Stereoselective Synthesis of Medium-Sized Cyclic Compounds by Means of Tandem Reactions of a Cyclic Oxosulfonium Ylide with Acetates of Baylis−Hillman Adducts

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Treatment of a five-membered cyclic oxosulfonium ylide **3** with β-acetoxy-α-methylene ketones in the presence of two equimolar amounts of base afforded the cycloheptene oxide derivatives **7a–i** as single stereoisomers in 19–77% yields. The products were considered to form through a Michael-type addition of the ylide, followed by elimination of the acetoxy group and an intramolecular Corey–Chaykovsky reaction. On the other hand, the same treatment, when using a six-membered oxosulfonium ylide, gave the corresponding cyclooctene oxide derivatives in moderate yields, with the products formed in a ca. 4:1 mixture of stereoisomers, a fact correlated with differences in the configuration of the sulfur atom in the sulfinyl group.

Introduction

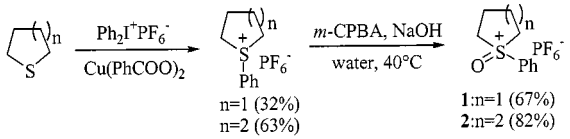
The development of efficient methods for the synthesis of medium-sized carbocycles such as seven- and eight-membered ring systems is a subject of great interest because these ring systems are found in a large number of natural products and are the basic framework of numerous biologically active compounds.[1] In particular, the construction of functionalized medium-sized ring compounds by means of tandem (domino or cascade) reactions[2] from easily accessible substrates is regarded as highly versatile, because these represent an efficient method, minimizing synthetic steps and simplifying laboratory operations. They also frequently supply the functionalized molecules in a highly stereoselective manner.

Although a wide variety of sequential reaction courses for the synthesis of medium-sized ring compounds has been described in recent reviews,[2,3] further development to expand the versatility of those tandem reactions that stereoselectively provide functionalized medium-sized carbocycles would be highly significant from the synthetic point of view.

Recently, we have developed novel tandem reactions between a five-membered cyclic oxosulfonium ylide and β-acetoxy-α-methylene ketones derived from Baylis−Hillman adducts,[4] in analogy with the tandem reactions, found in our laboratory, of a cyclic phosphonium ylide.[5] In these tandem reactions, a Michael-type addition, an elimination, and an intramolecular Corey−Chaykovsky reaction[6] proceed sequentially in one-pot fashion to provide a cycloheptene oxide derivative with a high level of stereoselectivity. In this paper, we describe in detail the tandem Michael/intramolecular Corey−Chaykovsky reactions communicated earlier in preliminary form,[7] and report the similar reactions of a six-membered oxosulfonium ylide, investigated with the goal of synthesizing the corresponding cyclooctene oxide derivatives.

Results and Discussion

Five- and six-membered cyclic oxosulfonium salts **1** and **2** were prepared by arylation[8] of tetramethylene or pentamethylene sulfide, using a diphenyliodonium salt in the presence of a catalytic amount of copper(II) benzoate followed by oxidation of the resulting cyclic sulfonium salts by *m*-CPBA in alkaline aqueous media[9] (Scheme 1).



Scheme 1. Preparation of cyclic oxosulfonium salts

It was first attempted to induce reaction between a five-membered oxosulfonium ylide **3**, generated from **1** using LHMDS as a base, and 4-hexen-3-one, in order to elucidate the reactivity of the cyclic oxosulfonium ylide towards enones. It had been found that the reaction between a five-

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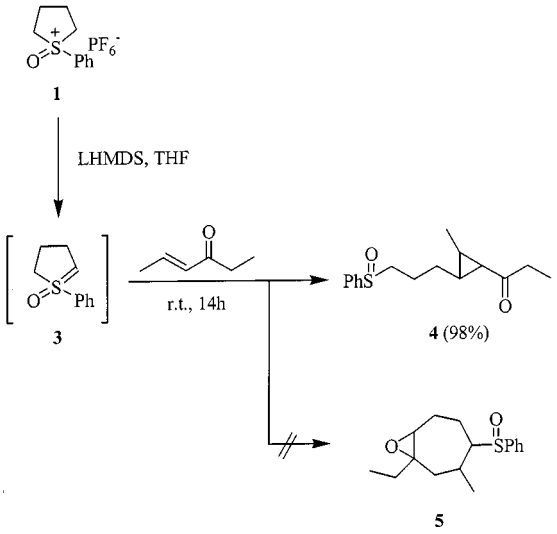
membered cyclic phosphonium ylide and enones provided cycloheptene derivatives, through a Michael-type addition followed by regeneration of the ylide and an intramolecular Wittig reaction.[5] With **3**, however, the reaction gave a cyclopropane derivative **4**[10] in 98% yield, instead of a cycloheptene oxide derivative **5** (Scheme 2).

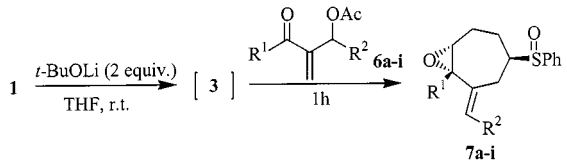


Scheme 2. Reaction of ylide **3** with 4-hexen-3-one

The fact that tandem reactions similar to those of the cyclic phosphonium ylide did not take place was assumed to be due to the intramolecular nucleophilic substitution of an enolate anion, accompanied by a ring-opening reaction, being faster than the regeneration of the ylide. If the enolate anion were to be removed through elimination of a leaving group attached at the position adjacent to the forming enolate anion after the Michael-type addition of the ylide, it might be expected that the undesirable ring-opening reaction would be prevented. We therefore next examined the reaction when β-acetoxy-α-methylene ketones **6a−i** were used as substrates, in the presence of two equimolar amounts of base. Treatment of **3** with **6a−i** in the presence of two equimolar amounts of *t*BuOLi gave 19−77% yields of cycloheptene oxide derivatives **7a−i**, which were presumed to be formed by means of a Michael-type addition of the ylide followed by elimination of an acetoxy group and an intramolecular Corey−Chaykovsky reaction (Table 1).

The reaction was complete within 1 h at room temperature, in spite of the multiple transformations involved in the conversion. Moreover, although many stereoisomers were possible, in view of the *exo*-methylene geometry and the relative configuration of a sulfinyl group, an oxirane ring, and a sulfur atom, all of the cycloheptene oxide derivatives **7a−i** were single stereoisomers. No peaks ascribable to other possible isomers were observed in their ^{1}H NMR and ^{13}C NMR spectra. To clarify the stereochemistry of the products, the NOESY spectrum of compound **7c** was analyzed. Correlation was observed between a vinylic proton and a methyl group bound to the oxirane ring, but none was found between the methylene protons in an ethyl

Table 1. Reaction of β-acetoxy-α-methylene ketones with **3**



Entry	R^1	R^2	Product	Yield[a] (%)
1	Me	*i*-Pr	**7a**	74
2	Me	H	**7b**	19
3	Me	Me	**7c**	56
4	Me	Et	**7d**	66
5	Me	Ph	**7e**	67
6	Et	H	**7f**	24
7	Et	Et	**7g**	62
8	*n*-C_5H_{11}	Ph	**7h**	62
9	*i*-Pr	Ph	**7i**	77

[a] Isolated yield.

group and the methyl group. Additionally, correlation was observed between neighboring protons, as shown in Figure 1.

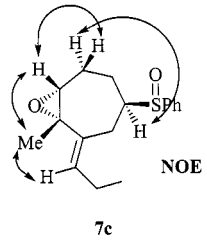


Figure 1. NOE correlation in **7c**

It was therefore indicated that the resulting product was the cycloheptene oxide derivative **7c**, with the phenylsulfinyl group attached to the cycloheptane ring *trans* to the oxirane ring and with (*E*) geometry in the trisubstituted olefin moiety. However, the configuration of the sulfur atom in the sulfinyl group could not be determined from the NOESY spectrum. Cycloheptene oxide derivative **7i** was then analyzed both by NOESY spectroscopy and by X-ray analysis in order to elucidate the complete structure of the products. Correlations similar to those in **7c** were observed in the NOESY spectrum of **7i**, thus suggesting that **7i** had the same stereochemical relationship between its cycloheptene ring substituents as **7c** did. Moreover, the X-ray analysis showed that the sulfur atom in the sulfinyl group had the configuration shown in Figure 2.

These stereochemical outcomes suggested that the product had originated from an intermediate **A′**, possessing a rigid thiabicyclo[3.2.1]octane ring system in which the C−O$^-$ bond and the C−S$^+$ bond were in an antiperiplanar relationship suitable for the subsequent intramolecular nucleophilic substitution (Scheme 3). On the other hand, the

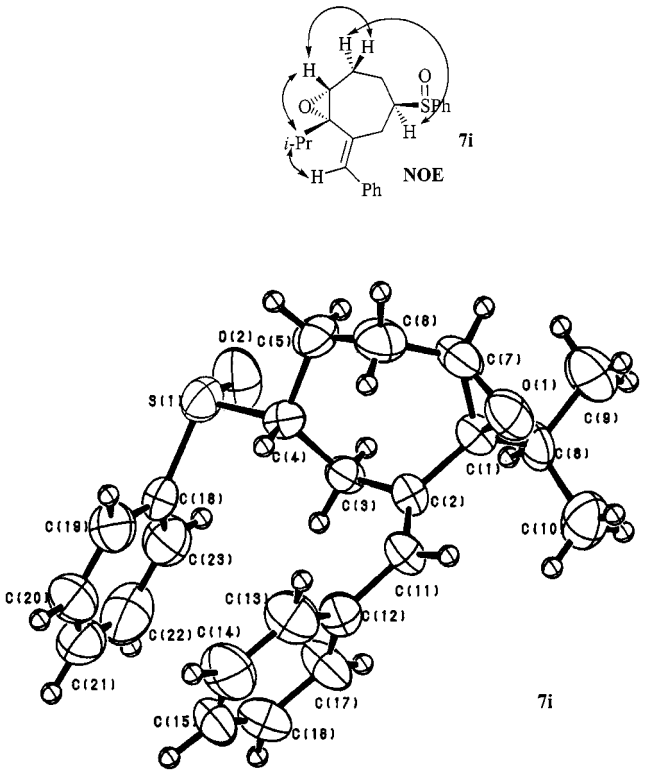


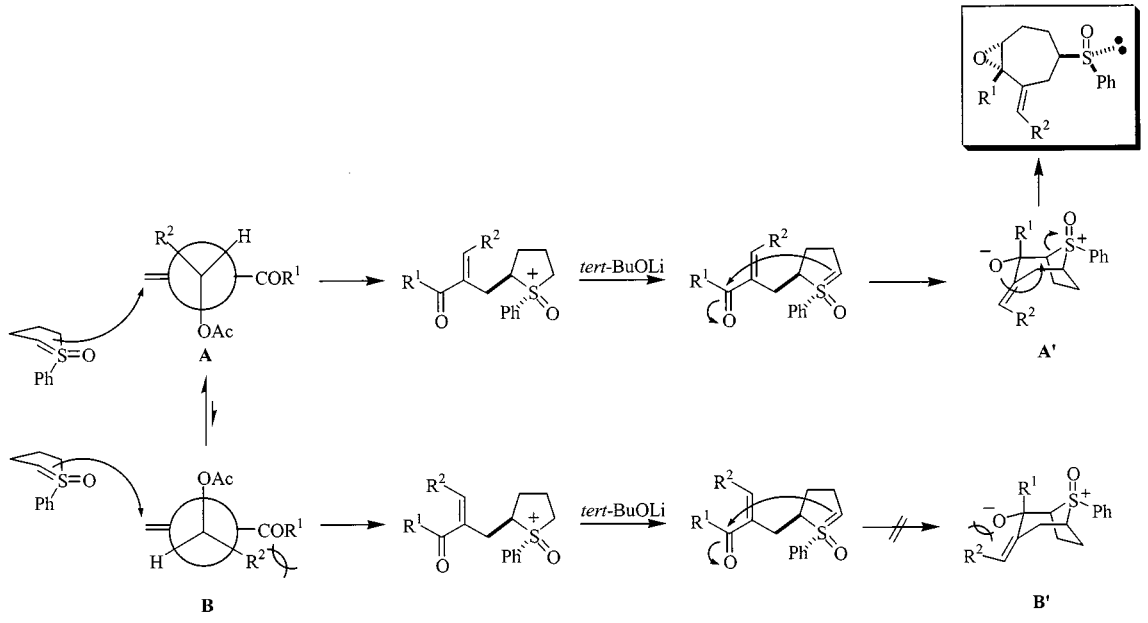
Figure 2. NOE correlation and ORTEP drawing of **7i**

intermediate **A′** was assumed to have been generated by a highly stereocontrolled S_N2' reaction between the oxosulfonium ylide and the enones, in which the oxosulfonium ylide approached conformer **A** of the enone from the direction *trans* to a phenyl group attached to the sulfur atom. That the attack of the ylide occurred predominantly from the direction *trans* to the phenyl group was assumed to be due to steric repulsion by the benzene ring. In addition, of the two possible enone conformers attacked by the ylide, conformer **B** was expected to be unfavorable because of steric interaction between substituent R and a carbonyl group. Consequently, of the other possible intermediates, the intermediate **A′** was generated predominantly.

We next examined the reaction between a six-membered oxosulfonium ylide and β-acetoxy-α-methylene ketones, for purposes of potential application to production of cyclooctene oxide derivatives. The reaction between the six-membered oxosulfonium ylide **8**, generated from **2** in the presence of two equimolar amounts of base, and enone **6a** was examined under sets of several reaction conditions.

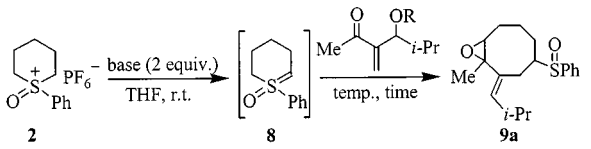
Although, when *t*BuOK was used as a base, the reaction afforded a complex mixture; when *t*BuOLi or LHMDS were used, the same procedure provided the desired cyclooctene oxide derivative **9a**, which was assumed to have been formed through tandem reactions similar to those undergone by the five-membered oxosulfonium ylide. However, the yields of the product were smaller than those obtained when using the five-membered ylide. Although reactions using substrates with different leaving groups were attempted under different reaction temperatures, the reaction conditions as optimized for the five-membered oxosulfonium ylide still provided the best results. In addition, treatment of the ylide **8** with some β-acetoxy-α-methylene ketones **6a−i** was investigated under the most effective reaction conditions (Table 2, Entry 6), with cyclooctene oxide derivatives **9a−i** subsequently being obtained in 7−46% yield (Table 3). The largest yields were observed when the enone possessed a bulky substituent (R^2) at the β-position of the β-acetoxy-α-methylene ketone.

All of the resulting products from this reaction using six-membered ylide **8** were obtained as ca. 4:1 mixtures of stereoisomers, irrespective of reaction conditions and substrates, except for the reaction of **6i** (Table 3, Entry 9). No



Scheme 3. Reaction mechanism of β-acetoxy-α-methylene ketones with **3**

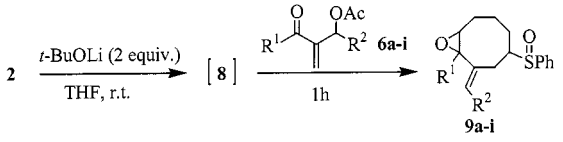
Table 2. Reaction of β-acetoxy-α-methylene ketones with **8**



Entry	Base	R	Temp.	Time(h)	Yield (%)[a]
1	*t*-BuOK	COMe	r.t.	4.5	- [b]
2	LHMDS	COMe	r.t.	17	20
3	*t*-BuOLi	COMe	0°C	1	22
4	*t*-BuOLi	COMe	-20°C - r.t.	2-1	32
5	*t*-BuOLi	COMe	r.t. - reflux	2	39
6	*t*-BuOLi	COMe	r.t.	1	46
7	*t*-BuOLi	$COCCl_3$	r.t.	1	22
8	*t*-BuOLi	$COCH(CH_3)_2$	r.t.	1	40
9	*t*-BuOLi	$COCH_2Ph$	r.t.	1	31

[a] Yields of a mixture of isomers whose ratio was ca. 4:1. The ratio was determined by ^1H NMR spectroscopy. – [b] A complex mixure was obtained.

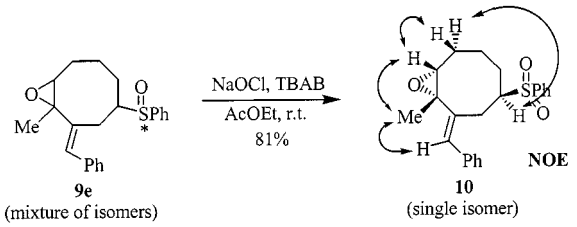
Table 3. Reaction of β-acetoxy-α-methylene ketones with **8**



Entry	R^1	R^2	Product	Yield (%)[a]	Ratio of isomers[b]
1	Me	*i*-Pr	**9a**	46	4:1
2	Me	H	**9b**	7	4:1
3	Me	Me	**9c**	14	4:1
4	Me	Et	**9d**	26	4:1
5	Me	Ph	**9e**	45	4:1
6	Et	H	**9f**	10	4:1
7	Et	Et	**9g**	32	4:1
8	n-C_5H_{11}	Ph	**9h**	45	4:1
9	*i*-Pr	Ph	**9i**	31	9:1

[a] Yields of a mixture of isomers. – [b] Determined by ^1H NMR spectroscopy.

peaks ascribable to other possible isomers were observed in the ^1H NMR and ^{13}C NMR spectra of the products. To obtain information about the stereochemistry of the isomers of the resulting cyclooctene oxide derivatives, we attempted to convert the sulfoxide **9e** into the corresponding sulfone. Treatment of the ca. 4:1 isomer mixture of **9e** with 5% sodium hypochlorite solution in the presence of tetrabutylammonium bromide (TBAB)[11] provided the corresponding sulfone **10** in 81% yield (Scheme 4) and as a single stereoisomer. In addition, it was found from the NOESY spectrum of the sulfone **10** that the stereochemistry of the substituents on the cyclooctane ring had been retained, as shown in Scheme 4. Accordingly, these results indicated that the isomers of the cyclooctene oxide derivatives **9a–i** were a function of different configurations at the sulfur atom.



Scheme 4. Oxidation of sulfoxide **9e**

Moreover, it was established from the X-ray analysis of the sulfoxide **9a** (Figure 3) that the sulfur atom in the major isomer had the same configuration as in the cycloheptene oxide derivative **7i**. These results suggested that the initial Michael-type addition of the six-membered oxosulfonium ylide **8** to the enones had occurred competitively from the directions both *trans* and *cis* to the benzene ring in oxosulfonium ylide **8**, to give a mixture of two isomers of the cyclooctene oxide derivatives, via two intermediates in which the configurations at the sulfur atom were different (Scheme 5).

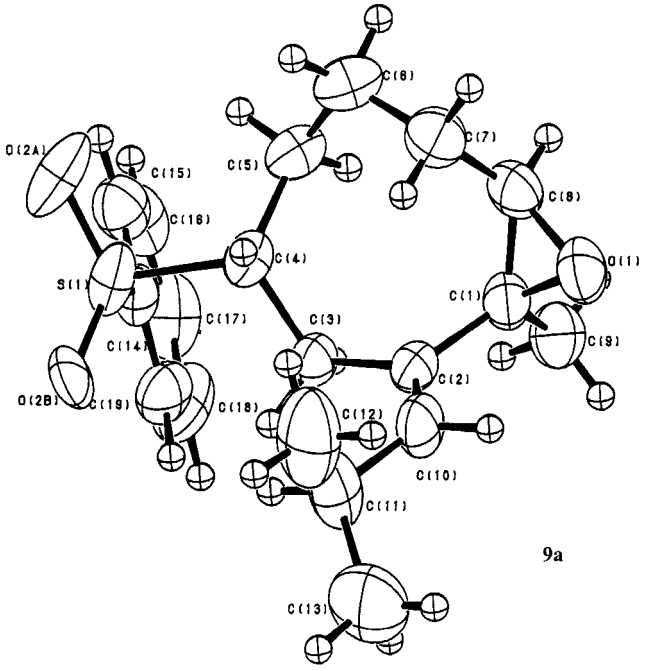
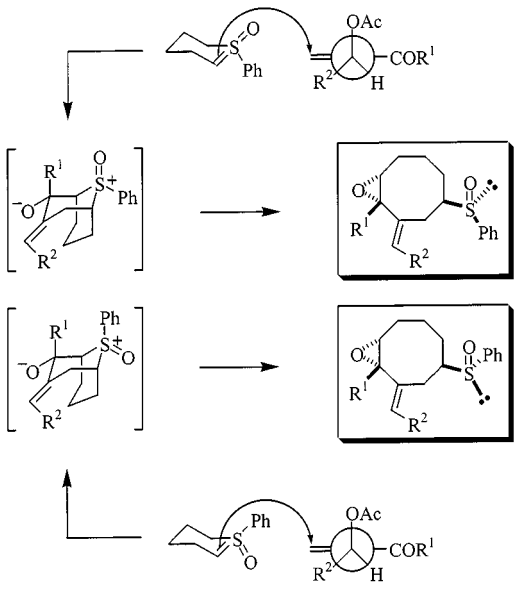


Figure 3. ORTEP drawing of **9a**; the two oxygen atoms [O(2A) and O(2B)] on the sulfur atom [S(1)] indicate that this compound **9a** is an (*R*)/(*S*) mixture of the sulfoxide; the ratio of these isomers was estimated to be ca. 4:1 based upon their atom site occupancies [0.8 for O(2A), 0.2 for O(2B)]



Scheme 5. Reaction mechanism of β-acetoxy-α-methylene ketones with **8**

Conclusion

In conclusion, we have developed a novel tandem reaction between cyclic oxosulfonium ylides and acetates of Baylis−Hillman adducts for the stereoselective synthesis of cycloheptene oxide or cyclooctene oxide derivatives. Further studies on the application of this method to the synthesis of other complex molecules and natural products are currently underway.

Experimental Section

NMR: Bruker DRX 500, Bruker DRX 400, JEOL JNMFX 90A (500 and 125 MHz, 400 and 100 MHz, 90 and 22.5 MHz, for ^{1}H and ^{13}C, respectively). For ^{1}H and ^{13}C NMR, [D$_6$]acetone as solvent, $\delta_H = 2.04$ and $\delta_C = 29.8$ or δ from TMS as reference standard. NOESY spectra were recorded with a 400-MHz NMR spectrometer. − MS: JEOL JMS600 (70 eV or FAB). − IR: JASCO A-100. − X-ray: Rigaku AFC5S. − Melting points are uncorrected. − Reactions were run in dried glassware under nitrogen. THF was distilled from sodium benzophenone ketyl prior to use. Flash column chromatography was carried out on silica gel 60 (Cica-MERCK). The β-acetoxy-α-methylene ketones were prepared by treatment of the corresponding aldehydes with unsaturated ketones in the presence of DABCO in THF,[4] followed by acylation with the corresponding acid chlorides and pyridine. The preparation of the five-membered oxosulfonium hexafluorophosphate **1**, the reaction between the five-membered oxosulfonium ylide **3** and 4-hexen-3-one and β-acetoxy-α-methylene ketones **6a−e**, and the spectroscopic data of the products were reported in ref.[7]

Six-Membered Oxosulfonium Hexafluorophosphate 2: A mixture of pentamethylene sulfide (2.66 g, 26.03 mmol), diphenyliodonium hexafluorophosphate (11.08 g, 26.01 mmol), and copper benzoate (0.20 g, 0.025 equiv.) was heated at 80 °C for 18 h. After having cooled to room temperature, the solidified mixture was dissolved in a small amount of acetone. The acetone solution was then poured into an excess of ether. The precipitated solid was filtered and purified by recrystallization from ethanol. The colorless sulfonium salt was obtained as a colorless solid in 63% yield; m.p. 170−171 °C. *m*-Chloroperoxybenzoic acid (70%, 11.40 g, 6 equiv.) was added to a solution of NaOH (2.78 g, 9 equiv.) in water (250 mL), and the resulting mixture was stirred at room temperature for 30 min. The sulfonium salt (2.50 g, 7.71 mmol) was then added, and the resulting mixture was stirred at 40 °C for 18 h. Aqueous hydrochloric acid (10%) was added dropwise at room temperature, and the mixture was washed several times with diethyl ether. The aqueous layer was then concentrated under reduced pressure, and the residue was purified by recrystallization from ethanol to give oxosulfonium salt **2** in 82% yield as a colorless solid; m.p. 204−205 °C. − ^{1}H NMR: δ = 7.94−8.35 (m, 5 H, aromatic H), 4.42−4.50 (m, 2 H, SCH_2), 4.31−4.37 (m, 2 H, SCH_2), 2.46−2.58 (m, 4 H), 1.99−2.08 (m, 2 H). − ^{13}C NMR: δ = 138.16, 131.87, 130.54, 127.97, 50.89, 22.18, 21.25. − IR (KBr): $\tilde{\nu}$ = 1060 (S=O), 820 (P−F) cm^{-1}. − MS: *m*/*z* = 194 [M$^+$ − HPF_6]. − $C_{11}H_{15}F_6OPS$ (340.3): calcd. C 38.83, H 4.44; found C 38.67, H 4.41.

General Procedure for Treatment of a Five-Membered Oxosulfonium Ylide 3 with β-Acetoxy-α-methylene Ketones 6f−i: Five-membered oxosulfonium salt **1** (100 mg, 0.31 mmol) was added to a solution of *t*BuOH (2.2 equiv.) and *n*-butyllithium (1.5 M sol. in *n*-hexane, 2.2 equiv.) in dry THF (2 mL). After the mixture had been stirred at room temperature for 10 min, a solution of an enone (0.31 mmol) in dry THF (2 mL) was then added dropwise, and the resulting solution was stirred at room temperature for 1 h. The mixture was then quenched with water and extracted with diethyl ether. The combined organic layer was washed with brine, dried with Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate as eluent).

***rel*-(1*S*,4*R*,7*R*)-1-Ethyl-2-methylene-4-[(*R*)-phenylsulfinyl]-8-oxabicyclo[5.1.0]octane (7f):** Colorless syrup (hexane/ethyl acetate, 1:2). − ^{1}H NMR: δ = 7.55−7.68 (m, 5 H, aromatic H), 5.10 (d, *J* = 1.5 Hz, 1 H, vinylic H), 5.03 (brs, 1 H, vinylic H), 2.96−2.99 (m, 1 H), 2.64−2.72 (m, 1 H), 2.24−2.39 (m, 3 H), 1.99−2.03 (m, 1 H), 1.79−1.88 (m, 1 H), 1.54−1.63 (m, 1 H), 1.37−1.48 (m, 2 H), 0.87 (t, *J* = 7.4 Hz, 3 H, CH_3CH_2). − ^{13}C NMR: δ = 145.50, 144.08, 131.68, 129.89, 125.61, 117.28, 66.11, 65.53, 60.33, 31.42, 28.45, 27.97, 24.93, 8.78. − IR (neat): $\tilde{\nu}$ = 1080 (oxirane), 1040 (S=O) cm^{-1}. − MS: *m*/*z* = 277 [M$^+$ + 1]. − HRMS: calcd. for $C_{16}H_{21}O_2S$ [M$^+$ + 1] 277.1262, found [M$^+$ + 1] 277.1232.

***rel*-(1*S*,2*E*,4*R*,7*R*)-1-Ethyl-4-[(*R*)-phenylsulfinyl]-2-propylidene-8-oxabicyclo[5.1.0]octane (7g):** Colorless syrup (hexane/ethyl acetate, 1:2). − ^{1}H NMR: δ = 7.55−7.72 (m, 5 H, aromatic H), 5.40 (t, *J* = 7.4 Hz, 1 H, vinylic H), 2.88−2.92 (m, 1 H), 2.51−2.58 (m, 1 H), 2.29−2.40 (m, 2 H), 2.10−2.16 (m, 1 H), 1.96−2.03 (m, 1 H), 1.70−1.80 (m, 2 H), 1.52−1.58 (m, 2 H), 1.20−1.39 (m, 2 H), 0.83 (t, *J* = 7.4 Hz, 3 H, CH_3CH_2), 0.78 (t, *J* = 7.4 Hz, 3 H, CH_3CH_2). − ^{13}C NMR: δ = 144.04, 134.19, 133.19, 131.41, 129.73, 125.21, 65.88, 65.29, 59.68, 29.05, 28.25, 26.05, 25.24, 20.61, 14.19, 8.76. − IR (neat): $\tilde{\nu}$ = 1095 (oxirane), 1040 (S=O) cm^{-1}. − MS: *m*/*z* = 305 [M$^+$ + 1]. − HRMS: calcd. for $C_{18}H_{25}O_2S$ [M$^+$ + 1] 305.1575, found [M$^+$ + 1] 305.1612.

***rel*-(1*S*,2*E*,4*R*,7*R*)-1-Pentyl-2-(phenylmethylene)-4-[(*R*)-phenylsulfinyl]-8-oxabicyclo[5.1.0]octane (7h):** Colorless solid; m.p. 127.5−129 °C (hexane/ethyl acetate, 1:2). − ^{1}H NMR: δ = 6.79−7.71 (m, 10 H, aromatic H), 6.48 (s, 1 H, vinylic H),

0.86−3.08 (m, 19 H). − ^{13}C NMR: δ =143.62, 137.89, 137.00, 131.69, 131.65, 130.00, 129.20, 128.70, 127.49, 125.28, 66.21, 63.85, 60.30, 35.63, 32.64, 28.48, 26.36, 25.47, 24.95, 23.24, 14.29. − IR (KBr): ṽ = 1090 (oxirane), 1035 (S=O) cm^{-1}. − MS: *m*/*z* = 395 [M$^+$ + 1]. − HRMS: calcd. for $C_{25}H_{31}O_2S$ [M$^+$ + 1] 395.2045, found [M$^+$ + 1] 395.2098.

***rel*-(1*S*,2*E*,4*R*,7*R*)-1-(1-Methylethyl)-2-(phenylmethylene)-4-[(*R*)-phenylsulfinyl]-8-oxabicyclo[5.1.0]octane (7i):** Colorless solid; m.p. 125.5−126.5 °C (hexane/ethyl acetate, 1:2). − ^{1}H NMR: δ = 7.57−7.64 (m, 5 H, aromatic H), 6.87−7.10 (m, 5 H, aromatic H), 6.46 (s, 1 H, vinylic H), 3.11−3.14 (m, 1 H), 2.75−2.83 (m, 1 H), 2.68−2.72 (m, 1 H), 2.37−2.44 (m, 1 H), 2.28−2.34 (m, 1 H), 2.19−2.26 (m, 1 H), 1.78−1.92 (m, 2 H), 1.29−1.38 (m, 1 H), 0.98 (d, *J* = 6.8 Hz, 3 H), 0.91 (d, *J* = 6.8 Hz, 3 H). − ^{13}C NMR: δ = 143.02, 136.68, 136.64, 132.31, 131.15, 129.50, 128.83, 128.33, 127.05, 124.84, 68.45, 63.31, 58.82, 32.04, 28.50, 25.99, 25.49, 18.63, 17.44. − IR (KBr): ṽ = 1080 (oxirane), 1040 (S=O) cm^{-1}. − MS: *m*/*z* = 367 [M$^+$ + 1]. − HRMS: calcd. for $C_{23}H_{27}O_2S$ [M$^+$ + 1] 367.1732, found [M$^+$ + 1] 367.1716.

General Procedure for the Treatment of Six-Membered Oxosulfonium Ylide 8 with β-Acetoxy-α-methylene Ketones 6a−i: Six-membered oxosulfonium salt **2** (100 mg, 0.29 mmol) was added to a solution of *t*BuOH (2.2 equiv.) and *n*-butyllithium (1.5 M sol. in *n*-hexane, 2.2 equiv.) in dry THF (2 mL) and the mixture was stirred at room temperature for 10 min. A solution of an enone (0.29 mmol) in dry THF (2 mL) was then added dropwise to the mixture and the resulting solution was stirred at room temperature for 1 h. The mixture was then quenched with water and extracted with diethyl ether. The combined organic layer was washed with brine, dried with Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate as eluent).

***rel*-(1*R*,2*E*,4*S*,8*S*)-1-Methyl-2-(2-methylpropylidene)-4-(phenylsulfinyl)-9-oxabicyclo[6.1.0]nonane (9a):** Colorless solid; m.p. 126−127 °C (hexane/ethyl acetate, 1:2). − ^{1}H NMR (a mixture of isomers): δ = 7.58−7.74 (m, 5 H, aromatic H), 5.29 (d, *J* = 9.9 Hz, 0.2 H, vinylic H), 5.24 (d, *J* = 9.9 Hz, 0.8 H, vinylic H), 2.97−3.02 (m, 0.2 H), 2.78−2.81 (m, 0.8 H), 2.62−2.67 (m, 1 H), 2.27−2.36 (m, 1 H), 2.19−2.26 (m, 1 H), 1.82−1.93 (m, 3 H), 1.68−1.78 (m, 1 H), 1.50−1.60 (m, 1 H), 1.33−1.42 (m, 1 H), 1.31 (s, 2.4 H), 1.27 (s, 0.6 H), 0.96−1.07 (m, 1 H), 0.86 (d, *J* = 6.6 Hz, 0.6 H), 0.82 (d, *J* = 6.6 Hz, 0.6 H), 0.75 (d, *J* = 6.6 Hz, 4.8 H). − ^{13}C NMR (major isomer): δ = 144.44, 137.31, 133.90, 131.75, 129.80, 125.86, 63.81, 63.03, 62.42, 28.73, 27.89, 26.69, 25.86, 24.19, 23.40, 23.09, 21.90. − ^{13}C NMR (minor isomer): δ = 143.92, 137.31, 133.70, 131.93, 129.80, 126.24, 64.37, 63.80, 62.42, 29.40, 26.89, 26.37, 25.91, 24.56, 23.46, 23.23, 21.90. − IR (KBr): ṽ = 1070 (oxirane), 1040 (S=O) cm^{-1}. − MS: *m*/*z* = 319 [M$^+$ + 1]. − HRMS: calcd. for $C_{19}H_{27}O_2S$ [M$^+$ + 1] 319.1732, found [M$^+$ + 1] 319.1737.

***rel*-(1*S*,4*R*,8*R*)-1-Methyl-2-methylene-4-(phenylsulfinyl)-9-oxabicyclo[6.1.0]nonane (9b):** Colorless solid; m.p. 120−124 °C (hexane/ethyl acetate, 1:2). − ^{1}H NMR (a mixture of isomers): δ = 7.54−7.73 (m, 5 H, aromatic H), 5.05−5.07 (m, 0.4 H, vinylic H), 5.02 (d, *J* = 2.4 Hz, 0.8 H, vinylic H), 4.90 (brs, 0.8 H, vinylic H), 2.60−2.71 (m, 2 H), 2.38−2.45 (m, 1 H), 2.09−2.24 (m, 2 H), 1.84−1.92 (m, 1 H), 1.66−1.76 (m, 1 H), 1.18−1.44 (m, 5 H), 0.98−1.10 (m, 1 H). − ^{13}C NMR (major isomer): δ = 147.25, 131.98, 129.80, 126.25, 125.84, 115.77, 64.35, 64.18, 62.97, 35.01, 26.42, 25.86, 24.27, 21.65. − IR (KBr): ṽ = 1090 (oxirane), 1040 (S=O) cm^{-1}. − MS: *m*/*z* = 277 [M$^+$ + 1]. − HRMS: calcd. for $C_{16}H_{21}O_2S$ [M$^+$ + 1] 277.1262, found [M$^+$ + 1] 277.1263.

***rel*-(1*R*,2*E*,4*S*,8*S*)-2-Ethylidene-1-methyl-4-(phenylsulfinyl)-9-oxabicyclo[6.1.0]nonane (9c):** Colorless solid; m.p. 119−123 °C (hexane/ethyl acetate, 1:2). − ^{1}H NMR (a mixture of isomers): δ = 7.54−7.75 (m, 5 H, aromatic H), 5.54 (q, *J* = 7.0 Hz, 0.2 H, vinylic H), 5.49 (q, *J* = 7.0 Hz, 0.8 H, vinylic H), 3.05−3.09 (m, 0.2 H), 2.75−2.85 (m, 0.8 H), 2.60−2.66 (m, 1 H), 2.22−2.34 (m, 2 H), 1.66−1.92 (m, 3 H), 1.46−1.57 (m, 1.6 H), 1.24−1.36 (m, 6.4 H), 0.89−1.06 (m, 1 H). − ^{13}C NMR (major isomer): δ = 144.28, 136.95, 131.79, 129.80, 126.03, 123.81, 63.00, 62.93, 62.75, 28.31, 27.64, 25.88, 24.16, 21.75, 12.00. − IR (KBr): ṽ = 1080 (oxirane), 1030 (S=O) cm^{-1}. − MS: *m*/*z* = 291 [M$^+$ + 1]. − HRMS: calcd. for $C_{17}H_{23}O_2S$ [M$^+$ + 1] 291.1419, found [M$^+$ + 1] 291.1435. − $C_{17}H_{22}O_2S$ (290.4): calcd. C 70.31, H 7.64; found C 70.41, H 7.84.

***rel*-(1*R*,2*E*,4*S*,8*S*)-1-Methyl-4-(phenylsulfinyl)-2-propylidene-9-oxabicyclo[6.1.0]nonane (9d):** Colorless solid; m.p. 109−110.5 °C (hexane/ethyl acetate, 1:2). −^{1}H NMR (a mixture of isomers): δ = 7.59−7.75 (m, 5 H, aromatic H), 5.49 (t, *J* = 7.5 Hz, 0.2 H, vinylic H), 5.44 (t, *J* = 7.5 Hz, 0.8 H, vinylic H), 3.01−3.04 (m, 0.2 H), 2.79−2.81 (m, 0.8 H), 2.63−2.67 (m, 1 H), 2.28−2.34 (m, 1 H), 2.23−2.26 (m, 1 H), 1.50−1.92 (m, 6 H), 1.28−1.37 (m, 4 H), 0.98−1.08 (m, 1 H), 0.87 (t, *J* = 7.5 Hz, 0.6 H), 0.78 (t, *J* = 7.5 Hz, 2.4 H). − ^{13}C NMR (major isomer): δ = 144.33, 135.65, 131.78, 131.52, 129.80, 125.96, 63.51, 63.01, 62.59, 28.52, 27.78, 25.88, 24.19, 21.87, 20.43, 14.41. − ^{13}C NMR (minor isomer): δ = 143.60, 135.67, 131.89, 131.56, 129.76, 126.21, 63.81, 63.04, 62.59, 29.35, 26.29, 25.92, 24.50, 21.85, 20.65, 14.48. − IR (KBr): ṽ = 1090 (oxirane), 1030 (S=O) cm^{-1}. − MS: *m*/*z* = 305 [M$^+$ + 1]. − HRMS: calcd. for $C_{18}H_{25}O_2S$ [M$^+$ + 1] 305.1575, found [M$^+$ + 1] 305.1651. − $C_{18}H_{24}O_2S$ (304.4): calcd. C 71.01, H 7.95; found C 71.13, H 8.18.

***rel*-(1*R*,2*E*,4*S*,8*S*)-1-Methyl-2-(phenylmethylene)-4-(phenylsulfinyl)-9-oxabicyclo[6.1.0]nonane (9e):** Colorless solid; m.p. 135−136 °C (hexane/ethyl acetate, 1:2). − ^{1}H NMR (a mixture of isomers): δ = 7.08−7.74 (m, 10 H, aromatic H), 6.61 (s, 0.2 H, vinylic H), 6.59 (s, 0.8 H, vinylic H), 3.35−3.40 (m, 0.2 H), 3.12−3.16 (m, 0.8 H), 2.74−2.80 (m, 1 H), 2.66−2.72 (m, 1 H), 2.27−2.38 (m, 1 H), 2.08−2.16 (m, 1 H), 1.90−1.97 (m, 1 H), 1.72−1.84 (m, 1 H), 1.54−1.65 (m, 1 H), 1.34−1.45 (m, 4 H), 1.11−1.22 (m, 1 H). − ^{13}C NMR (major isomer): δ = 143.41, 138.89, 137.25, 132.05, 130.30, 129.87, 129.22, 129.16, 127.45, 126.08, 63.62, 63.06, 62.57, 28.43, 27.60, 25.94, 24.40, 21.65. − ^{13}C NMR (minor isomer): δ = 142.18, 138.98, 137.36, 131.94, 130.18, 129.77, 129.48, 129.20, 127.63, 126.15, 63.58, 63.09, 62.44, 30.07, 25.97, 25.87, 24.50, 21.65. − IR (KBr): ṽ = 1080 (oxirane), 1030 (S=O) cm^{-1}. − MS: *m*/*z* = 353 [M$^+$ + 1]. − HRMS: calcd. for $C_{22}H_{25}O_2S$ [M$^+$ + 1] 353.1575, found [M$^+$ + 1] 353.1552. − $C_{22}H_{24}O_2S$ (352.5): calcd. C 74.96, H 6.86; found C 75.22, H 6.94.

***rel*-(1*S*,4*R*,8*R*)-1-Ethyl-2-methylene-4-(phenylsulfinyl)-9-oxabicyclo[6.1.0]nonane (9f):** Colorless solid; m.p. 101.5−103 °C (hexane/ethyl acetate, 1:2). − ^{1}H NMR (a mixture of isomers): δ = 7.59−7.74 (m, 5 H, aromatic H), 5.16 (brs, 0.2 H, vinylic H), 5.07 (d, *J* = 4 Hz, 0.2 H, vinylic H), 5.02 (d, *J* = 4 Hz, 0.8 H, vinylic H), 4.99 (s, 0.8 H, vinylic H), 2.70−2.79 (m, 1 H), 2.60−2.68 (m, 1 H), 2.41−2.51 (m, 1 H), 2.18−2.25 (m, 1 H), 2.09−2.13 (m, 1 H), 1.94−2.03 (m, 1 H), 1.85−1.93 (m, 1 H), 1.68−1.78 (m, 1 H), 1.24−1.45 (m, 3 H), 1.06−1.20 (m, 1 H), 0.81−0.92 (m, 3 H). − ^{13}C NMR (major isomer): δ = 145.04, 143.54, 132.02, 129.80, 126.34, 117.30, 66.08, 64.33, 62.11, 34.92, 27.29, 26.42, 25.49, 24.30, 8.84. − IR (KBr): ṽ = 1080 (oxirane), 1030 (S=O) cm^{-1}. − MS: *m*/*z* = 291 [M$^+$ + 1]. − HRMS: calcd. for $C_{17}H_{23}O_2S$ [M$^+$ + 1] 291.1418, found [M$^+$ + 1] 291.1455.

***rel*-(1*R*,2*E*,4*S*,8*S*)-1-Ethyl-4-(phenylsulfinyl)-2-propylidene-9-oxabicyclo[6.1.0]nonane (9g):** Colorless solid; m.p. 142−143.5 °C (hexane/ethyl acetate, 1:2). − ^{1}H NMR (a mixture of isomers): δ = 7.55−7.73 (m, 5 H, aromatic H), 5.47 (t, *J* = 7.6 Hz, 0.2 H, vinylic H), 5.43 (t, *J* = 7.6 Hz, 0.8 H, vinylic H), 3.02 (d, *J* = 12 Hz, 0.2 H), 2.81 (d, *J* = 12 Hz, 0.8 H), 2.65−2.72 (m, 1 H), 2.51−2.58 (m, 1 H), 2.23−2.35 (m, 2 H), 1.47−2.02 (m, 5 H), 0.77−1.38 (m, 10 H). − ^{13}C NMR (major isomer): δ = 144.48, 133.54, 133.10, 131.78, 129.81, 125.98, 66.23, 63.62, 62.14, 28.51, 27.77, 27.44, 25.57, 24.27, 20.53, 14.47, 8.86. − IR (neat): ṽ = 1080 (oxirane), 1035 (S=O) cm^{-1}. − MS: *m*/*z* = 319 [M$^+$ + 1]. − HRMS: calcd. for $C_{19}H_{27}O_2S$ [M$^+$ + 1] 319.1732, found [M$^+$ + 1] 319.1744. − $C_{19}H_{26}O_2S$ (318.5): calcd. C 71.66, H 8.23; found C 71.15, H 8.26.

***rel*-(1*R*,2*E*,4*S*,8*S*)-1-Pentyl-2-(phenylmethylene)-4-(phenylsulfinyl)-9-oxabicyclo[6.1.0]nonane (9h):** Colorless solid (hexane/ethyl acetate, 1:2). − ^{1}H NMR (a mixture of isomers): δ = 7.08−7.70 (m, 10 H, aromatic H), 6.59 (s, 0.2 H, vinylic H), 6.57 (s, 0.8 H, vinylic H), 3.35−3.39 (m, 0.2 H), 3.10−3.13 (m, 0.8 H), 2.65−2.79 (m, 2 H), 2.26−2.37 (m, 1 H), 2.05−2.18 (m, 2 H), 1.89−1.93 (m, 1 H), 1.75−1.82 (m, 1 H), 1.56−1.68 (m, 1 H), 0.74−1.45 (m, 12 H). − ^{13}C NMR (major isomer): δ = 143.47, 137.29, 137.11, 132.02, 131.57, 129.87, 129.20, 129.18, 127.42, 126.03, 66.10, 62.15, 62.15, 34.34, 32.42, 28.23, 27.63, 25.46, 25.02, 24.49, 23.16, 14.27. − ^{13}C NMR (minor isomer): δ = 142.90, 137.42, 137.27, 131.92, 131.43, 131.33, 129.76, 129.47, 127.62, 126.12, 68.24, 66.15, 64.15, 34.34, 32.42, 28.23, 27.63, 25.72, 24.98, 24.59, 23.59, 14.27. − IR (KBr): ṽ = 1440 (Ph), 1070 (oxirane), 1030 (S=O) cm^{-1}. − MS: *m*/*z* = 409 [M$^+$ + 1]. − HRMS: calcd. for $C_{26}H_{33}O_2S$ [M$^+$ + 1] 409.2201, found [M$^+$ + 1] 409.2215.

***rel*-(1*R*,2*E*,4*S*,8*S*)-1-(1-Methylethyl)-2-(phenylmethylene)-4-(phenylsulfinyl)-9-oxabicyclo[6.1.0]nonane (9i):** Colorless solid; m.p. 126−129 °C (hexane/ethyl acetate, 1:2). − ^{1}H NMR (a mixture of isomers): δ = 7.08−7.70 (m, 10 H, aromatic H), 6.56 (s, 0.1 H, vinylic H), 6.53 (s, 0.9 H, vinylic H), 3.35−3.38 (m, 0.1 H), 3.07−3.10 (m, 0.9 H), 3.01 (dd, *J* = 10.8, 3.1 Hz, 1 H), 2.68−2.74 (m, 1 H), 2.31−2.37 (m, 1 H), 2.16−2.26 (m, 1 H), 2.08−2.15 (m, 1 H), 1.89−1.95 (m, 1 H), 1.75−1.85 (m, 1 H), 1.52−1.62 (m, 1 H), 1.37−1.47 (m, 1 H), 1.24−1.33 (m, 1 H), 0.94 (d, *J* = 6.8 Hz, 2.7 H), 0.91 (d, *J* = 6.8 Hz, 0.3 H), 0.81 (d, *J* = 6.8 Hz, 2.7 H), 0.78 (d, *J* = 6.8 Hz, 0.3 H). − ^{13}C NMR (major isomer): δ = 143.32, 137.48, 137.30, 132.07, 132.01, 129.86, 129.16, 129.16, 127.40, 126.00, 68.70, 62.38, 60.15, 28.70, 28.31, 27.67, 25.64, 24.43, 18.96, 16.90. − IR (KBr): ṽ = 1080 (oxirane), 1040 (S=O), cm^{-1}. − MS: *m*/*z* = 381 [M$^+$ + 1]. − HRMS: calcd. for $C_{24}H_{29}O_2S$ [M$^+$ + 1] 381.1888, found [M$^+$ + 1] 381.1963.

***rel*-(1*R*,2*E*,4*S*,8*S*)-1-Methyl-2-(phenylmethylene)-4-(phenylsulfonyl)-9-oxabicyclo[6.1.0]nonane (10):** Aqueous NaOCl (5%, 2 equiv., 560.2 mg) was added to a solution of sulfoxide (**9e**) (67.0 mg, 0.19 mmol) and *n*Bu$_4$NBr (25.7 mg, 0.08 mmol) in 4 mL of ethyl acetate. The mixture was stirred vigorously at room temperature. After the sulfoxide had been completely consumed (43 h), the mixture was then added to water and extracted with ether. The combined organic layer was washed with brine, dried with Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate, 3:1 as eluent) to give **10** in 81% yield as a colorless solid; m.p. 159−160 °C. − ^{1}H NMR: δ = 7.62−7.94 (m, 5 H, aromatic H), 7.05−7.15 (m, 5 H, aromatic H), 6.62 (s, 1 H, vinylic H), 3.23−3.27 (m, 1 H), 3.06−3.13 (m, 1 H), 2.82 (dd, *J* = 10.9, 3.1 Hz, 1 H), 2.54−2.60 (m, 1 H), 2.19−2.26 (m, 1 H), 1.93−2.00 (m, 1 H), 1.78−1.88 (m, 1 H), 1.61−1.70 (m, 1 H), 1.43−1.53 (m, 4 H), 1.11−1.22 (m, 1 H). − ^{13}C NMR: δ = 138.93, 137.86, 137.03, 134.75, 131.16, 130.23, 129.79, 129.15, 129.14, 127.57, 63.71, 63.62, 62.95, 30.48, 26.20, 25.89, 24.34, 21.67. − IR (KBr): ṽ = 1440 (Ph), 1300 (SO_2), 1140 (SO_2), 1080 (oxirane) cm^{-1}. − MS: *m*/*z* = 369 [M$^+$ + 1]. − HRMS: calcd. for $C_{22}H_{25}O_3S$ [M$^+$ + 1] 369.1524, found [M$^+$ + 1] 369.1502.

Crystal Data and Structure Refinements. − Compound 7i: Empirical formula: $C_{23}H_{26}O_2S$; molecular mass: 366.52; temperature: 294 K; wavelength: 0.71069 Å; crystal system: tetragonal; space group: $I4_1/a$ (# 88); unit cell dimensions: *a* = 25.289(6) Å, *c* = 12.48(1) Å; *V* = 7982(6) Å^3; *Z* = 16; density (calcd.): 1.220 g/cm^3; μ = 1.67 cm^{-1}; *F*(000): 3136; crystal dimensions: 0.240×0.400×0.660 mm; 2θ range for data collection: 19.98−24.85°; reflections collected: 4630; independent reflections: 4435 [*R*(int) = 0.060]; structure solution: Direct Methods; refinement method: full-matrix least squares; data/parameter: 1315/235; goodness-of-fit: 1.59; reflection/parameter ratio: 5.6; R/R_W: 0.076/0.071; largest diff. peak and hole: 0.29 and −0.31e$^-$/Å^3. − **Compound 9a:** Empirical formula: $C_{19}H_{26}O_2S$; molecular mass: 318.47; temperature: 294 K; wavelength: 0.71069 Å; crystal system: monoclinic; space group: $P2_1/n$ (# 14); unit cell dimensions: *a* = 7.112(5) Å, *b* = 17.714(5) Å, *c* = 14.297(3) Å, β = 91.56(3)°; *V* = 1800(1) Å^3; *Z* = 4; density (calcd.): 1.175 g/cm^3; μ = 1.76 cm^{-1}; *F*(000): 688; crystal dimensions: 0.320×0.440×0.880 mm; 2θ range for data collection: 24.0−32.5°; reflections collected: 4609; independent reflections: 4275 [*R*(int) = 0.064]; structure solution: Direct Methods; refinement method: full-matrix least squares; data/parameter: 1768/209; goodness-of-fit: 1.62; reflection/parameter ratio: 8.46; R/R_W: 0.070:0.070; largest diff. peak and hole: 0.27 and −0.27e$^-$/Å^3. − Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-150203 (**7i**) and -150204 (**9a**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.au.uk].

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