DOI: 10.1002/adsc.201600118
Advanced Synthesis & Catalysis

Expeditious and Convenient Synthesis of Polycyclic Difluoroboron Complexes of 2-Oxoindoline-3-carboxamides by Tandem Reaction

Shanyan Mo,[a] Chuangchuang Xu,[a] and Jiaxi Xu[a,*]

[a] State Key Laboratory of Chemical Resource Engineering, Department of Organic Chemistry, Faculty of Science, Beijing University of Chemical Technology, Beijing 100029, People's Republic of China
Fax: (+86)-10-6443-5565; phone: (+86)-10-6443-5565; e-mail: jxxu@mail.buct.edu.cn

Received: January 26, 2016; Revised: February 23, 2016; Published online: April 19, 2016

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/adsc.201600118.

Abstract: *N*-Aryl-2-cyanodiazoacetamides produce polycyclic difluoroboron 2-oxoindoline-3-carboxamide complexes (up to pentacyclic conjugative and fused systems) directly and expeditiously in the presence of boron trifluoride etherate. The boron trifluoride serves as both a catalyst and reactant in the tandem reaction. The tandem reaction includes the carbene aromatic C–H insertion, hydrolysis of the cyano group into an amide group, and boronation of the two amide carbonyl groups. The synthetic method features the advantages of wide substrate scope and excellent chemoselectivity.

Keywords: boron trifluoride; cyanoacetates; difluoroboron complexes; malonamides; 2-oxoindolines; tandem reaction

Introduction

Difluoroboron (BF_2) complexes of N,N- and N,O-based ligands are generally highly fluorescent substances in the solution, film, and solid state.[1] Recently, difluoroboron complexes of β-dicarbonyl compounds have been widely investigated.[2–5] β-Diketonates, possessing two carbonyls, can easily react with boron trifluoride etherate ($BF_3{\cdot}OEt_2$) to form six-membered heterocyclic difluoroboron complexes. By installing different substituted conjugative groups, large molar emission ratios and high quantum yields could be realized for the BF_2 complexes of β-diketonates, which could serve as photochemical reagents, two-photon materials, and near-IR probes.[2–5] Recently, various BF_2 complexes of β-diketonates,[2–5] β-keto esters,[6] and β-keto amides[7] have been synthesized and extensively studied. However, an investigation of malonamide-type BF_2 complexes is very rare.[8]

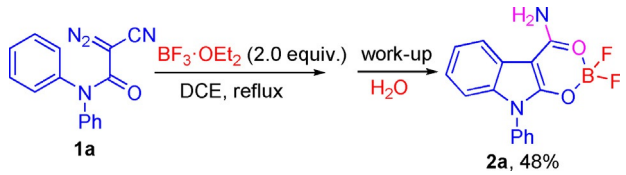
The carbene aromatic C–H insertion of diazoacetanilides, which generates a cyclic amide (lactam) functional group, is a powerful protocol for the oxindole skeleton construction.[9] It was reported that 2-cyano-2-diazoacetanilides produced 3-cyanooxindoles under the catalysis of Rh(II) compounds.[10] In addition, it was also described that the electrophilicity of the cyano group was improved by coordination with a Lewis acid,[11] resulting in favorable hydrolysis of the cyano group into an amide in the presence of water. Moreover, Lewis acids are also effective catalysts for carbene generation from diazo compounds.[12] Thus, we envisioned that Lewis acid $BF_3{\cdot}OEt_2$ could be applied as a catalyst first for the generation of 3-cyanooxindoles from 2-cyano-2-diazoacetanilides, secondly for hydrolysis of the cyano group into an amide, converting 3-cyanooxindoles into malonamide-type products 2-oxoindoline-3-carboxamides, and finally react with 2-oxoindoline-3-carboxamides to afford the corresponding BF_2 complexes of 2-oxoindoline-3-carboxamides.

Herein, we describe a tandem reaction to synthesize BF_2 complexes of 2-oxoindoline-3-carboxamides. In our approach, 2-cyano-2-diazoacetanilides **1** undergo a carbene aromatic C–H insertion, subsequent hydrolysis of the cyano group into an amide group, and finally, boronation of the two carbonyl groups, leading to the generation of the BF_2 complexes. The boron trifluoride etherate serves as a catalyst as well as a reactant. In the current method, a series of polyheterocyclic BF_2 complexes **2** of 2-oxoindoline-3-carboxamides **3** was synthesized.

Results and Discussion

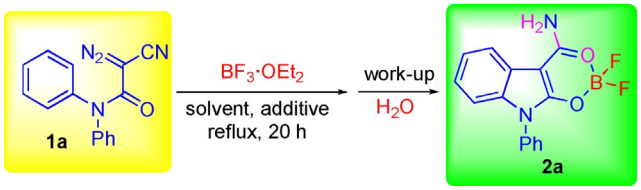
2-Cyano-2-diazoacetamides (**1**) were synthesized from 2-cyanoacetamides **4**, which were in turn prepared from cyanoacetic acid or cyanoacetic chloride and the corresponding secondary amines, by diazo transformation with the use of triflic azide under basic conditions. 2-Cyano-2-diazo-*N*-phenylacetanilide (**1a**) was selected as a model substrate and treated with $BF_3{\cdot}OEt_2$, affording the desired BF_2 complex of 1-phenyl-2-oxoindoline-3-carboxamide (**3a**), 4-amino-2,2-difluoro-9-phenyl-2,9-dihydro-[1,3,2]dioxaborinino[4,5-*b*]indol-3-ium-2-uide (**2a**), successfully in 48% yield after work-up in our first trial in 1,2-dichloroethane (DCE) (Scheme 1). The yield was improved to 77% in acetonitrile with 4-nitrophenol as an additive after optimization (Table 1, entry 15). The structure of **2a** was confirmed by ^{1}H, ^{13}C, ^{19}F, and ^{11}B NMR, IR, HR-MS, and X-ray diffraction analyses[13] (Figure 1).

For reaction optimization, several commonly used solvents were tested, revealing that acetonitrile was the best solvent for the reaction, while diethyl ether was almost completely not applicable (Table 1, entries 1–5). The loading amounts of $BF_3{\cdot}OEt_2$ were further screened, and the results indicated that better yields were obtained when 2.5 equivalents of $BF_3{\cdot}OEt_2$ were employed (Table 1, entries 6–9). To adjust the pH value for the hydrolysis of the cyano group, different protonic acids were added. Satisfactorily, except for *p*-nitrobenzoic acid, the addition of other protonic acids [TsOH, $(CF_3)_2CHOH$, *p*-$O_2NC_6H_4OH$] led to better yields, and *p*-nitrophenol was found to be the best additive for the reaction (Table 1, entries 11–13). After evaluating the loading



Scheme 1. Tandem reaction of 2-cyano-2-diazo-*N*,*N*-diphenylacetamide (**1a**).

Table 1. Optimization of the reaction conditions.



Entry	Solvent	$BF_3{\cdot}OEt_2$ (equiv.)	Additive (mol%)	Yield [%][a]
1	DCE	2.0	none	48
2	toluene	2.0	none	37
3	DCM	2.0	none	37
4	MeCN	2.0	none	57
5	ether	2.0	none	trace
6	MeCN	1.0	none	49
7	MeCN	1.5	none	54
8	MeCN	2.5	none	63
9	MeCN	3.0	none	61
10	MeCN	2.5	TsOH (10)	71
11	MeCN	2.5	*p*-$O_2NC_6H_4CO_2H$ (10)	56
12	MeCN	2.5	$(CF_3)_2CHOH$ (10)	66
13	MeCN	2.5	*p*-$O_2NC_6H_4OH$ (10)	72
14	MeCN	2.5	*p*-$O_2NC_6H_4OH$ (20)	75
15	MeCN	2.5	*p*-$O_2NC_6H_4OH$ (15)	77
16	MeCN	2.5	*p*-$O_2NC_6H_4OH$ (5)	72

[a] Isolated yield after flash chromatography. All reactions were performed on 0.38 mmol (100 mg) scale in 5 mL of solvent.

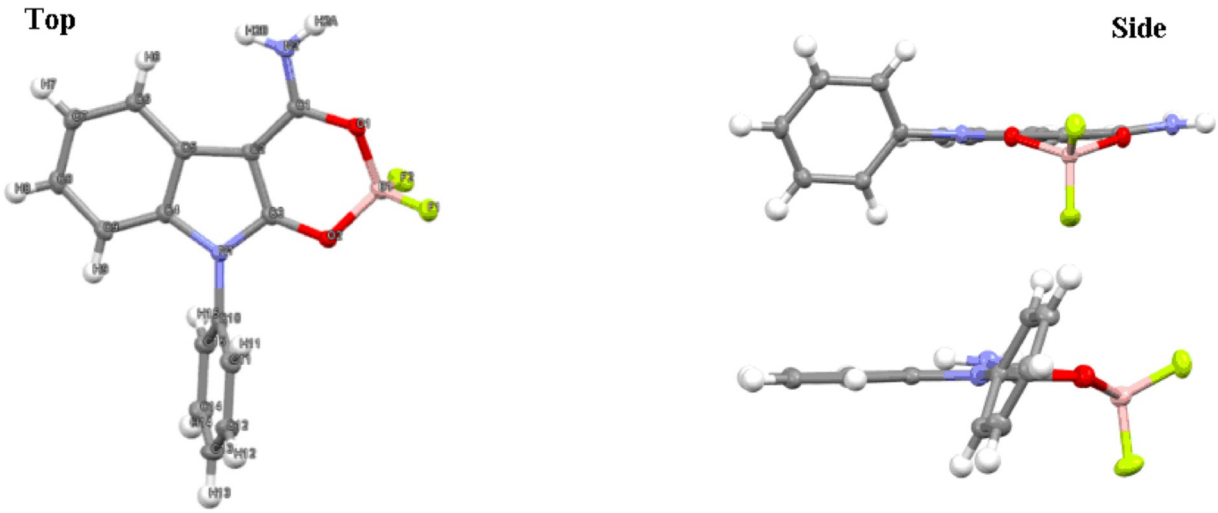
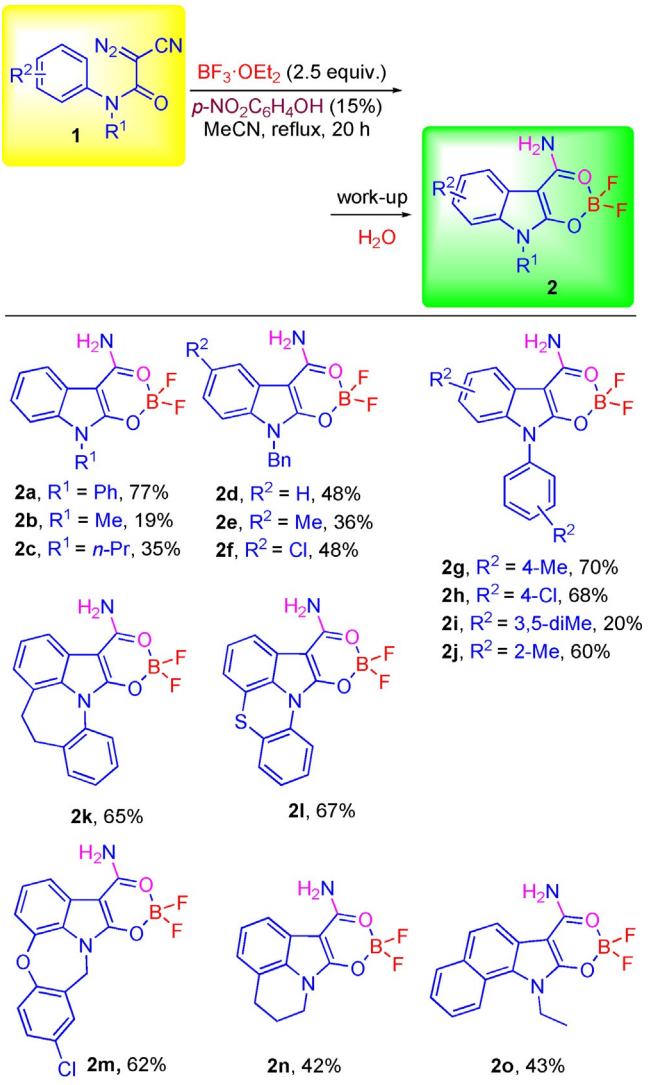


Figure 1. X-ray diffraction analytical structure of the BF_2 complex (**2a**) of 1-phenyl-2-oxoindoline-3-carboxamide (**3a**).

Table 2. Substrate scope.[a]

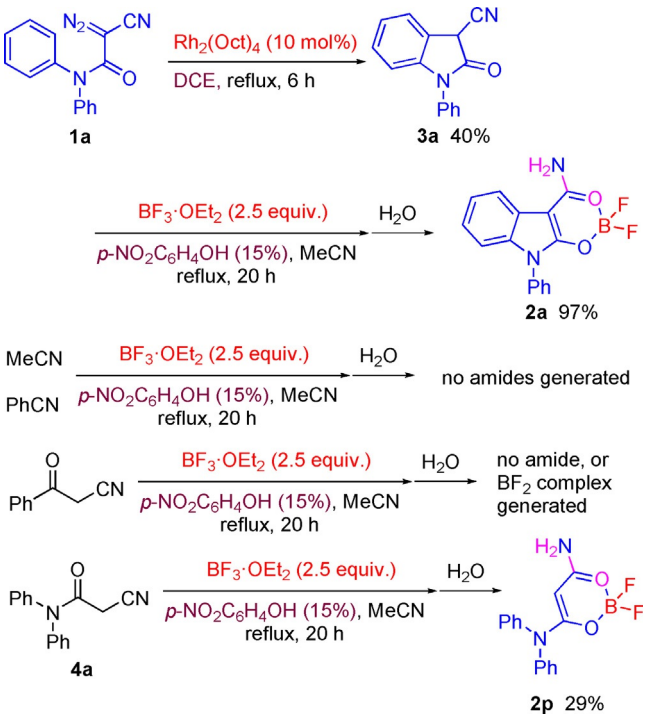


[a] Isolated yield. All reactions were performed under the optimized conditions on a 100 mg scale of **1**.

amount of the additive, the optimal yield of 77% was achieved when 15% of the additive was utilized (Table 1, entries 13–16).

After establishing the optimal reaction conditions, the substrate scope was examined with a diverse array of 2-cyano-2-diazoacetanilides **1**, and the results are summarized in Table 2. The effect of the *N*-substituent group was investigated. The results indicate that the substrates with *N*-alkyl and *N*-benzyl groups produced the corresponding desired products exclusively, showing excellent chemospecificity, only aromatic C–H insertion occurred (Table 2, **2a**–**2d**). The electronic effect of the substituents on the aromatic ring does not affect the yields obviously in the reactions (Table 2, **2d–2f**, **2g**, **2h**, **2j**). The steric effect of the substituents on the aromatic ring was also studied. Not surprisingly, all of them were converted into the desired products **2**. The substrate **1i** with 3,5-dimethyl groups on the aromatic ring furnished product **2i** in only 20% yield due to steric bulkiness (Table 2, **2i**). The reactions of 2-cyano-2-diazoacetanilides **1k–1n** derived from cyclic secondary amines were all successful, producing polycyclic BF_2 complexes **2k–2n** in 42–67% yields (Table 2, **2k–2n**). The *N*-naphthyl substituted substrate **1o** afforded the polycyclic BF_2 complex as well (Table 2, **2o**).

To get a mechanistic insight of the reaction, some designed experiments were conducted. At first, we used $Rh_2(Oct)_4$ (dirhodium tetraoctanoate) instead of $BF_3{\cdot}OEt_2$ as the catalyst for the model reaction.[10] 3-Cyano-1-phenyl-2-oxindole (**3a**) was obtained in 40% yield and it was further converted into the BF_2 complex **2a** under the optimized reaction conditions in the presence of $BF_3{\cdot}OEt_2$, indicating that the tandem reaction intermediate is 3-cyano-1-phenyl-2-oxindole (**3a**). To verify hydrolysis of the cyano group under the catalysis of $BF_3{\cdot}OEt_2$, acetonitrile, benzonitrile, 2-cyanoacetophenone, and 2-cyano-*N*,*N*-diphenylacetamide (**4a**) were examined under the optimal reaction conditions. The results reveal that no reaction occurred for acetonitrile, benzonitrile, and 2-cyanoacetophenone. However, 2-cyano-*N*,*N*-diphenylacetamide (**4a**) was partially converted into the corresponding BF_2 complex (**2p**) of *N*,*N*-diphenylmalonamide in 29% yield after work-up (Scheme 2). The results indicate that the rigid vicinal *cis*-hydroxy (or carbonyl, which can enolize into hydroxy) group is required for

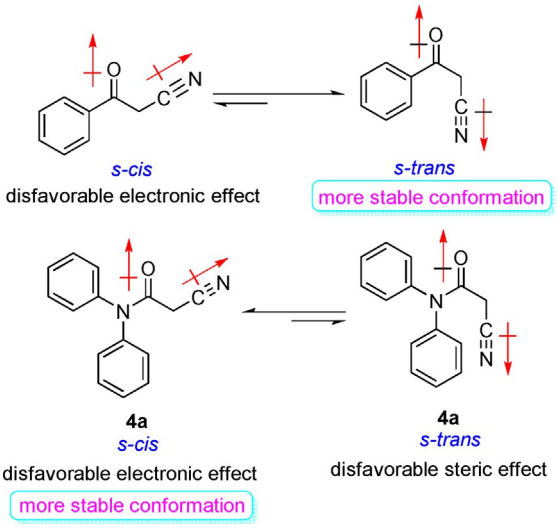


Scheme 2. Designed reactions for investigations on the mechanism of the tandem reaction.

hydrolysis of the cyano group. Even freely rotable vicinal oxo nitriles cannot be hydrolyzed in the presence of boron trifluoride.

Simple nitriles, such as acetonitrile and benzonitrile, which lack the chelating coordination sites, cannot be hydrolyzed under the catalysis of boron trifluoride. A freely rotatable vicinal oxo nitrile, 2-cyanoacetophenone, is also inert for the BF_3-catalyzed hydrolysis. However, 2-cyano-*N,N*-diphenylacetamide (**4a**) can be partially hydrolyzed under the same conditions, further generating difluoroboron complex (**2p**) in 29% yield after work-up (Scheme 2).

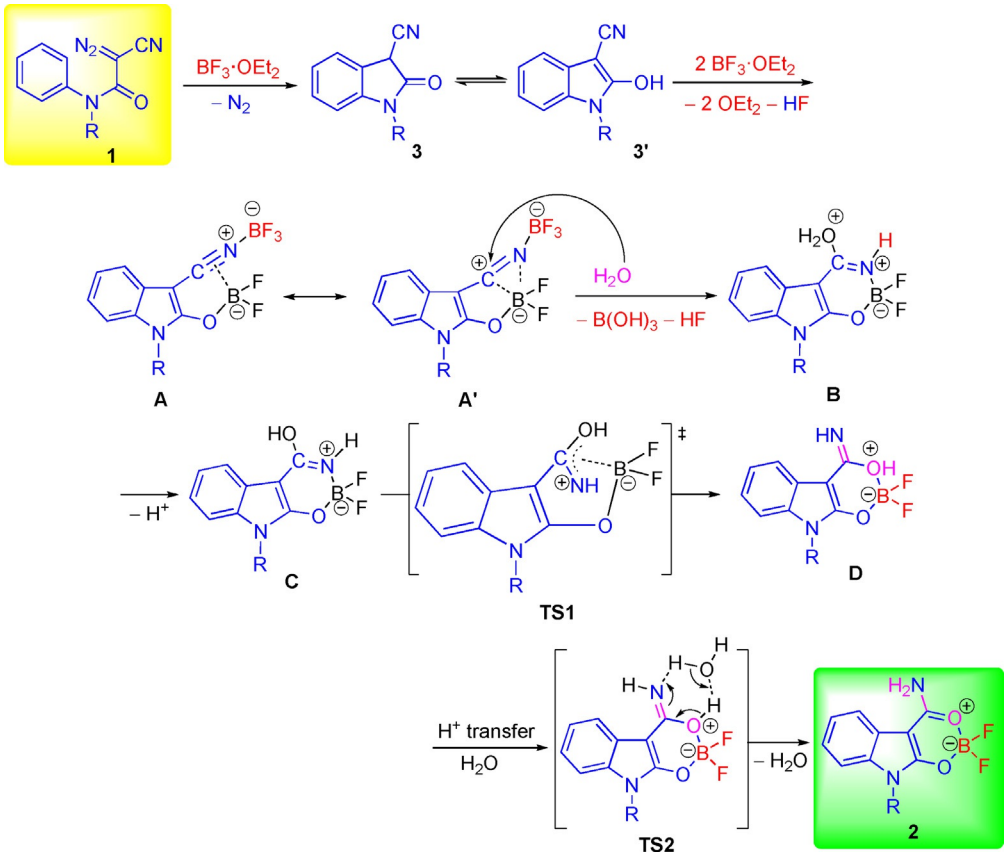
After carefully analyzing their structural features, we can rationalize that the *s-cis* conformation of the oxo and cyano groups in the substrates is required for the hydrolysis. 2-Cyanoacetophenone favorably exists in the *s-trans* conformation due to the lower molecular dipole moment (electronic repulsion). However, 2-cyano-*N,N*-diphenylacetamide (**4a**) exists in both *s-cis* and *s-trans* conformations due to the balance between molecular dipole moment and steric hindrance. This is the reason why cyanoacetamide **4a** can be partially hydrolyzed and 2-cyanoacetophenone cannot under BF_3-catalysis (Scheme 3). In the *s-cis* conformation, the boron atom of difluoroborate, generated from boron trifluoride and enol of **4a**, can coordinate with one of the π bonds in the cyano group. The coordination increases the electrophilicity of the cyano group



Scheme 3. Rationale for the BF_3-catalyzed hydrolysis of 2-cyano-*N,N*-diphenylacetamide (**4a**).

in cyanoacetamide **4a**, which is favorably hydrolyzed by water. The fact that 3-cyano-1-phenyl-2-oxindole (**3a**) can be efficiently hydrolyzed can thus be understood, since its oxo and cyano groups are locked in an *s-cis* conformation.

We thus propose the tandem reaction mechanism as shown in Scheme 4. An aromatic carbene C–H in-

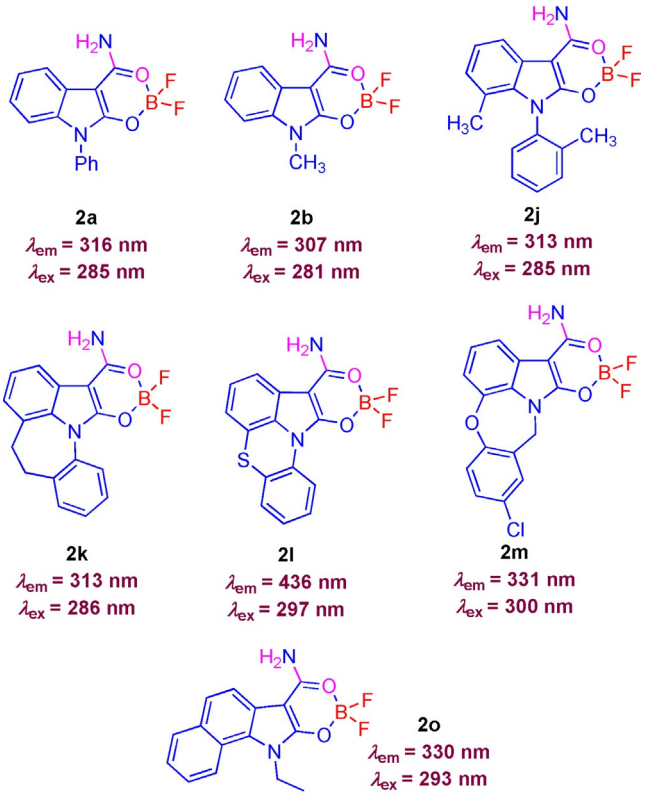


Scheme 4. Proposed mechanism for the tandem reaction.

sertion of 2-diazo-2-cyanoacetanilides **1** catalyzed by the Lewis acid $BF_3{\cdot}OEt_2$ provides 3-cyanooxindoles **3**, which tautomerize into 2-hydroxyindoles **3′**. Subsequently, the hydroxy group of **3′** reacts with BF_3 and another molecule of BF_3 coordinates with the cyano group of **3′**, leading to the formation of difluoroborates **A**, in which the boron atom in the difluoroborate group also coordinates with one of the π bonds of the cyano group. The difluoroborates **A** can resonate into unsaturated azaboririne forms **A′**, activating in the original C≡N bond. During work-up, water attacks the carbon atom of the azaboririne ring in resonance forms **A′** nucleophilically through a nucleophilic three-membered ring opening reaction.[14] Meanwhile, because the coordination between the cyano group and BF_3 is just Lewis acid-base bonding, which is reversible, water destroys the C≡N–BF_3 complexes, resulting in the formation of intermediates **B**, which can lose a proton to give intermediates **C**. The intermediates **C** favorably convert into intermediates **D** through transition states **TS1** because the boron atom is a hard acid and the oxygen atom is a harder base than the nitrogen atom, based on Pearson's hard and soft acid-base concept. The intermediates **D** undergo a water-participating proton transfer to give rise to the final products **2** through six-membered ring transition states **TS2** because the direct proton 1,3-shift is orbital-symmetry forbidden. The protonic solvent-participating proton transfer has been observed and rationalized previously in our studies on Claisen and benzidine rearrangements.[15] The difluoroboron complexes **2** show better stability to water during work-up. The above mechanistic analysis reveals that the boron atom shows more stable coordination with the oxygen atom than with the nitrogen atom. Thus, the function of the additive 4-nitrophenol in the reaction can be rationalized as follows: it first reacts with BF_3 to generate 4-nitrophenyl difluoroborate, which is a softer acid comparing with BF_3 and coordinates better with the soft nitrogen atom in the cyano group, promoting more efficient hydrolysis of the cyano group (the step from **A′** to **B** in Scheme 4).

The fluorescence properties of representative BF_2 complexes **2** were measured (Table 3). The results showed that the measured products exhibit low emission wavelengths (λ_{em} = 307–436 nm) and excitation wavelengths (λ_{ex} = 281–300 nm). With different R^1 and R^2 substituents, the λ_{em} and λ_{ex} values of BF_2 complexes **2a**, **2b**, **2j**, and **2k** are almost the same. The BF_2 complexes **2m** and **2o** show higher λ_{em} and λ_{ex} than **2a**, **2b**, **2j**, and **2k**, but lower than **2l**. BF_2 complex **2l** shows the highest λ_{em}, presumably due to the good conjugative property of its structure. Thus, the fluorescence properties indicate that installation of more conjugative and fused rings are required to get higher λ_{em}.[16]

Table 3. Fluorescence properties of representative difluoroboron complexes **2**.[a]



[a] Measured at a concentration of 1.0×10^{-5} dm^{-3} at 25 °C with DMSO as solvent.

Conclusions

We have developed an expeditious and convenient synthesis of difluoroboron complexes of oxindole-3-carboxamides from 2-cyanodiazoacetanilides and boron trifluoride etherate. This tandem reaction includes carbene aromatic C–H insertion, hydrolysis of nitriles, and boronation of two carbonyl groups. The boron trifluoride serves as a catalyst as well as a reactant. The reaction mechanism is proposed on the basis of some designed experiments. The current method provides an efficient way to prepare the difluoroboron complexes of malonamide-type compounds from 2-cyanodiazoacetanilides.

Experimental Section

General Information

Melting points were measured on a Yanaco MP-500 melting point apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer. Chemical shifts are reported in ppm with TMS as an inter-

nal standard. ^{31}F and ^{11}B NMR spectra were recorded at 375 MHz and 193 MHz on Bruker 400 MHz and 600 MHz spectrometers, respectively, with $BF_3{\cdot}OEt_2$ as an external standard. The IR spectra (KBr pellets, ν [cm^{-1}]) were taken on a Nicolet 370 MCT FT-IR spectrometer. The high resolution mass spectra were obtained with ESI ionization using an Agilent LC/MSD TOF mass spectrometer. Column chromatography was carried out on silica gel (200–300 mesh) with petroleum ether (PE, 60 °C-90 °C) and ethyl acetate (EA) as the eluent. All reactions were followed by thin-layer chromatography (TLC) where practical, using silica gel 60 F_{254} fluorescent treated silica gel plates, which were visualized under UV light (254 nm). For the reactions conducted under anhydrous conditions, solvents were refluxed with drying reagents and freshly distilled prior to use. Dichloromethane (DCM) and acetonitrile were dried over calcium hydride. 1,2-Dichloroethane (DCE) and chloroform were dried by phosphorus pentoxide. Toluene and benzene were dried over sodium wire with benzophenone as an indicator. Reagents used were obtained from commercial suppliers and used without purification except triethylamine (TEA) which was dried over calcium hydride and freshly distilled prior to use.

General Procedure for the Preparation of 2-Cyanoacetamides 4a–i and 4m–o using DCC/DMAP as Condensation Reagent[17]

To a solution of a secondary amine (10 mmol) and 2-cyanoacetic acid (93.5 mg, 11 mmol) in CH_2Cl_2 (10 mL) was added a solution of DCC (*N,N'*-dicyclohexylcarbodiimide, 226.6 mg, 11 mmol) and DMAP [4-(*N,N*-dimethylamino)pyridine, 6 mg, 0.05 mmol] in CH_2Cl_2 (20 mL) at 0 °C. The resulting solution was stirred for 1 h. During this period a white solid (1,3-dicyclohexylurea, DCU) was precipitated which was subsequently filtered. After removal of the solvent under reduced pressure, the resulting crude product was recrystallized from EtOH to afford the pure amide 4.

2-Cyano-*N,N*-diphenylacetamide (4a): yield: 2.00 g (88%, 10 mmol scale); colorless crystals; mp 161–162 °C, Lit.[18] 154–156 °C; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.47–7.23 (m, 10 H), 3.41 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.6, 141.4, 130.5, 129.1, 128.4, 126.9, 125.8, 113.9, 26.7; IR (KBr): ν = 2260 (CN), 1676 cm^{-1} (C=O).

2-Cyano-*N*-methyl-*N*-phenylacetamide (4b): yield: 1.43 g (82%, 10 mmol scale); colorless crystals; mp 87–89 °C, Lit.[19] 76–79 °C; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.51–7.47 (m, 2 H), 7.45–7.41 (m, 1 H), 7.26–7.23 (m, 2 H), 3.32 (s, 3 H), 3.25 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.6, 142.3, 130.4, 128.9, 127.0, 114.1, 37.8, 25.3; IR (KBr): ν = 2259 (CN), 1668 cm^{-1} (C=O).

2-Cyano-*N*-phenyl-*N*-propylacetamide (4c): yield: 1.84 g (91%, 10 mmol scale); colorless crystals; mp 60–64 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.51–7.42 (m, 3 H), 7.23–7.21 (m, 2 H), 3.69 (t, J = 7.6 Hz, 2 H), 3.19 (s, 2 H), 1.56 (sixtet, J = 7.6 Hz, 2 H), 0.91 (t, J = 7.6 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.4, 140.9, 130.3, 129.0, 127.9, 114.2, 51.5, 25.7, 20.6, 11.0; IR (KBr): ν = 2254 (CN), 1670 cm^{-1} (C=O); HR-MS (ESI): m/z = 203.1179, calcd. for $C_{12}H_{15}N_2O$ ($[M+H]^+$): 203.1179.

***N*-Benzyl-2-cyano-*N*-phenylacetamide (4d):** yield: 1.25 g (50%, 10 mmol scale); colorless crystals; mp 94–97 °C, Lit.[18] 91–94 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.37 (m, 3 H), 7.32–7.22 (m, 3 H), 7.22–7.11 (m, 2 H), 7.07–6.91 (m, 2 H), 4.89 (s, 2 H), 3.21 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.7, 140.6, 136.1, 130.2, 129.2, 129.1, 128.5, 128.2, 127.9, 114.1, 53.7, 25.7; IR (KBr): ν = 2259 (CN), 1664 cm^{-1} (C=O).

***N*-Benzyl-2-cyano-*N*-(*p*-tolyl)acetamide (4e):** yield: 2.53 g (96%, 10 mmol scale); colorless crystals; mp 104–106 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.25 (m, 3 H), 7.19–7.15 (m, 4 H), 6.87–6.84 (m, 2 H), 4.86 (s, 2 H), 3.21 (s, 2 H), 2.35 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.8, 139.3, 137.9, 136.2, 130.8, 129.0, 128.5, 127.9, 127.8, 114.1, 53.7, 25.7, 21.1; IR (KBr): ν = 2259 (CN), 1670 cm^{-1} (C=O); HR-MS (ESI): m/z = 265.1335, calcd. for $C_{17}H_{17}N_2O$ ($[M+H]^+$): 265.1335.

***N*-Benzyl-*N*-(4-chlorophenyl)-2-cyanoacetamide (4f):** yield: 4.6 g (84%, 19 mmol scale); colorless crystals; mp 100–102 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.35 (d, J = 8.5 Hz, 2 H), 7.31–7.24 (m, 3 H), 7.19–7.13 (m, 2 H), 6.94 (d, J = 8.5 Hz, 2 H), 4.86 (s, 2 H), 3.22 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.5, 138.9, 135.7, 135.2, 130.4, 129.6, 129.0, 128.6, 128.0, 113.9, 53.7, 25.7; IR (DCM): ν = 2261 (CN), 1673 cm^{-1} (C=O); HR-MS (ESI): m/z = 307.0620, calcd. for $C_{16}H_{13}ClN_2NaO$ ($[M+Na]^+$): 307.0609.

2-Cyano-*N,N*-di(*p*-tolyl)acetamide (4g): yield: 1.02 g (46%, 8.3 mmol scale); colorless crystals; mp 78–80 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.09 (m, 8 H), 3.40 (s, 2 H), 2.38 (s, 3 H), 2.31 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.7, 139.2, 139.1, 138.9, 136.7, 131.0, 129.7, 128.0, 125.6, 114.1, 26.6, 21.0, 20.9; IR (KBr): ν = 2260 (CN), 1674 cm^{-1} (C=O); HR-MS (ESI): m/z = 287.1167, calcd. for $C_{17}H_{16}N_2NaO$ ($[M+Na]^+$): 287.1155.

***N,N*-Di(4-chlorophenyl)-2-cyanoacetamide (4h):** yield: 1.23 g (66%, 6.1 mmol scale); colorless crystals; mp 138–140 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.18 (m, 8 H), 3.42 (s, 2 H).^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.6, 131.0, 129.7, 129.4, 127.1, 113.6, 26.8; IR (KBr): ν = 2260 (CN), 1681 cm^{-1} (C=O); HR-MS (ESI): m/z = 305.0247, calcd. for $C_{15}H_{10}Cl_2N_2O$ ($[M+H]^+$): 305.0243.

2-Cyano-*N,N*-di(3,5-dimethylphenyl)acetamide (4i): yield: 1.09 g (67%, 5.5 mmol scale); colorless crystals; mp 205–207 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.03–6.85 (m, 6 H), 3.40 (s, 2 H), 2.34 (s, 6 H), 2.28 (s, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.7, 141.3, 140.3, 138.8, 130.6, 128.8, 125.7, 123.7, 114.1, 26.5, 21.2; IR (KBr): ν = 2258 (CN), 1686 cm^{-1} (C=O); HR-MS (ESI): m/z = 293.1660, calcd. for $C_{19}H_{21}N_2O$ ($[M+H]^+$): 293.1648.

3-(2-Chlorodibenzo[*b,f*][1,4]oxazepin-10(11*H*)-yl)-3-oxopropanenitrile (4m): yield: 0.30 g (75%, 1.34 mmol scale); colorless crystals; mp 166–168 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.43 (m, 1 H), 7.37–7.34 (m, 2 H), 7.31–7.27 (m, 1 H), 7.22–7.19 (m, 1 H), 7.14 (d, J = 8.8 Hz, 2 H), 5.69 (s, 1 H), 4.26 (s, 1 H), 3.39 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.7, 153.3, 152.1, 132.6, 130.9, 128.8, 128.7, 128.7, 127.7, 125.9, 125.7, 122.5, 122.4, 113.5, 48.6, 25.3; IR (KBr): ν = 2261 (CN), 1685 cm^{-1} (C=O); HR-MS (ESI):299.0598, m/z = calcd. for $C_{16}H_{12}ClN_2O_2$ ($[M+H]^+$): 299.0582.

3-(3,4-Dihydroquinolin-1(2*H*)-yl)-3-oxopropanenitrile (4n): yield: 0.88 g (88%, 5 mmol scale); colorless oil; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.26–7.04 (m, 4 H), 3.82 (s, 2 H), 3.65 (s, 2 H), 2.74 (s, 2 H), 2.04–1.96 (m, 2 H); ^{13}C NMR

(100 MHz, $CDCl_3$): δ = 161.3, 137.6, 134.6, 128.8, 126.7, 123.6, 114.2, 43.4, 26.4, 25.8, 23.6; IR (KBr): ν = 2258 (CN), 1667 cm^{-1} (C=O); HR-MS (ESI): m/z = 223.0853, calcd. for $C_{12}H_{12}N_2NaO$ ($[M+H]^+$): 223.0842.

2-Cyano-*N*-ethyl-*N*-(naphthalen-1-yl)acetamide (4o): yield: 0.76 g (64%, 5 mmol scale); colorless crystals; mp 95–97 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.98–7.95 (m, 2H), 7.78 (d, J = 8.0 Hz, 1H), 7.66–7.59 (m, 2H), 7.57–7.52 (m, 1H), 7.40 (d, J = 7.2 Hz, 1H), 4.27 (dq, J = 14.1, 7.2 Hz, 1H), 3.51 (dq, J = 14.1, 7.2 Hz, 1H), 3.17 (dd, J = 18.2, 0.8 Hz, 1H), 3.00 (d, J = 18.2 Hz, 1H), 1.21 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.2, 136.5, 134.9, 130.0, 129.9, 129.0, 128.2, 127.2, 126.7, 125.7, 121.6, 114.1, 44.8, 25.5, 13.1; IR (KBr): ν = 2259 (CN), 1671 cm^{-1} (C=O); HR-MS (ESI): m/z = 239.1198, calcd. for $C_{15}H_{15}N_2O$ ($[M+H]^+$): 239.1198.

General Procedure for the Preparation of 2-Cyanoacetamides 4j–l using 2-Cyanoacetic Chloride as Acylating Reagent[19]

To a stirred suspension of 2-cyanoacetic acid (553 mg, 6.5 mmol) in CH_2Cl_2 (25 mL) was added oxalyl chloride (762 mg, 6 mmol) followed by seven drops of DMF at 0 °C. The reaction mixture was stirred at room temperature for 3 h.

To the above clear pale yellow solution was added a solution of a secondary amine (5 mmol) in dichloromethane (20 mL) followed by triethylamine (1.26 g, 12.5 mmol) at 0 °C. The reaction mixture was stirred for 24 hrs and then washed with water (25 mL) and 1 mol/L HCl (25 mL). The organic layer was dried over $MgSO_4$ and then evaporated. The resulting residue was purified by silica gel chromatography (petroleum ether/EtOAc, *v/v,* 6:1–2:1) to give the amide **4**.

2-Cyano-*N*,*N*-di(*o*-tolyl)acetamide (4j): yield: 0.26 g (26%, 3.8 mmol scale); colorless crystals; mp 179–180 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.33–7.24 (m, 5H), 7.17 (td, J = 7.5, 1.2 Hz, 1H), 7.10 (td, J = 7.7, 1.1 Hz, 1H), 6.91–6.88 (m, 1H), 3.39 (s, 2H), 2.38 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.1, 140.5, 139.4, 135.5, 134.9, 132.5, 131.4, 129.2, 129.0, 127.8, 127.4, 126.6, 125.9, 113.8, 26.1, 19.0, 18.1; IR (KBr): ν = 2258 (CN), 1681 cm^{-1} (C=O); HR-MS (ESI): m/z = 265.1345, calcd. for $C_{17}H_{17}N_2O$ ($[M+H]^+$): 265.1335.

3-(10,11-Dihydro-5*H*-dibenzo[*b*,*f*]azepin-5-yl)-3-oxopropanenitrile (4k): yield: 0.86 g (66%, 5 mmol scale); colorless crystals; mp 192–194 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.14 (m, 8H), 3.54–3.27 (m, 4H), 2.91–2.82 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.7, 140.7, 138.9, 137.9, 134.2, 130.8, 130.5, 129.6, 128.1, 128.0, 127.9, 127.0, 126.8, 113.7, 30.7, 30.1, 25.7; IR (KBr): ν = 2259 (CN), 1679 cm^{-1} (C=O); HR-MS (ESI): m/z = 263.1190, calcd. for $C_{17}H_{17}N_2O$ ($[M+H]^+$): 263.1179.

3-Oxo-3-(10*H*-phenothiazin-10-yl)propanenitrile (4l): yield: 0.80 g (60%, 5 mmol scale); colorless crystals; mp 202–204 °C; ^1H NMR (400 MHz, DMSO-d_6): δ = 7.68 (d, J = 7.0 Hz, 2H), 7.61 (dd, J = 7.7, 1.2 Hz, 2H), 7.44 (ddd, J = 7.7, 7.0, 1.2 Hz, 2H), 7.36 (dd, J = 7.0, 7.0 Hz, 2H), 4.17 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 162.3, 137.3, 128.1, 127.6, 127.0, 115.2, 26.4; IR (KBr): ν = 2259 (CN), 1670 cm^{-1} (C=O); HR-MS (ESI): m/z = 267.0583, calcd. for $C_{15}H_{11}N_2OS$ ($[M+H]^+$): 267.0587.

General Procedure for the Synthesis of 2-Cyano-2-diazoacetamides 1 *via* Diazo Transformation[20]

Sodium azide (2.34 g, 36 mmol) was dissolved in a mixture of H_2O (10 mL) and CH_2Cl_2 (5 mL) and the resulting solution was cooled to 0 °C in an ice-water bath. To this vigorously stirred solution was added triflic anhydride (1 mL, 6 mmol) dropwise through a syringe during 10 min. After being stirred at 0 °C for 2 h, the organic phase was separated and the aqueous phase was extracted with 5 mL of CH_2Cl_2. The combined organic phase was washed with 10 mL of saturated aqueous $NaHCO_3$, then dried over Na_2SO_4 and used in the next step immediately.

An amide **4** (5 mmol) was dissolved in 10 mL of CH_3CN, then the freshly prepared solution of triflic azide in CH_2Cl_2 was added under N_2 at 0 °C with cooling in an ice-water bath. After addition of triethylamine (758 mg, 7.5 mmol) the resulting mixture was stirred at room temperature for 18 h. The solution was concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography to give the pure product **1**.

2-Cyano-2-diazo-*N*,*N*-diphenylacetamide (1a): yield: 1.20 g (92%, 5 mmol scale); yellow crystals; mp 96–99 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.43–7.38 (m, 4H), 7.36–7.33 (m, 2H), 7.28–7.25 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.8, 141.3, 129.7, 128.1, 127.4, 106.9; IR (DCM): ν = 2218 (CN), 2129 (CN_2), 1735 cm^{-1} (C=O); HR-MS (ESI): m/z = 263.0925, calcd. for $C_{15}H_{11}N_4O$ ($[M+H]^+$): 263.0927.

2-Cyano-2-diazo-*N*-methyl-*N*-phenylacetamide (1b):[17] yield: 0.90 g (90%, 5 mmol scale); yellow oil; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.48–7.44 (m, 3H), 7.29–7.24 (m, 2H), 3.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.2, 141.2, 130.1, 129.5, 127.7, 107.2, 39.1; IR (DCM): ν = 2180 (CN), 2135 (CN_2), 1729 cm^{-1} (C=O).

2-Cyano-2-diazo-*N*-phenyl-*N*-propylacetamide (1c): yield: 1.02 g (90%, 5 mmol scale); yellow oil; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.48–7.43 (m, 3H), 7.26–7.21 (m, 2H), 3.72 (t, J = 7.6 Hz, 2H), 1.59 (sixtet, J = 7.6 Hz, 2H), 0.92 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.9, 139.7, 130.0, 129.6, 128.7, 107.2, 52.8, 20.8, 11.0; IR (DCM): ν = 2216 (CN), 2125 (CN_2), 1729 cm^{-1} (C=O); HR-MS (ESI): m/z = 229.1083, calcd. for $C_{12}H_{13}N_4O$ ($[M+H]^+$): 229.1084.

***N*-Benzyl-2-cyano-2-diazo-*N*-phenylacetamide (1d):** yield: 1.24 g (90% yield, 5 mmol scale); yellow crystals; mp 46–47 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.40 (m, 1H), 7.38–7.34 (m, 2H), 7.30–7.26 (m, 3H), 7.21–7.19 (m, 2H), 7.07–7.05 (m, 2H), 4.93 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.3, 139.5, 136.1, 129.9, 129.7, 128.9, 128.5, 127.9, 107.0, 54.9; IR (DCM): ν = 2215 (CN), 2121 (CN_2), 1638 cm^{-1} (C=O); HR-MS (ESI): m/z = 277.1092, calcd. for $C_{16}H_{13}N_4O$ ($[M+H]^+$): 277.1084.

***N*-Benzyl-2-cyano-2-diazo-*N*-(*p*-tolyl)acetamide (1e):** yield: 1.00 g (69%, 5 mmol scale); yellow crystals; mp 95–96 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.25 (m, 3H), 7.21–7.19 (m, 2H), 7.15 (d, J = 8.0 Hz, 2H), 6.92 (d, J = 8.0 Hz, 2H), 4.89 (s, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.4, 140.0, 136.8, 136.2, 130.4, 128.9, 128.6, 128.5, 127.8, 107.2, 54.9, 21.2; IR (DCM): ν = 2213 (CN),

2124 (CN_2), 1724 cm^{-1} (C=O); HR-MS (ESI): m/z = 291.1244, calcd. for $C_{17}H_{15}N_4O$ ($[M+H]^+$): 291.1240.

***N*-Benzyl-*N*-(4-chlorophenyl)-2-cyano-2-diazoacetamide (1f):** yield: 1.42 g (91%, 5 mmol scale); yellow crystals; mp 103–105 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.33 (d, J = 8.6 Hz, 2H), 7.31–7.26 (m, 3H), 7.21–7.14 (m, 2H), 6.97 (d, J = 8.6 Hz, 2H), 4.89 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.2, 137.9, 135.7, 135.7, 130.2, 130.1, 128.9, 128.6, 128.1, 107.0, 54.8; IR (DCM): ν = 2216 (CN), 2124 (CN_2), 1638 cm^{-1} (C=O); HR-MS (ESI): m/z = 311.0704, calcd. for $C_{16}H_{12}ClN_4O$ ($[M+H]^+$): 311.0694.

2-Cyano-2-diazo-*N*,*N*-di(*p*-tolyl)acetamide (1g): yield: 555 mg (95%, 2 mmol scale); yellow crystals; mp 100–103 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.19 (d, J = 8.4 Hz, 4H), 7.13 (d, J = 8.4 Hz, 4H), 2.36 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.7, 138.9, 130.2, 127.0, 126.1, 107.1, 21.1; IR (DCM): ν = 2216 (CN), 2124 (CN_2), 1650 cm^{-1} (C=O); HR-MS (ESI): m/z = 291.1249, calcd. for $C_{17}H_{15}N_4O$ ($[M+H]^+$): 291.1240.

***N*,*N*-Di(4-chlorophenyl)-2-cyano-2-diazoacetamide (1h):** yield: 331 mg (50%, 2 mmol scale); yellow crystals; mp 125–128 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.38 (d, J = 8.7 Hz, 4H), 7.17 (d, J = 8.7 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9, 139.4, 134.2, 130.0, 128.4, 106.7; IR (DCM): ν = 2218 (CN), 2133 (CN_2), 1648 cm^{-1} (C=O): HR-MS (ESI): m/z = 331.0156, calcd. for $C_{15}H_9Cl_2N_4O$ ($[M+H]^+$): 331.0148.

2-Cyano-2-diazo-*N*,*N*-di(3,5-dimethylphenyl)acetamide (1i): yield: 492 mg (77%, 2 mmol scale); yellow crystals; mp 149–151 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 6.97 (s, 2H), 6.87 (s, 4H), 2.30 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.6, 141.1, 139.4, 129.8, 125.0, 107.1, 21.2; IR (DCM): ν = 2215 (CN), 2120 (CN_2), 1647 cm^{-1} (C=O); HR-MS (ESI): m/z = 319.1571, calcd. for $C_{19}H_{19}N_4O$ ($[M+H]^+$): 319.1553.

2-Cyano-2-diazo-*N*,*N*-di(*o*-tolyl)acetamide (1j): yield: 264 mg (91%, 1 mmol scale); yellow crystals; mp 61–63 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.26 (m, 5H), 7.21–7.07 (m, 2H), 6.88–6.82 (m, 1H), 2.37 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.3, 139.8, 134.6, 132.3, 131.2, 129.5, 127.2, 126.8, 125.9, 106.8, 18.7, 18.0; IR (DCM): ν = 2216 (CN), 2130 (CN_2), 1654 (cm^{-1} (C=O); HR-MS (ESI): m/z = 291.1248, calcd. for $C_{17}H_{15}N_4O$ ($[M+H]^+$): 291.1240.

2-Diazo-3-(10,11-dihydro-5*H*-dibenzo[*b*,*f*]azepin-5-yl)-3-oxopropanenitrile (1k): yield: 403 mg (70%); yellow crystals; mp 98–100 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.41 (d, J = 7.8 Hz, 2H), 7.36–7.32 (m, 2H), 7.30–7.26 (m, 4H), 3.51–3.42 (m, 2H), 2.96–2.87 (m, 2H).; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.0, 139.4, 130.5, 129.3, 128.2, 127.2, 106.8, 30.4; IR (KBr): ν = 2214 (CN), 2128 (CN_2), 1645 (cm^{-1} (C=O); HR-MS (ESI): m/z = 289.1079, calcd. for $C_{17}H_{13}N_4O$ ($[M+H]^+$): 289.1084.

2-Diazo-3-oxo-3-(10*H*-phenothiazin-10-yl)propanenitrile (1l): yield: 295 mg (50%, 2 mmol scale); yellow crystals; mp 155–157 °C; ^1H NMR (400 MHz, DMSO-d_6): δ = 7.65 (dd, J = 8.0, 1.2 Hz, 2H), 7.46 (dd, J = 7.8, 1.5 Hz, 2H), 7.36 (ddd, J = 8.0, 7.6, 1.5 Hz, 2H), 7.30 (ddd, J = 7.8, 7.6, 1.2 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 158.8, 137.4, 133.0, 128.1, 127.8, 127.5, 126.4, 106.7; IR (KBr): ν = 2218 (CN), 2131 (CN_2), 1652 (cm^{-1} (C=O); HR-MS (ESI): m/z = 293.0494, calcd. for $C_{15}H_9N_4OS$ ($[M+H]^+$): 293.0492.

3-(2-Chlorodibenzo[*b*,*f*][1,4]oxazepin-10(11*H*)-yl)-2-diazo-3-oxopropanenitrile (1m): yield: 132 mg (61%, 0.67 mmol scale); yellow crystals; mp 149–151 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.46 (td, J = 8.2, 1.7 Hz, 1H), 7.32 (ddd, J = 9.4, 8.1, 1.4 Hz, 2H), 7.25 (dd, J = 7.4, 1.4 Hz, 1H), 7.23–7.11 (m, 3H), 5.56 (s, 1H), 4.30 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.4, 153.9, 152.3, 131.8, 131.5, 128.8, 128.6, 128.6, 125.6, 125.6, 122.6, 122.2, 106.7, 49.5; IR (KBr): ν = 2218 (CN), 2124 (CN_2), 1648 cm^{-1} (C=O); HR-MS (ESI): m/z = 325.0503, calcd. for $C_{16}H_{10}ClN_4O_2$ ($[M+H]^+$): 325.0487.

2-Diazo-3-(3,4-dihydroquinolin-1(2*H*)-yl)-3-oxopropanenitrile (1n): yield: 286 mg (63%, 2 mmol scale); yellow crystals; mp 125–127 °C; ^1H NMR (400 MHz, $CDCl_3$): δ = 7.30–7.19 (m, 4H), 3.82 (t, J = 6.7 Hz, 2H), 2.73 (t, J = 6.7 Hz, 2H), 2.00 (p, J = 6.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.2, 137.0, 133.0, 128.8, 126.8, 126.5, 123.7, 108.0, 45.1, 26.4, 23.9; IR (KBr): ν = 2218 (CN), 2125 (CN_2), 1640 cm^{-1} (C=O); HR-MS (ESI): m/z = 227.0932. calcd. for $C_{12}H_{11}N_4O$ ($[M+H]^+$): 227.0927.

2-Cyano-2-diazo-*N*-ethyl-*N*-(naphthalen-1-yl)acetamide (1o): yield: 202 mg (77%, 1 mmol scale); yellow oil; ^1H NMR (400 MHz, $CDCl_3$): δ = 8.03 (d, J = 8.3 Hz, 1H), 7.98–7.94 (m, 1H), 7.81 (d, J = 7.9 Hz, 1H), 7.65–7.57 (m, 2H), 7.55–7.50 (m, 1H), 7.42 (dd, J = 7.2, 1.0 Hz, 1H), 4.39–4.27 (m, 1H), 3.59 (dq, J = 14.2, 7.1 Hz, 1H), 1.25 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.6, 135.2, 134.6, 131.2, 130.8, 128.9, 127.9, 127.9, 127.0, 125.4, 121.7, 107.0, 46.1, 13.2; IR (KBr): ν = 2218 (CN), 2125 (CN_2), 1640 cm^{-1} (C=O); HR-MS (ESI): m/z = 227.0932, calcd. for $C_{12}H_{11}N_4O$ ($[M+H]^+$): 227.0927.

General Procedure for the Preparation of the Difluoroboron Complexes 2 of Oxindole-3-carboxamides

A solution of **1** (100 mg), $BF_3{\cdot}OEt_2$ (2.5 equiv.) and the additive (0.15 equiv.) in 5 mL of CH_3CN was refluxed for 20 h. Then water (5 mL) was added followed by the addition of 5 mL of EtOAc. The organic phase was separated and the aqueous phase was extracted with 5 mL of CH_2Cl_2. The combined organic phase was concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography to give the pure product **2**.

4-Amino-2,2-difluoro-9-phenyl-2,9-dihydro-[1,3,2]dioxaborinino[4,5-*b*]indol-3-ium-2-uide (2a): yield: 88 mg (77%); colorless crystals; mp 220–223 °C; ^1H NMR (400 MHz, DMSO-d_6): δ = 9.48 (s, 1H), 8.83 (s, 1H), 8.08 (d, J = 7.6 Hz, 1H), 7.65 (t, J = 7.2, 7.2 Hz, 2H), 7.58 (dd, J = 7.2, 7.2 Hz, 1H), 7.54 (d, J = 7.2 Hz, 2H), 7.28 (dd, J = 7.9, 7.0 Hz, 1H), 7.20 (dd, J = 7.6, 7.0 Hz, 1H), 7.13 (d, J = 7.9 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 164.4, 161.0, 133.7, 132.8, 129.8, 128.9, 126.9, 123.0, 122.9, 120.9, 118.6, 110.4, 81.4; ^{19}F NMR (376 MHz, DMSO-d_6): δ = −141.9, −142.0; ^{11}B NMR (193 MHz, DMSO-d_6): δ = 1.08; IR (KBr): ν = 656, 693, 736, 748, 768, 882, 1024, 1044, 1076, 1107, 1142, 1180, 1206, 1256, 1308, 1384, 1455, 1484, 1508, 1549, 1586, 1601, 1622, 1651, 2921, 3378, 3487 cm^{-1}; HR-MS (ESI) m/z = 301.0965, calcd. for $C_{15}H_{12}BF_2N_2O_2$ ($[M+H]^+$): 301.0954.

4-Amino-2,2-difluoro-9-methyl-2,9-dihydro-[1,3,2]dioxaborinino[4,5-*b*]indol-3-ium-2-uide (2b): yield: 23 mg (19%); colorless crystals; mp 180–182 °C; ^1H NMR (400 MHz,

DMSO-d_6): δ = 9.23 (s, 1H), 8.59 (s, 1H), 7.99–7.96 (m, 1H), 7.45–7.42 (m, 2H), 7.25–7.19 (m, 2H), 3.57 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 163.9, 161.4, 133.8, 122.3, 122.3, 120.7, 118.3, 110.2, 80.7, 27.2; ^{19}F NMR (376 MHz, DMSO-d_6): δ = −141.8, −141.8; ^{11}B NMR (193 MHz, DMSO-d_6): δ = 1.12; IR (KBr): ν = 616, 748, 773, 991, 1024, 1113, 1170, 1264, 1326, 1406, 1455, 1514, 1580, 1595, 1622, 2934, 3372 cm^{-1}); HR-MS (ESI): m/z = 261.0811, calcd. for $C_{10}H_{10}BF_2N_2O_2$ ([M+H]$^+$): 261.0789.

4-Amino-2,2-difluoro-9-propyl-2,9-dihydro-[1,3,2]dioxaborinino[4,5-*b*]indol-3-ium-2-uide (2c): yield: 40 mg (35%); colorless crystals; mp 259–260 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.24 (s, 1H), 8.60 (s, 1H), 7.99–7.97 (m, 1H), 7.51–7.47 (m, 1H), 7.23–7.18 (m, 2H), 4.04 (t, J = 7.2 Hz, 2H), 1.72 (sixtet, J = 7.2 Hz, 2H), 0.85 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 164.2, 160.9, 133.1, 122.3, 122.2, 120.8, 118.4, 110.4, 104.5, 80.6, 42.2, 21.5, 10.9; ^{19}F NMR (376 MHz, DMSO-d_6): δ = −142.1, −142.2; ^{11}B NMR (193 MHz, DMSO-d_6): δ = 1.13; IR (KBr): ν = 757, 1045, 1298, 1383, 1459, 1491, 1509, 1561, 1611, 1638, 1648, 1655, 1676, 1686, 1701, 1719, 2853, 2925, 3369 cm^{-1}; HR-MS (ESI): m/z = 267.1127, calcd. for $C_{12}H_{14}BF_2N_2O_2$ ([M+H]$^+$): 267.1111.

4-Amino-9-benzyl-2,2-difluoro-2,9-dihydro-[1,3,2]dioxaborinino[4,5-*b*]indol-3-ium-2-uide (2d): yield: 55 mg (48%); colorless crystals; mp 163–165 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.34 (s, 1H), 8.70 (s, 1H), 8.00 (d, J = 7.1 Hz, 1H), 7.43 (d, J = 7.8 Hz, 1H), 7.36–7.31 (m, 2H), 7.28–7.26 (m, 3H), 7.22–7.14 (m, 2H), 5.32 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 164.1, 161.3, 136.1, 132.9, 128.7, 127.7, 127.1, 122.5, 122.4, 120.9, 118.5, 110.7, 80.9, 43.9; ^{19}F NMR (376 MHz, DMSO-d_6): δ = −142.1, −142.1; ^{11}B NMR (193 MHz, DMSO-d_6): δ = 1.18; IR (KBr): ν = 704, 747, 770, 1027, 1081, 1142, 1238, 1263, 1332, 1383, 1456, 1479, 1510, 1555, 1598, 1625, 1642, 1701, 2927, 3375, 3481 cm^{-1}; HR-MS (ESI): m/z = 315.1125, calcd. for $C_{16}H_{14}BF_2N_2O_2$ ([M+H]$^+$): 315.1111.

4-Amino-9-benzyl-2,2-difluoro-6-methyl-2,9-dihydro-[1,3,2]dioxaborinino[4,5-*b*]indol-3-ium-2-uide (2e): yield: 40 mg (36%); colorless crystals; mp 203–205 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.27 (s, 1H), 8.61 (s, 1H), 7.84 (s, 1H), 7.34–7.23 (m, 6H), 6.97 (d, J = 8.2 Hz, 1H), 5.28 (s, 2H), 1.99 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 164.0, 161.2, 136.1, 131.6, 131.0, 128.7, 127.6, 127.1, 123.3, 121.0, 118.7, 110.4, 80.7, 43.9, 21.1; ^{19}F NMR (376 MHz, DMSO-d_6): δ = −142.1, −142.1; ^{11}B NMR (193 MHz, DMSO-d_6): δ = 1.17. IR (KBr): ν = 560, 703, 828, 1021, 1082, 1142, 1240, 1264, 1312, 1456, 1508, 1555, 1597, 1630, 2924, 3376, 3485 cm^{-1}; HR-MS (ESI): m/z = 329.1286, calcd. for $C_{17}H_{16}BF_2N_2O_2$ ([M+H]$^+$): 329.1267.

4-Amino-9-benzyl-6-chloro-2,2-difluoro-2,9-dihydro-[1,3,2]dioxaborinino[4,5-*b*]indol-3-ium-2-uide (2f): yield: 53 mg (48%); colorless crystals; mp 226–228 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.45 (s, 1H), 8.87 (s, 1H), 8.17 (d, J = 1.9 Hz, 1H), 7.46 (d, J = 8.6 Hz, 1H), 7.36–7.24 (m, 5H), 7.20 (dd, J = 8.6, 1.9 Hz, 1H), 5.33 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 163.9, 161.7, 135.8, 131.5, 128.8, 127.8, 127.4, 127.1, 122.3, 122.1, 118.1, 112.2, 80.9, 44.1; ^{19}F NMR (376 MHz, DMSO-d_6): δ = −142.0, −142.1; ^{11}B NMR (193 MHz, DMSO-d_6): δ = 1.11; IR (KBr): ν = 700, 722, 737, 833, 1028, 1045, 1093, 1143, 1191, 1263, 1360, 1384, 1402, 1454, 1493, 1583, 1599, 1636, 1720, 2216, 2927, 3351 cm^{-1}; HR-MS (ESI): m/z = 371.0551, calcd. for $C_{16}H_{12}BClF_2N_2NaO_2$ ([M+Na]$^+$): 371.0541.

4-Amino-2,2-difluoro-6-methyl-9-(*p*-tolyl)-2,9-dihydro-[1,3,2]dioxaborinino[4,5-*b*]indol-3-ium-2-uide (2g): yield: 79 mg (70%); colorless crystals; mp 238–240 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.40 (s, 1H), 8.73 (s, 1H), 7.92 (s, 1H), 7.43 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 7.00 (s, 2H), 2.41 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 164.3, 160.9, 138.4, 132.1, 132.0, 130.4, 130.2, 126.4, 123.6, 120.9, 118.8, 110.1, 81.2, 21.1, 20.7; ^{19}F NMR (376 MHz, DMSO-d_6): δ = −141.9, −142.0; ^{11}B NMR (193 MHz, DMSO-d_6): δ = 1.06; IR (KBr): ν = 881, 1025, 1048, 1076, 1142, 1180, 1384, 1461, 1487, 1517, 1552, 1598, 1631, 2927, 2973, 3387 cm^{-1}; HR-MS (ESI): m/z = 329.1278, calcd. for $C_{17}H_{16}BF_2N_2O_2$ ([M+H]$^+$): 329.1267.

4-Amino-6-chloro-9-(4-chlorophenyl)-2,2-difluoro-2,9-dihydro-[1,3,2]dioxaborinino[4,5-*b*]indol-3-ium-2-uide (2h): yield: 76 mg (68%); colorless crystals; mp >300 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.62 (s, 1H), 9.02 (s, 1H), 8.26 (d, J = 1.8 Hz, 1H), 7.72 (d, J = 8.7 Hz, 2H), 7.60 (d, J = 8.7 Hz, 2H), 7.22 (dd, J = 8.6, 1.8 Hz, 1H), 7.16 (d, J = 8.6 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 164.2, 161.3, 133.7, 132.1, 131.4, 129.9, 128.7, 127.9, 122.6, 122.3, 118.2, 111.9, 81.5; ^{19}F NMR (376 MHz, DMSO-d_6): δ = −141.7, −141.8; ^{11}B NMR (193 MHz, DMSO-d_6): δ = 0.99; IR (KBr): ν = 627, 657, 670, 694, 708, 717, 736, 750, 771, 805, 831, 859, 942, 958, 1015, 1044, 1069, 1093, 1115, 1143, 1180, 1207, 1256, 1289, 1322, 1384, 1407, 1428, 1457, 1483, 1500, 1553, 1578, 1603, 1621, 1647, 2930, 3107, 3204, 3277, 3373, 3482, 3568 cm^{-1}; HR-MS (ESI): m/z = 369.0193, calcd. for $C_{15}H_{10}BClF_2N_2O_2$ ([M+H]$^+$): 369.0175.

4-Amino-9-(3,5-dimethylphenyl)-2,2-difluoro-5,7-dimethyl-2,9-dihydro-[1,3,2]dioxaborinino[4,5-*b*]indol-3-ium-2-uide (2i): yield: 22 mg (20%); colorless crystals; mp 226–228 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.29 (s, 1H), 7.79 (s, 1H), 7.22 (s, 1H), 7.07 (s, 2H), 6.87 (s, 1H), 6.67 (s, 1H), 2.67 (s, 3H), 2.38 (s, 6H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 164.8, 161.5, 139.3, 135.0, 132.8, 130.6, 128.3, 126.4, 124.8, 118.1, 108.4, 82.5, 21.3, 20.9, 20.7; ^{19}F NMR (376 MHz, DMSO-d_6): δ = −145.5, −145.6; ^{11}B NMR (193 MHz, DMSO-d_6): δ = 0.87; IR (KBr): ν = 741, 770, 837, 914, 1036, 1075, 1142, 1180, 1239, 1276, 1383, 1475, 1506, 1534, 1589, 1637, 2924, 3377, 3512 cm^{-1}; HR-MS (ESI): m/z = 357.1584, calcd. for $C_{19}H_{20}BF_2N_2O_2$ ([M+H]$^+$): 357.1580.

4-Amino-2,2-difluoro-8-methyl-9-(*o*-tolyl)-2,9-dihydro-[1,3,2]dioxaborinino[4,5-*b*]indol-3-ium-2-uide (2j): yield: 68 mg (60%); colorless crystals; mp 236–239 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.44 (s, 1H), 8.75 (s, 1H), 7.93 (d, J = 7.6 Hz, 1H), 7.55–7.39 (m, 4H), 7.16 (dd, J = 7.6, 7.6 Hz, 1H), 6.94 (d, J = 7.6 Hz, 1H), 1.97 (s, 3H), 1.73 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 164.3, 161.5, 136.7, 134.2, 131.3, 130.5, 130.0, 129.5, 126.9, 125.7, 122.6, 121.4, 121.3, 116.6, 81.1, 17.4, 16.8; ^{19}F NMR (376 MHz, DMSO-d_6): δ = −141.6, −141.7, −141.8, −141.9, −142.8, −142.8, −143.0, −143.0; ^{11}B NMR (193 MHz, DMSO-d_6): δ = 1.03; IR (KBr): ν = 618, 634, 655, 729, 742, 769, 782, 878, 1030, 1093, 1124, 1174, 1264, 1297, 1319, 1354, 1410, 1456, 1481, 1505, 1557, 1590, 1616, 1645, 1651, 2928, 3267, 3370, 3478 cm^{-1}; HR-MS (ESI): m/z = 329.1280, calcd. for $C_{17}H_{16}BF_2N_2O_2$ ([M+H]$^+$): 329.1267.

14-Amino-12,12-difluoro-5,12-dihydro-4*H*-benzo[6,7]azepino[3,2,1-*hi*][1,3,2]dioxaborinino[4,5-*b*]indol-13-ium-12-uide (2k): yield: 73 mg (65%); colorless crystals; mp 235–237 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.57 (s, 1H), 8.81 (s, 1H), 7.89 (d, J = 7.7 Hz, 1H), 7.68 (d, J = 7.9 Hz, 1H), 7.45–7.38 (m, 2H), 7.35–7.30 (m, 1H), 7.18 (dd, J = 7.7, 7.5 Hz, 1H), 7.05 (d, J = 7.5 Hz, 1H), 3.14–3.00 (m, 4H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 164.4, 161.0, 136.8, 134.7, 131.5, 130.1, 127.4, 127.3, 126.8, 124.6, 124.3, 122.5, 121.6, 116.1, 83.1, 33.5, 33.2; ^{19}F NMR (376 MHz, DMSO-d_6): δ = −142.4; ^{11}B NMR (193 MHz, DMSO-d_6): δ = 2.11; IR (KBr): ν = 636, 651, 760, 788, 882, 939, 1030, 1115, 1248, 1280, 1319, 1361, 1441, 1487, 1557, 1592, 1615, 1651, 2928, 3365, 3480 cm^{-1}; HR-MS (ESI): m/z = 327.1113, calcd. for $C_{17}H_{14}BF_2N_2O_2$ ([M+H]$^+$): 327.1111.

4-Amino-2,2-difluoro-2*H*-[1,3,2]dioxaborinino[5′,4′:4,5]-pyrrolo[3,2,1-*kl*]phenothiazin-3-ium-2-uide (2l): yield: 76 mg (67%); colorless crystals; mp 251–253 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.62 (s, 1H), 8.79 (s, 1H), 8.24 (d, J = 8.3 Hz, 1H), 7.61 (d, J = 7.8 Hz, 1H), 7.28–7.23 (m, 1H), 7.20–7.17 (m, 1H), 7.14–7.12 (m, 1H), 7.08 (dd, J = 7.8, 7.6 Hz, 1H), 6.81 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 164.1, 159.8, 131.8, 127.8, 127.2, 126.8, 126.8, 125.4, 120.5, 120.1, 118.2, 117.2, 115.8, 115.4, 83.4; ^{19}F NMR (376 MHz, DMSO-d_6): δ = −141.9, −142.0; ^{11}B NMR (193 MHz, DMSO-d_6): δ = 0.96; IR (KBr): ν = 644, 744, 774, 828, 1026, 1076, 1143, 1196, 1308, 1438, 1474, 1551, 1601, 1645, 2925, 3366 cm^{-1}; HR-MS (ESI): m/z = 331.0526, calcd. for $C_{15}H_{10}BF_2N_2O_2S$ ([M+H]$^+$): 331.0519.

4-Amino-11-chloro-6,6-difluoro-6,9-dihydrobenzo[6,7][1,4]oxazepino[2,3,4-*hi*][1,3,2]dioxaborinino[4,5-*b*]indol-5-ium-6-uide (2m): yield: 69 mg (62%); colorless crystals; mp >300 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.39 (s, 1H), 8.71 (s, 1H), 7.83 (d, J = 2.5 Hz, 1H), 7.74 (d, J = 7.7 Hz, 1H), 7.46 (dd, J = 8.6, 2.5 Hz, 1H), 7.37 (d, J = 8.6 Hz, 1H), 7.15 (dd, J = 7.8, 7.7 Hz, 1H), 7.06 (d, J = 7.8 Hz, 1H), 5.40 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 164.1, 159.6, 156.9, 143.1, 130.3, 130.2, 129.4, 128.9, 123.4, 123.4, 123.3, 123.1, 114.5, 112.7, 81.2, 43.0; ^{19}F NMR (376 MHz, DMSO-d_6): δ = −141.6, −141.6; ^{11}B NMR (193 MHz, DMSO-d_6): δ = 1.15; IR (KBr): ν = 965, 1073, 1141, 1180, 1455, 1471, 1486, 1505, 1520, 1538, 1557, 1614, 1633, 1645, 1651, 1682, 2925, 3564, 3585, 3626 cm^{-1}; HR-MS (ESI): m/z = 363.0514, calcd. for $C_{16}H_{11}BClF_2N_2O_3$ ([M+H]$^+$): 363.0514.

11-Amino-9,9-difluoro-4,5,6,9-tetrahydro-[1,3,2]dioxaborinino[5′,4′:4,5]pyrrolo[3,2,1-*ij*]quinolin-10-ium-9-uide (2n): yield: 50 mg (42%); colorless crystals; mp 242–244 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.14 (s, 1H), 8.54 (s, 1H), 7.77 (d, J = 7.6 Hz, 1H), 7.09 (t, J = 7.6 Hz, 1H), 6.96 (d, J = 7.6 Hz, 1H), 3.99 (t, J = 5.6 Hz, 2H), 2.87 (t, J = 5.6 Hz, 2H), 2.08 (quintet, J = 5.6 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 164.1, 160.1, 130.1, 122.1, 122.0, 120.4, 119.1, 116.0, 81.0, 39.6, 23.7, 21.2; ^{19}F NMR (376 MHz, DMSO-d_6): δ = −141.7, −141.7; ^{11}B NMR (193 MHz, DMSO-d_6): δ = 1.10; IR (KBr): ν = 746, 776, 888, 923, 1022, 1075, 1123, 1172, 1214, 1243, 1296, 1355, 1372, 1446, 1461, 1485, 1514, 1566, 1584, 1608, 1627, 1654, 1689, 2929, 3390, 3506 cm^{-1}; HR-MS (ESI): m/z = 265.0954, calcd. for $C_{12}H_{12}BF_2N_2O_2$ ([M+H]$^+$): 256.0954.

7-Amino-11-ethyl-9,9-difluoro-9,11-dihydrobenzo[*g*]-[1,3,2]dioxaborinino[4,5-*b*]indol-8-ium-9-uide (2o): yield: 50 mg (43%); colorless crystals; mp 204–207 °C; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.46 (s, 1H), 8.84 (s, 1H), 8.34 (d, J = 8.6 Hz, 1H), 8.21 (d, J = 8.6 Hz, 1H), 8.02 (d, J = 7.9 Hz, 1H), 7.79 (d, J = 8.6 Hz, 1H), 7.62 (dd, J = 8.6, 7.2 Hz, 1H), 7.47 (dd, J = 7.9, 7.2 Hz, 1H), 4.57 (q, J = 7.0 Hz, 2H), 1.43 (t, J = 7.0 Hz, 3H); ^{13}C NMR (400 MHz, DMSO-d_6): δ = 164.4, 159.8, 130.5, 129.3, 126.7, 125.4, 123.7, 123.3, 121.2, 120.2, 118.1, 118.0, 82.1, 38.3, 14.7; ^{19}F NMR (376 MHz, DMSO-d_6): δ = −141.9, −142.0; ^{11}B NMR (193 MHz, DMSO-d_6): δ = 1.22; IR (KBr): ν = 616, 1037, 1118, 1332, 1405, 1458, 1474, 1500, 1535, 1560, 1591, 1638, 1648, 1654, 1686, 1701, 1719, 2935, 3370, 3568 cm^{-1}; HR-MS (ESI): m/z = 303.1126, calcd. for $C_{15}H_{14}BF_2N_2O_2$ ([M+H]$^+$): 303.1111.

2,2-Difluoro-N^4,N^4-diphenyl-2*H*-1λ^3,3,2λ^4-dioxaborinine-4,6-diamine (2p): yield: 69 mg (29%, 118 mg scale); colorless crystals; mp 169–172 °C; R_f = 0.15 (silica gel plate, ethyl acetate-petroleum ether 1:3, v/v); ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.02 (s, 1H), 7.92 (s, 1H), 7.47–7.43 (m, 4H), 7.40–7.30 (m, 6H,), 4.25 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 169.5, 166.2, 141.5, 129.6, 127.8, 127.5, 66.5; ^{19}F NMR (376 MHz, DMSO-d_6): δ = −143.19 (d, J = 22.9 Hz); ^{11}B NMR (193 MHz, DMSO-d_6): δ = 0.58; IR (KBr): ν = 3488, 3385, 2849, 1637, 1589, 1560, 1540, 1490, 1458, 1426, 1295, 1104, 1047, 1026, 994, 761, 700 cm^{-1}; HR-MS (ESI): m/z = 303.1119, calcd for $C_{15}H_{13}BF_2N_2O_2$ ([M+H]$^+$): 303.1111.

Preparation of 2-Oxo-1-phenylindoline-3-carbonitrile (3a)

2-Cyano-2-diazo-*N*,*N*-diphenylacetamide (**1a**) (277 mg, 1.06 mmol) and dirhodium tetraoctanoate (82.6 mg, 0.11 mmol) were dissolved in dichloromethane (5 mL). The reaction mixture was refluxed for 2 h. After removal of the solvent under reduced pressure, the resulting residue was purified by silica gel chromatography (methanol/dichloromethane 20:1, v/v) to give the crude product **3a**. Finally, the crude product **3a** was recrystallized from a mixture of ethyl acetate-petroleum ether to afford the pure white solid product **3a**; yield: 113 mg (40%); mp 152–156 °C, Lit.[21] 154–158 °C; R_f = 0.45 (silica gel plate, methanol-dichloromethane 1:10, v/v). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.58–7.45 (m, 5H), 7.42–7.40 (m, 2H), 7.34 (t, J = 8.0 Hz, 1H), 7.20 (t, J = 8.0 Hz, 1H), 6.83 (d, J = 8.0 Hz, 1H), 4.75 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.4, 144.0, 133.3, 130.4, 130.0, 129.0, 126.5, 125.1, 124.2, 119.9, 114.0, 110.5, 37.0.

Acknowledgements

This work was supported in part by the National Basic Research Program of China (No. 2013CB328905) and the National Natural Science Foundation of China (Nos. 21372025 and 21572017). Miss Jianxiu Fang is thanked for her generous experimental help.

References

[1] For recent reviews, see: a) Y. Ni, J. S. Wu, *Org. Biomol. Chem.* **2014**, *12*, 3774–3791; b) G. Ulrich, R. Ziessel, A.

Harriman, *Angew. Chem.* **2008**, *120*, 1202–1219; *Angew. Chem. Int. Ed.* **2008**, *47*, 1184–1201. For recent examples, see: c) U. Balijapalli, S. K. Iyer, *Eur. J. Org. Chem.* **2015**, 5089–5098; d) W. Zheng, B. B. Wang, C. H. Li, J. X. Zhang, C. Z. Wan, J. H. Huang, J. Liu, Z. Shen, X. Z. You, *Angew. Chem.* **2015**, *127*, 9198–9202; *Angew. Chem. Int. Ed.* **2015**, *54*, 9070–9074; e) Y. Kubota, T. Niwa, J. Y. Jin, K. Funabiki, M. Matsui, *Org. Lett.* **2015**, *17*, 3174–3177; f) S. M. Barbon, V. N. Staroverov, J. B. Gilroy, *J. Org. Chem.* **2015**, *80*, 5226–5235; g) A. G. Montalban, A. J. Herrera, J. Johannsen, A. J. P. White, D. J. Williams, *Tetrahedron* **2014**, *70*, 7358–7362; h) C. J. Yu, L. J. Jiao, P. Zhang, Z. Y. Feng, C. Cheng, Y. Wei, X. L. Mu, E. H. Hao, *Org. Lett.* **2014**, *16*, 3048–3051; i) I. S. Tamgho, A. Hasheminasab, J. T. Engle, V. N. Nemykin, C. J. Ziegler, *J. Am. Chem. Soc.* **2014**, *136*, 5623–5626.

[2] S. Xu, R. E. Evans, T. Liu, G. Zhang, J. N. Demas, C. O. Trindle, C. L. Fraser, *Inorg. Chem.* **2013**, *52*, 3597–3610, and references cited therein.

[3] H. Maeda, T. Shirai, S. Uemura, *Chem. Commun.* **2013**, *49*, 5310–5312.

[4] P. Galer, R. C. Korosec, M. Vidmar, B. Sket, *J. Am. Chem. Soc.* **2014**, *136*, 7383–7394.

[5] J. N. Wilson, J. Wigenius, D. R. G. Pitter, Y. Qiu, M. Abrahamsson, F. Westerlund, *J. Phys. Chem. B* **2013**, *117*, 12000–12006.

[6] a) B. Stefane, *Org. Lett.* **2010**, *12*, 2900–2903; b) B. Stefane, S. Polanc, *Tetrahedron* **2007**, *63*, 10902–10913; c) Z. C. Gyarmati, P. Csomos, G. Bernath, P. Valtamo, H. Kivelae, G. Argay, A. Kalman, K. Klika, K. Pihlaja, *J. Heterocycl. Chem.* **2004**, *41*, 187–199; d) J. Christoffers, B. Kreidler, S. Unger, W. Frey, *Eur. J. Org. Chem.* **2003**, 2845–2853.

[7] See recent examples: a) E. Giziroglu, A. Nesrullajev, N. Orhan, *J. Mol. Struct.* **2014**, *1056–1057*, 246–253; b) X. Liu, Q. Zhang, X. Xin, R. Zhang, N. Zhang, Y. Liang, D. Dong, *RSC Adv.* **2014**, *4*, 36234–36240; c) A. Yajima, A. Kawajiri, A. Mori, R. Katsuta, T. Nukada, *Tetrahedron Lett.* **2014**, *55*, 4350–4354; d) K. E. Judd, M. F. Mahon, L. Caggiano, *Synthesis* **2009**, 2809–2817; e) K. Zyabrev, A. Doroshenko, E. Mikitenko, Y. Slominskii, A. Tolmachev, *Eur. J. Org. Chem.* **2008**, 1550–1558.

[8] a) J. Fabian, H. Hartmann, *J. Phys. Org. Chem.* **2004**, *17*, 359–369; b) K. Hartke, B. Krug, R. Hoffmann, *Liebigs Ann. Chem.* **1984**, 370–380.

[9] For the related recent work in our group: a) S. Y. Mo, Z. H. Yang, J. X. Xu, *Eur. J. Org. Chem.* **2014**, 3923–3929; b) Z. H. Yang, J. X. Xu, *Chem. Commun.* **2014**, *50*, 3136–3138.

[10] S. Miah, A. M. Z. Slawin, C. J. Moody, S. M. Sheehan, J. P. Marino Jr, M. A. Semones, A. Padwa, *Tetrahedron* **1996**, *52*, 2489–2514.

[11] Y. Nakao, A. Yada, S. Ebata, T. Hiyama, *J. Am. Chem. Soc.* **2007**, *129*, 2428–2429.

[12] a) Z. H. Yang, K. I. Son, S. Q. Li, B. N. Zhou, J. X. Xu, *Eur. J. Org. Chem.* **2014**, 6380–6383; b) H. L. Wang, Z. Li, G. W. Wang, S. D. Yang, *Chem. Commun.* **2011**, *47*, 11336–11338.

[13] CCDC 1407219 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

[14] For reviews on nucleophilic ring opening of three-membered heterocycles, see: a) L. G. Ma, J. X. Xu, *Prog. Chem.* **2004**, *16*, 220–235; b) C. Zhou, J. X. Xu, *Prog. Chem.* **2011**, *23*, 174–189.

[15] a) S. L. Hou, X. Y. Li, J. X. Xu, *J. Org. Chem.* **2012**, *77*, 10856–10869; b) S. L. Hou, X. Y. Li, J. X. Xu, *Org. Biomol. Chem.* **2014**, *12*, 4952–4963.

[16] a) M. E. El-Khouly, S. Fukuzumi, F. D'Souza, *ChemPhysChem* **2014**, *15*, 30–34; b) A. Bessette, G. S. Hanan, *Chem. Soc. Rev.* **2014**, *43*, 3342–3405; c) H. Maeda, *Eur. J. Org. Chem.* **2007**, 5313–5325; d) H. Lu, J. Mack, Y. Yang, Z. Shen, *Chem. Soc. Rev.* **2014**, *43*, 4778–4823.

[17] H. Lutjens, A. Zickgraf, H. Figler, J. Linden, R. A. Olsson, P. J. Scammells, *J. Med. Chem.* **2003**, *46*, 1870–1877.

[18] A. Manikowski, Z. Kolarska, *Synth. Commun.* **2009**, *39*, 3621–3363.

[19] Y. Kobayashi, T. Harayama, *Org. Lett.* **2009**, *11*, 1603–1606.

[20] D. Marcoux, S. Azzi, A. B. Charette, *J. Am. Chem. Soc.* **2009**, *131*, 6970–6972.

[21] J. L. Lv, Z. N. Daisy, J. Deng, Y. F. Du, K. Zhao, *J. Org. Chem.* **2014**, *79*, 1111–1119.

