on silica gel eluting with CH_2Cl_2 and then 10% EtOAc/CH_2Cl_2 as an orange solid; 30 mg (77%). Recrystallization from benzene afforded **31** as fine red needles; mp >265 °C dec; NMR δ 8.45 (d, 1, H_{12}, $J_{11,12}$ = 10 Hz), 8.3-7.65 (m, 8), 6.60 (d, 1, H_{11}); mass spectrum, (chemical ionization, methane), *m/e* (relative intensity) 283 (M + 1, 100), 255 (6).

***trans*-9,10-Dihydro-9,10-dihydroxybenzo[*j*]fluoranthene (32).** A suspension of quinone **31** (30 mg, 0.11 mmol) in 95% EtOH (20 mL) was stirred in the dark at 0 °C with potassium borohydride (60 mg, 1.1 mmol). Oxygen was bubbled through the solution for 2 h. After that time, the colorless solution was poured into water and extracted several times with EtOAc. The extracts were combined, washed with 0.1 N HCl, water, and brine and dried over K_2CO_3. After removal of the solvent, the residue was purified by flash chromatography on silica gel eluting first with $CHCl_3$ and then 5% MeOH/$CHCl_3$. The dihydrodiol **32** was obtained as a white solid; 18 mg (58%). The spectral characteristics and chromatographic behavior of this compound were identical with those previously described.[21]

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Dichotomous Regiochemistry of Aldehyde and Ketone in the Reaction with Dithio-Substituted Crotyllithium

Jim-Min Fang,* Bor-Cherng Hong, and Li-Fan Liao

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

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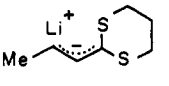
The crotyllithium compound **1** generated from (*E*)-2-(1-propen-1-yl)-1,3-dithiane reacted with an aldehyde to give γ-products in favor of the anti isomer. This regio- and diastereoselective reaction is applicable to syntheses of trans β,γ-disubstituted γ-lactones, including natural products of (±)-eldanolide and (±)-trans quercus lactone. The γ(1,2)-adducts obtained from the reaction of **1** and enals underwent alkoxy-Cope rearrangements on treatment with KH. The consequence is virtually complete α(1,4)-addition of crotyllithium **1** to α,β-unsaturated aldehydes. Crotyllithium **1** reacted with ketones at either the α- or the γ-site, depending on the nature of respective ketone. The regiochemistry is well interpreted by the hard and soft acids and bases principle, when the steric effect is a minor controlling factor. The effects of HMPA and reaction temperature on the regioselectivity were also evaluated.

The regioselective reactions of unsymmetric allylic anions have been extensively studied.[1] The controlling factors of regioselectivity include the effect of substituents,[2] the nature of attacking electrophiles,[3,4] the nature of solvents,[5] and the nature of counter cations.[6] However, no consistent rule is so far established to interpret the observed regioselectivity. The dithianylidene anion, an unsymmetric allylic anion with dithio substituents, can function as an equivalent of α,β-unsaturated acyl anion when reaction takes place at the α-site, while the anion can function as an equivalent of β-anion of carboxylic acid when reaction occurs at the γ-site. Thus, a proper manipulation of the ambident property of dithianylidene anions would provide a versatile method in organic synthesis. Furthermore, enlightened by the recent research on the diastereoselective reaction of crotyl anions,[7] we have found that dithio-substituted crotyllithium **1** indeed adds to aldehydes in a regio- and diastereoselective manner.[8] We herein report the unusual dichotomous regiochemistry of aldehyde and ketone in the reaction with crotyllithium **1**.

Table I. Reaction of Crotyllithium 1 and Aldehydes

entry	electrophile	addition products α:γ	addition products (anti/syn)	total yields, %
1	MeCHO	<5:95	(80/20)	86
2	$MeCH_2CHO$	<5:95	(~100/0)	91
3	$Me(CH_2)_2CHO$	<5:95	(~100/0)	89
4	Me_2CHCHO	<5:95	(~100/0)	93
5	$Me(CH_2)_3CHO$	<5:95	(~100/0)	93
6	$Me_2C{=}CHCH_2CHO$	<1:100	(~100/0)	90
7	$CH_2{=}CHCHO$	<1:100	(75/25)	87
8	$MeCH{=}CHCHO$	<1:100	(84/16)	88
9	$PhCH{=}CHCHO$	<1:100	(85/15)	86
10	2-furaldehyde	<1:100	(~100/0)	84
11	PhCHO	<1:100	(75/25)	92



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Results and Discussion

Treatment of crotonaldehyde with an equivalent amount of 1,3-propanedithiol in the presence of magnesium perchlorate yielded the vinylogous dithiane **2** in the *E* form.[8] Dithiane **2** was readily deprotonated by *n*-BuLi in THF solution to give the desired crotyllithium **1**.[9] Previous

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(2) Ikeda, Y.; Furuta, K.; Meguriya, N.; Ikeda, N.; Yamamoto, H. *J. Am. Chem. Soc.* **1982**, *104*, 7663.
(3) Murphy, W. S.; Wattanasin, S. *J. Chem. Soc., Perkin Trans 1* **1980**, 2678.
(4) Atlani, P. M.; Biellmann, J. F.; Dube, S.; Vicens, J. J. *Tetrahedron Lett.* **1974**, 2665.
(5) Ziegler, F. E.; Fang, J. M.; Tam, C. C. *J. Am. Chem. Soc.* **1982**, *104*, 7174.
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(7) Hoffmann, R. V. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 555.
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(9) Ziegler, F. E.; Mencel, J. J. *Tetrahedron Lett.* **1983**, *24*, 1859.

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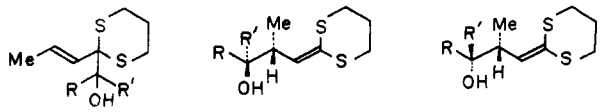

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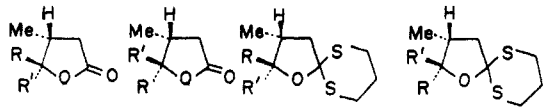
preparation of 1 from 2-propylidene-1,3-dithiane could not be realized without the assistance of a cosolvent of HMPA.[10] Thus, the present method is not only beneficial to evaluate the effect of HMPA in subsequent reactions, but also important to achieve the anticipated regio- and diastereoselectivities.

Reaction with Aldehydes. The resulting crotyllithium 1 was cooled to −78 °C and treated with appropriate electrophiles. The reaction with electrophiles of D_2O, iodomethane, and chlorotrimethylsilane occurred exclusively at the α-carbon of 1 to afford products of **3**, **4**, and **5**, respectively. On the other hand, crotyllithium 1 reacted with aldehydes dominantly at the γ-site (Table I). The structure of γ-addition product was characterized by the appearance of a doublet at ~δ 1.0 attributable to the resonance of a γ-CH_3 group in the ^1H NMR spectrum. The structure of the γ-adduct was also diagnostic in the mass spectrum, which exhibited a base peak at m/z 159 owing to the fragmentation at the newly formed C–C bond. Besides the high regioselectivity, the γ-addition was also diastereoselective (anti/syn ≥ 3/1). The ratio of products was carefully determined by the HPLC and NMR analyses, and occasionally calibrated by isolated weights of products. The structures of anti and syn isomers were rigorously determined by analysis of corresponding trans and cis γ-lactones. For example, the reaction of 1 and benzaldehyde gave exclusively the γ-adducts **7k** and **8k**



9 10 11 12

a, R = Me; R′ = H
b, R = CH_2Me; R′ = H
c, R = $(CH_2)_2Me$; R′ = H
d, R = $CHMe_2$; R′ = H
e, R = $(CH_2)_3Me$; R′ = H
f, R = $CH_2CH{=}CMe_2$; R′ = H
g, R = $CH{=}CH_2$; R′ = H
h, R = CH=CHMe; R′ = H
i, R = CH=CHPh; R′ = H
j, R = 2-furyl; R′ = H
k, R = Ph; R′ = H
l, R, R′ = $(CH_2)_4$
m, R, R′ = $(CH_2)_5$
n, R, R′ = $(CH_2)_2CH(t\text{-Bu})(CH_2)_2$
o, R, R′ = $(CH_2)_6$
p, R = CH_2Me; R′ = Me
q, R = R′ = CH_2Me
r, R = $(CH_2)_4Me$; R′ = Me
s, R = R′ = $CHMe_2$
t, R = CO_2Et; R′ = Me
u, R = Ph; R′ = Me
v, R = R′ = Ph
w, R, R′ = $CH{=}CH(CH_2)_2$
x, R, R′ = $CH{=}CH(CH_2)_3$
y, R = $CH{=}CH_2$; R′ = Me
z, R = $CH{=}CMe_2$; R′ = Me

in a ratio of 77:23 as revealed by HPLC and ^1H NMR analyses. Two diastereomers were separated and subjected to hydrolysis ($HgCl_2$, aqueous MeOH), respectively.[8] The major adduct with anti configuration (**7k**) yielded a product of trans lactone **9k**, and the minor adduct **8k** with syn configuration resulted in the cis lactone **10k**. Compound **10k** was recognized by appearance of a methyl resonance (d, J = 6 Hz) at the unusually high field (δ 0.66) owing to the shielding effect of the adjacent phenyl group.[11] However, the corresponding methyl resonance of the trans lactone **9k** occurred at a normal position of δ 1.17. For similar reason, trans lactone **9k** exhibited the γ-H resonance (d, J = 9 Hz) at a relatively higher field (δ 4.95) than the corresponding resonance (δ 5.62, d, J = 6 Hz) of cis lactone **10k**. Similarly, the reaction of crotyllithium 1 with

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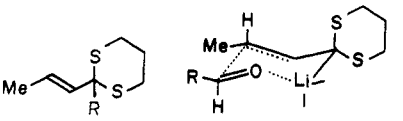
(11) Hoppe, D.; Bronneke, A. *Tetrahedron Lett.* **1983**, *24*, 1687.

Table II. Reaction of Crotyllithium 1 and Modest Size Ketones

entry	electrophile	addition products α:γ	(anti/syn)	total yields, %
1	cyclopentanone	100:<1		85
2	cyclohexanone	82:18		92
3	4-*tert*-butylcyclohexanone	80:20		90
4	cycloheptanone	100:<1		86
5	2-butanone	84:16	(77/23)	93
6	3-pentanone	85:15		91
7	2-heptanone	92:8		92

pentanal and 4-methyl-3-pentenal (Table I, entries 5 and 6) gave anti adducts **7e** and **7f**, respectively. Subsequent hydrolysis of **7e** and **7f** thus culminated in expedient synthesis of a plant constituent (±)-trans quercus lactone (**9e**)[12] and an insect pheromone (±)-eldanolide (**9f**).[13]

To account for the high regioselectivity and anti selectivity in the reaction of crotyllithium 1 with aldehydes, a chelation model with the chair-like transition state is proposed (A).[8] In the absence of a dipolar agent, such as



A

2, R = H
3, R = D
4, R = Me
5, R = $SiMe_3$
13, R = CH_2CH_2CHO
14, R = $CH(Me)CH_2CHO$

HMPA, the reaction conceivably proceeded via a chelation transition state to give γ-adducts. The original *E* configuration of 1 was retained in the chair form to avoid interaction of the methyl group with dithio substituents. The R group was favorably oriented at the equatorial position to yield the observed anti configuration of γ-adducts.

The anti γ-adducts **7** were prone to cyclization.[14] For example, a pure sample of compound **7k**, obtained by chromatography from a μ-Porasil column, underwent cyclization to give a spiro dithiane **11k**, on standing for 10 h in the refrigerator. Compound **7i** also turned to **11i** on standing in a $CDCl_3$ solution. The process was presumably catalyzed by existence of a trace amount of mineral acid.[15] Similarly, cyclization of the syn γ-adduct **8** was effected to afford the spiro dithiane **12** by treatment with a catalytic amount of acetic acid. Subsequent hydrolysis of spiro dithianes **11** and **12** eventually led to γ-lactones **9** and **10**.

The reaction of crotyllithium 1 with α,β-unsaturated aldehydes afforded allyl alcohols (Table I, entries 7–9). These allyl alcohols were able to undergo alkoxy-Cope rearrangements on treatment with KH.[16] Thus, allyl alcohols **7g** and **8g** were transformed into a product **13**, and allyl alcohols **7h** and **8h** were converted to the aldehyde **14**. The overall reactions can be visualized as the α-(1,4)-additions of vinylogous dithiane **2** to acrolein and crotonaldehyde. Treatment of **7h** with KH in the presence of 1 equiv of acrolein afforded a single product **14**. Since compound **13** was not formed in this case, the experiment unambiguously demonstrated that an intramolecular

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(13) Fang, J. M.; Hong, B. C. *Synth. Commun.* **1986**, *16*, 523.
(14) Seebach, D.; Kolb, -M. *Liebigs Ann. Chem.* **1977**, 811.
(15) Suzuki, K.; Tomooka, K.; Matsumoto, T.; Katayama, E.; Tsuichihashi, G. I. *Tetrahedron Lett.* **1985**, *26*, 3711.
(16) Ziegler, F. E.; Chakraborty, U. R.; Wester, R. T. *Tetrahedron Lett.* **1982**, 3237.

Table III. Reaction of Crotyllithium 1 with Bulky and Unsaturated Ketones

entry	electrophile	addition products α:γ	addition products (anti/syn)	total yields, %
1	diisopropyl ketone	<1:100		32
2	ethyl pyruvate	<1:100	(48/52)	86
3	acetophenone	<1:100	(76/24)	91
4	benzophenone	<1:100		93
5	2-cyclopentenone	100:<1		89
6	2-cyclohexenone	44:56	(75/25)	86
7	methyl vinyl ketone	<1:100	(60/40)	87
8	mesityl oxide	<1:100	(~100/0)	90

process rather than a dissociation-recombination mechanism was involved in the above transformation.[16]

Reaction with Ketones. In contrast to the result with aldehydes, crotyllithium 1 reacted predominantly at the α-site with the ketones shown in Table II. This phenomenon has been observed in certain related instances.[14,17] The structure of α-addition product (**6**) was readily recognized from the ^{1}H NMR spectrum, in which the resonance of α-H disappeared but the resonance of the vinyl methyl group was retained as a doublet at ~δ 1.8. The reaction of crotyllithium 1 and 4-*tert*-butylcyclohexanone resulted in three products (**6n**-ax-OH/**6n**-eq-OH/**7n**-ax-OH = 44/36/20) out of four possible isomers. The major isomer of α-adducts was tentatively assigned as the energetically favorable isomer having the hydroxyl group orienting at the axial position. The assignment was supported by the eluting order of two isomers on a μ-Porasil column, i.e., the **6n**-OH_{ax} isomer had a shorter retention time because its hydroxyl group was rather hindered for interaction with silica gel. In the mass spectrum, the **6n**-OH_{ax} isomer also showed a relatively intense signal corresponding to the fragment of $[M - H_2O]^+$.[18] The γ-adduct was also tentatively assigned as the thermodynamically stable isomer having the bulky substituent of dithiane group at the equatorial position.

Table III shows the result of the reaction of crotyllithium 1 with the bulky and/or the unsaturated ketones. Except for entries 5 and 6, exclusive γ-selectivity was observed. The reaction with an unsymmetric ketone resulted in two diastereomers of the γ-adduct. These isomers were transformed into corresponding γ-lactones for structural correlation (see above). The result indicated the preference of the anti isomer in the γ-additions except entry 2. Noteworthily, the (1,2)-adducts derived from the reaction of 1 with 2-cyclopentenone and 2-cyclohexenone were successfully isolated by means of the liquid chromatography. The (1,2)-adducts have been reported to be unstable, and feasible to undergo alkoxy-Cope rearrangements in prolonged reaction time to give corresponding (1,4)-adducts.[16]

Interpretation of Regiochemistry. Comparing the result shown in Tables I–III, one can not simply interpret the regiochemistry by the steric effect. Considering the α-site of crotyllithium 1 is more hindered than the γ-site, one would expect 1 to react at the γ-site with a bulky ketone, such as diisopropyl ketone. However, one would have difficulty in explaining the different regioselectivities of crotyllithium 1 in reactions with those ketones having similar sizes. Furthermore, one would even be perplexed by the observed regioselectivities of aldehydes and ketones. Why should relatively large ketones preferred the conjested α-site of 1, while smaller aldehydes favored the γ-site? Since the steric effect is not sufficient to interpret the regioselectivity, in our opinion, the electronic effect should play the role.

Although revelation of the real reaction pathway awaits further experimental evidence, a plausible interpretation of the observed regiochemistry is based on the hard and soft acids and bases principle (HSAB principle) as it is appraised in precedent.[19] Accordingly, the α-carbon of crotyllithium 1 is a relatively hard nucleophilic center because it is the position for hard electrophiles, as evidenced in the reaction with very hard electrophiles of D_2O and Me_3SiCl. The hardness at α-carbon is presumed to be the consequence of polarization by the dithio substituents. The hardness of a carbonyl compound is also counted on the substituents attached to the carbonyl carbon. It is considered that R^- is harder than H^-, so that the carbonyl carbon ($O{=}C^{2+}/2R^-$) of a ketone (R_2CO) is harder than the corresponding center ($O{=}C^{2+}/R^-,H^-$) of an aldehyde (RCHO). For this reason, the hard electrophile of ketones added to 1 at the relatively hard α-site, while the soft electrophile of aldehydes reacted at the relatively soft γ-site.

The absolute α-regioselectivity resulting in the reaction of 1 with cyclopentanone, cycloheptanone, and 2-cyclopentenone infers that these ketones might preferably coordinate with the crotyllithium prior to the carbon–carbon bond formation. The dipolarization process can be thought of as a consequence of releasing the ring strains and simultaneous generation of the extremely hard electrophilic centers. Due to delocalization of π-electrons, the open-chain conjugated ketones are relatively soft electrophiles and thus exhibit the γ-regioselectivity on reaction with 1. Interestingly, the reaction of crotyllithium 1 and α,β-unsaturated carbonyl compounds did not yield any conjugate addition product.

Ethyl pyruvate is usually considered as a hard electrophile for an electron-withdrawing group (carboxylate group) is attached to the carbonyl center ($O{=}C^{2+}/CH_3^-,EtO_2C^-$). However, the observed γ-regioselectivity is contradictory to the steric effect and contradictory to the HSAB principle. We surmize that the transition state may involve a chelation of the crotyllithium with both carbonyl and carboxyl groups to give the abnormal regioselection.

Comparison experiments on the reactivity of aldehydes and ketones were carried out. A THF solution of crotyllithium 1 was treated with a 1:1 mixture of propanal and 3-pentanone at −78 °C for 2 min. The reaction was quenched, and the product mixture was found to be composed of 93% α-adduct **6q** (from 3-pentanone) and 7% of γ-adduct **7b** (from propanal). Similar reaction also revealed that the α-addition of 2-butanone was much faster than the γ-addition of *n*-butanal. This result is in agreement with the HSAB principle, i.e., the hard–hard interaction is faster than the soft–soft interaction. When crotyllithium 1 was treated with mixed electrophiles of benzaldehyde and acetophenone in the above conditions, the reaction provided 70% γ-adducts **7k** + **8k** (from benzaldehyde) and 30% γ-adducts **7u** + **8u** (from acetophenone). This case clearly indicates the steric effect but indifference in the hardness of two electrophiles.

The influence of cosolvent HMPA and reaction temperature on the regiochemistry was studied. Table IV shows the α-addition products increased in the presence of 3 equiv of HMPA (entries 4, 5, 6, and 8), whereas the γ-addition products increased at higher reaction temperature (entries 8 and 9).[5]

(17) Kozikowski, A. P.; Chen, Y. Y. *J. Org. Chem.* **1980**, *45*, 2236.
(18) Green, M. M. *Top. Stereochem.* **1976**, *9*, 35.
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Table IV. Effects of Temperature and Cosolvent HMPA on the Reaction of Crotyllithium 1 with Electrophiles

entry	electrophile	products ratio (α:γ) THF, −78 °C	THF, 25 °C	THF–HMPA, 25 °C
1	D_2O	100:<1	100:<1	100:<1
2	MeI	100:<1	100:<1	100:<1
3	Me_3SiCl	100:<1	100:<1	100:<1
4	$Me(CH_2)_2CHO$	<5:95	<5:95	84:16
5	Me_2CHCHO	<5:95	<5:95	76:24
6	PhCHO	<1:100	<1:100	11:89
7	cyclopentanone	100:<1	100:<1	100:<1
8	cyclohexanone	82:18	24:76	95:<5
9	4-*t*-Bu-cyclohexanone	80:20	60:40	
10	cycloheptanone	100:<1	100:<1	100:<1
11	2-heptanone	100:<1	100:<1	100:<1
12	benzophenone	<1:100	<1:100	<1:100

Conclusion

We have demonstrated that aldehyde and ketone display dichotomous regiochemistry in a delicate reaction system involving crotyllithium 1. The regioselectivity is closely related to the nature of carbonyl compounds. The HSAB principle is a good index to reconcile the observed regioselectivity when the steric effect is a minor controlling factor. Soft electrophiles, such as aldehydes and most of unsaturated ketones, preferred the reaction of the γ-site of 1. Hard electrophiles, such as modest size ketones, favored the reaction at the α-site of 1, although this site is actually more conjested than the γ-site. Introduction of dithio substituents to a crotyllithium species not only serves as a latent functionality of carboxylic acid, but also impedes the E/Z isomerization to reach the high diastereoselectivity. Therefore, E form dithio-substituted crotyllithium 1 reacted with aldehydes via the chelation transition state to afford the γ-addition products in a high percentage of the anti isomer. This methodology is applicable to syntheses of trans β,γ-disubstituted lactones, including natural products of eldanolide and trans quercus lactone. The $\gamma(1,2)$-addition of crotyllithium 1 and conjugated aldehydes, followed by an alkoxy-Cope rearrangement, provides the $\alpha(1,4)$-adducts. This method is potentially useful in synthesis of 5-en-4-oxo aldehydes.

Experimental Section

Elemental analyses were carried out on the Perkin-Elmer 240c elemental analyzer. Infrared spectra were run on the Jasco IRA-1 spectrometer or the Perkin-Elmer 1310 infrared spectrophotometer. The proton nuclear magnetic resonance spectra were recorded on the Varian EM-390 (90 MHz) spectrometer or the Jeol JNM-FX100 (100 MHz) spectrometer or the Bruker AM-300 WB (300 MHz) spectrometer. Chemical shifts are reported in parts per million downfield from tetramethylsilane. Mass spectra were recorded on the Jeol JMS-D300 spectrometer operating at an ionizing voltage of 70 eV. Merck silica gel 60 F sheets were used for analytic thin-layer chromatography. Flash chromatography was performed as described by Still.[20] High-pressure liquid chromatography was carried out on a Waters Associates M45 liquid chromatograph, equipped with the ultraviolet and refractive index detectors. The sample was analyzed and/or separated on a μ-Porasil column (0.78 cm × 25 cm) by elution with gradient of ethyl acetate and hexane. The flow rate of the indicated elution solvent is maintained at 5 mL/min, and the retention time of a compound is recorded accordingly.

Reactions requiring anhydrous conditions were performed under a nitrogen atmosphere, and the apparatuses were dried at 120 °C for at least 1 h before use. THF was distilled from sodium benzophenone ketyl under N_2. Dry HMPA and diisopropylamine were distilled from CaH_2 under N_2. Other chemicals were commercially available reagent grade and were purified according to the standard procedure.[21] Commercial *n*-BuLi was standardized by the method of Kofron.[22] (*E*)-2-(1-propen-1-yl)-1,3-dithiane (2) was prepared according to the previously reported procedure.[8] *n*-Pentanal was prepared by oxidation of *n*-pentanol with chromic acid.[23] 4-Methyl-3-pentenal was prepared from hydrolysis of 2-(2′-ethoxycyclopropyl)-2-propanol.[24] Ethyl pyruvate was prepared by oxidation of ethyl lactate with potassium permanganate.[25] All reactions of 1 and carbonyl compounds (Tables I–IV) have been repeated from 2 to 5 times. The ratio of products was determined by the HPLC and ^1H NMR analyses and occasionaly assisted with measurement of isolation weights of products.

General Procedure for Reaction of Crotyllithium 1 with Electrophiles. Under an atmosphere of nitrogen, *n*-BuLi (1.1 mmol, 1.6 M in hexane) was added dropwise to a solution of dithiane 2 (1.0 mmol) in anhydrous THF at −30 °C. After stirring for 20–60 min, the resulting solution of crotyllithium 1 was cooled to −78 °C. A solution of appropriate electrophile (1 mmol) in THF (1 mL) was added dropwise, and it may be accompanied by HMPA (3 mmol) in appropriate cases (Table IV). After being stirred for 10–20 min, the reaction was quenched by addition of methanol. The mixture was concentrated in vacuo, and the residue was taken up with ether. The ethereal solution was washed 3 times with brine, dried (Na_2SO_4), and concentrated in vacuo to give the addition products. Separation of products was accomplished by using the flash chromatography and/or the HPLC.

Deuteriated Water. 3: IR (neat) 3020, 2940, 1650 cm^{-1}; MS, m/z (relative intensity) 161 (40, M^+), 159 (100), 146 (13), 86 (30), 85 (36); ^1H NMR ($CDCl_3$) δ 1.74 (3 H, d, J = 6 Hz), 1.80–2.25 (2 H, m), 2.79–2.99 (4 H, m), 5.55 (1 H, d, J = 15 Hz), 5.87 (1 H, dq, J = 15, 6 Hz).

Chlorotrimethylsilane. 4: IR (neat) 2953, 2910, 2851 cm^{-1}; MS, m/z (relative intensity) 232 (39, M^+), 217 (12), 159 (81), 127 (65), 85 (50), 73 (100); ^1H NMR (CCl_4) δ 0.21 (9 H, s), 1.78 (3 H, d, J = 6.5 Hz), 2.10–2.40 (2 H, m), 2.70–3.07 (4 H, m), 5.43 (1 H, d, J = 15 Hz), 5.68 (1 H, dq, J = 15, 6.5 Hz).

Iodomethane. 5: IR (neat) 3020, 2980, 2920, 2860, 1580 cm^{-1}; MS, m/z (relative intensity) 174 (25, M^+), 159 (62), 99 (60), 85 (100); ^1H NMR ($CDCl_3$) δ 1.64 (3 H, s), 1.76 (3 H, d, J = 6 Hz), 1.85–2.10 (2 H, m), 2.65–2.95 (4 H, m), 5.55 (1 H, d, J = 15 Hz), 5.90 (1 H, dq, J = 15, 6 Hz). Anal. Calcd for $C_8H_{14}S_2$: C, 55.12; H, 8.09. Found: C, 55.37; H, 8.12.

Acetaldehyde. *γ-anti*-7a: R_t (10% EA) 16.4 min; IR (neat) 3400, 2975, 2935, 2880 cm^{-1}; MS, m/z (relative intensity) 204 (100, M^+), 189 (7), 171 (23), 159 (59), 130 (78); ^1H NMR ($CDCl_3$) δ 0.92 (3 H, d, J = 6.8 Hz), 1.09 (3 H, d, J = 6.2 Hz), 1.84 (1 H, s, OH), 2.05–2.13 (2 H, m), 2.62–2.77 (1 H, m), 2.78–2.91 (4 H, m), 3.52–3.66 (1 H, m), 5.76 (1 H, d, J = 9.8 Hz). ***γ-syn*-8a**: R_t (10% EA) 16.2 min; ^1H NMR ($CDCl_3$) δ 0.94 (3 H, d, J = 6.7 Hz), 1.08 (3 H, d, J = 6.3 Hz), 1.84 (1 H, s, OH), 2.05–2.13 (2 H, m), 2.62–2.77 (1 H, m), 2.78–2.91 (4 H, m), 3.52–3.66 (1 H, m), 5.74 (1 H, d, J = 9.8 Hz). Anal. Calcd for $C_9H_{16}OS_2$: C, 52.90; H, 7.89. Found: C, 52.63; H, 7.80.

Propanal. *γ-anti*-7b: R_t (15% EA) 13.7 min; IR (neat) 3700–3100, 3000–2800, 1480–1400 cm^{-1}; MS, m/z (relative intensity) 218 (11, M^+), 159 (100), 85 (27); ^1H NMR ($CDCl_3$) δ 0.88–1.15 (6 H, m, two methyls), 1.28–1.72 (2 H, m), 2.02–2.32 (3 H, m, $SCCH_2$– and OH), 2.68–3.00 (5 H, m), 3.22–3.44 (1 H, m, C*H*OH), 5.85 (1 H, d, J = 10 Hz). Anal. Calcd for $C_{10}H_{18}OS_2$: C, 55.00; H, 8.31. Found: C, 54.83; H, 8.28.

Butanal. α-6c: R_t (10% EA) 4.4 min; IR (neat) 3470, 2960, 2880, 1580 cm^{-1}; MS, m/z (relative intensity) 232 (85, M^+), 159 (65), 125 (65), 106 (100), 83 (95); ^1H NMR ($CDCl_3$) δ 0.96 (3 H, t, J = 6 Hz), 1.29–1.70 (4 H, m), 1.81 (3 H, dd, J = 6, 1 Hz), 1.86–2.11 (2 H, m), 2.70–2.94 (4 H, m), 5.55 (1 H, dq, J = 15, 1 Hz), 6.05 (1 H, dq, J = 15, 6 Hz). Anal. Calcd for $C_{11}H_{20}OS_2$: C, 56.85; H, 8.67. Found: C, 56.72; H, 8.66. ***γ-anti*-7c**: R_t (10%

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EA) 7.0 min; IR (neat) 3440, 2950, 2910, 1570 cm^{-1}; MS, *m/z* (relative intensity) 232 (0.03, M^+), 159 (100), 85 (30); ^1H NMR ($CDCl_3$) δ 0.96 (3 H, t, J = 6 Hz), 1.00 (3 H, d, J = 6 Hz), 1.20–1.65 (4 H, m), 1.95–2.32 (3 H, m), 2.65–3.00 (5 H, m), 3.20–3.50 (1 H, m), 5.88 (1 H, d, J = 10 Hz). Anal. Calcd for $C_{11}H_{20}OS_2$: C, 56.85; H, 8.67. Found: C, 56.77; H, 8.76.

2-Methylpropanal. **α-6d**: R_t (10% EA) 4.3 min; IR (neat) 3490, 2976, 2935, 2875 cm^{-1}; MS, *m/z* (relative intensity) 232 (5, M^+), 189 (4), 160 (88), 159 (100), 145 (20), 118 (13), 85 (70); ^1H NMR (CCl_4) δ 0.92 (3 H, d, J = 7 Hz), 1.03 (3 H, d, J = 7 Hz), 1.30–1.45 (1 H, m), 1.83 (3 H, d, J = 6 Hz), 1.70–2.20 (2 H, m), 2.29 (1 H, s, OH), 2.40–3.00 (4 H, m), 3.63 (1 H, d, J = 2.5 Hz), 5.60 (1 H, d, J = 15 Hz), 6.02 (1 H, dq, J = 15, 6 Hz). **γ-*anti*-7d**: R_t (10% EA) 9.4 min; IR (neat) 3440, 2960, 2920, 2870, 1580 cm^{-1}; MS, *m/z* (relative intensity) 232 (14, M^+), 159 (100), 85 (28); ^1H NMR ($CDCl_3$) δ 0.95 (6 H, d, J = 6 Hz), 0.98 (3 H, d, J = 6 Hz), 1.60–1.87 (2 H, m), 1.95–2.28 (2 H, m), 2.78–2.98 (4 H, m), 3.10 (1 H, t, J = 6 Hz, C*H*OH), 5.89 (1 H, d, J =10 Hz). Anal. Calcd for $C_{11}H_{20}OS_2$: C, 56.85; H, 8.67. Found: C, 56.75; H, 8.74.

Pentanal. **γ-*anti*-7e**: R_t (8% EA) 7.4 min; IR (neat) 3700–3100, 1560 cm^{-1}; MS, *m/z* (relative intensity) 246 (8, M^+), 159 (100), 85 (23); ^1H NMR ($CDCl_3$) δ 0.80–1.05 (6 H, m), 1.10–1.60 (6 H, m), 1.92–2.30 (3 H, m), 2.68–2.98 (5 H, m), 3.20–3.52 (1 H, m, C*H*OH), 5.72 (1 H, d, J = 10 Hz). Anal. Calcd for $C_{12}H_{22}OS_2$: C, 58.49; H, 9.00. Found: C, 58.20; H, 8.98.

4-Methyl-3-pentenal. **γ-*anti*-7f**: R_t (10% EA) 6.7 min; IR (neat) 3600–3200 (OH), 3000, 2800, 1440 cm^{-1}; MS, *m/z* (relative intensity) 258 (10, M^+), 159 (100), 145 (9), 122 (7), 106 (10), 85 (30); ^1H NMR (CCl_4) δ 0.98 (3 H, d, J = 6 Hz, CH_3), 1.65 (6 H, d, J = 9 Hz, vinyl methyls), 1.90–2.28 (4 H, m), 2.55–2.91 (6 H, m), 3.39 (1 H, dt, J = 7, 6 Hz, C*H*OH), 5.10 (1 H, t, J = 7 Hz), 5.79 (1 H, d, J = 9 Hz). Anal. Calcd for $C_{13}H_{22}OS_2$: C, 60.42; H, 8.58. Found: C, 60.49; H, 8.63.

Acrolein. **γ-*anti*-7g**: R_t (10% EA) 7.7 min; IR (neat) 3450 (OH), 3096 (C=CH), 1675, 1640 (C=C), 1580, 1450, 1420 cm^{-1}; ^1H NMR (CCl_4) δ 0.95 (3 H, d, J = 6.8 Hz, CH_3), 1.52 (1 H, br s, OH), 1.95–2.25 (2 H, m, $SCCH_2$), 2.40–2.98 (5 H, m, SCH_2C and MeCH), 3.85 (1 H, C*H*OH), 5.02 (1 H, br d, J = 6 Hz), 5.21 (1 H, br d, J = 13 Hz), 5.69 (1 H, d, J = 10 Hz, CH=CS), 5.52–6.02 (1 H, m). **γ-*syn*-8g**: R_t (10% EA) 6.8 min; IR (neat) 3450, 3096, 1675, 1640, 1580, 1450, 1420 cm^{-1}; MS, *m/z* (relative intensity) 216 (1.2, M^+), 161 (10), 160 (11), 159 (100), 106 (5), 85 (30); ^1H NMR (CCl_4) δ 0.95 (3 H, d, J = 6.8 Hz, CH_3), 2.00–2.29 (2 H, m), 2.65–2.95 (4 H, m), 3.00–3.31 (1 H, m), 3.78–4.02 (1 H, m), 5.02 (1 H, br d, J = 6 Hz), 5.21 (1 H, br d, J = 13 Hz), 5.69 (1 H, d, J = 10 Hz, CH=CS), 5.52–6.02 (1 H, m). Anal. Calcd for $C_{10}H_{16}OS_2$: C, 55.51; H, 7.45. Found: C, 55.60; H, 7.51.

Crotonaldehyde. **γ-*anti*-7h**: R_t (15% EA) 6.6 min; IR (neat) 3440, 2990, 2895, 2700, 1660 cm^{-1}; MS, *m/z* (relative intensity) 230 (5, M^+), 161 (46), 150 (51) 159 (92), 106 (26), 85 (100); ^1H NMR (CCl_4) δ 0.95 (3 H, d, J = 6.8 Hz, CH_3), 1.20 (1 H, br s, OH), 1.70 (3 H, d, J = 6.0 Hz, vinyl CH_3), 1.95–2.30 (2 H, m, $SCCH_2$), 2.35–2.95 (5 H, m, SCH_2), 3.84 (1 H, br t, J = 5.5 Hz, C*H*OH), 5.40–5.60 (2 H, m), 5.68 (1 H, d, J = 10 Hz, CH=CS). Anal. Calcd for $C_{11}H_{18}OS_2$: C, 57.35; H, 7.88. Found: C, 57.29; H, 7.92. **γ-*syn*-8h**: R_t (15% EA) 6.2 min. IR (neat) 3440, 2990, 2895, 2700, 1660 cm^{-1}; MS, *m/z* (relative intensity) 230 (5, M^+), 161 (46), 160 (51), 159 (92), 106 (26), 85 (100); ^1H NMR (CCl_4) δ 0.95 (3 H, d, J = 6.8 Hz), 1.20 (1 H, br s), 1.70 (3 H, d, J = 6.0 Hz), 1.95–2.30 (2 H, m), 2.35–2.95 (5 H, m), 3.84 (1 H, br t, J = 5.5 Hz), 5.40–5.60 (2 H, m), 5.68 (1 H, d, J = 10 Hz).

Cinnamaldehyde. **γ-*anti*-7i**: R_t (15% EA) 8.7 min; IR (neat) 3490, 3070, 3020, 2975, 2945, 2890, 1680, 1595, 743, 685 cm^{-1}; MS, *m/z* (relative intensity) 292 (4, M^+), 159 (100), 106 (84); ^1H NMR (CCl_4) δ 1.01 (3 H, d, J = 7 Hz, CH_3), 1.70–1.90 (1 H, br s, OH), 1.95–2.30 (2 H, m), 2.70–2.98 (5 H, m), 4.02 (1 H, dd, J = 6, 6 Hz, C*H*OH), 5.75 (1 H, d, J = 10 Hz, CH=CS), 6.08 (1 H, dd, J = 15, 6.5 Hz), 6.49 (1 H, d, J = 15 Hz), 7.07–7.48 (5 H, m). Anal. Calcd for $C_{16}H_{20}OS_2$: C, 65.71; H, 6.89. Found: C, 65.50; H, 6.90. **γ-*syn*-8i**: R_t (15% EA) 8.3 min; IR (neat) 3490, 3070, 3020, 2975, 2945, 2890, 1680, 1595, 743, 685 cm^{-1}; MS, *m/z* (relative intensity) 292 (4, M^+), 159 (100), 106 (84); ^1H NMR (CCl_4) δ 1.01 (3 H, d, J = 7 Hz), 1.35–1.50 (1 H, m, OH), 1.95–2.30 (2 H, m), 2.70–2.95 (5 H, m), 4.07 (1 H, dd, J = 6.5, 6.0 Hz, C*H*OH), 5.73 (1 H, d, J = 10 Hz), 6.12 (1 H, dd, J = 15, 6.5 Hz), 6.51 (1 H, d, J = 15 Hz), 7.07–7.48 (5 H, m).

2-Furaldehyde. **γ-*anti*-7j**: R_t (15% EA) 11.6 min; IR (neat) 3435, 2913, 1666, 1410 cm^{-1}; MS, *m/z* (relative intensity) 256 (1, M^+), 161 (29), 160 (33), 159 (100), 106 (9), 85 (57); ^1H NMR ($CDCl_3$) δ 0.91 (3 H, d, J = 7 Hz), 2.00–2.54 (3 H, m), 2.70–3.00 (5 H, m), 4.45 (1 H, d, J = 8 Hz, C*H*OH), 5.85 (1 H, d, J = 9.5 Hz), 6.20–6.40 (2 H, m), 7.37 (1 H, br s). Anal. Calcd for $C_{12}H_{16}OS_2$: C, 56.22; H, 6.29. Found: C, 56.00; H, 6.38.

Benzaldehyde. **α-6k**: R_t (25% EA) 3.8 min; IR (neat) 3443, 3029, 2911, 2855, 1600 cm^{-1}; MS, *m/z* (relative intensity) 266 (1, M^+), 159 (100), 145 (55), 107 (10); ^1H NMR ($CDCl_3$) δ 1.75 (3 H, dd, J = 6, 1 Hz), 4.87 (1 H, s), 5.41 (1 H, dq, J = 15, 1 Hz), 5.88 (1 H, dq, J = 15, 6 Hz). Anal. Calcd for $C_{14}H_{18}OS_2$: C, 63.12; H, 6.81. Found: C, 63.29; H, 6.79. **γ-*anti*-7k**: R_t (25% EA) 4.6 min; IR (neat) 3440, 1600, 1580 cm^{-1}; MS, *m/z* (relative intensity) 266 (10, M^+), 159 (57), 106 (100); ^1H NMR ($CDCl_3$) δ 0.85 (3 H, d, J = 6 Hz), 1.97–2.25 (2 H, m), 2.70–2.97 (4 H, m), 3.00–3.23 (1 H, m), 4.40 (1 H, d, J = 6 Hz, C*H*OH), 5.85 (1 H, d, J = 9 Hz, vinyl), 7.35 (5 H, br s). Anal. Calcd for $C_{14}H_{18}OS_2$: C, 63.12; H, 6.81. Found: C, 62.42; H, 6.80. **γ-*syn*-8k**: R_t (25% EA) 4.3 min; ^1H NMR ($CDCl_3$) δ 0.98 (3 H, d, J = 6 Hz), 2.01–2.28 (2 H, m), 2.72–2.98 (4 H, m), 3.02–3.23 (1 H, m), 4.60 (1 H, d, J = 6 Hz), 5.78 (1 H, d, J = 10 Hz), 7.35 (5 H, br s).

Cyclopentanone. **α-6l**: IR (neat) 3460, 2920, 1600 cm^{-1}; MS, *m/z* (relative intensity) 244 (5, M^+), 159 (100), 85 (89); ^1H NMR ($CDCl_3$) δ 1.30–2.20 (11 H, m), 1.95 (3 H, d, J = 6.5 Hz, CH_3), 2.42–3.00 (4 H, m), 5.52 (1 H, d, J = 15 Hz), 5.97 (1 H, dq, J = 15, 6.5 Hz). Anal. Calcd for $C_{12}H_{20}OS_2$: C, 58.97; H, 8.25. Found: C, 59.25; H, 8.16.

Cyclohexanone. **α-6m**: R_t (5% EA) 6.0 min; IR (neat) 3480, 2900, 2840, 1580 cm^{-1}; MS, *m/z* (relative intensity) 258 (3, M^+), 159 (100), 85 (87); ^1H NMR ($CDCl_3$) δ 1.21–1.98 (10 H), 1.90 (3 H, dd, J = 6, 1 Hz, CH_3), 1.92–2.21 (2 H, m), 2.60–2.90 (4 H, m), 5.48 (1 H, dq, J = 15, 1 Hz), 5.89 (1 H, dq, J = 15, 6 Hz). Anal. Calcd for $C_{13}H_{22}OS_2$: C, 60.42; H, 8.58. Found: C, 60.45; H, 8.59. **γ-6m**: R_t (5% EA) 12.2 min; IR (neat) 3470, 2890, 2800, 1580 cm^{-1}; MS, *m/z* (relative intensity) 258 (0.02, M^+), 240 (0.4), 159 (100), 99 (52), 85 (86); ^1H NMR ($CDCl_3$) δ 1.00 (3 H, d, J = 6 Hz, CH_3), 1.35–1.70 (10 H), 1.80–2.20 (3 H, m), 2.67–2.97 (4 H, m), 5.95 (1 H, d, J = 9 Hz, vinyl H). Anal. Calcd for $C_{13}H_{22}OS_2$: C, 60.42; H, 8.58. Found: C, 61.00; H, 8.20.

4-*tert*-Butylcyclohexanone. **α-6n-OH_{ax}**: R_t (10% EA) 3.6 min; IR (neat) 3519, 2964, 2919, 2871 cm^{-1}; MS, *m/z* (relative intensity) 314 (0.7, M^+), 299 (1), 296 (0.3), 281 (2), 160 (100), 159 (41), 145 (63), 118 (12), 95 (11), 85 (47); ^1H NMR (CCl_4) δ 0.82 (9 H, s), 1.10–2.10 (12 H, m), 1.85 (3 H, d, J = 6 Hz, CH_3), 2.43–2.97 (4 H, m), 5.52 (1 H, d, J =15 Hz), 5.92 (1 H, dq, J = 15, 6 Hz). Anal. Calcd for $C_{17}H_{30}OS_2$: C, 64.91; H, 9.61. Found: C, 64.94; H, 9.60. **α-6n-OH_{eq}**: R_t (10% EA) 4.0 min; IR (neat) 3532, 2961, 2915, 2868 cm^{-1}; MS, *m/z* (relative intensity) 314 (3, M^+), 299 (0.5), 296 (1), 281 (1), 160 (100), 159 (23), 145 (31), 118 (9), 95 (9), 85 (23); ^1H NMR (CCl_4) δ 0.82 (9 H, s), 1.15–2.20 (12 H, m), 1.85 (3 H, d, J = 6 Hz, CH_3), 2.40–2.97 (4 H, m), 5.52 (1 H, d, J = 15 Hz), 5.92 (1 H, dq, J = 15, 6 Hz). **γ-*anti*-7n-OH_{ax}**: R_t R_t (10% EA) 4.6 min; IR (neat) 3493, 2958, 2919, 2871 cm^{-1}; MS, *m/z* (relative intensity) 314 (2, M^+), 281 (1), 207 (2), 160 (100), 159 (23), 145 (27), 118 (8), 95 (7), 85 (22); ^1H NMR (CCl_4) δ 0.83 (9 H, s), 0.95 (3 H, d, J = 6.5 Hz), 1.03–1.77 (8 H), 1.90–2.67 (4 H, m), 2.70–2.95 (4 H, m), 5.76 (1 H, d, J = 11 Hz).

Cycloheptanone. **α-6o**: R_t (5% EA) 5.0 min; IR (neat) 3500, 2940, 1580 cm^{-1}; MS, *m/z* (relative intensity) 272 (15, M^+), 254 (12), 159 (100), 113 (69), 95 (77); ^1H NMR ($CDCl_3$) δ 1.35–1.72 (8 H), 1.85 (3 H, dd, J = 6, 1 Hz), 1.75–2.10 (6 H), 2.20 (1 H, s, OH), 2.58–2.95 (4 H), 5.55 (1 H, dq, J = 15, 1 Hz), 5.97 (1 H, dq, J = 15, 6 Hz). Anal. Calcd for $C_{14}H_{24}OS_2$: C, 61.71; H, 8.88. Found: C, 61.84; H, 8.88.

2-Butanone. **α-6p**: R_t (5% EA) 4.4 min; IR (neat) 3500, 2968, 2936, 2919 cm^{-1}; MS, *m/z* (relative intensity) 232 (3, M^+), 214 (9), 203 (3), 160 (92), 159 (100), 145 (64), 118 (31); ^1H NMR (CCl_4) δ 0.92 (3 H, t, J = 7.5 Hz), 1.21 (3 H, s), 1.27–2.15 (5 H, m), 1.89 (3 H, d, J = 7.0 Hz), 2.45–3.00 (4 H, m), 5.53 (1 H, d, J = 16.5 Hz), 5.95 (1 H, dq, J = 16.5, 7.0 Hz). Anal. Calcd for $C_{11}H_{20}OS_2$: C, 56.85; H, 8.67. Found: C, 56.82; H, 8.44. **α-6p** (diastereomeric isomers): R_t (5% EA) 9.0 min; IR (neat) 3469, 2934, 2878, 2828, 1582 cm^{-1}; MS, *m/z* (relative intensity) 232 (3, M^+), 217 (3), 203 (11), 160 (100), 159 (80), 145 (30), 118 (17); ^1H NMR (CCl_4) δ 0.75–1.60 (13 H, m), 1.95–2.30 (2 H, m), 2.60–2.95 (4 H, m), 5.73

(d, J = 10 Hz, CH=C of syn isomer), 5.78 (d, J = 10 Hz, CH=C of anti isomer).

3-Pentanone. **α-6q**: R_t (5% EA) 3.6 min; IR (neat) 3525, 2973, 2934 cm^{-1}; MS, m/z (relative intensity) 246 (33, M^+), 239 (36), 217 (20), 160 (100), 159 (96), 145 (44), 85 (64); ^1H NMR (CCl_4) δ 0.75–1.02 (6 H, m), 1.50–2.25 (6 H, m), 2.40–3.00 (4 H, m), 3.60 (1 H, s, OH), 5.52 (1 H, d, J = 15 Hz), 5.82 (1 H, dq, J = 15, 6 Hz). Anal. Calcd for $C_{12}H_{22}OS_2$: C, 58.49; H, 9.00. Found: C, 58.55; H, 9.03. **γ-7q**: R_t (5% EA) 6.4 min; IR (neat) 3525, 2973, 2934 cm^{-1}; MS, m/z (relative intensity) 246 (33, M^+), 239 (36), 217 (20), 160 (100), 159 (96), 145 (44), 85 (64); ^1H NMR (CCl_4) δ 0.75–1.10 (6 H, m), 0.87 (3 H, d, J = 6.5 Hz), 1.20–1.50 (4 H, m), 1.73 (1 H, m), 1.90–2.30 (2 H), 2.40–2.67 (1 H, m, CH), 2.70–2.95 (4 H, m), 5.82 (1 H, d, J = 10 Hz).

2-Heptanone. **α-6r**: R_t (5% EA) 6.4 min; IR (neat) 3490, 2950, 1580 cm^{-1}; MS, m/z (relative intensity) 274 (4, M^+), 259 (6), 229 (5), 203 (15), 159 (100), 115 (21), 97 (6); ^1H NMR ($CDCl_3$) δ 1.02–1.73 (5 H), 1.30 (3 H, s), 1.15–1.65 (6 H, m), 1.82 (3 H, dd, J = 6, 1 Hz), 1.72–2.01 (2 H), 2.63–2.96 (4 H, m), 5.55 (1 H, dq, J = 15, 1 Hz), 6.00 (1 H, dq, J = 15, 6 Hz). Anal. Calcd for $C_{14}H_{26}OS_2$: C, 61.26; H, 9.55; Found: C, 61.07; H, 9.51. **α-6r** (diastereomeric isomers): IR (neat) 3500, 2990, 2970, 2850, 1680 cm^{-1}; MS, m/z (relative intensity) 274 (8, M^+), 269 (6), 267 (8), 203 (19), 160 (84), 159 (100), 145 (62); ^1H NMR (CCl_4) δ 0.97 (3 H, d, J = 6.5 Hz), 0.80–1.53 (14 H, m), 2.00–2.50 (3 H, m), 2.75–3.00 (5 H, m), 5.83 (d, J = 10 Hz, CH=C of syn isomer), 5.90 (d, J = 10 Hz, CH=C of anti isomer).

Diisopropyl Ketone. **γ-7s**: R_t (4% EA) 6.8 min; IR (neat) 3566, 2971, 2939, 2919, 2885 cm^{-1}; MS, m/z (relative intensity) 274 (36, M^+), 231 (39), 167 (35), 160 (100), 159 (82), 106 (64); ^1H NMR (CCl_4) δ 0.95 (15 H, m), 1.75–2.30 (4 H, m), 2.70–2.90 (4 H, m), 2.95–3.20 (1 H, m), 3.57 (1 H, s, OH), 5.86 (1 H, d, J = 10.5 Hz).

Ethyl Pyruvate. **γ-*anti*-7t**: R_t (10% EA) 6.2 min; IR (neat) 3532, 2986, 2939, 2919, 2885, 1725 (C=O) cm^{-1}; MS, m/z (relative intensity) 276 (0.6, M^+), 203 (6), 161 (10), 159 (100), 145 (3); ^1H NMR (CCl_4) δ 0.98 (3 H, d, J = 6.5 Hz), 1.28 (3 H, s), 1.27 (3 H, t, J = 7 Hz), 2.00–2.30 (2 H, m), 2.70–2.90 (5 H, m), 3.02 (1 H, s, OH), 4.14 (2 H, q, J = 7 Hz), 5.75 (1 H, d, J = 10.5 Hz). **γ-*syn*-8t**: R_t (10% EA) 5.8 min; mp 71–72 °C; IR (neat) 3532, 2986, 2939, 2919, 2885, 1725 cm^{-1}; MS, m/z (relative intensity) 276 (0.5, M^+), 203 (6), 161 (11), 160 (10), 159 (100), 145 (2); ^1H NMR (CCl_4) δ 0.87 (3 H, d, J = 6.5 Hz), 1.24 (3 H, s), 1.31 (3 H, t, J = 7 Hz), 2.00–2.30 (2 H, m), 2.60–2.90 (5 H, m), 2.95 (1 H, s, OH), 4.20 (2 H, q, J = 7 Hz), 5.81 (1 H, s, J = 10.5 Hz). Anal. Calcd for $C_{12}H_{20}O_3S_2$: C, 52.14; H, 7.29. Found: C, 52.03; H, 7.25.

Acetophenone. **γ-*anti*-7u**: R_t (5% EA) 6.4 min; IR (neat) 3493, 3081, 3034, 2977, 2936, 2915, 2881, 1668 cm^{-1}; MS, m/z (relative intensity) 280 (2, M^+), 174 (4), 161 (21), 160 (61), 159 (100), 145 (6), 132 (6), 121 (14), 106 (12), 85 (26); ^1H NMR (CCl_4) δ 0.89 (3 H, d, J = 7 Hz), 1.46 (3 H, s), 1.74 (1 H, s, OH), 1.82–2.20 (2 H, m), 2.40–2.80 (4 H, m), 2.82–3.20 (1 H, m), 5.67 (1 H, d, J = 11 Hz), 7.00–7.45 (5 H, m). Anal. Calcd for $C_{15}H_{20}OS_2$: C, 64.24; H, 7.19. Found: C, 64.43; H, 7.17. **γ-*syn*-8u**: R_t (5% EA) 5.6 min; IR (neat) 3501, 3060, 3030, 2977, 2936, 2915, 2881, 1668 cm^{-1}; MS, m/z (relative intensity) 280 (1, M^+), 263 (0.7), 229 (2), 174 (3), 161 (28), 160 (78), 159 (100), 145 (8), 121 (20); ^1H NMR (CCl_4) δ 0.73 (3 H, d, J = 7 Hz), 1.44 (3 H, s), 2.00–2.30 (2 H, m), 2.50 (1 H, s, OH), 2.70–3.25 (5 H, m), 5.90 (1 H, d, J = 10.5 Hz), 7.00–7.50 (5 H, m).

Benzophenone. **γ-7v**: R_t (15% EA) 3.5 min; IR (neat) 3490, 3020, 2930, 1580 cm^{-1}; MS, m/z (relative intensity) 342 (0.05, M^+), 324 (0.2), 183 (14), 159 (100), 85 (18), 77 (16); ^1H NMR ($CDCl_3$) δ 0.92 (3 H, d, J = 6 Hz), 1.95–2.28 (3 H, m), 2.60–2.83 (4 H, m), 6.05 (1 H, d, J = 9 Hz), 7.15–7.35 (6 H), 7.43–7.60 (4 H). Anal. Calcd for $C_{20}H_{22}OS_2$: C, 70.13; H, 6.47. Found: C, 70.02; H, 6.40.

2-Cyclopentenone. **α-6w**: R_t (5% EA) 8.4 min; IR (neat) 3485, 2946, 2919, 2853, 1610 cm^{-1}; MS, m/z (relative intensity) 242 (6, M^+), 224 (86), 191 (8), 160 (17), 159 (35), 150 (51), 117 (100); ^1H NMR (CCl_4) δ 1.60–2.05 (3 H, m), 1.83 (3 H, d, J = 6 Hz), 2.10–2.55 (4 H, m), 2.60–2.90 (4 H, m), 5.49 (1 H, d, J = 15 Hz), 5.63–6.20 (3 H, m). Anal. Calcd for $C_{12}H_{18}OS_2$: C, 59.46; H, 7.48. Found: C, 59.47; H, 7.49. **γ(1,4)-Adduct (Major Isomer)**: R_t (5% EA) 11.2 min; IR (neat) 2969, 2932, 2910, 2881, 1736 cm^{-1}; MS, m/z (relative intensity) 242 (7, M^+), 224 (100), 209 (29), 189 (17), 177 (32), 161 (15), 160 (60), 159 (100), 150 (27), 149 (29), 135 (20); ^1H NMR (CCl_4) δ 1.01 (3 H, d, J = 6.5 Hz), 1.35–2.70 (10 H, m), 2.75–2.95 (4 H, m), 5.65 (1 H, d, J = 10 Hz). **γ(1,4)-Adduct (Minor Isomer)**: R_t (5% EA) 12.4 min; IR (neat) 2969, 2932, 2910, 2881, 1736 cm^{-1}; MS, m/z (relative intensity) 242 (8, M^+), 224 (98), 209 (32), 189 (21), 177 (27), 161 (16), 160 (27), 159 (100), 150 (39), 149 (36), 136 (30); ^1H NMR (CCl_4) δ 1.01 (3 H, d, J = 6.5 Hz), 1.35–2.70 (10 H, m), 2.77–2.95 (4 H, m), 5.65 (1 H, d, J = 10 Hz).

2-Cyclohexenone. **α-6x**: R_t (8% EA) 6.0 min. IR (neat) 3476, 2937, 2919, 2869, 1642 cm^{-1}. MS, m/z (relative intensity) 256 (6, M^+), 238 (31), 229 (14), 160 (80), 159 (100), 131 (36), 117 (27), 106 (19); ^1H NMR (CCl_4) δ 1.20–2.45 (9 H, m), 1.97 (3 H, d, J = 6 Hz), 2.57–2.95 (4 H, m), 5.50 (1 H, d, J = 15.5 Hz), 5.70–6.10 (3 H, m). Anal. Calcd for $C_{13}H_{20}OS_2$: C, 60.89; H, 7.86. Found: C, 60.80; H, 7.90. **γ(1,2)-*anti*-7x**: R_t (8% EA) 9.0 min; IR (neat) 3480, 2950, 2922, 2880, 1640, 1580 cm^{-1}; MS, m/z (relative intensity) 256 (8, M^+), 238 (16), 191 (6), 160 (22), 159 (100), 130 (8), 106 (37); ^1H NMR (CCl_4) δ 0.97 (3 H, d, J = 7 Hz), 1.20 (1 H, s, OH), 1.35–2.45 (2 H, m), 2.50–2.95 (5 H, m), 5.55–5.73 (2 H, m), 5.79 (1 H, d, J = 10.5 Hz). **γ(1,2)-*syn*-8x**: R_t (8% EA) 10.4 min; IR (neat) 3480, 2950, 2922, 2880, 1640, 1580 cm^{-1}; MS, m/z (relative intensity) 256 (8, M^+), 238 (59), 223 (14), 191 (22), 160 (26), 159 (100), 130 (26), 106 (58); ^1H NMR (CCl_4) δ 0.95 (3 H, d, J = 7Hz), 1.13 (1 H, s, OH), 1.35–2.45 (2 H, m), 2.50–2.95 (5 H, m), 5.45–5.85 (2 H, m), 5.76 (1 H, d, J = 10.5 Hz).

Methyl Vinyl Ketone. **γ-*anti*-7y**: R_t (10% EA) 6.2 min; IR (neat) 3485, 2971, 2936, 2876, 1639 cm^{-1}; MS, m/z (relative intensity) 230 (14, M^+), 212 (4), 197 (3), 160 (13), 159 (100), 106 (72); ^1H NMR (CCl_4) δ 0.92 (3 H, d, J = 6.5 Hz), 1.18 (3 H, s), 1.95 (1 H, s, OH), 2.00–2.30 (2 H, m), 2.50–3.00 (5 H, m), 5.00 (1 H, dd, J = 10, 1 Hz), 5.16 (1 H, dd, J = 18, 1 Hz), 5.69 (1 H, d, J = 10.5 Hz), 5.87 (1 H, dd, J = 18, 10 Hz). Anal. Calcd for $C_{11}H_{18}OS_2$: C, 57.35; H, 7.88. Found: C, 57.25; H, 7.75. **γ-*syn*-8y**: R_t (10% EA) 5.8 min; IR (neat) 3490, 2969, 2934, 2871, 1643 cm^{-1}; MS, m/z (relative intensity) 230 (19, M^+), 215 (2), 172 (9), 160 (13), 159 (98), 106 (100); ^1H NMR (CCl_4) δ 0.92 (3 H, d, J = 6.5 Hz), 1.18 (3 H, s), 1.40 (1 H, s, OH), 1.95–2.30 (2 H, m), 2.53–2.95 (5 H, m), 5.00 (1 H, dd, J = 10, 1 Hz), 5.16 (1 H, dd, J = 18, 1 Hz), 5.75 (1 H, d, J = 10 Hz), 5.84 (1 H, dd, J = 18, 10 Hz).

Mesityl Oxide. **γ-*anti*-7z**: R_t (10% EA) 4.6 min; IR (neat) 3485, 2969, 2927, 2876, 1655 cm^{-1}; MS, m/z (relative intensity) 258 (12, M^+), 183 (3), 159 (3), 151 (30), 138 (13), 123 (80), 110 (63), 109 (68), 106 (100); ^1H NMR (CCl_4) δ 0.93 (3 H, d, J = 6 Hz), 1.19 (3 H, s), 1.43 (1 H, s, OH), 1.67 (3 H, s), 1.82 (3 H, s), 1.93–2.35 (2 H, m), 2.55–3.00 (5 H, m), 5.10 (1 H, s), 5.71 (1 H, d, J = 11 Hz). Anal. Calcd for $C_{13}H_{22}OS_2$: C, 60.42; H, 8.58. Found: C, 60.42; H, 8.61.

General Procedure for Formation of Lactones 9 and 10. γ-Adduct **7** or **8** (1 mmol) was dissolved in 40 mL of MeOH/H_2O (v/v = 8/92), and 3 mmol of $HgCl_2$ was added. The mixture was refluxed for 5 h under a N_2 atmosphere, concentrated in vacuo, and extracted 3 times with ethyl acetate. The combined extracts were washed with brine, dried (Na_2SO_4), concentrated in vacuo, and purified by chromatography to give ~95% yield of the desired lactone.

***trans*-β-Methyl-γ-methyl-γ-lactone 9a**: IR (neat) 2971, 2932, 1778 (C=O) cm^{-1}; MS, m/z (relative intensity) 114 (46, M^+), 99 (100), 87 (98); ^1H NMR ($CDCl_3$) δ 1.10 (3 H, d, J = 6.5 Hz), 1.36 (3 H, d, J = 6.3 Hz), 2.12–2.23 (2 H, m), 2.50–2.70 (1 H, m), 4.10 (1 H, dq, J = 6.5, 6.3 Hz). Anal. Calcd for $C_6H_{10}O_2$: C, 63.14; H, 8.83. Found: C, 63.08; H, 8.80.

***trans*-β-Methyl-γ-ethyl-γ-lactone 9b**: IR (neat) 2970, 2930, 1780 cm^{-1}; MS, m/z (relative intensity) 128 (100, M^+), 99 (84), 71 (35). ^1H NMR ($CDCl_3$) δ 1.03 (3 H, t, J = 7 Hz), 1.12 (3 H, d, J = 6 Hz), 1.35–1.75 (2 H, m), 1.85–2.75 (3 H, m), 3.80 (1 H, m). Anal. Calcd for $C_7H_{12}O_2$: C, 65.60; H, 9.44. Found: C, 65.79; H, 9.50.

***trans*-β-Methyl-γ-propyl-γ-lactone 9c**: IR (neat) 3000, 2800, 1780 cm^{-1}; MS, m/z (relative intensity) 142 (6, M^+), 99 (100), 71 (53); ^1H NMR ($CDCl_3$) δ 0.80–1.03 (3 H, m), 1.13 (3 H, d, J = 6 Hz), 1.30–1.75 (4 H, m), 1.85–2.75 (3 H, m), 3.88 (1 H, m). Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.06; H, 9.88.

***trans*-β-Methyl-γ-isopropyl-γ-lactone 9d**: IR (neat) 2960, 1780 cm^{-1}; MS, m/z (relative intensity) 142 (18, M^+), 99 (50), 71 (100); ^1H NMR ($CDCl_3$) δ 0.95 (3 H, d, J = 6 Hz), 0.97 (3 H, d, J = 6 Hz), 1.25 (3 H, d, J = 6 Hz), 1.67–2.05 (1 H, m), 1.97–2.73

(3 H, m), 3.80 (1 H, t, J = 6 Hz, γ-H). Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.60; H, 9.91.

Trans Quercus Lactone (9e): IR (neat) 2960, 2800, 1780 cm^{-1}; MS, m/z (relative intensity) 156 (3, M$^+$), 99 (100), 71 (34); ^{1}H NMR ($CDCl_3$) δ 0.80–1.03 (3 H, m), 1.10 (3 H, d, J = 6 Hz, β-CH_3), 1.20–1.75 (6 H, m), 1.85–2.70 (3 H, m), 3.87 (1 H, m, γ-H). Anal. Calcd for $C_9H_{16}O_2$: C, 69.19; H, 10.32. Found: C, 69.25; H, 10.28.

Eldanolide (9f): R_t (10% EA) 10.5 min. IR (neat) 2995, 2960, 1780 cm^{-1}; MS, m/z (relative intensity) 168 (19, M$^+$), 153 (7), 125 (8), 109 (11), 99 (100), 71 (64), 43 (50); ^{1}H NMR ($CDCl_3$) δ 1.15 (3 H, d, J = 6 Hz, β-CH_3), 1.69 (6 H, d, J = 7 Hz, vinyl methyls), 2.00–2.78 (5 H, m), 4.08 (1 H, td, J = 7, 6 Hz, γ-H), 5.19 (1 H, t, J = 7 Hz, vinyl H).

***trans*-β-Methyl-γ-(2-phenylethenyl)-γ-lactone 9i**: IR (neat) 3490, 3070, 3020, 2975, 2945, 2890, 1775, 1650, 750, 687 cm^{-1}; MS, m/z (relative intensity) 202 (78, M$^+$), 160 (47), 133 (72), 131 (100), 105 (55); ^{1}H NMR (CCl_4) δ 1.18 (3 H, d, J = 6 Hz), 1.90–2.80 (3 H, m), 4.42 (1 H, dd, J = 6.5, 6.5 Hz), 6.06 (1 H, dd, J = 15, 6.5 Hz), 6.61 (1 H, d, J = 15 Hz), 7.12–7.40 (5 H, m). Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.45; H, 7.00.

***trans*-β-Methyl-γ-phenyl-γ-lactone 9k**: R_t (15% EA) 3.1 min; IR (neat) 3080, 1780, 1600 cm^{-1}; MS, m/z (relative intensity) 176 (54, M$^+$), 107 (100), 105 (81), 77 (25); ^{1}H NMR ($CDCl_3$) δ 1.17 (3 H, d, J = 6 Hz), 2.19–2.63 (3 H, m), 4.95 (1 H, d, J = 9 Hz), 7.34 (5 H, br s). Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 75.12; H, 6.98.

***trans*-β-Methyl-γ-methyl-γ-phenyl-γ-lactone 9u**: IR (neat) 3060, 3029, 2977, 2937, 2880, 1770, 1602, 1445 cm^{-1}; MS, m/z (relative intensity) 190 (16, M$^+$), 175 (49), 121 (100), 105 (80); ^{1}H NMR (CCl_4) δ 1.14 (3 H, d, J = 6 Hz), 1.51 (3 H, s), 1.90–2.90 (3 H, m), 7.10–7.45 (5 H, m). Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 76.05; H, 7.40.

***cis*-β-Methyl-γ-methyl-γ-lactone 10a**: IR (neat) 2970, 2930, 1780 cm^{-1}; MS, m/z (relative intensity) 114 (32, M$^+$), 99 (86), 87 (48), 71 (100); ^{1}H NMR ($CDCl_3$) δ 0.99 (3 H, d, J = 6.8 Hz), 1.26 (3 H, d, J = 6.6 Hz), 2.12–2.23 (2 H, m), 2.50–2.70 (1 H, m), 4.63 (1 H, dq, J = 6.5, 6.3 Hz). Anal. Calcd for $C_6H_{10}O_2$: C, 63.14; H, 8.83. Found: C, 63.21; H, 8.78.

***cis*-β-Methyl-γ-phenyl-γ-lactone 10k**: R_t (15% EA) 3.3 min; IR (neat) 3080, 2970, 1780, 1600 cm^{-1}; MS, m/z (relative intensity) 176 (50, M$^+$), 107 (100), 105 (75), 77 (30); ^{1}H NMR ($CDCl_3$) δ 0.66 (3 H, d, J = 6 Hz), 2.70–2.97 (3 H, m), 5.62 (1 H, d, J = 6 Hz), 7.34 (5 H, br s). Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.25; H, 6.45.

***cis*-β-Methyl-γ-methyl-γ-phenyl-γ-lactone 10u**: IR (neat) 3070, 3020, 1770, 1600 cm^{-1}; MS, m/z (relative intensity) 190 (7, M$^+$), 175 (32), 121 (100); ^{1}H NMR (CCl_4) δ 0.67 (3 H, d, J = 6 Hz), 1.68 (3 H, s), 1.90–2.90 (3 H, m), 7.10–7.45 (5 H, m). Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.92; H, 7.50.

Trans spiro dithiane 11h: R_t (15% EA) 4.2 min. IR (neat) 2985, 2910, 2890, 2834, 1666, 1442, 1416 cm^{-1}; MS, m/z (relative intensity) 230 (5, M$^+$), 161 (46), 160 (51), 159 (92), 106 (26), 85 (100); ^{1}H NMR (CCl_4) δ 0.97 (3 H, d, J = 6 Hz), 1.75 (3 H, d, J = 5.5 Hz), 1.90–2.22 (3 H, m), 2.23–2.80 (4 H, m), 3.20–3.60 (2 H, m), 3.88 (1 H, dd, J = 7.5, 6 Hz), 5.20–5.90 (2 H, m). Anal. Calcd for $C_{11}H_{18}OS_2$: C, 57.35; H, 7.88. Found: C, 57.44; H, 7.80.

Trans spiro dithiane 11i: R_t (15% EA) 4.8 min; IR (neat) 3070, 3020, 2975, 2945, 2890, 1650, 750, 685 cm^{-1}; MS, m/z (relative intensity) 292 (8, M$^+$), 202 (38), 160 (20), 144 (100), 129 (43), 106 (95); ^{1}H NMR (CCl_4) δ 1.03 (3 H, d, J = 6 Hz), 1.55–2.80 (7 H, m), 3.15–3.68 (2 H, m), 4.10 (1 H, dd, J = 8.5, 8.3 Hz), 6.13 (1 H, dd, J = 15, 6.5 Hz), 6.56 (1 H, d, J = 15 Hz), 7.07–7.48 (5 H, m). Anal. Calcd for $C_{16}H_{20}OS_2$: C, 65.71; H, 6.89. Found: C, 65.55; H, 6.90.

Trans spiro dithiane 11k: R_t (15% EA) 7.7 min; IR (neat) 3070, 3020, 2975, 2890, 750, 685 cm^{-1}; MS, m/z (relative intensity) 266 (18, M$^+$), 192 (2), 160 (14), 118 (23), 106 (100); ^{1}H NMR (CCl_4) δ 1.00 (3 H, d, J = 6 Hz), 1.80–2.23 (2 H, m), 2.40–2.94 (4 H, m), 3.20–3.69 (2 H, m), 4.57 (1 H, d, J = 9 Hz), 7.31 (5 H, br s). Anal. Calcd for $C_{14}H_{18}OS_2$: C, 63.12; H, 6.81. Found: C, 63.31; H, 6.78.

Cis spiro dithiane 12i: R_t (15% EA) 4.4 min; IR (neat) 3070, 3020, 1650 cm^{-1}; MS, m/z (relative intensity) 292 (6, M$^+$), 202 (30), 144 (100), 129 (62); ^{1}H NMR (CCl_4) δ 0.97 (3 H, d, J = 6.5 Hz), 1.55–2.80 (7 H, m), 3.15–3.68 (2 H, m), 4.68 (1 H, dd, J = 8.5, 6.5 Hz), 6.10 (1 H, dd, J = 15, 6.5 Hz), 6.53 (1 H, d, J = 15 Hz), 7.07–7.48 (5 H, m). Anal. Calcd for $C_{16}H_{20}OS_2$: C, 65.71; H, 6.89. Found: C, 65.75; H, 6.87.

Cis spiro dithiane 12k: R_t (15% EA) 7.1 min; IR (neat) 3080, 3040, 2970, 2880, 760, 690 cm^{-1}; MS, m/z (relative intensity) 266 (12, M$^+$), 160 (24), 118 (22), 106 (100); ^{1}H NMR (CCl_4) δ 0.66 (3 H, d, J = 7 Hz), 1.80–2.23 (2 H, m), 2.34–2.94 (4 H, m), 3.23–3.80 (2 H, m), 5.24 (1 H, d, J = 6 Hz), 7.14 (5 H, br s). Anal. Calcd for $C_{14}H_{18}OS_2$: C, 63.12; H, 6.81. Found: C, 63.31; H, 6.78.

General Procedure for Alkoxy-Cope Rearrangement. The γ(1,2)-adduct (**7g**, **7h**, **8g**, or **8h**), obtained from the reaction of enal and crotyllithium **1**, was treated with KH (10 equiv) in THF for 16 h at 0° to 25 °C. The reaction was quenched with saturated NH_4Cl. The mixture was extracted with ethyl acetate and purified by chromatography to afford α(1,4)-adduct (**13** or **14**) in ~72% yield.

Aldehyde 13: R_t (10% EA) 5.3 min; IR (neat) 2920, 2852, 2817, 2715, 1678 cm^{-1}; MS, m/z (relative intensity) 216 (74, M$^+$), 201 (4), 187 (4), 172 (11), 159 (50), 142 (23), 132 (20), 113 (23), 100 (100), 85 (77); ^{1}H NMR (CCl_4) δ 1.78 (3 H, d, J = 6 Hz), 1.64–3.20 (10 Hz), 5.33 (1 H, d, J = 15 Hz), 5.85 (1 H, dq, J = 15, 6 Hz), 9.72 (1 H, br s, CHO). Anal. Calcd for $C_{10}H_{16}OS_2$: C, 55.51; H, 7.45. Found: C, 55.64; H, 7.43.

Aldehyde 14: R_t (10% EA) 4.2 min; IR (neat) 2920, 2852, 2817, 2713, 1713, 1678 cm^{-1}; MS, m/z (relative intensity) 230 (45, M$^+$), 159 (100), 114 (59), 85 (41); ^{1}H NMR (CCl_4) δ 1.03 (3 H, d, J = 6.5 Hz), 1.82 (3 H, d, J = 6 Hz), 1.68–3.20 (9 H, m), 5.32 (1 H, d, J = 15.6 Hz), 5.88 (1 H, dq, J = 15.6, 6 Hz), 9.68 (1 H, br s, CHO). Anal. Calcd for $C_{11}H_{18}OS_2$: C, 57.35; H, 7.87. Found: C, 57.24; H, 7.84.

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