Coordination-Induced Intramolecular Double Cyclization: Synthesis of Boron-Bridged Dipyridylvinylenes and Dithiazolylvinylenes

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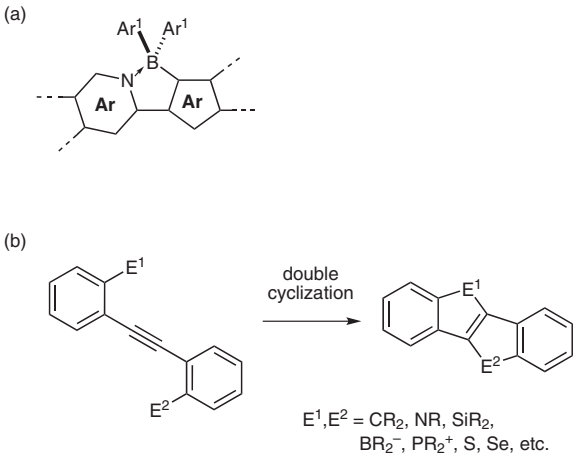
Received 22 October 2008

Abstract: Di(heteroaryl)acetylenes having a pyridyl or thiazolyl as the heteroaryl group underwent a reaction with bromodibenzoborole to produce coordination complexes, which were further treated with water to promote the intramolecular cascade double cyclization to produce the dibenzoborolyl-bridged ladder di(heteroaryl)vinylenes. For the thiazolyl derivative, further derivatization at the terminal positions produced a bis(dimesitylboryl)-substituted derivative. The ladder molecules prepared showed an intense emission in the fluorescence spectra as well as reversible reduction waves at low reduction potentials in the cyclic voltammetry.

Key words: boron, acetylene, N-heteroaryl, cascade cyclization, π-electron systems

Ladder π-electron systems, having fully fused polycyclic skeletons, are promising materials in organic electronics, since their rigid and flat skeletons without any conformational disorder give rise to a set of intriguing properties, such as intense fluorescence, high carrier mobility, and high thermal stability. A number of fascinating ladder materials have been synthesized and used in organic light emitting diodes as well as organic thin film transistors.[1] In the design of new ladder systems, one crucial issue is how to modify the electronic structure in order to provide the required property to the π skeleton. In this regard, we recently reported that the incorporation of boryl groups into a N-heteroaryl-based π-conjugated skeleton so as to form the intramolecular B–N coordination is a useful strategy for endowing the electron-accepting character to the resulting ladder π skeleton (Scheme 1a).[2,3] Indeed, the prepared B–N-coordinated thienylthiazole π-electron systems showed high performances as an electron-transporting material.[2] The other issue in the development of new ladder systems is how to achieve their efficient synthesis. A facile and general synthetic method that can produce a series of ladder systems is particularly demanded. In this regard, the intramolecular double cyclization (IDC) of *o*,*o*′-disubstituted diphenylacetylene precursors is a new powerful tool to synthesize ladder oligo(*p*-phenylenevinylene) (LOPV) skeletons (Scheme 1b).[4] Several types of the IDC reactions, proceeding via the acetylene reduction,[5] nucleophilic cascade cyclization,[6–9] or synchronous double radical cyclization,[10–12] have allowed us to synthesize a series of LOPV derivatives containing various bridging moieties, such as methylene,[10] SiR_2,[5] S and Se,[6,7,11,12] BR_2^- and PR_2^+,[8] and P(=O)R[9] (Scheme 1). All these reactions require the synthesis of the appropriate precursors having the requisite functional groups at the *o*,*o*′-positions of the diphenylacetylene skeleton, prior to conducting the IDC reactions. In contrast, we now present a new strategy for the IDC reaction, that is, the pre-coordination of the N-heteroaryl ring to the boron atom[13,14] for the construction of the requisite *o*,*o*′-disubstituted diarylacetylene precursor. In this article, we disclose the coordination-induced IDC reaction starting from the di(N-heteroaryl)acetylenes and haloboranes. This reaction produces a series of ladder π-electron systems with the intramolecular B–N coordination, which would be promising materials with highly electron-accepting properties for application in the organic electronic devices. Therefore, their fundamental photophysical and electrochemical properties have also been investigated.

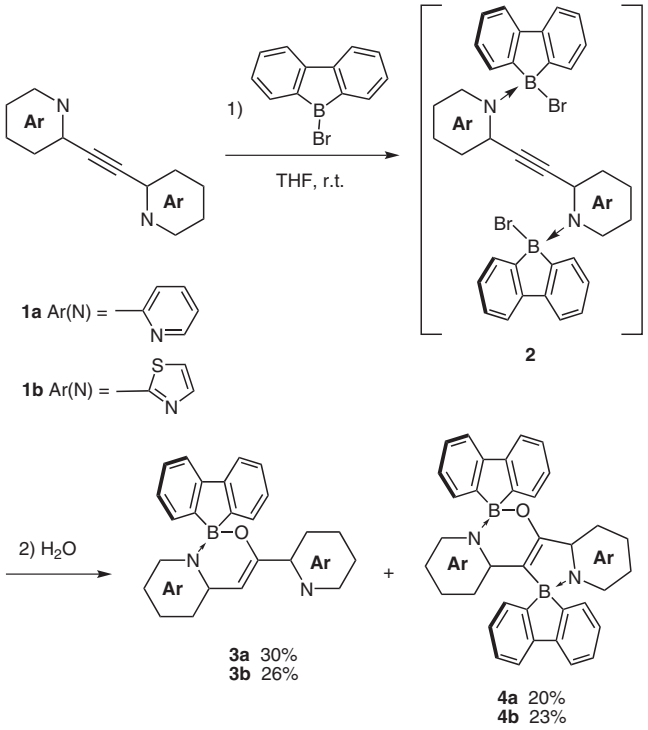


Scheme 1 Design toward a new ladder π skeleton: (a) intramolecular B–N coordination for effective electronic modulation, and (b) intramolecular double cyclization (IDC) as a useful synthetic tool

Coordination-Induced Intramolecular Double Cyclization

We first employed di(2-pyridyl)acetylene (**1a**) as the starting material (Scheme 2). When compound **1a** was reacted with bromodibenzoborole in THF at room temperature, the bis(borylpyridine) complex **2a** was immediately produced as a yellow precipitate. Whereas this complex can be isolated by recrystallization as a stable compound,

SYNTHESIS 2009, No. 1, pp 0127–0132
Advanced online publication: 12.12.2008
DOI: 10.1055/s-0028-1083271; Art ID: C05208SS



Scheme 2 Coordination-induced double cyclization

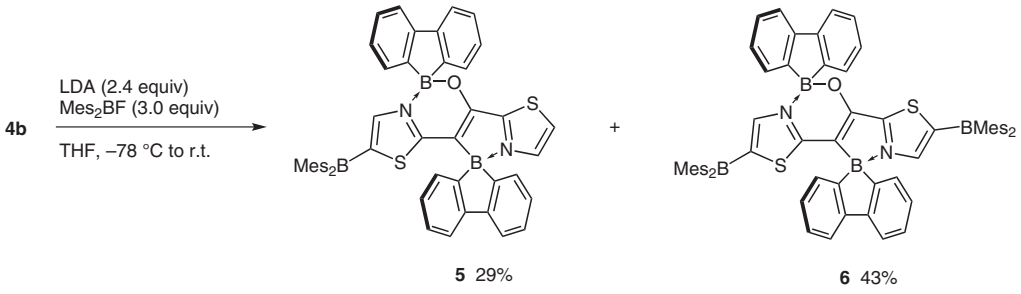
we directly used it without purification for the subsequent reaction. Thus, the treatment of **2a** with a stoichiometric amount of water under refluxing conditions followed by silica gel column chromatography produced two products, the mono-cyclized **3a** and double-cyclized **4a** in 30 and 20% yield, respectively. The structures of these products were verified by ^{1}H, ^{13}C, and ^{11}B NMR spectroscopies, mass spectrometry, and finally by X-ray crystallography for **4a** (vide infra).[15] The mechanism of this reaction is unclear at this stage, but is presumably that after formation of the hydroxyborole, the nucleophilic cascade cyclization occurs to produce the doubly cyclized product **4a**. In order to retard the formation of the mono-cyclized **3a**, we tried the addition of several bases, such as Ag_2O, however, this resulted in no improvement. For the present reaction, the use of bromodibenzoborole is essential. The use of $BF_3{\cdot}OEt_2$ or dimesitylboron fluoride, instead of the bromodibenzoborole, only resulted in no reaction. Presumably, the high Lewis acidity and high reactivity of the bromodibenzoborole may play an important role in promoting this reaction.

This IDC reaction has an advantage that the synthesis of complex precursor molecules is not necessary and should be applicable to other N-heteroaryl derivatives. Indeed, we found that the reaction also proceeded when we employed di(2-thiazolyl)acetylene (**1b**) as the starting material and obtained the mono-cyclized product **3b** and double-cyclized product **4b** in 26 and 23% yields, respectively, as shown in Scheme 2.

The double-cyclized products **4a** and **4b** have good solubilities in the common organic solvents (for example, 39.2 mg/mL in THF for **4a** and 16.8 mg/mL in THF for **4b**), despite their rigid bis(spiro) frameworks. These high solubilities are probably due to their unsymmetrical structures.

Utility as a Building Unit for More Extended π-Electron Materials

As the building unit for more complex π-electron materials, the thiazolyl derivative **4b** has a great advantage such as its facile functionalization at the terminal positions (5-position of the thiazole rings). To demonstrate the utility of **4b**, we conducted the incorporation of the boryl groups onto the terminal positions, since this is an effective way to enhance the electron-accepting ability.[16] Thus, the lithiation with LDA in the presence of dimesitylboron fluoride produced the monoboryl derivative **5** and diboryl derivative **6** in 29 and 43% yields, respectively (Scheme 3). These derivatives were isolated by silica gel column chromatography as stable compounds. Although the formation of the monoborylated product was simply due to the incomplete dilithiation, the regioselectivity of the monolithiation may have some implications. Thus, this result suggests the possible synthesis of unsymmetrically difunctionalized derivatives, which would be the basis for further precise syntheses, such as the synthesis of regioregular polymeric materials or donor-acceptor-type molecules. The regioselectivity of the monolithiation is probably due to the difference in the electronic effect of the bridging moieties. The oxy(dibenzoborolyl) bridge may be slightly more electron-withdrawing than the dibenzoborolyl group and thus may more stabilize the produced anion on the adjacent thiazole ring.



Scheme 3 Borylation of thiazolyl derivative **4b**

Crystal Structures of the Ladder Skeleton Having Intramolecular B–N Coordination

Among the produced compounds, the crystal structures of **4a** and **4b** were determined by X-ray crystallography,[15] whose ORTEP drawings are shown in Figure 1. In both crystal structures, two crystallographically independent molecules are included in the crystal lattice. In all these structures, the B–O-containing six-membered ring takes the half-chair conformation, in which the boron atom is deviated from the plane by 0.35–0.41 Å in **4a** and 0.48–0.50 Å in **4b**. In the dipyridyl derivative **4a**, except for the boron atom in the six-membered ring, the other part of the ladder π-conjugated skeleton maintains a rather coplanar structure. The dihedral angles between the two terminal pyridine rings are 5.52° and 11.85°. In contrast, the dithiazolyl derivative **4b** has more distorted π-conjugated frameworks. The dihedral angles between the two outer thiazole rings are 7.47° and 23.36°, suggesting a more severe ring strain in this ladder skeleton. As for the intramolecular B–N distance, in both compounds, no significant difference is observed between that in the B–O-containing six-membered ring [1.607(3)–1.623(4) Å] and that in the five-membered ring [1.596(2)–1.626(5) Å].

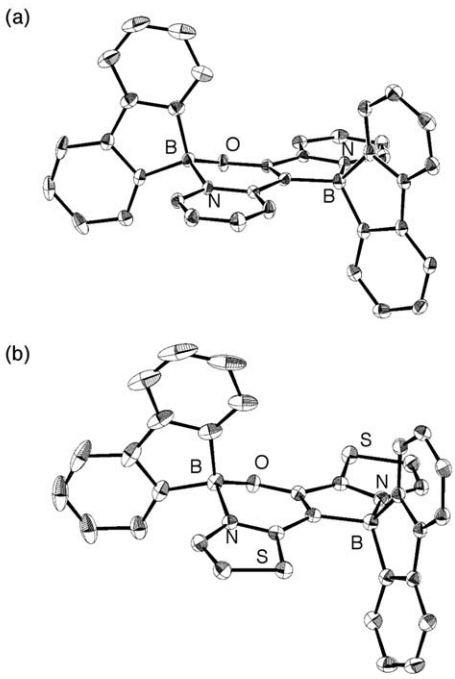


Figure 1 ORTEP drawings of (a) **4a** and (b) **4b** (50% probability for thermal elipsoids); hydrogen atoms are omitted for clarity

Photophysical and Electrochemical Properties

The UV/vis absorption and fluorescence spectra of compounds **3–6** are shown in Figure 2, the data of which are summarized in Table 1.

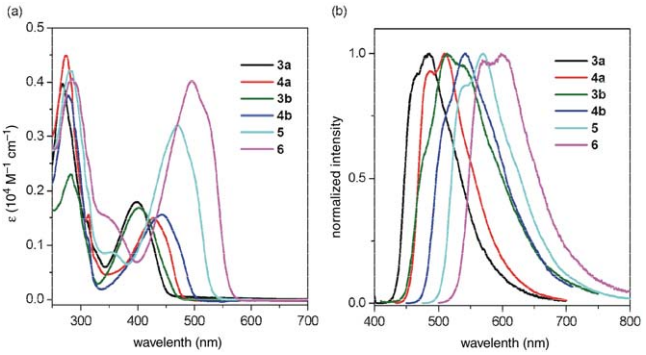


Figure 2 Photophysical properties of **3–6**: (a) UV/vis absorption spectra; and (b) fluorescence spectra in CH_2Cl_2

Table 1 Photophysical Data of Compounds **3–6** in CH_2Cl_2

	UV/vis absorption[a]		Fluorescence[b]	
Compound	λ_{max} (nm)	log ε	λ_{max} (nm)	Φ_f[c]
3a	398	4.25	485	0.22
4a	428	4.17	510	0.85
3b	402	4.23	510	0.06
4b	443	4.19	541	0.42
5	471	4.50	570	0.65
6	495	4.60	598	0.28

[a] Only the longest absorption maxima are given.
[b] Excited at the longest absorption maxima.
[c] Absolute fluorescence quantum yield determined by a calibrated integral sphere system.

In the absorption spectra, the doubly cyclized compounds **4a** and **4b** have an absorption maximum at 428 and 443 nm, respectively. These absorption bands can be assigned to the π-π* transition of the ladder π skeletons. These λ_{max} values are about 30–40 nm longer than those of the respective mono-cyclized **3a** and **3b**, demonstrating the extent of the electronic effect of the second boryl bridges. The DFT calculations of **4a** and **4b** at the B3LYP-6-31G(d) level suggested that the incorporation of the second boryl bridges decreases the π* (LUMO) level by about –0.3 eV, while it does not affect the energy level of the π orbital (HOMO-2). In both compounds, the HOMO and HOMO-1 are mainly localized on the dibenzoborole moieties.

In the fluorescence spectra, **4a** and **4b** show intense green and yellow fluorescences with the maximum wavelengths at 510 and 540 nm, respectively. These values are again longer by 25–30 nm compared to the respective mono-cyclized derivatives **3a** and **3b**. Notably, the fluorescence quantum yields of **4a** and **4b** are much higher that those of **3a** and **3b**, probably due to the rigid ladder structure in **4a** and **4b**.

The extension of the π-conjugation by the incorporation of the boryl groups generally results in the bathochromic

shifts in the absorption and fluorescence spectra. Indeed, the monoborylated **5** and diborylated **6** show the red-shifted absorption and fluorescence maxima compared to those of **4a** and **4b**. Notably, the fluorescence maximum of **6** reaches 598 nm with a reddish orange emission color.

Table 2 Electrochemical Properties of Compounds **3–6** in CH_2Cl_2[a]

Compound	E_{ox}^1 (V)[b]	E_{ox}^2 (V)[b]	E_{red}^1 (V)	E_{red}^2 (V)
3a	+1.05		–2.29[b]	
4a	+0.95	+1.08	–2.05	
3b	+1.12		–2.00	
4b	+0.94	+1.06	–1.82	–2.41[b]
5	+0.99	+1.10	–1.63	–2.18[b]
6	+1.02	+1.12	–1.36	–1.71

[a] Measurements conditions: sample 1 mM with Bu_4NPF_6 (0.1 M) at a scan rate of 100 mVs^{-1}. All potentials versus a ferrocene/ferrocenium couple.
[b] Peak potentials.

The electrochemical properties of compounds **3–6** were also investigated by cyclic voltammetry in CH_2Cl_2, the data of which are summarized in Table 2. All of the compounds showed reversible reduction waves, except for the mono-cyclized **3a**, while the oxidation waves for these compounds are irreversible processes. The difference in the reversibility of the reduction process between **3a** and **4a** demonstrates the significance of the ladder structure on the stabilization of the produced radical anion species. It is also worth noting that the borylated compounds **5** and **6** showed the first reversible reduction waves at rather low reduction potentials. Moreover, the diborylated **6** exhibited a second reduction as a reversible process. The structural modification from **3b** to **6** resulted in a decrease of the reduction potential by 0.64 V. This value well demonstrates the effectiveness of the p-π* conjugation between the π* orbital of the ladder skeleton and the vacant p-orbitals of the terminal boryl groups.

Conclusion

We have developed a new type of intramolecular double cyclization starting from the di(N-heteroaryl)acetylenes with bromodibenzoborole, which proceeds through the formation of the B–N coordination complex. This method has a significant advantage such that a simple procedure using simple precursors allows us to produce various heteroaryl-containing ladder π-conjugated skeletons. Thus the prepared ladder π systems with the intramolecular B–N coordination show intriguing photophysical and electrochemical properties, such as intense emission and reversible reduction waves at low reduction potentials in the cyclic voltammetry. The utility of the ladder di(2-thiazolyl)vinylene derivative as a building unit is also worth noting, since its facile functionalization would allow us to synthesize a variety of functional π-electron materials. Further structural modification as well as the application of these materials in organic electronic devices are now in progress in our laboratory.

Melting points were measured on a Yanaco MP-S3 instrument. ^1H, ^{13}C, and ^{11}B NMR spectra were recorded on a Jeol AL-400 spectrometer (400 MHz for ^1H, 100 MHz for ^{13}C, and 128 MHz for ^{11}B) in $CDCl_3$. Mass spectra were measured with a Jeol JMS700. UV/vis absorption and fluorescence spectra were performed with a Shimadzu UV-3150 spectrometer and a Hitachi F-4500 spectrometer, respectively. Quantum yields were determined with a Hamamatsu C9920-01 calibrated integral sphere system. TLC was performed on plates coated with 0.25 mm thickness of silica gel 60 F-254 (Merck). Column chromatography was performed using neutral silica gel PSQ 60B (Fuji Silysia Chemical). Di(2-pyridyl)acetylene (**1a**) and di(2-thiazolyl)acetylene (**1b**) were prepared according to the literature.[17,18] *B*-Bromodibenzoborole was prepared according to the literature.[19] The other materials were purchased from common commercial sources and used without additional purification. All reactions were performed under argon, unless otherwise stated. X-ray crystal structure determination was performed on a Rigaku Single Crystal CCD X-ray Diffractometer. Crystals of **4a** and **4b** suitable for X-ray structural analysis were obtained by recrystallization from a $CHCl_3$–hexane mixed solvent. Theoretical calculations were conducted using Gaussian 03 program.[20]

Intramolecular Double Cyclization of Di(heteroaryl)acetylenes; Compounds 3a and 4a; Typical Procedure

To a mixture of **1a** (200 mg, 1.11 mmol) and bromodibenzoborole (674 mg, 2.77 mmol) was added anhyd THF (30 mL) at r.t. After heating the mixture with stirring at 80 °C for 2 h, H_2O (1.1 M soln in THF; 1 mL, 1.1 mmol) was added to the resulting suspension. The mixture was stirred at the same temperature for 24 h. After removal of the solvents, purification by column chromatography on silica gel (CH_2Cl_2–hexane) followed by recrystallization from CH_2Cl_2–hexane gave 120 mg (0.33 mmol) of **3a** and 115 mg (0.22 mmol) of **4a** in 30% and 20% yield, respectively.

3a

Yellow solid; mp 208–209 °C.

^1H NMR (400 MHz, $CDCl_3$): δ = 6.90 (t, J_{HH} = 6.4 Hz, 1 H), 7.09 (t, J_{HH} = 7.2 Hz, 3 H), 7.26–7.34 (m, 4 H), 7.58 (d, J_{HH} = 7.2 Hz, 2 H), 7.64 (d, J_{HH} = 6.4 Hz, 4 H), 7.72 (t, J_{HH} = 7.6 Hz, 1 H), 7.93 (d, J_{HH} = 8.0 Hz, 1 H), 8.65 (d, J_{HH} = 4.4 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 95.33, 119.17, 120.63, 121.76, 122.47, 124.56, 126.87, 128.31, 130.05, 136.75, 140.31, 141.11, 148.42, 148.78, 152.49, 152.71, 164.51.

^{11}B NMR (128 MHz, $CDCl_3$): δ = 6.62.

HRMS (EI): *m/z* calcd for $C_{24}H_{17}BN_2O$: 360.1434; found: 360.1440.

4a

Yellow solid; mp >300 °C.

^1H NMR (400 MHz, $CDCl_3$): δ = 6.56 (d, J_{HH} = 8.4 Hz, 1 H), 6.80 (t, J_{HH} = 6.4 Hz, 1 H), 7.12–7.21 (m, 7 H), 7.29–7.41 (m, 5 H), 7.66–7.71 (m, 5 H), 7.83 (t, J_{HH} = 7.6 Hz, 3 H), 7.89–7.96 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 119.06, 119.27, 119.56, 121.35, 122.49, 123.75, 126.72, 126.93, 127.63, 128.33, 130.00, 130.13, 140.71, 140.77, 141.45, 142.43, 148.39, 150.59, 152.26, 155.33, 159.05.

^{11}B NMR (128 MHz, $CDCl_3$): δ = 1.32, 7.46.

HRMS (EI): *m/z* calcd for $C_{36}H_{24}B_2N_2O$: 522.2075; found: 522.2089.

3b

Yield: 26%; yellow solid; mp 183–184 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.84 (d, J_{HH} = 4.0 Hz, 1 H), 6.91 (d, J_{HH} = 4.0 Hz, 1 H), 7.06 (s, 1 H), 7.10 (t, J_{HH} = 8.0 Hz, 2 H), 7.30 (d, J_{HH} = 7.6 Hz, 2 H), 7.48–7.52 (m, 3 H), 7.64 (d, J_{HH} = 7.6 Hz, 2 H), 7.94 (d, J_{HH} = 3.2 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 88.96, 114.82, 119.13, 123.03, 126.79, 128.45, 129.95, 135.11, 144.20, 148.22, 159.73, 164.46, 165.43.

^{11}B NMR (128 MHz, $CDCl_3$): δ = 6.27.

HRMS (EI): *m/z* calcd for $C_{20}H_{13}BN_2OS_2$: 372.0562; found: 372.0580.

4b

Yield: 23%; yellow solid; mp 290–292 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.76 (d, J_{HH} = 3.6 Hz, 1 H), 6.89 (d, J_{HH} = 3.6 Hz, 1 H), 7.12–7.19 (m, 6 H), 7.28–7.38 (m, 6 H), 7.57 (d, J_{HH} = 7.2 Hz, 2 H), 7.65 (d, J_{HH} = 7.6 Hz, 2 H), 7.79 (d, J_{HH} = 7.6 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 116.99, 119.26, 119.57, 121.71, 126.60, 126.89, 127.85, 128.55, 129.91, 130.02, 134.89, 135.03, 148.25, 150.72, 156.44, 165.32, 168.83.

^{11}B NMR (128 MHz, $CDCl_3$): δ = –0.56, 6.81.

HRMS (EI): *m/z* calcd for $C_{32}H_{20}B_2N_2OS_2$: 534.120; found: 534.1194.

Functionalization of Compound 4b

To a solution of **4b** (50.0 mg, 0.094 mmol) and dimesitylboron fluoride (75.3 mg, 0.28 mmol) in anhyd THF (10 mL) was added LDA (0.83 M in THF, 0.28 mL, 0.23 mmol) dropwise at –78 °C. The resulting mixture was stirred at the same temperature for 1 h and then was allowed to warm to r.t. with stirring overnight. After removal of the solvent, the residual sticky red oil was passed through a silica gel column (CH_2Cl_2–hexane, 1:2) followed by recrystallization from a $CHCl_3$–hexane mixed solvent to give pure products **5** (21 mg, 0.027 mmol) and **6** (41 mg, 0.040 mmol).

5

Yield: 29%; orange solid; mp 208–210 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.80 (s, 12 H), 2.19 (s, 6 H), 6.62 (s, 4 H), 7.07 (s, 1 H), 7.11–7.17 (m, 6 H), 7.28–7.35 (m, 6 H), 7.56 (d, J_{HH} = 6.8 Hz, 2 H), 7.61 (d, J_{HH} = 7.6 Hz, 2 H), 7.73 (d, J_{HH} = 7.2 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.00, 23.13, 119.26, 119.65, 122.21, 126.52, 126.86, 127.78, 128.35, 128.50, 129.67, 129.90, 129.94, 134.90, 139.40, 140.49, 146.46, 148.23, 150.76, 157.71, 168.05, 171.99.

^{11}B NMR (128 MHz, $CDCl_3$): δ = –0.03, 6.97, 65.56.

HRMS (EI): *m/z* calcd for $C_{50}H_{41}B_3N_2OS_2$: 782.2939; found: 782.2936.

6

Yield: 43%; red solid; mp 260–262 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.79 (s, 12 H), 2.00 (s, 12 H), 2.19 (s, 6 H), 2.24 (s, 6 H), 6.62 (s, 4 H), 6.75 (s, 4 H), 7.08 (s, 1 H), 7.10–7.16 (m, 6 H), 7.25–7.31 (m, 5 H), 7.43 (s, 1 H), 7.53 (d, J_{HH} = 7.2 Hz, 2 H), 7.59 (d, J_{HH} = 7.6 Hz, 2 H), 7.70 (d, J_{HH} = 7.6 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.00, 21.03, 23.14, 23.29, 119.18, 119.70, 126.49, 126.78, 127.73, 128.35, 128.43, 128.61, 129.62, 129.71, 139.44, 140.08, 140.48, 140.50, 144.51, 146.41, 148.25, 150.67, 157.59, 171.68, 174.83.

^{11}B NMR (128 MHz, $CDCl_3$): δ = –0.01, 6.43, 65.95.

HRMS (APCI): *m/z* calcd for $C_{68}H_{63}N_2S_2B_4O$ [$(M + H)^+$]: 1031.4754; found: 1031.4749.

Acknowledgment

This work was partly supported by Grants-in-Aid (No. 19675001 and 17069011) from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

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