Synthesis of Azaaromatic–Borane Intramolecular Complexes by Palladium-Catalyzed Reaction of Azaaromatic Halides with Alkynyl(triaryl)borates

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Dedicated to Professor *Dieter Seebach* on the occasion of his 75th birthday

A diversity-oriented method to synthesize (*E*)-azastilbenes having an intramolecular B–N coordination bond from alkynyl(triaryl)borates and azaaromatic halides is described. The obtained π-conjugated compounds exhibit an intense blue fluorescence and a high electron affinity, indicating their potential to be used as n-type light-emitting materials.

Introduction. – Aza-π-conjugated compounds equipped with an intramolecular B–N coordination bond have attracted growing attention because of their interesting properties such as a high electron affinity [1], an intense fluorescence [2], and photochromism [3][4]. The conventional methods for their synthesis typically consist of initial lithiation of a parent N-containing π-conjugated framework and the following nucleophilic substitution reaction with haloboranes. However, electron-deficient azaaromatics such as isoquinolines and pyrazines are prone to undergo undesired side reactions upon treatment with lithiating agents [5]. A new method for the synthesis of a wide variety of azaaromatic–borane complexes is yet to be developed [6].

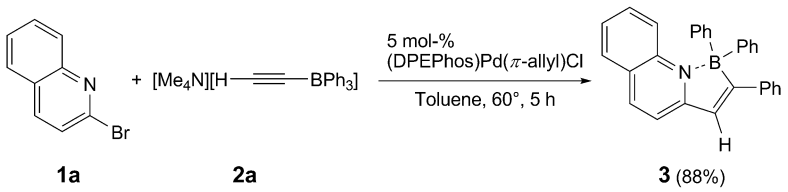
We previously developed the Pd-catalyzed reaction of alkynyl(aryl)borates (aryl = Ar^1) with aryl halides (aryl = Ar^2) [7]. Two aryl groups, Ar^1 and Ar^2, were incorporated across the C≡C bond to produce (trisubstituted alkenyl)boranes. This protocol was successfully applied to the synthesis of amine–borane complexes [8] and pyridine *N*-oxide–borane complexes [9]. Herein, we describe a diversity-oriented method for the synthesis of (*E*)-azastilbene derivatives having an intramolecular B–N coordination bond from alkynyl(triaryl)borates and azaaromatic halides. The obtained π-conjugated compounds exhibit an intense blue fluorescence and a high electron affinity, demonstrating their potential to be used as n-type light-emitting materials.

Results and Discussion. – 2-Bromoquinoline (**1a**) and alkynylborate **2a** were reacted under the slightly modified conditions of the previously reported Pd-catalyzed reaction [7b][9][1]). A toluene solution (1 ml) of **1a** (0.20 mmol), **2a** (0.20 mmol), and (DPEPhos)Pd(π-allyl)Cl (DPEPhos = bis[2-(diphenylphosphino)phenyl]ether = (oxydi-2,1-phenylene)bis(diphenylphosphine); 5 mol-%) was heated at 60° for 5 h

[1]) The preliminary screening of ligands revealed that DPEPhos gave a result superior to other ligands such as XANTPhos, BINAP, and DPPF.

(*Scheme 1*). The reaction efficiently took place, and the following chromatography afforded analytically pure quinoline–borane complex **3** in 88% yield.

Scheme 1

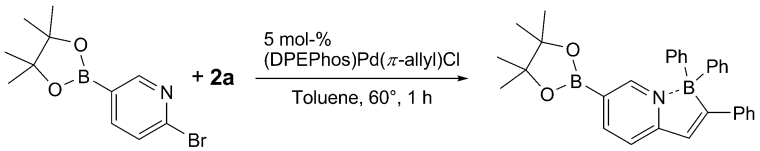


1a **2a** **3** (88%)

The broad scope of this Pd-catalyzed reaction was compiled in *Table 1*. Not only 2-bromoquinoline (**1a**), but also 8-bromoquinoline (**1b**) participated in the reaction to furnish six-membered azaboracycle **4** in 81% yield (*Entry 1*). Isoquinoline, pyrimidine, and pyrazine moieties were all suitably and underwent the present reaction (*Entries 2–5*), whereas these are prone to decompose upon lithiation [5]. The alkynylborates **2d–2f**, which are equipped with various aryl groups, undergoing the Pd-catalyzed reaction, afforded the corresponding azaaromatic–borane complexes **10–12** (*Entries 7–9*).

Excellent functional-group compatibility was demonstrated by the reaction of 2-bromopyridines bearing functional groups which were potentially reactive towards Pd catalysts. The pinacolatoboryl moiety was tolerated on the pyridine ring, yielding pinacolatoboryl-substituted pyridine–borane complex **13** in 82% yield (*Scheme 2*). When 2 equiv. of 2,5-dibromopyridine **1i** was used, the 2-Br group reacted in preference to the 5-Br group, as was the case with the Pd-catalyzed cross-coupling reactions (*Scheme 3*) [10]. The 5-bromopyridine–borane complex **14** was obtained in 78% yield. These boryl and Br groups remaining in the products served as footholds for the subsequent *Suzuki–Miyaura* cross-coupling reaction. Treatment of **13** and **14** with a catalytic amount of $Pd[P(t\text{-}Bu)_3]_2$ in the presence of NaOH in THF/H_2O provided bipyridne **15** in 84% yield (*Scheme 4*).

Scheme 2



1h **13** (82%)

Thus, a wide variety of azaaromatic–borane intramolecular complexes were successfully synthesized through the Pd-catalyzed reaction of alkynylborates with azaaromatic halides. We next examined the electrochemical properties of the quinoline–borane complex **3** to demonstrate a high electron affinity of the products. *Table 2* contains its characteristic properties in comparison with Alq (=tris(8-hydroxyquinolinato)aluminum), the most conventional fluorescent material with a high electron affinity. The cyclic voltammogram of quinoline–borane complex **3** showed a reversible reduction wave with the potential peak V_{pc} of -1.80 V, which was

Table 1. *Aza-π-Conjugated Compounds Having B–N Coordination Bond*[a])

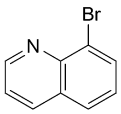
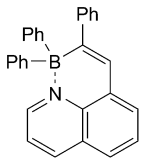
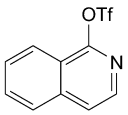
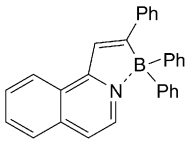
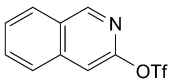
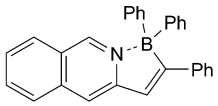
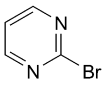
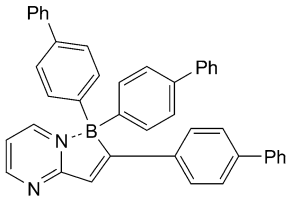
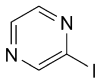
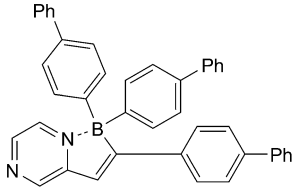
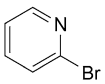
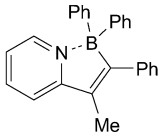
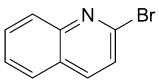
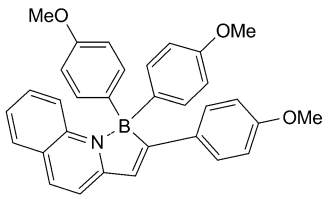
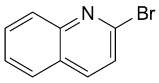
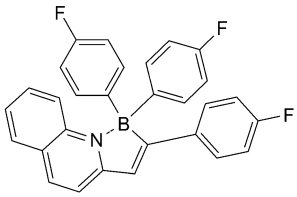
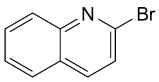
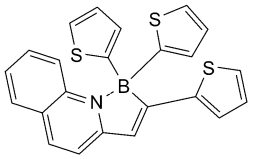
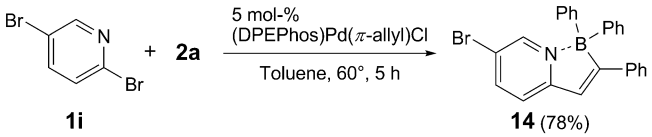
Entry	Azaaromatic halides **1**	Alkynylborates **2**	Products	Yield [%]
1	**1b** 	**2a** [Me_4N][H—≡—BPh_3]	**4** 	84
2	**1c** 	**2a** [Me_4N][H—≡—BPh_3]	**5** 	81
3	**1d** 	**2a** [Me_4N][H—≡—BPh_3]	**6** 	80
4	**1e** 	**2b** [Me_4N][H—≡—$B(C_6H_4\text{-}4\text{-}Ph)_3$]	**7** 	67
5	**1f** 	**2b** [Me_4N][Me—≡—BPh_3]	**8** 	43
6	**1g** 	**2c** [Me_4N][Me—≡—BPh_3]	**9** 	87
7	**1a** 	**2d** [Me_4N][H—≡—$B(C_6H_4\text{-}4\text{-}OMe)_3$]	**10** 	89

Table 1 (cont.)

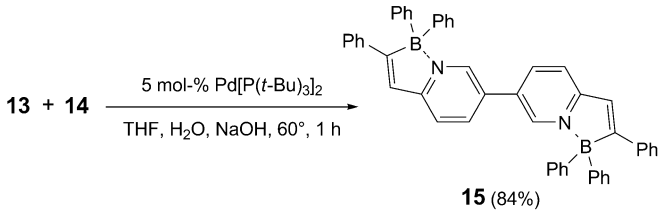
Entry	Azaaromatic halides **1**	Alkynylborates **2**	Products	Yield [%]
8	**1a** 	**2e** $[Me_4N][H{\equiv}B(C_6H_4\text{-}4\text{-}F)_3]$	**11** 	66
9	**1a** 	**2f** $[Me_4N][H{\equiv}B(2\text{-thienyl})_3]$	**12** 	84

[a]) Reaction conditions: 1.0 equiv. of aryl halide, 1.0 equiv. of alkynylborate, 5 mol-% (DPEPhos)Pd(π-allyl)Cl, toluene (0.2M), 60°, 5 h.

Scheme 3



Scheme 4



less negative than that of Alq (−2.14 V under the same conditions). The LUMO level of **3** was calculated as 3.8 eV, which was significantly higher than that of Alq (3.0 eV). These results indicate that **3** has an even higher electron affinity than Alq. The photophysical properties are also compiled in *Table 2*. The quinoline–borane complex **3** showed a sky blue fluorescence (λ_{max} 473 nm in CH_2Cl_2) with the quantum yield of 0.26, whereas Alq exhibited a green fluorescence (λ_{max} 526 nm, Φ 0.17) [11]. These electrochemical and photochemical properties demonstrated the potential usefulness of this class of molecules as the *n*-type blue light-emitting materials.

Table 2. *Photophysical and Electrochemical Properties of* **3**

Compounds	V_{pc}/V[a])	HOMO/eV[b])	LUMO/eV[c])	λ_{em}/nm	Φ
3	– 1.80	6.6	3.8	473[d])	0.26[d])
Alq	– 2.14	5.7	3.0	526[e])	0.17[e])

[a]) In γ-butyrolactone with Bu_4NClO_4 at a scan rate of 100 mVs^{-1}. Potentials *vs.* Fc/Fc^+. [b]) Determined by UPS. [c]) Calculated from the HOMO and the UV absorption edge. [d]) Taken from [8]. [e]) Taken from [11].

In summary, we have synthesized (*E*)-azastilbenes having an intramolecular B–N coordination by the Pd-catalyzed reaction of azaaromatic halides with alkynyl(triaryl)borates. This method is versatile enough to incorporate a wide variety of azaaromatics including those vulnerable to the conventional lithiating conditions. The obtained π-conjugated compounds exhibit a strong fluorescence and a high electron affinity, *i.e.*, with a potential to be used as the n-type light-emitting materials.

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Experimental Part

General. Unless otherwise noted, all chemicals and anh. solvents were obtained from commercial suppliers. Toluene was dried over sodium benzophenone ketyl. (DPEPhos)Pd(π-allyl)Cl [12] and alkynyl borates **2** [9] were prepared according to the reported procedures. Column chromatography (CC): silica gel *60 N* (*Kanto*). Prep. TLC: Silica gel *60 PF_{254}* (*Merck*). Gel permeation chromatography (GPC): *Japan Analytical Industry LC-908* or *LC-9204*. NMR Spectra: *Varian Gemini 2000* (^{1}H: 300 and ^{13}C: 75 MHz), *Varian Mercury vx* (^{1}H: 400 and ^{13}C: 100 MHz), *JEOL JNM-A500* (^{1}H: 500 and ^{13}C: 150 MHz), or *Varian 400-MR Auto Tune X5* (^{11}B: 128 MHz) spectrometers; unless otherwise noted, $CDCl_3$ was used as a solvent; chemical Shifts in δ ppm referenced to a residual $CDCl_3$ (δ 7.26 for ^{1}H, δ 77.0 for ^{13}C), CD_3CN (δ 1.94 for ^{1}H, δ 1.32 for ^{13}C), and $BF_3 \cdot OEt_2$ (δ 0.00 for ^{11}B). HR-MS: *Applied Biosystems Voyager Elite* or *JEOL JMS-HX110A* spectrometer.

Alkynylborate **2b**. ^{1}H-NMR (CD_3CN): 2.22 (*s*, 1 H); 3.00 (*s*, 12 H); 7.24 – 7.30 (*m*, 3 H); 7.37 – 7.43 (*m*, 12 H); 7.53 (*d*, *J* = 7.2, 6 H); 7.62 (*d*, *J* = 7.8, 6 H). ^{13}C-NMR (CD_3CN): 56.0; 125.5; 127.1; 127.4; 129.5; 135.9; 136.1; 143.4. ^{11}B-NMR (CD_3CN): – 12.6. HR-FAB-MS: 495.2293 ($[M-(Me_4N)]^-$, $C_{38}H_{28}B^-$; calc. 495.2284).

Alkynylborate **2f**. ^{1}H-NMR (CD_3CN): 2.21 (*s*, 1 H); 2.92 (*s*, 12 H); 6.90 – 6.91 (*m*, 6 H); 7.13 – 7.14 (*m*, 6 H). ^{13}C-NMR (CD_3CN): 56.0; 124.5; 127.2; 128.6. ^{11}B-NMR (CD_3CN): – 18.0. HR-FAB-MS: 285.0031 ($[M-(Me_4N)]^-$, $C_{14}H_{10}BS_3^-$; calc.285.0038).

Pd-Catalyzed Reaction of 2-Bromoquinoline (**1a**) *with Alkynylborate* **2a**. *A Typical Procedure*. In an oven-dried flask was placed (DPEPhos)Pd(π-allyl)Cl (3.6 mg, 5 μmol) and **2a** (34.7 mg, 0.10 mmol). The flask was then evacuated and purged by Ar three times. A toluene soln. (0.5 ml) of 2-bromoquinoline (21.2 mg, 0.10 mmol) was added to the flask, and then the mixture was stirred at 60°. After 5 h, H_2O was added. The resulting mixture was extracted with CH_2Cl_2 (3 ×), washed with H_2O (once), brine (once), dried ($MgSO_4$), and concentrated. The residue was purified by prep. TLC to give quinoline–borane complex **3** (34.8 mg, 0.088 mmol, 88% yield). The spectra of the obtained **3** were identical to the reported data [8].

Quinoline–Borane Complex **4**. ^{1}H-NMR ($CDCl_3$): 7.03 – 7.19 (*m*, 12 H); 7.32 – 7.35 (*m*, 4 H); 7.43 (*dd*, *J* = 8.4, 6.0, 1 H); 7.66 – 7.68 (*m*, 3 H); 8.33 (*dd*, *J* = 8.1, 1.5, 1 H); 8.79 (*dd*, *J* = 8.4, 2.1, 1 H). ^{13}C-NMR ($CDCl_3$): 121.0; 124.88; 124.94; 125.2; 125.9; 127.1; 127.3; 127.9; 129.1; 129.4; 130.0; 133.6; 134.0; 138.7; 141.0; 146.0; 149.5. Two kinds of C-atoms bound to B-atom were not detected due to quadrupolar relaxation. ^{11}B-NMR ($CDCl_3$): 1.7. HR-EI-MS: 395.1848 (M^+, $C_{29}H_{22}BN^+$; calc. 395.1845).

Isoquinoline–Borane Complex **5**. ^{1}H-NMR ($CDCl_3$): 7.18 – 7.42 (*m*, 14 H); 7.73 – 7.81 (*m*, 3 H); 7.84 – 7.87 (*m*, 2 H); 7.92 (*s*, 1 H); 8.10 (*d*, *J* = 6.6, 1 H); 8.51 (*d*, *J* = 7.5, 1 H). ^{13}C-NMR ($CDCl_3$): 117.8; 118.4; 123.8; 125.8; 126.8; 127.1; 127.5; 128.19; 128.21; 128.5; 128.8; 132.5; 133.8; 134.7; 137.0; 138.7; 160.8. Two kinds of C-atoms bound to B-atom were not detected due to quadrupolar relaxation. ^{11}B-NMR ($CDCl_3$): 3.7. HR-APCI-MS: 396.1914 ($[M+H]^+$, $C_{29}H_{23}BN^+$; calc. 396.1918).

Isoquinoline–Borane Complex **6**. ^{1}H-NMR ($CDCl_3$): 7.09 – 7.22 (*m*, 10 H); 7.34 – 7.37 (*m*, 4 H); 7.43 (*td*, *J* = 8.4, 0.9, 1 H); 7.58 – 7.61 (*m*, 2 H); 7.65 – 7.70 (*m*, 2 H); 7.75 – 7.79 (*m*, 2 H); 8.93 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$): 114.6; 121.3; 125.3; 125.8; 126.5; 127.0; 127.4; 127.8; 128.0; 128.2; 129.1; 133.2; 133.8; 138.3; 138.9; 147.2; 153.9. Two kinds of C-atoms bound to B-atom were not detected due to quadrupolar relaxation. ^{11}B-NMR ($CDCl_3$): 3.8. HR-EI-MS: ($C_{29}H_{22}BN$ $(M)^+$ 395.1845) 395.1843.

Pyrimidine–Borane Complex **7**. ^{1}H-NMR ($CDCl_3$): 7.07 (*dd*, *J* = 5.4, 4.8, 1 H); 7.29 – 7.63 (*m*, 26 H); 7.84 – 7.87 (*m*, 2 H); 8.52 (*dd*, *J* = 6.6, 5.7, 1 H); 8.88 (*dd*, *J* = 4.5, 2.1, 1 H). ^{13}C-NMR ($CDCl_3$): 115.1; 121.5; 126.4; 126.79; 126.88; 126.92; 127.0; 127.4; 128.6; 128.7; 129.4; 134.2; 136.6; 138.9; 140.4; 141.3; 142.1; 150.0; 161.2; 168.4. Two kinds of C-atoms bound to B-atom were not detected due to quadrupolar relaxation. ^{11}B-NMR ($CDCl_3$): 2.9. HR-EI-MS: 574.2578 (M^+, $C_{42}H_{31}BN_2^+$; calc. 574.2583).

Pyrazine–Borane Complex **8**. ^{1}H-NMR ($CDCl_3$): 7.31 – 7.64 (*m*, 26 H); 7.83 (*d*, *J* = 8.4), 8.27 (br. *s*, 1 H); 8.44 (br. *s*, 1 H); 9.01 (br. *s*, 1 H). ^{13}C-NMR ($CDCl_3$): 117.8; 126.5; 126.8; 126.91; 126.92; 127.0; 127.5; 128.6; 128.7; 129.1; 134.1; 135.8; 136.8; 139.1; 140.2; 140.4; 141.3; 141.9; 143.3; 146.4; 154.0; 185.3. ^{11}B-NMR (CD_3CN): 3.4. HR-ACPI-MS: 575.2650 ($[M+H]^+$, $C_{42}H_{32}BN_2^+$; calc. 575.2653).

Pyridine–Borane Complex **9**. ^{1}H-NMR ($CDCl_3$): 2.17 (*s*, 3 H); 7.03 – 7.05 (*m*, 1 H); 7.11 – 7.31 (*m*, 13 H); 7.48 (*dt*, *J* = 8.4, 1.5, 1 H); 7.53 (*d*, *J* = 8.0, 2 H); 7.93 (*t*, *J* = 8.0, 1 H); 8.23 (*d*, *J* = 5.6, 1 H). ^{13}C-NMR ($CDCl_3$): 11.8; 117.7; 119.5; 125.5; 126.1; 127.2; 127.5; 127.9; 128.3; 133.3; 140.3; 140.9; 143.1; 161.8. Two kinds of C-atoms bound to B-atom were not detected due to quadrupolar relaxation. ^{11}B-NMR ($CDCl_3$): 3.4. HR-EI-MS: 359.1854 (M^+, $C_{26}H_{22}BN^+$; calc. 359.1845).

Quinoline–Borane Complex **10**. ^{1}H-NMR ($CDCl_3$): 3.73 (*s*, 6 H); 3.76 (*s*, 3 H); 6.73 – 6.79 (*m*, 6 H); 7.08 (*s*, 1 H); 7.27 (*d*, *J* = 8.4, 4 H); 7.34 – 7.44 (*m*, 2 H); 7.46 – 7.50 (*m*, 2 H); 7.62 (*d*, *J* = 8.8, 1 H); 7.79 (*dd*, *J* = 7.8, 1.0, 1 H); 7.92 (*d*, *J* = 8.8, 1 H); 8.26 (*d*, *J* = 8.8, 1 H). ^{13}C-NMR ($CDCl_3$): 54.8; 55.1; 113.0; 113.5; 118.1; 120.0; 122.8; 125.3; 126.1; 128.5; 126.1; 128.5; 129.9; 131.1; 131.8; 134.4; 140.8; 141.5; 157.5; 160.0; 162.1. Two kinds of C-atoms bound to B-atom were not detected due to quadrupolar relaxation. ^{11}B-NMR ($CDCl_3$): 4.0. HR-EI-MS: 485.2164 (M^+, $C_{32}H_{28}BNO_3^+$; calc. 485.2162).

Quinoline–Borane Complex **11**. ^{1}H-NMR ($CDCl_3$): 6.81 – 6.95 (*m*, 6 H); 7.08 (*s*, 1 H); 7.18 – 7.23 (*m*, 4 H); 7.32 – 7.37 (*m*, 2 H); 7.42 – 7.49 (*m*, 2 H); 7.71 (*d*, *J* = 8.7, 1 H); 7.76 – 7.79 (*m*, 1 H); 7.86 – 7.89 (*m*, 1 H); 8.39 (*d*, *J* = 8.7, 1 H). ^{13}C-NMR ($CDCl_3$): 114.3 (*d*, *J*(C,F) = 19.1); 115.2 (*d*, *J*(C,F) = 21.3); 118.2; 121.9; 122.7; 126.0; 126.4; 128.8; 129.8 (*d*, *J*(C,F) = 8.1); 131.6; 134.6 (*d*, *J*(C,F) = 6.5); 135.2; 141.4; 141.6; 161.6 (*d*, *J*(C;F) = 241.5); 162.0; 163.0 (*d*, *J*(C,F) = 247.5). Two kinds of C-atoms bound to B-atom were not detected due to quadrupolar relaxation. ^{11}B-NMR ($CDCl_3$): 3.6. HR-EI-MS: 449.1562 (M^+, $C_{32}H_{19}BNF_3^+$; calc. 449.1563).

Quinoline–Borane Complex **12**. ^{1}H-NMR ($CDCl_3$): 6.90 – 6.93 (*m*, 1 H); 7.02 – 7.05 (*m*, 3 H); 7.23 – 7.32 (*m*, 6 H); 7.37 (*t*, *J* = 7.8, 1 H); 7.46 – 7.54 (*m*, 2 H); 7.74 (*d*, *J* = 7.8, 1 H); 8.16 (*d*, *J* = 8.4, 1 H); 8.22 (*d*, *J* = 8.1, 1 H). ^{13}C-NMR ($CDCl_3$): 118.1; 119.8; 122.4; 125.7; 126.3; 126.4; 127.2; 127.7; 128.0; 128.6; 130.4; 130.8; 131.6; 141.2; 141.8; 142.2; 161.4. ^{11}B-NMR ($CDCl_3$): 0.5. HR-EI-MS: 413.0545 (M^+, $C_{23}H_{16}BNS_3^+$; calc. 413.0538).

Pyridine–Borane Complex **13**. ^{1}H-NMR ($CDCl_3$): 1.33 (*s*, 12 H); 7.19 – 7.29 (*m*, 10 H); 7.37 – 7.40 (*m*, 4 H); 7.51 (*d*, *J* = 8.0, 1 H); 7.64 – 7.67 (*m*, 2 H); 8.23 (*d*, *J* = 8.0, 1.2, 1 H); 8.63 (*s*, 1 H). ^{13}C-NMR ($CDCl_3$): 24.8; 84.5; 118.7; 121.2; 125.7; 127.4; 128.1; 128.4; 128.5; 134.0; 138.5; 145.9; 148.7; 161.9. Three kinds of C-atoms bound to B-atom were not detected due to quadrupolar relaxation. ^{11}B-NMR ($CDCl_3$): 3.3; 28.7. HR-ACPI-MS: 472.2611 ($[M+H]^+$, $C_{31}H_{32}B_2NO_2^+$; calc. 472.2614).

Pyridine–Borane Complex **14**. ^{1}H-NMR ($CDCl_3$): 7.17 – 7.38 (*m*, 15 H); 7.62 – 7.64 (*m*, 2 H); 7.90 (*dd*, *J* = 8.8, 2.0, 1 H); 8.36 (*d*, *J* = 2.0, 1 H). ^{13}C-NMR ($CDCl_3$): 114.3; 120.1; 120.2; 126.1; 127.6; 128.2; 128.4; 128.7; 133.8; 138.2; 142.9; 144.2; 148.4; 159.0; 183.3. ^{11}B-NMR ($CDCl_3$): 4.2. HR-ACPI-MS: 424.0857 ($[M+H]^+$, $C_{25}H_{20}BNBr^+$; calc. 424.0867).

Pyridine–Borane Complex **15**. In an oven-dried flask was placed **13** (23.6 mg, 0.050 mmol), **14** (21.2 mg, 0.050 mmol), and NaOH (6.5 mg, 1.5 mmol). The flask was then evacuated and purged by Ar

three times. A THF soln. (0.5 ml) of $Pd[P(t\text{-}Bu)_3]_2$ (1.3 mg, 2.5 μmol) and subsequently H_2O (5 μl) were added, and then the mixture was stirred at 60°. After 1 h, H_2O was added. The mixture was extracted with CH_2Cl_2 (3 ×), washed with H_2O (once), brine (once), dried ($MgSO_4$), and concentrated. The residue was purified by prep. TLC, and GPC to gave **15** (28.9 mg, 0.042 mmol, 84% yield). ^{1}H-NMR ($CDCl_3$): 7.16–7.30 (*m*, 28 H); 7.55–7.62 (*m*, 6 H); 7.85 (*dd*, $J = 8.4, 2.0$, 2 H); 8.33 (*d*, $J = 1.6$, 2 H). ^{13}C- and ^{11}B-NMR could not be recorded due to the low solubility. HR-ACPI-MS: 689.3268 ($[M+H]^+$, $C_{50}H_{39}B_2N_2^+$; calc. 689.3294).

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