A Regiocontrolled Synthesis of Substituted Indoles by Palladium-Catalyzed Coupling of 2-Bromonitrobenzenes and 2-Bromoacetanilides

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The palladium-catalyzed cross-coupling reaction of 2-bromonitrobenzenes or 2-bromoacetanilides with ethylene has been used to produce a variety of substituted indoles. The mild reaction conditions and selectivity inherent in the coupling reaction have been utilized to produce regiochemically pure 4-, 5-, 6-, and 7-substituted indoles.

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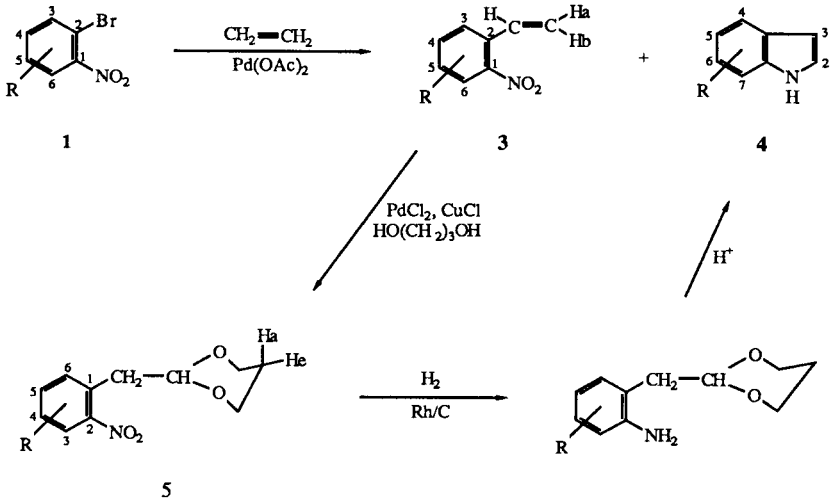
The biochemical importance of many indole derivatives has spured continual efforts towards new or improved methods for synthesis of the indole nucleus [1]. However, methods involving electrophilic ring closures, such as the Fischer or Bischler Syntheses, are generally not regiospecific when utilized for the synthesis of certain substituted indoles and result in the formation of mixture of isomers [2]. For example, the Fischer indole synthesis with *meta*-substituted phenylhydrazones gives mixtures of 4- and 6-substituted indoles. Similarly, the Fischer indole synthesis with phenylhydrazone of 2-butanone gives a mixture of 3-ethylindole and 2,3-dimethylindole [3]. Furthermore, the Fischer or Bischler Syntheses are normally in applicable to indoles containing only electron-withdrawing groups [2]. The Leimgruber-Batcho procedure is particularly useful for the synthesis of 2,3-unsubstituted indoles, but the procedure generally does not tolerate sensitive functionality [4].

In recent years, a variety of heterocyclic compounds can be synthesized using intramolecular nucleophilic attack on palladium complexed olefins as the ring forming step [5]. In this way, Hegedus reported the palladium-catalyzed synthesis of indoles from *o*-allylanilines [6] and from 2-ethenylaniline *p*-toluenesulfoamides [7]. The synthesis of indoles from 2-bromoacetanilides and methyl γ-bromocrotonate using a palladium-catalyst was also studied [8]. Stille *et al.* described the palladium-catalyzed regiospecific synthesis of indoles from 2-bromoanilines and vinylstannes [9]. We also mentioned an efficient synthesis of indoles based on a variety of palladium-catalyzed reaction



1 3 4 5

1a, 3a:	R = H	**4a:**	R = H	**5a:**	R = H
1b:	R = 3-COOMe	**4b:**	R = 4-COOMe	**5c:**	R = 5-OMe
1c, 3c:	R = 4-OMe	**4c:**	R = 5-OMe	**5d:**	R = 5 -Me
1d, 3d:	R = 4 -Me	**4d:**	R = 5 -Me	**5e:**	R = 5-COOMe
1e, 3e:	R = 4-COOMe	**4e:**	R = 5-COOMe	**5f:**	R = 4-OMe
1f, 3f:	R = 5-OMe	**4f:**	R = 6-OMe	**5g:**	R = 4-Me
1g, 3g:	R = 5-Me	**4g:**	R = 6-Me	**5h:**	R = 4-COOMe
1h, 3h:	R = 5-COOMe	**4h:**	R = 6-COOMe	**5i:**	R = 3-COOMe
1i, 3i:	R = 6-COOMe	**4i:**	R = 7-COOMe		

Figure 1

[10,11]. Herein, we wish to report the development of palladium-catalyzed reaction for the preparation of indoles from readily obtainable 2-bromonitrobenzenes **1** or 2-bromoacetanilides **2** and ethylene.

Results and Discussion.

Synthesis from 2-Bromonitrobenzenes (1).

The over-all reaction Scheme is presented in Figure 1. Literature methods for the synthesis of 2-ethenylnitrobenzenes **3** are characterized by low yields and intolerance toward functional groups [12]. The palladium-catalyzed cross-coupling reaction of alkenes with aryl bromides or iodides is a mild, high yield method of carbon-carbon bond formation [13]. Plevyak and Heck have previously reported that, in the pressure of 120 psi of ethylene, the reaction of 2-bromonitrobenzene in acetonitrile solution with ethylene using triethylamine as base and 1 mole % palladium acetate, plus 2 mole % tri-*o*-tolylphosphine as catalyst at 120° resulted the formation of 2-nitrostyrene (55%) and 2,2'-dinitrostilbene (5%) [14]. This reaction has been used to connect ethenyl group to aromatic rings; the utility of the procedure is that a wide variety of substituents can be tolerated on the coupling partners.

In our case, in the presence of 1% palladium acetate, 2% tri-*o*-tolylphosphine, and triethylamine as catalyst, 3-bromo-4-nitroanisole (**1c**), 3-bromo-4-nitrotoluene (**1d**), 4-bromo-3-nitrotoluene (**1g**), methyl 4-bromo-3-nitrobenzoate (**1h**), and methyl 3-bromo-2-nitrobenzoate (**1i**) regioselectively undergo palladium-catalyzed substitution at 120° for 24 hours under a pressure of 25 atmospheres of ethylene to form 2-ethenylnitrobenzene derivatives **3c**, **3d**, **3g**, **3h** and **3i** in fair yields. However, under similar conditions, 2-bromonitrobenzene (**1a**), methyl 3-bromo-4-nitrobenzoate (**1e**), and 4-bromo-3-nitroanisole (**1f**) reacted with ethylene to lead a formation of a mixture of 2-ethenylnitrobenzene derivatives **3a**, **3e** and **3f** and indole derivatives **4a**, **4e**, **4f** and the reaction of methyl 2-bromo-3-nitrobenzoate (**1b**) and ethylene afforded only methyl indole-4-carboxylate (**4b**) (Table 1). In the Heck reaction of **1a**, **1b**, **1e** and **1f** with ethylene, the mechanism of the indole formation is obscure. Presumably, by hydrio-palladium intermediate **a** which formed in the Heck reaction, the substitution raction products **3** are reduced to 2-ethenylaniline derivatives **b** and an intramolecular aminopalladation of **b** may lead to a formation of indole derivatives **4a**, **4b**, **4e** and **4f**.

The palladium-catalyzed oxidation of terminal olefins with water, which is well-known as the Wacker reaction, produce methyl ketones [15]. A similar reaction with alcohols gives their ketals (eq 1). These products arise *via* the attack of oxygen nucleophiles at the non-terminal olefinic carbon (C_2). On the other hand, Hosokawa *et al.* have recently found that terminal olefins bearing electron-withdrawing groups, upon treatment with diols in the presence of a palladium(II) catalyst, afforded cyclic acetals *via* attack at the C_1 carbon (eq 2) [16]. For example, in the presence of palladium(II) chloride and copper(I) chloride, 2-ethenyltoluene reacted with ethylene glycol under an oxygen atomosphere (1 atmosphere) and led to the formation of *o*-tolylacetaldehyde ethylene glycol acetal (77%).

Table 1

Heck Reaction of 2-Bromonitrobenzenes 1 with Ethylene

Entry	1	Products (yields % [a])
1	1a	3a (43) + 4a (22.5)
2	1b	4b (40)
3	1c	3c (94)
4	1d	3d (74)
5	1e	3e (52) + 4e (17)
6	1f	3f (32) + 4f (48)
7	1g	3g (70)
8	1h	3h (58)
9	1i	3i (75)

[a] Yields were based on 1.

In our case, in the present of palladium(II) chloride (0.1 equivalent) and copper(I) chloride (1 equivalent) in dimethoxyethane, compounds **3** are regioselectively acetalized at the terminal carbon (C_1) by propane-1,3-diol at 50-60° under an oxygen atmosphere (1 atmosphere). As a result, a fairly good yield of cyclic acetals **5** was obtained. In Table 2 are summarized the results of the acetalization of **3** to **5**.

Table 2

Palladium-Catalyzed Formation of Acetals 5 from 3

Entry	3	Products 5 (yields %)
1	3a	5a (90)
2	3c	5c (85)
3	3d	5d (90)
4	3e	5e (78)
5	3f	5f (80)
6	3g	5g (85)
7	3h	5h (75)
8	3i	5i (74)

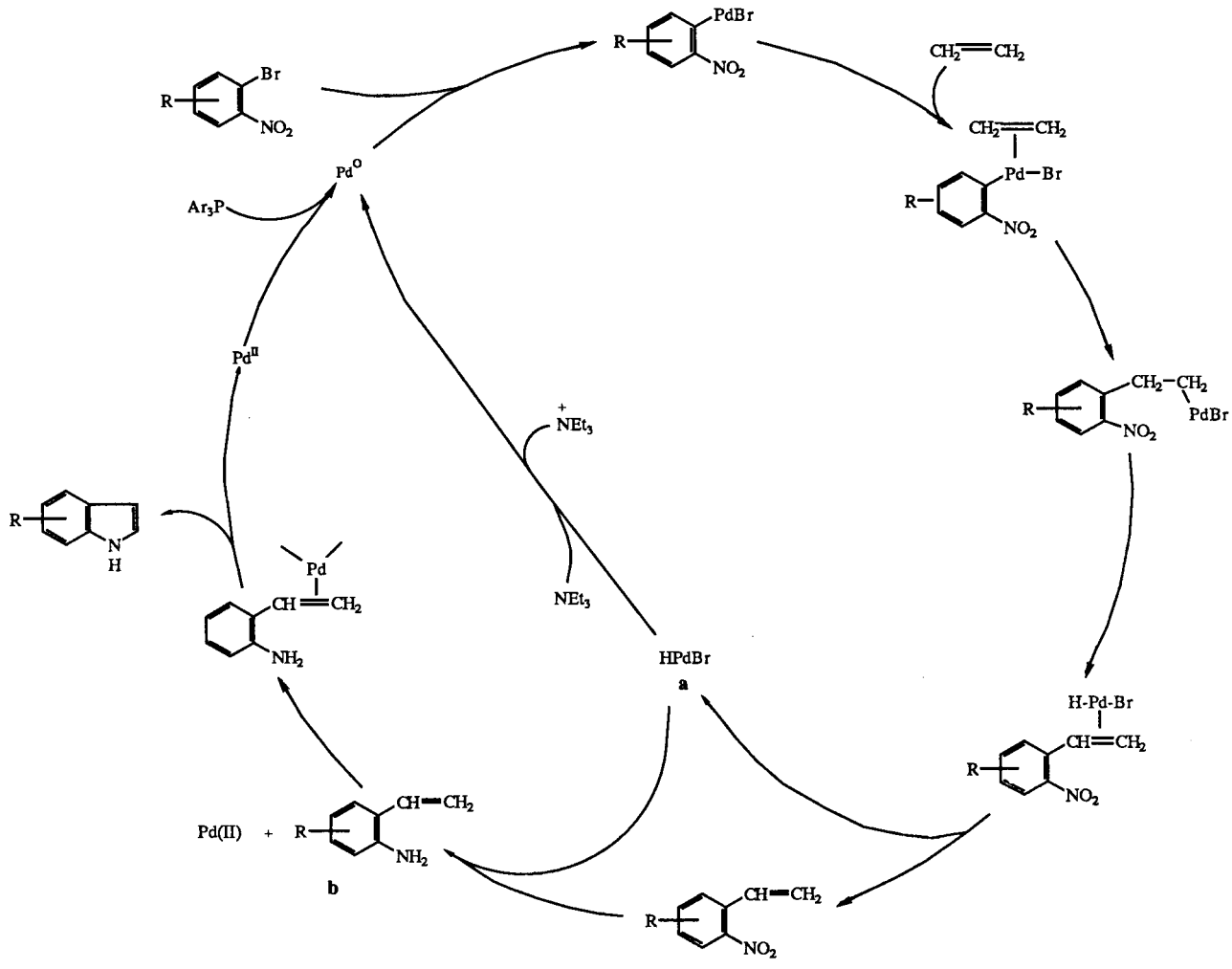
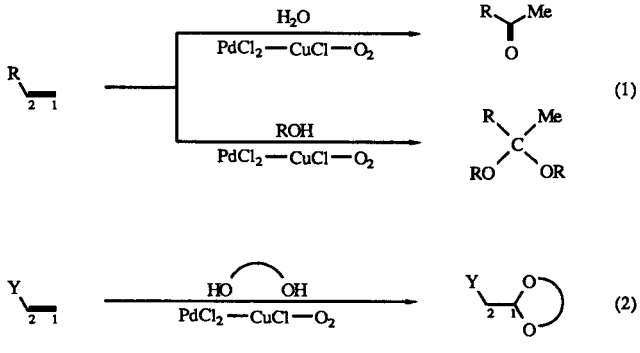


Figure 2



The reductive cyclization of the acetals **5** to the corresponding indoles **4** were carried out by using a variety of reagents, including H_2/Pd, H_2/Rh, Fe/HOAc, and Zn/HOAc. We found that the reductive cyclization of **5** to **4** was performed by catalytic hydrogenation with rhodium-carbon catalyst, followed by treatment with dilute hydrochloric acid.

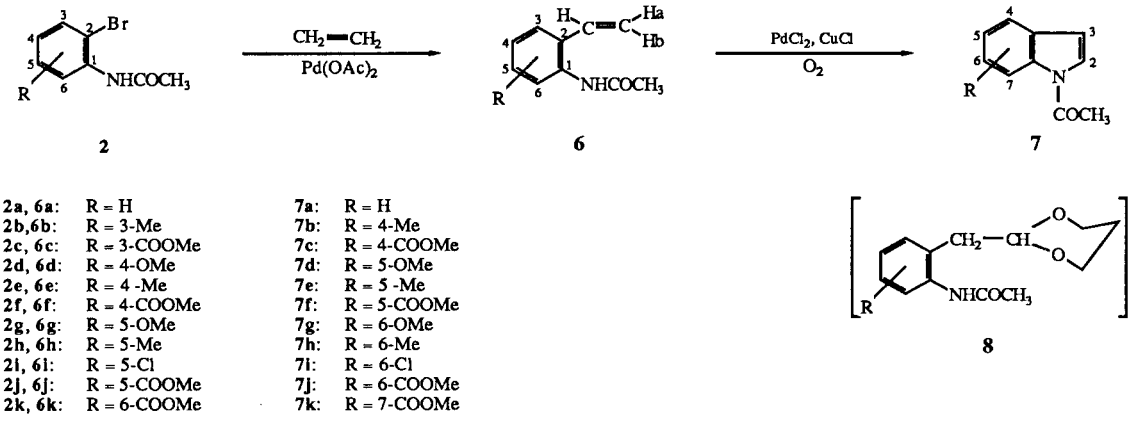
Table 3

Conversion of Acetals **5** to Indoles **4** by Catalytic Hydrogenation by Rhodium-Carbon

Entry	5	Products 4 (yields %)
1	**5a**	**4a** (75)
2	**5c**	**4c** (68)
3	**5d**	**4d** (64)
4	**5e**	**4e** (75)
5	**5f**	**4f** (70)
6	**5g**	**4g** (67)
7	**5h**	**4h** (65)
8	**5i**	**4i** (73)

Synthesis of Indoles from 2-Bromoacetanilides **2**.

The over-all reaction scheme is presented in Figure 3.



2a, 6a:	R = H	**7a:**	R = H
2b,6b:	R = 3-Me	**7b:**	R = 4-Me
2c, 6c:	R = 3-COOMe	**7c:**	R = 4-COOMe
2d, 6d:	R = 4-OMe	**7d:**	R = 5-OMe
2e, 6e:	R = 4 -Me	**7e:**	R = 5 -Me
2f, 6f:	R = 4-COOMe	**7f:**	R = 5-COOMe
2g, 6g:	R = 5-OMe	**7g:**	R = 6-OMe
2h, 6h:	R = 5-Me	**7h:**	R = 6-Me
2i, 6i:	R = 5-Cl	**7i:**	R = 6-Cl
2j, 6j:	R = 5-COOMe	**7j:**	R = 6-COOMe
2k, 6k:	R = 6-COOMe	**7k:**	R = 7-COOMe

Figure 3

Hegedus *et al.*. previously reported that, although palladium(II)-catalyzed cyclization of 2-ethenylaniline to indole was efficient (74%) [6], the analogous conversion of 3-bromo-2-ethenylaniline to 4-bromoindole was slow and inefficient [7]. We also described that the catalytic closure by lithium chloropalladate in ethanol of 2-ethenyl-4-methoxycarbonylaniline to methyl 4-indolecarboxylate was unsuccessful [11]. Thus, we have developed a synthesis of 1-acetylindoles **7** starting with **2**, conversion to 2-ethenylacetanilides **6**, and following with palladium-catalyzed cyclization to **7**. In the presence of pallasium(II) acetate, tri-*o*-tolylphosphine, and triethylamine, **2** undergos palladium-catalyzed substitution with ethylene to form **6** in moderate yields (Table 4). Meanwhile, Hegedus *et al.* reported that

Table 4

Heck Reaction of 2-Bromoacetanilides 2 with Ethylene

Entry	2	Products 6 (yields % [a])
1	**2a**	**6a** (76)
2	**2b**	**6b** (63)
3	**2c**	**6c** (54)
4	**2d**	**6d** (64)
5	**2e**	**6e** (84)
6	**2f**	**6f** (67)
7	**2g**	**6g** (75)
8	**2h**	**6h** (66)
9	**2i**	**6i** (63)
10	**2j**	**6j** (78)
11	**2k**	**6k** (55)

[a] Yields were based on 2.

Table 5

Palladium-Catalyzed Conversion of 6 to 1-Acetylindoles 7

Entry	6	Products 7 (yields %)
1	**6a**	**7a** (61)
2	**6b**	**7b** (49)
3	**6c**	**7c** (67)
4	**6d**	**7d** (54)
5	**6e**	**7e** (55)
6	**6f**	**7f** (65)
7	**6g**	**7g** (35)
8	**6h**	**7h** (60)
9	**6i**	**7i** (64)
10	**6j**	**7j** (57)
11	**6k**	**7k** (62)

the palladium-catalyzed closure of 3-bromo-2-ethenylacetanilide to 1-acetyl-4-bromoindole was slow with cupric acetate as reoxidant, and very slow with *p*-benzoquinone [7]. We found that, in the presence of palladium(II) chloride and copper(I) chloride in propane-1,3-diol under an oxygen atmosphere (1 atmosphere), compounds **6** are regioselectively cyclized to the corresponding **7** rather than are acetalized at the terminal carbon of the olefinic bond in **6** to form cyclic acetals **8**. In Table 5 are summarized the results of the cyclization of **6** to **7**.

EXPERIMENTAL

The ir and ^{1}H nmr spectra were recorded on Hitachi 260-10 and Hitachi R-90H spectrometers, respectively, in deuteriochloroform with TMS as internal standard in the latter case. The mass spectrum was recorded on a Hitachi RMU-6M spectrom-

eter. Melting points were taken with a Gallenkamp melting point apparatus and are uncorrected.

General Procedure for the Heck Reaction of 2-Bromonitrobenzenes **1** with Ethylene.

In 100 ml stainless autoclave, a mixture of 20 mmoles of **1**, 0.045 g (0.20 mmole) of palladium(II) acetate, 0.122 g (0.40 mmole) of tri-*o*-tolylphosphine, 2.02 g (20 mmoles) of triethylamine in 30 ml of acetonitrile was stirred at 120° under an ethylene pressure (30 atmospheres) for 24 hours. The cooled reaction mixture was diluted with ether and water. 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-hexane (1:1)), followed by recrystallization from ethanol.

In the case of the reaction with **1c**, **1d**, **1g**, **1h** and **1i**, only 2-ethenylnitrobenzene derivatives **3c**, **3d**, **3g**, **3h** and **3i** were obtained, but the reaction with **1a**, **1e** and **1f** afforded a mixture of 2-ethenylnitrobenzenes **3a**, **3e** and **3f** and indoles **4a**, **4e** and **4f**, respectively. On the other hand, the reaction with **1b** led to the formation of indole derivative **4b**. The structure of the products was confirmed by a mixed-melting point determination with authentic sample and the observation of the ir, ^{1}H nmr, and mass spectra. The results are summarized in Table 1.

2-Ethenylnitrobenzene (**3a**).

This compound was obtained from **1a** as pale yellow oil; ir (neat): 1530, 1345 (-NO_2), 980, 920 (-CH=CH_2), 1600, 1580, 760 cm^{-1} (*o*-disubst Ar-H); ^{1}H nmr: δ 5.36 (d, 1H, J = 10.6 Hz, Ar-C=CH_a), 5.73 (d, 1H, J = 17 Hz, Ar-C=CH_b), 7.16 (d-d, 1H, J = 10.6 and 17 Hz, Ar-CH=C-), 7.33-7.93 ppm (m, 4H, Ar-H); ms: m/z 149 (M$^+$).

Anal. Calcd. for $C_8H_7NO_2$: C, 64.42; H, 4.73; N, 9.39. Found: C, 64.37; H, 4.64; N, 9.31.

Indole (**4a**).

This compound was obtained from **1a** accompanied by **3a**, as colorless crystals, mp 53° (lit [17], mp 52-53°).

Methyl 4-Indolecarboxylate (**4b**).

This compound was obtained from **1b** as colorless crystals, mp 63°, (lit [18] mp 64-65°).

3-Ethenyl-4-nitroanisole (**3c**).

This compound was obtained from **1c** as a yellow oil; ir (neat): 1525, 1335 (-NO_2), 985, 920 (-CH=CH_2), 1600, 1580, 880, 830 cm^{-1} (1,2,4-trisubst Ar-H); ^{1}H-nmr: δ 3.84 (s, 3H, -OCH_3), 5.40 (d, 1H, J = 12 Hz, Ar-C=CH_a), 5.64 (d, 1H, J = 18 Hz, Ar-C=CH_b), 6.80 (d-d, 1H, J = 3 and 10 Hz, C_6-H), 6.93 (d, 1H, J = 3 Hz, C_2-H), 7.22 (d-d, 1H, J = 12 and 18 Hz, Ar-CH=C-), 7.91 (d, 1H, J = 10 Hz, C_5-H); ms: m/z 179 (M$^+$).

Anal. Calcd. for $C_9H_9NO_3$: C, 60.33; N, 5.06; N, 7.82. Found: C, 60.25; H, 4.96; N, 7.74.

3-Ethenyl-4-nitrotoluene (**3d**).

This compound was obtained from **1d** as a yellow oil; ir (neat): 1510, 1340 (-NO_2), 985, 920 (-CH=CH_2), 1600, 1580, 890, 830 cm^{-1} (1,2,4-trisubst Ar-H); ^{1}H nmr: δ 2.38 (s, 3H, Ar-CH_3), 5.45 (d, 1H, J = 11 Hz, Ar-C=CH_a), 5.61 (d, 1H, J = 17 Hz, Ar-C=CH_b), 6.90-7.20 (m, 2H, Ar-CH=C- + C_6-H), 7.30 (d, 1H, J = 2 Hz, C_2-H), 7.75 ppm (d, 1H, J = 8 Hz, C_5-H); ms: m/z 163 (M$^+$).

Anal. Calcd. for $C_9H_9NO_2$: C, 66.24; H, 5.56; N, 8.58. Found: C, 66.18; H, 5.49; N, 8.54.

Methyl 3-Ethenyl-4-nitrobenzoate (**3e**).

This compound was obtained from **1e** as a yellow oil, accompanied by **4e**; ir (neat): 1725 (-COOMe), 1525, 1335 (-NO_2), 980, 920 (-CH=CH_2), 1600, 1580, 890, 835 cm^{-1} (1,2,4-trisubst Ar-H); ^{1}H nmr: δ 3.97 (s, 3H, -COOCH_3), 5.53 (d, 1H, J = 11 Hz, Ar-C=CH_a), 5.83 (d, 1H, J = 17 Hz, Ar-C=CH_b), 7.06 (d-d, 1H, J = 11 and 17 Hz, Ar-CH=C-), 7.83 (d, 1H, J = 3 Hz, C_2-H), 7.96 (d-d, 1H, J = 3 and 8 Hz, C_6-H), 8.19 ppm (d, 1H, J = 8 Hz, C_5-H); ms: m/z 207 (M$^+$).

Anal. Calcd. for $C_{10}H_9NO_4$: C, 57.97; H, 4.38; N, 6.76. Found: C, 57.90; H, 4.35; N, 6.71.

Methyl 5-Indolecarboxylate (**4e**).

This compound was obtained from **1e** as colorless crystals, accompanied by **3e**, mp 124-125°; ir (potassium bromide): 3325 (-NH), 1690 (-COOMe), 1600, 1580, 900, 810 cm^{-1} (1,2,4-trisubst Ar-H); ^{1}H nmr: δ 3.91 (s, 3H, -COOCH_3), 6.60 (d, 1H, C_3-H), 7.20 (d, 1H, C_2-H), 7.32 (d, 1H, C_7-H), 7.86 (d-d, 1H, C_6-H), 8.40 (d, 1H, C_4-H), 8.82 ppm (br-s, 1H, -NH); ms: m/z 175 (M$^+$).

Anal. Calcd. for $C_{10}H_9NO_2$: C, 68.56; H, 5.18; N, 8.00. Found: C, 68.47; H, 5.05; N, 7.92.

4-Ethenyl-3-nitroanisole (**3f**).

This compound was obtained from **1f** as a yellow oil, accompanied by **4f**; ir (neat): 1520, 1335 (-NO_2), 985, 915 (-CH=CH_2), 1600, 1580, 860, 810 cm^{-1} (1,2,4-trisubst Ar-H); ^{1}H nmr: δ 3.82 (s, 3H, -OCH_3), 5.34 (d, 1H, J = 11 Hz, Ar-C=CH_a), 5.60 (d, 1H, J = 17 Hz, Ar-C=CH_b), 6.89-7.56 ppm (m, 4H, Ar-CH=C- + Ar-H); ms: m/z 179 (M$^+$).

Anal. Calcd. for $C_9H_9NO_3$: C, 60.33; H, 5.06; N, 7.82. Found: C, 60.27; H, 4.94; N, 7.75.

6-Methoxyindole (**4f**).

This compound was obtained from **1f** as colorless crystals, accompanied by **3f**, mp 89-90° (lit [19] mp 88-90°).

4-Ethenyl-3-nitrotoluene (**3g**).

This compound was obtained from **1g** as a yellow oil; ir (neat): 1525, 1330 (-NO_2), 980, 920 (-CH=CH_2), 1600, 1580, 880, 810 cm^{-1} (1,2,4-trisubst Ar-H); ^{1}H nmr: δ 2.35 (s, 3H, -CH_3), 5.36 (d, 1H, J = 11 Hz, Ar-C=CH_a), 5.65 (d, 1H, J = 17 Hz, Ar-C=CH_b), 7.05 (d-d, 1H, J = 11 and 17 Hz, Ar-CH=C-), 7.28-7.65 ppm (m, 3H, Ar-H); ms: m/z 163 (M$^+$).

Anal. Calcd. for $C_9H_9NO_2$: C, 66.24; H, 5.56; N, 8.58. Found: C, 66.20; H, 5.57; N, 8.50.

Methyl 4-Ethenyl-3-nitrobenzoate (**3h**).

This compound was obtained from **1h** as slightly yellow crystals, mp 65°; ir (potassium bromide): 1720 (-COOMe), 1530, 1360 (-NO_2), 980, 910 (-CH=CH_2), 1600, 1580, 890, 820 cm^{-1} (1,2,4-trisubst Ar-H); ^{1}H nmr: δ 3.96 (s, 3H, -COOCH_3), 5.61 (d, 1H, J = 11 Hz, Ar-C=CH_a), 5.86 (d, 1H, J = 17 Hz, Ar-C=CH_b), 7.20 (d-d, 1H, J = 11 and 17 Hz, Ar-CH=C-), 7.72 (d, 1H, C_5-H), 8.21 (d-d, 1H, C_6-H), 8.52 ppm (d, 1H, C_2-H); ms: m/z 207 (M$^+$).

Anal. Calcd. for $C_{10}H_9NO_4$: C, 57.97; H, 4.38; N, 6.76. Found: C, 57.93; H, 4.33; N, 6.68.

Methyl 3-Ethenyl-2-nitrobenzoate (**3i**).

This compound was obtained from **1i** as slightly yellow crystals, mp 88-90°; ir (potassium bromide): 1720 (-COOMe), 1530,

1370 ($-NO_2$), 990, 930 ($-CH=CH_2$), 1600, 1580, 765 (1,2,3-trisubst Ar-H); ^1H nmr: δ 3.89 (s, 3H, $-COOCH_3$), 5.52 (d, 1H, J = 11 Hz, Ar-C=CH_a), 5.85 (d, 1H, J = 17 Hz, Ar-C=CH_b), 6.63 (d-d, 1H, J = 11 and 17 Hz, Ar-CH=C-), 7.52 (m, 1H, C_5-H), 7.75-7.98 ppm (m, 2H, C_4-H + C_6-H); ms: m/z 207 (M^+).

Anal. Calcd. for $C_{10}H_9NO_4$: C, 57.97; H, 4.38; N, 6.76. Found: C, 57.88; H, 4.35; N, 6.72.

General Procedure of Acetalization of **3**.

In 50 ml flask fitted with a rubber balloon filled with oxygen and a teflon-coated magnetic stirring bar were placed palladium(II) chloride (0.248 g, 1.4 mmoles) and copper(I) chloride (1.386 g, 14 mmoles). Into the flask was added a solution of **3** (14 mmoles) and 1,3-propanediol (1 ml, 14 mmoles) in 1,2-dimethoxyethane (25 ml), and the resulting suspended solution was stirred for 24 hours at 50-60° under an oxygen atmosphere. After the reaction mixture was cooled to room temperature, ether (50 ml) was added to the mixture. The resulting insoluble materials were removed by filteration, and the filtrate was concentrated. The residue was then purified by means of silica gel column chromatography (benzene). The yields of acetals **5** are summarized in Table 2.

2-[(2-Nitrophenyl)methyl]-1,3-dioxane (**5a**).

This compound was obtained as colorless crystals, mp 69-70°; ir (potassium bromide): 1530, 1350 ($-NO_2$), 1600, 1580, 745 cm^{-1} (*o*-disubst Ar-H); ^1H nmr: δ 1.17-1.45 (m, 1H, -O-C-CH_a-C-O-), 1.80-2.30 (m, 1H, -O-C-CH_e-C-O-), 3.23 (d, 2H, Ar-CH_2-), 3.45-4.17 (m, 4H, -CH_2-C-C-O-), 4.76 (t, 1H, Ar-C-CH-O-), 7.27-7.90 ppm (m, 4H, Ar-H); ms: m/z 223.

Anal. Calcd. for $C_{11}H_{13}NO_4$: C, 59.18; H, 5.87; N, 6.28. Found: C, 59.12; H, 5.78; N, 6.21.

2-[(5-Methoxy-2-nitrophenyl)methyl]-1,3-dioxane (**5c**).

This compound was obtained as slightly yellow crystals, mp 114-115°; ir (potassium bromide): 1525, 1335 ($-NO_2$), 1600, 1580, 880, 830 cm^{-1} (1,2,4-trisubst Ar-H); ^1H nmr: δ 1.17-1.51 (m, 1H, -O-C-CH_a-C-O-), 1.80-2.35 (m, 1H, -O-C-CH_e-C-O-), 3.27 (Ar-CH_2-), 3.57-4.30 (m, 4H, -O-CH_2-C-C-O-), 3.89 (s, 1H, -OCH_3), 4.83 (t, 1H, Ar-C-CH-O-), 6.85 (d-d, 1H, C_5-H), 6.90 (d, 1H, C_6-H), 8.00 ppm (d, 1H, C_3-H); ms: m/z 253 (M^+).

Anal. Calcd. for $C_{12}H_{15}NO_5$: C, 56.91; H, 5.97; N, 5.53. Found: C, 56.78; H, 5.86; N, 5.39.

2-[(5-Methyl-2-nitrophenyl)methyl]-1,3-dioxane (**5d**).

This compound was obtained as slightly yellow crystals, mp 74-75°; ir (potassium bromide): 1520, 1350 ($-NO_2$), 1600, 1580, 895, 840 cm^{-1} (1,2,4-trisubst Ar-H); ^1H nmr: δ 1.29 (m, 1H, -O-C-CH_a-C-O-), 1.78-2.28 (m, 1H, -O-C-CH_e-C-O-), 2.39 (s, 3H, -CH_3), 3.19 (d, 2H, Ar-CH_2-), 3.70-4.02 (m, 4H, -O-CH_2-C-C-O-), 4.77 (t, 1H, Ar-C-CH-O-), 7.05-7.33 (m, 2H, C_4-H + C_6-H), 7.76 ppm (d, 1H, C_3-H); ms: m/z 237 (M^+).

Anal. Calcd. for $C_{12}H_{15}NO_4$: C, 60.75; H, 6.37; N, 5.90. Found: C, 60.66; H, 6.26; N, 5.81.

2-[(5-Methoxycarbonyl-2-nitrophenyl)methyl]-1,3-dioxane (**5e**).

This compound was obtained as slightly yellow crystals, mp 91-93°; ir (potassium bromide): 1720 (-COOMe), 1530, 1380 ($-NO_2$), 1600, 1580, 865, 840 cm^{-1} (1,2,4-trisubst Ar-H); ^1H nmr: δ 1.16-1.45 (m, 1H, -O-C-CH_a-C-O-), 1.73-2.31 (m, 1H, -O-C-CH_e-C-O-), 3.24 (d, 2H, Ar-CH_2-), 3.80-4.24 (m, 4H, -O-CH_2-C-C-O-), 3.94 (s, 3H, $-COOCH_3$), 4.77 (t, 1H, Ar-C-CH-O-), 7.81 (d, 1H, C_6-H), 7.92-8.17 ppm (m, 2H, C_3-H + C_4-H); ms: m/z 281 (M^+).

Anal. Calcd. for $C_{13}H_{15}NO_6$: C, 55.51; H, 5.38; N, 4.98. Found: C, 55.43; H, 5.34; N, 4.86.

2-[(4-Methoxy-2-nitrophenyl)methyl]-1,3-dioxane (**5f**).

This compound was obtained as slightly yellow crystals, mp 62-63°; ir (potassium bromide): 1530, 1350 ($-NO_2$), 1600, 1580, 870, 820 cm^{-1} (1,2,4-trisubst Ar-H); ^1H nmr: δ 1.18-1.36 (m, 1H, -O-C-CH_a-C-O-), 1.68-2.26 (m, 1H, -O-C-CH_e-C-O-), 3.28 (d, 2H, Ar-CH_2-), 3.86 (s, 3H, $-OCH_3$), 3.84-4.18 (m, 4H, -O-CH_2-C-C-O-), 4.73 (t, 1H, Ar-C-CH-O-), 7.14-7.75 ppm (m, 3H, Ar-H); ms: m/z 253 (M^+).

Anal. Calcd. for $C_{12}H_{15}NO_5$: C, 56.91; H, 5.97; N, 5.52. Found: C, 56.73; H, 5.84; N, 5.47.

2-[(4-Methyl-2-nitrophenyl)methyl]-1,3-dioxane (**5g**).

This compound was obtained as slightly yellow oil; ir (neat): 1535, 1345 ($-NO_2$), 1600, 1580, 890, 835 cm^{-1} (1,2,4-trisubst Ar-H); ^1H nmr: δ 1.15-1.40 (m, 1H, -O-C-CH_a-C-O-), 1.75-2.20 (m, 1H, -O-C-CH_e-C-O-), 2.37 (s, 3H, Ar-CH_3), 3.17 (d, 2H, Ar-CH_2-), 3.50-4.16 (m, 4H, -O-CH_2-C-C-O-), 4.72 (t, 1H, Ar-C-CH-O-), 7.26-7.30 (m, 2H, C_5-H + C_6-H), 7.65 ppm (d, 1H, C_3-H); ms: m/z 237 (M^+).

Anal. Calcd. for $C_{12}H_{15}NO_4$: C, 60.75; H, 6.37; N, 5.90. Found: C, 60.72; H, 6.35; N, 5.85.

2-[(4-Methoxycarbonyl-2-nitrophenyl)methyl]-1,3-dioxane (**5h**).

This compound was obtained as slightly yellow crystals, mp 104-106°; ir (potassium bromide): 1720 (-COOMe), 1530, 1360 ($-NO_2$), 1600, 1580, 890, 820 cm^{-1} (1,2,4-trisubst Ar-H); ^1H nmr: δ 1.13-1.50 (m, 1H, -O-C-CH_a-C-O-), 1.73-2.36 (m, 1H, -O-C-CH_e-C-O-), 3.28 (d, 2H, Ar-CH_2-), 3.45-4.30 (m, 4H, -O-CH_2-C-C-O-), 3.94 (s, 3H, $-COOCH_3$), 4.80 (t, 1H, Ar-C-CH-), 7.51 (d, 1H, C_6-H), 8.14 (d-d, 1H, C_5-H), 8.48 ppm (d, 1H, C_3-H); ms: m/z 281 (M^+).

Anal. Calcd. for $C_{13}H_{15}NO_6$: C, 55.51; H, 5.38; N, 4.98. Found: C, 55.47; H, 5.33; N, 4.89.

[(3-Methoxycarbonyl-2-nitrophenyl)methyl]-1,3-dioxane (**5i**).

This compound was obtained as slightly yellow crystals, mp 123-124°; ir (potassium bromide): 1720 (-COOMe), 1530, 1365 ($-NO_2$), 1600, 1580, 770, 695 cm^{-1} (1,2,3-trisubst Ar-H); ^1H nmr: δ 1.21-1.30 (m, 1H, -O-C-CH_a-C-O-), 1.72-2.27 (m, 1H, -O-C-CH_e-C-O-), 2.87 (d, 2H, Ar-CH_2-), 3.67-4.03 (m, 4H, -O-CH_2-C-C-O-), 3.84 (s, 3H, $-COOCH_3$), 4.68 (t, 1H, Ar-C-CH-), 7.44 (t, 1H, C_5-H), 7.62 (d-d, 1H, C_6-H), 7.83 ppm (d-d, 1H, C_4-H); ms: m/z 281 (M^+).

Anal. Calcd. for $C_{13}H_{15}NO_6$: C, 55.51; H, 5.38; N, 4.98. Found: C, 55.43; H, 5.27; N, 4.90.

General Procedure for Reductive Cyclization of Acetals **5** by Catalytic Hydrogenation.

A solution of 5 mmoles of acetal **5** in 100 ml of ethanol containing 200 mg of 10% rhodium-carbon was hydrogenated at 1 atmosphere and at room temperature. After stirring for 3 hours, the theoretical amount of hydrogen had been taken up. After the reaction mixture was purged with nitrogen and the catalyst was removed by filtration, 20 ml of 10% hydrochloric acid was added to the filtrate and the mixture was stirred at room temperature for 3 hours. Evaporation of the ethanol, extraction with chloro-

form, and column chromatography on silica gel (benzene) gave the product. The yields of indoles **4** are summarized in Table 3.

Data for Indoles **4** Prepared by Reductive Cyclization.

All of the indoles **4** prepared by the above procedures had melting points in agreement with literature values and exhibited ir and ^{1}H nmr spectra consistent with the assigned structure.

Indole (**4a**).

This compound had mp 51-53° (lit [17], mp 52-53°).

5-Methoxyindole (**4c**).

This compound had mp 55-56° (lit [19], mp 54-55°).

5-Methylindole (**4d**).

This compound had mp 59-60° (lit [20], mp 58-59°).

Methyl 5-Indolecarboxylate (**4e**).

This compound had mp 124-125°; ir (potassium bromide): 3325 (-NH), 1690 (-COOMe), 1600, 1580, 900, 810 cm^{-1} (1,2,4-trisubst Ar-H); ^{1}H nmr: δ 3.91 (s, 3H, -COOCH_3), 6.60 (d, 1H, C_3-H), 7.19 (d, 1H, C_2-H), 7.32 (d, 1H, C_7-H), 7.87 (d-d, 1H, C_6-H), 8.40 (d, 1H, C_4-H), 8.82 ppm (br-s, 1H, -NH); ms: m/z 175 (M$^+$).

Anal. Calcd. for $C_{10}H_9NO_2$: C, 68.56; H, 5.18; N, 8.00. Found: C, 68.45; H, 5.11; N, 7.89.

6-Methoxyindole (**4f**).

This compound had mp 89-90° (lit [19], mp 88-90°).

6-Methylindole (**4g**).

This compound had bp 81-83° (1 mm/Hg) (lit [21], bp 75-78° (1 mm/Hg)).

Methyl 6-Indolecarboxylate (**4h**).

This compound had mp 78-80° (lit [22], mp 78-79°).

Methyl 7-Indolecarboxylate (**4i**).

This compound had mp 44-45°; ir (potassium bromide): 3410 (-NH), 1695 (-COOMe), 1600, 1580, 750, 720 cm^{-1} (1,2,3-trisubst Ar-H); ^{1}H nmr: δ 3.86 (s, 3H, -COOCH_3), 6.54 (d, 1H, C_3-H), 7.06 (t, 1H, C_5-H), 7.17 (d, 1H, C_2-H), 7.72-7.90 (m, 2H, C_4-H + C_6-H), 9.85 ppm (br-s,1H, -NH); ms: m/z 175 (M$^+$).

Anal. Calcd. for $C_{10}H_9NO_2$: C, 68.56; H, 5.18; N, 8.00. Found: C, 68.54; H, 5.10; N, 7.98.

General Procedure for the Heck Reaction of 2-Bromoacetanilides **2** with Ethylene.

The procedure was essentially the one described for the Heck reaction of **1** with ethylene. The products **6** were purified by column chromatography (silica gel, benzene), followed by recrystallization from ethanol. The results are summarized in Table 4.

2-Ethenylacetanilide (**6a**).

This compound was obtained from **2a** as colorless crystals, mp 62-63°; ir (potassium bromide): 3220 (-NH), 1640, 1530, 1300 (-NHCO-), 990, 915 (-CH=CH_2), 1600, 1580, 770, 745 cm^{-1} (*o*-disubst Ar-H); ^{1}H nmr: δ 2.13 (s, 3H, -NCOCH_3), 5.34 (d, 1H, J = 11 Hz, Ar-C=CH_a), 5.63 (d, 1H, J = 17 Hz, Ar-C=CH_b), 6.81 (d-d, 1H, J = 11 and 17 Hz, Ar-CH=C-), 7.02-7.86 ppm (m, 5H, 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, 74.41; H, 6.81; N, 8.57.

2-Ethenyl-3-methylacetanilide (**6b**).

This compound was obtained from **2b** as colorless crystals, mp 118-119°; ir (potassium bromide): 3370 (-NH), 1650, 1530, 1290, (-NHCO-), 990, 930 (-CH=CH_2), 1600, 1580, 780, 750 cm^{-1} (1,2,-3-trisubst Ar-H); ^{1}H nmr: δ 2.13 (s, 3H, -NCOCH_3), 2.27 (s, 3H, Ar-CH_3), 5.41 (d-d, 1H, J = 1.5 and 11 Hz, Ar-C=CH_a), 5.69 (d-d, 1H, J = 1.5 and 17 Hz, Ar-C=CH_b), 6.64 (d-d, 1H, J = 11 and 17 Hz, Ar-CH=C-), 6.95 (m, 1H, C_5-H), 7.16 (m, 1H, C_4-H), 7.50 (br-s, 1H, -NH), 8.02 ppm (m, 1H, C_6-H); ms: m/z 175 (M$^+$).

Anal. Calcd. for $C_{11}H_{13}NO$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.26; H, 7.39; N, 7.90.

2-Ethenyl-3-methoxycarbonylacetanilide (**6c**).

This compound was obtained from **2c** as colorless crystals, mp 80-81°; ir (potassium bromide): 3260 (-NH), 1730 (-COOMe), 1660, 1530, 1330 (-NHCO-), 985, 930 (-CH=CH_2), 1600, 1580, 765, 680 cm^{-1} (1,2,3-trisubst Ar-H); ^{1}H nmr: δ 2.13 (s, 3H, -NCOCH_3), 3.83 (s, 3H, -COOCH_3), 5.32 (d-d, 1H, J = 1.5 and 11 Hz, Ar-C=CH_a), 5.66 (d-d, 1H, J = 1.5 and 17 Hz, Ar-C=CH_b), 6.98 (d-d, 1H, J = 11 and 17 Hz, Ar-CH=C-), 7.33 (m, 1H, C_5-H), 7.61 (d-d, 1H, C_6-H), 7.70 (-NH), 8.41 ppm (m, 1H, C_4-H); ms: m/z 219 (M$^+$).

Anal. Calcd. for $C_{12}H_{13}NO_3$: C, 65.74; H, 5.98; N, 6.39. Found: C, 65.66; H, 5.94; N, 6.36.

2-Ethyenyl-4-methoxyacetanilide (**6d**).

This compound was obtained from **2d** as colorless crystals, mp 108-109°; ir (potassium bromide): 3220 (-NH), 1640, 1530, 1350 (-NHCO-), 990, 920 (-CH=CH_2), 1600, 1580, 880, 820 cm^{-1} (1,2,4-trisubst Ar-H); ^{1}H nmr: δ 2.08 (s, 3H, -NCOCH_3), 3.78 (s, 3H, -OCH_3), 5.28 (d, 1H, J = 12 Hz, Ar-C=CH_a), 5.62 (d, 1H, J = 18 Hz, Ar-C=CH_b), 6.70 (d-d, 1H, J = 12 and 18 Hz, Ar-CH=C-), 6.76 (d-d, 1H, C_5-H), 6.96 (d, 1H, C_5-H, 7.29 (d, 1H, C_3-H), 7.78 ppm (br-s, 1H, -NH); ms: m/z 191 (M$^+$).

Anal. Calcd. for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.33. Found: C, 69.01; H, 6.77; N, 7.25.

2-Ethenyl-4-methylacetanilide (**6e**).

This compound was obtained from **2e** as colorless crystals, mp 84-86°; ir (potassium bromide): 3270 (-NH), 1655, 1535, 1365 (-NHCO-), 980, 905 (-CH=CH_2), 1600, 1580, 880, 820 cm^{-1} 1,2,4-trisubst Ar-H); ^{1}H nmr: δ 2.12 (s, 3H, -NCOCH_3), 2.30 (s, 3H, Ar-CH_3), 5.32 (d, 1H, J = 12 Hz, Ar-C=CH_a), 5.63 (d, 1H, J = 17 Hz, Ar-C=CH_b), 6.76 (d-d, 1H, J = 12 an 17 Hz, Ar-CH=C-), 6.80-7.54 ppm (m, 4H, Ar-H + -NH); ms: m/z 175 (M$^+$).

Anal. Calcd. for $C_{11}H_{13}NO$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.33; H, 7.39; N, 7.90.

2-Ethenyl-4-methoxycarbonylacetanilide (**6f**).

This compound was obtained from **2f** as colorless crystals, mp 125-127°; ir (potassium bromide): 3240 (-NH), 1720 (-COOMe), 1650, 1540, 1350 (-NHCO-), 975, 910 (-CH=CH_2), 1600, 1580, 885, 840 cm^{-1} (1,2,4-trisubst Ar-H); ^{1}H nmr: δ 2.14 (-NCOCH_3), 3.78 (s, 3H, -COOCH_3), 5.42 (d, 1H, J = 11 Hz, Ar-C=CH_a), 5.61 (d, 1H, J = 17 Hz, Ar-C=CH_b), 6.74 (d-d, 1H, J = 11 and 17 Hz, Ar-CH=C-), 7.68 (m, 2H, C_5-H + C_6-H), 8.07 ppm (m, 2H, C_3-H + -NH); ms: m/z 219 (M$^+$).

2-Ethenyl-5-methoxyacetanilide (**6g**).

This compound was obained from **2g**, as colorless crystals, mp 100-102°; ir (potassium bromide): 3200 (-NH), 1640, 1540, 1360, (-NHCO-), 980, 905 (-CH=CH_2), 1600, 1580, 850, 810 cm^{-1}

(1,2,4-trisubst Ar-H); ^{1}H nmr: δ 2.16 (s, 3H, -NCOCH_3), 3.76 (s, 3H, -OCH_3), 5.26 (d, 1H, J = 11 Hz, Ar-C=CH_a), 5.52 (d, 1H, J = 17 Hz, Ar-C=CH_b), 6.57 (d-d, 1H, J = 11 and 17 Hz, Ar-CH=C-), 6.87-7.52 ppm (m, 4H, Ar-H + -NH); ms: m/z 191 (M^+).

Anal. Calcd. for $C_{11}H_{13}NO_2$: C, 69.09; H, 6.85; N, 7.33. Found: C, 68.95; H, 6.78; N, 7.27.

2-Ethenyl-5-methylacetanilide (**6h**).

This compound was obtained from **2h** as colorless crystals, mp 127-129°; ir (potassium bromide): 3270 (-NH), 1660, 1575, 1350 (-NHCO-), 995, 905 (-CH=CH$_2$), 1600, 1580, 880, 815 cm^{-1} (1,2,4-trisubst Ar-H); ^{1}H nmr: δ 2.05 (-NCOCH_3), 2.27 (s, 3H, Ar-CH_3), 5.26 (d, 1H, J = 12 Hz, Ar-C=CH_a), 5.57 (d, 1H, J = 17 Hz, Ar-C=CH_b), 6.71 (d-d, 1H, J = 12 and 17 Hz, Ar-CH=C-), 6.96-7.46 ppm (m, 4H, Ar-H + -NH); ms: m/z 175 (M^+).

Anal. Calcd. for $C_{11}H_{13}NO$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.22; H, 7.35; N, 7.88.

2-Ethenyl-5-chloroacetanilide (**6i**).

This compound was obtained from **2i** as colorless crystals, mp 145-146°; ir (potassium bromide): 3250 (-NH), 1655, 1570, 1350 (-NHCO-), 980, 915 (-CH=CH$_2$), 1600, 1580, 870, 830 cm^{-1} (1,2,4-trisubst Ar-H): ^{1}H nmr: δ 2.13 (s, 3H, -NHCOCH$_3$), 5.38 (d, 1H, J = 12 Hz, Ar-C=CH_a), 5.62 (d, 1H, J = 17 Hz, Ar-C=CH_b), 6.70 (d-d, 1H, J = 12 and 17 Hz, Ar-CH=C-), 7.07 (d-d, 1H, C$_4$-H), 7.31 (d, 1H, C$_3$-H), 7.51 (br-s, 1H, -NH), 7.77 ppm (d, 1H, C$_6$-H); ms: m/z 196 (M^+).

Anal. Calcd. for $C_{10}H_{10}ClNO$: C, 61.42; H, 5.15; N, 7.16. Found: C, 61.36; H, 5.10; N, 7.09.

2-Ethenyl-5-methoxycarbonylacetanilide (**6j**).

This compound was obtained from **2j**, as colorless crystals, mp 143-144°; ir (potassium bromide): 3250 (-NH), 1720 (-COOMe), 1660, 1560, 1360 (-NHCO-), 990, 920 (-CH=CH$_2$), 1600, 1580, 900, 840 cm^{-1} (1,2,4-trisubst Ar-H); ^{1}H nmr: δ 2.17 (s, 3H, -NCOCH_3), 3.87 (s, 1H, -COOCH_3), 5.37 (d, 1H, J = 12 Hz, Ar-C=CH_a), 5.74 (d, 1H, J = 19 Hz, Ar-C=CH_b), 6.78 (d-d, 1H, J = 12 and 19 Hz, Ar-CH=C-), 7.46 (d, 1H, C$_3$-H), 7.79 (d-d, 1H, C$_4$-H), 7.99 (br-s, 1H, -NH), 8.25 ppm (d, 1H, C$_6$-H); ms: m/z 219 (M^+).

Anal. Calcd. for $C_{12}H_{13}NO_3$: C, 65.74; N, 5.98; N, 6.39. Found: C, 65.59; H, 5.91; N, 6.27.

2-Ethenyl-6-methoxycarbonylacetanilide (**6k**).

This compound was obtained from **2k** as colorless crystals, 111-112°; ir (potassium bromide): 3220 (-NH), 1730 (-COOMe), 1650, 1520, 1350 (-NHCO-), 990, 910 (-CH=CH$_2$), 1600, 1580, 780, 700 cm^{-1} (1,2,3-trisubst Ar-H); ^{1}H nmr: δ 2.18 (s, 3H, -NCOCH_3), 3.88 (s, 3H, -COOCH_3), 5.30 (d-d, 1H, J = 1.5 and 11 Hz, Ar-C=CH_a), 5.70 (d-d, 1H, J = 1.5 and 17 Hz, Ar-C=CH_b), 6.80 (d-d, 1H, J = 11 and 17 Hz, Ar-CH=C-), 7.10 (t, 1H, C$_4$-H), 7.66-7.90 (m, 2H, C$_3$-H + C$_5$-H), 9.05 ppm (br-s, 1H, -NH); ms: m/z 219 (M^+).

Anal. Calcd. for $C_{12}H_{13}NO_3$: C, 65.74; H, 5.98; N, 6.39. Found: C, 65.66; H, 5.91; N, 6.27.

General Procedure of Palladium-Catalyzed Cyclization of **6** to 1-Acetylindoles **7**.

The procedure was essentially the one described for the palladium-catalyzed acetalization of **3** to **5**. The results are summarized in Table 6.

1-Acetylindole (**7a**).

This compound was obtained from **6a** as a colorless oil, bp 135-138° (6 mm/Hg) (lit [23], bp 144-145 (10 mm/Hg)).

1-Acetyl-4-methylindole (**7b**).

This compound was obtained from **6b** as a colorless oil, bp 158-160° (11 mm/Hg) (lit [24], bp 172 (15 mm/Hg)).

1-Acetyl-4-methoxycarbonylindole (**7c**).

This compound was obtained from **6c** as a colorless crystals, mp 130-131°; ir (potassium bromide): 1690 (-NCO- + -COOMe), 1600, 1580, 770 cm^{-1} (1,2,3-trisubst Ar-H); ^{1}H nmr: δ 2.62 (s, 3H, -NCOCH_3), 3.96 (s, 3H, -COOCH_3), 7.31 (d, 1H, C$_3$-H), 7.36 (t, 1H, C$_6$-H), 7.47 (d, 1H, C$_2$-H), 7.96 (d, 1H, C$_5$-H), 8.65 ppm (d, 1H, C$_7$-H); ms: m/z 217 (M^+).

Anal. Calcd. for $C_{12}H_{11}NO_3$: C, 66.35; H, 5.10; N, 6.45. Found: C, 66.32; H, 5.03; N, 6.39.

1-Acetyl-5-methoxyindole (**7d**).

This compound was obtained from **6d**, as colorless crystals, mp 81-82° (lit [25], mp 80-81°).

1-Acetyl-5-methylindole (**7e**).

This compound was obtained from **6e** as colorless crystals, mp 61-63°; ir (potassium bromide): 1690 (-NCO-), 1600, 1585, 885, 830 cm^{-1} (1,2,4-trisubst Ar-H); ^{1}H nmr: δ 2.40 (s, 3H, Ar-CH_3), 2.52 (s, 3H, -NCOCH_3), 6.49 (d, 1H, C$_3$-H), 7.11 (m, 2H, C$_4$-H + C$_6$-H), 7.28 (d, 1H, C$_2$-H), 8.25 ppm (d, 1H, C$_7$-H); ms: m/z 173 (M^+).

Anal. Calcd. for $C_{11}H_{11}NO$: C, 76.27; H, 6.40; N, 8.09. Found: C, 76.20; H, 6.32; N, 8.03.

1-Acetyl-5-methoxycarbonylindole (**7f**).

This compound was obtained from **6f** as colorless crystals, mp 166-167°; ir (potassium bromide): 1700 (-NCO- + -COOMe), 1600, 1580, 880, 825 cm^{-1} (1,2,4-trisubst Ar-H); ^{1}H nmr: δ 2.59 (s, 3H, -NCOCH_3), 3.91 (-COOCH_3), 6.63 (d, 1H, C$_3$-H), 7.42 (d, 1H, C$_2$-H), 7.96 (d-d, 1H, C$_6$-H), 8.22 (d, 1H, C$_4$-H), 8.40 ppm (d, 1H, C$_7$-H); ms: m/z 217 (M^+).

Anal. Calcd. for $C_{12}H_{11}NO_3$: C, 66.35; H, 5.10; N, 6.45. Found: C, 66.30; H, 5.07; N, 6.47.

1-Acetyl-6-methoxyindole (**7g**).

This compound was obtained from **6g** as colorless crystals, mp 45-46°; ir (potassium bromide): 1700 (-NCO-), 1605, 1585, 870, 815 cm^{-1} (1,2,4-trisubst Ar-H); ^{1}H nmr: δ 2.58 (s, 3H, -NCOCH_3), 4.86 (s, 3H, -OCH_3), 6.52 (d, 1H, C$_3$-H), 6.87 (d-d, 1H, C$_5$-H), 7.25 (d, 1H, C$_2$-H), 7.37 (d, 1H, C$_4$-H), 8.20 ppm (d, 1H, C$_7$-H); ms: m/z 189 (M^+).

Anal. Calcd. for $C_{11}H_{11}NO_2$: C, 69.82; H, 5.86; N, 7.40. Found: C, 69.75; H, 5.76; N, 7.34.

1-Acetyl-6-methylindole (**7h**).

This compound was obtained from **6h** as colorless oil, bp 146-149° (5 mm/Hg), ir (neat): 1700 (-NCO-), 1600, 1575, 995, 905 cm^{-1} (1,2,4-trisubst Ar-H); ^{1}H nmr: δ 2.43 (s, 3H, Ar-CH_3), 2.49 (s, 3H, -NCOCH_3), 6.46 (d, 1H, C$_3$-H), 7.03 (d, 1H, C$_5$-H), 7.17 (d, 1H, C$_2$-H), 7.35 (d, 1H, C$_4$-H), 8.23 ppm (s, 1H, C$_7$-H); ms: m/z 173 (M^+).

Anal. Calcd. for $C_{11}H_{11}NO$: C, 76.27; H, 6.40; N, 8.09. Found: C, 76.18; H, 6.33; N, 7.97.

1-Acetyl-6-chloroindole (**7i**).

This compound was obtained from **6i** as colorless crystals, mp 63-64°; ir (potassium bromide): 1700 (-NCO-), 1600, 1580, 890, 805 cm^{-1} (1,2,4-trisubst Ar-H); ^1H nmr: δ 2.60 (-NCOCH_3), 6.59 (d, 1H, C_3-*H*), 7.21 (d-d, 1H, C_5-*H*), 7.37 (d, 1H, C_2-*H*), 7.44 (d, 1H, C_4-*H*), 8.45 ppm (d, 1H, C_7-*H*); ms: m/z 193 (M^+).

Anal. Calcd. for $C_{10}H_8ClNO$: C, 62.03; H, 4.16; N, 7.23. Found: C, 61.89; H, 4.09; N, 7.14.

1-Acetyl-6-methoxycarbonylindole (**7j**).

This compound was obtained from **6j** as colorless crystals, mp 128-129°; ir (potassium bromide): 1700 (-NCO- + -COOMe), 1600, 1580, 900, 830 cm^{-1} (1,2,4-trisubst Ar-H); ^1H nmr: δ 2.62 (s, 3H, -NCOCH_3), 3.92 (s, 3H, -COOCH_3), 6.61 (d, 1H, C_3-*H*), 7.53 (d, 1H, C_4-*H*), 7.55 (d, 1H, C_2-*H*), 7.83 (d, 1H, C_5-*H*), 9.03 ppm (d, 1H, C_7-*H*); ms: m/z 217 (M^+).

Anal. Calcd. for $C_{12}H_{11}NO_3$: C, 66.35; H, 5.10; N, 6.45. Found: C, 66.32; H, 5.05; N, 6.39.

1-Acetyl-7-methoxycarbonylindole (**7k**).

This compound was obtained from **6k** as colorless crystals, mp 86-87°; ir (potassium bromide): 1725 (-COOMe), 1705 (-NCO-), 1600, 1580, 780, 685 cm^{-1} (1,2,3-trisubst Ar-H); ^1H nmr: δ 2.63 (s, 3H, -NCOCH_3), 3.94 (s, 3H, -COOCH_3), 6.67 (d, 1H, C_3-*H*), 7.20-7.47 (m, 2H, C_2-*H* + C_5-*H*), 7.54 (d-d), 1H, C_4-*H*), 7.67 ppm (d-d, 1H, C_6-*H*); ms: m/z 217 (M^+).

Anal. Calcd. for $C_{12}H_{11}NO_3$: C, 66.35; H, 5.10; N, 6.45. Found: C, 66.32; H, 5.05; N, 6.39.

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