Synthesis of Isocoumarin, 1-Isoquinolone and 4(1*H*)-Quinolone Derivatives *via* Seleno-intermediates

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The reaction of 2-styrylbenzoic acids **2** with *N*-phenylselenosuccinimide (N-PSS) affords 3-phenyl-iso-coumarin derivatives **3** and 3,4-dihydro-3-phenyl-4-(phenylseleno)isocoumarins **4** *via* selenolactonization. The reaction of 2-styrylbenzamides **5** and 1-(2-aminophenyl)-3-phenyl-2-peropen-1-one derivatives **11** with N-PSS also resulted in the formation of 1-isoquinolone **6** and 4(1*H*)-quinolone derivatives **12**, respectively.

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Much attention has been paid to the methodology for the introduction of oxygen or nitrogen functional groups to olefins accompanied by the addition of the arylseleno moiety, and many types of reactions have been reported in the literature [1]. Selenoetherification [2], selenolactonization [3], or selenoamidation [4] are particularly favorable for the expansion of functional groups, because the resulting seleno-intermediates are convertible to various heterocycles. Typical examples involving heterocycles are shown in figure 1.

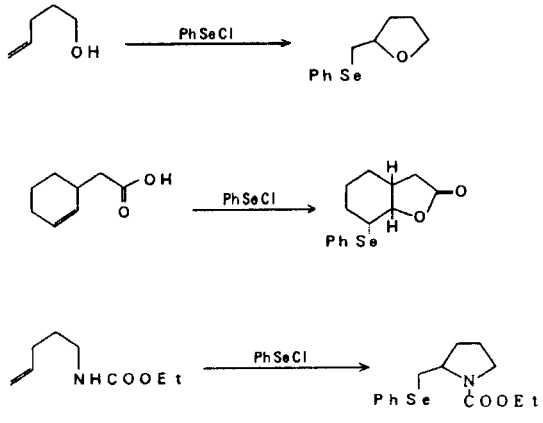

Figure 1

Such reactions usually proceed in good yield under mild conditions, and the proposed strategy involves making oxygen or nitrogen-carbon bonds, as in **A** or **B**, to generate the heterocycle.

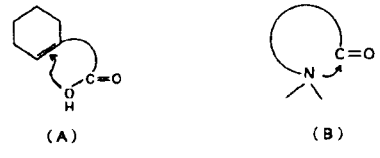

Figure 2

On the other hand, the isocoumarins are unsaturated lactones which are found in nature and display a wide variety of biological activities [5]. They have been prepared by cyclization of homophthalic acids [6], 2-carboxybenzyl ketones [7], and 2-vinylbenzoic acids [8], or by the conversion of alkylidenephthalides [9]. Previously, Hegedus *et al.* reported that 2-bromobenzoic acids were treated with π-allyl nickel bromide to produce 2-allylbenzoic acids which were cyclized to isocoumarins by treatment with palladium chloride, and that the palladium-assisted cyclization of 2-allylbenzamides proceeded to afford 1-isoquinolones [10]. We also described the palladium-catalyzed synthesis of isocoumarins and 1-isoquinolones from 2-vinylbenzoic acids and 2-vinylbenzamides [11].

Previously, we reported the synthesis of indoles from 2-vinylacetanilides *via* amidoselenation [12]. Herein, we wish to describe the development of intramolecular selenolactonization or amidoselenation for the preparation of 3-phenylisocoumarins **3**, 3-phenyl-1-isoquinolones **6** or 2-phenyl-4(1*H*)-quinolones **12** from readily obtainable 2-styrylbenzoic acids **2**, 2-styrylbenzamides **5** or 1-(2-acetylaminophenyl)-3-phenyl-2-propen-1-ones **11**, respectively.

Results and Discussion.

Synthesis of Isocoumarins **3** from 2-Styrylbenzoic Acids **2**.

The overall reaction scheme is presented in Figure 3.

The starting materials, 2-styrylbenzoic acid (**2a**), 4-methyl-2-styrylbenzoic acid (**2b**), 3-methyl-2-styrylbenzoic acid (**2c**), 4-chloro-2-styrylbenzoic acid (**2d**) and 5-carboxy-2-styrylbenzoic acid (**2e**) were synthesized by the Heck reaction of styrene with the corresponding alkyl 2-bromobenzoates **1**, followed by hydrolysis.

Numerous studies have reported that the reaction with benzeneseleneyl halides affords lactones or cyclic ethers through the addition of a phenylseleno group to the dou-

ble bond and subsequent cyclization by carbon-oxygen bond formation [2,3]. For example, in the reaction of unsaturated acid derivatives **C** with benzeneselenenyl halide, cyclization by the oxygen atom proceeded through the attack of an acid oxygen atom on an episelenium ion intermediate to form oxygen heterocycles bearing the phenylseleno moiety **D** (Figure 4).

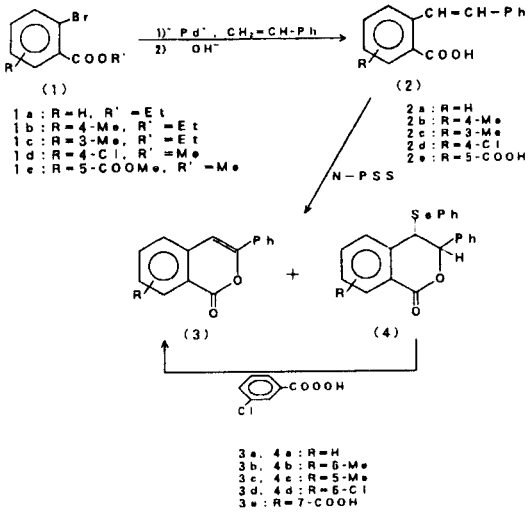

Figure 3

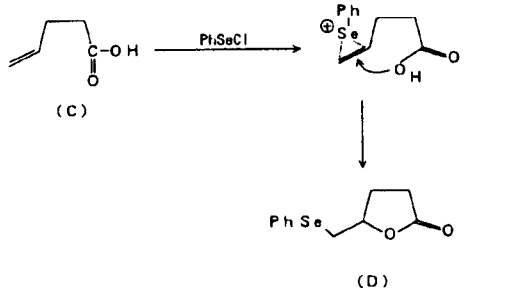

Figure 4

Clive *et al.* [13] previously reported that the reaction of 2-styrylbenzoic acid (**2a**) with benzeneselenyl chloride in ether afforded the mixture of 3,4-dihydro-3-phenyl-4-(phenylseleno)isocoumarin (**4a**) and 1,3-dihydro-3-[phenyl(phenylseleno)methyl]isobenzofuran-1-one. In our case, however, the reaction of **2** with *N*-phenylselenosuccinimide (N-PSS) (2.4 equivalents) in dichloromethane did not provide, as a main product, an intramolecular selenolactonization intermediate **4**, and resulted in the formation of 3-phenylisocoumarins **3** by a spontaneous elimination of the phenylseleno moiety from **4**, and 3,4-dihydro-3-phenyl-4-(phenylseleno)isocoumarins **4** as a minor product. The results are summarized in Table 1. Usually, the selenolactonization proceeds through the addition of the selenium reagent to the double bond and the subsequent carbon-oxygen bond formation. A few selenolactonizations proceeding concomitantly with elimination of phenylseleno group from **4** have been reported. For example, Kocor and Bersz [14] previously reported that the phenylselenolactonization of (*E*)- and (*Z*)-3-β-methoxychola-5,17(20)-dien-24-oic acids was accompanied by a spontaneous elimination of the phenylseleno moiety and resulted in the formation of unsaturated lactones. On the other hand, the amidoselenation of 2-styrylacetanilide with N-PSS also proceeded with elimination of the phenylseleno group and resulted in the formation of *N*-acetyl-2-phenylindole and *N*-acetyl-2-phenyl-3-(phenylseleno)indole [12].

The structure of the products **3** and **4** was confirmed by the observation of the ir and ^{1}H nmr spectra and by a mixed-melting-point determination with an authentic sample. The oxidation of the minor product **4** with 3-chloroperbenzoic acid afforded 3-phenylisocoumarins **3**.

Synthesis of 1-Isoquinolones **6** from 2-Styrylbenzamides **5**.

The overall reaction scheme is presented in Figure 5, and the starting materials **5** were synthesized by the reaction of **2** with thionyl chloride, followed by the amidation with ammonium carbonate.

The reaction of 2-styrylbenzamide (**5a**) with N-PSS in dichloromethane proceeded in the formation of an intramolecular amidoselenation product, 1-keto-3-phenyl-4-(phenylseleno)-1,2,3,4-tetrahydroisoquinoline (**7a**), and did not provide a product **6a** formed by an elimination of the phenylseleno moiety from **7a**. Under similar conditions, however, the reaction of 4-methyl-2-styrylbenzamide (**5b**) and 4-chloro-2-styrylbenzamide (**5c**) with N-PSS afforded 3-phenyl-1-isoquinolones **6b, 6c**, as the main products, and 1-keto-3-phenyl-4-(phenylseleno)-1,2,3,4-tetrahydroisoquinolines **7b, 7c**, as the minor products. The results were summarized in Table 1.

The structure of products **6** and **7** was confirmed by the observation of the ir and ^{1}H nmr spectra and by a mixed-melting-point determination with an authentic sample. Furthermore, the oxidation of product **7** with 3-chloroperbenzoic acid resulted in the formation of **6**.

Synthesis of 4(1*H*)-Quinolones **12** from 1-(2-Acylaminophenyl)-3-phenyl-2-propen-1-ones **11**.

The over-all reaction scheme is presented in Figure 6, and the starting materials **11** were synthesized by the reaction of 2-nitroacetophenones **8** with benzaldehyde, followed by the reduction and acylation.

The reaction of non-acylated compound, 1-(2-aminophenyl)-3-phenyl-2-propen-1-one (**10a**) with N-PSS in dichloromethane proceeded in the direction of phenylselenation on the aromatic ring, and led to the formation of the product **14** rather than an intramolecular

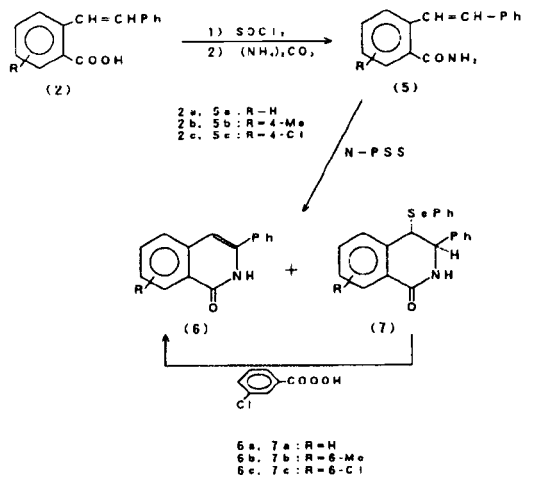

Figure 5

amidoselenation product **12**. The reaction of 1-(2-acetylaminophenyl)-3-phenyl-2-propen-1-ones **11a**, **11c**, **11d** with N-PSS afforded the intramolecular amidoselenation products **12a**, **12c**, **12d**, respectively, and did not afford the phenylseleno elimination products from **12**. However, 1-[2-(trifluoroacetylamino)phenyl]-3-phenyl-2-propen-1-one (**11b**) with N-PSS was very slow and did not proceed in the formation of an intramolecular amidoselenation product **12b**. The results are summarized in Table 1.

The structure of the products **12a**, **12c**, **12d** was confirmed by the observation of ir and ^1H nmr spectra. Moreover, the reduction of **12a**, **12c** and **12d** with

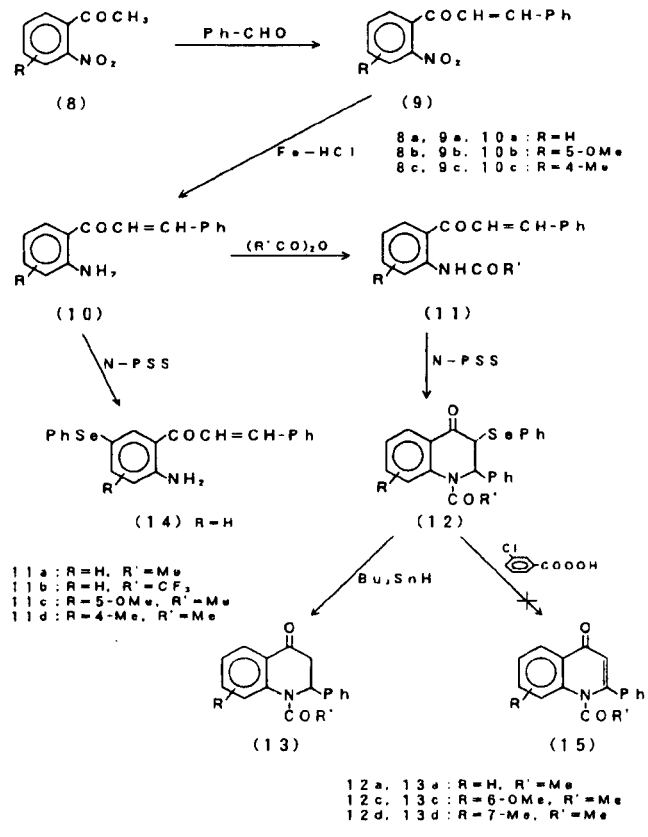

Figure 6

Table 1

Intramolecular Cyclization of 2-Styrylbenzoic Acid (**2**), 2-Styrylbenzamide (**5**) and 1-(2-Acylaminophenyl)-3-phenyl-2-propen-1-ones **11** using N-PSS.

Run	Starting material	N-PSS (equivalent)	Solvent [a] (ml)	Reaction conditions [b]	Yield [c] Product	Recovered
1	**2a**	2.4	CH_2Cl_2 (80 + 80)	rt 24 h	**3a** (81) + **4a** (9)	–
2	**2b**	2.4	CH_2Cl_2 (80 + 80)	rt 24 h	**3b** (64) + **4b** (9)	–
3	**2c**	2.4	CH_2Cl_2 (80 + 80)	rt 24 h	**3c** (54) + **4c** (29)	–
4	**2d**	2.4	THF (50 + 50)	rt 24 h	**3d** (52) + **4d** (11)	–
5	**2e**	2.4	THF (50 + 50)	rt 24 h	**3e** (54) –	–
6	**5a**	2.5	THF (90 + 100)	rt 24 h	– **7a** (35)	**5a** (65)
7	**5b**	2.5	CH_2Cl_2 (60 + 70)	rt 24 h	**6b** (60) + **7b** (12)	–
8	**5c**	2.5	THF (120 + 130)	rt 24 h, reflux 15 h	**6c** (12) + **7c** (13)	–
9	**10a**	1.0	CH_2Cl_2 (100 + 100)	rt 24 h	**14** (49)	–
10	**11a**	1.0	CH_2Cl_2 (100 + 100)	rt 36 h, reflux 52 h	**12a** (32)	**11a** (55)
11	**11a**	2.4	CH_2Cl_2 (200 + 200)	rt 24 h, reflux 24 h	**12a** (46)	**11a** (22)
12	**11a**	2.4	CH_2Cl_2 (100 + 100)	rt 46 h, reflux 27 h	**12a** (60)	**11a** (8)
13	**11b**	1.0	CH_2Cl_2 (100 + 100)	rt 24 h, reflux 24 h	-	**11b** (77)
14	**11c**	2.4	CH_2Cl_2 (100 + 100)	rt 24 h, reflux 24 h	**12c** (41)	**11c** (42)
15	**11d**	2.4	CH_2Cl_2 (100 + 100)	rt 24 h, reflux 24 h	**12d** (64)	**11d** (13)

[a] For example, in Run 1, into the mixture of **2a** in dichloromethane (80 ml) was added a solution of N-PSS (2.4 equivalents) in dichloromethane (80 ml) at room temparature. [b] For example, in Run 8, into the mixture of **5c** in tetrahydrofuran (120 ml) was added a solution of N-PSS in tetrahydrofuran (130 ml) at room temparature. After stirring for 24 hours at the same temperature, the reaction mixture was refluxed for 15 hours. [c] Isolated yield based on the starting material.

tributyltin hydride afforded 1-*N*-acetyl-4-keto-2-phenyl-1,2,3,4-tetrahydroquinolines **13a**, **13c**, **13d**, respectively, however, the reaction of **12a**, **12c** and **12d** with 3-chloroperbenzoic acid proceeded in the formation of polymerization product and did not afford 1-*N*-acetyl-2-phenyl-4(1*H*)quinolone derivative **15**.

EXPERIMENTAL

Melting points were determined with a Gallenkamp melting point determination apparatus and are uncorrected. The ir spectra were taken with a Hitachi 260-10 spectrometer. The ^{1}H nmr spectra were recorded with a Hitachi R-9OH (90 MHz) instrument in deuteriochloroform using TMS as internal standard. Mass spectra were measured on a Hitachi RMU-6M mass spectrometer.

N-Phenylselenosuccinimide (N-PSS) was prepared by the reported procedure [15].

General Procedure for the Synthesis of 2-Styrylbenzoic Acids **3**.

In a 200 ml autoclave, a mixture of alkyl 2-bromobenzoate (1) (39 mmoles), styrene (5.10 g, 49 mmoles), palladium(II) acetate (0.18 g, 0.8 mmoles), tri-*o*-tolylphosphine (0.48 g, 1.6 mmoles) and dry triethylamine (4.97 g, 49 mmoles) in acetonitrile (90 ml) was heated at 100° for 24 hours under a nitrogen atmosphere. After cooling, the reaction mixture was filtered and the filtrate was evaporated to dryness under reduced pressure. Without further purification, the residue was treated with 15% aqueous sodium hydroxide solution at room temperature or at 90-100°.

After stirring for 8 hours, the reaction mixture was acidified with 5% hydrochloric acid solution. The precipitates were filtered off and purified by recrystallization from benzene or benzene-hexane. The structure of the products was confirmed by a mixed-melting-point determination with an authentic sample and the observation of the ir and ^{1}H nmr spectra.

2-Styrylbenzoic Acid (**2a**).

This compound was obtained from ethyl 2-bromobenzoate (**1a**) as colorless crystals, mp 159-161° (lit [16], mp 158-160°).

4-Methyl-2-styrylbenzoic Acid (**2b**).

This compound was obtained from ethyl 2-bromo-4-methylbenzoate (**1b**) as colorless crystals, mp 186-188°; ir (potassium bromide): 3000-2500, 1660 (–COOH), 960 (*trans* –CH=CH–), 885, 830, 770, 690 cm^{-1} (Ar–H); ^{1}H nmr: δ 2.25 (s, 3H, $-CH_3$), 7.18-7.68 (m, 10H, –CH=CH– + Ar–H), 10.8 ppm (br-s, 1H, –COOH); ms: m/z 238 (M$^+$).

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.72; H, 6.08.

3-Methyl-2-styrylbenzoic Acid (**2c**).

This compound was obtained from ethyl 2-bromo-3-methylbenzoate (**1c**) as colorless crystals, mp 153-154°; ir (potassium bromide): 3050-2500, 1690 (–COOH), 970 (*trans* –CH=CH–), 790, 750, 690 cm^{-1} (Ar–H); ^{1}H nmr: δ 2.28 (s, 3H, $-CH_3$), 7.25-7.51 (m, 10H, –CH=CH– + Ar–H), 11.5 ppm (br-s, 1H, –COOH); ms: m/z 238 (M$^+$).

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.57; H, 5.81.

4-Chloro-2-styrylbenzoic Acid (**2d**).

This compound was obtained from methyl 2-bromo-4-chlorobenzoate (**1d**) as colorless crystals, mp 203-205°; ir (potassium bromide): 3100-2500, 1680 (–COOH), 965 (*trans* –CH=CH–), 880, 830, 765, 690 cm^{-1} (Ar–H); ^{1}H nmr: δ 7.08-7.81 (m, 10H, –CH=CH– + Ar–H), 11.3 ppm (br-s, 1H, –COOH); ms: m/z 259 (M$^+$).

Anal. Calcd. for $C_{15}H_{11}O_2Cl$: C, 69.64; H, 4.28. Found: C, 69.55; H, 4.19.

5-Carboxy-2-styrylbenzoic Acid (**2e**).

This compound was obtained from dimethyl 4-bromoisophthalate (**1e**) as colorless crystals, mp 285-286°; ir (potassium bromide): 3100-2500, 1680 (–COOH), 960 (*trans* –CH=CH–), 880, 835, 750, 700 cm^{-1} (Ar–H); ^{1}H nmr: δ 7.13-7.65 (m, 10H, Ar–H), 10.8 ppm (br-s, 2H, –COOH); ms: m/z 268 (M$^+$).

Anal. Calcd. for $C_{16}H_{12}O_4$: C, 71.64; H, 4.51. Found: C, 71.56; H, 4.42.

General Procedure for the Synthesis of 2-Styrylbenamides **6**.

After a mixture of 2-styrylbenzoic acids **2** (20 mmoles) and thionyl chloride (10.8 g) was refluxed for 3 hours, the excess thionyl chloride was evaporated to dryness under reduced pressure. The residue was stirred with ammonium carbonate (3.13 g, 32.6 mmoles) in dry benzene (70 ml) at room temperature for 24 hours. The benzene layers was successively washed with a saturated aqueous sodium hydrogen carbonate solution and water, dried over anhydrous magnesium sulfate, filtered and evaporated to dryness under reduced pressure. The residue was recrystallized from ethanol or benzene.

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

This compound was obtained from **2a** as colorless crystals, yield 84%, mp 189-190° (lit [17], mp 190-192°).

4-Methyl-2-styrylbenzamide (**5b**).

This compound was obtained from **2b** as colorless crystals, yield 80%, mp 187-188°, ir (potassium bromide): 3380, 3170 ($-NH_2$), 1630 ($-CONH_2$), 965 (*trans* –CH=CH–), 830, 750, 690 cm^{-1} (Ar–H); ^{1}H nmr: δ 2.26 (s, 3H, $-CH_3$), 7.15-7.80 (m, 10H, –CH=CH– + Ar–H), 8.13 ppm (br-s, 2H, $-NH_2$); ms: m/z 237 (M$^+$).

Anal. Calcd. for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90. Found: C, 81.02; H, 6.43; N, 5.86.

4-Chloro-2-styrylbenzamide (**5c**).

This compound was obtained from **2d** as colorless crystals, yield 87%, mp 245-247°, ir (potassium bromide): 3350, 3180 ($-NH_2$), 1640 ($-CONH_2$), 960 (*trans* –CH=CH–), 820, 765, 690 cm^{-1} (Ar–H); ^{1}H nmr: δ 7.08-7.78 (m, 10H, –CH=CH– + Ar–H), 8.06 ppm (br-s, 2H, $-NH_2$): ms: m/z 257 (M$^+$)

Anal. Calcd. for $C_{15}H_{12}NOCl$: C, 69.91; H, 4.69; N, 5.43. Found: C, 69.83; H, 4.61; N, 5.36.

General Procedure for the Synthesis of 1-(2-Nitrophenyl).

3-Phenyl-2-propen-1-one (**9**).

Into a mixture of sodium methoxide (2.70 g, 50 mmoles) and benzaldehyde (7.63 g, 72 mmoles) in ethanol (70 ml) was added a solution of 2-nitroacetophenone (**8**) (71 mmoles) at room temperature with stirring. After 3 hours, the reaction mixture was added to a mixture of water (300 ml) and concentrated

hydrochloric acid (7 ml). The precipitates were filtered off and recrystallized from ethanol.

1-(2-Nitrophenyl)-3-phenyl-2-propen-1-one (**9a**).

This compound was obtained from 2-nitroacetophenone (**8a**) as yellow crystals, yield 88%, mp 127-129° (lit [18], mp 128°).

1-(5-Methoxy-2-nitrophenyl)-3-phenyl-2-propen-1-one (**9b**).

This compound was obtained from 5-methoxy-2-nitroacetophenone (**8b**) as pale yellow crystals, yield 77%, mp 110-120° (lit [19], mp 112°).

1-(4-Methyl-2-nitrophenyl)-3-phenyl-2-propen-1-one (**9c**).

This compound was obtained from 4-methyl-2-nitroacetophenone (**8c**) as yellow crystals, yield 90%, mp 70-71°, ir (potassium bromide): 1640 (–C=O), 1530, 1350 ($-NO_2$), 970 (*trans* –CH=CH–), 880, 770, 690 cm^{-1} (Ar–H); ^1H nmr: δ 2.42 (s, 3H, $-CH_3$), 7.72-8.10 ppm (m, 10H, –CH=CH– + Ar–H); ms: m/z 267 (M^+).

Anal. Calcd. for $C_{16}H_{13}NO_3$: C, 71.90; H, 4.90; N, 5.24. Found: C, 71.82; H, 4.83; N, 5.16.

General Procedure for the Synthesis of 1-(2-Aminophenyl)-3-phenyl-2-propen-1-one (**10**).

Into a mixture of **9** (5.5 mmoles) and iron powder (1.3 g, 25 mmoles) in methanol (50 ml) was added a solution of concentrated hydrochloric acid (0.20 ml) in water (2 ml) at room temperature under stirring. The reaction mixture was then heated under reflux for 20 hours and filtered. The filtrate was evaporated under reduced pressure to dryness and the residue was dissolved in ether (200 ml). The ether phase was successively washed with a saturated aqueous sodium hydrogen carbonate solution and a saturated aqueous sodium chloride solution, dried over anhydrous magnesium sulfate, filtered and concentrated. The residue was recrystallized from ethanol or benzene.

1-(2-Aminophenyl)-3-phenyl-2-propen-1-one (**10a**).

This compound was obtained from **9a** as yellow crystals, yield 97%, mp 70-72°(lit [20], mp 71-72°).

1-(2-Amino-5-methoxyphenyl)-3-phenyl-2-propen-1-one (**10b**).

This compound was obtained from **9b** as yellow crystals, yield 89%, mp 145-147°, ir (potassium bromide): 3450, 3330 ($-NH_2$), 1640 (–C=O), 970 (*trans* –CH=CH–), 820, 760, 700 cm^{-1} (Ar–H); ^1H nmr: δ 3.86 (s, 3H, $-CH_3$), 6.36 (br-s, 2H, $-NH_2$), 6.84-8.04 ppm (m, 10H, –CH=CH– + Ar–H); ms: m/z 253 (M^+).

Anal. Calcd. for $C_{16}H_{15}NO_2$: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.72; H, 5.82; N, 5.48.

1-(2-Amino-4-methylphenyl)-3-phenyl-2-propen-1-one (**10c**).

This compound was obtained from **9c** as yellow crystals, yield 90%, mp 52-54°, ir (potassium bromide): 3370, 3260 ($-NH_2$), 1630 (–C=O), 970 (*trans* –CH=CH–), 850, 760, 690 cm^{-1}; ^1H nmr: δ 2.06 (s, 3H, $-CH_3$), 6.46 (br-s, 2H, $-NH_2$), 6.54-8.10 ppm (m, 10H, –CH=CH– + Ar–H); ms: m/z 237 (M^+).

Anal. Calcd. for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90. Found: C, 80.87; H, 6.31; N, 5.83

General Procedure for the Synthesis of 1-(2-Acylaminophenyl)-3-phenyl-2-propen-1-one (**11**).

Into a solution of **10** (1.90 mmoles) in benzene (50 ml) was successively added acid anhydride (7.80 mmoles) and pyridine (0.62 ml) at room temperature. After stirring for 20 hours at 60°, the benzene layer was successively washed with a 5% hydrochloric acid solution, a saturated aqueous sodium hydrogen carbonate solution and a saturated aqueous sodium chloride solution, dried over anhydrous magnesium sulfate, filtered, and concentrated. The residue was recrystallized from ethanol.

1-(2-Acetylaminophenyl)-3-phenyl-2-propen-1-one (**11a**).

This compound was obtained from **10a** and acetic anhydride as pale yellow crystals, yield 86%, mp 92-93° (lit [20], mp 92-93°).

1-[2-(Trifluoroacetylamino)phenyl]-3-phenyl-2-propen-1-one (**11b**).

This compound was obtained from **10a** and trifluoroacetic anhydride as pale yellow crystals, yield 85%, mp 120-121°, ir (potassium bromide): 3100 (–NH), 1730 (–C=O), 1640 (–NHC=O), 970 (*trans* –CH=CH–), 760, 730, 690 cm^{-1} (Ar–H); ^1H nmr: δ 7.00-8.13 (m, 10H, –CH=CH– + Ar–H), 8.62 (d-d, 1H, $-C_3-H$), 12.8 ppm (br-s, 1H, –NH); ms: m/z 319 (M^+).

Anal. Calcd. for $C_{17}H_{12}NO_2F_3$: C, 63.95; H, 3.79; N, 4.39. Found: C, 63.83; H, 3.70; N, 4.32.

1-(2-Acetylamino-5-methoxyphenyl)-3-phenyl-2-propen-1-one (**11c**).

This compound was obtained from **10b** and acetic anhydride as pale yellow crystals, yield 74%, mp 136-137°, ir (potassium bromide): 3275 (–NH), 1710 (–C=O), 1650 (–NHCO–), 980 (*trans* –CH=CH–), 840, 780, 690 cm^{-1} (Ar–H); ^1H nmr: δ 2.19 (s, 3H, $-COCH_3$), 3.83 (s, 3H, $-OCH_3$), 7.00-8.10 (m, 9H, –CH=CH– + Ar–H), 8.55 (d, 1H, Ar–H), 10.97 ppm (br-s, 1H, –NH); ms: m/z 295 (M^+).

Anal. Calcd. for $C_{18}H_{17}NO_3$: C, 73.20; H, 5.80; N, 4.74. Found: C, 73.29; H, 5.87; N, 4.65.

1-(2-Acetylamino-4-methylphenyl)-3-phenyl-2-propen1-one (**11d**).

This compound was obtained from **10c** and acetic anhydride as pale yellow crystals, yield 87%, mp 116-118°, ir (potassium bromide): 3225 (–NH), 1680 (–C=O), 1640 (–NHC=O), 990 (*trans* –CH=CH–), 810, 760, 690 cm^{-1} (Ar–H); ^1H nmr: δ 2.23 (s, 3H, $-CH_3$), 2.39 (s, 3H, $-COCH_3$), 6.87-7.93 (m, 9H, –CH=CH– + Ar–H), 8.58 (d, 1H, $-C_3-H$), 11.69 ppm (br-s, 1H, –NH); ms: m/z 279 (M^+).

Anal. Calcd. for $C_{18}H_{17}NO_2$: C, 77.40; H, 6.13; N, 5.01. Found: C, 77.27; H, 6.05; N, 4.87.

General Procedure for the Reaction of the Compounds **2, 5** and **11** with N-PSS.

To a 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 **2, 5, 10a** or **11** (4.0 mmoles) in dry dichloromethane (50 ml) under a 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 eluent] to afford products. In the case of **2**, the products were diphenyl diselenide (first elution, mp 62-63°), 3,4-dihydro-3-phenyl-4-(phenylseleno)isocoumarin **4** (second elution) and 3-phenylisocoumarin **3** (third elution). In the case of **5**, the products were diphenyl diselenide (first elution), 1-keto-3-phenyl-4-(phenylseleno)-1,2,3,4-tetrahydroisoquinoline **7** (second elution) and 3-

phenyl-1-isoquinolinone **6** (third elution). In the case of **11**, the reaction resulted in the formation of diphenyl diselenide (first elution) and 1-*N*-acetyl-4-keto-2-phenyl-3-(phenylseleno)-1,2,3,4-tetrahydroquinoline **12** (second elution). The results are summarized in Table 1.

3-Phenylisocoumarin (**3a**).

This compound was obtained from **2a** as colorless crystals, accompanied by **4a** (Run 1), mp 90-92° (lit [21], mp 90-91°).

3,4-Dihydro-3-phenyl-4-(phenylseleno)isocoumarin (**4a**).

This compound was obtained as colorless crystals, mp 124-125°, ir (potassium bromide): 1710 (-COO-), 755, 690 cm^{-1} (Ar-H); ^1H nmr: δ 4.85 (d, 1H, J = 2 Hz, $-C_3-H$), 5.82 (d, 1H, J = 2 Hz, $-C_4-H$), 7.13-7.56 (m, 13H, $-C_5-H$ + $-C_6-H$ + $-C_7-H$ + phenyl ring protons), 8.02 ppm (d-d, 1H, C_8-H); ms: m/z 379 (M^+).

Anal. Calcd. for $C_{21}H_{16}O_2Se$: C, 66.50; H, 4.25. Found: C, 66.62; H, 4.34.

6-Methyl-3-phenylisocoumarin (**3b**).

This compound was obtained from **2b** as colorless crystals, accompanied by **4b** (Run 2), mp 124-125°; ir (potassium bromide): 1720 (-C=O), 880, 835, 750, 700 cm^{-1} (Ar-H); ^1H nmr: δ 2.43 (s, 3H, $-CH_3$), 6.80 (s, 1H, -C=C-H), 7.13-7.57 (m, 5H, -phenyl protons), 7.79 (d, 1H, $-C_5-H$), 7.80 (d-d, 1H, $-C_7-H$), 8.11 ppm (d, 1H, $-C_8-H$); ms: m/z 236 (M^+).

Anal. Calcd. for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12. Found: C, 81.25; H, 5.03.

3,4-Dihydro-6-methyl-3-phenyl-4-(phenylseleno)isocoumarin (**4b**).

This compound was obtained as colorless crystals, mp 140-141°; ir (potassium bromide): 1720 (-C=O), 860, 830, 760, 700 cm^{-1} (Ar-H); ^1H nmr: δ 2.30 (s, 1H, $-CH_3$), 4.80 (d, 1H, J = 2 Hz, $-C_4-H$), 5.76 (d, 1H, J = 2 Hz, $-C_3-H$), 6.93-7.40 (m, 10H, phenyl protons), 7.50 (d, 1H, $-C_5-H$), 7.53 (d-d, 1H, $-C_7-H$), 7.90 ppm (d, 1H, $-C_8-H$); ms: m/z 393 (M^+).

Anal. Calcd. for $C_{22}H_{18}O_2Se$: C, 67.18; H, 4.61. Found: 67.25; H, 4.58.

5-Methyl-3-phenylisocoumarin (**3c**).

This compound was obtained from **2c** as colorless crystals, accompanied by **4c** (Run 3), mp 138-139°; ir (potassium bromide): 1720 (-C=O), 750, 690 cm^{-1} (Ar-H); ^1H nmr: δ 2.39 (s, 3H, $-CH_3$), 6.80 (s, 1H, -C=C-H), 7.30-7.49 (m, 5H, phenyl protons), 7.71-7.82 (m, 2H, $-C_6-H$ + $-C_7-H$), 8.00 ppm (s, 1H, $-C_8-H$); ms: m/z 236 (M^+).

Anal. Calcd. for $C_{16}H_{12}O_2$: C, 81.34; H, 5.12. Found: C, 81.27; H, 5.04.

3,4-Dihydro-5-methyl-3-phenyl-4-(phenylseleno)isocoumarin (**4c**).

This compound was obtained as colorless crystals, mp 167-168°; ir (potassium bromide): 1710 (-C=O), 760, 690 cm^{-1} (Ar-H); ^1H nmr: δ 2.31 (s, 3H, $-CH_3$), 4.82 (d, 1H, J = 2 Hz, $-C_4-H$), 5.75 (d, 1H, J = 2 Hz, $-C_3-H$), 7.01-7.78 (m, 12H, phenyl protons + $-C_6-H$ + $-C_7-H$), 7.82 ppm (s, 1H, $-C_8-H$); ms: m/z 393 (M^+).

Anal. Calcd. for $C_{22}H_{18}O_2Se$: C, 67.18; H, 4.61. Found: C, 67.25; H, 4.57.

6-Chloro-3-phenylisocoumarin (**3d**).

This compound was obtained from **2d** as colorless crystals, accompanied by **4d** (Run 4), mp 178-179°; ir (potassium bromide): 1710 (-C=O), 860, 830, 750, 690 cm^{-1} (Ar-H); ^1H nmr: δ 6.84 (s, 1H, -C=C-H), 7.24-7.41 (m, 5H, phenyl protons), 7.65-7.87 (m, 2H, $-C_4-H$ + $-C_7-H$), 8.11 ppm (d, 1H, $-C_8-H$); ms: m/z 256 (M^+).

Anal. Calcd. for $C_{15}H_9O_2Cl$: C, 70.19; H, 3.53. Found: C, 70.08; H, 3.44.

3,4-Dihydro-6-chloro-3-phenyl-4-(phenylseleno)isocoumarin (**4d**).

This compound was obtained as colorless crystals, mp 201-203°; ir (potassium bromide): 1720 (-C=O), 880, 830, 760, 690 cm^{-1} (Ar-H); ^1H nmr: δ 4.87 (d, 1H, J = 2 Hz, $-C_4-H$), 5.77 (d, 1H, J = 2 Hz, $-C_3-H$), 7.04-7.84 ppm (m, 13H, Ar-H); ms: m/z 413 (M^+).

Anal. Calcd. for $C_{21}H_{15}O_2ClSe$: C, 60.96; H, 3.65. Found: C, 60.88; H, 3.52.

7-Carboxy-3-phenylisocoumarin (**3e**).

This compound was obtained from **2e** as colorless crystals, accompanied by **4e** (Run 5), mp > 250°; ir (potassium bromide): 3100-2500 (-COOH), 1710 (-C=O), 860, 830, 760, 700 cm^{-1} (Ar-H); ^1H nmr: δ 7.45-7.76 (m, 6H, phenyl protons + -C=C-H), 7.90 (m, 2H, $-C_5-H$ + $-C_6-H$), 8.28 (d, 1H, $-C_8-H$), 8.64 ppm (s, 1H, -COOH); ms: m/z 266 (M^+).

Anal. Calcd. for $C_{16}H_{10}O_4$: C, 72.18; H, 3.79. Found: C, 72.03; H, 3.72.

1-Keto-3-phenyl-4-(phenylseleno)-1,2,3,4-tetrahydroisoquinoline (**7a**).

This compound was obtained from **5a** as colorless crystals (Run 6), mp 96-97°; ir (potassium bromide): 3050 (-NH), 1780 (-C=O), 760, 750, 690 cm^{-1} (Ar-H); ^1H nmr: δ 4.65 (d, 1H, J = 4 Hz, $-C_4-H$), 5.84 (d, 1H, J = 4 Hz, $-C_3-H$), 6.50-8.10 ppm (m, 15H, Ar-H); ms: m/z 378 (M^+).

Anal. Calcd. for $C_{21}H_{17}NOSe$: C, 66.67; H, 4.53; N, 3.70. Found: 66.58; H, 4.47; N, 3.61.

6-Methyl-3-phenyl-1-isoquinolone (**6b**).

This compound was obtained from **5b** as colorless crystals, accompanied by **7b** (Run 7), mp 175-176°; ir (potassium bromide): 3400, 3150-2850 (-NH), 1680 (-C=O), 800, 740, 690 cm^{-1} (Ar-H); ^1H nmr: δ 2.48 (s, 3H, $-CH_3$), 6.48 (s, 1H, C_4-H), 7.18-8.32 ppm (m, 9H, Ar-H + -NH); ms: m/z 235 (M^+).

Anal. Calcd. for $C_{16}H_{13}NO$: C, 81.68; H, 5.57, N, 5.95. Found: C, 81.60; H, 5.49; N, 5.87.

1-Keto-6-methyl-3-phenyl-4-(phenylseleno)-1,2,3,4-tetrahydroisoquinoline (**7b**).

This compound was obtained as colorless crystals, mp 117-120°; ir (potassium bromide): 3100, 1770 (-C=O), 830, 800, 750, 690 cm^{-1} (Ar-H); ^1H nmr: δ 2.44 (s, 3H, $-CH_3$), 4.61 (d, 1H, J = 4 Hz, $-C_4-H$), 5.80 (d, 1H, J = 4 Hz, $-C_3-H$), 6.71-8.02 ppm (m, 14H, Ar-H + -NH); ms: m/z 392 (M^+).

Anal. Calcd. for $C_{22}H_{19}NOSe$: C, 67.35; H, 4.88; N, 3.57. Found: C, 67.26; H, 4.75; N, 3.41.

6-Chloro-3-phenyl-1-isoquinolone (**6c**).

This compound was obtained from **5c** as colorless crystals, accompanied by **7c** (Run 8), mp 208-210°; ir (potassium bro-

mide): 3400, 3150-2850 (–NH), 1685 (–C=O), 820, 800, 750, 690 cm^{-1} (Ar–H); ^{1}H nmr: δ 6.52 (s, 1H, $-C_4-H$), 7.15-8.28 ppm (m, 9H, Ar–H + –NH); ms: m/z 255 (M$^+$).

Anal. Calcd. for $C_{15}H_{10}NOCl$: C, 70.46; H, 3.94; N, 5.48. Found: C, 70.58; H, 4.07; N, 5.38.

1-Keto-6–chloro-3-phenyl-4-(phenylseleno)-1,2,3,4-tetrahydroisoquinoline (**7c**).

This compound was obtained as colorless crystals, mp 194-196°; ir (potassium bromide): 3100 (–NH), 1760 (–C=O), 830, 800, 760, 700 cm^{-1} (Ar–H); ^{1}H nmr: δ 4.68 (d, 1H, J = 4 Hz, $-C_4-H$), 5.88 (d, 1H, J = 4 Hz, $-C_3-H$), 6.67-8.03 ppm (m, 14H, Ar–H + –NH); ms: m/z 412 (M$^+$).

Anal. Calcd. for $C_{21}H_{16}NOClSe$: C, 61.11; H, 3.91; N, 3.39. Found: C, 61.02; H, 3.78; N, 3.27.

1-[2-Amino-5-(phenylseleno)phenyl]-3-phenyl-2-propen-1-one (**14**).

This compound was obtained from **10a** as yellow crystals (Run 9), mp 113-114°; ir (potassium bromide): 3410, 3300 ($-NH_2$), 1640 (–C=O), 970 (–CH=CH–), 830, 770, 690 cm^{-1} (Ar–H); ^{1}H nmr: δ 6.47 (br-s, 2H, $-NH_2$), 6.62 (d, 1H, J = 9 Hz, Ar–H), 7.06-8.02 (m, 13H, Ar–H + –CH=CH–), 8.11 ppm (d, 1H, J = 2 Hz, Ar–H); ms: m/z 378 (M$^+$).

Anal. Calcd. for $C_{21}H_{17}NOSe$: C, 66.67; H, 4.53; N, 3.70. Found: C, 66.55; H, 4.41; N, 3.62.

The structure of **14** was determined by the observation of the ir and ^{1}H nmr spectra and by the reductive conversion of **14** into **10a** (mp 70-72°, lit [20] mp 71-72°) with tributyltin hydride.

1-*N*-Acetyl-4-keto-2-phenyl-3-(phenylseleno)-1,2,3,4-tetrahydroquinoline (**12a**).

This compound was obtained from **11a** as colorless crystals (Run 10, 11, 12), mp 117-118°; ir (potassium bromide): 1680 (–C=O), 1660 (–CON–), 760, 730, 690 cm^{-1} (Ar–H); ^{1}H nmr: δ 2.48 (s, 3H, $-CH_3$), 4.62 (d, 1H, J = 2 Hz. $-C_2-H$) 6.43 (d, 1H, J = 2 Hz, $-C_3-H$), 7.12 (s, 5H, -Se-Ph ring protons), 7.20-7.80 (m, 8H, $-C_6-H$ + $-C_7-H$ + $-C_8-H$ + –C-Ph ring protons), 7.88-8.05 ppm (d, 1H, $-C_5-H$); ms: m/z 420 (M$^+$).

Anal. Calcd. for $C_{23}H_{19}NO_2Se$: C, 65.72; H, 4.56; N, 3.33. Found: C, 65.59; H, 4.43; N, 3.27.

1-*N*-Acetyl-4-keto-6-methoxy-2-phenyl-3-(phenylseleno)-1,2,3,4-tetrahydroquinoline (**12c**).

This compound was obtained from **11c** as pale yellow oil (Run 14); ir (neat): 1680 (–C=O), 1650 (–CON–), 770, 730, 690 cm^{-1} (Ar–H); ^{1}H nmr: δ 2.46 (s, 3H, $-COCH_3$), 3.75 (s, 3H, $-OCH_3$), 4.60 (d, 1H, J = 2 Hz, $-C_2-H$), 6.41 (d, 1H, J = 2 Hz, $-C_3-H$), 6.54-7.82 ppm (m, 13H, Ar–H); ms: m/z 450 (M$^+$).

Anal Calcd. for $C_{24}H_{21}NO_3Se$: C, 64.00; H, 4.70; N, 3.11. Found: C, 63.87; H, 4.61; N, 2.98.

1-*N*-Acetyl-4-keto-7-methyl-2-phenyl-3-(phenylseleno)-1,2,3,4-tetrahydroquinoline **12d**.

This compound was obtained from **11d** as pale yellow crystals (Run 15), mp 157-159°; ir (potassium bromide): 1670 (–C=O), 1660 (–CON–), 830, 760, 690 cm^{-1} (Ar–H); ^{1}H nmr: δ 2.32 (s, 3H, $-COCH_3$), 2.46 (s, 3H, Ar–CH_3), 4.55 (d, 1H, J = 2 Hz, $-C_2-H$), 6.36 (d, 1H, J = 2 Hz, $-C_3-H$), 6.58-7.90 ppm (m, 13H, Ar–H); ms: m/z 434 (M$^+$).

Anal. Calcd. for $C_{24}H_{21}NO_2Se$: C, 66.36; H, 4.87; N, 3.22. Found: C, 66.31; H, 4.79; N, 3.13.

Oxidative Removal of Phenylseleno group from **4** and **7** with 3-Chloroperbenzoic Acid.

Into a solution of **4** or **7** (2.5 mmoles) in dry dichloromethane (20 ml) was gradually added 3-chloroperbenzoic acid (0.45 g, 2.6 mmoles) in dry dichloromethane (12 ml) at -20° under nitrogen atmosphere. After stirring for 20 minutes at the same temperature, a solution of diisopropylamine (0.40 g, 3.9 mmoles) in dichloromethane (10 ml) was added dropwise and the mixture was stirred for 4 hours at room temperature. After an excess of 3-chloroperbenzoic acid was removed by column chromatography on alumina, the product was purified by column chromatography on silica gel [eluent, chloroform].

3-Phenylisocoumarin (**3a**).

This compound was obtained from **4a** as colorless crystals in 63% yield, mp 90-92° (lit [21], mp 90-91°).

6-Methyl-3-phenylisocoumarin (**3b**).

This compound was obtained from **4b** as colorless crystals in 72% yield, mp 124-125°.

5-Methyl-3-phenylisocoumarin (**3c**).

This compound was obtained from **4c** as colorless crystals in 78% yield, mp 138-139°.

6-Chloro-3-phenylisocoumarin (**3d**).

This compound was obtained from **4d** as colorless crystals in 68%, mp 178-179°.

3-Phenyl-1-isoquinolone (**6a**).

This compound was obtained from **7a** as colorless crystals in 54% yield, mp 197-199° (lit [22], mp 198-199°).

6-Methyl-3-phenyl-1-isoquinolone (**6b**).

This compound was obtained from **7b** as colorless crystals in 68% yield, mp 175-176°.

6-Chloro-3-phenyl-1-isoquinolone (**6c**).

This compound was obtained from **7c** as colorless crystals in 60% yield, 208-210°.

Reductive Removal of Phenylseleno Group from **12** with Tributyltin Hydride.

In a Schlenk tube, to a solution of **12** (2.5 mmoles) in dry toluene (20 ml) was added a solution of 2,2'-azobisisobutyronitrile (AIBN, 8 mg, 0.05 mmole) in dry toluene (5 ml) under nitrogen atmosphere, and tributyltin hydride (1.0 ml, 5.1 mmoles) was injected from a syringe. The resulting mixture was heated at 110° for 1 hour using an oil bath while stirring magnetically. After evaporation of the solvent, the residue was purified by column chromatography on silica gel using hexane as the eluent. The structure of product **13** was determined by a mixed-melting-point determination with an authentic sample and by the observation of the ir, ^{1}H nmr and mass spectra.

1-*N*-Acetyl-4-keto-2-phenyl-1,2,3,4-tetrahydroquinoline (**13a**).

This compound was obtained from **12a** as colorless crystals in 85% yield, mp 164-166° (lit [20], mp 166-167°).

1-*N*-Acetyl-4-keto-6-methoxy-2-phenyl-1,2,3,4-tetrahydroquinoline (**13c**).

This compound was obtained from **12c** as colorless crystals in 89% yield, mp 148-149°, ir (potassium bromide): 1680 (–C=O),

1660 (–NCO–), 830, 790, 700 cm^{-1}; ^1H nmr: δ 2.37 (s, 3H, $-COCH_3$), 3.20-3.37 (m, 2H, $-CH_2-$), 3.72 (s, 3H, $-OCH_3$), 6.30-6.48 (m, 1H, –CH–), 6.79-7.44 ppm (m, 8H, Ar–H); ms: m/z 295 (M^+).

Anal. Calcd. for $C_{18}H_{17}NO_3$: C, 73.20; H, 5.80; N, 4.74. Found: C, 73.12; H, 5.67; N, 4.65.

1-*N*-Acetyl-4-keto-7-methyl-2-phenyl-1,2,3,4-tetrahydroquinoline (**13d**).

This compound was obtained from **12d** as colorless crystals in 90% yield, mp 137-138°, ir (potassium bromide): 1680 (–C=O), 1670 (–NCO–), 840, 790, 690 cm^{-1}; ^1H nmr: δ 2.29 (s, 3H, $-CH_3$), 2.40 (s, 3H, $-COCH_3$), 2. 94-3.50 (m, 2H, $-CH_2-$), 6.10-6.48 (m, 1H, –CH–), 6.72-7.86 ppm (m, 8H, Ar–H); ms: m/z 279 (M^+).

Anal. Calcd. for $C_{18}H_{17}NO_2$: C, 77.40; H, 6.13; N, 5.01. Found: C, 77.49; H, 6.23; N, 5.12.

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