Synthesis of 3-[5-(biphenyl-4-yl)pyrrol-2-yl]-1-phenylprop-2-yn-1-ones by palladium-free cross-coupling between pyrroles and haloalkynes on aluminum oxide

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Cross-coupling of 2-(biphenyl-4-yl)pyrroles derived from 1-(biphenyl-4-yl)ethanone oximes and acetylene with 3-bromo-1-phenylprop-2-yn-1-one on aluminum oxide gave 3-[5-(biphenyl-4-yl)pyrrol-2-yl]-1-phenylprop-2-yn-1-ones in 35—46% yields.

Key words: (biphenyl-4-yl) ketoximes, acetylene, pyrroles, biaryls, bromoalkynes, alkynylation, active surface, aluminum oxide.

Pyrrole derivatives are widely used for the synthesis of analogs to natural compounds[1] and as pharmacophores[2—5] and building blocks in drug design.[6,7] Alkynylpyrroles can serve as versatile synthons for their preparation. At the same time, most of the known methods devised for alkynylation of the pyrrole ring, including the Sonogashira reaction (palladium-catalyzed cross-coupling of halopyrroles with terminal acetylenes[8]) involve preliminary functionalization of the pyrrole ring. Documented examples of direct alkynylation of pyrroles are very few: palladium-catalyzed cross-coupling of N-fused pyrroles with haloalkynes,[9] AuCl-catalyzed reactions of pyrroles with trialkylsilylethynylbenziodoxolones,[10] Ph_3PAuCl-catalyzed oxidative alkynylation of *N*-benzylpyrrole with methyl propiolate in the presence of $PhI(OAc)_2$,[11] and reactions of *N*-methoxycarbonylpyrrole with (halo)(trifluoroacetyl)alkynes.[12]

Recently, we have developed a novel method for introduction of an alkyne substituent into position 2 of the pyrrole ring[13—15] or into position 3 of the indole ring.[16] The method involves cross-coupling of nonfunctionalized pyrroles or indoles with electrophilic haloalkynes on the active surfaces of metal oxides and metal salts. The reaction can be conducted at room temperature, with no special conditions required (palladium, bases, solvents, or inert atmosphere). In addition, an important advantage is that this method allows the synthesis of alkynylpyrroles with electron-withdrawing substituents at the triple bond.

The compounds obtained can be useful as antineoplastics,[17] antibacterial agents,[18] and HIV-integrase inhibitors as well as can be used to treat immunodeficiency,[19] psoriasis, arthritis, and detrimental effects of chemotherapy.[20] At the same time, a number of natural and synthetic entities with high biological activity are based on functionalized arylpyrroles.[21—28]

In the present work, we propose a convenient approach to the synthesis of earlier unknown alkynylpyrroles **1a—d** containing aryl substituents in positions 2 and 3 of the pyrrole ring. The approach involves cross-coupling of 2-(biphenyl-4-yl)pyrroles **2a**,**b** and their N-vinyl derivatives **2c**,**d** with 3-bromo-1-phenylprop-2-yn-1-one on Al_2O_3 (Scheme 1). The reaction was carried out by periodically grinding the reactants with aluminum oxide (used in a tenfold excess with respect to the mixture of the reactants). The conversion of the starting materials was monitored and the ratio of the products was checked by ^1H NMR spectroscopy for samples withdrawn from the reaction mixture and dissolved in $CDCl_3$. The cross-coupling conditions were optimized by varying the reaction temperature and the composition of the active surface in the ethynylation of compound **2c** as an example. It turned out that when the reaction is carried out under standard conditions[13] (Al_2O_3, room temperature, an equimolar ratio of the reactants) for 1 h, the final reaction mixture contains the unreacted pyrrole **2c** and product **1c** in a ratio of 2 : 1. Addition of CuCl or CdO to aluminum oxide (10% of the weight of Al_2O_3) increases the yield of compound **1c**

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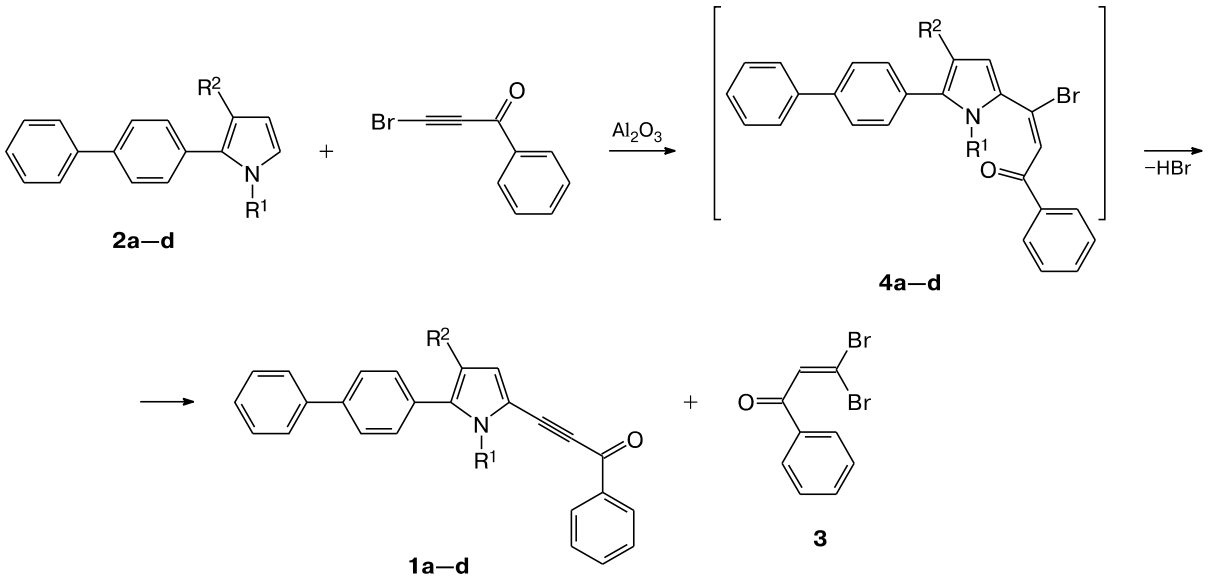
Scheme 1



1, **2**, **4**: R^1 = H, R^2 = H (**a**); R^1 = H, R^2 = Ph (**b**); R^1 = CH=CH_2, R^2 = H (**c**); R^1 = CH=CH_2, R^2 = Ph (**d**)

only slightly (by 5 and 7%, respectively). When the reaction temperature is raised to 50 °C and aluminum oxide is used, the fraction of product **1c** is twice as high as that achieved in the room-temperature synthesis. The same ratio of products **2c** and **1c** (1 : 1) at 50 °C is observed in the presence of CuCl or CdO.

Note that the final reaction mixtures contain large amounts of unreacted pyrrole **2c** but never 3-bromo-1-phenylprop-2-yn-1-one. Instead, its adduct with HBr (liberated upon the ethynylation) is detected. The spectral characteristics of this adduct 3,3-dibromo-1-phenylprop-2-en-1-one (**3**) (see Scheme 1) agree with the literature data.[29] For this reason, further we carried out cross-coupling at 50 °C using a twofold molar excess of a bromoalkyne. The content of the target products under these conditions was nearly doubled (**1a—d** : **2a—d** ≈ 2 : 1). The preparative yields of 2-alkynyl-1-vinylpyrroles **1c**,**d** were 46 and 43%, respectively; the yields of 1-unsubstituted 2-alkynylpyrroles **1a,b** were 35 and 36%, respectively.

Clearly, the alkynylation of pyrroles **2a—d** occurs by their nucleophilic addition to the activated triple bond of a bromoalkyne followed by HBr elimination from intermediates **4a—d**, which leads to alkynylpyrroles **1a—d** (see Scheme 1).

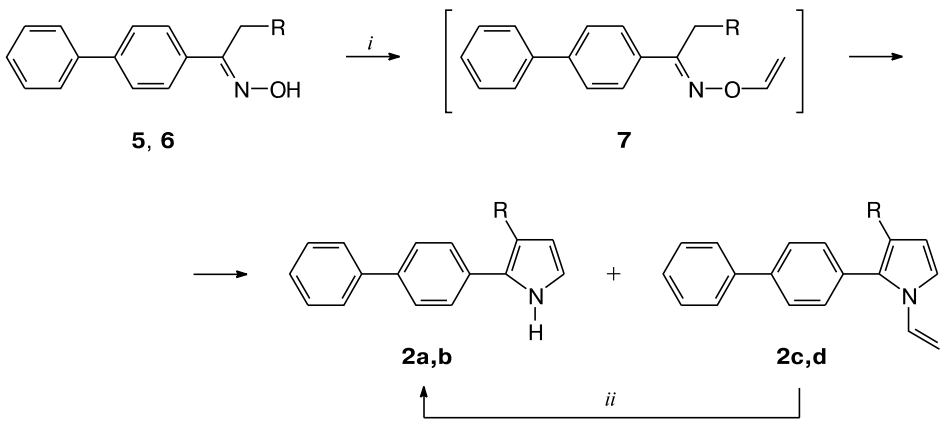
Intermediates **4a**,**b** stabilized by a strong intramolecular hydrogen bond involving the NH proton were detected in the reaction mixtures; adduct **4a** was isolated in the individual state.

The IR spectra of alkynylpyrroles **1a—d** show intense absorption bands at 2166—2176 (C≡C), 1623—1627 (C=O), and 3281—3284 (NH, **1a**,**b**) or 1642—1643 cm^{-1} (N—CH=CH_2, **1c**,**d**). Their ^{13}C NMR spectra contain characteristic signals for the pyrrole and benzene rings as well as signals at δ_C 177.5—177.3 (C=O) and 87.7—88.4 and 93.4—95.7 (C≡C). In the ^1H NMR spectra of alkynylpyrroles **1a—d**, the signals for the *ortho*-protons of the benzoyl fragment are shifted downfield (δ_H 8.17—8.18) and are distant from the signals for the *meta*- and *para*-protons of the benzene rings which are manifested as complicated multiplets at δ_H 7.18—7.65.

Compounds **2a—d** (including earlier unknown pyrroles **2b**,**d**) employed in the synthesis of alkynylpyrroles **1a—d** were prepared by the Trofimov reaction[30—33] from 1-(biphenyl-4-yl)ethanone oximes **5** and **6** and acetylene in the superbasic system MOH—DMSO (Scheme 2). It turned out that a reaction of ketoxime **5** with acetylene under the conditions of selective synthesis of 2-phenylpyrrole[34] (equimolar amount of KOH, DMSO—H_2O (10 vol.% of DMSO), 110 °C, 3 h) mainly gives 1-vinylpyrrole **2c** (**2c** : **2a** ≈ 4 : 1). Under these conditions, 2-(biphenyl-4-yl)-3-phenyl-1-vinylpyrrole (**2d**) is selectively obtained from ketoxime **6** and acetylene. When the reaction temperature is lowered to 90 °C, with the other conditions being unchanged, ketoxime **5** reacts with acetylene incompletely and the final reaction mixture contains unreacted oxime **5**, pyrrole **2a**, 1-vinylpyrrole **2c**, and the reaction intermediate *O*-vinyl oxime **7** in a ratio of 1 : 0.3 : 0.5 : 0.2 (see Scheme 2). In the system LiOH—DMSO, which selectively catalyzes construction of a pyrrole ring and is inactive in vinylation of 2-arylpyrroles,[35] the above reaction (100 °C, 3 h) also mainly affords 1-vinylpyrrole **2c** (**2c** : **2a** = 2.5 : 1).

Since the reactions of oximes **5** and **6** with acetylene are not selective, the target 1-unsubstituted pyrroles **2a**,**b**

Scheme 2



R = H (**2a**,**c**, **5**), Ph (**2b**,**d**, **6**)

Reagents and conditions: *i*. C_2H_2, MOH (M = Li, K), DMSO, Δ; *ii*. $Hg(OAc)_2$, MeCN, H_2O.

were synthesized by devinylation of 1-vinylpyrroles **2c**,**d** (see Scheme 2) in the presence of mercuric acetate (MeCN—H_2O (2 : 1), room temperature, 2 h, 55—60 °C, 15 min).[36] Compounds **2c**,**d** were selectively obtained from ketoximes **5** and **6** and acetylene under the following conditions: KOH—DMSO, 100 °C, 3 h.

To sum up, the cross-coupling of 2-(biphenyl-4-yl)pyrroles, which can easily be prepared by the Trofimov reaction of appropriate ketoximes with acetylene, with 3-bromo-1-phenylprop-2-yn-1-one on the active surface of aluminum oxide gave 3-[5-(biphenyl-4-yl)pyrrol-2-yl]-1-phenylprop-2-yn-1-ones. No special conditions (palladium, bases, solvents, or inert atmosphere) are required for the alkynylation to occur. The presence of reactive triple and double bonds in the compounds obtained makes them promising for further modification, specifically for use as drug precursors.

Experimental

IR spectra were recorded on a Bruker IFS-25 spectrometer (KBr pellets) in the 400—4000 cm^{-1} range. ^1H and ^{13}C NMR spectra were recorded on a Bruker DPX 400 instrument (400.13 and 100.6 MHz, respectively) in $CDCl_3$ or DMSO-d_6 with HMDS as the internal standard. For signal assignments and structural identification of the compounds obtained, 2D heteronuclear experiments (^1H—^{13}C HSQC and HMBC) were used. ^{15}N NMR spectra were recorded using a 2D ^1H—^{15}N HMBC procedure. Aluminum oxide (pH 9.5) was washed with distilled water and ethanol and dried to a constant weight.

Reactions of pyrroles 2a—d with 3-bromo-1-phenylprop-2-yn-1-one on aluminum oxide. Pyrrole **2a—d** (1 mmol) and a bromoalkyne (1 : 1 or 1 : 2) were thoroughly ground in a porcelain mortar with aluminum oxide (used in a tenfold excess with respect to the weight of the reactants) or with Al_2O_3—CuCl (10 : 1) or Al_2O_3—CdO (10 : 1) for 5 min. The temperature rose to 28—30 °C and the mixture turned bright yellow, with a gradual change to brown. The reaction mixture was kept at room temperature or at 50 °C for 1 h and then analyzed by ^1H NMR spectroscopy ($CDCl_3$). The ratio of the reaction products was determined from the integral intensity of the signals for the H(3) and H(4) protons (for pyrroles **1a—d**, **2a—d**, and **4**) and that of the signal for the =CH proton (for product **3**, δ 7.83).

3-[5-(Biphenyl-4-yl)pyrrol-2-yl]-1-phenylprop-2-yn-1-ones 1a—d (general procedure). Pyrrole **2a—d** (1 mmol) and 3-bromo-1-phenylprop-2-yn-1-one (2 mmol) were thoroughly ground in a porcelain mortar with aluminum oxide (used in a tenfold with respect to the weight of the reactants) for 5 min. The reaction mixture was transferred to a flask, heated on a water bath at 50 °C for 1 h, and chromatographed on Al_2O_3. The following fractions were collected: (1) a mixture of 3-bromo-1-phenylprop-2-yn-1-one and 3,3-dibromo-1-phenylprop-2-en-1-one (**3**) (with hexane as an eluent), (2) compound **4a** (for pyrrole **1a**, with hexane—diethyl ether (3 : 1) as an eluent), (3) unreacted pyrroles **2a—d** (with hexane—diethyl ether (1 : 1) as an eluent), and (4) the target products **1a—d** (with hexane—diethyl ether (1 : 3) as an eluent).

3-[5-(Biphenyl-4-yl)pyrrol-2-yl]-1-phenylprop-2-yn-1-one (1a). Yield 0.121 g (35%, or 44% for a 80% conversion of pyrrole **2a**), yellow needles, m.p. 210—212 °C. Found (%): C, 86.16; H, 4.78; N, 3.74. $C_{25}H_{17}NO$. Calculated (%): C, 86.43; H, 4.93; N, 4.03. ^1H NMR ($CDCl_3$), δ: 6.62 (m, 1 H, H(4)); 6.94 (m, 1 H, H(3)); 7.31 (m, 1 H, Ph); 7.44 (m, 2 H, Ph); 7.49 (m, 2 H, Ph); 7.61 (m, 5 H, Ph); 7.65 (m, 2 H, Ph); 8.18 (m, 2 H, H_o PhCO); 9.00 (br.s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 88.4, 93.5, 108.6, 111.1, 122.7, 125.1, 127.0, 127.7, 127.9, 128.7, 129.0, 129.4, 129.9, 133.9, 137.1, 137.2, 140.3, 140.9, 177.5. IR, ν/cm^{-1}: 3284 (NH), 2164 (C≡C), 1623 (CO).

3-[5-(Biphenyl-4-yl)-4-phenylpyrrol-2-yl]-1-phenylprop-2-yn-1-one (1b). Yield 0.152 g (36%, or 46% for a 79% conversion of pyrrole **2b**), bright yellow needles, m.p. 227—228 °C. Found (%): C, 87.64; H, 4.85; N, 3.52. $C_{31}H_{21}NO$. Calculated (%): C, 87.92; H, 5.00; N, 3.31. ^1H NMR ($CDCl_3$), δ: 7.02 (d, 1 H, H(3), J = 2.6 Hz); 7.36 (m, 6 H, Ph); 7.45 (m, 4 H, Ph); 7.51 (m, 2 H, Ph); 7.56 (m, 5 H, Ph); 8.18 (m, 2 H, H_o PhCO); 9.06 (br.s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 88.1, 93.4, 110.4, 122.6, 124.8, 126.8, 127.0, 127.6, 127.7, 128.0, 128.5, 128.6, 128.7, 129.0, 129.4, 130.5, 133.7, 134.0, 135.0, 137.1, 140.3, 141.0, 177.5. IR, ν/cm^{-1}: 3281 (NH), 2166 (C≡C), 1623 (CO).

3-[5-(Biphenyl-4-yl)-1-vinylpyrrol-2-yl]-1-phenylprop-2-yn-1-one (1c). Yield 0.171 g (46%, or 57% for a 80% conversion of pyrrole **2c**), light yellow transparent plates, m.p. 118—119 °C. Found (%): C, 87.21; H, 4.84; N, 3.83. $C_{27}H_{19}NO$. Calculated (%): C, 86.84; H, 5.13; N, 3.75. ^{1}H NMR ($CDCl_3$), δ: 5.29 (d, 1 H, $=CH_2$, J = 8.8 Hz); 5.71 (d, 1 H, $=CH_2$, J = 15.8 Hz); 6.39 (d, 1 H, H(4), J = 3.9 Hz); 6.94 (dd, 1 H, HC=, J = 8.8 Hz, J = 15.8 Hz); 7.02 (d, 1 H, H(3), J = 3.9 Hz); 7.36 (m, 1 H, Ph); 7.49 (m, 6 H, Ph); 7.62 (m, 5 H, Ph); 8.17 (m, 2 H, H_o PhCO). ^{13}C NMR, δ: 88.3, 95.7, 110.0, 111.7, 113.5, 123.7, 127.2, 127.5, 127.9, 128.8, 129.1, 129.5, 129.6, 130.6, 131.2, 133.9, 137.3, 139.1, 140.5, 141.3, 177.5. IR, ν/cm^{-1}: 2168 (C≡C), 1643 (C=C), 1625 (C=O).

3-[5-(Biphenyl-4-yl)-4-phenyl-1-vinylpyrrol-2-yl]-1-phenylprop-2-yn-1-one (1d). Yield 0.194 g (43%, or 52% for a 82% conversion of pyrrole **2d**), light yellow transparent plates, m.p. 138—139 °C. Found (%): C, 88.04; H, 5.05; N, 2.91. $C_{33}H_{23}NO$. Calculated (%): C, 88.17; H, 5.16; N, 3.12. ^{1}H NMR ($CDCl_3$), δ: 5.19 (d, 1 H, $=CH_2$, J = 8.8 Hz); 5.67 (d, 1 H, $=CH_2$, J = 15.8 Hz); 6.81 (dd, 1 H, HC=, J = 8.8 Hz, J = 15.8 Hz); 7.18 (m, 6 H, H(3), Ph); 7.36 (m, 3 H, Ph); 7.47 (m, 4 H, Ph); 7.62 (m, 5 H, Ph); 8.17 (m, 2 H, H_o PhCO). ^{13}C NMR ($CDCl_3$), δ: 87.7, 95.3, 109.0, 112.1, 123.1, 125.4, 126.5, 127.0, 127.2, 127.7, 128.2, 128.4, 128.6, 128.9, 129.3, 129.7, 130.7, 131.4, 134.3, 135.0, 137.1, 133.7, 140.1, 141.3, 177.3. IR, ν/cm^{-1}: 2169 (C≡C), 1642 (C=C), 1627 (CO).

(*E*)-3-[5-(Biphenyl-4-yl)pyrrol-2-yl]-3-bromo-1-phenylprop-2-en-1-one (4a). Yield 5%, red needles, m.p. 210—211 °C. Found (%): C, 69.87; H, 4.08; Br, 18.26; N, 3.44. $C_{25}H_{18}BrNO$. Calculated (%): C, 70.10; H, 4.24; Br, 18.65; N, 3.27. ^{1}H NMR ($CDCl_3$), δ: 6.80 (m, 1 H, H(4)); 7.13 (m, 1 H, H(3)); 7.35 (s, 1 H, HC=); 7.43 (m, 1 H, Ph); 7.45 (m, 4 H, Ph); 7.48 (m, 1 H, Ph); 7.56 (m, 2 H, Ph); 7.70 (m, 2 H, Ph); 7.85 (m, 2 H, Ph); 8.02 (m, 2 H, H_o PhCO); 14.58 (br.s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 110.1, 116.5, 124.4, 124.9, 126.6, 127.2, 127.4, 128.0, 128.3, 128.5, 129.7, 130.8, 132.2, 134.2, 138.0, 139.1, 140.0, 140.6, 187.3. IR, ν/cm^{-1}: 3448 (NH), 1623 (CO).

2-(Biphenyl-4-yl)-1-vinylpyrrole (2c). A 250-mL rotating steel autoclave was charged with 4-acetylbiphenyl oxime (5.25 g, 0.0248 mol), KOH (1.39 g, 0.0248 mol), and DMSO (120 mL). The reaction mixture was saturated with acetylene gas and heated at 100 °C for 3 h. On cooling to room temperature, the reaction mixture was discharged and diluted with water (1 : 3). The product was extracted with diethyl ether (5×100 mL). The extracts were combined, dried with K_2CO_3, and concentrated. The residue was passed through aluminum oxide on a Schott filter funnel with a sintered disk (hexane as an eluent). The yield of 1-vinylpyrrole **2c** in the individual state was 3.2 g (53%), white crystals, m.p. 126—127 °C (*cf.* Ref. 37: m.p. 120—122 °C). Found (%): C, 88.12; H, 6.38; N, 5.54. $C_{18}H_{15}N$. Calculated (%): C, 88.13; H, 6.16; N, 5.71. ^{1}H NMR ($CDCl_3$), δ: 4.82 (d, 1 H, $=CH_2$, J = 8.8 Hz); 5.30 (d, 1 H, $=CH_2$, J = 15.6 Hz); 6.42 (m, 2 H, H(3), H(4)); 7.07 (dd, 1 H, HC=, J = 15.6 Hz, J = 8.8 Hz); 7.24 (m, 1 H, H(5)); 7.45 (m, 1 H, Ph); 7.55 (m, 4 H, Ph); 7.73 (m, 4 H, Ph). ^{13}C NMR ($CDCl_3$), δ: 99.0, 110.1, 110.2, 118.6, 127.1, 127.2, 127.5, 128.9, 129.6, 131.5, 132.1, 134.0, 140.0, 140.7. IR, ν/cm^{-1}: 1640 (N—CH=CH_2).

2-(Biphenyl-4-yl)pyrrole (2a). A suspension of 1-vinylpyrrole **2c** (1.271 g, 0.00518 mol) and mercuric acetate (1.165 g, 0.00518 mol) in aqueous acetonitrile (2 : 1, 200 mL) was stirred at room temperature for 2 h and then heated at 55—60 °C for 15 min. On completion of the reaction, the reaction mixture was diluted with water (100 mL). The crystals that formed were filtered off, dried, and purified by flash chromatography (Al_2O_3, hexane—Et_2O (1 : 1)). The yield of compound **2a** was 0.500 g (44%), greenish crystals, m.p. 213—215 °C. Found (%): C, 87.38; H, 5.85; N, 6.23. $C_{16}H_{13}N$. Calculated (%): C, 87.64; H, 5.98; N, 6.39. ^{1}H NMR (DMSO-d_6), δ: 6.13 (m, 1 H, H(3)); 6.56 (m, 1 H, H(4)); 6.86 (m, 1 H, H(5)); 7.33 (m, 1 H, Ph); 7.45 (m, 2 H, Ph); 7.65 (m, 2 H, Ph); 7.68 (m, 2 H, Ph); 7.72 (m, 2 H, Ph); 11.40 (br.s, 1 H, NH). ^{13}C NMR (DMSO-d_6), δ: 106.0, 109.3, 119.7, 123.9, 126.3, 127.0, 127.3, 129.0, 130.8, 132.2, 136.9, 139.9. ^{15}N NMR (DMSO-d_6), δ: −228.4. IR, ν/cm^{-1}: 3433, 3395 (NH).

2-(Biphenyl-4-yl)-3-phenyl-1-vinylpyrrole (2d). A 250-mL rotating steel autoclave was charged with 1-(biphenyl-4-yl)-2-phenylethanone oxime (5.75 g, 0.020 mol), KOH (1.12 g, 0.02 mol), and DMSO (100 mL). The reaction mixture was saturated with acetylene gas and heated at 100 °C for 3 h. On cooling to room temperature, the reaction mixture was discharged and diluted with water (1 : 3). The product (almost pure compound **2d**, ^{1}H NMR data) was extracted with diethyl ether. The extract was concentrated and the residue was passed through aluminum oxide on a Schott filter funnel with a sintered disk (hexane as an eluent). The yield of 3-phenyl-1-vinylpyrrole **2d** in the individual state was 2.57 g (40%), white crystals, m.p. 113—114 °C. Found (%): C, 89.41; H, 5.78; N, 4.38. $C_{24}H_{19}N$. Calculated (%): C, 89.68; H, 5.96; N, 4.36. ^{1}H NMR ($CDCl_3$), δ: 4.63 (d, 1 H, $=CH_2$, J = 9.1 Hz); 5.15 (d, 1 H, $=CH_2$, J = 15.9 Hz); 6.51 (d, 1 H, H(4), J = 3.2 Hz); 6.76 (dd, 1 H, HC=, J = 15.9 Hz, J = 9.1 Hz); 7.08 (m, 1 H, Ph); 7.16 (m, 2 H, Ph); 7.17 (d, 1 H, H(5), J = 3.2 Hz); 7.20 (m, 2 H, Ph); 7.32 (m, 3 H, Ph); 7.42 (m, 2 H, Ph); 7.58 (m, 2 H, Ph); 7.61 (m, 2 H, Ph). ^{13}C NMR ($CDCl_3$), δ: 98.4, 110.8, 117.3, 124.2, 125.6, 127.1, 127.2, 127.6, 128.0, 128.3, 128.9, 129.6, 130.8, 131.7, 131.9, 136.0, 140.4, 140.5. ^{15}N NMR ($CDCl_3$), δ: −207.6. IR, ν/cm^{-1}: 1636 (N—CH=CH_2).

2-(Biphenyl-4-yl)-3-phenylpyrrole (2b). A suspension of *N*-vinylpyrrole **2d** (1.6 g, 0.005 mol) and mercuric acetate (1.12 g, 0.005 mol) in aqueous acetonitrile (2 : 1, 200 mL) was stirred at room temperature for 2 h and then heated at 55—60 °C for 15 min. On completion of the reaction, the reaction mixture was diluted with water (100 mL). The crystals that formed were filtered off, dried, and purified by flash chromatography (Al_2O_3, hexane—Et_2O (1 : 1)). The yield of compound **2b** was 0.89 g (62%), white crystals, m.p. 184—185 °C. Found (%): C, 89.12; H, 5.49; N, 4.51. $C_{22}H_{17}N$. Calculated (%): C, 89.46; H, 5.80; N, 4.74. ^{1}H NMR ($CDCl_3$), δ: 6.43 (dd, 1 H, H(4), J = 2.5 Hz, J = 2.8 Hz); 6.89 (dd, 1 H, H(5), J = 2.5 Hz, J = 2.8 Hz); 7.20 (m, 1 H, Ph); 7.27 (m, 2 H, Ph); 7.33 (m, 1 H, Ph); 7.41 (m, 6 H, Ph); 7.53 (m, 2 H, Ph); 7.59 (m, 2 H, Ph); 8.27 (br.s, 1 H, NH). ^{13}C NMR ($CDCl_3$), δ: 111.3, 118.3, 122.4, 125.8, 126.9, 127.3, 127.4, 127.8, 128.0, 128.4, 128.6, 128.9, 132.4, 136.7, 139.4, 140.6. IR, ν/cm^{-1}: 3409 (NH).

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