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Selective Synthesis of Tripyrranes, Tetrapyrranes, and Corroles

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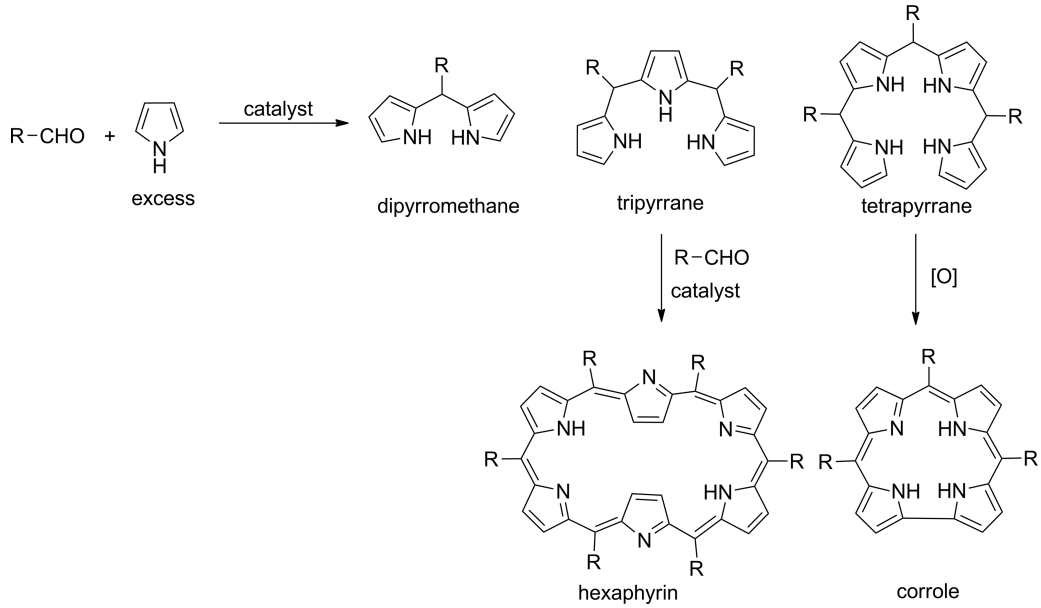
A new, catalytic, and general methodology was developed for the direct synthesis of unsymmetrical AB-type tripyrranes by reaction of dipyrromethanesulfonamides with pyrrole. Key structure dipyrromethanesulfonamides were synthesized by the addition of *meso*-substituted dipyrromethanes to $Cu(OTf)_2$-activated tosylimines. The introduced method enables selective preparation of tetrapyrranes in high yields by tuning the conditions of the addition reaction. The oxidation of tetrapyrranes by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone afforded only corresponding A_3- and *trans*-A_2B-corroles.

Introduction

Porphyrins and their expanded and contracted analogs have found widespread applications in catalysis, medicinal chemistry, materials science, and supramolecular chemistry.[1] Acyclic oligopyrromethanes, such as dipyrromethanes, tripyrranes, and tetrapyrranes are important precursors for the construction of these heteroaromatics. Among these, *meso*-substituted dipyrromethanes have been an indispensable structure in synthetic porphyrin chemistry.[2] Thereupon, the first studies in the literature mainly focused on the chemistry of *meso*-substituted dipyrromethanes. In the following years, growing interest in the synthesis of expanded and contracted porphyrins has increased the synthetic importance of tripyrranes and tetrapyrranes, because they are crucial building blocks for these macrocyclic heteroaromatics (Scheme 1).[3]

Acid-catalyzed condensation of aldehyde and pyrrole is the most straightforward method for the synthesis of oligopyrroles should identical *meso*-substituents be desired. This method requires excessive amounts of pyrrole to suppress the polymerization reaction and usually forms dipyrromethanes as a main product and other oligocondensates (tripyrranes, tetrapyrranes, and so on) as side products.[4] The necessity for long chromatographic separation of all



Scheme 1. Building blocks for hexaphyrins and corroles.

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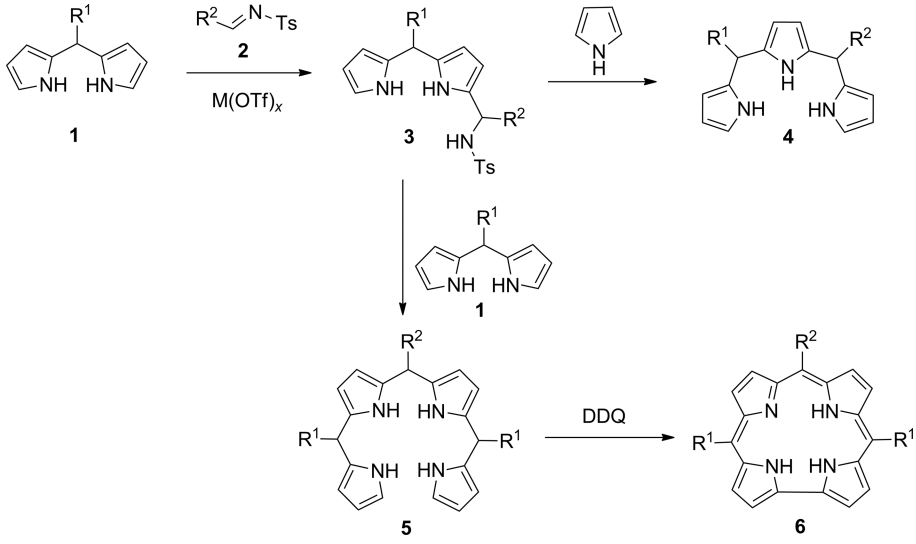


Scheme 2. Preparation of tripyrranes **4** and tetrapyrranes **5**.

oligopyrroles and low yields of tripyrranes and tetrapyrranes are drawbacks of this method. The major synthetic limitation of this method is that it is not possible to place different substituents selectively at the methylene bridge in tripyrranes or tetrapyrranes. Although reported methods are mainly focused on the synthesis of symmetrical oligopyrroles, a very limited number of methods for unsymmetrical derivatives have been developed to date, which include the treatment of pyrroles or dipyrromethanes with 2-(acetoxymethyl)pyrroles,[5] reactions of dipyrromethane carbinols with dipyrromethanes[6] or pyrroles.[7]

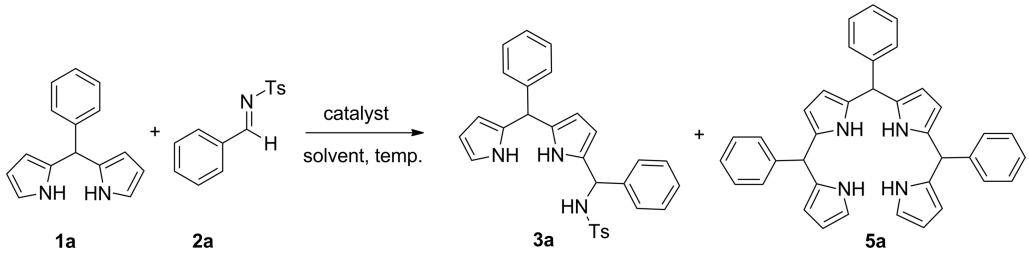
Due to the importance of oligopyrromethanes in porphyrin chemistry, developing a new method for the synthesis of tripyrranes and tetrapyrranes with non-identical substituents at the methylene bridges is in great demand. A new stepwise method for the synthesis of these compounds would also establish a convenient synthetic procedure to build up more complex members of the porphyrinoid family. Among them, corroles, analogs of porphyrins that have one less carbon atom, are the most well-known contracted porphyrinoids because of their interesting properties, such as stabilization of higher oxidation states of metal ions, higher fluorescence quantum yields, and larger Stokes shifts.[8] Despite these features, synthetic developments for corroles remained stagnant until 1999, at which time Gross and Paolesse published three papers on the direct syntheses of A_3-type *meso*-substituted corroles by reaction of pyrrole with aldehydes.[9] Thereafter, some other methods were developed to form A_3 and A_2B corroles by oxidative ring closure of bilanes.[10a,10b] Then, Gryko made an important contribution to the large-scale preparation of *meso*-substituted triarylcorroles.[10c] These improvements allowed their use in various fields ranging from materials chemistry to photophysics.[11] Although significant synthetic progress has been made for *meso*-substituted corroles, there is still a need for alternative synthetic approaches.

Previously, we have successfully developed facile protocols for the synthesis of *meso*-substituted dipyrromethanes, porphyrins, and [26]hexaphyrin by using tosylimines as effective reagents in the presence of metal triflate catalysts.[12] As part of our ongoing research on oligopyrromethanes and macrocyclic aromatic compounds, herein we present an efficient synthetic methodology for symmetrical or unsymmetrical tripyrranes **4** and tetrapyrranes **5** by starting from dipyrromethanesulfonamides **3**. In addition, the use of tetrapyrranes for the synthesis of A_3 as well as *trans*-A_2B corroles **6** is described (Scheme 2).

Results and Discussion

Synthesis of Dipyrromethanesulfonamides

Our study was initiated by optimizing the synthesis of dipyrromethanesulfonamides by using the reaction of 5-phenyldipyrromethane (**1a**) with *N*-benzylidene-4-methylbenzenesulfonamide (**2a**; Scheme 3).



Scheme 3. Preparation of dipyrromethanesulfonamide **3a** and bilane **5a**.

In accordance with our previously reported procedure for the synthesis of pyrrolesulfonamides,[12f] initial conditions for the reaction were chosen as 10% $Cu(OTf)_2$, dipyrromethane **1a**/tosylimine **2a** (3:1), tetrahydrofuran (THF), 0 °C (Table 1, Entry 1). Under these conditions, dipyrromethanesulfonamide **3a** and bilane **5a** were obtained in 60 and 10% yields, respectively. Next, the influence of the **1a/2a** ratio was investigated (Table 1, Entries 1–3). When the ratio of **1a/2a** was taken as 1:1 (Table 1, Entry 3), the yield of dipyrromethanesulfonamide slightly increased to 65%, and the yield of bilane decreased to 2%. The ratio 1:1 for **1a/2a** was chosen as the optimum ratio for further reactions. Subsequently, the effect of temperature on the dipyrromethanesulfonamide formation was studied. The reaction at room temperature furnished **3a** in decreased yield with a sharp increase in the yield of **5a** (Table 1, Entry 4). By lowering the temperature to –20 °C a decrease in the yield of **3a** (40%) occurred (Table 1, Entry 5). The best result was obtained at 0 °C. Then the effects of different solvents on the reaction were investigated. Among the screened solvents (Table 1, Entries 3, 6–11), THF was found to be the best. Next, we explored the effect of different catalysts, including Lewis acids and clays on the model reaction (Table 1, Entries 12–21). $ZnCl_2$, Mont. K-10, CuBr and $InCl_3$ gave **3a** in low yields (15–30% yields; Table 1, Entries 16, 18, 20, and 21). Comparable yields were obtained if $Cu(OTf)_2$, $Yb(OTf)_3$, $Gd(OTf)_3$, or $FeCl_3$ were used (Table 1, Entries 3, 12–14). Among these catalysts, $Cu(OTf)_2$ formed the desired product **3a** in the highest yield (65%), and it was chosen as the optimal catalyst for the synthesis of dipyrromethanesulfonamides.

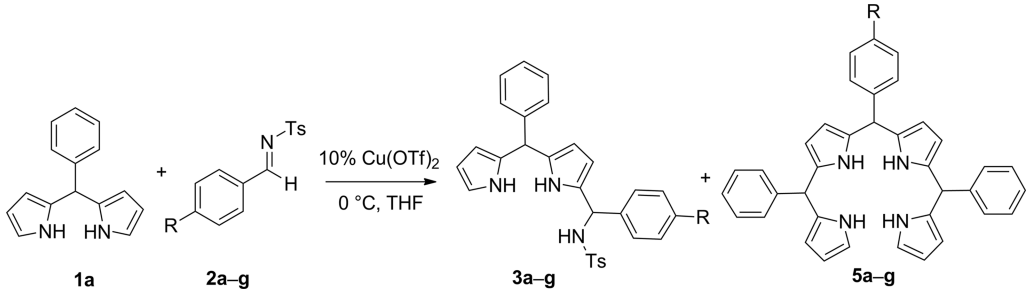
Table 1. Optimization of conditions for dipyrromethanesulfonamide synthesis.[a]

Entry	Temp. [°C]	Solvent	**1a/2a**	Catalyst	Yield [%][b] **3a**	**5a**
1	0	THF	3:1	$Cu(OTf)_2$	60	10
2	0	THF	2:1	$Cu(OTf)_2$	63	5
3	0	THF	1:1	$Cu(OTf)_2$	65	2
4	r.t.	THF	1:1	$Cu(OTf)_2$	48	27
5	–20	THF	1:1	$Cu(OTf)_2$	40	–
6	0	DMF	1:1	$Cu(OTf)_2$	< 1	–
7	0	CH_3CN	1:1	$Cu(OTf)_2$	< 1	–
8	0	toluene	1:1	$Cu(OTf)_2$	55	13
9	0	CH_2Cl_2	1:1	$Cu(OTf)_2$	43	10
10	0	CH_3OH	1:1	$Cu(OTf)_2$	30	5
11	0	$CHCl_3$	1:1	$Cu(OTf)_2$	48	15
12	0	THF	1:1	$Gd(OTf)_3$	60	5
13	0	THF	1:1	$Yb(OTf)_3$	58	6
14	0	THF	1:1	$FeCl_3$	55	10
15	0	THF	1:1	$NiCl_2$	–	–
16	0	THF	1:1	$ZnCl_2$	15	–
17	0	THF	1:1	LiCl	–	–
18	0	THF	1:1	Mont. K-10[c]	30	–
19	0	THF	1:1	Mont. KSF[c]	–	–
20	0	THF	1:1	CuBr	25	–
21	0	THF	1:1	$InCl_3$	20	–

[a] All reactions were performed with **1a** (0.10 mmol), **2a** (0.10 mmol), and catalyst (0.01 mmol) in solvent (1.5 mL). [b] Isolated yields after column chromatography. [c] Clay catalyst (100 mg) was used.

With the optimized conditions in hand, a range of dipyrromethanesulfonamides **3a**–**3g** were synthesized by using tosylimines **2a**–**2g** with different substituents on the phenyl ring. Compounds **2a**, **2b**, and **2e**–**2g** gave the corresponding products with different diastereomeric ratios in the range 50–71:29–50 (Table 2, Entries 1, 2, 5–7). Results of substituent effects on the reaction are depicted in Table 2. Reaction of **1a** with tosylimines that bear halogens or methoxy groups gave the desired products **3b**–**3e** in moderate yields (Table 2, Entries 2–5). Tosylimines that bear strongly electron-withdrawing cyano and nitro groups formed the corresponding addition products **3f** and **3g** in

Table 2. Synthesis of dipyrromethanesulfonamides.[a]



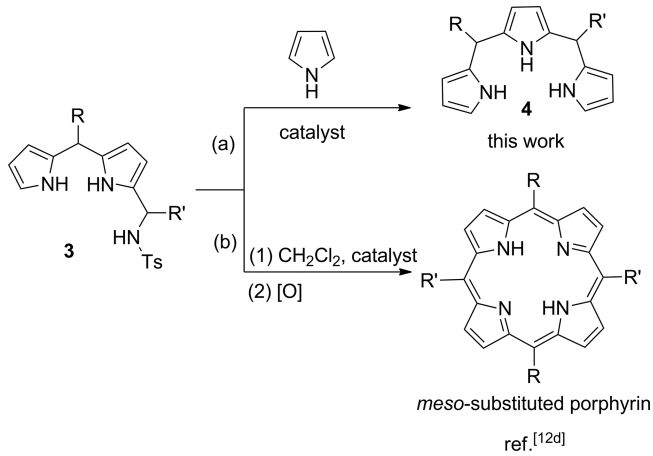
Entry	**2**	R	Yield [%][b] **3a**–**3g** (*dr*)	**5a**–**5g**
1	**2a**	H	65 (50:50)	2
2	**2b**	F	65 (71:29)	8
3	**2c**	Cl	52 (–)	3
4	**2d**	Br	63 (–)	2
5	**2e**	CH_3O	45 (52:48)	3
6	**2f**	CN	68 (69:31)	5
7	**2g**	NO_2	70 (63:37)	2

[a] All reactions were performed with **1a** (1.0 mmol), **2** (1.0 mmol), and $Cu(OTf)_2$ (0.1 mmol) in THF (15 mL). [b] Isolated yields after column chromatography.

slightly higher yields (Table 2, Entries 6 and 7). In all reactions, side products **5a**–**5g** were formed in very low yields (2–8%; Table 2, Entries 1–7).

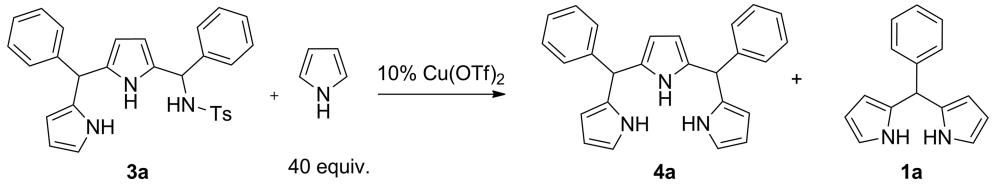
Synthesis of Tripyrranes

After completion of the synthesis of dipyrromethanesulfonamides, our next goal was to use them to construct oligopyrrolic structures. Although there are various methods that involve acid-catalyzed condensation of pyrrole with aldehydes for the syntheses of symmetrical tripyrranes,[13] the only synthetic protocol for unsymmetrical AB-type tripyrranes was reported by Osuka et al.[7] The method consists of three steps: (i) benzoylation of dipyrromethanes; (ii) reduction of the benzoyl group; and (iii) reaction of dipyrromethane carbinols with pyrrole. In addition, the method requires Grignard reagents and inert reaction conditions. Consequently, we directed our attention toward the synthesis of unsymmetrical tripyrranes **4** by nucleophilic substitution reaction of pyrrole with dipyrromethanesulfonamides **3** (Scheme 4a) under mild reaction conditions. We have recently shown that dipyrromethanesulfonamides afforded *meso*-substituted porphyrins if the reaction was carried out in dichloromethane at room temperature (Scheme 4b).[12d] To avoid this cyclisation reaction and access the desired tripyrranes **4**, pyrrole was used both as solvent and reactant.



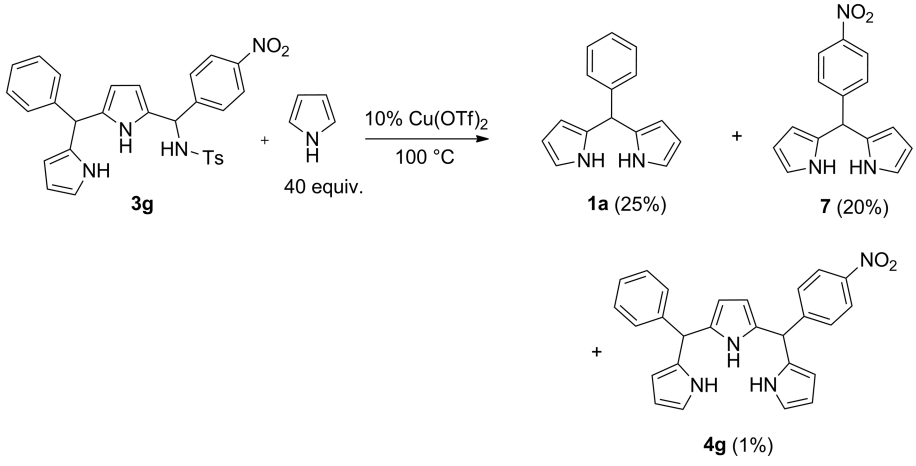
Scheme 4. Synthesis of tripyrranes **4**.

We have examined the reaction conditions for dipyrromethanesulfonamide **3a** and pyrrole in detail with various catalysts. The best yield (35%) was obtained with 40 equiv. of pyrrole in the presence of $Cu(OTf)_2$ catalyst (see Supporting Information, Table S1, Entry 3). In an attempt to increase the yield of tripyrrane product, the reaction was run at different temperatures (Scheme 5). The yield of **4a**



Temperature [°C]	Yield [%] **4a**	Yield [%] **1a**
0	15	–
r.t.	35	–
50	52	–
80	15	30
100	–	40

Scheme 5. Effect of temperature on the preparation of **4a**.



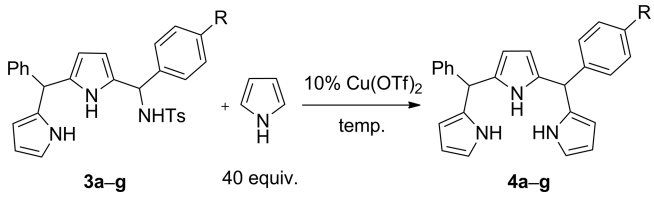
Scheme 6. Fragmentation of tripyrrane at high temperature.

improved by increasing the temperature from room temp. to 50 °C and reached 52% yield. Further increases in temperature decreased the yield of **4a** and caused the formation of 5-phenyldipyrromethane (**1a**). At 100 °C, **1a** was isolated as the only product in 40% yield (Scheme 5).

To understand the course of the reaction at high temperatures and test the sensitivity of the reaction to temperature, the same reaction was repeated by using dipyrromethanesulfonamide **3g** that bears two different substituents (phenyl and *p*-nitrophenyl) at 100 °C. After chromatographic separation, 5-phenyldipyrromethane (**1a**), 5-(*p*-nitrophenyl)dipyrromethane (**7**), and 5-phenyl-10-(*p*-nitrophenyl)tripyrrane (**4g**) were isolated in 25, 20 and 1% yields, respectively (Scheme 6).

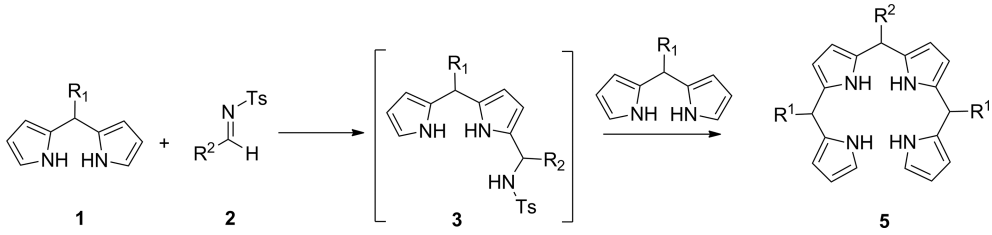
The formation of **1a** and **7** above 50 °C could be explained by temperature-dependent fragmentation of tripyrrane **4g** formed under the applied reaction conditions. As a result, the temperature was found to be the most important parameter for the formation of tripyrrane structures. In the next step, all reactions were performed at different temperatures for each substituent. The optimal temperatures for each one are depicted in Table 3. The optimal temperature was found to be 60 °C for halogen-bearing tripyrranes **4b**–**4d** (Table 3, Entries 2–4) and 50 °C for phenyl and methoxy substituents (Table 3, Entries 1 and 5). Dipyrromethanesulfonamides that bear electron-withdrawing cyano and nitro groups produced the corresponding products **4f** and **4g** at 80 °C (Table 3, Entries 6 and 7). This new synthetic

Table 3. Synthesis of tripyrranes.[a]



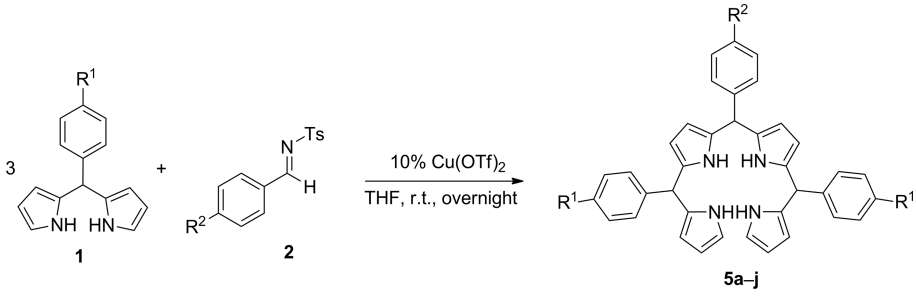
Entry	Temperature [°C]	R	Product	Yield [%][b]
1	50	H	**4a**	52
2	60	F	**4b**	55
3	60	Cl	**4c**	80
4	60	Br	**4d**	70
5	50	CH_3O	**4e**	67
6	80	CN	**4f**	60
7	80	NO_2	**4g**	80

[a] All reactions were performed with **3** (0.25 mmol), pyrrole (10 mmol), and $Cu(OTf)_2$ (0.025 mmol). [b] Isolated yields after column chromatography.



Scheme 7. Synthesis of bilanes through dipyrromethanesulfonamide intermediates.

Table 4. Synthesis of bilanes.[a]



Entry	R^1	R^2	Product	Yield [%][b]
1	H	H	**5a**	55
2	H	F	**5b**	65
3	H	Cl	**5c**	58
4	H	Br	**5d**	70
5	H	CH_3O	**5e**	60
6	H	CN	**5f**	75
7	H	NO_2	**5g**	85
8	F	F	**5h**	50
9	Cl	Cl	**5i**	65
10	NO_2	NO_2	**5j**	34

[a] All reactions were performed with **1** (3.0 mmol), **2** (1.0 mmol), and $Cu(OTf)_2$ (0.1 mmol). [b] Isolated yields after column chromatography.

strategy has rendered possible the synthesis of tripyrranes bearing different substituents at the 5- and 10-positions in moderate to high yields.

Synthesis of Bilanes

Encouraged by the results of the tripyrrane synthesis, the scope of the strategy was expanded for the synthesis of bilanes through dipyrromethanesulfonamide intermediates (Scheme 7). The advantage of this methodology is that it enables the selective synthesis of A_3- or A_2B-bilanes without any side product.

It was found that under the optimized conditions for dipyrromethanesulfonamides, the reaction of tosylimines with 3 equiv. of dipyrromethanes at room temperature afforded the corresponding A_3- and A_3B-bilanes **5a**–**5j**. The experimental results are summarized in Table 4. For tosylimines bearing halogen and methoxy substituents, the reaction resulted in the desired products **5b**–**5e** in moderate to good yields (Table 4, Entries 2–5). When the reaction was run with tosylimines substituted with electron-withdrawing cyano and nitro groups, the yields of bilanes increased to 75 and 85%, respectively (Table 4, Entries 6 and 7).

Synthesis of Corroles

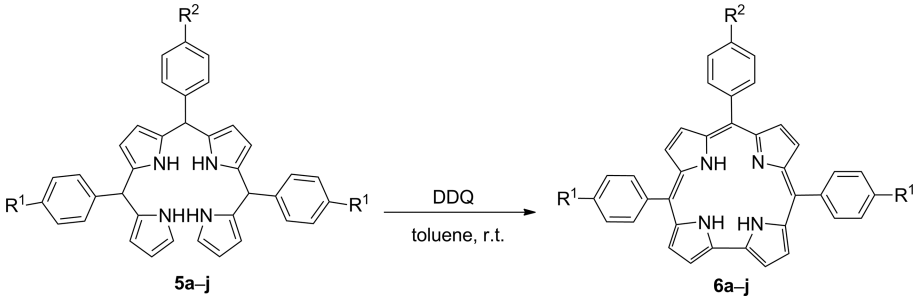
After the synthesis of bilanes as precursors of corroles, we focused on the oxidation of these important building blocks to obtain *meso*-substituted A_3- and A_2B-corroles. A number of synthetic protocols are available for the preparation of *meso*-substituted triarylcorroles by condensation reactions of aldehydes with pyrrole or dipyrromethanes. These methods mainly need time-consuming chromatographic separation procedures because of the formation of some other aromatic macrocycles. By the introduced methodology, the selective synthesis of tetrapyrranes in high yields could be a significant advantage in the formation of corroles without side products. Therefore, we directed our efforts toward the synthesis of *meso*-substituted corroles by oxidation of tetrapyrranes. Optimization of the reaction conditions is the most important step in corrole synthesis. For this purpose, various reaction parameters (solvent, bilane concentration, and temperature) were investigated. Initially, the role of solvent on the oxidation of **5a** was explored. All solvents except CH_3OH afforded 33–82% yield of the desired corrole **6a** (Table 5, Entries 1–7). The highest yield was obtained in toluene (82%), and thus it was chosen as the solvent for further studies. Next, the effect of the

Table 5. Optimization of the conditions for the corrole synthesis.[a]

Entry	Solvent	Concentration of **5a** [mM]	Yield [%][b]
1	CH_2Cl_2	5	57
2	THF	5	64
3	CH_3CN	5	33
4	DMF	5	44
5	CH_3OH	5	–
6	$CHCl_3$	5	36
7	toluene	5	82
8	toluene	1	49
9	toluene	2.5	70
10	toluene	10	66
11	toluene	20	60
12	toluene	40	58
13	toluene	80	48
14	toluene	5	34[c]

[a] All reactions were performed with **5a** (0.10 mmol) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ; 0.15 mmol). [b] Isolated yields after column chromatography. [c] At reflux temperatures in toluene.

Table 6. Synthesis of corroles by oxidation of tetrapyrranes.[a]



5a–j **6a–j**

Entry	R^1	R^2	Product	Yield [%][b]
1	H	H	**6a**	82
2	H	F	**6b**	53
3	H	Cl	**6c**	42
4	H	Br	**6d**	41
5	H	CH_3O	**6e**	32
6	H	CN	**6f**	22
7	H	NO_2	**6g**	34
8	F	F	**6h**	59
9	Cl	Cl	**6i**	35
10	NO_2	NO_2	**6j**	25

[a] All reactions were performed with **5** (0.2 mmol) and DDQ (0.3 mmol). [b] Isolated yields after column chromatography.

concentration of bilane **5a** on the yield of corrole **6a** was studied (Table 5, Entries 8–13). The optimum concentration of bilane was determined as 5 mM. When the reaction mixture was heated at reflux in toluene for 12 h, a sharp decrease in the reaction yield was observed (34%; Table 5, Entry 14).

Then, the direct synthesis of A_3- and *trans*-A_2B-corroles from the corresponding tetrapyrranes under the optimized conditions was performed. The highest yield of A_3-corrole was obtained for phenyl-substituted tetrapyrrane **5a** with a yield of 82% (Table 6, Entry 1). Halogen-bearing tetrapyrranes **5h** and **5i** gave the corresponding A_3-type corroles in 59 and 35% yields, respectively (Table 6, Entries 8 and 9). The electron-withdrawing nitro group on the tetrapyrrane decreased the reaction yield, and 5,10,15-tris(4-nitrophenyl) corrole (**6j**) was obtained in 27% yield (Table 6, Entry 10). Unsymmetrical tetrapyrranes that with halogens, electron-withdrawing (CN and NO_2), and electron-donating (CH_3O) groups, were employed to synthesize *trans*-A_2B-corroles (Table 6, Entries 2–7). Tetrapyrranes with halogen substituents **5b**–**5d** gave of corroles **6b**–**6d** in moderate 41–53% yields (Table 6, Entries 2–4). Electron-donating methoxy-substituted tetrapyrrane **5e** provided **6e** in 36% yield (Table 6, Entry 5). The lowest yield of *trans*-A_2B-corrole was 22% obtained with tetrapyrranes that had the electron-withdrawing cyano substituent, (Table 6, Entry 6). Compounds **6a**–**6f** and **6h**–**6j** were fully characterized by ^1H NMR and UV/Vis spectroscopy and HRMS analysis. Because compound **6g** was not very soluble, a good-quality NMR spectrum was not recorded. This compound was characterized by UV/Vis spectroscopy and HRMS analysis.

Conclusions

Dipyrromethanesulfonamide derivatives have been synthesized by $Cu(OTf)_2$-catalysed addition of *meso*-substituted dipyrromethanes to tosylimines. A new and general method has been developed to access unsymmetrical AB-type tripyrranes by using dipyrromethanesulfonamides, which have important applications in the syntheses of various aromatic macrocycles. The same synthetic strategy has been applied to the synthesis of A_3- and A_2B-tetrapyrranes just by tuning the reaction conditions. Tetrapyrranes have been obtained in high yields at room temperature under mild reaction conditions. A_3- and *trans*-A_2B-corroles have been directly synthesized by oxidizing the corresponding tetrapyrranes with DDQ.

Experimental Section

General Information: All reagents were purchased from commercial suppliers and used without purification. Thin layer chromatography was performed on pre-coated silica gel 60 F254 plates (0.060–0.200 mm). Silica gel (230–400 mesh) was used for column chromatography. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded with a Bruker Ultrashield FT NMR spectrometer. Chemical shifts (δ) are reported downfield from tetramethylsilane. Data for ^1H NMR spectra are reported as follows: s = singlet, d = doublet, dd = doublet of doublets, m = multiplet, br. s = broad singlet. High-resolution mass spectra (HRMS) were recorded with an Agilent 1200/6210 high-resolution-mass time-of-flight (TOF) LC/MS spectrometer. Samples were dissolved and measured in MeOH or CH_3CN. Infrared spectra were recorded with an ATR (Nicolet iS10) instrument. Tosylimines **1** were synthesized in high yields by the reaction of *p*-toluenesulfonamide and aldehydes in the presence of *p*-toluenesulfonic acid. Dipyrromethanes **2**[12e] were synthesized in accordance to reported procedures. Peaks that represent both the major and minor diastereomers are donated by an asterisk (*). Square brackets indicate peaks that arise from the minor diastereomer as applicable.

General Procedure for the Synthesis of Dipyrromethanesulfonamides 3a–3g: A mixture of tosylimine **2** (1 mmol) and $Cu(OTf)_2$ (0.1 mmol) was stirred in THF (10 mL) at 0 °C for 30 min. A solution of dipyrromethane **1** (1 mmol) in THF (5 mL) was added dropwise. The reaction was monitored by TLC. After completion of the reaction, the mixture was passed through a short column packed with silica gel and eluted with ethyl acetate to remove $Cu(OTf)_2$. The eluent was evaporated under reduced pressure. The crude product was purified by flash column chromatography with silica gel 60 (230–400 mesh; ethyl acetate/hexane, 1:6).

4-Methyl-*N*-(phenyl{5-[phenyl(1*H*-pyrrol-2-yl)methyl]-1*H*-pyrrol-2-yl}methyl)benzenesulfonamide (3a):[12d] Brown viscous oil (65% yield). *dr* = 50:50. R_f = 0.45 (EtOAc/hexane, 1:3). IR (ATR): $\tilde{\nu}_{max}$ = 3349, 3066, 2919, 2848, 1700, 1597, 1493, 1453, 1320, 1260, 1153, 1089, 1027, 801, 724, 698, 664, 557 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.37 (s, 6 H)*, 5.17–5.24 (m, 2 H)*, 5.32 (d, J = 5.6 Hz, 2 H)*, 5.43–5.47 (m, 4 H)*, 5.61–5.65 (m, 2 H)*, 5.83 (br. s, 2 H)*, 6.08 (br. s, 2 H)*, 6.60 (br. s, 2 H)*, 7.08–7.28 (m, 24 H)*, 7.52 (d, J = 8.2 Hz, 4 H)*, 7.90 (br. s, 2 H)*, 8.27 (br. s, 1 H), [8.29 (br. s, 1 H)] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6*, 44.1*, 55.9*, 107.4*, 107.4, [107.4], [108.6], 108.6, 108.6*, 117.2, [117.2], 127.0*, 127.3*, 127.3*, 127.8*, [128.5], 128.5, 128.6, [128.6], 129.4*, 130.1*, 130.2*, 132.2*, [133.8], 133.8, [137.5], 137.5, 138.9*, 142.1*, 143.1* ppm. HRMS (ESI): calcd. for $C_{29}H_{26}N_3O_2S$ $[M - H]^-$ 480.1751; found 480.1754.

***N*-[(4-Fluorophenyl){5-[phenyl(1*H*-pyrrol-2-yl)methyl]-1*H*-pyrrol-2-yl}methyl]-4-methylbenzenesulfonamide (3b):** Brown viscous oil (65% yield). *dr* = 71:29. R_f = 0.49 (EtOAc/hexane, 1:3). IR (ATR): $\tilde{\nu}_{max}$ = 3367, 2961, 2918, 1704, 1600, 1507, 1451, 1259, 1224, 1154, 1091, 1027, 845, 793, 725, 664, 578 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.34 (s, 6 H)*, 5.26 (s, 1 H), [5.29 (s, 1 H)], 5.40–5.47 (m, 4 H)*, 5.59 (br. s, 2 H)*, 5.77 (br. s, 2 H)*, 6.02 (br. s, 4 H)*, [6.50 (br. s, 1 H)], 6.52 (br. s, 1 H), 6.74–6.80 (m, 4 H)*, 6.99–7.24 (m, 18 H)*, 7.44 (d, J = 8.0 Hz, 4 H)*, 8.07 (br. s, 2 H)*, 8.54 (br. s, 1 H), [8.59 (br. s, 1 H)] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.5, [21.6], 44.0*, 55.3*, 107.2*, 107.3*, 108.4*, 108.6*, 115.1 (d, $^2J_{C,F}$ = 21.5 Hz)*, 117.2, [117.3], 126.5*, 126.8*, 128.4*, 128.4*, 129.1 (d, $^3J_{C,F}$ = 8.0 Hz)*, 129.6*, 129.8, [129.9], 132.5*, [134.1], 134.1, 134.7*, 134.7*, [137.3], 137.3, [142.2], 142.2, 143.1*, 162.1 (d, $^1J_{C,F}$ = 245.3 Hz)* ppm. HRMS (ESI): calcd. for $C_{29}H_{27}FN_3O_2S$ $[M + H]^+$ 500.1803; found 500.1740.

***N*-[(4-Chlorophenyl){5-[phenyl(1*H*-pyrrol-2-yl)methyl]-1*H*-pyrrol-2-yl}methyl]-4-methylbenzenesulfonamide (3c):** Brown viscous oil (52% yield). R_f = 0.40 (EtOAc/hexane, 1:3). IR (ATR): $\tilde{\nu}_{max}$ = 3385, 3279, 2928, 1723, 1581, 1495, 1322, 1152, 1085, 1038, 912, 810, 722 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.37 (s, 3 H), 5.32 (br. s, 1 H), 5.38 (d, J = 8.2 Hz, 1 H), 5.46 (s, 1 H), 5.49 (br. s, 1 H), 5.67 (br. s, 1 H), 5.85 (br. s, 1 H), 6.12 (br. s, 1 H), 6.64 (br. s, 1 H), 7.01 (d, J = 8.4 Hz, 2 H), 7.08–7.17 (m, 5 H), 7.20–7.31 (m, 4 H), 7.49 (d, J = 8.0 Hz, 2 H), 7.96 (br. s, 1 H), 8.23 (br. s, 1 H)

ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.5, 44.0, 55.2, 107.3, 107.3, 108.4, 108.6, 117.3, 127.0, 127.1, 128.3, 128.5, 128.6, 128.7, 129.5, 129.5, 132.3, 133.7, 134.2, 136.9, 137.1, 141.8, 143.6 ppm. HRMS (ESI): calcd. for $C_{29}H_{25}ClN_3O_2S$ [M – H]$^-$ 514.1361; found 514.1364.

***N*-[(4-Bromophenyl){5-[phenyl(1*H*-pyrrol-2-yl)methyl]-1*H*-pyrrol-2-yl}methyl]-4-methylbenzenesulfonamide (3d):** Brown viscous oil (63% yield). R_f = 0.43 (EtOAc/hexane, 1:3). IR (ATR): $\tilde{\nu}_{max}$ = 3370, 3255, 2925, 1664, 1597, 1487, 1322, 1156, 1097, 1069, 1030, 1010, 908, 810, 770 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.39 (s, 3 H), 5.12 (d, J = 7.2 Hz, 1 H), 5.34 (s, 1 H), 5.44 (d, J = 7.2 Hz, 1 H), 5.49 (br. s, 1 H), 5.66–5.69 (m, 1 H), 5.86 (br. s, 1 H), 6.14 (br. s, 1 H), 6.67 (br. s, 1 H), 6.97 (d, J = 8.3 Hz, 2 H), 7.11–7.18 (m, 5 H), 7.23–7.33 (m, 4 H), 7.51 (d, J = 8.0 Hz, 2 H), 7.90 (br. s, 1 H), 8.14 (br. s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.5, 44.0, 55.3, 107.3, 107.4, 108.4, 108.6, 117.3, 121.9, 127.1, 128.3, 128.7, 129.0, 129.4, 129.6, 131.5, 132.1, 134.1, 136.9, 137.5, 141.7, 143.7 ppm. HRMS (ESI): calcd. for $C_{29}H_{25}BrN_3O_2S$ [M – H]$^-$ 558.0856; found 558.0811.

***N*-[(4-Methoxyphenyl){5-[phenyl(1*H*-pyrrol-2-yl)methyl]-1*H*-pyrrol-2-yl}methyl]-4-methylbenzenesulfonamide (3e):** Brown viscous oil (45% yield). *dr* = 52:48. R_f = 0.33 (EtOAc/hexane, 1:3). IR (ATR): $\tilde{\nu}_{max}$ = 3350, 3251, 2917, 1708, 1598, 1511, 1452, 1259, 1160, 1089, 1034, 817 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.34 (s, 6 H)*, 3.71 (s, 6 H)*, 5.27 (br. s, 1 H), [5.30 (s, 1 H)], 5.38 (d, J = 7.2 Hz, 2 H)*, 5.43–5.47 (m, 2 H)*, 5.57–5.61 (m, 4 H)*, 5.78 (br. s, 1 H), [5.79 (br. s, 1 H)], 6.00–6.05 (m, 2 H)*, [6.52 (br. s, 1 H)], 6.54 (br. s, 1 H), 6.62 (d, J = 8.4 Hz, 4 H)*, 6.95 (d, J = 8.4 Hz, 4 H)*, 7.05 (d, J = 8.0 Hz, 4 H)*, 7.12 (d, J = 8.0 Hz, 4 H)*, 7.20–7.28 (m, 6 H)*, 7.47 (d, J = 8.0 Hz, 4 H)*, 8.01 (br. s, 2 H)*, 8.40 (br. s, 1 H), [8.45 (br. s, 1 H)] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.4*, 43.8*, 54.9*, 55.2*, [107.0], 107.1, 107.1*, [108.1], 108.1, 108.2, [108.2], 113.5*, 116.9, [117.0], 126.4*, 126.6*, 127.0*, [128.2], 128.3, 128.3*, 129.2*, 129.4*, 130.2, [130.2], 130.8, [130.8], 132.2*, [133.5], 133.6, 137.2, [137.3], 142.0*, 158.9* ppm. HRMS (ESI): calcd. for $C_{30}H_{28}N_3O_3S$ [M – H]$^-$ 510.1857; found 510.1858.

***N*-[(4-Cyanophenyl){5-[phenyl(1*H*-pyrrol-2-yl)methyl]-1*H*-pyrrol-2-yl}methyl]-4-methylbenzenesulfonamide (3f):** Brown viscous oil (68% yield). *dr* = 69:31. R_f = 0.21 (EtOAc/hexane, 1:3). IR (ATR): $\tilde{\nu}_{max}$ = 3366, 3261, 2923, 2228, 1705, 1560, 1494, 1429, 1323, 1155, 1091, 1030, 919, 856, 812, 771, 725 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.36 (s, 6 H)*, 5.25 (s, 1 H), [5.29 (s, 1 H)], 5.37–5.40 (m, 2 H)*, 5.48–5.54 (m, 2 H)*, 5.60 (br. s, 2 H)*, 5.74–5.83 (m, 3 H)*, 5.91 (d, J = 8.2 Hz, 1 H), 5.99–6.03 (m, 2 H)*, [6.45 (br. s, 1 H)], 6.50 (br. s, 1 H), 7.03–7.11 (m, 8 H)*, 7.15–7.24 (m, 10 H)*, 7.36 (d, J = 8.2 Hz, 4 H)*, 7.40–7.45 (m, 4 H)*, 7.95 (br. s, 2 H)*, 8.43 (br. s, 1 H), [8.53 (br. s, 1 H)] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.5*, 43.9*, 55.4*, [107.3], 107.4, 107.5*, [108.4], 108.4, 108.9*, 111.6*, 117.3, [117.4], 118.1*, [126.9], 127.0, 128.1*, 128.3*, 128.3*, 128.4*, 128.5*, 129.5*, 131.9*, 132.2*, [134.6], 134.6, [137.0], 137.0, [141.8], 141.9, 143.7*, 144.0* ppm. HRMS (ESI): calcd. for $C_{30}H_{25}N_4O_2S$ [M – H]$^-$ 505.1704; found 505.1785.

4-Methyl-*N*-[(4-nitrophenyl){5-[phenyl(1*H*-pyrrol-2-yl)methyl]-1*H*-pyrrol-2-yl}methyl]benzenesulfonamide (3g): Brown viscous oil (70% yield). *dr* = 63:37. R_f = 0.26 (EtOAc/hexane, 1:3). IR (ATR): $\tilde{\nu}_{max}$ = 3363, 2961, 2924, 1705, 1519, 1493, 1346, 1259, 1155, 1090, 1030, 862, 793, 725 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.32 (s, 6 H)*, 5.27 (s, 1 H), [5.29 (s, 1 H)], 5.39 (br. s, 2 H)*, 5.56 (br. s, 2 H)*, 5.60 (br. s, 4 H)*, 5.77 (br. s, 2 H)*, 6.01 (br. s, 2 H)*, [6.49 (br. s, 1 H)], 6.52 (br. s, 1 H), 7.03 (d, J = 7.8 Hz, 4 H)*, 7.08 (d, J = 7.8 Hz, 4 H)*, 7.18–7.26 (m, 10 H)*, 7.44 (d, J = 7.8 Hz, 4 H)*, 7.91 (d, J = 7.8 Hz, 4 H)*, 8.03 (br. s, 2 H)*, 8.57 (br. s, 1 H), [8.60 (br. s, 1 H)] ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.5*, 43.9*, 55.2*, 107.3*, 107.5*, 108.4*, 108.9*, 117.3*, 123.3*, 126.9*, 127.0*, 128.2*, 128.3*, 128.5*, 129.5*, 132.3*, 134.8*, 136.9*, 141.9*, 143.7*, 145.9*, 147.2* ppm. HRMS (ESI): calcd. for $C_{29}H_{25}N_4O_4S$ [M – H]$^-$ 525.1602; found 525.1636.

General Procedure for the Synthesis of Tripyrranes 4a–4g: Dipyrromethanesulfonamide **3** (0.25 mmol) was dissolved in excess pyrrole (10 mmol). $Cu(OTf)_2$ (0.025 mmol) was added to the reaction mixture at the temperature indicated in Table 4. The reaction was monitored by TLC. After completion of the reaction, the mixture was passed through a short column packed with silica gel and eluted with ethyl acetate to remove $Cu(OTf)_2$. The eluent was evaporated under reduced pressure. The crude product was purified by flash column chromatography with silica gel 60 (230–400 mesh; ethyl acetate/hexane, 1:6).

2-(Phenyl{5-[phenyl(1*H*-pyrrol-2-yl)methyl]-1*H*-pyrrol-2-yl}methyl)-1*H*-pyrrole (4a):[4g] Black viscous oil (52% yield). R_f = 0.63 (EtOAc/hexane, 1:3). IR (ATR): $\tilde{\nu}_{max}$ = 3362, 3059, 3023, 2925, 1698, 1450, 1247, 1028, 963, 884, 767, 717, 698 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.17 (br. s, 2 H), 5.60–5.63 (m, 2 H), 5.72 (br. s, 2 H), 5.97 (br. s, 2 H), 6.46 (br. s, 2 H), 7.02–7.06 (m, 4 H), 7.08–7.20 (m, 6 H), 7.54 (br. s, 1 H), 7.64 (br. s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 44.0, 107.3, 107.6, 108.6, 117.1, 126.9, 128.4, 128.6, 132.3, 132.4, 142.2 ppm. HRMS (ESI): calcd. for $C_{26}H_{22}N_3$ [M – H]$^-$ 376.1819; found 376.1850.

2-[(4-Fluorophenyl){5-[phenyl(1*H*-pyrrol-2-yl)methyl]-1*H*-pyrrol-2-yl}methyl]-1*H*-pyrrole (4b): Black viscous oil (55% yield). R_f = 0.44 (EtOAc/hexane, 1:3). IR (ATR): $\tilde{\nu}_{max}$ = 3366, 3106, 3023, 2921, 1712, 1507, 1219, 1026, 849, 774, 731, 695 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.17 (s, 1 H), 5.19 (s, 1 H), 5.53 (br. s, 1 H), 5.56 (br. s, 1 H), 5.64 (br. s, 1 H), 5.67 (br. s, 1 H), 5.92 (br. s, 2 H), 6.47 (br. s, 2 H), 6.80 (t, J = 8.1 Hz, 2 H), 6.93–7.02 (m, 4 H), 7.03–7.15 (m, 3 H), 7.49 (br. s, 1 H), 7.66 (br. s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 43.3, 44.1, 107.3, 107.3, 107.6, 108.6, 108.7, 115.3 (d, $^2J_{C,F}$ = 21.2 Hz), 117.0, 117.1, 127.0, 128.3, 128.6, 129.8 (d, $^3J_{C,F}$ = 7.8 Hz), 132.0, 132.0, 132.1, 132.4, 137.8, 142.0, 161.8 (d, $^2J_{C,F}$ = 244.8 Hz) ppm. HRMS (ESI): calcd. for $C_{26}H_{21}FN_3$ [M – H]$^-$ 394.1725; found 394.1754.

2-[(4-Chlorophenyl){5-[phenyl(1*H*-pyrrol-2-yl)methyl]-1*H*-pyrrol-2-yl}methyl]-1*H*-pyrrole (4c): Black viscous oil (80% yield). R_f = 0.50 (EtOAc/hexane, 1:3). IR (ATR): $\tilde{\nu}_{max}$ = 3370, 3094, 2929, 1704, 1483, 1176, 1081, 967, 884, 762, 719, 697 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.25–5.32 (m, 2 H), 5.63–5.67 (m, 2 H), 5.77 (br. s, 2 H), 6.04–6.07 (m, 2 H), 6.62 (br. s, 2 H), 7.00–7.24 (m, 9 H), 7.70 (br. s, 1 H), 7.86 (br. s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 43.5, 44.1, 107.2, 107.3, 107.5, 107.6, 108.4, 108.5, 117.2, 117.4, 127.0, 128.3, 128.6, 128.7, 129.7, 131.8, 132.0, 132.4, 132.6, 132.7, 140.6, 141.9 ppm. HRMS (ESI): calcd. for $C_{26}H_{21}ClN_3$ [M – H]$^-$ 410.1429; found 410.1447.

2-[(4-Bromophenyl){5-[phenyl(1*H*-pyrrol-2-yl)methyl]-1*H*-pyrrol-2-yl}methyl]-1*H*-pyrrole (4d):[7] Black viscous oil (70% yield). R_f = 0.49 (EtOAc/hexane, 1:3). IR (ATR): $\tilde{\nu}_{max}$ = 3468, 2929, 1715, 1499, 1101, 1042, 1014, 904, 727, 648 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.26 (br. s, 1 H), 5.30 (br. s, 1 H), 5.63–5.70 (m, 2 H), 5.75–5.81 (m, 2 H), 6.03–6.10 (m, 2 H), 6.61 (br. s, 2 H), 6.98 (d, J = 8.3 Hz, 2 H), 7.11 (d, J = 7.4 Hz, 2 H), 7.16–7.22 (m, 1 H), 7.23 (d, J = 7.4 Hz, 2 H), 7.34 (d, J = 8.3 Hz, 2 H), 7.68 (br. s, 1 H), 7.84 (br. s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 43.5, 44.0, 107.2, 107.3, 107.5, 107.6, 108.4, 108.5, 117.3, 117.4, 120.8, 127.0, 128.3, 128.7, 130.1, 131.6, 131.9, 132.4, 132.7, 141.1, 141.9 ppm. HRMS (ESI): calcd. for $C_{26}H_{21}BrN_3$ [M – H]$^-$ 454.0924; found 454.0940.

2-[(4-Methoxyphenyl)(1*H*-pyrrol-2-yl)methyl]-5-[phenyl(1*H*-pyrrol-2-yl)methyl]-1*H*-pyrrole (4e):[7] Black viscous oil (67% yield). R_f = 0.57 (EtOAc/hexane, 1:3). IR (ATR): $\tilde{\nu}_{max}$ = 3362, 3094, 3035, 2925, 1715, 1519, 1243, 1168, 1034, 845, 766, 715 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.77 (s, 3 H), 5.28 (s, 1 H), 5.33 (s, 1 H), 5.70 (br. s, 2 H), 5.81 (br. s, 2 H), 6.04–6.09 (m, 2 H), 6.60 (br. s, 2 H), 6.79 (d, J = 8.6 Hz, 2 H), 7.05 (d, J = 8.6 Hz, 2 H), 7.15 (d, J = 7.4 Hz, 2 H), 7.21–7.30 (m, 3 H), 7.64 (br. s, 1 H), 7.80 (br. s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 43.1, 44.0, 54.9, 107.0, 107.1, 107.2, 107.4, 108.4, 108.4, 113.7, 116.7, 116.8, 126.7, 128.2, 128.4, 129.2, 131.9, 132.1, 132.4, 132.5, 134.0, 142.0, 158.4 ppm. HRMS (ESI): calcd. for $C_{27}H_{24}N_3O$ $[M - H]^-$ 406.1925; found 406.1925.

4-[{5-[Phenyl(1*H*-pyrrol-2-yl)methyl]-1*H*-pyrrol-2-yl}(1*H*-pyrrol-2-yl)methyl]benzonitrile (4f): Black viscous oil (60% yield). R_f = 0.40 (EtOAc/hexane, 1:3). IR (ATR): $\tilde{\nu}_{max}$ = 3360, 3040, 2915, 2227, 1715, 1495, 1259, 1090, 1027, 787, 721, 674 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.33 (s, 1 H), 5.37 (s, 1 H), 5.61–5.65 (m, 1 H), 5.71 (br. s, 1 H), 5.75 (br. s, 1 H), 5.81 (br. s, 1 H), 6.07 (br. s, 2 H), 6.61 (br. s, 1 H), 6.64 (br. s, 2 H), 7.13 (d, J = 7.0 Hz, 2 H), 7.20–7.30 (m, 4 H), 7.55 (d, J = 8.2 Hz, 2 H), 7.72 (br. s, 1 H), 7.82 (br. s, 1 H), 7.89 (br. s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 44.1, 44.1, 107.4, 107.8, 108.0, 108.7, 108.9, 111.1, 117.2, 117.6, 118.3, 127.1, 128.3, 128.6, 129.1, 130.6, 130.7, 131.9, 132.2, 133.0, 135.0, 141.8, 147.5 ppm. HRMS (ESI): calcd. for $C_{27}H_{21}N_4$ $[M - H]^-$ 401.1772; found 401.1797.

2-[(4-Nitrophenyl)(1*H*-pyrrol-2-yl)methyl]-5-[phenyl(1*H*-pyrrol-2-yl)methyl]-1*H*-pyrrole (4g): Black viscous oil (80% yield). R_f = 0.34 (EtOAc/hexane, 1:3). IR (ATR): $\tilde{\nu}_{max}$ = 3383, 3080, 2920, 1712, 1514, 1344, 1259, 1089, 1027, 787, 721, 700 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.33 (s, 1 H), 5.41 (s, 1 H), 5.64 (br. s, 1 H), 5.71 (br. s, 1 H), 5.75 (br. s, 1 H), 5.80 (br. s, 1 H), 6.06 (br. s, 2 H), 6.59–6.67 (m, 2 H), 7.12 (d, J = 7.0 Hz, 2 H), 7.17–7.34 (m, 5 H), 7.76 (br. s, 1 H), 7.82 (br. s, 1 H), 7.93 (br. s, 1 H), 8.10 (d, J = 8.3 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 43.9, 44.1, 107.3, 107.8, 108.0, 108.7, 109.0, 117.2, 117.7, 123.7, 127.1, 128.3, 128.6, 129.1, 130.5, 130.6, 132.0, 133.1, 135.0, 141.8, 147.0, 149.5 ppm. HRMS (ESI): calcd. for $C_{26}H_{21}N_4O_2$ $[M - H]^-$ 421.1670; found 421.1698.

General Procedure for the Synthesis of Bilanes 5a–5j: A mixture of tosylimine **2** (1 mmol) and $Cu(OTf)_2$ (0.1 mmol) was stirred in THF (3 mL) at room temperature for 30 min. A solution of dipyrromethane **1** (3 mmol) in THF (5 mL) was added dropwise. The reaction was monitored by TLC, and the reaction was complete in 18 h. The mixture was passed through a short column packed with silica gel and eluted with ethyl acetate to remove $Cu(OTf)_2$. The eluent was evaporated under reduced pressure. The crude product was purified by flash column chromatography with silica gel 60 (230–400 mesh; ethyl acetate/hexane, 1:5).

2-[Phenyl(1*H*-pyrrol-2-yl)methyl]-5-(phenyl{5-[phenyl(1*H*-pyrrol-2-yl)methyl]-1*H*-pyrrol-2-yl}methyl)-1*H*-pyrrole (5a):[12d] Black viscous oil (55% yield). R_f = 0.47 (EtOAc/hexane, 1:3). IR (ATR): $\tilde{\nu}_{max}$ = 3420, 3102, 3062, 2959, 1698, 1492, 1451, 1260, 1074, 766, 718, 698 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.19 (br. s, 1 H), 5.29 (br. s, 2 H), 5.66 (br. s, 4 H), 5.80 (br. s, 2 H), 6.07 (br. s, 2 H), 6.58 (br. s, 2 H), 7.00–7.34 (m, 15 H), 7.67 (br. s, 2 H), 7.81 (br. s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 44.0, 44.1, 107.2, 107.4, 107.5, 108.5, 117.1, 126.9, 128.3, 128.4, 128.5, 128.5, 130.2, 132.2, 132.2, 132.4, 133.5, 142.1 ppm. HRMS (ESI): calcd. for $C_{37}H_{31}N_4$ $[M - H]^-$ 531.2554; found 531.2578.

2-[(4-Fluorophenyl){5-[phenyl(1*H*-pyrrol-2-yl)methyl]-1*H*-pyrrol-2-yl}methyl]-5-[phenyl(1*H*-pyrrol-2-yl)methyl]-1*H*-pyrrole (5b): Black viscous oil (65% yield). R_f = 0.43 (EtOAc/hexane, 1:3). IR (ATR): $\tilde{\nu}_{max}$ = 3362, 3059, 3023, 2960, 2929, 2874, 1715, 1601, 1503, 1456, 1423, 1219, 1156, 1089, 1030, 967, 908, 845, 758, 723 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.21 (br. s, 1 H), 5.32 (br. s, 2 H), 5.65 (br. s, 2 H), 5.69 (br. s, 2 H), 5.82 (br. s, 2 H), 6.09 (br. s, 2 H), 6.61 (br. s, 2 H), 6.91–6.97 (m, 2 H), 7.06–7.11 (m, 6 H), 7.22–7.30 (m, 6 H), 7.72 (br. s, 2 H), 7.87 (br. s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 43.2, 43.9, 107.1, 107.3, 107.4, 108.4, 115.1 (d, $^2J_{C,F}$ = 21.2 Hz), 117.0, 126.9, 128.2, 128.4, 129.7 (d, $^3J_{C,F}$ = 7.8 Hz), 131.9, 132.2, 132.3, 137.7 (d, $^4J_{C,F}$ = 3.1 Hz), 141.9, 161.6 (d, $^1J_{C,F}$ = 244.3 Hz) ppm. HRMS (ESI): calcd. for $C_{37}H_{30}FN_4$ $[M - H]^-$ 549.2460; found 549.2487.

2-[(4-Chlorophenyl){5-[phenyl(1*H*-pyrrol-2-yl)methyl]-1*H*-pyrrol-2-yl}methyl]-5-[phenyl(1*H*-pyrrol-2-yl)methyl]-1*H*-pyrrole (5c): Black viscous oil (58% yield). R_f = 0.49 (EtOAc/hexane, 1:3). IR (ATR): $\tilde{\nu}_{max}$ = 3420, 3098, 3058, 2923, 1728, 1489, 1089, 1028, 913, 764, 724, 700 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.18 (br. s, 1 H), 5.32 (br. s, 2 H), 5.66 (br. s, 2 H), 5.70 (br. s, 2 H), 5.83 (br. s, 2 H), 6.08–6.12 (m, 2 H), 6.61 (br. s, 2 H), 7.06 (d, J = 8.2 Hz, 2 H), 7.11–7.19 (m, 5 H), 7.21–7.31 (m, 5 H), 7.68 (br. s, 2 H), 7.83 (br. s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 43.4, 43.9, 107.1, 107.4, 108.4, 117.0, 126.8, 128.2, 128.5, 129.5, 131.6, 132.2, 132.3, 132.6, 140.5, 141.9 ppm. HRMS (ESI): calcd. for $C_{37}H_{30}ClN_4$ $[M - H]^-$ 565.2164; found 565.2175.

2-[(4-Bromophenyl){5-[phenyl(1*H*-pyrrol-2-yl)methyl]-1*H*-pyrrol-2-yl}methyl]-5-[phenyl(1*H*-pyrrol-2-yl)methyl]-1*H*-pyrrole (5d): Black viscous oil (70% yield). R_f = 0.46 (EtOAc/hexane, 1:3). IR (ATR): $\tilde{\nu}_{max}$ = 3425, 3059, 2925, 1664, 1585, 1487, 1392, 1259, 1073, 1026, 1006, 908, 723, 695 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.23 (s, 1 H), 5.36 (br. s, 2 H), 5.67 (br. s, 2 H), 5.72 (br. s, 2 H), 5.85 (br. s, 2 H), 6.13 (br. s, 2 H), 6.68 (br. s, 2 H), 7.02 (d, J = 8.4 Hz, 2 H), 7.14–7.20 (m, 5 H), 7.23–7.32 (m, 5 H), 7.39 (d, J = 8.4 Hz, 2 H), 7.72 (br. s, 2 H), 7.90 (br. s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 43.6, 44.0, 107.1, 107.2, 107.4, 107.5, 108.4, 117.2, 127.0, 128.4, 128.6, 128.6, 130.1, 131.6, 132.4, 132.5, 141.1, 141.9 ppm. HRMS (ESI): calcd. for $C_{37}H_{30}BrN_4$ $[M - H]^-$ 609.1659; found 609.1669.

2-[(4-Methoxyphenyl){5-[phenyl(1*H*-pyrrol-2-yl)methyl]-1*H*-pyrrol-2-yl}methyl]-5-[phenyl(1*H*-pyrrol-2-yl)methyl]-1*H*-pyrrole (5e): Black viscous oil (60% yield). R_f = 0.32 (EtOAc/hexane, 1:3). IR (ATR): $\tilde{\nu}_{max}$ = 3305, 3059, 2919, 1710, 1601, 1509, 1247, 1174, 1030, 883, 761, 724, 699 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.76 (s, 3 H), 5.19 (s, 1 H), 5.31 (s, 2 H), 5.64–5.68 (m, 4 H), 5.80 (br. s, 2 H), 6.04–6.08 (m, 2 H), 6.59–6.63 (m, 2 H), 6.74–6.78 (m, 2 H), 7.02 (d, J = 8.4 Hz, 2 H), 7.11–7.30 (m, 10 H), 7.66 (br. s, 2 H), 7.84 (br. s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 43.2, 43.9, 55.0, 107.1, 107.3, 108.4, 113.7, 116.8, 126.7, 128.2, 128.4, 129.1, 131.9, 132.2, 132.4, 134.0, 134.8, 142.0, 158.3 ppm. HRMS (ESI): calcd. for $C_{38}H_{33}N_4O$ $[M - H]^-$ 561.2660; found 561.2673.

4-(Bis{5-[phenyl(1*H*-pyrrol-2-yl)methyl]-1*H*-pyrrol-2-yl}methyl)-benzonitrile (5f): Black viscous oil (75% yield). R_f = 0.37 (EtOAc/hexane, 1:3). IR (ATR): $\tilde{\nu}_{max}$ = 3348, 3080, 2923, 2224, 1669, 1603, 1494, 1260, 1091, 1029, 766, 723, 699 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.28 (s, 1 H), 5.32 (s, 2 H), 5.59 (br. s, 2 H), 5.68 (br. s, 2 H), 5.79 (br. s, 2 H), 6.05–6.09 (m, 2 H), 6.61 (br. s, 2 H), 7.12 (d, J = 7.4 Hz, 4 H), 7.18–7.29 (m, 8 H), 7.52 (d, J = 8.1 Hz, 2 H), 7.69 (br. s, 2 H), 7.81 (br. s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 44.0, 44.1, 107.3, 107.7, 107.9, 108.6, 111.0, 117.1, 127.0, 128.2, 128.5, 129.0, 130.4, 131.9, 132.1, 132.7, 141.7, 147.4 ppm. HRMS (ESI): calcd. for $C_{38}H_{30}N_5$ $[M - H]^-$ 556.2507; found 556.2532.

2-[(4-Nitrophenyl){5-[phenyl(1*H*-pyrrol-2-yl)methyl]-1*H*-pyrrol-2-yl}methyl]-5-[phenyl(1*H*-pyrrol-2-yl)methyl]-1*H*-pyrrole (5g): Black viscous oil (85% yield). R_f = 0.29 (EtOAc/hexane, 1:3). IR (ATR): $\tilde{\nu}_{max}$ = 3417, 3078, 2980, 1712, 1597, 1515, 1448, 1420, 1349, 1156, 1093, 1026, 912, 861, 758, 719 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.30 (s, 1 H), 5.31 (s, 2 H), 5.63 (br. s, 2 H), 5.70 (br. s, 2 H), 5.81 (br. s, 2 H), 6.07 (br. s, 2 H), 6.58 (br. s, 2 H), 7.13 (d, J = 7.4 Hz, 4 H), 7.21–7.30 (m, 8 H), 7.79 (br. s, 2 H), 7.82 (br. s, 2 H), 8.06 (d, J = 8.3 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 43.9, 44.0, 107.3, 107.8, 107.9, 108.6, 117.3, 123.6, 127.0, 128.3, 128.6, 129.1, 130.5, 132.1, 133.0, 141.9, 146.8, 149.6 ppm. HRMS (ESI): calcd. for $C_{37}H_{30}N_5O_2$ [M – H]$^-$ 576.2405; found 576.2429.

2-[(4-Fluorophenyl)(1*H*-pyrrol-2-yl)methyl]-5-[(4-fluorophenyl)-{5-[(4-fluorophenyl)(1*H*-pyrrol-2-yl)methyl]-1*H*-pyrrol-2-yl}methyl]-1*H*-pyrrole (5h): Black viscous oil (50% yield). R_f = 0.44 (EtOAc/hexane, 1:3). IR (ATR): $\tilde{\nu}_{max}$ = 3464, 3374, 1692, 1597, 1507, 1408, 1215, 1152, 1097, 916, 849, 774, 762, 727 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.25 (br. s, 1 H), 5.33 (br. s, 2 H), 5.67 (br. s, 4 H), 5.81 (br. s, 2 H), 6.12 (br. s, 2 H), 6.67 (br. s, 2 H), 6.93–6.99 (m, 6 H), 7.07–7.14 (m, 6 H), 7.75 (br. s, 2 H), 7.94 (br. s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 43.3, 43.4, 107.3, 107.5, 107.6, 108.6, 115.4 (d, $^2J_{C,F}$ = 21.2 Hz), 117.3, 129.7, 129.9 (d, $^3J_{C,F}$ = 7.3 Hz), 132.1, 132.1, 132.8, 132.8, 137.7, 161.8 (d, $^1J_{C-F}$ = 244.6 Hz) ppm. HRMS (ESI): calcd. for $C_{37}H_{28}F_3N_4$ [M – H]$^-$ 585.2272; found 585.2289.

2-[(4-Chlorophenyl)(1*H*-pyrrol-2-yl)methyl]-5-[(4-chlorophenyl){5-[(4-chlorophenyl)(1*H*-pyrrol-2-yl)methyl]-1*H*-pyrrol-2-yl}methyl]-1*H*-pyrrole (5i): Black viscous oil (65% yield). R_f = 0.47 (EtOAc/hexane, 1:3). IR (ATR): $\tilde{\nu}_{max}$ = 3445, 2937, 2862, 1719, 1582, 1491, 1385, 1101, 908, 841, 758, 727 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.21 (br. s, 1 H), 5.29 (br. s, 2 H), 5.67 (br. s, 4 H), 5.81 (br. s, 2 H), 6.11 (br. s, 2 H), 6.66 (br. s, 2 H), 7.04–7.09 (m, 6 H), 7.22–7.38 (m, 6 H), 7.74 (br. s, 2 H), 7.90 (br. s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 43.5, 43.5, 107.4, 107.6, 107.7, 108.5, 117.6, 128.7, 129.7, 129.7, 131.9, 132.0, 132.1, 132.8, 140.5, 140.5 ppm. HRMS (ESI): calcd. for $C_{37}H_{28}Cl_3N_4$ [M – H]$^-$ 633.1385; found 633.1431.

2-[(4-Nitrophenyl)(1*H*-pyrrol-2-yl)methyl]-5-[(4-nitrophenyl){5-[(4-nitrophenyl)(1*H*-pyrrol-2-yl)methyl]-1*H*-pyrrol-2-yl}methyl]-1*H*-pyrrole (5j): Black viscous oil (34% yield). R_f = 0.25 (1:3 EtOAc/hexane). IR (ATR): $\tilde{\nu}_{max}$ = 3411, 2966, 2868, 1702, 1602, 1516, 1345, 1115, 915, 865, 830, 774, 729 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.34 (br. s, 1 H), 5.41 (br. s, 2 H), 5.62 (br. s, 4 H), 5.77 (br. s, 2 H), 6.09 (br. s, 2 H), 6.68 (br. s, 2 H), 7.18–7.28 (m, 6 H), 7.79 (br. s, 2 H), 7.92 (br. s, 2 H), 8.06–8.11 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 43.9, 43.9, 107.8, 107.9, 108.3, 108.8, 118.2, 123.9, 123.9, 129.2, 130.6, 131.2, 131.5, 147.0, 147.0, 148.9, 149.2 ppm. HRMS (ESI): calcd. for $C_{37}H_{28}N_7O_6$ [M – H]$^-$ 666.2107; found 666.2173.

General Procedure for the Synthesis of Corroles 6a–6j: DDQ (0.3 mmol) was added to the solution of bilane **5** (0.2 mmol) in toluene (40 mL) at room temperature under argon. The reaction was complete in 1 h. The mixture was passed through a short column packed with silica gel and eluted with ethyl acetate. The eluent was evaporated under reduced pressure. The crude product was purified by flash column chromatography with silica gel 60 (230–400 mesh; ethyl acetate/hexane, 1:10).

5,10,15-Triphenylcorrole (6a):[8f] Green solid (82% yield). R_f = 0.74 (EtOAc/hexane, 1:3). UV/Vis (toluene): λ_{max} (log ε) = 414 (5.14), 575 (4.32), 613 (4.22), 645 (4.15) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.18 (br. s, 3 H), 7.72 (br. s, 5 H), 7.80 (br. s, 4 H), 8.14 (br. s, 2 H), 8.33 (br. s, 4 H), 8.52 (br. s, 4 H), 8.85 (br. s, 4 H) ppm. HRMS (ESI): calcd. for $C_{37}H_{27}N_4$ [M + H]$^+$ 527.2230; found 527.2284.

10-(4-Fluorophenyl)-5,15-diphenylcorrole (6b): Green solid (53% yield). R_f = 0.71 (EtOAc/hexane, 1:3). UV/Vis (toluene): λ_{max} (log ε) = 416 (4.32), 567 (3.72), 615 (3.56), 650 (3.56) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68–7.73 (m, 4 H), 7.81 (br. s, 4 H), 8.11 (br. s, 2 H), 8.35 (br. s, 4 H), 8.50 (br. s, 2 H), 8.57 (br. s, 2 H), 8.88 (br. s, 2 H), 8.92 (br. s, 2 H) ppm. HRMS (ESI): calcd. for $C_{37}H_{26}FN_4$ [M + H]$^+$ 545.2136; found 545.2207.

10-(4-Chlorophenyl)-5,15-diphenylcorrole (6c): Green solid (42% yield). R_f = 0.72 (EtOAc/hexane, 1:3). UV/Vis (toluene): λ_{max} (log ε) = 416 (4.47), 573 (4.86), 614 (3.91), 649 (3.80) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (br. s, 4 H), 7.81 (br. s, 4 H), 8.10 (br. s, 2 H), 8.35 (br. s, 4 H), 8.52 (br. s, 2 H), 8.60 (br. s, 2 H), 8.89 (br. s, 2 H), 8.96 (br. s, 2 H) ppm. HRMS (ESI): calcd. for $C_{37}H_{26}ClN_4$ [M + H]$^+$ 561.1841; found 561.1910.

10-(4-Bromophenyl)-5,15-diphenylcorrole (6d): Green solid (41% yield). R_f = 0.76 (EtOAc/hexane, 1:3). UV/Vis (toluene): λ_{max} (log ε) = 416 (4.71), 576 (4.52), 615 (4.41), 650 (4.39) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.32 (br. s, 3 H), 7.68–8.20 (m, 10 H), 8.32 (br. s, 4 H), 8.48 (br. s, 4 H), 8.79 (br. s, 2 H), 8.84 (br. s, 2 H) ppm. HRMS (ESI): calcd. for $C_{37}H_{26}BrN_4$ [M + H]$^+$ 605.1335; found 605.1276.

10-(4-Methoxyphenyl)-5,15-diphenylcorrole (6e):[14] Green solid (32% yield). R_f = 0.72 (EtOAc/hexane, 1:3). UV/Vis (toluene): λ_{max} (log ε) = 421 (3.89), 514 (2.65), 614 (2.79), 649 (2.83) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.10 (s, 3 H), 7.60–7.88 (m, 8 H), 8.17 (br. s, 2 H), 8.36 (br. s, 4 H), 8.57 (br. s, 4 H), 8.79–9.00 (m, 4 H) ppm. HRMS (ESI): calcd. for $C_{38}H_{29}N_4O$ [M + H]$^+$ 557.2336; found 557.2322.

10-(4-Cyanophenyl)-5,15-diphenylcorrole (6f):[3g] Green solid (22% yield). R_f = 0.72 (EtOAc/hexane, 1:3). UV/Vis (toluene): λ_{max} (log ε) = 421 (4.73), 578 (3.90), 614 (3.76), 649 (3.62) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ = –2.11 (br. s, 3 H), 7.60–7.90 (m, 6 H), 8.09 (br. s, 2 H), 8.20–8.70 (m, 10 H), 8.85 (br. s, 4 H) ppm. HRMS (ESI): calcd. for $C_{38}H_{26}N_5$ [M + H]$^+$ 552.2183; found 552.2160.

10-(4-Nitrophenyl)-5,15-diphenylcorrole (6g):[3g] Green solid (34% yield). R_f = 0.73 (EtOAc/hexane, 1:3). UV/Vis (toluene): λ_{max} (log ε) = 421 (4.98), 582 (4.26), 608 (4.11), 648 (3.86) nm. HRMS (ESI): calcd. for $C_{37}H_{26}N_5O_2$ [M + H]$^+$ 572.2081; found 572.2131.

5,10,15-Tris(4-fluorophenyl)corrole (6h):[10] Green solid (59% yield). R_f = 0.73 (EtOAc/hexane, 1:3). UV/Vis (toluene): λ_{max} (log ε) = 418 (4.72), 520 (3.78), 614 (3.89), 648 (3.88) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52 (br. s, 6 H), 8.11 (br. s, 2 H), 8.31 (br. s, 4 H), 8.53 (br. s, 4 H), 8.84 (br. s, 2 H), 8.99 (br. s, 2 H) ppm. HRMS (ESI): calcd. for $C_{37}H_{24}F_3N_4$ [M + H]$^+$ 581.1948; found 581.1912.

5,10,15-Tris(4-chlorophenyl)corrole (6i): Green solid (35% yield). R_f = 0.78 (EtOAc/hexane, 1:3). UV/Vis (toluene): λ_{max} (log ε) = 420 (4.67), 526 (3.89), 618 (4.02), 654 (4.00) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (br. s, 2 H), 7.82 (br. s, 4 H), 8.11 (br. s, 2 H), 8.30 (br. s, 4 H), 8.57 (br. s, 4 H), 8.88 (br. s, 2 H), 9.01 (br. s, 2 H) ppm. HRMS (ESI): calcd. for $C_{37}H_{24}Cl_3N_4$ [M + H]$^+$ 629.1061; found 629.1038.

5,10,15-Tris(4-nitrophenyl)corrole (6j):[8f] Green solid (25% yield). R_f = 0.70 (EtOAc/hexane, 1:3). UV/Vis (toluene): λ_{max} (log ε) = 450 (4.39), 593 (3.84) nm. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.38 (d, J = 8.5 Hz, 2 H), 8.55 (d, J = 8.7 Hz, 4 H), 8.59 (d, J = 4.6 Hz, 2 H), 8.64–8.69 (m, 4 H), 8.72 (d, J = 8.4 Hz, 4 H), 8.91 (d, J = 4.6 Hz, 2 H), 9.11 (d, J = 4.3 Hz, 2 H) ppm. HRMS (ESI): calcd. for $C_{37}H_{24}N_7O_6$ [M + H]$^+$ 662.1783; found 662.1710.

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