Resolution of Homoallylic Alcohols Containing Dithioketene Acetal Functionalities. Synthesis of Optically Active γ-Lactones by a Combination of Chemical and Enzymatic Methods

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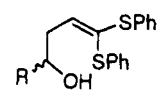
Racemic homoallylic alcohols **1–3** containing dithioketeneacetal functionalities were prepared by addition of aldehydes to the allylic anions of ketene dithioacetals or 2-alkenyl-1,3-dithiane in a regio- and stereoselective manner. Lipase-catalyzed hydrolyses of the corresponding acetates **7–9** afforded optically active alcohols **1–3**, which were treated with mercuric chloride to give γ-lactones such as natural hop lactone, whiskey lactone, and cognac lactone.

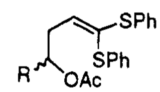
Introduction

Many natural products contain γ-lactone moieties. For example, γ-propenyl-γ-lactone is found in hop,[1] β-methyl-γ-butyl-γ-lactones (quercus lactones) are gradients of aged whiskey,[2] β-methyl-γ-pentyl-γ-lactones are natural flavor components of cognac,[3] and β-methyl-γ-(3-methyl-2-butenyl)-γ-lactone (eldanolide) is a pheromone of the African sugarcane borer.[4] We have synthesized such γ-lactones by hydrolyses of the homoallylic alcohols obtained by condensation of aldehydes with the allylic anions generated from ketene dithioacetals or 2-propenyl-1,3-dithiane (**4–6**).[5] Advantageously, the reaction is γ-regioselective and the relative stereochemistry of the β- and γ-substituents in **3** is controlled. Racemic **1–3** can be kinetically resolved using lipase-catalyzed reactions, and the optically active homoallylic alcohols containing dithioketene acetal functionalities can be converted to γ-lactones such as natural hop lactone, whiskey lactone, and cognac lactone.



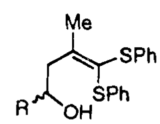
1a-s

1a R = Me
1b R = Et
1c R = *n*-Pr
1d R = *i*-Pr
1e R = C_6H_5
1f R = *o*-MeC_6H_4
1g R = *m*-MeC_6H_4
1h R = *p*-MeC_6H_4
1i R = *p*-(*i*-Pr)C_6H_4
1j R = *o*-$MeOC_6H_4$
1k R = *m*-$MeOC_6H_4$
1l R = *m*-$CF_3C_6H_4$
1m R = *p*-$CF_3C_6H_4$
1n R = *m*-FC_6H_4
1o R = *p*-FC_6H_4
1p R = *o*-ClC_6H_4
1q R = *m*-ClC_6H_4
1r R = *m*-BrC_6H_4
1s R = CH_2=CMe



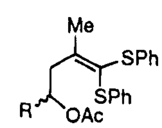
7a-s

7a R = Me
7b R = Et
7c R = *n*-Pr
7d R = *i*-Pr
7e R = C_6H_5
7f R = *o*-MeC_6H_4
7g R = *m*-MeC_6H_4
7h R = *p*-MeC_6H_4
7i R = *p*-(*i*-Pr)C_6H_4
7j R = *o*-$MeOC_6H_4$
7k R = *m*-$MeOC_6H_4$
7l R = *m*-$CF_3C_6H_4$
7m R = *p*-$CF_3C_6H_4$
7n R = *m*-FC_6H_4
7o R = *p*-FC_6H_4
7p R = *o*-ClC_6H_4
7q R = *m*-ClC_6H_4
7r R = *m*-BrC_6H_4
7s R = CH_2=CMe



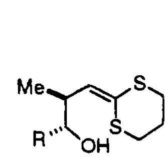
2a-g

2a R = Me
2b R = Et
2c R = *n*-Pr
2d R = *i*-Pr
2e R = C_6H_5
2f R = *n*-Bu
2g R = *n*-C_5H_{11}



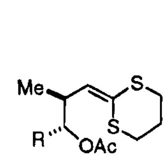
8a-g

8a R = Me
8b R = Et
8c R = *n*-Pr
8d R = *i*-Pr
8e R = C_6H_5
8f R = *n*-Bu
8g R = *n*-C_5H_{11}



3a-d

3a R = Et
3b R = *n*-Bu
3c R = *n*-C_5H_{11}
3d R = *n*-C_6H_{13}



9a-d

9a R = Et
9b R = *n*-Bu
9c R = *n*-C_5H_{11}
9d R = *n*-C_6H_{13}

Results and Discussion

The allylic anion generated from the ketene dithioacetal (**4** or **5**) or the 2-propenyl-1,3-dithiane (**6**) in THF was treated with a variety of aldehydes to give the homoallylic alcohols **1–3**. Compounds **3** had the threo configuration as they were obtained via chairlike six-membered cyclic transition states.[5] A number of lipases, such as lipases AP6, MY, AY-30, OF, AK, PS, M-AP10, CE-10, R-10, GC-4, N, and type 1 as well as porcine pancreas lipase were tested in order to resolve the homoallylic alcohols **1**. Acetylation of some homoallylic alcohols (Table 1) can be conducted in the presence of vinyl acetate by catalysis with lipases MY or AY, though the enantioselectivity was usually low. Acetylations of **1d**, **2d**, and **2e** by catalysis with lipase MY (entries 6,

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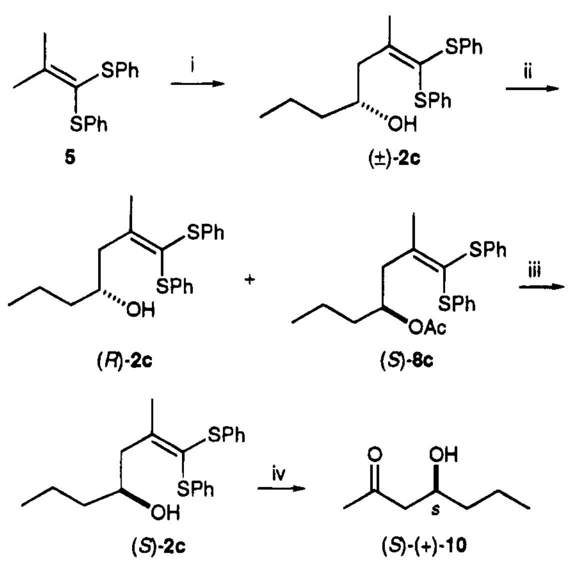
(1) Naya, Y.; Kotake, M. *Inst. Food. Chem., Osaka, Japan* **1968**, *89*, 1113.
(2) (a) Masuda, M.; Nishimura, K. *Phytochemistry* **1971**, *10*, 1401. (b) Masuda, M.; Nishimura, K. *Chem. Lett.* **1981**, 1333. (c) Hoppe, D.; Bronneke, A. *Tetrahedron Lett.* **1983**, *24*, 1687.
(3) (a) Ortuno, R. M.; Merce, R.; Font, J. *Tetrahedron* **1987**, *43*, 4497. (b) Nishimura, K. *Chem. Today* **1987**, *189*, 30. (c) Ebata, T.; Mastsumoto, K; Yoshikoshi, H.; Koseki, K.; Kawakami, H.; Matsushita, H. *Hetercoycles* **1990**, *31*, 1585.
(4) Kunesch, G.; Zagatti, P.; Lallemand, J. Y.; Debal, A.; Vigneron, J. P. *Tetrahedron Lett.* **1981**, *22*, 5271.
(5) (a) Fang, J.-M.; Hong, B.-C. *Synth. Commun.* **1986**, *16*, 523. (b) Fang, J.-M.; Liao, L.-F.; Hong, B.-C. *J. Org. Chem.* **1986**, *51*, 2828. (c) Fang, J.-M.; Hong, B.-C.; Liao, L.-F. *J. Org. Chem.* **1987**, *52*, 855

0022-3263/94/1959-6018$04.50/0

Table 1. Acetylation of Homoallylic Alcohols 1 and 2 with Vinyl Acetate in Hexane by Catalysis with Lipases

entry	alcohol substrate	R =	lipase	reaction time (h)	conversn (%)	acetate product	ee_p (%)	confign of major enantiomer	ee_s (%) of remaining substrate	*E*
1	**1a**	Me	MY	3	80	**7a**	8	*S*	8	1.3
2	**1a**	Me	AY	1	50	**7a**	6	*S*	6	1.2
3	**1b**	Et	MY	13	50	**7b**	4	*S*	4	1.1
4	**1b**	Et	AY	9	50	**7b**	12	*S*	26	1.5
5	**1c**	*n*-Pr	MY	25	50	**7c**	6	*S*	16	1.3
6	**1d**	*i*-Pr	MY	150	20	**7d**	93	*R*	16	32
7	**2a**	Me	MY	12	50	**8a**	40	*S*	40	3.3
8	**2a**	Me	AY	12	50	**8a**	40	*S*	39	3.4
9	**2b**	Et	MY	48	50	**8b**	46	*S*	52	4.4
10	**2b**	Et	AY	48	47	**8b**	69	*S*	69	11
11	**2c**	*n*-Pr	MY	100	25	**8c**	73	*S*	24	8
12	**2c**	*n*-Pr	AY	25	44	**8c**	86	*S*	67	27
13	**2d**	*i*-Pr	MY	150	13	**8d**	96	*R*	22	60
14	**2e**	C_6H_5	MY	240	10	**8e**	98	*R*	15	114

Scheme 1[a]



[a] Key: (i) BuLi, THF, *n*-C_3H_7CHO, −78 °C, 10 min; 85%; (ii) lipase, vinyl acetate (10 equiv), hexane, see Table 1; (iii) aqueous KOH (30%), MeOH, 25 °C, 3 h; 98%; (iv) O_3, CH_2Cl_2, −78 °C; Me_2S, 25 °C.

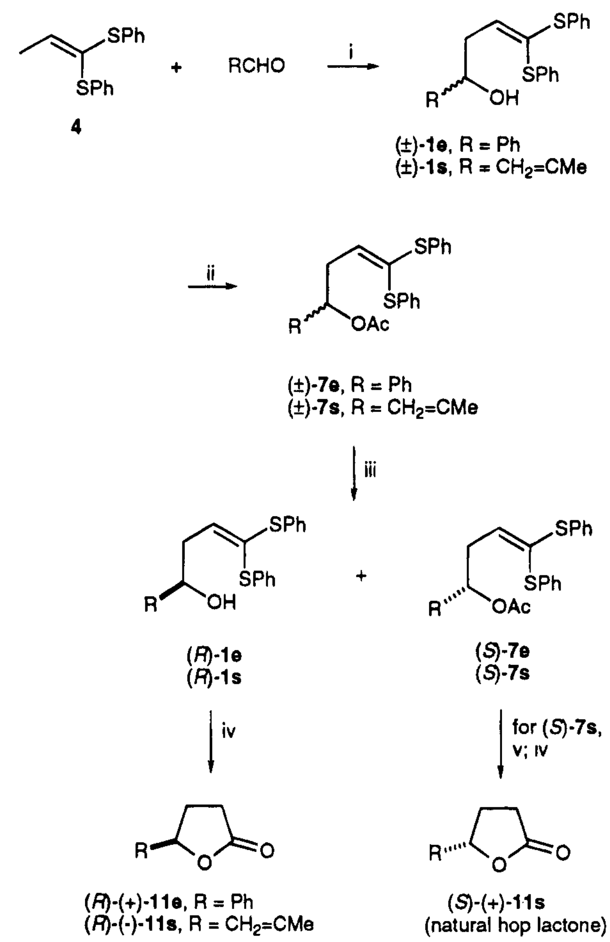
13, and 14, R = *i*-Pr or Ph) were sluggish but gave acetates **7d**, **8d**, and **8e** in high optical purity (≥93% ee).

Reaction mixture components were separated by silica gel chromatography, and the enantiomeric excess of the remaining substrate, ee_s, and the product, ee_p, were determined by HPLC using a Chiracel OD column. The *E* value was calculated according to $E = \ln[1 - c(1 + ee_p)]/\ln[1 - c(1 - ee_p)]$,[6] where conversion, *c*, was deduced from analysis of the reaction mixture by GC, HPLC, or ^{1}H NMR spectroscopy. The acetate **8c** (86% ee), obtained by the lipase-catalyzed reaction (entry 12, Table 1), was saponified and ozonized to give (+)-4-hydroxy-2-heptanone[7] in favor of the (*S*)-configuration (Scheme 1).

Alternatively, lipase-catalyzed hydrolyses of racemic acetates **7** and **8** were carried out in the presence of cosolvents (Tables 2 and 3). The rate of hydrolysis of **7e** (R = Ph) by lipase MY was adequate using either DMF, hexane, or toluene. The hydrolysis in phosphate buffer (pH 7.5) with 10% DMF appeared to be superior, giving alcohol **1e** in higher enantioselectivity (compare entries 3–5, Table 2).

(6) Chen, C.-J.; Fujimoto, Y.; Girdaukas, G.; Sih, C. J. *J. Am. Chem. Soc.* **1982**, *104*, 7294.
(7) Narasaka, K.; Miwa, T.; Hayashi, H.; Ohta, M. *Chem. Lett.* **1984**, 1399.

Scheme 2[a]



[a] Key: (i) BuLi, THF, −78 °C, 10 min; 85%; (ii) Ac_2O, Et_3N, DMAP cat., CH_2Cl_2, 25 °C, 1 h; 98%; (iii) lipase, DMF, phosphate buffer (pH 7.5); see Table 2; (iv) $HgCl_2$, aqueous MeOH (10%), reflux, 5h; 85%; (v) aqueous KOH (30%), MeOH, 25 °C, 3 h; 98%.

Compounds **7f-r** containing either electron-donating or electron-withdrawing groups on the phenyl ring were substrates for the lipase-catalyzed reaction. Lipases MY and AY catalyzed the hydrolyses of acetates **7d-s** in the same stereospecific manner. The major enantiomer of alcohol products **1d-s** in each case has the longer retention time on the Chiracel OD column. As delineated in Scheme 2, lipase-catalyzed hydrolyses gave homoallylic alcohols **1e** (R = Ph) and **1s** (R = CH_2=CMe) in favor of the (*R*)-configuration. Product **1e** (91% ee) was treated with $HgCl_2$ to give the optically active γ-phenyl-γ-lactone **11e**,[8] $[\alpha]_D$ +18° (*c* = 1.1, $CHCl_3$). The (*R*)-enantiomer of

Table 2. Lipase-Catalyzed Hydrolysis of Acetates 7 in Organic Solvent/Phosphate Buffer (pH 7.5) Solution

entry	acetate substrate	R =	lipase	organic solvent	reaction time (h)	conversn (%)	alcohol product	ee_p (%)	confign of major enantiomer	ee_s (%) of remaining substrate	*E*
1	**7d**	*i*-Pr	MY	hexane	240	35	**1d**	95	*R*	50	58
2	**7d**	*i*-Pr	MY	DMF	216	42	**1d**	95	*R*	68	72
3	**7e**	C_6H_5	MY	hexane	120	37	**1e**	79	*R*	45	13
4	**7e**	C_6H_5	MY	toluene	300	50	**1e**	75	*R*	99	34
5	**7e**	C_6H_5	MY	DMF	120	50	**1e**	82	*R*	87	33
6	**7e**	C_6H_5	AY	DMF	168	41	**1e**	91	*R*	64	40
7	**7f**	*o*-MeC_6H_4	MY	DMF	120	20	**1f**	93	*R*	27	35
8	**7g**	*m*-MeC_6H_4	MY	DMF	130	30	**1g**	91	*R*	45	33
9	**7g**	*m*-MeC_6H_4	AY	DMF	210	32	**1g**	87	*R*	47	23
10	**7h**	*p*-MeC_6H_4	MY	DMF	160	44	**1h**	87	*R*	71	30
11	**7i**	*p*-(*i*-Pr)C_6H_4	MY	DMF	288	45	**1i**	94	*R*	70	64
12	**7j**	*o*-$MeOC_6H_4$	MY	DMF	120	35	**1j**	92	*R*	50	39
13	**7k**	*m*-$MeOC_6H_4$	MY	DMF	120	23	**1k**	96	*R*	37	70
14	**7l**	*m*-$CF_3C_6H_4$	MY	DMF	130	40	**1l**	98	*R*	51	164
15	**7l**	*m*-$CF_3C_6H_4$	AY	DMF	120	20	**1l**	97	*R*	19	79
16	**7m**	*p*-$CF_3C_6H_4$	MY	DMF	144	28	**1m**	96	*R*	28	70
17	**7n**	*m*-FC_6H_4	MY	DMF	120	38	**1n**	94	*R*	56	57
18	**7o**	*p*-FC_6H_4	MY	DMF	120	40	**1o**	96	*R*	54	113
19	**7p**	*o*-ClC_6H_4	MY	DMF	130	33	**1p**	98	*R*	47	125
20	**7q**	*m*-ClC_6H_4	MY	DMF	120	48	**1q**	97	*R*	84	190
21	**7q**	*m*-ClC_6H_4	AY	DMF	120	42	**1q**	89	*R*	66	34
22	**7r**	*m*-BrC_6H_4	MY	DMF	310	20	**1r**	81	*R*	20	11
23	**7s**	CH_2=CMe	MY	DMF	120	37	**1s**	82	*R*	42	13
24	**7s**	CH_2=CMe	AY	DMF	240	55	**1s**	75	*R*	95	222

Table 3. Lipase-Catalyzed Hydrolysis of Acetates 8 in DMF/Phosphate Buffer (pH 7.5) Solution (1:9)

entry	acetate substrate	R =	lipase	reaction time (h)	conversn (%)	alcohol product	ee_p (%)	confign of major enantiomer	ee_s (%) of remaining substrate	*E*
1	**8a**	Me	MY	24	50	**2a**	23	*S*	21	2
2	**8a**	Me	AY	24	70	**2a**	20	*S*	37	4.4
3	**8b**	Et	MY	120	43	**2b**	56	*S*	31	4
4	**8b**	Et	AY	120	48	**2b**	57	*S*	54	6
5	**8c**	*n*-Pr	MY	120	45	**2c**	61	*S*	40	6
6	**8c**	*n*-Pr	AY	120	40	**2c**	65	*S*	36	7
7	**8d**	*i*-Pr	MY	450	30	**2d**	77	*R*	36	11
8	**8d**	*i*-Pr	AY	360	35	**2d**	91	*R*	55	37
9	**8e**	C_6H_5	MY	144	47	**2e**	66	*R*	53	8
10	**8e**	C_6H_5	AY	48	25	**2e**	74	*R*	24	8
11	**8f**	*n*-Bu	MY	137	45	**2f**	72	*S*	48	10
12	**8f**	*n*-Bu	AY	137	45	**2f**	82	*S*	67	20
13	**8g**	*n*-C_5H_{11}	MY	220	15	**2g**	97	*S*	21	120
14	**8g**	*n*-C_5H_{11}	AY	216	15	**2g**	99	*S*	12	220

Table 4. Lipase-Catalyzed Hydrolysis of Acetates 9 in DMF/Phosphate Buffer (pH 7.5) Solution (1:9)

entry	acetate substrate	R =	lipase	reaction time (h)	conversn (%)	alcohol product	ee_p (%)	confign of major enantiomer	ee_s (%) of remaining substrate	*E*
1	**9a**	Et	MY	48	40	**3a**	88	2*S*,3*R*	55	27
2	**9a**	Et	AY	48	38	**3a**	91	2*S*,3*R*	52	35
3	**9b**	*n*-Bu	MY	70	30	**3b**	91	2*S*,3*R*	44	33
4	**9b**	*n*-Bu	AY	70	25	**3b**	98	2*S*,3*R*	35	139
5	**9b**	*n*-Bu	AY	480	53	**3b**	85	2*S*,3*R*	95	48
6	**9c**	*n*-C_5H_{11}	MY	144	40	**3c**	85	2*S*,3*R*	58	22
7	**9c**	*n*-C_5H_{11}	AY	51	37	**3c**	93	2*S*,3*R*	65	52
8	**9c**	*n*-C_5H_{11}	AY	240	24	**3c**	96	2*S*,3*R*	30	66
10	**9d**	*n*-C_6H_{13}	MY	216	40	**3d**	81	2*S*,3*R*	58	17
10	**9d**	*n*-C_6H_{13}	AY	216	30	**3d**	94	2*S*,3*R*	37	46

alcohol **1s** (95% ee) was similarly converted to (−)-hop lactone **11s**. The natural hop lactone is dextrorotatory[1] and by these data has the (*S*)-configuration.

The combined chemical and enzymatic method was used in an expedient synthesis of a whisky lactone **12b** and a cognac lactone **12c** containing trans *β*- and *γ*-substituents (Scheme 3). The racemic alcohol **3b** (R = *n*-C_4H_9) obtained by condensation of 2-propenyl-1,3-dithiane and pentanal was converted to the corresponding acetate **9b** (Ac_2O, Et_3N). Racemic **9b** was subjected to lipase-catalyzed hydrolysis to give the optically active alcohol **3b** having the (2*S*,3*R*)-configuration (Table 4). Subsequent treatment with $HgCl_2$ afforded the natural trans quercus lactone **12b**.[2] By a similar procedure, the optically active alcohol **3c** (R = *n*-C_5H_{11}) was obtained and subsequently transformed into the natural cognac lactone **12c**.[3] The remaining acetates (2*R*,3*S*)-**9b,c** were saponified and treated with $HgCl_2$ to give unnatural antipodes of whiskey lactone and cognac lactone.

In summary, we have demonstrated the synthesis of varied optically active alcohols **1**−**3** via lipase-catalyzed

(8) Manzocchi, A.; Rosangela, C.; Fiecchi, A.; Santaniello, E. *J. Chem. Soc., Perkin Trans. 1* **1987**, 2753.

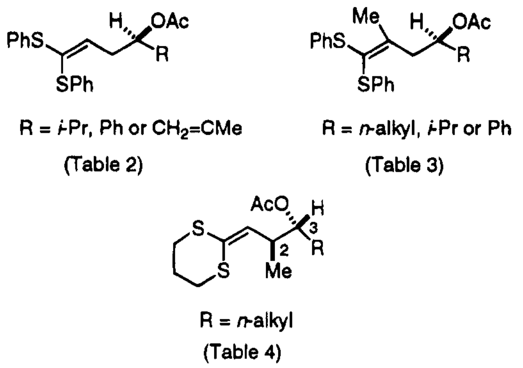
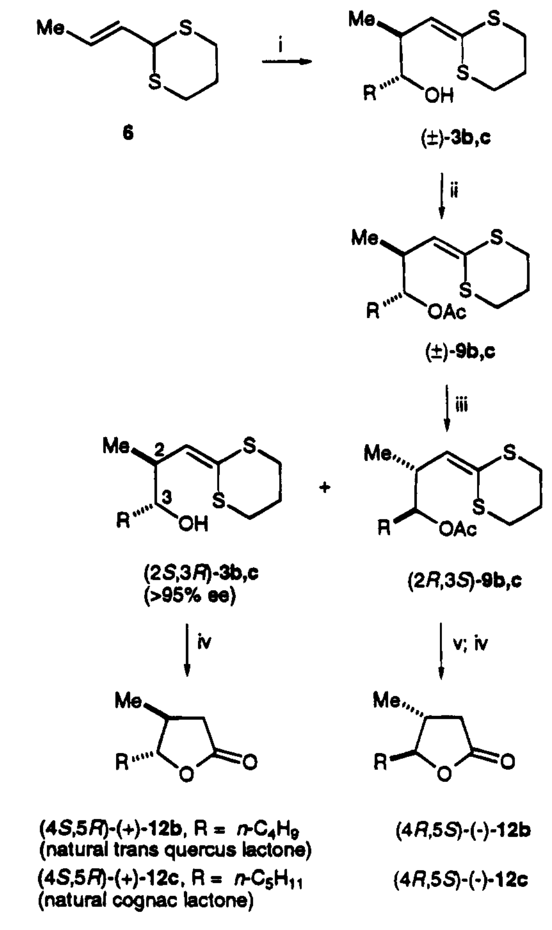


Figure 1. Preferable enantiomers for lipase-catalyzed hydrolyses.

Scheme 3[a]



[a] Key: (i) BuLi, THF, n-C_4H_9CHO or n-$C_5H_{11}CHO$, −78 °C, 10 min; 85%; (ii) Ac_2O, Et_3N, cat. DMAP, CH_2Cl_2, 25 °C, 1 h; 98%; (iii) lipase, DMF, phosphate buffer (pH 7.5), see Table 4; (iv) $HgCl_2$, aqueous MeOH (10%), reflux, 5 h; 92%.

hydrolyses of racemic acetates **7**−**9**. Alcohols **1s**, **3b**, and **3c** are precursors of natural γ-lactones. The enantiomeric preference for lipase-catalyzed hydrolyses of **7**−**9** are shown in Figure 1. (*R*)-Enantiomers of **7d** (R = *i*-Pr), **7e-r** (R = XC_6H_4), and **7s** (R = CH_2=CMe) were selectively hydrolyzed with 75−98% ee (Table 2). The result indicates a model for the enzymatic hydrolysis. The molecule orients with the bis(phenylthio) group on the left-hand side and the R group on the right-hand side, while the reacting acetoxy group positions on the front face. A similar orientation of substrates **8**, regardless of the nature of R groups (*n*-alkyl, *i*-Pr, or Ph) also accounts for the observed enantioselective hydrolyses (Table 3). Lipase-catalyzed acetylations of alcohols **1** and **2** (Table 1) follow the same trend, i.e., preference for formation of (*R*)-enantiomers of acetates **7a**, **8d**, and **8e** (R = *i*-Pr or Ph) and (*S*)-enantiomers of **7a-c** and **8a-c** (R = *n*-alkyl). Lipase-catalyzed hydrolysis of **9**, however, appears to favor the (2*S*,3*R*)-enantiomer having the molecule oriented as shown in Figure 1. From the literature,[9] alcohols containing sulfanyl or sulfonyl groups have been resolved by enzymatic methods. Several models[10] have been proposed to interpret enantioselectivity in lipase-catalyzed reactions, though no single model can fit all the experimental results.

Experimental Section

The ^{1}H NMR spectra were recorded at 200 or 300 MHz using tetramethylsilane as internal standard. ^{13}C NMR spectra were recorded at 50 or 75 MHz. The mass spectra were recorded at an ionizing voltage of 70 or 20 eV. HPLC was carried out on a chromatograph using a μ-Porasil column (7 μm, 25 cm × 0.78 cm) with a 5 mL/min flow rate of elution. Enantiomeric excess of the remaining substrate, ee_s, and the product, ee_p, were determined by HPLC using a Chiracel OD column (0.46 cm i.d. × 25 cm) with 1 mL/min flow rate of elution. The E value was calculated according to $E = \ln[1 - c(1 + ee_p)]/\ln[1 - c(1 - ee_p)]$,[6] where c is conversion.

Lipase AP6 (*Aspergillus niger*), lipase PS (*Pseudomonas* sp.), lipase N (*Rhizopus niveus*), lipase F-AP15 (*Rhizopus oryzae*), lipase AY-30 (*Candida cylindracea*), lipase CE-10 (*Humicola* sp.), lipase GC-4 (*Geotrichum candidum*), lipase R-10 (*Penicillium roqueforti*), lipase AK (*Pseudomonas* sp.), and lipase M-AP10 (*Mucor meihei*), were purchased from Amano Pharm. ipase OF (*C. cylindracea*) and lipase MY (*C. cylindracea*) were from Meito-Sangyo Co., Ltd, Japan. Porcine pancreas lipase (PPL) and lipase type 1 (wheat) were from Sigma, USA. These crude enzymes were used for enzymatic reactions without further purification.

General Procedure for Synthesis of Racemic Homoallylic Alcohols 1−3 and Their Acetates 7−9. Under an atmosphere of nitrogen, butyllithium (4.3 mL of 1.6 M solution in hexane) was added drop by drop to a cold (−20 °C) THF (10 mL) solution of dithioketene acetal or dithiane (5 mmol, **4**, **5**, or **6**). The mixture was stirred for 30 min and cooled to −78 °C, and a THF (2 mL) solution of the appropriate aldehyde (6 mmol) was added drop by drop. The mixture was stirred for 10 min and quenched by addition of a solution of acetic acid (0.9 mL, 15 mmol) in THF (2 mL). The mixture was washed with saturated $NaHCO_3$ and extracted three times with EtOAc. The combined EtOAc extracts were washed with brine, dried (Na_2SO_4), and concentrated under reduced pressure. The residue was chromatographed on a silica gel column by elution with gradients of EtOAc in hexane (10−20%) to give homoallylic alcohols **1**−**3** in 85−95% yields.

Triethylamine (10 mmol) and acetic anhydride (16 mmol) were added to a cold (0 °C) solution of the homoallylic alcohol

(9) (a) Fuganti, C.; Grasselli, P.; Servi, S.; Lazzarine, A.; Casati, P. *Tetrahedron* **1988**, *44*, 2575. (b) Bianchi, D.; Cesti, P.; Golini, P. *Tetrahedron* **1989**, *45*, 869. (c) Gu, R. L.; Sih, C. J. *Tetrahedron Lett.* **1990**, *31*, 3283. (d) Jacobs, H. K.; Mueller, B. H.; Gopalan, A. S. *Tetrahedron* **1992**, *48*, 8891. (e) Goergens, U.; Schneider, M. P. *Tetrahedron Asymmetry* **1992**, *3*, 1149. (f) Oyama, K.; Nishimura, S.; Nonaka, Y.; Kihara, K.; Hashimoto, T. *J. Org. Chem.* **1981**, *46*, 5242. (g) Isowa, Y.; Ohmori, M.; Ichikawa, T.; Mori, K. *Tetrahedron Lett.* **1979**, 2611. (h) Sakina, K.; Kawazura, K.; Morihara, K.; Tajima, H. *Chem. Pharm. Bull.* **1988**, *36*, 4345. (i) Matos, J. R.; West, J. B.; Wong, C.-H. *Biotechnol. Lett.* **1987**, *9*, 233.

(10) (a) Oberhauser, T.; Faber, K.; Griengl, H. *Tetrahedron* **1989**, *45*, 1679. (b) Roberts, S. M. *Phill. Trans. R. Soc. London B* **1989**, *45*, 1679. (c) Xie, Z.-F.; Suemune, H.; Sakai, K. *Tetrahedron Asymmetry* **1990**, *1*, 395. (d) Burgess, K.; Jennings, L. D. *J. Am. Chem. Soc.* **1990**, *112*, 7434. (e) Kazlauskai, R. J.; Weissfoch, A. N. E.; Rappaport, A. T.; Cuccia, L. A. *J. Org. Chem.* **1991**, *56*, 2656 and references cited therein. (f) Burgess, K.; Jennings, L. D. *J. Am. Chem. Soc.* **1991**, *113*, 6129. (g) Kim, M.-J.; Cho, H. *J. Chem. Soc., Chem. Commun.* **1992**, 1411. (h) O'Hagan, D.; Zaid, N. A. *J. Chem. Soc., Perkin Trans. 1* **1992**, 947. (i) Wimmer, Z. *Tetrahedron* **1992**, *48*, 8431. (j) Takano, S.; Yamane, T.; Takahashi, M.; Ogasawara, K. *Tetrahedron Asymmetry* **1992**, *3*, 837.

(4 mmol) and a small amount of 4-(dimethylamino)pyridine (10 mg) in CH_2Cl_2 (10 mL). The mixture was stirred for 1 h, concentrated, diluted with brine, and extracted with EtOAc. The organic phase was dried (Na_2SO_4), concentrated, and purified on a silica gel column by elution with gradients of EtOAc in hexane (3–10%) to give the corresponding acetates **7–9** in 90–98% yields.

General Procedure for Lipase-Catalyzed Acetylation of Homoallylic Alcohols 1 and 2. The alcohol (1 mmol) was stirred (800–1000 rpm) with vinyl acetate (10 mmol) and a lipase (0.3 g) in hexane (5 mL) at room temperature (25–27 °C). An aliquot of the reaction mixture was occasionally taken and filtered, and the filtrate was analyzed by GC, HPLC, or ^{1}H NMR to determine the conversion. After the mixture was stirred for the period indicated in Table 1, 30–55% of the alcohol was converted to the corresponding acetate. The mixture was filtered, and the filtrate was concentrated and chromatographed on a silica gel column by elution with gradients of EtOAc in hexane (3–15%) to give optically active acetate and alcohol. Enantiomeric excess of the remaining alcohol was determined by HPLC using a Chiracel OD column with elution of 2-propanol in hexane (0.5–10%). In order to determine the optical purity of the product, the acetate was converted to the corresponding alcohol by saponification in aqueous KOH (30%, 1 mL)/MeOH (10 mL) at room temperature for 3 h. The optical purity of the alcohol was similarly determined by HPLC, and its value was taken as that of the acetate.

General Procedure for Lipase-Catalyzed Hydrolysis of Racemic Acetates 7–9. The acetate (1 mmol) and a lipase (0.3 g) in a mixed solvent of DMF (0.8 mL) and phosphate buffer (7.2 mL, pH 7.5) were stirred (800–1000 rpm) at room temperature (25–27 °C) for the period indicated in Tables 2–4 to reach 30–55% conversion. The mixture was filtered, and the filtrate was analyzed by GC, HPLC, or ^{1}H NMR to determine the percent conversion to product. The alcohol products **1–3** and the starting materials **7–9** were separated by chromatography, and their values of optical purity were determined by HPLC as described above. In the entries 1, 3, and 4 of Table 2, the ratio of cosolvent hexane (or toluene) to phosphate buffer was 1:3.

The physical and spectral data of **3–6** were previously reported.[5,11]

5,5-Bis(phenylthio)-4-penten-2-ol (1a): oil; TC (15% EtOAc in hexane) R_f = 0.25; IR (neat) 3355 cm^{-1}; MS m/z (rel intensity) 302 (M$^+$, 100), 257 (90); ^{1}H NMR (CDCl$_3$) δ 7.28–7.18 (10 H, m), 6.37 (1 H, t, J = 7.4 Hz), 3.90 (1 H, dq, J = 6.2, 6.0 Hz), 2.60 (2 H, dd, J = 7.2, 7.8 Hz), 1.21 (3 H, d, J = 6.2 Hz); ^{13}C NMR (CDCl$_3$) δ 138.6 (d), 136.0 (s), 135.0 (s), 133.9 (s), 131.6 (d, 2 C), 130.4 (d, 2 C), 128.8 (d, 2 C), 128.7 (d, 2 C), 127.4 (d), 126.8 (d), 67.4 (d), 40.6 (t), 23.2 (q); HRMS calcd for $C_{17}H_{18}OS_2$ (M$^+$) 302.0799, found 302.0801; HPLC (Chiracel OD, 2-propanol/hexane (3:97)) t_R 15.8 min (R-isomer), 18.7 min (S-isomer).

6,6-Bis(phenylthio)-5-hexen-3-ol (1b): oil; ^{13}C NMR (CDCl$_3$) δ 139.3 (d), 134.0 (s, 2 C), 131.6 (d, 2 C), 131.5 (s), 130.4 (d, 2 C), 128.8 (d, 2 C), 128.7 (d, 2 C), 127.4 (d), 126.8 (d), 72.7 (d), 38.6 (t), 30.0 (t), 9.5 (q); HRMS calcd for $C_{18}H_{20}OS_2$ (M$^+$) 316.0955, found 316.0955; HPLC (Chiracel OD, 2-propanol/hexane (3:97)) t_R 18.7 min (R-isomer), 21.9 min (S-isomer).

1,1-Bis(phenylthio)-1-hepten-4-ol (1c): oil; ^{13}C NMR (CDCl$_3$) δ 139.3 (d), 134.0 (s, 2 C), 131.6 (d, 4 C), 130.4 (d), 128.8 (d, 2 C), 128.7 (d), 127.4 (d), 126.8 (d), 71.0 (d), 39.3 (t), 39.1 (t), 18.7 (q); HRMS calcd for $C_{19}H_{22}OS_2$ (M$^+$) 330.1112 Found 330.1118; HPLC (Chiracel OD, 2-propanol/hexane (5:95)) t_R 11.9 min (R-isomer), 14.5 min (S-isomer).

6,6-Bis(phenylthio)-2-methyl-5-hexen-3-ol (1d): oil; ^{13}C NMR (CDCl$_3$) δ 140.1 (d), 134.0 (s), 131.4 (s), 130.9 (s), 130.4 (d, 2C), 128.7 (d, 2 C), 128.6 (d, 2 C), 127.3 (d), 126.7 (d), 76.1 (d), 36.2 (t), 33.5 (d), 18.7 (q), 17.2 (q); HRMS calcd for $C_{19}H_{22}OS_2$ (M$^+$) 330.1112, found 330.1112; HPLC (Chiracel OD, 2-propanol/hexane (10:90)) t_R 8.1 min (S-isomer), 10.7 min (R-isomer).

4,4-Bis(phenylthio)-1-phenyl-3-butenol (1e): oil; ^{13}C NMR (CDCl$_3$) δ 143.4 (s), 138.0 (d), 134.0 (s), 133.8 (s), 131.7 (d, 2 C), 130.4 (d, 2 C), 128.8 (d, 4 C), 128.6 (s), 128.5 (d, 2 C), 127.6 (d), 127.4 (d), 126.8 (d), 125.8 (d, 2 C), 75.6 (d), 40.6 (t); HRMS calcd for $C_{22}H_{20}OS_2$ (M$^+$) 364.0956, found 364.0961; HPLC (Chiracel OD, 2-propanol/hexane (10:90)) t_R 15.9 min (S-isomer), 17.4 min (R-isomer).

4,4-Bis(phenylthio)-1-(*o*-methylphenyl)-3-butenol (1f): oil; ^{13}C NMR (CDCl$_3$) δ 141.5 (s), 138.2 (d), 134.4 (s), 134.1 (s), 134.0 (s), 133.7 (s), 131.8 (d, 2 C), 130.4 (d), 130.3 (d, 2 C), 128.8 (d, 2 C), 128.6 (d, 2 C), 127.4 (d), 127.3 (d), 126.7 (d), 126.3 (d), 125.3 (d), 70.0 (d), 39.3 (t), 19.0 (q); HRMS calcd for $C_{23}H_{22}OS_2$ (M$^+$) 378.1112, found 378.1086; HPLC (Chiracel OD, 2-propanol/hexane (20:80)) t_R 5.9 min (S-isomer), 9.6 min (R-isomer).

4,4-Bis(phenylthio)-1-(*m*-methylphenyl)-3-butenol (1g): oil; ^{13}C NMR (CDCl$_3$) δ 143.4 (s), 138.4 (s), 138.0 (s), 134.0 (s), 133.8 (s), 131.6 (d, 2 C), 130.3 (d, 2 C), 128.7 (d, 2 C), 128.6 (d, 2 C), 128.3 (d, 2 C), 127.3 (d, 2 C), 126.7 (d), 126.4 (d), 122.9 (d), 73.5 (d), 40.5 (t), 21.4 (q), 14.1 (q); HRMS calcd for $C_{23}H_{22}OS_2$ (M$^+$) 378.1112, found 378.1112; HPLC (Chiracel OD, 2-propanol/hexane (10:90)) t_R 9.3 min (S-isomer), 10.5 min (R-isomer).

4,4-Bis(phenylthio)-1-(*p*-methylphenyl)-3-butenol (1h): oil; ^{13}C NMR (CDCl$_3$) δ 140.5 (s), 138.6 (d), 137.2 (d), 135.9 (s), 135.6 (s), 134.0 (s), 133.8 (s), 131.6 (d, 2 C), 131.5 (d, 2 C), 128.9 (d), 128.7 (d, 2 C), 128.5 (d, 2 C), 127.3 (d), 126.7 (d), 125.8 (d, 2 C), 73.4 (d), 40.1 (t), 21.0 (q); HRMS calcd for $C_{23}H_{22}OS_2$ (M$^+$) 378.1112, found 378.1112; HPLC (Chiracel OD, 2-propanol/hexane (10:90)) t_R 14.8 min (S-isomer), 17.6 min (R-isomer).

4,4-Bis(phenylthio)-1-(*p*-(methylethyl)phenyl)-3-butenol (1i): oil; ^{13}C NMR (CDCl$_3$) δ 148.4 (s), 140.9 (d), 138.3 (d), 134.0 (d), 133.8 (d), 131.7 (d, 2 C), 131.7 (s), 130.4 (d, 2 C), 128.7 (d, 2 C), 128.6 (d, 2 C), 127.4 (d), 126.7 (d), 126.5 (d, 2 C), 125.8 (d, 2 C), 73.5 (d), 40.5 (t), 33.8 (d), 24.0 (q, 2 C); HRMS calcd for $C_{25}H_{26}OS_2$ (M$^+$) 406.1425, found 406.1419; HPLC (Chiracel OD, 2-propanol/hexane (20:80)) t_R 10.4 min (S-isomer), 14.0 min (R-isomer).

4,4-Bis(phenylthio)-1-(*o*-methoxyphenyl)-3-butenol (1j): oil; ^{13}C NMR (CDCl$_3$) δ 156.5 (s), 139.8 (d), 134.3 (s), 134.1 (s), 131.5 (d, 2 C), 131.2 (s), 131.0 (s), 130.3 (d, 2 C), 128.7 (d, 2 C), 128.6 (d, 2 C), 128.5 (d), 127.2 (d),127.1 (d), 126.6 (d), 120.8 (d), 110.6 (d), 70.6 (d), 55.3 (q), 39.0 (t); HRMS calcd for $C_{23}H_{22}O_2S_2$ (M$^+$) 394.1061, found 394.1067; HPLC (Chiracel OD, 2-propanol/hexane (5:95)) t_R 14.4 min (S-isomer), 18.4 min (R-isomer).

4,4-Bis(phenylthio)-1-(*m*-methoxyphenyl)-3-butenol (1k): oil; ^{13}C NMR (CDCl$_3$) δ 159.8 (s), 145.2 (s), 138.0 (d), 134.0 (s), 133.8 (s), 132.0 (s), 131.8 (d, 2 C), 130.4 (d, 2 C), 129.5 (d), 128.8 (d, 2 C), 128.7 (d, 2 C), 127.4 (d), 126.8 (d), 118.2 (d), 113.3 (d), 11.3 (d), 73.6 (d), 55.2 (q), 40.5 (t); HRMS calcd for $C_{23}H_{22}O_2S_2$ (M$^+$) 394.1061, found 394.1070; HPLC (Chiracel OD, 2-propanol/hexane (10:90)) t_R 13.7 min (S-isomer), 15.6 min (R-isomer).

4,4-Bis(phenylthio)-1-(*m*-(trifluoromethyl)phenyl)-3-butenol (1l): oil; ^{13}C NMR (CDCl$_3$) δ 144.5 (d), 136.0 (d), 135.7 (s), 133.3 (s), 133.0 (s), 132.1 (d, 2 C), 131.0 (s), 130.3 (d, 2 C), 129.2 (d), 128.9 (d, 3 C), 128.7 (d, 2 C), 127.7 (d), 126.9 (d), 124.3 (d), 122.6 (d), 72.9 (d), 40.5 (t); HRMS calcd for $C_{23}H_{19}F_3OS_2$ (M$^+$) 432.0829, found 432.0838; HPLC (Chiracel OD, 2-propanol/hexane (10:90)) t_R 6.4 min (S-isomer), 10.4 min (R-isomer).

4,4-Bis(phenylthio)-1-(*p*-(trifluoromethyl)phenyl)-3-butenol (1m): oil; ^{13}C NMR (CDCl$_3$) δ 147.4 (s), 135.9 (d), 133.7 (s), 133.4 (s), 133.1 (s), 132.2 (d, 2 C), 130.4 (d, 2 C), 126.9 (d), 126.2 (d), 125.5 (d), 125.1 (d), 125.2 (d), 72.9 (d), 40.5 (t); HRMS calcd for $C_{23}H_{19}F_3OS_2$ (M$^+$) 432.0829, found 432.0834; HPLC (Chiracel OD, 2-propanol/hexane (20:80)) t_R 12.3 min (S-isomer), 15.8 min (R-isomer).

4,4-Bis(phenylthio)-1-(*m*-fluorophenyl)-3-butenol (1n): oil; ^{13}C NMR (CDCl$_3$) δ 164.5 (s), 146.1, 136.6, 136.1, 135.7, 133.9, 133.5, 132.8, 132.1, 130.4, 130.1, 130.0, 128.9, 128.7,

(11) (a) Dziadulewicz, E.; Hodgson, D.; Gallagher, T. *J. Chem. Soc., Perkin Trans. 1* **1988**, 3367. (b) Kolb, M. *Synthesis* **1990**, 171.

128.6, 127.7, 126.9, 121.4, 114.6, 114.3, 112.9, 112.7, 73.0 (d), 40.5 (t); HRMS calcd for $C_{22}H_{19}OS_2F$ (M^+) 382.0861, found 382.0844; HPLC (Chiracel OD, 2-propanol/hexane (20:80)) t_R 7.4 min (*S*-isomer), 11.1 min (*R*-isomer).

4,4-Bis(phenylthio)-1-(*p*-fluorophenyl)-3-butenol (1o): oil; ^{13}C NMR (CDCl$_3$) δ 139.2 (s), 137.2 (d), 133.9 (s), 133.6 (s), 132.4 (s), 131.9 (d, 2 C), 130.4 (d, 2 C), 128.8 (d, 2 C)128.7 (d, 2 C), 127.6 (d), 127.4 (d), 126.8 (d), 115.5 (d), 115.1 (d), 72.9 (d), 40.6 (t); HRMS calcd for $C_{22}H_{19}OS_2F$ (M^+) 382.0861, found 382.0850; HPLC (Chiracel OD, 2-propanol/hexane (10:90)) t_R 9.0 min (*S*-isomer), 12.5 min (*R*-isomer).

4,4-Bis(phenylthio)-1-(*o*-chlorophenyl)-3-butenol (1p): oil; ^{13}C NMR (CDCl$_3$) δ 137.3 (d), 131.9 (d, 4 C), 130.4 (d, 2 C), 129.4 (s, 2 C), 128.8 (d, 2 C), 128.6 (d, 2 C), 127.5 (d, 2 C), 127.3 (s), 127.1 (s), 126.8 (d, 2 C), 69.9 (d), 38.8 (t); HRMS calcd for $C_{22}H_{19}OS_2Cl$ (M^+) 398.0565, found 398.0567; HPLC (Chiracel OD, 2-propanol/hexane (5:95)) t_R 23.6 min (*S*-isomer), 26.1 min (*R*-isomer).

4,4-Bis(phenylthio)-1-(*m*-chlorophenyl)-3-butenol (1q): oil; ^{1}H NMR (CDCl$_3$) δ 7.32−7.05 (14 H, m), 6.18 (1 H, t, J = 7.2 Hz), 4.72 (1 H, t, J = 6.4 Hz), 2.86 (2 H, dd, J = 7.2, 6.4 Hz); HRMS calcd for $C_{22}H_{19}OS_2Cl$ (M^+) 398.0565, found 398.0596; HPLC (Chiracel OD, 2-propanol/hexane (10:90)) t_R 12.9 min (*S*-isomer), 14.9 min (*R*-isomer).

4,4-Bis(phenylthio)-1-(*m*-bromophenyl)-3-butenol (1r): oil; ^{13}C NMR (CDCl$_3$, 50 MHz) δ 145.8 (s), 136.2 (d), 135.7 (s), 133.5 (s), 132.9 (s), 132.1 (d, 2 C), 130.7 (d), 130.4 (d), 130.0 (d), 129.0 (d), 128.9 (d, 2 C), 128.8 (d), 128.7 (d, 2 C), 127.7 (d), 126.9 (d), 126.8 (d), 124.5 (d), 122.5(s), 72.9 (d), 40.4 (t); HRMS calcd for $C_{22}H_{17}O^{81}BrS_2$ (M^+) 441.9900, found 441.9869; HPLC (Chiracel OD, 2-propanol/hexane (5:95)) t_R 8.5 min (*S*-isomer), 13.0 min (*R*-isomer).

6,6-Bis(phenylthio)-2-methyl-1,5-hexadien-3-ol (1s): oil; ^{13}C NMR (CDCl$_3$, 50 MHz) δ 146.6 (s), 138.7 (d), 135.7 (s), 134.0 (s), 131.7 (d, 2 C), 131.5 (s), 130.4 (d, 2 C), 128.8 (d, 2 C), 128.7 (d, 2 C), 127.4 (d), 126.8 (d), 111.4 (d), 74.8 (d), 36.8 (t), 17.9 (q); HRMS calcd for $C_{19}H_{20}OS_2$ (M^+) 328.0956, found 328.0948; HPLC (Chiracel OD, 2-propanol/hexane (20:80)) t_R 8.5 min (*S*-isomer), 13.0 min (*R*-isomer).

5,5-Bis(phenylthio)-4-methyl-4-penten-2-ol (2a): oil; TLC (10% EtOAc in hexane) R_f = 0.2; IR (neat) 3383 cm^{-1}; MS m/z (rel intensity) 316 (M^+, 100), 297 (10), 271 (32), 206 (28), 161 (55), 97 (68); ^{1}H NMR (CDCl$_3$) δ 7.25−7.10 (10 H, m), 4.09 (1 H, m), 2.93 (1 H, dd, J = 13.0 , 8.3 Hz), 2.68 (1 H, dd, J = 13.0, 5.0 Hz), 2.24 (3 H, s), 1.27 (2 H, d, J = 6.2 Hz); ^{13}C NMR (CDCl$_3$) δ 152.4 (s), 135.4 (s, 2 C), 129.5 (s, 2 C), 128.5 (d, 4 C), 126.2 (s), 126.0 (d), 123.8 (s), 67.3 (d), 46.8 (t), 23.8 (q), 22.9 (q); HRMS calcd for $C_{18}H_{20}OS_2$ (M^+) 316.0955, found 316.0963; HPLC (Chiracel OD, 2-propanol/hexane (5:95)) t_R 6.5 min (*S*-isomer), 8.3 min (*R*-isomer).

6,6-Bis(phenylthio)-5-methyl-5-hexen-3-ol (2b): oil; ^{13}C NMR (CDCl$_3$) δ 153.0 (s), 135.0 (s, 2 C), 129.4 (d, 2 C), 129.2 (d, 2 C), 128.6 (d, 4 C), 126.3 (d), 126,1 (d), 123.3 (s), 72.5 (d), 44.9 (t), 30.9 (t), 23.0 (q), 10.0 (q); HRMS calcd for $C_{19}H_{22}OS_2$ (M^+) 330.1112, found 330.1180; HPLC (Chiracel OD, 2-propanol/hexane (5:95)) t_R 9.1 min (*S*-isomer), 11.3 min (*R*-isomer).

1,1-Bis(phenylthio)-2-methyl-1-hepten-4-ol (2c): oil; ^{13}C NMR (CDCl$_3$) δ 153.0 (s), 135.5 (s, 2 C), 129.4 (d, 2 C), 129.1 (d, 2 C), 128.6 (d, 4 C), 126.2 (d), 126.0 (d), 123.7 (s), 70.9 (d), 45.3 (t), 40.2 (t), 23.0 (q), 18.8 (q), 14.0 (q); HRMS calcd for $C_{20}H_{24}OS_2$ (M^+) 344.1268, found 344.1263; HPLC (Chiracel OD, 2-propanol/hexane (10:90)) t_R 6.4 min (*S*-isomer), 9.3 min (*R*-isomer).

6,6-Bis(phenylthio)-2,5-dimethyl-5-hexen-3-ol (2d). Oil; ^{13}C NMR (CDCl$_3$) δ 154.0 (s), 135.5 (s, 2 C), 130.1 (d, 2 C), 129.7 (d, 2 C), 129.3 (d, 4 C), 126.9 (d), 126.7 (d), 123.1 (s), 78.2 (d), 42.9 (t), 35.0 (d), 23.5 (q), 19.4 (q), 17.9 (q); HRMS calcd for $C_{20}H_{24}OS_2$ (M^+) 344.1265, found 344.1263; HPLC (Chiracel OD, 2-propanol/hexane (3:97)) t_R 13.4 min (*R*-isomer), 17.0 min (*S*-isomer).

4,4-Bis(phenylthio)-3-methyl-1-phenyl-3-butenol (2e): oil; ^{13}C NMR (CDCl$_3$) δ 151.8 (s), 143.8 (s), 135.5 (s), 135.4 (s), 129.7 (d, 2 C), 129.1 (d, 2 C), 128.6(d, 6 C), 127.0 (d, 2 C), 126.3-(d), 126.0 (d), 125.9 (d), 123.8 (s), 73.7 (d), 46.8 (t), 23.0 (q); HRMS calcd for $C_{23}H_{22}OS_2$ (M^+) 378.1112, found 378.1086; HPLC (Chiracel OD, 2-propanol/hexane (10:90)) t_R 9.3 min (*R*-isomer), 14.0 min (*S*-isomer).

1,1-Bis(phenylthio)-2-methyl-1-octen-4-ol (2f): oil; ^{13}C NMR (CDCl$_3$) δ 153.1 (s), 135.6 (s), 135.5 (s), 129.5 (d, 2 C), 129.1 (d, 2 C), 128.6 (d, 4 C), 126.2 (d), 126.0 (d), 123.7 (s), 71.1 (d), 45.4 (t), 37.7 (t), 27.8 (t), 23.0 (q), 22.6 (t), 14.0 (q); HRMS calcd for $C_{21}H_{26}OS_2$ (M^+) 358.1425, found 358.1419; HPLC (Chiracel OD, 2-propanol/hexane (10:90)) t_R 5.7 min (*S*-isomer), 7.5 min (*R*-isomer).

1,1-Bis(phenylthio)-2-methyl-1-nonen-4-ol (2g). Oil; ^{13}C NMR (CDCl$_3$) δ 153.0 (s), 135.6 (s, 2 C), 129.4 (d, 2 C), 128.6 (d, 4 C), 126.2 (d), 126.0 (d), 123.6 (s), 71.1 (d), 45.4 (t), 38.0 (t), 31.7 (t), 25.3 (t), 22.9 (t), 22.5 (q), 14.0 (q); HRMS calcd for $C_{22}H_{28}OS_2$ (M^+) 372,1581, found 372.1586; HPLC (Chiracel OD, 2-propanol/hexane (10:90)) t_R 4.7 min (*S*-isomer), 6.4 min (*R*-isomer).

1-(1,3-Dithianylidene)-2-methyl-3-pentanol (3a): HPLC (Chiracel OD, 2-propanol/hexane (1:99)) t_R 18.6 min (2*S*,3*R*-isomer), 20.8 min (2*R*,3*S*-isomer).

1-(1,3-Dithianylidene)-2-methyl-3-heptanol (3b): HPLC (Chiracel OD, 2-propanol/hexane (1:99)) t_R 13.1 min (2*S*,3*R*-isomer), 14.7 min (2*R*,3*S*-isomer).

1-(1,3-Dithianylidene)-2-methyl-3-octanol (3c): HPLC (Chiracel OD, 2-propanol/hexane (1:99)) t_R 12.8 min (2*S*,3*R*-isomer), 14.6 min (2*R*,3*S*-isomer).

1-(1,3-Dithianylidene)-2-methyl-3-nonanol (3d): HPLC (Chiracel OD, 2-propanol/hexane (1:99)) t_R 11.4 min (2*S*,3*R*-isomer), 13.3 min (2*R*,3*S*-isomer).

5,5-Bis(phenylthio)-4-penten-2-yl acetate (7a): oil; TLC (10% EtOAc in hexane) R_f = 0.4; IR (neat) 1731 cm^{-1}; MS m/z (rel intensity) 345 (M^++1, 12), 344 (1), 284 (100), 207 (50); ^{1}H NMR (CDCl$_3$) δ 7.33−7.16 (10 H, m), 6.23 (1 H, t, J = 7.4 Hz), 4.99 (1 H, m), 2.71 (2 H, dd, J = 6.4, 6.4 Hz), 2.01 (3 H, s), 1.24 (3 H, d, J = 6.3 Hz); ^{13}C NMR (CDCl$_3$) δ 170.4 (s), 137.0, 133.9, 133.7, 132.5, 132.0, 130.5 (d, 2 C), 128.9 (d, 2 C), 128.7 (d, 2 C), 127.5 (d), 126.9 (d), 125.8, 69.8 (d), 37.3 (t), 21.2 (q), 19.7 (q); HRMS calcd for $C_{19}H_{20}O_2S_2$ (M^+) 344.0904, found 344.0909.

6,6-Bis(phenylthio)-5-hexen-3-yl acetate (7b): oil; IR (neat) 1724 cm^{-1}; ^{13}C NMR (CDCl$_3$) δ 170.6 (s), 137.2 (d), 133.9 (s), 133.7 (s), 132.2 (s), 131.9 (d, 2 C), 130.5 (d, 2 C), 128.8 (d, 2 C), 128.6 (d, 2 C), 127.6 (d), 126.8 (d), 74.3 (d), 35.2 (t), 26.8 (t), 21.2 (q), 9.6 (q); HRMS calcd for $C_{20}H_{22}O_2S_2$ (M^+) 358.1061, found 358.1034.

1,1-Bis(phenylthio)-1-hepten-4-yl acetate (7c): oil; IR (neat) 1730 cm^{-1}; ^{13}C NMR (CDCl$_3$, 50 MHz) δ 170.6 (s), 137.3 (d), 133.9 (s), 133.1 (s), 132.3 (s), 132.0 (d, 2 C), 130.5 (d, 2 C), 128.8 (d, 2 C), 128.7 (d, 2 C), 127.6 (d), 126.9 (d), 72.9 (d), 36.0 (t), 35.7 d), 21.2 (q), 18.5 (q), 13.9 (q); HRMS calcd for $C_{21}H_{24}O_2S_2$ (M^+) 372.1217, found 372.1225

6,6-Bis(phenylthio)-2-methyl-5-hexen-3-yl acetate (7d): oil; ^{13}C NMR (CDCl$_3$) δ 170.6 (s), 137.7 (d), 134.0 (s, 2 C), 133.8 (s), 132.1 (d, 2 C), 130.5 (d, 2 C), 128.9 (d, 2 C), 128.7 (d, 2 C), 127.6 (d), 126.9 (d), 76.5 (d), 33.2 (t), 31.5 (d), 21.1 (q), 18.7 (q), 17.8 (q); HRMS calcd for $C_{21}H_{24}O_2S_2$ (M^+) 372.1217, found 372.1198

4,4-Bis(phenylthio)-1-phenyl-3-butenyl acetate (7e): oil; IR (neat) 1724 cm^{-1}; ^{13}C NMR (CDCl$_3$) δ 169.8 (s), 139.4 (s), 135.9 (d), 133.7 (s), 133.4 (s), 132.9 (s), 132.0 (d, 2 C), 130.4 (d, 2 C), 128.7 (d, 2 C), 128.6 (d, 2 C), 128.4 (d, 2 C), 128.0 (d, 2 C), 127.5 (d), 126.8 (d), 126.3 (d, 2 C), 74.5 (d), 37.7 (t), 21.0 (q); HRMS calcd for $C_{24}H_{22}O_2S_2$ (M^+) 406.1061, found 406.1069.

4,4-Bis(phenylthio)-1-(*o*-methylphenyl)-3-butenyl acetate (7f): oil; IR (neat) 1727 cm^{-1}; ^{13}C NMR (CDCl$_3$) δ 169.9 (s), 138.0 (s), 135.9 (d), 133.8 (s), 133.8 (s), 133.4 (s), 133.0 (s), 132.2 (d, 2 C), 130.4 (d, 2 C), 128.8 (d, 2 C), 128.7 (d, 2 C), 127.8 (d), 127.7 (d), 126.8 (d), 126.1 (d), 125.8 (d), 71.6 (d), 37.0 (t), 21.1 (q), 19.1 (q); HRMS calcd for $C_{25}H_{24}O_2S_2$ (M^+) 420.1217, found 420.1216.

4,4-Bis(phenylthio)-1-(*m*-methylphenyl)-3-butenyl acetate (7g): oil; IR (neat) 1733 cm^{-1}; ^{13}C NMR (CDCl$_3$) δ 169.7 (s), 139.3 (s), 137.9 (s), 136.2 (d), 133.7 (s), 133.4 (s), 132.6 (s), 131.8 (d, 2 C), 130.3 (d, 2 C), 128.7 (d, 3 C), 128.5 (d, 2 C), 128.2 (d), 127.4 (d), 126.9 (d), 123.3 (d), 74.5 (d), 37.7 (t), 21.3 (q), 21.0 (q); HRMS calcd for $C_{25}H_{24}O_2S_2$ (M^+) 420.1217, found 420.1216.

4,4-Bis(phenylthio)-1-(*p*-methylphenyl)-3-butenyl acetate (7h): oil; IR(neat) 1729 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 170.0 (s), 137.7 (s), 136.5 (s), 136.4 (d), 133.8 (s), 133.5 (s), 132.7 (s), 131.9 (d, 2 C), 130.5 (d, 2 C), 129.1 (d, 2 C), 128.8 (d, 2 C), 128.6 (d, 2 C), 127.5 (d), 126.8 (d), 126.4 (d, 2 C), 74.5 (d), 37.7 (t), 21.1 (q); HRMS calcd for $C_{25}H_{24}O_2S_2$ (M^+) 420.1217, found 420.1216.

4,4-Bis(phenylthio)-1-(*p*-(methylethyl)phenyl)-3-butenyl acetate (7i): oil; IR (neat) 1734 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 170.0 (s), 148.7 (s). 136.9 (s), 136.2 (d), 133.8 (s), 133.5 (s), 132.8 (s), 132.0 (d, 2 C), 130.5 (d, 2 C), 128.8 (d, 2 C), 127.6 (d), 126.9 (d), 126.5 (d, 4 C), 74.6 (d), 37.8 (t), 33.7 (d), 23.9 (q, 2 C), 21.2 (q); HRMS calcd for $C_{27}H_{28}O_2S_2$ (M^+) 448.1530, found 448.1523; HPLC (Chiracel OD, 2-propanol/hexane (20:80)) t_R 4.7 min (*S*-isomer), 5.2 min (*R*-isomer).

4,4-Bis(phenylthio)-1-(*o*-methoxyphenyl)-3-butenyl acetate (7j): oil; IR (neat) 1737 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 169.6 (s), 155.8 (s), 137.6(d), 134.0 (s), 133.7 (s), 131.9 (s), 131.6 (d, 2 C), 130.2 (d, 2 C), 128.6 (d, 3 C), 128.5 (d, 2 C), 127.9 (d), 127.2 (d), 126.6 (d), 126.1 (d), 120.3 (d), 120.3 (d), 110.4 (d), 69.3 (d), 55.2 (q), 36.5 (t), 21.0 (q); HRMS calcd for $C_{25}H_{24}O_3S_2$ (M^+) 436.1167, found 436.1165; HPLC (Chiracel OD, 2-propanol/hexane (5:95)) t_R 5.8 min (*S*-isomer), 7.9 min (*R*-isomer).

4,4-Bis(phenylthio)-1-(*m*-methoxyphenyl)-3-butenyl acetate (7k): oil; IR (neat) 1732 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 169.9 (s), 156.0 (s), 137.8 (d), 134.1 (s), 133.9 (s), 132.0 (s), 131.8 (d, 2 C), 130.4 (d, 2 C), 128.7 (d, 2 C), 128.6 (d, 2 C), 128.1 (s), 127.4 (d), 127.3 (d), 126.7 (d), 126.3 (d), 120.5 (d), 110.5 (d), 69.5(d), 55.4 (q), 36.6 (t), 21.2 (q); HRMS calcd for $C_{25}H_{24}O_3S_2$ (M^+) 436.1167, found 436.1160.

4,4-Bis(phenylthio)-1-(*m*-(trifluoromethyl)phenyl)-3-butenyl acetate (7l): oil; IR (neat) 1730 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 169.8 (s), 141.1 (d), 134.4, 133.8, 132.3, 130.4, 130.0, 129.8, 129.2, 129.1, 128.9, 128.7, 128.5, 128.2, 127.8, 126.9, 126.5, 124.6, 73.9 (d), 37.6 (t), 21.0 (q); HRMS calcd for $C_{24}H_{21}F_3O_2S_2$ (M^+) 474.0935, found 474.0934; HPLC (Chiracel OD, 2-propanol/hexane (10:90)) t_R 3.6 min (*S*-isomer), 3.8 min (*R*-isomer).

4,4-Bis(phenylthio)-1-(*p*-(trifluoromethyl)phenyl)-3-butenyl acetate (7m): oil; IR (neat) 1733 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 169.9 (s), 143.6 (s), 134.1 (d), 134.0 (s), 133.5 (s), 133.1 (s), 132.4 (d, 2 C), 130.5 (d, 2 C), 129.9 (s), 128.9 (d, 2 C), 128.7 (d, 2 C), 127.9 (d), 127.0 (d), 126.7 (d), 125.5 (d, 2 C), 125.4 (d), 74.0 (d), 37.6 (t), 21.0 (q); HRMS calcd for $C_{25}H_{21}O_2S_2F_3$ (M^+) 474.0935, found 474.0934.

4,4-Bis(phenylthio)-1-(*m*-fluorophenyl)-3-butenyl acetate (7n): oil; IR (neat) 1731 cm^{-1}; MS *m/z* (rel intensity) 424 (M^+, 8), 365 (50), 257 (100); ^{1}H NMR ($CDCl_3$) δ 7.30−7.05 (14 H, m), 6.04 (1 H, t, J = 7.4 Hz), 5.79 (1 H, t, J = 6.3 Hz), 2.99 (2 H, dd, J = 7.4, 6.3 Hz), 2.09 (3 H, s); HRMS calcd for $C_{24}H_{21}O_2S_2F$ (M^+) 424.0967, found 424.0972; HPLC (Chiracel OD, 2-propanol/hexane (5:95)) t_R 9.1 min (*S*-isomer), 10.7 min (*R*-isomer).

4,4-Bis(phenylthio)-1-(*p*-fluorophenyl)-3-butenyl acetate (7o): oil; IR (neat) 1731 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 169.9 (s), 164.0, 160.8, 135.4 (s), 135.3 (d), 133.7 (s), 133.4 (s), 132.2 (d, 2 C), 130.5 (d), 130.4 (d, 2 C), 128.8 (d, 2 C), 128.7 (d, 2 C), 128.3 (d), 128.2 (d), 127.5 (d), 126.9 (d), 115.5 (d), 115.2 (d), 74.0 (d), 37.7 (t), 21.1 (q); HRMS calcd for $C_{18}H_{20}OS_2$ (M^+) 424.0967, found 424.0973; HPLC (Chiracel OD, 2-propanol/hexane (3:97)) t_R 8.8 min (*S*-isomer), 10.2 min (*R*-isomer).

4,4-Bis(phenylthio)-1-(*o*-chlorophenyl)-3-butenyl acetate (7p): oil; IR (neat) 1738 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 169.5 (s), 137.4 (s), 135.2 (d), 133.7 (s), 133.4 (s), 133.3 (d), 132.2 (d), 132.0 (s), 130.4 (d, 2 C), 129.5 (d), 128.9 (d), 128.8 (d, 2 C), 128.6 (d, 2 C), 127.6 (d), 127.1 (d), 126.9 (d), 126.8 (d), 71.3 (d), 36.4 (t), 21.0 (q); HRMS calcd for $C_{24}H_{21}O_2S_2Cl$ (M^+) 440.0671, found 440.0663; HPLC (Chiracel OD, 2-propanol/hexane (10:90)) t_R 3.6 min (*S*-isomer), 3.8 min (*R*-isomer).

4,4-Bis(phenylthio)-1-(*m*-chlorophenyl)-3-butenyl acetate (7q): oil; IR (neat) 1736 cm^{-1}; ^{13}C NMR ($CDCl_3$, 50 MHz) δ 169.7 (s), 141.6 (s), 134.4 (d), 134.3 (s), 133.7 (s), 133.6 (s), 133.1 (s), 132.3 (d, 2 C), 130.4 (d,2 C), 129.7 (d), 128.8 (d, 2 C), 128.6 (d, 2 C), 128.1 (d), 127.7 (d), 126.9 (d), 126.4 (d), 124.5 (d), 73.8 (d), 37.5 (d), 20.9 (q); HRMS calcd for $C_{24}H_{21}O_2S_2Cl$ (M^+) 440.0671, found 440.0683; HPLC (Chiracel OD, 2-propanol/hexane (5:95)) t_R 7.1 min (*S*-isomer), 7.7 min (*R*-isomer).

4,4-Bis(phenylthio)-1-(*m*-bromophenyl)-3-butenyl acetate (7r): oil; ^{13}C NMR ($CDCl_3$) δ 169.7 (s), 141.9 (s), 134.3 (d), 133.7 (s), 133.6 (s), 133.1 (s), 132.3 (d), 131.1 (d, 2 C), 130.4 (d, 2 C), 130.0 (d), 129.3 (d), 128.9 (d, 2 C), 128.7 (d, 2 C), 127.8 (d), 126.9 (d), 125.0 (d), 122.5 (s), 73.8 (d), 37.6 (t), 21.0 (q); HRMS calcd for $C_{24}H_{21}O_2{}^{79}BrS_2$ (M^+) 484.0166, found 484.0151; HPLC (Chiracel OD, 2-propanol/hexane (5:95)) t_R 8.1 min (*S*-isomer), 8.9 min (*R*-isomer).

6,6-Bis(phenylthio)-2-methyl-1,5-hexadien-3-yl acetate (7s): oil; IR (neat) 1734 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 169.9 (s), 142.3 (s), 136.6 (d), 133.9 (s), 133.6 (s), 132.4 (s), 132.0 (d, 2 C), 128.8 (d, 2 C), 128.6 (d, 2 C), 127.5 (d), 126.8 (d), 112.9 (t), 75.7 (d), 34.3 (t), 21.0 (q), 18.4 (q); HRMS calcd for $C_{21}H_{22}O_2S_2$ (M^+) 370.1061, found 370.1025.

5,5-Bis(phenylthio)-4-methyl-4-penten-2-yl acetate (8a): oil; TLC (5% EtOAc in hexane) R_f = 0.30; IR (neat) 1730 cm^{-1}; MS *m/z* (rel intensity) 358 (M^+, 25), 298 (65), 221 (100); ^{1}H NMR ($CDCl_3$) δ 7.24−7.05 (10 H, m), 5.23 (1 H, m), 3.08 (1 H, dd, J = 13.2, 8.7 Hz), 2.74 (1 H, dd, J = 13.2, 4.7 Hz), 2.20 (3 H, s), 2.00 (3 H, s), 1.29 (3 H, d, J = 6.2 Hz); ^{13}C NMR ($CDCl_3$) δ 170.3 (s), 150.3 (s), 135.2 (s, 2 C), 129.7 (d, 2 C), 129.6 (d, 2 C), 128.4 (d, 4 C), 126.3 (d), 126.2 (d), 125.2 (s), 69.3 (d), 44.0 (t), 22.5 (q), 21.2 (q), 20.2 (q); HRMS calcd for $C_{20}H_{22}O_2S_2$ (M^+) 358.1061, found 358.1041.

6,6-Bis(phenylthio)-5-methyl-5-hexen-3-yl acetate (8b): oil; IR (neat) 1731 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 170.4 (s), 150.4 (s), 135.3 (s, 2 C), 129.8 (d, 4 C), 128.5 (d, 4 C), 126.3 (d, 2 C), 125.2 (s), 73.7 (d), 41.7 (t), 27.5 (t), 22.6 (q), 21.1 (q), 9.6 (q); HRMS calcd for $C_{21}H_{24}O_2S_2$ (M^+) 372.1217, found 372.1204.

1,1-Bis(phenylthio)-2-methyl-1-hepten-4-yl acetate (8c): oil; IR (neat) 1732 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 170.5 (s), 150.6 (s), 135.4 (s, 2 C), 129.9 (d, 2 C), 129.8 (d, 2 C), 128.5 (d, 4 C), 126.3 (d, 2 C), 125.2 (s), 72.4 (d), 42.2 (d), 36.8 (t), 22.7 (q), 21.2 (q), 18.6 (t), 13.8 (q); HRMS calcd for $C_{22}H_{26}O_2S_2$ (M^+) 386.1374, found 386.1374.

6,6-Bis(phenylthio)-2,5-dimethyl-5-hexen-3-yl acetate (8d): oil; IR (neat) 1726 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 170.3 (s), 150.6 (s), 135.3 (s), 135.2 (s), 129.9 (d, 2 C), 129.7 (d, 2 C), 128.4 (d, 4 C), 126.2 (d), 126.17 (d), 125.0 (s), 76.5 (d), 39.2 (t), 32.2 (d), 22.6 (q), 21.0 (q), 18.3 (q), 17.6 (q); HRMS calcd for $C_{23}H_{24}OS_2$ (M^+) 386.1374, found 386.1376.

4,4-Bis(phenylthio)-3-methyl-1-phenyl-3-butenyl acetate (8e): oil; IR (neat) 1736 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 170.0 (s), 149.5 (s), 139.7 (s), 135.3 (s), 135.2 (s), 130.0 (d, 2 C), 129.5 (d, 2 C), 128.5 (d, 4 C), 128.1 (d), 126.6 (d, 2 C), 126.4 (d), 126.2 (d), 126.0 (s), 74.5 (d), 44.0 (t), 22.6 (q), 21.2 (q); HRMS calcd for $C_{25}H_{24}O_2S_2$ (M^+) 420.1218, found 420.1224.

1,1-Bis(phenylthio)-2-methyl-1-octen-4-yl acetate (8f): oil; IR (neat) 1733 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 170.3 (s), 150.4 (s), 135.3 (s), 135.2 (s), 129.7 (d, 2 C), 129.68 (d, 2 C), 128.4 (d, 4 C), 126.2 (d, 2 C), 125.2 (s), 72.5 (d), 42.0 (t), 34.3 (t), 27.3 (t), 22.5 (q), 22.3 (t), 21.1 (q), 13.8 (q); HRMS calcd for $C_{23}H_{28}O_2S_2$ (M^+) 440.1530, found 400.1536.

1,1-Bis(phenylthio)-2-methyl-1-nonen-4-yl acetate (8g): oil; IR (neat) 1731 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 170.6 (s),150.7 (s), 135.5 (s), 134.4 (s), 129.9 (d, 2 C), 129.8 (d, 2 C), 128.6 (d, 4 C), 126.4 (d, 2 C), 125.6 (s), 72.8 (d), 42.2 (t), 34.7 (t), 31.6 (t), 25.0 (t), 22.7 (q), 22.5 (t), 21.3 (q), 14.0 (q); HRMS calcd for $C_{24}H_{30}O_2S_2$ (M^+) 414.1687, found 414.1677.

1-(1,3-Dithianylidene)-2-methyl-3-pentyl acetate (9a): oil; TLC (5% EtOAc in hexane) R_f = 0.3; IR (neat) 1731 cm^{-1}; MS *m/z* (rel intensity) 261 (M^++1, 18), 260 (1), 200 (30), 159 (100); ^{1}H NMR ($CDCl_3$) δ 5.75 (1 H, d, J = 9.8 Hz), 4.69 (1 H, m), 2.87 (1H, m), 2.84 - 2.74 (4 H, m), 2.13 - 2.04 (2 H, m), 1.98 (3 H, s), 1.47 (2 H, m), 0.91 (3 H, d, J = 4.2 Hz), 0.78 (3 H, t, J = 5.0 Hz); ^{13}C NMR ($CDCl_3$) δ 170.7 (s), 134.5 (d), 127.3 (s), 78.1 (s), 37.3 (t), 30.2 (t), 29.6 (t), 25.2 (t), 25.1 (t), 20.9 (q), 16.7 (q), 9.8 (q); HRMS calcd for $C_{13}H_{22}O_2S_2$ (M^+) 260.0904, found 260.0912.

1-(1,3-Dithianylidene)-2-methyl-3-heptyl acetate (9b): oil; IR (neat) 1730 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 170.8 (s), 134.7 (d), 127.3 (s), 76.8 (d), 37.3 (d), 31.9 (t), 30.3 (t), 29.7 (t), 27.6 (t), 25.1 (t), 22.5 (t), 21.0 (q), 16.7 (q), 13.9 (q); HRMS calcd for $C_{14}H_{24}O_2S_2$ (M^+) 288.1217, found 288.1216.

1-(1,3-Dithianylidene)-2-methyl-3-octyl acetate (9c): oil; IR (neat) 1731 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 170.6 (s), 134.5 (d), 127.2 (s), 76.7 (d), 37.6 (d), 32.1 (t), 31.5 (t), 30.2 (t), 29.6 (t), 25.0 (t), 24.9 (t), 22.3 (t), 20.9 (q), 16.7 (q), 13.8 (q); HRMS calcd for $C_{15}H_{26}O_2S_2$ (M^+) 302.1374, found 302.1348.

1-(1,3-Dithianylidene)-2-methyl-3-nonyl acetate (9d): oil; IR (neat) 1731 cm^{-1}; ^{13}C NMR ($CDCl_3$, 50 MHz) δ 170.6 (s), 134.6 (d), 127.2 (s), 76.9 (d), 37.6 (d), 32.2 (t), 31.6 (t), 30.2 (t), 29.6 (t), 29.0 (t), 25.3 (t), 25.0 (t), 22.4 (t), 20.9 (q), 16.7 (q), 14.0 (q); HRMS calcd for $C_{16}H_{28}O_2S_2$ (M^+) 316.1530, found 316.1530.

(*S*)-4-Hydroxy-2-heptanone (10). A cold (−78 °C) solution of (*S*)-**2c** (0.18 g, 0.47 mmol, 86% ee) in CH_2Cl_2 (30 mL) was treated with ozone. The reaction was monitored by TLC analysis. After complete consumption of (*S*)-**8c**, Me_2S (0.5 mL) was added. The mixture was warmed to room temperature and stirring maintained for 4 h. The mixture was concentrated and separated by silica gel chromatography and HPLC (EtOAc/hexane (1:1)) to give (*S*)-**10** (20 mg, 38%), $[\alpha]^{25}_D$ +44° (c = 0.18, $CHCl_3$) (lit.[7] $[\alpha]_D$ +35.1° (c = 2.1, $CHCl_3$, 58% ee)). Two isomers of 3-hydroxy-3-methyl-5-propyl-2,3,4,5-tetrahydrofuran-2-one (37%, 55:45) were also isolated as side products.

5-Phenyl-2,3,4,5-tetrahydrofuran-2-one (11e). The alcohol **1e** (60 mg, 91% ee favoring (*R*)-configuration), obtained from lipase-catalyzed hydrolysis of acetate **7e** (entry 6 of Table 2), was treated with $HgCl_2$ by a procedure silimar to that for hop lactone to give (+)-**11e** (24 mg, 90%) in favor of the (*R*)-configuration (91% ee), $[\alpha]^{25}_D$ +18° (c = 1.1, $CHCl_3$) (lit.[8] $[\alpha]_D$ +32.5° (c = 1, MeOH)).

5-(Methylethenyl)-2,3,4,5-tetrahydrofuran-2-one (Hop Lactone) (11s). (*S*)-Alcohol **1s** (0.44 g, 1.34 mmol) with 95% ee, obtained by saponification of the recovered acetate (*S*)-**7s** (95% ee) in entry 24 of Table 2, was treated with $HgCl_2$ (0.39 g, 1.47 mmol) in 10% MeOH (10 mL) at reflux for 5 h. The mixture was concentrated and extracted three times with EtOAc. The combined extracts were washed with brine, dried (Na_2SO_4), concentrated, and separated by silica gel chromatography (EtOAc/hexane (1:9)) to give hop lactone (0.15 g, 85%) with $[\alpha]^{25}_D$ +10° (c = 1.5, EtOH). Hop lactone in nature has been reported to have optical rotation $[\alpha]_D$ +8° (c = 0.25, EtOH).[1] (*R*)-**1s** (75% ee, entry 24 of Table 2)) was similarly converted to (*R*)-hop lactone, $[\alpha]^{25}_D$ −6.5° (c = 2.6, EtOH).

5-Butyl-4-methyl-2,3,4,5-tetrahydrofuran-2-one (Quercus Lactone) (12b). The alcohol **3b** (0.22 g, 85% ee favoring the (2*S*,3*R*)-configuration), obtained from lipase-catalyzed hydrolysis of acetate **9b**, was treated with $HgCl_2$ by a procedure similar to that for hop lactone to give trans quercus lactone (153 mg, 92%) in favor of (4*S*,5*R*)-configuration (85% ee), $[\alpha]^{25}_D$ +68° (c = 1.2, MeOH) (lit.[2] $[\alpha]_D$ +79° (c = 1.04, MeOH)). Hydrolysis of (2*R*,3*S*)-**3b** (95% ee) gave (4*R*,5*S*)-quercus lactone (95% ee), $[\alpha]^{25}_D$ −75° (c = 1.0, MeOH).

5-Pentyl-4-methyl-2,3,4,5-tetrahydrofuran-2-one (Cognac Lactone) (12c). The alcohol **3c** (100 mg, 94% ee favoring the (2*S*,3*R*)-configuration), obtained from lipase-catalyzed hydrolysis of acetate **9c**, was treated with $HgCl_2$ by a procedure silimar to that for hop lactone to give trans cognac lactone (65 mg, 92%) in favor of (4*S*,5*R*)-configuration (96% ee), $[\alpha]^{25}_D$ +75° (c = 1.0, CH_2Cl_2), lit.[3] $[\alpha]_D$ +79.5° (c = 1.12, CH_2Cl_2). Hydrolysis of (2*R*,3*S*)-**3c** (37% ee) gave (4*R*,5*S*)-cognac lactone, $[\alpha]_D^{25}$ −35° (c = 2.9, CH_2Cl_2).

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Supplementary Material Available: NMR spectra and additional spectral data of new compounds (65 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; ordering information is given on any current masthead page.