A Straightforward Synthesis of 2-(1-Vinyl-1*H*-pyrrol-2-yl)-1*H*-benzimidazoles from 1-Vinyl-1*H*-pyrrole-2-carbaldehydes and *o*-Phenylenediamine

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Abstract: Hitherto inaccessible 1-vinylpyrrole–benzimidazole ensembles have been synthesized by the condensation of 1-vinyl-1*H*-pyrrole-2-carbaldehydes with *o*-phenylenediamine either directly or via the intermediate Schiff bases of the 1-vinyl-1*H*-pyrrole-2-carbaldehydes (1% TFA, DMSO, air atmosphere, 60–70 °C, 1 h) in yields up to 89%, the intermediate Schiff bases of exclusively *E* configuration being isolated in 91–98% yield (1% TFA, DMSO, r.t., 30 min). The synthesized 2-(1-vinyl-1*H*-pyrrol-2-yl)-1*H*-benzimidazoles are intensely fluorescent, covering the practically important blue region (λ_{max} 343–417 nm, Stokes shift 31–91 nm).

Key words: 1-vinyl-1*H*-pyrrole-2-carbaldehydes, pyrrolylbenzimidazoles, *o*-phenylenediamine, Schiff bases, oxidative condensation

Functionalized pyrrole–benzimidazole scaffolds play a great role in biology and medicine as anti-infection[1a,b] drugs, artificial gene regulators,[1c,d] and antiviral and antitumor[1e] agents. Thienylpyrrole–benzimidazoles possess excellent solvatochromic properties, high thermal stability and good optical nonlinearity.[2] 4,4-Difluoro-4-bora-3a,4a-diaza-*s*-indacene (BODIPY) dyes based on benzimidazolylpyrroles show pronounced photostability and high extinction coefficients.[3]

So far, however, no pyrrolylbenzimidazoles containing a *N*-vinyl group in the pyrrole counterpart are known. These compounds are also of special interest as candidates for pharmaceuticals owing to the presence of two pharmacophores: the 1-vinyl-1*H*-pyrrole and benzimidazole[1] moieties. Furthermore, the *N*-vinyl group opens opportunities for a number of chemical modifications, such as addition reactions and polymerization, that allow tailor-made materials to be designed.

The known protocols for the synthesis of 2-(pyrrol-2-yl)benzimidazoles are based on the condensation of *o*-phenylenediamine with pyrrole-2-carbaldehydes,[4] pyrrol-2-ylglyoxalic acid,[5] imidoethers of pyrrole-2-carbonic acid[6] or *N*-(ethoxycarbonyl)thioamides.[7] Also, for the synthesis of such compounds, a reductive cyclization of *o*-nitroaniline with pyrrole-2-carbaldehydes[2,8] and the Trofimov reaction[9] of 2-acetyl-1-methylbenzimidazole oxime and acetylene in the system potassium hydroxide–dimethyl sulfoxide[10] have been employed.

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1-Vinyl-1*H*-pyrrole-2-carbaldehydes, now available[11] from the formylation of 1-vinyl-1*H*-pyrroles, represent highly reactive building blocks for the synthesis of functionalized pyrroles.[12] However, the synthetic procedures often used to obtain pyrrolylbenzimidazoles from pyrrole-2-carbaldehydes (see above) require special catalysts [e.g., silicotungstic heteropolyacid ($H_4SiW_{12}O_{40}$)][4d] and oxidants (copper salts,[4a] hypervalent iodine[4e]), and long heating (90–100 °C).[4a,c] In the case of 1-vinyl-1*H*-pyrrole-2-carbaldehydes, the aforementioned procedures might be inconvenient and even unsuitable due to the well-known sensitivity of the *N*-vinyl group toward acids and oxidants.[13]

The present work reports the condensation of 1-vinyl-1*H*-pyrrole-2-carbaldehydes **1b**,**d**,**f–i** with *o*-phenylenediamine to afford the previously unknown 1-vinylpyrrole–benzimidazole derivatives **3b**,**d**,**f–i** and the intermediate 1-vinyl-1*H*-pyrrole-2-carbaldehyde Schiff bases **2b**,**d**,**f–i**. Non-vinylated 1*H*-pyrrole-2-carbaldehydes **1a**,**c**,**e** were also involved in the condensation for comparison.

The intermediate 1-vinyl-1*H*-pyrrole-2-carbaldehyde Schiff bases **2b**,**d**,**f–i** are formed at ambient temperature in dimethyl sulfoxide (DMSO) in the presence of catalytic amounts of trifluoroacetic acid (TFA) almost quantitatively, in 91–98% yield (Table 1). We have used TFA because, as our previous investigations have shown,[14] this acid catalyzes the transformation of 1-vinyl-1*H*-pyrrole-2-carbaldehydes into the Schiff bases leaving the vinyl group intact.

According to ^{1}H NMR monitoring, 1-vinyl-1*H*-pyrrole-2-carbaldehydes **1b** and **1f** are completely consumed in 20–30 minutes after the beginning of the reaction. In the absence of the acid, the reaction did not take place even after 20 hours (as determined by GLC).

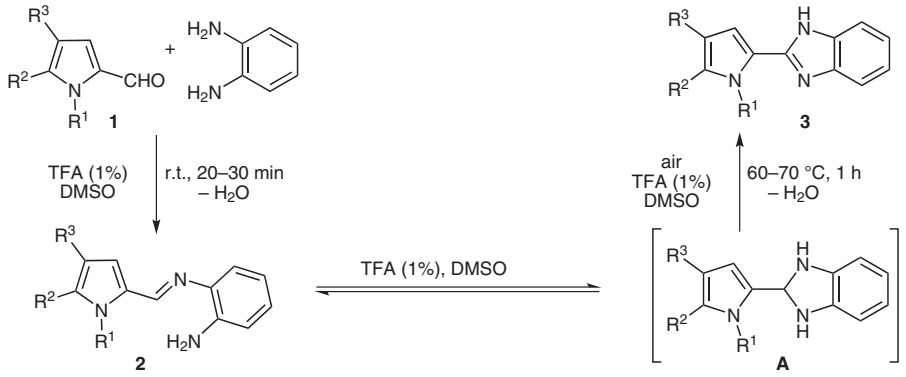
All of the Schiff bases synthesized exist as the *E*-isomers exclusively. This fact was confirmed by 2D NOESY experiments showing NOE correlations between the HC=N proton and H-3 of the pyrrole moiety, as well as between the HC=N proton and H-6 of the benzene ring.

Interestingly, in the case of 4,5,6,7-tetrahydro-1*H*-indole-2-carbaldehyde (**1c**), a pyrrole with electron-donating substituents, the reaction does not occur under the above conditions and the initial pyrrolecarbaldehyde is recovered completely. Increasing the temperature up to 130 °C results in only 58% conversion of **1c** (30 min), the yield of

2c being 91% based on the pyrrole consumed. At the same time, with 1-vinyl-4,5,6,7-tetrahydro-1*H*-indole-2-carbaldehyde (**1d**) the reaction is accomplished within 30 minutes to furnish the corresponding Schiff base **2d** in quantitative yield (Table 1). This fact is an illustration of the strong electron-withdrawing effect of the *N*-vinyl substituent, which is transmitted to the carbonyl group significantly increasing its electrophilicity.

It is known[15] that non-vinylated structural analogues of Schiff bases **2b**,**d**,**f–i** are potent block synthons for supramolecular complexes. It could be expected that introduction of the highly reactive *N*-vinyl group into these molecules would greatly expand their synthetic potential.

Table 1 Synthesis of 1*H*-Pyrrole-2-carbaldehyde Schiff Bases **2** and 2-(1*H*-Pyrrol-2-yl)-1*H*-benzimidazoles **3**



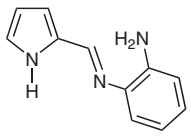
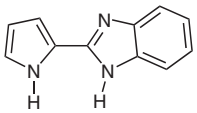
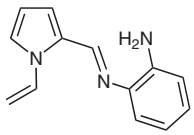
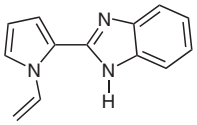
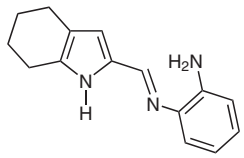
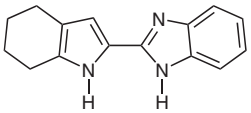
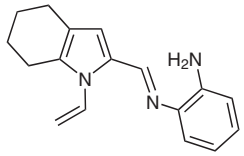
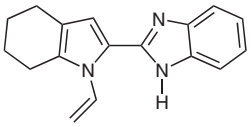
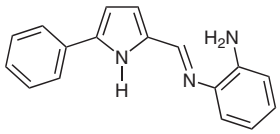
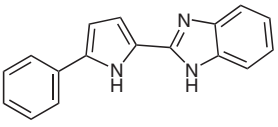
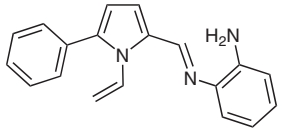
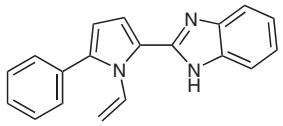
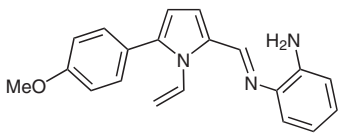
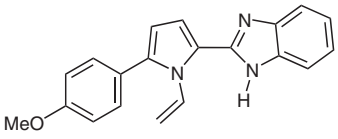
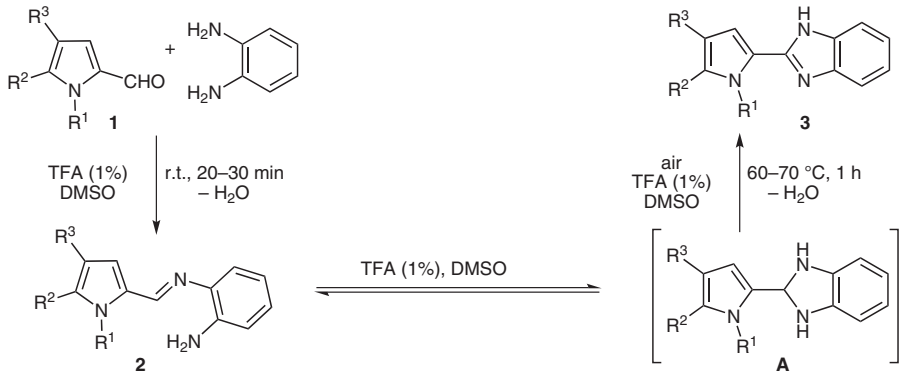
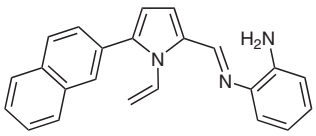
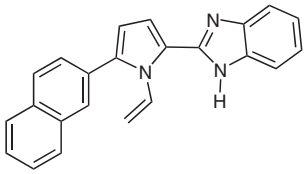
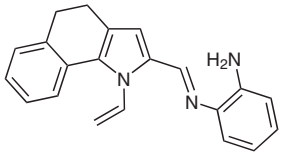
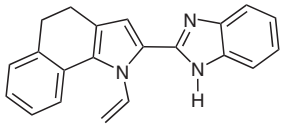
Product	Schiff base **2**	Yield (%)	Product	Benzimidazole **3**	Yield (%)
2a		98	**3a**		83
2b		96	**3b**		58 (61)[a]
2c		91[b]	**3c**		–[c]
2d		98	**3d**		41 (42)[a]
2e		92	**3e**		77
2f		97	**3f**		84 (89)[a]
2g		96	**3g**		82 (86)[a]

Table 1 Synthesis of 1*H*-Pyrrole-2-carbaldehyde Schiff Bases **2** and 2-(1*H*-Pyrrol-2-yl)-1*H*-benzimidazoles **3** (continued)



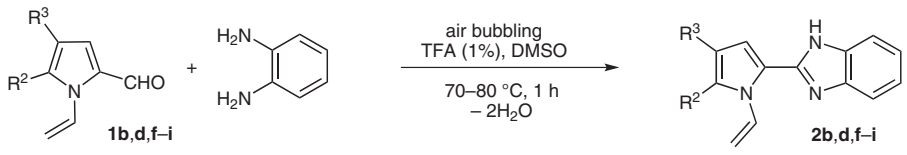
Product	Schiff base **2**	Yield (%)	Product	Benzimidazole **3**	Yield (%)
2h		95	**3h**		62 (65)[a]
2i		97	**3i**		71 (74)[a]

[a] In a one-pot reactor with air bubbling (see Scheme 1).
[b] Conversion of **1c** at 130 °C: 58%.
[c] Not obtained.

(1-Vinylpyrrolyl)benzimidazoles **3b**,**d**,**f**–**i** were prepared by heating (60–70 °C, 1 h) the corresponding 1-vinyl-1*H*-pyrrole-2-carbaldehyde Schiff bases **2b**,**d**,**f**–**i** in DMSO in the presence of catalytic amounts of TFA (Table 1). From common knowledge,[16] DMSO could act as a probable oxidant of the intermediate benzimidazoline **A**; however, our experiments with Schiff base **2f** have shown that the aromatization takes place exclusively due to oxidation by air oxygen. Noteworthy, air bubbling through a heated (60–70 °C) solution of Schiff base **2f** in DMSO quantitatively yields the corresponding benzimidazole even in the absence of the acid. Heating (60–70 °C) compound **2f** in the presence of acid in freshly distilled (oxygen-free) DMSO under argon does not give benzimidazole **3f**, even in trace amounts.

When 5-phenyl-1-vinyl-1*H*-pyrrole-2-carbaldehyde (**1f**) is heated (70–80 °C) with *o*-phenylenediamine (1:1 molar ratio) in DMSO in the presence of TFA, the reaction does not proceed to the end, stopping at the stage when the reaction mixture contains ca. equimolar amounts of intermediate **2f** and the final product **3f**. Further heating at higher temperature (130 °C, 30 min) does not alter the ratio of **2f** to **3f** in the reaction mixture. The inhibition is likely due to the released water that then participates in hydrolysis of the intermediate imidazoline **A**.

Pyrrolylbenzimidazole **3f** was synthesized in 76% yield in a one-pot procedure directly from 5-phenyl-1-vinyl-1*H*-pyrrole-2-carbaldehyde (**1f**) and *o*-phenylenediamine under azeotropic removal of water with benzene. Also, benzimidazole **3f** was selectively prepared in 89% yield directly from 5-phenyl-1-vinyl-1*H*-pyrrole-2-carbaldehyde (**1f**) under air bubbling (70–80 °C). This fact is likely to be the result of a simultaneous increase in the oxidant (O_2) concentration in the reaction mixture and removal of the released water from the reactor by air flow. 2-(1-Vinyl-1*H*-pyrrol-2-yl)-1*H*-benzimidazoles **3b**,**d**,**g**–**i** were synthesized in a similar manner, the yields being comparable (even slightly higher) to those resulting from the two-step protocol (Scheme 1, Table 1).



Scheme 1

Thus, the synthesis of (1-vinylpyrrolyl)benzimidazoles has been carried out directly from 1-vinyl-1*H*-pyrrole-2-carbaldehydes and *o*-phenylenediamine avoiding the stage of isolation of the intermediate Schiff bases.

The synthesis of diverse benzimidazoles, including 2-(1*H*-pyrrol-2-yl)-1*H*-benzimidazole (**3a**) in 81% yield, by the oxidation of a mixture of aldehydes with *o*-phenylenediamine with air oxygen in dioxane (100 °C, 28 h) has been reported.[4c] According to our procedure, compound **3a** was synthesized in 83% yield under milder conditions (60–70 °C) and in much shorter time (1 h), which clearly demonstrates the advantages of the developed method.

If necessary, the *N*-vinyl group can be removed almost quantitatively by consecutive treatment of 1-vinyl-1*H*-pyrroles with mercury acetate and sodium borohydride.[17] Therefore, 1-vinylpyrrole–benzimidazole ensembles should be considered as the corresponding protected *N*-H compounds.

All of the 2-(1-vinyl-1*H*-pyrrol-2-yl)-1*H*-benzimidazoles **3b**,**d**,**f–i** fluoresce intensely (λ_{max} 343–417 nm, Stokes shift 31–91 nm) (Table 2).

Table 2 UV/Vis and Fluorescence Spectroscopic Data for (1-Vinylpyrrolyl)benzimidazoles **3b**,**d**,**f–i** (in MeCN)

Compound	Absorption		Emission	Stokes shift (nm)
	λ_{max} (nm)	log ε	λ_{max} (nm)	
3b	312	4.37	343 (sh)	31
		4.57	360	48
		4.46	378 (sh)	66
3d	328	4.39	360 (sh)	32
		4.55	376	48
		4.42	390 (sh)	62
3f	330	4.63	392	62
			405 (sh)	75
3g	321	4.55	412	91
3h	333	4.75	417	84
3i	356	4.27	396 (sh)	40
		4.44	417	61

Comparison of the UV spectra of 2-phenyl-1-vinyl-1*H*-pyrrole[18] and the corresponding benzimidazole derivative **3f** as well as of benzimidazoles **3a**[6] and **3b** shows that the introduction of the benzimidazole substituent to position 2 of the pyrrole ring leads to a bathochromic shift (60 nm) and induces a hyperchromic effect ($\Delta\log \varepsilon = 0.6$).

One can suppose that due to the high photostability of pyrrolylbenzimidazole derivatives,[3] as well as the ability of (1-vinylpyrrolyl)benzimidazoles **3g–i** to fluoresce in the practically important blue region of visible light, these compounds may find an application in optoelectronics.

In conclusion, efficient methods for the synthesis of hitherto unknown 1-vinyl-1*H*-pyrrole-2-carbaldehyde Schiff bases functionalized with an amino group and the corresponding 1-vinylpyrrole–benzimidazole ensembles have been developed. The methods involve the condensation of available 1-vinyl-1*H*-pyrrole-2-carbaldehydes with *o*-phenylenediamine in DMSO in the presence of catalytic amounts of TFA. The synthesized 1-vinyl-1*H*-pyrrole-2-carbaldehyde Schiff bases and 1-vinylpyrrole–benzimidazole compounds are potent building blocks for drug design and precursors of advanced optoelectronic materials.

^{1}H (400.13 MHz) and ^{13}C (101.61 MHz) NMR spectra were recorded on a Bruker DPX 400 or AV-400 spectrometer, with HMDS as an internal standard. In order to attribute ^{1}H and ^{13}C peaks, 2D homonuclear COSY and NOESY routines, as well as 2D heteronuclear HSQC and HMBC techniques, were used. IR spectra were recorded on a Bruker IFS 25 spectrometer. GLC analysis was performed on an Agilent 6890N instrument. 1-Vinyl-1*H*-pyrrole-2-carbaldehydes were obtained according to ref.[11b] Other chemicals (Aldrich) and solvents were commercial grade.

N-(1*H*-Pyrrol-2-ylmethylene)benzene-1,2-diamines 2; General Procedure

A mixture of a 1*H*-pyrrole-2-carbaldehyde **1** (2 mmol), *o*-phenylenediamine (0.22 g, 2 mmol) and TFA (1% with respect to the combined mass of both reagents) in DMSO (2 mL) was stirred at 20–25 °C for 30 min. The reaction mixture was diluted with aq 1% $NaHCO_3$ soln (8 mL), extracted with Et_2O (5 × 5 mL) and the extracts were dried (K_2CO_3). The solvent was evaporated under reduced pressure to give **2** as a colored powder.

N-(1*H*-Pyrrol-2-ylmethylene)benzene-1,2-diamine (2a)

Yield: 0.36 g (98%) from 0.19 g (2 mmol) of **1a**.

Yellow crystals; mp 116–118 °C.

IR (KBr): 3406, 3057, 3014, 2968, 2926, 1703, 1602, 1552, 1541, 1497, 1480, 1452, 1438, 1416, 1377, 1337, 1296, 1260, 1209, 1193, 1162, 1134, 1119, 1099, 1050, 1009, 970, 935, 912, 870, 836, 813, 785, 759, 706, 669, 652, 602, 474 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.54 (br s, 1 H, NH), 8.45 (s, 1 H, CH=N), 6.99 (m, 2 H, Ar), 6.89 (m, 1 H, Ar), 6.67 (d, $^3J_{3'-4'}$ = 3.9 Hz, 1 H, H-3′), 6.44 (dd, $^3J_{3'-4'}$ = 3.9 Hz, $^3J_{4'-5'}$ = 8.7 Hz, 1 H, H-4′), 5.18 (d, $^3J_{4'-5'}$ = 8.7 Hz, 1 H, H-5′), 4.99 (br s, 2 H, NH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.0 (1 C, C=N), 141.7, 138.9 (2 C, Ar), 127.0 (1 C, C-2′), 121.2 (1 C, C-5′), 119.8, 119.0, 117.0, 115.9 (4 C, Ar), 112.9 (1 C, C-3′), 109.9 (1 C, C-4′).

Anal. Calcd for $C_{11}H_{11}N_3$ (185.23): C, 71.33; H, 5.99; N, 22.69. Found: C, 71.55; H, 5.53; N, 22.32.

N-[(1-Vinyl-1*H*-pyrrol-2-yl)methylene]benzene-1,2-diamine (2b)

Yield: 0.40 g (96%) from 0.24 g (2 mmol) of **1b**.

Yellow crystals; mp 93–96 °C.

IR (KBr): 3098, 3051, 2923, 2853, 1730, 1642, 1624, 1594, 1582, 1504, 1465, 1451, 1425, 1395, 1352, 1327, 1281, 1273, 1229, 1148, 1114, 1075, 1028, 1004, 981, 962, 873, 848, 798, 764, 748, 723, 716, 673, 616, 590, 579, 479, 440 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.35 (s, 1 H, CH=N), 8.23 (dd, $^3J_{A-X}$ = 9.0 Hz, $^3J_{B-X}$ = 15.9 Hz, 1 H, H_X), 7.24 (d, $^3J_{4'-5'}$ = 8.4 Hz, 1 H, H-5′), 7.00, 6.94, 6.73, 6.70 (m, 4 H, Ar), 6.69 (d, $^3J_{3'-4'}$ = 3.4 Hz, 1 H, H-3′), 6.28 (dd, $^3J_{3'-4'}$ = 3.4 Hz, $^3J_{4'-5'}$ = 8.4 Hz, 1 H, H-4′), 5.19 (d, $^3J_{B-X}$ = 15.9 Hz, 1 H, H_B), 4.80 (d, $^3J_{A-X}$ = 9.0 Hz, 1 H, H_A), 4.08 (br s, 2 H, NH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.0 (1 C, C=N), 143.0, 142.3 (2 C, Ar), 128.5 (1 C, C_α), 126.4 (1 C, C-2′), 124.0, 122.9, 117.9,

117.3 (4 C, Ar), 116.6 (1 C, C-5′), 108.8 (1 C, C-4′), 107.0 (1 C, C-3′), 95.9 (1 C, C_β).

Anal. Calcd for $C_{13}H_{13}N_3$ (211.27): C, 73.91; H, 6.20; N, 19.89. Found: C, 73.52; H, 6.22; N, 19.32.

***N*-(4,5,6,7-Tetrahydro-1*H*-indol-2-ylmethylene)benzene-1,2-diamine (2c)**

Yield: 0.26 g (91%; conversion: 58%) from 0.30 g (2 mmol) of **1c**.

Orange crystals; mp 117–119 °C.

IR (KBr): 3411, 3027, 2968, 2926, 2869, 2837, 2725, 1639, 1602, 1552, 1541, 1497, 1480, 1452, 1438, 1416, 1377, 1337, 1296, 1260, 1209, 1193, 1162, 1134, 1119, 1099, 1050, 1009, 970, 935, 912, 870, 836, 813, 785, 759, 736, 706, 669, 652, 602, 474 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 9.54 (br s, 1 H, NH), 8.45 (s, 1 H, CH=N), 7.31 (m, 1 H, Ar), 6.99 (m, 2 H, Ar), 6.89 (m, 1 H, Ar), 6.67 (s, 1 H, H-3′), 4.99 (br s, 2 H, NH_2), 2.64 (m, 2 H, H-7′), 2.50 (m, 2 H, H-5′), 1.85 (m, 2 H, H-6′), 1.76 (m, 2 H, H-4′).

Anal. Calcd for $C_{15}H_{17}N_3$ (239.32): C, 75.28; H, 7.16; N, 17.56. Found: C, 75.72; H, 7.22; N, 17.12.

***N*-[(1-Vinyl-4,5,6,7-tetrahydro-1*H*-indol-2-yl)methylene]benzene-1,2-diamine (2d)**

Yield: 0.52 g (98%) from 0.35 g (2 mmol) of **1d**.

Orange viscous oil.

IR (KBr): 3479, 3379, 1640, 1615, 1597, 1575, 1566, 1503, 1495, 1478, 1458, 1447, 1410, 1389, 1355, 1331, 1317, 1305, 1292, 1266, 1218, 1193, 1155, 1132, 1086, 1054, 1034, 951, 893, 875, 856, 843, 818, 805, 761, 747, 711, 684, 648, 614, 587, 486, 433 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.31 (s, 1 H, CH=N), 7.68 (dd, $^3J_{A-X}$ = 8.8 Hz, $^3J_{B-X}$ = 15.9 Hz, 1 H, H_X), 6.94, 6.74 (m, 2 H, Ar), 6.71 (m, 2 H, Ar), 6.56 (s, 1 H, H-3′), 5.07 (d, $^3J_{B-X}$ = 15.9 Hz, 1 H, H_B), 5.03 (d, $^3J_{A-X}$ = 8.8 Hz, 1 H, H_A), 4.20 (br s, 2 H, NH_2), 2.70 (m, 2 H, H-7′), 2.54 (m, 2 H, H-4′), 1.82 (m, 2 H, H-6′), 1.75 (m, 2 H, H-5′).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.3 (1 C, C=N), 142.5, 142.1 (2 C, Ar), 135.4 (1 C, C-7a′), 132.7 (1 C, Cα), 129.8 (1 C, C-2′), 126.5 (1 C, Ar), 121.0 (1 C, C-3a′), 118.6 (1 C, Ar), 118.0 (1 C, C-3′), 116.7, 115.0 (2 C, Ar), 105.9 (1 C, C_β), 24.7, 23.4, 23.1, 23.0 (4 C, C-4′, C-5′, C-6′, C-7′).

Anal. Calcd for $C_{17}H_{19}N_3$ (265.36): C, 76.95; H, 7.22; N, 15.84. Found: C, 76.54; H, 7.18; N, 15.80.

***N*-[(5-Phenyl-1*H*-pyrrol-2-yl)methylene]benzene-1,2-diamine (2e)**

Yield: 0.48 g (92%) from 0.34 g (2 mmol) of **1e**.

Yellow crystals; mp 159–162 °C.

IR (KBr): 3397, 3044, 3000, 2968, 2926, 2725, 1602, 1552, 1541, 1497, 1480, 1452, 1438, 1416, 1377, 1337, 1296, 1260, 1209, 1193, 1162, 1134, 1119, 1099, 1050, 1009, 970, 935, 912, 870, 836, 785, 759, 736, 706, 669, 652, 602, 474 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 9.49 (br s, 1 H, NH), 8.28 (s, 1 H, CH=N), 7.52 (m, 2 H, Ar), 7.38 (m, 2 H, Ar), 7.25 (m, 1 H, Ar), 6.99 (m, 2 H, Ar), 6.74 (m, 2 H, Ar), 6.69 (d, $^3J_{3'-4'}$ = 3.9 Hz, 1 H, H-3′), 6.58 (d, $^3J_{3'-4'}$ = 3.9 Hz, 1 H, H-4′), 4.18 (br s, 2 H, NH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.6 (1 C, C=N), 142.4, 139.1, 131.0 (3 C, Ar), 130.8 (1 C, C-5′), 129.1 (2 C, Ar), 128.0 (1 C, C-2′), 126.4, 125.5, 124.0, 122.3, 120.2, 115.5 (7 C, Ar), 113.0 (1 C, C-3′), 109.4 (1 C, C-4′).

Anal. Calcd for $C_{17}H_{15}N_3$ (261.33): C, 78.13; H, 5.79; N, 16.08. Found: C, 78.58; H, 5.28; N, 15.89.

***N*-[(5-Phenyl-1-vinyl-1*H*-pyrrol-2-yl)methylene]benzene-1,2-diamine (2f)**

Yield: 0.56 g (97%) from 0.39 g (2 mmol) of **1f**.

Yellow crystals; mp 102–104 °C.

IR (KBr): 3456, 3360, 3025, 2990, 1711, 1635, 1607, 1589, 1566, 1541, 1508, 1488, 1462, 1454, 1420, 1407, 1381, 1337, 1322, 1310, 1267, 1230, 1215, 1188, 1153, 1134, 1077, 1045, 1026, 1011, 966, 938, 918, 878, 834, 782, 765, 755, 744, 712, 697, 659, 645, 631, 608, 578, 560, 537, 501, 488, 464, 419 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.45 (s, 1 H, CH=N), 7.44 (m, 5 H, Ar), 7.37 (dd, $^3J_{A-X}$ = 8.7 Hz, $^3J_{B-X}$ = 15.7 Hz, 1 H, H_X), 7.35, 7.31 (m, 2 H, Ar), 6.93 (d, $^3J_{3'-4'}$ = 3.9 Hz, 1 H, H-3′), 6.74 (m, 2 H, Ar), 6.36 (d, $^3J_{3'-4'}$ = 3.9 Hz, 1 H, H-4′), 5.13 (d, $^3J_{A-X}$ = 8.7 Hz, 1 H, H_A), 4.92 (d, $^3J_{B-X}$ = 15.7 Hz, 1 H, H_B), 4.16 (br s, 2 H, NH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.6 (1 C, C=N), 143.1, 142.1, 131.5, 130.3 (5 C, Ar), 129.3 (1 C, C_α), 128.6 (1 C, C-5′), 128.1, 126.3 (3 C, Ar), 125.6 (1 C, C-2′), 124.4, 122.7, 120.0, 115.3 (4 C, Ar), 105.9 (1 C, C_β), 104.4 (1 C, C-4′), 104.1 (1 C, C-3′).

Anal. Calcd for $C_{19}H_{17}N_3$ (287.36): C, 79.41; H, 5.96; N, 14.62. Found: C, 79.65; H, 6.00; N, 14.88.

***N*-{[5-(4-Methoxyphenyl)-1-vinyl-1*H*-pyrrol-2-yl]methylene}benzene-1,2-diamine (2g)**

Yield: 0.61 g (96%) from 0.45 g (2 mmol) of **1g**.

Orange crystals; mp 123–125 °C.

IR (KBr): 3476, 3377, 3013, 2894, 2800, 1643, 1621, 1588, 1575, 1555, 1513, 1484, 1471, 1451, 1438, 1401, 1398, 1344, 1331, 1320, 1303, 1288, 1259, 1227, 1200, 1155, 1129, 1091, 1047, 1037, 955, 888, 869, 853, 848, 818, 800, 773, 744, 716, 694, 649, 632, 572, 545, 524, 497, 465 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.44 (s, 1 H, CH=N), 7.36 (m, 4 H, Ar), 6.96 (dd, $^3J_{A-X}$ = 8.7 Hz, $^3J_{B-X}$ = 15.9 Hz, 1 H, H_X), 6.90 (d, $^3J_{o-m}$ = 8.64 Hz, 2 H, H_o), 6.75 (d, $^3J_{o-m}$ = 8.64 Hz, 2 H, H_m), 6.72 (d, $^3J_{3'-4'}$ = 3.9 Hz, 1 H, H-3′), 6.30 (d, $^3J_{3'-4'}$ = 3.9 Hz, 1 H, H-4′), 5.12 (d, $^3J_{A-X}$ = 8.7 Hz, 1 H, H_A), 4.92 (d, $^3J_{B-X}$ = 15.9 Hz, 1 H, H_B), 4.17 (br s, 2 H, NH_2), 3.82 (s, 3 H, OMe).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 157.1 (1 C, *C*OMe), 148.5 (1 C, C=N), 143.2, 142.4, 131.0 (4 C, Ar), 129.7 (1 C, C_α), 128.5 (1 C, C-5′), 125.1 (1 C, C-2′), 124.6, 124.3, 122.9, 120.8, 115.8, 114.5 (7 C, Ar), 105.7 (1 C, C_β), 104.2 (1 C, C-3′), 103.5 (1 C, C-4′), 56.0 (1 C, OCH_3).

Anal. Calcd for $C_{20}H_{19}N_3O$ (317.38): C, 75.69; H, 6.03; N, 13.24. Found: C, 75.65; H, 6.11; N, 13.68.

***N*-{[5-(Naphthalen-2-yl)-1-vinyl-1*H*-pyrrol-2-yl]methylene}benzene-1,2-diamine (2h)**

Yield: 0.64 g (95%) from 0.49 g (2 mmol) of **1h**.

Yellow crystals; mp 177–180 °C.

IR (KBr): 3460, 3365, 3101, 3050, 2860, 1643, 1616, 1595, 1571, 1497, 1482, 1453, 1440, 1417, 1383, 1369, 1350, 1327, 1321, 1304, 1290, 1271, 1263, 1248, 1216, 1195, 1186, 1154, 1131, 1048, 1036, 1014, 975, 962, 931, 896, 860, 841, 822, 791, 771, 746, 712, 694, 677, 640, 629, 599, 557, 481, 472, 427, 398 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.48 (s, 1 H, CH=N), 7.93 (s, 1 H, Ar), 7.83 (m, 4 H, Ar), 7.54 (m, 3 H, Ar), 7.50 (dd, $^3J_{A-X}$ = 8.6 Hz, $^3J_{B-X}$ = 15.7 Hz, 1 H, H_X), 7.10 (m, 1 H, Ar), 6.99 (d, $^3J_{3'-4'}$ = 4.1 Hz, 1 H, H-3′), 6.73 (m, 2 H, Ar), 6.47 (d, $^3J_{3'-4'}$ = 4.1 Hz, 1 H, H-4′), 5.13 (d, $^3J_{A-X}$ = 8.6 Hz, 1 H, H_A), 4.92 (d, $^3J_{B-X}$ = 15.7 Hz, 1 H, H_B), 4.18 (br s, 2 H, NH_2).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.9 (1 C, C=N), 143.3, 142.5, 139.4, 138.0, 135.0, 133.2, 131.1 (7 C, Ar), 129.9 (1 C, C_α), 129.2 (1 C, Ar), 128.0 (1 C, C-5′), 127.6, 126.7 (2 C, Ar), 125.4 (1 C, C-

2′), 124.5, 123.8, 122.8, 120.2, 119.9, 117.5 (6 C, Ar), 106.2 (1 C, C_β), 105.5 (1 C, C-4′), 104.7 (1 C, C-3′).

Anal. Calcd for $C_{23}H_{19}N_3$ (337.42): C, 81.87; H, 5.68; N, 12.45. Found: C, 81.21; H, 6.04; N, 12.88.

_N_-[(1-Vinyl-4,5-dihydro-1_H_-benzo[_g_]indol-2-yl)methylene]benzene-1,2-diamine (2i)
Yield: 0.61 g (97%) from 0.45 g (2 mmol) of **1i**.

Yellow crystals; mp 125–128 °C.

IR (KBr): 3480, 3379, 3022, 2924, 2857, 1640, 1615, 1597, 1575, 1566, 1503, 1495, 1478, 1459, 1447, 1410, 1389, 1355, 1331, 1317, 1305, 1292, 1266, 1218, 1193, 1155, 1132, 1086, 1054, 1034, 951, 893, 875, 856, 844, 818, 805, 761, 747, 718, 684, 647, 636, 587, 555, 521, 487, 466, 434 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.41 (s, 1 H, CH=N), 7.66 (m, 2 H, Ar), 7.47 (dd, $^3J_{A–X}$ = 8.3 Hz, $^3J_{B–X}$ = 15.7 Hz, 1 H, H_X), 7.18 (m, 1 H, Ar), 7.11 (m, 1 H, Ar), 7.06 (m, 2 H, Ar), 6.85 (s, 1 H, H-3′), 6.73 (m, 2 H, Ar), 5.40 (d, $^3J_{A–X}$ = 8.3 Hz, 1 H, H_A), 5.32 (d, $^3J_{B–X}$ = 15.7 Hz, 1 H, H_B), 4.19 (br s, 2 H, NH_2), 2.89 (t, $^3J_{4′–5′}$ = 7.2 Hz, 2 H, H-4′), 2.68 (t, $^3J_{4′–5′}$ = 7.2 Hz, 2 H, H-5′).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.8 (1 C, C=N), 143.1, 142.4, 136.0, 133.8, 131.0 (5 C, Ar), 130.1 (1 C, C_α), 127.5, 125.8 (2 C, Ar), 125.0 (1 C, Ar), 124.8, 124.2, 122.9, 121.8 (4 C, Ar), 121.4 (1 C, C-2′), 118.9 (1 C, C-3′), 115.8 (1 C, Ar), 105.7 (1 C, C_β), 103.2 (1 C, Ar), 30.5 (1 C, C-5′), 27.7 (1 C, C-4′).

Anal. Calcd for $C_{21}H_{19}N_3$ (313.40): C, 80.48; H, 6.11; N, 13.41. Found: C, 80.63; H, 6.09; N, 13.21.

2-(1_H_-Pyrrol-2-yl)-1_H_-benzimidazoles 3 from the Intermediate Schiff Bases 2; General Procedure
A mixture of a _N_-(1_H_-pyrrol-2-ylmethylene)benzene-1,2-diamine **2** (2 mmol) and TFA (1% with respect to the mass of **2**) in DMSO (2 mL) was stirred at 60–70 °C for 1 h. The reaction mixture was diluted with aq 1% $NaHCO_3$ soln (8 mL), extracted with Et_2O (5 × 5 mL) and the extracts were dried (K_2CO_3). The solvent was evaporated and the crude product was passed through a neutral alumina column (benzene) to give **3**.

2-(1-Vinyl-1_H_-pyrrol-2-yl)-1_H_-benzimidazoles 3 Directly from the 1-Vinyl-1_H_-pyrrole-2-carbaldehydes 1 Using Air Bubbling; General Procedure
A mixture of a 1-vinyl-1_H_-pyrrole-2-carbaldehyde **1** (2 mmol), _o_-phenylenediamine (0.22 g, 2 mmol) and TFA (1% with respect to the combined mass of both reagents) in DMSO (2 mL) was stirred at 70–80 °C for 1 h with continuous air bubbling. The reaction mixture was diluted with aq 1% $NaHCO_3$ soln (8 mL), extracted with Et_2O (5 × 5 mL) and the extracts were dried (K_2CO_3). The solvent was evaporated and the crude product was passed through a neutral alumina column (benzene) to give **3**.

2-(1_H_-Pyrrol-2-yl)-1_H_-benzimidazole (3a)
Yield: 0.30 g (83%) from 0.37 g (2 mmol) of **2a**.

Yellow crystals; mp 261–262 °C (MeOH) (Lit.[4b] 260–261 °C).

IR (KBr): 3410, 3063, 2921, 2851, 1627, 1602, 1516, 1454, 1394, 1271, 1226, 1169, 1127, 1035, 1009, 989, 925, 882, 797, 763, 741, 605, 582, 436 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 9.76 (br s, 2 H, NH), 7.48 (m, 2 H, Ar), 7.33 (d, $^3J_{3′–4′}$ = 3.8 Hz, 1 H, H-3′), 7.22 (m, 2 H, Ar), 6.80 (d, $^3J_{4′–5′}$ = 8.8 Hz, 1 H, H-5′), 6.58 (dd, $^3J_{3′–4′}$ = 3.8 Hz, $^3J_{4′–5′}$ = 8.8 Hz, 1 H, H-4′).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 145.1 (1 C, C-2), 136.6 (1 C, C-3a), 135.0 (1 C, C-7a), 119.6, 119.4 (2 C, Ar), 117.8 (1 C, C-5′), 114.7, 114.6 (2 C, Ar), 114.3 (1 C, C-2′), 108.5 (1 C, C-4′), 101.3 (1 C, C-3′).

Anal. Calcd for $C_{11}H_9N_3$ (183.21): C, 72.11; H, 4.95; N, 22.94. Found: C, 71.98; H, 5.02; N, 22.92.

2-(1-Vinyl-1_H_-pyrrol-2-yl)-1_H_-benzimidazole (3b)
Yield: 0.24 g (58%) from 0.42 g (2 mmol) of **2b**; yield: 0.26 g (61%) from 0.24 g (2 mmol) of **1b**.

Orange crystals; mp 75–78 °C.

IR (KBr): 3431, 3098, 2922, 2851, 2782, 1643, 1625, 1583, 1508, 1481, 1465, 1451, 1408, 1395, 1351, 1327, 1283, 1273, 1229, 1208, 1146, 1128, 1076, 1043, 1028, 1005, 981, 962, 873, 798, 764, 748, 717, 673, 615, 590, 581, 479, 438 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 9.18 (br s, 1 H, NH), 8.32 (dd, $^3J_{A–X}$ = 8.9 Hz, $^3J_{B–X}$ = 15.9 Hz, 1 H, H_X), 7.77 (m, 1 H, Ar), 7.40 (m, 1 H, Ar), 7.27 (m, 1 H, H-5′), 7.10 (m, 2 H, Ar), 6.67 (m, 1 H, H-4′), 6.31 (m, 1 H, H-3′), 5.24 (d, $^3J_{B–X}$ = 15.9 Hz, 1 H, H_B), 4.86 (d, $^3J_{A–X}$ = 8.9 Hz, 1 H, H_A).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 139.4 (1 C, C-3a), 137.7 (1 C, C-7a), 131.5 (1 C, C-2), 127.5 (1 C, C_α), 119.7, 119.6 (2 C, Ar), 115.7 (1 C, C-5′), 115.3, 115.2 (2 C, Ar), 111.8 (1 C, C-2′), 105.7 (1 C, C-3′), 102.7 (1 C, C-4′), 95.0 (1 C, C_β).

Anal. Calcd for $C_{13}H_{11}N_3$ (209.25): C, 74.62; H, 5.30; N, 20.08. Found: C, 74.52; H, 5.22; N, 20.31.

2-(1-Vinyl-4,5,6,7-tetrahydro-1_H_-indol-2-yl)-1_H_-benzimidazole (3d)
Yield: 0.22 g (41%) from 0.53 g (2 mmol) of **2d**; yield: 0.22 g (42%) from 0.35 g (2 mmol) of **1d**.

Orange crystals; mp 145–147 °C.

IR (KBr): 3441, 3059, 2928, 2850, 1641, 1619, 1597, 1563, 1497, 1477, 1457, 1438, 1421, 1389, 1368, 1326, 1288, 1238, 1214, 1155, 1129, 1105, 1058, 1006, 959, 946, 883, 868, 800, 741, 680, 633, 583, 551, 488, 464, 434 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.93 (br s, 1 H, NH), 7.77 (dd, $^3J_{A–X}$ = 9.1 Hz, $^3J_{B–X}$ = 15.9 Hz, 1 H, H_X), 7.33 (m, 1 H, Ar), 7.29 (m, 1 H, Ar), 7.15 (m, 2 H, Ar), 6.47 (s, 1 H, H-3′), 5.07 (d, $^3J_{B–X}$ = 15.9 Hz, 1 H, H_B), 5.01 (d, $^3J_{A–X}$ = 9.1 Hz, 1 H, H_A), 2.70 (m, 2 H, H-7′), 2.50 (m, 2 H, H-4′), 1.78 (m, 2 H, H-6′), 1.67 (m, 2 H, H-5′).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 139.6 (1 C, C-3a), 137.8 (1 C, C-7a), 133.8 (1 C, C-2), 130.1 (1 C, C_α), 120.4 (1 C, C-7a′), 119.6, 119.5, 115.3, 115.1 (4 C, Ar), 111.9 (1 C, C-3a′), 111.5 (1 C, C-2′), 104.7 (1 C, C_β), 97.3 (1 C, C-3′), 25.9, 24.9 (2 C, C-5′, C-6′), 22.4, 22.3 (2 C, C-4′, C-7′).

Anal. Calcd for $C_{17}H_{17}N_3$ (263.34): C, 77.54; H, 6.51; N, 15.96. Found: C, 77.21; H, 6.73; N, 15.68.

2-(5-Phenyl-1_H_-pyrrol-2-yl)-1_H_-benzimidazole (3e)
Yield: 0.40 g (77%) from 0.52 g (2 mmol) of **2e**.

Yellow crystals; mp 120–123 °C.

IR (KBr): 3407, 3053, 2922, 2851, 1628, 1606, 1544, 1496, 1477, 1458, 1446, 1414, 1388, 1356, 1319, 1294, 1267, 1241, 1224, 1155, 1066, 1046, 1015, 998, 934, 915, 904, 856, 840, 787, 754, 740, 680, 572, 552, 541, 501, 437 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 9.76 (br s, 2 H, NH), 7.50 (m, 5 H, Ar), 7.33 (m, 4 H, Ar), 6.80 (m, 1 H, H-3′), 6.58 (m, 1 H, H-4′).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 146.0 (1 C, C-2), 136.9 (1 C, C-3a), 134.7 (1 C, C-7a), 131.6 (1 C, Ar), 129.9 (1 C, C-5′), 129.3, 125.9, 125.0, 119.4, 119.3, 114.8, 114.4 (9 C, Ar), 113.8 (1 C, C-2′), 107.7 (1 C, C-3′), 101.8 (1 C, C-4′).

Anal. Calcd for $C_{17}H_{13}N_3$ (259.31): C, 78.74; H, 5.05; N, 16.20. Found: C, 78.41; H, 4.94; N, 16.32.

2-(5-Phenyl-1-vinyl-1*H*-pyrrol-2-yl)-1*H*-benzimidazole (3f)
Yield: 0.48 g (84%) from 0.57 g (2 mmol) of **2f**; yield: 0.51 g (89%) from 0.39 g (2 mmol) of **1f**.

Orange-red viscous oil.

IR (KBr): 3424, 3051, 2923, 2739, 2657, 1642, 1622, 1600, 1573, 1535, 1476, 1462, 1449, 1438, 1407, 1395, 1369, 1343, 1327, 1289, 1270, 1223, 1150, 1115, 1074, 1027, 1005, 962, 909, 885, 784, 758, 741, 694, 655, 617, 577, 514, 492, 439, 398 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 10.27 (br s, 1 H, NH), 7.70 (dd, $^3J_{A-X}$ = 8.6 Hz, $^3J_{B-X}$ = 15.8 Hz, 1 H, H_X), 7.39–7.32 (m, 5 H, Ar), 7.21 (m, 4 H, Ar), 6.80 (d, $^3J_{3'-4'}$ = 3.8 Hz, 1 H, H-3′), 6.29 (d, $^3J_{3'-4'}$ = 3.8 Hz, 1 H, H-4′), 4.93 (d, $^3J_{A-X}$ = 8.6 Hz, 1 H, H_A), 4.69 (d, $^3J_{B-X}$ = 15.8 Hz, 1 H, H_B).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 139.3 (1 C, C-3a), 137.3 (1 C, C-7a), 132.5 (1 C, C-2), 131.0, 130.5, 130.3 (3 C, Ar), 128.7 (1 C, C_α), 128.3, 127.9, 127.1 (3 C, Ar), 126.7 (1 C, C-5′), 119.6, 119.3, 115.3, 115.0 (4 C, Ar), 110.8 (1 C, C-2′), 106.2 (1 C, C_β), 98.7 (1 C, C-3′), 97.5 (1 C, C-4′).

Anal. Calcd for $C_{19}H_{15}N_3$ (285.35): C, 79.98; H, 5.30; N, 14.73. Found: C, 79.56; H, 5.11; N, 14.91.

2-[5-(4-Methoxyphenyl)-1-vinyl-1*H*-pyrrol-2-yl]-1*H*-benzimidazole (3g)
Yield: 0.52 g (82%) from 0.63 g (2 mmol) of **2g**; yield: 0.54 g (86%) from 0.45 g (2 mmol) of **1g**.

Orange crystals; mp 146–148 °C.

IR (KBr): 3428, 3116, 2922, 2851, 1643, 1623, 1606, 1571, 1543, 1505, 1444, 1402, 1334, 1299, 1272, 1218, 1198, 1180, 1035, 954, 892, 806, 755, 745, 678, 614, 580, 468 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 9.31 (br s, 1 H, NH), 7.75 (dd, $^3J_{A-X}$ = 8.6 Hz, $^3J_{B-X}$ = 15.8 Hz, 1 H, H_X), 7.34 (m, 5 H, Ar), 6.91 (m, 3 H, Ar), 6.76 (d, $^3J_{3'-4'}$ = 3.8 Hz, 1 H, H-3′), 6.28 (d, $^3J_{3'-4'}$ = 3.8 Hz, 1 H, H-4′), 4.99 (d, $^3J_{A-X}$ = 8.6 Hz, 1 H, H_A), 4.74 (d, $^3J_{B-X}$ = 15.8 Hz, 1 H, H_B), 3.58 (s, 3 H, OMe).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 155.5 (1 C, *C*OMe), 139.2 (1 C, C-3a), 137.7 (1 C, C-7a), 132.9 (1 C, C-2), 131.2 (2 C, Ar), 128.8 (1 C, C_α), 127.5 (1 C, C-5′), 125.4, 119.8, 119.6, 115.4, 114.9 (7 C, Ar), 110.9 (1 C, C-2′), 105.9 (1 C, C_β), 99.3 (1 C, C-3′), 96.9 (1 C, C-4′), 55.5 (1 C, OCH_3).

Anal. Calcd for $C_{20}H_{17}N_3O$ (315.37): C, 76.17; H, 5.43; N, 13.32. Found: C, 76.47; H, 5.33; N, 13.23.

2-[5-(Naphthalen-2-yl)-1-vinyl-1*H*-pyrrol-2-yl]-1*H*-benzimidazole (3h)
Yield: 0.42 g (62%) from 0.67 g (2 mmol) of **2h**; yield: 0.44 g (65%) from 0.49 g (2 mmol) of **1h**.

Orange crystals; mp 237–240 °C (dec).

IR (KBr): 3435, 3050, 2920, 2850, 1642, 1624, 1599, 1579, 1536, 1499, 1455, 1439, 1411, 1392, 1371, 1342, 1325, 1300, 1288, 1274, 1251, 1228, 1220, 1166, 1148, 1130, 1068, 1030, 1016, 1004, 978, 962, 914, 895, 880, 859, 836, 820, 800, 783, 765, 750, 740, 705, 677, 648, 610, 577, 475, 442, 427 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 9.13 (br s, 1 H, NH), 7.93 (s, 1 H, Ar), 7.84–7.82 (m, 5 H, Ar), 7.79 (dd, $^3J_{A-X}$ = 8.7 Hz, $^3J_{B-X}$ = 15.8 Hz, 1 H, H_X), 7.54 (m, 1 H, Ar), 7.49 (m, 2 H, Ar), 7.43 (m, 2 H, Ar), 6.82 (d, $^3J_{3'-4'}$ = 3.8 Hz, 1 H, H-3′), 6.45 (d, $^3J_{3'-4'}$ = 3.8 Hz, 1 H, H-4′), 5.01 (d, $^3J_{A-X}$ = 8.7 Hz, 1 H, H_A), 4.75 (d, $^3J_{B-X}$ = 15.8 Hz, 1 H, H_B).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 139.9 (1 C, C-7a), 138.3 (1 C, C-3a), 138.0, 135.5, 133.1 (3 C, Ar), 132.9 (1 C, C-2), 131.1, 130.7, 129.6 (3 C, Ar), 129.2 (1 C, C_α), 127.5 (1 C, C-5′), 127.2, 126.7, 123.7, 119.8, 119.7, 115.4, 113.1 (8 C, Ar), 111.0 (1 C, C-2′), 108.6 (1 C, C_β), 99.0 (1 C, C-4′), 97.7 (1 C, C-3′).

Anal. Calcd for $C_{23}H_{17}N_3$ (335.41): C, 82.36; H, 5.11; N, 12.53. Found: C, 82.18; H, 5.18; N, 11.68.

2-(1*H*-Benzimidazol-2-yl)-1-vinyl-4,5-dihydro-1*H*-benzo[*g*]indole (3i)
Yield: 0.44 g (71%) from 0.63 g (2 mmol) of **2i**; yield: 0.46 g (74%) from 0.45 g (2 mmol) of **1i**.

Yellow crystals; mp 149–151 °C.

IR (KBr): 3435, 3053, 3020, 2925, 1639, 1622, 1600, 1585, 1571, 1529, 1495, 1446, 1425, 1388, 1330, 1304, 1289, 1272, 1226, 1199, 1183, 1159, 1146, 1122, 1070, 1045, 1005, 966, 938, 905, 895, 807, 762, 747, 737, 706, 666, 645, 617, 584, 502, 469, 441 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 9.21 (br s, 1 H, NH), 7.90 (dd, $^3J_{A-X}$ = 8.5 Hz, $^3J_{B-X}$ = 15.6 Hz, 1 H, H_X), 7.77 (m, 1 H, Ar), 7.66 (m, 2 H, Ar), 7.40 (m, 1 H, Ar), 7.22 (m, 2 H, Ar), 7.16 (m, 1 H, Ar), 7.09 (m, 1 H, Ar), 6.64 (s, 1 H, H-3), 5.27 (d, $^3J_{A-X}$ = 8.5 Hz, 1 H, H_A), 5.23 (d, $^3J_{B-X}$ = 15.6 Hz, 1 H, H_B), 2.89 (t, $^3J_{4-5}$ = 7.3 Hz, 2 H, H-4), 2.65 (t, $^3J_{4-5}$ = 7.3 Hz, 2 H, H-5).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 139.1 (1 C, C-3a′), 138.0 (1 C, C-7a′), 135.9 (1 C, Ar), 133.4 (1 C, C-2′), 132.9, 130.9 (2 C, Ar), 129.1 (1 C, C_α), 126.8, 125.4, 124.1 (3 C, Ar), 121.0 (1 C, C-9b), 119.6, 119.5, 115.7, 115.4 (4 C, Ar), 112.2 (1 C, C-3a), 110.5 (1 C, C-2), 106.3 (1 C, C_β), 97.0 (1 C, C-3), 30.9 (1 C, C-5), 23.3 (1 C, C-4).

Anal. Calcd for $C_{21}H_{17}N_3$ (311.39): C, 81.00; H, 5.50; N, 13.49. Found: C, 79.97; H, 6.18; N, 13.75.

2-(5-Phenyl-1-vinyl-1*H*-pyrrol-2-yl)-1*H*-benzimidazole (3f) Directly from 5-Phenyl-1-vinyl-1*H*-pyrrole-2-carbaldehyde (1f) Using Azeotropic Distillation
A mixture of 5-phenyl-1-vinyl-1*H*-pyrrole-2-carbaldehyde (**1f**; 0.25 g, 1.3 mmol), *o*-phenylenediamine (0.15 g, 1.3 mmol), TFA (4 mg, 1% with respect to the combined mass of both reagents) and benzene (5 mL) in DMSO (5 mL) was stirred at 85–90 °C until the benzene was completely distilled off (about 45 min). The reaction mixture was diluted with aq 1% $NaHCO_3$ soln (8 mL), extracted with Et_2O (5 × 5 mL) and the extracts were dried (K_2CO_3). The solvent was evaporated and the crude product was passed through a neutral alumina column (benzene) to give **3f**; yield: 0.28 g (76%).

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