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Ring-Closing Metathesis of Titanium–Carbene Complexes Prepared from Thioacetals Having a Carbon–Carbon Double Bond

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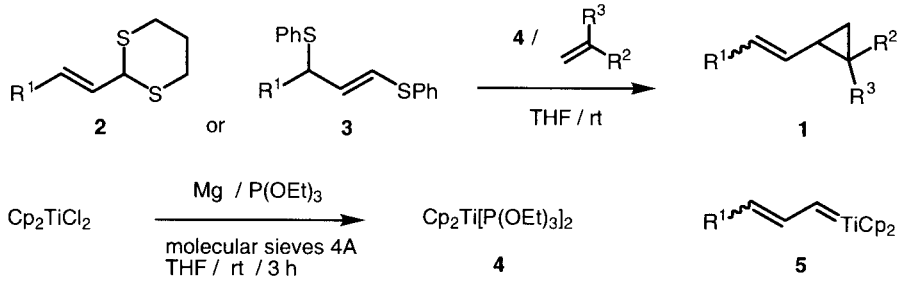
Abstract—The ring-closing metathesis proceeded to give cycloalkenes in good yields when diphenyl thioacetals having a carbon–carbon double bond were treated with the low-valent titanium species $Cp_2Ti[P(OEt)_3]_2$ in THF at room temperature and then at reflux. This methodology is successfully applied to the preparation of cyclic ethers and sulfides. © 2000 Published by Elsevier Science Ltd.

Introduction

In the course of study on the desulfurizative metallation of organosulfur compounds,[1] we found that vinylcyclopropanes **1** were produced by the desulfurization of β,γ-unsaturated thioacetals **2** or 1,3-bis(phenylthio)propene derivatives **3** with the low-valent titanium species $Cp_2Ti[P(OEt)_3]_2$ **4** in the presence of terminal olefins. The newly developed titanium reagent **4** is easily prepared by the reduction of titanocene dichloride with magnesium in the presence of triethyl phosphite and molecular sieves 4A (Scheme 1).[2]

This finding initiated our work with carbene chemistry; the experimental results described above indicate that vinylcarbene complexes **5** would be produced by the reduction of thioacetals **2** or their congeners **3** with titanocene(II) species **4**. The preparation and reactions of titanium–carbene complexes have been extensively studied since the discovery of Tebbe reagent.[3] However this chemistry has a great drawback of lacking the general method for the preparation of alkylidenetitanium species. Therefore we expected that the desulfurization of thioacetals would become a practical method for the preparation of such species. Indeed, the organotitanium species thus formed showed the reactivity characteristic of titanium–carbenes. Their reactions with various carbonyl compounds including carboxylic acid derivatives produced conjugated dienes in good yields.[4a] Furthermore, we found that the treatment of diphenyl thioacetals derived from saturated aldehydes with **4** produced the similar organotitanium species which reacted with carbonyl compounds[4] and alkynes[5] to give the corresponding olefins and conjugated dienes, respectively. On the basis of these experimental results, we tentatively propose that the active species formed from saturated thioacetal is also a titanium–carbene complex **6**.

In contrast to the vinylcarbene complex **5**, the reaction of **6** with a simple terminal alkene gave a multi-component mixture of unsaturated hydrocarbons. It is assumed that



Scheme 1.

Keywords: thioacetal; titanium and compounds; metathesis; cyclization.

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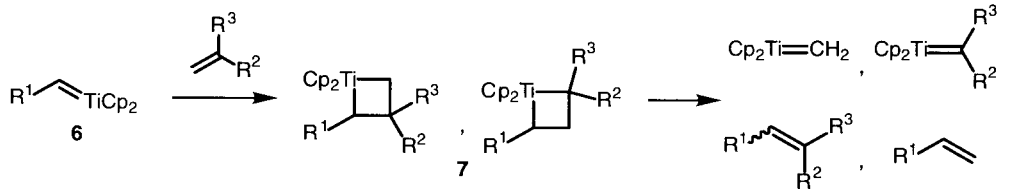


Scheme 2.

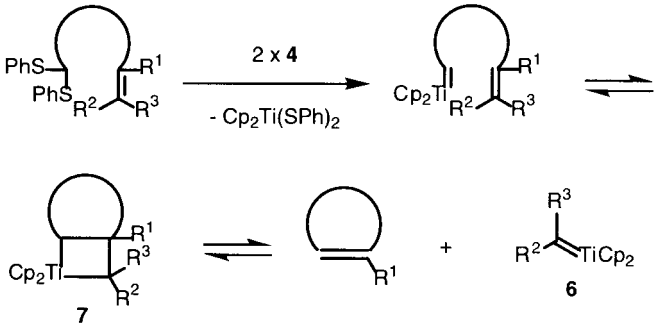
this complexity would arise from lack of regioselectivity in the formation of titanacyclobutane intermediates **7**, which may decompose to form new carbene complexes and olefins by metathesis-type process (Scheme 2). We then examined the influence of substituents of olefin on the geometry of the intermediate titanacycle **7** and found that γ-substituted allylsilanes were stereoselectively obtained when allyltrialkylsilanes were employed as an olefin component.[6]

Another approach to regioselective formation of titanacycle intermediate **7** is to modify the reaction in an intramolecular fashion. The transition metal catalyzed ring-closing metathesis (RCM) of dienes is a useful method for the preparation of various cyclic compounds.[7] Ruthenium,[8] molybdenum,[9] tungsten[10] and rhenium[11] complexes have been employed as catalysts for such transformations. Nicolaou et al. reported the preparation of cyclic ethers from unsaturated esters by RCM using the Tebbe or Petasis reagent, in which the alkylidenetitanocene was suggested to serve as an intermediate.[12] The formation of metathesis products by the titanocene(II)-promoted reaction of thioacetals with allylsilanes prompted us to explore RCM using thioacetals that have a carbon–carbon double bond. This transformation proceeds via the formation of titanacyclobutane intermediate **7** by the intramolecular reaction of titanium–carbene complex with a carbon–carbon double bond and the subsequent elimination of alkylidenetitanocene **6** (Scheme 3).[13]

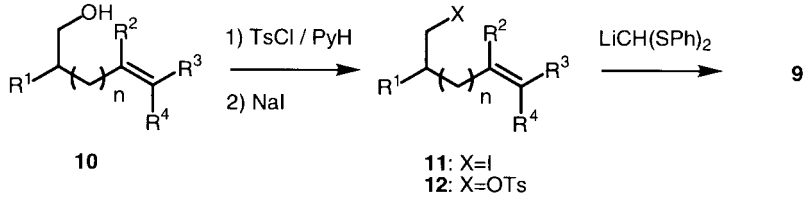
Results and Discussion

Initially the preparation of cycloalkenes **8** was studied. The starting thioacetals **9** were prepared from the unsaturated alcohols **10**. After the transformation of **10** to the iodides **11** via the tosylate **12**, **11** were treated with bis(phenylthio)-methyllithium to produce the thioacetals **9** in good overall yields from **10** (**9a**; 72%, **9b**; 78%, **9c**; 68%, **9d**; 72%, **9e**; 73%, **9f**; 76%, **9g**; 62%, **9h**; 75%, **9i**; 78%) (Scheme 4). When the thioacetal **9a** was treated with the low-valent titanium **4** at room temperature for 17 h, a small amount of 4-(3-phenylpropyl)cyclopentene **8a**, the RCM product, was obtained along with 1-methyl- and 1-methylene-3-(3-phenylpropyl)cyclopentanes **13** and **14**. The reaction of **9b** with **4** at room temperature for 2 h followed by the treatment with D_2O produced **8a** and the dideuterio compound **15** (Scheme 5). The formation of **13** and **15** suggests that the titanacyclobutane **7** was produced as an intermediate. It is reasonable to assume that **14** was formed through the β-hydride elimination of **7**.

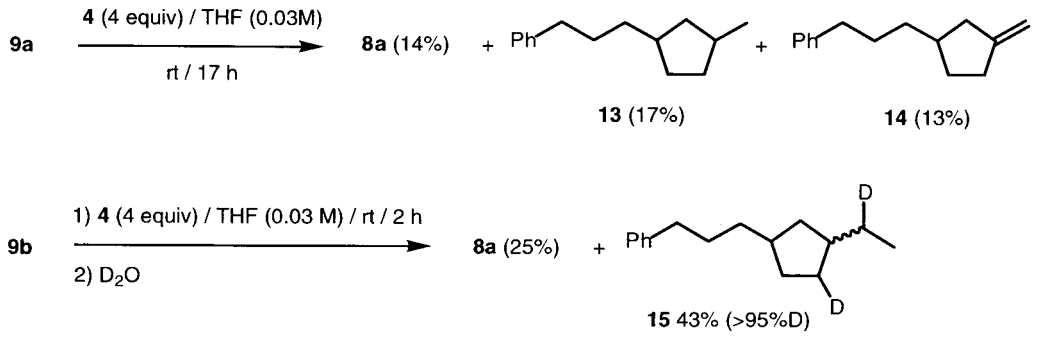
In order to accelerate the elimination of alkylidenetitanocene **6**, the reaction mixture was refluxed for 1 h after the treatment of thioacetal **9a** with **4** at room temperature for 2 h to afford the RCM product **8a** in 71% yield. When benzophenone (1.5 equiv.) was added to the reaction mixture prior to heating, 1,1-diphenylethylene was produced in 10% yield along with **8a** (59%).[14] This result supports our assumption



Scheme 3.

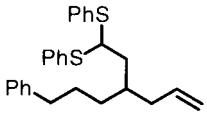
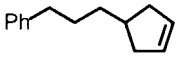
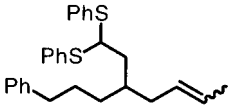
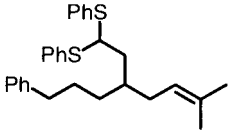
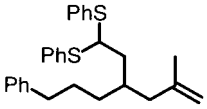
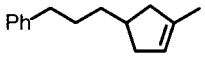
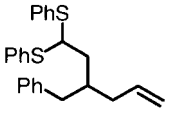
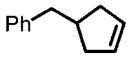
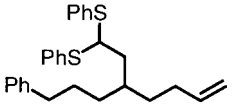
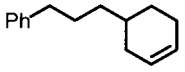
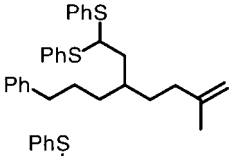
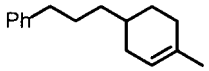
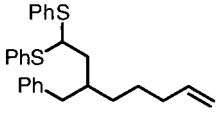
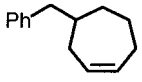
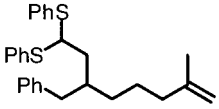
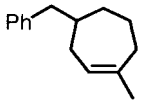


Scheme 4.

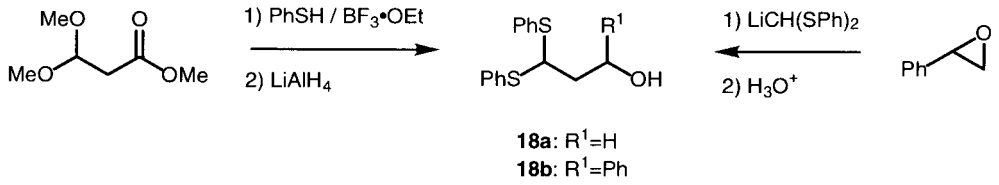


Scheme 5.

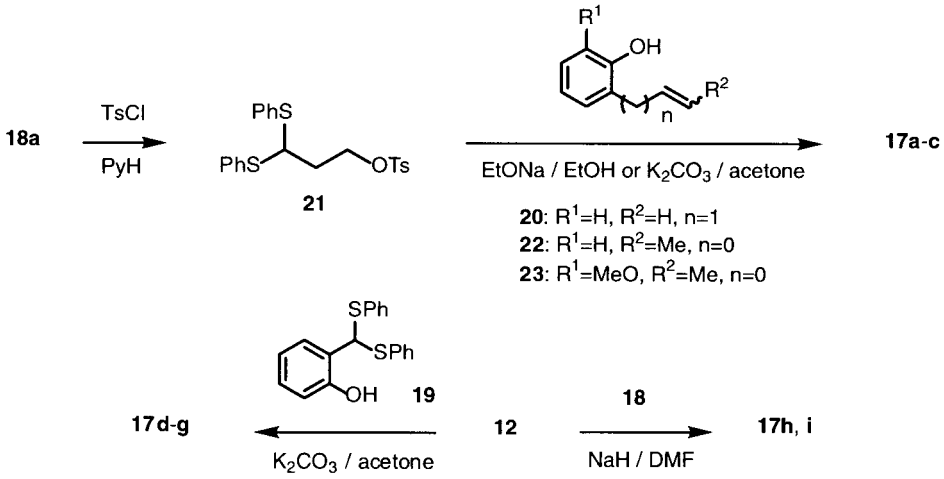
Table 1. Preparation of Cycloalkenes **8**

Entry	Thioacetal **9**	Titanocene (II) **4** (equiv.)/Concentration of **9** (M)	Product **8**	Yield (%)
1	 **9a**	3/0.03	 **8a**	71
2[a]	 **9b**[b]	3/0.1	**8a**	67
3[a]	 **9c**	3/0.1	**8a**	8
4	 **9d**	3/0.03	 **8b**	87
5[c]	 **9e**	4/0.03	 **8c**	74
6[a]	 **9f**	3/0.1	 **8d**	50
7	 **9g**	3/0.03	 **8e**	87
8[c,d]	 **9h**	3/0.03	 **8f**	58
9	 **9i**	4/0.015	 **8g**	81[e]

[a] Carried out at room temperature for 1 h and then at reflux for 1 h.
[b] *E:Z*=82:18.
[c] Carried out at room temperature for 2 h and then at reflux for 3 h.
[d] 1-Benzyl-4-methylcycloheptane was obtained as a by-product in 9% yield.
[e] Contaminated with 6-benzyl-2-methyloct-1-ene (3%). The yield was corrected for the contaminant.



Scheme 6.



Scheme 7.

that alkylidene-titanocene **6** is formed by the decomposition of titanacycle intermediate **7**. In a similar manner, five, six, and seven-membered cycloalkenes were obtained in good yields (Table 1). In the case of the thioacetal having a trisubstituted double bond **9c**, the major product isolated was a desulfurized acyclic hydrocarbon, 5-ethyl-2-methyl-8-phenyloct-2-ene, and the RCM product **8a** was obtained in only 8% yield. The tendency to produce methyl group substituted olefins in better yields than their unsubstituted congeners was observed in these reactions. The composition of equilibrium depicted in Scheme 3 is largely dependent on the number and position of substituents on carbon–carbon double bond. The equilibrium ratio is also dependent on the ring size; the formation of 1-benzyl-4-methylcycloheptane by the reaction of **9h** indicates that a considerable amount of the titanacyclobutane intermediate remained even after the reaction mixture was refluxed for 3 h (Entry 8).

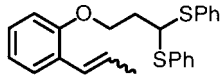
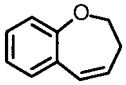
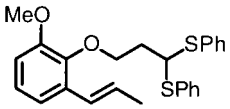
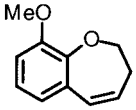
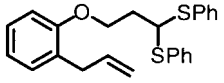
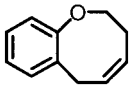
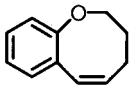
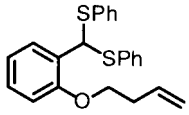
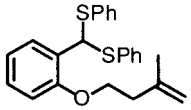
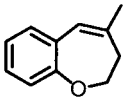
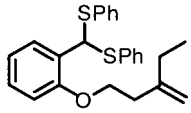
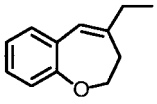
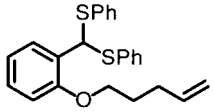
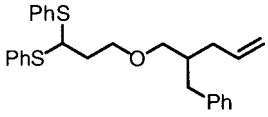
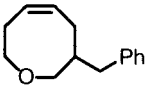
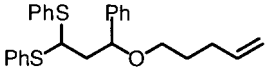
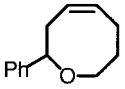
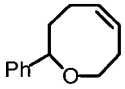
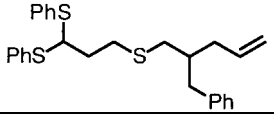
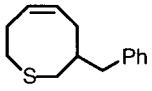
Next we examined the application of this methodology to the construction of cyclic ethers **16**. The acyclic unsaturated ethers **17** were prepared by the Williamson synthesis using γ-hydroxy thioacetals **18a** and **b** or salicylaldehyde diphenyl thioacetal (**19**). The hydroxy thioacetal **18a** was easily prepared by the treatment of commercially available methyl 3,3-dimethoxypropanoate with thiophenol in the presence of $BF_3{\cdot}OEt_2$ and the following reduction with $LiAlH_4$ (Scheme 6).[15] The phenyl group substituted alcohol **18b** was obtained in 93% yield by the reaction of styrene oxide with bis(phenylthio)methyllithium. The condensation of 2-allylphenol (**20**) with the tosylate **21** prepared from **18a** gave the thioacetal **17c** in 83% yield. Similarly the thioacetals **17a** and **b** were prepared by the reactions of **21** with 2-(prop-1-enyl)phenol (**22**) and 2-methoxy-6-(prop-1-enyl)phenol (**23**) in 85 and 83% yields, respectively. These phenols were obtained by the base-catalyzed isomerization of the corresponding allylphenols.[16] The condensation of the tosylates **12** with **18** or **19** gave **17d–i** in good yields (**17d**; 63%, **17e**; 53%, **17f**; 69%, **17g**; 69%, **17h**; 64%, **17i**; 81%) (Scheme 7).

Similarly to the preparation of cycloalkenes, the treatment of the thioacetals **17** with titanocene(II) species **4** and subsequent thermal decomposition of the intermediate afforded the seven- and eight-membered unsaturated cyclic ethers **16** (Table 2). In some cases, the isomerization of double bond was observed (entries 3, 4 and 10). As shown in Table 2, this new cyclization is applicable to not only cyclic ethers fused with a benzene ring but also monocyclic compounds. The formation of the latter rings would be a conformationally less favorable process than the formation of bicyclic compounds. The cyclic sulfide **24** was also obtained by the RCM of the sulfide **25**. The starting material **25** was easily prepared in 89% yield by the reaction of tosylate **21** with the thiolate prepared in situ from the corresponding thiolester **26** (Scheme 8).

Conclusion

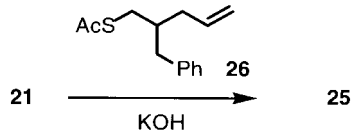
We have established a new cyclization reactions of thioacetals that have a carbon–carbon double bond promoted with the low-valent titanium reagent **4**. Because the starting materials were easily prepared using the organosulfur building blocks, the present reaction provides a versatile synthetic tool for the construction of cyclic compounds. Although we have no direct experimental evidence for the

Table 2. Preparation of unsaturated cyclic ethers **16**

Entry	Thioacetal **17**	Titanocene (II) **4** (equiv.)/Concentration of **17** (M)	Product **16**	Yield (%)
1[a]	 **17a**[b]	4/0.03	 **16a**	75
2[a]	 **17b**	3/0.03	 **16b**	73
3[c]	 **17c**	4/0.015	 **16c**  **16d** (82:18)	70
4	**17c**	3/0.015	**16c** **16d** (98:2)	61
5	 **17d**	3/0.03	**16a**	69
6	 **17e**	3/0.03	 **16e**	71
7	 **17f**	3/0.03	 **16f**	69
8[d]	 **17g**	3/0.03	**16d**	65
9[d]	 **17h**	3/0.03	 **16g**	56
10[d]	 **17i**	3/0.03	 **16h**  **16i**	64[e]
11[d]	 **25**	3/0.03	 **24**	50

[a] Carried out at room temperature for 1 h and then at reflux for 1 h.
[b] *E*:*Z*=96:4.
[c] Carried out at room temperature for 2 h and then at reflux for 3 h.
[d] The thioacetal was added dropwise over 3 h.
[e] A mixture of regioisomers (55:45).

intermediary of titanium–carbene complex, the formation of RCM product indicates that this reaction proceeds through the initial formation of such species. This active organotitanium species should be reactive toward a variety of organic molecules other than those having a carbon–carbon or carbon–oxygen multiple bond. Indeed we have already found their reactions with alkanenitriles,[17] group 14 metal hydrides,[18] and *tert*-alkyl halides.[19] Further study on the titanocene(II)-promoted reaction of thioacetal is now in progress.



Scheme 8.

Experimental

General

Melting points were determined with a Yanaco MP-S3 micromelting point apparatus. ^{1}H (500 MHz) and ^{13}C

(125 MHz) NMR spectra were measured in $CDCl_3$ on a Jeol ALPHA-500 instrument. Chemical shifts are reported (δ scale) from internal tetramethylsilane for ^1H and from $CDCl_3$ for ^{13}C spectroscopies. IR spectra were recorded on a Jeol Diamond-20 FT-IR spectrometer; absorptions are reported in cm^{-1}. Elemental analyses were performed on a Perkin Elmer 2400II.

Materials

Wakogel B-5F was used for preparative thin layer chromatography (PTLC) and Merck Si 60 was used for column chromatography as an adsorbent. THF was distilled from sodium and benzophenone. Magnesium turnings were purchased from Nacalai Tesque Inc. (Kyoto, Japan).

Preparation of thioacetals having a carbon–carbon double bond 9

Preparation of 4-[2,2-bis(phenylthio)ethyl]-7-phenylhept-1-ene (9a). To a pyridine (1.4 ml) solution of 2-(3-phenylpropyl)-4-penten-1-ol (878 mg, 4.3 mmol) was added *p*-toluenesulfonyl chloride (902 mg, 4.73 mmol) at 0°C, and the reaction mixture was stirred overnight. The mixture was diluted with water (10 ml) and the organic materials were extracted with ether (15 ml×2). The extracts were combined, washed with 1 M HCl (5 ml×3), water, and brine, and dried (Na_2SO_4). The crude tosylate was obtained by removal of the solvent under reduced pressure. The tosylate and sodium iodide (2.13 g, 14.2 mmol) were dissolved in acetone (6 ml), and the mixture was reflux for 2 h. After cooling, the reaction mixture was diluted with water (30 ml) and the organic materials were extracted with ether (20 ml×2). The combined extracts were washed with a saturated Na_2SO_3 solution and brine, dried (Na_2SO_4), and condensed under reduced pressure to give the crude iodide. To a THF solution of bis(phenylthio)methane (999 mg, 4.3 mmol) was added a hexane solution of butyllithium (2.8 ml, 4.4 mmol) at 0°C under argon. After 15 min, the crude iodide in THF (5 ml) was added and the reaction mixture was stirred for 2 h. The reaction was quenched by addition of a saturated NH_4Cl solution and the organic materials were extracted with ether (20 ml×2). The combined extracts were dried (Na_2SO_4) and condensed under reduced pressure. The residue was purified by silica gel column chromatography to afford **9a** (1.30 g, 72%). **9a:** IR (neat) 3074, 3060, 2931, 1637, 1583, 1479, 1439, 1024, 999, 914, 748, 690. ^1H NMR 1.20–1.33 (m, 2H), 1.47–1.57 (m, 2H), 1.69–1.83 (m, 2H), 1.91–2.07 (m, 3H), 2.48–2.59 (m, 2H), 4.40 (t, 1H, J=7.5 Hz), 4.88–4.97 (m, 2H), 5.63 (ddt, 1H, J=16.9, 10.2, 6.7 Hz), 7.10–7.21 (m, 3H), 7.22–7.33 (m, 8H), 7.38–7.47 (m, 4H). ^{13}C NMR 27.92, 32.53, 34.72, 35.96, 37.58, 40.08, 56.63, 116.53, 125.65, 127.70, 128.22, 128.34, 128.82, 132.84, 132.94, 134.05, 136.14, 142.39. Anal. Calcd for $C_{27}H_{30}S_2$: C, 77.46; H, 7.22. Found: C, 77.72; H, 7.20.

In a similar manner, the following thioacetals **9** were obtained.

5-[2,2-Bis(phenylthio)ethyl]-8-phenyloct-2-ene (9b). (E:Z=82:18) IR (neat) 3060, 3024, 2933, 1602, 1583, 1479, 1439, 1026, 968, 748, 698, 690. ^1H NMR 1.19–1.32 (m, 2H), 1.48–1.61 (m, 2.54H), 1.58 (dd, 2.46H, J=6.1, 0.9 Hz), 1.66–1.82 (m, 2H), 1.86–2.04 (m, 3H), 2.49–2.59 (m, 2H), 4.41 and 4.40 (2t, 1H, J=7.5 Hz), 5.21 (ddt, 0.82H, J=15.3, 6.7, 1.5 Hz), 5.31 (dq, 0.82H, J=15.3, 6.1 Hz), 5.18–5.35 (m, 0.18H), 5.45 (dq, 0.18H, J=11.0, 6.7 Hz), 7.11–7.20 (m, 3H), 7.24–7.33 (m, 8H), 7.40–7.47 (m, 4H). ^{13}C NMR 12.92, 17.95, 17.97, 27.98, 28.09, 30.45, 32.63, 32.78, 35.02, 35.35, 35.97, 36.04, 36.15, 40.04, 40.33, 56.65, 125.31, 125.62, 126.93, 127.63, 127.68, 127.97, 128.21, 128.36, 128.47, 128.80, 128.81, 132.75, 132.85, 132.87, 132.99, 134.09, 134.14, 142.47. Anal. Calcd for $C_{28}H_{32}S_2$: C, 77.73, H, 7.45. Found: C, 77.94, H, 7.44.

5-[2,2-Bis(phenylthio)ethyl]-2-methyl-8-phenyloct-2-ene (9c). IR (neat) 3059, 3024, 2929, 1603, 1583, 1479, 1439, 1024, 748, 690. ^1H NMR 1.20–1.32 (m, 2H), 1.47–1.56 (m, 2H), 1.52 (s, 3H), 1.63 (s, 3H), 1.67–1.81 (m, 2H), 1.86–2.00 (m, 3H), 2.53 (t, 2H, J=7.5 Hz), 4.41 (t, 1H, J=7.5 Hz), 4.93–5.01 (m, 1H), 7.10–7.15 (m, 2H), 7.15–7.20 (m, 1H), 7.22–7.31 (m, 8H), 7.39–7.46 (m, 4H). ^{13}C NMR 17.84, 25.83, 28.12, 31.67, 32.89, 35.54, 36.03, 40.26, 56.60, 122.06, 125.62, 127.62, 128.21, 128.37, 128.81, 132.74, 132.89, 134.09, 134.14, 142.48. Anal. Calcd for $C_{29}H_{34}S_2$: C, 77.97; H, 7.67. Found: C, 78.07; H, 7.66.

4-[2,2-Bis(phenylthio)ethyl]-2-methyl-7-phenylhept-1-ene (9d). IR (neat) 3060, 3024, 2933, 1647, 1583, 1479, 1439, 1026, 891, 748, 690. ^1H NMR 1.21–1.30 (m, 2H), 1.43–1.56 (m, 2H), 1.66 (s, 3H), 1.72–1.80 (m, 2H), 1.84–1.90 (m, 1H), 1.92–2.07 (m, 2H), 2.52 (t, 2H, J=7.6 Hz), 4.41 (t, 1H, J=7.5 Hz), 4.61 (s, 1H), 4.71 (s, 1H), 7.09–7.14 (m, 2H), 7.16–7.21 (m, 1H), 7.23–7.32 (m, 8H), 7.39–7.45 (m, 4H). ^{13}C NMR 22.13, 22.15, 27.64, 32.72, 36.03, 40.56, 42.96, 56.67, 112.30, 125.66, 127.60, 127.70, 128.23, 128.36, 128.83, 132.66, 132.89, 134.14, 134.25, 142.42, 143.98. Anal. Calcd for $C_{28}H_{32}S_2$: C, 77.73; H, 7.45. Found: C, 77.92; H, 7.45.

4-Benzyl-6,6-bis(phenylthio)hex-1-ene (9e). IR (neat) 3074, 3060, 2920, 1639, 1583, 1479, 1439, 1026, 991, 914, 744, 702, 692. ^1H NMR 1.74–1.88 (m, 2H), 1.95–2.08 (m, 2H), 2.26–2.35 (m, 1H), 2.47 (dd, 1H, J=13.4, 7.0 Hz), 2.56 (dd, 1H, J=13.4, 7.0 Hz), 4.38 (t, 1H, J=7.5 Hz), 4.94–5.01 (m, 2H), 5.68 (ddt, 1H, J=16.9, 10.2, 7.2 Hz), 7.05–7.10 (m, 2H), 7.16–7.20 (m, 1H), 7.21–7.31 (m, 8H), 7.31–7.37 (m, 2H), 7.37–7.42 (m, 2H). ^{13}C NMR 36.95, 37.64, 39.83, 40.23, 56.57, 117.03, 125.93, 127.65, 127.79, 128.30, 128.78, 128.81, 129.19, 132.84, 133.28, 133.47, 133.99, 135.90, 140.30. Anal. Calcd for $C_{25}H_{26}S_2$: C, 76.88; H, 6.71. Found: C, 76.77; H, 6.65.

5-[2,2-Bis(phenylthio)ethyl]-8-phenyloct-1-ene (9f). IR (neat) 3060, 3026, 2929, 1639, 1583, 1479, 1439, 1024, 999, 910, 748, 690. ^1H NMR 1.21–1.37 (m, 4H), 1.44–1.58 (m, 2H), 1.76 (t, 2H, J=7.0 Hz), 1.82–1.97 (m, 3H), 2.53 (t, 2H, J=7.5 Hz), 4.35 (t, 1H, J=7.3 Hz), 4.87–5.00 (m, 2H), 5.73 (ddt, 1H, J=16.9, 10.2, 6.7 Hz), 7.09–7.23 (m, 3H), 7.23–7.35 (m, 8H), 7.39–7.48 (m, 4H). ^{13}C NMR 27.63, 30.43, 32.25, 32.41, 34.40, 36.02, 40.28, 56.68, 114.41, 125.65, 127.68, 127.71, 128.23, 128.35, 128.83, 132.63, 132.81, 132.90, 134.10, 134.13, 138.77, 142.39.

Anal. Calcd for $C_{28}H_{32}S_2$: C, 77.73; H, 7.45. Found: C, 77.78; H, 7.43.

5-[2,2-Bis(phenylthio)ethyl]-2-methyl-8-phenyloct-1-ene (9g). IR (neat) 3060, 3024, 2931, 1647, 1583, 1479, 1439, 1024, 887, 746, 690. ^{1}H NMR 1.24–1.31 (m, 2H), 1.31–1.39 (m, 2H), 1.46–1.56 (m, 2H), 1.66 (s, 3H), 1.76 (t, 2H, *J*=7.0 Hz), 1.81–1.89 (m, 3H), 2.54 (t, 2H, *J*=7.5 Hz), 4.36 (t, 1H, *J*=7.5 Hz), 4.60 (s, 1H), 4.66 (s, 1H), 7.10–7.21 (m, 3H), 7.23–7.33 (m, 8H), 7.41–7.46 (m, 4H). ^{13}C NMR 22.50, 27.66, 31.07, 32.29, 34.25, 34.56, 36.02, 40.30, 56.73, 109.74, 125.65, 127.68, 127.70, 128.22, 128.35, 128.83, 132.84, 132.87, 134.13, 134.14, 142.39, 145.91. Anal. Calcd for $C_{29}H_{34}S_2$: C, 77.97; H, 7.67. Found: C, 78.08; H, 7.64.

6-Benzyl-8,8-bis(phenylthio)oct-1-ene (9h). IR (neat) 3060, 3026, 2929, 1639, 1583, 1479, 1439, 1024, 999, 912, 741, 700, 690. ^{1}H NMR 1.18–1.41 (m, 4H), 1.75–1.84 (m, 2H), 1.92–2.01 (m, 2H), 2.14–2.24 (m, 1H), 2.47 (dd, 1H, *J*=13.6, 7.0 Hz), 2.56 (dd, 1H, *J*=13.6, 7.0 Hz), 4.32 (t, 1H, *J*=7.5 Hz), 4.89–5.01 (m, 2H), 5.73 (ddt, 1H, *J*=17.1, 10.1, 6.7 Hz), 7.04–7.08 (m, 2H), 7.16–7.37 (m, 11H), 7.37–7.42 (m, 2H). ^{13}C NMR 25.31, 32.76, 33.83, 37.06, 40.26, 40.45, 56.70, 114.48, 125.84, 127.61, 127.77, 128.25, 128.76, 128.81, 129.16, 132.71, 133.31, 133.60, 134.11, 138.68, 140.51. Anal. Calcd for $C_{27}H_{30}S_2$: C, 77.46; H, 7.22. Found: C, 77.58; H, 7.18.

6-Benzyl-8,8-bis(phenylthio)-2-methyloct-1-ene (9i). IR (neat) 3060, 3024, 2931, 1647, 1583, 1479, 1439, 1024, 887, 737, 700, 690. ^{1}H NMR 1.16–1.28 (m, 2H), 1.28–1.44 (m, 2H), 1.66 (s, 3H), 1.77–1.82 (m, 2H), 1.91 (t, 2H, *J*=7.5 Hz), 2.14–2.24 (m, 1H), 2.47 (dd, 1H, *J*=13.4, 7.0 Hz), 2.56 (dd, 1H, *J*=13.4, 6.7 Hz), 4.32 (t, 1H, *J*=7.5 Hz), 4.60 (s, 1H), 4.67 (s, 1H), 7.04–7.09 (m, 2H), 7.14–7.20 (m, 1H), 7.20–7.30 (m, 8H), 7.30–7.35 (m, 2H), 7.38–7.42 (m, 2H). ^{13}C NMR 22.35, 24.04, 32.99, 37.10, 37.85, 40.28, 40.50, 56.67, 109.87, 125.84, 127.60, 127.77, 128.25, 128.76, 128.80, 129.15, 132.70, 133.30, 133.58, 134.07, 140.52, 145.72. Anal. Calcd for $C_{28}H_{32}S_2$: C, 77.73; H, 7.45. Found: C, 77.59; H, 7.58.

Cyclization of 9

Cyclization of 9d. Finely powdered molecular sieves 4A (150 mg), magnesium turnings (40 mg, 1.65 mmol), and Cp_2TiCl_2 (374 mg, 1.5 mmol) were placed in a flask and dried by heating with a heat gun under reduced pressure (2–3 mmHg). During this procedure, care was taken not to sublime Cp_2TiCl_2. After cooling, THF (6.7 ml) and $P(OEt)_3$ (0.52 ml, 3 mmol) were added successively with stirring at room temperature under argon. Within 15 min, the reaction mixture turned dark green and then dark brown with slight evolution of heat. After 3 h, the unsaturated thioacetal **9d** (216 mg, 0.5 mmol) in THF (10 ml) was added to the reaction mixture, which was further stirred for 2 h. Then the reaction mixture was refluxed for 1 h. After cooling, the reaction was quenched with 1 M NaOH (10 ml) and vigorously stirred for 20 min. The insoluble materials were filtered off through celite and washed with ether (50 ml). The organic phase was separated and dried (Na_2SO_4). After removal of the solvent, the residue was purified by PTLC (hexane) to yield 1-methyl-4-(3-phenylpropyl)cyclopentene (**8b**) (87 mg, 87%). **8b:** IR (neat) 3027, 2925, 2844, 1655, 1604, 1496, 1452, 1014, 789, 748, 698. ^{1}H NMR 1.38–1.47 (m, 2H), 1.57–1.66 (m, 2H), 1.68 (s, 3H), 1.84–1.97 (m, 2H), 2.22–2.38 (m, 2H), 2.38–2.47 (m, 1H), 2.60 (t, 1H, *J*=7.6 Hz), 5.20–5.24 (m, 1H), 7.13–7.20 (m, 3H), 7.23–7.29 (m, 2H). ^{13}C NMR 16.73, 30.24, 36.14, 36.43, 38.40, 39.18, 43.34, 123.42, 125.55, 128.20, 128.36, 139.51, 142.85. Anal. Calcd for $C_{15}H_{20}$: C, 89.94; H,10.06. Found: C, 90.24; H, 10.34.

In a similar manner, the following cycloalkenes **8** were obtained.

4-(3-Phenylpropyl)cyclopentene (8a). IR (neat) 3062, 3026, 2924, 2844, 1604, 1496, 1452, 748, 698. ^{1}H NMR 1.39–1.48 (m, 2H), 1.58–1.69 (m, 2H), 1.90–2.00 (m, 2H), 2.18–2.29 (m, 1H), 2.40–2.51 (m, 2H), 2.60 (t, 2H, *J*=7.6 Hz), 5.65 (s, 2H), 7.14–7.19 (m, 3H), 7.23–7.29 (m, 2H). ^{13}C NMR 30.29, 36.14, 36.17, 37.56, 38.91, 125.56, 128.20, 128.35, 129.91, 142.78. Anal. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 90.65; H, 10.00.

4-Benzylcyclopentene (8c). IR (neat) 3064, 3030, 2935, 2850, 1614, 1498, 1454, 744, 700, 671. ^{1}H NMR 2.02–2.11 (m, 2H), 2.38–2.47 (m, 2H), 2.53–2.63 (m, 1H), 2.68 (d, 2H, *J*=7.6 Hz), 5.67 (s, 2H), 7.15–7.21 (m, 3H), 7.25–7.32 (m, 2H). ^{13}C NMR 38.56, 38.87, 42.27, 125.67, 128.18, 128.83, 129.74, 141.81. Anal. Calcd for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 91.00; H, 9.02.

4-(3-Phenylpropyl)cyclohexene (8d). IR (neat) 3024, 2914, 2854, 1653, 1604, 1496, 1452, 910, 746, 698, 654. ^{1}H NMR 1.15–1.38 (m, 3H), 1.49–1.78 (m, 5H), 1.99–2.04 (m, 3H), 2.60 (t, 2H, *J*=7.7 Hz), 5.65 (s, 2H), 7.14–7.21 (m, 3H), 7.24–7.31 (m, 2H). ^{13}C NMR 25.26, 28.82, 28.91, 31.87, 33.40, 36.19, 36.34, 125.56, 126.61, 127.01, 128.21, 128.35, 142.81. Anal. Calcd for $C_{15}H_{20}$: C, 89.94; H, 10.06. Found: C, 90.25; H, 10.22.

1-Methyl-4-(3-phenylpropyl)cyclohexene (8e). IR (neat) 3026, 2912, 1604, 1496, 1452, 800, 746, 698. ^{1}H NMR 1.15–1.36 (m, 3H), 1.42–1.53 (m, 1H), 1.55–1.70 (m, 3H), 1.63 (s, 3H), 1.70–1.77 (m, 1H), 1.85–2.11 (m, 3H), 2.59 (t, 2H, *J*=7.8 Hz), 5.34 (s, 1H), 7.14–7.19 (m, 3H), 7.23–7.29 (m, 2H). ^{13}C NMR 23.55, 28.98, 29.36, 30.16, 32.06, 33.25, 36.16, 36.23, 120.63, 125.56, 128.21, 128.36, 133.94, 142.86. Anal. Calcd for $C_{16}H_{22}$: C, 89.66; H, 10.34. Found: C, 89.47; H, 10.17.

4-Benzylcycloheptene (8f). IR (neat) 3022, 2914, 2837, 1653, 1604, 1495, 1452, 750, 698. ^{1}H NMR 1.29–1.43 (m, 2H), 1.65–1.81 (m, 2H), 1.85–1.99 (m, 2H), 2.02–2.20 (m, 3H), 2.53 (d, 2H, *J*=7.3 Hz), 5.64–5.71 (m, 1H), 5.78–5.85 (m, 1H), 7.10–7.22 (m, 3H), 7.24–7.31 (m, 2H). ^{13}C NMR 25.82, 28.77, 34.09, 38.04, 39.15, 43.54, 125.66, 128.11, 129.18, 130.40, 132.89, 141.42. Anal. Calcd for $C_{14}H_{18}$: C, 90.26; H, 9.74. Found: C, 90.63; H, 9.98.

4-Benzyl-1-methylcycloheptene (8g). IR (neat) 3028, 2913, 2848, 1604, 1496, 1454, 847, 748, 698. ^{1}H NMR 1.28–1.39 (m, 2H), 1.62–1.75 (m, 2H), 1.70 (s, 3H), 1.81–1.95 (m, 2H), 1.95–2.08(m, 2H), 2.08–2.18 (m,

1H), 2.45–2.53 (m, 2H), 5.38–5.44 (m, 1H), 7.10–7.19 (m, 3H), 7.22–7.29 (m, 2H). ^{13}C NMR 25.12, 26.08, 33.40, 33.99, 38.32, 39.20, 43.59, 123.72, 125.59, 128.07, 129.17, 141.20, 141.51. Anal. Calcd for $C_{15}H_{20}$: C, 89.94; H, 10.06. Found: C, 89.86; H, 10.40.

The dideuterio compound, 1-[1-^{2}H]ethyl-3-(3-phenylpropyl)[5-^{2}H]cyclopentane (**15**), (47 mg, 43%) was obtained by the reaction of **9b** (216 mg, 0.5 mmol) at room temperature for 2 h followed by the treatment with D_2O (0.5 ml). **15**: IR (neat) 3028, 2933, 2146, 1496, 1454, 1030, 748, 698. ^{1}H NMR 0.59–0.69 (m, 1H), 0.85 (d, J=7.3 Hz, 3H), 1.09–1.19 (m, 1H), 1.23–1.38 (m, 3H), 1.56–1.88 (m, 6H), 1.88–1.96 (m, 1H), 2.58 (t, J=7.8 Hz, 2H), 7.13–7.19 (m, 3H), 7.24–7.29 (m, 2H). ^{13}C NMR 12.94, 28.89 (t, J=19 Hz), 30.64, 30.83 (t, J=20 Hz), 31.50, 36.26, 36.32, 40.06, 40.22, 41.79, 125.52, 128.20, 128.37, 142.96.

Preparation of the ethers having a carbon–carbon double bond and a diphenyl thioacetal moiety 17

Preparation of 1-phenyl-3,3-bis(phenylthio)propanol (18b). To a THF (100 ml) solution of bis(phenylthio)-methane (11.62 g, 50 mmol) was added a hexane solution of butyllithium (35.6 ml, 55 mmol) at 0°C with stirring under argon. After 30 min, styrene oxide (6.8 ml, 60 mmol) was added and the reaction mixture was stirred for 1.5 h. The reaction was quenched by addition of a saturated NH_4Cl solution (30 ml) and the organic materials were extracted with ether (50 ml×2). The combined extracts were dried (Na_2SO_4) and condensed under reduced pressure. The residue was purified by silica gel column chromatography (hexane:AcOEt=9:1) to give **18b** (16.37 g, 93%). **18b:** IR (neat) 3444, 3062, 2918, 1585, 1481, 1441, 1026, 744, 694. ^{1}H NMR 2.10 (ddd, 1H, J=14.7, 8.9, 4.3 Hz), 2.18 (br d, 1H, J=2.2 Hz), 2.34 (ddd, 1H, J=14.7, 9.2, 5.5 Hz), 4.60 (dd, 1H, J=8.9, 5.5 Hz), 5.13 (dt, 1H, J=8.9, 4.1 Hz), 7.25–7.36 (m, 11H), 7.42–7.47 (m, 4H). ^{13}C NMR 44.58, 54.51, 71.74, 125.77, 127.69, 127.79, 127.83, 128.57, 128.92, 132.51, 132.72, 133.50, 133.76, 143.54. Anal. Calcd for $C_{21}H_{20}OS_2$: C, 71.55; H, 5.72. Found: C, 71.37; H, 5.73.

Preparation of 1-[3,3-bis(phenylthio)propoxy]-2-(prop-1-enyl)benzene (17a). To a pyridine (1.4 ml) solution of **18a** (1.11 g, 4 mmol) was added *p*-toluenesulfonyl chloride (839 mg, 4.4 mmol) at 0°C under argon, and the reaction mixture was stirred for 12 h. The mixture was diluted with water (10 ml) and the organic materials were extracted with ether (15 ml×2). The extracts were combined, washed with 1 M HCl (5 ml×3), water, and brine, and dried (Na_2SO_4). To an acetone (6.7 ml) solution of the crude tosylate **21** obtained by removal of the solvent under reduced pressure were added K_2CO_3 (663 mg, 4.8 mmol) and 2-(prop-1-enyl)phenol **22** (644 mg, 4.8 mmol), and the mixture was refluxed for 20 h. The reaction mixture was diluted with water (30 ml) and the organic materials were extracted with ether (20 ml×2). The combined extracts were washed with water and brine, dried (Na_2SO_4), and condensed under reduced pressure. The residue was purified by silica gel column chromatography (hexane:AcOEt=95:5) to give **17a** (1.34 g, 85%) (*E*:*Z*=96:4). **17a:** IR (neat) 3059, 3033, 2929, 1597, 1581, 1489, 1452, 1439, 1244, 1051, 1026, 972, 752, 690. ^{1}H NMR 1.81 (dd, 0.12H, J=7.0, 1.8 Hz), 1.87 (dd, 2.88H, J=6.7, 1.5 Hz), 2.33 (dt, 2H, J=7.3, 5.8 Hz), 4.23 (t, 2H, J=5.8 Hz), 4.78 (t, 1H, J=7.0 Hz), 5.79 (dq, 0.04H, J=11.6, 7.0 Hz), 6.19 (dq, 0.96H, J=15.9, 6.7 Hz), 6.47 (dd, 0.04H, J=11.6, 1.8 Hz), 6.65 (dd, 0.96H, J=15.9, 1.5 Hz), 6.78–6.85 (m, 1H), 6.86–6.95 (m, 1H), 7.10–7.15 (m, 1H), 7.22–7.31 (m, 6H), 7.38 (dd, 1H, J=7.6, 1.5 Hz), 7.43–7.48 (m, 4H). ^{13}C NMR (*E* isomer) 18.97, 35.60, 54.71, 64.88, 111.98, 120.89, 125.52, 126.30, 126.35, 127.11, 127.68, 127.73, 128.92, 132.50, 133.90, 155.03. Anal. Calcd for $C_{24}H_{24}OS_2$: C, 73.43; H, 6.16. Found: C, 73.42; H, 6.12.

In a similar manner, the following thioacetals **17** were obtained.

(*E*)-2-[3,3-Bis(phenylthio)propoxy]-1-methoxy-3-(prop-1-enyl)benzene (17b). IR (neat) 3059, 3035, 2935, 1654, 1576, 1475, 1460, 1439, 1271, 1209, 1090, 1068, 1024, 972, 744, 690. ^{1}H NMR 1.81 (dd, 1H, J=6.7, 1.5 Hz), 2.28 (dt, 2H, J=7.0, 6.0 Hz), 3.74 (s, 3H), 4.19 (t, 2H, J=6.0 Hz), 4.91 (t, 1H, J=7.0 Hz), 6.21 (dq, 1H, J=15.9, 6.7 Hz), 6.68 (d, 1H, J=15.9, 1.5 Hz), 6.74 (dd, 1H, J=7.9, 1.5 Hz), 6.98 (t, 1H, J=7.9 Hz), 7.04 (dd, 1H, J=7.9, 1.5 Hz), 7.23–7.34 (m, 6H), 7.46–7.54 (m, 4H). ^{13}C NMR 18.83, 36.31, 54.00, 55.62, 69.94, 110.47, 117.85, 123.93, 125.19, 127.21, 127.52, 128.83, 132.18, 132.53, 133.90, 144.75, 152.87. Anal. Calcd for $C_{25}H_{26}O_2S_2$: C, 71.05; H, 6.20. Found: C, 71.09; H, 6.11.

1-Allyl-2-[3,3-bis(phenylthio)propoxy]benzene (17c). IR (neat) 3074, 3060, 2927, 1637, 1585, 1495, 1454, 1439, 1248, 1025, 914, 754, 692. ^{1}H NMR 2.32 (dt, 2H, J=7.0, 5.8 Hz), 3.31 (d, 2H, J=6.4 Hz), 4.22 (t, 2H, J=5.8 Hz), 4.77 (t, 1H, J=7.0 Hz), 4.94–5.02 (m, 2H), 5.87–5.97 (m, 1H), 6.83 (d, 1H, J=7.9 Hz), 6.90 (dt, 1H, J=7.3, 0.9 Hz), 7.13 (dd, 1H, J=7.3, 1.8 Hz), 7.17 (dt, 1H, J=7.9, 1.5 Hz), 7.24–7.35 (m, 6H), 7.43–7.52 (m, 4H). ^{13}C NMR 34.38, 35.72, 54.36, 64.39, 111.07, 115.32, 120.64, 127.32, 127.63, 128.35, 128.89, 129.82, 132.38, 133.91, 136.85, 156.11. Anal. Calcd for $C_{24}H_{24}OS_2$: C, 73.43; H, 6.16. Found: C, 73.32; H, 6.09.

Preparation of 1-(3-methylbut-3-enyloxy)-2-[bis(phenylthio)methyl]benzene (17e). To an acetone (15 ml) solution of the crude tosylate prepared from 3-methyl-3-buten-1-ol (947 mg, 11 mmol) and *p*-toluenesulfonyl chloride (2.31 g, 12.1 mmol) was added K_2CO_3 (1.52 mg, 11 mmol) and 2-bis(phenylthio)methylphenol (**19**) (3.25 g, 10 mmol). After being refluxed for 20 h, the reaction mixture was diluted with water (40 ml) and the organic materials were extracted with ether (30 ml×2). The combined extracts were dried (Na_2SO_4) and condensed under reduced pressure. The residue was purified by silica gel column chromatography (hexane:AcOEt=98:2) to give **17e** (2.09 g, 53%). **17e:** IR (neat) 3064, 2968, 1657, 1572, 1491, 1263, 1221, 1057, 897, 860, 756. ^{1}H NMR 1.75 (s, 3H), 2.45 (t, 2H, J=6.4 Hz), 4.03 (t, 2H J=6.4 Hz), 4.77 (s, 1H), 4.80 (s, 1H), 6.13 (s, 1H), 6.80 (d, 1H, J=8.2 Hz), 6.90 (t, 1H, J=7.5 Hz), 7.15–7.23 (m, 7H), 7.31–7.36 (m, 4H), 7.60 (d, 1H, J=7.9 Hz). ^{13}C NMR 22.45, 37.31, 52.01, 66.33, 111.27, 112.33, 120.79, 127.16, 128.02, 128.60, 128.90, 128.99, 131.60, 135.27, 141.93, 154.86. Anal. Calcd for $C_{24}H_{24}OS_2$: C, 73.43; H, 6.16. Found: C, 73.47; H, 6.20.

In a similar manner, the following thioacetals **17** were obtained.

1-(But-3-enyloxy)-2-[bis(phenylthio)methyl]benzene (17d). IR (neat) 3076, 2937, 1643, 1583, 1491, 1248, 1026, 989, 906, 748, 690. ^{1}H NMR 2.50 (tq, 2H, *J*=6.7, 1.2 Hz), 3.98 (t, 2H, *J*=6.7 Hz), 5.04–5.16 (m, 2H), 5.85 (ddt, 1H, *J*=17.1, 10.4, 6.7 Hz), 6.10 (s, 1H), 6.80 (dd, 1H, *J*=8.2, 0.9 Hz), 6.91 (dt, 1H, *J*=7.6, 0.9 Hz), 7.16–7.24 (m, 7H), 7.31–7.36 (m, 4H), 7.58 (dd, 1H, *J*=7.6, 1.8 Hz). ^{13}C NMR 33.74, 52.28, 67.49, 111.46, 117.12, 120.88, 127.23, 128.15, 128.64, 128.97, 129.00, 131.73, 134.51, 135.30, 154.90. Anal. Calcd for $C_{23}H_{22}OS_2$: C, 72.98; H, 5.86. Found: C, 73.01; H, 5.96.

1-(3-Ethylbut-3-enyloxy)-2-[bis(phenylthio)methyl]benzene (17f). IR (neat) 3078, 2970, 1647, 1585, 1489, 1248, 1026, 741. ^{1}H NMR 1.03 (t, 3H, *J*=7.3 Hz), 2.06 (q, 2H, *J*=7.3 Hz), 2.47 (t, 2H, *J*=6.7 Hz), 4.03 (t, 2H, *J*=6.7 Hz), 4.79 (s, 1H), 4.81 (s, 1H), 6.12 (s, 1H), 6.80 (d, 1H, *J*=8.2 Hz), 6.90 (t, 1H, *J*=7.6 Hz), 7.15–7.24 (m, 7H), 7.30–7.36 (m, 4H), 7.58 (d, 1H, *J*=7.6 Hz). ^{13}C NMR 12.27, 28.91, 35.82, 52.03, 66.73, 109.98, 111.29, 120.77, 127.17, 128.61, 128.92, 128.99, 131.63, 135.28, 147.47, 154.90. Anal. Calcd for $C_{25}H_{26}OS_2$: C, 73.85; H, 6.45. Found: C, 74.07; H, 6.48.

1-(Pent-4-enyloxy)-2-[bis(phenylthio)methyl]benzene (17g). IR (neat) 3060, 2941, 1641, 1583, 1481, 1248, 1099, 1001, 914, 748, 690. ^{1}H NMR 1.81–1.89 (m, 2H), 2.19 (dt, 2H, *J*=7.6, 6.7 Hz), 3.94 (t, 2H, *J*=6.4 Hz), 4.95–5.04 (m, 2H), 5.81 (ddt, 1H, *J*=17.1, 10.1, 6.7 Hz), 6.08 (s, 1H), 6.79 (d, 1H, *J*=8.2 Hz), 6.88 (t, 1H, *J*=7.6 Hz), 7.06–7.22 (m, 7H), 7.30–7.36 (m, 4H), 7.57 (d, 1H, *J*=7.6 Hz). ^{13}C NMR 28.45, 30.16, 52.64, 67.44, 111.37, 115.23, 120.66, 127.23, 127.93, 128.66, 128.90, 129.00, 131.67, 135.34, 137.68, 155.05. Anal. Calcd for $C_{24}H_{24}OS_2$: C, 73.43; H, 6.16. Found: C, 73.81; H, 6.21.

Preparation of 2-benzylpent-4-enyl 3,3-bis(phenylthio)-propyl ether (17h). To a flask charged with NaH (55% dispersion in mineral oil, 52 mg, 1.2 mmol) was added a DMF (0.5 ml) solution of **18a** (276 mg, 1 mmol) dropwise at room temperature under argon. After the evolution of hydrogen was terminated, the tosylate prepared from 2-benzylpent-4-en-1-ol (212 mg, 1.2 mmol) and *p*-toluenesulfonyl chloride (252 mg, 1.32 mmol) in DMF (0.4 ml) was added at 0°C and the reaction mixture was warmed up to room temperature. After being stirred for 19 h, the reaction was quenched by addition of water (5 ml) and the organic materials were extracted with ether (10 ml×3). The combined extracts were dried (Na_2SO_4) and condensed under reduced pressure. The residue was purified by PTLC (hexane:AcOEt=98:2) to give **17h** (278 mg, 64%). **17h:** IR (neat) 3062, 2920, 1639, 1583, 1481, 1438, 1117, 1026, 995, 741, 692. ^{1}H NMR 1.87–1.98 (m, 1H), 2.02–2.14 (m, 4H), 2.63 (dd, 1H, *J*=13.6, 7.5 Hz), 2.57 (dd, 1H, *J*=13.6, 6.9 Hz), 3.22 (dd, 2H, *J*=5.5, 1.5 Hz), 3.60 (dt, 2H, *J*=6.8, 1.2 Hz), 4.69 (dt, 1H, *J*=7.0, 2.1 Hz), 4.97–5.04 (m, 2H), 5.72–5.82 (m, 1H), 7.11–7.20 (m, 3H), 7.22–7.32 (m, 8H), 7.44–7.49 (m, 4H). ^{13}C NMR 35.46, 36.20, 37.25, 40.33, 54.30, 67.44, 72.15, 116.37, 125.79, 127.46, 127.48, 128.17, 128.85, 129.22, 132.21, 132.27, 134.28, 136.73, 140.58. Anal. Calcd for $C_{27}H_{30}OS_2$: C, 74.61; H, 6.96. Found: C, 74.73; H, 6.92.

In a similar manner, 1-phenyl-3,3-bis(phenylthio)propyl pent-4-enyl ether (**17i**) was obtained. **17i:** IR (neat) 3059, 2937, 1639, 1583, 1439, 1342, 1097, 912, 737, 690. ^{1}H NMR 1.57–1.65 (m, 2H), 1.89 (dddd, 1H, *J*=14.7, 9.5, 4.3, 1.5 Hz), 2.01–2.11 (m, 2H), 2.36 (dddd, 1H, *J*=14.7, 9.5, 5.0, 1.7 Hz), 3.20 (dt, 1H, *J*=9.2, 6.4 Hz), 3.31 (dt, 1H, *J*=9.2, 6.4 Hz), 4.62–4.68 (m, 2H), 4.89–4.99 (m, 2H), 5.76 (ddt, 1H, *J*=17.1, 10.4, 6.7 Hz), 7.21–7.35 (m, 11H), 7.41–7.46 (m, 4H). ^{13}C NMR 29.10, 30.39, 44.59, 54.10, 68.23, 78.97, 114.63, 126.54, 127.40, 127.59, 127.69, 128.44, 128.85, 132.11, 132.48, 133.96, 134.21, 138.29, 141.79. Anal. Calcd for $C_{26}H_{28}OS_2$: C, 74.24; H, 6.71. Found: C, 74.05; H, 6.78.

Preparation of 2-benzylpent-4-enyl 3,3-bis(phenylthio)-propyl sulfide (25). To an ethanol (2 ml) solution of KOH (85%, 0.28 g, 6 mmol) was added an ethanol (4 ml) solution of S-2-benzylpent-4-enyl thioacetate (**26**) (703 mg, 3 mmol) under argon, and the reaction mixture was stirred for 2.5 h at room temperature. After cooling to 0°C, the crude tosylate **21**, prepared from **18a** (912 mg, 3.3 mmol) and *p*-toluenesulfonyl chloride (692 mg, 3.6 mmol), in ethanol (1 ml) was added and the reaction mixture was gradually warmed up to room temperature. After being stirred overnight, the reaction mixture was diluted with water (10 ml) and the organic materials were extracted with ether (10 ml×3). The combined extracts were dried (Na_2SO_4) and condensed under reduced pressure. The residue was purified by silica gel column chromatography (hexane:AcOEt=10:1) to give **25** (1.21 g, 89%). **25:** IR (neat) 3060, 2916, 1639, 1583, 1481, 1439, 914, 744, 690. ^{1}H NMR 1.86–1.93 (m, 1H), 2.02 (q, 2H, *J*=7.0 Hz), 2.11 (t, 2H, *J*=7.0 Hz), 2.34 (dd, 1H, *J*=12.7, 6.3 Hz), 2.37 (dd, 1H, *J*=12.7, 6.3 Hz), 2.59 (dd, 1H, *J*=13.7, 7.0 Hz), 2.66 (dd, 1H, *J*=13.7, 7.0 Hz), 2.72 (t, 2H, *J*=7.0 Hz), 4.60 (t, 1H, *J*=6.9 Hz), 5.00–5.07 (m, 2H), 5.67–5.77 (m, 1H), 7.12–7.21 (m, 3H), 7.23–7.33 (m, 8H), 7.43–7.49 (m, 4H). ^{13}C NMR 29.97, 35.26, 35.71, 36.95, 39.09, 39.98, 56.66, 117.04, 125.97, 127.80, 128.28, 128.92, 129.21, 132.80, 133.82, 136.11, 140.24. Anal. Calcd for $C_{27}H_{30}S_3$: C, 71.95; H, 6.71. Found: C, 71.95; H, 6.61.

Cyclization of 17 and 25

The reactions of **17** and **25** were performed with a similar procedure described above, and the following cyclic ethers and sulfide were obtained.

2,3-Dihydro-1-benzoxepin (16a). IR (neat) 3024, 2960, 2929, 1488, 1452, 1444, 1248, 1215, 1111, 997, 773, 756, 741. ^{1}H NMR 2.67 (ddt, 2H, *J*=4.9, 4.6, 1.8 Hz), 4.24 (t, 2H, *J*=4.9 Hz), 5.97 (dt, 1H, *J*=11.6, 4.6 Hz), 6.33 (dt, 1H, *J*=11.6, 1.8 Hz), 6.98–7.00 (m, 2H), 7.12 (dt, 1H, *J*=7.6, 1.5 Hz), 7.17 (dd, 1H, *J*=7.6, 1.5 Hz). ^{13}C NMR 34.23, 69.47, 119.86, 122.32, 126.79, 127.87, 128.69, 130.21, 132.67, 158.87. Anal. Calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.90. Found: C, 82.56; H, 7.10.

2,3-Dihydro-9-methoxy-1-benzoxepin (16b). Mp: 69–69.5°C. IR (KBr) 3024, 3014, 2925, 1576, 1487, 1460,

1442, 1263, 1207, 987, 796, 739. ^{1}H NMR 2.68 (ddt, 2H, *J*=4.9, 4.6, 1.8 Hz), 3.86 (s, 3H), 4.31 (t, 2H, *J*=4.9 Hz), 5.98 (dt, 1H, *J*=11.6, 4.6 Hz), 6.30 (dt, 1H, *J*=11.6, 1.8 Hz), 6.74–6.80 (m, 2H), 6.91 (t, 1H, *J*=7.9 Hz). ^{13}C NMR 34.18, 56.03, 70.17, 110.36, 121.83, 124.52, 127.41, 128.51, 130.65, 148.33, 150.32. Anal. Calcd for $C_{11}H_{12}O_2$: C, 74.98; H, 6.86. Found: C, 74.80; H, 6.87.

A mixture of 3,6-dihydro-2*H*-1-benzoxocin (16c) and 3,4-dihydro-2*H*-1-benzoxocin (16d) (82: 18). IR (neat) 3018, 2927, 2871, 1491, 1441, 1286, 1252, 1223, 1103, 1005, 775, 733, 704. ^{1}H NMR 1.69–1.76 (m, 0.36H), 2.30–2.42 (m, 2H), 3.41 (d, 1.64H, *J*=6.7 Hz), 4.05 (t, 1.64H, *J*=5.2 Hz), 4.27 (dt, 0.36H, *J*=5.5, 2.1 Hz), 5.62 (dt, 0.82H, *J*=11.0, 7.6 Hz), 5.76 (ddt, 0.18H, *J*=11.9, 7.0, 1.8 Hz), 5.91 (ddt, 0.82H, *J*=11.0, 6.7, 0.9 Hz), 6.33 (d, 0.18H, *J*=11.9 Hz), 6.95–7.05 (m, 2H), 7.06–7.11 (m, 0.36H), 7.11–7.22 (m, 1.64H). ^{13}C NMR (**16c**): 27.86, 32.34, 73.59, 122.63, 124.17, 126.44, 127.91, 129.39, 133.10, 136.85, 157.42. Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.62; H, 7.53.

3,4-Dihydro-2*H*-1-benzoxocin (16d). IR (neat) 3022, 2945, 1641, 1495, 1257, 1211, 1065, 752. ^{1}H NMR 1.68–1.76 (m, 2H), 2.34–2.42 (m, 2H), 4.27 (t, 2H, *J*=5.7 Hz), 5.75 (dt, 1H, *J*=11.6, 7.0 Hz), 6.35 (d, 1H, *J*=11.6 Hz), 6.96–7.01 (m, 2H), 7.06–7.11 (m, 1H), 7.15–7.21 (m, 1H). ^{13}C NMR 23.79, 26.54, 71.11, 121.89, 122.57, 127.36, 128.35, 128.69, 130.08, 131.27, 156.11. Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.38; H, 7.75.

4-Methyl-2,3-dihydro-1-benzoxepin (16e). IR (neat) 3064, 2968, 1657, 1491, 1263, 1221, 1057, 756. ^{1}H NMR 1.95 (s, 3H), 2.59 (t, 2H, *J*=4.9 Hz), 4.21 (t, 2H, *J*=4.9 Hz), 6.14 (s, 1H), 6.91 (d, 1H, *J*=7.6 Hz), 6.94 (dt, 1H, *J*=7.3, 1.2 Hz), 7.05 (dt, 1H, *J*=7.6, 1.8 Hz), 7.10 (dd, 1H, *J*=7.6, 1.5 Hz). ^{13}C NMR 26.42, 38.63, 68.84, 119.65, 122.30, 124.90, 126.64, 126.93, 132.24, 139.00, 158.68. Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.44; H, 7.52.

4-Ethyl-2,3-dihydro-1-benzoxepin (16f). IR (neat) 3064, 2964, 1651, 1570, 1489, 1263, 1063, 1026, 889, 864, 756. ^{1}H NMR 1.11 (t, 3H, *J*=7.6 Hz), 2.21 (q, 2H, *J*=7.6 Hz), 2.60 (t, 2H, *J*=4.9 Hz), 4.22 (t, 2H, *J*=4.9 Hz), 6.13 (s, 1H), 6.88–6.96 (m, 2H), 7.05 (dt, 1H, *J*=7.6, 1.5 Hz), 7.12 (d, 1H, *J*=7.6 Hz). ^{13}C NMR 12.99, 33.03, 36.83, 68.81, 119.58, 122.18, 123.47, 126.46, 126.96, 132.49, 144.43, 158.53. Anal. Calcd for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.69; H, 8.19.

3-Benzyl-3,4,7,8-tetrahydro-2*H*-oxocin (16g). IR (neat) 3024, 2929, 1645, 1454, 1281, 1117, 748, 698. ^{1}H NMR 1.94–2.04 (m, 2H), 2.08–2.26 (m, 2H), 2.29–2.40 (m, 1H), 2.54 (dd, 1H, *J*=13.4, 7.9 Hz), 2.62 (dd, 1H, *J*=13.4, 7.3 Hz), 3.47 (dd, 1H, *J*=11.9, 5.5 Hz), 3.57–3.65 (m, 2H), 3.68–3.77 (m, 1H), 5.73 (dt, 1H, *J*=10.4, 7.9 Hz), 5.85 (dt, 1H, *J*=10.4, 7,9 Hz), 7.15–7.21 (m, 3H), 7.25–7.30 (m, 2H). ^{13}C NMR 28.61, 29.38, 38.19, 43.23, 72.04, 73.25, 125.84, 128.28, 129.04, 129.41, 130.15, 140.89. Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.95; H, 9.20.

A mixture of 8-phenyl-3,4,7,8-tetrahydro-2*H*-oxocin (16h) and 2-phenyl-3,4,7,8-tetrahydro-2*H*-oxocin (16i) (55: 45). IR (neat) 3020, 2933, 1645, 1454, 1273, 1097, 1028, 754, 721, 698. ^{1}H NMR 1.45–1.55 (m, 0.55H), 1.73–1.90 (m, 0.90H), 1.94–2.03 (m, 0.55H), 2.08–2.22 (m, 1.45H), 2.38–2.45 (m, 0.55H), 2.48–2.68 (m, 2H), 3.46 (ddd, 0.55H, *J*=12.2, 9.8, 2.4 Hz), 3.58 (dt, 0.45H, *J*=11.8, 3.4 Hz), 3.97–4.06 (m, 1H), 4.38–4.46 (m, 1H), 5.76–5.94 (m, 2H), 7.12–7.38 (m, 5H). ^{13}C NMR 23.62, 24.05, 29.43, 30.60, 35.48, 37.92, 68.73, 70.82, 81.31, 82.73, 125.44, 125.91, 126.78, 127.05, 127.53 128.16, 128.18, 128.87, 131.31, 131.63, 143.53, 144.52. Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.82; H, 8.75.

3-Benzyl-3,4,7,8-tetrahydro-2*H*-thiacin (24). IR (neat) 3026, 2925, 1653, 1497, 1456, 1415, 1342, 1273, 1030, 748, 725, 698. ^{1}H NMR 2.06–2.15 (m, 1H), 2.15–2.26 (m, 1H), 2.34–2.44 (m, 1H), 2.44–2.72 (m, 8H), 5.60 (dt, 1H, *J*=10.4, 7.6 Hz), 5.74 (dt, 1H, *J*=10.4, 7.6 Hz), 7.12–7.22 (m, 3H), 7.25–7.31 (m, 2H). ^{13}C NMR 29.59, 30.39, 33.98, 35.18, 40.18, 43.33, 125.90, 128.31, 129.10, 130.03, 130.16, 140.75. Anal. Calcd for $C_{14}H_{18}S$: C, 77.01; H, 8.31. Found: C, 76.87; H, 8.25.

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References

1. (a) Takeda, T.; Ando, K.; Mamada, A.; Fujiwara, T. *Chem. Lett.* **1985**, 1149–1152. (b) Takeda, T.; Oshima, H.; Inoue, M.; Togo, A.; Fujiwara, T. *Chem. Lett.* **1987**, 1345–1348. (c) Takeda, T.; Ogawa, S.; Ohta, N.; Fujiwara, T. *Chem. Lett.* **1987**, 1967–1970. (d) Yamaguchi, J.; Tamada, Y.; Takeda, T. *Bull. Chem. Soc. Jpn* **1993**, *66*, 607–612. (e) Takeda, T.; Miura, I.; Horikawa, Y.; Fujiwara, T. *Tetrahedron Lett.* **1995**, *36*, 1495–1498. (f) Horikawa, Y.; Nomura, T.; Watanabe, M.; Miura, I.; Fujiwara, T.; Takeda, T. *Tetrahedron Lett.* **1995**, *36*, 8835–8838.

2. Horikawa, Y.; Nomura, T.; Watanabe, M.; Fujiwara, T.; Takeda, T. *J. Org. Chem.* **1997**, *62*, 3678–3682.

3. Dörwalt, F. Z. *Metal Carbenes in Organic Synthesis*, Wiley–VCH: Weinheim, 1999.

4. (a) Horikawa, Y.; Watanabe, M.; Fujiwara, T.; Takeda, T. *J. Am. Chem. Soc.* **1997**, *119*, 1127–1128. (b) Takeda, T.; Watanabe, M.; Nozaki, N.; Fujiwara, T. *Chem. Lett.* **1998**, 115–116. (c) Rahim, M. A.; Taguchi, H.; Watanabe, M.; Fujiwara, T.; Takeda, T. *Tetrahedron Lett.* **1998**, 39, 2153–2156. (d) Takeda, T.; Watanabe, M.; Rahim, M. A.; Fujiwara, T. *Tetrahedron Lett.* **1998**, *39*, 3753–3756. (e) Fujiwara, T.; Iwasaki, N.; Takeda, T. *Chem. Lett.* **1998**, 741–742. (f) Rahim, M. A.; Fujiwara, T.; Takeda, T. *Synlett* **1999**, 1029–1032.

5. Takeda, T.; Shimokawa, H.; Miyachi, Y.; Fujiwara, T. *Chem. Commun.* **1997**, 1055–1056.

6. Fujiwara, T.; Takamori, M.; Takeda, T. *Chem. Commun.* **1998**, 51–52.

7. (a) Schuster, M.; Blechert, S. *Angew. Chem. Int. Ed. Engl.* **1997**,

36, 2036–2056. (b) Grubbs, R. H.; Chang, S. *Tetrahedron* **1998**, *54*, 4413–4450.
8. (a) Fu, G. C.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 9856–9857. (b) Miller, S. J.; Kim, S.-H.; Chen, Z.-R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 2108–2109. (c) Grubbs, R. H.; Miller, S. J.; Fu, G. C. *Acc. Chem. Rec.* **1995**, *28*, 446–452.
9. (a) Fu, G. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**,*114*, 5426–5427. (b) Fu, G. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 7324–7325. (c) Fu, G. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 3800–3801. (d) Fujimura, O.; Fu, G. C.; Grubbs, R. H. *J. Org. Chem.* **1994**, *59*, 4029–4031.
10. (a) Tsuji, J; Hashiguchi, S. *Tetrahedron Lett.* **1980**, *21*, 2955–2958. (b) Tsuji, J.; Hashiguchi, S. *J. Organomet. Chem.* **1981**, *218*, 69–80. (c) Couturier, J.-L.; Tanaka, K.; Leconte, M.; Basset, J.-M.; Ollivier, J. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 112–115. (d) Leconte, M.; Jourdan, I.; Pagano, S.; Lefebvre, F.; Basset, J.-M. *J. Chem. Soc., Chem. Commun.* **1995**, 857–858.
11. (a) Warwel, S.; Kätker, H.; Rauenbusch, C. *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 702–703. (b) Junga, H.; Blechert, S. *Tetrahedron Lett.* **1993**, *34*, 3731–3733. (c) Toreki, R.; Schrock, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 2448–2449. (d) Toreki, R.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1992**, *114*, 3367–3380.
12. Nicolaou, K. C.; Postema, M. H. D.; Claiborne, C. F. *J. Am. Chem. Soc.* **1996**, *118*, 1565–1566.
13. Preliminary communication: Fujiwara, T.; Takeda, T. *Synlett* **1999** 354–356.
14. The olefination product, 1,1-diphenylpropene, was also produced in 22% yield when benzophenone (1.5 equiv.) was heated with the organotitanium species formed from the ether **17a**.
15. Rahim, M. A.; Fujiwara, T.; Takeda, T. *Tetrahedron* **2000**, *56*, 763–770.
16. Tarbell, D. S. *Org. React.* **1944**, *2*, 27.
17. Takeda, T.; Taguchi, H.; Fujiwara, T. *Tetrahedron Lett.* **2000**, *41*, 65–68.
18. Takeda, T.; Nozaki, N.; Fujiwara, T. *Tetrahedron Lett.* **1998**, *39*, 3533–3536.
19. Takeda, T.; Nozaki, N.; Saeki, N.; Fujiwara, T. *Tetrahedron Lett.* **1999**, *40*, 5353–5356.