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A Modular Synthesis of Unsymmetrical Tetraarylazadipyrromethenes

Michael J. Hall, Shane O. McDonnell, John Killoran, and Donal F. O'Shea*

Centre for Synthesis and Chemical Biology, Conway Institute, Department of Chemistry, University College Dublin, Belfield, Dublin 4, Ireland

donal.f.oshea@ucd.ie

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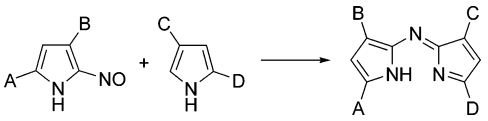

A stepwise route to unsymmetrical tetraarylazadipyrromethenes by a condensation of 2,4-diaryl-5-nitroso-pyrroles with 2,4-diarylpyrroles is described. This modular building-block approach allows for the introduction of up to four different aryl substituents on the azadipyrromethene and is tolerant of a varied substituent set. An efficient synthesis of the 2,4-diarylpyrroles building blocks from 1,3-diaryl-4-nitro-butan-1-ones by nitro hydrolysis to a keto-aldehyde and subsequent ammonia condensation reaction has been achieved. The facile conversion of 2,4-diarylpyrroles into their α-nitroso analogues by their reaction with sodium nitrite generated the second building block required for the synthesis.

Introduction

The dipyrrin class **1** was first described in the porphyrin synthesis work of Hans Fischer, and later in 1968 their boron difluoro analogues **2** were reported (Figure 1).[1] Since that time derivatives of **2** have become widely utilized fluorophores with many protein, nucleotide, oligonucleotide, and enzyme conjugated analogues now commercially available for use as fluorescent probes for a range of biological processes.[2] Other applications have been explored including their use as inputs into molecular wires,[3] as laser dyes,[4] as metal ion fluorescent sensors,[5] as probes for lipid membrane[6] and protein dynamics,[7] and as labels for DNA sequencing.[8] Their value lies in their high fluorescent quantum yields and photostability with emission wavelength between 500 and 600 nm. We have recently described synthetic routes to the bridging nitrogen analogues, the pyrrol-2-yl-pyrrol-2-ylidene-amines **3** (azadipyrromethene or azadipyrrin) and their BF_2 analogues **4**, which offer an optical advantage of a bathochromic shift of approximately 150 nm in absorption and emission wavelength (Figure 1).[9] We have shown how structural modification of the core photosensitizer can give rise to control of the photophysical properties of this compound class for the development of photodynamic therapeutic agents.[9b,c]

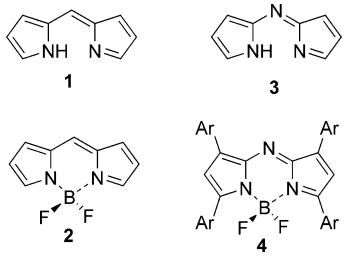

FIGURE 1. Dipyrrins and azadipyrromethenes (azadipyrrin).

In addition, the tetra-aryl-BF_2 analogues **4** have strong absorptions and emissions profiles in the spectral region

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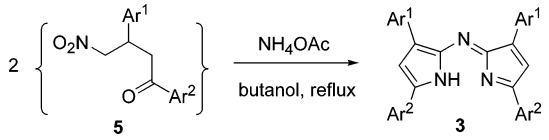
SCHEME 1. Synthesis of Symmetrical Tetraarylazadipyrromethenes



between 650 and 750 nm, which is a highly sought-after region of the spectrum for optical applications. This emerging class of chromophore offers an alternative to the other compound classes with related near-infrared spectral characteristics, such as the phthalocyanines, azaporphyrins and cyanines dyes, with apparent potential for application in the areas of fluorescent biochemical assaying and biomolecular probes. A key area of interest is the application of near-infrared dyes for real time in vivo fluorescence imaging for biomedical diagnostic applications, which is achievable as a result of efficient penetration of light through body tissue and the low autofluorescence of endogenous chromophores in this spectral region.[10]

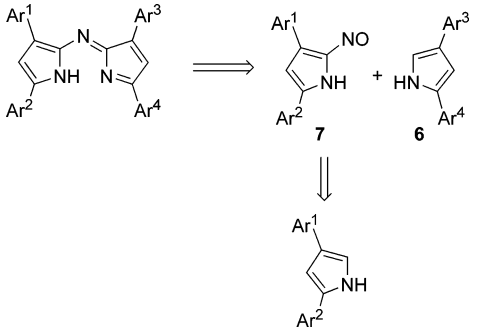
The chromophore class **3** was first reported over 60 years ago but remained unstudied until it attracted our interest and we reported their spectral properties and conversion into their corresponding BF_2 chelated analogues.[11] We have detailed an optimized synthetic route to the tetra-aryl *C*-2 symmetric derivatives **3** from the reaction of 1,3-diaryl-4-nitro-butan-1-ones **5** with ammonium acetate (Scheme 1).[9b] Although this approach is synthetically very accessible, a limitation of this route is that two molecules of **5** ultimately combine to yield **3** and consequently only symmetrical derivatives containing two pairs of aryl substituents can be generated.

As part of our ongoing work on tetraarylazadipyrromethenes and their chelated analogues we required a stepwise synthesis of unsymmetrical systems, which would facilitate the introduction of differing substituents on each of the aryl rings. This type of synthetic control would be required for fine-tuning of both spectroscopic and solubility properties of the compounds and allow the introduction of specific functional groups for both molecular sensors and bioconjugated analogues. The modular approach we chose to develop was to couple one-half of the molecule with the other by the reaction of 2,4-diarylpyrroles **6** with their corresponding α-nitroso analogues **7** (Scheme 2).

Results and Discussion

Synthesis of 2,4-Diaryl-1*H*-pyrroles. To pursue this synthetic strategy we required a versatile synthesis of 2,4-diarylpyrroles. Despite their synthetic importance, direct methods for making 2,4-diarylpyrroles **6** are limited, especially if two different aryl substituents are required. Routes to symmetrical substituted 2,4-diarylpyrroles include SmI_2-mediated reductive dimerization

SCHEME 2. Proposed Route to Unsymmetrical Tetraarylazadipyrromethenes



of phenacyl azides,[12] reaction of hexacarbonylmolybdenum with 3-aryl-2*H*-azirines,[13] and Grignard-mediated dimerization of acetophenone oximes.[14] Rhodium- and zirconium-catalyzed reaction of alkynes, amines, and carbon monoxide have been reported as procedures to unsymmetrically substituted derivatives, but these methods require high-pressure CO conditions.[15,16]

Our approach was to exploit the 1-nitro-4-butanones **5** as our initial substrate as it would be a starting material common to our previously reported symmetrical synthesis.[9b] Our aim was to develop a direct transformation to the 2,4-diarylpyrroles **6** by a sequential Nef transformation of **5** into a 1,4-keto-aldehyde that would be converted to the desired pyrroles by an ammonia condensation reaction.[17] The starting point of the synthesis was the diaryl α,β-unsaturated ketones (chalcones) **8** of which **8a**,**c**,**h** were commercially available and the remainder **8b**,**d**,**e**,**f**,**g**,**i**,**j** were synthesized by an aldol/dehydration reaction of the corresponding aldehyde and acetophenone in high yield (see Supporting Information, p S5). The two aldehydes (4-diethylaminomethyl-benzaldehyde and 4-morpholin-4-ylmethyl-benzaldehyde) required for the synthesis of **8e**, **8f**, and **8j** were not commercially available and were synthesized from the reaction of 4-bromomethylbenzaldehyde[18] with the corresponding amine (see SI p S3). 1,4-Addition of nitromethane to **8a**−**j** using diethylamine as base in methanol at reflux provided us with a set of 1,3-diaryl-4-nitro-butan-1-ones **5a**−**j** in isolated yields of 68−93% (Table 1).

This facile two-step procedure provided the substrates **5** for the pyrrole generation. Deprotonation of **5** with KOH in MeOH, with THF as a cosolvent to maintain a homogeneous solution, generated a nitro-stabilized anion, which upon hydrolysis with H_2SO_4 gave the 1-keto-4-dimethylacetals intermediates **9**. The intermediate ketal **9a** (Ar^1, Ar^2 = Ph) was isolated by silica gel chromatography in 73% yield; however in subsequent examples this was deemed unnecessary and the unpurified material was converted directly to the pyrrole without isolation.

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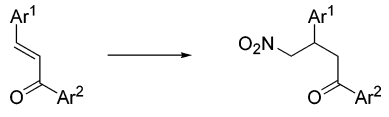
TABLE 1. Synthesis of 1,3-Diaryl-4-nitro-butan-1-ones 5a–j[a]



8a-j **5a-j**

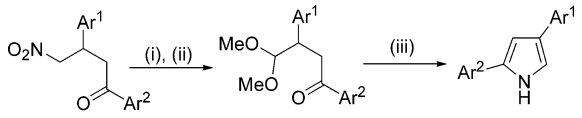
entry	substrate	Ar^1	Ar^2	5	yield (%)
1	**8a**	C_6H_5	C_6H_5	**5a**	*b*
2	**8b**	*p*-$Me_2NC_6H_4$	C_6H_5	**5b**	87
3	**8c**	*p*-$MeOC_6H_4$	C_6H_5	**5c**	*b*
4	**8d**	*p*-BrC_6H_4	C_6H_5	**5d**	*b*
5	**8e**	*p*-$Et_2NCH_2C_6H_4$	C_6H_5	**5e**	92
6	**8f**	*p*-$O(CH_2CH_2)_2NCH_2C_6H_4$	C_6H_5	**5f**	81
7	**8g**	*p*-$CH_3CONHC_6H_4$	C_6H_5	**5g**	68
8	**8h**	C_6H_5	*p*-$MeOC_6H_4$	**5h**	*b*
9	**8i**	C_6H_5	*p*-FC_6H_4	**5i**	93
10	**8j**	*p*-$Et_2NCH_2C_6H_4$	*p*-$MeOC_6H_4$	**5j**	86

[a] Conditions: $MeNO_2$, Et_2NH, MeOH, reflux, 16 h. [b] Previously reported in ref 9b.

Subsequent acetal deprotection and condensation with NH_4OAc in acetic acid provided the 2,4-diaryl-1*H*-pyrroles **6a–j** in good isolated yields (Table 2).

The pyrrole products were purified by recrystallization or alumina column chromatography and could be stored with no special precautions for prolonged periods of time. Despite the relatively harsh conditions of the Nef reaction we were pleased to find that the reaction sequence tolerated a diverse set of aryl substituents, underlining this approach as a new general route to diarylpyrrole synthesis.

TABLE 2. Synthesis of 2,4-Diaryl-1*H*-pyrrole Building Blocks 6a–j[a]



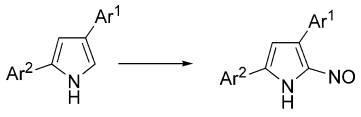
5a-j **9** **6a-j**

entry	substrate	Ar^1	Ar^2	pyrrole	yield (%)
1	**5a**	C_6H_5	C_6H_5	**6a**	70
2	**5b**	*p*-$Me_2NC_6H_4$	C_6H_5	**6b**	52
3	**5c**	*p*-$MeOC_6H_4$	C_6H_5	**6c**	68
4	**5d**	*p*-BrC_6H_4	C_6H_5	**6d**	63
5	**5e**	*p*-$Et_2NCH_2C_6H_4$	C_6H_5	**6e**	70
6	**5f**	*p*-$O(CH_2CH_2)_2N$-$CH_2C_6H_4$	C_6H_5	**6f**	71
7	**5g**	*p*-$CH_3CONHC_6H_4$	C_6H_5	**6g**	52
8	**5h**	C_6H_5	*p*-$MeOC_6H_4$	**6h**	72
9	**5i**	C_6H_5	*p*-FC_6H_4	**6i**	65
10	**5j**	*p*-$Et_2NCH_2C_6H_4$	*p*-$MeOC_6H_4$	**6j**	59

[a] Conditions: (i) KOH, MeOH/THF, rt, 1 h; (ii) H_2SO_4, MeOH, 0 °C to rt; 1 h; (iii) NH_4OAc, AcOH, 100 °C, 1 h.

The penultimate step was the transformation of the diarylpyrroles **6a**,**c**,**h**,**i** into their corresponding α-nitroso derivatives **7a–d**, which was readily achieved by their reaction with sodium nitrite in ethanol/aqueous HCl (Table 3). This reaction was very efficient for selective nitrosation at the unsubstituted α-pyrrole position, with the products isolated by direct precipitation from the reaction mixture in high yields. The nitroso-pyrroles **7** are stable solids, which can be obtained analytically pure following alumina chromatography.

TABLE 3. Generation of Nitroso-pyrrole Building Blocks 7a–d[a]



6 **7a-d**

entry	pyrrole	Ar^1	Ar^2	nitroso-pyrrole	yield (%)
1	**6a**	Ph	Ph	**7a**	79
2	**6c**	*p*-$MeOC_6H_4$	Ph	**7b**	86
3	**6h**	Ph	*p*-$MeOC_6H_4$	**7c**	92
4	**6i**	Ph	*p*-FC_6H_4	**7d**	83

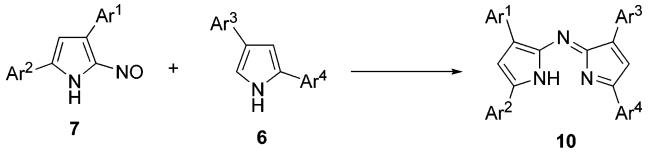
[a] Conditions: $NaNO_2$, EtOH, HCl (aq), rt, 30 min.

Synthesis of Unsymmetrical Tetraarylazadipyrromethenes. The cross-condensation of **7a–d** with the diarylpyrroles **6** was achieved by stirring the two components in acetic anhydride/acetic acid mixture at 100 °C for 1 h during which time a deep blue color developed. Reaction products were isolated by addition of ice to the cooled reaction mixture and extraction with dichloromethane with purification by recrystallization or chromatography. Encouragingly, the key condensation reaction was tolerant of a range of both electronically divergent and chemically sensitive functional groups, with the unsymmetrical tetraarylazadipyrromethenes **10a–k** isolated in excellent yields in all but one case (Table 4). Our route allowed for the generation of derivatives containing one to four differently substituted aryl rings depending upon the pyrrole building blocks used. The versatility of this approach is highlighted by **10j**, which has the four different aryl group substituents: phenyl (Ph), an electron-withdrawing group (F), an electron-donating group (OMe), and a basic amine group ($CH_2N(Et)_2$) (entry 10). This ability to readily generate poly-functionalized analogues of **10** will facilitate the optimization of this chromophore class to a wide range of applications.

As the pyrrole rings of compounds **10** could be envisaged to exist with either an *E* or *Z* orientation about the bridging nitrogen atom, solid-state evidence was sought to determine the structural features of this compound class. Compound **10b** was crystallized by slow evaporation of a chloroform solution at room temperature, in the monoclinic space group $P2_1/n$. The X-ray structure analysis of **10b** proved that the aza-dipyrrole unit is essentially planar, with both pyrrole units adopting the same orientation in the solid state (see ORTEP diagram in SI p S8). The comparable nitrogen–carbon bond lengths for the bridging nitrogen to both pyrrole rings of N(1)–C(1) = 1.340(6) Å and N(1)–C(18) = 1.314(5) Å demonstrated the conjugated nature of the chromophore (full details in SI p S12). Notably, the tautomeric nature of the pyrrole NH between both pyrrole units was established as there was an unequal sharing of the pyrrole hydrogen between both pyrrole rings, with two-thirds occupancy on N2 and one-third on N3 (see SI p S20).

^1H and ^{13}C NMR confirmed the unsymmetrical nature of **10** with two β-pyrrole signals observed in the proton spectrum and a doubling of the signal numbers in the

TABLE 4. Synthesis of Unsymmetrical Tetraarylazadipyrromethenes[a]



entry	7	Ar^1	Ar^2	6	Ar^3	Ar^4	product	yield (%)
1	**7a**	Ph	Ph	**6b**	*p*-$Me_2NC_6H_5$	Ph	**10a**	35
2	**7a**	Ph	Ph	**6c**	*p*-$MeOC_6H_4$	Ph	**10b**	86
3	**7a**	Ph	Ph	**6d**	*p*-BrC_6H_4	Ph	**10c**	92
4	**7a**	Ph	Ph	**6e**	*p*-$Et_2NCH_2C_6H_4$	Ph	**10d**	94
5	**7a**	Ph	Ph	**6f**	*p*-$O(CH_2CH_2)_2NCH_2C_6H_4$	Ph	**10e**	90
6	**7a**	Ph	Ph	**6g**	*p*-$CH_3CONHC_6H_4$	Ph	**10f**	78
7	**7a**	Ph	Ph	**6i**	Ph	*p*-FC_6H_4	**10g**	88
8	**7b**	Ph	*p*-$MeOC_6H_4$	**6j**	*p*-$Et_2NCH_2C_6H_4$	*p*-$MeOC_6H_4$	**10h**	94
9	**7c**	*p*-$MeOC_6H_4$	Ph	**6c**	Ph	*p*-$MeOC_6H_4$	**10i**	72
10	**7d**	Ph	*p*-FC_6H_4	**6j**	*p*-$Et_2NCH_2C_6H_4$	*p*-$MeOC_6H_4$	**10j**	88
11	**7d**	Ph	*p*-FC_6H_4	**6c**	Ph	*p*-$MeOC_6H_4$	**10k**	94

[a] Conditions: acetic anhydride, acetic acid, 100 °C, 1 h.

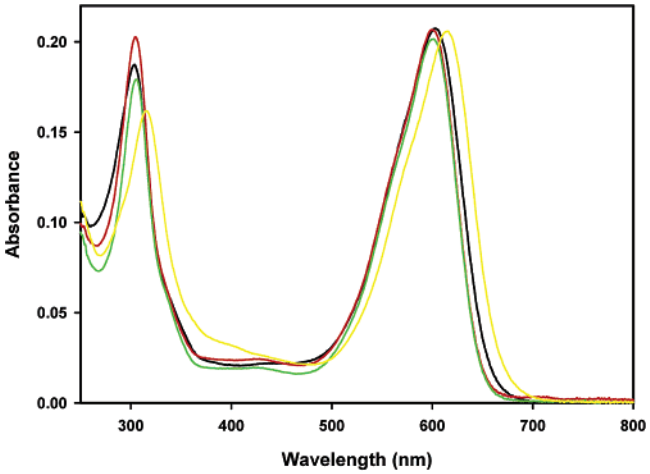


FIGURE 2. UV−vis spectra of **10b** (black), **10c** (green), **10e** (red), and **10i** (yellow) in $CHCl_3$ at 4×10^{-6} M concentration.

carbon spectrum when compared to the previously reported symmetrical examples. As expected the UV−vis spectra of **10a**−**k** all displayed a strong absorbance with high extinction coefficients in the region of 600 nm with wavelength of maximum absorbance being dependent upon aryl substituents (Figure 2 and SI p S24).

As previously shown for symmetrical analogues it would be anticipated that the conversion of **10a**−**k** into their BF_2 chelated analogues would result in a bathochromic shift of absorbance maximum in the range of 50−70 nm, an increase in extinction coefficient, and the provision of a high fluorescence quantum yield.[9b]

Conclusions

We have demonstrated a straightforward three-step route from readily available starting materials to a valuable class of diarylpyrroles with a range of aromatic substituents. We have subsequently used these compounds as building blocks to access a number of unsymmetrical tetraarylazadipyrromethenes carrying varying aryl substituents. Both the pyrrole synthesis and the coupling of pyrrole with α-nitroso-pyrrole is tolerant of a wide range of functional groups. The described robust new routes to unsymmetrical tetraarylazadipyrromethenes together with our previously reported methods for the synthesis of symmetrical derivatives should open the way to exploitation of this compound class for a diverse range of applications. Work in our group is currently focused on examining the spectroscopic properties of the BF_2 chelated analogues and their application as biomolecular sensors and labels and as targeted PDT agents.

Experimental Section

General Procedure for Synthesis of 1,3-Diaryl-4-nitrobutan-1-ones, 5a−j. A solution of 1,3-diarylpropenone **8a**−**j** (5 mmol) in MeOH (50 mL) was treated with diethylamine (2.6 mL, 25 mmol) and nitromethane (1.4 mL, 25 mmol) and heated under reflux for 16 h.

5b,g,i: The solution was cooled, partitioned between CH_2Cl_2 (100 mL) and water (100 mL), and acidified with 1 M HCl. The aqueous layer was extracted with a further portion of CH_2Cl_2 (100 mL), and the combined organics were washed with water (100 mL) and brine (100 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the resulting oil was purified by column chromatography on silica gel (Et_2O/cyclohexane) or by crystallization from methanol or ethanol.

5e,f,j: The solution was cooled, partitioned between CH_2Cl_2 (100 mL) and water (100 mL) and extracted with CH_2Cl_2 (100 mL). The combined organics were extracted with 1 M HCl (200 mL), and the aqueous layer was then neutralized with 2 M NaOH and extracted with CH_2Cl_2 (2×100 mL). The combined organics were washed with water (100 mL) and brine (100 mL) and dried over Na_2SO_4. The solvent was removed under reduced pressure, and the resulting oil was purified by column chromatography on alumina (Et_2O/cyclohexane) or by crystallization from methanol or ethanol.

3-(4-Dimethylamino-phenyl)-4-nitro-1-phenyl-butan-1-one (5b). Colorless solid (1.36 g, 87%), mp 114−115 °C (MeOH). ^1H NMR ($CDCl_3$) δ: 7.88−7.92 (m, 2H), 7.51−7.57 (m, 1H), 7.40−7.46 (m, 2H), 7.13 (d, $J = 8.7$ Hz, 2H), 6.67 (d, $J = 8.7$ Hz, 2H), 4.76 (dd, $J = 12.3$, 6.8 Hz, 1H), 4.61 (dd, $J = 12.3$, 7.9 Hz, 1H), 4.06−4.15 (m, 1H), 3.31−3.47 (m, 2H), 2.89 (s, 6H). ^{13}C NMR ($CDCl_3$) δ: 197.5, 150.3, 136.8, 133.6, 128.9, 128.3, 128.3, 126.6, 113.0, 80.2, 42.0, 40.6, 38.8. IR (KBr) cm^{-1}: 1680. ES-MS: *m/z* 313 $[M + H]^+$. HRMS calcd for $C_{18}H_{21}N_2O_3$ $[M + H]^+$ 313.1552, found 313.1557. Anal. Calcd for $C_{18}H_{20}N_2O_3$: C, 69.21; H, 6.45; N, 8.97. Found: C, 69.40; H, 6.39; N, 8.83.

3-(4-Diethylaminomethyl-phenyl)-4-nitro-1-phenyl-butan-1-one (5e). Colorless solid (1.63 g, 92%), mp 92−93 °C

(MeOH). ^{1}H NMR ($CDCl_3$) δ: 7.91 (d, J = 7.3 Hz, 2H), 7.55−7.60 (m, 1H), 7.43−7.48 (t, m 2H), 7.30 (d, J = 8.1 Hz, 2H), 7.21 (d, J = 8.1 Hz, 2H), 4.80−4.85 (m, 1H), 4.64−4.71 (m, 1H), 4.19−4.26 (m, 1H), 3.52 (s, 2H), 3.37−3.50 (m, 2H), 2.50 (q, J = 7.1 Hz, 4H), 1.02 (t, J = 7.1 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 197.0, 139.8, 137.5, 136.5, 133.6, 129.5, 128.8, 128.1, 127.3, 79.7, 57.1, 46.7, 41.7, 39.1, 11.7. IR (KBr disk) cm^{-1}: 1689. ES-MS: *m/z* 355 [M + H]$^+$. HRMS calcd for $C_{21}H_{27}N_2O_3$ [M + H]$^+$ 355.2022, found 355.2029. Anal. Calcd for $C_{21}H_{26}N_2O_3$: C, 71.16; H, 7.39; N, 7.90. Found: C, 71.21; H, 7.44; N, 7.77.

3-(4-Morpholin-4-ylmethyl-phenyl)-4-nitro-1-phenyl-butan-1-one (5f). Colorless solid (1.49 g, 81%), mp 109−110 °C (MeOH). ^{1}H NMR ($CDCl_3$) δ: 7.91 (d, J = 7.8 Hz, 2H), 7.55−7.60 (m, 1H), 7.43−7.48 (m, 2H), 7.29 (d, J = 8.1 Hz, 2H), 7.23 (d, J = 8.1 Hz, 2H), 4.82 (dd, J = 12.4, 6.6 Hz, 1H), 4.68 (dd, J = 12.4, 8.1 Hz, 1H), 4.17−4.27 (m, 1H), 3.69 (t, J = 4.5 Hz, 4H), 3.47 (s, 2H), 3.39−3.50 (m, 2H), 2.41 (t, J = 4.5 Hz, 4H). ^{13}C NMR ($CDCl_3$) δ: 196.9, 138.0, 137.4, 136.4, 133.6, 129.9, 128.8, 128.0, 127.4, 79.6, 79.6, 63.0, 53.6, 41.6, 39.0. IR (KBr disk) cm^{-1}: 1690. ES-MS: *m/z* 369 [M + H]$^+$. HRMS calcd for $C_{21}H_{25}N_2O_4$ [M + H]$^+$ 369.1814, found 369.1831. Anal. Calcd for $C_{21}H_{24}N_2O_4$: C, 68.46; H, 6.57; N, 7.60. Found: C, 68.85; H, 6.55; N, 7.36.

***N*-[4-(1-Nitromethyl-3-oxo-3-phenyl-propyl)-phenyl]-acetamide (5g).** Colorless solid (1.11 g, 68%), mp 82−84 °C (EtOH). ^{1}H NMR (DMSO-d_6) δ: 9.88 (s, 1H), 7.90 (d, J = 7.2 Hz, 2H), 7.58−7.63 (m, 1H), 7.44−7.51 (m, 4H), 7.26 (d, J = 8.5 Hz, 2H), 4.93 (dd, J = 12.7, 5.7, 1H), 4.78 (dd, J = 12.7, 9.8, 1H), 3.94−3.99 (m, 1H), 3.40−3.57 (m, 2H), 1.98 (s, 3H).^{13}C NMR (DMSO-d_6) δ: 197.9, 168.7, 138.8, 136.8, 134.8, 133.8, 129.2, 128.5, 128.4, 119.5, 80.2, 41.6, 39.1, 24.4. IR (KBr disk) cm^{-1}: 1687. ES-MS: *m/z* 327 [M + H]$^+$. HRMS calcd for $C_{18}H_{19}N_2O_4$ [M + H]$^+$ 327.1345, found 327.1361. Anal. Calcd for $C_{18}H_{18}N_2O_4$: C, 66.25; H, 5.56; N, 8.58. Found: C, 65.96; H, 5.69; N, 8.29.

1-(4-Fluoro-phenyl)-4-nitro-3-phenyl-butan-1-one (5i). Colorless solid (1.34 g, 93%), mp 70−71 °C (EtOH). ^{1}H NMR ($CDCl_3$) δ: 7.90−7.95 (m, 2H), 7.19−7.34 (m, 5H), 7.06−7.12 (m, 2H), 4.81 (dd, J = 12.5, 6.6 Hz, 1H), 4.67 (dd, J = 12.5, 8.0 Hz, 1H), 4.16−4.25 (m, 1H), 3.44 (dd, J = 17.7, 6.6 Hz, 1H), 3.37 (dd, J = 17.7, 7.4 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ: 195.3, 165.9 (d, J = 255.2 Hz), 139.1, 132.8, 130.7 (d, J = 9.4 Hz), 129.1, 127.9, 127.5, 115.9 (d, J = 21.7 Hz), 79.5, 41.4, 39.3. IR (KBr disk) cm^{-1}: 1686. ES-MS: *m/z* 286 [M − H]$^-$. HRMS calcd for $C_{16}H_{13}NO_3F$ [M − H]$^-$ 286.0879, found 286.0872. Anal. Calcd for $C_{16}H_{14}FNO_3$: C, 66.86; H, 4.91; N, 4.88. Found: C, 66.81; H, 4.94; N, 4.90.

3-(4-Diethylaminomethyl-phenyl)-1-(4-methoxy-phenyl)-4-nitro-butan-1-one (5j). Yellow oil (1.65 g, 86%). ^{1}H NMR ($CDCl_3$) δ: 7.90 (d, J = 8.8 Hz, 2H), 7.29 (d, J = 8.2 Hz, 2H), 7.21 (d, J = 8.2 Hz, 2H), 6.92 (d, J = 8.8 Hz, 2H), 4.82 (dd, J = 12.4, 6.4 Hz, 1H), 4.67 (dd, J = 12.4, 8.1 Hz, 1H), 4.14−4.24 (m, 1H), 3.86 (s, 3H), 3.52 (s, 2H), 3.30−3.45 (m, 2H), 2.50 (q, J = 7.1 Hz, 4H), 1.03 (t, J = 7.1 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 199.5, 170.0, 167.8, 143.7, 141.6, 134.4, 133.5, 131.3, 117.9, 83.7, 61.1, 59.6, 50.7, 45.3, 43.2, 15.7. IR (neat) cm^{-1}: 1679. ES-MS: *m/z* 385 [M + H]$^+$. HRMS calcd for $C_{22}H_{29}N_2O_4$ [M + H]$^+$ 385.2127, found 385.2142. Anal. Calcd for $C_{22}H_{28}N_2O_4$: C, 68.73; H, 7.34; N, 7.29. Found: C, 68.43; H, 7.30; N, 6.99.

General Procedure for Synthesis of 2,4-Diaryl-1*H*-pyrroles, 6a−j. A stirred solution of **5a−j** (2 mmol) in MeOH (20 mL) and THF (40 mL) at room temperature was treated with KOH (0.56 g, 10 mmol). After 1 h the mixture was added dropwise to a solution of H_2SO_4 (4 mL) in MeOH (20 mL) at 0 °C, following which the solution was allowed to warm to room temperature and stirred for a further 1 h. Water (50 mL) and ice (50 mL) were added, and the mixture was neutralized with aqueous 4 M NaOH and extracted with dichloromethane (2 × 50 mL). The combined extracts were washed with water (50 mL) and brine (50 mL) and dried over Na_2SO_4.The solvent was removed under reduced pressure to provide **9** as an oil, which was carried into the next stage without further purification. The oil was treated with acetic acid (10 mL) and NH_4OAc (0.77 g, 10 mmol), and the resulting solution was heated at 100 °C for 1 h. The reaction mixture was cooled to room temperature, ice (50 mL) was added, and the mixture carefully neutralized with aqueous 4 M NaOH. The solution extracted with dichloromethane (2 × 50 mL), the combined extracts were washed with water (50 mL) and brine (50 mL) and dried over Na_2SO_4, and the solvent removed under reduced pressure. Purification by column chromatography on alumina (Et_2O, cyclohexane) or by recrystallization from EtOH.

2,4-Diphenyl-1*H*-pyrrole (6a). Light pink solid (0.31 g, 70%), mp 178−180 °C (EtOH). ^{1}H NMR ($CDCl_3$) δ: 8.45 (bs, 1H), 7.50−7.58 (m, 4H), 7.34−7.42 (m, 4H), 7.17−7.27 (m, 2H), 7.15 (d, J = 3.8 Hz, 1H), 6.83 (d, J = 3.8 Hz, 1H). ^{13}C NMR (DMSO-d_6) δ: 136.2, 133.2, 132.8, 129.2, 129.0, 126.2, 125.5, 125.2, 124.9, 123.9, 117.1, 103.7. IR (KBr disk) cm^{-1}: 3439. ES-MS: *m/z* 220 [M + H]$^+$. HRMS calcd for $C_{16}H_{14}N$ [M + H]$^+$ 220.1126, found 220.1133. Anal. Calcd for $C_{16}H_{13}N$: C, 87.64; H, 5.98; N, 6.39. Found: C, 87.46; H, 6.03; N, 6.40.

4-(4-Dimethylamino-phenyl)-2-phenyl-1*H*-pyrrole (6b). Light brown solid (0.34 g, 52%), mp 201−204 °C (EtOH). ^{1}H NMR (DMSO-d_6) δ: 11.29 (bs, 1H), 7.71 (d, J = 7.2 Hz, 2H), 7.47 (d, J = 8.8 Hz, 2H), 7.38−7.41 (m, 2H), 7.17−7.22 (m, 2H), 6.87 (s, 1H), 6.77 (d, J = 8.8 Hz, 2H), 2.93 (s, 6H). ^{13}C NMR (DMSO-d_6) δ: 148.8, 133.3, 132.2, 129.1, 125.9, 125.7, 125.6, 124.9, 123.7, 115.5, 113.4, 103.3, 40.9. IR (KBr disk) cm^{-1}: 3422. ES-MS: *m/z* 263 [M + H]$^+$. HRMS calcd for $C_{18}H_{19}N_2$ [M + H]$^+$ 263.1548, found 263.1556. Anal. Calcd for $C_{18}H_{18}N_2$: C, 82.41; H, 6.92; N, 10.68. Found: C, 82.11; H, 6.90; N, 10.66.

4-(4-Methoxy-phenyl)-2-phenyl-1*H*-pyrrole (6c). Light brown solid (0.34 g, 68%), mp 190−191 °C (EtOH). ^{1}H NMR (DMSO-d_6) δ: 11.34 (s, 1H), 7.61 (d, J = 7.5 Hz, 2H), 7.50 (d, J = 8.6 Hz, 2H), 7.31−7.36 (m, 2H), 7.21 (s, 1H), 7.11−7.16 (m, 1H), 6.88 (d, J = 8.6 Hz, 2H), 6.86 (s, 1H), 3.72 (s, 3H). ^{13}C NMR (DMSO-d_6) δ: 153.5, 129.1, 128.4, 125.0, 124.8, 121.9, 120.9, 119.7, 112.0, 110.3, 99.4, 51.3. IR (KBr disk) cm^{-1}: 3427. ES-MS: *m/z* 250 [M + H]$^+$. HRMS calcd for $C_{17}H_{16}NO$ [M + H]$^+$ 250.1223, found 250.1232. Anal. Calcd for $C_{17}H_{15}NO$: C, 81.90; H, 6.06; N, 5.62. Found: C, 81.61; H, 6.12; N, 5.60.

4-(4-Bromo-phenyl)-2-phenyl-1*H*-pyrrole (6d). Light blue solid (0.38 g, 63%), mp 215−218 °C (EtOH). ^{1}H NMR (DMSO-d_6) δ: 11.50 (s, 1H), 7.66 (d, J = 7.3 Hz, 2H), 7.56 (d, J = 8.5 Hz, 2H), 7.46 (d, J = 8.5 Hz, 2H), 7.32−7.38 (m, 3H), 7.13−7.18 (m, 1H), 6.95 (s, 1H). ^{13}C NMR (DMSO-d_6) δ: 135.5, 132.9, 132.8, 131.8, 129.2, 126.8, 126.3, 123.9, 123.8, 118.0, 117.6, 103.6. IR (KBr disk) cm^{-1}: 3435. ES-MS: *m/z* 298 [M + H]$^+$. HRMS calcd for $C_{16}H_{13}BrN$ [M + H]$^+$ 298.0231, found 298.0233. Anal. Calcd for $C_{16}H_{12}BrN$: C, 64.45; H, 4.06; N, 4.70. Found: C, 64.30; H, 4.13; N, 4.61.

Diethyl-[4-(5-phenyl-1*H*-pyrrol-3-yl)-benzyl]-amine (6e). Light pink solid (0.43 g, 70%), mp 116−117 °C (EtOH). ^{1}H NMR (DMSO-d_6) δ: 11.40 (s, 1H), 7.66 (d, J = 7.3 Hz, 2H), 7.52 (d, J = 8.1 Hz, 2H), 7.32−7.36 (m, 2H), 7.28 (s, 1H), 7.22 (d, J = 8.1 Hz, 2H), 7.12−7.16 (m, 1H), 6.91 (s, 1H), 3.47 (s, 2H), 2.43 (q, J = 7.1 Hz, 4H), 0.94 (t, J = 7.1 Hz, 6H). ^{13}C NMR (DMSO-d_6) δ: 133.0, 130.7, 129.2, 128.6, 125.4, 125.2, 122.3, 121.2, 120.7, 119.9, 112.9, 99.7, 53.2, 42.6, 8.2. IR (KBr disk) cm^{-1}: 3383, 1604. ES-MS: *m/z* 305 [M + H]$^+$. HRMS calcd for $C_{21}H_{25}N_2$ [M + H]$^+$ 305.2018, found 305.2018. Anal. Calcd for $C_{21}H_{24}N_2$: C, 82.85; H, 7.95; N, 9.20. Found: C, 82.57; H, 7.90; N 8.93.

4-[4-(5-Phenyl-1*H*-pyrrol-3-yl)-benzyl]-morpholine (6f). Light pink solid (0.45 g, 71%), mp 166−167 °C (EtOH). ^{1}H NMR ($CDCl_3$) δ: 8.48 (bs, 1H), 7.51−7.53 (m, 4H), 7.35−7.40 (m, 1H), 7.28−7.33 (m, 2H), 7.21−7.24 (m, 2H), 7.13 (s, 1H), 6.81 (s, 1H), 3.72 (t, J = 4.5 Hz, 4H), 3.50 (s, 2H), 2.48 (t, J = 4.5 Hz, 4H). ^{13}C NMR ($CDCl_3$) δ: 135.0, 134.5, 133.1, 132.5, 129.6, 129.0, 126.5, 125.0, 123.9, 115.5, 104.0, 67.1, 63.3, 53.7. IR (KBr disk) cm^{-1}: 3420. ES-MS: *m/z* 317 [M − H]$^-$. HRMS

calcd for $C_{21}H_{23}N_2O$ [M + H]$^+$ 319.1810, found 319.1798. Anal. Calcd for $C_{21}H_{22}N_2O$: C, 79.21; H, 6.96; N, 8.80. Found: C, 79.03; H, 6.97; N, 8.64.

***N*-[4-(5-Phenyl-1*H*-pyrrol-3-yl)-phenyl]-acetamide (6g).** Light tan solid (0.29 g, 52%), mp 214−216 °C (EtOH). ^{1}H NMR (DMSO-d_6) δ: 11.38 (s, 1H), 9.87 (s, 1H), 7.67 (d, J = 7.2 Hz, 2H), 7.51−7.56 (m, 4H), 7.37 (t, J = 7.8 Hz, 2H), 7.27 (d, J = 4.1 Hz, 1H), 7.14−7.17 (m, 1H), 6.90 (d, 4.1 Hz, 1H), 2.04 (s, 3H). ^{13}C NMR (DMSO-d_6) δ: 168.4, 137.1, 133.1, 132.5, 131.1, 129.1, 126.1, 125.0, 123.8, 119.7, 116.5, 103.5, 24.4. IR (KBr) cm^{-1}: 3412, 1657, 1601. ES-MS: *m/z* 277 [M + H]$^+$. HRMS calcd for $C_{18}H_{17}N_2O$ [M + H]$^+$ 277.1341, found 277.1345.

2-(4-Methoxy-phenyl)-4-phenyl-1*H*-pyrrole (6h). Light pink solid (0.36 g, 72%), mp 206−208 °C (EtOH). ^{1}H NMR (DMSO-d_6) δ: 11.28 (bs, 1H), 7.45−7.56 (m, 4H), 7.25−7.30 (m, 3H), 7.06−7.09 (m, 1H), 6.89−6.92 (m, 2H), 6.78 (s, 1H), 3.73 (s, 3H). ^{13}C NMR (DMSO-d_6) δ: 154.2, 132.5, 129.0, 125.2, 122.3, 121.6, 121.4, 121.2, 121.0, 122.4, 110.8, 98.6, 51.7. IR (KBr disk) cm^{-1}: 3387. ES-MS: *m/z* 250 [M + H]$^+$. HRMS calcd for $C_{17}H_{16}NO$ [M + H]$^+$ 250.1232, found 250.1237.

2-(4-Fluoro-phenyl)-4-phenyl-1*H*-pyrrole (6i). Light pink solid (0.31 g, 65%), mp 176−178 °C, (EtOH). ^{1}H NMR (DMSO-d_6) δ: 11.47 (bs, 1H), 7.71−7.75 (m, 2H), 7.63 (d, J = 7.4 Hz, 2H), 7.30−7.36 (m, 3H), 7.13−7.22 (m, 3H), 6.94 (s, 1H). ^{13}C NMR (DMSO-d_6) δ: 158.7, 155.4, 132.2, 127.9, 125.8, 125.0, 121.7, 120.9, 113.0, 112.2, 111.9, 99.6. IR (KBr disk) cm^{-1}: 3429. ES-MS: *m/z* 236 [M − H]$^-$. HRMS calcd for $C_{16}H_{11}FN$ [M − H]$^-$ 236.0874, found 236.0864. Anal. Calcd for $C_{16}H_{12}$-FN: C, 80.99; H, 5.10; N, 5.90. Found: C, 80.79; H, 5.14; N 5.79.

Diethyl-{4-[5-(4-methoxy-phenyl)-1*H*-pyrrol-3-yl]-benzyl}-amine (6j). Light pink solid (0.46 g, 59%), mp 182−184 °C (EtOH). ^{1}H NMR (DMSO-d_6) δ: 11.38 (s, 1H), 7.59 (d, J = 8.3 Hz, 2H), 7.49 (d, J = 7.6 Hz, 2H), 7.19−7.24 (m, 3H), 6.92 (d, J = 8.3 Hz, 2H), 6.75 (s, 1H), 3.73 (s, 3H), 3.45 (s, 2H), 2.42 (q, J = 7.0 Hz, 4H), 0.95 (t, J = 7.0 Hz, 6H). ^{13}C NMR (DMSO-d_6) δ: 154.3, 133.1, 131.1, 129.0, 125.5, 122.5, 121.5, 121.2, 120.9, 112.3, 110.9, 98.6, 53.5, 51.8, 42.8, 8.4. IR (KBr disk) cm^{-1}: 3445. ES-MS: *m/z* 335 [M + H]$^+$; HRMS calcd for $C_{22}H_{27}N_2O$ [M + H]$^+$ 335.2123, found 335.2122. Anal. Calcd for $C_{22}H_{26}N_2O$: C, 79.00; H, 7.84; N, 8.38. Found: C, 78.89; H, 7.83; N, 8.40.

General Procedure for Synthesis 2,4-Diaryl-5-nitroso-pyrroles (7a−d). To a stirred solution of **6** (1 mmol) in EtOH (10 mL) was added concentrated HCl (0.2 mL), followed by a dropwise addition of aqueous $NaNO_2$ (80 mg, 1.15 mmol, in 2 mL of H_2O). The solution was stirred for 30 min and cooled to 0 °C, and another portion of concentrated HCl (1 mL) was added. The solution was allowed to stir for 1 h, and the resulting red solid was collect by filtration and washed with Et_2O. The solid was dissolved in minimal EtOH, an excess of aqueous NaOAc and ice was added, and the solution was stirred for 1 h. The resulting solid was collected by filtration dried and purified by chromatography on alumina (EtOAc/cyclohexane).

2-Nitroso-3,5-diphenyl-1*H*-pyrrole (7a). Green solid (0.20 g, 79%), mp 138−140 °C. ^{1}H NMR ($CDCl_3$) δ: 8.16−8.19 (m, 2H), 7.80−7.83 (m, 2H), 7.47−7.51 (m, 6H), 7.14 (s, 1H), (NH not observed). ^{13}C NMR ($CDCl_3$) δ: 162.7, 147.6, 141.8, 132.1, 131.2, 129.8, 129.5, 129.3, 129.0, 128.8, 127.1, 112.4. IR (KBr disk) cm^{-1}: 3287. ES-MS: *m/z* 249 [M + H]$^+$. HRMS calcd for $C_{16}H_{13}N_2O$ [M + H]$^+$ 249.1028, found 249.1028. Anal. Calcd for $C_{16}H_{12}N_2O$: C, 77.40; H, 4.87; N, 11.28. Found: C, 77.35; H, 4.97; N, 11.23.

3-(4-Methoxy-phenyl)-2-nitroso-5-phenyl-1*H*-pyrrole (7b). Green solid (0.24 g, 86%), mp 173−174 C. ^{1}H NMR ($CDCl_3$) δ: 8.17 (d, J = 8.9 Hz, 2H), 7.78−7.82 (m, 2H), 7.48−7.52 (m, 3H), 7.07 (s, 1H), 7.02 (d, J = 8.9, 2H), 3.89 (s, 3H), (NH not observed). ^{13}C NMR ($CDCl_3$) δ: 163.1, 161.2, 141.4, 131.0, 129.4, 126.8, 124.5, 114.4, 111.8, 131.3, 55.4. IR (KBr disk) cm^{-1}: 3303. EI-MS: *m/z* 279 [M + H]$^+$. HRMS calcd for $C_{17}H_{15}N_2O_2$ [M + H]$^+$ 279.1134, found 279.1145.

5-(4-Methoxy-phenyl)-2-nitroso-3-phenyl-1*H*-pyrrole (7c). Yellow solid (0.26 g, 92%), mp 171−173 °C. ^{1}H NMR ($CDCl_3$) δ: 8.11−8.13 (m, 2H), 7.87 (d, J = 8.4 Hz, 2H), 7.45−7.50 (m, 3H), 7.13 (s, 1H), 6.99 (d, J = 8.4 Hz, 2H), 3.86 (s, 3H), (NH not observed). ^{13}C NMR ($CDCl_3$) δ: 163.4, 162.6, 152.6, 143.1, 131.8, 129.5, 129.5, 129.2, 128.7, 121.9, 114.9, 114.5, 55.5. IR (KBr disk) cm^{-1}: 3452. ES-MS: *m/z* 279.1 [M + H]$^+$. HRMS calcd for $C_{17}H_{15}N_2O_2$ [M + H]$^+$ 279.1134, found 279.1131.

5-(4-Fluoro-phenyl)-2-nitroso-3-phenyl-1*H*-pyrrole (7d). Yellow solid (0.22 g, 83%), mp 176−178 °C. ^{1}H NMR ($CDCl_3$) δ: 8.10−8.13 (m, 2H), 7.89−7.94 (m, 2H), 7.45−7.48 (m, 3H), 7.15−7.20 (m, 2H), 7.12 (s, 1H), (NH not observed). ^{13}C NMR ($CDCl_3$) δ: 164.6 (d, J = 254.7 Hz), 163.2, 150.2, 142.9, 131.7, 129.7, 129.6, 129.4 (d, J = 8.9 Hz), 128.8, 125.8 (d, J = 3.2 Hz), 116.7 (d, J = 22.0 Hz), 114.0. IR (KBr disk) cm^{-1}: 3451. ES-MS: *m/z* 267 [M + H]$^+$. HRMS calcd for $C_{16}H_{10}FN_2O$ [M − H]$^-$ 265.0777, found 265.0784. Anal. Calcd for $C_{16}H_{11}FN_2O$: C, 72.17; H, 4.16; N, 10.52. Found: C, 71.81; H, 4.19; N, 10.18.

4,4-Dimethoxy-1,3-diphenyl-butan-1-one (9a). A stirred solution of **5a** (1.35 g, 5 mmol) in MeOH (50 mL) and THF (100 mL) at room temperature was treated with KOH (1.4 g, 25 mmol). After 1 h the mixture was added dropwise to a solution of H_2SO_4 (10 mL) in MeOH (50 mL) at 0 °C, following which the solution was allowed to warm to room temperature and stirred for a further 1 h. Half of the solvent was removed under reduced pressure, and the remainder was added to water (100 mL) and ice (50 mL). The mixture was neutralized with aqueous 4 M NaOH and extracted with dichloromethane (2 × 200 mL). The combined extracts were dried over Na_2SO_4, and the solvent was removed under reduced pressure to provide an oil that was purified by column chromatography on silica gel (EtOAc/cycloheaxne) to give **9a** as a colorless solid (1.04 g, 73%), mp 80−82 °C, (MeOH). ^{1}H NMR ($CDCl_3$) δ: 7.93 (d, J = 7.0 Hz, 2H), 7.50−7.55 (m, 1H), 7.42 (t, J = 7.4 Hz, 2H), 7.25−7.34 (m, 4H), 7.16−7.22 (m, 1H), 4.49 (d, J = 5.4 Hz, 1H), 3.72−3.79 (m, 1H), 3.55 (dd, J = 17.2, 5.1 Hz, 1H), 3.36 (s, 3H), 3.30−3.39 (m, 1H), 3.31 (s, 3H). ^{13}C NMR ($CDCl_3$) δ: 198.6, 140.6, 137.3, 132.8, 128.6, 128.4, 128.3, 128.0, 126.7, 107.9, 55.3, 54.8, 44.1, 39.6. IR (KBr disk) cm^{-1}: 1680. ES-MS: *m/z* 307 [M + Na]$^+$; HRMS calcd for $C_{18}H_{20}O_3Na$ [M + Na]$^+$ 307.1310, found 307.1313. Anal. Calcd for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: C, 75.77; H, 7.29.

General Procedure for Synthesis of Unsymmetrical Tetraarylazadipyrromethenes (10a−k). 1-Nitroso-2,4-diarylpyrrole **7** (0.5 mmol) and 2,4-diarylpyrrole **6** (0.5 mmol) were dissolved in AcOH (2.5 mL) and acetic anhydride (0.5 mL) and heated to 100 °C for 1 h. During the course of the reaction an intense blue color formed. Ice (20 mL) and 2 M NaOH (20 mL) was added, and the mixture was stirred for 30 min, extracted with CH_2Cl_2 (2 × 100 mL), and washed aqueous $NaHCO_3$ (100 mL), water (100 mL), and brine (100 mL). The combined organics were dried over Na_2SO_4, and the solvent was removed under reduced pressure to provide the product as a dark blue solid. Purification was by silica gel or alumina column chromatography.

(3,5-Diphenyl-1*H*-pyrrol-2-yl)-[3-(4-dimethylamino-phenyl)-5-phenylpyrrol-2-ylidene]-amine (10a). Dark blue metallic solid (0.086 g, 35%), mp 238−240 °C (silica; CH_2Cl_2/pentane 3:2). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.98−8.09 (m, 6H), 7.85−7.89 (m, 2H), 7.31−7.55 (m, 9H), 7.10 (s, 2H), 6.73−6.78 (m, 2H), 3.05 (s, 6H), (NH not observed). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 160.9, 153.8, 150.8, 149.3, 146.3, 146.0, 139.7, 134.5, 133.0, 132.4, 130.5, 129.3, 129.3, 129.2, 129.2, 128.4, 127.7, 127.2, 126.1, 122.2, 113.8, 112.5, 112.1, 40.5. IR (KBr disk) cm^{-1}: 1606. HRMS calcd for $C_{34}H_{29}N_4$ [M + H]$^+$ 493.2392, found 493.2402. Anal. Calcd for $C_{34}H_{28}N_4$: C, 82.90; H, 5.73; N, 11.37. Found: C, 82.70; H, 5.71; N, 11.26. λ max ($CHCl_3$): 593 nm. ϵ = 37,000 L mol^{-1} cm^{-1}.

(3,5-Diphenyl-1*H*-pyrrol-2-yl)-[3-(4-methoxy-phenyl)-5-phenyl-pyrrol-2-ylidene]-amine (10b). Dark blue metallic solid (0.21 g, 86%), mp 267−269 °C (silica; CH_2Cl_2/EtOAc 3:1). ^{1}H NMR ($CDCl_3$) δ: 8.01−8.05 (m, 4H), 7.88−7.93 (m, 4H), 7.33−7.54 (m, 9H), 7.14 (s, 1H), 7.12 (s, 1H), 6.94 (d, J = 8.9 Hz, 2H), 3.88 (s, 3H), (NH not observed). ^{13}C NMR ($CDCl_3$) δ: 159.8, 157.7, 152.2, 151.3, 147.8, 134.5, 141.2, 133.9, 132.3, 132.0, 130.4, 130.2, 129.7, 129.1, 129.1, 128.2, 127.8, 126.8, 126.4, 126.2, 114.5, 113.7, 55.4. IR (KBr disk) cm^{-1}: 3457. ES-MS: *m/z* 480 [M + H]$^+$. HRMS calcd for $C_{33}H_{26}N_3O$ [M + H]$^+$ 480.2076, found 480.2077. Anal. Calcd for $C_{33}H_{25}N_3O$: C, 82.65; H, 5.25; N, 8.76. Found: C, 82.45; H, 5.27; N, 8.70. λ max ($CHCl_3$): 601 nm. ϵ = 47,000 L mol^{-1} cm^{-1}.

[3-(4-Bromo-phenyl)-5-phenyl-pyrrol-2-ylidene]-(3,5-diphenyl-1*H*-pyrrol-2-yl)-amine (10c). Dark blue metallic solid (0.24 g, 92%), mp 282−285 °C (silica; CH_2Cl_2/EtOAc 3:1). ^{1}H NMR (10% TFA/$CDCl_3$) δ: 11.77 (s, 2H), 7.89−7.95 (m, 4H), 7.22−7.58 (m, 17H). ^{13}C NMR (10% TFA/$CDCl_3$) δ: 156.3, 155.3, 149.1, 146.9, 136.3, 135.9, 133.7, 133.4, 131.9, 131.6, 131.3, 130.6, 130.4, 130.2, 129.7, 128.7, 127.8, 127.6, 126.9, 125.2, 116.2, 115.2. (KBr disk) cm^{-1}: 3420. ES-MS: *m/z* 528 [M + H]$^+$. HRMS calcd for $C_{32}H_{23}N_3Br$ [M + H]$^+$ 528.1075, found 528.1091. λ max ($CHCl_3$): 601 nm. ϵ = 45,000 L mol^{-1} cm^{-1}.

[3-(4-Diethylamino-methyl-phenyl)-5-phenyl-pyrrol-2-ylidene]-(3,5-diphenyl-1*H*-pyrrol-2-yl)-amine (10d). Dark blue metallic solid (0.25 g, 94%), mp 162−165 °C (alumina; CH_2Cl_2/EtOAc 9:1). ^{1}H NMR ($CDCl_3$) δ: 8.01 (d, J = 6.7 Hz, 2H), 7.96 (d, J = 8.1 Hz, 2H), 7.84−7.88 (m, 4H), 7.34−7.48 (m, 11H), 7.11 (s, 1H), 7.10 (s, 1H), 3.63 (s, 2H), 2.58 (q, J = 7.1 Hz, 4H), 1.09 (t, J = 7.1 Hz, 6H), (NH not observed). ^{13}C NMR ($CDCl_3$) δ: 155.7, 154.1, 150.1, 149.1, 142.8, 142.1, 139.8, 133.8, 132.2, 132.1, 130.0, 129.8, 129.3, 129.0, 128.8, 128.2, 127.8, 126.6, 126.4, 114.8, 114.4, 57.4, 46.8, 11.8. IR (KBr disk) cm^{-1}: 3440. ES-MS: *m/z* 535 [M + H]$^+$. HRMS calcd for $C_{37}H_{35}N_4$ [M + H]$^+$ 535.2862, found 535.2880. Anal. Calcd for $C_{37}H_{34}$-
N_4: C, 83.11; H, 6.41; N, 10.48. Found: C, 82.72; H, 6.39; N, 10.25. λ max ($CHCl_3$): 600 nm. ϵ = 45,000 L mol^{-1} cm^{-1}.

(3,5-Diphenyl-1H-pyrrol-2-yl)-[3-(4-morpholin-4-ylmethyl-phenyl)-5-phenyl-pyrrol-2-ylidene]-amine (10e). Dark blue metallic solid (0.25 g, 90%), mp 238−241 °C, (alumina; CH_2Cl_2/EtOAc 9:1). ^{1}H NMR ($CDCl_3$) δ: 8.02−8.07 (m, 4H), 7.95 (d, J = 7.2 Hz, 4H), 7.37−7.57 (m, 11H), 7.20 (s, 1H), 7.19 (s, 1H), 3.74−3.80 (m, 4H), 3.57 (s, 2H), 2.49−2.53 (m, 4H), (NH not observed). ^{13}C NMR ($CDCl_3$) δ: 155.6, 155.1, 150.0, 149.7, 142.8, 138.0, 134.0, 132.9, 132.4, 132.4, 129.3, 129.3, 129.3, 129.2, 128.4, 128.2, 126.8, 126.7, 115.0, 115.0, 67.3, 63.5, 53.9. IR (KBr disk) cm^{-1}: 3465. ES-MS: *m/z* 549 [M + H]$^+$. HRMS calcd for $C_{37}H_{33}N_4O$ [M + H]$^+$ 549.2654, found 549.2672. Anal. Calcd for $C_{37}H_{32}N_4O$: C, 80.99; H, 5.88; N, 10.21. Found: C, 81.30; H, 6.09; N, 9.95. λ max ($CHCl_3$): 600 nm. ϵ = 47,000 L mol^{-1}cm^{-1}.

***N*-{4-[2-(3,5-Diphenyl-1*H*-pyrrol-2-ylimino)-5-phenyl-2H-pyrrol-3-yl]-phenyl}-acetamide (10f).** Dark blue metallic solid (0.20 g, 78%), mp 343−345 °C, (silica; CH_2Cl_2/EtOAc 3:1). ^{1}H NMR (10%TFA/$CDCl_3$) δ: 11.84 (bs, 1H), 11.64 (bs, 1H), 8.85 (bs, 1H), 7.67 (d, J = 7.5 Hz, 2H), 7.61 (d, J = 7.0 Hz, 2H), 7.23−7.42 (m, 10H), 7.11−7.16 (m, 5H), 7.09 (s, 1H), 7.00 (s, 1H), 3.35 (s, 3H). ^{13}C NMR (10%TFA/$CDCl_3$) δ: 173.6, 155.1, 155.0, 148.6, 146.9, 138.1, 135.6, 133.4, 133.3, 131.1, 131.0, 130.5, 130.3, 129.5, 128.7, 128.2, 127.6, 127.4, 126.5, 126.4, 121.0, 115.4, 144.5, 22.9. IR (KBr disk) cm^{-1}: 3451, 3282, 1658. ES-MS: *m/z* 507 [M + H]$^+$. HRMS calcd for $C_{36}H_{27}$-NO_2 [M + H]$^+$ 507.2185, found 507.2192. λ max ($CHCl_3$): 604 nm. ϵ = 41,000 L mol^{-1}cm^{-1}.

(3,5-Diphenyl-1*H*-pyrrol-2-yl)-[5-(4-fluoro-phenyl)-3-phenyl-pyrrol-2-ylidene]-amine (10g). Dark blue metallic solid (0.21 g, 88%), mp 288−291 °C, (silica; CH_2Cl_2/EtOAc 3:1). ^{1}H NMR ($CDCl_3$) δ: 8.04−8.08 (m, 4H), 7.97−8.02 (m, 2H), 7.89 (d, J = 7.2 Hz, 2H), 7.36−7.57 (m, 9H), 7.24−7.26 (m, 2H), 7.21 (s, 1H), 7.16 (s, 1H), (NH not observed). ^{13}C NMR ($CDCl_3$) δ: 165.3, 163.3, 158.0, 152.3, 151.4, 147.0, 144.7, 141.2, 133.9, 133.9, 133.6, 131.9, 129.9, 129.3, 129.3, 129.2, 129.0, 128.4, 128.0, 126.3, 116.5, 116.3, 113.4. IR (KBr disk) cm^{-1}: 3424. ES-MS: *m/z* 468 [M + H]$^+$. HRMS calcd for $C_{32}H_{23}N_3F$ [M + H]$^+$ 468.1876, found 468.1897. λ max ($CHCl_3$): 597 nm. ϵ = 44,000 L mol^{-1}cm^{-1}.

[3-(4-Diethylamino-methyl-phenyl)-5-(4-methoxy-phenyl)-pyrrol-2-ylidene]-[5-(4-methoxy-phenyl)-3-phenyl-1*H*-pyrrol-2-yl]-amine (10h). Dark blue metallic solid (0.28 g, 94%), mp 165−168 °C, (alumina; CH_2Cl_2/EtOAc 9:1). ^{1}H NMR ($CDCl_3$) δ: 8.01 (d, J = 8.1 Hz, 2H), 7.96 (d, J = 8.2 Hz, 2H), 7.76−7.81 (m, 4H), 7.31−7.41 (m, 5H), 7.04 (s, 1H), 7.02 (s, 1H), 6.95 (d, J = 8.8 Hz, 2H), 6.94 (d, J = 8.8 Hz, 2H), 3.83 (s, 3H), 3.82 (s, 3H), 3.63 (s, 2H), 2.58 (q, J = 7.1 Hz, 4H), 1.09 (t, J = 7.1 Hz, 6H), (NH not observed). ^{13}C NMR ($CDCl_3$) δ: 161.1, 161.0, 154.8, 153.3, 149.9, 148.8, 142.3, 141.5, 139.5, 134.0, 132.4, 129.0, 128.7, 128.1, 128.1, 127.9, 127.6, 125.0, 124.9, 114.5, 114.1, 113.8, 57.5, 55.4, 46.8, 11.8. IR (KBr disk) cm^{-1}: 3457. ES-MS: *m/z* 595 [M + H]$^+$. HRMS calcd for $C_{39}H_{39}N_4O_2$ [M + H]$^+$ 595.3073, found 595.3079. Anal. Calcd for $C_{39}H_{38}$-N_4O_2: C, 78.76; H, 6.44; N, 9.42. Found: C, 78.56; H, 6.49; N, 9.21. λ max ($CHCl_3$): 621 nm. ϵ = 41,000 L mol^{-1}cm^{-1}.

[5-(4-Methoxy-phenyl)-3-phenyl]-1*H*-pyrrol-2-yl)-[3-(4-methoxy-phenyl)-5-phenyl-pyrrol-2-ylidene]-amine (10i). Dark blue metallic solid (0.18 g, 72%), mp 294−296 °C, (silica; CH_2Cl_2/EtOAc 3:1). ^{1}H NMR (1%TFA/$CDCl_3$) δ: 8.01 (d, J = 8.4 Hz, 2H), 7.93−7.95 (m, 2H), 7.51−7.56 (m, 4H), 7.44−7.47 (m, 4H), 7.24−7.29 (m, 2H), 7.20 (s, 1H), 7.11 (s, 1H), 6.98 (d, J = 8.4 Hz, 2H), 6.71 (d, J = 8.4 Hz, 2H), 3.89 (s, 3H), 3.87 (s, 3H), (NH not observed). ^{13}C NMR (1%TFA/$CDCl_3$) δ: 164.1, 161.1, 155.1, 153.5, 135.8, 135.5, 132.4, 132.1, 131.6, 130.4, 130.3, 129.9, 129.4, 128.5, 127.4, 124.7, 119.5, 116.5, 115.7, 115.3, 114.1, 113.2, 112.7, 55.7, 55.5. IR (KBr disk) cm^{-1}: 3425. ES-MS: *m/z* 510 [M + H]$^+$. HRMS calcd for $C_{34}H_{28}N_3O_2$ [M + H]$^+$ 510.2182, found 510.2203. Anal. Calcd for $C_{34}H_{27}N_3O_2$: C, 80.13; H, 5.34; N, 8.25. Found: C, 79.85; H, 5.32; N, 8.11. λ max ($CHCl_3$): 615 nm. ϵ = 53,000 L mol^{-1}cm^{-1}.

[3-(4-Diethylamino-methyl-phenyl)-5-(4-methoxy-phenyl)-pyrrol-2-ylidene]-[5-(4-flouro-phenyl)-3-phenyl-1*H*-pyrrol-2-yl]-amine (10j). Dark blue metallic solid (0.26 g, 88%), mp 202−203 °C, (alumina; CH_2Cl_2/EtOAc 9:1). ^{1}H NMR ($CDCl_3$) δ: 8.01 (d, J = 7.0 Hz, 2H), 7.96 (d, J = 8.2 Hz, 2H), 7.88 (d, J = 8.8 Hz, 2H), 7.74−7.80 (m, 2H), 7.32−7.41 (m, 5H), 7.12−7.18 (m, 2H), 7.13 (s, 1H), 6.98−7.01 (m, 2H), 6.98 (s, 1H), 3.88 (s, 3H), 3.63 (s, 2H), 2.58 (q, J = 7.1 Hz, 4H), 1.09 (t, J = 7.1 Hz, 6H). ^{13}C NMR ($CDCl_3$) δ: 161.8, 159.6, 152.9, 148.2, 148.1, 144.7, 140.1, 139.5, 134.0, 131.9, 128.9, 128.7, 128.2, 125.0, 116.4, 116.3, 114.6, 112.1, 57.5, 55.5, 46.8, 11.9. IR (KBr disk) cm^{-1}: 3459. ES-MS: *m/z* 583 [M + H]$^+$. HRMS calcd for $C_{38}H_{36}FN_4O$ [M + H]$^+$ 583.2873, found 583.2884. Anal. Calcd for $C_{38}H_{35}FN_4O$: C, 78.32; H, 6.05; N, 9.61. Found: C, 78.47; H, 6.13; N, 9.57. λ max ($CHCl_3$): 607 nm. ϵ = 42,000 L mol^{-1}cm^{-1}.

[5-(4-Fluoro-phenyl)-3-phenyl-1*H*-pyrrol-2-yl]-[5-(4-methoxy-phenyl)-3-phenyl-pyrrol-2-ylidene]-amine (10k). Dark blue metallic solid (0.23 g, 94%), mp 265−268 °C, (silica; CH_2Cl_2/EtOAc 3:1). ^{1}H NMR ($CDCl_3$) δ: 7.98−8.01 (m, 4H), 7.85 (d, J = 8.0 Hz, 2H), 7.74−7.79 (m, 2H), 7.32−7.42 (m, 6H), 7.09−7.18 (m, 2H), 7.12 (s, 1H), 6.96−7.01 (m, 2H), 6.99 (s, 1H), 3.88 (s, 3H), (NH not observed). ^{13}C NMR ($CDCl_3$) δ: 161.8, 159.0, 152.4, 149.0, 146.5, 144.5, 134.0, 134.0, 133.5, 129.1, 128.9, 128.7, 128.2, 128.1, 127.8, 127.7, 127.7, 125.0, 116.5, 116.4, 116.1, 114.6, 112.4, 55.5. IR (KBr disk) cm^{-1}: 3463. ES-MS: *m/z* 498 [M + H]$^+$. HRMS calcd for $C_{33}H_{25}FN_3O$ [M + H]$^+$ 498.1982, found 498.1993. Anal. Calcd for $C_{33}H_{24}$-FN_3O: C, 79.66; H, 4.86; N, 8.45. Found: C 79.23; H, 4.94; N, 7.90. λ max ($CHCl_3$): nm 606. ϵ = 46,000 L mol^{-1}cm^{-1}.

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Supporting Information Available: Experimental procedures and characterization data for **8b**,**e**,**f**,**g**,**i**,**j**, 4-morpholin-4-ylmethyl-benzaldehyde, and 4-diethylaminomethyl-benzaldehyde. ^{1}H and ^{13}C NMR spectra for **6a**−**j**, **7a**−**d**, **9a**, and **10a**−**k**. UV−vis spectra of **10a**−**k**. X-ray crystallographic data of **10b** as a CIF file with ORTEP drawing. This material is available free of charge via the Internet at http://pubs.acs.org.

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