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Pyridone fused boron-dipyrromethenes: synthesis and properties†

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In this paper a general procedure for the introduction of pyridone moiety was developed, using a Friedländer reaction, for post-modification of ready-made BODIPY core, from which three pyridone-fused BODIPYs **1**, **2** and **3** were generated. This method is complementary to the classical method for obtaining aromatic ring-fused BODIPYs, which begins with the condensation of the corresponding aromatic ring-fused pyrroles. These pyridone-fused BODIPYs are distinctive, possessing favorable photophysical characteristics with strong absorption, high bright orange fluorescence and easy reduction due to the electron-withdrawing effect of the fused pyridone moiety. More important, these BODIPYs bear reactive functions which are applicable in proteins labeling by bioorthogonal chemical reactions.

Introduction

Boron-dipyrromethene (BODIPY) derivatives are of high interest and well known to be attractive functional groups for the construction of molecular sensors and light-harvesting systems, owing to their valuable photophysical properties, such as high fluorescence quantum yields, relatively high absorption coefficients, and high photo- and chemostability.[1] Thus, there is great attention to the engineering of BODIPYs. Thanks to the easy modification of the BODIPY core, the preparation of sophisticated BODIPY dyes resolving specific problems have been established.[2–5]

One of the most commonly studied synthetic strategies available for the modification of the BODIPY core is the nucleophilic substitutions of halogen atoms at the 3- and/or 5-positions.[6–7] Until now, a series of oxygen-, nitrogen-, and sulfur-centred nucleophiles substituted at the 3- and/or 5-positions of BODIPY dyes have been introduced. Of special interest is that the 3,5-substituents could alter the electronic properties of BODIPY dyes significantly, demonstrating the fast and easy variation of the dye to optimize the spectroscopic properties. However, most studies just stop at this step, no further post-functionality for the synthesis of constrained molecules with a precise molecular architecture, which are well programmed to generate upgraded functionality and desired physicochemical properties. Our group has reported a route, using a 3-chloro-BODIPY precursor, for efficient synthesis of α-amino-β-formylated BODIPYs.[6a] The structure of this BODIPY represents an aromatic 2-amino-substituted carbonyl compound, a precursor for the Friedländer reaction which is one of the simplest methods to construct quinoline ring systems.[8] Therefore, it can be envisioned that a general procedure for the introduction of pyridone onto a single BODIPY core can be developed by the Friedländer reaction, which can be used to get pyridone-fused BODIPYs and is complementary to the classical method for obtaining aromatic ring-fused BODIPYs.

It is demonstrated that the fusion of aryl moieties can result in an extension of the π-system while retaining the rigidity and increasing the planarity of the BODIPYs. Therefore, several reports have been published concerning this method to obtain the rigid ring fused constrain BODIPY molecules.[9,10] However, the main synthetic approach for the fusion of aryl moieties into the BODIPYs begins with the condensation of the corresponding aromatic ring-fused pyrroles.[9] The post-modification of the ready-made BODIPY core to get aromatic ring-fused BODIPY molecules has not been investigated well. Hence, we envisioned the possibility to introduce the fusion of aromatic moieties into the BODIPY core by a post-functionalization approach. Herein, we report the synthesis of three pyridone-fused BODIPYs *via* modified Friedländer reaction conditions, as well as the spectroscopic properties investigated in various solvents. These rigid pyridone ring-fused BODIPYs are distinctive, possessing favorable photophysical characteristics.

Results and discussion

Synthesis

To synthesize the designed BODIPYs **1**, **2** and **3**, the key synthetic precursor BODIPY **4** was firstly prepared as shown in

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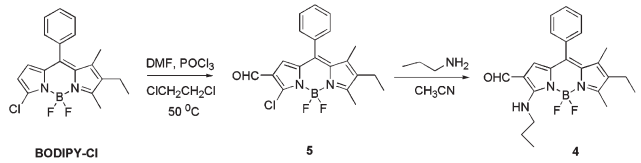
†Electronic supplementary information (ESI) available: UV-vis absorption and emission spectra, fluorescence decay profile, ^{1}H NMR, ^{13}C NMR spectra of the new compounds. See DOI: 10.1039/c2ob26791h



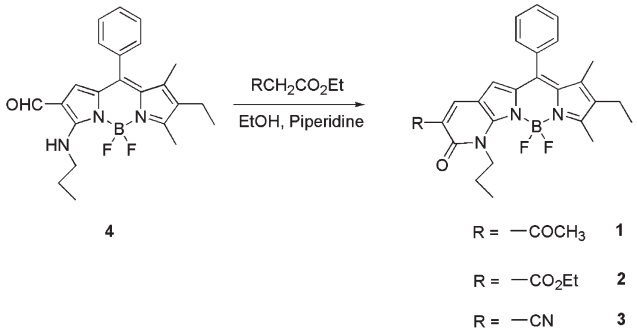
Scheme 1 Synthesis of BODIPY **4**.

Scheme 1. Previously, we reported a route to get the analogue of compound **4**, starting from **BODIPY-Cl**, followed by S_NAr substitution with an amine nucleophile and subsequent β-formylation.[6a] While this approach was successful, the nucleophilic substitution step needed refluxing in CH_3CN for the reaction to proceed at an acceptable rate. Enhancement of the electron deficiency at the 3-position must increase the reactivity towards nucleophiles. To prove this concept, treatment of **BODIPY-Cl** was first adopted by Vilsmeier–Haack reactions using $DMF/POCl_3$ in chloroform with 89% yield of **5** formation. As expected, nucleophilic substitution of **5** with propylamine readily takes place at room temperature with high yield. This observation is consistent with the difference in reactivity between 3,5-dichloro-BODIPYs and monochlorinated BODIPYs.[6,7d]

It is well known that fusion of the pyridine moiety to a phenyl ring by the Friedländer reaction results in a quinoline system. The Friedländer reaction requires an aromatic 2-amino-substituted carbonyl compound and an appropriately substituted carbonyl derivative containing a reactive α-methylene group as reactive substrates. While BODIPY **4** is an aromatic 2-amino-substituted aldehyde, it can be envisioned that a general procedure for the introduction of pyridone onto a single BODIPY core can be developed by the Friedländer reaction, complementary to the classical method to get aromatic-ring fused BODIPYs. To demonstrate the capacity, BODIPY **4** was subjected to Friedländer reactions with ethyl acetoacetate, diethyl malonate, and ethyl cyanoacetate in EtOH in the presence of piperidine as shown in Scheme 2, from which **1**, **2** and **3** were generated in 26%–31% yield under refluxing.

The chemical structures for **1**, **2** and **3** were confirmed by ^1H NMR, ^{13}C NMR, HRMS analysis. The important features, two typical chemical shifts as singlet, can be observed in ^1H NMR spectra. The pyridone protons appears in the region of 7.8–8.6 ppm, while that of 1-pyrrole protons in 6.4–6.5 ppm.

From the viewpoint of molecular structure, BODIPYs **1**, **2** and **3** bear reactive function ketone, ester and cyano, respectively. These reactive functions are applicable in proteins labeling by chemical reactions, such as reactions between ketones and oxyamino-containing reagents.[11,12] This bioorthogonal reaction has found wide application in the conjugation of biomolecules. To demonstrate our designed BODIPYs can be exploited as ligation reagents for modification of proteins, we here have confined ourselves only to investigate whether **1** could react with small molecules containing oxyamino groups. If this reaction could be performed smoothly, then **1** would



Scheme 2 Synthesis of **1**, **2** and **3** under Friedländer reaction conditions.

find application in modification of proteins incorporated oxyamino groups. As expected, when methoxyamine or 1,2-bis(oxyamino)ethane was mixed with **1**, a new peak for the condensation product was detected by HPLC analysis after 1 h. The identity of each product was confirmed by mass spectrometry (Fig. S1†), which revealed a mass of 505.2286 for the reaction with methoxyamine and a mass of 550.2648 for **1** with 1,2-bis(oxyamino)ethane.

Spectroscopic properties

Spectroscopic evaluation of **1**, **2** and **3** was performed in several solvents of varying polarity (Fig. 1 and 2, Fig. S2–S3,†

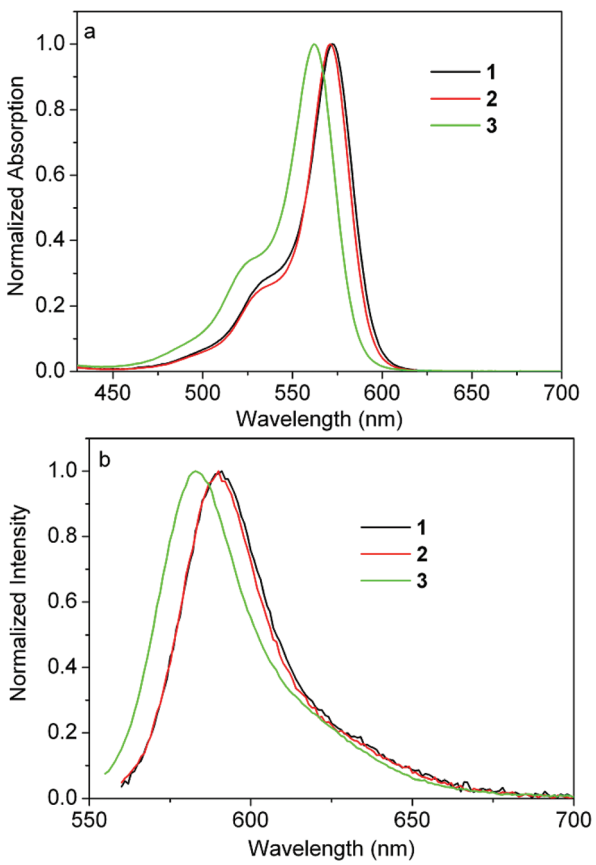


Fig. 1 (a) The normalized absorption and (b) emission of **1**, **2** and **3** in toluene.

Table 1). All dyes showed typical absorption and emission features of BODIPY dyes in solutions as shown in Fig. 1, with strong absorption and high fluorescence quantum yields.

The absorption of the three dyes displays a main S_0–S_1 absorption band with a vibrational transition on the higher-energy side as a shoulder. **1** and **2** exhibit almost the same absorption spectra with the band centered at 542–572 nm, whereas **3** shows a 10 nm hypsochromic shift in the absorption. Consistent with typical BODIPYs, no significant solvent-dependent spectra variations were observed, with the maximum being shifted hypsochromically (~28 nm) when the solvent is changed from a nonpolar solvent to a polar one (Table 1).

Similar to the absorption spectra, no significant solvatochromic effect was observed in the fluorescence spectra. The fluorescence maxima display less than 20 nm hypsochromically shifts upon increasing solvent polarity. The maximum emission wavelength of **1** and **2** is in 578–591 nm range, while that of **3** centered between 569 and 583 nm. Notably, the fusion of pyridone into BODIPY core results in bathochromic shifts in the absorption (~30 nm) and emission spectra (~50 nm), when compared to the simple BODIPYs in the literature.[1b] All three dyes exhibit bright orange fluorescence with relatively high quantum yields and small Stokes shifts. The fluorescence quantum yield decreases with increasing solvent polarity, which is consistent with that of other BODIPY systems.

The fluorescence decay of **1**, **2** and **3** in pure solvents is monoexponential, with a fluorescence lifetime corresponding to the orientation polarizability of the solvent. The representative fluorescence lifetime of **1** (Fig. 3) decreases from 3.0 ns to 2.0 ns with increasing the polarity of solvents from CH_2Cl_2 to CH_3CN. The rates of radiative and nonradiative decays were then calculated from the measured fluorescence lifetimes and quantum yields and are presented in Table 2. These values are in close agreement with those reported for other BODIPY chromophores.[13]

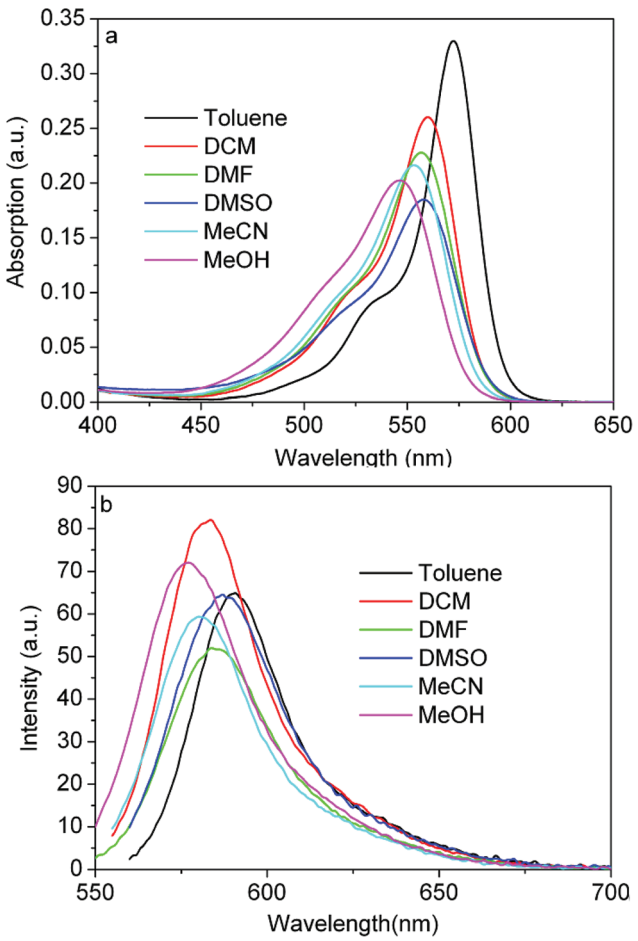


Fig. 2 (a) The absorption and (b) emission of **1** in different solvents.

Electrochemical properties

The redox properties of **1**, **2** and **3** (Fig. 4) were investigated by cyclic voltammetric (CV) experiments, which were performed in CH_2Cl_2 containing Bu_4NPF_6 as supporting electrolyte at a scan rate of 100 mV s^{-1} at room temperature. All reported potentials are calibrated against the ferrocene/ferrocenium (Fc/Fc^+) couple. Based on comparison of the results with the CVs of the reported BODIPY derivatives in the literatures,[14–16] the quasi-reversible oxidation processes with half-wave potentials occurring in the range between *ca.* 1.3 and 1.5 V are attributed to the oxidation of the BODIPY unit to form the corresponding radical cation. The reversible reductions observed in the cyclic voltammograms of **1**, **2**, and **3** are shifted to less negative potentials when compared to the reversible reduction of the BODIPY core,[14–16] due to the electron-withdrawing effect of the fused pyridone moiety. This trend is reflected in the reduction of nitro substituted BODIPYs. By switching a cyano

Table 1 Photophysical properties of **1**, **2** and **3** in several solvents of varying polarity

	λ_{abs} (nm)			λ_{em} (nm)			Φ		
Solvent	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**
Toluene	572	571	562	591	590	583	0.61	0.37	0.43
CH_2Cl_2	560	558	545	582	581	572	0.51	0.27	0.41
DMF	557	557	544	584	581	578	0.40	0.22	0.31
DMSO	558	556	545	587	585	579	0.48	0.31	0.37
Acetonitrile	553	552	540	580	572	572	0.30	0.23	0.26
Methanol	547	542	532	578	571	569	0.38	0.24	0.32

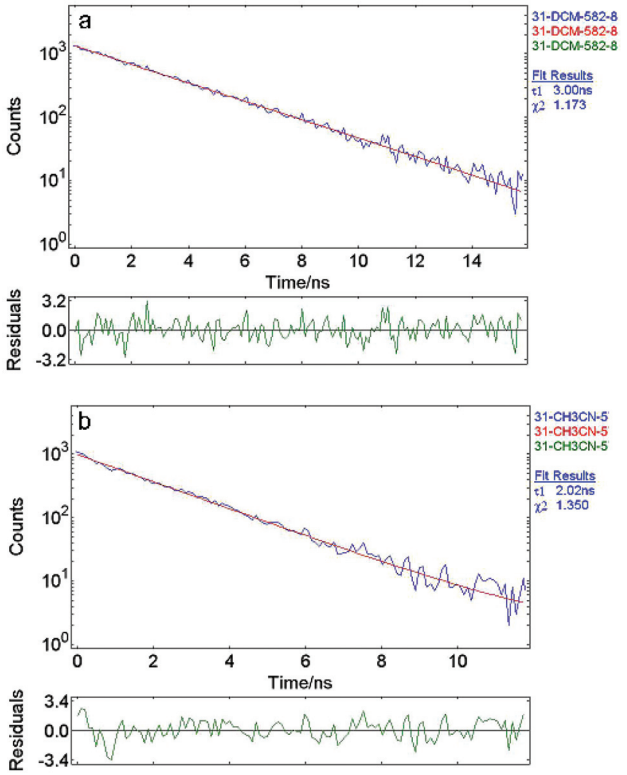


Fig. 3 Fluorescent decay profiles of **1** in (a) CH_2Cl_2 and (b) CH_3CN.

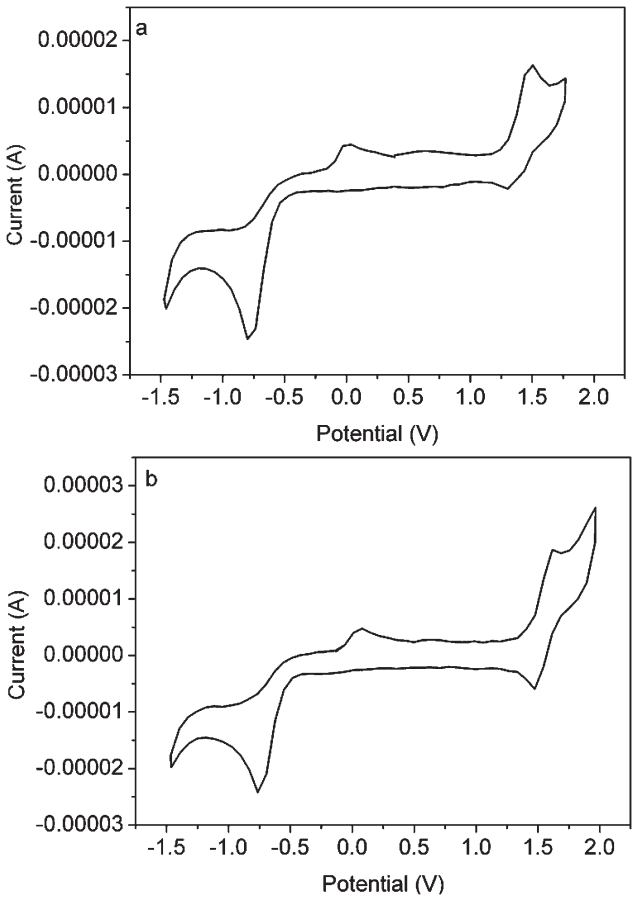


Fig. 4 Cyclic voltammograms of **1** (a) and **3** (b) in CH_2Cl_2 using tetrabutylammonium hexafluorophosphate as supporting electrolyte with a scan rate of 100 mV s^{-1}.

Table 2 Time-resolved fluorescence of **1**, **2** and **3** in CH_2Cl_2 and CH_3CN

Solvent		CH_2Cl_2	CH_3CN
τ/ns	**1**	3.00	2.02
	2	2.60	1.64
	3	3.33	2.27
K_f (10^9 s^{-1})	**1**	0.17	0.15
	2	0.10	0.14
	3	0.12	0.11
K_{nr} (10^9 s^{-1})	**1**	0.16	0.35
	2	0.28	0.47
	3	0.17	0.33

Table 3 Electrochemical data for **1**, **2** and **3** in CH_2Cl_2

Compound	$E_{ox,\,1/2}$ (V) *vs.* ferrocene	$E_{red,\,1/2}$ (V) *vs.* ferrocene
1	1.40	−0.40
2	1.32	−0.41
3	1.54	−0.35

moiety in compound **3** for a nitro group in the model compound (for synthesis and structure see ESI†), the reversible reduction is further shifted to less negative potential at −0.25 V. These results indicate these compounds are quite easily reduced (Table 3).

Conclusions

Three pyridone-fused BODIPYs **1**, **2** and **3** are reported in this paper. The main synthetic approach for the fusion of aryl moieties into BODIPYs begins with the condensation of the corresponding aromatic ring-fused pyrroles. In this paper a general procedure for the introduction of a pyridone moiety was developed by post-modification of the ready-made BODIPY core using a Friedländer reaction, which can be a complementary approach to get aromatic ring-fused BODIPYs.

These rigid pyridone ring-fused BODIPYs are distinctive, possessing favorable photophysical characteristics. All dyes showed strong absorption and high bright orange fluorescence with relatively high quantum yields and small Stokes shifts. Electrochemical study revealed that these compounds are easily reduced due to the electron-withdrawing effect of the fused pyridone moiety.

More importantly, BODIPYs **1**, **2** and **3** bear reactive ketone, ester and cyano functions, respectively. These reactive functions are applicable in proteins labeling by chemical reactions. The efficient reactions of **1** with small molecules containing oxyamino groups demonstrate our designed BODIPYs can be exploited as ligation reagents for modification of proteins.

Experimental section

All chemicals were purchased from commercial suppliers unless otherwise specified. Propylamine and 1,2-dichloroethane were used as received without further purification. Anhydrous *N*,*N*-dimethylformamide (DMF) was dried over CaH_2 and distillated immediately prior to use. 3-Chloro-5,7-dimethyl-6-ethyl-8-phenyl-BODIPY[6a] was prepared according to literature procedures.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV-400 spectrometer with chemical shifts reported in ppm at room temperature. Mass spectra were measured on a HP 1100 LC-MS spectrometer. UV-vis absorption spectra were recorded on a Varian Cary 100 spectrophotometer. Fluorescence spectra were measured with a Varian Cary Eclipse Fluorescence spectrophotometer. Spectral-grade solvents were used for measurements of UV-vis absorption and fluorescence.

Synthesis of 5

A mixture of DMF (3 mL) and $POCl_3$ (3 mL) was stirred in an ice bath for 5 min under argon. After being warmed to room temperature, it was stirred for additional 30 min. A solution of 3-chloro-5,7-dimethyl-6-ethyl-8-phenyl-BODIPY (0.3 g, 0.84 mmol) in 1,2-dichloroethane (10 mL) was then added, and the resulting mixture was stirred for 2 h at 50 °C. The reaction mixture was cooled to room temperature and slowly poured into saturated aqueous $NaHCO_3$ under ice-cold conditions. After being warmed to room temperature, the reaction mixture was further stirred for 1 h, extracted with CH_2Cl_2 and washed with water. The organic layers were dried over anhydrous Na_2SO_4, and evaporated *in vacuo*. The crude product was further purified using column chromatography (silica gel, EtOAc–hexane = 40 : 1) to give **5** (0.265 g, 82%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.08 (t, J = 7.6 Hz, 3H), 1.51 (s, 3H), 2.41 (q, J = 7.6 Hz, 2H), 2.72 (s, 3H), 6.66 (s, 1H), 7.30–7.37 (m, 2H), 7.47–7.62 (m, 3H), 9.88 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.5, 13.8, 13.9, 17.2, 122.2, 125.2, 128.7, 128.8, 129.9, 132.5, 133.4, 135.7, 138.9, 139.1, 140.5, 143.9, 168.4, 183.9; HRMS (ESI) calcd for $C_{20}H_{19}BN_2OF_2Cl$: 387.1247; found: 387.1252 $[M + H]^+$.

Synthesis of 4

To a solution of **5** (0.2 g, 0.52 mmol) in 20 mL CH_3CN was added propylamine (85 μL, 1.03 mmol), and the reaction mixture was stirred at room temperature for 4 h. Excess CH_3CN was removed under vacuum, and the residue was dissolved in ethyl acetate, washed with H_2O, dried over Na_2SO_4. The crude product was purified by flash chromatography (silica gel, eluent: hexane–EtOAc = 30 : 1) to afford **4** (0.27 g, 89%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.04 (t, J = 7.6 Hz, 3H), 1.11 (t, J = 7.4 Hz, 3H), 1.44 (s, 3H), 1.71–1.87 (m, 2H), 2.39 (q, J = 7.6 Hz, 2H), 2.59 (s, 3H), 3.85 (t, J = 6.9 Hz, 2H), 6.67 (s, 1H), 7.29–7.39 (m, 2H), 7.41–7.58 (m, 3H), 9.56 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.3, 11.8, 12.7, 14.5, 17.2, 23.3, 46.2, 117.5, 128.3, 129.0, 129.4, 131.1, 132.0, 133.5, 134.1, 134.5, 136.8, 137.3, 154.1, 157.6, 185.3; HRMS (ESI) calcd for $C_{23}H_{25}BN_3OF_2$: 408.2059; found: 408.2031 $[M - H]^-$.

Synthesis of 1

To a solution of **4** (0.1 g, 0.26 mmol) in anhydrous EtOH was added a drop of piperidine and ethyl acetoacetate (66 μL, 0.52 mmol), the resulting mixture was refluxed for 2 h, Excess EtOH was removed under vacuum, and the residue was dissolved in CH_2Cl_2, washed with H_2O, dried over Na_2SO_4. The crude product was purified by flash chromatography (silica gel, eluent: hexane–EtOAc = 10 : 1) to afford **1** (0.037 g, 30%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.06–1.12 (m, 6H), 1.48 (s, 3H), 1.80–1.92 (m, 2H), 2.43 (q, J = 7.5 Hz, 2H), 2.70 (s, 3H), 2.72 (s, 3H), 4.64 (t, J = 8.0 Hz, 2H), 6.50 (s, 1H), 7.35–7.38 (m, 2H), 7.51–7.61 (m, 3H), 8.23 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.3, 12.2, 13.6, 14.1, 17.3, 21.6, 31.0, 46.2, 113.9, 122.6, 123.6, 128.7, 129.0, 129.6, 133.6, 134.0, 135.7, 137.4, 138.1, 140.5, 141.4, 150.7, 161.9, 163.9, 197.8; HRMS (ESI) calcd for $C_{27}H_{29}BN_3O_2F_2$: 476.2321; found: 476.2280 $[M + H]^+$.

Synthesis of 2

The procedure was similar to that described for the synthesis of **1** except diethyl malonate was used instead of ethyl acetoacetate. Yield: 31%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.05–1.10 (m, 6H), 1.38 (t, J = 7.1 Hz, 3H), 1.48 (s, 3H), 1.80–1.92 (m, 2H), 2.42 (q, J = 7.6 Hz, 2H), 2.69 (s, 3H), 4.37 (q, J = 7.14 Hz, 2H), 4.62 (m, 2H), 6.47 (s, 1H), 7.32–7.41 (m, 2H), 7.49–7.61 (m, 3H), 8.23 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.2, 12.1, 13.5, 14.1, 14.3, 17.3, 21.5, 46.3, 61.0, 113.3, 115.5, 123.2, 128.6, 129.1, 129.5, 133.8, 135.5, 137.9, 138.6, 140.4, 141.1, 150.6, 159.9, 163.4, 165.4; HRMS (ESI) calcd for $C_{28}H_{31}BN_3O_3F_2$: 506.2427; found: 506.2425 $[M + H]^+$.

Synthesis of 3

The procedure was similar to that described for the synthesis of **1** except ethyl cyanoacetate was used instead of ethyl acetoacetate. Yield: 22%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.08 (t, J = 7.6 Hz, 6H), 1.49 (s, 3H), 1.84 (m, 2H), 2.43 (q, J = 7.6 Hz, 2H), 2.71(s, 3H), 4.63 (t, J = 8.0 Hz, 2H), 6.42 (s, 1H), 7.34–7.40 (m, 2H), 7.51–7.63 (m, 3H), 7.86 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.1, 12.2, 13.8, 14.0, 17.3, 21.4, 46.8, 99.4, 113.0, 116.4, 121.4, 128.8, 129.0, 129.8, 133.3, 134.6, 135.8, 139.0, 140.4, 140.5, 142.2, 149.6, 160.4, 165.8; HRMS (ESI) calcd for $C_{26}H_{26}BN_4OF_2$: 459.2168; found: 459.2165 $[M + H]^+$.

Acknowledgements

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