Convenient Synthesis of Allylic Sulfides and Application to Allylic Carbon–Carbon Bond Formation[1)]

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Allylic sulfides were synthesized from allylic alcohols 1 using *S,S'*-bis(1-phenyl-1*H*-tetrazol-5-yl) dithiocarbonate (2) by means of a single-step reaction. The allylic sulfides were coupled with a Grignard reagent or carbanion in the presence of a catalytic amount of copper(I) bromide or palladium(0).

Keywords *S,S'*-bis(1-phenyl-1*H*-tetrazol-5-yl) dithiocarbonate; carbon–carbon bond formation; cross-coupling reaction; allylic sulfide; copper(I) bromide; palladium(0)

The cross-coupling reaction involving allylic sulfide is among the most important methods of carbon–carbon bond formation and various regioselective reactions are catalyzed by transition metal complexes.[2-5)] For example, some cross-coupling reactions of allylic sulfides and Grignard reagents have been reported.[4-7)] In most cases, allylic sulfides are prepared by the reactions of allylic halides and thiolate, allylic alcohols and tributylphosphine-disulfides, or allylic carbonates and alkylthiotrimethylsilane in the presence of a catalyst such as palladium.[8)]

Recently, we reported on the use of the coupling reagent *S,S'*-bis(1-phenyl-1*H*-tetrazol-5-yl) dithiocarbonate (**2**) to generate esters, macrolides, and peptides from carboxylic acids and nucleophiles.[9,10)]

In this report, we would like to describe out observations on the utility of the reagent (**2**) for single-step syntheses of allylic sulfides from allylic alcohols, and we show that allylic sulfides can undergo cross-coupling reactions with nucleophiles. A solution of an allylic alcohol and **2** in acetonitrile or acetone was stirred at room temperature in the presence of tertiary amine to afford allylic sulfides, **4** and/or **5**, with liberation of carbon dioxide. The possible reaction mechanism providing **4** and/or **5** is proposed to be as follows. The hydroxy group of the allylic alcohol attacks the carbonyl group of the reagent (**2**) to give intermediate **3** with liberation of 1-phenyltetrazol-5-thiol (**6**). The sulfinyl anion arising from eliminated 1-phenyltetrazol-5-thiol (**6**) attacks the α-carbon of **3** to generate **4**, or the γ-carbon to generate **5** with liberation of carbon dioxide (Chart 1).

The results obtained starting with various allylic alcohols are summarized in Table I.

As shown in Table I, in the case of primary allylic alcohols, acetonitrile solutions of branched allylic alcohols **1** and **2** with triethylamine as a base were stirred to afford allylic sulfides **4** in high yields (runs 1—5). The allylic sulfides **4** were produced similarly in high yields from γ-aromatic-substituted and cyclic allylic alcohols (runs 6—8). The β-carbon configurations of geranyl (run 3) and neryl (run 4) were maintained in these reactions. Therefore, these reactions probably proceeded regioselectively (runs 1—8).

In the case of secondary allylic alcohols, the reaction of **2** and 3-buten-2-ol produced two products, **4i** and **5i** (runs 9—11). The structures of **4i** and **5i** were determined by the proton nuclear magnetic resonance (^{1}H-NMR) analysis. The chemical shift due to $-C\underline{H}=CH_2$ (1H) of **4i** was 5.93 ppm and the *J* values were 7.0, 10.5, and 17.0 Hz. The chemical shift for $-C\underline{H}_2S$ (2H) of **5i** was 3.99 ppm and the $J_{1',2'}$ value was 7.5 Hz. The ratio of **4i** to **5i** was determined from their integration curves in the NMR spectra. Thus, the ratio at room temperature was 2.0 : 1.0 whereas the ratio under reflux was 1.0 : 1.1 in acetonitrile containing triethylamine. Furthermore, using 4-dimethylaminopyridine (DMAP) as a basic catalyst, the ratio of **4i** to **5i** was 4.0 : 1.0 in acetone (run 11). The reaction of cyclic allylic alcohols also proceeded to give sulfides in reasonable yields (runs 12 and 13).

In the case of a tertiary allylic alcohol such as linalool, two products, **4l** and **5l**, were obtained (runs 14 and 15). The structures of **4l** and **5l** were determined by ^{1}H-NMR. The chemical shift due to $-C\underline{H}=CH_2$ (1H) of **4l** was 6.00 ppm and the *J* values were 6.0 and 10.0 Hz. The chemical shift due to $-C\underline{H}_2S-$ (2H) of **5l** was 4.07 ppm and the $J_{1',2'}$ value was 8.0 Hz. The ratios of **4l** to **5l** were determined from their integration curves in the NMR

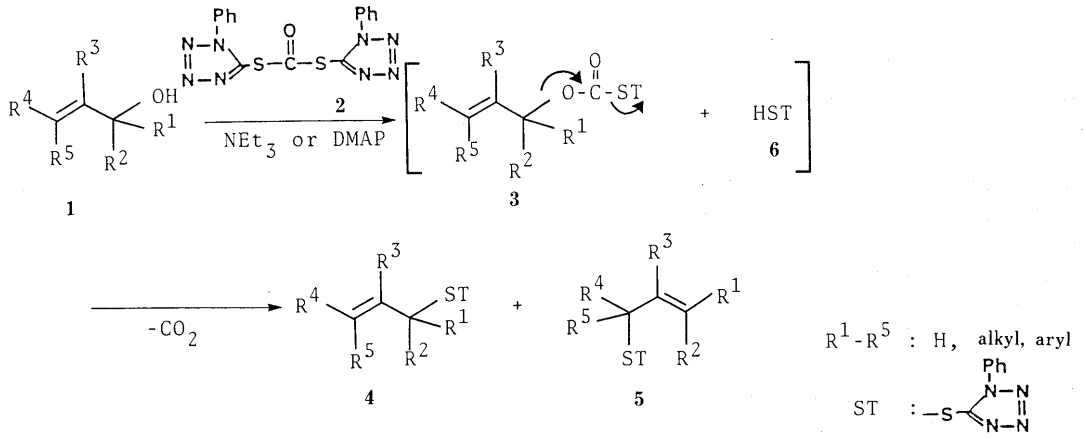
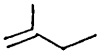
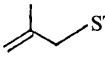
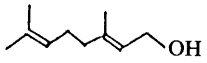
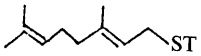
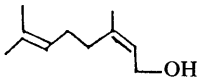
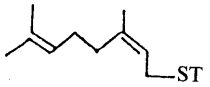
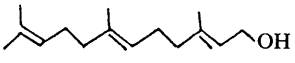
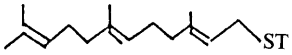
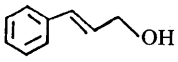
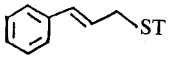
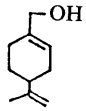
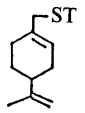
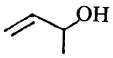
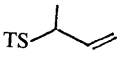
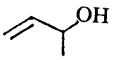
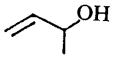
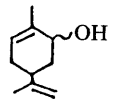
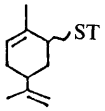
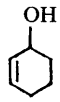
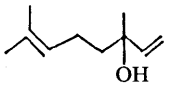
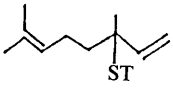
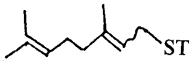
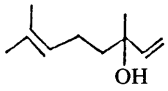


Chart 1

TABLE I. Reaction of Allylic Alcohols **1** with Reagent (**2**)

Run	Alcohol	Time (h)	Base/solv.	Yield (%)	Product[a]	
1		24	NEt_3/CH_3CN	83		**4a**
2		24	NEt_3/CH_3CN	91		**4b**
3		24	NEt_3/CH_3CN	89		**4c**
4		24	NEt_3/CH_3CN	91		**4d**
5		24	NEt_3/CH_3CN	89		**4e**
6		24	NEt_3/CH_3CN	87		**4f**
7		24	NEt_3/CH_3CN	89		**4g**
8		24	NEt_3/CH_3CN	98		**4h**
9		24	NEt_3/CH_3CN (r.t.)	71	 **4i**  **4i**:**5i** = 2.0:1.0	**5i**
10		6	NEt_3/CH_3CN (reflux)	60	**4i**:**5i** = 1.0:1.1	
11		24	DMAP/acetone	63	**4i**:**5i** = 4.0:1.0	
12		24	DMAP/acetone	57		**4j**
13		24	DMAP/acetone	73		**4k**
14		24[b]	DMAP/acetone	38	 **4l**  **4l**:**5l** = 1.0:23.8	**5l**
15		1[b]	DMAP/acetone	26	**4l**:**5l** = 1.0:13.7	

a) Ph
ST = –S– (N–N, N–N). b) The starting alcohols of runs 14 and 15 were recovered in 40 and 60% yields, respectively. r.t. = room temperature.

spectra. When the reaction was allowed to proceed overnight, the ratio of **4l** to **5l** was 1.0:23.8. When the reaction time was reduced to 1 h, the ratio changed to 1.0:13.7.

In short, the reactions of primary allylic alcohols afforded allylic sulfides in high yields, whereas the yields of allylic sulfides from secondary and tertiary allylic alcohols decreased owing to steric hindrance.

The results obtained from allylic alcohols having arylmethyl and propargyl alcohol moieties are summarized in Table II.

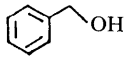
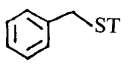
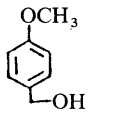
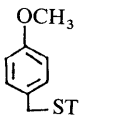
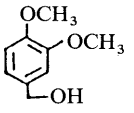
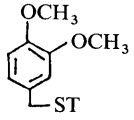
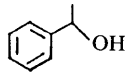
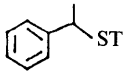
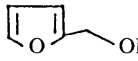
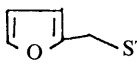
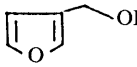
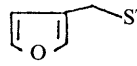
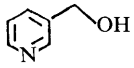
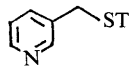
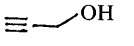
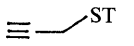
In the case of primary benzylic alcohols, a solution of **2** and a benzylic alcohol with triethylamine as a base in acetonitrile was stirred to afford benzylic sulfides in high yield (runs 16 and 17). The yield of the corresponding sulfide from a secondary benzylic alcohol was slightly decreased in the same conditions (run 19).

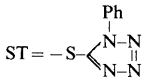
Arylmethyl alcohols, furfuryl and pyridylmethyl alcohols, reacted with **2** under the same conditions to afford the corresponding sulfides in good yields (runs 21 and 22). When a nonpolar solvent such as benzene was used, the corresponding sulfides were obtained from benzyl and furfuryl alcohols in similarly good yields (runs 18 and 20).

In the case of propargyl alcohol having a triple bond, the reaction proceeded smoothly to give the desired product in good yield (run 23).

The yields of sulfides from arylmethyl alcohols are good, as in the cases of allylic alcohols.

TABLE II. Reaction of Benzylic Alcohols **1** and Propargyl Alcohol with Reagent (**2**)

Run	Alcohol	Time (h)	Base/solv.	Yield (%)	Product[a]	
16		24	NEt_3/CH_3CN	99		**4m**
17		24	NEt_3/CH_3CN	84		**4n**
18		3	NEt_3/benzene[b]	99		**4o**
19		24	NEt_3/CH_3CN	56		**4p**
20		3	NEt_3/benzene[b]	85		**4q**
21		24	NEt_3/CH_3CN	95		**4r**
22		24	NEt_3/CH_3CN	95		**4s**
23		24	NEt_3/CH_3CN	70		**4t**

a) 

b) The solvent of run 18 and run 19 in page 4106 of Ref. 1. should be corrected from CH_3CN to benzene.

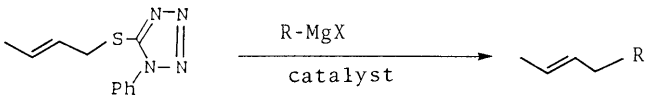


Chart 2

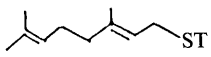
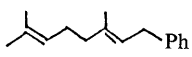
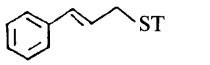
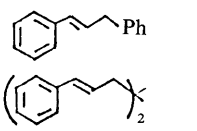
Thus, now we are able readily to prepare allylic sulfides. We then tried to use these sulfides for the formation of carbon–carbon bonds. To this end, the coupling reaction was carried out using sulfides **4** and carbon-nucleophiles in the presence of a catalyst such as CuBr or palladium(0).

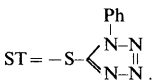
In the case of the CuBr-catalyzed Grignard reaction, we propose the reaction process shown in Chart 2, and the results of the coupling reactions are summarized in Table III.

The reaction of geranyl sulfide and phenylmagnesium bromide in the presence of a catalytic amount of CuBr (0.11 eq) gave a cross-coupling product (**6**) together with biphenyl as a homo-coupling product (run 24). When cinnamyl sulfide was used, a cross-coupling product (**7**) and a small amount of dimer (**8**) were obtained under the same conditions in the ratio of **7**:**8**=6.2:1.0 (run 25). In the case of a secondary allylic sulfide, **4k**, the coupling reaction proceeded under the same conditions to afford the cross-coupling product (**9**) together with biphenyl (run 26). The yields of these cross-coupling products were good to excellent and the yields from primary sulfides (runs 24 and 25) were higher than that from a secondary sulfide (run 26).

It is known that palladium in the presence of the phosphine ligand catalyzes the reaction of allylic derivatives and carbanion[11] or sulfinate[12] to give the coupling products. The reaction process of allylic sulfide and

TABLE III. Grignard Reaction of Allylic Sulfides **4**

Run	Allylic sulfide[a]	Yield (%)	Product	
24		77		**6**
25		92	 **7**:**8**=6.2:1.0	**7** **8**
26		69		**9**

a) 

nucleophile with palladium-phosphine as a catalyst is shown in Chart 3 and the results of the coupling reactions are summarized in Table IV.

Now we would like to describe in detail the reactions of primary allylic sulfides and soft nucleophiles in the presence of catalysts (see Table VI). A mixture of geranyl sulfide and sodium methyl phenylsulfonylacetate in the presence of a catalytic amount of $Pd(PPh_3)_4$ (0.038 eq) was refluxed in acetonitrile, resulting in regioselective alkylation (run 27). In the case of sodium *p*-tolylsulfinate as a nucleophile under the same conditions, two products (**11** and **12**) were obtained in the ratio of **11**:**12**=1.0:4.6. The ratio of 11 to 12 was

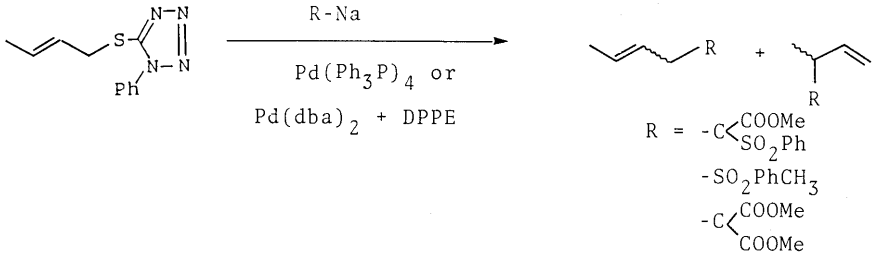
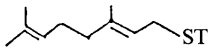
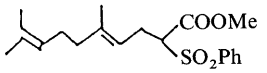
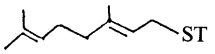
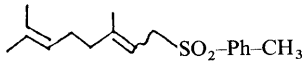
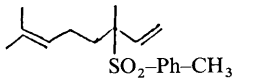
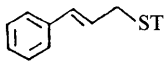
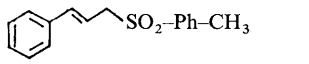
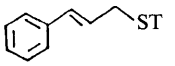
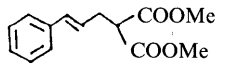
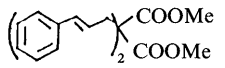
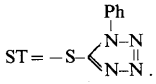


Chart 3

TABLE IV. Coupling-Reaction of Allylic Sulfides **4** with Nucleophiles

Run	Allylic sulfide[a)]	Nucleophile	Catalyst	Yield (%)	Product	
27		NaC(COOMe)(SO$_2$Ph)	Pd(Ph$_3$P)$_4$	69		**10**
28		NaSO$_2$–Ph–CH$_3$ (*p*)	Pd(Ph$_3$P)$_4$	66		**11**
						**12**
					11:**12** = 1.0:4.6	
29		NaSO$_2$–Ph–CH$_3$ (*p*)	Pd(Ph$_3$P)$_4$	96		**13**
30		NaC(COOMe)(COOMe)	Pd(dba)$_2$ + DPPE	91		**14**
						**15**
					14:**15** = 10.0:1.0	
31		NaSO$_2$–Ph–CH$_3$ (*p*)	Pd(Ph$_3$P)$_4$	75		**16**

a) 

different from that in Kotake *et al.*'s report[12] where geranyl acetate and sodium *p*-tolylsulfinate in the presence of Pd(Ph$_3$P)$_4$ were used, but we have no reasonable explanation for this discrepancy at present (run 28). A mixture of cinnamyl sulfide and sodium *p*-tolylsulfinate afforded the coupling product (**13**) under the same conditions (run 29). A mixture of cinnamyl sulfide and sodium malonate in the presence of a catalytic amount of palladium dibenzylideneacetone (Pd(dba)$_2$) (0.01 eq) and diphenylphosphino ethane (DPPE) (0.025 eq) was refluxed in tetrahydrofuran (THF) to afford a coupling product (**14**) and the side-reaction product (**15**) in the ratio of **14**:**15** = 10.0:1.0 (run 30). Furthermore, 2-cyclohexyl sulfide as a secondary sulfide and sodium *p*-tolylsulfinate reacted in the presence of a catalytic amount of Pd(Ph$_3$P)$_4$ under the same conditions to afford the coupling product (**16**) in satisfactory yield (75%) (run 31).

Finally, the synthesis of dendrolasin (**17**), which had been isolated from mendibular gland of the ant *Lasius* (*Dendrolasius*) *fulginosus* LATR,[13] was achieved. Geranyl sulfide and 3-furylmethylmagnesium bromide[14] as the Grignard reagent reacted in the presence of a catalytic amount of CuBr (0.11 eq) at −78 °C to furnish dendrolasin

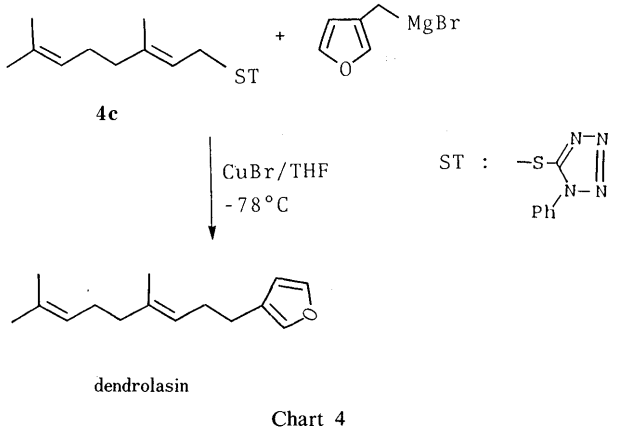


Chart 4

regioselectively in 86% yield (Chart 4).

In conclusion, **2** was found to be a versatile reagent for the syntheses of allylic sulfides of type **4**, and was so stable that it could be stored for several months at room temperature. Furthermore, the allylic sulfides **4** underwent carbon–carbon bond formation in good yield. By the use

of **4c**, the natural product dendrolasin was conveniently and regioselectively synthesized in good yield.

Experimental

Melting points were measured with a Yamato melting point apparatus and are uncorrected. Thin-layer chromatography (TLC) was performed on Silica gel GE254 (Merck) plates, and the spots were detected under ultraviolet (UV) light irradiation and by spraying with 5% aqueous sulfuric acid solution. Field desorption mass spectra (FD-MS), fast atom bombardment mass spectra (FAB-MS), and infrared (IR) spectra were measured with JEOL JMS-DX 300, JMS-3100, and JASCO IR-A2 instruments, respectively. The NMR spectra were measured in chloroform-*d* ($CDCl_3$) except for run 27 (in benzene-d_6) with Varian T-60, EM-390, XL-300, and XL-400 spectrometers.

1-Phenyl-5-(2-propenylthio)-1*H*-tetrazole (4a) (Run 1) A typical experimental procedure was as follows. A solution of triethylamine (191 mg, 1.0 mmol) in acetonitrile (0.5 ml) was added to a solution of 2-propenol (58 mg, 1.0 mmol) and *S*,*S*′-bis(1-phenyl-1*H*-tetrazol-5-yl) dithiocarbonate (**2**) (134 mg, 1.1 mol) in acetonitrile (10 ml). The mixture was stirred at room temperature for 24 h, then evaporated and ethyl acetate was added to the residue. The organic layer was washed with 4% $NaHCO_3$, 0.5 N HCl, and saturated brine, dried over Na_2SO_4, and evaporated. The residue was subjected to TLC on silica-gel (benzene). Yield 83%, oil. MS *m/z*: 218 (M^+). *Anal.* Calcd for $C_{10}H_{10}N_4S$: C, 55.02; H, 4.61; N, 25.66. Found: C, 54.87; H, 4.63; N, 25.63. IR ν_{max}^{neat} cm^{-1}: 3100, 1600. ^{1}H-NMR (60 MHz) δ: 4.03 (2H, d, J=6.0 Hz, $-CH_2S-$), 5.08—6.33 (3H, m, $CH_2=CH-$), 7.53 (5H, s, Ph).

5-(2-Methyl-2-propenylthio)-1-phenyl-1*H*-tetrazole (4b) (Run 2) Yield 91%, oil. MS *m/z*: 232 (M^+). *Anal.* Calcd for $C_{11}H_{12}N_4S$: C, 56.87; H, 5.20; N, 24.11. Found: C, 57.15; H, 5.25; N, 24.19. IR ν_{max}^{neat} cm^{-1}: 3080, 2950, 1600. ^{1}H-NMR (60 MHz) δ: 1.80 (3H, s, $-CH_3$), 4.03 (2H, s, $-CH_2S-$), 4.95 (2H, d, J=9.0 Hz, $CH_2=$), 7.50 (5H, s, Ph).

5-[(*E*)-3,7-Dimethyl-2,6-octadienylthio]-1-phenyl-1*H*-tetrazole (4c) (Run 3) Yield 89%, oil. MS *m/z*: 314 (M^+). *Anal.* Calcd for $C_{17}H_{22}N_4S$: C, 64.93; H, 7.05; N, 17.81. Found: C, 64.97; H, 7.06; N, 18.00. IR ν_{max}^{neat} cm^{-1}: 2920, 1600. ^{1}H-NMR (400 Hz) δ: 1.58, 1.65 (6H, s, $(CH_3)_2C=$), 1.74 (3H, s, $-CH_2C(C\underline{H}_3)=$), 1.98—2.11 (4H, m, $-CH_2CH_2-$), 4.07 (2H, d, J=8.0 Hz, $-CH_2S-$), 5.01—5.06 (1H, m, $C(CH_3)_2=C\underline{H}-$), 5.37—5.43 (1H, m, $=C\underline{H}CH_2S-$), 7.50—7.61 (5H, m, Ph).

5-[(*Z*)-3,7-Dimethyl-2,6-octadienylthio]-1-phenyl-1*H*-tetrazole (4d) (Run 4) Yield 91%, oil. MS *m/z*: 314 (M^+). *Anal.* Calcd for $C_{17}H_{22}N_4S$: C, 64.93; H, 7.05; N, 17.81. Found: C, 64.82; H, 7.01; N, 17.54. IR ν_{max}^{neat} cm^{-1}: 2960, 1660, 1600. ^{1}H-NMR (300 MHz) δ: 1.58, 1.65, 1.72 (9H, s, $-CH_3\times3$), 2.00—2.20 (4H, m, $-CH_2CH_2-$), 4.05 (2H, dd, J=0.7, 8.0 Hz, $-CH_2S-$), 5.09 (1H, t, J=8.0 Hz, $(CH_3)_2C=C\underline{H}-$), 5.42 (1H, t, J=8.0 Hz, $=C\underline{H}CH_2S-$), 7.30—7.70 (5H, m, Ph).

1-Phenyl-5-[(2*E*,6*E*)-3,7,11-trimethyl-2,6,10-dodecatrienylthio]-1*H*-tetrazole (4e) (Run 5) Yield 89%, oil. MS *m/z*: 382 (M^+). *Anal.* Calcd for $C_{22}H_{30}N_4S$: C, 69.07; H, 7.90; N, 14.64. Found: C, 69.04; H, 7.93; N, 14.62. IR ν_{max}^{neat} cm^{-1}: 2950, 1600. ^{1}H-NMR (400 MHz) δ: 1.56—1.77 (12H, s, $-CH_3\times4$), 1.92—2.20 (8H, br, $-CH_2CH_2-\times2$), 4.07 (2H, d, J=8.0 Hz, $-CH_2S-$), 5.02—5.04 (2H, m, $C(CH_3)_2=C\underline{H}-$, $-CH_2C(CH_3)=C\underline{H}-CH_2CH_2-$), 5.37—5.46 (1H, m, $=C\underline{H}CH_2S-$), 7.49—7.63 (5H, m, Ph).

1-Phenyl-5-(3-phenyl-2-propenylthio)-1*H*-tetrazole (4f) (Run 6) Yield 87%, mp 56—57 °C. MS *m/z*: 294 (M^+). *Anal.* Calcd for $C_{16}H_{14}N_4S$: C, 65.28; H, 4.79; N, 19.03. Found: C, 65.31; H, 4.80; N, 19.22. IR ν_{max}^{neat} cm^{-1}: 3030, 1595. ^{1}H-NMR (60 MHz) δ: 4.19 (2H, d, J=7.0 Hz, $-CH_2S-$), 6.03—6.88 (2H, m, $-CH=CH-$), 7.30, 7.53 (10H, s, Ph×2).

5-[(1*R*,5*R*)-2-(6,6-Dimethylbicyclo[3.3.1]hept-2-enyl)methylthio]-1-phenyl-1*H*-tetrazole (5-(−)-Myrtenylthio-1-phenyl-1*H*-tetrazole) (4g) (Run 7) Yield 89%, oil. MS *m/z*: 312 (M^+). *Anal.* Calcd for $C_{17}H_{20}N_4S$: C, 65.29; H, 6.45; 17.92. Found: C, 65.35; H, 6.45; N, 17.93. IR ν_{max}^{neat} cm^{-1}: 2910, 1600. ^{1}H-NMR (90 MHz) δ: 0.78, 1.29 (6H, s, $-CH_3\times2$), 1.17 (1H, t, J=8.4 Hz, $-CH_2C\underline{H}C=$), 1.87—2.52 (5H, m, $-C\underline{H}_2C\underline{H}C\underline{H}_2CH-$), 4.03 (2H, s, $-CH_2S-$), 5.67 (1H, m, $=CH-$), 7.57 (5H, m, Ph).

5-[(*S*)-(4-Isopropenyl-1-cyclohexenyl)methylthio]-1-phenyl-1*H*-tetrazole (5-[(−)-Perillylthio]-1-phenyl-1*H*-tetrazole) (4h) (Run 8) Yield 98%, mp 89—90 °C. MS *m/z*: 312 (M^+). *Anal.* Calcd for $C_{17}H_{20}N_4S$: C, 65.35; H, 6.45; N, 17.93. Found: C, 65.11; H, 6.39; N, 17.80. IR ν_{max}^{neat} cm^{-1}: 2920, 1650, 1600. ^{1}H-NMR (90 MHz) δ: 1.22—1.66 (2H, m, $-C\underline{H}C\underline{H}_2CH_2-$), 1.70 (3H, s, $-CH_3$), 1.87—2.39 (5H, m, $-CH_2C\underline{H}C\underline{H}_2C\underline{H}_2-$), 4.03 (2H, br s, $-CH_2S-$), 4.72 (2H, dd, J=0.9, 1.2 Hz, $-C=C\underline{H}_2$), 5.87 (1H, m, $=CH-$), 7.57 (5H, s, Ph).

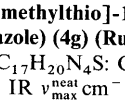
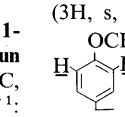
5-(1-Methyl-2-propenylthio)-1-phenyl-1*H*-tetrazole (4i) and 5-(2-Butenylthio)-1-phenyl-1*H*-tetrazole (5i) (Runs 9—11) The reaction was carried out by the same procedure as used in the typical experiment except that the reaction mixture was refluxed for 6 h in run 10. The reaction was carried out by the same procedure as used in the typical experiment except that acetone was used as the reaction solvent and DMAP (122 mg, 1 mmol) as the base in run 11. Yields were 71% (run 9), 60% (run 10), and 63% (run 11). Ratios of **4i** to **5i** were 2.0 : 1.0 (run 9), 1.0 : 1.1 (run 10), and 4.0 : 1.0 (run 11). **4i**: Oil. MS *m/z*: 232 (M^+). *Anal.* Calcd for $C_{11}H_{12}N_4S$: C, 56.87; H, 5.20; N, 24.11. Found: C, 57.08; H, 5.21; N, 24.09. IR ν_{max}^{neat} cm^{-1}: 3100, 2800, 1600. ^{1}H-NMR (400 MHz) δ: 1.59 (3H, d, J=7.0 Hz, $-C(C\underline{H})_3CH=$), 4.63 (1H, dq, J=7.0, 7.0 Hz, $-SC\underline{H}(CH_3)-$), 5.13, 5.33 (2H, d×2, J=10.5, 17.0 Hz, $-CH=C\underline{H}_2$), 5.93 (2H, ddd, J=7.0, 10.5, 17.0 Hz, $-CH=C\underline{H}_2$), 7.56 (5H, br s, Ph). **5i**: Oil. MS *m/z*: 232 (M^+). *Anal.* Calcd for $C_{11}H_{12}N_4S$: C, 56.87; H, 5.20; N, 24.11. Found: C, 57.02; H, 5.23; N, 24.13. IR ν_{max}^{neat} cm^{-1}: 3040, 2925, 1600. ^{1}H-NMR (400 MHz) δ: 1.68 (3H, br d, J=7.5 Hz, $-CH_3$), 3.99 (2H, br d, J=7.5 Hz, $-CH_2S-$), 5.63 (1H, m, $=C\underline{H}CH_2S-$), 5.84 (1H, dq, J=6.5, 13.0 Hz, $CH_3C\underline{H}=$), 7.56 (5H, m, Ph).

5-[(−)-5-Isopropenyl-2-methyl-2-cyclohexenylthio]-1-phenyl-1*H*-tetrazole (5-[(−)Carveylthio]-1-phenyl-1*H*-tetrazole) (4j) (Run 12) The reaction was carried out by the same procedure as used in the typical experiment except that acetone was used as the reaction solvent and DMAP as the base in run 12. Yield 57%, oil. MS *m/z*: 312 (M^+). *Anal.* Calcd for $C_{13}H_{20}N_4S$: C, 65.35; H, 6.45; N, 17.93. Found: C, 65.64; H, 6.45; N, 17.77. IR ν_{max}^{neat} cm^{-1}: 2900, 1640, 1600. ^{1}H-NMR (300 MHz) δ: 1.69, 1.71, 1.78, 1.83 (s, $-CH_3\times4$ (isomer)), 1.88—2.62 (m, $-CH_2CHCH_2CHS-\times2$ (isomer)), 4.68, 4.72 (br s, $=CH_2\times2$ (isomer)), 5.66—5.72 (m, $-C=CH-\times2$ (isomer), 7.46—7.61 (m, Ph×2 (isomer)).

5-(2-Cyclohexenylthio)-1-phenyl-1*H*-tetrazole (4k) (Run 13) The reaction was carried out by the same procedure as used in the typical experiment except that acetone was used as the reaction solvent and DMAP as the base in run 13. Yield 73%, oil. MS *m/z*: 258 (M^+). *Anal.* Calcd for $C_{13}H_{14}N_4S$: C, 60.44; H, 5.46; N, 21.68. Found: C, 60.36; H, 5.51; N, 21.83. IR ν_{max}^{neat} cm^{-1}: 2900, 1650, 1600. ^{1}H-NMR (90 MHz) δ: 1.56—2.30 (6H, m, $-(CH_2)_3-$), 4.75 (1H, m, $-C\underline{H}S-$), 5.73—6.12 (2H, m, $-CH=CH-$), 7.60 (5H, m, Ph).

5-(1,5-Dimethyl-1-vinyl-4-hexenylthio)-1-phenyl-1*H*-tetrazole (4l) and 5-(3,7-Dimethyl-2,6-octadienylthio)-1-phenyl-1*H*-tetrazole (5l) (Runs 14 and 15) The reactions were carried out by the same procedure as used in the typical experiment except that acetone was used as the reaction solvent and DMAP as the base in run 14. Furthermore, the reaction time was changed to 1 h in run 15. Yields were 38% (run 14) and 26% (run 15), as the mixture. Ratios of **4l** to **5l** were 1.0 : 23.8 (run 14) and 1.0 : 13.7 (run 15). **4l** and **5l**: Foam. HRMS *m/z* Calcd for $C_{17}H_{22}N_4S$: (M^+) 314.15639. Found: (M^+) 314.15643. IR ν_{max}^{neat} cm^{-1}: 2900, 1600. ^{1}H-NMR (300 MHz) δ: 1.58, 1.66, 1.74 (s, $-CH_3\times3$ (**5l**)), 1.60, 1.68, 1.75 (s, $-CH_3\times3$ (**4l**)), 1.94—2.89 (m, $-CH_2CH_2-$), 4.07 (d, J=8.0 Hz, $-CH_2S-$ (**5l**)), 5.08—5.60 (m, $=CH$, $(CH_3)_2C=C\underline{H}-$ (**4l**), $=CH-\times2$ (**5l**)), 6.00 (dd, J=6.0, 10.0 Hz, $-CH=CH_2$ (**4l**)), 7.02 (m, Ph×2).

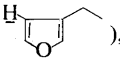
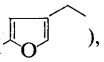
5-Benzylthio-1-phenyl-1*H*-tetrazole (4m) (Run 16) Yield 99%, mp 70—71 °C. MS *m/z*: 268 (M^+). *Anal.* Calcd for $C_{14}H_{12}N_4S$: C, 62.66; H, 4.50; N, 20.87. Found: C, 62.47; H, 4.46; N, 20.74. IR ν_{max}^{KBr} cm^{-1}: 3030, 1600. ^{1}H-NMR (60 MHz) δ: 4.65 (2H, s, $-CH_2S-$), 7.05—7.45 (5H, m, Ph), 7.52 (5H, s, Ph).

5-(4-Methoxybenzylthio)-1-phenyl-1*H*-tetrazole (4n) (Run 17) Yield 84%, oil. HRMS *m/z* Calcd for $C_{15}H_{14}N_4OS$: (M^+) 298.08874. Found: (M^+) 298.08869. IR ν_{max}^{neat} cm^{-1}: 2940, 1610. ^{1}H-NMR (300 MHz) δ: 3.79 (3H, s, $-OCH_3$), 4.59 (2H, s, $-CH_2S-$), 6.84 (2H, dt, J=2.0, 9.0 Hz, ), 7.34 (2H, dt, J=2.5, 8.5 Hz, ), 7.53 (5H, s, Ph).

5-(3,4-Dimethoxybenzylthio)-1-phenyl-1*H*-tetrazole (4o) (Run 18) The reaction was carried out by the same procedure as used in the typical experiment expect that benzene was used as the reaction solvent in run 18. Yield 99%, mp 84—86 °C. MS *m/z*: 328 (M^+). *Anal.* Calcd for $C_{16}H_{16}N_4O_2S$: C, 58.52; H, 4.91; N, 17.06. Found: C, 58.47; H, 4.97; N, 16.99. IR ν_{max}^{KBr} cm^{-1}: 2950, 1595. ^{1}H-NMR (60 MHz) δ: 3.87 (6H, s, $-OCH_3\times2$), 4.57 (2H, s, $-CH_2S-$), 6.77—7.44 (3H, m, Ph), 7.48 (5H, s, Ph).

(±)-5-(α-Methylbenzylthio)-1-phenyl-1*H*-tetrazole (4p) (Run 19) Yield 56%, oil. HRMS *m/z* Calcd for $C_{15}H_{14}N_4S$: (M^+) 282.09383. Found: (M^+) 282.09287. IR ν_{max}^{neat} cm^{-1}: 3050, 2970, 1600. ^{1}H-NMR (300 MHz) δ: 1.88 (3H, d, J=7.0 Hz, $-CH_3$), 5.21 (1H, q, J=7.0 Hz, $-C\underline{H}(CH_3)S-$), 7.20—7.61 (10H, m, Ph×2).

5-(2-Furfurylthio)-1-phenyl-1*H*-tetrazole (4q) (Run 20) The reaction was carried out by the same procedure as used in the typical experiment except that benzene was used as the reaction solvent in run 20. Yield 85%, oil. MS *m/z*: 258 (M^+). *Anal.* Calcd for $C_{12}H_{10}N_4OS$: C, 55.80; H, 3.90; N, 21.69. Found: C, 55.50; H, 3.75; N, 21.78. IR ν_{max}^{neat} cm^{-1}: 3050, 1600. ^{1}H-NMR (60 MHz) δ: 4.67 (2H, s, $-CH_2S-$), 6.27—6.52, 7.20—7.41 (3H, m, furan), 7.53 (5H, s, Ph).

5-(3-Furfurylthio)-1-phenyl-1*H*-tetrazole (4r) (Run 21) Yield 95%, oil. HRMS *m/z* Calcd for $C_{12}H_{10}N_4OS$: (M^+) 258.05746. Found: (M^+) 258.05619. IR ν_{max}^{neat} cm^{-1}: 3130, 1590. ^{1}H-NMR (300 MHz) δ: 4.88 (2H, s, $-CH_2S-$), 6.42 (1H, m, ), 7.36 (1H, m, ), 7.52 (1H, m, ), 7.54 (5H, s, Ph).

1-Phenyl-5-(3-pyridinylmethylthio)-1*H*-tetrazole (4s) (Run 22) Yield 95%, mp 72—74 °C. HRMS *m/z* Calcd for $C_{13}H_{11}N_5S$: (M^+) 269.07344. Found: (M^+) 269.07354. IR ν_{max}^{neat} cm^{-1}: 3070, 1600, 1240. ^{1}H-NMR (300 MHz) δ: 4.60 (2H, s, $-CH_2S-$), 7.20—7.28, 7.78—7.85, 8.50—8.55, 8.65—8.70 (4H, m, pyridine), 7.44—7.61 (5H, m, Ph).

1-Phenyl-5-propargylthio-1*H*-tetrazole (4t) (Run 23) Yield 60%, mp 97—98 °C. MS *m/z*: 216 (M^+). *Anal.* Calcd for $C_{10}H_8N_4S$: C, 55.53; H, 3.72; N, 25.90. Found: C, 55.47; H, 3.72; N, 25.62. IR ν_{max}^{KBr} cm^{-1}: 3250, 1595, 2100. ^{1}H-NMR (60 MHz) δ: 2.23—2.42 (1H, m, $CH\equiv C-$), 4.18 (2H, d, J=7.0 Hz, $-CH_2S-$), 7.58 (5H, s, Ph).

(*E*)-Methyl-1-phenyl-2,6-octadiene (6) (Run 24) A solution of 2 M-PhMgBr (1 ml, 2 mmol) and CuBr (8 mg, 0.055 mol, 0.11 eq) was added to a solution of **4c** (167 mg, 0.5 mmol) in THF (5 ml) and the mixture was stirred at room temperature under argon for 3 h, then quenched with saturated NH_4Cl (5 ml) and concentrated. Ether was added to the residue. The organic layer was washed with water, 4% $NaHCO_3$, and saturated brine, dried over Na_2SO_4, and evaporated. The residue was subjected to TLC on silica-gel (*n*-hexane). Yield 77%, oil. HRMS *m/z* Calcd for $C_{16}H_{22}$: (M^+) 214.17204. Found: (M^+) 214.17275. IR ν_{max}^{neat} cm^{-1}: 2900, 1600. ^{1}H-NMR (400 MHz) δ: 1.61, 1.69 (6H, s×2, $C(C\underline{H}_3)_2=CH-$), 1.72 (3H, d, J=1.5 Hz, $-CH_2C(C\underline{H}_3)=$), 2.03—2.28 (4H, m, $-C\underline{H}_2C\underline{H}_2-$), 3.36 (2H, d, J=7.5 Hz, $-CH_2Ph$), 5.11 (1H, m, $C(CH_3)_2=C\underline{H}-$), 5.35 (1H, tq, J=1.5, 7.5 Hz, $=C\underline{H}CH_2Ph$), 7.15—7.40 (5H, m, Ph).

(*E*)-1,3-Diphenylpropene (7) and (*E,E*)-1,6-Diphenyl-1,5-hexadiene (8) (Run 26) The reaction was carried out by the same procedure as used in run 24 except for overnight reaction and a different solvent system for TLC (*n*-hexane : pentane = 10 : 4). Yield 92% (**7** : **8** = 6.2 : 1.0). **7**: Oil. HRMS *m/z* Calcd for $C_{15}H_{14}$: (M^+) 194.10948. Found: (M^+) 194.10955. IR ν_{max}^{neat} cm^{-1}: 3025, 1600. ^{1}H-NMR (90 MHz) δ: 3.52 (2H, d, J=5.4 Hz, $-CH_2Ph$), 6.10—6.60 (2H, m, $-CH=CH-$), 7.00—7.53 (10H, m, Ph×2). **8**: Oil. HRMS *m/z* Calcd for $C_{18}H_{18}$: (M^+) 234.14076. Found: (M^+) 234.14057. IR ν_{max}^{neat} cm^{-1}: 2930, 1600. ^{1}H-NMR (300 MHz) δ: 2.40 (4H, dd, J=3.0, 3.5 Hz, $-CH_2-$×2), 6.24 (4H, br d, J=16.0 Hz, $PhCH=CH-$×2), 6.44 (4H, br d, J=16.0 Hz, $PhCH=CH-$×2), 7.30 (10H, m, Ph×2).

1-Phenyl-2-cyclohexene (9) (Run 26) The reaction was carried out by the same procedure as used in run 24 except for the reaction time of 4 h. Yield 69%, oil. HRMS *m/z* Calcd for $C_{12}H_{14}$: (M^+) 158.10948. Found: (M^+) 158.10960. IR ν_{max}^{neat} cm^{-1}: 2930, 1650, 1600. ^{1}H-NMR (90 MHz) δ: 1.27—2.29 (6H, m, $-(CH_2)_3-$), 3.29 (1H, m, $-CHPh$), 5.66 (1H, m, $-CH_2C\underline{H}=CH-$), 5.90 (1H, m, $-CH_2CH=C\underline{H}-$), 7.24 (5H, m, Ph).

(*E*)-Methyl 5,8-Dimethyl-2-phenylsulfonyl-4,8-decadienoate (10) (Run 27) A solution of **4c** (157 mg, 0.5 mmol) and $Pd(Ph_3P)_4$ (22 mg, 0.019 mmol, 0.038 eq) in dry acetonitrile (3 ml) was stirred for 15 min. Further, 60% NaH (80 mg, 2.0 mmol) was added to a solution of sodium methyl phenylsulfonylacetate (429 mg, 2 mmol) in acetonitrile. After stirring for 15 min, this solution was added to the above solution. The mixture was refluxed for 6 h under argon and then quenched with saturated NH_4Cl (5 ml). The reaction mixture was concentrated and ethyl acetate was added to the residue. The organic layer was washed with 4% $NaHCO_3$, 0.5 N HCl, and saturated brine, dried with Na_2SO_4, and evaporated. The residue was subjected to TLC on silica-gel (ether : *n*-hexane = 1 : 10). Yield 69%, oil. HRMS *m/z* Calcd for $C_{19}H_{26}O_4S$: (M^+) 350.15503. Found: (M^+) 350.15359. IR ν_{max}^{neat} cm^{-1}: 2930, 1750, 1590, 1330. ^{1}H-NMR (400 MHz, benzene-d_6) δ: 1.52 (3H, br s, $-CH_2C(C\underline{H}_3)=CH-$), 1.61, 1.75 (6H, br s×2, $C(C\underline{H}_3)_2=CH-$), 1.95—2.19 (4H, m, $-CH_2CH_2-$), 2.85—3.05 (2H, m, $-CH_2S-$), 3.33 (3H, s, $-COOCH_3$), 4.11 (1H, dd, J=2.0, 5.5 Hz, $-C\underline{H}(COOCH_3)(SO_2Ph)$), 5.02 (1H, m, $-CH_2C(CH_3)=C\underline{H}-$), 5.19 (1H, m, $(CH_3)_2C=C\underline{H}-$), 6.95—7.10, 7.91—7.98 (5H, m, Ph).

3,7-Dimethyl-1-(*p*-tolylsulfonyl)-2,6-octadiene (11) and 3,7-Dimethyl-3-(*p*-tolylsulfonyl)-1,6-octadiene (12) (Run 28) A solution of sodium *p*-tolylsulfonate (256 mg, 2 mmol) in dry methanol (5 ml) and $Pd(Ph_3P)_4$ (35 mg, 0.03 mmol, 0.061 eq) were successively added to a solution of **4c** (157 mg, 0.5 mmol) in dry THF (10 ml). The mixture was refluxed for 24 h under argon, then quenched with water (5 ml), and concentrated. Ethyl acetate was added to the residue. The organic layer was washed with 4% $NaHCO_3$ and saturated brine, dried with Na_2SO_4, and evaporated. The residue was subjected to TLC on silica-gel (benzene). Yield 66% as a mixture (**11** : **12** = 1.0 : 4.6). Oil. HRMS *m/z* Calcd for $C_{17}H_{24}O_2S$: (M^+ + H) 293.15739. Found: (M^+ + H) 293.15562. IR ν_{max}^{neat} cm^{-1}: 2930, 1640, 1600. ^{1}H-NMR (300 MHz) δ: **11**: 1.31 (3H, br s, $-CH_2C(C\underline{H}_3)=$), 1.56, 1.65 (6H, br s, $C(C\underline{H}_3)_2=$), 1.97 (4H, m, $-CH_2CH_2-$), 2.40 (3H, s, $-PhCH_3$), 3.75 (2H, d, J=8.0 Hz, $-CH_2SO_2-$), 5.03 (1H, m, $C(CH_3)_2=C\underline{H}-$), 5.14 (1H, t, J=8.0 Hz, $=C\underline{H}CH_2SO_2-$), 7.29, 7.71 (4H, m, $-PhCH_3$). **12**: 1.33 (3H, br s, $-CH_2C(C\underline{H}_3)(SO_2PhCH_3)-$), 1.52, 1.63 (6H, br s×2, $C(CH_3)_2=$), 1.80—1.94 (4H, m, $-CH_2CH_2-$), 2.40 (3H, s, $-PhCH_3$), 5.03 (1H, m, $C(CH_3)=C\underline{H}-$), 5.03, 5.32 (2H, d×2, J=17.0, 10.5 Hz, $=CH_2$), 5.88 (1H, dd, J=10.5, 17.0 Hz, $-C\underline{H}=CH_2$).

(*E*)-3-Phenyl-1-(*p*-tolylsulfonyl)-2-propene (13) (Run 29) The reaction was carried out by the same procedure as used in run 28 except for a different amount of $Pd(Ph_3P)_4$ (25 mg, 0.02 mmol, 0.043 eq), refluxing time of 6 h, and a different quenching solution (saturated NH_4Cl). Yield 96%, mp 116—118 °C. HRMS *m/z* Calcd for $C_{16}H_{16}O_2S$: (M^+) 272.08701. Found: (M^+) 272.08771. IR ν_{max}^{neat} cm^{-1}: 2930, 1600, 1320. ^{1}H-NMR (90 MHz) δ: 2.40 (3H, s, $-CH_3$), 3.94 (2H, d, J=7.5 Hz, $-CH_2SO_2-$), 6.13 (1H, dq, J=7.5, 15.0 Hz, $-CH=C\underline{H}CH_2-$), 6.43 (1H, d, J=15.0 Hz, $PhC\underline{H}=CH-$), 7.10—7.46, 7.66—7.90 (9H, m, Ph×2).

Dimethyl (*E*)-3-Phenyl-2-propenylmalonate (14) and Dimethyl Bis[(*E*)-3-phenyl-2-propenyl]malonate (15) (Run 30) DPPE (5 mg, 0.0125 mmol, 0.025 eq) and $Pd(dba)_2$ (3 mg, 0.0052 mmol, 0.01 eq) were added to a solution of **4l** (147 mg, 0.5 mmol) in dry THF (2 ml). Further, 60% NaH (80 mg, 2.0 mmol) was added to a solution of sodium dimethyl malonate (264 mg, 2 mmol) in dry THF (10 ml), and this mixture was added to the above solution. The whole was refluxed under argon. After 1 h, treatment was carried out in the same way as used in run 27 except for a different solvent system for TLC (ethyl acetate : benzene : *n*-hexane = 1 : 25 : 6). Yield 91% (**14** : **15** = 10.0 : 1.0). **14**: Oil. MS *m/z*: 248 (M^+). *Anal.* Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.80; H, 6.50. IR ν_{max}^{neat} cm^{-1}: 2970, 1740, 1600. ^{1}H-NMR (300 MHz) δ: 2.80 (2H, ddd, J=1.5, 7.0, 7.5 Hz, $=CHC\underline{H}_2-$), 3.53 (1H, t, J=7.5 Hz, $-CH_2C\underline{H}(COOCH_3)_2$), 3.73, 3.75 (6H, s, $-COOCH_3$×2), 6.13 (1H, dt, J=7.0, 15.5 Hz, $=C\underline{H}CH_2-$), 6.47 (1H, d, J=15.5 Hz, $PhC\underline{H}=$), 7.30—7.40 (5H, m, Ph). **15**: Oil. MS *m/z*: 364 (M^+). *Anal.* Calcd for $C_{23}H_{24}O_4$: C, 75.80; H, 6.64. Found: C, 76.13; H, 6.64. IR ν_{max}^{neat} cm^{-1}: 2950, 1740, 1600. ^{1}H-NMR (300 MHz) δ: 2.86 (4H, dd, J=1.0, 7.5 Hz, $-CH_2-$×2), 3.75 (6H, s, $-COOCH_3$×2), 6.08 (2H, dt, J=7.5, 15.5 Hz, $=C\underline{H}CH_2-$×2), 6.48 (2H, d, J=15.5 Hz, $PhCH=$×2), 7.33 (10H, m, Ph×2).

3-*p*-Tolylsulfonycyclohexane (16) (Run 31) The reaction was carried out by the same procedure as used in run 28 except for the refluxing time of 4 h and a different quenching solution (saturated NH_4Cl). Yield 75%, mp 58—59 °C. HRMS *m/z* Calcd for $C_{13}H_{16}O_2S$: (M^+ + H) 237.09483. Found: (M^+ + H) 237.09601. IR ν_{max}^{neat} cm^{-1}: 2950, 1600, 1140. ^{1}H-NMR (90 MHz) δ: 1.14—2.14 (6H, m, $-(CH_2)_3-$), 2.36 (3H, s, $-CH_3$), 3.71 (1H, m, $-CHSO_2-$), 5.79 (1H, dd, J=3.0. 10.5 Hz, $-CH_2CH=C\underline{H}-$), 6.10 (1H, ddd, J=3.0, 6.0, 10.5 Hz, $-CH_2C\underline{H}=CH-$), 7.16—7.90 (4H, m, Ph).

Dendrolasin (17) A solution of 3-furylmethyl bromide (322 mg, 2 mmol) in dry THF (4 ml) was dropped into a solution of magnesium turnings (100 mg, 4 mmol) in dry THF (1 ml) for 90 min in an ice bath under argon. The mixture was dropped into a solution of **4c** (160 mg, 0.51 mmol) and CuBr (8 mg, 0.056 mmol, 0.11 eq) in dry THF (2 ml) over 1 h at −78 °C under argon and the mixture was stirred overnight at room temperature. The reaction mixture was quenched with saturated NH_4Cl and concentrated, and ether was added to the residue. The organic layer was washed with 4% $NaHCO_3$, 0.5 N HCl, and saturated brine, dried over Na_2SO_4 evaporated. The residue was distilled under 3 Torr at 130 °C. The product was found to be identical with an authentic sample by TLC. Yield 86%.

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