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NOVEL 1,1',5,5'-TETRAARYL-2,2'-BIPYRROLES: THEIR SYNTHESIS AND PHYSICAL PROPERTIES

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Abstract – We report a new type of 2,2'-bipyrrole derivatives that bear four aryl groups at the 1, 1', 5 and 5' positions. These compounds were synthesized by two routes: (i) the reaction of 1,8-diaryl-2,7-ditosyl-1,7-octadiene-3,5-diynes (**4**) with anilines was performed in the presence of CuCl at 150 ^{o}C; (ii) the above compound (**4**) was converted to a 1-aryl-4-(1,5-diaryl-2-pyrrolyl)butadiynes (**7**), which were subjected to the reaction with anilines in the presence of CuCl in DMF at 150 ^{o}C. The conformation between the two pyrrole rings of the 1,1',5,5'-tetraaryl-2,2'-bipyrrole is also discussed from X-Ray crystal structure and UV-VIS spectrum.

INTRODUCTION

Development of new π-conjugated systems is a significant subject of many recent studies because the systems promise numerous optical, electrochemical, and electric properties. Among many kinds of π-systems, a pyrrole ring plays an important role in the interesting features of π-functional materials[1] such as polypyrroles,[2] phthalocyanines,[3] and porphyrins.[4] The pyrrole ring is so fairly electron-rich to donate its π-electron(s) intra- or intermolecularly. Recently, we reported a novel π-system, 1-aryl-2,5-di(2-thienyl)pyrrole,[5] in which the 1-aryl group contributes effectually toward developing the π-system as electroluminescent materials, metal-lustrous pigments, and so on.[6] This is because the 1-aryl group stands perpendicular to the parent π-system so that affects the coplanarity to a lesser extent, impedes the stacking of the π-systems, and as a result increases the solubility of the π-system. Against these background, we were interested in 1,1',5,5'-tetraaryl-2,2'-bipyrroles (**I**). Some 2,2'-bipyrrole ring

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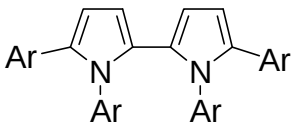
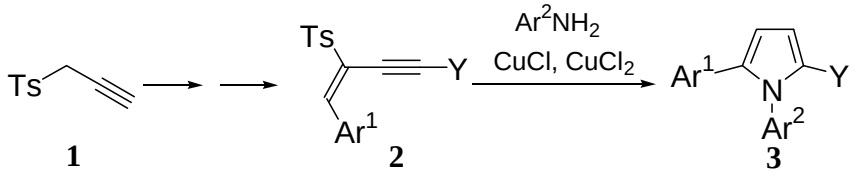
This paper is dedicated to the memory of the Emeritus Professor Kenji Koga of Tokyo University.

systems are also known to exhibit intriguing physical properties for developing functional materials.[7] However, to our surprise, there are no reports describing these compounds (**I**). Here, we report the synthetic route of **I** and their some physical properties.



I

Hitherto, several synthetic methods have been reported to form the 2,2'-bipyrrole derivatives:[8] (i) metal-catalyzed homo-coupling reactions with 2-halopyrroles or pyrrole (Cu,[8b,c,d,g,j] Ni,[8b,h] Pd[8m]); (ii) Paal-Knorr type condensation reaction;[8l] (iii) the coupling of pyrrolidinones with pyrrole;[8e,k] and (iv) the trifluoromethanesulfonate-mediated reaction of donor-acceptor cyclopropanes with 2-cyanopyrroles.[8a] These methods have been performed for synthesizing 1,1'-unsubstituted or 1,1'-alkyl-substitued 2,2'-bipyrroles. In a recent paper, we reported the preparation of 2,5-disubstituted 1-arylpyrroles (**3**) by the Cu ion-mediated reaction of anilines with 1-aryl-2-tosyl-1-alken-3-ynes (**2**) that are easily prepared from 3-tosylpropyne (**1**) (Scheme 1).[9] Thus, we decided to employ this type of 1-arylpyrrole ring construction for synthesis of **I**.

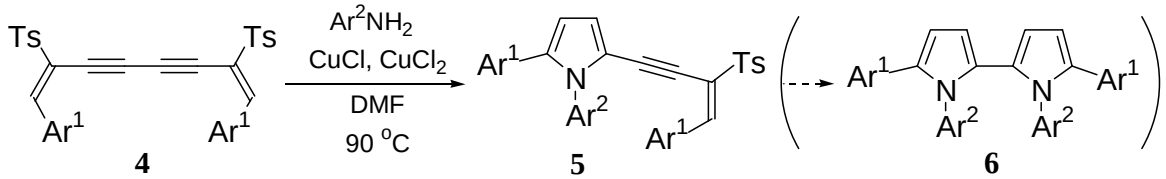


1 **2** **3**

Scheme 1

RESULTS AND DISCUSSION

As reported previously,[9] a 1,8-diaryl-2,7-ditosyl-1,7-octadiene-3,5-diyne (**4**), which was prepared from **1** (see EXPERIMENTAL), reacted with anilines (3.2 equiv.) in DMF (the concentration of **4**: 0.2 M) in the presence of CuCl (1.6 equiv.) and $CuCl_2$ (0.16 equiv.) at 90 °C to give a monopyrrole derivative (**5**). Under these conditions, the corresponding 2,2'-bipyrrole (**6**) was not detected in the reaction mixture (Scheme 2).



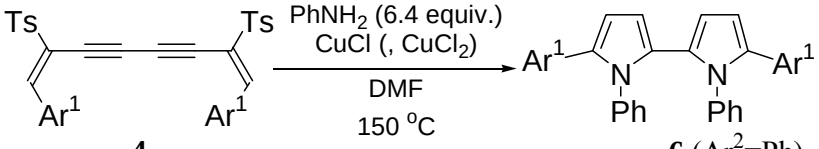
4 **5** **6**

Scheme 2

First of all, the reaction temperature was raised from 90 °C to 150 °C and 6.4 mol-equiv. of aniline was used. The results under various conditions are summarized in Table 1. In the reaction using 0.2 M concentration of **4** (Ar^1=Ph), the 2,2'-bipyrrole derivative (**6**; Ar^1=Ar^2=Ph) was formed, but the yield was very low (5%) and **5** (Ar^1=Ar^2=Ph) was obtained in 42% yield. In this reaction, the concentrations of the

substrate and the reagents become lower as the reaction proceeds. When the initial concentration of **4** (Ar^1=Ph) was increased up to 5.0 M, the expected **6** (Ar^1=Ph) was obtained in 20% yield. It is noteworthy that, in the absence of $CuCl_2$, the yield of the desired 2.2'-bipyrrole (**6**; Ar^1=Ph) was slightly raised to 28%.

Table 1. Direct Synthesis of 2,2'-Bipyrroles (**6**) from **4**.

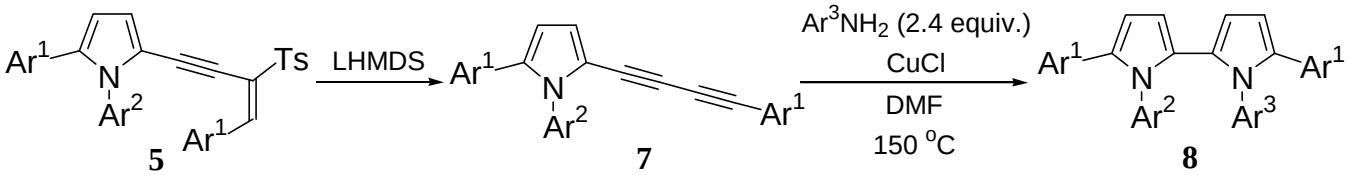


4 **6** (Ar^2=Ph)

Entry	Ar^1	CuCl (equiv.)	$CuCl_2$ (equiv.)	Conc. (M)	Yield (%)
1	Ph	3.2	0.32	0.2	5[a]
2		3.2	0.32	5.0	20
3		3.2	0	5.0	28
4	*m*-$MeOC_6H_4$	3.2	0	5.0	23

a **5** (Ar^1=Ph, Ar^2=Ph) was obtained in 42%.

In spite of our effort to gain a higher yield of the expected **6** under various reaction conditions (reaction temperature and reagent amount), the best yield was below 30%. This is probably because the high reaction temperature (150 °C) is not suitable to the reaction of aniline with the 2-tosyl-1-alken-3-yne part of **4** and **5**. Therefore, we examined the stepwise sequence *via* a diyne intermediate (**7**) (Scheme 3): (i) the pure monopyrrole (**5**) that was formed under mild conditions (at 90 °C) is isolated in a pure form; (ii) the pure **5** is converted to the diyne intermediate (**7**); and then (iii) the reaction of **7** with anilines is performed under forced conditions. This sequence is so advantageous over the above-mentioned synthesis that we can select different aryl groups at the 1 and 1' positions of the 2,2'-bipyrrole ring.



5 **7** **8**

Scheme 3

As described in the literature,[9] various monopyrroles (**5**) can be prepared by the reaction of **4** with anilines (3.2 equiv.), CuCl (1.6 equiv.), and $CuCl_2$ (0.16 equiv.) in 0.2 M DMF at 90 °C. Furthermore, we synthesized the monopyrroles (**5**) that have *p*-bromophenyl group. The results are

Table 2. Preparation of Diyne Compounds (**7**) from **4**.

Entry	Ar^1	Ar^2	**4** → **5**[a]		**5** → **7**[e]
			Time (h)	Yield (%)	Yield (%)
1	Ph	Ph	8	62[b]	80
2	*p*-$MeOC_6H_4$	*p*-BrC_6H_4	9	8[c]	—
3	*m*-$MeOC_6H_4$	*p*-BrC_6H_4	8	64[d]	66
4	*p*-BrC_6H_4	*p*-$MeOC_6H_4$	10	39[d]	64

a Conditions: **4** (1.0 equiv.), Ar^2NH_2 (3.2 equiv.), CuCl (1.6 equiv.), and $CuCl_2$ (0.16 equiv.); DMF (0.2 M); 90 °C. b Ref. 9. c The starting material was recovered in 69%. d CuBr/$CuBr_2$ was used instead of CuCl/$CuCl_2$.
e Conditions: **5** (1 equiv.) and LHMDS (10 equiv.); THF; rt; 4 h.

summarized in Table 2. In the reaction of **4** (Ar^1=*p*-$MeOC_6H_4$), the monopyrrole (**5**; Ar^1= *p*-$MeOC_6H_4$) was given in a low yield (8%). It is likely that the electron-donating ability of *p*-MeO group retards the nucleophilic attack of aniline on the 1-position of **4**. Since a Br-Cl halogen exchange occurred in the reaction of **4** (Ar^1=*p*-BrC_6H_4), we employed CuBr (1.6 equiv.) and $CuBr_2$ (0.16 equiv.) (Entry 4 in Table 2). The thus-obtained **5** was subjected to the dehydrosulfonylation reaction with an excess amount (10 equiv.) of LHMDS to give the diyne (**7**) in good to high yields (Table 2).[10]

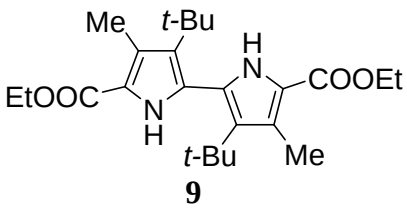
It was reported that a conjugated alkadiyne reacted with ammonia, alkylamines, or anilines by a catalytic amount of CuCl to give a pyrrole derivative.[11] According to this procedure, we subjected the diyne (**7**) to the reaction with anilines (2.4 equiv.) and CuCl (1.2 equiv.) in DMF (5.0 M) at 150 °C. As the results are shown in Table 3, the desired 1,1',5,5'-tetraaryl-2,2'-bipyrrole derivatives (**8**) were obtained. The solvent (DMF) is not always necessary. In case the aniline itself is liquid, the aniline can be utilized as a solvent. This is the case when aniline or *p*-fluoroaniline was used in the reaction (Entries 2 and 3 in Table 3). It is noteworthy that CuBr could be also employed instead of CuCl, but the yield of **6** was comparable as shown in Table 3 (Entry 8).

Table 3. Formation of 2,2'-Bipyrroles (**8**) from **7**.[a]

Entry	Ar^1	Ar^2	Ar^3	Yield (%)
1	Ph	Ph	Ph	82
2	Ph	Ph	Ph	82[b]
3	Ph	Ph	*p*-FC_6H_4	84[b]
4	Ph	Ph	*p*-$MeOC_6H_4$	42
5	Ph	Ph	*p*-AcC_6H_4	62
6	Ph	Ph	*p*-$NO_2C_6H_4$	53
7	*m*-$MeOC_6H_4$	*p*-BrC_6H_4	*p*-BrC_6H_4	73
8	*p*-BrC_6H_4	*p*-$MeOC_6H_4$	*p*-$MeOC_6H_4$	48[c]

a Conditions: **7** (1.0 equiv.), Ar^3NH_2 (2.4 equiv.), and CuCl (1.2 equiv.); DMF (5.0 M); 150 °C; 1 h. b DMF was not used. c CuBr was used instead of CuCl.

With the desired 1,1',5,5'-tetraaryl-2,2'-bipyrroles in hand, we investigated the conformation around the 2-2' bond of the 1,1',5,5'-tetraaryl-2,2'-bipyrrole. There are some literatures that report the conformation of 2,2'-bipyrrole derivatives (**9**-**12**) from their X-Ray crystallographic analyses. The conformation between the pyrrole rings in the former two 2,2'-bipyrroles (**9**[8c] and **10**[8h]) is largely twisted probably due to the steric hindrance between the bulky groups (*tert*-butyl or bromo group) at the 3 and 3' positions, while the latter two (**11**[7c] and **12**[8g]) adopt a flat conformation because of the



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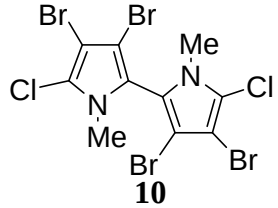

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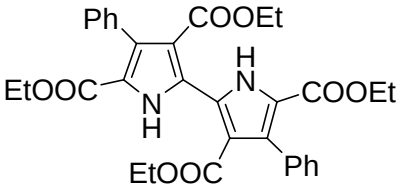

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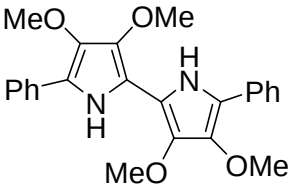

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intramolecular hydrogen bonding. Fortunately, we obtained single crystals of **6** (Ar^1=Ar^2=Ph) with a good quality, which were given by crystallization from ethyl acetate-hexane. The crystal structure of **6** (Ar^1=Ar^2=Ph) was shown in Figure 1.[12]

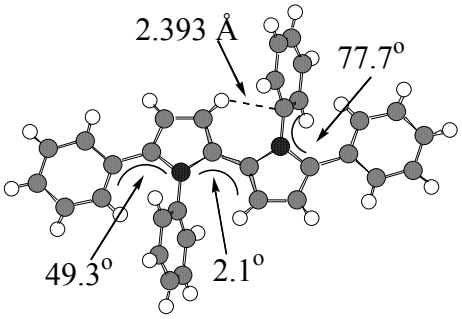

Figure 1. The crystal structure of **6** (Ar^1=Ar^2=Ph).

Interestingly, the 2,2'-bipyrrole π-system of **6** (Ar^1=Ar^2=Ph) adopts a planar conformation with an anti relationship between the two pyrrole rings (torsion angle of N1-C2-C2'-C3': 2.1°). Four phenyl rings are twisted from the 2,2'-bipyrrole π -system (dihedral angle: 49.3° and 77.7°, respectively). The so-called CH-π interaction[13] was observed between the *ipso*-carbon of phenyl group substituted at 1 (and 1') position and the proton at the 3 position of the pyrrole (C…H: 2.393 Å). In order to obtain more information about the conformation of the 2,2'-bipyrrole π-system, a solution UV-VIS spectrum of **6** (Ar^1=Ar^2=Ph) was measured in THF (Figure 2). If two pyrrole rings are fully twisted, the absorption maxima of **6** (Ar^1=Ar^2=Ph) would be approximately same to that of 1,2-diphenylpyrrole. This estimation was supported by the fact that the λ_{max} (288 nm) of **9** that adopts a twisted conformation in a crystalline state and in a solution is similar to that (284 nm) of 3-*tert*-butyl-2,4-dimethyl-5-ethoxycarbonylpyrrole.[8c] In contrast, the planar conformation of **11** remains unchanged in a CH_2Cl_2 solution and in a crystalline state because of the intramolecular hydrogen bonding. Indeed, its λ_{max} was shown at a longer wavelength (346 nm) than that (275 nm) of 3,5-bis(ethoxycarbonyl)-4-phenylpyrrole in a solution.[5c] The λ_{max} of **6** (Ar^1=Ar^2=Ph) appeared at 304 nm with the absorption edge near 380 nm. The λ_{max} is longer only by 28 nm than that (280 nm) of 1,2-diphenylpyrrole.[14] A small difference between these absorption maxima suggests that two pyrrole rings of **6** (Ar^1=Ar^2=Ph) are largely twisted to one another. The most stable conformation of **6** (Ar^1=Ar^2=Ph) in a gas phase was calculated by the PM3 method. The calculated conformation is a twisted one (the dihedral angle of N1-C2-C2'-C3': 88.9°), as shown in Figure 3. Thus, we suppose that the

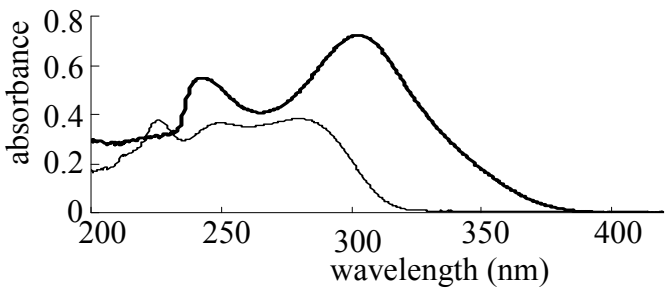

Figure 2. UV-VIS spectra of **6** (Ar^1=Ar^2=Ph) (bold line) and 1,2-diphenylpyrrole (narrow line).

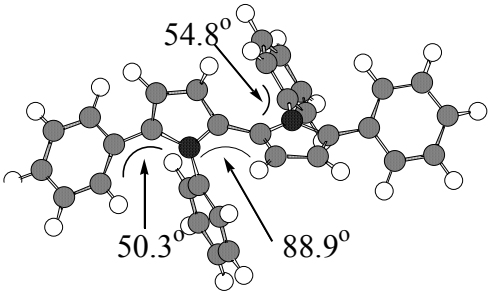

Figure 3. The most stable conformation of **6** (Ar^1 =Ar^2=Ph) calculated by PM 3 method.

coplanarity of two pyrrole rings of **6** (Ar^1=Ar^2=Ph) in a crystalline state is dissolved in a solution.

In conclusion, we synthesized a new type of 2,2'-bipyrrole derivatives (**6** and **8**) that bear four aryl groups at 1, 1', 5 and 5' positions starting from 1,8-diaryl-2,7-ditosyl-1,7-octadiene-3,5-diynes (**4**). The reaction of **4** with anilines in the presence of CuCl at an elevated temperature (150 °C) formed the desired **6** directly, but the yields are relatively lower (up to 28%). An alternative synthetic route from **4** to **6** is *via* a diyne intermediate (**7**), which forms **8** on treatment with anilines in the presence of CuCl in DMF at 150 °C. The conformation between the two pyrrole rings of the 1,1',5,5'-tetraaryl-2,2'-bipyrrole was also revealed from X-Ray crystal structure and UV-VIS spectrum: a flat conformation is adopted in a crystalline state, while a twisted conformation is predominant in a solution.

EXPERIMENTAL

General Procedures. Melting points were determined with Yanaco MP-J3 and values were uncorrected. NMR spectra were recorded at 300 MHz (proton) and at 75 MHz (carbon-13) on Varian GEMINI 2000 spectrometer with TMS as internal standard. *J*-Values are given in Hz. IR spectra were measured on a JASCO FT/IR-350 spectrophotometer. Elemental analyses (EA) and high-resolution mass spectroscopy (HRMS) were carried out by the Chemical Analysis Center of Chiba University.

Synthesis of (*E*)-1-phenyl-2-tosyl-1-buten-3-yne (2; Ar^1=Ph, Y=H). A Typical Procedure. To a solution of *n*-BuLi (14 mL, 1.6 *M* in hexane, 22 mmol) in dry THF (76 mL), was dropwise added a solution of 3-tosylpropyne (3.83 g, 19.7 mmol) in dry THF (20 mL) at –78 °C. After being stirred for 5 min at the same temperature, benzaldehyde (2.30 mL, 22.6 mmol) was added and then stirred for 5 min. After acetic anhydride (2.30 mL, 24 mmol) was added, the resulting mixture was stirred at –78 °C for 1 h and quenched with sat. aqueous NH_4Cl (100 mL). The mixture was extracted with diethyl ether (30 mL × 3) and the combined organic layers were dried over $MgSO_4$. Evaporation in vacuo and column chromatography (alumina; hexane : EtOAc = 3 : 1) provided **2** (Ar^1=Ph, Y=H) (3.67 g, 66%) as yellow solid. Recrystallization from hexane-EtOAc gave pale yellow crystals: mp 140.8-142.8 °C; ^{1}H NMR ($CDCl_3$) δ 2.44 (s, 3H), 3.70 (d-like, *J* = 0.7 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.40-7.46 (m, 3H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.96 (d, *J* = 8.9 Hz, 2H), 8.00 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 21.6, 75.8, 90.8, 123.7, 128.8 (×2), 129.8, 130.4, 131.8, 132.5, 135.8, 143.9, 144.8; IR (KBr/cm^{-1}) 3244, 3064, 2922, 2092, 1597, 1450, 1304, 1147, 1088, 820, 667, 563. *Anal.* Calcd for $C_{17}H_{14}O_2S$: C, 72.31; H, 5.00. Found: C, 72.23; H, 4.90.

(*E*)-1-(3-Methoxyphenyl)-2-tosyl-1-buten-3-yne (2; Ar^1=3-$MeOC_6H_4$, Y=H). Colorless crystals: mp 94.0-95.0 °C (hexane-EtOAc); ^{1}H NMR ($CDCl_3$) δ 2.44 (s, 3H), 3.72 (t-like, *J* = 0.7 Hz, 1H), 3.81 (s, 3H), 7.01 (ddd, *J* = 8.2, 2.6 and 0.8 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 1H,), 7.34 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 7.7 Hz, 1H), 7.62 (t-like, *J* = 2.1 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 2H), 7.98 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 21.6,

55.3, 76.0, 90.9, 114.3, 118.1, 123.4, 123.8, 128.7, 129.7 (×2), 133.6, 135.7, 143.8, 144.7, 159.6; IR (KBr/cm^{-1}) 3244, 3045, 2940, 2836, 2090, 1606, 1455, 1313, 1247, 1157, 667. *Anal*. Calcd for $C_{18}H_{16}O_3S$: C, 69.21; H, 5.16. Found: C, 69.19; H, 5.22.

(*E*)-1-(4-Methoxyphenyl)-2-tosyl-1-buten-3-yne (2; Ar^1=4-MeOC$_6$H$_4$, Y=H). Pale yellow crystals; mp 143.0-144.0 °C (hexane-EtOAc); ^{1}H NMR ($CDCl_3$) δ 2.44 (s, 3H), 3.68 (d-like, *J* = 0.7 Hz, 1H), 3.85 (s, 3H), 6.92 (d, *J* = 8.9 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.86 (d, *J* = 8.2 Hz, 2H), 7.94 (s, 1H), 7.96 (d, *J* = 8.9 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.5, 55.3, 76.2, 90.2, 114.2, 120.5, 125.2, 128.6, 129.7, 132.4, 136.2, 143.6, 144.5, 162.5; IR (KBr/cm^{-1}) 3252, 3066, 2934, 2838, 2091, 1592, 1512, 1316, 1265, 1153, 664. *Anal*. Calcd for $C_{18}H_{16}O_3S$: C, 69.21; H, 5.16. Found: C, 69.04; H, 5.11.

(*E*)-1-(4-Bromophenyl)-2-tosyl-1-buten-3-yne (2; Ar^1=4-BrC$_6$H$_4$, Y=H). Pale purple crystals: mp 109.5-110.5 °C (hexane-EtOAc); ^{1}H NMR ($CDCl_3$) δ 2.45 (s, 3H), 3.75 (d-like, *J* = 0.7 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.55 (d, *J* = 8.7 Hz, 2H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.93 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 21.6, 75.7, 91.5, 124.4, 126.3, 128.9, 129.8, 131.3, 131.6, 132.2, 135.5, 142.4, 145.0; IR (KBr/cm^{-1}) 3252, 3066, 2934, 2838, 2091, 1592, 1512, 1316, 1265, 1153, 664. *Anal*. Calcd for $C_{17}H_{13}O_2BrS$: C, 56.52; H, 3.63. Found: C, 56.36; H, 3.58.

Synthesis of (1*E*,7*E*)-1,8-diphenyl-2,7-ditosyl-1,7-ocutadiene-3,5-diyne (4; Ar^1=Ph). A Typical Procedure. After pyridine (37.0 mL) was added to a solution of $Cu(OAc)_2$ (3.34 g, 18.4 mmol) in dry MeOH (80.0 mL), the mixture was stirred at rt for 30 min. Further, a solution of **2** (Ar^1=Ph, Y=H) (2.59 g, 9.18 mmol) in dry MeOH (240 mL) was dropwise added over 30 min and the resulting mixture was stirred at room temperature for 3 h. The mixture was poured into 1 *M* H_2SO_4 (430 mL). The precipitated yellow solid (**4**; Ar^1=Ph) (2.30 g, 89%) was gathered by filtration and washed with MeOH. Recrystallization from EtOAc gave yellow crystals: mp 211.0-212.0 °C; ^{1}H NMR ($CDCl_3$) δ 2.46 (s, 6H), 7.37 (d, *J* = 8.1 Hz, 4H), 7.42-7.53 (m, 6H), 7.87 (d, *J* = 8.2 Hz, 4H), 7.91 (d, *J* = 7.1 Hz, 4H), 8.08 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 21.6, 78.3, 85.4, 123.5, 124.0, 128.8, 129.1, 130.0, 130.5, 132.5, 135.9, 145.2, 145.9; IR (KBr/cm^{-1}) 3064, 2924, 1589, 1450, 1319, 1153, 1088, 813, 665, 607, 563. *Anal*. Calcd for $C_{34}H_{26}O_4S_2$: C, 72.57; H, 4.66. Found: C, 72.32; H, 4.74.

(1*E*,7*E*)-1,8-Di(3-methoxyphenyl)-2,7-ditosyl-1,7-octadiene-3,5-diyne (4; Ar^1=3-MeOC$_6$H$_4$). Yellow crystals: mp 242.0-243.0 °C (EtOAc); ^{1}H NMR ($CDCl_3$) δ 2.47 (s, 6H), 3.78 (s, 6H), 7.05 (ddd, *J* = 7.8, 2.6 and 1.2 Hz, 2H), 7.34 (t, *J* = 8.1 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 4H,), 7.41 (d, *J* = 7.7 Hz, 2H), 7.57 (t-like, *J* = 1.8 Hz, 2H), 7.85 (d, *J* = 8.2 Hz, 4H), 8.04 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 21.6, 55.3, 78.4, 85.4, 113.8, 119.3, 123.6, 123.7, 128.7, 130.0 (×2), 133.7, 135.9, 145.2, 146.1, 159.9; IR (KBr/cm^{-1}) 3041, 2990, 2962, 2834, 1567, 1320, 1273, 1151, 1088, 665. *Anal.* Calcd for $C_{36}H_{30}O_6S_2$: C, 69.43; H, 4.86. Found: C, 69.32; H, 4.94.

(1*E*,7*E*)-1,8-Di(4-methoxyphenyl)-2,7-ditosyl-1,7-octadiene-3,5-diyne (4; Ar^1=4-$MeOC_6H_4$). Yellow crystals: mp 192.5-193.5 °C (EtOAc); ^{1}H NMR ($CDCl_3$) δ 2.46 (s, 6H), 3.88 (s, 6H), 6.95 (d, *J* = 8.8 Hz, 4H), 7.35 (d, *J* = 8.5 Hz, 4H), 7.86 (d, *J* = 8.4 Hz, 4H), 7.92 (d, *J* = 8.7 Hz, 4H), 8.00 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 21.6, 55.5, 78.6, 85.3, 114.5, 120.3, 125.4, 128.6, 129.9, 132.7, 136.4, 144.8, 145.5, 163.1; IR (KBr/cm^{-1}) 3033, 2963, 2840, 1582, 1511, 1317, 1266, 1176, 1149, 665. *Anal*. Calcd for $C_{36}H_{30}O_6S_2$: C, 69.43; H, 4.86. Found: C, 69.28; H, 4.75.

(1*E*,7*E*)-1,8-Di(4-bromophenyl)-2,7-ditosyl-1,7-octadiene-3,5-diyne (4; Ar^1=4-BrC_6H_4). Yellow crystals: mp 222.5-223.5 °C (EtOAc); ^{1}H NMR ($CDCl_3$) δ 2.48 (s, 6H), 7.38 (d, *J* = 8.0 Hz, 4H), 7.58 (d, *J* = 8.5 Hz, 4H), 7.77 (d, *J* = 8.7 Hz, 4H), 7.85 (d, *J* = 8.4 Hz, 4H), 8.02 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 21.7, 78.4, 85.7, 124.1, 127.1, 128.8, 130.0, 131.3, 131.6, 132.4, 135.6, 144.6, 145.4; IR (KBr/cm^{-1}) 3062, 2922, 1583, 1487, 1321, 1153, 1087, 813, 671, 582. *Anal.* Calcd for $C_{34}H_{24}O_4Br_2S_2$: C, 56.68; H, 3.36. Found: C, 56.61; H, 3.35.

Direct Synthesis of 1,1',5,5'-Tetraphenyl-2,2'-bipyrrole (6; Ar^1=Ar^2=Ph) from 4 (Ar^1=Ph). A Typical Procedure. A mixture of **4** (Ar^1=Ph) (113 mg, 0.20 mmol), aniline (0.12 mL, 1.3 mmol), and CuCl (64 mg, 0.64 mmol) in dry DMF (0.04 mL) was stirred at 150 °C for 1 h under N_2 atmosphere. The reaction mixture was cooled down to rt and $CHCl_3$ (5 mL) was added. The precipitated insoluble solid was filtered off and washed with $CHCl_3$ (about 5 mL). The filtrate and the washing were combined and evaporated in vacuo to give black solid (110 mg), which was subjected to column chromatography on silica gel (hexane : EtOAc = 3 : 1) to give **6** (Ar^1=Ar^2=Ph) (24.6 mg, 28%) as yellow solid. Recrystallization from hexane-EtOAc gave pale yellow crystals: mp 198.5-199.5 °C; ^{1}H NMR ($CDCl_3$) δ 6.31 (d, *J* = 3.6 Hz, 2H), 6.37 (d, *J* = 3.6 Hz, 2H), 6.59 (dd, *J* = 7.9 and 1.0 Hz, 4H), 6.96-7.11 (m, 16H); ^{13}C NMR ($CDCl_3$) δ 109.5, 113.2, 126.0, 126.2, 127.4, 127.8 (×2), 128.2, 128.4, 133.2, 134.7, 138.7; IR (KBr/cm^{-1}) 3053, 2781, 1597, 1496, 1375, 1236, 1072, 754, 696. *Anal*. Calcd for $C_{32}H_{24}N_2$: C, 88.04; H, 5.54; N, 6.42. Found: C, 87.77; H, 5.59; N, 6.29.

5,5'-Di(3-methoxyphenyl)-1,1'-diphenyl-2,2'-bipyrrole (6; Ar^1=3-$MeOC_6H_4$, Ar^2=Ph). Pale yellow crystals: mp 175.0-176.0 °C (hexane-EtOAc); ^{1}H NMR ($CDCl_3$) δ 3.52 (s, 6H), 6.29 (d, *J* = 3.6 Hz, 2H), 6.38 (d, *J* = 3.7 Hz, 2H), 6.46 (dd-like, *J* = 2.4 and 1.6 Hz, 2H), 6.59-6.65 (m, 8H), 7.00-7.08 (m, 8H); ^{13}C NMR ($CDCl_3$) δ 54.9, 109.5, 112.3, 113.2, 113.4, 120.9, 126.3, 127.4, 127.8, 128.3, 128.8, 134.4, 134.5, 138.8, 158.9; IR (KBr/cm^{-1}) 3056, 3008, 2951, 1599, 1498, 1487, 1371, 1219, 1038, 837, 771, 702. *Anal.* Calcd for $C_{34}H_{28}N_2O_2$: C, 82.23; H, 5.68; N, 5.64. Found: C, 81.92; H, 5.91; N, 5.56.

Synthesis of (*E*)-4-(1,5-Diphenyl-2-pyrrolyl)-1-phenyl-2-tosyl-1-buten-3-yne (5; Ar^1=Ar^2=Ph). A Typical Procedure. To a solution of CuCl (79.2 mg, 0.80 mmol) and $CuCl_2$ (10.8 mg, 0.080 mmol) in dry DMF (1.25 mL), which was bubbled through by N_2 for 30 min, was added aniline (0.15 mL, 1.6 mmol) at rt. After being stirred for 15 min at that temperature, a solution of **4** (Ar^1=Ph) (280 mg, 0.50

mmol) in dry DMF (3.8 mL) was added to the reaction mixture and stirred at 90 °C for 8 h. After adding ethyl acetate (30 mL) at rt, the mixture was washed with brine (100 mL × 3). The aqueous layers were extracted with ethyl acetate (50 mL × 3). The combined organic layers were washed with 2 *M* HCl (100 mL) and water (100 mL). The organic layer was dried over $MgSO_4$. Evaporation in vacuo and column chromatography (silica gel; hexane : EtOAc = 3 : 1) provided **5** (Ar^1=Ar^2=Ph) (152 mg, 62%) as a yellow solid. Recrystallization from EtOAc gave yellow crystals: mp 192.5-193.5 °C; ^{1}H NMR ($CDCl_3$) δ 2.40 (s, 3H), 6.45 (d, *J* = 3.8 Hz, 1H), 6.73 (d, *J* = 3.8 Hz, 1H), 7.07-7.10 (m, 2H), 7.19-7.28 (m, 9H), 7.32-7.41 (m, 4H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.69 (d, *J* = 7.3 Hz, 2H), 7.74 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 21.5, 86.8, 95.4, 110.8, 117.6, 118.6, 124.6, 127.2, 128.0, 128.1, 128.2, 128.4, 128.7 (×2), 129.2, 129.5, 130.0, 130.9, 131.9, 133.1, 136.3, 137.7, 138.3, 139.0, 144.3; IR (KBr/cm^{-1}) 3060, 2923, 2852, 2173, 1595, 1446, 1318, 1256, 1150, 1086, 751, 665. *Anal*. Calcd for $C_{33}H_{25}NO_2S$: C, 79.33; H, 5.04; N, 2.80. Found: C, 79.09; H, 5.13; N, 2.78.

(*E*)-4-[1-(4-Bromophenyl)-5-(4-methoxyphenyl)-2-pyrrolyl]-1-(4-methoxyphenyl)-2-tosyl-1-buten-3-yne (5; Ar^1=4-$MeOC_6H_4$, Ar^2=4-BrC_6H_4). Yellow crystals: mp 88.0-89.0 °C (hexane-$CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 2.42 (s, 3H), 3.78 (s, 3H), 3.85 (s, 3H), 6.36 (d, *J* = 3.8 Hz, 1H), 6.71 (d, *J* = 3.7 Hz, 1H), 6.76 (d, *J* = 8.7 Hz, 2H), 6.77 (d, *J* = 9.1 Hz, 2H), 7.00 (d, *J* = 8.9 Hz, 2H), 7.11 (d, *J* = 8.7 Hz, 2H), 7.26 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.7 Hz, 2H), 7.66 (d, *J* = 9.1 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.72 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 21.6, 55.2, 55.5, 87.2, 94.4, 110.3, 113.9, 114.1, 116.5, 118.5, 121.5, 121.6, 124.2, 125.9, 128.3, 129.5 (×2), 129.7, 131.9, 132.1, 136.7, 137.2, 137.4, 139.3, 144.1, 158.9, 161.9; IR (KBr/cm^{-1}) 3448, 3067, 2934, 2837, 2176, 1591, 1491, 1256, 1175, 1150, 665. *Anal.* Calcd for $C_{35}H_{28}NO_4BrS$: C, 65.83; H, 4.42; N, 2.19. Found: C, 65.86; H, 4.51; N, 2.24.

(*E*)-4-[1-(4-Bromophenyl)-5-(3-methoxyphenyl)-2-pyrrolyl]-1-(3-methoxyphenyl)-2-tosyl-1-buten-3-yne (5; Ar^1=3-$MeOC_6H_4$, Ar^2=4-BrC_6H_4). Yellow crystals: mp 154.0-155.0 °C (EtOAc); ^{1}H NMR ($CDCl_3$) δ 2.41 (s, 3H), 3.65 (s, 3H), 3.80 (s, 3H), 6.44 (d, *J* = 4.0 Hz, 1H), 6.61 (t-like, *J* = 2.1 Hz, 1H), 6.66 (dt, *J* = 7.7 and 1.5 Hz, 1H), 6.73 (d, *J* = 3.8 Hz, 1H), 6.76 (dd, *J* = 8.4 and 2.3 Hz, 1H), 6.95 (ddd, *J* = 8.1, 2.6 and 1.8 Hz, 1H), 7.12 (d, *J* = 8.5 Hz, 2H), 7.14 (t, *J* = 8.0 Hz, 1H), 7.19 (t, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 7.4 Hz, 2H), 7.30 (d, *J* = 8.2 Hz, 1H), 7.40 (t-like, *J* = 1.8 Hz, 1H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.59 (d, *J* = 8.4 Hz, 2H), 7.77 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 21.6, 55.0, 55.3, 87.0, 94.9, 111.3, 113.2, 113.8, 114.9, 116.9, 117.2, 118.9, 120.9, 121.8, 122.5, 124.7, 128.4, 129.4, 129.5, 129.6, 129.7, 132.2, 132.9, 134.3, 136.3, 137.2, 137.4, 140.0, 144.5, 159.4, 159.7; IR (KBr/cm^{-1}) 3448, 3064, 2958, 2834, 2182, 1598, 1491, 1302, 1258, 1151, 666. *Anal.* Calcd for $C_{35}H_{28}NO_4BrS$: C, 65.83; H, 4.42; N, 2.19. Found: C, 65.86; H, 4.51; N, 2.24.

(*E*)-4-[5-(4-Bromophenyl)-1-(4-methoxyphenyl)-2-pyrrolyl]-1-(4-bromophenyl)-2-tosyl-1-buten-3-yne (5; Ar^1=4-BrC_6H_4, Ar^2=4-$MeOC_6H_4$). Yellow crystals: mp 200.5-201.5 °C (hexane-EtOAc); ^{1}H

NMR ($CDCl_3$) δ 2.42 (s, 3H), 3.84 (s, 3H), 6.43 (d, *J* = 4.0 Hz, 1H), 6.71 (d, *J* = 4.0 Hz, 1H), 6.90 (d, *J* = 9.1 Hz, 2H), 6.95 (d, *J* = 8.7 Hz, 2H), 7.14 (d, *J* = 9.1 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.7 Hz, 2H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.65 (s, 1H), 7.68 (d, *J* = 8.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 21.6, 55.4, 87.0, 96.3, 110.8, 114.5, 117.6, 118.6, 121.3, 125.1, 125.3, 128.7, 129.0, 129.6, 129.7, 130.8, 131.2, 131.5, 131.9, 132.0, 136.1, 136.7, 137.1, 144.7, 159.4; IR (KBr/cm^{-1}) 3059, 2954, 2835, 2177, 1583, 1510, 1248, 1153, 1074, 835, 673. *Anal.* Calcd for $C_{34}H_{25}NO_3Br_2S$: C, 59.40; H, 3.67; N, 2.04. Found: C, 59.62; H, 3.67; N, 2.02.

Synthesis of 1,5-Diphenyl-2-(4-phenylbutadiynyl)pyrrole (7; Ar^1=Ar^2=Ph). A Typical Procedure. To a THF solution of LHMDS, which was prepared from *n*-BuLi (2.5 mL, 1.60 *M* in hexane, 4.0 mmol) and hexamethyldisilazane (0.93 mL, 4.4 mmol) in THF (2 mL) (0 °C, 30 min), was added a THF solution (3 mL) of **5** (Ar^1=Ar^2=Ph) (200 mg, 0.40 mmol) and the resulting solution was stirred at rt for 4 h. After quenching with sat. aqueous NH_4Cl (10 mL), the reaction mixture was extracted with ethyl acetate (15 mL × 3). The combined organic layers were dried over $MgSO_4$, evaporated in vacuo, and the residue was subjected to column chromatography on alumina (hexane : EtOAc = 3 : 1) to give (**7**; Ar^1=Ar^2=Ph) (0.109 g, 80%) as orange solid. Recrystallization from hexane-EtOAc gave pale orange crystals: mp 174.5-175.5 °C; ^1H NMR ($CDCl_3$) δ 6.41 (d, *J* = 4.0 Hz, 1H), 6.83 (d, *J* = 3.9 Hz, 1H), 7.08-7.11 (m, 2H), 7.18 (dd-like, *J* = 5.2 and 1.9 Hz, 3H), 7.23-7.27 (m, 2H), 7.32 (dt-like, *J* = 7.1 and 1.1 Hz, 3H), 7.37 (dt-like, *J* = 7.3 and 1.4 Hz, 3H), 7.45 (dd-like, *J* = 8.0 and 2.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 74.1, 74.3, 78.7, 83.4, 110.4, 117.1, 119.4, 122.0, 127.0, 127.8, 128.1, 128.3 (×2), 128.9, 129.0, 132.1, 132.3, 137.1, 138.3; IR (KBr/cm^{-1}) 3051, 2921, 2199, 2141, 1596, 1498, 1486, 1343, 1045, 834, 770. *Anal*. Calcd for $C_{26}H_{17}N$: C, 90.93; H, 4.99; N, 4.08. Found: C, 90.60; H, 5.06; N, 4.08.

1-(4-Bromophenyl)-5-(3-methoxyphenyl)-2-[4-(3-methoxyphenyl)butadiynyl]pyrrole (7; Ar^1=3-$MeOC_6H_4$, Ar^2=4-BrC_6H_4). Pale orange crystals: mp 183.5-184.5 °C (EtOAc-EtOH); ^1H NMR ($CDCl_3$) δ 3.65 (s, 3H), 3.79 (s, 3H), 6.41 (d, *J* = 4.0 Hz, 1H), 6.61 (dd, *J* = 2.5 and 1.6 Hz, 1H), 6.67 (dt, *J* = 7.7 and 1.5 Hz, 1H), 6.74 (ddd, *J* = 8.4, 2.5 and 1.0 Hz, 1H), 6.81 (d, *J* = 3.8 Hz, 1H), 6.91 (ddd, *J* = 8.4, 2.6 and 1.1 Hz, 1H), 7.00 (dd, *J* = 2.6 and 1.4 Hz, 1H), 7.08 (dt, *J* = 7.6 and 1.2 Hz, 1H), 7.13 (t, *J* = 8.0 Hz, 1H), 7.14 (d, *J* = 8.7 Hz, 2H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.52 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 55.0, 55.2, 73.6, 73.8, 79.1, 83.7, 110.9, 113.2, 113.7, 116.1, 116.9, 117.1, 119.7, 120.9, 121.7, 122.8, 125.0, 129.4 (×2), 129.6, 132.2, 133.0, 137.0, 137.4, 159.4 (×2); IR (KBr/cm^{-1}) 3011, 2950, 2202, 2141, 1594, 1491, 1474, 1219, 1032, 834, 770. *Anal*. Calcd for $C_{28}H_{20}NO_2Br$: C, 69.72; H, 4.18; N, 2.90. Found: C, 69.94; H, 4.30; N, 2.90.

5-(4-Bromophenyl)-1-(4-methoxyphenyl)-2-[4-(4-bromophenyl)butadiynyl]pyrrole. (7; Ar^1= 4-BrC_6H_4, Ar^2=4-$MeOC_6H_4$). Pale yellow crystals: mp 217.0-218.0 °C (hexane-EtOAc); ^1H NMR ($CDCl_3$) δ 3.84 (s, 3H), 6.38 (d, *J* = 3.8 Hz, 1H), 6.78 (d, *J* = 4.1 Hz, 1H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.95

(d, *J* = 8.5 Hz, 2H), 7.14 (d, *J* = 8.8 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 55.4, 74.6, 75.4, 78.6, 82.3, 110.3, 114.2, 117.6, 119.2, 120.9, 121.1, 123.4, 128.8, 129.6, 130.9 (×2), 131.6, 133.7, 136.0, 159.1; IR (KBr/cm^{-1}) 3010, 2933, 2200, 2146, 1610, 1587, 1512, 1483, 1250, 1009, 825, 773. *Anal*. Calcd for $C_{27}H_{17}NOBr_2$: C, 61.04; H, 3.23; N, 2.64. Found: C, 60.95; H, 3.36; N, 2.58.

A Stepwise Synthesis of 1,1'-Di(4-bromophenyl)-5,5'-di(3-methoxyphenyl)-2,2'-bipyrrole (8; Ar^1= 3-MeOC$_6$H$_4$, Ar^2=Ar^3=4-BrC$_6$H$_4$). A Typical Procedure. A suspension of 4-bromoaniline (496 mg, 2.88 mmol), **7** (Ar^1=3-MeOC$_6$H$_4$, Ar^2=4-BrC$_6$H$_4$) (580 mg, 1.20 mmol), and CuCl (143 mg, 1.44 mmol) in DMF (0.24 mL) was stirred at 150 °C for 1 h under N_2 atmosphere. The reaction mixture was cooled to rt, ethyl acetate (30 mL) was added and the precipitated solid was filtered off. The filtrate was evaporated in vacuo and the residue was subjected to column chromatography on silica gel (hexane : EtOAc = 3 : 1) to give **8** (Ar^1=3-MeOC$_6$H$_4$, Ar^2=Ar^3=4-BrC$_6$H$_4$) (569 mg, 73%) as pale yellow solid. Recrystallization from hexane-EtOAc gave pale yellow crystals: mp 185.0-186.0 °C; ^{1}H NMR ($CDCl_3$) δ 3.61 (s, 6h), 6.40 (d, *J* = 8.7 Hz, 4H), 6.41 (d, *J* = 2.9 Hz, 2H), 6.42 (d, *J* = 3.8 Hz, 2H), 6.52 (t-like, *J* = 1.5 Hz, 2H), 6.56 (dt, *J* = 7.7 and 1.5 Hz, 2H), 6.68 (ddd, *J* = 8.2, 2.6 and 0.8 Hz, 2H), 7.06 (t, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 8.7 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 54.9, 109.5, 112.3, 113.2, 113.4, 120.9, 126.3, 127.4, 127.8, 128.3, 128.8, 134.4, 134.5, 138.8, 158.9; IR (KBr/cm^{-1}) 3448, 3011, 2950, 2202, 2141, 1594, 1491, 1474, 1219, 1032, 834, 770. *Anal*. Calcd for $C_{34}H_{26}N_2O_2Br_2$: C, 62.40; H, 4.00; N, 4.28. Found: C, 62.33; H, 4.15; N, 4.18.

1-(4-Fluorophenyl)-1',5,5'-triphenyl-2,2'-bipyrrole (8; Ar^1=Ar^2=Ph, Ar^3=4-FC$_6$H$_4$). Pale yellow crystals: mp 207.5-208.5 °C (EtOAc-EtOH); ^{1}H NMR ($CDCl_3$) δ 6.34-6.38 (m, 4H), 6.50 (dd, *J* = 8.8 and 4.7 Hz, 2H), 6.58 (dd, *J* = 8.2 and 1.8 Hz, 2H), 6.68 (t, *J* = 8.8 Hz, 2H), 6.94-7.05 (m, 7H), 7.08-7.14 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 109.5, 109.6, 113.4 (×2), 114.9, 115.2, 126.1, 126.2, 126.3, 127.0, 127.4, 127.6, 127.8, 127.9, 128.2, 128.4, 129.0, 129.2, 132.9, 133.1, 134.7, 134.8, 138.7, 162.5; IR (KBr/cm^{-1}) 3053, 2781, 1597, 1496, 1375, 1236, 1072, 754, 696. *Anal*. Calcd for $C_{32}H_{23}N_2F$: C, 84.56; H, 5.10; N, 6.16. Found: C, 84.25; H, 5.18; N, 5.97.

1-(4-Methoxyphenyl)-1',5,5'-triphenyl-2,2'-bipyrrole (8; Ar^1=Ar^2=Ph, Ar^3=4-MeOC$_6$H$_4$). Pale yellow glassy solid (purified by preparative GPC; elution solvent=$CHCl_3$): ^{1}H NMR ($CDCl_3$) δ 3.73 (s, 3H), 6.27 (d, *J* = 3.6 Hz, 1H), 6.29 (d, *J* = 3.6 Hz, 1H), 6.37 (d, *J* = 3.6 Hz, 1H), 6.38 (d, *J* = 3.6 Hz, 1H), 6.60 (d-like, *J* = 1.4 Hz, 4H), 6.68 (dd, *J* = 8.0 and 1.9 Hz, 2H), 6.98-7.02 (m, 4H), 7.06-7.16 (m, 9H); ^{13}C NMR ($CDCl_3$) δ 55.2, 109.2, 109.5, 113.0, 113.2, 113.5, 126.0, 126.1, 126.4, 127.5, 127.6, 127.9 (×2), 128.0, 128.3. 128.4, 128.5, 128.9, 131.9, 133.3 (×2), 134.7, 134.8, 139.0, 158.0; IR (KBr/cm^{-1}) 3057, 2931, 2835, 1601, 1512, 1498, 1452, 1248, 833, 756, 698. *Anal.* Calcd for $C_{33}H_{26}N_2O \cdot 0.08CHCl_3$: C, 83.45; H, 5.52; N, 5.88. Found: C, 83.41; H, 5.70; N, 5.83. HRMS (FAB$^+$) Calcd for $C_{33}H_{26}N_2O$: M. 466.2045, found: m/z 466.2032.

1-(4-Acetylphenyl)-1',5,5'-triphenyl-2,2'-bipyrrole (8; Ar^1=Ar^2=Ph, Ar^3=4-AcC_6H_4). Pale yellow glassy solid (purified by preparative GPC; elution solvent=$CHCl_3$); ^{1}H NMR ($CDCl_3$) δ 2.52 (s, 3H), 6.42 (d, *J* = 3.7 Hz, 1H), 6.42 (s, 2H), 6.44 (d, *J* = 3.7 Hz, 1H), 6.48 (d, *J* = 7.6 Hz, 2H), 6.62 (d, *J* = 8.6 Hz, 2H), 6.94-7.05 (m, 7H), 7.09-7.16 (m, 6H), 7.58 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 26.4, 109.7, 110.4, 113.6, 114.1, 126.2, 126.3, 126.5, 126.9, 127.4, 127.5, 127.9, 128.1, 128.3, 128.4, 128.5, 128.6, 132.9, 133.0, 134.5, 134.8, 135.0, 138.6, 143.0, 197.4; IR (KBr/cm^{-1}) 3059, 2924, 2854, 1684, 1601, 1496, 1383, 1263, 842, 756, 698. *Anal.* Calcd for $C_{34}H_{26}N_2O$·0.07$CHCl_3$: C, 84.04; H, 5.40; N, 5.75. Found: C, 83.91; H, 5.65; N, 5.66. HRMS (FAB^+) Calcd for $C_{34}H_{26}N_2O$: M. 478.2045, found: m/z 478.2019.

1-(4-Nitrophenyl)-1',5,5'-triphenyl-2,2'-bipyrrole (8; Ar^1=Ar^2=Ph, Ar^3=4-$NO_2C_6H_4$). Yellow crystals: mp 180.1-180.9 °C (EtOAc-EtOH); ^{1}H NMR ($CDCl_3$) δ 6.42-6.44 (m, 4H), 6.50 (d, *J* = 3.7 Hz, 1H), 6.52 (d, *J* = 3.6 Hz, 1H), 6.58 (d, *J* = 9.1 Hz, 2H), 6.90-7.01 (m, 7H), 7.08-7.18 (m, 6H), 7.78 (d, *J* = 8.9 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 110.0, 111.1, 113.9, 114.7, 123.6, 126.2, 126.3, 126.5, 126.9, 127.2, 127.5, 127.7, 128.0, 128.3, 128.4, 128.6, 128.7, 132.5, 132.8, 134.9, 135.3, 138.5, 144.3, 145.3; IR (KBr/cm^{-1}) 3060, 2927, 2856, 1724, 1597, 1522, 1496, 1383, 1342, 854, 758, 698. *Anal*. Calcd for $C_{32}H_{23}N_3O_2$: C, 79.81; H, 4.81; N, 8.73. Found: C, 79.59; H, 4.72; N, 8.61.

5,5'-Di(4-bromophenyl)-1,1'-di(4-methoxyphenyl)-2,2'-bipyrrole (8; Ar^1=4-BrC_6H_4, Ar^2=Ar^3=4-$MeOC_6H_4$). Pale yellow crystals: mp 201.5-202.5 °C (EtOH); ^{1}H NMR ($CDCl_3$) δ 3.75 (s, 6H,), 6.16 (d, *J* = 3.7 Hz, 2H), 6.32 (d, *J* = 3.7 Hz, 2H), 6.59 (d, *J* = 9.2 Hz, 4H), 6.63 (d, *J* = 9.2 Hz, 4H), 6.84 (d, *J* = 8.7 Hz, 4H), 7.08 (d, *J* = 8.7 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 55.4, 109.5, 113.1, 113.7, 120.0, 127.9, 129.0, 129.8, 131.1, 131.7, 132.2, 133.6, 158.3; IR (KBr/cm^{-1}) 3049, 2956, 2835, 1736, 1512, 1481, 1296, 1250, 1032, 831, 771. *Anal*. Calcd for $C_{34}H_{26}N_2O_2Br_2$: C, 62.40; H, 4.00; N, 4.28. Found: C, 62.60; H, 4.03; N, 4.29.

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