Diastereoselective Synthesis of Five- and Seven-Membered Rings by [2+2+1], [3+2], [3+2+2], and [4+3] Carbocyclization Reactions of β-Substituted (Alkenyl)(methoxy)carbene Complexes with Methyl Ketone Lithium Enolates

José Barluenga,* Jorge Alonso, and Francisco J. Fañanás[a]

Abstract: β-Substituted alkenylcarbene complexes react with methyl ketone lithium enolates to give different carbocyclization products depending on the structure of the lithium enolate, on the metal of the carbene complex, and on the reaction media. Thus, the reactions of aryl and alkyl methyl ketone lithium enolates with β-substituted alkenyl chromium and tungsten carbene complexes in diethyl ether afford 1,3-cyclopentanediol derivatives derived from a formal [2+2+1] carbocyclization reaction. However, the lithium enolates of acetone and tungsten complexes furnish formal [3+2+2] carbocyclization products. In the case of alkynyl methyl ketone lithium enolates, competitive formal [2+2+1] and [3+2] carbocyclization reactions occur and 1,3-cyclopentanediol and 3-cyclopentenol derivatives are formed. Conversely, alkenyl methyl ketone lithium enolates react with alkenylcarbene complexes under the same reaction conditions to form 2-cycloheptenone derivatives by a formal [4+3] carbocyclization reaction. Finally, when the reaction was performed in the presence of a coordinating medium, the [3+2] carbocyclization pattern was observed independently of the nature of the methyl ketone lithium enolate used.

Keywords: carbenes · carbocycles · cyclization · enolates

Introduction

The design of new methods for the selective synthesis of medium-size carbocycles continues to be of great interest for organic chemists[1] due to the importance of carbocyclic skeletons in biologically relevant compounds.[2] Organometallic compounds have considerably contributed in the development of important processes for the construction of cyclic products with different ring sizes.[3] In this context, Fischer carbene complexes, which have been revealed as extraordinarily useful tools for synthesizing a wide variety of complex molecules,[4] have turned out to be a solid asset for the preparation of cyclization products.[5] In particular, stabilized Group 6 alkenylcarbene complexes are recognized as valuable building blocks for the preparation of five- and seven-membered carbo- and heterocycles. In fact, there are diverse examples in which these compounds act as a C_3 component for the formation of five- and seven-membered rings. Thus, reactions of alkenylcarbene complexes with alkynes,[4c,6] electronically neutral 1,3-dienes,[7] electron-rich 1,3-dienes,[8] 1-amino-1-aza-1,3-dienes,[9] electron-poor alkenes,[10] enamines,[11] ynamines,[12] imines,[13] and isonitriles[14] give rise to five-membered rings by a formal [3+2] cyclization process. In this last case, if the isonitrile stoichiometry is changed, a new cyclopentane ring can also be formed by a formal [3+1+1] cyclization reaction.[14,15] The participation of alkenylcarbene complexes as a C_1 component in the formation of five-membered rings is rather uncommon. Thus, when these complexes react with electronically neutral 1,3-dienes[7] or 1-amino-1-azadienes,[9] cyclopentene and pyrrole derivatives arising from a formal [4+1] cyclization reaction are obtained. Nevertheless, 1,3-diamino-1,3-dienes and chromium alkenylcarbene complexes can also undergo a [4+1] cyclization reaction.[16] Alkenylcarbene complexes can also take part in the construction of seven-membered rings, generally as a C_3 component. Certainly, they react with both electron-rich[17] and electron-poor dienes[18] or azadienes[19] to give the corresponding [4+3] cyclization adducts. Recently,[20] a nickel-mediated [3+2+2]

[a] Prof. Dr. J. Barluenga, Dr. J. Alonso, Dr. F. J. Fañanás
Instituto Universitario de Química Organometálica "Enrique Moles"
Unidad Asociada al CSIC, Universidad de Oviedo
Julián Clavería 8, 33006 Oviedo (Spain)
Fax: (+34) 985-103-450
E-mail: barluenga@uniovi.es

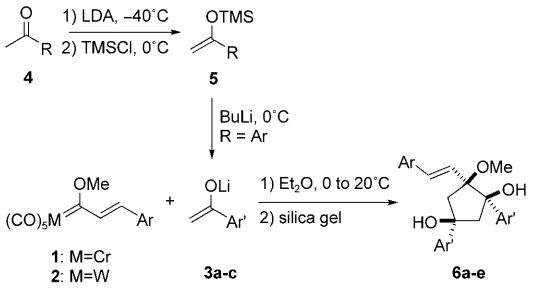
 DOI: 10.1002/chem.200500164

cyclization reaction of alkenyl chromium carbene complexes and alkynes has been described in which the carbene complexes act as a C_3 unit. Alternatively, while lithium enolates add to α,β-unsaturated carbene complexes in a Michael fashion,[21] Casey and Brunsvold[21a] described only an example in which the lithium enolate of acetone added to these complexes through 1,2-nucleophilic attack to furnish α,β-unsaturated ketones. In this context, we have recently[22] reported the novel and solvent-controlled diastereoselective [3+2] and [4+1] cyclization reactions of α,β-substituted (alkenyl)(methoxy)carbene complexes and methyl ketone lithium enolates to form five-membered carbocyclic rings. Herein, we present the reaction of β-substituted (alkenyl)-(methoxy)carbene complexes and lithium enolates derived from methyl ketones to afford five- and seven-membered carbocyclic rings in a diastereoselective way. Formal [2+2+1], [3+2], [3+2+2], and [4+3] cyclization reactions are observed and the reaction outcome depends on the nature of the substituent on the lithium enolate, the metal of the carbene complex, and the presence or absence of a strong coordinating cosolvent in the reaction medium.

Results and Discussion

Since the results of the reaction of β-substituted alkenyl carbene complexes **1**, **2** and lithium enolates **3** are highly dependent on the nature of the R group of the enolate, the results and discussion have been systematized according to the structure of the methyl ketones **4**, which are the precursors of the lithium enolates **3** (Scheme 1).

Abstract in Spanish: *Los complejos alquenilcarbeno β-sustituidos reaccionan con enolatos de litio de metil cetonas para dar diferentes productos de carbociclación dependiendo de la estructura del enolato de litio, del metal del complejo carbeno y del medio de reacción. Así, la reacción de enolatos de litio de aril y alquil metil cetonas con complejos alquenilcarbeno de cromo y wolframio β-sustituidos en dietil eter origina derivados de 1,3-ciclopentanodiol, derivados de una reacción de carbociclación formal [2+2+1]. Sin embargo, el enolato de litio de la acetona y complejos de wolframio dan lugar a productos de carbociclación formal [3+2+2]. En el caso de enolatos de litio de alquinil metil cetonas, se observa la formación de una mezcla de derivados de 1,3-ciclopentanodiol y 3-ciclopentenol derivados de reacciones de carbociclación formal [2+2+1] y [3+2] competitivas. Por el contrario, los enolatos de litio de alquenil metil cetonas reaccionan con complejos alquenilcarbeno en las mismas condiciones de reacción para generar derivados de 2-cicloheptenona a través de una reacción de carbociclación formal [4+3] Finalmente, cuando la reacción se lleva a cabo en presencia de PMDTA, un medio coordinante, se observa el modelo de carbociclación formal [3+2], independientemente de la naturaleza del enolato de litio utilizado.*



Scheme 1. Reaction of carbene complexes **1** or **2** with aryl methyl ketone lithium enolates **3a–c** to give 1,3-cyclopentanediol derivatives **6a–e**. LDA = lithium diisopropylamide, TMS = trimethylsilyl.

Aryl methyl ketones—Formal [2+2+1] cyclizations: When β-substituted (alkenyl)(methoxy)carbene complexes **1** (M = Cr) or **2** (M = W) were treated with two equivalents of aryl methyl ketone lithium enolates **3a–c**, generated by the reaction of the corresponding silyl enol ethers **5** with butyllithium at 0 °C, in diethyl ether at temperatures of 0–20 °C, 1,3-cyclopentanediol derivatives **6a–e** were obtained, after hydrolysis with silica gel, in moderate yield and as single diastereoisomers (Scheme 1 and Table 1). Compounds **6a–e** can be considered as the result of a three-component, formal [2+2+1] carbocyclization reaction, in which three quaternary stereogenic centers have been generated with complete diastereoselectivity. The structure and relative configuration of the stereogenic centers of compounds **6a–e** were determined by 2D NMR spectroscopic analysis (COSY, HMQC, HMBC, and NOESY).

It is interesting to note that the use of one equivalent of the lithium enolate **3a–c** under the same reaction conditions led to the formation of compounds **6a–e** in lower yields and the recovery of almost half of the carbene complexes **1**. Remarkably, the reaction only works when the lithium enolates **3** were prepared from silyl enol ethers **5** and with diethyl ether as solvent. When the same reaction was carried out with tetrahydrofuran (THF) as the solvent, a mixture of unidentified products was observed. When enolates **3** were formed by deprotonation of the corresponding aryl methyl ketones **4** with LDA in THF and were then treated with carbene complexes **1** or **2**, the open-chain adducts, derived from a 1,2-addition reaction, were formed.[20a] Probably, the presence of diisopropylamine in the reaction medium inhibited the progress of the reaction. With regard to the carbene complex, both chromium and tungsten derivatives were competent in this chemistry, although the yields obtained with the former were slightly higher. In particular, the most noticable difference was observed in the reaction with the lithium enolate **3c**. Although compound **6c** could be obtained in low yield from carbene complex **1a**, the same reaction did not proceed with the tungsten carbene complex **2a**.

Alkyl methyl ketones—Formal [2+2+1] and [3+2+2] cyclizations: Taking into account the results described above for the aryl methyl ketone lithium enolates **3a–c**, we decided to

Table 1. Synthesis of 1,3-cyclopentanediol derivatives **6a–e** from carbene complexes **1** and **2** and aryl methyl ketone lithium enolates **3a–c**.

Carbene complex	Ar	Enolate[a]	Ar′	Product	Yield [%][b]
1a	Ph	**3a**	Ph	**6a**	51
2a	Ph	**3a**	Ph	**6a**	49
1a	Ph	**3b**	4-$MeOC_6H_4$	**6b**	55
2a	Ph	**3b**	4-$MeOC_6H_4$	**6b**	43
1a	Ph	**3c**	2-furyl	**6c**	28
1b	2-furyl	**3a**	Ph	**6d**	52
2b	2-furyl	**3a**	Ph	**6d**	52
1b	2-furyl	**3b**	4-$MeOC_6H_4$	**6e**	42
2b	2-furyl	**3b**	4-$MeOC_6H_4$	**6e**	34

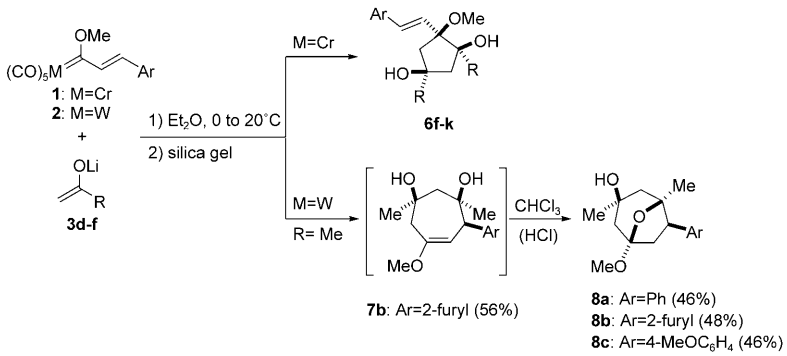
[a] Enolates **3** were generated by reaction of the corresponding silyl enol ether **5** with butyllithium at 0°C. [b] Yield after product isolation and based on starting carbene complexes **1** or **2**.

investigate the behavior of alkyl methyl ketone lithium enolates towards carbene complexes **1** and **2**. The reaction of two equivalents of lithium enolates **3d–f** with chromium carbene complexes **1** in diethyl ether at 20°C gave rise, after hydrolysis, to 1,3-cyclopentanediol derivatives **6f–k** in moderate yields and as a mixture of diastereoisomers (Scheme 2 and Table 2).

A different reaction outcome was observed when tungsten carbene complexes **2** were used. Treatment of carbene complexes **2** with the lithium enolate of acetone, **3d**, under the same reaction conditions as those described above led, after hydrolysis, to cycloheptenediol derivatives **7**, which could be isolated in the case of **7b** in moderate yield. In general, cycloheptenediol derivatives **7** were characterized as the 8-oxabicyclo[3.2.1]octane derivatives **8**, generated by simple dissolution of the former in chloroform containing hydrogen chloride. Both products **7b** and **8** were obtained as unique diastereoisomers, as deduced from the 2D NMR spectroscopy analysis (Scheme 2). The global reaction can be considered as formal [3+2+2] cyclization of three components. Unfortunately, attempts to extend this transformation to other alkyl methyl ketone lithium enolates failed and the corresponding cycloheptenediol derivatives were not formed.

Alkynyl methyl ketones—Formal [2+2+1] and [3+2] cyclizations: Considering the influence of the nature of the R group of the lithium enolate and the metal of the carbene complex, we decided to study further the behavior of lithium enolates derived from alkynyl methyl ketones in this chemistry. Treatment of carbene complexes **1** or **2** with lithium enolates **3g** or **3h** under the same reaction conditions as those described before led to separable mixtures of the corresponding 1,3-cyclopentanediol derivatives **6l–p** and 3-cyclopentenol derivatives **9a–e**, both as single diastereoisomers (Scheme 3 and Table 3). The former compounds correspond, as before, to a formal [2+2+1] cyclization of three components and the latter products indicate a formal [3+2] cyclization of two components.

It is difficult to explain the influence of the R^1 substituent of the alkynyl lithium enolate and the metal of the carbene complex in the product distribution. Remarkably, compounds **6** are obtained as *Z*/*E* mixtures in different ratios in almost all the cases (Table 3, entries 6–8 and 10).



Scheme 2. Reaction of carbene complexes **1** or **2** with alkyl methyl ketone lithium enolates **3d–f** to give 1,3-cyclopentanediol derivatives **6f–k**, 5-cycloheptene-1,3-diols **7**, and 8-oxabicyclo[3.2.1]octanes **8**.

Table 2. Synthesis of 1,3-cyclopentanediol derivatives **6f–k** from chromium carbene complexes **1** and alkyl methyl ketone lithium enolates **3d–f**.

Carbene complex	Ar	Enolate[a]	R	Product	Yield [%][b]	*de* [%]
1a	Ph	**3d**	Me	**6f**	36	90
1b	2-furyl	**3d**	Me	**6g**	44	80
1b	2-furyl	**3e**	$Ph(CH_2)_2$	**6h**	40	67
1c	4-$MeOC_6H_4$	**3d**	Me	**6i**	42	50
1c	4-$MeOC_6H_4$	**3e**	$Ph(CH_2)_2$	**6j**	38	95
1c	4-$MeOC_6H_4$	**3f**	*i*Bu	**6k**	41	90

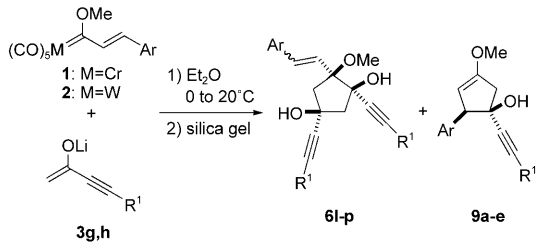
[a] Enolates **3** were generated by reaction of the corresponding silyl enol ether **5** with butyllithium at 20°C. [b] Yield after product isolation and based on starting carbene complexes **1**.

Alkenyl methyl ketones—Formal [4+3] cyclizations:[23] Finally, we have applied the reaction of β-substituted alkenyl carbene complexes **1** and **2** to alkenyl methyl ketone lithium enolates. When the reaction was performed with enolates **3i–l**, 2-cycloheptenone derivatives **10** were obtained in moderate yields and as single diastereoisomers (Scheme 4 and

Table 3. Synthesis of 1,3-cyclopentanediol derivatives **6l–p** and 3-cyclopentenol derivatives **9a–e** from carbene complexes **1** and **2** and alkynyl methyl ketone lithium enolates **3g** and **3h**.

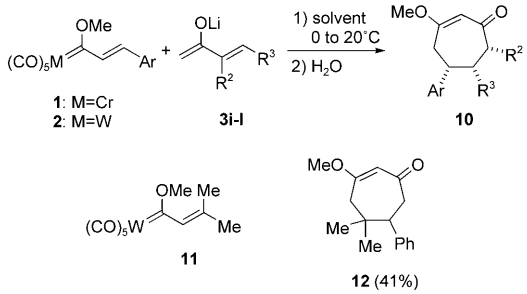
Entry	Carbene complex	Ar	Enolate[a]	R^1	Product **6** (yield [%])[b]	Product **9** (yield [%])[b]
1	**1a**	Ph	**3g**	Bu	**6l** (14)	**9a** (52)
2	**2a**	Ph	**3g**	Bu	**6l** (9)	**9a** (61)
3	**1a**	Ph	**3h**	TMS	–	**9b**[c] (80)
4	**2a**	Ph	**3h**	TMS	**6m** (11)	**9b** (59)
5	**1b**	2-furyl	**3h**	TMS	–	**9c**[d] (69)
6	**2b**	2-furyl	**3h**	TMS	**6n**[e] (54)	**9c** (19)
7	**1c**	4-$MeOC_6H_4$	**3g**	Bu	**6o**[f] (19)	**9d** (52)
8	**2c**	4-$MeOC_6H_4$	**3g**	Bu	**6o**[f] (63)	**9d** (20)
9	**1c**	4-$MeOC_6H_4$	**3h**	TMS	–	**9e** (68)
10	**2c**	4-$MeOC_6H_4$	**3h**	TMS	**6p**[g] (20)	**9e** (42)

[a] Enolates **3** were generated by reaction of the corresponding silyl enol ether **5** with butyllithium at 0 °C. [b] Yield after product isolation and based on starting carbene complexes **1** or **2**. [c] Obtained as a separable 88:12 mixture of diastereoisomers. [d] Obtained as a separable 94:6 mixture of diastereoisomers. [e] Obtained as a nonseparable 1.3:1 mixture of *Z*/*E* diastereoisomers. [f] Obtained as a nonseparable 1:1.4 mixture of *Z*/*E* diastereoisomers. [g] Obtained as a nonseparable 1:2 mixture of *Z*/*E* diastereoisomers.



Scheme 3. Reaction of carbene complexes **1** or **2** with alkynyl methyl ketone lithium enolates **3g**,**3h** to give 1,3-cyclopentanediol derivatives **6l–p** and 3-cyclopentenols **9a–e**.

and diethyl ether was used when the enolate was formed by treatment of the corresponding silyl enol ether with butyllithium. The solvent does not seem to have an influence on the formation of the final product **10**, either in the diastereoselectivity or the chemical yield, when the Ar, R^2, or R^3 groups do not have heteroatoms (Table 4, entries 4, 5). However, when either the carbene complex or the lithium enolate contain a heteroatom at certain positions in their structure, an interesting reaction variation was noticed as a function of the reaction conditions. For example, in the reaction of tungsten carbene complex **2a** with lithium enolate **3l**, containing a dihydropyran moiety in its structure, cycloheptenone **10d** was not formed when the reaction was performed in THF, while in diethyl ether product **10d** was obtained in 52% yield (Table 4, entries 6, 7). In a similar way, cycloheptenone **10e**



Scheme 4. Synthesis of 2-cycloheptenone derivatives **10** and **12** by reaction of carbene complexes **1**, **2**, or **11** with alkenyl methyl ketone lithium enolates **3i–l**.

Table 4). The relative *cis* configuration of product **10** was determined on the basis of the coupling constant ($J_{H5,H6}$ = 5.5 Hz) and NOESY experiments. In a similar way, the β,β-disubstituted carbene complex **11** reacted with the lithium enolate **3i** to give, after hydrolysis, the 2-cycloheptenone derivative **12** in 41% yield (Scheme 4). The formation of compounds **10** and **11** can be considered as a formal [4+3] cyclization reaction, in which two carbon–carbon bonds and two or three stereogenic centers have been generated.

From the results summarized in Table 4, the following conclusions can be extracted. The reaction outcome does not depend on the nature of the metal of the carbene complex and the yields of the reactions are comparable (Table 4 entries 1, 2). The solvent used depended on the method used for the formation of the enolate. Thus, THF was used when the lithium enolate was generated by deprotonation of the corresponding ketone **4** with LDA

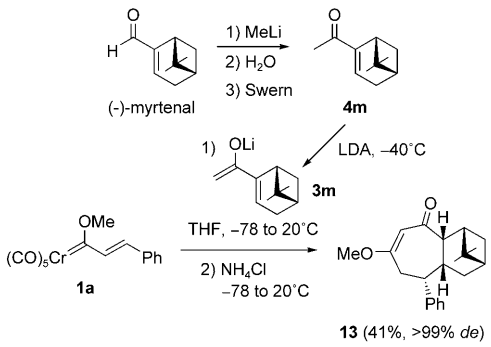
Table 4. Synthesis of 2-cycloheptenone derivatives **10** from carbene complexes **1** and **2** and alkenyl methyl ketone lithium enolates **3i–l**.

Entry	Carbene complex	M	Ar	Enolate[a]	R^2	R^3	Solvent	Product	Yield [%][b]
1	**1a**	Cr	Ph	**3i**	H	H	THF	**10a**	46
2	**2a**	W	Ph	**3i**	H	H	THF	**10a**	48
3	**1a**	Cr	Ph	**3j**	H	Me	THF	**10b**	44
4	**1a**	Cr	Ph	**3k**	H	Ph	THF	**10c**	51
5	**1a**	Cr	Ph	**3k**	H	Ph	Et_2O	**10c**	53
6	**2a**	W	Ph	**3l**	$O(CH_2)_3$		THF	–[c]	
7	**2a**	W	Ph	**3l**	$O(CH_2)_3$		Et_2O	**10d**	53
8	**1b**	Cr	2-furyl	**3k**	H	Ph	THF	–[c]	
9	**2b**	W	2-furyl	**3k**	H	Ph	THF	**10e**	6
10	**2b**	W	2-furyl	**3k**	H	Ph	Et_2O	**10e**	46
11	**1c**	Cr	4-$MeOC_6H_4$	**3i**	H	H	THF	**10f**	52
12	**1c**	Cr	4-$MeOC_6H_4$	**3k**	H	Ph	THF	**10g**	43

[a] Enolates **3** were generated by deprotonation of the corresponding ketone **4** with LDA when the reaction was carried out in THF and by treatment of the corresponding silyl enol ether **5** with butyllithium at 0 °C when the reaction was performed in diethyl ether. [b] Yield after product isolation and based on starting carbene complexes **1** and **2**. [c] No defined product was observed.

was not formed when the chromium carbene complex **1b** (Ar = 2-furyl) reacted with the lithium enolate **3k**, and only a 6% yield of **10e** was obtained from the tungsten carbene **2b** when the reaction was performed in THF (Table 4, entries 8, 9). However, the seven-membered ring **10e** was obtained in 46% yield when the reaction was carried out in diethyl ether (Table 4, entry 10). It seems that both the solvent and/or the presence of diisopropylamine in the reaction medium could be responsible for the different result of the reaction. In this context, we carried out an experiment in the absence of diisopropylamine by treating carbene complex **1b** with lithium enolate **3k**, generated by the reaction of silyl enol ether **5k** and butyllithium, in THF under the same reaction conditions, but unfortunately an intractable mixture of compounds was obtained and the 2-cycloheptenone derivative **10e** was not observed.

Given the complete diastereoselectivity for **10** in all the cases examined, we carried out a reaction with the homochiral enolate derived from ketone **4m** (Scheme 5), which is easily obtained by treatment of (−)-myrtenal with methyllithium and further Swern oxidation of the resulting mixture of diastereoisomeric alcohols. The reaction of the enolate **3m** with chromium carbene complex **1a** at −78 to 20 °C followed by hydrolysis at −78 °C with a solution of ammonium chloride afforded the fused tricyclic compound **13** in 41% yield with diastereoselectivity higher than 99%. The structure and absolute configuration of the new stereogenic centers were unequivocally determined by 2D NMR spectroscopy analysis.

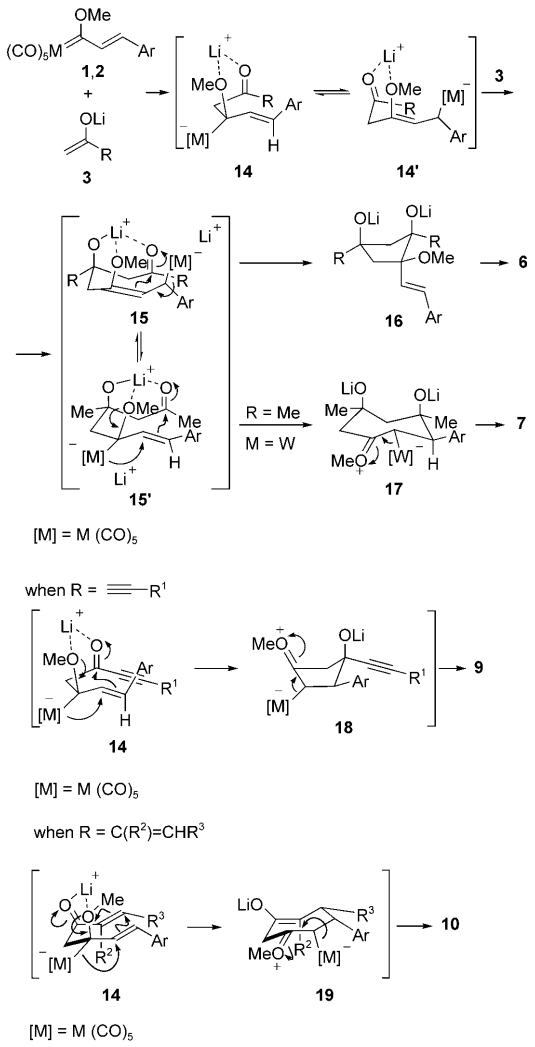


Scheme 5. Synthesis of tricyclic compound **13** from homochiral lithium enolate **3m**, derived from (−)-myrtenal, and chromium carbene complex **1a**.

Mechanistic proposals: In Scheme 6, tentative mechanisms to rationalize the different results obtained in the reaction of β-substituted alkenylcarbene complexes **1** or **2** with methyl ketone lithium enolates **3** are presented. We assume that a 1,2-addition of the lithium enolates **3** to the carbene complexes **1** or **2** occurs first to form intermediates **14**, which could be in equilibrium with **14′** derived from an 1,3-migration[24] of the pentacarbonylmetal. The evolution of these intermediates depends on the nature of the R group of the lithium enolate, on the metal of the carbene complex, and on the solvent. Thus, when R is an alkyl, aryl, or alkynyl group and the reaction is carried out in diethyl ether, the lithium atom could coordinate to the oxygen atoms of the carbonyl and methoxy groups, thereby increasing the rigidity of intermediates **14** or **14′** and the electrophilic character of the carbonyl group. In these circumstances, addition of a second molecule of lithium enolate **3** to the carbonyl group of intermediates **14** or **14′**, giving the new intermediates **15** or **15′**, could be preferred over an intramolecular ring closing. A nucleophilic attack of the γ-carbon atom of the allylpentacarbonylmetallate on the carbonyl group in intermediates **15** would lead to the cyclic systems **16**, which after hydrolysis, would give rise to the 1,3-cyclopentanediol derivatives **6**. Alternatively, compounds **6** could be formed by an attack of the α-carbon atom of the allyl metallate moiety of intermediates **15′** on the carbonyl group. However, the formation of compounds **6** as *Z*/*E* isomers in some cases (see Table 3) supports the former proposal rather than the latter. On the other hand, in cases where R = Me and M = W, the evolution would be from intermediates **15′**, which would undergo a cyclization reaction induced by a 1,2-migration[25] of the pentacarbonyltungsten fragment to afford the seven-membered intermediate **17**. Further elimination of the metal moiety would furnish, after hydrolysis and metal decoordination, the cycloheptenediol derivatives **7**. The reason why the last reaction only works with R = Me and evolves in a different manner to the other cases is not clear. Possibly, the difference could be attributed to steric effects hindering the addition of a second molecule of alkyl enolate to tungsten intermediates **14** or **14′**. On the other hand, the formation of seven-membered rings in the reaction of the lithium enolate of acetone and tungsten complexes could be due to the greater steric volume of the tungsten fragment favoring the formation of intermediates **15′** over **15**. Moreover, the high diastereoselectivity found in the formation of compounds **6** and **7** could be attributed to transition states with the same geometric disposition as intermediates **15** and **15′**, respectively, in which the coordination of the three oxygen atoms to the lithium atom would favor these dispositions.

Alternatively, and only when R is an alkynyl group (R = ≡–R^1) due to its shorter size compared with the alkyl and aryl groups, intermediates **14** could undergo a cyclization reaction promoted by an 1,2-migration of the pentacarbonylmetal fragment to give the five-membered ring intermediates **18**, which after elimination of the metal moiety, hydrolysis, and metal decoordination would afford the 3-cyclopentenol derivatives **9** (Scheme 6). The formation of a unique diastereoisomer of **9** is a consequence of the more favorable *trans* disposition of the aryl and alkynyl groups in the lithium-coordinated intermediate **14**, which would avoid the steric interactions between these groups.

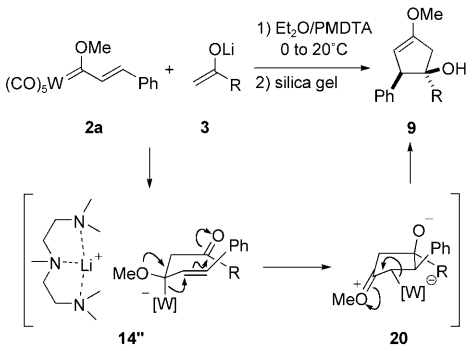
Finally, when the R substituent is an alkenyl group (R = $C(R^2)$=CHR^3), the evolution is also different and, in this case, intermediates **14** undergo a cyclization induced by a 1,2-migration of the pentacarbonylmetal group, in which a Michael addition is involved, thereby furnishing the seven-membered intermediates **19**. Subsequent elimination of the



Scheme 6. Mechanistic proposal for the formation of compounds **6**, **7**, **9**, and **10**.

metal fragment followed by hydrolysis, metal decoordination, and double bond isomerization, gives rise to 2-cycloheptenone derivatives **10** (Scheme 6). The generation of the *cis* diastereoisomers can be explained by invoking a chairlike transition state, derived from **14** and presumably favored by the internal coordination of the oxygen atoms to the lithium atom. The importance of this coordination in the outcome of the reaction is manifested by the fact that the presence of other heteroatoms, either in the carbene complex or lithium enolate, influences the result of the reaction and the fact the seven-membered rings **10** are formed in diethyl ether but not, or in very low yields, in THF. The coordination of the lithium atom to the other heteroatoms or to THF could disfavor the chairlike conformation of intermediate **14** and, therefore, the ring closing. Furthermore, the presence of diisopropylamine in the reaction medium could lead to decomposition of intermediate **14**.

As stated in all the mechanistic proposals presented above, the coordination of the oxygen atoms to the lithium atom has been proposed as a key feature for the diastereoselective formation of the final products. In order to verify the validity of this statement, we carried out a set of reactions with carbene complex **2a** and lithium enolates **3**, generated from the reaction of the corresponding silyl enol ethers **5** and butyllithium, in diethyl ether at temperatures of 0–20 °C and in the presence of *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDTA). In these cases, the formal [3+2] cyclization products **9** were formed in moderate yields and as single diastereoisomers, independently of the nature of the R substituent of the lithium enolate **3** used (Scheme 7 and Table 5).



Scheme 7. Reaction of carbene complex **2a** with lithium enolates **3** in the presence of PMDTA to give 3-cyclopentenol derivatives **9** and a proposal for the mechanism of product formation.

Table 5. Synthesis of 3-cyclopentenol derivatives **9** from carbene complex **2a** and lithium enolates **3** in the presence of PMDTA.

Enolate[a]	R	Product	Yield [%][b]
3a	Ph	**9f**	53
3d	Me	**9g**[c]	64
3f	*i*Bu	**9h**	51
3h	C≡CTMS	**9b**[d]	61
3k	(*E*)-PhCH=CH	**9i**	20

[a] Enolates **3** were generated by reaction of the corresponding silyl enol ether **5** with butyllithium at 0 °C. [b] Yield after product isolation and based on starting carbene complex **2a**. [c] A small amount of compound **6f** was also obtained (22 %, >95 % *de*). [d] Obtained as a separable 95:5 mixture of diastereoisomers.

In order to prove the influence of the metal in the reaction outcome, a reaction was carried out with the chromium carbene complex **1a** and the lithium enolate **3d** under the same reaction conditions and compound **9g** was obtained in 55 % yield and also as a single diastereoisomer.

The formation of **9** when PMDTA was used can be rationalized in terms of coordination of the lithium atom to the triamine; this coordination lowers the rigidity of the transition structure derived from **14**″, thereby favoring the approach of the allylic carbon atom of the σ-allyltungsten moiety to the carbonyl atom and giving the cyclization intermediates **20**. The elimination of the metal fragment and the final hydrolysis would furnish the 3-cyclopentenol derivatives **9**. The diastereoselectivity found can also be under-

stood by assuming that the phenyl and the R groups would adopt a *trans* disposition in the transition structure to avoid steric interactions.

Conclusion

We have described the reaction of β-substituted alkenylcarbene complexes and methyl ketone lithium enolates. The reaction outcome is highly dependent on the structure of the lithium enolate, on the metal of the carbene complex, and on the reaction medium. Thus, in a noncoordinating medium, aryl and alkyl methyl ketone lithium enolates react with β-substituted alkenyl chromium and tungsten carbene complexes to give 1,3-cyclopentanediol derivatives derived from a formal [2+2+1] carbocyclization reaction. Only for the lithium enolate of acetone with tungsten complexes was a formal [3+2+2] carbocyclization reaction observed. Both carbocyclization reactions involve two equivalents of alkyl or aryl lithium enolates and one equivalent of carbene complex. In the case of alkynyl lithium enolates, competitive formation of five-membered rings by formal [2+2+1] and [3+2] carbocyclization reactions occurs. Conversely, alkenyl methyl ketone lithium enolates react with alkenylcarbene complexes under the same reaction conditions to form seven-membered carbocycles by formal [4+3] carbocyclization reactions. This last cyclization pattern has been successfully applied in the diastereoselective transformation of a natural product, (−)-myrtenal. On the other hand, when the reaction is performed in a coordinating medium, in the presence of PMDTA, the [3+2] carbocyclization pattern was observed, independently of the nature of the methyl ketone lithium enolate used. Mechanistic proposals for all cyclization patterns, taking into account all the factors above mentioned, have also been discussed herein. Finally, it is important to point out the simplicity of the starting materials, methyl ketones and Fischer-type carbene complexes. Investigations to clarify the mechanism of the reactions, the application of this method to organic synthesis, and the search for a version leading to enantiopure products are underway in our laboratories.

Experimental Section

General: All reactions involving organometallic species were carried out under an atmosphere of dry N_2 by using oven-dried glassware and syringes. THF and Et_2O were distilled from sodium/benzophenone under N_2 immediately prior to use. TLC was performed on aluminum-backed plates coated with silica gel 60 with F_{254} indicator (Scharlau). Flash column chromatography was carried out on commercial and deactivated silica gel 60 (230–240 mesh). (Deactivated silica gel was prepared as follows: Silica gel (125 g) was stirred with a 4% aqueous solution of K_2HPO_4 (500 mL) for 3 h. After filtration, the resulting solid was oven-dried at 100 °C for 2 d.) ^{1}H NMR (200, 300 MHz) and ^{13}C NMR (50.5, 75.5 MHz) spectra were measured at room temperature on Bruker AC-200, AV-300, and DPX-300 instruments, with tetramethylsilane (δ = 0.0 ppm, ^{1}H NMR) and $CDCl_3$ (δ = 77.0 ppm, ^{13}C NMR) or C_6D_6 (δ = 127.8 ppm, ^{13}C NMR) as internal standards. Carbon multiplicities were assigned by DEPT techniques. Two-dimensional NMR experiments (COSY, HMQC, HMBC, and NOESY) were recorded on a Bruker AMX-400 (400 MHz) instrument. High-resolution mass spectra were determined on a Finnigang MAT95 spectrometer. Elemental analyses were carried out on a Perkin–Elmer 2400 microanalyzer.

Materials: Butyllithium (1.6 N in hexanes) was purchased from Acros Organics; methyl ketones **4**, silyl enol ethers **5a** and **5d**, diisopropylamine, and PMDTA were purchased from Aldrich and used without further purification, except PMDTA, which was dried prior to use. The other silyl enol ethers **5** were prepared in a similar way to the literature procedures.[26] (Alkenyl)(methoxy)carbene complexes **1**, **2**,[27] and **11**[28] were prepared according to literature procedures. Ketones **4g** and **4l** were prepared by addition of the corresponding organocuprate to acetyl bromide.[29]

General procedure for the preparation of compounds 6 and 7: In a flame-dried round-bottomed flask, enolates **3** were prepared by treatment of silyl enol ethers **5** (1 mmol) with BuLi (0.63 mL, 1.6 N in hexanes, 1 mmol) in diethyl ether (10 mL), at room temperature for 30 min for silyl enol ethers **5d** and **5f**, and at 0 °C for 30 min for the rest of the silyl enol ethers **5**. Carbene complexes **1** or **2** (0.4 mmol) were then added at 0 °C and the mixture was warmed to room temperature and stirred for 30 min. The reaction mixture was quenched with a small amount of silica gel, solvents were removed, and the resulting residue was purified by flash column chromatography on silica gel (hexanes/ethyl acetate 10:1→3:1) to give compounds **6** and **7**.

(1*R,3*R**,4*S**)-4-Methoxy-1,3-diphenyl-4-[(*E*)-styryl]-1,3-cyclopentanediol (6a)**: Silyl enol ether **5a** (192 mg, 1 mmol), BuLi (0.63 mL, 1.6 N in hexanes, 1 mmol), and carbene complex **1a** (135 mg, 0.4 mmol) or **2a** (188 mg, 0.4 mmol) afforded **6a** (79 mg, 51% from **1a**; 76 mg, 49% from **2a**) as a colorless oil. ^{1}H NMR (300 MHz, C_6D_6): δ = 7.96–7.18 (m, 15H; ArH), 6.43 (d, J = 16.5 Hz, 1H; =C*H*Ph), 5.19 (d, J = 16.5 Hz, 1H; =CHC), 5.39 (s, 1H; OH), 4.70 (t, J = 1.7 Hz, 1H; OH), 3.07 (dd, J = 14.3, 1.7 Hz, 1H; PhCC*H*HCPh), 2.55 (dd, J = 14.3, 1.7 Hz, 1H; PhCCH*H*CPh), 2.98 (d, J = 15.2 Hz, 1H; C*H*HCOMe), 2.72 (d, J = 15.2 Hz, 1H; CH*H*COMe), 2.91 ppm (s, 3H; OMe); ^{13}C NMR (75.5 MHz, C_6D_6): δ = 146.9, 141.7, 136.2, 133.0, 130.0, 128.7, 128.3, 128.1, 127.8, 127.3, 127.0, 126.8, 126.6, 125.7, 89.3, 86.5, 78.9, 51.9, 49.6, 48.7 ppm; HRMS (70 EV, EI): m/z: calcd for $C_{25}H_{21}O$: 337.1592; found: 337.1579 $[M-H_2O-MeO]^+$; elemental analysis calcd (%) for $C_{26}H_{26}O_3$: C 80.80, H 6.78; found: C 80.98, H 6.59.

(1*R,3*R**,4*S**)-4-Methoxy-1,3-bis(4-methoxyphenyl)-4-[(*E*)-styryl]-1,3-cyclopentanediol (6b)**: Silyl enol ether **5b** (222 mg, 1 mmol), BuLi (0.63 mL, 1.6 N in hexanes, 1 mmol), and carbene complex **1a** (135 mg, 0.4 mmol) or **2a** (188 mg, 0.4 mmol) afforded **6b** (98 mg, 55%, from **1a**; 77 mg, 43% from **2a**) as a colorless oil. ^{1}H NMR (300 MHz, C_6D_6): δ = 7.85, 7.49, 6.87 (3d, J = 8.8 Hz, 6H; ArH), 7.11–7.02 (m, 7H; ArH), 6.49 (d, J = 16.5 Hz, 1H; =C*H*Ph), 5.81 (d, J = 16.5 Hz, 1H; =CHC), 5.38, 4.70 (2s, 2H; 2×OH), 3.48, 3.38, 2.98 (3s, 9H; 3×OMe), 3.09 (d, J = 14.2 Hz, 1H; ArCC*H*HCAr), 2.62 (d, J = 14.2 Hz, 1H; ArCCH*H*CAr), 3.04 (d, J = 15.1 Hz, 1H; C*H*HCOMe), 2.79 ppm (d, J = 15.1 Hz, 1H; CH*H*COMe); ^{13}C NMR (75.5 MHz, C_6D_6): δ = 159.2, 159.0, 139.2, 136.3, 133.9, 133.0, 130.3, 128.7, 128.1, 128.0, 126.9, 126.6, 113.7, 113.2, 89.4, 86.3, 78.6, 54.7, 54.5, 51.9, 49.6, 49.1 ppm; HRMS (70 EV, EI): m/z: calcd for $C_{28}H_{26}O_3$: 410.1882; found: 410.1884 $[M-2H_2O]^+$.

(1*R,3*S**,4*S**)-1,3-Bis(2-furyl)-4-methoxy-4-[(*E*)-styryl]-1,3-cyclopentanediol (6c)**: Silyl enol ether **5c** (182 mg, 1 mmol), BuLi (0.63 mL, 1.6 N in hexanes, 1 mmol), and carbene complex **1a** (135 mg, 0.4 mmol) afforded **6c** (41 mg, 28%) as a colorless oil. ^{1}H NMR (300 MHz, C_6D_6): δ = 7.18–7.05 (m, 5H; ArH), 7.03, 6.97 (2d, J = 1.8 Hz, 2H; 2×=CHO), 6.63 (d, J = 16.2 Hz,1H; =C*H*Ph), 5.85 (d, J = 16.2 Hz, 1H; =CHC), 6.55, 6.03 (2d, J = 3.3 Hz, 2H; 2×C*H*CH=CHO), 6.09, 5.96 (2dd, J = 3.3, 1.8 Hz, 2H; 2×C*H*=CHO), 4.44, 4.37 (2s, 2H; 2×OH), 3.08, 3.07, 2.49, 2.46 (4d, J = 14.4 Hz, 4H; 2×CH_2), 2.86 ppm (s, 3H; OMe); ^{13}C NMR (75.5 MHz, C_6D_6): δ = 158.5, 155.0, 142.6, 141.2, 136.8, 133.1, 129.3, 128.6, 128.1, 126.7, 110.6, 110.1, 107.1, 105.4, 89.3, 83.2, 76.8, 51.9, 47.9, 46.6 ppm; HRMS (70 EV, EI): m/z: calcd for $C_{22}H_{18}O_3$: 330.1250; found: 330.1252 $[M-2H_2O]^+$.

(1*R,3*R**,4*S**)-4-[(*E*)-2-(2-Furyl)ethenyl]-4-methoxy-1,3-diphenyl-1,3-cyclopentanediol (6d)**: Silyl enol ether **5a** (192 mg, 1 mmol), BuLi (0.63 mL, 1.6 N in hexanes, 1 mmol), and carbene complex **1b** (131 mg, 0.4 mmol) or **2b** (184 mg, 0.4 mmol) afforded **6d** (76 mg, 52% from **1b**; 76 mg, 52% from **2b**) as a colorless oil. ^{1}H NMR (400 MHz, C_6D_6): δ = 7.92–7.06 (m, 10H; ArH), 6.91 (d, J = 1.9 Hz, 1H; =CHO), 6.18 (d, J = 16.4 Hz, 1H; 2-FuC*H*=), 5.84 (d, J = 16.4 Hz, 1H; =CHC), 6.02 (dd, J = 3.3, 1.9 Hz, 1H; C*H*=CHO), 5.90 (d, J = 3.3 Hz, 1H; C*H*CH=CHO), 5.39, 4.65 (2s, 2H; 2×OH), 3.03 (dd, J = 14.3, 1.9 Hz, 1H; PhCC*HH*CPh), 2.55 (dd, J = 14.3, 1.9 Hz, 1H; CPhCH*HC*Ph), 2.88 (s, 3H; OMe), 2.84 (d, J = 15.2 Hz, 1H; C*H*HCOMe), 2.70 ppm (dd, J = 15.2, 1.2 Hz, 1H; CH*H*COMe); ^{13}C NMR (100.6 MHz, C_6D_6): δ = 152.0, 147.0, 142.4, 141.6, 128.3, 127.8, 127.7, 127.3, 126.9, 126.8, 125.6, 121.5, 111.3, 108.7, 89.2, 86.6, 78.8, 51.9, 49.9, 49.1 ppm; HRMS (70 EV, EI): m/z: calcd for $C_{24}H_{20}O_2$: 340.1463; found: 340.1471 $[M-2H_2O]^+$; elemental analysis calcd (%) for $C_{24}H_{24}O_4$: C 76.57, H 6.43; found: C 76.80, H 6.19.

(1*R,3*R**,4*S**)-4-[(*E*)-2-(2-Furyl)ethenyl]-4-methoxy-1,3-bis(4-methoxyphenyl)-1,3-cyclopentanediol (6e)**: Silyl enol ether **5b** (222 mg, 1 mmol), BuLi (0.63 mL, 1.6 N in hexanes, 1 mmol), and carbene complex **1b** (131 mg, 0.4 mmol) or **2b** (184 mg, 0.4 mmol) afforded **6e** (73 mg, 42% from **1b**; 59 mg, 34% from **2b**) as a colorless oil. ^{1}H NMR (200 MHz, C_6D_6): δ = 7.74, 7.32, 6.94, 6.76 (4d, J = 8.9 Hz, 8H; ArH), 6.79 (d, J = 1.8 Hz, 1H; =CHO), 6.18 (d, J = 16.4 Hz, 1H; 2-FuCH=), 5.88 (d, J = 16.4 Hz, 1H; =CHC), 5.91 (dd, J = 3.3, 1.8 Hz, 1H; C*H*=CHO), 5.82 (d, J = 3.3 Hz, 1H; C*H*CH=CHO), 5.29 (s, 1H; OH), 4.53 (br s, 1H; OH), 3.38, 3.26 (2s, 6H; 2×OMe), 2.98 (d, J = 14.1 Hz, 1H; ArCC*H*HCAr), 2.53 (d, J = 14.1 Hz, 1H; ArCCH*H*CAr), 2.83 (s, 3H; OMe), 2.82 (d, J = 15.1 Hz, 1H; C*H*HCOMe), 2.68 ppm (d, J = 15.1 Hz, 1H; CH*H*COMe); ^{13}C NMR (75.5 MHz, C_6D_6): δ = 159.1, 158.9, 152.1, 142.3, 139.3, 133.8, 128.2, 128.1, 126.8, 121.4, 113.7, 113.2, 111.3, 108.7, 89.4, 86.3, 78.5, 54.6, 54.4, 51.9, 49.8, 49.5 ppm; HRMS (70 EV, EI): m/z: calcd for $C_{24}H_{24}O_4$: 400.1675; found: 400.1692 $[M-2H_2O]^+$.

(1*R,3*S**,4*S**)-4-Methoxy-1,3-dimethyl-4-[(*E*)-styryl]-1,3-cyclopentanediol (6f)**: Silyl enol ether **5d** (144 mg, 1 mmol), BuLi (0.63 mL, 1.6 N in hexanes, 1 mmol), and carbene complex **1a** (135 mg, 0.4 mmol) afforded **6f** (38 mg, 36%, 90% *de*) as a colorless oil. ^{1}H NMR (300 MHz, C_6D_6, major diasteromer): δ = 7.22–7.08 (m, 5H; ArH), 6.36 (d, J = 16.4 Hz, 1H; =C*H*Ph), 5.98 (d, J = 16.4 Hz, 1H; =CHC), 3.61 (br s, 1H; CO*H*-COMe), 3.34 (s, 1H; CH_2CO*H*CH_2), 2.89 (s, 3H; OMe), 2.19 (d, J = 14.8 Hz, 1H; C*H*HCOMe), 1.98 (d, J = 14.8 Hz, 1H; CH*H*COMe), 2.05 (d, J = 14.2 Hz, 1H; MeCC*H*HCMe), 1.69 (2d, J = 14.2 Hz, 2H; MeCCH*H*CMe), 1.36 (s, 3H; CH_2C*Me*CH_2), 1.10 ppm (s, 3H; C*Me*-COMe); ^{13}C NMR (75.5 MHz, C_6D_6, major diasteromer): δ = 136.5, 132.4, 129.5, 128.7, 128.1, 126.6, 88.9, 82.7, 75.1, 53.4, 51.4, 46.3, 28.6, 22.9 ppm; HRMS (70 EV, EI): m/z: calcd for $C_{16}H_{22}O_3$: 262.1569; found: 262.1565 $[M]^+$.

(1*S,3*R**,4*S**)-4-[2-(2-Furyl)ethenyl]-4-methoxy-1,3-dimethyl-1,3-cyclopentanediol (6g)**: Silyl enol ether **5d** (144 mg, 1 mmol), BuLi (0.63 mL, 1.6 N in hexanes, 1 mmol), and carbene complex **1b** (131 mg, 0.4 mmol) afforded **6g** (44 mg, 44%, 80% *de*) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, major diastereomer): δ = 7.38 (d, J = 2.0 Hz, 1H; = CHO), 6.41 (dd, J = 3.1, 2.0 Hz, 1H; C*H*=CHO), 6.34 (d, J = 16.3 Hz, 1H; 2-FuC*H*=), 6.03 (d, J = 16.3 Hz, 1H; =CHC), 6.29 (d, J = 3.1 Hz, 1H; C*H*CH=CHO), 3.64, 3.45 (2br s, 2H; 2×OH), 3.22 (s, 3H; OMe), 2.33 (d, J = 14.8 Hz, 1H; C*H*HCOMe), 2.19 (d, J = 14.8 Hz, 1H; CH*H*COMe), 2.04 (d, J = 14.5 Hz, 1H; MeCC*H*HCMe), 1.88 (d, J = 14.5 Hz, 1H; MeCCH*H*CMe), 1.34, 1.13 ppm (2s, 6H; 2×Me); ^{13}C NMR (75.5 MHz, $CDCl_3$, major diastereomer): δ = 151.9, 142.2, 127.4, 120.7, 111.4, 108.5, 88.6, 82.9, 75.5, 53.0, 52.1, 46.4, 28.3, 22.9 ppm.

(1*S,3*R**,4*S**)-4-[2-(2-Furyl)ethenyl]-4-methoxy-1,3-diphenethyl-1,3-cyclopentanediol (6h)**: Silyl enol ether **5e** (220 mg, 1 mmol), BuLi (0.63 mL, 1.6 N in hexanes, 1 mmol), and carbene complex **1b** (131 mg, 0.4 mmol) afforded **6h** (69 mg, 40%, 67% *de*) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$, major diastereomer): δ = 7.42–7.16 (m, 11H; ArH and =CHO), 6.42 (dd, J = 3.1, 1.9 Hz, 1H; C*H*=CHO), 6.38 (d, J = 16.3 Hz, 1H; 2-FuCH=), 6.04 (d, J = 16.3 Hz, 1H; =CHC), 6.32 (d, J = 3.1 Hz, 1H; C*H*CH=CHO), 4.10, 3.58 (2br s, 2H; 2×OH), 3.31 (s, 3H; OMe), 3.04–1.66 ppm (m, 12H; CH_2CCH_2 and 2CH_2CH_2Ph); ^{13}C NMR (75.5 MHz, $CDCl_3$, major diastereomer): δ = 151.7, 142.7, 142.3, 128.3, 127.6, 125.6, 120.3, 111.4, 108.7, 88.7, 84.8, 77.8, 52.4, 47.9, 47.1, 43.9, 37.8, 30.6, 30.4 ppm; HRMS (70 EV, EI): m/z: calcd for $C_{28}H_{32}O_4$: 432.2301; found: 432.2286 $[M]^+$.

(1*S,3*R**,4*S**)-4-Methoxy-4-[2-(4-methoxyphenyl)ethenyl]-1,3-dimethyl-1,3-cyclopentanediol (6i)**: Silyl enol ether **5d** (144 mg, 1 mmol), BuLi (0.63 mL, 1.6 N in hexanes, 1 mmol), and carbene complex **1c** (147 mg, 0.4 mmol) afforded **6i** (49 mg, 42%, 50% *de*) as a colorless oil ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38 (d, J = 8.8 Hz, 2H; ArH, minor diastereomer), 7.36 (d, J = 8.8 Hz, 2H; ArH, major diastereomer), 6.89 (d, J = 8.8 Hz, 4H; ArH, both diastereomers), 6.58, 6.03 (2d, J = 16.5 Hz, 2H; CH=CH, minor diastereomer), 6.47, 5.95 (2d, J = 16.4 Hz, 2H; CH=CH, major diastereomer), 3.82 (s, 6H; 2×MeO, both diastereomers), 3.28 (s, 6H; 2×MeO both diastereomers), 3.75, 3.71 (s, 2H; 2×OH, minor diastereomer), 3.62, 3.53 (s, 2H; 2×OH, major diastereomer), 3.28 (s, 3H; MeO, major diastereomer), 3.12 (s, 3H; MeO, minor diastereomer), 2.38–1.90 (m, 8H; 4CH_2, both diastereomers), 1.40, 1.34 (2s, 6H; 2×Me, minor diastereomer), 1.39, 1.18 ppm (2s, 6H; 2×Me, major diastereomer); ^{13}C NMR (75.5 MHz, $CDCl_3$, major diastereomer): δ = 159.5, 132.0, 127.7, 127.6, 126.3, 114.0, 88.9, 82.7, 75.5, 55.2, 53.4, 51.8, 45.7, 28.2, 23.1 ppm; HRMS (70 EV, EI): m/z: calcd for $C_{17}H_{24}O_4$: 292.1675; found: 292.1674 $[M]^+$.

(1*S,3*R**,4*S**)-4-Methoxy-4-[2-(4-methoxyphenyl)ethenyl]-1,3-diphenethyl-1,3-cyclopentanediol (6j)**: Silyl enol ether **5e** (220 mg, 1 mmol), BuLi (0.63 mL, 1.6 N in hexanes, 1 mmol), and carbene complex **1c** (147 mg, 0.4 mmol) afforded **6j** (72 mg, 38%, >95% *de*) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38–7.19 (m, 12H; ArH), 6.90 (d, J = 8.8, 2H; ArH), 6.49 (d, J = 16.3 Hz, 1H; =CHAr), 5.98 (d, J = 16.3 Hz, 1H; =CHC), 4.07, 3.62 (2br s, 2H; 2×OH), 3.86, 3.31 (2s, 6H; 2OMe), 3.04–1.58 ppm (m, 12H; CH_2CCH_2, 2CH_2CH_2Ph); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 159.5, 142.7, 131.6, 128.7, 128.3, 127.7, 126.8, 125.7, 114.0, 88.9, 84.7, 77.8, 55.2, 52.4, 48.0, 46.6, 43.8, 37.9, 30.6, 30.3 ppm; HRMS (70 EV, EI): m/z: calcd for $C_{31}H_{36}O_4$: 472.2614; found: 472.2598 $[M]^+$.

(1*S,3*R**,4*S**)-1,3-Diisobutyl-4-methoxy-4-[2-(4-methoxyphenyl)ethenyl]-1,3-cyclopentanediol (6k)**: Silyl enol ether **5f** (172 mg, 1 mmol), BuLi (0.63 mL, 1.6 N in hexanes, 1 mmol), and carbene complex **1c** (147 mg, 0.4 mmol) afforded **6k** (62 mg, 41%, 90% *de*) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38 (d, J = 8.5 Hz, 2H; ArH), 6.91 (d, J = 8.5 Hz, 2H; ArH), 6.53 (d, J = 16.5 Hz, 1H; =CHAr), 5.92 (d, J = 16.5 Hz, 1H; = CHC), 4.02, 3.36 (2s, 2H; 2×OH), 3.83, 3.23 (2s, 6H; 2×OMe), 2.31–1.14 (m, 10H; CH_2CCH_2 and 2×CH_2CH), 1.07–0.88 ppm (m, 12H; 4Me); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 159.4, 131.2, 129.0, 127.6, 127.5, 114.0, 89.2, 85.3, 78.4, 55.3, 52.2, 50.3, 49.1, 47.5, 43.9, 24.8, 24.7, 24.6, 24.5, 24.3 ppm; HRMS (70 EV, EI): m/z: calcd for $C_{23}H_{36}O_4$: 376.2614; found: 376.2601 $[M]^+$.

(1*S,3*R**,4*R**)-4-(2-Furyl)-1,3-dimethyl-6-methoxy-5-cycloheptene-1,3-diol (7b)**: Silyl enol ether **4d** (144 mg, 1 mmol), BuLi (0.63 mL, 1.6 N in hexanes, 1 mmol), and carbene complex **1b** (184 mg, 0.4 mmol) afforded **7b** (56 mg, 56%) as a colorless oil. ^{1}H NMR (400 MHz, C_6D_6): δ = 7.16 (d, J = 1.0 Hz, 1H; =CHO), 6.22 (dd, J = 3.0, 1.0 Hz, 1H; C*H*=CHO), 6.19 (d, J = 3.0 Hz, 1H; C*H*CH=CHO), 4.76 (d, J = 5.2 Hz, 1H; CH=), 3.52 (d, J = 5.2 Hz, 1H; CH), 3.41, 3.25 (2s, 2H; 2×OH), 3.17 (s, 3H; OMe), 2.48 (d, J = 14.5 Hz, 1H; C*H*HCOMe), 2.34 (dt, J = 14.5, 2.0 Hz, 1H; CH*H*COMe), 1.84 (dd, J = 14.5, 2.0 Hz, 1H; COHC*H*HCOH), 1.28 (d, J = 14.5 Hz, 1H; COHCH*H*COH), 1.07 (s, 3H; CH_2C*Me*CH_2), 0.91 ppm (s, 3H; CHC*Me*); ^{13}C NMR (100.6 MHz, C_6D_6): δ = 158.4, 157.4, 140.6, 110.3, 106.1, 96.2, 73.3, 69.5, 55.0, 54.0, 46.0, 45.2, 32.7, 30.3 ppm; HRMS (70 EV, EI): m/z: calcd for $C_{14}H_{20}O_4$: 252.1362; found: 252.1359 $[M]^+$; elemental analysis calcd (%) for $C_{14}H_{20}O_4$: C 66.65, H 7.99; found: C 66.79, H 7.86.

General procedure for the preparation of compounds 8: The reaction described before to obtain compound **7** was performed. The resulting residue was filtered through a small amount of silica gel (hexanes/ethyl acetate 2:1). The solvents were removed, and the resulting mixture was dissolved in $CHCl_3$ (3 mL) and left for 24 h. The solvent was then removed, and the residue was purified by flash column chromatography on silica gel (hexanes/ethyl acetate 10:1→5:1).

(1*S,3*S**,5*S**,6*S**)-1-Methoxy-3,5-dimethyl-6-phenyl-8-oxabicyclo-[3.2.1]octan-3-ol (8a)**: Silyl enol ether **4d** (144 mg, 1 mmol), BuLi (0.63 mL, 1.6 N in hexanes, 1 mmol), and carbene complex **1a** (188 mg, 0.4 mmol) afforded **8a** (48 mg, 46 %) as a colorless oil. ^{1}H NMR (300 MHz, C_6D_6): δ = 7.33–7.14 (m, 5H; ArH), 3.46 (s, 3H; MeO), 2.78 (dd, J = 9.2, 4.3 Hz, 1H; C*H*Ph), 2.54 (br s, 1H; OH), 2.47–2.39 (m, 2H; MeOC*H*H, C*H*HCH), 2.26 (dd, J = 13.9, 9.2 Hz, 1H; CH*H*CH), 1.85 (d, J = 13.9 Hz, 1H; MeCC*H*HCMe), 1.73 (d, J = 13.7 Hz, 1H; MeOCH*H*), 1.51 (d, J = 13.9 Hz, 1H; MeCCH*H*CMe), 1.31, 0.98 ppm (2s, 6H; 2× Me); ^{13}C NMR (75.5 MHz, C_6D_6): δ = 144.5, 128.8, 128.6, 126.5, 106.0, 81.8, 69.7, 52.6, 52.1, 50.0, 47.7, 45.1, 29.9, 25.6 ppm.

(1*S,3*S**,5*S**,6*R**)-6-(2-Furyl)-1-methoxy-3,5-dimethyl-8-oxabicyclo-[3.2.1]octan-3-ol (8b)**: Silyl enol ether **4d** (144 mg, 1 mmol), BuLi (0.63 mL, 1.6 N in hexanes, 1 mmol), and carbene complex **1b** (184 mg, 0.4 mmol) afforded **8b** (48 mg, 48 %) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36 (d, J = 1.7 Hz, 1H; =CHO), 6.33 (dd, J = 3.1, 1.7 Hz, 1H; C*H*=CHO), 6.13 (d, J = 3.1 Hz, 1H; C*H*CH=CHO), 3.51 (s, 3H; MeO), 3.19 (dd, J = 9.5, 5.3 Hz, 1H; 2-FuC*H*), 2.65 (br s, 1H; OH), 2.43 (dd, J = 14.0, 5.3 Hz, 1H; C*H*HCH), 2.24 (dd, J = 14.0, 9.5 Hz, 1H; CH*H*CH), 2.21 (dd, J = 14.0 Hz, 1H; MeOC*H*H), 1.93 (d, J = 14.0 Hz, 1H; MeCC*H*HCMe), 1.94 (d, J = 14.0 Hz, 1H; MeOCH*H*), 1.82 (d, J = 14.0 Hz, 2H; MeCCH*H*CMe), 1.40, 1.03 ppm (2s, 6H; 2× Me); ^{13}C NMR (75.5 MHz, C_6D_6): δ = 156.4, 141.4, 110.0, 106.5, 105.5, 81.3, 70.0, 51.8, 50.0, 48.7, 45.5, 39.0, 29.8, 24.4 ppm; HRMS (70 EV, EI): m/z: calcd for $C_{14}H_{20}O_4$: 252.1362; found: 252.1351 $[M]^+$.

(1*S,3*S**,5*S**,6*S**)-1-Methoxy-6-(4-methoxyphenyl)-3,5-dimethyl-8-oxabicyclo[3.2.1]octan-3-ol (8c)**: Silyl enol ether **4d** (144 mg, 1 mmol), BuLi (0.63 mL, 1.6 N in hexanes, 1 mmol), and carbene complex **1c** (200 mg, 0.4 mmol) afforded **8c** (54 mg, 46 %) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.17, 6.83 (2d, J = 8.8 Hz, 4H; ArH), 3.80, 3.51 (2s, 6H; 2× MeO), 2.97 (dd, J = 9.1, 4.1 Hz, 1H; CH), 2.74 (br s, 1H; OH), 2.48 (dd, J = 13.9, 9.1 Hz, 1H; C*H*HCH), 2.32 (d, J = 13.9 Hz, 1H; O_2CC*H*HC), 2.28 (dd, J = 13.9, 4.1 Hz, 1H; CH*H*CH), 1.93 (d, J = 14.0 Hz, 1H; CMeC*H*HCMe), 1.89 (d, J = 13.9 Hz, 1H; O_2CCH*H*C), 1.79 (d, J = 14.0 Hz, 1H; CMeCH*H*CMe), 1.39, 0.92 ppm (2s, 6H; 2× Me); ^{13}C NMR (100.6 MHz, C_6D_6): δ = 158.1, 135.9, 129.4, 113.4, 105.9, 82.0, 70.4, 55.1, 51.8, 51.7, 50.5, 47.6, 45.0, 29.5, 25.5 ppm; HRMS (70 EV, EI): m/z: calcd for $C_{17}H_{24}O_4$: 292.1675; found: 292.1673 $[M]^+$; elemental analysis calcd (%) for $C_{17}H_{24}O_4$: C 69.84, H 8.27; found: C 69.95, H 8.21.

General procedures for the preparation of compounds 6l–p and 9a–e: These compounds were prepared by using the method described before for compounds **6a–k**. The only difference was the amount of lithium enolate, as 0.8 mmol were generated from silyl enol ethers **4** (0.8 mmol) and BuLi (0.5 mL, 1.6 N in hexanes, 0.8 mmol).

(1*R,3*R**,4*S**)-1,3-Bis(1-hexynyl)-4-methoxy-4-[(*E*)-styryl]-1,3-cyclopentanediol (6l) and (1*R**,2*R**)-1-(1-hexynyl)-4-methoxy-2-phenyl-3-cyclopentenol (9a)**: Silyl enol ether **5g** (157 mg, 1 mmol), BuLi (0.63 mL, 1.6 N in hexanes, 1 mmol), and carbene complex **1a** (135 mg, 0.4 mmol) or **2a** (188 mg, 0.4 mmol) afforded **6l** (22 mg, 14 % from **1a**; 14 mg, 9 % from **2a**) and **9a** (56 mg, 52 % from **1a**; 66 mg, 61 % from **2a**) as colorless oils.

Compound 6l: ^{1}H NMR (300 MHz, C_6D_6): δ = 7.46–7.02 (m, 5H; ArH), 6.88 (d, J = 16.4 Hz, 1H; =CHPh), 6.57 (d, J = 16.4 Hz, 1H; =CHC), 3.63, 3.38 (2s, 2H; 2× OH), 2.98 (d, J = 14.6 Hz, 1H; HOCC*H*HCOH), 2.77 (d, J = 14.6 Hz, 1H; HOCC*H*HCOMe), 2.70 (d, J = 14.6 Hz, 1H; HOCCH*H*COH), 2.48 (d, J = 14.6 Hz, 1H; HOCCH*H*COMe), 2.03, 1.93 (2t, J = 6.9 Hz, 4H; 2× C*H*$_2$Pr), 1.31–1.19 (m, 8H; 2× C*H*$_2$C*H*$_2$Me), 0.72, 0.66 ppm (2t, J = 7.4 Hz, 6H; 2× Me); ^{13}C NMR (75.5 MHz, C_6D_6): δ = 136.8, 129.9, 128.7, 128.1, 126.8, 88.6, 86.5, 84.5, 83.2, 80.0, 79.2, 71.2, 54.4, 52.0, 48.9, 30.9, 30.7, 22.0, 21.9, 18.4, 13.5, 13.4 ppm; HRMS (70 EV, EI): m/z: calcd for $C_{26}H_{34}O_3$: 394.2508; found: 394.2501 $[M]^+$.

Compound 9a: ^{1}H NMR (200 MHz, C_6D_6): δ = 7.58–7.17 (m, 5H; ArH), 4.47 (s, 1H; C*H*Ph), 4.40 (s, 1H; =CH), 3.31 (s, 3H; OMe), 3.27 (d, J = 17.7 Hz, 1H; C*H*HCOH), 3.11 (d, J = 17.7 Hz, 1H; CH*H*COH), 2.12 (t, J = 6.5 Hz, 2H; C*H*$_2$Pr), 1.49 (s, 1H; OH), 1.44–1.28 (m, 4H; C*H*$_2$C*H*$_2$Me), 0.89 ppm (t, J = 6.9 Hz, 3H; Me); ^{13}C NMR (75.5 MHz, C_6D_6): δ = 159.7, 138.7, 129.7, 128.3, 127.5, 94.0, 84.2, 83.9, 72.5, 60.8, 56.0, 48.3, 30.8, 22.0, 18.4, 13.5 ppm; HRMS (70 EV, EI): m/z: calcd for $C_{18}H_{22}O_2$: 270.1620; found: 270.1610 $[M]^+$; elemental analysis calcd (%) for $C_{18}H_{22}O_2$: C 79.96, H 8.20; found: C 80.10, H 8.01.

(1*R,3*R**,4*S**)-4-Methoxy-1,3-bis(trimethylsilylethynyl)-4-[(*E*)-styryl]-1,3-cyclopentanediol (6m) and (1*R**,2*R**)-4-methoxy-1-(trimethylsilylethynyl)-2-phenyl-3-cyclopentenol (9b)**: Silyl enol ether **5h** (170 mg, 1 mmol), BuLi (0.63 mL, 1.6 N in hexanes, 1 mmol), and carbene complex **1a** (135 mg, 0.4 mmol) or **2a** (188 mg, 0.4 mmol) afforded **6m** (19 mg, 11 % from **2a**) and **9b** (92 mg, 80 %, 76 % *de* from **1a**; 68 mg, 59 % from **2a**) as colorless oils.

Compound 6m: ^{1}H NMR (200 MHz, C_6D_6): δ = 7.59–7.12 (m, 5H; ArH), 6.97 (d, J = 16.0 Hz, 1H; =CHPh), 6.66 (d, J = 16.0 Hz, 1H; =CHC), 3.69, 3.28 (2s, 2H; 2× OH), 3.22–2.53 (m, 4H; 2× CCH$_2$C), 0.22, 0.16 ppm (2s, 18H; 6× Me); HRMS (70 EV, EI): m/z: calcd for $C_{24}H_{34}O_3Si_2$: 426.2046; found: 426.2042 $[M]^+$.

Compound 9b: ^{1}H NMR (200 MHz, C_6D_6): δ = 7.59–7.19 (m, 5H; ArH), 4.48 (s, 1H; C*H*Ph), 4.33 (s, 1H; =CH), 3.28 (s, 3H; OMe), 3.23 (d, J = 16.3 Hz, 1H; C*H*H), 3.06 (d, J = 16.3 Hz, 1H; CH*H*), 1.47 (s, 1H; OH), 0.27 ppm (s, 9H; 3× Me); ^{13}C NMR (75.5 MHz, C_6D_6): δ = 159.5, 138.2, 129.4, 128.3, 128.1, 109.9, 93.7, 87.6, 72.5, 60.6, 56.0, 47.9, −0.3 ppm; HRMS (70 EV, EI): m/z: calcd for $C_{17}H_{22}O_2Si$: 286.1389; found: 286.1391 $[M]^+$.

(1*R,3*R**,4*S**)-4-[(*Z*/*E*)-2-(2-Furyl)ethenyl]-4-methoxy-1,3-bis(trimethylsilylethynyl)-1,3-cyclopentanediol (6n) and (1*R**,2*S**)-2-(2-furyl)-4-methoxy-1-(trimethylsilylethynyl)-3-cyclopentenol (9c)**: Silyl enol ether **5h** (170 mg, 1 mmol), BuLi (0.63 mL, 1.6 N in hexanes, 1 mmol), and carbene complex **1b** (131 mg, 0.4 mmol) or **2b** (184 mg, 0.4 mmol) afforded **6n** (90 mg, 54 %, *cis*:*trans* 1.3:1 from **2b**) and **9c** (76 mg, 69 %, 88 % *de* from **1b**; 21 mg, 19 % from **2b**) as colorless oils.

Compound 6n: ^{1}H NMR (300 MHz, C_6D_6): δ = 7.13 (d, J = 1.7 Hz, 1H; = CHO, *trans* diastereomer), 6.99 (d, J = 1.7 Hz, 1H; =CHO, *cis* diastereomer), 6.96 (d, J = 3.4 Hz, 1H; C*H*CH=CHO, *cis* diastereomer), 6.79, 6.72 (2d, J = 16.5 Hz, 2H; CH=CH, *trans* diastereomer), 6.60, 5.80 (2d, J = 13.1 Hz, 2H; CH=CH *cis* diastereomer), 6.31 (d, J = 3.4 Hz, 1H; C*H*CH=CHO, *trans* diastereomer), 6.20–6.16 (m, 2H; C*H*=CHO), 3.70, 3.65, 3.38, 3.26 (4br s, 4H; 4× OH), 3.20–2.38 (m, 8H; 2× CH$_2$CCH$_2$), 3.19 (s, 3H; OMe, *cis* diastereomer), 2.91 (s, 3H; OMe, *trans* diastereomer), 0.25, 0.20 (2s, 18H; 6× MeSi, *trans* diastereomer), 0.18, 0.14 ppm (2s, 18H; 6× MeSi, *cis* diastereomer); ^{13}C NMR (75.5 MHz, C_6D_6): δ = 152.5, 151.1, 142.4, 142.3, 128.1, 125.1, 122.7, 113.2, 112.1, 111.5, 110.0, 109.9, 109.1, 108.9, 106.0, 105.0, 90.5, 90.3, 88.4, 88.3, 86.6, 79.3, 77.9, 71.3, 71.2, 54.6, 53.6, 53.5, 52.4, 52.1, 48.6, −0.3, −0.4, −0.5, −0.6 ppm.

Compound 9c: ^{1}H NMR (300 MHz, C_6D_6, major diastereomer): δ = 7.16 (d, J = 1.8 Hz, 1H; =CHO), 6.23 (d, J = 3.1 Hz, 1H; C*H*CH=CHO), 6.18 (dd, J = 3.1, 1.8 Hz, 1H; C*H*=CHO), 4.56–4.53, 4.27–4.25 (2m, 2H; C*H*C*H*-2-Fu), 3.18 (s, 3H; OMe), 3.14 (d, J = 15.9 Hz, 1H; C*H*H), 3.03 (d, J = 15.9 Hz, 1H; CH*H*), 2.02 (br s, 1H; OH), 0.22 ppm (s, 9H; 3× Me); ^{13}C NMR (75.5 MHz, C_6D_6, major diastereomer): δ = 159.3, 153.3, 142.3, 110.4, 109.8, 108.2, 92.0, 87.1, 72.3, 55.9, 54.8, 47.9, −0.3 ppm; HRMS (70 EV, EI): m/z: calcd for $C_{15}H_{20}O_3Si$: 276.1182; found: 276.1184 $[M]^+$.

(1*R,3*R**,4*S**)-1,3-Bis(1-hexynyl)-4-methoxy-4-[(*Z*/*E*)-2-(4-methoxyphenyl)ethenyl]-1,3-cyclopentanediol (6o) and (1*R**,2*R**)-1-(1-hexynyl)-4-methoxy-2-(4-methoxyphenyl)-3-cyclopentenol (9d)**: Silyl enol ether **5g** (157 mg, 1 mmol), BuLi (0.63 mL, 1.6 N in hexanes, 1 mmol), and carbene complex **1c** (147 mg, 0.4 mmol) or **2c** (200 mg, 0.4 mmol) afforded **6o** (32 mg, 19 %, *cis*:*trans* 1:1.4 from **1c**; 107 mg, 63 %, *cis*:*trans* 1:1.4 from **2c**) and **9d** (62 mg, 52 % from **1c**; 24 mg, 20 % from **2c**) as colorless oils.

Compound 6o: ^{1}H NMR (300 MHz, C_6D_6): δ = 7.59 (d, J = 8.7 Hz, 2H; ArH, *cis* diastereomer), 7.58, 6.94 (2d, J = 8.7 Hz, 4H; ArH, *trans* diastereomer), 6.88, 6.50 (2d, J = 16.4 Hz, 2H; CH=CH, *trans* diastereomer), 6.83–6.74 (m, 6H; ArH), 6.61, 5.98 (2d, J = 13.1 Hz, 2H; CH=CH, *cis* diastereomer), 3.71–3.48 (m, 4H; 4× OH), 3.32, 3.28, 3.24, 2.98 (4s, 12H; 4× MeO), 3.30–2.50 (m, 8H; 2× CH$_2$CCH$_2$), 2.08–0.63 ppm (m, 18H; 2× Bu); ^{13}C NMR (75.5 MHz, C_6D_6): δ = 160.0, 159.7, 134.7, 133.2, 131.8, 129.6, 128.1, 126.5, 114.2, 113.6, 88.7, 88.0, 86.5, 84.6, 83.2, 81.0, 79.3, 78.1, 71.2, 54.6, 54.5, 54.3, 51.9, 48.9, 30.9, 30.7, 30.5, 22.0, 21.9, 18.5, 18.3, 13.5 ppm.

Compound 9d: ^{1}H NMR (300 MHz, C_6D_6): δ = 7.42, 6.83 (2d, J = 8.8 Hz, 4H; ArH), 4.39, 4.31 (2s, 2H; ArC*H*, =CH), 3.31, 3.22 (2s, 6H, 2× MeO), 3.18 (d, J = 15.9 Hz, 1H; C*H*HCOMe), 3.03 (d, J = 15.9 Hz, 1H; CH*H*COMe), 2.02 (t, J = 6.8 Hz, 2H; CH_2Pr), 1.37–1.24 (m, 5H; CH_2CH_2Me, OH), 0.75 ppm (t, J = 6.9 Hz, 3H; Me); ^{13}C NMR (75.5 MHz, C_6D_6): δ = 159.6, 130.4, 130.2, 113.9, 94.3, 84.4, 83.8, 72.4, 60.1, 56.0, 54.5, 48.2, 30.9, 21.9, 18.4, 13.5 ppm; HRMS (70 EV, EI): m/z: calcd for $C_{19}H_{24}O_3$: 300.1725; found: 300.1730 $[M]^+$.

(1*R,3*R**,4*S**)-4-Methoxy-4-[(*Z*/*E*)-2-(4-methoxyphenyl)ethenyl]-1,3-bis(trimethylsilylethynyl)-1,3-cyclopentanediol (6p) and (1*R**,2*R**)-2-methoxy-2-(4-methoxyphenyl)-1-(trimethylsilylethynyl)-3-cyclopentenol (9e)**: Silyl enol ether **5h** (170 mg, 1 mmol), BuLi (0.63 mL, 1.6 N in hexanes, 1 mmol), and carbene complex **1c** (147 mg, 0.4 mmol) or **2c** (200 mg, 0.4 mmol) afforded **6p** (36 mg, 20%, *cis*:*trans* 1:2 from **2c**) and **9e** (86 mg, 68% from **1c**; 53 mg, 42% from **2c**) as colorless oils.

Compound 6p: ^{1}H NMR (300 MHz, C_6D_6): δ = 7.66, 6.85 (2d, J = 8.4 Hz, 4H; ArH, *cis* diastereomer), 7.58, 6.94 (2d, J = 8.4 Hz, 4H; ArH, *trans* diastereomer), 6.98, 6.62 (2d, J = 16.4 Hz, 2H; CH=CH, *trans* diastereomer), 6.68, 6.01 (2d, J = 13.1 Hz, 2H; CH=CH, *cis* diastereomer), 3.39, 3.22 (2s, 6H; 2×MeO, *cis* diastereomer), 3.36, 2.99 (2s, 6H; 2×MeO, *trans* diastereomer), 3.35–2.42 (m, 12H; 4×OH and 2×CH_2CCH_2), 0.24, 0.20 (2s, 18H; 6×MeSi, *trans* diastereomer), 0.21, 0.18 ppm (2s, 18H; 6× MeSi, *cis* diastereomer).

Compound 9e: ^{1}H NMR (300 MHz, C_6D_6): δ = 7.38, 6.81 (2d, J = 8.4 Hz, 4H; ArH), 4.38, 4.24 (2s, 2H; ArC*H*, =CH), 3.30, 3.18 (2s, 6H; 2× OMe), 3.13 (d, J = 15.9 Hz, 1H; C*H*H), 2.96 (d, J = 15.9 Hz, 1H; CH*H*), 1.48 (s, 1H; OH), 0.16 ppm (s, 9H; 3×MeSi); ^{13}C NMR (75.5 MHz, C_6D_6): δ = 159.7, 159.4, 130.4, 129.8, 114.0, 110.1, 94.0, 87.4, 72.5, 59.9, 56.1, 54.5, 47.7, −0.2 ppm; HRMS (70 EV, EI): m/z: calcd for $C_{18}H_{24}O_3Si$: 316.1495; found: 316.1483 $[M]^+$.

General procedures for the preparation of compounds 10 and 12: *Method A*: The compounds were prepared following the procedure described before for compounds **9a–e**.

Method B: Alternatively, when chromium carbene complexes were used, compounds **10** were prepared by treatment of ketones **4** (0.44 mmol) with LDA (1 equiv) at −30°C for 30 min in THF (10 mL). Carbene complexes **1** (0.4 mmol) were then added, and the mixture was warmed to room temperature and stirred for 1 h. The reaction was quenched with water (10 mL) and extracted with diethyl ether (3×50 mL). The solvents were removed, and the residue was dissolved in hexanes/ethyl acetate (5:1; 25 mL). Air was bubbled through the mixture, and the solution was exposed to direct sunlight for 3 h. The resulting suspension was filtered through Celite, the solvents removed, and the obtained residue was purified by flash column chromatography on silica gel (hexanes/ethyl acetate 5:1→2:1) to give compounds **10** or **12**. Compounds **10d** and **10e** were purified on deactivated silica gel (hexanes/ethyl acetate 10:1→5:1).

3-Methoxy-5-phenyl-2-cycloheptenone (10a): *Method B*: Ketone **4i** (31 mg, 0.44 mmol), LDA (0.44 mmol), and carbene complex **1a** (135 mg, 0.4 mmol) or **2a** (188 mg, 0.4 mmol) afforded compound **10a** (40 mg, 46%, from **1a**; 42 mg, 48% from **2a**) as a colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.36–7.19 (m, 5H; ArH), 5.48 (s, 1H; CH=), 3.65 (s, 3H; OMe), 3.26–1.91 ppm (m, 7H; CH_2C*H*PhCH_2CH_2); ^{13}C NMR (50.5 MHz, $CDCl_3$): δ = 202.1, 175.1, 145.9, 128.6, 126.5, 126.4, 105.3, 55.8, 41.5, 40.8, 39.7, 30.0 ppm; HRMS (70 EV, EI): m/z: calcd for $C_{14}H_{16}O_2$: 216.1150; found: 216.1165 $[M]^+$.

***cis*-3-Methoxy-6-methyl-5-phenyl-2-cycloheptenone (10b)**: *Method B*: Ketone **4j** (57 mg, 0.44 mmol), LDA (0.44 mmol), and carbene complex **1a** (135 mg, 0.4 mmol) afforded compound **10b** (40 mg, 44%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.05 (m, 5H; ArH), 5.45 (s, 1H; CH=), 3.62 (s, 3H; OMe), 3.29 (ddd, J = 11.0, 5.5, 2.2 Hz, 1H; C*H*Ph), 3.11 (dd, J = 16.9, 11.0 Hz, 1H; C*H*HCOMe), 2.68–2.56 (m, 3H; CH_2CO, CH*H*COMe), 2.37–2.28 (m, 1H; C*H*Me), 0.68 ppm (d, J = 6.8 Hz, 3H; Me); ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 201.0, 176.8, 143.3, 128.2, 127.5, 126.3, 105.4, 55.7, 49.8, 46.0, 35.4, 33.0, 16.4 ppm; HRMS (70 EV, EI): m/z: calcd for $C_{15}H_{18}O_2$: 230.1307; found: 230.1299 $[M]^+$.

***cis*-3-Methoxy-5,6-diphenyl-2-cycloheptenone (10c)**: *Method B*: Ketone **4k** (64 mg, 0.44 mmol), LDA (0.44 mmol), and carbene complex **1a** (135 mg, 0.4 mmol) afforded compound **10c** (60 mg, 51%) as a colorless oil.

Method A: Silyl enol ether **5k** (174 mg, 0.8 mmol), BuLi (0.50 mL, 1.6 N in hexanes, 0.8 mmol), and carbene complex **1a** (135 mg, 0.4 mmol) afforded **10c** (62 mg, 53%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.18–6.73 (m, 10H; ArH), 5.62 (s, 1H; CH=), 3.93–2.67 (m, 6H; CH_2CHCHCH_2), 3.73 ppm (s, 3H; OMe); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 200.8, 175.5, 142.0, 140.8, 128.1, 127.8, 127.7, 126.3, 126.2, 105.4, 55.8, 46.7, 46.4, 45.0, 36.8 ppm; HRMS (70 EV, EI): m/z: calcd for $C_{20}H_{20}O_2$: 292.1463; found: 292.1472 $[M]^+$.

(4a*R,5*R**,9a*R**)-3,4,4a,5,6,9a-Hexahydro-7-methoxy-5-phenyl-2*H*-cyclohepta[*b*]pyran-9-one (10d)**: *Method A*: Silyl enol ether **5l** (158 mg, 0.8 mmol), BuLi (0.50 mL, 1.6 N in hexanes, 0.8 mmol), and carbene complex **2a** (188 mg, 0.4 mmol) in diethyl ether (10 mL) afforded **10d** (58 mg, 53%) as a colorless oil. ^{1}H NMR (400 MHz, C_6D_6): δ = 7.22–6.84 (m, 5H; ArH), 5.56 (s, 1H; CH=), 4.41 (d, J = 4.2 Hz, 1H; OCH), 3.84–3.78 (m, 1H; C*H*HO), 3.53–3.47 (m, 1H; CH*H*O), 3.32–3.26 (m, 1H; C*H*CHPh), 3.17 (dd, J = 12.7, 3.7 Hz, 1H; C*H*Ph), 3.06 (s, 3H; OMe), 2.48 (d, J = 16.6 Hz, 1H; CH*H*CHPh), 2.25–2.21 (m, 1H; C*H*CHPh), 1.52–1.04 ppm (m, 4H; OCH_2CH_2CH_2); ^{13}C NMR (100.6 MHz, C_6D_6): δ = 197.1, 173.8, 144.6, 128.5, 127.3, 126.4, 103.8, 85.3, 65.2, 54.8, 44.0, 41.4, 36.3, 24.6, 22.1 ppm; HRMS (70 EV, EI): m/z: calcd for $C_{17}H_{20}O_3$: 272.1412; found: 272.1416 $[M]^+$; elemental analysis calcd (%) for $C_{17}H_{20}O_3$: C 74.97, H 7.40; found: C 75.09, H 7.24.

***cis*-5-(2-Furyl)-3-methoxy-6-phenyl-2-cycloheptenone (10e)**: *Method B*: Ketone **4k** (64 mg, 0.44 mmol), LDA (0.44 mmol), and carbene complex **2b** (184 mg, 0.4 mmol) afforded compound **10e** (7 mg, 6%) as a colorless oil.

Method A: Silyl enol ether **5k** (174 mg, 0.8 mmol), BuLi (0.50 mL, 1.6 N in hexanes, 0.8 mmol), and carbene complex **2b** (184 mg, 0.4 mmol) afforded **10e** (52 mg, 46%) as a colorless oil. ^{1}H NMR (400 MHz, C_6D_6): δ = 7.11–6.66 (m, 5H; ArH), 6.89 (d, J = 1.8 Hz, 1H; =CHO), 5.86 (dd, J = 3.3, 1.8 Hz, 1H; C*H*=CHO), 5.51 (s, 1H; =C*H*COMe), 5.44 (d, J = 3.3 Hz, 1H; C*H*CH=CHO), 2.98 (s, 3H; OMe), 3.47–2.83 (m, 5H; CH_2C*H*CHCH_2), 2.46 ppm (ddd, J = 16.2, 4.2, 1.3 Hz, 1H; CH_2CHC*H*CH_2); ^{13}C NMR (100.6 MHz, C_6D_6): δ = 199.0, 171.4, 155.1, 142.2, 141.0, 127.9, 127.5, 126.3, 109.9, 106.7, 105.1, 55.0, 46.3, 43.5, 40.2, 35.9 ppm; HRMS (70 EV, EI): m/z: calcd for $C_{18}H_{18}O_3$: 282.1256; found: 282.1259 $[M]^+$; elemental analysis calcd (%) for $C_{18}H_{18}O_3$: C 76.57, H 6.43; found: C 76.69, H 6.29.

3-Methoxy-5-(4-methoxyphenyl)-2-cycloheptenone (10f): *Method B*: Ketone **4i** (31 mg, 0.44 mmol), LDA (0.44 mmol), and carbene complex **1c** (147 mg, 0.4 mmol) afforded compound **10f** (51 mg, 52%) as a colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.12, 6.87 (2d, J = 6.9 Hz, 4H; ArH), 5.49 (s, 1H; CH=), 3.83, 3.65 (2s, 6H; 2×OMe), 3.23–1.86 ppm (m, 7H; CH_2CHCH_2CH_2); ^{13}C NMR (50.5 MHz, $CDCl_3$): δ = 202.1, 175.0, 158.1, 138.1, 127.5, 114.0, 105.3, 55.8, 55.2, 41.1, 40.7, 40.0, 30.1 ppm; HRMS (70 EV, EI): m/z: calcd for $C_{15}H_{18}O_3$: 246.1256; found: 246.1255 $[M]^+$.

***cis*-3-Methoxy-5-(4-methoxyphenyl)-6-phenyl-2-cycloheptenone (10g)**: *Method B*: Ketone **4k** (64 mg, 0.44 mmol), LDA (0.44 mmol), and carbene complex **1c** (147 mg, 0.4 mmol) afforded compound **10g** (55 mg, 43%) as a colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.16–6.66 (m, 9H; ArH), 5.59 (s, 1H; CH=), 3.73, 3.70 (2s, 6H; 2×OMe), 3.53–3.19 (m, 4H; C*H*HC*H*C*H*CH*H*), 2.90 (dd, J = 15.3, 3.1 Hz, 1H; CH*H*CH), 2.70 ppm (d, J = 17.0 Hz, 1H; CHCH*H*); ^{13}C NMR (50.5 MHz, $CDCl_3$): δ = 201.2, 175.5, 157.9, 141.2, 134.2, 128.9, 128.1, 127.8, 126.4, 113.1, 105.3, 55.8, 55.2, 46.4, 45.9, 45.1, 37.3 ppm; HRMS (70 EV, EI): m/z: calcd for $C_{21}H_{22}O_3$: 322.1569; found: 322.1550 $[M]^+$.

3-Methoxy-5,5-dimethyl-6-phenyl-2-cycloheptenone (12): *Method B*: Ketone **4k** (64 mg, 0.44 mmol), LDA (0.44 mmol), and carbene complex **11** (169 mg, 0.4 mmol) afforded compound **12** (47 mg, 48%) as a colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.32–7.02 (m, 5H; ArH), 5.43 (d, J = 2.2 Hz, 1H; CH=), 3.70 (s, 3H; OMe), 3.04 (dd, J = 16.6, 11.3 Hz, 1H; CHC*H*H), 2.87 (d, J = 11.3 Hz, 1H; CH), 2.83 (d, J = 14.6 Hz, 1H; C*H*HCMe$_2$), 2.71 (d, J = 16.6 Hz, 1H; CHCH*H*), 2.20 (dd, J = 14.6, 2.2 Hz, 1H; CH*H*CMe$_2$), 1.05, 0.65 ppm (2s, 6H; 2×Me); ^{13}C NMR (50.5 MHz, $CDCl_3$): δ = 203.5, 173.5, 142.3, 129.2, 127.6, 126.2, 103.7, 55.8,

49.1, 46.6, 46.5, 35.0, 27.9, 25.5 ppm; HRMS (70 EV, EI): *m/z*: calcd for $C_{16}H_{20}O_2$: 244.1463; found: 244.1465 $[M]^+$; elemental analysis calcd (%) for $C_{16}H_{20}O_2$: C 78.65, H 8.25; found: C 78.50, H 8.13.

1-{(1*R*,5*S*)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl}ethanone (4m): MeLi (1 equiv, 6.7 mL, 1.5 M in diethyl ether) was added dropwise to a solution of (−)-myrtenal (1.52 g, 10 mmol) in diethyl ether (20 mL) at −78 °C, thereby warming the mixture to room temperature; it was then stirred for 10 min. The reaction was quenched with water (20 mL) and extracted in diethyl ether (3×20 mL). After removing solvents, the obtained crude residue was used in the next step without further purification. Dimethyl sulfoxide (4 equiv, 3.12 g, 40 mmol) was added dropwise to a solution of oxalyl chloride (2 equiv, 2.54 g, 20 mmol) in CH_2Cl_2 (20 mL) at −78 °C. After the reaction mixture had been stirred for 5 min, a solution of the residue from the previous step in CH_2Cl_2 (30 mL) was added dropwise and the resulting mixture was stirred for 30 min. Triethylamine (6.5 equiv, 9 mL, 65 mmol) was then added and the reaction was warmed to room temperature. After stirring for 12 h, the reaction was quenched with water (30 mL) and extracted with diethyl ether. The solvents were removed, and the resulting residue was purified by flash column chromatography on silica gel (hexanes/ethyl acetate 10:1→5:1) to afford compound **4m** as a pale yellow oil (1.26 g, 76 %). $[\alpha]_D^{20} = -29.7$ ($c = 0.77$, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 6.68$–6.64 (m, 1H; CH=), 2.86–1.98, 0.98–0.94 (2m, 6H; CH_2CHCH_2CH), 2.18 (s, 3H; MeCO), 1.21, 0.62 ppm (2s, 6H; 2×Me); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 196.9$, 149.4, 137.4, 40.0, 39.1, 37.1, 32.3, 30.9, 25.6, 24.7, 20.6 ppm; HRMS (70 EV, EI): *m/z*: calcd for $C_{11}H_{16}O$: 164.1201; found: 164.1195 $[M]^+$.

(1*S*,2*S*,7*R*,8*R*,10*S*)-5-Methoxy-11,11-dimethyl-7-phenyltricyclo[8.1.1.0^{2,8}]-dodec-4-en-3-one (13): Ketone **4m** (73 mg, 0.44 mmol) was added to a solution of lithium diisopropylamide (0.44 mmol) in THF (10 mL) at −40 °C and the mixture was stirred for 30 min and then cooled to −78 °C. A solution of carbene complex **1a** (188 mg, 0.4 mmol) in THF (5 mL) was added dropwise and the reaction mixture was slowly warmed overnight. The reaction mixture was cooled again to −78 °C and a saturated solution of ammonium chloride (5 mL) was added. The mixture was warmed to room temperature and extracted with diethyl ether (3× 20 mL). Solvents were removed and the resulting crude residue was dissolved hexanes/ethyl acetate (5:1, 20 mL). Air was bubbled through the mixture and the solution was exposed to direct sunlight for 1 h. The obtained suspension was filtered on celite, the solvents were removed, and the resulting residue was purified by flash column chromatography on silica gel (hexanes/ethyl acetate 20:1→5:1) to afford compound **13** as a colorless oil (51 mg, 41 %). $[\alpha]_D^{20} = -59.3$ ($c = 0.44$, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.34$–7.17 (m, 5H; ArH), 5.57 (s, 1H; CH=), 3.62 (s, 3H; OMe), 3.53–3.41 (m, 2H; CH*H*C*H*Ph), 3.11 (dd, $J = 10.2$, 5.1 Hz, 1H; CHCO), 2.83 (apparent q, $J = 5.7$ Hz, 1H; CHPhC*H*), 2.74 (q, $J =$ 10.2 Hz, 1H; $CH_2CHCHCO$), 2.65 (d, $J = 16.2$ Hz, 1H; C*H*HCHPh), 2.20–2.14 (m, 1H; CHPhCHC*H*H), 1.98–1.84 (m, 2H; $CHPhCHCH_2CHCHH$), 1.51–1.36 (m, 2H; CHPhCHCH*H*CHC*H*H), 1.18, 0.76 ppm (2s, 6H; 2×Me); ^{13}C NMR (100.6 MHz, C_6D_6): $\delta = 202.5$, 172.8, 144.9, 128.6, 128.5, 125.9, 106.8, 54.6, 54.6, 46.3, 44.0, 40.0, 39.4, 35.8, 34.8, 28.1, 26.3, 23.1, 22.3 ppm; HRMS (70 EV, EI): *m/z*: calcd for $C_{21}H_{26}O_2$: 310.1933; found: 310.1939 $[M]^+$; elemental analysis calcd (%) for $C_{21}H_{26}O_2$: C 81.25, H 8.44; found: C 81.33, H 8.35.

General procedures for the preparation of compounds 9b,f–i: BuLi (1 equiv) was added to a solution of silyl enol ethers **5a**,**d**,**f**,**h**,**k** (0.8 mmol) in diethyl ether (10 mL) at 20 °C for silyl enol ethers **5d**,**f** or at 0 °C for silyl enol ethers **5a**,**h**,**k**, and the reaction mixture was then stirred for 30 min. PMDTA (0.50 mL, 2.4 mmol) was then added at 0 °C, and the mixture was stirred for further 10 min. Carbene complex **2a** (188 mg, 0.4 mmol) was then added and the reaction was warmed to room temperature and stirred for 30 min. After that, a small amount of silica gel was added, the solvents were removed, and the resulting residue was purified by flash column chromatography on silica gel (hexanes/ethyl acetate 10:1→3:1).

(1*R,2*S**)-4-Methoxy-1,2-diphenyl-3-cyclopentenol (9f)**: Silyl enol ether **5a** (154 mg, 0.8 mmol), BuLi (0.50 mL, 1.6 N in hexanes, 0.8 mmol), and carbene complex **2a** (188 mg, 0.4 mmol) afforded **9f** (56 mg, 53 %) as a colorless oil. ^{1}H NMR (300 MHz, C_6D_6): $\delta = 7.47$–7.05 (m, 10H; ArH), 4.44–4.40 (m, 2H; =CH, C*H*Ph), 3.39 (s, 3H; OMe), 3.17 (d, $J = 16.3$ Hz, 1H; C*H*H), 3.01 (d, $J = 16.3$ Hz, 1H; CH*H*), 1.61 ppm (s, 1H; OH); ^{13}C NMR (50.5 MHz, C_6D_6): $\delta = 159.7$, 147.5, 138.6, 129.0, 128.4, 128.0, 127.4, 126.6, 125.4, 94.4, 80.6, 61.6, 56.1, 50.0 ppm; HRMS (70 EV, EI): *m/z*: calcd for $C_{18}H_{18}O_2$: 266.1307; found: 266.1302 $[M]^+$.

(1*R,2*R**)-4-Methoxy-1-methyl-2-phenyl-3-cyclopentenol (9g)**: Silyl enol ether **5d** (144 mg, 0.8 mmol), BuLi (0.50 mL, 1.6 N in hexanes, 0.8 mmol), and carbene complex **2a** (188 mg, 0.4 mmol) afforded **9g** (52 mg, 64 %) as a colorless oil along with compound **6f** (22 mg, 22 %, >95 % *de*). ^{1}H NMR (300 MHz, C_6D_6): $\delta = 7.28$–7.20 (m, 5H; ArH), 4.44 (brs, 1H; CH=), 3.88 (brs, 1H; C*H*Ph), 3.48 (s, 3H; OMe), 2.63 (d, $J = 16.1$ Hz, 1H; C*H*H), 2.58 (d, $J = 16.1$ Hz, 1H; CH*H*), 1.61 (brs, 1H; OH), 0.91 ppm (s, 3H; Me); ^{13}C NMR (75.5 MHz, C_6D_6): $\delta = 158.5$, 142.2, 128.2, 126.6, 95.8, 79.4, 61.0, 55.7, 47.7, 25.6 ppm; HRMS (70 EV, EI): *m/z*: calcd for $C_{13}H_{16}O_2$: 204.1150; found: 204.1159 $[M]^+$.

(1*R,2*R**)-1-Isobutyl-4-methoxy-2-phenyl-3-cyclopentenol (9h)**: Silyl enol ether **5a** (138 mg, 0.8 mmol), BuLi (0.50 mL, 1.6 N in hexanes, 0.8 mmol), and carbene complex **2a** (188 mg, 0.4 mmol) afforded **9h** (50 mg, 51 %) as a colorless oil. ^{1}H NMR (300 MHz, C_6D_6): $\delta = 7.26$–7.16 (m, 5H; ArH), 4.46 (ddd, $J = 3.3$, 2.6, 0.8 Hz, 1H; CH=), 3.70 (d, $J =$ 2.6 Hz, 1H; C*H*Ph), 3.37 (s, 3H; OMe), 2.80 (dd, $J = 16.1$, 3.3 Hz, 1H; CC*H*HC), 2.52 (dd, $J = 16.1$, 0.8 Hz, 1H; CCH*H*C), 1.91–1.82 (m, 1H; C*H*Me_2), 1.75 (brs, 1H; OH), 1.28 (dd, $J = 14.4$, 5.3 Hz, 1H; C*H*HCH), 1.03 (dd, $J = 14.4$, 6.4 Hz, 1H; CH*H*CH), 0.88 (d, $J = 6.7$ Hz, 3H; Me), 0.86 ppm (d, $J = 6.3$ Hz, 3H; Me); ^{13}C NMR (75.5 MHz, C_6D_6): $\delta = 160.0$, 142.3, 128.6, 128.3, 126.6, 96.6, 81.8, 63.2, 55.9, 46.7, 45.8, 24.7, 24.3 ppm; HRMS (70 EV, EI): *m/z*: calcd for $C_{16}H_{22}O_2$: 246.1620; found: 246.1619 $[M]^+$.

(1*R,2*R**)-4-Methoxy-2-Phenyl-1-[(*E*)-styryl]-3-cyclopentenol (9i)**: Silyl enol ether **5k** (174 mg, 0.8 mmol), BuLi (0.50 mL, 1.6 N in hexanes, 0.8 mmol), and carbene complex **2a** (188 mg, 0.4 mmol) afforded **9i** (23 mg, 20 %) as a colorless oil. ^{1}H NMR (300 MHz, C_6D_6): $\delta = 7.35$–7.06 (m, 10H; ArH), 6.63 (d, $J = 15.9$ Hz, 1H; =C*H*Ph), 6.41 (d, $J = 15.9$ Hz, 1H; =C*H*COH), 4.42 (s, 1H; =C*H*COMe), 4.04 (s, 1H; C*H*Ph), 3.39 (s, 3H; OMe), 3.28 (s, 1H; OH), 2.90 (d, $J = 15.8$ Hz, 1H; C*H*H), 2.82 ppm (d, $J = 15.8$ Hz, 1H; CH*H*); ^{13}C NMR (75.5 MHz, C_6D_6): $\delta = 160.3$, 142.1, 137.3, 135.6, 130.0, 129.2, 126.7, 94.5, 79.8, 58.7, 56.1, 46.8 ppm.

Acknowledgements

Financial support for this work was provided by the Ministerio de Ciencia y Tecnología (project BQU2001-3853) and Junta del Principado de Asturias (project PR-01-GE-9) of Spain.

[1] a) T. Hudlicky, J. D. Price, *Chem. Rev.* **1989**, *89*, 1467–1486; b) R. D. Little in *Comprehensive Organic Synthesis*, *Vol. 5* (Eds.: B. M. Trost, I. Fleming), Pergamon Press, Oxford, **1991**, Chapter 3.1B, pp. 239–270; c) D. M. T. Chan in *Comprehensive Organic Synthesis*, *Vol. 5* (Eds.: B. M. Trost, I. Fleming), Pergamon Press, Oxford, **1991**, Chapter 3.2, pp. 271–314; d) S. E. Denmark in *Comprehensive Organic Synthesis*, *Vol. 5* (Eds.: B. M. Trost, I. Fleming), Pergamon Press, Oxford, **1991**, Chapter 6.3, pp. 751–784; e) M. Lautens, W. Klute, W. Tam, *Chem. Rev.* **1996**, *96*, 49–92.

[2] a) T. L. Ho, *Carbocycle Construction in Terpene Synthesis*, VCH, New York, **1988**; b) T. Hudlicky, F. Rulin, T. C. Lovelace, J. W. Reed in *Studies in Natural Products Chemistry* (Ed.: T. Atta-Ur-Rahman), Elsevier Science, Essex, UK, **1989**.

[3] H.-W. Frühauf, *Chem. Rev.* **1997**, *97*, 523–526.

[4] For recent reviews, see: a) K. H. Dötz, P. Tomuschat, *Chem. Soc. Rev.* **1999**, *28*, 187–198; b) J. W. Herndon, *Tetrahedron* **2000**, *56*, 1257–1280; c) A. de Meijere, H. Schirmer, M. Duetsch, *Angew. Chem.* **2000**, *112*, 4124–4162; *Angew. Chem. Int. Ed.* **2000**, *39*, 3964–4002; d) M. A. Sierra, *Chem. Rev.* **2000**, *100*, 3591–3637; e) J. Barluenga, F. J. Fañanás, *Tetrahedron* **2000**, *56*, 4597–4628; f) J. Barluen-

ga, J. Flórez, F. J. Fañanás, *J. Organomet. Chem.* **2001**, *624*, 5–17; g) J. Barluenga, *Pure Appl. Chem.* **2002**, *74*, 1317–1325; h) J. Barluenga, M. Tomás, J. Santamaría, *Chem. Rev.* **2004**, *104*, 2259–2283; i) *Metal Carbenes in Organic Synthesis: Topics in Organometallic Chemistry*, *Vol. 13* (Ed.: K. H. Dötz), Springer, Berlin, **2004**; j) J. Barluenga, M. A. Fernández-Rodriguez, E. Aguilar, *J. Organomet. Chem.* **2005**, *690*, 539–587.

[5] a) W. D. Wulff in *Comprehensive Organometallic Chemistry II*, *Vol 12* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon, Oxford, **1995**, pp. 469–547; b) J. Barluenga, F. Rodríguez, F. J. Fañanás, J. Flórez in *Metal Carbenes in Organic Synthesis: Topics in Organometallic Chemistry*, *Vol. 13* (Ed.: K. H. Dötz), Springer, Berlin, **2004**, pp. 59–121.

[6] For a rhodium-promoted [3+2] cyclization of alkenylcarbene complexes and alkynes, see: J. Barluenga, R. Vicente, L. A. López, E. Rubio, M. Tomás, C. Álvarez-Rúa, *J. Am. Chem. Soc.* **2004**, *126*, 470–471.

[7] a) F. Zaragoza Dörwald, *Angew. Chem.* **2003**, *115*, 1372–1374; *Angew. Chem. Int. Ed.* **2003**, *42*, 1332–1334; b) J. Barluenga, S. López, J. Flórez, *Angew. Chem.* **2003**, *115*, 241–243; *Angew. Chem. Int. Ed.* **2003**, *42*, 231–233.

[8] a) M. Hoffmann, M. Buchert, H.-U. Reissig, *Angew. Chem.* **1997**, *109*, 281–283; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 283–285; b) M. Hoffmann, M. Buchert, H.-U. Reissig, *Chem. Eur. J.* **1999**, *5*, 876–882.

[9] J. Barluenga, A. Ballesteros, J. Santamaría, M. Tomás, *J. Organomet. Chem.* **2002**, *643*, 363–368.

[10] a) A. Wienand, H.-U. Reissig, *Chem. Ber.* **1991**, *124*, 957–965; b) M. Hoffmann, H.-U. Reissig, *Synlett* **1995**, 625–627; c) J. Barluenga, M. Tomás, A. L. Suárez-Sobrino, *Synthesis* **2000**, 935–940.

[11] a) A. G. Meyer, R. Aumann, *Synlett* **1995**, 1011–1013; b) R. Aumann, A. G. Meyer, R. Fröhlich, *Organometallics* **1996**, *15*, 5018–5027; c) R. Aumann, M. Kössmeier, A. Jäntti, *Synlett* **1998**, 1120–1122; d) J. Barluenga, M. Tomás, A. Ballesteros, J. Santamaría, C. Brillet, S. García-Granda, A. Piñera-Nicolás, J. T. Vázquez, *J. Am. Chem. Soc.* **1999**, *121*, 4516–4517.

[12] R. Aumann, H. Heinen, M. Dartmann, B. Krebs, *Chem. Ber.* **1991**, *124*, 2343–2347.

[13] a) H. Kagoshima, T. Akiyama, *J. Am. Chem. Soc.* **2000**, *122*, 11741–11742; b) H. Kagoshima, T. Okamura, T. Akiyama, *J. Am. Chem. Soc.* **2001**, *123*, 7182–7183.

[14] a) R. Aumann, H. Heinen, *Chem. Ber.* **1985**, *118*, 4186–4195; b) R. Aumann, H. Heinen, *Chem. Ber.* **1986**, *119*, 3801–3811.

[15] R. Aumann, H. Heinen, C. Krüger, *Chem. Ber.* **1987**, *120*, 1287–1291.

[16] J. Barluenga, F. Aznar, M. Fernández, *Chem. Eur. J.* **1997**, *3*, 1629–1637.

[17] a) W. D. Wulff, D. C. Yang, C. K. Murray, *J. Am. Chem. Soc.* **1988**, *110*, 2653–2655; b) W. D. Wulff, W. E. Bauta, R. W. Kaesler, P. J. Lankford, R. A. Miller, C. K. Murray, D. C. Yang, *J. Am. Chem. Soc.* **1990**, *112*, 3642–3659; c) J. Barluenga, F. Aznar, C. Valdés, A. Martín, S. García-Granda, E. Martín, *J. Am. Chem. Soc.* **1993**, *115*, 4403–4404; d) J. Barluenga, F. Aznar, A. Martín, S. García-Granda, M. A. Salvadó, P. Pertierra, *J. Chem. Soc. Chem. Commun.* **1993**, 319–321; e) J. Barluenga, F. Aznar, A. Martín, J. T. Vázquez, *J. Am. Chem. Soc.* **1995**, *117*, 9419–9426; see also refs. [8b] and [16].

[18] J. Barluenga, F. Aznar, A. Martín, *Organometallics* **1995**, *14*, 1429–1433.

[19] a) J. Barluenga, M. Tomás, A. Ballesteros, J. Santamaría, R. J. Carbajo, F. López-Ortiz, S. García-Granda, P. Pertierra, *Chem. Eur. J.* **1996**, *2*, 88–97; b) J. Barluenga, M. Tomás, A. Ballesteros, J. Santamaría, A. L. Suárez-Sobrino, *J. Org. Chem.* **1997**, *62*, 9229–9235.

[20] J. Barluenga, P. Barrio, L. A. López, M. Tomás, S. García-Granda, C. Álvarez-Rúa, *Angew. Chem.* **2003**, *115*, 3116–3119; *Angew. Chem. Int. Ed.* **2003**, *42*, 3008–3011.

[21] a) C. P. Casey, W. Brunsvold, *Inorg. Chem.* **1977**, *16*, 391–396; b) S. Aoki, T. Fujimura, E. Nakamura, *J. Am. Chem. Soc.* **1992**, *114*, 2985–2990; c) E. Nakamura, K. Tanoka, T. Fujimura, S. Aoki, P. G. Villiard, *J. Am. Chem. Soc.* **1993**, *115*, 9015–9020; d) J. Barluenga, J. Montserrat, J. Flórez, S. García-Granda, E. Martín, *Chem. Eur. J.* **1995**, *1*, 236–242.

[22] J. Barluenga, J. Alonso, F. J. Fañanás, *J. Am. Chem. Soc.* **2003**, *125*, 2610–2616.

[23] For a previous communication, see: J. Barluenga, J. Alonso, F. Rodríguez, F. J. Fañanás, *Angew. Chem.* **2000**, *112*, 2555–2558; *Angew. Chem. Int. Ed.* **2000**, *39*, 2460–2462.

[24] For 1,3-metal migrations, see: a) H. F. Sleiman, L. McElwee-White, *J. Am. Chem. Soc.* **1988**, *110*, 8700–8701; b) L. S. Hegedus, B. R. Lundmark, *J. Am. Chem. Soc.* **1989**, *111*, 9194–9198; c) C. T. Maxey, H. F. Sleiman, S. T. Massey, L. McElwee-White, *J. Am. Chem. Soc.* **1992**, *114*, 5153–5160; d) H. Fischer, A. Schlageter, W. Bidell, A. Früh, *Organometallics* **1991**, *10*, 389–391; e) J. Barluenga, M. Tomás, E. Rubio, J. A. López-Pelegrín, S. García-Granda, M. Pérez-Priede, *J. Am. Chem. Soc.* **1999**, *121*, 3065–3071.

[25] For 1,2-metal migrations, see: a) H. Fischer, T. Meisner, J. Hofmann, *Chem. Ber.* **1990**, *123*, 1799–1804; b) K. H. Dötz, C. Christoffers, P. Knochel, *J. Organomet. Chem.* **1995**, *489*, C84–C86; c) J. Barluenga, M. Tomás, E. Rubio, J. A. López-Pelegrín, S. García-Granda, P. Pertierra, *J. Am. Chem. Soc.* **1996**, *118*, 695–696; d) N. Iwasawa, K. Maeyama, M. Saitou, *J. Am. Chem. Soc.* **1997**, *119*, 1486–1487; e) N. Iwasawa, K. Maeyama, *J. Org. Chem.* **1997**, *62*, 1918–1919; f) N. Iwasawa, T. Ochiai, K. Maeyama, *Organometallics* **1997**, *16*, 5137–5139; g) N. Iwasawa, T. Ochiai, K. Maeyama, *J. Org. Chem.* **1998**, *63*, 3164–3165; h) J. Barluenga, E. Rubio, J. A. López-Pelegrín, M. Tomás, *Angew. Chem.* **1999**, *111*, 1163–1165; *Angew. Chem. Int. Ed.* **1999**, *38*, 1091–1093.

[26] M. E. Jung, C. A. McCombs, Y. Takeda, Y.-G. Pan, *J. Am. Chem. Soc.* **1981**, *103*, 6677–6685.

[27] a) R. Aumann, H. Heinen, *Chem. Ber.* **1987**, *120*, 587–588; b) K. H. Dötz, R. Noack, K. Karms, *Tetrahedron* **1990**, *46*, 1235–1252.

[28] W. D. Wulff, W. E. Bauta, R. W. Kaesler, P. J. Lankford, R. A. Miller, C. K. Murray, D. C. Yang, *J. Am. Chem. Soc.* **1990**, *112*, 3642–3659.

[29] G. H. Posner, C. E. Whitten, J. J. Sterling, *J. Am. Chem. Soc.* **1973**, *95*, 7788–7800.

Received: February 15, 2005
Please note: Minor changes have been made to this manuscript since its publication in *Chemistry—A European Journal* Early View. The Editor
Published online: June 15, 2005