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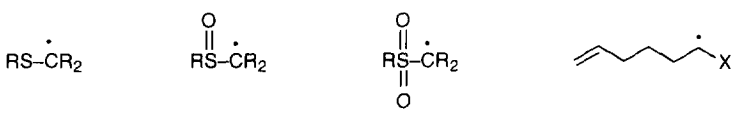
Generation and Intramolecular Cyclization of α-Sulfinyl and α-Sulfonyl Radicals

Bor-Wen Ke, Chao-Hsiung Lin and Yeun-Min Tsai*

Department of Chemistry, National Taiwan University, Taipei, Taiwan 106, Republic of China

Abstract: α-Phenylsulfinyl and α-Phenylsulfonyl radicals are generated by the reactions of α-chlorosulfoxides and α-chlorosulfones with tributyltin hydride, respectively. High reaction concentration (0.2 M) is required to ensure efficient generations of these radicals. The 5-*exo*-type intramolecular cyclizations of these radicals are studied. The cyclization is most successful when the olefin is terminally substituted with an ester group. The sulfinyl group only induces mild diastereoselectivity on the cyclization. © 1997 Elsevier Science Ltd.

Radicals carrying α-sulfur functionalities (**1–3**) are potentially useful reactive intermediates. Because of the rich chemistry that organosulfur compounds exhibit,[1] the combination of sulfur functionalities with radicals will greatly enhance their synthetic utilities.[2-4] We have been interested in the study of intramolecular cyclizations of this type of radicals and performed a systematic comparison of the electron rich α-sulfenyl radical **4** and the more electron deficient radicals **5** and **6**.[5,6] On the other hand, the influence of the chiral center of the sulfinyl group in **5** on the stereoselectivity of the cyclization has also been examined.[6] Others have also independently developed novel application of α-sulfinyl radicals in asymmetric synthesis.[3a] Herein, we report our full investigation about α-sulfinyl and α-sulfonyl radicals.



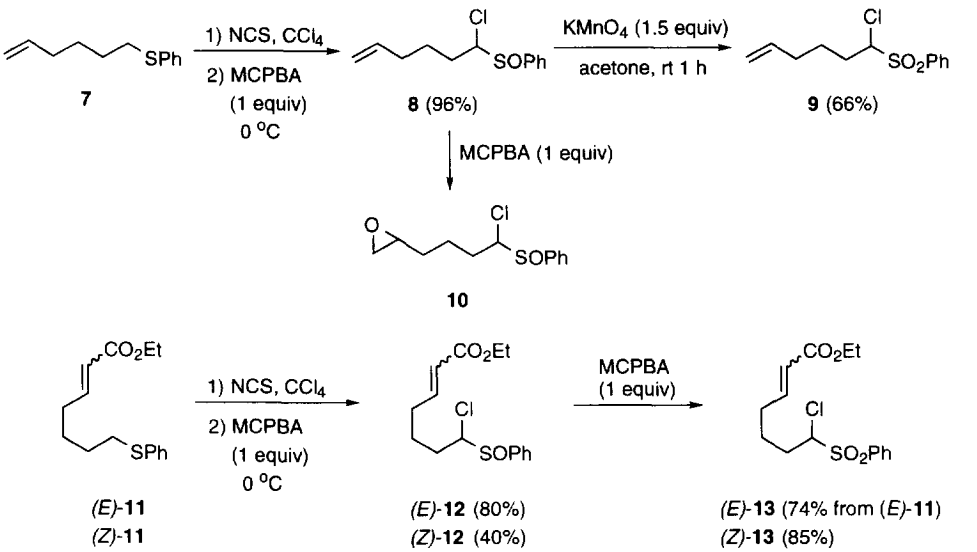
1 **2** **3**

4 X = SR
5 X = SOR
6 X = SO_2R

RESULTS AND DISCUSSION

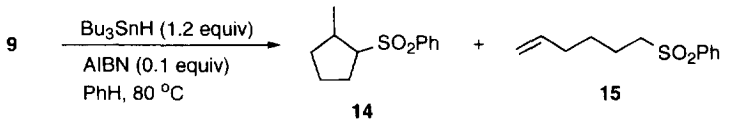
As shown in Scheme 1, sulfide **7**[7] was treated with NCS in carbon tetrachloride to give the corresponding α-chlorosulfide.[8] The crude chloride was oxidized with one equivalent of MCPBA at 0 °C to afford α-chlorosulfoxide **8** in 96% yield. In contrast to α-chlorosulfide, sulfoxide **8** was stable and could be purified by

Scheme 1



column chromatography. Sulfoxide **8** existed as a mixture of two diastereomers in a ratio of 2.2/1 determined by ^{1}H NMR integration. Since both isomers generate the same radical following treatment with tributyltin hydride, this mixture was used in subsequent cyclization studies. Further oxidation of **8** with another equivalent of MCPBA at room temperature did not give the desired sulfone **9**, but instead gave epoxide **10**. The presence of an electron withdrawing chlorine substituent probably made the oxidation of sulfoxide more difficult. We found that potassium permanganate in acetone[9] successfully oxidized the sulfoxide **8** to afford **9** in 66% yield. Similarly, (*E*)-**11**[5] was converted to (*E*)-**12** in 80% yield as a mixture of two diastereomers

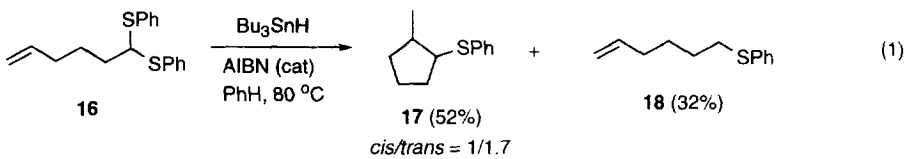
Table 1. Optimization of the Reaction Condition for Radical Cyclization of α-Chlorosulfone **9**.[a]



entry	final concentration (M)[a]	addition time of Bu_3SnH (hr)	**14** (% yield)[b,c]	**15** (% yield)[b]	total yield[d]
1[e]	0.05	6	54	19	73
2	0.05	1	53	31	84
3	0.2	2	46	31	77

[a]A solution of tributyltin hydride and AIBN in benzene was added over the specified time to a refluxing solution of **9** in benzene. Equal amount of benzene was used to prepare the two solutions, and the concentration specified here is the final concentration relative to **9**. [b]Based on the ^{1}H NMR integration. [c]The *cis/trans* ratio was determined by ^{1}H NMR integration to be 2.3/1. [d]Isolation yield. [e]Unreacted **9** was recovered in 20%.

(3.2/1). Because the olefin in (*E*)-**12** was electron deficient and less prone to be oxidized by MCPBA, treatment of (*E*)-**12** with another equivalent of MCPBA successfully gave sulfone (*E*)-**13**. With two equivalents of MCPBA, the chlorosulfide obtained from (*E*)-**11** could be oxidized directly to give (*E*)-**13** in 74% yield. Similarly, (*Z*)-**12** (40%; a 2/1 mixture) and (*Z*)-**13** (85% from (*Z*)-**12**) were also prepared.



We have chosen sulfone **9** to optimize the radical cyclization reaction with tributyltin hydride because the structure determination of the products was easier than the case of **8**. Initial attempts of the cyclization showed that **9** was unreactive. However, with careful deoxygenation of the solvent, the reaction of **9** with tributyltin hydride occurred. As shown in entry 1 of Table 1, under the normally used concentration of 0.05 M for radical cyclizations and slow addition (6 h) of tributyltin hydride (1.2 equiv), the reaction gave 73% yield of a mixture of **14** and **15** (**14/15** = 2.8/1) in addition to 20% of recovered **9**. Under the same condition, the cyclization of dithioacetal **16** (eq 1) afforded 52% of **17** and 32% of **18**.[5] Compared with **16**, the cyclization of **9** gave relatively more **14** than **15**. The observed difference can be explained by considering α-sulfonyl radical as an electrophilic radical, therefore the rate of cyclization to an electron rich alkyl substituted olefin would be faster.[10] However, the highly electron deficient α-sulfonyl radical should be very unstable[11] and is more difficult to generate. We believed that this is the reason that the cyclization of **9** was not completed in entry 1 (Table 1). In order to facilitate the generation of α-sulfonyl radical, we shortened the addition time of stannane (entry 2) to 1 h, and the reaction was complete. However, due to higher in situ concentration of tributyltin hydride, lower ratio of **14/15** was observed. We also performed the reaction at a higher concentration (entry 3) of 0.2 M and still obtained 46% of cyclization. Since the latter condition is operationally very practical, we used this condition for the rest of our studies except that 1.5 equivalent of tributyltin hydride was used.

To provide authentic samples of the cyclization products for structural determination, we prepared *cis*- and *trans*-**17** from *trans*- and *cis*-**19**, respectively, using Walker's method (Scheme 2).[5,12] Oxidation of *cis*- and *trans*-**17** with one equivalent of MCPBA gave *cis*-**20** (78%) and *trans*-**20** (75%), which existed as a pair of

Scheme 2

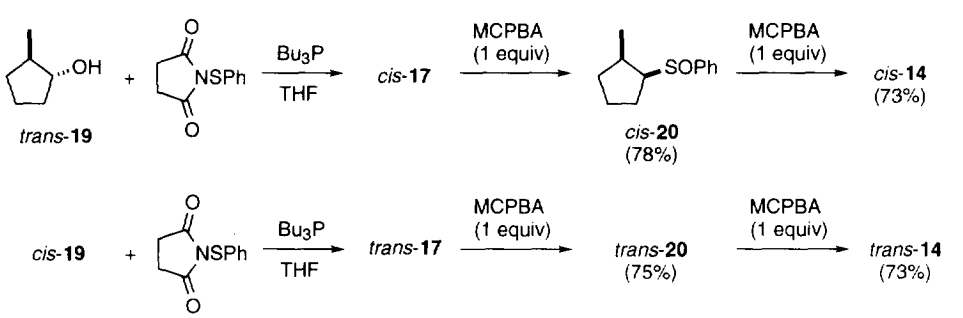
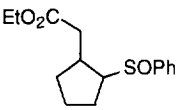
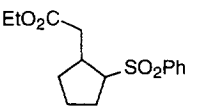
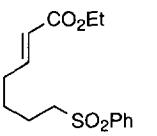


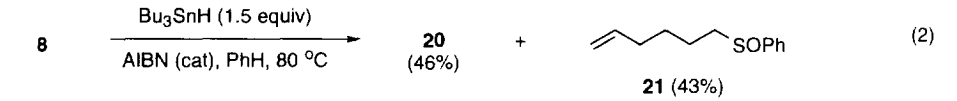
Table 2. Radical Cyclizations of **12** and **13**.

entry	starting material	cyclization product (% yield; *cis/trans* ratio)[a]	diastereomeric ratio[a] *cis*	diastereomeric ratio[a] *trans*	reduction product (% yield)
1	*(E)*-**12**	 **22** (68; 3/1)	4/1	2/1	–
2	*(Z)*-**12**	**22** (88; 2.3/1)	5/1	1.3/1	–
3	*(E)*-**13**	 **23** (81; 2.3/1)	–	–	 *(E)*-**24** (2)
4	*(Z)*-**13**	**23** (73; 1/1)	–	–	*(Z)*-**24** (1)

[a]Ratio was determined by ^{1}H NMR integration.

diastereomers in a ratio of 1.5/1 and 2/1, respectively. Oxidation of *cis*- and *trans*-**20** with another equivalent of MCPBA yielded *cis*-**14** (73%) and *trans*-**14** (73%).

The reaction of **8** with tributyltin hydride gave 46% of cyclization product **20** and 43% of **21** (eq 2). Since we have authentic samples of the isomers of **20**, the *cis/trans* ratio was determined as 1/1 by ^{1}H NMR integration. The *cis*-isomer of **20** was a 1.5/1 mixture of two diastereomers, and *trans*-**20** was a 2/1 mixture. Thus, the sulfur chiral center only induced moderate selectivity for the cyclization.



(2)

As shown in Table 2, with α,β-unsaturated ester as radicalphile, α-chlorosulfoxide **12** and α-chlorosulfone **13** cyclized effectively with a little or no reduction product. Interestingly, both electron-withdrawing and electron-donating substituents on olefin enhance the rate of intramolecular cyclizations of α-sulfonyl radical. These results indicated that α-sulfonyl radical was on the borderline between nucleophilic and electrophilic behavior.[13]

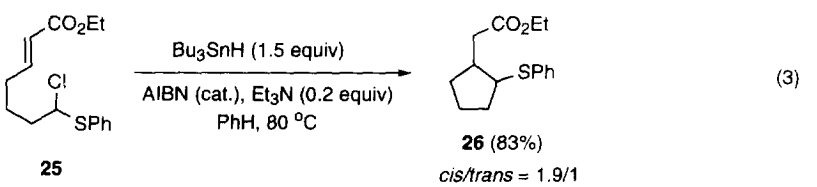
Previously, we studied the cyclization of α-chlorosulfide **25** (eq 3) and obtained sulfide **26** as a 1.9/1 mixture of *cis/trans* isomers.[5] We took this mixture and oxidized it with MCPBA to afford successively **22** and **23** with the same *cis/trans* ratio as **26**. Therefore, we were able to obtain spectroscopic information of

Table 3. Characteristic ^{1}H NMR Absorptions of **14**, **20**, **22** and **23**.[a]

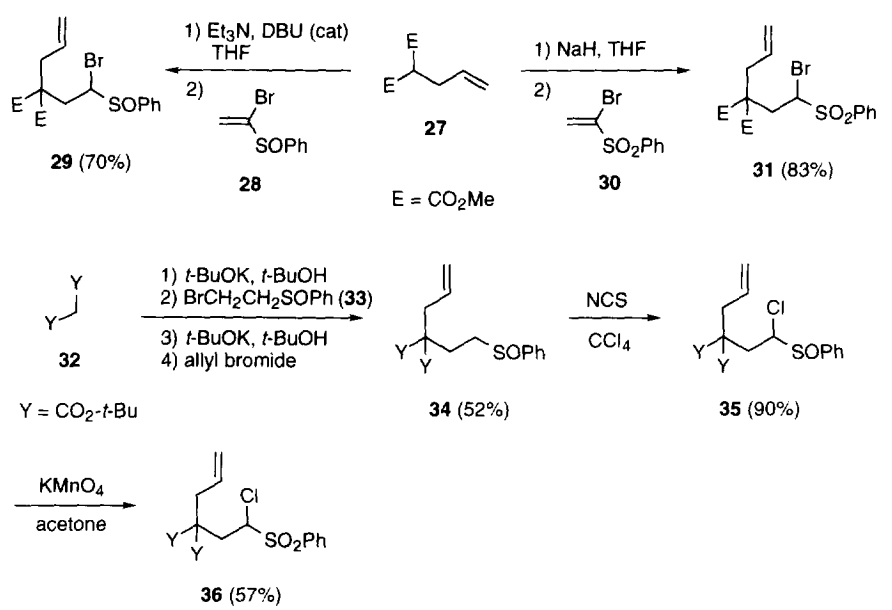
		chemical shift of SC-H (δ)	
entry	compound	*cis*-isomer	*trans*-isomer
1	**14**	3.37	3.10
2	**23**	3.61	3.45
3	**20**[b]	2.88 (major); 3.09 (minor)	2.49 (major); 2.67 (minor)
4	**22**[b]	3.20 (major); 3.30 (minor)	2.83 (major); 2.93 (minor)

[a]The spectra were taken using $CDCl_3$ as solvent. [b]Two diastereomers epimeric at sulfur.

these isomers and determined the product ratio as shown in Table 2. A particularly informative signal is the ^{1}H NMR absorption of the proton on the carbon with sulfur group attached. In accordance with the trend observed in sulfone **14** and sulfoxide **20** (Table 3, entries 1, 3), the signal of the *cis*-isomer always occurred at lower field while that of the *trans*-isomer occurred at higher field. Similar trend was also observed in the case of sulfides.[5]



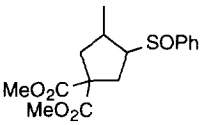
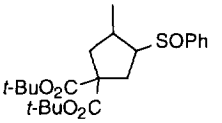
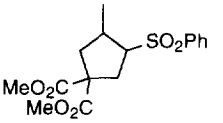
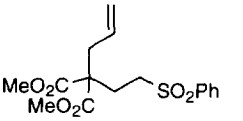
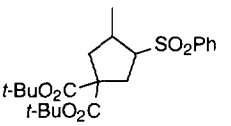
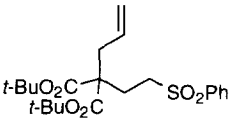
Scheme 3



We also synthesized **29**, **31**, **35** and **36** as shown in Scheme 3. Deprotonation of malonate **27** with base followed by Michael addition to sulfoxide **28**[14] or sulfone **30**[15] gave α-bromosulfoxide **29** (70%) and α-bromosulfone **31**[4c] (83%). The sulfoxide **29** we obtained was a mixture of two diastereomers (3.3/1) and was used directly in our cyclization study. Successive alkylation of di-*t*-butyl malonate (**32**) with 2-bromoethyl phenyl sulfoxide (**33**) and allyl bromide in *t*-butanol with potassium *t*-butoxide as base gave sulfoxide **34** (52%). Chlorination of **34** was carried out with NCS in carbon tetrachloride[8] and afforded α-chlorosulfoxide **35** in 90% yield as a 3/1 mixture of two diastereomers. Oxidation of **35** with potassium permanganate in acetone[9] gave α-chlorosulfone **36** in 57% yield.

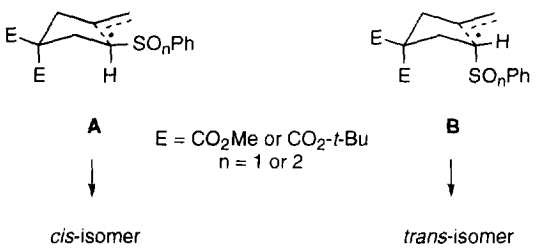
Due to the Thorpe-Ingold effect,[16] the cyclizations shown in Table 4 all gave higher ratio of cyclization product versus reduction product as compared with the model cases of **8** and **9**. There was no apparent difference by using bromide or chloride. α-Bromosulfoxide **29** (entry 1) and α-bromosulfone **31** (entry 3)

Table 4. Radical Cyclizations of **29**, **31**, **35** and **36**.

entry	starting material	cyclization product (% yield; *cis/trans* ratio)[a]	diastereomeric ratio[a] *cis*	*trans*	reduction product (% yield)
1	**29**	 **37** (60; 1.9/1)	2/1	1.5/1	–
2	**35**	 **38** (51; 1/1.8)	3/1	1.5/1	**34** (9)
3	**31**	 **39** (70; 2.3/1)	–	–	 **40** (4)
4	**36**	 **41** (62; 1.2/1)	–	–	 **42** (5)

[a]Ratio was determined by ^{1}H NMR integration.

gave higher *cis/trans* ratios of cyclization products as compared with the cyclizations of **35** (entry 2) and **36** (entry 4). This was probably due to the size difference of methoxycarbonyl and *t*-butoxycarbonyl groups. Assuming the cyclization occurs through chair transition states[17] as shown in **A** and **B**, the bulkier *t*-butoxycarbonyl group at pseudoaxial position will increase the energy of **A** and **B**. Therefore, the rates of cyclizations in the cases with *t*-butoxycarbonyl groups will be slower than those with methoxycarbonyl groups. In fact, more reduction products were observed in entries 2 and 4, indicating that these cyclizations are slower. In our previous study of α-sulfenyl radical,[5] we observed that more *cis*-product was obtained for a faster cyclization. Likewise, similar trend was observed in present study. In the cases of faster cyclizations as in **29** and **31**, higher *cis/trans* product ratios were observed. The corresponding **35** and **36** gave lower *cis/trans* product ratios, indicating that these cyclizations were slower. One may expect that the bulkier *t*-butoxycarbonyl group increases the 1,3-diaxial interaction in **B** and disfavors the formation of the *trans*-isomer. However, our results indicated that this factor is not decisive in controlling the *cis/trans* ratio.



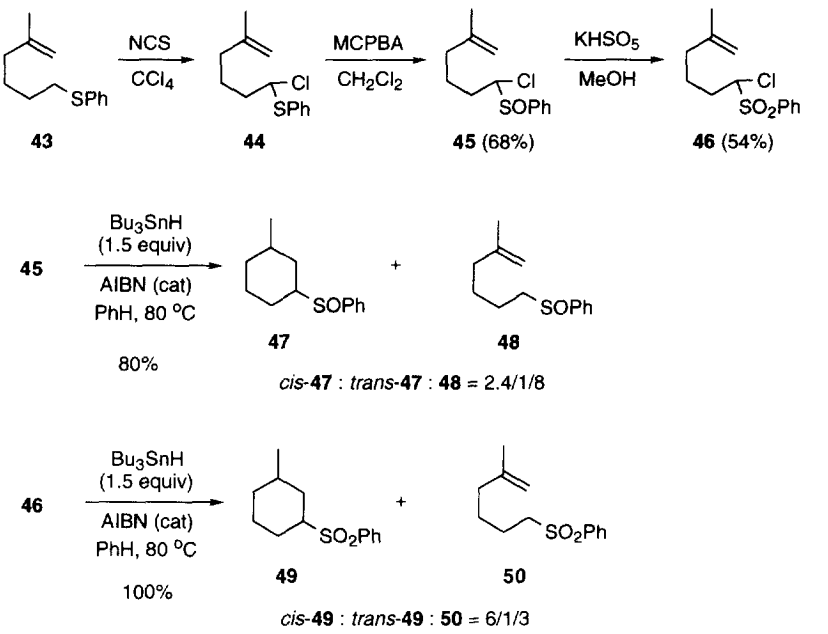
The stereochemistry of the cyclization products was determined by comparison of their ^{1}H NMR spectra with those of sulfoxide **20** and sulfone **14** (Table 5). The absorptions of the protons on the carbon with sulfur attached and the methyl group on the cyclopentane ring all appeared at lower field for the *cis*-isomers. Most characteristically, the chemical shifts of the ring-methyl groups of all the *cis*-isomers appeared at δ 1.37 ± 0.14, and those of the *trans*-isomers appeared at δ 0.98 ± 0.19.

Table 5. Comparison of ^{1}H NMR Absorptions of **37**, **38**, **39** and **41** with **20** and **14**.

		absorption of SC-H (δ)		absorption of ring-methyl (δ)	
entry	compound	*cis*-isomer	*trans*-isomer	*cis*-isomer	*trans*-isomer
1	**37** (major)	3.05	2.89	1.50	0.89
	37 (minor)	3.29	2.79	1.38	1.16
2	**38** (major)	3.02	2.87	1.45	0.92
	38 (minor)	2.67	2.60	–[a]	1.08
3	**20** (major)	2.88	2.49	1.40	0.79
	20 (minor)	3.09	2.67	1.23	1.00
4	**39**	3.55	3.21	1.35	1.01
5	**41**	3.50	3.23	1.35	1.02
6	**14**	3.37	3.10	1.28	0.94

[a]Overlapped with the signals of *t*-butyl group at 1.35–1.50 and could not be identified clearly.

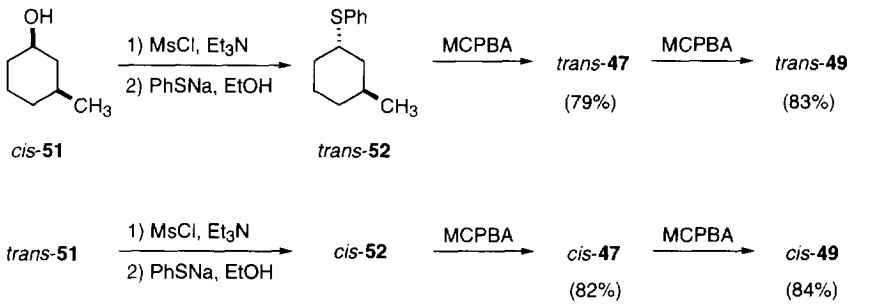
Scheme 4



Subsequently, we synthesized α-chlorosulfoxide **45** and α-chlorosulfone **46** (Scheme 4) using methods described above, except that the oxidation of **45** was accomplished by using potassium hydrogen persulfate in methanol.[18] The reaction of **45** with tributyltin hydride gave a mixture (80% yield) of 6-*endo* cyclization product **47** and reduction product **48**. The ratio of *cis*-**47** : *trans*-**47** : **48** was determined by ^{1}H NMR integration to be 2.4/1/8. The *cis*- and *trans*-isomer of **47** existed as a mixture of diastereomers, and we were not able to determine their ratios. Interestingly, the sulfone **46** cyclized even better to give in quantitative yield of a mixture of **49** and **50**. The ratio of *cis*-**49** : *trans*-**49** : **50** was determined to be 6/1/3.

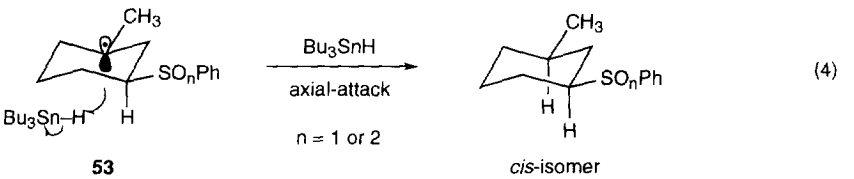
The structures of these products were unequivocally determined by alternative synthesis. As shown in Scheme 5, *cis*- and *trans*-**51** were converted to the corresponding mesylates followed by displacement of the

Scheme 5



mesylate groups with phenylthio groups with inversion of the stereochemistry to give *trans*- and *cis*-**52**, respectively. Oxidation with MCPBA provided us authentic samples of the isomers of **47** and **49**.

It is well known in the 5-hexenyl radical system that alkyl substituent at C-5 severely hinders the attack of radical at C-5 and reduces the rate of 5-*exo*-trig cyclization by about 50 fold.[19,20] Therefore, it is not surprising that α-chlorosulfide **44** did not give any cyclization product when treated with tributyltin hydride. In comparison with **44**, α-chlorosulfone **46** gave a very high portion of 6-*endo* cyclization product. We believe that this was due to the higher reactivity of α-sulfonyl radical. Although 5-*exo* cyclization in the case of **46** was also slow, the 6-*endo* cyclization was fast enough to compete with straight reduction. The 6-*endo* cyclization would give radical **53** (eq 4) and the stereochemical course was determined at the hydrogen abstraction step. It is well known that cyclohexyl radical prefers to abstract hydrogen from axial site,[21] therefore, *cis*-isomer was expected to be the major product derived from **53**.



53 *cis*-isomer (4)

In summary, we found that α-sulfinyl and α-sulfonyl radicals could be generated by the reaction of α-chorosulfoxide and α-chlorosulfone with tributyltin hydride. Intramolecular cyclizations were best performed in high concentration (0.2 M) with tributyltin hydride added slowly over 2 h. These radicals appeared to be quite reactive and gave moderate to good yields of cyclization products. The cyclizations were most successful when the olefin was substituted with an ester group or when the system exhibited Thorpe-Ingold effect. The chiral center on sulfoxide only imposed moderate stereo-control of the cyclization. In the case of α-sulfonyl radical, when 5-*exo* cyclization was slow as in **46**, 6-*endo* cyclization became the predominate process.

EXPERIMENTAL SECTION

^1H and ^{13}C NMR spectra were recorded on Bruker AM-300WB (operating at 300 and 75 MHz) or Bruker AC-200 (operating at 200 and 50 MHz) spectrometers with tetramethysilane (TMS) or $CHCl_3$ as internal standards and $CDCl_3$ as the solvent. Infrared spectra were taken on a Perkin-Elmer 938G instrument. Mass spectra were recorded on a Finigan TSQ-46C spectrometer. Exact masses were recorded on JEOL JMS-HX 110 or SX-102A spectrometers. Combustion analyses were done on a Perkin-Elmer 240C instrument. Benzene and THF were distilled from sodium benzophenone ketyl under N_2. All reactions were performed under a blanket of N_2 or Ar.

6-Chloro-6-phenylsulfinyl-1-hexene (8). A mixture of 403 mg (2.09 mmol) of **7**[7] and 289 mg (2.16 mmol) of NCS in 4.5 mL of carbon tetrachloride was stirred at room temperature overnight and then filtered. The filtrate was concentrated in vacuo to give 487 mg of a pale yellow oil. The oil was dissolved in 4 mL of dichloromethane and cooled in an ice-water bath followed by the addition of 430 mg (2.12 mmol) of MCPBA (85%) in one portion. The reaction mixture was stirred at the same temperature for 1.5 h and then partitioned between 100 mL of dichloromethane and 40 mL of 1 N sodium hydroxide solution. The organic layer was

dried ($MgSO_4$) and concentrated. The residual oil was chromatographed over silica gel (eluted with hexane/ethyl acetate, 88/12) to give 491 mg (96%) of **8** (a 2.2/1 mixture of two diastereomers) as a pale yellow oil: IR (neat) 3060, 2929, 1635, 1440, 1085, 1050, 913, 748, 688 cm^{-1}; ^1H NMR (300 MHz) δ 1.45–1.65 (m, 1 H), 1.65–1.87 (m, 1 H), 1.87–2.33 (m overlapped with q, J = 7 Hz, at 2.06, 4 H, allyl and others), 4.38 (dd, J = 10, 2 Hz, 1 H, CHCl of the major isomer), 4.51 (dd, J = 9, 4 Hz, 1 H, CHCl of the minor isomer), 4.90 (br d, J = 10 Hz, 1 H, $=CH_2$), 4.99 (br d, J = 18 Hz, 1 H, $=CH_2$), 5.73 (ddt, J = 18, 10, 7 Hz, 1H, =CH–), 7.45–7.58 (m, 3 H, ArH), 7.60–7.75 (m, 2 H, ArH); ^{13}C NMR (50 MHz) of the major isomer at δ 24.9, 30.4, 32.3, 76.3, 115.1, 125.0, 128.6, 131.3, 136.9, 139.0, minor isomer at δ 24.1, 29.8, 32.2, 76.7, 115.1, 125.3, 128.7, 131.6, 136.7, 140.5; MS *m/z* (rel intensity) 243 (M^++1, 12), 205 (3), 126 (100), 97 (3), 78 (20), 55 (5); HRMS calcd for $C_{12}H_{15}ClOS$ *m/z* 242.0532, found 242.0526.

6-Chloro-6-phenylsulfonyl-1-hexene (9). To 124 mg (0.48 mmol) of **8** in 2 mL of acetone was added 93 mg (0.48 mmol) of potassium permanganate and the resulting mixture was stirred at room temperature overnight. The resulting reaction mixture was filtered over Celite, and the filtrate was partitioned between 50 mL of ether and 30 mL of brine. The ether layer was dried ($MgSO_4$) and concentrated. The residual oil was chromatographed over silica gel (eluted with hexane/ethyl acetate, 83/17) to give 87 mg (66%) of **9** as a pale yellow oil: IR (neat) 3061, 2952, 1636 , 1581, 1443, 1300, 1144, 1085 cm^{-1}; ^1H NMR (200 MHz) δ 1.40–1.92 (m, 3 H), 2.08 (q, J = 7 Hz, 2 H, allyl), 2.28–2.48 (m, 1 H), 4.63 (dd, J = 10, 2 Hz, 1 H, CHCl), 4.95 (br d, J = 10 Hz, 1 H, $=CH_2$), 5.01 (br d, J = 18 Hz, 1 H, $=CH_2$), 5.72 (ddt, J = 18, 10, 7 Hz, 1H, =CH–), 7.56 (t, J = 7 Hz, 2 H, ArH), 7.68 (t, J = 7 Hz, 1 H, ArH), 7.95 (d, J = 7 Hz, 2 H, ArH). ^{13}C NMR (50 MHz) δ 25.0, 29.9, 32.6, 74.7, 115.6, 129.0, 129.9, 134.5, 135.0, 137.1. Anal. Calcd for $C_{12}H_{15}ClO_2S$: C, 55.69; H, 5.84. Found: C, 55.53; H, 6.09.

Ethyl (*E*)-7-phenylsulfinyl-2-heptenoate ((*E*)-12) Using the same procedure for the preparation of **8**, the reaction of (*E*)-**11**[5] (0.316 g, 1.20 mmol) gave 0.300 g (80%) of (*E*)-**12** (a 3.2/1 mixture of two diastereomers) as a pale yellow oil: IR (neat) 3075, 2932, 1706, 1649, 1187, 1085, 1046 cm^{-1}; ^1H NMR (200 MHz) δ 1.30 (t, J = 7 Hz, 3 H, CH_3), 1.55–2.10 (m, 4 H), 2.25 (q, J = 7 Hz, 2 H, allyl), 4.15 (q, J = 7 Hz, 2 H, OCH_2), 4.42 (dd, J = 9, 3 Hz, 1 H, CHCl of the major isomer), 4.58 (dd, J = 9, 3 Hz, 1 H, CHCl of the minor isomer), 5.82 (d, J = 15 Hz, 1 H, =CHCO), 6.91 (dt, J = 15, 7 Hz, 1 H, =CH), 7.50–7.85 (m, 5 H, ArH); ^{13}C NMR (50 MHz) δ 14.1, 23.7, 24.5, 30.4, 30.5, 31.1, 60.1, 76.4, 75.9, 122.1, 125.4, 125.6, 127.8, 128.8, 128.9, 129.2, 131.8, 132.1, 147.2, 166.2. Anal. Calcd for $C_{15}H_{19}ClO_3S$: C, 57.22; H, 6.08. Found: C, 57.19; H, 6.03 .

Ethyl (*Z*)-7-phenylsulfinyl-2-heptenoate ((*Z*)-12) Using the same procedure for the preparation of **8**, the reaction of (*Z*)-**11**[5] (85 mg, 0.32 mmol) gave 41 mg (40%) of (*Z*)-**12** (a 2/1 mixture of two diastereomers) as a pale yellow oil: IR (neat) 3057, 2938, 1711, 1651, 1308, 1274, 1187, 1089, 1050 cm^{-1}; ^1H NMR (200 MHz) δ 1.29 (t, J = 7 Hz, 3 H, CH_3), 1.45–2.10 (m, 3 H), 2.14–2.48 (m, 1 H), 2.50–2.95 (m, 2 H), 4.15 (q, J = 7 Hz, 2 H, OCH_2), 4.48 (dd, J = 11, 3 Hz, 1 H, CHCl of the minor isomer), 4.65 (dd, J = 11, 3 Hz, 1 H, CHCl of the major isomer), 5.78 (d, J = 11 Hz, 1 H, =CHCO), 6.15 (dt, J = 11, 7 Hz, 1 H, =CH), 7.40–7.96 (m, 5 H, ArH); ^{13}C NMR (50 MHz) of the major isomer at δ 14.2, 23.9, 27.8, 29.8, 59.9, 74.2, 121.0, 128.3, 129.0, 132.8, 137.9, 147.9, 166.1, the minor isomer at δ 14.2, 24.9, 27.3, 29.6, 59.9, 72.2, 121.0,

127.8, 129.9, 134.4, 135.1, 146.4, 165.9. Anal. Calcd for $C_{15}H_{19}ClO_3S$: C, 57.22; H, 6.08. Found: C, 57.19; H, 6.03 .

Ethyl (*E*)-7-phenylsulfonyl-2-heptenoate ((*E*)-13) Using the same procedure for the preparation of **8** except using two equivalents of MCPBA, the reaction of (*E*)-**11**[5] (92 mg, 0.35 mmol) gave 85 mg (74%) of (*E*)-**13** as a pale yellow oil: IR (CH_2Cl_2) 3055, 2933, 1706, 1649, 1325, 1308, 1152, 998 cm^{-1}; ^1H NMR (200 MHz) δ 1.27 (t, *J* = 7 Hz, 3 H, CH_3), 1.60–1.96 (m, 3 H), 2.25 (q, *J* = 7 Hz, 2 H, allyl), 2.30–2.51 (m, 1 H), 4.15 (q, *J* = 7 Hz, 2 H, OCH_2), 4.60 (dd, *J* = 10, 3 Hz, 1 H, CHCl), 5.80 (d, *J* = 17 Hz, 1 H, =CHCO), 6.87 (dt, *J* = 17, 7 Hz, 1 H, =CH), 7.53–7.73 (m, 3 H, ArH), 7.90-7.96 (m, 2 H, ArH); ^{13}C NMR (50 MHz) δ 14.2, 24.4, 30.0, 31.1, 60.2, 74.4, 122.3, 129.1, 129.9, 134.5, 135.0, 147.0, 166.2. Anal. Calcd for $C_{15}H_{19}ClO_4S$: C, 54.46; H, 5.79. Found: C, 54.38; H, 5.69.

Ethyl (*Z*)-7-phenylsulfonyl-2-heptenoate ((*Z*)-13) A mixture of 56 mg (0.18 mmol) of (*Z*)-**12** and 36 mg (0.18 mmol) of MCPBA (85%) was stirred at room temperature overnight. The resulting mixture was partitioned between 30 mL of dichloromethane and 10 mL of 1 N sodium hydroxide solution. The organic layer was dried (Na_2SO_4) and concentrated. The residual oil was chromatographed over silica gel (eluted with hexane/ethyl acetate, 85/15) to give 49 mg (85%) of (*Z*)-**13** as a pale yellow oil: IR (neat) 3056, 2927, 1705, 1637, 1324, 1194, 1152 cm^{-1}; ^1H NMR (200 MHz) δ 1.28 (t, *J* = 7 Hz, 3 H, CH_3), 1.55–2.00 (m, 3 H), 2.32–2.55 (m, 1 H), 2.55–2.90 (m, 2 H), 4.18 (q, *J* = 7 Hz, 2 H, OCH_2), 4.78 (dd, *J* = 12, 3 Hz, 1 H, CHCl), 5.81 (d, *J* = 11 Hz, 1 H, =CHCO), 6.17 (dt, *J* = 11, 7 Hz, 1 H, =CH), 7.60 (t, *J* = 8 Hz, 2 H, ArH), 7.73 (t, *J* = 8 Hz, 1 H, ArH), 7.96 (d, *J* = 8 Hz, 2 H, ArH); ^{13}C NMR (50 MHz) δ 14.2, 25.0, 27.4, 29.9, 60.0, 74.3, 121.1, 129.1, 130.0, 132.1, 134.5, 148.0, 166.2; MS *m/z* (rel intensity) 331 (M^++1, 50), 319 (100), 291 (10), 285 (50), 257 (25), 223 (75), 199 (7), 189 (28), 177 (50), 171 (5), 159 (15), 149 (35), 143 (55), 131 (10), 125 (45), 113 (58), 107 (30), 99 (35), 95 (25), 85 (7), 77 (90), 67 (10), 43 (10); HRMS calcd for $C_{15}H_{19}ClO_4S$ *m/z* 330.0693, found *m/z* 330.0683.

General procedure for radical cyclization reactions. A solution of tributyltin hydride (1.5 mmol) and AIBN (0.1 mmol) in deoxygenated benzene (2.5 mL) was added over 2 h to a refluxing solution of the substrate (1 mmol) in deoxygenated benzene (2.5 mL). The resulting solution was heated for another 2 h and then directly concentrated in vacuo. A few drops of wet triethylamine was added to the residue,[22] and the resulting mixture was chromatographed over silica gel using hexane/ethyl acetate as eluent to separate the products.

Radical cyclization of 8: *cis*-2-methylcyclopentyl phenyl sulfoxide (*cis*-20), *trans*-2-methylcyclopentyl phenyl sulfoxide (*trans*-20), and 6-phenylsulfinyl-1-hexene (21). According to the general procedure of radical cyclization, the reaction of **8** (87 mg, 0.36 mmol) gave 35 mg (46%) of **20** (*cis/trans* = 1/1) and 32 mg (43%) of **21**. By comparison with authentic samples prepared from oxidation of *cis*-**17** and *trans*-**17**, *cis*-**20** was a 1.5/1 mixture of two diastereomers and *trans*-**20** was a 2/1 mixture of two diastereomers. *cis*-**20**: IR (neat) 3039, 2960, 1440, 1084, 1067, 1037, 1021, 998 cm^{-1}; ^1H NMR (300 MHz) of the minor isomer at δ 1.11–1.63 (m overlapped with d, *J* = 8 Hz, at 1.23, 5 H, $CH_3$and others), 1.42–1.60 (m, 2 H), 1.69–1.85 (m, 2 H), 2.60–2.68 (m, 1 H), 3.09 (td, *J* = 9, 7 Hz, 1 H, CHS), 7.43–7.47 (m, 3 H,

ArH), 7.64–7.68 (m, 2 H, ArH), and the major isomer at δ 1.36–1.52 (m overlapped with d, J = 7 Hz, at 1.40, 6H, CH_3 and others), 1.70–1.82 (m, 2 H), 2.12–2.37 (m, 2 H), 2.88 (q, J = 7 Hz, 1 H, CHS), 7.38–7.56 (m, 5 H, ArH); ^{13}C NMR (75 MHz) of the major isomer at δ 15.3, 22.4, 24.6, 33.9, 35.7, 70.3, 125.2, 129.0, 131.2, 144.0, and the minor isomer (50 MHz) at δ 16.2, 21.2, 23.9, 34.8, 38.0, 67.9, 124.3, 127.6, 128.9, 130.2; MS *m/z* (rel intensity) 209 (M^++1, 100), 126 (82), 110 (2), 97 (2), 83 (30), 78 (8), 67 (2), 55 (20); HRMS calcd for $C_{12}H_{16}OS$ *m/z* 208.0922, found *m/z* 208.0924. ***trans*-20**: IR (neat) 3051, 2949, 1439, 1084, 1042cm^{-1}; ^1H NMR (200 MHz) δ 0.79 (d, J = 7 Hz, 3 H, CH_3 of the major diastereomer), 1.00 (d, J = 7 Hz, 3 H, CH_3 of the minor diastereomer),1.12–2.82 (m, 7 H), 2.49 (ddd, J = 20, 15, 7 Hz, 1 H, CHS of the major diastereomer), 2.67 (q, J = 7 Hz, 1 H, CHS of the minor diastereomer), 7.43–7.63 (m, 5 H, ArH); ^{13}C NMR (75 MHz) δ 19.2, 21.0, 22.1, 22.3, 24.2, 25.1, 27.7, 28.5, 33.7, 35.0, 70.6, 71.5, 124.4, 124.7, 128.9, 130.6, 130.8, 143.3; MS *m/z* (rel intensity) 209 (M^++1, 100), 126 (82), 110 (2), 97 (2), 83 (30), 78 (8), 67 (2), 55 (20); HRMS calcd for $C_{12}H_{16}OS$ *m/z* 208.0922, found *m/z* 208.0924. **21**: IR (neat) 3061, 2917, 1630, 1435, 1084, 1067, 1042 cm^{-1}; ^1H NMR (200 MHz) δ 1.35–1.90 (m, 4 H), 2.04 (q, J = 7 Hz, 2 H, allyl), 2.77 (t, J = 7 Hz, 2 H, CH_2S), 4.91 (br d, J = 10 Hz, 1 H, $=CH_2$), 4.95 (br d, J = 18 Hz, 1 H, $=CH_2$), 5,73 (ddt, J = 18, 10, 7 Hz, 1 H, =CH–), 7.42–7.69 (m, 5 H, ArH); ^{13}C NMR (50 MHz) δ 21.5, 27.7, 33.1, 57.0, 115.0, 123.9, 129.1, 130.8, 137.7, 143.9; MS *m/z* (rel intensity) 209 (M^++1, 100), 191 (80), 136 (3), 126 (75), 117 (2), 9 (3), 83 (15), 78 (20), 67 (3), 55 (50); HRMS calcd for $C_{12}H_{16}OS$ *m/z* 208.0922, found *m/z* 208.0922.

Radical cyclization of 9: *cis*-2-methylcyclopentyl phenyl sulfone (*cis*-14), *trans*-2-methylcyclopentyl phenyl sulfone (*trans*-14), and 6-phenylsulfonyl-1-hexene (15). According to the general procedure of radical cyclization, the reaction of **9** (186 mg, 0.72 mmol) gave 59 mg (77%) of a mixture of **14** and **15**. By comparison with authentic samples prepared from oxidation of *cis*-**17** and *trans*-**17**, the ratio determined by ^1H NMR integration was *cis*-**14** : *trans*-**14** : **15** = 1 : 2.3 : 1.7. *cis*-**14** : IR (neat) 3058, 2960, 1443, 1381, 1302, 1145, 1085 cm^{-1}; ^1H NMR (200 MHz) δ 1.28 (d, J = 7 Hz, 3 H, CH_3), 1.54–2.29 (m, 6 H), 2.41–2.68 (m, 1 H), 3.37 (q, J = 8 Hz, 1 H, CHS), 7.48–7.70 (m, 3 H, ArH), 7.58–8.01 (m, 2 H, ArH); ^{13}C NMR (50 MHz) δ 15.8, 22.4, 26.1, 34.2, 36.7, 67.1, 127.9, 129.0, 133.2, 140.8; MS *m/z* (rel intensity) 225 (M^++1, 70), 183 (3), 143 (52), 125 (25), 91 (2), 83 (100), 67 (5), 55 (15); HRMS calcd for $C_{12}H_{17}O_2S$ *m/z* 225.0949, found *m/z* 225.0948. *trans*-**14** : IR (neat) 3058, 2956, 1443, 1299, 1144, 1085 cm^{-1}; ^1H NMR (200 MHz) δ 0.94 (d, J = 7 Hz, 3 H, CH_3), 1.13–1.33 (m, 2 H), 1.42–2.21 (m, 4 H), 2.48 (m, 1 H), 3.10 (dt, J = 9, 7 Hz, 1 H, CHS), 7.49–7.68 (m, 3 H, ArH), 7.88 (d, J = 8 Hz, 2 H, ArH); ^{13}C NMR (50 MHz) δ 22.7, 24,8, 28.3, 35.4, 35.7, 70.8, 128.5, 129.1, 133.4, 139.0; MS *m/z* (rel intensity) 225 (M^++1, 70), 183 (3), 143 (52), 125 (25), 91 (2), 83 (100), 67 (5), 55 (15); HRMS calcd for $C_{12}H_{17}O_2S$ *m/z* 225.0949, found *m/z* 225.0948. **15**: IR (neat) 3066, 2932, 1636, 1443, 1303, 1146, 1085 cm^{-1}; ^1H NMR (200 MHz) δ 1.41 (quintet, J = 7 Hz, 2 H, CH_2), 1.62–1.78 (m, 2 H), 1.98 (q, J = 7 Hz, 2 H, allyl), 3.05 (dd, J = 8, 5 Hz, 2 H, CH_2S), 4.89 (br d, J = 10 Hz, 1 H, $=CH_2$), 4.91 (br d, J = 18 Hz, 1 H, $=CH_2$), 5.66 (ddt, J = 18, 10, 7 Hz, 1H, =CH–), 7.52 (t, J = 7 Hz, 2 H, ArH), 7.62 (t, J = 7 Hz, 1 H, ArH), 7.86 (d, J = 7 Hz, 2 H, ArH); ^{13}C NMR (50 MHz) δ 22.0, 27.3, 32.9, 56.0, 115.2, 127.9, 129.2, 133.5, 137.4, 139.0; MS *m/z* (rel intensity) 225 (M^++1, 100), 136 (3), 123 (2), 83 (52); HRMS calcd for $C_{12}H_{16}O_2S$ *m/z* 224.0871, found *m/z* 224.0869.

Radical cyclization of (*E*)-12: ethyl *cis*-2-(2-phenylsulfinylcyclopentyl)acetate (*cis*-22), and ethyl *trans*-2-(2-phenylsulfinylcyclopentyl)acetate (*trans*-22). According to the general procedure of radical cyclization, the reaction of *E*-**12** (189 mg, 0.602 mmol) gave 114 mg (68%) of a mixture of *cis*-**22** and *trans*-**22** in a ratio of 3/1. The *cis*-isomer was a 4/1 mixture of two diastereomers and the *trans*-isomer was a 2/1 mixture of two stereoisomers. *cis*-**22**: IR of the major isomer (neat) 2969, 1727, 1606, 1037, and IR of the minor isomer (neat) 3051, 2953, 1722, 1645, 1578, 1439, 1173, 1083, 1039, 749 cm^{-1}; ^1H NMR (200 MHz) of the major isomer δ 1.30 (t, J = 7 Hz, 3 H, CH_3), 1.39–1.54 (m, 3 H), 1.76–1.88 (m, 2 H), 2.04–2.25 (m, 1 H), 2.56–2.79 (m, 1 H), 2.82 (dd, J = 18, 7 Hz, 1 H, CH_2CO), 3.14 (dd, J = 18, 10 Hz, 1 H, CH_2CO), 3.20 (q, J = 7 Hz, 1 H, CHS), 4.20 (q, J = 7 Hz, 2 H, OCH_2), 7.42–7.54 (m, 5 H, ArH); ^1H NMR (200 MHz) of the minor isomer δ 1.29 (t, J = 7 Hz, 3 H, CH_3), 1.35–2.05 (m, 6 H), 2.55 (dd, J = 15, 9 Hz, 1 H, CH_2CO), 2.78–3.02 (m, 1 H), 3.20 (dd, J = 15, 5 Hz, 1 H, CH_2CO), 3.30 (q, J = 7 Hz, 1 H, CHS), 4.18 (q, J = 7 Hz, 2 H, OCH_2), 7.45–7.55 (m, 3 H, ArH), 7.66–7.76 (m, 2 H, ArH); ^{13}C NMR (50 MHz) of the major isomer at δ 14.2, 20.3, 24.1, 32.6, 35.5, 40.1, 60.5, 65.6, 124.0, 128.8, 130.1, 143.0, 172.9, the minor isomer at δ 14.2, 22.8, 26.0, 31.4, 34.6, 38.8, 60.4, 68.5, 125.5, 129.2, 131.5, 143.6, 172.5; MS *m/z* (rel intensity) 280 (M^+, 50), 263 (12), 250 (30), 234 (85), 218 (60), 199 (2), 184 (20), 175 (15), 167 (35), 155 (82), 149 (80), 141 (23), 125 (100), 109 (98), 97 (12), 81 (55), 77 (30), 67 (50), 61 (2), 57 (10); HRMS calcd for $C_{15}H_{20}O_3S$ *m/z* 280.1133, found *m/z* 280.1136. *trans*-**22**: IR (neat) 3046, 2962, 1726, 1443, 1182, 1087, 1042 cm^{-1}; ^1H NMR (200 MHz) δ 1.18–1.76 (m overlapped with two t, J = 7 Hz, at 1.24 and 1.28, 6 H, CH_3 and others), 1.78–2.40 (m overlapped with d, J = 7 Hz, at 2.34, 5 H, CH_3 and others), 2.52–3.00 (m overlapped with sextet, J = 7 Hz, at 2.63, and q, J = 7 Hz, at 2.83 (CHS of the major diastereomer), and q, J = 9 Hz, at 2.93 (CHS of the minor diastereomer), 2 H), 3.98–4.22 (two overlapped q, J = 7 Hz, at 4.07 (minor) and 4.13 (major), 2 H, OCH_2), 7.40–7.71 (m, 5 H, ArH); ^{13}C NMR (50 MHz) δ 14.2, 22.9, 24.3, 24.9, 26.2, 32.7, 33.0, 35.8, 36.7, 37.4, 39.4, 60.2, 60.5, 67.8, 68.9, 124.2, 124.7, 129.0, 130.7, 131.1, 143.0, 171.7; MS *m/z* (rel intensity) 280 (M^+, 50), 263 (12), 250 (30), 234 (85), 218 (60), 199 (2), 184 (20), 175 (15), 167 (35), 155 (82), 149 (80), 141 (23), 125 (100), 109 (98), 97 (12), 81 (55), 77 (30), 67 (50), 61 (2), 57 (10); HRMS calcd for $C_{15}H_{20}O_3S$ *m/z* 280.1133, found *m/z* 280.1136.

Radical cyclization of (*Z*)-12. According to the general procedure of radical cyclization, the reaction of (*Z*)-**12** (41 mg, 0.13 mmol) gave 32 mg (88%) of a mixture of *cis*-**22** and *trans*-**22** in a ratio of 2.3/1. The *cis*-isomer was a 5/1 mixture of two diastereomers and the *trans*-isomer was a 1.3/1 mixture of two stereoisomers.

Radical cyclization of (*E*)-13: ethyl *cis*-2-(2-phenylsulfonylcyclopentyl)acetate (*cis*-23), ethyl *trans*-2-(2-phenylsulfonylcyclopentyl)acetate (*trans*-23), and ethyl (*E*)-6-phenylsulfonyl-2-heptenoate ((*E*)-24). According to the general procedure of radical cyclization, the reaction of (*E*)-**13** (95 mg, 0.29 mmol) gave 69 mg (81%) of a mixture of *cis*-**23** and *trans*-**23** in a ratio of 2.3/1, and 2 mg (2%) of (*E*)-**24**. *cis* and *trans*-**23**: IR (neat) 3063, 2962, 1729, 1446, 1304, 1179, 1145, 1086, 723, 692 cm^{-1}; ^1H NMR (200 MHz) δ 1.18–1.30 (m, overlapped with two t, J = 7 Hz, at 1.24 for the *trans* isomer, and at 1.25 for the *cis* isomer, 3 H, CH_3), 1.20–2.18 (m, 6 H), 2.28 (dd, J = 16, 9 Hz, 1 H, CH_2CO_2 of the *trans* isomer), 2.52 (dd, J = 16, 5 Hz, 1 H, CH_2CO of the *trans* isomer), 2.65 (dd, J = 16, 9 Hz, 1 H, CH_2CO of the *cis* isomer), 2.70–2.82 (m, 1 H), 3.18 (dd, J = 16, 5 Hz, 1 H, CH_2CO of the *cis* isomer), 3.45 (td, J = 7, 5.5 Hz, 1 H, CHS of the *trans* isomer), 3.61 (q, J = 7 Hz, 1 H, CHS of the *cis* isomer), 4.02–4.20 (two overlapped q, J =

7 Hz, at 4.10 for the *trans* isomer, and 4.12 for the *cis* isomer, 2 H, OCH_2), 7.50–7.70 (m, 3 H, ArH), 7.80–7.96 (m, 2 H, ArH); ^{13}C NMR (50 MHz) δ 14.1, 22.6, 24.6, 27.4, 28.1, 31.4, 32.7, 34.6, 37.0, 38.9, 39.1, 60.3, 65.2, 67.8, 128.0, 128.5, 129.1, 133.3, 133.6, 136.4, 139.9, 171.7, 172.6. Anal. Calcd for $C_{15}H_{20}O_4S$: C, 60.78; H, 6.80. Found: C, 60.65; H, 6.56. (*E*)-**24** : IR (neat) 3050, 2929, 1708, 1644, 1440, 1364, 1304, 1266, 1184, 1086, 1040 cm^{-1}; ^1H NMR (200 MHz) δ 1.19 (t, *J* = 7 Hz, 3 H, CH_3), 1.37–1.85 (m, 4 H), 2.12 (br q, *J* = 7 Hz, 2 H, allyl), 2.71 (t, *J* = 7 Hz, 2 H, CH_2S), 4.08 (q, *J* = 7 Hz, 2 H, OCH_2), 5.70 (br d, *J* = 16 Hz, 1 H, =CHCO), 6.80 (dt, *J* = 16, 7 Hz, 1 H, =CH–), 7.35–7.60 (m, 5 H, ArH); ^{13}C NMR (50 MHz) δ 14.1, 21.5, 26.9, 31.4, 56.6, 60.0, 121.8, 123.8, 129.1, 130.8, 143.6, 147.6, 166.2; MS *m/z* (rel intensity) 297 (M^++1, 25), 287 (5), 273 (3), 250 (40), 223 (5), 199(3), 155 (7), 143 (5), 127 (8), 108 (98), 99 (5), 80 (100), 67 (5), 57 (5), 43 (5); HRMS calcd for $C_{15}H_{20}O_4S$ *m/z* 296.1083, found *m/z* 296.1076.

Radical cyclization of (*Z*)-13. According to the general procedure of radical cyclization, the reaction of (*Z*)-**13** (49 mg, 0.15 mmol) gave 32 mg (73%) of a mixture of *cis*-**23** and *trans*-**23** in a ratio of 1/1. About 1% of (*Z*)-**24** was observed by ^1H NMR in a separate chromatographic fraction, and the structure was confirmed by alternative synthesis *via* oxidation of (*Z*)-**11**. (*Z*)-**24** : IR (neat) 3051, 2927, 1702, 1632, 1439, 1301, 1181, 1145, 1084 cm^{-1}; ^1H NMR (200 MHz) δ 1.25 (t, *J* = 7 Hz, 3 H, CH_3), 1.40–1.85 (m, 4 H), 2.62 (q, *J* = 7 Hz, 2 H, allyl), 3.10 (dd, *J* = 7, 6 Hz, 2 H, CH_2S), 4.12 (q, *J* = 7 Hz, 2 H, OCH_2), 5.73 (d, *J* = 11 Hz, 1 H, =CHCO), 6.10 (dt, *J* = 11, 7 Hz, 1 H, =CH–C), 7.45–7.71 (m, 3 H, ArH), 7.88 (d, *J* = 8 Hz, 2 H, ArH); ^{13}C NMR (50 MHz) δ 14.2, 22.2, 27.4, 28.0, 55.9, 59.9, 120.7, 128.0, 129.2, 133.6, 139.2, 148.5, 166.2; MS *m/z* (rel intensity) 297 (M^++1, 25), 287 (5), 273 (3), 250 (40), 223 (5), 199(3), 155 (7), 143 (5), 127 (8), 108 (98), 99 (5), 80 (100), 67 (5), 57 (5), 43 (5); HRMS calcd for $C_{15}H_{20}O_4S$ *m/z* 296.1083, found *m/z* 296.1076.

Dimethyl 2-(2-propenyl)-2-[2-bromo-2-(phenylsulfinyl)ethyl]propanedioate (29). A solution of 297 mg (1.73 mmol) of **27**, 0.240 mL (1.73 mmol) of triethylamine and 13 μL (0.086 mmol) of DBU in 0.7 mL of anhydrous DMF was stirred at room temperature for 5 min. To the resulting solution was added dropwise over 6 min a solution of 200 mg (0.864 mmol) of **28**[14] in 1 mL of anhydrous DMF. The resulting solution was stirred for another 2.5 h and then partitioned between 40 mL of ether and 10 mL of water. The organic layer was washed with 10 mL of water, 10 mL of brine, dried ($MgSO_4$) and concentrated. The residual oil was chromatographed over silica gel (eluted with hexane/ethyl acetate, 4/1) to give 243 mg (70%) of **29** (a 3.3/1 mixture of two stereoisomers) as a pale yellow oil: IR (neat) 3061, 2953, 1733, 1638, 1440, 1291, 1210, 1088, 1054 cm^{-1}; ^1H NMR (300 MHz) δ 2.42 (dd, *J* = 17, 9 Hz, 1 H, CH–C–Br), 2.63 (dd, *J* = 14, 9 Hz, 1 H, allyl), 2.76 (dd, *J* = 14, 9 Hz, 1 H, allyl), 3.08 (dd, *J* = 14, 2 Hz, 1 H, CH–C–Br), 3.70 (s, 3 H, OCH_3), 3.75 (s, 3 H, OCH_3), 4.78 (dd, *J* = 9, 2 Hz, 0.77 H, CHBr of the major isomer), 4.83 (dd, *J* = 9, 2 Hz, 0.23 H, CHBr of the minor isomer), 5.02–5.22 (m, 2 H, $=CH_2$), 5.53 (ddt, *J* = 15, 10, 7 Hz, 1H, =CH–), 7.45–7.80 (m, 5 H, ArH); ^{13}C NMR (50 MHz) δ 34.3, 35.8, 37.5, 37.9, 52.7, 52.9, 55.9, 56.4, 83.5, 84.2, 120.2, 120.4, 125.5, 126.0, 128.8, 129.0, 131.0, 131.9, 132.2, 139.8, 140.8, 170.1, 170.3. Anal. Calcd for $C_{16}H_{19}BrO_5S$: C, 47.65; H, 4.75. Found: C, 47.41; H, 4.62.

Dimethyl 2-(2-propenyl)-2-[2-bromo-2-(phenylsulfonyl)ethyl]propanedioate (31). To a solution of 157 mg (0.913 mmol) of **27** in 1 mL of THF at 0 °C was added 22.7 mg (o.757 mmol) of sodium hydride (80% dispersion in mineral oil) in one portion. The resulting mixture was stirred at the same temperature for 30 min followed by the addition of a solution of 180 mg (0.729 mmol) of **30**[15] and then stirred for another 40 min at 0 °C. The resulting mixture was partitioned between 100 mL of ether and 30 mL of 3 N hydrochloric acid solution. The organic layer was washed with 30 mL of water, 30 mL of brine, dried ($MgSO_4$) and concentrated. The residual oil was chromatographed over silica gel (eluted with hexane/ethyl acetate, 3/1) to give 254 mg (83%) of **31** as a colorless liquid: IR (neat) 3058, 2951, 1962, 1731, 1636 , 1443, 1432, 1327, 1309, 1289, 1211, 1155, 1083 cm^{-1}; ^1H NMR (300 MHz) δ 2.47 (dd, J = 16, 10 Hz, 1 H, CH–C–Br), 2.61 (dd, J = 15, 8 Hz, 1 H, allyl), 2.73 (dd, J = 15, 8 Hz, 1 H, allyl), 3.17 (dd, J = 16, 2 Hz, 1 H, CH–C–Br), 3.68 (s, 3 H, OCH_3), 3.69 (s, 3 H, OCH_3), 4.91 (dd, J = 10, 2 Hz, 1 H, CHBr), 5.03–5.17 (m, 2 H, $=CH_2$), 5.50 (ddt, J = 18, 10, 7 Hz, 1H, =CH–), 7.57 (t, J = 8 Hz, 2 H, ArH), 7.69 (t, J = 8 Hz, 1 H, ArH), 7.93 (d, J = 8 Hz, 2 H, ArH); ^{13}C NMR (75 MHz) δ 34.8, 37.4, 52.8, 53.0, 55.8, 60.0, 120.5, 129.1, 130.1, 130.8, 134.6, 134.8, 170.0, 170.1; MS *m/z* (rel intensity) 419 (M^+, 10), 387 (5), 358 (30), 327 (10), 277 (50), 217 (35), 185 (15), 171 (30), 157 (10), 137 (100), 125 (35), 109 (15), 93 (25), 77 (15), 59 (15); HRMS calcd for $C_{16}H_{19}BrO_6S$ *m/z* 418.0086, found *m/z* 418.0071.

2-Bromoethyl phenyl sulfoxide (33). A mixture of 1.00 g (4.61 mmol) of 2-bromoethyl phenyl sulfide[23,24] and 1.34 g (2.30 mmol) of monoperoxyphthalic acid magnesium salt (85%) in 10 mL of ethanol and 0.1 mL of water was stirred at room temperature for 12 h. The resulting mixture was poured into 30 mL of water and extracted with dichloromethane (50 mL x 2). The combined organic layers were dried (Na_2SO_4) and concentrated. The residual oil was chromatographed over silica gel (eluted with hexane/ethyl acetate, 7/3) to give 0.951 g (89%) of **33** as a pale yellow liquid: IR (neat) 3055, 1477, 1443, 1250, 1099, 1085, 1070, 998 cm^{-1}; ^1H NMR (200 MHz) δ 3.32 (t, J = 5 Hz, 2 H, CH_2), 3.47 (dt, 2 H, J = 7, 5 Hz, CH_2Br), 3.78 (dt, 2 H, J = 7, 5 Hz, CH_2Br), 7.52–7.70 (m, 5 H, ArH); ^{13}C NMR (50 MHz) δ 23.1, 58.9, 123.8, 129.4, 131.3, 142.3; MS *m/z* (rel intensity) 234 (M^+, 17), 232 (20), 125 (100), 109 (90), 107 (80), 97 (55), 77 (80); HRMS calcd for C_8H_9BrOS *m/z* 231.9558, found *m/z* 231.9558.

Di-*t*-butyl 2-(2-propenyl)-2-[2-(phenylsulfinyl)ethyl]propanedioate (34). A mixture of 0.991 g (4.58 mmol) of **32** and 0.513 g (4.58 mmol) of potassium *t*-butoxide in 5 mL of *t*-butyl alcohol was stirred at room temperature for 30 min, followed by the addition of 0.971 g (4.17 mmol) of **33** in one portion. The reaction mixture was stirred for another 20 min and partitioned between 40 mL of dichloromethane and 20 mL of water. The aqueous layer was extracted with 40 mL of dichloromethane, and the combined organic layers were dried (Na_2SO_4) and concentrated. The residual oil was chromatographed over silica gel (eluted with hexane/ethyl acetate, 7/3) to give 1.409 g of a pale yellow oil which appeared as a mixture of the desired coupling product and unreacted **32**. The mixture was dissolved in 10 mL of *t*-butyl alcohol followed by the addition of 0.857 g (7.65 mmol) of potassium *t*-butoxide and then heated at 80 °C for 15 min. To the reaction mixture was added 0.500 mL (5.74 mmol) of allyl bromide and then stirred at the same temperature for 8 h. The resulting mixture was poured into 30 mL of water and extracted with dichloromethane (30 mL x 3). The combined organic layers were dried (Na_2SO_4) and concentrated. The residual oil was chromatographed over silica gel (eluted with hexane/ethyl acetate, 7/3) to give 0.972 g of **34** (52%) as a pale yellow oil: IR (neat)

3075, 2976, 1723, 1639, 1369, 1303, 1252, 1145, 1048 cm^{-1}; ^1H NMR (300 MHz) δ 1.31 (s, 9 H, CH_3), 1.32 (s, 9 H, CH_3), 1.88–2.05 (m, 2 H, CH_2–C–S), 2.41 (d, *J* = 7 Hz, 2 H, allyl), 2.62 (td, *J* = 13, 5 Hz, 1 H, CH_2S), 2.74 (td, *J* = 13, 5 Hz, 1 H, CH_2S), 4.93 (d, *J* = 10 Hz, 1 H, =CH_2), 4.94 (d, *J* = 15 Hz, 1 H, =CH_2), 5.43 (ddt, *J* = 15, 10, 7 Hz, 1 H, =CH–), 7.41–7.43 (m, 3 H, ArH), 7.52–7.54 (m, 2 H, ArH); ^{13}C NMR (75 MHz) δ 24.2, 27.6, 37.0, 51.7, 56.8, 81.7, 119.0, 123.9, 129.0, 130.9, 131.6, 143.3, 169.3; MS *m/z* (rel intensity) 409 (M^+, 50), 353 (38), 335 (10), 313 (8), 297 (30), 279 (5), 227 (12), 171 (100), 153 (21), 125 (12), 109 (15), 81 (7), 57 (39); HRMS calcd for $C_{22}H_{33}O_5S$ *m/z* 409.2049, found *m/z* 409.2047.

Di-*t*-butyl 2-(2-propenyl)-2-[2-chloro-2-(phenylsulfinyl)ethyl]propanedioate (35). A mixture of 822 mg (2.01 mmol) of **34** and 296 mg (2.21 mmol) of NCS in 5 mL of carbon tetrachloride was stirred at room temperature for 17 h and then filtered. The filtrate was concentrated and the residual oil was chromatographed over silica gel (eluted with hexane/ethyl acetate, 4/1) to give 796 mg (90%) of **35** (a 3/1 mixture of two diastereomers) as a pale yellow oil: IR (neat) 3063, 2976, 1718, 1640, 1369, 1309, 1257, 1153, 1084, 1056 cm^{-1}; ^1H NMR (300 MHz) δ 1.44 (s, 9 H, *t*-Bu), 1.47 (s, 9 H, *t*-Bu), 2.10 (dd, *J* = 15, 9 Hz, 1 H, CH–C–Cl), 2.60 (dd, *J* = 15, 8 Hz, 1 H, allyl), 2.75 (dd, *J* = 15, 8 Hz, 1 H, allyl), 2.95 (dd, *J* = 15, 2 Hz, 1 H, CH–C–Cl), 4.62 (dd, *J* = 9, 2 Hz, 1 H, CHCl of the minor isomer), 4.65 (dd, *J* = 9, 2 Hz, 1 H, CHCl of the major isomer), 5.10 (dd, *J* = 10, 2 Hz, 1 H, =CH_2), 5.15 (dd, *J* = 15, 2 Hz, 1 H, =CH_2), 5.60 (ddt, *J* = 15, 10, 7 Hz, 1H, =CH–), 7.45–7.85 (m, 5 H, ArH); ^{13}C NMR (50 MHz) δ 27.5, 30.6, 33.4, 36.9, 53.3, 56.4, 71.4, 82.0, 82.3, 119.6, 125.6, 128.7, 131.3, 131.9, 138.3, 168.9, 169.0. Anal. Calcd for $C_{22}H_{31}ClO_5S$: C, 59.64; H, 7.05. Found: C, 59.12; H, 6.90.

Di-*t*-butyl 2-(2-propenyl)-2-[2-chloro-2-(phenylsulfonyl)ethyl]propanedioate (36). Using the same procedure for the preparation of **9**, the reaction of **35** (213 mg, 0.418 mmol) gave 124 mg (57%) of **36** as a pale yellow oil: IR (neat) 3071, 2979, 1724, 1640, 1369, 1332, 1250, 1153, 1085 cm^{-1}; ^1H NMR (200 MHz) δ 1.40 (s, 9 H, *t*-Bu), 1.45 (s, 9 H, *t*-Bu), 2.29 (dd, *J* = 15, 10 Hz, 1 H, CH–C–Cl), 2.53 (dd, *J* = 15, 7 Hz, 1 H, allyl), 2.70 (dd, *J* = 15, 7 Hz, 1 H, allyl), 3.08 (dd, *J* = 15, 2 Hz, 1 H, CH–C–Cl), 4.75 (dd, *J* = 10, 2 Hz, 1 H, CHCl), 5.02–5.18 (m, 2 H, =CH_2), 5.58 (ddt, *J* = 15, 10, 7 Hz, 1H, =CH–), 7.55 (t, *J* = 8 Hz, 2 H, ArH), 7.69 (t, *J* = 8 Hz, 1 H, ArH), 7.92 (d, *J* = 8 Hz, 2 H, ArH); ^{13}C NMR (50 MHz) δ 27.8, 33.4, 36.7, 58.4, 71.0, 82.3, 82.6, 119.9, 129.1, 130.2, 131.4, 134.6, 134.9, 168.9. Anal. Calcd for $C_{22}H_{31}ClO_6S$: C, 57.57; H, 6.81. Found: C, 57.42; H, 7.10.

Radical cyclization of 29: dimethyl *cis*-3-methyl-4-phenylsulfinyl-1,1-cyclopentanedicarboxylate (*cis*-37), dimethyl *trans*-3-methyl-4-phenylsulfinyl-1,1-cyclopentanedicarboxylate (*trans*-37). According to the general procedure of radical cyclization, the reaction of **29** (133 mg, 0.33 mmol) gave 60 mg (60%) of **37** (*cis/trans* = 1.9/1). The *cis*-isomer was a 2/1 mixture of two stereoisomers, and the *trans*-isomer was a 1.5/1 mixture of two stereoisomers. *cis*-**37**: IR (neat) 3012, 2919, 1723, 1439, 1213, 1165, 1084, 1069, 1041, 1020 cm^{-1}; ^1H NMR (200 MHz) of the major isomer δ 1.50 (d, *J* = 7 Hz, 3 H, CH_3), 2.00–2.21 (m, 2 H), 2.35 (dd, *J* = 15, 6 Hz, 1 H), 2.40–2.80 (m overlapped with dd, *J* = 15, 6 Hz, at 2.75, 2 H), 3.05 (q, *J* = 8 Hz, 1 H, CHS), 3.67 (s, 3 H, OCH_3), 3.75 (s, 3 H, OCH_3), 7.35–7.60 (m, 5 H, ArH); ^{13}C NMR (50 MHz) of the major isomer δ 15.9, 28.9, 36.3, 41.9, 52.8, 59.0, 66.1, 124.0, 124.2, 129.2, 130.5, 171.1; ^1H NMR (200 MHz) of the minor isomer δ 1.38 (d, *J* = 7 Hz, 3 H, CH_3), 1.85 (dd, *J* = 15, 7 Hz, 1

H), 2.22 (dd, J = 11, 7 Hz, 2 H), 2.53 (dd, J = 15, 7 Hz, 1 H), 2.65-2.92 (m, 1 H, CHMe), 3.29 (q, J = 7 Hz, 1 H, CHS), 3.65 (s, 3 H, OCH_3), 3.73 (s, 3 H, OCH_3), 7.43–7.59 (m, 3 H, ArH), 7.68–7.80 (m, 2 H, ArH); ^{13}C NMR (50 MHz) of the minor isomer δ 15.8, 28.8, 36.2, 41.8, 52.8, 58.9, 66.0, 124.1, 129.1, 130.4, 142.6, 171.1, 172.6; MS *m/z* (rel intensity) 323 (M^+–1, 100), 313 (32), 307 (12), 299 (7), 285 (20), 275 (7), 263 (7), 247 (12), 236 (13), 197 (55), 183 (22), 165 (39), 153 (12), 137 (98), 125 (38), 109 (22), 97 (22), 83 (18), 78 (12); HRMS calcd for $C_{16}H_{20}O_5S$ *m/z* 324.1031, found *m/z* 324.1033. *trans*-**37**: IR (neat) 2948, 1726, 1439, 1257, 1200, 1142, 1085, 1044 cm^{-1}; ^1H NMR (200 MHz) of the major isomer δ 0.89 (d, J = 7 Hz, 3 H, CH_3), 1.88 (dd, J = 15, 10 Hz, 1 H), 2.27–2.73 (m, 4 H), 2.89 (q, J = 8 Hz, 1 H, CHS), 3.69 (s, 3 H, OCH_3), 3.76 (s, 3 H, OCH_3), 7.43–7.59 (m, 3 H, ArH), 7.60–7.73 (m, 2 H, ArH); ^{13}C NMR (50 MHz) of the major isomer δ 17.9, 30.2, 34.8, 42.3, 52.9, 58.0, 70.0, 124.0, 129.2, 130.8, 133.2, 172.5; ^1H NMR (200 MHz) of the minor isomer δ 1.16 (d, J = 7 Hz, 3 H, CH_3), 1.75 (dd, J = 15, 10 Hz, 1 H), 1.98–2.02 (m, 1 H), 2.30–2.52 (m, 1 H, CHMe), 2.55-2.72 (m, 2 H), 2.79 (dd, J = 15, 7 Hz, 1 H, CHS), 3.68 (s, 3 H, OCH_3), 3.76 (s, 3 H, OCH_3), 7.43–7.62 (m, 5 H, ArH); ^{13}C NMR (50 MHz) of the minor isomer δ 20.3, 34.4, 35.4, 42.6, 53.0, 59.2, 69.7, 124.8, 129.2, 131.3, 142.8, 171.3, 171.9; MS *m/z* (rel intensity) 325 (M^++1, 68), 308 (2), 293 (15), 250 (1), 199 (28), 167 (12), 139 (100), 126 (5), 107 (30), 79 (18), 59 (3); HRMS calcd for $C_{16}H_{20}O_5S$ *m/z* 324.1031, found *m/z* 324.1026.

Radical cyclization of 35: di-*t*-butyl *cis*-3-methyl-4-phenylsulfinyl-1,1-cyclopentanedicarboxylate (*cis*-38), di-*t*-butyl *trans*-3-methyl-4-phenylsulfinyl-1,1-cyclopentanedicarboxylate (*trans*-38). According to the general procedure of radical cyclization, the reaction of **35** (48 mg, 0.11 mmol) gave 26 mg (60%) of a mixture of *cis*-**38**, *trans*-**38** and **34** (*cis*-**38**/*trans*-**38**/**34** = 2/3.7/1). The diastereomeric ratio of *cis*-**38** was 3/1, and that of the *trans*-**38** was 1.5/1. The major diastereomer of *cis*-**38**: ^1H NMR (200 MHz) δ 1.34 (s, 9 H, *t*-Bu), 1.41–1.51 (s at 1.43, overlapped with d, J = 7 Hz, at 1.45, 12 H, t-Bu and CH_3 at C-3), 1.91–2.09 (m, 2 H), 2.12 (dd, J = 15, 8 Hz, 1 H), 2.41–2.71 (m overlapped with dd, J = 15, 8 Hz, at 2.63, 1 H), 3.02 (q, J = 8 Hz, 1 H, CHS), 7.41–7.61 (m, 5 H, ArH); MS *m/z* (rel intensity) 409 (M^++1, 30), 353 (100), 335 (15), 297 (55), 279 (6), 235 (10), 171 (95), 153 (30), 125 (85), 109 (8), 81 (10), 57 (63); HRMS calcd for $C_{22}H_{32}O_5S$ *m/z* 408.1971, found *m/z* 408.1968. Characteristic ^1H NMR (200 MHz) for the minor diastereomer of *cis*-**38** at δ 1.32 (s, 9 H, *t*-Bu), 1.41 (s, 9 H, *t*-Bu), 2.67 (q, J = 5 Hz, 1 H, CHS), for the major diastereomer of *trans*-**38** at δ 0.92 (d, J = 7 Hz, 3 H, CH_3 at C-3), 1.40 (s, 9 H, *t*-Bu), 1.45 (s, 9 H, *t*-Bu), 2.30 (dd, J = 14, 8 Hz, 1 H), 2.87 (q, J = 8 Hz, 1 H, CHS), for the minor diastereomer of *trans*-**38** at δ 1.08 (d, J = 7 Hz, 3 H, CH_3 at C-3), 1.37 (s, 9 H, *t*-Bu), 1.43 (s, 9 H, *t*-Bu), 2.01 (dd, J = 14, 8 Hz, 1 H), 2.60 (q, J = 8 Hz, 1 H, CHS).

Radical cyclization of 31: dimethyl *cis*-3-methyl-4-phenylsulfonyl-1,1-cyclopentanedicarboxylate (*cis*-39), dimethyl *trans*-3-methyl-4-phenylsulfonyl-1,1-cyclopentanedicarboxylate (*trans*-39) and dimethyl 2-(2-propenyl)-2-[2-(phenylsulfonyl)ethyl]propanedioate (40). According to the general procedure of radical cyclization, the reaction of **31** (80 mg, 0.19 mmol) gave 48 mg (74%) of a mixture of *cis*-**39**, *trans*-**39** and **40** in a ratio of 17.5/7.5/1 (*cis*-**39**/*trans*-**39**/**40**). *cis*-**39**: IR (neat) 2949, 1730, 1442, 1303, 1273, 1204, 1169, 1145, 1085 cm^{-1}; ^1H NMR (300 MHz) δ 1.35 (d, J = 7 Hz, 3 H, CH_3), 2.31–2.40 (m, 3 H), 2.55–2.75 (eight line m, 2 H), 3.55 (q, J = 8 Hz, 1 H, CHS), 3.65 (s, 3 H, OCH_3), 3.74 (s, 3 H, OCH_3), 7.54 (t, J = 7 Hz, 2 H, ArH), 7.62 (t, J = 7 Hz, 1 H, ArH), 7.88 (d, J = 7 Hz, 2 H, ArH); ^{13}C NMR

(75 MHz) δ 15.7, 34.7, 36.5, 41.7, 53.1, 58.3, 65.6, 128.2, 129.2, 133.6, 139.9, 171.2, 172.4; MS *m/z* (rel intensity) 341 (M^++1, 25), 309 (30), 280 (20), 249 (10), 199 (55), 167 (15), 139 (100), 125 (10), 107 (45), 79 (30); HRMS calcd for $C_{16}H_{20}O_6S$ *m/z* 340.0980, found *m/z* 340.0976. *trans*-**39**: IR (neat) 3057, 2950, 1730, 1442, 1260, 1203, 1146, 1085 cm^{-1}; ^1H NMR (200 MHz) δ 1.01 (d, *J* = 7 Hz, 3 H, CH_3), 1.76 (dd, *J* = 12, 8 Hz, 1 H), 2.50–2.72 (m overlapped with d, *J* = 8 Hz, at 2.51, 4 H, CH_2), 3.21 (q, *J* = 8 Hz, 1 H, CHS), 3.66 (s, 3 H, OCH_3), 3.70 (s, 3 H, OCH_3), 7.54 (t, *J* = 7 Hz, 2 H, ArH), 7.63 (t, *J* = 7 Hz, 1 H, ArH), 7.86 (d, *J* = 7 Hz, 2 H, ArH); ^{13}C NMR (75 MHz) δ 19.7, 35.1, 35.7, 42.3, 53.0, 58.5, 69.4, 128.5, 129.3, 133.8, 138.4, 170.9, 171.8; MS *m/z* (rel intensity) 341 (M^++1, 25), 309 (30), 280 (20), 249 (10), 199 (60), 167 (15), 139 (100), 125 (10), 107 (45), 79 (30); HRMS calcd for $C_{16}H_{20}O_6S$ *m/z* 340.0980, found *m/z* 340.0976. **40**: IR (neat) 3063, 2949, 1720, 1635, 1442, 1142, 1085, 1071 cm^{-1}; ^1H NMR (300 MHz) δ 2.12–2.29 (m, 2 H), 2.54 (d, *J* = 8 Hz, 2 H, allyl), 3.09–3.21 (m, 2 H, CH_2S), 3.64 (s, 6 H, OCH_3), 4.92–5.08 (m, 2 H, $=CH_2$), 5.45 (ddt, *J* = 15, 10, 7 Hz, 1H, =CH–), 7.54 (t, *J* = 7 Hz, 2 H, ArH), 7.63 (t, *J* = 7 Hz, 1 H, ArH), 7.86 (d, *J* = 7 Hz, 2 H, ArH); ^{13}C NMR (50 MHz) δ 25.9, 37.9, 51.7, 52.7, 65.1, 119.9, 128.0, 129.3, 131.1, 133.8, 138.6, 170.3; MS *m/z* (rel intensity) 341 (M^++1, 15), 309 (10), 280 (45), 249 (15), 199 (100), 171 (10), 143 (10), 139 (80), 125 (10), 107 (65), 79 (60), 71 (15), 67 (5), 59 (20), 45 (5); HRMS calcd for $C_{16}H_{20}O_6S$ *m/z* 340.0980, found *m/z* 340.0978.

Radical cyclization of 36: di-*t*-butyl *cis*-3-methyl-4-phenylsulfonyl-1,1-cyclopentanedicarboxylate (*cis*-41), di-*t*-butyl *trans*-3-methyl-4-phenylsulfonyl-1,1-cyclopentanedicarboxylate (*trans*-41) and di-*t*-butyl 2-(2-propenyl)-2-[2-(phenylsulfonyl)ethyl]propanedioate (42). According to the general procedure of radical cyclization, the reaction of **36** (90 mg, 0.11 mmol) gave 29 mg (34%) of *cis*-**41**, 24 mg (28%) of *trans*-**41** and 4 mg (5%) of **42**. *cis*-**41**: IR (neat) 3059, 2971, 1713, 1366, 1282, 1148, 1085 cm^{-1}; ^1H NMR (300 MHz) δ 1.20–1.51 (m, 21 H, overlapped with two s at 1.34 and 1.43), 2.19–2.31 (m, 3 H), 2.53–2.68 (m, 2 H), 3.50 (dt, *J* = 10, 8 Hz, 1 H, CHS), 7.50–7.68 (m, 3 H, ArH), 7.82–7.91 (m, 2 H, ArH); ^{13}C NMR (75 MHz) δ 15.9, 27.7, 27.8, 34.0, 36.1, 41.4, 59.7, 65.8, 81.6, 81.8, 128.1, 129.2, 133.4, 140.2, 169.9, 171.2; MS *m/z* (rel intensity) 425 (M^++1, 11), 369 (100), 351 (10), 313 (90), 295 (22), 250 (7), 223 (2), 171 (20), 153 (3), 143 (2), 125 (30), 108 (15), 81 (5), 57 (30), 49 (2); HRMS calcd for $C_{22}H_{33}O_6S$ *m/z* 425.1998, found *m/z* 425.1983. *trans*-**41**: IR (neat) 3059, 2971, 1713, 1366, 1282, 1148, 1085 cm^{-1}; ^1H NMR (200 MHz) δ 1.02 (d, *J* = 7 Hz, 3 H, CH_3 at C-3), 1.38 (s, 9 H, *t*-Bu), 1.42 (s, 9 H, *t*-Bu), 1.53–1.63 (m, 1 H), 2.30–2.73 (m, 3 H), 3.23 (q, *J* = 7 Hz, 1 H, CHS), 7.50–7.71 (m, 3 H, ArH), 7.88 (d, *J* = 8 Hz, 2 H, ArH); ^{13}C NMR (50 MHz) δ 19.9, 27.7, 27.8, 34.9, 35.4, 41.9, 59.7, 69.5, 81.7, 81.9, 128.5, 129.2, 133.7, 138.7, 169.6, 170.8; MS *m/z* (rel intensity) 425 (M^++1, 11), 369 (100), 351 (10), 313 (90), 295 (22), 250 (7), 223 (2), 171 (20), 153 (3), 143 (2), 125 (30), 108 (15), 81 (5), 57 (30), 49 (2); HRMS calcd for $C_{22}H_{33}O_6S$ *m/z* 425.1998, found *m/z* 425.1983. **42**: IR (neat) 3063, 2973, 1720, 1637, 1367, 1305, 1253, 1149 cm^{-1}; ^1H NMR (200 MHz) δ 1.39 (s, 18 H, CH_3), 2.00–2.13 (a six line m, 2 H), 2.45 (d, *J* = 7 Hz, 2 H, allyl), 3.00–3.10 (a five line m, 2 H), 4.92–5.06 (m, 2 H, $=CH_2$), 5.38–5.58 (m, 1H, =CH–), 7.49–7.68 (m, 3 H, ArH), 7.88 (br d, *J* = 8 Hz, 2 H, ArH); ^{13}C NMR (50 MHz) δ 25.7, 27.8, 37.3, 51.9, 56.6, 81.8, 119.4, 128.1, 129.3, 131.5, 133.7, 138.7, 169.2; MS *m/z* (rel intensity) 425 (M^++1, 40), 369 (100), 313 (80), 287 (8), 277 (12), 266 (12), 250 (10), 171 (20), 143 (5), 119 (10), 108 (10), 97 (3), 80 (20), 71 (3), 57 (45); HRMS calcd for $C_{22}H_{33}O_6S$ *m/z* 425.1998, found *m/z* 425.1990.

6-Chloro-2-methyl-6-phenylsulfinyl-1-hexene (45). Using the same procedure for the preparation of **8**, the reaction of **43** (0.370 g, 1.80 mmol) gave 0.315 g (68%) of **45** (a 10/1 mixture of two diastereomers) as a pale yellow oil: IR (neat) 3069, 2935, 1113, 1091, 1052 cm^{-1}; ^1H NMR (200 MHz) δ 1.50–1.90 (m overlapped with br s at 1.70, 5 H, $=CCH_3$ and $=C-C-CH_2$), 2.05 (br t, J = 7 Hz, 2 H, allyl), 2.13–2.33 (m, 2 H, CH_2-C-Cl), 4.41 (dd, J = 9, 4.5 Hz, 1 H, CHCl of the minor isomer), 4.57 (dd, J = 9, 4.5 Hz, 1 H, CHCl of the major isomer), 4.68 (s, 1 H, $=CH_2$), 4.73 (s, 1 H, $=CH_2$), 7.50–7.58 (m, 3 H, ArH), 7.61–7.73 (m, 2 H, ArH); ^{13}C NMR (50 MHz) of the major isomer δ 22.1, 24.0, 30.7, 36.7, 76.4, 110.8, 125.5, 128.8, 131.8, 139.2, 144.4; MS *m/z* (rel intensity) 257 (M^+, 100), 239 (33), 221 (8), 143 (5), 126 (35), 95 (45), 77 (8), 67 (4), 51 (3); HRMS calcd for $C_{13}H_{17}ClOS$ *m/z* 256.0689, found *m/z* 256.0677.

6-Chloro-2-methyl-6-phenylsulfonyl-1-hexene (46). A mixture of 220 mg (0.85 mmol) of **45** and 143 mg (0.94 mmol) of potassium peroxymonosulfate in 1 mL of methanol was stirred at room temperature for 15 h and then partitioned between 30 mL of 2 N sodium hydroxide solution and 60 mL of dichloromethane. The organic layer was dried (Na_2SO_4) and concentrated. The residual oil was chromatographed over silica gel (eluted with hexane/ethyl acetate, 4/1) to give 126 mg (54%) of **46** as a pale yellow oil: IR (neat) 3068, 2933, 1445, 1326, 1215, 1152, 1085 cm^{-1}; ^1H NMR (200 MHz) δ 1.40–1.95 (m overlapped with br s at 1.68, 5 H, $=CCH_3$ and $=C-C-CH_2$), 2.04 (t, J = 7 Hz, 2 H, allyl), 2.25–2.48 (m, 2 H, CH_2-C-Cl), 4.57–4.80 (m overlapped with two br s at 4.65 and 4.71, 3 H, CHCl and $=CH_2$), 7.30–7.78 (m, 3 H, ArH), 7.78–8.08 (m, 2 H, ArH); ^{13}C NMR (50 MHz) δ 22.1, 23.7, 30.1, 36.6, 74.8, 110.0, 129.0, 130.0, 134.4, 135.2, 144.2; MS *m/z* (rel intensity) 273 (M^+, 49), 185 (2), 169 (4), 143 (23), 130 (65), 95 (100), 89 (2), 81 (3), 77 (12), 67 (10), 51 (7); HRMS calcd for $C_{13}H_{17}ClO_2S$ *m/z* 272.0637, found *m/z* 272.0642.

Radical cyclization of 45: 3-methylcyclohexyl phenyl sulfoxide (47) and 2-methyl-6-phenylsulfinyl-1-hexene (48). According to the general procedure of radical cyclization, the reaction of **45** (120 mg, 0.47 mmol) gave 83 mg (80%) of a mixture of **47** and **48** in a ratio of 2.4/1/8 (*cis*-**47**/*trans*-**47**/**48**). *cis*-**47**: IR (neat) 2920, 1440, 1085, 1035 cm^{-1}; ^1H NMR (200 MHz) δ 0.68–1.48 (m overlapped with d, J = 7 Hz, at 0.86, 11 H, CH_3 and others), 1.48–1.95 (m, 4 H), 2.52 (br t, J = 10 Hz, 1 H, CHS), 7.40–7.58 (m, 5 H, ArH); ^{13}C NMR (50 MHz) δ 22.3, 23.0, 25.0, 25.3, 25.7, 31.7, 32.0, 32.0, 32.3, 33.9, 34.1, 62.5, 62.7, 124.7, 127.9, 128.7, 129.0, 130.7, 133.5, 138.3, 141.5; MS *m/z* (rel intensity) 223 (M^++1, 20), 170 (8), 141 (7), 126 (100), 110 (3), 97 (21), 94 (8), 78 (19), 55 (25), 51 (9); HRMS calcd for $C_{13}H_{18}OS$ *m/z* 222.1079, found *m/z* 222.1061. *trans*-**47**: IR (neat) 3053, 2924, 1441, 1085, 1040 cm^{-1}; ^1H NMR (200 MHz) δ 0.78 (d, J = 7 Hz, 3 H, CH_3 for one of diastereomer), 0.83 (d, J = 7 Hz, 3 H, CH_3 for the other of diastereomer), 0.95–2.15 (m, 9 H), 2.72 (br s, 1 H, CHS), 7.40–7.58 (m, 5 H, ArH); ^{13}C NMR (50 MHz) δ 20.2, 20.4, 21.1, 24.0, 25.9, 27.2, 27.9, 31.4, 32.7, 33.2, 61.7, 125.0, 128.8, 131.0, 142.6; MS *m/z* (rel intensity) 223 (M^++1, 10), 205 (8), 126 (100), 97 (30), 78 (20), 69 (5), 55 (65), 51 (4); HRMS calcd for $C_{13}H_{18}OS$ *m/z* 222.1078, found *m/z* 222.1058. **48**: IR (neat) 3070, 2861, 1645, 1476, 1443, 1087, 1071, 1037, 999 cm^{-1}; ^1H NMR (200 MHz) δ 1.20–1.65 (m overlapped with s at 1.50, 3 H, 7 H, $=CCH_3$ and others), 1.85 (t, J = 7 Hz, 2 H, allyl), 2.62 (t, J = 7 Hz, 2 H, CH_2S), 4.45 (s, 1 H, $=CH_2$), 4.50 (s, 1 H, $=CH_2$), 7.25–7.50 (m, 5 H, ArH); ^{13}C NMR (50 MHz) δ 21.6, 22.1, 26.4, 37.0, 57.0, 110.2, 123.6, 129.0, 130.7, 143.6, 144.7; MS *m/z* (rel intensity) 223 (M^++1, 12), 205 (7), 136 (3), 126 (31), 109 (5), 97

(45), 77 (27), 69 (12), 55 (100), 51 (25), 41 (54); HRMS calcd for $C_{13}H_{18}OS$ *m/z* 222.1078, found *m/z* 222.1058.

Radical cyclization of 46: 3-methylcyclohexyl phenyl sulfone (49) and 2-methyl-6-phenylsulfonyl-1-hexene (50). According to the general procedure of radical cyclization, the reaction of **46** (70 mg, 0.26 mmol) gave 61 mg (100%) of a mixture of **49** and **50** in a ratio of 6/1/3 (*cis*-**49**/*trans*-**49**/**50**). *cis*-**49**: IR (neat) 3056, 2924, 1442, 1302, 1268, 1143, 1081 cm^{-1}; ^1H NMR (200 MHz) δ 0.87 (d, *J* = 7 Hz, 3 H, CH_3), 1.00–2.02 (m, 9 H), 2.90 (tt, *J* = 10, 3 Hz, 1 H, CHS), 7.42–7.62 (m, 3 H, ArH), 7.82 (d, *J* = 7 Hz, 2 H, ArH); ^{13}C NMR (50 MHz) δ 22.3, 24.8, 25.0, 31.9, 33.2, 33.7, 63.4, 113.4, 128.9, 133.5, 137.2; MS *m/z* (rel intensity) 239 (M^++1, 100), 143 (12), 125 (8), 110 (3), 97 (31), 81 (3), 77 (8), 69 (2), 55 (21), 51 (5); HRMS calcd for $C_{13}H_{18}O_2S$ *m/z* 238.1028, found *m/z* 238.1027. *trans*-**49**: IR (neat) 3058, 2930, 1442, 1301, 1144, 1083 cm^{-1}; ^1H NMR (200 MHz) δ 0.89 (d, *J* = 7 Hz, 3 H, CH_3), 1.20–2.00 (m, 8 H), 2.14 (br s, 1 H), 3.10 (quintet, *J* = 3 Hz, 1 H, CHS), 7.27–7.67 (m, 3 H, ArH), 7.84 (d, *J* = 7 Hz, 2 H, ArH); ^{13}C NMR (50 MHz) δ 18.5, 19.6, 25.6, 26.9, 31.0, 31.1, 59.1, 127.6, 128.9, 133.5, 136.6; MS *m/z* (rel intensity) 239 (M^++1, 100), 143 (12), 125 (8), 110 (3), 97 (31), 81 (3), 77 (8), 69 (2), 55 (21), 51 (5); HRMS calcd for $C_{13}H_{18}O_2S$ *m/z* 238.1028, found *m/z* 238.1027. **50**: IR (neat) 3065, 2930, 1644, 1444, 1304, 1147, 1087 cm^{-1}; ^1H NMR (200 MHz) δ 1.30–1.80 (m overlapped with quintet, *J* = 7 Hz, at 1.46 and s at 1.65, 7 H, $=CCH_3$ and others), 1.95 (t, *J* = 8 Hz, 2 H, allyl), 3.07 (dd, *J* = 8, 6 Hz, 2 H, CH_2S), 4.58 (s, 1 H, $=CH_2$), 4.65 (s, 1 H, $=CH_2$), 7.43–7.65 (m, 3 H, ArH), 7.78 (d, *J* = 8 Hz, 2 H, ArH); ^{13}C NMR (50 MHz) δ 22.1, 22.2, 26.1, 37.0, 56.1, 110.6, 128.0, 129.2, 133.6, 139.1, 144.5; MS *m/z* (rel intensity) 239 (M^++1, 54), 143 (15), 95 (100), 81 (58), 77 (30), 67 (11), 55 (23), 51 (12), 41 (25); HRMS calcd for $C_{13}H_{18}O_2S$ *m/z* 238.1028, found *m/z* 238.1017.

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