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室温下电化学合成保护型有机硼酸 RB(dan)

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摘要 报道了室温条件下保护型有机硼酸 RB(dan) (R＝烷基或芳基)的电化学合成. 在室温条件下, 在一个不分隔电解池中, 1,8-二氨基萘和硼酸可以顺利地参与反应得到多种 RB(dan) (R＝烷基或芳基)化合物. 该转化具有广泛的底物范围, 避免了使用高温或过渡金属催化剂, 使其更可持续和再生.
关键词 电化学合成; 硼酸; 保护基; 室温

Electrochemical Synthesis of Masked Organoboronic Acids RB(dan) at Room Temperature

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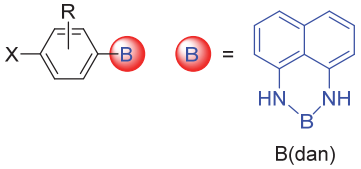
Abstract An electrochemical room-temperature synthesis of masked organoboronic acids RB(dan) (R＝alkyl or aryl) has been developed. At room temperature, 1,8-diaminonaphthalene and boronic acids can smoothly participate in this reaction to provide a wide variety of RB(dan) (R＝alkyl or aryl) in an undivided cell. The transformation has broad substrate scope and avoids using high-temperature or transition-metal catalysts, making it more sustainable and renewable.
Keywords electrochemical synthesis; boronic acids; masked group; room temperature

1 Introduction

Organoboronic acids are one group of important reaction substrates because they are widely used in organic synthesis chemistry for the construction of medicine and material. For instance, organoboronic acids are important substrates for the Suzuki-Miyaura cross-coupling reactions, which have become an essential methodology to construct new C—C bonds.[1] Due to the high reactivity, the borane group is usually masked by the easy-to-remove group to obtain good chemical selectivity in synthesizing complex molecules.[2] For example, 1,8-diaminonaphthalene has been found to be a good boron-masking group, which reacts with organoboronic acids giving aryl-B(dan) moiety (Scheme 1).[3-7] Interestingly, B(dan) also received extensive attention due to the characterization of aggregation-induced emissive.[8] As such, great efforts have been attracted to the development of general and efficient methods to construct the R-B(dan) frameworks in current organic synthesis.[9-12] Classical methods for the synthesis of R-B(dan) have focused on condensation reactions in high temperatures, coupling reactions using transition-metal catalysis.[6,13-14] Despite impressive advances, these approaches have disadvantages involving complex operations which often involve substrate adaptability and harsh reaction conditions.



Scheme 1 Masked haloarylboronic acids using 1,8-diaminonaphthalene

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In order to address these shortcomings, a condensation-dehydrating reaction of Ar-B(OH)$_2$ with 1,8-diaminonaphthalene has been proven to be an important advance for the construction of aryl-B(dan) moiety in an atom- and step-economical manner. Since Maitlis and coworkers[15-18] have pioneered a condensation-dehydrating reaction of Ar-B(OH)$_2$ with 1,8-diaminonaphthalene for assembling aryl-B(dan) moiety at high temperatures, a high-temperature condensation-dehydrating reaction has been widely used in the synthesis of aryl-B(dan). Higher temperatures are usually needed to reduce the reaction time, such as 150 ℃.[19]

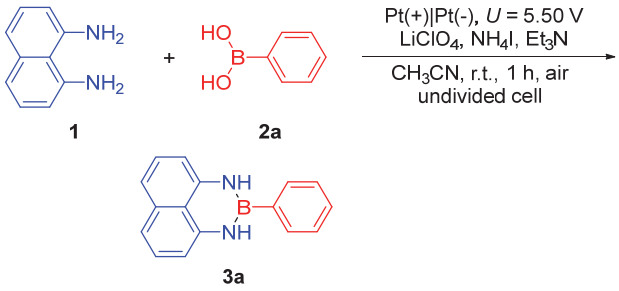
In 2018, Bao/Ren and coworkers[8] developed a mild strategy where room temperature was involved in the condensation-dehydrating reaction of Ar-B(OH)$_2$ with 1,8-diaminonaphthalene to give aryl-B(dan) moiety at 8 h. Meanwhile, a catalytic amount of $FeCl_3$ was utilized to execute the condensation-dehydrating of Ar-B(OH)$_2$ with 1,8-diaminonaphthalene in MeCN at room temperature to give aryl-B(dan) at 2 h.[20] Therefore, discovering mild and green tactics that consist of condensation-dehydrating, especially avoiding the use of transition-metal catalysts at room temperature to construct the aryl-B(dan) scaffolds is still in demand.

Organic electrochemical synthesis has been developed as an efficient and atom-economical approach for the formation of new bonds.[21-25] The electric current has been superior to the expensive metal and toxic oxidants, so the electrochemical methods have been attractive for organic synthesis and widely applied in many chemical transformations.[26-33] Although these strategies provide a series of valuable molecules, the R-B(dan) scaffolds have not been obtained via electrochemistry by far. Herein, we developed an electrochemical dehydrating condensation of 1,8-diaminonaphthalene with boronic acids at room temperature in 1 h (Scheme 2).

2 Result and discussion

We began our study by optimizing the reaction conditions for the condensation-dehydrating reaction of 1,8-diaminonaphthalene **1** and Ar-B(OH)$_2$ **2a** (Table 1). The

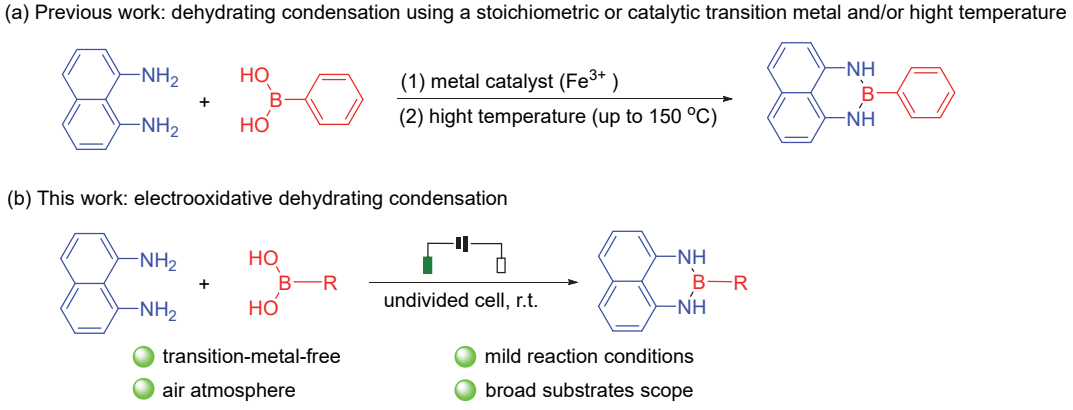
Table 1 Optimization of the reaction conditions[a]



1 2a 3a

Entry	Variation from the standard condition	Yield[b]/%
1	None	90
2	0.5 h instead of 1 h	80
3	2 h instead of 1 h	85
4	^{n}Bu$_4$NClO$_4$ instead of LiClO$_4$	46
5	^{n}Bu$_4$NBF$_4$ instead of LiClO$_4$	55
6	^{n}Bu$_4$NI instead of NH$_4$I	68
7	No NH$_4$I	Trace
8	5.0 V instead of 5.5 V	67
9	4.0 V instead of 5.5 V	61
10	6.0 V instead of 5.5 V	51
11	10 mA in constant current	30
12	DMSO instead of MeCN	Trace
13	DMF instead of MeCN	n.r.
14	MeOH instead of MeCN	35
15	H$_2$O instead of MeCN	Trace
16	60 ℃ instead of r.t.	80
17	C(+)|C(−) instead of Pt(+)|Pt(−)	63
18	C(+)|Pt(−) instead of Pt(+)|Pt(−)	66
19	GF(+)|Pt(−) instead of Pt(+)|Pt(−)	81
20	No current	33
21	No Et$_3$N	62
22[c]	Large-scale reaction	75

[a] Reaction conditions: Pt plate anode (10 mm×10 mm×0.1 mm), Pt plate cathode (10 mm×10 mm×0.1 mm), constant voltage=5.5 V, **1** (0.5 mmol), **2a** (0.5 mmol), NH$_4$I (0.25 mmol), LiClO$_4$ (0.1 mmol), Et$_3$N (0.1 mmol), MeCN (10 mL), air, room temperature, 1 h, undivided cell. [b] Isolated yield. [c] Reaction conditions: Pt plate anode (20 mm×20 mm×0.2 mm), Pt plate cathode (20 mm×20 mm×0.2 mm), constant voltage=5.5 V, **1** (2.5 mmol), **2a** (2.5 mmol), NH$_4$I (1.25 mmol), LiClO$_4$ (0.5 mmol), Et$_3$N (0.1 mmol), MeCN (50 mL), air, room temperature, 3 h, undivided cell.



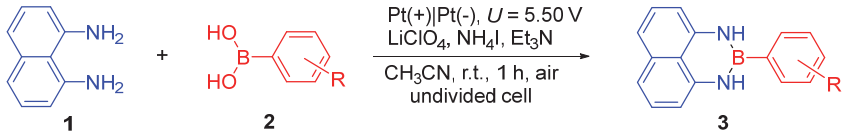
Scheme 2 Electrochemical synthesis of R-B(dan) frameworks

setup for constant voltage electrolysis consisted of an undivided cell (a three-necked round-bottomed flask) equipped with a Pt plate anode and Pt plate cathode.

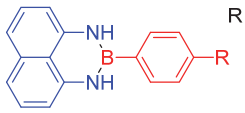
The reaction was conducted using 1 equiv. of **1** and **2a** at room temperature in the presence of 20 mol% $LiClO_4$ and 50 mol% NH_4I. When the reaction was carried out in MeCN under 5.5 V constant voltage in the undivided cell, the condensation-dehydrating product **3a** was obtained in 90% yield. A shorter or longer reaction time was insufficient to effectively form product **3a** (Entries 2, 3). Changing the electrolyte from $LiClO_4$ to ^{n}Bu$_4$NClO$_4$, ^{n}Bu$_4$NBF$_4$, or ^{n}Bu$_4$NI resulted in a reduced product yield (Entries 4～6). 0.5 equiv. NH_4I was needed for this condensation-dehydrating reaction (Entry 7). Both increasing or decreasing the voltage afforded the final product in lower yield (Entries 8～10). The constant current (10 mA) in this reaction provided low yield (Entry 11). As for the reaction solvent, dimethyl sulfoxide (DMSO), *N*,*N*-dimethylformamide (DMF), MeOH, and H_2O exhibited lower product yields when compared with MeCN (Entries 12～15). Moreover, increasing the reaction temperature to 60 ℃ gave the corresponding product in 80% yield (Entry 16). Replacing the Pt plate with a glassy carbon electrode led to poor reaction efficiency (Entries 16, 17). Graphite felt as anthode gave good reaction yield (Entry 18). Finally, the control experiment indicated that electricity and Et_3N were essential for the reaction (Entries 19～20). The scalability of the reaction was demonstrated by the facile preparation of 0.457 g of product **3a** (Entry 21). Therefore, this protocol can be used as a practical method to synthesize the aryl-B(dan) scaffolds.

With the best conditions in hand, the scope of the electrolytic protocol was investigated in regard the scope of the aryl boronic acids as starting material (Table 2). A variety of aryl boronic acids with *para*-substituted electrondonating or electron-withdrawing groups on the aromatic ring

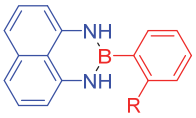
Table 2 Scope of aryl boronic acids (**1**) used in the reaction[a]



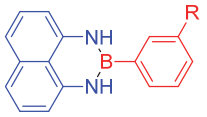
1 **2** **3**



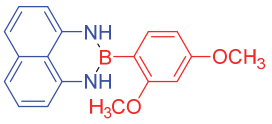
R = H, **3a** 90%[b]; 4-CH_3, **3b** 40%[b]; 4-OCH_3, **3c** 63%[b]; 4-F, **3d** 53%[b]; 4-CF_3, **3e** 54%[b]; 4-Cl, **3f** 50%[b]; 4-Br, **3g** 67%[b]; 4-OH, **3h** 62%[b]; 4-CN, **3i** 90%[b]



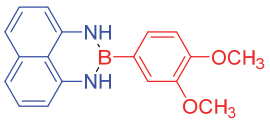
R = 2-CH_3, **3j** 34%[b]; 2-OCH_3, **3k** 49%[b]; 2-F, **3l** 49%[b]; 2-Cl, **3m** 56%[b]; 2-Br, **3n** 74%[b]; 2-OH, **3o** 49%[b]; 2-CN, **3p** 96%[b]



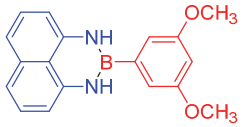
R = 3-CH_3, **3q** 58%[b]; 3-OCH_3, **3r** 69%[b]; 3-F, **3s** 64%[b]; 3-CF_3, **3t** 61%[b]; 3-Cl, **3u** 44%[b]; 3-Br, **3v** 74%[b]; 3-Vinyl, **3w** 24%[b]



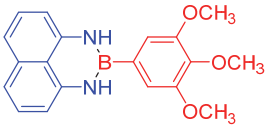
3x 30%[b]



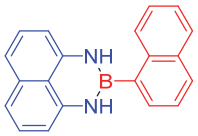
3y 68%[b]



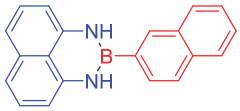
3z 90%[b]



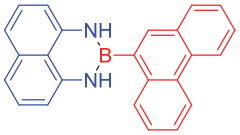
3aa 50%[b]



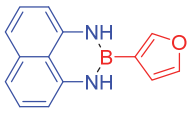
3ab 27%[b]



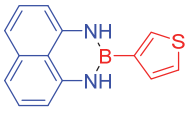
3ac 70%[b]



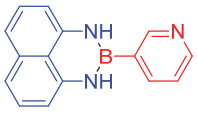
3ad 64%[b]



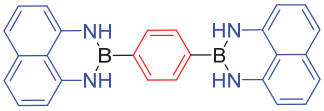
3ae 44%[b]



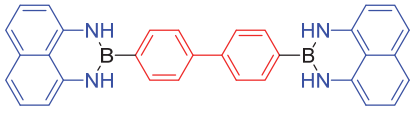
3af 74%[b]



3ag 95%[b]



3ah 31%[b]



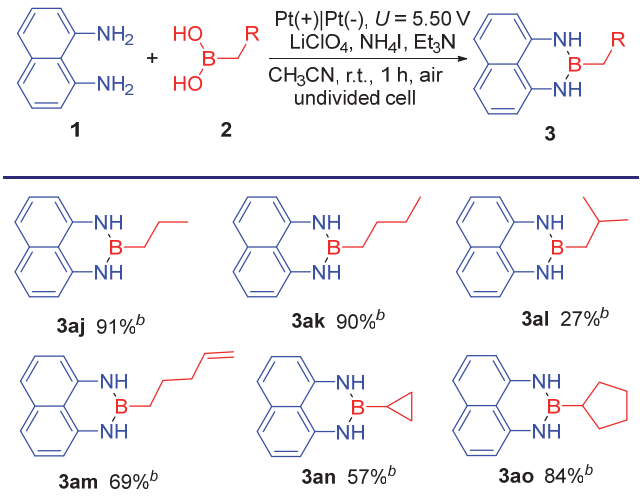
3ai 37%[b]

[a] Reaction conditions: Pt plate anode (10 mm×10 mm×0.1 mm), Pt plate cathode (10 mm×10 mm×0.1 mm), constant voltage=5.5 V, **1** (0.5 mmol), **2a** (0.5 mmol), NH_4I (0.25 mmol), $LiClO_4$ (0.1 mmol), Et_3N (0.1 mmol), MeCN (10 mL), air, room temperature, undivided cell. [b] Isolated yield.

led to the desired products in moderate to pretty good yield. It is particularly noteworthy that functional groups, such as Me, MeO, F, Cl, Br, CF_3, OH, and CN were well-tolerated in the reaction (Table 2, **3b**～**3i**). Compared with the *para*-substituent substrate and model substrate, the *ortho*-substitution led to slightly decreased yields (Table 2, **3j**～**3o**) because of the steric hindrance effect. Notably, the substrate group CN gave pretty good yields whether in *para*- or *ortho*-substitution (Table 2, **3i**, **3p**). Aryl boronic acids possessing a chlorine substituent at C(2), C(3), or C(4) of phenyl all gave their corresponding products in acceptable yield (Table 2, **3f**, **3m**, **3u**), thereby facilitating additional modification at the halogenated positions. A poly-substituted aryl boronic acid gave the desired product in good yield (Table 2, **3x**～**3aa**). A substrate bearing a naphthyl or phenanthryl group was successfully applied in the reaction, furnishing the aryl-B(dan) product with a low to good yield (Table 2, **3ab**～**3ad**). Interestingly, heterocyclic aromatic boronic acids gave the desired product in moderate to good yield (Table 2, **3ae**～**3ag**). Finally, both 1,2-phenylenediboronic acid and 4,4'-biphenyldiboronic acid reacted with 1,8-diaminonaphthalene to furnish the desired product in acceptable yield (Table 2, **3ah**～**3ai**).

Subsequently, the generality of the electrochemical condensation reactions of alkyl boronic acids **2** was examined (Table 3). Compare to the branched-chain alkyl boronic acids (**3al**), the alkyl boronic acids with straight chains displayed good activity in this electrochemical intermolecular condensation-dehydrating reaction (**3aj**～**3ak**). Gratifyingly, the straight chain alkyl boronic acid with a terminal double bond was compatible in this electrochemical condensation transformation, which gave the corresponding product with 69% yield (**3am**). In addition,

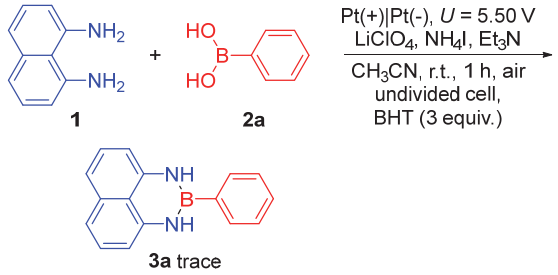
Table 3 Scope of alkyl boronic acids used in the reaction[a]



[a] Reaction conditions: Pt plate anode (15 mm×15 mm×0.2 mm), Pt plate cathode (15 mm×15 mm×0.2 mm), constant current=9 mA, **1a** (0.5 mmol), **2a** (0.5 mmol), **3a** (0.75 mmol), NH_4I (0.25 mmol), $LiClO_4$ (0.1 mmol), Et_3N (0.1 mmol), MeCN (10 mL), Ar, room temperature, undivided cell. [b] Isolated yield.

both cyclopropyl and cyclopentyl boronic acids were tolerated and the reaction gave moderate to good yields (**3an**～**3ao**).

To shed light on the electrochemical condensation-dehydrating reaction mechanism, the control reaction was conducted as shown in Scheme 3. Firstly, the reaction was suppressed in the presence of 1.0 equiv. of 2,6-di-*tert*-butyl-4-methylphenol (BHT), suggesting that a radical process may be involved in the transformation. Secondly, the cyclic voltammetric (CV) experiments were also conducted to investigate the reaction process. Based on the results, it's not too difficult to find that the NH_4I obviously susceptible to oxidation. In addition, when using NH_4I and phenylboronic acid, the lower oxidation potential indicated that phenylboronic acid may react with I^-.



Scheme 3 Control experiments of electrochemical synthesis of boronic acids R-B(dan)

Based on the literature reported and the mechanistic studies mentioned above,[34-36] a plausible mechanism was proposed as shown in Scheme 4. Initially, the single electron transfer (SET) oxidation process of iodide is involved, generating an iodine radical. And then the iodine is released, which reacts with phenylboronic acid **2a** to generate intermediate **A** with the fast extrusion of HI. Subsequently, the interaction of the intermediate **A** and 1,8-diaminonaphthalene **1** is involved to afford intermediate **B**. The transfer H^+ to intermediate **B** produces intermediate **C**. Finally, after releasing of HIO, the corresponding product **3a** is yielded. In addition, the hypoiodous reacted with triethylamine to form amine salt to accelerate the reaction.

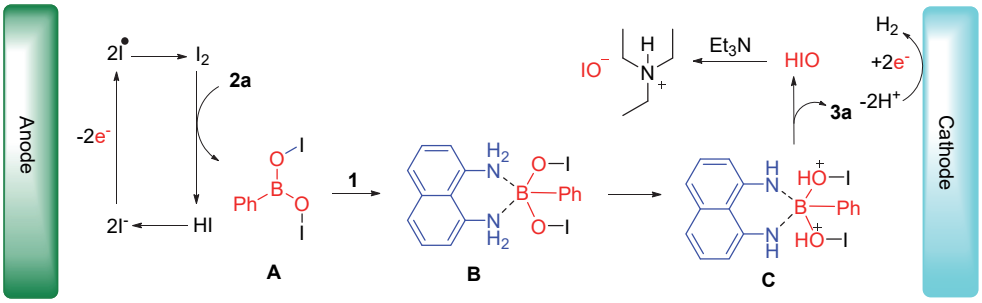
3 Conclusions

In summary, we have successfully developed an efficient electrochemical condensation-dehydrating reaction used for the synthesis of the aryl-B(dan) scaffolds. Our electrochemical synthetic method is compatible with a wide range of boronic acids. Notably, this methodology has been achieved without the use of an external oxidant or transition-metal catalyst, and the scalability of the reaction is also beneficial for industrial production.

4 Experimental section

4.1 General experimental information

All experiments were carried out under air atmosphere.



Scheme 4 Plausible mechanism for the electrochemical synthesis of bronic acids R-B(dan) reaction

All chemicals and solvents used in the experiments were obtained from commercial sources and used directly without further treatment. ^{1}H NMR and ^{13}C NMR spectra were recorded in 400 MHz apparatus and the frequencies for ^{1}H NMR and ^{13}C NMR test were 400 and 100 MHz, respectively. The chemical shifts were reported with TMS as internal standard. Melting points were tested in an X-4A instrument without correcting temperature and the HRMS were obtained under ESI model in a mass spectrometer equipped with time of flight (TOF) analyzer.

4.2 General procedure for the synthesis of R-B(dan) frameworks

A 10-mL oven-dried undivided three-necked bottle was equipped with a platinum plate (10 mm×10 mm×0.1 mm) cathode and a platinum plate (10 mm×10 mm×0.1 mm) anode which was connected to a DC-regulated power supply. Naphthalene-1,8-diamine **1a** (0.3 mmol), phenylboronic acid **2a** (0.4 mmol), NH_4I (0.3 mmol), and $LiClO_4$ (0.1 mol/L) dissolved in 10 mL of CH_3CN were added to the cell and electrolyzed at a constant voltage at 5.50 V. The electrolysis was terminated when the starting materials were consumed as determined by thin-layer chromatography (TLC). After electrolysis, the reaction mixture was diluted in 40 mL of ethyl acetate, washed with a saturated solution of brine (15 mL×3), dried (Na_2SO_4), and concentrated in a vacuum, and the resulting residue was purified by silica gel column chromatography (petroleum/ethyl acetate) to afford the products desired product **3a**.

2-Phenyl-2,3-dihydro-1*H*-naphtho[1,8-de][1,3,2]diazaborinine (**3a**):[18] Isolated in 90% yield as a brown solid. m.p. 91～92 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.672～7.648 (m, 2H), 7.518～7.438 (m, 3H), 7.167 (t, J=7.6 Hz, 2H), 7.082 (d, J=8.4 Hz, 2H), 6.432 (d, J=7.3 Hz, 2H), 6.050 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.01, 136.28, 131.39, 130.25, 128.22, 127.59, 119.78, 117.76, 105.98.

2-(*p*-Tolyl)-2,3-dihydro-1*H*-naphtho[1,8-de][1,3,2]-diazaborinine (**3b**):[18] Isolated in 40% yield as a brown solid. m.p. 194～195 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.533 (d, J=7.6 Hz 2H), 7.251 (d, J=7.6 Hz, 2H), 7.133 (t, J=8 Hz, 2H), 7.043 (dd, J=8.4, 1.2 Hz, 2H), 6.398 (dd, J=7.2, 1.2 Hz, 2H), 6.012 (s, 2H), 2.392 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.11, 140.36, 136.28, 131.41, 129.00, 127.58, 119.72, 117.65, 105.90, 21.56.

2-(4-Methoxyphenyl)-2,3-dihydro-1*H*-naphtho[1,8-de]-[1,3,2]diazaborinine (**3c**):[19] Isolated in 63% yield as a gray solid. m.p. 163～165 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.588 (d, J=8.4 Hz, 2H), 7.166 (t, J=8.4 Hz, 2H), 7.079 (d, J=8.4 Hz, 2H), 6.986 (d, J=8.8 Hz, 2H), 6.423 (d, J=7.2 Hz, 2H), 6.012 (s, 2H), 3.860 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.27, 141.13, 136.25, 132.94, 127.56, 119.58, 117.57, 113.74, 105.85, 55.09.

2-(4-Fluorophenyl)-2,3-dihydro-1*H*-naphtho[1,8-de]-[1,3,2]diazaborinine (**3d**):[18] Isolated in 53% yield as a white solid. m.p. 133～134 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.435～7.409 (m, 2H), 7.318 (dd, J=9.2, 2.8 Hz, 1H), 7.170～7.131 (m, 3H), 7.071 (dd, J=8.4, 1.2 Hz, 2H), 6.428 (dd, J=7.2, 1.2 Hz, 2H), 5.998 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 164.28 (d, J=248.0 Hz), 140.86, 136.25, 133.42 (d, J=8.0 Hz), 127.59, 119.69, 117.89, 115.35 (d, J=21.0 Hz), 106.04; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −109.94.

2-(4-(Trifluoromethyl)phenyl)-2,3-dihydro-1*H*-naphtho-[1,8-de][1,3,2] diazaborinine (**3e**):[18] Isolated in 54% yield as a yellow solid. m.p. 129～131 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.709～7.662 (m, 4H), 7.173 (t, J=8.4 Hz, 2H), 7.104 (d, J=8.4 Hz, 2H), 6.423 (d, J=7.2 Hz, 2H), 5.986 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.56, 136.23, 132.00, 131.84 (q, J=32.0 Hz), 127.60, 124.06 (q, J=270.0 Hz), 124.79 (q, J=4.0 Hz), 119.87, 118.15, 106.23; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −62.70.

2-(4-Chlorophenyl)-2,3-dihydro-1*H*-naphtho[1,8-de]-[1,3,2]diazaborinine (**3f**):[18] Isolated in 50% yield as a gray solid. m.p. 148～151 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.380 (s, 2H), 7.988 (d, J=6.8 Hz, 2H), 7.529 (d, J=8.4 Hz, 2H), 7.096 (t, J=7.6 Hz, 2H), 6.919 (d, J=8.0 Hz, 2H), 6.614 (dd, J=7.2, 2.0 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 142.28, 136.01, 135.12, 134.66, 127.81, 127.74, 119.80, 116.47, 105.80.

2-(4-Bromophenyl)-2,3-dihydro-1*H*-naphtho[1,8-de]-[1,3,2]diazaborinine (**3g**):[18] Isolated in 67% yield as a white solid. m.p. 143～145 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.385 (s, 2H), 7.927 (d, J=8.0 Hz, 2H), 7.672 (d, J=8.0 Hz, 2H), 7.100 (t, J=7.6 Hz, 2H), 6.923 (d, J=8.0 Hz, 2H), 6.623 (d, J=7.6 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 142.27, 136.00, 134.88, 130.71, 127.74, 124.11, 119.82, 119.80, 105.81.

4-(1*H*-Naphtho[1,8-de][1,3,2]diazaborinin-2(3*H*)-yl)-

phenol (**3h**):[19] Isolated in 62% yield as a reddish brown solid. m.p. 223～225 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.668 (s, 1H), 8.128 (s, 2H), 7.804～7.777 (m, 2H), 7.070 (t, J=7.6 Hz, 2H), 6.879 (dd, J=8.4, 1.2 Hz, 2H), 6.843～6.822 (m, 2H), 6.580 (dd, J=7.6, 1.2 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 159.27, 142.56, 135.96, 134.42, 127.63, 119.41, 115.97, 114.73, 105.47.

4-(1*H*-Naphtho[1,8-de][1,3,2]diazaborinin-2(3*H*)-yl)-benzonitrile (**3i**):[19] Isolated in 90% yield as a yellow solid. m.p. 221～225 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.431 (s, 2H), 8.104 (d, J=8.4 Hz, 2H), 7.912 (dd, J=8.4, 2.0 Hz, 2H), 7.092 (t, J=8.0 Hz, 2H), 6.929 (d, J=7.6 Hz, 2H), 6.585 (d, J=7.2 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 142.01, 135.96, 133.36, 131.24, 127.70, 119.93, 119.00, 116.67, 112.36, 105.91.

2-(*o*-Tolyl)-2,3-dihydro-1*H*-naphtho[1,8-de][1,3,2]diazaborinine (**3j**):[18] Isolated in 34% yield as a gray solid. m.p. 78～79 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.438 (d, J=7.2 Hz, 1H), 7.312 (t, J=7.2 Hz, 1H), 7.216 (d, J=4.0 Hz, 2H), 7.122 (t, J=8.0 Hz, 2H), 7.048 (d, J=8.4 Hz, 2H), 6.329 (d, J=7.2 Hz, 2H), 5.808 (s, 2H), 2.483 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.03, 140.59, 136.27, 132.19, 129.63, 129.27, 127.58, 125.24, 119.69, 117.76, 105.86, 22.38.

2-(2-Methoxyphenyl)-2,3-dihydro-1*H*-naphtho[1,8-de]-[1,3,2]diazaborinine (**3k**): Isolated in 49% yield as a brown solid. m.p. 85～87 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.967 (s, 2H), 7.730 (dd, J=7.6, 2.0 Hz, 1H), 7.444～7.400 (m, 1H), 7.075 (t, J=7.6 Hz, 2H), 7.034～6.999 (m, 2H), 6.902 (d, J=8.0 Hz, 2H), 6.572 (d, J=7.2 Hz, 2H), 3.851 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 163.34, 142.29, 136.01, 134.44, 131.50, 127.72, 120.22, 119.63, 116.21, 110.51, 105.72, 55.29. HRMS (ESI) calcd for $C_{17}H_{15}BN_2O$ $[M+H]^+$ 275.1350, found 275.1343.

2-(2-Fluorophenyl)-2,3-dihydro-1*H*-naphtho[1,8-de]-[1,3,2]diazaborinine (**3l**):[20] Isolated in 49% yield as a white solid. m.p. 91～93 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.503～7.464 (m, 1H), 7.420～7.362 (m, 1H), 7.182～7.145 (m, 1H), 7.127～7.016 (m, 5H), 6.356 (dd, J=7.2, 1.2 Hz, 2H), 6.206 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 166.82 (d, J=243.0 Hz), 140.80, 136.22, 133.20 (d, J=9.0 Hz), 132.21 (d, J=10.0 Hz), 127.55, 124.14 (d, J=3.0 Hz), 119.84, 117.77, 115.50 (d, J=25.0 Hz), 106.06; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −105.99.

2-(2-Chlorophenyl)-2,3-dihydro-1*H*-naphtho[1,8-de]-[1,3,2]diazaborinine (**3m**):[18] Isolated in 56% yield as a purple solid. m.p. 86～88 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.528 (dd, J=7.2, 1.6 Hz, 1H), 7.436～7.297 (m, 3H), 7.160 (t, J=8.4 Hz, 2H), 7.087 (d, J=8.0 Hz, 2H), 6.389 (dd, J=7.2, 1.2 Hz, 2H), 6.087 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.80, 137.75, 136.23, 133.82, 130.93, 129.46, 127.56, 126.43, 119.78, 117.85, 106.03.

2-(2-Bromophenyl)-2,3-dihydro-1*H*-naphtho[1,8-de]-[1,3,2]diazaborinine (**3n**): Isolated in 74% yield as a gray solid. m.p. 81～82 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.553 (d, J=7.6 Hz, 1H), 7.422 (dd, J=7.2, 1.6 Hz, 1H), 7.307 (t, J=7.2 Hz, 1H), 7.253～7.204 (m, 1H), 7.105 (t, J=8.0 Hz, 2H), 7.035 (d, J=8.0 Hz, 2H), 6.326 (d, J=7.2 Hz, 2H), 5.945 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.75, 136.23, 134.02, 132.52, 131.00, 127.56, 126.83, 126.66, 119.77, 117.87, 106.03.

2-(1*H*-naphtho[1,8-de][1,3,2]diazaborinin-2(3*H*)-yl)-phenol (**3o**): Isolated in 49% yield as a reddish brown solid. m.p. 96～98 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.670 (s, 1H), 8.120 (s, 2H), 7.785～7.764 (m, 2H), 7.064 (t, J=8.0 Hz, 2H), 6.874 (dd, J=8.0, 0.8 Hz, 2H), 6.830～6.809 (m, 2H), 6.569 (dd, J=7.2, 0.8 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 162.06, 142.23, 136.01, 134.56, 131.37, 127.75, 119.52, 118.85, 116.16, 115.30, 105.64.

2-(1*H*-naphtho[1,8-de][1,3,2]diazaborinin-2(3*H*)-yl)-benzonitrile (**3p**): Isolated in 96% yield as a yellow solid. m.p. 94～96 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.336 (s, 2H), 7.881 (d, J=7.6 Hz, 1H), 7.780～7.719 (m, 2H), 7.638～7.596 (m, 1H), 7.094 (t, J=8.0 Hz, 2H), 6.953 (d, J=8.4 Hz, 2H), 6.498 (d, J=7.2 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 141.94, 135.98, 133.55, 132.60, 132.17, 129.74, 127.66, 119.98, 119.59, 116.73, 114.63, 105.87. HRMS (ESI) calcd for $C_{17}H_{13}BN_3$ $[M+H]^+$ 270.1197, found 270.1195.

2-(*m*-Tolyl)-2,3-dihydro-1*H*-naphtho[1,8-de][1,3,2]diazaborinine (**3q**):[18] Isolated in 58 % yield as a gray solid. m.p. 98～99 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.328 (d, J=10.0 Hz, 2H), 7.407～7.329 (m, 2H), 7.198 (t, J=8.0 Hz, 2H), 7.114 (d, J=8.0 Hz, 2H), 6.444 (d, J=7.2 Hz, 2H), 6.053 (s, 2H), 2.466 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.05, 137.57, 136.25, 132.08, 130.98, 128.41, 128.11, 127.56, 119.75, 117.66, 105.92, 21.48.

2-(3-Methoxyphenyl)-2,3-dihydro-1*H*-naphtho[1,8-de]-[1,3,2]diazaborinine (**3r**):[19] Isolated in 69% yield as a yellow solid. m.p. 114～116 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.334 (t, J=7.6 Hz, 1H), 7.168 (d, J=7.2 Hz, 1H), 7.133～7.094 (m, 3H), 7.033 (d, J=8.0 Hz, 2H), 6.89 (dd, J=8.4, 2.0 Hz, 1H), 6.358 (d, J=7.2 Hz, 2H), 5.963 (s, 2H), 3.819 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.33, 140.95, 136.27, 129.44, 127.55, 123.68, 119.80, 117.76, 116.89, 115.39, 105.99, 55.16.

2-(3-Fluorophenyl)-2,3-dihydro-1*H*-naphtho[1,8-de]-[1,3,2]diazaborinine (**3s**):[19] Isolated in 64% yield as a white solid. m.p. 93～95 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.448～7.378 (m, 2H), 7.311 (dd, J=8.8, 1.6 Hz, 1H), 7.173 (t, J=8.0 Hz, 3H), 7.101 (d, J=8.4 Hz, 2H), 6.417 (dd, J=7.2, 1.2 Hz, 2H), 5.989 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.75 (d, J=246.0 Hz), 140.69, 136.21, 129.98 (d, J=8.0 Hz), 127.55, 126.96 (d, J=3.0 Hz), 119.80, 117.95, 117.75, 117.01 (d, J=21.0 Hz), 106.12; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −123.06.

2-(3-(Trifluoromethyl)phenyl)-2,3-dihydro-1*H*-naphtho-[1,8-de][1,3,2] diazaborinine (**3t**):[20] Isolated in 61% yield as a yellow solid. m.p. 99～102 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.880 (s, 1H), 7.782～7.728 (m, 2H), 7.547 (t, J=7.6 Hz, 1H), 7.169 (t, J=8.4 Hz, 2H), 7.098 (dd, J=8.4, 1.2 Hz, 2H), 6.424 (d, J=7.2 Hz, 2H), 6.004 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.56, 136.20, 134.67,130.32 (q, J=32.0 Hz), 128.52, 127.93 (q, J=4.0

Hz), 124.24 (q, J=270.0 Hz), 126.74 (q, J=4.0 Hz), 119.83, 118.11, 106.24; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −62.42.

2-(3-Chlorophenyl)-2,3-dihydro-1*H*-naphtho[1,8-de]-[1,3,2]diazaborinine (**3u**):[18] Isolated in 44% yield as a brown solid. m.p. 119～120 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.594～7.586 (m, 1H), 7.484～7.460 (m, 2H), 7.366 (t, J=7.6 Hz, 1H), 7.163 (t, J=8.4 Hz, 2H), 7.091 (dd, J=8.4, 1.2 Hz, 2H), 6.404 (dd, J=7.2, 1.2 Hz, 2H), 5.958 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.63, 136.20, 134.44, 131.33, 130.15, 129.64, 129.36, 127.56, 119.79, 118.00, 106.16.

2-(3-Bromophenyl)-2,3-dihydro-1*H*-naphtho[1,8-de]-[1,3,2]diazaborinine (**3v**):[19] Isolated in 74% yield as a white solid. m.p. 123～125 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.748～7.740 (m, 1H), 7.613～7.585 (m, 1H), 7.516 (d, J=7.2 Hz, 1H), 7.301 (t, J=7.6 Hz, 1H), 7.158 (t, J=8.0 Hz, 2H), 7.086 (dd, J=8.4, 1.2 Hz, 2H), 6.401 (dd, J=7.2, 1.2 Hz, 2H), 5.953 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.62, 136.19, 134.24, 133.06, 129.92, 129.80, 127.56, 122.95, 119.79, 118.00, 106.16.

2-(3-Vinylphenyl)-2,3-dihydro-1*H*-naphtho[1,8-de]-[1,3,2]diazaborinine (**3w**):[19] Isolated in 24% yield as a orange solid. m.p. 86～88 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.613 (d, J=7.6 Hz, 1H), 7.513 (d, J=7.2 Hz, 1H), 7.418 (t, J=7.2 Hz, 1H), 7.318 (t, J=7.2 Hz, 1H), 7.145 (t, J=7.6 Hz, 2H), 7.083～7.014 (m, 3H), 6.359 (d, J=7.2 Hz, 2H), 5.863～5.723 (m, 3H), 5.319 (d, J=10.8Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.21, 140.95, 137.57, 136.28, 132.41, 129.57, 127.58, 127.31, 125.22, 119.70, 117.85, 115.72, 105.91.

2-(2,4-Dimethoxyphenyl)-2,3-dihydro-1*H*-naphtho[1,8-de][1,3,2]diazaborinine (**3x**): Isolated in 30% yield as a pink solid. m.p. 128～129 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.800 (s, 2H), 7.707 (d, J=8.0 Hz, 1H), 7.057 (t, J=7.6 Hz, 2H), 6.877 (dd, J=8.0, 0.8 Hz, 2H), 6.612～6.541 (m, 4H), 3.864 (s, 3H), 3.810 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 165.24, 162.57, 142.25, 135.94, 135.69, 127.66, 119.36, 116.05, 105.63, 105.13, 97.81, 55.38, 55.24. HRMS (ESI) calcd for $C_{18}H_{18}BN_2O_2$ $[M+H]^+$ 305.1456, found 305.1451.

2-(3,4-Dimethoxyphenyl)-2,3-dihydro-1*H*-naphtho[1,8-de][1,3,2]diazaborinine (**3y**): Isolated in 68% yield as a purple solid. m.p. 126～127 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.185 (s, 2H), 7.541～7.514 (m, 2H), 7.089 (t, J=8.0 Hz, 2H), 7.022 (d, J=7.6 Hz, 1H), 6.897 (d, J=8.0 Hz, 2H), 6.594 (dd, J=7.6, 2.4 Hz, 2H), 3.865 (s, 3H), 3.802 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 150.66, 148.35, 142.50, 136.00, 127.69, 126.18, 119.51, 116.11, 113.72, 111.18, 105.49, 55.79, 55.38. HRMS (ESI) calcd for $C_{18}H_{18}BN_2O_2$ $[M+H]^+$ 305.1456, found 305.1453.

2-(3,5-Dimethoxyphenyl)-2,3-dihydro-1*H*-naphtho[1,8-de][1,3,2]diazaborinine (**3z**): Isolated in 90% yield as a brown solid. m.p. 129～130 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.226 (s, 2H), 7.100～7.062 (m, 4H), 6.901 (dd, J=8.4, 1.2 Hz, 2H), 6.592 (s, 1H), 6.582～6.570 (m, 2H), 3.812 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 160.27, 142.34, 135.99, 127.68, 119.76, 116.29, 110.37, 105.63, 102.01, 55.29. HRMS (ESI) calcd for $C_{18}H_{18}BN_2O_2$: $[M+H]^+$ 305.1456, found 305.1451.

2-(3,4,5-Trimethoxyphenyl)-2,3-dihydro-1*H*-naphtho-[1,8-de][1,3,2]diazaborinine (**3aa**): Isolated in 50% yield as a purple solid. m.p. 137～139 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.212 (s, 2H), 7.228 (s, 2H), 7.100 (t, J=7.6 Hz, 2H), 6.910 (d, J=8.0 Hz, 2H), 6.586 (dd, J=7.2, 2.0 Hz, 2H), 3.880 (s, 6H), 3.705 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 152.69, 142.41, 139.49, 136.03, 127.70, 119.63, 116.25, 110.14, 105.51, 60.04, 56.20. HRMS (ESI) calcd for $C_{19}H_{20}BN_2O_3$ $[M+H]^+$ 335.1567, found 335.1569.

2-(Naphthalen-1-yl)-2,3-dihydro-1*H*-naphtho[1,8-de]-[1,3,2]diazaborinine (**3ab**):[18] Isolated in 27% yield as a gray solid. m.p. 140～142 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.214～8.185 (m, 1H), 7.928～7.980 (m, 2H), 7.699 (dd, J=6.8, 1.2 Hz, 1H), 7.754～7.497 (m, 3H), 7.167 (t, J=8.0 Hz, 2H), 7.102 (dd, J=8.4, 1.2 Hz, 2H), 6.385 (dd, J=7.2, 1.2 Hz, 2H), 6.025 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.05, 136.35, 135.34, 133.20, 130.63, 129.48, 128.73, 127.86, 127.62, 126.19, 125.80, 125.35, 119.89, 117.92, 105.99.

2-(Naphthalen-2-yl)-2,3-dihydro-1*H*-naphtho[1,8-de]-[1,3,2]diazaborinine (**3ac**):[18] Isolated in 70% yield as a yellow solid. m.p. 139～140 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.554 (s, 1H), 8.472 (s, 2H), 8.067 (d, J=8.4 Hz, 1H), 7.985～7.934 (m, 3H), 7.577～7.553 (m, 2H), 7.125 (t, J=7.6 Hz, 2H), 6.940 (d, J=8.0 Hz, 2H), 6.680 (d, J=7.2 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 142.46, 136.04, 133.97, 133.28, 132.60, 129.38, 128.23, 127.75, 127.66, 126.77, 126.74, 126.13, 119.82, 116.37, 105.76.

2-(Phenanthren-9-yl)-2,3-dihydro-1*H*-naphtho[1,8-de]-[1,3,2]diazaborinine (**3ad**):[19] Isolated in 64% yield as a gray solid. m.p. 143～145 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.760 (d, J=8.0 Hz, 1H), 8.710 (d, J=8.0 Hz, 1H), 8.240 (dd, J=8.0, 1.2 Hz, 1H), 7.963 (s, 1H), 7.902 (dd, J=7.6, 1.6 Hz, 1H), 7.721～7.668 (m, 2H), 7.649～7.598 (m, 2H), 7.178 (t, J=8.0 Hz, 2H), 7.117 (d, J=8.4 Hz, 2H), 6.345 (d, J=6.8 Hz, 2H), 6.068 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.02, 136.35, 133.57, 132.34, 131.17, 130.72, 129.97, 128.70, 128.67, 127.63, 127.17, 126.74, 126.73, 126.49, 123.16, 122.52, 119.91, 117.95, 106.03.

2-(Furan-3-yl)-2,3-dihydro-1*H*-naphtho[1,8-de][1,3,2]-diazaborinine (**3ae**):[19] Isolated in 44% yield as a brown solid. m.p. 73～75 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.705 (s, 1H), 7.572～7.564 (m, 1H), 7.154 (t, J=8.0 Hz, 2H), 7.074 (d, J=8.0 Hz, 2H), 6.559 (s, 1H), 6.392 (dd, J=7.2, 0.8 Hz, 2H), 5.876 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.01, 143.38, 140.78, 136.22, 127.54, 119.64, 117.73, 111.56, 105.84.

2-(Thiophen-3-yl)-2,3-dihydro-1*H*-naphtho[1,8-de]-[1,3,2]diazaborinine (**3af**):[19] Isolated in 74% yield as a gray solid. m.p. 79～81 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.689～7.677 (m, 1H), 7.476～7.458 (m, 1H), 7.342

(dd, J=4.8, 1.2 Hz, 1H), 7.220～7.164 (m, 2H), 7.128～7.094 (m, 2H), 6.420 (d, J=7.2 Hz, 2H), 5.972 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 140.86, 136.21, 131.25, 129.70, 127.54, 126.13, 119.65, 117.71, 105.92.

2-(Pyridin-3-yl)-2,3-dihydro-1*H*-naphtho[1,8-de][1,3,2]-diazaborinine (**3ag**):[19] Isolated in 95% yield as a dark green solid. m.p. 140～142 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 9.047 (s, 1H), 8.628 (d, J=4.8 Hz, 1H), 8.382 (s, 2H), 8.258 (d, J=7.6 Hz, 1H), 7.469～7.438 (m, 1H), 7.090 (t, J=7.6 Hz, 2H), 6.924 (d, J=8.0 Hz, 2H), 6.574 (d, J=7.2 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 153.31, 150.83, 142.11, 140.42, 136.07, 127.84, 123.44, 119.92, 116.75, 105.97.

1,4-Bis(1*H*-naphtho[1,8-de][1,3,2]diazaborinin-2(3*H*)-yl)benzene (**3ah**):[20] Isolated in 31% yield as a red brown solid. m.p. 223～225 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.345～8.328 (m, 4H), 8.035～8.013 (m, 4H), 7.100 (t, J=8.0 Hz, 4H), 6.919 (d, J=8.0 Hz, 4H), 6.658～6.623 (m, 4H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 142.38, 136.01, 131.90, 127.70, 119.80, 116.32, 105.71.

4,4'-Bis(1*H*-naphtho[1,8-de][1,3,2]diazaborinin-2(3*H*)-yl)-1,1-biphenyl (**3ai**):[20] Isolated in 37% yield as an orange solid. m.p. 234～235 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.357 (s, 4H), 8.090～8.070 (m, 4H), 7.858～7.838 (m, 4H),7.105 (t, J=8.0 Hz, 4H), 6.923 (dd, J=8.4, 1.2 Hz, 4H), 6.638 (dd, J=7.6, 1.2 Hz, 4H); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 142.37, 141.34, 135.97, 133.39, 127.67, 125.95, 119.73, 116.28, 105.69.

2-Isopropyl-2,3-dihydro-1*H*-naphtho[1,8-de][1,3,2]diazaborinine (**3aj**):[19] Isolated in 91% yield as a purple liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.137 (t, J=8.0 Hz, 2H), 7.045 (dd, J=8.4, 1.2 Hz, 2H), 6.317 (dd, J=7.6, 1.2 Hz, 2H), 5.624 (s, 2H), 1.544～1.450 (m, 2H), 1.030 (t, J=7.6 Hz, 3H), 0.871 (t, J=8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.16, 136.23, 127.50, 119.47, 117.21, 105.32, 18.10, 17.02.

2-Butyl-2,3-dihydro-1*H*-naphtho[1,8-de][1,3,2]diazaborinine (**3ak**):[19] Isolated in 98% yield as a dark purple liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.157 (t, J=8.0 Hz, 2H), 7.07 (d, J=8.0 Hz, 2H), 6.328 (dd, J=7.2, 1.2 Hz, 2H), 5.624 (s, 2H), 1.462～1.410 (m, 4H), 1.013～0.977 (m, 3H), 0.898～0.860 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.16, 136.21, 127.48, 119.44, 117.18, 105.30, 26.92, 25.44, 13.95.

2-Isobutyl-2,3-dihydro-1*H*-naphtho[1,8-de][1,3,2]diazaborinine (**3al**):[18] Isolated in 27% yield as a purple solid. m.p. 69～70 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.111 (t, J=8.4 Hz, 2H), 7.017 (dd, J=8.0, 0.8 Hz, 2H), 6.305 (dd, J=7.2, 0.8 Hz, 2H), 5.625 (s, 2H), 1.887～1.786 (m, 1H), 0.996 (d, J=6.4 Hz, 6H), 0.816 (d, J=7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.18, 136.24, 127.52, 119.48, 117.26, 105.34, 25.54, 25.39.

2-(Pent-4-en-1-yl)-2,3-dihydro-1*H*-naphtho[1,8-de]-[1,3,2]diazaborinine (**3am**):[19] Isolated in 69% yield as a yellow oil liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.161～7.115 (m, 2H), 7.048 (dd, J=8.4, 1.2 Hz, 2H), 6.314 (dd, J=7.6, 1.2 Hz, 2H), 5.927～5.825 (m, 1H), 5.619 (s, 2H), 5.114～5.019 (m, 2H), 2.178～2.118 (m, 2H), 1.593～1.516 (m, 2H), 0.905～0.864 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.09, 138.72, 136.21, 127.49, 119.46, 117.27, 114.72, 105.35, 36.35, 24.07. HRMS (ESI) calcd for $C_{15}H_{18}BN_2$ $[M+H]^+$ 237.1558, found 237.1562.

2-Cyclopropyl-2,3-dihydro-1*H*-naphtho[1,8-de][1,3,2]-diazaborinine (**3an**):[18] Isolated in 57% yield as a purple solid. m.p. 60～62 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.121 (t, J=8.4 Hz, 2H), 7.030 (dd, J=8.4, 0.8 Hz, 2H), 6.300 (dd, J=7.2, 1.2 Hz, 2H), 5.453 (s, 2H), 0.773～0.725 (m, 2H), 0.477～0.437 (m, 2H), −0.041～0.119 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.06, 136.20, 127.48, 119.31, 117.20, 105.33, 3.93.

2-Cyclopentyl-2,3-dihydro-1*H*-naphtho[1,8-de][1,3,2]-diazaborinine (**3ao**):[18] Isolated in 94% yield as a brown solid. m.p. 80～82 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.149 (t, J=8.0 Hz, 2H), 7.055 (dd, J=8.4, 1.2 Hz, 2H), 6.337 (dd, J=7.2, 1.2 Hz, 2H), 5.628 (s, 2H), 1.926～1.852 (m, 2H), 1.742～1.367 (m, 4H), 1.40～1.367 (m, 2H), 1.274～1.182 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 141.21, 136.23, 127.49, 119.48, 117.18, 105.35, 29.19, 26.50.

Supporting Information Copies of ^{1}H NMR and ^{13}C NMR spectra of products **3a**～**3ao** and cyclic voltammetry experiments. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn.

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