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4-Penteneselenothioic Acid *S*-Alkyl Esters: Synthesis *via* the Seleno-Claisen Rearrangement

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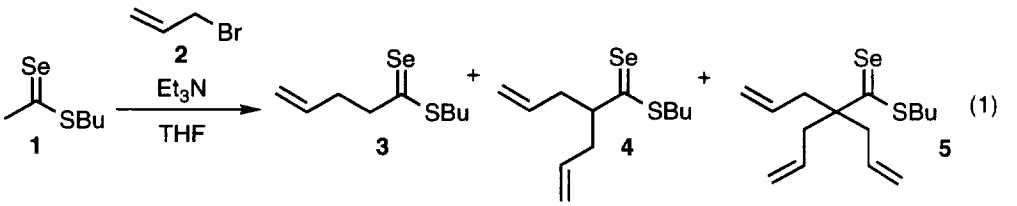
Abstract: Selenothioic acid *S*-alkyl esters were reacted with allylic bromides in the presence of Et_3N. Mono-, di- or tri-allylatd products were selectively formed by changing reaction temperatures, times and allylic bromides used. The reaction proceeded with high regio- and stereoselectivity *via* the seleno-Claisen rearrangement. The selective synthesis of monoallylated esters was also attained by the reaction of *in-situ* generated lithium eneselenolates with allylic bromides. © 1997 Elsevier Science Ltd.

In the course of our studies on the chemistry of sulfur and selenium isologues of carboxylic acid derivatives, we have recently succeeded in the first synthesis and isolation of selenothioic acid *S*-alkyl esters.[1] Their high reactivity toward a variety of heavy metal salts[2] and electron deficient alkynes[3] has also been demonstrated. Furthermore, the esters react with allylic bromides in the presence of Et_3N even at -78 °C to give α-allylated esters.[4] Herein we report the methods for the synthesis of 4-penteneselenothioic acid *S*-alkyl esters *via* the seleno-Claisen rearrangement.

Selenothioacetic acid *S*-butyl ester (**1**) was reacted with two equiv of 3-bromo-1-propene (**2**) and Et_3N in THF at 0 °C for 2 h to give diallylated ester **4** selectively in 80% yield (eq 1). A similar reaction of ester **1** with 3.0 equiv of **2** and Et_3N under the reflux in THF for 48 h gave triallylated ester **5** in 90% yield. These esters **1**, **4**, and **5** exhibited intensive colors depending on the substituents. Esters **1** and **4** were from deep pink to deep purple, whereas **5** showed deep blue color.

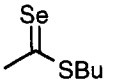
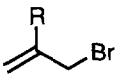
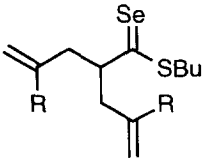
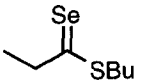
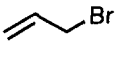
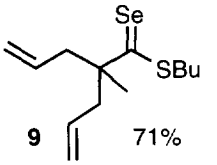
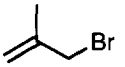
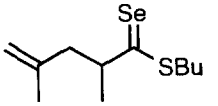
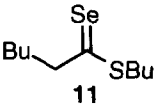
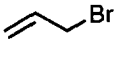
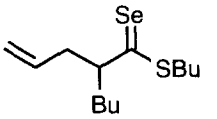
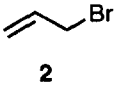
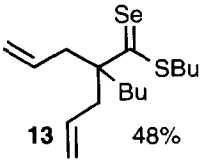


0 °C, 2 h	0%	80%	0%
66 °C, 48 h	0%	0%	90%

In the reaction of eq 1 the construction of a quaternary carbon center was realized in a single operation by the repetition of the allylation of ester **1** at the α-position of selenocarbonyl group. On the contrary, attempts to

synthesize monoallylated ester **3** as a single product resulted in the formation of a mixture involving **1**, **3**, and **4** even in the reaction at -78 °C. These results are in sharp contrast to a similar reaction using thioamides[5] and dithioesters.[6] Selective synthesis of monoallylated products from thioamides and dithioesters is possible, and their triallylation has been reported to be unsuccessful.[5] Moreover, the reaction of dithioesters requires more than two days to give monoallylated products with allylic bromides in the presence of a base.[6]

Table 1. Allylation of Selenothioic Acid *S*-Alkyl Esters [a]

entry	ester	allylic bromide	temp., time	product, yield [b]
	 **1**	 **6**		
1		**6a** R = Br	0 °C, 4 h	**7a** 59%
2		**6b** R = CO_2Et	25 °C, 23 h	**7b** 68%
3		**6c** R = CH_3	66 °C, 14 h	**7c** 72%
4 [c]	 **8**	 **2**	66 °C, 48 h	 **9** 71%
5 [d]		 **6c**	0 °C, 1 h	 **10** 79%
6 [e]	 **11**	 **2**	0 °C, 3.5 h	 **12** 99%
7		 **2**	66 °C, 48 h	 **13** 48%

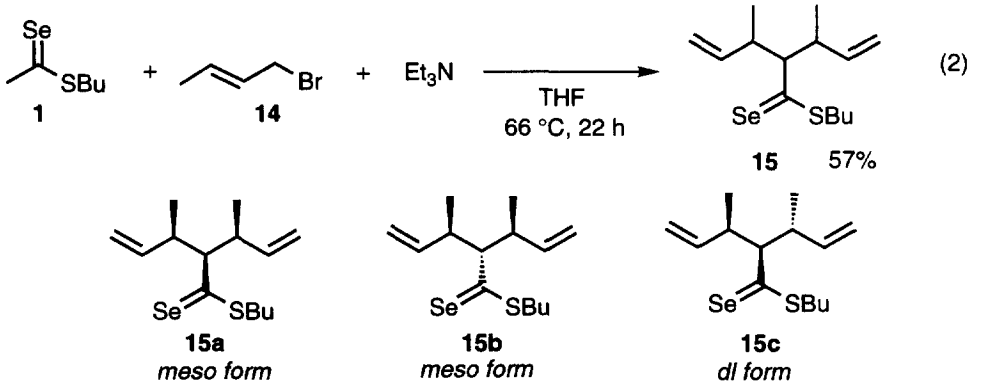
[a] The reaction was carried out with ester (1 mmol), allylic bromide (2 mmol), and Et_3N (2 mmol) in THF (5 mL) unless otherwise noted. [b] Isolated yield. [c] **8** (5 mmol), **2** (10 mmol), and Et_3N (10 mmol) were used. [d] **8** (5 mmol), **6c** (5 mmol), and Et_3N (5 mmol) were used. [e] **11** (1 mmol), **2** (1 mmol), and Et_3N (1 mmol) were used.

It should also be noted that the process from **1** to **4** is complete under much milder conditions than the formally analogous reaction between one of ordinary esters, i.e. diethyl malonate, and **2** leading to 1,6-dien-4-dicarboxylate.[7]

The results of the reactions of esters **1**, **8**, and **11** with a variety of allylic bromides **2**, **6a–6c** in the presence of Et_3N in THF are summarized in Table 1. As for the reactions of **1** with substituted allylic bromides **6**, diallylation proceeded smoothly to give the corresponding esters **7** (entries 1–3), although the attempts to introduce three allylic groups to **1** were not successful even at higher temperatures for longer reaction time and gave a complex mixture in the cases of **6a** and **6b**. Functional groups such as bromine and ethoxycarbonyl groups tolerated the present reaction conditions.

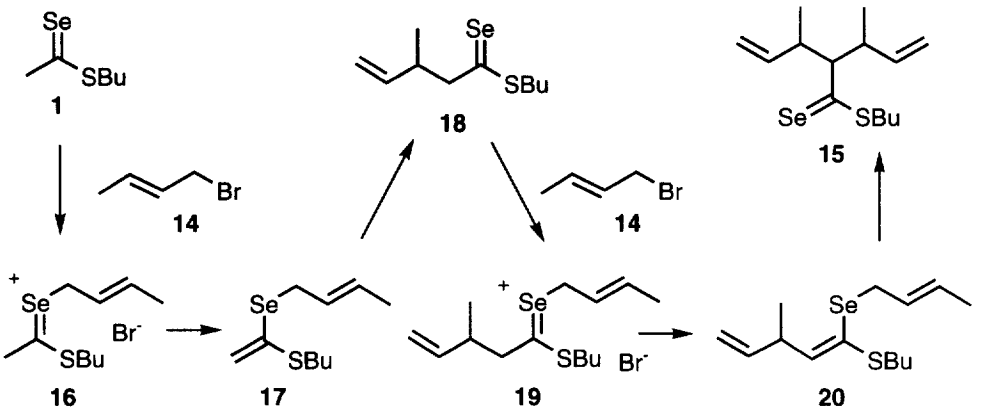
As for the allylation of **8** and **11**, it highly depended on the substitution patterns of the esters and allylic bromides whether monoallylated or diallylated products were formed. For example, the reaction using 3-bromo-2-methyl-1-propene (**6c**) yielded monoallylated ester **10** in high yield (entry 5). In the reaction of ester **11**, monoallylation proceeded selectively at 0 °C for 3.5 h to give **12** in 99% yield (entry 6). Similarly to the reaction of **1** the synthesis of esters **9** and **13** having quaternary carbon centers at the α-position of the selenocarbonyl group was attained by the reactions of **8** and **11** with **2** at 66 °C for 48 h (entries 4, 7). In these two cases sterically more hindered **13** was obtained in lower yield.

The allylation of ester **1** with 4-bromo-2-butene (**14**) was also carried out (eq 2). The reaction of **1** with two equiv of **14** and Et_3N at 66 °C in THF gave ester **15** as a stereoisomeric mixture in 57% yield. A similar diallyation with **14** has been known for diethyl malonate. However, the regiochemical course of the present reaction is in sharp contrast to the case of diethyl malonate where allylic carbon adjacent to bromine of **14** was introduced to α-carbon of carbonyl groups of diethyl malonate.[7b] As for **15**, the formation of three stereoisomers, i.e. two *meso* forms **15a**, **15b**, and *dl* form **15c** is possible. Among them, one of *meso* forms **15a** or **15b** and *dl* form **15c** were obtained in a ratio of 82 to 18. Thus, three contiguous stereocenters are constructed in one operation, and their stereochemistry has been controlled to some extent. On the basis of the simplicity of the ^1H and ^{13}C NMR spectra for two *meso* forms **15a** and **15b** their structures were easily differentiated from *dl* form, although the structures of two *meso* forms have not been determined.



The plausible reaction pathway from **1** to **15** is shown in Scheme 1. In the first step, ester **1** may interact with **14** to form selenoxonium ion intermediate **16**. Then, proton abstraction from **16** may give allyl

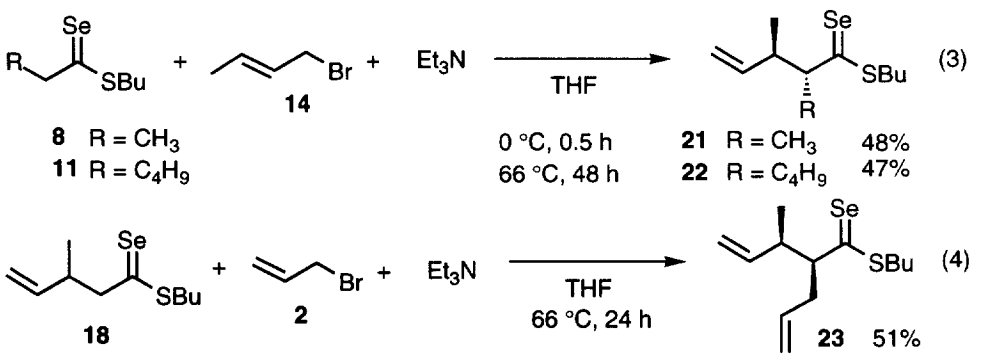
vinyl selenide intermediate **17**. The following seleno-Claisen rearrangement of **17** may lead to ester **18**. A similar process may be repeated from **18** to end up as a formation of ester **15** *via* **19** and **20**.



Scheme 1

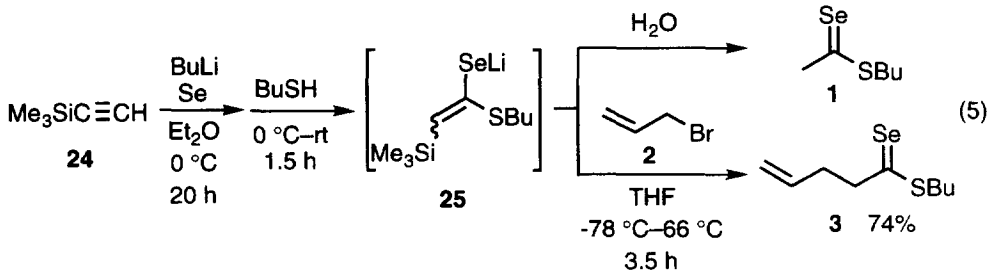
To isolate some intermediates the reaction in eq 2 was carried out at lower temperatures. The reaction at -78 °C for 10 min followed by the addition of water gave monoallylated product **18** in 37% yield. When **1** was treated with two equiv of **14** at 25 °C for 4 h, allyl vinyl selenide **20** was quantitatively obtained with an *E* and *Z* selectivity of 11 : 89. These results have suggested the intermediacy of **18** in eq 2 and that the seleno-Claisen rearrangement can proceed even at -78 °C. Furthermore, the reactivity of **1** and **18** toward **14** is competitive at room temperature, but the seleno-Claisen rearrangement of **17** takes place more easily than that of **20**. Nevertheless, the present seleno-Claisen rearrangement appears to proceed more quickly than that of allyl vinyl selenides leading to selenoaldehydes.[8,9] The introduction of an electron donating group such as alkylthio group to allyl vinyl selenides enhances the easiness of the seleno-Claisen rearrangement analogous to the ordinary Claisen rearrangement.[11]

The reaction in Scheme 1 involves two stereodetermining steps if the rearrangement proceeds through chair-form transition state:[11] the formation of allyl vinyl selenide **20** and the seleno-Claisen rearrangement of **20**. The high stereoselectivity in the former step is proved by the predominant formation of a *Z*-isomer of **20**.

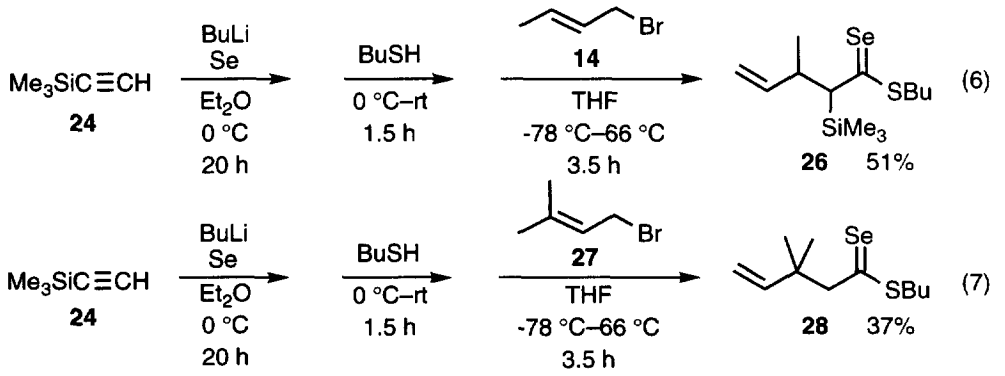


Although more studies are necessary to disclose the factors to control the stereochemistry in the latter step,[12] a similar highly stereoselective allylation was demonstrated by the reactions of **8**, **11** and **18** with **14** and **2** (eqs 3 and 4). In each case only one of stereoisomers **21**, **22**,[13] or **23**[15] was obtained, although in moderate yields.

Finally, alternative synthetic routes to 4-penteneselenothioic acid *S*-alkyl esters were developed. Ester **1** is prepared by the reaction of trimethylsilylacetylene (**24**) with BuLi, Se, and butanethiol followed by hydrolysis (eq 5). In this reaction lithium eneselenolate **25** is considered as a putative intermediate.[16] Therefore, 3-bromo-1-propene (**2**) was added to the reaction mixture of eq 5 prior to the aqueous work-up.[17] Interestingly, monoallylated ester **3** was selectively obtained in good yield.



The use of **14** and 1-bromo-3-methyl-2-butene (**27**) gave esters **26**[18,19] and **28** in 51 and 37% yields, respectively (eqs 6 and 7). The high regioselectivity of the reaction where more substituted carbon atoms of **14** and **27** are attached to α-carbons of selenocarbonyl group has suggested that the reaction of eqs 6 and 7 also involves the seleno-Claisen rearrangement. Thus, allylation with **14** and **27** initially takes place between selenium atom of **25** and less substituted carbon atoms of **14** and **27**. Noteworthy is that the trimethylsilyl group in **24** remained in the product **26** when **14** was employed as an allylic bromide, whereas protodesilylation[20] of the products proceeded completely to give **28** in the reaction with **27**.



In summary, we have demonstrated two types of methods for the synthesis of 4-penteneselenothioic acid *S*-alkyl esters. These reactions proceed highly efficiently to afford mono-, di- or tri-allylated esters selectively. The reaction proceeds via the seleno-Claisen rearrangement and exhibits high regio- and diastereoselectivity.

The present results have provided operationally simple routes to selenothioic acid *S*-alkyl esters and have proved their high potential utilities among selenocarbonyl compounds, which generally require cumbersome preparative procedures.[21] Further studies on the unique properties of selenothioic acid *S*-alkyl esters are in progress.

Experimental

Materials. All solvents and reagents were obtained from commercial sources and used without further purification unless otherwise indicated. Triethylamine was distilled from potassium hydroxide. Tetrahydrofuran and diethyl ether were distilled from benzophenone-ketyl. Selenothioic acid *S*-butyl esters **1**, **8**, and **11** were prepared by the literature procedure.[16]

Characterization. ^{1}H NMR spectra were measured on a JEOL α–400 (400 MHz) in $CDCl_3$. Chemical shifts of protons are reported in δ values referred to tetramethylsilane as an internal standard, and the following abbreviations were used; s: singlet, d: doublet, q: quartet, qui: quintet, sex: sextet, m: multiplet. ^{13}C NMR spectra were determined on a JEOL α-400 (100 MHz). ^{77}Se NMR spectra were recorded on a JEOL α-400 (76 MHz). IR spectra were obtained on a PERKIN-ELMER FT-IR 1640 spectrometer. The mass spectra (MS) were taken on SHIMADZU GCMS-QP1000 (A) (EI/CI, mode) or GCMS 9020DF high resolution mass spectrometers. Elemental analyses were carried out by Elemental Analysis Center in Kyoto University.

A typical experimental procedure for the allylation of selenothioic acid S-alkyl esters are represented by the synthesis of 2-(2-propenyl)-4-penteneselenothioic acid S-butyl ester (4)

To a THF solution (50 mL) of selenothioic acid *S*-butyl ester **1** (10.0 mmol, 1.97 g) and 3-bromo-1-propene (**2**) (19.6 mmol, 1.73 mL) was added Et_3N (20 mmol, 2.8 mL) at 0 °C. The resulting solution was stirred at 0 °C for 2 h. The reaction mixture was poured into ice/water and extracted with ether. The combined organic layer was dried over anhydrous magnesium sulfate and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel using hexane as eluent to give 2.2 g (80 %) of **4**: IR (neat) 3077, 2959, 2930, 2873, 2362, 2088, 1832, 1718, 1686, 1560, 1543, 1508, 1464, 1438, 1415, 1397, 1380, 1354, 1273, 1242, 1148, 990, 916, 745, 670, 618 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.94 (t, J = 7.4 Hz, 3H, CH_3), 1.45 (sex, J = 7.4 Hz, 2H, CH_2), 1.70 (qui, J = 7.4 Hz, 2H, CH_2), 2.42 (td, J = 7.1, 6.3 Hz, 2H, CH_2), 2.60 (dt, J = 7.9, 7.1 Hz, 2H, CH_2), 3.27 (t, J = 7.4 Hz, 2H, SCH_2), 3.40 (tt, J = 7.9, 6.3 Hz, 1H, CH), 4.99 (dd, J = 10.2, 1.2 Hz, 2H, CH=C*H*H), 5.03 (dd, J = 17.0, 1.2 Hz, 2H, CH=CH*H*), 5.73 (ddt, J = 17.0, 10.2, 7.1 Hz, 2H, C*H*=CH_2) ; ^{13}C NMR ($CDCl_3$) δ 13.7 (CH_3), 22.3 (CH_2), 28.9 (CH_2), 39.4 (CH_2), 41.1 (SCH_2), 64.4 (CH), 116.9 (CH=*C*H_2), 135.2 (*C*H=CH_2), 247.9 (C=Se); EIMS (*m/z*) 276 (M^+); Anal. Calcd for $C_{12}H_{20}SSe$: C, 52.35; H, 7.32. Found: C, 52.21: H, 7.51.

2,2-Bis(2-propenyl)-4-penteneselenothioic acid S-butyl ester (5): IR (neat) 3076, 3006, 2959, 2930, 2873, 2360, 1837, 1639, 1442, 1416, 1323, 1271, 1100, 993, 973, 916, 818, 701, 657, 614, 563 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.95 (t, J = 7.4 Hz, 3H, CH_3), 1.46 (sex, J = 7.4 Hz, 2H, CH_2), 1.73 (qui, J = 7.4 Hz, 2H, CH_2), 2.72 (d, 7.1 Hz, 6H, CH_2), 3.23 (t, J = 7.4 Hz, 2H, SCH_2), 5.05 (dd, J = 17.1, 1.3 Hz, 3H, CH=C*H*H), 5.09 (dd, J = 9.8, 1.3 Hz, 3H, CH=CH*H*), 5.71 (ddt, J = 17.1, 9.8, 7.1 Hz 3H, C*H*=CH_2) ; ^{13}C NMR ($CDCl_3$) δ 13.7 (CH_3), 22.4 (CH_2), 28.7 (CH_2), 41.3 (CH_2), 43.2 (CH_2), 64.3 (CH), 118.3 (CH=*C*H_2), 133.5 (*C*H=CH_2), 251.6 (C=Se); EIMS (*m/z*) 316 (M^+); Anal. Calcd for $C_{15}H_{24}SSe$: C, 57.13; H, 7.67. Found: C, 57.42: H, 7.59.

*4-Bromo-2-(2-bromo-2-propenyl)-4-penteneselenothioic acid S-butyl ester (**7a**)*: IR (neat) 2957, 2929, 2872, 2088, 1628, 1464, 1425, 1236, 1151, 1100, 1025, 893, 760, 622, 601, 562, 538, 489 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.94 (t, J = 7.5 Hz, 3H, CH_3), 1.45 (sex, J = 7.5 Hz, 2H, CH_2), 1.72 (qui, J = 7.5 Hz, 2H, CH_2), 2.73 (dd, J = 14.4, 5.5 Hz, 2H, CH_2), 3.02 (dd, J = 14.4, 8.4 Hz, 2H, CH_2), 3.25 (t, J = 7.5 Hz, 2H, SCH_2), 4.13 (tt, J = 8.4, 5.5 Hz, 1H, CH), 5.43 (s, 2H, CBr=C*H*H), 5.55 (s, 2H, CBr=CH*H*); ^{13}C NMR ($CDCl_3$) δ 13.7 (CH_3), 22.2 (CH_2), 28.6 (CH_2), 39.8 (CH_2), 47.5 (CH_2), 58.9 (CH), 120.0 (CBr=*C*H_2), 130.0 (*C*Br=CH_2), 244.3 (C=Se); EIMS *(m/z)* 353 (M^+-Br); Anal. Calcd for $C_{12}H_{18}Br_2SSe$: C, 33.28; H, 4.19. Found: C, 33.66; H, 4.44.

*4-Ethoxycarbonyl-2-(2-ethoxycarbonyl-2-propenyl)-4-penteneselenothioic acid S-butyl ester (**7b**)*: IR (neat) 2960, 2932, 2874, 2346, 1716, 1630, 1444, 1399, 1369, 1329, 1308, 1227, 1183, 1029, 950, 904, 859, 816, 722, 611 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.92 (t, J = 7.4 Hz, 3H, CH_3), 1.32 (t, J = 7.3 Hz, 6H, CH_3), 1.40 (sex, J = 7.4 Hz, 2H, CH_2), 1.65 (qui, J = 7.4 Hz, 2H, CH_2), 2.75 (dd, J = 14.3, 5.6 Hz, 2H, CH_2), 2.80 (dd, J = 14.3, 8.4 Hz, 2H, CH_2), 3.19 (t, J = 7.4 Hz, 2H, SCH_2), 4.00(tt, J = 8.4, 5.6 Hz, 1H, CH), 4.22 (q, J = 7.3 Hz, 4H, OCH_2), 5.53 (s, 2H, C=CH*H*), 6.14 (s, 2H, C=C*H*H); ^{13}C NMR ($CDCl_3$) δ 13.6 (CH_3), 14.2 (CH_3), 22.1 (CH_2), 28.6 (CH_2), 39.2 (CH_2), 39.4 (CH_2), 60.2 (CH), 60.6 (OCH), 127.4 (C=*C*H_2), 137.0 (*C*=CH_2), 166.6 (C=O), 247.1 (C=Se); CIMS (*m/z*) 421 (M^++1); Anal. Calcd for $C_{18}H_{28}O_4SSe$: C, 51.54; H, 6.73. Found: C, 51.29; H, 6.64.

*4-Methyl-2-(2-methyl-2-propenyl)-4-peneteneselenothioic acid S-butyl ester (**7c**)*: IR (neat) 3075, 2961, 2931, 2361, 1649, 1442, 1375, 1245, 1219, 1109, 1065, 987, 892, 744, 608, 578, 504 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.94 (t, J = 7.4 Hz, 3H, CH_3), 1.44 (sex, J = 7.4 Hz, 2H, CH_2), 1.70 (qui, J = 7.4 Hz, 2H, CH_2), 1.75 (s, 6H, CH_3), 2.37 (dd, J = 13.9, 5.9 Hz, 2H, CH_2), 2.61 (dd, J = 13.9, 8.3 Hz, 2H, CH_2), 3.25 (t, J = 7.4 Hz, 2H, SCH_2), 3.74 (tt, J = 8.3, 5.9 Hz, 1H, CH), 4.70 (s, 2H, C=C*H*H), 4.75 (s, 2H, C=CH*H*); ^{13}C NMR ($CDCl_3$) δ 13.7 (CH_3), 22.2 (CH_3), 22.3 (CH_2), 28.8 (CH_2), 39.4 (CH_2), 45.2 (CH_2), 60.6 (CH), 113.1 (C=*C*H_2), 142.4 (*C*=CH_2), 248.7 (C=Se); EIMS (*m/z*) 304 (M^+); Anal. Calcd for $C_{14}H_{24}SSe$: C, 55.43; H, 7.97. Found: C, 55.29; H, 8.12.

*2-Methyl-2-(2-propenyl)-4-penteneselenothioic acid S-butyl ester (**9**)*: IR (neat) 3076, 2960, 2929, 2873, 2346, 1832, 1639, 1560, 1456, 1436, 1415, 1394, 1378, 1293, 1229, 1152, 1099, 992, 916, 828, 707, 617, 566 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 0.95 (t, J = 7.3 Hz, 3H, CH_3), 1.46 (sex, J = 7.6 Hz, 2H, CH_2), 1.52 (s, 3H, CH_3), 1.73 (qui, J = 7.5 Hz, 2H, CH_2), 2.43 (dd, J = 13.4, 7.2 Hz, 2H, CH_2), 2.86 (dd, J = 13.8, 6.8 Hz, 2H, CH_2), 3.20 (t, J= 7.4 Hz, 2H, SCH_2), 5.01-5.06 (m, 4H, CH=CH_2), 5.65-5.76 (m, 2H, C*H*=CH_2); ^{13}C-NMR ($CDCl_3$) δ 13.7, 22.4, 24.8, 28.7, 41.4, 48.4, 61.6, 118.1, 133.8, 253.2; EIMS (*m/z*): 289 (M^+); Anal. Calcd for $C_{13}H_{22}SSe$: C, 53.96; H: 7.66. Found: C, 54.00; H, 7.83.

*2,4-Dimethyl-4-penteneselenothioic acid S-butyl ester (**10**)*: IR (neat) 3075, 2961, 2346, 1794, 1686, 1651, 1560, 1455, 1418, 1396, 1374, 1348, 1292, 1270, 1207, 1146, 1097, 1031, 999, 965, 924, 822, 787, 745, 587, 558, 503; ^1H-NMR ($CDCl_3$) δ 0.95(t, J = 7.3 Hz, 3H, CH_3), 1.31 (d, J = 6.6 Hz, 3H, CH_3), 1.45 (sex, J = 7.4 Hz, 2H, CH_2, 1.72 (qui, J = 7.5 Hz, 2H, CH_2), 1.74 (s, 3H, CH_3), 2.34 (dd, J = 7.0, 0.9 Hz, 1H, CH_2), 2.60 (dd, J = 6.8, 0.7 Hz, 1H, CH_2), 3.23 (t, J = 7.6 Hz, 2H, SCH_2), 3.61 (sex, J = 6.8 Hz, 1H, CHCSe), 4.71 (s, 1H, C=C*H*H), 4.76 (s, 1H, C=CH*H*); ^{13}C-NMR ($CDCl_3$) δ 13.7, 22.3, 22.4, 22.5, 28.9, 39.5, 46.9, 57.4, 113.0, 142.7, 251.5; EIMS (*m/z*): 263 (M^+); HRMS calcd for $C_{11}H_{20}SSe$ 264.04499. Found: 264.04322.

2-(2-Propenyl)hexaneselenothioic acid S-butyl ester (12): IR (neat) 3077, 2958, 2929, 2859, 2346, 1640, 1465, 1379, 1153, 989, 914, 730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.86 (t, J = 7.3 Hz, 3H, CH_3), 0.95 (t, J = 7.5 Hz, 3H, CH_3), 1.23-1.31 (m, 4H, CH_2), 1.45 (sex, J = 7.3 Hz, 2H, CH_2), 1.72 (qui, J = 7.3 Hz, 2H, CH_2), 1.88-1.96 (m, 2H, CH_2) 2.38 (ddd, J = 13.7, 13.2, 7.0 Hz, 1H, C*H*H) 2.60 (ddd, J = 13.7, 13.2, 7.0 Hz, 1H, CH*H*), 3.26 (t, J = 7.5 Hz, 2H, SCH_2), 3.35 (ddt, J = 13.7, 8.8, 5.0 Hz, 1H, CH), 4.96 (dd, J = 10.1, 2.0 Hz, 1H, CH=C*H*H), 5.01 (dd, J = 17.1, 2.0, Hz, 1H, CH=CH*H*), 5.72 (ddt, J = 17.1, 10.1, 7.0 Hz, 1H, C*H*=CH_2); ^{13}C NMR ($CDCl_3$) δ 13.6, 13.9, 22.2, 22.6, 28.8, 29.2, 36.6, 39.3, 41.9, 64.8, 116.6, 135.5, 249.8; CIMS (*m/z*) 293 (M^++1); Anal. Calcd for $C_{13}H_{24}SSe$: C, 53.59; H, 8.30. Found: C, 53.65; H, 8.06.

2,2-Bis(2-propenyl)hexaneselenothioic acid S-butyl ester (13): IR (neat) 3076, 2958, 2871, 2872, 1834, 1638, 1456, 1415, 1379, 1262, 1228, 1147, 1099, 994, 970, 915, 917, 730, 678, 582 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.84 (t, J = 7.1 Hz, 3H, CH_3), 0.93 (t, J = 7.4 Hz, 3H, CH_3), 1.21 (m, 4H, CH_2), 1.45 (sex, J = 7.4 Hz, 2H, CH_2), 1.72 (qui, J = 7.4 Hz, 2H, CH_2), 1.89 (m, 2H, CH_2), 2.66 (d, J = 7.1 Hz, 2H, CH_2), 2.69 (d, J = 7.1 Hz, 2H, CH_2), 3.21 (t, J = 7.4 Hz, 2H, SCH_2), 5.03 (d, J = 9.8 Hz, 2H, CH=CH*H*), 5.04 (d, J = 17.1 Hz, 2H, CH=C*H*H), 5.67 (ddt, J = 17.1, 9.8, 7.1 Hz, 2H, C*H*=CH_2); EIMS (*m/z*): 332 (M^+); ^{13}C NMR ($CDCl_3$) δ 13.7, 14.0, 22.4, 23.2, 25.5, 28.7, 39.2, 41.2, 43.1, 64.5, 118.0, 133.9, 253.5; HRMS Calcd for $C_{16}H_{28}SSe$: 332.10755. Found: 332.10929.

*3-Methyl-2-(1-methyl-2-propenyl)-4-penteneselenothioic acid S-butyl ester (**meso-15a**)*: IR (neat) 3077, 2961, 2829, 2873, 2346, 1686, 1639, 1458, 1417, 1377, 1271, 1123, 996, 914, 887, 843, 723 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 (t, J = 7.4 Hz, 3H, CH_3), 1.00 (d, J = 6.6 Hz, 6H, CH_3), 1.48 (sex, J = 7.4 Hz, 2H, CH_2), 1.63 (qui, J = 7.4 Hz, 2H, CH_2), 2.76 (dq, J = 7.3, 6.6 Hz, 2H, CH), 3.16 (t, J = 7.4 Hz, 2H, SCH_2), 3.30 (t, J = 7.3 Hz, 1H, CH), 4.92 (dd, J = 10.0, 2.0 Hz, 2H, C=C*H*H), 4.98 (dd, J = 17.3, 2.0 Hz, 2H, C=CH*H*), 5.68 (ddd, J = 17.3, 10.0, 7.1 Hz, 4H, C*H*=C); ^{13}C NMR ($CDCl_3$) δ 13.7, 16.7, 22.3, 28.8, 40.0, 74.2, 114.3, 142.3, 243.1; EIMS (*m/z*) 304 (M^+); HRMS Calcd for $C_{14}H_{24}SSe$: 304.07627. Found: 304.08008. ***(meso-15b)***: ^1H NMR ($CDCl_3$) δ 0.94 (t, J = 7.3 Hz, 3H, CH_3), 1.10 (d, J = 6.8 Hz, 6H, CH_3), 1.45 (sex, J = 7.3 Hz, 2H, CH_2), 1.71 (qui, J = 7.3 Hz, 2H, CH_2), 2.77 (dq, J = 7.3, 6.8 Hz, 2H, CH), 3.23 (t, J = 7.3 Hz, 2H, SCH_2), 3.35 (t, J = 7.3 Hz, H, CH), 5.01 (dd, J = 9.9, 1.7 Hz, 2H, C=C*H*H), 5.09 (dd, J = 17.6, 1.7 Hz, 2H, C=CH*H*), 5.99 (ddd, J = 17.6, 9.9, 7.4 Hz, 2H, C*H*=C); ^{13}C NMR ($CDCl_3$) δ 13.7, 17.9, 22.2, 28.9, 39.3, 70.4, 115.4, 142.0, 242.2. ***(dl-15c)***: ^1H NMR ($CDCl_3$) δ 0.87 (t, J = 7.3 Hz, 3H, CH_3), 0.99 (d, J = 6.8 Hz, 6H, CH_3), 1.38 (sex, J = 7.3 Hz, 2H, CH_2), 1.63 (qui, J = 7.3 Hz, 2H, CH_2), 2.63 (dq, J = 7.3, 6.8 Hz, 1H, CH), 2.85 (dq, J = 7.3, 6.8 Hz, 1H, CH), 3.16 (t, J = 7.3 Hz, 2H, SCH_2), 3.30 (t, J = 7.3 Hz, 1H, CH), 4.85-5.50 (m, 4H, C=CH_2), 5.70 (ddd, J = 17.0, 10.4, 7.3 Hz, 1H, C*H*=C), 6.03 (ddd, J = 17.0, 10.4, 7.3 Hz, 1H, C*H*=C); ^{13}C NMR ($CDCl_3$) δ 13.7, 16.7, 18.4, 18.9, 22.3, 28.8, 39.3, 40.1, 40.6, 114.8, 115.1, 142.1, 142.3, 243.1.

3-Methyl-4-penteneselenothioic acid S-butyl ester (18): IR (neat) 3079, 2959, 2929, 2872, 1654, 1639, 1560, 1458, 1417, 1374, 1229, 1124, 990, 940, 914, 835, 682 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.93 (t, J = 7.3 Hz, 3H, CH_3), 1.06 (d, J = 6.3 Hz, 3H, CH_3), 1.45 (sex, J = 7.3 Hz, 2H, CH_2), 1.71 (m, 2H, CH_2), 2.91(m, 2H, CH_2), 2.86-2.99 (m, 1H, CH), 3.23 (t, J = 7.6 Hz, 2H, SCH_2), 4.94 (dd, J = 10.2, 1.2 Hz, 1H, C=CH*H*), 5.00 (dd, J = 7.0, 1.2 Hz, 1H, C=C*H*H), 5.75 (ddd, J = 17.1, 10.2, 7.0 Hz, 1H, CH=C); ^{13}C NMR ($CDCl_3$) δ 13.7, 19.1, 22.3, 28.9, 39.5, 40.7, 63.6, 113.7, 142.1, 242.1; EIMS (*m/z*) 250 (M^+); Anal. Calcd for $C_{10}H_{18}SSe$: C, 48.18; H, 7.28. Found: C, 48.03; H, 7.22.

*Z-3-Methyl-5-butylthio-6-selena-deca-1,4,8-triene (**20**)*: ^{1}H NMR ($CDCl_3$) δ 0.91 (t, J = 7.3 Hz, 3H, CH_3), 1.07 (d, J = 6.8 Hz, 3H, CH_3), 1.41 (sex, J = 7.3 Hz, 2H, CH_2), 1.55 (qui, J = 7.3 Hz, 2H, CH_2), 1.66 (d, J = 3.9 Hz, 3H, CH_3), 2.71 (t, J = 7.3 Hz, 1H, SCH_2), 2.73 (t, J = 7.3 Hz, 1H, SCH_2), 3.40-3.42 (m, 2H, $SeCH_2$), 3.51-3.54 (m, 1H, CH), 4.94-5.01 (m, 1H, C=C*H*H), 5.52-5.55 (m, 2H, CH=CH), 5.60-5.80 (m, 1H, C=CH*H*), 5.91 (d, J = 9.0 Hz, 1H, C=CH); HRMS Calcd for $C_{14}H_{24}SSe$: 304.07627. Found: 304.08008.

*2,3-Dimethyl-4-penteneselenothioic acid S-butyl ester (**21**)*: IR (neat) 2958, 2930, 2872, 2362, 1691, 1629, 1464, 1379, 1225, 1198, 1092, 893, 744, 590 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.96 (t, J = 7.6 Hz, 3H, CH_3), 0.98 (d, J = 6.4 Hz, 3H, CH_3), 1.27 (d, J = 6.6 Hz, 3H, CH_3), 1.47 (sex, J = 7.6 Hz, 2H, CH_2), 1.73 (qui, J = 7.6 Hz, 2H, CH_2), 2.71 (tq, J = 9.3, 6.4 Hz, 1H, CH), 3.20 (dq, J = 9.3, 6.6 Hz, 1H, CH), 3.27 (dt, J = 7.6, 5.6 Hz, 2H, SCH_2), 5.03 (dd, J = 9.7, 0 85 Hz, 1H, CH=C*H*H) 5.10 (dd, J = 17.0, 0.85 Hz, 1H, CH=CH*H*), 5.72 (ddd, J = 17.0, 9.7, 9.3 Hz, 1H, C*H*=CH_2). Irradiation at δ 1.27 showed a doublet (J = 9.3 Hz) at δ 3.20. Irradiation at δ 2.71 showed a quartet (J = 6.6 Hz) at δ 3.20. ^{13}C NMR ($CDCl_3$) δ 13.7 (CH_3), 19.1 (CH_3), 21.9 (CH_3), 22.3 (CH_2), 28.9 (CH_2), 39.5 (SCH_2), 45.5 (CH), 64.6 (CH), 115.2 (*C*H=CH_2), 141.7 (CH=*C*H_2), 251.1 (C=Se); EIMS (*m/z*) 264 (M^+), 209 (M^+-crotyl); HRMS Calcd for $C_{11}H_{20}SSe$: 264.04499. Found: 264.04075.

*2-(1-Methyl-2-propenyl)hexaneselenothioic acid S-butyl ester (**22**)*: IR (neat) 3076, 2958, 2928, 2859, 1639, 1458, 1417, 1378, 1295, 1142, 1074, 994, 901, 838, 730, 689, 588 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.76 (t, J = 7.0 Hz, 3H, CH_3), 0.88 (d, J = 7.2 Hz, 3H, CH_3), 0.89 (t, J = 7.4 Hz, 3H, CH_3), 1.00-1.34 (m, 4H, CH_2), 1.40 (sex, J = 7.4 Hz, 2H, CH_2), 1.57-1.68 (m, 1H, CH_2), 1.66 (qui, J = 7.4 Hz, 2H, CH_2), 1.75-1.84 (m, 1H, CH_2), 2.68 (dquint, J = 9.9, 7.2 Hz, 1H, CH), 3.00 (dt, J = 9.9, 2.4 Hz, 1H, CH), 3.23 (dt, J = 7.4, 2.4 Hz, 2H, SCH_2), 4.95 (dd, J = 10.1, 1.4 Hz, 1H, C=C*H*H), 5.01 (dd, J = 17.1, 1.4 Hz, 2H, C=CH*H*), 5.63 (ddd, J = 17.1, 10.1, 7.1 Hz, 1H, CH=C). Double irradiation at δ 1.66 and 1.87 showed a doublet (J = 9.9 Hz) at δ 3.00. ^{13}C NMR ($CDCl_3$) δ 13.7, 13.9, 19.1, 22.3, 22.6, 28.9, 29.4, 35.4, 39.5, 45.3, 70.2, 115.1, 142.3, 249.9; EIMS (*m/z*) 306 (M^+); HRMS Calcd for $C_{14}H_{26}SSe$: 306.09191. Found: 306.09394.

*3-Methyl-2-(2-propenyl)-4-penteneselenothioic acid S-butyl ester (**23**)*: IR (neat) 3077, 2959, 2929, 2873, 1718, 1640, 1457, 1436, 1417, 1373, 1246, 1217, 1108, 994, 915, 844, 692 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.95 (t, J = 7.5 Hz, 3H, CH_3), 0.97 (d, J = 6.8 Hz, 3H, CH_3), 1.45 (sex, J = 7.5 Hz, 2H, CH_2), 1.71 (qui, J = 7.5 Hz, 2H, CH_2), 2.46-2.49 (m, 1H, CH_2), 2.54-2.59 (m, 1H, CH_2), 2.70 (ddq, J = 9.4, 7.2, 6.8 Hz, 1H, CH), 3.14 (dt, J = 9.4, 3.7 Hz, 1H, CH), 3.27 (t, J = 7.5 Hz, 2H, SCH_2), 4.90 (dd, J = 10.0, 1.5 Hz, 1H, C=C*H*H), 4.94 (dd, J = 17.2, 1.5 Hz, 1H, C=C*H*H), 5.06 (dd, J = 10.1, 1.6 Hz, 1H, C=CH*H*), 5.11 (dd, J = 17.2, 1.6 Hz, 1H, C=CH*H*), 5.63 (ddt, J = 17.2, 10.0, 7.2 Hz, 2H, CH=C), 5.72 (ddd, J = 17.2, 10.1, 9.1 Hz, 2H, CH=C). Double irradiation at δ 2.46 and 2.58 showed a doublet (J = 9.4 Hz) at δ 3.14. Double irradiation at δ 0.97 and 2.58 showed a doublet (J = 9.4 Hz) at δ 2.70. ^{13}C NMR ($CDCl_3$) δ 13.7, 19.0, 22.3, 28.8, 39.4 , 40.2, 44.9, 69.8, 115.6, 116.3, 135.6, 141.8, 247.7; EIMS (*m/z*) 290 (M^+); HRMS Calcd for $C_{13}H_{22}SSe$: 290.06063. Found: 290.05808.

*A typical experimental procedure for the synthesis of monoallylated selenothioic acid S-alkyl esters is represented by the synthesis of 4-penteneselenothioic acid S-butyl ester (**3**)*:

To an Et_2O solution (3 mL) of trimethylsilylacetylene (**24**) (0.145 mL, 1.0 mmol) was added butyllithium (0.625 mL, 1.0 mmol) at 0 °C. After stirring at this temperature for 15 min, selenium powder

(0.083 g, 1.1 mmol) was added at 0 °C, and this was stirred at room temperature for 5 min. To this was added 1-butanethiol (0.215 mL, 2.0 mmol) at 0 °C, and this was stirred at 0 °C for 30 min and at room temperature for additional 1 h. Then, THF (3 mL) and 3-bromo-1-propene (**2**) (0.18 mL, 2.0 mmol) were added sequentially to the reaction mixture at -78 °C, and it was stirred at this temperature for 15 min and at room temperature for 15 min . After stirring at reflux temperature for 3 h, the reaction mixture was poured into water, and extracted with ether. The organic layer was dried over magnesium sulfate and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel using hexane as eluent to give 0.175 g (74%) of **3** as a deep pink oil: IR (neat) 3078, 2959, 2930, 2873, 1685, 1641, 1560, 1458, 1438, 1207, 1137, 990, 916, 875, 760, 650 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.95 (t, J = 7.3 Hz, 3H, CH_3), 1.46 (sex, J = 7.4 Hz, 2H, CH_2), 1.73 (sex, J = 7.4 Hz, 2H, CH_2), 2.61-2.67 (m, 2H, CH_2), 3.01 (t, J = 7.6 Hz, 2H, CH_2), 3.24 (t, J = 7.4 Hz, 2H, SCH_2), 5.00 (dd, J = 10.3, 1.5 Hz, 1H, C=C*H*H), 5.08 (dd, J = 17.1, 1.5 Hz, 1H, C=CH*H*), 5.84 (ddt, J = 17.1, 13.5, 6.7 Hz, 1H, CH=C); ^{13}C NMR ($CDCl_3$) δ 13.7, 22.3, 28.9, 35.3, 40.7, 56.4, 115.9, 136.2, 243.1; EIMS (*m/z*) 236 (M^+); Anal. Calcd for $C_9H_{16}SSe$: C, 45.95; H, 6.86. Found: C, 45.65; H, 6.89.

3-Methyl-2-trimethylsilyl-4-penteneselenothioic acid S-butyl ester (26): IR (neat) 3077, 2958, 2929, 2874, 1639, 1560, 1458, 1419, 1368, 1294, 1248, 1183, 1145, 1102, 1062, 1036, 998, 980, 916, 895, 842, 755, 689, 622, 519 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.11 (s, 9H, CH_3), 0.93 (t, J = 7.4 Hz, 3H, CH_3), 1.01 (d, J = 6.1 Hz, 3H, CH_3), 1.44 (sex, J = 7.4 Hz, 2H, CH_2, 1.65-1.73 (m, 2H, CH_2), 3.22 (dd, J = 8.1, 7.0 Hz, 1H, SCH_2), 3.28-3.33 (m, 2H, CHSi, CH), 3.31(dd, J = 8.3, 7.0 Hz, 1H, SCH_2), 5.00 (dd, J = 10.2, 1.7 Hz, 1H, C=C*H*H), 5.14 (dd, J = 17.2, 1.7 Hz, 1H, C=CH*H*), 5.76 (ddd, J = 17.2, 10.2, 9.0 Hz, 1H, C=CH); ^{13}C NMR ($CDCl_3$) δ -1.5, 13.7, 21.0, 22.3, 29.2, 39.7, 43.6, 69.7, 114.5, 143.2, 246.3; EIMS (*m/z*) 322 (M^+); Anal. Calcd for $C_{13}H_{26}SSeSi$: C, 48.57; H, 8.15. Found: C, 48.51; H, 8.39.

3,3-Dimethyl-4-penteneselenothioic acid S-butyl ester (28): IR (neat) 3084, 2960, 2928, 2872, 1638, 1459, 1414, 1380, 1203, 1172, 1107, 981, 913, 812 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.94 (t, J = 7.3 Hz, 3H, CH_3), 1.17 (s, 6H, $C(CH_3)_2$), 1.45 (sex, J = 7.3 Hz, 2H, CH_2), 1.71 (q, J = 7.4 Hz, 2H, CH_2), 3.19 (s, 2H, CCH_2), 3.19 (t, J = 7.6 Hz, 2H, SCH_2), 4.93 (dd, J = 17.3, 1.2 Hz, 1H, C=C*H*H), 4.95 (dd, J = 11.0, 1.2 Hz, 1H, C=CH*H*), 5.95 (dd, J = 17.3, 11.0 Hz, 1H, CH=C); ^{13}C NMR ($CDCl_3$) δ 13.7, 22.3, 27.1, 28.8 , 36.5 ($C(CH_3)$), 41.8, 69.6, 111.2, 147.1, 238.5; EIMS (*m/z*) 263 (M^+); Anal. Calcd for $C_{11}H_{20}SSe$: C, 50.25; H, 7.67. Found: C, 50.20; H, 7.90.

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9 Although the direct comparison of the reaction rate between the thio-[10] and seleno-Claisen rearrangement is not easy, the latter one proceeds as smoothly as the former one even if a selenocarbonyl group, which has been believed to be an unstable functional group, is formed in the latter case.

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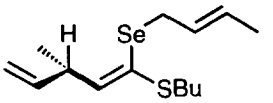
12. In the latter step, 2-butenyl group can approach to a vinyl group from the side close to either methyl group or vinyl group if **20** adopts an eclipse comformation through the bond depicted with bold line as shown right.



20

13. The stereochemical assignment of the products was based on the coupling constant (J = 9.3 Hz for **21**, J = 9.9 for **22**) between the protons attached to the α-carbon of the selenocarbonyl group and to the allylic carbon. The coupling constant observed for **21** and **22** was close to typical values for *erythro* isomers.[14] The stereochemistry of **22** was further confirmed by a phase sensitive NOESY spectrum.

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15. On the basis of a phase sensitive NOESY spectrum the product **23** was tentatively assigned to be a *threo* isomer.

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18. Ester **26** was obtained as a stereoisomeric mixture in a ratio of 92 : 8, although the stereochemistry has not been determined.

19. Protodesilylation of **26** with KF in MeOH proceeded smoothly to give ester **18**.

20. The protodesilylation was complete mainly during the purification of the products by column chromatography on silica gel. In some cases the silyl group was partly replaced with proton in the aqueous work-up.

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