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Do the Electronic Effects of Sulfur Indeed Control the π-Selectivity of γ-Sulfenyl Enones? An Investigation†

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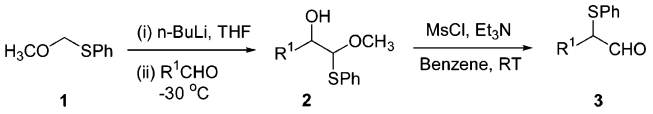
The electronic effects of sulfur in γ-sulfenyl enones are not transmitted to the carbonyl carbon through the π bond as reported previously. The diastereoselectivity is rather controlled by a combination of several other factors. The steric effects arising from the substituents on the sulfur atom and the γ-carbon and the bulk of the nucleophile constitute the major control elements.

Introduction

The influence of a heteroatom that is vinylogously adjacent to a center of nucleophilic attack has received much attention.[1] Sato et al.[2] have studied the hydride reduction of γ-sulfenyl enones. The observed high *anti*-to-S selectivity was attributed to the electronic effect of sulfur that was transmitted to the reaction center through the π bond. It was emphasized that the observed selectivity was neither steric- nor chelation-controlled. Wipf et al.[3] have reported high *anti*-to-O selection from the reactions of 4,4-disubstituted cyclohexadienones with Grignard reagents in support of a dipolar control model that allowed a nucleophile to approach the carbonyl function from the positive end of the molecular dipole. Felkin−Anh−Cieplak-type hyperconjugative orbital stabilization[4] in the TS was considered secondary. This dipolar control model, when applied to the above γ-sulfenyl enones, predicts *syn*-to-S addition.

In contrast, Fleming et al.[5] observed a complete loss of selectivity from hydride reduction of γ-methoxy enones that led them to conclude that the Cram selectivity[6] was largely steric in origin. Reetz et al.[7] made a similar observation from the addition of alkyllithium and Grignard reagents to γ-amino and γ-alkoxy enals and concluded that the possible electronic and steric effects were not transmitted from the heteroatom to the reaction center through the π-system. Dumaritin et al.[8] observed no or very little selectivity from the reduction of 1,1-bis-ethoxy-5-*tert*-butyldiphenylsilyloxy-3-hexen-2-one. Our own investigation of nucleophilic additions to 6-methyl-1-oxa-4-thiaspiro[4.5]dec-6-ene-7-carbaldehyde, a substrate that possessed both sulfur and oxygen at the γ-carbon, showed only a marginal *anti*-to-S selection.[9] However, if the rationale of electronic effects[2] were true, high *anti*-to-S selectivity must have prevailed for the combined electronic effects of the two heteroatoms. Likewise, had the dipolar control model been at work, *the syn*-to-S selectivity must have predominated.

SCHEME 1



1 2 3

The above contrasts led us to probe steric effects, and thus, we investigated the hydride reduction of variously substituted γ-sulfenyl enones in detail. We describe our results herein to demonstrate conclusively that the observed selectivity is predominantly steric-in-origin and that the solvent and the low temperature also contributed to it.

Starting Materials

The γ-sulfenyl enones **7** were prepared by Wittig−Horner reaction of the corresponding α-sulfenyl aldehydes **3** that, in turn, were prepared by following the protocols given in Schemes 1 and 2. The α-sulfenyl esters **5** were reduced to the alcohols **6** that were oxidized to furnish the α-sulfenyl aldehydes **3**. The protocol outlined in Scheme 2 offers the flexibility of incorporating different substituents on sulfur as required for our studies. The α-sulfenyl aldehydes with R^1 = Et, $(CH_2)_4$, $(CH_2)_5$, and

† Dedicated fondly to Professor Sukh Dev on the occasion of his 80th birthday.

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(1) Mengel, A.; Reiser, O. *Chem. Rev.* **1999**, *99*, 1191.

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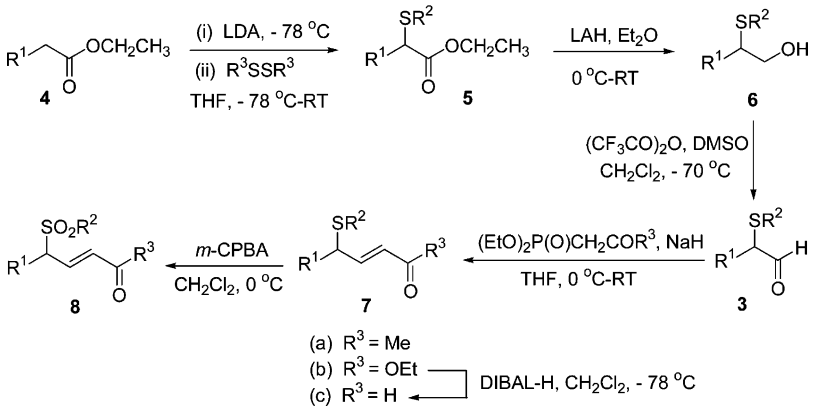
SCHEME 2



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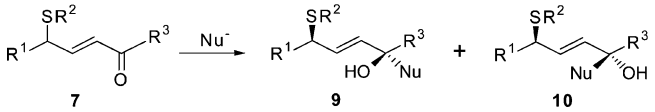

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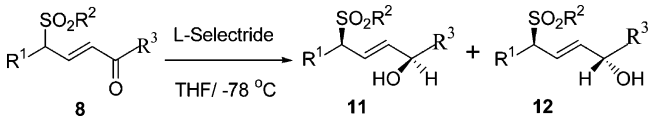

CH_2CH_2Ph and R^2 = Ph were prepared by the protocol given in Scheme 1.[10,11] All other α-sulfenyl aldehydes were prepared as outlined in Scheme 2.

Results and Discussion

Since, in all but one substrate, the substituent on sulfur was Ph and the substituent on the γ-carbon was a large alkyl group (*t*-Bu, *i*-Pr, *n*-C_6H_{13}, *n*-C_7H_{15}), the observed selectivity could very well be a consequence of large group steric effects. Further, since the C−S bond is almost orthogonal to the plane of the enone function with S−C−C=C dihedral angle at ∼106°,[12] the Ph on sulfur is likely to shield one face of the enone and thus direct a nucleophile to the other face. An evaluation of steric and electronic effects was therefore necessary, and we chose to study both the SPh- and SMe-substrates (**7**, R^2 = Ph, Me) (Scheme 3). Again, since the bulk of R^3 was shown by the earlier investigators[2] not to influence the selectivity appreciably (e.g., the *anti*-to-S selectivity was reduced from 97:3 to 94:6 to 91:9 on changing R^3 from *t*-Bu to *i*-Pr to Me, respectively, for the substrate with R^1 = *t*-Bu and R^2 = Ph), we chose to study the substrates with R^3 = Me. This allowed us to probe the steric effects of R^1, R^2, and the hydride reagent.

1. Steric Effects of R^1 and R^2. The ratios of the alcohols **9** and **10** formed from L-Selectride reduction of several γ-sulfenyl enones **7a** are collected in Table 1.[13] The PhS-substrates showed considerably higher *anti*-to-S selectivity than the corresponding MeS-substrates. This is likely to be due to a more effective shielding of the *syn*-to-S face of the enone by Ph than by Me that guides Selectride to the *anti*-to-S face of the carbonyl function. The selectivity was constant at about 67:33 for R^1 = *n*-Bu, *i*-Pr, *t*-Bu, and *n*-C_8H_{17} for the MeS-substrates just as it was constant at about 86:14 for the PhS-substrates. The only exception was the substrate with R^1 = *t*-Bu and R^2 = Ph when the selectivity increased to 91:9. Interestingly, irrespective of the substituent on the sulfur, the selectivity had increased further to 100:0 when the γ-carbon was part of a ring system (entries 11−14). The *anti*-to-S selectivity was confirmed from the X-ray structure of the 4-bromobenzoate of the sulfone derived from the alcohol at entry 13 (Figure 1).

A notable observation was made to the effect that the *anti*-to-S selectivity had decreased from about 86:14 to 78:22 for the PhS-bearing substrate when R^1 was changed from *n*-Bu/*i*-Pr to CH_2CH_2Ph (entry 2/4 vs 15). This is likely to be due to a competitive shielding of the *anti*-to-S face of the enone by the Ph present in R^1 in much the same manner as the Ph on S was expected to shield the *syn*-to-S face. This argument draws support from the

TABLE 1. Diastereoselectivity of Hydride Addition to γ-Sulfenyl Enones 7a[a,b]

entry	R^1	R^2	R^3	yield[c] (%)	ratio **9**:**10**[d]
1	C_2H_5	Ph	Me	96	71:29
2	*n*-C_4H_9	Ph	Me	92	85:15
3	*n*-C_4H_9	Me	Me	94	66:34
4	*i*-C_3H_7	Ph	Me	94	86:14
5	*i*-C_3H_7	Me	Me	92	68:32
6	*t*-C_4H_9	Ph	Me	94	91:9[e]
7	*t*-C_4H_9	Me	Me	92	68:32
8	*n*-C_6H_{13}	Ph	Me	91	85:15
9	*n*-C_8H_{17}	Ph	Me	94 (98)	83:17 (63:37)
10	*n*-C_8H_{17}	Me	Me	93 (97)	66:34 (54:46)
11	*c*-C_5H_8[f]	Ph	Me	90	100:0
12	*c*-C_5H_8[f]	Me	Me	97	100:0
13	*c*-C_6H_{10}[f]	Ph	Me	94	100:0
14	*c*-C_6H_{10}[f]	Me	Me	93	100:0
15	$-CH_2CH_2Ph$	Ph	Me	94	79:21
16	$-CH_2CH_2Ph$	Me	Me	93	55:45[g]

[a] All the reactions were carried out in THF at −78 °C for 30 min using 2 equiv of L-Selectride. [b] Values in the parentheses are the results from reduction with 1 equiv of $NaBH_4$ in MeOH at −78 °C. [c] Isolated yields. [d] Determined from ^1H integrals of CH(OH)*Me* and S*Me* for PhS- and MeS-substrates, unless indicated otherwise. [e] Determined from ^1H integrals of C*H*(SPh). [f] The γ-carbon atom is part of the ring system. [g] Determined from ^1H integrals of OCO*Me* of the corresponding mixture of acetates.

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(12) Dorgio, A. E.; Morokuma, K. *J. Am. Chem. Soc.* **1989**, *111*, 6524.
(13) The distributions of diastereomers formed from the hydride reductions of SPh and SMe enones were determined, respectively, from ^1H integrals of S*Me* and CH(OH)*Me*.

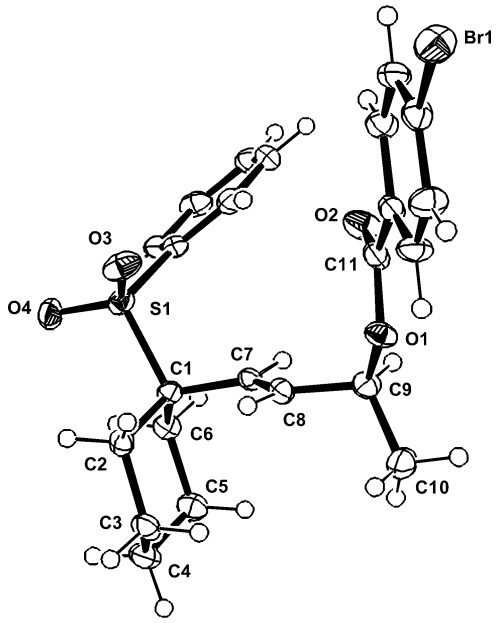

FIGURE 1. ORTEP plot of the X-ray crystal structure of the sulfone/4-bromobenzoate of the product in entry 13, Table 1. Selected bond lengths (Å), bond angles (deg), and torsional angles (deg): C(7)C(8) 1.314(3), S(1)C(1) 1.837(2); C(7)C(1)S-(1) 107.95(16); C(8)C(7)C(1) 126.4(2), S(1)C(1)C(7)C(8) 102.4 (2), C(7)C(8)C(9)O(1) 130.2(2).

TABLE 2. Reduction of γ-Sulfonyl Enones 8 with L-Selectride[a]

entry	R^1	R^2	R^3	yield **11** + **12**[b] (%)	ratio **11**:**12**[c]
1	C_2H_5	Ph	Me	90	75:25
2	*t*-C_4H_9	Ph	Me	93	100:0
3	*t*-C_4H_9	Me	Me	91	65:35

[a] The reductions were carried out under conditions identical to those for the reductions of the corresponding sulfenyl enones. [b] Isolated yields. [c] Determined by ^{1}H integrals of CH(OH)*Me* for SO_2Ph materials and the integral of SO_2*Me* for entry 3.

observation that the *anti*-to-S selectivity for the corresponding MeS-derivative had also decreased from about 67:33 to 55:45 (entry 16). Our results, therefore, support significant steric effects on the observed selectivity that contrasts the "only electronic effects" argument.[2] The electronic effects arising from the sulfur[14] influence primarily the stable conformers distribution in compliance with the stereoelectronic effects that favor the carbon−sulfur bond to be aligned orthogonal to the plane of the enone function.

2. Effect of Reversing the Electronic Effects of Sulfur. We substantiate our claim that the preferred *anti*-to-S addition of nucleophiles to the γ-sulfenyl enones is due primarily to the steric effects and that the electronic effects of sulfur are less importrant in the diastereocontrol from the results obtained from L-Selectride reduction of the γ-sulfonyl enones **8**. The sulfur has changed from being electron-donating in **7** to electron-attracting in **8** (Table 2). Obviously, an addition *syn*-to-S must predominate if the selectivity were indeed controlled by only the electronic effects of the sulfur. In the event, not only did the *anti*-addition predominate but it was also enhanced somewhat in comparison to that for the corresponding sulfenyl substrates. For instance, the selectivity had increased from 71:29 to 75:25 for the substrate with $R^1 = C_2H_5$ and R^2 = Ph and from 91:9 to 100:0 for the substrate with R^1 = *t*-Bu and R^2 = Ph. The stereostructure of the product with R^1 = *t*-Bu and R^2 = Ph was confirmed from its X-ray structure (Figure 2). It is important to note that the carbon−sulfur bond is almost orthogonal to the plane of the olefinic bond in the product alcohol. Ab initio MO calculations at the B3LYP/6-31G* level[15] suggest that the *s-cis*-**8** ($R^1 = R^3$ = Me, R^2 = Ph) is slightly favored over the *s-trans*-**8** by 0.22 kcal/mol and that both the conformers possessed the carbon−sulfur and C−H bonds, respectively, orthogonal to and in-plane of the enone function.

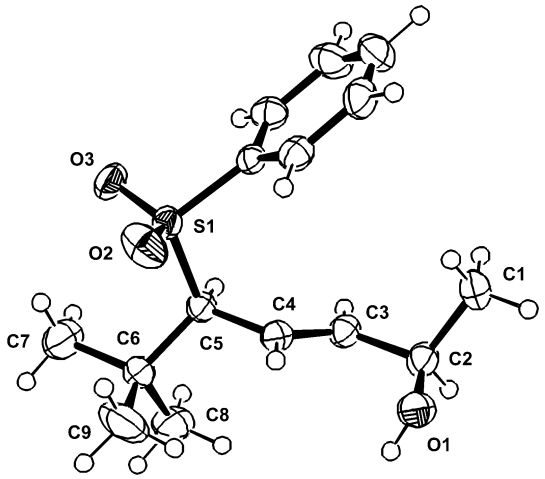

FIGURE 2. ORTEP plot of the X-ray crystal structure the alcohol in entry 2, Table 2. Selected bond lengths (Å), bond angles (deg), and torsional angles (deg): C(3)C(4) 1.312(3); S(1)C(5) 1.8062(19); C(4)C(5)S(1) 108.29(12), C(3)C(4)C(5) 124.15(17); S(1)C(5)C(4)C(3) −112.12(15), C(4)C(3)C(2)O(1) 12.4 (3).

3. Effect of the Bulk of the Hydride Reagent. We studied next the effect of the bulk of the reducing agent and performed selected reactions with $NaBH_4$ at −78 °C. These results are also collected in Table 1. In both the cases, $NaBH_4$ gave only marginal *anti*-to-S selectivity. The considerable drop in the *anti*-to-S selectivity is instructive. The bulk of the hydride reagent is obviously much more important than the bulks of the substituents in the substrate for the diastereocontrol. The large bulk of L-Selectride coupled with those of Ph or Me on S ensured the high selectivities observed throughout by the previous investigators.[2]

$NaBH_4$ is less sensitive to the bulks of R^1 and R^2 than L-Selectride because of its relatively much smaller size. It can, therefore, approach both the faces of the enone with considerably reduced discrimination. Had it been

(14) The electron-donating abilities of σ-bonds increases in the order: $\sigma_{CO} < \sigma_{CC} < \sigma_{CH} < \sigma_{CS}$. Epiotis, N. D.; Cherry, W. R.; Shaik, S.; Yates, R. L.; Bernardi, F. *Top. Curr. Chem*. **1977**, 70.

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TABLE 3. Reactions of γ-Sulfenyl Enones 7a with L-Selectride under Different Conditions[a]

entry	R^1	R^2	R^3	solvent	T (°C)	yield **9** + **10**[b] (%)	**9**:**10**[c]
1	*n*-C_4H_9	Ph	Me	THF	−78	92	85:15
2	*n*-C_4H_9	Ph	Me	toluene	−78	90	74:26
3	*n*-C_4H_9	Ph	Me	THF/HMPA (10:1)	−78	92	76:24
4	*n*-C_4H_9	Ph	Me	THF/HMPA (10:5)	−78	87	73:27
5	*n*-C_8H_{17}	Ph	Me	THF	−78	92	85:15
6	*n*-C_8H_{17}	Ph	Me	THF	−40	93	75:25
7	*n*-C_8H_{17}	Ph	Me	THF	0	94	66:34

[a] All the reactions were carried out for 30 min with 2 equiv of L-Selectride. [b] Isolated yields. [c] Ratios were calculated from ^{1}H integrals of CH(OH)*Me*.

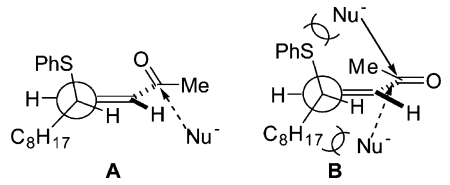

FIGURE 3.

due to the electronic effects of S, the *anti*-to-S selectivity from reduction with $NaBH_4$ will be expected to be, more or less, similar to the selectivity observed from reduction with L-Selectride.

4. Effect of Solvent and Temperature. The solvent and temperature also contributed to the selectivity. We have studied R^1 = *n*-Bu and *n*-C_8H_{17} with R^2 = Ph and R^3 = Me for the study of the effects of solvent and temperature, respectively. The results are collected in Table 3. The selectivity dropped from 85:15 in THF to 74:26 in toluene. The solvent THF will be expected to increase the total bulk of L-Selectride by complexation with Li^+ cation that, in turn, will increase the *anti*-to-S selectivity. Such a complexation is less likely in toluene. The increase in the polarity of the solvent by the addition of HMPA reduced the selectivity (*cf.* entries 3 and 4). HMPA will be expected to solvate Li^+ and remove it away from tri-*sec*-butyl borohydride. The bulk of the nucleophile is, therefore, reduced, and poor *anti*-to-S selectivity is observed.

The selectivity was reduced from 85:15 observed at − 78 °C to 75:25 and 66:34 at −40 °C and 0 °C (entries 5 and 7), respectively, under otherwise identical conditions. This is likely because the contribution from the s-*trans* conformer is raised at higher temperatures. Studies on the conformational preferences of similar methyl enones have revealed that they received contribution from both the *s-cis* and the *s-trans* conformers.[16] The incoming nucleophile encounters steric interactions with the phenyl on S and *n*-C_8H_{17} in the *s-trans* conformer **B** during the additions syn and anti to the sulfur, respectively (Figure 3).[4,17] The steric interactions with the phenyl on S will, however, be larger than the steric interactions with *n*-C_8H_{17} due to the improved conformational closeness of the former to the reaction center. The *anti*-to-S approach of a nucleophile will then generate the product **10** that will be formed, in principle, from the *syn*-to-S approach of a nucleophile to the *s-cis* conformer **A**. This results in the loss of selectivity.

TABLE 4. Reactions of γ-Sulfenyl Enals 7c with RMgI[a]

Sl no.	R^1	R^2	R^3	R	yield **9** + **10**[b] (%)	**9**:**10**
1	*t*-C_4H_9	Ph	H	Me	84	58:42[c]
2	*t*-C_4H_9	Ph	H	Ph	87	72:28[c]
3	*c*-C_6H_{10}[d]	Ph	H	Me	89	100:0

[a] The reactions were carried out in THF at − 78 °C for 2 h using 2 equiv of freshly prepared RMgI (1 M solution in Et_2O). [b] Isolated yields. [c] Determined by ^{1}H integrals for C*H*(SPh). [d] The γ-carbon is part of the ring system.

The above steric interactions are absent in the *anti*-to-S approach of a nucleophile to the *s-cis* conformer **A**. The *syn*-to-S approach, however, will experience steric interactions from the phenyl on S that, as stated above, is conformationally fairly close to the reaction center. This will allow the *s-cis* conformer **A** to react faster than the *s-trans* conformer **B**. The predominant formation of **9** over **10** even at 0 °C suggests that it is possibly the *s-cis* conformer **A** that reacted in preference to the *s-trans* conformer **B**. The high selectivity observed with the single methyl ketone studied by the previous investigators[2] was thereofre supported additionally by the low temperature (−78 °C) at which the reaction was performed. The methyl ketone reacted primarily (or even exclusively) through the *s-cis* conformer at −78 °C (vide infra).

5. Reaction of the Corresponding Enal with Grignard Reagents. With a 2-fold objective of (a) evaluating the rationale that the substituent on sulfur indeed controlled the selectivity and (b) indirectly confirming the fact that the methyl ketones **7** indeed reacted largely through the *s-cis* conformation at −78 °C, we considered reacting the γ-sulfenyl enals **7c** with MeMgI to generate the same products as those formed from the hydride reduction of the corresponding methyl ketone and also with PhMgI to assess the impact of the bulk of the nucleophile additionally.[18] The results are collected in Table 4. Enals exist in the *s-trans* conformation predominantly.[16] Our own ab initio MO calculatiuons of the *s-cis*-**7c** and *s-trans*-**7c** ($R^1 = R^2$ = Me) at B3LYP/6-31G* level indicated the *s-trans* conformer to be 1.48 kcal/mol more stable than the *s-cis* conformer.

For the reasons discussed above for the transition structure **B**, more *anti*-to-S reaction must take place than the alternate *syn*-to-S variant. In the event, MeMgI exhibited **9c**:**10c** = 58:42 selectivity that was raised to 72:28 on reaction with PhMgI. Whereas the 58:42 diastereocontrol observed with MeMgI is too small to support the "only electronic effects" argument, the increase in the *anti*-to-S selectivity in the reaction with PhMgI clearly supports the steric effects argument. The increased steric interactions of the phenyl on S with PhMgI than that with MeMgI appears responsible for the enhanced *anti*-to-S approach of the former reagent. The cycloderivative at entry 3 reacted with remarkable *anti*-to-S control. The major product **9** that is formed from the *anti*-to-S addition

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(17) (a) Bürgi, H. B. *Angew. Chem.* 1975, *87*, 461. (b) Bürgi, H. B. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 460. (c) Bürgi, H. B.; Dunitz, J. D. *Acc. Chem. Res.* **1983**, *16*, 153.

(18) The enals were obtained from the reduction of the corresponding γ-sulfenyl esters with diisobutylaluminum hydride.

TABLE 5. Diastereoselectivities of 7g and 7f with Different Hydride Agents

entry	substrate	reducing agent	solvent	*T* (°C)	yield **9** + **10**[a] (%)	**9**:**10**[b]
1	**7f**	L-Selectride	THF	−78	95	97:3
2	**7g**	L-Selectride	THF	−78	95	68:32
3	**7g**	L-Selectride	THF	0	95	64:36
4	**7g**	$NaBH_4$	MeOH	−78	97	45:55
5	**7g**	$LiAlH_4$	Et_2O	−78	96	40:60

[a] Isolated yield. [b] Ratios were calculated from ^{1}H integrals of −C*H*(OH).

of MeMgI to *s-trans*-**7c** (R^1 = *t*-Bu, R^2 = Ph) could be formed from the *anti*-to-S hydride reduction of the methyl ketone **7** (R^1 = *t*-Bu, R^2 = Ph, R^3 = Me) only if the latter reacted through its *s-cis* form.

6. Computational Evidence That Favors *s-cis*-7a over *s-trans*-7a (the Methyl Ketone 7a). The methyl ketones similar to **7a** have been reported[16] to exist as a equilibrium mixture of the *s-cis* and the *s-trans* forms, and it has been, more or less, a common belief that the latter form is the more stable of the two. Our experimental results presented above indicated otherwise, and thus, we took to ab initio MO calculations of the species **7d** (**7a**, R^1 = Me, R^2 = Ph) and **7e** (**7a**, R^1 = R^2 = Me) at the B3LYP/6-31G* level of theory. The *s-cis*-**7d** was 0.72 kcal/mol more stable than the *s-trans*-**7d**. Likewise, *s-cis*-**7e** was 0.30 kcal/mol more stable than *s-trans*-**7e**. The higher concentration of the *s-cis* form at equilibrium at −78 °C coupled with its above-discussed superior reactivity could very well be taken to understand that it was mainly the *s-cis* form of each methyl ketone (Table 1) that had reacted. The carbon−sulfur bond is at a torsion angle of 106.5° and 111.8° with the double bond in the computed *s-cis*-**7d** and *s-cis*-**7e**, respectively. Further, the C5−H bond on C5 of the main skeleton is *syn* with the C3−H bond.

7. Fixing the *s-cis* Conformation of the Enone and Estimating the Selectivity. To eliminate doubts in regard to the discussions presented above for the involvement of the *s-cis* conformer of the methyl ketone, we opted to study the substrates **7f** (**7**, R^1 = R^3 = *t*-Bu and R^2 = Ph) and **7g** (**7**, R^1 = R^3 = *t*-Bu and R^2 = Me) as this secures fully the *s-cis* form of the enone and allows one to study the steric effects of both the substituent on S (Ph vs Me) and the reducing agent. The stereochemical data are collected in Table 5. The considerable drop in the selectivity from 97:3 for **7f** to 68:32 for **7g** from reduction with L-Selectride demonstrates the dramatic steric effect of the substituent on the sulfur. It is to be noted that the above selectivity of **7g** is the same as that of **7a** (R^1 = *t*-Bu, R^2 = Me, entry 7, Table 1). This could possibly be taken as evidence to the fact that the latter reacted almost exclusively through the *s-cis* form at −78 °C. Further, the drop in the selectivity of **7g** from 68:32 from reduction with L-Selectride to 45:55 from reduction with $NaBH_4$ or 40:60 from reduction with $LiAlH_4$ demonstrates the significance of the bulk of the hydride source in the control of the overall selectivity. The purported electronic effects of sulfur stand evaporated. A comparison of the results at entries 2 and 3 demonstrates a very small change in the selectivity on change in the temperature. The comparatively much larger drop in the selectivity of **7a** at higher temperatures must, therefore, be due to the larger participation of the *s-trans* form that reacted preferably *anti* to the S.

Conclusion

In conclusion, the preferred *anti*-to-S addition of nucleophiles to γ-sulfenyl enones is not due to the electronic effects of sulfur that was earlier considered to be transmitted to the reaction center through the olefinic bond. It is rather due to a combination of the steric effects arising from the substituents on sulfur and the γ-carbon, the large bulk of L-Sselectride, the low reaction temperature (−78 °C), and THF as the reaction solvent. It was the best combination of all these parameters that lead to the very high *anti*-to-S selectivity observed by the previous investigators.

Experimental Section

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$. The ^{1}H and ^{13}C positions are reported in δ relative to TMS used as an internal standard and the central line for $CDCl_3$, respectively. The solvents were removed under reduced pressure on a rotovap. The chromatographic separations were performed over silica gel (100−200 mesh) using mixtures of EtOAc and hexane.

General Procedure for the Preparation of γ-Sulfenyl Alcohols 6. A solution of ester **4** (5 mmol) in THF (5 mL) was added slowly to a solution of LDA (6 mmol) in THF (3 mL) under stirring at −78 °C. After 10 min, a solution of disulfide (7.5 mmol) in THF (4 mL) was added, all at once, at the same temperature, and the reaction mixture was allowed to warm to room temperature. It was then diluted with ether, washed with 2% HCl, H_2O, and brine, concentrated, and filtered through a short column of silica gel to afford **5**. A solution of **5** in Et_2O (10 mL) was added to an ethereal suspension of LAH at 0 °C and was gradually warmed to room temperature. After 6 h, the reaction was quenched with EtOAc. The contents were filtered and the filtrate was concentrated. The crude material was purified by column chromatography to afford **6**.

General Procedure[19] for the Preparation of γ-Sulfenyl Aldehydes 3 from 6. $(CF_3CO)_2O$ (2.25 mmol, 0.32 mL) in dry CH_2Cl_2 (2 mL) was added to a solution of dry DMSO (3.0 mmol, 0.21 mL) in CH_2Cl_2 at −70 °C at such a rate that the temperature of the reaction mixture did not rise above −60 °C. The addition took 10 min. The contents were stirred at the same temperature for 15 min before the alcohol **6** (1.5 mmol) in CH_2Cl_2 (2 mL) was added. The mixture was stirred for another 45 min, and dry diisopropylamine (4.2 mmol, 0.58 mL) was added drop by drop in about 10 min. The cooling bath was then removed, and the contents were stirred for 45 min. The reaction mixture was diluted with CH_2Cl_2, and the organic solution was washed with H_2O and brine. The residue obtained from concentration was filtered through a short column, and the product **3** thus obtained was used directly for further reaction.

Preparation of γ-Sulfenyl Enone 7a from 3. To a suspension of NaH (1.2 mmol) in THF (2 mL) was added diethyl (2-oxopropyl)phosphonate (1.2 mmol, 0.233 g) in THF (4 mL) at 0 °C over 10 min. When all the NaH had dissolved, aldehyde **3** (1 mmol) in THF (4 mL) was added. The cooling bath was removed, and the contents were stirred for 12 h. The reaction mixture was diluted with Et_2O, washed with saturated aqueous NH_4Cl and brine, and concentrated. The residue was filtered through a silica gel column to afford the enone **7a**.

(19) Muncuso, A. J.; Swern, D. *Synthesis*, **1981**, 165.

Preparation of γ-Sulfenyl Ester 7b from 3. To a suspension of NaH (1.2 mmol) in THF (2 mL) was added triethyl phosphonoacetate (1.2 mmol, 0.269 g) in THF (4 mL) at 0 °C. After all the NaH had dissolved, the aldehyde **3** (1 mmol) in THF (4 mL) was added at the same temperature. The cooling bath was removed, and the contents were stirred for 12 h. The reaction mixture was diluted with Et_2O, washed with saturated aqueous NH_4Cl and brine, and concentrated. The residue was filtered through a silica gel column to afford the ester **7b**.

General Procedure for the Preparation of γ-Sulfonyl Enones 8 from 7a. To a stirred solution of enone **7a** (0.2 mmol) in 4 mL of CH_2Cl_2 at −10 °C was added *m*-CPBA (0.4 mmol, 0.098 g, 70%), and the resultant mixture was stirred at the same temperature for 30 min. The reaction mixture was then diluted CH_2Cl_2, washed with saturated aqueous $NaHCO_3$, water, brine, concentrated, and purified using radial chromatography to obtain γ-sulfonyl enones **8** in >80% yield.

General Procedure for the L-Selectride Reduction of γ-Sulfenyl Enones 7a and γ-Sulfonyl Enones 8. To a solution of **7a** or **8** (0.1 mmol) in THF (1 mL) was added L-Selectride (1.0 M THF solution, 0.2 mmol, 0.2 mL) at −78 °C. After being stirred for 30 min, the reaction was mixed with MeOH (0.1 mL), 1 N NaOH (0.1 mL), and 30% H_2O_2 (0.1 mL). The resulting mixture was allowed to warm to room temperature and stirred for 30 min. Extraction with EtOAc, evaporation of the solvent, and filtration of the crude material through a short silica gel column provided the diastereomeric mixture of **9** and **10** or **11** and **12**, respectively.

General Procedure for $NaBH_4$ Reduction of γ-Sulfenyl Enones 7a at −78 °C. To a solution of **7a** (0.1 mmol) in MeOH (1 mL) was added a solution of $NaBH_4$ (0.1 mmol, 4 mg) in MeOH (1 mL) at −78 °C. The contents were stirred at this temperature for 30 min. MeOH was removed, and the residue was taken in Et_2O, washed with saturated aqueous NH_4Cl, dried, and concentrated to furnish the mixture of alcohols **9** and **10**.

General Procedure for $LiAlH_4$ Reduction of the γ-Sulfenyl Enones 7g at −78 °C. $LiAlH_4$ (0.2 mmol, 8 mg) was added to a solution of **7g** (0.1 mmol) in Et_2O (1 mL) at −78 °C. The contents were stirred at this temperature for 30 min. EtOAc (2 mL) and water (2 drops) were added to destroy the excess $LiAlH_4$. It was then filtered and concentrated. The residue, thus obtained, was filtered through a short silica gel column to obtain the mixture of the corresponding alcohols **9** and **10**.

General Procedure for the Grignard Addition to γ-Sulfenyl Enals 7c. Freshly prepared Grignard reagent (1 M solution in Et_2O, 0.2 mmol) was added to a solution of γ-sulfenyl enal **7c** (0.1 mmol) in THF (1 mL) at −78 °C. After being stirred for 2 h, the reaction mixture was diluted with Et_2O and washed with water. Evaporation of the solvent and filtration of the residue through a short silica gel column provided a mixture of **9** and **10**.

2 (R^1 = Et). Identical with the one reported previously.[20]

2 (R^1 = $C(CH_2)_4$, 80%, liquid): ^{1}H NMR δ 7.54−7.52 (m, 2H), 7.33−7.24 (m, 3H), 4.67 (s, 1H), 3.45 (s, 3H), 2.37 (bs, 1H), 1.95−1.56 (m, 8H); ^{13}C NMR δ 135.8, 132.7, 129.1, 127.4, 101.3, 84.7, 57.5, 36.8, 24.4.

2 (R^1 = $C(CH_2)_5$, 84%, liquid): ^{1}H NMR δ 7.55−7.52 (m, 2H), 7.32−7.25 (m, 3H), 4.49 (s, 1H), 3.42 (s, 3H), 2.29 (bs, 1H), 1.73−1.54 (m, 10H); ^{13}C NMR δ 136.1, 132.7, 129.1, 127.3, 104.1, 74.1, 57.7, 33.1, 32.7, 25.7, 21.7, 21.3.

2 (R^1 = $PhCH_2CH_2$−, 68%, liquid). Less polar diastereomer: ^{1}H NMR δ 7.48−7.14 (m, 10H), 4.44 (d, *J* = 6.8 Hz, 1H), 3.62−3.57 (m, 1H), 3.47 (s, 3H), 2.90−2.83 (m, 1H), 2.69−2.60 (m, 1H), 2.09−2.01 (m, 1H). 1.87−1.78 (m, 1H); ^{13}C NMR δ 142.0, 133.8, 132.3, 129.0, 128.4, 128.3, 128.0, 125.7, 97.1, 71.3, 56.9, 34.4, 31.9. More polar diastereomer: ^{1}H NMR δ 7.39−7.15 (m, 10H), 4.39 (d, *J* = 7.3 Hz, 1H), 3.64−3.59 (m, 1H), 3.51 (s, 3H), 2.87−2.80 (m, 1H), 2.76−2.63 (m, 1H), 2.26−2.17 (m, 1H), 1.84−1.75 (m, 1H); ^{13}C NMR δ 141.8, 133.9, 132.2, 128.8, 128.5, 128.3, 127.8, 125.7, 94.5, 71.9, 56.7, 34.3, 31.5.

6 (R^1 = *n*-Bu, R^2 = Ph, 70%, liquid): ^{1}H NMR δ 7.45−7.43 (m, 2H), 7.32−7.26 (m, 3H), 3.65−3.61 (dd, *J* = 11.4, 4.9 Hz, 1H), 3.53−3.49 (dd, *J* = 11.5, 6.4 Hz, 1H), 3.18−3.12 (m, 1H), 2.41 (bs, 1H), 1.69−1.28 (m, 6H), 0.91 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR δ 133.4, 132.7, 128.9, 127.3, 63.6, 52.5, 30.8, 29.2, 22.5, 13.9.

6 (R^1 = *n*-Bu, R^2 = Me, 68%, liquid): ^{1}H NMR δ 3.68−3.64 (dd, *J* = 11.2, 4.6 Hz, 1H), 3.51−3.46 (dd, *J* = 11.2, 7.3 Hz, 1H), 2.70−2.64 (m, 1H), 2.20 (bs, 1H), 2.03 (s, 3H), 1.60−1.30 (m, 6H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR δ 62.7, 50.0, 30.4, 29.2, 22.5, 13.9, 11.8.

6 (R^1 = *i*-Pr, R^2 = Ph, 80%, liquid): ^{1}H NMR δ 7.46−7.43 (m, 2H), 7.30−7.22 (m, 3H), 3.73−3.69 (dd, *J* = 11.5, 5.5 Hz, 1H), 3.62−3.58 (dd, *J* = 11.5, 6.7 Hz, 1H), 3.07−3.03 (q, *J* = 5.9 Hz, 1H), 2.10−1.95 (m, 1H), 1.05 (d, *J* = 6.6 Hz, 3H), 1.04 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR δ 135.2, 131.7, 128.8, 126.8, 62.4, 60.1, 29.4, 20.3, 19.3.

6 (R^1 = *i*-Pr, R^2 = Me, 67%, liquid): ^{1}H NMR δ 3.76−3.72 (dd, *J* = 11.2, 4.3 Hz, 1H), 3.55−3.50 (dd, *J* = 11.2, 8.0 Hz, 1H), 2.50−2.45 (m, 1H), 2.08 (s, 3H), 1.95−1.86 (m, 1H), 1.03 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR δ 61.7, 58.6, 29.5, 20.4, 19.9, 14.2.

6 (R^1 = *t*-Bu, R^2 = Ph, 88%, liquid): ^{1}H NMR δ 7.49−7.46 (m, 2H), 7.29−7.18 (m, 3H), 3.93−3.89 (dd, *J* = 11.7, 4.2 Hz, 1H), 3.62−3.56 (dd, *J* = 11.7, 8.5 Hz, 1H), 3.06−3.03 (dd, *J* = 8.5, 4.2 Hz, 1H), 2.35 (bs, 1H), 1.06 (s, 9H); ^{13}C NMR δ 137.0, 131.4, 129.0, 126.7, 67.0, 61.7, 35.0, 28.1.

6 (R^1 = *t*-Bu, R^2 = Me, 64%, liquid): ^{1}H NMR δ 3.88−3.84 (dd, *J* = 11.5, 4.2 Hz, 1H), 3.45−3.40 (dd, *J* = 11.5, 9.3 Hz, 1H), 2.59 (bs, 1H), 2.42−2.38 (dd, *J* = 9.3, 4.2 Hz, 1H), 2.18 (s, 3H), 1.03 (s, 9H); ^{13}C NMR δ 65.5, 61.1, 34.8, 27.9, 17.9.

6 (R^1 = *n*-C_6H_{13}, R^2 = Ph, 73% liquid): ^{1}H NMR δ 7.45−7.42 (m, 2H), 7.31−7.25 (m, 3H), 3.64−3.60 (dd, *J* = 11.2, 4.6 Hz, 1H), 3.53−3.49 (dd, *J* = 11.2, 6.3 Hz, 1H), 3.17−3.11 (quintet, *J* = 6.0 Hz, 1H), 2.33 (bs, 1H), 1.67−1.28 (m, 10H), 0.88 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR δ 133.5, 132.8, 128.9, 127.4, 63.7, 52.6, 31.6, 31.2, 29.0, 27.0, 22.5, 14.0.

6 (R^1 = *n*-C_8H_{17}, R^2 = Ph, 71% liquid): ^{1}H NMR δ 7.44−7.41 (m, 2H), 7.29−7.21 (m, 3H), 3.63−3.59 (dd, *J* = 11.5, 5.0 Hz, 1H), 3.53−3.49 (dd, *J* = 11.5, 6.1 Hz, 1H), 3.16−3.10 (m, 1H), 2.47 (bs, 1H), 1.66−1.48 (m, 4H), 1.27 (bm, 10H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR δ 133.6, 132.6, 128.8, 127.2, 63.7, 52.4, 31.8, 31.2, 29.3, 29.1, 27.0, 22.6, 14.0.

6 (R^1 = *n*-C_8H_{17}, R^2 = Me, 64%, liquid): ^{1}H NMR δ 3.67−3.63 (dd, *J* = 11.2, 4.8 Hz, 1H), 3.52−3.47 (dd, *J* = 11.2, 7.1 Hz, 1H), 2.69−2.63 (m, 1H), 2.37 (bs, 1H), 2.02 (s, 3H), 1.59−1.34 (m, 4H), 1.28−1.27 (bm, 10H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR δ 62.8, 49.9, 31.8, 30.7, 29.4, 29.2, 27.0, 22.6, 14.0, 11.8.

6 (R^1 = $C(CH_2)_4$, R^2 = Me, 75%, liquid): ^{1}H NMR δ 3.42 (s, 2H), 2.63 (bs, 1H), 1.96 (s, 3H), 1.86−1.77 (m, 2H), 1.74−1.61 (m, 6H); ^{13}C NMR δ 65.3, 58.1, 35.3, 24.6, 11.1.

6 (R^1 = $C(CH_2)_5$, R^2 = Me, 77%, liquid): ^{1}H NMR δ 3.38 (s, 2H), 2.59 (bs, 1H), 1.89 (s, 3H), 1.72−1.54 (m, 4H), 1.54−1.25 (m, 6H); ^{13}C NMR δ 66.7, 51.4, 32.0, 25.9, 21.3, 8.8.

6 (R^1 = $PhCH_2CH_2$, R^2 = Me, 67%, liquid): ^{1}H NMR δ 7.27−7.14 (m, 5H), 3.62−3.58 (dd, *J* = 11.5, 5.1 Hz, 1H), 3.53−3.49 (dd, *J* = 11.5, 6.8 Hz, 1H), 2.87−2.80 (m, 1H), 2.76−2.68 (m, 1H), 2.64−2.57 (m, 1H), 1.99 (s, 3H), 1.93−1.84 (m, 1H), 1.80−1.70 (m, 1H); ^{13}C NMR δ 141.3, 128.22, 128.20, 125.7, 62.9, 48.7, 32.8, 32.0, 11.7.

7a (R^1 = Et, R^2 = Ph, R^3 = Me, 75%, liquid): ^{1}H NMR δ 7.37−7.35 (m, 2H), 7.30−7.24 (m, 3H), 6.59−6.52 (dd, *J* = 16.0, 9.4 Hz, 1H), 5.70 (d, *J* = 16.0 Hz, 1H), 3.57−3.51 (dt, *J* = 8.4, 7.6 Hz, 1H), 2.17 (s, 3H), 1.85−1.68 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR δ 198.1, 146.3, 133.6, 133.1, 130.4, 128.8, 127.9, 52.9, 27.0, 26.7, 11.9. Anal. Calcd for $C_{13}H_{16}OS$: C, 70.87; H, 7.32. Found: C, 70.72 H, 7.24.

(20) Rawal, V. H.; Akiba, M.; Cava, M. P. *Synth. Commun.* **1984**, *14*, 1129.

8 (R^1 = Et, R^2 = Ph, R^3 = Me): ^{1}H NMR δ 7.83−7.81 (m, 2H), 7.69−7.65 (m, 1H), 7.61−7.52 (m, 2H), 6.51−6.44 (dd, J = 16.1, 9.6 Hz, 1H), 5.96 (d, J = 16.1 Hz, 1H), 3.60−3.54 (dt, J = 10.3, 3.4 Hz, 1H), 2.27−2.22 (m, 1H), 2.24 (s, 3H), 1.83−1.72 (m, 1H), 0.96 (t, J = 7.6 Hz, 3H); ^{13}C NMR δ 196.9, 137.2, 137.0, 134.1, 129.1, 128.9, 128.1, 70.0, 27.3, 20.7, 11.2. Anal. Calcd for $C_{13}H_{16}O_3S$: C, 61.88; H, 6.39. Found: C, 61.69; H, 6.30.

7a (R^1 = *n*-Bu, R^2 = Ph, R^3 = Me, 65%, liquid): ^{1}H NMR δ 7.36−7.33 (m, 2H), 7.29−7.23 (m, 3H), 6.57−6.51 (ddd, J = 15.9, 9.4, 0.9 Hz, 1H), 5.65 (d, J = 15.9 Hz, 1H), 3.63−3.57 (dt, J = 8.5, 6.8 Hz, 1H), 2.15 (s, 3H), 1.78−1.64 (m, 2H), 1.46−1.29 (m, 4H), 0.90 (t, J = 6.8 Hz, 3H); ^{13}C NMR δ 197.9, 146.3, 133.5, 133.0, 130.0, 128.7, 127.7, 51.1, 33.0, 29.3, 26.8, 22.2, 13.7. Anal. Calcd for $C_{15}H_{20}OS$: C, 72.53; H, 8.12. Found: C, 72.40; H, 7.98.

7a (R^1 = *n*-Bu, R^2 = R^3 = Me, 68%, liquid): ^{1}H NMR δ 6.45−6.38 (ddd, J = 15.8, 9.5, 1.2 Hz, 1H), 5.86 (d, J = 15.8 Hz, 1H), 3.08−3.02 (m, 1H), 2.21 (s, 3H), 1.88 (s, 3H), 1.65−1.49 (m, 2H), 1.35−1.20 (m, 4H), 0.81 (t, J = 7.1 Hz. 3H); ^{13}C NMR δ 198.3, 146.7, 130.1, 48.5, 32.9, 29.3, 26.8, 22.2, 13.7. Anal. Calcd for $C_{10}H_{18}OS$: C, 64.46; H, 9.74. Found: C, 64.34; H, 9.64

7a (R^1 = *i*-Pr, R^2 = Ph, R^3 = Me, 79%, liquid): ^{1}H NMR δ 7.36−7.32 (m, 2H), 7.29−7.22 (m, 3H), 6.63−6.56 (dd, J = 15.9, 10.0 Hz, 1H), 5.63 (d, J = 15.9 Hz, 1H), 3.44−3.40 (dd, J = 10, 6.7 Hz, 1H), 2.15 (s, 3H), 2.07−1.96 (m, 1H), 1.12 (d, J = 6.8 Hz, 3H), 1.04 (d, J = 6.8 Hz, 3H); ^{13}C NMR δ 198.0, 144.8, 133.7, 133.5, 130.7, 128.8, 127.7, 59.3, 31.9, 27.0, 20.6, 20.0. Anal. Calcd for $C_{14}H_{18}OS$: C, 71.75; H, 7.74. Found: C, 71.60; H, 7.65.

7a (R^1 = *i*-Pr, R^2 = R^3 = Me, 75%, liquid): ^{1}H NMR δ 6.58−6.51 (dd, J = 15.6, 10.3 Hz, 1H), 5.93 (d, J = 15.6 Hz, 1H), 2.93−2.89 (dd, J = 10.2, 7.0 Hz, 1H), 2.30 (s, 3H), 1.96 (s, 3H), 1.96−1.89 (m, 1H), 1.06 (d, J = 6.7 Hz, 3H), 1.00 (d, J = 6.7 Hz, 3H); ^{13}C NMR δ 198.2, 145.1, 130.7, 56.6, 31.7, 26.9, 20.5, 20.1, 14.4. Anal. Calcd for $C_9H_{16}OS$: C, 62.74; H, 9.36. Found: C, 62.60; H, 9.25.

7a (R^1 = *t*-Bu, R^2 = Ph, R^3 = Me, 80%, liquid): ^{1}H NMR δ 7.35−7.32 (m, 2H), 7.28−7.23 (m, 3H), 6.72−6.65 (dd, J = 15.6, 10.5 Hz, 1H), 5.48 (d, J = 15.6 Hz, 1H), 3.31 (d, J = 10.5 Hz, 1H), 2.14 (s, 3H), 1.11 (s, 9H); ^{13}C NMR δ 198.0, 143.8, 134.1, 133.8, 130.2, 128.8, 127.8, 65.0, 34.5, 27.9, 27.0. Anal. Calcd for $C_{15}H_{20}OS$: C, 72.53; H, 8.12. Found: 72.38; H, 8.00.

7b (R^1 = *t*-Bu, R^2 = Ph, R^3 = OEt, 82%, liquid): ^{1}H NMR δ 7.36−7.34 (m, 2H), 7.29−7.23 (m, 3H), 6.93−6.87 (dd, J = 15.4, 10.7 Hz, 1H), 5.30 (d, J = 15.4 Hz, 1H), 4.17−4.11 (m, 2H), 3.30 (d, J = 10.5 Hz, 1H), 1.25 (t, J = 7.2 Hz, 3H), 1.10 (s, 9H); ^{13}C NMR δ 166.1, 145.2, 134.5, 133.6, 128.9, 127.6, 120.9, 64.6, 60.2, 34.6, 27.9, 14.2. Anal. Calcd for $C_{16}H_{22}O_2S$: C, 69.03; H, 7.97. Found: C, 68.93; H, 7.85.

7c (R^1 = *t*-Bu, R^2 = Ph, R^3 = H, 76%, liquid): ^{1}H NMR δ 9.47 (d, J = 8.0 Hz, 1H), 7.35−7.32 (m, 2H), 7.30−7.25 (m, 3H), 6.79−6.72 (dd, J = 15.4, 10.7 Hz, 1H), 5.57−5.51 (d, J = 15.4, 7.8 Hz, 1H), 3.44 (d, J = 10.7 Hz, 1H), 1.13 (s, 9H); ^{13}C NMR δ 193.4, 153.8, 133.8, 131.7, 129.1, 128.1, 64.8, 34.5, 27.8. Anal. Calcd for $C_{14}H_{18}OS$: C, 71.76; H, 7.75. Found: C, 71.67; H, 7.64.

8 (R^1 = *t*-Bu, R^2 = Ph, R^3 = Me, colorless solid, mp 77−78 °C): ^{1}H NMR δ 7.78−7.76 (m, 2H), 7.63−7.57 (m, 1H), 7.52−7.49 (m, 2H), 6.72−6.65 (dd, J = 16.1, 11.0 Hz, 1H), 5.48 (d, J = 16.1 Hz, 1H), 3.44 (d, J = 10.7 Hz, 1H), 2.16 (s, 3H), 1.28 (s, 9H); ^{13}C NMR δ 196.8, 139.3, 137.7, 136.9, 133.8, 128.9, 128.5, 77.5, 36.1, 29.0, 27.0. Anal. Calcd for $C_{15}H_{20}O_3S$: C, 64.26; H, 7.19. Found: C, 64.10; H, 7.06.

7a (R^1 = *t*-Bu, R^2 = R^3 = Me, 78%, liquid): ^{1}H NMR δ 6.56−6.50 (dd, J = 15.6, 10.7 Hz, 1H), 5.80 (d, J = 15.6 Hz, 1H), 2.74 (d, J = 10.5 Hz, 1H), 2.20 (s, 3H), 1.84 (s, 3H), 0.94 (s, 9H); ^{13}C NMR δ 198.0, 143.9, 130.3, 61.8, 34.0, 27.7, 26.8, 14.7. Anal. Calcd for $C_{10}H_{18}OS$: C, 64.46; H, 9.74. Found: C, 64.30; H, 9.64.

7g (7; R^1 = R^3 = *t*-Bu, R^2 = Me, 78%, colorless solid, mp 53−55 °C): ^{1}H NMR δ 6.78−6.71 (dd, J = 14.9, 11.0 Hz, 1H), 6.28 (d, J = 14.9 Hz, 1H), 2.83 (d, J = 11.0 Hz, 1H), 1.88 (s, 3H), 1.14 (s, 9H), 0.99 (s, 9H); ^{13}C NMR δ 203.9, 143.0, 123.9, 62.0, 42.8, 34.2, 27.9, 26.2, 14.9. Anal. Calcd for $C_{13}H_{24}OS$: C, 68.37; H, 10.60. Found: 68.27; H, 10.47.

8 (R^1 = *t*-Bu, R^2 = R^3 = Me, colorless solid, mp 62−63 °C): ^{1}H NMR δ 6.90−6.83 (dd, J = 15.8, 11.0 Hz, 1H), 6.25 (d, J = 15.8 Hz, 1H), 3.45 (d, J = 11.0 Hz, 1H), 2.82 (s, 3H), 2.36 (s, 3H), 1.23 (s, 9H); ^{13}C NMR δ 197.0, 138.4, 137.0, 76.0, 41.9, 35.9, 28.8, 27.3; HRMS calcd m/z for $C_{10}H_{18}O_3S$ 218.0977, found m/z 218.0960.

7a (R^1 = *n*-C_6H_{13}, R^2 = Ph, R^3 = Me, 70%, colorless solid, mp 50−52° C): ^{1}H NMR δ 7.38−7.34 (m, 2H), 7.30−7.24 (m, 3H), 6.57−6.51 (dd, J = 15.8, 9.4 Hz, 1H), 5.66 (d, J = 15.8 Hz, 1H), 3.63−3.57 (m, 1H), 2.16 (s, 3H), 1.82−1.62 (m, 2H), 1.49−1.24 (m, 8H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR δ 198.2, 146.6, 133.6, 133.2, 130.2, 128.8, 127.9, 51.3, 33.5, 31.5, 28.9, 27.2, 27.0, 22.5, 14.0. Anal. Calcd for $C_{17}H_{24}OS$: C, 73.86; H, 8.75. Found: C, 73.70; H, 8.64.

7a (R^1 = *n*-C_8H_{17}, R^2 = Ph, R^3 = Me, 68%, colorless solid, 54−55 °C): ^{1}H NMR δ 7.37−7.33 (m, 2H), 7.30−7.25 (m, 3H), 6.57−6.51 (dd, J = 15.8, 9.5 Hz, 1H), 5.66 (d, J = 15.6 Hz, 1H), 3.63−3.57 (dt, J = 8.8, 6.4 Hz, 1H), 2.16 (s, 3H), 1.80−1.62 (m, 2H), 1.47−1.39 (m, 2H), 1.37−1.27 (m, 10H), 0.88 (t, J = 6.7 Hz, 3H);. ^{13}C NMR δ 198.2, 146.6, 133.7, 133.2, 130.2, 128.9, 127.9, 51.3, 33.5, 31.8, 29.3, 29.22, 29.15, 27.3, 27.0, 22.6, 14.1; HRMS calcd m/z for $C_{19}H_{28}OS$ 304.1861, found m/z 304.1855.

7a (R^1 = *n*-C_8H_{17}, R^2 = R^3 = Me, 71%, liquid): ^{1}H NMR δ 6.45−6.39 (dd, J = 15.9, 9.5 Hz, 1H), 5.88 (d, J = 15.9 Hz, 1H), 3.09−3.03 (m, 1H), 2.21 (s, 3H), 1.89 (s, 3H), 1.62−1.52 (m, 2H), 1.34−1.29 (m, 1H), 1.23−1.20 (m, 11H), 0.81 (t, J = 6.8 Hz, 3H); ^{13}C NMR δ 198.1, 146.7, 130.2, 48.5, 33.2, 31.7, 29.22, 29.15, 29.1, 27.2, 26.8, 22.5, 13.9, 13.7. Anal. Calcd for $C_{14}H_{26}OS$: C, 69.36; H, 10.81. Found: C, 69.22; H, 10.69.

7a (R^1= $C(CH_2)_4$, R^2 = Ph, R^3 = Me, 75%, liquid): ^{1}H NMR δ 7.38−7.26 (m, 5H), 6.90 (d, J = 16.1 Hz, 1H), 5.51 (d, J = 16.1 Hz, 1H), 2.22 (s, 3H), 2.01−1.66 (m, 8H); ^{13}C NMR δ 198.5, 149.9, 136.5, 132.0, 129.0, 128.5, 127.2, 60.6, 36.4, 27.1, 23.1; HRMS calcd m/z for $C_{15}H_{18}OS$ 246.1078, found m/z 246.1064.

7a (R^1 = $C(CH_2)_4$, R^2 = R^3 = Me, 78%, liquid): ^{1}H NMR δ 6.78 (d, J = 16.1 Hz, 1H), 5.89 (d, J = 16.1 Hz, 1H), 2.30 (s, 3H), 1.92−1.82 (m, 6H), 1.87 (s, 3H), 1.73−1.67 (m, 2H); ^{13}C NMR δ 198.7, 149.4, 127.2, 55.9, 36.0, 26.8, 23.2, 12.3. Anal. Calcd for $C_{10}H_{16}OS$: C, 65.17; H, 8.75. Found: C, 65.00; H, 8.64.

7a (R^1 = $C(CH_2)_5$, R^2 = Ph, R^3 = Me, 71%, liquid): ^{1}H NMR δ 7.36−7.26 (m, 5H), 6.64 (d, J = 16.4 Hz, 1H), 5.41 (d, J = 16.4 Hz, 1H), 2.20 (s, 3H), 1.85−1.70 (m, 7H), 1.55−1.36 (m, 3H); ^{13}C NMR δ 198.5, 150.4, 137.6, 130.4, 129.3, 128.5, 127.6, 53.8, 35.0, 27.2, 25.7, 22.6. Anal. Calcd for $C_{16}H_{20}OS$: C, 73.80; H, 7.74. Found: C, 73.65; H, 7.62.

7b (R^1 = $C(CH_2)_5$, R^2 = Ph, R^3 = OMe, 77%, liquid): ^{1}H NMR δ 7.39−7.25 (m, 5H), 6.85 (d, J = 16.1 Hz, 1H), 5.19 (d, J = 16.1 Hz, 1H), 4.21−4.15 (q, J = 16.1 Hz, 2H), 1.84−1.69 (m, 6H), 1.51−1.37 (m, 4H), 1.28 (t, J = 7.2 Hz, 3H); ^{13}C NMR δ 198.5, 150.4, 137.6, 130.4, 129.3, 128.5, 127.6, 53.8, 35.0, 27.2, 25.7, 22.6. Anal. Calcd for $C_{17}H_{22}O_2S$: C, 70.31; H, 7.64. Found: C, 70.16; H, 7.56.

7c (R^1 = $C(CH_2)_5$, R^2 = Ph, R^3 = H, 67%, liquid): ^{1}H NMR δ 9.53 (d, J = 7.6 Hz, 1H) 7.37−7.32 (m, 3H), 7.30−7.26 (m, 2H), 6.66 (d, J = 15.9 Hz, 1H), 5.49−5.43 (dd, J = 15.8, 7.8 Hz, 1H), 1.88−1.71 (m, 6H), 1.56−1.36 (m, 4H); ^{13}C NMR δ 193.9, 160.6, 137.5, 129.9, 129.5, 129.3, 128.6, 53.9, 34.9, 25.6, 22.5. Anal. Calcd for $C_{15}H_{18}OS$: C, 73.14; H, 7.37. Found: C, 73.03; H, 7.27.

7a (R^1 = $C(CH_2)_5$, R^2 = R^3 = Me, 65%, liquid): ^{1}H NMR δ 6.55 (d, J = 16.3 Hz, 1H), 5.86 (d, J = 16.3 Hz, 1H), 2.31 (s, 3H), 1.80 (s, 3H), 1.77−1.68 (m, 6H), 1.54−1.38 (m, 4H); ^{13}C

NMR δ 198.9, 150.0, 127.3, 48.9, 34.2, 26.8, 25.7, 22.2, 10.3. Anal. Calcd for $C_{11}H_{18}OS$: C, 66.62; H, 9.15. Found: C, 66.54; H, 9.00.

7a (R^1 = $PhCH_2CH_2$, R^2 = Ph, R^3 = Me, 74%, liquid): ^{1}H NMR δ 7.34−7.16 (m, 10H), 6.60−6.53 (dd, *J* = 15.8, 9.3 Hz, 1H), 5.65 (d, *J* = 15.8 Hz, 1H), 3.62−3.56 (td, *J* = 8.6, 7.6 Hz, 1H), 2.79 (t, *J* = 7.6 Hz, 2H), 2.14 (s, 3H), 2.11−1.97 (m, 2H); ^{13}C NMR δ 198.0, 146.0, 140.5, 133.7, 132.7, 130.3, 128.9, 128.5, 128.4, 128.0, 126.2, 50.3, 34.8, 33.1, 27.0. Anal. Calcd for $C_{19}H_{20}OS$: C, 76.98; H, 6.80. Found: C, 76.85; H, 6.70.

7a (R^1 = $PhCH_2CH_2$, R^2 = R^3 = Me, 79%, liquid): ^{1}H NMR δ 7.30−7.26 (m, 2H), 7.20−7.15 (m, 3H), 6.54−6.48 (dd, *J* = 15.9, 9.5 Hz, 1H), 5.92 (d, *J* = 15.8 Hz, 1H), 3.15−3.09 (td, *J* = 9.0, 7.6 Hz, 1H), 2.73 (t, *J* = 7.6 Hz, 2H), 2.27 (s, 3H), 2.03−1.92 (m, 2H), 1.94 (s, 3H); ^{13}C NMR δ 198.2, 146.1, 140.6, 130.3, 128.4, 128.3, 126.0, 47.5, 34.5, 33.1, 26.8, 13.5. Anal. Calcd for $C_{14}H_{18}OS$: C, 71.75; H, 7.74. Found: C, 71.62; H, 7.63.

9 (R^1 = Et, R^2 = Ph, R^3 = Me, less polar alcohol, major isomer, liquid): ^{1}H NMR δ 7.39−7.37 (m, 2H), 7.30−7.21 (m, 3H), 5.49−5.42 (dd, *J* = 15.4, 9.1 Hz, 1H), 5.31−5.26 (dd, *J* = 15.4, 6.4 Hz, 1H), 4.19−4.12 (quintet, *J* = 6.4 Hz, 1H), 3.52−3.46 (dt, *J* = 8.1, 6.4 Hz, 1H), 1.79−1.58 (m, 2H), 1.12 (d, *J* = 6.3 Hz, 3H), 1.0 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR δ 135.9, 134.6, 133.5, 130.4, 128.6, 127.3, 68.1, 52.9, 27.4, 23.0, 11.9. Anal. Calcd for $C_{13}H_{18}OS$: C, 70.22; H, 8.16. Found: C, 70.10; H, 8.05.

10 (R^1 = Et, R^2 = Ph, R^3 = Me, more polar alcohol, minor isomer, liquid): ^{1}H NMR δ 7.38−7.36 (m, 2H), 7.29−7.21 (m, 3H), 5.49−5.43 (dd, *J* = 15.4, 9.0 Hz, 1H), 5.32−5.26 (dd, *J* = 15.4, 6.6 Hz, 1H), 4.20−4.13 (quintet, *J* = 6.4 Hz, 1H), 3.51−3.45 (dt, *J* = 8.4, 6.0 Hz, 1H), 1.79−1.58 (m, 2H), 1.07 (d, *J* = 6.4 Hz, 3H), 1.01 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR δ 135.8, 134.5, 133.4, 130.4, 128.6, 127.2, 68.3, 53.0, 27.4, 23.2, 11.9. Anal. Calcd for $C_{13}H_{18}OS$: C, 70.22; H, 8.16. Found: C, 70.14; H, 8.08.

Mixture of 11 and 12 (R^1 = Et, R^2 = Ph, R^3 = Me): ^{1}H NMR δ 7.85−7.81 (m), 7.64−7.62 (m), 7.56−7.52 (m), 5.54−5.40 (m), 4.28−4.22 (m), 3.44−3.37 (m), 2.20−2.11 (m), 1.74−1.62 (m), 1.14 (d, *J* = 6.6 Hz, major isomer), 1.12 (d, *J* = 6.3 Hz, minor isomer), 0.94 (t, *J* = 7.3 Hz); ^{13}C NMR δ 143.6, 137.6, 133.6, 129.1, 128.8, 121.3, 121.1, 70.2, 67.7, 22.9, 20.5, 11.2; HRMS calcd *m*/*z* for $C_{13}H_{18}O_3S$ 254.0977, found *m*/*z* 254.0970.

Mixture of alcohols 9 and 10 (R^1 = *n*-Bu, R^2 = Ph, R^3 = Me, liquid): ^{1}H NMR δ 7.39−7.34 (m), 7.30−7.22 (m), 5.47−5.41 (dd, *J* = 15.4, 9.2 Hz), 5.27−5.22 (dd, *J* = 15.4, 6.4 Hz), 4.17−4.10 (quintet, *J* = 6.4 Hz), 3.58−3.51 (m), 1.73−1.55 (m), 1.46−1.25 (m), 1.00 (d, *J* = 6.3 Hz, major isomer), 1.05 (d, *J* = 6.3 Hz, minor isomer), 0.89 (t, *J* = 7.4 Hz); ^{13}C NMR δ 135.6, 135.5, 134.6, 134.5, 133.5, 133.4, 130.6, 128.6, 127.3, 127.2, 68.2, 68.1, 51.4, 51.3, 33.9, 29.4, 23.1, 23.0, 22.4, 13.9. Anal. Calcd for $C_{15}H_{22}OS$: C, 71.95; H, 8.86. Found: C, 71.80, H, 8.75.

Mixture of 9 and 10 (R^1 = *n*-Bu, R^2 = R^3 = Me, liquid): ^{1}H NMR δ 5.56−5.51 (dd, *J* = 15.4, 5.9 Hz, major isomer), 5.55−5.50 (dd, *J* = 15.4, 6.1 Hz, minor isomer), 5.45−5.39 (dd, *J* = 15.4, 9.2 Hz), 4.38−4.32 (quintet, *J* = 6.1 Hz), 3.05−2.99 (dt, *J* = 8.6, 6.3 Hz), 1.99 (s, major isomer), 1.97 (s, minor isomer), 1.75−1.48 (m), 1.38−1.25 (m), 1.30 (d, *J* = 6.4 Hz, minor isomer), 1.29 (d, *J* = 6.4 Hz, major isomer), 0.89 (t, *J* = 7.1 Hz); ^{13}C NMR δ 135.4, 131.0, 130.8, 68.3, 48.8, 33.8, 29.5, 23.7, 22.4, 13.9, 13.8. Anal. Calcd for $C_{10}H_{20}OS$: C, 63.77; H, 10.70. Found: C, 63.70; H, 10.60.

Mixture of 9 and 10 (R^1 = *i*-Pr, R^2 = Ph, R^3 = Me, liquid): ^{1}H NMR δ 7.39−7.34 (m), 7.29−7.20 (m), 5.51−5.45 (m), 5.24−5.19 (m), 4.15−4.10 (quintet, *J* = 6.3 Hz), 3.43−3.39 (m), 1.98−1.89 (m), 1.11−1.00 (overlapping doublets); ^{13}C NMR δ 136.4, 136.3, 135.1, 133.5, 133.4, 128.7, 128.6, 127.2, 68.3, 68.2, 59.1, 32.1, 29.7, 23.2, 23.0, 20.7, 19.7. Anal. Calcd for $C_{14}H_{20}OS$: C, 71.13; H, 8.53. Found: C, 71.00; H, 8.45.

Mixture of 9 and 10 (R^1 = *i*-Pr, R^2 = R^3 = Me, liquid): ^{1}H NMR δ 5.55−5.43 (m), 4.38−4.32 (quintet, *J* = 6.1 Hz), 2.86−2.82 (m), 1.98 (s, major isomer), 1.96 (s, minor isomer), 1.87−1.81 (m), 1.31 (d, *J* = 6.3 Hz, minor isomer), 1.30 (d, *J* = 6.3 Hz, major isomer), 1.01 (d, *J* = 6.6 Hz, minor isomer), 1.00 (d, *J* = 6.8 Hz, major isomer), 0.98 (d, *J* = 6.6 Hz, minor isomer), 0.96 (d, *J* = 6.8 Hz, major isomer); ^{13}C NMR δ 136.2, 136.1, 128.9, 128.8, 68.5, 68.4, 56.8, 32.0, 29.7, 23.9, 23.8, 20.7, 19.9, 19.8, 14.4, 14.3. Anal. Calcd for $C_9H_{18}OS$: C, 62.02; H, 10.41. Found: C, 61.94; H, 10.31.

9 (R^1 = *t*-Bu, R^2 = Ph, R^3 = Me, less polar alcohol, major isomer, liquid): ^{1}H NMR δ 7.36−7.33 (m, 2H), 7.26−7.18 (m, 3H), 5.55−5.49 (dd, *J* = 15.1, 10.2 Hz, 1H), 5.06−5.01 (dd, *J* = 15.1, 6.6 Hz, 1H), 4.10−4.04 (quintet, *J* = 6.4 Hz, 1H), 3.28 (d, *J* = 10.2 Hz, 1H), 1.04 (d, *J* = 6.4 Hz, 3H), 1.03 (s, 9H); ^{13}C NMR δ 136.0, 135.5, 134.0, 128.6, 128.4, 127.2, 68.2, 64.8, 34.4, 28.0, 23.0; HRMS calcd *m*/*z* for $C_{15}H_{22}OS$ 250.1391, found *m*/*z* 250.1385.

10 (R^1 = *t*-Bu, R^2 = Ph, R^3 = Me, more polar alcohol, minor isomer, liquid): ^{1}H NMR δ 7.34−7.32 (m, 2H), 7.26−7.19 (m, 3H), 5.59−5.52 (dd, *J* = 15.4, 10.2 Hz, 1H), 5.09−5.04 (dd, *J* = 15.4, 6.7 Hz, 1H), 4.14−4.07 (quintet, *J* = 6.4 Hz, 1H), 3.27 (d, *J* = 10.2 Hz, 1H), 1.06 (s, 9H), 0.99 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR δ 135.7, 135.4, 133.9, 128.6, 128.3, 127.1, 68.3, 64.9, 34.4, 28.0, 23.2; HRMS calcd *m*/*z* for $C_{15}H_{22}OS$ 250.1391, found *m*/*z* 250.1382.

9 (R^1 = *t*-Bu, R^2 = R^3 = Ph, less polar alcohol, major isomer, liquid): ^{1}H NMR δ 7.40−7.12 (m, 10H), 5.76−5.69 (ddd, *J* = 15.1, 10.4, 1.1 Hz, 1H), 5.26−5.20 (dd, *J* = 15.1, 6.4 Hz, 1H), 5.02 (d, *J* = 6.6 Hz, 1H), 3.38 (d, *J* = 10.5 Hz, 1H), 1.08 (s, 9H); ^{13}C NMR δ 142.5, 135.4, 133.8, 130.1, 128.7, 128.3, 127.45, 127.42, 127.3, 126.1, 74.1, 64.6, 34.5, 28.0. Anal. Calcd for $C_{20}H_{24}OS$: C, 76.88; H, 7.75. Found: C, 76.74; H, 7.66.

10 (R^1 = *t*-Bu, R^2 = R^3 = Ph, more polar alcohol, minor isomer, liquid): ^{1}H NMR δ 7.28−7.08 (m, 10H), 5.77−5.71 (ddd, *J* = 15.1, 10.2, 1.0 Hz, 1H), 5.29−5.23 (dd, *J* = 15.1, 6.9 Hz, 1H), 5.05 (d, *J* = 7.1 Hz, 1H), 3.32 (d, *J* = 10.2 Hz, 1H), 1.10 (s, 9H); ^{13}C NMR δ 142.7, 135.1, 133.7, 133.6, 130.3, 128.6, 128.3, 127.4, 127.1,126.1, 74.6, 64.5, 34.5, 28.1. Anal. Calcd for $C_{20}H_{24}OS$: C, 76.88; H, 7.75. Found: C, 76.78; H, 7.64.

11 (R^1 = *t*-Bu, R^2 = Ph, R^3 = Me, colorless solid, mp 134 °C): ^{1}H NMR δ 7.82−7.80 (m, 2H), 7.61−7.57 (m, 1H), 7.53−7.49 (m, 2H), 5.71−5.64 (ddd, *J* = 15.1, 10.7, 1.2 Hz, 1H), 5.07−5.02 (dd, *J* = 15.4, 5.9 Hz, 1H), 4.15−4.08 (quintet, *J* = 6.4 Hz, 1H), 3.33 (d, *J* = 10.7 Hz, 1H), 1.24 (s, 9H), 1.00 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR δ 143.0, 140.2, 133.2, 128.7, 128.6, 121.5, 77.6, 67.6, 35.6, 29.0, 22.6; HRMS calcd *m*/*z* for $C_{15}H_{22}O_3S$ 282.1290, found *m*/*z* 282.1287.

Mixture of 9 and 10 (R^1 = *t*-Bu, R^2 = R^3 = Me, liquid): ^{1}H NMR δ 5.57−5.44 (m), 4.38−4.34 (m), 2.75 (d, *J* = 10 Hz, minor isomer), 2.74 (d, *J* = 9.8 Hz, major isomer), 1.96 (s, major isomer), 1.93 (s, minor isomer), 1.31 (d, *J* = 6.4 Hz, minor isomer), 1.30 (d, *J* = 6.3 Hz, major isomer), 1.00 (s, minor isomer), 0.99 (s, major isomer); ^{13}C NMR δ 136.0, 135.9, 128.2, 128.1, 68.5, 68.4, 62.19, 62.15, 34.1, 27.9, 23.9, 23.8, 14.8, 14.7. Anal. Calcd for $C_{10}H_{20}OS$: C, 63.77; H, 10.70. Found: C, 63.64; H, 10.60.

Mixture of 9 and 10 (R^1 = R^3 = *t*-Bu, R^2 = Me, liquid): ^{1}H NMR δ 5.64−5.43 (m), 3.82 (d, *J* = 6.8 Hz, minor isomer), 3.78 (d, *J* = 7.0 Hz, major isomer), 2.78 (d, *J* = 10.3 Hz, minor isomer), 2.77 (d, *J* = 9.8 Hz, major isomer), 1.98 (s, major isomer), 1.97 (s, minor isomer), 1.01 (s, minor isomer), 1.00 (s, minor isomer), 0.93 (s, minor isomer), 0.925 (s, major isomer); ^{13}C NMR δ 131.7, 131.4, 131.1, 131.0, 80.8, 80.3, 62.6, 34.9, 34.2, 28.0, 25.8, 14.9. Anal. Calcd for $C_{13}H_{26}OS$: C, 67.78; H, 11.38. Found: C, 67.65; H, 11.24.

Mixture of 11 and 12 (R^1 = *t*-Bu, R^2 = R^3 = Me, liquid): ^{1}H NMR δ 5.93−5.78 (m), 4.46−4.39 (m), 3.31 (d, *J* = 9.8 Hz, minor isomer), 3.30 (d, *J* = 9.8 Hz, major isomer), 2.84 (s, major isomer), 2.81 (s, minor isomer), 1.32 (d, *J* = 6.6 Hz), 1.20 (s, minor isomer), 1.18 (s, major isomer); ^{13}C NMR δ 143.1, 143.0, 122.6, 122.3, 76.43, 76.39, 67.9, 67.8, 41.60, 41.56, 35.3, 28.8, 23.3, 23.1. Anal. Calcd for $C_{10}H_{20}O_3S$: C, 54.51; H, 9.15. Found: C, 54.44; H, 9.06.

Mixture of 9 and 10 (R^1 = *n*-C_6H_{13}, R^2 = Ph, R^3 = Me, liquid): ^{1}H NMR δ 7.39−7.35 (m), 7.30−7.23 (m), 5.47−5.41 (ddd, J = 15.4, 9.2, 1.0 Hz), 5.27−5.21 (dd, J = 15.4, 7.1 Hz), 4.17−4.11 (m), 3.58−3.52 (m), 1.73−1.54 (m), 1.43−1.36 (m), 1.34−1.21 (m), 1.10 (d, J = 6.4 Hz, major isomer), 1.05 (d, J = 6.4 Hz, minor isomer), 0.88 (t, J = 7.1 Hz); ^{13}C NMR δ 135.6, 135.5, 134.6, 133.6, 133.5, 130.8, 130.7, 128.6, 127.3, 127.2, 68.2, 68.1, 51.4, 34.2, 31.6, 28.9, 27.3, 23.2, 23.0, 22.6, 14.0. Anal. Calcd for $C_{17}H_{26}OS$: C, 73.33; H, 9.41. Found: C, 73.20; H, 9.33.

Mixture of 9 and 10 (R^1 = *n*-C_8H_{17}, R^2 = Ph, R^3 = Me, liquid): ^{1}H NMR δ 7.32−7.28 (m), 7.23−7.15 (m), 5.41−5.35 (dd, J = 15.4, 9.3 Hz), 5.21−5.16 (dd, J = 15.4, 6.4 Hz, minor isomer), 5.20−5.15 (dd, J = 15.4, 6.4 Hz, major isomer), 4.11−4.04 (quintet, J = 6.4 Hz), 3.51−3.45 (m), 1.65−1.47 (m), 1.37−1.29 (m), 1.25−1.13 (m), 1.03 (d, J = 6.4 Hz, major isomer), 0.99 (d, J = 6.4 Hz, minor isomer), 0.81 (t, J = 7.0 Hz); ^{13}C NMR δ 135.7, 134.6, 133.6, 133.5, 130.8, 128.6, 127.33, 127.25, 68.2, 51.4, 34.2, 31.8, 29.4, 29.3, 29.2, 27.3, 23.2, 23.0, 22.6, 14.1. Anal. Calcd for $C_{19}H_{30}OS$: C, 74.45; H, 9.87. Found: C, 74.35; H, 9. 78.

Mixture of 9 and 10 (R^1 = *n*-C_8H_{17}, R^2 = R^3 = Me, liquid): ^{1}H NMR δ 5.56−5.504 (dd, J = 15.1, 6.1 Hz major isomer), 5.55−5.495 (dd, J = 15.1, 6.1 Hz, minor isomer), 5.45−5.39 (dd, J = 15.1, 9.0 Hz), 4.38−4.31 (quintet, J = 6.2 Hz), 3.04−2.99 (dt, J = 8.5, 6.2 Hz), 1.98 (s, major isomer), 1.96 (s, minor isomer), 1.65−1.47 (m), 1.40−1.21 (m), 0.88 (t, J = 7.1 Hz); ^{13}C NMR δ 135.4, 135.3, 131.0, 130.9, 68.4, 68.3, 48.9, 48.8, 34.21, 34.15, 31.8, 29.4, 29.3, 29.2, 27.3, 23.8, 23.7, 22.6, 14.1, 13.8. Anal. Calcd for $C_{14}H_{28}OS$: C, 68.79; H, 11.55. Found: C, 68.65; H, 11.47.

9 (R^1 = $C(CH_2)_4$, R = Ph, R^3 = Me, liquid): ^{1}H NMR δ 7.43−7.41 (m, 2H), 7.33−7.26 (m, 3H), 5.82 (d, J = 15.6 Hz, 1H), 5.10−5.05 (dd, J = 15.6 Hz, 6.8 Hz, 1H), 4.25−4.19 (quintet, J = 6.4 Hz, 1H), 1.97−1.64 (m, 8H), 1.45 (bs, 1H), 1.16 (d, J = 6.4 Hz, 3H); ^{13}C NMR δ 136.5, 135.0, 133.4, 132.0, 128.5, 128.3, 68.7, 60.7, 37.4, 37.2, 23.2; HRMS calcd *m*/*z* for $C_{15}H_{20}OS$ 248.1235, found *m*/*z* 248.1224.

4-Bromobenzoate of 9 (R^1= $C(CH_2)_4$, R^2 = Ph, R^3 = Me, liquid): ^{1}H NMR δ 7.88 (d, J = 5.0 Hz, 2H), 7.58 (d, J = 5.0 Hz, 2H), 7.40−7.38 (m, 2H), 7.26−7.15 (m, 3H), 6.01−5.96 (dd, J = 15.6, 0.9 Hz, 1H), 5.74−5.51 (m, 1H), 5.16−5.10 (dd, J = 15.6, 6.8 Hz, 1H), 1.96−1.65 (m, 8H), 1.34 (d, J = 6.6 Hz, 3H);. ^{13}C NMR δ 164.9, 137.4, 136.5, 133.0, 131.6, 131.1, 129.6, 128.4, 128.3, 127.9, 127.1, 71.7, 60.6, 37.2, 37.1, 23.2, 20.5.

9 (R^1 = $C(CH_2)_4$, R^2 = R^3 = Me, liquid): ^{1}H NMR δ 5.72 (d, J = 15.6 Hz, 1H), 5.49−5.43 (dd, J = 15.6, 6.6 Hz, 1H), 4.39−4.32 (quintet, J = 6.4 Hz, 1H), 1.89 (s, 3H), 1.87−1.63 (m, 8H), 1.30 (d, J = 6.4 Hz, 3H); ^{13}C NMR δ 134.2, 132.0, 68.7, 56.0, 37.0, 36.7, 23.9, 23.4, 12.3; HRMS calcd *m*/*z* for $C_{10}H_{18}OS$ 186.1078, found *m*/*z* 186.1064.

Acetate of 9 (R^1 = $C(CH_2)_4$, R^2 = R^3 = Me, liquid): ^{1}H NMR δ 5.75 (d, J = 14.6 Hz, 1H), 5.42−5.36 (m, 2H), 2.04 (s, 3H), 1.87 (s, 3H), 1.87−1.61 (m, 8H), 1.33 (d, J = 6.1 Hz, 3H); ^{13}C NMR δ 171.8, 136.0, 127.5, 70.8, 36.9, 36.7, 29.7, 23.4, 21.4, 20.8, 12.3.

9 (R^1 = $C(CH_2)_5$, R^2 = Ph, R^3 = Me, liquid): ^{1}H NMR δ 7.42−7.40 (m, 2H), 7.33−7.26 (m, 3H), 5.55 (d, J = 15.9 Hz, 1H), 5.03−4.97 (dd, J = 15.8, 6.8 Hz, 1H), 4.24−4.18 (quintet, J = 6.5 Hz, 1H), 1.81−1.68 (m, 6H), 1.50−1.37 (m, 4H), 1.15 (d, J = 6.4 Hz, 3H); ^{13}C NMR δ 137.7, 135.3, 132.6, 131.9, 128.7, 128.2, 68.9, 53.7, 36.02, 35.97, 25.9, 23.1, 22.6; HRMS calcd *m*/*z* for $C_{16}H_{22}OS$ 262.1391, found *m*/*z* 262.1376.

4-Bromobenzoate of 9 (R^1 = $C(CH_2)_5$, R^2 = Ph, R^3 = Me, liquid): ^{1}H NMR δ 7.88 (d, J = 7.3 Hz, 2H), 7.58 (d, J = 7.3 Hz, 2H), 7.39−7.37 (m, 2H), 7.26−7.15 (m, 3H), 5.72 (d, J = 16.0 Hz, 1H), 5.58−5.52 (quintet, J = 6.6 Hz, 1H), 5.08−5.03 (dd, J = 16.0, 5.6 Hz, 1H), 1.85−1.65 (m, 6H), 1.54−1.32 (m, 4H), 1.34−1.32 (dd, J = 6.3, 1.1 Hz, 3H); ^{13}C NMR δ 164.9, 137.7, 131.61, 131.55, 131.4, 131.1, 129.6, 128.6, 128.1, 127.8, 127.6, 71.8, 53.4, 35.74, 35.69, 25.9, 22.5, 20.53, 20.45.

The above material was oxidized with *m*-CPBA to furnish the corresponding sulfone as a colorless solid: mp 124 °C; ^{1}H NMR δ 7.89−7.86 (m, 2H), 7.76−7.73 (m, 2H), 7.61−7.54 (m, 3H), 7.43−7.39 (m, 2H), 5.63−5.48 (m, 3H), 2.07−1.89 (m, 4H), 1.74−1.58 (m, 3H), 1.41 (d, J = 6.1 Hz, 3H), 1.38−1.16 (m, 3H); ^{13}C NMR δ 164.8, 137.1, 135.0, 133.4, 131.7, 131.1, 130.8, 129.1, 128.2, 128.1, 71.1, 67.7, 28.6, 28.4, 25.1, 21.5, 20.1; ESMS [M + NH_4] 494.2 and 496.2 (1:1).

9 (R^1 = $C(CH_2)_5$, R^2 = R^3 = Me, liquid): ^{1}H NMR δ 5.52−5.40 (m, 2H), 4.40−4.34 (quintet, J = 6.4 Hz, 1H), 1.83 (s, 3H), 1.71−1.60 (m, 7H), 1.51−1.36 (m, 3H), 1.31 (d, J = 6.4 Hz, 3H); HRMS calcd *m*/*z* for $C_{11}H_{20}OS$ 200.1235, found *m*/*z* 200.1230.

4-Bromobenzoate of 9 (R^1 = $C(CH_2)_5$, R^2 = R^3 = Me, liquid): ^{1}H NMR δ 7.91 (d, J = 6.8 Hz, 2H), 7.58 (d, J = 6.8 Hz, 2H), 5.66−5.60 (m, 2H), 5.49−5.44 (dd, J = 16.1, 6.3 Hz, 1H), 1.81 (s, 3H), 1.72−1.62 (m, 6H), 1.49−1.35 (m, 4H). 1.47 (d, J = 6.4 Hz, 3H); ^{13}C NMR δ 165.0, 137.2, 131.6, 131.1, 129.6, 127.9, 127.5, 72.0, 48.7, 35.1, 34.9, 26.0, 22.3, 20.9, 10.4.

Mixture of 9 and 10 (R^1 = Ph CH_2CH_2, R^2 = Ph, R^3 = Me, liquid): ^{1}H NMR δ 7.36−7.17 (m), 5.52−5.46 (m), 5.29−5.23 (m), 4.19−4.13 (m), 3.58−3.52 (m), 2.81−2.69 (m), 2.07−1.88 (m), 1.12 (d, J = 6.4 Hz, major isomer), 1.06 (d, J = 6.4 Hz, minor isomer); ^{13}C NMR δ 141.2, 136.1, 135.9, 134.2, 133.6, 133.5, 130.2, 128.63, 128.61, 128.49, 128.47, 128.4, 127.43, 127.36, 126.0, 68.2, 68.1, 50.5, 50.4, 35.6, 33.3, 23.1, 23.0. Anal. Calcd for $C_{19}H_{22}OS$: C, 76.46; H, 7.43. Found: C, 76.32; H, 7.38.

Mixture of alcohols 9 and 10 (R^1 = $PhCH_2CH_2$, R^2 = R^3 = Me, liquid): ^{1}H NMR δ 7.30−7.26 (m), 7.21−7.17 (m), 5.57−5.42 (m), 4.39−4.33 (m), 3.06−3.00 (dt, J = 8.0, 6.6 Hz), 2.75−2.69 (m), 2.00−1.84 (m), 1.98 (s, major isomer), 1.96 (s, minor isomer), 1.64 (bs), 1.30 (d, J = 6.3 Hz); ^{13}C NMR δ 141.4, 135.9, 135.8, 130.5, 130.3, 128.4, 125.9, 68.44, 68.36, 48.02, 47.95, 35.5, 33.3, 23.7, 23.6, 13.7. Anal. Calcd for $C_{14}H_{20}OS$: C, 71.14; H, 8.52. Found: C, 71.05; H, 8.45.

Acetate of alcohols 9 and 10 (R^1 = $PhCH_2CH_2$, R^2 = R^3 = Me, liquid): ^{1}H NMR δ 7.30−7.26 (m), 7.21−7.16 (m), 5.55−5.34 (m), 3.05−2.98 (m), 2.75−2.67 (m), 2.06 (s, minor isomer), 2.05 (s, major isomer), 1.98−1.81 (m), 1.95 (s), 1.34 (d, J = 6.6 Hz); ^{13}C NMR δ 170.3, 141.3, 132.5, 132.3, 131.2, 128.44, 128.36, 125.9, 70.4, 70.3, 47.9, 47.8, 35.42, 35.37, 33.3, 21.4, 20.7, 20.5, 13.6, 13.5.

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Supporting Information Available: The Crystallographic Information Files (CIF) for 4-bromobenzoate of the sulfone derived from the alcohol **9** (R^1 = *cy*-C_6H_{10}, R^2 = Ph, R^3 = Me) and the alcohol **11** (R^1 = *t*-Bu, R^2 = Ph, R^3 = Me) and the coordinates of the optimized geometries of *s-cis*-**8** and *s-trans*-**8** (R^1 = R^3 = Me, R^2 = Ph), *s-cis*-**7d** and *s-trans*-**7d** (**7a**; R^1 = Me, R^2 = Ph), *s-cis*-**7e** and *s-trans*-**7e** (**7a**; R^1 = R^2 = Me), and *s-cis*-**7c** and *s-trans*-**7c** (R^1 = R^2 = Me). This material is available free of charge via the Internet at http://pubs.acs.org.

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