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Efficient Synthesis of meso-Substituted Corroles in a H_2O−MeOH Mixture

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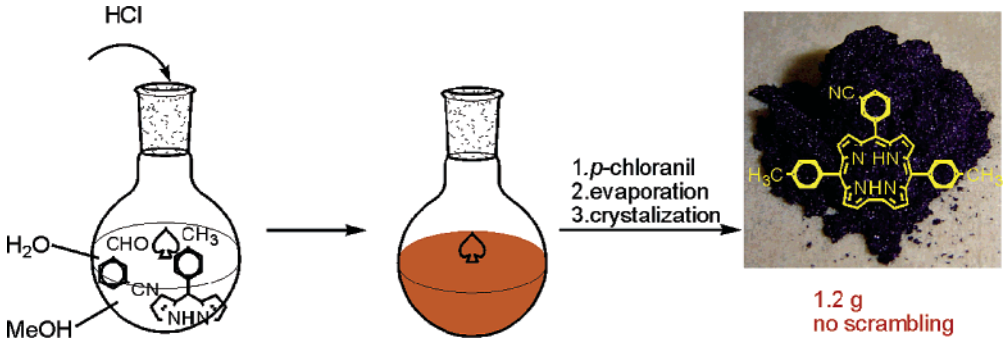

New and efficient conditions for the synthesis of meso-substituted corroles were developed. The first step, involving the reaction of aldehydes with pyrrole, was carried out in a water−methanol mixture in the presence of HCl. A relatively narrow distribution of aldehyde−pyrrole oligocondensates was obtained through careful control of their solubility in the reaction medium. After thorough optimization of various reaction parameters (cosolvent, reagent, and acid concentration), high yields of bilanes were obtained. Additionally, the bilane derived from 4-cyanobenzaldehyde was isolated, and the oxidative macrocyclization reaction was performed under various reaction conditions (different solvents, different concentrations, and various oxidants). As a result, triphenylcorrole was obtained in the highest yield (32%) reported to date. The scope and limitations studied showed that this method was particularly efficient for moderately reactive aldehydes and those bearing electron-donating groups (yields 14−27%). Using these conditions, corroles bearing strongly electron-donating groups were obtained for the first time. In addition, it was found that the reaction of unhindered dipyrromethanes with aldehydes under analogous conditions afforded *trans*-A_2B-corroles in very high yields (45−56%; 8-fold higher than previously reported) without scrambling. The fact that scrambling was not observed in this reaction despite a very high HCl concentration (0.3 M) is unprecedented. Detailed studies on the oxidation of bilane, derived from sterically hindered dipyrromethane, allowed us to unequivocally establish that the yield of macrocyclization is insensitive to the concentration. It was found the ^{1}H NMR spectra of corroles in deuterated TFA gave very sharp signals.

Introduction

Corroles, one carbon shorter analogues of porphyrins, recently emerged as an independent area of research.[1] Their coordination chemistry,[2] photophysics,[3] synthesis,[4] chemical transformations,[5] electrochemistry,[6] and other properties[7] have recently been studied in great detail. Optimization of corrole synthesis has been a frequent focus of research activities[8] since the initial reports by Gross et al.[4a] and Paolesse et al.,[4b,9] revealing one-pot syntheses of meso-substituted corroles from aldehydes and pyrrole. Refinement of reaction conditions has improved corrole yields to 15−20%. A broader investigation of the physicochemical properties and practical applicability of corroles necessitates the development of powerful new methods for their synthesis, and although there has been dramatic progress in recent years, there is still tremendous room for improvement.

The one-pot synthesis of meso-substituted A_3-corroles from aldehydes and pyrroles consists of two independent steps. The first step is an acid-mediated electrophilic substitution to yield

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a mixture of various aldehyde−pyrrole oligocondensates, including bilane (tetrapyrrane), a direct precursor of corrole. The second step is the oxidative ring closure. Maximizing bilane formation while minimizing the formation of dipyrromethanes (DPMs), tripyrrane, and higher oligocondensates, is a difficult task due to the similar reactivity of all these compounds. An independent improvement of both processes (i.e., bilane formation and its macrocyclization) is the key to success, but the optimization of the first step seems to be more crucial. Initial attempts concentrated on the fine-tuning of the reaction conditions, depending on the reactivity of various aldehydes.[8c] Although these results were satisfactory (especially for aldehydes with electron-withdrawing groups), there was still room for further improvements. The inspiration for this work came from an intriguing paper by Kral and co-workers,[10] describing the synthesis of dipyrromethanes in water. The authors took advantage of the difference in water solubility between the substrates (aldehyde, pyrrole) and the product (dipyrromethane). Exploiting this solubility difference, it was possible to essentially stop the reaction at the dipyrromethane level using only a 6-fold excess of pyrrole. Furthermore, the authors briefly mentioned that the addition of MeOH to the reaction mixture led to a decrease in the yield of dipyrromethanes, probably due to the formation of higher oligocondensates. This could be attributed to the better solubility of dipyrromethanes in H_2O/MeOH mixtures, which permits further reaction. We reasoned that careful optimization of the aldehyde/pyrrole ratio in conjunction with the amount of MeOH might be a perfect way for narrowing the distribution of oligocondensates and, thus, open the way to a more efficient synthesis of corroles. Here we describe the synthesis of A_3-corroles as well as *trans*-A_2B-corroles in an H_2O/MeOH mixture, which resulted from this study.

Results and Discussion

A_3-Corroles. Model Optimization Study. The reaction of benzaldehyde (**1**) with pyrrole was chosen as a model system for the optimization study because the yield of corrole **5** can be easily compared with several existing procedures[8] (Scheme 1). The highest yield of corrole **5** (17%)[11] has been reported by Paolesse and co-workers.[8d] On the basis of the paper by Kral et al.,[10] we chose the following initial conditions for the first acid-catalyzed step: [ald. **1**] = 18 mM; ald. **1**/pyrrole = 3:4; [HCl] = 0.12 M; H_2O/MeOH = 1:1 (Table 1, entry 1). Benzaldehyde (**1**) reacted with pyrrole under these conditions to give a pink suspension of oligocondensates. These products were extracted with CH_2Cl_2 and oxidized with DDQ. Though Geier and co-workers[4g] showed that DDQ is not the best oxidizing agent for the synthesis of triphenylcorrole **5** because it causes its partial decomposition, it was chosen in our study for convenience (reaction with *p*-chloranil required a much longer time). The use of DDQ would certainly decrease the yields in comparison to *p*-chloranil, but the relative differences in the yields between reactions under different conditions would remain the same.

Under the reaction conditions initially chosen, corrole **5** was obtained in a reasonable 14% yield. Initially we concentrated our efforts on examining the influence of the benzaldehyde (**1**)/pyrrole ratio on the yield of corrole **5** (Table 1, entries 1−3). The best yield (21%) was obtained when the ratio was 1:2 (Table 1, entry 2). Hence, for further reactions, it was kept constant at this value. Subsequently, solvent effects were investigated by replacing MeOH with other water-miscible, polar solvents such as *i*-PrOH, CH_3CN, DMF, and THF.

We observed that bilanes were formed in negligible amounts in all solvents studied, and only traces of corrole **5** were detected (Table 1, entries 4−7). Such poor results were primarily due to

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(11) Intrigued by the big difference in yields between two procedures reported by Paolesse and co-workers (11% for neat reaction and 21% for synthesis in CH_2Cl_2, respectively),[8d] we repeated their experiments with very carefully purified, freshly distilled benzaldehyde. We found that the yields are exactly 17% regardless of the method used (each experiment was repeated three times by different researchers), which is in contrast to what is reported. Consequently, benzaldehyde was freshly purified and distilled before the present study to ensure repeatability of the results.

SCHEME 1

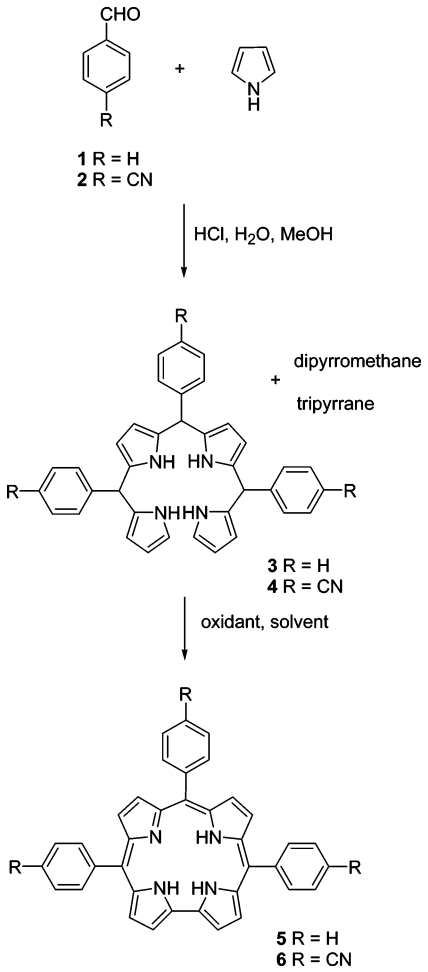


TABLE 1. Optimization of Conditions of the Benzaldehyde (1) Reaction with Pyrrole, Leading to Corrole 5[a]

entry	ald. **1** (mM)	ald. **1**/pyrrole	HCl (mM)	H_2O/cosolvent (v/v)	cosolvent	yield of corrole **5**[b] (%)
1	18	3/4	0.12	1/1	MeOH	14
2	12	1/2	0.12	1/1	MeOH	21
3	6	1/4	0.12	1/1	MeOH	16
4	12	1/2	0.12	1/1	*i*-PrOH	1
5	12	1/2	0.12	1/1	CH_3CN	0
6	12	1/2	0.12	1/1	DMF	0
7	12	1/2	0.12	1/1	THF	1
8	12	1/2	0.12	2/1	MeOH	15
9	12	1/2	0.12	1/2	MeOH	5
10	12	1/2	0.06	1/1	MeOH	19
11	12	1/2	0.36	1/1	MeOH	20
12[c]	12	1/2	0.12	1/1	MeOH	21
13[d]	12	1/2	0.12	1/1	MeOH	19
14	24	1/2	0.24	1/1	MeOH	22
15	36	1/2	0.36	1/1	MeOH	17
16	48	1/2	0.48	1/1	MeOH	15
17[e]	25	1/2	0.25	1/1	MeOH	32

[a] All reactions were performed under the following constant conditions: first step, 1 h, room temperature; second step, $CHCl_3$, DDQ (1 equiv versus aldehyde), room temperature. [b] Isolated yields. [c] Time of the first step was 3 h. [d] Time of the first step was 16 h. [e] DDQ was replaced with *p*-chloranil.

the improved solubility of the initially formed products and higher oligocondensates in these solvents. Unexpectedly, only dipyrromethane and tripyrrane were detected in THF. Increasing or decreasing the H_2O/MeOH ratio led to a sharp decrease in the yield of corrole **5** (entries 8 and 9). When more MeOH was used, the yield of *trans*-A_2B_2-porphyrin increased. Because the concentration of an acid catalyst usually has a profound effect on the yield of porphyrinoids, we next analyzed the role of HCl concentration on the corrole **5** yield. Surprisingly, the concentration of HCl had a negligible effect on the yield of corrole **5** (entries 10 and 11). Extending the reaction time to 3 h or even 16 h also did not improve the outcome of the process (entries 12 and 13). Large volumes of solvents (MeOH and H_2O) would be required for preparative-scale synthesis if optimal conditions were to be used directly. To eliminate this disadvantage, we attempted to decrease the volume of the solvents (entries 14−16). It should be noted that increasing the concentration of starting materials should theoretically lead to the earlier precipitation of dipyrromethanes and, hence, a decrease in the yield of bilane. We observed that while a 2-fold increase in concentration did not influence the yield of corrole **5**, a further increase gave corrole **5** in lower yield. Finally, control experiments under optimized conditions with *p*-chloranil instead of DDQ (entry 17) led to a substantial increase in the yield of corrole **5** to 32% (confirming previous observations[4g]).

TABLE 2. Optimization of Conditions for the Conversion of Bilane 4 into Corrole 6[a]

entry	solvent	yield of corrole **6**[b] (%)
1	MeOH	49
2	CH_3CN	72
3	THF	52
4	$CHCl_3$	62
5[c]	CH_2Cl_2	56
6	toluene	30

[a] All reactions were performed under the following constant conditions: [bilane **4**] = 1.1 mM, *p*-chloranil (3 equiv versus bilane **4**), 65 °C, 1 h. [b] Isolated yields. [c] Temperature was 42 °C.

Oxidation Study. Our previous studies left some questions concerning the dependence of corrole yield on the concentration of bilane.[8c] Given the importance of this factor, we decided to unequivocally establish the concentration dependence of the bilane macrocyclization using pure bilane starting material rather than a complicated mixture of oligocondensates. This would simultaneously provide the maximal yield that could be reached for this process.[4e,8a] Because the bilane derived from 4-cyanobenzaldehyde (**2**) is relatively stable and can be purified on a reasonable scale, it was chosen for these studies. Bilane **4** was obtained as a mixture of diastereo- and regioisomers using the new optimized conditions in 31% yield (Scheme 1).

Initially, we explored the role of solvent on the oxidation of **4** with *p*-chloranil (Table 2). The rationale behind this study was not only to maximize the yield, but also to check how broad a range of solvents could be used to perform this reaction. Corrole **6** was obtained in all solvents examined. We found that the macrocyclization reaction afforded 60−70% yield of corrole **6** in $CHCl_3$, CH_2Cl_2, and in CH_3CN. Significantly lower yields were obtained in toluene, MeOH, or DMF. Although CH_3CN gave the highest yield (72%), $CHCl_3$ was chosen as the solvent of choice for further studies because it made purification easier.

The influence of reaction concentration on the yield of corrole **6** was studied next.[12] The results of this study conducted in $CHCl_3$ are presented in Figure 1 and show that there is an

(12) The relationship between yields of corroles and dilution of the reaction mixture after the first step was studied several times by us, but the results were very inconsistent. Studies on pure bilane should remove any uncertainty concerning this issue.

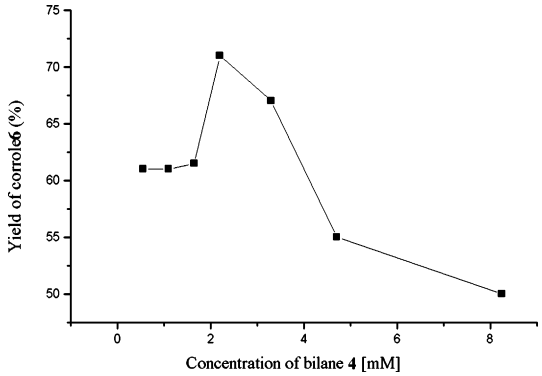


FIGURE 1. Dependence of the yield of corrole **6** on the concentration of bilane **4**.

optimal concentration of tetrapyrrane (~2.2 mM). The yield of bilanes in the first step is around 30−50%. Hence, it can be calculated from the above data that, in reactions carried out without purification of tetrapyrranes, for 1 mmol of starting aldehyde, ~45−75 mL of $CHCl_3$ should be used for the oxidation step to ensure the highest yield of corroles.

Although the yields for the transformation of bilanes into corroles were high with DDQ or *p*-chloranil, we also investigated other oxidizing agents. One of the rationales behind this study was to look for putative intermediates, such as biladienes, of the oxidation process. We observed that mild oxidizing agents such as *p*-benzoquinone could transform bilane **4** to corrole **6**. Though this process was very slow in CH_2Cl_2 at rt, we did not detect any trace intermediates, which indicates that the final step of this process must be very fast and the lifetime of the intermediates is rather short.

Because the reaction could not be driven to completion with a $CHCl_3$ reflux, it was carried out in toluene. After 16 h of reflux, tetrapyrrane **4** could not be detected and the yield of corrole **6** was 45%, a higher value than with *p*-chloranil in the same solvent (Table 2). Based on the work by Paolesse et al.,[4a] we also tried molecular oxygen as the oxidizing agent. The reaction of bilane **4** performed in boiling acetic acid gave rise to a significant amount of 5,10,15,20-tetrakis-(4-cyanophenyl)-porphyrin and only a low yield of corrole **6**, indicating bilane scrambling was occurring. We also tried [bis(trifluoroacetoxy)-iodo]benzene (PIFA), which is known to promote oxidative dimerization of aromatic compounds. However, we found that PIFA afforded only a 10% yield of corrole **6**.

Scope of the HCl/H_2O/MeOH Procedure. The optimized conditions (first step, [ald.] = 25 mM, [HCl] = 0.25 M, H_2O/MeOH = 1:1, ald./pyrrole = 1:2; second step, *p*-chloranil [1 equiv versus aldehyde], $CHCl_3$, 60 mL for 1 mmol of aldehyde) were subsequently used for the synthesis of a broad spectrum of A_3-corroles (Table 3).

The initial experiments performed at a 2.5-fold larger scale than the optimization study showed that some dipyrromethanes precipitated too fast. Due to the detrimental effect of the addition of more MeOH (Table 1, entry 9), we decided to decrease the concentration of reagents as well as HCl and increase the reaction time (Table 1, entry 12). The yield of corroles **7** and **10** improved significantly, and these conditions were used for further studies.

Nevertheless, the reaction results depended significantly on the aldehyde used in the reaction. In general, for aldehydes similar to benzaldehyde (**7**−**10**, 4-methylbenzaldehyde, 4-fluorobenzaldehyde, etc.), the reaction worked very well and gave yields exceeding previous results (22−27%). In contrast, for aldehydes bearing electron-withdrawing groups (**13**−**16**, 4-cyanobenzaldehyde, 4-carboxymethylbenzaldehyde, etc.), yields were moderate and usually very similar to those reported earlier (10−23%). In all these cases, the amount of porphyrins formed was 1−3%. Interestingly, the reaction with C_6F_5CHO did not result in the corresponding corrole, and sterically hindered aldehyde **17** afforded corrole **30** in low yield.

TABLE 3. Comparison of Reaction Yields of Different A_3-Corroles

aromatic aldehyde	corrole	yield[a] (%)
C_6H_5CHO, **1**	**5**	27 (17)[b]
4-$CH_3C_6H_4CHO$, **7**	**20**	25 (15)[b]
4-FC_6H_4CHO, **8**	**21**	25 (2.5)[b]
4-BrC_6H_4CHO, **9**	**22**	22 (10)[b]
4-$MeOC_6H_4CHO$, **10**	**23**	22 (15)[b]
3,4-$(OCH_2CO_2Me)C_6H_3CHO$, **11**	**24**	17
3,4,5-$(MeO)_3C_6H_2CHO$, **12**	**25**	14
4-$NO_2C_6H_4CHO$, **13**	**26**	10 (22)[b]
4-CNC_6H_4CHO, **2**	**6**	21 (13)[b]
3-CNC_6H_4CHO, **14**	**27**	23 (15)[b]
4-$CF_3C_6H_4CHO$, **15**	**28**	16 (19)[b]
4-$(CO_2Me)C_6H_4CHO$, **16**	**29**	17 (14)[b]
2,6-$Cl_2C_6H_3CHO$, **17**	**30**	8 (14)[b]
2,6-$(MeO)_2C_6H_4CHO$, **18**		0
2-formylthiophen, **19**	**31**	5

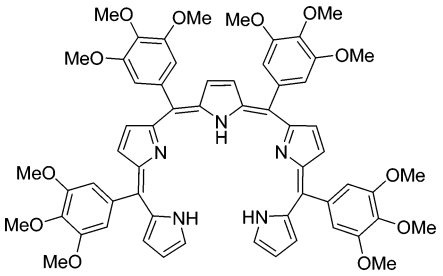
[a] Isolated yields. [b] Values in parentheses indicate the highest yields obtained using previous methods.

Given the intrinsic polarity of aldehydes bearing electron-donating groups, we reasoned that they could give good yields of bilanes and, hence, corroles under H_2O/MeOH/HCl conditions. The use of *p*-chloranil (milder than DDQ) should eliminate problems with their further oxidation. Eventually, we found that 3,4,5-trimethoxybenzaldehyde (**12**) reacted with pyrrole giving the corresponding tetrapyrrane, which could be oxidized to corrole **25** in 14% yield. Surprisingly, this corrole was stable enough to be purified with typical bench conditions. Notably, it was shown that aldehyde **11**, which bears hydrolytically labile ester groups, afforded corrole **24** in 17% yields. The reaction of 2,6-dimethoxybenzaldehyde (**18**) with pyrrole afforded corrole, but this compound was so unstable that it could not be purified.[4a] On the other hand, 2-formylthiophene (**19**) subjected to optimized reaction conditions gave corrole **31**, although in a surprisingly low yield (5%). Presumably, the yield suffers due to the participation of the electron-rich thiophene ring in the electrophilic substitution. As expected with pyridine-4-carboxaldehyde, the respective corrole formed in trace amounts because salt formation prevents the favorable solubility controlled aldehyde−pyrrole oligocondensates distribution. Taken together, the results of the condensation of aldehydes with pyrrole in the H_2O/MeOH/HCl system are superior to earlier studies.[4b,c,8]

Characterization of the Side Products of the Reaction. In all cases, chromatographic purification afforded an olive-green−brown band immediately before the corrole band. We once hypothesized that it can be radical cations of corrole,[4d] but this view has been criticized.[8d] To gather additional information on the structure of these species, we carried out two simple experiments: (1) we reacted triphenylcorrole (**5**) with 1 equiv of *p*-chloranil (quantitative formation of olive-green−brown

band) and then added NH_2NH_2[13] (anhydrous, as THF soln.); (2) we collected olive-green bands from several experiments and added NH_2NH_2. In both cases, we regenerated the respective corroles. There are two conclusions that can be drawn from these experiments: (1) the olive-green species cannot be open-chain compounds as previously proposed;[8d] (2) we think that hydrazine acts as a mild reducing agent that reacts with the compound that is easily and reversibly formed from corrole and an oxidant. All corrole-forming reactions can be quenched with hydrazine to increase the yield of corrole.

Furthermore, we observed that the pentapyrrotetramethenes described by Gross et al.[14] were ubiquitous side-products that formed under the reaction conditions from pentapyrranes. They were observed as a characteristic red spot on the TLC plate, located just below the corrole in virtually every case. In one case, the reaction of 3,4,5-trimethoxybenzaldehyde with pyrrole, pentapyrrotetramethene **32** was isolated in 5.5% yield, and its structure was confirmed by NMR and MS techniques (Structure 1).



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***trans*-A_2B-Corroles Study with Model Unhindered Dipyrromethane.** Reactions of dipyrromethanes with aldehydes leading to *trans*-A_2B-corroles have been extensively studied by us[4d,15c] and other groups.[4c,8c,15a,b,d] Previous studies showed that reasonable yields of corroles could be obtained for sterically hindered dipyrromethanes[4c,15b] and for dipyrromethanes bearing electron-withdrawing groups.[15c] However, from unhindered 5-phenyldipyrromethane (**33**) and its analogues, corroles could be prepared only in very low yields (6−7%).[4c] All attempts to increase the yield by an increase in the acid concentration led to significant scrambling.[4c] To our delight, 5-phenyldipyrromethane (**33**) reacted with 4-cyanobenzaldehyde (**2**) under the optimized conditions (Scheme 2) to afford the respective corrole **44** in 38% yield *with no detectable scrambling* (Table 4, entry 1).

Encouraged by this remarkable result, we conducted a short optimization study with this model reaction (Table 4). When oxidation with *p*-chloranil was performed under milder conditions (room temperature, overnight), the yield increased to 44%, with a concomitant decrease in the olive-green side product (entry 2). An increase in the concentration of substrates to 5 mM and 10 mM resulted in corrole **43** in 51−54% yield (entry 3 and 4), while further increases led to a substantial decrease in yield (entry 5). Altering the stoichiometric ratio of substrates did not change the outcome of this reaction (entries 6 and 7). Analogous to A_3-corroles synthesis, the ratio of MeOH to H_2O was studied. When the ratio of MeOH to H_2O was increased from 1:1 to 2:1, the yield of corrole **43** significantly decreased to 18% (entry 8). In contrast, reversing the ratio (i.e., H_2O/MeOH = 2:1) led to essentially the same yield (entry 9). Notably, this represents an 8-fold improvement over the previously reported[4d] yield for the same conversion.

Scope of the HCl/H_2O/MeOH. The optimized procedure (Table 4, entry 3), which does not differ significantly from one employed for the preparation of A_3-corroles from aldehydes and pyrrole was subsequently used to examine the scope of the corrole formation. Dipyrromethanes **34**−**37** bearing electron-withdrawing or electron-donating groups and various aldehydes **1**, **2**, **14**, **15**, **41** were employed (Scheme 2). Results showed that *trans*-A_2B-corroles could be obtained in yields of 45−55% with no detectable scrambling. The only examples that gave lower yields were 5-(4-methoxyphenyl)dipyrromethane (**36**) and 5-(pentafluorophenyl)dipyrromethane (**38**). It is noteworthy that the amounts of porphyrins formed under these conditions were negligible.

To prove the scalability of this process, a large scale preparation of corrole **45** was attempted. The reaction of dipyrromethane **34** with aldehyde **15** performed at a 20-mmol scale (10-fold increase) furnished 1.5 g of corrole **45** in essentially the same yield as in the small scale. Importantly, it was also found that 1.2 g of corrole **45** could be obtained without any chromatography by crystallization of the crude product from EtOH and CH_2Cl_2.

Study with Sterically Hindered Dipyrromethanes. While expanding the scope of the *trans*-A_2B-corroles' synthesis to include sterically hindered dipyrromethanes, we did observed solubility problems. The reaction of mesityldipyrromethane (**39**) with 4-cyanobenzaldehyde (**2**; Scheme 3) carried out under previously optimized reaction conditions gave very low conversion. The combined effect of a higher ratio of MeOH to H_2O, a higher concentration of acid, and longer reaction time (first step, [ald.] = 5.0 mM, [HCl] = 0.4 M, H_2O/MeOH = 1:2, ald./DPM = 1:2, 2 h, rt; second step, *p*-chloranil [3 equiv versus aldehydes], $CHCl_3$) afforded corrole **50** in 30% yield (the same as reported).[8c] To determine the source of this difference, we conducted a study of the oxidation of bilane derived from a sterically hindered dipyrromethane.[16] Bilane **53** was obtained, using the H_2O/MeOH/HCl method in 49% yield as white crystals, and fully characterized (Scheme 3). Because this compound was crystalline, it could be obtained in a very pure state, which is very rare for bilanes.

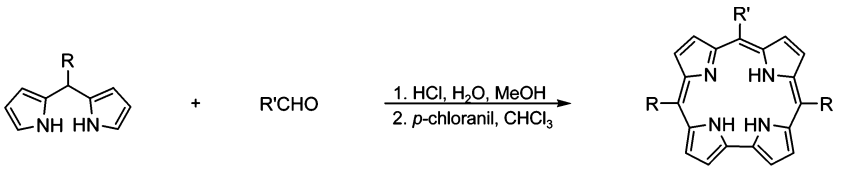
The yield of corrole **50** was essentially concentration independent (60 ± 2%) when the oxidation of bilane **53** with *p*-chloranil was performed under various concentrations (20 mM, 4.0 mM, 1.0 mM, and 0.5 mM). The macrocyclization was equally efficient for bilanes bearing sterically hindered and unhindered substituents. The difference in the yield of corroles was thus influenced by the first step of the synthesis. We also carried out the oxidation of tetrapyrrane **53** with DDQ, which resulted in a slightly lower yield of corrole **50** (55%). Corrole **51** was synthesized from 5-(2,6-dichlorophenyl)dipyrromethane (**40**; prepared using the new Lindsey procedure for sterically

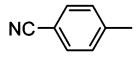
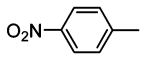
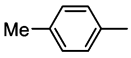
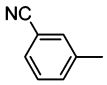
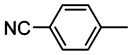
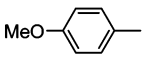
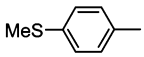
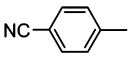
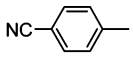
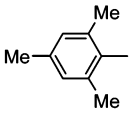
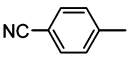
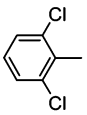
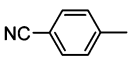
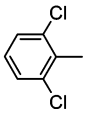
(13) Hydrazine hydrate was used by Paolesse and co-workers to remove the excess of *p*-chloranil from a,c-biladiene oxidations to *β*-substituted corroles: Paolesse, R.; Froiio, A.; Nardis, S.; Mastroianni, M.; Russo, M.; Nurco, D. J.; Smith, K. M. *J. Porphyrins Phthalocyanines* **2003**, *7*, 585−592.

(14) Gross, Z.; Galili, N.; Simkhovich, L.; Saltsman, I.; Botoshansky, M.; Blaser, D.; Boese, R.; Goldberg, I. *Org. Lett.* **1999**, *1*, 599−602.

(15) (a) Asokan, C. V.; Smeets, S.; Dehaen, W. *Tetrahedron Lett*. **2001**, *42*, 4483−4485. (b) Gryko, D. T.; Piechota, K. E. *J. Porphyrins Phthalocyanines* **2002**, *6*, 81−97. (c) Gryko, D. T.; Koszarna, B. *Synthesis* **2004**, 2205−2209. (d) Andrioletti, B.; Rose, E. *J. Chem. Soc., Perkin Trans 1* **2002**, 715−716. (e) Barbe, J.-M.; Canard, G.; Brandès, S.; Guilard, R. *Eur. J. Org. Chem*. **2005**, 4601−4611.

SCHEME 2[a]



DPM	R	Aldehyde	R'	Corrole	Yield[a]
33		**2**		**43**	56%(7)
33		**14**		**44**	53%(6)
34		**15**		**45**	51%
35		**1**		**46**	47%
36		**41**		**47**	13% (6)
37		**2**		**48**	42%
38		**2**		**49**	20%(19)
39		**2**		**50**	30%(31)
40		**2**		**51**	27%(13)
40		**42**		**52**	16%(19)

[a] Values in parentheses indicate the highest yield obtained using previous methods.

hindered dipyrromethanes)[17] and 4-cyanobenzaldehyde (**2**) in 27% yield, 2-fold higher than previously reported.[8c] Recently described phlorin−dipyrrin conjugates[18] were also detected in small amounts in these reactions, which further confirms the idea of solubility-controlled distribution of products (hexapyrranes, which are direct precursors of phlorin−dipyrrin conjugates, could not form in sizable amounts). Interestingly, dipyrromethane **40** reacted with pyridine-4-carboxaldehyde (**43**) under slightly altered reaction conditions (first step, [ald.] = 5.0 mM, [HCl] = 0.78 M, H_2O/MeOH = 2:1, **43**:**40** = 1:2, 2 h, rt; second step, DDQ [3 equiv versus aldehydes], $CHCl_3$) to give corrole **55** in 16% yield (similar to previous results).[15b]

It is well-known that the ^{1}H NMR spectra of free-base corroles often display significant signal broadening. This phenomenon is particularly strong for meso-substituted corroles possessing unhindered substituents. Some of the spectra, which we initially obtained in $CDCl_3$ or THF-d_8, had broad signals that spread across the entire aromatic region. Consequently, we decided to perform spectra with the addition of a small amount of CD_3OD, a procedure that was successfully used by Lee et al.[8a] and Geier et al.[4g] We obtained much clearer spectra for

(16) An additional motivation came from our previous studies,[4d,8c,15b] which left some inconsistency about the dependence of the yield of the macrocyclization of such bilanes on their concentration.

(17) Laha, J. K.; Dhanalekshmi, S.; Taniguchi, M.; Ambroise, A.; Lindsey, J. S. *Org. Process Res. Dev.* **2003**, *7*, 799−812.

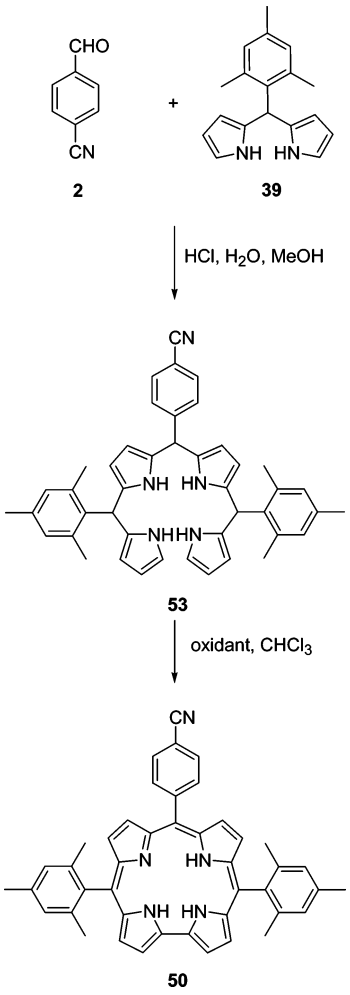
(18) Gryko, D. T.; Koszarna, B. *Eur. J. Org. Chem.* **2005**, 3314−3318.

TABLE 4. Optimization of Conditions of the 4-Cyanobenzaldehyde (2) Reaction with 5-Phenyldipyrromethane (33)[a]

entry	ald. **2** (mM)	ald. **2**/DPM **33**	HCl (M)	H_2O/MeOH (v/v)	yield of corrole **43**[b] (%)
1[c]	2.5	1/2	0.30	1/1	38
2	2.5	1/2	0.30	1/1	44
3	5.0	1/2	0.30	1/1	54
4	10	1/2	0.30	1/1	51
5	20	3/4	1.20	1/1	19
6	5.0	3/4	0.30	1/1	50
7	5.0	1/3	0.30	1/1	50
8	5.0	1/2	0.20	1/2	18
9	5.0	1/2	0.20	2/1	53

[a] All reactions were performed under the following constant conditions: first step, 1 h, room temperature; second step, $CHCl_3$, *p*-chloranil (1.5 equiv versus dipyrromethane **33**), room temperature, 16 h. [b] Isolated yields. [c] Oxidation was performed under reflux for 1 h.

SCHEME 3



corroles **31**, **45**, and **46**. During our study we also found that spectra performed in pure deuterated TFA afforded sharp signals, and so we obtained ^{1}H NMR for corroles **24**, **25**, and **48** in this solvent. Pyrrolic N−H signals were obviously not detected in either solvent.

Conclusions

The acid-catalyzed formation of bilanes (tetrapyrranes) from aldehydes and pyrrole in H_2O/cosolvent mixtures has been studied in-depth and, as a result, a broad variety of A_3-corroles has been synthesized in the highest yields yet reported. In addition, it was found that (1) the macrocyclization of tetrapyrranes is strongly solvent-dependent and can be performed with yields up to 73% (MeCN); (2) corroles bearing strongly electron-donating substituents (like 3,4,5-trimethoxyphenyl) are stable enough for purification; (3) methyl ester groups are stable under the conditions of the first acid-catalyzed step; (4) linear pentapyrrotetramethenes are typical side products in this reaction; (5) *p*-benzoquinone can also be used for the oxidation of bilanes to corroles; (6) *p*-chloranil gave higher yields than DDQ in all cases except aldehydes with strong electron-withdrawing groups; and (7) quenching the corrole-forming reactions with hydrazine hydrate reduces the amount of olive-green−brown side product, probably via its reduction to corrole.

We discovered that the reaction of sterically unhindered dipyrromethanes with aldehydes can be performed in an H_2O/MeOH system with a high HCl concentration *without any scrambling*. Although not fully explicable, this result led to the development of a procedure that gives *trans*-A_2B-corroles in yields up to 56% and in turn makes these compounds easily accessible on a large scale. Furthermore, it was observed that the macrocyclization of bilanes bearing sterically hindered groups led to corroles in the same yield as bilanes bearing unhindered groups.

The conditions described in this paper provide by far the best yields in both a one-pot synthesis of A_3-corroles (20−30%) from a wide range of aromatic aldehydes and in the [2+1] synthesis of *trans*-A_2B-corroles from sterically unhindered dipyrromethanes. The unexpected discovery of scrambling-free high-acid concentration conditions opens new avenues of research in porphyrinoid chemistry.

Experimental Section

All chemicals were used as received unless otherwise noted. Reagent grade solvents (CH_2Cl_2, hexanes, cyclohexane) were distilled prior to use. All reported ^{1}H and ^{13}C NMR spectra were recorded on 500- or 400-MHz spectrometers. Chemical shifts (δ ppm) were determined with TMS as the internal reference; *J* values are given in Hz. UV−vis spectra were recorded in toluene. Chromatography was performed on silica (Kieselgel 60, 200−400 mesh), or dry column vacuum chromatography (DCVC)[19] was performed on preparative thin-layer chromatography silica. Mass spectra were obtained via electrospray MS (ESI-MS). The purity of all new corroles was established on the basis of ^{1}H NMR spectra and elemental analysis. Aldehyde **11**[15c] and dipyrromethanes **33**,[17] **34**−**36**,[20] **37**,[21] and **38**−**39**[17] were prepared as described in the literature.

General Procedures for the Investigation of the Reaction Conditions. Optimization of Conditions of the Benzaldehyde (1) Reaction with Pyrrole Leading to Corrole 5 (Table 1). Reactions were performed under the following conditions: benzaldehyde (1 mmol, 102 μL) and pyrrole (2 mmol, 140 μL) were dissolved in a specific amount of H_2O−cosolvent mixture. Subsequently, HCl_{aq} (36%, 0.85 mL) was added, and the reaction was stirred at room temperature. The progress of the reaction was monitored by periodic removal of aliquots (containing precipitated solid) from the reaction mixture and vial extraction with CH_2Cl_2, followed by TLC examination (SiO_2, CH_2Cl_2/hexanes, 3:1). Fu-

(19) Pedersen, D. S.; Rosenbohm, C. *Synthesis* **2001**, 2431−2434.
(20) Littler, B. J.; Miller, M. A.; Hung, C. H.; Wagner, R. W.; O′Shea, D. F.; Boyle, P. D.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 1391−1396.
(21) Clausen, C.; Gryko, D. T.; Yasseri, A. A.; Diers, J. R.; Bocian, D. F.; Kuhr, W. G.; Lindsey, J. S. *J. Org. Chem.* **2000**, *65*, 7371−7378.

migration of the developed TLC plates with bromine vapor (CAUTION—fume hood) stains the dipyrromethane bright red, the tripyrrane purple, and the bilane brown. Additionally, spots were compared with authentic samples of dipyrromethane **33** and diphenyltripyrrane, obtained using known procedures.[17,22] After 1h, there was no further progress in the reaction. The reaction was worked up by extraction with $CHCl_3$. The organic layer was washed twice with H_2O, dried (Na_2SO_4), filtered, and diluted to 300 mL with $CHCl_3$. Then DDQ or *p*-chloranil (1 equiv versus aldehyde) was added, and the mixture was gently refluxed for 1 h. Corrole **5** and tetraphenylporphyrin were detected via a TLC comparison of the reaction mixture with authentic samples. The yield of corrole **5** was determined by the chromatographic separation (SiO_2, CH_2Cl_2/hexanes, 3:2) and the subsequent chromatographical purification (SiO_2, CH_2Cl_2/hexanes, 1:1).

Optimization of Conditions of the Conversion of Bilane 4 into Corrole 6. Bilane **4** (0.164 mmol, 99.7 mg) was dissolved in a given solvent (150 mL), and *p*-chloranil (0.492 mmol, 121 mg) was added. The reaction mixture was heated at 65 °C for 1 h. After cooling to room temperature, the resulting solution was washed with a saturated solution of $NaHCO_3$, dried (Na_2SO_4), and filtrated. The yield of corrole **6** was determined by the chromatographic separation (SiO_2, CH_2Cl_2/hexanes, 3:2).

Optimization of Conditions of the 4-Cyanobenzaldehyde (2) Reaction with 5-Phenyldipyrromethane (33; Table 4). Samples of the 4-cyanobenzaldehyde (0.5 or 0.75 mmol) and 5-phenyldipyrromethane (1 or 1.5 mmol) were dissolved in MeOH (12.5−100 mL). Subsequently, the solution of HCl_{aq} (36%, 1−5 mL) in H_2O (12.5−100 mL) was added, and the reaction was stirred at room temperature. The progress of the reaction was monitored by the periodic removal of aliquots from the reaction mixture (containing precipitated solid) and vial extraction with CH_2Cl_2, followed by TLC examination (SiO_2, CH_2Cl_2/hexanes, 3:1). Fumigation of the developed TLC plates with bromine vapor (CAUTION—fume hood) stains the dipyrromethane bright red, the tripyrrane purple, and the bilane brown. The presence of remaining 5-phenyldipyrromethane **33** was detected by a comparison with authentic sample. The presence of higher oligocondensates was estimated based on the intensity of more polar spots on the TLC plate. After 1 h, *p*-chloranil (1.5 equiv versus dipyrromethane **33**) was added and again TLC examination and a comparison with authentic samples of corrole **43**[4d] and 5,15-diphenyl-10,20-bis(4-cyanophenyl)porphyrin[23] allowed us to identify these compounds. The yield of corrole **43** was determined by the chromatographic separation (SiO_2, CH_2Cl_2/hexanes, 3:2) and crystallization from hot EtOH.

Optimization of Conditions of the Conversion of Bilane 53 into Corrole 50. Bilane **53** (0.1 mmol, 64 mg) was dissolved in a specific amount of $CHCl_3$, an oxidant (0.30 mmol) was added, and the reaction mixture was stirred overnight at room temperature. The yield of corrole was determined by the chromatographic separation (SiO_2, CH_2Cl_2/hexanes, 2:3).

General Procedure for the Preparation of A_3-Corroles. Aldehyde (5 mmol) and pyrrole (697 μL, 10 mmol) were dissolved in MeOH (200 mL), and H_2O (200 mL) was added. Subsequently, HCl_{aq} (36%, 4.25 mL) was added, and the reaction was stirred at room temperature for 3 h. The mixture was extracted with $CHCl_3$, and the organic layer was washed twice with H_2O, dried (Na_2SO_4), filtered, and diluted to 300 mL with $CHCl_3$. *p*-Chloranil (1.23 g, 5 mmol) was added, and the mixture was refluxed for 1 h. The purification details are described for each case as follows.

5,10,15-Triphenylcorrole (5). The reaction mixture was passed over a silica column (CH_2Cl_2), and all fractions containing corrole were combined and evaporated. The subsequent chromatography (silica, CH_2Cl_2/hexanes, 1:1) and crystallization (CH_2Cl_2/hexanes) afforded pure corrole (235 mg, 27%): ESI-HR calcd exact mass ($C_{37}H_{27}N_4$), 527.2230; found, 527.2255 [M + H^+]. Anal. Calcd for $C_{37}H_{26}N_4$: C, 84.38; H, 4.98; N, 10.64. Found: C, 84.17; H, 5.00; N, 10.41. Other analytical data are consistent with literature values.[4b]

5,10,15-Tris(4-cyanophenyl)corrole (6). The reaction mixture was washed with a saturated solution of $NaHCO_3$, dried (Na_2SO_4), and filtered. The resulting solution was concentrated to about 50 mL and chromatographed (silica, CH_2Cl_2/hexanes, 1:1 then 2:1, 4:1) to give pure corrole (208 mg, 21%): ESI-HR calcd exact mass ($C_{40}H_{24}N_7$), 602.2088; found, 602.2084 [M + H^+]. Anal. Calcd for $C_{40}H_{23}N_7$: C, 79.85; H, 3.85; N, 16.30. Found: C, 79.73; H, 3.95; N, 16.25. Other analytical data are consistent with literature values.[8c]

5,10,15-Tris(4-methylphenyl)corrole (20). The reaction mixture was washed with a saturated solution of $NaHCO_3$, dried (Na_2SO_4), and filtered. The mixture was concentrated to half the volume and passed over a silica column (silica, CH_2Cl_2/hexanes, 2:3). The subsequent chromatography (silica, CH_2Cl_2/hexanes, 2:3) afforded pure corrole (240 mg, 25%): ESI−HR calcd exact mass ($C_{40}H_{33}N_4$), 569.2600; found, 569.2718 [M + H^+]. Anal. Calcd for $C_{40}H_{32}N_4$: C, 84.48; H, 5.67; N, 9.85. Found: C, 84.27; H, 5.70; N, 9.83. Other analytical data are consistent with literature values.[4b]

5,10,15-Tris(4-fluorophenyl)corrole (21). The reaction mixture was evaporated to about 50 mL and passed over a silica column (CH_2Cl_2). All fractions containing corrole were combined, evaporated with silica, and rechromatographed (silica, CH_2Cl_2/hexanes, 1:1) to give corrole containing a few impurities. The subsequent crystallization from CH_2Cl_2 afforded almost pure corrole, which was suspended in hot EtOH and filtered to give pure crystals (229 mg, 25%): ESI−HR calcd exact mass ($C_{37}H_{24}N_4F_3$), 581.1948; found, 581.1955 [M + H^+]. Anal. Calcd for $C_{37}H_{23}N_4F_3$: C, 76.54; H, 3.99; N, 9.65. Found: C, 76.56; H, 3.76; N, 9.48. Other analytical data are consistent with literature values.[8a]

5,10,15-Tris(4-bromophenyl)corrole (22). The reaction mixture was evaporated to dryness, suspended in hot EtOH, and filtered to give corrole containing a few impurities. The subsequent crystallization from CH_2Cl_2 gave crystals of pure product (207 mg). Because the second filtrate contained corrole, after evaporation with silica, it was chromatographed (DCVC, silica, cyclohexane then CH_2Cl_2/cyclohexane, 1:3) to give almost pure product, which was crystallized from CH_2Cl_2 to afford an additional 73 mg of corrole **22** (22%). Anal. Calcd for $C_{37}H_{23}N_4Br_3 \times 0.5CH_2Cl_2$: C, 55.90; H, 3.00; N, 6.95. Found: C, 55.88; H, 2.89; N, 6.74. Other analytical data are consistent with literature values.[4b]

5,10,15-Tris(4-methoxyphenyl)corrole (23). The reaction mixture was washed with a saturated solution of $NaHCO_3$, dried (Na_2SO_4), and filtered. The resulting solution was concentrated to half the volume and passed over a silica column (silica, CH_2Cl_2/hexanes, 3:2). The fractions containing corrole were evaporated to dryness and crystallized from CH_2Cl_2/hexanes to give pure corrole (222 mg, 22%): ESI-HR calcd exact mass ($C_{40}H_{33}N_4O_3$), 617.2547; found, 617.2552 [M + H^+]. Anal. Calcd for $C_{40}H_{32}N_4O_3 \times 0.5H_2O$: C, 76.78; H, 5.32; N, 8.95. Found: C, 77.04; H, 5.17; N, 8.79. Other analytical data are consistent with literature values.[4b]

5,10,15-Tris[3,4-bis(methoxycarbonylmethoxy)phenyl]-corrole (24). The reaction mixture was evaporated to dryness and chromatographed (silica, CH_2Cl_2 then CH_2Cl_2/EtOAc, 98:2, 95:5, 9:1). All fractions containing corrole were combined and evaporated to dryness. The residue was crystallized from acetone/hexanes. Because some impurities were still present, the crystals were recrystallized from CH_2Cl_2/hexanes to afford pure corrole (304 mg, 17%) as dark fine crystals: $R_f = 0.68$ (silica, CH_2Cl_2/acetone, 4:1); ^{1}H NMR (400 MHz, CF_3COOD) δ 3.99 (s, 3H), 4.01 (s, 6H), 4.02 (s, 3H), 4.08 (s, 3H), 4.11 (s, 3H), 4.97 (s, 4H), 5.01 (s, 4H), 5.09 (s, 4H), 6.77 (s, 2H), 7.02−7.11 (m, 2H), 7.19 (s, 1H), 7.27 (d, J = 8.6 Hz, 2H), 7.36 (d, J = 4.3 Hz, 2H), 7.47 (d, J = 1.8 Hz, 1H), 7.49 (s, 1H), 7.53 (d, J = 4.3 Hz, 2H), 7.58 (d, J = 1.8 Hz, 2H), 7.70 (d, J = 1.8 Hz, 1H), 7.72 (d, J = 1.8 Hz, 1H); ESI-MS obsd 1055.3 [M + H^+]; ESI-HR calcd exact mass ($C_{55}H_{50}N_4O_{18}Na$),

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1077.3012; found, 1077.3033 [M + Na^+]; λ_{abs} (toluene, $\epsilon \times 10^{-3}$) 424 (127.8), 526 (8.3), 565 (16.5), 621 (14.3), 653 (14.8) nm. Anal. Calcd for $C_{55}H_{50}N_4O_{18} \times CH_3OH$: C, 61.87; H, 5.01; N, 5.15. Found: C, 62.17; H, 5.20; N, 5.32.

5,10,15-Tris(3,4,5-trimethoxyphenyl)corrole (25). The reaction mixture was concentrated under reduced pressure and passed over a silica column (silica, CH_2Cl_2 then CH_2Cl_2/acetone, 96:4). All fractions containing corrole were combined and evaporated to dryness. The residue was crystallized from acetone/cyclohexane to give pure corrole (164 mg). Because the filtrate contained corrole, it was rechromatographed (DCVC, silica, CH_2Cl_2 then CH_2Cl_2/acetone, 99:1) to obtain product which was crystallized from acetone/cyclohexane to give an additional 22 mg of corrole (yield = 14%). R_f = 0.71 (silica, CH_2Cl_2/acetone, 95:5); ^{1}H NMR (400 MHz, CF_3COOD) δ 3.97 (s, 6H), 4.08 (s, 15H), 4.23 (s, 6H), 6.83 (s, 2H), 6.84 (s, 2H), 6.87 (s, 2H), 7.35 (s, 2H), 7.47 (d, J = 4.3 Hz, 2H), 7.52 (d, J = 4.3 Hz, 2H), 7.62 (d, J = 4.3 Hz, 2H); ESI-MS obsd 797.3 [M + H^+]; ESI-HR calcd exact mass ($C_{46}H_{45}N_4O_9$), 797.3181; found, 797.3182 [M + H^+]; λ_{abs} (toluene, $\epsilon \times 10^{-3}$) 423 (116.0), 570 (18.0), 621 (15.2), 653 (13.4) nm. Anal. Calcd for $C_{46}H_{44}N_4O_9 \times CH_3OH$: C, 68.10; H, 5.84; N, 6.76. Found: C, 68.01; H, 5.82; N, 6.59.

Pentapyrrotetramethene (32). All fractions containing a red compound were combined and evaporated to dryness. The residue was rechromatographed (DCVC, silica, CH_2Cl_2 then CH_2Cl_2/acetone 98.5:1.5, 97:3, 95.5:4.5) to give the product containing a few impurities. The subsequent crystallization from CH_2Cl_2/cyclohexane afforded pure crystals (71 mg, 5.5%). R_f = 0.72 (silica, CH_2Cl_2/acetone, 9:1). ^{1}H NMR (100 MHz, $CDCl_3$) δ 3.80 (s, 12H), 3.88 (br s, 12H), 3.90 (s, 6H), 3.94 (s, 6H), 5.94 (br s, 2H), 6.14 (br s, 2H), 6.30−6.65 (m, 8H), 6.72 (br s, 6H), 6.82 (s, 2H), 12.61 (br s, 3H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 56.3, 60.9, 61.0, 109.1, 110.5, 114.4, 119.9, 125.7, 128.5, 128.9, 133.6, 134.0, 134.1, 135.4, 135.6, 137.6, 137.9, 146.5, 151.5, 151.9, 152.7, 165.9; ESI-MS obsd 1042.4 [M + H^+]; ESI-HR calcd exact mass ($C_{60}H_{60}N_5O_{12}$), 1042.4233; found, 1042.4245 [M + H^+]; λ_{abs} (toluene, $\epsilon \times 10^{-3}$) 353 (41.1), 395 (39.5), 459 (25.6), 503 (52.9), 825 (7.3), 904 (8.9) nm.

5,10,15-Tris(4-nitrophenyl)corrole (26). The reaction mixture was passed over a chromatography column (silica, CH_2Cl_2). All fractions containing corrole were combined and evaporated to dryness. The residue was crystallized from CH_2Cl_2 to give pure corrole (107 mg, 10%): ESI-HR calcd exact mass ($C_{37}H_{24}N_7O_6$), 662.1783; found, 662.1809 [M + H^+]. Anal. Calcd for $C_{37}H_{23}N_7O_6 \times 0.5H_2O$: C, 66.27; H, 3.61; N, 14.62. Found: C, 66.26; H, 3.42; N, 14.57. Other analytical data are consistent with literature values.[4b]

5,10,15-Tris(3-cyanophenyl)corrole (27). The reaction mixture was evaporated to dryness and chromatographed (silica, toluene then toluene/EtOAc, 98:2). The subsequent chromatography (silica, toluene/EtOAc, 99:1) and crystallization from THF/Et_2O afforded pure corrole (226 mg, 23%): ESI-HR calcd exact mass ($C_{40}H_{24}N_7$), 602.2088; found, 602.2085 [M + H^+]. Anal. Calcd for $C_{40}H_{23}N_7$: C, 79.85; H, 3.85; N, 16.30. Found: C, 79.48; H, 3.55; N, 16.11. Other analytical data are consistent with literature values.[8c]

5,10,15-Tris[(4-trifluoromethyl)phenyl]corrole (28). The reaction mixture was concentrated to half the volume and passed over a silica column (silica, CH_2Cl_2/hexanes, 1:1). The subsequent chromatography of all fractions containing corrole (silica, CH_2Cl_2/hexanes, 2:3) and crystallization from CH_2Cl_2/hexanes afforded pure corrole (198 mg, 16%): ESI-HR calcd exact mass ($C_{40}H_{24}F_9N_4$), 731.1852; found, 731.1862 [M + H^+]. Anal. Calcd for $C_{40}H_{23}F_9N_4$: C, 65.76; H, 3.17; N, 7.67. Found: C, 65.28; H, 2.87; N, 7.41. Other analytical data are consistent with literature values.[8c]

5,10,15-Tris(4-carboxymethylphenyl)corrole (29). The reaction mixture was evaporated to dryness and chromatographed (silica, toluene/EtOAc, 95:5). A second chromatography (silica, toluene/EtOAc, 99:1) and crystallization from CH_2Cl_2/hexanes afforded pure corrole (203 mg, 17%). Anal. Calcd for $C_{43}H_{32}N_4O_6 \times H_2O$: C, 71.86; H, 4.77; N, 7.80. Found: C, 72.09; H, 4.62; N, 7.60. Other analytical data are consistent with literature values.[8c]

5,10,15-Tris(2,6-dichlorophenyl)corrole (30). The reaction mixture was evaporated with silica and chromatographed (silica, CH_2Cl_2/hexanes, 1:9 then 1:4, 1:2). All fractions containing corrole were combined and evaporated to dryness. The residue was crystallized from CH_2Cl_2/hexanes to give pure corrole (95 mg, 7.8%). Anal. Calcd for $C_{37}H_{20}N_4Cl_6$: C, 60.60; H, 2.75; N, 7.64. Found: C, 60.66; H, 2.84; N, 7.39. Other analytical data are consistent with literature values.[4a]

5,10,15-Tris(2-thienyl)corrole (31). The reaction mixture was evaporated to about 50 mL and passed over a silica column (silica, CH_2Cl_2/hexanes, 2:3) to obtain corrole containing a few impurities. All fractions containing corrole were combined, evaporated with silica, and rechromatographed (DCVC, silica, CH_2Cl_2/hexanes, 1:3 then 2:3) to give almost pure product, which was crystallized from CH_2Cl_2/hexanes to afford pure corrole (46 mg, 5.0%): R_f = 0.43 (silica, CH_2Cl_2/hexane, 3:2); ^{1}H NMR (200 MHz, THF-d_8 + 10% CD_3OD) δ 7.46−7.64 (m, 3H), 7.82 (s, 1H), 7.92−8.95 (m, 5H), 8.62 (d, J = 4.2 Hz, 2H), 8.69 (d, J = 4.5 Hz, 2H), 8.91 (d, J = 3.8 Hz, 2H), 9.04 (d, J = 4.4 Hz, 2H); ESI-MS obsd 545.1 [M + H^+]; ESI-HR calcd exact mass ($C_{31}H_{21}N_4S_3$), 545.0923; found, 545.0897 [M + H^+]; λ_{abs} (toluene, $\epsilon \times 10^{-3}$) 428 (163.0), 530 (11.1), 578 (21.5), 629 (16.5), 664 (15.2) nm. Anal. Calcd for $C_{31}H_{20}N_4S_3$: C, 68.35; H, 3.70; N, 10.29. Found: C, 68.26; H, 3.64; N, 10.07.

5-(2,6-Dichlorophenyl)dipyrromethane (40). 2,6-dichlorobenzaldehyde (8.75 g, 50 mmol) was dissolved in pyrrole (347 mL, 5 mol), and $MgBr_2$ (4.6 g, 25 mmol) was added. The reaction mixture was stirred at room temperature for 1.5 h (slow darkening), and powdered NaOH (10 g, 0.25 mol) was added. The mixture was filtered through Celite, and the pyrrole was removed under vacuum. The residue was dissolved and passed over a short silica column (silica, AcOEt/hexanes, 1:3). All fractions containing product were combined, evaporated, and crystallized from hot cyclohexane to afford pure dipyrromethane **40** (8.7 g, 60%): mp 103−104 °C (lit.[23] mp 102−103 °C). Anal. Calcd for $C_{15}H_{12}N_2Cl_2$: C, 61.87; H, 4.15; N, 9.62. Found: C, 62.03; H, 4.18; N, 9.74. Other analytical data are consistent with literature values.[19]

General Procedure for the Preparation of *trans*-A_2B-Corroles from Unhindered Dipyrromethanes: Dipyrromethane (1 mmol) and aldehyde (0.5 mmol) were dissolved in MeOH (50 mL). Subsequently, a solution of HCl_{aq} (36%, 2.5 mL) in H_2O (50 mL) was added, and the reaction was stirred at room temperature for 1 h. The mixture was extracted with $CHCl_3$, and the organic layer was washed twice with H_2O, dried (Na_2SO_4), filtered, and diluted to 250 mL with $CHCl_3$. *p*-Chloranil (369 mg, 1.5 mmol) was added, and the mixture was stirred overnight at room temperature. The purification details are described for each case as follows.

10-(4-Cyanophenyl)-5,15-diphenylcorrole (43). The reaction mixture was concentrated to half the volume and passed over a silica column (silica, CH_2Cl_2/hexanes, 3:2). All fractions containing corrole were combined and evaporated to dryness. The resulting solid was suspended in boiling EtOH, cooled, and filtered to give pure corrole (155 mg, 56%): ESI-HR calcd exact mass ($C_{38}H_{26}N_5$), 552.2188; found, 552.2204 [M + H^+]. Anal. Calcd for $C_{38}H_{25}N_5 \times H_2O$: C, 80.12; H, 4.78; N, 12.29. Found: C, 80.45; H, 4.64; N, 12.15. Other analytical data are consistent with literature values.[4d]

10-(4-Nitrophenyl)-5,15-diphenylcorrole (44). The reaction mixture was concentrated to half the volume and passed over a silica column (silica, CH_2Cl_2/hexanes, 1:1). All fractions containing corrole were combined and evaporated to dryness. The resulting solid was suspended in boiling EtOH, cooled, and filtered to give almost pure product. The crystals was crystallized from CH_2Cl_2/hexanes to afford pure corrole (152 mg, 53%): ESI-HR calcd exact mass ($C_{37}H_{26}N_5O_2$), 572.2081; found, 572.2099 [M + H^+]. Anal. Calcd for $C_{37}H_{25}N_5O_2 \times H_2O$: C, 75.37; H, 4.62; N, 11.88. Found: C, 75.59; H, 4.52; N, 11.92. Other analytical data are consistent with literature values.[4d]

10-(3-Cyanophenyl)-5,15-bis(4-methylphenyl)corrole (45). The reaction mixture was concentrated to half the volume and passed over a silica column (silica, CH_2Cl_2/hexanes, 1:1). All fractions containing corrole were combined and evaporated to dryness. The resulting solid was suspended in boiling EtOH, cooled, and filtered to give pure corrole (149 mg, 51%): $R_f = 0.38$ (silica, CH_2Cl_2/hexane, 3:2); ^{1}H NMR (200 MHz, THF-d_8 + 1% CD_3OD) δ 2.64 (s, 6H), 7.63 (d, $J = 7.8$ Hz, 4H), 7.92 (t, $J = 7.8$ Hz, 1H), 8.08 (d, $J = 7.8$ Hz, 1H), 8.22 (d, $J = 7.8$ Hz, 4H), 8.37 (d, $J = 4.6$ Hz, 2H), 8.42−8.54 (m, 4H), 8.81 (d, $J = 4.8$ Hz, 2H), 8.91 (d, $J = 4.4$ Hz, 2H); ESI-MS obsd 580.3 [M + H$^+$]; ESI-HR calcd exact mass ($C_{40}H_{30}N_5$), 580.2496; found, 580.2518 [M + H$^+$]; λ_{abs} (toluene, $\epsilon \times 10^{-3}$) 422 (126.4), 521 (8.1), 582 (15.4), 615 (12.6), 651 (9.7) nm. Anal. Calcd for $C_{40}H_{29}N_5$: C, 82.88; H, 5.04; N, 12.08. Found: C, 82.69; H, 4.98; N, 12.14. **Large Scale Preparation.** Dipyrromethane **34** (2.36 g, 10 mmol) and 3-cyanobenzaldehyde **15** (650 mg, 5 mmol) were dissolved in MeOH (500 mL). Subsequently, the solution of HCl_{aq} (36%, 25 mL) in H_2O (500 mL) was added, and the reaction was stirred at room temperature for 1 h. The mixture was extracted with $CHCl_3$, and the organic layer was washed twice with H_2O, dried (Na_2SO_4), filtered, and diluted to 1.25 L with $CHCl_3$. *p*-Chloranil (3.69 g, 15 mmol) was added, and the mixture was stirred overnight at room temperature. The whole reaction mixture was evaporated to dryness and boiled with EtOH (70 mL). After cooling in the refrigerator, it was filtered to afford crystals, which were dissolved in hot THF and precipitated with cyclohexane. Filtration gave crystals of corrole **45** (794 mg). Both filtrates were combined, evaporated to the dryness, and suspended in CH_2Cl_2. Filtration gave crystals comprised of corrole and 2,3,5,6-tetrachlorohydroquinone. The latter one was removed quantitatively by washing several times with warm EtOH to give pure corrole **45** (446 mg). The filtrate was evaporated to dryness with silica and chromatographed (DCVC, silica, cyclohexane then CH_2Cl_2/cyclohexane, 2:3) to afford a fraction containing corrole contaminated with other compounds. The resulting solid was crystallized from THF/EtOH to give an additional crop of product (292 mg). Total yield, 1.532 g (53%).

10-Phenyl-5,15-bis(4-cyanophenyl)corrole (46). The reaction mixture was concentrated to half the volume and passed over a silica column (silica, CH_2Cl_2/hexanes, 3:2). All fractions containing corrole were combined and evaporated to dryness. The resulting solid was suspended in boiling EtOH, cooled, and filtered to give pure corrole (136 mg, 47%): $R_f = 0.54$ (silica, CH_2Cl_2/hexane, 3:2); ^{1}H NMR (200 MHz, THF-d_8 + 10% CD_3OD) δ 7.76 (s, 3H), 8.19 (d, $J = 7.6$ Hz, 6H), 8.53 (d, $J = 5.0$ Hz, 8H), 8.83 (d, $J = 4.4$ Hz, 2H), 8.99 (d, $J = 3.6$ Hz, 2H); ESI-MS obsd 577.2 [M + H$^+$]; ESI-HR calcd exact mass ($C_{39}H_{25}N_6$), 577.1921; found, 577.1899 [M + H$^+$]; λ_{abs} (toluene, $\epsilon \times 10^{-3}$) 432 (114.3), 577 (17.8), 629 (12.8), 655 (12.9) nm. Anal. Calcd for $C_{39}H_{24}N_6$: C, 81.23; H, 4.20; N, 14.57. Found: C, 81.24; H, 4.02; N, 14.51.

10-(Pentafluorophenyl)-5,15-bis(4-methoxyphenyl)corrole (47). The reaction mixture was evaporated to dryness and chromatographed (silica, CH_2Cl_2/hexanes, 1:1). All fractions containing corrole were combined, evaporated, and crystallized from CH_2Cl_2/hexanes to afford pure corrole (44 mg, 13%): ESI-HR calcd exact mass ($C_{39}H_{26}N_4O_2F_5$), 677.1970; found, 677.1953 [M + H$^+$]. Anal. Calcd for $C_{39}H_{25}N_4O_2F_5$: C, 69.23; H, 3.72; N, 8.28. Found: C, 69.16; H, 3.74; N, 8.22. Other analytical data are consistent with literature values.[4d]

10-(4-Cyanophenyl)-5,15-bis(4-methylthiophenyl)corrole (48). The reaction mixture was concentrated to half the volume and passed over a silica column (silica, CH_2Cl_2/hexanes, 3:2). All fractions containing corrole were combined and evaporated to dryness. The resulting solid was suspended in boiling EtOH, cooled, and filtered to give pure corrole (136 mg, 42%): $R_f = 0.48$ (silica, CH_2Cl_2/hexane, 3:1); ^{1}H NMR (400 MHz, CF_3COOD) δ 2.67 (s, 6H), 6.69 (s, 2H), 7.30 (d, $J = 3.4$ Hz, 2H), 7.42 (s, 2H), 7.52 (d, $J = 3.4$ Hz, 2H), 7.58, 7.86 (AA′BB′, $J = 8.0$ Hz, 2 × 4H), 7.65, 7.90 (AA′BB′, $J = 8.0$ Hz, 2 × 2H); ESI-MS obsd 644.2 [M + H$^+$]; ESI-HR calcd exact mass ($C_{40}H_{30}N_5S_2$), 644.1937; found, 644.1925 [M + H$^+$]; λ_{abs} (toluene, $\epsilon \times 10^{-3}$) 426 (100.3), 589 (17.1), 618 (16.0), 653 (10.7) nm. Anal. Calcd for $C_{40}H_{29}N_5S_2 \times CH_3OH$: C, 72.89; H, 4.92; N, 10.36. Found: C, 73.04; H, 4.55; N, 10.23.

10-(4-Cyanophenyl)-5,15-bis(pentafluorophenyl)corrole (49). In this case, DDQ instead of *p*-chloranil was used as the oxidizing agent. The reaction mixture was concentrated to half the volume and passed over a silica column (silica, CH_2Cl_2/hexanes, 1:1). All fractions containing corrole were combined and evaporated to dryness. A second chromatography (silica, hexanes/acetone, 9:1 then 6:1) afforded pure corrole (73 mg, 20%). Anal. Calcd for $C_{38}H_{15}N_5F_{10}$: C, 62.39; H, 2.07; N, 9.57. Found: C, 62.17; H, 1.87; N, 9.63. Other analytical data are consistent with literature values.[4d]

General Procedure for the Preparation of *trans*-A_2B-Corroles from Hindered Dipyrromethanes. Dipyrromethane (1 mmol) and aldehyde (0.5 mmol) were dissolved in MeOH (100 mL). Subsequently, a solution of HCl_{aq} (36%, 5 mL) in H_2O (50 mL) was added, and the reaction was stirred at room temperature for 2 h. The mixture was extracted with $CHCl_3$, and the organic layer was washed twice with H_2O, dried (Na_2SO_4), filtered, and diluted to 250 mL with $CHCl_3$. *p*-Chloranil (369 mg, 1.5 mmol) was added, and the mixture was stirred overnight at room temperature. The purification details are described for each case as follows.

10-(4-Cyanophenyl)-5,15-dimesitylcorrole (50). The reaction mixture was evaporated to dryness and chromatographed (silica, CH_2Cl_2/hexanes, 2:3) to afford pure corrole (97 mg, 31%). Anal. Calcd for $C_{44}H_{37}N_5$: C, 83.12; H, 5.87; N, 11.02. Found: C, 83.32; H, 6.05; N, 10.51. Other analytical data are consistent with literature values.[4d]

10-(4-Cyanophenyl)-5,15-bis(2,6-dichlorophenyl)corrole (51). The reaction mixture was evaporated to dryness and chromatographed (silica, toluene/hexanes, 4:1). A second chromatography (DCVC, silica, acetone/hexanes, 1:9 then 1:6) afforded pure corrole (93 mg, 27%): ESI-HR calcd exact mass ($C_{38}H_{22}N_5Cl_4$), 688.0624; found, 688.0624 [M + H$^+$]. Anal. Calcd for $C_{38}H_{21}N_5Cl_4$: C, 66.20; H, 3.07; N, 10.16. Found: C, 65.92; H, 3.29; N, 10.05. Other analytical data are consistent with literature values.[8c]

10-(4-Pyridyl)-5,15-bis(2,6-dichlorophenyl)corrole (52). Pyridine-4-carboxaldehyde (54 μL, 0.5 mmol) was dissolved in H_2O (50 mL), and HCl_{aq} (36%, 2.5 mL) was added. To this mixure was added 2,6-dichlorophenyldipyrromethane (292 mg, 1 mmol) in EtOH (25 mL). The reaction was stirred overnight at room temperature. NaOH (1.6 g) solution in H_2O (50 mL) was added, followed by CH_2Cl_2 (50 mL). The organic phase was isolated, washed twice with water, dried (Na_2SO_4), filtered, and diluted to 250 mL with $CHCl_3$. DDQ (260 mg, 1.15 mmol) in THF (5 mL) was added, and the mixture was stirred at room temperature for 15 min. The reaction mixture was concentrated to half the volume and passed over a silica column (silica, CH_2Cl_2 then acetone/hexanes, 5:95) to afford pure corrole (54 mg, 16%): ESI-HR calcd exact mass ($C_{36}H_{22}N_5Cl_4$), 664.0624; found, 664.0608 [M + H$^+$]. Anal. Calcd for $C_{36}H_{21}N_5Cl_4$: C, 64.98; H, 3.18; N, 10.53. Found: C, 64.71; H, 3.38; N, 10.41. Other analytical data are consistent with literature values.[8c]

5,10,15-Tris(4-cyanophenyl)tetrapyrrane (4). Samples of 4-cyanobenzaldehyde **2** (7.9 g, 60 mmol) and pyrrole (8.34 mL, 120 mmol) were dissolved in a mixture of MeOH (1 L) and H_2O (1 L). Subsequently, HCl_{aq} (36%, 30 mL) was added, and the reaction was stirred at room temperature for 2 h. The mixture was extracted with CH_2Cl_2, and the organic layer was washed twice with H_2O, dried (Na_2SO_4), and filtered. The reaction mixture was evaporated to dryness and chromatographed (silica, EtOAc/hexanes, 9:1 then 4:1, 3:2, 1:1). All fractions containing product were combined and rechromatographed (silica, toluene/EtOAc, 4:1). Removal of the solvent afforded the product as an amorphous solid (3.75 g, 31%).%): $R_f = 0.53$ (silica, acetone/hexane, 2:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.32−5.33 (m, 1H), 5.42 (d, $J = 4.7$ Hz, 2H), 5.66−5.70 (m, 2H), 5.78−5.87 (m, 2H), 6.13−6.17 (m, 2H), 6.25

(q, $J = 2.2$ Hz, 1H), 6.72−6.74 (m, 2H), 6.80−6.85 (m, 1H), 7.23−7.32 (m, 6H), 7.51−7.60 (m, 6H), 7.91 (br s, 2H), 8.02 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 43.98, 44.02, 44.05, 107.72, 108.08, 108.14, 108.69, 110.73, 110.81, 117.66, 117.86, 117.93, 118.00, 118.61, 118.70, 118.77, 126.98, 127.68, 128.20, 128.56, 128.91, 129.11, 129.16, 130.70, 130.92, 131.21, 131.47, 131.53, 132.34, 147.40, 171.20; ν_{max} (KBr) 723, 769, 1021, 1250, 1414, 1500, 1605, 2228, 3368 cm^{-1}; ESI-MS obsd 630.2 [M + Na$^+$]; ESI-HR calcd exact mass ($C_{40}H_{29}N_7Na$), 630.2377; found, 630.2372 [M + Na$^+$]. This compound is a mixture of regio- and stereoisomers.

10-(4-Cyanophenyl)-5,15-dimesityltetrapyrrane (53). Samples of 5-mesityldipyrromethane **33** (2.64 g, 10 mmol) and 4-cyanobenzaldehyde **2** (655 mg, 5 mmol) were dissolved in MeOH (500 mL). Subsequently, HCl_{aq} (36%, 25 mL) in H_2O (500 mL) was added, and the reaction mixture was stirred at room temperature for a night. The mixture was extracted with CH_2Cl_2, and the organic layer was washed twice with H_2O, dried (Na_2SO_4), and filtered. After evaporation, the reaction mixture was chromatographed (silica, EtOAc/hexanes, 9:1 then 4:1). All fractions containing product were collected and evaporated to dryness. A subsequent crystallization from EtOAc/hexanes gave pure tetrapyrrane (468 mg). Because the filtrate contained product, it was chromatographed (silica, EtOAc/hexanes, 9:1 then 4:1) to give pure tetrapyrrane as an oil that was crystallized from EtOAc/hexanes. Filtration gave crystals (558 mg) and an additional portion of product as a foamlike solid (554 mg). Total yield, 1.58 g (49%); mp 203−205 °C; $R_f = 0.69$ (silica, acetone/hexane, 2:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.02 (br s, 12H), 2.26 (br s, 6H), 5.33 (br s, 1H), 5.67−5.70 (m, 2H), 5.80−5.83 (m, 4H), 5.89−5.93 (m, 2H), 6.13−6.16 (m, 2H), 6.63−6.65 (m, 2H), 6.83 (br s, 4H), 7.25−7.28 (m, 2H), 7.54−7.57 (m, 2H), 7.74 (br s, 2H), 7.83 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.53, 20.74, 38.31, 44.07, 44.11, 106.35, 106.38, 106.41, 106.85, 106.87, 106.89, 107.88, 107.91, 107.92, 108.54, 110.59, 110.61, 116.31, 116.34, 118.82, 128.00, 129.03, 129.67, 129.68, 129.71, 130.29, 131.03, 131.06, 131.09, 131.41, 131.45, 131.49, 132.22, 134.18, 136.60, 137.38, 147.88; ν_{max} (KBr) 765, 856, 1028, 1091, 1453, 1606, 2236, 2916, 3361 cm^{-1}; ESI-MS obsd 664.3 [M + Na$^+$]; ESI-HR calcd exact mass ($C_{44}H_{43}N_5Na$), 664.3411; found, 664.3433 [M + Na$^+$]; Anal. Calcd for $C_{44}H_{43}N_5$: C, 82.34; H, 6.75; N, 10.91. Found: C, 82.56; H, 6.85; N, 10.70. This compound is a mixture of regio- and stereoisomers.

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Supporting Information Available: ^{1}H NMR spectra of corroles **24**, **25**, **31**, **45**, **46**, and **48** and UV−vis absorption spectrum of pentapyrromethene **32**. This material is available free of charge via the Intenet at http://pubs.acs.org.

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