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Expedient one-step synthesis of nitrogen stilbene analogs by transition metal-free hydroamination of arylacetylenes with pyrroles

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ABSTRACT

A novel family of nitrogen stilbene analogs, 1-styrylpyrroles, has been synthesized in good to excellent yields by a straightforward facile transition metal-free addition of pyrroles to arylacetylenes in the KOH/DMSO system (90–120 °C, 5–13 h). Thermodynamically controlled *E*/*Z*-isomer ratio of 1-styrylpyrroles depends on structure of both pyrroles and acetylenes ranging from ca. 100% *E*-stereoselectivity (for the pair unsubstituted pyrrole—phenylacetylene) to 90, 96% *Z*-stereoselectivity (for the pairs: 2-phenylpyrrole—phenylacetylene and 2-(2-thienyl)pyrrole—phenylacetylene, respectively).

1. Introduction

Diverse stilbene derivatives are abundant in nature (plant antioxidants, e.g., resveratrol[1] and pterostilbene[2]) and widely used in medicine. Owing to the ability of stilbenes to reversible *E*/*Z*-isomerization, they belong to 'intellectual' molecules and can be applied for the information recording and storage,[3] also for construction of the molecular muscle fiber mimic.[4] As fluorescence labels with unique photochrome properties, substituted stilbenes gain a growing interest particularly for the investigation of dynamical processes in biological membranes.[5] They are also employed for detection of Hg^{2+} at micromolar concentrations.[6] Heteroaromatic analogs of stilbenes, according to the quantum chemical calculations, possess a superior potential of nonlinear-optical materials compared to the parent aromatic compounds.[7]

To the best of our knowledge, no general methods for the synthesis of pyrrole analogs of stilbenes were reported in the literature. Some of their representatives have been prepared by either transition metal catalyzed reactions or multi-step procedures. For instance, *E*-1-styrylpyrrole (with 30% admixture of α-regioisomer) was synthesized by palladium-catalyzed Heck arylation of 1-vinylpyrrole with iodobenzene,[8] and also by copper-catalyzed cross-coupling of pyrrole with styrylbromide (CuI, tetradentate ligand, Cs_2CO_3).[9] Vinylation of pyrrole, indole, carbazole and their derivatives with styrylbromide by palladium-phosphine complexes resulted in the stilbene analogs in 30–99% yields.[10] Isolation of *E*-1-styrylpyrrole from the products of 5-methyl-1*H*-pyrrolo[1,2-*c*]thiazole-2,2-dioxide thermolysis (230 °C) was mentioned.[11] Unexpectedly, three functionalized 1-styrylpyrroles were isolated (9–42% yields) from the products mixture of the reaction of substituted 7-methyl-3-cyanoindolizine and dimethyl acetylenedicarboxylate.[12] 1-[(*Z*)-2-Styryl]-3-phenyl-4,5,6,7-tetrahydroindole was formed in 14% yield when cyclohexanone oxime was treated with phenylacetylene in the KOH/DMSO system at 80 °C.[13] A remote analog of 1-styrylpyrrole, *E*-9-styrylcarbazole, was a product of the reaction of 9-[2-(triethoxysilyl)ethenyl]-9*H*-carbazole with iodobenzene in the presence of $Pd_2(dba)_3$.[14] The same stilbenoid was also obtained by multi-step syntheses[15] where a general step was alkylation of carbazole with chloromethylthiobenzene followed by treatment of the intermediate with *m*-chloroperbenzoic acid, $NaIO_4$, acetyl chloride, and *n*-BuLi. 1-Styrylpyrrole(indole)-2-carboxylic acids were prepared by the reaction between potassium salts of 2-pyrrole(indole)carboxylic acids and phenyloxirane in the presence of NaH (DMF, 110–120 °C).[16]

All the above publications are limited in number and deal with the protocols, which are neither general nor atom-economic often

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using hardly accessible starting materials. A general and straightforward method for the synthesis of nitrogen stilbene analogs might be based on the addition of pyrroles to aryl(hetaryl)acetylenes. Such an assumption follows from the known easy nucleophilic addition of aryl(hetaryl)pyrroles to acetylene in the superbasic KOH/DMSO system.[17] In the same system, the isopropynylation of pyrroles, indoles, di- and triazoles with propyne/allyne mixtures was successfully accomplished.[18]

A straightforward general route to pyrrole analogs of stilbenes could be a hydroamination of arylacetylenes with pyrroles. Currently, for the reactions of such type, transition metal catalysis is successfully applied.[19] However, in some cases, more general fundamental and closer to nature acid-based catalysis (e.g., organic catalysis) could also demonstrate certain advantages, particularly from the simplicity, safety and ecological points. Indeed, during the past decades, catalysis by superbases has occupied a solid position in the acetylene chemistry.[20]

In this line, the formation of *Z*-1-styrylindole and *Z*-9-styrylcarbazole (in 80 and 97% yields, respectively) from the corresponding heterocycles and phenylacetylene in the superbasic KOH/DMSO system (50–75 mol % KOH, 100–110 °C, 2.5–7.5 h) was described.[21] Later, *Z*-1-styrylpyrrole and -indole were synthesized (in 79 and 65% yields) by the same reaction (20 mol % $CsOH \cdot H_2O$, NMP, 90–120 °C, 12–24 h).[22] Most recently, similar results were published for the addition of azoles to diverse substituted acetylenes (KOH/DMSO, 120 °C), but with pyrrole, only one analog of stilbene was reported.[23] Thus, until now the question whether the above approach is general and efficient for the pyrrole series remains pending. Therefore we have thoroughly investigated the transition metal-free superbase catalyzed nucleophilic addition of substituted pyrroles **1a**–**f** to arylacetylenes **2a**–**e** and ethynylpyridine **2f** under the action KOH/DMSO system.

2. Results and discussion

The experiments have shown that reaction proceeds readily at 90–120 °C and the ratio **1**/**2**/KOH=1:1–2:0.1–1 to afford regiospecifically substituted 1-styrylpyrroles **3a**–**p** in a yield up to 94% (Table 1).

As seen from Table 1, the reaction tolerates a wide range of substituents (comprising electron-donating and electron-withdrawing groups) both in the pyrrole ring and acetylene, thus demonstrating a general character of the synthesis. Expectedly, the yield of adduct depends on the reaction conditions and the structure of reactants (Table 2), though not always significantly.

In the case unsubstituted pyrrole **1a** and phenylacetylene **2a**, the adduct yield just slightly responses to the changing of the reaction conditions: 81–86% for the 90–120 °C temperature, 20–100 mol % of KOH. The same is true for the reaction between 4,5,6,7-tetrahydroindole **1c** and acetylene **2a**: the yields are 93 and 89% for 90 and 120 °C, respectively.

Much more sensitive toward the reaction conditions was the yield of 1-styryl-2-phenylpyrrole **3l**, the adduct of 2-phenylpyrrole (**1d**) to phenylacetylene (**2a**), which spanned 18–68% interval (Table 2), at a higher concentration of KOH, the adduct yield being increased. A higher temperature (120 °C) led to the yield drop (34%) accompanied by the pyrrole conversion decrease due to phenylacetylene oligomerization (the dimer, 1,4-diphenyl-1-buten-3-yne, was detectable in the crude product).

A similar behavior (including oligomerization of phenylacetylene) was observed for the addition of 2-(2-thienyl)pyrrole (**1e**) to phenylacetylene (**2a**) (Table 2).

The yield–structure relationship is in agreement with the reaction mechanism, which essentially represents the classic nucleophilic addition to the carbon–carbon triple bond (Table 1). Indeed, electron-donating substituents in the pyrrole ring and electron-withdrawing substituents in the acetylene facilitate the reaction and otherwise (Table 1): actually the best yields were attained for the adducts **3h**, **3j** (4,5,6,7-tetrahydroindole **1c** to phenylacetylene **2a** and 3-fluorophenylacetylene **2d**).

The *E*/*Z*-isomer ratio of the adducts is controlled by the reaction conditions as expected from the reaction mechanism. In fact, as one can deduce from Table 2, the adducts initially formed as the *Z*-isomers (kinetic control, according to the classic trans-nucleophilic addition rule).[24] Then the *Z*-isomers undergo *Z*→*E*-isomerization until reaching the equilibrium state, i.e., the reaction stereochemistry is thermodynamically controlled. As seen from Table 1, the reaction is highly *E*-stereoselective (92–100% for the adducts **3a**, **3d**–**f**) and *Z*-stereoselective (85–100% for the adducts **3b**, **3i**, **3l**–**m**, **3o**).

The NMR monitoring of the addition of pyrrole **1a** to acetylene **2a** (KOH/DMSO-d_6, 90 °C) has shown that after 10 min the *E*/*Z* ratio is 1:9, which gradually changes with further heating in favor of the *E*-isomer to reach a 1:1 ratio after 4 h. This is the evidence that *Z*-isomer **3a** is kinetically controlled. The NMR monitoring has revealed a rapid H/D exchange between DMSO-d_6, pyrrole, and phenylacetylene: after mixing of the reactants in KOH/DMSO-d_6 suspension, in the NMR tube, the signals of NH–, acetylenic protons, and olefinic protons of adduct **3a** are not observed, the *E*/*Z* ratio being evaluated via the relative intensity of the pyrrole protons of *E*- and *Z*-isomers. These results indicate the following equilibriums to be realized (Scheme 1):

Our ab initio calculations (Table 3) of the free energy differences between *E*- and *Z*-isomers of 1-styrylpyrroles are in a good agreement with the experimental *E*/*Z* ratios of pyrrole-, 2-methylpyrrole-, and 4,5,6,7-tetrahydroindole-derived 1-styrylpyrroles (Table 1).

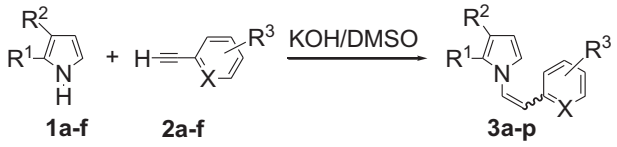
A peculiar feature for the *Z*-configurations of all the adducts is a substantially distorted coplanarity of the double bond: the N1–C2–C3–C4 dihedral angle is 7.2° in **3a**, 4.8° in **3g**, and 6.6° in **3h** (Fig. 1).

A close correspondence of the experimental *E*/*Z*-isomer ratios with the equilibrium values were confirmed by special experiments. So, pure *Z*-isomers of adducts **3h** and **3l** were heated (125–130 °C) in DMSO for 7 and 15 h to give 30:70 and 16:84 *E*/*Z* mixtures of isomers, respectively, thus fitting satisfactorily to the values observed for the corresponding addition reactions (25:75 and 10:90, Table 1). The more stable pure isomers *E*-**3a**, *Z*-**3h**, and *Z*-**3l** in benzene-d_6 upon UV irradiation (Hg-lamp) were considerably enriched by less stable isomers: by 75, 35, and 40%, respectively.

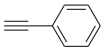
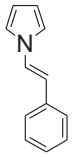
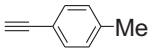
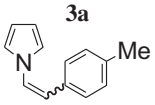
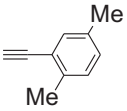
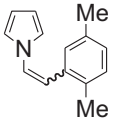
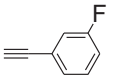
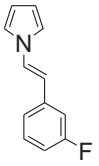
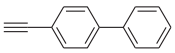
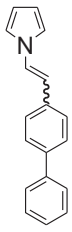
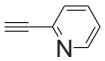
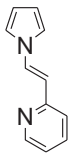
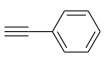
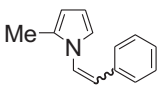
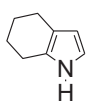
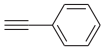
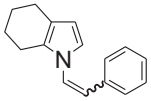
1-Styrylpyrroles *E*-**3a**, *E*-**3f**, and *Z*-**3a** are heterocyclic analogs of *trans*- and *cis*-stilbene and have similar intensities and locations of the long-wave absorption and fluorescence bands ($\lambda_{max,abs}$=295 nm, ε_{max}=28,500 $M^{-1}\,cm^{-1}$, $\lambda_{max,fl}$=350 nm and $\lambda_{max,abs}$=276 nm, ε_{max}=11,200 $M^{-1}\,cm^{-1}$, $\lambda_{max,fl}$=440 nm for *E*- and *Z*-stilbene, respectively) (Table 4). The substitution of the benzene cycle by the pyrrole ring (*E*-**3a** and *Z*-**3a**) or two benzene cycles by the pyrrole and pyridine moieties (*E*-**3f**) effects mainly the Φ_f values, which for isomers *E*-**3a** (Φ_f=0.003) and *E*-**3f** (Φ_f=0.001) are significantly lower than those for *E*-stilbene (Φ_f=0.023),[25] while the fluorescence of isomer *Z*-**3a** has not been registered [Φ_f of (*Z*-stilbene) ~ 10^{-4}].[26] Like stilbene, *E*- and *Z*-isomers of 1-styrylpyrroles under the action of UV light are transformed into the corresponding *Z*- and *E*-forms.

In the presence of air (oxygen) in the solution, the photoisomerization *Z*-**3a**→*E*-**3a** competes with the formation of photocyclization product, pyrrolo[2,1-*a*]isoquinoline. The latter are identified in small amounts by intense fluorescence (which increases in the course of irradiation) with typical for plain indolizines structured spectrum.[28]

Table 1
Synthesis of substituted 1-styrylpyrroles from pyrroles and arylacetylenes

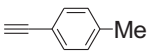
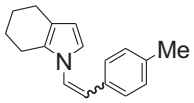
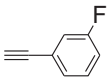
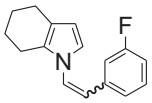
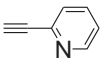
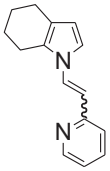
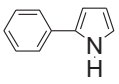
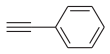
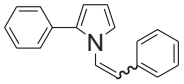
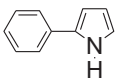
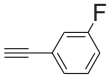
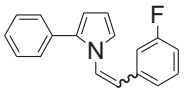
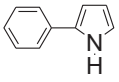
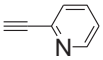
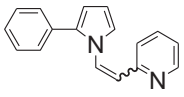
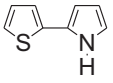
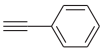
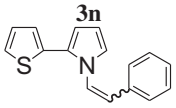
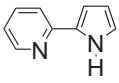
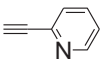
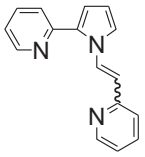


1a-f **2a-f** **3a-p**

Pyrrole	Acetylene	1-Styrylpyrrole	Yield,[a] %	Conversion of pyrrole **1**,[b] %	Ratio of *E*/*Z*-isomers[b]
 **1a**	 **2a**	 **3a**	86	100	100:0
 **1a**	 **2b**	 **3b**	87	100	15:85
 **1a**	 **2c**	 **3c**	89	100	20:80
 **1a**	 **2d**	 **3d**	86	100	100:0
 **1a**	 **2e**	 **3e**	88	100	92:8
 **1a**	 **2f**	 **3f**	87	100	100:0
 **1b**	 **2a**	 **3g**	86	100	33:67
 **1c**	 **2a**	 **3h**	93	100	25:75

(*continued on next page*)

Table 1 (*continued*)

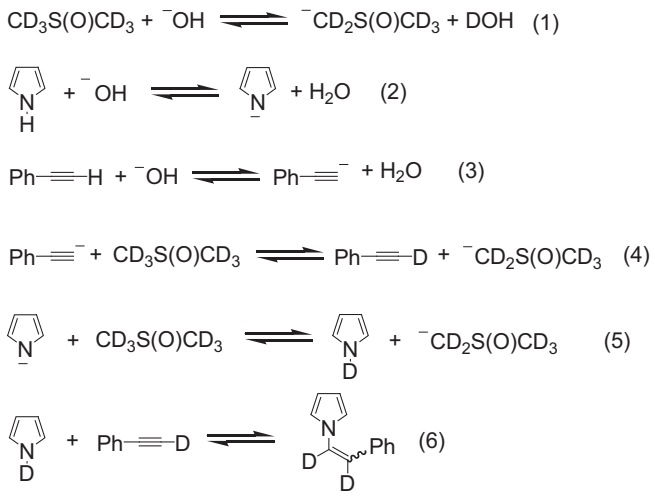
Pyrrole	Acetylene	1-Styrylpyrrole	Yield,[a] %	Conversion of pyrrole **1**,[b] %	Ratio of *E*/*Z*-isomers[b]
 **1c**	 **2b**	 **3i**	59	70	4:96
 **1c**	 **2d**	 **3j**	94	100	37:63
 **1c**	 **2f**	 **3k**	75	95	75:25
 **1d**	 **2a**	 **3l**	68	90	10:90
 **1d**	 **2d**	 **3m**	61	80	6:94
 **1d**	 **2f**	 **3n**	53	75	55:45
 **1e**	 **2a**	 **3o**	51	80	4:96
 **1f**	 **2f**	 **3p**	48	75	67:33

[a] Isolated yields were noted.
[b] According to ^{1}H NMR data of the crude product.

Table 2
The effect of the reaction conditions on the pyrrole conversion, the adducts yields and the *E*/*Z*-isomer ratio for the addition of pyrroles **1a**, **1c**–**e** to the phenylacetylene **2a**

Pyrrole	Ratio of components			Temperature, °C	Time, h	Conversion of pyrrole, %	Isolated yield, %	Ratio of *E*/*Z*-isomers
	Pyrrole	Acetylene	KOH					
1a	1	1	1	90	5	100	83	50:50
1a	1	1	1	120	5	100	86	100:0
1a	1	1	0.2	90	5	100	81	15:85
1c	1	1	1	90	5	100	93	25:75
1c	1	1	1	120	5	100	89	24:76
1d	1	2	1	90	13	90	68	10:90
1d	1	1	1	120	8	72[a]	34[b]	5:95
1d	1	2	0.5	100	8	90	60	0:100
1d	1	1	0.1	120	12	18[c]	18[c]	0:100
1e	1	2	1	90	6.5	80	51	4:96
1e	1	2	0.5	100	10	70[a]	38[b,d]	3:97

[a] Unreacted pyrrole was isolated by chromatography on Al_2O_3 (hexane/ether=4:1).
[b] 1,4-Diphenyl-1-buten-3-yne was detected in the reaction mixture due to dimerization of phenylacetylene (^{1}H NMR and GC–MS).
[c] According to GLC of the reaction mixture for 1–12 h.
[d] Decomposition and resinification products were detected in the reaction mixture (^{1}H NMR, GLC, and GC–MS).



Scheme 1.

Table 3
The energy difference (Δ*G*, kcal/mol) between *E*- and *Z*-isomers and *E*/*Z*-isomer ratio for selected 1-styrylpyrroles (MP2/6-311++G**//B3LYP/6-31G*)

1-Styrylpyrrole	Δ*G*	*K*	*E*/*Z*
3a	−1.50	0.08	92:8
3g	0.35	1.79	36:64
3h	0.79	3.76	21:79

3. Conclusions

In conclusion, a transition metal-free hydroamination of arylacetylenes with substituted pyrroles in the superbasic system KOH/DMSO at moderate temperatures (90–120 °C) provides a general straightforward route to nitrogen analogs of stilbenes, diversely substituted 1-styrylpyrroles. The hydroamination stereochemistry is controlled kinetically on the initial stages of the reaction and thermodynamically in the end of the process depending on the reactants structure and the reaction conditions that allows individual *E*- or *Z*-stereoisomers of the adducts to be isolated. The novel pyrrole analogs of stilbenes thus synthesized represent promising highly potent synthetic intermediates, building blocks for drug design, and precursors for optoelectronic advanced materials, particularly for molecular optical switches, biological labels, sensors, and information recording/storage devices.

4. Experimental section

4.1. General

The IR spectra were recorded on a Bruker IFS25 spectrophotometer from samples prepared as KBr pellets or thin films. The NMR spectra were measured from solutions in $CDCl_3$ on Bruker DPX-400 and AV-400 spectrometers (400.1 MHz for ^1H, 100.6 MHz for ^{13}C, 40.5 MHz for ^{15}N, and 376.5 MHz for ^{19}F) using hexamethyldisiloxane (^1H, ^{13}C), nitromethane (^{15}N), and trichlorofluoromethane (^{19}F) as internal references. The assignments of ^1H and ^{13}C NMR spectra were performed by COSY, NOESY, HSQC, and HMBC experiments.

Table 4
Spectroscopic and photophysical characteristics of 1-styrylpyrroles in MeCN at 22 °C

Styrylpyrrole	$\lambda_{max,abs}$, nm	Absorption coefficient (ε, M^{-1} cm^{-1})	$\lambda_{max,fl}$, nm	$\lambda_{max,ex}$, nm	Fluorescence quantum yield[a] (Φ_f)
E-**3a**	291	27,000	360	291	0.003
Z-**3a**	266	9200	n.f.[b]	n.f.[b]	n.f.[b]
E-**3e**	317	38,500	383	317	0.006
E-**3f**	276; 312	23,000	379	276; 313	0.001

[a] Relative to carbazole (Φ_f=0.259 in MeCN in the presence of O_2).[27]
[b] n.f.—not fluoresce.

UV/vis absorption spectra were measured on a Lambda-35 (Perkin–Elmer) spectrophotometer. The absorption coefficients have been determined with accuracy of ±100 M^{-1} cm^{-1}. Excitation and emission spectra were measured on an LS-55 steady state fluorescence spectrometer (Perkin–Elmer). For samples, a right-angle configuration was used and to avoid re-absorption, the maximum absorbance was kept below 0.05. In the case of fluorescent *E*-isomers, the excitation spectra matched well the absorption spectra. The solvent used was MeCN (spectroscopic grade) from Sigma–Aldrich. The fluorescence quantum yields (Φ_f) were measured on an FLSP-920 combined steady state and time resolved fluorescence spectrometers (Edinburgh Instruments). Φ_f of the styrylpyrrole systems were calculated using the following relationship: $\Phi_f=\Phi_{ref}F_{sampl}A_{ref}/F_{ref}A_{sampl}$. Here, *F* denotes the integral of the corrected fluorescence spectrum, *A* is the absorbance at the excitation wavelength, ref and sampl denote parameters from the reference and unknown experimental samples, respectively.

The equilibrium geometries and Gibbs free energy corrections were calculated within a density functional theory with a hybrid Becke's three-parameter exchange functional[29] and Lee, Yang, and Parr gradient-corrected correlation functional[30] using the 6-31G* basis set. Energy of most stable conformers of *E*- and *Z*-isomers was refined using the extended 6-311++G** basis set with the correlation effects included in the Moller–Plesset second order perturbation theory. The calculations were made using Gaussian-98 package.[31]

Pyrrole **1a**, arylacetylenes **2a**–**e**, and ethynylpyridine **2f** are commercial products. Pyrroles **1b**–**f** are prepared from the corresponding ketoximes and acetylene by the Trofimov reaction.[32]

4.2. Synthesis of the 1-styrylpyrroles 3a–p

To a solution of pyrroles **1a**–**e** (2.0 mmol) and acetylenes **2a**–**f** (2.0 mmol) in DMSO (7 mL) was rapidly added powdered KOH·0.5H_2O (0.130 g, 2.0 mmol). In the case of the synthesis of **3p**:

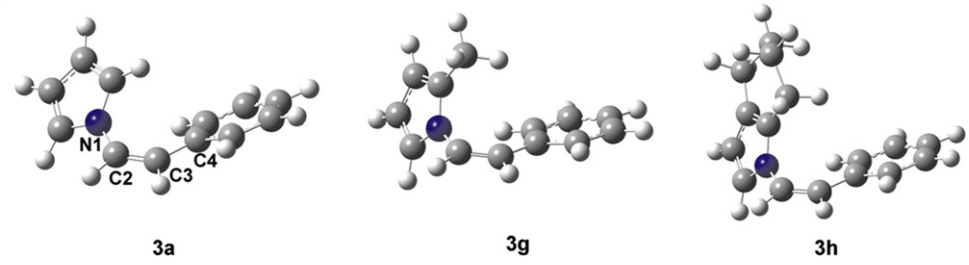


Fig. 1. The B3LYP/6-31G* structures of *Z*-styrylpyrroles.

to a solution of pyrrole **1f** (0.130 g, 0.9 mmol) and acetylene **2f** (0.093 g, 0.9 mmol) in DMSO (3.2 mL) was rapidly added powdered $KOH·0.5H_2O$ (0.059 g, 0.9 mmol). The suspension was stirred at heating on oil bath for 5–13 h. The reaction mixture was poured into ice water (25–30 mL), neutralized with NH_4Cl, extracted with ether (4×15 mL). The ether extract was washed with water (2×10 mL) and dried over K_2CO_3 overnight. The crude product was obtained after filtration and evaporation of the solvent. The residue obtained was dried in vacuo and purified by column chromatography (Al_2O_3, eluent: hexane or silica gel, eluent: benzene) to give the corresponding 1-styrylpyrroles **3a**–**p**.

*4.2.1. 1-[(E)-2-Phenylethenyl]-1H-pyrrole (**3a**).* Yield: 0.291 g (86%); beige crystals; mp 104–106 °C (hexane) (Table 1); R_f (25% Et_2O/benzene) 0.91. IR (KBr): 3436, 1659, 1521, 1482, 1449, 1340, 1308, 1097, 1072, 940, 749, 728, 692, 612, 583, 507 cm^{-1}. ^1H NMR (400.1 MHz, $CDCl_3$): δ=6.29–6.31 (m, 2H, H-3, H-4), 6.61 (d, $^3J_{(H\text{-}\beta,H\text{-}\alpha)}$=14.4 Hz, 1H, CH^{β}=), 6.99–7.01 (m, 2H, H-2, H-5), 7.24–7.26 (m, 1H, H^p, Ph), 7.28 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=14.4 Hz, 1H, CH^{α}=), 7.33–7.37 (m, 2H, H^m, Ph), 7.38–7.42 (m, 2H, H^o, Ph) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=110.4 (C-3, C-4, pyrrole), 114.3 (C-β), 119.1 (C-2, C-5, pyrrole), 125.7 (Co, Ph), 126.9 (C-α), 127.0 (C^p, Ph), 128.8 (C^m, Ph), 135.6 (C^i, Ph) ppm. ^{15}N NMR (40.5 MHz, $CDCl_3$): δ=−207.6 ppm. Anal. Calcd for $C_{12}H_{11}N$: C, 85.17; H, 6.55; N, 8.28. Found: C, 85.38; H, 6.61; N, 8.07.

*4.2.2. 1-[(Z)-2-Phenylethenyl]-1H-pyrrole (**3a**).* Colorless oil (silica gel, eluent—benzene) (Table 2); R_f (25% Et_2O/benzene) 0.91. IR (film): 1655, 1599, 1485, 1447, 1416, 1357, 1287, 1248, 1087, 1075, 964, 855, 773, 728, 696, 612, 603, 547 cm^{-1}. ^1H NMR (400.1 MHz, $CDCl_3$): δ=6.10 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=9.5 Hz, 1H, CH^{β}=), 6.13–6.15 (m, 2H, H-3, H-4), 6.64–6.66 (m, 2H, H-2, H-5), 6.73 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=9.5 Hz, 1H, CH^{α}=), 7.17–7.21 (m, 2H, H^o, Ph), 7.24–7.26 (m, 1H, H^p, Ph), 7.27–7.29 (m, 2H, H^m, Ph) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=109.5 (C-3, C-4, pyrrole), 118.2 (C-β), 120.9 (C-2, C-5, pyrrole), 126.4 (C-α), 127.5 (C^p, Ph), 128.4 (C^m, Ph), 128.8 (Co, Ph), 134.6 (C^i, Ph) ppm. ^{15}N NMR (40.5 MHz, $CDCl_3$): δ=−213.4 ppm. Anal. Calcd for $C_{12}H_{11}N$: C, 85.17; H, 6.55; N, 8.28. Found: C, 85.27; H, 6.64; N, 8.31.

*4.2.3. 1-[(Z/E)-2-(4-Methylphenyl)ethenyl]-1H-pyrrole (**3b**).* Yield: 0.319 g (87%); pale yellow oil (mixture of *Z*- and *E*-isomers), (silica gel, eluent—benzene); R_f (25% Et_2O/benzene) 0.96. IR (film): 3102, 3033, 2954, 2922, 2852, 1702, 1690, 1652, 1610, 1564, 1513, 1485, 1420, 1357, 1287, 1248, 1089, 1074, 965, 875, 866, 821, 727, 613, 603, 545 cm^{-1}. ^1H NMR (400.1 MHz, $CDCl_3$) for *Z*-isomer: δ=2.39 (s, 3H, Me), 6.13 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=9.5 Hz, 1H, CH^{β}=), 6.20–6.22 (m, 2H, H-3, H-4), 6.71–6.73 (m, 2H, H-2, H-5), 6.74 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=9.5 Hz, 1H, CH^{α}=), 7.10–7.16 (m, 4H, Ho, H^m, Ph); for *E*-isomer: δ=2.41 (s, 3H, Me), 6.34–6.36 (m, 2H, H-3, H-4), 6.62 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=14.7 Hz, 1H, CH^{β}=), 7.03–7.05 (m, 2H, H-2, H-5), 7.19–7.23 (m, 2H, Ho, Ph), 7.32–7.36 (m, 2H, H^m, Ph), 7.33 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=14.7 Hz, 1H, CH^{α}=) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$) for *Z*-isomer: δ=21.3 (Me), 109.3 (C-3, C-4, pyrrole), 118.7 (C-β), 120.8 (C-2, C-5, pyrrole), 125.9 (C-α), 128.7 (Co, Ph), 129.2 (C^m, Ph), 132.1 (C^i, Ph), 137.4 (C^p, Ph); for *E*-isomer: δ=21.2 (Me), 110.4 (C-3, C-4, pyrrole), 114.4 (C-β), 119.3 (C-2, C-5, pyrrole), 125.8 (Co, Ph), 126.2 (C-α), 129.6 (C^m, Ph), 132.9 (C^i, Ph), 136.8 (C^p, Ph) ppm. ^{15}N NMR (40.5 MHz, $CDCl_3$) for *Z*-isomer: δ=−213.1; for *E*-isomer: δ=−208.2 ppm. Anal. Calcd for $C_{13}H_{13}N$: C, 85.21; H, 7.15; N, 7.64. Found: C, 85.09; H, 7.19; N, 7.53.

*4.2.4. 1-[(Z/E)-2-(2,5-Dimethylphenyl)ethenyl]-1H-pyrrole (**3c**).* Yield: 0.351 g (89%); yellow oil (mixture of *Z*- and *E*-isomers); R_f (25% Et_2O/benzene) 0.90. IR (film): 3104, 3036, 3016, 2950, 2922, 2859, 1702, 1657, 1612, 1526, 1498, 1485, 1425, 1329, 1288, 1249, 1090, 1075, 966, 931, 836, 808, 766, 727, 616 cm^{-1}. ^1H NMR (400.1 MHz, $CDCl_3$) for *Z*-isomer: δ=2.16 (s, 3H, 2-Me), 2.27 (s, 3H, 5-Me), 5.98 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=9.8 Hz, 1H, CH^{β}=), 6.07–6.09 (m, 2H, H-3, H-4), 6.55–6.57 (m, 2H, H-2, H-5), 6.75 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=9.8 Hz, 1H, CH^{α}=), 6.98–7.03 (m, 2H, H-4, H-6, Ph), 7.09–7.11 (m, 1H, H-3, Ph); for *E*-isomer: δ=2.34 (s, 6H, Me), 6.29–6.31 (m, 2H, H-3, H-4), 6.76 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=14.4 Hz, 1H, CH^{β}=), 6.99–7.01 (m, 2H, H-2, H-5), 7.03–7.07 (m, 1H, H-4, Ph), 7.08–7.10 (m, 1H, H-3, Ph), 7.17 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=14.4 Hz, 1H, CH^{α}=), 7.23–7.27 (m, 1H, H-6, Ph) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$) for *Z*-isomer: δ=19.4 (2-Me), 21.0 (5-Me), 109.4 (C-3, C-4, pyrrole), 114.1 (C-β), 120.9 (C-2, C-5, pyrrole), 126.6 (C-α), 128.3 (C-4, Ph), 129.6 (C-6, Ph), 130.4 (C-3, Ph), 133.3 (C-5, Ph), 134.9 (C-1, Ph), 135.4 (C-2, Ph); for *E*-isomer: δ=19.6 (2-Me), 21.1 (5-Me), 110.4 (C-3, C-4. pyrrole), 112.6 (C-β), 119.2 (C-2, C-5, pyrrole), 125.7 (C-6, Ph), 127.2 (C-4, Ph), 127.6 (C-α), 128.9 (C-3, Ph), 132.5 (C-5, Ph), 134.4 (C-1, Ph), 135.7 (C-2, Ph) ppm. ^{15}N NMR (40.5 MHz, $CDCl_3$) for *Z*-isomer: δ=−210.3; for *E*-isomer: δ=−207.4 ppm. Anal. Calcd for $C_{14}H_{15}N$: C, 85.24; H, 7.66; N, 7.10. Found: C, 85.35; H, 7.53; N, 7.21.

*4.2.5. 1-[(E)-2-(3-Fluorophenyl)ethenyl]-1H-pyrrole (**3d**).* Yield: 0.322 g (86%); yellow powder; mp 62–63 °C (silica gel, eluent—benzene); R_f (25% Et_2O/benzene) 0.94. IR (KBr): 1661, 1612, 1582, 1524, 1482, 1447, 1337, 1278, 1239, 1144, 1096, 1072, 965, 936, 861, 783, 729, 682, 615 cm^{-1}. ^1H NMR (400.1 MHz, $CDCl_3$): δ=6.33–6.35 (m, 2H, H-3, H-4), 6.57 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=14.7 Hz, 1H, CH^{β}=), 6.95–6.99 (m, 1H, H-4, Ph), 7.01–7.03 (m, 2H, H-2, H-5), 7.10–7.14 (m, 1H, H-2, Ph), 7.16–7.20 (m, 1H, H-6, Ph), 7.30–7.34 (m, 1H, H-5, Ph), 7.32 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=14.7 Hz, 1H, CH^{α}=) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=110.9 (C-3, C-4, pyrrole), 112.1 (d, $^2J_{(C,F)}$=22.1 Hz, C-2, Ph), 113.0 (C-β), 113.7 (d, $^2J_{(C,F)}$=21.6 Hz, C-4, Ph), 119.2 (C-2, C-5, pyrrole), 121.7 (d, $^4J_{(C,F)}$=2.5 Hz, C-6, Ph), 128.0 (C-α), 130.3 (d, $^3J_{(C,F)}$=8.0 Hz, C-1, Ph), 130.3 (d, $^3J_{(C,F)}$=8.5 Hz, C-5, Ph), 163.2 (d, $^1J_{(C,F)}$=245.2 Hz, C-3, Ph) ppm. ^{15}N NMR (40.5 MHz, $CDCl_3$): δ=−208.8 ppm. ^{19}F NMR (376.5 MHz, $CDCl_3$): δ=−113.0 (m) ppm. Anal. Calcd for $C_{12}H_{10}FN$: C, 76.99; H, 5.38; F, 10.15; N, 7.48. Found: C, 76.85; H, 5.35; F, 9.97; N, 7.22.

*4.2.6. 1-[(Z/E)-2-[1,1′-Biphenyl]-4-ylethenyl]-1H-pyrrole (**3e**).* Yield: 0.432 g (88%); *E*-isomer is pale yellow powder; mp 207–208 °C (petroleum ether 40–70 °C); *Z*-isomer is detected by ^1H NMR. IR (KBr) for *E*-isomer: 1656, 1484, 1334, 1314, 1097, 1074, 968, 936, 852, 764, 724, 692, 610 cm^{-1}. ^1H NMR (400.1 MHz, $CDCl_3$) for *Z*-isomer: δ=6.09 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=9.4 Hz, 1H, CH^{β}=), 6.11–6.13 (m, 2H, H-3, H-4), 6.66–6.68 (m, 2H, H-2, H-5), 6.71 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=9.4 Hz, 1H, CH^{α}=), 7.30–7.50 (m, 9H, Ph); for *E*-isomer: δ=6.26–6.28 (m, 2H, H-3, H-4), 6.61 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=14.7 Hz, 1H, CH^{β}=), 6.98–7.00 (m, 2H, H-2, H-5), 7.30–7.34 (m, 1H, H-4′, Ph), 7.33 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=14.7 Hz, 1H, CH^{α}=), 7.39–7.46 (m, 4H, H-3′, H-5′; H-2, H-6, Ph), 7.54–7.58 (m, 2H, H-3, H-5, Ph), 7.58–7.60 (m, 2H, H-2′, H-6′, Ph) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$) for *E*-isomer: δ=110.6 (C-3, C-4, pyrrole), 113.9 (C-β), 119.2 (C-2, C-5, pyrrole), 126.2 (C-2, C-6, Ph), 127.0 (C-α), 127.0 (C-2′, C-6′, Ph), 127.4 (C-4′, Ph), 127.5 (C-3, C-5, Ph), 128.9 (C-3′, C-5′, Ph), 134.9 (C-1, Ph), 139.9 (C-4, Ph), 140.7 (C-1′, Ph) ppm. ^{15}N NMR (40.5 MHz, $CDCl_3$) for *E*-isomer: δ=−208.2 ppm. Anal. Calcd for $C_{18}H_{15}N$: C, 88.13; H, 6.16; N, 5.71. Found: C, 88.29; H, 6.12; N, 5.87.

*4.2.7. 1-[(E)-2-(2-Pyridinyl)ethenyl]-1H-pyrrole (**3f**).* Yield: 0.296 g (87%); white powder; mp 106–108 °C (silica gel, eluent—benzene); R_f (25% Et_2O/benzene) 0.90. IR (KBr): 1660, 1584, 1559, 1521, 1490, 1468, 1430, 1336, 1280, 1148, 1100, 1090, 1073, 968, 951, 852, 772, 765, 737, 615, 600 cm^{-1}. ^1H NMR (400.1 MHz, $CDCl_3$): δ=6.26–6.28 (m, 2H, H-3, H-4), 6.56 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=14.2 Hz, 1H, CH^{β}=), 6.99–7.01 (m, 2H, H-2, H-5), 7.05–7.09 (m, 1H, H-5, pyridine), 7.14–7.18 (m, 1H, H-3, pyridine), 7.57–7.61 (m, 1H, H-4, pyridine), 7.89 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=14.2 Hz, 1H, CH^{α}=), 8.48–8.52 (m, 1H, H-6, pyridine) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=110.1 (C-3, C-4, pyrrole), 112.6 (C-β),

119.6 (C-2, C-5, pyrrole), 121.5 (C-5, pyridine), 121.8 (C-3, pyridine), 130.7 (C-α), 136.7 (C-4, pyridine), 149.6 (C-6, pyridine), 154.8 (C-2, pyridine) ppm. ^{15}N NMR (40.5 MHz, $CDCl_3$): δ=−208.8 (pyrrole), −82.6 (pyridine) ppm. Anal. Calcd for $C_{11}H_{10}N_2$: C, 77.62; H, 5.92; N, 16.46. Found: C, 77.91; H, 5.86; N, 16.39.

*4.2.8. 2-Methyl-1-[(Z/E)-2-phenylethenyl]-1H-pyrrole (**3g**).* Yield: 0.315 g (86%); yellow oil (mixture of *Z*- and *E*-isomers) (Al_2O_3, eluent—hexane); R_f (25% Et_2O/benzene) 0.93. IR (film): 3068, 3029, 2924, 1649, 1564, 1485, 1451, 1417, 1331, 1299, 1146, 1075, 975, 936, 846, 778, 701, 597, 505 cm^{-1}. ^{1}H NMR (400.1 MHz, $CDCl_3$) for *Z*-isomer: δ=2.17 (s, 3H, Me), 5.94 (dd, $^3J_{(H\text{-}3,H\text{-}4)}$=3.4 Hz, $^4J_{(H\text{-}3,H\text{-}5)}$=1.5 Hz, 1H, H-3), 6.05 (dd, $^3J_{(H\text{-}4,H\text{-}3)}$=3.4 Hz, $^3J_{(H\text{-}4,H\text{-}5)}$=2.9 Hz, 1H, H-4), 6.25 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=9.1 Hz, 1H, CH^{β}=), 6.50 (dd, $^3J_{(H\text{-}5,H\text{-}4)}$=2.9 Hz, $^4J_{(H\text{-}5,H\text{-}3)}$=1.5 Hz, 1H, H-5), 6.65 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=9.1 Hz, 1H, CH^{α}=), 7.03–7.07 (m, 2H, H^o, Ph), 7.18–7.22 (m, 1H, H^p, Ph), 7.22–7.26 (m, 2H, H^m, Ph); for *E*-isomer: δ=2.33 (s, 3H, Me), 5.95 (dd, $^3J_{(H\text{-}3,H\text{-}4)}$=3.4 Hz, $^4J_{(H\text{-}3,H\text{-}5)}$=1.5 Hz, 1H, H-3), 6.18 (dd, $^3J_{(H\text{-}4,H\text{-}3)}$=3.4 Hz, $^3J_{(H\text{-}4,H\text{-}5)}$=2.9 Hz, 1H, H-4), 6.57 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=14.4 Hz, 1H, CH^{β}=), 7.05 (dd, $^3J_{(H\text{-}5,H\text{-}4)}$=2.9 Hz, $^4J_{(H\text{-}5,H\text{-}3)}$=1.5 Hz, 1H, H-5), 7.21–7.25 (m, 1H, H^p, Ph), 7.30 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=14.4 Hz, 1H, CH^{α}=), 7.32–7.36 (m, 2H, H^m, Ph), 7.38–7.42 (m, 2H, H^o, Ph) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$) for *Z*-isomer: δ=11.9 (Me), 107.1 (C-3, pyrrole), 108.1 (C-4, pyrrole), 119.1 (C-5, pyrrole), 122.9 (C-β), 124.5 (C-α), 127.3 (C^p, Ph), 128.0 (C^m, Ph), 128.1 (C-2, pyrrole), 128.2 (Co, Ph), 134.2 (C^i, Ph); for *E*-isomer: δ=11.9 (Me), 108.2 (C-3, pyrrole), 109.3 (C-4, pyrrole), 114.8 (C-β), 116.2 (C-5, pyrrole), 124.1 (C-α), 125.3 (Co, Ph), 126.6 (C^p, Ph), 128.4 (C^m, Ph), 128.8 (C-2, pyrrole), 135.7 (C^i, Ph) ppm. ^{15}N NMR (40.5 MHz, $CDCl_3$) for *Z*-isomer: δ=−215.4; for *E*-isomer: δ=−208.9 ppm. Anal. Calcd for $C_{13}H_{13}N$: C, 85.21; H, 7.15; N, 7.64. Found: C, 85.14; H, 7.36; N, 7.82.

*4.2.9. 1-[(E/Z)-2-Phenylethenyl]-4,5,6,7-tetrahydro-1H-indole (**3h**).* Yield: 0.416 g (93%). Individual *Z*-isomer **3h** is yellow oil (Al_2O_3, eluent—hexane); R_f (17% Et_2O/hexane) 0.82; *E*-isomer **3h** is detected by NMR. IR (film) for *Z*-isomer: 3080, 3058, 3026, 2927, 2845, 1703, 1650, 1598, 1494, 1447, 1481, 1447, 1381, 1292, 1138, 1073, 1029, 913, 781, 769, 695, 632, 551 cm^{-1}. ^{1}H NMR (400.1 MHz, $CDCl_3$) for *Z*-isomer: δ=1.69–1.78 (m, 4H, CH_2), 2.44–2.49 (m, 4H, CH_2), 5.89 (d, $^3J_{(H\text{-}2,H\text{-}3)}$=2.7 Hz, 1H, H-3), 6.08 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=9.3 Hz, 1H, CH^{β}=), 6.45 (d, $^3J_{(H\text{-}2,H\text{-}3)}$=2.7 Hz, 1H, H-2), 6.57 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=9.3 Hz, 1H, CH^{α}=), 7.10–7.14 (m, 2H, Ho, Ph), 7.20–7.24 (m, 2H, H^m, Ph), 7.28–7.32 (m, 1H, H^p, Ph); for *E*-isomer: δ=1.82–1.87 (m, 4H, CH_2), 2.60–2.65 (m, 4H, CH_2), 6.05 (d, $^3J_{(H\text{-}2,H\text{-}3)}$=2.8 Hz, 1H, H-3), 6.51 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=14.4 Hz, 1H, CH^{β}=), 6.95 (d, $^3J_{(H\text{-}2,H\text{-}3)}$=2.8 Hz, 1H, H-2), 7.18–7.22 (m, 1H, H^p, Ph), 7.22 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=14.4 Hz, 1H, CH^{α}=), 7.28–7.32 (m, 2H, H^m, Ph), 7.33–7.37 (m, 2H, H^o, Ph) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$) for *Z*-isomer: δ=22.1 (CH_2-7), 23.0 (CH_2-4), 23.2 (CH_2-6), 23.3 (CH_2-5), 108.4 (C-3, pyrrole), 118.4 (C-9), 118.5 (C-2, pyrrole), 119.6 (C-β), 124.3 (C-α), 127.9 (C-8), 128.4 (C^m, Ph), 128.7 (Co, Ph), 128.8 (C^p, Ph), 135.3 (C^i, Ph); for *E*-isomer: δ=22.1 (CH_2-7), 23.1 (CH_2-4), 23.2 (CH_2-5), 23.4 (CH_2-6), 109.8 (C-3, pyrrole), 113.7 (C-β), 115.5 (C-2, pyrrole), 119.5 (C-9), 124.4 (C-α), 125.7 (Co, Ph), 126.8 (C^p, Ph), 127.5 (C^m, Ph), 128.3 (C-8), 136.4 (C^i, Ph) ppm. Anal. Calcd for $C_{16}H_{17}N$: C, 86.05; H, 7.67; N, 6.27. Found: C, 86.21; H, 7.53; N, 6.09.

*4.2.10. 1-[(Z/E)-2-(4-Methylphenyl)ethenyl]-4,5,6,7-tetrahydro-1H-indole (**3i**).* Yield: 0.280 g (59%). Individual *Z*-isomer **3i** is pale yellow cereous oil (Al_2O_3, eluent—hexane); R_f (25% Et_2O/benzene) 0.89; *E*-isomer **3i** is detected by NMR. IR (KBr) for *Z*-isomer: 2928, 2851, 1653, 1591, 1511, 1481, 1435, 1384, 1290, 1158, 1142, 937, 874, 821, 812, 753, 728, 719, 704, 632, 609, 540 cm^{-1}. ^{1}H NMR (400.1 MHz, $CDCl_3$) for *Z*-isomer: δ=1.69–1.77 (m, 4H, CH_2), 2.29 (s, 3H, Me), 2.42–2.50 (m, 4H, CH_2), 5.89 (d, $^3J_{(H\text{-}2,H\text{-}3)}$=2.9 Hz, 1H, H-3), 6.06 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=9.1 Hz, 1H, CH^{β}=), 6.47 (d, $^3J_{(H\text{-}2,H\text{-}3)}$=2.9 Hz, 1H, H-2), 6.53 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=9.1 Hz, 1H, CH^{α}=), 6.98–7.02 (m, 2H, H^m, Ph), 7.02–7.06 (m, 2H, H^o, Ph); for *E*-isomer: δ=1.77–1.87 (m, 4H, CH_2), 2.36 (s, 3H, Me), 2.53–2.66 (m, 4H, CH_2), 6.08 (d, $^3J_{(H\text{-}2,H\text{-}3)}$=2.9 Hz, 1H, H-3), 6.51 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=14.4 Hz, 1H, CH^{β}=), 7.21 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=14.4 Hz, 1H, CH^{α}=), 6.97 (d, $^3J_{(H\text{-}2,H\text{-}3)}$=2.9 Hz, 1H, H-2), 7.13–7.17 (m, 2H, H^m, Ph), 7.26–7.30 (m, 2H, Ho, Ph) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$) for *Z*-isomer: δ=21.0 (Me), 22.2 (CH_2-7), 23.0 (CH_2-4), 23.5 (CH_2-6), 23.8 (CH_2-5), 108.4 (C-3, pyrrole), 118.3 (C-9), 118.5 (C-2, pyrrole), 119.8 (C-β), 123.3 (C-α), 127.7 (C-8), 128.8 (Co, Ph), 130.5 (C^m, Ph), 132.5 (C^i, Ph), 138.8 (C^p, Ph); for *E*-isomer: δ=21.2 (Me), 22.1 (CH_2-7), 23.2 (CH_2-4), 23.3 (CH_2-6), 23.5 (CH_2-5), 109.6 (C-3, pyrrole), 114.0 (C-β), 115.5 (C-2, pyrrole), 119.4 (C-9), 123.7 (C-α), 125.6 (Co, Ph), 128.2 (C-8), 129.5 (C^m, Ph), 133.5 (C^i, Ph), 136.6 (C^p, Ph) ppm. ^{15}N NMR (40.5 MHz, $CDCl_3$) for *Z*-isomer: δ=−207.2; for *E*-isomer: δ=−213.6 ppm. Anal. Calcd for $C_{17}H_{19}N$: C, 86.03; H, 8.07; N, 5.90. Found: C, 86.27; H, 8.15; N, 5.73.

*4.2.11. 1-[(Z/E)-2-(3-Fluorophenyl)ethenyl]-4,5,6,7-tetrahydro-1H-indole (**3j**).* Yield: 0.454 g (94%); orange oil (mixture of *E*- and *Z*-isomers) (silica gel, eluent—benzene); R_f (25% Et_2O/benzene) 0.94. IR (film): 3068, 3036, 2928, 2849, 1654, 1611, 1593, 1581, 1481, 1443, 1381, 1305, 1138, 930, 881, 785, 707, 684 cm^{-1}. ^{1}H NMR (400.1 MHz, $CDCl_3$) for *Z*-isomer: δ=1.75–1.80 (m, 4H, CH_2), 2.40–2.41 (m, 4H, CH_2), 5.94 (d, $^3J_{(H\text{-}2,H\text{-}3)}$=2.9 Hz, 1H, H-3), 6.06 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=9.4 Hz, 1H, CH^{β}=), 6.46 (d, $^3J_{(H\text{-}2,H\text{-}3)}$=2.9 Hz, 1H, H-2), 6.65 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=9.4 Hz, 1H, CH^{α}=), 6.83–6.87 (m, 1H, H-2, Ph), 6.90–6.94 (m, 1H, H-4, Ph), 6.95–6.99 (m, 1H, H-6, Ph), 7.20–7.24 (m, 1H, H-5, Ph); for *E*-isomer: δ=1.77–1.89 (m, 4H, CH_2), 2.53–2.67 (m, 4H, CH_2), 6.10 (d, $^3J_{(H\text{-}2,H\text{-}3)}$=2.9 Hz, 1H, H-3), 6.48 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=14.4 Hz, 1H, CH^{β}=), 6.90–6.94 (m, 1H, H-4, Ph), 6.97 (d, $^3J_{(H\text{-}2,H\text{-}3)}$=2.9 Hz, 1H, H-2), 7.06–7.10 (m, 1H, H-2, Ph), 7.11–7.15 (m, 1H, H-6, Ph), 7.26 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=14.4 Hz, 1H, CH^{α}=), 7.28–7.32 (m, 1H, H-5, Ph) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$) for *Z*-isomer: δ=22.0 (CH_2-7), 23.1 (CH_2-6), 23.3 (CH_2-5), 23.5 (CH_2-4), 108.9 (C-3, pyrrole), 114.3 (d, $^2J_{(C,F)}$=21.3 Hz, C-4, Ph), 115.5 (d, $^2J_{(C,F)}$=22.0 Hz, C-2, Ph), 118.1 (C-β), 118.4 (C-2, pyrrole), 118.8 (C-9), 124.6 (d, $^4J_{(C,F)}$=2.9 Hz, C-6, Ph), 125.3 (C-α), 127.8 (C-8), 129.8 (d, $^3J_{(C,F)}$=8.5 Hz, C-5, Ph), 137.5 (d, $^3J_{(C,F)}$=8.0 Hz, C-1, Ph), 162.8 (d, $^1J_{(C,F)}$=245.4 Hz, C-3, Ph); for *E*-isomer: δ=22.0 (CH_2-7), 23.2 (CH_2-5), 23.4 (CH_2-6), 23.5 (CH_2-4), 110.3 (C-3, pyrrole), 112.0 (d, $^2J_{(C,F)}$=22.0 Hz, C-2, Ph), 112.3 (C-β), 113.4 (d, $^2J_{(C,F)}$=21.3 Hz, C-4, Ph), 115.5 (C-2, pyrrole), 119.9 (C-9), 121.5 (d, $^4J_{(C,F)}$=2.6 Hz, C-6, Ph), 125.4 (C-α), 128.4 (C-8), 130.2 (d, $^3J_{(C,F)}$=8.5 Hz, C-5, Ph), 138.9 (d, $^3J_{(C,F)}$=8.0 Hz, C-1, Ph), 163.3 (d, $^1J_{(C,F)}$=245.2 Hz, C-3, Ph) ppm. ^{15}N NMR (40.5 MHz, $CDCl_3$) for *Z*-isomer: δ=−219.8; for *E*-isomer: δ=−214.3 ppm. Anal. Calcd for $C_{16}H_{16}FN$: C, 79.64; H, 6.68; F, 7.87; N, 5.80. Found: C, 79.82; H, 6.57; F, 7.69; N, 5.69.

*4.2.12. 1-[(Z/E)-2-(2-Pyridinyl)ethenyl]-4,5,6,7-tetrahydro-1H-indole (**3k**).* Yield: 0.336 g (75%); orange oil (mixture of *E*- and *Z*-isomers) (silica gel, eluent—benzene); R_f (25% Et_2O/benzene) 0.60. IR (film): 3069, 3002, 2928, 2845, 1652, 1588, 1560, 1487, 1469, 1430, 1378, 1307, 1268, 1237, 1209, 1198, 1170, 1147, 1136, 991, 944, 835, 790, 766, 741, 705, 696, 631, 604, 589 cm^{-1}. ^{1}H NMR (400.1 MHz, $CDCl_3$) for *Z*-isomer: δ=1.75–1.85 (m, 4H, CH_2), 2.49–2.50 (m, 4H, CH_2), 5.93 (d, $^3J_{(H\text{-}2,H\text{-}3)}$=2.9 Hz, 1H, H-3), 6.19 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=9.5 Hz, 1H, CH^{β}=), 6.64 (d, $^3J_{(H\text{-}2,H\text{-}3)}$=2.9 Hz, 1H, H-2), 6.78 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=9.5 Hz, 1H, CH^{α}=), 7.06–7.10 (m, 1H, H-3, pyridine), 7.10–7.12 (m, 1H, H-5, pyridine), 7.53–7.55 (m, 1H, H-4, pyridine), 8.58–8.60 (m, 1H, H-6, pyridine); for *E*-isomer: δ=1.75–1.85 (m, 4H, CH_2-5,6), 2.48–2.50 (m, 2H, CH_2-4), 2.70–2.72 (m, 2H, CH_2-7), 6.10 (d, $^3J_{(H\text{-}2,H\text{-}3)}$=2.9 Hz, 1H, H-3), 6.52 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=14.2 Hz, 1H, CH^{β}=), 7.02 (d, $^3J_{(H\text{-}2,H\text{-}3)}$=2.9 Hz, 1H, H-2), 7.06–7.08 (m, 1H, H-5, pyridine), 7.17–7.19 (m, 1H, H-3, pyridine), 7.60–7.62 (m, 1H, H-4, pyridine), 7.90 (d, $^3J_{(H\text{-}\alpha,H\text{-}}$

β)=14.2 Hz, 1H, CH$^{\alpha}$=), 8.51–8.53 (m, 1H, H-6, pyridine) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$) for *Z*-isomer: δ=22.0 (CH_2-7), 23.1 (CH_2-6), 23.2 (CH_2-4), 23.5 (CH_2-5), 108.8 (C-3, pyrrole), 118.7 (C-β), 118.7 (C-9), 119.0 (C-2, pyrrole), 121.9 (C-5, pyridine), 123.7 (C-3, pyridine), 126.7 (C-α), 128.0 (C-8), 136.0 (C-4, pyridine), 149.4 (C-6, pyridine), 154.8 (C-2, pyridine); for *E*-isomer: δ=22.1 (CH_2-7), 23.1 (CH_2-6), 23.1 (CH_2-4), 23.4 (CH_2-5), 110.7 (C-3, pyrrole), 111.7 (C-β), 115.8 (C-2, pyrrole), 120.0 (C-9), 121.1 (C-5, pyridine), 121.5 (C-3, pyridine), 128.2 (C-α), 129.0 (C-8), 136.6 (C-4, pyridine), 149.4 (C-6, pyridine), 155.3 (C-2, pyridine) ppm. ^{15}N NMR (40.5 MHz, $CDCl_3$) for *Z*-isomer: δ=−218.5 (pyrrole), −69.8 (pyridine); for *E*-isomer: δ=−213.7 (pyrrole), −83.8 (pyridine) ppm. Anal. Calcd for $C_{15}H_{16}N_2$: C, 80.32; H, 7.19; N, 12.49. Found: C, 80.61; H, 7.24; N, 12.18.

*4.2.13. 2-Phenyl-1-[(Z/E)-2-phenylethenyl]-1H-pyrrole (**3l**).* Yield: 0.334 g (68%). Individual *Z*-isomer is yellow oil (Al_2O_3, eluent—hexane); R_f (25% Et_2O/hexane) 0.88; *E*-isomer is detected by NMR. IR (film) for *Z*-isomer: 1649, 1602, 1494, 1467, 1416, 1316, 1176, 1167, 1076, 1029, 759, 717, 696, 606 cm^{-1}. ^{1}H NMR (400.1 MHz, $CDCl_3$) for *Z*-isomer: δ=6.24 (dd, $^3J_{(H\text{-}4,H\text{-}3)}$=3.4 Hz, $^3J_{(H\text{-}4,H\text{-}5)}$=2.7 Hz, 1H, H-4), 6.28 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=9.1 Hz, 1H, CH$^{\beta}$=), 6.40 (dd, $^3J_{(H\text{-}3,H\text{-}4)}$=3.4 Hz, $^4J_{(H\text{-}3,H\text{-}5)}$=1.7 Hz, 1H, H-3), 6.68 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=9.1 Hz, 1H, CH$^{\alpha}$=), 6.70 (dd, $^3J_{(H\text{-}5,H\text{-}4)}$=2.7 Hz, $^4J_{(H\text{-}5,H\text{-}3)}$=1.7 Hz, 1H, H-5), 7.22–7.27 (m, 3H, Ho, H^p, Ph_{styryl}), 7.28–7.33 (m, 3H, H^m, Ph_{styryl}; H$^{p\prime}$, $Ph_{pyrrole}$), 7.38–7.42 (m, 2H, H$^{m\prime}$, $Ph_{pyrrole}$), 7.51–7.55 (m, 2H, H$^{o\prime}$, $Ph_{pyrrole}$); for *E*-isomer: δ=6.39 (dd, $^3J_{(H\text{-}3,H\text{-}4)}$=3.4 Hz, $^4J_{(H\text{-}3,H\text{-}5)}$=1.7 Hz, 1H, H-3), 6.40 (dd, $^3J_{(H\text{-}4,H\text{-}3)}$=3.4 Hz, $^3J_{(H\text{-}4,H\text{-}5)}$=3.4 Hz, 1H, H-4), 6.71 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=14.4 Hz, 1H, CH$^{\beta}$=), 7.23 (dd, $^3J_{(H\text{-}5,H\text{-}4)}$=3.4 Hz, $^4J_{(H\text{-}5,H\text{-}3)}$=1.7 Hz, 1H, H-5), 7.24–7.26 (m, 1H, H^p, Ph_{styryl}), 7.33–7.40 (m, 4H, Ho, H^m, Ph_{styryl}), 7.40 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=14.4 Hz, 1H, CH$^{\alpha}$=), 7.35–7.45 (m, 5H, H$^{o\prime}$, H$^{m\prime}$, H$^{p\prime}$, $Ph_{pyrrole}$) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$) for *Z*-isomer: δ=109.2 (C-3, pyrrole), 109.5 (C-4, pyrrole), 122.1 (C-β), 122.7 (C-5, pyrrole), 126.3 (C-α), 126.7 (C$^{p\prime}$, $Ph_{pyrrole}$), 127.7 (C^p, Ph_{styryl}), 128.2 (C$^{o\prime}$, $Ph_{pyrrole}$), 128.3 (C^m, Ph_{styryl}), 128.3 (C$^{m\prime}$, $Ph_{pyrrole}$), 128.7 (Co, Ph_{styryl}), 132.8 (C$^{i\prime}$, $Ph_{pyrrole}$), 133.6 (C-2, pyrrole), 134.5 (C^i, Ph_{styryl}); for *E*-isomer: δ=110.3 (C-3, pyrrole), 110.3 (C-4, pyrrole), 116.4 (C-β), 118.9 (C-5, pyrrole), 125.9 (C-α), 126.0 (Co, Ph_{styryl}), 126.8 (C^p, Ph_{styryl}), 127.5 (C$^{p\prime}$, $Ph_{pyrrole}$), 128.7 (C^m, Ph_{styryl}), 128.7 (C$^{m\prime}$, $Ph_{pyrrole}$), 129.3 (C$^{o\prime}$, $Ph_{pyrrole}$), 132.4 (C$^{i\prime}$, $Ph_{pyrrole}$), 134.6 (C-2, pyrrole), 135.8 (C^i, Ph_{styryl}) ppm. ^{15}N NMR (40.5 MHz, $CDCl_3$) for *Z*-isomer: δ=−218.5; for *E*-isomer: δ=−211.5 ppm. Anal. Calcd for $C_{18}H_{15}N$: C, 88.13; H, 6.16; N, 5.71. Found: C, 88.27; H, 6.33; N, 5.49.

*4.2.14. 2-Phenyl-1-[(Z/E)-2-(3-fluorophenyl)ethenyl]-1H-pyrrole (**3m**).* Yield: 0.321 g (61%). Individual *Z*-isomer is red oil (silica gel, eluent—benzene); R_f (25% Et_2O/benzene) 0.89; *E*-isomer was detected by ^{1}H NMR. IR (film): 1651, 1610, 1582, 1494, 1486, 1467, 1441, 1415, 1320, 1251, 1178, 1131, 1077, 879, 787, 757, 717, 697, 693, 663, 635, 522 cm^{-1}. ^{1}H NMR (400.1 MHz, $CDCl_3$) for *Z*-isomer: δ=6.20 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=9.1 Hz, 1H, CH$^{\beta}$=), 6.24 (dd, $^3J_{(H\text{-}4,H\text{-}3)}$=3.4 Hz, $^3J_{(H\text{-}4,H\text{-}5)}$=2.9 Hz, 1H, H-4), 6.38 (dd, $^3J_{(H\text{-}3,H\text{-}4)}$=3.4 Hz, $^4J_{(H\text{-}3,H\text{-}5)}$=1.7 Hz, 1H, H-3), 6.67 (dd, $^3J_{(H\text{-}5,H\text{-}4)}$=2.9 Hz, $^4J_{(H\text{-}5,H\text{-}3)}$=1.7 Hz, 1H, H-5), 6.71 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=9.1 Hz, 1H, CH$^{\alpha}$=), 6.85–6.87 (m, 1H, H-2, Ph_{styryl}), 6.92–6.94 (m, 1H, H-4, Ph_{styryl}), 6.96–6.98 (m, 1H, H-6, Ph_{styryl}), 7.20–7.24 (m, 1H, H-5, Ph_{styryl}), 7.26–7.30 (m, 1H, H$^{p\prime}$, $Ph_{pyrrole}$), 7.34–7.38 (m, 2H, H$^{m\prime}$, $Ph_{pyrrole}$), 7.44–7.48 (m, 2H, H$^{o\prime}$, $Ph_{pyrrole}$); for *E*-isomer: δ=6.35 (dd, $^3J_{(H\text{-}3,H\text{-}4)}$=3.3 Hz, $^4J_{(H\text{-}3,H\text{-}5)}$=1.6 Hz, 1H, H-3), 6.38 (dd, $^3J_{(H\text{-}4,H\text{-}3)}$=3.3 Hz, $^3J_{(H\text{-}4,H\text{-}5)}$=2.9 Hz, 1H, H-4), 6.64 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=14.7 Hz, 1H, CH$^{\beta}$=), 6.80–6.90 (m, 3H, H-2, H-4, H-6, Ph_{styryl}), 7.17–7.21 (m, 1H, H-5, Ph_{styryl}), 7.23 (dd, $^3J_{(H\text{-}5,H\text{-}4)}$=2.9 Hz, $^4J_{(H\text{-}5,H\text{-}3)}$=1.6 Hz, 1H, H-5), 7.30–7.40 (m, 5H, H$^{o\prime}$, H$^{m\prime}$, H$^{p\prime}$, $Ph_{pyrrole}$), 7.42 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=14.7 Hz, 1H, CH$^{\alpha}$=) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$) for *Z*-isomer: δ=109.7 (C-3, pyrrole), 114.7 (d, $^2J_{(C,F)}$=21.3 Hz, C-4, Ph_{styryl}), 115.5 (d, $^2J_{(C,F)}$=22.3 Hz, C-2, Ph_{styryl}), 121.0 (C-β), 124.6 (d, $^4J_{(C,F)}$=2.8 Hz, C-6, Ph_{styryl}), 126.9 (C$^{p\prime}$, $Ph_{pyrrole}$), 127.5 (C-α), 128.3 (C$^{o\prime}$, $Ph_{pyrrole}$), 128.4 (C$^{m\prime}$, $Ph_{pyrrole}$), 129.9 (d, $^3J_{(C,F)}$=8.4 Hz, C-5, Ph_{styryl}), 132.8 (C$^{i\prime}$, $Ph_{pyrrole}$), 133.9 (C-2, pyrrole), 136.8 (d, $^3J_{(C,F)}$=8.2 Hz, C-1, Ph_{styryl}), 162.8 (d, $^1J_{(C,F)}$=245.6 Hz, C-3, Ph_{styryl}) ppm. ^{15}N NMR (40.5 MHz, $CDCl_3$) for *Z*-isomer: δ=−219.1 ppm. Anal. Calcd for $C_{18}H_{14}FN$: C, 82.11; H, 5.36; F, 7.22; N, 5.32. Found: C, 82.25; H, 5.48; F, 7.08; N, 5.21.

*4.2.15. 2-Phenyl-1-[(Z/E)-2-(2-pyridinyl)ethenyl]-1H-pyrrole (**3n**).* Yield: 0.262 g (53%); yellow oil (mixture of *E*- and *Z*-isomers), (Al_2O_3, eluent—hexane); R_f (25% Et_2O/hexane) 0.48. IR (film): 3079, 3060, 2929, 1650, 1602, 1585, 1563, 1496, 1465, 1434, 1415, 1328, 1307, 1286, 1240, 1172, 1150, 1078, 1051, 991, 980, 949, 915, 868, 841, 795, 786, 759, 741, 717, 699, 663, 639, 617, 607, 568, 514 cm^{-1}. ^{1}H NMR (400.1 MHz, $CDCl_3$) for *Z*-isomer: δ=6.23 (dd, $^3J_{(H\text{-}4,H\text{-}3)}$=3.4 Hz, $^3J_{(H\text{-}4,H\text{-}5)}$=3.0 Hz, 1H, H-4), 6.38 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=9.3 Hz, 1H, CH$^{\beta}$=), 6.39 (dd, $^3J_{(H\text{-}3,H\text{-}4)}$=3.4 Hz, $^4J_{(H\text{-}3,H\text{-}5)}$=1.6 Hz, 1H, H-3), 6.77 (dd, $^3J_{(H\text{-}5,H\text{-}4)}$=3.0 Hz, $^4J_{(H\text{-}5,H\text{-}3)}$=1.6 Hz, 1H, H-5), 6.85 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=9.3 Hz, 1H, CH$^{\alpha}$=), 7.11–7.18 (m, 2H, H-3, H-5, pyridine), 7.26–7.30 (m, 1H, H$^{p\prime}$, Ph), 7.35–7.38 (m, 2H, H$^{m\prime}$, Ph), 7.45–7.49 (m, 2H, H$^{o\prime}$, Ph), 7.54–7.58 (m, 1H, H-4, pyridine), 8.57–8.61 (m, 1H, H-6, pyridine); for *E*-isomer: δ=6.34 (dd, $^3J_{(H\text{-}3,H\text{-}4)}$=3.5 Hz, $^4J_{(H\text{-}3,H\text{-}5)}$=1.6 Hz, 1H, H-3), 6.38 (dd, $^3J_{(H\text{-}4,H\text{-}3)}$=3.5 Hz, $^3J_{(H\text{-}4,H\text{-}5)}$=3.0 Hz, 1H, H-4), 6.71 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=14.2 Hz, 1H, CH$^{\beta}$=), 7.07–7.11 (m, 1H, H-5, pyridine), 7.19–7.23 (m, 1H, H-3, pyridine), 7.28 (dd, $^3J_{(H\text{-}5,H\text{-}4)}$=3.0 Hz, $^4J_{(H\text{-}5,H\text{-}3)}$=1.6 Hz, 1H, H-5), 7.35–7.39 (m, 1H, H$^{p\prime}$, Ph), 7.44–7.46 (m, 4H, H$^{o\prime}$, H$^{m\prime}$, Ph), 7.59–7.63 (m, 1H, H-4, pyridine), 7.94 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=14.2 Hz, 1H, CH$^{\alpha}$=), 8.47–8.51 (m, 1H, H-6, pyridine) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$) for *Z*-isomer: δ=109.8 (C-3, pyrrole), 109.9 (C-4, pyrrole), 121.9 (C-β), 122.1 (C-5, pyridine), 122.9 (C-5, pyrrole), 123.7 (C-3, pyridine), 127.0 (C$^{p\prime}$, Ph), 128.4 (C$^{o\prime}$, Ph), 128.5 (C$^{m\prime}$, Ph), 129.0 (C-α), 132.6 (C$^{i\prime}$, Ph), 134.1 (C-2, pyrrole), 136.1 (C-4, pyridine), 149.6 (C-6, pyridine), 154.1 (C-2, pyridine); for *E*-isomer: δ=110.9 (C-3, pyrrole), 111.2 (C-4, pyrrole), 114.9 (C-β), 118.8 (C-5, pyrrole), 121.3 (C-3, pyridine), 121.5 (C-5, pyridine), 127.5 (C$^{p\prime}$, Ph), 128.7 (C$^{m\prime}$, Ph), 129.4 (C$^{o\prime}$, Ph), 129.6 (C-α), 132.3 (C$^{i\prime}$, Ph), 135.3 (C-2, pyrrole), 136.6 (C-4, pyridine), 149.5 (C-6, pyridine), 154.9 (C-2, pyridine) ppm. ^{15}N NMR (40.5 MHz, $CDCl_3$) for *Z*-isomer: δ=−218.5 (pyrrole), −69.2 (pyridine); for *E*-isomer: δ=−211.2 (pyrrole), −81.9 (pyridine) ppm. Anal. Calcd for $C_{17}H_{14}N_2$: C, 82.90; H, 5.73; N, 11.37. Found: C, 82.73; H, 5.54; N, 11.02.

*4.2.16. 1-[(Z/E)-2-Phenylethenyl]-2-(2-thienyl)-1H-pyrrole (**3o**).* Yield: 0.256 g (51%). Individual *Z*-isomer is pale yellow oil (Al_2O_3, eluent—hexane); R_f (25% Et_2O/hexane) 0.75; *E*-isomer was detected by NMR. IR (film) for *Z*-isomer: 1648, 1574, 1505, 1494, 1465, 1448, 1432, 1409, 1346, 1299, 1204, 1162, 1073, 1029, 944, 843, 781, 693, 605, 559, 498 cm^{-1}. ^{1}H NMR (400.1 MHz, $CDCl_3$) for *Z*-isomer: δ=6.15 (dd, $^3J_{(H\text{-}4,H\text{-}3)}$=3.4 Hz, $^3J_{(H\text{-}4,H\text{-}5)}$=2.9 Hz, 1H, H-4), 6.32 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=9.1 Hz, 1H, CH$^{\beta}$=), 6.41 (dd, $^3J_{(H\text{-}3,H\text{-}4)}$=3.4 Hz, $^4J_{(H\text{-}3,H\text{-}5)}$=1.5 Hz, 1H, H-3), 6.59 (dd, $^3J_{(H\text{-}5,H\text{-}4)}$=2.9 Hz, $^4J_{(H\text{-}5,H\text{-}3)}$=1.5 Hz, 1H, H-5), 6.74 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=9.1 Hz, 1H, CH$^{\alpha}$=), 7.01 (dd, $^3J_{(H\text{-}4',H\text{-}5')}$=5.1 Hz, $^3J_{(H\text{-}3',H\text{-}4')}$=3.7 Hz, 1H, H-4′, thiophene), 7.09 (dd, $^3J_{(H\text{-}3',H\text{-}4')}$=5.1 Hz, $^4J_{(H\text{-}3',H\text{-}5')}$=1.2 Hz, 1H, H-3′, thiophene), 7.09–7.13 (m, 2H, Ho, Ph), 7.18–7.22 (m, 1H, H^p, Ph), 7.21 (dd, $^3J_{(H\text{-}4',H\text{-}5')}$=5.1 Hz, $^4J_{(H\text{-}3',H\text{-}5')}$=1.2 Hz, 1H, H-5′, thiophene), 7.21–7.25 (m, 2H, H^m, Ph); for *E*-isomer: δ=6.30 (dd, $^3J_{(H\text{-}4,H\text{-}3)}$=3.4 Hz, $^3J_{(H\text{-}4,H\text{-}5)}$=2.8 Hz, 1H, H-4), 6.37 (dd, $^3J_{(H\text{-}3,H\text{-}4)}$=3.4 Hz, $^4J_{(H\text{-}3,H\text{-}5)}$=1.5 Hz, 1H, H-3), 6.65 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=14.4 Hz, 1H, CH$^{\beta}$=), 7.03 (dd, $^3J_{(H\text{-}3',H\text{-}4')}$=3.7 Hz, $^4J_{(H\text{-}3',H\text{-}5')}$=1.2 Hz, 1H, H-3′, thiophene), 7.08 (dd, $^3J_{(H\text{-}4',H\text{-}5')}$=5.1 Hz, $^3J_{(H\text{-}3',H\text{-}4')}$=3.7 Hz, 1H, H-4′, thiophene), 7.19 (dd, $^3J_{(H\text{-}5,H\text{-}4)}$=2.8 Hz, $^4J_{(H\text{-}5,H\text{-}3)}$=1.5 Hz, 1H, H-5), 7.23–7.27 (m, 1H, H^p, Ph), 7.31 (dd, $^3J_{(H\text{-}4',H\text{-}5')}$=5.1 Hz, $^4J_{(H\text{-}3',H\text{-}5')}$=1.2 Hz, 1H, H-5′, thiophene), 7.34–7.36 (m, 4H, Ho, H^m, Ph), 7.50 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=14.4 Hz,

1H, CH^{α}=) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$) for *Z*-isomer: δ=109.8 (C-4, pyrrole), 110.1 (C-3, pyrrole), 122.8 (C-5, pyrrole), 124.3 (C-β), 124.5 (C-5′, thiophene), 125.0 (C-3′, thiophene), 125.9 (C-α), 126.7 (C-2, pyrrole), 127.4 (C-4′, thiophene), 128.0 (C^{p}, Ph), 128.5 (C^{m}, Ph), 128.9 (Co, Ph), 134.3 (C^{i}, Ph), 134.9 (C-2′, thiophene); for *E*-isomer: δ=110.6 (C-4, pyrrole), 111.7 (C-3, pyrrole), 117.2 (C-β), 119.4 (C-5, pyrrole), 125.5 (C-α), 125.7 (C-5′, thiophene), 126.1 (Co, Ph), 126.7 (C-3′, thiophene), 127.3 (C-2, pyrrole), 127.3 (C^{p}, Ph), 127.6 (C-4′, thiophene), 127.7 (C^{m}, Ph), 133.9 (C-2′, thiophene), 135.8 (C^{i}, Ph) ppm. ^{15}N NMR (40.5 MHz, $CDCl_3$) for *Z*-isomer: δ=−218.4 ppm; for *E*-isomer: δ=−210.6 ppm. Anal. Calcd for $C_{16}H_{13}NS$: C, 76.46; H, 5.21; N, 5.57; S, 12.76. Found: C, 76.29; H, 5.32; N, 5.54; S, 12.47.

*4.2.17. 1-[(E)-2-(2-Pyridinyl)ethenyl]-2-(2-pyridinyl)-1H-pyrrole (**3p**).* Yield: 0.107 g (48%). Individual *E*-isomer is pale brown cereous oil (silica gel, eluent—10% Et_2O/benzene); R_f (25% Et_2O/benzene) 0.45; *Z*-isomer was detected by ^1H NMR in the crude product. IR (film) for *E*-isomer: 3102, 3080, 3047, 3003, 1651, 1645, 1587, 1563, 1484, 1471, 1448, 1412, 1327, 1313, 1249, 1236, 1201, 1182, 1150, 1095, 1080, 1068, 1046, 999, 949, 841, 786, 769, 741, 719, 698, 610, 604, 517 cm^{-1}. ^1H NMR (400.1 MHz, $CDCl_3$) for *Z*-isomer: δ=6.19 (dd, $^3J_{(H\text{-}4,H\text{-}3)}$=3.3 Hz, $^3J_{(H\text{-}4,H\text{-}5)}$=2.9 Hz, 1H, H-4), 6.40 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=9.2 Hz, 1H, CH^{β}=), 6.71 (dd, $^3J_{(H\text{-}3,H\text{-}4)}$=3.3 Hz, $^4J_{(H\text{-}3,H\text{-}5)}$=1.4 Hz, 1H, H-3), 7.00 (dd, $^3J_{(H\text{-}5,H\text{-}4)}$=2.9 Hz, $^4J_{(H\text{-}5,H\text{-}3)}$=1.4 Hz, 1H, H-5), 6.95 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=9.2 Hz, 1H, CH^{α}=), 7.00–7.10 (m, 2H, H-5, H-5′, pyridine), 7.50–7.65 (m, 4H, H-4, H-3, H-4′, H-3′ pyridine), 8.52–8.60 (m, 2H, H-6, H-6′, pyridine); for *E*-isomer: δ=6.36 (dd, $^3J_{(H\text{-}4,H\text{-}3)}$=3.7 Hz, $^3J_{(H\text{-}4,H\text{-}5)}$=3.2 Hz, 1H, H-4), 6.64 (dd, $^3J_{(H\text{-}3,H\text{-}4)}$=3.7 Hz, $^4J_{(H\text{-}3,H\text{-}5)}$=1.6 Hz, 1H, H-3), 6.73 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=14.4 Hz, 1H, CH^{β}=), 7.06 (m, 1H, H-5, pyridine), 7.11–7.15 (m, 1H, H-5′, $pyridine_{pyrrole}$), 7.27–7.31 (m, 1H, H-3, pyridine), 7.35 (dd, $^3J_{(H\text{-}5,H\text{-}4)}$=3.2 Hz, $^4J_{(H\text{-}5,H\text{-}3)}$=1.6 Hz, 1H, H-5), 7.53–7.60 (m, 2H, H-3′, $pyridine_{pyrrole}$; H-4, pyridine), 7.63–7.67 (m, 1H, H-4′, $pyridine_{pyrrole}$), 8.50–8.54 (m, 1H, H-6, pyridine), 8.63–8.67 (m, 1H, H-6′, $pyridine_{pyrrole}$), 8.85 (d, $^3J_{(H\text{-}\alpha,H\text{-}\beta)}$=14.4 Hz, 1H, CH^{α}=) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$) for *E*-isomer: δ=110.8 (C-4, pyrrole), 112.9 (C-3, pyrrole), 115.1 (C-β), 120.5 (C-5, pyrrole), 120.8 (C-3, pyridine), 120.9 (C-5′, $pyridine_{pyrrole}$), 121.2 (C-5, pyridine), 122.4 (C-3′, $pyridine_{pyrrole}$), 131.3 (C-α), 132.8 (C-2, pyrrole), 136.3 (C-4, pyridine), 136.4 (C-4′, $pyridine_{pyrrole}$), 148.9 (C-6′, $pyridine_{pyrrole}$), 149.3 (C-6, pyridine), 151.6 (C-2′, $pyridine_{pyrrole}$), 155.1 (C-2, pyridine) ppm. ^{15}N NMR (40.5 MHz, $CDCl_3$) for *E*-isomer: δ=−211.8 (pyrrole), −79.6 (N-2, pyridine), −74.6 (N-2′, $pyridine_{pyrrole}$) ppm. Anal. Calcd for $C_{16}H_{13}N_3$: C, 77.71; H, 5.30; N, 16.99. Found: C, 77.83; H, 5.49; N, 17.04.

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