Rational Syntheses of Porphyrins Bearing up to Four Different Meso Substituents

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Porphyrins bearing specific patterns of substituents are crucial building blocks in biomimetic and materials chemistry. We have developed methodology that avoids statistical reactions, employs minimal chromatography, and affords up to gram quantities of regioisomerically pure porphyrins bearing predesignated patterns of up to four different meso substituents. The methodology is based upon the availability of multigram quantities of dipyrromethanes. A procedure for the diacylation of dipyrromethanes using EtMgBr and an acid chloride has been refined. A new procedure for the preparation of unsymmetrical diacyl dipyrromethanes has been developed that involves (1) monoacylation with EtMgBr and a pyridyl benzothioate followed by (2) introduction of the second acyl unit upon reaction with EtMgBr and an acid chloride. The scope of these acylation methods has been examined by preparing multigram quantities of diacyl dipyrromethanes bearing a variety of substituents. Reduction of the diacyl dipyrromethane to the corresponding dipyrromethane-dicarbinol is achieved with $NaBH_4$ in methanolic THF. Porphyrin formation involves the acid-catalyzed condensation of a dipyrromethane-dicarbinol and a dipyrromethane followed by oxidation with DDQ. Optimal conditions for the condensation were identified after examining various reaction parameters (solvent, temperature, acid, concentration, time). The conditions identified (2.5 mM reactants in acetonitrile containing 30 mM TFA at room temperature for <7 min) provided reaction without detectable scrambling (LD-MS) for aryl-substituted dipyrromethanes, and trace scrambling for alkyl-substituted dipyrromethanes. The desired porphyrins were obtained in 14−40% yield. The synthesis is compatible with diverse functionalities: amide, aldehyde, carboxylic acid, ester, nitrile, ether, bromo, iodo, ethyne, TMS-ethyne, TIPS-ethyne, perfluoroarene. In total 30 porphyrins of the types A_3B, *trans*-A_2B_2, *trans*-AB_2C, *cis*-A_2B_2, *cis*-A_2BC, and ABCD were prepared, including >1-g quantities of three porphyrins.

Introduction

Meso-substituted porphyrins bearing specific patterns of functional groups are valuable components in the synthesis of porphyrin-based biomimetic systems and molecular materials. Indeed, the level of architectural sophistication that can be achieved in such systems is closely tied to the availability of suitable porphyrin building blocks. As a result, we have devoted considerable effort to the development of methodologies for the synthesis of diverse porphyrin building blocks.[1,2]

The seven types of meso-substituted porphyrins are shown in Chart 1. Our goals in developing syntheses of these classes of porphyrins are as follows: (1) achieve broad scope, (2) employ minimal chromatography, and (3) obtain up to 1-g quantities of porphyrin. The objective of broad scope has motivated the use of mild reaction conditions, while the desire to avoid chromatography and to work on a reasonable scale has prompted the development of rational approaches that do not require the separation of a mixture of porphyrins.

The strategy for the synthesis of meso-substituted porphyrins depends on the pattern of different substituents. The routes employed generally become more elaborate as the number of different substituents increases. The best methods to prepare each of the seven classes of meso-substituted porphyrins (lacking β-substituents) are summarized as follows:

(1) A_4-porphyrins are readily synthesized under mild conditions and at high concentration in the one-flask reaction of pyrrole and the corresponding aldehyde.[3]

(2) A_3B-porphyrins have been prepared by reaction of pyrrole and two aldehydes, affording a statistical mixture of all six substituted products, which were then separated by chromatography.[2,4] The chromatographic separation was generally lengthy and afforded only small quantities (typically <100 mg) of the desired porphyrin.

(3) *trans*-A_2B_2-porphyrins have been typically prepared by reaction of an aldehyde and a dipyrromethane. In any acid-catalyzed reaction involving polypyrromethanes, acid-catalyzed fragmentation followed by an alternate recombination is an ever-present possibility. These processes ultimately scramble the meso-substituents and result in a mixture of porphyrins.[5] We readily identified conditions that afford *trans*-A_2B_2-porphyrins without

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(2) Lindsey, J. S. In *The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, CA, 2000; Vol. 1, pp 45−118.

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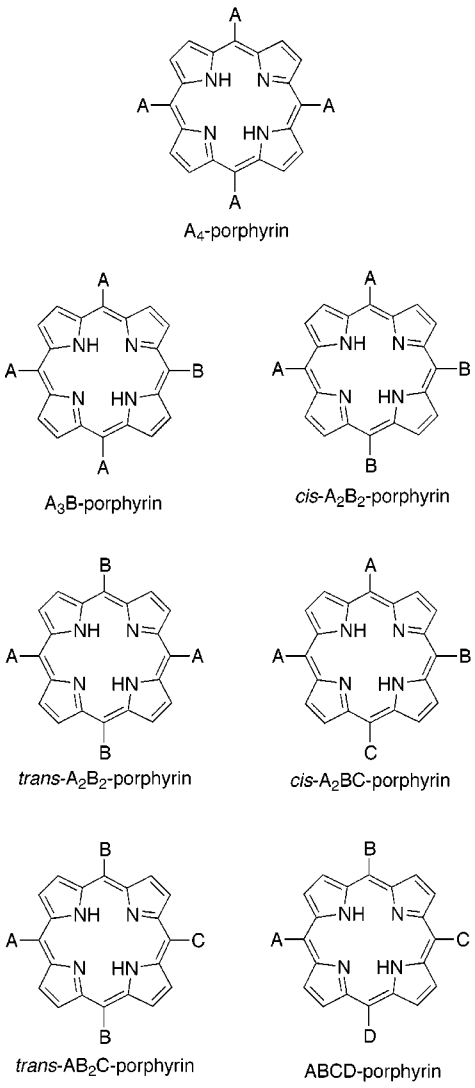
Chart 1



scrambling from the condensation of a dipyrromethane bearing a sterically hindered substituent, such as a mesityl group, at the 5-position with an aldehyde. A high level of scrambling is observed under the same conditions with a dipyrromethane bearing a sterically unhindered substituent. After an extensive study, we identified conditions that minimized scrambling for sterically unhindered dipyrromethanes, but the porphyrin yield was poor. Recently we showed that the self-condensation of a dipyrromethane-monocarbinol (derived from a monoacyl dipyrromethane) provides a general method for the rational synthesis of *trans*-A_2B_2-porphyrins in good yield without scrambling.[6] The greater reactivity of the dipyrromethane-monocarbinol compared with the dipyrromethane + aldehyde condensation enables reaction under mild acid conditions without scrambling.

(4) *cis*-A_2B_2-porphyrins have been prepared rationally in milligram quantities by reaction of a tripyrrane with a pyrrole-dicarbinol.[7] Statistical syntheses requiring extensive chromatographic separation have involved mixed condensations of two aldehydes and pyrrole,[2,4] or a linked dialdehyde, an aldehyde, and pyrrole.[8]

(5) *trans*-AB_2C-porphyrins have been prepared by statistical reaction of a dipyrromethane and two aldehydes, or of two dipyrromethanes and one aldehyde. In each case the resulting three porphyrins (assuming no acidolytic scrambling) are then separated chromatographically. In pursuit of rational routes to *trans*-AB_2C-porphyrins, we have previously reported methods for diacylation of dipyrromethanes and reduction of the resulting diacyl dipyrromethanes to the corresponding dipyrromethane-dicarbinol.[9] However, the lack of suitable conditions for performing the dipyrromethane-dicarbinol + dipyrromethane reaction stymied the implementation of this rational route (as also occurred with ABCD-porphyrins, vide infra). An alternative route to this class of porphyrins involves treating a 5,15-disubstituted porphyrin with an organolithium reagent, quenching with water, and then treating with an alkyl iodide followed by oxidation.[10]

(6) *cis*-A_2BC-porphyrins have not been prepared via rational routes.

(7) ABCD-porphyrins have been prepared in small amounts by a rational approach involving sequential introduction of acyl groups (or their equiv) onto the dipyrromethane nucleus, followed by reduction to the dipyrromethane-dicarbinol, and then condensation of the dipyrromethane-dicarbinol with a dipyrromethane.[9] The methods for monoacylation or diacylation were only partially selective, in each case affording a mixture of unreacted, monoacylated, and diacylated species which were separated by chromatography. The condensation conditions for the dipyrromethane-dicarbinol + dipyrromethane reaction afforded regioisomerically pure porphyrin in low yield (<10%). The limitations in dipyrromethane chemistry and the low yield of porphyrin formation limited the scale to milligram quantities of porphyrins. All acid catalysis conditions examined that gave higher yields of porphyrins also resulted in scrambling. Scrambling must be avoided altogether in the synthesis of porphyrins bearing three or four different substituents due to the large number of possible products. This route to ABCD-porphyrins in principle encompasses the syntheses of porphyrins bearing two or three different substituents; however, the low yield, small scale, and prohibitive levels of chromatography have effectively limited the applications of this approach. Other routes to ABCD-porphyrins have also been plagued by one or more of these problems.[11]

In this paper, we describe methods for the synthesis of the five types of meso-substituted porphyrins (A_3B, *trans*-AB_2C, *cis*-A_2B_2, *cis*-A_2BC, and ABCD) that previously have been inaccessible by rational routes on a reasonable scale (up to 1 g) with minimal chromatography. Dipyrromethanes provide the starting point for each porphyrin target. We describe refined conditions for the diacylation of dipyrromethanes, essential precursors to A_3B- and *trans*-AB_2C-porphyrins. Then we build on our recent method for selective monoacylation of a dipyrromethane to achieve sequential acylation, thereby providing the unsymmetrical diacyl dipyrromethane pre-

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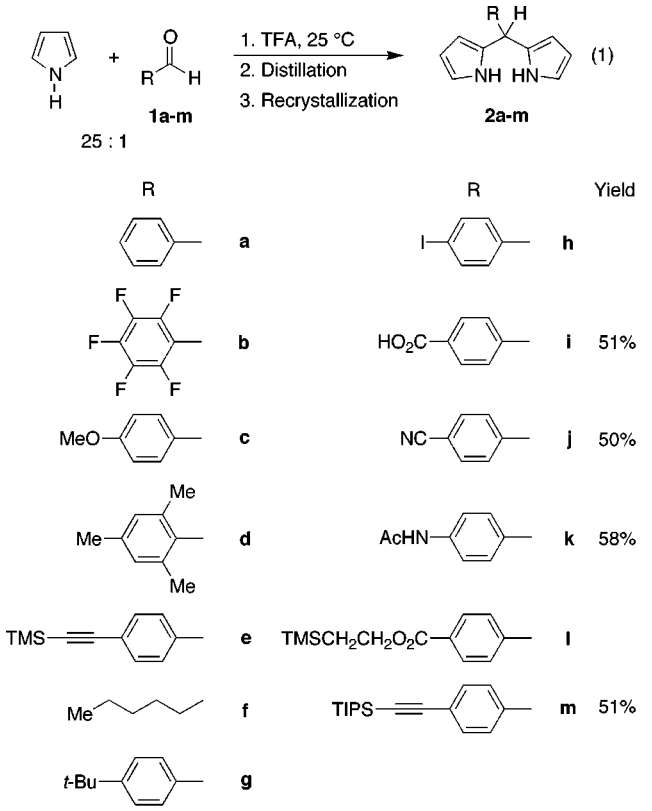
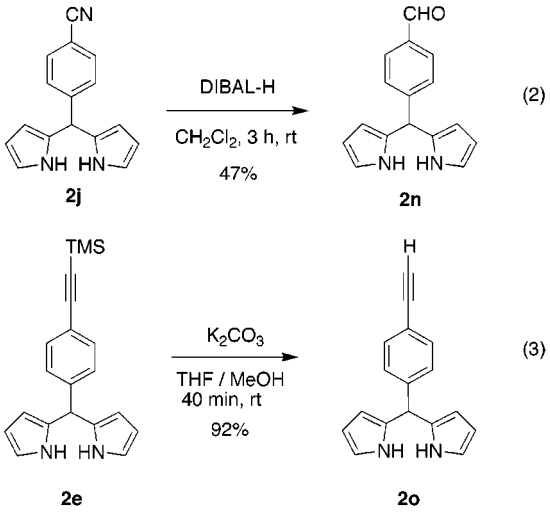
cursors to *cis*-A_2B_2-, *cis*-A_2BC-, and ABCD-porphyrins. Conditions also have been refined for the reduction of diacyl dipyrromethanes to the corresponding dipyrromethane-dicarbinols. A lengthy study has been performed of the acid-catalyzed condensation of a dipyrromethane-dicarbinol and a dipyrromethane in order to achieve the highest possible yield without detectable scrambling.[12] These routes have proved successful in the majority of cases examined and broaden the scope of accessible porphyrin model systems.

Results and Discussion

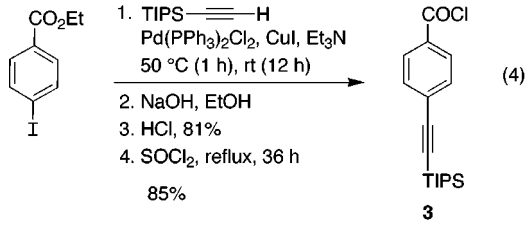
I. Methodology for Preparing Porphyrin Precursors

Synthesis of Dipyrromethanes. The dipyrromethanes were prepared by a one-flask reaction of an aldehyde with pyrrole.[13,14] Aldehydes were obtained commercially (**1a**−**d**, **1f**−**k**), prepared as described in the literature (**1l**),[15] or obtained via the Pd-mediated coupling[16] of 4-bromobenzaldehyde with trimethylsilylacetylene and triisopropylsilylacetylene, respectively (**1e** and **1m**). According to a refined procedure,[13] each aldehyde was dissolved in excess pyrrole at room temperature, treated with TFA for a few min, and the resulting dipyrromethane was purified either by bulb-to-bulb distillation followed by recrystallization or filtration through a pad of silica followed by recrystallization (eq 1). Distillation (or filtration through silica) removes most higher molecular weight oligomers and recrystallization removes N-confused dipyrromethane. In this manner, dipyrromethanes **2a**−**d**,[13] **2e**,[17] **2f**,[14] **2g**,[6] **2h**,[13] and **2l**[6] prepared previously and new dipyrromethanes **2i**−**k,m** were obtained on a multigram scale in analytically pure form. Reduction of **2j** with DIBAL-H afforded dipyrromethane **2n** in 92% yield (eq 2). Treatment of **2e** with K_2CO_3 in THF/methanol afforded dipyrromethane **2o** in 92% yield (eq 3). The availability of pure dipyrromethanes in gram quantities forms the foundation of our rational routes to meso-substituted porphyrins.





Diacylation of Dipyrromethanes. Dipyrromethanes with identical acyl groups at the 1- and 9-positions are key precursors to A_3B-, *trans*-A_2B_2-, and *trans*-AB_2C-porphyrins. An early study showed that treatment of a dipyrromethane with excess EtMgBr in THF followed by excess acid chloride produced both the diacylated dipyrromethane and monoacylated dipyrromethane.[9,17] The following section summarizes a lengthy series of studies that attempted to produce the diacyl dipyrromethane as the sole product. The best conditions identified were then applied to a variety of dipyrromethanes and acid chlorides. The acid chlorides employed were commercially available, except for acid chloride **3**. The Pd-catalyzed coupling of ethyl 4-iodobenzoate with triisopropylsilylacetylene followed by saponification according to a procedure[18] for the preparation of 4-ethynylbenzoic acid afforded the required carboxylic acid. Subsequent reaction with thionyl chloride gave acid chloride **3** (eq 4).



(i) Optimization of Reaction Conditions. For the optimization study we chose the reaction of 5-phenyl-

(12) The limit of detection of scrambled porphyrins by laser-desorption mass spectrometry (LD-MS) is approximately 1 part in 100. Thus, for a porphyrin yield of 25%, any putative single scrambled (nonisomeric) porphyrin would be present in no greater than 0.25% yield. Note that the MS method cannot exclude scrambling leading exclusively to isomeric porphyrins (e.g., trans to cis). However, rearrangement processes leading to isomers would be expected to form a distribution of porphyrin products, including those of other masses. See ref 6.

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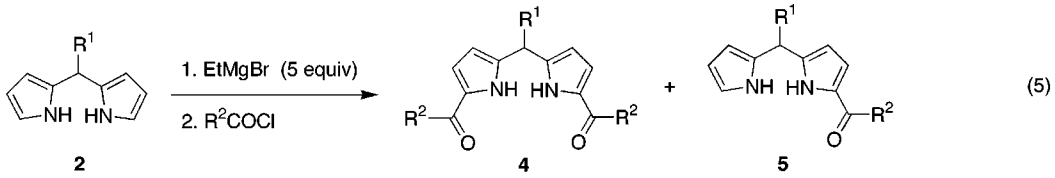
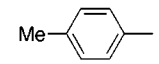
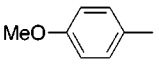
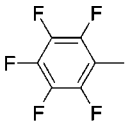
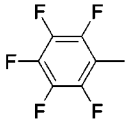
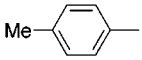
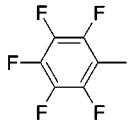
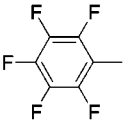
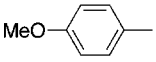
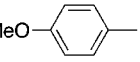
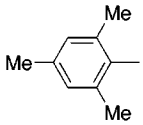
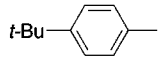
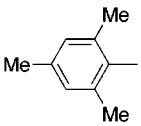
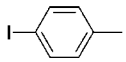
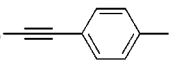
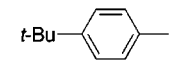
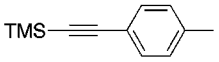
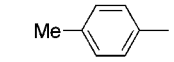
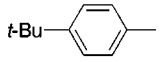
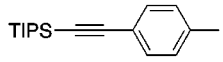
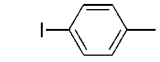
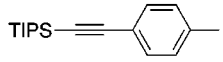
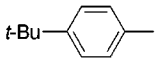
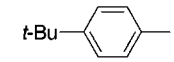
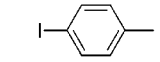
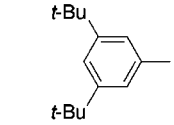
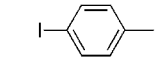
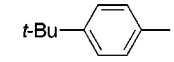
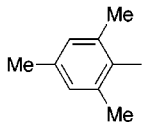
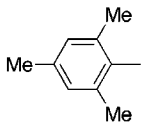


R^1	R^2	Diacyl Product	Yield
		**4a**	70%
		**4b**	66%
		**4c**	29%
		**4d**	51%
		**4e**	25%
		**4f**	69%
		**4g**	83%
		**4h**	59%
		**4i**	65%
		**4j**	40%
n-Pentyl	*n*-Pentyl	**4k**	60%
		**4l**	38%
		**4m**	39%
		**4n**	58%
		**4o**	24%
		**4p**	44%
		**4q**	19%

dipyrromethane (**2a**) with EtMgBr and *p*-toluoyl chloride as our model system. This reaction affords diacylated dipyrromethane **4a** and monoacylated dipyrromethane **5a** (R^1 = phenyl, R^2 = *p*-tolyl) as shown in eq 5. To improve the yield of the diacylated compound we altered the reaction solvent, solvent for EtMgBr, temperature, concentration, and ratio of dipyrromethane:EtMgBr:acid chloride. The chelating agent TMEDA was also added to some reactions. The ratio of **4a**:**5a** in the crude reaction product was determined with ^{1}H NMR spectroscopy by integration of the peaks due to the pyrrolic NH (monoacyl at δ 8.25, 9.65 ppm; diacyl at δ 11.60 ppm) and/or the meso CH (monoacyl at δ 5.60 ppm; diacyl at δ 5.72 ppm) of the acyl dipyrromethanes. A detailed description of these studies is included in the Supporting Information. Our major findings are as follows: (1) The best results were obtained with 0.05 M dipyrromethane and a 1:5:2.2 molar ratio of dipyrromethane:EtMgBr:acid chloride in toluene (rather than THF) at room temperature for 10 min. These conditions afford the diacylated and monoacylated dipyrromethanes (**4a**, **5a**) in a typical ratio of 5:1. (2) A decrease in the amount of EtMgBr (2 mol equiv) caused a substantial decline in diacylated product. (3) A larger excess of *p*-toluoyl chloride did not further increase the amount of diacylated product. (4) Reaction in toluene was superior to reaction in THF, with no greater than a 2:1 ratio of diacylated:monoacylated species obtained in THF. (5) The reaction could be performed at 6-fold higher concentration (0.3 M dipyrromethane) while maintaining the same 1:5:2.2 ratio of dipyrromethane:EtMgBr:RCOCl without significant change in the diacylated:monoacylated ratio (~4:1). Although these refined conditions do not afford the diacylated product exclusively, the higher ratio of diacylated:monoacylated species facilitates purification compared to previous methods. Note that pure diacyl dipyrromethanes are essential for the success of these rational routes.[19]

(ii) Scope of the Refined Diacylation Procedure. The refined procedure was applied to a variety of dipyr-

(17) Cho, W.-S.; Kim, H.-J.; Littler, B. J.; Miller, M. A.; Lee, C.-H.; Lindsey, J. S. *J. Org. Chem.* **1999**, *64*, 7890−7901.

(18) Yashima, E.; Matsushima, T.; Okamoto, Y. *J. Am. Chem. Soc.* **1997**, *119*, 6345−6359.

(19) A monoacyl dipyrromethane yields a dipyrromethane-monocarbinol on reduction that readily undergoes self-condensation yielding the corresponding *trans*-A_2B_2-porphyrin.[6] Thus, the presence of a monoacyl dipyrromethane impurity in a diacyl dipyrromethane (derived from an intermediate in the diacylation of a dipyrromethane, or the starting material in the acylation of a monoacyl dipyrromethane) will likely lead to an unwanted porphyrin contaminant. The success of the rational syntheses relies on the use of pure dipyrromethanes and diacyl dipyrromethanes.

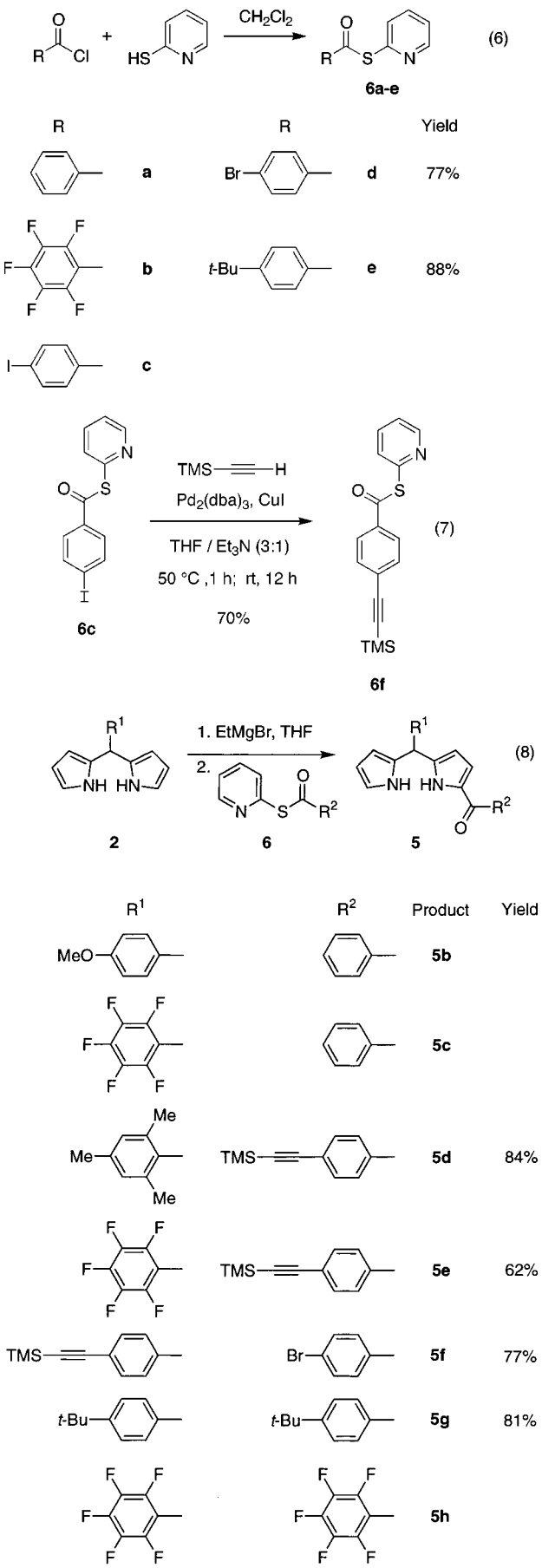
Table 1. Optimization of Reaction Conditions for Acylation of Monoacyl Dipyrromethanes[a]

entry	substrate[b] (mmol)	solvent (2 mL)	EtMgBr[c] (mmol)	*p*-toluoyl chloride (mmol)	product: substrate (**7a**:**5b**)[d]
1	0.50	THF	1.25	0.75	1.0:1.0
2	0.50	toluene	1.25	0.75	1.5:1.0
3	0.50	toluene	1.50	1.00	1.8:1.0
4	0.50	toluene	2.00	1.50	2.3:1.0
5	0.50	toluene	2.50	2.00	19:1.0
6	0.50	toluene	3.00	1.50	>20:1[e]

[a] All reactions were performed at room temperature. [b] 1-Benzoyl-5-(4-methoxyphenyl)dipyrromethane (**5b**). [c] EtMgBr was used as a 1.0 M solution in THF. [d] The ratio was determined by ^{1}H NMR spectroscopic analysis of crude reaction samples. [e] No unreacted substrate could be detected by ^{1}H NMR spectroscopy.

romethanes (1−15 mmol) and acid chlorides (eq 5). In each case the crude reaction product was examined by ^{1}H NMR spectroscopy. The ratio of diacylated and monoacylated products generally ranged from 1:1 to 5:1 (see Experimental Section). In most cases purification was achieved by column chromatography followed by precipitation from boiling aqueous 2-propanol. In some cases further purification was required, which was achieved by a second crystallization from CH_2Cl_2−hexanes or methanol. The reaction readily afforded reasonable yields of diacyl dipyrromethanes in most cases, with the following noticeable exceptions: (1) Reaction with pentafluorobenzoyl chloride gave low yields (**4c**, **4e**). Our attempts to improve the yield of **4e** by varying the amounts of EtMgBr, lowering the temperature, or using sequential addition of EtMgBr and the acid chloride were unsuccessful. (2) Reactions involving 5-(4-iodophenyl)-dipyrromethane required two chromatographic columns followed by recrystallization to obtain pure samples of compounds **4m**, **4o**, and **4p**. (3) The diacylation with 3,5-di-*tert*-butylbenzoyl chloride afforded a rather low yield of the desired compound **4o**. (4) A_3B-porphyrins in which A is mesityl and B incorporates a synthetic handle have proved to be very useful building blocks in materials chemistry.[15,20] Diacylation of 5-mesityldipyrromethane with mesitoyl chloride furnished the corresponding diacyl dipyrromethane **4q** in only 19% yield.

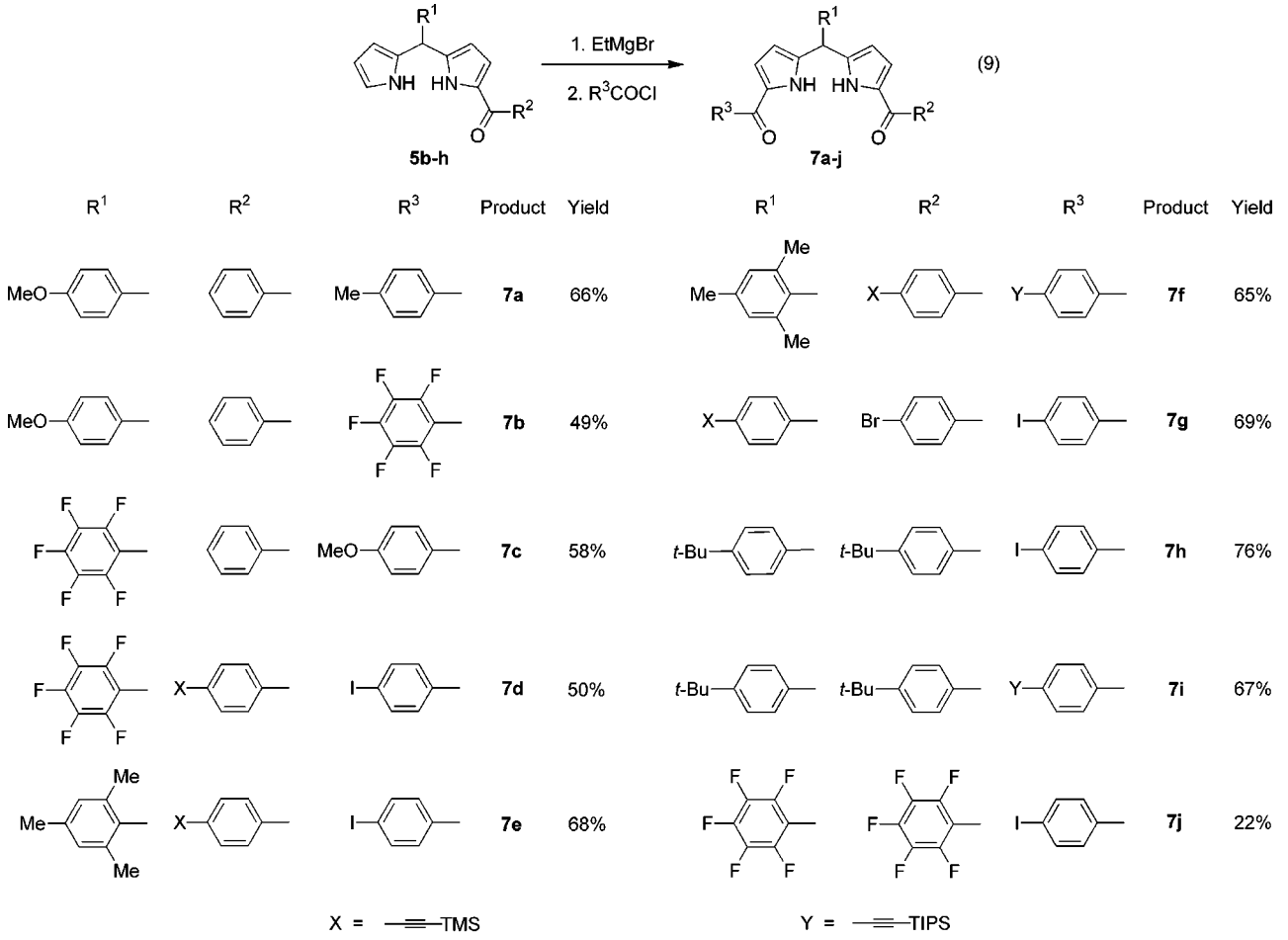
Sequential Acylation of Dipyrromethanes. Dipyrromethanes bearing two different acyl groups at the 1- and 9-positions are required precursors to *cis*-A_2B_2-, *cis*-A_2BC- and ABCD-porphyrins.[9,11] We recently reported that treatment of a dipyrromethane with EtMgBr followed by an *S*-2-pyridyl-substituted benzothioate (**6**) is an efficient procedure for the preparation of 1-acyl dipyrromethanes (**5**) in multigram quantities.[6,21] Our previous approach toward unsymmetrical diacyl dipyrromethanes involved alkylation of a 1-acyldipyrromethane at the 9-position with a benzoxathiolium tetrafluoroborate, but this route entailed preparation of the benzoxathiolium derivative and then oxidative hydrolysis of the 1-acyl-9-alkyldipyrromethane in order to unveil the 9-acyl moiety.[9] For a more simple procedure, we envisioned that further treatment of the 1-acyldipyrromethane with EtMgBr followed by an acid chloride should enable the introduction of a second acyl group at the 9-position.



(i) Preparation of Monoacyl Dipyrromethanes. *S*-2-Pyridyl-substituted benzothioates **6a**−**c** were pre-

(20) Lammi, R. K.; Ambroise, A.; Balasubramanian, T.; Wagner, R. W.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Am. Chem. Soc.* **2000**, *122*, 7579−7591.

(21) Strachan, J. P.; O'Shea, D. F.; Balasubramanian, T.; Lindsey, J. S. *J. Org. Chem.* **2000**, *65*, 3160−3172.



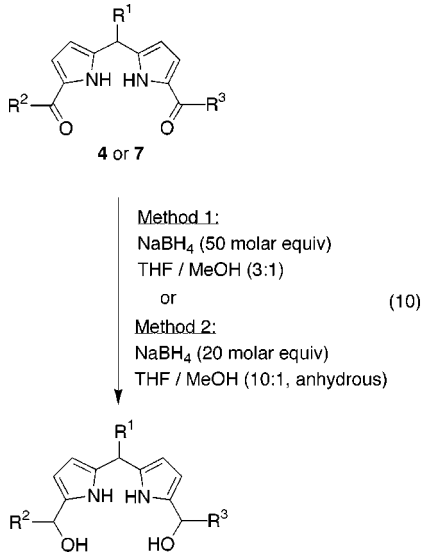
pared as reported from the corresponding acid chlorides and 2-mercaptopyridine (eq 6).[6] Thioesters **6d** and **6e** were prepared in the same manner in 77% and 88% yields, respectively. Thioester **6f** was synthesized by coupling thioester **6c** with trimethylsilylacetylene using $Pd_2(dba)_3$ and TEA (instead of $Pd(PPh_3)_2Cl_2$ and *N*,*N*-diisopropylethylamine) (eq 7). These conditions gave an improved yield and a shorter reaction time.[6] Monoacyl dipyrromethanes **5b**,[6] **5c**,[6] **5h**,[21] and **5d**−**g** were synthesized from the corresponding dipyrromethanes and thioesters (eq 8).

(ii) Model Acylation Study. We chose the reaction of 1-benzoyl-5-(4-methoxyphenyl)dipyrromethane[6] (**5b**) and *p*-toluoyl chloride as a model system for optimization of conditions. Thus, a solution of **5b** (0.50 mmol) in THF (2 mL, 0.25 M) at room temperature was treated with EtMgBr (1.25 mmol) followed by *p*-toluoyl chloride (0.75 mmol) (eq 9). TLC and ^{1}H NMR analysis indicated the presence of equal amounts of the desired diacyl dipyrromethane **7a** and the starting monoacyl dipyrromethane (entry 1, Table 1). The use of toluene rather than THF as solvent improved conversion to the diacyl dipyrromethane (entry 2). In toluene, as the amount of EtMgBr and acid chloride increased, so did the consumption of starting material (entries 3−6). Complete consumption of the monoacyl dipyrromethane was achieved upon treatment of **5b** with 6 equiv of EtMgBr and 3 equiv of *p*-toluoyl chloride (entry 6). The desired diacyl dipyrromethane **7a** was isolated in 66% yield after column chromatography. This procedure where the monoacyl dipyrromethane is treated all-at-once with 6 equiv of EtMgBr followed by 3 equiv of acid chloride is referred to as procedure A.

(iii) Scope of Acylation of Monoacyl Dipyrromethanes. The monoacyl dipyrromethanes **5b**−**e** were converted to diacyl dipyrromethanes **7a**−**e** using procedure A (eq 9). Treatment of monoacyl dipyrromethane **5b** with EtMgBr followed by pentafluorobenzoyl chloride furnished a 1:10 mixture of **5b** and **7b**. Column chromatography afforded **7b** in 49% yield. Similarly, **5c** was treated with *p*-anisoyl chloride to obtain **7c** in 58% yield. In contrast, treatment of monoacyl dipyrromethanes **5d** or **5e** with EtMgBr followed by 4-iodobenzoyl chloride produced a complex mixture. The desired products **7e** and **7d** were isolated in about 50% yield from the crude mixture via column chromatography, but the difficulty of these separations prompted us to develop a modified procedure.

To minimize the amount of free EtMgBr present at any time, we added small portions of the EtMgBr (2, 2, 1 equiv) and acid chloride (1, 1, 0.5 equiv) sequentially and repeatedly at 10 min intervals (procedure B) rather than the entire amounts all-at-once (procedure A). Analytically pure diacyl dipyrromethanes **7e**−**i** were prepared via procedure B in good yields and substantial quantities (2−5 g) in a straightforward manner. In the preparation of diacyl dipyrromethane **7j**, the ^{1}H NMR spectrum of the product initially isolated indicated the presence of up to 20% of an unidentified product. Recrystallization from methanol afforded pure **7j** in 22% yield.

Reduction of Diacyl Dipyrromethanes. The reduction of diacyl dipyrromethanes can be achieved with

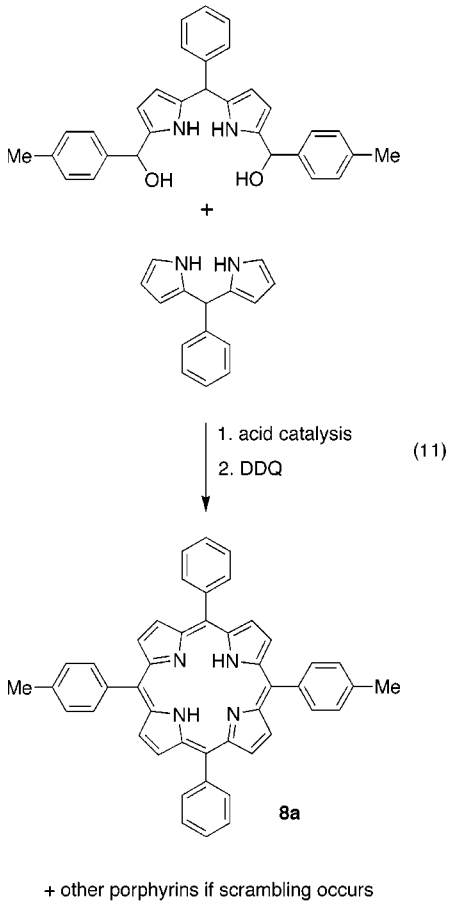


excess $NaBH_4$ (50 molar equiv) in THF/methanol (3:1) as shown in eq 10.[9,17] This method (reduction method 1) worked well in all cases examined with the exception of **7d**, where partial cleavage of the trimethylsilyl group occurred. (It is noteworthy that the TMS-ethynylphenyl group at the 5-position of diacyl dipyrromethanes **4i** and **4j** was compatible with such reduction conditions.) Deprotection of a TMS-ethynyl group has been reported using $NaBH(OMe)_3$,[22] a likely species in the reaction mixture. As a model study, we examined a variety of conditions for cleanly reducing the TMS-ethyne substituted monoacyl dipyrromethane **5d** (excess $NaBH_4$ in diglyme, 2-propanol/THF or 2-propanol instead of THF/methanol) but without success. The reduction of **5d** was finally accomplished with the TMS-ethyne group intact with a 10:1 mixture of anhydrous THF/methanol and only 10 molar equiv of $NaBH_4$. Application of this procedure (reduction method 2) to diacyl dipyrromethane **7f** (1 mmol scale, 0.75 g) using 20 mmol of $NaBH_4$ afforded the corresponding dicarbinol with the TMS-ethyne group intact. In summary, method 1 uses a large amount of $NaBH_4$ (50 molar equiv) in reagent grade THF/methanol (3:1). Method 2 uses a smaller excess of $NaBH_4$ (20 molar equiv) in anhydrous THF/methanol (10:1). The latter method is attractive because (1) less $NaBH_4$ is used and (2) TMS-ethyne groups remain intact. Method 2 was developed during the course of this work and has been used exclusively for all subsequent reductions.

Attempted reduction of 1,9-dimesitoyl-5-mesityldipyrromethane (**4q**) to the corresponding dicarbinol was unsuccessful with either method or with a variety of other hydride reducing agents ($NaBH_4-CeCl_3$, BH_3-THF, $LiAlH_4$, $NaAlH_4$, $LiBH_4$). Thus at present, mesityl groups cannot be introduced into the porphyrin nucleus via acylation of a dipyrromethane.

II. Nonscrambling Conditions for the Condensation of a Dipyrromethane-Dicarbinol and a Dipyrromethane

The development of nonscrambling conditions is essential for the rational synthesis of porphyrins in condensations employing dipyrromethanes. We readily identified conditions for the nonscrambling condensation of a sterically hindered dipyrromethane and an aldehyde,



but identification of nonscrambling conditions for the condensation of a sterically unhindered dipyrromethane and an aldehyde proved more difficult.[5] We eventually identified conditions that gave little or no scrambling for the latter reaction, albeit in less than 10% yield: condensation at 10 mM in acetonitrile at 0 °C with $BF_3 \cdot Et_2O$ in the presence of NH_4Cl, followed by DDQ oxidation.[5]

We applied these conditions to the reaction of a dipyrromethane-dicarbinol and a dipyrromethane (10 mM each), and also to the reaction of heteroatom-substituted substrates (a furylpyrromethane-dicarbinol or thienylpyrromethane-dicarbinol) leading to the corresponding heteroatom-substituted (N_3O, N_3S) porphyrins.[17] Compared to the dipyrromethane + aldehyde condensation, the dipyrromethane-dicarbinol + dipyrromethane condensation proceeded much more rapidly, gave higher yields and produced no detectable scrambled byproducts.[12] However, the elimination of scrambling was critically dependent on using a minimum amount of acid. With 1 mM $BF_3 \cdot Et_2O$, capricious variations in the reaction rate and isolated yield of porphyrin were observed. Increasing the acid concentration to 2 mM overcame some of the variability, but increasing the $BF_3 \cdot Et_2O$ concentration to 5 mM resulted in the production of scrambled byproducts.

For the rational syntheses described herein, we undertook a detailed study aimed at refining the low-scrambling reaction conditions for the dipyrromethane-dicarbinol + dipyrromethane condensation. This study had two principal aims: (1) maximize the yield with no scrambling; (2) find conditions that produce consistent kinetics and yields. We employed a model system employing dipyrromethane **2a** and the dipyrromethane-dicarbinol derived from **4a** to obtain *trans*-A_2B_2-porphyrin

(22) Myers, A. G.; Harrington, P. M.; Kuo, E. Y. *J. Am. Chem. Soc.* **1991**, *113*, 694−695.

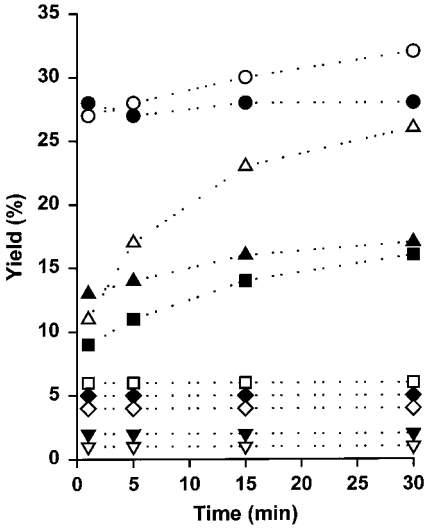


Figure 1. Effect of the reaction solvent on the porphyrin yield. Reactions were performed with 2.5 mM dipyrromethane-dicarbinol (derived from **4a**) and 2.5 mM dipyrromethane (**2a**) at room-temperature catalyzed by 20 mM TFA. The yield of porphyrin **8a** was determined spectroscopically upon oxidation of reaction aliquots with DDQ. See text for results of the scrambling assay. Legend: ○ nitromethane; ● acetonitrile; △ CH_2Cl_2; ▲ $CHCl_3$; ■ toluene; □ DMF; ◆ ethyl acetate; ◇ DMSO; ▼ diethyl ether; ▽ THF.

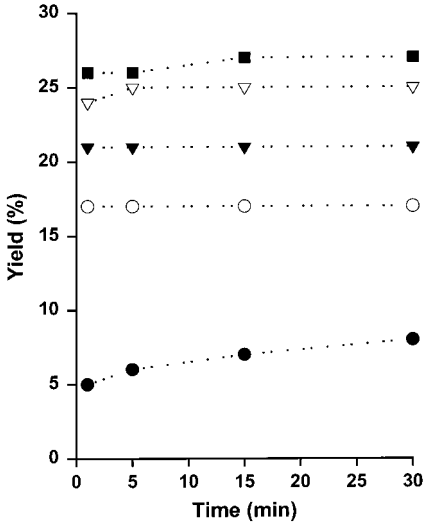


Figure 2. Effect of the TFA concentration on the porphyrin yield. Reactions were performed with 2.5 mM dipyrromethane-dicarbinol (derived from **4a**) and 2.5 mM dipyrromethane (**2a**) in acetonitrile at room temperature. The yield of porphyrin **8a** was determined spectroscopically upon oxidation of reaction aliquots with DDQ. No scrambling was detected at any concentration. Legend: ● 1.00 mM TFA; ○ 3.16 mM TFA; ▼ 10.0 mM TFA; ▽ 31.6 mM TFA; ■ 100 mM TFA.

8a (eq 11). In this system, the combination of phenyl and *p*-tolyl substituents allows resolution of scrambled porphyrins in the LD-MS spectrum while minimizing steric and electronic differences.

Acid Catalyst. Both $BF_3{\cdot}Et_2O/NH_4Cl$ and TFA afforded *trans*-porphyrins with minimal scrambling from the dipyrromethane + aldehyde condensation. We decided to focus on TFA for two reasons: (1) $BF_3{\cdot}Et_2O/NH_4Cl$ afforded capricious results in the dipyrromethane-dicarbinol + dipyrromethane condensations in the heteroatom porphyrin study,[17] and (2) a detailed study into the pyrrole + aldehyde condensation showed that reactions performed with TFA produced more consistent reaction kinetics and porphyrin yields compared to those performed using the $BF_3{\cdot}Et_2O/NH_4Cl$ catalyst system.[5] Because the pyrrole + aldehyde and dipyrromethane + aldehyde condensations catalyzed by TFA in previous studies showed little or no salt effect, all reactions were performed with no added salts. (See the Supporting Information of ref 5 for a thorough description of studies comparing TFA and $BF_3{\cdot}Et_2O$ in the dipyrromethane + aldehyde reaction.)

Solvent. We examined the dipyrromethane-dicarbinol + dipyrromethane condensation in 10 different solvents. The reaction conditions chosen were based on the optimal conditions for the pyrrole + aldehyde condensation under TFA catalysis; 10 mM pyrrole, 10 mM aldehyde, and 20 mM TFA. Because the dipyrromethane building blocks each contain two pyrrole units, 2.5 mM dipyrromethane-dicarbinol and 2.5 mM dipyrromethane were used to maintain an overall "pyrrole" and "aldehyde" concentration of 10 mM. The solvents examined fell into three major categories (Figure 1). (1) DMF, ethyl acetate, DMSO, diethyl ether, and THF gave a reaction that was complete within 1 min and afforded the porphyrin in poor yield (<6%) but with no scrambling at all times. (2) CH_2Cl_2, $CHCl_3$ (containing 0.75% ethanol), and toluene gave an initial fast reaction within 1 min that afforded ~10% porphyrin yield with no scrambling. From 1 to 30 min the porphyrin yield continued to increase, but the improvement in yield was outweighed by the production of scrambled porphyrins. After 30 min in CH_2Cl_2 and toluene, severe scrambling had occurred, but in $CHCl_3$ only a small amount of the scrambled products was detected. (3) CH_3CN and CH_3NO_2 gave the highest yields. Reaction in acetonitrile was complete within 1 min and showed no increase in yield up to 30 min, and no scrambling was detected by LD-MS at all timepoints. In contrast, reaction in nitromethane produced a small increase in yield from 1 to 30 min, but this was accompanied by the production of small amounts of scrambled byproducts. Therefore, acetonitrile was the solvent used in the subsequent studies.

Acid Concentration. The effect of the concentration of TFA (1.00 mM to 100 mM) was examined on the yield and extent of scrambling in acetonitrile at room temperature. Figure 2 shows that an increase in the amount of acid led to an increase in the porphyrin yield. No scrambling was detected by LD-MS at all timepoints, even at 100 mM TFA.

Concentration of Dipyrromethane-Dicarbinol and Dipyrromethane. Large volumes of solvent are required for preparative-scale syntheses if the reaction is performed with the dipyrromethane-dicarbinol and dipyrromethane at 2.5 mM. Therefore, we studied whether the reaction could be performed at a 4-fold higher concentration. The reactions were performed in acetonitrile at room temperature and over a TFA concentration range from 10.0 mM to 316 mM. As shown in Figure 3, reaction at 10 mM dipyrromethane-dicarbinol and dipyrromethane resulted in a lower yield of porphyrin compared with reaction at 2.5 mM. The higher acid concentration employed at higher reactant concentration also resulted in scrambling at long reaction times. No scrambling was detected at 1 min over the range of TFA concentration studied. At 30 min the reactions catalyzed by 10.0 mM and 31.6 mM showed no scrambling, but the reactions

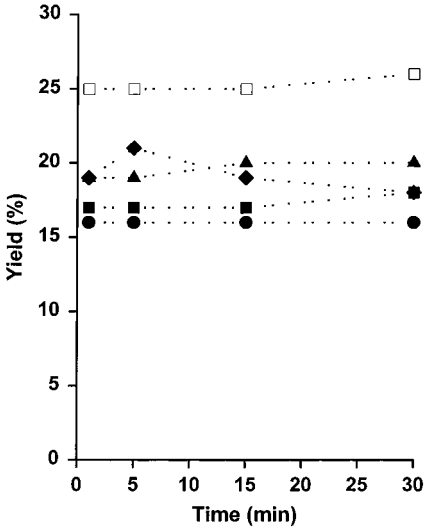


Figure 3. Effect of a higher concentration of reactants on the porphyrin yield. Reactions were performed with dipyrromethane-dicarbinol (derived from **4a**) and dipyrromethane (**2a**) (10 mM each) in acetonitrile at room temperature. The yield of porphyrin **8a** was determined spectroscopically upon oxidation of reaction aliquots with DDQ. See text for results of the scrambling assay. Legend: ● 10.0 mM TFA; ■ 31.6 mM TFA; ▲ 100 mM TFA; ◆ 316 mM TFA. (□ Calibration reaction performed with 2.5 mM dipyrromethane-dicarbinol, 2.5 mM dipyrromethane, and 31.6 mM TFA.)

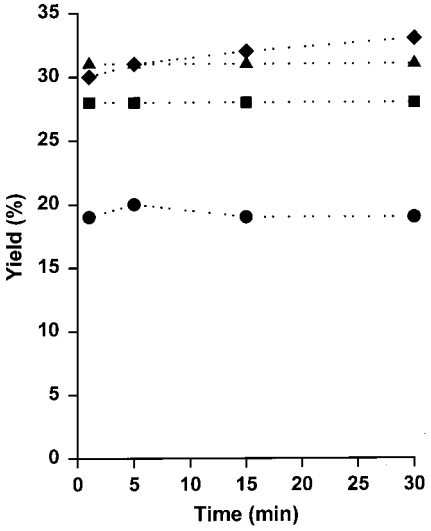


Figure 4. Effect of temperature on the porphyrin yield. Reactions were performed with 2.5 mM dipyrromethane-dicarbinol (derived from **4a**) and 2.5 mM dipyrromethane (**2a**) in acetonitrile catalyzed by 31.6 mM TFA. The yield of porphyrin **8a** was determined spectroscopically upon oxidation of reaction aliquots with DDQ. Legend: ● −20 °C to −30 °C; ■ 0 °C; ▲ room temperature; ◆ 40 °C.

catalyzed by 100 mM and 316 mM TFA produced scrambled products that were detected by LD-MS. The extent of scrambling was related to the acid concentration because trace scrambling was observed with 100 mM TFA, but severe scrambling was seen with 316 mM TFA.

Reaction Temperature. Finally, we studied the effect of different reaction temperatures on the porphyrin yield for the condensation of 2.5 mM dipyrromethane-dicarbinol and dipyrromethane in acetonitrile catalyzed by 31.6 mM TFA. As shown in Figure 4, the porphyrin yield decreased at lower reaction temperatures, but the decline in yield was only pronounced when the solvent was cooled close to its freezing point.

Optimal Reaction Conditions. From the data presented above we conclude that the optimal condensation conditions are 2.5 mM dipyrromethane-dicarbinol and 2.5 mM dipyrromethane with 31.6 mM TFA in acetonitrile at room temperature. The reaction is complete within 1 min and proceeds with no detectable scrambling. For convenience we have employed 30 mM TFA for all synthetic applications. The significant advantages of the optimized conditions compared to those previously employed in the heteroatom porphyrin study (10 mM dipyrromethane-dicarbinol and 10 mM dipyrromethane catalyzed by 1.0 mM $BF_3{\cdot}Et_2O$ in acetonitrile at 0 °C in the presence of 100 mM NH_4Cl)[17] are as follows: (1) higher yield (30% vs 15%); (2) the reaction rate, porphyrin yield, and extent of scrambling are less sensitive to the exact amount of acid catalyst added; (3) reaction conditions are more simple (no added salt, no cooling in an ice-bath). These refined conditions have already proved effective in several applications.[21,23,24]

III. Synthesis of Porphyrins

To prepare the target porphyrins, the desired diacyl dipyrromethane was reduced to the corresponding dicarbinol (using method 1 or 2; see Experimental Section), and then immediately condensed with the desired dipyrromethane under the optimal conditions delineated above (2.5 mM of each dipyrromethane species in acetonitrile containing 30 mM TFA at room temperature, followed within a few minutes by oxidation with DDQ). A sample from each porphyrin-forming reaction was analyzed by LD-MS to examine for the presence of scrambled porphyrin products. The porphyrins were isolated by a simple process involving the following steps: (1) filtration through a pad of alumina to remove quinone species, (2) removal of solvent under reduced pressure, (3) one silica gel chromatography procedure, and (4) recrystallization, trituration of a suspension in hot alcohol, or sonication of a suspension in alcohol.

***Trans*-A_2B_2-porphyrins.** The best syntheses of *trans*-A_2B_2-porphyrins employ condensation of a dipyrromethane + aldehyde[5] or self-condensation of a dipyrromethane-monocarbinol.[6] While the synthesis of a *trans*-A_2B_2-porphyrin by the condensation of an A-dipyrromethane and a BAB-dipyrromethane-dicarbinol[25] has little preparative merit, this route is useful for studies of scrambling and examination of substituent effects. Thus, porphyrin **8a** (eq 11) was prepared for scrambling studies, and porphyrin **8b** (Scheme 1) was prepared in order to examine the effect of the strongly electron-withdrawing pentafluorophenyl group (vide infra).

A_3B-porphyrins. A_3B-porphyrins can be prepared in two different ways, involving either an A_3-dipyrromethane-dicarbinol + B-dipyrromethane, or an ABA-dipyrromethane-dicarbinol + A-dipyrromethane (Scheme 1). The former route was followed for porphyrins **9a**−**i**, while the latter was employed for porphyrin **9j**. The efficacy of the reaction was slightly different with aryl versus alkyl substituted dipyrromethanes.

(23) Miller, M. A.; Lammi, R. K.; Prathapan, S.; Holten, D.; Lindsey, J. S. *J. Org. Chem.* **2000**, *65*, 6634−6649.

(24) (a) 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. (b) Li, J.; Gryko, D.; Dabke, R. B.; Diers, J. R.; Bocian, D. F.; Kuhr, W. G.; Lindsey, J. S. *J. Org. Chem.* **2000**, *65*, 7379−7390.

(25) In the term XYZ-dipyrromethane-dicarbinol, the X, Y, and Z refer to the 1-, 5-, and 9-positions, respectively.

A_3B-porphyrins (A = aryl): The diacyl dipyrromethanes **4f** and **4e** were reduced using $NaBH_4$ and the resulting dicarbinols were condensed with 5-phenyldipyrromethane (**2a**) to give porphyrins **9a** and **9b** in 27% and 18% yields, respectively. In the case of **9b** (A = pentafluorophenyl), further column chromatography was required to obtain the pure porphyrin. The porphyrins **9c** and **9d** were prepared in 25% and 18% yields by reducing **4n** followed by condensation with **2h** and **2i**, respectively. The dicarbinol obtained after the reduction of **4i** when condensed with 5-(4-*tert*-butylphenyl)dipyrromethane (**2g**) afforded the porphyrin **9j** in 27% yield. LD-MS analysis of crude reaction samples showed no scrambling during the synthesis of these porphyrins.

A_3B-porphyrins (A = pentyl): Porphyrins **9e**−**i** were prepared by the condensation of the tripentyldipyrromethane-dicarbinol derived from **4k** with various meso-substituted dipyrromethanes (Scheme 1). The LD-MS analysis of crude reaction samples revealed no scrambling during the formation of porphyrins **9g** and **9i**, but low levels of scrambling were detected in the formation of porphyrins **9e**, **9f**, and **9h**. In the latter cases, purification by column chromatography on silica followed by trituration with refluxing ethanol furnished the pure porphyrin products. The synthesis of porphyrins **9e**−**i** show that electron-donating groups at the 5-position of the dipyrromethane increase the yield of the porphyrin during the condensation. The yields range from 35% (4-acetamidophenyl) to 14% (pentafluorophenyl).

***Trans*-AB_2C-porphyrins.** Retrosynthetic analysis of *trans*-AB_2C-porphyrins reveals two distinct approaches involving either a BAB-dipyrromethane-dicarbinol + C-dipyrromethane (Scheme 1) or an ABC-dipyrromethane-dicarbinol + B-dipyrromethane (Scheme 2). The former route is more efficient as only one diacylation procedure is required, while the latter route requires sequential introduction of the two acyl units. Several noteworthy observations were made during the course of these syntheses. (1) Porphyrin **10a** was prepared from **4d** and **2a** in 36% yield, consistent with other reactions (vide infra) in which a pentafluorophenyl group in the 5-position of the dipyrromethane-dicarbinol increased the porphyrin yield. (2) The synthesis of porphyrin-carboxaldehyde **10d** from **4o** and formyl-substituted dipyrromethane **2n** illustrates the high chemoselectivity of the condensation. Reaction occurs much faster at the carbinol than at the formyl group, affording the intact porphyrin-carboxaldehyde **10d** in 17% yield as the only porphyrin product. (3) A 0.9-g batch (22% yield) of porphyrin **10e** was prepared from **4p** and the ester-substituted dipyrromethane (**2l**). (4) Since the mesitoyl group could not be reduced to the corresponding carbinol, we used an ABC-dipyrromethane-dicarbinol + B-dipyrromethane to prepare the desired *trans*-AB_2C-porphyrin **10f**, where B = mesityl (Scheme 2). This route requires synthesis of the unsymmetrical diacyl dipyrromethane but provides the only rational route at present to obtain the desired porphyrin with mesityl groups occupying trans-positions. (5) No scrambling was detected upon LD-MS analysis of the crude reaction samples during the synthesis of any of these *trans*-AB_2C-porphyrins.

***Cis*-A_2B_2-porphyrins.** Retrosynthetic analysis reveals that regardless of the disconnection, the dipyrromethane must be sequentially acylated with two different groups, one of which introduces the same substituent that is present at the 5-position. The synthesis of three *cis*-A_2B_2-porphyrins is shown in Scheme 2. The diacyl dipyrromethanes **7h** and **7i** were reduced to the corresponding dicarbinols and condensed with dipyrromethanes **2h** and **2m** to afford porphyrins **11a** (1.18 g) and **11b** (0.53 g), respectively. The diacyl dipyrromethane **7j** (bearing two pentafluorophenyl groups) on reduction followed by condensation with **2h** furnished a mixture of products along with desired porphyrin **11c**. LD-MS analysis of this sample gave a peak consistent with the corresponding mono-pentafluorophenyl-substituted corrole in addition to the desired porphyrin which could not be obtained in pure form. Corrole formation is known to be favored with electron-withdrawing substituents.[26] LD-MS analysis of the crude reaction samples showed no scrambling during the synthesis of the other porphyrins in this set.

***Cis*-A_2BC-porphyrins.** The synthesis of a *cis*-A_2BC-porphyrin requires an unsymmetrical diacyl dipyrromethane. One approach involves an ABC-dipyrromethane-dicarbinol + A-dipyrromethane, while an alternative approach employs an AAB-dipyrromethane-dicarbinol + C-dipyrromethane. Porphyrins **12a**−**c** were prepared via the former route in yields of 16−29%. Reduction method 2 was employed with diacyl dipyrromethanes bearing TMS or TIPS-ethyne groups (**7f**, **7g**). Porphyrin **12d** was prepared following the second route from diacyl dipyrromethane **7h** and dipyrromethane **2e** in 26% yield (Scheme 2). LD-MS analysis of the crude reaction samples showed no scrambling during the synthesis of these porphyrins.

ABCD-porphyrins. Five ABCD-porphyrins were prepared as shown in Scheme 2. Noteworthy observations from this set are as follows. (1) Reduction of diacyl dipyrromethane **7e** (method 1) and reaction with dipyrromethane **2m** resulted in a 1:1 mixture of desired porphyrin **13b** and desilylated porphyrin (loss of TMS) in 25% total yield. Upon application of reduction method 2, porphyrin **13b** was obtained in good yield (1.05 g, 27%) without loss of the TMS group and with no detectable scrambling. (2) Porphyrins **13b** and **13d** each bear three functional groups that can be selectively manipulated and are potential building blocks for the construction of "T-shaped" porphyrin architectures. The former contains one iodo group and two protected ethynes, while the latter contains three ethynes that can be reacted sequentially (unprotected, TMS-protected, and TIPS-protected). (3) Porphyrin **13e**, prepared in >1-g quantity, bears four different functional groups for sequential elaboration via Pd coupling reactions. LD-MS analysis of the crude reaction samples indicated no detectable scrambling in any of these reactions.

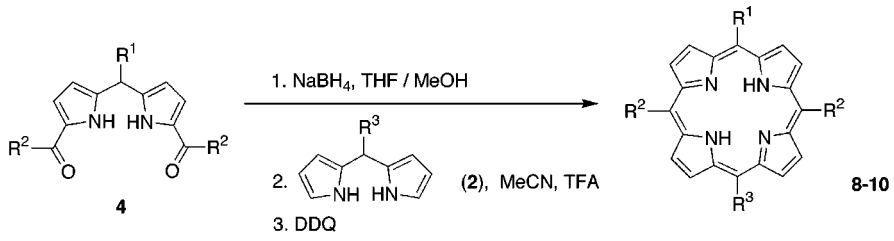
(IV) Tactical Considerations

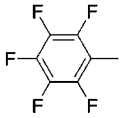
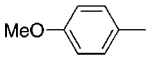
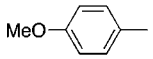
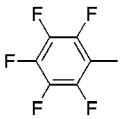
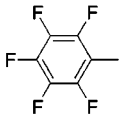
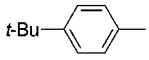
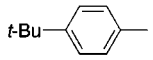
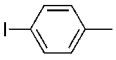
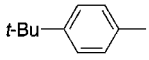
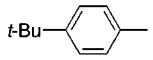
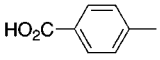
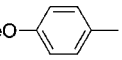
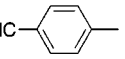
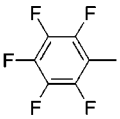
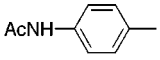
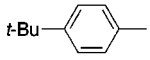
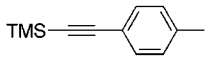
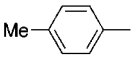
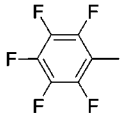
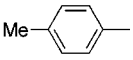
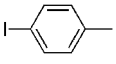
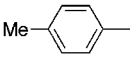
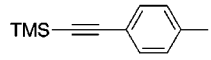
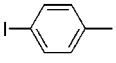
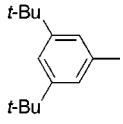
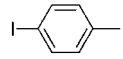
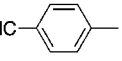
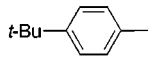
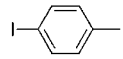
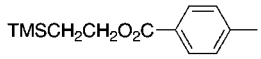
The rational routes to porphyrins described herein are compatible with diverse functionalities: amide, aldehyde, carboxylic acid, ester, nitrile, ether, bromo, iodo, ethyne, TMS-ethyne, TIPS-ethyne, and perfluoroarene. The successful formation of the porphyrin in optimal yield requires appropriate placement of substituents in the dipyrromethane precursors, taking into consideration electronic effects, steric effects, and functional group reactivity.

Effect of Substituents on the Dipyrromethane-Dicarbinol + Dipyrromethane Condensation. The reactions of a number of the dipyrromethanes and

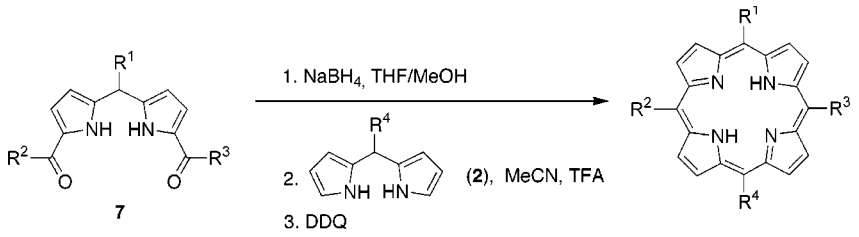
(26) Gross, Z.; Galili, N.; Saltsman, I. *Angew. Chem., Int. Ed.* **1999**, *38*, 1427−1429.

Scheme 1



Components	R^2	R^1	R^3	Product	Yield
BAB + A		***Trans*-A_2B_2-Porphyrins**			
4c + 2a			$R^1 = R^3$	**8b**	24%
A_3 + B		**A_3B-Porphyrin**			
4f + 2a				**9a**	27%
4e + 2a				**9b**	18%
4n + 2h				**9c**	25%
4n + 2i				**9d**	18%
4k + 2a	*n*-Pentyl	*n*-Pentyl		**9e**	22%
4k + 2c	*n*-Pentyl	*n*-Pentyl		**9f**	28%
4k + 2j	*n*-Pentyl	*n*-Pentyl		**9g**	18%
4k + 2b	*n*-Pentyl	*n*-Pentyl		**9h**	14%
4k + 2k	*n*-Pentyl	*n*-Pentyl		**9l**	35%
ABA + A					
4i + 2g				**9j**	27%
BAB + C		***Trans*-AB_2C-Porphyrins**			
4d + 2a				**10a**	36%
4a + 2h				**10b**	21%
4j + 2h				**10c**	26%
4o + 2n				**10d**	17%
4p + 2l				**10e**	22%

Scheme 2



Components	R^2	R^1	R^3	R^4	Product	Yield
ABC + B		***Trans*-AB_2C-Porphyrin**				
7f + 2d	TMS	Me, Me, Me	TIPS	$R^1 = R^4$	**10f**	24%
AAB + B		***Cis*-A_2B_2-Porphyrin**				
7h + 2h	*t*-Bu	$R^1 = R^2$	I	$R^3 = R^4$	**11a**	24%
7i + 2m	*t*-Bu	$R^1 = R^2$	TIPS	$R^3 = R^4$	**11b**	24%
7j + 2h	F, F, F, F, F	$R^1 = R^2$	I	$R^3 = R^4$	**11c**	not pure
ABC + A		***Cis*-A_2BC-Porphyrin**				
7b + 2a		MeO	F, F, F, F, F	$R^2 = R^4$	**12a**	20%
7c + 2a		F, F, F, F, F	MeO	$R^2 = R^4$	**12a**	29%
7f + 2e	TMS	Me, Me, Me	TIPS	$R^2 = R^4$	**12b**	16%
7g + 2h	I	TMS	Br	$R^2 = R^4$	**12c**	21%
AAB + C						
7h + 2e	*t*-Bu	$R^1 = R^2$	I	TMS	**12d**	26%
ABC + D		**ABCD-Porphyrin**				
7a + 2g		MeO	Me	*t*-Bu	**13a**	21%
7e + 2m	TMS	Me, Me, Me	I	TIPS	**13b**	27%
7d + 2m	TMS	F, F, F, F, F	I	TIPS	**13c**	40%
7f + 2o	TMS	Me, Me, Me	TIPS	H	**13d**	26%
7g + 2m	Br	TMS	I	TIPS	**13e**	25%

dipyrromethane-dicarbinols provide insight into the electronic effects of substituents. The outcome is quite different for the 5-position of a dipyrromethane and the 5-position of a dipyrromethane-dicarbinol. For substituents at the 5-position of a dipyrromethane, the yield increases with electron-releasing strength. A clear trend is seen in the formation of porphyrins **9e**−**i**, where the yield increases from 14% (pentafluorophenyl) to 35% (4-acetamidophenyl). Conversely, for substituents at the 5-position of a dipyrromethane-dicarbinol, a higher yield is obtained with pentafluorophenyl (**13c**, 40%) than with mesityl (**13b**, 27%). In general, the presence of a pentafluorophenyl group at the 5-position of a dipyrromethane-dicarbinol affords high yields, as observed with porphyrins **10a** (36%) and **12a** (formed from **7c** + **2a**; 29% yield). These results are consistent with those observed during the self-condensation of dipyrromethane-monocarbinols.[6]

The final condensation is quite tolerant of the substituents in the dipyrromethane-dicarbinol or dipyrromethane. Significant problems have been encountered in only a few cases. (1) Dipyrromethane-dicarbinols bearing two or three pentafluorophenyl groups can give side reactions. With one pentafluorophenyl group at either the 5-position (**10a**, **12a** from **7c** + **2a**, **13c**) or at one of the carbinol positions (**12a** from **7b** + **2a**), the reaction proceeded smoothly and gave porphyrin in yields of 20−40%. With pentafluorophenyl groups at both of the carbinol positions (**8b**), reaction also proceeded smoothly (24%). However, with pentafluorophenyl groups at the 5-position and one (**11c**) or both of the carbinol positions (**9b**), the reaction was not clean and further purification was required to obtain the desired porphyrin. (2) The tripentyl-substituted dipyrromethane-dicarbinol reacts poorly. A low level of scrambling was observed in the syntheses of porphyrins **9e**, **9f**, and **9h**, though in each case the target porphyrin could be purified by chromatography. (3) Dipyrromethanes bearing heterocyclic substituents (e.g., pyridyl) react very poorly under these conditions but can be reacted with dipyrromethane-dicarbinols without scrambling under modified condensation conditions.[27]

A striking example of the selective and mild nature of the dipyrromethane-dicarbinol + dipyrromethane condensation is provided by the formation of the porphyrin-carboxaldehyde **10d**. The direct synthesis of **10d** without using an aldehyde protecting group was prompted by our observation that the reaction of a dipyrromethane-carbinol is much faster than the reaction of a dipyrromethane and an aldehyde.[28] (This observation underpinned the development of the nonscrambling synthesis of *trans*-A_2B_2-porphyrins by the self-condensation of a sterically unhindered dipyrromethane-monocarbinol.[6]) Porphyrin-carboxaldehydes are useful building blocks but have formerly only been prepared with the aldehyde in masked form. This direct synthesis of a porphyrin-carboxaldehyde suggests the possibility of incorporating a variety of very sensitive, unprotected groups in the dipyrromethane unit with subsequent conversion to the corresponding porphyrin.

(ii) Order of Introduction of Groups. The rational routes to the porphyrins described herein rely on the preparation of diacyl dipyrromethanes and their subsequent reduction to the corresponding dicarbinol. Despite the use of EtMgBr and acid chlorides, the scope of compatible functional groups (e.g., alkyl, bromophenyl, iodophenyl, methoxyphenyl, TMS-ethynylphenyl, TIPS-ethynylphenyl, pentafluorophenyl) incorporated into diacyl dipyrromethanes is substantial. The broad compatibility likely reflects the rapid formation of the pyrrolic magnesium bromide derivative of the dipyrromethane, which is substantially less reactive than EtMgBr. Evidence of such diminished reactivity stems from the ability to introduce a second acyl unit into a monoacyl dipyrromethane (by treatment with EtMgBr followed by an acid chloride) without significant attack on the first acyl unit. Still, the reaction conditions required to convert a dipyrromethane to a dipyrromethane-dicarbinol are far more demanding than those in forming the dipyrromethane itself. Given these different reaction conditions, and the fact that up to four different groups can be incorporated in the meso-substituted porphyrin, the issue arises as to the optimal order and components in which the groups should be introduced.[29] In exploring the generality of these routes, involving the preparation of 27 diacyl dipyrromethanes and 30 porphyrins, the following heuristics have emerged concerning the order of introduction of various groups (precursors to the porphyrin meso substituents).

(1) A substituent that is vulnerable to attack by EtMgBr or reduction by $NaBH_4$ [e.g., acetamide (**9i**), terminal ethyne (**13d**), aldehyde (**10d**), carboxylic acid (**9d**), ester (**10e**), nitrile (**9g**)] should be introduced during the final condensation through the incoming dipyrromethane.

(2) The dipyrromethane to be acylated should carry the most resistant of the required groups at the 5-position (e.g., **13d**).

(3) In successive acylation yielding an unsymmetrical diacyl dipyrromethane, the group that is more resistant to attack by EtMgBr should be introduced in the first acylation via the thioester reagent (e.g., **7d**, **7e**, **7g**, **7h**).

(4) The inability to reduce a mesitoyl-substituted dipyrromethane requires that mesityl groups be introduced at the 5-position of a dipyrromethane or dipyrromethane-dicarbinol (e.g., **10f**, **13b**, **13d**).

Conclusion

The synthesis of porphyrins bearing different meso substituents has presented a number of challenges. Porphyrins bearing two different substituents (A_3B, *trans*-A_2B_2, *cis*-A_2B_2) have been available via a statistical condensation of pyrrole with two aldehydes, albeit in small quantities following extensive chromatography. Porphyrins with three (*cis*-A_2BC, *trans*-AB_2C) or four (ABCD) different substituents require rational syntheses. The success of rational syntheses requires the absence of acidolytic scrambling of the location of substituents at all stages of the synthesis. As such, the rational synthesis of substituted porphyrins involves methodology at the other extreme from the one-flask pyrrole−aldehyde condensation leading to A_4-porphyrins. The rational

(27) Gryko, D.; Lindsey, J. S. *J. Org. Chem.* **2000**, *65*, 2249−2252.
(28) Geier, G. R., III.; Lindsey, J. S. Manuscripts in preparation.

(29) For a given ABCD-porphyrin, there are four possible dipyrromethane-dicarbinol + dipyrromethane condensations, and two possible orderings for introducing the two acyl units into each of the corresponding diacyl dipyrromethanes. Thus there are eight possible routes for preparing a given ABCD-porphyrin. Note that this is an ordering issue and does not involve isomers of the given ABCD-porphyrin. See Supporting Information for consideration of routes to the other classes of meso-substituted porphyrins.

methodology developed herein has four stages: (1) a one-flask synthesis of dipyrromethanes, (2) preparation of a symmetrical diacyl dipyrromethane by diacylation or an unsymmetrical diacyl dipyrromethane by sequential acylation, (3) reduction of the diacyl dipyrromethane to the dipyrromethane-dicarbinol, and (4) nonscrambling condensation of a dipyrromethane-dicarbinol + dipyrromethane followed by oxidation to give the porphyrin. Refinement has been made to steps 2−4 in order to achieve broad scope, minimal chromatography, and ease of implementation. The diacyl dipyrromethanes are analytically pure and are available in multigram quantities. Although the yields of the dipyrromethane-dicarbinol + dipyrromethane reaction range from only 14 to 40%, the absence of detectable scrambling in almost all cases greatly diminishes the chromatography required for purification. In general, we find that with the requisite starting materials (pyrrole- and carbonyl-containing compounds) in hand, 0.1−1 g quantities of a porphyrin can be prepared in a straightforward manner in about one week. The rational routes described encompass A_3B-, *trans*-AB_2C-, *cis*-A_2B_2-, *cis*-A_2BC-, and ABCD-porphyrins. The ability to prepare significant quantities of such porphyrins in pure form may prove useful in a variety of biomimetic and materials applications.

Experimental Section

General. ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra were obtained in $CDCl_3$ unless noted otherwise. Absorption spectra were collected routinely. Elemental analyses were performed by Atlantic Microlab, Inc. Melting points are uncorrected. Bulb-to-bulb distillations were performed using a standard-size Kugelrohr short path distillation apparatus (Aldrich). Silica gel (Baker, 40 μm average particle size) and alumina (Fisher, 80−200 mesh) were used for column chromatography. The $CHCl_3$ was reagent grade and contained 0.75% ethanol. Dipyrromethanes were prepared as described previously and analyzed for purity by gas chromatography.[9] The dipyrromethanes, diacyl dipyrromethanes, and dipyrromethane-dicarbinols were easily detected in TLC upon exposure to Br_2 vapor.

The acylations with acid chlorides were performed in freshly distilled toluene (from CaH_2). The acid chlorides were of reagent grade and were used as obtained. In all acylation procedures involving EtMgBr and an acid chloride, TLC analysis indicated the presence of fast-migrating dark impurities (not characterized) which were readily removed during chromatographic purification. Purification of the diacyl dipyrromethanes was increasingly difficult with the presence of increased amounts of unreacted monoacyl dipyrromethane. Isolation of the diacyl dipyrromethanes following column chromatography generally was achieved by (a) slow precipitation from hot 2-propanol/water, or (b) slow precipitation from CH_2Cl_2/hexanes (or in other solvents as specified) at room temperature with slow evaporation of the solvent on standing. In general, the diacyl dipyrromethanes were obtained as amorphous pale brown solids rather than crystalline materials.

The reduction of the diacyl dipyrromethanes were performed in THF/methanol. In method 1, the THF and methanol were of reagent grade (A.C.S.). In method 2, the THF was freshly distilled from Na/benzophenone and anhydrous methanol was used as received from Aldrich.

Porphyrin-forming reactions were performed in reagent-grade (A.C.S.) acetonitrile obtained from Fisher (used without any further purification). Porphyrins (from reaction samples or following purification) were analyzed by laser desorption ionization mass spectrometry (LD-MS) without a matrix.[30] The progress of the porphyrin-forming reactions was monitored spectroscopically and the extent of scrambling in the crude reaction mixture was determined as described previously.[5,31] In some cases, the final step in purification involved a procedure in which the porphyrin product was suspended in alcohol and the suspension was sonicated for a few minutes in a standard benchtop ultrasonic cleaning bath, followed by filtration.

Aldehydes **1a**−**d** and **1f**−**k** were obtained commercially. The following compounds were prepared as described in the literature: aldehyde **1l**;[15] dipyrromethanes **2a**−**d**,[13] **2e**,[17] **2f**,[14] **2g**,[6] **2h**,[13] and **2l**;[6] monoacyl dipyrromethanes **5b**, **5c**, and **5h**;[6] *S*-2-pyridyl benzothioates **6a**−**c**.[6]

Studies of the Dipyrromethane-Dicarbinol + Dipyrromethane Condensation. A sample of **4a** (275 mg, 0.60 mmol) was reduced by $NaBH_4$ (1.13 g, 30.0 mmol) in THF/methanol (3:1, 40 mL) to afford upon workup the corresponding dipyrromethane-dicarbinol as a foamlike solid (reduction method 1). Due to the limited stability of the dipyrromethane-dicarbinol, 60 mL of acetonitrile was immediately added, and a 10-mL portion of the dipyrromethane-dicarbinol was placed in each of five separate reaction flasks (10 mmol each). For the study examining the effect of the reaction solvent, the acetonitrile was then removed under vacuum, and the solvent of interest was added. For all other reactions additional acetonitrile was added if required to give the desired reagent concentration, and then **2a** was added. The reactions were then performed in sets of five, starting one reaction every 6 min by the addition of TFA. The reaction yield and extent of scrambling were determined at 1, 5, 15, and 30 min by UV−vis spectroscopy and LD-MS, respectively, as described previously.[5]

4-[2-(Trimethylsilyl)ethynyl]benzaldehyde (1e).[32] Prepared by an improved procedure (see Supporting Information).

4-[2-(Triisopropylsilyl)ethynyl]benzaldehyde (1m). 4-Bromobenzaldehyde (4.62 g, 25.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.105 g, 0.15 mmol), and CuI (0.57 g, 3.0 mmol) were placed in a Schlenk flask which was thoroughly flushed with argon. Then degassed triethylamine (50 mL) followed by triisopropylsilylacetylene (5.47 g, 30.0 mmol) were introduced, and the flask was sealed. The contents of the flask were stirred at 80 °C for 12 h. Then the reaction mixture was cooled to room temperature, the solids were removed by filtration, and the filtrate was concentrated. The crude brown oil was bulb-to-bulb distilled (130−140 °C at 0.02 mmHg) to obtain a colorless liquid (6.05 g, 84%). ^{1}H NMR δ 1.14 (m, 21H), 7.61 (d, J = 8.1 Hz, 2H), 7.82 (d, J = 8.1 Hz, 2H), 10.00 (s, 1H); ^{13}C NMR δ 11.4, 18.8, 95.9, 106.1, 129.6, 129.9, 132.7, 135.6, 191.6. Anal. Calcd for $C_{18}H_{26}OSi$: C, 75.46; H, 9.15. Found: C, 75.37; H, 9.09.

5-(4-Carboxyphenyl)dipyrromethane (2i). Following a general procedure,[13] a mixture of pyrrole (60 mL, 0.86 mol) and 4-carboxybenzaldehyde (2.60 g, 17.3 mmol) was flushed with argon for 5 min and treated with TFA (0.133 mL, 1.73 mmol), and the mixture was stirred for 5 min. 0.1 M aq NaOH (50 mL) and ethyl acetate (100 mL) were added, and the layers were separated. The aqueous layer was acidified with dil HCl solution and extracted again with ethyl acetate. The combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated to remove the excess pyrrole. Column chromatography [silica, CH_2Cl_2/ethyl acetate (3:1)] afforded a pale brown oil which was dissolved in a 1:20 mixture of water and ethanol and was allowed to crystallize at 0 °C overnight, affording a blue solid that was filtered and dried in vacuo (2.35 g, 51%). mp 149−150 °C; ^{1}H NMR (acetone-d_6) δ 5.55 (s, 1H), 5.76 (m, 2H), 6.05 (m, 2H), 6.70 (m, 2H), 7.34 (d, J = 8.1 Hz, 2H), 7.96 (d, J = 8.1 Hz, 2H), 9.75 (br, 2H) (acid hydrogen not observed); ^{13}C NMR δ 44.9, 107.7, 108.3, 118.2, 129.4, 129.6, 130.5, 133.3, 149.9, 167.9. Anal. Calcd for $C_{16}H_{14}N_2O_2$: C, 72.16; H, 5.30; N, 10.52. Found: C, 71.50; H, 5.38; N, 10.25.

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5-(4-Cyanophenyl)dipyrromethane (2j). A sample of 4-cyanobenzaldehyde (3.8 g, 29 mmol) was reacted with excess pyrrole following the reported procedure.[13] After preliminary workup (wash with 0.1 M aq NaOH, remove pyrrole by rotary evaporation), the crude product was purified by column chromatography [silica, CH_2Cl_2/ethyl acetate (1:1)] to obtain a pale yellow oil which was recrystallized from hot ethyl acetate. The white needles thus obtained were filtered and dried in vacuo (5.1 g, 50%). ^{1}H NMR (acetone-d_6) δ 5.58 (s, 1H), 5.77 (m, 2H), 6.02 (AB quartet, J = 3.0 Hz, 2H), 6.72 (AB quartet, J = 3.0 Hz, 2H), 7.38 (d, J = 8.1 Hz, 2H), 7.64−7.68 (m, 2H), 9.77 (br, 2H). Other analytical data (mp, ^{13}C NMR) are consistent with literature values.[33]

5-(4-Acetamidophenyl)dipyrromethane (2k). A sample of 4-acetamidobenzaldehyde (4.0 g, 25 mmol) was reacted with excess pyrrole following the general procedure.[13] After preliminary workup (wash with 0.1 M aq NaOH, remove pyrrole by rotary evaporation), the crude product was purified by column chromatography [silica, CH_2Cl_2/ethyl acetate (4:1)] to obtain a yellow oil which was dissolved in a 1:20 mixture of water and ethanol. The resulting yellow solid was filtered and dried in vacuo (4.0 g, 58%). mp 158−160 °C; ^{1}H NMR (acetone-d_6) δ 2.04 (s, 3H), 5.39 (s, 1H), 5.72 (m, 2H), 5.97 (m, 2H), 6.66 (m, 2H), 7.10 (m, 2H), 7.52 (d, J = 7.8 Hz, 2H), 9.13 (br, 1H), 9.65 (br, 2H); ^{13}C NMR (acetone-d_6) δ 24.4, 44.6, 107.5, 108.3, 117.9, 120.0, 129.7, 134.4, 138.9, 139.6. Anal. Calcd for $C_{17}H_{17}N_3O$: C, 73.10; H, 6.13; N, 15.04. Found: C, 73.08; H, 6.17; N, 15.06.

5-{4-[2-(Triisopropylsilyl)ethynyl]phenyl}dipyrromethane (2m). A sample of **1m** (5.72 g, 20.0 mmol) was reacted with excess pyrrole following the general procedure.[13] After preliminary workup (wash with 0.1 M aq NaOH, remove pyrrole by rotary evaporation), the crude oil was bulb-to-bulb distilled (180−190 °C at 0.02 mmHg) to obtain a pale yellow oil which was dissolved in a 1:20 mixture of water and methanol and was allowed to crystallize at 0 °C overnight. The resulting grayish amorphous solid was filtered and dried in vacuo (4.15 g, 51%). mp 80−81 °C; ^{1}H NMR δ 1.12 (m, 21H), 5.46 (s, 1H), 5.89 (m, 2H), 6.15 (m, 2H), 6.69 (m, 2H), 7.14 (m, 2H), 7.43 (m, 2H), 7.91 (br, 2H); ^{13}C NMR δ 11.4, 18.7, 43.8, 90.7, 106.9, 107.5, 108.5, 117.5, 128.3, 132.14, 132.3, 142.4. Anal. Calcd for $C_{26}H_{34}N_2Si$: C, 77.56; H, 8.51; N, 6.96. Found: C, 77.44; H, 8.54; N, 6.94.

5-(4-Formylphenyl)dipyrromethane (2n). A solution of **2j** (1.0 g, 4.0 mmol) in CH_2Cl_2 (22 mL) was treated dropwise with a solution of DIBAL-H (1 M in hexanes, 8.0 mL, 8.0 mmol) at room temperature. The reaction mixture was stirred at room temperature for about 3 h and then quenched with 100 mL of satd aq NH_4Cl and stirred for a further 2 h. More CH_2Cl_2 (50 mL) was added, and the aqueous layer was removed. The organic layer appeared as an emulsion, to which 10% aq NaOH (100 mL) was added. The aqueous phase was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried (Na_2SO_4), and concentrated to dryness. The light brown residue was purified by column chromatography (silica, CH_2Cl_2) to afford a pale yellow solid (0.47 g, 47%). mp 117−118 °C; ^{1}H NMR δ 5.55 (s, 1H), 5.90 (s, 2H), 6.17−6.20 (m, 2H), 6.73−6.75 (m, 2H), 7.34 (d, J = 7.8 Hz, 2H), 7.80 (d, J = 8.1 Hz, 2H), 8.04 (br, 2H), 9.96 (s, 1H); ^{13}C NMR δ 44.3, 107.9, 108.8, 118.0, 129.3, 130.3, 131.6, 135.4, 149.5, 192.3. Anal. Calcd for $C_{16}H_{14}N_2O$: C, 76.78; H, 5.64; N, 11.19. Found: C, 76.73; H, 5.65; N, 11.08.

5-(4-Ethynylphenyl)dipyrromethane (2o). Solid K_2CO_3 (0.35 g) was added to a solution of dipyrromethane **2e** (0.96 g, 3.0 mmol) in THF/methanol (25 mL, 4:1). The mixture was stirred for 40 min at room temperature and then concentrated. The residue was dissolved in CH_2Cl_2 and washed with water and brine. The organic layer was dried (Na_2SO_4) and filtered through a bed of silica. Recrystallization from CH_2Cl_2/hexanes afforded colorless needles (0.68 g, 92%). mp 109−110 °C; ^{1}H NMR δ 3.08 (s, 1H), 5.46 (s, 1H), 5.91 (s, 2H), 6.18 (m, 2H), 6.70 (s, 2H), 7.18 (d, J = 8.1 Hz, 2H), 7.47 (d, J = 8.1 Hz, 2H), 7.89 (br, 2H); ^{13}C NMR δ 44.4, 78.0, 84.1, 108.1, 109.2, 118.2, 121.3, 129.1, 132.5, 133.0. Anal. Calcd for $C_{17}H_{14}N_2$: C, 82.90; H, 5.73; N, 11.37. Found: C, 82.66; H, 5.72; N, 11.39.

4-[2-(Triisopropylsilyl)ethynyl]benzoyl Chloride (3). Ethyl 4-iodobenzoate (13.8 g, 50.0 mmol), $Pd(PPh_3)_2Cl_2$ (0.21 g, 0.30 mmol), and CuI (0.57 g, 3.0 mmol) were placed in a Schlenk flask, and the flask was thoroughly flushed with argon. Then degassed triethylamine (100 mL) followed by triisopropylsilylacetylene (10.94 g, 60.00 mmol) were introduced, and the flask was sealed. The contents of the flask were stirred at 50 °C for 1 h and then at room temperature for a further 12 h. The solids were filtered and the filtrate was concentrated. The crude brown oil was dissolved in ethanol (500 mL), and aq NaOH (2 M, 100 mL) was added. The homogeneous reaction mixture was stirred for 12 h at room temperature. Then the reaction mixture was diluted with water (400 mL) and washed with ether. The aqueous layer was acidified with concentrated HCl and extracted with ether. The combined ether layers were dried (Na_2SO_4) and concentrated. The faintly colored oil was dissolved in hexanes and allowed to crystallize, affording colorless crystals (12.15 g, 81%). mp 93−94 °C; ^{1}H NMR δ 1.14 (m, 21H), 7.56 (d, J = 8.1 Hz, 2H), 8.04 (d, J = 8.1 Hz, 2H) (acid hydrogen not observed); ^{13}C NMR δ 11.4, 18.8, 95.2, 106.2, 128.8, 129.3, 130.2, 132.2, 172.0. Anal. Calcd for $C_{18}H_{26}O_2Si$: C, 71.47; H, 8.66. Found: C, 71.48; H, 8.66. The acid (10.57 g, 35.00 mmol) was dissolved in benzene (25 mL), thionyl chloride (12.8 mL, 175 mmol) was added, and the mixture was refluxed for 36 h. The volatile components were removed by vacuum evaporation (water aspirator), and the faintly colored oil was bulb-to-bulb distilled (150−160 °C at 0.02 mmHg) to afford a pale yellow liquid (9.56 g, 85%). ^{1}H NMR δ 1.17 (m, 21H), 7.60 (d, J = 8.1 Hz, 2H), 8.07 (d, J = 8.1 Hz, 2H); ^{13}C NMR δ 11.4, 18.8, 97.4, 105.5, 130.9, 131.3, 132.4, 132.5, 167.8. Anal. Calcd for $C_{18}H_{25}ClOSi$: C, 67.36; H, 7.85. Found: C, 67.37; H, 7.87.

General Procedure for Diacylation, Exemplified for 1,9-Bis(4-methylbenzoyl)-5-phenyldipyrromethane (4a). A solution of EtMgBr (25.0 mL, 25.0 mmol) was added slowly to a stirred, tap-water-cooled flask containing a solution of 5-phenyldipyrromethane (**2a**, 1.11 g, 5.00 mmol) in toluene (100 mL) under an Ar atmosphere. An exothermic reaction with gas evolution ensued. The resulting brown solution was stirred for 30 min at room temperature. Then a solution of *p*-toluoyl chloride (1.65 mL, 12.5 mmol) in toluene (12.5 mL) was added over 10 min. The solution darkened, and the mixture was stirred for an additional 10 min. The reaction was quenched by adding satd aq NH_4Cl (75 mL). Ethyl acetate (100 mL) was then added. The organic phase was washed successively with water and brine and then dried ($MgSO_4$). The solvent was removed under reduced pressure to afford a brown oil. ^{1}H NMR analysis of the crude reaction mixture indicated a 4.4:1 product ratio (diacyl dipyrromethane versus monoacyl dipyrromethane). The crude product was then purified by column chromatography [silica, CH_2Cl_2/ethyl acetate (95:5)], and the main fractions containing the desired diacyl dipyrromethane were collected. Removal of solvent afforded a yellow foam which was dissolved in hot 2-propanol (25 mL). Precipitation with water (1−2 mL) afforded an amorphous solid. Recrystallization from CH_2Cl_2/hexanes afforded pure **4a** (1.61 g, 70%). Analytical data are consistent with literature values.[17]

1,9-Bis(4-methoxybenzoyl)-5-phenyldipyrromethane (4b). Following the general diacylation procedure, reaction of **2a** (0.67 g, 3.0 mmol) and *p*-anisoyl chloride (1.28 g, 7.50 mmol) afforded a 3.3:1 product ratio; column chromatography [silica, hexanes/ethyl acetate (13:7)] followed by precipitation from 2-propanol/water gave an amorphous solid (0.97 g, 66%). mp 120−121 °C; ^{1}H NMR δ 3.84 (s, 6H), 5.65 (s, 1H), 5.92 (m, 2H), 6.51 (m, 2H), 6.89 (d, J = 8.7 Hz, 4H), 7.33−7.42 (m, 3H), 7.53 (d, J = 7.2 Hz, 2H), 7.78 (d, J = 8.7 Hz, 4H), 11.46 (br, 2H); ^{13}C NMR δ 45.4, 55.7, 111.3, 113.6, 120.4, 127.7, 129.1, 129.2, 131.3, 131.4, 132.1, 140.9, 162.7, 183.7; FAB-MS obsd 490.1916,

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calcd 490.1893 ($C_{31}H_{26}N_2O_4$). Anal. Calcd for $C_{31}H_{26}N_2O_4$: C, 75.90; H, 5.34; N, 5.71. Found: C, 75.48; H, 5.48; N, 5.60.

1,9-Bis(pentafluorobenzoyl)-5-phenyldipyrromethane (4c). Following the general diacylation procedure, reaction of **2a** (0.45 g, 2.0 mmol) and pentafluorobenzoyl chloride (0.72 mL, 5.0 mmol) afforded a 5.3:1 product ratio; column chromatography [silica, hexanes/ethyl acetate (17:3)] followed by slow precipitation from CH_2Cl_2/hexanes gave an amorphous solid (0.35 g, 29%). mp 150−151 °C; ^{1}H NMR δ 5.66 (s, 1H), 6.15 (m, 2H), 6.70 (m, 2H), 7.22−7.48 (m, 5H), 9.62 (br, 2H); ^{13}C NMR δ 44.4, 112.0, 122.4, 128.2, 128.3, 129.3, 131.4, 138.0, 142.3, 172.2; FAB-MS obsd 610.0773, calcd 610.0739 ($C_{29}H_{12}F_{10}N_2O_2$). Anal. Calcd for $C_{29}H_{12}F_{10}N_2O_2$: C, 57.06; H, 1.98; N, 4.59. Found: C, 58.18; H, 2.46; N, 4.37.

1,9-Bis(4-methylbenzoyl)-5-(pentafluorophenyl)dipyrromethane (4d). Following the general diacylation procedure, reaction of **2b** (0.62 g, 2.0 mmol) with *p*-toluoyl chloride (0.66 mL, 5.0 mmol) afforded a 1.9:1 product ratio; column chromatography [silica, CH_2Cl_2/ethyl acetate (19:1)] followed by slow precipitation from CH_2Cl_2/hexanes gave an amorphous solid (0.56 g, 51%). mp 155−156 °C; ^{1}H NMR δ 2.38 (s, 6H), 6.06 (m, 2H), 6.16 (s, 1H), 6.61(m, 2H), 7.22 (d, J = 8.1 Hz, 4H), 7.70 (d, J = 8.1 Hz, 4H), 11.49 (br, 2H); ^{13}C NMR δ 22.0, 33.9, 110.9, 120.5, 129.3, 130.1, 131.9, 135.7, 136.2, 143.1, 184.8; FAB-MS obsd 548.1518, calcd 548.1523 ($C_{31}H_{21}F_5N_2O_2$). Anal. Calcd for $C_{31}H_{21}F_5N_2O_2$: C, 67.88; H, 3.86; N, 5.11. Found: C, 68.16; H, 3.85; N, 5.08.

1,9-Bis(pentafluorobenzoyl)-5-(pentafluorophenyl)-dipyrromethane (4e). Following the general diacylation procedure, reaction of **2b** (0.31 g, 1.0 mmol) and pentafluorobenzoyl chloride (0.36 mL, 2.5 mmol) afforded a product ratio of <0.9:1 (estimated, due to overlapping peaks); column chromatography [silica, CH_2Cl_2/ethyl acetate (49:1)] followed by slow precipitation from CH_2Cl_2/hexanes gave an amorphous solid (0.18 g, 25%). mp > 225 °C (dec); ^{1}H NMR (DMSO-d_6) δ 6.01 (d, J = 3.9 Hz, 2H), 6.04 (s, 1H), 6.87 (d, J = 3.9 Hz, 2H), 12.69 (br, 2H); FAB-MS obsd 700.0307, calcd 700.0268 ($C_{29}H_7F_{15}N_2O_2$). Anal. Calcd for $C_{29}H_7F_{15}N_2O_2$: C, 53.77; H, 1.89; N, 4.05. Found: C, 48.84; H, 1.06; N, 4.14 (**4e** did not furnish satisfactory elemental analysis data). Alternatively, **4e** was obtained by stepwise addition of acylating reagents. Thus a solution of **2b** (0.94 g, 3.0 mmol) in toluene (60 mL) was treated with a solution of EtMgBr (6.0 mL, 6.0 mmol) and a solution of pentafluorobenzoyl chloride (0.43 mL, 3.0 mmol) in toluene. After 10 min, the addition of EtMgBr (6.0 mL, 6.0 mmol) and acid chloride (0.43 mL, 3.0 mmol) was repeated. After a further 10 min, the remaining portions of EtMgBr (3.0 mL, 3.0 mmol) and acid chloride (0.21 mL, 1.5 mmol) were added. After reaction for 10 min, the reaction mixture was quenched. Purification of the crude product was performed as before, affording **4e** (0.51 g, 24%) with the same purity as above.

1,9-Bis(4-methoxybenzoyl)-5-(4-methoxyphenyl)dipyrromethane (4f). Following the general diacylation procedure, reaction of **2c** (0.63 g, 2.5 mmol) with *p*-anisoyl chloride (1.06 g, 6.25 mmol) afforded a 2.5:1 product ratio; column chromatography [silica, CH_2Cl_2/ethyl acetate (3:1)] followed by slow precipitation from CH_2Cl_2/hexanes gave an amorphous solid (0.89 g, 69%). mp 109−110 °C; ^{1}H NMR δ 3.82 (s, 3H), 3.85 (s, 6H), 5.58 (s, 1H), 5.96 (m, 2H), 6.57 (m, 2H), 6.92 (m, 6H), 7.40 (d, J = 8.7 Hz, 2H), 7.81 (d, J = 8.7 Hz, 4H), 11.00 (br, 2H); ^{13}C NMR δ 44.3, 55.5, 55.6, 110.9, 113.5, 114.5, 120.1, 130.0, 131.2, 131.7, 140.6, 162.7, 183.5; FAB-MS obsd 520.2012, calcd 520.1998 ($C_{32}H_{28}N_2O_5$). Anal. Calcd for $C_{32}H_{28}N_2O_5$: C, 73.83; H, 5.42; N, 5.38. Found: C, 73.53; H, 5.46; N, 5.32.

1,9-Bis(4-*tert*-butylbenzoyl)-5-mesityldipyrromethane (4g). Following the general diacylation procedure, reaction of **2d** (1.32 g, 5.00 mmol) with 4-*tert*-butylbenzoyl chloride (2.44 mL, 12.5 mmol) resulted in no detectable monoacyl compound; column chromatography [silica, hexanes/ethyl acetate (8:2)] followed by slow precipitation from hexanes gave an amorphous solid (2.42 g, 83%). mp 144−145 °C; ^{1}H NMR δ 1.34 (s, 18H), 2.21 (s, 6H), 2.32 (s, 3H), 6.08 (m, 2H), 6.14 (s, 1H), 6.75 (m, 2H), 6.93 (s, 2H), 7.43 (d, J = 8.1 Hz, 4H), 7.74 (d, J = 8.1 Hz, 4H), 10.43 (br, 2H); ^{13}C NMR δ 20.8, 20.9, 31.1, 34.9, 39.1, 110.3, 120.5, 124.9, 129.1, 130.3, 130.4, 133.0, 135.6, 137.5, 139.4, 154.9, 183.7; FAB-MS obsd 584.3409, calcd 584.3403 ($C_{40}H_{44}N_2O_2$). Anal. Calcd for $C_{40}H_{44}N_2O_2$: C, 82.15; H, 7.58; N, 4.79. Found: C, 82.09; H, 7.64; N, 4.80.

1,9-Bis(4-iodobenzoyl)-5-mesityldipyrromethane (4h). Following the general diacylation procedure, reaction of **2d** (1.32 g, 5.00 mmol) with *p*-iodobenzoyl chloride (2.93 g, 12.5 mmol) afforded a 1.7:1 product ratio; column chromatography [silica, hexanes/ethyl acetate (17:3)] followed by slow precipitation from CH_2Cl_2/hexanes gave an amorphous solid (2.14 g, 59%). mp > 225 °C (dec); ^{1}H NMR δ 2.22 (s, 6H), 2.32 (s, 3H), 5.96 (m, 2H), 6.19 (s, 1H), 6.58 (m, 2H), 6.93 (s, 2H), 7.40 (d, J = 8.1 Hz, 4H), 7.74 (d, J = 8.1 Hz, 4H), 11.34 (br, 2H); ^{13}C NMR δ 20.8, 39.2, 98.9, 110.7, 121.0, 129.9, 130.4, 130.7, 132.7, 137.2, 137.4, 140.3, 182.7; FAB-MS obsd 724.0080, calcd 724.0084 ($C_{32}H_{26}I_2N_2O_2$). Anal. Calcd for $C_{32}H_{26}I_2N_2O_2$: C, 53.06; H, 3.62; N, 3.87. Found: C, 53.10; H, 3.61; N, 3.81.

1,9-Bis(4-*tert*-butylbenzoyl)-5-{4-[2-(trimethylsilyl)-ethynyl]phenyl}dipyrromethane (4i). Following the general diacylation procedure, reaction of **2e** (1.59 g, 5.00 mmol) with 4-*tert*-butylbenzoyl chloride (2.15 mL, 12.5 mmol) afforded a 3:1 product ratio; column chromatography [silica, hexanes/ethyl acetate (17:3)] followed by slow precipitation from hexanes gave an amorphous solid (2.09 g, 65%). mp 178−180 °C; ^{1}H NMR δ 0.31 (s, 9H), 1.36 (s, 18H), 5.67 (s, 1H), 5.92 (m, 2H), 6.55 (m, 2H), 7.42 (d, J = 7.8 Hz, 4H), 7.48 (s, 4H), 7.70 (d, J = 7.8 Hz, 4H), 11.60 (br, 2H); ^{13}C NMR δ −0.06, 31.1, 34.9, 44.9, 94.3, 104.9, 111.0, 120.6, 122.0, 124.9, 128.7, 129.5, 131.1, 132.4, 135.5, 140.2, 140.9, 155.1, 184.4; FAB-MS obsd 638.3355, calcd 638.3329 ($C_{42}H_{46}N_2O_2Si$). Anal. Calcd for $C_{42}H_{46}N_2O_2Si$: C, 78.95; H, 7.26; N, 4.38; Found: C, 78.78; H, 7.21; N, 4.43.

1,9-Bis(4-methylbenzoyl)-5-{4-[2-(trimethylsilyl)ethynyl]-phenyl}dipyrromethane (4j). Following the general diacylation procedure, reaction of **2e** (1.59 g, 5.00 mmol) with *p*-toluoyl chloride (1.65 mL, 12.5 mmol) afforded a 1.8:1 product ratio; column chromatography [silica, hexanes/ethyl acetate (8:2)] followed by slow precipitation from 2-propanol gave an amorphous solid (1.11 g, 40%). Analytical data are consistent with literature values.[17]

1,9-Dihexanoyl-5-pentyldipyrromethane (4k). Following the general diacylation procedure, reaction of **2f** (1.08 g, 5.00 mmol) with hexanoyl chloride (1.74 mL, 12.5 mmol) resulted in no detectable monoacyl compound; column chromatography [silica, hexanes/ethyl acetate (9:1)] followed by recrystallization from 2-propanol/water gave yellow crystals (1.24 g, 60%). mp 128−129 °C; ^{1}H NMR δ 0.85 (m, 9H), 1.31 (m, 14H), 1.69 (m, 4H), 2.09 (m, 2H), 2.76 (t, J = 7.2 Hz, 4H), 4.18 (t, J = 8.1 Hz, 1H), 6.09 (m, 2H), 6.85 (m, 2H), 10.79 (br, 2H); ^{13}C NMR δ 13.8, 13.9, 22.4, 25.3, 27.4, 31.5, 31.6, 33.1, 37.7, 38.0, 107.7, 117.9, 131.3, 141.9, 191.3; FAB-MS obsd 413.3171, calcd 413.3168 ($C_{26}H_{40}N_2O_2$). Anal. Calcd for $C_{26}H_{40}N_2O_2$: C, 75.68; H, 9.77; N, 6.79. Found: C, 75.95; H, 9.74; N, 6.82.

1,9-Bis{4-[2-(triisopropylsilyl)ethynyl]benzoyl}-5-(4-*tert*-butylphenyl)dipyrromethane (4l). Following the general diacylation procedure, reaction of **2g** (1.39 g, 5.00 mmol) in toluene (100 mL) with **3** (4.01 g, 12.5 mmol) afforded a 2:1 product ratio; column chromatography [silica, CH_2Cl_2/ethyl acetate (60:1)] followed by slow precipitation from 2-propanol/water gave an amorphous solid (1.61 g, 38%). mp 151−152 °C; ^{1}H NMR δ 1.13 (s, 42H), 1.34 (s, 9H), 5.61 (s, 1H), 6.00 (m, 2H), 6.56 (m, 2H), 7.39 (m, 4H), 7.49 (d, J = 8.1 Hz, 4H), 7.71 (d, J = 8.1 Hz, 4H), 11.07 (br, 2H); ^{13}C NMR δ 11.6, 18.9, 31.7, 34.9, 44.8, 94.1, 106.6, 111.7, 121.0, 126.2, 127.2, 128.7, 129.7, 131.9, 137.1, 137.8, 141.6, 150.8, 183.7; FAB-MS obsd 846.5005, calcd 846.4976 ($C_{55}H_{70}N_2O_2Si_2$). Anal. Calcd for $C_{55}H_{70}N_2O_2Si_2$: C, 77.96; H, 8.33; N, 3.31. Found: C, 77.78; H, 8.33; N, 3.34.

1,9-Bis{4-[2-(triisopropylsilyl)ethynyl]benzoyl}-5-(4-iodophenyl)dipyrromethane (4m). Following the general diacylation procedure, reaction of **2h** (0.35 g, 1.0 mmol) with **3** (0.80 g, 2.5 mmol) resulted in no detectable monoacyl compound; column chromatography [silica, CH_2Cl_2/ethyl acetate (9:1)] followed by slow precipitation from ethanol gave

an amorphous solid (0.36 g, 39%). mp 212−214 °C; ^{1}H NMR δ 1.17 (s, 42H), 5.64 (s, 1H), 5.97 (m, 2H), 6.49 (m, 2H), 7.38 (d, J = 8.1 Hz, 2H), 7.52 (d, J = 8.7 Hz, 4H), 7.69 (d, J = 8.7 Hz, 4H), 7.76 (d, J = 8.1 Hz, 2H), 11.75 (br, 2H); ^{13}C NMR δ 11.2, 18.6, 44.7, 93.2, 94.0, 106.2, 111.6, 120.9, 127.0, 129.5, 130.9, 131.0, 131.6, 137.2, 138.0, 140.0, 140.7, 183.5; FAB-MS obsd 916.3311, calcd 916.3316 ($C_{51}H_{61}IN_2O_2Si_2$). Anal. Calcd for $C_{51}H_{61}IN_2O_2Si_2$: C, 66.79; H, 6.70; N, 3.05. Found: C, 66.70; H, 6.80; N, 3.01.

1,9-Bis(4-*tert*-butylbenzoyl)-5-(4-*tert*-butylphenyl)dipyrromethane (4n). Following the general diacylation procedure, reaction of **2g** (4.17 g, 15.0 mmol) in toluene (300 mL) with 4-*tert*-butylbenzoyl chloride (7.30 mL, 37.5 mmol) afforded a 1.9:1 product ratio; column chromatography [silica, CH_2Cl_2/ethyl acetate (10:1)] followed by slow precipitation from 2-propanol/water gave an amorphous solid (5.21 g, 58%). mp 140−142 °C; ^{1}H NMR δ 1.34 (s, 9H), 1.36 (m, 18H), 5.61 (s, 1H), 6.09 (m, 2H), 6.77 (m, 2H), 7.28 (d, J = 7.2 Hz, 2H), 7.39 (d, J = 8.1 Hz, 2H), 7.46 (d, J = 7.2 Hz, 4H), 7.77 (d, J = 8.1 Hz, 4H), 10.09 (br, 2H); ^{13}C NMR δ 31.4, 31.6, 34.8, 35.2, 44.5, 111.1, 120.6, 125.3, 126.1, 128.5, 129.5, 131.2, 135.8, 140.7, 150.6, 155.4, 184.5; FAB-MS obsd 598.3544, calcd 598.3559 ($C_{41}H_{46}N_2O_2$). Anal. Calcd for $C_{41}H_{46}N_2O_2$: C, 82.24; H, 7.74; N, 4.68. Found: C, 81.91; H, 7.69; N, 4.77.

1,9-Bis(3,5-di-*tert*-butylbenzoyl)-5-(4-iodophenyl)dipyrromethane (4o). Following the general diacylation procedure, reaction of **2h** (1.04 g, 3.00 mmol) with 3,5-di-*tert*-butylbenzoyl chloride (1.90 g, 7.50 mmol) afforded a 0.7:1 product ratio; column chromatography [silica, CH_2Cl_2/ethyl acetate (15:1)] followed by slow precipitation from 2-propanol/water gave an amorphous solid (0.56 g, 24%). mp 172−175 °C; ^{1}H NMR δ 1.05 (s, 36H), 5.47 (s, 1H), 5.70 (m, 2H), 6.25 (m, 2H), 7.24 (m, 8H), 7.47 (d, J = 7.8 Hz, 2H), 12.18 (br, 2H); ^{13}C NMR δ 31.6, 35.2, 45.3, 93.1, 111.4, 121.3, 124.5, 125.8, 131.4, 131.5, 138.1, 138.3, 140.7, 150.6, 185.8; FAB-MS obsd 780.3184, calcd 780.3152 ($C_{45}H_{53}IN_2O_2$). Anal. Calcd for $C_{45}H_{53}IN_2O_2$: C, 69.22; H, 6.84; N, 3.59. Found: C, 68.82; H, 6.74; N, 3.63.

1,9-Bis(4-*tert*-butylbenzoyl)-5-(4-iodophenyl)dipyrromethane (4p). Following the general diacylation procedure, reaction of **2h** (3.48 g, 10.0 mmol) with 4-*tert*-butylbenzoyl chloride (5.90 mL, 25.0 mmol) afforded a 1.6:1 product ratio; column chromatography [silica, CH_2Cl_2/ethyl acetate (10:1)] followed by slow precipitation from 2-propanol/water gave an amorphous solid (2.93 g, 44%). mp 168−169 °C; ^{1}H NMR δ 1.26 (s, 18H), 5.61 (s, 1H), 5.88 (m, 2H), 6.78 (m, 2H), 7.15 (d, J = 8.1 Hz, 2H), 7.24 (d, J = 8.5 Hz, 4H), 7.50 (m, 6H), 11.83 (br, 2H); ^{13}C NMR δ 32.7, 46.1, 94.4, 112.5, 122.2, 126.5, 131.1, 132.4, 132.7, 137.0, 139.3, 141.8, 141.9, 156.6, 185.9; FAB-MS obsd 668.1917, calcd 668.1900 ($C_{37}H_{37}IN_2O_2$). Anal. Calcd for $C_{37}H_{37}IN_2O_2$: C, 66.47; H, 5.58; N, 4.19. Found: C, 66.42; H, 5.64; N, 4.11.

1,9-Dimesitoyl-5-mesityldipyrromethane (4q). Following the general diacylation procedure, reaction of **2d** (0.53 g, 2.0 mmol) in toluene (40 mL) with mesitoyl chloride (0.83 mL g, 5.0 mmol), followed by column chromatography [silica, CH_2Cl_2/ethyl acetate (98:2)] and recrystallization from CH_2Cl_2/hexanes gave yellowish plates (0.23 g, 19%). (A ratio of monoacyl and diacyl dipyrromethanes could not be determined by ^{1}H NMR analysis of the crude reaction mixture.) mp 159−161 °C; ^{1}H NMR 2.08 and 2.15 (2s, 18H), 2.28, 2.29 and 2.30 (3s, 9H), 5.88 (s, 1H), 6.11 (m, 1H), 6.41 (s, 1H), 6.58 (s, 1H), 6.83 (s, 2H), 6.85 (s, 2H), 6.87 (m, 1H), 6.90 (s, 2H), 8.19 (br, 1H), 9.02 (br, 1H). Anal. Calcd for $C_{38}H_{40}N_2O_2$: C, 81.98; H, 7.24; N, 5.03. Found: C, 81.78; H, 7.41; N, 5.01.

General Monoacylation Procedure, Exemplified for 1-{4-[2-(Trimethylsilyl)ethynyl]benzoyl}-5-mesityldipyrromethane (5d). A solution of EtMgBr in THF (25 mL, 25 mmol, 1 M) was added to a solution of 5-mesityldipyrromethane (**2d**, 2.64 g, 10.0 mmol) in dry THF (10 mL) at room temperature. After stirring for 10 min, the flask was cooled to −78 °C, and a solution of *S*-2-pyridyl 4-[2-(trimethylsilyl)-ethynyl]benzothioate (**6f**, 3.11 g, 10.0 mmol) in THF (10 mL) was added. Then the cooling bath was removed, the mixture was stirred for 30 min, and then the reaction mixture was quenched with satd aq NH_4Cl. The organic layer was washed with brine, dried (Na_2SO_4), and concentrated. Column chromatography [silica, CH_2Cl_2 → CH_2Cl_2/ethyl acetate (95:5)] afforded a foamlike solid. Recrystallization from hexanes provided a yellowish amorphous solid (3.92 g, 84%). mp 131−132 °C; ^{1}H NMR δ 0.26 (s, 9H), 2.08 (s, 6H), 2.29 (s, 3H), 5.94 (s, 1H), 6.12 (m, 2H), 6.21 (m, 1H), 6.68 (m, 1H), 6.79 (m, 1H), 6.89 (s, 2H), 7.53 (d, J = 8.1 Hz, 2H), 7.79 (d, J = 8.1 Hz, 2H), 7.85 (br, 1H), 9.24 (br, 1H); ^{13}C NMR δ 0.03, 20.8, 20.9, 38.7, 97.2, 104.4, 107.3, 109.0, 110.3, 117.1, 120.7, 126.6, 128.8, 129.1, 129.8, 130.7, 131.9, 133.1, 137.3, 137.5, 138.1, 141.4, 183.2. Anal. Calcd for $C_{30}H_{32}N_2OSi$: C, 77.54; H, 6.94; N, 6.03. Found: C, 77.47; H, 6.94; N, 6.03.

1-{4-[2-(Trimethylsilyl)ethynyl]benzoyl}-5-(pentafluorophenyl)dipyrromethane (5e). Following the general monoacylation procedure, reaction of **2b** (2.81 g, 9.00 mmol) and **6f** (2.80 g, 9.00 mmol) followed by column chromatography [silica, CH_2Cl_2/ethyl acetate (98:2)] and then crystallization from methanol afforded pale yellow needles (2.85 g, 62%). mp 167 °C; ^{1}H NMR δ 0.28 (s, 9H), 5.93 (s, 1H), 6.07 (m, 2H), 6.13 (m, 1H), 6.69 (m, 1H), 6.77 (m, 1H), 7.55 (d, J = 8.1 Hz, 2H), 7.77 (d, J = 8.1 Hz, 2H), 8.49 (br, 1H), 10.38 (br, 1H); ^{13}C NMR δ 0.00, 33.4, 97.8, 104.2, 108.5, 109.0, 110.6, 114.9, 118.8, 120.9, 126.6, 127.2, 129.1, 131.0, 132.0, 137.5, 138.3, 143.4, 184.1. Anal. Calcd for $C_{27}H_{21}F_5N_2OSi$: C, 63.27; H, 4.13; N, 5.47. Found: C, 63.27; H, 4.14; N, 5.42.

1-(4-Bromobenzoyl)-5-{4-[2-(trimethylsilyl)ethynyl]-phenyl}dipyrromethane (5f). Following the general monoacylation procedure, reaction of **2e** (4.77 g, 15.0 mmol) and **6d** (4.41 g, 15.0 mmol) followed by column chromatography [silica, CH_2Cl_2/ethyl acetate (98:2)] and then slow precipitation from CH_2Cl_2/hexanes afforded a pale yellow amorphous powder (5.81 g, 77%). mp 151−152 °C (dec); ^{1}H NMR δ 0.25 (s, 9H), 5.54 (s, 1H), 5.97 (br, 1H), 6.06 (m, 1H), 6.17 (m, 1H), 6.69 (m, 1H), 6.78 (m, 1H), 7.12 (d, J = 8.1 Hz, 2H), 7.38 (d, J = 8.1 Hz, 2H) 7.58−7.68 (m, 4H), 8.20 (br, 1H), 9.83 (br, 1H); ^{13}C NMR δ 0.68, 44.5, 105.3, 108.7, 109.1, 111.8, 118.7, 122.2, 127.4, 128.8, 131.0, 131.2, 132.2, 132.8, 137.6, 141.8, 142.9, 184.2. Anal. Calcd for $C_{27}H_{25}BrN_2OSi$: C, 64.67; H, 5.02; N, 5.59. Found: C, 64.92; H, 5.21; N, 5.39.

1-(4-*tert*-Butylbenzoyl)-5-(4-*tert*-butylphenyl)dipyrromethane (5g). Following the general monoacylation procedure, reaction of **2g** (5.56 g, 20.0 mmol) and **6e** (5.43 g, 20.0 mmol) followed by column chromatography [silica, CH_2Cl_2/ethyl acetate (98:2)] and then slow precipitation from hexanes/CH_2Cl_2 afforded colorless amorphous granules (7.11 g, 81%). mp 198−200 °C; ^{1}H NMR δ 1.29 (s, 9H), 1.37 (s, 9H), 5.55 (s, 1H), 6.02 (br, 1H), 6.12 (m, 1H), 6.16 (m, 1H), 6.67 (m, 1H), 6.83 (m, 1H), 7.14 (m, 2H), 7.31 (m, 2H), 7.48 (m, 2H), 7.75 (m, 2H), 8.34 (br, 1H), 9.93 (br, 1H); ^{13}C NMR δ 31.3, 31.4, 34.5, 35.1, 43.7, 107.7, 108.2, 110.7, 117.9, 121.5, 125.3, 125.6, 128.0, 129.1, 130.9, 131.6, 135.8, 138.0, 142.5, 149.9, 155.4, 184.8. Anal. Calcd for $C_{30}H_{34}N_2O$: C, 82.15; H, 7.81; N, 6.39. Found: C, 81.98; H, 8.07; N, 6.13.

***S*-2-Pyridyl 4-bromobenzothioate (6d).** Treatment of 2-mercaptopyridine (7.18 g, 64.6 mmol) with 4-bromobenzoyl chloride (14.17 g, 64.6 mmol) in CH_2Cl_2 (300 mL) according to the reported procedure,[6] followed by recrystallization from ethyl acetate/hexanes, afforded colorless needles (14.62 g, 77%). mp 132−133 °C; ^{1}H NMR δ 7.29−7.33 (m, 1H), 7.59−7.62 (m, 2H), 7.67−7.78 (m, 2H), 7.83−7.87 (m, 2H), 8.64−8.66 (m, 1H); ^{13}C NMR δ 124.5, 129.6, 129.7, 131.5, 132.8, 135.9, 137.9, 151.1, 151.2, 189.0. Anal. Calcd for $C_{12}H_8BrNOS$: C, 49.00; H, 2.74; N, 4.76. Found: C, 49.26; H, 2.76; N, 4.77.

***S*-2-Pyridyl 4-*tert*-butylbenzothioate (6e).** Treatment of 2-mercaptopyridine (4.44 g, 40.0 mmol) with 4-*tert*-butylbenzoyl chloride (7.86 g, 40.0 mmol) in CH_2Cl_2 (200 mL) according to the reported procedure,[6] followed by recrystallization from hexanes, afforded colorless flakes (9.56 g, 88%). mp 91−92 °C; ^{1}H NMR δ 1.35 (s, 9H), 7.30−7.35 (m, 1H), 7.50 (m, 2H), 7.72−7.79 (m, 2H), 7.96 (m, 2H), 8.67 (m, 1H); ^{13}C NMR δ 31.7, 35.9, 124.2, 126.5, 128.2, 131.5, 134.5, 137.7, 151.1, 152.2, 158.4, 189.4. Anal. Calcd for $C_{16}H_{17}NOS$: C, 70.81; H, 6.31; N, 5.16. Found: C, 70.97; H, 6.38; N, 5.16.

***S*-2-Pyridyl 4-[2-(trimethylsilyl)ethynyl]benzothioate (6f).** The following is a refined procedure. A mixture of **6c** (10.23 g, 30.0 mmol), $Pd_2(dba)_3$ (0.46 g, 0.50 mmol), PPh_3 (1.05 g, 4.00 mmol), and CuI (0.57 mg, 3.0 mmol) was placed in a Schlenk flask. The flask was pump-filled with Ar three times, and then a degassed (argon) mixture of THF (60 mL) and triethylamine (20 mL) was introduced followed by trimethylsilylacetylene (4.24 mL, 36.0 mmol). The flask was sealed tightly, and the contents were stirred for 1 h at 50 °C and 12 h at room temperature. The solid was filtered off, and the filtrate was concentrated. Flash column chromatography [silica, hexanes/ethyl acetate (4:1)] afforded a brown solid. Recrystallization (ethyl acetate) afforded pale yellow crystals (6.54 g, 70%). Analytical data are consistent with literature values.[6]

Procedure A for Acylation of Monoacyl Dipyrromethanes, Exemplified for 1-Benzoyl-5-(4-methoxyphenyl)-9-(4-methylbenzoyl)dipyrromethane (7a). 1-Benzoyl-5-(4-methoxyphenyl)dipyrromethane (**5b**, 0.18 mg, 0.50 mmol) was dissolved in dry toluene (2 mL). To this solution, EtMgBr (3.0 mL, 3.0 mmol, 1.0 M solution in THF) was slowly added at room temperature under argon. After stirring for 10 min, *p*-toluoyl chloride (0.20 mL, 1.5 mmol) was added, and stirring was continued for 30 min. Then satd aq NH_4Cl (10 mL) and ethyl acetate (10 mL) were added. The organic layer was separated, dried (Na_2SO_4), and concentrated. Column chromatography of the residue [silica, CH_2Cl_2/ethyl acetate (95:5)] afforded 0.16 g (66%) of a yellow amorphous powder. ^{1}H NMR δ 2.38 (s, 3H), 3.81 (s, 3H), 5.62 (s, 1H), 5.96 (m, 2H), 6.53 (m, 2H), 6.90 (m, 2H), 7.18 (d, J = 8.1 Hz, 2H), 7.35−7.48 (m, 5H), 7.67 (d, J = 8.1 Hz, 2H), 7.75 (m, 2H), 11.48 (br, 2H); ^{13}C NMR δ 24.2, 46.8, 57.9, 113.6, 113.7, 116.8, 123.1, 123.5, 130.6, 131.3, 132.2, 132.3, 132.5, 133.5, 133.7, 134.1, 135.1, 138.2, 140.9, 143.6, 144.1, 144.7, 161.5, 186.9, 187.1. Anal. Calcd for $C_{31}H_{26}N_2O_3$: C, 78.46; H, 5.52; N, 5.90. Found: C, 78.10; H, 5.62; N, 5.77.

1-Benzoyl-5-(4-methoxyphenyl)-9-(pentafluorobenzoyl)-dipyrromethane (7b). Following acylation procedure A, reaction of **5b** (0.23 g, 0.65 mmol) and pentafluorobenzoyl chloride (0.29 mL, 2.0 mmol) followed by column chromatography [silica, CH_2Cl_2/ethyl acetate (95:5)] and recrystallization from ether/hexanes afforded colorless needles (0.18 g, 49%). mp 123−124 °C; ^{1}H NMR δ 3.76 (s, 3H), 5.68 (s, 1H), 6.07 (m, 2H), 6.61 (m, 1H), 6.77 (m, 3H), 7.11 (m, 2H), 7.40−7.55 (m, 3H), 7.76−7.79 (m, 2H), 10.45 and 10.72 (br, 2H); ^{13}C NMR δ 43.6, 55.3, 110.9, 112.0, 114.3, 121.4, 122.7, 128.3, 129.2, 129.6, 131.1, 131.3, 132.0, 138.3, 140.7, 144.4, 159.1, 171.9, 185.1. Anal. Calcd for $C_{30}H_{19}F_5N_2O_3$: C, 65.46; H, 3.48; N, 5.09. Found: C, 65.57; H, 3.51; N, 4.93.

1-Benzoyl-5-(pentafluorophenyl)-9-(4-methoxybenzoyl)-dipyrromethane (7c). Following acylation procedure A, reaction of **5c** (0.21 g, 0.50 mmol) and *p*-anisoyl chloride (0.20 mL, 1.5 mmol) followed by column chromatography [silica, CH_2Cl_2/ethyl acetate (95:5)] and recrystallization from ether/hexanes afforded colorless needles (0.16 g, 58%). mp 124−125 °C; ^{1}H NMR δ 3.87 (s, 3H), 6.11 (m, 3H), 6.68 (m, 2H), 6.93 (m, 2H), 7.41−7.54 (m, 3H), 7.79−7.85 (m, 4H), 10.68 (br, 2H); ^{13}C NMR δ 33.7, 55.5, 110.6, 110.7, 113.6, 119.7, 120.6, 128.3, 129.6, 129.9, 130.6, 131.4, 131.5, 131.9, 132.0, 135.6, 136.5, 138.1, 139.3, 139.6, 143.5, 146.9, 162.9, 183.5, 184.7. Anal. Calcd for $C_{30}H_{19}F_5N_2O_3$: C, 65.46; H, 3.48; N, 5.09. Found: C, 65.40; H, 3.56; N, 5.07.

1-(4-Iodobenzoyl)-5-(pentafluorophenyl)-9-{4-[2-(trimethylsilyl)ethynyl]benzoyl}dipyrromethane (7d). Following acylation procedure A, reaction of **5e** (2.05 g, 4.00 mmol) and 4-iodobenzoyl chloride (3.19 g, 12.0 mmol) followed by column chromatography [silica, hexanes/2-propanol (9:1)] and slow precipitation from ethanol furnished a pink amorphous solid (1.48 g, 50%). mp 135−136 °C; ^{1}H NMR δ 0.26 (s, 9H), 6.07 (m, 2H), 6.13 (s, 1H), 6.59 (m, 2H), 7.47−7.52 (m, 4H), 7.70−7.80 (m, 4H), 11.05 (br, 2H); ^{13}C NMR δ −0.1, 33.5, 97.5, 99.4, 104.1, 110.7, 113.6, 120.4, 126.9, 127.9, 129.3, 130.9, 131.1, 131.6, 136.2, 136.5, 136.9, 137.1, 137.4, 138.9, 143.5, 146.2, 183.3. Anal. Calcd for $C_{34}H_{24}F_5IN_2O_2Si$: C, 54.99; H, 3.26; N, 3.77. Found: C, 55.19; H, 3.39; N, 3.62.

Procedure B for Acylation of Monoacyl Dipyrromethanes, Exemplified for 1-(4-Iodobenzoyl)-5-mesityl-9-{4-[2-(trimethylsilyl)ethynyl]benzoyl}dipyrromethane (7e). To a stirred solution of monoacyl dipyrromethane **5d** (2.32 g, 5.00 mmol) in dry toluene (20 mL) at room temperature was added EtMgBr (10 mL, 10 mmol, 1 M in THF) slowly under argon, and the mixture was stirred for 5 min. To the resulting mixture was added 4-iodobenzoyl chloride (1.33 g, 5.00 mmol). After 10 min, the same process was repeated once. After stirring for 10 min (TLC indicated incomplete but relatively clean reaction), the mixture was treated with additional EtMgBr (5.0 mL, 5.0 mmol, 1 M in THF) followed by 4-iodobenzoyl chloride (0.67 g, 2.5 mmol). After stirring the contents for 20 min, satd aq NH_4Cl and ethyl acetate were added. The organic layer was separated, dried (Na_2SO_4), and concentrated. Purification by column chromatography [silica, CH_2Cl_2/ethyl acetate (98:2)] followed by slow precipitation from CH_2Cl_2/methanol afforded a pink amorphous solid (2.36 g, 68%). mp 147−148 °C; ^{1}H NMR δ 0.27 (s, 9H), 2.25 (s, 6H), 2.33 (s, 3H), 5.94 (m, 2H), 6.21 (s, 1H), 6.58 (m, 2H), 6.94 (s, 2H), 7.40 (d, J = 7.8 Hz, 2H), 7.46 (d, J = 8.1 Hz, 2H), 7.63 (d, J = 7.8 Hz, 2H), 7.73 (d, J = 8.1 Hz, 2H), 11.42 (br, 2H); ^{13}C NMR δ 0.7, 21.8, 40.1, 99.7, 105.2, 111.6, 122.0, 127.2, 130.0, 130.8, 131.1, 131.2, 131.7, 132.4, 133.8, 138.0, 138.1, 138.3, 138.5, 141.1, 141.4, 183.5. Anal. Calcd for $C_{37}H_{35}IN_2O_2Si$: C, 63.97; H, 5.08; N, 4.03. Found: C, 63.85; H, 5.06; N, 3.91.

1-{4-[2-(Triisopropylsilyl)ethynyl]benzoyl}-5-mesityl-9-{4-[2-(trimethylsilyl)ethynyl]benzoyl}dipyrromethane (7f). Following acylation procedure B, reaction of **5d** (2.32 g, 5.00 mmol) and **3** (4.00 g, 12.5 mmol) followed by column chromatography [silica, CH_2Cl_2/ethyl acetate (98:2)] and slow precipitation from 2-propanol afforded a brown amorphous solid (2.45 g, 65%). mp 148−150 °C; ^{1}H NMR δ 0.30 (s, 9H), 1.18 (s, 21H), 2.33 (s, 6H), 2.37 (s, 3H), 5.94−5.95 (m, 2H), 6.32 (s, 1H), 6.58 (s, 2H), 6.98 (s, 2H), 7.49−7.52 (m, 4H), 7.66 (m, 4H), 11.93 (br, 2H); ^{13}C NMR δ 0.06, 11.4, 18.8, 21.1, 39.5, 93.6, 97.1, 104.4, 104.5, 106.6, 110.9, 121.4, 121.5, 126.4, 126.7, 129.4, 130.4, 131.7, 131.7, 133.4, 137.1, 137.7, 137.8, 137.9, 140.8, 182.8. Anal. Calcd for $C_{48}H_{56}N_2O_2Si_2$: C, 76.96; H, 7.53; N, 3.74. Found: C, 76.68; H, 7.57; N, 3.60.

1-(4-Bromobenzoyl)-5-{4-[2-(trimethylsilyl)ethynyl]-phenyl}-9-(4-iodobenzoyl)dipyrromethane (7g). Monoacyl dipyrromethane **5f** (4.51 g, 9.00 mmol) and 4-iodobenzoyl chloride (6.00 g, 22.5 mmol) were reacted following acylation procedure B. TLC analysis indicated the presence of a trace amount of monoacyl dipyrromethane. Column chromatography [silica, CH_2Cl_2/ethyl acetate (95:5)] followed by slow precipitation from ethanol afforded a pink amorphous solid (4.61 g, 69%). mp > 225 °C; ^{1}H NMR δ 0.25 (s, 9H), 5.63 (s, 1H), 5.91 (m, 2H), 6.46 (m, 2H), 7.42 (d, J = 8.1 Hz, 2H), 7.48 (s, 4H), 7.55 (m, 4H), 7.74 (d, J = 8.1 Hz, 2H), 11.77 (br, 2H); ^{13}C NMR δ 0.19, 45.1, 94.9, 99.5, 104.8, 111.8, 121.1, 122.6, 126.9, 128.9, 130.9, 131.4, 131.5, 132.6, 136.7, 137.3, 137.4, 140.7, 141.3, 183.4, 183.6. Anal. Calcd for $C_{34}H_{28}BrIN_2O_2Si$: C, 55.83; H, 3.86; N, 3.83. Found: C, 55.53; H, 3.84; N, 3.73.

1-(4-*tert*-Butylbenzoyl)-5-(4-*tert*-butylphenyl)-9-(4-iodobenzoyl)dipyrromethane (7h). Monoacyl dipyrromethane **5g** (4.39 g, 10.0 mmol) and 4-iodobenzoyl chloride (6.65 g, 25.0 mmol) were reacted following acylation procedure B. TLC analysis indicated the presence of a trace amount of monoacyl dipyrromethane. Column chromatography [silica, CH_2Cl_2/ethyl acetate (95:5)] followed by slow precipitation from CH_2Cl_2/methanol afforded a brown amorphous solid (5.12 g, 76%). mp 158−160 °C; ^{1}H NMR δ 1.35 (s, 18H), 5.64 (s, 1H), 5.98−6.03 (m, 2H), 6.57 (m, 1H), 6.63 (m, 1H), 7.39 (m, 4H), 7.42 (m, 2H), 7.50 (m, 2H), 7.71−7.78 (m, 4H), 11.13 (br, 2H); ^{13}C NMR δ 31.8, 32.0, 35.2, 35.6, 45.1, 99.6, 111.7, 112.0, 121.1, 121.5, 125.6, 126.4, 129.0, 130.1, 131.2, 131.7, 136.1, 137.6, 137.9, 138.2, 141.4, 142.5, 150.9, 155.8, 184.0. Anal. Calcd for $C_{37}H_{37}IN_2O_2$: C, 66.47; H, 5.58; N, 4.19. Found: C, 66.81; H, 5.70; N, 4.08.

1-(4-*tert*-Butylbenzoyl)-5-(4-*tert*-butylphenyl)-9-{4-[2-(triisopropylsilyl)ethynyl]benzoyl}dipyrromethane (7i).

Following acylation procedure B, reaction of **5g** (2.19 g, 5.00 mmol) and **3** (4.00 g, 12.5 mmol) followed by column chromatography [silica, CH_2Cl_2/ethyl acetate (95:5)] and slow precipitation from ethanol afforded a brown amorphous solid (2.42 g, 67%). mp 148−151 °C (dec); ^{1}H NMR δ 1.12 (s, 21H), 1.35 (s, 18H), 5.62 (s, 1H), 6.03 (m, 2H), 6.61−6.67 (m, 2H), 7.34−7.53 (m, 8H), 7.75 (d, J = 9.0 Hz, 4H), 10.73 (br, 2H); ^{13}C NMR δ 11.9, 19.3, 31.8, 32.0, 35.2, 35.6, 45.1, 94.3, 107.0, 111.7, 112.0, 121.2, 121.4, 121.5, 125.6, 126.4, 127.4, 129.1, 130.1, 130.2, 131.5, 131.8, 132.2, 136.2, 137.7, 138.4, 141.5, 150.9, 155.7, 184.1, 185.0. Anal. Calcd for $C_{48}H_{58}N_2O_2Si$: C, 79.73; H, 8.09; N, 3.87. Found: C, 79.69; H, 8.13; N, 3.73.

1-(4-Iodobenzoyl)-5-(pentafluorophenyl)-9-(pentafluorobenzoyl)dipyrromethane (7j). Monoacyl dipyrromethane **5h** (2.53 g, 5.00 mmol) and 4-iodobenzoyl chloride (1.33 g, 5.0 mmol) were reacted following acylation procedure B. TLC analysis indicated the presence of a considerable amount of monoacyl dipyrromethane. Then additional EtMgBr (5.0 mL, 5.0 mmol, 1.0 M) followed by 4-iodobenzoyl chloride (0.67 g, 2.5 mmol) were added. Column chromatography [silica, CH_2Cl_2/ethyl acetate (95:5)] followed by slow precipitation from hexanes afforded a pink amorphous solid which was found to be a mixture of two compounds (^{1}H NMR analysis). The desired compound was obtained as a cotton-like solid (0.81 g, 22%) after recrystallization from methanol. ^{1}H NMR δ 6.06 (s, 1H), 6.18 (m, 2H), 6.65 (m, 1H), 6.76 (m, 1H), 7.54 (m, 2H), 7.82 (m, 2H), 10.27 (br, 2H); FAB-MS obsd 735.9728, calcd 735.9706. Anal. Calcd for $C_{29}H_{11}F_{10}IN_2O_2$: C, 47.31; H, 1.51; N, 3.80. Found: C, 45.99; H, 1.81; N, 3.63.

General Procedures for Porphyrin Formation: Reduction of Diacyl Dipyrromethanes. Method 1.[17] A sample of $NaBH_4$ (50 mmol, 50 mol equiv) was added in small portions (every 5 min) to a stirred solution of a diacyl dipyrromethane (**4** or **7**, 1.0 mmol) in THF/methanol (3:1, 80 mL) in a round-bottomed flask open to the atmosphere. A significant evolution of gas occurred throughout the course of this reaction. The progress of the reduction was monitored by TLC [alumina, CH_2Cl_2/ethyl acetate]. After the reaction was complete (about 40 min), the reaction mixture was quenched with water (20 mL) and poured into CH_2Cl_2 (100 mL). The organic phase was isolated, washed with water (2 × 100 mL), and dried (K_2CO_3). Removal of solvent afforded the dicarbinol as a foamlike solid.

Method 2. A sample of $NaBH_4$ (20 mmol, 20 mol equiv) was added in small portions (every 2 min) to a stirred solution of a diacyl dipyrromethane (**4** or **7**, 1.0 mmol) in dry THF/methanol (10:1, 44 mL) in a round-bottomed flask. The flask, fitted with a vented rubber septum and flooded with argon, was opened as needed to add the $NaBH_4$. A modest evolution of gas occurred throughout the course of this reaction. The progress of the reduction was monitored by TLC [alumina, CH_2Cl_2/ethyl acetate]. After the reaction was complete (about 40 min), the reaction mixture was poured into a stirred mixture of satd aq NH_4Cl (100 mL) and CH_2Cl_2 (100 mL). The satd aq NH_4Cl is essential to buffer the solution (e.g., thereby avoiding cleavage of TMS groups). The organic phase was isolated, washed with water (2 × 100 mL), and dried (Na_2SO_4). Removal of solvent afforded the dicarbinol as a foamlike solid.

Exemplary Large-scale Procedure, Given for 5-(4-Iodophenyl)-10-mesityl-15-{4-[2-(trimethylsilyl)ethynyl]phenyl}-20-{4-[2-(triisopropylsilyl)ethynyl]phenyl}porphyrin (13b). A sample of diacyl dipyrromethane **7e** (2.50 g, 3.60 mmol) was dissolved in dry THF/methanol (10:1, 160 mL) at room temperature in a 500-mL round-bottomed flask fitted with a vented rubber septum and flooded with argon. The septum was removed as needed to add $NaBH_4$ (2.72 g, 72.0 mmol, 20 mol equiv) in small portions (~0.5 g, every 2 min) with rapid stirring (reduction method 2). The progress of the reduction was monitored by TLC analysis [alumina, CH_2Cl_2/ethyl acetate (3:2)] of reaction aliquots. After the reaction was complete (about 40 min), the reaction mixture was poured into a stirred mixture of satd aq NH_4Cl (200 mL) and CH_2Cl_2 (400 mL) in a 1-L beaker. The organic phase was removed in a 1-L separatory funnel, washed with water (2 × 200 mL), dried (Na_2SO_4), and placed in a 2-L round-bottomed flask. Removal of solvent on a rotary evaporator under reduced pressure yielded the dicarbinol as a foamlike solid. To the 2-L flask containing the dipyrromethane-dicarbinol (3.6 mmol assuming quantitative reduction) was added dipyrromethane **2m** (1.45 g, 3.60 mmol) followed by reagent grade (A.C.S.) acetonitrile (1.44 L). The mixture was stirred for 5 min to achieve dissolution, and then TFA (3.33 mL, 43.2 mmol, 30 mM) was added in a steady slow stream over the course of 1 min with efficient stirring. The reaction was monitored by absorption spectroscopy after a total elapsed time of 1 and 2.5 min following the completion of TFA addition. [Reaction monitoring was performed by injecting a 25 μL reaction aliquot into a solution of DDQ (300 μL, 0.01 M in toluene); then 25 μL of the resulting oxidized mixture was dissolved in CH_2Cl_2/EtOH (3:1, 3 mL), and the absorption spectrum was recorded.[5,31]] The yield of porphyrin was about the same at the first (1 min) and second timepoints (2.5 min), indicating the dipyrromethane-dicarbinol + dipyrromethane condensation was complete. Then (elapsed time of 3.5 min after the addition of TFA) DDQ (2.45 g, 10.8 mmol) was added, and the mixture was stirred at room temperature for 1 h. Then triethylamine (6.02 mL, 43.2 mmol) was added, and the entire reaction mixture was filtered (to remove quinone species) through a pad of alumina (7.5 × 15 cm) and eluted with CH_2Cl_2 (~2 L) until the eluant was no longer dark. The resulting porphyrin-containing solution was concentrated by rotary evaporation to give a dark solid. The solid was redissolved in CH_2Cl_2 (100 mL) and passed through a pad of silica (7.5 × 20 cm) with CH_2Cl_2 elution to remove non-porphyrin products. Fractions were collected to obtain the porphyrin (fast-eluting) free of non-porphyrinic materials (slow-eluting). The purple fractions were combined and concentrated by rotary evaporation to give a purple solid. Recrystallization from CH_2Cl_2/methanol afforded a crystalline purple solid (1.05 g, 27%). ^{1}H NMR δ -2.71 (br, 2H), 0.41 (s, 9H), 1.29 (s, 21H), 1.86 (s, 6H), 2.65 (s, 3H), 7.31 (s, 2H), 7.91 (m, 4H), 7.96 (d, J = 8.1 Hz, 2H), 8.10 (d, J = 8.1 Hz, 2H), 8.18 (apparent t, J = 8.1 Hz, 4H), 8.74−8.86 (m, 8H); LD-MS obsd 1060.31; FAB-MS obsd 1058.3601, calcd 1058.3636 ($C_{63}H_{63}IN_4Si_2$).

Exemplary Small-scale Procedure, Given for 5,15-Diphenyl-10,20-bis(pentafluorophenyl)porphyrin (8b). A solution of diacyl dipyrromethane **4c** (0.18 g, 0.30 mmol) in dry THF/methanol (10:1, 13.2 mL) in a 50-mL round-bottomed flask (fitted with a rubber septum and flooded with argon) was reduced by adding portions of $NaBH_4$ (total amount 0.23 g, 6.0 mmol) (reduction method 2). After the reduction was complete (TLC monitoring as for **13b**), the reaction mixture was poured into satd aq NH_4Cl (20 mL) and CH_2Cl_2 (40 mL) in a 200-mL beaker. The organic layer was separated in a separatory funnel, washed twice with water, dried (Na_2SO_4), and placed in a 250-mL round-bottomed flask. Removal of the solvent by rotary evaporation under vacuum yielded the dicarbinol as a foamlike solid. Then 5-phenyldipyrromethane (**2a**, 67 mg, 0.30 mmol) and reagent-grade (A.C.S.) acetonitrile (120 mL) were added, and the mixture was stirred to achieve a homogeneous solution. Then TFA (0.280 mL, 3.65 mmol) was added in a slow steady stream over 5−10 s with rapid stirring. Reaction monitoring (as described for **13b**) showed rapid reaction, and after 5 min of elapsed time, DDQ (0.20 g, 0.90 mmol) was added. After stirring for 1 h at room temperature, triethylamine (0.507 mL, 3.65 mmol) was added, and the entire reaction mixture was filtered through a pad of alumina (4 × 8 cm) and eluted with CH_2Cl_2 (~150 mL) until the eluant was no longer dark. The resulting porphyrin solution was concentrated, redissolved in CH_2Cl_2 (30 mL), and passed through a pad of silica (4 × 8 cm) with CH_2Cl_2 elution to remove non-porphyrinic pigments. The purple fractions were combined and concentrated to give a purple solid which was recrystallized from CH_2Cl_2/methanol (58 mg, 24% from **4c**). ^{1}H NMR δ −2.83 (br, 2H), 7.78−7.84 (m, 6H), 8.20−8.25 (m, 4H), 8.80 (d, J = 4.5 Hz, 4H), 8.95 (d, J = 4.5 Hz, 4H); LD-MS obsd 796.50; FAB-MS obsd 794.1514, calcd 794.1528 ($C_{44}H_{20}F_{10}N_4$).

Notes Concerning the Porphyrin-Forming Reaction. (1) The condensation was monitored by absorption spectroscopy in order to add DDQ at the appropriate time (i.e., after condensation has leveled off). Samples were removed for

spectroscopic monitoring (DDQ oxidation and absorption spectroscopy) after 1 min, 2.5 min, 4 min, etc. If the yield was essentially the same for two successive timepoints, bulk oxidation was performed by adding DDQ to the reaction mixture. This generally occurred for the first and second timepoints (indicating the reaction was complete in ≤1 min); given manual constraints in experimentation the bulk oxidation was then generally started at ∼3.5 min following the completion of the addition of TFA. In the following procedures, the times given for DDQ oxidation reflect the number of timepoints collected [always 2 (addition of DDQ after 3−5 min), sometimes 3 (addition of DDQ after 5−7 min)] in spectroscopic yield monitoring of porphyrin formation. (2) The last sample obtained in spectroscopic yield monitoring also was examined by LD-MS to check for the presence of scrambled porphyrin products. (3) In the following procedures, "standard workup" refers to the following sequence of steps: (i) treatment with a sufficient amount of triethylamine to neutralize the TFA, (ii) filtration through alumina, (iii) evaporation of the solvent, (iv) dissolution in CH_2Cl_2 followed by column chromatography on silica, (v) evaporation of the solvent to obtain the porphyrin as a purple solid. Any further purification procedures are specified in individual preparations.

5,10,15-Tris(4-methoxyphenyl)-20-phenylporphyrin (9a). Reduction (method 2) of **4f** (0.26 g, 0.50 mmol) followed by condensation with **2a** (0.11 g, 0.50 mmol) for 4 min, oxidation with DDQ (0.34 g, 1.5 mmol), and standard workup and recrystallization from CH_2Cl_2/methanol furnished a purple solid (94 mg, 27% from **4f**). ^{1}H NMR δ −2.76 (br, 2H), 4.09 (s, 9H), 7.28 (d, J = 7.8 Hz, 6H), 7.74−7.76 (m, 3H), 8.12 (d, J = 7.8 Hz, 6H), 8.20−8.23 (m, 2H), 8.82−8.87 (m, 8H); LD-MS obsd 705.01; FAB-MS obsd 704.2780, calcd 704.2787 ($C_{47}H_{36}N_4O_3$).

5,10,15-Tris(pentafluorophenyl)-20-phenylporphyrin (9b). Reduction (method 2) of **4e** (0.21 g, 0.30 mmol) followed by condensation with **2a** (67 mg, 0.30 mmol) for 6 min, oxidation with DDQ (0.20 g, 0.90 mmol), and standard workup with an additional gravity column chromatography [silica, $CHCl_3$/hexanes (1:2)] furnished a purple solid (47 mg, 18% from **4e**). ^{1}H NMR δ −2.85 (br, 2H), 7.76−7.84 (m, 3H), 8.19−8.23 (m, 2H), 8.81 (d, J = 4.5 Hz, 2H), 8.89 (m, 4H), 8.96 (d, J = 4.5 Hz, 2H); LD-MS obsd 885.83; FAB-MS obsd 884.1083, calcd 884.1057 ($C_{44}H_{15}F_{15}N_4$).

5,10,15-Tris(4-*tert*-butylphenyl)-20-(4-iodophenyl)porphyrin (9c). Reduction (method 2) of **4n** (2.56 g, 4.30 mmol) followed by condensation with **2h** (1.50 g, 4.30 mmol) for 4 min, oxidation with DDQ (2.92 g, 13.0 mmol), and standard workup furnished a purple solid which was suspended in methanol, sonicated for 5 min, filtered, and dried (0.98 g, 25% from **4n**). ^{1}H NMR δ −2.78 (br, 2H), 1.61 (s, 27H), 7.75 (d, J = 8.1 Hz, 6H), 7.94 (d, J = 8.1 Hz, 2H), 8.09 (d, J = 8.1 Hz, 2H), 8.13 (d, J = 8.1 Hz, 4H), 8.14 (d, J = 8.1 Hz, 2H), 8.79 (d, J = 4.5 Hz, 2H), 8.88−8.91 (m, 6H); LD-MS obsd 908.96; FAB-MS obsd 908.3301, calcd 908.3315 ($C_{56}H_{53}IN_4$).

5,10,15-Tris(4-*tert*-butylphenyl)-20-(4-carboxyphenyl)-porphyrin (9d). Reduction (method 2) of **4n** (0.18 g, 0.30 mmol) followed by condensation with **2i** (80 mg, 0.30 mmol) for 5 min, oxidation with DDQ (0.20 g, 0.90 mmol), and use of polar solvents in the standard workup (alumina, THF/acetic acid (10:1); silica, CH_2Cl_2/methanol (10:1)) furnished a purple solid which was suspended in methanol, sonicated for 5 min, filtered, and dried (44 mg, 18% from **4n**). ^{1}H NMR δ −2.55 (br, 2H), 1.64 (s, 27H), 7.79 (d, J = 7.8 Hz, 6H), 8.17 (d, J = 8.1 Hz, 6H), 8.38 (d, J = 8.7 Hz, 2H), 8.54 (d, J = 8.1 Hz, 2H), 8.81 (d, J = 4.5 Hz, 2H), 8.91−8.95 (m, 6H) (acid hydrogen not observed); LD-MS obsd 828.19; FAB-MS obsd 826.4264, calcd 826.4247 ($C_{57}H_{54}N_4O_2$).

5,10,15-Tripentyl-20-phenylporphyrin (9e). Reduction (method 1) of **4k** (0.25 g, 0.60 mmol) followed by condensation with **2a** (0.13 g, 0.60 mmol) for 6 min, oxidation with DDQ (0.41 g, 1.8 mmol), and standard workup gave a purple solid which was suspended in boiling ethanol for a few min, cooled, filtered, and dried (78 mg, 22% from **4k**). ^{1}H NMR δ −2.71 (br, 2H), 0.96−1.04 (m, 9H), 1.48−1.62 (m, 6H), 1.72−1.85 (m, 6H), 2.57−4.45 (m, 6H), 4.90−5.12 (m, 6H), 7.75−7.78 (m, 3H), 8.19 (d, J = 7.2 Hz, 2H), 8.81 (d, J = 5.1 Hz, 2H), 9.39 (d, J = 5.1 Hz, 2H), 9.52−9.54 (m, 4H); LD-MS obsd 597.28; FAB-MS obsd 596.3887, calcd 596.3879 ($C_{41}H_{48}N_4$).

5,10,15-Tripentyl-20-(4-methoxyphenyl)porphyrin (9f). Reduction (method 1) of **4k** (0.25 g, 0.60 mmol) followed by condensation with **2c** (0.15 g, 0.60 mmol) for 4 min, oxidation with DDQ (0.41 g, 1.8 mmol), and standard workup gave a purple solid which was suspended in boiling ethanol for a few min, cooled, filtered, and dried (0.11 g, 28% from **4k**). ^{1}H NMR δ −2.78 (br, 2H), 0.94−1.02 (m, 9H), 1.49−1.60 (m, 6H), 1.75−1.80 (m, 6H), 2.49−2.50 (m, 6H), 4.21 (s, 3H), 4.91−5.01 (m, 6H), 7.27 (m, 2H), 8.07 (m, 2H), 8.83 (d, J = 5.1 Hz, 2H), 9.37 (d, J = 4.5 Hz, 2H), 9.49−9.53 (m, 4H); LD-MS obsd 626.24; FAB-MS obsd 626.3969, calcd 626.3985 ($C_{42}H_{50}N_4O$).

5,10,15-Tripentyl-20-(4-cyanophenyl)porphyrin (9g). Reduction (method 1) of **4k** (0.25 g, 0.60 mmol) followed by condensation with **2j** (0.15 g, 0.60 mmol) for 5 min, oxidation with DDQ (0.41 g, 1.8 mmol), and standard workup gave a purple solid which was suspended in boiling ethanol for a few min, cooled, filtered, and dried (68 mg, 18% from **4k**). ^{1}H NMR δ −2.75 (br, 2H), 0.94−1.02 (m, 9H), 1.49−1.58 (m, 6H), 1.74−1.82 (m, 6H), 2.47−2.55 (m, 6H), 4.90−4.97 (m, 6H), 8.03.(d, J = 7.2 Hz, 2H), 8.26 (d, J = 8.1 Hz, 2H), 8.66 (d, J = 4.5 Hz, 2H), 9.38 (d, J = 5.1 Hz, 2H), 9.49−9.54 (m, 4H); LD-MS obsd 623.76; FAB-MS obsd 621.3830, calcd 621.3831 ($C_{42}H_{47}N_5$).

5,10,15-Tripentyl-20-(pentafluorophenyl)porphyrin (9h). Reduction (method 1) of **4k** (0.25 g, 0.60 mmol) followed by condensation with **2b** (0.19 g, 0.60 mmol) for 4 min, oxidation with DDQ (0.41 g, 1.8 mmol), and standard workup gave a purple solid which was suspended in boiling ethanol for a few min, cooled, filtered, and dried (57 mg, 14% from **4k**). ^{1}H NMR δ −2.65 (br, 2H), 0.95−1.02 (m, 9H), 1.48−1.60 (m, 6H), 1.73−1.83 (m, 6H), 2.47−2.56 (m, 6H), 4.94−5.15 (m, 6H), 8.71 (d, J = 4.2 Hz, 2H), 9.45 (d, J = 5.1 Hz, 2H), 9.48 (d, J = 5.1 Hz, 2H), 9.54 (d, J = 4.5 Hz, 2H); LD-MS obsd 686.83; FAB-MS obsd 686.3410, calcd 686.3408 ($C_{41}H_{43}F_5N_4$).

5,10,15-Tripentyl-20-(4-acetamidophenyl)porphyrin (9i). Reduction (method 1) of **4k** (0.25 g, 0.60 mmol) followed by condensation with **2k** (0.17 g, 0.60 mmol) for 7 min, oxidation with DDQ (0.41 g, 1.8 mmol), and standard workup gave a purple solid which was suspended in boiling ethanol for a few min, cooled, filtered, and dried (0.14 g, 35% from **4k**). ^{1}H NMR δ −2.77 (br, 2H), 0.94−1.02 (m, 9H), 1.46−1.61 (m, 6H), 1.71−1.85 (m, 6H), 2.35 (s, 3H), 2.45−2.59 (m, 6H), 4.89−5.10 (m, 6H), 7.49 (s, 1H), 7.86 (d, J = 8.1 Hz, 2H), 8.11 (d, J = 8.1 Hz, 2H), 8.80 (d, J = 4.5 Hz, 2H), 9.36 (d, J = 5.1 Hz, 2H), 9.49−9.54 (m, 4H); LD-MS obsd 653.98; FAB-MS obsd 653.4130, calcd 653.4094 ($C_{43}H_{51}N_5O$).

5,10,15-Tris(4-*tert*-butylphenyl)-20-{4-[2-(trimethylsilyl)-ethynyl]phenyl}porphyrin (9j). Reduction (method 1) of **4i** (0.45 g, 0.70 mmol) followed by condensation with **2g** (0.19 g, 0.70 mmol) for 5 min, oxidation with DDQ (0.48 g, 2.1 mmol), and standard workup furnished a purple solid which was suspended in ethanol, sonicated for 5 min, filtered, and dried (0.17 g, 27% from **4i**). ^{1}H NMR δ −2.75 (br, 2H), 0.37 (s, 9H), 1.60 (s, 27H), 7.75 (d, J = 8.1 Hz, 6H), 7.87 (d, J = 8.1 Hz, 2H), 8.12−8.18 (m, 8H), 8.78 (d, J = 4.5 Hz, 2H), 8.80−8.90 (m, 6H); LD-MS obsd 880.73; FAB-MS obsd 878.4782, calcd 878.4744 ($C_{61}H_{62}N_4Si$).

5-Phenyl-15-(pentafluorophenyl)-10,20-bis(4-methylphenyl)porphyrin (10a). Reduction (method 2) of **4d** (0.22 g, 0.40 mmol) followed by condensation with **2a** (0.89 g, 0.40 mmol) for 4 min, oxidation with DDQ (0.27 g, 1.2 mmol), and standard workup furnished a purple solid which was recrystallized from CH_2Cl_2/methanol (0.11 g, 36% from **4d**). ^{1}H NMR δ −2.75 (br, 2H), 2.73 (s, 6H), 7.57 (d, J = 7.2 Hz, 4H), 7.76−7.80 (m, 3H), 8.10 (d, J = 7.2 Hz, 4H), 8.21−8.24 (m, 2H), 8.76 (d, J = 5.1 Hz, 2H), 8.85 (d, J = 4.2 Hz, 2H), 8.88 (d, J = 5.1 Hz, 2H), 8.97 (d, J = 5.1 Hz, 2H); LD-MS obsd 732.89; FAB-MS obsd 732.2294, calcd 732.2312 ($C_{46}H_{29}F_5N_4$).

5-(4-Iodophenyl)-15-phenyl-10,20-bis(4-methylphenyl)-porphyrin (10b). Reduction (method 1) of **4a** (0.23 g, 0.50 mmol) followed by condensation with **2h** (0.17 g, 50 mmol) for 5 min, oxidation with DDQ (0.34 g, 1.5 mmol), and standard workup gave a purple solid which was suspended in boiling ethanol for a few min, cooled, filtered, and dried (82 mg, 21%

from **4a**). ^{1}H NMR δ −2.78 (br, 2H), 2.73 (s, 6H), 7.55 (d, J = 8.1 Hz, 4H), 7.74−7.76 (m, 3H), 7.93−7.96 (m, 8H), 8.09 (d, J = 8.1 Hz, 6H), 8.20−8.22 (m, 2H), 8.80−8.90 (m, 4H); LD-MS obsd 770.50; FAB-MS obsd 768.1749, calcd 768.1750 ($C_{46}H_{33}IN_4$).

5-(4-Iodophenyl)-15-{4-[2-(trimethylsilyl)ethynyl]phenyl}-10,20-bis(4-methylphenyl)porphyrin (10c). Reduction (method 1) of **4j** (0.83 g, 1.5 mmol) followed by condensation with **2h** (0.52 g, 1.5 mmol) for 5 min, oxidation with DDQ (1.02 g, 4.5 mmol), and standard workup furnished a purple solid which was suspended in methanol, sonicated for 5 min, filtered, and dried (0.34 g, 26% from **4j**). ^{1}H NMR δ −2.82 (br, 2H), 0.40 (s, 9H), 2.70 (s, 6H), 7.55 (d, J = 8.1 Hz, 4H), 7.85−7.87 (m, 2H), 7.92−7.95 (m, 2H), 8.06−8.10 (m, 6H), 8.13−8.16 (m, 2H), 8.80 (apparent t, J = 5.0 Hz, 4H), 8.86−8.88 (m, 4H); LD-MS obsd 866.22; FAB-MS obsd 864.2137, calcd 864.2145 ($C_{51}H_{41}IN_4Si$).

5-(4-Formylphenyl)-15-(4-iodophenyl)-10,20-bis(3,5-di-*tert*-butylphenyl)porphyrin (10d). Reduction (method 2) of **4o** (0.13 g, 0.17 mmol) followed by condensation with **2n** (43 mg, 0.17 mmol) for 5 min, oxidation with DDQ (0.12 g, 0.50 mmol), and standard workup furnished a brown solid which was suspended in methanol, sonicated for 5 min, filtered and dried (29 mg, 17% from **4o**). ^{1}H NMR δ −2.81 (br, 2H), 1.48 (s, 36H), 7.76−7.77 (m, 2H), 7.90−7.93 (m, 2H), 8.00−8.07 (m, 6H), 8.22 (d, J = 8.1 Hz, 2H), 8.36 (d, J = 8.1 Hz, 2H), 8.72 (d, J = 4.5 Hz, 2H), 8.78 (d, J = 5.1 Hz, 2H), 8.85−8.88 (m, 4H), 10.34 (s, 1H); LD-MS obsd 993.43; FAB-MS obsd 992.3922, calcd 992.3890 ($C_{61}H_{61}IN_4O$).

5-{4-[2-(Trimethylsilyl)ethoxycarbonyl]phenyl}-15-(4-iodophenyl)-10,20-bis(4-*tert*-butylphenyl)porphyrin (10e). Reduction (method 2) of **4p** (2.73 g, 4.0 mmol) followed by condensation with **2l** (1.47 g, 4.0 mmol) for 5 min, oxidation with DDQ (2.72 g, 12.0 mmol), and standard workup furnished a purple solid which was suspended in methanol, sonicated for 5 min, filtered, and dried (0.90 g, 22% from **4p**). ^{1}H NMR δ −2.77 (br, 2H), 0.21 (s, 9H), 1.27−1.37 (m, 2H), 1.64 (s, 18H), 4.60−4.68 (m, 2H), 7.79 (d, J = 8.7 Hz, 4H), 7.98 (d, J = 8.7 Hz, 2H), 8.12 (d, J = 8.1 Hz, 2H), 8.16 (d, J = 8.1 Hz, 4H), 8.33 (d, J = 8.7 Hz, 2H), 8.46 (d, J = 8.1 Hz, 2H), 8.81 (d, J = 5.1 Hz, 2H), 8.84 (d, J = 4.5 Hz, 2H), 8.94 (d, J = 4.5 Hz, 4H); LD-MS obsd 997.65; FAB-MS obsd 996.3288, calcd 996.3296 ($C_{58}H_{57}IN_4O_2Si$).

5,15-Dimesityl-10-{4-[2-(triisopropylsilyl)ethynyl]phenyl}-20-{4-[2-(trimethylsilyl)ethynyl]phenyl}-porphyrin (10f). Reduction (method 2) of **7f** (0.75 g, 1.0 mmol) followed by condensation with **2d** (0.26 g, 1.0 mmol) for 3.5 min, oxidation with DDQ (0.68 g, 3.0 mmol), and standard workup furnished a purple solid (0.24 g, 24%). ^{1}H NMR δ −2.62 (br, 2H), 0.40 (s, 9H), 1.28 (s, 21H), 1.85 (s, 12H), 2.65 (s, 6H), 7.30 (s, 4H), 7.88 (d, J = 8.1 Hz, 2H), 7.89 (d, J = 8.1 Hz, 2H), 8.19 (d, J = 8.1 Hz, 4H), 8.72 (d, J = 5.4 Hz, 4H), 8.77−8.82 (m, 4H); LD-MS obsd 976.64; FAB-MS obsd 974.5164, calcd 974.5139 ($C_{66}H_{70}N_4Si_2$).

5,10-Bis(4-*tert*-butylphenyl)-15,20-bis(4-iodophenyl)-porphyrin (11a). Reduction (method 2) of **7h** (3.34 g, 5.00 mmol) followed by condensation with **2h** (1.74 g, 5.00 mmol) for 3.5 min, oxidation with DDQ (3.40 g, 15.0 mmol), and standard workup furnished a purple solid which was suspended in methanol, sonicated for 5 min, filtered, and dried (1.18 g, 24%). ^{1}H NMR δ -2.81 (br, 2H), 1.61 (s, 18H), 7.77 (d, J = 8.1 Hz, 4H), 7.95 (d, J = 8.1 Hz, 4H), 8.08−8.14 (m, 8H), 8.81−8.90 (m, 8H); LD-MS obsd 979.82; FAB-MS obsd 978.1697, calcd 978.1656 ($C_{52}H_{44}I_2N_4$).

5,10-Bis(4-*tert*-butylphenyl)-15,20-bis{4-[2-(triisopropylsilyl)ethynyl]phenyl}porphyrin (11b). Reduction (method 2) of **7i** (1.44 g, 2.00 mmol) followed by condensation with **2m** (0.800 g, 2.00 mmol) for 3.5 min, oxidation with DDQ (1.36 g, 6.00 mmol), and standard workup including recrystallization from CH_2Cl_2/methanol afforded a crystalline purple solid (0.53 g, 24%). ^{1}H NMR δ −2.77 (br, 2H), 1.27 (s, 42H), 1.62 (s, 18H), 7.78 (d, J = 8.1 Hz, 4H), 7.90 (d, J = 8.1 Hz, 4H), 8.15 (d, J = 8.1 Hz, 4H), 8.18 (d, J = 8.1 Hz, 4H), 8.83−8.92 (m, 8H); LD-MS obsd 1090.30; FAB-MS obsd 1086.6432, calcd 1086.6391 ($C_{74}H_{86}N_4Si_2$).

5-(4-Methoxyphenyl)-10-(pentafluorophenyl)-15,20-diphenylporphyrin (12a). Reduction (method 2) of **7b** (0.11 g, 0.20 mmol) followed by condensation with **2a** (44 mg, 0.20 mmol) for 3.5 min, oxidation with DDQ (136 mg, 0.60 mmol), and standard workup including recrystallization from CH_2Cl_2/methanol afforded a crystalline purple solid (28 mg, 20%). ^{1}H NMR δ −2.70 (br, 2H), 4.10 (s, 3H), 7.26−7.32 (m, 2H), 7.76−7.81 (m, 6H), 8.13−8.26 (m, 6H), 8.80−9.02 (m, 8H); LD-MS obsd 734.56; FAB-MS obsd 734.2146, calcd 734.2105 ($C_{45}H_{27}F_5N_4O$). Alternatively, reduction (method 2) of **7c** (0.14 g, 0.25 mmol) followed by reaction with **2a** (56 mg, 0.25 mmol) afforded porphyrin **12a** (54 mg, 29%).

5-Mesityl-10,15-bis{4-[2-(trimethylsilyl)ethynyl]phenyl}-20-{4-[2-(triisopropylsilyl)ethynyl]phenyl}porphyrin (12b). Reduction (method 2) of **7f** (0.38 g, 0.50 mmol) followed by condensation with **2e** (0.18 g, 0.50 mmol) for 3.5 min, oxidation with DDQ (0.34 g, 1.5 mmol), and standard workup furnished a purple solid (82 mg, 16%). ^{1}H NMR δ −2.75 (br, 2H), 0.42 (s, 18H), 1.29 (s, 21H), 1.87 (s, 6H), 2.66 (s, 3H), 7.32 (s, 2H), 7.90−7.92 (m, 6H), 8.17−8.21 (m, 6H), 8.75−8.89 (m, 8H); LD-MS obsd 1029.35; FAB-MS obsd 1028.5092, calcd 1028.5065 ($C_{68}H_{72}N_4Si_3$).

5-(4-Bromophenyl)-10-{4-[2-(trimethylsilyl)ethynyl]phenyl}-15,20-bis(4-iodophenyl)porphyrin (12c). Reduction (method 2) of **7g** (0.73 g, 1.0 mmol) followed by condensation with **2h** (0.35 g, 1.0 mmol) for 3.5 min, oxidation with DDQ (0.68 g, 3.0 mmol), and standard workup furnished a purple solid (0.22 g, 21%). ^{1}H NMR δ −2.83 (br, 2H), 0.42 (s, 9H), 7.90 (m, 8H), 8.07 (m, 6H), 8.16 (m, 2H), 8.85 (s, 8H); LD-MS obsd 1043.99; FAB-MS obsd 1039.9875, calcd 1039.9904 ($C_{49}H_{35}BrI_2N_4Si$).

5,10-Bis(4-*tert*-butylphenyl)-15-(4-iodophenyl)-20-{4-[2-(trimethylsilyl)ethynyl]phenyl}porphyrin (12d). Reduction (method 2) of **7h** (0.67 g, 1.0 mmol) followed by condensation with **2e** (0.32 g, 1.0 mmol) for 3.5 min, oxidation with DDQ (0.68 g, 3.0 mmol), and standard workup furnished a purple solid (0.25 g, 26%). ^{1}H NMR δ −2.78 (br, 2H), 0.40 (s, 9H), 1.63 (s, 18H), 7.79 (d, J = 7.2 Hz, 4H), 7.89 (d, J = 8.1 Hz, 2H), 7.97 (d, J = 8.1 Hz, 2H), 8.12 (d, J = 8.1 Hz, 2H), 8.16 (d, J = 8.1 Hz, 2H), 8.18 (d, J = 7.2 Hz, 4H), 8.81−8.93 (m, 8H); LD-MS obsd 950.77; FAB-MS obsd 948.3074, calcd 948.3084 ($C_{57}H_{53}IN_4Si$).

5-(4-*tert*-Butylphenyl)-10-(4-methylphenyl)-15-(4-methoxyphenyl)-20-phenylporphyrin (13a). Reduction (method 1) of **7a** (0.16 g, 0.33 mmol) followed by condensation with **2g** (0.094 g, 0.33 mmol) for 3.5 min, oxidation with DDQ (0.227 g, 1.00 mmol), and standard workup furnished a purple solid which was suspended in ethanol, sonicated for 5 min, filtered, and dried (51 mg, 21%). ^{1}H NMR δ −2.76 (br, 2H), 1.60 (s, 9H), 2.70 (s, 3H), 4.08 (s, 3H), 7.28 (m, 2H), 7.55 (d, J = 8.1 Hz, 2H), 7.75 (m, 5H), 8.13 (m, 6H), 8.20−8.23 (m, 2H), 8.81−8.88 (m, 8H); LD-MS obsd 715.55; FAB-MS obsd 714.3346, calcd 714.3359 ($C_{50}H_{42}N_4O$).

5-(4-Iodophenyl)-10-(pentafluorophenyl)-15-{4-[2-(trimethylsilyl)ethynyl]phenyl}-20-{4-[2-(triisopropylsilyl)-ethynyl]phenyl}porphyrin (13c). Reduction (method 2) of **7d** (0.74 g, 1.0 mmol) followed by condensation with **2m** (0.40 g, 1.0 mmol) for 3.5 min, oxidation with DDQ (0.68 g, 3.0 mmol), and standard purification furnished a brown solid which was suspended in methanol, sonicated for 5 min, filtered and dried to give a reddish-brown solid (0.44 g, 40%). ^{1}H NMR δ −2.82 (br, 2H), 0.38 (s, 9H), 1.26 (s, 21H), 7.88−7.96 (m, 6H), 8.11−8.17 (m, 6H), 8.78−8.92 (m, 8H); LD-MS obsd 1108.58; FAB-MS obsd 1106.2678, calcd 1106.2695 ($C_{60}H_{52}F_5IN_4Si_2$).

5-(4-Ethynylphenyl)-10-{4-[2-(triisopropylsilyl)ethynyl]phenyl}-15-mesityl-20-{4-[2-(trimethylsilyl)ethynyl]phenyl}porphyrin (13d). Reduction (method 2) of **7f** (0.75 g, 1.0 mmol) followed by condensation with **2o** (0.25 g, 1.0 mmol) for 3.5 min, oxidation with DDQ (0.68 g, 3.0 mmol), and standard workup including recrystallization from CH_2Cl_2/methanol afforded a crystalline purple solid (0.25 g, 26%). ^{1}H NMR δ −2.67 (br, 2H), 0.43 (s, 9H), 1.30 (s, 21H), 1.88 (s, 6H), 2.67 (s, 3H), 3.35 (s, 1H), 7.32 (s, 2H), 7.92 (d, J = 8.1 Hz, 2H), 7.93 (d, J = 8.1 Hz, 4H), 8.21 (d, J = 8.1 Hz, 6H),

8.76−8.89 (m, 8H); LD-MS obsd 958.27; FAB-MS obsd 956.4665, calcd 956.4670 ($C_{65}H_{64}N_4Si_2$).

5-(4-Bromophenyl)-10-{4-[2-(triisopropylsilyl)ethynyl]-phenyl}-15-(4-iodophenyl)-20-{4-[2-(trimethylsilyl)ethynyl]-phenyl}porphyrin (13e). Reduction (method 2) of **7g** (2.92 g, 4.00 mmol) followed by condensation with **2m** (1.62 g, 4.00 mmol) for 3.5 min, oxidation with DDQ (2.72 g, 12.0 mmol), and standard workup including recrystallization from CH_2Cl_2/methanol afforded a purple solid (1.12 g, 25%). ^{1}H NMR δ −2.82 (br, 2H), 0.41 (s, 9H), 1.28 (s, 21H), 7.89−7.97 (m, 8H), 8.08−8.18 (m, 8H), 8.85 (m, 8H); LD-MS obsd 1098.02; FAB-MS obsd 1094.2288, calcd 1094.2272 ($C_{60}H_{56}BrIN_4Si_2$).

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Supporting Information Available: ^{1}H NMR and LD-MS spectra for all new porphyrins; improved experimental procedure for synthesis of **1e**; procedures and tables of data for refinement of the procedure giving symmetrical diacyl dipyrromethanes; and complete retrosynthetic analyses for the five types of porphyrins. This material is available free of charge via the Internet at http://pubs.acs.org.

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