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Pyrrolidinamine, Piperidinamine and Tetrahydropyridazine Derivatives from Selenium Promoted Cyclization of Alkenyl Phenylhydrazones

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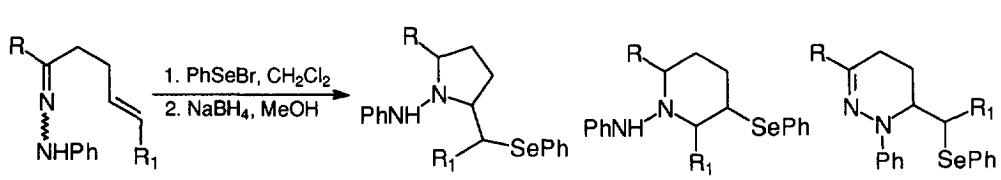
Abstract: Upon treatment with phenylselenenyl bromide, alkenyl phenylhydrazones give rise to cyclization reactions affording, after reduction with sodium borohydride, either pyrrolidinamine and piperidinamine or tetrahydropyridazine derivatives depending on the geometrical structure of the starting substrates. © 1997 Elsevier Science Ltd.

The ring closure reactions, which occur when an alkene containing a suitably positioned nitrogen nucleophile is treated with an electrophilic reagent, represent a convenient synthetic pathway for the preparation of a variety of nitrogen heterocyclic compounds. Primary alkenyl amines do not give the desired ring closure reactions which can instead be readily effected starting from primary N-protected alkenyl amines.[1,2] Several new examples of these reactions have been described in recent years.[3] Much attention has been recently devoted to the cyclization reactions of alkenes in which the internal nitrogen nucleophile is that of an imidate,[4] an oxime,[5-7] an O-allyl oxime[8-10] or an imine.[11,12] In these compounds the imino nitrogen atom is sufficiently nucleophilic to attack the carbon atom of the seleniranium ion intermediate formed from the interaction of the electrophilic reagent with the olefinic double bond. Thus, lactams and cyclic nitrones are formed from imidates and oximes, respectively, and cyclic iminium salts, which can evolve in different ways, are produced from O-allyl oximes and from imines.

We now report that similar cyclization reactions can also be effected starting from the alkenyl hydrazones by treatment with phenylselenenyl bromide. An imino and an amino nitrogen atom are present in these molecules and it can be expected that both can give rise to cyclization leading to pyrrolidinamine and piperidinamine (after reduction of the initially formed iminium salts) or to tetrahydropyridazine derivatives, respectively (Scheme 1).

Scheme 1



The phenylhydrazones **1-6** (Table 1), necessary for the present investigation, were easily obtained from the corresponding aldehydes or ketones by reaction with phenylhydrazine under standard conditions. As indicated by ^{1}H and ^{13}C NMR, the crude products were constituted by one of the two geometrical isomers sligthly contaminated by the other isomer and/or by other products. These hydrazones were not very stable and readily decomposed on standing or on attempted purification by column chromatography. The crude products were therefore directly used for the cyclization reactions. The geometry of the hydrazone function was established by ^{13}C NMR, by measuring the chemical shift differences between the α carbons of the phenylhydrazones and those of the corresponding ketones or aldehydes, according to the procedure previously proposed for dimethylhydrazones, oximes and p-toluenesulfonylhydrazones.[13] As expected on the basis of simple steric considerations, the hydrazones **1**, **2**, **4-6** have the *E* and the hydrazone **3** has the *Z* configuration.

The cyclization reactions were carried out by adding phenylselenenyl bromide to the solution of the crude phenylhydrazones **1-6** in dichloromethane at room temperature. The progress of the reaction was monitored by TLC. After 1-2 h, methanol and sodium borohydride were added and the solution was stirred at room temperature for 1-2 h. The reaction mixtures were poured on water and worked up in the usual way. The reaction products **7-12** were obtained in a pure form by column chromatography on silica gel. The results of these experiments are summarized in Table 1. These reactions are proposed to proceed through the initial formation of the seleniranium ion intermediates **13**, **15** and **17**, which are trapped stereoselectively by one of the two nitrogen atoms to afford the cyclization products (Scheme 2). *Anti* addition is generally observed in these selenium induced cyclizations.[2,3] On this basis the structure indicated in Scheme 2 is proposed for compound **10**.

Scheme 2

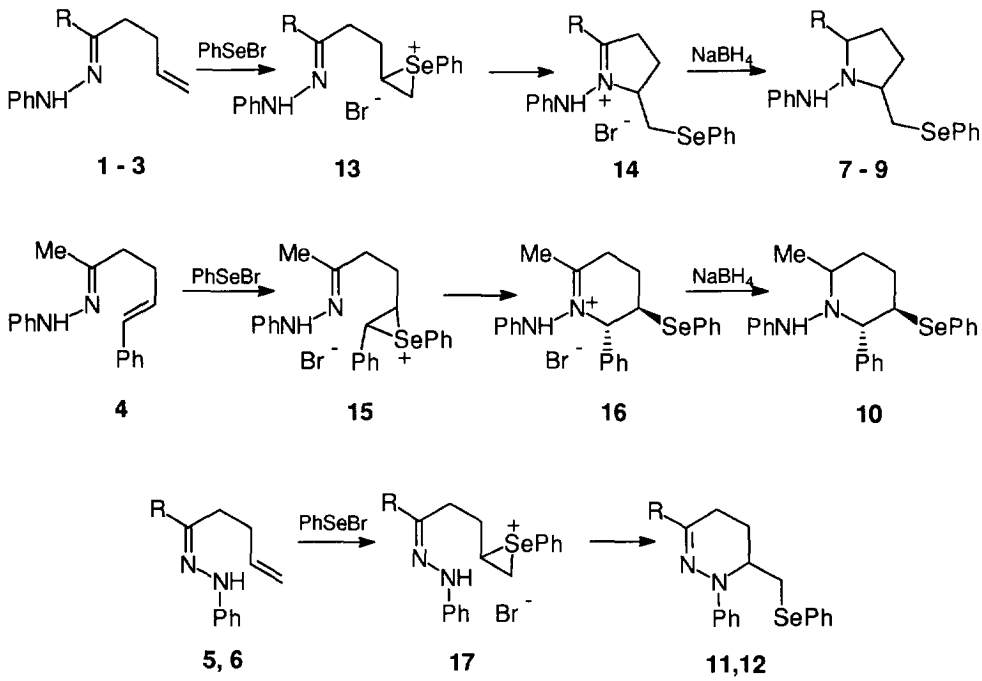
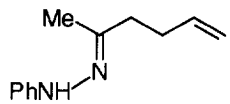
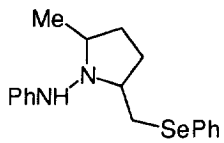
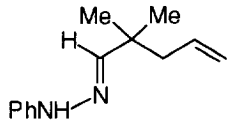
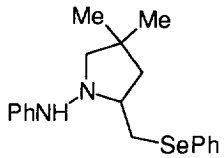
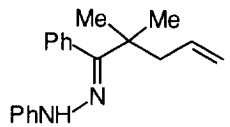
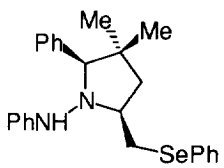
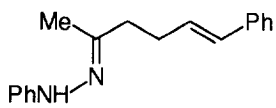
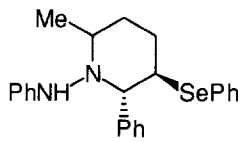
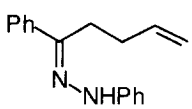
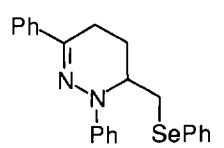
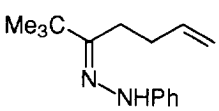
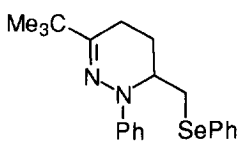


Table 1. Conversion of Alkenyl Phenylhydrazones into Pyrrolidinamines, Piperidinamines or Tetrahydropyridazines with PhSeBr in dichloromethane at room temperature.

	Alkenyl Phenylhydrazone	Reaction time[a] (h)		Reaction Product	% Yield[b]
1		1	**7**		65[c]
2		1	**8**		58
3		2	**9**		66[d]
4		2	**10**		55[c]
5		1	**11**		68
6		1	**12**		40

a. Time necessary for the reactions of the alkenyl phenylhydrazones with PhSeBr before the addition of $NaBH_4$.

b. Calculated on the amount of the ketone or the aldehyde employed for the preparation of the alkenyl phenylhydrazones.

c. 1:1 Mixture of two stereoisomers which could not be separated.

d. Single stereoisomer.

In the case of the phenylhydrazones **1-4** the ring closure occurs through the imino nitrogen atom and affords the cyclic iminium bromides **14** and **16**, which are then reduced to the pyrrolidinamines **7-9** or to the piperidinamine **10**. On the contrary, in the case of the phenylhydrazones **5** and **6**, cyclization occurs through the amino nitrogen atom and the tetrahydropyridazines **11** and **12** are produced. After treatment with sodium borohydride these two compounds remained unchanged. Thus, the perhydropyridazines are either not formed under these conditions or they are easily oxidized to the tetrahydro derivatives, as observed in similar cases.[14]

Compounds **7** and **10** were constituted by a 1:1 mixture of the two possible stereoisomers which could not be separated. Compound **9** instead was formed as a single stereoisomer. The structure reported in Table 1 is proposed on the basis of the results of differential NOE and NOESY experiments.

The results presented in Scheme 2 and summarized in Table 1 indicate that in every case the cyclization reaction is a regiospecific process which takes place with a Markovnikov orientation. Under the conditions employed no isomerization of the phenylhydrazone function takes place and the structure of the reaction products is strictly determined by the geometry of the starting alkenyl phenylhydrazone. The presently described selenium induced cyclization of alkenyl phenylhydrazones represents a new process which can be conveniently used to synthesize pyrrolidinamines, piperidinamines or tetrahydropyridazines derivatives.

EXPERIMENTAL

Melting points were determined on a capillary melting point apparatus and are uncorrected. GLC analyses and MS spectra were carried out with an HP 5890 gaschromatograph (dimethyl silicone column, 12.5 m) equipped with an HP 5971 Mass Selective Detector; for the ions containing selenium only the peak arising from the selenium-80 isotope is given. ^1H and ^{13}C NMR spectra were recorded at 200 and 50.32 MHz, respectively, on a Bruker AC 200 instrument; $CDCl_3$ was used as solvent and TMS as standard. Elemental analyses were carried out on a Carlo Erba 1106 Elemental Analyzer and were in good agreement with the calculated values.

Synthesis of Alkenyl Phenylhydrazones. 5-Hexen-2-one, 2,2-dimethyl-4-pentenal were commercial products. 2,2-Dimethyl-1-phenyl-4-penten-1-one,[15] 6-phenyl-(5*E*)-hexen-2-one,[16] 1-phenyl-4-penten-1-one,[17] 2,2-dimethyl-6-hepten-3-one,[18] were prepared according to the procedures described in the literature. The phenylhydrazones were obtained from the corresponding aldehyde or ketone according to a standard procedure.[19]

The appropriate aldehyde or ketone (10 mmol) dissolved in EtOH (4 mL) was added to a solution of phenylhydrazine hydrochloride (12 mmol) and sodium acetate (15 mmol) in H_2O (20 mL) under Argon. The mixture was stirred at room temperature or at 50 °C for 1-15 h and then was poured into a 10% aqueous solution of Na_2CO_3 and extracted with CH_2Cl_2. The organic layer was dried (Na_2SO_4), evaporated under reduced pressure and the labile reddish brown residue, stored under Argon, was directly used for the cyclization reaction. Physical and spectral data of phenylhydrazones are reported below.

The configurations of these phenylhydrazones were assigned on the basis of their ^{13}C NMR spectra.[13] The chemical shifts of the two methylenic carbons in compounds **1**, **4**, **5** and **6** were assigned on the basis of the results of HETCOR experiments.

5-Hexen-2-one phenylhydrazone (1): oil; ^1H NMR δ 7.28 (dd, 2 H, *J* = 7.4, 8.0 Hz), 7.18 (d, 2 H, *J* = 8.0 Hz), 6.86 (t, 1 H, *J* = 7.3 Hz), 6.03-5.8 (m, 1 H), 5.18-4.97 (m, 2 H), 2.55-2.3 (m, 4 H), 1.85 (s, 3 H); (C_6D_6) 7.15 (dd, 2 H, *J* = 7.4, 8.0 Hz) 7.05 (d, 1 H, *J* = 8.0 Hz), 6.75 (t, 1 H, *J* = 7.3 Hz), 6.65 (br s, 1 H), 5.95-5.7 (m, 1 H), 5.1-4.85 (m, 2 H), 2.3-2.15 (m, 4 H), 1.3 (s, 3 H); ^{13}C NMR δ 145.8, 137.8, 128.8, 119.3, 115.6, 112.8, 37.9 (C_3), 30.5 (C_4), 14.2; (C_6D_6) 146.6, 144.7, 138.4, 128.5, 119.7, 114.9, 113.4, 38.3 (C_3), 31.0 (C_4), 14.0. MS *m/z* (relative intensity) 188 (M^+, 39), 159 (6), 147 (9), 132 (11), 106 (87), 93 (100), 83 (48), 77 (28), 65 (42), 55 (14), 42 (20), 41 (13).

2,2-Dimethyl-4-pentenal phenylhydrazone (2): viscous oil; ^1H NMR δ 7.2 (dd, 2 H, *J* = 7.5, 8.4 Hz), 7.05 (br s, 1 H), 6.95 (dd, 2 H, *J* = 1.0, 8.4 Hz), 6.82 (s, 1 H), 6.78 (tt, 1 H, *J* = 1.0, 7.4 Hz), 5.92-5.69 (m, 1 H), 5.09-4.96 (m, 2 H), 2.18 (d, 2 H, *J* = 7.3 Hz), 1.09 (s, 6 H); ^{13}C NMR δ 147.8, 145.6, 134.8, 129.1, 119.3, 117.3, 112.5, 45.5 (C_2), 37.3 (C_3), 25.6. MS *m/z* (relative intensity) 202 (M^+, 28), 161 (98), 146 (19), 134 (25), 93 (77), 92 (100), 77 (22), 65 (46), 41 (32).

2,2-Dimethyl-1-phenyl-4-penten-1-one phenylhydrazone (3): oil; ^1H NMR δ 7.4 (t, 2 H, *J* = 6.9 Hz), 7.2-7.0 (m, 5 H), 6.82 (d, 2 H, *J* = 7.5 Hz), 6.71 (t, 1 H, *J* = 6.7 Hz), 6.05-5.78 (m, 1 H), 5.1-4.99 (m, 2 H), 3.9 (br s, 1 H), 2.32 (d, 2 H, *J* = 7.1 Hz), 1.18 (s, 6 H); ^{13}C NMR δ 152.9, 145.3, 135.5, 133.5, 128.9, 128.5, 128.4, 119.2, 116.9, 112.5, 44.9 (C_3), 40.8 (C_2), 26.3. MS *m/z* (relative intensity) 278 (M^+, 46), 277 (66), 237 (74), 195 (20), 173 (25), 144 (23), 134 (65), 115 (12), 104 (60), 92 (100), 91 (26), 77 (48), 65 (58), 41 (38).

6-Phenyl-(5*E*)-hexen-2-one phenylhydrazone (4): oil; ^1H NMR δ 7.38-7.12 (m, 7 H), 7.06 (dd, 2 H, *J* = 1.1, 8.5 Hz), 6.85 (br s, 1 H), 6.81 (tt, 1 H, *J* = 1.1, 7.0 Hz), 6.41 (d, 1 H, *J* = 15.9 Hz), 6.23 (dt, 1 H, *J* = 6.0, 15.9 Hz) 2.58-2.38 (m, 4 H), 1.82 (s, 3 H); ^{13}C NMR δ 145.7, 145.5, 137.5, 130.1, 129.8, 128.9, 128.3, 126.7, 125.8, 119.3, 112.8, 38.3 (C_3), 29.8 (C_4), 14.4. MS *m/z* (relative intensity) 264 (M^+, 8), 173 (20), 133 (47), 117 (80), 115 (33), 105 (51), 92 (31), 77 (100), 51 (12).

1-Phenyl-4-penten-1-one phenylhydrazone (5): oil; ^1H NMR δ 7.78-7.6 (m, 2 H), 7.5-7.0 (m, 6 H), 7.0-6.6 (m, 3 H), 5.8 (ddt, 1 H, *J* = 6.6, 10.2, 16.8 Hz), 5.18-4.85 (m, 2 H), 2.76-2.6 (m, 2 H), 2.38-2.2 (m, 2 H); ^{13}C NMR δ 145.1, 143.9, 138.1, 137.0, 129.1, 128.3, 127.8, 125.4, 120.1, 116.0, 113.2, 29.7 (C_3), 24.8 (C_2).

2,2-Dimethyl-6-hepten-3-one phenylhydrazone (6): oil; ^1H NMR δ 7.25-7.1 (m, 2 H), 7.08-6.99 (m, 2 H), 6.8-6.7 (m, 1 H), 6.01-5.75 (m, 1 H), 5.2-5.0 (m, 2 H), 2.38-2.18 (m, 4 H), 1.19 (s, 9 H); ^{13}C NMR δ 154.1, 146.1, 137.5, 129.0, 119.3, 115.2, 112.8, 38.6 (C_2), 29.6 (C_5), 28.0, 24.5 (C_4). MS *m/z* (relative intensity) 230 (M^+, 17), 188 (6), 173 (5), 139 (18), 97 (32), 93 (100), 77 (36), 65 (38), 57 (39), 55 (13), 41 (28).

Cyclization of Alkenyl Phenylhydrazones. General Procedure. Phenylselenenyl bromide (2.4 mmol) was added portionwise to the solution of the phenylhydrazones **1-6** (2 mmol) in dichloromethane (10 mL) at room temperature. The progress of the reaction was monitored by TLC and after 1-2 h, methanol (10 mL) and sodium borohydride (3 mmol) were added ant the solution was stirred at room temperature for 1-2 h. The reaction was poured on water and extracted with CH_2Cl_2. The organic layer was dried (Na_2SO_4) evaporated and the residue was chromatographed through a silica gel column using petroleum ether/diethyl ether (95:5) as eluant. The products and the yields are summarized in Table 1. Physical and spectral data are reported below.

1*N*-Phenyl-2-methyl-5-(phenylseleno)methyl-1-pyrrolidinamine (7) (1:1 mixture of cis and trans isomers): oil; ^{1}H NMR δ 7.48-7.3 (m, 4 H), 7.28-7.05 (m, 10 H), 6.9-6.78 (m, 4 H), 6.78-6.61 (m, 2 H), 4.72 (br s, 1 H), 4.15 (br s, 1 H), 3.5-3.35 (m, 1 H), 3.32-3.05 (m, 3 H), 3.05-2.77 (m, 3 H), 2.63 (ddq, 1 H, *J* = 6.4, 6.5, 9.1 Hz), 2.18-1.78 (m, 4 H), 1.77-1.38 (m, 4 H), 1.0 (d, 3 H, *J* = 6.0 Hz), 0.96 (d, 3 H, *J* = 6.4 Hz); ^{13}C NMR δ 150.1, 149.0, 132.1, 129.0, 126.5, 118.7, 118.4, 113.0, 112.5, 68.5, 64.9, 61.9, 56.3, 32.3, 31.9, 28.9, 28.8, 27.4, 27.2, 19.4, 14.8. MS *m/z* (relative intensity) 346 (M^+, 4), 175 (100), 158 (4), 93 (13), 92 (44), 77 (12), 65 (11). Anal. Calcd for $C_{18}H_{22}N_2Se$: C, 62.60; H, 6.42; N, 8.11. Found: C, 62.53; H, 6.34; N, 8.19.

1*N*-Phenyl 4,4-dimethyl-2-(phenylseleno)methyl-1-pyrrolidinamine (8): oil; ^{1}H NMR δ 7.48-7.38 (m, 2 H), 7.28-7.09 (m, 5 H), 6.9 (d, 2 H, *J* = 8.5 Hz), 6.75 (t, 1 H, *J* = 7.4 Hz), 4.15 (br s, 1 H), 3.31-3.17 (m, 1 H), 3.12 (d, 1 H, *J* = 8.6 Hz), 3.05-2.86 (m, 2 H), 2.12 (d, 1 H, *J* = 8.6 Hz), 1.85 (dd, 1 H, *J* = 7.7, 13.2 Hz), 1.51 (dd, 1 H, *J* = 8.1, 13.2 Hz), 1.2 (s, 3 H), 1.05 (s, 3 H); ^{13}C NMR δ 149.2, 132.0, 131.1, 129.0, 128.9, 126.4, 119.0, 113.0, 70.1, 66.8, 44.5, 34.4, 31.9, 30.5, 29.1. MS *m/z* (relative intensity) 360 (M^+, 5), 267 (1), 189 (100), 157 (4), 92 (57), 77 (20), 65 (16), 55 (20), 41 (15). Anal. Calcd for $C_{19}H_{24}N_2Se$: C, 63.50; H, 6.73; N, 7.80. Found: C, 63.41; H, 6.66; N, 7.87.

1*N*,2-Diphenyl-3,3-dimethyl-5-(phenylseleno)methyl-1-pyrrolidinamine (9): mp 78-79.5 °C; ^{1}H NMR (CD_3OD) δ 7.38-7.27 (m, 2 H), 7.25-7.0 (m, 10 H), 6.75 (dd, 2 H, *J* = 1.0, 7.9 Hz), 6.62 (tt, 1 H, *J* = 1.0, 7.7 Hz), 4.6 (br s, 1 H), 4.0 (s, 1 H), 3.98-3.872 (dd, 1 H,2 (m, 1 H), 3.3 (dd, 1 H, *J* = 3.5, 11.7 Hz), 2.93 (dd, 1 H, *J* = 9.5, 11.7 Hz), 2.1 (dd, 1 H, *J* = 8.4, 13.1 Hz), 1. *J* = 6.0, 13.1 Hz), 1.18 (br s, 3 H), 0.7 (s, 3 H); ^{13}C NMR (DMSO-d_6) δ 149.0, 139.1, 130.5, 130.4, 129.0, 128.8, 127.9, 127.4, 126.6, 126.1, 116.8, 111.5, 75.9, 56.7, 45.2, 38.2, 29.3, 27.8, 24.5. Anal. Calcd for $C_{25}H_{28}N_2Se$: C, 68.95; H, 6.48; N, 6.43. Found: C, 68.87; H, 6.56; N, 6.40.

1*N*,2-Diphenyl-6-methyl-3-(phenylseleno)-1-piperidinamine (10) (1:1 mixture of two stereoisomers): oil; ^{1}H NMR δ 7.4-6.91 (m, 22 H), 6.91-6.8 (m, 2 H), 6.73-6.53 (m, 4 H), 6.52-6.38 (m, 2 H), 4.69 (br s, 1 H), 4.19 (br s, 1 H), 4.1-3.88 (m, 1 H), 3.6-3.3 (m, 4 H), 2.6-2.4 (m, 1 H), 2.15-1.5 (m, 8 H), 1.11 (d, 3 H, *J* = 6.5 Hz), 1.07 (d, 3 H, *J* = 6.1 Hz); ^{13}C NMR δ 149.5, 147.9, 139.9, 135.5, 128.7, 127.9, 127.8, 127.4, 118.3, 117.4, 112.9, 112.3, 78.3, 68.3, 63.5, 53.2, 48.2, 47.1, 34.6, 33.2, 31.2, 27.0, 20.8. Anal. Calcd for $C_{24}H_{26}N_2Se$: C, 68.40; H, 6.22; N, 6.65. Found: C, 68.49; H, 6.32; N, 6.54.

1,3-Diphenyl-6-(phenylseleno)methyl-1,4,5,6-tetrahydropyridazine (11): oil; ^{1}H NMR δ 7.8-7.68 (m, 2 H), 7.68-7.52 (m, 2 H), 7.4-7.12 (m, 8 H), 7.09 (dd, 2 H, *J* = 1.0, 8.5 Hz), 6.8 (tt, 1 H, *J* = 1.0, 7.7 Hz), 4.27 - 4.13 (m, 1 H), 3.14 (ddd, 1 H, *J* = 1.6, 3.2, 12.8 Hz), 2.86 (dd, 1 H, *J* = 11.7, 12.8 Hz), 2.76-2.57 (m, 2 H), 2.56-2.31 (m, 1 H), 2.05-1.82 (m, 1 H); ^{13}C NMR δ 145.9, 139.7, 138.6, 134.3, 131.8, 129.3, 129.1, 128.3, 127.8, 127.7, 124.5, 119.8, 113.5, 50.1, 27.0, 19.5, 17.6. MS *m/z* (relative intensity) 406 (M^+, 2), 235 (100), 157 (3), 143 (11), 104 (7), 77 (23). Anal. Calcd for $C_{23}H_{22}N_2Se$: C, 68.14; H, 5.47; N, 6.91. Found: C, 68.06; H, 5.53; N, 6.86.

3-(*tert*-Butyl)-1-phenyl-6-(phenylseleno)methyl-1,4,5,6-tetrahydropyridazine (12): oil; ^{1}H NMR δ 7.65-7.5 (m, 2 H), 7.38-7.25 (m, 3 H), 7.15 (dd, 2 H, *J* = 7.2, 8.0 Hz), 6.94 (dd, 2 H, *J* = 1.0, 8.0 Hz), 6.74 (tt, 1 H, *J* = 1.0, 7.2 Hz), 4.12-3.99 (m, 1 H), 3.08 (ddd, 1 H, *J* = 1.5, 3.0, 12.6 Hz), 2.75 (dd, 1 H, *J* = 11.7, 12.6 Hz), 2.47 (ddt, 1 H, *J* = 2.0, 4.2, 13.0 Hz), 2.35-1.9 (m, 2 H), 1.88-1.67 (m, 1 H), 1.1 (s, 9 H); ^{13}C NMR δ 151.0, 146.4, 134.1, 129.1, 128.9, 128.6, 127.6, 118.6, 112.8, 49.6, 38.3, 28.1, 26.9, 19.9, 15.6. MS *m/z* (relative intensity) 386 (M^+, 3), 216 (16), 215 (100), 159 (14), 91 (8), 77 (17), 57 (33), 41 (10). Anal. Calcd for $C_{21}H_{26}N_2Se$: C, 65.44; H, 6.80; N, 7.27. Found: C, 65.35; H, 6.92; N, 7.33.

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