Reaction of Allenyl Selenoketene, Generated by [3,3] Sigmatropic Rearrangement, with Amines

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Many syntheses of heterocyclic compounds containing selenium have been extensively investigated because of their interesting reactivities[1] and potential pharmaceutical significance.[2] We are interested in the synthesis of novel heterocyclic compounds containing selenium.[3] We found a new evidence for allenyl selenoketene formation via a [3,3] sigmatropic rearrangement by trapping with primary amines and its cyclization by new pathway. To the best of our knowledge, though there are examples of a ketene−allene cycloaddition in the literature,[4] a selenoketene−allene cycloaddition has not been reported.[5] Reactions with various kinds of secondary amines also were investigated. We describe here the reaction of 2-pentynyl phenylethynyl selenide with primary and secondary amines.

Results and Discussion

The reaction leading to 2-imino-2*H*-5,6-dihydroselenine **5** is summarized in Scheme 1. In a typical procedure, 2-pentynyl chloride was added to THF solution of the lithium alkyne selenolate **2**, generated in situ from phenylacetylene **1**, *n*-BuLi, and elementary selenium, and the mixture was stirred at 0 °C for 1.5 h. Subsequent silica gel flash column chromatography afforded 2-pentynyl phenylethynyl selenide **3** in a 87% yield. The mixture of **3** and *n*-butylamine **4a** in benzene was refluxed for 5 h. After standard workup, 2-butylimino-4-ethyl-3-phenyl-2*H*-5,6-dihydroselenine **5a** was isolated in a 88% yield as an orange liquid.

The reactions using other primary amines **4** were investigated and gave **5** in 57−88% yields (Table 1). Under optimized conditions, **5a** was obtained, while **6a** was obtained in a low yield under conditions of lower temperature or shorter reaction times (Table 1, entries 2, 3). The spectra of **6a** was typical of a terminal allene.[6] Previously, though an allenyl selenoketene **7** was suggested to be formed from alkynyl propargyl selenide, it could not be isolated.[7] The isolation of **6a**, bearing a terminal allene, could secure the formation of an allenyl selenoketene intermediate **7** in the present reaction

Table 1. Reaction of 2-Pentynyl Phenylethynyl Selenide 3 and Primary Amines 4 in Benzene

entry	primary amine **4** (R)	yield (%)[a] **5a−d**	**6a−d**
1[b]	**4a**, $CH_3(CH_2)_3$	88	trace
2[c]	**4a**, $CH_3(CH_2)_3$	58	2
3[d]	**4a**, $CH_3(CH_2)_3$	29	6
4[b]	**4b**, $CH_3(CH_2)_2$	60	2
5[b]	**4c**, $C_6H_5(CH_2)_2$	65	2
6[b]	**4d**, $C_6H_5CH_2$	57	3

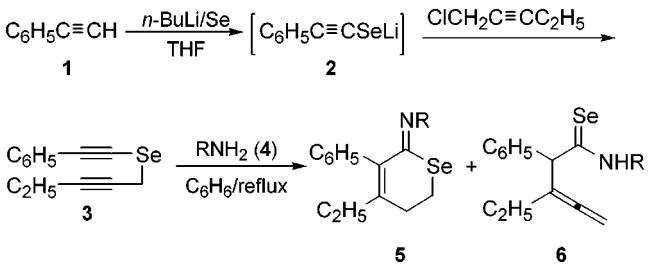
[a] Isolated yield. [b] Reaction mixture was refluxed for 5 h. [c] Refluxed for 3 h. [d] At 70 °C for 5 h.

Table 2. Reaction of 2-Pentynyl Phenylethynyl Selenide 3 and Secondary Amines 8 in THF

entry	secondary amine **8** (R_1)	yield (%)[a] **9a−f** (*E*/*Z*)[b]
1	**8a**, CH_3CH_2	43 (56/44)[c]
2	**8b**, $CH_3(CH_2)_2$	35 (50/50)[c]
3	**8c**, $(CH_3)_2CH$	—[d]
4	**8d**, C_6H_5	—[d]
5	**8e**, -C_4H_8-	54 (66/34)[c]
6	**8f**, -C_5H_{10}-	59 (64/36)[c]

[a] Isolated yield. [b] The stereochemistry of the isomers was confirmed by NOESY. [c] The ratio of each isomer was calculated by ^{1}H NMR measurement. [d] No reaction.

Scheme 1



(1) (a) Katritzky, A. R.; Rees, C. W.; Scriven, E. F. V. *Comprehensive Heterocyclic Chemistry II*; Pergamon: New York, 1996; Vols. 1−11. (b) Back, T. G. *Organoselenium Chemistry: A Practical Approach*; Oxford University Press: Cary, NC, 1999. (c) Wirth, T. *Organoselenium Chemistry. Modern Developments in Organic Synthesis*; Springer: New York, 2000.

(2) (a) Kumar, Y.; Green, R.; Borysko, K. Z.; Wise, D. S.; Wotring, L. L.; Townsend, L. B. *J. Med. Chem.* **1993**, *36*, 3843. (b) Koketsu, M.; Ishihara, H.; Wu, W.; Murakami, K.; Saiki, I. *Eur. J. Pharm. Sci.* **1999**, *9*, 157. (c) Wu, W.; Murakami, K.; Koketsu, M.; Yamada, Y.; Saiki, I. *Anticancer Res.* **1999**, *19*, 5375. (d) Cho, S. I.; Koketsu, M.; Ishihara, H.; Matsushita, M.; Nairn, A. C.; Fukazawa, H.; Uehara, Y. *Biochim. Biophys. Acta* **2000**, *1475*, 207.

(3) (a) Koketsu, M.; Miyajima Y.; Ishihara, H. *Chem. Lett.* **1998**, 645. (b) Koketsu, M.; Hiramatsu S.; Ishihara, H. *Chem. Lett.* **1999**, 485. (c) Koketsu, M.; Suzuki N.; Ishihara, H. *J. Org. Chem.* **1999**, *64*, 6473. (d) Koketsu, M.; Senda, T.; Yoshimura K.; Ishihara, H. *J. Chem. Soc., Perkin Trans. 1* **1999**, 453.

(4) (a) Brady, W. T.; Stockton, G. A. *J. Am. Chem. Soc.* **1973**, *95*, 7447. (b) Bampfield, H. A.; Brook, P. R.; McDonald, W. S. *J. Chem. Soc., Chem. Commun.* **1975**, 132. (c) Bertrand, M.; Gil, G.; Junino, A.; Maurin, R. *Tetrahedron* **1985**, *41*, 2759. (d) Brady, W. T.; Giang, Y. S. F.; Marchand, A. P.; Wu, A. H. *J. Org. Chem.* **1987**, *52*, 3457. (e) Tidwell, T. T. Ketenes; Wiley: New York, 1995. (f) Huang, W.; Tidwell, T. T. *Synthesis* **2000**, *3*, 457. (g) McCaleb, K. L.; Halcomb, R. L. *Org. Lett.* **2000**, *2*, 2631.

(5) Examples of intramolecular cycloadditions with allenes: (a) Landor, S. R. *The Chemistry of the Allenes*; Academic Press: New York, 1982. (b) *Allenes in Organic Synthesis*; Schuster, H. F., Coppola, G. M., Eds.; Wiley-Interscience: New York, 1984. (c) Crimmins, M. T. *Chem. Rev.* **1988**, *88*, 1453. (d) Arredondo, V. M.; Tian, S.; McDonald, F. E.; Marks, T. J. *J. Am. Chem. Soc.* **1999**, *121*, 3633. (e) van Henegouwen, W. G. B.; Fieseler, R. M.; Rutjes, F.; Hiemstra, H. *Angew. Chem., Int. Ed.* **1999**, *38*, 2214. (f) Brummond, K. M.; Lu, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 5087. (g) Villar, F.; Equey, O.; Renaud, P. *Org. Lett.* **2000**, *2*, 1061.

(6) Typical spectra of an allene **6a**: IR (neat) 852, 1955 cm^{-1}; ^{1}H NMR δ 4.73−4.84 (m, 2H); ^{13}C NMR δ 79.2, 105.4, 205.9, see: (a) Munson, J. W. In *The Chemistry of Ketenes, Allenes and Related Compounds*; Patai, S., Ed.; Wiley-Interscience Publication: New York, 1980; p 179. (b) Runge, W. Spectroscopic Properties of Allenes., In *The Chemistry of the Allenes*; Landor, S. R., Ed., Academic Press: New York, 1982; vol. 3, p 777.

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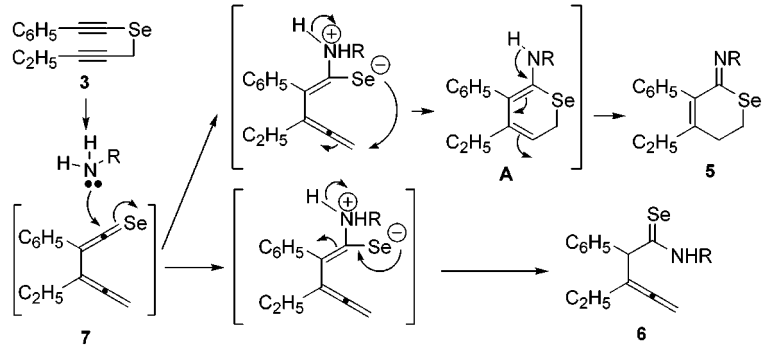
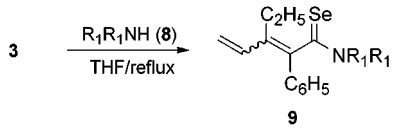
Scheme 2



Scheme 3



process and be explained by the mechanism presented in Scheme 2. Subsequent nucleophilic attack of allenyl selenoketene **7**, which was generated from **3** through a [3,3] sigmatropic rearrangement, by primary amine **4** afforded the observed products **5** and **6** (Scheme 2).

Our attention next turned to the reaction of **3** with various secondary amines **8** (Scheme 2). The results are shown in Table 2. Diethylamine **8a**, di-*n*-propylamine **8b**, pyrrolidine **8e**, and piperidine **8f** all smoothly trapped allenyl selenoketene **7**, affording the corresponding $\alpha\beta,\gamma\delta$-unsaturated selenoamides **9a**−**f** as an inseparable mixture of *E*/*Z* isomers (Table 2, entries 1, 2, 5, 6). In contrast, the reaction with diisopropylamine **8c** and diphenylamine **8d** gave no desired products (Table 2, entries 3, 4), suggesting that these amines might not be able to attack the center of selenoketene because of the steric hindrance. In the case of the reaction with primary amine, intermediate **A** was generated in situ and it smoothly formed stable cyclic compound **5** via hydrogen transfer (Scheme 2). On the other hand, the reaction with secondary amine could not generate sterically labile intermediate **A** bearing dialkyl groups; therefore, it might be thought to be give only $\alpha\beta,\gamma\delta$-unsaturated selenoamides **9**.

Experimental Section

2-Pentynyl Phenylethynyl Selenide 3. To a solution of phenylacetylene (0.51 g, 5.0 mmol) in dry tetrahydrofuran (30 mL) was added *n*-butyllithium, in *n*-hexane (3.3 mL, 5.0 mmol), and the mixture was stirred at 0 °C for 30 min under an argon atmosphere. Then selenium powder (0.40 g, 5.0 mmol) was added to the mixture and stirred at room temperature for 1 h. Moreover, 2-pentynyl chloride (0.56 g, 5.5 mmol) was added to the reaction mixture and stirred at 0 °C for 1.5 h. The mixture was extracted with diethyl ether and washed with saturated NaCl solution. The organic layer was dried over sodium sulfate and evaporated to dryness. The residue was purified by flash chromatography on silica gel with *n*-hexane:diethyl ether (50:1) to give 1.07 g **3** (87%) as a greenish yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.13 (t, 3H, J = 7.6 Hz, CH_3), 2.23 (qt, 2H, J = 7.6, 2.4 Hz, CH_2), 3.60 (t, 2H, J = 2.4 Hz, CH_2), 7.28−7.31 (m, 3H, Ar), 7.41−7.44 (m, 2H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.6, 13.8, 15.5, 70.5, 74.2, 87.5, 101.7, 123.3, 128.2, 131.5; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 236.2; HRMS: m/z = 247.1983, calcd for $C_{13}H_{12}Se$, found 247.1975.

2-Butylimino-4-ethyl-3-phenyl-2*H*-5,6-dihydroselenine 5a. To a solution of 2-pentynyl phenylethynyl selenide **3** (0.25 g, 1.0 mmol) in dry benzene (20 mL) was added *n*-butylamine **4a** (0.20 mL, 2.0 mmol). The mixture was stirred at reflux for 5 h under an argon atmosphere. The mixture was extracted with diethyl ether and washed with saturated NaCl solution. The organic layer was dried over sodium sulfate and evaporated to dryness. The residue was purified by thin-layer chromatography on silica gel with *n*-hexane:diethyl ether (10:1) to give **5a** 0.28 g (88%) as an orange liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.84 (t, 3H, J = 7.2 Hz, CH_3), 0.95 (t, 3H, J = 7.2 Hz, CH_3), 1.23 (m, 2H, CH_2), 1.51 (m, 2H, CH_2), 1.95 (q, 2H, J = 7.4 Hz, CH_2), 2.78 (t, 2H, J = 6.0 Hz, Se−CH_2), 3.01 (t, 2H, J = 6.2 Hz, =C−CH_2), 3.30 (t, 2H, J = 7.2 Hz, N−CH_2), 7.08 (d, 2H, J = 6.8 Hz, Ar), 7.26 (m, 3H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.6, 13.8, 19.2, 20.6, 30.4, 30.6, 32.1,56.4, 125.2, 127.4, 129.7, 135.3, 140.3, 147.6, 154.6; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 322.9; HRMS: m/z = 320.3364, calcd for $C_{17}H_{23}NSe$, found 320.3352. Anal. Calcd for $C_{17}H_{23}NSe$: C, 63.74; H, 7.24; N, 4.37. Found: C, 63.65; H, 7.12; N, 4.51.

4-Ethyl-3-phenyl-2-propylimino-2*H*-5,6-dihydroselenine 5b. 5b (0.19 g, 60%) was obtained as an orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.74 (t, 3H, J = 7.6 Hz, CH_3), 0.87 (t, 3H, J = 7.6 Hz, CH_3), 1.47 (m, 2H, CH_2), 1.87 (q, 2H, J = 7.6 Hz, CH_2), 2.70 (t, 2H, J = 6.0 Hz, Se−CH_2), 2.93 (t, 2H, J = 6.0 Hz, =C−CH_2), 3.19 (t, 2H, J = 7.2 Hz, N−CH_2), 7.00 (d, 2H, J = 6.8 Hz, Ar), 7.11−7.23 (m, 3H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.9, 12.6, 19.2, 21.7, 23.3, 30.4, 30.6, 58.2, 126.0, 128.1, 129.7, 135.2, 140.2, 147.7, 155.0; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 323.0; HRMS: m/z = 306.3095, calcd for $C_{16}H_{21}NSe$, found 306.3078. Anal. Calcd for $C_{16}H_{21}NSe$: C, 62.74; H, 6.91; N, 4.57. Found: C, 62.71; H, 6.89; N, 4.60.

4-Ethyl-2-phenethylimino-3-phenyl-2*H*-5,6-dihydroselenine 5c. 5c was obtained (0.24 g, 65%) as an orange oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, 3H, J = 7.6 Hz, CH_3), 1.93 (q, 2H, J = 7.6 Hz, CH_2), 2.72 (t, 2H, J = 6.0 Hz, Se−CH_2), 2.82 (t, 2H, J = 7.2 Hz, CH_2), 2.94 (t, 2H, J = 6.2 Hz, =C−CH_2), 3.50 (t, 2H, J = 7.2 Hz, CH_2), 7.03−7.34 (m, 5H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.5, 19.0, 30.3, 30.4, 36.4, 57.8, 125.6−139.7, 140.4, 147.9, 155.9; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 322.9; HRMS: m/z = 368.3803, calcd for $C_{21}H_{23}NSe$, found 368.3792. Anal. Calcd for $C_{21}H_{23}NSe$: C, 68.47; H, 6.29; N, 3.80. Found: C, 68.51; H, 6.35; N, 3.62.

2-Benzylimino-4-ethyl-3-phenyl-2*H*-5,6-dihydroselenine 5d. 5d (0.20 g, 57%) was obtained as an yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (t, 3H, J = 7.6 Hz, CH_3), 1.97 (q, 2H, J = 7.6 Hz, CH_2), 2.77 (t, 2H, J = 6.0 Hz, Se−CH_2), 3.01 (t, 2H, J = 6.0 Hz, =C−CH_2), 4.54 (s, 2H, CH_2), 7.12−7.34 (m, 5H, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.5, 19.3, 30.3, 30.5, 59.1, 126.1−139.7, 140.0, 148.3, 156.8; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 328.1; HRMS: m/z = 354.3535, calcd for $C_{20}H_{21}NSe$, found 351.3532. Anal. Calcd for $C_{20}H_{21}NSe$: C, 67.79; H, 5.97; N, 3.95. Found: C, 67.78; H, 5.94; N, 3.99.

***N*-Butyl-3-ethyl-2-phenyl-3,4-pentadieneselenoamide 6a.** To a solution of 2-pentynyl phenylethynyl selenide **3** (0.25 g, 1.0 mmol) in dry diethyl ether (20 mL) was added *n*-butylamine **4a** (0.20 mL, 2.0 mmol). The mixture was stirred at 70 °C for 5 h

(7) (a) Schaumann E.; Grabley, F.-F. *Tetrahedron Lett.* **1980**, *21*, 4251. (b) Shimada, K.; Akimoto, S.; Itoh, H.; Nakamura, H.; Takikawa, Y. *Chem. Lett.* **1994**, 1743. (c) Shimada, K.; Akimoto, S.; Takikawa, Y.; Kabuto C. *Chem. Lett.* **1994**, 2283.

under an argon atmosphere. The mixture was extracted with diethyl ether and washed with saturated NaCl solution. The organic layer was dried over sodium sulfate and evaporated to dryness. The residue was purified by thin-layer chromatography on silica gel with *n*-hexane:diethyl ether (10:1) to give **6a** 0.02 g (6%) as an yellow oil; IR (neat) 852, 1530, 1955 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.82 (t, 3H, J = 7.2 Hz, CH_3), 0.97 (t, 3H, J = 7.2 Hz, CH_3), 1.22 (m, 2H, CH_2), 1.53 (m, 2H, CH_2), 1.99 (m, 2H, CH_2), 3.50−3.66 (m, 2H, N−CH_2), 4.73−4.84 (m, 2H, =CH_2), 5.02 (s, 1H, CH), 7.20−7.29 (m, 5H, Ar), 7.81 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.8, 13.4, 19.8, 25.3, 29.3, 49.0, 68.4, 79.2, 105.4, 126.5, 127.9, 128.7, 137.4, 205.6, 205.9; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 581.3; MS (CI): m/z = 322 [M^+ + 1]. Anal. Calcd for $C_{17}H_{23}NSe$: C, 63.74; H, 7.24; N, 4.37. Found: C, 63.71; H, 6.36; N, 4.11.

3-Ethyl-2-phenyl-*N*-propyl-3,4-pentadieneselenoamide 6b. A yellow oil; IR (neat) 853, 1453, 1955 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.81 (t, 3H, J = 7.2 Hz, CH_3), 0.97 (t, 3H, J = 7.2 Hz, CH_3), 1.50−1.67 (m, 2H, CH_2), 1.90−2.05 (m, 2H, CH_2), 3.43−3.76 (m, 2H, N−CH_2), 4.73−4.84 (m, 2H, =CH_2), 5.02 (s, 1H, CH), 7.21−7.27 (m, 5H, Ar), 7.83 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.1, 11.8, 20.7, 25.3, 50.9, 68.4, 79.3, 105.4, 127.6, 127.9, 128.7, 205.8, 205.9; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 581.2; MS (CI): m/z = 308 [M^+ + 1]. Anal. Calcd for $C_{16}H_{21}NSe$: C, 62.74; H, 6.91; N, 4.57. Found: C, 62.71; H, 6.89; N, 4.55.

3-Ethyl-*N*-phenethyl-2-phenyl-3,4-pentadieneselenoamide 6c. A yellow oil; IR (neat) 857, 1453, 1935 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.96 (t, 3H, J = 7.6 Hz, CH_3), 1.89−2.00 (m, 2H, CH_2), 2.92 (t, 2H, J = 7.2 Hz, CH_2), 3.85−3.99 (m, 2H, N−CH_2), 4.58−4.73 (m, 2H, CH_2), 5.03 (s, 1H, CH), 7.06−7.29 (m, 5H, Ar), 7.87 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.9, 25.3, 33.3, 50.0, 68.6, 79.2, 1085.4, 126.7, 127.6, 128.0, 128.4, 128.7, 128.8, 137.3, 137.5, 205.9; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 592.8; MS (CI): m/z = 370 [M^+ + 1]. Anal. Calcd for $C_{21}H_{23}NSe$: C, 68.47; H, 6.29; N, 3.80. Found: C, 68.42; H, 6.13; N, 3.85.

***N*-Benzyl-3-ethyl-2-phenyl-3,4-pentadieneselenoamide 6d.** A yellow oil; IR (neat) 855, 1454, 1954 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.02 (t, 3H, J = 7.2 Hz, CH_3), 1.97−2.11 (m, 2H, CH_2), 4.71−4.91 (m, 2H, =CH_2), 5.16 (s, 1H, CH) 7.79−7.32 (m, 5H, Ar), 8.06 (br s, 1H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.8, 25.3, 53.5, 68.3, 79.5, 105.3, 127.6, 127.7, 127.9, 128.0, 128.6, 128.7, 135.0, 137.3, 206.6; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 609.5; HRMS: m/z = 354.3535, calcd for $C_{20}H_{21}NSe$, found 351.3513.

***N*,*N*-Diethyl-3-ethyl-2-phenyl-2,4-pentadieneselenoamide 9a.** To a solution of 2-pentynyl phenylethynyl selenide (0.25 g, 1.0 mmol) in dry benzene (20 mL) was added diethylamine **8a** 0.21 mL (2.0 mmol). The mixture was stirred at reflux for 5 h under an argon atmosphere. The mixture was extracted with diethyl ether and washed with saturated NaCl solution. The organic layer was dried over sodium sulfate and evaporated to dryness. The residue was purified by thin-layer chromatography on silica gel with *n*-hexane:diethyl ether (10:1) to give **9a** (0.27 g, 43%) as a yellow oil; IR (neat) 1495 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.75 (t, J = 7.5 Hz, CH_3), 0.96 (t, J = 7.4 Hz, CH_3), 1.01 (t, J = 7.6 Hz, CH_3), 1.11 (t, J = 7.6 Hz, CH_3), 1.25 (t, J = 7.5 Hz, CH_3), 2.13−2.47 (m, CH_2), 3.31−3.71 (m, CH_2), 3.76−4.28 (m, CH_2), 5.07 (d, J = 9.2 Hz, CH_2), 5.19 (d, J = 10.8 Hz, CH_2), 5.28 (d, J = 17.6 Hz, CH_2), 5.33 (d, J = 17.6 Hz, CH_2), 6.34 (dd, J = 10.4, 6.8 Hz, CH), 6.56 (dd, J = 11.2, 6.4 Hz, CH), 7.20−7.28 (m, Ar), 7.55−7.59 (m, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.7, 10.8, 12.2, 12.5, 12.6, 14.0, 20.9, 23.2, 48.0, 48.3, 48.6, 115.5, 115.8, 127.6−130.3, 134.2, 134.3, 135.5, 136.4, 142.2, 142.5, 202.5, 203.1; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 668.2, 680.7; HRMS: m/z = 320.3364, calcd for $C_{17}H_{23}NSe$, found 320.3364. Anal. Calcd for $C_{17}H_{23}NSe$: C, 63.74; H, 7.24; N, 4.37. Found: C, 63.65; H, 7.12; N, 4.45.

***N*,*N*-Di-*n*-propyl-3-ethyl-2-phenyl-2,4-pentadieneselenoamide 9b. 9b** (0.12 g, 35%) was obtained as a yellow oil; ^1H NMR (400 MHz, $CDCl_3$) δ 0.68 (t, J = 7.2 Hz, CH_3), 0.79 (t, J = 7.4 Hz, CH_3), 0.93 (t, J = 7.6 Hz, CH_3), 0.95 (t, J = 7.6 Hz, CH_3), 1.09 (t, J = 7.4 Hz, CH_3), 1.19 (t, J = 7.4 Hz, CH_3), 1.76−1.90 (m, CH_2), 2.24−2.53 (m, CH_2), 3.23−3.29 (m,CH_2), 3.57−3.60 (m, CH_2), 3.69−3.78 (m, CH_2), 3.91−3.98 (m, CH_2), 4.02−4.08 (m, 2H, CH_2), 4.18−4.25 (m, CH_2), 5.16 (d, J = 12.0 Hz, CH_2), 5.26 (d, J = 11.6 Hz, CH_2), 5.36 (d, J = 17.6 Hz, CH_2), 5.40 (d, J = 16.4 Hz, CH_2), 6.43 (dd, J = 11.2, 6.4 Hz, CH), 6.67 (dd, J = 11.2, 6.4 Hz, CH), 7.27−7.36 (m, Ar), 7.64−7.68 (m, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.7, 10.9, 11.1, 12.6, 14.1, 18.8, 18.9, 20.3, 20.5, 20.9, 23.3, 55.5, 55.8, 115.3, 115.8, 127.6−130.3, 134.4, 134.5, 135.6, 136.4, 142.4, 142.7, 203.1, 203.6; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 678.1, 694.1; HRMS: m/z = 348.3901, calcd for $C_{19}H_{27}NSe$, found 348.3889. Anal. Calcd for $C_{19}H_{27}NSe$: C, 65.50; H, 7.81; N, 4.02. Found: C, 65.52; H, 7.84; N, 4.01.

***N*-(3-Ethyl-2-phenyl-1-selenoxo-2,4-pentadienyl)pyrrolidine 9e. 9e** (0.17 g, 54%) was obtained as a yellow oil; IR (neat) 1445 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.97 (t, J = 7.6 Hz, CH_3), 1.12 (t, J = 7.6 Hz, CH_3), 1.90−2.06 (m, CH_2), 2.31−2.40 (m, CH_2), 2.48−2.57 (m, 2H, CH_2), 3.38 (t, J = 6.2 Hz, CH_2), 3.05−3.11 (m, CH_2), 3.38−3.41 (m, CH_2), 3.67−3.72 (m, CH_2), 3.79−3.86 (m, CH_2), 5.07 (d, J = 12.4 Hz, CH_2), 5.21 (d, J = 11.6 Hz, CH_2), 5.30 (d, J = 17.2 Hz, CH_2), 5.36 (d, J = 16.0 Hz, CH_2), 6.29 (dd, J = 10.8, 6.8 Hz, CH), 6.49 (dd, J = 11.2, 6.0 Hz, CH), 7.19−7.29 (m, Ar), 7.48−7.54 (m, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.6, 14.0, 20.9, 22.9, 24.17, 24.25, 26.2, 26.3, 52.7, 52.8, 55.8, 56.0, 116.0, 116.2, 127.7−130.7, 133.0, 133.8, 134.1, 134.3, 135.1, 136.2, 143.1, 143.4, 199.3, 199.7; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 688.8, 689.3; HRMS: m/z = 318.3205, calcd for $C_{17}H_{21}NSe$, found 318.3205. Anal. Calcd for $C_{17}H_{21}NSe$: C, 64.15; H, 6.65; N, 4.40. Found: C, 64.12; H, 6.60; N, 4.45.

***N*-(3-Ethyl-2-phenyl-1-selenoxo-2,4-pentadienyl)piperidine 9f. 9f** (0.20 g, 59%) was obtained as a yellow oil; IR (neat) 1491 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.05 (t, J = 7.2 Hz, CH_3), 1.20 (t, J = 7.4 Hz, CH_3), 1.37−1.47 (m, CH_2), 1.50−1.81 (m, CH_2), 2.19−2.54 (m, CH_2), 3.56−3.65 (m, CH_2), 3.72−3.79 (m, CH_2), 4.08−4.13 (m, CH_2), 4.31−4.42 (m, CH_2), 4.56−4.64 (m, CH_2), 5.14 (d, J = 11.2 Hz, CH_2), 5.26 (d, J = 11.2 Hz, CH_2), 5.35 (d, J = 17.6 Hz, CH_2), 5.40 (d, J = 21.2 Hz, CH_2), 6.37 (dd, J = 11.2, 6.4 Hz, CH), 6.62 (dd, J = 11.2, 6.4 Hz, CH), 7.27−7.27 (m, Ar), 7.55−7.63 (m, Ar); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.7, 13.8, 20.8, 22.4, 23.0, 23.6, 24.1, 25.0, 25.1, 25.4, 25.8, 25.9, 26.0, 53.1, 53.2, 53.5, 53.6, 54.9, 55.5, 58.2, 115.6, 115.7, 126.0−130.2, 129.1, 130.3, 134.0, 134.1, 135.7, 136.7, 141.8, 142.1, 201.5, 202.1; ^{77}Se NMR (76 MHz, $CDCl_3$) δ 625.0, 626.5; HRMS: m/z = 332.3474, calcd for $C_{18}H_{23}NSe$, found 332.3456. Anal. Calcd for $C_{18}H_{23}NSe$: C, 65.05; H, 6.98; N, 4.21. Found: C, 65.00; H, 6.89; N, 4.22.

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