JOC Article

^{15}N NMR Chemical Shifts for the Identification of Dipyrrolic Structures

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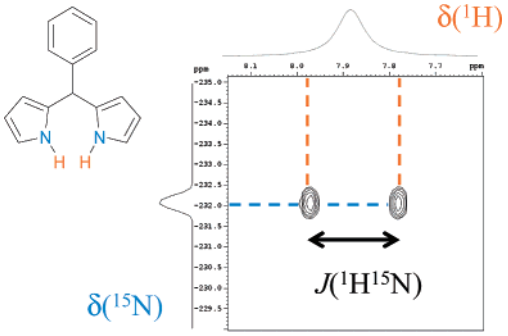

A variety of dipyrromethanes and dipyrromethenes have been prepared, and their ^{15}N NMR chemical shifts have been measured by two-dimensional correlation to ^{1}H NMR signals. The nitrogen atoms in five examples of dipyrromethanes consistently exhibit chemical shifts around −231 ppm, relative to nitromethane. Seven examples of hydrobromide salts of meso-unsubstituted dipyrromethenes consistently display ^{15}N chemical shifts around −210 ppm, while their corresponding zinc(II) complexes exhibit chemical shifts around −170 ppm. The presence of electron-withdrawing substituents on one of the pyrrolic rings of dipyrromethenes affects the chemical shifts of both of the nitrogen nuclei in the molecule. Boron difluoride complexes of meso-unsubstituted dipyrromethenes display ^{15}N chemical shifts around −190 ppm. Two examples of free-base dipyrromethenes bearing substituents at the meso-position exhibit ^{15}N chemical shifts at approximately −156 ppm, and for the zinc complexes of these compounds at −162 ppm. One-bond nitrogen−hydrogen coupling constants, when measurable, were consistently in the range of −96 Hz. Since the measured ^{15}N chemical shifts have such a high regularity correlated to structure, they can be used as diagnostic indications for identifying the structure of dipyrrolic compounds.

Introduction

Research that has been conducted into nitrogen NMR of pyrrole derivatives has focused upon the ^{14}N and ^{15}N NMR spectra of pyrroles, polypyrroles, and cyclic tetrapyrroles such as porphyrins and corrinoids.[1,2] There have been two reports of investigations of the ^{15}N NMR spectrum of bilirubin,[3,4] a linear tetrapyrrolic dipyrrinone, but, to the best of our knowledge, there are no reports of nitrogen NMR data for dipyrrolic compounds such as dipyrromethanes (Figure 1) and only one spectrum for a dipyrromethene compound.[5] Dipyrromethanes are frequently synthesized as precursors to porphyrins and dipyrromethenes,[6] which are both important ligands in the design of macromolecular structures.[7,8] Boron difluoride complexes of dipyrromethenes, known as BODIPY dyes, have found importance as fluorescent dyes for biological samples.[9,10]

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(7) Halper, S. R.; Cohen, S. M. *Inorg. Chem.* **2005**, *44*, 486−488.
(8) Sazanovich, I. V.; Kirmaier, C.; Hindin, E.; Yu, L.; Bocian, D. F.; Lindsey, J. S.; Holten, D. *J. Am. Chem. Soc.* **2004**, *126*, 2664−2665.

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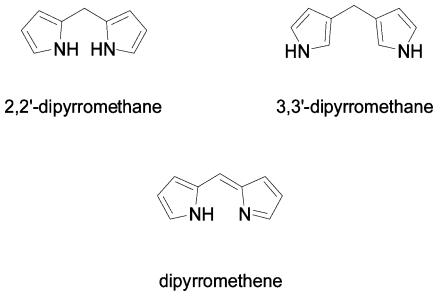


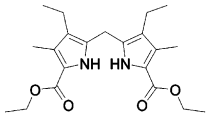
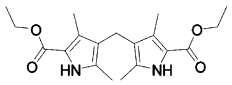
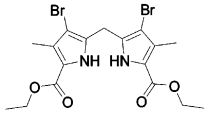
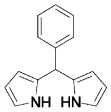
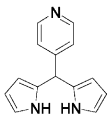
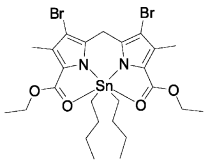
FIGURE 1. General structures of dipyrromethanes and dipyrromethenes.

The acquisition of ^{15}N NMR data suffers from a low natural abundance (0.365%) and a low magnetogyric ratio, resulting in low sensitivity.[2] The use of natural abundance ^{15}N NMR experiments has recently become routine as a result of advances in inverse detection techniques such as heteronuclear multiple bond correlation (HMBC) and heteronuclear single quantum coherence (HSQC) spectroscopy, alleviating the reliance upon costly isotopically enriched samples and insensitive nuclei enhanced by polarization transfer (INEPT) experiments. Furthermore, improvements in probe design and electronics, in addition to the remarkable stability of modern NMR spectrometers, have greatly reduced losses due to poor pulse calibrations in the sensitivity-improved pulsed field gradient selective HSQC experiments.[11,12] The research presented here describes an ^{15}N NMR study of a series of dipyrrolic molecules to demonstrate the usefulness of these easy and practical NMR experiments in the characterization of dipyrrolic compounds.

Results and Discussion

In this study, non-decoupled ^{15}N HSQC experiments were used to obtain ^{15}N NMR chemical shift data. Each experiment had an acquisition time of approximately 1 h for samples that had a concentration of about 0.2 M, thus making these experiments suitable as a spectroscopic probe for routine analysis of reaction mixtures and crude products. A series of dipyrrolic compounds were prepared for comparison of their ^{15}N chemical shifts. Table 1 presents the structures and ^{15}N NMR data for a series of dipyrromethanes, **1**−**5**. Comparison of **1** and **2** shows that there is little difference in $\delta(^{15}N)$ between 2,2′- and 3,3′-dipyrromethanes. The two compounds exhibit chemical shifts nearly identical to that of pyrrole, which exhibits a resonance at −231.4 ppm.[1] As well, the one-bond nitrogen−hydrogen coupling constants, $^1J(^{15}N^1H)$, are highly uniform around −96 Hz, similar again to that of pyrrole at −96.5 Hz.[1] The replacement of the ethyl substituents in **1** with bromine substituents results in a deshielding change for the ^{15}N NMR signal as seen for compound **3**. The presence of a substituent in the meso-position of the dipyrromethane, such as the phenyl and pyridyl rings in **4** and **5**, respectively, appear to have a similar effect upon the chemical shift of the ^{15}N nuclei as the ester functional groups in **1** and **2**. The chemical shift of the nitrogen atom in the pyridine ring of compound **5** was measured and found to be −73.3 ppm, which is similar to previously reported data for pyridine derivatives.[1] The consistency of the chemical shifts makes it certain that a generalization of $\delta(^{15}N) \approx -230$ ppm can be made for most dipyrromethanes.

TABLE 1. Data for ^{15}N Chemical Shifts, Relative to Nitromethane, and $^1J_{NH}$ for Dipyrromethane Compounds 1−6, Obtained from Solutions in $CDCl_3$

Structure	δ ^{15}N (ppm)	$^1J(^{15}N^1H)$ (Hz)
 **1**	-231.8	-96
 **2**	-231.4	-97
 **3**	-226.8	-97
 **4**	-232.1	-94
 **5**	-232.2 -73.3	-96
 **6**	-194.1	n/a

Tin complexes of dipyrromethanes have found use in the preparation of 1,9-diacyldipyrromethanes.[13] The complexation of tin(IV), as in tin-bound dipyrromethane **6**, results in a significant change in $\delta(^{15}N)$, shifting 32.7 ppm less shielded relative to the uncomplexed ligand, dipyrromethane **3**. This result is not comparable to the only reported values for tin(IV) complexes of pyrrolic molecules[14] as the oxygen atoms of the ester functional groups of **6** are involved in bonding interactions with the tin center, creating a hexacoordinate tin environment.[15] It has been observed that complexation of *N*,*N*′-(dipyrrolyl-α-methyl)-*N*-methylamines with titanium(IV), zirconium(IV), and

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(10) Gabe, Y.; Urano, Y.; Kikuchi, K.; Kojima, H.; Nagano, T. *J. Am. Chem. Soc.* **2004**, *126*, 3357−3367.
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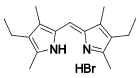
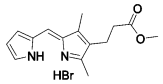
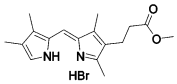
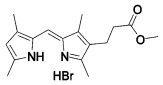
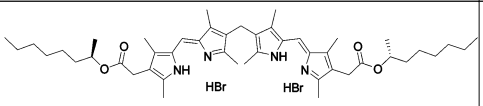
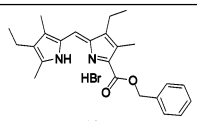
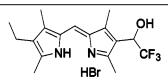
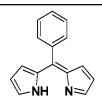
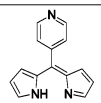
(12) Kontaxis, G.; Stonehouse, J.; Laue, E. D.; Keeler, J. *J. Magn. Reson. A* **1994**, *111*, 70−76.
(13) Tamaru, S.-i.; Yu, L.; Youngblood, W. J.; Muthukumaran, K.; Taniguchi, M.; Lindsey, J. S. *J. Org. Chem.* **2004**, *69*, 765−777.
(14) Wrackmeyer, B. *J. Organomet. Chem.* **1985**, *297*, 265−272.
(15) Kitamura, C.; Yamashita, Y. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1443−1447.

TABLE 2. Data for ^{15}N Chemical Shifts, Relative to Nitromethane, and $^1J_{NH}$ for Dipyrromethene Compounds 7−15, Obtained from Solutions in $CDCl_3$

Structure	δ ^{15}N (ppm)	$^1J(^{15}N^1H)$ (Hz)
 **7**	-213.7	-95
 **8**	-207.8 -210.0	-95 -95
 **9**	-210.7 -213.6	-96 -95
 **10**	-211.5 -212.3	-96 -95
 **11**	-211.6 -212.0	-95 -95
 **12**	-202.7 -224.6	-94 -97
 **13**	-210.9 -212.3	-96 -95
 **14**	-156.2	n/a
 **15**	-156.1 -68.0	n/a

halfnium(IV) resulted in deshielded shifting of the ^{14}N chemical shift.[16] The ligand displayed a chemical shift of −234 ppm, typical for a pyrrole, which changed to −84, −128, and −131 ppm, respectively, upon formation of the three complexes.[16]

As seen in Table 2, compounds **7**−**15** represent molecules with dipyrromethene structure. In the absence of a meso-substituent, these compounds are best synthesized and stored as their salt with hydrobromic acid.[17] As seen from the data listed in Table 2, the ^{15}N chemical shift of dipyrromethene hydrobromide salts can be highly generalized as $\delta(^{15}N) \approx -210$ ppm. One signal is observed for the two nitrogen atoms in **7** because they are identical upon considering resonance. This is supported by the lack of distinction in the ^1H NMR spectrum (see Experimental Section) between the hydrogens on substituents of the pyrrole ring containing the formally cationic nitrogen atom and the ring containing the neutral pyrrole-like nitrogen atom of this compound. The symmetry of protonated dipyrromethenes is further supported by X-ray photoelectron spectroscopy experiments.[18] The only known previously reported dipyrromethene ^{15}N chemical shift is for 3,3′,4,4′,5,5′-hexamethyldipyrromethene.[5] It was found that the protonated dipyrromethene exhibited a $\delta(^{15}N)$ of −209.2 ppm in deuterated chloroform,[5] which corresponds well with the results reported here for protonated dipyrromethenes.

It is apparent that the values of $\delta(^{15}N)$ for the two nitrogen atoms in asymmetric dipyrromethene hydrobromide salts, such as **8**−**13**, are dependent not only upon the structure of the pyrrole ring in which they are contained, but also upon the structure of the pyrrole ring with which it is in conjugation. This is best illustrated by the structurally related series of compounds **8**−**10**. Not one constant chemical shift is observed between the three compounds for the nitrogen atom contained within the unvarying ring that bears a methyl propanoate substituent. Therefore, the substituents of the variable ring can be seen to influence not only the chemical shift of the nitrogen atom within that ring, but also that of the adjacent ring. Covalent attachment of two dipyrromethene hydrobromide salt systems, as in bis(dipyrromethene) **11**, appears to have no effect upon $\delta(^{15}N)$. The presence of a strong electron-withdrawing group attached to the carbon adjacent to the nitrogen atom in a dipyrromethene hydrobromide salt, such as for benzyl ester-functionalized compound **12**, has the effect of increasing the chemical shift of one nitrogen atom, while decreasing that of the other from the typical chemical shift of −210 ppm. Through the use of nuclear Overhauser effect (nOe) experiments, the nitrogen chemical shifts were assigned (Supporting Information). The chemical shift of the nitrogen atom in the ester-substituted ring was found to be −224.6 ppm, and that of the nitrogen atom in the trialkylated ring was found to be −202.7 ppm. The presence of a strong electron-withdrawing group attached to the carbon β to the nitrogen atom, as for trifluoroethanol-functionalized **13**, does not appear to result in any significant deviation from the typical chemical shift for dipyrromethene hydrobromide salts. Therefore, it appears that electron-withdrawing substituents in the 5-position affect the nitrogen chemical shift to a greater extent than those in the 3- and 4-positions. As well, the one-bond nitrogen−hydrogen coupling constants were measured to be −94 Hz for the more deshielded nitrogen and −97 Hz for the more shielded. These results reveal deviations from the $^1J(^{15}N^1H)$ values for compounds **7**−**11** and **13**, which are consistently around −95 or −96 Hz.

The protonation shift for 3,3′,4,4′,5,5′-hexamethyldipyrromethene has been reported as 47.2 ppm shielding.[5] The differences in chemical shifts between the two nitrogen atoms in non-symmetrical dipyrromethenes **8**−**13** are not sufficiently large to represent protonation shifts. Therefore, in a manner similar to the symmetrization of dipyrromethene **7** by resonance, the ^{15}N NMR spectra for compounds **8**−**13** also exhibit the nitrogen atoms of these molecules as existing in an electronic environment that is between formally cationic and neutral, and the differences in ^{15}N NMR chemical shift likely arise merely from differences in ring substitution patterns.

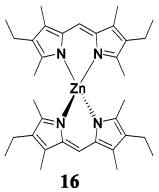
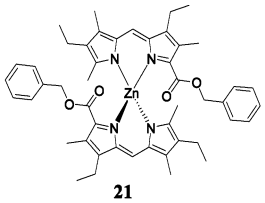
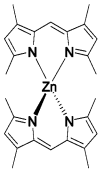
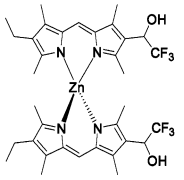
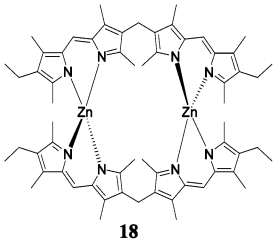
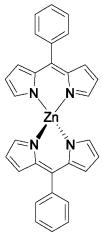
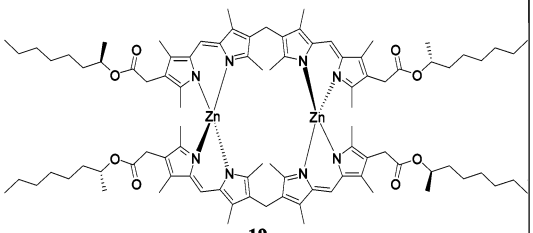
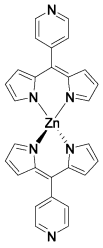
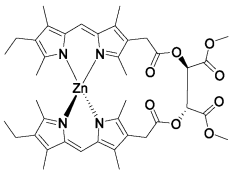
Compounds **14** and **15** present examples of meso-substituted dipyrromethenes that are stable in their free-base forms. The

(16) Li, Y.; Turnas, A.; Ciszewski, J. T.; Odom, A. L. *Inorg. Chem.* **2002**, *41*, 6298−6306.

(17) Jones, R. A.; Bean, G. P. *The Chemistry of Pyrroles*; Organic Chemistry, Vol. 34; Academic Press: London, 1977.

(18) Falk, H. *The Chemistry of Linear Oligopyrroles and Bile Pigments*; Springer-Verlag: New York, 1989.

TABLE 3. Data for ^{15}N Chemical Shifts, Relative to Nitromethane, for Zinc(II) Dipyrromethene Complexes 16−24, Obtained from Solutions in $CDCl_3$

Structure	δ ^{15}N (ppm)	Structure	δ ^{15}N (ppm)
 **16**	-169.5	 **21**	-152.8 -174.9
 **17**	-167.5	 **22**	-166.6 -170.2
 **18**	-166.3 -171.1	 **23**	-162.2
 **19**	-165 -172	 **24**	-162.5 -69.0
 **20**	-167.5 -170.5		

chemical shift of these compounds, −156 ppm, is drastically different from those of the *meso*-H dipyrromethene hydrobromides **7**−**13** but, more importantly, very similar to the ^{15}N NMR chemical shift of the free-base of 3,3′,4,4′,5,5′-hexamethyldipyrromethene, which was reported to be −162.0 ppm in deuterated chloroform.[5] This change in ^{15}N chemical shift compared to compounds **7**−**13** is likely due to the protonation of the imine-type nitrogen atom in the dipyrromethene hydrobromides. The protonation shift for the structurally related compound tetraphenylporphyrin is 55 ppm shielding.[19] Making the reasonable assumption that the protonation shift for dipyrromethenes is approximately equal to that of porphyrins, the chemical shifts of the hydrobromide salts of the meso-aromatic dipyrromethenes would be in the same range as the hydrobromide salts of the *meso*-H dipyrromethenes. The chemical shift of the pyridyl-nitrogen in compound **15** was measured and found to be 5.3 ppm more deshielded than the corresponding atom in the related dipyrromethane, **5**.

Only one signal is observed in the ^{15}N NMR spectrum for the two nitrogen atoms in each of compounds **14** and **15**. The protonated *meso*-H dipyrromethene **7** gives NMR spectra indicative of a symmetrical system due to equivalence of the nitrogen atoms through resonance. X-ray photoelectron spectroscopy experiments show that free-base dipyrromethenes appear symmetrical due to a rapid tautomerization involving the exchange of a hydrogen atom between the two nitrogen

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atoms.[18] The coalescence temperature for the similar tautomerization in tetraphenylporphyrin free base has been measured using ^{15}N NMR to be approximately 288 K.[19]

The ^{15}N chemical shift of zinc(II) dipyrromethene complexes **16**−**22** (Table 3) can be generalized as ∼−170 ppm. As observed for the protonated *meso*-H dipyrromethenes **8**−**13**, zinc(II) complexes of symmetrical dipyrromethenes exhibit only one ^{15}N NMR signal for the two nitrogen atoms in each dipyrromethene molecule. As well, the values of δ(^{15}N) for the two nitrogen atoms in zinc(II) complexes of non-symmetrical dipyrromethenes are very similar and likely represent a value between a formally anionic nitrogen and a neutral imine-like nitrogen. Studies involving the X-ray photoelectron spectrum of a zinc(II) complex of a symmetrical dipyrromethene show that the equivalence seen in ^{15}N NMR spectra arise from symmetry in the molecule due to resonance.[18]

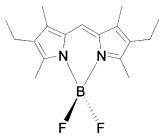
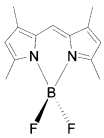
The corresponding zinc(II) complexes of several of the previously mentioned dipyrromethenes were prepared, and comparison of their zinc(II) complexation shifts shows a consistent, 44.2 ppm deshielding from **7** to **16**, 43.4 ppm (average) deshielding from **11** to **19**, 49.8 ppm (average) from **12** to **21**, and 43.2 ppm (average) deshielding from **13** to **22**. As seen for the related compound, **12**, the two nitrogen atoms of **21** exhibit δ(^{15}N) values above and below the average chemical shift for the class of compounds. Using nOe experiments (Supporting Information), we assigned the nitrogen atom in the ester-substituted ring to δ(^{15}N) of −174.9 ppm and the nitrogen atom of the trialkyl ring to −152.8 ppm. These data are consistent with the ^{15}N chemical shifts observed for **12**, with the nitrogen of the trialkylated ring being more deshielded.

The meso-substituted dipyrromethenes exhibit a shift of approximately 6 ppm shielding upon zinc(II) complexation. The zinc(II) complexes of dipyrromethenes can therefore be approximated to chemical shifts more deshielded than free-base dipyrromethenes, but more shielded than dipyrromethene hydrobromide salts. The chemical shift of the nitrogen atom in the pyridine ring of **24** did not change significantly upon complexation of the zinc(II) ion by the dipyrromethene nitrogens in the same molecule. This supports the discrete 2:1 dipyrromethene/zinc(II) structure proposed for this compound in solution rather than the coordination polymer structure that has also been observed for metal complexes of this type.[20,21] The zinc(II) complexation shift for the meso-substituted dipyrromethenes presented here is similar in magnitude, but opposite in sign of the zinc(II) complexation shift measured for free-base tetraphenylporphyrin.[19] Two boron difluoride dipyrromethene complexes, **25** and **26**, exhibited ^{15}N chemical shifts around −193 ppm (Table 4). Complexation of dipyrromethene hydrobromide salts by both boron difluoride and zinc(II) results in a deshielding of the ^{15}N nuclei as seen by comparison of the related structures **7**, **16**, and **25**. The change is greater for zinc(II) complexation than for boron difluoride complexation. Similar to previous dipyrromethene compounds, these molecules exhibit only one signal in their ^{15}N NMR spectra for two nitrogen atoms.

Conclusion

With modern NMR spectrometers, natural abundance ^{15}N experiments are routine. The addition of ^{15}N NMR chemical shift determination to the characterization of dipyrrolic derivatives enables a more definitive structural confirmation for those compounds whose ^{1}H and ^{13}C NMR spectra are ambiguous. For example, the ^{1}H and ^{13}C NMR spectra for dipyrromethene free bases and dipyrromethene metal complexes appear similar, whereas ^{15}N NMR reveals the dramatic change in the electronic environment about the nitrogen atoms that occurs as a result of the reaction. The systematic interpretation of substituent effects upon δ(^{15}N) is still not straightforward.[14,22] It has been shown previously that a correlation between δ(^{15}N) and electron-withdrawing strength of substituents on pyrrole nitrogen atoms does not exist due to the strong anisotropic influence.[22] It was found that the paramagnetic shift contribution, which is affected by the hybridization of the nitrogen atom, is the most significant term in ^{15}N chemical shifts.[22] Consequently, the electron-withdrawing strength of substituents on the rings of the dipyrrolic molecules studied here cannot be used to predict ^{15}N chemical shifts, and vice versa, without conducting computational studies of the molecules. However, comparison of the data between the different classes of dipyrrolic molecules reveals a pattern for δ(^{15}N) that may be used to probe the character of the pyrrolic nitrogen atom and determine the presence of pyrroles, dipyrromethanes, dipyrromethenes, and their complexes. A summary of the ^{15}N NMR chemical shift data for compounds **1**−**26** and a comparison to previously reported data for pyrrole are presented in Figure 2. The outlying values for the meso-unsubstituted dipyrromethene hydrobromide salts and the meso-unsubstituted dipyrromethene zinc(II) complexes arise from compounds **12** and **21**, respectively. Figure 2 illustrates the characteristic ^{15}N NMR chemical shift values that were found for the series of dipyrrolic molecules studied. It can be seen that these values are diagnostic for the structure of the dipyrrolic compound.

TABLE 4. Data for ^{15}N Chemical Shifts, Relative to Nitromethane, for Boron Difluoride Dipyrromethene Complexes 25 and 26, Obtained from Solutions in $CDCl_3$

Structure	δ ^{15}N (ppm)
 **25**	-194.6
 **26**	-192.1

Experimental Section

Materials and General Procedure. Nuclear magnetic resonance experiments for ^{1}H, ^{11}B, ^{13}C, ^{15}N, and ^{119}Sn nuclei were conducted using a 500 MHz spectrometer using a BBO probe equipped with *z*-axis gradients. The shift scales were referenced as outlined in the IUPAC Recommendations of 2001.[23] NMR experiments for ^{19}F nuclei were conducted using a 250 MHz spectrometer. The chemical shifts in ^{19}F NMR spectra are reported using trichlorofluoromethane

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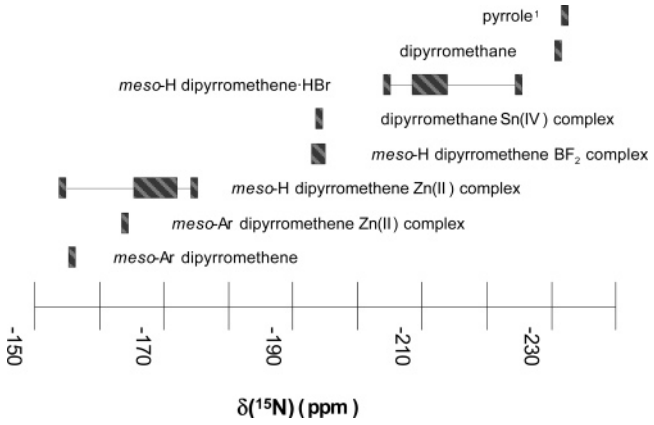

FIGURE 2. Summary of ^{15}N chemical shifts relative to nitromethane for molecules with a variety of dipyrrolic structures in comparison to pyrrole.

(0.0 ppm) as an external reference. Melting points are reported uncorrected. Mass spectrometry was performed using electrospray ionization. Chromatography was performed using 230−400 mesh ultrapure silica. With the exclusion of solvents, chemicals used in the preparations were received from suppliers and used without further purification.

The following compounds were prepared by established procedures: diethyl 3,3′-diethyl-4,4′-dimethyl-2,2′-dipyrromethane-5,5′-dicarboxylate (**1**),[24] diethyl 2,2′,4,4′-tetramethyl-3,3′-dipyrromethane-5,5′-dicarboxylate (**2**),[25] *meso*-phenyldipyrromethane (**4**),[6] *meso*-(4-pyridyl)dipyrromethane (**5**),[26] bis(3-[(*R*)-1-(methylheptyloxycarbonyl)-methyl]-2,2′,4,4′-tetramethyldipyrromethene) hydrobromide (**11**),[27] *meso*-phenyldipyrromethene (**14**),[28] zinc(II) di[bis(3-ethyl-2,2′,4,4′-tetramethyldipyrromethene)] (**18**),[25] zinc(II) di[bis(3-[(*R*)-1-(methylheptyloxycarbonyl)-methyl]-2,2′,4,4′-tetramethyldipyrromethene)] (**19**),[27] zinc(II) dimethyl-(L)tartrate-*O*,*O*′-(4-ethyl-2,2′,5,5′-tetramethyldipyrromethene-4-propanoate) (**20**),[29] zinc(II) di(*meso*-phenyldipyrromethene) (**23**),[30] and *N*,*N*′-difluoroboryl-3,3′,5,5′-tetramethyldipyrromethene (**26**).[31,32]

Diethyl 3,3′-Dibromo-4,4′-dimethyl-2,2′-dipyrromethane-5,5′-dicarboxylate (3). The product was prepared following a literature procedure:[33] ^{1}H NMR ($CDCl_3$) δ 10.72 (s, 2H), 4.17 (q, 4H, J = 7.0 Hz), 4.00 (s, 2H), 2.25 (s, 6H), 1.32 (t, 6H, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$) δ 162.2, 130.9, 126.3, 118.6, 101.4, 61.2, 24.8, 14.4, 12.1.

Diethyl *N*,*N*′-(Dibutyl)tin(IV)-3,3′-dibromo-4,4′-dimethyl-2,2′-dipyrromethane-5,5′-dicarboxylate (6). Triethylamine (0.58 mL, 0.42 mmol) was added to a mixture of diethyl 3,3′-dibromo-4,4′-dimethyl-2,2′-dipyrromethane-5,5′-dicarboxylate (**3**) (0.100 g, 0.22 mmol) and dibutyltin dichloride (0.061 g, 0.20 mmol) in dichloromethane (2 mL). After being stirred at room temperature for 6 h, methanol (5 mL) was added and the product was crystallized by partial removal of solvent using a rotary evaporator without applying heating. The solution was filtered, and the residue was rinsed with methanol to give 0.0825 g (53%) of the product as a colorless crystalline solid: ^{1}H NMR ($CDCl_3$) δ 7.04 (s, 1H), 4.35 (q, 1H, J = 7.0 Hz), 4.02 (s, 2H), 2.32 (s, 6H), 1.37 (t, 6H, J = 7.0 Hz), 1.32−1.36 (m, 8H), 1.16−1.22 (m, 4H), 0.75 (t, 3H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 166.8, 138.6, 128.1, 121.4, 101.8, 61.3, 27.1, 26.1, 24.6, 14.5, 13.5, 12.1; ^{119}Sn NMR ($CDCl_3$) δ −247.1; mp 110−111 °C; MS (−ve), *m*/*z* 704.9 (97%, M − 1).

4,4′-Diethyl-3,3′,5,5′-tetramethyldipyrromethene Hydrobromide (7). Aqueous hydrobromic acid (48% (w/v)) (0.7 mL, 4.2 mmol) was added to a solution of ethyl 4-ethyl-3,5-dimethylpyrrole-2-carboxylate[34] (1.016 g, 5.2 mmol) in aqueous formic acid (96% (w/v)) (2.7 mL). After being heated to reflux for 1 h, the mixture was cooled to room temperature. Further cooling to 4 °C caused the product to crystallize. The solution was filtered, and the residue was rinsed with cold methanol to give 0.512 g (58%) of the product as a red solid: ^{1}H NMR ($CDCl_3$) δ 12.87 (br s, 2H), 7.04 (s, 1H), 2.65 (s, 6H), 2.42 (q, 4H, J = 7.5 Hz), 2.27 (s, 6H), 1.07 (t, 6H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 153.7, 141.4, 130.5, 126.1, 118.7, 17.3, 14.5, 12.8, 10.1; mp 214−218 °C (dec); MS (+ve), *m*/*z* 257.2 (M + 1 − HBr).

3,5-Dimethyl-4-(methylpropanoate)dipyrromethene Hydrobromide (8). Hydrogenolysis of benzyl 3,5-dimethyl-4-(methylpropanoate)pyrrole-2-carboxylate[35] (0.103 g, 0.33 mmol) was performed using a catalytic amount of 10 mol % palladium on activated carbon (0.010 g) in tetrahydrofuran (8 mL) and triethylamine (1 drop). After being stirred for 16 h under 1 atm of hydrogen gas, the mixture was filtered through a plug of Celite to remove the palladium catalyst. Methanol (1 mL), pyrrole-2-carboxaldehyde (0.031 g, 0.33 mmol), and aqueous hydrobromic acid (48% (w/v)) (0.17 mL, 1.0 mmol) were added to the filtrate. After being stirred for 1 h, the mixture was concentrated by partial removal of solvent using a rotary evaporator and the product was precipitated by the addition of diethyl ether. The solution was filtered, and the residue was rinsed with cold methanol to give 0.098 g (90%) of the product as a red-brown solid: ^{1}H NMR ($CDCl_3$) δ 14.34 (br s, 1H), 14.00 (br s, 1H), 7.72 (s, 1H), 7.21 (s, 1H), 7.11 (s, 1H), 6.52−6.53 (m, 1H), 3.67 (s, 3H), 2.78 (t, 2H, J = 7.5 Hz), 2.73 (s, 3H), 2.50 (t, 2H, J = 7.5 Hz), 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 172.6, 161.4, 146.1, 138.5, 132.6, 129.6, 129.4, 127.9, 125.3, 115.0, 52.1, 33.6, 19.4, 13.6, 10.5; mp 148−151 °C (dec); MS (+ve), *m*/*z* 259.3 (M + 1 − HBr).

3,3′,4′,5-Tetramethyl-4-(methylpropanoate)dipyrromethene Hydrobromide (9). Hydrogenolysis of benzyl 3,5-dimethyl-4-(methylpropanoate)pyrrole-2-carboxylate[35] (0.100 g, 0.32 mmol) was performed using a catalytic amount of 10 mol % palladium on activated carbon (0.010 g) in tetrahydrofuran (8 mL) and triethylamine (1 drop). After being stirred for 16 h under 1 atm of hydrogen gas, the mixture was filtered through a plug of Celite to remove the palladium catalyst. Methanol (1 mL), 3,4-dimethylpyrrole-2-carboxaldehyde[36] (0.040 g, 0.32 mmol), and aqueous hydrobromic acid (48% (w/v)) (0.17 mL, 1.0 mmol) were added to the filtrate. After being stirred for 1 h, the mixture was concentrated by partial removal of solvent using a rotary evaporator and the product was precipitated by the addition of diethyl ether. The solution was filtered, and the residue was rinsed with cold methanol to give 0.086 g (73%) of the product as a brown solid: ^{1}H NMR ($CDCl_3$) δ 13.21 (br s, 1H), 13.10 (br s, 1H), 7.52−7.53 (m, 1H), 7.16 (s, 1H), 3.67 (s, 3H), 2.78−2.73 (m, 5H), 2.48 (t, 2H, J = 7.5 Hz), 2.33 (s, 3H), 2.27 (s, 3H), 2.06 (s, 3H); ^{13}C NMR ($CDCl_3$) δ

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172.8, 157.5, 144.3, 141.7, 139.8, 128.2, 127.6, 127.1, 124.9, 121.2, 52.1, 33.8, 19.5, 13.4, 10.5, 10.3, 10.2; mp 195−198 °C (dec); MS (+ve), *m*/*z* 287.3 (M + 1 − HBr).

3,3′,5,5′-Tetramethyl-4-(methylpropanoate)dipyrromethene Hydrobromide (10). Hydrogenolysis of benzyl 3,5-dimethyl-4-(methylpropanoate)pyrrole-2-carboxylate[35] (0.102 g, 0.32 mmol) was performed using a catalytic amount of 10 mol % palladium on activated carbon (0.010 g) in tetrahydrofuran (8 mL) and triethylamine (1 drop). After being stirred for 16 h under 1 atm of hydrogen gas, the mixture was filtered through a plug of Celite to remove the palladium catalyst. Methanol (1 mL), 3,5-dimethylpyrrole-2-carboxaldehyde[37] (0.040 g, 0.32 mmol), and aqueous hydrobromic acid (48% (w/v)) (0.17 mL, 1.0 mmol) were added to the filtrate. After being stirred for 1 h, the mixture was concentrated by partial removal of solvent using a rotary evaporator and the product was precipitated by the addition of diethyl ether. The solution was filtered, and the residue was rinsed with cold methanol to give 0.067 g (56%) of the product as a red solid: ^{1}H NMR ($CDCl_3$) δ 13.08 (br s, 1H), 13.03 (br s, 1H), 7.07 (s, 1H), 6.15 (s, 1H), 3.67 (s, 3H), 2.75 (t, 2H, J = 7.5 Hz), 2.69 (s, 3H), 2.67 (s, 3H), 2.47 (t, 2H, J = 7.5 Hz), 2.36 (s, 3H), 2.31 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 172.8, 155.2, 154.9, 145.8, 142.9, 127.2, 126.9, 126.3, 119.8, 117.5, 51.9, 33.9, 19.5, 14.6, 13.0, 12.3, 10.4; mp 164−168 °C (dec); MS (+ve), *m*/*z* 287.2 (M + 1 − HBr).

Benzyl 3,4′-Diethyl-3′,4,5′-trimethyldipyrromethene-5-carboxylate Hydrobromide (12). The product was prepared following a literature procedure:[38] ^{1}H NMR ($CDCl_3$) δ 14.49 (br s, 1H), 12.25 (br s, 1H), 7.63−7.65 (m, 1H), 7.37−7.28 (m, 5H), 7.20 (s, 1H), 5.48 (s, 2H), 2.79 (s, 3H), 2.69 (q, 2H, J = 7.5 Hz), 2.42 (q, 2H, J = 7.5 Hz), 2.31 (s, 3H), 2.24 (s, 3H), 1.13−1.10 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 165.8, 159.8, 146.3, 145.6, 136.0, 135.0, 133.4, 131.1, 129.5, 128.4, 128.3, 127.3, 125.2, 121.0, 66.7, 18.2, 17.2, 16.4, 14.0, 13.7, 10.4, 9.8; mp 147−152 °C (dec); MS (+ve), *m*/*z* 377.1 (M + 1 − HBr).

4′-Ethyl-3,3′,5,5′-tetramethyl-4-(2,2,2-trifluoro-1-hydroxyethyl)dipyrromethene Hydrobromide (13). Hydrogenolysis of benzyl 3,5-dimethyl-4-(2,2,2-trifluoro-1-hydroxyethyl)pyrrole-2-carboxylate[39,40] (1.003 g, 3.1 mmol) was performed using a catalytic amount of 10 mol % palladium on activated carbon (0.329 g) in tetrahydrofuran (40 mL). After being stirred for 3 days under 1 atm of hydrogen gas, the mixture was filtered through a plug of Celite to remove the palladium catalyst. The filtrate was concentrated by partial removal of solvent using a rotary evaporator, and the carboxylic acid was precipitated by addition of chloroform. The solution was filtered to give 3,5-dimethyl-4-(2,2,2-trifluoro-1-hydroxyethyl)pyrrole-2-carboxylic acid as a white powder 0.640 g (87%). A suspension of the carboxylic acid in ethanolamine (5 mL) was heated to 200 °C for 45 min and then poured into ice water. The aqueous mixture was extracted with dichloromethane, washed with water, washed with brine, and dried over anhydrous sodium sulfate, and the solvent was removed using a rotary evaporator. A solution of the residue in chloroform was concentrated under vacuum to give the α-free compound as a yellow solid (72%). Aqueous hydrobromic acid (48% (w/v)) (0.30 mL, mmol) was added to a solution of 2,4-dimethyl-3-(2,2,2-trifluro-1-hydroxyethyl)pyrrole (0.384 g, 2.0 mmol) and 3-ethyl-2,4-dimethylpyrrole-2-carboxaldehyde[41] (0.302 g, 2.0 mmol) in tetrahydrofuran (25 mL). After 30 min, the mixture was concentrated by partial removal of the solvent using a rotary evaporator and the product was precipitated by the addition of diethyl ether. The solution was filtered to give 0.399 g (57%) of the product as a red solid: ^{1}H NMR ($CDCl_3$) δ 12.69 (br s, 1H), 12.52 (br s, 1H), 7.45 (s, 1H), 6.83 (br s, 1H), 5.27 (q, 1H, J = 8.0 Hz), 2.60 (s, 3H), 2.58 (s, 3H), 2.42−2.47 (m, 5H), 2.34 (s, 3H), 1.04 (t, 3H, J = 8.0 Hz); ^{13}C NMR ($CDCl_3$) δ 158.1, 151.7, 145.2, 143.9, 132.6, 128.5, 126.4 (q, J = 281 Hz), 126.2, 122.3, 121.9, 65.8 (q, J = 32 Hz), 17.4, 15.0, 14.1, 13.6, 11.1, 10.7; ^{19}F NMR ($CDCl_3$) δ −78.2 (d, J = 7.7 Hz); mp 190 °C (dec); MS (ESI+), 327.1 (M + 1 − HBr).

***meso*-(4-Pyridyl)dipyrromethene (15).** A solution of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (0.169 g, 0.73 mmol) in toluene (50 mL) was added dropwise to a solution of *meso*-(4-pyridyl)dipyrromethane[26] (**5**) (0.163 g, 0.73 mmol) in chloroform (80 mL) at 0 °C. After the addition was complete (10 min), the solution was filtered through a plug of Celite and the solvent was removed using a rotary evaporator. The crude mixture was purified by silica flash chromatography (gradient 1:9 → 2:8 EtOAc/CH_2Cl_2) to give 0.025 g (16%) of the product as a yellow film after removal of the solvent: ^{1}H NMR ($CDCl_3$) δ 8.72 (dd, 2H, J = 4.5 Hz, J = 1.5 Hz), 7.67 (s, 2H), 7.42 (dd, 2H, J = 4.5 Hz, J = 1.5 Hz), 6.52 (dd, 2H, J = 4.5 Hz, J = 1.0 Hz), 6.41 (dd, 2H, J = 4.5 Hz, J = 1.0 Hz); ^{13}C NMR ($CDCl_3$) δ 149.5, 145.4, 144.7, 140.3, 138.4, 128.4, 125.3, 118.5; MS (+ve), *m*/*z* 222.3 (M + 1).

Zinc(II) Bis(4,4′-diethyl-3,3′,5,5′-tetramethyldipyrromethene) (16). A solution of zinc acetate dihydrate (0.044 g, 0.2 mmol) and sodium acetate trihydrate (0.027 g, 0.2 mmol) in methanol (10 mL) was added to a solution of 4,4′-diethyl-3,3′,5,5′-tetramethyldipyrromethene hydrobromide (**7**) (0.028 g, mmol) in chloroform (10 mL). After the reaction mixture was stirred for 30 min, the solvent was removed by using a rotary evaporator and the crude mixture was dissolved in dichloromethane. The solution was filtered through a plug of silica, and the solvent was removed using a rotary evaporator to give 0.20 g (83%) of the product as a fuscia solid: ^{1}H NMR ($CDCl_3$) δ 6.96 (s, 2H), 2.34 (q, 8H, J = 7.5 Hz), 2.22 (s, 12H), 1.89 (s, 12H), 1.01 (t, 12H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 156.4, 136.5, 135.7, 129.6, 120.7, 18.2, 15.3, 14.7, 10.1; mp 145−149 °C; MS (+ve), *m*/*z* 257.2 (100%, ligand), 574.4 (12%, M).

Zinc(II) Bis(3,3′,5,5′-tetramethyldipyrromethene) (17). A solution of zinc acetate dihydrate (1.790 g, 7.9 mmol) and sodium acetate trihydrate (1.066 g, 7.9 mmol) in methanol (60 mL) was added to a solution of 3,3′,5,5′-tetramethyldipyrromethene hydrobromide[42] (0.443 g, 1.6 mmol) in chloroform (60 mL). After the reaction mixture was stirred for 30 min, the solvent was removed by using a rotary evaporator and the crude mixture was dissolved in dichloromethane. The solution was filtered through a plug of silica, and the solvent was removed using a rotary evaporator to give 0.33 g (44%) of the product as a fuscia solid: ^{1}H NMR ($CDCl_3$) δ 7.02 (s, 2H), 5.98 (s, 4H), 2.31 (s, 12H), 1.95 (s, 12H); ^{13}C NMR ($CDCl_3$) δ 157.9, 142.1, 136.7, 122.0, 116.9, 16.6, 12.0; mp > 250 °C; MS (+ve), *m*/*z* 201.1 (100%, ligand), 462.1 (74%, M).

Zinc(II) Bis(benzyl 3,4′-diethyl-3′,4,5′-trimethyldipyrromethene-5-carboxylate) (21). A solution of zinc acetate dihydrate (0.690 g, 3.2 mmol) and sodium acetate trihydrate (0.435 g, 3.2 mmol) in methanol (8 mL) was added to a solution of benzyl 3,4′-diethyl-3′,4,5′-trimethyldipyrromethene-5-carboxylate hydrobromide (**12**) (0.286 g, 0.63 mmol) in chloroform (10 mL). After the reaction mixture was stirred for 30 min, the solvent was removed by using a rotary evaporator and the crude mixture was dissolved in dichloromethane. The solution was filtered through a plug of silica, and the solvent was removed using a rotary evaporator to give 0.25 g (48%) of the product as a fuscia solid: ^{1}H NMR ($CDCl_3$) δ 7.07−7.00 (m, 6H), 6.89 (s, 2H), 6.76−6.75 (m, 4H), 4.77 (d, 2H, J = 12.5 Hz), 4.55 (d, 2H, J = 12.5 Hz), 2.63−2.61 (m, 4H), 2.29−2.27 (m, 10H), 2.10 (s, 6H), 1.74 (s, 6H), 1.09 (t, 6H, J = 7.5 Hz),

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1.00 (t, 6H, $J = 7.5$ Hz); ^{13}C NMR ($CDCl_3$) δ 168.3, 162.8, 142.5, 140.9, 139.8, 137.4, 136.1, 135.3, 135.2, 127.9, 127.6, 127.3, 127.0, 121.5, 64.6, 18.1, 18.0, 17.2, 14.6, 14.5, 10.9, 9.9; mp 162−163 °C; MS (+ve), *m*/*z* 377.2 (14%, ligand), 837.4 (100%, M + Na).

Zinc(II) Bis[4′-ethyl-3,3′,5,5′-tetramethyl-4-(2,2,2-trifluoro-1-hydroxyethyl)dipyrromethene] (22). Zinc acetate dihydrate (0.070 g, 0.32 mmol), sodium acetate trihydrate (0.046 g, 0.34 mmol), and 4′-ethyl-3,3′,5,5′-tetramethyl-4-(2,2,2-trifluoro-1-hydroxyethyl)-dipyrromethene (**13**) (0.050 g, 0.14 mmol) were dissolved in methanol (7 mL). After being stirred for 30 min, the solvent was removed using a rotary evaporator. The crude mixture was dissolved in ethyl acetate, washed with water, washed with brine, and dried over anhydrous sodium sulfate, and the solvent was removed using a rotary evaporator. The residue was extracted with boiling hexanes and decanted, and the solvent was then removed using a rotary evaporator to give 0.027 g (64%) of the product as an iridescent orange solid: ^1H NMR ($CDCl_3$) δ 7.04 (s, 2H), 5.04−5.06 (m, 2H), 2.34−2.37 (m, 10H), 2.22 (d, 6H, $J = 1.5$ Hz), 2.20 (br s, 2H), 1.97−1.99 (m, 6H), 1.87−1.91 (m, 6H), 1.02 (t, 6H, $J = 7.5$ Hz); ^{13}C NMR ($CDCl_3$) δ 161.5, 153.3, 139.6, 137.8, 134.9, 134.8, 132.3, 125.6 (q, $J = 280$ Hz), 121.8, 117.9, 68.4 (m), 18.23, 15.6, 15.5, 15.1, 10.7, 10.6; ^{19}F NMR ($CDCl_3$) δ 235; mp 197−198 °C; MS (+ve), *m*/*z* 327.2 (58%, ligand), 715.1 (27%, M + 1), 737.1 (100%, M + Na).

Zinc(II) Bis[*meso*-(4-pyridyl)dipyrromethene] (24). A solution of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (0.129 g, 0.57 mmol) in benzene (40 mL) was added slowly dropwise to a solution of *meso*-(4-pyridyl)dipyrromethane[26] (**5**) (0.128 g, 0.57 mmol) in chloroform (60 mL) at 0 °C. After the reaction mixture was stirred for 10 min, the solvent was removed using a rotary evaporator. Triethylamine (0.4 mL) and a solution of zinc chloride (0.040 g, 0.29 mmol) in methanol (1 mL) were added to a solution of the crude mixture in methanol (20 mL) and chloroform (20 mL). After being stirred for 16 h at reflux under a nitrogen atmosphere, the solvent was removed by rotary evaporation. The product was obtained as a mixture with (**15**) as an iridescent red solid: ^1H NMR ($CDCl_3$) δ 8.74 (dd, 4H, $J = 4.5$ Hz, $J = 1.5$ Hz), 7.57 (s, 4H), 7.50 (dd, 4H, $J = 4.5$ Hz, $J = 1.5$ Hz), 6.64 (dd, 4H, $J = 4.0$ Hz, $J = 1.0$ Hz), 6.41 (dd, 4H, $J = 4.0$ Hz, $J = 1.0$ Hz); ^{13}C NMR ($CDCl_3$) δ 150.9, 149.2, 147.1, 145.1, 139.7, 132.8, 125.4, 118.1; mp > 250 °C; MS (+ve), *m*/*z* 222.2 (100%, ligand), 505.2 (14%, M).

***N*,*N*′-Difluoroboryl-4,4′-diethyl-3,3′,5,5′-tetramethyldipyrromethene (25).** The product was prepared following a literature procedure:[43] ^1H NMR ($CDCl_3$) δ 6.94 (s, 1H), 2.49 (s, 6H), 2.37 (q, 4H, $J = 7.5$ Hz), 2.16 (s, 6H), 1.06 (t, 6H, $J = 7.5$ Hz); ^{11}B NMR ($CDCl_3$) δ 0.91 (t, $J = 33.7$ Hz); ^{13}C NMR ($CDCl_3$) δ 154.8, 136.8, 132.6, 131.8, 118.8, 17.5, 14.8, 12.7, 9.6; ^{19}F NMR ($CDCl_3$) δ −147.4 (q, $J = 34.1$ Hz); mp 187−188 °C.

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Supporting Information Available: Copies of ^{13}C NMR spectra for **3**, **6**−**10**, **12**, **13**, **15**−**17**, **21**, **22**, **24**, and **25**; NOESY spectra used to assign ^1H NMR signals for **12** and **21**. This material is available free of charge via the Internet at http://pubs.acs.org.

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