Rational Synthesis of Trans-Substituted Porphyrin Building Blocks Containing One Sulfur or Oxygen Atom in Place of Nitrogen at a Designated Site

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The use of heteroatom-substituted porphyrins in bioorganic and materials chemistry requires the ability to position a variety of substituents in a controlled manner about the porphyrin periphery. We describe a rational route to *trans*-AB_2C-type porphyrins bearing one oxygen atom (N_3O) or one sulfur atom (N_3S) in a designated location in the porphyrin core. The synthesis involved four stages: (1) Acid-catalyzed condensation of a furyl- or thienylcarbinol in excess pyrrole afforded the aryl-substituted furyl- or thienylpyrromethane in high yield. (2) Treatment of the furyl- or thienylpyrromethane with an acid chloride catalyzed by $SnCl_4$ or $AlCl_3$ afforded the corresponding diketo product. (3) Reduction with $NaBH_4$ in alcoholic solvents gave the furyl- or thienylpyrromethanediols. (4) Reaction of a furylpyrromethanediol, thienylpyrromethanediol, or dipyrromethanediol with a dipyrromethane in a one-flask process of condensation followed by oxidation gave the corresponding porphyrin. Reaction conditions previously identified to minimize scrambling in a dipyrromethane−aldehyde condensation were found to be effective in this application. Thus, reaction with 10 mM reactants in acetonitrile at 0 °C containing $BF_3{\cdot}Et_2O$ and NH_4Cl followed by oxidation with DDQ resulted in the desired porphyrin (10−20% yields) without acidolysis. In this manner, N_3O-, N_3S-, or N_4-porphyrins bearing 5-(*p*-iodophenyl), 15-[4-(2-(trimethylsilyl)ethynyl)-phenyl], and 10,20-di-*p*-tolyl groups have been made. This set of trans-substituted porphyrin building blocks is expected to be useful in the synthesis of biomimetic energy transduction systems.

Introduction

The ability to systematically tune the properties of the porphyrin macrocycle is of central importance to a broad range of studies in biomimetic and materials chemistry. One approach for altering the porphyrin involves replacement of one or more of the four pyrrolic nitrogen atoms with heteroatoms such as oxygen, sulfur, selenium, or tellurium. Such heteroatom porphyrins have altered metal coordination properties,[1] acid−base strength,[2] redox potentials,[3] electronic energy levels[4] (as evidenced by the shifted absorption and fluorescence spectra),[5] and excited-state lifetimes.[6] We recently proposed that a set of heteroatom porphyrins arranged in a linear series with a progressive decrease in energy levels could provide the basis for an energy cascade.[7] Such an array could be used for the vectorial flow of excited-state energy in light-harvesting arrays. To systematically exploit the distinctive properties afforded by heteroatom substitution requires the ability to locate the heteroatom in a specified position in the core of the porphyrin with respect to different substituents arranged about the porphyrin perimeter.

Heteroatom-substituted porphyrins were first prepared by Broadhurst and Grigg, who performed a 3 + 1 condensation of a *β*-substituted tripyrrane and 2,5-diformyl furan (or thiophene) to give the N_3O (or N_3S) porphyrin.[8] The synthesis of meso-substituted, heteroatom-substituted porphyrins was pioneered by Ulman and Manassen, who reacted 2,5-bis(α-phenyl-α-hydroxymethyl)thiophene with pyrrole in toluene containing chloroacetic acid to afford the NSNS tetra-*p*-tolylporphyrin.[9] Alternatively, the thiophenediol was converted by reaction with pyrrole to a dihydrotripyrrin analogue, which upon reaction with a 2,5-bis(α-aryl-α-hydroxymethyl)thiophene afforded the NSNS-porphyrin bearing two types of meso substituents in a cis configuration.[10] More recently, Latos−Grazynski and Chmielewski reacted a 2,5-bis(α-aryl-α-hydroxymethyl)thiophene with an aldehyde and pyrrole, affording the N_3S-porphyrin bearing two types of meso substituents in a cis configuration (eq 1).[11] This strategy afforded the core-modified

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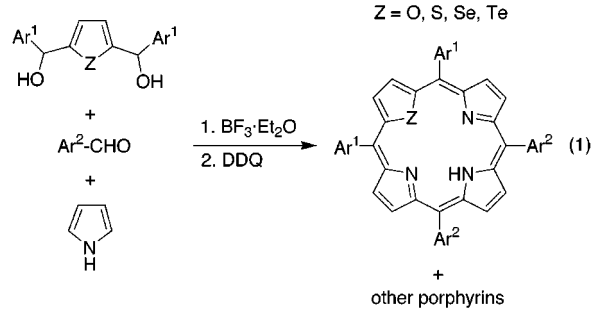
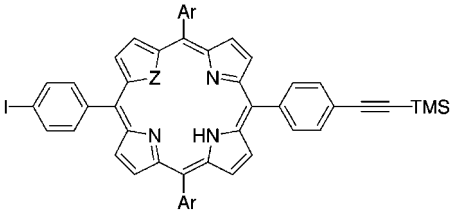


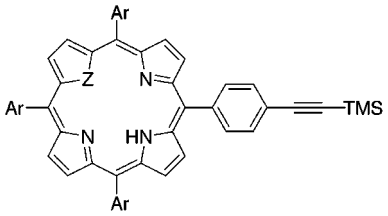
porphyrins with replacement of one nitrogen atom with an oxygen,[12] sulfur,[13] selenium,[14] or tellurium atom.[15] The reaction of 2-(α-phenyl-α-hydroxy)methyl-5-hydroxymethylfuran with *p*-tolualdehyde and pyrrole gave the 5-phenyl-10,15-di-*p*-tolyl-21-thiaporphyrin, the only example of a core-modified porphyrin with three different meso substituents.[12] These mixed condensations afford heteroatom porphyrins possessing a cis configuration of meso substituents among a mixture of porphyrins and require chromatographic separation. The reliance on statistical condensations in these methods limits access to heteroatom porphyrin building blocks.

Our groups have been working toward the development of porphyrin building blocks for the modular construction of biomimetic assemblies and molecular devices. In Korea, we have explored routes to a variety of core-modified porphyrins, including porphyrins containing one or two heteroatoms, N-confused porphyrins, and N-confused heteroatom porphyrins.[16−19] In the U.S., we have developed and refined an efficient one-flask synthesis of 5-substituted dipyrromethanes,[20,21] investigated a stepwise approach toward porphyrins bearing four different meso substituents,[22] and identified nonscrambling conditions for the dipyrromethane−aldehyde condensation leading to trans-substituted porphyrins.[23] A major emphasis in this latter work has been to develop rational (nonstatistical) syntheses of multiply substituted porphyrins and to minimize the use of chromatography at all stages. Here we present rational routes to porphyrin building blocks containing one oxygen atom (N_3O) or one sulfur atom (N_3S) with regiospecific control over the location of the heteroatom as well as the meso-substituted functional groups. Porphyrins with no core modification (N_4) also are available by this general route.

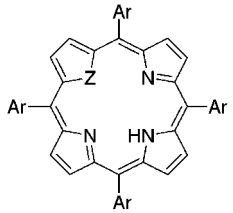
Chart 1



Bifunctional building block
Z = NH, O, or S



Monofunctional building block
Z = NH, O, or S



Benchmark, Z = NH, O, or S

Results and Discussion

The building block porphyrins required for a linear array are shown in Chart 1. The bifunctional building blocks (AB_2C-type) possess a trans configuration of iodo and ethyne groups that provide versatile handles for incorporation into a variety of architectures.[24] Two aryl groups are included at the remaining meso positions for solubility purposes. We initially hoped to use mesityl groups because these have been used previously to solubilize multiporphyrin arrays.[25] However, because we were unable to find suitable reduction conditions for sterically hindered mesitoyl groups (vide infra), we chose to employ *p*-tolyl groups instead. We also prepared monofunctional building blocks (A_3B-type) containing one ethyne group and tetraarylporphyrins (A_4-type) to serve as benchmarks for the building block porphyrins.

Our synthetic strategy toward these building blocks and the benchmarks involves the synthesis of furyl- or thienylpyrromethanes, bis-acylation, and then reduction to afford the corresponding diol and condensation of the diol with a dipyrromethane to form the porphyrin (Scheme 1). This strategy parallels that employed in our prior synthesis of porphyrins with four different meso substituents and is critically dependent on the use of nonscrambling conditions in the final condensation.[22]

In principle, either the dipyrromethane or the furyl/thienylpyrromethane could be converted to the corresponding diol. In a brief study (described in the Supporting Information), we showed that condensation of a furylpyrromethane or a thienylpyrromethane with a

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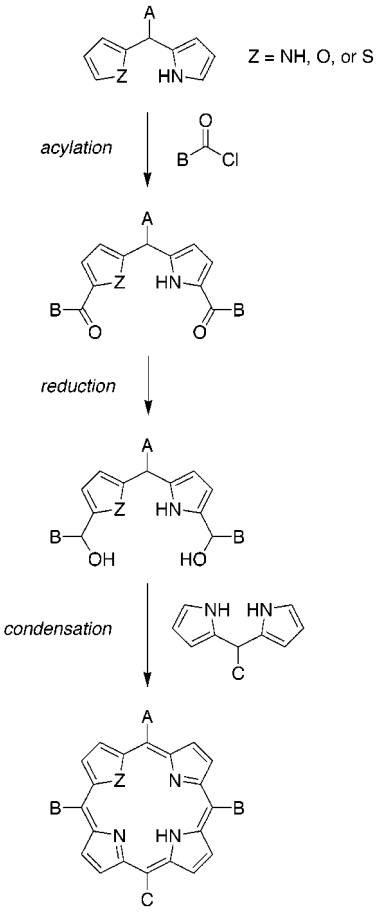
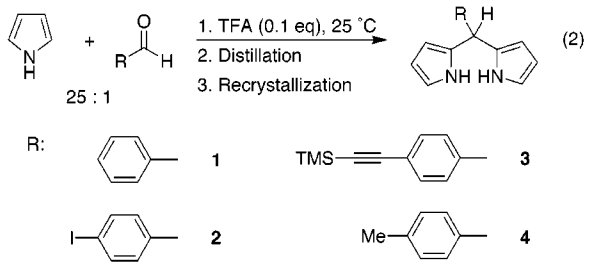
Scheme 1



dipyrromethanediol also affords heteroatom porphyrins. However, we did not pursue this synthetic approach further because in any condensation between a dipyrromethanediol and a furyl/thienylpyrromethane there is the complicating factor of differential reactivity between the pyrrole ring and the furyl/thienyl ring.[26] In contrast, incorporating the heteroatom into the diol moiety minimizes the reactivity differences and allows condensation with a symmetrical dipyrromethane.

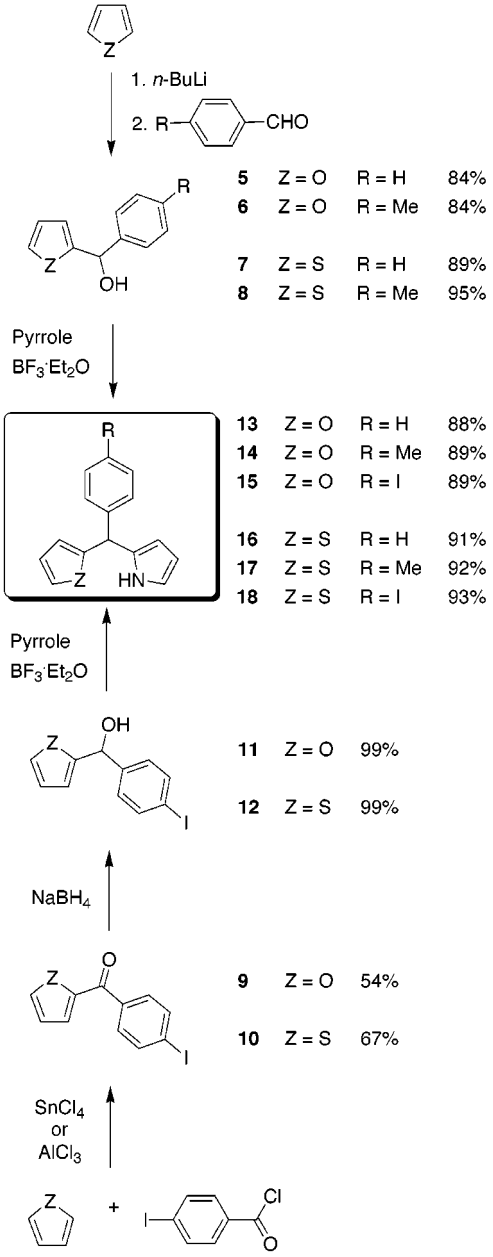
(1) Synthesis of Furyl-, Thienyl-, or Dipyrromethanes. Dipyrromethanes **1**−**4** were prepared by condensation of the aldehyde in neat excess pyrrole (eq 2).[21] Bulb-to-bulb distillation removed the higher oligo-



mers and recrystallization removed the N-confused dipyrromethane, readily affording multigram batches of pure dipyrromethane.

The furylpyrromethanes and thienylpyrromethanes were prepared as shown in Scheme 2. Treatment of furan or thiophene with *n*-butyllithium[27] followed by an aro-

Scheme 2



matic aldehyde afforded the corresponding 2-α-hydroxymethylated compounds **5**−**8** in high yield (84−95%). A small amount of deiodination occurred during the reaction of *p*-iodobenzaldehyde with lithiated furan or thiophene. Therefore, we developed a complementary two-step route to *p*-iodophenyl carbinols that utilized Freidel-Crafts acylation of furan[28] or thiophene[29] with *p*-iodobenzoyl chloride to give the ketone (**9** or **10**) (54−67%), followed by reduction with $NaBH_4$ to afford the 2-α-hydroxymethylated compounds **11** or **12** (99%) with no deiodination.

On the basis of the conditions previously employed for the formation of dipyrromethanes from 2-(α-hydroxy)-methylpyrroles,[20] carbinols **5**−**8**, **11**, or **12** were treated

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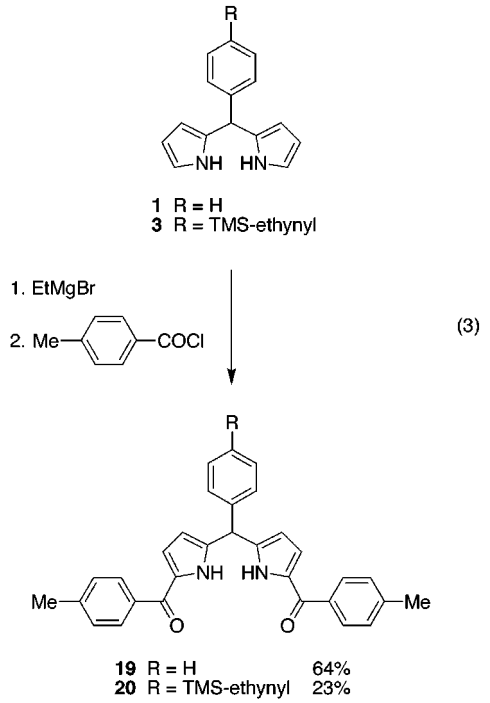
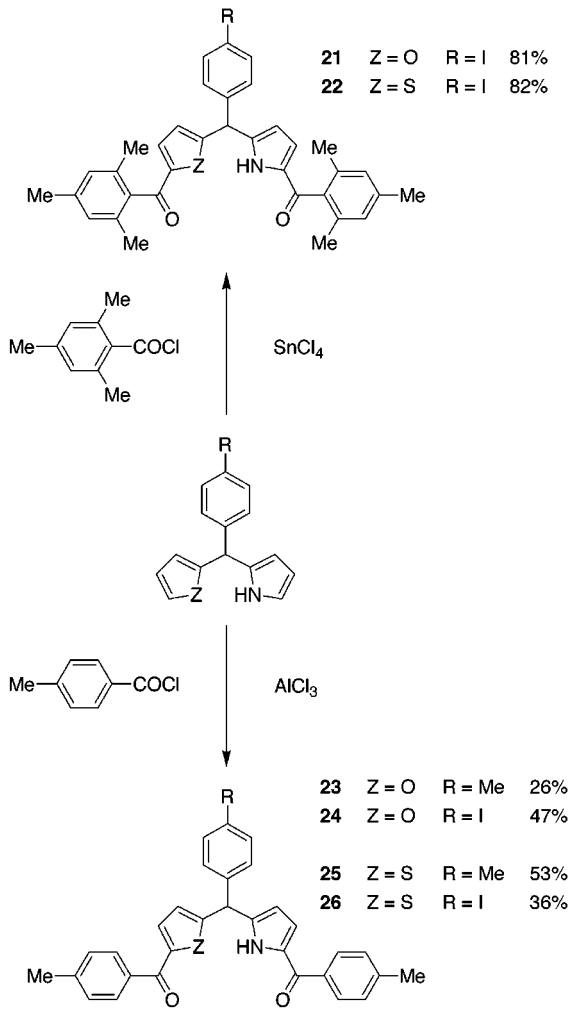
with $BF_3 \cdot Et_2O$ (1 mol equiv)[30] in neat excess pyrrole (23−66 mol equiv)[31] to afford furyl- and thienylpyrromethanes **13**−**18** in excellent yield (88−93%). Examination of the crude reaction mixtures produced from each furyl- or thienylcarbinol by GC−MS showed the presence of a byproduct of mass identical to that of the desired product. We assigned this impurity as the "N-confused" pyrrol-3-yl species by analogy to the byproduct formed in the condensation of an aldehyde in neat excess pyrrole.[21] Purification of the crude reaction mixture by column chromatography, bulb-to-bulb distillation, or direct recrystallization, followed by recrystallization from ethanol or washing with hexanes, afforded pure furylpyrromethanes **13**−**15**. GC analysis of thienylpyrromethanes **16**−**18** showed that approximately 1% of the pyrrol-3-yl species remained after the standard purification procedures. These materials are readily available on a multigram scale and were used directly in the acylation step.

(2) Acylation of the Furylpyrromethanes, Thienylpyrromethanes, and Dipyrromethanes. In our previous study on the acylation of dipyrromethanes, we were most interested in developing conditions that led to the monoacyldipyrromethane.[22] Optimal ratios for monoacylation (63%) with little diacylation (19%) were found to be 5-phenyldipyrromethane (**1**) (1.0 mol equiv), EtMgBr (2.2 mol equiv), and *p*-toluoyl chloride (1.4 mol equiv). Use of a larger excess of the acylation reagents [**1**: EtMgBr/*p*-toluoyl chloride (1.0: 3.0: 2.2 mol equiv)] increased the quantity of the diacyldipyrromethane (33%) relative to the monoacyldipyrromethane (41%). In this study, to further increase the amount of diacyldipyrromethane produced, we utilized an even greater excess of the Grignard reagent and the acid chloride. Thus, treatment of **1** with EtMgBr (5 mol equiv) in THF followed by *p*-toluoyl chloride (5 mol equiv) gave 64% of the diacylated product (**19**) and 31% of the monoacylated product (eq 3).[32] Identical treatment of 5-(*p*-iodophenyl)-



dipyrromethane (**2**) afforded a similar mixture of diacylated and monoacylated products, but also there was deiodination of the dipyrromethane. Therefore, the desired iodoethynylporphyrin was prepared using a complementary route via diacylation of 5-[4-(2-trimethylsilyl)-ethynyl)phenyl]dipyrromethane (**3**) affording **20**. In each case, column chromatography enabled isolation of gram batches of the diacyldipyrromethane free from the monoacyldipyrromethane.

Scheme 3



Because furan and thiophene rings are unable to form a species analogous to an N-metalated pyrrole, diacylation of the furyl- or thienylpyrromethanes cannot be achieved using Grignard reagents. Previously, the 1,9-diacylation of dithienylmethane or difurylmethane was achieved under Freidel−Crafts reaction conditions,[19] so we studied analogous conditions for the diacylation of furyl- or thienylpyrromethanes (Scheme 3). Our objective was to achieve clean acylation of both heterocyclic nuclei without forming excessive amounts of mono- or multiacylated products, since such a mixture would be difficult to separate. Initial studies focused on the acylation of the furylpyrromethane **15** with mesitoyl chloride (2.5 mol equiv) utilizing $SnCl_4$ (3.8 mol equiv). Purification of

(30) Use of TFA as an alternate catalyst was briefly examined. Reaction of **11** in pyrrole (64 mol equiv) catalyzed by TFA (1 mol equiv) also gave furylpyrromethane **15** in excellent yield (88%). However, reaction of **12** using TFA (1 mol equiv) gave **18** in 28% yield. More TFA (4 mol equiv) increased the yield to 76%.

(31) The furyl-/thienylpyrromethane yields were insensitive to the excess of pyrrole over the range studied (23−66 mol equiv).

(32) Greater than 5-fold excesses of ethylmagnesium bromide and *p*-toluoyl chloride did not significantly increase the ratio of diacyldipyrromethane to monoacyldipyrromethane.

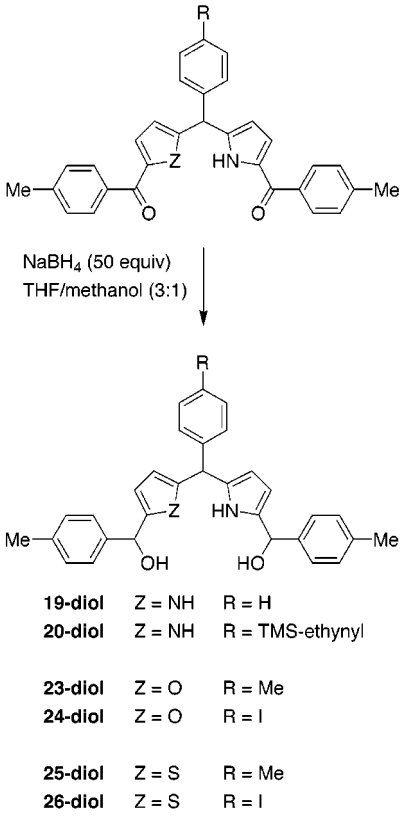
the crude product mixture by flash column chromatography readily removed the small amounts of the mono- and triacyl byproducts and afforded the diacylated product **21** in 81% yield. Identical treatment of thienylpyrromethane **18** gave **22** in 82% yield.

We were ultimately unable to reduce the sterically hindered mesitoyl groups (vide infra), so we used *p*-toluoyl substituents instead. However, changing mesitoyl chloride for *p*-toluoyl chloride resulted in a more complex mixture of products that was difficult to separate. For example, when **15** was treated with *p*-toluoyl chloride (2.5 mol equiv) and $SnCl_4$ (3.8 mol equiv), the diacyl compound **24** was isolated in 39% yield, but only after lengthy chromatography.[33] The use of more $SnCl_4$ (5.5 mol equiv) gave indiscriminate acylation. Use of $AlCl_3$ (3.8 mol equiv) as an alternate Lewis acid for reaction of **15** with *p*-toluoyl chloride (2.5 mol equiv) gave a crude reaction mixture that proved much easier to purify, affording pure **24** in 47% yield after a single flash column. Comparable results were obtained upon reaction of furyl- and thienylpyrromethanes **14**, **17**, and **18**. Thus, diacyl compounds **23**−**26** were readily prepared in 0.4−1.2 g batches (26−53% yield) by $AlCl_3$-catalyzed acylation with *p*-toluoyl chloride followed by column chromatography.

(3) Reduction To Form the Diol. In our prior synthesis of porphyrins bearing four different meso substituents, the diacyldipyrromethane intermediates were reduced to the corresponding dipyrromethanediols using a large excess of $NaBH_4$ in THF/ethanol (1:1), but the reduction product was used directly in the next step and not characterized.[22] Other reports have utilized $LiAlH_4$ in THF to reduce aroylpyrroles.[16,34] We examined these reaction conditions for the reduction of diacyldipyrromethane **19** and attempted to isolate and characterize the dipyrromethanediol product.

A detailed description of these diketone reduction studies is included in the Supporting Information. The key findings were as follows: (1) treatment of **19** with $LiAlH_4$ in THF led to over-reduction of the acyl-moiety; ^{1}H NMR spectroscopy showed the presence of one benzylic group, not the expected two hydroxymethyl groups. (2) No reduction was observed when **19** was treated with $NaBH_4$ in neat THF. (3) No reaction was observed over 1 h when **19** was treated with $NaBH_4$ (5 mol equiv) in THF/ethanol (1:1). (4) Treatment of **19** with $NaBH_4$ (10 mol equiv) in THF/methanol (7:3) gave reduction to the diol. The facile reduction in methanol likely involves a reducing agent derived by reaction of $NaBH_4$ with methanol, since $NaBH_4$ is known to decompose rapidly in methanol.[35]

In general, the *p*-toluoyl-substituted compounds (**19**, **20**, and **23**−**26**) were effectively reduced to the diol using a large excess of $NaBH_4$ (50−100 mol equiv) in THF/methanol (1:1−3:1) (eq 4). In each case, the reaction was followed by TLC; initially, a monoreduced species was observed, but further reduction afforded the diol as a single component with a lower R_f value that was readily



isolated if the reaction was quenched and worked up under nonacidic conditions. Examination of the crude reaction product by ^{1}H NMR and IR spectroscopy showed complete reduction of the carbonyl groups to hydroxy groups with no over-reduction as well as no dehalogenation of any *p*-iodophenyl groups.[36] ^{1}H NMR spectroscopy showed that a mixture of diastereomers was produced (each diol contains three stereocenters), but all attempts to separate the diastereomers by column chromatography resulted in decomposition. Although the furyl-, thienyl-, or dipyrromethanediols can be handled for a few hours, significant decomposition yielding dark materials occurred over 2 days upon storage in the freezer. Therefore, the crude diols were not purified or stored but were directly condensed with the dipyrromethane.

The sterically hindered mesitoyl-substituted dipyrromethanes **21** and **22** were not reduced under the conditions applied for the reduction of **19**, **20**, and **23**−**26**. Use of stronger reducing agents ($LiAlH_4$, $NaAlH_4$, $LiBH_4$) in a variety of solvents afforded complex mixtures. Accordingly, the mesityl-substituted heteroatom porphyrins could not be prepared despite the attractive solubility features imparted by mesityl groups that have been observed in other porphyrin building blocks.[25]

(4) Examination of Reaction Conditions for Porphyrin Formation. We recently employed a rapid small-scale assay based on LD-MS to identify reaction conditions that minimize acid-catalyzed scrambling during the condensation of sterically unhindered dipyrromethanes with aldehydes to form trans-substituted porphyrins.[23] We applied the same assay in this study to survey conditions for the related condensation of a dipyrromethanediol and a dipyrromethane. We chose the

(33) The complex mixture arises from the production of monoacylation and triacylation. The identity of the major byproducts produced in the acylation of compounds **24**, **25**, and **26** have been provisionally assigned by ^{1}H NMR spectroscopy of isolated samples. (Original NMR spectra of these byproducts are provided in the Supporting Information.)

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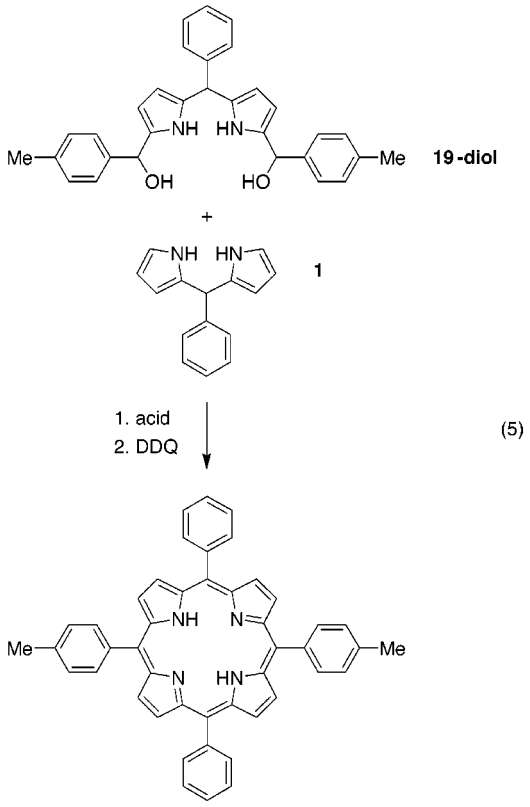
(36) ^{1}H NMR spectroscopy requires neutralization of the commercially supplied $CDCl_3$ over K_2CO_3 in order to prevent rapid acid-catalyzed decomposition of the diols.

condensation of **19-diol** with 5-phenyldipyrromethane (**1**) as our model system (eq 5) for two reasons: (1) The combination of phenyl and *p*-tolyl substituents allows resolution of scrambled porphyrins in the LD-MS spectrum while minimizing steric and electronic differences and is analogous to the model system used in the dipyrromethane-aldehyde study. (2) Both materials are readily available.



During our study to prepare porphyrins bearing four different meso substituents (ABCD-type porphyrins), we identified that in $CHCl_3$ use of TFA gave less scrambling than $BF_3{\cdot}Et_2O$.[22] We therefore screened the condensation of **19-diol** and **1** under two sets of reaction conditions. (1) Conditions similar to those used in the ABCD study: dipyrromethanediol (10 mM) and dipyrromethane (10 mM) in CH_2Cl_2 catalyzed by TFA (17.8 mM). (2) Low-scrambling conditions identified in the dipyrromethane/aldehyde condensation: dipyrromethanediol (10 mM) and dipyrromethane (10 mM) in acetonitrile at 0 °C in the presence of NH_4Cl (100 mmol/L) catalyzed by $BF_3{\cdot}Et_2O$ (1 mM). The time dependency of the spectroscopic yield and the extent of scrambling are shown in Figure 1. Both reactions have an initial phase (<1 min) during which the porphyrin is rapidly formed with no detectable scrambling. However, for the reaction in CH_2Cl_2 the spectroscopic yield continues to increase from 1 to 30 min in tandem with an undesirable increase in the amount of scrambling. In contrast, the reaction in acetonitrile shows no increase in either the spectroscopic yield or scrambling from 1 to 30 min. Thus, the previously identified low-scrambling conditions were even more effective in the dipyrromethanediol/dipyrromethane condensation versus dipyrromethane/aldehyde condensation because (1) the reaction was much more rapid (<1 min vs ca. 4 h), (2) yields were higher (14% vs 9%), and (3) scrambling was eliminated (undetectable vs trace).[37]

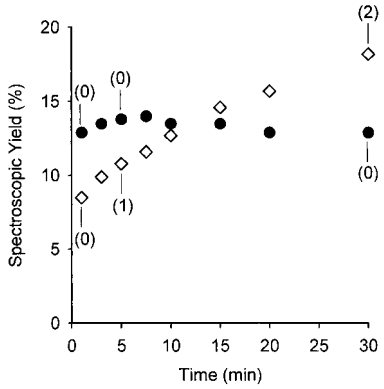
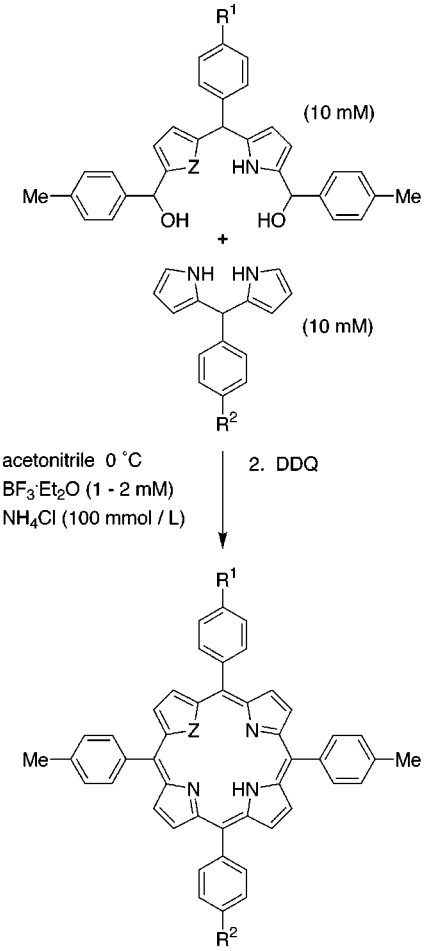


Figure 1. Yield (determined spectroscopically) vs time for reaction of **19-diol** (10 mM) and **1** (10 mM) (see eq 5). ◇: with TFA (17.8 mM) in CH_2Cl_2 at room temperature. ●: with $BF_3{\cdot}Et_2O$ (1.0 mM) and NH_4Cl (100 mmol/L) in acetonitrile at 0 °C. Scrambling levels[23] are shown in parentheses: 0 = no scrambling; 1 = trace scrambling; 2 = significant scrambling.

(5) Preparation of the Heteroatom Porphyrins. We applied reaction conditions of diol (10 mM) and dipyrromethane (10 mM) in acetonitrile at 0 °C catalyzed by $BF_3{\cdot}Et_2O$ (1 mM) in the presence of NH_4Cl (100 mmol/L) to the preparation of porphyrins **27**−**33** (eq 6). Spectroscopic monitoring of the reactions forming N_4-porphyrin **27** and N_3O-porphyrins **28**−**30** showed that the yield rapidly maximized (within 5 min) in each case. In contrast, condensations forming N_3S-porphyrins **31**−**33** gave inconsistent yields and rates of reaction when catalyzed by 1 mM $BF_3{\cdot}Et_2O$. This problem increased with the scale of the condensation, and in certain cases no porphyrin was formed even after 2 h. Increasing the amount of $BF_3{\cdot}Et_2O$ to 2 mM gave reliably fast reactions (complete within 20 min) with no detectable scrambling. In exploring higher acid concentrations for forming thiaporphyrin **30**, we found that 5 mM $BF_3{\cdot}Et_2O$ resulted in a crude reaction mixture comprising species consistent with scrambled byproducts (LD-MS analysis). These results show that an intermediate acid concentration is most effective in achieving porphyrin formation in good yield without detectable scrambling.

(6) Physical Properties of the Heteroatom Porphyrins. Oxaporphyrins are significantly more basic than thiaporphyrins or N_4-porphyrins,[2] a feature that had three significant ramifications in the isolation and characterization procedures of the N_3O-porphyrins. (1) The basicity of the N_3O-porphyrins (**28**−**30**) required separation of the porphyrin from the black nonporphyrin pigments produced in the DDQ oxidation step to be performed using basic alumina. The N_3S-porphyrins (**31**−**33**) were substantially less basic than the N_3O-porphyrins and could be separated from the DDQ oxidation byproducts using nonbasic alumina. Final purification of porphyrins **27**−**33** was achieved by recrystallization from ethanol or methanol. The nonporphyrin pigments were typically not isolated or characterized; however, during the preparation of 5,10,15,20-tetra-*p*-tolyl-21-oxaporphyrin (**28**) we also isolated an N_3O-tri(*p*-tolyl)corrole produced in less than 1% yield.[38]

(37) The signal-to-noise ratio of LD-MS typically exceeded 100:1. The MS method cannot exclude the selective scrambling yielding only the *cis*-porphyrin or the movement of the heteroatom within the core. However, rearrangement processes leading to such isomers would be expected to form a distribution of porphyrin products, including those of other masses. See ref 23.



27	Z = NH	R^1 = TMS-ethynyl	R^2 = I	10%
28	Z = O	R^1 = Me	R^2 = Me	12%
29	Z = O	R^1 = Me	R^2 = TMS-ethynyl	10%
30	Z = O	R^1 = I	R^2 = TMS-ethynyl	10%
31	Z = S	R^1 = Me	R^2 = Me	19%
32	Z = S	R^1 = Me	R^2 = TMS-ethynyl	18%
33	Z = S	R^1 = I	R^2 = TMS-ethynyl	11%

(2) The absorption spectrum of an N_3O-porphyrin in neat CH_2Cl_2 typically shows a long-wavelength shoulder on the Soret band due to formation of the protonated porphyrin. Addition of triethylamine, or use of a more basic solvent such as CH_2Cl_2/ethanol (3:1), causes disappearance of the shoulder. The N_3S-porphyrin is less easily protonated and can be examined in CH_2Cl_2 alone.

(3) The ^{1}H NMR spectrum of the N_3O-porphyrins collected in commercially supplied $CDCl_3$ results in disappearance of the N−H resonance. Treatment of the $CDCl_3$ with K_2CO_3 results in sharp peaks. The N_3S-porphyrins are less sensitive and can be examined in $CDCl_3$ without base treatment.

The ^{1}H NMR spectrum of porphyrin **30** or **33** revealed the asymmetric structure around the macrocycle. Due to the regiospecific placement of a furan or thiophene ring and three types of meso substituents, each pyrrole unit is unique. Using a 300 MHz spectrometer, all of the resonances arising from the β-protons were clearly separated, confirming the integrity of the AB_2C-type heteroatom porphyrin.

The UV−vis absorption spectra in toluene of the N_3O- and N_3S-porphyrins displayed the $Q_x(0,0)$ band at ∼675 or ∼680 nm, respectively, to be compared with that of the N_4-porphyrin (**27**) at 649 nm. The Soret band of the N_3O- or N_3S-porphyrins appeared at ∼423 or ∼432 nm, respectively, to be compared with that of the N_4-porphyrin at 422 nm. The Soret band of the N_3O- or N_3S-porphyrins exhibited $\epsilon_{\lambda max}$ ∼(2−3) × 10^5 M^{-1} cm^{-1} with slight broadening (fwhm 15−19 nm). Previous comparisons of the effects of oxygen substitution on spectral properties relied on an N_3O-porphyrin bearing only three meso substituents, which displayed the $Q_x(0,0)$ band at 664 nm.[7,12] Thus, the N_3O- and N_3S-porphyrins bearing identical substituents exhibit very similar red-shifts compared with the parent N_4-porphyrin. Knowledge of the effects of heteroatom substitution on electronic energy levels is essential for the rational design of energy transduction systems based on heteroatom porphyrins.

The emission spectra in toluene of the N_3O- and N_3S-porphyrins are characteristically red-shifted. The Q(0,0) and Q(0,1) bands of the N_3O-porphyrins appeared at ∼679 and ∼750 nm, respectively, while those of the N_3S-porphyrins appeared at ∼686 and ∼757 nm, to be compared with the N_4-porphyrin standard tetraphenylporphyrin (TPP), which emits at 652 and 718 nm. The fluorescence quantum yield of N_3O-porphyrins **28** and **29** were 0.093 and 0.097 respectively, which are similar to that of TPP (Φ_f = 0.11). The N_3S-porphyrins **31** and **32** exhibited fluorescence quantum yields of 0.023 and 0.016, respectively. The diminished fluorescence intensity of N_3S-porphyrins compared to TPP has been noted previously.[6b,c]

Conclusion

We have developed a rational route to trans-AB_2C-type porphyrins bearing one oxygen atom (N_3O) or one sulfur atom (N_3S) in a designated location in the porphyrin core. The key step in this route involves porphyrin formation via condensation of a furylpyrromethanediol or thienylpyrromethanediol with a dipyrromethane without any acid-catalyzed scrambling. Typically, the single porphyrin product is readily isolated in excellent purity in 10−20% yield utilizing only trivial chromatography followed by recrystallization. Simple and general synthetic methods that readily allow the preparation of the diols in gram batches have been developed. Therefore, the synthetic route described in this paper enables the rapid preparation of trans-AB_2C-type porphyrins with control over the placement of a heteroatom within the porphyrin core and the meso substituents around the porphyrin perimeter.

Experimental Section

General Methods. ^{1}H and ^{13}C NMR spectra and absorption spectra were collected routinely. Elemental analyses were

(38) The corrole structure must arise via the acid-catalyzed cleavage of a polypyrrane, but the site of the α,α-linkage cannot be conclusively determined from the spectral data collected: ^{1}H NMR ($CDCl_3$) δ 9.52 (d, J = 4.2 Hz, 1 H), 9.22 (m, 1 H), 9.04 (d, J = 3.6 Hz, 1 H), 8.87 (m, 3 H), 8.74 (m, 1 H), 8.63 (d, J = 4.2 Hz, 1 H), 8.18 (m, 4 H), 8.06 (d, J = 7.2 Hz, 2 H), 7.62 (d, J = 8.1 Hz, 2 H), 7.61 (d, J = 8.1 Hz, 2 H), 7.53 (d, J = 8.1 Hz, 2 H), 2.70 (s, 9 H), −2.93 (br s, 1 H); λ_{abs} (toluene) nm 405, 486, 554, 607, 423; $C_{40}H_{31}N_3O$ calcd exact mass 569.2467, obsd 568.8 (LD-MS); obsd 569.2493 (FAB-MS). Therefore, at present the exact mechanism leading to production of the corrole is uncertain. Further studies are required to determine whether corrole production is ubiquitous from the condensation of a furylpyrromethanediol, thienylpyrromethanediol, or dipyrromethanediol with a dipyrromethane catalyzed by BF_3·Et_2O in acetonitrile in the presence of NH_4Cl.

performed by Atlantic MicroLab, Inc. Melting points are uncorrected. A standard-size Kugelrohr short-path distillation apparatus was purchased from Aldrich Chemical Co. Column chromatography was performed on silica (Baker, 40 μm average particle size), alumina (Fisher, 80−200 mesh), and basic alumina (Fisher, Brockman activity I, 60−325 mesh). The furyl-, thienyl-, and dipyrromethanes were examined by GC analysis. Samples were analyzed with a GC system equipped with a FID detector [temperature gradient: temperature 1, 100 °C (3 min); temperature 2, 270 °C (10 min); rate 10 °C/min, total run time 30 min]. GC−MS analysis was performed identically to confirm the identity of N-confused product. In each case, the estimated percentage of N-confused product is based on relative peak areas without calibration based on working curves concerning the response of the FID detector.

The quantitative absorption spectral measurements were performed using a HP8453 spectrometer with 1-nm resolution (for comparison, *meso*-tetraphenylporphyrin has fwhm = 13 nm in toluene). Fluorescence spectra and emission yield determinations were made as previously described.[40]

For acylation reactions, CH_2Cl_2 was distilled from K_2CO_3. THF was distilled from Na/benzophenone. All other chemicals are reagent grade and were used as obtained. Unless otherwise indicated, all reagents were obtained from Aldrich Chemical Co., and all solvents were obtained from Fisher Scientific. 4-Iodobenzaldehyde was obtained from Karl Industries, Inc. The furyl-, thienyl-, and dipyrromethanes and their corresponding diols were easily visualized upon exposure of TLC plates to Br_2 vapor.

Porphyrins (from crude reaction mixtures, or following purification) were analyzed by laser desorption ionization mass spectrometry (LD-MS) without a matrix[39] using a Bruker Proflex II spectrometer without calibration. The progress of the N_4- and N_3S-porphyrin-forming reactions was monitored spectroscopically, and the extent of scrambling in the crude reaction mixture was determined as described previously.[22] Due to the basicity of the N_3O-porphyrins, two modifications were made to the standard monitoring procedure: (1) 25 μL of triethylamine was added to the solution in the cuvette (containing crude oxidized spectroscopic aliquots diluted in CH_2Cl_2/ethanol (3:1)) prior to UV−vis analysis. (2) The crude oxidized spectroscopic aliquots were spotted directly onto an LD-MS target without prior filtration through a pad of silica in a Pasteur pipet.

5-[4-(2-(Trimethylsilyl)ethynyl)phenyl]dipyrromethane (3). A solution of 4-(2-(trimethylsilyl)ethynyl)benzaldehyde[41] (3.53 g, 17.3 mmol) in pyrrole (30 mL, 0.43 mol) was degassed with a stream of Ar for 10 min. Then TFA (133 μL, 1.73 mmol) was added, the reaction mixture was stirred for 5 min, and ethyl acetate and 0.1 M NaOH were added. The organic phase was washed with 0.1 M NaOH and water and then dried (Na_2SO_4) and the solvent removed. Bulb-to-bulb distillation [170−180 °C (0.03 mmHg)] and then recrystallization (ethanol) afforded colorless crystals (3.48 g, 63%): mp 120 °C; ^{1}H NMR ($CDCl_3$) δ 8.01 (br s, 1 H), 7.41 (d, J = 7.9 Hz, 2 H), 7.14 (d, J = 7.9 Hz, 2 H), 6.69 (m, 2 H), 6.15 (m, 2 H), 5.87 (m, 2 H), 5.44 (s, 1 H), 0.25 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 142.47, 132.13, 131.87, 128.21, 121.69, 117.36, 108.41, 107.31, 104.76, 94.23, 43.69, −0.10; m/z 318.1549 (HRMS), $C_{20}H_{22}N_2Si$ requires 318.1552.

2-(α-Hydroxy-α-phenyl)methylfuran (5). Furan (0.77 mL, 11 mmol) was added to a solution of TMEDA (2.5 mL, 17 mmol) and *n*-butyllithium (4.5 mL, 11 mmol, 2.5 M in hexanes) in hexanes (25 mL). The mixture was heated at reflux for 30 min and then allowed to cool slightly and directly introduced into an ice-cold solution of benzaldehyde (0.60 mL, 5.9 mmol) in THF (30 mL) using a double-tipped needle. The solution was stirred for an additional 30 min at room temperature, quenched with saturated aqueous NH_4Cl, and extracted with diethyl ether. The organic layer was dried (Na_2SO_4) and the solvent removed. Column chromatography (silica; CH_2Cl_2) afforded an oil (0.86 g, 84%). Spectroscopic data were identical to those previously reported.[42]

2-[α-Hydroxy-α-(*p*-tolyl)]methylfuran (6). Furan (2.00 mL, 27.5 mmol), TMEDA (6.50 mL, 43.1 mmol), *n*-butyllithium (1.6 M in hexanes, 18.0 mL, 28.8 mmol), and hexanes (70 mL) were treated as described for **5** to afford a yellow solid (2.90 g, 84%): mp 36−37 °C; ^{1}H NMR ($CDCl_3$) δ 7.39 (d, J = 2.2 Hz, 1 H), 7.32 (d, J = 8.0 Hz, 2 H), 7.18 (d, J = 8.0 Hz, 2 H), 6.31 (m, 1 H), 6.12 (m, 1 H), 5.80 (d, J = 3.7 Hz, 1 H), 2.36 (s, 3 H), 2.31 (br d, J = 4.7 Hz, 1 H); ^{13}C NMR ($CDCl_3$) δ 156.07, 142.47, 137.88, 137.81, 129.15, 126.53, 110.15, 107.24, 70.02, 21.13; m/z 188.0833 (HRMS), $C_{12}H_{12}O_2$ requires 188.0837.

2-(α-Hydroxy-α-phenyl)methylthiophene (7). Thiophene (0.51 mL, 6.37 mmol), TMEDA (1.50 mL, 9.94 mmol), *n*-butyllithium (2.5 M in hexanes, 2.8 mL, 7.00 mmol), and benzaldehyde (0.64 mL, 6.3 mmol) in hexanes (15 mL) were treated as described for **5** to afford a solid (1.06 g, 89%): mp 55 °C (lit.[43] mp 55.5 °C). Spectroscopic data were identical to those previously reported.[43]

2-[α-Hydroxy-α-(*p*-tolyl)]methylthiophene (8). Thiophene (4.40 mL, 55.0 mmol), TMEDA (9.40 mL, 62.3 mmol), *n*-butyllithium (37.0 mL, 59.2 mmol, 1.6 M in hexanes), and *p*-tolualdehyde (5.59 mL, 47.5 mmol) in hexanes (80 mL) were treated as described for **5** to afford an oil that solidified upon standing in a freezer for 1 week. Washing the solid with hexanes afforded a tan solid (9.18 g, 95%): mp 48 °C; ^{1}H NMR ($CDCl_3$) δ 7.33 (d, J = 7.5 Hz, 2 H), 7.25 (m, 1 H), 7.17 (d, J = 7.5 Hz, 2 H), 6.93 (m, 1 H), 6.88 (m, 1 H), 6.02 (d, J = 3.6 Hz, 1 H), 2.37 (d, J = 3.6 Hz, 1 H), 2.35 (s, 3 H). Anal. Calcd for $C_{12}H_{12}OS$: C, 70.55; H, 5.92. Found: C, 70.42; H, 5.82.

2-(4-Iodobenzoyl)furan (9). A sample of $AlCl_3$ (0.34 g, 2.6 mmol) was added to an ice-cold solution of furan (0.25 mL, 3.4 mmol) and 4-iodobenzoyl chloride (0.45 g, 1.7 mmol) in CH_2Cl_2 (30 mL). The mixture was then heated at reflux for 2 h, an additional sample of $AlCl_3$ (0.57 g, 4.3 mmol) was added, and the heating was continued for 1 h. The mixture was combined with saturated aqueous $NaHCO_3$ and then extracted with $CHCl_3$. The organic layer was washed with water and then dried ($MgSO_4$), and the solvent was removed to afford a black solid. Column chromatography [silica; CH_2Cl_2/hexanes (1:1)] and then recrystallization (ethanol/water) afforded a pale yellow powder (0.27 g, 54%): mp 64 °C; ^{1}H NMR ($CDCl_3$): δ 7.88−7.85 (m, 2 H), 7.73−7.69 (m, 3 H), 7.25 (d, J = 3.7 Hz, 1 H), 6.62−6.60 (m, 2 H). Anal. Calcd for $C_{11}H_7IO_2$: C, 44.32; H, 2.37; I, 42.57. Found: C, 44.50; H, 2.35; I, 42.67.

2-(4-Iodobenzoyl)thiophene (10). A sample of $SnCl_4$ (0.90 mL, 7.7 mmol) was added to an ice-cold solution of thiophene (0.43 mL, 5.4 mmol) and 4-iodobenzoyl chloride (1.4 g, 5.2 mmol) in benzene (20 mL). The mixture was heated at reflux for 4 h, an additional sample of $SnCl_4$ (1.5 mL, 13 mmol) was added, and the heating was continued for 12 h. The mixture was combined with 10 vol % HCl and then extracted with CH_2Cl_2. The organic layer was washed with water and then dried ($MgSO_4$) and the solvent removed to afford a black solid. Column chromatography [silica; CH_2Cl_2/hexanes (2:1)] and then recrystallization (ethanol) afforded colorless crystals (1.09 g, 67%): mp 105.5 °C (lit.[28] mp 106.5 °C); ^{1}H NMR ($CDCl_3$) δ 7.88−7.84 (m, 2 H), 7.74 (m, 1 H), 7.63−7.55 (m, 3 H), 7.17 (dd, 1 H, J = 5.1, 3.7 Hz). Anal. Calcd for $C_{11}H_7IOS$: C, 42.06; H, 2.25; I, 40.40. Found: C, 42.22; H, 2.23; I, 40.49.

2-[α-Hydroxy-α-(4-iodophenyl)]methylfuran (11). A sample of $NaBH_4$ (0.17 g, 4.4 mmol) was added to a solution of **9** (0.39 g, 1.3 mmol) in THF/methanol (5:1, 30 mL). The mixture was stirred at room temperature for 10 min, quenched

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with water, and extracted with CH_2Cl_2 and the organic layer dried (Na_2SO_4). Removal of the solvent afforded a brown solid (0.39 g, 99%): mp 48 °C; ^{1}H NMR ($CDCl_3$) δ 7.67 (d, J = 8.1 Hz, 2 H), 7.36 (m, 1 H), 7.15 (d, J = 8.1 Hz, 2 H), 6.29 (m, 1 H), 6.09 (d, J = 3.0 Hz, 1 H), 5.72 (s, 1 H), 2.73 (br s, 1 H). Anal. Calcd for $C_{11}H_9IO_2$: C, 44.03; H, 3.02. Found: C, 44.40; H, 3.07.

2-[α-Hydroxy-α-(4-iodophenyl)]methylthiophene (12). A solution of **10** (0.74 g, 2.4 mmol) in THF/methanol (5:1, 30 mL) was treated with $NaBH_4$ (0.55 g, 15 mmol) as described for **11** to afford a gray solid (0.74 g, 99%): mp 85 °C; ^{1}H NMR ($CDCl_3$) δ 7.69 (d, J = 8.1 Hz, 2 H), 7.25 (m, 1 H), 7.20 (d, J = 8.1 Hz, 2 H), 6.95 (m, 1 H), 6.89 (m, 1 H), 6.01 (d, J = 3.7 Hz, 1 H), 2.38 (d, J = 3.7 Hz, 1 H). Anal. Calcd for $C_{11}H_9IOS$: C, 41.79; H, 2.87. Found: C, 42.04; H, 2.89.

Phenyl(furan-2-yl)(pyrrol-2-yl)methane (13). A solution of **5** (1.05 g, 6.04 mmol) and pyrrole (10.0 mL, 144 mmol) cooled by a water bath was degassed with N_2 for 5 min, and then BF_3·Et_2O (0.80 mL, 6.3 mmol) was added. The mixture was stirred for 30 min, quenched with 0.1 M NaOH, and extracted with ethyl acetate. The combined organic layers were washed with water and then dried ($MgSO_4$), and the solvent was removed to afford a black solid. Column chromatography (silica; CH_2Cl_2) afforded a colorless oil (1.19 g, 88%): ^{1}H NMR ($CDCl_3$) δ 8.04 (br s, 1 H), 7.38−7.19 (m, 6 H), 6.71 (m, 1 H), 6.32 (m, 1 H), 6.15 (q, J = 2.9 Hz, 1 H), 6.06 (d, J = 2.9 Hz, 1 H), 5.93 (m, 1 H), 5.46 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 155.58, 141.95, 131.03, 128.51, 128.41, 128.28, 127.02, 117.29, 110.15, 108.21, 107.41, 107.21, 44.20; m/z 223.0991 (HRMS), $C_{15}H_{13}NO$ requires 223.0997. GC detected no phenyl(furan-2-yl)(pyrrol-3-yl)methane.

(*p*-Tolyl)(furan-2-yl)(pyrrol-2-yl)methane (14). Compound **6** (1.24 g, 6.58 mmol) was treated with pyrrole (30 mL, 430 mmol) and BF_3·Et_2O (0.84 mL, 6.6 mmol) as described for **13**. Column chromatography (silica; CH_2Cl_2) afforded a colorless oil (1.39 g, 89%): ^{1}H NMR ($CDCl_3$) δ 8.04 (bs, 1 H), 7.36 (m, 1 H), 7.14−7.08 (m, 4 H), 6.71 (m, 1 H), 6.31 (m, 1 H), 6.15 (m, 1 H), 6.05 (m, 1 H), 5.93 (m, 1 H), 5.42 (s, 1 H), 2.33 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 155.81, 141.88, 137.65, 136.65, 131.25, 129.25, 128.18, 117.16, 110.12, 108.25, 107.24, 107.08, 43.85, 21.00; m/z 237.1153 (HRMS), $C_{16}H_{15}NO$ requires 237.1154. GC detected no (*p*-tolyl)(furan-2-yl)(pyrrol-3-yl)methane.

(4-Iodophenyl)(furan-2-yl)(pyrrol-2-yl)methane (15). Compound **11** (0.39 g, 1.3 mmol) was treated with pyrrole (5.0 mL, 72 mmol) and BF_3·Et_2O (0.17 mL, 1.3 mmol) as described for **13**. Column chromatography [silica; CH_2Cl_2/hexanes (1:2)] then recrystallization (ethanol) afforded a pink solid (0.41 g, 89%): mp 78 °C; ^{1}H NMR ($CDCl_3$) δ 8.04 (br s, 1 H), 7.61 (m, 2 H), 7.36 (m, 1 H), 6.93 (m, 2 H), 6.71 (m, 1 H), 6.32 (dd, J = 2.7 and 1.5 Hz, 1 H), 6.14 (q, J = 2.9 Hz, 1 H), 6.06 (m, 1 H), 5.90 (m, 1 H), 5.39 (s, 1 H). Anal. Calcd for $C_{15}H_{12}INO$: C, 51.60; H, 3.46; N, 4.01. Found: C, 51.73; H, 3.50; N, 3.94. GC detected no (4-iodophenyl)(furan-2-yl)(pyrrol-3-yl)methane.

Phenyl(thien-2-yl)(pyrrol-2-yl)methane (16). Compound **7** (0.598 g, 3.14 mmol) was treated with pyrrole (5.0 mL, 72 mmol) and BF_3·Et_2O (0.4 mL, 3.16 mmol) as described for **13**, except that the reaction flask was not placed in a water bath. Recrystallization of the crude product (hexanes) afforded a pink solid (0.68 g, 91%): mp 54−55 °C; ^{1}H NMR ($CDCl_3$) δ 7.90 (br s, 1 H), 7.35−7.20 (m, 6 H), 6.94 (dd, J = 5.1 and 3.7 Hz, 1 H), 6.81 (m, 1 H), 6.71 (m, 1 H), 6.16 (q, J = 2.9 Hz, 1 H), 5.93 (m, 1 H), 5.67 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 146.76, 142.76, 133.06, 128.51, 128.28, 126.99, 126.57, 125.73, 124.50, 117.16, 108.21, 107.47, 45.59; m/z 239.0769 (HRMS), $C_{15}H_{13}NS$ requires 239.0760. GC detected **16** (16.34 min, 98.7%) and phenyl(thien-2-yl)(pyrrol-3-yl)methane (17.65 min, 1.3%).

(*p*-Tolyl)(thien-2-yl)(pyrrol-2-yl)methane (17). Compound **8** (5.20 g, 25.5 mmol) was treated with pyrrole (44.2 mL, 0.64 mol) and BF_3·Et_2O (3.07 mL, 25.0 mmol) as described for **13** to afford an oil (5.96 g, 92%): ^{1}H NMR ($CDCl_3$) δ 7.74 (br s, 1 H), 7.30−7.23 (m, 5 H), 7.04 (dd, J = 5.1 and 3.6 Hz, 1 H), 6.92 (m, 1 H), 6.75 (m, 1 H), 6.26 (m, 1 H), 6.06 (m, 1 H), 5.72 (s, 1 H), 2.30 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 147.09, 139.85, 136.58, 133.29, 129.22, 128.18, 126.54, 125.63, 124.40, 127.10, 108.18, 107.34, 45.27, 21.00; m/z 253.0938 (HRMS), $C_{16}H_{15}NS$ requires 253.0925. GC detected **17** (16.44 min, 98.4%) and (*p*-tolyl)(thien-2-yl)(pyrrol-3-yl)methane (17.73 min, 1.6%).

(4-Iodophenyl)(thien-2-yl)(pyrrol-2-yl)methane (18). Compound **12** (0.74 g, 2.3 mmol) was treated with pyrrole (8.0 mL, 120 mmol) and BF_3·Et_2O (0.31 mL, 2.4 mmol) as described for **13**, except that the solid crude product was directly recrystallized (hexanes or ethanol) to afford a brown solid (0.80 g, 93%): mp 91 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (br s, 1 H), 7.60 (d, J = 8.2 Hz, 2 H), 7.17 (d, J = 5.0 Hz, 1 H), 6.97 (d, J = 8.2 Hz, 2 H), 6.91 (dd, J = 4.9 and 3.6 Hz, 1 H), 6.75 (d, J = 3.0 Hz, 1 H), 6.65 (m, 1 H), 6.12 (m, 1 H), 5.88 (s, 1 H), 5.56 (s, 1 H). Anal. Calcd for $C_{15}H_{12}INS$: C, 49.33; H, 3.31; N, 3.84. Found: C, 49.34; H, 3.37; N, 3.76. GC detected **18** (20.69 min, 98.7%) and (4-iodophenyl)(thien-2-yl)(pyrrol-3-yl)methane (22.22 min, 1.3%).

1,9-Bis(*p*-toluoyl)-5-phenyldipyrromethane (19). A solution of ethylmagnesium bromide (10.0 mL, 10 mmol, 1.0 M in THF) was carefully added to a stirred solution of 5-phenyldipyrromethane[21] (**1**) (444 mg, 2.0 mmol) in THF (5 mL) under Ar. An exothermic reaction with gas evolution ensued. After 30 min, a solution of *p*-toluoyl chloride (1.32 mL, 10.0 mmol) in THF (5.0 mL) was slowly added. The reaction mixture was stirred for an additional 2 h and then quenched with saturated aqueous NH_4Cl and extracted with CH_2Cl_2. The organic phase was washed with water and then dried ($MgSO_4$) and the solvent removed to afford a dark oil. Column chromatography [silica; CH_2Cl_2/ethyl acetate (20:1 to 5:1 gradient elution)] initially afforded the monoacylated byproduct 1-(*p*-toluoyl)-5-phenyldipyrromethane[22] (209 mg, 31%) as a foam. Further elution afforded **19** (585 mg, 64%) as an amorphous solid.[22]

1,9-Bis(*p*-toluoyl)-5-[4-(2-(trimethylsilyl)ethynyl)phenyl]dipyrromethane (20). Compound **3** (3.00 g, 9.42 mmol) was treated with ethylmagnesium bromide (47.1 mL, 47 mmol, 1.0 M in THF) and *p*-toluoyl chloride (6.23 mL, 47.1 mmol) as described for **19**, affording a pale brown solid. Recrystallization (ethanol) afforded a colorless solid (1.22 g, 23%): mp 242−243 °C; ^{1}H NMR ($CDCl_3$) δ 11.05 (br s, 2 H), 7.69 (d, J = 9.0 Hz, 4 H), 7.49 (d, J = 9.0 Hz, 2 H), 7.42 (d, J = 8.1 Hz, 2 H), 7.21 (d, J = 7.8 Hz, 4 H), 6.58 (m, 2 H), 5.95 (m, 2 H), 5.63 (s, 1 H), 2.40 (s, 6 H), 0.26 (s, 9 H); IR (cm^{-1}) 1614 (s, C=O). Anal. Calcd for $C_{36}H_{34}N_2O_2Si$: C, 77.94; H, 6.18; N, 5.05. Found: C, 77.86; H, 6.22; N, 4.97.

(4-Iodophenyl)[5-(mesitoyl)furan-2-yl][5-(mesitoyl)-pyrrol-2-yl]methane (21). A sample of $SnCl_4$ (0.40 mL, 3.4 mmol) was added to an ice-cold solution of **15** (0.32 g, 0.9 mmol) and mesitoyl chloride (0.38 mL, 2.3 mmol) in toluene (20 mL). The mixture was stirred for 40 min at room temperature, and then 2.0 M HCl was added. The solution was extracted with ethyl acetate, and the combined organic phases were washed with 0.1 M NaOH and water and then dried (Na_2SO_4). Two bands were observed by TLC [silica; hexanes/ethyl acetate (3:1)] at R_f 0.67 (monoacyl product) and 0.55 (**21**). The solvent was removed and the resulting solid purified by column chromatography [silica; hexanes/ethyl acetate (3:1)]. Compound **21** eluted as the second band. Recrystallization (ethanol) afforded a tan solid (0.47 g, 81%): mp 109−110 °C; ^{1}H NMR ($CDCl_3$) δ 9.42 (br s, 1 H), 7.68 (d, J = 8.1 Hz, 2 H), 6.99 (d, J = 8.1 Hz, 2 H), 6.86 (s, 4 H), 6.83 (d, J = 2.9 Hz, 1 H), 6.38 (m, 1 H), 6.18 (d, J = 2.9 Hz, 1 H), 5.94 (m, 1 H), 5.53 (s, 1 H), 2.31 (s, 6 H), 2.15 (s, 6 H), 2.14 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 189.09, 187.35, 159.78, 152.84, 138.88, 138.30, 137.97, 136.36, 135.61, 134.55, 134.45, 134.39, 132.71, 130.38, 128.28, 128.12, 121.46, 120.33, 111.03, 110.73, 93.45, 44.43, 21.10, 19.39, 19.19; m/z 641.1415 (HRMS), $C_{35}H_{32}INO_3$ requires 641.1427.

(4-Iodophenyl)[5-(mesitoyl)thien-2-yl][5-(mesitoyl)pyrrol-2-yl]methane (22). A mixture of **18** (0.418 g, 1.14 mmol) and mesitoyl chloride (0.48 mL, 2.9 mmol) was treated with $SnCl_4$ (0.51 mL, 4.4 mmol) as described for **21**, except that the reaction time was 45 min. Two bands were observed by TLC [silica; hexanes/ethyl acetate (5:1)] at R_f 0.57 (monoacyl product) and 0.43 (**22**). The solvent was removed and the resulting solid purified by column chromatography [silica; hexanes/ethyl acetate (5:1)]. Compound **22** eluted as the second band. Recrystallization (ethanol) afforded a yellow solid (0.63

g, 82%): mp 124−125 °C; ^{1}H NMR ($CDCl_3$) δ 9.64 (br s, 1 H), 7.68 (d, J = 8.8 Hz, 2 H,), 7.16 (d, J = 3 Hz, 1 H), 7.01 (d, J = 8.8 Hz, 2 H), 6.87 (s, 4 H), 6.78 (d, J = 3.0 Hz, 1 H), 6.40 (br s, 1 H), 5.99 (m, 1 H), 5.67 (s, 1 H), 2.31 (s, 6 H), 2.16 (m, 12 H); ^{13}C NMR ($CDCl_3$) δ 189.45, 155.36, 144.47, 140.63, 140.37, 138.91, 138.59, 138.24, 136.62, 134.88, 134.65, 134.39, 132.84, 130.51, 128.48, 128.38, 127.80, 120.59, 111.13, 93.61, 46.28, 21.33, 19.62, 19.55; m/z 657.1223 (HRMS), $C_{35}H_{32}INSO_2$ requires 657.1199.

(*p*-Tolyl)[5-(*p*-toluoyl)furan-2-yl][5-(*p*-toluoyl)pyrrol-2-yl]methane (23). A solution of **14** (935 mg, 3.94 mmol) in CH_2Cl_2 (10 mL) was added to an ice-cold solution of *p*-toluoyl chloride (1.19 mL, 8.97 mmol) and $AlCl_3$ (1.35 g, 10.13 mmol) in CH_2Cl_2 (40 mL) under Ar. The mixture was stirred for 2 h at room temperature, saturated aqueous $NaHCO_3$ was carefully added followed by $CHCl_3$, and the mixture was filtered through Celite to remove insoluble salts. The organic phase was isolated and then washed successively with saturated aqueous $NaHCO_3$, 2 M NaOH, and water, and then dried ($MgSO_4$) and the solvent removed. TLC [silica; hexanes/ethyl acetate (3:1)] showed many bands, including R_f 0.23 (**23**). Column chromatography [silica; hexanes/ethyl acetate (3:1)] afforded **23** (540 mg) contaminated with a small amount of an impurity. Further column chromatography [silica; hexanes/ethyl acetate (3:1)] followed by recrystallization (ethanol) afforded pure **23** as a solid (443 mg, 26%): mp 66 °C; ^{1}H NMR ($CDCl_3$) δ 9.33 (br s, 1 H), 7.82 (d, J = 8.1 Hz, 2 H), 7.77 (d, J = 8.1 Hz, 2 H), 7.28−7.24 (m, 4 H), 7.18−7.16 (m, 5 H), 6.81 (m, 1 H), 6.29 (d, J = 2.9 Hz, 1 H), 6.11 (m, 1 H), 5.60 (s, 1 H), 2.42 (s, 6 H), 2.35 (s, 3 H); IR (cm^{-1}) 1640 (m, C═O), 1605 (s, C═O). Anal. Calcd for $C_{32}H_{27}NO_3$: C, 81.16; H, 5.75; N, 2.96. Found: C, 80.98; H, 5.91; N, 2.90.

(4-Iodophenyl)[5-(*p*-toluoyl)furan-2-yl][5-(*p*-toluoyl)-pyrrol-2-yl]methane (24). A solution of **15** (1.38 g, 3.96 mmol) in CH_2Cl_2 (10 mL) was treated with *p*-toluoyl chloride (1.30 mL, 9.83 mmol) and $AlCl_3$ (1.91 g, 14.3 mmol) in CH_2Cl_2 (100 mL) as described for **23**, except that the reaction time was 4 h. TLC [silica; hexanes/ethyl acetate (3:1)] showed bands at R_f 0.69 (monoacyl product, trace), 0.53 (monoacyl product, 0.64 g, 34%), 0.46 (**24**), and 0.15 (triacyl product, trace). Column chromatography [silica; CH_2Cl_2/ethyl acetate (25:1)] afforded **24** contaminated with a small amount of an unidentified impurity. Further column chromatography [silica; CH_2Cl_2/ethyl acetate (10/1)] afforded pure **24** as a tan solid (1.10 g, 47%): mp 74−75 °C; ^{1}H NMR ($CDCl_3$) δ 9.41 (br s, 1 H), 7.83−7.77 (m, 4 H), 7.70 (d, J = 8.1 Hz, 2 H), 7.29−7.26 (m, 4 H), 7.17 (d, J = 3.7 Hz, 1 H), 7.03 (d, J = 8.8 Hz, 2 H), 6.82 (m, 1 H), 6.30 (d, J = 3.7 Hz, 1 H), 6.09 (m, 1 H), 5.59 (s, 1 H), 2.43 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 184.77, 182.05, 159.17, 152.32, 143.50, 142.79, 138.49, 138.14, 138.04, 135.59, 134.62, 131.42, 130.55, 129.61, 129.32, 129.22, 121.30, 120.37, 110.90, 93.55, 44.60, 21.81, 21.75; IR (cm^{-1}) 1640 (m, C═O), 1605 (s, C═O); m/z 585.0810 (HRMS), $C_{31}H_{24}IN_3O$ requires 585.0801.

(*p*-Tolyl)[5-(*p*-toluoyl)thien-2-yl][5-(*p*-toluoyl)pyrrol-2-yl]methane (25). A solution of **17** (0.401 g, 1.58 mmol) in CH_2Cl_2 (5 mL) was treated with *p*-toluoyl chloride (0.48 mL, 3.6 mmol) and $AlCl_3$ (0.55 g, 4.1 mmol) in CH_2Cl_2 (30 mL) as described for **23**, except that the reaction time was 14 h. TLC [silica; hexanes/ethyl acetate (3:1)] showed bands at R_f 0.56 (monoacyl product, trace), 0.46 (monoacyl product, 0.25 g, 26%), 0.38 (**25**), and 0.13 (triacyl product, trace). Column chromatography [silica; $CHCl_3$/ethyl acetate (24:1)] afforded **25** as a solid (0.41 g, 53%): mp 76−77 °C; ^{1}H NMR ($CDCl_3$) δ 9.54 (br s, 1 H), 7.80−7.74 (m, 4 H), 7.49 (d, J = 3.9 Hz, 1 H), 7.30−7.27 (m, 4 H), 7.22−7.16 (m, 4 H), 6.91 (d, J = 3.9 Hz, 1 H), 6.83 (m, 1 H), 6.14 (m, 1 H), 5.73 (s, 1 H), 2.44 (s, 6 H), 2.36 (s, 3 H); IR (cm^{-1}) 1605 (s, C═O); Anal. Calcd for $C_{32}H_{27}NO_2S$: C, 78.49; H, 5.56; N, 2.86. Found: C, 78.24; H, 5.53; N, 2.77.

(4-Iodophenyl)[5-(*p*-toluoyl)thien-2-yl][5-(*p*-toluoyl)-pyrrol-2-yl]methane (26). A solution of **18** (1.01 g, 2.77 mmol) in CH_2Cl_2 (10 mL) was treated with *p*-toluoyl chloride (1.27 g, 8.22 mmol) and $AlCl_3$ (1.46 g, 1.09 mmol) in CH_2Cl_2 (100 mL) as described for **23**, except that the reaction time was 10 h. TLC analysis showed two bands at R_f 0.59 (monoacyl product, 35%) and 0.35 (**26**). Purification by column chromatography [silica; $CHCl_3$/ethyl acetate, (24:1)] afforded **26** a pale green solid (600 mg, 36%): mp 104−106 °C; ^{1}H NMR ($CDCl_3$) δ 9.86 (br s, 1 H), 7.77 (d, J = 8.1 Hz, 2 H), 7.74 (d, J = 8.1 Hz, 2 H), 7.66 (d, J = 8.3 Hz, 2 H), 7.47 (d, J = 3.9 Hz, 1 H), 7.29−7.26 (m, 4 H), 7.03 (d, J = 8.3 Hz, 2 H), 6.87 (d, J = 3.8 Hz, 1 H), 6.82 (m, 1 H), 6.10 (m, 1 H), 5.73 (s, 1 H), 2.43 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 187.80, 184.73, 154.1, 143.31, 143.21, 142.80, 140.27, 139.82, 138.16, 135.52, 135.23, 134.67, 131.27, 130.43, 129.45, 129.27, 129.25, 129.18, 127.39, 120.15, 110.95, 93.53, 46.01, 21.72; m/z 601.0585 (HRMS), $C_{31}H_{24}INO_2S$ requires 601.0573.

1,9-Bis[α-hydroxy-α-(*p*-tolyl)methyl]-5-phenyldipyrromethane (19-diol). A sample of $NaBH_4$ (1.33 g total, 35.2 mmol, 50 mol equiv) was carefully added in small portions (∼400 mg each) over 20 min to a stirred solution of **19** (323 mg, 0.704 mmol) in THF/methanol (2:1, 20 mL). The progress of the reduction was followed by TLC [alumina; ethyl acetate/hexanes (1:1)]. Within 5 min, a new spot at R_f 0.5 was observed (monoreduced product), but this new component was fully converted to a second spot at R_f 0.2 (diol) after 40 min. The reaction mixture was quenched with water and then extracted with CH_2Cl_2. The organic phase was dried (K_2CO_3) and the solvent removed to afford a pale yellow oil: ^{1}H NMR ($CDCl_3$) δ 10.24 (m, 2 H), 7.39−7.19 (m, 5 H), 7.17−7.04 (m, 8 H), 5.75−5.64 (m, 4 H), 5.45−5.30 (m, 3 H), 2.33 (br s, 6 H), 1.96−1.91 (br m, 2 H); IR (cm^{-1}) 3290 (br s, OH).

5-(4-Iodophenyl)-15-[4-(2-(trimethylsilyl)ethynyl)-phenyl]-10,20-di(*p*-tolyl)porphyrin (27). A solution of compound **20** (224 mg, 0.40 mmol) in THF/methanol (3:1, 20 mL) was reduced with $NaBH_4$ (800 mg, 21.1 mmol) as described for **19-diol** to afford an oil (**20-diol**): ^{1}H NMR ($CDCl_3$) δ 10.11 (br m, 2 H), 7.43−7.35 (m, 2 H), 7.31−7.23 (m, 2 H), 7.13−7.10 (m, 8 H), 5.74−5.61 (m, 4 H), 5.39−5.30 (m, 3 H), 2.33 (br s, 6 H), 0.25 (s, 9 H); IR (cm^{-1}) 3290 (br m, OH).

Due to limited stability **20-diol** (ca. 0.40 mmol) was immediately dissolved in acetonitrile (40 mL) and 5-(4-iodophenyl)dipyrromethane[21] (**2**) (149 mg, 0.40 mmol) was added. The solution was cooled in an ice bath under Ar for 10 min, and then NH_4Cl (214 mg, 4.0 mmol) was added followed by BF_3·Et_2O (5.0 μL, 0.04 mmol, 1 mM). The solution instantly darkened, and the progress of the reaction was followed by UV spectroscopy. After 5 min, the spectroscopic porphyrin yield had stopped increasing, and then DDQ (136 mg, 0.60 mmol) and triethylamine (ca 0.5 mL) were added and the mixture was stirred at room temperature for 1 h. The entire reaction mixture was then filtered through a pad of alumina (eluted with CH_2Cl_2) until the eluant was no longer dark. Removal of the solvent gave a dark solid that was fully redissolved in CH_2Cl_2/hexanes (1:1, 50 mL) and filtered through a pad of silica [CH_2Cl_2/hexanes (1:1)]. The porphyrin eluted as a purple band. Removal of the solvent followed by recrystallization (ethanol) afforded a purple solid (36 mg, 10% from **20**): ^{1}H NMR ($CDCl_3$) δ 8.90−8.86 (m, 4 H), 8.81−8.78 (m, 4 H), 8.15 (d, J = 8.1 Hz, 2 H), 8.09−8.07 (m, 6 H), 7.94 (d, J = 8.1 Hz, 2 H), 7.86 (d, J = 8.1 Hz, 2 H), 7.55 (d, J = 8.1 Hz, 4 H), 2.70 (s, 6 H), 0.37 (s, 9 H), −2.81 (br s, 2 H); λ_{abs} (toluene) nm (ϵ, mM^{-1} cm^{-1}), 422 (330, fwhm = 15 nm), 516 (14), 552 (8.0), 593 (4.4), 649 (3.7); $C_{51}H_{41}IN_4Si$ calcd mass 864.2, obsd 863.8 (LD-MS); calcd exact mass 864.2145, obsd 864.2148 (FAB-MS).

5,10,15,20-Tetra(*p*-tolyl)-23*H*-21-oxaporphyrin (28). A solution of **23** (102 mg, 0.21 mmol) in THF/methanol (7:3, 20 mL) was reduced as described for **19-diol** to afford an oil (**23-diol**): ^{1}H NMR ($CDCl_3$): δ 8.72−8.55 (br m, 1 H), 7.19−7.04 (m, 12 H), 5.86−5.80 (m, 2 H), 5.69−5.49 (m, 4 H), 5.26 (m, 1 H), 3.56−3.11 (br m, 2 H), 2.32−2.29 (m, 9 H); IR (cm^{-1}) 3345 (br s, OH).

Condensation of freshly prepared **23-diol** (98 mg, 0.21 mmol) and 5-(*p*-tolyl)dipyrromethane[21] (**4**) (48 mg, 0.20 mmol) in acetonitrile (20 mL) in the presence of NH_4Cl (110 mg, 21 mmol) catalyzed by BF_3·Et_2O (20.4 μL, 0.021 mmol, 1.01 M in acetonitrile, 1.0 mM) was performed as described for **27**. DDQ (139 mg, 0.610 mmol) and triethylamine (10 μL) were added after 20 min. After 1 h of stirring at room temperature, the mixture was combined with water and extracted with ethyl

acetate. The organic phases were combined and dried (Na_2SO_4), and the solvent was removed. Flash column chromatography [silica; 30 mm diameter × 100 mm; THF/CH_2Cl_2 (1:9)] separated a fast moving black band that contained a corrole[38] (less than 1% yield) from desired porphyrin that eluted slowly. The column was then eluted using THF/CH_2Cl_2 (1:1) until no red fluorescence was observed in the eluant using a UV lamp (365 nm). Further purification by flash column chromatography [basic alumina (Brockman activity I); CH_2Cl_2] eluted an unidentified fast-moving blue band. The porphyrin was then eluted as a bright green band using ethyl acetate/hexanes (1:5). Removal of the solvent followed by recrystallization (ethanol) afforded a purple solid (17 mg, 12% from **23-diol**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.17 (s, 2 H), 8.87 (s, 2 H), 8.61 (d, J = 4.6 Hz, 2 H), 8.54 (d, J = 4.6 Hz, 2 H), 8.06−8.04 (m, 8 H), 7.54−7.52 (m, 8 H), 2.70 (s, 6 H), 2.69 (s, 6 H), −1.53 (br s, 1 H); λ_{abs} (toluene) nm (ϵ, mM^{-1} cm^{-1}), 422 (160, fwhm = 19 nm), 509 (16), 541 (6.1), 613 (5.3), 675 (4.0); λ_{em} (toluene) 679, 750 nm; $C_{48}H_{37}N_3O$ calcd mass 671.3, obsd 673.1 (LD-MS); calcd exact mass 672.3015 (MH^+), obsd 672.3027 (FAB-MS).

5,10,20-tri(*p*-tolyl)-15-[4-(2-(trimethylsilyl)ethynyl)phenyl]-23*H*-21-oxaporphyrin (29). A solution of compound **23** (159 mg, 0.336 mmol) in THF/methanol (3:1, 40 mL) was reduced as described for **19-diol** to afford **23-diol** as an oil.

Condensation of **23-diol** (ca. 0.336 mmol) and **3** (106 mg, 0.336 mmol) in acetonitrile (33 mL) in the presence of NH_4Cl (178 mg, 3.36 mmol) catalyzed by $BF_3{\cdot}Et_2O$ (33 μL, 33 mmol, 1 M in acetonitrile, 1 mM) was performed as described for **27**. DDQ (151 mg, 0.665 mmol) was added after 10 min. The crude product was dissolved in CH_2Cl_2 and purified by flash column chromatography [basic alumina (Brockman activity I); hexanes/ethyl acetate (6:1)]. A blue band containing no porphyrin eluted first, followed by a green band that contained the porphyrin and some unidentified nonporphyrin pigments. The pigments were removed by reoxidation with DDQ (151 mg) in toluene (25 mL) at reflux for 1 h. Once the mixture had cooled to room temperature, triethylamine (ca 100 μL) was added and the mixture filtered through a chromatography pad [basic alumina (Brockman activity I); hexanes/ethyl acetate (6:1)] to afford a purple solid (25 mg, 10% from **23**): ^{1}H NMR ($CDCl_3$) δ 9.19 (m, 2 H), 8.89 (m, 1H), 8.81 (m, 1 H), 8.62 (m, 1 H), 8.59−8.54 (m, 3 H), 8.12 (d, J = 8.1 Hz, 2 H), 8.05 (d, J = 7.3 Hz, 6 H), 7.84 (d, J = 8.1 Hz, 2 H), 7.53 (d, J = 7.3 Hz, 6 H), 2.69 (s, 9 H), 0.37 (s, 9 H), −1.60 (br s, 1 H); λ_{abs} (toluene) nm (ϵ, mM^{-1} cm^{-1}), 423 (290, fwhm = 15 nm), 509 (26), 541 (7.1), 615 (4.1), 676 (5.8); λ_{em} (toluene) 680, 751 nm; $C_{52}H_{43}N_3OSi$ calcd mass 753.4, obsd 754.5 (LD-MS); calcd exact mass 754.3254 (MH^+), obsd 754.3262 (FAB-MS).

5-(4-Iodophenyl)-15-[4-(2-(trimethylsilyl)ethynyl)phenyl]-10,20-di(*p*-tolyl)-23*H*-21-oxaporphyrin (30). A solution of **24** (530 mg, 0.905 mmol) in methanol/ethanol (2:1, 150 mL) was reduced as described for **19-diol** to afford an oil (**24-diol**): ^{1}H NMR ($CDCl_3$) δ 8.21 (m, 1 H), 7.60 (d, J = 8.1 Hz, 2 H), 7.28−7.23 (m, 4 H), 7.15 (d, J = 7.3 Hz, 4 H), 6.93 (d, J = 8.1 Hz, 2 H) 5.96 (m, 1 H), 5.91 (m, 1 H), 5.81−5.76 (m, 1 H), 5.73−5.66 (m, 3 H), 5.66 (m, 1 H), 5.30−5.29 (m, 1 H), 2.35 (s, 6 H), 2.21 (br s, 2 H); IR (cm^{-1}) 3355 (br s, OH); *m*/*z* 589.1123 (HRMS) $C_{31}H_{28}INO_3$ requires 589.1114.

Condensation of **24-diol** (424 mg, 0.719 mmol) and **3** (228 mg, 0.718 mmol) in acetonitrile (72 mL) in the presence of NH_4Cl (383 mg, 7.17 mmol) catalyzed by $BF_3{\cdot}Et_2O$ (9.1 μL, 0.072 mmol) was performed as described for **27**. Samples of DDQ (1.13 g, 4.97 mmol) and triethylamine (0.50 mL) were added after 20 min, and the mixture was stirred for an additional 1 h at room temperature before being combined with water and extracted with ethyl acetate. The organic layer was dried (Na_2SO_4) and the solvent removed. Column chromatography [silica; 50 mm diameter × 100 mm; THF/CH_2Cl_2 (1:9)] separated unidentified fast moving black materials from the desired porphyrin that eluted slowly. The column was eluted until no red fluorescence was observed in the eluant using a UV lamp (365 nm). Further purification [basic alumina (Brockman activity I): 35 mm diameter × 200 mm; ethyl acetate/hexanes (1:6)] eluted the desired porphyrin as a green band. Recrystallization (ethanol) afforded a purple solid (55 mg, 9% from **24**-diol): ^{1}H NMR ($CDCl_3$) δ 9.22 (d, J = 5.1 Hz, 1 H), 9.14 (d, J = 5.1 Hz, 1 H), 8.90 (d, J = 5.1 Hz, 1 H), 8.82 (d, J = 5.1 Hz, 1 H), 8.64 (d, J = 4.5 Hz, 1 H), 8.56 (m, 2 H), 8.50 (d, J = 5.1 Hz, 1 H), 8.13−8.03 (m, 8 H), 7.92−7.84 (m, 4 H), 7.56−7.53 (m, 4 H), 2.70 (s, 3 H), 2.69 (s, 3 H), 0.37 (s, 9 H); λ_{abs} (toluene) nm (ϵ, mM^{-1} cm^{-1}) 424 (270, fwhm = 19 nm), 510 (26), 542 (7.8), 615 (5.0), 675 (6.4); $C_{51}H_{40}IN_3OSi$ calcd mass 865.2, obsd 867.0 (LD-MS); calcd exact mass 866.2064 (MH^+), obsd 866.2077 (MH^+) (FAB-MS).

5,10,15,20-Tetra(*p*-tolyl)-23*H*-21-thiaporphyrin (31). A solution of compound **25** (238 mg, 0.486 mmol) in THF/methanol (1:1, 50 mL) was reduced by $NaBH_4$ (1.84 g, 48.6 mmol) as described for **19-diol** to afford an oil (**25-diol**): ^{1}H NMR ($CDCl_3$) δ 8.08 (br s, 1 H), 7.29−7.20 (m, 4 H), 7.15−7.05 (m, 8 H), 6.62 (m, 1 H), 6.56 (m, 1 H), 5.86 (m, 1 H), 5.76 (m, 2 H), 5.68 (m, 1 H), 5.43 (s, 1 H), 2.43 (br s, 2 H), 2.33−2.30 (m, 9 H); IR (cm^{-1}) 3375 (br s, OH); *m*/*z* 493.2062 (HRMS), $C_{32}H_{31}NO_2S$ requires 493.2076.

Condensation of **25-diol** (ca. 0.49 mmol) and 5-(*p*-tolyl)-dipyrromethane[21] (**4**) (115 mg, 0.486 mmol) in acetonitrile (49 mL) in the presence of NH_4Cl (260 mg, 4.86 mmol) catalyzed $BF_3{\cdot}Et_2O$ (49 μL, 49 mmol, 1 M stock in acetonitrile, 1 mM) was performed as described for **27**. DDQ (221 mg, 0.972 mmol) was added after 18 min and the mixture stirred for 1 h. Triethylamine (ca. 1 mL) was added and the entire reaction mixture filtered through an alumina pad (CH_2Cl_2). TLC (silica; CH_2Cl_2) showed the crude product contained the desired porphyrin contaminated with some pigments, so the crude product was reoxidized with DDQ (227 mg, 1.0 mmol) in toluene (50 mL) at reflux for 1 h. Addition of triethylamine (ca. 1 mL) and CH_2Cl_2 (25 mL) to the cooled mixture followed by filtration through an alumina pad (CH_2Cl_2) afforded the porphyrin and trace amounts of undesired non-porphyrin pigments. Final purification by flash column chromatography [silica; CH_2Cl_2/hexanes (1:1)] followed by recrystallization (ethanol) afforded a purple solid (50 mg, 15% from **25**): ^{1}H NMR ($CDCl_3$) δ 9.75 (s, 2 H), 8.93 (d, J = 1.5 Hz, 2 H), 8.68 (d, J = 5.1 Hz, 2 H), 8.61 (d, J = 4.4 Hz, 2 H), 8.13 (d, J = 8.1 Hz, 2 H), 8.07 (d, J = 7.6 Hz, 2 H), 7.62 (d, J = 8.1 Hz, 2 H), 7.54 (d, J = 7.3 Hz, 2 H), 2.70 (s, 12 H), −2.68 (br s, 1 H); λ_{abs} (toluene) nm (ϵ, mM^{-1} cm^{-1}), 431 (190, fwhm = 17 nm), 515 (27), 550 (11), 621 (5.9), 680 (8.2); λ_{em} (toluene) 686, 756 nm; $C_{48}H_{37}N_3S$ calcd mass 687.3, obsd 688.6 (LD-MS); calcd exact mass 688.2786 (MH^+), obsd 688.2787 (FAB-MS).

5,10,20-Tri(*p*-tolyl)-15-[4-(2-(trimethylsilyl)ethynyl)-phenyl]-23*H*-21-thiaporphyrin (32). A solution of compound **25** (98 mg, 0.20 mmol) in THF/methanol (3:1, 16 mL) was reduced by $NaBH_4$ (378 mg, 10.0 mmol) as described for **19-diol** to afford **25-diol** as an oil.

Condensation of **25-diol** (ca. 0.20 mmol) and **3** (64 mg, 0.20 mmol) in acetonitrile (20 mL) in the presence of NH_4Cl (108 mg, 2.0 mmol) catalyzed $BF_3{\cdot}Et_2O$ (5.0 μL, 0.40 mmol, 2.0 mM) was performed as described for **27**. DDQ (68 mg, 0.30 mmol) was added after 4 min, and the mixture stirred for 1 h. Triethylamine (ca. 0.5 mL) was added and the entire reaction mixture filtered through an alumina pad (CH_2Cl_2). Removal of the solvent afforded a black solid that was purified by filtration through a silica pad [CH_2Cl_2/hexanes (1:1)] followed by recrystallization (methanol) to afford a purple solid (29 mg, 18% from **25**): ^{1}H NMR ($CDCl_3$) δ 9.76 (s, 2 H), 8.96 (d, J = 2.1 Hz, 1 H), 8.95 (d, J = 1.5 Hz, 1 H), 8.88 (d, J = 2.1 Hz, 1 H), 8.86 (d, J = 1.5 Hz, 1 H), 8.70 (d, J = 4.5 Hz, 1 H), 8.69 (d, J = 4.5 Hz, 1 H), 8.62 (d, J = 4.5 Hz, 1 H), 8.55 (d, J = 4.5 Hz, 2 H), 8.14 (d, 8 H), 8.07 (d, J = 7.2 Hz, 4 H), 7.86 (d, J = 8.1 Hz, 4 H), 7.63 (d, 8 H), 7.556 (d, J = 7.2 Hz, 4 H) 2.70 (s, 9 H), 0.38 (s, 9 H), −2.72 (s, 1 H); λ_{abs} (toluene) nm (ϵ, mM^{-1} cm^{-1}), 432 (250, fwhm = 17 nm), 515 (18), 551 (6.5), 621 (2.5), 681 (4.6); λ_{em} (toluene) 687, 758 nm; $C_{52}H_{43}N_3SSi$ calcd mass 769.3, obsd 770.7 (LD-MS); calcd exact mass 769.2947, obsd 769.2930 (FAB-MS).

5-(4-Iodophenyl)-15-[4-(2-(trimethylsilyl)ethynyl)-phenyl]-10,20-di(*p*-tolyl)-23*H*-21-thiaporphyrin (33). A solution of compound **26** (120 mg, 0.20 mmol) in THF/methanol (3:1, 16 mL) was reduced by $NaBH_4$ (378 mg, 10.0 mmol) as described for **19-diol** to afford an oil (**26-diol**): ^{1}H NMR

($CDCl_3$) δ 8.07 (br s, 1 H), 7.59 (d, J = 7.3 Hz, 2 H), 7.28 (d, J = 7.3 Hz, 2 H), 7.22 (d, J = 8.1 Hz, 2 H), 7.16−7.12 (m, 4 H), 6.95 (d, J = 7.3 Hz, 2 H), 6.64 (m, 1 H), 6.55 (m, 1 H), 5.88 (s, 1 H), 5.77 (m, 1H), 5.73−5.70 (m, 2H), 5.42 (s, 1 H), 2.34 (s, 6 H), 2.25 (br s, 2 H); IR (cm^{-1}) 3400 (br s, OH).

Condensation of **26-diol** (ca. 0.20 mmol) and **3** (64 mg, 0.20 mmol) in acetonitrile (20 mL) in the presence of NH_4Cl (108 mg, 2.0 mmol) catalyzed $BF_3 \cdot Et_2O$ (5.0 μL, 0.40 mmol, 2.0 mM) was performed as described for **27**. DDQ (68 mg, 0.30 mmol) was added after 18 min and the mixture stirred for 1 h. Triethylamine (ca. 0.5 mL) and CH_2Cl_2 (50 mL) were added, and the entire reaction mixture was filtered through an alumina pad (CH_2Cl_2). Removal of the solvent afforded a black solid that was purified by filtration through a silica pad [CH_2Cl_2/hexanes (1:1)] followed by recrystallization (ethanol) to afford a purple solid (19 mg, 11% from **26**): ^{1}H NMR ($CDCl_3$) δ 9.77 (d, J = 5.2 Hz, 1 H), 9.68 (d, J = 5.2 Hz, 1 H), 8.96 (dd, J = 5.2, 1.5 Hz, 1H), 8.88 (dd, J = 5.2, 1.5 Hz), 8.70 (d, J = 4.4 Hz, 1 H), 8.63 (m, 2 H), 8.55 (d, J = 4.4 Hz, 1 H), 8.15−8.11 (m, 4 H), 8.16 (d, J = 8.1 Hz, 2 H), 7.96 (d, J = 8.8 Hz, 2 H), 7.85 (d, J = 8.1 Hz, 2 H), 7.62 (d, J = 7.3 Hz, 2 H), 7.53 (d, J = 8.1 Hz, 2 H), 2.70 (s, 6 H), 0.37 (s, 9 H); λ_{abs} (toluene) nm (ϵ, mM^{-1} cm^{-1}), 432 (280, fwhm = 15 nm), 515 (50), 550 (37), 621 (30), 679 (30); $C_{51}H_{40}IN_3SSi$ calcd mass 881.2, obsd 883.4 (LD-MS); calcd exact mass 881.1757, obsd 881.1793 (FAB-MS).

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Supporting Information Available: Full descriptions of the study into the condensation of a furylpyrromethane or a thienylpyrromethane with a dipyrromethanediol, and the study into the reduction of diacyldipyrromethanes to dipyrromethanediols; ^{1}H NMR spectra of compounds **3**, **6**, **13**, **14**, **16**, **17**, **21**, **22**, **24**, byproducts of **24**, byproducts of **25**, **26**, a byproduct of **26**, **19-diol**, **20-diol**, the diols of **23**−**26**, **27**, the corrole byproduct of **28**, **29**−**34**, and **34-diol**; LD-MS spectra of porphyrins **27**, **29**−**33**, and the corrole byproduct of **28**; UV−vis absorption spectra of porphyrins **27** and **29**−**33**; emission spectra of porphyrins **28**, **29**, **31**, and **32**. This material is available free of charge via the Internet at http://pubs.acs.org.

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