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Convenient and highly efficient synthesis of boron–dipyrrins bearing an arylboronate center

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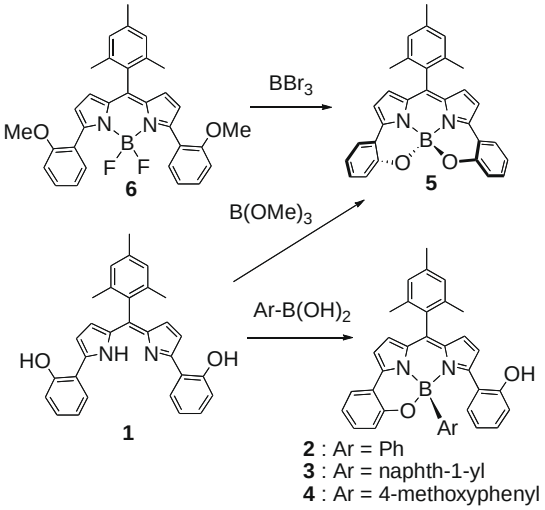
ABSTRACT

Novel boron–dipyrrins bearing an aryl group and a phenyloxy group linked directly to the boron center have been prepared in high yields from arylboronic acid. The unique coordination geometry around the boron was determined by an X-ray crystallographic analysis. The complexes showed a strong fluorescence, and alkylation of the OH group shifted the emission to a longer wavelength with a larger Stokes shift.

Boron dipyrrins containing a BF_2 unit[1] (*F*-BODIPYs) have been attracting considerable interest in many research areas because of their intense absorption and fluorescence.[2] Various substituents have been introduced into the *F*-BODIPY skeleton to modify the original optical properties for applications such as biological labeling[3] and electroluminescent devices,[4] and laser dyes[5]. Substitution of the fluorine atoms on the boron also changes the properties.[6,7] To date, boron dipyrrins bearing alkyl,[7c] alkyloxy,[6b] aryl,[7b,c] aryloxy,[6a,b] and ethynyl[7a,c] groups have been prepared on the basis of this substitution. The dipyrrin complexes bearing one or two aryl group(s) at the boron center (*Ar*-BODIPYs) are of great interest because (1) the optical properties would be modified by introducing various aromatic chromophores, (2) fluorescent sensoring of an appropriate guest is expected when the aromatic moiety has the binding site, and because (3) the *Ar*-BODIPYs usually show an intense fluorescence. However, substitution of the fluorine atoms with an aryl-Grignard or aryl-lithium reagent is the only reported way for the *Ar*-BODIPY preparation, but the yields are moderate.[7b,c] Hence, the high-yield one-step synthesis of *Ar*-BODIPYs from the dipyrrin ligands and readily available boron-containing compounds has been strongly desired in order to obtain a variety of boron dipyrrins with valuable properties.

Recently, we synthesized the boron dipyrrin **5** from the dipyrrin ligand **1** by the reaction with $B(OMe)_3$,[8] and not from *F*-BODIPY **6**.[9] Our synthetic method is very useful because the non-fluorinated boron dipyrrin is readily obtained via a one-step reaction from the free ligand **1** (Scheme 1). We expected that the reaction of **1** with arylboronic acid afforded a variety of *Ar*-BODIPY derivatives such as **2** in one-step by using the huge library of boronic acids. Furthermore, the chiral boron center in the *Ar*-BODIPYs would be utilized for chiral recognition or for circularly polarized luminescence.

In this Letter, we describe the convenient high-yield synthesis, characterization, and optical properties of novel *Ar*-BODIPYs **2**–**4**



Scheme 1. Synthesis of the boron dipyrrins. Only one of the enantiomers is shown for **2**–**5**.

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and **7**–**9** bearing an aryl ring and a phenyloxy group at the boron center. To the best of our knowledge, this is the first example of dipyrrins with N, N, O, C atoms coordinating to the boron.

The reaction of **1** with phenylboronic acid and 1-naphthylboronic acid quantitatively afforded *Ar*-BODIPYs **2** and **3**, respectively (Table 1, entries 1 and 2).[10] The reaction with 4-methoxyphenylboronic acid also gave *Ar*-BODIPY **4** in high yield, although a small amount of BODIPY **5** was also obtained (entry 3). In case of 4-dimethylaminophenylboronic acid and anthracence-9-boronic acid, **5** was isolated as a single product instead of *Ar*-BODIPY (entries 4 and 5). **4** was gradually converted to **5** in chloroform under reflux. This reaction involves the cleavage of the B–C bond and the formation of the B–O bond. The initial step is probably the electrophilic attack of the phenol proton of **4** on the *ipso*-carbon.[11] The proposed mechanism agrees with the exclusive formation of **5** in the case of highly electron-rich arylboronic acids.[11]

Since the optical properties of some boron–dipyrrins bearing a phenol OH group are different from those of the corresponding alkoxy derivatives,[12] we alkylated the residual OH group of **2**. The reaction of **2** with methyl iodide, butyl bromide, and benzyl bromide afforded **7**, **8,** and **9** in 79%, 75%, and 98% yields, respectively (Scheme 2).[13] These alkoxy dipyrrins show different emission properties when compared to **2** (vide infra).

Compounds **2, 3, 4, 7, 8,** and **9** were identified by spectroscopic measurements (^{1}H, ^{13}C, and ^{11}B NMR, ESI-mass) and elemental analysis. The ^{1}H NMR spectra of these compounds indicate a C_1 symmetric dipyrrin skeleton. For example, the pyrrolic-β protons of **2** afford four doublets at 6.35, 6.68, 6.79, and 6.84 ppm. The methyl protons of the mesityl group of **2** appeared at 2.14, 2.32, and 2.39 ppm as a singlet. The ^{11}B NMR of **2** shows a broad singlet at 2.55 ppm, suggesting a tetrahedral geometry around the boron atom.[14] In the presence of europium tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorate] as a chiral shift reagent, the methyl signal of **2** at 2.14 ppm split into two signals due to the diastereotopic complex formation. This fact shows that the chiral configuration of the boron center is stable at least on the NMR timescale.

The X-ray crystallographic analysis of **2** confirmed the unique structure of the *Ar*-BODIPY (Fig. 1).[15,16]

The compound crystallized as a racemate in the centrosymmetric space group $P\bar{1}$. The two pyrrole nitrogen atoms and phenol oxygen O(2) of the dipyrrin ligand bind to the boron atom, which is

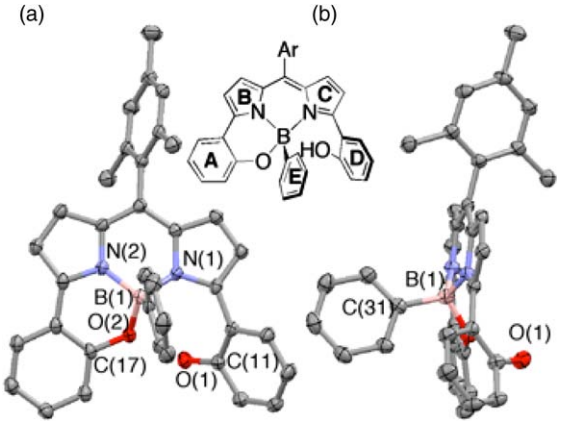


Figure 1. Crystal structure of **2**. Thermal ellipsoids are plotted at 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): B1–N1 1.562(3), B1–N2 1.542(3), B1–O2 1.479(3), B1–C31 1.611(3).

connected to the phenyl ring E. The chiral boron center adopts a distorted tetrahedral geometry with the N–B–N, C–B–N, and C–B–O bond angles of 104.3°, 108.0°, and 111.7°, respectively. The A ring and the two B and C pyrrole rings are nearly coplanar with the maximum mean plane deviation of 0.27 Å. The boron atom is out of the bis-pyrrolic plane by 0.44 Å. The length of the boron–carbon bond (1.61 Å) is similar to that of the boron–dipyrrin bearing two phenyl groups at the boron center.[7b] The phenol ring D is tilted with respect to the pyrrole ring C, and the dihedral angle between C and D is 54°. The distance between the two oxygens in the A and D rings is 2.61 Å, indicative of OH···O hydrogen bonding.

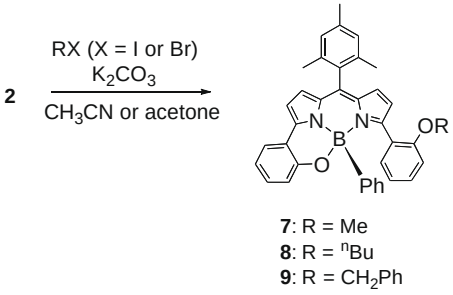
The absorption and fluorescence spectral data of the obtained *Ar*-BODIPY are summarized in Table 2. All the compounds show a strong absorption band around 590 nm and an intense fluorescence with a quantum yield of 0.59–0.68. Wavelengths of the absorption band maximum (λ_{max}) of **2**–**4** (588 nm) are longer than that of the *F*-BODIPY **6** (λ_{max} 550 nm). The B–O linkage in **2**–**4** may cause the red shift. The **A** ring, which is nearly coplanar with the pyrrole rings, probably contributes to extending the conjugation.[6a] Compounds **7**–**9** bearing an alkoxy or a benzyloxy phenyl group show larger Stokes shifts when compared to those of **2** (Table 2).

This fact suggests the larger conformational changes of **7**–**9** than those of **2** in the excited state. The rotational motion of the phenol substituents in **7**–**9**, and lack of the intramolecular hydrogen bond observed in **2** may account for the larger shifts.

The results in this study would provide a facile, efficient, and versatile way to afford boron–dipyrrins bearing various aryl groups at the boron center. The chiral *Ar*-BODIPYs should be used for producing interesting chiral properties and functions such as circularly polarized luminescence and chiral recognition. The separation of the enantiomers and the investigation of the properties are the subject of a current study.

Table 1
Condensation of **1** and arylboronic acid for the synthesis of *Ar*-BODIPYs

Entry	Ar	Products
1	Phenyl	**2**(quant)
2	Naphth-1-yl	**3**(quant)
3	4-Methoxyphenyl	**4**(92%), **5**(8%)
4	4-Dimethylaminophenyl	**5**(85%)
5	Anthr-9-yl	**5**(quant)



Scheme 2. Alkylation of **2**. Only one of the enantiomers is shown for **7**–**9**.

Table 2
Spectroscopic data for the various *Ar*-BODIPYs in chloroform at 298 K

	λ_{max} (nm)	λ_{flu} (nm)	Stokes shift (cm^{-1})	Φ_f[a]
2	588	614	730	0.65
3	588	615	750	0.68
4	588	613	690	0.63
7	595	644	1280	0.59
8	597	643	1200	0.60
9	596	642	1200	0.62

[a] Determined under aerated conditions.

Acknowledgment

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References and notes

1. Treibs, A.; Kreuzer, F.-H. *Justus Liebigs Ann. Chem.* **1968**, *718*, 208–223.
2. (a) Loudet, A.; Burgess, K. *Chem. Rev.* **2007**, *107*, 4891–4932; (b) Ulrich, G.; Ziessel, R.; Harriman, A. *Angew. Chem., Int. Ed.* **2008**, *47*, 1184–1201.
3. (a) Karolin, J.; Johansson, L. B.-A.; Strandberg, L.; Ny, T. *J. Am. Chem. Soc.* **1994**, *116*, 7801–7806; (b) Reents, R.; Wagner, M.; Kuhlmann, J.; Waldmann, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 2711–2714.
4. Bonardi, L.; Kanaan, H.; Camerel, F.; Jolinat, P.; Retailleau, P.; Ziessel, R. *Adv. Funct. Mater.* **2008**, *18*, 401–413.
5. Arbeloa, T. L.; Arbeloa, F. L.; Arbeloa, I. L.; García-Moreno, I.; Costela, A.; Sastre, R.; Amat-Guerri, F. *Chem. Phys. Lett.* **1999**, *299*, 315–321.
6. (a) Kim, H.; Burghart, A.; Welch, M. B.; Reigenspies, J.; Burgess, K. *Chem. Commun.* **1999**, 1889–1890; (b) Tahtaoui, C.; Thomas, C.; Rohmer, F.; Klots, P.; Duportail, G.; Mély, Y.; Bonnet, D.; Hibert, M. *J. Org. Chem.* **2007**, *72*, 269–272.
7. (a) Ulrich, G.; Goze, C.; Guardigli, M.; Roda, A.; Ziessel, R. *Angew. Chem., Int. Ed.* **2005**, *44*, 3694–3698; (b) Goze, C.; Ulrich, G.; Mallon, L. J.; Allen, B. D.; Harriman, A.; Ziessel, R. *J. Am. Chem. Soc.* **2006**, *128*, 10231–10239; (c) Harriman, A.; Izzet, G.; Ziessel, R. *J. Am. Chem. Soc.* **2006**, *128*, 10868–10875; (d) Ulrich, G.; Goze, C.; Goeb, S.; Retailleau, P.; Ziessel, R. *New J. Chem.* **2006**, *30*, 982–986.
8. Ikeda, C.; Ueda, S.; Nabeshima, T., *Chem. Commun.* **2009**, doi:10.1039/B820141B.
9. The reported compound possesses a 4-iodophenyl group at the *meso* position. See Ref.[6a].
10. *General procedure for the synthesis of Ar*-Bodipys **2**–**4**: To a stirred solution containing **1** (44.4 mg, 0.100 mmol) in chloroform (20 mL) was added arylboronic acid (0.120 mmol), and the mixture was heated to reflux for 3 h. After being cooled, the solvent was evaporated and the resulting residue was purified by column chromatography on silica gel using chloroform as the eluent to give *Ar*-Bodipy.
Compound **2**: Black solid. >99% yield. Mp 230 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.14 (s, 3H), 2.32 (s, 3H), 2.39 (s, 3H), 6.35 (d, J = 4.0 Hz, 1H), 6.68 (d, J = 4.0 Hz, 1H), 6.75 (dd, J = 8.0, 1.3 Hz, 2H), 6.79 (d, J = 4.0 Hz, 1H), 6.84 (d, J = 4.0 Hz, 1H), 6.86–6.98 (m, 5H), 6.99 (s, 1H), 7.02 (s, 1H), 7.06 (dd, J = 7.8, 1.8 Hz, 1H), 7.12 (dd, J = 7.8, 1.0 Hz, 1H), 7.24 (dd, J = 7.8, 1.0 Hz, 1H), 7.32 (td, J = 7.8, 1.6 Hz, 1H), 7.41 (td, J = 7.8, 1.8 Hz, 1H), 7.49 (dd, J = 7.8, 1.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.1, 20.4, 21.2, 115.7, 118.5, 119.9, 120.1, 120.7, 120.8, 120.9, 124.6, 126.2, 126.5, 126.8, 127.9, 128.2, 128.3, 130.1, 130.8, 130.9, 131.6, 133.1, 133.8, 136.7, 136.9, 137.1, 138.6, 143.3, 149.6, 153.7, 154.7, 155.1. ^{11}B NMR ($CDCl_3$, 128 MHz) δ 2.55 (s). MS(ESI) observed m/z 533.28 ($[M+H]^+$), calcd for $C_{36}H_{30}BN_2O_2$ m/z 533.24. Anal. Calcd for $C_{36}H_{29}BN_2O_2{\cdot}0.1CHCl_3$: C, 79.65; H, 5.69; N, 5.15. Found: C, 79.63; H, 5.68; N, 5.15.
Compound **3**: Black solid. >99% yield. Mp 270–271 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.13 (s, 3H), 2.40 (s, 3H), 2.48 (s, 3H), 6.23 (d, J = 4.0 Hz, 1H), 6.65 (d, J = 4.0 Hz, 1H), 6.79 (d, J = 4.5 Hz, 1H), 6.82 (d, J = 4.0 Hz, 1H), 6.83–6.89 (m, 2H), 6.90–6.95 (m, 2H), 7.01 (s, 1H), 7.02 (d, J = 7.3 Hz, 1H), 7.05 (s, 1H), 7.17 (t, J = 7.6 Hz, 1H), 7.19 (d, J = 8.6 Hz, 1H), 7.23–7.32 (m, 2H), 7.40–7.45 (m, 3H), 7.56 (d, J = 7.6 Hz, 1H), 7.95 (d, J = 8.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.1, 20.8, 21.2, 116.3, 119.0, 119.8, 120.6, 120.9, 121.0, 123.9, 124.2, 124.5, 126.2, 127.4, 127.9, 128.1, 128.3, 128.4, 128.5, 130.2, 130.8, 131.5, 131.6, 133.1, 133.2, 134.4, 135.9, 136.9, 137.0, 137.2, 138.7, 143.2, 150.3, 153.2, 154.1, 155.1. ^{11}B NMR ($CDCl_3$, 128 MHz) δ 2.96 (s). MS(ESI) observed m/z 583.30 ($[M+H]^+$), calcd for $C_{40}H_{32}BN_2O_2$ m/z 583.26. Anal. Calcd for $C_{40}H_{31}BN_2O_2{\cdot}0.05CHCl_3$: C, 81.74; H, 5.32; N, 4.76. Found: C, 81.63; H, 5.61; N, 4.76.
Compound **4**: Black solid. 92% yield. Mp 225–226 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.13 (s, 3H), 2.31 (s, 3H), 2.39 (s, 3H), 3.60 (s, 3H), 6.35 (d, J = 4.0 Hz, 1H), 6.43 (d, J = 8.6 Hz, 2H), 6.67 (d, J = 8.6 Hz, 2H), 6.68 (d, J = 4.0 Hz, 1H), 6.82 (d, J = 4.0 Hz, 1H), 6.88 (d, J = 4.0 Hz, 1H), 6.90 (td, J = 7.8, 1.0 Hz, 1H), 6.96 (td, J = 7.8, 1.0 Hz, 1H), 6.99 (s, 1H), 7.01 (s, 1H), 7.10 (m, 2H), 7.25 (dd, J = 7.8, 1.0 Hz, 1H), 7.32 (td, J = 7.8, 1.6 Hz, 1H), 7.41 (td, J = 7.8, 1.6 Hz, 1H), 7.50 (dd, J = 7.8, 1.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.1, 20.4, 21.2, 54.7, 112.3, 115.6, 118.5, 119.9, 120.1, 120.7, 120.8, 120.9, 124.7, 126.2, 127.9, 128.1, 128.2, 128.3, 130.1, 130.8, 131.6, 132.1, 133.0, 133.7, 136.7, 136.9, 137.1, 138.6, 143.2, 149.5, 153.7, 154.7, 155.2, 158.3. ^{11}B NMR ($CDCl_3$, 128 MHz) δ 2.68 (s). MS(ESI) observed m/z 563.29 ($[M+H]^+$), calcd for $C_{37}H_{32}BN_2O_3$ m/z 563.25. Anal. Calcd for $C_{37}H_{31}BN_2O_3{\cdot}0.5H_2O$: C, 77.76; H, 5.64; N, 4.90. Found: C, 78.06; H, 5.78; N, 4.91.
11. (a) Kuivila, H. G.; Nahabedian, K. V. *J. Am. Chem. Soc.* **1961**, *83*, 2159–2163; (b) Coopper, J. N.; Powell, R. E. *J. Am. Chem. Soc.* **1963**, *85*, 1590–1592; (c) Nishida, H.; Takada, N.; Yoshimura, M. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2600–2604.
12. Baruah, M.; Qin, W.; Basarić, N.; De Borggraeve, W. M.; Boens, N. *J. Org. Chem.* **2005**, *70*, 4152–4157.
13. *Compound* **7:** To a stirred solution containing **2** (53.2 mg, 0.100 mmol) and K_2CO_3 (0.138 g, 0.100 mmol) in acetonitrile (20 mL) was added methyl iodide (7.4 μL, 1.2 mmol), and the stirred mixture was heated to reflux under N_2 for 10 h. The resulting mixture was poured into water and the organic layer was separated. The aqueous phase was extracted with chloroform. The combined organic phases were dried over sodium sulfate, filtered, and the solvents were evaporated in vacuo. The obtained black solid was purified by column chromatography over silica gel with chloroform/hexane (2:1) to give **7** (43.0 mg, 79%). Black solid. Mp 194–195 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.15 (s, 3H), 2.34 (s, 3H), 2.39 (s, 3H), 3.48 (s, 3H), 6.47 (d, J = 4.0 Hz, 1H), 6.64 (d, J = 4.0 Hz, 1H), 6.68 (d, J = 4.0 Hz, 1H), 6.72 (d, J = 4.0 Hz, 1H), 6.77 (t, J = 7.8 Hz, 1H), 6.81 (d, J = 8.2 Hz, 2H), 6.87–6.93 (m, 5H), 6.98 (s, 1H), 7.00 (s, 1H), 7.05 (t, J = 7.8 Hz, 1H), 7.23 (td, J = 7.8, 1.6 Hz, 1H), 7.41–7.45 (m, 2H), 7.68 (dd, J = 7.8, 1.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.1, 20.5, 21.2, 55.7, 110.7, 114.6, 118.4, 119.0, 119.2, 119.8, 120.8, 122.3, 125.8, 125.9, 126.6, 126.8, 127.6, 128.2, 130.6, 131.1, 132.5, 133.1, 133.2, 136.6, 136.8, 137.0, 138.3, 142.1, 149.4, 154.6, 156.8, 158.0. ^{11}B NMR ($CDCl_3$, 128 MHz) δ 2.80 (s). MS(ESI) observed m/z 547.29 ($[M+H]^+$), calcd for $C_{37}H_{32}BN_2O_2$ m/z 547.26. Anal. Calcd for $C_{37}H_{31}BN_2O_2{\cdot}0.2CHCl_3$: C, 78.34; H, 5.51; N, 4.91. Found: C, 78.05; H, 5.77; N, 4.62.
Compound **8**: To a stirred solution containing **2** (29.1 mg, 0.055 mmol) and K_2CO_3 (11.4 mg, 0.083 mmol) in acetonitrile (20 mL) was added 1-bromobutane (0.50 mL of a 0.12 M solution in acetonitrile, 0.061 mmol). The resulting mixture was treated as described for **7** to give **8** (24.4 mg, 75%). Black solid. Mp 176–177 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.70 (t, J = 7.6 Hz, 3H), 1.05–1.15 (m, 2H), 1.32–1.40 (m, 2H), 2.14 (s, 3H), 2.30 (s, 3H), 2.38 (s, 3H), 3.39–3.46 (m,1H), 3.67–3.72 (m, 1H), 6.49 (d, J = 4.0 Hz, 1H), 6.61 (d, J = 4.0 Hz, 1H), 6.68 (d, J = 4.0 Hz, 1H), 6.72 (d, J = 4.0 Hz, 1H), 6.72–6.91 (m, 8H), 6.97 (s, 1H), 7.00 (s, 1H), 7.07 (t, J = 7.6 Hz, 1H), 7.21 (t, J = 8.0 Hz, 1H), 7.42–7.37 (m, 2H), 7.78 (d, J = 7.2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.8, 19.0, 20.0, 20.3, 21.2, 31.2, 68.3, 112.1, 114.3, 118.5, 119.0, 119.1, 119.9, 121.4, 122.7, 125.7, 125.9, 126.5, 126.9, 127.3, 128.2, 130.6, 131.1, 132.4, 132.9, 133.1, 136.7, 136.8, 137.1, 138.2, 142.0, 149.0, 155.3, 156.8, 157.7. ^{11}B NMR ($CDCl_3$, 128 MHz) δ 2.85 (s). MS(ESI) observed m/z 588.29 ($[M+H]^+$), calcd for $C_{40}H_{38}BN_2O_2$ m/z 588.31. Anal. Calcd for $C_{40}H_{37}BN_2O_2{\cdot}0.5H_2O$: C, 80.40; H, 6.41; N, 4.69. Found: C, 80.67; H, 6.60; N, 4.48.
Compound **9**: To a stirred solution containing **2** (18.2 mg, 0.034 mmol) and K_2CO_3 (7.1 mg, 0.051 mmol) in acetone (20 mL) was added benzyl bromide (0.50 mL of a 84 mM solution in acetonitrile, 0.042 mmol). The resulting mixture was treated as described for **7** to give **9** (20.7 mg, 98%). Black solid. Mp 165–166 °C. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.14 (s, 3H), 2.35 (s, 3H), 2.39 (s, 3H), 4.46 (d, J = 11.9 Hz, 1H), 4.74 (d, J = 11.9 Hz, 1H), 6.50 (d, J = 4.0 Hz, 1H), 6.62 (d, J = 4.0 Hz, 1H), 6.70 (d, J = 4.0 Hz, 1H), 6.76 (d, J = 4.0 Hz, 1H), 6.77 (t, J = 7.2 Hz, 1H), 6.80-6.86 (m, 5H), 6.92 (dd, J = 8.4, 2.1 Hz, 2H), 6.98–7.01 (m, 4H), 7.10–7.16 (m, 4H), 7.23 (td, J = 7.6, 1.6 Hz, 1H), 7.40–7.45 (m, 2H), 7.80 (dd, J = 7.6, 1.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.0, 20.3, 21.2, 70.6, 112.9, 114.7, 118.5, 119.2, 119.6, 119.8, 121.2, 123.2, 125.8, 126.0, 126.6, 126.7, 126.9, 127.1, 127.6, 127.9, 128.2, 130.6, 131.1, 132.5, 133.0, 133.2, 136.6, 136.8, 137.0, 137.3, 138.3, 142.1, 149.4, 154.6, 156.7, 157.4. ^{11}B NMR ($CDCl_3$, 128 MHz) δ 2.68 (s). MS(ESI) observed m/z 622.27 ($[M+H]^+$), calcd for $C_{43}H_{36}BN_2O_2$ m/z 622.29. Anal. Calcd for $C_{43}H_{35}BN_2O_2$: C, 81.59; H, 5.58; N, 4.42. Found: C, 81.74; H, 5.96; N, 4.22.
14. Islam, T. M. B.; Yoshino, K.; Sasane, A. *Anal. Sci.* **2003**, *19*, 455–460.
15. *Crystallographic analysis of* **2:** deep red prism (0.5 × 0.2 × 0.2 mm^3), $C_{36}H_{29}BN_2O_2$ (M = 532.42), triclinic, a = 8.1638(6), b = 12.7262(11), c = 13.3910(12) Å, α = 83.874(3)°, β = 81.820(2)°, γ = 81.777(2)° V = 1357.6(2) $Å^3$, space group $\bar{P}$ (No. 2), Z = 2, ρ_{calcd} = 1.302 g/cm^3, T = 120 K, μ(Mo Kα) = 0.092 mm^{-1}, collected refections, 13,321, unique, 6140 (R_{int} = 0.0438), R_1 = 0.0539 ($I/2\sigma(I)$), wR_2 = 0.1302 (all data) GOF (F^2) = 1.078. CCDC 716494 contains the supplementary crystallographic data for this Letter. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
16. Sheldrick, G. M. SHELXL-97. Program for crystal structure refinement, University of Göttingen, 1997.