Pergamon

Tetrahedron 54 (1998) 1601–1614

TETRAHEDRON

γ-Oxygenated-α,β-Unsaturated Sulfones in Radical Cyclizations and Cascade Processes

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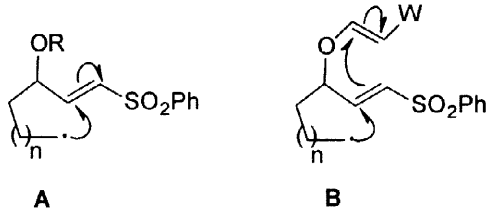
Received 16 September 1997; accepted 20 November 1997

Abstract: A wide variety of radical precursors having the structure of γ–oxygenated-α,β-unsaturated sulfone (substrates **1-4**) have been prepared. Both 5-hexenyl and 6-heptenyl radicals, generated by reaction of substrates **1-4** with Bu_3SnH/AIBN, underwent an efficient cyclization *via* intramolecular addition to the vinyl sulfone moiety. By introduction of a double bond joined to the oxygen at γ-position, a cascade process based on two sequential radical cyclizations took place, affording highly substituted 2-oxa[3.3.0] or 9-oxa[4.3.0] bicyclic compounds.

INTRODUCTION

In recent years, methods for ring construction based on the intramolecular addition of radicals to carbon-carbon double bonds have gained a great attention, owing to the mild conditions required for the radical generation and the wide functional group tolerance usually displayed in this type of reaction.[1] As 6- and, particularly, 5-exo closures are very favoured processes, six and five membered rings are frequently prepared by this methodology, specially when base- or acid-sensitive functionalities are present.

Although much less studied than α,β-unsaturated esters, α,β-unsaturated sulfones are known to be good substrates for the conjugate addition of radicals, both in intermolecular and intramolecular processes.[2] Furthermore, the resulting α-sulfonyl radical obtained after radical cyclization could be a useful intermediate for the generation of a second C-C bond *via* intramolecular addition to a suitably located carbon-carbon multiple bond.[3] In connection with our interest in developing highly efficient stereoselective processes using γ-hydroxyvinyl sulfones as readily available starting materials in organic synthesis,[4] we recently undertook the study of their radical cyclizations from proper radical precursors (**A**, figure 1). Following an earlier communication,[5] we describe herein this work in detail, as well as its application to radical cascade cyclizations *via* intramolecular addition of the α-sulfonyl radical intermediate to a second carbon-carbon double bond attached to the oxygen at γ-position (**B**, figure 1).



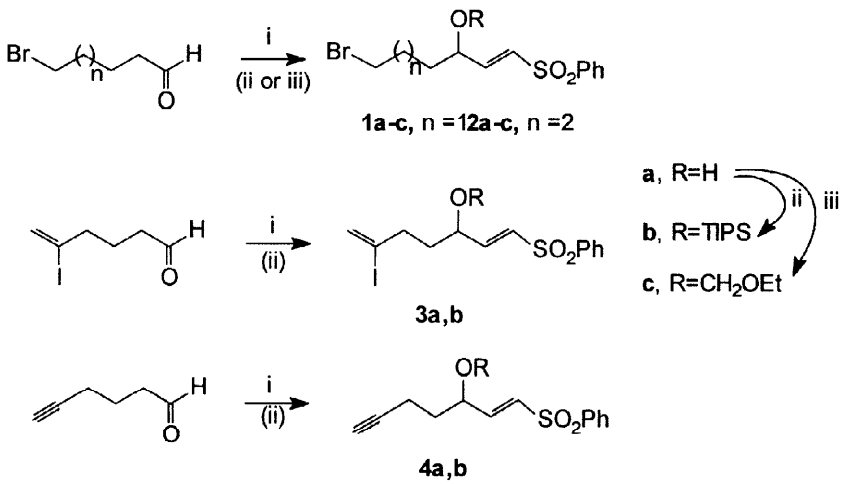
A **B**

Figure 1

PII: S0040-4020(97)10368-4

RESULTS AND DISCUSSION

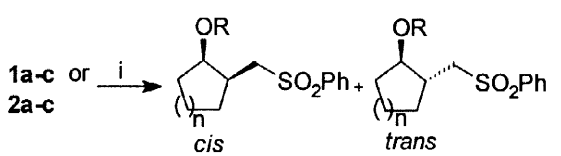
Radical cyclizations. Both the alkyl radical precursors, **1a** and **2a**, and the vinyl radical precursors, **3a** and **4a**, were prepared in good yields (81%, 79%, 70% and 84%, respectively) by our usual one-step procedure for the synthesis of γ-hydroxy-α,β-unsaturated sulfones, based on the condensation of sulfonyl sulfinyl methanes with aldehydes[6] (scheme 1). From these alcohols (substrates **a**), their TIPS derivatives (substrates **b**) and ethoxymethyl derivatives (substrates **c**) were prepared in very high yield (90-95%) by reaction with TIPSOTf/ 2,6-lutidine and with $ClCH_2OEt$/ DIPEA, respectively. The radical precursors **1-4** were subjected to the tin hydride method (Bu_3SnH/AIBN) in refluxing benzene. In tables 1 and 2 the results obtained from substrates **1-2** and **3-4** are shown, respectively.



i:$PhSO_2$~SOTol, piperidine, CH_2Cl_2, 0 °C ii: TIPSOTf, 2,6-lutidine, CH_2Cl_2, rt. iii: $ClCH_2OEt$, DIPEA, CH_2Cl_2, rt.

Scheme 1

Table 1: Radical cyclization of vinylsulfones **1-2**

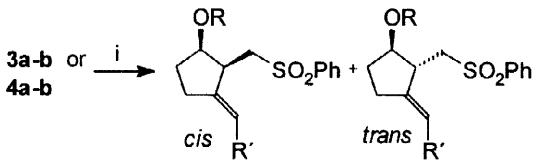


i: Bu_3SnH, AIBN, C_6H_6, Δ **5a-c**, n=1 **6a-c**, n=2

Entry	Vinylsulfone	n	OR	Product	Yield (%)[a]		*cis/trans*
					cis	*trans*	
1	**1a**	1	OH	**5a**	81	---	>98/<2
2	**1b**	1	OTIPS	**5b**	55	23	70/30
3	**1c**	1	OCH_2OEt	**5c**	52	27	66/34
4	**2a**	2	OH	**6a**	50	30	63/37
5	**2b**	2	OTIPS	**6b**	70[b]		55/45
6	**2c**	2	OCH_2OEt	**6c**	45	30	60/40

[a]In pure isomers after chromatographic separation. [b]*cis*-**6b** + *trans*-**6b** could not be separated by silica gel chromatography.

Table 2: Radical cyclization of vinylsulfones **3-4**



i:Bu_3SnH, AIBN, C_6H_6, Δ

7a-b, R'=H
8a-b, R'=Bu_3Sn

Entry	Vinylsulfone	R'	OR	Product	Yield (%)[a]		*cis/trans*
					cis	*trans*	
1	**3a**	H	OH	**7a**	46	30	60/40
2	**3b**	H	OTIPS	**7b**	43	28	60/40
3	**4a**	$SnBu_3$	OH	**8a**	56	24	70/30
4	**4b**	$SnBu_3$	OTIPS	**8b**	77[b]		65/35

[a]In pure isomers after chromatographic separation. [b]*cis*-**8b** + *trans*-**8b** could not be separated by silica gel chromatography.

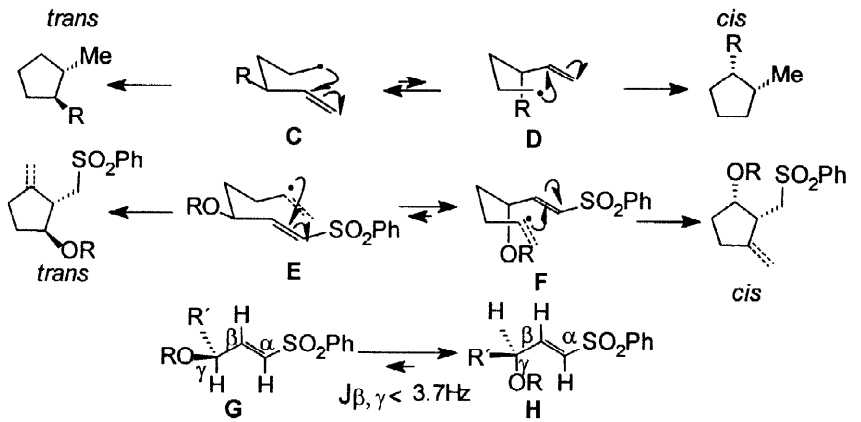
It is noteworthy that although substrates **1-4** were treated with Bu_3SnH (1.2 equiv)/AIBN (10 mol%) without using slow addition techniques or highly diluted conditions, good yields in cyclized products were obtained in all cases (70-81%). The absence of reduced starting material under these conditions indicates that the cyclization is quite fast compared to reduction, showing that the α,β-unsaturated sulfone acts as an excellent radical acceptor. This result is particularly significant in the case of substrates **2** (6-heptenyl radical precursors), whose 6-*exo* ring closure should be much slower than the 5-*exo* ring closure of substrates **1**, **3** and **4** (5-hexenyl radical precursors).

Concerning the stereoselectivity, only in the case of substrate **1a** did the cyclization occurr with very high stereoselectivity, being detected by ^{1}H-NMR showing only the *cis* cyclopentanol **5a**. With the rest of the substrates, regardless of the nature of both OR group and radical precursor, the stereoselectivity was rather low and homogeneous leading to a *cis/trans* mixture of cyclized products in which the *cis* isomer predominates (d.e.=10-40%). Moreover, the stereoselectivity appears to be hardly dependent on the temperature. Thus, the cyclization of **4a** in toluene at 0°C, promoted by reaction with Bu_3SnH in the presence of Et_3B[7] (10 equiv), afforded the same *cis/trans* ratio of isomers **8a** obtained in benzene at 80°C (entry 4, table 2).

These stereochemical results do not fit well with the Beckwith model, usually used to predict the stereoselectivity in the cyclization of substituted 5-hexenyl radicals.[8] According to this model a 4-substituted hexenyl radical should afford the *trans* rather than the *cis* isomer in majority, because of the higher stability of the chair like transition state **C** compared with transition state **D**, which presents the substituent in axial orientation[9] (scheme 2). In our case the favored formation of the *cis* isomers **5-8** would indicate a preference for participation of transition state **F** (similar to **D**) instead of transition state **E** (similar to **C**). This behavior could be due to a combination of two factors:

Firstly, the smaller 1,3-*syn*-diaxial interaction of an oxygenated function in 4 position, compared with that of the alkyl substituent usually considered in the Beckwith model, would determine a decrease in the steric difference between the axially and equatorially substituted transition states, consequently enhancing the ratio of the *cis* isomer.

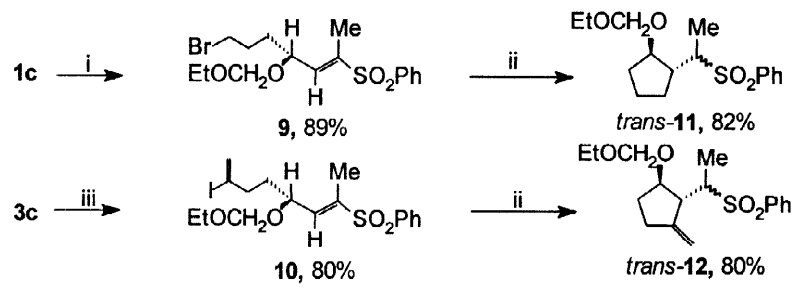
Secondly, taking into account the conformational analysis around the C_β-C_γ bond of substrates **1-4**, the conformation **H** (OR/H_α in 1,3-parallel arrangement) should be more stable than conformation **G** (H_α/H_γ in 1,3-parallel arrangement), as it is deduced from the low value of $J_{\beta,\gamma}$ (≤3.7 Hz for all substrates **1-4**). This conformational effect would favour the transition state **F** (conformationally similar to **H**) to a larger extent than **E** (conformationally similar to **G**) in the radical cyclizations. Similar conformational arguments have been invoked by other authors to explain the stereoselectivity observed in nucleophilic additions to other types of allylic alcohols.[10] However, we do not have a conclusive explanation to the fact that the cyclization of **1a** is completely *cis*-stereoselective (d.e≥96%), whereas the cyclization of the rest of the substrates is only moderately *cis* stereoselective (d.e.=10-40%).



Scheme 2

If this analysis based on conformational ground state criteria is correct, the cyclization should become *trans*-stereoselective if a carbon substituent was incorporated at the α-position of vinylsulfones **1-4**, because now in order to avoid an important R/OR 1,3-allylic strain[11] the most populated conformation around the C_β-C_γ bond would be like **G**. To confirm this assumption the α-methyl derivatives **9** and **10** were prepared in 89% and 80% yields by α-deprotonation of **1c** and **3c** with n-BuLi and LHMDS (THF, -78°C), respectively, followed by methylation with methyl iodide. As expected, substrates **9** and **10** showed a high value for $J_{\beta\gamma}$ (8.7 Hz), characteristic of the major participation of a **G** like conformation.

We were pleased to find that, effectively, the treatment of **9** and **10** with Bu_3SnH/AIBN under the usual conditions (benzene, 80°C, 3h) afforded exclusively the *trans*-cyclopentanols **11** and **12**, respectively, as an inseparable 1:1 mixture of epimers at the sulfonylic carbon (scheme 3). After flash chromatography compounds *trans*-**11** and *trans*-**12** were isolated in 82% and 80% yields, respectively.

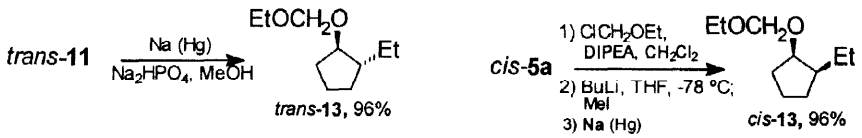


i: a) BuLi, THF, -78 °C; b) MeI, -78 °C. ii: Bu_3SnH, AIBN, C_6H_6 Δ. iii: a) LHMDS, THF, -78 °C; b) MeI, -78 °C.

Scheme 3

Configurational assignment. The *cis-trans* stereochemistry of products **5-12** has been unambiguously established by a combination of chemical correlations and NMR studies.

A) *Chemical correlations*: The silyl ethers **b** and ketal derivatives **c** have been transformed into the corresponding alcohols **a** by straighforward chemical hydrolysis. On the other hand, *trans*-**5b** was correlated with commercially available *trans*-2-methyl cyclopentanol by desulfonylation (Na-Hg, Na_2HPO_4, MeOH) and further silyl deprotection (TBAF, CH_2Cl_2). Tributyltin derivatives **8** were converted to the methylidene cyclopentanes **7** by protonolysis with AcOH in MeOH. The *trans* stereochemistry of **11** was demonstrated by its transformation into the ethoxymethyl ketal of *trans*-2-ethylcyclopentanol (*trans*-**13**) after desulfonylation (Na-Hg, MeOH, Na_2HPO_4). Additionally, for comparison purposes the diastereomer *cis*-**13** was stereoselectively prepared from *cis*-**5a** in three steps: ketal formation, methylation of the sulfonyl carbanion and desulfonylation (scheme 4).



Scheme 4

B) *NMR-studies:* As is usual in *cis/trans* 1,2-disubstituted cyclohexanes[12] and cyclopentanes[13], we observed that in ^{1}H-NMR H_1 and H_2 appeared more deshielded in the *cis* isomers than in the *trans* ones, whereas the opposite was observed in ^{13}C-NMR for the chemical shift of the CH_2 attached to the sulfonyl group.[14] Moreover, in the cyclohexanes *cis*-**6** the small value of $J_{1,2}$ (≤3.0 Hz) was indicative of a *cis* stereochemistry. These stereochemical assignments were confirmed in the case of cyclopentanes **8** by study of the NOESY spectra of *cis*-**8a** and *trans*-**8a** (figure 2). Thus, an important NOE was observed between H_1 and H_2 in the *cis* isomer, whereas this effect was absent in the *trans* isomer. Additionally, in the latter a significant nOe between OH and H_2 was detected. On the other hand, the nOe between the olefinic hydrogen and the CH_2SO_2Ph moiety demonstrated the (E) configuration of the double bond of these compounds.

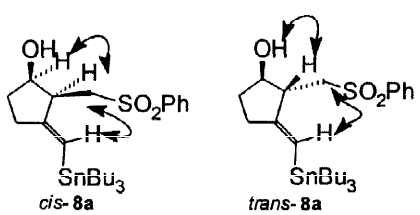
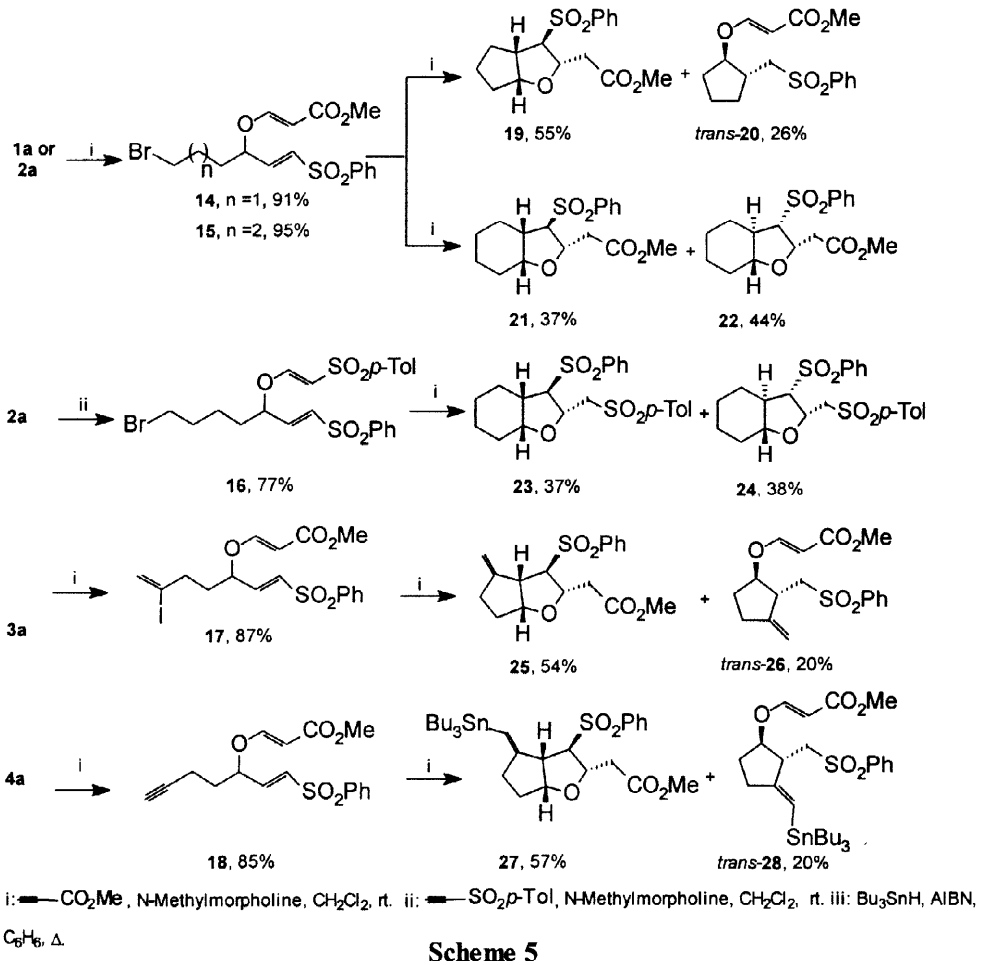


Figure 2: Significant NOE's of *cis*-**8a** and *trans*-**8a**

Cascade processes. Sequential transformations (cascade reactions) have become a rapidly expanding area of research, because the formation of two or more carbon-carbon bonds in a single step is a highly attractive method of enhancing the efficiency of organic synthesis.[15] In this regard, radical mediated and transition metal-catalyzed cascade reactions are the most frequently used processes, owing to their generality and functional group tolerance. In particular, we planned to expand the synthetic usefulness of the radical cyclizations of γ-hydroxyvinyl sulfone derivatives by their use in cascade reactions.



Scheme 5

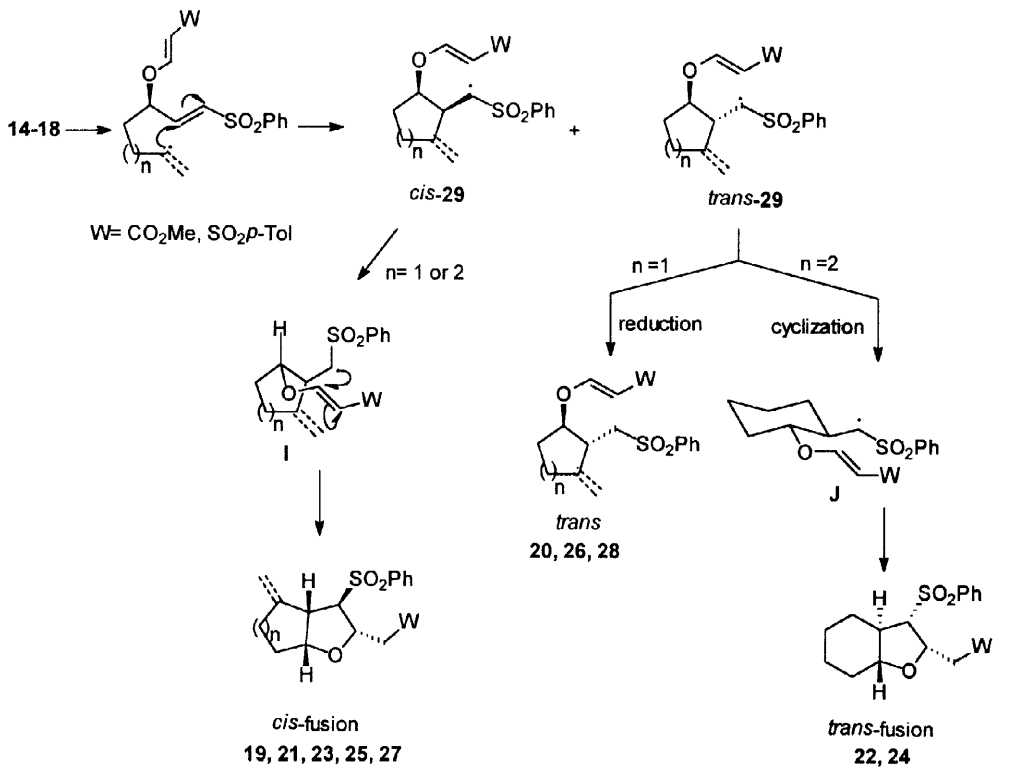
For this goal, the highly functionalized acyclic precursors **14-18** were readily prepared in high yield (77-95%) by addition of the corresponding alcohols to ethyl propiolate (or phenyl ethynyl sulfone) in the presence of N-methyl morpholine.[16] From these substrates a second carbon-carbon bond could be created by intramolecular addition of the α-sulfonyl radical intermediate to the new double bond (5-*exo*-closure), leading to the formation of [3.3.0] or [4.3.0] bicyclic products.

The compounds **14-18** were treated with Bu_3SnH/AIBN under the usual non diluted conditions, affording in all cases and in good yields two products which were readily separated by silica gel chromatography (scheme 5). The major component of each pair of compounds proved to have a bicyclic structure (compounds **19**, **21**, **23**, **25** and **27**), demonstrating that two consecutive radical cyclizations had taken place in a highly stereoselective manner. On the other hand, whereas in the cyclization of **15** and **16** (coming both from **2a**, the acyclic precursor with the longest side chain) the second product was also bicyclic (**22** and **24**, respectively), in the case of **14**, **17** and **18** the minor compound was a cyclopentane of *trans* configuration (*trans*-**20**, *trans*-**26**, and *trans*-**28**).

These results can be rationalized as is depicted in scheme 6. Like the cyclizations of substrates **1-4**, the first cyclization of substrates **14-18** would be moderately *cis*-stereoselective leading to a mixture of the α-sulfonyl radical intermediates *cis*-**29** and *trans*-**29**. In the case of the radical *cis*-**29**, regardless the size of the ring (n=1 or 2), this evolves by a fast second cyclization, giving the corresponding *cis*-fused bicyclic product ([3.3.0] or [4.3.0], respectively). In contrast, the mechanistic pathway of the radical intermediate *trans*-**29** would be quite dependent on the size of the cycle. In the case of the cyclohexane ring (n=2) its behavior is parallel to that of *cis*-**29**, evolving again by a

fast second cyclization to afford *trans*-[4.3.0]bicyclic products. However, the radical *trans*-**29** having a cyclopentane ring (n=1) evolves exclusively by hydrogen abstraction instead of cyclization, giving the corresponding *trans*-cyclopentanols (**20, 26** and **28**). This different behavior is most likely due to the strain that would be associated with the formation of a *trans*-fused [3.3.0]bicyclic derivative from *trans*-**29** (n=1).

It is noteworthy that, unlike the first radical cyclization, the second cyclization from both *cis*-**29** and *trans*-**29** is in all cases fully stereoselective, leading to the formation of a single isomer. To explain these high stereoselectivities we postulate that both cyclizations occur through the most sterically favorable chair-like transition states[8] (**I** and **J** in scheme 6). In radical *trans*-**29** (transition state **J**) all substituents would be in equatorial positions, whereas in *cis*-**29** (transition state **I**) the sulfonyl group would adopt an *anti* relationship with regard to the contiguous C-C bond.



Scheme 6

Configurational assignment. The stereochemistry of the bicyclic products has been established by NMR, the values of the coupling constants and the NOESY experiments being particularly diagnostic. In figure 3 are depicted the most important data. In *cis*-fused [4.3.0] products the low value of $J_{1,6}$ (≤3.8Hz), characteristic of the gauche arrangement of H_1 and H_6, and especially the strong NOE´s between H_1, H_6 and H_8, which prove their location on the same side of the molecule is very significant. Also, the NOE´s between H_7 and the hydrogens contiguous to the ester moiety and those of the *ortho* position of the arylsulfonyl group with H_6 and H_8 are relevant. Accordingly, the same NOE´s were observed for the *cis*-fused [3.3.0] products, although in this case owing to the presence of two fused five membered rings there is an important change in the value of the coupling constants.

By similar arguments, in the *trans* fused [4.3.0] products the *syn* arrangement of H_1, H_7, and H_8 was deduced from the strong NOE´s between them. Moreover, this assignment is supported by the NOE´s of H_6 with the arylsulfonyl group and one of the hydrogens contiguous to the ester moiety, and by the high value of $J_{1,6}$ (10.7 Hz).

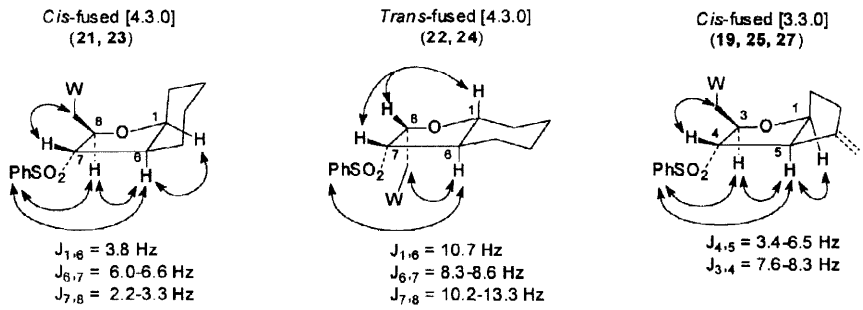


Figure 3: Significant coupling constants and NOE's of[3.3.0] and [4.3.0] bicyclic products.

In summary, by combination of the ready synthetic access to radical precursors having structures of γ-hydroxyvinyl sulfone and the efficiency of the vinyl sulfone moiety as radical acceptor, substituted cyclopentanes, cyclohexanes, 2-oxa[3.3.0] and 9-oxa[4.3.0]bicyclic products have been prepared in a highly stereoselective manner. As γ-hydroxy–α,β-unsaturated phenyl sulfones can be readily prepared in enantiomerically pure form[6c] the procedure should be readily applied to the preparation of enantiomerically pure bicyclic products.

EXPERIMENTAL SECTION

General methods. ^{1}H-NMR (200 or 300 MHz) and ^{13}C-NMR (50 or 75 MHz) spectra were recorded in $CDCl_3$. Elemental analyses were performed in this University on a Perkin-Elmer Model 2400 CHN analyser. Chromatography was performed on DC-Alufolien 0.2 mm silica gel 60-F plates (MERCK). Visualisation was accomplished with UV light and ethanolic phosphomolybdic acid solution followed by heating. Flash chromatography was performed on silica gel MERCK-60 (230-400 mesh). All reactions involving the use of *n*-BuLi, LHMDS, TIPSOTf, $ClCH_2OEt$ and Bu_3SnH were carried out under argon atmosphere with dry solvents.

Typical procedure for the preparation of (E)-γ-hydroxy-α,β-unsaturated phenylsulfones: (E)-6-Bromo-1-(phenylsulfonyl)hex-1-en-3-ol (1a) : To a solution of 1.37 g (4.68 mmol) of *p*-tolylsulfinylmethyl phenyl sulfone[6] in 10 mL of CH_2Cl_2, cooled at 0 °C, were added sequentially 0.92 mL (9.37 mmol) of piperidine and 1.16 g (7.03 mmol) of 5-bromopentanal. After being stirred for 5 h at 0 °C, the reaction mixture was quenched with 5% HCl (10 mL). The mixture was extracted with CH_2Cl_2 (2 x 15 mL) and the combined organic layers were dried (Na_2SO_4) and evaporated. The residue was purified by flash chromatography (hexane-ethyl acetate 4:1) to afford 1.21 g (81%) of **1a**. M.p.: 89-90 °C. ^{1}H-NMR: 7.90-7.85 (m, 2H), 7.63-7.52 (m, 3H), 6.95 (dd, *J*=14.7 and 3.5 Hz, 1H), 6.65 (dd, *J*=14.7 and 1.5 Hz, 1H), 4.90 (m, 1H), 3.41 (t, *J*=7.1 Hz, 2H), 2.75 (m, 1H), 2.10-1.63 (m, 4H). ^{13}C-NMR: 148.0, 139.8, 133.5, 129.8, 129.2, 127.5, 69.2, 34.3, 33.2, 28.2. Anal. Calcd for $C_{12}H_{15}BrO_3S$: C, 45.15; H, 4.74; S, 10.04; found: C, 45.28; H, 5.04; S, 10.37.

(E)-7-Bromo-1-(phenylsulfonyl)hept-1-en-3-ol (2a): By the same procedure, the reaction of 1.0 g (3.40 mmol) of *p*-tolylsulfinylmethyl phenyl sulfone, 0.67 mL (6.80 mmol) of piperidine and 0.91 g (5.10 mmol) of 6-bromohexanal afforded 0.93 g (79%) of **2a**. M.p.: 60-61 °C. ^{1}H-NMR: 7.98-7.81 (m, 2H), 7.61-7.58 (m, 3H), 6.99 (dd, *J*=15 and 3.4 Hz, 1H), 6.65 (dd, *J*=15 and 1.4 Hz, 1H), 4.50 (m, 1H), 3.51 (t, *J*=7.1 Hz, 2H), 2.75 (m, 2H), 1.9 (m, 2H) 1.6 (m, 2H). ^{13}C-NMR: 148.53, 139.8, 133.3, 129.1, 129.2, 127.2, 69.2, 34.9, 31.9, 25.4, 23.5. Anal. Calcd for $C_{13}H_{17}BrO_3S$: C, 46.86; H, 5.14; S, 9.62; found: C, 47.20; H, 5.02; S 9.39.

(E)-6-Iodo-1-(phenylsulfonyl)hepta-1,6-dien-3-ol (3a): By the same procedure, the reaction of 0.48 g (1.66 mmol) of *p*-tolylsulfinylmethyl phenyl sulfone, 0.31 mL (3.32 mmol) of piperidine and 570 mg (2.57 mmol) of 5-iodo-5-hexenal afforded 0.51 g (70%) of **3a**. M.p.: 80-81 °C. ^{1}H-NMR: 7.91-7.83 (m, 2H), 7.65-7.49 (m, 3H), 7.0 (dd, *J*=15 Hz and 3.6 Hz, 1H), 6.62 (dd, *J*=15 and 1.6 Hz, 1H), 6.05 (m, 1H), 5.71 (m, 1H), 4.91 (m, 1H), 2.51 (m, 2H), 1.63-2.0 (m, 2H). ^{13}C-NMR: 148.0, 139.7, 133.4, 129.6, 129.2, 127.3, 126.4, 110.3, 68.2, 40.6, 35.0. Anal. Calcd for $C_{13}H_{14}O_3S$: C, 41.28; H, 4.00; S, 8.48; found: C, 41.65; H, 3.98; S, 8.41.

(E)-1-(Phenylsulfonyl)hept-1-en-6-in-3-ol (4a): By the same procedure, the reaction of 0.5 g (1.71 mmol) of *p*-tolylsulfinylmethyl phenyl sulfone, 0.33 mL (3.42 mmol) of piperidine and 252 mg (2.62 mmol) of 5-hexynal afforded 0.33 g (84%) of **4a**. M.p.: 136-137 °C. ^{1}H-NMR: 7.91-7.85 (m, 2H), 7.65-7.49 (m, 3H), 7.03 (dd, *J*=14.9 and 3.5 Hz, 1H), 6.65 (dd, *J*=14.9 and 1.9 Hz, 1H), 4.51 (m, 1H), 2.41 (m, 2H), 2.01 (t, *J*=2.7 Hz, 1H), 2.95-1.63 (m, 2H). ^{13}C-NMR (CD_3OD): 150.2, 142.1, 134.7, 130.9, 130.5, 128.6, 84.0, 73.2, 51.5, 69.4, 35.9. Anal. Calcd for $C_{13}H_{14}O_3S$: C, 62.38; H, 5.64; S, 12.87; found: C, 62.39; H, 5.46; S, 13.02.

Typical procedure for the preparation of (E)-γ-(triisopropylsilyloxy)-α,β-unsaturated phenyl sulfones: (E)-6-Bromo-1-(phenylsulfonyl)-3-(triisopropylsilyloxy)-1-hexene (1b): To a solution of 100 mg (0.31 mmol) of **1a** in dry CH_2Cl_2 (3 mL) were added sequentially 55 μL (0.47 mmol) of 2,6-lutidine and 80 μL (0.37 mmol) of TIPSOTf.

After being stirred for 6 h at rt, saturated aqueous NH_4Cl (10 mL) was added. The organic layer was separated, dried (Na_2SO_4) and evaporated. The residue was purified by flash chromatography (hexane-ethyl acetate 9:1) to afford 135.7 mg (95%) of **1b**. ^{1}H-NMR: 7.88-7.83 (m, 2H), 7.71-7.52 (m, 3H), 6.96 (dd, *J*=14.7 and 3.6 Hz, 1H), 6.57 (dd, *J*=14.7 and 1.9 Hz, 1H), 4.61 (m, 1H), 3.39 (t, *J*=5.9 Hz, 2H), 1.98-1.65 (m, 4H), 0.93 (m, 21H). ^{13}C-NMR: 148.1, 140.2, 133.3, 130.5, 129.2, 127.4, 70.0, 35.1, 33.5, 26.7, 17.8, 12.0. MS *m*\z (relative intesity): 433 (M^+-^{i}Pr, 22), 431 (21), 391 (40), 389 (38), 291 (5), 289(5), 167 (17), 165 (21). HRMS (M^+-^{i}Pr) calcd for $C_{18}H_{29}BrO_3SSi$ *m*\z 433.0703 found 433.0712.

(E)-7-Bromo-1-(phenylsulfonyl)-3-(triisopropylsilyloxy)-1-heptene (2b): By the same procedure, the reaction of 100 mg (0.30 mmol) of **2a**, 52 μL (0.45 mmol) of 2,6-lutidine and 78 μL (0.36 mmol) of TIPSOTf afforded 139 mg (95%) of **2b**. ^{1}H-NMR (300MHz): 7.85-7.83 (m, 2H), 7.61-7.49 (m, 3H), 6.95 (dd, *J*=14.7 and 3.2 Hz, 1H), 6.56 (dd, *J*=14.7 and 1.6 Hz, 1H), 4.55 (m, 1H), 3.45 (t, *J*=7.2 Hz, 2H), 1.89-1.75 (m, 2H), 1.31- 1.71 (m, 4H), 1.10 (m, 21H). ^{13}C-NMR (75 MHz): 148.5, 140.4, 133.2 , 130.3, 129.2, 127.5, 70.7, 36.1, 33.2, 32.6 , 22.4, 17.8, 12.1. HRMS (FAB+) calcd for $C_{22}H_{38}{}^{81}BrO_3SSi$ 491.1485, found 491.1473.

(E)-6-Iodo-1-(phenylsulfonyl)-3-(triisopropylsilyloxy)hepta-1,6-diene (3b): By the same procedure, the reaction of 75 mg (0.19 mmol) of **3a**, 35 μL (0.29 mmol) of 2,6-lutidine and 32 μL (0.14 mmol) of TIPSOTf afforded 96.5 mg (91%) of **3b**. ^{1}H-NMR: 7.91-7.83 (m, 2H), 7.65-7.49 (m, 3H), 7.03 (dd, *J*=14.9 and 3.5 Hz, 1H), 6.62 (dd, *J*=14.9 and 1.7 Hz, 1H), 6.05 (m, 1H), 5.74 (m, 1H), 4.56 (m, 1H), 2.51(m, 2H), 2.01-1.63 (m, 2H), 0.99 (m, 21H). ^{13}C-NMR: 147.9, 141.1, 133.3, 130.7, 129.2, 127.5, 126.0, 110.7, 69.6, 39.6, 36.5, 17.6, 12.2.

(E)-1-(Phenylsulfonyl)-3-(triisopropylsilyloxy)hept-1-en-6-yne (4b): By the same procedure, the reaction of 100 mg (0.40 mmol) of **4a**, 70 μL (0.60 mmol) 2,6-lutidine and 104 μL (0.48 mmol) of TIPSOTf afforded 152 mg (93%) of **4b**. ^{1}H-NMR: 7.91-7.83 (m, 2H), 7.65-7.49 (m, 3H), 7.03 (dd, *J*=14.9 and 3.5 Hz, 1H), 6.65 (dd, *J*=14.9 and 1.8 Hz, 1H), 4.71 (m, 1H), 2.41 (m, 2H), 2.01 (t, *J*=2.7 Hz, 1H), 1.63-2.95 (m, 2H), 1.10 (m, 21H). ^{13}C-NMR: 147.5, 140.1, 133.2, 130.4, 129.0, 127.3, 83.0, 69.6, 69.2, 35.5, 17.7, 13.2, 12.2. MS *m*\z (relative intensity): 363 (M^+-^{i}Pr, 5), 255 (68), 191 (38), 121 (44), 75 (78). HRMS (M^+-^{i}Pr) calcd for $C_{19}H_{27}O_3SSi$ *m*\z 363.1454 found 363.1457.

Typical procedure for the preparation of (E)-γ-ethoxymethoxy-α,β-unsaturated phenyl sulfones: (E)-6-Bromo-3-(ethoxymethoxy)-1-(phenylsulfonyl)-1-hexene (1c): To a solution of 300 mg (0.93 mmol) of **1a** in 12 mL of dry CH_2Cl_2 were added sequentially 0.32 mL (1.86 mmol) of N,N-diisopropylethylamine and 0.34 mL (3.75 mmol) of chloromethyl ethyl ether. The solution was stirred for 12 h at rt, saturated aqueous NH_4Cl (10 mL) was added. The organic layer was separated, washed with saturated aqueous Na_2CO_3 (2 x 10 mL), dried (Na_2SO_4) and evaporated. The residue was purified by flash chromatography (hexane-ethyl acetate 8:1) to afford 319 mg (90%) of **1c**.^{1}H-NMR: 7.95-7.85 (m, 2H), 7.70-7.49 (m, 3H), 6.90 (dd, *J*=14.9 and 3.5 Hz, 1H), 6.55 (dd, *J*=14.9 and 1.6 Hz, 1H), 4.61 (m, 2H), 4.35 (m, 1H), 3.55 (m, 4H), 1.90-1.65 (m, 4H), 1.12 (t, *J*=6.8 Hz, 3H). ^{13}C-NMR: 145.4, 140.5, 133.4, 131.2, 129.3, 127.6, 93.7, 73.8, 63.9, 44.4, 31.6, 27.8, 14.9.

(E)-7-Bromo-3-(ethoxymethoxy)-1-(phenylsulfonyl)-1-heptene (2c): By the same procedure, the reaction of 100 mg (0.30 mmol) of **2a**, 0.10 mL (0.60 mmol) of N,N-diisopropylethylamine and 86 μL (0.90 mmol) of chloromethyl ethyl ether afforded 105.6 mg (90%) of **2c**. ^{1}H-NMR: 7.95-7.83 (m, 2H), 7.69-7.52 (m, 3H), 6.90 (dd, *J*=14.8 and 3.5 Hz, 1H), 6.55 (dd, *J*=14.8 and 3.5 Hz, 1H), 4.65 (m, 2H), 4.30 (m, 1H), 3.55 (m, 4H), 1.89-1.45 (m, 6H), 1.12 (t, *J*=6.8 Hz, 3H). ^{13}C-NMR: 145.8, 140.0, 133.1, 130.5, 129.0, 127.2, 93.5, 74.1, 63.4, 44.6, 33.3, 31.8 , 21.8, 14.7.

(E)-3-(Ethoxymethoxy)-6-Iodo-1-(phenylsulfonyl)hepta-1,6-diene (3c): By the same procedure, the reaction of 50 mg (0.13 mmol) of **3a**, 41 μL (0.26 mmol) of N,N-diisopropylethylamine and 35.1 μL (0.13 mmol) of chloromethyl ethyl ether afforded 51 mg (88%) of **3c**. ^{1}H-NMR: 7.90-7.83 (m, 2H), 7.63-7.51 (m, 3H), 6.90 (dd, *J*=14.9 and 3.5 Hz, 1H), 6.55 (dd, *J*=14.9 and 1.7 Hz, 1H), 6.05 (m, 1H), 5.68 (m, 1H), 4.61 (m, 2H), 4.35 (m, 1H), 3.58 (m, 2H), 2.51 (dt, *J*=7.5 and 3.1 Hz, 2H), 1.70-1.95 (m, 2H), 1.17 (t, *J*=6.9 Hz, 3H). ^{13}C-NMR: 145.3, 140.0, 133.4, 131.1, 129.2, 127.6, 126.4, 110.3, 93.8, 73.2, 63.8, 40.4, 33.9, 14.8. HRMS (FAB+) calcd for $C_{16}H_{22}IO_4S$ 437.0297, found 437.0283.

(E)-7-Bromo-4-(ethoxymethoxy)-2-(phenylsulfonyl)-2-heptene (9): 141 μL of (0.35 mmol) 2.5 M *n*-BuLi in hexane were slowly added to a solution of 122 mg (0.32 mmol) of **1c** in dry THF (3 mL). After 5 min at -78 °C, 47 μL (0.48 mmol) of MeI were added. After being stirred for 15 min at -78 °C, the mixture was treated with saturated aqueous solution of NH_4Cl (10 mL) and extracted with CH_2Cl_2 (2 x 10 mL). The combined organic layers were dried (Na_2SO_4) and concentrated. The residue was purified by flash chromatography (hexane-ethyl acetate 8:1) to afford 113 mg (89%) of **9**. ^{1}H-NMR: 7.91-7.85 (m, 2H), 7.75-7.50 (m, 3H), 6.75 (dq, *J*=1.5 and 8.7 Hz, 1H), 4.61 (m, 2H), 4.35 (m, 1H), 3.65 (m, 4H), 2.01-1.65 (m, 4H), 1.90 (d, *J*=1.5 Hz, 3H), 1.12 (t, *J*=6.8 Hz, 3H). ^{13}C-NMR: 139.8, 139.4, 138.7, 133.4, 129.2, 128.1, 93.2, 71.4, 63.6, 44.5, 31.8, 28.0, 14.9, 11.8. MS *m*\z (relative intensity): 331, 333 (M^+-$CH_2OCH_2CH_3$, 0.8), 269 (7), 211 (5), 143 (5), 77 (22), 59 (100). HRMS (M^+-$CH_2OCH_2CH_3$) calcd for $C_{13}H_{16}BrO_3S$ *m*\z 332.9980 found 332.9982.

(E)-4-(Ethoxymethoxy)-7-iodo-2-(phenylsulfonyl)octa-2,7-diene (10): To a solution of 80 mg (0.18 mmol) of **3c** in 5 mL of dry THF were added 408 μL (0.20 mmol) of 0.5 M LHMDS in THF. After 5min at -78° C, 27 μL (0.27 mmol) of MeI were added and the solution was stirred at -78° C for 15 min. After the same work up shown for the preparation of **9**, 66 mg (80%) of **10** were obtained. ^{1}H-NMR: 7.91-7.85 (m, 2H), 7.75-7.50 (m, 3H), 6.75 (dq, *J*=1.5 and 8.7 Hz, 1H), 6.01 (m, 1H), 5.71 (m, 1H), 4.61 (m, 2H), 4.35 (m, 1H), 3.65 (m, 2H), 2.55 (m, 2H), 1.93 (d, *J*=1.5 Hz, 3H), 1.85-1.62 (m, 2H), 1.12 (t, *J*=6.8 Hz, 3H). ^{13}C-NMR: 139.7, 139.3, 138.6, 133.4, 129.1, 128.0, 126.3, 110.6, 93.4, 70.5, 63.6, 40.6, 34.0, 14.9, 12.0.

Typical procedure for the reaction of γ-hydroxy-α,β-unsaturated sulfones with methyl propiolate: Methyl (E)-3-[4-bromo-1-[(E)-2-(phenylsulfonyl)ethenyl]butoxy]propenoate (14): To a solution of 710 mg (2.22 mmol) of **1a** in 10 mL of dry CH_2Cl_2, were added sequentially 255 μL (2.44 mmol) of N-methylmorpholine and 226 μL (2.44 mmol) of methyl propiolate. After stirring at rt for 8 h, the reaction mixture was treated with saturated aqueous NH_4Cl (10mL). The organic layer was separated, dried (Na_2SO_4) and evaporated. The residue was purified by flash chromatography (hexane-ethyl acetate 4:1) to afford 816.1 mg (91%) of **14**. ^{1}H-NMR: 7.90-7.85 (m, 2H), 7.63-7.52 (m, 3H), 7.42 (d, *J*= 12.2 Hz, 1H), 6.92 (dd, *J*=15.3 and 3.6 Hz, 1H), 6.67 (dd, *J*=15.3 and 1.4 Hz, 1H), 5.25 (d, *J*=12.2 Hz, 1H), 4.65 (m, 1H), 3.69 (s, 3H), 3.41 (m, 2H), 1.63 (m, 4H).^{13}C-NMR: 167.2, 160.3, 142.1, 139.3, 133.6, 131.8, 129.3, 127.5, 98.8, 79.0, 51.0, 32.5, 32.2, 27.4. . MS *m*\z (relative intesity): 373 (M^+- OCH_3, 0.2), 371 (0.2) 303 (11), 301 (10), 263 (15), 261 (16), 125 (100), 77 (80). HRMS (FAB+) calcd for $C_{16}H_{20}{}^{79}BrO_5S$ 403.0209, found 403.0214.

Methyl (E)-3-[5-bromo-1-[(E)-2-(phenylsulfonyl)ethenyl]pentyloxy]propenoate (15): By the same procedure, the reaction of 155 mg (0.46 mmol) of **2a**, 57 μL (0.51 mmol) of N-methylmorpholine and 48 μL (0.51 mmol) of methyl propiolate afforded 185 mg (95%) of **15**. ^{1}H-NMR: 7.91-7.85 (m, 2H), 7.65-7.49 (m, 3H), 7.40 (d, *J*=12.5 Hz, 1H), 6.89 (dd, *J*=14.7 and 3.5 Hz, 1H), 6.52 (dd, *J*=14.7 and 1.4 Hz, 1H), 5.25 (d, *J*=12.5 Hz, 1H), 4.56 (m, 1H), 3.65 (s, 3H), 3.35 (t, *J*=5.9 Hz, 2H), 1.91-1.72 (m, 4H), 1.40-1.61 (m, 2H).^{13}C-NMR: 167.1, 160.3, 142.4, 139.4, 133.4, 131.4, 129.1, 127.3, 98.5, 79.4, 50.9, 32.8, 32.6, 31.7, 22.8. HRMS (FAB+) calcd for $C_{17}H_{22}{}^{79}BrO_5S$ 417.0373, found 417.0371.

(E)-7-Bromo-1-(phenylsulfonyl)-3-[(E)-2-(*p*-tolylsulfonyl)ethenyloxy)]-1-heptene (16): To a solution of 108 mg (0.32 mmol) of **2a** in 8 mL of dry CH_2Cl_2 were added sequentially 38.3 μL (0.35 mmol) of N-methylmorpholine and 62.3 mg (0.35 mmol) *p*-tolylsulfonylacetilene[17]. After stirring at rt. for 48 h, the reaction mixture was treated with saturated aqueous NH_4Cl (10mL). The organic layer was separated, dried (Na_2SO_4) and evaporated. The residue was purified by flash chromatography (hexane-ethyl acetate 4:1) to afford 128 mg (77%) of **16**. ^{1}H-NMR: 7.90-7.86 (m, 2H), 7.77-7.33 (AA'BB' system, 4H), 7.65-7.49 (m, 3H), 7.41 (d, *J*=12.6 Hz, 1H), 6.89 (dd, *J*=14.9 and 3.2 Hz, 1H), 6.52 (dd, *J*=14.9 and 1.4 Hz, 1H), 5.81 (d, *J*=12.6 Hz, 1H), 4.66 (m, 1H), 3.38 (t, *J*=6.2 Hz, 2H), 2.46 (s, 3H), 1.91-1.72 (m, 2H), 1.40-1.61 (m, 2H), 1.2-0.9 (m, 2H). ^{13}C-NMR: 158.4, 148.1, 139.5, 133.8, 132.3, 129.9, 129.5, 129.3, 127.7, 127.6, 126.9, 109.7, 80.9, 33.1, 32.8, 31.9, 23.0, 21.5.

Methyl (E)-3-[4-iodo-1-[(E)-2-(phenylsulfonyl)ethenyl]-4-pentenyloxy]propenoate (17) : By the same procedure, the reaction of 53 mg (0.14mmol) of **3a** in 3 mL of dry CH_2Cl_2, 15 μL (0.15 mmol) of N-methylmorpholine and 14 μL (0.15 mmol) of methyl propiolate afforded 57 mg (87%) of **17**. ^{1}H-NMR: 7.91-7.83 (m, 2H), 7.65-7.49 (m, 3H), 7.38 (d, *J*=11.7 Hz, 1H), 6.95 (dd, *J*=14.9 and 3.5 Hz, 1H), 6.52 (dd, *J*=14.9 and 1.5 Hz, 1H), 6.05 (m, 1H), 5.71 (m, 1H), 5.25 (d, *J*=11.7 Hz, 1H), 4.59 (m, 1H), 3.67 (s, 3H), 2.49 (m, 2H), 1.83-2.1 (m, 2H). ^{13}C-NMR: 167.4, 160.4, 160.2, 142.1, 133.7, 132.1, 129.4, 127.7, 127.5, 109.0, 99.1, 78.1, 51.2, 40.1, 33.3. . MS *m*\z (relative intesity): 253 (M^+- OCH_2=CH_2CO_2Me, 10), 321 (35), 219 (16), 125 (80), 77 (100). HRMS (FAB+) calcd for $C_{17}H_{22}IO_5S$ 463.0084, found 463.0076.

Methyl (E)-3-[1-[(E)-2-(phenylsulfonyl)ethenyl)]-4-pentinyloxy]propenoate (18): By the same procedure, the reaction of 84 mg (0.34 mmol) of **4a** in 4 mL of dry CH_2Cl_2, 50 μL (0.38 mmol) of N-methylmorpholine and 34 μL (0.38 mmol) of methyl propiolate, afforded 57 mg (85%) of **17**. ^{1}H-NMR: 7.87-7.85 (m, 2H), 7.61-7.49 (m, 3H), 7.38 (d, *J*= 12.5 Hz, 1H), 6.91 (dd, *J*=15.1 and 4.3 Hz, 1H), 6.51 (dd, *J*=15.1 and 1.5 Hz, 1H), 5.23 (d, *J*= 12.5 Hz, 1H), 4.75 (m, 1H), 3.61(s, 3H), 2.22-2.35 (m, 2H), 2.0 (t, *J*=2.6 Hz, 1H), 1.88 (m, 2H). ^{13}C-NMR: 167.3, 160.5, 141.9, 140.0, 139.3, 133.6, 131.9, 129.2, 127.6, 98.9, 81.6, 78.2, 70.2, 32.4, 12.9. . MS *m*\z (relative intesity): 303 (M^+- OCH_3, 4), 233 (16), 193 (14), 125 (100), 91 (58), 77 (62). HRMS (M^+- OCH_3) calcd for $C_{16}H_{15}O_4S$ *m*\z 303.0687 found 303.0691.

Typical procedure for the radical cyclizations: *cis*-2-[(phenylsulfonyl)methyl]cyclopentanol (*cis*-5a): To a solution of 300 mg (0.93 mmol) of **1a** in 30 mL of dry benzene were added, at rt, in one portion, 240 μL (1.02 mmol) of Bu_3SnH and 16 mg (0.09 mmol) of AIBN. The resulting mixture was immediately heated at 80 °C for 3 h. The solvent was evaporated under reduced pressure and the residue was purified by flash chromatography; first eluting with hexane to separate the organotin by-products, followed by elution with hexane-ethyl acetate 6:1 to afford 169 mg (81%) of ***cis*-5a**. ^{1}H-NMR: 7.96-7.85 (m, 2H), 7.70-7.49 (m, 3H), 4.45 (m, 1H), 3.49 (dd, *J*=9.1 and 14.1 Hz, 1H), 3.89 (dd, *J*=6.6 and 14.1 Hz, 1H), 2.43 (d, *J*=1.7 Hz, 1H), 2.35-2.10 (m, 2H), 2.05-1.23 (m, 4H). ^{13}C-NMR: 139.3, 133.6, 129.2, 127.7, 72.8, 56.2, 39.5, 34.2, 29.6, 22.0.

***cis* and *trans* 2-[(Phenylsulfonyl)methyl]-1-(triisopropylsilyloxy)cyclopentane (5b):** By the same procedure, the reaction of 87 mg (0.18 mmol) of **1b** in 8 mL of dry benzene, 58 μL (0.21 mmol) of Bu_3SnH and 3.3 mg (0.02 mmol) of AIBN afforded 40 mg (55%) of *cis*-**5b** and 17 mg (23%) of *trans*-**5b** (hexane-ethyl acetate 10:1 as eluent). *cis*-**5b:** ^{1}H-NMR: 7.93-7.88 (m, 2H), 7.69-7.51 (m, 3H), 4.32 (m, 1H), 3.52 (dd, *J*=4.0 and 14.3 Hz, 1H), 3.08 (dd, *J*=8.8 and 14.3 Hz, 1H), 2.22 (m, 1H), 1.54-1.90 (m, 6H), 1.02 (m, 21H). ^{13}C-NMR (75 MHz): 140.0, 133.5, 129.1, 127.9, 78.5, 43.1, 33.6, 28.6, 26.7, 20.8, 17.9, 12.1. .MS *m\z* (relative intesity): 353 (M^+- ^{i}Pr, 100), 255 (5), 191 (6), 121 (16). *trans*-**5b:** ^{1}H-NMR (300 MHz): 7.92-7.88 (m, 2H), 7.68-7.51 (m, 3H), 3.85 (m, 1H), 3.40 (dd, *J*=2.8 and 14 Hz, 1H), 2.91 (dd, *J*=10.4 and 14 Hz, 1H), 2.08 (m, 1H), 1.54-1.90 (m, 6H), 1.02 (m, 21H). ^{13}C-NMR: 140.0, 133.4, 129.2, 127.8, 75.5, 56.5, 39.6, 34.1, 28.4, 21.0, 18.0, 12.3. MS *m\z* (relative intesity): 353 (M^+- ^{i}Pr, 100), 255 (5), 191 (6), 121 (16), 77 (25). HRMS (M^+- ^{i}Pr) calcd for $C_{18}H_{29}O_3SSi$ *m\z* 353.1611 found 353.1608.

***cis* and *trans* 1-(Ethoxymethoxy)-2-[(phenylsulfonyl)methyl]cyclopentane (5c):** By the same procedure, the reaction of 55 mg (0.14 mmol) of **1c** in 7 mL of dry benzene, 43 μL (0.16 mmol) of Bu_3SnH and 1.64 mg (0.01 mmol) of AIBN afforded 22.6 mg (52%) of *cis*-**5c** and 11 mg (27%) of *trans*-**5c** (hexane-ethyl acetate 8:1 as eluent). *cis*-**5c:**^{1}H-NMR: 7.93-7.81 (m, 2H), 7.71-7.49 (m, 3H), 4.60 (m, 2H), 4.01 (m,1H), 3.48 (q, *J*=6.5 Hz, 2H), 3.45 (dd, *J*=6.6 and 8.3 Hz, 1H), 3.24 (dd, *J*=8.3 and 14.8 Hz, 1H), 2.32 (m, 1H), 1.85-1.22 (m, 6H), 1.12 (t, *J*=6.5 Hz, 3H). ^{13}C-NMR: 140.2, 133.5, 129.2, 127.8, 94.2, 79.9, 63.5, 56.5, 38.7, 31.3, 21.6, 17.5, 15. MS *m\z* (relative intesity): 253 (M^+-OCH_2CH_3, 5), 200 (4), 157 (2), 143 (8), 81 (20). HRMS (M^+- OCH_2CH_3) calcd for $C_{13}H_{17}O_3S$ *m\z* 253.0899 found 253.0898. *trans*-**5c:** ^{1}H-NMR: 7.90-7.81 (m, 2H), 7.72-7.49 (m, 3H), 4.56, (m, 2H), 3.66 (m,1H), 3.49 (q, *J*=6.5 Hz, 2H), 3.36 (dd, *J*=3.3 and 16.1 Hz, 1H), 2.92 (dd, *J*=10.8 and 16.1 Hz, 1H), 2.21 (m, 1H), 1.90-1.27 (m, 6H), 1.12 (t, *J*=6.5 Hz, 3H). ^{13}C-NMR: 140.3, 133.5, 129.2, 127.9, 94.5, 83.3, 63.3, 59.8, 40.3, 30.9, 27.8, 26.8, 15.0.

***cis* and *trans* 2-[(Phenylsulfonyl)methyl]cyclohexanol (6a):** By the same procedure, the reaction of 67 mg (0.20 mmol) of **2a** in 10 mL of dry benzene, 66 μL (0.24 mmol) of Bu_3SnH and 33 mg (0.02 mmol) of AIBN afforded 25.5 mg (50%) of *cis*-**6a** and 15 mg (30%) of *trans*-**6a** (hexane-ethyl acetate 6:1 as eluent). *cis*-**6a:** ^{1}H-NMR: 7.98-7.91 (m, 2H), 7.71-7.51 (m, 3H), 4.10 (m, 1H), 3.37(dd, *J*= 6 and 12 Hz, 1H), 2.94 (dd, *J*=5.9 and 12 Hz, 1H), 2.3 (m, 1H), 1.8-1.2 (m, 8H). ^{13}C-NMR: 140.5, 133.5, 129.2 , 127.7, 67.9, 57.9, 36.3, 32.3, 24.4, 20.08. *trans*-**6a:** ^{1}H-NMR: 7.93-7.83 (m, 2H), 7.72-7.51 (m, 3H), 3.62 (dd, *J*=4 and 14 Hz, 1H), 3.25 (m, 1H), 2.95 (dd, *J*=6.4 and 14 Hz, 1H), 2.21-1.52 (m, 5H), 1.35 (m, 4H). ^{13}C-NMR: 140.1, 133.6, 129.2, 127.8, 71.7, 59.1, 35.8, 31.9, 25.2, 24.6, 19.1.

***cis* and *trans* 2-[(Phenylsulfonyl)methyl]-1-(triisopropylsilyloxy)cyclohexane (6b):** By the same procedure, the reaction of 78 mg (0.16 mmol) of **2b** in 5 mL of dry benzene, 83 μL (0.19 mmol) of Bu_3SnH and 3.5 mg (0.02 mmol) of AIBN afforded after chromatographic purification (hexane-ethyl acetate 8:1) 46 mg (70%) of an inseparable 60/40 mixture of *cis/trans*-**6b**. ^{1}H-NMR (*cis*-**6b** + *trans*-**6b**): 7.95-7.88 (m, *cis* + *trans*), 7.70-7.51 (m, *cis* + *trans*), 3.91 (m, 1H, *cis*), 3.70 (dd, *J*=2.2 and 13.9 Hz, 1H, *cis*), 3.43 (dd, *J*=3.1 and 14.0 Hz, 1H, *cis*), 3.39 (m, 1H, *trans*), 3.06 (dd, *J*=9.1 and 14.2 Hz, 1H, *trans*), 2.83 (dd, *J*=10.2 and 14.1 Hz, 1H, *trans*), 2.33 and 2.03-1.2 (m, *cis* + *trans*), 0.98 (m, *cis* + *trans*). ^{13}C-NMR (*cis*-**6b** + *trans*-**6b**): 141.1, 141.0, 133.3, 129.2, 129.1, 127.8, 127.7, 73.5, 71.1, 58.4, 55.2, 40.8, 36.9, 35.1, 32.2, 29.9, 26.9, 24.4, 24.0, 22.3, 21.8, 18.1, 13.5. HRMS (FAB+) calcd for $C_{22}H_{39}{}^{79}BrO_3SSi$ 411.2362, found 411.2389.

***cis* and *trans* 1-(Ethoxymethoxy)-2-[(phenylsulfonyl)methyl]cyclohexane (6c):** By the same procedure, the reaction of 60 mg (0.15 mmol) of **2c** in 7 mL of dry benzene, 50 μL (0.17 mmol) of Bu_3SnH and 3.3 mg (0.015 mmol) of AIBN afforded 22.2 mg (45%) of *cis*-**6c** and 15 mg (30%) of *trans*-**6c** (hexane-ethyl acetate 6:1 as eluent). cis-**6c:** ^{1}H-NMR: 7.91-7.88 (m, 2H), 7.70-7.53 (m, 3H,), 4.57 (m, 2H), 3.76 (m, 1H), 3.50 (m, 2H), 3.51 (dd, *J*=4.9 and 14.3 Hz, 1H), 3.51 (dd, *J*=6.9 and 14.3 Hz, 1H), 2.98 (m, 1H), 1.21-1.85 (m, 8H), 1.15 (t, *J*=7.1 Hz, 3H). ^{13}C-NMR: 140.0, 133.5, 129.2, 127.7, 93.6, 74.6, 63.4, 57.5, 35.5, 29.4, 27.3, 23.9, 20.7, 15.0. MS *m\z* (relative intesity): 253 (M^+-$CH_2OCH_2CH_3$, 6), 235 (3), 143 (2), 125 (10), 77 (25). HRMS (FAB+) calcd for $C_{16}H_{25}O_4S$ 313.1473, found 313.1488. *trans*-**6c:** ^{1}H-NMR (300 MHz): 7.91-7.88 (m, 2H), 7.70-7.51 (m, 3H), 4.61 (AB system, *J*=7.2 Hz, 2H), 3.61 (dd, *J*= 3.6 and *J*=16.0 Hz, 1H), 3.52 (q, *J*=7.2 Hz, 2H), 3.12 (m, 1H), 2.85 (dd, *J*=13.2 and 16.0 Hz, 1H), 2.30 (m, 1H), 2.06-1.85 (m, 4H), 1.7 (m, 1H), 1.57 (m, 1H), 1.18 (m, 2H), 1.15 (t, *J*=7.2 Hz, 3H). ^{13}C-NMR: 140.3, 133.4, 129.2, 127.7, 93.6, 78.6, 63.5, 58.3, 38.8, 32.0, 31.0, 24.9, 24.2, 14.9.

***cis* and *trans* 3-Methylene-2-[(phenylsulfonyl)methyl]cyclopentanol (7a):** By the same procedure, the reaction of 150 mg (0.40 mmol) **3a** in 20 mL of dry benzene, 135 μL (0.48 mmol) of Bu_3SnH and 8.8 mg (0.04 mmol) of AIBN afforded 45.3 mg (46%) of *cis*-**7a** and 30.2 mg (30%) of *trans*-**7a** (hexane-ethyl acetate 8:1 as eluent), *cis*-**7a**: ^{1}H-NMR: 8.01-7.95 (m, 2H), 7.70-7.55 (m, 3H), 5.05 (m, 1H), 4.68 (m, 2H), 3.49 (dd, *J*=12.5 and 13.6, 1H), 3.31 (dd, *J*=2.5 and 13.6, 1H), 2.91 (m, 1H), 2.75-2.11 (m, 2H), 1.98-1.85 (m, 2H). ^{13}C-NMR: 151.3, 139.3, 133.9, 129.4, 127.7, 107.0, 72.6, 55.2, 43.7, 32.0, 29.5. *trans*-**7a**: ^{1}H-NMR: : 8.01-7.95 (m, 2H), 7.70-7.55 (m, 3H), 5.05 (m, 1H), 4.76 (m, 1H), 4.25 (m, 1H), 3.44 (dd, *J*=1.7 and 14.4 Hz, 1H), 3.18 (dd, *J*=8.7 and 14.4 Hz, 1H), 2.75 (m, 1H), 2.65-2.01 (m, 4H). ^{13}C-NMR: 151.1, 138.7, 134.0, 129.4, 128.1, 107.9, 78.0, 60.5, 46.1, 32.0, 29.3.

***cis* and *trans* 3-Methylene-2-[(phenylsulfonyl)methyl]-1-(triisopropylsilyloxy)cyclopentane (7b):** By the same procedure, the reaction of 110 mg (0.20 mmol) of **3a** in 10 mL of dry benzene, 72 μL (0.24 mmol) of Bu_3SnH and

4.5 mg (0.02 mmol) of AIBN afforded 34.7 mg (43%) of *cis*-**7b** and 23.1 mg (28%) of *trans*-**7b** (hexane-ethyl acetate 8:1 as eluent). *cis*-**7b**: ^{1}H-NMR: 7.98-7.90 (m, 2H), 7.66-7.51 (m, 3H), 4.95 (m, 1H), 4.83 (m, 1H), 4.55 (q, *J*=4.1 Hz, 1H), 3.69 (dd, *J*=6.6 and 15.6 Hz, 1H), 3.12 (dd, *J*=5.0 and 15.6 Hz, 1H), 2.91 (m, 1H), 2.70-2.21 (m, 2H), 1.88-1.78 (m, 2H), 1.05 (m, 21H). ^{13}C-NMR: 150.5, 140.1, 133.5, 129.2, 127.9, 107.7, 74.3, 54.4, 44.3, 32.9, 28.5, 18.0, 12.5. HRMS (FAB+) calcd for $C_{22}H_{37}O_3SSi$ 409.2228, found 409.2232. *trans*-**7b**: ^{1}H-NMR: 7.98-7.90 (m, 2H), 7.66-7.51 (m, 3H), 5.02 (m, 1H), 4.93 (m, 1H), 4.23 (q, *J*=4.6 Hz, 1H), 3.17 (m, 2H), 2.81 (m, 1H), 2.69-2.20 (m, 2H), 1.98-1.55 (m, 2H), 1.05 (m, 21H). ^{13}C-NMR: 150.8, 139.9, 133.6, 129.2, 127.9, 109.0, 77.2, 59.3, 47.9, 32.9, 28.7, 18.0, 12.3. MS *m\z* (relative intensity): 365 (M^+-^{i}Pr, 100), 255 (23), 191 (15), 135 (16), 93 (29), 77 (31). HRMS (M^+-^{i}Pr) calcd for $C_{19}H_{29}O_3SSi$ *m\z* 365.1609 found 365.1608.

***cis* and *trans* 2-[(Phenylsulfonyl)methyl]-3-[(tributylstannyl)methylene]cyclopentanol (8a):** By the same procedure, the reaction of 143 mg (0.58 mmol) of **4a**, in 20 mL of dry benzene, 240 μL (0.70 mmol) of Bu_3SnH and 11 mg (0.05 mmol) of AIBN afforded 176 mg (56%) of *cis*-**8a** and 75.2 mg (24%) of *trans*-**8a** (hexane-ethyl acetate 8:1 as eluent). *cis*-**8a**: ^{1}H-NMR: 8.01-7.95 (m, 2H), 7.70-7.49 (m, 3H), 5.51 (m, 1H), 4.67 (m, 1H), 3.31-3.53 (m, 2H), 2.93 (m, 1H), 2.71 (d, *J*=1.6 Hz, 1H), 2.65-2.20 (m, 2H), 2.05-1.83 (m, 2H), 1.61-1.23 and 0.95 (m, 27H). ^{13}C-NMR: 159.7, 139.3, 133.8, 129.4, 127.8, 119.0, 72.6, 55.8, 45.8, 32.1, 31.9, 29.2, 27.6, 13.6, 11.9. MS *m\z* (relative intesity): 541 (M^+, 0.5) 485 (100), 429 (17), 371 (13), 261 (9), 197 (38),.93 (77), 77 (100). HRMS (M^+) calcd for $C_{25}H_{42}O_3SSn$ *m\z* 541.1794 found 591.1798. *trans*-**8a**: ^{1}H-NMR: 8.02-7.95 (m, 2H), 7.70-7.49 (m, 3H), 5.50 (m, 1H), 4.15 (m, 1H), 3.97 (d, *J*=1.5 Hz, 1H), 3.53 (dd, J=1.4 and 15.6 Hz), 3.16 (dd, J=11.2 and 15.6 Hz), 2.81 (m, 1H), 2.55-2.11 (m, 2H), 1.83-1.63 (m, 2H), 1.61-1,23 and 0.95 (m, 27H). ^{13}C-NMR: 158.4, 138.8, 134.0, 130.9, 127.5, 120.6, 78.0, 61.1, 48.4, 32.6, 31.8, 28.9, 27.6, 13.6, 11.9.

***cis* and *trans* 2-[(Phenylsulfonyl)methyl]-3-[(tributylstannyl)methylene]-1-(triisopropylsilyloxy)-cyclopentane (8b):** The reaction of 85 mg (0.21 mmol) of **4b** in 10 mL of dry benzene, 240 μL (0.25 mmol) of Bu_3SnH and 4.4 mg (0.02 mmol) of AIBN afforded a 65/35 crude mixture of *cis/trans*-**8b**. ^{1}H-NMR (*cis*-**8b** + *trans*-**8b**): 8.00-7.91 (m, *cis* + *trans*), 7.70-7.45 (m, *cis* + *trans*), 6.81 (m, 1H, *cis*), 5.09 (m, 1H, *trans*), 4.66 (m, 1H, *cis*), 4.45 (m, 1H, *trans*), 3.60 (dd, *J*= 9.1 and 13.3, 2H, *cis*), 3.13 (m, 2H, *cis* + *trans*), 2.89 (m, *cis* + *trans*), 2.65-2.21 (m, *cis* + *trans*), 1.98-1.85 (m, *cis* + *trans*), 1.78-0.70 (m, *cis* + *trans*). When this mixture was purified by flash chromatography (hexane-ethyl acetate 6:1) only the de-stannylated products 7b (77% yield) were isolated.

***trans*-1-(Ethoxymethoxy)-2-[1-(phenylsulfonyl)ethyl]cyclopentane (*trans*-11):** By the same procedure, the reaction of 100 mg (0.25 mmol) of **9** in 15 mL of dry benzene, 82 μL (0.30 mmol) of Bu_3SnH and 4.9 mg (0.03 mmol) of AIBN afforded 65 mg (82%) of *trans*-**11** as a 1:1 mixture of epimers at the sulfonylic carbon (hexane-ethyl acetate 4:1 as eluent) ^{1}H-NMR: 7.95-7.85 (m, 4H), 7.66-7.50 (m, 6H), 4.71 (m, 2H), 4.65 (m, 2H), 4.16 (q, *J*=5.2 Hz, 1H), 3.76 (q, *J*=7.1 Hz, 1H), 3.57 (m, 4H), 3.42 (dq, *J*=3.0 and 7.1 Hz, 1H), 3.15 (m, 1H), 2.41 (m, 1H), 2.33 (m, 1H), 1.85-1.45 (m, 12H), 1.20 (m, 6H), 0.92 (t, *J*=7.0 Hz, 6H). ^{13}C-NMR: 138.5, 133.4, 129.0, 128.6, 94.5, 81.0, 63.5, 63.3, 62.4, 59.9, 46.2, 43.4, 32.9, 31.1, 29.5, 26.8, 23.1, 15.0. HRMS (FAB+) calcd for $C_{16}H_{25}O_4S$ 313.1466, found 313.1473.

***trans*-1-(Ethoxymethoxy)-2-[1-(phenylsulfonyl)ethyl]-3-methylencyclopentane (*trans*-12):** By the same procedure, the reaction of 75 mg (0.16 mmol) of **12** in 10 mL of dry benzene, 55 μL (0.20 mmol) of Bu_3SnH and 3.28 mg (0.02 mmol) of AIBN afforded 43 mg (80%) of *trans*-**12** as a 1:1 mixture of epimers at the sulfonylic carbon (hexane-ethyl acetate 4:1 as eluent) ^{1}H-NMR: 7.95-7.85 (m, 4H), 7.66-7.50 (m, 6H), 5.25 (m, 1H), 5.13 (m, 1H), 5.04 (m, 2H), 4.85 (m, 6H), 4.48 (m, 1H), 4.17 (m, 1H), 3.61 (m, 4H), 3.22 (m, 2H), 2.20-2.55 (m, 2H), 1.91-1.71 (m, 2H), 1.25 (m, 12H). ^{13}C-NMR: 150.1, 139.2, 134.0, 129.2, 127.5, 107.4, 94.3, 81.2, 64.1, 63.2, 62.4, 60.0, 46.1, 43.4, 32.7, 31.1, 29.8, 26.0, 23.1, 16.1. HRMS (FAB M-OEt) calcd for $C_{15}H_{19}O_3S$ 279.1047, found 279.1054.

Cascade cyclization of 14: By the same general procedure described for the radical cyclization, the reaction of 186 mg (0.46 mmol) of **14** in 18 mL of dry benzene, 240 μL (0.55 mmol) of Bu_3SnH and 8.8 mg (0.05 mmol) of AIBN afforded 82 mg (55%) of **19** and 19.2 mg (26%) of *trans*-**20** (hexane-ethyl acetate 4:1 as eluent) **(1S*, 3R*, 4S*, 5R*)-3-[(Methoxycarbonyl)methyl]-2-oxa-4-(phenylsul-fonyl)bicyclo-[3.3.0]octane (19)** M.p.: 165-166 °C. ^{1}H-NMR : 7.98-7.91 (m, 2H), 7.70-7.51 (m, 3H), 4.51 (m, 2H), 3.70 (s, 3H), 3.34 (dd, *J*=6.5 and 8.3 Hz, 1H), 3.01 (m, 1H), 2.84 (dd, *J*=1.6 and 15.8 Hz, 1H), 2.06 (dd, *J*= 8.1 and 15.8 Hz, 1H), 1.85 (m, 1H), 2.56 (m, 4H), 1.14 (m, 1H). ^{13}C-NMR: 170.6, 138.3, 134.0, 129.4, 128.6, 84.7, 75.3, 73.2, 51.7, 46.0, 38.0, 33.2, 32.3, 23.6. MS *m\z* (relative intensity): 324 (M^+, 0.8), 293 (54), 251 (7), 182 (100), 153 (17), 123 (41), 109 (32), 77 (48). HRMS (M^+) calcd for $C_{16}H_{20}O_5S$ *m\z* 324.1036 found 324.1040. **(E)-3-[(1R*, 2R*)-2-[(phenylsulfonyl)methyl]cyclopentanyloxy]propenoate (*trans*-20):** ^{1}H-NMR: 7.96-7.89 (m, 2H), 7.70-7.51 (m, 3H), 7.47 (d, *J*=13.2 Hz, 1H), 5.18 (d, *J*=13.2 Hz, 1H), 4.25 (m, 1H), 3.71 (s, 3H), 3.23 (dd, *J*=6.2 and 13.3 Hz, 1H), 3.06 (dd, *J*=8.2 and 13.3 Hz, 1H), 2.45 (m, 1H), 2.25-1.91 (m, 2H), 1.73 (m, 2H), 1.48-1.21 (m, 2H). ^{13}C-NMR: 168.0, 161.2, 140.0, 133.8, 129.4, 128.6, 128.0, 97.6, 86.5, 59.0, 51.1, 40.4, 30.7, 30.0, 28.2, 17.2. HRMS (FAB+) calcd for $C_{16}H_{21}O_5S$ 325.1098, found 325.1109.

Cascade cyclization of 15: By the same procedure, the reaction of 137 mg (0.32 mmol) of **15** in 11 mL of dry benzene, 104 μL (0.38 mmol) of Bu_3SnH and 5.3 mg (0.03 mmol) of AIBN afforded 48 mg (37%) of **21** and 41 mg (44%) of **22** (hexane-ethyl acetate 4:1 as eluent). **(1S*, 6R*, 7S*, 8R*)-8-[(Methoxycarbonyl)-methyl]-9-oxa-7-**

(phenyl-sulfonyl)bicyclo[4.3.0]nonane (21): ^{1}H-NMR: 7.98-7.87 (m, 2H), 7.78-7.56 (m, 3H), 4.61 (m, 1H), 3.99 (m, 1H), 3.71 (s, 3H), 3.25 (dd, *J*=3.1 and 6.0 Hz, 1H), 2.51 (m, 2H), 2.0 (m, 1H), 1.0-1.82 (m, 8H). ^{13}C-NMR: 170.4, 138.0, 134.0, 129.4, 128.1, 77.1, 74.0, 70.6, 51.9, 40.5, 40.0, 29.0, 27.1, 24.3, 20.5. **(1R*, 6R*, 7S*, 8S*)-8-[(Methoxycarbonyl)methyl]-9-oxa-7-(phenylsulfonyl)-bicyclo[4.3.0]nonane (22).** ^{1}H-NMR (benzene-d_6): 7.75 (m, 2H), 6.85-7.0 (m, 3H), 5.89 (dt, *J*=4.3 and 9.7 Hz, 1H), 3.83 (dd, *J*=4.3 and 16.2 Hz, 1H), 3.51 (dd, *J*=9.2 and 16.2 Hz, 1H), 3.41 (s, 3H), 3.15 (dd, *J*= 8.6 and 10.0 Hz, 1H), 2.75 (dt, *J*=3.7 and 10.1 Hz, 1H), 2.0 (m, 1H), 1.85 (m, 1H), 1.63 (m, 4H), 1.15 (m, 1H), 0.85 (m, 2H). ^{13}C-NMR: 170.1, 139.0, 134.0, 129.1, 129.0, 85.1, 75.0, 69.0, 53.7, 47.6, 38.5, 33.5, 29.3, 26.6, 25.5.

Cascade cyclization of 16: By the same procedure, the reaction of 100 mg (0.19 mmol) of **16** in 10 mL of dry benzene, 62 μL (0.23 mmol) of Bu_3SnH and 3.5 mg (0.02 mmol) of AIBN afforded 31 mg (37%) of **23** and 32 mg (38%) of **24** (hexane-ethyl acetate 6:1 as eluent) **(1S*, 6R*, 7S*, 8R*)-9-Oxa-7-(phenylsulfonyl)-8-[(*p*-tolylsulfonyl)-methyl]bicyclo[4.3.0]nonane (23):** ^{1}H-NMR (300 MHz): 7.85 (m, 2H), 7.69-7.32 (AA'BB' system, 4H), 7.51-7.68 (m, 3H), 4.55 (m, 1H), 3.91 (m, 1H), 3.36 (dd, *J*=7.5 and 13.7 Hz, 1H), 3.19 (dd, *J*=2.2 and 6.6 Hz, 1H), 3.04 (dd, *J*=2.7 and 13.7 Hz, 1H), 2.50 (m, 1H), 2.45 (s, 3H), 1.81 (m, 2H), 1.65 (m, 2H), 1.53 (m, 2H), 1.17 (m, 2H). ^{13}C-NMR: 144.7, 138.5, 137.1, 134.2, 129.6, 129.2, 128.6, 127.7, 77.6, 73.9, 72.5, 60.7, 39.9, 29.0, 27.1, 24.0, 21.6, 19.8. **(1R*, 6R*, 7S*, 8S*)-9-Oxa-7-(phenylsulfonyl)-8-[(*p*-tolylsulfonyl)-methyl]bicyclo[4.3.0]nonane (24):** ^{1}H-NMR: 7.98-7.69 (m, 2H), 7.69-7.32 (AA'BB' system, 4H), 7.51-7.68 (m, 3H), 4.81 (m, 1H), 4.10 (m, 1H), 4.01-3.61 (m, 2H), 3.85 (dd, *J*=8.3 and 13.3 Hz, 1H), 2.51 (s, 3H), 2.0 (m, 2H), 1.01-1.82 (m, 6H). ^{13}C-NMR: 44.4, 138.2, 136.9, 134.3, 129.5, 129.3, 128.3, 128.1, 83.5, 73.0, 69.7, 57.5, 45.9, 30.5, 27.8, 25.2, 23.5, 21.6.

Cascade cyclization of 17: By the same procedure, the reaction of 50 mg (0.11 mmol) **17** in 5 mL of dry benzene, 36 μL (0.13 mmol) Bu_3SnH and 1.8 mg (0.01 mmol) of AIBN afforded. 19.5 mg (54%) of **25** and 7.2 mg (20%) of *trans*-**26** (hexane-ethyl acetate 4:1 as eluent). **(1S*, 3R*, 4S*, 5R*)-3-[(Methoxy-carbonyl)methyl]-4-methylene-2-oxa-4-(phenylsulfonyl)bicyclo[3.3.0]octane (25):** ^{1}H-NMR: 7.98-7.93 (m, 2H), 7.75-7.56 (m, 3H), 4.77 (m, 1H), 4.63 (dt, *J*=3.8 Hz y *J*=7.6 Hz, 1H), 4.51 (t, *J*=5.0 Hz, 1H), 4.09 (m, 1H), 3.66 (s, 3H), 3.56 (dd, *J*=3.9 Hz, *J*=7.6 Hz, 1H), 3.33 (m, 1H), 2.61 (dd, *J*=3.8 and 16.3 Hz, 1H), 2.56 (dd, *J*=7.0 and 16.4 Hz, 1H), 2.45 (m, 1H), 2.20 (m, 1H), 1.98 (m, 1H), 1.51-1.70 (m, 2H). ^{13}C-NMR: 171.4, 153.9, 139.2, 135.3, 130.7, 129.9, 109.7, 86.5, 78.7, 76.4, 52.9, 51.7, 40.0, 31.7, 28.9. MS *m/z* (relative intensity): 305, (M^+- OCH_3, 2), 262 (12), 194 (72), 120 (73), 93 (69), 77 (48). HRMS (M^+- OCH_3) calcd for $C_{16}H_{17}O_4S$ *m/z* 305.0850 found 305.0847. **Methyl (E)-3-[(1R*, 2R*)-3-methylene-2-[(phenylsulfonyl)methyl]cyclopentanyloxy]propenoate (*trans*-26):** ^{1}H-NMR: 8.01-7.93 (m, 2H), 7.75-7.56 (m, 3H), 7.51 (d, *J*=12.5 Hz, 1H), 5.32 (d, *J*=12.5 Hz, 1H), 5.15 (m, 1H), 4.91 (m, 1H), 4.68 (m, 1H), 3.73 (s, 3H), 3.15 (m, 2H), 2.45 (m, 1H), 1.98 (m, 2H), 1.51-1.70 (m, 2H). ^{13}C-NMR: 168.0, 160.0, 149.9, 138.9, 133.9, 129.4, 128.0, 109.5, 98.0, 85.3, 59.0, 51.1, 44.7, 29.6, 29.2. HRMS (FAB+) calcd for $C_{17}H_{21}O_5S$ 337.1098, found 337.1084.

Cascade cyclization of 18 By the same procedure, the reaction of 76 mg (0.24 mmol) of **18** in 10 mL of dry benzene, 77 μL (0.28 mmol) of Bu_3SnH and 3.5 mg (0.02 mmol) of AIBN afforded 87.3 mg (57%) of **27** and 29.3 mg (20%) of *trans*-**28** (hexane-ethyl acetate 8:1 as eluent). **(1S*, 3R*, 4S*, 5R*)-3-[(Methoxy-carbonyl)methyl]-2-oxa-5-[(E)-(tributylstannyl)methylene]-4-(phenylsulfonyl)bicyclo[3.3.0]octane (27):** ^{1}H-NMR: 7.98-7.93 (m, 2H), 7.75-7.56 (m, 3H), 4.93 (m, 1H), 4.69 (dt, *J*=3.8 and *J*=7.8Hz, 1H), 4.52 (t, *J*=4.9Hz, 1H), 3.67 (s, 3H), 3.50 (dd, *J*=3.4 and *J*=7.6, 1H), 3.34 (m, 1H), 2.73 (dd, *J*=3.6 and 15.9 Hz, 1H), 2.56 (dd, *J*=6.4 and 15.9 Hz, 1H), (2.47 (m, 1H), 2.10 (m, 2H), 1.68 (m, 1H), 1.51-0.60 (m, 27H). ^{13}C-NMR: 170.3, 161.7, 138.2, 134.0, 130.7, 129.4, 128.8, 121.7, 85.4, 75.8, 53.1, 51.7, 39.5, 32.3, 30.5, 29.0, 27.1, 13.6, 9.7. **Methyl (E)-3-[(1R*, 2R*)-2-[(phenyl-sulfonyl)methyl]-3-[(E)-(tributylstannyl)methylene]cyclopentanyloxy]prope-noate (*trans*-28):** ^{1}H-NMR: 8.01-7.93 (m, 2H), 7.75-7.56 (m, 3H), 7.56 (d, *J*=12.5 Hz, 1H), 5.72 (m, 1H), 5.31 (d, *J*=12.5 Hz, 1H), 4.71 (m, 1H), 3.73 (s, 3H), 3.25 (m, 2H), 2.49-2.15 (m, 3H), 2.03 (m, 2H), 1.51-0.60 (m, 27H). ^{13}C-NMR: 160.9, 138.9, 133.9, 130.8, 129.4, 128.8, 128.1, 122.8, 97.9, 85.2, 71.7, 59.5, 47.2, 31.3, 30.9, 29.0, 27.1, 13.6, 9.7.

***cis*-1-(Ethoxymethoxy)-2-ethylcyclopentane (*cis*-13):** To a solution of 56 mg (0.18 mmol) of *cis*-**11** (prepared from *cis*-**5a**) in 4 mL of MeOH were added 500 mg of 4% powdered Na(Hg) and 96 mg of Na_2HPO_4. The suspension was stirred at rt. for 2 h. The reaction was poured into water and extracted with ether (20 mL). The combined organic layers were dried (Na_2SO_4) and evaporated, to afford 29 mg (96%) of *cis*-**13**. ^{1}H-NMR: 4.71 (m, 2H), 4.05 (m, 1H), 3.66 (m, 2H), 1.85-1.28 (m, 9H), 1.22 (t, *J*=7.5 Hz, 3H), 0.91 (t, *J*=7.3, 3H). ^{13}C-NMR: 93.6, 79.4, 63.1, 47.0, 31.5, 28.9, 21.9, 21.6, 15.0, 13.0.

***trans*-1-(Ethoxymethoxy)-2-ethylcyclopentane (*trans*-13):** The same procedure described above was applied to the reaction of 50 mg (0.16 mmol) of trans-**11**, 500 mg of 4% Na(Hg) and 96 mg of Na_2HPO_4. in 4mL of MeOH, affording 26 mg (96%) of *trans*-**13**. ^{1}H-NMR: 4.70 (m, 2H), 3.75 (m, 1H), 3.59 (m, 2H), 1.91-1.05 (m, 9H), 1.22 (t, *J*=7.5 Hz, 3H), 0.92 (t, *J*=7.3, 3H). ^{13}C-NMR: 93.8, 83.3, 62.9, 47.5, 31.7, 27.5, 26.6, 22.2, 15.0, 12.5.

Acknowledgement. We thank *Dirección General de Investigación Científica y Técnica* (DGICYT) for financial support (PB93-244).

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