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Generation and characterization of aliphatic selenothioic acid salts

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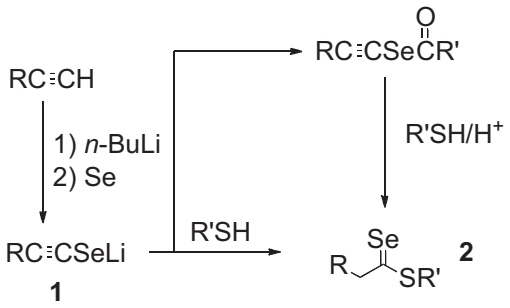
ABSTRACT

The reaction of thioic acid *O*-methyl esters with in situ generated aluminum 2-(trimethylsilyl)ethylselenolate gave selenothioic acid *Se*-(2-trimethylsilyl)ethyl esters in 56–78% yields. The resulting four esters were treated with a THF solution of tetrabutylammonium fluoride (TBAF) to generate selenothioic acid ammonium salts in low to good yields. The efficiency of the generation of the salts depended on the substituents α to the selenocarbonyl group. Fluoride ion in TBAF partly worked as a base to deprotonate from the esters to generate ammonium enethiolates as by-products. Methylation of the acid salts with methyl iodide took place selectively at the selenium atom to give selenothioic acid Se-methyl esters in 48–68% yields. Instead of TBAF, Me_4NF and KF/18-crown-6 were used to generate the salts with other counter cations. The spectroscopic properties of the esters and salts suggested that resonance structures involving carbon–selenium double bonds also contribute to the resonance hybrids of the salts.

1. Introduction

It is important that we clarify the properties of selenium isologues of dithioic acids[1] and their salts[2] in organic chemistry because the replacement of a sulfur atom in organosulfur compounds with a selenium atom may give rise to compounds with greater instability and unique properties.[3] In fact, dithioic acid, salts and their esters (RC(S)SR′)[4] have been well-known compounds for over 100 years, and their application as metal ligands,[5] organocatalysts,[6] and key synthetic compounds[7] has been intensively continued even in very recent years. The synthesis of dithioic acid esters has generally used commercially available carbon disulfide (CS_2). In contrast, a similar approach to selenium isologues is not an easy way since carbon selenide sulfide (CSeS)[8] is highly labile and not readily available. Although selenium isologues are still of theoretical interest,[9] selenothioic acid *S*-esters and *Se*-esters had been ambiguous species[10] until Kato and co-workers established several synthetic methods[11] leading to these compounds. For the synthesis of aliphatic selenothioic acid *S*-esters, lithium alkyneselenolates **1** generated from terminal alkynes are used as key precursors (Scheme 1). Their reactions with alkanethiols gave a series of the corresponding esters **2**. Alternatively, acylation of lithium alkyneselenolates led to selenoic acid *Se*-alkynyl esters, and the subsequent addition of thiols under acidic conditions gave the esters **2**. In the former case, the use of silylacetylenes was highly effective, whereas a range of terminal acetylenes could be used in the latter.



Scheme 1. Synthesis of selenothioic acid *S*-esters **2**.

With these methods, a variety of selenothioic acid *S*-esters **2**[12] were prepared, and new reactions using them were developed.[13] For example, in allylation of the ester **2a** with excess allyl bromide in the presence of Et_3N, three allyl groups were effectively introduced to the carbon atom α to the selenocarbonyl group to give the ester **2b** (Scheme 2).[14] The further reaction of **2b** with tetrabutylammonium fluoride (Bu_4NF, TBAF) led to the first example of aliphatic selenothioic acid ammonium salt **3a** (Scheme 3).[15] Despite the fact that tremendous amounts of examples of dithioic acid salts have been reported, as their selenium isologues an inner salt bearing a selenothiocarboxyl group was only reported around the same time.[16] Formation of the salt **3a** was accompanied by the elimination of trimethylsilyl fluoride and ethylene from **2b**. We report here the details of the generation of aliphatic selenothioic acid salts and their characterization.

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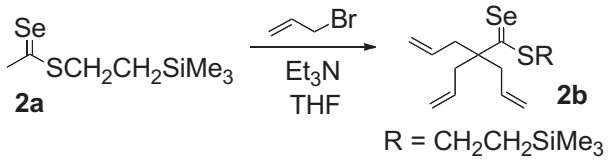
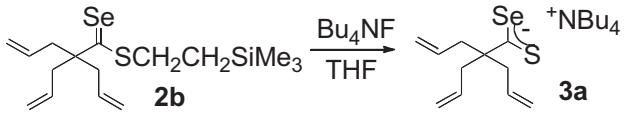


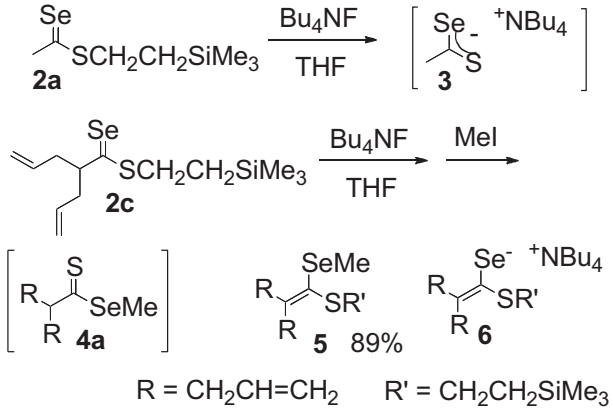
Scheme 2. Triallylation of selenothioic acid *S*-ester **2a**.



Scheme 3. Generation of selenothioic acid salt **3a**.

2. Results and discussion

Initially, enolizable selenothioic acid *S*-2-(trimethylsilyl)ethyl esters were subjected to the reaction with TBAF. To confirm the formation of the desired salt **3a**, alkyl halides were added to the reaction mixture of **3** and TBAF (Scheme 4).

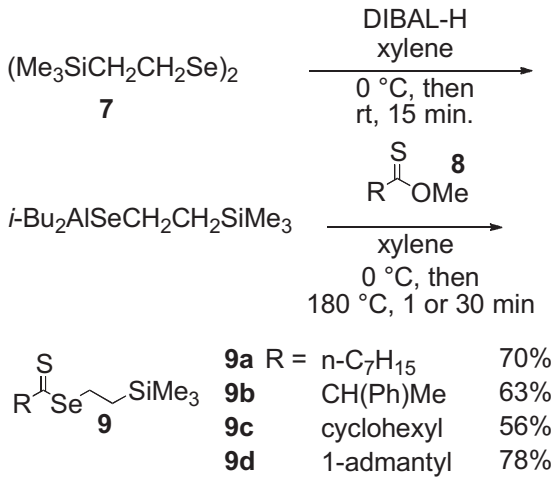


Scheme 4. Attempts to generate selenothioic acid salts **3**.

However, the reaction of the ester **2a** with TBAF and alkyl halides gave complex mixtures. In contrast, the reaction of **2c** with TBAF followed by methylation proceeded smoothly, but did not give the desired ester **4a**. Instead, selenothioketene acetal **5** was obtained in 89% yield. This suggested the formation of ammonium eneselenolate **6**, and the methylation of **6** selectively takes place at the selenium atom. In this case, Bu_4NF acts as a base to deprotonate the α-proton of the ester **2c** even if the fluoride ion shows high affinity toward a silicon atom. As starting esters with less acidic α-protons, the use of selenothioic *Se*-2-(trimethylsilyl)ethyl esters **9** was envisioned, since the acidity of α-protons is believed to be reduced on going from C=Se, to C=S, and C=O.

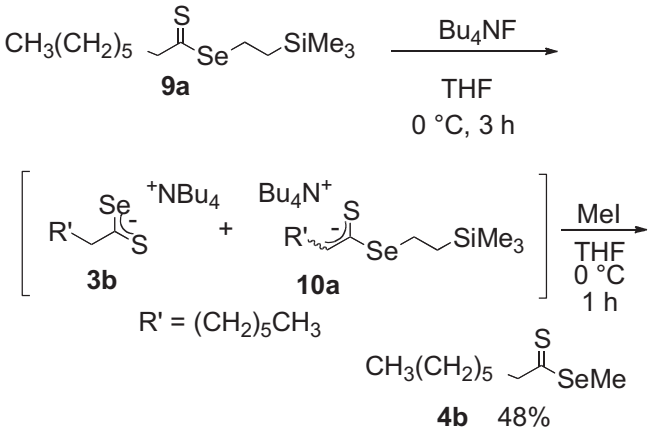
Aliphatic selenothioic acid *Se*-2-(trimethylsilyl)ethyl esters **9** were prepared by reacting aluminum 2-(trimethylsilyl)ethylselenolate generated in situ from diselenide **7**[17] and DIBAL–H with the corresponding thioic acid *O*-methyl esters **8** (Scheme 5). In the reaction at 180 °C for 1 min, the desired products **9a**–**9c** were obtained, whereas a longer reaction time (30 min) was necessary for the synthesis of *Se*-ester **9d**. These *Se*-esters **9** are stable under an atmosphere of inert gas at room temperature.

The generation of selenoic acid salts from esters **9** was then carried out (Schemes 6, 7, and 9). Ester **9a** was treated with a THF solution of TBAF. The reaction mixture gradually changed from yellow to red. After the mixture was stirred at 0 °C for 0.5 h, the



Scheme 5. Synthesis of selenothioic acid *Se*-esters **9**.

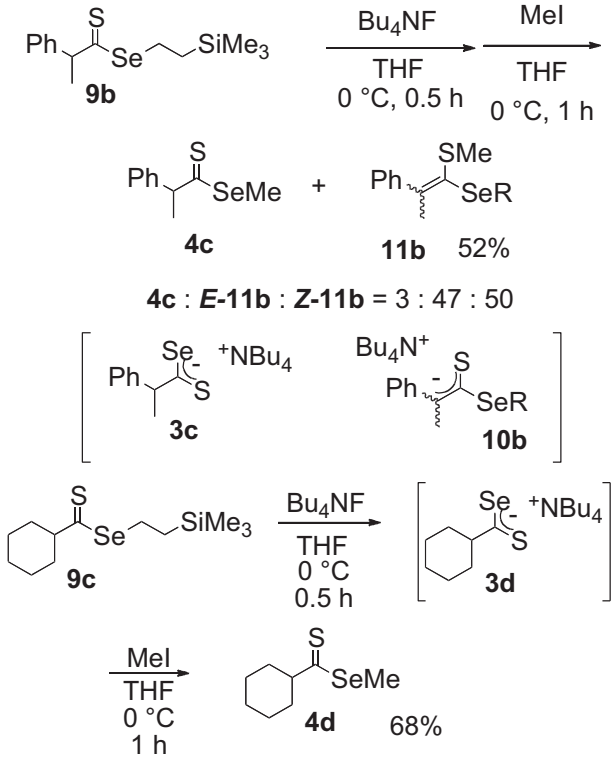
solvent was removed under reduced pressure to give a red oil. The NMR spectra of the red oil implied the formation of the desired selenothioic acid salt **3b** along with the formation of ammonium enethiolate **10a** as a mixture of *E* and *Z* isomers. Nevertheless, the treatment of the reaction mixture of **9a** and TBAF after 3 h with methyl iodide gave selenothioic acid *Se*-methyl ester **4b** as an isolable product. Although the selectivity of the reaction that leads to the salt **3b** was not high, our idea that the desilylethylation from **9** led to salts **3** worked to some extent.



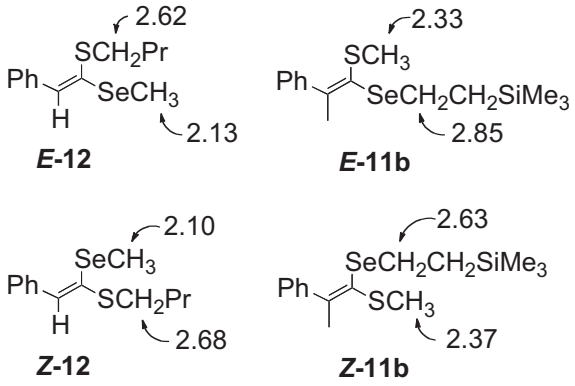
Scheme 6. Generation of selenothioic acid salt from **9a** and its methylation.

To reduce the deprotonation from the site α to the thiocarbonyl group, α,α-disubstituted selenothioic acid *Se*-esters **9b** and **9c** were then used as starting materials (Scheme 7). In the NMR spectra of the mixture of **9b** and TBAF, the signals ascribed to the salt **3c** were observed, but methylation of the reaction mixture mainly gave selenothioketene acetal **11b** as a stereoisomeric mixture along with a small amount of **4c**. Therefore, deprotonation from **9b** predominantly takes place at the position α to thiocarbonyl group of **9b** to generate **10b**. The stereochemistry of **11b** was determined by comparing ^{1}H NMR spectra of **11b** with those of similar compound **12**[18] (Scheme 8). The protons of alkyl groups attached to the sulfur atom oriented at the cis-position of a phenyl group in *E*-**11b** and *E*-**12** were observed at higher regions than those in *Z*-**11b** and *Z*-**12**. Similar tendencies were observed for the protons of alkyl groups attached to the selenium atom. In contrast to the reaction of **9b**, desilylethylation from the ester **9c** with TBAF proceeded followed

by the methylation to give ester **4d** in 68% yield. The isolation of the salt **3d** as a pure form was not successful since excess TBAF could not be removed, but NMR spectra showed **3d** was formed in good yield.



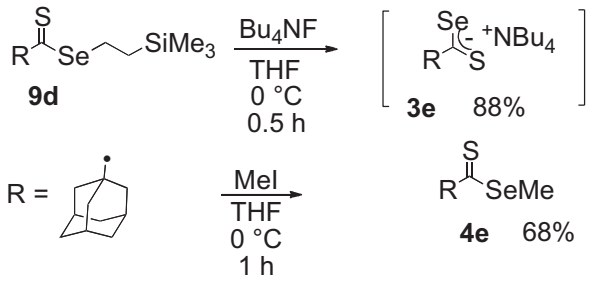
Scheme 7. Generation of selenothioic acid salts from **9b** and **9c** and their methylation.



Scheme 8. Chemical shifts of selenothioketene acetals **11b** and **12** in ^{1}H NMR spectra.

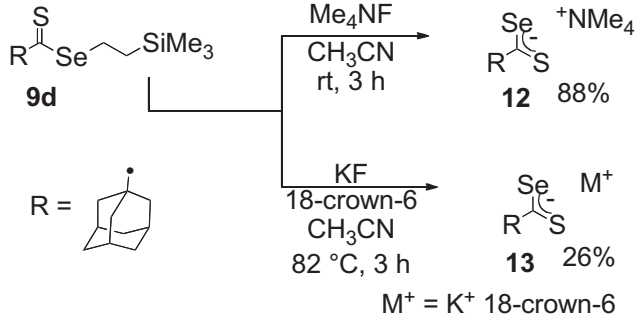
Adamantanecarboselenothioic acid *Se*-ester **9d** was used as an example of trisubstituted esters (Scheme 9). The crude products were washed with hexane several times, and concentrated in vacuo to form the desired salt **3e** as a red-brown oil. The NMR spectra of the salt showed that it was formed in a pure form, although they were slightly contaminated with unreacted TBAF. Methylation of the salt **3e** also took place selectively at the selenium atom to give selenothioic acid *Se*-ester **4e** in good yields.

Finally, the generation of selenothioic acid salts with other counter cations was examined (Scheme 10). Instead of a THF solution of TBAF, Me_4NF and KF were used in CH_3CN. In the latter case, 18-crown-6 was also used as an additive. The reactions proceeded smoothly, and the starting ester **9d** was consumed within 3 h. The



Scheme 9. Generation of selenothioic acid salt from **9d** and its methylation.

precipitates were filtered through a glass filter, and the reaction mixture was concentrated. To the residue was added Et_2O, and the filtration of the solution gave the corresponding salts **12** and **13** as deep green and gray solids, respectively.



Scheme 10. Generation of selenothioic acid salts **12** and **13** from **9d**.

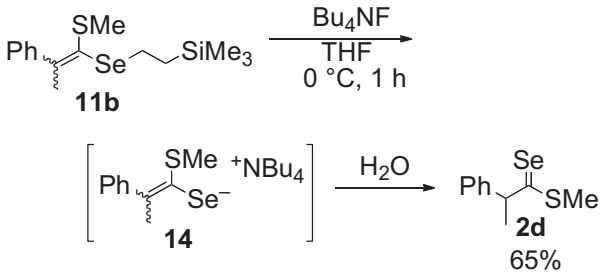
The spectroscopic properties of some esters and salts are summarized in Table 1. As observed for aromatic selenothioic acid esters and salts, in ^{77}Se and ^{13}C NMR spectra, the signals due to esters **9c** and **9d** were observed at ca. 830 ppm, i.e., at higher fields than those due to salts **3d** and **3e**. These values are larger than those of selenoic acid *O*-esters and selenoamides, which clearly possess carbon–selenium double bonds in the compounds.[3c,19] The coupling constants between the carbon and selenium bonds of salts **3** were greater than those of esters **9**. In the UV/vis spectra, the longest wavelengths of salts **3** were red-shifted compared to those of esters **9**. These results suggested resonance structures involving selenium–carbon double bonds also contribute to the resonance hybrids of salts **3**.

Table 1
Spectroscopic properties of esters **9** and salts **3**

Compd	δ		$^{1}J_{C=Se}$[a] (Hz)	UV/vis[b] λ_{max} (nm)
	^{77}Se NMR[a]	^{13}C NMR[a]		
9c	836.6	252.0	168.5	477
9d	827.8	258.9	172.3	486
3d	1090.7	273.4	—[c]	522
3e	1064.0	279.6	209.2	575

[a] $CDCl_3$ was used for **9** and THF-d_8 was used for **3**.
[b] THF was used as a solvent.
[c] Not determined.

Additionally, selenothioketene acetal **11b** was used as a precursor of selenothioic acid *S*-ester **2d** (Scheme 11). The reaction of **11b** with TBAF went to completion within 1 h, and aqueous workup of the reaction mixture gave **2d** as a stable purple oil in good yield.



Scheme 11. Conversion of **11b** to selenothioic acid ester **2d**.

3. Conclusion

In summary, the generation and characterization of aliphatic selenothioic acid salts were described. As precursors of the salts, selenothioic acid *Se*-(2-trimethylsilyl)ethyl esters were prepared by the reaction of thioic acid *O*-methyl esters with aluminum 2-(trimethylsilyl)ethylselenolate. Treatment of the esters with TBAF could lead to the salts. Deprotonation from the esters competitively took place depending on the substituents α to the thiocarbonyl group. Methylation of the salts occurred selectively at the selenium atom of the salts to give selenothioic acid *Se*-esters with high efficiency. The spectroscopic properties of the salts suggested that carbon–selenium bonds have a double-bond character.

4. Experimental section

4.1. General information

Characterization: Melting points were measured by a Yanagimoto micromelting point apparatus (uncorrected). The IR spectra were obtained on a PERKIN ELMER FT-IR 1640 and JASCO FT/IR 410 spectrophotometers. The ^{1}H NMR spectra were measured on a JEOL α-400 (399.7 MHz) in $CDCl_3$, THF-d_8, and DMSO-d_6. Chemical shifts of protons are reported in δ values referred to tetramethylsilane as an internal standard. The ^{13}C (100.4 MHz) NMR spectra and the ^{77}Se (76.2 MHz) NMR spectra were measured on the spectrometer JEOL α-400. The ^{77}Se chemical shifts are expressed in δ values deshielded with respect to Me_2Se as an external standard. UV/vis spectra were measured on a JASCO U best 55 or HITACHI U-4000. The mass spectra (MS) were taken on SHIMADZU GCMS QP1000 (EI mode) and GCMS 9020DF high resolution mass spectrometers. The high resolution mass spectroscopy (HRMS) was taken on JEOL JMS-GCmate II GCMS SYSTEM. Elemental analyses were carried out by Elemental Analysis Center of Kyoto University.

Materials: Diethyl ether (Et_2O) and tetrahydrofuran (THF) were distilled from sodium/benzophenone ketyl prior to use. Acetonitrile and dichloromethane (CH_2Cl_2) were distilled from phosphorus pentoxide. Xylene was distilled from calcium hydride. Anhydrous tetramethylammonium fluoride[20] was obtained from the tetramethylammonium fluoride tetrahydrate by removal of the water under reduced pressure (150 °C/1.0 mmHg) with stirring for about 1 h. Xylene, methyl iodide, and potassium fluoride were purchased from Nacalai Tesque, Inc., and used without further purification. 18-Crown-6 ether, tetrabutylammonium fluoride (in THF), and tetramethylammonium fluoride tetrahydrate were purchased from Aldrich Chemical Company, Inc., and used without further purification. Diisobutylaluminum hydride (DIBAL–H) 1.0 M hexane solution was purchased from Kanto Chemical Co., Inc. and used without further purification. Silica gel used in column chromatography was silica gel 60N from Kanto Chemical Co., Inc.

4.2. Synthetic procedure of selenothioacetic acid *S*-(2-trimethylsilyl)ethyl ester (2a)

In a 300 mL three-necked flask, BuLi (12.8 mL, 20.0 mmol) was added to an Et_2O (200 mL) solution of (trimethylsilyl)acetylene (2.8 mL, 20.0 mmol) at 0 °C. After the stirring at 0 °C for 10 min, powder selenium (1.58 g, 20.0 mmol) was added to the resulting mixture at 20 °C, and it was stirred for 20 min. To this was added 2-(trimethylsilyl)ethanethiol (3.2 mL 20.0 mmol) at 0 °C, and the mixture was stirred for 30 min. The reaction mixture was poured into water, and extracted with Et_2O. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel using hexane as an eluent to give 2.68 g of **2a** (56%) as a purple oil; IR (neat) 2953, 2902, 1654, 1560, 1418, 1357, 1249, 1166, 1136, 1107, 1009, 1008, 824 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.06 (s, 9H, $SiMe_3$), 1.00 (m, 2H, CH_2Si), 2.55 (s, 3H, CH_3), 3.20 (m, 2H, SCH_2); ^{13}C NMR ($CDCl_3$) δ −1.8, 14.4, 44.9, 38.2 (SCH_2), 44.9 (CH_3), 237.8 (C=Se, $^1J_{C-Se}$=222.3 Hz); ^{77}Se NMR ($CDCl_3$, Me_2Se) δ 1501.9; MS (EI) *m*/*z* 240. Anal. Calcd for $C_7H_{16}SSeSi$; C, 35.13; H, 6.74. Found: C, 35.35; H, 7.03.

4.3. Synthetic procedure for 2-(2-propenyl)-4-penteneselenothioic acid *S*-2-(trimethylsilyl)ethyl ester (2c)

In a 50 mL three-necked flask, to a solution of ester **2a** (0.723 g, 3.0 mmol) and 3-bromo-1-propene (0.51 mL, 5.9 mmol) in 20 mL of THF was added Et_3N (0.84 mL, 0.59 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 2 h. The reaction mixture was poured into water, and extracted with Et_2O. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel using hexane as an eluent to give 0.43 g of **2c** (56%) as a purple oil; IR (neat) 3077, 2953, 2904, 1641, 1560, 1508, 1438, 1250, 1165, 1007, 916, 858 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.06 (s, 9H, $SiMe_3$), 0.98 (m, 2H, CH_2Si), 2.39 (ddd, *J*=5.9, 7.1, 13.4 Hz, 2H, CH_2), 2.61 (ddd, *J*=7.0, 8.2, 15.1 Hz, 2H, CH_2), 3.22 (m, 2H, SCH_2), 3.37 (tt, *J*=5.8, 8.4 Hz, 1H, CH), 4.96–5.04 (m, 4H, CH_2), 5.71 (ddt, *J*=7.01, 10.2, 17.1 Hz, 2H, CH); ^{13}C NMR ($CDCl_3$) δ −1.7, 14.3, 36.2, 41.1, 64.2, 116.9, 135.3, 248.0 (C=Se, $^1J_{C-Se}$=224.3 Hz); ^{77}Se NMR ($CDCl_3$, Me_2Se) δ 1423.9; MS (EI) *m*/*z* 320. Anal. Calcd for $C_{13}H_{24}SSeSi$; C, 48.88; H, 7.57. Found: C, 48.63; H, 7.47.

4.4. Reaction of ester 2c with TBAF and methyl iodide leading to selenothioketene acetal 5

In a 20 mL two-necked flask, tetrabutylammonium fluoride (0.3 mL, 0.3 mmol) was added to a THF (5 mL) solution of ester **2c** (0.096 g, 0. 3 mmol) at 0 °C. After stirring at 0 °C for 3 h, methyl iodide (0.05 mL, 0.8 mmol) was added at 0 °C, and the stirring was continued for 1 h. The reaction mixture was poured into water, and extracted with Et_2O. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel using hexane as an eluent to give 0.098 g of **5** (89%) as a yellow oil; IR 3079, 2954, 2897, 1637, 1425, 1380, 1249, 1161, 1081, 993, 941, 912, 861 cm^{-1}; ^{1}H NMR δ 0.00 (s, 9H, $SiMe_3$), 0.80 (m, 2H, CH_2), 2.15 (s, 3H, SeMe), 2.69 (m, 2H, CH_2), 3.20 (dt, *J*=1.5, 6.3 Hz, 2H, CH_2), 3.25 (dt, *J*=1.5, 6.6 Hz, 2H), 5.01 (m, 4H, CH_2), 5.71 (m, 2H, CH); ^{13}C NMR δ −1.7, 8.1, 17.5, 31.2, 39.7, 41.3, 115.9, 124.5, 135.3, 135.5, 147.4; ^{77}Se NMR ($CDCl_3$, Me_2Se) δ 170.5; MS (EI) *m*/*z* 334; HRMS calcd for $C_{14}H_{26}SSeSi$ (M^+): 334.0690, found: 334.0701.

4.5. General procedure for the synthesis of selenothioic acid *Se*-(2-trimethylsilyl)ethyl esters 9

In a 20 mL two-necked round-bottom flask, a xylene solution of 1.0 M DIBAL–H in hexane (2.5 mL, 2.5 mmol) was added to a xylene

solution (2 mL) of diselenide **7** (0.360 g, 1.00 mmol) at 0 °C, and the mixture was stirred at 25 °C for 15 min. A xylene solution (2 mL) of thioic acid *O*-methyl ester **8** (4.00 mmol) was added to the resulting mixture at 0 °C, and the mixture was heated at 180 °C. The reaction mixture was poured onto ice/water mixture, and extracted with Et_2O. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel using hexane as an eluent to give **9** as a yellow oil.

*4.5.1. Octaneselenothioic acid Se-2-(trimethylsilyl)ethyl ester (**9a**).* A yellow oil; IR (neat) 2925, 2855, 1794, 1719, 1460, 1401, 1249, 869 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.05 (s, 9H, $SiMe_3$), 0.86 (t, J=6.8 Hz, 3H, CH_3), 0.99–1.04 (m, 2H, CH_2Si), 1.26–1.32 (m, 8H, CH_2), 1.80 (quint, J=7.3 Hz, 2H, CH_2), 3.02 (t, J=7.6 Hz, 2H, CH_2), 3.20–3.25 (m, 2H, $SeCH_2$); ^{13}C NMR ($CDCl_3$) δ −1.79, 14.1, 16.4, 22.6, 28.8, 29.0, 29.3, 31.4, 31.7, 55.6, 246.0 (C=S: $^1J_{C-Se}$=166.7 Hz); ^{77}Se NMR ($CDCl_3$, Me_2Se) δ 851.4; UV/vis (THF) λ_{max} (log ε) 476 (1.51), 339 (4.24), 269 (4.10), 221 (4.49) nm; MS (EI) m/z 323 (M^+); HRMS Calcd for $C_{13}H_{28}SSeSi$: (M^+) 324.0846, Found: 324.0824.

*4.5.2. dl-2-Phenylpropaneselenothioic acid Se-2-(trimethylsilyl)ethyl ester (**9b**).* An orange oil; IR (neat) 3027, 2953, 2925, 1600, 1493, 1451, 1248, 861, 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.04 (s, 9H, $SiMe_3$), 0.94–0.99 (m, 2H, CH_2Si), 1.70 (d, J=6.8 Hz, 3H, CH_3), 3.16–3.21 (m, 2H, $SeCH_2$), 4.58 (q, J=7.2 Hz, 1H, CH), 7.24 (t, J=6.3 Hz, 1H, Ar), 7.31 (t, J=7.1 Hz, 2H, Ar), 7.40 (d, J=6.8 Hz, 2H, Ar); ^{13}C NMR ($CDCl_3$) δ −1.82, 16.0, 22.4, 29.1, 62.8, 127.2, 127.8, 128.5, 142.0, 248.9 (C=S: $^1J_{C-Se}$=169.9 Hz); ^{77}Se NMR ($CDCl_3$, Me_2Se) δ 848.5; UV/vis (THF) λ_{max} (log ε) 480 (1.77), 341 (4.18), 227 (4.65) nm; MS (EI) m/z 329 (M^+). Anal. Calcd for $C_{14}H_{22}SSeSi$: C, 51.04; H, 6.73. Found: C, 50.97; H, 6.61.

*4.5.3. Cyclohexanecarboselenothioic acid Se-2-(trimethylsilyl)ethyl ester (**9c**).* A yellow oil; IR (neat) 2930, 2853, 1447, 1248, 1185, 927, 860, 782, 695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.05 (s, 9H, $SiMe_3$), 0.98–1.03 (m, 2H, CH_2Si), 1.15–1.38 (m, 3H, cyclohexyl), 1.59–1.73 (m, 3H, cyclohexyl), 1.78–1.82 (m, 2H, cyclohexyl), 1.90–1.94 (m, 2H, cyclohexyl), 3.12–3.24 (m, 3H, cyclohexyl, $SeCH_2$); ^{13}C NMR ($CDCl_3$) δ −1.78, 16.3, 25.7, 26.1, 28.2, 34.7, 63.4, 252.0 (C=S: $^1J_{C-Se}$=168.5 Hz); ^{77}Se NMR ($CDCl_3$, Me_2Se) δ 836.6; UV/vis (THF) λ_{max} (log ε) 477 (1.37), 338 (4.18), 274 (4.41), 221 (4.47) nm; MS (EI) m/z 307 (M^+) 127 (M^+−$SeCH_2CH_2SiMe_3$); HRMS calcd for $C_{12}H_{24}SSeSi$: (M^+) 308.0533, found: 308.0530.

*4.5.4. Adamantanecarboselenothioic acid Se-2-(trimethylsilyl)ethyl ester (**9d**).* An orange solid; mp 72–74 °C; IR (KBr) 2901, 2847, 1448, 1342, 1246, 1150, 1051, 1035, 858, 836 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.05 (s, 9H, $SiMe_3$), 0.96–1.01 (m, 2H, CH_2Si), 1.68–2.12 (m, 15H, Ad), 3.15–3.20 (m, 2H, $SeCH_2$); ^{13}C NMR ($CDCl_3$) δ −1.75, 15.8, 28.2, 29.1, 36.6, 44.1, 56.9, 258.9 (C=S: $^1J_{C-Se}$=172.3 Hz); ^{77}Se NMR ($CDCl_3$, Me_2Se) δ 827.8; UV/vis (THF) λ_{max} (log ε) 486 (1.56), 340 (4.09), 274 (4.52), 231 (4.45) nm; MS (EI) m/z 359 (M^+). Anal. Calcd for $C_{16}H_{28}SSeSi$: C, 53.45; H, 7.85. Found: C, 53.52; H, 8.03.

4.6. General procedure for the reaction of selenothioic acid *Se*-2-(trimethylsilyl)ethyl esters 9 with tetrabutylammonium fluoride and the methylation of the resulting solution

In a 20 mL two-necked flask, tetrabutylammonium fluoride (0.2 mL, 0.2 mmol) was added to a THF solution of selenothioic acid *Se*-2-(trimethylsilyl)ethyl esters **9** (0.2 mmol) at 0 °C. After being stirred at 0 °C for an appropriate time, the reaction mixture was concentrated to give selenothioic acid salts **3** and/or enethiolates **10**. For methylation of the salts **3** and/or **10**, the methyl iodide was added to the reaction mixture of **9** and Bu_4NF, and the mixture was stirred at 0 °C for 1 h. The reaction mixture was poured into water, and extracted with CH_2Cl_2. The organic layer was collected, dried over $MgSO_4$, and concentrated to give crude products, which were purified by column chromatography on silica gel to give the corresponding methylated products **4** and/or **11**.

*4.6.1. Tetrabutylammonium octaneselenothioate (**3b**).* ^1H NMR (THF-d_8) δ 0.88 (t, J=7.5 Hz, 3H, CH_3), 0.98 (t, J=7.3 Hz, 12H, CH_3), 1.29–1.39 (m, 8H, CH_2), 1.42 (sex, J=7.3 Hz, 8H, CH_2), 1.74 (br, 8H, CH_2), 3.52 (br, 8H, CH_2), the protons (CH_2CSSe) were not identified; ^{13}C NMR (THF-d_8): δ 267.1 (C=Se); ^{77}Se NMR (THF-d_8, Me_2Se): δ 1114.2.

*4.6.2. Octaneselenothioic acid Se-methyl ester (**4b**).* A yellow oil; IR (neat) 3423, 3068, 2925, 1794, 1723, 1598, 1579, 1385, 1145, 963, 876 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.86 (t, J=6.8 Hz, 3H, CH_3), 1.26–1.41 (m, 8H, CH_2), 1.82 (quint, J=7.6 Hz, 2H, CH_2), 2.53 (s, 3H, $SeCH_3$), 3.06 (t, J=7.8 Hz, 2H, CH_2); ^{13}C NMR ($CDCl_3$) δ 13.7, 14.1, 22.6, 28.7, 29.0, 31.4, 31.7, 55.1, 245.3 (C=S: $^1J_{C-Se}$=162.8 Hz); ^{77}Se NMR ($CDCl_3$, Me_2Se) δ 721.6; UV/vis (THF) λ_{max} (log ε) 469 (1.47), 330 (4.11), 270 (4.26), 220 (4.47) nm; HRMS calcd for $C_9H_{18}SSe$: (M^+) 238.0294, found: 238.0281.

*4.6.3. Tetrabutylammonium phenylpropaneselenothioate (**3c**).* ^1H NMR (THF-d_8) δ 0.96 (t, J=7.3 Hz, 12H, CH_3), 1.37 (sex, J=7.3 Hz, 8H, CH_2), 1.55 (d, J=6.8 Hz, 3H, CH_3), 1.65 (br, 8H, CH_2), 3.33 (br, 8H, CH_2), 5.04 (q, J=7.2 Hz, 1H, CH), 7.03–7.15 (m, 1H, Ar), 7.63 (t, J=7.3 Hz, 2H, Ar), 8.28 (d, J=7.8 Hz, 2H, Ar); ^{13}C NMR (THF-d_8) δ 14.2, 20.6, 24.4, 24.9, 59.2, 73.0, 125.7, 127.7, 128.5, 146.6 (Ar), 268.4 (C=Se: $^1J_{C-Se}$=205.6 Hz); ^{77}Se NMR (THF-d_8, Me_2Se) δ 1144.7.

*4.6.4. Tetrabutylammonium E-1-(2-trimethylsilylethylseleno)-2-phenyl-1-propenethiolate (E-**10b**).* ^1H NMR (THF-d_8) δ 0.05 (s, 9H, $SiMe_3$), 0.96 (t, J=7.3 Hz, 12H, CH_3), 1.37 (sex, J=7.3 Hz, 8H, CH_2), 1.65 (br, 8H, CH_2), 2.14 (s, 3H, CH_3), 3.16–3.21 (m, 2H, $SeCH_2$), 3.33 (br, 8H, CH_2), 7.03–7.15 (m, 1H, Ar), 7.63 (t, J=7.3 Hz, 2H, Ar), 8.28 (d, J=7.8 Hz, 2H, Ar); ^{13}C NMR (THF-d_8) δ 2.0, 14.2, 20.6, 21.4, 22.9, 24.9, 30.7, 59.2, 124.8, 125.7, 127.7, 128.5 (Ar), 141.2, 146.6; ^{77}Se NMR (THF-d_8, Me_2Se) δ 462.5.

*4.6.5. Tetrabutylammonium Z-1-(2-trimethylsilylethylseleno)-2-phenyl-1-propenethioalte (Z-**10b**).* ^1H NMR (THF-d_8) δ −0.01 (s, 9H, $SiMe_3$), 0.96 (t, J=7.3 Hz, 12H, CH_3), 1.37 (sex, J=7.3 Hz, 8H, CH_2), 1.65 (br, 8H, CH_2), 2.34 (s, 3H, CH_3), 3.00–3.04 (m, 2H, $SeCH_2$), 3.33 (br, 8H, CH_2), 7.03–7.15 (m, 1H, Ar), 7.63 (t, J=7.3 Hz, 2H, Ar), 8.28 (d, J=7.8 Hz, 2H, Ar); ^{13}C NMR (THF-d_8) δ 2.0, 14.2, 20.6, 20.8, 24.9, 30.5, 30.9, 59.2, 124.6, 125.7, 127.7, 128.5, 140.6, 146.6; ^{77}Se NMR (THF-d_8, Me_2Se) δ 438.8.

*4.6.6. Phenylpropaneselenothioic acid Se-methyl ester (**4c**).* ^1H NMR ($CDCl_3$) δ 1.73 (d, J=6.8 Hz, 3H, CH_3), 2.47 (s, 3H, $SeCH_3$), 4.59 (q, J=7.1 Hz, 1H, CH), 7.23–7.41 (m, 5H, Ar); ^{13}C NMR ($CDCl_3$) δ 13.5, 22.6, 62.5, 125.5, 127.4, 127.5, 141.9, 248.9; ^{77}Se NMR ($CDCl_3$, Me_2Se) δ 720.7.

*4.6.7. (E)-1-(Methylthio)-1-(trimethylsilylethylseleno)-2-phenylpropene (E-**11b**).* IR (neat) 2952, 2917, 1599, 1489, 1439, 1418, 1366, 1248, 1148, 1074, 1027, 1011, 859, 757, 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.05 (s, 9H, $SiMe_3$), 1.01–1.06 (m, 2H, CH_2Si), 2.12 (s, 3H SCH_3), 2.33 (s, 3H, CH_3), 2.87–2.92 (m, 2H, $SeCH_2$), 7.13–7.36 (m, 5H, Ar); ^{13}C NMR ($CDCl_3$) δ −1.78, 18.7, 19.1, 23.4, 24.7, 124.8, 126.3, 127.9, 128.0, 144.9, 147.3; ^{77}Se NMR ($CDCl_3$, Me_2Se) δ 331.7; MS (EI) m/z 343 (M^+); HRMS calcd for $C_{15}H_{24}SSeSi$: (M^+) 344.05332, found: 344.05496.

*4.6.8. (Z)-1-(Methylthio)-1-(trimethylsilylethylseleno)-2-phenylpropene (**11b**).* IR (neat) 2952, 2917, 1599, 1489, 1439, 1418,

1366, 1248, 1148, 1074, 1027, 1011, 859, 757, 697 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.04 (s, 9H, $SiMe_3$), 0.79–0.84 (m, 2H, CH_2Si), 2.35 (s, 3H, CH_3), 2.37 (s, 3H SCH_3), 2.60–2.65 (m, 2H, $SeCH_2$), 7.13–7.36 (m, 5H, Ar); ^{13}C NMR ($CDCl_3$) δ −1.88, 18.2, 19.7, 23.3, 27.1, 124.2, 126.9, 127.8, 128.0 (Ar), 144.0, 147.2; ^{77}Se NMR ($CDCl_3$, Me_2Se) δ 312.8; MS (EI) m/z 343 (M^+); HRMS calcd for $C_{15}H_{24}SSeSi$: (M^+) 344.05332, found: 344.05496.

*4.6.9. Tetrabutylammonium cyclohexanecarboselenothioate (**3d**).* A red oil; IR (neat) 2959, 2930, 2873, 2044, 1834, 1463, 1384, 1232, 1147, 1110, 1065, 1032, 935, 885, 862 cm^{-1}; ^1H NMR (THF-d_8) δ 0.99 (t, J=7.6 Hz, 12H, CH_3), 1.12–1.22, 1.28–1.33, 1.59–1.62, 1.85–1.89 (m, 10H, cyclohexyl), 1.43 (sex, J=7.6 Hz, 8H, CH_2), 1.73 (m, 8H, CH_2), 3.37–3.51 (m, 9H, CH_2, cyclohexyl); ^{13}C NMR (THF-d_8) δ 14.2, 20.7, 25.0, 27.4, 27.6, 36.2, 59.5, 67.9, 273.4 (C=Se); ^{77}Se NMR (THF-d_8, Me_2Se) δ 1090.7; UV/vis (THF) λ_{max} (log ε) 522 (2.26), 340 (3.18), 305 (3.22), 224 (3.65) nm.

*4.6.10. Cyclohexanecarboselenothioic acid Se-methyl ester (**4d**).* A yellow oil; IR (neat) 2925, 2852, 1447, 1241, 1188, 1035, 926 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.16–1.41 (m, 2H, cyclohexyl), 1.65–1.75 (m, 2H, cyclohexyl), 1.78–1.83 (m, 3H, cyclohexyl), 1.92–1.96 (m, 3H, cyclohexyl), 2.50 (s, 3H, $SeCH_3$), 3.21 (tt, J=3.4, 11.5 Hz, 1H, cyclohexyl); ^{13}C NMR ($CDCl_3$) δ 12.7, 25.6, 26.1, 34.8, 63.4, 251.3 (C=S: $^1J_{C-Se}$=164.2 Hz); ^{77}Se NMR ($CDCl_3$, Me_2Se) δ 707.0; UV/vis (THF) λ_{max} (log ε) 475 (1.53), 331 (3.99), 271 (4.01), 218 (4.42) nm; MS (EI) m/z 221 (M^+); HRMS calcd for $C_8H_{14}SSe$: (M^+) 221.9981, found: 221.9961.

*4.6.11. Tetrabutylammonium adamantanecarboselenothioate (**3e**).* A red-brown oil; IR (neat) 2959, 2042, 1834, 1471, 1384, 1233, 1152, 1110, 1005, 893, 804, 739 cm^{-1}; ^1H NMR (THF-d_8) δ 0.99 (t, J=7.3 Hz, 12H, CH_3), 1.43 (sex, J=7.3 Hz, 8H, CH_2), 1.62–1.68, 1.70–1.78 (m, 14H, Ad, CH_2), 1.96 (br, 2H, Ad), 2.26 (d, J=2.9 Hz, 7H, Ad), 3.46 (t, J=7.3 Hz, 8H, CH_2); ^{13}C NMR (THF-d_8) δ 14.2, 20.7, 24.9, 31.2, 38.3, 46.4, 58.3, 59.3, 279.6 (C=Se: $^1J_{C-Se}$=209.2 Hz); ^{77}Se NMR (THF-d_8, Me_2Se) δ 1064.0; UV/vis (THF) λ_{max} (log ε) 575 (1.58), 295 (3.61), 254 (3.52), 220 (3.93) nm.

*4.6.12. Adamantaneselenothioic acid Se-methyl ester (**4e**).* A yellow solid; mp 70–76 °C; IR (KBr) 2902, 2844, 1637, 1447, 1401, 1341, 1259, 1186, 1050, 1037, 907, 833, 737 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.69–1.76, 2.08–2.14 (m, 15H, Ad), 2.46 (s, 3H, $SeCH_3$); ^{13}C NMR (THF-d_8) δ 12.9 ($SeCH_3$), 29.0, 36.5, 44.2, 56.9 (Ad), 258.2 (C=S: $^1J_{C-Se}$=168.1 Hz); ^{77}Se NMR ($CDCl_3$, Me_2Se) δ 703.6; UV/vis (THF) λ_{max}(log ε) 483 (1.58), 336 (4.15), 239 (3.82), 226 (4.44) nm; MS (EI) m/z 273 (M^+). Anal. Calcd for $C_{12}H_{18}SSe$: C, 52.74; H, 6.64. Found: C, 52.79; H, 6.44.

4.7. Synthetic procedure for tetramethylammonium adamantaneselenothioate (12)

In a 20 mL two-necked flask, adamantanecarboselenothioic acid *Se*-2-(trimethylsilyl)ethyl ester (**9d**) (0.441 g, 1.23 mmol) was added to a CH_3CN (3 mL) suspension of tetramethylammonium fluoride (0.255 g, 2.74 mmol) at 20 °C. After stirring at 20 °C for 3 h, the reaction mixture was filtered through a glass filter (G4) to separate the insoluble parts, and the solvent was removed under reduced pressure. To this was added Et_2O (5 mL) and at 20 °C, the mixture was stirred for 5 min. Filtration of the resulting deposits gave 0.334 g (82%) of **12** as a deep green solid; mp: 206–212 °C (decomp.); IR (KBr) 3013, 2902, 2844, 2103, 1524, 1488, 1404, 1256, 1004, 949, 896 cm^{-1}; ^1H NMR (DMSO-d_6) δ 1.56, 1.93, 2.04 (br s, 15H, Ad), 3.12 (s, 12H, NMe_4); ^{13}C NMR (DMSO-d_6) δ 29.0, 36.6, 44.8, 54.2, 56.9, 278.5; ^{77}Se NMR (DMSO-d_6) δ 1079.1; UV/vis (THF) λ_{max} (log ε) 561 (1.34), 349 (3.35), 228 (3.61) nm.

4.8. Synthetic procedure for potassium adamantaneselenothioate 18-crown-6 ether complex (13)

In a 20 mL two-necked flask, a solution of adamantane carboselenothioic acid *Se*-2-(trimethylsilyl)ethyl ester **9d** (0.302 g, 0.804 mmol) in CH_3CN (10 mL) was added to a suspension of potassium fluoride (0.073 g, 1.26 mmol) and 18-crown-6 ether (0.222 g, 0.840 mmol) in the same solvent (2 mL) at 20 °C. The mixture was heated at 82 °C for 3 h. The insoluble parts were filtered out. The solvent was evaporated under reduced pressure. To the residue was added Et_2O (7 mL) at 20 °C, followed by stirring for 10 min. Filtration of the resulting precipitates gave 0.150 g (26%) of **13** as a gray solid; ^1H NMR (DMSO-d_6) δ 1.53–2.06 (m, 15H, Ad), 3.54 (s, 24H, 18-Crown-6); ^{13}C NMR (DMSO-d_6) δ 28.4, 36.7, 44.4, 53.4 (Ad), 69.4 (18-Crown-6), 271.9 (C=Se); ^{77}Se NMR (DMSO-d_6) δ 1334.1.

4.9. Synthetic procedure for phenylpropaneselenothioic acid *S*-methyl ester (2d)

In a 20 mL two-necked flask, tetrabutylammonium fluoride (0.5 mL, 0.5 mmol) was added to a THF solution (3 mL) of ketene selenothioacetal **11b** (0.171 g, 0.50 mmol) at 0 °C. It was stirred at that temperature for 1 h. The reaction mixture was poured into water, and extracted with Et_2O. The organic layer was dried over $MgSO_4$ and concentrated in vacuo. The residue was purified by column chromatography on silica gel using hexane (R_f=0.02) as an eluent to give 0.079 g (65%) of **2d** as a purple oil: IR (neat) 3069, 3025, 2971, 1599, 1492, 1450, 1412, 1369, 1128, 1016, 903, 763, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.79 (d, J=7.3 Hz, 3H, CH_3), 2.59 (s, 3H, SCH_3), 4.65 (q, J=7.0 Hz, 1H, CH), 7.14–7.46 (m, 5H, Ar); ^{13}C NMR ($CDCl_3$) δ 23.1, 24.1, 63.9, 127.2, 127.6, 128.4, 141.4, 249.0 (C=Se: $^1J_{C-Se}$=224.7 Hz); ^{77}Se NMR ($CDCl_3$, Me_2Se) δ 1509.5; UV/vis (THF) λ_{max} (log ε) 562 (1.81), 272 (3.62), 242 (3.83), 220 (4.37) nm; MS (EI) m/z 243 (M^+); HRMS calcd for $C_{10}H_{18}SSe$: (M^+) 243.9825, found: 243.9813.

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