

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

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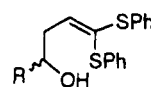
Racemic homoallylic alcohols **1–3** containing dithioaceteneacetal functionalities were prepared by addition of aldehydes to the allylic anions of ketene dithioacetals or 2-alkenyl-1,3-dithiane in a regio- and stereoselective manner. Lipase-catalyzed hydrolyses of the corresponding acetates **7–9** 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 dithioacetene acetal functionalities can be converted to γ -lactones such as natural hop lactone, whiskey lactone, and cognac lactone.

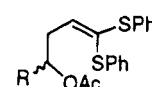
Results and Discussion

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 three 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



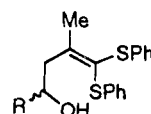
1a-s

- 1a R = Me
1b R = Et
1c R = *n*-Pr
1d R = *i*-Pr
1e R = C₆H₅
1f R = *o*-MeC₆H₄
1g R = *m*-MeC₆H₄
1h R = *p*-MeC₆H₄
1i R = *p*-(*i*-Pr)C₆H₄
1j R = *o*-MeOC₆H₄
1k R = *m*-MeOC₆H₄
1l R = *m*-CF₃C₆H₄
1m R = *p*-CF₃C₆H₄
1n R = *m*-FC₆H₄
1o R = *p*-FC₆H₄
1p R = *o*-ClC₆H₄
1q R = *m*-ClC₆H₄
1r R = *m*-BrC₆H₄
1s R = CH₂=CMe



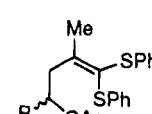
7a-s

- 7a R = Me
7b R = Et
7c R = *n*-Pr
7d R = *i*-Pr
7e R = C₆H₅
7f R = *o*-MeC₆H₄
7g R = *m*-MeC₆H₄
7h R = *p*-MeC₆H₄
7i R = *p*-(*i*-Pr)C₆H₄
7j R = *o*-MeOC₆H₄
7k R = *m*-MeOC₆H₄
7l R = *m*-CF₃C₆H₄
7m R = *p*-CF₃C₆H₄
7n R = *m*-FC₆H₄
7o R = *p*-FC₆H₄
7p R = *o*-ClC₆H₄
7q R = *m*-ClC₆H₄
7r R = *m*-BrC₆H₄
7s R = CH₂=CMe



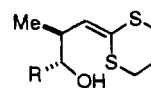
2a-g

- 2a R = Me
2b R = Et
2c R = *n*-Pr
2d R = *i*-Pr
2e R = C₆H₅
2f R = *n*-Bu
2g R = *n*-C₅H₁₁



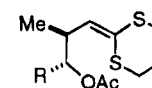
8a-g

- 8a R = Me
8b R = Et
8c R = *n*-Pr
8d R = *i*-Pr
8e R = C₆H₅
8f R = *n*-Bu
8g R = *n*-C₅H₁₁



3a-d

- 3a R = Et
3b R = *n*-Bu
3c R = *n*-C₅H₁₁
3d R = *n*-C₆H₁₃



9a-d

- 9a R = Et
9b R = *n*-Bu
9c R = *n*-C₅H₁₁
9d R = *n*-C₆H₁₃

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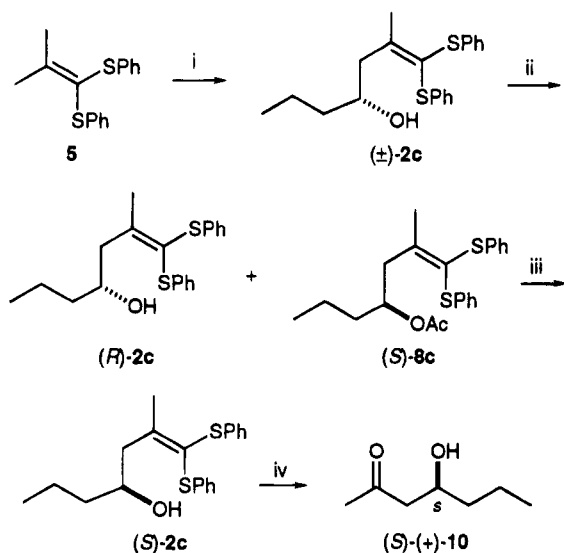
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the enantioselectivity was usually low. Acetylations of **1d**, **2d**, and **2e** by catalysis with lipase MY (entries 6,

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)	conversion (%)	acetate product	ee _p (%)	confign of major enantiomer	ee _s (%) of remaining substrate	<i>E</i>
1	1a	Me	MY	3	80	7a	8	<i>S</i>	8	1.3
2	1a	Me	AY	1	50	7a	6	<i>S</i>	6	1.2
3	1b	Et	MY	13	50	7b	4	<i>S</i>	4	1.1
4	1b	Et	AY	9	50	7b	12	<i>S</i>	26	1.5
5	1c	<i>n</i> -Pr	MY	25	50	7c	6	<i>S</i>	16	1.3
6	1d	<i>i</i> -Pr	MY	150	20	7d	93	<i>R</i>	16	32
7	2a	Me	MY	12	50	8a	40	<i>S</i>	40	3.3
8	2a	Me	AY	12	50	8a	40	<i>S</i>	39	3.4
9	2b	Et	MY	48	50	8b	46	<i>S</i>	52	4.4
10	2b	Et	AY	48	47	8b	69	<i>S</i>	69	11
11	2c	<i>n</i> -Pr	MY	100	25	8c	73	<i>S</i>	24	8
12	2c	<i>n</i> -Pr	AY	25	44	8c	86	<i>S</i>	67	27
13	2d	<i>i</i> -Pr	MY	150	13	8d	96	<i>R</i>	22	60
14	2e	C ₆ H ₅	MY	240	10	8e	98	<i>R</i>	15	114

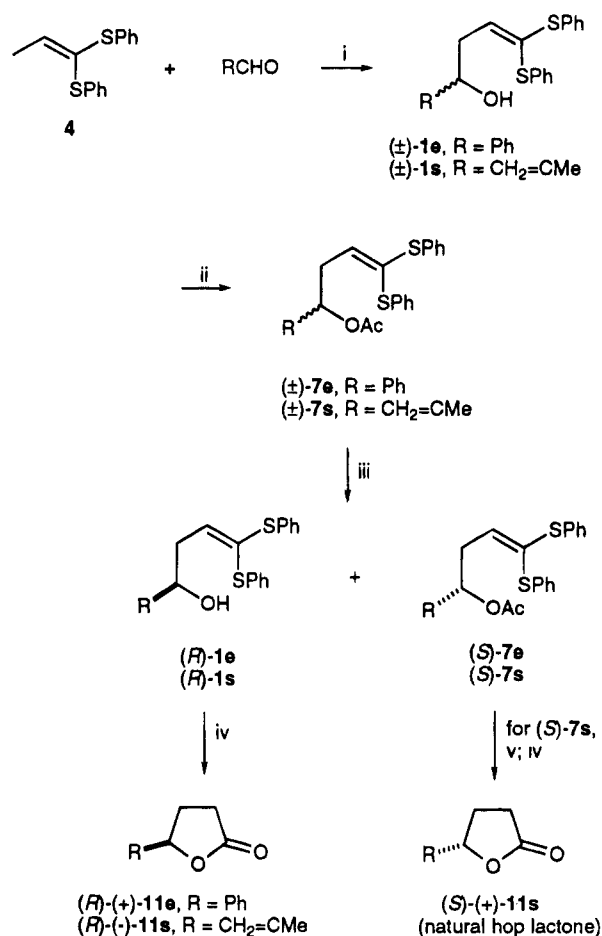
Scheme 1^a

^a Key: (i) BuLi, THF, *n*-C₃H₇CHO, -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) O₃, CH₂Cl₂, -78 °C; Me₂S, 25 °C.

13, and **14**, R = *i*-Pr or Ph) were sluggish but gave acetates **7d**, **8d**, and **8e** in high optical purity ($\geq 93\%$ 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 ¹H 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-heptanone⁷ 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).

Scheme 2^a

^a Key: (i) BuLi, THF, -78 °C, 10 min; 85%; (ii) Ac₂O, Et₃N, DMAP cat., CH₂Cl₂, 25 °C, 1 h; 98%; (iii) lipase, DMF, phosphate buffer (pH 7.5); see Table 2; (iv) HgCl₂, 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 = CH₂=CMe) in favor of the (*R*)-configuration. Product **1e** (91% ee) was treated with HgCl₂ to give the optically active γ -phenyl- γ -lactone **11e**,⁸ [α]_D +18° (*c* = 1.1, CHCl₃). The (*R*)-enantiomer of

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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)	conversion (%)	alcohol product	ee _p (%)	confign of major enantiomer	ee _s (%) of remaining substrate	<i>E</i>
1	7d	<i>i</i> -Pr	MY	hexane	240	35	1d	95	<i>R</i>	50	58
2	7d	<i>i</i> -Pr	MY	DMF	216	42	1d	95	<i>R</i>	68	72
3	7e	C ₆ H ₅	MY	hexane	120	37	1e	79	<i>R</i>	45	13
4	7e	C ₆ H ₅	MY	toluene	300	50	1e	75	<i>R</i>	99	34
5	7e	C ₆ H ₅	MY	DMF	120	50	1e	82	<i>R</i>	87	33
6	7e	C ₆ H ₅	AY	DMF	168	41	1e	91	<i>R</i>	64	40
7	7f	<i>o</i> -MeC ₆ H ₄	MY	DMF	120	20	1f	93	<i>R</i>	27	35
8	7g	<i>m</i> -MeC ₆ H ₄	MY	DMF	130	30	1g	91	<i>R</i>	45	33
9	7g	<i>m</i> -MeC ₆ H ₄	AY	DMF	210	32	1g	87	<i>R</i>	47	23
10	7h	<i>p</i> -MeC ₆ H ₄	MY	DMF	160	44	1h	87	<i>R</i>	71	30
11	7i	<i>p</i> -(<i>i</i> -Pr)C ₆ H ₄	MY	DMF	288	45	1i	94	<i>R</i>	70	64
12	7j	<i>o</i> -MeOC ₆ H ₄	MY	DMF	120	35	1j	92	<i>R</i>	50	39
13	7k	<i>m</i> -MeOC ₆ H ₄	MY	DMF	120	23	1k	96	<i>R</i>	37	70
14	7l	<i>m</i> -CF ₃ C ₆ H ₄	MY	DMF	130	40	1l	98	<i>R</i>	51	164
15	7l	<i>m</i> -CF ₃ C ₆ H ₄	AY	DMF	120	20	1l	97	<i>R</i>	19	79
16	7m	<i>p</i> -CF ₃ C ₆ H ₄	MY	DMF	144	28	1m	96	<i>R</i>	28	70
17	7n	<i>m</i> -FC ₆ H ₄	MY	DMF	120	38	1n	94	<i>R</i>	56	57
18	7o	<i>p</i> -FC ₆ H ₄	MY	DMF	120	40	1o	96	<i>R</i>	54	113
19	7p	<i>o</i> -ClC ₆ H ₄	MY	DMF	130	33	1p	98	<i>R</i>	47	125
20	7q	<i>m</i> -ClC ₆ H ₄	MY	DMF	120	48	1q	97	<i>R</i>	84	190
21	7q	<i>m</i> -ClC ₆ H ₄	AY	DMF	120	42	1q	89	<i>R</i>	66	34
22	7r	<i>m</i> -BrC ₆ H ₄	MY	DMF	310	20	1r	81	<i>R</i>	20	11
23	7s	CH ₂ =CMe	MY	DMF	120	37	1s	82	<i>R</i>	42	13
24	7s	CH ₂ =CMe	AY	DMF	240	55	1s	75	<i>R</i>	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)	conversion (%)	alcohol product	ee _p (%)	confign of major enantiomer	ee _s (%) of remaining substrate	<i>E</i>
1	8a	Me	MY	24	50	2a	23	<i>S</i>	21	2
2	8a	Me	AY	24	70	2a	20	<i>S</i>	37	4.4
3	8b	Et	MY	120	43	2b	56	<i>S</i>	31	4
4	8b	Et	AY	120	48	2b	57	<i>S</i>	54	6
5	8c	<i>n</i> -Pr	MY	120	45	2c	61	<i>S</i>	40	6
6	8c	<i>n</i> -Pr	AY	120	40	2c	65	<i>S</i>	36	7
7	8d	<i>i</i> -Pr	MY	450	30	2d	77	<i>R</i>	36	11
8	8d	<i>i</i> -Pr	AY	360	35	2d	91	<i>R</i>	55	37
9	8e	C ₆ H ₅	MY	144	47	2e	66	<i>R</i>	53	8
10	8e	C ₆ H ₅	AY	48	25	2e	74	<i>R</i>	24	8
11	8f	<i>n</i> -Bu	MY	137	45	2f	72	<i>S</i>	48	10
12	8f	<i>n</i> -Bu	AY	137	45	2f	82	<i>S</i>	67	20
13	8g	<i>n</i> -C ₅ H ₁₁	MY	220	15	2g	97	<i>S</i>	21	120
14	8g	<i>n</i> -C ₅ H ₁₁	AY	216	15	2g	99	<i>S</i>	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)	conversion (%)	alcohol product	ee _p (%)	confign of major enantiomer	ee _s (%) of remaining substrate	<i>E</i>
1	9a	Et	MY	48	40	3a	88	2 <i>S</i> ,3 <i>R</i>	55	27
2	9a	Et	AY	48	38	3a	91	2 <i>S</i> ,3 <i>R</i>	52	35
3	9b	<i>n</i> -Bu	MY	70	30	3b	91	2 <i>S</i> ,3 <i>R</i>	44	33
4	9b	<i>n</i> -Bu	AY	70	25	3b	98	2 <i>S</i> ,3 <i>R</i>	35	139
5	9b	<i>n</i> -Bu	AY	480	53	3b	85	2 <i>S</i> ,3 <i>R</i>	95	48
6	9c	<i>n</i> -C ₅ H ₁₁	MY	144	40	3c	85	2 <i>S</i> ,3 <i>R</i>	58	22
7	9c	<i>n</i> -C ₅ H ₁₁	AY	51	37	3c	93	2 <i>S</i> ,3 <i>R</i>	65	52
8	9c	<i>n</i> -C ₅ H ₁₁	AY	240	24	3c	96	2 <i>S</i> ,3 <i>R</i>	30	66
10	9d	<i>n</i> -C ₆ H ₁₃	MY	216	40	3d	81	2 <i>S</i> ,3 <i>R</i>	58	17
10	9d	<i>n</i> -C ₆ H ₁₃	AY	216	30	3d	94	2 <i>S</i> ,3 <i>R</i>	37	46

alcohol **1s** (95% ee) was similarly converted to (–)-hop lactone **11s**. The natural hop lactone is dextrorotatory¹ 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*-C₄H₉) obtained by condensation of 2-propenyl-1,3-dithiane and pentanal was converted to the correspond-

ing acetate **9b** (Ac₂O, Et₃N). 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 HgCl₂ afforded the natural trans quercus lactone **12b**.² By a similar procedure, the optically active alcohol **3c** (R = *n*-C₅H₁₁) 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 HgCl₂ to give unnatural antipodes of whisky lactone and cognac lactone.

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

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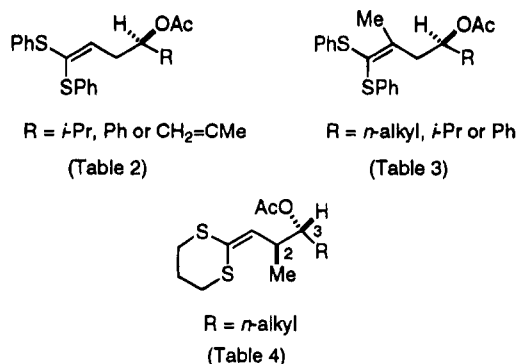
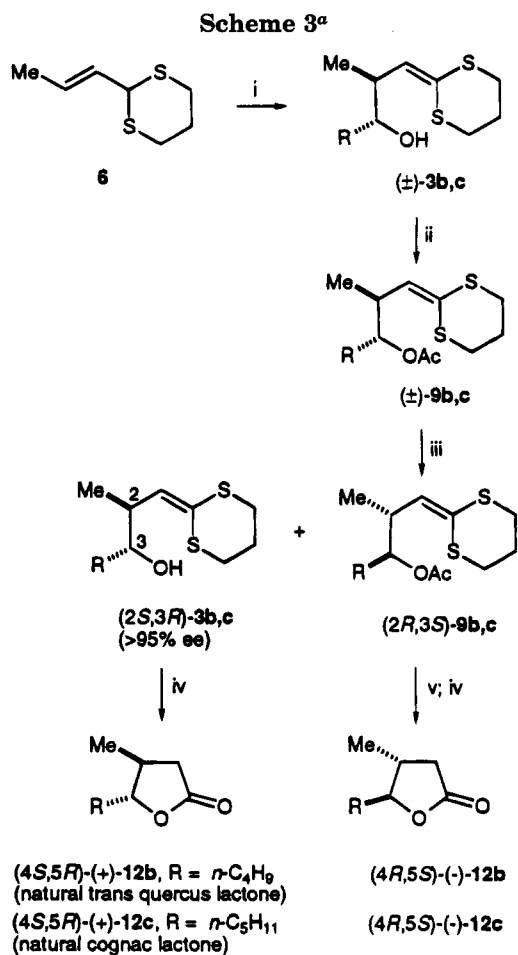


Figure 1. Preferable enantiomers for lipase-catalyzed hydrolyses.



^a Key: (i) BuLi, THF, *n*-C₄H₉CHO or *n*-C₅H₁₁CHO, -78 °C, 10 min; 85%; (ii) Ac₂O, Et₃N, cat. DMAP, CH₂Cl₂, 25 °C, 1 h; 98%; (iii) lipase, DMF, phosphate buffer (pH 7.5), see Table 4; (iv) HgCl₂, 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 = XC₆H₄), and **7s** (R = CH₂=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 (*2S,3R*)-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 models¹⁰ have been proposed to interpret enantioselectivity in lipase-catalyzed reactions, though no single model can fit all the experimental results.

Experimental Section

The ¹H NMR spectra were recorded at 200 or 300 MHz using tetramethylsilane as internal standard. ¹³C 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 μ m, 25 cm \times 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 Chiralcel OD column (0.46 cm i.d. \times 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. Lipase 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 dithioacetone 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 NaHCO₃ and extracted three times with EtOAc. The combined EtOAc extracts were washed with brine, dried (Na₂SO₄), 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

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(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 ^1H 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 ^1H 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); ^1H 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 $\text{C}_{17}\text{H}_{18}\text{OS}_2$ (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 $\text{C}_{18}\text{H}_{20}\text{OS}_2$ (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 $\text{C}_{19}\text{H}_{22}\text{OS}_2$ (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, 2 C), 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 $\text{C}_{19}\text{H}_{22}$ -

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 $\text{C}_{22}\text{H}_{20}\text{OS}_2$ (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 $\text{C}_{23}\text{H}_{22}\text{OS}_2$ (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), 126.7 (d), 126.3 (d), 125.3 (d), 70.0 (d), 39.3 (t), 19.0 (q); HRMS calcd for $\text{C}_{23}\text{H}_{22}\text{OS}_2$ (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 $\text{C}_{23}\text{H}_{22}\text{OS}_2$ (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 $\text{C}_{25}\text{H}_{26}\text{OS}_2$ (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 $\text{C}_{23}\text{H}_{22}\text{O}_2\text{S}_2$ (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 $\text{C}_{23}\text{H}_{22}\text{O}_2\text{S}_2$ (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 $\text{C}_{23}\text{H}_{19}\text{F}_3\text{OS}_2$ (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 $\text{C}_{23}\text{H}_{19}\text{F}_3\text{OS}_2$ (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,

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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; 1H 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); 1H 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); 1H 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 $\text{C}_{25}\text{H}_{24}\text{O}_2\text{S}_2$ (M^+) 420.1217, found 420.1216.

4,4-Bis(phenylthio)-1-(*p*-methylethylphenyl)-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 $\text{C}_{27}\text{H}_{28}\text{O}_2\text{S}_2$ (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 $\text{C}_{25}\text{H}_{24}\text{O}_3\text{S}_2$ (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 $\text{C}_{25}\text{H}_{24}\text{O}_3\text{S}_2$ (M^+) 436.1167, found 436.1160.

4,4-Bis(phenylthio)-1-(*m*-trifluoromethylphenyl)-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 $\text{C}_{24}\text{H}_{21}\text{F}_3\text{O}_2\text{S}_2$ (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*-trifluoromethylphenyl)-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 $\text{C}_{25}\text{H}_{21}\text{O}_2\text{S}_2\text{F}_3$ (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); ^1H 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 $\text{C}_{24}\text{H}_{21}\text{O}_2\text{S}_2\text{F}$ (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 $\text{C}_{18}\text{H}_{20}\text{OS}_2$ (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 $\text{C}_{24}\text{H}_{21}\text{O}_2\text{S}_2\text{Cl}$ (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 $\text{C}_{24}\text{H}_{21}\text{O}_2\text{S}_2\text{Cl}$

(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 $\text{C}_{24}\text{H}_{21}\text{O}_2\text{BrS}_2$ (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 $\text{C}_{21}\text{H}_{22}\text{O}_2\text{S}_2$ (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); ^1H 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 $\text{C}_{20}\text{H}_{22}\text{O}_2\text{S}_2$ (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 $\text{C}_{21}\text{H}_{24}\text{O}_2\text{S}_2$ (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 $\text{C}_{22}\text{H}_{26}\text{O}_2\text{S}_2$ (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 $\text{C}_{23}\text{H}_{24}\text{OS}_2$ (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 $\text{C}_{25}\text{H}_{24}\text{O}_2\text{S}_2$ (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 $\text{C}_{23}\text{H}_{28}\text{O}_2\text{S}_2$ (M^+) 440.1530, found 440.1536.

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 $\text{C}_{24}\text{H}_{30}\text{O}_2\text{S}_2$ (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); ^1H NMR (CDCl_3) δ 5.75 (1 H, d, $J = 9.8$ Hz), 4.69 (1 H, m), 2.87 (1 H, 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 $\text{C}_{13}\text{H}_{22}\text{O}_2\text{S}_2$ (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 $\text{C}_{14}\text{H}_{24}\text{O}_2\text{S}_2$ (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 $\text{C}_{15}\text{H}_{26}\text{O}_2\text{S}_2$ (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 $\text{C}_{16}\text{H}_{28}\text{O}_2\text{S}_2$ (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 ($\text{EtOAc}/\text{hexane}$ (1:1)) to give (*S*)-**10** (20 mg, 38%), $[\alpha]_D^{25} +44^\circ$ ($c = 0.18$, CHCl_3) (lit.⁷ $[\alpha]_D +35.1^\circ$ ($c = 2.1$, 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 similar to that for hop lactone to give (+)-**11e** (24 mg, 90%) in favor of the (*R*)-configuration (91% ee), $[\alpha]_D^{25} +18^\circ$ ($c = 1.1$, CHCl_3) (lit.⁸ $[\alpha]_D +32.5^\circ$ ($c = 1$, 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 ($\text{EtOAc}/\text{hexane}$ (1:9)) to give hop lactone (0.15 g, 85%) with $[\alpha]_D^{25} +10^\circ$ ($c = 1.5$, EtOH). Hop lactone in nature has been reported to have optical rotation $[\alpha]_D +8^\circ$ ($c = 0.25$, EtOH).¹ (*R*)-**1s** (75% ee, entry 24 of Table 2) was similarly converted to (*R*)-hop lactone, $[\alpha]_D^{25} -6.5^\circ$ ($c = 2.6$, 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), $[\alpha]_D^{25} +68^\circ$ ($c = 1.2$, MeOH) (lit.² $[\alpha]_D +79^\circ$ ($c = 1.04$, MeOH)). Hydrolysis of (2*R*,3*S*)-**3b** (95% ee) gave (4*R*,5*S*)-quercus lactone (95% ee), $[\alpha]_D^{25} -75^\circ$ ($c = 1.0$, 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 similar to that for hop lactone to give trans cognac lactone (65 mg, 92%) in favor of (4*S*,5*R*)-configuration (96% ee), $[\alpha]_D^{25} +75^\circ$ ($c = 1.0$, CH_2Cl_2), lit.³ $[\alpha]_D +79.5^\circ$ ($c = 1.12$, CH_2Cl_2). Hydrolysis of (2*R*,3*S*)-**3c** (37% ee) gave (4*R*,5*S*)-cognac lactone, $[\alpha]_D^{25} -35^\circ$ ($c = 2.9$, 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.