1665–1495 cm^{-1} (C=C); MS (EI, 40 °C): *m*/*z* (%): 220 (2) [M^+], 91 (100) [$C_7H_7^+$]; HRMS: *m*/*z*: calcd for $C_{14}H_{20}O_2$: 220.1463; found: 220.1447. (*E*)-**13p**: IR (film): $\tilde{\nu}$ = 3435 (O–H), 3085–2835 (=C–H, C–H), 1670–1495 cm^{-1} (C=C); MS (EI, 60 °C): *m*/*z* (%): 220 (1) [M^+], 91 (100) [$C_7H_7^+$]. The following signal can be assigned to 4-phenylbutan-2-ol: δ = 3.82 ppm (m, 1H; 2-H).

(*E*)- and (*Z*)-1-Methoxydec-1-en-4-ol (13d): The reaction was performed with heptanal (**8d**) (0.114 g, 1.00 mmol) and **12** (0.140 g, 2.00 mmol) in accordance with the general procedure. Chromatography on aluminium oxide (activity III) using *n*-hexane/ethyl acetate (90:10 to 80:20) yielded a mixture of (*E*)-**13d** and (*Z*)-**13d** (0.081 g, 43%, *E*:*Z* 55:45) as a colourless oil. IR (film): $\tilde{\nu}$ = 3440 (O–H), 3040 (=C–H), 2960–2830 (C–H), 1655 cm^{-1} (C=C); MS (EI, 30 °C): *m*/*z* (%): 186 (1) [M^+], 101 (100) [$M^+ - C_5H_9O_2$]; HRMS: *m*/*z*: calcd for $C_{10}H_{19}O$ [$M^+ - OCH_3$]: 155.1436; found 155.1453; elemental analysis calcd (%) for $C_{11}H_{22}O_2$ (186.3): C 70.92, H 11.90; found C 70.94, H 11.65.

1-(3-Methoxybut-2-enyl]cyclopentanol (24): Cyclopentanone (**8a**) (0.084 g, 1.00 mmol) and **23** (0.126 g, 1.50 mmol) were treated with SmI_2 and HMPA under the described conditions. Chromatography on aluminium oxide (activity III) using *n*-hexane/ethyl acetate (90:10 to 70:30) afforded **24** (0.031 g, 18%, purity > 70%) as a colourless oil. ^1H NMR (270 MHz, $CDCl_3$): δ = 4.40 (t, ^3J = 7.9 Hz, 1H; 2′-H), 3.47 (s, 3H; OCH_3), 2.22 (d, ^3J = 7.9 Hz, 2H; 1′-H), 1.87–1.50 (m, 9H; 2-H, 3-H, 4-H, 5-H, OH), 1.76 ppm (s, 3H; 4′-H).

4-*tert*-Butyl-1-(2-oxaspiro[4.5]deca-3,6,9-trien-4-ylmethyl)cyclohexanol (27), 4-*tert*-butyl-1-(2-oxaspiro[4.5]deca-3,6,8-trien-4-ylmethyl)cyclohexanol (28) and 4-*tert*-butyl-1-[(2*E*)/(2*Z*)-3-benzyloxyprop-2-enyl]cyclohexanol (26): The reaction was carried out according to the general procedure using **25** (0.219 g, 1.50 mmol) and 4-*tert*-butylcyclohexanone (**8b**) (0.154 g, 1.00 mmol). Chromatography on aluminium oxide (activity III) with *n*-hexane/ethyl acetate (95:5 to 75:25) followed by separation by HPLC [nucleosil 50–5, *n*-hexane/isopropanol (98:2), 64 mL min^{-1}, 65 bar] afforded (*E*)-**26** (0.044 g, 15%, purity > 95%), **27** (0.061 g, 20%), **28** (0.024 g, 8%, *dr* > 97:3) and (*Z*)-**26** (0.036 g, 12%, *dr* > 97:3) all as colourless solids. **27**: m.p. 98–100 °C; ^1H NMR (500 MHz, $CDCl_3$): δ = 6.34 (s, 1H; 3′-H), 5.84 (td, ^3J = 3.3, 10.2 Hz, 1H; 7′-H, 9′-H), 5.56 (td, ^4J = 2.1, ^3J = 10.2 Hz, 2H; 6′-H, 10′-H), 4.05 (s, 2H; 1′-H), 2.62 (m, 2H; 8′-H), 2.10 (s, 2H; 4′-CH_2), 1.81–1.78, 1.63–1.60, 1.34–1.29, 1.06–0.99 (4m, 2H, 2H, 2H, 3H; 2-H, 3-H, 4-H, 5-H, 6-H), 1.77 (br s, 1H; OH), 0.82 ppm (s, 9H; $C(CH_3)_3$); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 142.8 (d, C-3′), 129.8 (d, C-6′, C-10′), 125.4 (d, C-7′, C-9′), 116.2 (s, C-4′), 81.2 (t, C-1′), 71.7 (s, C-1), 50.4 (s, C-5′), 47.3 (d, C-4), 38.5, 24.5 (2t, C-2, C-3, C-5, C-6), 32.2, 27.5 (s, q, $C(CH_3)_3$), 30.3 (t, 4′-CH_2), 26.0 ppm (t, C-8′); IR (film): $\tilde{\nu}$ = 3340 (O–H), 3025–2815 (=C–H, C–H), 1660–1630 cm^{-1} (C=C); MS (EI, 80 °C): *m*/*z* (%): 302 (1) [M^+], 148 (100) [$M^+ - C_{10}H_{18}O$]; HRMS: *m*/*z*: calcd for $C_{20}H_{30}O_2$: 302.2246; found 302.2240. **28**: m.p. 117–118 °C; ^1H NMR (500 MHz, $CDCl_3$): δ = 6.29 (s, 1H; 3′-H), 5.94 (dd, ^3J = 5.1, 9.6 Hz, 1H; 7′-H), 5.86–5.79, 5.74–5.67 (2m, each 1H; 8′-H, 9′-H), 5.51 (d, ^3J = 9.6 Hz, 1H; 6′-H), AB system (δ_A = 4.06, δ_B = 3.97, $^2J_{AB}$ = 8.8 Hz, each 1H; 1′-H), 2.55–2.46, 2.34–2.27 (2m, each 1H; 10′-H), 2.25 (s, 2H; 4′-CH_2), 1.92–1.81, 1.67–1.60, 1.41–1.23, 1.07–0.97 (4m, 2H, 3H, 3H, 2H; 2-H, 3-H, 4-H, 5-H, 6-H, OH), 0.82 ppm (s, 9H; $C(CH_3)_3$); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 141.9 (d, C-3′), 130.7, 125.1, 124.5, 123.2 (4d, C-6′, C-7′, C-8′, C-9′), 117.0 (s, C-4′), 80.9 (t, C-1′), 72.0 (s, C-1), 48.3 (s, C-5′), 47.4 (d, C-4), 39.5, 38.3, 24.6, 24.5 (4t, C-2, C-3, C-5, C-6), 33.8 (t, C-10′), 30.5 (t, 4′-CH_2), 32.2, 27.6 ppm (s, q, $C(CH_3)_3$); IR (film): $\tilde{\nu}$ = 3340 (O–H), 3050–2800 (=C–H, C–H), 1650 cm^{-1} (C=C); MS (EI, 90 °C): *m*/*z* (%): 302 (1) [M^+], 148 (100) [$M^+ - C_{10}H_{18}O$]; HRMS: *m*/*z*: calcd for $C_{20}H_{28}O$ [$M^+ - H_2O$]: 284.2140; found 284.2153. (*E*)-**26**: m.p. 64–65 °C; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.38–7.28 (m, 5H; Ph), 6.36 (d, ^2J = 12.6 Hz, 1H; 3′-H), 4.87 (td, ^3J = 7.9, 12.6 Hz, 1H; 2′-H), 4.77 (s, 2H; OCH_2), 2.13 (d, ^3J = 7.9 Hz, 2H; 1′-H), 1.73–1.62, 1.40–1.34, 1.10–0.98 (3m, 5H, 2H, 3H; 2-H, 3-H, 4-H, 5-H, 6-H, OH), 0.85 ppm (s, 9H; $C(CH_3)_3$); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 148.5 (d, C-3′), 137.0, 128.5, 127.9, 127.5 (s, 3d, Ph), 98.9 (d, C-2′), 71.4 (s, C-1), 71.2 (t, OCH_2), 47.5 (d, C-4), 38.1, 24.2 (2t, C-2, C-3, C-5, C-6), 34.8 (t, C-1′), 32.2, 27.6 ppm (s, q, $C(CH_3)_3$); IR (film): $\tilde{\nu}$ = 3435 (O–H), 3090–2865 (=C–H, C–H), 1670–1650 cm^{-1} (C=C); MS (EI, 50 °C): *m*/*z* (%): 302 (1) [M^+], 91 (100) [$C_7H_7^+$]; HRMS: *m*/*z*: calcd for $C_{16}H_{21}O_2$ [$M^+ - C_4H_9$]: 245.1541; found 245.1562. (*Z*)-**26**: m.p. 52–53 °C; ^1H NMR (500 MHz, $CDCl_3$): δ = 7.36–7.28 (m, 5H; Ph), 6.23 (td, ^4J = 1.1, ^3J = 6.3 Hz, 1H; 3′-H), 4.80 (s, 2H; OCH_2), 4.51 (dt, ^3J = 7.8, 6.3 Hz, 1H; 2′-H), 2.36 (dd, ^4J = 1.1, ^3J = 7.8 Hz, 2H; 1′-H), 1.86 (br s, 1H; OH), 1.81–1.77, 1.65–1.62, 1.38–1.32, 1.15–1.06, 1.03–0.95 (5m, 2H, 2H, 2H, 2H, 1H; 2-H, 3-H, 4-H, 5-H, 6-H), 0.83 ppm (s, 9H; $C(CH_3)_3$); ^{13}C NMR (126 MHz, $CDCl_3$): δ = 146.7 (d, C-3′), 137.3, 128.5, 127.9, 127.4 (s, 3d, Ph), 101.9 (d, C-2′), 73.8 (t, OCH_2), 72.6 (s, C-1), 47.5 (d, C-4), 38.5, 24.5 (2t, C-2, C-3, C-5, C-6), 31.3 (t, C-1′), 32.2, 27.6 ppm (s, q, $C(CH_3)_3$); IR (film): $\tilde{\nu}$ = 3330 (O–H), 3090–2840 (=C–H, C–H), 1665 cm^{-1} (C=C); MS (EI, 100 °C): *m*/*z* (%): 302 (1) [M^+], 91 (100) [$C_7H_7^+$]; HRMS: *m*/*z*: calcd for $C_{20}H_{30}O_2$: 302.2246; found 302.2262.

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