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Boron-Complexation Strategy for Use with 1-Acyldipyrromethanes

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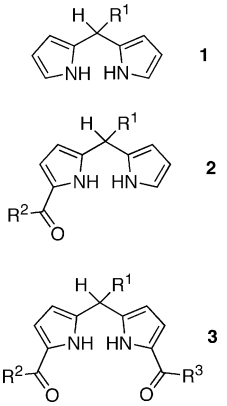
1-Acyldipyrromethanes are important precursors in rational syntheses of diverse porphyrinic compounds. 1-Acyldipyrromethanes are difficult to purify, typically streaking upon chromatography and giving amorphous powders upon attempted crystallization. A solution to this problem has been achieved by reacting the 1-acyldipyrromethane with a dialkylboron triflate (e.g., Bu_2B-OTf or 9-BBN-OTf) to give the corresponding *B*,*B*-dialkyl-*B*-(1-acyldipyrromethane)boron(III) complex. The reaction is selective for a 1-acyldipyrromethane in the presence of a dipyrromethane. The 1-acyldipyrromethane−boron complexes are stable to routine handling, are soluble in common organic solvents, are hydrophobic, crystallize readily, and chromatograph without streaking. The 1-acyldipyrromethane can be liberated in high yield from the boron complex upon treatment with 1-pentanol. Alternatively, the 1-acyldipyrromethane−boron complex can be used in the formation of a *trans*-A_2B_2-porphyrin. In summary, the boron-complexation strategy has broad scope and greatly facilitates the isolation of 1-acyldipyrromethanes.

Introduction

Rational syntheses of a variety of porphyrinic compounds bearing diverse patterns of meso-substituents have been developed recently. The porphyrinic compounds include porphyrins,[1−3] chlorins,[4] corroles,[5] and bilanes.[6] The syntheses begin with dipyrromethanes (**1**) and, depending on desired substitution pattern, also employ 1-acyldipyrromethanes (**2**) and 1,9-diacyldipyrromethanes (**3**) (Chart 1).[1,2] 1-Acyldipyrromethanes are readily prepared from the corresponding dipyrromethane, and 1,9-diacyldipyrromethanes can be prepared by 9-acylation of a 1-acyldipyrromethane or by 1,9-diacylation of a dipyrromethane. Although the acylation procedures work reasonably well, purification is difficult owing to the lack of crystallinity of the acyldipyrromethanes. Accordingly, the mixture containing the acyldipyrromethane is usually separated by chromatography, which can be tedious owing to the tendency of the acyldipyrromethanes to streak on chromatographic media.

CHART 1



One of our objectives over the past few years has been to increase the scale of porphyrin syntheses, which entails decreasing if not eliminating reliance on chromatography for purification. Toward this goal, we recently developed a simple procedure for isolating a 1,9-diacyldipyrromethane from the diacylation reaction mixture by forming a dialkyltin complex (Chart 2, **4**).[7] Dipyrromethanes, 1-acyldipyrromethanes, or 1,8-diacyldipyrromethanes did not give tin complexes. The tin complex of a 1,9-diacyldipyrromethane was hydrophobic and crystalline, greatly facilitating isolation. In addition, the tin complex readily underwent decomplexation upon treatment with dilute trifluoroacetic acid. The availability of the tin-complexation procedure has enabled routine synthesis of multigram quantities of 1,9-diacyldipyrromethanes.

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[‡] University of Notre Dame.

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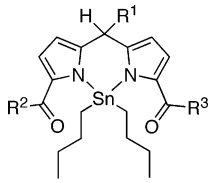
CHART 2



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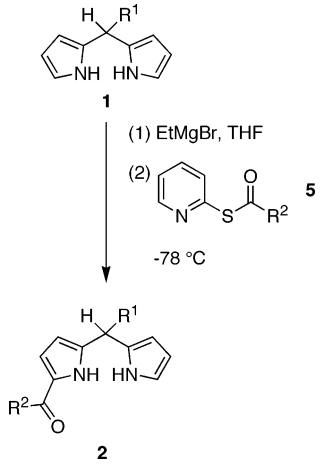
SCHEME 1

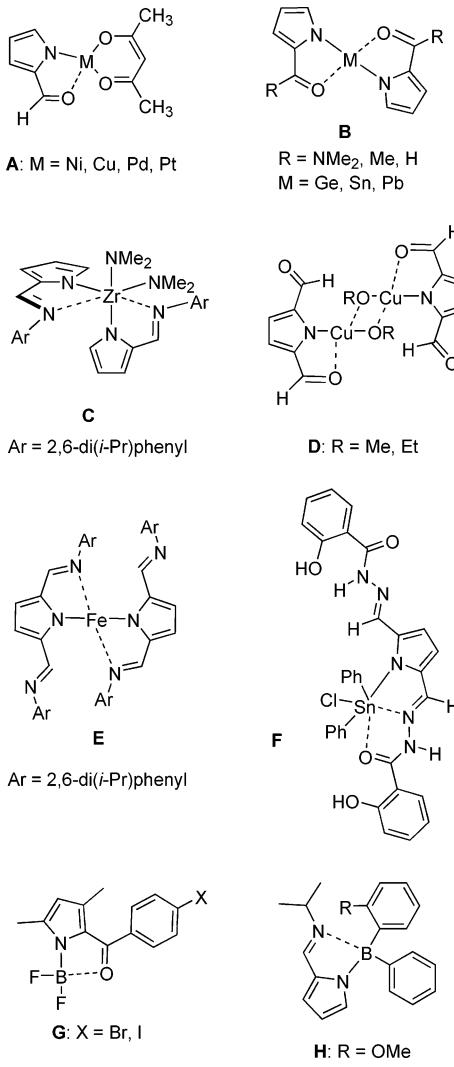


1 **5** **2**

The beneficial impact of the tin-complexation procedure prompted us to explore an analogous method for isolating a 1-acyldipyrromethane from the mixture formed upon 1-acylation of a dipyrromethane. The synthesis of a 1-acyldipyrromethane (**2**) is achieved by treatment of a dipyrromethane (**1**) with EtMgBr in THF at room temperature followed by addition of a pyridyl thioester (**5**) in THF at −78 °C.[2] The product mixture consists of unreacted dipyrromethane (**1**), the 1-acyldipyrromethane (**2**), and pyridyl thioester and/or other byproducts (Scheme 1). A suitable complexation aid for application to such a mixture must meet several criteria, including the following: (1) afford reaction with diverse 1-acyldipyrromethanes, (2) resist complex formation with other species in the reaction mixture, particularly the dipyrromethane, (3) yield a crystalline solid, (4) exhibit sufficient stability for routine handling, and (5) undergo decomplexation under mild conditions to liberate the 1-acyldipyrromethane in pure form.

A number of metal complexes of 2-acylpyrroles are known, as shown in Chart 3. Pyrrole-2-carboxaldehyde forms a stable coordination complex (**A**) in conjunction with acetylacetone and copper(II), nickel(II), palladium(II), or platinum(II).[8] Pyrrole-2-acyl species and imino derivatives therefrom also form complexes with various metals or coordination centers (**B**,[9] **C**,[10] **D**,[11] **E**,[10] and **F**[12]). We began our search for suitable metal complexes of

CHART 3



1-acyldipyrromethanes on the basis of the known complexes of 2-acylpyrroles. Note that 1-acyldipyrromethanes and 2-acylpyrroles each contain the same α-acylpyrrole motif.

In this paper, we report the development of a boron-complexation strategy for the isolation and purification of 1-acyldipyrromethanes formed upon acylation of dipyrromethanes. We also describe use of the 1-acyldipyrromethane−boron complexes in porphyrin-forming reactions following similar procedures employed with 1-acyldipyrromethanes. The ability to complex the 1-acyldipyrromethane greatly facilitates purification and enables synthesis of 1-acyldipyrromethanes at the multigram scale.

Results and Discussion

Identification of Suitable 1-Acyldipyrromethane-Coordination Complexes. A variety of metal reagents were examined as potential complexation aids for 1-acyldipyrromethanes. The metal reagents include $Mg(OAc)_2 \cdot 4H_2O$, $Sc(OTf)_3$, TiF_4, $MnCl_2$, $Mn(OAc)_2$, $FeBr_3$, $Fe(OAc)_2$, $Fe(acac)_3$, $Co(OAc)_2 \cdot 4H_2O$, $Ni(OAc)_2 \cdot 4H_2O$, $Cu(OAc)_2 \cdot H_2O$, $Zn(OAc)_2 \cdot 2H_2O$, GeI_4, $MoCl_3$, $RuCl_3 \cdot H_2O$, $Pd(OAc)_2$, $Pd(CH_3CN)_2Cl_2$, Ag(OTf), $CdCl_2$, $InCl_3$, $In(OAc)_3$, SnF_4,

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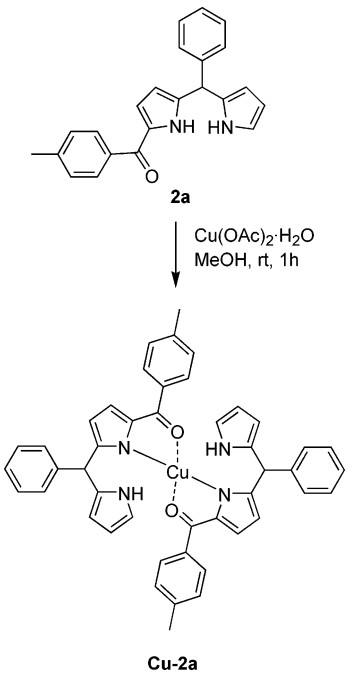
SCHEME 2



$SbCl_5$, $TeCl_4$, CeI_3, $EuCl_3$, $Dy(OTf)_3$, $Yb(OTf)_3$, Tl(OAc), and $BiCl_3$. The conditions employed treatment of a methanolic solution of **2a**[2] (100 mM) with the metal reagent (50 mM) at room temperature for 1 h. Most of the reagents examined gave multiple components. A readily isolable complex was obtained only with Cu-$(OAc)_2 \cdot H_2O$, affording **Cu-2a** as a green precipitate (Scheme 2). Although the formation of **Cu-2a** was promising, copper was found to have three limitations as a complexing agent: (1) the **Cu-2a** complex underwent decomplexation upon silica TLC; (2) formation of the complex was quite substrate-selective; a copper complex was obtained for 1-*p*-toluoyl-5-phenyldipyrromethane (**2a**) but not with 1-pentafluorobenzoyl-5-(pentafluorophenyl)dipyrromethane (**2e**)[1]; and (3) the **Cu-2a** complex was an amorphous solid rather than a crystalline product.

1-Acyldipyrromethane−Boron Complexes. To meet the objectives of broad applicability and formation of crystalline products, we turned to investigate boron complexes. The first boron derivative of a dipyrromethane species apparently was reported by Treibs et al.,[13] who reacted BF_3-etherate with a dipyrrin to obtain a difluoroboron−dipyrrin complex. A wide variety of such difluoroboron−dipyrrin (BODIPY) derivatives have been prepared owing to their high fluorescence yields.[14] The boron−difluoride complexes of dipyrrins are exceptionally resistant to decomplexation.[13−15] 2-Ketopyrroles are also known to form stable boron−difluoride complexes (**G**, Chart 3).[15] A dialkylboron complex of a 2-iminopyrrole also is known (**H**, Chart 3).[16]

We thought that boron complexes with *B*,*B*-dialkyl substituents might afford the appropriate balance of stability and susceptibility to decomplexation for our studies. A variety of compounds containing *N*-(dialkylboryl)pyrrole[17−25] or *N*-(diarylboryl)pyrrole[26] motifs have been prepared. Thus, reaction of **2a** and Bu_2B-OTf in CH_2Cl_2 containing TEA at room temperature afforded the corresponding boron complex **6a-BBu$_2$** in 93% yield (Scheme 3). The boron complex was readily isolated by passage through a pad of silica. The generality of the complexation of 1-acyldipyrromethane **2a** with various boron reagents was examined. The complex of **2a** with 9-BBN gave an orange-yellow solid, whereas the boron complex with dibutyl or dimethyl substituents gave an orange oil. On the other hand, no complex was obtained with $BF_3 \cdot O(Et)_2$ or *B*-bromocatechol borane. Owing to the high yield and formation of a crystalline product, we primarily used 9-BBN complexes for further study.

The selectivity of boron complexation was examined next. Dipyrromethane **1a** did not give a boron complex (TLC analysis). However, a trace amount of a byproduct, tentatively assigned as dipyrrin−boron complex **7** on the basis of ^1H NMR and absorption spectroscopy, was observed. The reaction of 1,9-diacyldipyrromethane **3a**[1] and Bu_2B-OTf in CH_2Cl_2 containing TEA at room temperature afforded the corresponding bis-boron complex **3a-(BBu$_2$)$_2$** (Scheme 4). Thus, the complexation process is selective for the α-acylpyrrole motif but does not distinguish 1-acyl versus 1,9-diacyldipyrromethanes.

The generality of the complexation with 9-BBN-OTf was examined with various 1-acyldipyrromethanes (Scheme 5). The requisite 1-acyldipyrromethanes **2a**,[2] **2d**,[7] **2e**,[1] **2f**,[2] **2g**,[1] **2h**,[7] and **2i**[27] are known compounds, whereas **2b** and **2c** were prepared herein following the general method.[2] In each case, the resulting boron complex was hydrophobic and easily isolated by passage of the mixture through a pad of silica. The complexation of 1-acyldipyrromethanes **2a**−**d** and **2g** with 9-BBN-OTf

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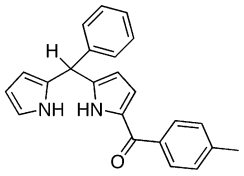
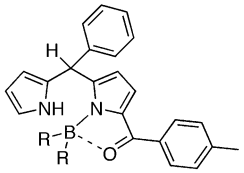
(26) (a) Cornelissen-Gude, C.; Retting, W. *J. Phys. Chem. A* **1999**, *103*, 4371−4377. (b) Kehr, G.; Fröhlich, R.; Wibbeling, B.; Erker, G. *Chem. Eur. J.* **2000**, *6*, 258−266.
(27) Tomizaki, K.-Y.; Lysenko, A. B.; Taniguchi, M.; Lindsey, J. S. *Tetrahedron* **2004**, *60*, 2011−2023.

SCHEME 3



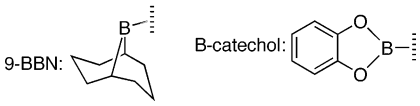
2a

R_2BX
TEA/CH_2Cl_2
rt, 1 h

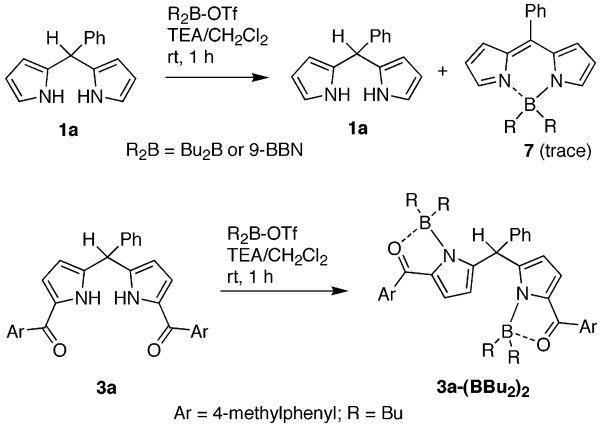


6a-BR$_2$

R_2B	X	Complex	Yield
Bu_2B	OTf	**6a-BBu$_2$**	93%
Me_2B	Br	**6a-BMe$_2$**	91%
9-BBN	OTf	**6a-BBN**	94%
F_2B	F	**6a-BF$_2$**	0%
B-Catechol	Br	**6a-B(cat)**	0%



SCHEME 4

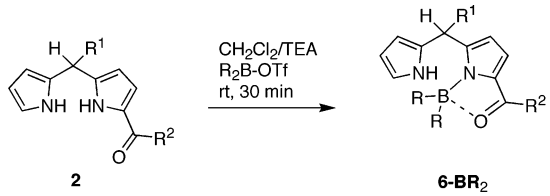


gave **6a-BBN**−**6d-BBN** and **6g-BBN** in excellent yields (87−97%). The reaction of **2e** or **2f** with 9-BBN-OTf gave complete reaction (TLC analysis), but partial decomplexation occurred upon passage through a silica pad, affording a mixture of **2e** and **6e-BBN** or **2f** and **6f-BBN**. Isolation of the unstable mesityl-substituted complex **6f-BBN** was circumvented by reaction of **2f** with Bu_2B-OTf, which gave **6f-BBu$_2$** as a stable product in 89% yield. The same approach with the pentafluorophenyl-substituted **2e** gave **6e-BBu$_2$**, which was isolated in pure form by silica pad separation but underwent facile decomplexation to **2e** upon further handling.

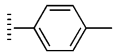
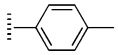
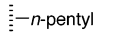
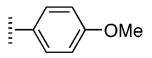
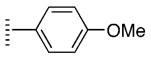
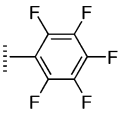
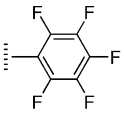
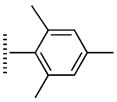
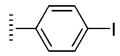
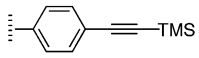
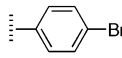
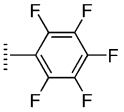
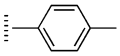
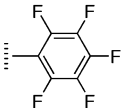
To check the effect of the presence of a single pentafluorophenyl group at the 5-position or 1-acyl position, boron complexation reactions of **2h** and **2i** were investigated. The reaction of **2h** (5-pentafluorophenyl substituent) with 9-BBN-OTf or Bu_2B-OTf gave a stable complex (**6h-BBN** or **6h-BBu$_2$**) in excellent yield. However, reaction of **2i** (1-pentafluorobenzoyl substituent) with 9-BBN-OTf gave a complex (**6i-BBN**) that proved unstable, whereas the reaction of **2i** with BBu_2-OTf gave **6i-BBu$_2$** in 89% yield. Thus, the presence of the pentafluorophenyl group is potentially deleterious only at the 1-acyl position.

It is noteworthy that among the complexes examined herein, almost all 9-BBN complexes of 1-acyldipyrromethanes were solids (the all-pentyl **6c-BBN** was the one exception), whereas almost all dibutylboron complexes of 1-acyldipyrromethanes were oils (**6f-BBu$_2$** was the one exception). Regardless of state, the boron complexes typically are yellow-orange, whereas the uncomplexed 1-acyldipyrromethanes are off-white solids. The 1-acyldipyrromethane−boron complexes are stable to water and routine handling. Unlike 1-acyldipyrromethanes, the 1-acyldipyrromethane−boron complexes

SCHEME 5



2 **6-BR$_2$**

2	R^1	R^2	R_2B	Product (Yield)
2a			9-BBN	**6a-BBN** (94%)
2b			9-BBN	**6b-BBN** (91%)
2c			9-BBN	**6c-BBN** (87%)
2d			9-BBN	**6d-BBN** (97%)
2e			9-BBN	**6e-BBN** [a]
			Bu_2B	**6e-BBu$_2$** (97%)
2f			9-BBN	**6f-BBN** [a]
			Bu_2B	**6f-BBu$_2$** (89%)
2g			9-BBN	**6g-BBN** (96%)
2h			9-BBN	**6h-BBN** (93%)
			Bu_2B	**6h-BBu$_2$** (90%)
2i			9-BBN	**6i-BBN** [a]
			Bu_2B	**6i-BBu$_2$** (89%)

[a] The product partially decomplexed upon chromatography (silica, CH_2Cl_2).

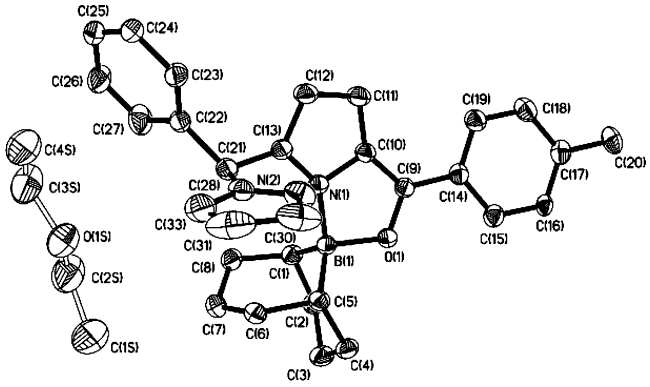


FIGURE 1. ORTEP drawing of the X-ray structure of **6a-BBN**. The diethyl ether solvate molecule is also illustrated. All ellipsoids are contoured at the 50% level, and hydrogens are omitted for clarity.

can be precipitated/crystallized from CH_2Cl_2/hexanes, are relatively nonpolar, and do not streak upon chromatography.

Characterization. The spectral changes upon boron complexation of a 1-acyldipyrromethane include the appearance of the characteristic absorption at ca. 340−390 nm. The ^{13}C NMR spectra show the downfield shift (∼8 ppm) of the carbonyl carbon. The ^1H NMR spectra show (1) disappearance of the NH resonance of the acylpyrrole unit, (2) a ∼0.4 ppm upfield shift of the unsubstituted pyrrolic NH resonance, (3) a downfield shift (∼0.2 ppm) of the meso-proton, (4) a downfield shift (∼1 ppm) of the *β*-protons of the acylpyrrole, and (5) multiplets from the diastereotopic alkyl moieties attached to the boron atom. An example of a boron complex with freely rotating alkyl substituents is provided by **6a-BMe$_2$**, where a distinct singlet (0.04, 0.15 ppm) is observed owing to the different magnetic environment for each methyl group (*syn* or *anti* with respect to the meso-substituent). In the rigid 9-BBN complexes, a further difference in magnetic environment stems from whether the alkyl boron groups are proximal or distal to the α-carbonyl unit. For example, in **6a-BBN**, the 9-BBN bridgehead protons give two partially overlapping multiplets (centered at ∼0.7 ppm) and the remaining methylene protons give complex multiplets in the low-field region (1.6−2.4 ppm).

The ^{11}B NMR spectra of selected samples (**6a-BBN**−**6d-BBN**, and **6g-BBN**) each showed a single peak at ∼13 ppm relative to the ^{11}B standard, $BF_3{\cdot}O(Et)_2$ (0 ppm). For comparison, the boron signal in the unacylated *N*-(9-borabicyclo[3.3.1]non-9-yl)pyrrole appears at 59.9 ppm.[23] The relative upfield shift of the dialkylboron acylated pyrrole complex is characteristic of organoboron species with coordination in the lone p orbital of the boron atom.[28] Elemental analyses for some of the boron complexes were satisfactory while others showed unsatisfactory results for carbon. This discrepancy may stem from solvent inclusion in the crystal lattice of the boron complexes. However, FABMS analysis of each complex was satisfactory.

X-ray structural analysis was performed on **6a-BBN** (Figure 1). Complexation results in near coplanarity of the boron atom, α-carbonyl, and pyrrole unit. Selected bond lengths and angles are shown in Supporting Information. The C−O bond length (1.298 Å) is longer than for that in 2-benzoylpyrrole (1.234 Å),[29] suggesting some enolate character. At the same time, the C−C bond between the carbonyl carbon and the α-carbon of the acylpyrrole (1.402 Å) is significantly shorter than that in 2-benzoylpyrrole (1.445 Å),[29] suggesting partial multiple bond character. Similar structural features were reported for the 2-ketopyrrole−BF_2 complex.[15] Coordination of the carbonyl group and the pyrrolic nitrogen atom to the boron atom effectively masks two groups that can participate in hydrogen bonding. The ensheathed α-acylpyrrole motif is the source of the striking change in physical properties (polarity, crystallinity) upon conversion of a 1-acyldipyrromethane to the corresponding dialkylboron complex.

Boron Complexation as Purification Aid for 1-Acyldipyrromethanes. An integrated procedure consisting of 1-acylation and subsequent boron complexation was developed. The two steps are carried out as follows:

(i) The dipyrromethane (**1**) is treated with 2.0 molar equiv of EtMgBr followed by 1.0 molar equiv of a Mukaiyama reagent[30] (**5**). The reaction mixture is quenched with aqueous NH_4Cl, and the organic layer is separated and concentrated, affording the crude product **2** (vide infra). Note that the use of boron complexation to isolate the 1-acyldipyrromethane enables use of a stoichiometric quantity of EtMgBr, rather than an excess as employed previously to ensure complete consumption of the Mukaiyama reagent.[2]

(ii) The residue (**2**) is dissolved in CH_2Cl_2 and treated with TEA and R_2B-OTf at room temperature for 1 h. Passage of the reaction mixture over a pad of silica using CH_2Cl_2/hexanes as eluant readily affords the boron complex.

In this manner, each member in a series of dipyrromethanes (**1a**−**f**,[31] **1g**[32]) was reacted with the appropriate Mukaiyama reagent (**5a**−**e**,[2] **5f**) followed by boron complexation with Bu_2B-OTf or 9-BBN-OTf. The corresponding boron complexes of **2a**−**c** and **2f**−**h** were readily obtained in good yield, whereas that of **2d** was prepared by a slightly modified procedure (Scheme 6).

A slight modification to the general boron-complexation method was explored to further streamline workup. The modification entails use of a solvent for complexation that results in precipitation of the 1-acyldipyrromethane−boron complex. Thus, the reaction of **2a** with 9-BBN-OTf in the presence of TEA in toluene afforded a precipitate, which largely consisted of **6a-BBN** and the TfOH·TEA salt. Washing with water and methanol afforded the desired 1-acyldipyrromethane−boron complex **6a-BBN**. This procedure was employed with 8.88 g of **2a**, affording a precipitate (9.63 g, 52%) of analytically pure **6a-BBN**. Silica pad separation of the filtrate afforded additional

(28) Wrackmeyer, B. *Annu. Rep. NMR Spectrosc.* **1988**, *20*, 61−203.

(29) English, R. B.; McGillivray, G.; Smal, E. *Acta Crystallogr.* **1980**, *B36*, 1136−1141.

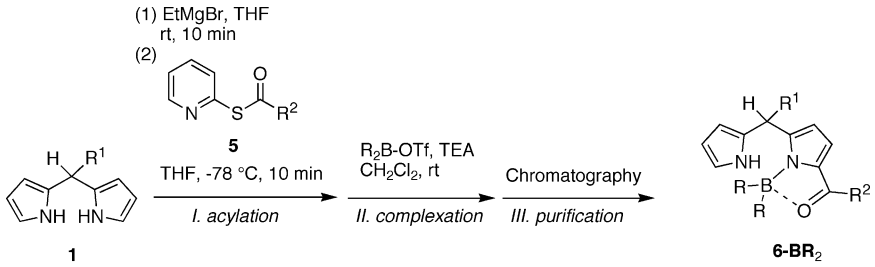
(30) Araki, M.; Sakata, S.; Takei, H.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 1777−1780.

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

(32) 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.

(33) Geier, G. R., III; Callinan, J. B.; Rao, P. D.; Lindsey, J. S. *J. Porphyrins Phthalocyanines* **2001**, *5*, 810−823.

SCHEME 6



1 + 5	R^1	R^2	R_2B	Product (Yield)
1a + 5a			9-BBN	**6a-BBN** (67%)
1b + 5a	—H		9-BBN	**6b-BBN** (60%)
1c + 5f	—*n*-pentyl	—*n*-pentyl	9-BBN	**6c-BBN** (60%)
1d + 5b	—OMe	—OMe	9-BBN	**6d-BBN** (66%)
1f + 5d		—I	Bu_2B	**6f-BBu$_2$** (68%)
1g + 5e	—TMS	—Br	9-BBN	**6g-BBN** (71%)
1e + 5a			9-BBN	**6h-BBN** (58%)

material (1.77 g), giving an overall yield of 62%. This procedure is well suited for synthesis at the multigram level. No change in solvent was required for use with **2d**; the boron complex **6d-BBN** precipitated upon formation in CH_2Cl_2. Note that dipyrromethanes **1a**−**f** were prepared by a streamlined procedure with minimal or no reliance on chromatography,[31] and **1g** was prepared herein by the same procedure; accordingly, the overall route to form a 1-acyldipyrromethane can now be implemented with limited or no use of chromatography.

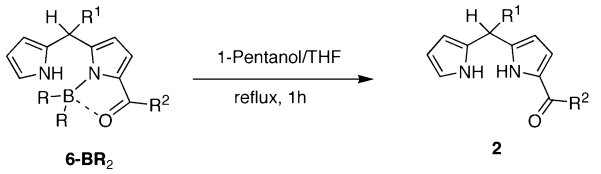
Decomplexation of 1-Acyldipyrromethane−Boron Complex. A simple method for decomplexation of the 1-acyldipyrromethane−boron complexes was investigated using **6a-BBN** as a test case. The cleavage of the B−N bond in alkyl or arylamines has been achieved with acids,[34,35] bases,[35] or ethanolamine.[35] The similar cleavage of *N*-(dialkylboron)pyrroles has been achieved with acids[19,24] or ethanol.[24] Given the potential lability of the 1-acyldipyrromethane to acidic conditions, we focused on neutral reaction conditions. Smooth decomplexation was obtained in refluxing solvents composed of H_2O/THF or ROH/THF, where ROH is methanol, neopentyl glycol, ethanolamine, poly(ethylene glycol), 1,3-propanediol, pentaerythritol, or poly(vinyl alcohol). In many cases, isolation could be achieved in nearly pure form without chromatography. A key factor in choice of alcohol is to avoid chromatography altogether for separation of the 1-acyldipyrromethane and the derivative formed upon reaction of ROH and the dibutylboron or 9-BBN species. We found that 1-pentanol generally afforded superior results. Accordingly, treatment of **6a-BBN** with excess 1-pentanol in refluxing THF for 1 h followed by solvent removal, trituration with hot hexanes for 5 min, and recrystallization/precipitation from CH_2Cl_2/hexanes afforded **2a** in 83% yield (Scheme 7).

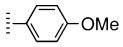
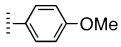
Application of these decomplexation conditions to **6a-BBN**, **6b-BBN**, and **6d-BBN** afforded **2a**, **2b**, and **2d**, respectively, in excellent yields (Scheme 7). The boron complex **6f-BBu$_2$** was decomplexed with neat 1-pentanol at 80 °C for 1 h followed by the workup procedure described above. Decomplexation of **6c-BBN** with 1-pentanol in THF at reflux for 1 h afforded **2c**, which was isolated upon passage through a pad of alumina.

Use of 1-Acyldipyrromethane−Boron Complexes in Porphyrin Formation. The reduction of a 1-acyldipyrromethane affords the corresponding dipyrromethane-1-carbinol, which upon self-condensation and oxidation affords the *trans*-A_2B_2 porphyrin.[2,33] The 1-acyldipyrromethane−boron complexes were examined as precursors to *trans*-A_2B_2 porphyrins, thereby avoiding the

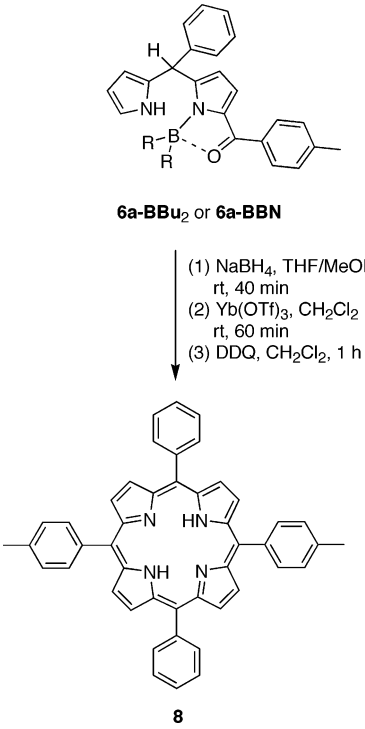
(34) Bar-Haim, G.; Kol, M. *J. Org. Chem.* **1997**, *62*, 6682−6683.
(35) Bar-Haim, G.; Kol, M. *Tetrahedron Lett.* **1998**, *39*, 2643−2644.

SCHEME 7



6a-BR$_2$	R^1	R^2	R$_2$B	Product (Yield)
6a-BBN			9-BBN	**2a** (83%)
6b-BBN			9-BBN	**2b** (81%)
6c-BBN			9-BBN	**2c** (82%)
6d-BBN			9-BBN	**2d** (80%)
6f-BBu$_2$			Bu$_2$B	**2f** (65%)

SCHEME 8



boron-decomplexation procedure. Thus, the boron complex **6a-BBu$_2$** was treated with $NaBH_4$ in THF/methanol for 40 min. TLC analysis indicated complete consumption of **6a-BBu$_2$** and formation of a new polar spot. The reaction mixture was worked up in the standard way and the product was subjected to acid-catalyzed self-condensation [$Yb(OTf)_3$ in CH_2Cl_2][33] followed by oxidation with DDQ. Porphyrin **8** was obtained in 26% yield (Scheme 8). The boron complex **6a-BBN** was treated similarly, affording porphyrin **8** in 17% yield. In both cases, no other porphyrin species were observed upon LD-MS[36] analysis of the crude reaction mixtures. For comparison, the reaction of the uncomplexed 1-acyldipyrromethane **2a** affords porphyrin **8** in 25% yield.[33]

Conclusion

Advances in porphyrin chemistry stem both from identification of new routes and from development of refined syntheses of critical intermediates. 1-Acyldipyrromethanes are essential intermediates in the synthesis of *trans*-A_2B_2, *trans*-AB_2C, *cis*-A_2B_2, *cis*-AB_2C, and ABCD porphyrins; diverse chlorins; A_2B, AB_2, and ABC corroles; and bilanes. The boron-complexation strategy provides a facile method for the isolation of a 1-acyldipyrromethane from the crude acylation mixture. Formation of the boron complex alters the structure by blocking the pyrrolic nitrogen and carbonyl oxygen atoms, thereby ensheathing sites that can engage in hydrogen bonding. The resulting 1-acyldipyrromethane−boron complex is typically less polar than the corresponding 1-acyldipyrromethane, has high solubility in organic solvents, chromatographs as a sharp band, and crystallizes readily. The boron-complexation strategy can be used for the purification of a wide variety of 1-acyldipyrromethanes. The 1-acyldipyrromethane−boron complexes can be decomplexed to give the 1-acyldipyrromethanes in excellent yields. Alternatively, reduction of a 1-acyldipyrromethane−boron complex followed by self-condensation of the resulting dipyrromethane-carbinol affords the corresponding *trans*-A_2B_2 porphyrin. The ability to isolate and handle 1-acyldipyrromethanes as dialkylboron complexes should increase the scale of 1-acyldipyrromethane syntheses and facilitate the preparation of a wide variety of porphyrinic compounds.

Experimental Section

Noncommercial Compounds. Dipyrromethanes **1a**−**f** were prepared as described in the literature and analyzed for purity by gas chromatography.[31] 1-Acyldipyrromethanes **2a**,[2] **2d**,[7] **2e**,[1] **2f**,[2] **2g**,[1] **2h**,[7] **2i**;[27] 1,9-diacyldipyrromethane **3a**;[1] and the Mukaiyama reagents **5a**−**e**[2] and **5f**[5] were prepared as described in the literature.

5-[4-(Trimethylsilylethynyl)phenyl]dipyrromethane (1g). Following a standard procedure,[31] a solution of 4-(trimethylsilylethynyl)benzaldehyde (7.00 g, 35.0 mmol) in pyrrole (347 mL) was degassed for 10 min. Then $InCl_3$ (1.11 g, 5.00 mmol) was added. The mixture was stirred at room temperature under argon. After 1.5 h, NaOH (6.00 g, 0.15 mol, 20−40 mesh beads) was added, and the stirring was continued for an additional 45 min. The mixture was filtered, and the filtrate was concentrated under high vacuum. The resulting oil was triturated with hexanes (50 mL), and the volatile components were evaporated. This procedure was repeated four times, affording a white solid. Crystallization from ethanol afforded off-white crystals (7.66 g, 69%): mp 122−123 °C (lit.[32] 120 °C). ^{1}H NMR spectral data are consistent with reported values:[32] ^{1}H NMR δ 0.26 (s, 9H), 5.45 (s, 1H), 5.88−5.92 (m, 2H), 6.13−6.19 (m, 2H), 6.67−6.71 (m, 2H), 7.14 (d, J = 8.0 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H), 7.83−7.90 (br, 2H). Anal. Calcd for $C_{18}H_{20}N_2$: C, 75.42; H, 6.96; N, 8.80. Found: C, 75.40; H, 6.88; N, 8.75.

1-(4-Methylbenzoyl)dipyrromethane (2b). Following a standard procedure[2] (but with a 500 mM solution of **1b** rather than 1 M owing to limited solubility), a solution of **1b** (0.731 g, 5.00 mmol) in THF (10 mL) at room temperature under argon was treated with EtMgBr (12.5 mL, 12.5 mmol, 1.0 M solution in THF) for 10 min. The solution was cooled to −78

(36) (a) Fenyo, D.; Chait, B. T.; Johnson, T. E.; Lindsey, J. S. *J. Porphyrins Phthalocyanines* **1997**, *1*, 93−99. (b) Srinivasan, N.; Haney, C. A.; Lindsey, J. S.; Zhang, W.; Chait, B. T. *J. Porphyrins Phthalocyanines* **1999**, *3*, 283−291.

°C. Then a solution of **5a** (1.15 g, 5.00 mmol) in THF (5.0 mL) was added. The reaction mixture was stirred at −78 °C for 10 min and at room temperature for 20 min. Standard workup and chromatography [silica, CH_2Cl_2/ethyl acetate (9:1)] afforded a pale brown solid (0.812 g, 62%): mp 172−174 °C; ^{1}H NMR δ 2.43 (s, 3H), 4.09 (s, 2H), 6.03−6.06 (m, 1H), 6.08−6.12 (m, 1H), 6.14−6.18 (m, 1H), 6.51−6.55 (m, 1H), 6.80−6.86 (m, 1H), 7.27 (d, J = 8.0 Hz, 2H), 7.76 (d, J = 8.0 Hz, 2H), 9.25−9.28 (br, 1H), 10.94−10.98 (br, 1H); ^{13}C NMR δ 21.8, 26.8, 106.4, 108.3, 110.3, 117.7, 123.1, 128.2, 129.3, 130.7, 136.0, 141.2, 142.7, 185.6. Anal. Calcd for $C_{17}H_{16}N_2O$: C, 77.25; H, 6.10; N, 10.60. Found: C, 76.52; H, 5.89; N, 10.33.

1-Hexanoyl-5-pentyldipyrromethane (2c). Following a standard procedure,[2] a solution of **1c** (1.08 g, 5.00 mmol) in THF (5.0 mL) under argon at room temperature was treated with EtMgBr (12.5 mL, 12.5 mmol, 1.0 M solution in THF) for 10 min. The solution was cooled to −78 °C, and then a solution of **5f** (1.05 g, 5.00 mmol) in THF (5.0 mL) was added. The reaction mixture was stirred at −78 °C for 10 min and at room temperature for 20 min. Standard workup and chromatography [silica, CH_2Cl_2/ethyl acetate (9:1)] afforded a light yellow oil (0.986 g, 63%): ^{1}H NMR δ 0.81−0.90 (m, 6H), 1.22−1.37 (m, 10H), 1.68−1.76 (m, 2H), 2.00−2.06 (m, 2H), 2.74 (t, J = 7.6 Hz, 2H), 4.05 (t, J = 7.6 Hz, 1H), 6.02−6.06 (m, 1H), 6.08−6.14 (m, 2H), 6.64−6.68 (m, 1H), 6.88−6.91 (m, 1H), 8.94−8.98 (br, 1H), 10.16−10.20 (br, 1H); ^{13}C NMR δ 14.1, 14.2, 22.7, 26.2, 27.7, 31.85, 31.87, 33.8, 38.1, 38.3, 105.0, 108.1, 108.5, 117.3, 119.5, 131.1, 133.0, 144.8, 191.9. Anal. Calcd for $C_{20}H_{30}N_2O$: C, 76.39; H, 9.62; N, 8.91. Found: C, 76.15; H, 9.80; N, 8.77.

Screening Protocol for Metal Complexation of 1-Acyldipyrromethanes. A solution of **2a** (0.017 g, 0.050 mmol) in methanol (0.5 mL) was treated with a solution of a metal reagent (0.025 mmol) in methanol (0.5 mL). The mixture was stirred at room temperature for 1 h. The reaction was monitored visually for precipitate formation. The reaction mixture was examined by TLC (silica, CH_2Cl_2/ethyl acetate, 9:1) and by absorption spectroscopy.

Bis[1-(4-methylbenzoyl)-5-phenyldipyrromethan-10-yl]copper(II) (Cu-2a). A solution of **2a** (0.25 mmol, 85 mg) in methanol (2.5 mL) was treated with a warm solution of $Cu(OAc)_2 \cdot H_2O$ (0.30 mmol, 26 mg) in methanol (1 mL). The mixture was stirred at room temperature for 20 min. The resulting precipitate was filtered. The filtered material was washed with methanol and dried in vacuo to afford a green powder (75 mg, 81%): Anal. Calcd for $C_{46}H_{38}CuN_4O_2$: C, 74.42; H, 5.16; N, 7.55. Found: C, 73.93; H, 5.22; N, 7.40. λ_{abs} 380 nm.

10-(Dibutylboryl)-1-(4-methylbenzoyl)-5-phenyldipyrromethane (6a-BBu$_2$). A solution of **2a** (0.340 g, 1.00 mmol) in CH_2Cl_2 (2 mL) was treated with TEA (0.335 mL, 2.40 mmol) followed by Bu_2B-OTf (2.00 mL, 2.00 mmol, 1.0 M in CH_2Cl_2). After 30 min, the mixture was passed through a pad of silica (4 × 8 cm) eluting with CH_2Cl_2. The product eluted as a fast-moving yellow band, which upon concentration afforded an orange oil (0.431 g, 93%): ^{1}H NMR δ 0.36−0.52 (m, 2H), 0.61 (t, J = 7.2 Hz, 3H), 0.65−1.18 (m, 13H), 2.47 (s, 3H), 5.60 (s, 1H), 5.85−5.88 (m, 1H), 6.13−6.17 (m, 1H), 6.45 (d, J = 4.0 Hz, 1H), 6.68−6.72 (m, 1H), 7.20−7.38 (m, 8H), 7.79−7.83 (br, 1H), 8.11 (d, J = 8.0 Hz, 2H); ^{13}C NMR δ 14.3, 14.4, 22.2, 22.6, 22.7, 26.17, 26.24, 27.1, 27.5, 44.2, 107.9, 108.8, 117.4, 117.8, 119.3, 127.3, 128.0, 128.77, 128.83, 129.98, 130.01, 132.2, 134.2, 141.5, 145.4, 150.1, 176.5; FABMS obsd 465.3074 [(M + H)$^+$], calcd 465.3077 ($C_{31}H_{37}BN_2O$). Anal. Calcd for $C_{31}H_{37}BN_2O$: C, 80.17; H, 8.03; N, 6.03. Found: C, 79.98; H, 8.06; N, 5.95. λ_{abs} 393 nm.

10-(Dimethylboryl)-1-(4-methylbenzoyl)-5-phenyldipyrromethane (6a-BMe$_2$). A solution of **2a** (0.340 g, 1.00 mmol) in CH_2Cl_2 (2 mL) was treated with TEA (0.335 mL, 2.40 mmol) followed by Me_2B-Br (0.390 mL, 1.00 mmol). After 30 min, the mixture was passed through a pad of silica (4 × 8 cm) eluting with CH_2Cl_2. The product eluted as a fast-moving yellow band, which upon concentration afforded an orange oil (0.344 g, 91%): ^{1}H NMR δ 0.04 (s, 3H), 0.15 (s, 3H), 2.48 (s, 3H), 5.66 (s, 1H), 5.87−5.92 (m, 1H), 6.15−6.19 (m, 1H), 6.43 (d, J = 4.0 Hz, 1H), 6.70−6.75 (m, 1H), 7.24−7.38 (m, 8H), 7.84−7.88 (br, 1H), 8.11 (d, J = 8.0 Hz, 2H); ^{13}C NMR δ 6.8, 22.1, 44.1, 107.9, 108.6, 117.5, 118.3, 119.3, 127.3, 128.1, 128.8, 128.9, 129.95, 129.99, 132.0, 133.1, 141.4, 145.5, 150.1, 176.1; FABMS obsd 381.2158 [(M + H)$^+$], calcd 381.2138 ($C_{25}H_{25}BN_2O$). Anal. Calcd for $C_{25}H_{25}BN_2O$: C, 78.96; H, 6.63; N, 7.37. Found: C, 78.66; H, 6.60; N, 7.28. λ_{abs} 393 nm.

10-(9-Borabicyclo[3.3.1]non-9-yl)-1-(4-methylbenzoyl)-5-phenyldipyrromethane (6a-BBN). A solution of **2a** (0.680 g, 2.00 mmol) in CH_2Cl_2 (4 mL) was treated with TEA (0.670 mL, 4.80 mmol) followed by 9-BBN-OTf (8.00 mL, 4.00 mmol, 0.5 M in hexanes). After 30 min, the mixture was passed through a pad of silica (4 × 8 cm) eluting with CH_2Cl_2. The product eluted as a fast-moving yellow band, which upon concentration afforded a yellow-orange solid (0.863 g, 94%): mp 187 °C (dec); ^{1}H NMR δ 0.66−0.71 (m, 2H), 1.65−1.84 (m, 6H), 1.95−2.25 (m, 6H), 2.48 (s, 3H), 5.83−5.86 (m, 1H), 6.01 (s, 1H), 6.13−6.17 (m, 1H), 6.41 (d, J = 4.0 Hz, 1H), 6.69−6.73 (m, 1H), 7.18 (d, J = 8.0 Hz, 2H), 7.22−7.38 (m, 6H), 7.83−7.87 (br, 1H), 8.11 (d, J = 8.0 Hz, 2H); ^{13}C NMR δ 22.0, 23.8, 25.1, 25.9, 26.4, 30.5, 30.8, 34.48, 34.54, 44.7, 108.1, 108.5, 117.4, 118.2, 120.8, 127.0, 128.1, 128.4, 128.6, 129.7, 129.9, 132.3, 134.8, 142.1, 145.0, 151.9, 174.4; ^{11}B NMR δ 12.34; FABMS obsd 460.2674 [M$^+$], calcd 460.2686 ($C_{31}H_{33}BN_2O$). Anal. Calcd for $C_{31}H_{33}BN_2O$: C, 80.87; H, 7.22; N, 6.08. Found: C, 78.96; H, 7.13; N, 5.85. λ_{abs} 381 nm.

10-(9-Borabicyclo[3.3.1]non-9-yl)-1-(4-methylbenzoyl)-dipyrromethane (6b-BBN). Following the procedure for **6a-BBN**, reaction of **2b** (0.529 g, 2.00 mmol) afforded a yellow-orange solid (0.696 g, 91%): mp 147 °C (dec); ^{1}H NMR δ 0.71−0.78 (m, 2H), 1.67−1.75 (m, 4H), 1.76−1.91 (m, 4H), 1.98−2.14 (m, 2H), 2.16−2.26 (m, 2H), 2.48 (s, 3H), 4.34 (s, 2H), 6.03−6.06 (m, 1H), 6.16−6.18 (m, 1H), 6.36 (d, J = 4.0 Hz, 1H), 6.69−6.72 (m, 1H), 7.29 (d, J = 4.0 Hz, 1H), 7.36 (d, J = 8.0 Hz, 2H), 7.90−7.94 (br, 1H), 8.11 (d, J = 8.0 Hz, 2H); ^{13}C NMR δ 22.1, 24.0, 25.2, 26.8, 29.5, 31.5, 34.5, 107.1, 108.7, 117.5, 118.3, 120.7, 128.2, 128.7, 129.8, 129.9, 135.3, 145.0, 149.5, 174.1; ^{11}B NMR δ 12.74; FABMS obsd 384.2395 [M$^+$], calcd 384.2373 ($C_{25}H_{29}BN_2O$). Anal. Calcd for $C_{25}H_{29}BN_2O$: C, 78.13; H, 7.61; N, 7.29. Found: C, 78.17; H, 7.58; N, 7.09. λ_{abs} 380 nm.

10-(9-Borabicyclo[3.3.1]non-9-yl)-1-hexanoyl-5-pentyldipyrromethane (6c-BBN). Following the procedure for **6a-BBN**, reaction of **2c** (0.529 g, 2.00 mmol) afforded an orange oil (0.758 g, 87%): ^{1}H NMR δ 0.55−0.64 (m, 2H), 0.82−0.94 (m, 6H), 1.19−1.54 (m, 12H), 1.62−1.91 (m, 8H), 1.96−2.17 (m, 6H), 2.81 (t, J = 8.0 Hz, 2H), 4.43 (t, J = 8.0 Hz, 1H), 6.03−6.06 (m, 1H), 6.13−6.17 (m, 1H), 6.39 (d, J = 4.0 Hz, 1H), 6.62−6.67 (m, 1H), 7.05 (d, J = 4.0 Hz, 1H), 7.76−7.80 (br, 1H); ^{13}C NMR δ 14.1, 14.2, 22.5, 22.6, 22.7, 24.0, 25.0, 25.8, 26.3, 27.6, 30.7, 30.8, 31.5, 31.7, 32.2, 34.19, 32.22, 36.4, 39.2, 105.2, 108.5, 117.0, 117.57, 117.63, 133.5, 136.5, 154.8, 184.3; ^{11}B NMR δ 13.22; FABMS obsd 434.3481 [M$^+$], calcd 434.3468 ($C_{28}H_{43}BN_2O$). Anal. Calcd for $C_{28}H_{43}BN_2O$: C, 77.41; H, 9.98; N, 6.45. Found: C, 75.22; H, 9.90; N, 6.40. λ_{abs} 345 nm.

10-(9-Borabicyclo[3.3.1]non-9-yl)-1-(4-methoxybenzoyl)-5-(4-methoxyphenyl)dipyrromethane (6d-BBN). Following the procedure for **6a-BBN**, reaction of **2d** (0.773 g, 2.00 mmol) afforded a yellow-brown solid (0.986 g, 97%): mp 72−73 °C; ^{1}H NMR δ 0.64−0.74 (m, 2H), 1.62−1.86 (m, 6H), 1.98−2.24 (m, 6H), 3.79 (s, 3H), 3.92 (s, 3H), 5.82−5.87 (m, 1H), 5.96 (s, 1H), 6.12−6.17 (m, 1H), 6.40 (d, J = 4.0 Hz, 1H), 6.69−6.72 (m, 1H), 6.84 (d, J = 8.0 Hz, 2H), 7.05 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 4.0 Hz, 1H), 7.84−7.88 (br, 1H), 8.21 (d, J = 8.0 Hz, 2H); ^{13}C NMR δ 24.0, 25.2, 26.0, 26.5, 30.6, 30.9, 34.6, 34.7, 44.0, 55.4, 55.8, 107.9, 108.6, 114.0, 114.7, 117.4, 117.8, 120.5, 123.5, 129.6, 130.0, 133.0, 134.4, 134.5, 151.7, 158.6, 164.4, 173.8; ^{11}B NMR δ 12.69; FABMS obsd 506.2749 [M$^+$], calcd 506.2741 ($C_{32}H_{35}BN_2O_3$).

Anal. Calcd for $C_{32}H_{35}BN_2O_3$: C, 75.89; H, 6.97; N, 5.53. Found: C, 74.75; H, 7.37; N, 5.01. λ_{abs} 388 nm.

10-(Dibutylboryl)-1-(pentafluorobenzoyl)-5-pentafluorophenyldipyrromethane (6e-BBu$_2$). Following the procedure for **6a-BBu$_2$**, reaction of **2e** (0.506 g, 1.00 mmol) afforded an orange oil (0.608 g, 97%): ^{1}H NMR δ 0.13−0.35 (m, 2H), 0.58−1.39 (m, 16H), 5.94 (s, 1H), 6.00 (s, 1H), 6.15−6.20 (m, 1H), 6.61 (d, J = 4.0 Hz, 1H), 6.74−6.80 (m, 1H), 7.04−7.10 (m, 1H), 8.05−8.09 (br, 1H); ^{13}C NMR δ 14.1, 14.3, 20.9, 21.4, 26.0, 26.2, 26.9, 27.4, 33.5, 33.9, 108.5, 109.2, 109.4, 111.3, 118.8, 119.6, 119.7, 119.8, 122.1, 122.3, 127.0, 136.9 (m), 138.0, 139.6 (m), 142.1 (m), 142.9 (m), 143.9 (m), 144.4 (m), 145.5 (m), 146.4 (m), 147.0 (m), 150.6, 166.0. This compound partially decomplexed to **2e** upon handling as a result of exposure to moisture.

10-(Dibutylboryl)-1-(4-iodobenzoyl)-5-mesityldipyrromethane (6f-BBu$_2$). Following the procedure for **6a-BBu$_2$**, reaction of **2f** (0.494 g, 1.00 mmol) afforded a yellow-orange solid (0.548 g, 89%): mp 53−54 °C; ^{1}H NMR δ −0.25− −0.17 (m, 1H), 0.24−0.39 (m, 2H), 0.55−0.98 (m, 13H), 1.14−1.27 (m, 2H), 2.15 (s, 6H), 2.62 (s, 3H), 5.88 (s, 1H), 5.90−5.93 (m, 1H), 6.16−6.20 (m, 1H), 6.50 (d, J = 4.0 Hz, 1H), 6.66−6.70 (m, 1H), 6.83 (s, 2H), 7.17 (d, J = 4.0 Hz, 1H), 7.80−7.84 (br, 1H), 7.85−7.94 (m, 4H); ^{13}C NMR δ 14.3, 14.5, 20.9, 21.2, 21.8, 26.1, 26.2, 27.3, 27.5, 40.1, 101.9, 108.0, 108.9, 116.8, 117.0, 122.8, 130.0, 130.1, 130.6, 130.9, 134.8, 135.3, 136.9, 137.2, 138.6, 153.0, 174.7; FABMS obsd 619.2390 [(M + H)$^+$], calcd 619.2357 ($C_{33}H_{40}BIN_2O$). Anal. Calcd for $C_{33}H_{40}BIN_2O$: C, 64.09; H, 6.52; N, 4.53. Found: C, 64.08; H, 6.62; N, 4.40. λ_{abs} 404 nm.

10-(9-Borabicyclo[3.3.1]non-9-yl)-1-(4-bromobenzoyl)-5-[4-(2-trimethylsilyl)ethynylphenyl]dipyrromethane (6g-BBN). Following the procedure for **6a-BBN**, reaction of **2g** (0.529 g, 2.00 mmol) afforded a yellow-orange solid (1.19 g, 96%): mp 172 °C (dec); ^{1}H NMR δ 0.24 (s, 9H), 0.64−0.73 (m, 2H), 1.64−1.85 (m, 6H), 1.94−2.09 (m, 4H), 2.12−2.24 (m, 2H), 5.83 (s, 1H), 6.00 (s, 1H), 6.13−6.18 (m, 1H), 6.39 (d, J = 4.0 Hz, 1H), 6.71−6.75 (m, 1H), 7.09 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 4.0 Hz, 1H), 7.40 (d, J = 8.0 Hz, 2H), 7.68−7.74 (m, 2H), 7.82−7.86 (br, 1H), 8.02−8.10 (m, 2H); ^{13}C NMR δ 0.18, 23.8, 25.1, 25.9, 26.6, 30.7, 30.8, 34.6, 44.8, 94.7, 104.9, 108.4, 108.8, 117.9, 118.7, 121.6, 122.1, 128.4, 129.2, 129.7, 131.0, 131.7, 132.4, 132.6, 132.7, 135.1, 142.4, 152.5, 173.2; ^{11}B NMR δ 13.98; FABMS obsd 620.2057 [M$^+$], calcd 620.2030 ($C_{35}H_{38}BBrN_2OSi$). Anal. Calcd for $C_{35}H_{38}BBrN_2OSi$: C, 67.64; H, 6.16; N, 4.51. Found: C, 67.41; H, 6.26; N, 4.43. λ_{abs} 388 nm.

10-(9-Borabicyclo[3.3.1]non-9-yl)-1-(4-methylbenzoyl)-5-(pentafluorophenyl)dipyrromethane (6h-BBN). Following the procedure for **6a-BBN**, reaction of **2h** (0.430 g, 1.00 mmol) afforded a yellow-orange solid (0.512 g, 93%): mp 154−156 °C (dec); ^{1}H NMR δ 0.58−0.64 (m, 1H), 0.68−0.74 (m, 1H), 1.58−1.85 (m, 6H), 1.94−2.24 (m, 6H), 2.50 (s, 3H), 5.79 (s, 1H), 6.12−6.18 (m, 1H), 6.30 (s, 1H), 6.60 (d, J = 4.0 Hz, 1H), 6.62−6.68 (m, 1H), 7.38 (d, J = 4.0 Hz, 1H), 7.39 (d, J = 8.0 Hz, 2H), 7.75−7.78 (br, 1H), 8.15 (d, J = 8.0 Hz, 2H); ^{13}C NMR δ 22.2, 23.9, 25.1, 26.3, 27.2, 29.8, 31.3, 34.67, 34.71, 36.3, 106.9, 109.2, 117.4, 118.3, 120.56, 120.60, 120.64, 127.9, 129.6, 130.07, 130.14, 135.9, 136.8 (m), 139.4 (m), 142.0 (m), 144.4 (m), 145.8, 146.4, 146.9 (m), 175.9; FABMS obsd 550.2229 [M$^+$], calcd 550.2215 ($C_{31}H_{28}BF_5N_2O$). Anal. Calcd for $C_{31}H_{28}BF_5N_2O$: C, 67.65; H, 5.13; N, 5.09. Found: C, 68.05; H, 5.23; N, 4.92. λ_{abs} 377 nm.

10-(Dibutylboryl)-1-(4-methylbenzoyl)-5-(pentafluorophenyl)dipyrromethane (6h-BBu$_2$). Following the procedure for **6a-BBu$_2$**, reaction of **2h** (0.430 g, 1.00 mmol) afforded an orange oil (0.497 g, 90%): ^{1}H NMR δ 0.16−0.35 (m, 2H), 0.54−1.25 (m, 16H), 2.48 (s, 3H), 5.94−6.02 (m, 2H), 6.14−6.18 (m, 1H), 6.57 (d, J = 4.0 Hz, 1H), 6.72−6.78 (m, 1H), 7.24 (d, J = 4.0 Hz, 1H), 7.38 (d, J = 8.0 Hz, 2H), 8.06−8.10 (br, 1H), 8.12 (d, J = 8.0 Hz, 2H); ^{13}C NMR δ 14.2, 14.4, 21.5, 21.8, 22.2, 26.1, 26.3, 27.1, 27.6, 33.7, 107.9, 109.0, 117.4, 118.3, 119.68, 119.72, 119.76, 127.7, 128.0, 130.1, 130.2, 135.0, 145.6, 146.1, 177.6; FABMS obsd 555.2627 [(M + H)$^+$], calcd 555.2606 ($C_{31}H_{32}BF_5N_2O$). Anal. Calcd for $C_{31}H_{32}BF_5N_2O$: C, 67.16; H, 5.82; N, 5.05. Found: C, 67.00; H, 5.78; N, 4.91. λ_{abs} 386 nm.

10-(Dibutylboryl)-1-(pentafluorobenzoyl)dipyrromethane (6i-BBu$_2$). Following the procedure for **6a-BBu$_2$**, reaction of **2i** (0.340 g, 1.00 mmol) afforded an orange oil (0.412 g, 89%): ^{1}H NMR δ 0.58−0.68 (m, 2H), 0.74−0.92 (m, 10H), 1.00−1.08 (m, 2H), 1.16−1.30 (m, 4H), 4.09 (s, 2H), 6.04−6.09 (m, 1H), 6.14−6.20 (m, 1H), 6.45 (d, J = 4.0 Hz, 1H), 6.70−6.75 (m, 1H), 7.01−7.06 (m, 1H), 7.90−7.93 (br, 1H); ^{13}C NMR δ 14.4, 22.0, 26.2, 27.3, 107.6, 109.1, 117.8, 120.21, 120.26, 120.30, 121.9, 126.9, 137.5, 152.1, 164.1; FABMS obsd 465.2179 [(M + H)$^+$], calcd 465.2137 ($C_{24}H_{26}BF_5N_2O$). Anal. Calcd for $C_{24}H_{26}BF_5N_2O$: C, 62.09; H, 5.64; N, 6.03. Found: C, 61.31; H, 5.63; N, 5.93. λ_{abs} 382 nm.

Acylation-Boron Complexation Procedure, Exemplified for 6a-BBN. A solution of EtMgBr (20.0 mL, 20.0 mmol, 1.0 M in THF) was added slowly to a solution of **1a** (2.22 g, 10.0 mmol) in THF (10 mL) under argon. The resulting mixture was stirred at room temperature for 10 min and then cooled to −78 °C. A solution of *S*-2-pyridyl 4-methylbenzothioate (**5a**, 2.29 g, 10.0 mmol) in THF (10 mL) was added. The solution was stirred at −78 °C for 10 min and then warmed to room temperature. The reaction mixture was quenched by addition of saturated aqueous NH_4Cl (40 mL). The mixture was extracted with ethyl acetate (30 mL). The organic layer was washed (water and brine), dried (Na_2SO_4), and filtered. The filtrate was concentrated. The crude product (a red-orange oil) thus obtained was dissolved in CH_2Cl_2 (20 mL) and treated with TEA (3.35 mL, 24.0 mmol) followed by 9-BBN-OTf (40 mL, 20.0 mmol, 0.5 M in hexane) with stirring at room temperature. A precipitate formed that largely consisted of the salt of TEA and triflic acid. After 1 h, the mixture was poured onto a pad of silica (4 × 8 cm) eluting with CH_2Cl_2. The product eluted as a fast-moving yellow band, which upon concentration afforded a yellow-orange solid (3.12 g, 67%) with satisfactory characterization data (mp, ^{1}H NMR spectrum, and FABMS) as reported above.

Note: The use of boron complexation to isolate the 1-acyldipyrromethane enables use of stoichiometric quantities of reagents rather than excess as employed previously. Thus, the 1-acylation of dipyrromethanes was conducted with slight modification to the standard procedure. Previously, 2.5 molar equiv of EtMgBr was used for the acylation of dipyrromethane (**1**) with 1.0 molar equiv of a Mukaiyama reagent (**5**) in order to avoid cochromatography of the unreacted **5** and the product **2**.[2] (The unreacted Mukaiyama reagent is consumed by EtMgBr, affording the ketone.[30]) Given that the 1-acyldipyrromethane is to be isolated as a boron complex, complete consumption of the Mukaiyama reagent is not necessary.

Scale-Up Procedure. A solution of EtMgBr (80.0 mL, 80.0 mmol, 1.0 M in THF) was added slowly to a solution of **1a** (8.88 g, 40.0 mmol) in THF (40 mL) under argon. The resulting mixture was stirred at room temperature for 10 min and then cooled to −78 °C. A solution of *S*-2-pyridyl 4-methylbenzothioate (**5a**, 9.16 g, 40.0 mmol) in THF (40 mL) was added. The solution was stirred at −78 °C for 10 min and then warmed to room temperature. The reaction mixture was quenched by addition of saturated aqueous NH_4Cl. The mixture was extracted with ethyl acetate. The organic layer was dried (Na_2SO_4) and filtered. The filtrate was concentrated. The crude product (a red-orange oil) thus obtained was dissolved in toluene (80 mL) and treated with TEA (13.4 mL, 96.0 mmol) followed by 9-BBN-OTf (160 mL, 80.0 mmol, 0.5 M in hexanes) with stirring at room temperature. A precipitate formed immediately, which largely consisted of the title compound and the salt of TEA and triflic acid. After 1 h, the mixture was filtered through a Büchner funnel using coarse filter paper. The filtered material was washed with water, washed with methanol, and then dried in vacuo to afford a yellow powder (9.63 g, 52%). The filtrate was concentrated and passed

through a silica pad eluting with CH_2Cl_2/hexanes, affording 1.77 g of the title compound. The combined yield is 11.4 g (62%) and the characterization data are satisfactory (mp, ^{1}H NMR, ^{13}C NMR, and FABMS spectra) as reported above.

10-(9-Borabicyclo[3.3.1]non-9-yl)-1-(4-methylbenzoyl)-dipyrromethane (6b-BBN). Following the acylation-complexation procedure, reaction of **1b** (1.46 g, 10.0 mmol) with EtMgBr (20.0 mL, 20.0 mmol, 1.0 M in THF) followed by treatment with **5a** (2.29 g, 10.0 mmol) afforded crude **2b**. Boron complexation with TEA (3.35 mL, 24.0 mmol) and 9-BBN-OTf (40.0 mL, 20.0 mmol, 0.5 M in hexanes) in CH_2Cl_2 followed by passage through a pad of silica [CH_2Cl_2/hexanes (1:1)] afforded a solid, which upon trituration with hexanes afforded yellow crystals (2.30 g, 60%) with satisfactory characterization data (mp, ^{1}H NMR, and elemental analysis) as reported above.

10-(9-Borabicyclo[3.3.1]non-9-yl)-1-hexanoyl-5-pentyl-dipyrromethane (6c-BBN). Following the acylation-complexation procedure, reaction of **1c** (2.16 g, 10.0 mmol) with EtMgBr (20.0 mL, 20.0 mmol, 1.0 M in THF) followed by treatment with **5f** (2.09 g, 10.0 mmol) afforded crude **2c**. Boron complexation with TEA (3.35 mL, 24.0 mmol) and 9-BBN-OTf (40.0 mL, 20.0 mmol, 0.5 M in hexanes) in CH_2Cl_2 followed by passage through a pad of silica [CH_2Cl_2/hexanes (1:1)] afforded an orange oil (2.59 g, 60%) with satisfactory characterization data (^{1}H NMR and ^{13}C NMR spectra and FABMS) as reported above.

10-(9-Borabicyclo[3.3.1]non-9-yl)-1-(4-methoxybenzoyl)-5-(4-methoxyphenyl)dipyrromethane (6d-BBN). Following the acylation-complexation procedure, reaction of **1d** (2.45 g, 10.0 mmol) with EtMgBr (20.0 mL, 20.0 mmol, 1.0 M in THF) followed by treatment with **5b** (2.45 g, 10.0 mmol) afforded crude **2d**. Boron complexation with TEA (3.35 mL, 24.0 mmol) and 9-BBN-OTf (40.0 mL, 20.0 mmol, 0.5 M in hexanes) in CH_2Cl_2 afforded a yellow-orange precipitate. The precipitate was filtered and dissolved in 50 mL of CH_2Cl_2. The solution was washed with water and brine, dried (Na_2SO_4), and concentrated to dryness. The resulting yellow solid was stirred in Et_2O for 1 min, filtered, washed with Et_2O and hexanes, dissolved in 20 mL of CH_2Cl_2, and concentrated to dryness, affording yellow crystals (2.81 g, 56%). The filtrates (from reaction mixture and stirring in Et_2O) were combined, concentrated, and filtered through a pad of silica CH_2Cl_2/hexanes (1:1), affording additional product (0.52 g). The total yield is 3.33 g (66%), and the characterization data are satisfactory (mp, ^{1}H NMR, and elemental analysis).

10-(Dibutylboryl)-1-(4-iodobenzoyl)-5-mesityldipyrromethane (6f-BBu$_2$). Following the acylation-complexation procedure, reaction of **1f** (2.64 g, 10.0 mmol) with EtMgBr (20.0 mL, 20.0 mmol, 1.0 M in THF) followed by treatment with **5d** (2.29 g, 10.0 mmol) afforded crude **2f**. Boron complexation with TEA (3.35 mL, 24.0 mmol) and dibutylboron triflate (20.0 mL, 20.0 mmol, 1.0 M in CH_2Cl_2) in CH_2Cl_2 followed by passage through a pad of silica [CH_2Cl_2/hexanes (1:2)] afforded a golden-yellow amorphous powder (4.23 g, 68%) with satisfactory characterization data (mp, ^{1}H NMR, and elemental analysis) as reported above.

10-(9-Borabicyclo[3.3.1]non-9-yl)-1-(4-bromobenzoyl)-5-[4-(trimethylsilylethynyl)phenyl]dipyrromethane (6g-BBN). Following the acylation-complexation procedure, reaction of **1g** (3.18 g, 10.0 mmol) with EtMgBr (20.0 mL, 20.0 mmol, 1.0 M in THF) followed by treatment with **5e** (2.93 g, 10.0 mmol) afforded crude **2g**. Boron complexation with TEA (3.35 mL, 24.0 mmol) and 9-BBN-OTf (40.0 mL, 20.0 mmol, 0.5 M in hexanes) in CH_2Cl_2 followed by passage through a pad of silica [CH_2Cl_2/hexanes (1:1)] afforded orange-yellow crystals (4.38 g, 71%) with satisfactory characterization data (mp, ^{1}H NMR, and elemental analysis) as reported above.

10-(9-Borabicyclo[3.3.1]non-9-yl)-1-(4-methylbenzoyl)-5-(pentafluorophenyl)dipyrromethane (6h-BBN). Following the acylation-complexation procedure, reaction of **1h** (3.12 g, 10.0 mmol) with EtMgBr (20.0 mL, 20.0 mmol, 1.0 M in THF) followed by treatment with **5a** (2.29 g, 10.0 mmol) afforded crude **2h**. Boron complexation with TEA (3.35 mL, 24.0 mmol) and 9-BBN-OTf (40.0 mL, 20.0 mmol, 0.5 M in hexanes) in CH_2Cl_2 followed by passage through a pad of silica [CH_2Cl_2/hexanes (1:1)] afforded yellow crystals (3.17 g, 58%) with satisfactory characterization data (mp, ^{1}H NMR, and elemental analysis) as reported above.

Decomplexation Procedure, Exemplified for 6a-BBN → 2a. A solution of **6a-BBN** (0.230 g, 0.500 mmol) in THF (0.8 mL) was treated with 1-pentanol (0.2 mL). The reaction mixture was heated at reflux. After 1 h, TLC (silica/CH_2Cl_2) examination showed almost complete consumption of boron complex **6a-BBN**. The mixture was concentrated to dryness, and the resulting oily residue was treated with 5 mL of hexanes. The oil solidified upon standing for 5 min. The mixture was heated gently under reflux for 5 min (the solid dissolved completely). The mixture was cooled, affording a precipitate upon standing for a few hours. The solvent was decanted. The solid was dissolved in a minimal amount of CH_2Cl_2 (~0.2 mL), and the title compound was precipitated upon addition of hexanes. The precipitate was collected and dried in vacuo to afford a dark-yellow powder (0.118 g, 66%). The hexanes solution was concentrated to half of the starting volume. The resulting precipitate was filtered, dissolved in a minimal volume of CH_2Cl_2, and precipitated upon addition of hexanes, affording an additional 0.030 g of title compound. The combined yield (0.148 g) is 83%: mp 64−65 °C (lit.[2] 70−72 °C); ^{1}H NMR ($CDCl_3$) δ 2.42 (s, 3H), 5.54 (s, 1H), 5.99 (s, 1H), 6.04−6.08 (m, 1H), 6.16−6.20 (m, 1H), 6.72 (s, 1 H), 6.79−6.83 (m, 1H), 7.36−7.22 (m, 8H), 7.75 (d, J = 8.0 Hz, 2H), 7.97−8.00 (br, 1H) 9.34−9.37 (br, 1H); FABMS obsd 340.1593 [M^+], calcd 340.1576 ($C_{23}H_{20}N_2O$).

Notes: High ratios of 1-pentanol/THF can be used and result in faster reaction (20 min) but can cause interference upon crystallization. In most cases, it is important to remove 1-pentanol completely because of the high solubility of 1-acyldipyrromethanes in 1-pentanol.

1-(4-Methylbenzoyl)dipyrromethane (2b). Following the decomplexation procedure, a sample of **6b-BBN** (0.74 g, 2.0 mmol) was dissolved in THF (3 mL) and 1-pentanol (1 mL) was added. The mixture was refluxed for 1 h, concentratedm and treated with 5 mL of hexanes. The resulting precipitate was filtered, washed with hexanes, and dried under vacuo to give pale yellow crystals (0.43 g, 81%) with satisfactory characterization data (mp, ^{1}H NMR, and elemental analysis) as described above.

1-Hexanoyl-5-pentyldipyrromethane (2c). Following the decomplexation procedure, reaction of **6c-BBN** (0.869 g, 2.00 mmol) with 1-pentanol (1.00 mL, 10.0 mmol) in THF at reflux afforded a crude product. The crude product was passed through a pad of alumina [CH_2Cl_2 → CH_2Cl_2/ethyl acetate (4:1)] affording a light yellow oil (0.514 g, 82%) with satisfactory characterization data (^{1}H NMR, elemental analysis) as described above.

1-(4-Methoxybenzoyl)-5-(4-methoxyphenyl)dipyrromethane (2d). Following the decomplexation procedure, a suspension of **6d-BBN** (1.01 g, 2.00 mmol) in THF (3.2 mL) and 1-pentanol (0.8 mL) was refluxed for 1.5 h. The mixture was concentrated, and the residue was dissolved in a small volume of CH_2Cl_2 and treated with hexanes. An oily precipitate was formed. The solvent was decanted. The residue was dried under vacuum, washed thoroughly with hexanes, and dried again to afford a pale brown amorphous powder (0.610 g, 78%): mp 58−61 °C (dec) (lit.[7] 113−114 °C). The ^{1}H NMR data and elemental analysis data were consistent with those for the same compound obtained by a different route.[7]

1-(4-Iodobenzoyl)-5-mesityldipyrromethane (2f). A sample of **6f-BBu$_2$** (1.24 g, 2.00 mmol) was dissolved in 1-pentanol (4.0 mL). The solution was heated at 70−80 °C. After 1 h the mixture was concentrated, and 20 mL of hexanes was added. The mixture was heated at reflux for 2 min and then cooled to room temperature. After standing overnight at −15 °C, the precipitate was collected, dissolved in a minimum

volume of CH_2Cl_2, and precipitated with hexanes. The precipitate was collected and dried in vacuo to afford a dark powder (0.639 g, 65%): mp 166−170 °C (lit.[2] 163 °C). The ^1H NMR and elemental analysis data were consistent with those for the same compound obtained by a different route.[2]

5,15-Bis(4-methylphenyl)-10,20-diphenylporphyrin (8) from 6a-BBu$_2$. A sample of 1-acyldipyrromethane−boron complex **6a-BBu$_2$** (0.116 g, 0.250 mmol) was dissolved in dry THF/methanol (3:1, 6 mL) at room temperature in a round-bottomed flask fitted with a vented rubber septum and flooded with argon. The septum was removed as needed to add $NaBH_4$ (0.238 g, 6.25 mmol, 25 mol equiv) in small portions with rapid stirring. 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 saturated aqueous NH_4Cl and CH_2Cl_2. The organic phase was separated, washed with water, dried (Na_2SO_4), and concentrated under reduced pressure to yield the monocarbinol as a foamlike solid. To the flask containing the dipyrromethanemoncarbinol (0.250 mmol assuming quantitative reduction) was added reagent-grade CH_2Cl_2 (50 mL). The mixture was stirred for 5 min to achieve dissolution, and then $Yb(OTf)_3$ (0.010 g, 0.016 mmol, 0.32 mM) was added. The reaction was monitored by absorption spectroscopy [by injecting a 50 μL reaction aliquot into a solution of DDQ (300 μL, 0.01 M in toluene); then 50 μL of the resulting oxidized mixture was dissolved in CH_2Cl_2/EtOH (3:1, 3 mL), and the absorption spectrum was recorded]. After acid-catalyzed condensation for 60 min, DDQ (0.085 g, 0.375 mmol) was added. The mixture was stirred at room temperature for 1 h. TEA was added, and the entire reaction mixture was passed through a pad of silica and eluted with CH_2Cl_2 until the eluant was no longer purple. The resulting porphyrin-containing solution was concentrated by rotary evaporation to give a purple solid. The solid was triturated with methanol and dried in vacuo, affording a crystalline purple solid (0.021 g, 26%). The characterization data (^1H NMR, LDMS, and UV−vis spectra) were consistent with the reported values.[2]

5,15-Bis(4-methylphenyl)-10,20-diphenylporphyrin (8) from 6a-BBN. Following the porphyrin formation procedure for **8** from **6a-BBu$_2$**, reaction of **6a-BBN** (0.460 g, 1.00 mmol) afforded a purple solid (0.054 g, 17%) with satisfactory characterization data (^1H NMR, LDMS, and UV−vis spectra).

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Supporting Information Available: ^1H NMR spectra for each new compound and crystallographic data for **6a-BBN**. This material is available free of charge via the Internet at http://pubs.acs.org.

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