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Boronic ester of a phthalocyanine precursor with a salicylaldimino moiety

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ABSTRACT

4-(4-Formyl-3-hydroxyphenoxy)phthalonitrile (**3**) and its condensation product with 2-aminophenol have been synthesized to reach 4-(3-hydroxy-4-(((2-hydroxyphenyl)imino)-methyl)phenoxy)phthalonitrile (**5**), a tridentate ligand possessing ONO binding sites. Subsequent condensation of phenylboronic acid with **5** afforded a novel boronic ester of a Schiff base with a phthalonitrile group (**7**). Boronate **7** displays high stability and can be handled in air due to the presence of coordinative B–N and covalent B–O bonds in its structure. The novel compounds were characterized by elemental analyses, IR, UV–vis, mass, ^{1}H-, ^{13}C- and ^{11}B NMR spectra.

1. Introduction

There is considerable interest in the synthesis and characterization of organoboron compounds due to their interesting applications, for example in medicinal chemistry, as enzyme inhibition, potent and selective serine protease inhibition. Likewise, organoboron compounds have been used as anticancer agents in boron neutron capture therapy, a binary form of cancer treatment that relies on delivering a compound containing boron-10 selectively to tumour tissues prior to irradiation by neutrons [1–4]. Some boron compounds also present cytotoxic activity [5]. Furthermore, compounds containing boronic acids [$RB(OH)_2$] or boronate esters [$RB(OR')_2$] have been used extensively as intermediates in Suzuki–Miyaura cross-coupling reactions for a variety of applications [2,6]. They also display a wide range of applications as materials with fluorescence [7], electro-optical and non-linear optical properties [8–10]. Boron-based compounds of the type R_2BOAr (including many variations on Ar) have attracted a great deal of attention as emitting materials due to their increased stability compared to aluminium-based emitters and the strong π-electron accepting behaviour of the empty pz orbital at the boron centre [11–13]. In addition, four-coordinated organoboron compounds with a π-conjugated chelate backbone have emerged recently as highly attractive materials for a number of applications including emitters and electron-transport materials for organic light-emitting diodes (OLEDs) or organic field effect transistors, photoresponsive materials, and sensory and imaging materials [14].

The traditional organic synthesis of macrocyclic compounds involves several steps, as a consequence, the products are obtained in low yields. As an alternative method, coordinative connections are preferred for the formation of a number of organic and inorganic macrocycles and these processes usually occur through self-assembly [15,16]. The presence of metal ions with the appropriate ionic radius has also allowed the synthesis of coordinating systems via the template effect [17,18].

Although boron takes part between metals and non-metals in the periodic table of the elements, most of its physical and chemical properties and those of the compounds derived from it are typical for nonmetallic species. Its capacity to form coordinative bonds with a series of ligands typically used for metal-complexation is the most prominent feature in the chemistry of boron that reflects a relationship to metal compounds [19,20]. Boron forms coordinative bonds with nitrogen, oxygen, sulphur or phosphorus atoms with small charge separations. The ease of boron macrocyclic synthesis is due to this versatility of boron atom to react with donor atoms (e.g. N and O), thus favouring self-assembly processes [21]. The synthesis of boron macrocycles that contain coordinative bonds between the nitrogen and boron atoms has been achieved using the above method, and dimeric, trimeric, tetrameric and pentameric species have been reported [15,22,23].

The advantage of macrocyclic boronates lies in their easy, one step synthesis from readily available starting materials [24]. The presence of boron in the macromolecular structure gained unusual and interesting properties to these macrocyclic boronates [7,8].

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The use of tridentate ligands in coordination chemistry provides a facile means to stabilize transition metals [25] and main group elements [26] taking advantage of the chelate effect. Thus, it has been reported that tridentate ligands having an ONO donor set of atoms react with main group elements to give stable heterocycles [27]. The results of the studies based on these boronates have shown that in all cases boron atom is tetracoordinated and forms a dative bond with the nitrogen atom; the characteristics of the dative bond as well as the rigidity of the tridentate ligands employed gave rise to monomeric molecules and, through a self-assembly procedure, to specific di-, tri- and tetrameric molecules [28–30]. Moreover, the reaction is dependent on steric, as well as electronic factors. All these compounds showed high hydrolytic and oxidative stability [31] due to the presence of coordinative N–B and covalent B–O bonds (the tetracoordination of the boron atoms) [32,33]. In this context, the reactions between the molecules containing nitrogen atoms as Lewis bases with compounds having boron atoms as Lewis acids has been studied intensively [1,23,34].

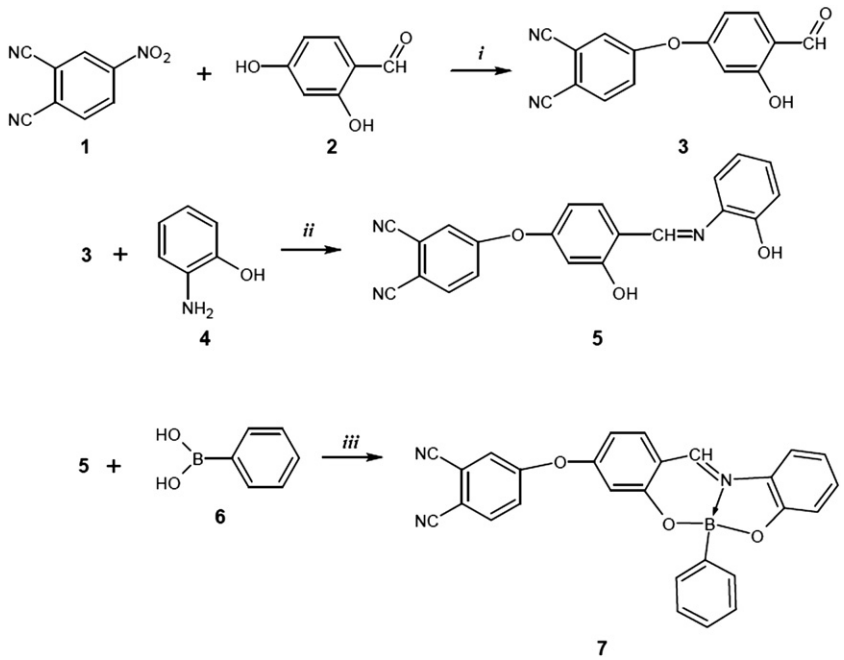
Recently, there has been a great attention for boron products of imines and related substrates prepared from the condensation of boronic or borinic acid with polydentate Schiff base ligands which can function in both bridging and chelating capacities [17,20,23,35]. These compounds have a number of applications, including their use in bifunctional catalysis, molecular recognition, fluorescent chemosensors, fungicidal additives, chiral sensors, electroluminescent devices, and non-linear optical studies [36]. Farfán et al. [37] have investigated the imino Diels–Alder reactions with organoboron esters prepared by the condensation of the salicylaldimines with phenylboronic acid ($PhB(OH)_2$) or phenylborinic acid (Ph_2BOH) and have discovered that related systems are potential candidates for third order non-linear optical studies. Their previous studies reported the possible applications of boron adduct in Imino Diels–Alder (IDA) reaction as the presence of the coordination bond between the nitrogen and boron atoms polarizes the imine bond and increases the selective reactivity of this bond [38]. At present, there is extending interest in this type of compounds because of their being efficient catalysts in propylene polymerization reactions via the formation of a boron cation [39].

Continuing our studies on the preparation and characterization of boronated tetrapyrolle derivatives and their precursors [40,41], in the present study we report the synthesis of a phthalonitrile derivative possessing ONO binding sites and its phenylboronic ester. The new compounds were fully characterized by elemental analyses, FTIR, ^1H NMR, ^{13}C NMR, ^{11}B NMR and UV–vis spectral data.

2. Results and discussion

Scheme 1 shows the synthesis of the target phthalonitrile derivatives **3**, **5** and **7**. In the first step of this study, 4-(4-formyl-3-hydroxyphenoxy)phthalonitrile (**3**) was prepared by a base-catalyzed nucleophilic aromatic displacement of 4-nitrophthalonitrile (**1**) with 2,4-dihydroxybenzaldehyde (**2**). The reaction was carried out as a single step synthesis by using K_2CO_3 as the base at room temperature in dry dimethylformamide under N_2 atmosphere. It has been reported that among the two phenolic OH groups in **2**, the *ortho*-hydroxy group was less acidic due to the intramolecular H-bonding with the carbonyl group, making it possible to selectively react the more acidic *para*-hydroxy group first using weaker bases or lower temperatures [42]. Therefore, the product was compound **3**, not a mixture of isomers. The second step was the preparation of a phthalonitrile derivative having a Schiff's base structure required for the esterification reaction with phenylboronic acid. 4-(3-Hydroxy-4-(((2-hydroxyphenyl)imino)methyl)phenoxy)phthalonitrile (**5**) was prepared through a condensation reaction between equimolar amount of compound **3** and 2-aminophenol in ethanol with a yield of 82%. The subsequent reaction of compound **5** with phenylboronic acid in THF under reflux gave the desired boronate **7** in relatively high yield (78%). In order to efficiently remove the byproduct water, the reaction was performed in the presence of 3 Å molecular sieves.

This novel bicyclic compound **7** is very stable to hydrolysis and can be handled in air due to the presence of coordinative B–N and covalent B–O bonds in its structure [43–45]. Furthermore, as the strength of the B–N bond depends on the polarization of the coordinative bond and the degree of substitution on the nitrogen and boron atoms, the stability of this phenyl boron heterocycles **7**



Scheme 1. Synthetic route for compounds **3**, **5**, **7** (i) DMF, K_2CO_3, r.t.; (ii) Ethanol, reflux; (iii) THF, reflux, molecular sieves.

can be attributed to the strong acidity of the boron atom produced by the electron-withdrawing behaviour of the phenyl group [46].

The preparation methods followed in the present study were easy and afforded compounds **5** and **7** in relatively high yields. Together with the fact that esterification reactions are essentially in equilibrium with the precursors, a reaction mechanism based on self assembly of these components can be proposed [47]. The relatively high yield of the reaction in the present case can be a consequence of this interaction.

Characterizations of the products involved a combination of methods including elemental analysis, ^{1}H and ^{13}C NMR, UV–vis, FTIR, mass spectra and also ^{11}B NMR for boronated compound. Spectral data on the newly synthesized compounds are consistent with the proposed structures.

The IR spectrum of dinitrile compound **3** confirmed the proposed structure by the disappearance of the aromatic $-NO_2$ band at 1548 cm^{-1} and the appearance of an intense new absorption at 1246 cm^{-1} attributable to aromatic C–O–C [48]. In addition, the characteristic C≡N stretching vibrations appeared as a single intense peak at expected frequency (2233 cm^{-1}) [49]. Furthermore, the presence of aromatic C–H peaks around 3078–2971 cm^{-1}, C=O peak at 1738 cm^{-1} and O–H peaks around 3300 cm^{-1} in the IR spectrum of **3** are the additional evidences for the formation of compound **3** [50].

In the ^{1}H NMR spectrum of **3**, aromatic protons of benzaldehyde group appeared at 7.76–7.72, 6.80–6.78 and 6.45 ppm as doublet, doublet, singlet, respectively, while those of phthalonitrile groups appeared at lower fields at 8.06, 7.84 and 7.43 ppm as doublet, singlet, doublet, respectively. Also the CH=O and O–H protons were observed as singlets at 11.00 and 9.87 ppm respectively. The ^{13}C NMR of **3** exhibited the expected signals between 186.95 ppm and 107.48 ppm for aromatic carbons. The carbon attached to the OH group in the benzaldehyde part was observed at 157.23 ppm and the signal for the formyl carbon was observed at 186.95 ppm. Furthermore, the presence of nitrile groups in compound **3** was also evidenced by signals at 116.72 and 115.65 ppm.

The formation of compound **5**, the molecule with an ONO binding core, was confirmed by the presence of O–H peaks around 3330 cm^{-1}, aromatic CH peaks around 3063–2964 cm^{-1}, C≡N peaks at 2200 cm^{-1}, aromatic C–O–C peaks around 1227 cm^{-1} in the IR spectrum. Schiff base structure of **5** was also confirmed by the disappearance of CH=O absorption band (1738 cm^{-1}) and appearance of an intense band attributed to the CH=N group at 1585 cm^{-1}. This imine proton was also well characterized by the singlet peak at 8.73 ppm in ^{1}H NMR spectrum. Due to the differences in their chemical environments, the protons of OH groups showed different chemical shift values (14.14 ppm and 9.71 ppm) and the aromatic protons were appeared in the range of 7.64–6.24 ppm.

The ^{13}C NMR spectrum of compound **5** showed aromatic carbons in the range of δ 169.05 and 103.96 ppm. The azomethine carbon appeared at 164.75 ppm and the nitrile carbons were observed at 117.63 and 116.96 ppm. Also the aromatic carbon atoms adjacent to the OH groups came out at 160.13 and 149.96 ppm.

The IR spectra for compound **7** showed the disappearance of the bands corresponding to the OH groups, which are present in the Schiff's base **5** around 3330 cm^{-1}. Another important diagnostic parameter would be the value of the B–N and B–O stretching frequency. In the spectrum of compound **7**, B–N and B–O peaks appeared at 1440 cm^{-1} and 1344–1312 cm^{-1} respectively. Furthermore, the formation of the N–B coordinative bond was established by the observation of the CH=N stretching band at 1601 cm^{-1}. This band is shifted to higher wavenumbers compared to the same band in the compound **5** (1585 cm^{-1}). This is due to the B–N intramolecular coordination which serves to reduce the electron density in the C=N bond [51]. Also, aromatic CH peaks came out around 3068–2870 cm^{-1} and the intense C≡N peak was observed at 2223 cm^{-1}.

Most identical differences between ^{1}H NMR spectra of compounds **5** and **7** are the disappearance of OH chemical shifts in the latter and appearance of new chemical shifts in the aromatic region arising from the protons of benzene group condensed on to the compound **5**. The imine proton was observed at 8.19 ppm. The aromatic protons appear in the range of 8.17–6.42 ppm.

The characteristic signal in the ^{13}C NMR spectrum for the imine group appeared at 151.64 ppm and shifted to higher field with respect to that of compound **5** (164.75 ppm). The signals attributed to the phenolic carbon atoms of phenylboronic acid moiety at 135.78, 135.66, 131.21, 128.28, 128.03 and 127.33 ppm also confirmed the binding of phenylboronic acid with compound **5**. The existence of the N→B bond in compound **7** was also established by ^{11}B NMR which showed a signal at 7.44 ppm, characteristic for the tetracoordinated boron atom [52].

2.1. UV–vis spectra of compounds *2*, *3*, *5* and *7*

The compound **7** presented in this paper is an example of four-coordinated organoboron compound that possesses a chelate π-conjugated backbone. In this kind of compounds, boron influences the electronic properties of the π system by stabilizing the chelate and enhancing the π conjugation. These dual roles of boron makes this class of compounds good candidates for their possible use in OLEDs as emitters and electron-transport materials [14].

The UV–vis spectra of compounds **2**, **3**, **5** and **7** in THF are given in Fig. 1. The UV–vis spectrum of 2,4-dihydroxybenzaldehyde presented three absorptions at 234, 278 and 313 nm in THF. The phthalonitrile **3** exhibited bands at 246 and 268 nm with higher absorbance values than those of compound **2** at 234 and 278 nm. This increase in the absorbance values can be attributed to the $\pi-\pi^*$ transitions of the phenoxy group attached to the structure by the aromatic substitution reaction of 2-nitrophthalonitrile (**1**) and 2,4-dihydroxybenzaldehyde (**2**). Furthermore, the band at 313 nm disappeared in the UV–vis spectrum of phthalonitrile **3**. The UV–vis spectrum of phthalonitrile **5** was characterized by the presence of three absorption maxima at 242, 280 and 345 nm. The broad maximum in **5** at 345 nm is due to the $n-\pi^*$ electronic transition of the azomethine group while the bands at 242 and 280 nm are due to the $\pi-\pi^*$ electronic transitions. Significant spectral changes occurred in the spectrum of compound **5** after the formation of boronate **7** through the condensation reaction of phenylboronic acid and Schiff base **5**. The peak at 345 nm of compound **5** was blue shifted (by 35 nm) to 311 nm and its absorbance value increased. In addition, the appearance of a broad band around 430–440 nm indicated the formation of the proposed boronate ester of the Schiff base with a phthalonitrile group [53,54] (Fig. 1).

In conclusion, three novel phthalonitrile derivatives, 4-(4-formyl-3 hydroxyphenoxy)-phthalonitrile (**3**), 4-(3-hydroxy-4-(((2-hydroxyphenyl)imino)methyl)-phenoxy)phthalonitrile (**5**) and phenylboronic acid ester of 4-(3-hydroxy-4-(((2-hydroxyphenyl) imino)-methyl)-phenoxy)phthalonitrile (**7**) have been prepared. Phthalonitrile **7** displays high stability in air due to the presence of coordinative B–O and dative B–N bonds in its structure. All of the presented compounds in this paper were characterized by elemental analyses, IR, UV–vis, mass, ^{1}H NMR, ^{13}C NMR spectra and ^{11}B NMR spectrum for boron compound. Spectral data and gradual increase in their solubility confirmed the successful preparation of the proposed phthalonitrile derivatives. Further studies to convert the phthalonitrile precursors with or without boronic ester groups to phthalocyanines are under investigation.

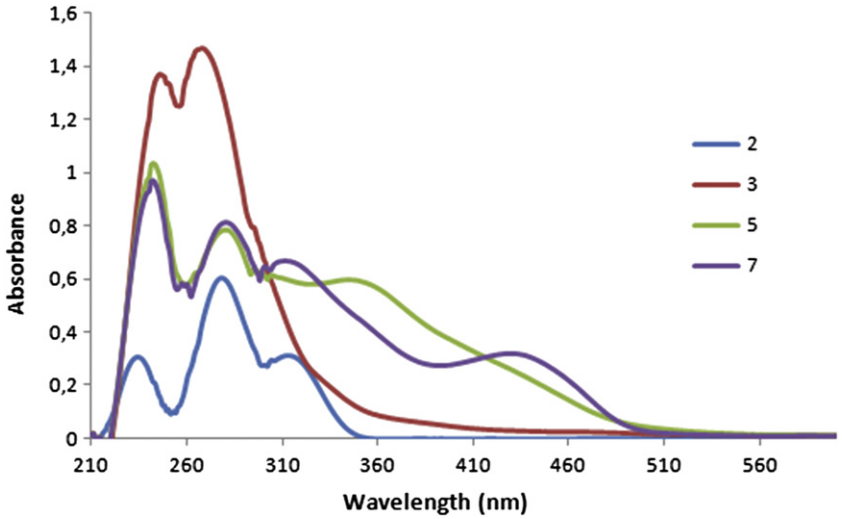


Fig. 1. Absorption spectra of compounds **2**, **3**, **5** and **7** in THF.

3. Experimental

All reagents and solvents were of reagent grade quality, obtained from commercial suppliers. The solvents were stored over molecular sieves (4 Å). 4-Nitrophthalonitrile (**1**) was synthesized as reported in the literature [55]. 2,4-Dihydroxybenzaldehyde (**2**) and phenylboronic acid were used as supplied commercially. The progress of the reactions was monitored by TLC (SiO_2). IR spectra were recorded on a Perkin–Elmer Spectrum One FTIR (ATR sampling accessory) spectrophotometer, electronic spectra in the UV–vis region were recorded with an Scinco S-3100 single beam UV/vis PDA spectrophotometer. ^{1}H NMR spectra were recorded on a Varian UNITY INOVA 500 MHz spectrophotometer using TMS as internal reference. ^{13}C- and ^{11}B NMR spectra were recorded on a Bruker Ultra Shield Plus 400 MHz spectrometer. Boron trifluouride diethyl etherate was used as an external standard in ^{11}B NMR spectra. Elemental analyses were performed on a Thermo Flash EA 1112.

3.1. Synthesis of 4-(4-formyl-3-hydroxyphenoxy)phthalonitrile (*3*)

4-Nitrophthalonitrile (1.0 g, 5.78 mmol) and 2,4-dihydroxybenzaldehyde (1.197 g, 8.66 mmol) were dissolved in 10 ml dry DMF. After dissolution, finely ground anhydrous potassium carbonate (4.2 g, 30 mmol) was added in portions over 2 h with efficient stirring. The reaction mixture was stirred vigorously at room temperature under N_2 for 48 h. The progress of the reaction was monitored by TLC. The reaction mixture was poured into 250 ml of cold water and stirred for 30 min. The pH of the solution was adjusted to 1 by addition of 1 N HCl solution. The precipitated solid was filtered, washed with water until the filtrate was neutral. Then the solid product was dissolved in ethanol and the solution was refluxed for 30 min in the presence of activated carbon. The hot solution was filtered and then the solvent was evaporated to dryness. The solid product was washed with hexane and dried *in vacuo*. Yield: 0.488 g (32%); m.p. 181 °C. FTIR ν_{max}/cm^{-1}: 3300(broad, O–H), 3078–2971 (Ar–H), 2233 (C≡N), 1738 (C=O), 1656 (C=C), 1591, 1483, 1457, 1374, 1309, 1246 (C–O–C), 1168, 1098, 1042, 980, 876, 815, 666. ^{1}H NMR (d_6-DMSO): 11.00 (1H, s, OH), 9.87 (1H, s, CH=O), 8.06 (1H, d, J = 7.9 Hz, Ar–H), 7.84 (1H, s, Ar–H), 7.74 (1H, d, J = 7.7 Hz, Ar–H), 7.43 (1H, d, J = 7.4 Hz, Ar–H), 6.79 (1H, d, J = 7.4 Hz, Ar–H), 6.45 (1H, s, Ar–H); ^{13}C NMR (d_6-DMSO): 186.95 (CH=O), 164.95 (Ar C), 160.58 (Ar C), 157.23 (Ar C), 136.30 (Ar CH), 132.47 (Ar CH), 123.1 (Ar CH), 122.57 (Ar CH), 119.65 (Ar C), 116.72 (C≡N), 115.65 (C≡N), 115.31 (Ar C), 113.81 (Ar CH), 108.86 (Ar C), 107.48 (Ar CH); UV–vis (THF): λ_{max}/nm: 246, 268; Calcd. for $C_{15}H_8N_2O_3$: C, 68.18; H, 3.05; N, 10.60%. Found: C, 68.27; H, 3.25; N, 10.54%.

3.2. Synthesis of 4-(3-hydroxy-4-(((2-hydroxyphenyl)imino) methyl)phenoxy)phthalonitrile (*5*)

To a solution of 200.0 mg (0.757 mmol) **3** in 20 ml of ethanol, a solution of 2-aminophenol (90.8 mg, 0.832 mmol) in 15 ml of ethanol was added. The reaction mixture was refluxed for 24 h and then the hot mixture was filtered. The filtrate was evaporated to dryness to give compound **5** as a golden brown solid. Yield: 0.220 g (82%). m.p. 214 °C. FTIR ν_{max}/cm^{-1}: 3330 (OH), 3063–2964 (Ar–H), 2220 (C≡N), 1585 (CH=N), 1510, 1458, 1342, 1227 (C–O–C), 1099, 1035, 829, 745, 666; ^{1}H NMR (d_6-DMSO): 14.14 (1H, s, OH), 9.71 (1H, s, OH), 8.73 (1H, s, CH=N), 8.19 (1H, d, J = 7.9 Hz, Ar–H), 7.64 (1H, s, Ar–H), 7.28 (1H, d, J = 7.8 Hz, Ar–H), 7.13 (1H, d, J = 7.6 Hz, Ar–H), 7.05–7.03 (1H, m, Ar–H), 6.94 (1H, d, J = 7.4 Hz, Ar–H), 6.82 (1H, m, Ar–H), 6.66–6.61 (1H, m, Ar–H), 6.39 (1H, d, J = 7.5 Hz, Ar–H), 6.24 (1H, s, Ar–H); ^{13}C NMR (d_6-DMSO): 169.05 (Ar C–O), 164.75 (CH=N), 160.13 (Ar C), 156.26 (Ar C), 149.96 (Ar C), 143 (Ar C), 134.39 (Ar CH), 133.53 (Ar CH), 126.13 (Ar CH), 124.60 (Ar CH), 124.43 (Ar CH), 119.39 (Ar CH), 119.01 (Ar CH), 117.63 (C≡N), 116.96 (C≡N), 116.23 (Ar CH), 114.40 (Ar C), 112.09 (Ar C), 109.37 (Ar CH), 106.40 (Ar C), 103.96 (Ar CH); UV–vis (THF): λ_{max}/nm: 242, 280, 345; Calcd. for $C_{21}H_{13}N_3O_3$: C, 70.98; H, 3.69; N, 11.83%. Found: C, 71.12; H, 3.45; N, 11.75%.

3.3. Synthesis of compound *7*

100 mg (0.28 mmol) of compound **5** was dissolved in 25 ml THF and then poured into a solution of benzenboronic acid (34 mg, 0.28 mmol) in 15 ml THF. The reaction mixture was refluxed in 100 ml round bottom flask charged with 3 Å molecular sieves (1.20 g) in order to remove the water released from the esterification reaction. After 6 h reflux, the mixture was filtered to remove the molecular sieves. The solvent was evaporated under reduced pressure and the product was washed with hexane. Yield: 97 mg (78%). m.p. 140 °C. FTIR ν_{max}/cm^{-1}: 3068–2870 (Ar–CH), 2223 (C≡N), 1601 (CH=N), 1556, 1471, 1440, 1344, 1312, 1258, 1232

(C–O–C), 1177, 1119, 1087, 1015, 945, 859, 802, 746, 699; ^{1}H NMR ($CDCl_3$): 8.19 (1H, s, CH=N), 8.17 (1H, d, J = 8.1 Hz, Ar–H), 7.69–7.67 (1H, s, Ar–H), 7.53 (1H, d, J = 8.2 Hz, Ar–H), 7.46–7.43 (2H, m, Ar–H), 7.35–7.33 (3H, m, Ar–H), 7.26 (1H, d, J = 7.8 Hz, Ar–H), 7.21 (1H, m, Ar–H), 7.11–7.06 (1H, m, Ar–H), 7.00–6.98 (1H, m, Ar–H), 6.91 (1H, d, J = 7.6 Hz, Ar–H), 6.83 (1H, d, J = 7.9 Hz, Ar–H), 6.42 (1H, s, Ar–H); ^{13}C NMR ($CDCl_3$): 169.92 (Ar C–O–B), 163.77 (Ar C), 160.81 (Ar C–O–B), 157.25 (Ar C), 151.64 (CH=N), 150.35 (Ar C), 144.60 (Ar CH), 135.78 (Ar CH-meta-B), 135.66 (Ar CH-meta-B), 133.57 (Ar CH), 131.21 (Ar C-ortho-B), 128.28 (Ar CH-para-B), 128.03 (Ar CH-para-B), 127.33 (Ar CH-para-B), 125.56 (Ar CH), 121.44 (Ar CH), 120.32 (Ar CH), 119.42 (Ar CH), 117.14 (Ar CH), 115.73 (C≡N), 115.20 (C≡N), 114.77 (Ar C), 114.42 (Ar CH), 112.17 (Ar C), 110.42 (Ar CH), 107.05 (Ar C), 105.66 (Ar CH); ^{11}B NMR, ($CDCl_3$, ppm): 7.44 (s, tetracoordinated B); UV–vis (THF): λ_{max}/nm: 242, 280, 311, 429; Calcd. for $C_{27}H_{16}BN_3O_3$: C, 73.49; H, 3.65; N, 9.52%. Found: C, 73.65; H, 3.45; N, 9.75%.

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