Synthesis of Indoles *via* Amidoselenation

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The reaction of 2-styrylacetanilides (**2**) with *N*-phenylselenosuccinimide affords 1-*N*-acetyl-2-phenyl-3-phenylselenoindoles (**3**) and 1-*N*-acetyl-2-phenylindoles (**4**). The reaction of 2-vinylacetanilides (**5**) with phenylselenenyl bromide proceeds to form indoles *via* an intramolecular amidoselenation.

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The chemistry of organoselenium compounds is of interest owing to their fertile and easily manipulated nature [1]. For utilization in organic syntheses, one of the key reactions is the introduction of nitrogen functional groups to olefins accompanied by the addition of phenylseleno moiety. This methodology has been utilized in the selective formation of phenylseleno substituted pyrrolidine or piperidine derivatives from *N*-alkenylamides or -urethanes through an intramolecular amidoselenation [2].

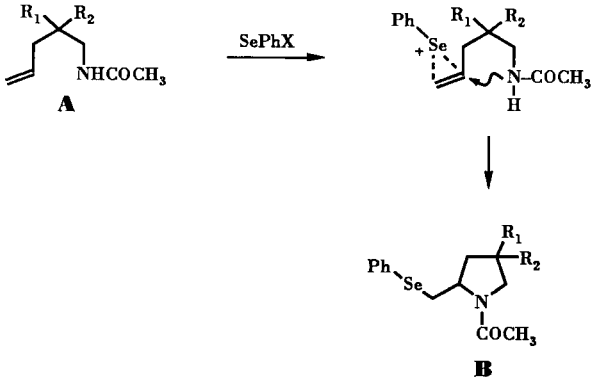
On the other hand, the indole nucleus is common to a large number of and a wide variety of biologically active, naturally occurring compounds, and numerous approaches of its synthesis have been reported. We wish herein to report the synthesis of indole derivative from 2-styrylacetanilides **2** or 2-vinylacetanilides **5** *via* amidoselenation.

Results and Discussion.

Intramolecular Amidoselenation of 2-Styrylacetanilide (**2**).

Numerous studies have reported that the reactions of olefinic amides with benzeneselenenyl halides afford lactams or cyclic amines through the addition of a phenylseleno group to the double bond and subsequent cyclization by the carbon-nitrogen bond formation [2]. For example, by the reactions of *N*-(4-pentenyl)acetamide derivatives **A** with benzeneselenenyl halide, cyclization by the nitrogen atom proceeded through the attack of a amide nitrogen atom on an episelenonium ion intermediate to form nitrogen heterocycles bearing the phenylseleno moiety **B** [2d] (Scheme 1).

Scheme 1

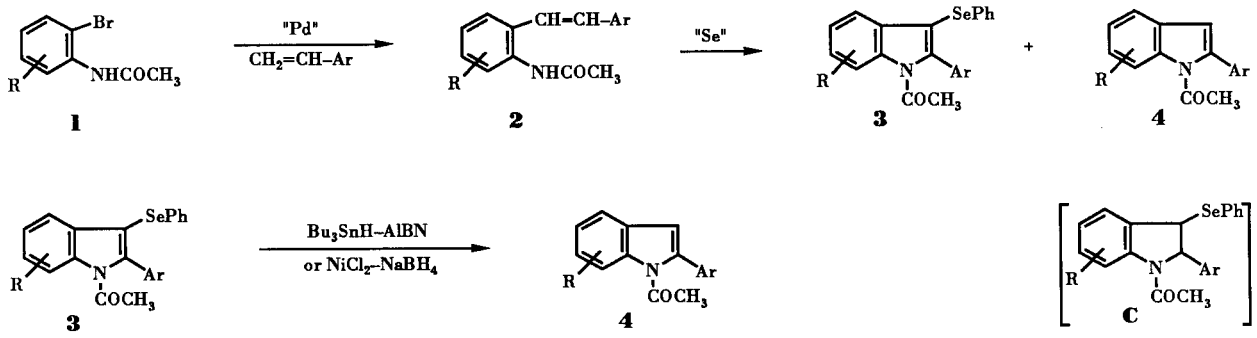


In our case, however, the reaction of 4-methyl-2-styrylacetanilide (**2c**) with benzeneselenenyl chloride (2.4 equivalents) in dry acetonitrile did not provide an intramolecular amidoselenation intermediate **c** and results directly in the formation of 1-*N*-acetyl-5-methyl-2-phenyl-3-phenylselenoindole (**3c**) and 1-*N*-acetyl-5-methyl-2-phenylindole (**4c**) in 61 and 16% yields, respectively, accompanied by recovered **2c** (15%) (Table 1, run 3). The results of the reaction of **2c** with various selenation agents, diphenyldiselenide, benzeneselenenyl bromide, *N*-phenylselenophthalimide (N-PSP) and *N*-phenylselenosuccinimide (N-PSS), under various conditions, were showed in Table 1. Among these reactions, in the presence of *p*-toluenesulfonic acid as catalylst, the reaction of **2c** with 2.4 equivalents of N-PSS in dry dichloromethane at room temperature for 48 hours affords best result (run 6); therefore, the amidoselenation of 2-styrylacetanilide (**2a**), 3-methyl-2-styrylacetanilide (**2b**), 5-methoxy-2-styrylacetanilide (**2d**), 5-ethoxycarbonyl-2-styrylacetanilide (**2e**), and 2-[2-(2-naphthylvinyl)acetanilide (**2f**) carried out under the same conditions (Table 1).

The structure of **4c** was confirmed as 1-*N*-acetyl-5-methyl-2-phenylindole by spectroscopic data and by comparison with an authentic sample. The ir spectrum of **3c** indicated the occurrence of tertiary amido bond at 1685 cm^{-1}. However, the ^1H nmr spectrum of this product did not contain signals in the range of δ 2.37 to 7.00 ppm, except signals of methyl protons (δ 1.94 and 2.37 ppm), indicating the absence of methylene or methine groups in the molecule, and the ^{13}C nmr spectrum of **3c** contains seven quarternary aromatic carbon signals. Furthermore, the reaction of **4c** with a equimol of N-PSS in dichloromethane resulted in the formation of **3c**. Consequently, the structure was confirmed as 1-*N*-acetyl-5-methyl-2-phenyl-3-phenylselenoindole for **3c**.

The reaction of **2c** with 1.2 equivalents of N-PSS afforded **4c** (54% yield) as the main product, accompanied by **3c** (9% yield) (run 5), however, the reaction with 2.4

Scheme 2



1

2

3 + **4**

3 → **4**

C

1a: R = H
1b: R = 3-Me
1c: R = 4-Me
1d: R = 5-OMe
1e: R = 5-COOEt

2a: R = H, Ar = -Ph
2b: R = 3-Me, Ar = -Ph
2c: R = 4-Me, Ar = -Ph
2d: R = 5-OMe, Ar = -Ph
2e: R = 5-COOEt, Ar = -Ph
2f: R = H, Ar = 2-Naphthyl

3a,4a: R = H, Ar = -Ph
3b,4b: R = 4-Me, Ar = -Ph
3c,4c: R = 5-Me, Ar = -Ph
3d,4d: R = 6-OMe, Ar = -Ph
3e,4e: R = 6-COOEt, Ar = -Ph
3f,4f: R = H, Ar = 2-Naphthyl

equivalents of N-PSS resulted in the formation of **3c** (82%) as the main product, accompanied by **4c** (10%) (run 6). Moreover, monitoring by tlc (silica gel) showed that the reaction proceeds at first in the formation of **4c**, followed by the formation of **3c**. The above observations indicated that the amidoselenation of **2** directly yielded 1-*N*-acetylindoles **4**, and that the following reaction of **4** with N-PSS resulted to form 1-*N*-acetyl-2-phenyl-3-phenylselenoindoles **3**. The amidoselenation of olefins usually proceeds though the addition of selenium reagent to the double bond and the subsequent carbon-nitrogen bond formation, however, the course of the amidoselenation proceeding concomit-

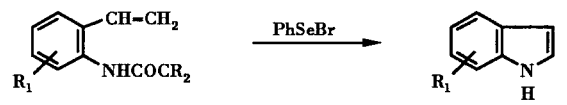
Table 1

Intramolecular Cyclization of 2-Styrylacetanilides **2** Using Selenium Compounds

Run	Starting material	Reagent (equivalents)		Time, hours	Temp (°C)	Product: yield (%) [a] **3**	**4**	Recovered **2**
1	**2c**	PhSeBr [b]	(2.0)	48	rt	4	33	48
2	**2c**	PhSeCl [c]	(1.2)	84	40	8	30	35
3	**2c**	PhSeCl [c]	(2.4)	84	40	61	16	12
4	**2c**	N-PSP [d]	(1.0)	44	reflux	12	47	15
5	**2c**	N-PSS [e]	(1.2)	78	40	9	54	25
6	**2c**	N-PSS [f]	(2.4)	48	rt	82	10	–
7	**2c**	PhSeSePh [g]	(1.0)	24	70	7	48	35
8	**2c**	PhSeSePh [g]	(2.0)	24	70	66	28	–
9	**2a**	N-PSS [f]	(2.4)	48	rt	78	2	–
10	**2b**	N-PSS [f]	(2.4)	48	rt	74	8	–
11	**2d**	N-PSS [f]	(2.4)	48	rt	78	4	–
12	**2e**	N-PSS [f]	(2.4)	48	rt	62 + 28	–	–
13	**2f**	N-PSS [f]	(2.4)	48	rt	50	45	–

[a] Isolated yield based on **2**. [b] Carried out using **2c** (4.0 mmoles) and benzeneselenenyl bromide (8.0 mmoles) in tetrahydrofuran (70 ml) under a nitrogen atmosphere. [c] To a solution of **2c** (8.0 mmoles) in acetonitrile (80 ml) was added a solution of benzeneselenenyl chloride in acetonitrile (50 ml), and after stirring at room temperature for 60 hours, the mixture was warmed at 40° for 24 hours under a nitrogen atmosphere. [d] To a solution of **2c** (2.33 mmoles) in dry dichloromethane (24 ml) was added a solution of N-PSP in dichloromethane (100 ml), and after stirring at room temperature for 4 hours, the mixture was refluxed for additional 40 hours, the mixture was refluxed for additional 40 hours under a nitrogen atmosphere. [e] To a solution of N-PSS (4.8 mmoles) and *p*-toluenesulfonic acid monohydrate (0.48 mmoles) in dichloromethane (40 ml), and after stirring at room temperature for 54 hours the mixture was warmed at 40° for an additional 24 hours, under a nitrogen atmosphere. [f] See experimental. [g] A solution of PhSeSePh, ammonium peroxydisulfate (2.4 mmoles) and **2c** (4.0 mmoles) in acetonitrile (35 ml) was warmed at 70° under a nitrogen atmosphere. [h] *N*-Deacetyl derivative **3e'** (28% yield) was obtained as a byproduct.

Scheme 3



5 **6**

5a: $R_1 = H, R_2 = -CH_3$
5b: $R_1 = 5\text{-}CH_3, R_2 = -CH_3$
5c: $R_1 = H, R_2 = -CF_3$
5b: $R_1 = 5\text{-}CH_3, R_2 = -CF_3$

6a: $R_1 = H$
6b: $R_1 = 6\text{-}CH_3$

antly with elimination of the phenyseleno group was not reported to our knowledge. Kocor and Beata [3] reported previously that the phenylselenolactonization of (*E*)- and (*Z*)-3β-methoxychol-5-,17(20)-dien-24-acids was accompanied by a spontaneous elimination of the phenylseleno moiety and resulted in the formation of unsaturated lactones. Therefore, it seems of interest to gain insight into the reaction of **2** with N-PSS.

The reductive removal of a phenylseleno group from 3-phenylseleno derivatives **3** was carried out using tri-*n*-butyltin hydride [4] in the presence of 2,2′-azobisisobutyronitrile (AIBN) in good yield, however, the nickel boride reduction [2d,5] was also effective for the replacement of a phenylseleno group by a hydrogen atom to afford **4** in less yield than that of tri-*n*-butyltin hydride reduction (Table 2).

The reaction of 2-vinylacetanilide (**5a**) with phenylselenenyl bromide (2 equivalents) in THF as the solvent at room temperature, indole (**6a**) was directly produced with no formation of the 3-phenylseleno derivative **6′** (run 1), however, the yield was poor (17%). It was increased to 40% by changing the starting material from **5a** to 2-vinyltrifluoroacetanilide (**5c**). The formation of **6** probably proceeds through the addition of a phenylseleno group to the double bond of **5**, by subsequent cyclization by carbon-nitrogen bond formation, with spontaneous elimination of a phenylseleno moiety, and by following hydrolysis of the *N*-acyl gorup with hydrobromic acid which was produced in the reaction. On the other hand, the reaction of **5a** with N-PSS in dichloromethane did not afford the amidoselenation product. These results are summarized in Table 3.

Table 2

Reductive Removal of Phenylseleno Group from **3**

Run	Starting material	Reducing agent	Time, hours	Yield (%) [a] Product	Recovered
1	**3a**	*n*-Bu_3SnH-AIBN [b]	6.5	**4a** (82)	**3a** (18)
2	**3b**	*n*-Bu_3SnH-AIBN [b]	16	**4b** (78)	**3b** (22)
3	**3b**	*n*-Bu_3SnH-AIBN [b]	1	**4c** (82)	**3c** (14)
4	**3c**	$NiCl_2$-$NaBH_4$ [c]	31	**4c** (49)	**3c** (48)
5	**3c**	$NiCl_2$-$NaBH_4$ [d]	37	**4c** (64)	**3c** (34)
6	**3d**	*n*-Bu_3SnH-AIBN [b]	24	**4d** (69)	**3d** (13)
7	**3e**	*n*-Bu_3SnH-AIBN [b]	24	**4e** (80)	– –
8	**3f**	*n*-Bu_3SnH-AIBN [b]	24	**4f** (97)	**3f** (2)

[a] Isolated yield based on 3. [b] Carried out using phenylseleno derivative (2.5 mmoles), AIBN (0.05 mmole), and tri-*n*-butyltin hydride (5.1 mmoles) in tetrahydrofuran at 110° (see Experimental). [c] To a mixture of **3c** (2.8 mmoles) and nickel dichloride hexahydrate (21 mmoles) in methanol-tetrahydrofuran (1:9, 300 ml) was added sodium borohydride (42 mmoles) at 0°, and the mixture was stirred at 0° for 1 hour, and at room temperature for additional 30 hours. [d] To a mixture of **3c** (2.8 mmoles) and nickel dichloride hexahydrate (21 mmoles) in methanol-tetrahydrofuran (1:9, 300 ml) was added sodium borohydride (42 mmoles) at 0°. After vigorous stirring at 0° for 1 hour and then at room temperature for 12 hours, the resulting mixture was refluxed for additional 24 hours.

Table 3

Intramolecular Cyclization of 2-Vinylacetanilides **5**

Run	Starting material	Reagent	Solvent	Time, hours	Temp (°C)	Product Yield (%) [a]
1	**5a**	PhSeBr [b]	THF	19	rt	**6a** (17)
2	**5a**	PSS [c]	CH_2Cl_2	48	rt	– –
3	**5b**	PhSeBr [b]	THF	12	rt	**6b** (25)
4	**5c**	PhSeBr [b]	THF	12	rt	**6a** (40)
5	**5d**	PhSeBr [b]	THF	12	rt	**6b** (45)

[a] Isolated yield based on **5**. [b] Carried out using benzeneselenenyl bromide (13 mmoles) and **5** (6.5 mmoles) in tetrahydrofuran (25 ml) (see Experimental). [c] To a solution of N-PSS (16 mmoles) and *p*-toluenesulfonic acid monohydrate (1.6 mmoles) in dichloromethane (120 ml) was added a solution of **5a** (6.7 mmoles) in dichloromethane (50 ml) under a nitrogen atmosphere.

EXPERIMENTAL

Melting points were determined with a Gallenkamp melting point determination apparatus and were uncorrected. The ir spectra were taken with a Hitachi 260-10 spectrometer. The ^1H- and ^{13}C-nmr spectra were recorded with a Hitachi R-90H (90 MHz) instrument in deuteriochloroform using TMS as internal standard. Mass spectra were measured on a Hitachi RMU-6M mass spectrometer.

Literature methods were used to prepare the following compounds: diphenyldiselenide [6], benzeneselenenyl chloride [6], *N*-phenylselenophthalimide (N-PSP) [8], *N*-phenylselenosuccinimide (N-PSS) [9]. Benzeneselenenyl bromide was usually prepared *in situ* by the reported procedure [7] and used directly.

General Procedure for the Synthesis of 2-Styrylacetanilides **2**.

A mixture of *o*-bromoacetanilides (0.42 mmole), styrene (0.40 g, 3.86 mmoles), triethylamine (0.39 g, 3.86 mmoles), tri-*o*-tolylphosphine (0.08 g, 0.27 mmole) and palladium(II) acetate (0.007 g, 0.032 mmole) in dry xylene (10 ml) was heated at 100° under nitrogen atmosphere. After 6 hours additional portions of palladium(II) acetate (0.032 g, 0.15 mmole) and tri-*o*-tolylphosphine (0.159 g, 0.525 mmole) wee added and the mixture was heated for additional 3 hours. The reaction mixture was then poured into water and extracted with ether. The ether phase was separated,

washed with water, dried over anhydrous magnesium sulfate, filtered and concentrated. The residue was then purified by column chromatography (silica gel, benzene), followed by recrystallization from ethanol.

The structure of the products **2** was confirmed by a mixed-melting point determination with authentic sample and by the observation of the ir, ^{1}H nmr, and mass spectra.

2-Styrylacetanilide (**2a**).

This compound was obtained from **1a** as colorless crystals, mp 139-140° (lit [10], mp 140°), yield, 69%.

3-Methyl-2-styrylacetanilide (**2b**).

This compound was obtained from **1b** as colorless crystals, mp 111-112°, yield 69%; ir (potassium bromide): 3250 (-NH), 1650 (-NHCO-), 960 (*trans* -CH=CH-), 760, 690 cm^{-1} (Ar-H); ^{1}H nmr: δ 2.06 (s, 3H, -$COCH_3$), 2.31 (s, 3H, Ar-CH_3), 6.82 (d, 2H, J = 16.5 Hz, -CH=CH-), 7.03 + 7.13-7.60 + 7.84-8.02 ppm (m, 9H, Ar-H + -NH); ms: m/z 251 [M$^+$].

Anal. Calcd. for $C_{17}H_{17}NO$: C, 81.24; H, 6.82; N, 5.57. Found: C, 81.19; H, 6.75; N, 5.48.

4-Methyl-2-styrylacetanilide (**2c**).

This compound was obtained from **1c** as colorless crystals, mp 161-162°, yield 72%; ir (potassium bromide): 3270 (-NH), 1650 (-NHCO-), 965 (*trans* -CH=CH-), 810, 710 cm^{-1} (Ar-H); ^{1}H nmr: δ 2.01 (s, 3H, -$COCH_3$), 2.24 (s, 3H, Ar-CH_3), 6.90 (d, 2H, J = 12 Hz, -CH=CH-), 7.10-7.48 (m, 8H, Ar-H), 7.54 ppm (br s, 1H, -NH); ms: m/z 251 [M$^+$].

Anal. Calcd. for $C_{17}H_{17}NO$: C, 81.24; H, 6.82; N, 5.57. Found: C, 81.16; H, 6.71; N, 5.46.

5-Methoxy-2-styrylacetanilide (**2d**).

This compound was obtained from **1d** as colorless crystals, mp 179-180°, yield 82%; ir (potassium bromide): 3230 (-NH), 1645 (-NHCO-), 975 (*trans* -CH=CH-), 960, 850, 800, 750, 710 cm^{-1} (Ar-H); ^{1}H nmr: δ 2.10 (s, 3H, -$COCH_3$), 3.74 (s, 3H, -OCH_3), 6.70 (br s, 1H, -NH), 6.90 (d, 2H, J = 12 Hz, -CH=CH-), 7.10-7.60 ppm (m, 8H, Ar-H); ms: m/z 267 [M$^+$].

Anal. Calcd. for $C_{17}H_{17}NO_2$: C, 76.38; H, 6.41; N, 5.24. Found: C, 76.35; H, 6.37; N, 5.19.

5-Ethoxycarbonyl-2-styrylacetanilide (**2e**).

This compound was obtained from **1e** as colorless crystals, mp 185-186°, yield 75%; ir (potassium bromide): 3240 (-NH), 1705 (ester), 1650 (-NHCO-), 960 (*trans* -CH=CH-), 935, 815, 790, 710 cm^{-1} (Ar-H); ^{1}H nmr: δ 1.36 (t, 3H, -CH_3),2.13 (s, 3H, -$COCH_3$), 4.32 (q, 2H, -CH_2-), 7.01 + 7.23-7.82 (m, 10H, -CH=CH- + Ar-H), 8.16 ppm (br s, 1H, -NH); ms: m/z 309 [M$^+$].

Anal. Calcd. for $C_{19}H_{19}NO_3$: C, 73.76; H, 6.19; N, 4.53. Found: C, 73.68; H, 6.15; N, 4.46.

2-[2-(2-Naphthyl)vinyl]acetanilide (**2f**).

This compound was prepared by the reaction of **1a** with 2-vinylnaphthalene in the presence of palladium catalyst using the method described above, colorless crystals, mp 215-216°, yield 59%; ir (potassium bromide): 3250 (-NH), 1650 (-NHCO-), 950 (*trans* -CH=CH-), 810, 740 cm^{-1} (Ar-H); ^{1}H nmr: δ 2.17 (s, 3H, -$COCH_3$), 7.20-7.60 (m, 6H, -CH=CH- + Ar-H), 7.70-7.96 (m, 7H, naphthalene ring protons), 9.60 ppm (s, 1H, -NH); ms: m/z 287 [M$^+$].

Anal. Calcd. for $C_{20}H_{17}NO$: C, 83.59; H, 5.96; N, 4.88. Found: C, 83.56; H, 5.87; N, 4.85.

Synthesis of 2-Vinylacetanilides (**5**).

2-Vinylacetanilide (**5a**).

This compound was synthesized by the reaction of 2-vinylaniline with acetic anhydride, colorless crystals, mp 89-90°, yield 97%; ir (potassium bromide): 3220 (-NH), 1640 (-NHCO-), 1000, 920 (-CH=CH_2), 745 cm^{-1} (Ar-H); ^{1}H nmr: δ 2.15 (s, 3H, -$COCH_3$), 5.35 (d, 1H, J = 12 Hz, Ar-C=CH-), 6.65 (d, 1H, J = 18 Hz, Ar-C=CH-), 6.80 (d-d, 1H, J = 12 and 18 Hz, Ar-CH=C-), 7.08-7.86 (Ar-H + -NH); ms: m/z 161 [M$^+$].

Anal. Calcd. for $C_{10}H_{11}NO$: C, 74.51; H, 6.88; N, 8.69. Found: C, 74.45; H, 6.83; N, 8.64.

5-Methyl-2-vinylacetanilide (**5b**).

This compound was synthesized according to the literature method, mp 127-129°, (lit [11], mp 127-129°).

2-Vinyltrifluoroacetanilide (**5c**).

This compound was synthesized by the reaction of 2-vinylaniline with trifluoroacetic anhydride, colorless crystals, mp 69-70°, yield 93%; ir (potassium bromide): 3270 (-NH), 1700 (-NHCO-), 980, 910 (-CH=CH_2), 755 cm^{-1} (Ar-H); ^{1}H nmr: δ 5.45 (d, 1H, J = 13.5 Hz, Ar-C=CH-), 5.64 (d, 1H, J = 21 Hz, Ar-C=CH-), 6.80 (d-d, 1H, J = 13.5 and 21 Hz, Ar-CH=C-), 7.15-7.50 + 7.65-7.80 (m, 4H, Ar-H), 8.00 ppm (br s, 1H, -NH); ms: m/z 215 [M$^+$].

Anal. Calcd. for $C_{10}H_8F_3NO$: C, 55.82; H, 3.75; N, 6.51. Found: C, 55.77; H, 3.66; N, 6.55.

5-Methyl-2-vinyltrifluoroacetanilide (**5d**).

This compound was synthesized by the reaction of 5-methyl-2-vinylaniline with trifluoroacetic anhydride in benzene, colorless crystals, mp 109-110°, yield 95%; ir (potassium bromide): 3250 (-NH), 1700 (-NHCO-), 990, 910, 875, 805 cm^{-1}; ^{1}H nmr: δ 2.28 (s, 3H, -CH_3), 5.47 (d, 1H, J = 13 Hz, Ar-C=C-H), 5.76 (d, 1H, J = 20 Hz, Ar-C=C-H), 6.87 (d, 1H, J = 13 and 20 Hz, Ar-CH=C-), 7.08-7.51 (m, 3H, Ar-H), 7.69 ppm (br s, 1H, -NH); ms: m/z 229 [M$^+$].

Anal. Calcd. for $C_{11}H_{10}F_3NO$: C, 57.64; H, 4.36; N, 6.11. Found: C, 57.58; H, 4.29; N, 6.03.

General Procedure for the Reaction of 2-Styrylacetanilides **2a-f** with *N*-Phenylselenosuccinimide (N-PSS) (Table 1, runs 6, 9, 10, 11, 12 and 13).

To the solution of N-PSS (2.44 g, 9.6 mmoles) and *p*-toluenesulfonic acid monohydrate (0.18 g, 0.96 mmole) in dry dichloromethane (50 ml) was added dropwise the solution of **2a-f** (4.0 mmoles) in dry dichloromethane (50 ml) under nitrogen atmosphere and the resulting mixture was stirred at room temperature for 2 days. After evaporation of solvents under reduced pressure, the residue was purified by column chromatography [silica gel, hexane-benzene (1:1) as eluant] to afford diphenyldiselenide (first elution, mp 62-63°), 1-*N*-acetyl-2-phenylindoles **4a-f** (second elution), and 1-*N*-acetyl-2-phenyl-3-(phenylseleno)indoles **3a-f** (third elution). The results are summarized in Table 1.

1-*N*-Acetyl-2-phenyl-3-(phenylseleno)indole (**3a**).

This compound was obtained from **2a** as colorless crystals, accompanied by **4a**, mp 116-117°; ir (potassium bromide): 1700 (-NCO-), 1600, 1580, 760, 700 cm^{-1} (o-di- and mono-subst Ar-H); ^{1}H nmr: δ 1.94 (s, 3H, -CH_3), 7.05 (s, 5H, -Se-C_6H_5), 7.35 (s, 5H,

$-C_2-C_6H_5$), 7.12-7.60 (m, 3H, $-C_4-H$ + $-C_5-H$ + $-C_6-H$), 8.35 ppm (d-d, 1H, $-C_7-H$); ^{13}C nmr: δ 27.5 ($-CH_3$), 115.8, 120.6, 123.9, 125.7, 125.9, 128.8, 128.9, 129.5, 130.1, 130.3 (non-substituted aromatic carbons), 108.6, 130.7, 131.9, 132.8, 136.9, 142.7 (substituted aromatic carbons), 170.7 ppm (-C=O); ms: m/z 390 [M$^+$].

Anal. Calcd. for $C_{22}H_{17}NOSe$: C, 67.69; H, 4.39; N, 3.59. Found: C, 67.61; H, 4.28; N, 3.51.

1-*N*-Acetyl-2-phenylindole (**4a**).

This compound was obtained as colorless oil and the structure was established by comparision of ir and ^1H nmr spectra with those of an authentic sample [12].

1-*N*-Acetyl-4-methyl-2-phenyl-3-(phenylseleno)indole (**3b**).

This compound was obtained from **2b** as colorless crystals, accompanied by **4b**, mp 143°; ir (potassium bromide): 1700 (-NCO-), 1600, 1570, 780, 700 cm^{-1} (1,2,3-tri- and mono-subst Ar-H); ^1H nmr: δ 1.94 (s, 3H, $-COCH_3$), 2.70 (s, 3H, Ar-CH_3), 7.06 (s, 5H, $-Se-C_6H_5$), 7.35 (s, 5H, $-C_2-C_6H_5$), 7.13-7.58 (m, 2H, $-C_5-H$ + $-C_6-H$), 8.29 ppm (d-d, 1H, $-C_7-H$); ^{13}C nmr: δ 19.2 (Ar-CH_3), 27.5 (acetyl $-CH_3$), 113.4, 123.9, 125.3, 126.1, 128.0, 128.1, 129.4, 130.0, 130.5 (non-substituted aromatic carbons), 106.4, 125.3, 131.9, 133.2, 134.9, 137.1, 143.9 (substituted aromatic carbons), 170.9 ppm (-C=O); ms: m/z 404 [M$^+$].

Anal. Calcd. for $C_{23}H_{19}NOSe$: C, 68.31; H, 4.73; N, 3.46. Found: C, 68.17; H, 4.68; N, 3.42.

1-*N*-Acetyl-4-methylindole (**4b**).

This compound was obtained as colorless oil; ir (neat): 1700 (-NCO-), 1600, 1560, 780, 700 cm^{-1} (1,2,3-tri- and mono-subst Ar-H); ^1H nmr: δ 2.05 (s, 3H, $-COCH_3$), 2.50 (s, 3H, Ar-CH_3), 6.63 (s, 1H, $-C_3-H$), 6.98-7.35 (m, 2H, $-C_5-H$ + $-C_6-H$), 7.41 (s, 5H, $-C_2-C_6H_5$), 8.18 ppm (d, 1H, $-C_7-H$); ms: m/z 249 [M$^+$].

Anal. Calcd. for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N, 5.62. Found: C, 81.85; H, 6.01; N, 5.56.

1-*N*-Acetyl-5-methyl-2-phenyl-3-(phenylseleno)indole (**3c**).

This compound was obtained as colorless crystals from **2c**, accompanied by **4c**, mp 113-114°; ir (potassium bromide): 1685 (-NCO-), 1600, 1580, 870, 810, 700 cm^{-1} (1,2,4-tri- and mono-subst Ar-H); ^1H nmr: δ 1.94 (s, 3H, $-COCH_3$), 2.37 (s, 3H, Ar-CH_3), 7.00-7.25 (m, 7H, $-Se-C_6H_5$ + $-C_4-H$ + $-C_6-H$), 7.34 (s, 5H, $-C_2-C_6H_5$), 8.25 ppm (d, 1H, $-C_7-H$); ^{13}C nmr: δ 21.3 (Ar-CH_3), 27.5 (acety $-CH_3$), 115.7, 120.4, 125.8, 127.1, 128.2, 128.9, 129.3, 130.3, 130.6 (non-substituted aromatic carbons), 108.3, 129.6, 131.0, 133.0, 133.6, 135.1, 143.0 (substituted aromatic carbons), 170.6 ppm (C=O); ms: m/z 404 [M$^+$].

Anal. Calcd. for $C_{23}H_{19}NOSe$: C, 68.31; H, 4.73; N, 3.46. Found: C, 68.23; H, 4.65; N, 3.38.

1-*N*-Acetyl-5-methyl-2-phenylindole (**4c**).

This compound was obtained as colorless crystals, mp 70-71° (lit [13], mp 71.5-72.5°).

1-*N*-Acetyl-6-methoxy-2-phenyl-3-(phenylseleno)indole (**3d**).

This compound was obtained as colorless oil from **2d**, accompanied by **4d**; ir (neat): 1700 (-NCO-), 1600, 1585, 950, 840, 810, 710 cm^{-1}; ^1H nmr: δ 1.96 (s, 3H, $-COCH_3$), 3.85 (s, 3H, $-OCH_3$), 6.86 (d-d, 1H, $-C_5-H$), 7.00-7.13 (m, 5H, $-Se-C_6H_5$), 7.36 (s, 5H, $-C_2-C_6H_5$), 7.37-7.45 (m, 1H, $-C_4-H$), 7.98 ppm (d, 1H, $-C_7-H$); ^{13}C nmr: δ 27.6 (acetyl $-CH_3$), 55.6 ($-OCH_3$), 100.1, 113.2, 121.1, 125.9, 128.2, 128.8, 129.5, 130.0, 130.3 (non-substituted aromatic carbons), 108.6, 124.5, 131.9, 133.0, 137.8, 141.3, 158.9 (substituted aromatic carbons), 171.0 ppm (-C=O); ms: m/z 420 [M$^+$].

Anal. Calcd. for $C_{23}H_{19}NO_2Se$: C, 65.71; H, 4.55; N, 3.33. Found: C, 65.65; H, 4.47; N, 3.29.

1-*N*-Acetyl-6-methoxy-2-phenylindole (**4d**).

This compound was obtained as colorless crystals, mp 86-87° (lit [13], mp 88-89°).

1-*N*-Acetyl-6-ethoxycarbonyl-2-phenyl-3-(phenylseleno)indole (**3e**).

This compound was obtained as colorless crystals from **2e**, accompanied by **3e'**, mp 140-141°; ir (potassium bromide): 1715 (-COOEt + -NCO-), 1600, 1580, 985, 840, 710 cm^{-1} (1,2,4-tri- and mono-subst Ar-H); ^1H nmr: δ 1.40 (t, 3H, $-CH_3$), 2.00 (s, 3H, $-COCH_3$), 4.40 (q, 2H, $-CH_2-$), 7.09 (s, 5H, $-Se-C_6H_5$), 7.41 (s, 5H, $-C_2-C_6H_6$), 7.56 (d, 1H, $-C_4-H$), 7.96 (d, 1H, $-C_5-H$), 9.00 cm^{-1} (s, 1H, $-C_7-H$); ^{13}C nmr: δ 14.4 (ester $-CH_3$), 27.6 (acetyl $-CH_3$), 60.9 (ester $-CH_2-$), 120.3, 125.2, 126.2, 127.9, 128.4, 128.9, 129.7, 130.0, 130.2 (non-substituted aromatic carbons), 108.5, 117.6, 131.5, 132.4, 134.4, 136.3, 145.4 (substituted aromatic carbons), 166.7 (ester -C=O), 170.6 ppm (acetyl -C=O); ms: m/z 462 [M$^+$].

Anal. Calcd. for $C_{25}H_{21}NO_3Se$: C, 64.93; H, 4.57; N, 3.03. Found: C, 64.90; H, 4.48; N, 2.95.

6-Ethoxycarbonyl-2-phenyl-3-(phenylseleno)indole (**3e'**).

This compound was probably formed by hydrolysis of **3e**, and was obtained as colorless cyrstals, mp 186°; ir (potassium bromide): 3350 (-NH), 1695 (-COOEt + $-COCH_3$), 1570, 1530, 880, 820, 690 cm^{-1} (1,2,4-tri and mono-subst Ar-H); ^1H nmr: δ 1.40 (t, 3H, $-CH_3$), 4.40 (q, 2H, $-CH_2-$), 7.12 (s, 5H, $-Se-C_6H_5$), 7.23-7.80 (m, 8H, -NH + $-C_2-C_6H_5$ + $-C_4-H$ + $-C_5-H$), 8.24 ppm (s, 1H, $-C_7-H$); ms: m/z 420 [M$^+$].

Anal. Calcd. for $C_{23}H_{19}NO_2Se$: C, 65.71; H, 4.55; N, 3.33. Found: C, 65.66; H, 4.47; N, 3.26.

1-*N*-Acetyl-2-(2-naphthyl)-3-(phenylseleno)indole (**3f**).

This compound was obtained as colorless crystals from **2f**, accompanied by **4f**, mp 122-124°; ir (potassium bromide): 1700 (-NCO-), 1600, 1560, 810, 760 cm^{-1}; ^1H nmr: δ 1.94 (s, 3H, $-COCH_3$), 7.01-7.88 (m, 16H, aromatic ring protons), 8.92 ppm (d-d, 1H, $-C_7-H$); ^{13}C nmr: δ 27.8 (acetyl $-CH_3$), 115.8, 120.4, 123.4, 124.9, 125.3, 126.1, 126.3, 126.5, 126.6, 127.4, 127.6, 127.8, 128.1, 130.5 (non-substituted aromatic carbons), 106.3, 125.3, 128.9, 131.3, 132.5, 132.9, 137.7, 139.5 (substituted aromatic carbons), 170.9 ppm (acetyl -C=O); ms: m/z 440.

Anal. Calcd. for $C_{26}H_{19}NOSe$: C, 70.90; H, 4.35; N, 3.18. Found: C, 70.78; H, 4.45; N, 3.02.

1-*N*-Acetyl-2-(2-naphthyl)indole (**4f**).

This compound was obtained as colorless crystals, mp 91-92°; ir (potassium bromide): 1700 (-NCO-), 1600, 1560, 810, 760 cm^{-1}; ^1H nmr: δ 1.98 (s, 3H, $-COCH_3$), 6.58 (s, 1H, $-C_3-H$), 7.05-7.90 (m, 10H, aromatic protons), 8.34 ppm (d-d, 1H, $-C_7-H$); ms: m/z 285 [M$^+$].

Anal. Calcd. for $C_{20}H_{15}NO$: C, 84.18; H, 5.30; N, 4.91. Found: C, 84.01; H, 5.17; N, 4.82.

Reaction of 1-*N*-Acetyl-5-methyl-2-phenylindole (**4c**) with N-PSS.

To the solution of N-PSS (1.47 g, 5.8 mmoles) and *p*-toluenesulfonic acid monohydrate (0.11 g, 0.58 mmole) in dry dichlorometh-

ane (60 ml) was added dropwise the solution of **4c** (0.60 g, 2.4 mmoles) in dichloromethane (50 ml) and the resulting mixture was stirred for 24 hours at room temperature. After evaporation of the solvents, the residue were purified by column chromatography (silica gel, benzene) and the colorless crystals of **3c** (mp 113-114°, 0.93 g, 96% yield) were obtained.

Reductive Removal of Phenylseleno Group from **3** to **4** with Tributyltin Hydride.

In a Schlenk tube, to a solution of 3-phenylseleno derivative **3** (2.5 mmoles) in dry toluene (15 ml) was added a solution of 2,2'-azobisisobutyronitrile (AIBN, 0.008 g, 0.05 mmole) in dry toluene (3 ml) under a nitrogen atmosphere, and tri-*n*-butyltin hydride (1.0 ml, 5.1 mmoles) was injected from a syringe. The resulting mixture was heated at 110° for 1 hour using oil bath under stirring magnetically. Evaporation of the solvent and column chromatography of the residue over silica gel with hexane/ethyl acetate (2:1) gave a colorless crystals of **4**. The results are summarized in Table 2.

General Procedure for the Reaction of 2-Vinylacetanilide **5** with Benzeneselenenyl Bromide (Table 3).

Under a nitrogen atmosphere, to a solution of benzeneselenenyl bromide (6.5 mmoles) in dry THF (25 ml) was added a solution of **5** (6.5 mmoles) in the same solvent (20 ml) at room temperature and the mixture was stirred at ambient temperature for 12 hours. Saturated aqueous sodium hydrogencarbonate (30 ml) was added, and the products were extracted with dichloromethane. The orgnaic layer was washed with brine, dried over anhydrous magnesium sulfate, and evaporated. Column chromatography (alumina, benzene) afforded indole derivative (**6**).

Indole (**6a**).

This compound was obtained from **5a** or **5c** as colorless crystals, mp 50-51° (lit [14], mp 52-53°).

6-Methylindole (**6b**).

This compound was obtained from **5b** or **5d** as a pale yellow oil and the structure was determinated by the comparison of ir and ^{1}H nmr spectra with those of the authentic sample (lit [15], bp 75-78°/1 mm Hg).

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