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Radical Cyclization Using a Thioacetal Group for Radical Generation

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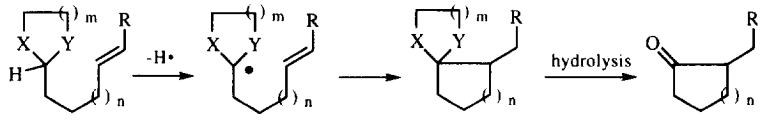
Abstract: The generation and cyclization of several heterocyclic radicals were investigated. The hydrogen abstraction from 1,3-dithiane, 1,3-dithiolane, and 1,3-oxathiane rings by a benzophenone triplet generated the corresponding heterocyclic radicals, which gave the cyclized products by intramolecular addition to α,β-unsaturated esters. Diastereoselective radical cyclization using chiral acetals was also investigated.

Radical cyclization has recently become a powerful tool for constructing carbocyclic or heterocyclic skeletons, and various applications to the synthesis of natural products have been reported.[1] Generally, the key carbon radical is generated by the reductive cleavage of a carbon-halogen (or other heteroatom) bond using a trialkylstannane. In addition to this stannane method, hydrogen abstraction is also useful, since a wide range of substrate structures is available. We were interested in the reaction depicted in Scheme 1, in which X and Y are heteroatoms. Here, we expected that the methine hydrogen at C2 would be selectively abstracted using photochemically excited aromatic ketones due to stabilization by the two adjacent heteroatoms. If the resulting carbon radical could cyclize, the reaction would present a new method for preparing cycloalkanones after hydrolysis and the acetal group could be considered as the equivalent of an acyl radical.[2,3] We were also interested in diastereoselectivity (ρ selectivity) in cyclization using a chiral acetal.[4] Some of these results have previously been reported as a preliminary communication.[5]



Scheme 1.

Substrates: Figure 1 summarizes the structures which we examined. These substrates were prepared according to the standard procedures shown in Schemes 2-5.

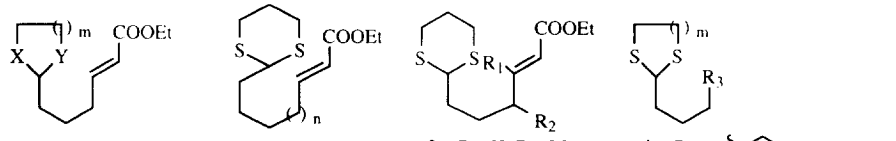
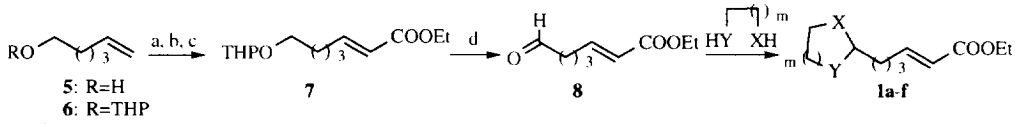
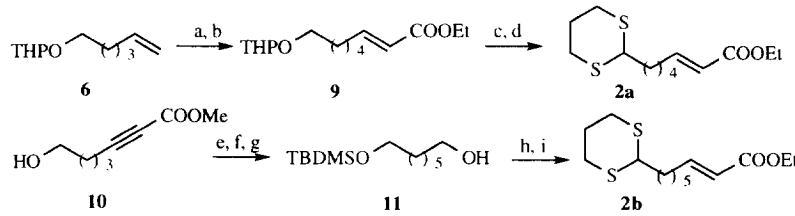


Fig. 1. Summarizes the Structures Examined.



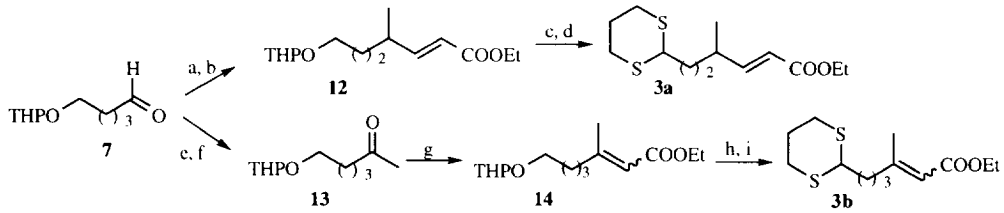
key; a DHP, cat. *c* HCl; b i) NMO, OsO_4, ii) $NaClO_4$, aq. MeOH; c $Ph_3P{=}CHCO_2Et$; d i) MeOH, cat. TsOH, ii) PCC.

Scheme 2. Synthesis of 1.



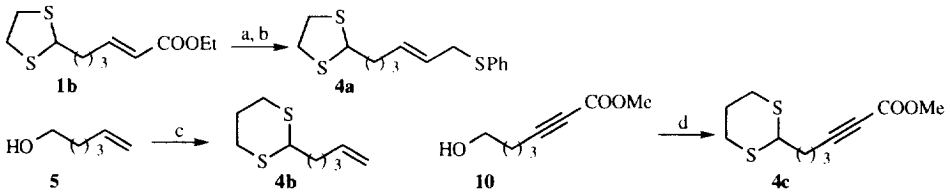
key; a i) BH_3, THF, H_2O_2, b i) PCC, ii) $Ph_3P{=}CHCO_2Et$, c i) cat. TsOH, MeOH, ii) PCC, d) $HS(CH_2)_3SH$, $BF_3{\cdot}OEt_2$, e H_2, Pd/C, f TBDMS-Cl, imidazole, g LAH, h i) TBAF, ii) PCC, iii) $Ph_3P{=}CHCO_2Et$, i $HS(CH_2)_3SH$, $BF_3{\cdot}OEt_2$.

Scheme 3. Synthesis of 2.



key; a i) *sec*-$BuNH_2$, ii) LDA, MeI, b $Ph_3P{=}CHCO_2Et$, c i) TsOH, MeOH, ii) PCC, d $HS(CH_2)_3SH$, $BF_3{\cdot}OEt_2$, e MeLi, f PCC, g $(EtO)_2P(O)CH_2CO_2Et$, NaH, h i) TsOH, MeOH, ii) PCC, i $HS(CH_2)_3SH$, $BF_3{\cdot}OEt_2$.

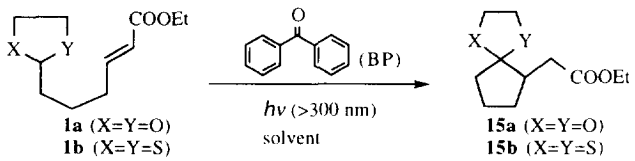
Scheme 4. Synthesis of 3.



key; a DIBAL, b PhSSPh, nBu_3P, c i) Swern ox., ii) $HS(CH_2)_3SH$, $BF_3{\cdot}OEt_2$, d i) PCC, ii) $HS(CH_2)_3SH$, $BF_3{\cdot}OEt_2$.

Scheme 5. Synthesis of 4.

Radical Cyclizations: Although the hydrogen abstraction at high temperature using a peroxide as a radical initiator has been used to generate carbon radicals, these conditions have only limited applicability because of the low regioselectivity of this reaction. The photochemical generation and reaction of α-oxycarbon radicals was reported by Fraser-Reid *et al.* in 1972.[6] Irradiation of alcohols or acetals at 350 nm in the presence of benzophenone (BP) generated carbon radicals, which reacted with enones derived from D-glucose. Since they used alcohols or acetals as solvents in most of their reactions, no information is available about the efficiencies in either radical generation or addition. These efficiencies are likely influenced by the structure of the radical-generating group. Both steps must be efficient to use this reaction for radical cyclization. Therefore, we first investigated radical cyclization using several heterocycles as radical-generating groups to test the reactivity of the generation and cyclization steps (eq. 1).



1a (X=Y=O)
1b (X=Y=S)

15a (X=Y=O)
15b (X=Y=S)

(1)

Irradiation of **1a** (12.5 mM) and BP (2 mM) in acetonitrile with a Pyrex-filtered medium-pressure mercury vapor lamp at room temperature for 7 h gave the cyclized product **15a** at a yield of only 3%, and instead resulted in recovery of **1a** (30%). We next investigated the reaction of dithiolane **1b**. Irradiation of **1b** under the same conditions gave the cyclized product **15b** at a yield of 11 %, as shown in Table 1. With a greater concentration of BP (6.8 mM), the reaction was faster and the yield of **15b** improved to 43% (run 2). A large solvent effect was observed in this reaction. Although the reactions in polar solvents proceeded slowly, the reactions in non-polar solvents, especially in benzene, gave a clean reaction (runs 3-6). The best result was obtained when 24 mM of **1b** was irradiated in the presence of 14 mM of BP for 20 min, to give **15b** at a yield of 63% along with **1b** at 14% (run 7). Reactions in the presence of acetone or acetophenone instead of BP resulted only in isomerization of the olefin geometry.

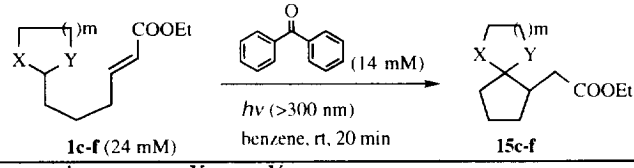
The cyclization of other substrates was investigated under the optimized conditions described above (Table 2). Dithiane **1c** was as effective as dithiolane **1b**, and oxathiolane **1d** also gave a cyclized product in a moderate yield. On the other hand, the reactions of substrates containing nitrogen heterocycles, such as

Table 1. Radical Reaction of 1b.

run	**1b** (mM)	solvent	BP (mM)	time (min)	**15b** (%)[a]	recovery of **1b**[a]
1	12.5	CH_3CN	2	300	11[b]	50[b]
2	12	CH_3CN	6.8	90	43[b]	
3	12	CH_3CN	6.8	20	20	50
4	12	*t*-BuOH	6.8	20	1	62
5	12	*n*-hexane	6.8	20	31 (45)	31
6	12	benzene	6.8	20	57 (60)	5
7	24	benzene	14	20	63 (73)	14
8	12	acetone	0	20	0	100[c]
9	12	benzene	0[d]	20	0	100[e]

a The yields were determined by ^{1}H-NMR using CH_2Cl_2 as an internal standard. Yields based on recovered **1b** are shown in parentheses. b Isolated yield. c A mixture of olefin isomers (*trans*:*cis*=9:1). d Acetophenone (6.8 mM) was used instead of benzophenone. e A mixture of olefin isomers (*trans*:*cis*=2:1).

Table 2. Radical Cyclizations of 1c, 1d, 1e, and 1f.



1c-f (24 mM) **15c-f**

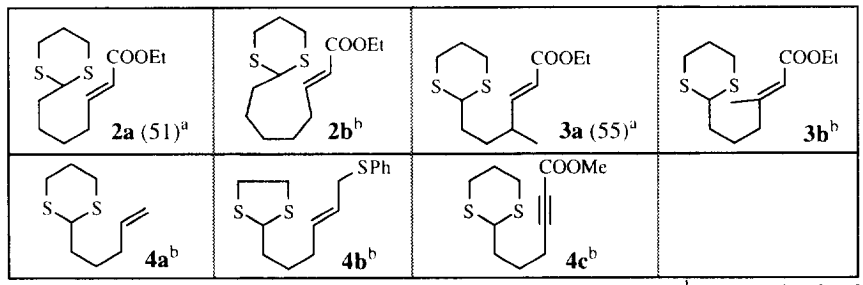
run	substrate	X	Y	m	yield of **15** (%)[a]	recovery of **1** (%)[a]
1	**1c**	S	S	2	60	19
2	**1d**	S	O	1	24	30
3	**1e**	S	NPh	1	b	
4	**1f**	NPh	NPh	1	b	

a The yields were determined by ^{1}H-NMR using CH_2Cl_2 as an internal standard. b Complex mixture.

thiazolidine and imidazolidine rings, gave only complex mixtures.

The scope and the limitations of this reaction were investigated further (Table 3). Although a six-membered ring was formed from **2a**, no cyclization was observed with **2b**, which was expected to give a seven-membered ring as a product. In the reaction of **3b**, a methyl substitution at the β-position of the unsaturated ester completely prohibited the formation of a five-membered ring. However, γ-methyl unsaturated ester **3a** cyclized to give a mixture of products (**16**) in which the trans isomer was predominated (*trans*:*cis* =9:1). The stereochemistry of the products was determined by NOE experiments with the separated *cis* **16**. Characteristic NOEs are shown in Figure 2. Alkenes without an electron-withdrawing substituent and an alkynyl ester failed to trap heterocyclic radicals.

Table 3. Effects of Chain Length, Substituent, and Radical Acceptor.



a The yields of cyclized products are shown in parentheses and were determined by ^{1}H-NMR using CH_2Cl_2 as an internal standard. b A cyclized product was not obtained and the starting material was recovered in about 70% yield.

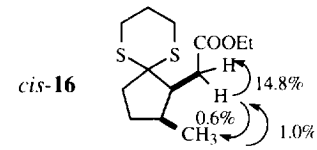


Fig. 2. Diagnostic NOEs observed in *cis*-16.

Discussion: The effect of heteroatoms on the rate of hydrogen abstraction at the α-carbon has been reported by Oae et al.[7a] They measured the rate of hydrogen abstraction from the substituted methane by t-BuO• at 130 °C. The relative rates of hydrogen abstraction from toluene, anisole, thioanisole, and dimethylaniline were

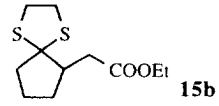
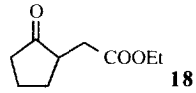
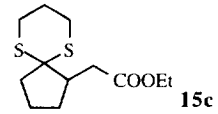
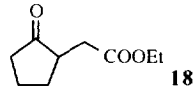
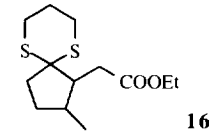
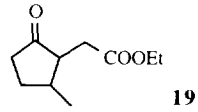
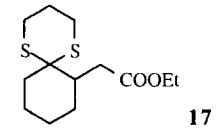
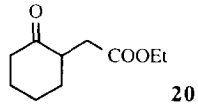
1.00, 1.44, 2.12, and 81.9, respectively. These enhanced rates were considered the result of stabilization of the carbon radicals by the electron-releasing effects of the heteroatoms.[7] In the case of sulfur compounds, interaction of the d orbital is also important.

As expected, dithiolane **1b** and dithiane **1c** are more reactive than dioxolane **1a**. Although better results were expected with nitrogen-containing heterocycles, the reactions of **1e** and **1f** gave complex mixtures and no desired products were isolated. These results may be attributed to non-regioselective hydrogen abstraction from the substrate and products.

The nucleophilic nature of the radicals, which can add to electron-deficient alkenes, is reflected in the data in Table 3. The unsuccessful results with **3b** and **4c** may be explained by the unfavorable interaction between the dithiane ring and the unsaturated esters in the transition state.

Hydrolysis of dithioacetals: The resulting dithioacetals were hydrolyzed to cyclopentanones (**18** and **19**) and cyclohexanone **20** using two conditions (A: methyl iodide in aqueous ether, B: bis(trifluoroacetoxy)iodobenzene in aqueous methanol[8]). Conditions and yields of the hydrolysis are summarized in Table 4.

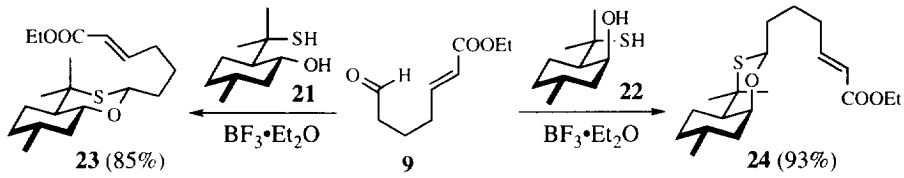
Table 4. Hydrolysis of Dithioacetals.

run	substrate	conditions[a]	product	yield, %
1	 **15b**	A B	 **18**	55 64
2	 **15c**	A B	 **18**	83 34
3	 **16**	B	 **19**	78
4	 **17**	A	 **20**	75

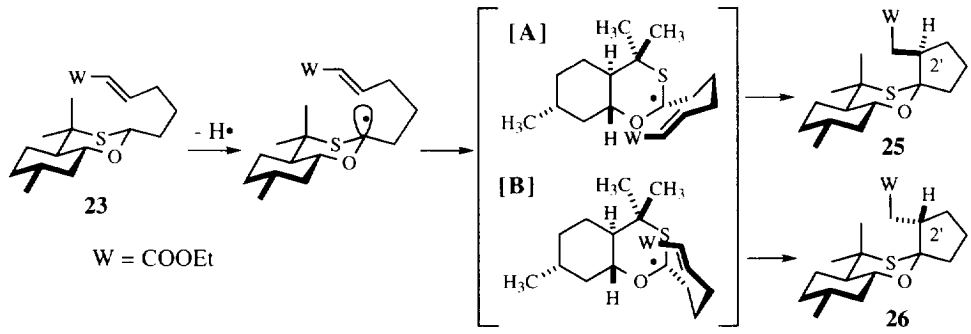
a Conditions A: CH_3I (excess), EtOH-H_2O (20:1), reflux, B: $(CF_3COO)_2IC_6H_5$ (1.7 eq), MeOH-H_2O (20:1), 0 °C.

Diastereoselective radical cyclization using chiral acetals: We next examined diastereoselective radical cyclization using chiral acetals under the conditions described above. The acetalization of ethyl 6-formyl-2-hexenoate **9** using two chiral hydroxythiols, **21** and **22**, which are easily prepared from (*R*)-(+)-pulegone,[9] in the presence of Lewis acid gave **23** and **24**, respectively (Scheme 6).

The importance of the stereoelectronic effect in hydrogen abstraction from the cyclic and acyclic substrates containing more than one heteroatom has been demonstrated both experimentally and theoretically.[7b-e,10] Therefore, hydrogen abstraction from **23** should generate the axial radical, which would be stabilized by the overlap of lone pairs. Cyclization may proceed through chair transition state **A** or **B**.



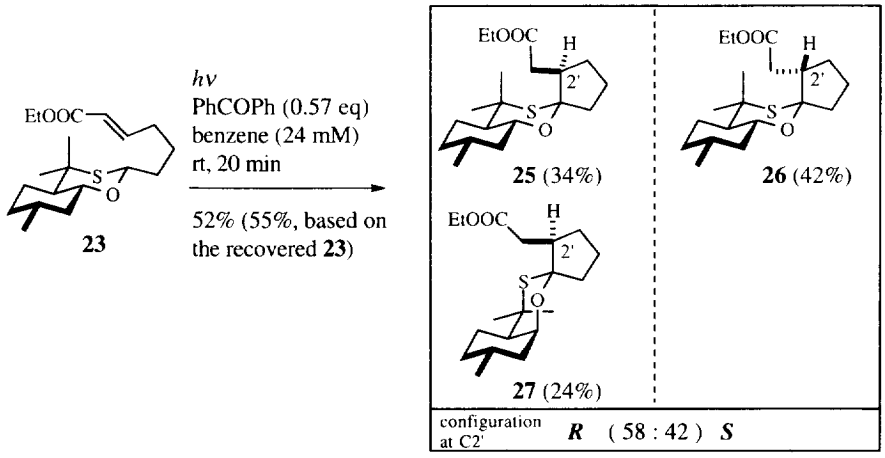
Scheme 6.



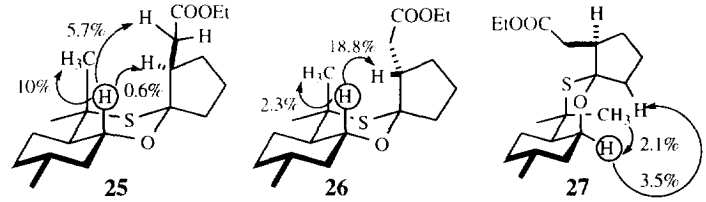
Scheme 7.

Transition state **A** is most likely favored because there is less interaction between the axial methyl group on the oxathiane ring and the ethoxy carbonyl group. Therefore, the formation of **25** might predominate (Scheme 7).

Irradiation of a benzene solution of **23** through a Pyrex filter in the presence of benzophenone at room temperature for 20 min gave a separable mixture of three cyclized products **25**, **26**, and **27**, in a ratio of 1.42 : 1.75 : 1 in a combined yield of 52% (Scheme 8). Spectroscopic analysis revealed the structures of products **25** and **26**, which were expected based on an analysis of the transition state of this reaction. NOE experiments clarified the configuration at the C2' position of each product (Figure 3). Thus, irradiation of the methine



Scheme 8.

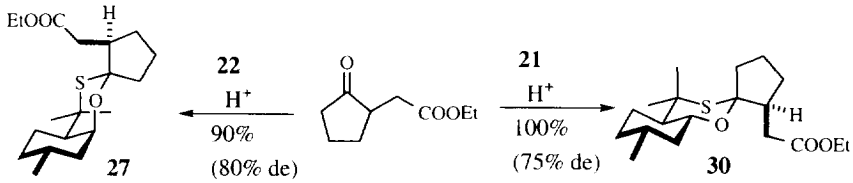


NMR data of circled hydrogen ($CDCl_3$, δ, Hz)	3.47 (ddd, 10, 10, 4.5)	3.61 (ddd, 10, 10, 4)	4.06 (broad s)

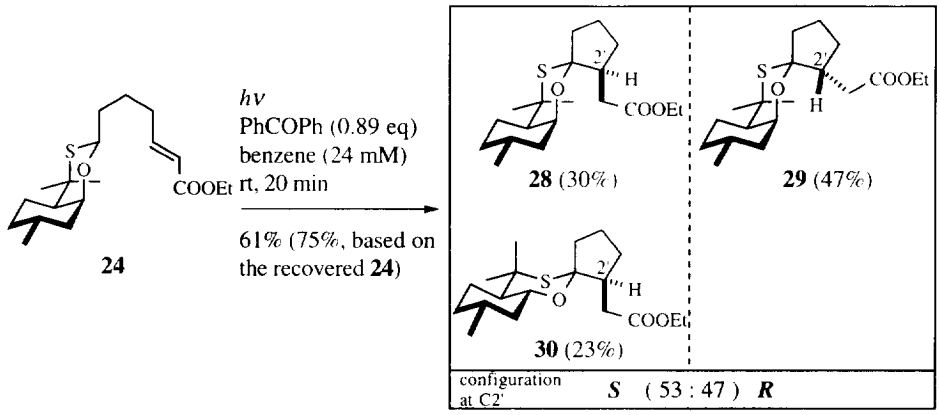
Fig. 3 Observed NOEs for 25, 26 and 27.

hydrogen (circled in the structure) at the oxygen-substituted carbon (C8a position) in **25** showed 5.7 % NOE at the methylene hydrogen in the side chain and 0.6% NOE at the methine hydrogen at the C2' position. On the other hand, in **26**, a strong NOE was observed between the methine hydrogen at the C8a position and the methine hydrogen at the C2' position. Therefore, the absolute configuration at C2' for **25** was determined to be *R* and that in **26** was *S*.

In the ^{1}H-NMR spectrum of **27**, a signal assigned to a methine hydrogen at the C8a position was shifted downfield about 0.5 ppm compared to those in the spectra of **25** and **26**. Furthermore, the coupling constants were smaller. These dada suggest the presence of a cis-fused bicyclic oxathiane ring which resulted from the inversion of the oxathiane ring. Fortunately, **27** was identical to the major product obtained from the reaction of **22** and (2-oxocyclopentyl)acetate (eq. 2).[11] The absolute configuration at C2' in **27** had been determined to be *R* by an X-ray analysis of the carboxylic acid obtained from **27**. Therefore, the asymmetric induction in the cyclization of **23** is 16% d.e.



Cyclization of **24** under the same conditions as those for **23** gave an inseparable mixture of three products, **28**, **29**, and **30**, at a yield of 61% (Scheme). Treatment of the mixture with lithium aluminum hydride, followed by benzylation, gave three isomers of benzyl ethers, **31**, **32**, and **33**, which were separated by column chromatography. Compounds **31** and **32** were stereoisomers at the C2' stereogenic center and their stereochemistry was determined by NOE experiments (Figure 4). Compound **32** showed stronger NOE between the methine hydrogens at the C2' position and the C8a position than **31**. Therefore, the absolute configuration at C2' in **31** was determined to be *S* and that in **32** was *R*. The ^{1}H-NMR spectrum of **33** suggested inversion of the oxathiane ring, as in **27** (Figure 4). Chromatography of the mixture of carboxylic acids obtained by hydrolysis of the reaction products separated an acid **34** from other two isomers (eq. 3), and the structure of **34** was confirmed by direct comparison with authentic **34** prepared by asymmetric acetalization using **21** (eq. 2).[11] Since the absolute configuration at C2' in **34** was *S*, the ratio and the structures of cyclized products, **28**, **29**, and **30**, are shown in Scheme 9 and the asymmetric induction in this reaction was only 6% d.e.



Scheme 9.

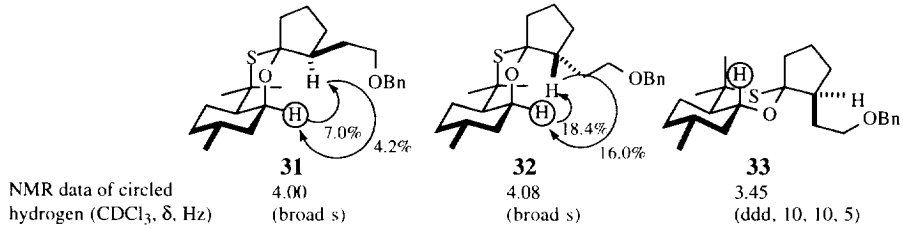
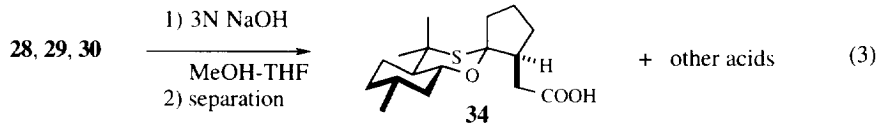
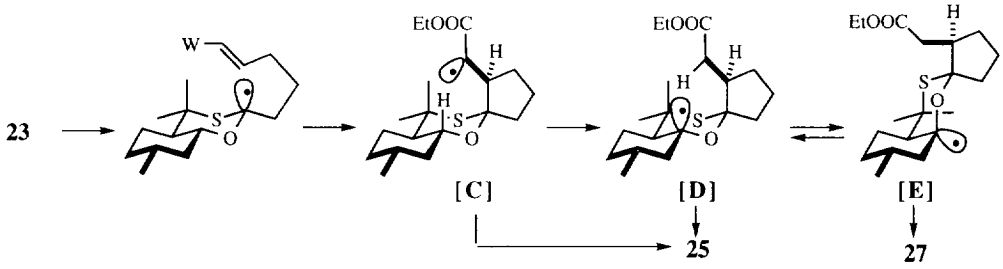


Fig. 4 Observed NOEs for 31, 32 and 33.



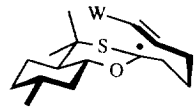


Scheme 10.

Compounds **23** and **24** gave the cyclized products in better yields than the simple oxathiane **1d**. This might be due to the fact that there are no abstractive hydrogen atoms at an α-carbon to the sulfur atom in the products. Inversion of the oxathiane rings in the reactions of **23** and **24**, which result in **27** and **30**, respectively, can be explained as follows. Cyclization of **23** may generate the radical intermediate [C] which

would rearrange to the radical [D] by a 1,5-hydrogen migration, as shown in Scheme 10. The radical intermediate [D], in which the radical robe is oriented in an axial configuration, would be equilibrated with radical [E] by inversion of the radical center to minimize the unfavorable steric interaction between an axial methyl and the acetate side chain. The hydrogen abstraction of both [C] and [D] gives the product **25**, while the radical [E] gives **27**. A similar mechanism can be used to explain the formation of **30**. The participation of a half-chair transition state [F], which gives **26** as shown in Figure 5, may explain the low diastereoselectivity in these reactions. Further efforts to improve the selectivity using a different type of chiral acetal are underway.

[F]



W=COOEt

Fig. 5. A Half-Chair Transition State in the Reaction of 23.

EXPERIMENTAL

General: Anhydrous solvents were obtained by distillation from benzophenone ketyl (diethyl ether, tetrahydrofurane, toluene) or from calcium hydride (dichrolomethane, acetonitrile). IR spectra were recorded on a JASCO IRA-2 spectrophotometer. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a JEOL JNM EX-400, JNM GX-270, JNM FX-100 or JNM FX-90Q spectrometer. Chemical shifts are reported in ppm (δ) from tetramethylsilane. NMR data for ^{13}C DEPT experiments are reported as quaternary (C), tertiary (CH), secondary (CH_2), and primary (CH_3) carbon atoms. Mass spectra were recorded on a JEOL JMS-DX303 spectrometer. Optical rotations were recorded on a JASCO DIP-370 polarimeter.

6-(2-Tetrahydropyranyl)oxy-1-hexene (6). A few drops of conc. H_2SO_4 was added to a mixture of 5-hexen-1-ol (**5**, 10 g, 0.10 mol) and 3,4-dihydro-2H-pyrane (15 g, 0.18 mol). The mixture was stirred for 3 h at room temperature. The mixture was diluted with ether and washed with saturated NaCl solution. After the organic layers were dried over $MgSO_4$, the solvent was removed *in vacuo*, and the residue was purified by chromatography on silica gel (ether:*n*-hexane=1:9) affording **6** (17.03 g, 92%). IR (neat) 2950, 1645 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 5.81 (ddt, *J*= 17.0, 10.0, 7.0 Hz, 1H), 5.01 (ddt, *J*= 17.0, 2.0, 1.0 Hz, 1H), 4.95 (ddt, *J*= 10.0, 2.0, 1.5 Hz, 1H), 4.58 (dd, *J*= 4.5, 3.0 Hz, 1H), 3.87 (ddd, *J*= 11.5, 7.5, 3.0 Hz, 1H), 3.74 (dt, *J*= 10.0, 6.5 Hz, 1H), 3.57-3.46 (m, 1H), 3.38 (dt, *J*= 10.0, 6.5 Hz, 1H), 2.08 (dtdd, *J*= 7.0, 7.0, 2.0, 1.0 Hz, 2H), 1.88-1.78 (m, 1H), 1.76-1.67 (m, 1H), 1.66-1.44 (m, 8H). LRMS m/e 183 (M^+-1), 141, 126, 101, 98, 85, 67, 55, 41. HRMS calcd $C_{11}H_{20}O_2$ 184.1458; obs 184.1463.

Ethyl 7-(2-tetrahydropyranyl)oxy-2-heptenoate (7). A mixture of **6** (6.40 g, 34.8 mmol), *N*-methylmorpholine-*N*-oxide (75.2 mmol), and osmium tetroxide (0.25 M *t*-BuOH solution, 9.8 mL, 2.45 mmol) in 200 mL of acetone was stirred for 2 h at room temperature. Sodium hydrosulphite (4.30 g, 2.47 mmol) was added and the mixture was stirred overnight. After the mixture was filtered through a Celite pad, the filtrate was concentrated *in vacuo*. Water was added to the residue and the product was extracted with ethyl acetate after salting out with NaCl. The combined extracts were dried and concentrated *in vacuo*. Purification of the residue by chromatography on silica gel (ethyl acetate) gave 5-(2-tetrahydropyranyl)oxy-1,2-hexanediol (6.00 g, 79%). A solution of 5-(2-tetrahydropyranyl)oxy-1,2-hexanediol (6.00 g, 28.07 mmol) in 70 mL of MeOH was added to a solution of sodium metaperiodate (6.62 g, 30.90 mmol) in water (60 mL) and the mixture was stirred for 3 h at 0 °C. After the insoluble materials were removed by filtration, the filtrate was concentrated *in vacuo*. The aqueous solution was saturated with NaCl, and then the product was extracted with ether. The combined extracts were washed with saturated NaCl, dried, and concentrated *in vacuo*. Purification of the residue by chromatography on silica gel (ethyl acetate) gave 6-(2-tetrahydropyranyl)oxy-1-pentanal (5.5 g, 95%). IR (neat) 2925, 2850, 2700, 1715 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 9.40 (t, *J*= 2.0 Hz, 1H), 4.57 (dd, *J*= 5.0, 3.0 Hz, 1H), 3.86 (ddd, *J*= 11.5, 7.5, 3.0 Hz, 1H), 3.76 (dt, *J*= 10.0, 6.5 Hz, 1H), 3.54-3.46 (m, 1H), 3.40 (dt, *J*= 10.0, 6.5 Hz, 1H), 2.48 (td, *J*= 10.0, 6.5, 1H), 1.88-1.48 (m, 11H). ^{13}C-NMR ($CDCl_3$, ppm) δ 202.49 (CHO), 98.92 (CH), 66.98 (CH_2), 62.38 (CH_2), 43.64 (CH_2), 30.73 (CH_2), 29.17 (CH_2), 25.46 (CH_2), 19.65 (CH_2), 19.06 (CH_2). LRMS m/e 128, 115, 111, 101, 85, 67, 56, 41. HRMS calcd $C_{10}H_{18}O_3$ 186.1256 ; obs 186.1284.

To a solution of 6-(2-tetrahydropyranyl)oxy-1-pentanal (1.50 g, 8.06 mmol) in 10 mL of CH_2Cl_2 was added triphenylcarboethoxyphosphorane (3.65 g, 1.92 mmol), and the mixture was stirred for 6 h at room temperature. After the solvent was removed *in vacuo*, the residue was purified by chromatography on silica gel (ethyl acetate:*n*-hexane=1:1) affording **7** (1.87 g, 91%). IR (neat) 2895, 2800, 1710, 1640 cm^{-1}. ^1H-NMR ($CDCl_3$, ppm) δ 6.96 (dt, *J*= 16.0, 7.0 Hz, 1H), 5.83 (dt, *J*= 16.0, 1.5 Hz, 1H), 4.57 (dd, *J*= 4.5, 3.0 Hz, 1H), 4.18 (q, *J*= 7.0 Hz, 2H), 3.86 (ddd, *J*= 11.5, 7.5, 3.0 Hz, 1H), 3.75 (dt, *J*= 10.0, 6.5 Hz, 1H), 3.54-3.46 (m, 1H), 3.39 (dt, *J*= 10.0, 6.5 Hz, 1H), 2.24 (ddd, *J*= 7.5, 7.5, 1.5 Hz, 2H), 1.88-1.76 (m, 1H), 1.76-1.48 (m, 9H), 1.29 (t, *J*= 7.0 Hz, 3H). ^{13}C-NMR ($CDCl_3$, ppm) δ 166.71 (COO), 148.98 (C), 121.54 (CH), 98.88 (CH), 67.14 (CH_2), 62.35 (CH_2), 60.15 (CH_2), 31.97 (CH_2), 30.76 (CH_2), 29.24 (CH_2), 25.49 (CH_2), 24.84 (CH_2), 19.66 (CH_2), 14.28 (CH_3). LRMS m/e 256 (M^+), 238, 227, 211, 201, 184, 172, 155, 127, 101, 85, 81, 67, 55, 41. HRMS calcd $C_{14}H_{24}O_4S$ 256.1665; obs 256.1675.

Ethyl 6-formyl-2-hexenoate (8). A mixture of **7** (1.87 g, 7.32 mmol) and a catalytic amount of *p*-toluenesulfonic acid in anhydrous MeOH (30 mL) was stirred for 3 h at room temperature. Saturated $NaHCO_3$ solution was added to the reaction and the mixture was concentrated *in vacuo* to give a residue, which was extracted with ether. The combined extracts were washed with saturated NaCl solution, dried, and concentrated *in vacuo*. Purification of the residue by chromatography on silica gel (ethyl acetate:*n*-hexane=1:3) gave ethyl 7-hydroxy-2-heptenoate (1.1 g, 74%). IR (neat) 3400, 2950, 1720, 1700, 1650 cm^{-1}. ^1H-NMR ($CDCl_3$, ppm) δ 6.96 (dt, *J*= 15.5, 7.0 Hz, 1H), 5.83 (dt, *J*= 15.5, 1.5 Hz, 1H), 4.18 (q, *J*= 7.0 Hz, 2H), 3.66 (broad t, *J*= 6.0 Hz, 2H), 2.24 (dtd, *J*= 7.0, 7.0, 1.5 Hz, 2H), 1.65-1.50 (m, 4H), 1.28 (t, *J*= 7.0 Hz, 3H). ^{13}C-NMR ($CDCl_3$, ppm) δ 166.71 (COO), 148.79 (CH), 121.65 (CH), 62.55 (CH_2), 60.20 (CH_2), 32.11 (CH_2), 31.88 (CH_2), 24.27 (CH_2), 14.28 (CH_3). LRMS m/e 173 (M^++1), 154, 142, 126, 114, 97, 86, 81, 73, 68, 60, 55, 41. HRMS calcd $C_9H_{16}O_3$ 172.1100; obs 172.1071. Anal. Calcd for $C_9H_{16}O_3$: C, 62.77; H, 9.36. Found: C, 61.85, H, 9.61.

Pyridinium chlorochromate (578 mg, 2.69 mmol) and Celite (600 mg) were added to a solution of 7-hydroxy-2-heptenoate (308.2 mg, 1.79 mmol) in anhydrous CH_2Cl_2. The suspension was stirred for 2 h at room temperature. Then the reaction mixture was diluted with ether and filtered through a Frolisil column. The column was further eluted with ether and the combined elutes were concentrated to give 271.8 mg (89%) of ethyl 6-formyl-2-hexenoate (**8**). IR (neat) 2950, 2750, 1720, 1660 cm^{-1}. ^1H-NMR ($CDCl_3$, ppm) δ 9.78 (t, *J*= 1.5 Hz, 1H), 6.92 (dt, *J*= 15.5, 7.0 Hz, 1H), 5.84 (dt, *J*= 15.5, 1.5 Hz, 1H), 4.14 (q, *J*= 7.0 Hz, 2H), 2.49 (td, *J*= 7.0, 1.5 Hz, 2H), 2.25 (dtd, *J*= 7.0, 7.0, 1.5 Hz, 2H), 1.81 (quint, *J*= 7.0 Hz, 2H), 1.29 (t, *J*= 7.0 Hz, 3H). ^{13}C-NMR ($CDCl_3$, ppm) δ 201.55 (CHO), 166.46 (COO), 147.49 CH), 122.35 (CH), 60.30 (CH_2), 42.98 (CH_2), 31.27 (CH_2), 20.39 (CH_2), 14.27 (CH_3). LRMS m/e 171 (M^++1), 149, 142, 125, 114, 99, 86, 81, 68, 60, 55, 41. HRMS calcd $C_9H_{14}O_3$ 170.0943; obs 170.0943.

Ethyl 7,7-ethylenedioxy-2-heptenoate (1a). A solution of **8** (278 mg, 1.64 mmol), ethylene glycol (121 mg, 1.97 mmol), and a catalytic amount of *p*-toluenesulfonic acid in benzene (30 mL) was heated to reflux for 1 h while resulting water was removed azeotropically. The solution was cooled to room temperature, and then diluted with ether. The mixture was washed with saturated $NaHCO_3$ solution and saturated NaCl solution, successively. The organic layer was dried over $MgSO_4$ and concentrated *in vacuo* to give **1a** (281 mg, 80%). IR (neat) 2975, 1720, 1660 cm^{-1}. ^1H-NMR ($CDCl_3$, ppm) δ 6.95 (dt, *J*= 15.5, 7.0 Hz, 1H), 5.87 (dt, *J*= 15.5, 1.5 Hz, 1H), 4.86 (t, *J*= 4.5 Hz, 1H), 4.18 (q, *J*= 7.0 Hz, 2H), 4.01-3.91 (m, 4H), 2.25 (dtd, *J*= 7.0, 7.0, 1.5 Hz, 2H), 1.73-1.65 (m, 2H), 1.65-1.55 (m, 2H), 1.28 (t, *J*= 7.0 Hz, 3H). ^{13}C-NMR ($CDCl_3$, ppm) δ 166.66 (CO), 148.59 (CH), 121.71 (CH), 104.21 (CH), 64.91 (CH_2), 60.15 (CH_2), 33.21 (CH_2), 31.91 (CH_2), 22.33 (CH_2), 14.27 (CH_3). LRMS m/e 213 (M^+-1), 169, 152, 141, 125, 108, 99, 81, 73, 68, 55, 45, 41. HRMS calcd $C_{11}H_{18}O_4$ 214.1205; obs 214.1176. Anal. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47. Found: C, 61.41, H, 8.58.

Ethyl 6-(2-dithiolanyl)-2-hexenoate (1b). A mixture of **8** (407 mg, 2.39 mmol), 1,2-ethanedithiol (0.2 mL, 2.38 mmol), and a catalytic amount of $BF_3 \cdot OEt_2$ in anhydrous CH_2Cl_2 (30 mL) was stirred for 1 h at room temperature. Usual workup and chromatography on silica gel (ether:*n*-hexane=1:9) gave **1b** (470 mg, 80%). IR (neat) 2925, 1720, 1650 cm^{-1}. ^1H-NMR ($CDCl_3$, ppm) δ 6.94 (dt, *J*= 15.5, 7.0 Hz, 1H), 5.83 (dt, *J*= 15.5, 1.5 Hz, 1H), 4.47 (t, *J*= 7.0 Hz, 1H), 4.18 (q, *J*= 7.0 Hz, 2H), 3.28-3.16 (m, 4H), 1.88-1.81 (m, 4H), 1.67-1.58 (m, 2H), 1.29 (t, *J*= 7.0 Hz, 3H). ^{13}C-NMR ($CDCl_3$, ppm) δ 166.58 (COO), 148.24 (CH), 121.85 (CH), 60.20 (CH_2), 53.36 (CH), 38.44 (CH_2), 36.43 (CH_2), 31.69 (CH_2), 27.47 (CH_2), 14.27 (CH_3). LRMS m/e 246 (M^+), 218, 201, 185, 173, 139, 131, 120, 105, 99, 87, 81, 73, 67, 61, 53, 45, 41.

HRMS calcd $C_{11}H_{18}O_2S_2$ 246.0749; obs 246.0719. Anal. Calcd for $C_{11}H_{18}O_2S_2$: C, 53.62; H, 7.36; S, 26.03. Found: C, 53.42, H, 7.43; S, 25.93.

Ethyl 6-(2-dithianyl)-2-hexenoate (1c). A mixture of **8** (411 mg, 2.42 mmol), 1,3-propanedithiol (0.2 mL, 2.00 mmol), and a catalytic amount of BF_3•OEt_2 in anhydrous CH_2Cl_2 (30 mL) was stirred for 1 h at room temperature. Usual workup and chromatography on silica gel (ether:*n*-hexane=1:9) gave **1c** (492 mg, 78%). IR (neat) 2900, 1725 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 6.93 (dt, *J*= 15.5, 7.0 Hz, 1H), 5.83 (dt, *J*= 15.5, 2.0 Hz, 1H), 4.18 (q, *J*= 7.0 Hz, 2H), 4.04 (t, *J*= 7.0 Hz, 1H), 2.88 (ddd, *J*= 14.0, 11.0, 3.0 Hz, 2H), 2.83 (ddd, *J*= 14.0, 4.0, 4.0 Hz, 2H), 2.23 (dtd, *J*= 7.0, 7.0, 2.0 Hz, 2H), 2.12 (dtt, *J*= 14.0, 4.0, 3.0 Hz, 2H), 1.82-1.64 (m, 5H), 1.29 (t, *J*= 7.0 Hz, 3H). ^{13}C-NMR ($CDCl_3$, ppm) δ 166.31 (COO), 147.95 (CH), 121.73 (CH), 59.99 (CH), 47.06 (CH), 34.66 (CH_2), 31.48 (CH_2), 30.23 (CH_2), 25.81 (CH_2), 24.89 (CH_2), 14.12 (CH_3). LRMS m/e 260 (M^+), 215, 187, 173, 154, 145, 134, 119, 106, 99, 91, 87, 81, 74, 67, 59, 53, 41. HRMS calcd $C_{12}H_{20}O_2S_2$ 260.0900; obs 260.0922.

Ethyl 6-(2-oxathiolanyl)-2-hexenoate (1d). A mixture of **8** (37 mg, 0.18 mmol), 2-mercaptoethanol (0.02 mL, 0.29 mmol), and a catalytic amount of BF_3•OEt_2 in anhydrous CH_2Cl_2 (3 mL) was stirred for 1 h at room temperature. Usual workup and chromatography on silica gel (ether:*n*-hexane=1:9) gave **1d** (44.8 mg, 89%). IR (neat) 2950, 1720, 1660 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 6.94 (dt, *J*= 15.5, 7.0 Hz, 1H), 5.83 (dt, *J*= 15.5, 1.5 Hz, 1H), 5.08 (t, *J*= 6.0 Hz, 1H), 4.34 (ddd, *J*= 9.0, 5.5, 4.0 Hz, 1H), 4.18 (q, *J*= 7.0 Hz, 2H), 3.78 (ddd, *J*= 9.0, 8.0, 6.5 Hz, 1H), 3.07-2.99 (m, 2H), 1.99-1.87 (m, 2H), 1.85-1.75 (m, 2H), 1.73-1.51 (m, 2H), 1.29 (t, *J*= 7.0 Hz, 3H). ^{13}C-NMR ($CDCl_3$, ppm) δ 166.60 (CO), 143.37 (CH), 121.82 (CH), 86.50 (CH), 71.31 (CH_2), 60.19 (CH_2), 35.74 (CH_2), 32.72 (CH_2), 31.84 (CH_2), 24.69 (CH_2), 14.27 (CH_2). LRMS m/e 230 (M^+), 223, 213, 201, 185, 170, 157, 152, 141, 124, 115, 104, 99, 89, 81, 73, 69, 61, 55, 41. HRMS calcd $C_{11}H_{18}O_3S$ 230.0977; obs 230.0784. Anal. Calcd for $C_{11}H_{18}O_3S$: C, 57.36; H, 7.88; S, 13.92. Found: C, 57.14, H, 7.81; S, 13.71.

Ethyl 6-(*N*-phenylthiazolidin-2-yl)-2-hexenoate (1e). A mixture of **8** (85 mg, 0.50 mmol) and 2-mercaptoethylphenylamine (80 mg, 0.50 mmol) in anhydrous benzene (2 mL) was stirred for 1 h at room temperature. Evaporation of the solvent *in vacuo* gave **1e** (160 mg, quant.), which was used without further purification because of its instability. ^{1}H-NMR (90 MHz, $CDCl_3$) δ 7.26-6.28 (m, 6H), 5.80 (dt, *J*= 16.0 Hz, 1.5 Hz 1H), 4.80 (dd, *J*= 6.0 Hz, 4.5 Hz, 1H), 4.17 (q, *J*= 7.0 Hz, 2H) , 3.80-2.44 (m, 4H), 2.38-2.02 (m, 2H), 2.02 -1.39 (m, 4H), 1.27 (t, *J*= 7.0 Hz, 3H).

Ethyl 6-(*N*,*N*-diphenylimidazolidin-2-yl)-2-hexenoate (1f). A mixture of **8** (85 mg, 0.50 mmol) and 2-mercaptoethylphenylamine (106 mg, 0.50 mmol) in anhydrous benzene (2 mL) was stirred for 1 h at room temperature. Evaporation of the solvent *in vacuo* gave **1f** (180 mg, quant.), which was used without further purification. ^{1}H-NMR (100 MHz, $CDCl_3$) δ 7.60-7.10 (m, 4H), 7.00-6.50 (m, 7H), 5.70 (dt, *J*= 16.0 Hz, *J*= 1.5 Hz 1H), 5.40 (t, *J*= 2.0 Hz, 1H), 4.12 (q, *J*= 7.0 Hz, 2H) 3.80-3.60 (m, 4H), 2.20-1.90 (m, 4H), overlapping peaks 1.96-1.20 (m) and 1.25 (t, *J*= 7.0 Hz, total 5H).

Ethyl 8-(2-tetrahydropyranyl)oxy-2-octenoate (9). A THF solution of diborane (0.2 M, 10.8 mL, 6.5 mmol) was added to a solution of **6** (1.0 g, 5.4 mmol) in THF (10 mL) at 0 °C and the mixture was stirred for 1 h at room temperature. Then water (1.92 mL), 3N NaOH (1.74 mL) and 30% hydrogen peroxide (1.74 mL) were added to the mixture successively, and the mixture was stirred overnight. After the layers were separated, the aqueous layer was extracted with ether. The combined organic layers were washed with water, dried and concentrated *in vacuo*. Purification of the residue by chromatography on silica gel (ether:*n*-hexane=1:2) gave 6-(2-tetrahydropyranyl)oxy-1-hexanol (0.94 g, 86%). IR (neat) 3350, 2875, 2800, 1440, 1420 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 4.57 (dd, *J*= 5.0, 3.0 Hz, 1H), 3.87 (ddd, *J*= 10.0, 6.0, 3.0 Hz, 1H), 3.74 (dt, *J*= 7.5, 6.0 Hz, 1H), 3.64 (t, *J*= 6.0 Hz, 2H), 3.54-3.47 (m, 1H), 3.39 (dt, *J*= 7.5, 6.0 Hz, 1H), 1.88-1.78 (m, 1H), 1.76-1.66 (m, 1H), 1.66-1.46 (m, 8H), 1.46-1.35 (m, 5H). ^{13}C-NMR ($CDCl_3$, ppm) δ 98.94 (CH), 67.54 (CH_2), 62.93 (CH_2), 62.44 (CH_2), 32.74 (CH_2), 30.82 (CH_2), 29.72 (CH_2), 26.06 (CH_2), 25.57 (CH_2), 25.51 (CH_2), 19.75 (CH). LRMS m/e 201 (M^+-1), 184, 144, 136, 129, 117, 101, 85, 71, 67, 55, 41. HRMS calcd $C_{11}H_{22}O_3$ 202.1570; obs 202.1587.

A mixture of 6-(2-tetrahydropyranyl)oxy-1-hexanol (3.6 g, 17.8 mmol), pyridinium chlorochromate (5.75 g, 26.7 mmol), and Celite (6 g) in anhydrous CH_2Cl_2 (100 mL) was stirred for 2 h at room temperature. The mixture was diluted with ether and filtered through a Florisil column. Concentration of the filtrate gave a residue which was purified by chromatography on silica gel (ether:*n*-hexane=1:4) affording 6-(2-tetrahydropy-

ranyl)oxyhexanal (2.41 g, 68%). IR (neat) 2900, 2825, 2700, 1720 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 9.77 (t, *J*= 2.0 Hz, 1H), 4.57 (dd, *J*= 5.0, 3.0 Hz, 1H), 3.86 (ddd, *J*= 11.5, 7.0, 3.0 Hz, 1H), 3.74 (dt, *J*= 10.0, 7.0 Hz, 1H), 3.53-3.46 (m, 1H), 3.39 (dt, *J*= 10.0, 7.0 Hz, 1H), 2.44 (ddd, *J*= 7.0, 2.0 Hz, 2H), 1.88-1.77 (m, 1H), 1.75-1.47 (m, 9H), 1.47-1.37 (m, 2H). ^{13}C-NMR ($CDCl_3$, ppm) δ 202.61 (CO), 98.96 (CH), 67.28 (CH_2), 62.42 (CH_2), 43.86 (CH_2), 30.78 (CH_2), 29.52 (CH_2), 25.93 (CH_2), 25.49 (CH_2), 21.97 (CH_2), 19.72 (CH_2). LRMS m/e 199 (M^+-1), 170, 156, 149, 129, 115, 99, 85, 81, 67, 55, 41. HRMS calcd $C_{11}H_{20}O_3$ 200.1413; obs 200.1396. Anal. Calcd for $C_{11}H_{20}O_3$: C, 65.97; H, 10.07. Found: C, 65.56, H, 10.30.

A mixture of 6-(2-tetrahydropyranyl)oxyhexanal (2.4 g, 12 mmol) and (carbethoxymethylene)triphenylphosphorane (6.3 g, 18 mmol) in anhydrous CH_2Cl_2 (10 mL) was stirred for 6 h at room temperature. The solvent was removed *in vacuo* and the residue was purified by chromatography on silica gel (ethyl acetate:*n*-hexane=1:4) affording **9** (2.9 g, 90%). IR (neat) 2925, 2850, 1720, 1650 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 6.96 (dt, *J*= 15.5, 7.0 Hz, 1H), 5.81 (dt, *J*= 15.5, 2.0 Hz, 1H), 4.57 (dd, *J*= 5.0, 3.0 Hz, 1H), 4.18 (q, *J*= 7.0 Hz, 2H), 3.86 (ddd, *J*= 12.0, 8.0, 3.0 Hz, 1H), 3.73 (dt, *J*= 10.0, 7.0 Hz, 1H), 3.53-3.47 (m, 1H), 3.38 (dt, *J*= 10.0, 7.0 Hz, 1H), 2.21 (dtd, *J*= 7.0, 7.0, 2.0 Hz, 2H), 1.88-1.77 (m, 1H), 1.75-1.66 (m, 1H), 1.66-1.35 (m, 10H), 1.28 (t, *J*= 7.0 Hz, 3H). ^{13}C-NMR ($CDCl_3$, ppm) δ 166.75 (C), 149.18 (CH), 121.42 (CH), 98.94 (CH), 67.42 (CH_2), 62.42 (CH_2), 60.13 (CH_2), 32.12 (CH_2), 30.80 (CH_2), 29.52 (CH_2), 27.89 (CH_2), 25.84 (CH_2), 25.51 (CH_2), 19.73 (CH_2), 14.30 (CH_3). LRMS m/e 269 (M^+-1), 241, 225, 215, 197, 187, 170, 156, 141, 127, 101, 95, 85, 81, 67, 55, 41. HRMS calcd $C_{15}H_{26}O_4$ 270.1857; obs 270.1832. Anal. Calcd for $C_{15}H_{26}O_4$: C, 66.63; H, 9.69. Found: C, 66.54, H, 9.77.

Ethyl 7-(2-dithianyl)-2-heptenoate (2a). A mixture of **9** (290 mg, 1.07 mmol) and a catalytic amount of *p*-toluenesulfonic acid in anhydrous methanol (3 mL) was stirred for 3 h at room temperature. Usual workup and chromatography on silica gel (ethyl acetate:*n*-hexane=1:1) gave ethyl 8-hydroxy-2-octenoate (164 mg, 82%). IR (neat) 3400, 2930, 1720, 1700, 1650 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 6.96 (dt, *J*= 16.0, 7.0 Hz, 1H), 5.82 (dt, *J*= 16.0, 1.5 Hz, 1H), 4.18 (q, *J*= 7.0 Hz, 2H), 3.64 (t, *J*= 7.0 Hz, 2H), 2.22 (dtd, *J*= 7.0, 7.0, 1.5 Hz, 2H), 1.58 (broad quintet, *J*= 7.0 Hz, 2H), 1.54-1.35 (m, 4H), 1.29 (t, *J*= 7.0 Hz, 3H). ^{13}C-NMR ($CDCl_3$, ppm) δ 166.75 (CO), 149.03 (CH), 121.47 (CH), 62.75 (CH_2), 60.17 (CH_2), 32.48 (CH_2), 32.12 (CH_2), 27.84 (CH_2), 25.31 (CH_2), 14.27 (CH_3). LRMS m/e 187 (M^+), 168, 156, 141, 127, 112, 107, 99, 95, 86, 81, 73, 67, 61, 55, 41. HRMS calcd $C_{10}H_{18}O_3$ 186.1256; obs 186.1266. Anal. Calcd for $C_{10}H_{18}O_3$: C, 64.45; H, 9.74. Found: C, 64.36, H, 9.68.

A mixture of ethyl 8-hydroxy-2-octenoate (148 mg, 0.80 mmol), pyridinium chlorochromate (540 mg, 1.6 mmol), and Celite (540 mg) in anhydrous CH_2Cl_2 (20 mL) was stirred for 2 h at room temperature. The mixture was diluted with ether and filtered through a Florisil column. Concentration of the filtrate gave a residue which was purified by chromatography on silica gel (ether:*n*-hexane=1:1) affording ethyl 7-formyl-2-heptenoate (120 mg, 81%). IR (neat) 2950, 1720, 1660 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 9.77 (t, *J*= 1.5 Hz, 1H), 6.93 (dt, *J*= 15.5, 7.0 Hz, 1H), 5.82 (dt, 15.5, 1.5 Hz, 1H), 4.18 (q, *J*= 7.0 Hz, 2H), 2.46 (td, 7.0, 1.5 Hz, 2H), 2.23 (dtd, *J*= 7.0, 7.0, 1.4 Hz, 2H), 1.72-1.62 (m, 2H), 1.55-1.46 (m, 2H), 1.29 (t, *J*= 7.0 Hz, 3H). ^{13}C-NMR ($CDCl_3$, ppm) δ 202.05 (CHO), 166.57 (COO), 148.24 (CH), 121.85 (CH), 60.20 (CH), 43.58 (CH_2), 31.84 (CH_2), 27.51 (CH_2), 21.53 (CH_2), 14.27 (CH_3). LRMS m/e 185 (M^++1), 156, 138, 127, 121, 110, 99, 94, 86, 81, 73, 67, 60, 55, 41. HRMS calcd $C_{10}H_{16}O_3$ 184.1100; obs 184.1111.

A mixture of ethyl 7-formyl-2-heptenoate (400 mg, 2.17 mmol), 1,3-propanedithiol (0.22 mL, 2.20 mmol), and a catalytic amount of BF_3•OEt_2 in anhydrous CH_2Cl_2 (30 mL) was stirred for 1 h at room temperature. Usual workup and chromatography on silica gel (ether:*n*-hexane=1:9) gave **2a** (482 mg, 81%). IR (neat) 2975, 1730, 1660 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 6.94 (dt, *J*= 15.0, 7.0 Hz, 1H), 5.81 (dt, *J*= 15.0, 1.5 Hz, 1H), 4.71 (q, *J*= 7.0 Hz, 2H), 4.04 (t, *J*= 7.0 Hz, 1H), 2.88 (ddd, *J*= 14.0, 11.0, 3.0 Hz, 2H), 2.82 (ddd, *J*= 14.0, 4.0, 4.0 Hz, 2H), 2.21 (dtd, *J*= 7.0, 7.0, 1.5 Hz, 2H), 2.12 (dtt, *J*= 14.0, 4.0, 3.0 Hz, 1H), 1.86 (dtt, *J*= 14.0, 11.0, 4.0 Hz, 1H), 1.76 (broad q, *J*= 7.0 Hz, 1H), 1.60-1.44 (m, 5H), 1.28 (t, *J*= 7.0 Hz, 3H). ^{13}C-NMR ($CDCl_3$, ppm) δ 166.24 (CO), 148.39 (CH), 121.29 (CH), 59.78 (CH_2), 47.07 (CH), 34.89 (CH_2), 31.60 (CH_2), 30.14 (CH_2), 27.34 (CH_2), 25.86 (CH_2), 25.73 (CH_2). LRMS m/e 274 (M^+), 229, 199, 186, 166, 119, 106, 99, 93, 85, 73, 59, 55, 45, 41. HRMS calcd $C_{13}H_{22}O_2S_2$ 274.1056; obs 274.1073.

7-*tert*-Butyldimethylsilyloxy-1-heptanol (11). A mixture of **10** (530 mg, 3.40 mmol) and a catalytic amount of 5% palladium carbon in methanol (20 mL) was stirred overnight at room temperature under hydrogen atmosphere. The mixture was filtered and the solvent was evaporated to give methyl 7-hydroxyheptanoate (480 mg, 88%), which was used for next step without further purification. IR (neat) 3350,

2900, 1720 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 3.67 (s, 3H), 3.64 (t, *J*= 7.0 Hz, 2H), 2.32 (t, *J*= 7.0 Hz, 2H), 1.70-1.50 Hz, (m, 5H), 1.44-1.30 (m, 4H). ^{13}C-NMR ($CDCl_3$, ppm) δ 174.23 (CO), 62.84 (CH_2), 51.45 (CH_3), 33.98 (CH_2), 32.54 (CH_2), 28.88 (CH_2), 25.39 (CH_2), 24.86 (CH_2). LRMS m/e 161 (M^++1), 143, 130, 111, 101, 93, 87, 83, 74, 69, 59, 55, 43. HRMS calcd $C_8H_{16}O_3$ 160.1100; obs 160.1098.

A mixture of methyl 7-hydroxyheptanoate (1.16 g, 7.25 mmol), *tert*-butyldimethylchlorosilane (1.2 g, 8.00 mmol), and imidazole (0.5 g, 7.36 mmol) in DMF (10 mL) was stirred for 3 h at room temperature. Usual workup and chromatography on silica gel (ethyl acetate:*n*-hexane=1:9) gave methyl 7-*tert*-butyldimethylsilyloxyheptanoate (1.67 g, 84%). IR (neat) 2950, 2875, 1745 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 3.62 (s, 3H), 3.55 (t, *J*= 6.5 Hz, 2H), 2.26 (t, *J*= 7.0 Hz, 2H), 1.65-1.53 (m, 2H), 1.52-1.42 (m, 2H), 1.34-1.24 (m, 4H), 0.89 (s, 9H), 0.41 (s, 6H). ^{13}C-NMR ($CDCl_3$, ppm) δ 174.25 (CO), 63.13 (CH_2), 51.41(CH), 34.05 (CH_2), 32.66 (CH_2), 28.97 (CH_2), 25.99 (CH_3), 25.49 (CH_2), 24.96 (CH_2), 18.36 (C), -5.27 (CH_3). LRMS m/e 275 (M^++1), 259, 243, 227, 217, 185, 155, 143, 129, 115, 101, 89, 83, 75, 69, 59, 55, 47, 41. HRMS calcd $C_{14}H_{31}O_3Si$ 275.2042; obs 275.2045.

A mixture of methyl 7-*tert*-butyldimethylsilyloxyheptanoate (500 mg, 1.82 mmol) and lithium aluminum hydride (50 mg, 1.35 mmol) in ether (15 mL) was stirred at 0 °C. Usual workup afforded **11** (403.2 mg, 90%). IR (neat) 3350, 2950, 2875, 1460 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 3.63 (t, *J*= 6.5 Hz, 2H), 3.59 (t, *J*= 7.0, 2H), 1.61-1.46 (m, 5H), 1.40-1.26 (m, 5H), 0.89 (s, 9H), 0.41 (s, 6H). ^{13}C-NMR ($CDCl_3$, ppm) δ 63.28 (CH_2), 63.08 (CH_2), 32.83 (CH_2), 32.77 (CH_2), 29.26 (CH_2), 26.01 (CH_2), 25.82 (CH_3), 25.77 (CH_2), 18.40 (C), 5.25 (CH_3). LRMS m/e 247 (M^++1), 189, 171, 143, 129, 115, 105, 97, 93, 89, 75, 69, 55. HRMS calcd $C_{13}H_{30}O_2Si$ 246.2016; obs 246.2039.

Ethyl 8-(2-dithianyl)-2-octenoate (2b). A mixture of **11** (400 mg, 1.63 mmol), pyridinium chlorochromate (700 mg, 3.26 mmol), and Celite (700 mg) in anhydrous CH_2Cl_2 (30 mL) was stirred for 2 h at room temperature. The mixture was diluted with ether and filtered through a Florisil column. Concentration of the filtrate gave 7-*tert*-butyldimethylsilyloxyheptanal (300 mg, 76%), which was used for next step without further purification. IR (neat) 2925, 2850, 1730 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 9.76 (t, *J*= 2.0 Hz, 1H), 3.60 (t, *J*= 6.5 Hz, 2H), 2.42 (td, *J*= 7.0, 2.0 Hz, 2H), 1.69-1.59 (m, 2H), 1.56-1.47 (m, 2H), 1.40-1.30 (m, 4H), 0.89 (s, 9H), 0.04 (s, 6H). ^{13}C-NMR ($CDCl_3$, ppm) δ 202.82 (CHO), 63.10 (CH_2), 43.87 (CH_2), 32.63 (CH_2), 28.99 (CH_2), 25.99 (CH_3), 25.62 (CH_2), 22.11 (CH_2), 18.38 (C), -5.25 (CH_3). LRMS m/e 243 (M^+-1), 227, 203, 185, 129, 105, 93, 83, 75, 55, 47, 41. HRMS calcd $C_{13}H_{28}O_2Si$ 244.1859; obs 244.1877.

A mixture of 7-*tert*-butyldimethylsilyloxyheptanal (300 mg, 1.28 mmol) and (carbethoxymethylene)-triphenylphosphorane (680 mg, 1.92 mmol) in anhydrous CH_2Cl_2 (30 mL) was stirred for 6 h at room temperature. The solvent was removed *in vacuo* and the residue was purified by chromatography on silica gel (ethyl acetate:*n*-hexane=1:9) affording ethyl 9-*tert*-butyldimethylsilyloxy-2-nonenate (390 mg, quant.). IR (neat) 2950, 2875, 1720, 1655 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 6.96 (dt, *J*= 15.5, 7.0 Hz, 1H), 5.81 (dt, *J*= 15.5, 1.5 Hz, 1H), 4.18 (q, *J*= 7.0 Hz, 2H), 3.59 (t, *J*= 6.5 Hz, 2H), 2.19 (ddd, *J*= 7.0, 7.0, 1.5 Hz, 2H), 1.55-1.42 (m, 4H), 1.37-1.30 (m, 4H), 1.28 (t, *J*= 7.0, 3H), 0.88 (s, 9H), 0.05 (s, 6H). ^{13}C-NMR ($CDCl_3$, ppm) δ 166.81 (CO), 149.36 (CH), 121.33 (CH), 63.39 (CH_2), 60.13 (CH_2), 32.74 (CH_2), 32.15 (CH_2), 28.95 (CH_2), 28.04 (CH_2), 25.99 (CH_3), 25.62 (CH_2), 18.38 (C), 14.30 (CH3), -5.25 (CH_3). LRMS m/e 315 (M^++1), 299, 257, 229, 211, 167, 155, 129, 115, 109, 103, 99, 95, 85, 81, 75, 67, 59, 55, 45. HRMS calcd $C_{17}H_{34}O_3Si$ 314.2278; obs 314.2256.

A THF solution of tetra-*n*-butylammonium fluoride (1 M solution, 1 mL, 1 mmol) was added to ethyl 9-*tert*-butyldimethylsilyloxy-2-nonenate (100 mg, 0.32 mmol) and the mixture was stirred for 2 h at room temperature. Usual workup and chromatography on silica gel (ethyl acetate:*n*-hexane=1:1) gave ethyl 9-hydroxy-2-nonenate (61 mg, 93%). IR (neat) 3400, 2950, 2860, 1720, 1700, 1650 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 6.96 (dt, *J*= 15.5, 7.0 Hz, 1H), 5.81 (dt, *J*= 15.5, 1.5 Hz, 1H), 4.18 (q, *J*= 7.0, 2H), 3.64 (t, *J*= 6.5 Hz, 2H), 2.20 (ddd, *J*= 7.0, 7.0, 1.5 Hz, 2H), 1.63-1.52 (m, 2H), 1.52-1.42 (m, 3H), 1.42-1.32 (m, 4H), 1.28 (t, *J*= 7.0, 3H). ^{13}C-NMR ($CDCl_3$, ppm) δ 166.79 (CO), 149.23 (CH), 121.40 (CH), 62.95 (CH_2), 60.17 (CH_2), 32.66 (CH_2), 32.10 (CH_2), 28.93 (CH_2), 28.00 (CH_2), 25.55 (CH_2), 14.30 (CH_3). LRMS m/e 201 (M^++1), 182, 170, 155, 136, 127, 109, 99, 94, 86, 81, 73, 67, 55, 41. HRMS calcd $C_{11}H_{20}O_3$ 200.1413; obs 200.1392.

A mixture of ethyl 9-hydroxy-2-nonenate (57.4 mg, 0.29 mmol), pyridinium chlorochromate (150 mg, 0.70 mmol), and Celite (150 mg) in anhydrous CH_2Cl_2 (2 mL) was stirred for 2 h at room temperature. The mixture was diluted with ether and filtered through a Florisil column. Concentration of the filtrate gave a

residue which was purified by chromatography on silica gel (ethyl acetate:*n*-hexane=1:3) affording ethyl 8-formyl-2-octenoate (43.3 mg, 77%). IR (neat) 2950, 1720, 1660 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 9.77 (t, *J*= 1.5 Hz, 1H), 6.94 (dt, *J*= 15.5, 7.0 Hz, 1H), 5.81 (dt, *J*= 15.5, 1.0 Hz, 1H), 4.18 (q, *J*= 7.0 Hz, 2H), 2.41 (td, *J*= 7.0, 1.5 Hz, 2H), 2.21 (ddd, *J*= 7.0, 7.0, 1.5 Hz, 2H), 1.65 (quintet, *J*= 7.0, 2H), 1.49 (broad quintet, *J*= 7.0, 2H), 1.41-1.32 (m, 2H), 1.29 (t, *J*= 7.0, 3H). ^{13}C-NMR ($CDCl_3$, ppm) δ 202.43 (CHO), 166.68 (CO_{OEt2}), 148.79 (CH), 121.60 (CH), 60.19 (CH_2), 43.75 (CH_2), 31.91 (CH_2), 28.62 (CH_2), 27.78 (CH_2), 21.86 (CH_2), 14.28 (CH_3). LRMS m/e 199 (M^++1), 180, 170, 153, 135, 127, 107, 99, 95, 88, 81, 73, 67, 60, 55, 41. HRMS calcd $C_{11}H_{18}O_3$ 198.1256; obs 198.1244.

A mixture of ethyl 8-formyl-2-octenoate (470 mg, 2.37 mmol), 1,3-propanedithiol (0.22 mL, 2.20 mmol), and a catalytic amount of BF_3•OEt_2 in anhydrous CH_2Cl_2 (20 mL) was stirred for 1 h at room temperature. Usual workup and chromatography on silica gel (ether:*n*-hexane=1:4) gave **2b** (550 mg, 81%). IR (neat) 2950, 1720, 1660 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 4.18 (q, *J*= 7.0 Hz, 2H), 4.04 (t, *J*= 7.0 Hz, 1H), 2.88 (ddd, *J*= 14.0, 11.0, 3.0 Hz, 2H), 2.82 (ddd, *J*= 14.0, 4.0, 4.0 Hz, 2H), 2.20 (tdd, *J*= 7.0, 7.0, 1.5 Hz, 2H), 2.12 (dtt, *J*= 14.0, 4.0, 3.0 Hz, 1H), 1.86 (dtt, *J*= 14.0, 11.0, 4.0 Hz, 1H), 1.74 (broad quartet, *J*= 7.0 Hz, 2H), 1.57-1.42 (m, 5H), 1.39-1.31 (m, 3H), 1.28 (t, *J*= 7.0 Hz, 3H). ^{13}C-NMR ($CDCl_3$, ppm) δ 166.71 (CO), 149.05 (CH), 121.47 (CH), 60.13 (CH_2), 47.55 (CH), 35.33 (CH_2), 32.02 (CH_2), 30.50 (CH_2), 28.69 (CH_2), 27.76 (CH_2), 26.34 (CH_2), 26.04 (CH_2), 16.30 (CH_3). LRMS m/e 288 (M^+), 259, 243, 225, 213, 200, 180, 167, 145, 139, 119, 106, 93, 87, 73, 67, 55, 45, 41. HRMS calcd $C_{14}H_{24}O_2S_2$ 288.1219; obs 288.1191.

Ethyl 4-methyl-7-(2-tetrahydropyranyl)oxy-2-heptenoate (12). A mixture of **7** (2.14 g, 11.5 mmol) and *sec*-butylamine (2.3 mL, 23 mmol) was stirred overnight in anhydrous benzene (10 mL) in the presence of molecular sieves 4A at room temperature. Concentration of the mixture *in vacuo* gave crude enamine (2.5 g, 11 mmol), which was used without purification. A solution of *n*-butyllithium in hexane (1.5 M, 11.3 mL, 27 mmol) was added to a solution of diisopropylamine (2.4 mL, 27 mmol) in THF (20 mL) at -78 °C and the mixture was stirred for 10 min at -78 °C. After the mixture was warmed to 0 °C for 10 min, HMPA (1.91 mL, 11 mmol) and a solution of the crude enamine in THF (2 mL) were added. The mixture was cooled to -78 °C and stirred over 30 min, and then methyl iodide (0.81 mL, 13 mmol) was added. The mixture was gradually warmed to room temperature for 30 min. The reaction was quenched by addition of saturated NH_4Cl solution, and THF was evaporated. The aqueous solution was extracted with ether. The combined organic layers were washed with saturated NaCl solution, dried and concentrated *in vacuo*. Purification of the residue by chromatography on silica gel (ether:*n*-hexane=1:2) gave 2-methyl-5-(2-tetrahydropyranyl)-oxypentanal (1.9 g, 95%). IR (neat) 2950, 1730, 1460 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 9.64 (dd, *J*= 2.0, 1.0 Hz, 1H), 4.57 (dd, *J*= 4.5, 3.0 Hz, 1H) 3.86 (ddd, *J*= 11.0, 7.0, 3.0 Hz, 1H), 3.76 (dt, *J*= 10.0, 6.5 Hz, 1H), 3.54-3.47 (m, 1H), 3.40 (dt, *J*= 10.0, 6.5 Hz, 1H), 2.38 (dqd, *J*= 7.0, 7.0, 1.0 Hz, 1H), 1.90-1.76 (m, 2H), 1.76-1.40 (m, 8H), 1.12 (d, *J*= 7.0, 3H). ^{13}C-NMR ($CDCl_3$, ppm) δ 205.01 (CO), 98.98 (CH), 67.23 (CH_2), 62.44 (CH_2), 46.12 (CH), 30.76 (CH_2), 27.29 (CH_2), 27.18 (CH_2), 25.49 (CH_2), 19.68 (CH_2), 13.37 (CH_3). LRMS m/e 200 (M^+), 183, 149, 143, 129, 115, 99, 85, 81, 69, 57, 43. HRMS calcd $C_{11}H_{20}O_3$ 200.1413; obs 200.1402.

A mixture of 2-methyl-5-(2-tetrahydropyranyl)oxypentanal (1.90 g, 9.5 mmol) and (carbethoxymethylene)triphenylphosphorane (5.0 g, 14.3 mmol) in anhydrous CH_2Cl_2 (23 mL) was stirred for 6 h at room temperature. After the solvent was removed *in vacuo*, and then the residue was purified by chromatography on silica gel (ether:*n*-hexane=1:2) affording **12** (2.33 g, 91%). IR (neat) 2950, 1730 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 9.64 (dd, *J*= 2.0, 1.0 Hz, 1H), 4.57 (dd, *J*= 4.5, 3.0 Hz, 1H) 3.86 (ddd, *J*= 11.0, 7.0, 3.0 Hz, 1H), 3.76 (dt, *J*= 10.0, 6.5 Hz, 1H), 3.54-3.47 (m, 1H), 3.40 (dt, *J*= 10.0, 6.5 Hz, 1H), 2.38 (dqd, *J*= 7.0, 7.0, 1.0 Hz, 1H), 1.90-1.76 (m, 2H), 1.76-1.40 (m, 8H), 1.12 (d, *J*= 7.0, 3H). ^{13}C-NMR ($CDCl_3$, ppm) δ 205.01 (CO), 98.98 (CH), 67.23 (CH_2), 62.44 (CH_2), 46.12 (CH), 30.76 (CH_2), 27.29 (CH_2), 27.18 (CH_2), 25.49 (CH_2), 19.68 (CH_2), 13.37 (CH_3). LRMS m/e 200 (M^+), 183, 149, 143, 129, 115, 99, 85, 81, 69, 57, 43. HRMS calcd $C_{11}H_{20}O_3$ 200.1413; obs 200.1402.

Ethyl 6-(2-dithianyl)-4-methyl-2-hexenoate (3a). A mixture of **12** (2.30 g, 8.52 mmol) and a catalytic amount of *p*-toluenesulfonic acid in anhydrous methanol (3 mL) was stirred for 3 h at room temperature. Usual workup and chromatography on silica gel (ethyl acetate:*n*-hexane=1:1) gave ethyl 7-hydroxy-4-methyl-2-heptenoate (1.31 g, 82%). IR (neat) 3400, 2925, 1710, 1650 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 6.86 (dd, *J*= 15.5, 8.0 Hz, 1H), 5.79 (dd, *J*= 15.5, 1.0 Hz, 1H), 4.18 (q, *J*= 7.0 Hz, 2H), 3.64 (broad t, *J*= 6.0 Hz, 2H), 2.32 (dqd, *J*= 7.0, 7.0, 1.0 Hz, 2H), 1.61-1.51 (m, 2H), 1.51-1.42 (m, 2H), 1.29

(t, J= 7.0 Hz, 3H), 1.07 (d, J= 7.0 Hz, 3H). ^{13}C-NMR ($CDCl_3$, ppm) δ 166.88 (CO), 154.06 (CH), 120.02 (CH), 62.86 (CH_2), 60.22 (CH_2), 36.36 (CH), 32.13 (CH_2), 30.36 (CH_2), 19.48 (CH_3), 14.28 (CH_3). LRMS m/e 187 (M^++1), 168, 156, 141, 123, 113, 101, 95, 88, 85, 81, 73, 67, 55, 43. HRMS calcd $C_{10}H_{18}O_3$ 186.1256; obs 186.1241.

A mixture of ethyl 7-hydroxy-4-methyl-2-heptenoate (1.8 g, 10 mmol), pyridinium chlorochromate (3.00 g, 24 mmol), and Celite (3 g) in anhydrous CH_2Cl_2 (20 mL) was stirred for 2 h at room temperature. The mixture was diluted with ether and filtered through a Florisil column. Concentration of the filtrate gave a residue which was purified by chromatography on silica gel (ether:*n*-hexane=1:4) affording ethyl 6-formyl-4-methyl-2-hexenoate (1.1 g, 84%). IR (neat) 2950, 1710, 1640 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 9.77 (t, J= 1.5 Hz, 1H), 6.80 (dd, J= 10.5, 8.0 Hz, 1H), 5.80 (dd, J= 10.0, 1.0 Hz, 1H), 4.19 (q, J= 7.0 Hz, 2H), 2.45 (dddd, J= 9.0, 8.0, 1.5, 1.0 Hz, 2H), 2.35 (dqdd, J= 8.0, 7.0, 1.5, 1.0 Hz, 1H), 1.80-1.62 (m, 2H), 1.30 (t, J= 7.0 Hz, 3H), 1.09 (d, J= 7.0, 3H). ^{13}C-NMR ($CDCl_3$, ppm) δ 201.68 (CHO), 166.61 (CH), 152.76 (CH), 120.81 (CH), 60.35 (CH_2), 41.53 (CH_2), 35.92 (CH), 27.91 (CH_2), 19.44 (CH_3), 14.27 (CH_3). LRMS m/e 185 (M^++1), 166, 156, 139, 128, 121, 111, 99, 93, 81, 67, 60, 55, 41. HRMS calcd $C_{10}H_{16}O_3$ 184.1100; obs 184.1096.

A mixture of ethyl 6-formyl-4-methyl-2-hexenoate (400 mg, 2.17 mmol), 1,3-propanedithiol (0.22 mL, 2.20 mmol), and a catalytic amount of BF_3•OEt_2 in anhydrous CH_2Cl_2 (30 mL) was stirred for 1 h at room temperature. Usual workup and chromatography on silica gel (ether:*n*-hexane=1:9) gave **3a** (293 mg, 50%). IR (neat) 2950, 1720, 1650 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 6.83 (dd, J= 15.5, 8.0 Hz, 1H), 5.79 (dd, J= 15.5, 1.0 Hz, 1H), 4.13 (q, J= 7.0 Hz, 2H), 4.01 (t, J= 6.5 Hz, 1H), 2.88 (ddd, J= 15.0, 10.5, 3.0 Hz, 2H), 2.82 (ddd, J= 15.0, 4.0, 4.0 Hz, 2H), 2.32 (dqd, J= 7.0 Hz, 1H), 2.12 (dtt, J= 14.0, 4.0, 3.0 Hz, 1H), 1.86 (dtt, J= 14.0, 10.5, 4.0 Hz, 1H), 1.78-1.70 (m, 2H), 1.64-1.56 (m, 2H), 1.29 (t, J= 7.0 Hz, 3H), 1.07 (d, J= 7.0 Hz, 3H). ^{13}C-NMR ($CDCl_3$, ppm) δ 166.73 (CO), 153.47 (CH), 120.34 (CH), 60.24 (CH_2), 47.57 (CH), 36.32 (CH), 33.14 (CH_2), 32.88 (CH_2), 30.47 (CH_2), 26.01 (CH_2), 19.42 (CH_3), 14.28 (CH_3). LRMS m/e 274 (M^+), 229, 201, 166, 153, 145, 132, 119, 106, 93, 87, 81, 74, 69, 55, 45, 41. HRMS calcd $C_{13}H_{22}O_2S_2$ 274.1063; obs 274.1056.

6-(2-Tetrahydropyranyl)oxyhexan-2-one (13). A solution of methyllithium in ether (1.4 M, 25 mL, 35 mmol) was added to a solution of 5-(2-tetrahydropylanyl)oxypentanal (4.99 g, 26.8 mmol) in ether (40 mL) at -78 °C and the mixture was gradually warmed to room temperature with stirring. The reaction was quenched by addition of saturated NH_4Cl solution, and the separated aqueous layer was extracted with ether. The combined organic layers were washed with saturated NaCl solution, dried and concentrated *in vacuo*. Purification of the residue by chromatography on silica gel (ether:*n*-hexane=3:1) gave 6-(2-tetrahydropyranyl)oxy-2-hexanol (1.80 g, 33%). IR (neat) 3400, 2950, 1710 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 4.57 (dd, J= 5.0, 3.0 Hz, 1H), 3.87 (ddd, J= 11.0 , 7.0, 3.0 Hz, 1H), 3.82 (dq, J= 6.0, 6.0 Hz, 1H), 3.75 (dtd, J= 11.5, 7.0, 2.0 Hz, 1 H), 3.54-3.47 (m, 1H) 3.40 (dt, J= 9.5, 7.5 Hz, 1H), 1.88-1.77 (m, 1H), 1.76- 1.68 (m, 1H) 1.68-1.36 (m, 10H) 1.19 (d, J= 7.0 Hz, 3H). ^{13}C-NMR ($CDCl_3$, ppm) δ 98.98 (CH), 68.03 (CH), 67.52 (CH_2), 62.44 (CH_2), 39.10 (CH_2), 30.80 (CH_2), 29.66 (CH_2), 25.51 (CH_2), 22.48 (CH_2), 19.73 (CH_2). LRMS m/e 203 (M^++1), 203, 185, 117, 101, 85, 45. HRMS calcd $C_{11}H_{23}O_3$ 203.1648; obs 203.1645.

A mixture of 6-(2-tetrahydropyranyl)oxy-2-hexanol (1.8 g, 8.36 mmol), pyridinium chlorochromate (3.0 g, 24 mmol) and Celite (3.0 g) in anhydrous CH_2Cl_2 (50 mL) was stirred for 2 h at room temperature. The mixture was diluted with ether and filtered through a Florisil column. Concentration of the filtrate gave **13** (1.75 g, 98%), which was used without further purification. IR (neat) 2950, 1710 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 4.57 (dd, J= 5.0, 3.0 Hz, 1H), 3.86 (ddd, J= 12.0, 7.0, 3.0 Hz, 1H), 3.75 (dt, J= 10.0 Hz, 1H), 3.54-3.46 (m, 1H) 3.39 (dt, J= 10.0, 6.5 Hz, 1H), 2.47 (t, J= 7.5 Hz, 2H), 2.14 (s, 3H), 1.89-1.76 (m, 2H), 1.76-1.45 (m, 10H). ^{13}C-NMR ($CDCl_3$, ppm) δ 208.91 (CO), 98.92 (CH), 67.15 (CH_2), 43.47 (CH_2), 30.76 (CH_2), 29.87 (CH_3), 29.21 (CH_2), 25.49 (CH_2), 20.70 (CH_2), 19.68 (CH_2). LRMS m/e 203 (M^++1), 201, 115, 101, 99, 85, 43. HRMS calcd $C_{11}H_{21}O_3$ 201.1491; obs 201.1478.

Ethyl 3-methyl-7-(2-tetrahydropyranyl)oxy-2-heptenoate (14): Triethyl phoshonoacetate (1.8 mL, 9 mmol) was added to a suspension of sodium hydride (50% dispersion in mineral oil, 429 mg, 9 mmol) in DMF (5 mL) at 0 °C and the mixture was stirred for 30 min. A solution of **13** (500 mg, 2.3 mmol) in DMF (5 mL) was added and the mixture was stirred for 2 days at room temperature. The reaction was quenched by addition of saturated NaCl solution, and the solution was extracted with ether. The combined organic layers were washed with water and saturated NaCl solution successively, dried and concentrated *in vacuo*.

Purification of the residue by chromatography on silica gel (ether:*n*-hexane=1:2) gave **14** (1.65 g, 70%). IR (neat) 2925, 1710, 1640 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 5.69-5.64 (m, 1H), 4.60-4.55 (m, 1H), overlapping peaks 4.14 (q, *J*= 7.0 Hz) and 4.13 (q, *J*= 7.0 Hz, total 2H), 3.90-3.82 (m, 1H), 3.79-3.71 (m, 1H), 3.54-3.46 (m, 1H), 3.36-3.45 (m, 1H), 2.66 (t, *J*= 8.0 Hz, 0.5 H), 2.17 (t, *J*= 8.0 Hz, 1.5 Hz), 2.15 (d, *J*= 1.0 Hz, 2H), 1.89 (d, *J*= 1.0 Hz, 1H), 1.87-1.77 (m, 1H), 1.75-1.63 (m, 1H), 1.63-1.48 (m, 8H), overlapping peaks 1.28 (t, *J*= 7.0 Hz) and 1.27 (t, *J*= 7.0, total 3H). ^{13}C-NMR ($CDCl_3$, ppm) δ 166.88 and 166.37 (CO), 160.22 and 159.77 (C), 116.37 and 115.77 (CH), 98.92 (CH), 67.39 and 67.19 (CH_2). LRMS m/e 269 (M^+-1), 241, 225, 197, 169, 101, 85. HRMS calcd $C_{15}H_{25}O_4$ 269.1754; obs 269.1748.

Ethyl 6-(2-dithiolanyl)-3-methyl-2-hexenoate (3b). A mixture of **14** (1.65 g, 6.1 mmol) and a catalytic amount of *p*-toluenesulfonic acid in anhydrous methanol (30 mL) was stirred for 3 h at room temperature. The reaction was quenched by the addition of saturated $NaHCO_3$ solution. Usual workup and chromatography on silica gel (ethyl acetate:*n*-hexane=1:2) gave ethyl 7-hydroxy-3-methyl-2-heptenoate (0.93 g, 82%). IR (neat) 3400, 2925, 1710, 1640 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 5.69-5.65 (m, 1H), 4.14 and 4.13 (q, *J*= 7.0 Hz, total 2H), 3.74-3.63 (m, 2H), 2.62 (t, *J*= 7.5 Hz, 0.5 H), overlapping peaks 2.21-2.12 (m) and 2.16 (d, *J*= 1.5 Hz, total 3.5 H), 1.90 (d, *J*= 1.5 Hz, 1H), 1.64-1.52 (m, 5H), 1.28-1.26 (t, *J*= 7.0 Hz, 3H). ^{13}C-NMR ($CDCl_3$, ppm) δ 166.84 (CO), 160.83 and 159.56 (C), 116.09 and 115.84 (CH), 62.64 and 62.09 (CH_2), 59.59 (CH_2), 40.58 (CH_2), 32.64 and 32.19 (CH_2), 25.27 (CH_3), 24.23 and 23.59 (CH_2), 18.67 and 14.34 (CH_3). LRMS m/e 187 (M^+), 168, 156, 141, 122, 111, 95, 87, 82, 67, 55, 41. HRMS calcd $C_{10}H_{18}O_3$ 186.1256; obs 186.1281.

A mixture of ethyl 7-hydroxy-3-methyl-2-heptenoate (187 mg, 1.00 mmol), pyridinium chlorochromate (430 mg, 1.50 mmol), and Celite (430 mg) in anhydrous CH_2Cl_2 (5 mL) was stirred for 2 h at room temperature. The mixture was diluted with ether and filtered through a Florisil column. Concentration of the filtrate gave a residue, which was purified by chromatography on silica gel (ether:*n*-hexane=1:3) affording ethyl 6-formyl-3-methyl-2-hexenoate (156 mg, 85%). IR (neat) 2950, 1720, 1650 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 9.78 and 9.79 (t, *J*= 1.5 Hz, 1H), overlapping peaks 5.70 (broad s) and 5.66 (q, *J*= 1.5 Hz, total 1H), 4.15 and 4.13 (q, *J*= 7.0 Hz, 2H), 2.66 (t, *J*= 8.0, 0.5 H), overlapping peaks 2.50 (td, *J*= 7.0, 1.5 Hz) and 2.46 (td, *J*= 7.0, 1.5 Hz, total 2H), overlapping peaks 2.17 (td, *J*= 8.0, 1.5 Hz) and 2.16 (d, *J*= 1.5 Hz, total 3.5 H), 1.90 (d, *J*= 1.5 Hz, 1 H), 1.88-1.77 (m, 2H), overlapping peaks 1.28 and 1.26 (t, *J*= 7.0 Hz, 3H). ^{13}C-NMR ($CDCl_3$, ppm) δ 201.61 (CO), 166.62 and 158.28 (C), 117.12 and 116.46 (CH), 59.60 (CH_2), 43.40 and 42.98 (CH_2), 39.89 (CH_2), 32.39 (CH_2), 24.93 (CH_3), 20.45 and 19.64 (CH_2), 18.56 and 14.32 (CH_3). LRMS m/e 185 (M^++1), 166, 156, 139, 128, 121, 113, 100, 98, 88, 82, 67, 60, 55, 41. HRMS calcd $C_{10}H_{16}O_3$ 184.1100; obs 184.1078.

A mixture of ethyl 6-formyl-3-methyl-2-hexenoate (373 mg, 2.03 mmol), 1,3-propanedithiol (0.22 mL, 2.20 mmol), and a catalytic amount of BF_3•OEt_2 in anhydrous CH_2Cl_2 (30 mL) was stirred for 1 h at room temperature. Usual workup and chromatography on silica gel (ether:*n*-hexane=1:9) gave **3a** (443 mg, 80%). IR (neat) 2950, 1720, 1650 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 6.83 (dd, *J*= 15.5, 8.0 Hz, 1H), 5.79 (dd, *J*= 15.5, 1.0 Hz, 1H), 4.13 (q, *J*= 7.0 Hz, 2H), 4.01 (t, *J*= 6.5 Hz, 1H), 2.88 (ddd, *J*= 15.0, 10.5, 3.0 Hz, 2H), 2.82 (ddd, *J*= 15.0, 4.0, 4.0 Hz, 2H), 2.32 (septet, *J*= 7.0 Hz, 1H), 2.12 (dtt, *J*= 14.0, 4.0, 3.0 Hz, 1H), 1.86 (dtt, *J*= 14.0, 10.5, 4.0 Hz, 1H), 1.78-1.70 (m, 2H), 1.64-1.56 (m, 2H), 1.29 (t, *J*= 7.0 Hz, 3H), 1.07 (d, *J*= 7.0 Hz, 3H). ^{13}C-NMR ($CDCl_3$, ppm) δ 166.73 (CO), 153.47 (CH), 120.34 (CH), 60.24 (CH_2), 47.57 (CH), 36.32 (CH), 33.14 (CH_2), 32.88 (CH_2), 30.47 (CH_2, two carbons), 26.01 (CH_2), 19.42 (CH_3), 14.28 (CH_3). LRMS m/e 274 (M^+), 229, 201, 166, 153, 145, 132, 119, 106, 93, 87, 81, 74, 69, 55, 45, 41. HRMS calcd $C_{13}H_{22}O_2S_2$ 274.1063; obs 274.1056.

2-(6-Phenylthio-4-hexenyl)oxathiolane (4a). A solution of diisobutylaluminum hydride in toluene (1 M, 13.0 mL, 13.0 mmol) was added to a solution of **1b** (1.20 g, 4.88 mmol) in anhydrous CH_2Cl_2 (15 mL) at -78 °C and the mixture was stirred for 20 min. The reaction was quenched by addition of saturated NH_4Cl solution and the mixture was partitioned between water and chloroform. After the mixture was filtered through a Celite pad, the separated organic layer was dried and concentrated *in vacuo*. Purification of the residue by chromatography on silica gel (ethyl acetate:*n*-hexane=1:1) gave 6-(2-thiolanyl)-2-hexenol (818.5 mg, 95%). IR (neat) 3375, 2930, 2850, 1455, 1430 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 5.72-5.60 (m, 2H), 4.47 (t, *J*= 7.0 Hz, 1H), 4.09 (d, *J*= 4.0 Hz, 2H), 3.29-3.15 (m, 4H), 2.12-2.03 (m, 2H), 1.88-1.79 (m, 2H), 1.62-1.50 (m, 2H). ^{13}C-NMR ($CDCl_3$, ppm) δ 132.41 (CH), 129.59 (CH), 63.70 (CH_2), 53.22 (CH), 38.81 (CH_2), 38.41 (CH_2), 31.73 (CH_2), 28.64 (CH_2). LRMS m/e 204 (M^+), 187, 176, 158, 143, 131, 125, 120, 111, 105, 99, 93, 87, 81, 73, 67, 61. HRMS calcd $C_9H_{16}OS_2$ 204.0464; obs 204.0671.

Anal. Calcd for $C_9H_{16}OS_2$: C, 52.89; H, 7.89; S, 31.39. Found: C, 52.74, H, 7.92; S, 31.09.

A mixture of 6-(2-thiolanyl)-2-hexenol (30 mg, 0.17 mmol), diphenyldisulfide (53 mg, 0.26 mmol) and tri-*n*-butylphosphine (0.084 mL, 0.34 mmol) in anhydrous acetonitrile (2 mL) was stirred for 3 h at room temperature. The reaction mixture was diluted with ether. Then the mixture was washed with 20% NaOH and saturated NaCl solution successively, and dried. Purification of the residue by chromatography on silica gel (benzene:*n*-hexane=1:1) gave **4a** (25.5 mg, 57%). IR (neat) 2920, 1735, 1580 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 7.36-7.24 (m, 4H), 7.18 (tt, *J*= 7.0, 1.0 Hz, 1H), 5.55-5.43 (m, 2H), 4.42 (t, *J*= 7.0 Hz, 1H), 3.49 (dd, *J*= 6.0, 1.0 Hz, 2H), 3.26-3.14 (m, 4H), 2.20-1.96 (m, 2H), 1.76-1.69 (m, 2H), 1.48-1.39 (m, 2H). ^{13}C-NMR ($CDCl_3$, ppm) δ 136.08 (C), 133.52 (CH), 13.05 (CH), 128.75 (CH), 126.17 (CH), 125.66 (CH), 53.60 (CH), 38.62 (CH_2), 38.37 (CH_2), 36.50 (CH_2), 31.75 (CH_2), 28.66 (CH_2). LRMS m/e 297 (M^++1), 279, 235, 203, 187, 158, 131, 105, 93, 77, 67, 61, 53, 41. HRMS calcd $C_{15}H_{20}S_3$ 296.0729; obs 296.0699. Anal. Calcd for $C_{15}H_{20}S_3$: C, 60.76; H, 6.80; S, 32.24. Found: C, 60.71, H, 6.87; S, 32.29.

2-(5-Pentenyl)dithiane (4b). Dimethylsulfoxide (3.4 mL, 48 mmol) was added to a solution of oxalyl chloride (2.2 mL, 25 mmol) in anhydrous CH_2Cl_2 (20 mL) at -78 °C. Then, 5-hexenol (1.20 g, 12 mmol) was added and the mixture was stirred for 15 min under the same conditions. Triethylamine (14 mL, 10 mmol) was added and the mixture was stirred for further 15 min at -78 °C. The mixture was diluted with CH_2Cl_2, and then washed with 1N HCl and water successively. To the dried organic layer, 1,3-propanedithiol (0.84 mL, 8.38 mmol) and a catalytic amount of BF_3•OEt_2 were added, and the mixture was stirred for 1 h at room temperature. Usual workup and chromatography on silica gel (ether:*n*-hexane=1:9) gave **4b** (1.39 g, 62%). IR (neat) 2930, 1635 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 5.79 (ddt, *J*= 17.0, 11.0, 7.0 Hz, 1H), 5.02 (ddt, *J*= 17.0, 1.5, 1.5 Hz, 1H), 4.97 (broad d, *J*= 11.0 Hz, 1H), 4.05 (t, *J*= 7.0 Hz, 1H), 2.88 (ddd, *J*= 14.0, 11.0, 3.0 Hz, 2H), 2.82 (ddd, *J*= 14.0, 4.0, 4.0 Hz, 2H), 2.16-2.04 (m, 3H), 1.86 (dtt, *J*= 14.0, 11.0, 4.0 Hz, 1H), 1.80-1.74 (m, 2H), 1.66-1.54 (m, 2H). ^{13}C-NMR ($CDCl_3$, ppm) δ 137.86 (CH), 114.76 (CH), 47.24 (CH), 34.66 (CH_2), 33.03 (CH_2), 30.21 (CH_2), 25.84 (CH_2), 25.62 (CH_2). LRMS m/e 188 (M^+), 155, 145, 134, 119, 114, 106, 101, 91, 87, 80, 74, 69, 64, 60, 55, 45, 41. HRMS calcd $C_9H_{16}S_2$ 188.0690; obs 188.0674.

Methyl 6-(2-dithianyl)-2-hexynoate (4c). A mixture of methyl 7-hydroxy-2-heptynoate (1.0 g, 6.14 mmol), pyridinium chlorochromate (2.07 g, 9.62 mmol), and Celite (2 g) in anhydrous CH_2Cl_2 (30 mL) was stirred for 2 h at room temperature. The mixture was diluted with ether and filtered through a Florisil column. Concentration of the filtrate gave a residue which was dissolved in CH_2Cl_2 (20 mL). 1,3-propanedithiol (0.64 mL, 6.14 mmol) and a catalytic amount of BF_3•OEt_2 were added to the solution, and the mixture was stirred for 1 h at room temperature. Usual workup and chromatography on silica gel (ether:*n*-hexane=1:1) gave **4c** (960 mg, 64%). IR (neat) 2960, 2920, 2250, 1715 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 4.06 (t, *J*= 7.0 Hz, 1H), 3.76 (s, 3H), 2.88 (ddd, *J*= 14.0, 11.0, 3.0 Hz, 2H), 2.83 (ddd, *J*= 14.0, 4.0, 4.0 Hz, 2H), 2.39 (t, *J*= 7.0 Hz, 2H), 2.14 (dtt, *J*= 14.0, 4.0, 3.0, 1H), 1.92-1.75 (m, 5H). ^{13}C-NMR ($CDCl_3$, ppm) δ 153.93 (COO), 88.50 (C), 73.28 (C), 52.43 (CH_3), 46.62 (CH), 34.20 (CH_2, two carbons), 30.18 (CH_2), 25.79 (CH_2), 24.49 (CH_2), 18.20 (CH_2). LRMS m/e 244 (M^+), 212, 201, 185, 179, 170, 156, 151, 145, 138, 119, 111, 91, 87, 79, 65, 59, 51, 41. HRMS calcd $C_{11}H_{16}O_2S_2$ 244.0593; obs 244.0575.

General procedure for the reaction radical reaction of ethyl 6-(2-dithiolanyl)-2-hexenoate (1b): large scale conditions (Table 1, run 1). A solution of **1b** (307 mg, 1.25 mmol) and benzophenone (40 mg, 0.21 mmol) in acetonitrile (100 mL) was irradiated with a 300 W medium-pressure mercury lamp through a Pyrex filter for 5 h. Concentration and purification of the residue by chromatography on silica gel (ether:*n*-hexane=1:4) afforded 1,3-dithiolan-2-spiro-1'-(2'-ethoxycarbonylmethyl)cyclopentane (**15b**, 29.5 mg, 11%) along with recovery of **1b** (50%). Spectral data for **15b**: IR (neat) 2925, 1720 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 4.13 (q, *J*= 7.0 Hz, 2H), 3.35-3.17 (m, 4H), 2.80 (dd, *J*= 15.5, 4.0 Hz, 1H), 2.51 (tdd, *J*= 11.0, 8.0, 4.0 Hz, 1H), 2.36 (dd, *J*= 15.5, 11.0 Hz, 1H), 2.32-2.15 (m, 2H), 2.09 (dtd, *J*= 14.0, 8.0, 5.5 Hz, 1H), 1.80-1.66 (m, 2H), 1.38 (dtd, *J*= 14.0, 11.0, 8.0 Hz, 1H), 1.29 (t, *J*= 7.0 Hz, 2H). ^{13}C-NMR ($CDCl_3$, ppm) δ 173.26 (COO), 75.20 (C), 60.30 (CH_2), 47.02 (CH), 45.19 (CH_2), 39.39 (CH_2, two carbons), 36.30 (CH_2), 30.12 (CH_2), 21.40 (CH_2), 14.25 (CH_3). LRMS m/e 246 (M^+), 218, 201, 185, 172, 153, 144, 131, 118, 111, 97, 89, 85, 79, 71, 67, 61, 53, 41. HRMS calcd $C_{11}H_{18}O_2S_2$ 246.0744; obs 246.0753.

Small scale conditions (Table 1, run 3). A solution of **1b** (30 mg, 0.12 mmol) and benzophenone (12.5 mg, 0.068 mmol) in acetonitrile (10 mL) was irradiated with a 300 W medium-pressure mercury lamp through a Pyrex filter for 20 min. The reaction mixture was concentrated and benzophenone was removed by

chromatography on silica gel (ether:*n*-hexane=1:9). A mixture of **1b** (20%) and **15b** (50%) was eluted and the yield of the product was determined by ^{1}H-NMR using CH_2Cl_2 as an internal standard.

Radical reaction of ethyl 7,7-ethylenedioxy-2-heptenoate (1a, eq 1). A solution of **1a** (287 mg, 1.34 mmol) and benzophenone (39 mg, 0.21 mmol) in acetonitrile (107 mL) was irradiated for 7 h under the large scale conditions to afford 1,3-dioxolan-2-spiro-1'-(2'-ethoxycarbonylmethyl)cyclopentane (**15a**, 9.1 mg, 3%). IR (neat) 2925, 1720 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 4.15 (q, *J*= 7.0 Hz, 2H), 3.96-3.81 (m, 4H), 2.48 (dd, *J*= 14.0, 6.0 Hz, 1H), 2.48-2.37 (m, 1H), 2.23 (dd, *J*= 14.0, 8.5 Hz, 1H), 1.82-1.72 (m, 3H), 1.72-1.60 (m, 2H), 1.40 (dtd, *J*= 12.5, 9.0, 8.0 Hz, 1H), 1.28(t, *J*= 7.0, 3H).

Radical reaction of ethyl 6-(2-dithianyl)-2-hexenoate (1c). A solution of **1c** (63 mg, 0.25 mmol) and benzophenone (25 mg, 0.14 mmol) in benzene (10 mL) was irradiated for 25 min under the small scale conditions to give a mixture of 1,3-dithian-2-spiro-1'-(2'-ethoxycarbonyl)cyclopentane (**15c**, 60%) and **1c** (19%). A small amount of **15c** was further purified for spectroscopic analysis: IR (neat) 2950, 1730, 1440, 1420 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 4.15 (qd, *J*= 7.0, 1.0 Hz, 2H), 3.01 (ddd, *J*= 14.0, 11.0, 3.0 Hz, 1H), 2.90 (ddd, *J*= 14.0, 11.0, 3.0 Hz, 1H), 2.84 (dd, *J*= 15.5, 3.0 Hz, 1H), 2.82 (ddd, *J*= 14.5, 6.0, 4.0 Hz, 1H), 2.78 (ddd, *J*= 14.5, 6.0, 4.0 Hz, 1H), 2.55-2.46 (m, 2H), 2.32 (dd, *J*= 15.5, 10.5 Hz, 1H), 2.15 (ddd, *J*= 13.0, 10.0, 8.0 Hz, 1H), 2.10-2.00 (m, 2H), 1.91 (dtt, *J*= 13.5, 11.0, 3.0 Hz, 1H), 1.88-1.70 (m, 2H), 1.57 (dddd, *J*= 13.0, 10.0, 8.0, 6.0 Hz, 1H), 1.29 (t, *J*= 7.0 Hz, 3H). ^{13}C-NMR ($CDCl_3$, ppm) δ 173.02 (COO), 60.41 (CH_2), 59.35 (C), 47.02 (CH), 21.15 (CH_2), 36.05 (CH_2), 29.48 (CH_2), 28.42 (CH_2), 27.14 (CH_2), 25.77 (CH_2), 21.34 (CH_2), 14.27 (CH_3). LRMS m/e 260 (M^+), 227, 215, 185, 173, 153, 145, 139, 119, 106, 97, 85, 79, 71, 67, 59, 55, 45, 41. HRMS calcd $C_{12}H_{20}O_2S_2$ 260.0906; obs 260.0888.

Radical reaction of ethyl 6-(2-oxathiolanyl)-2-hexenoate (1d). A solution of **1d** (73 mg, 0.32 mmol) and benzophenone (25 mg, 0.14 mmol) in benzene (10 mL) was irradiated for 20 min under the small scale conditions to give 1,3-oxathian-2-spiro-1'-(2'-ethoxycarbonylmethyl)cyclopentane (**15d**, 17.8 mg, 24%) as a mixture of two diastereomers, along with a recovery of **1d** (30%). A diastereomer of **15d**: IR (neat) 2950, 1730, 1440 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 4.23 (ddd, *J*= 9.0, 6.0, 3.0 Hz, 1H), 4.13 (qd, *J*= 7.0, 1.5 Hz, 2H), 3.86 (ddd, *J*= 9.0, 9.0, 6.0 Hz, 1H) 3.20-2.93 (m, 2H), 2.68 (dd, *J*= 15.0, 4.0 Hz, 1H), 2.42 (tdd, *J*= 11.0, 8.0, 4.0 Hz, 1H), 2.26 (dd, *J*= 15.0, 11.0 Hz, 1H), 2.15-1.99 (m, 2H), 1.91 (ddd, *J*= 14.0, 10.0, 8.0 Hz, 1H), 1.81-1.62 (m, 1H), 1.51 (dtd, *J*= 14.0, 12.0, 8.0 Hz, 1H), 1.39-1.29 (m, 2H), 1.26 (t, *J*= 7.0, 3H). ^{13}C-NMR ($CDCl_3$, ppm) δ 173.63 (CO), 101.15 (C), 70.08 (CH_2), 60.24 (CH_2), 45.63 (CH), 40.97 (CH_2), 33.80 (CH_2), 33.65 (CH_2), 29.54 (CH_2), 21.18 (CH_2), 14.27 (CH_3). LRMS m/e 230 (M^+), 201, 185, 171, 157, 149, 143, 124, 115, 97, 88, 83, 79, 69, 60, 55, 45, 41. HRMS calcd $C_{11}H_{18}O_3S$ 230.0977; obs 230.0972. Another diastereomer of **15d**: IR (neat) 2950, 1730, 1440 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 4.20 (ddd, *J*= 9.0, 6.0, 4.0 Hz, 1H), 4.15 (qd, *J*= 7.0, 1.5 Hz, 2H), 3.96 (ddd, *J*= 9.0, 8.0, 5.5 Hz, 1H), 3.07-2.92 (m, 2H), 2.59 (d, dd, *J*= 15.0, 5.0 Hz, 1H), 2.52 (td, *J*= 9.0, 5.0 Hz, 1H), 2.26 (dd, *J*= 15.0, 9.0 Hz, 1H), 2.23 (dd, *J*= 8.0, 8.0 Hz, 2H), 2.15-1.99 (m, 2H), 1.81-1.60 (m, 1H), 1.39-1.29 (m, 2H), 1.26 (t, *J*= 7.0, 3H). ^{13}C-NMR ($CDCl_3$, ppm) δ 173.08 (CO), 104.08 (C), 70.43 (CH_2), 60.28 (CH_2), 45.03 (CH), 40.25 (CH_2), 37.36 (CH_2), 33.43 (CH_2), 29.11 (CH_2), 20.36 (CH_2), 14.27 (CH_3). LRMS m/e 230 (M^+), 201, 185, 171, 157, 143, 124, 115, 107, 97, 88, 83, 79, 69, 60, 55, 45, 41. HRMS calcd $C_{11}H_{18}O_3S$ 230.0977; obs 230.0954.

Radical reaction of ethyl 6-(2-dithianyl)-4-methyl-2-hexenoate (3a). A solution of ethyl 6-(2-dithianyl)-4-methyl-2-hexenoate (**3a**, 60 mg, 0.22 mmol) and benzophenone (25 mg, 0.14 mmol) in benzene (10 mL) was irradiated for 25 min under the small scale conditions to give 1,3-dithian-2-spiro-1'-(2'-ethoxycarbonylmethyl-3'-methyl)cyclopentane (**16**, 55%) as a mixture of two diastereomers (*trans*:*cis*=9:1), along with a recovery of **3a** (5%). A small amount of analytically pure **16** was obtained by column chromatography on silica gel (ethyl acetate:*n*-hexane=1:6). trans-**16**: IR (neat) 2950, 1730, 1460, 1420 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 4.09 (qd, *J*= 7.0, 1.5 Hz, 2H), 3.01 (ddd, *J*= 14.0, 11.5, 3.0 Hz, 1H), 2.90 (ddd, *J*= 14.0, 11.5, 3.0 Hz, 1H), 2.80 (dd, *J*= 15.5, 4.0 Hz, 1H), 2.66 (broad d, *J*= 14.5 Hz, 2H), 2.54 (ddd, *J*= 13.0, 8.0, 5.0 Hz, 4H), 2.27 (dd, *J*= 15.5, 9.5 Hz, 1H), 2.20 (ddd, *J*= 13.0, 9.0, 6.0 Hz, 1H), 2.06-1.90 (m, 1H), 1.86 (tdt, *J*= 13.5, 11.5, 3.0 Hz, 1H), 1.37-1.28 (m, 1H), 1.21 (t, *J*= 7.0 Hz, 3H), 0.95 (d, *J*= 6.0 Hz, 3H). ^{13}C-NMR ($CDCl_3$, ppm) δ 173.08 (C), 60.54 (C), 60.44 (CH_2), 54.66 (CH), 40.98 (CH_2), 38.52 (CH), 35.33 (CH_2), 31.46 (CH_2), 28.40 (CH_2), 26.85 (CH_2), 25.90 (CH_2), 20.10 (CH_3), 14.23 (CH_3). LRMS m/e 274 (M^+), 229, 199, 187, 167, 153, 145, 132, 121, 106, 93, 85, 79, 71, 55, 45, 41. HRMS calcd

$C_{13}H_{22}O_2S_2$ 274.1063; obs 274.1082. *cis*-**16**: IR (neat) 2850, 1730, 1460, 1440, 1420 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 4.16 (q, *J*= 7.0 Hz, 2H), 2.96 (ddd, *J*= 14.0, 8.5, 3.0 Hz, 1H), 2.85 (dd, *J*= 14.0, 7.0, 3.5 Hz, 1H), 2.81 (dd, *J*= 6.5, 3.5 Hz, 1H), 2.79 (dd, *J*= 6.5, 4.5 Hz, 1H), 2.74 (dd, *J*= 16.0, 4.0 Hz, 1H), 2.71-2.58 (m, 2H), 2.44 (dd, *J*= 16.0, 4.0 Hz, 1H), 2.41-2.30 (m, 1H), 2.10-1.82 (m, 2H), 1.50-1.34 (m, 2H), overlapping peaks 1.27 (t, *J*= 7.0) and 1.30-1.24 (m, total 4H), 0.97 (d, *J*= 6.5, 3H). ^{13}C-NMR ($CDCl_3$, ppm) δ 173.41 (C), 60.42 (CH_2), 59.58 (C), 49.27 (CH), 40.56 (CH_2), 34.46 (CH), 31.73 (CH_2), 30.98 (CH_2), 28.75 (CH_2), 37.78 (CH_2), 25.28 (CH_2), 17.38 (CH_3), 14.23 (CH_3). LRMS m/e 274 (M^+), 229, 199, 187, 167, 153, 145, 132, 121, 106, 93, 85, 79, 71, 67, 59, 55, 45, 41. HRMS calcd $C_{13}H_{22}O_2S_2$ 274.1063; obs 274.1034.

Radical reaction of ethyl 7-(2-dithianyl)-2-heptenoate (2a). A solution of **2a** (69 mg, 0.25 mmol) and benzophenone (29 mg, 0.16 mmol) in benzene (10 mL) was irradiated for 25 min under the small scale conditions to give 1,3-dithian-2-spiro-1'-(2'-ethoxycarbonylmethyl)cyclohexane (**17**, 51%), along with a recovery of **2a** (4%). Spectral data for **17**: IR (neat) 2900, 1710, 1650 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 4.14 (q, *J*= 7.0 Hz, 2H), 3.17 (dd, *J*= 19.0, 8.0 Hz, 1H), 3.05 (ddd, *J*= 15.0, 11.0, 3.0 Hz, 1H), 2.82 (ddd, *J*= 15.0, 11.0, 3.0 Hz, 1H), 2.70 (ddd, *J*= 14.0, 4.0, 3.0 Hz, 1H), 2.67 (ddd, *J*= 14.0, 4.0, 3.0 Hz, 1H), 2.62-2.50 (m, 1H), overlapping peaks 2.31 (dd, *J*= 19.0, 9.5 Hz) and 2.41-2.24 (m, total 2H), 2.02 (dtt, *J*= 14.0, 3.0, 3.0 Hz, 1H), 1.84 (dtt, *J*= 14.0, 11.0, 4.0 Hz, 1H), 1.78-1.55 (m, 5H), 1.54-1.43 (m, 1H), 1.43-1.31 (m, 1H), 1.26 (t, *J*= 7.0, 3H). ^{13}C-NMR ($CDCl_3$, ppm) δ 173.32 (CO), 60.30 (CH_2), 55.41 (C), 42.74 (CH), 37.07 (CH_2), 3.67 (CH_2), 27.40 (CH_2), 25.84 (CH_2), 25.71 (CH_2), 25.13 (CH_2), 24.56 (CH_2), 22.39 (CH_2), 14.23 (CH_3). LRMS m/e 274 (M^+), 246, 229, 201, 187, 167, 154, 145, 139, 126, 106, 93, 79, 71, 61, 55, 45. HRMS calcd $C_{13}H_{22}O_2S_2$ 274.1056; obs 274.1056.

General procedure for the hydrolysis of dithioacetals: hydrolysis of 1,3-dithiolan-2-spiro-1'-(2'-ethoxycarbonylmethyl)cyclopentane (15b). Method A; a solution of **15b** (53.6 mg, 0.22 mmol) and iodomethane (large excess) in 95% ethanol (15.8 mL) was heated for 2 days at refluxing temperature. The reaction mixture was cooled to room temperature and then neutralized by the addition of saturated $NaHCO_3$ solution. Usual workup and chromatography on silica gel (ether:*n*-hexane=1:2) gave ethyl (2-oxocyclopentyl)acetate (**18**) (20.6 mg, 55%), along with recovery of **15b** (13%). **Method B;** a mixture of **15b** (75.8 mg, 0.30 mmol) and [bis(trifluoroacetoxy)iodo]benzene (220 mg, 0.51 mmol) in 95% methanol was stirred at 0 °C. The reaction was quenched by addition of saturated $NaHCO_3$ solution. Usual workup and chromatography on silica gel (ether:*n*-hexane=1:2) gave **18** (33.6 mg, 64%). Spectral data for **18**: IR (neat) 2975, 1740 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 4.14 (q, *J*= 7.0 Hz, 2H), 2.74-2.66 (m, 1H), 2.56-2.24 (m, 5H), 2.18 (ddd, *J*= 19.0, 11.0, 9.0 Hz, 1H), 2.06 (dddt, *J*= 13.0, 9.0, 6.0, 2.0 Hz, 1H), 1.81 (ddtd, *J*= 16.0, 13.0, 9.0, 6.0 Hz, 1H), 1.62 (qd, *J*= 13.0, 6.0 Hz, 1H), 1.29 (t, *J*= 7.0 Hz, 3H). ^{13}C-NMR ($CDCl_3$, ppm) δ 219.13 (CO), 172.13 (COO), 60.63 (CH_2), 45.67 (CH), 37.47 (CH_2), 34.07 (CH_2), 30.91 (CH_3), 29.35 (CH_2), 20.65 (CH_2), 14.21 (CH_3), 1.29 (t, *J*= 7.0, 3H). LRMS m/e 170 (M^+), 141, 125, 114, 97, 88, 83, 79, 73, 69, 60, 55, 48, 41. HRMS calcd $C_9H_{14}O_3$ 170.0943; obs 170.0945.

Hydrolysis of 1,3-dithian-2-spiro-1'-(2'-ethoxycarbonylmethyl)cyclopentane (15c). 15c (56.8 mg, 0.22 mmol) was hydrolyzed using method A to give **18** (30.7 mg, 83%). On the other hand, **15c** (429 mg, 1.65 mmol) was hydrolyzed to **18** using method B in 34% yield (95 mg).

Hydrolysis of 1,3-dithian-2-spiro-1'-(2'-ethoxycarbonylmethyl)cyclohexane (17). 17 (81 mg, 0.30 mmol) was hydrolyzed using method B to give ethyl (2-oxocyclohexyl)acetate (**20**, 42 mg, 78%). IR (neat) 2900, 1730, 1700, 1440 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 4.14 (qd, *J*= 7.0, 2.0 Hz, 2H), 2.87 (dddd, *J*= 13.0, 7.0, 5.0, 5.0 Hz, 1H), 2.77 (dd, *J*= 16.0, 7.0 Hz, 1H), overlapping peaks 2.38 (dddd, 13.0, 13.0, 13.0, 5.5 Hz) and 2.46-2.32 (m, total 2H), overlapping peaks 2.14 (dd, *J*= 16.0, 5.0 Hz) and 2.20-2.06 (m, total 3H), 1.92-1.85 (m, 1H), 1.73 (dddt, *J*= 13.0, 13.0, 13.0, 3.5 Hz, 1H), 1.64 (dddd, *J*= 13.0, 13.0, 13.0, 4.0 Hz, 1H), 1.42 (dddd, *J*= 13.0, 13.0, 13.0, 4.0 Hz, 1H), 1.26 (t, *J*= 7.0 Hz, 3H). $_{13}$C-NMR ($CDCl_3$, ppm) δ 210.95 (CO), 172.59 (COO), 60.41 (CH_2), 47.13 (CH), 41.81 (CH_2), 34.46 (CH_2), 33.87 (CH_2), 27.78 (CH_2), 25.20 (CH_2), 14.17 (CH_3). LRMS m/e 184 (M^+), 139, 128, 121, 110, 97, 93, 88, 82, 67, 60, 55, 41. HRMS calcd $C_{10}H_{16}O_3$ 184.1040; obs 184.1077.

Hydrolysis of 1,3-dithian-2-spiro-1'-(2'-ethoxycarbonylmethyl)cyclopentane (16). 16 (269 mg, 0.98 mmol) was hydrolyzed using method A to give ethyl (*trans*-5-methyl-2-oxocyclopentyl)acetate (**19**,

136.5 mg, 75%). IR (neat) 2975, 1740, 1450, 1400 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 4.14 (q, *J*= 7.0 Hz, 2H), 2.62 (dd, *J*= 16.0, 4.5 Hz, 1H), 2.52 (dd, *J*= 16.0, 5.0 Hz, 1H), 2.38 (dd, *J*= 18.0, 10.0 Hz, 1H), 2.21 (dd, *J*= 18.0, 11.0 Hz, 1H), 2.16-2.10 (m, 1H), 2.06-1.90 (m, 2H), 1.50-1.37 (m, 1H), 1.26 (t, *J*= 7.0 Hz, 3H), 1.14 (d, *J*= 7.0 Hz, 3H). ^{13}C-NMR ($CDCl_3$, ppm) δ 218.73 (CO), 172.07 (CO), 30.31 (CH_2), 53.15 (CH), 37.55 (CH_2), 37.00 (CH), 32.26 (CH_2), 29.68 (CH_2), 19.11 (CH_3), 14.16 (CH_3). LRMS m/e 185 (M^++1), 169, 155, 139, 127, 123, 111, 97, 88, 83, 69, 60, 55, 41. HRMS calcd $C_{10}H_{16}O_3$ 184.1100; obs 184.1072.

Preparation of chiral acetals:

Ethyl (*E*)-6-[(2*R*,4a*R*,7*R*,8a*R*)-4a,5,6,7,8,8a-hexahydro-4,4,7-trimethyl-4*H*-1,3-bnzoxathiin-2-yl]-2-hexenoate (23). A mixture of **9** (1.63 g, 9.48 mmol), (1*R*, 2*R*, 5*R*)-2-(1-mercapto-1-methylethyl)-5-methylcyclohexanol (**21**, 1.63 mg, 8.67 mmol), and 0.1 mL of BF_3•OEt_2 in CH_2Cl_2 (40 mL) was stirred for 0.5 h at room temperature. Usual workup and chromatography on silica gel (ether:*n*-hexane=1:4) gave **23** (1.79 g, 61%). IR (neat) 2925, 1720, 1650, 1460 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 6.94 (dt, *J*= 16.0, 7.0 Hz, 1H), 5.82 (dt, *J*= 16.0, 1.5 Hz, 1H), 4.88 (dd, *J*= 7.0, 5.0 Hz, 1H), 4.18 (q, *J*= 7.0 Hz, 2H), 3.37 (ddd, *J*= 14.5, 14.5, 4.0 Hz, 1H), 2.22 (dtd, *J*= 7.0, 7.0, 1.5 Hz, 2H), 1.93 (dddd, *J*= 13.0, 4.5, 4.5, 2.5 Hz, 1H), 1.87-1.50 (m, 7H), overlapping peaks 1.50-1.36 (m) and 1.41 (s, total 6H), 1.28 (t, *J*= 7.0 Hz, 3H), 1.25 (s, 3H), 1.10 (ddd, *J*= 12.5, 12.5, 11.0 Hz, 1H), overlapping peaks 1.01-0.81(m) and 0.92 (s, total 6H). ^{13}C-NMR ($CDCl_3$, ppm) δ 166.57 (CO), 148.59 (CH), 121.67 (CH), 78.53 (CH), 77.18 (CH), 60.10 (CH_2), 50.70 (CH), 42.98 (C), 41.83 (CH_2), 35.02 (CH_2), 34.75 (CH_2), 31.84 (CH_2), 31.48 (CH), 29.57 (CH_3), 24.40 (CH_2), 24.01 (CH_2), 23.01 (CH_3), 22.08 (CH_3), 14.27 (CH_3). LRMS m/e 340 (M^+), 322, 311, 295, 267, 239, 225, 199, 171, 155, 137, 127, 109, 95, 88, 81, 75, 69, 55, 41. HRMS calcd $C_{19}H_{32}O_3S$ 340.2074; obs 340.2099.

Ethyl (*E*)-6-[(2*S*,4a*R*,7*R*,8a*S*)-4a,5,6,7,8,8a-hexahydro-4,4,7-trimethyl-4*H*-1,3-bnzoxathiin-2-yl]-2-hexenoate (24). A mixture of **9** (400 mg, 2.33 mmol), (1*S*, 2*R*, 5*R*)-2-(1-mercapto-1-methylethyl)-5-methylcyclohexanol (**22**, 400 mg, 2.12 mmol), and a catalytic amount of BF_3•OEt_2 in CH_2Cl_2 (10 mL) was stirred for 1h at room temperature. Usual workup and chromatography on silica gel (ether:*n*-hexane=1:4) gave **24** (672 mg, 93%). IR (neat) 2900, 1710, 1640, 1440 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 6.95 (dt, *J*= 16.0, 7.0 Hz, 1H), 5.82 (dt, *J*= 16.0, 1.5 Hz, 1H), 4.86 (dd, *J*= 6.0, 5.0 Hz, 1H), 4.18 (q, *J*= 7.0 Hz, 2H), 3.92 (broad s, 1H), 2.23 (dtd, *J*= 7.0, 7.0, 1.5 Hz, 2H), overlapping peaks 1.92-1.50 (m) and 1.52 (s, total 15H), 1.28 (t, *J*= 7.0 Hz, 3H), 1.16 (s, 3H), 1.06-0.97 (m, 2H), 0.90 (dddd, *J*= 13.0, 13.0, 13.0, 4.0 Hz, 1H), 0.82 (d, *J*= 7.0 Hz, 1H). ^{13}C-NMR ($CDCl_3$, ppm) δ 166.70 (CO), 148.81 (CH), 121.63 (CH), 79.35 (CH), 73.41 (CH), 60.15 (CH_2), 44.18 (CH), 44.04 (C), 41.39 (CH_2), 35.10 (CH_2), 34.62 (CH_2), 31.99 (CH_2), 29.52 (CH_3), 29.10 (CH_3), 25.86 (CH), 23.87 (CH_2), 22.33 (CH_2 and CH_3), 14.30 (CH_3). LRMS m/e 340 (M^+), 295, 225, 214, 199, 186, 171, 155, 137, 127, 111, 95, 86, 81, 69, 55, 41. HRMS calcd $C_{19}H_{32}O_3S$ 340.2074; obs 340.2055.

Radical reaction of ethyl (*E*)-6-[(2*R*,4a*R*,7*R*,8a*R*)-4a,5,6,7,8,8a-hexahydro-4,4,7-trimethyl-4*H*-1,3-bnzoxathiin-2-yl]-2-hexenoate (23). A solution of **23** (54 mg, 0.15 mmol) and benzophenone (25 mg, 0.14 mmol) in benzene (6.6 mL) was irradiated for 20 min under the small scall conditions. Concentration and purification of the residue by chromatography on silica gel (ether:*n*-hexane=1:9) afforded a mixture of **25**, **26**, and **27** (44.5 mg, 52%) along with recovery of **23** (3 mg, 6%). The mixture was separated by chromatography on silica gel (*n*-hexane:benzene:ether=30:3:1). Spectral data for (2*S*,4a*R*,7*R*,8a*R*,2'*R*)-4a,5,6,7,8a-hexahydro-(4,4,7)-trimethyl-4*H*-1,3-bezoxathiin-2-spiro-1'-(2'-ethoxycarbonylmethyl)cyclopentane (**25**): IR (neat) 2950, 1730, 1440 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 4.15 (q, *J*= 7.0, 2H), 3.47 (ddd, *J*= 4.5, 1.0, 1.0 Hz, 1H), 3.04 (broad s, 1H), 2.45 (dd, *J*= 15.0, 1.0 Hz, 1H), overlapping peaks 2.22-1.80 (m) and 1.48 (s, total 6H), overlapping peaks 1.80-1.34 (m) and 1.48 (s, total 9H), 1.27 (t, *J*= 7.0 Hz, 3H), 1.24 (s, 3H), 1.15-1.04 (m, 1H), overlapping peaks 1.40-0.88 (m) and 0.92 (d, *J*= 6.0, total 5H). ^{13}C-NMR ($CDCl_3$, ppm) δ 173.52 (CO), 91.88 (C), 72.38 (CH), 60.42 (CH_2), 49.40 (CH), 44.28 (CH), 43.69 (C), 42.01 (CH_2), 39.70 (CH_2), 34.86 (CH_2), 34.62 (CH_2), 31.47 (CH), 30.82 (C), 28.29 (CH_2), 26.04 (CH_3), 24.18 (CH_2), 22.11 (CH_3), 18.05 (CH_2), 14.28 (CH_3). LRMS m/e 340 (M^+), 311, 295, 267, 239, 225, 203, 182, 170, 155, 137, 125, 105, 95, 88, 81, 69, 55, 41. HRMS calcd $C_{19}H_{32}O_3S$ 340.2074; obs 340.2047. Spectral data for (2*S*,4a*R*,7*R*,8a*R*,2'*S*)-4a,5,6,7,8a-hexahydro-(4,4,7)-trimethyl-4*H*-1,3-bezoxathiin-2-spiro-1'-(2'-ethoxycarbonylmethyl)cyclopentane (**26**): IR (neat) 2950, 1720, 1650, 1450 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 4.15 (q, *J*= 7.0 Hz, 2H), 3.61 (ddd, *J*= 10.0, 10.0, 4.0 Hz, 1H), 3.04 (dd, *J*= 12.0, 6.0 Hz, 1H), 2.83 (ddd, *J*= 15.0, 3.0, 1.0 Hz, 1H), overlapping peaks 1.93 (dd,

J= 15.0, 12.0 Hz) and 2.40-1.57 (m, total 9H), overlapping peaks 1.57-1.34 (m) and 1.41 (s, total 6H), 1.26 (t, J= 7.0 Hz 3H), 1.21 (s, 3H), 1.12-0.8 (m, 2H), overlapping peaks 0.96-0.88 (m) and 0.91(d, J= 6.0, total 4H). ^{13}C-NMR ($CDCl_3$, ppm) δ 173.30 (CO), 91.84 (C), 69.99 (CH), 60.32 (CH_2), 49.84 (CH), 43.40 (C), 42.36 (CH_2 and CH), 39.67 (CH_2), 38.02 (CH_2), 34.73 (CH_2), 31.57 (CH), 29.98 (CH_3), 28.75 (CH_2), 25.46 (CH_3), 24.11 (CH_2), 22.11 (CH_3), 18.73 (CH_2), 14.28 (CH_3). LRMS m/e 340 (M^+), 311, 295, 267, 225, 203, 182, 170, 155, 137, 125, 105, 95, 88, 81, 69, 55, 41. HRMS calcd $C_{19}H_{32}O_3S$ 340.2074; obs 340.2085. Spectral data for (2*S*,4a*R*,7*R*,8a*S*,2'*R*)-4a,5,6,7,8a-hexahydro-(4,4,7)-trimethyl-4*H*-1,3-bezoxathiin-2-spiro-1'-(2'-ethoxycarbonylmethyl)cyclopentane (**27**): IR (neat) 3000, 1750, 1465 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 4.14 (qd, J= 7.0, 1.5 Hz, 2H), 4.06 (broad s, 1H), 2.91 (dd, J= 16.0, 3.5 Hz, 1H), 2.56 (ddd, J= 13.5, 8.0, 5.0 Hz, 1H), 2.40 (dd, J= 16.0, 10.5 Hz, 1H), 2.11 (ddd, J= 13.5, 10.0, 7.5 Hz, 1H), 1.92 (dddd, J= 12.0, 8.0, 7.5, 4.0 Hz, 1H), 1.88 (dddd, J= 12.0, 8.0, 7.5, 4.0 Hz, 1H), 1.83-1.57 (m, 6H), overlapping peaks 1.55 (s) and 1.58-1.40 (m, total 5H), 1.26 (t, J= 7.0 Hz, 3H), 1.12 (s, 3H), 1.09-1.95 (m, 2H), overlapping peaks 0.94-0.08 (m) and 0.83 (d, J= 6.5, total 4H). LRMS m/e 340 (M^+), 307, 267, 225, 170, 155, 137, 125, 113, 95, 81, 75, 69, 55, 41. HRMS calcd $C_{19}H_{32}O_3S$ 340.2094; obs 3340.2074. Anal. Calcd for $C_{19}H_{32}O_3S$: C, 67.02; H, 9.47; S, 9.42. Found: C, 67.21, H, 9.50, S, 9.56.

Radical reaction of ethyl (*E*)-6-[(2*S*,4a*R*,7*R*,8a*S*)-4a,5,6,7,8,8a-hexahydro-4,4,7-trimethyl-4*H*-1,3-bnzoxathiin-2-yl]-2-hexenoate (24). A solution of **24** (816 mg, 2.4 mmol) and benzophenone (375 mg, 2 mmol) in benzene (100 mL) was irradiated for 20 min under the large scall conditions to afford a mixture of **28**, **29**, and **30** (494 mg, 61%) along with recovery of **24** (158 mg, 19%). To a solution of the mixture of **28**, **29** and **30** (1.77 g, 5.21 mmol) in THF (25 mL), lithium aluminum hydride (222 mg, 5.8 mmol) was added in small portions at 0°C. The mixture was gradually warmed to room temperature over 1 h with stirring. The reaction was quenched by the addition of water (0.5 mL) and 10% NaOH (0.4 mL). Filtration and concentration of the reaction mixture gave a crude mixture of the alcohols (1.37 g, 85%). A solution of the resulting mixture of alcohols in DMF (3 mL) was added to a suspension of sodium hydride (60% dispersion, 280 mg, 6.97 mol) in DMF (30 mL) at 0°C and the mixture was stirred for 15 min. After the addition of benzyl bromide (0.84 mL, 6.97 mmol), the mixture was stirred overnight at room temperature. The reaction was quenched by addition of saturated NH_4Cl solution, and the separated aqueous layer was extracted with ether. The combined organic layers were washed with saturated NaCl solution, dried and concentrated *in vacuo*. Purification of the residue by chromatography on silica gel (ether:*n*-hexane=1:9) gave a mixture of **31**, **32**, and **33** (1.57 g, 89%). The ratio of the products was determined by ^{1}H-NMR. Analytically pure samples were isolated by chromatography on silica gel (*n*-hexane:benzene:ether=30:3:1). (2*R*,4a*R*,7*R*,8a*S*,2'*S*)-4a,5,6,7,8,8a-hexahydro-4,4,7-trimethyl-4*H*-benzoxatiin-2-spiro-1'-[2'-(2-benzyloxy)ethyl]cyclopentane (**31**): IR (neat) 2950, 2925, 2875, 1450 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 7.37-7.29 (m, 4H), 7.29-7.23 (m, 1H), 4.54 (d, 1H, J= 12.0 Hz), 4.48 (d, 1H, J= 12.0 Hz), 4.0 (broad s, 1H), 3.55 (ddd, 1H, J= 9.0, 6.5, 4.5 Hz), 3.46 (ddd, J= 9.0, 9.0, 5.5 Hz, 1H), 2.62 (dd, J= 11.0, 6.0 Hz, 1H), 2.10-1.98 (m, 2H), 1.95-1.70 (m, 7H), overlapping 1.70-1.48 (m) and 1.54 (s, total 6H), 1.30-1.20 (m, 1H), 1.15 (s, 3H), 1.08-0.98 (m, 2H), 0.94-0.88 (m, 2H), 0.85 (d, J= 6.0 Hz, 3H). ^{13}C-NMR ($CDCl_3$, ppm) δ 138.75 (C), 128.33 (CH), 127.45 (CH), 93.49 (C), 72.88 (CH_2), 69.04 (CH_2), 68.49 (CH), 44.90 (C), 44.44 (CH), 43.40 (CH), 41.44 (CH_2), 39.61 (CH_2), 34.75 (CH_2), 32.10 (CH_3), 29.96 (CH_3), 29.10 (CH_2), 27.25 (CH2), 25.62 (CH), 22.31 (CH_3), 21.73 (CH_2), 18.18 (CH_2). LRMS m/e 388 (M^+), 355, 297, 282, 254, 225, 199, 170, 149, 137, 127, 111, 91, 81, 69, 55, 41. HRMS calcd $C_{24}H_{36}O_2S$ 388.2438; obs 388.2425. (2*R*,4a*R*,7*R*,8a*S*,2'*R*)-4a,5,6,7,8,8a-hexahydro-4,4,7-trimethyl-4*H*-benzoxatiin-2-spiro-1'-[2'-(2-benzyloxy)ethyl]cyclopentane (**32**): IR (neat) 2900, 2850, 1495, 1450 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 7.39-7.31 (m, 4H), 7.31-7.23 (m, 1H), 4.54 (d, J= 21.0 Hz, 1H), 4.49 (d, 1H, J= 12.0 Hz), 4.08 (broad s, 1H), 3.55 (ddd, J= 9.0, 7.0, 4.5 Hz, 1H), 3.51 (ddd, J= 9.0, 8.0, 6.0 Hz, 1H), 2.58 (dd, J= 11.5, 7.0 Hz, 1H), 2.17 (broad quintet, J= 7.0 Hz, 1H), 1.97-1.60 (m, 8H), overlapping peaks 1.51 (s) and 1.60-1.46 (m, total 6H), 1.12 (s, 3H), 1.12-1.00 (m, 2H), 1.00-0.83 (m, 2H), 0.83 (d, J= 6.0 Hz, 3H). ^{13}C-NMR ($CDCl_3$, ppm) δ 138.84 (C), 128.42 (CH), 128.31 (CH), 127.80 (CH), 127.65 (CH), 127.41 (CH), 93.18 (C), 72.75 (CH_2), 69.18 (CH_2), 65.78 (CH), 44.37 (C), 43.60 (CH), 41.77 (CH_2), 41.64 (CH), 39.69 (CH_2), 34.75 (CH_2), 31.90 (CH_2), 31.84 (CH_3), 29.24 (CH_3), 28.06 (CH_2), 25.71 (CH), 22.37 (CH_3), 21.69 (CH_2), 19.02 (CH_2). LRMS m/e 388 (M^+), 355, 297, 282, 254, 225, 170, 149, 137, 127, 111, 91, 81, 69, 55, 41. HRMS calcd $C_{24}H_{36}O_2S$ 388.2438; obs 388.2432. (2*R*,4a*R*,7*R*,8a*R*,2'*S*)-4a,5,6,7,8,8a-hexahydro-4,4,7-trimethyl-4*H*-benzoxatiin-2-spiro-1'-[2'-(2-benzyloxy)ethyl]cyclopentane (**33**): IR (neat) 3000, 2900, 1465 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 7.42-7.30 (m, 5H), 7.30-7.23 (m, 1H), 4.54 (d, J= 12.0 Hz, 1H), 4.47 (d, J= 12.0 Hz, 1H), 3.60-3.50 (m, 2H), 3.45 (ddd, J= 10.0, 10.0, 5.0 Hz, 1H), 2.51 (ddd, J= 13.5, 8.0, 5.0 Hz, 1H), 2.18 (dtd, J= 13.5, 7.5, 3.0 Hz, 1H), 1.98 (ddd, J= 13.0, 10.0, 7.0 Hz, 1H), 1.86-1.54 (m, 9H),

1.43 (s, 3H), 1.43-1.20 (m, 3H), 1.20 (s, 3H), 1.02 (td, *J*= 13.0, 11.0 Hz, 1H), 0.91 (d, *J*= 6.5 Hz, 3H). ^{13}C-NMR ($CDCl_3$, ppm) δ 138.92 (C), 128.24 (CH), 127.60 (CH), 127.29 (CH), 89.37 (C), 72.55 (CH_2), 69.83 (CH_2), 69.62 (CH), 50.04 (CH), 48.30 (CH), 43.03 (C), 42.10 (CH_2), 40.56 (CH_2), 34.77 (CH_2), 31.49 (CH_3), 30.40 (CH), 28.88 (CH_2), 28.71 (CH_2), 26.08 (CH_3), 24.11 (CH_2), 22.55 (CH_2), 22.17 (CH_3).

Isolation of 34: A solution of the mixture of **28**, **29** and **30** (212 mg, 0.62 mmol) in a mixture solvent of methanol:THF:3N NaOH (1:1:3, 10 mL) was stirred overnight at room temperature. After the solution was acidified by 3N HCl, the mixture was extracted with ethyl acetate. The combined organic layers were washed with saturated NaCl solution, dried and concentrated in vacuo. Purification of the residue by chromatography on silica gel (ethyl acetate:*n*-hexane=1:1) gave a mixture of three acids (185 mg, 88%). Repeated chromatography on silica gel (ethyl acetate:*n*-hexane=1:1) gave analytically pure **34**. mp 122-124 °C. IR ($CHCl_3$) 2950, 1710, 1450, 1410 cm^{-1}. ^{1}H-NMR ($CDCl_3$, ppm) δ 3.51 (ddd, *J*= 10.5, 10.5, 4.5 Hz, 1H), 2.87 (dd, *J*= 16.5, 4.0 Hz, 1H), 2.54 (ddd, *J*= 13.0, 8.0, 5.5 Hz, 1H), 2.47 (dd, *J*= 16.5, 9.0 Hz, 1H), 2.22-1.89 (m, 3H), 1.89-1.56 (m, 5H), overlapping peaks 1.56-1.24 (m) and 1.44 (s, total 6H), 1.21 (s, 3H), 1.03 (ddd, *J*= 12.0, 12.0, 10.5 Hz, 1H), overlapping peaks 1.00-0.85 (m), 0.90 (d, *J*= 7.0 Hz, total 5H). ^{13}C-NMR ($CDCl_3$, ppm) δ 178.29 (CO), 89.30 (C), 70.15 (CH), 50.12 (CH), 47.37 (CH), 43.24 (C), 41.93 (CH_2), 40.16 (CH_2), 34.76 (CH_2), 34.20 (CH_2), 31.56 (CH), 30.24 (CH_3), 28.32 (CH_2), 25.95 (CH_3), 24.15 (CH_2), 22.39 (CH_2), 22.10 CH_3). LRMS m/e 312 (M^+), 283, 267, 225, 170, 155, 137, 123, 109, 95, 88, 81, 69, 55, 41. HRMS calcd $C_{17}H_{28}O_3S$ 312.1764; obs 312.1768. Anal. Calcd for $C_{17}H_{28}O_3S$: C, 65.34; H, 9.03; S, 10.26. Found: C, 65.17, H, 9.12, S, 10.06.

References and Notes

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1. a) Giese, B. *Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds;* Pergamon Press: Oxford, New York, 1986. b) Curran, D. P. *Synthesis*. **1988**, 417 and 489.
2. Recent studies in acyl radical chemistry; Crich, D.; Chen, C.; Hwang, J.-T.; Yuan, H.; Papadatos, A.; Walter, R. I. *J. Am. Chem. Soc.* **1994**, *116*, 8937 and references cited therein.
3. Cyclization using a 1,3-dithiolane ring as a radical-generating group has been reported previously; Winkler, J. D.; Sridar, V. *J. Am. Chem. Soc.*, **1986**, *108*, 1708. Highly activated benzylic dithioacetal has been used as a radical donor to construct the B ring of tetracyclines: Barton, D. H. R.; Clive, D. L. J.; Magnus, P. D.; Smith, G. *J. Chem. Soc. (C)*, **1971**, 2193.
4. For a review of the diastereoselective radical reactions: Porter, N. A.; Giese, B.; Curran, D. P. *Acc. Chem. Res.* **1991**, *24*, 296.
5. Nishida, A.; Nishida, M.; Yonemitsu, O. *Tetrahedron Lett.* **1990**, *31*, 7035.
6. Fraser-Reid, B.; Holder, N. L.; Yunker, M. B. *J. Chem. Soc. Chem. Commun.* **1972**, 1286; Walker, D. L.; Fraser-Reid, B. *J. Chem. Soc. Chem. Commun.* **1974**, 319; Fraser-Reid, B.; Holder, N. L.; Hicks, D. R; Walker, D. L. *Can. J. Chem.* **1977**, *55*, 3978; Fraser-Reid, B.; Anderson R. C.; Hicks, D. R; Walker, D. L. *Can. J. Chem.* **1977**, *55*, 3986.
7. For studies of α-heteroatom radicals; a) Uneyama, K.; Namba, H.; Oae, S.; *Bull. Chem. Soc. Jpn.*, **1968**, *41*, 1928. b) Malatesta, V.; Ingold, K. U. *J. Am. Chem. Soc.*, **1981**, *103*, 609. c) Beckwith, A. L. J.; Easton, C. J. *J. Am. Chem. Soc.*, **1981**, *103*, 615. d) Malatesta, V.; Scaiano, J. C. *J. Org. Chem.*, **1982**, *47*, 1455. e) Beckwith, A. L. J.; Brumby, S. *J. Chem. Soc. Perkin. Trans. II.*, **1987**, 1801. See also ref. 1.
8. Stork, G.; Zhao, K. *Tetrahedron Lett.* **1989**, *30*, 287.
9. Eliel, E. L.; Lynch, J. E. *Tetrahedron Lett.* **1981**, *22*, 2855.
10. Rychnovsky, S. D.; Skalitsky, D. J. *SYNLETT* **1995**, 555.
11. Nishida, M.; Nakaoka, K.; Ono, S.; Yonemitsu, O.; Nishida, A.; Kawahara, N.; Takayanagi, H. *J. Org. Chem.* **1993**, *58*, 5870.

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