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$BF_3 \cdot Et_2O$-mediated intramolecular cyclization of unsaturated amides: convenient synthesis of dihydroquinolin-2-one-BF_2 complexes†

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A facile and efficient synthesis of substituted dihydropyridone–BF_2 complexes is developed *via* intramolecular cyclization of α-acyl acrylamides and α-acyl cinnamamides mediated by $BF_3 \cdot Et_2O$.

Introduction

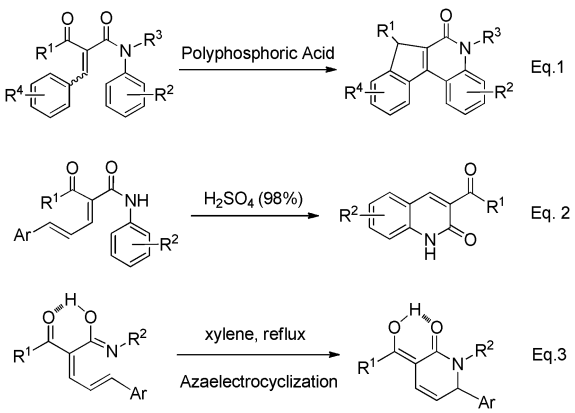
Over the past decades, pyridin-2(1*H*)-ones and their analogues have attracted considerable attention in chemical and biological fields.[1,2] These structural motifs can serve as efficient catalysts in a variety of proton-dependent reactions[3] and as valuable ligands in coordination chemistry.[4] Furthermore, pyridin-2(1*H*)-ones are versatile intermediates in the synthesis of a wide range of *aza*-heterocycles, such as pyridines, piperidines, indolizidines, quinolines and quinolizidines.[5,6] In particular, pyridin-2(1*H*)-one is a key unit in numerous natural products and synthetic organic compounds such as elfamycin, cerpegin and camptothecin,[7] along with diverse bio-, physio- and pharmacological activities. To date, a variety of synthetic approaches have been well established to access pyridin-2(1*H*)-ones and their analogues, which comprise the modification of the preconstructed heterocyclic ring by pyridinium salt chemistry[8] and *N*-alkylation,[9] the construction of heterocyclic skeletons from appropriately substituted open-chain precursors *via* metal-catalyzed sp^2 C–H bond amination,[10] ring closing metathesis,[11] and Diels–Alder reaction.[12]

On the other hand, organoboron compounds have emerged as one of the most important class of organic complexes for their excellent photophysical properties and potential use in molecular sensors,[13] biomolecular probes[14] and optoelectronic devices.[15] Among those reported work, β-dicarbonyl compounds are most used ligands, and the boron difluoride β-diketonates have been extensively investigated and their promising luminescence make them good candidates for optical imaging and sensing applications.[16,17]

During the course of our studies on the synthesis of heterocycles based on β-oxo amide derivatives, we developed the synthesis of a variety of substituted pyridin-2(1*H*)-ones under Vilsmeier conditions.[18] Most recently, we achieved the synthesis of indeno[2,1-*c*]quinolin-6(7*H*)-ones from α-acyl cinnamamides mediated by PPA (eqn (1), Scheme 1),[19] divergent synthesis of quinolin-2(1*H*)-ones (eqn (2), Scheme 1)[20] and pyridin-2(3*H*)-ones (eqn (3), Scheme 1) from 2-acyl penta-2,4-dienamides.[21] Encouraged by the previous work, we are interested to examine the reaction behaviors of unsaturated amides toward $BF_3 \cdot Et_2O$. By this research, we developed a facile and convenient synthesis of dihydropyridone–BF_2 complexes under very mild conditions. Herein, we will report our experimental results and present a proposed mechanism involved in the cyclization reactions.

Results and discussion

The substrates, unsaturated amides, were prepared by Knoevenagel condensation of commercially available β-oxo amides with aryl aldehydes in the presence of piperidine and acetic acid



Scheme 1 Reactions of α,β-unsaturated amides.

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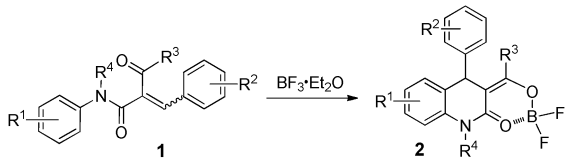
† Electronic supplementary information (ESI) available: Experimental details, spectral and analytical data, copies of ^1H NMR and ^{13}C NMR spectra for new compounds **1–3** and **5**, and CIF files for **2g** and **5d**. CCDC 922666 and 938933. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4ra06151a

in good yields according to reported procedures.[19–22] Then, we selected 2-benzylidene-3-oxo-*N*-phenylbutanamide **1a** as a model compound to investigate its reaction behavior in the presence of $BF_3 \cdot Et_2O$ (1.0 equiv.) in CH_2Cl_2 at room temperature. The reaction could proceed and furnished a product, which was characterized as 2,2-difluoro-4-methyl-5-phenyl-5,10-dihydro-2*H*-[1,3,2]dioxa-borinino[4,5-*b*]quinolin-1-ium-2-uide **2a** (in 76% yield) on the basis of its spectral and analytical data. A series of experiments revealed that the optimal results were obtained when the reaction of **1a** was performed with $BF_3 \cdot Et_2O$ (2.0 equiv.) in CH_2Cl_2 at room temperature, in which the yield of **2a** reached 88% (Table 1, entry 1).

Under the identical conditions as for **2a**, a range of reactions of α-acyl *N*-arylcinnamamides **1b–n** were carried out and some of the results are summarized in Table 2. All the reactions of **1b–g** bearing various electron-donating and electron-withdrawing substituents R^1 on the aryl amides proceeded smoothly to afford the corresponding dihydropyridone–BF_2 complexes **2b–g** in high yields (Table 1, entries 2–9). In the case of **1d**, 2,2-difluoro-4,8-dimethyl-5-phenyl-5,10-dihydro-2*H*-[1,3,2]dioxa-borinino-[4,5-*b*]quinolin-1-ium-2-uide **2d** was exclusively obtained in 79% yield, which suggests that **1d** underwent the cyclization reaction in a regioselective manner (Table 1, entry 4). The efficiency of the cyclization proved to be suitable for **1j–m** bearing various electron-donating and electron-withdrawing substituents R^2 on the benzene ring affording the corresponding substituted dihydropyridone–BF_2 complexes **2j–m** in very good yields (Table 1, entries 10–13). In the same fashion, the validity of this dihydropyridone–BF_2 complex synthesis was further evaluated by performing **1n** bearing secondary amide, in which dihydroquinolin-2-one-BF_2 complex **2n** was obtained in high yield (Table 1, entry 14). The structure of **2g** was further confirmed by the X-ray single crystal analysis (Fig. 1). The results shown above demonstrate the efficiency and synthetic interest of the cyclization reaction of variable α-acyl *N*-aryl cinnamamides **1**.

It should be mentioned that when dihydropyridone–BF_2 complex **2h** was treated with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 1.0 equiv.) in CH_2Cl_2 at room temperature for 1.0 h, 3-acyl-6-methoxy-4-phenylquinolin-2(1*H*)-one **3h** could be obtained in 80% yield (Scheme 2). Therefore, we provided a novel and convenient synthesis of dihydropyridone–BF_2 complexes **2** and an alternative synthesis of dihydroquinolin-2-ones **3** as well.

Table 1 Synthesis of substituted dihydroquinolin-2-one-BF_2 complexes **2** from α-Acyl *N*-arylcinnamamides **1**[a]

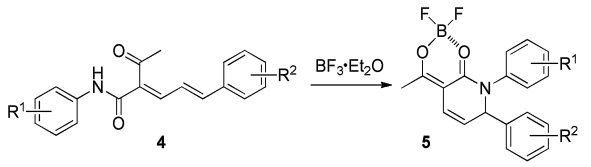


1 2

Entry	1	R^1	R^2	R^3	R^4	2	Yield[b] (%)
1	**1a**	H	H	Me	H	**2a**	88
2	**1b**	4-Me	H	Me	H	**2b**	81
3	**1c**	2-Me	H	Me	H	**2c**	82
4	**1d**	3-Me	H	Me	H	**2d**	79
5	**1e**	2,4-Me_2	H	Me	H	**2e**	80
6	**1f**	4-Cl	H	Me	H	**2f**	83
7	**1g**	4-MeO	H	Me	H	**2g**	96
8	**1h**	2-MeO	H	Me	H	**2h**	94
9	**1i**	H	H	Ph	H	**2i**	75
10	**1j**	H	4-Me	Me	H	**2j**	87
11	**1k**	H	2-Me	Me	H	**2k**	86
12	**1l**	H	2-MeO	Me	H	**2l**	85
13	**1m**	H	4-Cl	Me	H	**2m**	83
14	**1n**	H	H	Me	Et	**2n**	81

[a] Reagents and conditions: **1** (2.0 mmol), $BF_3 \cdot Et_2O$ (4.0 mmol), CH_2Cl_2 (5.0 mL), rt, 2.0–3.0 h. [b] Isolated yield.

Table 2 Synthesis of dihydropyridin-2(3*H*)-one-BF_2 complexes **5** from 2-acyl penta-2,4-dienamides[a]



4 5

Entry	4	R^1	R^2	5	Yield[b] (%)
1	**4a**	4-Me	H	**5a**	70
2	**4b**	4-MeO	H	**5b**	72
3	**4c**	4-Cl	H	**5c**	68
4	**4d**	2-Cl	4-MeO	**5d**	71
5	**4e**	2-Me	4-MeO	**5e**	63
6	**4f**	4-Me	4-Me	**5f**	65

[a] Reaction conditions: **1** (1.0 mmol), KOH (6.0 mmol), *t*-BuOH (10 mL), 80 °C. 1.0–2.0 h. [b] Isolated yields.

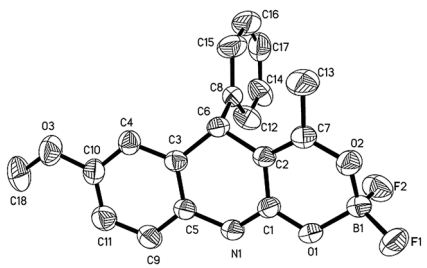
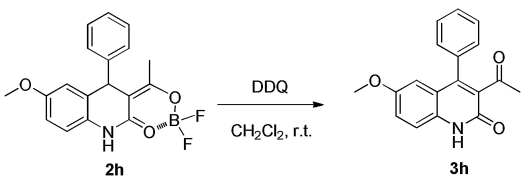


Fig. 1 ORTEP drawing of **2g**.



2h 3h

Scheme 2 Reaction of substituted dihydroquinolin-2-one-BF_2 complex **2h** with DDQ.

Encouraged by the above results, we intended to explore the reaction of 2-acyl penta-2,4-dienamides under identical reaction conditions as for **2a**. However, when 2-acyl-5-phenyl-*N*-(*p*-tolyl) penta-2,4-dienamide **4a** was subjected to CH_2Cl_2 in the presence of $BF_3 \cdot Et_2O$ at room temperature for 2.0 h, no reaction was observed. Then, the reaction of **4a** was performed in $(CH_2)_2Cl_2$ under reflux for 1.0 h and furnished a product, which was characterized as 2,2-difluoro-4-methyl-7-phenyl-8-(*p*-tolyl)-7,8-dihydro-2*H*-[1,3,2]dioxaborinino[4,5-*b*]pyridin-1-ium-2-uide **5a** (Table 2, entry 1).

Under the identical conditions as for **4a** in Table 2 entry 1, a series of reactions of 2-acyl penta-2,4-dienamides **4b–f** were carried out in the presence of $BF_3 \cdot Et_2O$, and some of the results are summarized in Table 2. All the reactions of **4b–f** bearing different aryl amide groups for R^1 and aryl groups for R^2 could proceed smoothly to afford the corresponding dihydropyridin-2(3*H*)-one-BF_2 complexes **5b–f** in good yields (Table 2, entries 2–7). The structure of **5d** was elucidated by NMR (^1H, ^{13}C) spectra and further confirmed by means of the X-ray single crystal analysis (Fig. 2).

In contrast to the conventional acid-catalyzed Knorr quinolin-2(1*H*)-one synthesis,[23] α-acyl *N*-aryl cinnamamides **1** were found to undergo a distinct intramolecular cyclization in which the nucleophilic addition site was on the β-carbon of the α,β-unsaturated carbonyl compounds **1** instead of their α-acyl groups. On the basis of the results obtained above and the reported literatures, a plausible mechanism for the synthesis of dihydroquinolin-2-one-BF_2 complexes **2** is presented in Scheme 3. Mediated by $BF_3 \cdot Et_2O$, α-acyl *N*-arylcinnamamide **1** is activated by the formation of BF_2-complex intermediate **A**,[17d,e] followed by an intramolecular Friedel–Crafts reaction to afford dihydropyridin-2(3*H*)-one-BF_2 complex **2**.[24] It is most possible that the BF_2-complex moiety could not provide enough activation to promote further intramolecular cyclization for **2** under the investigated conditions. As for 2-acyl penta-2,4-dienamides **4**, a BF_2-complex intermediate **B** is formed in the same way (Scheme 3). Here, it is worth noting that BF_2-complex intermediate **B** contains a 1-azatriene moiety, which under the investigated conditions may undergo a 6π-azaelectrocyclization reaction[21] instead of the Friedel–Crafts reaction as α-acyl *N*-aryl cinnamamide **1** did. Just like the role of hydrogen bond did in our previous work, the BF_2-complex structure provides the driving force to keep the azadiene N=C–C=C of **B** in a *cis* conformation that may favor the subsequent 6π-azaelectrocyclization, and also stabilize the structure of product **5**.

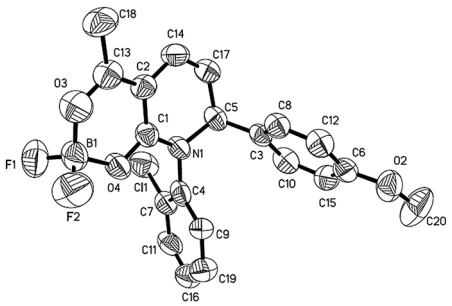
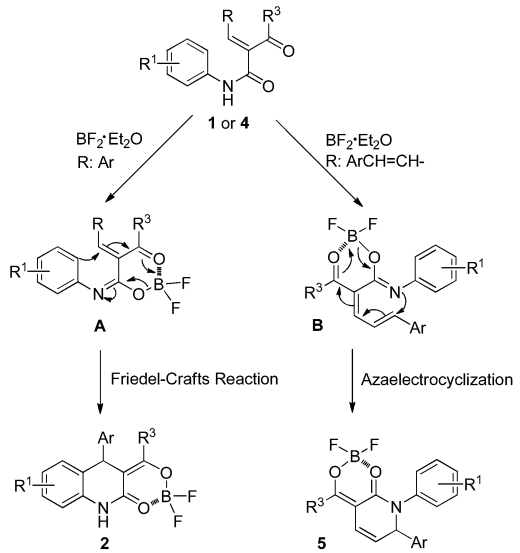


Fig. 2 ORTEP drawing of **5d**.



Scheme 3 Plausible mechanism for the reaction of unsaturated amides mediated by $BF_3 \cdot Et_2O$.

Conclusions

In summary, a facile and convenient synthesis of substituted dihydropyridone–BF_2 complexes **3** and **5** is developed *via* intramolecular cyclization of unsaturated amides, α-acyl *N*-arylcinnamamides **1** and 2-acyl penta-2,4-dienamides **4**, mediated by $BF_3 \cdot Et_2O$, respectively. The simple execution, readily available substrates, very mild conditions, good yields and wide range of synthetic potential of the products make this protocol much attractive. The extension of the scope of the methodology and its further applications are currently under investigation in our laboratory.

Experimental section

General

All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. The products were purified by column chromatography over silica gel. ^1H NMR and ^{13}C NMR spectra were recorded at 25 °C at 300 MHz and 100 MHz, respectively, with TMS as internal standard. IR spectra (KBr) were recorded on FTIR-spectrometer in the range of 400–4000 cm^{-1}. All melting points were determined in open capillary tubes in a Thiele apparatus and are uncorrected.

Typical procedure for the synthesis of substituted unsaturated amides 1 (1a as an example)

To a 100 mL round-bottomed flask was added 3-oxo-*N*-phenylbutanamide (0.89 g, 5.0 mmol), 4-methylbenzaldehyde (0.60 g, 5.0 mmol), piperidine (0.5 mmol), acetic acid (0.5 mmol) and ethanol (30 mL). Then the mixture was stirred for 8.0 h at room temperature. The resulting mixture was slowly poured into

saturated aqueous NaCl (100 mL), and extracted with dichloromethane (3 × 30 mL). The combined organic phase was washed with water (3 × 30 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the crude product was purified by flash chromatography (silica gel, petroleum ether : ethyl acetate10 : 1) to give **1a** as a colorless solid (1.20 g, 86%).

Substrates **1a–k** and **1n** are known compounds (**1a** and **1j**: *J. Indian Chem. Soc.*, 1981, **58**, 168, **1c** and **1d**: *Comptes Rendus Hebdomadaires des Seances de I´Academie des Sciences*, 1949, **228**, 576, **1b**, **1e–k** and **1n**: *Org. Lett.*, 2013, **15**, 776.)

2-(4-Methoxybenzylidene)-3-oxo-*N*-phenylbutanamide (1l) [*E*/*Z* = 4 : 25]. Colorless solid: mp 91–96 °C; ^{1}H NMR (300 MHz, $CDCl_3$) (minor *E*-isomer): δ 2.45 (s, 3H), 3.86 (s, 3H), 6.94 (d, J = 6.0 Hz, 2H), 7.14–7.16 (m, 1H), 7.28–7.33 (m, 2H), 7.57–7.63 (m, 4H), 8.21 (s, 1H), 9.39 (s, 1H); (major *Z*-isomer): δ 2.45 (s, 3H), 3.81 (s, 3H), 6.86 (d, J = 6.0 Hz, 2H), 7.16 (t, J = 6.0 Hz, 1H), 7.35 (t, J = 6.0 Hz, 2H), 7.53–7.57 (m, 5H), 7.88 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.7, 20.5, 22.2, 26.4, 30.9, 54.8, 59.9, 114.0, 119.7, 124.0, 128.5, 131.2, 131.9, 137.3, 140.5, 145.1, 161.3, 165.8, 195.4; Anal. calcd for $C_{18}H_{17}NO_3$: C, 73.20; H, 5.80; N, 4.74. Found: C, 72.81; H, 5.85; N, 4.69.

2-(4-Chlorobenzylidene)-3-oxo-*N*-phenylbutanamide (1m) [*E*/*Z* = 2 : 5]. Colorless solid: mp 122–127 °C; ^{1}H NMR (300 MHz, $CDCl_3$) (minor *E*-isomer): δ 2.17 (s, 3H), 7.11–7.18 (m, 2H), 7.27–7.35 (m, 2H), 7.47–7.50 (m, 2H), 7.52 (s, 2H), 7.58 (d, J = 6.0 Hz, 2H), 9.28 (s, 1H); (major *Z*-isomer): δ 2.43 (s, 3H), 7.11–7.18 (m, 1H), 7.20 (d, J = 12.0 Hz, 1H), 7.27–7.35 (m, 4H), 7.40 (d, J = 9.0 Hz, 1H), 7.45 (s, 1H), 7.47–7.50 (m, 2H), 8.11 (d, J = 4.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.4, 31.1, 119.5, 119.9, 124.2, 128.6, 130.5, 135.8, 136.8, 143.1, 160.3, 165.1, 195.4, 206.3; Anal. calcd for $C_{17}H_{14}ClNO_2$: C, 68.12; H, 4.71; N, 4.67. Found: C, 68.44; H, 4.75; N, 4.62.

Typical procedure for the synthesis of dihydropyridone–BF_2 complexes 2 (2a as an example)

To a 50 mL round bottomed flask was added **1a** (530.0 mg, 2.0 mmol), $BF_3{\cdot}Et_2O$ (5.0 mmol) and CH_2Cl_2 (10 mL). The mixture was stirred at room temperature for 1.0 h. After the substrate **1a** was consumed completely as indicated by TLC, the mixture was poured into ice water, and then extracted with dichloromethane (3 × 20 mL), the combined organic phase was washed with water (3 × 20 mL), and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the crude product was purified by flash chromatography (silica gel, petroleum ether : ethyl acetate 5 : 1) to give **2a** as colorless solid (551.1 mg, 88%).

2,2-Difluoro-4-methyl-5-phenyl-5,10-dihydro-2*H*-[1,3,2]dioxaborinino[4,5-*b*]quinolin-1-ium-2-uide (2a). Yellow solid: mp 239–240 °C; ^{1}H NMR (300 MHz, DMSO): δ 2.05 (s, 3H), 5.33 (s, 1H), 7.07 (d, J = 6.0 Hz, 1H), 7.11 (s, 1H), 7.17–7.22 (m, 2H), 7.25 (s, 1H), 7.28 (d, J = 2.4 Hz, 3H), 7.32 (d, J = 7.5 Hz, 1H), 12.08 (s, 1H); ^{13}C NMR (100 MHz, DMSO): δ 20.4, 41.5, 96.6, 117.2, 125.5, 126.4, 126.7, 126.9, 127.8, 129.0, 129.5, 132.4, 146.3, 163.8, 179.4; IR (KBr, cm^{-1}): 3352, 1624, 1610, 1593, 1526, 1493, 1333, 1119, 762, 706; Anal. calcd for $C_{17}H_{14}BF_2NO_2$: C, 65.21; H, 4.51; N, 4.47. Found: C, 65.52; H, 4.48; N, 4.54.

2,2-Difluoro-4,7-dimethyl-5-phenyl-5,10-dihydro-2*H*-[1,3,2]-dioxaborinino[4,5-*b*]quinolin-1-ium-2-uide (2b). Yellow solid: mp 210–212 °C; ^{1}H NMR (300 MHz, DMSO): δ 2.03 (s, 3H), 2.17 (s, 3H), 5.26 (s, 1H), 6.98 (d, J = 9.9 Hz, 1H), 7.03 (d, J = 9.9 Hz, 2H), 7.18 (t, J = 6.9 Hz, 1H), 7.25 (d, J = 6.9 Hz, 2H), 7.30 (t, J = 7.5 Hz, 2H), 12.01 (s, 1H); ^{13}C NMR (100 MHz, DMSO): δ 20.4, 41.7, 96.7, 117.1, 126.3, 126.8 (1), 126.8 (2), 128.4, 129.0, 129.8, 130.0, 134.9, 146.4, 163.5, 178.9; Anal. calcd for $C_{18}H_{16}BF_2NO_2$: C, 66.09; H, 4.93; N, 4.28. Found: C, 65.87; H, 4.90; N, 4.22.

2,2-Difluoro-4,9-dimethyl-5-phenyl-5,10-dihydro-2*H*-[1,3,2]-dioxaborinino[4,5-*b*]quinolin-1-ium-2-uide (2c). Colorless solid: mp 246–247 °C; ^{1}H NMR (300 MHz, DMSO): 2.09 (s, 3H), 2.34 (s, 3H), 5.31 (s, 1H), 6.99 (t, J = 7.5 Hz, 1H), 7.06 (d, J = 7.5 Hz, 1H), 7.12 (d, J = 7.5 Hz, 1H), 7.16–7.21 (m, 1H), 7.24–7.28 (m, 3H), 7.32 (d, J = 7.5 Hz, 1H), 11.22 (s, 1H); ^{13}C NMR (100 MHz, DMSO): δ 17.8, 20.5, 41.8, 97.0, 125.4, 126.1, 126.8, 127.0, 127.4, 128.1, 128.9, 129.2, 129.8, 130.9, 146.5, 164.6, 179.9; Anal. calcd for $C_{18}H_{16}BF_2NO_2$: C, 66.09; H, 4.93; N, 4.28. Found: C, 66.35; H, 4.88; N, 4.31.

2,2-Difluoro-4,8-dimethyl-5-phenyl-5,10-dihydro-2*H*-[1,3,2]-dioxaborinino[4,5-*b*]quinolin-1-ium-2-uide (2d). Yellow solid: mp 261–263 °C; ^{1}H NMR (300 MHz, DMSO): δ 2.04 (s, 3H), 2.33 (s, 3H), 5.27 (s, 1H), 5.76 (s, 1H), 6.90 (d, J = 7.8 Hz, 2H), 7.13 (d, J = 7.8 Hz, 1H), 7.19 (d, J = 7.5 Hz, 1H), 7.24 (d, J = 7.5 Hz, 2H), 7.30 (d, J = 7.5 Hz, 2H), 12.02 (s, 1H); ^{13}C NMR (100 MHz, DMSO): δ 20.4, 20.5, 41.2, 54.8, 96.7, 117.4, 123.5, 126.2, 126.7, 129.0, 129.3, 132.1, 137.3, 146.5, 163.8, 179.2; Anal. calcd for $C_{18}H_{16}BF_2NO_2$: C, 66.09; H, 4.93; N, 4.28. Found: C, 66.42; H, 5.00; N, 4.22.

2,2-Difluoro-4,7,9-trimethyl-5-phenyl-5,10-dihydro-2*H*-[1,3,2]-dioxaborinino[4,5-*b*]quinolin-1-ium-2-uide (2e). Yellow solid: mp 291–293 °C; ^{1}H NMR (300 MHz, DMSO): δ 2.08 (s, 3H), 2.14 (s, 3H), 2.30 (s, 3H), 5.24(s, 1H), 6.87 (s, 1H), 6.91 (s, 1H), 7.16–7.33 (m, 5H), 11.19 (s, 1H); ^{13}C NMR (100 MHz, DMSO): δ 17.5, 20.2, 20.4, 41.8, 96.9, 125.8, 126.6, 126.7, 126.8, 127.6, 128.4, 129.0, 130.3, 134.4, 146.4, 164.2, 179.3; IR (KBr, cm^{-1}): 3337, 1626, 1601, 1526, 1485, 1327, 1146, 731, 706; Anal. calcd for $C_{19}H_{18}BF_2NO_2$: C, 66.89; H, 5.32; N, 4.11. Found: C, 66.52; H, 5.39; N, 4.17.

7-Chloro-2,2-difluoro-4-methyl-5-phenyl-5,10-dihydro-2*H*-[1,3,2]dioxaborinino[4,5-*b*]quinolin-1-ium-2-uide (2f). Yellow solid: mp 218–219 °C; ^{1}H NMR (300 MHz, DMSO): δ 2.05 (s, 3H), 5.37 (s, 1H), 7.11 (d, J = 6.0 Hz, 1H), 7.20–7.24 (m, 1H), 7.28–7.36 (m, 6H), 12.20 (s, 1H); ^{13}C NMR (100 MHz, DMSO): δ 20.5, 41.3, 96.1, 119.0, 126.8, 127.1, 127.8, 128.5, 129.0, 129.2, 131.5, 145.8, 163.8, 179.9; IR (KBr, cm^{-1}): 3348, 3333, 1622, 1609, 1593, 1520, 1489, 1140, 746, 710, 696; Anal. calcd for $C_{17}H_{13}BClF_2NO_2$: C, 58.75; H, 3.77; N, 4.03. Found: C, 59.10; H, 3.69; N, 4.06.

2,2-Difluoro-7-methoxy-4-methyl-5-phenyl-5,10-dihydro-2*H*-[1,3,2]dioxaborinino[4,5-*b*]quinolin-1-ium-2-uide (2g). Yellow solid: mp 226–228 °C; ^{1}H NMR (400 MHz, DMSO): δ 2.03 (s, 3H), 3.66 (s, 3H), 5.29 (s, 1H), 6.82–6.85 (m, 2H), 7.02–7.05 (m, 1H), 7.17–7.22 (m, 1H), 7.25–7.29 (m, 3H), 7.32 (d, J = 7.5 Hz, 1H), 11.99 (s, 1H); ^{13}C NMR (100 MHz, DMSO): δ 21.2, 43.5, 55.5, 96.1, 113.2, 115.2, 118.0, 124.8, 126.9, 127.3, 129.2, 145.2, 157.5,

163.3, 181.0; IR (KBr, cm^{-1}): 3348, 1703, 1647, 1620, 1597, 1529, 1499, 1269, 1130, 733, 698; Anal. calcd for $C_{18}H_{16}BF_2NO_3$: C, 63.01; H, 4.70; N, 4.08. Found: C, 63.18; H, 4.69; N, 4.10.

Crystal data for **2g**: $C_{18}H_{16}BF_2NO_3$, colorless crystal, M = 343.13, monoclinic, $C2/c'$, a = 26.916(3) Å, b = 8.0515(9) Å, c = 17.954(2) Å, α = 90.00°, β = 123.571(2)°, γ = 90.00°, V = 3241.9(6) $Å^3$, Z = 8, T = 293(2) K, F000 = 1512, R = 0.0474.

2,2-Difluoro-9-methoxy-4-methyl-5-phenyl-5,10-dihydro-2*H*-[1,3,2]dioxaborinino[4,5-*b*]quinolin-1-ium-2-uide (2h). Colorless solid: mp 239–240 °C; ^{1}H NMR (300 MHz, DMSO): δ 2.06 (s, 3H), 3.83 (s, 3H), 5.28 (s, 1H), 6.84 (d, J = 8.1 Hz, 1H), 6.90 (d, J = 8.1 Hz, 1H), 7.04 (t, J = 8.1 Hz, 1H), 7.15–7.23 (m, 1H), 7.25–7.31 (m, 4H), 11.50 (s, 1H); ^{13}C NMR (100 MHz, DMSO): δ 20.5, 41.5, 56.1, 96.7, 110.2, 121.0, 121.6, 125.8, 126.7, 126.9, 127.4, 129.0, 146.2, 147.8, 164.0, 179.5; IR (KBr, cm^{-1}): 3319, 1608, 1593, 1543, 1495, 1271, 1103, 750; Anal. calcd for $C_{18}H_{16}BF_2NO_3$: C, 63.01; H, 4.70; N, 4.08. Found: C, 62.82; H, 4.74; N, 3.99.

2,2-Difluoro-4-methyl-5-(*p*-tolyl)-5,10-dihydro-2*H*-[1,3,2]dioxaborinino[4,5-*b*]quinolin-1-ium-2-uide (2i). Yellow solid: mp 192–194 °C; ^{1}H NMR (300 MHz, DMSO): δ 2.04 (s, 3H), 2.22 (s, 3H), 5.27 (s, 1H), 7.05–7.11 (m, 4H), 7.15 (d, J = 8.1 Hz, 2H), 7.19–7.25 (m, 2H), 12.04 (s, 1H); ^{13}C NMR (100 MHz, DMSO): δ 20.5, 41.2, 54.8, 96.6, 117.1, 125.4, 126.6, 127.7, 129.5 (1), 129.5 (2), 132.3, 136.0, 143.5, 163.7, 179.2; IR (KBr, cm^{-1}): 3344, 1628, 1595, 1526, 1491, 1329, 810, 762; Anal. calcd for $C_{18}H_{16}BF_2NO_2$: C, 66.09; H, 4.93; N, 4.28. Found: C, 65.79; H, 5.01; N, 4.33.

2,2-Difluoro-4-methyl-5-(*o*-tolyl)-5,10-dihydro-2*H*-[1,3,2]dioxaborinino[4,5-*b*]quinolin-1-ium-2-uide (2j). Yellow solid: mp 251–253 °C; ^{1}H NMR (300 MHz, DMSO): δ 1.92 (s, 3H), 2.34 (s, 3H), 5.52 (s, 1H), 7.03–7.08 (m, 3H), 7.12–7.18 (m, 3H), 7.20–7.26 (m, 2H), 12.08 (s, 1H); ^{13}C NMR (100 MHz, DMSO): δ 19.0, 20.8, 96.5, 117.0, 125.5, 125.8, 126.6, 126.9, 127.8, 129.3, 131.4, 132.3, 134.2, 144.4, 163.6, 179.0; IR (KBr, cm^{-1}): 3354, 1622, 1591, 1521, 1493, 1047, 764; Anal. calcd for $C_{18}H_{16}BF_2NO_2$: C, 66.09; H, 4.93; N, 4.28. Found: C, 66.41; H, 4.89; N, 4.32.

2,2-Difluoro-5-(4-methoxyphenyl)-4-methyl-5,10-dihydro-2*H*-[1,3,2]dioxaborinino[4,5-*b*]quinolin-1-ium-2-uide (2k). Yellow solid: mp 204–206 °C; ^{1}H NMR (300 MHz, DMSO): δ 2.04 (s, 3H), 3.68 (s, 3H), 5.26 (s, 1H), 6.86 (d, J = 9.0 Hz, 2H), 7.08 (t, J = 9.0 Hz, 2H), 7.17 (d, J = 9.0 Hz, 2H), 7.21–7.25 (m, 2H), 12.03 (s, 1H); ^{13}C NMR (100 MHz, DMSO): δ 20.8, 41.0, 55.4, 97.1, 114.7, 117.5, 125.8, 127.2, 128.0, 128.2, 129.9, 132.6, 139.0, 158.4, 164.1, 179.7; Anal. calcd for $C_{18}H_{16}BF_2NO_3$: C, 63.01; H, 4.70; N, 4.08. Found: C, 63.39; H, 4.77; N, 4.16.

5-(4-Chlorophenyl)-2,2-difluoro-4-methyl-5,10-dihydro-2*H*-[1,3,2]dioxaborinino[4,5-*b*]quinolin-1-ium-2-uide (2l). Yellow solid: mp 218–220 °C; ^{1}H NMR (300 MHz, DMSO): δ 2.07 (s, 3H), 5.40 (s, 1H), 7.10 (t, J = 7.5 Hz, 2H), 7.24 (t, J = 7.5 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H), 12.12 (s, 1H); ^{13}C NMR (100 MHz, DMSO): δ 20.5, 40.9, 96.3, 117.3, 125.6, 125.9, 128.0, 129.0, 129.5, 131.7, 132.4, 145.2, 163.7, 179.6; IR (KBr, cm^{-1}): 3333, 1630, 1595, 1529, 1493, 1323, 1057, 760, 719; Anal. calcd for $C_{17}H_{13}BClF_2NO_2$: C, 58.75; H, 3.77; N, 4.03. Found: C, 58.44; H, 3.84; N, 4.12.

2,2-Difluoro-4,5-diphenyl-5,10-dihydro-2*H*-[1,3,2]dioxaborinino[4,5-*b*]quinolin-1-ium-2-uide (2m). Colorless solid: mp 282–284 °C; ^{1}H NMR (400 MHz, DMSO): δ 5.36 (s, 1H), 6.90 (d, J = 7.6 Hz, 2H), 7.09–7.19 (m, 5H), 7.26 (t, J = 7.6 Hz, 1H), 7.37 (d, J = 7.6 Hz, 1H), 7.45–7.50 (m, 4H), 7.56 (t, J = 6.8 Hz, 1H), 12.41 (s, 1H); ^{13}C NMR (100 MHz, DMSO): δ 41.4, 97.2, 117.1, 125.7, 126.1, 126.3, 126.7, 127.8, 127.9, 128.6, 128.7, 129.4, 131.2, 132.4, 133.6, 145.6, 165.1, 174.8; IR (KBr, cm^{-1}): 3312, 1628, 1589, 1580, 1522, 1489, 1132, 762, 702; Anal. calcd for $C_{22}H_{16}BF_2NO_2$: C, 70.43; H, 4.30; N, 3.73. Found: C, 70.01; H, 4.19; N, 3.81.

10-Ethyl-2,2-difluoro-4-methyl-5-phenyl-5,10-dihydro-2*H*-[1,3,2]dioxaborinino[4,5-*b*]quinolin-1-ium-2-uide (2n). Colorless solid: mp 189–191 °C; ^{1}H NMR (400 MHz, DMSO): δ 1.31 (t, J = 6.9 Hz, 3H), 2.12 (s, 1H), 4.14–4.24 (m, 2H), 5.34 (s, 1H), 7.16–7.23 (m, 3H), 7.25–7.32 (m, 4H), 7.36 (d, J = 7.8 Hz, 1H), 7.39 (t, J = 7.8 Hz, 1H), 7.45 (d, J = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, DMSO): δ 13.0, 20.8, 39.1, 41.4, 97.5, 116.9, 126.3, 127.0, 127.4, 128.5, 129.5, 130.4, 133.8, 146.2, 163.6, 179.3; IR (KBr, cm^{-1}): 1603, 1580, 1518, 1487, 1337, 1138, 756, 700; Anal. calcd for $C_{19}H_{18}BF_2NO_2$: C, 66.89; H, 5.32; N, 4.11. Found: C, 67.23; H, 5.26; N, 4.17.

The procedure for the synthesis of substituted quinolin-2(1*H*)-one 3h

To a 50 mL round bottomed flask was added 2 h (686.3 mg, 2.0 mmol), DDQ (3.0 mmol) and CH_2Cl_2 (10 mL). The mixture was stirred at room temperature for 1.0 h. After the substrate **2g** was consumed completely as indicated by TLC, the mixture was poured into ice water, and then extracted with dichloromethane (3 × 20 mL), the combined organic phase was washed with water (3 × 20 mL), and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the crude product was purified by flash chromatography (silica gel, petroleum ether : ethyl acetate 4 : 1) to give **3h** as colorless solid (469.3 mg, 80%).

3-Acetyl-6-methoxy-4-phenylquinolin-2(1*H*)-one (3h). Yellow solid: mp 260–261 °C; ^{1}H NMR (400 MHz, DMSO): δ 2.21 (s, 3H), 3.57 (s, 3H), 6.64 (d, J = 2.4 Hz, 1H), 7.24–7.27 (dd, J_1 = 9.2 Hz, J_2 = 2.4 Hz, 1H), 7.31 (s, 1H), 7.33 (d, J = 2.4 Hz, 1H), 7.37 (d, J = 9.2 Hz, 1H), 7.48–7.53 (m, 3H), 12.14 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 31.4, 55.2, 109.0, 117.0, 119.5, 119.8, 128.5, 128.7, 133.0, 133.7, 134.2, 146.4, 154.2, 158.8, 201.7; IR (KBr, cm^{-1}): 3446, 1703, 1647, 1597, 1497, 1281, 733, 702; Anal. calcd for $C_{18}H_{15}NO_3$: C, 73.71; H, 5.15; N, 4.78. Found: C, 74.16; H, 5.20; N, 4.83.

Typical procedure for the synthesis of dihydropyridone–BF_2 complexes 5 (5a as an example)

To a 50 mL round bottomed flask was added 4a (610.7 mg, 2.0 mmol), $BF_3 \cdot Et_2O$ (3.0 mmol) and DCE (10 mL). The mixture was stirred at 80 °C for 2.0 h. After the substrate **4a** was consumed completely as indicated by TLC, the mixture was poured into ice water, and then extracted with dichloromethane (3 × 20 mL), the combined organic phase was washed with water (3 × 20 mL), and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure, and the crude product was purified by flash chromatography (silica gel, petroleum

ether : ethyl acetate 4 : 1) to give **5a** as a colorless solid (494.4 mg, 70%).

2,2-Difluoro-4-methyl-7-phenyl-8-(*p*-tolyl)-7,8-dihydro-2*H*-[1,3,2]dioxaborinino[4,5-*b*]pyridin-1-ium-2-uide (5a). Yellow solid: mp 189–192 °C; ^{1}H NMR (300 MHz, DMSO): δ 2.21 (s, 3H), 2.27 (s, 3H), 4.55 (d, J = 7.5 Hz, 1H), 6.04–6.11 (dd, J_1 = 15.6 Hz, J_2 = 7.5 Hz, 1H), 6.34 (d, J = 15.6 Hz, 1H), 6.84 (d, J = 8.1 Hz, 1H), 6.99 (d, J = 8.1 Hz, 1H), 7.04 (s, 1H), 7.18–7.29 (m, 5H), 8.20 (s, 1H); ^{13}C NMR (100 MHz, DMSO): δ 20.1, 20.6, 94.2, 117.0, 124.5, 126.5, 127.6, 128.0, 128.6, 129.8, 130.5, 131.9, 134.9, 136.2, 163.5, 178.6; IR (KBr, cm^{-1}): 3346, 1622, 1595, 1529, 1501, 1167, 816, 770, 746, 689; Anal. calcd for $C_{20}H_{18}BF_2NO_2$: C, 68.02; H, 5.14; N, 3.97. Found: C, 67.83; H, 5.21; N, 4.07.

2,2-Difluoro-8-(4-methoxyphenyl)-4-methyl-7-phenyl-7,8-dihydro-2*H*-[1,3,2]dioxaborinino[4,5-*b*]pyridin-1-ium-2-uide (5b). Yellow solid: mp 210–211 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.25 (s, 3H), 3.79 (s, 3H), 4.61 (d, J = 7.5 Hz, 1H), 6.08–6.16 (dd, J_1 = 15.6 Hz, J_2 = 7.5 Hz, 1H), 6.38 (d, J = 15.6 Hz, 1H), 6.76–6.79 (dd, J_1 = 8.7 Hz, J_2 = 2.7 Hz, 1H), 6.82 (d, J = 2.7 Hz, 1H), 6.91 (d, J = 8.7 Hz, 1H), 7.22–7.30 (m, 5H), 8.00 (s, 1H); ^{13}C NMR (100 MHz, DMSO): δ 19.9, 55.4, 93.8, 113.4, 114.6, 118.1, 126.0, 126.1, 126.4, 127.6, 128.1, 128.6, 131.8, 136.2, 157.0, 178.1; Anal. calcd for $C_{20}H_{18}BF_2NO_3$: C, 65.07; H, 4.91; N, 3.79. Found: C, 65.53; H, 4.85; N, 3.91.

8-(4-Chlorophenyl)-2,2-difluoro-4-methyl-7-phenyl-7,8-dihydro-2*H*-[1,3,2]dioxaborinino[4,5-*b*]pyridin-1-ium-2-uide (5c). Yellow solid: mp 219–221 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.28 (s, 3H), 5.43 (d, J = 3.9 Hz, 1H), 5.49–5.54 (dd, J_1 = 10.2 Hz, J_2 = 3.9 Hz, 1H), 6.46 (d, J = 10.2 Hz, 1H), 6.84 (d, J = 8.7 Hz, 1H), 7.06–7.10 (m, 2H), 7.26 (s, 1H), 7.27–7.31 (m, 1H), 7.32 (d, J = 1.5 Hz, 1H), 7.34 (d, J = 1.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.6, 68.5, 95.2, 118.0, 118.5, 127.7, 128.5, 129.1, 129.2, 129.6, 134.8, 135.8, 137.8, 164.8, 174.0; Anal. calcd for $C_{19}H_{15}BClF_2NO_2$: C, 61.08; H, 4.05; N, 3.75. Found: C, 61.53; H, 4.16; N, 3.86.

8-(2-Chlorophenyl)-2,2-difluoro-7-(4-methoxyphenyl)-4-methyl-7,8-dihydro-2*H*-[1,3,2]dioxaborinino[4,5-*b*]pyridin-1-ium-2-uide (5d) (*d*/*r* = 5 : 3). Yellow solid: mp 151–155 °C; ^{1}H NMR (major isomer) (400 MHz, DMSO): δ 2.29 (s, 3H), 3.73 (s, 3H), 5.50 (d, J = 4.0 Hz, 1H), 5.62–5.66 (dd, J_1 = 12.0 Hz, J_2 = 4.0 Hz, 1H), 6.42 (d, J = 8.0 Hz, 1H), 6.91 (d, J = 12.0 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 7.21 (t, J = 8.0 Hz, 1H), 7.44 (t, J = 8.0 Hz, 1H), 7.72 (d, J = 8.0 Hz, 1H); ^{1}H NMR (minor isomer) (400 MHz, DMSO): δ 2.27 (s, 3H), 3.68 (s, 3H), 5.57–5.60 (dd, J_1 = 12.0 Hz, J_2 = 4.0 Hz, 1H), 5.93 (s, 1H), 6.71 (d, J = 12.0 Hz, 1H), 6.78 (d, J = 12.0 Hz, 2H), 6.99 (d, J = 8.0 Hz, 2H), 7.35–7.39 (m, 2H), 7.49–7.53 (m, 1H), 7.87 (d, J = 8.0 Hz, 1H); ^{13}C NMR (100 MHz, DMSO): δ 19.7, 19.8, 55.4, 55.5, 66.0, 67.5, 95.2, 95.3, 113.8, 114.6, 118.0, 118.7, 119.2, 119.3, 128.1, 128.9, 130.4, 131.1, 134.4, 135.1, 159.9, 160.0, 163.8, 164.9, 173.3, 174.4; Anal. calcd for $C_{20}H_{17}BClF_2NO_3$: C, 59.52; H, 4.25; N, 3.47. Found: C, 59.91; H, 4.36; N, 3.40.

Crystal data for **5d**: $C_{20}H_{17}BClF_2NO_3$, colorless crystal, M = 871.29, P-1, a = 7.643(5) Å, b = 12.269(5) Å, c = 12.840(5) Å, α = 101.954(5)°, β = 104.028(5)°, γ = 98.284(5)°, V = 1118.6(10) Å^3, Z = 1, T = 293(2) K, F000 = 450, R = 0.0123.

2,2-Difluoro-7-(4-methoxyphenyl)-4-methyl-8-(*o*-tolyl)-7,8-dihydro-2*H*-[1,3,2]dioxaborinino[4,5-*b*]pyridin-1-ium-2-uide (5e). Yellow solid: mp 182–183 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.27 (s, 3H), 2.31 (s, 3H), 3.79 (s, 3H), 4.62 (d, J = 7.2 Hz, 1H), 5.94–6.01 (dd, J_1 = 15.6 Hz, J_2 = 7.2 Hz, 1H), 6.30 (d, J = 15.6 Hz, 1H), 6.81 (d, J = 8.7 Hz, 2H), 7.06–7.08 (m, 2H), 7.15–7.18 (m, 1H), 7.23 (s, 1H), 7.66 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.5, 20.7, 40.8, 55.3, 94.2, 114.0, 124.1, 124.4, 125.5, 127.4, 127.7, 128.6, 128.7, 129.7, 130.4, 159.4, 164.3, 181.7; IR (KBr, cm^{-1}): 1630, 1601, 1560, 1512, 1252, 1180, 827, 764; Anal. calcd for $C_{21}H_{20}BF_2NO_3$: C, 65.82; H, 5.26; N, 3.66. Found: C, 66.03; H, 5.31; N, 3.57.

2,2-Difluoro-4-methyl-7,8-di-*p*-tolyl-7,8-dihydro-2*H*-[1,3,2]dioxaborinino[4,5-*b*]pyridin-1-ium-2-uide (5f). Yellow solid: mp 219–221 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.24 (s, 3H), 2.30 (s, 3H), 2.31 (s, 3H), 4.57 (d, J = 7.5 Hz, 1H), 6.02–6.10 (dd, J_1 = 15.6 Hz, J_2 = 7.5 Hz, 1H), 6.34 (d, J = 15.6 Hz, 1H), 6.85 (d, J = 8.1 Hz, 1H), 7.03 (d, J = 8.1 Hz, 1H), 7.09 (d, J = 8.1 Hz, 3H), 7.21 (d, J = 8.1 Hz, 2H), 8.02 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.6, 20.9, 21.1, 40.8, 94.4, 116.9, 124.0, 126.4, 128.9, 129.0, 129.2, 129.6, 129.7, 129.8, 133.3, 135.8, 137.7, 163.8, 180.4; IR (KBr, cm^{-1}): 3344, 1626, 1599, 1529, 1500, 1207, 1163, 814; Anal. calcd for $C_{21}H_{20}BF_2NO_2$: C, 68.69; H, 5.49; N, 3.81. Found: C, 68.36; H, 5.54; N, 3.84.

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