有机化学 DOI: 10.6023/cjoc202108040 研究论文
Chinese Journal of Organic Chemistry ARTICLE

8-氨基喹啉骨架螯合的四配位 *B*,*B*-二芳基络合物的合成与计算研究

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摘要 尽管四配位有机硼配合物作为荧光材料已被广泛应用, 但硼中心上连接有两个芳基的配合物的合成方法仍然较少. 该类化合物的合成一般需要使用敏感的有机金属试剂. 本工作使用市售可得、化学稳定的芳基三氟硼酸钾盐作为二芳基硼结构的来源, 以 8-氨基喹啉作为螯合配体, 以中等至优异的产率获得了一系列先前难以制备的二芳基硼络合物. 此外, 对所得配合物的密度泛函理论计算研究揭示了其分子轨道分布.

关键词 光催化剂; 三氟硼酸钾; 四配位有机硼; 理论计算

Synthetic and Computational Study of Four-Coordinate *B*,*B*-Diaryl 8-Aminoquinolate Complexes

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Abstract Despite the wide application of four-coordinate organoboron compounds as fluorescent materials, the synthesis of such complexes, which contain two aryl groups on the boron centers, is relatively limited by the need for sensitive organometallic reagents. Herein, using stable and commercially available aryl trifluoroborate potassium salts as complexation reagents, a series of aminoquinolate-framed diarylboron complexes, which were difficult to access previously, have been obtained in moderate to excellent yields. Furthermore, density functional theory (DFT) study of the obtained complex shows its molecular orbital distribution.

Keywords photocatalyst; trifluoroborate potassium; four-coordinate organoboron; theoretical calculation

1 Introduction

Four-coordinate organoboron compounds, which contain π-conjugated chelate backbones (CB), have been under constant investigation over the past decades.[1] They have been documented to express unique optical properties and gained versatile optoelectronic applications in organic light-emitting diodes (OLEDs),[2] photoresponsive materials,[3] and sensory and imaging materials.[4] Therefore, their design and synthesis have also attracted substantial interest.

In this context, the modification of the chelate backbone, which is usually a monoanion to form one covalent bond and one dative bond with the sp^3 boron center respectively, has been the major trend, especially for the famous boron dipyrromethene (BODIPY) dyes.[5] In contrast, the synthetical methods for introducing hydrocarbyl groups to the boron centers are relatively far less explored. Traditionally, the nucleophilic substitution of (CB)BX_2 (X=halide) with organometallic reagents has been utilized to achieve this goal.[6] The reactions between halidediarylboron[7] or triarylboron,[8] which are also usually prepared from organometallic reagents, and chelation ligands are also used.[1e] However, due to the strong nucleophilicity of the organometallic reagents used, the functional group compatibility of these methods is highly restricted.

More recently, the organotrifluoroborates (RBF_3K),

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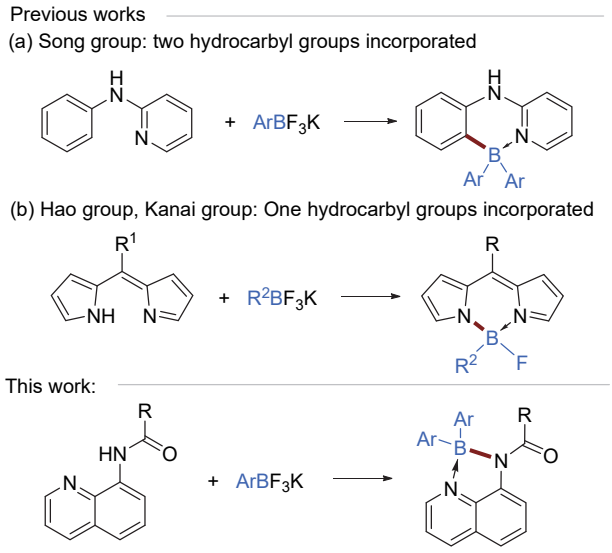
Received August 20, 2021; revised October 27, 2021; published online November 24, 2021.
Project supported by the National Natural Science Foundation of China (Nos. 21901214, 21963010) and the Natural Science Foundation of Shaanxi Province (No. 2020JQ-918).
国家自然科学基金(Nos. 21901214, 21963010)和陕西省自然科学基金(No. 2020JQ-918)资助项目.

usually stable solids with diverse attached functional groups, have been used to introduce the R_2B- or RFB-motifs to the four-coordinate organoboron compounds.[9] For example, Song's group[10] realized an elegant synthesis of four-coordinate triarylboranes using aryl trifluoroborates ($ArBF_3K$) in 2018. The boron atoms (Ar_2B-), which were substituted by two aryl groups from $ArBF_3K$, were incorporated into the final products (Scheme 1a). Later, Kanai's group[11] and Hao's group[12] independently reported their protocols on the concise synthesis of RFB-BODIPYs, where RBF_3K was used and only one hydrocarbyl group was introduced to boron atoms of BODIPYs (Scheme 1b). Herein, we disclose the synthesis of *B*,*B*-dihydrocarbyl-substituted organoboron compounds with aminoquinolate frames, using RBF_3K as the starting materials. This protocol can be well regulated to obtain the aim-products in good to excellent yields.



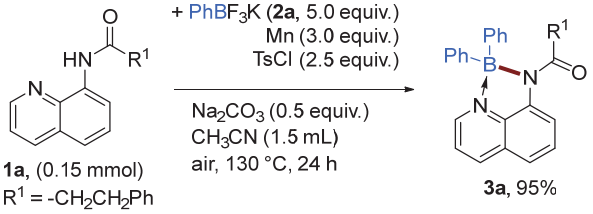
Scheme 1 Methods for introducing hydrocarbyl groups to the boron atoms using organotrifluoroborates

2 Results and discussion

The investigation was initiated by optimizing the reaction between 3-phenyl-*N*-(quinolin-8-yl) propenamide (**1a**) and phenyl trifluoroborate potassium (**2a**). After extensive experimentation, the *B*,*B*-diaryl product **3a** could be obtained in 95% yield under the following conditions (the standard conditions in Table 1): 5.0 equiv. of **2a**, 3.0 equiv. of Mn, 2.5 equiv. of *p*-toluenesulfonyl chloride (TsCl), 0.5 equiv. of Na_2CO_3, MeCN solution, stirring at 130 ℃ under air for 24 h. As indicated in Table 1, an array of variations from the standard conditions were screened, which were detrimental to the isolated yields to different degrees.

In the beginning, to explore the function of each additive in the standard conditions, control experiments were performed. In the absence of TsCl, this transformation was almost halted (Entry 1), indicating its critical role in the activation of $PhBF_3K$. When Mn was omitted, the product was obtained in 25% yield. The function of Mn was further

Table 1 Optimization of the reaction conditions[a]



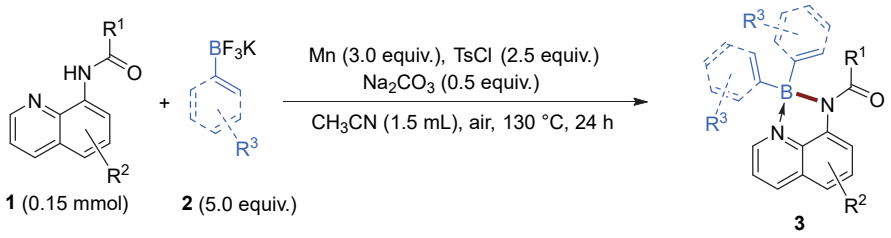
Entry	Variations from the 'standard' conditions	Yield[b]/%
	No 4-toluenesulfonyl chloride	5
	No Mn	25
	No Na_2CO_3	84
	K_2CO_3 instead of Na_2CO_3	80
	$NaHCO_3$ instead of Na_2CO_3	91
	NaOMe instead of Na_2CO_3	N.D.
	DMSO instead of CH_3CN	N.D.
	DMF instead of CH_3CN	53
	Toluene instead of CH_3CN	Trace
	1,4-Dioxane instead of CH_3CN	24
	Fe instead of Mn	32
	$MnCl_2$ instead of Mn	N.D.
	80 ℃ instead of 130 ℃	Trace

[a] Standard reaction conditions: **1a** (0.15 mmol, 1.0 equiv.), **2a** (0.75 mmol, 5.0 equiv.), Mn (0.45 mmol, 3.0 equiv.), 4-toluenesulfonyl chloride (0.375 mmol, 2.5 equiv.), Na_2CO_3 (0.075 mmol, 0.5 equiv.), CH_3CN (1.5 mL), stirring at 130 ℃ under air for 24 h. [b] Isolated yields. N.D.=not detected.

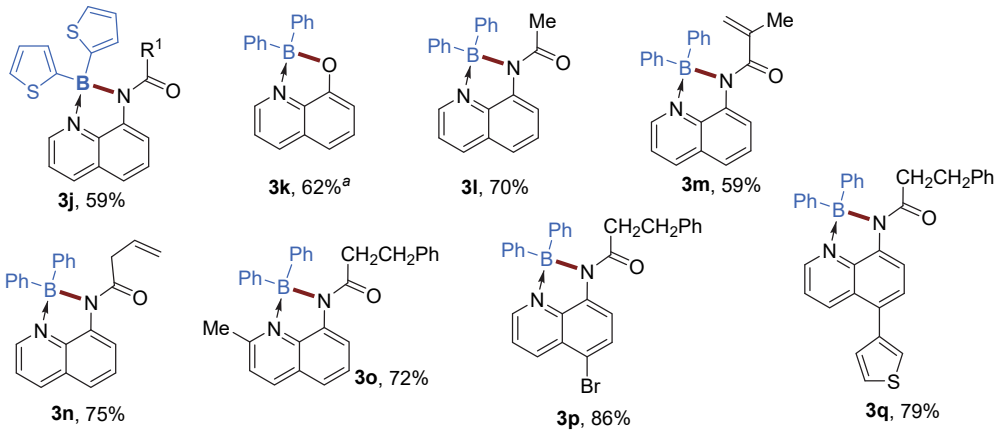
investigated by replacing it by $MnCl_2$, which was demonstrated to be completely ineffective (Entry 12). This implied if the zero-valent Mn acted as a reductant in the reaction mixture, its counter anions after oxidation should play an important role during the reaction. In comparison to TsCl and Mn, the added base Na_2CO_3 seemed to be less critical, since its absence only resulted in 10% decreased yield of **3a** (Entry 3). However, replacing it by a strong base NaOMe suppressed the transformation absolutely (Entry 6). The choice of solvent was also found to play a key role. While dimethyl sulfoxide (DMSO) and toluene solution showed no reactivity, *N*,*N*-dimethylformamide (DMF) and 1,4-dioxane solution resulted in the formation of the products, albeit in lower yields (Entries 7～10). Reducing the temperature to 80 ℃ also suppressed the transformation (Entry 13), which indicated that a high temperature should be necessary for this conversion.

With the optimal conditions in hand, the substrate scope of this synthetic protocol was then explored. As indicated in Table 2, different RBF_3Ks were first treated with **1a** under optimal conditions for the synthesis of aminoquinolate *B*,*B*-diarylboron (AQDAB) complexes. It should be noted that these diaryl organoboron compounds have been found to be competent photocatalysts in catalytic C—O bond construction and photooxidation.[13] Several substrates of this type and the corresponding characterization data have been disclosed therein, which were not included in Table 2.[13a] A variety of substituted phenyl trifluoroborates were competent starting materials, albeit of the electronic properties of these substituents (**3b**～**3i**). Alkoxy (**3b**, 90%; **3g**,

Table 2 Substrate scope of the *B*,*B*-diaryl products



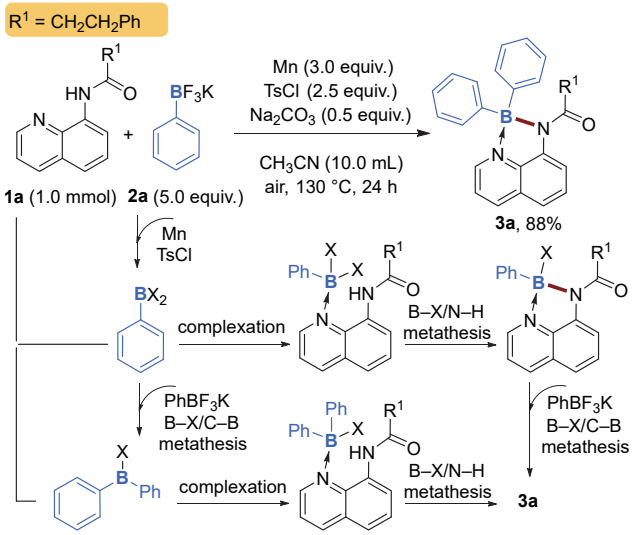
R^1 = CH_2CH_2Ph, R^2 = H		
3b	R^3 = *m*-OMe	90%
3c	R^3 = *m*-F	87%
3d	R^3 = *p*-Cl	79%
3e	R^3 = *p*-Br	90%
3f	R^3 = *p*-CN	68%
3g	R^3 = *p*-OCH_2Ph	80%
3h	R^3 = *p*-Ph	91%
3i	R^3 = *p*-^{t}Bu	31%



[a] 8-Hydroxyquinoline (0.15 mmol), TsCl (2.0 equiv.).

80%) and cyano (**3f**, 68%) groups were both compatible with reaction conditions. Good to excellent yields were obtained except for the *para-tert*-Bu case (**3i**, 31%). In addition, the *para*- or *meta*-halogen-substituted phenyl trifluoroborates also resulted in moderate to good yields (**3c**～**3e**). The compatibility of halogen atoms should pave the way for further decoration of the obtained products, due to the abundant possibilities of their functionalization. The biphenyl trifluoroborate salts could lead to the product **3h** containing extended aromatic system. Interestingly, thienyl trifluoroborates participated in the reaction efficiently, affording **3j** in 59% yield. Then, the variation of the chelation backbone was explored. The four-coordinate *N*,*O*-chelated diphenylborinate **3k** was obtained in 62% yield, using 8-hydroxyquinoline as the chelation ligand. For the acylated 8-aminoquinoline backbone, the substitution groups (R^1) on the amide motif could be changed to methyl, propen-2-yl, allyl, 3-buten-1-yl, affording the products **3l**～**3n** in moderate to good yields. Finally, the substitutions on the quinoline core were investigated. 2-Methyl on the 8-aminoquinoline led to **3o** in 72% yield, indicating the steric effect had limited effect on the output of the reaction. The 5-position could be substituted by bromide, and thienyl, and the corresponding products were all obtained in about 80% yields. Overall, this protocol was suitable for the confusion of various *N*,*N*- or *N*,*O*-chelation backbone with aryl/alkenyl fluoroborates, leading to *B*,*B*-dihydrocarbyl-substituted organoboron compounds.

Moreover, the synthesis of **3a** could be amplified easily to 1.0 mmol, and the isolated yield of **3a** was 88% in this case (Scheme 2). Based on the previous report[10-12,14] and our observation, plausible reaction pathways have been proposed in Scheme 2. Firstly, via the syngenetic function of Mn and TsCl, dihalide arylborane intermediate **A** could be obtained *in situ*. The following B—X/C—B cross-metathesis between **A** and aryltrifluoroborate would introduce the second aryl group onto the boron center of intermediate **B**. After the coordination of sp^2-N in the quinoline skeleton, the generated complex **C** had a pair of neighboring B—X and N—H bonds, whose metathesis eventually led to the target product. It should be noted that the sequence of these two metathesis processes might be reversed, which did not affect the formation of the product.



Scheme 2 An amplified reaction for the synthesis of **3a** and plausible reaction mechanisms

To gain additional insight into the synthesized photo-

catalyst, density functional theory (DFT) and time-dependent density functional theory calculations (TD-DFT)[15] were performed with the compounds **3**, using the Gaussian09 suite of programs.[16] In both cases, the combination of m062x/6-311g** was applied.[17] As shown in Figure 1, both HOMO and LUMO orbitals were delocalized over the acyl aminoquinolate backbone. While the HOMO orbital was delocalized mostly over the acyl aniline motif, with a significant participation of the amide unit, the LUMO orbital mainly delocalized at the quinoline unit, rendering limited overlap between these two orbitals. Then, TD-DFT calculations on this optimized structure suggested that lowest energy transition (S0→S1) involves exclusively the HOMO and the LUMO frontier orbitals, indicating a possible ligand-to-ligand charge transfer excitation process.[13a]

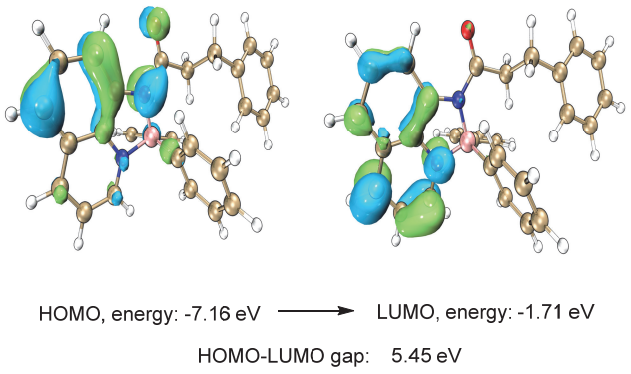


Figure 1 HOMO and LUMO orbitals of **3a**

3 Conclusions

In conclusion, a new synthetic strategy has been developed herein, to realize the chemoselective synthesis of B,B-diaryl four-coordinate organoboron products. Stable and readily available aryl trifluoroborates, with diverse functional groups, were utilized as the aryl sources, thus bypassing the disadvantage of commonly used aryl metallic reagents. This strategy also featured simple and convenient operation. Further exploration and application of such type of organoboron compounds are underway in our laboratory.

4 Experimental section

4.1 General Information

Unless otherwise noted, all reactions were carried out under air atmosphere. Analytical thin-layer chromatography (TLC) was performed on glass plates coated with 0.25 mm 230～400 mesh silica gel containing a fluorescent indicator. Visualization was accomplished by exposure to an ultraviolet lamp. All the products in this article are compatible with standard silica gel chromatography. Column chromatography was performed on silica gel (200～300 mesh) using standard methods.

NMR spectra were measured on a Bruker Ascend 400 spectrometer. ^{1}H NMR spectra were recorded at 400 MHz in NMR solvents and referenced internally to corresponding solvent resonance, and ^{13}C NMR spectra were recorded at 101 MHz and referenced to corresponding solvent resonance. Infrared spectra were collected on a Thermo Fisher Nicolet 6700 FT-IR spectrometer using ATR (Attenuated Total Reflectance) method. High resolution mass spectra (HRMS) were acquired on a Thermo Scientific LTQ Orbitrap XL with an ESI source.

Commercial reagents and solvent, such as Mn, TsCl and aryl trifluoroborates, were purchased from Adamas, J&K, Energy, Sigma-Aldrich, Alfa Aesar, Acros Organics, TCI and used as received unless otherwise stated.

4.2 Typical procedures for the synthesis of four-coordinate organoboron products

The synthesis of **3b**: A flame-dried 25 mL pressure reaction tube was placed with a stirring bar. Then, 3-phenyl-*N*-(quinolin-8-yl)propanamide (41.4 mg, 0.15 mmol, 1.0 equiv.), potassium 3-methoxyphenyltrifluoroborate (160.5 mg, 0.75 mmol, 5.0 equiv.), Mn (24.7 mg, 0.45 mmol, 3.0 equiv.), 4-toluenesulfonyl chloride (71.5 mg, 0.375 mmol, 2.5 equiv.), Na_2CO_3 (7.9 mg, 0.075 mmol, 0.5 equiv.) and CH_3CN (1.5 mL) were added. The resulting mixture was stirred at 130 ℃ for 24 h. The reaction mixture was filtered, concentrated and then purified by column chromatography on silica gel to give the target product.

4.3 Preparation and characterization data for isolated products

1-(2,2-Bis(3-methoxyphenyl)-2λ^4,3λ^4-[1,3,2]diazaborolo[4,5,1-ij]quinolin-1(2*H*)-yl)-3-phenylpropan-1-one (**3b**): The product was isolated by flash chromatography (*V*(petroleum ether)∶*V*(ethyl acetate)=3∶1) as a yellow solid (67.7 mg, 90% yield). m.p. 129.7～132.6 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.96 (d, *J*=8.0 Hz, 1H), 8.38 (d, *J*=5.2 Hz, 1H), 8.26 (d, *J*=8.4 Hz, 1H), 7.74 (t, *J*=8.0 Hz, 1H), 7.43 (t, *J*=2.8 Hz, 1H), 7.42～7.39 (m, 1H), 7.20 (t, *J*=8.0 Hz, 2H), 7.15～7.10 (m, 2H), 7.09～7.02 (m, 5H), 6.84 (d, *J*=7.2 Hz, 2H), 6.81～6.76 (m, 2H), 3.68 (s, 6H), 2.64～2.54 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.2, 159.2, 141.9, 141.6, 139.6, 139.2, 137.6, 132.6, 129.0, 128.4, 128.1, 127.6, 125.9, 125.6, 122.4, 119.6, 119.0, 117.2, 111.9, 55.1, 40.0, 31.6; IR (KBr) *v*: 3033, 2939, 1639, 1571, 1508, 1325, 1284, 1232, 1045, 767 cm^{-1}. HRMS (ESI) calcd for $C_{32}H_{30}BN_2O_3$ $[M+H]^+$ 501.2344, found 501.2348.

1-(2,2-Bis(3-Fluorophenyl)-2λ^4,3λ^4-[1,3,2]diazaborolo-[4,5,1-ij]quinolin-1(2*H*)-yl)-3-phenylpropan-1-one (**3c**): The product was isolated by flash chromatography (*V*(petroleum ether)∶*V*(ethyl acetate)=3∶1) as a yellow solid (62.0 mg, 87% yield). m.p. 172.7～174.1 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.98 (d, *J*=7.6 Hz, 1H), 8.40 (d, *J*=8.4 Hz, 1H), 8.35 (d, *J*=5.2 Hz, 1H), 7.80 (t, *J*=8.0 Hz, 1H), 7.54 (dd, *J*=8.4, 5.2 Hz, 1H), 7.51 (d, *J*=8.4 Hz, 1H), 7.26～7.20 (m, 4H), 7.18～7.05 (m, 5H), 6.97～6.89 (m, 2H), 6.86 (d, *J*=6.8 Hz, 2H), 2.69～2.61 (m, 2H), 2.54～2.46 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 175.8, 162.9 (d, *J*=245 Hz), 141.7, 141.3, 139.6 (d, *J*=10.5 Hz), 137.5, 132.8, 129.7 (d, *J*=7.2 Hz), 128.9 (d, *J*=2.4 Hz),

128.3, 128.2, 127.7, 125.7, 122.6, 119.7, 119.4, 119.2, 117.5, 114.2 (d, J=21 Hz), 39.9, 31.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −113.59; IR (KBr) ν: 3028, 1641, 1575, 1508, 1384, 1228, 786 cm^{-1}. HRMS (ESI) calcd for $C_{30}H_{24}BF_2N_2O$ $[M+H]^+$ 477.1944, found 477.1953.

1-(2,2-Bis(4-chlorophenyl)-2λ^4,3λ^4-[1,3,2]diazaborolo-[4,5,1-ij]quinolin-1(2*H*)-yl)-3-phenylpropan-1-one (**3d**): The product was isolated by flash chromatography (V(petroleum ether)∶V(ethyl acetate)=3∶1) as a yellow solid (60.4 mg, 79% yield). m.p. 77.3～81.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.00 (d, J=8.0 Hz, 1H), 8.43 (d, J=8.0 Hz, 1H), 8.34 (d, J=5.2 Hz, 1H), 7.82 (t, J=8.0 Hz, 1H), 7.57 (dd, J=8.4, 5.6 Hz, 1H), 7.53 (d, J=8.4 Hz, 1H), 7.36 (d, J=8.4 Hz, 4H), 7.24 (d, J=8.4 Hz, 4H), 7.21～7.14 (m, 2H), 7.14～7.09 (m, 1H), 6.87 (d, J=7.2 Hz, 2H), 2.74～2.65 (m, 2H), 2.54～2.42 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 175.1, 141.4, 141.0, 140.4, 139.5, 137.5, 133.8, 133.0, 131.6, 128.3, 128.3, 127.8, 126.0, 122.8, 119.6, 119.1, 117.9, 111.2, 39.9, 31.1; IR (KBr) ν: 3026, 1649, 1508, 1390, 1325, 1087, 827, 779 cm^{-1}. HRMS (ESI) calcd for $C_{30}H_{24}BCl_2N_2O$ $[M+H]^+$ 509.1353, found 509.1352.

1-(2,2-Bis(4-bromophenyl)-2l^4,3l^4-[1,3,2]diazaborolo-[4,5,1-ij]quinolin-1(2*H*)-yl)-3-phenylpropan-1-one (**3e**): The product was isolated by flash chromatography (V(petroleum ether)∶V(ethyl acetate)=3∶1) as a yellow solid (80.6 mg, 90% yield). m.p. 60.1～64.3 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.96 (d, J=8.0 Hz, 1H), 8.39 (d, J=8.0 Hz, 1H), 8.31 (d, J=5.2 Hz, 1H), 7.78 (t, J=8.0 Hz, 1H), 7.55～7.48 (m, 2H), 7.37 (d, J=8.0 Hz, 4H), 7.27 (d, J=8.0 Hz, 4H), 7.15 (t, J=6.8 Hz, 2H), 7.09 (t, J=7.2 Hz, 1H), 6.84 (d, J=7.2 Hz, 2H), 2.71～2.63 (m, 2H), 2.51～2.43 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 175.7, 141.7, 141.2, 139.7, 139.4, 137.5, 135.1, 132.8, 131.1, 128.4, 128.2, 127.7, 125.8, 122.6, 121.9, 119.2, 117.5, 39.8, 31.3; IR (KBr) ν: 3024, 164, 1506, 1386, 1325, 1074, 827, 773 cm^{-1}. HRMS (ESI) calcd for $C_{30}H_{24}BBr_2N_2O$ $[M+H]^+$ 597.0343, found 597.0340.

4,4'-(1-(3-Phenylpropanoyl)-2λ^4,3λ^4-[1,3,2]diazaborolo-[4,5,1-ij]quinoline-2,2(1*H*)-diyl)dibenzonitrile (**3f**): The product was isolated by flash chromatography (V(petroleum ether)∶V(ethyl acetate)=1∶1) as a yellow solid (49.8 mg, 68% yield). m.p. 100.0～106.3 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.00 (d, J=7.6 Hz, 1H), 8.51 (d, J=7.6 Hz, 1H), 8.33 (d, J=4.8 Hz, 1H), 7.85 (t, J=8.0 Hz, 1H), 7.64 (dd, J=8.4, 5.2 Hz, 1H), 7.59 (d, J=8.0 Hz, 1H), 7.55～7.47 (m, 8H), 7.20～7.09 (m, 3H), 6.88～6.80 (m, 2H), 2.70 (t, J=7.6 Hz, 2H), 2.37 (t, J=7.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 175.1, 141.4, 141.0, 140.4, 139.5, 137.51, 133.8, 133.0, 131.6, 128.3, 128.3, 127.8, 126.0, 122.8, 119.6, 119.1, 117.9, 111.2, 39.9, 31.1; IR (KBr) ν: 3026, 2225, 1650, 1508, 1390, 1325, 829, 784 cm^{-1}. HRMS (ESI) calcd for $C_{32}H_{24}BN_4O$ $[M+H]^+$ 491.2038, found 491.2042.

1-(2,2-Pis(4-(benzyloxy)phenyl)-2λ^4,3λ^4-[1,3,2]diazaborolo[4,5,1-ij]quinolin-1(2*H*)-yl)-3-phenylpropan-1-one (**3g**): The product was isolated by flash chromatography (V(petroleum ether)∶V(ethyl acetate)=2∶1) as a yellow solid (78.1 mg, 80% yield). m.p. 160.4～162.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.96 (d, J=7.6 Hz, 1H), 8.33 (d, J=5.2 Hz, 1H), 8.26 (d, J=8.4 Hz, 1H), 7.74 (t, J=8.0 Hz, 1H), 7.43～7.36 (m, 10H), 7.33 (t, J=7.2 Hz, 4H), 7.27 (t, J=7.2 Hz, 2H), 7.14～7.04 (m, 3H), 6.91～6.87 (m, 6H), 5.01 (s, 4H), 2.69～2.60 (m, 2H), 2.59～2.50 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 176.3, 158.3, 142.0, 141.7, 139.5, 139.0, 137.5, 137.3, 134.8, 132.6, 128.6, 128.5, 128.1, 128.0, 127.6, 127.6, 125.6, 122.5, 118.9, 117.2, 114.4, 69.9, 39.7, 31.5; IR (KBr) ν: 3026, 1649, 1596, 1506, 1390, 1174, 829, 698 cm^{-1}. HRMS (ESI) calcd for $C_{44}H_{38}BN_2O_3$ $[M+H]^+$ 653.2970, found 653.2969.

1-(2,2-Di([1,1'-biphenyl]-4-yl)-2l^4,3l^4-[1,3,2]diazaborolo-[4,5,1-ij]quinolin-1(2*H*)-yl)-3-phenylpropan-1-one (**3h**): The product was isolated by flash chromatography (V(petroleum ether)∶V(ethyl acetate)=3∶1) as a yellow solid (80.5 mg, 91% yield). m.p. 113.3～117.2 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.05 (d, J=8.0 Hz, 1H), 8.51 (dd, J=5.2, 0.8 Hz, 1H), 8.41 (dd, J=8.0, 0.8 Hz, 1H), 7.84 (t, J=8.4 Hz, 1H), 7.63～7.58 (m, 8H), 7.58～7.50 (m, 6H), 7.47～7.40 (m, 4H), 7.35～7.30 (m, 2H), 7.15～7.09 (m, 2H), 7.09～7.04 (m, 1H), 6.86 (d, J=6.8 Hz, 2H), 2.74～2.67 (m, 2H), 2.66～2.60 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 176.2, 142.0, 141.5, 141.3, 139.9, 139.6, 139.2, 137.7, 134.0, 132.7, 128.7, 128.5, 128.1, 127.7, 127.1, 127.1, 126.6, 125.6, 122.6, 119.1, 117.3, 39.9, 31.5; IR (KBr) ν: 3024, 1647, 1506, 1388, 1325, 1188, 75 4 cm^{-1}. HRMS (ESI) calcd for $C_{42}H_{34}BN_2O$ $[M+H]^+$ 593.2759, found 593.2755.

1-(2,2-Bis(4-(*tert*-butyl)phenyl)-2λ^4,3λ^4-[1,3,2]diazaborolo[4,5,1-ij]quinolin-1(2*H*)-yl)-3-phenylpropan-1-one (**3i**): The product was isolated by flash chromatography (V(petroleum ether)∶V(ethyl acetate)=5∶1) as a yellow solid (26.0 mg, 31% yield). m.p. 81.9～85.7 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.99 (d, J=7.6 Hz, 1H), 8.46 (dd, J=5.2, 0.8 Hz, 1H), 8.34 (d, J=8.4 Hz, 1H), 7.79 (t, J=8.4 Hz, 1H), 7.51 (dd, J=8.4, 5.2 Hz, 1H), 7.47 (d, J=8.0 Hz, 1H), 7.42 (d, J=8.4 Hz, 4H), 7.29 (d, J=8.2 Hz, 4H), 7.16～7.05 (m, 3H), 6.80～6.75 (m, 2H), 2.61～2.49 (m, 4H), 1.30 (s, 18H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 176.5, 149.7, 142.1, 141.7, 139.7, 138.8, 137.7, 133.3, 132.5, 128.6, 128.0, 127.5, 125.5, 124.7, 122.4, 118.9, 117.1, 40.1, 34.4, 31.8, 31.4; IR (KBr) ν: 3026, 2958, 1647, 1506, 1388, 1325, 827 cm^{-1}. HRMS (ESI) calcd for $C_{38}H_{42}BN_2O$ $[M+H]^+$ 553.3385, found 553.3388.

1-(2,2-Di(thiophen-2-yl)-2λ^4,3λ^4-[1,3,2]diazaborolo-[4,5,1-ij]quinolin-1(2*H*)-yl)-3-phenylpropan-1-one (**3j**): The product was isolated by flash chromatography (V(petroleum ether)∶V(ethyl acetate)=5∶1) as a yellow solid (39.7 mg, 59% yield). m.p. 208.8～211.7 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.98 (d, J=7.6 Hz, 1H), 8.44 (d, J=4.4 Hz, 1H), 8.41 (d, J=8.4 Hz, 1H), 7.81 (t, J=8.4 Hz, 1H), 7.56 (dd, J=8.4, 5.2 Hz, 1H), 7.52 (d, J=8.0 Hz, 1H), 7.40 (dd, J=4.4, 0.4 Hz, 2H), 7.38～7.32 (m, 2H), 7.15 (t, J=7.2 Hz, 2H), 7.12～7.05 (m, 3H), 6.88 (d, J=6.8 Hz, 2H), 2.78～2.72 (m, 2H), 2.71–2.65 (m, 2H); ^{13}C NMR

(101 MHz, $CDCl_3$) δ: 176.2, 141.6, 141.2, 140.3, 139.5, 136.6, 132.7, 131.6, 128.5, 128.1, 127.9, 127.7, 125.6, 122.4, 119.1, 117.4, 39.8, 31.7; IR (KBr) ν: 3082, 1645, 1510, 1386, 833, 713 cm^{-1}. HRMS (ESI) calcd for $C_{26}H_{22}BN_2OS_2$ $[M+H]^+$ 453.1261, found 453.1270.

2,2-Diphenyl-2*H*-2λ^4,3λ^4-[1,3,2]oxazaborolo[5,4,3-ij]quinolone (**3k**): The product was isolated by flash chromatography (V(petroleum ether)∶V(dichloromethane)∶V(ethyl acetate)=8∶1∶1) as a yellow solid (28.8 mg, 62% yield). m.p. 199.9～202.1 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.58 (d, J=4.8 Hz, 1H), 8.38 (d, J=8.4 Hz, 1H), 7.65 (t, J=8.0 Hz, 1H), 7.63～7.58 (m, 1H), 7.49～7.41 (m, 4H), 7.30～7.20 (m, 7H), 7.18 (d, J=7.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 158.8, 139.3, 138.8, 137.6, 132.9, 132.0, 128.5, 127.6, 127.0, 122.8, 112.2, 109.7.

1-(2,2-Diphenyl-2λ^4,3λ^4-[1,3,2]diazaborolo[4,5,1-ij]quinolin-1(2*H*)-yl)ethan-1-one (**3l**): The product was isolated by flash chromatography (V(petroleum ether)∶V(ethyl acetate)∶V(triethylamine)=3∶1∶0.3) as a yellow solid (36.8 mg, 70% yield). m.p. 220.4～222.0 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.93 (d, J=8.0 Hz, 1H), 8.38 (d, J=5.2 Hz, 1H), 8.30 (d, J=8.0 Hz, 1H), 7.75 (t, J=8.0 Hz, 1H), 7.56～7.40 (m, 6H), 7.33～7.19 (m, 6H), 1.92 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 174.4, 142.1, 139.6, 139.1, 137.6, 133.6, 132.6, 127.9, 127.6, 127.2, 122.5, 118.7, 117.1, 26.8; IR (KBr) ν: 3008, 1650, 1508, 1382, 1319, 1186, 825, 729 cm^{-1}. HRMS (ESI) calcd for $C_{23}H_{20}BN_2O$ $[M+H]^+$ 351.1663, found 351.1673.

1-(2,2-Diphenyl-2λ^4,3λ^4-[1,3,2]diazaborolo[4,5,1-ij]quinolin-1(2*H*)-yl)-2-methylprop-2-en-1-one (**3m**): The product was isolated by flash chromatography (V(petroleum ether)∶V(ethyl acetate)=3∶1) as a yellow solid (33.3 mg, 59% yield). m.p. 179.3～181.8 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.86 (d, J=7.6 Hz, 1H), 8.38～8.31 (m, 2H), 7.82 (t, J=8.0 Hz, 1H), 7.52 (dd, J=8.4, 0.8 Hz, 1H), 7.51～7.44 (m, 5H), 7.30～7.17 (m, 6H), 4.83 (s, 1H), 4.72～4.63 (m, 1H), 1.12 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 175.5, 142.8, 142.1, 139.8, 139.0, 137.7, 134.2, 132.4, 127.6, 127.5, 126.8, 122.6, 119.8, 117.8, 116.1, 19.9; IR (KBr) ν: 3068, 1623, 1508, 1382, 1234, 827, 707 cm^{-1}. HRMS (ESI) calcd for $C_{25}H_{22}BN_2O$ $[M+H]^+$ 377.1820, found 377.1829.

1-(2,2-Diphenyl-2λ^4,3λ^4-[1,3,2]diazaborolo[4,5,1-ij]quinolin-1(2*H*)-yl)but-3-en-1-one (**3n**): The product was isolated by flash chromatography (V(petroleum ether)∶V(ethyl acetate)=3∶1) as a yellow solid (42.4 mg, 75% yield). m.p. 221.6～223.7 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.96 (d, J=7.2 Hz, 1H), 8.44 (dd, J=5.2, 0.8 Hz, 1H), 8.39 (dd, J=8.4, 1.2 Hz, 1H), 7.80 (t, J=8.4 Hz, 1H), 7.57～7.53 (m, 1H), 7.53～7.47 (m, 5H), 7.32～7.30 (m, 1H), 7.30～7.26 (m, 4H), 5.75～5.62 (m, 1H), 4.91 (dd, J=10.4, 2.0 Hz, 1H), 4.71 (m, 1H), 2.99 (dt, J=6.9, 1.2 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 174.9, 142.0, 139.6, 139.1, 137.7, 135.7, 133.5, 132.7, 132.3, 128.0, 127.8, 127.6, 127.2, 122.5, 119.0, 117.4, 117.2, 43.0; IR (KBr) ν: 3070, 1639, 1512, 1386, 1269, 1168, 831, 707 cm^{-1}. HRMS (ESI) calcd for $C_{25}H_{22}BN_2O$ $[M+H]^+$ 377.1820, found 377.1826.

1-(4-Methyl-2,2-diphenyl-2l^4,3l^4-[1,3,2]diazaborolo-[4,5,1-ij]quinolin-1(2*H*)-yl)-3-phenylpropan-1-one (**3o**): The product was isolated by flash chromatography (V(petroleum ether)∶V(ethyl acetate)=3∶1) as a yellow solid (49.1 mg, 72% yield). m.p. 202.6～204.4 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ: 9.01 (d, J=7.6 Hz, 1H), 8.26 (d, J=8.4 Hz, 1H), 7.72 (t, J=8.4 Hz, 1H), 7.57～7.51 (m, 4H), 7.46 (d, J=8.0 Hz, 1H), 7.30～7.22 (m, 7H), 7.12 (t, J=6.8 Hz, 2H), 7.07 (t, J=6.8 Hz, 1H), 6.78 (d, J=6.8 Hz, 2H), 2.63～2.55 (m, 2H), 2.51～2.42 (m, 2H), 2.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 175.9, 153.8, 141.9, 141.7, 139.2, 138.2, 134.0, 131.3, 128.4, 128.1, 127.8, 127.0, 126.0, 125.5, 118.7, 117.3, 39.6, 31.3, 21.9; IR (KBr) ν: 3047, 1652, 1512, 1409, 1379, 1315, 840, 703 cm^{-1}. HRMS (ESI) calcd for $C_{31}H_{28}BN_2O$ $[M+H]^+$ 455.2289, found 455.2297.

1-(7-Bromo-2,2-diphenyl-2l^4,3l^4-[1,3,2]diazaborolo-[4,5,1-ij]quinolin-1(2*H*)-yl)-3-phenylpropan-1-one (**3p**): The product was isolated by flash chromatography (V(petroleum ether)∶V(dichloromethane)∶V(ethyl acetate)=2∶1∶0.1) as a yellow solid (66.8 mg, 86% yield). m.p. 177.8～181.2 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.90 (d, J=8.4 Hz, 1H), 8.63 (dd, J=8.4, 0.8 Hz, 1H), 8.47 (dd, J=5.2, 0.8 Hz, 1H), 8.01 (d, J=8.4 Hz, 1H), 7.64 (dd, J=8.4, 5.2 Hz, 1H), 7.50～7.44 (m, 4H), 7.32～7.26 (m, 6H), 7.17～7.11 (m, 2H), 7.11～7.05 (m, 1H), 6.83 (d, J=6.8 Hz, 2H), 2.65～2.59 (m, 2H), 2.57～2.50 m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 176.2, 141.9, 141.4, 140.3, 139.0, 138.4, 135.5, 133.4, 128.4, 128.1, 128.0, 127.4, 127.1, 125.6, 123.4, 119.5, 109.2, 39.8, 31.3; IR (KBr) ν: 3070, 1639, 1502, 1375, 1188, 779, 707 cm^{-1}. HRMS (ESI) calcd for $C_{30}H_{25}BBrN_2O$ $[M+H]^+$ 519.1238, found 519.1232.

1-(2,2-Diphenyl-7-(thiophen-3-yl)-2l^4,3l^4-[1,3,2]diazaborolo[4,5,1-ij]quinolin-1(2*H*)-yl)-3-phenylpropan-1-one (**3q**): The product was isolated by flash chromatography (V(petroleum ether)∶V(ethyl acetate)∶V(triethylamine)=3∶1∶0.3) as a yellow solid (62.2 mg, 79% yield). m.p. 234.4～237.1℃; ^1H NMR (400 MHz, $CDCl_3$) δ: 9.02 (d, J=8.0 Hz, 1H), 8.60 (dd, J=8.4, 0.8 Hz, 1H), 8.43 (dd, J=5.2, 1.2 Hz, 1H), 7.81 (d, J=8.0 Hz, 1H), 7.56～7.45 (m, 6H), 7.38 (dd, J=2.8, 1.2 Hz, 1H), 7.33～7.24 (m, 7H), 7.16～7.09 (m, 2H), 7.09～7.03 (m, 1H), 6.83 (d, J=6.8 Hz, 2H), 2.67～2.58 (m, 2H), 2.57～2.50 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 176.2, 141.5, 141.4, 139.7, 138.2, 138.0, 137.9, 133.5, 132.5, 128.7, 128.5, 128.1, 128.0, 127.2, 127.0, 126.3, 125.6, 125.6, 123.7, 122.5, 118.8, 39.9, 31.5; IR (KBr) ν: 3068, 1639, 1473, 1386, 1309, 1191, 783, 707 cm^{-1}. HRMS (ESI) calcd for $C_{34}H_{28}BN_2OS$ $[M+H]^+$ 523.2010, found 523.2005.

Supporting Information ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn/.

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