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## Synthesis, structure and photophysical properties of NIR aza-BODIPYs with –F/-N<sub>3</sub>/-NH<sub>2</sub> groups at 1,7-positions

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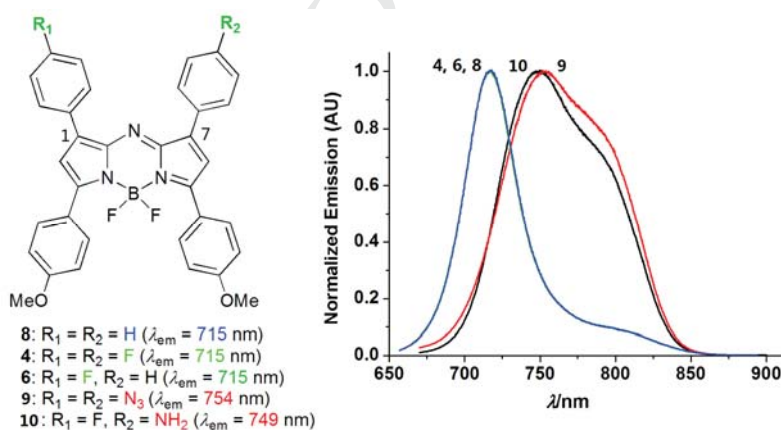
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**Abstract:** With 4-fluorostyrene as the starting material, symmetric/asymmetric fluorine-containing aza-difluoroboradiaza-*s*-indacenes (aza-BODIPYs) **3-6** at 1/7-position were successfully prepared. NaN<sub>3</sub> undertook nucleophilic aromatic substitution via replacement of F atoms of **4** to form the N<sub>3</sub>/NH<sub>2</sub>-containing aza-BODIPYs **9** and **10**. The solid-state structure of aza-BODIPY **4** was confirmed by single crystal X-ray analysis, the F-C<sub>ph</sub> bond distance of which was found to be shorter than those of the reported fluoride. These aza-BODIPYs absorb and emit in

the NIR region. Surprisingly, although the withdrawing group was introduced at 1/7 positions of **3-6**, the effect of the fluorine atoms to the photophysical properties is trifling. However, **9** and **10** with  $-N_3/-NH_2$  groups resulted in a remarkable bathochromic shift. Aza-BODIPY **10** could be also used as a turn-on fluorescent probe for pH value. Moreover, the main photophysical data are well supported and explained by cLR-PCM(CHCl<sub>3</sub>)-M06-2X/6-311+G(2d,p)/SOS-CIS(D) calculations.

**Keywords:** aza-BODIPY • NIR • fluorine • fluorescence • TD-DFT calculations

## 1. Introduction

Near-infrared (NIR) fluorescent dyes can greatly reduce background absorption, fluorescence, light scattering, and can be used as building blocks to improve the sensitivity of the probes and sensors [1]. More importantly, NIR fluorescent dyes with strong absorption and emission in the low energy regions (650-900 nm) have deep penetration in tissues which allows more efficient in vivo imaging and photodynamic therapy [2]. The safe, non-invasive nature of NIR fluorescent imaging has attracted great interests in the design and synthesis of novel NIR compounds [3]. Indeed, NIR derivatives such as azo, cyanine, quinone, and phthalocyanine dyes have been developed though, in most cases, insufficient photo-stability and/or difficult modification obstructed their applications [3]. Most NIR fluorescent dyes possess highly  $\pi$ -conjugated systems which lead to significantly reduced fluorescence quantum yields due to increased internal conversion. However, BODIPY and their derivatives are well-known to be highly fluorescent and very stable dyes, presenting tunable emission wavelengths and an exceptional insensitivity to the polarity of the medium [4]. Therefore, they are very promising candidates for biological labeling applications, and are already used in those fields [4,5].

By using an imine instead of a methane in BODIPY system to narrow the HOMO–LUMO gap one obtains aza-BODIPY that are known to be an attractive platform to reach NIR absorption (Fig. 1a) [6]. Furthermore, by introducing an electron-donating/withdrawing group one can further reduce the HOMO–LUMO gap by increasing the HOMO and/or decreasing the LUMO energy and reach more redshifted absorption and emission bands [7]. For instance, aza-BODIPYs with an electron-donating group such as  $-(p-NMe_2)Ph/-(p-OMe)Ph$  at 3/5-positions (Fig. 1b) exhibit bathochromic shift of the absorption/emission bands [8]. By contrast, aza-BODIPYs bearing an electron-withdrawing group (such as the  $-CN$  group) at 1/7-positions (Fig. 1c) are also known to undergo a redshift of the absorption/emission bands [9]. Since fluorine is a strong inductive acceptor, introduction of fluorine atom(s) in aza-BODIPY was considered in the present work. Importantly, the introduction of a fluorine atom into an organic molecule often induces significant, if not remarkable, variations of its chemical, physical and biological properties, due to the lipophilizing nature, strong electron-withdrawing nature and specific steric repulsion of fluorine [10]. In line with their widespread use

in both medicinal chemistry and in materials science, fluorinated molecules have attracted a considerable interest in the framework of molecular design. Therefore, studies on the characteristic of a fluorine-containing aza-BODIPY at 1/7-positions are of importance. We have been already exploring fluorides [11], and our most recent research interest lies in novel BODIPY/aza-BODIPY family of fluorescent dyes [12].

<Fig. 1>

## 2. Experimental methods

**2.1 General:** The melting points were measured using a SGW® X-4 melting point apparatus. <sup>1</sup>H NMR spectra were recorded on a Bruker AVANCE III 500 MHz spectrometer. <sup>1</sup>H NMR chemical shifts ( $\delta$ ) are given in ppm downfield from Me<sub>4</sub>Si, determined by chloroform ( $\delta$  = 7.26 ppm). <sup>13</sup>C NMR spectra were recorded on a Bruker AVANCE III 125 MHz spectrometer. <sup>13</sup>C NMR chemical shifts ( $\delta$ ) are reported in ppm with the internal CDCl<sub>3</sub> at  $\delta$  77.0 ppm as standard. HRMS (ESI) was measured by micro TOF-Q II.

Tetrahydrofuran (THF) was freshly distilled from Na/benzophenone, *n*-hexane was distilled over Na, and other solvents were distilled over CaH<sub>2</sub>. Merck silica gel 60 was used for the column chromatography. Fluorescence spectra were recorded on F-4600 spectrophotometer. UV/Vis spectra were recorded on UV-2550 spectrophotometer at room temperature. The refractive index of the medium was measured by 2 W Abbe's refractometer at 20 °C. The fluorescence quantum yields ( $\Phi_f$ ) of the BODIPY systems were calculated using the following relationship (equation 1):

$$\Phi_f = \Phi_{\text{ref}} F_{\text{sampl}} A_{\text{ref}} n_{\text{sampl}}^2 / F_{\text{ref}} A_{\text{sampl}} n_{\text{ref}}^2 \quad (1)$$

Here,  $F$  denotes the integral of the corrected fluorescence spectrum,  $A$  is the absorbance at the excitation wavelength, ref and sampl denote parameters from the reference and unknown experimental samples, respectively. The reference systems used was boronazadipyrromethene dye [13] as standard ( $\Phi_f$  = 0.36 in chloroform,  $\lambda_{\text{abs}}$  = 688 nm) for **3-6**, **9** and **10**.

**2.2 Computational details:** DFT, and TD-DFT calculations on molecules were carried out with the latest version of the Gaussian 09 program package [14], applying both a tightened self-consistent field convergence criterion ( $10^{-9}$ – $10^{-10}$  au) and an improved optimization threshold ( $10^{-5}$  au on average forces). For each molecule, we have optimized the geometry of both the ground and the first excited states, as well as computed the vibrational spectra of both states. The same DFT integration grid, namely the so-called ultrafine pruned (99,590) grid, was used for both the ground and excited states. All DFT and TD-DFT calculations were performed with the M06-2X hybrid exchange–correlation functional, that has been shown to be an adequate choice for investigating excited-state energies and structures of many classes of molecules [15]. Atoms were described with the 6-311+G(2d,p) basis sets. Solvation effects (here CHCl<sub>3</sub>) have been quantified using the Polarizable Continuum Model (PCM) [16].

Here, we have applied the corrected LR approach [17]. The SOS-CIS(D)/6-311+G(2d,p) energies were determined with the Q-Chem package using the resolution of identity (RI) scheme with the same basis set. The interested reader can find the whole applied computational protocol in ref. 18.

**Synthesis of 1-Fluoro-4-(1,2-dibromoethyl)benzene:** Under N<sub>2</sub>, Br<sub>2</sub> (0.42 ml, 8.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 ml) was dropwise added to 4-fluorostyrene (1.0 g, 8.1 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (40 ml) at 0 °C for 30 min. The color of the mixture changed from red to colorless. The reaction was allowed to warm up to room temperature slowly. After removal of the solvents by evaporation, the resulting crude mixture was recrystallization (*n*-hexane) to afford 1-fluoro-4-(1,2-dibromoethyl)benzene (1.82 g, 80%) as yellow solids.

### 2.3 Synthesis

**Synthesis of 3-(4-fluorophenyl)-2H-azirine:** Under N<sub>2</sub>, NaN<sub>3</sub> (840 mg, 12.9 mmol) was slowly added to 1-fluoro-4-(1,2-dibromoethyl)benzene (1.8 g, 6.3 mmol) in DMSO (20 ml) at 20 °C and stirred for 12 h at 25 °C. Then, 50% NaOH (1 ml) was added to the mixture and stirred for 24 h at 25 °C. The reaction was quenched with 10% NaHCO<sub>3</sub> (50 ml). The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 30 ml), and the organic layer was washed with brine (2 × 30 ml) and dried over anhydrous MgSO<sub>4</sub>. After removal of the solvents by evaporation, the red oil was obtained. Toluene (40 ml) was added the red oil and the mixture was refluxed for 2 h. After removal of the solvents by evaporation, the resulting crude mixture was separated by column chromatography (*n*-hexane : CH<sub>2</sub>Cl<sub>2</sub> = 1 : 1) to afford 3-(4-fluorophenyl)-2H-azirine (510 mg, 60%) as yellow oil. This mixture was direct used for the next step without further purification. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 7.22-7.25 (m, 2H), 7.13-7.17 (m, 2H), 2.34 (s, 2H).

**Synthesis of pyrrole 1:** Under N<sub>2</sub>, 1-tetralone (71.0 mg, 0.59 mmol) in DMSO (10 ml) was added to NaH (excess) in DMSO (10 ml) at -40 °C and stirred for 10 min. Then, 3-(4-fluorophenyl)-2H-azirine (80 mg, 0.59 mmol) in DMSO (5 ml) was added and the resulting mixture was stirred for 1 h at the same temperature. The reaction was allowed to warm up to room temperature slowly. It was quenched with water, neutralized with dilute HCl to a pH about 7. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 30 ml), and the organic layer was washed with brine (2 × 30 ml) and dried over anhydrous MgSO<sub>4</sub>. After removal of the solvents by evaporation, the resulting crude mixture was separated by column chromatography (*n*-hexane : CH<sub>2</sub>Cl<sub>2</sub> = 1 : 1) to afford pyrrole **1** as hoary solids (76.9 mg, 55%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 8.45 (br s, 1H), 7.50-7.53 (m, 4H), 7.40 (t, <sup>3</sup>J = 8.0 Hz, 2H), 7.25 (d, <sup>3</sup>J = 7.5 Hz, 1H), 7.80-7.09 (m, 1H), 7.05 (t, <sup>3</sup>J = 8.5 Hz, 2H), 6.76 (m, 1H). HRMS-MALDI (m/z): [M + H]<sup>+</sup> calcd for C<sub>16</sub>H<sub>13</sub>FN: 238.10265; found: 238.10268.

**Synthesis of pyrrole 2:** 6-Methoxytetralone (218 mg, 1.45 mmol) was used as the starting materials, and pyrrole **2** was obtained green solids (232.8 mg, 60%). <sup>1</sup>H NMR

(500 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.34 (br s, 1H), 7.51 (d,  $^3J = 9.0$  Hz, 1H), 7.50 (d,  $^3J = 9.0$  Hz, 1H), 7.44 (d,  $^3J = 9.0$  Hz, 2H), 7.02-7.06 (m, 3H), 6.94 (d,  $^3J = 8.5$  Hz, 2H), 6.65 (m, 1H), 3.84 (s, 1H). HRMS-MALDI (m/z): [M + H]<sup>+</sup> calcd for C<sub>17</sub>H<sub>15</sub>FNO: 268.11322; found: 268.11322.

**Synthesis of aza-BODIPY 3:** Sodium nitrite (6.9 mg, 0.1 mmol) was added to a suspension of pyrrole **1** (47.5 mg, 0.2 mmol) in a mixture of acetic acid/anhydride (1 ml/0.4 ml) at 0 °C, and was stirred for 10 min. The color changed from colorless to brown, then green, and finally dark green was observed. After 0.5 h stirring at room temperature, the mixture was heated at 80 °C for 0.5 h. Crushed ice was added to the mixture, the resulted dark green dye was filtered, washed with water. The dark green dye was dissolved in CH<sub>2</sub>Cl<sub>2</sub>, filtered through a pad of alumina (activity III). Solvent was removed under reduced pressure, and the residue was dissolved in dry 1,2-dichloroethane. Triethylamine (0.28 ml, 2.0 mmol) was added, followed by dropwise addition of BF<sub>3</sub>·Et<sub>2</sub>O (0.50 ml, 4.0 mmol) with stirring at room temperature. The mixture was stirred for 0.5 h, then heated in 80 °C for 0.5 h. The reaction was quenched with crushed ice, extracted with CH<sub>2</sub>Cl<sub>2</sub>, and purified by chromatography on silica gel followed by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane to afford aza-BODIPY **3** (24.5 mg, 46%) as coppery solids. M.p.: 240.0–240.8 °C (decomp.). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.02-8.04 (m, 8H), 7.48-7.50 (m, 6H), 7.16 (t,  $^3J = 8.5$  Hz, 4H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 159.6, 145.4, 143.0, 131.4, 131.2, 131.1, 131.0, 129.5, 128.6, 118.8, 115.8, 115.7. HRMS-MALDI (m/z): [M + Na]<sup>+</sup> calcd for C<sub>32</sub>H<sub>20</sub>BF<sub>4</sub>N<sub>3</sub>Na: 556.1584; found: 556.1583.

**Synthesis of aza-BODIPY 4:** Pyrrole **2** (53.6 mg, 0.2 mmol) was used as the starting materials, and aza-BODIPY **4** was obtained green solids (25.5 mg, 43%). M.p.: 290.0–291.0 °C (decomp.). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.08 (d,  $^3J = 8.5$  Hz, 4H), 8.01 (dd,  $^3J = 8.5$  Hz, 4H), 7.14 (t,  $^3J = 8.5$  Hz, 4H), 7.01 (d,  $^3J = 8.5$  Hz, 4H), 6.99 (s, 2H), 3.89 (s, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 161.9, 158.1, 145.1, 141.9, 131.6, 131.0, 128.6, 123.9, 118.3, 115.7, 115.5, 114.2. HRMS-MALDI (m/z): [M + H]<sup>+</sup> calcd for C<sub>34</sub>H<sub>25</sub>BF<sub>4</sub>N<sub>3</sub>O<sub>2</sub>: 594.19705; found: 594.19678.

**Synthesis of aza-BODIPY 5:** Sodium nitrite (11.6 mg, 0.16 mmol) was added to a suspension of 2,4-diphenyl-1*H*-pyrrole (36.9 mg, 0.16 mmol) in acetic acid (1 mL) at 0 °C, and was stirred for 10 min. The color changed from colorless to brown, then green, and finally brown was observed. The second pyrrole moiety **1** (40 mg, 0.16 mmol) was added, followed by addition of acetic anhydride (0.4 mL). The mixture turned blue immediately. After 0.5 h stirring, the mixture was heated at 80 °C for 0.5 h. Crushed ice was added to the mixture, the resulted blue dye was filtered, washed with water. The blue dye was dissolved in CH<sub>2</sub>Cl<sub>2</sub>, filtered through a pad of alumina (activity III). Solvent was removed under reduced pressure, and the residue was dissolved in dry 1,2-dichloroethane. Triethylamine (0.28 mL, 2.0 mmol) was added, followed by dropwise addition of BF<sub>3</sub>·Et<sub>2</sub>O (0.50 mL, 4.0 mmol) with stirring at room temperature. The mixture was stirred for 0.5 h, then heated in 80 °C for 0.5 h. The

reaction was quenched with crushed ice, extracted with CH<sub>2</sub>Cl<sub>2</sub>, and purified by chromatography on silica gel followed by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane to afford aza-BODIPY **5** (42.0 mg, 51%) as coppery solids. M.p.: 230–231.0 °C (decomp.). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 8.01-8.07 (m, 8H), 7.46-7.49 (m, 9H), 7.14 (t, (t, <sup>3</sup>J = 8.5 Hz, 2H), 7.04 (s, 1H), 6.98 (s, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 159.6, 159.3, 145.5, 145.3, 144.2, 142.8, 132.1, 131.4, 131.2, 131.1, 131.0, 130.9, 129.6, 129.5, 129.4, 129.3, 129.2, 128.6, 128.5, 126.4, 119.2, 118.6, 115.7, 115.6. HRMS-MALDI (m/z): [M + H]<sup>+</sup> calcd for C<sub>32</sub>H<sub>22</sub>BF<sub>3</sub>N<sub>3</sub>: 516.18534; found: 516.18463.

**Synthesis of aza-BODIPY 6:** 2-(4-methoxyphenyl)-4-phenyl-1H-pyrrole (25.0 mg, 0.093 mmol) and pyrrole **2** (24.1 mg, 0.096 mmol) was used as the starting materials, and aza-BODIPY **6** was obtained green solids (26.2 mg, 49%). M.p.: 257.0–258.0 °C (decomp.). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 8.01-8.10 (m, 8H), 7.41-7.48 (m, 3H), 7.13 (t, <sup>3</sup>J = 8.5 Hz, 2H), 7.04 (s, 1H), 7.01 (dd, <sup>3</sup>J = 8.5 Hz, <sup>4</sup>J = 3.0 Hz, 4H), 6.98 (s, 1H), 3.89 (s, 3H), 3.88 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 161.8, 158.2, 158.0, 157.9, 145.2, 145.1, 143.2, 141.7, 132.4, 131.5, 131.0, 130.9, 129.3, 129.2, 128.6, 128.5, 124.1, 123.9, 118.7, 118.6, 118.1, 115.6, 115.5, 114.2. HRMS-MALDI (m/z): [M + Na]<sup>+</sup> calcd for C<sub>34</sub>H<sub>25</sub>BF<sub>3</sub>N<sub>3</sub>NaO<sub>2</sub>: 598.1890; found: 598.1889.

**Synthesis of aza-BODIPY 9:** NaN<sub>3</sub> (8.8 mg, 0.13 mmol) was added to a solution of **4** (25.0 mg, 0.042 mmol) in DMF (4 ml), and then the mixture was stirred at 40 °C for 30 min. The reaction was quenched with water, extracted with CH<sub>2</sub>Cl<sub>2</sub>, and purified by chromatography on silica gel followed by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane to afford aza-BODIPY **9** (15.3 mg, 57%) as coppery solids. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 8.04 (d, <sup>3</sup>J = 8.5 Hz, 4H), 7.79 (d, <sup>3</sup>J = 8.5 Hz, 4H), 6.99 (d, <sup>3</sup>J = 8.5 Hz, 4H), 6.85 (s, 2H), 6.75 (d, <sup>3</sup>J = 8.5 Hz, 4H), 3.87 (s, 6H). HRMS-MALDI (m/z): [M - 4N + 5H]<sup>+</sup> calcd for C<sub>34</sub>H<sub>29</sub>BF<sub>2</sub>N<sub>5</sub>O<sub>2</sub>: 588.23769; found: 588.23730.

**Synthesis of aza-BODIPY 10:** NaN<sub>3</sub> (3.0 mg, 0.046 mmol) was added to a solution of **4** (27.4 mg, 0.046 mmol) in DMF (5 ml), and then the mixture was stirred at 40 °C for 1 h. The reaction was quenched with NaHS aqueous solution, extracted with CH<sub>2</sub>Cl<sub>2</sub>, and purified by chromatography on silica gel followed by recrystallization from CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane to afford aza-BODIPY **10** (13.5 mg, 50%) as coppery solids. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 8.08 (d, <sup>3</sup>J = 8.5 Hz, 2H), 8.03 (td, <sup>3</sup>J = 8.5 Hz, <sup>4</sup>J = 3.0 Hz, 4H), 7.96 (d, <sup>3</sup>J = 8.5 Hz, 2H), 7.15 (t, <sup>3</sup>J = 8.5 Hz, 2H), 7.00 (dd, <sup>3</sup>J = 8.5 Hz, <sup>4</sup>J = 3.0 Hz, 4H), 6.92 (s, 1H), 6.90 (s, 1H), 6.74 (d, <sup>3</sup>J = 8.5 Hz, 2H), 4.04 (br s, 2H), 3.88 (s, 6H). HRMS-MALDI (m/z): [M + H]<sup>+</sup> calcd for C<sub>34</sub>H<sub>27</sub>BF<sub>3</sub>N<sub>4</sub>O<sub>2</sub>: 591.21737; found: 591.21777.

### 3. Results and Discussion

To introduce the fluorine atom into the aza-BODIPY core, 4-fluorostyrene was selected as a starting material (Scheme 1). 1-Fluoro-4-(1,2-dibromoethyl)benzene was obtained in 80% yield by the reaction of 4-fluorostyrene with Br<sub>2</sub> at 0 °C. Followed by NaN<sub>3</sub>, DMSO, NaOH and reflux in toluene, the yellow oil 3-(4-fluorophenyl)-2*H*-azirine can be synthesized in 60% yield. Acetophenone was employed to react with 3-(4-fluorophenyl)-2*H*-azirine to give fluoro-containing pyrroles **1** (y. 55%) and **2** (y. 60%) in the presence of NaH (Scheme 1), respectively [19]. The clear 1:10 integral areas of the hydrogen signals in pyrrole **2** between the proton of N-*H* ( $\delta$  = 8.34 (br s, 1H)) and other protons of the pyrrole in the <sup>1</sup>H NMR spectrum were obtained (see ESI), indicating that the fluorine atom was successfully introduced into the pyrrole skeleton.

<Scheme 1>

<Scheme 2>

Using the pyrroles **1** and **2**, symmetric/asymmetric fluorine-containing aza-BODIPYs **3-6** were successfully synthesized in moderate yields under HOAc, Ac<sub>2</sub>O and NaNO<sub>2</sub>, followed by complexation with Et<sub>3</sub>N·BF<sub>3</sub>·Et<sub>2</sub>O, as described in the literature (Scheme 2) [19]. Their structures were unambiguously confirmed by detailed characterizations including NMR and ESI-HRMS analyses (see ESI).

Furthermore, the solid-state structure of aza-BODIPY **4** was clearly confirmed by single crystal X-ray analysis (Fig. 2 and see ESI). Selected bond lengths and angles are summarized in Fig. 2. The F2-C15 distances (1.278 Å) were found to be slightly shorter than the F-C<sub>ph</sub> bond of the reported fluoride (1.365 Å) by 0.09 Å [11c]. The other bond lengths for **4** are very similar to those found for **8** (R<sub>1</sub> = H, R<sub>2</sub> = OMe) (Fig. 1b) [13]. Additionally, the sp<sup>3</sup> hybridized boron center for **4** appears as a slightly distorted tetrahedron with angles. The dihedral angles C(11\*)-N(2)-C(11)-C(10) of 179.9° are nearly of the ideal value of 180°, thus indicating the plane skeleton of the aza-BODIPY core.

<Fig. 2>

Additionally, the derivative of the fluorine-containing aza-BODIPYs was found to be feasible (Scheme 3). NaN<sub>3</sub> undertook nucleophilic aromatic substitution (S<sub>N</sub>Ar) via replacement of the fluorine atoms of **4** to form N<sub>3</sub>-containing aza-BODIPY **9** by treatment of water, whereas it provides NH<sub>2</sub>-containing aza-BODIPY **10** by treatment of NaHS (Scheme 3) [20]. The proton of N-*H*<sub>2</sub> ( $\delta$  = 4.04 (br s, 2H)) and other distinct hydrogen signals for the asymmetric NH<sub>2</sub>-containing aza-BODIPY **10** in the <sup>1</sup>H NMR spectrum indicate clearly that the amino group was introduced into the aza-BODIPY **10** (see ESI).

<Scheme 3>

<Table 1>

The absorption and emission spectra of aza-BODIPYs **3-6** are shown in Fig. 3 whereas the photophysical data collected are listed in Table 1. Aza-BODIPYs **3-6**



have excellent optical properties. These dyes absorb and emit in the NIR region, with high molar extinction coefficients, high quantum yields and narrow full width at half maxima (FWHM). The profile curves including absorption and emission between **3/4** and **5/6** nearly overlap, and optical properties of every pair of aza-BODIPYs are very similar. Moreover, the pictures of **3-6** taken in  $\text{CHCl}_3$  under normal conditions reveal vivid colors, and the hues between pairs of **3/4** and **5/6** are also uniform (Fig. 3). To investigate the spectroscopic effects of the withdrawing group F atom, the spectral characteristics of **3-6** were respectively compared to those of the known dyes **7** ( $R_1 = R_2 = \text{H}$ ) [13] and **8** [13] (Fig. 1b and Table 1). By comparison with the absorption and emission maxima of **7** ( $\lambda_{\text{abs}} = 650$ ,  $\lambda_{\text{em}} = 672$  nm), it is clear that the effect of the fluorine atom in **3** and **5** is trifling. Moreover, extinction coefficients and quantum yields of dyes **3** and **5** in  $\text{CHCl}_3$  are nearly the same to those of dye **7** ( $79000 \text{ M}^{-1} \text{ cm}^{-1}$ ,  $\Phi_f = 0.34$ ). In addition, the photophysical properties of mono/bis-fluoro substituted aza-BODIPYs **4** and **6** bearing the  $-\text{OMe}$  group are also completely equivalent to those of aza-BODIPY **8**.

<Fig. 3>

Interestingly, the replacement of -F atoms with  $-\text{N}_3$  groups in **9** ( $\lambda_{\text{abs}} = 710$  nm) resulted in a remarkable bathochromic shift (22 nm) compared to that of the parent aza-BODIPY **4** ( $\lambda_{\text{abs}} = 688$ ) (Fig. 4 and Table 1), which is well in agreement with the reported literature [9]. Although the electronegativity of  $\text{N}_3$  group (-3.04) was well-known to be smaller than that of F atom (-4.0) [18], the effect of the  $\text{N}_3$  group at 1/7 position to photophysical properties in aza-BODIPY **9** is notable (Fig. 4 and Table 1), comparing to F-containing aza-BODIPYs **3-6** as described above. Aza-BODIPY **9** emits at 754 nm, possesses large Stokes' shift (44 nm) and has moderate quantum yield ( $\Phi_f = 0.26$ ). The absorption and emission maxima of **10** bearing the  $\text{NH}_2$ -donating group ( $\lambda_{\text{abs}} = 699$  nm,  $\lambda_{\text{em}} = 749$  nm) was obviously red shifted compared with **4** ( $\lambda_{\text{abs}} = 688$  nm,  $\lambda_{\text{em}} = 715$  nm), and the fluorescence of **10** became so weak (0.03) due to the intramolecular charge transfer (ICT) effect.

<Fig. 4>

Since having a  $-\text{NH}_2$  group in **10**, therefore, we continued to explore the response of the amino-containing aza-BODIPY **10** to pH value. Dimethylamino group ( $-\text{NMe}_2$ ) is well-known to be one of the fragments for the pH-responsive fluorescent probe frequently used for the purpose of the ICT effect.[21] In this ICT process, the excited state of the fluorophore can be quenched by the electron transfer from electron donating amine to the fluorophore; upon recognition of a proton, the electron transfer is "switched off" and in turn the emission of fluorescence is "switched on". Herein, the mechanism of aza-BODIPY **10** bearing a  $-\text{NH}_2$  group to pH value is same to that of the above description. Upon addition of hydrochloric acid to **10** with a  $-\text{NH}_2$  group

as the pH-sensitive functionality, **10** was protonated at relatively low pH value [8,22], and a distinctly hypochromatic shift occurs at pH 2 (Fig. 5a). A stepwise increase of the absorption intensity was observed in the 700 nm band of **10-H<sup>+</sup>** from the 710 nm of **10** in DMSO/H<sub>2</sub>O (2:1, v/v) (Fig. 5a). The absorption intensity of **10-H<sup>+</sup>** reached the maximum when 4 M HCl was used. The absorption band of **10-H<sup>+</sup>** is blue-shifted by about 10 nm compared to that of **10**. Furthermore, with decreasing pH, a remarkable increase in fluorescence intensity at 750 nm by about 6 folds when **10** was treated with 4M HCl. (Fig. 5b). So, aza-BODIPY **10** could be used as a turn-on fluorescent probe for pH value.

<Fig. 5>

Quantum chemical calculations were performed on the four fluorine-containing aza-BODIPY compounds **3–6** to support the absorption and emission results. We followed a strategy that was developed recently (see computational details) [23] and that gave excellent result for both the BODIPY and aza-BODIPY systems [24]. The main computed photophysical data at the best level of calculation, i.e. cLR-PCM(CHCl<sub>3</sub>)-M06-2X/6-311+G(2d,p)/SOS-CIS(D) are summarized in Table 2. The calculations confirmed the limited effect of adding a F atom at 1/7-positions, comparing for instance the calculated absorption and emission wavelengths of **4** and **6** with respect to those of **8**. This observation persists for the absorption/fluorescence crossing point energies ( $E^{\text{AFCP}}$ ) that can be compared to experimental  $E^{0-0}$  energies. Fig. 6 shows the density difference plots computed for the fluorine-containing aza-BODIPY dyes and the involvement of the fluorine atom is clearly limited in the excited-states, which is consistent with the measurements. CT parameters, i.e. the CT distance ( $d^{\text{CT}}$ ) and the transferred charge ( $q^{\text{CT}}$ ) were also calculated through Le Bahers' model (Table 2) [25]. Again the only substantial difference emerges when comparing CT distances of parent complexes with and without the methoxy group (**3** vs. **4** for instance). Similar calculations were realized on compounds **9** and **10** (Table 2 and Fig. 6) confirming the tendencies experimentally observed, such as the redshift of the absorption/emission when going from **3** and **4** to **9** and **10**. Replacing F by N<sub>3</sub> (**4** vs. **9**) slightly reduces the CT distance in agreement with the smaller electronegativity of N<sub>3</sub> with respect to F. Finally, the small calculated  $d^{\text{CT}}$  of **10** can be attributed to the strong dissymmetry induced by the replacement of only one fluorine group by NH<sub>2</sub> donating group.

<Table 2>

<Fig. 6>

#### 4. Conclusions

Utilizing 4-fluorostyrene as starting material, acetophenone was employed to react with 3-(4-fluorophenyl)-2*H*-azirine to give fluoro-containing pyrroles in the presence

of NaH. Fluorine-containing aza-BODIPYs **3-6** at 1/7-position were successfully synthesized by the reaction of fluoro-containing pyrroles **1** and **2** under HOAc, Ac<sub>2</sub>O and NaNO<sub>2</sub>, followed by complexation with Et<sub>3</sub>N-BF<sub>3</sub> · Et<sub>2</sub>O. NaN<sub>3</sub> undertook nucleophilic aromatic substitution to form N<sub>3</sub>-containing aza-BODIPY **9** by treatment of water, whereas it gives NH<sub>2</sub>-containing aza-BODIPY **10** by treatment of NaHS. The solid-state structure of aza-BODIPY **4** was confirmed by single crystal X-ray analysis, the F-C<sub>Ph</sub> bond distance of which was found to be shorter than those of the reported fluoride. The optical properties of fluorine-containing aza-BODIPYs **3-6** are very similar to those of the parent complexes. Surprisingly, the effect of the withdrawing -F group at 1/7-position on the photophysical properties is found to be almost negligible, comparing to those of the parent aza-BODIPYs **7** and **8**. However, the replacement of -F atoms with -N<sub>3</sub>/-NH<sub>2</sub> groups in **9** and **10** resulted in a remarkable bathochromic shift. The amino-containing aza-BODIPY **10** could be used as a turn-on fluorescent probe for pH value. The main photophysical data are well supported and explained by cLR-PCM(CHCl<sub>3</sub>)-M06-2X/6-311+G(2d,p)/SOS-CIS(D) calculations.

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**Fig. 1.** (a) BODIPY vs. aza-BODIPY. (b) Structures of some previously reported aza-BODIPYs [6,8,9].

**Scheme 1** Synthesis of fluorine-containing pyrroles **1** and **2**.

**Scheme 2** Synthesis of fluorine-containing aza-BODIPYs **3-6**.

**Fig. 2.** ORTEP diagram of **4** showing the thermal ellipsoids at the 30% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): B1-F1, 1.349(4); B1-N1, 1.518(5); N1-C8, 1.344(5); N1-C11, 1.365(5); N2-C11, 1.301(5); F2-C15, 1.278(9); C(11\*)-N(2)-C(11)-C(10), 179.9(5).

**Scheme 3** Synthesis of aza-BODIPYs **9** and **10**.

**Table 1** Photophysical properties of aza-BODIPYs **3-10** in CHCl<sub>3</sub> at 298 K.

**Fig. 3.** (a) Normalized absorption and (b) fluorescence spectra of aza-BODIPYs **3** (black curve), **4** (blue curve), **5** (red curve) and **6** (green curve) in CHCl<sub>3</sub> at 298 K. Photoimages of **3-6** under normal room illumination in CHCl<sub>3</sub> at 298 K.

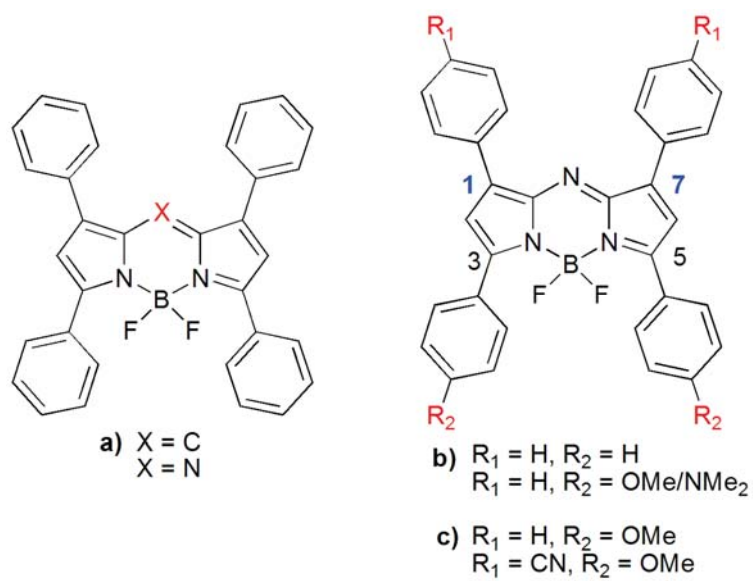
**Fig. 4.** (a) Normalized absorption and (b) fluorescence spectra of aza-BODIPYs **9** (red curve) and **10** (black curve) in CHCl<sub>3</sub> at 298 K.

**Fig. 5.** Absorption (a) and fluorescence (b) spectra (pH 7, 6, 5, 4, 3, 2, 1.8, 1.6, 1.4, 1.2, 1 and 1 M, 2 M, 4 M, 6 M of HCl) of 2 μM dye **10** in DMSO/H<sub>2</sub>O (2:1, v/v) as a function of pH.  $\lambda_{\text{ex}} = 700$  nm.

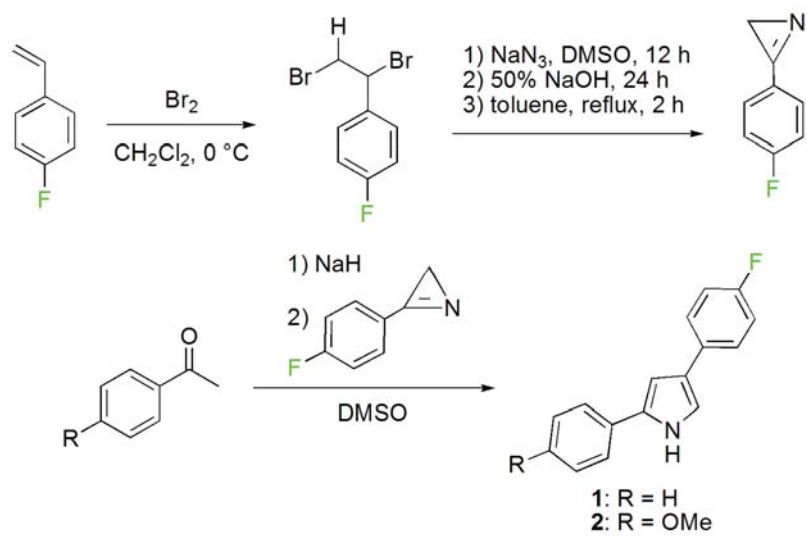
**Table 2** Computed  $\lambda_{\text{abs}}$  and  $\lambda_{\text{em}}$  (in nm), AFCP energy ( $E^{\text{AFCP}}$ , in nm), charge transfer distances ( $d^{\text{CT}}$ , in Å), and transferred charges ( $q^{\text{CT}}$ , in e) of aza-BODIPYs **3**, **4**, **5**, **6**, **8**, **9** and **10** at the cLR-PCM(CHCl<sub>3</sub>)-M06-2X/6-311+G(2d,p)/SOS-CIS(D).

**Fig. 6.** Density difference plots for (from left to right and top to bottom) aza-BODIPYs **3**, **4**, **5**, **6**, **9** and **10**. The blue (red) zones indicate density decrease (increase) upon transition.

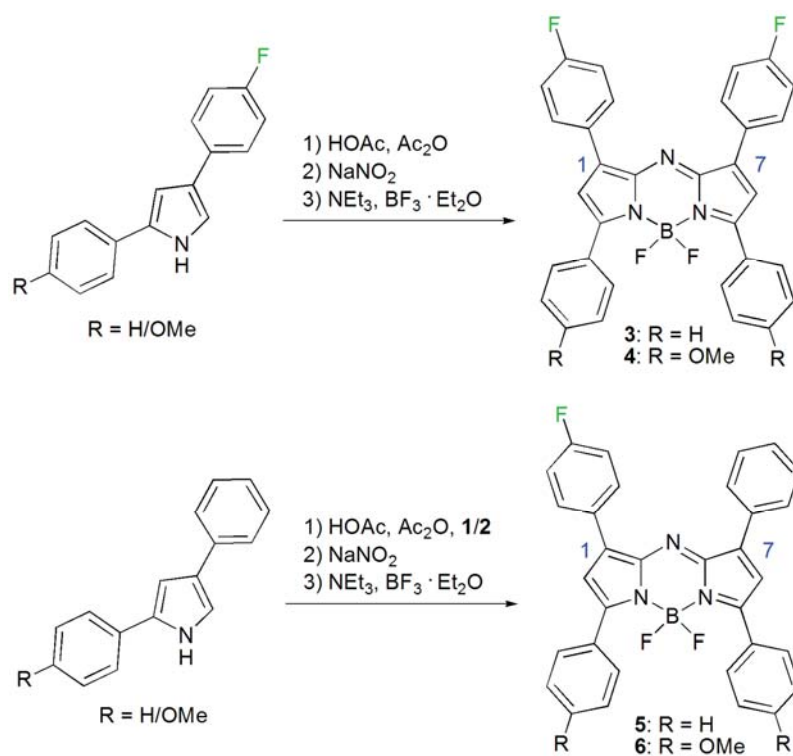
ACCEPTED MANUSCRIPT



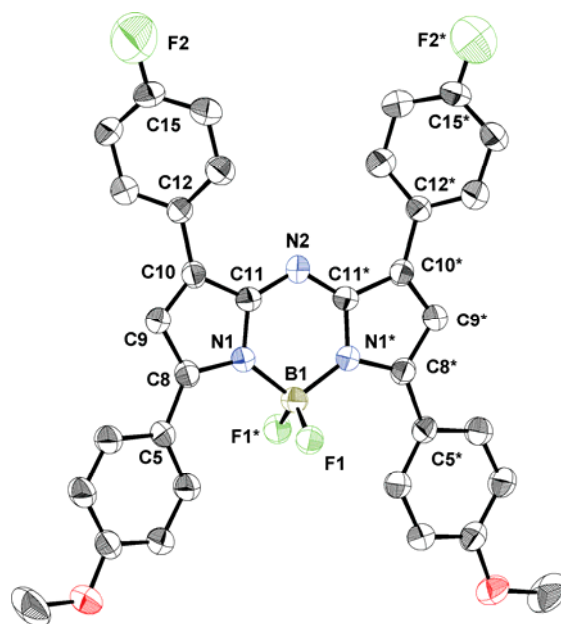
**Fig. 1** (a) BODIPY vs. aza-BODIPY. (b) Structures of some previously reported aza-BODIPYs [6,8,9].



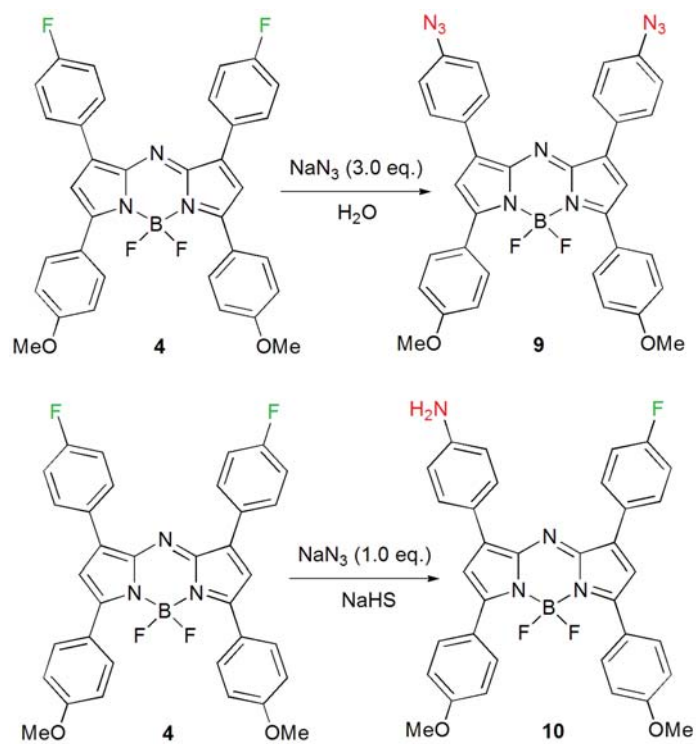
**Scheme 1** Synthesis of fluorine-containing pyrroles **1** and **2**.



**Scheme 2** Synthesis of fluorine-containing aza-BODIPYs 3-6.



**Fig. 2.** ORTEP diagram of **4** showing the thermal ellipsoids at the 30% probability level. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): B1-F1, 1.349(4); B1-N1, 1.518(5); N1-C8, 1.344(5); N1-C11, 1.365(5); N2-C11, 1.301(5); F2-C15, 1.278(9); C(11\*)-N(2)-C(11)-C(10), 179.9(5).

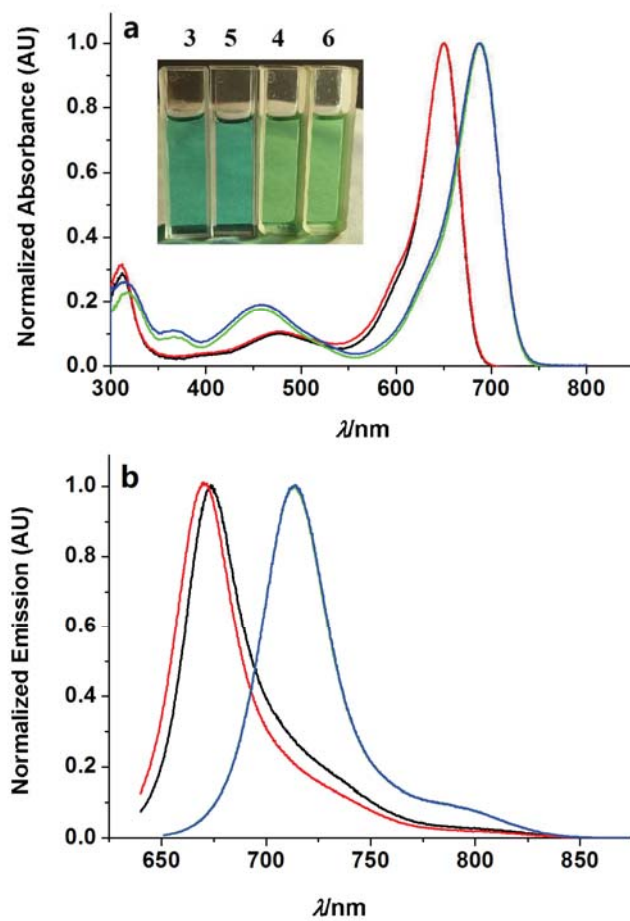


**Scheme 3** Synthesis of aza-BODIPYs **9** and **10**.

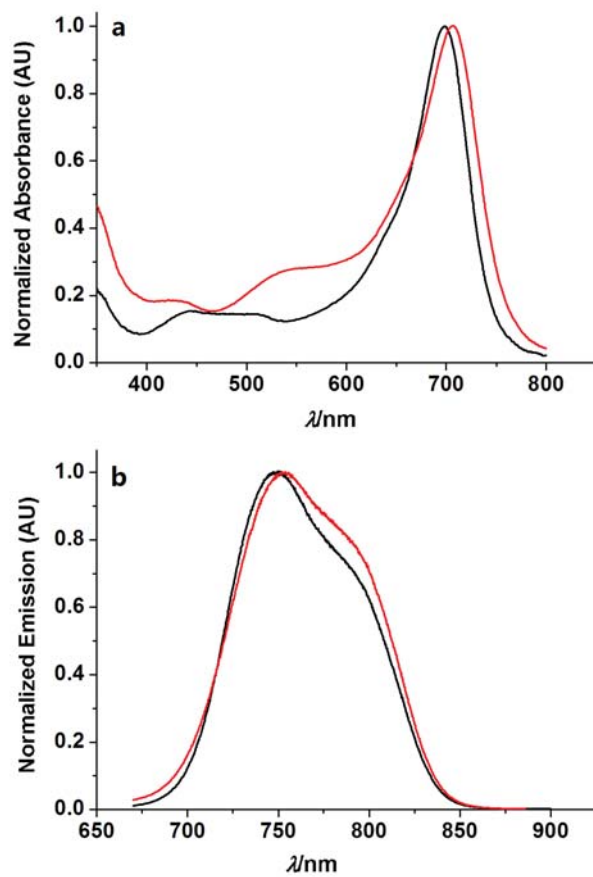
**Table 1** Photophysical properties of aza-BODIPYs **3-10** in CHCl<sub>3</sub> at 298 K.

Dye	$\lambda_{\text{abs}}/\lambda_{\text{em}}$ [nm]	Stokes' shift [cm <sup>-1</sup> ]	FWHM [nm]	$\epsilon$ [M <sup>-1</sup> cm <sup>-1</sup> ]	$\Phi_f$
<b>3</b>	650/674	25	49	80000	0.34
<b>4</b>	688/715	27	55	86000	0.36
<b>5</b>	650/672	25	49	79000	0.34
<b>6</b>	688/715	27	55	85000	0.36
<b>7</b> [13]	650/672	25	49	79000	0.34
<b>8</b> [13]	688/715	27	55	85000	0.36
<b>9</b>	710/754	44	86	67000	0.26
<b>10</b>	699/749	50	68	52000	0.03

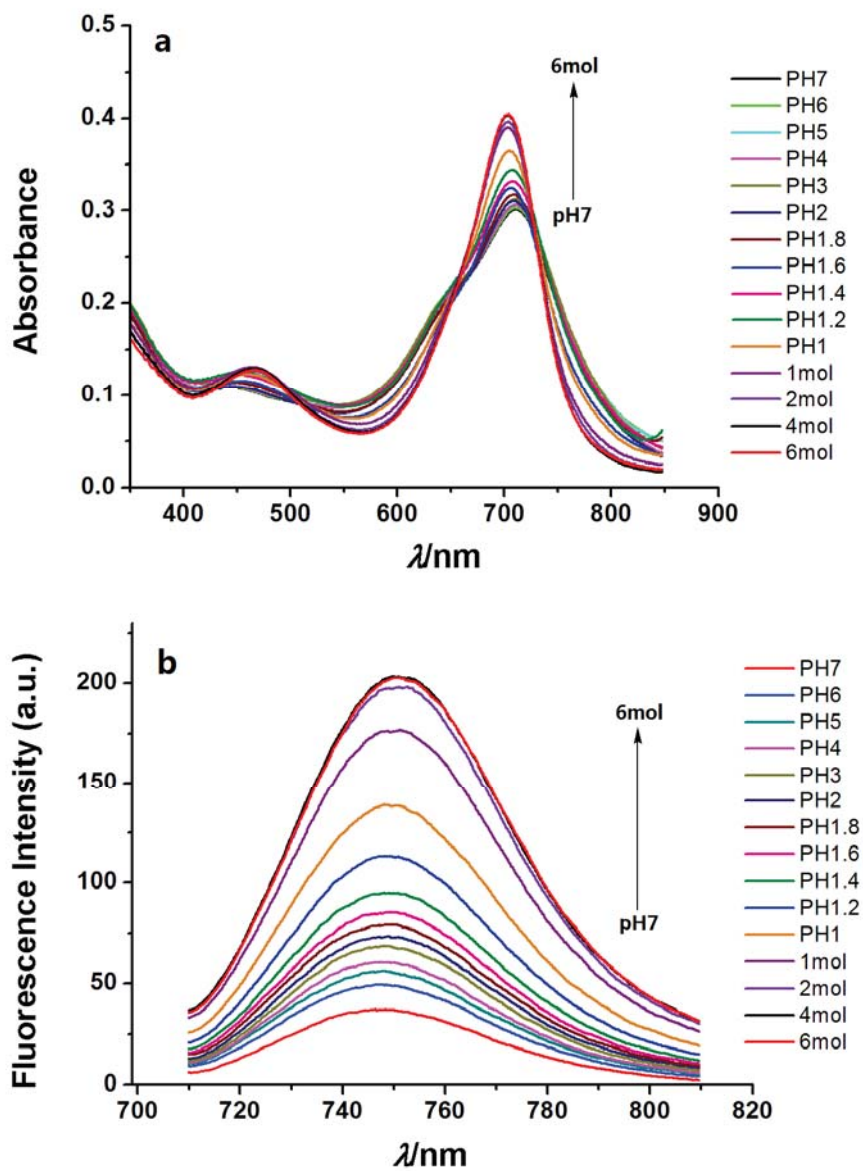




**Fig. 3.** (a) Normalized absorption and (b) fluorescence spectra of aza-BODIPYs **3** (black curve), **4** (blue curve), **5** (red curve) and **6** (green curve) in  $\text{CHCl}_3$  at 298 K. Photoimages of **3-6** under normal room illumination in  $\text{CHCl}_3$  at 298 K.



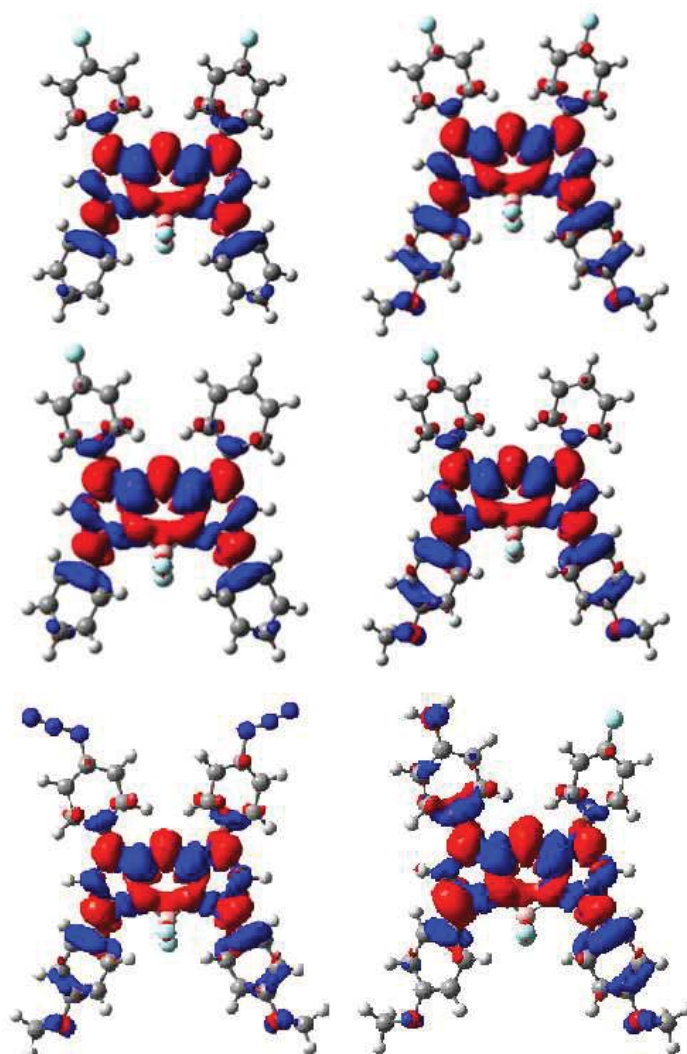
**Fig. 4.** (a) Normalized absorption and (b) fluorescence spectra of aza-BODIPYs **9** (red curve) and **10** (black curve) in  $\text{CHCl}_3$  at 298 K.



**Fig. 5.** Absorption (a) and fluorescence (b) spectra (pH 7, 6, 5, 4, 3, 2, 1.8, 1.6, 1.4, 1.2, 1 and 1 M, 2 M, 4 M, 6 M of HCl) of 3  $\mu$ M dye **10** in DMSO/H<sub>2</sub>O (2:1, v/v) as a function of pH.  $\lambda_{\text{ex}} = 700$  nm.

**Table 2** Computed  $\lambda_{\text{abs}}$  and  $\lambda_{\text{em}}$  (in nm), AFCP energy ( $E^{\text{AFCP}}$ , in nm), charge transfer distances ( $d^{\text{CT}}$ , in Å), and transferred charges ( $q^{\text{CT}}$ , in e) of aza-BODIPYs **3**, **4**, **5**, **6**, **8**, **9** and **10** at the cLR-PCM(CHCl<sub>3</sub>)-M06-2X/6-311+G(2d,p)/SOS-CIS(D).

Dye	$\lambda_{\text{abs}}$ [nm]	$\lambda_{\text{em}}$ [nm]	$E^{\text{AFCP}}$ [nm]	$d^{\text{CT}}$ [Å]	$q^{\text{CT}}$ [e]
<b>3</b>	664	717	706	0.56	0.34
<b>4</b>	704	770	755	1.44	0.39
<b>5</b>	664	717	710	0.61	0.34
<b>6</b>	703	769	752	1.44	0.39
<b>8</b>	702	768	752	1.47	0.39
<b>9</b>	714	783	769	1.11	0.38
<b>10</b>	716	798	770	0.56	0.39



**Fig. 6.** Density difference plots for (from left to right and top to bottom) aza-BODIPYs **3**, **4**, **5**, **6**, **9** and **10**. The blue (red) zones indicate density decrease (increase) upon transition.

ESI

**Synthesis, structure and photophysical properties of NIR  
aza-BODIPYs with -F/-N<sub>3</sub>/-NH<sub>2</sub> groups at 1,7-positions**

**Xin-Dong Jiang,<sup>a,b\*</sup> Jian Guan,<sup>a</sup> Jiuli zhao,<sup>a</sup> Boris Le Guennic,<sup>c,\*</sup> Denis  
Jacquemin,<sup>d</sup> Zhigang Zhang<sup>a</sup> Shangdong Chen<sup>a</sup> and Linjiu Xiao<sup>a</sup>**

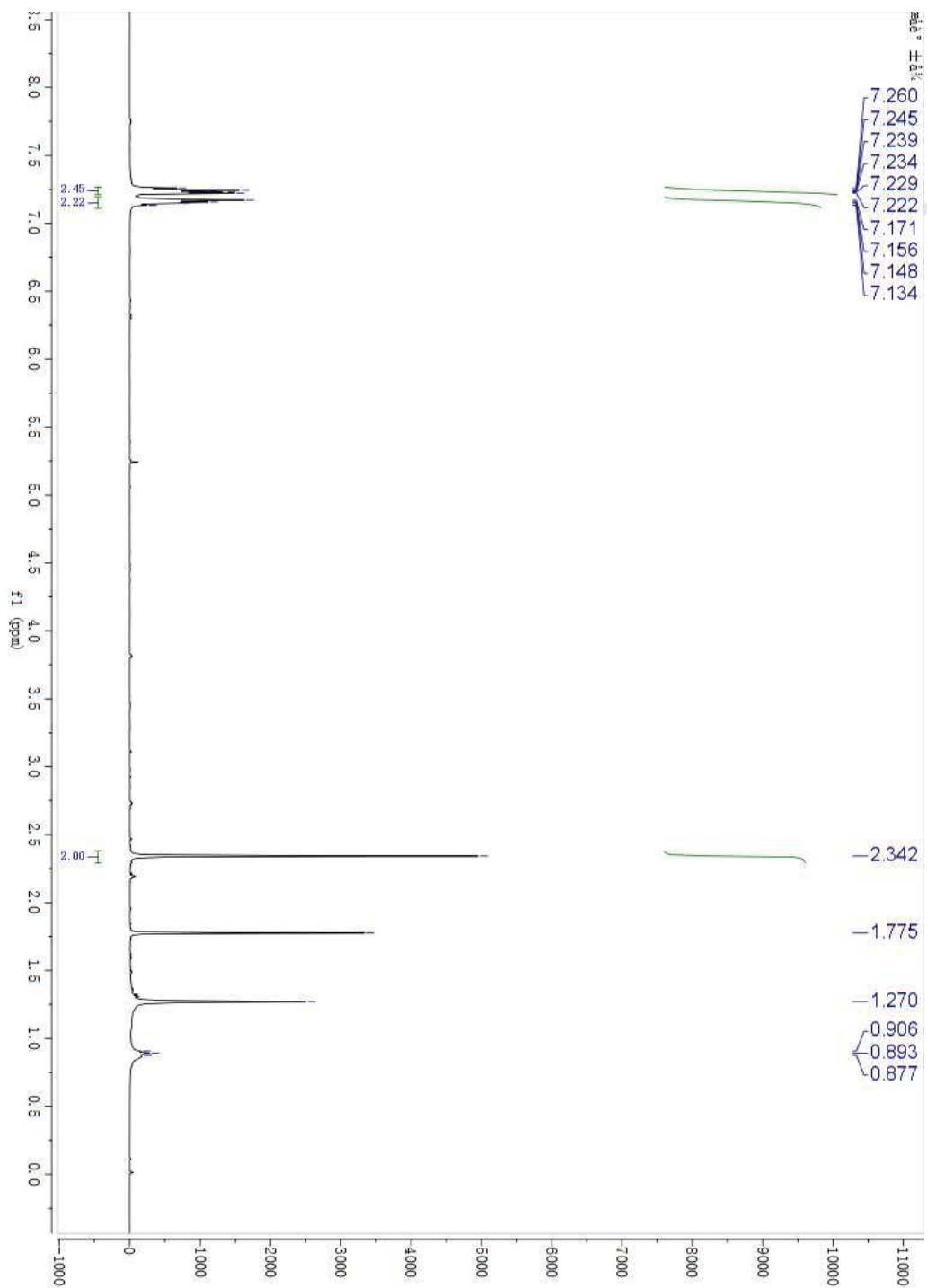
1 NMR

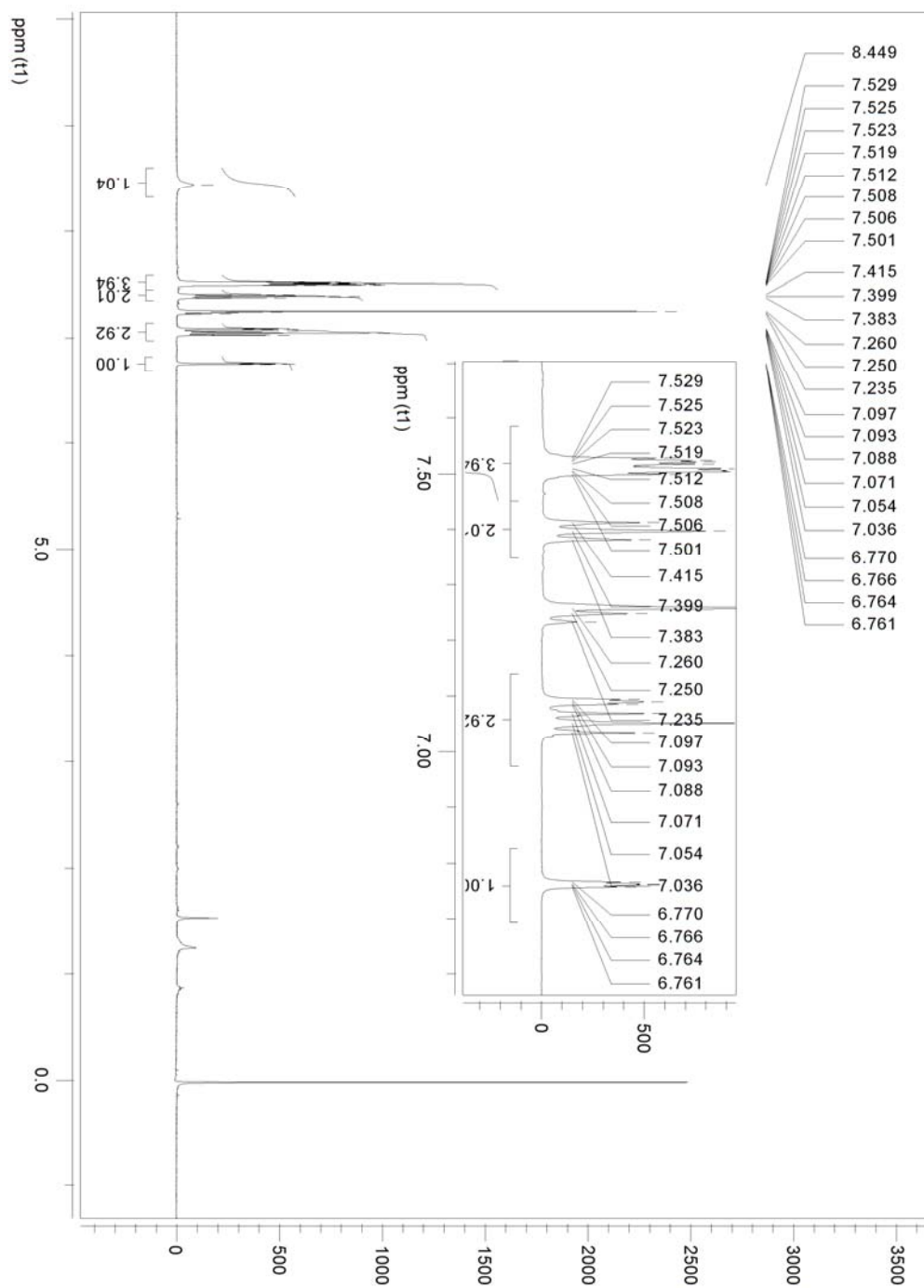
2 HRMS

3 X-ray single crystal diffraction data of **4**

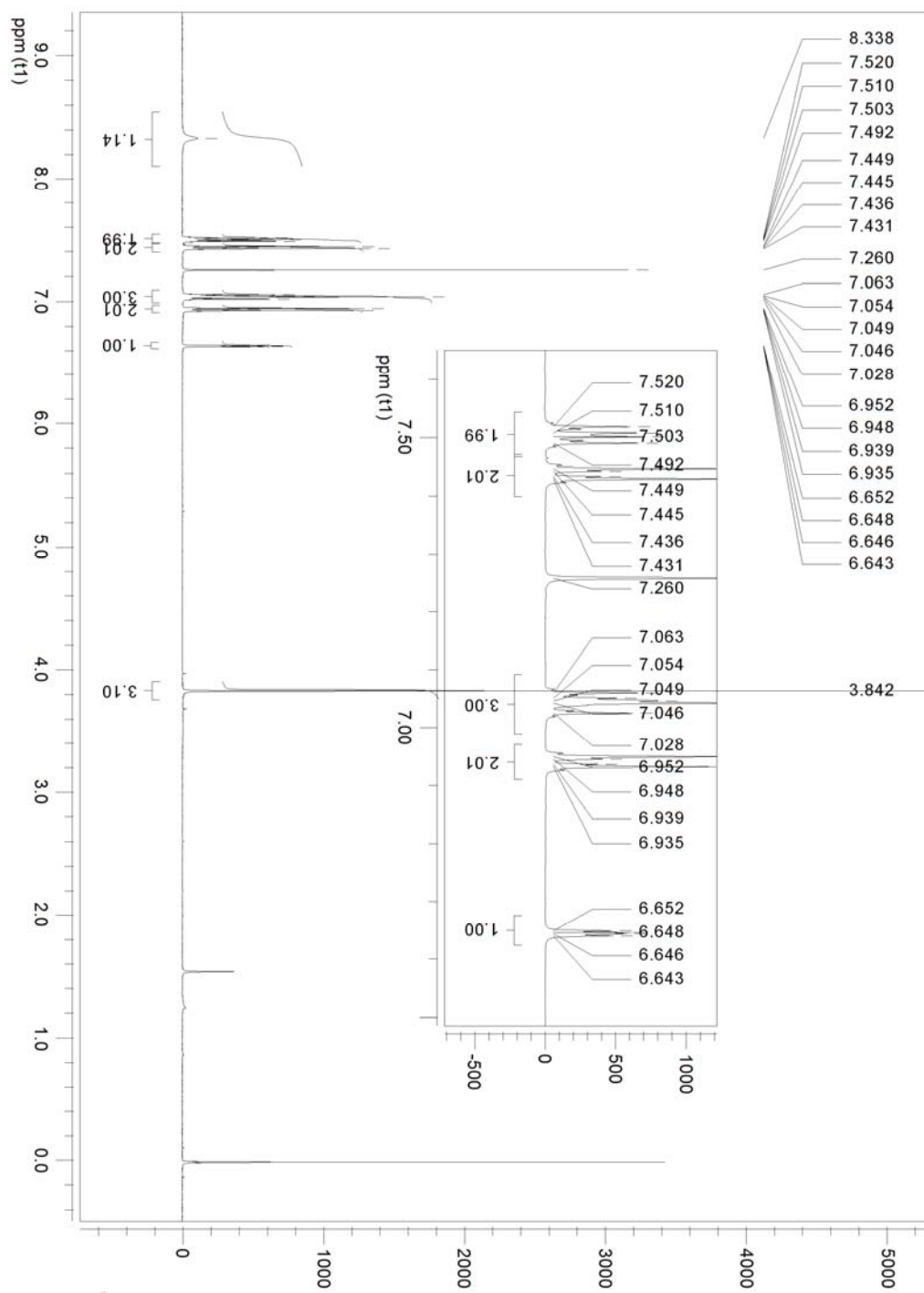
4 Ground state geometries in gas phase

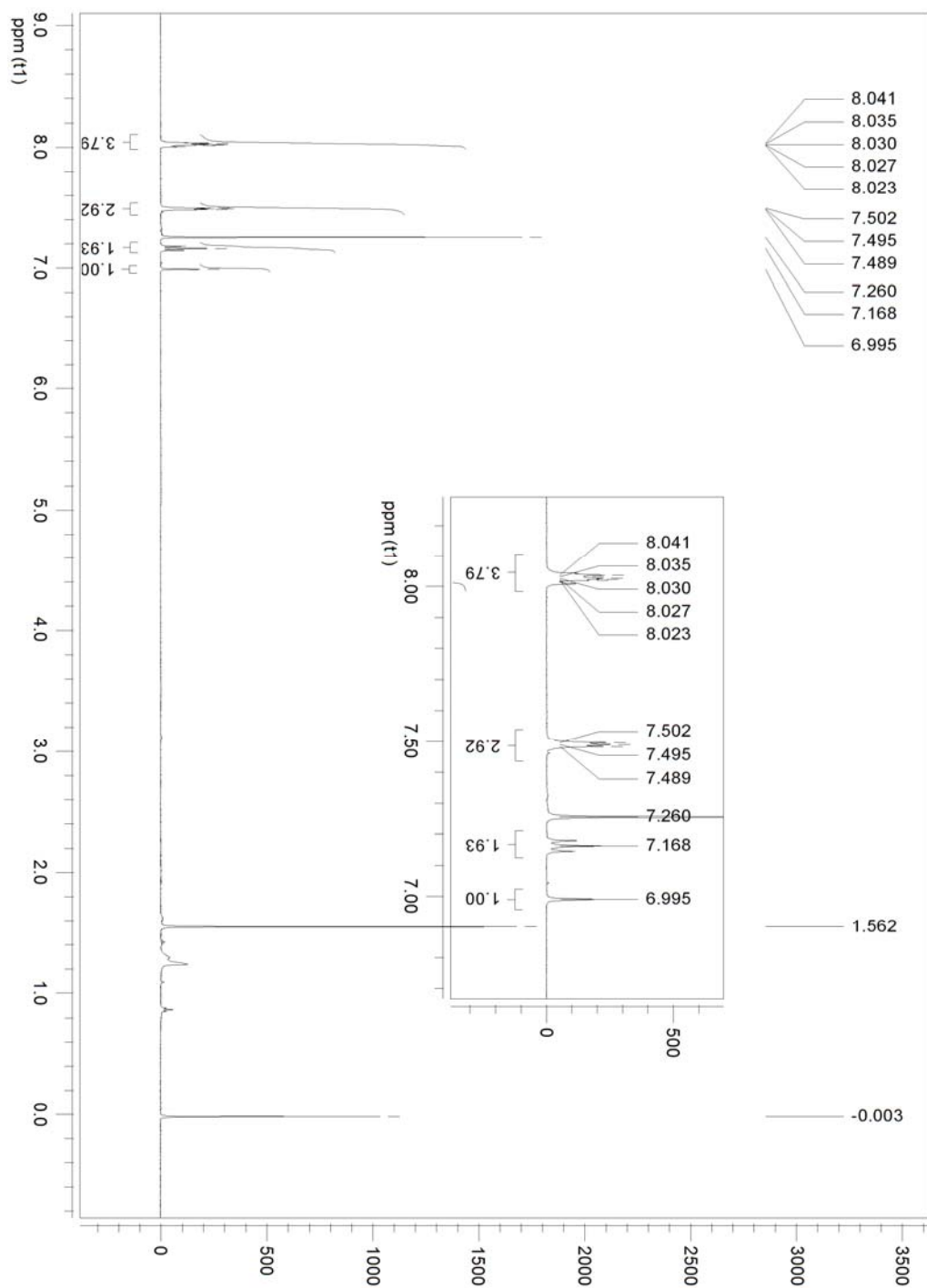
## 1. NMR

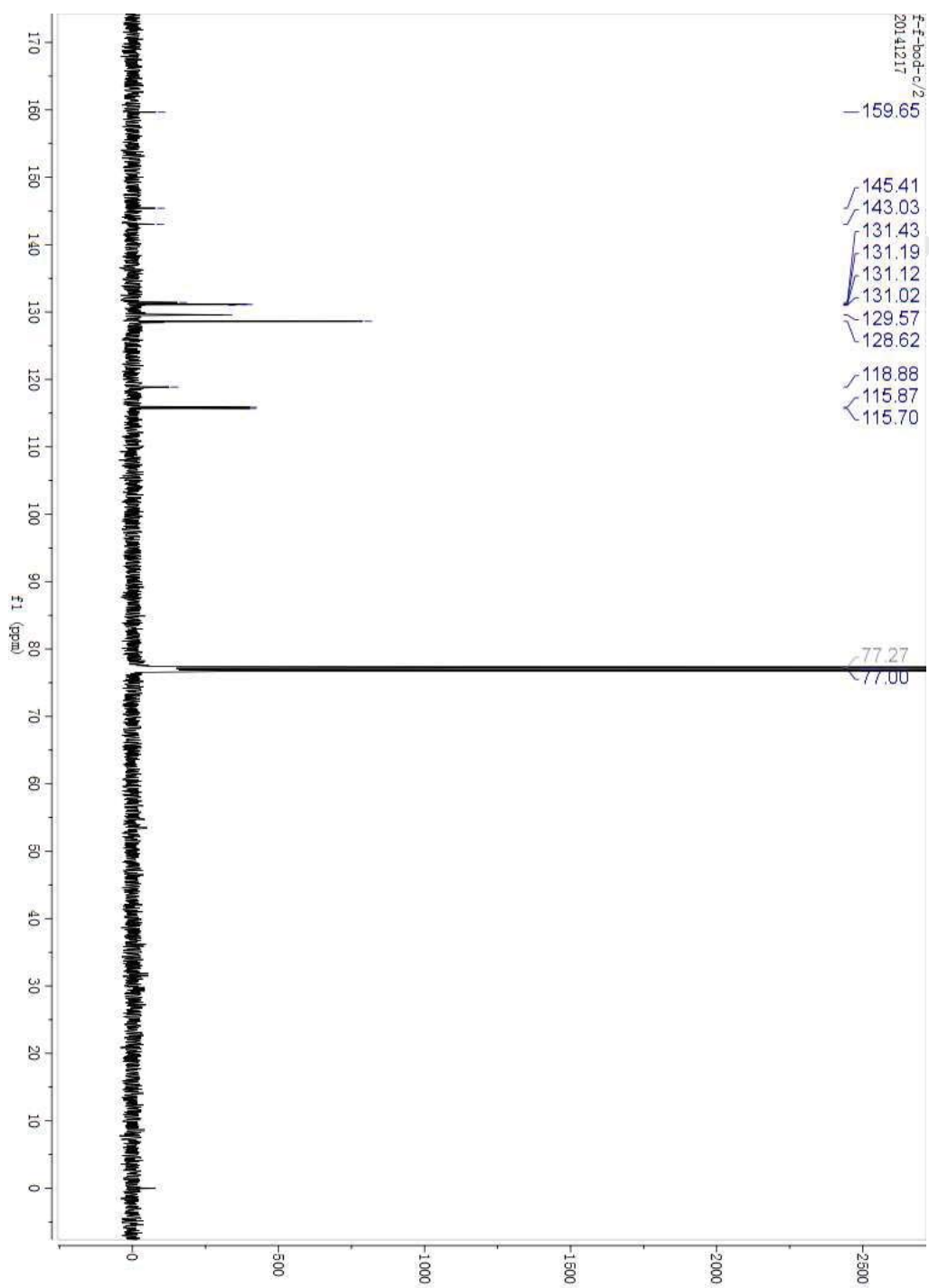
<sup>1</sup>H NMR of 3-(4-fluorophenyl)-2H-azirine

 $^1\text{H}$  NMR of pyrrole 1

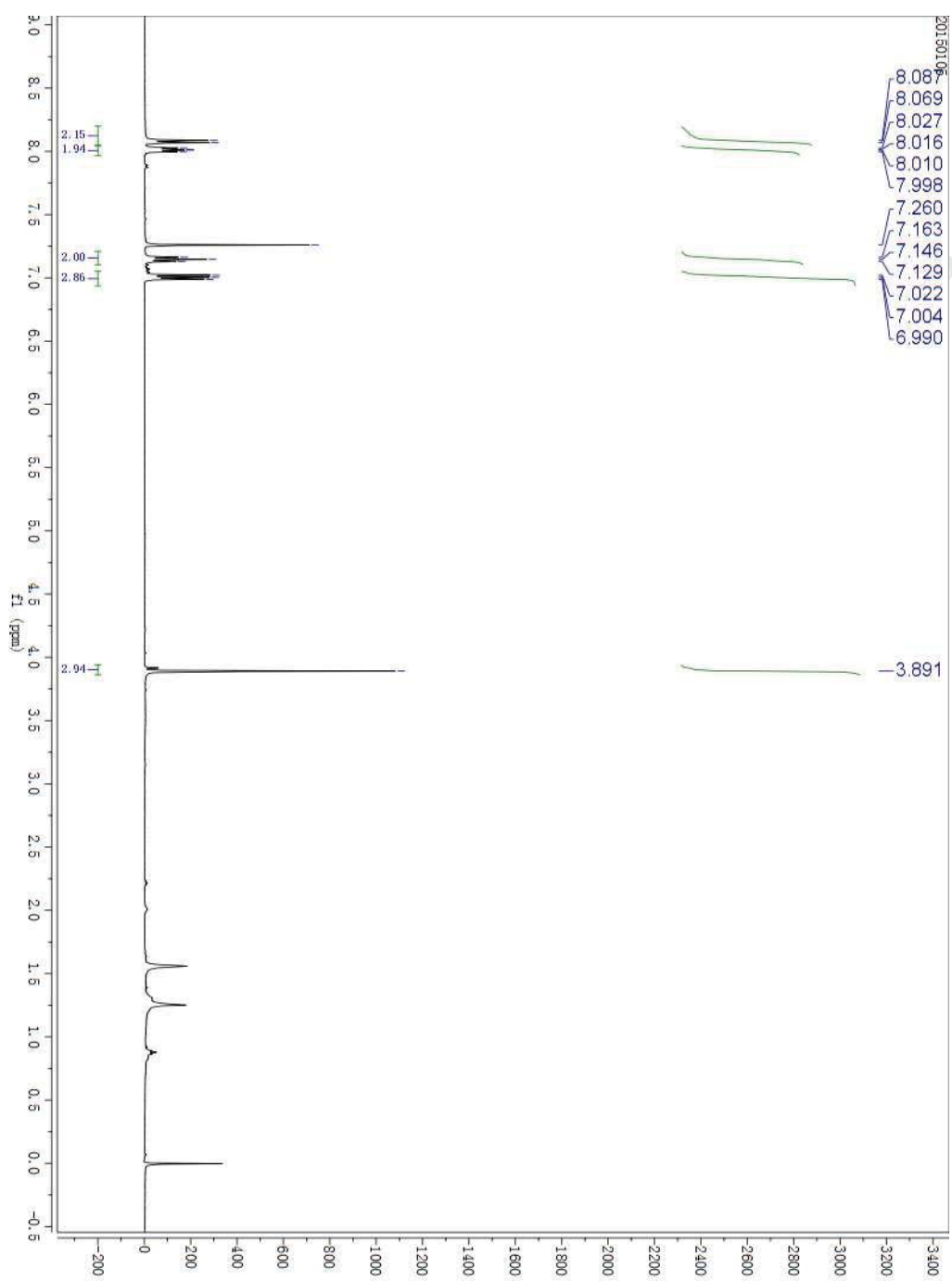


 $^1\text{H}$  NMR of pyrrole 2

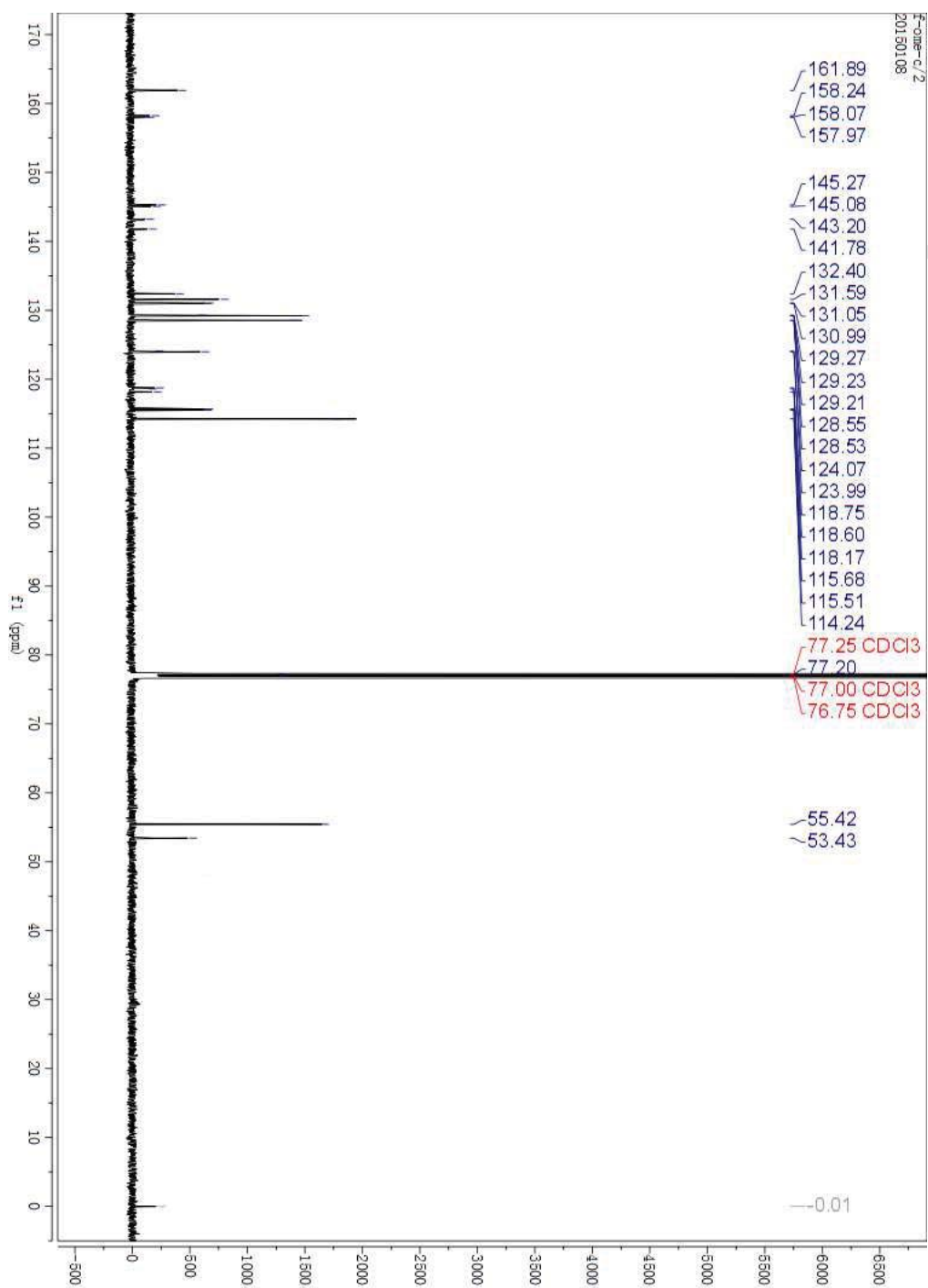
 $^1\text{H}$  NMR of aza-BODIPY 3



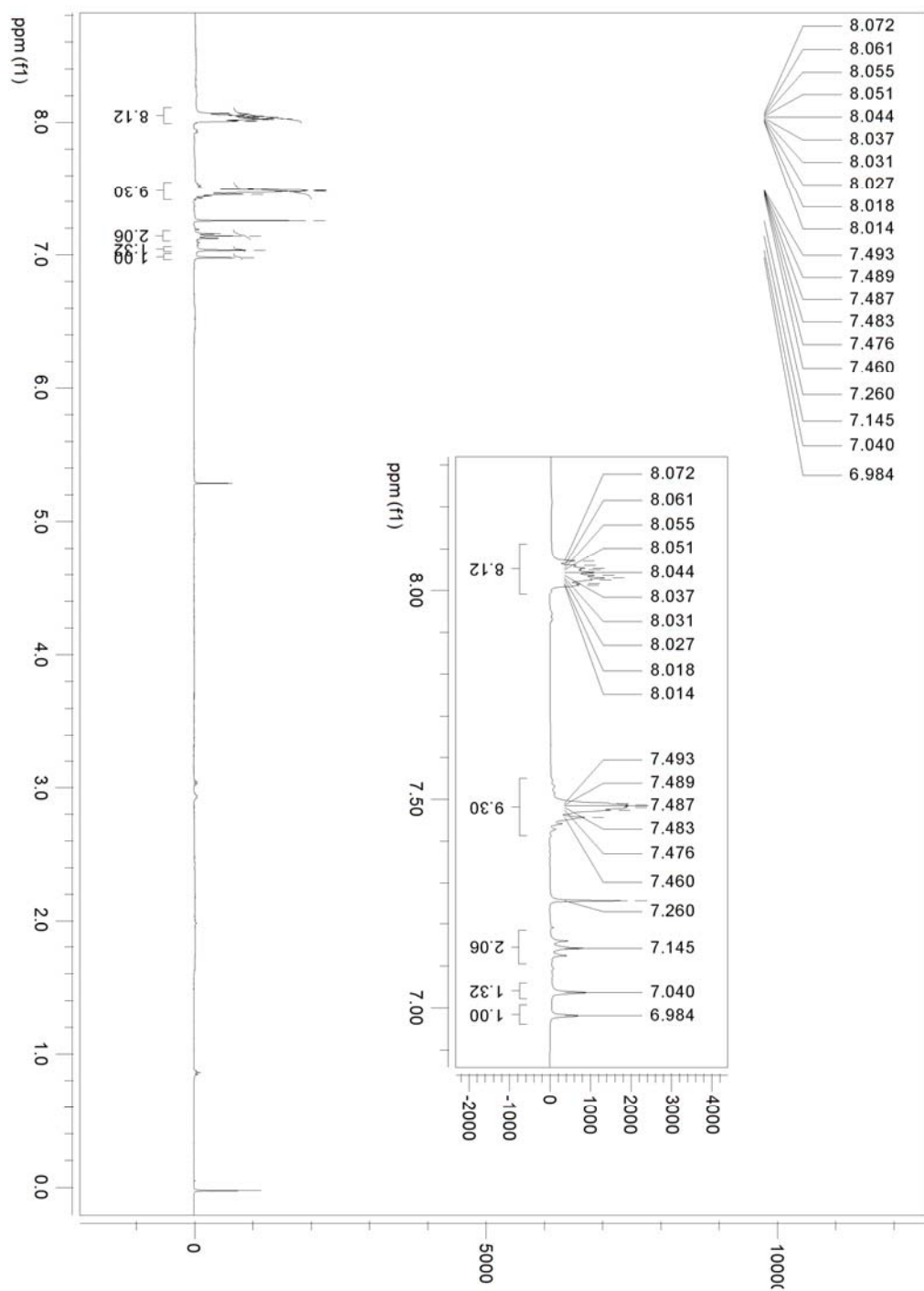
$^{13}\text{C}$  NMR of aza-BODIPY 3

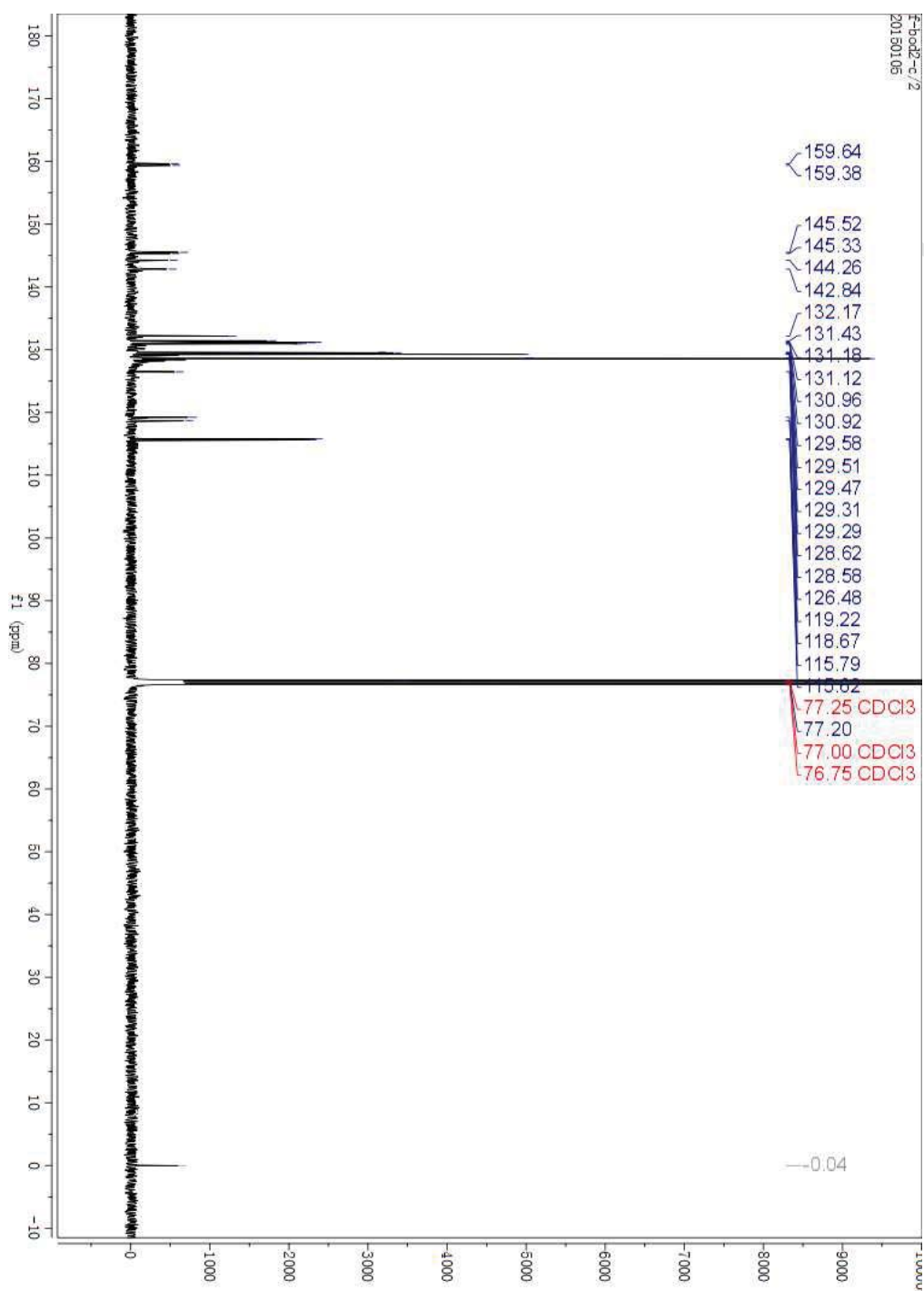


<sup>1</sup>H NMR of aza-BODIPY 4

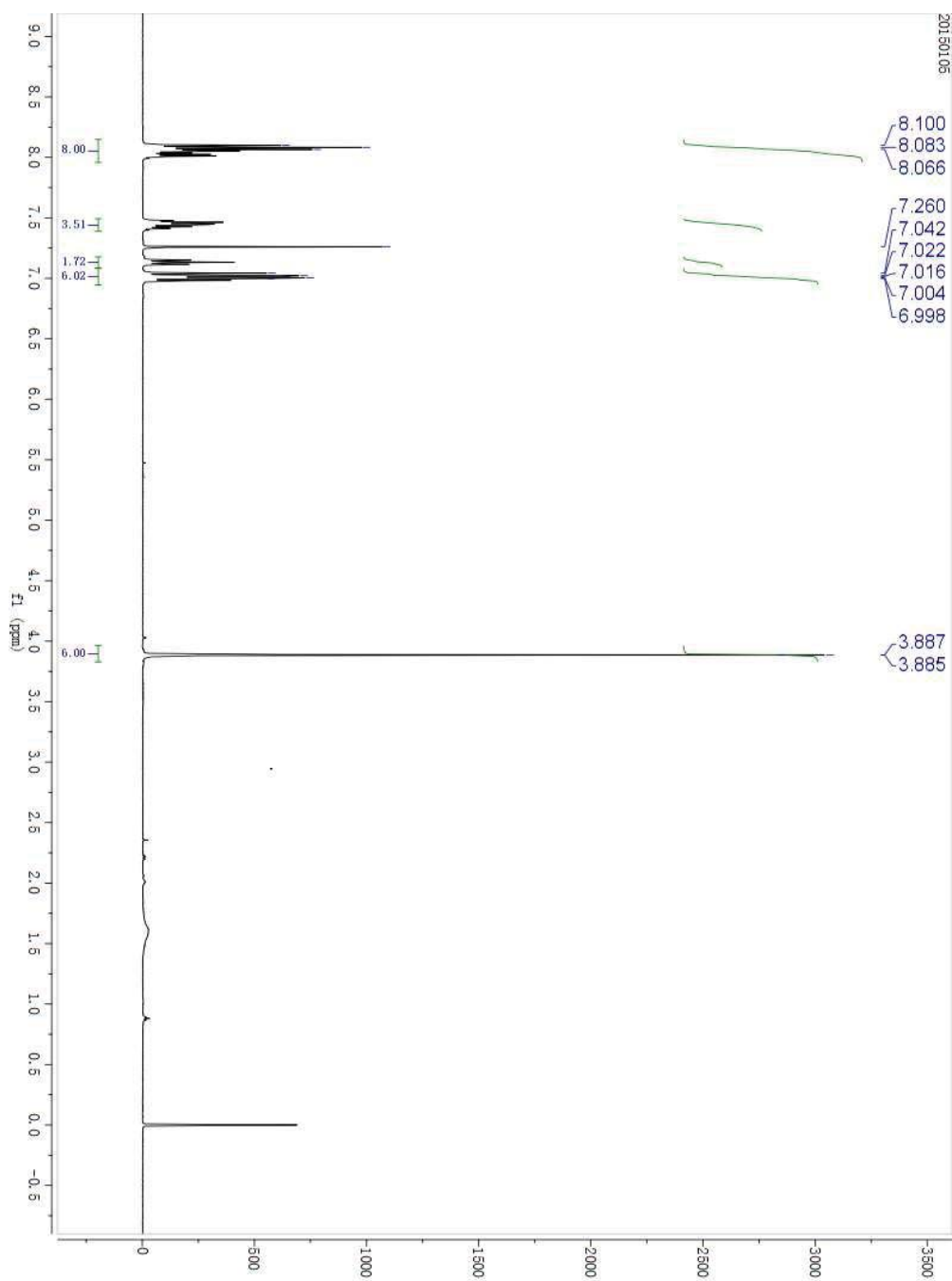


<sup>13</sup>C NMR of aza-BODIPY 4

 $^1\text{H}$  NMR of aza-BODIPY 5

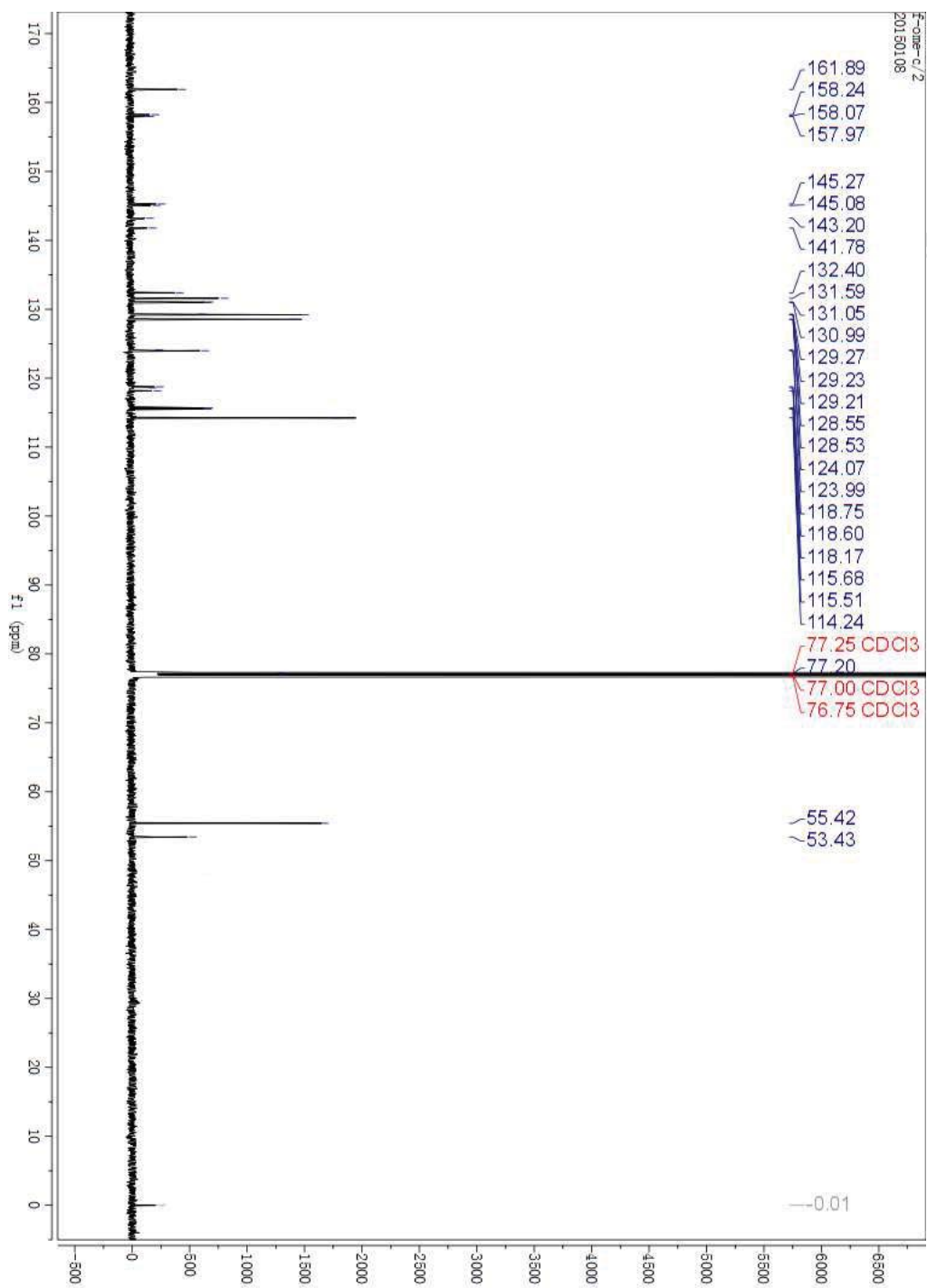


<sup>13</sup>C NMR of aza-BODIPY 5

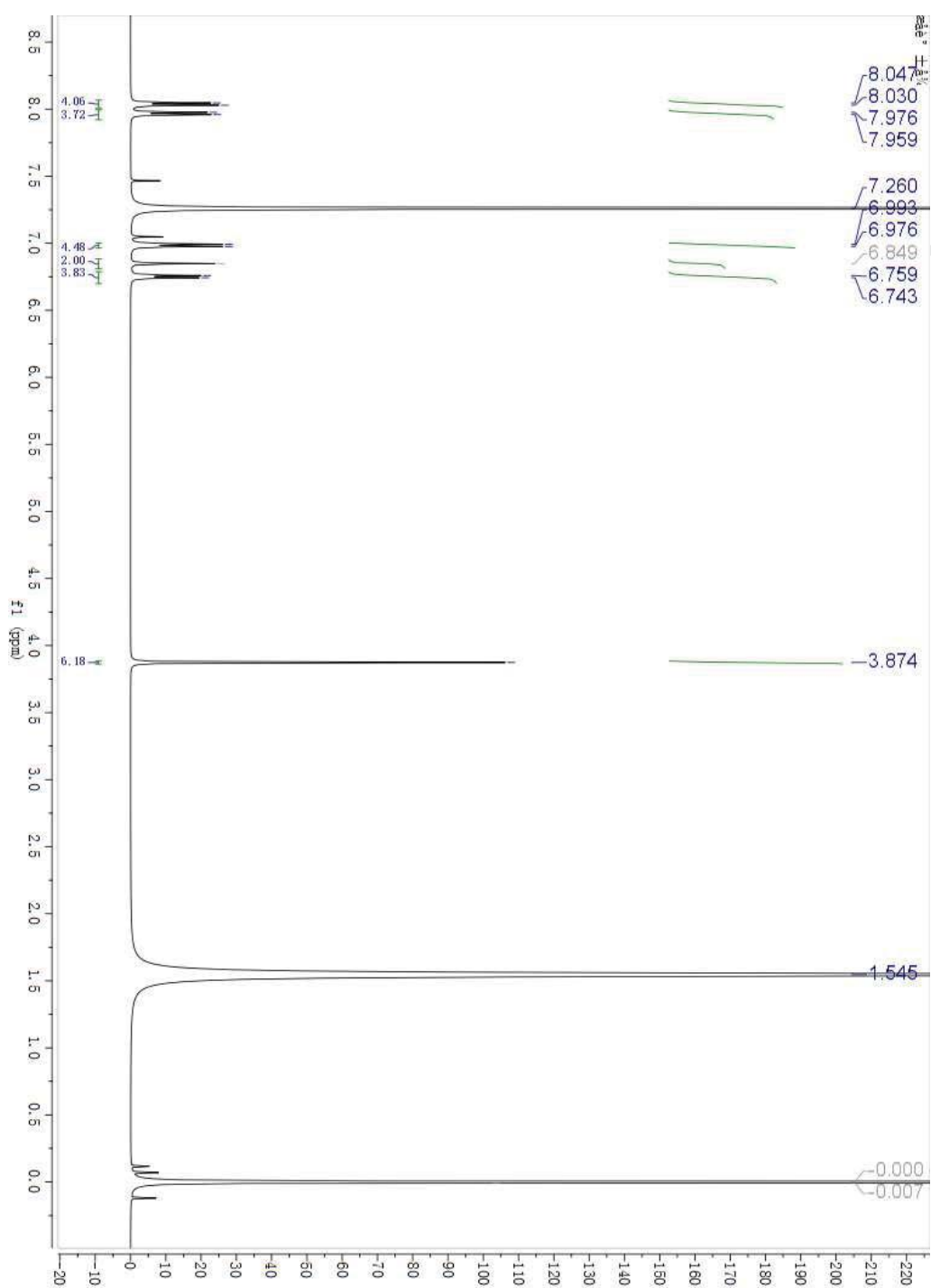


$^1\text{H}$  NMR of aza-BODIPY 6

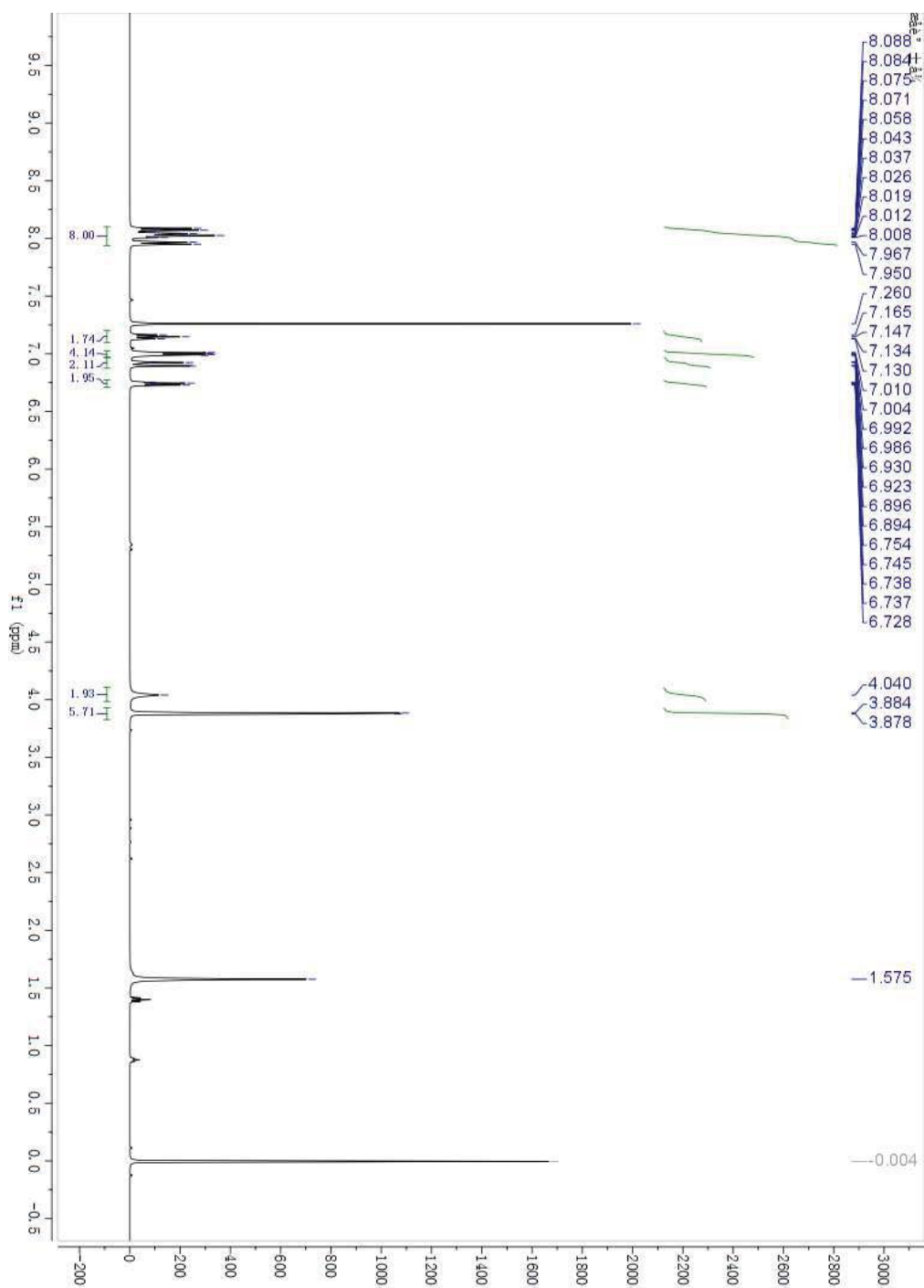




<sup>13</sup>C NMR of aza-BODIPY 6



<sup>1</sup>H NMR of aza-BODIPY 9

 $^1\text{H}$  NMR of aza-BODIPY 10

## 2. HRMS

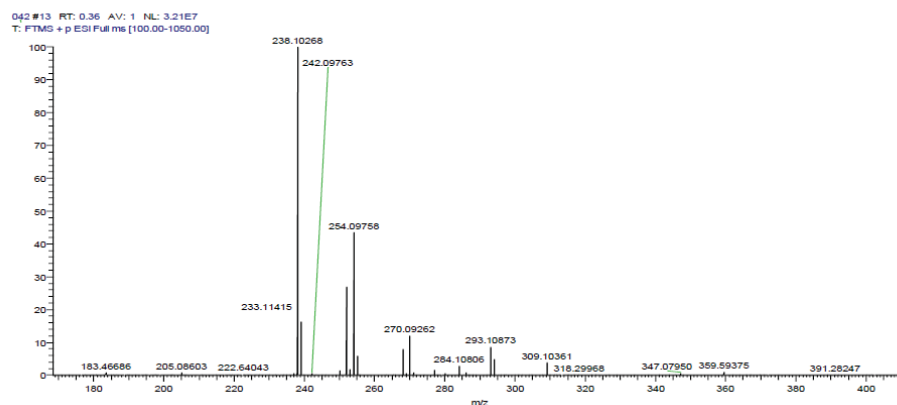
使用仪器：

Thermo Scientific LTQ Orbitrap XL

离子源：ESI

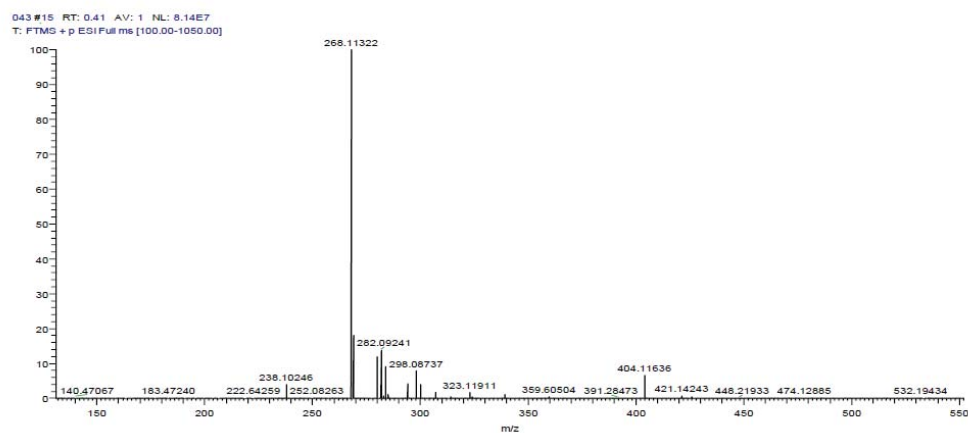
检测结果：

1. HRMS (ESI)  $m/z$  calcd for  $C_{16}H_{13}FN^+$  (M+H)<sup>+</sup> 238.10265, found 238.10268.



HRMS for 1

2. HRMS (ESI)  $m/z$  calcd for  $C_{17}H_{15}FNO^+$  (M+H)<sup>+</sup> 268.11322, found 268.11322.



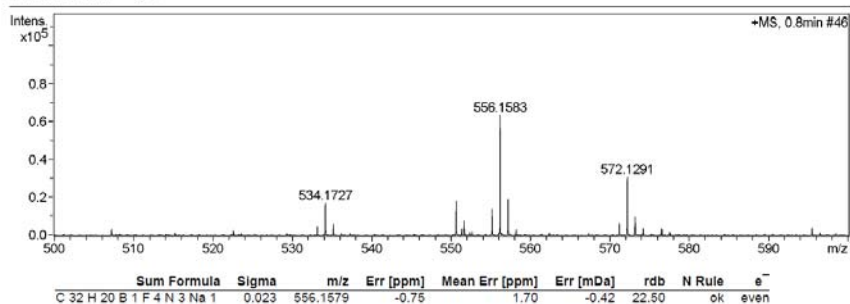
HRMS for 2

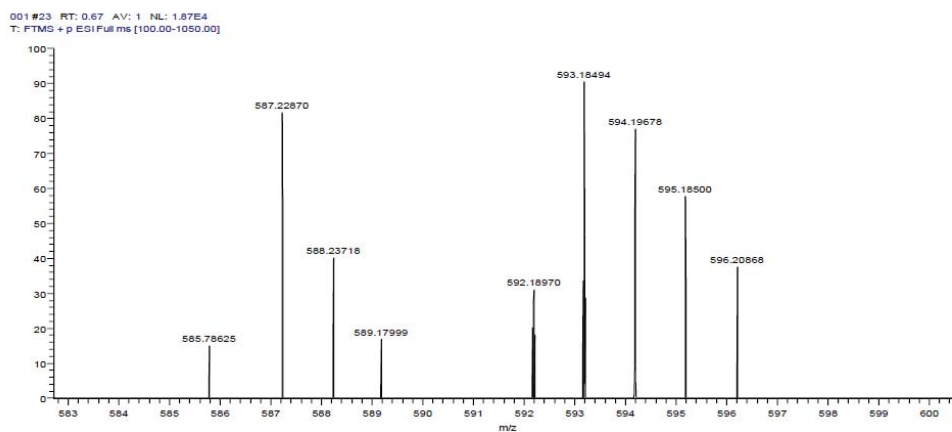
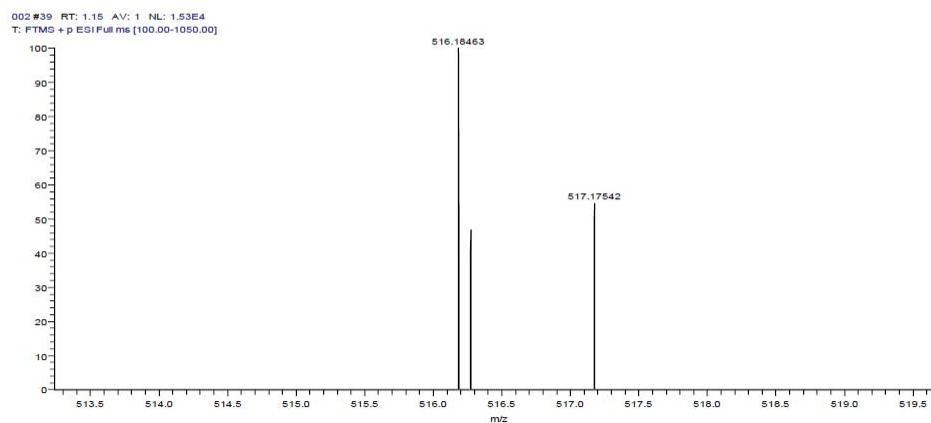
## Mass Spectrum Molecular Formula Report

**Analysis Info** D:\Data\20150115CEYANG\2.d  
**Analysis Name** Acquisition Date 1/15/2015 11:13:26 AM  
**Method** tune\_wide\_pos.m **Operator** micrOTOF-Q  
**Sample Name** 2 **Instrument / Ser#** Bruker Customer 125  
**Comment**

**Acquisition Parameter**  
Source Type ESI Ion Polarity Positive Set Nebulizer 0.3 Bar  
Focus Active Set Capillary 4500 V Set Dry Heater 180 °C  
Scan Begin 50 m/z Set End Plate Offset -500 V Set Dry Gas 4.0 l/min  
Scan End 3000 m/z Set Collision Cell RF 600.0 Vpp Set Divert Valve Source

**Generate Molecular Formula Parameter**  
Formula, min. C32H20B1F4N3Na  
Formula, max.  
Measured m/z 556.158 Tolerance 5 ppm Charge 1  
Check Valence no Minimum 0 Maximum 0  
Nitrogen Rule no Electron Configuration both  
Filter H/C Ratio no Minimum 0 Maximum 3  
Estimate Carbon yes



**3. HRMS (ESI) m/z calcd for  $C_{34}H_{25}BF_4N_3O_2^+$  (M+H)<sup>+</sup> 594.19705, found 594.19678.****HRMS for 4****4. HRMS (ESI) m/z calcd for  $C_{32}H_{22}BF_3N_3^+$  (M+H)<sup>+</sup> 516.18534, found 516.18463.****HRMS for 5**

## Mass Spectrum Molecular Formula Report

Analysis Info D:\Data\20150115CEYANG\3.d

Analysis Name

Acquisition Date 1/15/2015 11:16:31 AM

Method tune\_wide\_pos.m

Operator micrOTOF-Q

Sample Name 3

Instrument / Ser# Bruker Customer 125

Comment

## Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source

## Generate Molecular Formula Parameter

Formula, min. C34H25B1F3N3O2Na

Formula, max.

Measured m/z 598.189

Tolerance 5 ppm

Charge 1

Check Valence no

Minimum 0

Maximum 0

Nitrogen Rule no

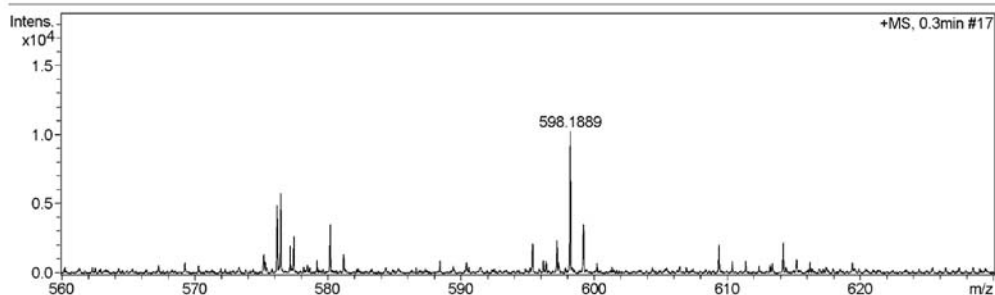
Electron Configuration both

Filter H/C Ratio no

Minimum 0

Maximum 3

Estimate Carbon yes



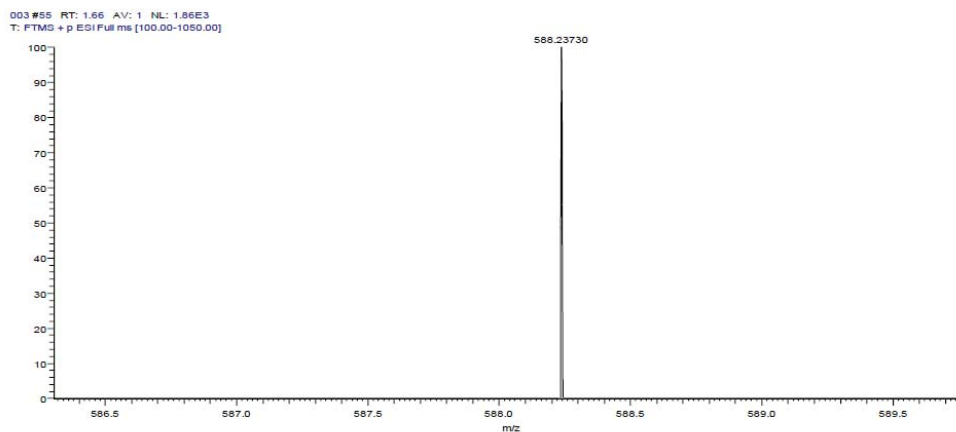
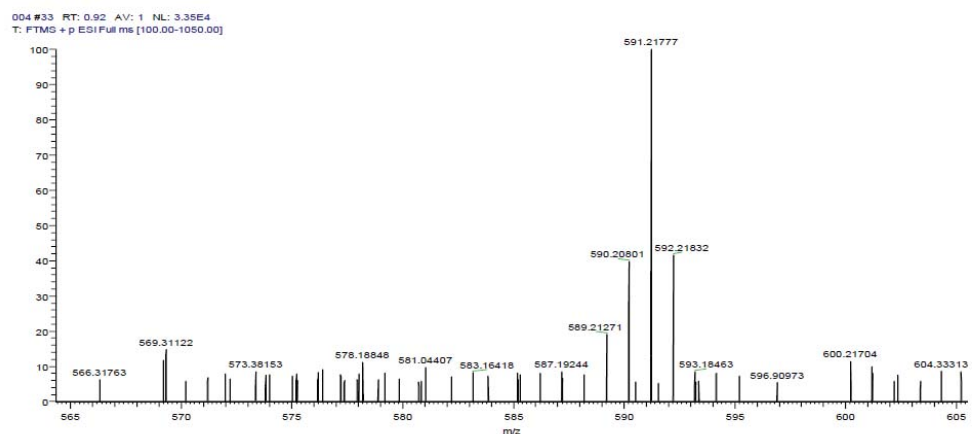
Sum Formula	Sigma	m/z	Err [ppm]	Mean Err [ppm]	Err [mDa]	rdb	N Rule	e <sup>-</sup>
C 34 H 25 B 1 F 3 N 3 Na 1 O 2	0.012	598.1884	-0.81	0.47	-0.49	22.50	ok	even

Bruker Daltonics DataAnalysis 3.4

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Page 1 of 1

HRMS for 6

**5. HRMS (ESI) m/z calcd for  $C_{34}H_{29}BF_2N_5O_2^+$  (M+H)<sup>+</sup> 588.23769, found 588.23730.****HRMS for 9****6. HRMS (ESI) m/z calcd for  $C_{34}H_{27}BF_3N_4O_2^+$  (M+H)<sup>+</sup> 591.21737, found 591.21777.****HRMS for 10**



### 3. X-ray single crystal diffraction data of 4

Crystals suitable for the X-ray structural determination were mounted on a Mac Science DIP2030 imaging plate diffractometer and irradiated with graphite monochromated Mo- $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) for the data collection. The unit cell parameters were determined by separately autoindexing several images in each data set using the DENZO program (MAC Science). For each data set, the rotation images were collected in 3 degree increments with a total rotation of 180 deg about the  $\phi$  axis. The data were processed using SCALEPACK. The structures were solved by a direct method with the SHELX-97 program. Refinement on  $F^2$  was carried out using the full-matrix least-squares by the SHELX-97 program. All non-hydrogen atoms were refined using the anisotropic thermal parameters. The hydrogen atoms were included in the refinement along with the isotropic thermal parameters (Table S1-S5).

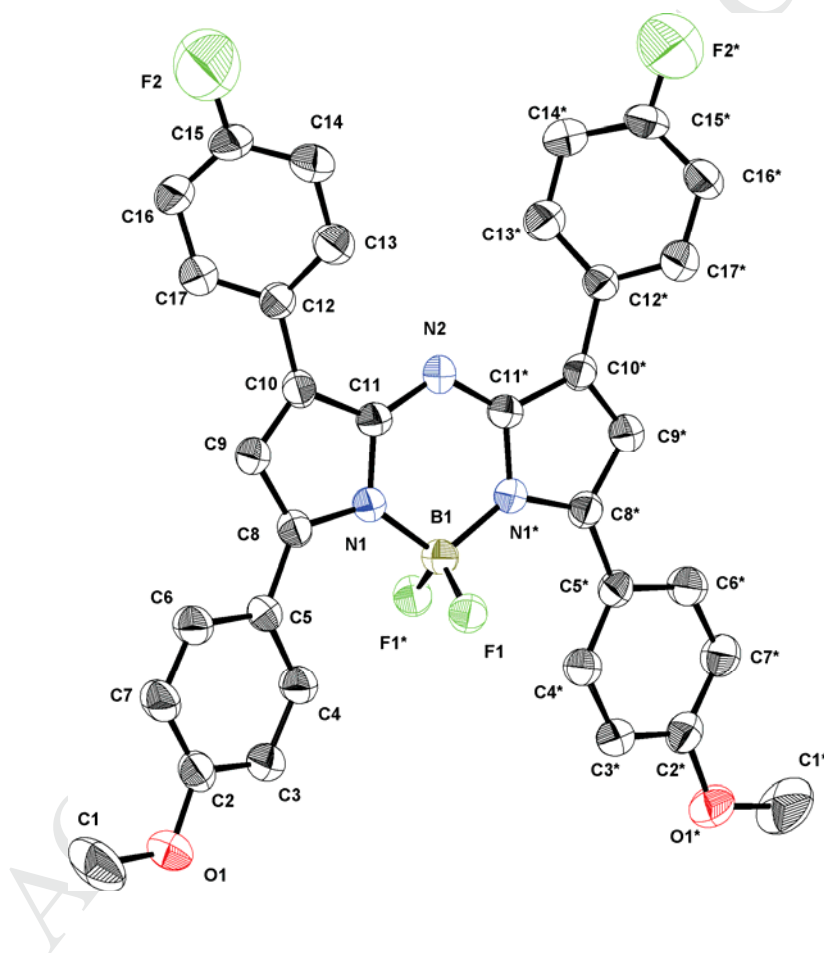


Table S1. Crystal data and structure refinement.

Identification code	shelx	
Empirical formula	C <sub>34</sub> H <sub>24</sub> B F <sub>4</sub> N <sub>3</sub> O <sub>2</sub>	
Formula weight	593.37	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	?	
Space group	Ia-3d	
Unit cell dimensions	a = 16.1853(2) Å	$\alpha = 90^\circ$ .
	b = 16.1853(2) Å	$\beta = 90^\circ$ .
	c = 19.9274(6) Å	$\gamma = 90^\circ$ .
Volume	5220.26(18) Å <sup>3</sup>	
Z	48	
Density (calculated)	9.060 Mg/m <sup>3</sup>	
Absorption coefficient	0.683 mm <sup>-1</sup>	
F(000)	14688	
Crystal size	0.40 x 0.30 x 0.20 mm <sup>3</sup>	
Theta range for data collection	3.24 to 28.38°.	
Index ranges	-21 ≤ h ≤ 21, -21 ≤ k ≤ 21, -26 ≤ l ≤ 26	
Reflections collected	23013	
Independent reflections	3276 [R(int) = 0.0867]	
Completeness to theta = 28.38°	99.8 %	
Max. and min. transmission	0.8756 and 0.7719	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	3276 / 0 / 202	
Goodness-of-fit on F <sup>2</sup>	2.181	
Final R indices [I > 2σ(I)]	R1 = 0.1437, wR2 = 0.3623	
R indices (all data)	R1 = 0.1832, wR2 = 0.4016	
Extinction coefficient	0.0002(6)	
Largest diff. peak and hole	1.077 and -0.724 e.Å <sup>-3</sup>	

Table S2. Atomic coordinates ( $\text{\AA} \times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ).  
 $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U^{ij}$  tensor.

	x	y	z	$U(\text{eq})$
F(1)	4356(2)	2252(2)	52(1)	68(1)
N(1)	4724(2)	3202(2)	885(2)	56(1)
N(2)	5000	2500	1895(2)	57(1)
C(11)	4754(3)	3150(3)	1568(2)	57(1)
C(8)	4405(3)	3946(3)	732(2)	58(1)
C(5)	4206(3)	4249(3)	81(2)	59(1)
C(10)	4471(3)	3893(3)	1848(2)	59(1)
O(1)	3564(2)	5205(2)	-1736(2)	89(1)
C(9)	4269(3)	4355(3)	1333(2)	65(1)
C(12)	4440(3)	4104(3)	2551(2)	60(1)
C(2)	3755(3)	4932(3)	-1130(2)	69(1)
C(3)	4209(3)	4242(3)	-1115(2)	72(1)
C(4)	4431(3)	3912(3)	-523(2)	71(1)
C(6)	3730(3)	4966(3)	42(2)	79(1)
C(15)	4374(4)	4560(4)	3832(2)	87(2)
C(13)	4194(3)	3561(3)	3029(3)	79(1)
C(17)	4604(3)	4870(3)	2739(3)	85(2)
C(7)	3504(4)	5296(3)	-541(2)	81(2)
B(1)	5000	2500	432(3)	55(2)
C(16)	4576(4)	5107(3)	3395(3)	90(2)
C(14)	4152(4)	3771(4)	3686(2)	88(2)
F(2)	4452(7)	4791(5)	4443(4)	270(4)
C(1)	3093(6)	5936(5)	-1790(4)	142(3)

Table S3. Bond lengths [Å] and angles [°].

---

F(1)-B(1)	1.349(4)
N(1)-C(8)	1.344(5)
N(1)-C(11)	1.365(5)
N(1)-B(1)	1.518(5)
N(2)-C(11)	1.301(5)
N(2)-C(11)#1	1.301(5)
C(11)-C(10)	1.403(6)
C(8)-C(9)	1.387(6)
C(8)-C(5)	1.425(6)
C(5)-C(4)	1.370(6)
C(5)-C(6)	1.396(6)
C(10)-C(9)	1.311(6)
C(10)-C(12)	1.442(6)
O(1)-C(2)	1.322(5)
O(1)-C(1)	1.411(8)
C(12)-C(17)	1.322(7)
C(12)-C(13)	1.356(7)
C(2)-C(3)	1.338(7)
C(2)-C(7)	1.376(7)
C(3)-C(4)	1.343(6)
C(6)-C(7)	1.330(6)
C(15)-F(2)	1.278(9)
C(15)-C(16)	1.285(8)
C(15)-C(14)	1.357(8)
C(13)-C(14)	1.355(7)
C(17)-C(16)	1.363(7)
B(1)-F(1)#1	1.349(4)
B(1)-N(1)#1	1.518(5)
C(8)-N(1)-C(11)	107.1(3)
C(8)-N(1)-B(1)	130.5(3)
C(11)-N(1)-B(1)	122.4(3)
C(11)-N(2)-C(11)#1	119.8(5)
N(2)-C(11)-N(1)	124.1(4)
N(2)-C(11)-C(10)	126.4(4)
N(1)-C(11)-C(10)	109.5(4)
N(1)-C(8)-C(9)	107.1(4)
N(1)-C(8)-C(5)	126.9(4)
C(9)-C(8)-C(5)	125.9(4)
C(4)-C(5)-C(6)	115.4(4)
C(4)-C(5)-C(8)	127.1(4)
C(6)-C(5)-C(8)	117.4(4)

C(9)-C(10)-C(11)	105.0(4)
C(9)-C(10)-C(12)	128.1(4)
C(11)-C(10)-C(12)	126.9(4)
C(2)-O(1)-C(1)	118.4(5)
C(10)-C(9)-C(8)	111.3(4)
C(17)-C(12)-C(13)	117.9(5)
C(17)-C(12)-C(10)	119.3(4)
C(13)-C(12)-C(10)	122.6(4)
O(1)-C(2)-C(3)	115.4(5)
O(1)-C(2)-C(7)	124.6(5)
C(3)-C(2)-C(7)	120.0(4)
C(2)-C(3)-C(4)	119.9(5)
C(3)-C(4)-C(5)	122.8(4)
C(7)-C(6)-C(5)	122.3(5)
F(2)-C(15)-C(16)	114.7(7)
F(2)-C(15)-C(14)	120.4(6)
C(16)-C(15)-C(14)	124.7(5)
C(14)-C(13)-C(12)	122.0(5)
C(12)-C(13)-C(16)	121.9(5)
C(6)-C(7)-C(2)	119.5(5)
F(1)-B(1)-F(1)#1	111.8(5)
F(1)-B(1)-N(1)	109.19(16)
F(1)#1-B(1)-N(1)	109.74(16)
F(1)-B(1)-N(1)#1	109.74(16)
F(1)#1-B(1)-N(1)#1	109.18(16)
N(1)-B(1)-N(1)#1	107.1(5)
C(15)-C(16)-C(17)	117.7(5)
C(13)-C(14)-C(15)	115.5(5)

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Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1/2,z+0

Table S4. Anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ). The anisotropic displacement factor exponent takes the form:  $-2\pi^2 [ h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12} ]$

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{23}$	$U^{13}$	$U^{12}$
F(1)	69(2)	65(2)	70(2)	-1(1)	-10(1)	2(1)
N(1)	65(2)	49(2)	53(2)	2(1)	1(2)	3(1)
N(2)	58(3)	48(2)	65(3)	0	0	0(2)
C(11)	64(2)	57(2)	48(2)	-1(2)	1(2)	3(2)
C(8)	61(2)	53(2)	61(2)	4(2)	4(2)	3(2)
C(5)	65(2)	54(2)	59(2)	5(2)	-6(2)	7(2)
C(10)	65(3)	49(2)	61(2)	4(2)	6(2)	1(2)
O(1)	103(3)	92(3)	72(2)	16(2)	-15(2)	6(2)
C(9)	77(3)	54(2)	63(2)	-2(2)	2(2)	7(2)
C(12)	66(3)	58(2)	56(2)	-1(2)	6(2)	7(2)
C(2)	72(3)	61(3)	73(3)	11(2)	-8(2)	-2(2)
C(3)	88(3)	66(3)	60(2)	3(2)	4(2)	4(2)
C(4)	86(3)	64(3)	62(3)	2(2)	1(2)	15(2)
C(6)	99(4)	71(3)	66(3)	1(2)	-1(3)	27(3)
C(15)	123(5)	88(4)	51(2)	-10(3)	9(3)	15(3)
C(13)	86(4)	76(3)	74(3)	5(2)	3(3)	4(3)
C(17)	115(4)	67(3)	71(3)	2(2)	-6(3)	7(3)
C(7)	94(4)	70(3)	78(3)	11(3)	-5(3)	29(3)
B(1)	53(3)	61(4)	52(3)	0	0	8(3)
C(16)	133(5)	69(3)	68(3)	-14(3)	-4(3)	21(3)
C(14)	111(4)	89(4)	62(3)	7(3)	10(3)	0(3)
F(2)	415(14)	190(7)	204(7)	-10(6)	73(7)	67(8)
C(1)	156(8)	139(6)	132(6)	54(5)	-13(5)	64(6)

Table S5. Hydrogen coordinates ( $\text{\AA} \times 10^4$ ) and isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ).

	x	y	z	U(eq)
H(9)	4060	4889	1367	78
H(3)	4370	3990	-1513	86
H(4)	4752	3436	-524	85
H(6)	3565	5222	438	94
H(13)	4050	3027	2902	95
H(17)	4743	5259	2414	101
H(7)	3179	5770	-549	97
H(16)	4698	5646	3522	108
H(14)	3983	3401	4015	105
H(1A)	3426	6401	-1664	213
H(1B)	2622	5901	-1498	213
H(1C)	2909	6003	-2245	213

Table S6. Torsion angles [°].

C(11)#1-N(2)-C(11)-N(1)	0.8(3)
C(11)#1-N(2)-C(11)-C(10)	179.9(5)
C(8)-N(1)-C(11)-N(2)	177.2(4)
B(1)-N(1)-C(11)-N(2)	-1.5(6)
C(8)-N(1)-C(11)-C(10)	-2.0(5)
B(1)-N(1)-C(11)-C(10)	179.2(3)
C(11)-N(1)-C(8)-C(9)	2.1(5)
B(1)-N(1)-C(8)-C(9)	-179.3(3)
C(11)-N(1)-C(8)-C(5)	-175.4(4)
B(1)-N(1)-C(8)-C(5)	3.3(7)
N(1)-C(8)-C(5)-C(4)	-12.5(8)
C(9)-C(8)-C(5)-C(4)	170.5(5)
N(1)-C(8)-C(5)-C(6)	167.4(5)
C(9)-C(8)-C(5)-C(6)	-9.6(7)
N(2)-C(11)-C(10)-C(9)	-178.1(4)
N(1)-C(11)-C(10)-C(9)	1.1(5)
N(2)-C(11)-C(10)-C(12)	3.8(7)
N(1)-C(11)-C(10)-C(12)	-176.9(4)
C(11)-C(10)-C(9)-C(8)	0.2(6)
C(12)-C(10)-C(9)-C(8)	178.2(5)
N(1)-C(8)-C(9)-C(10)	-1.4(6)
C(5)-C(8)-C(9)-C(10)	176.0(4)
C(9)-C(10)-C(12)-C(17)	-34.6(8)
C(11)-C(10)-C(12)-C(17)	143.0(5)
C(9)-C(10)-C(12)-C(13)	140.8(5)
C(11)-C(10)-C(12)-C(13)	-41.5(7)
C(1)-O(1)-C(2)-C(3)	-179.4(6)
C(1)-O(1)-C(2)-C(7)	2.2(8)
O(1)-C(2)-C(3)-C(4)	-179.6(5)
C(7)-C(2)-C(3)-C(4)	-1.2(8)
C(2)-C(3)-C(4)-C(5)	0.7(8)
C(6)-C(5)-C(4)-C(3)	-0.4(8)
C(8)-C(5)-C(4)-C(3)	179.5(5)
C(4)-C(5)-C(6)-C(7)	0.5(8)
C(8)-C(5)-C(6)-C(7)	-179.4(5)
C(17)-C(12)-C(13)-C(14)	-3.2(8)
C(10)-C(12)-C(13)-C(14)	-178.6(5)
C(13)-C(12)-C(17)-C(16)	3.6(8)
C(10)-C(12)-C(17)-C(16)	179.2(5)
C(5)-C(6)-C(7)-C(2)	-1.0(9)
O(1)-C(2)-C(7)-C(6)	179.6(5)
C(3)-C(2)-C(7)-C(6)	1.3(8)



C(8)-N(1)-B(1)-F(1)	-59.0(5)
C(11)-N(1)-B(1)-F(1)	119.5(4)
C(8)-N(1)-B(1)-F(1)#1	63.8(5)
C(11)-N(1)-B(1)-F(1)#1	-117.7(4)
C(8)-N(1)-B(1)-N(1)#1	-177.8(4)
C(11)-N(1)-B(1)-N(1)#1	0.7(3)
F(2)-C(15)-C(16)-C(17)	172.1(7)
C(14)-C(15)-C(16)-C(17)	-3.1(10)
C(12)-C(17)-C(16)-C(15)	-0.6(9)
C(12)-C(13)-C(14)-C(15)	-0.2(8)
F(2)-C(15)-C(14)-C(13)	-171.5(8)
C(16)-C(15)-C(14)-C(13)	3.4(10)

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Symmetry transformations used to generate equivalent atoms:

#1  $-x+1, -y+1/2, z+0$

**4. Ground state geometries in gas phase (M062X/6-311+G(2d,p))****Compound 3** E= -1819.96788515 a.u.

5	-2.0188870	0.0138560	0.3350060
9	-3.0272740	0.0012940	-0.5961060
9	-2.5129360	0.0474810	1.6404940
7	-1.0960220	-1.2445260	0.1814100
6	0.2921760	-1.1519410	0.2082710
7	0.9587420	-0.0164310	0.1877800
6	0.3141300	1.1296400	0.1231910
7	-1.0732940	1.2479980	0.1240010
6	-1.4122420	-2.5482270	0.0326460
6	-0.2245080	-3.3207940	-0.0368340
6	0.8550800	-2.4661510	0.0929870
6	-1.3685150	2.5540520	-0.0447040
6	-0.1679310	3.3023500	-0.1490980
6	0.8988090	2.4297490	-0.0378740
6	2.2809550	-2.7960780	0.0727170
6	2.7155920	-3.9553720	-0.5873310
1	1.9928900	-4.5834250	-1.0990190
6	4.0601840	-4.2989880	-0.6222400
1	4.4100290	-5.1879280	-1.1347680
6	4.9720160	-3.4661390	0.0107130
6	4.5830720	-2.3120230	0.6749250
1	5.3303210	-1.6962980	1.1631050
6	3.2337860	-1.9825340	0.7069900
1	2.9134640	-1.0898400	1.2313400
6	2.3286280	2.7507620	-0.0571120
6	3.2955780	1.8170870	-0.4643660
1	2.9875520	0.8267220	-0.7775630
6	4.6442640	2.1506470	-0.4747810
1	5.4015070	1.4413710	-0.7902960
6	5.0203160	3.4260920	-0.0804410
6	4.0950040	4.3777020	0.3237250
1	4.4337530	5.3607660	0.6305750
6	2.7507290	4.0310130	0.3327110
1	2.0179190	4.7575270	0.6699120
6	-2.7698250	-3.0990940	-0.0335910
6	-2.9885080	-4.2258970	-0.8405540
6	-4.2485860	-4.8060200	-0.9151610
1	-4.4074570	-5.6692630	-1.5533020
6	-5.3039470	-4.2761640	-0.1747830
6	-5.0912000	-3.1640110	0.6377100

1	-5.9081720	-2.7550160	1.2234600
6	-3.8347450	-2.5740630	0.7112450
1	-3.6713140	-1.7222550	1.3599050
6	-2.7165050	3.1278230	-0.1253640
6	-2.9140810	4.2366160	-0.9625800
6	-4.1631740	4.8375490	-1.0546580
1	-4.3052180	5.6858690	-1.7163550
6	-5.2291240	4.3473350	-0.3022430
6	-5.0374720	3.2537180	0.5398660
1	-5.8623730	2.8751300	1.1349020
6	-3.7920930	2.6428740	0.6312440
1	-3.6460660	1.8058900	1.3025780
1	-2.0896060	4.6089000	-1.5630850
1	-2.1709050	-4.6289810	-1.4305910
1	-0.1258300	4.3736710	-0.2877690
1	-0.2011370	-4.3993820	-0.1079480
9	6.3217680	3.7514770	-0.0896120
1	-6.2884870	-4.7298990	-0.2294940
1	-6.2050900	4.8174110	-0.3708510
9	6.2734970	-3.7889890	-0.0207170

**Compound 4 E= -2049.00336427 a.u.**

5	-1.3053530	0.0084970	0.4414670
9	-2.3325010	-0.0000150	-0.4713860
9	-1.7812100	0.0373940	1.7554680
7	-0.3893860	-1.2500670	0.2669160
6	0.9990330	-1.1578480	0.2497870
7	1.6662870	-0.0229310	0.2131600
6	1.0201350	1.1236980	0.1749680
7	-0.3664650	1.2435030	0.2191270
6	-0.7132420	-2.5547170	0.1256580
6	0.4741620	-3.3258650	0.0169240
6	1.5566540	-2.4716160	0.1126310
6	-0.6678160	2.5522150	0.0674590
6	0.5326270	3.2983160	-0.0687700
6	1.6002680	2.4239010	0.0036240
6	2.9815560	-2.8020070	0.0459330
6	3.3952810	-3.9585820	-0.6318780
1	2.6566430	-4.5847320	-1.1228110
6	4.7382340	-4.3021580	-0.7106500
1	5.0715080	-5.1892070	-1.2373730
6	5.6698110	-3.4717240	-0.1040610
6	5.3020510	-2.3201960	0.5762910

1	6.0644150	-1.7058620	1.0424310
6	3.9543090	-1.9910290	0.6524690
1	3.6505290	-1.0997820	1.1889790
6	3.0298350	2.7436710	-0.0558640
6	3.9824480	1.8126350	-0.5008980
1	3.6630810	0.8251800	-0.8119710
6	5.3308660	2.1444620	-0.5500600
1	6.0768490	1.4367620	-0.8946780
6	5.7211000	3.4157980	-0.1565660
6	4.8102310	4.3647280	0.2845130
1	5.1597840	5.3445850	0.5896100
6	3.4661770	4.0195240	0.3322410
1	2.7453460	4.7438650	0.6987430
6	-2.0668750	-3.1052050	0.0991910
6	-2.3045050	-4.2559290	-0.6626050
6	-3.5601100	-4.8493440	-0.7143680
1	-3.7082890	-5.7293400	-1.3281250
6	-4.6100100	-4.2935090	0.0228290
6	-4.3832220	-3.1491560	0.8005810
1	-5.2096250	-2.7442820	1.3749400
6	-3.1337550	-2.5618650	0.8378810
1	-2.9716460	-1.6919520	1.4619440
8	-5.8678130	-4.7872380	0.0518850
6	-6.1393700	-5.9469900	-0.7154620
1	-5.9643120	-5.7641040	-1.7811800
1	-5.5254480	-6.7913850	-0.3836780
1	-7.1917690	-6.1752600	-0.5529840
6	-2.0114450	3.1278000	0.0296300
6	-2.2259380	4.2682360	-0.7545960
6	-3.4698820	4.8842870	-0.8209850
1	-3.5996860	5.7548220	-1.4521720
6	-4.5320500	4.3627580	-0.0764090
6	-4.3285850	3.2295290	0.7234750
1	-5.1638300	2.8510090	1.3030330
6	-3.0905360	2.6193490	0.7753940
1	-2.9475130	1.7585960	1.4162160
8	-5.7804540	4.8804440	-0.0606460
6	-6.0284970	6.0290820	-0.8522860
1	-5.8533440	5.8214760	-1.9134500
1	-5.4004630	6.8688710	-0.5355670
1	-7.0770960	6.2795890	-0.6982200
1	-1.4123440	4.6691380	-1.3514590
1	-1.4991350	-4.6835160	-1.2521910
1	0.5744830	4.3707730	-0.1982660

1	0.4974810	-4.4044660	-0.0533070
9	7.0226010	3.7395990	-0.2030500
9	6.9700640	-3.7943040	-0.1783930

**Compound 5 E= -1720.72334179 a.u.**

5	-1.7906740	0.3791090	0.3377880
9	-2.7614470	0.6732920	-0.5869760
9	-2.2695680	0.4758930	1.6459610
7	-1.2218180	-1.0660150	0.1174950
6	0.1447270	-1.3346570	0.1180150
7	1.0795610	-0.4102030	0.1838640
6	0.7511150	0.8650830	0.2054450
7	-0.5583690	1.3357570	0.1828330
6	-1.8653500	-2.2394210	-0.0550650
6	-0.9171720	-3.2897250	-0.1592480
6	0.3483750	-2.7456120	-0.0439660
6	-0.5048250	2.6764920	0.0370110
6	0.8488920	3.0930430	-0.0352470
6	1.6529910	1.9743660	0.0895370
6	1.6341800	-3.4508080	-0.0592210
6	1.6859120	-4.7902490	0.3543350
1	0.7804270	-5.2756660	0.7066290
6	2.8868110	-5.4893040	0.3468610
1	2.9100180	-6.5231650	0.6765460
6	4.0581700	-4.8612980	-0.0737660
6	4.0178760	-3.5314720	-0.4883610
1	4.9251250	-3.0377400	-0.8229560
6	2.8178560	-2.8283890	-0.4852290
1	2.7912220	-1.7972320	-0.8175590
6	3.1148210	1.9021420	0.0635860
6	3.8115110	0.8493240	0.6786570
1	3.2614940	0.0687790	1.1909240
6	5.1993440	0.7982850	0.6407710
1	5.7514050	-0.0063330	1.1136390
6	5.8865280	1.8125610	-0.0096880
6	5.2347730	2.8728060	-0.6234690
1	5.8123520	3.6404250	-1.1259260
6	3.8475960	2.9089920	-0.5830390
1	3.3227700	3.7190440	-1.0799930
6	-3.3191810	-2.4184810	-0.1389590
6	-3.8136130	-3.4264920	-0.9807900
6	-5.1799420	-3.6589920	-1.0760200
1	-5.5494230	-4.4327490	-1.7411870

6	-6.0704500	-2.8968420	-0.3219010
6	-5.5857820	-1.9022450	0.5253090
1	-6.2750310	-1.3134750	1.1220700
6	-4.2203540	-1.6590670	0.6196330
1	-3.8501330	-0.8985230	1.2957020
6	-1.6594090	3.5790270	-0.0227300
6	-1.5637640	4.7255060	-0.8258720
6	-2.6162380	5.6299450	-0.8919450
1	-2.5346060	6.5061180	-1.5270150
6	-3.7730740	5.4077910	-0.1469450
6	-3.8704140	4.2768450	0.6615960
1	-4.7655180	4.1057890	1.2509610
6	-2.8241070	3.3640960	0.7267130
1	-2.8982050	2.4977190	1.3724470
1	-0.6695720	4.8907250	-1.4194080
1	-3.1227500	-4.0097440	-1.5819810
1	1.1670900	4.1238980	-0.1052250
1	-1.1707670	-4.3310890	-0.3005900
9	7.2267230	1.7676650	-0.0473140
1	4.9969850	-5.4061470	-0.0783910
1	-7.1381420	-3.0790170	-0.3929190
1	-4.5951740	6.1149240	-0.1951140

**Compound 6** E= -1949.75869866 a.u.

5	-1.1062760	0.1520520	0.4435550
9	-2.1100610	0.4046320	-0.4604470
9	-1.5667080	0.2295880	1.7613570
7	-0.4839410	-1.2669410	0.2112740
6	0.8923930	-1.4759130	0.1660760
7	1.7886700	-0.5122390	0.2028400
6	1.4053200	0.7476600	0.2405760
7	0.0769190	1.1614490	0.2642420
6	-1.0843960	-2.4675360	0.0571510
6	-0.0926320	-3.4748260	-0.0800820
6	1.1505250	-2.8764080	-0.0059380
6	0.0653160	2.5058910	0.1258360
6	1.3988360	2.9789550	0.0118530
6	2.2531120	1.8953630	0.1010280
6	2.4645380	-3.5264100	-0.0636940
6	2.5861030	-4.8639480	0.3411950
1	1.7135170	-5.3884390	0.7194730
6	3.8142880	-5.5122570	0.2919540
1	3.8909000	-6.5455930	0.6153460

6	4.9445190	-4.8343320	-0.1621090
6	4.8351680	-3.5056370	-0.5676880
1	5.7099040	-2.9726410	-0.9277710
6	3.6073570	-2.8534570	-0.5229790
1	3.5270960	-1.8226180	-0.8476250
6	3.7155350	1.8874450	0.0263510
6	4.4785250	0.8653430	0.6137200
1	3.9806660	0.0592130	1.1396060
6	5.8654470	0.8766620	0.5302940
1	6.4680300	0.0960590	0.9813250
6	6.4851050	1.9224320	-0.1377440
6	5.7667880	2.9536320	-0.7257970
1	6.2926860	3.7476540	-1.2437910
6	4.3813200	2.9271320	-0.6401700
1	3.8045220	3.7136420	-1.1169280
6	-2.5258570	-2.7097760	0.0181850
6	-3.0034420	-3.7646880	-0.7696280
6	-4.3578740	-4.0685590	-0.8379560
1	-4.6895350	-4.8817200	-1.4718630
6	-5.2668930	-3.3128100	-0.0916490
6	-4.8015190	-2.2630710	0.7127350
1	-5.5239450	-1.6997470	1.2937080
6	-3.4542910	-1.9634240	0.7664710
1	-3.1116400	-1.1636450	1.4106550
8	-6.6025290	-3.5198850	-0.0779590
6	-7.1153230	-4.5715770	-0.8769880
1	-6.8940700	-4.4048350	-1.9367270
1	-6.7055110	-5.5386460	-0.5658660
1	-8.1936680	-4.5666010	-0.7246000
6	-1.1234900	3.3562280	0.1071450
6	-1.0920770	4.5311350	-0.6539180
6	-2.1750480	5.4012340	-0.6963880
1	-2.1182890	6.2921530	-1.3096690
6	-3.3198170	5.1050070	0.0494530
6	-3.3603040	3.9384390	0.8261360
1	-4.2538820	3.7368750	1.4071730
6	-2.2819750	3.0758910	0.8542680
1	-2.3222880	2.1913790	1.4775890
8	-4.4275710	5.8786390	0.0883350
6	-4.4261420	7.0719140	-0.6755470
1	-4.3069780	6.8563910	-1.7428380
1	-3.6292040	7.7483000	-0.3479010
1	-5.3946380	7.5396080	-0.5042030
1	-0.2137760	4.7596020	-1.2500760

1	-2.3073300	-4.3449030	-1.3676060
1	1.6725690	4.0226140	-0.0573450
1	-0.3030730	-4.5270750	-0.2113840
9	7.8244550	1.9381850	-0.2188570
1	5.9047190	-5.3392380	-0.1993650

**Compound 8 E= -1850.51390976 a.u.**

5	-0.9147740	0.0099800	0.4371810
9	-1.9478460	0.0046140	-0.4693430
9	-1.3832000	0.0405250	1.7540870
7	-0.0040940	-1.2512460	0.2572740
6	1.3848300	-1.1637900	0.2312380
7	2.0549010	-0.0306410	0.1917220
6	1.4125390	1.1181170	0.1577440
7	0.0262220	1.2419120	0.2092020
6	-0.3333710	-2.5546730	0.1183510
6	0.8506060	-3.3296070	0.0013730
6	1.9370890	-2.4794690	0.0893910
6	-0.2721840	2.5513040	0.0587780
6	0.9296930	3.2939000	-0.0831980
6	1.9955670	2.4168930	-0.0158560
6	3.3607050	-2.8185460	0.0127550
6	3.7604980	-3.9789610	-0.6661280
1	3.0114890	-4.5987380	-1.1504680
6	5.1037850	-4.3251620	-0.7486940
1	5.3965890	-5.2238420	-1.2824430
6	6.0718720	-3.5153750	-0.1563730
6	5.6859550	-2.3602870	0.5212120
1	6.4339820	-1.7281980	0.9898440
6	4.3420860	-2.0130740	0.6109350
1	4.0460350	-1.1186390	1.1470030
6	3.4261450	2.7357700	-0.0833530
6	4.3744810	1.8057340	-0.5371680
1	4.0511250	0.8192550	-0.8481900
6	5.7217670	2.1472930	-0.5917110
1	6.4430910	1.4174200	-0.9465390
6	6.1454450	3.4163510	-0.2021970
6	5.2105930	4.3481500	0.2462790
1	5.5318330	5.3372170	0.5574400
6	3.8638900	4.0104810	0.3057240
1	3.1428130	4.7315670	0.6795310
6	-1.6893150	-3.1004320	0.1001900
6	-1.9359200	-4.2494130	-0.6612580
6	-3.1939400	-4.8385340	-0.7054530



1	-3.3490410	-5.7173970	-1.3191450
6	-4.2370710	-4.2799460	0.0390850
6	-4.0012840	-3.1372720	0.8165020
1	-4.8225560	-2.7300580	1.3965610
6	-2.7495010	-2.5543100	0.8463100
1	-2.5802980	-1.6854150	1.4699290
8	-5.4966050	-4.7694730	0.0757600
6	-5.7769740	-5.9269120	-0.6917040
1	-5.6082290	-5.7428730	-1.7582680
1	-5.1637580	-6.7739890	-0.3654400
1	-6.8290660	-6.1520330	-0.5228230
6	-1.6145510	3.1306930	0.0279670
6	-1.8300960	4.2711960	-0.7557510
6	-3.0726670	4.8908510	-0.8157040
1	-3.2033290	5.7614900	-1.4465840
6	-4.1322300	4.3727820	-0.0651470
6	-3.9276220	3.2395700	0.7343640
1	-4.7607900	2.8637240	1.3186580
6	-2.6909700	2.6259160	0.7799860
1	-2.5468250	1.7651240	1.4205270
8	-5.3793070	4.8940410	-0.0430490
6	-5.6282660	6.0423770	-0.8346530
1	-5.4592650	5.8331430	-1.8965190
1	-4.9962500	6.8808340	-0.5223020
1	-6.6753450	6.2960690	-0.6754170
1	-1.0184760	4.6694160	-1.3570830
1	-1.1357890	-4.6790990	-1.2564290
1	0.9744190	4.3662190	-0.2127350
1	0.8700870	-4.4081830	-0.0700000
1	7.1978960	3.6784880	-0.2471800
1	7.1215240	-3.7840830	-0.2226090

**Compound 9 E= -2177.67866629 a.u.**

5	-1.8822680	0.0262760	0.4515520
9	-2.9023820	0.0057230	-0.4690720
9	-2.3691160	0.0850420	1.7607230
7	-0.9738150	-1.2414000	0.3101760
6	0.4150280	-1.1594760	0.3076780
7	1.0907110	-0.0300580	0.2550570
6	0.4529420	1.1199680	0.1854110
7	-0.9329920	1.2497030	0.2120730
6	-1.3060250	-2.5464590	0.1896960
6	-0.1241720	-3.3280760	0.1096470

6	0.9645660	-2.4801190	0.2025840
6	-1.2241330	2.5573950	0.0301860
6	-0.0183020	3.2926440	-0.1079120
6	1.0437850	2.4130370	-0.0060030
6	2.3856250	-2.8230130	0.1614040
6	2.7997190	-4.0043510	-0.4706160
1	2.0628280	-4.6437770	-0.9472150
6	4.1387400	-4.3608590	-0.5257180
1	4.4339730	-5.2780210	-1.0273110
6	5.0983030	-3.5278140	0.0574070
6	4.7049070	-2.3481380	0.6934860
1	5.4625010	-1.7185210	1.1479820
6	3.3639710	-2.0026380	0.7479260
1	3.0665440	-1.0907430	1.2524410
6	2.4739370	2.7235720	-0.0566800
6	3.4343280	1.7752690	-0.4479660
1	3.1198520	0.7763910	-0.7257900
6	4.7801370	2.1039430	-0.4873030
1	5.5228640	1.3741380	-0.7921460
6	5.1983030	3.3905920	-0.1411700
6	4.2575250	4.3492770	0.2459980
1	4.5709680	5.3515390	0.5238560
6	2.9132410	4.0109010	0.2852910
1	2.1922390	4.7545300	0.6109550
6	-2.6638250	-3.0865180	0.1577090
6	-2.9027000	-4.2486540	-0.5860130
6	-4.1625610	-4.8328040	-0.6407680
1	-4.3114850	-5.7222350	-1.2405880
6	-5.2155810	-4.2555720	0.0751400
6	-4.9877890	-3.0992060	0.8346130
1	-5.8169520	-2.6774120	1.3925680
6	-3.7339960	-2.5213650	0.8748660
1	-3.5712280	-1.6414670	1.4846490
8	-6.4776170	-4.7388850	0.0996480
6	-6.7499290	-5.9107370	-0.6487600
1	-6.5624650	-5.7491460	-1.7158000
1	-6.1458140	-6.7532590	-0.2948780
1	-7.8056480	-6.1282390	-0.4931570
6	-2.5637530	3.1403000	-0.0337170
6	-2.7633670	4.2655910	-0.8432690
6	-4.0025910	4.8880930	-0.9341960
1	-4.1207080	5.7462500	-1.5843700
6	-5.0751710	4.3887150	-0.1893790
6	-4.8867520	3.2708130	0.6353360

1	-5.7299630	2.9095540	1.2143750
6	-3.6532040	2.6541010	0.7117790
1	-3.5219410	1.8058440	1.3715030
8	-6.3202920	4.9146260	-0.1960540
6	-6.5529220	6.0492910	-1.0120750
1	-6.3691260	5.8200590	-2.0673010
1	-5.9221970	6.8908800	-0.7056140
1	-7.6012030	6.3097440	-0.8730090
1	-1.9414840	4.6490030	-1.4402800
1	-2.0945790	-4.6930660	-1.1591610
1	0.0313260	4.3619040	-0.2589490
1	-0.1087220	-4.4079460	0.0606120
7	6.5935850	3.6323920	-0.2118740
7	6.4898880	-3.7977810	0.0533500
7	6.8433560	-4.8430990	-0.5062600
7	6.9676950	4.7722210	0.0903550
7	7.2731860	-5.7673270	-0.9890610
7	7.4153580	5.7758610	0.3444120

**Compound 10 E= -2005.11678847 a.u.**

5	-1.3069270	0.0239550	0.4386450
9	-2.3368660	0.0427130	-0.4725540
9	-1.7841970	0.0596430	1.7536190
7	-0.4192180	-1.2501210	0.2594150
6	0.9684350	-1.1885520	0.2454300
7	1.6628550	-0.0616120	0.2115640
6	1.0439340	1.0930360	0.1767420
7	-0.3432010	1.2399330	0.2217540
6	-0.7725080	-2.5501500	0.1177850
6	0.3948660	-3.3429610	0.0117670
6	1.4974020	-2.5077260	0.1087080
6	-0.6160250	2.5549600	0.0774330
6	0.5960890	3.2806560	-0.0540940
6	1.6524970	2.3904140	0.0126590
6	2.9154530	-2.8694820	0.0455720
6	3.3086570	-4.0272790	-0.6419020
1	2.5591740	-4.6321040	-1.1431610
6	4.6446390	-4.3994580	-0.7165660
1	4.9614020	-5.2883760	-1.2504220
6	5.5905300	-3.5961490	-0.0964270
6	5.2435330	-2.4445760	0.5944250
1	6.0157900	-1.8520600	1.0725330
6	3.9024670	-2.0876390	0.6669970

1	3.6145140	-1.1967540	1.2129850
6	3.0790360	2.6888110	-0.0470350
6	4.0420150	1.7283940	-0.4053240
1	3.7261360	0.7213360	-0.6514400
6	5.3872840	2.0503070	-0.4622080
1	6.1122560	1.2923780	-0.7476540
6	5.8306050	3.3495060	-0.1630030
6	4.8738180	4.3151580	0.1948540
1	5.1984750	5.3222890	0.4410640
6	3.5315130	3.9864150	0.2471830
1	2.8161620	4.7471190	0.5464150
6	-2.1409570	-3.0685450	0.0893980
6	-2.4100500	-4.2026830	-0.6855170
6	-3.6791530	-4.7687040	-0.7349050
1	-3.8505220	-5.6377230	-1.3583570
6	-4.7114170	-4.1995830	0.0158930
6	-4.4540670	-3.0700770	0.8047700
1	-5.2675610	-2.6530310	1.3889240
6	-3.1906780	-2.5117070	0.8414260
1	-3.0052080	-1.6521770	1.4734850
8	-5.9811500	-4.6665750	0.0479160
6	-6.2812080	-5.8103210	-0.7314680
1	-6.1095910	-5.6183540	-1.7962980
1	-5.6825150	-6.6715450	-0.4149750
1	-7.3370080	-6.0197180	-0.5648980
6	-1.9482110	3.1568410	0.0393460
6	-2.1380420	4.3051590	-0.7397520
6	-3.3697290	4.9451420	-0.8073930
1	-3.4808570	5.8208800	-1.4349380
6	-4.4439100	4.4406320	-0.0683080
6	-4.2648020	3.3001180	0.7270490
1	-5.1090170	2.9351400	1.3022620
6	-3.0391750	2.6654580	0.7792670
1	-2.9146880	1.7987090	1.4157710
8	-5.6821980	4.9820780	-0.0540960
6	-5.9061710	6.1377540	-0.8425910
1	-5.7314970	5.9304280	-1.9038920
1	-5.2636150	6.9646320	-0.5210750
1	-6.9504050	6.4073120	-0.6910050
1	-1.3149020	4.6929650	-1.3320530
1	-1.6178200	-4.6399240	-1.2859160
1	0.6524410	4.3530230	-0.1762190
1	0.3979290	-4.4220130	-0.0577070
9	6.8848790	-3.9462800	-0.1669760

7	7.1785570	3.6573280	-0.1630720
1	7.4072440	4.6361280	-0.2795330
1	7.7677710	3.0552490	-0.7233960

ACCEPTED MANUSCRIPT

- Aymmetric/asymmetric fluorine-containing aza-BODIPYs at 1/7-positions were prepared.
- The effect of the withdrawing -F group at 1/7-position on the photophysical properties is found to be almost negligible.
- The replacement of -F atoms with -N<sub>3</sub>/ $\text{-NH}_2$  groups resulted in a remarkable bathochromic shift.
- Aza-BODIPY with a -NH<sub>2</sub> group could be used as a turn-on fluorescent probe for pH value.