An Efficient Synthetic Method of 4-Penteneselenoamides: Four-Component Coupling Reaction of Terminal Acetylenes, Selenium, Amines, and Allylic Bromides

Toshiaki Murai, Tatsuya Ezaka, and Shinzi Kato*

Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido, Gifu 501-1193

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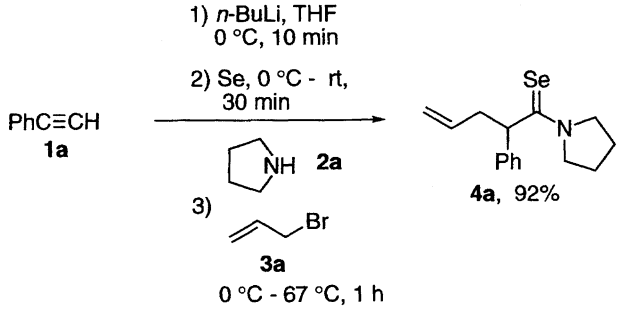
The reaction of lithium alkyneselenolates generated from terminal acetylenes, butyllithium, and selenium with amines and allylic bromides proceeded smoothly in THF at 67 °C to give 4-penteneselenoamides in moderate to high yields. The reaction may proceed via selenoketene intermediates bearing an allylic group, followed by the attack of amines to give the products. Aliphatic and aromatic acetylenes, silylacetylene, and enynes were employed as terminal acetylenes. One molar amount of secondary amines was effective, whereas an excess of primary amines was necessary. The reactions with 2-butenyl bromide exhibited high regioselectivity, although they gave the stereoisomeric mixtures. The reactions of silyl ethers of propargylic alcohols gave α,β-unsaturated selenoamides as a product.

The chemistry of selenium isologues of amides, i.e. selenoamides, has been of current interest.[1] Various synthetic methods have been devised over the last thirty years. However, the known methods have usually employed selenium reagents such as H_2Se, P_2Se_5, and $(R_3Si)_2Se$,[1c] which are not easily handled. Alternatively, several methods have employed elemental selenium to construct selenocarbamoyl groups.[2] These reactions generally involve the generation of selenoketene intermediates and give the selenoamides in less than 40% yields. This low yield is mainly due to the inefficient trapping of the selenoketene intermediates with amines. To improve the yields of the selenoamides, amines were used as a solvent in some cases.[2a,2b] Nevertheless, only a limited number of selenoketenes were generated, and the selenoamides bearing linear aliphatic carbon chains are mainly synthesized. In contrast, during the course of our studies on the synthesis of selenothioic acid *S*-esters[3] and selenoamides,[4] we have found that the four-component coupling reactions of terminal acetylenes, selenium, thiols[3d,3e] or amines,[4c] and allylic bromides cleanly proceeded through the selenoketene intermediates to form α,α-disubstituted selenocarbonyl compounds efficiently. Several reagents are necessary in the reactions, but all of the reagents have been used in nearly identical molar ratios. The procedure is also of great interest from the synthetic point of view since the increasing attention has been paid to multiple-component condensations involving carbon–carbon bond-forming reactions.[5] We report here the detail of the four-component coupling reaction leading to 4-pentenselenoamides. The differences of the reaction pathways between thiols and amines are also discussed.

Results and Discussion

We first examined the reaction of phenylacetylene (**1a**) under the modified reaction conditions of four-component coupling reaction using thiols.[3d] Namely, to a solution of THF and lithium alkyneselenolate **5**, generated in situ from phenylacetylene (**1a**), butyllithium, and selenium, were added pyrrolidine (**2a**) and allyl bromide (**3a**) at 0 °C. The resulting mixture was stirred at 67 °C for 1 h. The reaction, which is formally analogous to that with thiols, proceeded smoothly to give a 92% isolated yield of 4-penteneselenoamide **4a** (Scheme 1).

The reaction using thiols has been known to proceed via selenoketene intermediate **6** generated by the protonation of lithium alkyneselenolate **5** with thiols, followed by the nucleophilic attack of lithium thiolates to form lithium eneselenolates **7** (Chart 1).[3d] Subsequent reaction of **7** with allyl bromide (**3a**) affords the products **8**. To confirm the formation of the similar lithium eneselenolate **9**, the reaction mixture of pyrrolidine (**2a**) and **5** was monitored by ^1H and ^{13}C NMR spectra. The results have indicated that no reaction takes place between **2a** and **5**. This may be explained by the fact that **2a** is less acidic than thiols.[6] However, the addition of allyl bromide (**3a**) to the mixture of **2a** and **5** initiated the reaction exothermally. Accordingly, the reac-



Scheme 1.

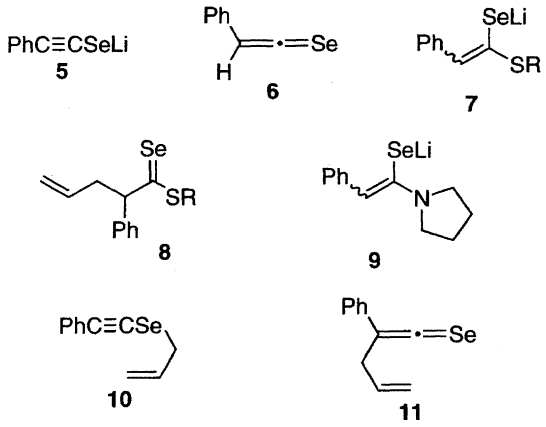
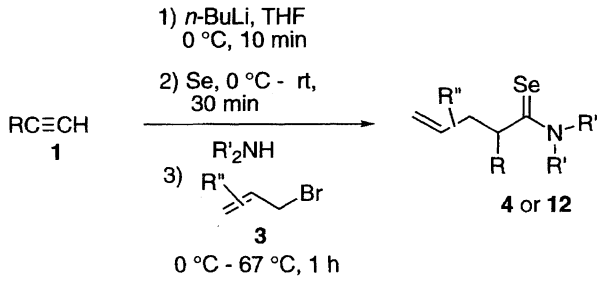


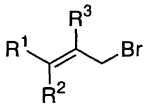
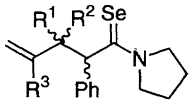
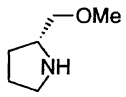
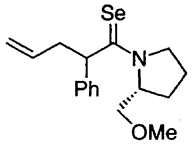
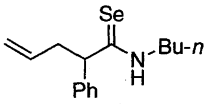
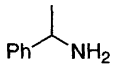
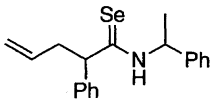
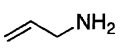
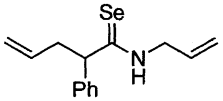
Chart 1.



Scheme 2.

tion may proceed through the selenoketene intermediate **11** formed from lithium alkyneselenolate **5** and allyl bromide (**3a**), unlike the reaction with thiols, although it is not clear

Table 1. Synthesis of 4-Penteneselenoamides **4** from Phenylacetylene, Selenium, Amines, and Allylic Bromides[a)]

Entry	Amines	Allylic bromides	Yield[b)] Selenoamides
			
1	**2a**	**3b** $R^1=CH_3$, $R^2=R^3=H$[c)]	**4b**, 82% (54 : 46)[d)]
2	**2a**	**3c** $R^1=R^2=H$, $R^3=CH_3$	**4c**, 76%
3[e)]	**2a**	**3d** $R^1=R^2=CH_3$, $R^3=H$	**4d**, 52%
4[e,f)]	 **2b**	**3a**	 **4e**, 66% (54:16:16:14)[d,g,h)]
5	n-$BuNH_2$ **2c**	**3a**	 **4f**, 67%
6	 **2d**	**3a**	 **4g**, 64% (53:47)[d,g,h)]
7[i)]	 **2e**	**3a**	 **4h**, 49%

a) The reaction was carried out as follows unless otherwise noted: To a THF solution (5 mL) of lithium alkyneselenolate **5** generated from phenylacetylene (**1a**) (2 mmol), n-BuLi (2 mmol), and Se (2 mmol) were added amines **2** (2 mmol) and allylic bromides **3** (2 mmol) at 0 °C. Then, the reaction mixture was stirred at 67 °C for 1 h. b) Isolated yield. c) **3b** ($E:Z=85:15$) was used. d) The ratio of the diastereoisomers is in parenthesis. e) After the addition of amine **2** and allylic bromide **3**, the reaction mixture was stirred at 67 °C for 30 min. f) The reaction was carried out on 1 mmol scale. g) The product involved the conformational isomers through the carbon-nitrogen single bond. h) The ratio of the diastereomers was determined by ^{77}Se NMR. i) After the addition of **2e** (10 mmol) and **3a**, the reaction mixture was stirred at 53 °C.

Table 2. Synthesis of 4-Peneteneselenoamides **4** from Terminal Acetylenes, Selenium, Amines, and Allylic Bromides[a)]

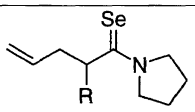
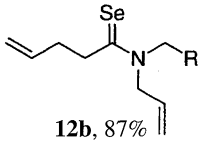
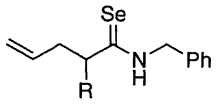
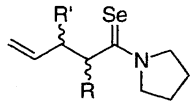
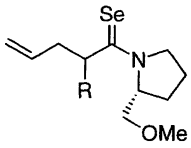
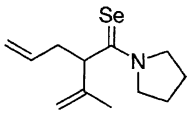
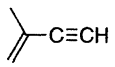
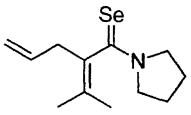
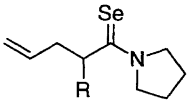
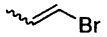
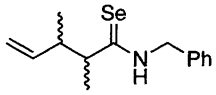
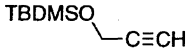
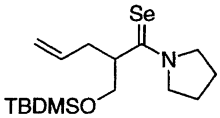
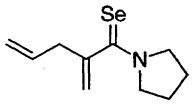
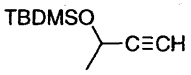
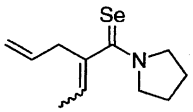
Entry	Acetylenes	Amines	Allylic bromides	Yield[b)] Selenoamides
1	$Me_3SiC{\equiv}CH$ **1b**	**2a**	**3a**	 **4i**:R=Me_3Si, **12a**:R=H 100% (**4i**:**12a**=84:16)[c)] **4i**, 94%[d)]
2[e)]	**1b**	**2f** : R = $CH{=}CH_2$	**3a**	 **12b**, 87%
3[f)]	**1b**	**2g** : R = Ph	**3a**	**12c**, 72% (58 : 42)[g,h)]
4	**1b**	$PhCH_2NH_2$ **2h**[i)]	**3a**	 **4j**:R=Me_3Si, **12d**:R=H 59% (**4j**:**12d**=64:36)
	RC≡CH 1c R = 			
5	**1c**	**2a**	**3a**	**4k**, R′ = H, 85%
6	**1c**	**2a**	**3b**[j)]	**4l**, R′ = CH_3, 69% (50 : 50)[h)]
7	**1c**	**2b**	**3a**	 **4m**, 77% (37:27:26:10)[h,k)]
				 **4n**, 32%
8	 **1d**	**2a**	**3a**	 **4n′**, 52%
				
9	*n*-BuC≡CH **1e**	**2a**	**3a**	**4o**, R=Bu-*n* 75%

Table 2. (Continued)

Entry	Acetylenes	Amines	Allylic bromides	Yield[b] Selenoamides
10[l]	 **13**	**2a**	**3a**	**4p**, R=CH_3 63%  **4q**
11[l]	**13**	**2h**	**3b**[i]	17% (56:44)[h,m] 66% (51:49)[h,n]
12	 **1f**	**2a**	**3a**	 **4r**, 15%
				 **4r′**, 62%
13	 **1g**	**2a**	**3a**	 **4s′**, 65% (E : Z = 58 : 42)

a) The reaction was carried out as follows unless otherwise noted: To a THF solution (5 mL) of lithium alkyneselenolates generated from terminal acetylenes **1** (2 mmol), *n*-BuLi (2 mmol), and Se (2 mmol) were added amines **2** (2 mmol) and allylic bromides **3** (2 mmol) at 0 °C. Then, the reaction mixture was stirred at 67 °C for 1 h. b) Isolated yield. c) After the addition of **2a** and **3a** the reaction mixture was stirred at 67 °C for 30 min. d) The reaction was carried out on 10 mmol scale in Et_2O. After the addition of **2a** and **3a**, the reaction mixture was stirred at 0 °C for 30 min, and then at room temperature for 70 h. e) The reaction was carried out on 15 mmol scale with three molar amount of **2f**. The reaction mixture was treated with KF and MeOH at room temperature for 10 h prior to aqueous workup. f) The reaction was carried out on 30 mmol scale. The reaction mixture was treated with KF and MeOH at room temperature for 16 h prior to aqueous workup. g) The product involved the conformational isomers through the carbon–nitrogen single bond. h) The ratio of the diastereoisomers is in parenthesis. i) Three molar amount of **2h** was used. j) **3b** (E : Z = 85 : 15) was used. k) The ratio of the diastereomers was determined by ^{77}Se NMR. l) 1-Propynyllithium was generated by the reaction of 1-bromo-1-propene (**13**) with 2.2 molar amount of *n*-BuLi at −78 °C for 2 h. m) The reaction was carried out on 30 mmol scale. n) Five molar amount of **2h** was used.

whether **11** is formed directly from **5** and **3a** or from **10** via the [3,3]-sigmatropic rearrangement on the basis of this result.[2c] Then, the nucleophilic attack of pyrrolidine (**2a**) to **11** may give 4-penteneselenoamide **4a**. Attempts to isolate the selenoketene **11** have not yet been successful, but the isolation of selenoketenes from the similar reactions of (trimethylsilyl)acetylene with 2-butenyl or prenyl (3-methyl-2-butenyl)bromides has been reported.[2d] The important point to obtain the product **4a** in high yields is to add **2a** and **3a** to a solution of **5** simultaneously. When **2a** was added after mixing **5** and **3a** for more than 1 h, the product **4a** was formed in only low yields, and the mixture of the decomposed products of **11** was observed. Accordingly, the selenoketene intermediate **11** has to be trapped with **2a** just after the formation of **11**.

The results of the reaction using phenylacetylene (**1a**), amines **2**, and allylic bromides **3** are summarized in Table 1. As allylic bromides, 2-butenyl, methallyl, and prenyl bromides **3b**—**3d** were employed (Entries 1—3). As for the reactions with **3b** and **3d**, the γ-carbon atoms of **3b** and **3d** were selectively introduced to the carbon atom α to the selenocarbonyl group, although the stereochemistry of **4b** was not controlled. These results have suggested that the reaction proceeds via the [3,3]-sigmatropic rearrangement of allylic alkynyl selenides similar to **10**. The use of primary amines also gave the products **4f**, **4g**, and **4h** in good yields (Entries 5—7).

The generality of the present method has been illustrated by the results in Scheme 2 and Table 2. A wide variety of the combination of acetylenes with allylic bromides and amines afforded the corresponding selenoamides in moderate to high yields. The aliphatic acetylenes, enynes, and silylacetylene

were applicable to the reaction. The reaction of (trimethylsilyl)acetylene (**1b**) with selenium, pyrrolidine (**2a**), and allyl bromide (**3a**) gave the selenoamide **4i** along with a small amount of the desilylated selenoamide **12a** under the reaction conditions analogous to the cases of **1a** (Entry 1). The selective formation of **4i** was achieved by carrying out the reaction in Et_2O. The complete desilylation of **4i** was further attained by treating **4i** with *n*-Bu_4NF to give **12a** in 87% yield. The use of KF and MeOH instead of *n*-Bu_4NF also afforded the desilylated selenoamides **12b** and **12c** in good yields (Entries 2 and 3). The selenocarbamoyl groups remained intact under these reaction conditions. The reactions of 1-ethynylcyclohexene (**1c**) and 1-hexyne (**1e**) proceeded smoothly to give the corresponding 4-penteneselenoamides **4k**—**4m** and **4o** (Entries 5—7, 9), whereas the reaction of 2-methyl-1-buten-3-yne (**1d**) gave the corresponding selenoamide **4n** along with the isomerized selenoamide **4n′** (Entry 8). In the synthesis of selenoamides **4p** and **4q**, 1-propynyllithium[7] was generated from 1-bromo-1-propene (**13**) and butyllithium (Entries 10 and 11). As for the reactions of 3-*t*-butyldimethylsiloxy-1-propyne (**1f**) and 3-*t*-butyldimethylsiloxy-1-butyne (**1g**), α,β-unsaturated selenoamides **4r′** and **4s′** were produced through the elimination of *t*-butyldimethylsilyloxy group, although it is a rather poor leaving group (Entries 12 and 13). A variety of primary and secondary amines such as (*R*)-(+)-2-(methoxymethyl)pyrrolidine (**2b**), diallylamine (**2f**), *N*-benzylallylamine (**2g**), and benzylamine (**2h**) were applicable to the present reaction (Entries 2—4, 7, and 11), although an excess of amines **2f** and **2h** was necessary to obtain the corresponding selenoamides in good yields (Entries 2, 4, and 11).

In summary, we have demonstrated that the four-component coupling reaction afforded 4-penteneselenoamides highly efficiently. The reaction exhibited high regioselectivity, although with poor stereoselectivity. A wide range of terminal acetylenes, amines, and allylic bromides can be employed in the reaction. The reaction may proceed via selenoketene intermediates formed by [3,3]-sigmatropic rearrangement of allylic alkynyl selenides. The operational simplicity of the present reaction has offered not only some useful synthetic methods of selenoamides but also some new carbon–carbon bond-forming reactions.

Experimental

General. All reactions were carried out under argon atmosphere. THF and Et_2O were distilled from sodium benzophenone ketyl prior to use. Melting points were determined on a Yanagimoto melting point apparatus without correction. The IR spectra were measured on a Perkin–Elmer FT-IR 1640 instrument. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) were recorded on a JEOL α-400 MHz spectrometer using TMS as the internal standard for ^{1}H NMR and $CDCl_3$ for ^{13}C NMR. The mass spectra were recorded on a Shimadzu GCMS QP1000 (EI/CI, model) mass spectrometer. High-performance liquid chromatography was performed on a model LC-908 (Japan Analytical Industry Co., Ltd.). Elemental analyses were carried out at the Elemental Analyses Center of Kyoto University.

Synthesis of 1-(2-Phenyl-1-selenoxo-4-pentenyl)pyrrolidine (4a). To a THF solution (5 mL) of phenylacetylene (**1a**) (0.22 mL, 2 mmol) was added butyllithium (1.6 M hexane solution, 1.25 mL, 2 mmol) at 0 °C; the mixture was stirred for 10 min at this temperature. To this was added selenium (0.158 g, 2 mmol), and the mixture was stirred for 30 min at room temperature. Then, pyrrolidine (**2a**) (0.17 mL, 2 mmol) and allyl bromide (**3a**) (0.17 mL, 2 mmol) were added successively at 0 °C, and the resulting solution was stirred at 67 °C for 1 h. The mixture was poured into saturated aqueous solution of NH_4Cl, and extracted with Et_2O three times. The combined organic layers were dried over Na_2SO_4 and concentrated. The residue was purified through column chromatography on silica gel (hexane–CH_2Cl_2, 3 : 1) to give **4a** (0.535 g, 92%) as a yellow oil.

4a: IR (neat) 3062, 3024, 2973, 2872, 1639, 1600, 1455, 1328, 1257, 1222, 1168, 1079, 1032, 996, 970, 920, 824, 768, 700, 645 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.84—2.14 (m, 4H, $NCH_2C\underline{H}_2$), 2.80 (dtt, J = 1.2, 7.3, 14.2 Hz, 1H, $PhCHC\underline{H}_2$), 3.19 (dtt, J = 1.2, 7.1, 14.2 Hz, 1H, $PhCHC\underline{H}_2$), 3.32—3.43 (m, 1H, NCH_2), 3.60—3.70 (m, 1H, NCH_2), 3.76—3.86 (m, 1H, NCH_2), 3.87 (t, J = 7.2 Hz, 1H, $PhC\underline{H}$), 3.91—4.01 (m, 1H, NCH_2), 4.96 (ddt, J = 1.2, 2.0, 10.1 Hz, 1H, $C\underline{H}_2$=CH), 5.03 (ddt, J = 1.2, 2.0, 17.1 Hz, 1H, $C\underline{H}_2$=CH), 5.75 (ddt, J = 7.0, 10.1, 17.1 Hz, 1H, CH_2=$C\underline{H}$), 7.21—7.33 (m, 3H, Ar), 7.47—7.53 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$) δ = 23.6, 26.2, 44.1, 51.5, 58.2, 58.4, 116.6, 127.1, 128.5, 128.7, 136.4, 138.8, 205.4; MS (EI) *m/z* 293 (M^+). Found: C, 61.42; H, 6.68%. Calcd for $C_{15}H_{19}NSe$: C, 61.64; H, 6.55%.

1- (3- Methyl- 2- phenyl- 1- selenoxo- 4- pentenyl)pyrrolidine (4b): Yellow oil; IR (neat) 3061, 3024, 2972, 2872, 1831, 1639, 1599, 1455, 1370, 1328, 1256, 1223, 1170, 1102, 1075, 1033, 995, 970, 916, 849, 809, 769, 703, 625, 612 cm^{-1}; ^{1}H NMR ($CDCl_3$) (Major diastereomer) δ = 0.81 (d, J = 6.8 Hz, 3H, CH_3), 1.84—2.20 (m, 4H, CH_2), 3.53—3.85 (m, 5H), 3.88—4.02 (m, 1H), 5.04 (dt, J = 1.1, 10.5 Hz, 1H, $C\underline{H}_2$=CH), 5.14 (dt, J = 1.5, 17.3 Hz, 1H, $C\underline{H}_2$=CH), 6.03 (ddd, J = 6.3, 10.6, 17.1 Hz, 1H, CH_2=$C\underline{H}$), 7.18—7.32 (m, 3H, Ar), 7.54—7.64 (m, 2H, Ar); (Minor diastereomer) δ = 1.17 (d, J = 6.3 Hz, 3H, CH_3), 1.84—2.20 (m, 4H, CH_2), 3.53—3.85 (m, 5H), 3.88—4.02 (m, 1H), 4.73—4.78 (m, 1H, $C\underline{H}_2$=CH), 4.88 (dt, J = 1.4, 17.1 Hz, 1H, $C\underline{H}_2$=CH), 5.51 (ddd, J = 7.3, 10.5, 17.6 Hz, 1H, CH_2=$C\underline{H}$), 7.18—7.32 (m, 3H, Ar), 7.54—7.64 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$) (Major diastereomer) δ = 17.1, 23.5, 26.1, 43.4, 51.6, 58.1, 64.2, 114.3, 127.2, 128.2, 129.7, 137.7, 142.5, 205.6; (Minor diastereomer) δ = 19.4, 23.5, 26.1, 45.0, 51.6, 58.3, 64.2, 114.4, 127.1, 128.1, 129.8, 137.9, 141.1, 205.4; MS (EI) *m/z* 307 (M^+). Found: C, 62.45; H, 6.90%. Calcd for $C_{16}H_{21}NSe$: C, 62.74; H, 6.91%.

1-(4-Methyl-2-phenyl-1-selenoxo-4-pentenyl)pyrrolidine (4c): Yellow solid; mp 77—79 °C; IR (KBr) 2962, 1646, 1600, 1439, 1330, 1259, 1220, 1186, 1170, 1158, 1077, 1042, 972, 896, 812, 784, 770, 726, 702 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.68 (s, 3H, CH_3), 1.85—2.03 (m, 3H, $NCH_2C\underline{H}_2$), 2.03—2.16 (m, 1H, $NCH_2C\underline{H}_2$), 2.74 (dd, J = 7.3, 14.6 Hz, 1H, $PhCHC\underline{H}_2$), 3.20 (dd, J = 6.8, 14.6 Hz, 1H, $PhCHC\underline{H}_2$), 3.44 (dt, J = 6.2, 12.3 Hz, 1H, NCH_2), 3.67 (dt, J = 6.3, 12.7 Hz, 1H, NCH_2), 3.80 (dt, J = 7.0, 14.0 Hz, 1H, NCH_2), 3.97 (dt, J = 7.0, 13.9 Hz, 1H, NCH_2), 4.06 (t, J = 7.1 Hz, 1H, $PhC\underline{H}$), 4.54 (s, 1H, $C\underline{H}_2$=CCH_3), 4.72 (s, 1H, $C\underline{H}_2$=CCH_3), 7.20—7.32 (m, 3H, Ar), 7.48—7.53 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$) δ = 23.3, 23.6, 26.2, 47.3, 51.4, 58.4, 56.2, 112.2, 127.0, 128.4, 128.6, 139.1, 143.3, 205.9; MS (EI) *m/z* 307 (M^+). Found: C, 62.88; H, 6.92%. Calcd for $C_{16}H_{21}NSe$: C, 62.74; H, 6.91%.

1-(3,3-Dimethyl-2-phenyl-1-selenoxo-4-pentenyl)pyrrolidine (4d): Yellow solid; mp 119—120 °C; IR (KBr) 2951, 1629, 1440, 1377, 1325, 1258, 1158, 1080, 1035, 1002, 906, 839, 783, 738, 706, 490 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.24 (s, 3H, CH_3), 1.29

(s, 3H, CH_3), 1.86—2.04 (m, 3H, $NCH_2C\underline{H}_2$), 2.05—2.18 (m, 1H, $NCH_2C\underline{H}_2$), 3.55 (dt, J = 6.1, 12.2 Hz, 1H, NCH_2), 3.70 (dt, J = 7.6, 12.2 Hz, 1H, NCH_2), 3.75 (dt, J = 7.4, 14.9 Hz, 1H, NCH_2), 3.98 (dt, J = 6.8, 13.7 Hz, 1H, NCH_2), 4.16 (s, PhC$\underline{H}$), 4.87 (dd, J = 1.3, 17.4 Hz, 1H, $C\underline{H}_2$=CH), 4.97 (dd, J = 1.3, 10.9 Hz, 1H, $C\underline{H}_2$=CH), 6.43 (dd, J = 10.7, 17.6 Hz, 1H, CH_2=C$\underline{H}$), 7.22—7.32 (m, 3H, Ar), 7.72—7.79 (m, 2H, Ar); ^{13}C NMR ($CDCl_3$) δ = 23.8, 26.4, 25.8, 26.7, 41.6, 52.0, 58.1, 67.4, 111.5, 127.2, 127.5, 131.8, 135.6, 146.6, 203.4; MS (EI) m/z 321 (M^+). Found: C, 63.69; H, 7.31%. Calcd for $C_{17}H_{23}NSe$: C, 63.74; H, 7.24%.

2- (Methoxymethyl)- 1- (2- phenyl- 1- selenoxo- 4- pentenyl)- pyrrolidine (4e): Yellow oil; IR (neat) 2976, 1639, 1600, 1442, 1328, 1254, 1167, 1118, 997, 916, 765, 702, 544 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.75—2.30 (m, 4H, $NCH_2C\underline{H}_2$), 2.70—2.90 (m, 1H, CH_2=CHC$\underline{H}_2$), 3.19, 3.36, 3.38 (s, 3H, OCH_3), 3.05—4.10 (m, 5.8H), 4.22—4.38 (m, 0.3H), 4.45—4.65 (m, 0.3H), 4.95—5.20 (m, 2.6H), 5.65—5.90 (m, 1H, CH_2=C$\underline{H}$), 7.20—7.60 (m, 5H, Ar). Found: m/z 337.09295. Calcd for $C_{17}H_{23}NOSe$: M, 337.09437.

***N*-Butyl-2-phenyl-4-penteneselenoamide (4f):** Yellow solid; mp 36—68 °C; IR (KBr) 3160, 1639, 1599, 1538, 1434, 1163, 1065, 988, 912, 757, 698, 594, 542, 478 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 0.87 (t, J = 7.4 Hz, 3H, CH_3), 1.26 (sextet, J = 7.4 Hz, 2H, $C\underline{H}_2CH_3$), 1.57 (quintet, J = 7.4 Hz, $C\underline{H}_2CH_2CH_3$), 2.76 (dt, J = 7.6, 15.1 Hz, 1H, CH_2=CHC$\underline{H}_2$), 3.25 (dt, J = 6.8, 13.7 Hz, 1H, CH_2=CHC$\underline{H}_2$), 3.62 (dt, J = 5.6, 7.3 Hz, 2H, NCH_2), 4.06 (dd, J = 6.3, 8.8 Hz, 1H, PhC$\underline{H}$C(=Se)), 4.94—5.00 (m, 1H, $C\underline{H}_2$=CH), 5.04—5.11 (m, 1H, $C\underline{H}_2$=CH), 5.71 (ddt, J = 6.8, 10.1, 17.0 Hz, 1H, CH_2=CH), 7.25—7.40 (m, 5H, Ar), 7.86 (brs, 1H, NH); ^{13}C NMR ($CDCl_3$) δ = 13.6, 19.9, 29.4, 39.8, 49.1, 63.5, 117.1, 127.7, 128.2, 128.9, 135.3, 138.4, 210.9; MS (EI) m/z 295 (M^+). Found: C, 61.29; H, 7.07%. Calcd for $C_{15}H_{21}NSe$: C, 61.22; H, 7.19%.

2- Phenyl- *N*- (1- phenylethyl)- 4- penteneselenoamide (4g): Pale yellow solid; mp 77—112 °C; IR (KBr) 3150, 1642, 1600, 1522, 1451, 1426, 1287, 1207, 1152, 1025, 995, 922, 888, 792, 754, 697, 600, 544, 520 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.51 (d, J = 6.8 Hz, 3H, CH_3), 2.69—2.83 (m, 1H, CH_2=CHC$\underline{H}_2$), 3.17—3.27 (m, 1H, CH_2=CHC$\underline{H}_2$), 4.00—4.08 (m, 1H, PhC$\underline{H}$C(=Se)), 4.93—5.01 (m, 1H, $C\underline{H}_2$=CH), 5.01—5.12 (m, 1H, $C\underline{H}_2$=CH), 5.64—5.77 (m, 1H, CH_2=C$\underline{H}$), 5.80—5.90 (m, 1H, C$\underline{H}CH_3$), 7.10—7.40 (m, 10H, Ar), 7.87 (brs, 1H, NH); ^{13}C NMR ($CDCl_3$) δ = 19.5, 19.6, 39.6, 39.7, 57.4, 63.7, 126.2, 127.8, 128.1, 128.2, 128.7, 129.0, 135.3, 138.5, 140.3, 210.1; MS (EI) m/z 343 (M^+). Found: C, 66.41; H, 6.23%. Calcd for $C_{19}H_{21}NSe$: C, 66.66; H, 6.18%.

***N*-Allyl-2-phenyl-4-penteneselenoamide (4h):** Yellow solid; mp 44—46 °C; IR (KBr) 3156, 1642, 1522, 1492, 1411, 1285, 1155, 1069, 1031, 998, 933, 892, 763, 701, 631, 585, 530, 481 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 2.78 (dddt, J = 1.4, 6.6, 8.6, 14.8 Hz, 1H, CH_2=CHC$\underline{H}_2$), 3.26 (ddt, J = 1.4, 6.6, 14.8 Hz, 1H, CH_2=CHC$\underline{H}_2$), 4.06 (dd, J = 6.6, 8.6 Hz, 1H, PhC$\underline{H}$), 4.28 (tt, J = 1.4, 5.6 Hz, 2H, NCH_2), 4.98 (dq, J = 1.4, 10.2 Hz, 1H, $C\underline{H}_2$=CHCH$_2$), 5.08 (dq, J = 1.4, 17.1 Hz, 1H, $C\underline{H}_2$=CHCH$_2$), 5.09 (dq, J = 1.4, 17.1 Hz, 1H, $C\underline{H}_2$=CHCH$_2$N), 5.17 (dq, J = 1.4, 10.4 Hz, 1H, $C\underline{H}_2$=CHCH$_2$N), 5.71 (ddt, J = 6.6, 10.2, 17.1 Hz, 1H, CH_2=C$\underline{H}$CH$_2$), 5.83 (ddt, J = 5.6, 10.4, 17.1 Hz, 1H, CH_2=C$\underline{H}$CH$_2$N), 7.25—7.40 (m, 5H, Ar), 7.79 (brs, 1H, NH); ^{13}C NMR ($CDCl_3$) δ = 40.0, 51.5, 63.7, 117.2, 118.5, 127.9, 128.3, 129.0, 131.0, 135.3, 138.4, 211.9; MS (EI) m/z 279 (M^+). Found: C, 60.32; H, 6.09%. Calcd for $C_{14}H_{17}NSe$: C, 60.43; H, 6.16%.

1-(1-Selenoxo-2-trimethylsilyl-4-pentenyl)pyrrolidine (4i): Yellow solid; mp 50—52 °C; IR (KBr) 2951, 1638, 1488, 1470, 1447, 1328, 1246, 1183, 1117, 1081, 1010, 969, 906, 838, 774, 756, 697, 632 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 0.09 (s, 9H, Me_3Si), 1.89—2.15 (m, 4H, $NCH_2C\underline{H}_2$), 2.38—2.47 (m, 1H, CH_2=CHC$\underline{H}_2$), 2.68 (dd, J = 3.5, 10.4 Hz, 1H, $Me_3SiC\underline{H}$), 3.12—3.22 (m, 1H, CH_2=CHC$\underline{H}_2$), 3.37—3.52 (m, 2H, NCH_2), 3.79—3.89 (m, 1H, NCH_2), 3.92—4.02 (m, 1H, NCH_2), 4.88 (ddt, J = 1.2, 1.7, 10.1 Hz, 1H, $C\underline{H}_2$=CH), 4.99 (dq, J = 1.7, 17.1 Hz, 1H, $C\underline{H}_2$=CH), 5.78 (dddd, J = 5.8, 7.4, 10.1, 17.1 Hz, 1H, CH_2=C$\underline{H}$); ^{13}C NMR ($CDCl_3$) δ = −2.4, 24.1, 26.2, 36.9, 49.0, 51.6, 57.3, 115.0, 138.5, 205.9; MS (EI) m/z 289 (M^+). Found: C, 50.02; H, 7.91%. Calcd for $C_{12}H_{23}NSeSi$: C, 49.98; H, 8.04%.

1-(1-Selenoxo-4-pentenyl)pyrrolidine (12a): Red brown solid; mp 32—34 °C; IR (KBr) 2965, 1640, 1495, 1446, 1342, 1329, 1257, 1222, 1181, 1090, 1040, 1006, 973, 960, 928, 866, 821, 767, 701, 651, 578, 565 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 1.98—2.07 (m, 2H, $NCH_2C\underline{H}_2$), 2.10—2.19 (m, 2H, $NCH_2C\underline{H}_2$), 2.55—2.63 (m, 2H, CH_2=CHC$\underline{H}_2$), 2.83—2.90 (m, 2H, CH_2C(=Se)), 3.54 (t, J = 6.8 Hz, 2H, NCH_2), 3.87 (t, J = 7.1 Hz, 2H, NCH_2), 5.02 (dq, J = 1.5, 10.2 Hz, 1H, $C\underline{H}_2$=CH), 5.10 (dq, J = 1.5, 17.0 Hz, 1H, $C\underline{H}_2$=CH), 5.88 (ddt, J = 6.7, 10.2, 17.0 Hz, 1H, CH_2=C$\underline{H}$); ^{13}C NMR ($CDCl_3$) δ = 24.1, 26.3, 33.2, 46.6, 51.4, 57.7, 115.6, 136.4, 202.8; MS (EI) m/z 217 (M^+). Found: C, 50.00; H, 7.00%. Calcd for $C_9H_{15}NSe$: C, 50.00; H, 6.99%.

Synthesis of *N*,*N*-Diallyl-4-penteneselenoamide (12b): To a THF solution (38 mL) of trimethylsilylacetylene (**1b**) (2.12 mL, 15 mmol) was added butyllithium (1.6 M hexane solution, 9.38 mL, 15 mmol, 1 M = 1 mol dm^{-3}) at 0 °C; this mixture was stirred for 10 min at this temperature. To this was added selenium (1.184 g, 15 mmol), and this mixture was stirred for 30 min at room temperature. Then, diallylamine (**2f**) (5.56 mL, 45 mmol) and allyl bromide (**3a**) (1.30 mL, 15 mmol) were added successively at 0 °C, and the resulting solution was stirred for 1 h at reflux temperature. Next, methanol (20 mL) and potassium fluoride (0.872 g, 15 mmol) were added at room temperature, and the mixture was stirred for 10 h. The mixture was poured into saturated aqueous solution of NH_4Cl, and extracted with Et_2O three times. The combined organic layers were dried over Na_2SO_4 and concentrated. The residue was purified through column chromatography on silica gel (hexane–Et_2O, 5 : 1) to give **12b** (3.171 g, 87%) as a yellow oil.

12b: IR (neat) 3079, 2979, 2919, 1641, 1496, 1411, 1341, 1282, 1248, 1183, 1091, 993, 924, 670, 552 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ = 2.55—2.63 (m, 2H, CH_2), 2.94—3.00 (m, 2H, CH_2), 4.17 (dt, J = 1.8, 4.9 Hz, 2H, NCH_2), 4.78 (d, J = 5.9 Hz, 2H, NCH_2), 4.99—5.34 (m, 6H, $C\underline{H}_2$=CH), 5.73—5.98 (m, 3H, CH_2=C$\underline{H}$); ^{13}C NMR ($CDCl_3$) δ = 34.2, 46.1, 53.4, 59.7, 115.8, 118.4, 119.0, 129.9, 130.4, 136.2, 209.7; MS (EI) m/z 243 (M^+). Found: C, 54.54; H, 7.02%. Calcd for $C_{11}H_{17}NSe$: C, 54.55; H, 7.07%.

***N*-Allyl-*N*-benzyl-4-penteneselenoamide (12c):** Yellow oil; IR (neat) 3077, 2918, 1641, 1604, 1496, 1452, 1353, 1243, 1178, 1078, 1029, 992, 919, 736, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) (Major isomer) δ = 2.64 (dt, J = 6.6, 7.9 Hz, 2H, CH_2=CHC$\underline{H}_2$), 3.01—3.09 (m, 2H, CH_2C(=Se)), 4.07—4.12 (m, 2H, $NC\underline{H}_2CH$=CH_2), 4.96—5.35 (m, 4H, $C\underline{H}_2$=CH), 5.48 (s, 2H, $NC\underline{H}_2Ph$), 5.68—6.01 (m, 2H, CH_2=C$\underline{H}$), 7.28—7.42 (m, 5H, Ar); (Minor isomer) δ = 2.59 (dt, J = 6.8, 7.8 Hz, 2H, CH_2=CHC$\underline{H}_2$), 3.01—3.09 (m, 2H, CH_2C(=Se)), 4.77—4.81 (m, 2H, $NC\underline{H}_2CH$=CH_2), 4.78 (s, 2H, $NC\underline{H}_2Ph$), 4.96—5.35 (m, 4H, $C\underline{H}_2$=CH), 5.68—6.01 (m, 2H, CH_2=C$\underline{H}$), 7.14 (d, J = 7.6 Hz, 2H, Ar), 7.28—7.42 (m, 3H, Ar); ^{13}C NMR ($CDCl_3$) (Major isomer) δ = 34.1, 46.1, 52.9, 59.6, 115.9, 118.4, 126.1, 127.7, 128.6, 129.8, 134.7, 136.1, 210.8; (Minor isomer) δ = 34.1, 46.6, 54.2, 59.7, 115.9, 119.1, 127.8, 128.0, 129.0, 130.2, 133.7, 136.0, 209.9. Found: m/z 293.06952. Calcd for $C_{15}H_{19}NSe$: M, 293.06817.

***N*-Benzyl-2-trimethylsilyl-4-penteneselenoamide (4j):** Yel-

low brown oil; IR (neat) 3205, 3032, 2955, 1639, 1605, 1520, 1410, 1306, 1249, 1158, 1094, 1030, 996, 914, 850, 754, 699, 626, 492 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.14 (s, 9H, Me_3Si), 2.36—2.45 (m, 1H, CH_2=CHC$\underline{H}_2$), 2.48 (dd, J = 3.4, 11.0 Hz, 1H, $Me_3SiC\underline{H}$), 3.02 (dddt, J = 1.4, 6.2, 11.0, 14.5 Hz, 1H, CH_2=CHC$\underline{H}_2$), 4.85 (t, J = 4.8 Hz, 2H, NCH_2), 4.96 (dq, J = 1.4, 10.1 Hz, 1H, C$\underline{H}_2$=CH), 5.06 (dq, J = 1.4, 17.1 Hz, 1H, C$\underline{H}_2$=CH), 5.80 (dddd, J = 6.2, 7.0, 10.1, 17.1 Hz, 1H, CH_2=C$\underline{H}$), 7.30—7.41 (m, 5H, Ar), 7.55 (br s, 1H, NH); ^{13}C NMR ($CDCl_3$) δ = −2.6, 34.9, 53.5, 54.0, 115.6, 128.3, 128.7, 129.0, 135.9, 137.4, 211.8; MS (EI) m/z 325 (M^+). Found: C, 55.27; H, 7.06%. Calcd for $C_{15}H_{23}NSeSi$: C, 55.54; H, 7.15%.

***N*-Benzyl-4-penteneselenoamide (12d):** Yellow solid; mp 47—49 °C; IR (KBr) 2933, 1640, 1600, 1539, 1452, 1340, 1236, 1150, 1059, 1025, 992, 956, 924, 898, 823, 748, 697, 646, 615, 552, 506 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 2.57 (tq, J = 1.3, 7.1 Hz, 2H, CH_2=CHC$\underline{H}_2$), 2.84 (t, J = 7.1 Hz, 2H, CH_2C(=Se)), 4.83 (d, J = 5.1 Hz, 2H, NCH_2), 5.01 (ddt, J = 1.3, 1.7, 10.1 Hz, 1H, C$\underline{H}_2$=CH), 5.09 (ddt, J = 1.3, 1.7, 17.2 Hz, 1H, C$\underline{H}_2$=CH), 5.80 (ddt, J = 7.1, 10.1, 17.2 Hz, 1H, CH_2=C$\underline{H}$), 7.31—7.41 (m, 5H, Ar), 8.05 (brs, 1H, NH); ^{13}C NMR ($CDCl_3$) δ = 33.4, 49.9, 53.9, 116.5, 128.4, 128.5, 129.0, 135.3, 136.0, 209.9; MS (EI) m/z 253 (M^+). Found: C, 56.98; H, 6.03%. Calcd for $C_{12}H_{15}NSe$: C, 57.15; H, 5.99%.

1- [2- (1- Cyclohexenyl)- 1- selenoxo- 4- pentenyl]pyrrolidine (4k): Yellow oil; IR (neat) 3072, 2922, 2659, 1720, 1639. 1455, 1372, 1327, 1256, 1221, 1169, 1140, 1081, 995, 966, 918, 822, 803, 721, 624, 579, 543 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.50—1.65 (m, 4H), 1.92—2.18 (m, 8H), 2.63 (dt, J = 7.1, 14.2 Hz, 1H, CH_2=CHC$\underline{H}_2$), 2.89 (dt, J = 7.1, 14.2 Hz, 1H, CH_2=CHC$\underline{H}_2$), 3.28 (t, J = 7.2 Hz, 1H, CHC(=Se)), 3.50—3.64 (m, 2H, NCH_2), 3.84—4.00 (m, 2H, NCH_2), 4.95—5.00 (m, 1H, C$\underline{H}_2$=CH), 5.03—5.10 (m, 1H, C$\underline{H}_2$=CH), 5.66 (s, 1H, CH=C), 5.80 (ddt, J = 7.0, 10.1, 17.1 Hz, 1H, CH_2=C$\underline{H}$); ^{13}C NMR ($CDCl_3$) δ = 22.3, 22.8, 23.7, 25.3, 26.2, 26.6, 39.8, 51.3, 58.4, 60.0, 116.0, 125.4, 135.0, 136.9, 205.6; MS (EI) m/z 297 (M^+). Found: C, 61.05; H, 7.95%. Calcd for $C_{15}H_{23}NSe$: C, 60.80; H, 7.82%.

1- [2- (1- Cyclohexenyl)- 3- methyl- 1- selenoxo- 4- pentenyl]-pyrrolidine (4l): Yellow solid; mp 84—95 °C; IR (KBr) 2926, 1640, 1442, 1326, 1255, 1187, 1070, 997, 907, 856, 816, 703, 585 cm^{-1}; ^1H NMR ($CDCl_3$) (one diastereomer) δ = 0.99 (d, J = 6.6 Hz, 3H, CH_3), 1.40—1.70 (m, 4H), 1.90—2.20 (m, 7H), 2.33—2.52 (m, 1H), 3.07 (d, J = 10.5 Hz, 1H, CHC(=Se)), 3.28—3.45 (m, 1H), 3.48—3.73 (m, 2H), 3.79—4.03 (m, 2H), 4.90—4.98 (m, 1H, C$\underline{H}_2$=CH), 5.01—5.09 (m, 1H, C$\underline{H}_2$=CH), 5.58—5.63 (m, 1H, CH=C), 5.71 (ddd, J = 8.1, 10.3, 17.3 Hz, 1H, CH_2=C$\underline{H}$); (the other diastereomer) δ = 0.98 (d, J = 6.8 Hz, 3H, CH_3), 1.40—1.70 (m, 4H), 1.90—2.20 (m, 7H), 2.33—2.52 (m, 1H), 3.14 (d, J = 10.5 Hz, 1H, CHC(=Se)), 3.28—3.45 (m, 1H), 3.48—3.73 (m, 2H), 3.79—4.03 (m, 2H), 4.90—4.98 (m, 1H, C$\underline{H}_2$=CH), 5.01—5.09 (m, 1H, C$\underline{H}_2$=CH), 5.62—5.66 (m, 1H, CH=C), 5.88 (ddd, J = 6.5, 10.5, 17.1 Hz, 1H, CH_2=C$\underline{H}$); ^{13}C NMR ($CDCl_3$) (one diastereomer) δ = 19.7 (CH_3), 22.2, 22.8, 23.6, 25.6, 26.2, 26.3, 42.0, 51.2, 58.4, 66.7, 113.5, 127.4, 134.9, 141.7, 204.5; (the other diasteromer) δ = 17.0, 22.3, 22.9, 23.6, 25.7, 26.2, 26.2, 39.9, 51.2, 58.2, 66.8, 113.9, 127.7, 134.4, 142.8, 204.4; MS (EI) m/z 311 (M^+). Found: C, 61.87; H, 8.30%. Calcd for $C_{16}H_{25}NSe$: C, 61.92; H, 8.12%.

1-[2-(1-Cyclohexenyl)-2-(methoxymethyl)-1-selenoxo-4-pentenyl]pyrrolidine (4m): Yellow oil; IR (neat) 3072, 2926, 1638, 1443, 1328, 1253, 1186, 1119, 995, 973, 916, 803, 626, 539 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.46—1.70 (m, 4H), 1.94—2.28 (m, 8H), 2.52—3.00 (m, 2H), 3.20—4.54 (m, 6H), 3.33, 3.34, 3.35 (s, 3H, OCH_3), 4.94—5.22 (m, 2H), 5.56—5.90 (m, 2H). Found: m/z 341.12536. Calcd for $C_{17}H_{27}NOSe$: M, 341.12565.

1-(2-Isopropenyl)-1-selenoxo-4-pentenyl)pyrrolidine (4n): Yellow oil; IR (neat) 3073, 2972, 1820, 1641, 1455, 1374, 1328, 1256, 1222, 1170, 1079, 1038, 996, 963, 907, 824, 764, 640, 582, 542 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.81 (dd, J = 0.7, 1.2 Hz, 3H, CH_3), 1.95—2.05 (m, 2H, $NCH_2C\underline{H}_2$), 2.05—2.17 (m, 2H, $NCH_2C\underline{H}_2$), 2.64 (dtt, J = 1.2, 7.1, 14.1 Hz, 1H, CH_2=CHC$\underline{H}_2$), 2.92 (dtt, J = 1.3, 7.1, 14.2 Hz, 1H, CH_2=CHC$\underline{H}_2$), 3.42 (t, J = 7.2 Hz, 1H, CHC(=Se)), 3.52—3.66 (m, 2H, NCH_2), 3.82—4.00 (m, 2H, NCH_2), 4.93—4.95 (m, 1H, C$\underline{H}_2$=CCH$_3$), 4.96 (quintet, J = 1.5 Hz, 1H, C$\underline{H}_2$=CCH$_3$), 5.00 (ddt, J = 1.0, 2.1, 10.3 Hz, 1H, C$\underline{H}_2$=CH), 5.09 (ddt, J = 1.5, 2.0, 17.1 Hz, 1H, C$\underline{H}_2$=CH), 5.80 (dddd, J = 6.5, 7.4, 10.1, 17.0 Hz, 1H, CH_2=C$\underline{H}$); ^{13}C NMR ($CDCl_3$) δ = 20.7, 23.7, 26.3, 39.6, 51.4, 58.4, 59.7, 114.2, 116.4, 136.4, 142.5, 204.9; MS (EI) m/z 257 (M^+). Found: C, 56.50; H, 7.43%. Calcd for $C_{12}H_{19}NSe$: C, 56.25; H, 7.47%.

1-(2-Isopropylidene-1-selenoxo-4-pentenyl)pyrrolidine (4n′): Yellow solid; mp 45—47 °C; IR (KBr) 2970, 1636, 1560, 1488, 1444, 1384, 1322, 1260, 1183, 1137, 987, 921, 876, 836, 731, 612, 576 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.62 (s, 3H, CH_3), 1.75 (s, 3H, CH_3), 1.92—2.12 (m, 4H, $NCH_2C\underline{H}_2$), 3.06—3.16 (m, 1H), 3.23—3.34 (m, 2H), 3.44—3.53 (m, 1H), 3.76—3.91 (m, 2H, NCH_2), 4.97—5.02 (m, 1H, C$\underline{H}_2$=CH), 5.11 (dq, J = 1.6, 17.1 Hz, 1H, C$\underline{H}_2$=CH), 5.85 (dddd, J = 6.8, 7.4, 9.9, 17.1 Hz, 1H, CH_2=C$\underline{H}$); ^{13}C NMR ($CDCl_3$) δ = 19.5, 21.6, 24.3, 26.1, 36.7, 52.9, 55.6, 116.2, 125.1, 137.4, 134.9, 202.4; MS (EI) m/z 257 (M^+). Found: C, 56.42; H, 7.44%. Calcd for $C_{12}H_{19}NSe$: C, 56.25; H, 7.47%.

1-(2-Allyl-1-selenoxohexyl)pyrrolidine (4o): Yellow oil; IR (neat) 3074, 2953, 1832, 1719, 1639, 1455, 1329, 1256, 1222, 1185, 1117, 998, 970, 915, 822, 732, 693, 611, 532 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 0.88 (t, J = 7.1 Hz, 3H, CH_3), 1.08—1.20 (m, 1H), 1.20—1.36 (m, 3H), 1.56—1.68 (m, 1H), 1.89—2.17 (m, 5H), 2.33 (dt, J = 6.8, 13.5, 1H, CH_2=CHC$\underline{H}_2$), 2.63 (dt, J = 7.1, 14.3 Hz, 1H, CH_2=CHC$\underline{H}_2$), 2.82—2.92 (m, 1H, n-BuC$\underline{H}$C(=Se)), 3.50—3.66 (m, 2H, NCH_2), 3.86—4.00 (m, 2H, NCH_2), 4.95—5.01 (m, 1H, C$\underline{H}_2$=CH), 5.05—5.13 (m, 1H, C$\underline{H}_2$=CH), 5.74 (dddd, J = 6.6, 7.9, 10.0, 16.8 Hz, 1H, CH_2=C$\underline{H}$); ^{13}C NMR ($CDCl_3$) δ = 13.9, 22.8, 23.7, 26.0, 29.5, 36.6, 41.2, 51.7, 57.7, 53.0, 116.7, 135.8, 209.9; MS (EI) m/z 273 (M^+). Found: C, 57.08; H, 8.48%. Calcd for $C_{13}H_{23}NSe$: C, 57.34; H, 8.51%.

Synthesis of 1-(2-Methyl-1-selenoxo-4-pentenyl)pyrrolidine (4p): To a THF solution (5 mL) of 1-bromo-1-propene (**13**) (0.17 mL, 2 mmol) was added butyllithium (1.6 M hexane solution, 2.75 mL, 4.4 mmol) at −78 °C; the mixture was stirred for 2 h at this temperature. To this was added selenium (0.158 g, 2 mmol), and the mixture was stirred for 30 min at room temperature. Then, pyrrolidine (**2a**) (0.17 mL, 2 mmol) and allyl bromide (**3a**) (0.17 mL, 2 mmol) were added successively at 0 °C, and the resulting solution was stirred for 1 h at reflux temperature. The mixture was poured into a saturated aqueous solution of NH_4Cl, and extracted with Et_2O three times. The combined organic layers were dried over Na_2SO_4 and concentrated. The residue was purified through column chromatography on silica gel (hexane–CH_2Cl_2, 5 : 1) to give **4p** (0.291 g, 63%) as a yellow oil:

4p: IR (neat) 3470, 3074, 2972, 1640, 1487, 1371, 1329, 1256, 1193, 1103, 1035, 995, 962, 919, 821, 696, 655, 560, 532 cm^{-1}; ^1H NMR ($CDCl_3$) δ = 1.25 (d, J = 6.8 Hz, 3H, CH_3), 1.95—2.05 (m, 2H, $NCH_2C\underline{H}_2$), 2.07—2.18 (m, 2H, $NCH_2C\underline{H}_2$), 2.33 (dt, J = 7.2, 13.9 Hz, 1H, $CH_3CHC\underline{H}_2$), 2.62 (dt, J = 6.7, 13.9 Hz, 1H, $CH_3CHC\underline{H}_2$), 2.94 (sextet, J = 6.8 Hz, 1H, $CH_3C\underline{H}$), 3.50—3.66 (m, 2H, NCH_2), 3.84—3.98 (m, 2H, NCH_2), 4.97—5.04 (m, 1H, C$\underline{H}_2$=CH), 5.04—5.13 (m, 1H, C$\underline{H}_2$=CH), 5.77 (dddd, J = 6.7, 7.2, 10.3, 16.9 Hz, 1H, CH_2=C$\underline{H}$); ^{13}C NMR ($CDCl_3$) δ = 21.0, 23.7,

26.0, 42.2, 46.9, 51.3, 57.7, 116.8, 135.8, 210.4; MS (EI) *m/z* 231 (M^+). Found: C, 52.29; H, 7.53%. Calcd for $C_{10}H_{17}NSe$: C, 52.17; H, 7.44%.

***N*-Benzyl-2,3-dimethyl-4-penteneselenoamide (4q):** Yellow oil; IR (neat) 3193, 2973, 1951, 1832, 1640, 1605, 1586, 1538, 1455, 1303, 1142, 1030, 999, 917, 889, 824, 746, 700, 616, 535, 497 cm^{-1}; ^1H NMR ($CDCl_3$) (Major diastereomer) $\delta = 1.01$ (d, $J = 6.6$ Hz, 3H, $C\underline{H}_3CHCH{=}CH_2$), 1.23 (d, $J = 6.6$ Hz, 3H, $C\underline{H}_3CHC(=Se)$), 2.46—2.72 (m, 2H, $CH_3CHC\underline{H}CH_3$), 4.75—4.93 (m, 2H, NCH_2), 4.94—5.12 (m, 2H, $C\underline{H}_2{=}CH$), 5.73 (ddd, $J = 7.3$, 10.4, 17.2 Hz, 1H, $CH_2{=}C\underline{H}$), 7.29—7.41 (m, 5H, Ar), 8.11 (brs, 1H, NH); (Minor diastereomer) $\delta = 1.06$ (d, $J = 6.3$ Hz, 3H, $C\underline{H}_3CHCH{=}CH_2$), 1.27 (d, $J = 6.4$ Hz, 3H, $C\underline{H}_3CHC(=Se)$), 2.46—2.72 (m, 2H, $CH_3C\underline{H}C\underline{H}CH_3$), 4.75—4.93 (m, 2H, NCH_2), 4.94—5.12 (m, 2H, $C\underline{H}_2{=}CH$), 5.64 (ddd, $J = 8.8$, 10.2, 17.1 Hz, 1H, $CH_2{=}C\underline{H}$), 7.29—7.41 (m, 5H, Ar), 7.98 (brs, 1H, NH); ^{13}C NMR ($CDCl_3$) (Major diastereomer) $\delta = 16.5$, 19.1, 43.9, 53.3, 58.8, 115.8, 128.3, 128.4, 129.0, 135.3, 140.8, 216.0; (Minor diastereomer) $\delta = 18.3$, 19.2, 42.8, 53.3, 58.8, 114.7, 128.3, 128.4, 128.9, 135.3, 141.2, 215.5; MS (EI) *m/z* 281 (M^+). Found: C, 59.75; H, 6.80%. Calcd for $C_{14}H_{19}NSe$: C, 60.00; H, 6.83%.

1-[2-(*t*-Butyldimethylsiloxymethyl)-1-selenoxo-4-pentenyl]-pyrrolidine (4r): Brown oil; IR (neat) 2952, 1639, 1491, 1450, 1330, 1256, 1189, 1098, 915, 837, 778, 670 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta = -0.02$ (s, 3H, SiMe), -0.01 (s, 3H, SiMe), 0.80 (s, 9H, $C(CH_3)_3$), 1.85—2.12 (m, 4H, $NCH_2C\underline{H}_2$), 2.31 (dt, $J = 7.0$, 14.0 Hz, 1H, $CH_2{=}CHC\underline{H}_2$), 2.61 (dt, $J = 7.0$, 14.0 Hz, 1H, $CH_2{=}CHC\underline{H}_2$), 3.12—3.22 (m, 1H, CHC(=Se)), 3.44—3.54 (m, 1H, NCH_2), 3.69 (dd, $J = 5.1$, 9.3 Hz, 1H, OCH_2), 3.78—3.91 (m, 3H, NCH_2), 4.94 (dd, $J = 1.2$, 10.0 Hz, 1H, $C\underline{H}_2{=}CH$), 5.04 (dd, $J = 1.2$, 17.1 Hz, $C\underline{H}_2{=}CH$), 5.71 (dddd, $J = 6.6$, 7.4, 10.0, 17.1 Hz, 1H, $CH_2{=}C\underline{H}$); ^{13}C NMR ($CDCl_3$) $\delta = -5.4$, -5.3, 18.1, 23.9, 25.8, 26.0, 37.6, 52.0, 55.2, 57.7, 68.2, 116.8, 135.6, 207.1. Found: *m/z* 361.13556. Calcd for $C_{16}H_{31}NOSeSi$: M, 361.13386.

1-(2-Methylene-1-selenoxo-4-pentenyl)pyrrolidine (4r′): Yellow brown oil; IR (neat) 3076, 2973, 2875, 1832, 1641, 1487, 1327, 1254, 1217, 1159, 1103, 1023, 997, 916, 872, 833, 697, 574, 547 cm^{-1}; ^1H NMR ($CDCl_3$) $\delta = 2.00$—2.13 (m, 4H, $NCH_2C\underline{H}_2$), 3.24 (dt, J=1.2, 7.3 Hz, 2H, $CH_2{=}CHC\underline{H}_2$), 3.53 (t, $J = 6.6$ Hz, 2H, NCH_2), 3.84 (t, $J = 7.1$ Hz, 2H, NCH_2), 4.93—4.96 (m, 2H, $C\underline{H}_2{=}C$), 5.09—5.14 (m, 1H, $C\underline{H}_2{=}CH$), 5.16 (dq, $J = 1.5$, 17.1 Hz, 1H, $C\underline{H}_2{=}CH$), 5.86 (ddt, $J = 7.2$, 10.0, 17.2 Hz, 1H, $CH_2{=}C\underline{H}$); ^{13}C NMR ($CDCl_3$) $\delta = 24.3$, 26.2, 39.7, 53.5, 56.0, 109.9, 117.8, 133.7, 152.6, 201.0; MS (EI) *m/z* 229 (M^+). Found: C, 52.64; H, 6.54%. Calcd for $C_{10}H_{15}NSe$: C, 52.63; H, 6.63%.

1-(2-Ethylidene-1-selenoxo-4-pentenyl)pyrrolidine (4s′): Yellow brown oil; IR (neat) 3074, 2972, 1832, 1638, 1492, 1448, 1381, 1326, 1252, 1174, 1078, 1028, 998, 917, 857, 726, 574 cm^{-1}; ^1H NMR ($CDCl_3$) (*E*-isomer) $\delta = 1.58$ (dt, $J = 1.3$, 6.8 Hz, 3H, CH_3), 1.95—2.14 (m, 4H, $NCH_2C\underline{H}_2$), 3.06—3.22 (m, 2H), 3.28—3.38 (m, 1H), 3.42—3.56 (m, 1H), 3.75—3.93 (m, 2H), 5.04—5.09 (m, 1H, $C\underline{H}_2{=}CH$), 5.09—5.16 (m, 1H, $C\underline{H}_2{=}CH$), 5.19 (tq, $J = 1.5$, 7.0 Hz, 1H, $CH_3C\underline{H}{=}C$), 5.84 (ddt, $J = 7.1$, 10.0, 17.0 Hz, 1H, $CH_2{=}C\underline{H}$); (*Z*-isomer) $\delta = 1.74$ (d, $J = 7.1$ Hz, 3H, CH_3), 1.95—2.14 (m, 4H, $NCH_2C\underline{H}_2$), 3.06—3.22 (m, 2H), 3.28—3.38 (m, 1H), 3.42—3.56 (m, 1H), 3.75—3.93 (m, 2H), 5.00—5.05 (m, 1H, $C\underline{H}_2{=}CH$), 5.09—5.16 (m, 1H, $C\underline{H}_2{=}CH$), 5.48 (q, $J = 6.9$ Hz, 1H, $CH_3C\underline{H}{=}C$), 5.77—5.90 (m, 1H, $CH_2{=}C\underline{H}$); ^{13}C NMR ($CDCl_3$) (*E*-isomer) $\delta = 14.4$, 24.3, 26.1, 40.2, 52.7, 55.5, 117.3, 117.7, 134.3, 144.7, 200.5; (*Z*-isomer) $\delta = 13.2$, 24.3, 26.1, 34.8, 53.8, 56.2, 116.5, 121.2, 134.3, 144.3, 202.3; MS (EI) *m/z* 243 (M^+). Found: C, 54.71; H, 7.05%. Calcd for $C_{11}H_{17}NSe$: C, 54.55; H, 7.07%.

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