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[3,3]Sigmatropic Ring Expansion of Cyclic Thionocarbonates. 13.[1] Synthesis of Medium-Membered Heterocyclic Allenes and Synthetic Application to Antifungal Constituent of *Sapium Japonicum*

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Abstract: *Cyclic allenes (**3a-k, 3n**) containing a SCOO moiety in the range of 8- to 11-membered ring were synthesized by the [3,3]sigmatropic rearrangement of the alkynyl cyclic thionocarbonates (**2**). Ring expansion of 6-membered cyclic thionocarbonates (**2i-k**) afforded a new type of strained 8-membered heterocyclic allenes (**3i-k**) in high yields. The MNDO optimized structure of **3i** indicated the allenyl moiety was bent and strained. The reactivity of 8-membered cyclic allenes was also examined. Further, using this methodology with a novel application of a SmI_2-HMPA reduction of the resulting heterocyclic allene (**3n**), an antifungal constituent of a Sapium japonicum, (±)-methyl 8-hydroxy-5,6-octadienoate (**24**), was synthesized.*

INTRODUCTION

In recent years there has been a wide-spread interest in reactivity of substituted allenes and their use in the synthesis of complex molecules.[2,3] Despite an increasing number of naturally occurring allenes, *e.g.*, allenic pheromones[4] or allenyl prostaglandins[5], chemistry of allenes involves many stereochemical and synthetic problems to be solved.[6]

We recently found[7] that the [3,3]sigmatropic ring expansion of allylic 8-membered thionocarbonates induced the highly stereoselective synthesis of either *Z* or *E* olefins in 10-membered thiolcarbonates. Formation of the 8-membered intermediates followed by their proposed transition states in the [3,3]sigmatropic rearrangements were investigated by experiments[8] and theoretical calculations.[9] Moreover, the utility of this methodology was demonstrated by a unique and stereoselective synthesis of (-)-yellow scale pheromone.[1] The yield and stereoselectivity of this reaction encouraged us to see if it could be applied to alkynyl cyclic

thionocarbonates (**2**), which after ring expansion would yield medium sized-heterocyclic allenes (**3**),[3,10] a class of compounds otherwise difficult to synthesize.[11]

We here report our conclusion to this study: (i) synthesis of 11, 10, and 9-membered heterocyclic allenes, (ii) synthesis and characterization of a new type of strained 8-membered heterocyclic allenes, (iii) application to the synthesis of (±)-methyl 8-hydroxy-5,6-octadienoate which is an antifungal constituent of *Sapium japonicum*. The synthesis also involves the first SmI_2-HMPA reduction of a cyclic thionocarbonate.

RESULTS AND DISCUSSION

Synthesis of Medium-membered Heterocyclic Allenes by [3,3]Sigmatropic Ring Expansion of Cyclic Thionocarbonates

The starting acetylene diol monothionocarbonates (**1**) used in the present study were easily prepared by addition of alkynyllithiums to the corresponding aldehydes or ketones.[7,12] The ^{1}H-NMR data of **1** are summarized in **Table 3**.

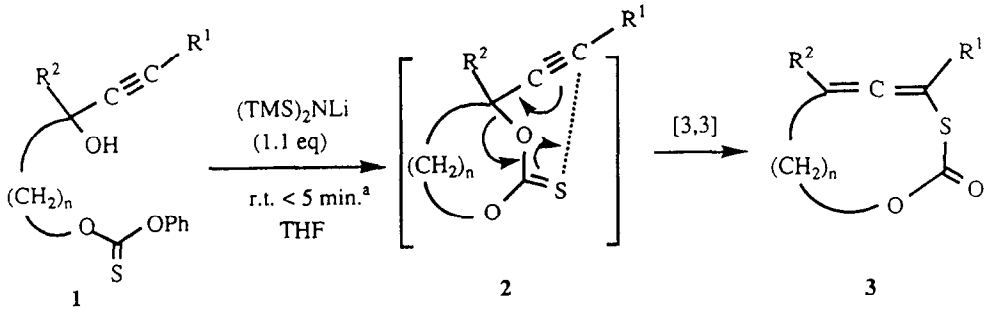
When a dry THF solution of lithium bis(trimethylsilyl)amide [$(TMS)_2NLi$] (1.1 eq) was rapidly added to a THF solution of **1b**, the formation of cyclic thionocarbonate (**2b**) and its spontaneous [3,3]sigmatropic rearrangement went to completion immediately. After usual workup the 10-membered allene (**3b**) was isolated by flash chromatography in 77% yield (**Table 1**, run 2). IR spectrum of **3b** showed a weak peak of C=C=C at 1950 cm^{-1}. Its ^{13}C-NMR spectrum indicated a characteristic allenic *sp* carbon at 202.4 ppm and two sp^2 carbons at 102.9 and 96.0 ppm, respectively. The structure was supported by the MS [*m/z*: 240 (M^+)]. Its isomeric purity was confirmed by VPC analysis using 5% silicon OV-17 column. It should be pointed out that the ease of this reaction may be attributed to the favorable conformation of the intermediate (**2b**) during the rearrangement (**Fig. 1**).

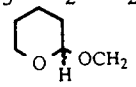
We next examined on the influence of the ring size of cyclic allene (**3**) of this reaction, the results of which are summarized in **Table 1**. Compounds [**1a** (n = 5), **1c** (n = 4), and **1g** (n = 3)] having a n-butyl group at R^1 position afforded 11-, 10-, and 9-membered cyclic allenes (**3a**, **3c**, and **3g**) in 28%, 66%, and 49% yields, respectively (**Table 1**, runs 1, 3, and 7). This result indicated that the 10-membered cyclic allene was apt to be formed easily. The cyclic allene formations could be applied for compounds (**1e** and **1f**) with a hydroxymethyl group protected by methoxymethoxymethyl or tetrahydropyranyl group (runs 5, 6) in modest yields. Compounds (**1d** and **1h**) having a bulky *tert*-butyl group also afforded 10- and 9-membered cyclic allenes (**3d** and **3h**) (runs 4, 8). These observation indicated that this reaction provided a convenient and flexible approach for the medium-membered cyclic allenes tethered by a SCOO moiety.

Synthesis of Strained 8-Membered Heterocyclic Allenes and Their Derivatives

Recent interests have focused on attempts to synthesize the highly strained cyclic allenes and to study their properties.[10,13] Decreasing the ring size of cyclic allenes results in deviation of both the normal C=C=C linearity and the orthogonality of the dihedral angle.[10] Seven- and six-membered cyclic allenes are known as important intermediates in organic synthesis.[10, 13] However, the most smallest isolable carbocyclic allene is 1-*tert*-butyl-1,2-cyclooctadiene.[14] Recently, two groups[15] independently reported synthesis of 6-membered silacyclic allenes bridged by long Si-Si bond which would release the ring strain. Although several methods have been reported to generate the cyclic allenes,[10] the sigmatropic rearrangement has been rarely used to synthesize the strained cyclic

Table 1. Synthesis of Medium-membered Heterocyclic Allenes (3) by the [3,3]Sigmatropic Ring Expansion of Cyclic Thionocarbonates (2)[a]



Run	1; No	n	R^1	R^2	3; Ring Size	No	Yield (%)[b]
1	**1a**	5	n-C_4H_9	H	11	**3a**	28[c]
2	**1b**	4	n-C_4H_9	CH_3	10	**3b**	77
3	**1c**	4	n-C_4H_9	H	10	**3c**	66
4	**1d**	4	*tert*-C_4H_9	H	10	**3d**	46[d]
5	**1e**	4	$CH_3OCH_2OCH_2$	H	10	**3e**	47
6	**1f**	4		H	10	**3f**	35
7	**1g**	3	n-C_4H_9	H	9	**3g**	49[e]
8	**1h**	3	*tert*-C_4H_9	CH_3	9	**3h**	33

a: Unless otherwise stated, the reactions were carried out according to the general procedure (see experimental); b: Isolated yield; c: Dimeric material was also obtained in 28% yield; d: The reaction was carried out at room temperature for 0.5 h; e: **1g** (40%) was recovered.

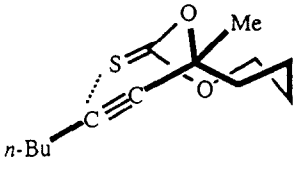
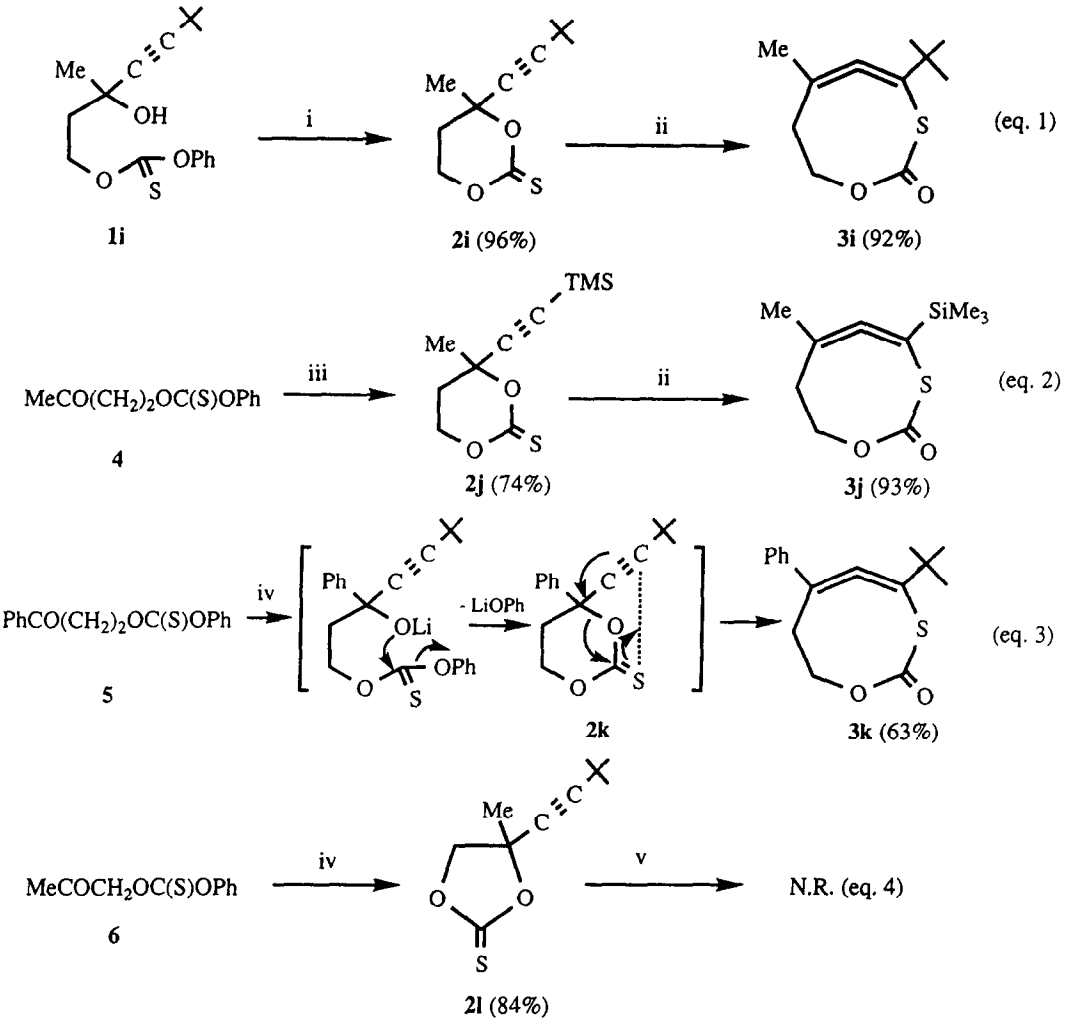


Figure 1. Favorable conformation of **2b**

allenes. From these viewpoints, we were interested in the synthesis of the strained cyclic allenes containing a divalent sulfur and oxygen atoms, according to our methodology.

While the strained cyclic allenes easily dimerize through a [2+2] cycloaddition,[10, 16] bulky alkyl groups on the allene moiety make possible to isolate the labile molecule.[10, 14] Treatment of diol monothionocarbonate (**1i**) having a *tert*-butyl group with (TMS)2NLi in THF at room temperature afforded a 6-membered cyclic thionocarbonate (**2i**) (96%), which was a substrate for the [3,3]sigmatropic ring expansion.[8] The rearrangement of **2i** expectedly proceeded by refluxing in benzene solution for 1.5 h to give a pure 8-membered heterocyclic

allene (**3i**) in 92% yield (**Scheme 1**, eq 1). The ^{1}H- and ^{13}C-NMR spectra of **3i** showed the four non-equivalent methylene protons and the allenic carbons at 202.9, 117.2 and 102.7 ppm, respectively. As we could

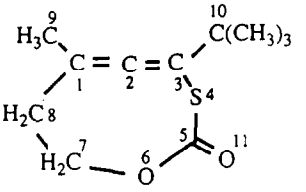


Scheme 1. Reagents and Conditions: (i) $(TMS)_2NLi$ (1.0 eq), THF, rt, 1.5 h; (ii) reflux in benzene, 1.5 h; (iii) TMSC ≡ CLi, THF, -70°C, 20 min.; (iv) *tert*-BuC ≡ CLi, THF, -70° → rt, 25 min; (v) reflux in toluene, 11 h

not obtain a suitable crystal of **3i** for X-ray analysis, the structure was estimated from MNDO calculation. The bond angle on the *sp* carbon, C1-C2-C3, is bent from linearity to 170.1°. The dihedral angle, CH_3-C1-C3-^{t}Bu, is twisted (64.3°) from vertical geometry. The bond angle of the *sp* carbon of **3i** corresponds to that of carbon skeletal nine-membered cyclic allene estimated from MNDO calculation by Johnson *et al.*[17] The optimized structure and dihedral angle around the allene bond were shown in **Figure 2**, and the selected bond distances and angles are summarized in **Table 2**.

Table 2. Selected Bond Lengths (Å) and Bond Angle (deg) in 3i by MNDO Calculation

Bond	Distance	Bond	Angle
C1 - C2	1.328	C2 - C1 - C8	116.8
C1 - C8	1.520	C2 - C1 - C9	115.1
C1 - C9	1.509	C8 - C1 - C9	126.9
C2 - C3	1.314	C1 - C2 - C3	170.1
C3 - S4	1.726	C2 - C3 - S4	114.1
C3 - C10	1.532	C2 - C3 - C10	127.4
S4 - C5	1.732	S4 - C3 - C10	118.5
C5 - O6	1.365	C3 - S4 - C5	105.2
O6 - C7	1.414	S4 - C5 - O6	116.2
C7 - C8	1.551	C5 - O6 - C7	125.1
C5 - O11	1.217	O6 - C7 - C8	110.0
		C1 - C8 - C7	115.5



Numbering of Selected Atoms of **3i**

Further, two 8-membered cyclic allenes (**3j** and **3k**) containing a TMS or a phenyl group could be similarly synthesized from ketones (**4** and **5**[18]) (**Scheme 1**, eqs 2 and 3). Interestingly, reaction of **5** with lithium acetylide directly afforded **3k** in 63% yield *via* a spontaneous rearrangement of the intermediate (**2k**). The **3i** and **3k** having a *tert*-butyl group were stable and required no special treatment in handling. As the 8-membered cyclic allene (**3j**) with a TMS group was rather unstable, its structure was confirmed as Diels-Alder adducts. Cycloaddition of **3j**, generated *in situ* from **2j**, with cyclopentadiene under uncatalyzed thermal conditions was carried out to give two stereoisomeric products (**7** and **8**) in 40% and 49% yields from **2j**, respectively (**Scheme 2**). Their structures were determined by their ^{1}H-NOE experiments indicated by arrows in **Scheme 2**. A 5-membered cyclic intermediate (**2l**), which is a substrate for 7-membered cyclic allene, did not produce at all even in refluxing toluene, only starting material being recovered (**Scheme 1**, eq 4). This would be due to a location restricted perpendicularly of the triple bond in **2l** for C=S bond.

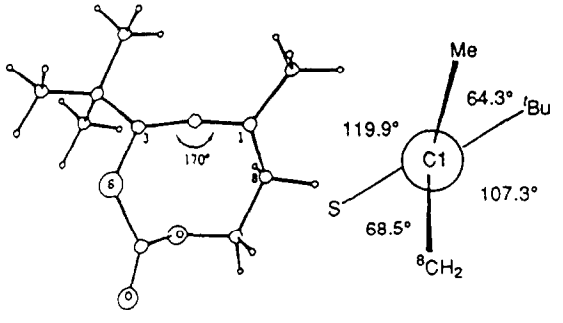


Figure 2. MNDO Estimated Structure of **3i** with Dihedral Geometry around the Allenic Moiety

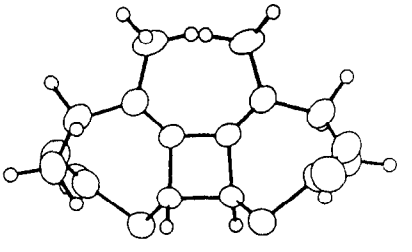
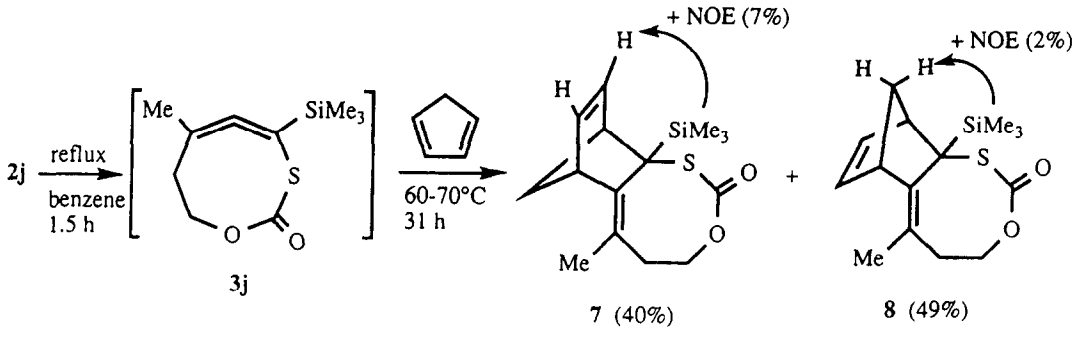
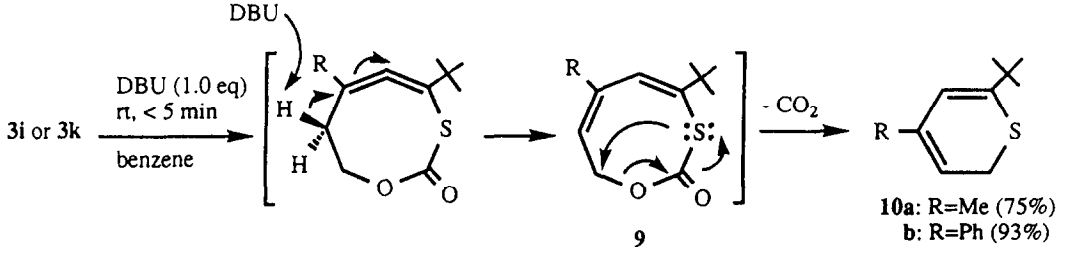


Figure 3. X-Ray Determined Structure of **11**



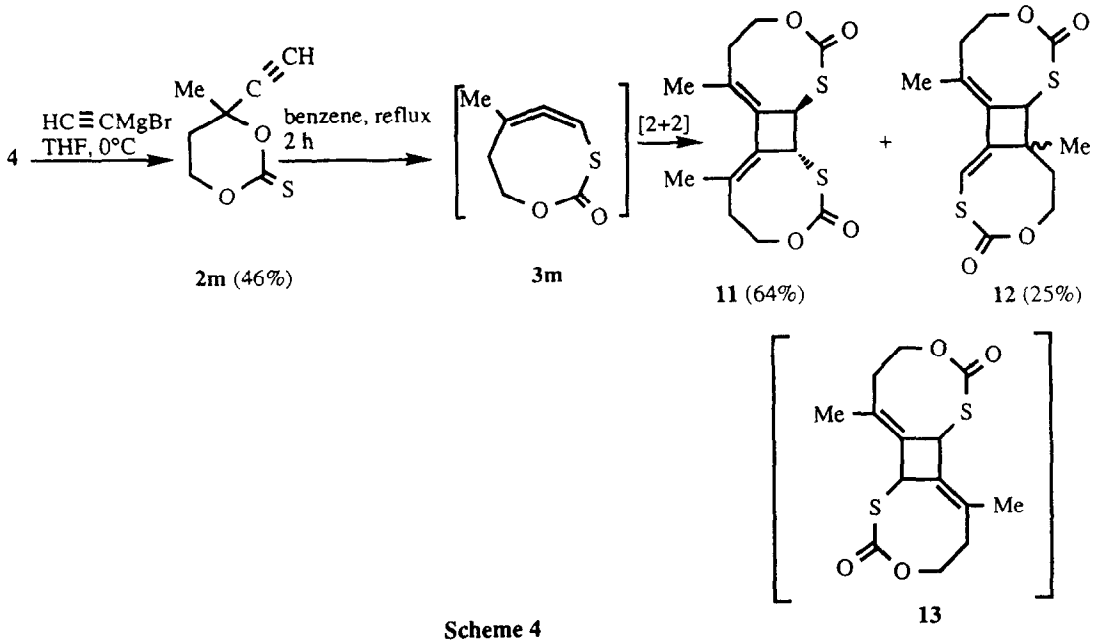
Scheme 2



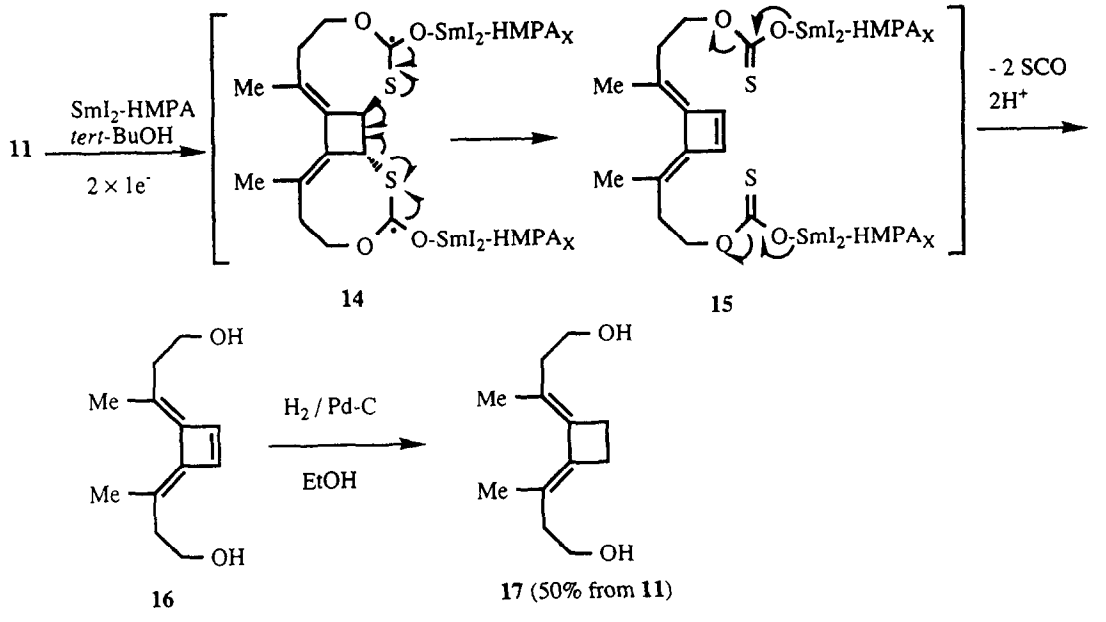
Scheme 3

We examined then the behavior of the 8-membered cyclic allenes (**3**) for base or acid. Intriguing point was a formation of 2*H*-thiopyran derivatives (**10**) by treatment of **3** with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (**Scheme 3**). When DBU was added to a colorless solution of **3i** or **3k** in THF, the color varied from initially deep blue to pale yellow at the end. After usual workup and chromatography, 2*H*-thiopyrans (**10a, 10b**) were isolated in high yields. A pathway for the conversion of **3** → **10** is suggested by a plausible mechanism (**Scheme 3**). The ring strain incurred in **3** would induce an isomerization of the double bond by the extraction of an allylic proton. Elimination of carbon dioxide from the resulting cyclic diene (**9**) would afford **10**. The observed color change may indicate the generation of **9** and CO_2 liberation. On the contrary, treatment of **3** with *p*-toluenesulfonic acid in THF was unreactive.

Attention was then addressed to the stability of the cyclic allene (**3m**) lacking a bulky substituent. Refluxing of the cyclic thionocarbonate (**2m**), prepared from ketone (**4**) and ethynylmagnesium bromide, in benzene afforded two dimeric products (**11** and **12**) in 64 and 25% yields, respectively. The formation of **11** and **12** is reasonably explained by the involvement of the strained cyclic allene (**3m**). However, we could not initially define the major product (**11**) (head-to-head dimer) and an other product (**13**) (head-to-tail dimer). Therefore, we attempted a reductive removal of the SCO moieties in **11** to determine the course of the dimerization. The reaction of **11** with lithium *p,p'*-di-*tert*-butylbiphenylide or lithium in liquid ammonia gave only decomposed materials at -70°C. Thus, our attention was directed to samarium (II) iodide (SmI_2),[19] widely noted not only for its moderate reducing power for organic compounds but also for its ease of handling in THF. Addition of **11** to a freshly



Scheme 4



Scheme 5

prepared SmI_2 in THF-HMPA successfully afforded a labile cyclobutene derivative (**16**) (**Scheme 5**). To our knowledge, the reaction of the thionocarbonates with SmI_2 has not been reported so far. The SmI_2 reduction of

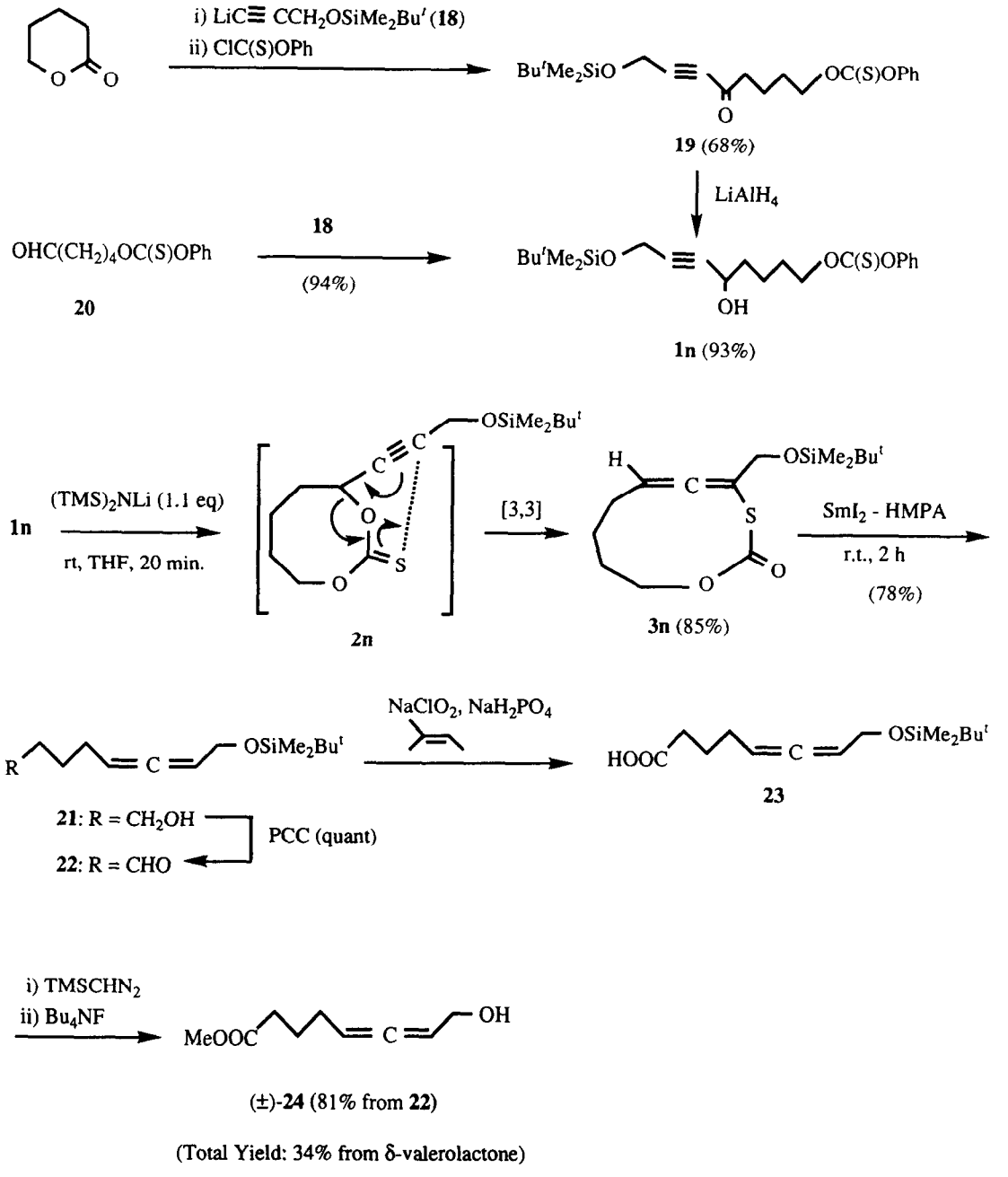
the dimer (**11**) would produce a diradical species (**14**) *via* two one-electron transfer process. Cleavage of C-S bonds of **14**, successive expulsions of 2 × SCO *via* **15** indicated by arrows, and then protonations would afford **16**. Catalytic hydrogenation of **16** yielded a diol (**17**) in 50% yield from **11**. This chemical transformation indicated that the major product (**11**) was a head-to-head dimer. The conjugate diene structure of **11** was also supported by UV [λ_{max} nm (ε) : 265 (4843)] spectral data. In the event, X-ray analysis[20] of **11** confirmed unequivocally the structure with *trans*-configuration of the four-membered ring (**Figure 3**). The planar structure of the minor product (**12**) was determined by spectroscopic data, but its configuration remained undetermined.

Synthetic Application to the Antifungal Constituent of *Sapium Japonicum*

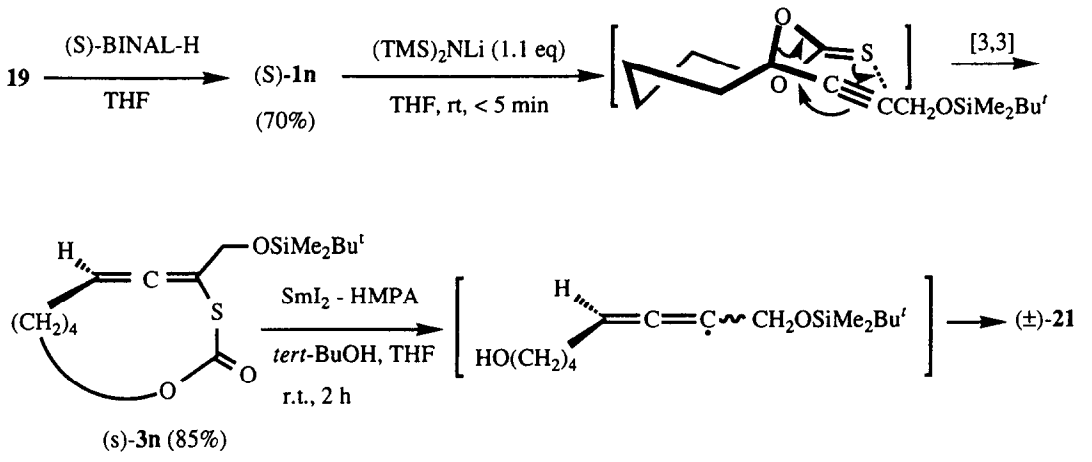
Sapium japonicum, a deciduous tree that is commonly found at the base of mountains in Japan, is resistant to certain types of fungal infections. This has been attributed to the presence of (*R*)-(-)-methyl 8-hydroxy-5,6-octadienoate (**24**), a strong antifungal agent, in its leaves.[21] Recently, several synthesis of allenic alcohol (**24**) have been accomplished.[5, 22] We developed a novel and efficient approach to (±)-**24** using the present methodology. This synthesis also features a novel application of the SmI_2-HMPA reduction to a key intermediate, 10-membered cyclic thiolcarbonate (**3n**).

The diol monothionocarbonate (**1n**), which was a substrate for the [3,3]sigmatropic rearrangement, was synthesized by two routes, as shown in **Scheme 6**. Addition of a lithium acetylide (**18**)[23], prepared from *tert*-butyldimethylsilylpropargyl ether, to a δ-valerolactone[22b] followed by a treatment with phenyl chlorothionoformate gave a ketone (**19**) in 68% yield. Reduction of **19** with $LiAlH_4$ in THF led to the required diol monothionocarbonate (**1n**) in 93% yield. This was also synthesized by addition of **18** to an aldehyde (**20**)[12] employed in our previous report. Reaction of **1n** with $(TMS)_2NLi$ afforded a 10-membered allene (**3n**) in 85% yield *via* the [3,3]sigmatropic rearrangement of a cyclic thionocarbonate (**2n**). As **3n** was unstable, it was immediately subjected to the SmI_2-HMPA reduction to afford an allenic alcohol (**21**) in 78% yield with the liberation of SCO[24]. A major advantage of this reduction is that the allenic function itself was unaffected. The primary alcohol moiety in **21** was readily converted to the aldehyde (**22**) by pyridinium chlorochromate (PCC), but unfortunately further oxidation to a carboxylic acid (**23**) was not easy because of the instability of the allenic moiety. After many trials, it was found that **22** was quantitatively converted to **23** by a use of sodium chlorite[25a] in the presence of NaH_2PO_4 and 2-methyl-2-butene.[25b, 26] Esterification of **23** with trimethylsilyldiazomethane[27] and deprotection with tetrabutylammonium fluoride gave the target compound [(±)-**24**] in 81% yield. Spectroscopic data for the synthetic material was identical in all respects with those reported for the isolated natural product.[5, 20, 21] Thus, synthesis of (±)-**24** was attained from δ-valerolactone in 34% overall yield.

Our interest was next addressed to the synthetic study of (-)-**24** (**Scheme 7**). The ketone (**19**) was thus converted into a chiral alcohol [(S)-**1n**] by (S)-BINAL-H[28] reduction in 70% yield. Treatment of (S)-**1n** with $(TMS)_2NLi$ afforded a chiral cyclic allene {(S)-**3n**, $[\alpha]_D$ -64.3° (c = 2.20, $CHCl_3$)}, whose absolute configuration was estimated from the transition state of the [3,3]sigmatropic rearrangement. However, the SmI_2-HMPA reduction of the chiral **3n** under the above condition brought about (±)-**21**. The same reduction of **3n** at -70°C for 0.5 h afforded only 30% yield of (±)-**21**. This failure may be attributed to the easy racemization of an allylic radical intermediate.


i) LiC≡ CCH2OSiMe2Bu' (18)
ii) ClC(S)OPh
Bu'Me2SiO
OC(S)OPh
19 (68%)
LiAlH4
18
OHC(CH2)4OC(S)OPh
(94%)
20
OH
1n (93%)
OSiMe2Bu'
(TMS)2NLi (1.1 eq)
1n
rt, THF, 20 min.
2n
[3,3]
SmI2 - HMPA
r.t., 2 h
(78%)
3n (85%)
NaClO2, NaH2PO4
R
HOOC
23
21: R = CH2OH
22: R = CHO
PCC (quant)
i) TMSCHN2
ii) Bu4NF
MeOOC
OH
(±)-24 (81% from 22)
(Total Yield: 34% from δ-valerolactone)

Scheme 6



Scheme 7

Experimental

General. Melting points (mp) were determined on a Yanagimoto micromelting point apparatus and were uncorrected. The IR spectra were recorded on a Shimadzu IR-435, and MS on a Hitachi M-80 spectrometers. The UV spectra were measured on a JASCO UVIDEC-505 spectrometer. ^{1}H- and ^{13}C-NMR spectra were taken with tetramethylsilane as an internal standard on a Varian Gemini-200 spectrometer in $CDCl_3$, unless otherwise noted. VPC analyses were performed with a Shimadzu GC-4BMPF gas chromatograph with a flame ionization detector using a 1.5% silicon OV-17 column (3 mm i.d. × 3 m). For column chromatography, SiO_2 (Merck 9385) was used. All reactions were carried out in an argon stream unless otherwise noted.

General Procedure for the Preparation of Diol Monothionocarbonates (1)[29]: *O*-(5-Hydroxy-5-methyl-6-undecynyl) *O*-Phenyl Thionocarbonate (1b) A 1.6 M hexane solution of n-butyllithium (1.6 ml, 2.5 mmol) was added dropwise with stirring to 1-hexyne (0.29 ml, 2.5 mmol) in anhydrous THF (2 ml) at -70°C. The mixture was stirred at the same temperature for 10 min. HMPA (1 ml) was added to the THF solution of 1-hexynyllithium thus prepared, and the resulting mixture was stirred for additional 10 min. *O*-5-Oxohexyl *O*-phenyl thionocarbonate[7] (524 mg, 2.1 mmol) in THF (2 ml) was subsequently added to the solution slowly at -70°C. The reaction mixture was stirred for 1 h, and was quenched with saturated ammonium chloride solution (1 ml), and was extracted with ether (50 ml × 2). The extract was washed with H_2O and brine, and was dried over anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography using EtOAc-n-hexane (1 : 4) for elution to give **1b** (590 mg, 85%). Yields and ^{1}H-NMR spectral data are summarized in **Table 3**.

General Procedure for the Preparation of Medium-membered Heterocyclic Allenes (3): 4-Butyl-6-methyl-1-oxa-3-thia-4,5-cyclodecadien-2-one (3b) A 1.0 M THF solution of $(TMS)_2NLi$[30] (0.66 ml, 0.66 mmol) was injected to a solution of **1b** (209 mg, 0.60 mmol) in THF (60 ml, 10^{-2} M) with stirring at room temperature. The reaction was quenched with H_2O within 5 min and the solvent was concentrated under reduced pressure to give a residue which was extracted with EtOAc-n-hexane (1:1). The

extract was washed with brine, dried over anhydrous Na_2SO_4 and then concentrated under reduced pressure. The residual oil was purified by column chromatography using 3% EtOAc-n-hexane for elution to give **3b** (116 mg, 77%). Yields and spectral data are summarized in **Table 1** and **Tables 4, 5**, respectively. VPC analysis (programmed at 140-270°C, 10°C/min); t_R = 13.6 min.

Table 3. Yields and ^{1}H-NMR Spectral Data of Monothionocarbonates (1)[a, 29]

Compound No.	Yield (%)	^{1}H-NMR δ ($CDCl_3$, ppm)
1a	64	0.90 (3H, t, *J* = 6.0 Hz, CH_3), 1.25-1.95 (12H, br m, 6 × CH_2), 2.21 (2H, td, *J* = 6.0, 2.0 Hz, C≡CCH_2), 4.20-4.50 (2H, overlapped, C≡CC*H*OH), 4.53 (2H, t, *J* = 6.0 Hz, OCH_2), 7.06-7.50 (5H, m, Ar)
1b	85	0.89 (3H, t, *J* = 7.0 Hz, CH_3), 1.20-2.00 (10H, br m, 5 × CH_2), 1.45 (3H, s, CHC*H*$_3$), 2.18 (2H, t, *J* = 7.0 Hz, ≡CCH_2), 4.53 (2H, t, *J* = 6.5 Hz, OCH_2), 7.05-7.45 (5H, m, ArH)
1c	57	0.88 (3H, t, *J* = 7.5 Hz, CH_3), 1.10-1.98 (10H, br, 5 × CH2), 2.20 (2H, t, *J* = 6.0 Hz, ≡CCH_2), 4.38 (1H, br, CH), 4.50 (2H, t, *J* = 6.0 Hz, OCH_2), 7.05-7.47 (5H, m, ArH)
1d	73	1.23 [9H, s, C(CH_3)3], 1.45-2.00 (6H, br m, 3 × CH_2), 4.55 (2H, t, *J* = 6.0 Hz, OCH_2), 7.07-7.50 (5H, m, ArH)
1e	55	1.55-2.01 (6H, br m, 3 × CH_2), 3.38 (3H, s, OCH_3), 4.26 (2H, d, *J* = 2.8 Hz, ≡CCH_2), 4.46 (1H, br t, *J* = 6.5 Hz, C*H*OH), 4.53 [2H, t, *J* = 7.5 Hz, CH_2OC(S)], 4.70 (2H, s, OCH_2O), 7.07-7.48 (5H, m, ArH)
1f	55	1.50-2.05 (12H, m, 6 × CH_2), 3.52-3.63 (1H, m, ≡CC*H*H), 3.81-3.94 (1H, m, ≡CCH*H*), 4.34 [2H, ddd, *J* = 19.0, 15.0, 2.5 Hz, CH_2 (6-position of ring)], 4.44-4.53 (1H, br t, *J* = 6.0 Hz, C*H*OH), 4.57 [2H, t, *J* = 6.0 Hz, CH_2OC(S)], 4.82-4.87 (1H, br s, OCHO), 7.12-7.52 (5H, m, ArH)
1g	40	0.93 (3H, t, *J* = 6.5 Hz, CH_3), 1.30-2.20 (8H, br m, 4 × CH_2), 2.24 (2H, br t, *J* = 6.0 Hz, ≡CCH_2), 4.45 (1H, br, C*H*OH), 4.60 [2H, t, *J* = 6.0 Hz, CH_2OC(S)], 7.10-7.55 (5H, m, ArH)
1h	60	1.21 [9H, s, C(CH_3)3], 1.50 (3H, s, CH_3), 1.72-1.85 (2H, m, OCH_2CH_2), 2.00-2.15 [2H, m, C(OH)C*H*$_2$], 4.60 (2H, t, *J* = 6.0 Hz, OCH_2), 7.09-7.51 (5H, m, ArH)
1i	44[b]	1.23 [9H, s, C(CH_3)3], 1.52 (3H, s, CH_3), 2.20 [2H, t, *J* = 7.5 Hz, C(OH)C*H*$_2$], 4.82 (2H, t, *J* = 7.5 Hz, OCH_2), 7.10-7.50 (5H, m, ArH)
1n	94	0.11 [6H, s, OSi(CH_3)$_2$], 0.90 [9H, s, SiC(CH_3)3], 1.66-1.98 (6H, m, 3 × CH_2), 4.36 (2H, s, ≡CCH_2), 4.45 (1H, br t, *J* = 7.5 Hz, C*H*OH), 4.54 (2H, t, *J* = 6.5 Hz, OCH_2), 7.08-7.49 (5H, m, ArH)

a: These were oily materials.
b: **2i** was also obtained in 13% yield. c: See experimental

Table 4. IR and MS Spectral Data of Cyclic Allenes (3)

Product No.[a]	IR (neat) ν (cm^{-1})[b] C=C=C	CO	Molecular Formula	HR-MS (*m/z*) Found	Calcd
3a	1950	1695	$C_{13}H_{20}O_2S$	240.1185	240.1183 (M^+)
3b	1950	1695	$C_{13}H_{20}O_2S$	240.1189	240.1183 (M^+)
3c	1950	1690	$C_{12}H_{18}O_2S$	226.1023	226.1026 (M^+)
3d	c	1690	$C_{12}H_{18}O_2S$	226.1035	226.1026 (M^+)
3e	1950	1680	$C_{11}H_{26}O_4S$	d	
3f	1950	1670	$C_{14}H_{20}O_4S$	284.1083	284.1081 (M^+)
3g	1950	1708	$C_{11}H_{16}O_2S$	212.0856	212.0870 (M^+)
3h	1950	1700	$C_{11}H_{16}O_2S$	213.0946	213.0948 (M^++1)
3i	c	1712	$C_{11}H_{16}O_2S$	213.0946	213.0948 (M^++1)
3j	1910	1710	$C_{10}H_{16}O_2SSi$	d	
3k	c	1700	$C_{16}H_{18}O_2S$	274.1026	274.1027 (M^+)
3n	1950	1685	$C_{15}H_{26}O_2SSi$	314.1354	314.1371 (M^+)

a: These are oily materials except for **3d** (wax), **3i** (wax, mp 36-37°C), **3k** (powder, mp 69-71°C);
b: The allenic peaks were very weak except for **3j**; c: Not observed; d: Reference 29

Table 5. ^{1}H- and ^{13}C-NMR Spectral Data of Cyclic Allenes (3)

Product No.	^{1}H- and ^{13}C-NMR ($CDCl_3$, ppm)
3a	0.90 (3H, t, J = 7.5 Hz, CH_3), 1.20-1.75 (10H, br m, 5 × CH_2), 1.75-2.45 (4H, br m, CH_2C=C=CCH_2), 4.06 (1H, m, OC*H*H), 4.52 (1H, m, OCH*H*), 5.27 (1H, m, =CH); 14.0, 22.1, 23.0, 24.9, 25.5, 26.8, 30.1, 35.7, 67.7, 93.4, 97.1, 170.0, 207.4
3b	0.87 (3H, t, J = 7.0 Hz, CH_2CH_3), 1.15-1.80 (8H, br , 4 × CH_2), 1.64 (3H, s, =CCH_3), 2.12 (3H, br t, J = 6.2 Hz, 3/2 × CH_2), 2.28-2.47 (1H, br, 1/2 × CH_2), 3.80 (1H, t, J = 11.0 Hz, 1/2 × OCH_2), 4.95 (1H, dd, J = 11.0, 3.8 Hz, 1/2 × OCH_2); 14.0, 16.7, 22.0, 24.4, 28.0, 30.2, 33.6, 34.2, 68.6, 96.0, 102.9, 170.1, 202.4
3c	0.88 (3H, t, J = 7.5 Hz, CH_3), 1.16-1.77 (8H, br, 4 × CH_2), 2.10-2,40 (4H, br, 2 × CH_2), 3.80-3.93 (1H, m, 1/2 × OCH_2), 4.85-4.98 (1H, m, 1/2 × OCH_2), 5.14 (1H, d quint, J = 9.9, 2.6 Hz, =CH); 13.9, 22.0, 26.2, 28.3, 28.7, 30.1, 33.6, 68.8, 94.7, 98.0, 169.4, 204.4
3d	1.14 [9H, s, $C(CH_3)_3$], 1.50-1.85 (4H, br, 2 × CH_2), 2.20-2.40 (2H, br, =CCH_2), 3.82 (1H, br t, J = 10.5 Hz, OC*H*H), 5.00 (1H, br d, J = 10.5 Hz, OCH*H*), 5.20 (1H, t, J = 7.5 Hz, =CH); 25.7, 28.2, 28.4, 29.2, 35.6, 68.7, 94.5, 108.8, 170.3, 203.7

3e 1.53-1.87 (4H, br m, 2 × CH_2), 2.15-2.45 (2H, br m, =CCH_2), 3.38 (3H, s, OCH_3), 3.89 (1H, dd, *J* = 11.5, 10.0 Hz, OC*H*H), 4.18 (2H, d, *J* = 3.2 Hz, =CCH_2O), 4.66 (2H, s, OCH_2O), 4.93 (1H, ddd, *J* = 10.5, 6.8, 3.0 Hz, OCH*H*), 5.30 (1H, dd, *J* = 9.9, 6.0 Hz, =CH);
26.2, 28.3, 28.5, 55.9, 67.8, 69.0, 95.5, 95.6, 169.0, 205.9

3f 1.40-1.92 (10H, br m, 5 × CH_2), 2.12- 2.47 (2H, m, =CCH_2), 3.45-3.58 (1H, m, C*H*HOTHP), 3.80-3.96 [2H, m, overlapped, CH*H*OTHP, C*H*HOC(O)], 4.12-4.36 (2H, m, OCH_2 of THP), 4.75 (1H, br d, *J* = 3.4 Hz, OCHO), 4.88-5.02 [1H, m, CH*H*O(CO)], 5.22-5.38 (1H, m, =CH);
19.1, 25.7, 26.3, 28.3, 28.7, 30.5, 62.2, 67.6, 68.8, 95.5, 96.9, 97.6, 169.1, 205.8

3g 0.92 (3H, t, *J* = 7.0 Hz, CH_3), 1.20-1.60 (4H, br m, 2 × CH2), 1.75-2.05 (2H, br m, CH_2), 2.10-2.45 (4H, br m, $CH_2C{=}C{=}CCH_2$), 3.90 (1H, td, *J* = 11.0, 5.0 Hz, OC*H*H), 4.92 (1H, dt, *J* = 11.0, 4.0 Hz, OCH*H*), 5.45 (1H, m, =CH);
14.0, 22.1, 25.5, 29.4, 30.1, 33.3, 68.6, 95.5, 101.8, 171.2, 206.7

3h 1.43 [9H, s, $C(CH_3)_3$], 1.73 (3H, s, CH_3), 1.82-2.10 (3H, br m, overlapped, CH_2, =CC*H*H), 2.35-2.50 (1H, br m, =CCH*H*), 3.80-3.96 (1H, m, OC*H*H), 4.87 (1H, dt, *J* = 10.5, 3.5 Hz, OCH*H*);
19.7, 28.5, 29.2, 32.0, 35.7, 68.6, 104.9, 111.2, 172.5, 202.9

3i 1.16 [9H, s, $C(CH_3)_3$], 1.68 (1H, ddd, *J* = 13.8, 2.6, 2.1 Hz, OC*H*H), 1.82 (3H, s, =CCH_3), 2.52 (1H, ddd, *J* = 13.8, 10.6, 5.8 Hz, OCH*H*), 4.42 (1H, ddd, *J* = 12.0, 5.8, 2.1 Hz, =CC*H*H), 4.55 (1H, ddd, *J* = 12.0, 10.6, 2.6 Hz, =OCH*H*);
19.8, 29.0, 29.5, 35.9, 71.3, 102.7, 117.2, 172.0, 202.9

3j 0.18 [9H, s, $Si(CH_3)_3$], 1.69 (1H, dt, *J* = 16.0, 2.5 Hz, OC*H*H), 2.53 (1H, ddd, *J* = 16.0, 10.0, 5.0 Hz, OCH*H*), 4.33-4.56 (2H, overlapped, =CCH_2);
-1.4, 18.8, 28.9, 70.5, 96.6, 99.9, 173.1, 210.8

3k 1.28 [9H, s, $C(CH_3)_3$], 2.57 (1H, dt, *J* = 14.0, 2.5 Hz, =CC*H*H), 2.73 (1H, ddd, *J* = 14.0, 10.0, 5.5 Hz, =CCH*H*), 4.57-4.70 (2H, m, OCH_2), 7.20-7.44 (5H, m, ArH);
25.5, 29.6, 36.5, 72.3, 108.8, 120.2, 126.8, 128.4, 129.3, 135.9, 171.4, 205.2

3n 0.08 [6H, s, $Si(CH_3)_2$], 0.90 [9H, s, $C(CH_3)_3$], 1.60-1.85 (4H, m, 2 × CH_2), 2.13-2.44 (2H, m, =CCH_2), 3.88 (1H, td, *J* = 11.3, 2.7 Hz, OC*H*H), 4.28 (2H, d, *J* = 2.8 Hz, $SiOCH_2$), 4.94 (1H, ddd, *J* = 11.3, 5.4, 2.5 Hz, OCH*H*), 5.23-5.37 (1H, m, =CH);
-5.1, 18.5, 26.0, 26.2, 28.4, 28.5, 64.5, 68.9, 96.0, 99.1, 169.4, 204.0

4-(3,3-Dimethyl-1-butynyl)-4-methyl-1,3-dioxan-2-thione (2i) A 1 M THF solution of $(TMS)_2NLi$[30] (1.18 ml, 1.18 mmol) was added to a solution of **1i** (362 mg, 1.18 mmol) in THF (40 ml) with stirring at room temperature. After 1.5 h, the reaction mixture was quenched with H_2O, then concentrated under reduced pressure. The residue was extracted with EtOAc-n-hexane (1:1) and the extract was washed with brine, dried over anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, the residue was

purified by column chromatography using 2.5% EtOAc-n-hexane for elution to give **2i** (239 mg, 96%) as white solid, which was recrystallized from n-hexane to give colorless needles, mp. 71-73°. IR (KBr) : 2230 cm^{-1} (C≡C). ^{1}H-NMR : 1.21 (9H, s, 3 × CH_3), 1.74 (3H, s, CH_3), 2.16-2.27 (2H, m, C*H*$_2$CH$_2$O), 4.50 (1H, dt, *J* = 11.2, 3.7 Hz, C*H*HO), 4.65-4.80 (1H, m, CH*H*O). *Anal.* Calcd. for $C_{11}H_{16}O_2S$: C, 62.22; H, 7.60. Found: C, 62.29; H, 7.64.

4-Methyl-4-(2-trimethylsilylethynyl)-1,3-dioxan-2-thione (2j) A 1.6 M n-hexane solution of n-butyllithium (0.63 ml, 1 mmol) was added with stirring to trimethylsilylacetylene (0.14 ml, 1 mmol) in THF (20 ml) at -70°C. After 0.5 h, a solution of **4** (224 mg, 1 mmol) in THF (10 ml) was added dropwise, and the resulting mixture was stirred at the same temperature for 20 min. The mixture was quenched with MeOH (0.2 ml) and extracted with EtOAc-n-hexane (1 : 2). The extract was washed with H_2O (× 2), 1% aqueous NaOH (× 2), and dried over anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography using 10% EtOAc-n-hexane for elution to give **2j** (169 mg, 74%) as white solid, which was recrystallized from n-hexane to give colorless needles, mp. 91-92°C. IR (KBr): 2170 cm^1(C≡C). ^{1}H-NMR : [0.16 (9H, s, Si(CH$_3$)$_3$], 1.74 (3H, s, CH_3), 2.20-2.32 (2H, m, C*H*$_2$CH$_2$O), 4.45-4.56 (1H, m, OC*H*H), 4.65-4.70 (1H, m, OCH*H*). *Anal.* Calcd. for $C_{10}H_{16}O_2SSi$: C, 52.59; H, 7.06. Found: C, 52.45; H, 6.99.

4-(3,3-Dimethyl-1-butynyl)-4-methyl-1,3-dioxolan-2-thione (2l)[29] A 1.6 M n-hexane solution of n-butyllithium (3.44 ml, 5.5 mmol) was added with stirring to tert-butylacetylene (0.68 ml, 5.5 mmol) in THF (30 ml) at -70°C. Then, a solution of **6** (1050 mg, 5.0 mmol) in THF (75 ml) was added, and the resulting mixture was stirred at the same temperature for 15 min. The mixture was quenched with H_2O and extracted with EtOAc-n-hexane (1: 2). The extract was washed in turn with H_2O (× 2), 1% aqueous NaOH (× 2), H_2O, brine, and dried over anhydrous Na_2SO_4. After evaporation of the solvent under reduced pressure, the residue was purified by column chromatography using 10% EtOAc-n-hexane for elution to give **2l** (829 mg, 84%) as an oil. IR (neat) : 2240 cm^{-1} (C≡C). ^{1}H-NMR : 1.21 (9H, s, 3 × CH_3), 1.78 (3H, s, CH_3), 4.38 (1H, d, *J* = 8.5 Hz, OC*H*H), 4.60 (1H, d, J = 8.5 Hz, OCH*H*).

4-*tert*-Butyl-6-methyl-1-oxa-3-thia-4,5-cyclooctadien-2-one (3i) A solution of **2i** (200 mg, 0.94 mmol) in benzene (25 ml) was refluxed for 1.5 h. The solvent was evaporated and the crude product was purified by column chromatography using 5% EtOAc-n-hexane for elution to give **3i**[31] (184 mg, 92%) as colorless oil. The oil turned to a white wax on standing.

4-*tert*-Butyl-6-phenyl-1-oxa-3-thia-4,5-cyclooctadien-2-one (3k) A 1.6 M hexane solution of n-butyllithium (0.38 ml, 0.61 mmol) was added to 3,3-dimethylbutyne (50 mg, 0.61 mmol) in THF (13 ml) at -70°C. The reaction temperature was raised to 0°C over 40 min, and then a solution of **5** (157 mg, 0.55 mmol) in THF (6 ml) was added to the mixture. The solution slowly changed from colorless to pale yellow. After being stirred for 25 min, the reaction was quenched with H_2O and extracted with with EtOAc-n-hexane (1 : 2). The extract was washed with H_2O, brine, dried over anhydrous Na_2SO_4, and evaporated under reduced pressure. The residual oil was purified by column chromatography using 2.5% EtOAc-n-hexane for elution to give **3k**[31] (95 mg, 63%) as a white powder, which was recrystallized from isopropanol-H_2O gave colorless pillars.

Diels Alder Cycloaddition of 3j with Cyclopentadiene A solution of **2j** (65 mg, 0.29 mmol) in benzene (5 ml) was refluxed for 1.5 h. The reaction was monitored by a thin-layer chromatography and, when completed the formation of **3j**, cyclopentadiene (1.5 ml) was added to the solution at room temperature. The resulting mixture was heated at 60-70°C for 5 h. Cyclopentadiene (1.5 ml) was again added to the mixture, and heating was allowed to continue for 19 h. At hourly intervals and upon continued heating, two portions of cyclopentadiene (1 ml × 2) were added. After heating for additional 6 h, the solvent was evaporated under reduced pressure and the resulting residue was chromatographed on a silica gel (8 g). Elution with 0.1-0.5% EtOAc-n-hexane gave **7** (34 mg, 40% from **2j**), while elution with 10% EtOAc-hexane gave **8** (41 mg, 49% from **2j**) as white wax, respectively.

(7R*,10S*,10aR*)-6-Methyl-10a-trimethylsilyl-5,7,10,10a-tetrahydro-7,10-methano-4*H*-3,1-benzoxathiocin-2-one (7) : IR (neat) : 1695 cm^{-1} (CO). ^{1}H-NMR : 0.18 [9H, s, $Si(CH_3)_3$], 1.60 (1H, d, J = 9.0 Hz, bridgehead), 1.90 (3H, s, CH_3), 2.11 (1H, dt, J = 20.0, 4.0 Hz, =C*H*H), 2.40 (1H, d, J = 9.0 Hz, bridgehead), 2.72 (1H, ddd, J = 20.0, 10.0, 4.0 Hz,. =CH*H*), 2.97 (1H, br s, C10-H), 3.66 (1H, br s, C7-H), 4.23 (1H, ddd, J = 20.0, 10.0, 4.0 Hz, OC*H*H), 4.57 (1H, dt, J = 10.0, 5.0 Hz, OCH*H*), 6.08 (1H, br s, C=CH), 6.24 (1H, br s, HC=C). ^{13}C-NMR : 1.71, 23.7, 37.6, 49.5, 50.4, 53.1, 56.7, 68.5, 125.9, 134.7, 139.2, 141.9, 172.9. EIMS *m/z* : 294 (M^+). HR-MS *m/z*: calcd for $C_{15}H_{22}O_2SSi$ 294.1109, Found: 294.1111.

(7S*,10R*,10aR*)-6-Methyl-10a-trimethylsilyl-5,7,10,10a-tetrahydro-7,10-methano-4*H*-3,1-benzoxathiocin-2-one (8) : IR (neat) : 1700 cm^{-1}(CO). ^{1}H-NMR : 0.26 [3H, s, $Si(CH_3)_3$], 1.50 (1H, d, J = 8.9 Hz, bridgehead), 1.58 (1H, dt, J = 8.9, 1.7 Hz, bridgehead), 1.84 (3H, s, $=CCH_3$), 1.90 (1H, ddd, J = 13.6, 7.0, 1.9 Hz, =CC*H*H), 3.25 (1H, ddd, J = 13.6, 10.6, 8.9 Hz, =CCH*H*), 3.25 (1H, br s, C7- or C10-H), 3.55 (1H, br s, C7- or C10-H), 4.11 (1H, ddd, J = 11.3, 10.0, 6.9, OC*H*H), 4.42 (1H, ddd, J = 11.3, 8.9, 1.9 Hz, OCH*H*), 6.32 (2H, br s, HC=CH). ^{13}C-NMR : 1.3, 20.5, 35.6, 47.1, 48.0, 53.4, 55.8, 67.3, 123.0, 137.2, 137.5, 143.6, 170.3. EIMS *m/z* : 294 (M^+). HR-MS *m/z* : calcd for $C_{15}H_{22}O_2SSi$ 294.1109, Found: 294.1103.

6-*tert*-Butyl-4-phenyl-2*H*-thiopyran (10b) A solution of DBU (15 mg, 0.1 mmol) in benzene (1 ml) was added to a solution of **3k** (27 mg, 0.1 mmol) in benzene (2 ml) at room temperature. During the addition of DBU, the color of the solution quickly changed to deep blue. After a few minutes, the blue color turned to pale yellow at the end. After evaporation the solvent, the residue was purified by column chromatography using 1% EtOAc-n-hexane for elution to give **10b** (21 mg, 92%) as an oil. ^{1}H-NMR : 1.28 [9H, s, $C(CH_3)_3$], 3.37 (2H, d, J = 8.3 Hz, SCH_2), 5.71 (1H, td, J = 8.3, 1.0 Hz, =C*H*CH_2), 6.41 (1H, d, J = 1.0 Hz, C5-H), 7.21-7.43 (5H, m, ArH). ^{13}C-NMR : 26.7, 29.8, 37.9, 111.1, 117.5, 126.8, 127.8, 128.9, 139.8, 141.5, 151.9. MS *m/z* : 230 (M^+). HR-MS *m/z* : calcd for $C_{15}H_{18}S$ 230.1128, Found: 230.1135.

6-*tert*-Butyl-4-methyl-2*H*-thiopyran (10a) Treatment of **3i** (36 mg, 0.17 mmol) with DBU (26 mg, 0.17 mmol) gave **10a**[29] (21 mg, 75%) as an oil, according the procedure described for the preparation of **10b**. ^{1}H-NMR : 1.20 [9H, s, $C(CH_3)_3$], 1.80 (3H, s, CH_3), 3.16 (2H, d, J = 5.0 Hz, CH_2), 5.22 (1H, br t, J = 5.0 Hz, =C*H*CH_2), 5.90 (1H, s, =CH). ^{13}C-NMR : 22.0, 26.2, 29.7, 37.4, 109.9, 118.9, 135.4, 149.6.

4-Ethynyl-4-methyl-1,3-dioxan-2-thione (2m) A 0.5 M THF solution of ethynylmagnesium bromide[30] (12.5 ml, 6.25 mmol) was added dropwise to a solution of **4** (1400 mg, 6.25 mmol) in THF (40 ml)

over 10 min with stirring at 0 °C, and then additional THF (6 ml) was added. After stirring was continued for 90 min at 0°C, the mixture was quenched with H_2O, and extracted with EtOAc-n-hexane (2 : 1). The extract was washed with 1% NaOH (× 3), H_2O, brine, and dried over anhydrous Na_2SO_4. After evaporation of the solvent, the residue was purified by column chromatography using successive 5%, 10%, 20%, and 50% EtOAc in n-hexane for elution to give **2m** (445 mg, 46%), mp. 67-69°C (colorless prisms) from benzene-ligroin, with recovery of **4** (152 mg, 11%). IR (KBr) : 2100 cm^{-1} (C≡C). ^{1}H-NMR : 1.80 (3H, s, CH_3), 2.29 (2H, dd, J = 7.5, 3.0 Hz, CH_2), 2.76 (1H, s, ≡CH), 4.54 (1H, dt, J = 10.5, 3.0 Hz, OC*H*H), 4.77 (1H, dt, J = 10.5, 7.5 Hz, OCH*H*). ^{13}C-NMR (C_6D_6) : 28.0, 32.5, 67.2, 76.0, 76.2, 81.1, 189.0. *Anal.* Calcd. for $C_7H_8O_2S$: C, 53.83; H, 5.16. Found: 53.80; H, 5.18.

Thermolysis of 2m A solution of **2m** (95 mg, 0.61 mmol) in benzene (5 ml) was refluxed for 2h. After evaporation of the solvent, the residue was purified by column chromatography using successive 10%, 20% and 30% EtOAc-hexane for elution to give **11** (61 mg, 64%) followed by **12** (24 mg, 25%).

***trans*-6,7-Dimethyl-4,5,8,9,12a,12b-hexahydrocyclobuta[1,2-*d*:4,3-*d'*]dioxathiocin-2,11-dione (11)** : mp. 220-231°C (as colorless prisms from benzene). IR (KBr) : 1687 cm^{-1} (CO). UV λ_{max} 265 nm (ε 4843). ^{1}H-NMR : 1.86 (6H, s, 2 × CH_3), 2.34 (2H, ddd, J = 17.5, 10.0, 5.0 Hz, 2 × =CC*H*H), 2.92 (2H, br d, J = 17.5, 2 × =CCH*H*), 4.27 (2H, s, 2 × CH), 4.30-4.45 (2H, m, OC*H*H), 4.52-4.68 (2H, m, OCH*H*). ^{13}C-NMR : 24.0, 36.4, 49.8, 69.4, 130.5, 136.3, 171.2. *Anal.* Calcd. for $C_{14}H_{16}O_4S_2$: C, 53.83; H, 5.16. Found: C, 53.56; H, 5.18.

6,12a-Dimethyl-4,5,11,12,12a,12b-hexahydrocyclobuta[1,2-*d*:3,4-*e'*]dioxathiocin-2,9-dione (12) : mp. 168-240°C (dec.) (as colorless mass form benzene). IR (KBr) : 1688, 1656 cm^{-1} (CO). UV λ_{max} : 293 nm. ^{1}H-NMR : 1.28 (3H, s, CH_3), 1.70 (1H, dd, J = 14.5, 1.75 Hz, C12-H), 1.95 (3H, s, =CCH_3), 2.06 (1H, dd, J = 14.5, 7.5 Hz, C12-H), 2.33 (1H, ddd, J = 14.5, 7.5, 1.5 Hz, C5-H), 2.92 (1H, br d, J = 14.5 Hz, C5-H), 4.37 (1H, s, C12b-H), 4.25-4.50 (1H, m, OC*H*H), 4.53-4.73 (1H, m, OCH*H*), 6.25 (1H, s, =CH). ^{13}C-NMR : 16.3, 27.3, 36.3, 37.4, 49.3, 55.3, 67.4, 68.9, 112.4, 132.8, 135.9, 152.1, 171.9, 172.9. *Anal.* Calcd. for $C_{14}H_{16}O_4S_2$: C, 53.83; H, 5.16. Found: C, 53.65; H, 5.18.

1,2-Bis[(*E*)-3-hydroxy-1-methylpropylidene]cyclobutane (17) Samarium metal (225 mg, 1.5 mmol) was added under a flow of an Argon (Ar) to an oven-dried round-bottomed flask containing a magnetic stirring bar and septum inlet. The flask and samarium were cooled under an Ar. THF (1.5 ml) followed by $C_2H_4I_2$ (351 mg, 1.25 mmol) were added, and the mixture was stirred at room temperature for 2 h. HMPA (0.22 ml, 1.25 mmol) was added, and the resulting purple solution was continued to stir for 10 min. A solution of *tert*-BuOH (9 mg, 0.12 mmol) in THF (1 ml) followed by a solution of **11** (16 mg, 0.05 mmol) in THF (1 ml) were added to the resulting SmI_2 solution at 0°C, and the mixture was stirred for 20 min at the same temperature. Ice was added and the reaction mixture was exposed to air with stiring for 10 min, then filtered with ether through a Celite pad. The filtrate was washed with H_2O (× 3), brine, and then dried over $MgSO_4$. The solvent was evaporated to give 1,2-bis[(*E*)-3-hydroxy-1-methylpropylidene]cyclobutene (**16**) (17 mg) as a crude oil, which was too labile to purify by column chromatography on silica gel. ^{1}H-NMR : 1.96 (6H, s, 2 × CH_3), 2.40 (4H, t, J = 6.0 Hz, 2 × =CCH_2), 3.73 (4H, t, J = 6.0 Hz, 2 × OCH_2), 6.87 (2H, s, =CH). EIMS *m/z* : 194 (M^+). A solution of **16** thus obtained in EtOH (7 ml) was hydrogenated over 10% palladium on carbon (12 mg) at 2 Kg/cm^2 for 1.5 h. The catalyst (17 mg) was further added and the hydrogenation was continued for an

additional 1 h. After the catalyst was filtered off, the solvent was evaporated *in vacuo*, and the residue was purified by column chromatography using 30% -50% EtOAc-n-hexane for elution to give **17** (5 mg, 50% based on **11**) as an oil. IR (neat) : 3340 cm^{-1} (OH). UV λ_{max} : 255 nm. ^{1}H-NMR : 1.82 (6H, s, 2 × CH_3), 2.27 (4H, t, J = 6.5 Hz, 2 × =CCH_2), 2.46 (4H, s, 2 × CH_2), 3.70 (4H, t, J = 6.5 Hz, 2 × OCH_2). ^{13}C-NMR : 19.9, 27.1, 38.2, 60.7, 121.7, 138.2. EIMS *m/z* : 196 (M^+). HR-MS *m/z* : calcd for $C_{12}H_{20}O_2$ 196.1462, Found: 196.1455.

***O*-(8-*tert*-Butyldimethylsilyloxy-5-oxo-6-octynyl) *O*-Phenyl Thionocarbonate (19)** A solution of lithium salt (1.2 mmol) of *tert*-butyldimethylsilylpropargyl ether[22b] in THF (6 ml) was added dropwise to a solution of δ-valerolactone (100 mg, 1.0 mmol) in dry THF (10 ml) with stirring at -70°C.[23] Dry ice-bath was removed, and the reaction mixture was stirred for 75 min, during the time of which the solution was warmed to room temperature. The reaction mixture was quenched with saturated aqueous ammonium chloride and diluted with ether (50 ml). The organic layer was separated, dried over $MgSO_4$, and evaporated *in vacuo* to give a pale brown oil (278 mg). A solution of phenyl chlorothionoformate (0.15 ml, 1.1 mmol) in acetonitrile (3 ml) was added slowly over 5 min to the solution of the oil thus obtained in acetonitrile (10 ml) in the presence of pyridine (87 mg, 1.1 mmol) and 4-DMAP (12 mg, 0.1 mmol) at 0°C. After 1.5 h, the solvent was evaporated under reduced pressure to give an oil, which was subsequently diluted with EtOAc-n-hexane (1 : 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 5% EtOAc-n-hexane for elution to give **19**[29] (275 mg, 68%) as an oil. IR (neat) : 2200 (C≡C), 1690 cm^{-1} (CO). ^{1}H-NMR : 0.13 [6H, s, $Si(CH_3)_2$], 0.92 [9H, s, $C(CH_3)_3$], 1.85 (4H, br, 2 × CH_2), 2.65 (2H, br t, J = 6.0 Hz, $COCH_2$), 4.48 (2H, s, ≡CCH_2), 4.53 [2H, br t, J = 6.0 Hz, $CH_2OC(S)O$)], 7.05-7.50 (5H, m, ArH).

***O*-(8-*tert*-Butyldimethylsilyloxy-5-hydroxy-6-octynyl) *O*-Phenyl Thionocarbonate (1n)** A solution of **19** (264 mg, 0.65 mmol) in THF (10 ml) was added dropwise with stirring to a solution of 1 M solution of $LiAlH_4$[30] in THF (0.65 ml, 0.65 mmol) at -70°C. After 10 min, the reaction was quenched with H_2O (1.0 ml). The whole was treated with anhydrous $MgSO_4$ and filtered through a Celite pad, and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography using 10% EtOAc-n-hexane for elution to give **1n** (247 mg, 93%) as an oil. The ^{1}H-NMR data are shown in **Table 3**. IR (neat) : 3650-3100 cm^{-1} (OH). MS *m/z* : 408 (M^+), 391 (M^+-OH). HR-MS *m/z* : calcd for $C_{21}H_{32}O_4SSi$ 408.1789, Found: 408.1790.

4-*tert*-Butyldimethylsilyloxymethyl-1-oxa-3-thia-4,5-cyclodecadien-2-one (3n) A fresh THF 1 M solution of $(TMS)_2NLi$[30] (1.13 ml, 1.13 mmol) was injected to a solution of **1n** (423 mg, 1.03 mmol) with stirring at room temperature. After 20 min, the reaction was quenched with H_2O, and workup and purification according to the general procedure described above afforded **3n** (323 mg, 85%)[32] as an oil. Spectroscopic data of **3n** are shown in **Tables 4** and **5**.

8-*tert*-Butyldimethylsilyloxy-5,6-octadienol (21) Samarium metal (0.75 g, 5 mmol) and 1,2-diiodoethane (1.24 g, 4.4 mmol) in anhydrous THF (10 ml) were stirred at room temperature under an Ar atmosphere for 2.5 h to give a deep blue solution. HMPA[24] (1.2 ml) followed by *tert*-BuOH (0.1 ml) were added to the solution at 0°C. After 0.5 h, a solution of **3n** (258 mg, 0.82 mmol) in THF (8 ml) was added and the

mixture was stirred at 0°C for 0.5 h followed by at room temperature for 2 h. Ice was added and the reaction mixture was exposed to air with stirring for 10 min, then filtered through a Celite pad. The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography using 20% EtOAc-n-hexane for elution to give **21** (164 mg, 78%) as an oil. IR (neat) : 3600-3050 (OH), 1962 cm^{-1} (C=C=C). ^{1}H-NMR : 0.10 [6H, s, $OSi(CH_3)_2$], 0.90 [9H, s, $C(CH_3)_3$], 1.40-1.68 (4H, m, 2 × CH_2), 2.05 (2H, m, $=CCH_2$), 3.65 (2H, t, J = 7.5 Hz, CH_2OH), 4.16 (2H, dd, J = 7.5, 4.0 Hz, CH_2OSi), 5.20 (2H, m, 2 × =CH). ^{13}C-NMR : -5.0, 18.5, 25.5, 26.1, 28.5, 32.3, 62.4, 62.8, 92.2, 92.5, 204.2. MS *m/z* : 255 (M^+-1). HR-MS *m/z* : calcd. for $C_{14}H_{27}O_2Si$ (M^+-1) 255.1778, Found: 255.1773.

8-*tert*-butyldimethylsilyloxy-5,6-octadienal (22) A solution of **21** (25 mg, 0.098 mmol) in CH_2Cl_2 (0.5 ml) was added to a suspension of PCC[30] (108 mg, 0.5 mmol) in CH_2Cl_2 (1.5 ml) with stirring at room temperature. After 1 h, the reaction mixture was treated with $MgSO_4$ and filtered through a Celite pad. The filtrate was concentrated under reduced pressure, and the residue was purified by column chromatography using 10% EtOAc-n-hexane for elution to give **22** (24 mg, quant) as a colorless oil. IR (neat) : 1963 (C=C=C), 1725 cm^{-1} (CO). ^{1}H-NMR : 0.10 [6H, s, $OSi(CH_3)_2$], 0.92 (9H, s, $C(CH_3)_3$], 1.78 (2H, quint, J = 7.5 Hz, CH_2), 2.08 (2H, m, $=CCH_2$), 2.51 (2H, t, J = 7.5 Hz, CH_2CHO), 4.20 (2H, dd, J = 7.5, 5.0 Hz, OCH_2), 5.21 (2H, m, 2 × =CH), 9.80 (1H, s, CHO). EIMS *m/z* : 253 (M^+-1). CIMS *m/z* : 255 (M^++1). HRMS *m/z* : clacd. for $C_{14}H_{25}O_2Si$ 253.1622, Found: 253.1622.]

(±)-Methyl 8-Hydroxy-5,6-octadienoate (24) A mixture of **22** (25 mg, 0.1 mmol), $NaClO_2$ (31 mg, 0.34 mmol), 2-methyl-2-butene (31 mg, 0.44 mmol), and NaH_2PO_4 $2H_2O$ (16 mg, 0.1 mmol) in H_2O (1 ml) and *tert*-BuOH (4 ml) was stirred at room temperature. After 0.5 h, the reaction mixture was neutralized with 1 *N* HCl (pH4) and extracted with CH_2Cl_2 (× 3, each 40 ml). The CH_2Cl_2 layer was washed with H_2O, brine, and dried over anhydrous Na_2SO_4. Evaporation of the solvent *in vacuo* gave 8-*tert*-butyldimethylsilyloxy-5,6-octadienoic acid (**23**, 25 mg) as a colorless oil. IR (neat) : 3700-2200 (OH), 1963 (C=C=C), 1723 cm^{-1} (CO). ^{1}H-NMR : 0.10 [6H, s, $OSi(CH_3)_2$], 0.91 [9H, s, $C(CH_3)_3$], 1.76 (2H, quint, J = 9.5 Hz, CH_2), 2.06 (2H, td, J = 7.5, 5.0 Hz, $=CCH_2$), 2.40 (2H, t, J = 9.5 Hz, CH_2COOH), 4.18 (2H, dd, J = 7.0, 4.0 Hz, OCH_2), 5.20 (2H, m, 2 × =CH). The carboxylic acid (**23**) was diluted with MeOH-benzene (1: 5, 2 ml), and a 10% solution of $TMSCHN_2$[33] in hexane (0.5 ml) was added dropwise to the mixture with stirring. After 10 min, the solvent was concentrated *in vacuo* to give a methyl ester (27 mg) {^{1}H-NMR : 0.08 [6H, s, $OSi(CH_3)_2$], 0.90 [9H, s, $C(CH_3)_3$], 1.73 (2H, quint, J = 8.0 Hz, CH_2), 2.02 (2H, td, J = 7.0, 5.0 Hz, $=CCH_2$), 2.35 (2H, t, J = 8.0 Hz, CH_2COOCH_3), 3.67 (3H, s, $COOCH_3$), 4.18 (2H, dd, J = 7.0, 4.0 Hz, OCH_2), 5.11-5.20 (1H, m, =CH), 5.20-5.30 (1H, m, =CH)} as a colorless oil. A solution of the methyl ester (27 mg, 0.095 mmol) in THF (3 ml) was added to a 1 M THF solution of Bu_4NF[30] (0.095 ml, 0.095 mmol) at 0°C. The mixture was stirred at 0°C for 15 min followed by at room temperature for 20 min. Ice was added to the mixture, and the THF was evaporated to give a crude oil. The oil was purified by silica gel (1 g) using EtOAc-n-hexane (1 : 1) for elution to give **24**[5,21,22] (13 mg, 81% based on **22**) as a colorless oil. IR (neat) : 3600-3000 (OH), 1963 (C=C=C), 1737 cm^{-1} (CO). ^{1}H-NMR : 1.78 (2H, quint, J = 9.0 Hz, CH_2), 2.04 (2H, td, J = 5.5, 3.5 Hz, $=CCH_2$), 2.39 (2H, t, J = 9.0 Hz, CH_2COOCH_3), 3.68 (3H, s, $COOCH_3$), 4.11 [(2H, br, CH_2OH) → (2H, dd, J = 5.0, 2.5 Hz) after D_2O treatment], 5.18-5.29 (1H, m, =CH), 5.29-5.40 (1H, m, =CH). ^{13}C-NMR : 24.3, 28.1, 33.4, 51.9, 61.0, 92.9, 93.0, 174.8, 204.1. MS m/z : 152 (M^+-H_2O). HR-MS *m/z* : calcd for $C_9H_{12}O_2$ (M^+-H_2O) 152.0837, Found: 152.0842.

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REFERENCES AND NOTES

1. Part, 12 : Harusawa, S.; Takemura, S.; Yoneda, R.; Kurihara, T. *Tetrahedron*, **1993**, *49*, 10577.
2. Öztung, A.; Imre, S.; Wagner, H.; Norte, M.; Fernandez, J. J.; González, R. *Tetrahedron*, **1991**, *47*, 2273.
3. Schuster, H. F.; Coppola, G. M.; "Allenes in Organic Synthesis," John Wiley & Sons, New York, 1984.
4. Mori, K.; Nukada, T.; Ebata, T. *Tetrahedron*, **1981**, *37*, 1343.
5. Goodsing, O. W.; Beard, C. C.; Jackson, D. Y.; Wren, D. L.; Cooper, G. F. *J. Org. Chem.*, **1991**, *56*, 1083.
6. Baumeler, A.; Eugster, C. H. *Helv. Chim. Acta*, **1991**, *74*, 469.
7. Harusawa, S.; Osaki, H.; Fujii, H.; Yoneda, R.; Kurihara, T. *Tetrahedron*, **1992**, *48*, 9433.
8. Harusawa, S.; Timii, S.; Takehisa, C.; Ohishi, H.; Yoneda, R.; Kurihara, T. *Chem. Pharm. Bull.*, **1992**, *40*, 2279.
9. Harusawa, S.; Osaki, H.; Yoneda, R.; Kurihara, T.; Ohishi, H. *Tetrahedron Lett.*, **1991**, *32*, 1203.
10. Reviews: Johnson, R. P.; *Chem. Rev.*, **1989**, *89*, 1111.
11. a) Illuminati, G.; Mandolini, L. Acc. Chem. Res., 1981, 14, 95. b) Moore, J. A., "Comprehensive Heterocyclic Chemistry," Vol. 7, ed. by Katritzky, A. R.; Rees, C. W. Pergamon Press, Oxford, 1984, p 653.
12. Harusawa, S.; Osaki, H.; Kurokawa, T.; Fujii, H.; Yoneda, R.; Kurihara, T. *Chem. Pharm. Bull.*, **1991**, *39*, 1659.
13. Yildiz, Y. K.; Seçen, H.; Krawiec, M.; Watson, W. H.; Balci, M. *J. Org. Chem.*, **1993**, *58*, 5355.
14. Price, J. D.; Johnson, R. P. *Tetrahedron Lett.*, **1986**, *27*, 4679.
15. a) Pang, Y.; Petrich, S. A.; Young, V. G. Jr.; Gordon, M. S.; Barton, T. J. *J. Am. Chem. Soc.*, **1993**, *115*, 2534. b) Shimizu, T.; Hojo, F.; Ando, W. *ibid.*, **1993**, *115*, 3111.
16. Moore, W. R.; Bach, R. D.; Ozretich, T. M. *J. Am. Chem. Soc.*, **1969**, *91*, 5918.
17. Angus, R. O. Jr.; Schmitt, M. W.; Johnson, R. P. *J. Am. Chem. Soc.*, **1985**, *107*, 532.
18. Kim, K. S.; Kim, S. J.; Song, Y. H.; Hahn, C. S. *Synthesis*, **1987**, 1017.
19. Molander, G. A., "Reduction with Samarium (II) Iodide," Organic Reactions, ed. by Paquette, L. A., John Wiley & Sons, Inc., New York, 1994, 46, pp 211-367.
20. Monoclinic, C2/1. More details on the crystal structure analysis were submitted to the Cambridge Crystallographic Data Centre.
21. Ohigashi, H.; Kawazu, K.; Egawa, H.; Mitsui, T. *Agr. Biol. Chem.*, **1972**, *36*, 1399.
22. a) Rodini, D. J.; Snider, B. B. *Tetrahedron Lett.*, **1980**, *21*, 3857. b) Huguet, J.; Reyes, M. del C. *ibid.*, **1990**, *31*, 4279. c) Back, T. G.; Dyck, B. P. ibid., 1992, 33, 4725.
23. Chabala, J. C.; Vincent, J. E. *Tetrahedron Lett.*, **1978**, 937.
24. The reaction was unreactive under lack of HMPA.

25. a) Lindgren, B. O.; Nilsson, T. *Acta Chem. Scand.*, **1973**, *27*, 888. b) Kraus, G. A.; Tashner, M. J. *J. Org. Chem.*, **1980**, *45*, 1175.
26. We wish to thank Dr. T. Aoyama at Nagoya City University for his valuable suggestion at the oxidation step.
27. Hashimoto, N.; Aoyama, T.; Shioiri, T. *Chem. Pharm. Bull.*, **1981**, *29*, 1475.
28. Noyori, R.; Tomino, I.; Yamada, M.; Nishizawa, M. *J. Am. Chem. Soc.*, **1984**, *106*, 6717.
29. The expected MS peaks were not obtained because of thermal instability.
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31. The spectral data are shown in Tables 4 and 5.
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