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Synthesis of 2-Benzoylethynylpyrroles by Cross Coupling of 2-Arylpyrroles with 1-Benzoyl-2-bromoacetylene over Aluminum Oxide

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Abstract—Cross coupling of 2-arylpyrrole with benzoylbromoacetylene over aluminum oxide at room temperature gave 45–94% of 2-(benzoylethynyl)-5-arylpyrroles. Intermediate 2-(2-benzoyl-1-bromoethenyl)-5-arylpyrroles were isolated in up to 19% yield. The reaction was accompanied by formation of less than 5% of adducts of the initial pyrroles with the cross-coupling products, 2-benzoyl-1,1-bis(5-arylpyrrol-2-yl)ethenes.

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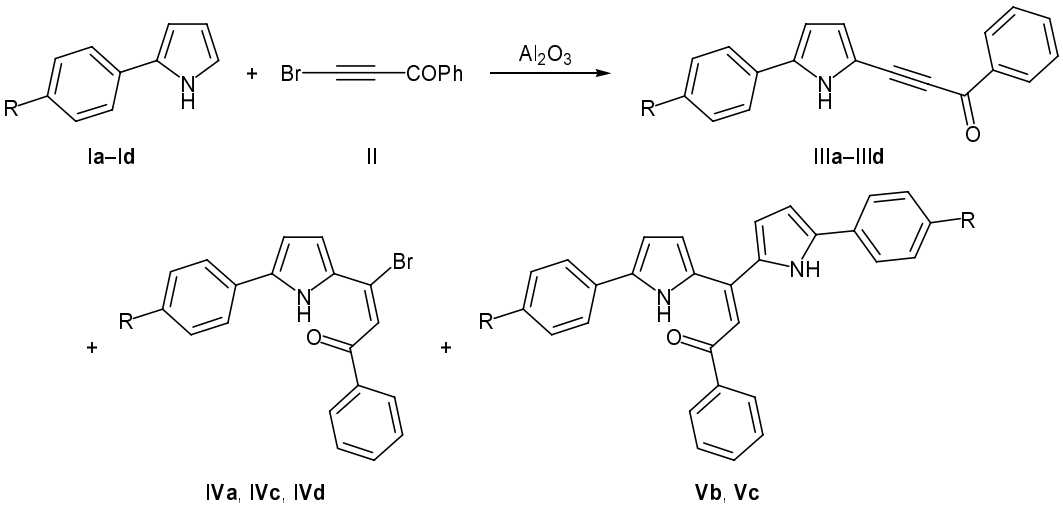
Design of new substances and materials with specified properties stimulates development of the chemistry of acetylene and its functional derivatives, including acetylenic ketones. The latter are widely spread in the nature [1] and are used in organic synthesis for the preparation of saturated polycyclic [2] and heterocyclic compounds [3]; in addition, they exhibit physiological activity [4]. Combination of acetylenic ketone and pyrrole fragments in a single molecule could give rise to synergistic effect and considerably extend the scope of application of polyfunctional pyrrole derivatives. However, the most widely used methods for the preparation of acetylenic ketones, in particular reactions of acetylenic nucleophiles with acyl chlorides in the presence of palladium or copper catalysts [5], are hardly applicable to the synthesis of acylethynylpyrroles because of inaccessibility of initial pyrrolylacetylenes. The Sonogashira reaction (cross coupling of haloarenes with acetylenes in the presence of palladium or copper compounds and a base [6]), which is widely used in the synthesis of arylacetylenes, has received limited application in the pyrrole series: only N-substituted halopyrroles or those containing electron-acceptor groups may be involved in this process; moreover, simple halopyrroles are characterized by low stability and low reactivity in the Sonogashira reaction [7].

We recently reported [8] on a new simple and efficient synthetic route to acylethynylpyrroles via cross coupling of acylbromoacetylenes with pyrroles having no halogen atoms. The reaction occurs over aluminum oxide surface at room temperature and requires no copper or palladium compound, base, and solvent. In the present work we performed a detailed study on the reaction of 2-arylpyrroles **Ia**–**Id** with 1-benzoyl-2-bromoacetylene (**II**) over aluminum oxide under mechanochemical activation with a view to obtain new information on this type of cross coupling, elucidate factors determining the product yield and ratio, and extend the series of accessible acylethynylpyrroles as promising compounds for fine organic synthesis and medicinal chemistry.

The reactions were carried out by intermittently grinding equimolar amounts of pyrrole **Ia**–**Id**, benzoylbromoacetylene **II**, and aluminum oxide (the latter was taken in a 10-fold excess with respect to the overall weight of the reactants) at room temperature over a period of 1 h. The yield of ethynylpyrroles **IIIa**–**IIId** was 45–94%. In addition, small amounts of compounds **IV** and **V** were formed (Scheme 1).

We previously presumed [8] that 2-(acylethynyl)pyrroles **III** are formed as a result of elimination of hydrogen bromide molecule from the primary pyrrole–acylbromoacetylene adducts, 2-(2-acyl-1-bromoethen-

Scheme 1.



Ia–Id **II** **IIIa–IIId**

IVa, IVc, IVd **Vb, Vc**

R = H (**a**), Me_2N (**b**), MeO (**c**), Cl (**d**).

Compound no.	Yield, %			
	a	**b**	**c**	**d**
III	69	45	62	94
IV	4	Traces	19	3
V	Traces	5	5	Traces

yl)pyrroles **IV**. To verify this assumption, the reactions of pyrroles **Ia**–**Id** with acetylene **II** were monitored by ^{1}H NMR spectroscopy (samples were withdrawn from the reaction mixtures at definite time intervals and dissolved in $CDCl_3$, and their ^{1}H NMR spectra were recorded). We have found that 2-arylpyrroles **Ia**, **Ic**, and **Id** react with compound **II** to give the corresponding 2-(benzoylethynyl)-5-arylpyrroles **IIIa**, **IIIc**, and **IIId** and 2-(2-benzoyl-1-bromoethenyl)-5-arylpyrroles **IVa**, **IVc**, and **IVd**, whose ratio changes only slightly with time (see table).

No 2-(2-benzoyl-1-bromoethenyl)-5-(4-dimethylaminophenyl)pyrrole (**IVb**) was detected in the reaction mixture obtained from pyrrole **Ib** and acetylene **II**: even after 10 min, the mixture contained only 2-(benzoylethynyl)-5-(4-dimethylaminophenyl)-1*H*-pyrrole (**IIIb**) and 2-benzoyl-1,1-bis[5-(4-dimethylaminophenyl)-1*H*-pyrrol-2-yl)ethene (**Vb**) together with the initial reactants.

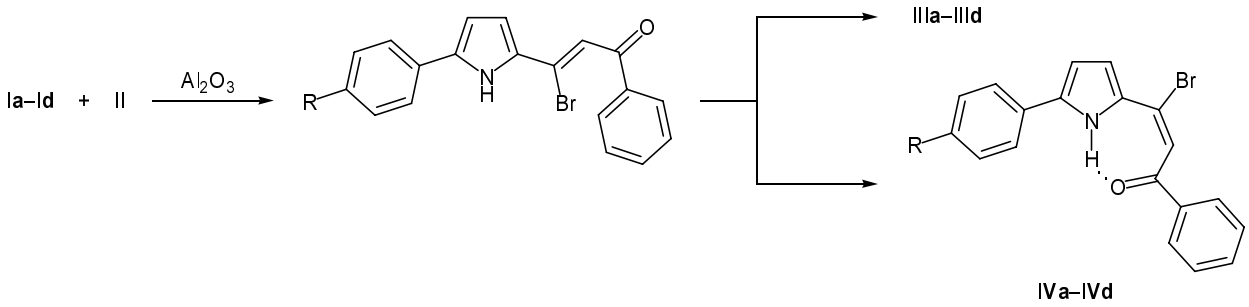
The fact that the product ratio does not change during the process may be rationalized as follows: pyrroles **Ia**–**Id** add to acetylene **II** according to the nucleophilic *trans*-addition pattern to give 2-[(*Z*)-2-benzoyl-1-bromoethenyl)pyrroles **IVa**–**IVd** (Scheme 2). The latter are transformed along two pathways: (1) elimination of hydrogen bromide leading to the formation of ethynylpyrroles **IIIa**–**IIId** and (2) isomerization to 2-[(*E*)-2-benzoyl-1-bromoethenyl)pyrroles stabilized by strong intramolecular hydrogen bond like that found previously in structurally related com-

Compositions[a] of the reaction mixtures (%) in the cross coupling of pyrroles **Ia**–**Id** with benzoylbromoacetylene **II** over Al_2O_3 at room temperature

Comp. no.	10 min				30 min				60 min			
	I	**III**	**IV**	**V**	**I**	**III**	**IV**	**V**	**I**	**III**	**IV**	**V**
Ia	Traces	75	25	Traces	Traces	74	26	Traces	Traces	78	22	3
Ib	39	51	Traces	10	36	64	Traces	Traces	21	70	Traces	9
Ic	27	53	17	3	21	59	19	Traces	11	64	22	3
Id	9	72	18	Traces	Traces	79	21	Traces	Traces	81	19	Traces

[a] The concentration of initial ketone **II** was the same as the concentration of initial pyrrole **I**.

Scheme 2.



pounds [9]. Since *cis*-elimination is slower than *trans*-elimination [10, 11], some amount of the *E* isomers of 2-(2-benzoyl-1-bromoethenyl)pyrroles is present in the reaction mixture.

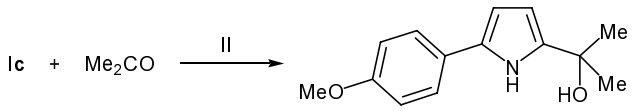
The formation of ethynylpyrroles **III** from 2-(2-benzoyl-1-bromoethenyl)pyrroles **IV** is supported by comparing the fractions of 2-(2-benzoyl-1-bromoethenyl)pyrroles **IV** in the crude product mixture with the yields of the isolated products. For example, pyrrole **Id** reacted with acetylene **II** in 1 h, yielding (according to the NMR data), 81% of ethynylpyrrole **IIId** and 19% of 2-(2-benzoyl-1-bromoethenyl)pyrrole **IVd**. Chromatographic separation of the product mixture on aluminum oxide gave 94% of **IIId** and 3% of **IVd**. Moreover, 2-(2-benzoyl-1-bromoethenyl)pyrrole **IVd** was found to undergo ready transformation into ethynylpyrrole **IIId** over aluminum oxide (conversion 92% in 1 h). These results indicate that bromoethenyl derivatives **IV** are by-products in the cross-coupling reaction. The *E* isomer of 2-(2-benzoyl-1-bromoethenyl)pyrrole **IVc** is more stable; we succeeded in converting compound **IVc** into ethynylpyrrole **IIIc** in 50% yield only by keeping for 24 h over aluminum oxide.

Apart from the major products, ethynylpyrroles **III** and intermediate 2-(2-benzoyl-1-bromoethenyl)pyrroles **IV**, in some cases the reaction mixtures contained small amounts of 2-benzoyl-1,1-dipyrrolylethenes **V**. Unlike ethynylpyrroles **III** whose concentration in the reaction mixture increased with time (at least during the first hour), the concentration of dipyrrolylethenes **V** remained almost unchanged.

^{1}H NMR monitoring of the reaction of pyrrole **Ib** with acetylene **II** over aluminum oxide (samples were withdrawn in 5, 30, and 60 min after mixing the reactants, and their ^{1}H NMR spectra were recorded both after withdrawal and after keeping for 5 h in chloroform) showed that the products undergo further transformations in solution. The signals of ethynylpyrrole **IIIb** disappeared almost completely, while the intensity of signals belonging to dipyrrolylethene **Vb** sharply increased so that the ratio **Ib**:**IIIb**:**Vb** became equal to 1:0.1:1. The presence of approximately equal amounts of compound **Vb** in samples of the reaction mixture, analyzed in 10–15 min after withdrawal, as well as among the products, may be due to its formation in solution (the isolation procedure also utilizes solvents). Therefore, 3–5% of dipyrrolylethene **Vb** was always isolated together with ethynylpyrrole **IIIb**. Pure ethynylpyrrole **IIIb** failed to react with compound **Ib** in chloroform: the ^{1}H NMR spectrum of an equimolar mixture of **IIIb** and **Ib** in chloroform, recorded in 24 h after mixing, contained only signals from the initial compounds.

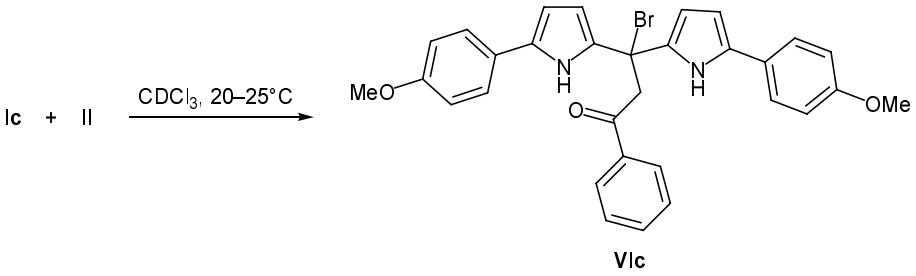
Presumably, the formation of dipyrrolylethene **Vb** from ethynylpyrrole **IIIb** and pyrrole **Ib** is catalyzed by traces of hydrogen bromide or benzoylbromoacetylene **II** present in the chloroform extract. The catalytic activity of bromoacetylene **II** (or hydrogen bromide liberated as a result of hydrolysis with traces of water) in nucleophilic addition of pyrroles to electron-deficient multiple bonds is confirmed as follows: when an equimolar mixture of pyrrole **Ic** and acetylene **II** in acetone was kept for 1 h in an NMR ampule, signals of the initial pyrrole disappeared from the spectrum, and new signals corresponding to 2-[5-(4-methoxyphenyl)-1*H*-pyrrol-2-yl]propan-2-ol appeared (Scheme 3).

Scheme 3.



In some cases, the ^{1}H NMR spectra of samples withdrawn from aluminum oxide in the initial stage (10 min) contained a couple of broadened signals at δ 5.6 and 12.1 ppm. We examined the reaction of pyrrole **Ic** with an equimolar amount of acetylene **II** in chloroform in an NMR ampule. After 10 min, signals

Scheme 4.

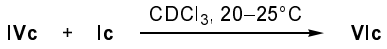


VIc

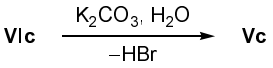
from initial pyrrole **Ic** disappeared completely, and broadened signals at δ 5.6 and 12.1 ppm emerged. According to the ^{1}H and ^{13}C NMR spectra, including two-dimensional homo- and heteronuclear correlation techniques, these signals belong to 2-benzoyl-1-bromo-1,1-bis(pyrrol-2-yl)ethane **VIc** (Scheme 4). The signal at δ 5.6 ppm was assigned to protons in the methylene group; the corresponding carbon atom gave a signal at δ_C 45.9 ppm (a triplet in the proton-coupled spectrum).

In the ESR spectrum of the reaction mixture obtained by dissolution of pyrrole **Ic** and acetylene **II** in $CHCl_3$ we observed a narrow (~0.65 mT) singlet with a *g* factor of 2.0026, indicating the presence of unpaired electrons at a concentration of 1.4×10^{17} spin/g. These data suggest that the process involves a single electron transfer stage (cf. [12]). Scheme 5 shows a probable mechanism of formation of dipyrrolylethane **VIc** on mixing pyrrole **Ic** with acetylene **II** without a solvent. The reaction includes formation of radical ion pair **A** which is converted into radical pair **B**. The ESR spectrum of the mixture contained a weak signal as an unresolved singlet with a width of about 0.9 mT and a *g* factor of 2.0031; the intensity of that signal increased twofold during 2 h and then remained unchanged for at least 24 h. The concentration of paramagnetic species attained $\sim1\times10^{17}$ spin/g. Presumably, the reaction of 2-(2-benzoyl-1-bromoethenyl)pyrrole **IVc** with initial pyrrole **Ic** also involves single electron transfer stage.

Dipyrrolylethane **VIc** was also formed in an NMR ampule ($CDCl_3$) from 2-(2-benzoyl-1-bromoethenyl)-pyrrole **IVc** and compound **Ic**.

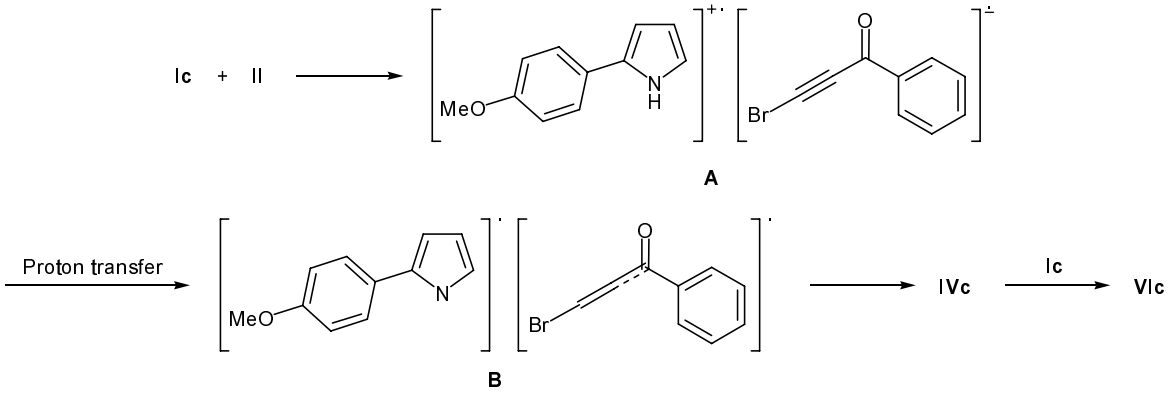


In carbon tetrachloride, the above reaction gives exclusively 2-(2-benzoyl-1-bromoethenyl)pyrrole **IVc**, the conversion of pyrrole **Ic** being 100% (according to the ^{1}H NMR data). Dipyrrolylethane **VIc** is stable in chloroform, but removal of the solvent leaves a dark blue powder with unknown structure. By treatment of a solution of dipyrrolylethane **VIc** in chloroform with aqueous potassium carbonate we isolated dipyrrolylethene **Vc**.



We also tried to effect cross coupling of pyrrole **Ic** with acetylene **II** over silica gel. In this case, the reaction at room temperature (1 h) gave 2-(2-benzoyl-1-bromoethenyl)pyrrole **IVc** as the major product, the conversion of pyrrole **Ic** was almost complete, and

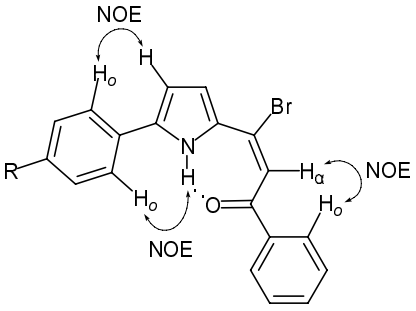
Scheme 5.



only traces of dipyrrolylethene **Vc** were detected by ^{1}H NMR spectroscopy. In the reaction of **II** with 2 equiv of **Ic**, dipyrrolylethane **VIc** was formed as the only product (NMR data).

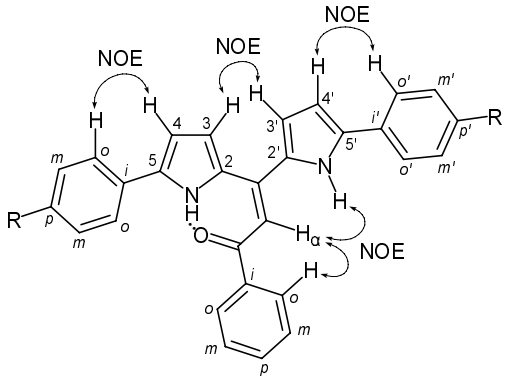
The IR spectra of ethynylpyrroles **IIIa**–**IIId** contained strong absorption bands typical of stretching vibrations of C≡C bond (2154–2170 cm^{-1}), carbonyl group (1613–1622 cm^{-1}), and N–H bond (3289–3332 cm^{-1}). Compounds **IIIa**–**IIId** displayed in the ^{13}C NMR spectra signals from the pyrrole and benzene rings, carbonyl carbon atom (δ_C 177.5–176.2 ppm), and carbon atoms at the triple bond (δ_C 89.5–90.2 and 92.5–94.3 ppm). In the ^{1}H NMR spectra of **IIIa**–**IIId**, as well as of **IVa**, **IVc**, **IVd**, **Vb**, and **Vc**, signals from the *ortho*-protons in the benzene ring were displaced downfield far from the signals belonging to the *meta*- and *para*-protons, the latter appearing as complex multiplets in the region δ 7.48–7.60 ppm. Protons in the benzene ring substituted at the *para*-position gave rise to two multiplets in the regions δ 6.74–7.41 and 7.40–7.80 ppm.

According to the ^{1}H NMR data, 2-(2-benzoyl-1-bromoethenyl)pyrroles **IVa**, **IVc**, and **IVd** are *Z* isomers with *s-cis* orientation of the carbonyl group with respect to the olefinic double bond. This conformation favors intramolecular hydrogen bonding between the NH proton and carbonyl oxygen atom. As a result, the NH proton signal is displaced strongly downfield (δ 14.58–14.63 ppm).



IVa, **IVc**, **IVd**

The NH group in one pyrrole ring of dipyrrolylethenes **Vb** and **Vc** is arranged *cis* with respect to the benzoyl group; as a result, strong intramolecular hydrogen bond N–H···O=C is formed, and the NH signal appears in the ^{1}H NMR spectrum in a weak field (δ 14.90–15.02 ppm). The other NH signal is located at δ 8.73–8.80 ppm. The spin systems of both pyrrole rings are reliably distinguished by the two-dimensional COSY spectra (cross peaks from the ring and NH protons). Signals from the ^{13}C nuclei were assigned using two-dimensional HSQC and HMBC techniques.



Vb, **Vc**

EXPERIMENTAL

The IR spectra (400–4000 cm^{-1}) were recorded in KBr on a Bruker IFS-25 spectrometer. The ^{1}H and ^{13}C NMR spectra were measured on Bruker DPX-250 (250.13 MHz for ^{1}H and 62.9 MHz for ^{13}C) and Bruker DPX-400 instruments (400.13 MHz for ^{1}H); $CDCl_3$ and DMSO-d_6 were used as solvents, and HMDS, as internal reference. Signals in the ^{1}H NMR spectra were assigned using two-dimensional homonuclear correlation techniques (COSY, NOESY) [13]. Signals from carbon nuclei were assigned on the basis of two-dimensional HSQC and HMBC spectra [14]. The HMBC spectra were recorded with pulse sequences optimized for direct ($^1J_{CH}$ = 160 Hz) and long-range couplings (J_{CH} = 15 Hz).

The reaction mixtures and products were analyzed by TLC on Silufol UV-254 plates using hexane–diethyl ether (1:1, 1:3) as eluent. Aluminum oxide (pH 9.5) was washed with distilled water and dried to a constant weight. Initial pyrroles were synthesized by the Trofimov reaction [15], and 2-benzoyl-1-bromoacetylene was prepared by bromination of benzoylacetylene as described in [16].

Reaction of 2-arylpyrroles Ia–Ic with benzoylbromoacetylene II (*general procedure*). A mixture of 2 mmol of pyrrole **Ia**–**Id**, 2 mmol of benzoylbromoacetylene, and a 10-fold amount of aluminum oxide was ground for 1 h at room temperature in a porcelain mortar. The mixture warmed up to 30°C and turned bright yellow; the color gradually changed to brown. The mixture was applied to a column charged with aluminum oxide, and the column was eluted first with hexane to isolate 2-(2-benzoyl-1-bromoethenyl)pyrroles **IVa**, **IVc**, and **IVd** and then with diethyl ether to isolate ethynylpyrroles **IIIa**–**IIId** and dipyrrolylethenes **Vb** and **Vc**.

The spectral parameters of compound **IIIa** were given in [8, 17], and of **IVa**, in [17].

2-(Benzoylethynyl)-5-(4-dimethylaminophenyl)-1*H*-pyrrole (IIIb). Orange–brown crystals. Yield 0.283 g (45%), mp 192°C. IR spectrum, ν, cm^{-1}: 1613 (C=O), 2154 (C≡C), 3325 (NH). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.02 s (6H, Me), 6.41 d.d (1H, 4-H, J = 3.9, 2.4 Hz), 6.74 m (2H, *m*-H, $Me_2NC_6H_4$), 6.92 d.d (1H, 3-H, J = 3.9, 2.4 Hz), 7.41 m (2H, *o*-H, $Me_2NC_6H_4$), 7.48 m (2H, *m*-H, COPh), 7.58 m (1H, *p*-H, COPh), 8.18 d (2H, *o*-H, COPh), 8.87 br.s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 40.4 (Me), 90.2 (C^{α}), 94.3 (C^{β}), 106.7 (C^4), 109.4 (C^2), 112.6 (C^m, $Me_2NC_6H_4$), 123.1 (C^3), 119.1 (C^i, $Me_2NC_6H_4$), 125.8 (C^o, $Me_2NC_6H_4$), 128.6 (C^m, COPh), 129.4 (C^o, COPh), 133.7 (C^p, COPh), 137.1 (C^i, COPh), 138.8 (C^5), 150.3 (C^p, $Me_2NC_6H_4$), 177.5 (C=O). Found, %: C 79.73; H 5.77; N 9.14. $C_{21}H_{18}N_2O$. Calculated, %: C 80.23; H 5.77; N 8.91.

2-(Benzoylethynyl)-5-(4-methoxyphenyl)-1*H*-pyrrole (IIIc). Yellow crystals. Yield 0.373 g (62%), mp 169–170°C. IR spectrum, ν, cm^{-1}: 1613 (C=O), 2162 (C≡C), 3332 (NH). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.84 s (3H, MeO), 6.47 d.d (1H, 4-H, J = 3.9, 2.4 Hz), 6.92 d.d (1H, 3-H, J = 3.9, 2.6 Hz), 6.95 m (2H, *m*-H, $MeOC_6H_4$), 7.46 m (2H, *o*-H, $MeOC_6H_4$), 7.51 m (2H, *m*-H, COPh), 7.60 m (1H, *p*-H, COPh), 8.18 m (2H, *o*-H, COPh), 8.93 br.s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 55.5 (MeO), 89.5 (C^{α}), 93.7 (C^{β}), 107.5 (C^4), 110.2 (C^2), 114.6 (C^m, $MeOC_6H_4$), 122.7 (C^3), 123.9 (C^i, $MeOC_6H_4$), 126.1 (C^o, $MeOC_6H_4$), 128.6 (C^m, COPh), 129.3 (C^o, COPh), 133.8 (C^p, COPh), 137.0 (C^i, COPh), 137.7 (C^5), 159.6 (C^p, $MeOC_6H_4$), 177.5 (C=O). Found, %: C 79.80; H 4.98; N 4.51. $C_{20}H_{15}NO_2$. Calculated, %: C 79.72; H 5.02; N 4.65.

2-(Benzoylethynyl)-5-(4-chlorophenyl)-1*H*-pyrrole (IIId). Yellow needles. Yield 0.575 g (94%), mp 188°C. IR spectrum, ν, cm^{-1}: 1622 (C=O), 2170 (C≡C), 3289 (NH). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 6.53 m (1H, 4-H), 6.88 m (1H, 3-H), 7.37 m (2H, *m*-H, ClC_6H_4), 7.48 m (4H, *m*-H, COPh, *o*-H, ClC_6H_4), 7.59 m (1H, *p*-H, COPh), 8.15 m (2H, *o*-H, COPh), 9.07 br.s (1H, NH). ^{13}C NMR spectrum (DMSO-d_6), δ_C, ppm: 89.6 (C^{α}) 92.5, (C^{β}) 109.1, (C^4), 110.3 (C^2), 122.9 (C^3), 126.5 (C^o, ClC_6H_4), 128.9 (C^o, COPh), 129.0 (C^m, COPh), 129.0 (C^m, ClC_6H_4), 129.9 (C^i, ClC_6H_4), 132.0 (C^p, ClC_6H_4), 134.3 (C^p, COPh), 136.3 (C^5), 136.4 (C^i, COPh), 176.2 (C=O). Found, %: C 74.51; H 3.96; Cl 11.92; N 4.58. $C_{19}H_{12}ClNO$. Calculated, %: C 74.64; H 3.96; Cl 11.59; N 4.58.

2-(2-Benzoyl-1-bromoethenyl)-5-(4-methoxyphenyl)-1*H*-pyrrole (IVc). Orange–red needles. Yield 0.145 g (19%), mp 138–139°C. IR spectrum, ν, cm^{-1}: 1623 (C=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.88 s (3H, MeO), 6.70 d.d (1H, 4-H, J = 3.9, 2.4 Hz), 7.02 m (2H, *m*-H, $MeOC_6H_4$), 7.13 d.d (1H, 3-H, J = 3.9, 2.0 Hz), 7.25 s (1H, α-H), 7.50 m (2H, *m*-H, COPh), 7.55 m (1H, *p*-H, COPh), 7.76 m (2H, *o*-H, $MeOC_6H_4$), 8.03 m (2H, *o*-H, COPh), 14.57 br.s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 55.5 (MeO), 109.9 (C^4), 114.7 (C^m, $MeOC_6H_4$), 116.0 (C^{α}), 124.0 (C^i, $MeOC_6H_4$), 125.1 (C^3), 126.5 (C^o, $MeOC_6H_4$), 128.4 (C^o, COPh), 128.7 (C^m, COPh), 130.7 (C^2), 132.5 (C^p, COPh), 134.6 (C^{β}), 139.1 (C^5), 139.6 (C^i, COPh), 159.9 (C^p, $MeOC_6H_4$), 187.5 (C=O). Found, %: C 62.71; H 4.50; Br 20.99; N 3.23. $C_{20}H_{16}BrNO_2$. Calculated, %: C 62.84; H 4.22; Br 20.90; N 3.66.

2-(2-Benzoyl-1-bromoethenyl)-5-(4-chlorophenyl)-1*H*-pyrrole (IVd). Yellow needles. Yield 0.023 g (3%), mp 119–120°C. IR spectrum, ν, cm^{-1}: 1624 (C=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 6.69 d.d (1H, 4-H, J = 4.1, 2.4 Hz), 7.06 d.d (1H, 3-H, J = 4.1, 2.2 Hz), 7.28 s (1H, α-H), 7.41 m (2H, *m*-H, ClC_6H_4), 7.48 m (2H, *m*-H, COPh), 7.54 m (1H, *p*-H, COPh), 7.69 m (1H, *o*-H, ClC_6H_4), 8.02 m (2H, *o*-H, COPh), 14.58 br.s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 110.6 (C^4), 117.2 (C^{α}), 124.8 (C^3), 126.2 (C^o, ClC_6H_4), 128.7 (C^o, COPh), 128.8 (C^m, COPh), 129.6 (C_m, ClC_6H_4), 130.0 (C^i, ClC_6H_4), 131.4 (C^2), 132.8 (C^p, COPh), 134.2 (C^{β}), 134.9 (C^p, ClC_6H_4), 137.4 (C^5), 139.4 (C^i, COPh), 187.6 (C=O). Found, %: C 59.15; H 3.11; Br 20.01; Cl 9.00; N 3.86. $C_{19}H_{13}BrClNO$. Calculated, %: C 59.02; H 3.39; Br 20.66; Cl 9.17; N 3.62.

2-Benzoyl-1,1-bis[5-(4-dimethylaminophenyl)-1*H*-pyrrol-2-yl]ethene (Vb). Dark violet crystals. Yield 0.05 g (5%), mp 257–258°C. IR spectrum, ν, cm^{-1}: 1612 (C=O), 3420 (NH). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.98 s (6H, NMe'$_2$), 3.02 s (6H, NMe_2), 6.48 d.d (1H, 4'-H, J = 3.2, 2.6 Hz), 6.66 d.d (1H, 4-H, J = 3.6, 2.3 Hz), 6.68 s (1H, α-H), 6.70 d (2H, *m*'-H, $Me_2NC_6H_4$, J = 8.7 Hz), 6.72 d.d (1H, 3'-H, J = 3.2, 2.8 Hz), 6.77 d (2H, *m*-H, $Me_2NC_6H_4$, J = 8.7 Hz), 6.96 d.d (1H, 3-H, J = 3.6, 2.0 Hz), 7.40 d (2H, *o*'-H, $Me_2NC_6H_4$, J = 8.7 Hz), 7.45 m (3H, *m*-H, *p*-H, COPh), 7.75 d (2H, *o*-H, $Me_2NC_6H_4$, J = 8.7 Hz), 8.02 m (2H, *o*-H, COPh), 8.73 br.s (1H, NH'), 15.02 br.s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C,

ppm: 40.5 (NMe_2), 40.6 (NMe_2), 106.4 ($C^{4'}$), 108.5 (C^{α}), 108.9 (C^4), 112.7 (C^m, $Me_2NC_6H_4$), 112.8 ($C^{m'}$, $Me_2NC_6H_4$), 114.9 ($C^{3'}$), 119.9 (C^i, $Me_2NC_6H_4$), 120.4 ($C^{i'}$, $Me_2NC_6H_4$), 121.6 (C^3), 125.5 ($C^{o'}$, $Me_2NC_6H_4$), 126.2 (C^o, $Me_2NC_6H_4$), 128.0 (C^o, COPh), 128.5 (C^m, COPh), 130.5 (C^2), 131.3 (C^p, COPh), 133.0 ($C^{2'}$), 136.0 ($C^{5'}$), 138.9 (C^5), 140.0 (C^{β}), 142.0 (C^i, COPh), 149.8 ($C^{p'}$, $Me_2NC_6H_4$), 150.3 (C^p, $Me_2NC_6H_4$), 188.3 (C=O). Found, %: C 79.41; H 6.66; N 10.80. $C_{33}H_{32}N_4O$. Calculated, %: C 79.17; H 6.44; N 11.19.

2-Benzoyl-1,1-bis[5-(4-methoxyphenyl)-1*H*-pyrrol-2-yl]ethene (Vc). Dark cherry crystals. Yield 0.047 g (5%), mp 208–209°C. IR spectrum, ν, cm^{-1}: 1606 (C=O), 3441 (NH). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.83 s (3H, MeO'), 3.86 s (3H, MeO), 6.58 d.d (1H, 4'-H, *J* 3.7, 2.7 Hz), 6.74 d.d (1H, 4-H, *J* = 4.1, 2.6 Hz), 6.80 s (1H, α-H), 6.82 d.d (1H, 3'-H, *J* = 3.7, 2.6 Hz), 6.97 d.d (1H, 3-H, *J* = 4.1, 2.1 Hz), 7.05 d (2H, *m*'-H, $MeOC_6H_4$), 7.15 d (2H, *m*-H, $MeOC_6H_4$), 7.46 m (3H, *m*-H, *p*-H, COPh), 7.50 d (2H, *o*'-H, $MeOC_6H_4$), 7.80 m (2H, *o*-H, $MeOC_6H_4$), 8.05 m (2H, *o*-H, COPh), 8.80 br.s (1H, NH'), 14.90 br.s (1H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 55.5 (MeO), 107.2 ($C^{4'}$), 109.2 (C^4), 109.7 (C^{α}), 114.6 ($C^{m'}$, $MeOC_6H_4$), 114.6 (C^m, $MeOC_6H_4$), 114.8 ($C^{3'}$), 121.2 (C^3), 124.5 (C^i, $MeOC_6H_4$), 124.8 ($C^{i'}$, $MeOC_6H_4$), 125.7 ($C^{o'}$, $MeOC_6H_4$), 126.3 (C^o, $MeOC_6H_4$), 128.1 (C^o, COPh), 128.5 (C^m, COPh), 130.7 (C^2), 131.7 (C^p, COPh), 133.7 ($C^{2'}$), 135.2 ($C^{5'}$), 137.7 (C^5), 140.2 (C^{β}), 141.5 (C^i, COPh), 159.0 ($C^{p'}$, $MeOC_6H_4$), 159.5 (C^p, $MeOC_6H_4$), 188.9 (C=O). Found, %: C 77.97; H 5.79; N 5.44. $C_{31}H_{26}N_2O_3$. Calculated, %: C 78.46; H 5.52; N 5.90.

2-Benzoyl-1-bromo-1,1-bis[5-(4-methoxyphenyl)-1*H*-pyrrol-2-yl]ethane (VIc). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 3.76 s (6H, MeO), 5.56 br.s (2H, CH_2), 6.78 br.s (2H, 4-H), 6.82 m (4H, *o*-H, MeO-C_6H_4), 7.17 br.s (2H, 3-H), 7.29 m (2H, *m*-H, COPh), 7.44 m (1H, *p*-H, COPh), 7.98 m (4H, *m*-H, MeO-C_6H_4), 8.15 m (2H, *o*-H, COPh), 12.08 br.s (2H, NH). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 45.9 (CH_2), 55.5 (MeO), 114.6 (C^m, $MeOC_6H_4$), 116.3 (C^4), 121.0 (C^i, $MeOC_6H_4$), 128.7 (C^m, COPh), 129.6 (C^o, COPh), 130.0 (C^o, $MeOC_6H_4$), 132.1 (C^3), 133.9 (C^p, COPh), 135.8 (C^i, COPh), 136.1 (C^2), 139.3 (C^{β}), 152.7 (C^5), 162.1 (C^p, $MeOC_6H_4$), 196.1 (C=O).

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