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[3,3]Sigmatropic Ring Expansion of Cyclic Thionocarbonates. 12.[1] Synthesis of (-)-Yellow Scale Pheromone

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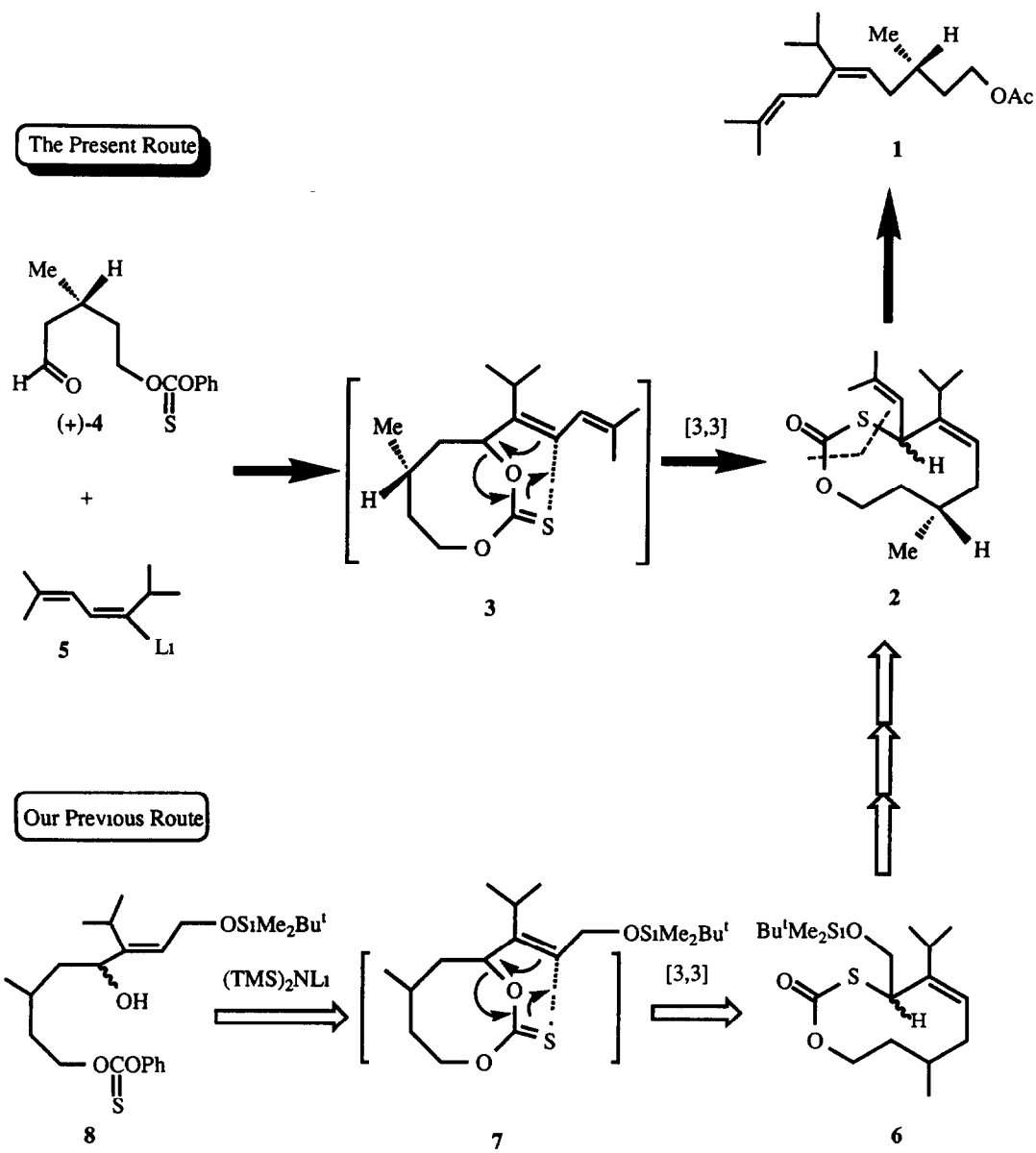
Abstract: *(-)-Yellow scale pheromone* ***1*** *has been synthesized by the route via [3,3]sigmatropic ring expansion of the 8-membered thionocarbonate* ***3*** *containing a diene moiety The key Z-10-membered intermediate* ***2*** *was exclusively synthesized by a one-pot conversion from a chiral aldehyde (+)-****4*** *and a dienyliodide* ***14***

The yellow scale, *Aonidiella citrina* (Coquillett),[2] causes widespread damage to citrus crops in addition to important ornamentals, and the sex pheromone offers the possibility of species-specific control of population Since the pheromone, (S,*E*)-(-)-3,9-dimethyl-6-isopropyl-5,8-decadienyl acetate **1**, was first isolated in 1979,[3] it has been synthesized by several routes [4]

We found that the [3,3]sigmatropic ring expansion of allylic cyclic thionocarbonates is extremely facile, and can be used in the highly stereoselective synthesis of either *Z* or *E* olefins in 10-membered thiolcarbonates (starting from 8-membered thionocarbonates) [5] In order to demonstrate the synthetic utility of this method, we recently reported a unique and stereoselective synthesis of (±)-yellow scale pheromone **1** [6] In the route (*Scheme 1*), the [3,3]sigmatropic ring expansion of 8-membered thionocarbonate **7** exclusively produced the *Z*-10-membered thiolcarbonate **6**, which was transformed *via* three steps into the key 10-membered intermediate **2** with all of the required carbon atoms of **1** Reductive removal of the SCO moiety in **2** with lithium in liquid ammonia or lithium *p,p'*-di-*tert*-butylbiphenylide (LDBB)-HMPA followed by acetylation afforded the pheromone (±)-**1** In continuation of the synthetic study of (-)-yellow scale pheromone, we have now developed a direct one-pot conversion to the key 10-membered thiolcarbonate **2** from a chiral aldehyde **4**, and the (-)-yellow scale pheromone **1** was synthesized *via* **2**

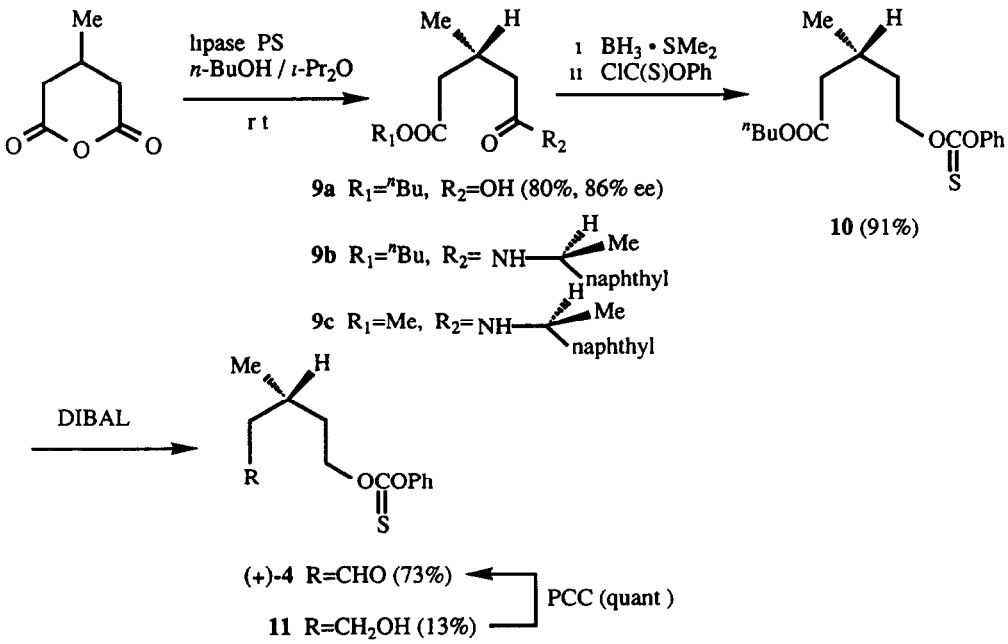
The chiral aldehyde **4** was prepared as follows A commercially available 3-methylglutaric anhydride was converted through the use of lipase PS (lipase from *Pseudomonas* sp)[7] to its half ester (R)-**9a** (80% yield, 86% ee) by modification[7b] of Oda procedure[8] (*Scheme 2*) The absolute configuration of **9a** was estimated from the data reported in the literature,[8] and its enantiomeric excess was determined by the HPLC and ^{1}H-NMR of the diastereomeric amide derivative **9c** (see Experimental) The half ester **9a** was then converted to the thionocarbonate **10** (91%) by successive treatments with diborane-dimethylsulfide followed by phenyl chlorothionoformate Diisobutylaluminum hydride (DIBAL) reduction of **10** gave the desired aldehyde (+)-**4** in 73% yield, along with an alcohol **11** in 13% yield Pyridinium chlorochromate (PCC) oxidation of **11** easily provided (+)-**4** The $[\alpha]_D$ value of **4** was nearly 0°, but, the variation of optical activity with the wavelength clearly gave a positive optical rotatory dispersion curve

Scheme 1


The Present Route
Me
H
OAc
1
Me
H
H
O
OCOPh
S
(+)-4
+
5
Li
Me
H
O
S
O
[3,3]
3
O
S
H
O
Me
H
2
Our Previous Route
OSiMe2But
OH
OCOPh
S
8
(TMS)2NLi
OSiMe2But
[3,3]
7
ButMe2SiO
O
S
H
O
6

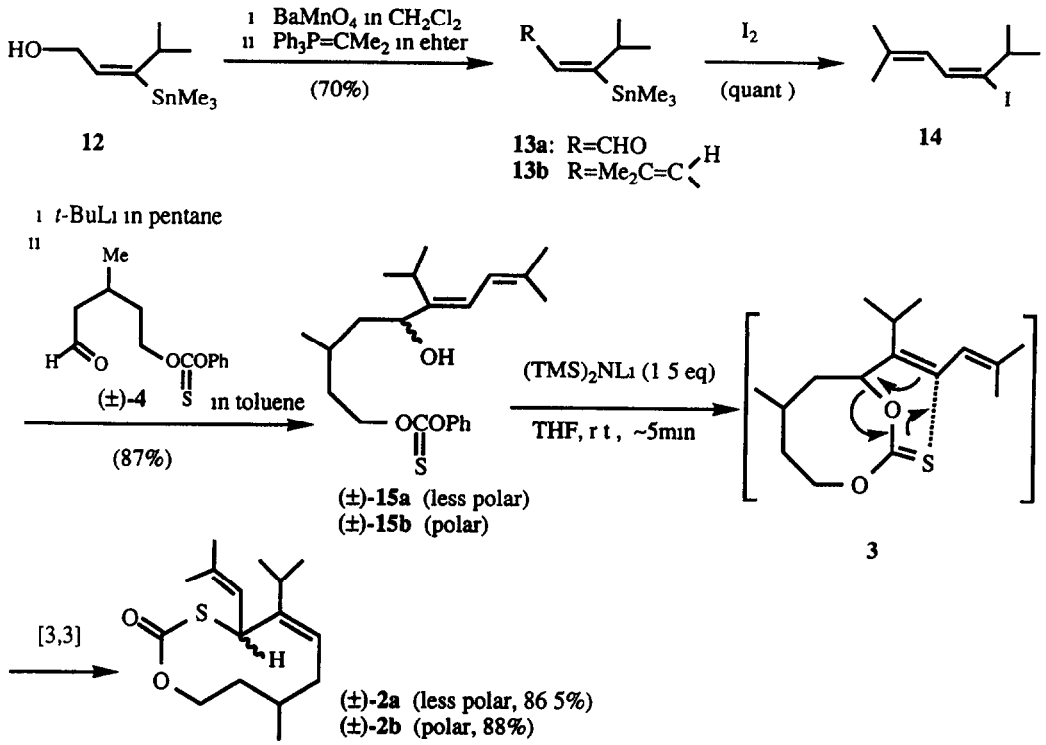
Oxidation of *E*-allylic alcohol **12**, prepared by the known procedure,[6,9] with $BaMnO_4$[10] gave the aldehyde **13a**, which was, without purification, subjected to the Wittig reaction to yield the dienylstannane **13b** in 70%

Scheme 2

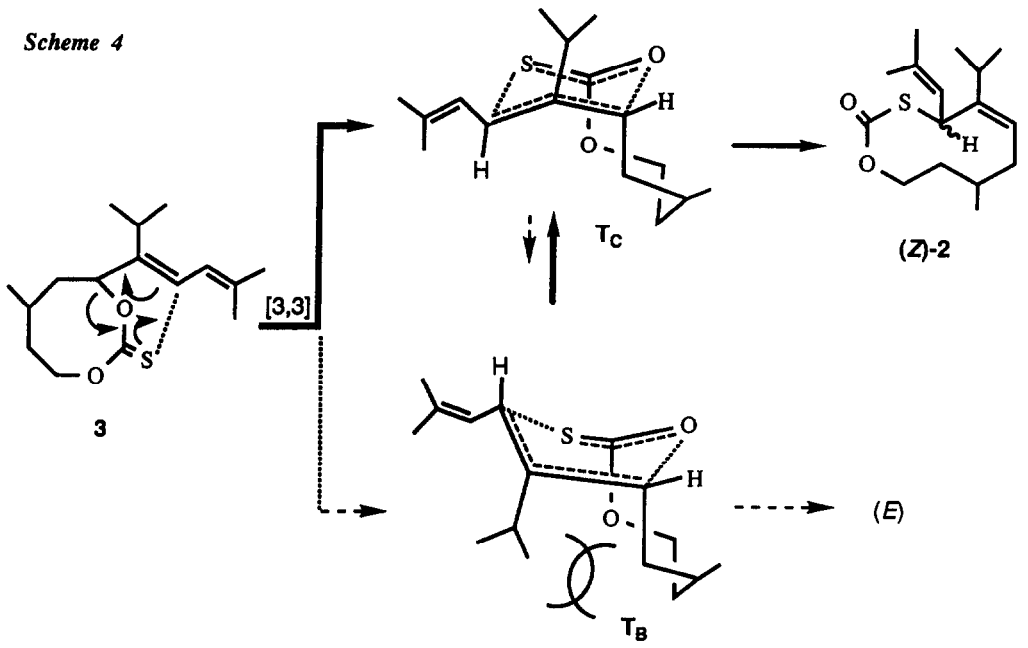


overall yield The ^{1}H-NMR of *E*-**13b** exhibited two peaks at δ 6 15 (d, *J*=11 2 Hz) and 6 28 [d, *J*=11 2 Hz ($^3J_{Sn-H}$=82 0 Hz)] due to olefinic protons The *E*-stereochemistry of the double bond was confirmed by a comparison with $^3J_{Sn-H}$ coupling constant[9] of its *Z*-isomer ($^3J_{Sn-H}$=140 0 Hz) [11] The dienylstannane **13b** was readily derived to the corresponding iodide **14** by treatment with iodine Many attempts to generate dienyllithium **5** by lithium-iodine exchange under various conditions in diethyl ether or THF were unsuccessful, because of the instability of generated **5** However, this problem could be overcomed by using pentane as solvent [12] Thus, addition of *t*-butyllithium (*t*-BuLi) to a pentane solution of **14** caused a white precipitate (LiI) at room temperature Subsequent addition of (±)-aldehyde 4[6] in toluene[13] at -78 °C afforded a 1 1 mixture of diastereomeric diol monothionocarbonates **15a,b**[14] (87% yield), which were separated by column chromatography Accordingly, the dienyllithium **5** formed in hydrocarbon solvents must be remarkably stabilized by its aggregation state in contrast to **5** in polar solvents Treatment of **15a** (**15b**) with lithium bis(trimethylsilyl)amide [$(TMS)_2NLi$][15] (1 5 eq) in THF at room temperature went to completion instantly *via* the [3,3]sigmatropic ring expansion of 8-membered thionocarbonates **3** Usual workup and purification by silica gel column chromatography exclusively gave the 10-membered thiolcarbonate **2a**[14] (**2b**[14]) in 86 5% (88%) yield, respectively (*Scheme 3*) Their ^{1}H-NMR data were completely corresponded with those of the diastereomeric mixture **2**, prepared by an alternative method in the preceding paper [6] This result clarified that the diol monothionocarbonates having a diene moiety could be suited to the [3,3]sigmatropic ring expansion of cyclic thionocarbonates

Scheme 3



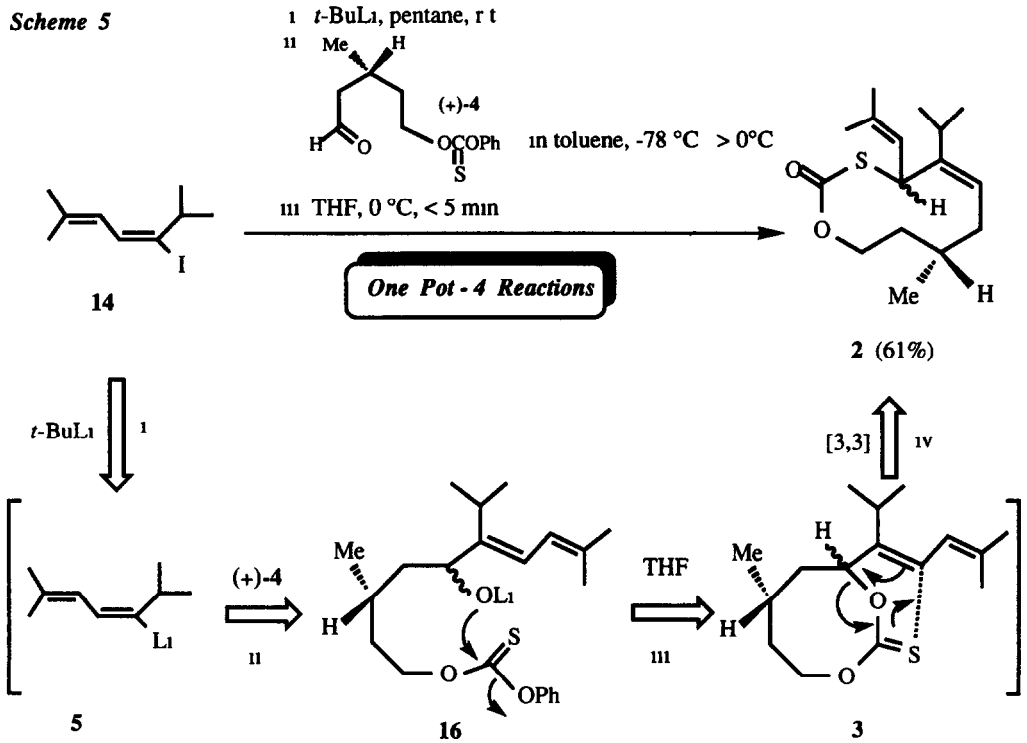
Scheme 4



The exclusive formation of the *Z*-double bond in **2** may be rationalized by the conformational preference of a chairlike transition state ($\mathbf{T_C}$) over the more congested boatlike transition state ($\mathbf{T_B}$) leading to the *E*-isomer (*Scheme 4*), as proposed from the previous studies [5]

We next aimed a one-pot formation of **2** from chiral aldehyde **4** and dienyliodide **14** in one reaction vessel without use of $(TMS)_2NLi$ Treatment of the dienyliodide **14** with *t*-BuLi in pentane at room temperature

Scheme 5



followed by addition of a solution of **4** in toluene at -78 °C, and then dilution of the reaction mixture with THF at 0 °C successfully afforded a 1 1 mixture of diastereomeric products **2** in 61% yield This conversion consists of four reactions as illustrated in *Scheme 5* i) Generation of dienyllithium **5** in pentane ii) Addition of **5** to the chiral aldehyde **4** iii) Cyclization of the lithium alkoxide **16** to 8-membered thionocarbonate **3** iv) The [3,3]sigmatropic ring expansion to the 10-membered product **2** It should be noted that THF is an indispensable solvent in promoting the steps iii and iv Both diastereomers **2** are utilized in the preparation of the yellow scale pheromone **1**, since a newly formed chiral center in **2** is not present in the final product We thus succeeded the facile synthesis of the key 10-membered intermediate **2** for the synthesis of pheromone **1** by simple one-pot procedure

Reductive desulfurization of **2** by LDBB-HMPA followed by acetylation finally afforded (-)-yellow scale pheromone **1** in 60% yield [6] The optical rotation of **1** was $[\alpha]_D$ -10 0° (*n*-hexane) {lit $[\alpha]_D$ -9 48° (*n*-hexane),[4e] $[\alpha]_D$ -9 83° (*n*-hexane),[4c] $[\alpha]_D$ -11 9° (*n*-hexane),[4d] and $[\alpha]_D$ -12 1° (*n*-hexane)[4g]}

Further synthetic applications of the [3,3]sigmatropic ring expansion of medium-membered thionocarbonates are also being investigated in our laboratories

Experimental

General The IR spectra were recorded on a Shimadzu IR-435, and MS on a Hitachi M-80 spectrometers The ^{1}H- and ^{13}C-NMR spectra were taken with tetramethylsilane as an internal standard on a Varian Gemini-200 spectrometers in $CDCl_3$ The ORD spectra were recorded with a JASCO ORD/UV-5 spectrometer and optical rotations were measured with a JASCO DIP-181 Digital Polarimeter HPLC analysis was carried out with a Waters Associates instrument [column, μ porasil, 3 9 mmx30 cm, eluent, 3% 2-propanol in hexane, detection, 280 nm] Unless otherwise noted, SiO_2 (Merck 9385) was used for column chromatography and the reactions were carried out under argon stream THF was distilled from sodium-benzophenone

3(R)-Monobutyl-3-methylpentanedioate (9a): *n*-Butanol (0 18 ml, 2 0 mmol) and lipase PS[7] (200 mg) were added to a vigorously stirred suspension of 3-methylglutaric anhydride (128 mg, 1 0 mmol) in diisopropyl ether (10 ml) according to a known procedure [8] The reaction mixture was stirred magnetically at ambident temperature for 37 h The workup afforded **9a** (80%, 86% ee) as a colorless oil

Determination of Diastereomeric Excess of 9a The half ester **9a** was converted to the diastereomeric amide **9b** of (S)-1-(1-naphthyl)ethylamine according to the literature[8], however, the enantiomeric excess could not determine at this stage The butyl ester moiety of **9b** was converted into the methyl ester through transesterification with heating in MeOH-toluene (1 1) in the presence of d-camphorsulfonic acid for 20 h The diastereomeric excess (d e) of the methyl ester homolog **9c** was determined as 86% by HPLC (flow rate 1 ml/min, R_t 28 and 30 min) The d e was also calculated as 86% from calculation of the peak areas at δ 3 61 and 3 64 in the ^{1}H-NMR spectrum of **9c** [oil IR ($CHCl_3$) 3420 (NH), 1720 (CO), 1650, 1495 cm^{-1} ^{1}H-NMR 0 99 (3H, d, *J*=6 0 Hz, C<u>H</u>$_3$CHCH$_2$), 1 67 (3H, d, *J*=6 0 Hz, C<u>H</u>$_3$CHNH), 1 98~2 57 (5H, m, 2xCH$_2$, CH$_3$C<u>H</u>CH$_2$), 3 61 and 3 64 (total 3H, each s, CH$_3$O/13 1), 5 87~6 03 (2H, br, NH, CH$_3$C<u>H</u>NH), 7 40~8 15 (7H, m, ArH) MS *m/z* 313 (M^+) HR-MS *m/z* calcd for $C_{19}H_{23}NO_3$ 313 1676, Found 313 1672

3(R)-*O*-4-Butoxycarbonyl-3-methylbutyl *O*-Phenyl Thionocarbonate (10): A 2 0 M borane-dimethyl sulfide complex in THF (0 59 ml, 1 18 mmol) was added dropwise over 5 min to a solution of (R)-**9a** (198 mg, 0 98 mmol) in THF (7 ml) in a dry flask at 0 °C The reaction mixture was stirred at 0 °C for 10 min , then at room temperature for 3 h The reaction mixture was quenched with H_2O, made slightly alkaline with saturated aqueous $NaHCO_3$, and extracted with ether (2x20 ml) The combined ether solution was washed with brine, and dried over anhydrous $MgSO_4$ Evaporation gave 3(R)-butyl 5-hydroxy-3-methylpentanoate (180 mg, 98%) [IR (neat) 3400 (OH), 1715 (CO) cm^{-1} ^{1}H-NMR 0 92 (3H, t, *J*=7 2 Hz, C<u>H</u>$_3$CH$_2$), 0 97 (3H, d, *J*=6 4 Hz, C<u>H</u>$_3$CH), 1 39 (2H, sept, *J*=7 2 Hz, CH$_3$C<u>H</u>$_2$), 1.47~1 68 (4H, m, CH$_3$CH$_2$C<u>H</u>$_2$, C<u>H</u>$_2$CH$_2$OH), 2 04~2 41 (3H, m, CH, CH$_2$O), 3 67 (2H, t, *J*=6 6 Hz, C<u>H</u>$_2$OH), 4 07 (2H, t, *J*=6 6 Hz, CH$_2$OCO)] as a colorless oil A solution of phenyl chlorothionoformate (0 35 ml, 2 54 mmol) in acetonitrile (2 5 ml) was added to a solution of the ester (459 mg, 2 44 mmol) in acetonitrile (10 ml) in the presence of pyridine (0 22 ml, 2 72 mmol) and 4-DMAP (30 mg, 0 25 mmol) at 0 °C The reaction mixture was stirred at 0 °C for 20 min, then at room temperature for 2 h The solvent was evaporated under reduced pressure to give an oil, which was subsequently diluted with EtOAc-hexane (3 1) The organic layer was washed with H_2O, brine, dried over anhydrous Na_2SO_4, and then evaporated *in vacuo* The residue was purified by column chromatography using EtOAc-hexane (1 3) for elution to give **10** (733 mg, 93%) as an oil IR (neat) 1720 (CO) cm^{-1} ^{1}H-NMR 0 94

(3H, t, J=7 3 Hz, C<u>H</u>$_3$CH$_2$), 1 04 (3H, d, J=6 3 Hz, C<u>H</u>$_3$CH), 1 38 (2H, sext, J=7 3 Hz, CH$_3$C<u>H</u>$_2$), 1 54~1 82 (3H, m, CH$_2$OCO, 1/2xCHC<u>H</u>$_2$CH$_2$), 1 92 (1H, dtd, J=21 6, 7 0, 1 8 Hz, 1/2xCHC<u>H</u>$_2$CH$_2$), 2 09~2 29 (2H, m, CH, 1/2xCHC<u>H</u>$_2$CO), 2 38 (1H, dd, J=17 2 Hz, 1/2xCHC<u>H</u>$_2$CO), 4 10 (2H, t, J=6 6 Hz, CH$_2$OCO), 4 58 (2H, td, J=7.0, 1 3 Hz, CH$_2$OCS), 7 06~7 49 (5H, m, ArH) MS m/z. 324 (M^+), 251 (M^+-OC$_4$H$_9$) HR-MS m/z calcd for $C_{17}H_{24}O_4S$ 324 1394, Found 324 1376

3(R)-*O*-(4-Formyl-3-methylbutyl) *O*-Phenyl Thionocarbonate (4) A 1 5 M solution of DIBAL in toluene (0 46 ml, 0 693 mmol) was added dropwise to a solution of **10** (102 mg, 0 315 mmol) in toluene (5 m l) in a dry flask at -78 °C After being stirred at -78 °C for 0 5 h, the reaction was quenched with saturated aqueous NH$_4$Cl The resulting turbidity was removed by filtration through a Celite pad, and washed with ether The combined ether solution was washed with H$_2$O, dried over anhydrous MgSO$_4$, and then evaporated under reduced pressure The residual oil was purified by column chromatography using EtOAc-hexane (3 7) for elution to give 4[6] (58 mg, 73%) and 3(S)-O-(5-hydroxy-3-methylpentyl) O-phenyl thionocarbonate **11**[6] (10 mg, 13%) ORD of **4** (c=1 62, EtOH) [α]^{20} (nm) ~0° (589), +4 9° (500), +18 5° (400), and +29 6° (350)

The alcohol **11** was converted to the aldehyde **4** by PCC oxidation in quantitative yield [6]

***E*-2,6-Dimethyl-5-trimethylstannyl-2,4-heptadiene (13b)** A suspension of BaMnO$_4$ (9 8 g, 38 3 mmol) and **12**[6] (1 225 g, 4 66 mmol) in CH$_2$Cl$_2$ (120 ml) was stirred at room temperature for 32 h Additional BaMnO$_4$ (9 8 g, 38 3 mmol) was added and the suspension was stirred at room temperature for another 16 h The reaction mixture was filtered through a Celite pad and washed with CH$_2$Cl$_2$ The combined solvent was evaporated under reduced pressure to give *E*-4-methyl-3-trimethylstannyl-2-pentenal **13a** (1 216 g, quant) {IR (neat) 1660 (CHO) cm^{-1} ^{1}H-NMR 0 26 [9H, s (J_{Sn-H}=53 5 Hz), 3xSnCH$_3$], 1 12 (6H, d, J=6 7 Hz, 2xC<u>H</u>$_3$CH), 3 86 (1H, sept, J=6 7 Hz, CH$_3$C<u>H</u>), 6 08 [1H, d, J=7 4 Hz (J_{Sn-H}=72 0 Hz), =CH], 10 09 (1H, d, J=7 4 Hz, CHO) MS m/z 262 (M^+)} as a pale yellow oil A 1 6 M solution of *n*-BuLi (0 75 ml, 1 20 mmol) was added to a suspension of isopropyltriphenylphosphonium bromide (462 mg, 1 20 mmol) in anhydrous ether (6 ml) in a dry flask at room temperature After the suspension was stirred for 2 5 h in a sealed flask, a solution of the aldehyde **13a** (285 mg, 1 09 mmol) in anhydrous ether (6 ml) was added to a resulting wine-red solution The mixture was stirred at room temperature for 38 h in a sealed flask The reaction mixture was then diluted with *n*-hexane, and the resulting insoluble precipitate was filtered through a Celite pad and washed with *n*-hexane The combined hexane solution was evaporated *in vacuo*, and the residue was purified by column chromatography (Mallinckrodt 60 Å SPECIAL/silica, 1 0 g) using *n*-hexane for elution to yield *E*-**13b** (220 mg, 70%) as a colorless oil ^{1}H-NMR 0 14 [9H, s (J_{Sn-H}=51 8 Hz), 3xSnCH$_3$], 0 98 (6H, d, J=6 7 Hz, 2xC<u>H</u>$_3$CH), 1 77 and 1 79 (each 3H, each s, 2x=CCH$_3$), 3 16 (1H, sept, J=6 7 Hz, CH), 6 15 [1H, d, J=11 2 Hz, HC=C(CH$_3$)2], 6 28 [1H, d, J=11 2 Hz (J_{Sn-H}=82 0 Hz), HC=CSn] MS m/z 288 (M^+) HR-MS m/z calcd for $C_{12}H_{24}Sn$ 288 0899, Found 288 0901

***E*-5-Iodo-2,6-dimethyl-2,4-heptadiene (14)** Iodine (276 mg, 1 087 mmol) was added to a stirred solution of **13b** (260 mg, 0 906 mmol) in dry ether (8 ml) at 0 ° The reaction mixture was stirred for 20 min at the same temperature and then treated with saturated aqueous Na$_2$S$_2$O$_3$ solution until the resulting brown color became colorless A 10% KF solution was added and the mixture was stirred for additional 15 min at room temperature The resulting turbidity was filtered off through a Celite pad, and washed with ether The combined ether solution was washed with saturated Na$_2$S$_2$O$_3$ solution, brine, and dried over anhydrous MgSO$_4$

Evaporation of the solvent under reduced pressure gave **14** (225 mg, quant) as a yellow oil ^{1}H-NMR· 0 94 (6H, d, *J*=6 4 Hz, 2xC<u>H</u>$_3$CH), 1 69 and 1 73 (each 3H s, 2x=CC<u>H</u>$_3$), 2 37 (1H, sept, *J*=6 4 Hz, CH), 6 02 [1H, br d, *J*=11 2 Hz, HC=C(CH$_3$)$_2$], 6 88 [1H, d, *J*=11 2 Hz, HC=CI)

(±)-*O*-[*E*-3,9-Dimethyl-5-hydroxy-6-isopropyl-6,8-decadienyl] *O*-Phenyl Thionocarbonates (15a, 15b) A 1 5 M *tert*-BuLi in pentane solution (2 1 ml, 3 12 mmol) was added to a solution of **14** (390 mg, 1 56 mmol) in pentane (10 ml) in a dry flask at room temperature The reaction mixture was stirred for 80 min during which a white precipitate deposited A solution of (±)-**4** (246 mg, 0 98 mmol) in toluene (7 ml) was then added at -78 °C and the reaction mixture was stirred at the same temperature for 110 min followed by at 0 °C for 15 min The reaction mixture was quenched with saturated aqueous NaHCO$_3$ and extracted with ether The organic solution was washed with H$_2$O (x2), brine, and dried over anhydrous MgSO$_4$ Evaporation of the solvent under reduced pressure gave an oily residue, which was purified by column chromatography using EtOAc-hexane (1 49) for elution to give a mixture (318 mg, 87%) of **15a**[14] (less polar) and **15b**[14] (polar), which could be separated in part by column chromatography (benzene EtOAc=30 1)

(±)-**15a** A colorless oil IR (neat)· 3420 (OH) cm^{-1} ^{1}H-NMR 1 04 (3H, d, *J*=6 6 Hz, C<u>H</u>$_3$CHCH$_2$), 1 08 and 1 16 (each 3H, each d, *J*=7 1 Hz, 2x=CCHC<u>H</u>$_3$), 1 23~2 08 (5H, br m, CH$_3$C<u>H</u>CH$_2$, CHC<u>H</u>$_2$CH, CHC<u>H</u>$_2$CH$_2$), 1 78 and 1 82 (each 3H, s, 2x=CCH$_3$), 2 90 (1H, quint, *J*=7 1 Hz, =CC<u>H</u>CH$_3$), 4 30 (1H, br d, *J*=10 0 Hz, C<u>H</u>OH), 4 61 (2H, br, CH$_2$OCS), 6 14 (1H, br d, *J*=11 6 Hz, CH$_3$C=C<u>H</u>), 6 32 (1H, d, *J*=11 6 Hz, C<u>H</u>=CCH), 7 05~7 52 (5H, m, ArH) MS *m/z* 358 (M$^+$-OH)

(±)-**15b**. A colorless oil IR (neat). 3420 (OH) cm^{-1} ^{1}H-NMR 1 03 (3H, d, *J*=6 6 Hz, C<u>H</u>$_3$CHCH$_2$), 1 10 and 1 17 (each 3H, d, *J*=7 1 Hz, 2x=CCHC<u>H</u>$_3$), 1 23~2 16 (5H, br m, CH$_3$C<u>H</u>CH$_2$, CHC<u>H</u>$_2$CH, CHC<u>H</u>$_2$CH$_2$), 1 78 and 1 83 (each 3H, each s, 2x=CCH$_3$), 2 88 (1H, quint, *J*=7 1 Hz, =CC<u>H</u>CH3), 4 28 (1H, t, *J*=6 9 Hz, C<u>H</u>OH), 4 48~4 72 (2H, m, CH$_2$OCS), 6 15 (1H, br d, *J*=11 6 Hz, CH$_3$C=C<u>H</u>), 6 29 (1H, d, *J*=11 6 Hz, <u>H</u>C=CCH), 7 06-7 50 (5H, m, ArH) MS *m/z* 358 (M$^+$-OH)

(±)-*Z*-5-Isopropyl-8-methyl-4-(2-methyl-1-propenyl)-7,8,9,10-tetrahydro-4*H*-1,3-oxathiecin-2-one (2a)· A 1 M solution of (TMS)$_2$NLi in THF (0 17 ml, 0 17 mmol) was injected rapidly to a solution of (±)-**15a** (41 8 mg, 0 11 mmol) in THF (12 ml) in a dry flask with a stirring at room temperature The reaction mixture was quenched by addition of H$_2$O within 5 min, and diluted with *n*-hexane-EtOAc (2 1) The organic layer was washed with H$_2$O, brine, and dried over anhydrous Na$_2$SO$_4$ Evaporation of the solvent under reduced pressure gave an oily residue, which was purified by column chromatography using 15% EtOAc in *n*-hexane for elution to give **2a**[14] (27 1 mg, 86.5%) as a colorless oil ^{1}H-NMR 1 06 and 1 14 (each 3H, d, *J*=6 9 Hz, 2x=CCHCH$_3$), 1 12 (3H, d, *J*=6 7 Hz, C<u>H</u>$_3$CHCH$_2$), 1 42 (1H, dt, *J*=16 0, 6 0 Hz, 1/2x C<u>H</u>$_2$CH$_2$O), 1 67~2 10 (3H, br m, 1/2xC<u>H</u>$_2$CH$_2$O, CH$_3$C<u>H</u>CH$_2$, 1/2x=CHC<u>H</u>$_2$), 1 77 (6H, br s, 2x=CCH$_3$), 2 52 (1H, dt, *J*=14 6, 12 0 Hz, 1/2x=CHCH$_2$), 2 57 (1H, sept, *J*=6 9 Hz, =C<u>H</u>CH$_3$), 4 01 (1H, td, *J*=11 3, 1 5 Hz, 1/2xCH$_2$O), 4 86 (1H, ddd, *J*=11 3, 4 6, 2 9 Hz, 1/2xCH$_2$O), 5.20 (1H, dt, *J*=9 4, 1 3 Hz, CH$_3$C=C<u>H</u>), 5 30 (1H, dd, *J*=12 0, 3 3 Hz, =CHCH$_2$), 5 45 (1H, d, *J*=9 4 Hz, SCH)

In the same manner as described above, (±)-**2b** (11 7 mg, 88%) was obtained from (±)-**15b** (17 7 mg, 0 05 mmol) and 1 0 M solution of (TMS)$_2$NLi (0 07 ml, 0 07 mmol) as a colorless oil ^{1}H-NMR 1 01 (3H, d, *J*=5 5 Hz, =CCHC<u>H</u>$_3$), 1 08 (3H, d, *J*=7 3 Hz, C<u>H</u>$_3$CHCH$_2$), 1 12 (3H, d, *J*=6 8 Hz, =CCHCH$_3$), 1 36~1 48 (2H, m, C<u>H</u>$_2$CH$_2$O), 1 73 (6H, br s, 2x=CCH$_3$), 1 84~2 16 (2H, m, 1/2x=CHC<u>H</u>$_2$, CH$_3$C<u>H</u>CH$_2$), 2 56 (1H, sept, *J*=6 8 Hz, =CC<u>H</u>CH$_3$), 2 98 (1H, td, *J*=13 4, 4 1 Hz, 1/2x=CHC<u>H</u>$_2$), 3 73

(1H, dd, J=13 2, 11 2 Hz, 1/2xCH$_2$O), 5 10 (1H, dt, J=11 2, 3 3 Hz, 1/2xCH$_2$O), 5 18 (1H, dt, J=9 4, 1 3 Hz, C<u>H</u>=CCH$_3$), 5 33~5 44 (1H, overlap, =C<u>H</u>CH$_2$), 5,44 (1H, br d, J=9 4 Hz, SCH)

One-Pot Synthesis of Key 10-Membered Intermediates 2 from Chiral Aldehyde (+)-4 and Dienyliodide 14: A 1 5 M solution of *tert*-BuLi (1 26 ml, 1 888 mmol) was added to a solution of **14** (236 mg, 0 944 mmol) in dry pentane (7 ml) in a dry flask at room temperature The reaction mixture was stirred for 30 min during which a white precipitate deposited, then cooled to -78 °C The chiral aldehyde (+)-4 (198 mg, 0 787 mmol) in toluene (7 ml) was added dropwise, and the resulting mixture was stirred at -78°C for 45 min followed by at 0 °C for 75 min Then, THF (60 ml) was rapidly added to the mixture at 0°C The reaction was quenched within 5 min and THF was evaporated *in vacuo* to give an oily residue, which was dissolved in ether The ether solution was washed with H$_2$O (x2), brine, and dried over anhydrous MgSO$_4$ Evaporation of the solvent under reduced pressure gave a crude oil, which was purified by column chromatography using 3% EtOAc in hexane for elution to give a 1 1 mixture of diastereomeric products **2** (132 mg, 61%) as a white wax ORD of (+)-**2**, (c=4 14, CHCl3) [α]^{19} (nm) +14 5 (589), +18 8 (500), +26 8 (450), and +39 9 (400)

(S,*E*)-(-)-3,9-Dimethyl-6-isopropyl-5,8-decadienyl Acetate (The Yellow Scale Pheromone) 1 Reductive desulfurization of **2** by LDBB-HMPA followed by acetylation according to our previous procedure[6] afforded **1** {60%, $[\alpha]_D^{21}$=-10 0° (c=1 30, hexane)} and (S)-3,9-dimethyl-6-isopropyl-6,8-decadienyl acetate {23%, $[\alpha]_D^{21}$=-11 0° (c=1 38, hexane)}

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11 Reaction of (*E*)-aldehyde **13a** with Wittig ylide, prepared from isopropyltriphenylphosphonium bromide and sodium methylsulfinylmethylide in DMSO, gave **Z-13b** (12%) {^{1}H-NMR. 0 20 [9H, s (J_{Sn-H}=52 5 Hz, Sn(CH_3)$_3$], 1.01 [6H, d, *J*=7.0 Hz, CH($C\underline{H}_3$)$_2$], 1 74 [6H, s, =C(CH_3)$_2$], 2 52 (1H, sept, *J*=7 0 Hz, CH), 5 80 [1H, d, *J*=10 5 Hz, $\underline{H}$C=C(CH_3)$_2$], 6 79 [1H, d, *J*=10 5 Hz (J_{Sn-H}=140 0 Hz)]}, and **Z-13a** (25%)

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13 Aldehyde **4** is insoluble in pentane

14 The relative configuration remains undetermined

15 Use of (TMS)$_2$NNa or (TMS)$_2$NK afforded **2** in low yield