

Supporting Information for

NIR-Absorbing and Emitting α,α -Nitrogen-Bridged BODIPY Dimers with Strong Excitonic Coupling

Long Wang,^a Cheng Cheng,^a Changjiang Yu,^{a,} Qinghua Wu,^b Zhengxin Kang,^a Hua Wang,^{a,*} Lijuan Jiao,^a and
Erhong Hao^{a,*}*

^aAnhui Laboratory of Molecule-Based Materials; The Key Laboratory of Functional Molecular Solids, Ministry of Education; School of Chemistry and Materials Science, Anhui Normal University, Wuhu 241002, China.

^bSchool of Pharmacy, Anhui University of Chinese Medicine, Hefei, 230012, China.

*E-mail: yuchj@ahnu.edu.cn, huaw2011@ahnu.edu.cn, haoehong@ahnu.edu.cn

Table of Contents

1. General information	S2
2. Synthesis and characterization.....	S4
3. Crystal data.....	S10
4. Photophysical data.....	S12
5. Reactive oxygen species properties	S14
6. Electrochemical data.....	S16
7. DFT calculation.....	S17
8. ¹ H, ¹³ C, ¹¹ B and ¹⁹ F NMR spectra of all new compounds.....	S30
9. HRMS spectra of all new compounds.....	S44
10. Author contribution statement.....	S45
11. References.....	S45

1. General information

Reagents and solvents were used as received from commercial suppliers (Energy Chemicals) unless noted otherwise. All reactions were performed in oven-dried or flame-dried glassware unless stated otherwise and were monitored by TLC using 0.25 mm silica gel plates with UV indicator (60F-254). Heating mantle was used for all the reaction that required heating. ^1H and ^{13}C spectra were recorded on a 400 or 500 MHz NMR spectrometer at room temperature. Chemical shifts (δ) are given in ppm relative to CDCl_3 (7.26 ppm for ^1H and 77.0 ppm for ^{13}C). Data for ^1H NMR and ^{13}C NMR are reported as follows: multiplicity (s = singlet, d = doublet, m = multiplet), coupling constant (Hz) and integration. High-resolution mass spectra (HRMS) were obtained using APCI-TOF, ESI-TOF or MALDI-TOF in positive mode.

Absorption and emission measurements. UV-visible absorption and fluorescence emission spectra were recorded on commercial spectrophotometers (Shimadzu UV-2450 and Edinburgh FS5 spectrometers). All measurements were made at 25 °C, using 5×10 mm cuvettes. Non-degassed, spectroscopic grade solvents and a 10 mm quartz cuvette were used. Relative fluorescence quantum efficiencies of BODIPY derivatives were obtained by comparing the areas under the corrected emission spectrum of the test sample in various organic solvents with Indocyanine Green ($\Phi = 0.12$ in DMSO).¹ Non-degassed, spectroscopic grade solvents and a 10 mm quartz cuvette were used. Dilute solutions ($0.01 < A < 0.05$) were used to minimize the reabsorption effects. Quantum yields were determined using the following equation:²

$$\Phi_X = \Phi_S (I_X/I_S) (A_S/A_X) (n_X/n_S)^2$$

Where Φ_S stands for the reported quantum yield of the standard, I stands for the integrated emission spectra, A stands for the absorbance at the excitation wavelength and n stands for the refractive index of the solvent being used. X subscript stands for the test sample, and S subscript stands for the standard.

X-ray structure analysis. Crystal of compound **2a** suitable for X-ray analysis was obtained via the slow diffusion of petroleum ether into their dichloromethane solution. The vial containing this solution was placed, loosely capped, to promote the crystallization. A suitable crystal was chosen and mounted on a glass fiber using grease. Data were collected using a Bruker APEX-II³ CCD diffractometer operating at $T = 293(2)$ K. The determination of unit cell parameters and data collections were performed with Mo $K\alpha$ radiation (λ) at 0.71073 Å. The total number of runs and images was based on

the strategy calculation from the program APEX2 (Bruker).⁴ The structure was solved by the structure solution program Olex2 (Dolomanov et al., 2009),⁵ and the model was refined with version 2014/7 of ShelXL (Sheldrick, 2015)⁶ using full matrix least squares on F² minimization. CCDC-2333069 (**2a**) containing the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Electron paramagnetic resonance (EPR) experiments. CW X-band EPR spectra for radicals were acquired on Bruker EMX instrument.

Singlet oxygen generation efficiency. A comparative study of the relative singlet oxygen generating efficiency of these dyes was performed in air-saturated solvents under light at 660 nm laser irradiation (10 mW/cm²) condition using 1,3-diphenylisobenzofuran (DPBF, 4 × 10⁻⁵ M) as a trap molecule.⁷ A commercial photosensitizer against 1,7-diphenyl-2,6-dibromo-3,5-di(4-methoxyphenyl)-azaBODIPY (azaBDP) (Φ_{Δ} = 0.74 in toluene) was used as reference.^{7c} The absorbance of BODIPY dyes and the reference azaBDP at 660 nm was kept around 0.1. The decrease of the absorbance band of DPBF at 415 nm was monitored. Singlet oxygen quantum yield (Φ_{Δ}) determinations were carried out using the chemical trapping method, and the Φ_{Δ} value was obtained by the relative method using azaBDP as the reference as shown in following equation:

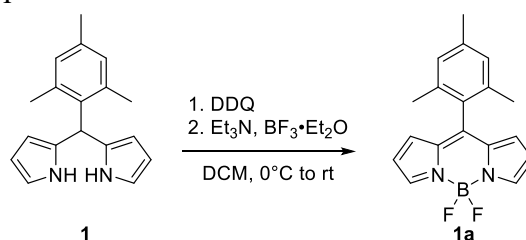
$$\Phi_{\Delta\text{sam}} = \Phi_{\Delta\text{ref}} [(m_{\text{sam}}/m_{\text{ref}})(L_{\text{ref}}/L_{\text{sam}})]$$

Where $\Phi_{\Delta\text{ref}}$ and $\Phi_{\Delta\text{sam}}$ are the singlet oxygen quantum yields for the standard azaBDP and photosensitizer (**2a-c**). m_{sam} and m_{ref} are the slope of the difference ($\Delta\text{O.D.}$) in the change in the absorption maximum wavelength of DPBF (415 nm), which are plotted against the photoirradiation time, L_{ref} and L_{sam} are the light harvesting efficiency, which is given by $L = 1 - 10^{-A}$ (“A” is the absorbance at the laser irradiation wavelength 660 nm).

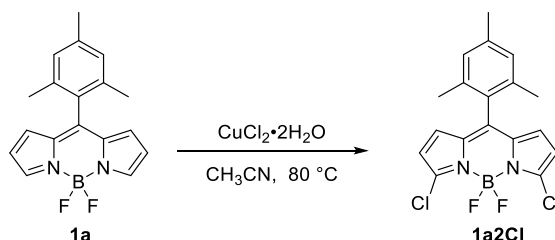
Electrochemical measurements. Cyclic voltammograms and differential pulse voltammograms of 1.0 mM **2a-c** and **1aNH₂** were measured in dichloromethane solution, containing 0.1 M TBAPF₆ as the supporting electrolyte, glassy carbon electrode as a working electrode, Pt wire as a counter electrode, and saturated calomel electrode (SCE) as reference electrode at 100 mV s⁻¹ of scanning rate at room temperature.

2. Synthesis and characterization

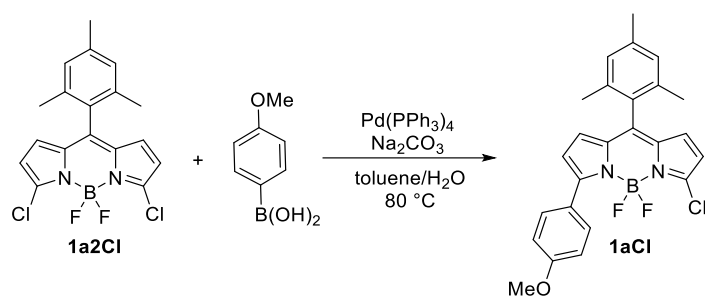
BODIPYs **1**,⁸ **1a2Cl**,⁹ **1aCl**,¹⁰ **1aNH₂**,¹⁰ **2**,⁸ **1b**,¹¹ **1bH**,¹² **1bCl**,¹⁰ **1bNH₂**¹⁰ were synthesized according to the previously reported literatures.



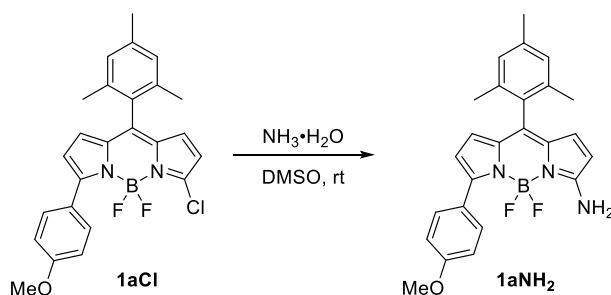
Syntheses of BODIPY **1a**: To a dry round-bottom flask loaded with **1** (462 mg, 1.75 mmol) and DDQ (398 mg, 1.75 mmol) was added CH₂Cl₂ (50 mL). The reaction mixture was stirred at 0 °C for 10 min. After that, triethylamine (4 mL), BF₃·Et₂O (4 mL) were added subsequently. Then the reaction mixture was warmed to room temperature and stirred for additional 2 h. Then the reaction mixture was washed with water, and 0.2 M aqueous solution of NaOH, and water. The organic layer was dried over anhydrous Na₂SO₄, filtered, and evaporated under vacuum. The crude product was purified by column chromatography on silica gel with dichloromethane / petroleum ether (1 : 2) as eluent to give the desired **1a** (201 mg, 37%) as an orange amorphous solid. ¹H NMR (300 MHz, CDCl₃) δ 7.91 (s, 2H), 6.95 (s, 2H), 6.68 (d, *J* = 4.2 Hz, 2H), 6.47 (d, *J* = 4.0 Hz, 2H), 2.36 (s, 3H), 2.10 (s, 6H); ¹¹B NMR (128 MHz, CDCl₃) δ 0.32 (t, *J* = 29.0 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -145.67 (q, *J* = 30.1 Hz).



Synthesis of BODIPY **1a2Cl**: To a dry round-bottom flask loaded with **1a** (62 mg, 0.2 mmol) and CuCl₂·2H₂O (102 mg, 0.6 mmol) was added CH₃CN (5 mL). The reaction mixture was stirred at 80°C for 6 h. After cooling down to room temperature, the reaction mixture was diluted with dichloromethane, and washed twice with water. The organic layer was dried over anhydrous Na₂SO₄, filtered, and evaporated under vacuum. The residue was purified by column chromatography on silica gel with ethyl acetate / petroleum ether (1 : 40) as eluent to give the desired **1a2Cl** (50 mg, 66%). ¹H NMR (300 MHz, CDCl₃) δ 6.95 (s, 2H), 6.61 (d, *J* = 4.2 Hz, 2H), 6.37 (d, *J* = 4.3 Hz, 2H), 2.35 (s, 3H), 2.09 (s, 6H); ¹¹B NMR (128 MHz, CDCl₃) δ 0.51 (t, *J* = 28.0 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -148.60 (q, *J* = 26.3 Hz).



Synthesis of BODIPY **1aCl**: To a dry round-bottom flask loaded with **1a2Cl** (75 mg, 0.2 mmol), 4-methoxyphenylboronic acid (30 mg, 0.2 mmol), Na₂CO₃ (2 mL, 1M, aqueous solution), and Pd (PPh₃)₄ (23 mg, 0.02 mmol) was added toluene (2 mL). The freeze-pump-thaw cycle was carried out three times. After that, the reaction mixture was stirred at 80 °C under an argon atmosphere for 2 h. After cooling to room temperature, the reaction mixture was diluted with dichloromethane, and washed twice with water. The organic layer was dried over anhydrous Na₂SO₄, filtered, and evaporated under vacuum. The residue was purified by column chromatography on silica gel with petroleum ether / dichloromethane (3 : 1) to give the desired **1aCl** (47 mg, 53%). ¹H NMR (500 MHz, CDCl₃) δ 8.00 (d, *J* = 8.5 Hz, 2H), 7.02 (d, *J* = 9.0 Hz, 2H), 6.96 (s, 2H), 6.69 (d, *J* = 4.0 Hz, 1H), 6.65 (d, *J* = 4.0 Hz, 1H), 6.48 (d, *J* = 4.0 Hz, 1H), 6.29 (d, *J* = 4.0 Hz, 1H), 3.88 (s, 3H), 2.36 (s, 3H), 2.14 (s, 6H); ¹¹B NMR (128 MHz, CDCl₃) δ 1.10 (t, *J* = 30.6 Hz); ¹⁹F NMR (376 MHz, CDCl₃) δ -140.99 (q, *J* = 30.1 Hz).

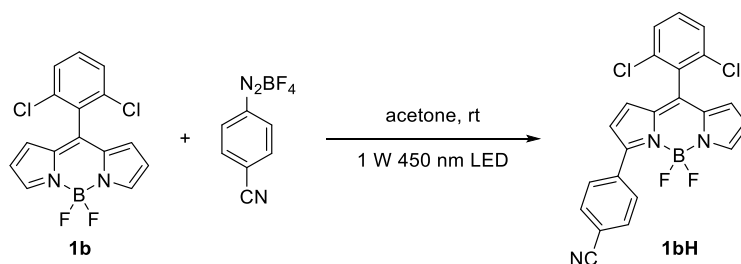


Syntheses of BODIPY **1aNh₂**: To 10 mL DMSO in a reaction tube were added **1aCl** (180 mg, 0.4 mmol) and NH₃·H₂O (2 mL). The reaction mixture was stirred at room temperature for 2 h. Then the reaction mixture was diluted with dichloromethane, and washed twice with water. The organic layer was dried over anhydrous Na₂SO₄, filtered, and evaporated under vacuum. The residue was purified by column chromatography on silica gel with ethyl acetate / petroleum ether (1 : 1) as eluent to give the desired **1aNh₂** (124 mg, 72%) as an orange amorphous solid. ¹H NMR (500 MHz, CDCl₃) δ 7.80 (d, *J* = 8.5 Hz, 2H), 6.97 (d, *J* = 8.5 Hz, 2H), 6.94 (s, 2H), 6.58 (d, *J* = 4.5 Hz, 1H), 6.31 (d, *J* = 3.3

Hz, 1H), 6.21 (d, $J = 3.7$ Hz, 1H), 5.94 (d, $J = 4.2$ Hz, 1H), 5.67 (s, 2H), 3.86 (s, 3H), 2.35 (s, 3H), 2.15 (s, 6H); ^{11}B NMR (128 MHz, CDCl_3) δ 1.50 (t, $J = 34.7$ Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -142.74 (q, $J = 37.6$ Hz).

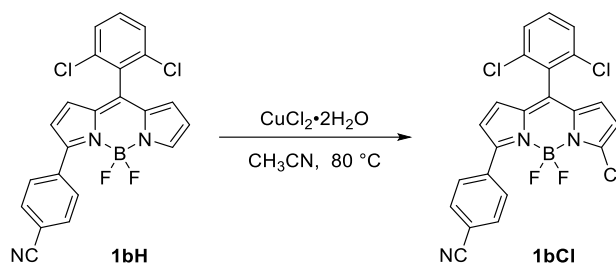


Syntheses of BODIPY **1b**: To a dry round-bottom flask loaded with **2** (580 mg, 2.0 mmol) and DDQ (454 mg, 2.0 mmol) was added CH_2Cl_2 (50 mL). The reaction mixture was stirred at 0 °C for 10 min. After that, triethylamine (4 mL), $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (4 mL) were added subsequently. Then the reaction mixture was warmed to room temperature and stirred for additional 2 h. Then the reaction mixture was washed with water, and 0.2 M aqueous solution of NaOH, and water. The organic layer was dried over anhydrous Na_2SO_4 , filtered, and evaporated under vacuum. The crude product was purified by column chromatography on silica gel with dichloromethane / petroleum ether (1 : 2) as eluent to give the desired **1b** (298 mg, 43%) as an orange amorphous solid. ^1H NMR (300 MHz, CDCl_3): $\delta = 7.95$ (s, 2 H), 7.53 - 7.41 (m, 3 H), 6.71 (d, $J = 3.9$ Hz, 2 H), 6.52 (d, $J = 3.6$ Hz, 2 H); ^{11}B NMR (128 MHz, CDCl_3) δ 0.30 (t, $J = 28.6$ Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -145.45 (q, $J = 57.4, 30.1$ Hz).

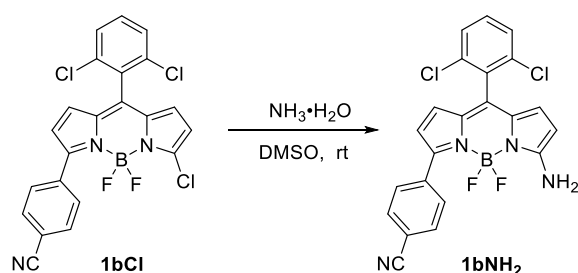


Syntheses of BODIPY **1bH**: To a dry Schlenk tube loaded with **1b** (34mg, 0.1 mmol) and 4-cyanobenzene diazonium tetrafluoroborate (26mg, 0.12 mmol) was add acetone (2.0 mL). The reaction mixture was irradiated with 1 W blue LED at room temperature for 1 h. Then the reaction mixture was diluted with dichloromethane, and washed twice with water. The organic layer was dried over anhydrous Na_2SO_4 , filtered, and evaporated under vacuum. The crude product was purified by column chromatography on silica gel with dichloromethane / petroleum ether (1 : 2) as eluent to give the desired **1bH** (24 mg, 54%) as a red amorphous solid. ^1H NMR (300 MHz, CDCl_3) δ : 8.10 (d, $J = 8.5$

Hz, 2H), 7.95 (s, 1H), 7.79 (d, $J = 8.5$ Hz, 2H), 7.59 - 7.40 (m, 3H), 6.74 (t, $J = 4.5$ Hz, 2H), 6.67 (d, $J = 4.0$ Hz, 1H), 6.56 (d, $J = 3.0$ Hz, 1H); ^{11}B NMR (128 MHz, CDCl_3) δ 0.80 (t, $J = 30.4$ Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -139.25 (q, $J = 30.1$ Hz).

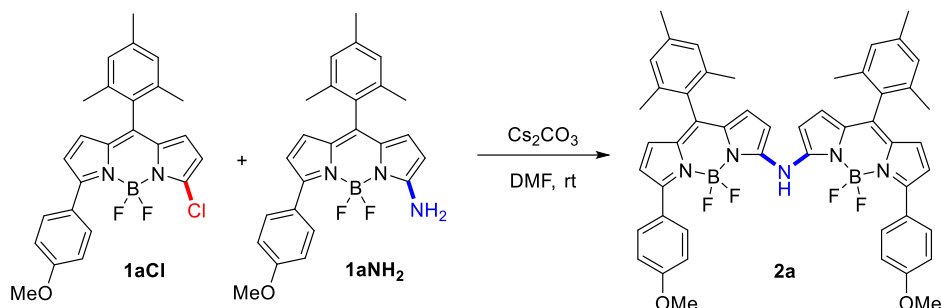


Syntheses of BODIPY **1bCl**: To a dry Schlenk tube loaded with **1bH** (219 mg, 0.5 mmol), and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (512 mg, 3.0 mmol) was added CH_3CN (20 mL). The reaction mixture was stirred at 80°C for 2 h. After cooling down to room temperature, the reaction mixture was diluted with dichloromethane, and washed twice with water. The organic layer was dried over anhydrous Na_2SO_4 , filtered and evaporated under vacuum. The residue was purified by column chromatography on silica gel with dichloromethane / petroleum ether (1 : 2) as eluent to give the desired **1bCl** (168 mg, 71%) as a red amorphous solid. ^1H NMR (400 MHz, CDCl_3) δ 8.07 (d, $J = 8.4$ Hz, 2H), 7.77 (d, $J = 8.4$ Hz, 2H), 7.59 - 7.39 (m, 3H), 6.81 - 6.62 (m, 3H), 6.43 (d, $J = 4.4$ Hz, 1H); ^{11}B NMR (128 MHz, CDCl_3) δ 0.93 (t, $J = 29.9$ Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -140.23 (q, $J = 30.08$ Hz).

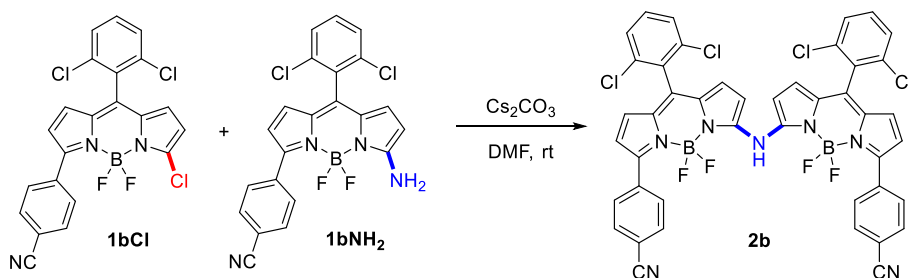


Syntheses of BODIPY **1bNH₂**: To 10 mL DMSO in a reaction tube were added BODIPY **1bCl** (236 mg, 0.5 mmol) and $\text{NH}_3 \cdot \text{H}_2\text{O}$ (2 mL). The reaction mixture was stirred at room temperature for 2 h. Then the reaction mixture was diluted with dichloromethane, and washed twice with water. The organic layer was dried over anhydrous Na_2SO_4 , filtered and evaporated under vacuum. The residue was purified by column chromatography on silica gel with ethyl acetate / petroleum ether (1 : 1) as eluent to give the desired **1bNH₂** (183 mg, 81%) as an orange amorphous solid. ^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, $J = 8.4$ Hz, 2H), 7.67 (d, $J = 8.4$ Hz, 2H), 7.49 - 7.44 (m, 2H), 7.41 - 7.33 (m, 1H),

6.68 (d, $J = 4.8$ Hz, 1H), 6.45 (d, $J = 4.0$ Hz, 1H), 6.21 (d, $J = 4.0$ Hz, 1H), 6.13 (d, $J = 4.8$ Hz, 1H), 6.02 (s, 2H); ^{11}B NMR (128 MHz, CDCl_3) δ 1.44 (t, $J = 34.5$ Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -141.67 (q, $J = 33.8$ Hz).

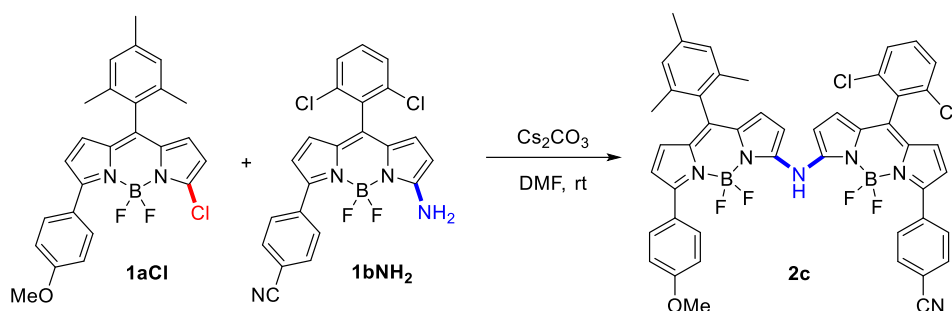


Synthesis of BODIPY **2a**: To a dry Schlenk tube loaded with **1aCl** (225 mg, 0.5 mmol), **1aNh₂** (237 mg, 0.55 mmol) and Cs_2CO_3 (325 mg, 1.0 mmol) was added DMF (5 mL). The reaction mixture was stirred at room temperature for 1 h. Then the reaction mixture was diluted with dichloromethane, washed twice with water. The organic layer was dried over anhydrous Na_2SO_4 , filtered, and evaporated under vacuum. The residue was purified by column chromatography on silica gel with dichloromethane / petroleum ether (1 : 1) as eluent to give the desired **2a** (245 mg, 58%) as a green amorphous solid. ^1H NMR (400 MHz, CDCl_3) δ 9.46 (s, 1H), 7.93 (d, $J = 9.2$ Hz, 4H), 7.00 - 6.94 (m, 8H), 6.61 (d, $J = 4.4$ Hz, 2H), 6.51 (d, $J = 4.0$ Hz, 2H), 6.47 (d, $J = 4.4$ Hz, 2H), 6.40 (d, $J = 4.8$ Hz, 2H), 3.86 (s, 6H), 2.36 (s, 6H), 2.15 (s, 12H); ^{13}C NMR (125 MHz, CDCl_3) δ 160.5, 155.2, 150.8, 138.6, 138.4, 137.2, 136.1, 131.7, 131.0, 130.7, 130.1, 128.2, 127.0, 125.4, 118.6, 113.9, 109.9, 55.4, 21.2, 20.1; HRMS (APCI) calcd for $\text{C}_{50}\text{H}_{46}\text{B}_2\text{F}_4\text{N}_5\text{O}_2$ $[\text{M}+\text{H}]^+$: 846.3774, found 846.3775; ^{11}B NMR (128 MHz, CDCl_3) δ 1.47 (t, $J = 34.0$ Hz); ^{19}F NMR (376 MHz, CDCl_3) δ -141.08 (q, $J = 33.8$ Hz).



Synthesis of BODIPY **2b**: To a dry Schlenk tube loaded with **1bCl** (47 mg, 0.1 mmol), **1bNh₂** (50 mg, 0.11 mmol) and Cs_2CO_3 (65 mg, 0.2 mmol) was added DMF (2 mL). The reaction mixture was stirred at room temperature for 1 h, Then the reaction mixture was diluted with dichloromethane, and washed twice with water. The organic layer was dried over anhydrous Na_2SO_4 , filtered, and evaporated under

vacuum. The residue was purified by column chromatography on silica gel with dichloromethane / petroleum ether (1 : 1.5) as eluent to give the desired **2b** (52 mg, 59%) as a green amorphous solid. **¹H NMR** (400 MHz, CDCl₃) δ 9.57 (s, 1H), 8.02 (d, *J* = 8.0 Hz, 4H), 7.72 (d, *J* = 8.0 Hz, 4H), 7.61 - 7.33 (m, 6H), 6.78 (d, *J* = 4.4 Hz, 2H), 6.60 (d, *J* = 4.0 Hz, 2H), 6.57 - 6.50 (m, 4H); **¹³C NMR** (100 MHz, CDCl₃) δ 152.5, 136.9, 135.9, 134.3, 132.7, 132.6, 132.1, 131.4, 131.2, 129.84, 129.81, 128.4, 126.3, 119.5, 118.9, 112.5, 112.4.; **HRMS** (MALDI-TOF) calcd for C₄₄H₂₃B₂Cl₄F₆N₇ [M]⁺: 889.0857, found 889.0850; **¹¹B NMR** (128 MHz, CDCl₃) δ 1.30 (t, *J* = 33.2 Hz); **¹⁹F NMR** (376 MHz, CDCl₃) δ -140.16 (q, *J* = 33.8 Hz).



Synthesis of BODIPY 2c: To a dry Schlenk tube loaded with **1aCl** (45 mg, 0.1 mmol), **1bNH₂** (50 mg, 0.11 mmol) and Cs₂CO₃ (65 mg, 0.2 mmol) was added DMF (5 mL). The reaction mixture was stirred at room temperature for 1 h. Then the reaction mixture was diluted with dichloromethane, and washed twice with water. The organic layer was dried over anhydrous Na₂SO₄, and evaporated under vacuum. The residue was purified by column chromatography on silica gel with dichloromethane / petroleum ether (1 : 1.5) as eluent to give the desired **2c** (55 mg, 64%) as a green amorphous solid. **¹H NMR** (400 MHz, CDCl₃) δ 9.59 (s, 1H), 8.04 (d, *J* = 8.0 Hz, 2H), 7.95 (d, *J* = 8.0 Hz, 2H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.50 - 7.38 (m, 3H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.96 (s, 2H), 6.76 (d, *J* = 4.8 Hz, 1H), 6.62 - 6.57 (m, 4H), 6.56 (d, *J* = 3.6 Hz, 1H), 6.41 (d, *J* = 4.0 Hz, 1H), 6.36 (d, *J* = 4.4 Hz, 1H), 3.92 (s, 3H), 2.36 (s, 3H), 2.15 (s, 6H); **¹³C NMR** (100 MHz, CDCl₃) δ 161.2, 157.9, 154.5, 149.7, 147.9, 140.4, 138.7, 137.5, 137.0, 136.9, 136.0, 135.3, 133.1, 132.1, 131.7, 131.6, 131.4, 131.2, 131.1, 129.8, 129.6, 129.2, 128.3, 128.2, 124.6, 123.9, 120.1, 119.3, 118.3, 114.0, 113.1, 111.5, 109.2, 55.6, 21.3, 20.1; **HRMS** (ESI) calcd for C₄₇H₃₄B₂Cl₂F₄N₆NaO [M+Na]⁺: 889.2191, found 889.2200; **¹¹B NMR** (128 MHz, CDCl₃) δ 1.38 (t, *J* = 34.0 Hz); **¹⁹F NMR** (376 MHz, CDCl₃) δ -140.28 (q, *J* = 37.6 Hz), -140.88 (q, *J* = 33.8 Hz).

3. Crystal data

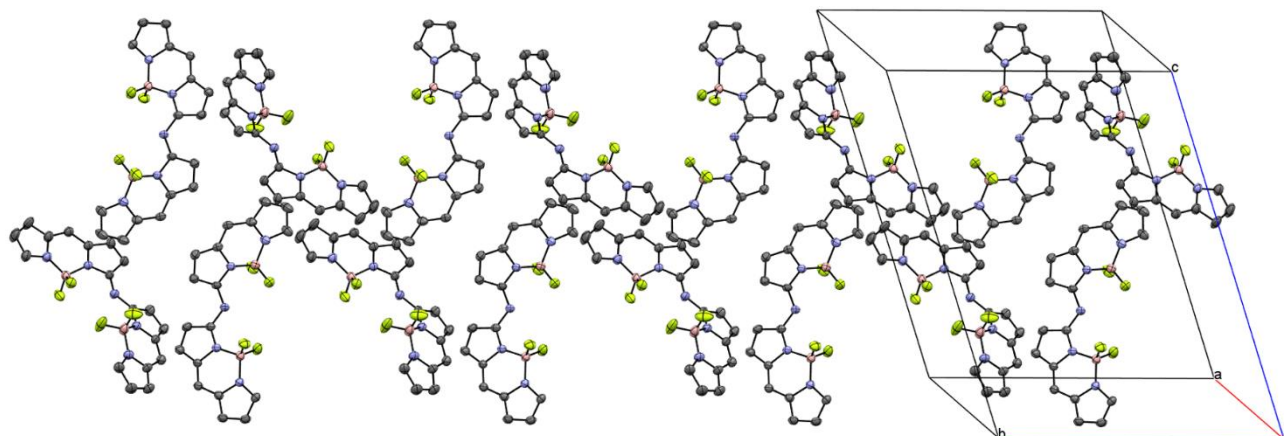
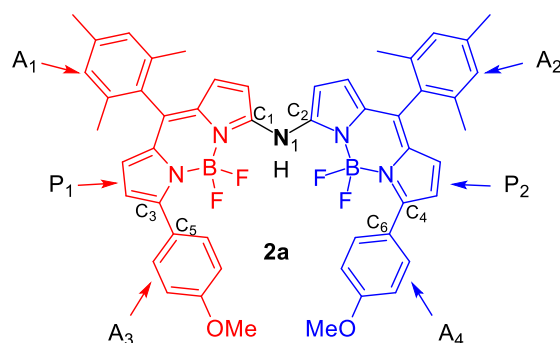


Figure S1. The packing of dimer **2a**. C, black; N, blue; B, yellow; F, green; Cl, dark green. Hydrogen atoms have been removed for clarity, *meso*-aryl and α -aryl substituents were simplified. Thermal ellipsoids are shown at the 30% probability level.

Table S1. Selected geometrical parameters of compound **2a** obtained from crystallography



	2a
the C1-N1 bond length (Å)	1.38(5)
the C2-N1 bond length (Å)	1.36(2)
the B-F bond length (Å)	1.37(9), 1.39(6)
the B-N bond length (Å)	1.35(4), 1.39(1)
	1.54(0), 1.54(5)
	1.54(0), 1.54(7)
dihedral angles between A ₁ and dipyrrin core P ₁ in (deg)	70.10
dihedral angles between A ₂ and dipyrrin core P ₂ in (deg)	75.04
dihedral angles between A ₃ and dipyrrin core P ₁ in (deg)	39.61
dihedral angles between A ₄ and dipyrrin core P ₂ in (deg)	37.52
dihedral angles of two dipyrrin cores in P ₁ and P ₂ (deg)	45.42

Table S2. Crystal data and structure refinement for **2a**

Crystal data	2a
CCDC	2333069
Empirical formula	C ₅₀ H ₄₅ B ₂ F ₄ N ₅ O ₂
Formula weight	845.53
Temperature/K	293.15
Crystal system	triclinic
Space group	P-1
a/Å	12.9120(16)
b/Å	16.473(2)
c/Å	22.588(3)
α/°	71.340(2)
β/°	83.507(2)
γ/°	79.792(2)
Volume/Å ³	4471.9(10)
Z	4
ρ _{calc} /cm ³	1.256
μ/mm ⁻¹	0.088
F(000)	1768.0
Crystal size/mm ³	0.19 × 0.18 × 0.17
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	1.906 to 49.998
Index ranges	-15 ≤ h ≤ 14, -19 ≤ k ≤ 19, -26 ≤ l ≤ 26
Reflections collected	32603
Independent reflections	15462 [R _{int} = 0.1418, R _{sigma} = 0.1532]
Data/restraints/parameters	15462/17/1139
Goodness-of-fit on F ²	0.966
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0819, wR ₂ = 0.2159
Final R indexes [all data]	R ₁ = 0.1584, wR ₂ = 0.2626
Largest diff. peak/hole / e Å ⁻³	0.52/-0.47

4. Photophysical data

Table S3. Spectroscopic and photophysical properties of BODIPYs **2a-c** in different solvents.

Dyes	Solvent	λ_{abs}^a (nm) ($\lg \varepsilon$) ^b	$\lambda_{\text{em}}^{\text{max}}$ (nm)	Φ_{F}^c	ss ^d (cm ⁻¹)
2a	Hexane	708 (4.92), 512 (5.02)	732	0.26	460
	Toluene	716 (4.95), 518 (5.06)	746	0.17	560
	Dichloromethane	703 (4.92), 510 (5.01)	738	<0.01	680
	Tetrahydrofuran	711 (4.90), 513 (4.97)	742	0.01	590
	Acetonitrile	692 (4.86), 503 (4.97)	735	<0.01	850
2b	Toluene	715 (5.00), 507 (5.02)	746	0.13	580
	Dichloromethane	703 (5.00), 501 (5.06)	743	<0.01	770
	Tetrahydrofuran	712 (4.91), 501 (4.73), 467 (4.69)	747	<0.01	660
	Acetonitrile	690 (4.92), 492 (4.95)	736	<0.01	910
2c	Hexane	711 (4.66), 505 (4.84)	767	<0.01	1030
	Toluene	719 (4.79), 510 (4.88)	782	<0.01	1120
	Dichloromethane	703 (4.73), 503 (4.79)	791	<0.01	1580
	Tetrahydrofuran	718 (4.79), 469 (4.65)	782	<0.01	1120
	Acetonitrile	701 (4.77), 461 (4.66)	804	<0.01	1830

^aMain, lowest-energy absorption band. ^bMolar absorption coefficient. ^cThe fluorescence quantum yields of **2a-c** were calculated using indocyanine Green ($\Phi_{\text{F}} = 0.12$ in DMSO) as the reference. The standard errors are less than 10%. ^dStokes shift.

Absorption and emission spectra of BODIPY 2a-c dimers at different solvents

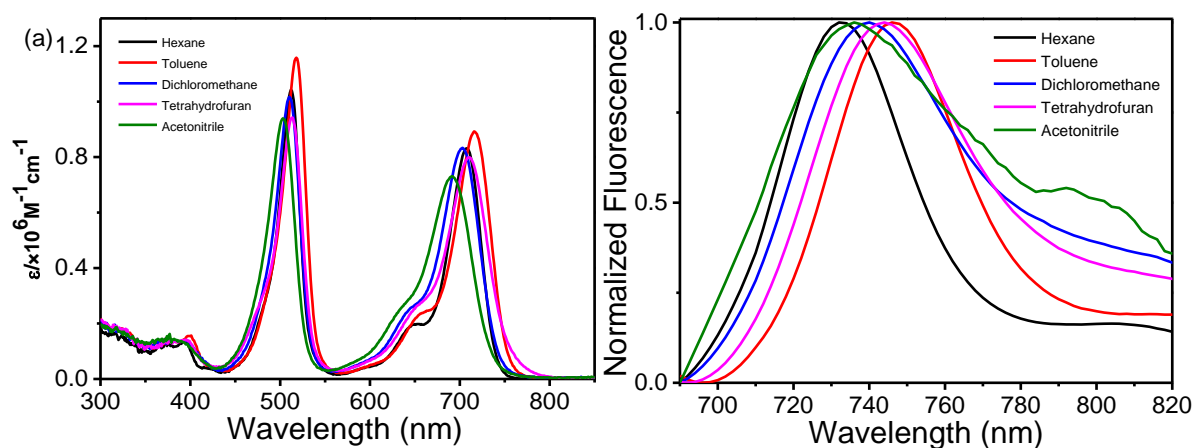


Figure S2. Absorption (a) and emission (b) spectra of compound **2a** (5 μM) recorded in different solvents, excited at 680 nm.

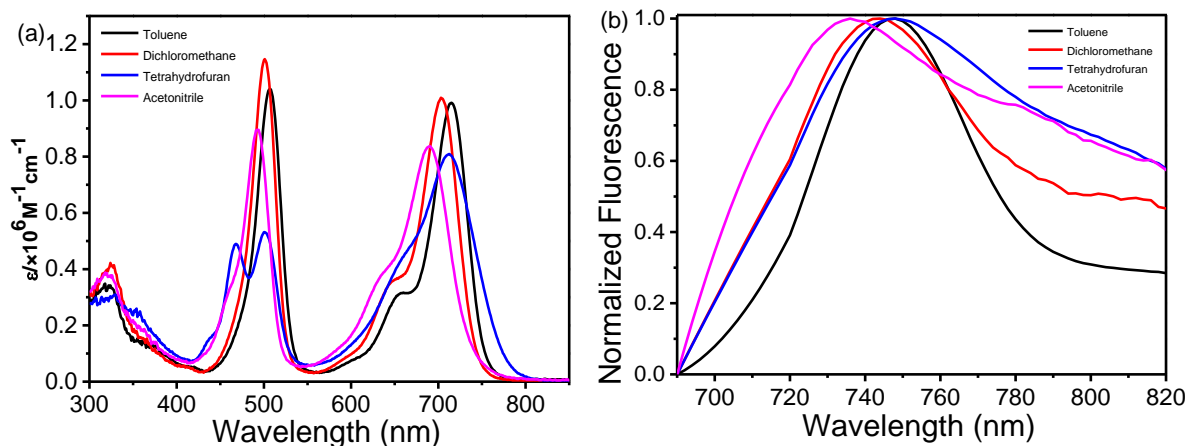


Figure S3. Absorption (a) and emission (b) spectra of compound **2b** (5 μM) recorded in different solvents, excited at 680 nm.

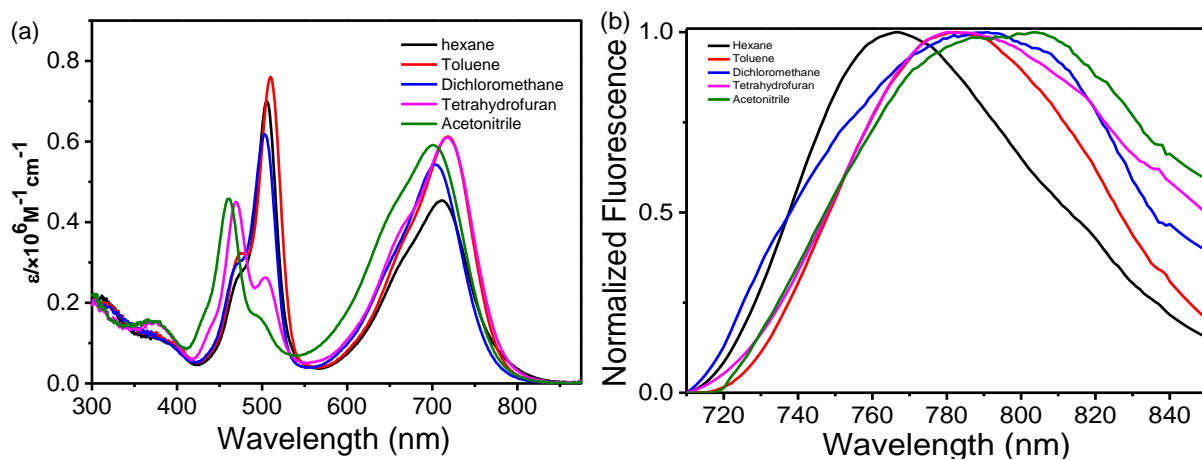


Figure S4. Absorption (a) and emission (b) spectra of compound **2c** (5 μM) recorded in different solvents, excited at 700 nm.

5. Reactive oxygen species properties

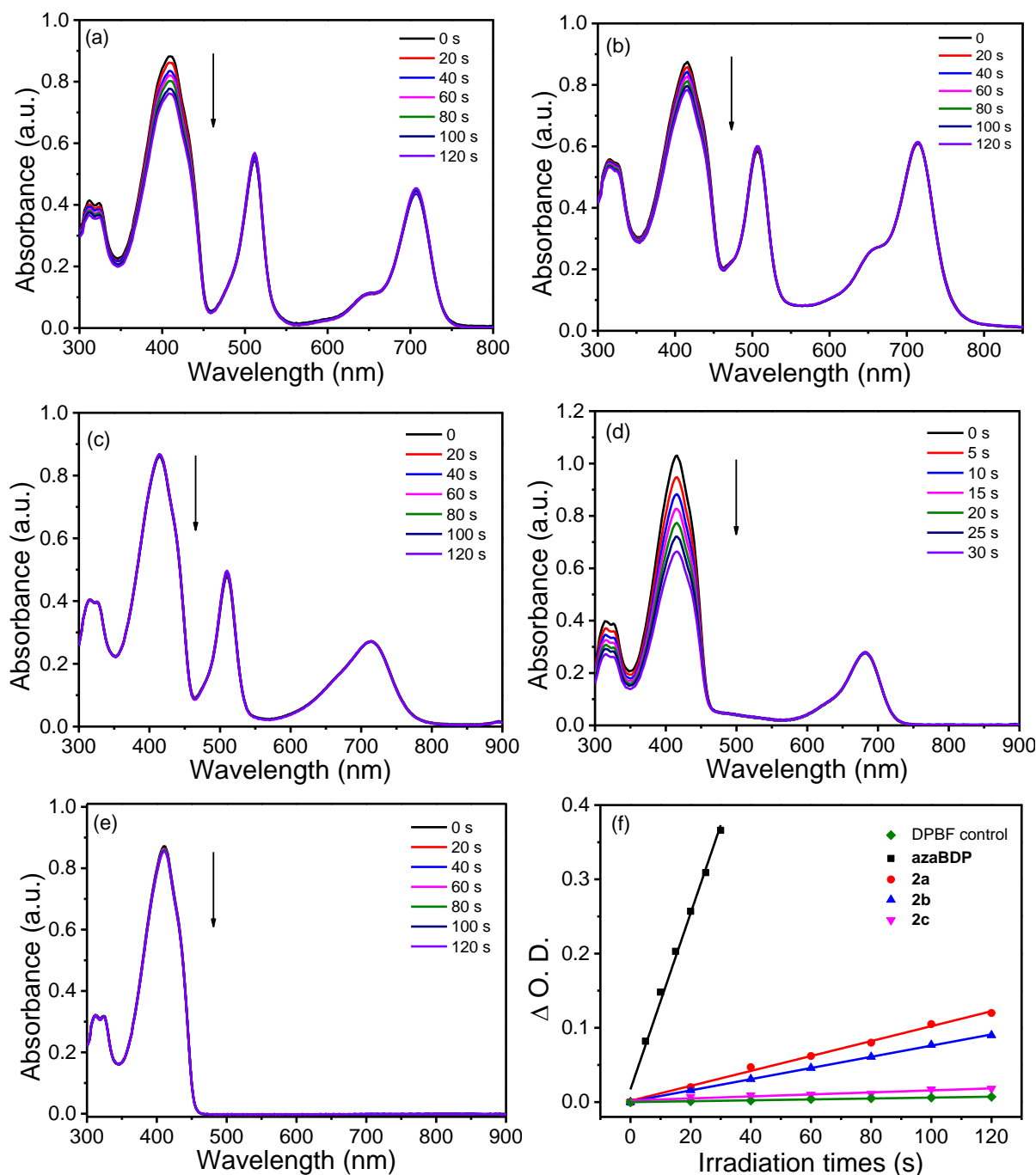


Figure S5. Absorption spectra of DPBF (initial absorbance around 0.90 at 410 nm) upon irradiation with 660 nm laser light in the presence of BODIPY **2a-c** and photosensitizer **azaBDP** (initial absorbance around 0.1 at 660 nm); (a) **2a** for 120 s (recorded at 20 s intervals) in toluene; (b) **2b** for 120 s (recorded at 20 s intervals) in toluene; (c) **2c** for 120 s (recorded at 20 s intervals) in toluene; (d) photosensitizer **azaBDP** for 30 s (recorded at 5 s intervals) in toluene; (e) absorption spectra of DPBF (initial absorbance around 1.0 at 415 nm) upon irradiation in toluene; (f) Comparative DPBF degradation profiles (absorbance at 415 nm) of **2a-c** and reference **azaBDP** in toluene. Singlet oxygen quantum yield of **2a-c** in toluene are 0.1, 0.04, 0.01, respectively.

Reactive oxygen species (ROS) trapping

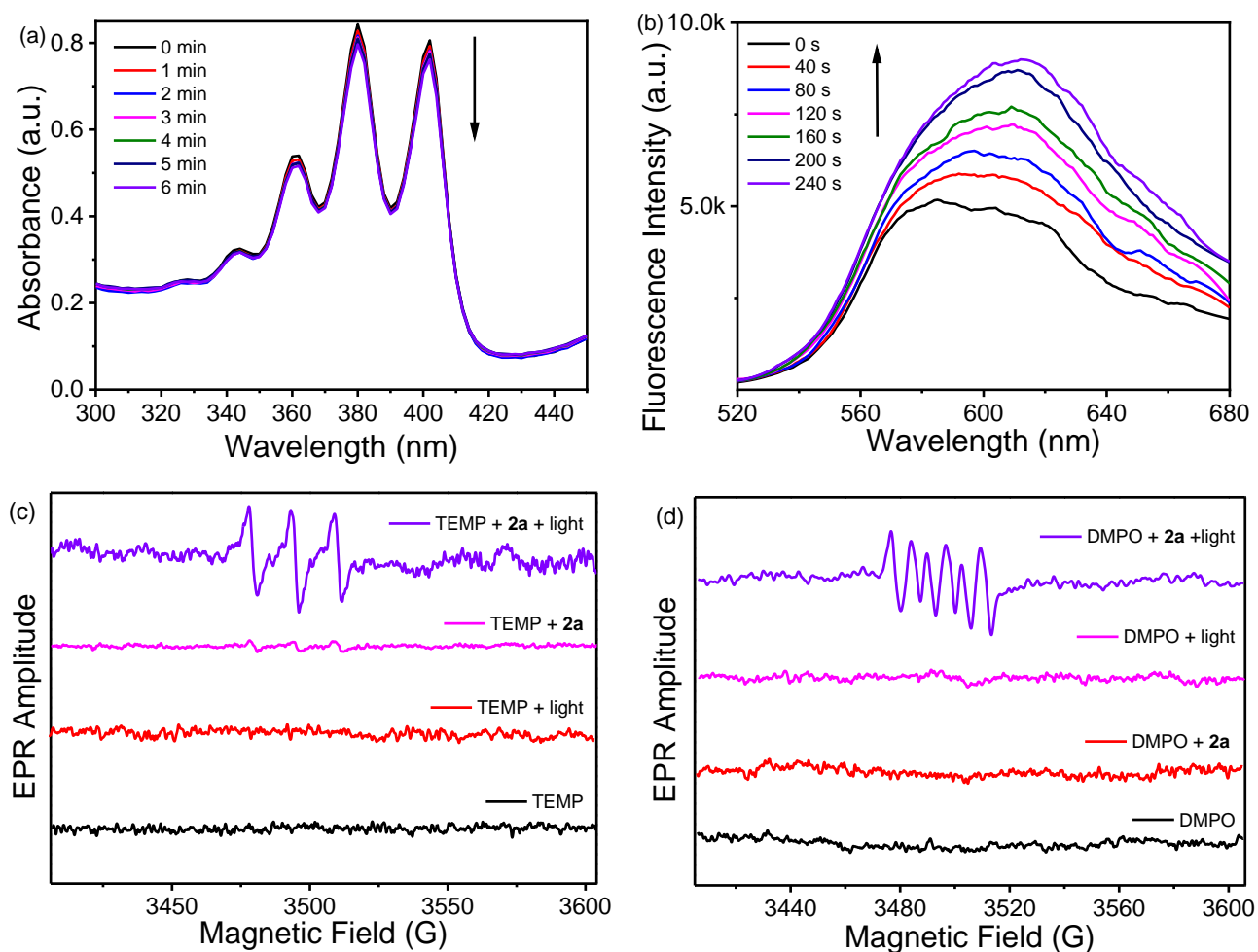


Figure S6. (a) Absorption spectra of 9,10-anthracenediyl-bis(methylene) dimalonic acid (ABDA) in the presence of **2a** in PBS/THF (v/v: 1/1) mixture under 660 nm light irradiation.¹⁰ (b) Fluorescence spectra of Dihydroethidium (DHE) in the presence of **2a** in chloroform under 660 nm light irradiation, and the excitation wavelength for spectra determination was 510 nm.¹⁰ (c) EPR spectra of **2a** (0.3 mM in toluene) for $^1\text{O}_2$ characterization with 2,2,6,6-tetramethyl-4-piperidone (TEMP, 50 mM) as the spin-trap reagent in different conditions.¹³ (d) EPR spectra of **2a** (0.3 mM, in toluene) for $\text{O}_2^{\bullet -}$ characterization with 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO, 200 mM) as the spin-trap reagent in different conditions.¹⁴

6. Electrochemical data

Table S4. Electrochemical data acquired at 100 mV/s, and HOMO-LUMO Gaps determined from spectroscopy of dyes 2a-c^a

dyes	$E_{1/2}^{\text{red}}$ (V)	$E_{\text{red}}^{\text{onset}}$ (V)	$E_{1/2}^{\text{ox}}$ (V)	$E_{\text{ox}}^{\text{onset}}$ (V)	LUMO (eV)	HOMO (eV)	E_g^e (eV)	E_g^o (eV)
2a	-1.42; -1.00	-0.85	1.05; 0.78	0.71	-3.55	-5.11	1.56	1.58
2b	-0.68; -1.12	-0.53	1.07	0.87	-3.87	-5.27	1.40	1.59
2c	-1.33; -0.79	-0.71	0.88	0.59	-3.69	-4.99	1.30	1.49

^a $E_{1/2}^{\text{red}}$ = half wave potentials of reversible reduction potential; $E_{\text{red}}^{\text{onset}}$ = the onset reduction potentials; $E_{1/2}^{\text{ox}}$ = half wave potentials of reversible oxidation potential; $E_{\text{ox}}^{\text{onset}}$ = the onset oxidation potentials; $E_{\text{LUMO}} = -e(E_{\text{red}}^{\text{onset}} + 4.4)$; $E_{\text{HOMO}} = -e(E_{\text{ox}}^{\text{onset}} + 4.4)$; E_g^e = bandgap, obtained from the intercept of the electrochemical data; $E_g^e = E_{\text{LUMO}} - E_{\text{HOMO}}$; E_g^o = bandgap, obtained from the intercept of the absorption spectra.

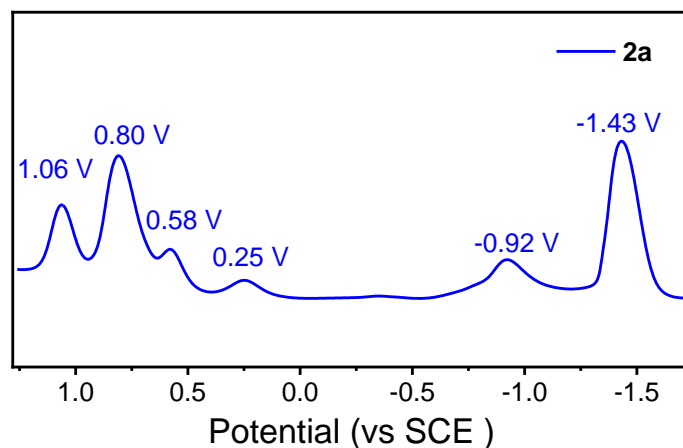


Figure S7. Differential pulse voltammogram of **2a** recorded in dichloromethane containing 0.1 M TBAPF₆ at room temperature.

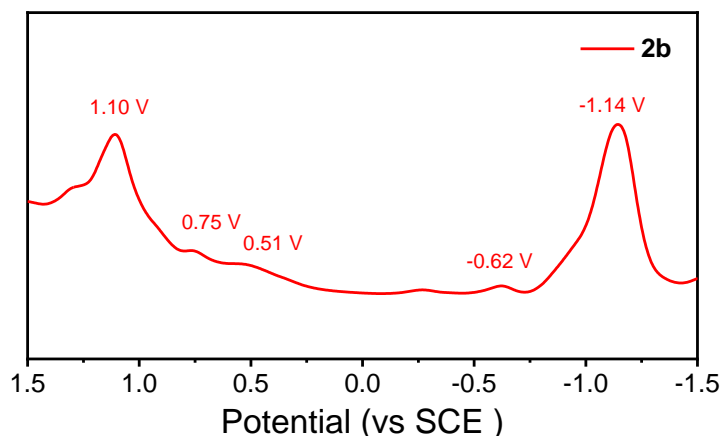


Figure S8. Differential pulse voltammogram of **2b** recorded in dichloromethane containing 0.1 M TBAPF₆ at room temperature.

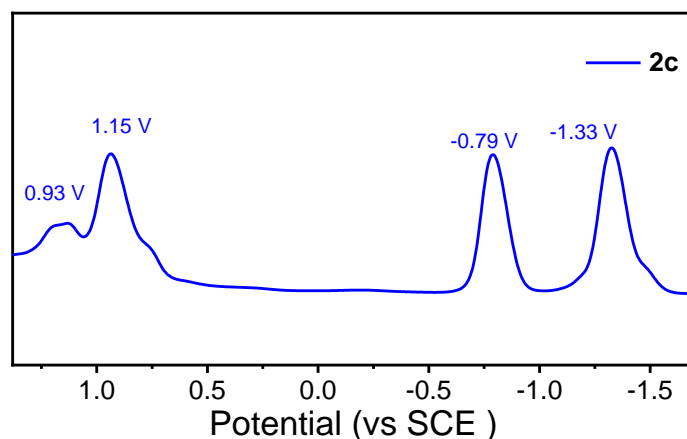


Figure S9. Differential pulse voltammogram of **2c** recorded in dichloromethane containing 0.1 M TBAPF₆ at room temperature.

7. DFT calculation

The ground state geometry was optimized by using DFT method at B3LYP/6-31G(d) level. The same method was used for vibrational analysis to verify that the optimized structures correspond to local minima on the energy surface. TD-DFT computations were used the optimized ground state geometries under the B3LYP/6-31+G (d, p) theoretical level. The calculated molecules in dichloromethane were done using the Self-Consistent Reaction Field (SCRF) method and Polarizable Continuum Model (PCM). All of the calculations were carried out by the methods implemented in Gaussian 09 package.¹¹

Table S5. Selected electronic excitation energies (eV) and oscillator strengths (f), configurations of the low-lying singlet excited states of **1aNH₂**, **2a** and **2c** calculated by TDDFT//B3LYP/6-31+G (d, p), based on the optimized ground state geometries.

	Electronic transition	TD//B3LYP/6-31+G(d, p)			
		Energy/ eV ^[a]	f ^[b]	Composition ^[c]	CI ^[d]
1aNH₂	S0→S1	2.4676 eV 502.45 nm	0.7100	HOMO → LUMO	0.7062
	S0→S2	3.2722 eV 378.90 nm	0.0051	HOMO -1 → LUMO	0.1212
				HOMO -2 → LUMO	0.6943
				HOMO -3 → LUMO	0.1015
	S0→S3	3.4465 eV 359.74 nm	0.0025	HOMO -1 → LUMO	0.1015
	S0→S4	3.4857 eV 355.69 nm	0.1702	HOMO -3 → LUMO	0.6985
HOMO -2 → LUMO				0.1059	
HOMO -1 → LUMO				0.1180	
HOMO -1 → LUMO				0.6706	
2a	S0→S1	1.8039 eV 687.32 nm	0.5220	HOMO → LUMO	0.7060
	S0→S2	2.2203 eV 558.41 nm	0.0003	HOMO -1 → LUMO	0.4833
				HOMO → LUMO +1	0.5143
	S0→S3	2.5433 eV 487.49 nm	1.2690	HOMO -1 → LUMO	0.5143
				HOMO → LUMO +1	0.4820
	S0→S7	3.1190 eV 397.51 nm	0.3284	HOMO -2 → LUMO	0.6532
HOMO -4 → LUMO				0.2250	
2c	S0→S1	1.7804 eV 696.39 nm	0.5183	HOMO → LUMO	0.7058
	S0→S2	2.2718 eV 545.76 nm	0.0609	HOMO -1 → LUMO	0.4609
				HOMO → LUMO +1	0.5337
	S0→S3	2.5971 eV 477.39 nm	1.2205	HOMO -1 → LUMO	0.5307
				HOMO → LUMO +1	0.4544
	S0→S6	3.0342 eV 408.62 nm	0.1965	HOMO -2 → LUMO	0.6356
HOMO -4 → LUMO				0.2194	
				HOMO -1 → LUMO +1	0.1327

[a] Only the selected low-lying excited states are presented. [b] Oscillator strength. [c] Only the main configurations are presented. [d] The CI coefficients are in absolute values.

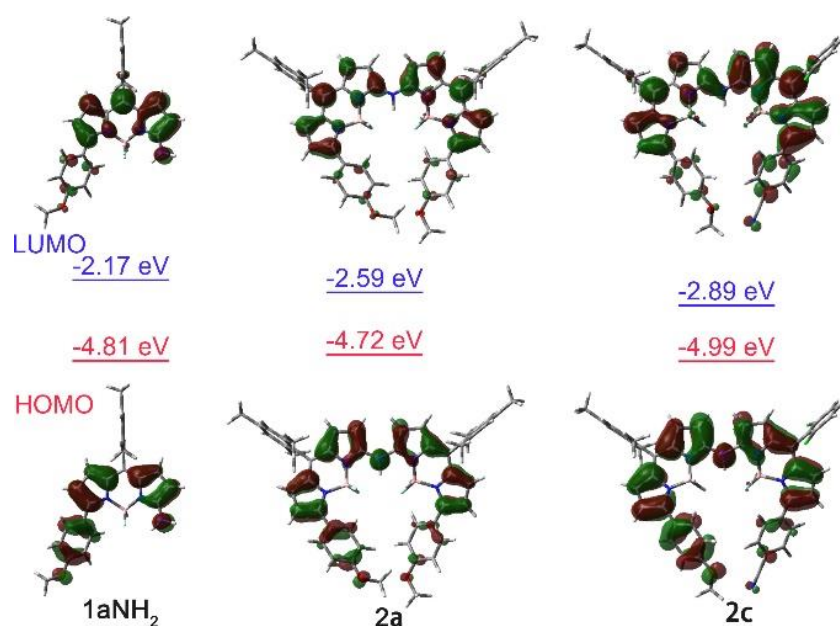


Figure S10. Molecular orbitals and energy levels of **1aNH₂**, **2a** and **2c**.

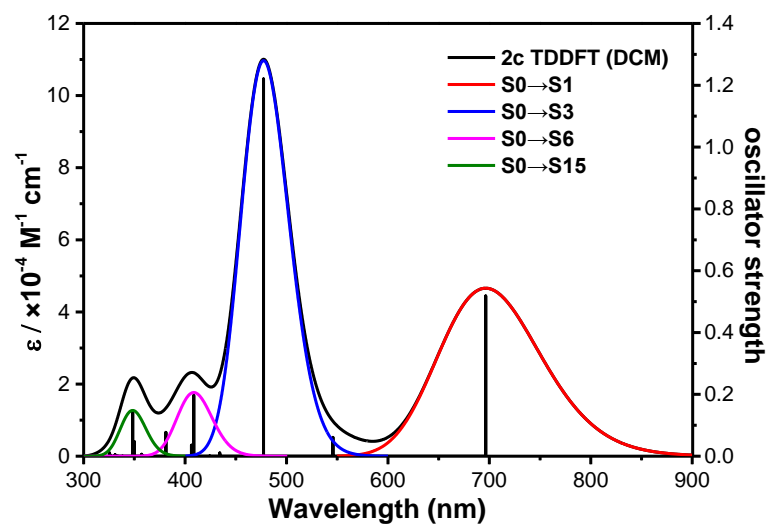


Figure S11. Calculated absorption of energy-minimized calculated **2c**.

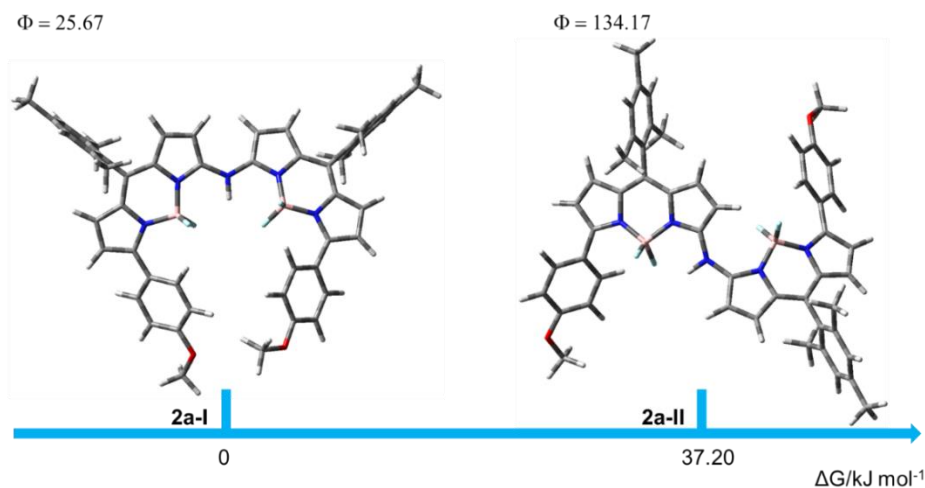


Figure S12. Calculated structures for the low-energy conformations of **2a** in dichloromethane (B3LYP/6-31G (d)). Φ : dihedral angle of two BODIPY units of different conformer.

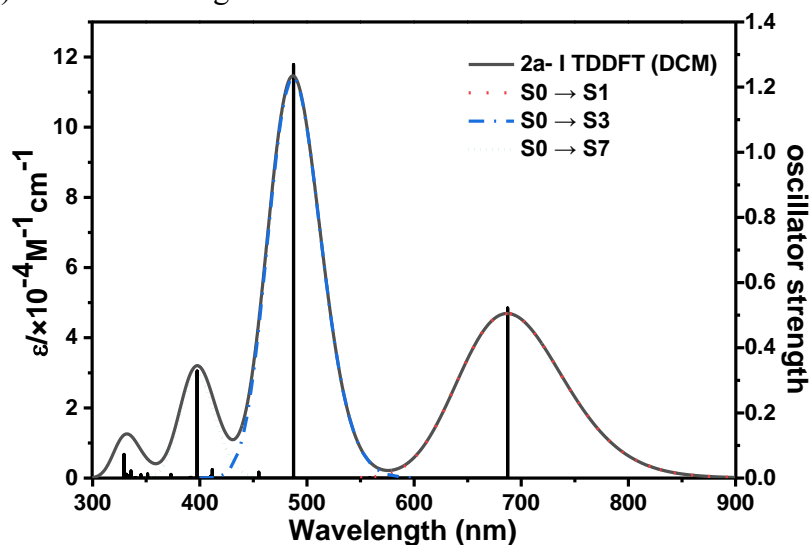


Figure S13. Calculated absorption of energy-minimized calculated **2a-I**.

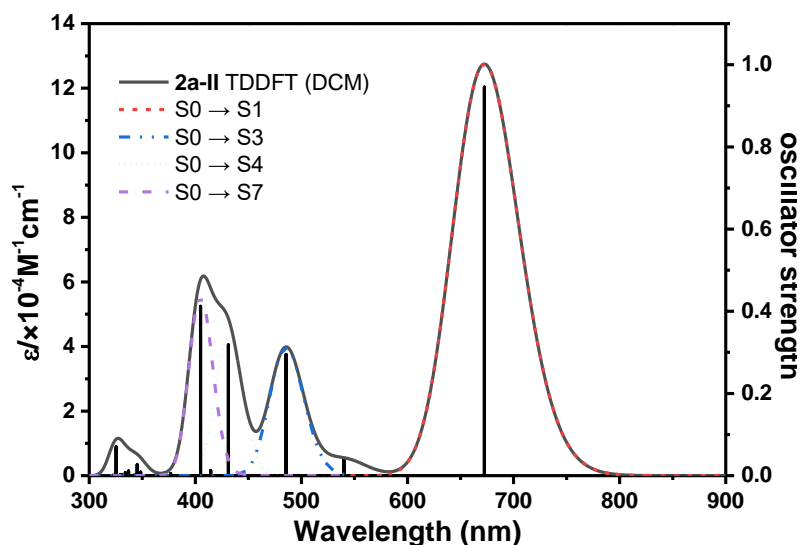


Figure S14. Calculated absorption of energy-minimized calculated **2a-II**.

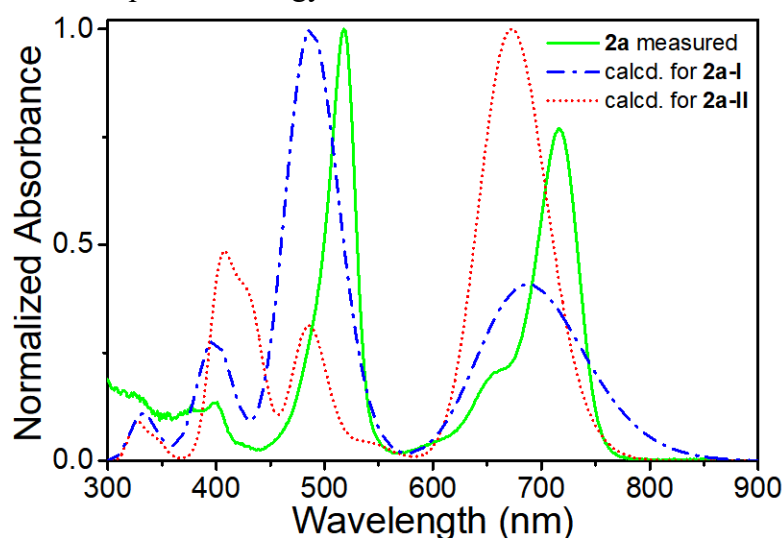


Figure S15. Comparison of measured and calculated absorption bands for the two calculated low-energy conformers of **2a** in CH_2Cl_2 .

DFT optimized coordinates for **1aNH₂** optimized S0 state Geometry by B3LYP/6-31G(d).

B	-0.86631800	1.46915300	0.24317200
C	-1.53179500	-1.07668000	0.04054400
C	-0.83188300	-2.30497500	-0.03789800
C	0.52786800	-2.02244300	-0.00959700
C	0.65814300	-0.61940900	0.06504900
C	1.82857700	0.16451200	0.02028000
C	1.73359700	1.54205700	-0.07015900
C	2.72266200	2.54819000	-0.25863500
C	2.07007900	3.75453500	-0.42215900
C	0.66805400	3.47904500	-0.32534000
C	3.16409500	-0.49846900	0.01836900
C	3.78996500	-0.81190900	-1.20196600
C	5.04270300	-1.43070700	-1.17505800

C	5.68246500	-1.74545400	0.02625100
C	5.03949500	-1.42157000	1.22397500
C	3.78643000	-0.80468800	1.24284900
C	3.12430800	-0.48759000	-2.51775700
C	7.02078600	-2.44323100	0.03156100
C	3.11467500	-0.46888900	2.55224400
F	-1.84589900	1.93654200	-0.64194500
F	-1.21643700	1.78467400	1.55680600
N	-0.62219900	-0.05864000	0.09501000
N	0.48000000	2.16361100	-0.10767700
H	-1.29964600	-3.27893800	-0.06798500
H	1.35513600	-2.71768900	-0.04350400
H	3.78755300	2.36350000	-0.29085800
H	5.52926500	-1.67317800	-2.11735900
H	5.52465100	-1.65455800	2.16940100
H	3.71238000	-0.86849100	-3.35767400
H	3.00330900	0.59380800	-2.64880600
H	2.12185100	-0.92623500	-2.57281200
H	7.62247100	-2.14793200	0.89757100
H	7.59326900	-2.21770800	-0.87406700
H	6.89855700	-3.53347000	0.07735700
H	2.90522200	0.60403700	2.62893300
H	3.74248600	-0.75700600	3.40023400
H	2.15210100	-0.98391000	2.64711800
C	-2.98811600	-0.93158600	0.06773900
C	-3.65455400	0.03749700	0.84450000
C	-3.76984600	-1.83516800	-0.66789500
C	-5.03784200	0.09632500	0.86811200
H	-3.08001300	0.73195900	1.44311700
C	-5.16194100	-1.78266800	-0.65253800
H	-3.27896300	-2.58035000	-1.28650200
C	-5.80440400	-0.80886100	0.12023800
H	-5.55476800	0.83646000	1.47027500
H	-5.72719300	-2.49138200	-1.24590000
O	-7.15672000	-0.66173300	0.21270100
C	-7.97381700	-1.55799900	-0.52086700
H	-9.00416300	-1.27029000	-0.30520200
H	-7.79200500	-1.47674500	-1.60065600
H	-7.81324600	-2.59792700	-0.20715300
N	-0.37099600	4.34706100	-0.39805400
H	-0.19987400	5.25771800	-0.79629100
H	-1.28215700	3.93374700	-0.56424600
H	2.50429100	4.72831300	-0.60222400

SCF done: -1431.33360742 a.u.

No imaginary Frequency.

DFT optimized coordinates for **2a-I** optimized S0 state Geometry by B3LYP/6-31G(d).

F	1.43821300	0.74351800	-0.07098400
F	2.02679600	-0.03219300	2.00345000
N	-2.41156800	-1.36715400	-0.10664400
F	-1.59867800	0.67300800	0.75208500
N	2.25708600	-1.49985100	0.10784800
N	-0.08040900	-1.58965700	-0.01287200
H	-0.04322400	-0.56953600	0.05021100
F	-1.79519600	0.49620600	-1.52300300
N	-3.84630600	0.67903900	-0.24931300
N	3.81027900	0.42435300	0.42816900
O	1.67255700	6.55281400	1.53473800
C	-1.32452700	-2.15764800	0.03100700
C	3.34783700	-2.34333300	-0.08962600
C	1.12846700	-2.21236500	-0.10409000
C	-3.54602700	-2.15197400	0.06179800
C	-4.94156300	-0.17917600	-0.08842000
C	-1.73574300	-3.50091400	0.26162900
H	-1.08450700	-4.34019500	0.44812300
C	-6.02398600	-2.41438900	0.23156200
C	-4.32221400	1.93956200	-0.47245600
C	2.84853900	-3.63067400	-0.42487700
H	3.46367100	-4.48870600	-0.65772300
C	-4.81016000	-1.56493000	0.06623800
C	1.46584300	-3.55645300	-0.44315300
H	0.76905500	-4.33161300	-0.72048700
C	4.64336900	-1.84208100	-0.03580600
C	-3.12351400	-3.48909400	0.27736500
H	-3.78562800	-4.32582400	0.45112100
C	5.80520800	-2.74652100	-0.26824400
C	6.25855700	-2.98067700	-1.57951900
C	3.59453000	2.92038600	0.74709400
C	4.85651400	-0.47228600	0.19110500
C	-6.61317000	-3.01514400	-0.89612800
C	2.33962800	5.40069600	1.22771000
C	6.44183800	-3.35219700	0.83083500
C	7.53025400	-4.19535200	0.59517400
H	8.02558800	-4.66315900	1.44321800
C	7.35175100	-3.83013000	-1.76940200
H	7.70788700	-4.00920200	-2.78153900
C	-6.56406900	-2.61341900	1.51564000
C	7.99794100	-4.44975400	-0.69685400
C	4.33566000	1.68102000	0.50721300

C	-6.12604700	0.59118700	-0.18637400
H	-7.12689900	0.19508800	-0.08559100
C	-8.30485700	-4.02451600	0.54620200
C	3.48523900	5.34200300	0.42678600
H	3.90479000	6.23522100	-0.02033800
C	2.43423800	3.00156300	1.54493300
H	2.03765600	2.11135100	2.01359200
C	1.81511000	4.22038400	1.77346300
H	0.93219600	4.28603800	2.40106400
C	-7.74647800	-3.81227500	-0.71687000
H	-8.20363000	-4.27851700	-1.58692800
B	2.34245300	-0.03998400	0.64551000
C	-5.74435100	1.89775700	-0.42784200
H	-6.38897300	2.75882400	-0.52998000
C	-7.69708100	-3.41976900	1.64949600
H	-8.11367300	-3.57951400	2.64161200
C	4.09527500	4.11187000	0.19689600
H	4.97075500	4.07535000	-0.44353300
C	6.06442700	0.26056500	0.13056500
H	7.04034500	-0.17275700	-0.03831700
O	-1.51283500	6.67520900	-1.68389600
C	-5.92940500	-1.97446700	2.72725300
H	-6.45525100	-2.26209100	3.64205600
H	-5.94355500	-0.88123000	2.65385800
H	-4.87888500	-2.26957000	2.82882200
C	5.74031900	1.59498100	0.31522600
H	6.42058600	2.43376700	0.35283300
B	-2.37640800	0.17696800	-0.31185400
C	9.15588900	-5.38947000	-0.92891900
H	9.86208900	-5.36835400	-0.09235200
H	9.70196700	-5.13335400	-1.84265500
H	8.80910300	-6.42579500	-1.03580800
C	5.96099300	-3.09251000	2.23799300
H	6.02984900	-2.02864000	2.49172300
H	6.55269900	-3.65635700	2.96467700
H	4.90937100	-3.37651100	2.35828900
C	5.58551200	-2.32247200	-2.75989400
H	4.53950100	-2.63666500	-2.85019800
H	6.09801300	-2.57460400	-3.69256900
H	5.57903500	-1.23169900	-2.65616200
C	-6.03496600	-2.80217100	-2.27429700
H	-5.98620300	-1.73617600	-2.52359600
H	-6.64017900	-3.30408000	-3.03453400
H	-5.01170700	-3.18851000	-2.34208700

C	2.26423100	7.78367000	1.14771000
H	2.31945100	7.88205100	0.05575700
H	3.27182900	7.88903100	1.56886700
H	1.61680800	8.56597700	1.54662400
C	-2.11610400	5.50708400	-1.33663800
C	-3.41410400	5.31519900	-1.83511200
H	-3.85079800	6.08746800	-2.45982900
C	-4.10418400	4.15284500	-1.54104200
H	-5.09486900	4.00845100	-1.96001600
C	-3.52910600	3.13581100	-0.74701000
C	-2.23296300	3.35195900	-0.25017100
H	-1.76172700	2.60729100	0.37357800
C	-1.53117200	4.51803500	-0.53764700
H	-0.53290600	4.63733400	-0.13329000
C	-9.54859000	-4.86332900	0.71150200
H	-10.45419000	-4.24704300	0.63591700
H	-9.57183000	-5.35605500	1.68905500
H	-9.61585600	-5.63587500	-0.06148200
C	-0.19855900	6.90538700	-1.19549700
H	0.50634500	6.15105100	-1.56838700
H	-0.17017800	6.90216900	-0.10071200
H	0.08891800	7.88926600	-1.57118500

SCF done: -2806.11088957 a.u.

No imaginary Frequency.

DFT optimized coordinates for **2a-II** optimized S0 state Geometry by B3LYP/6-31G(d).

F	1.57935500	1.18622400	-0.66128100
F	2.44161100	1.67119300	1.42593500
N	-2.08959000	-0.25646200	0.70750100
F	-2.10927700	-2.29804700	-0.53586800
N	2.47958000	-0.62409100	0.65192000
N	0.06112200	-1.17186100	0.71253900
H	-0.45777400	-1.98680900	0.39054800
F	-2.93946800	-2.34715000	1.58879800
N	-4.27984100	-1.19183500	-0.06443400
N	3.99238700	1.15333200	-0.32578500
O	1.59116500	6.79849900	-2.70650400
C	-0.76451300	-0.10379300	0.95152400
C	3.62662100	-1.40534700	0.86055900
C	1.40973400	-1.43153000	0.86732100
C	-2.72156200	0.94305900	1.03624000
C	-4.83946300	0.04964600	0.26491400
C	-0.51146200	1.19568600	1.47857100
H	0.45481700	1.58073900	1.75645200

C	-4.75245100	2.39805800	1.17045200
C	-5.29083200	-1.99159500	-0.52606300
C	3.22641500	-2.71409700	1.23030600
H	3.90222500	-3.52795300	1.45296700
C	-4.08363800	1.10456700	0.82170400
C	1.84869100	-2.73829500	1.21687000
H	1.18906300	-3.56357900	1.44940400
C	4.90482800	-0.94476800	0.53301400
C	-1.72919800	1.83977200	1.52233900
H	-1.91750300	2.85368200	1.84802900
C	6.09381900	-1.82542700	0.76645700
C	6.53916700	-2.70293400	-0.24427800
C	3.67192600	3.39221400	-1.45836400
C	5.07259300	0.30652800	-0.07629400
C	-5.29879700	2.57997000	2.45824700
C	2.31039500	5.69324100	-2.36362700
C	6.76862400	-1.76235900	2.00398400
C	7.88100100	-2.58469500	2.20743800
H	8.40308700	-2.53153800	3.16080300
C	7.65620900	-3.50680200	0.00693800
H	8.00049000	-4.18186300	-0.77410700
C	-4.82872400	3.43040700	0.21213700
C	8.33968500	-3.46670700	1.22501800
C	4.45511500	2.23365500	-1.01584500
C	-6.21869700	0.01221000	-0.02706900
H	-6.90213800	0.84030700	0.10107300
C	-6.00674200	4.83510600	1.83082600
C	3.32004300	5.12325600	-3.14888300
H	3.58640400	5.54280100	-4.11214100
C	2.65600400	3.98553700	-0.68019900
H	2.40945200	3.56700300	0.28706400
C	1.99005000	5.11542900	-1.12521400
H	1.21387300	5.57866500	-0.52422600
C	-5.91456400	3.79809300	2.76307000
H	-6.33233300	3.93831400	3.75819000
B	2.56427300	0.89590100	0.25593600
C	-6.49788400	-1.25633300	-0.51383800
H	-7.44727900	-1.62832600	-0.87383500
C	-5.45469800	4.63084000	0.56342700
H	-5.50979500	5.42765500	-0.17582600
C	3.98945700	3.99090900	-2.68842600
H	4.75835100	3.54709600	-3.31433100
C	6.23743500	0.88641400	-0.63527700
H	7.22757200	0.45376300	-0.59442600

O	-5.25368900	-7.36024800	-2.29155800
C	-4.24376900	3.26225300	-1.17258900
H	-4.43518900	4.14801600	-1.78568800
H	-4.67190600	2.39447700	-1.68715200
H	-3.15942600	3.10546100	-1.13618800
C	5.85026700	2.07246600	-1.23089300
H	6.48069400	2.78999500	-1.73754800
B	-2.85698700	-1.59175600	0.42927600
C	9.52476100	-4.36804000	1.48234400
H	10.24810500	-3.89690000	2.15645600
H	10.04364700	-4.62368600	0.55248400
H	9.21215100	-5.31116100	1.95037000
C	6.31393400	-0.82288300	3.09864900
H	6.31686400	0.22005000	2.76134300
H	6.96828300	-0.89757700	3.97221300
H	5.29092400	-1.04645000	3.42279200
C	5.83767900	-2.78754800	-1.58189700
H	4.78613300	-3.07545600	-1.46850200
H	6.32125100	-3.52656200	-2.22762100
H	5.84739500	-1.82418300	-2.10434100
C	-5.22373700	1.48989300	3.50399400
H	-5.70782000	0.56874300	3.15996600
H	-5.71388800	1.80472400	4.43015800
H	-4.18573600	1.23024000	3.74203200
C	1.87098300	7.42649600	-3.94802400
H	1.69003500	6.74870600	-4.79255900
H	2.90623500	7.78966200	-3.99222400
H	1.18809400	8.27535400	-4.01422600
C	-5.16926500	-6.05637500	-1.90025800
C	-6.21255500	-5.59579300	-1.08286000
H	-7.00283000	-6.28737700	-0.80810200
C	-6.21619000	-4.28465300	-0.63514100
H	-7.02175000	-3.94609500	0.00983200
C	-5.18071400	-3.38716600	-0.97354000
C	-4.14946200	-3.86350400	-1.79651000
H	-3.34763400	-3.19925300	-2.08761600
C	-4.13799400	-5.17994400	-2.25714600
H	-3.32538100	-5.50528500	-2.89666900
C	-6.70590000	6.12982000	2.17483000
H	-7.77649600	6.07976100	1.93449200
H	-6.28737000	6.97278600	1.61463400
H	-6.62432400	6.35819400	3.24290500
C	-4.22023500	-7.88434700	-3.11035300
H	-3.24467000	-7.83632900	-2.60895400

H	-4.15776400	-7.35514800	-4.07042800
H	-4.48230700	-8.92850200	-3.29101900

-2806.09671496

No imaginary frequency

DFT optimized coordinates for **2c** optimized S0 state Geometry by B3LYP/6-31G(d).

F	1.49945000	0.93652400	0.03993900
F	2.18894600	0.14554500	2.08198300
N	-2.22666900	-1.43693200	-0.10302100
F	-1.48801600	0.77633000	0.32716600
N	2.46197100	-1.25374800	0.13855000
N	0.12413400	-1.47395300	-0.01447000
H	0.09152900	-0.45024200	0.01798900
F	-2.03806900	0.25641000	-1.83375000
N	-3.86292900	0.45912400	-0.26015400
N	3.89917700	0.75777200	0.47385300
O	1.02484600	6.55314200	1.28928200
C	-1.07301800	-2.12074000	0.05913800
C	3.60022900	-2.02581300	-0.07167600
C	1.37976800	-2.02848700	-0.09678300
C	-3.28201100	-2.32345200	0.09298000
C	-4.87037300	-0.49239500	-0.09358400
C	-1.36104400	-3.49304300	0.34615900
H	-0.63230200	-4.25640700	0.57024100
C	-5.71666700	-2.82653700	0.26944700
C	-4.46842300	1.67087300	-0.44944000
C	3.18125900	-3.33150800	-0.43303100
H	3.84275300	-4.14969000	-0.68250500
C	-4.58984700	-1.86457100	0.08172800
C	1.79488000	-3.33835400	-0.45962500
H	1.14969300	-4.14810200	-0.76407400
C	4.87313000	-1.44329100	-0.01920000
C	-2.73297200	-3.61117800	0.36088400
H	-3.30814500	-4.50126300	0.57540000
C	6.08908800	-2.28055300	-0.26739600
C	6.56818300	-2.46183000	-1.58185400
C	3.48941200	3.22145200	0.75730900
C	5.00067000	-0.06527900	0.21473800
C	-6.30718600	-3.49310200	-0.81958700
C	1.88807200	5.52114900	1.08845200
C	6.75146700	-2.88350400	0.82275400
C	7.88537300	-3.66290900	0.57424200
H	8.39714600	-4.12481100	1.41628800
C	7.70713000	-3.24958000	-1.77972200

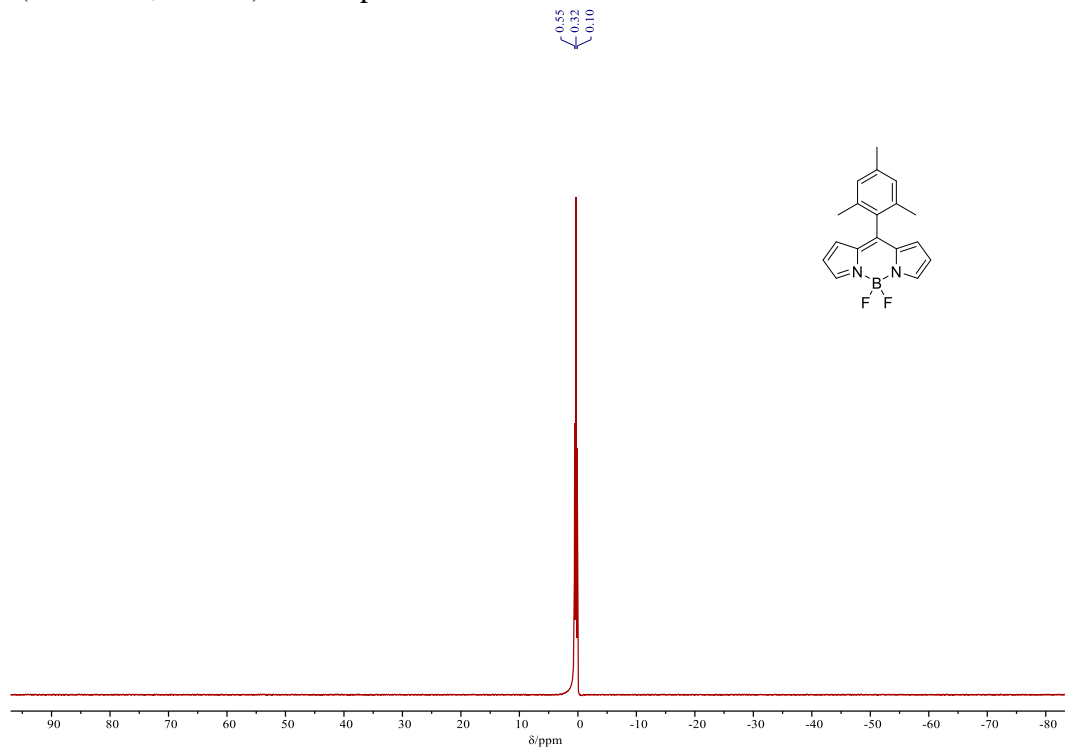
H	8.07906300	-3.38504200	-2.79340000
C	-6.24260100	-3.10973000	1.54306800
C	8.37852600	-3.86210300	-0.71829300
C	4.33297400	2.04692700	0.52230300
C	-6.12209300	0.15617900	-0.15708900
H	-7.08288400	-0.32443100	-0.03586200
C	-7.85147600	-4.64259000	0.62255400
C	2.97863800	5.54842400	0.20911400
H	3.20592900	6.43393300	-0.37279500
C	2.40806600	3.22560600	1.66363800
H	2.18724800	2.33754000	2.24225800
C	1.62780400	4.35655500	1.82925400
H	0.79882600	4.36313600	2.53029900
C	-7.36117000	-4.39125100	-0.65662700
H	-7.78579100	-4.88141000	-1.52548700
B	2.46603300	0.19614100	0.71749600
C	-5.87044800	1.49979800	-0.38626300
H	-6.59411100	2.30001300	-0.45694800
C	-7.29563200	-4.00460900	1.72884600
H	-7.66803200	-4.19261300	2.72956400
C	3.76662300	4.40879500	0.05945100
H	4.58897300	4.43123600	-0.65004000
C	6.15220600	0.75796600	0.11604400
H	7.15488700	0.39998600	-0.07352200
C	5.73578700	2.06412500	0.28807800
H	6.34891000	2.95474200	0.28974600
B	-2.36647000	0.07170300	-0.50668100
C	9.58791700	-4.73431600	-0.96247900
H	10.28698800	-4.69559100	-0.12024300
H	10.12694300	-4.42896100	-1.86549600
H	9.29901400	-5.78549500	-1.09604600
C	6.25964900	-2.69639900	2.24075800
H	6.26824100	-1.64033100	2.53430900
H	6.88770800	-3.24800100	2.94654200
H	5.22817700	-3.04789500	2.35966100
C	5.88241600	-1.81934000	-2.76736500
H	4.84601300	-2.16137100	-2.86921400
H	6.40820400	-2.05834300	-3.69647800
H	5.84685900	-0.72824000	-2.67021400
C	1.22855500	7.76367100	0.56451600
H	1.16126900	7.59935900	-0.51652700
H	2.19743600	8.21459400	0.81446400
H	0.42179200	8.43113800	0.86764700
C	-2.70584300	5.52293000	-1.10008500

C	-3.85290000	5.12279100	-1.80653900
H	-4.30804200	5.79816700	-2.52385200
C	-4.39076300	3.86184700	-1.58950900
H	-5.26537000	3.55123200	-2.15232000
C	-3.80242100	2.96375000	-0.67556400
C	-2.65703600	3.37986700	0.02857000
H	-2.18900500	2.71141200	0.73635800
C	-2.11422000	4.64197900	-0.17976000
H	-1.23345500	4.95666100	0.37108200
H	-8.67233600	-5.34047400	0.75827000
Cl	-5.71830100	-3.19941200	-2.44552900
Cl	-5.56590400	-2.32866400	2.96096700
C	-2.13582000	6.81968300	-1.31564100
N	-1.66328000	7.87028100	-1.48410000

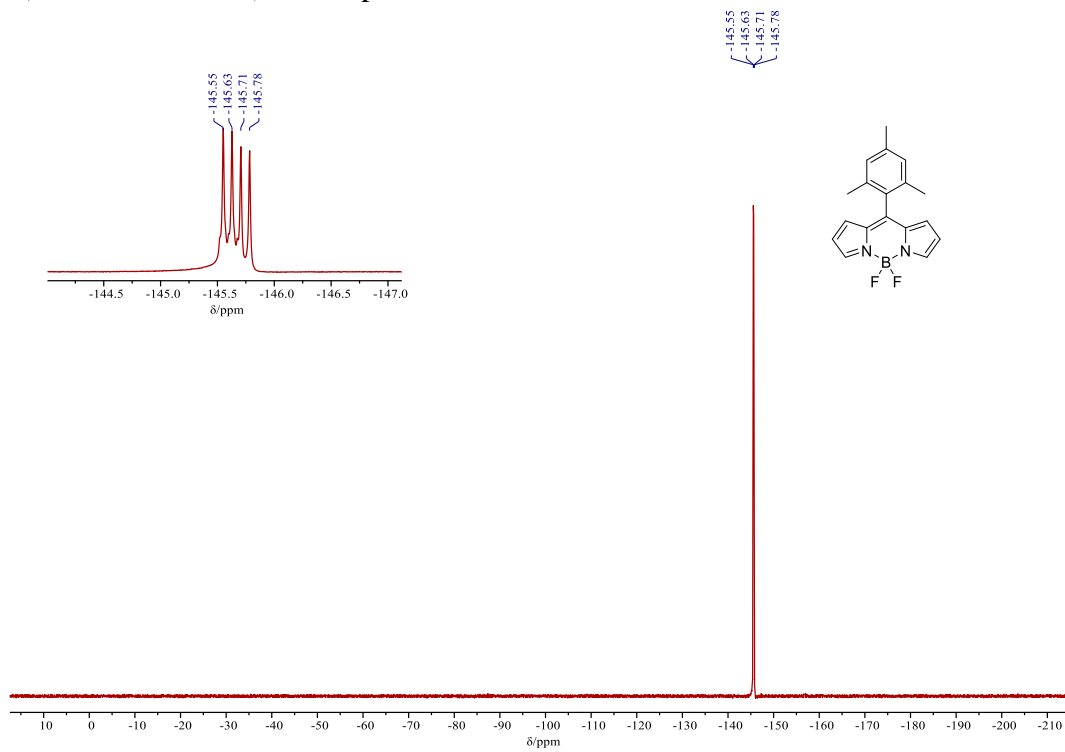
SCF done: -3585.06373696 a.u. No imaginary Frequency.

8. ^1H , ^{13}C , ^{11}B and ^{19}F NMR spectra of all new compounds.

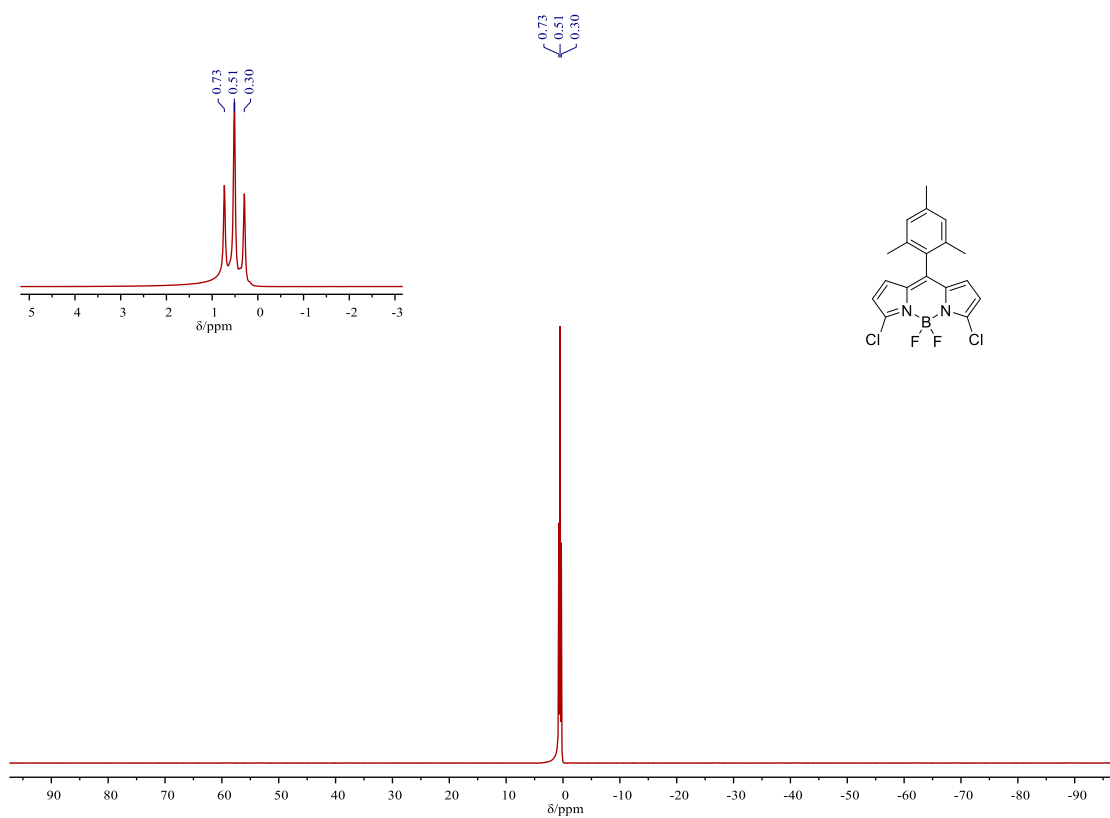
^{11}B NMR (128 MHz, CDCl_3) of compound **1a**.



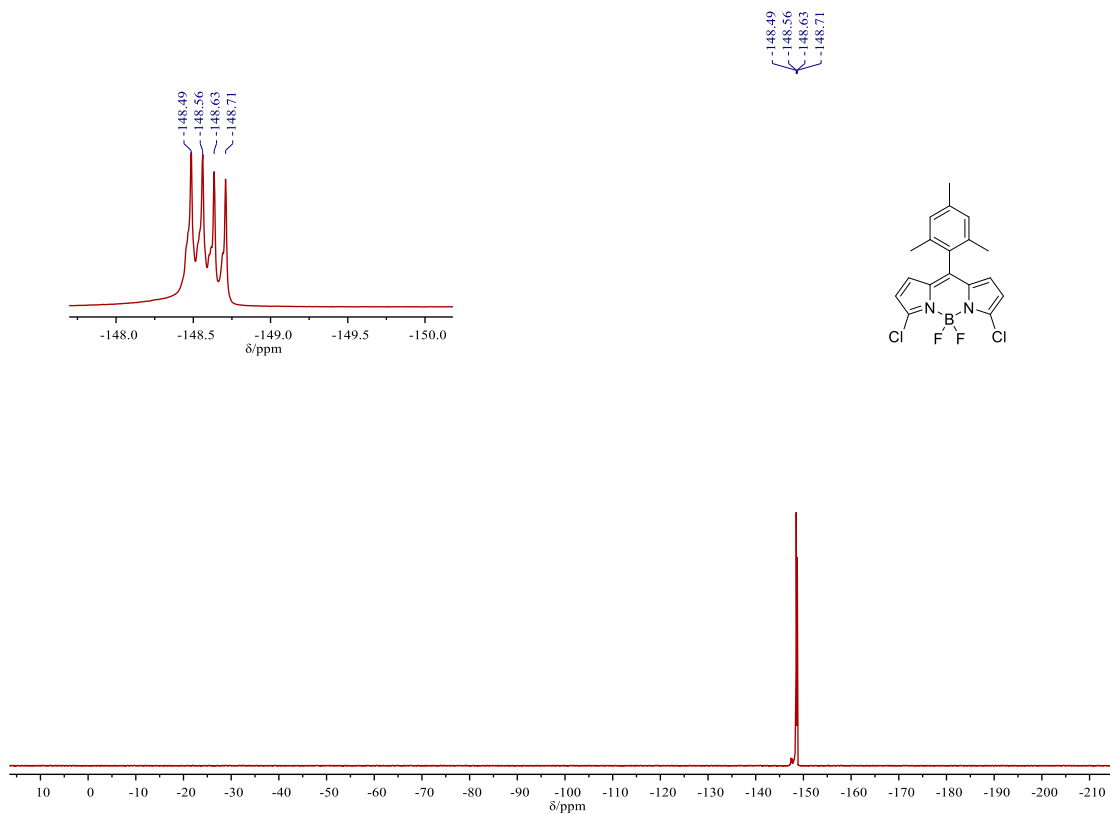
^{19}F NMR (376 MHz, CDCl_3) of compound **1a**.



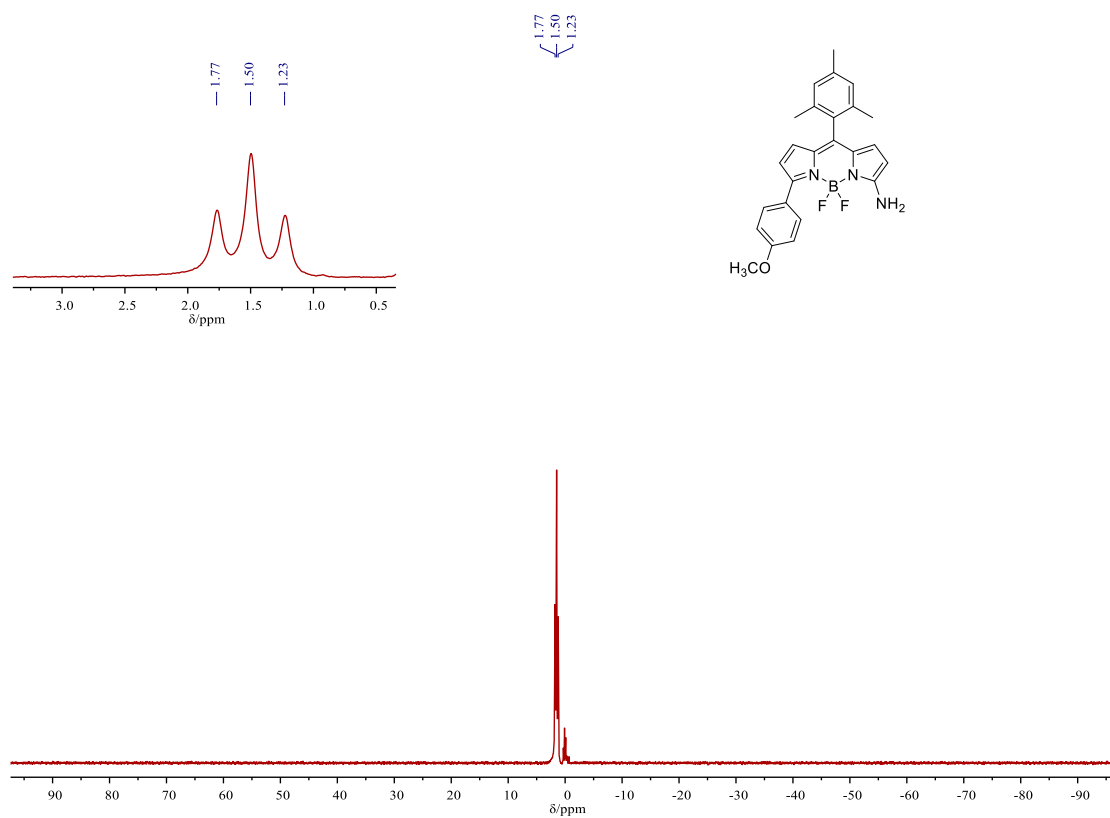
^{11}B NMR (128 MHz, CDCl_3) of compound **1a2Cl**.



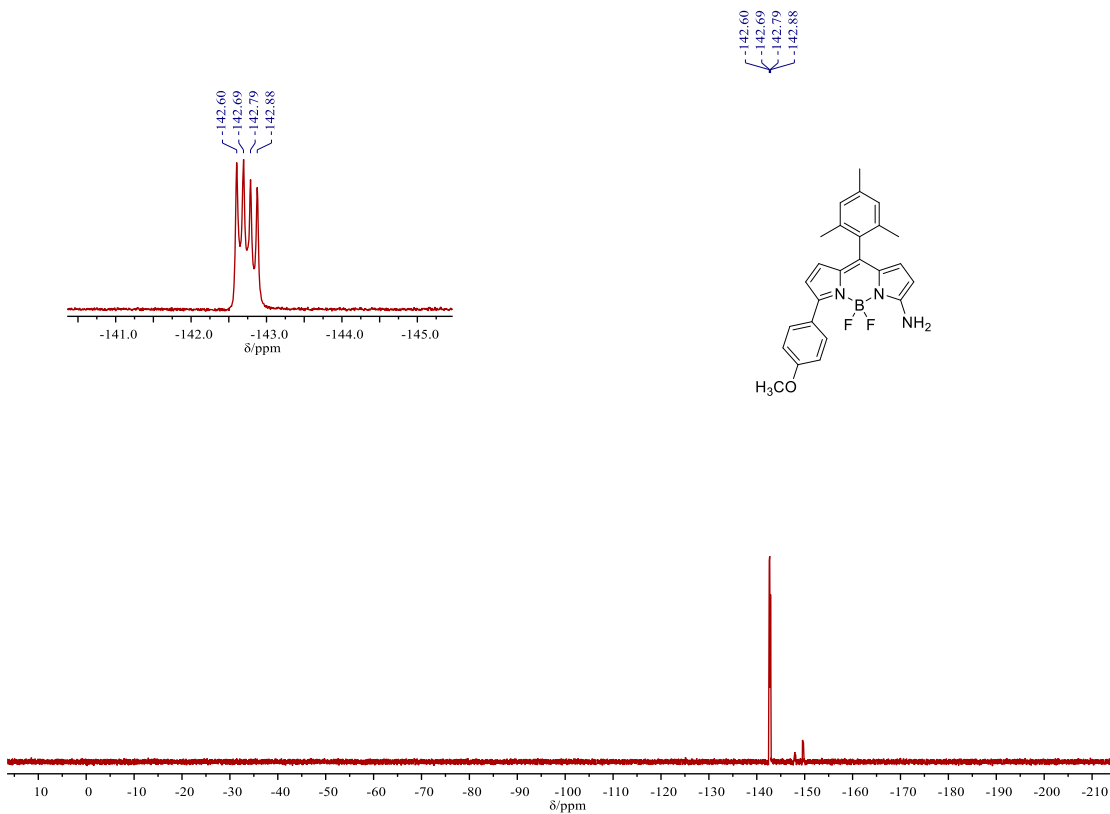
^{19}F NMR (376 MHz, CDCl_3) of compound **1a2Cl**.



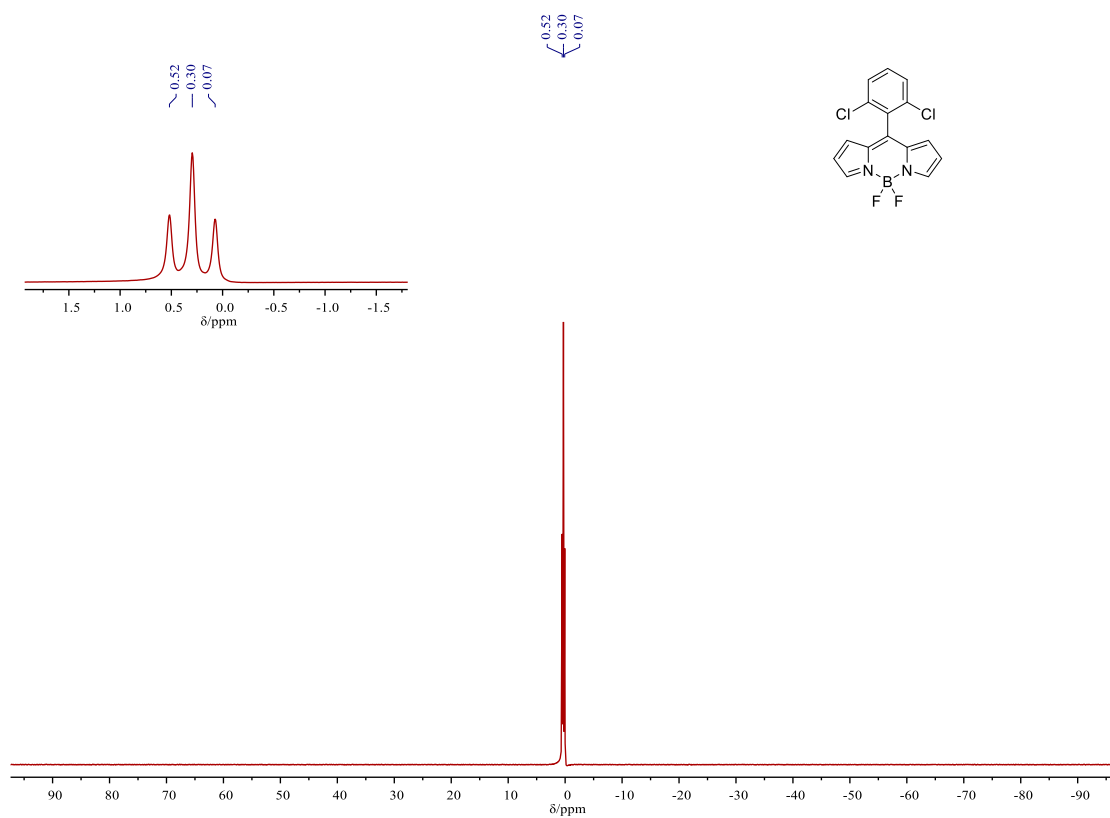
^{11}B NMR (128 MHz, CDCl_3) of compound **1aNH₂**.



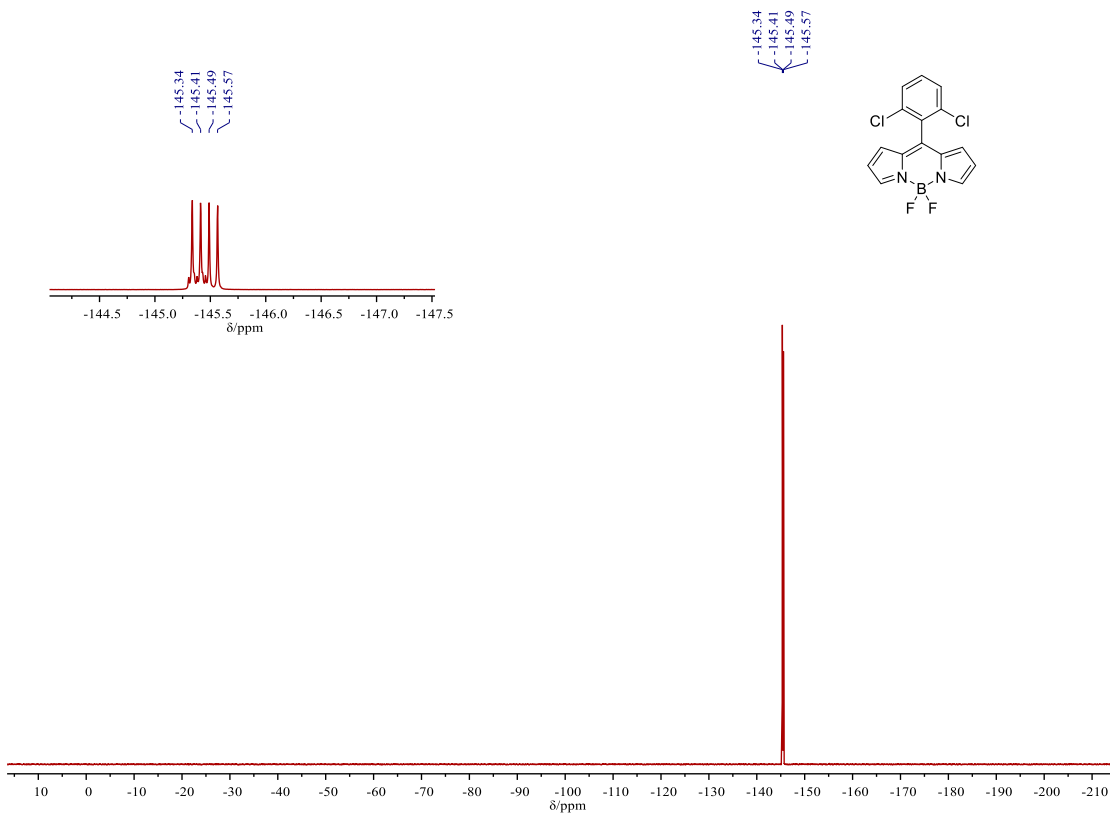
^{19}F NMR (376 MHz, CDCl_3) of compound **1aNH₂**.



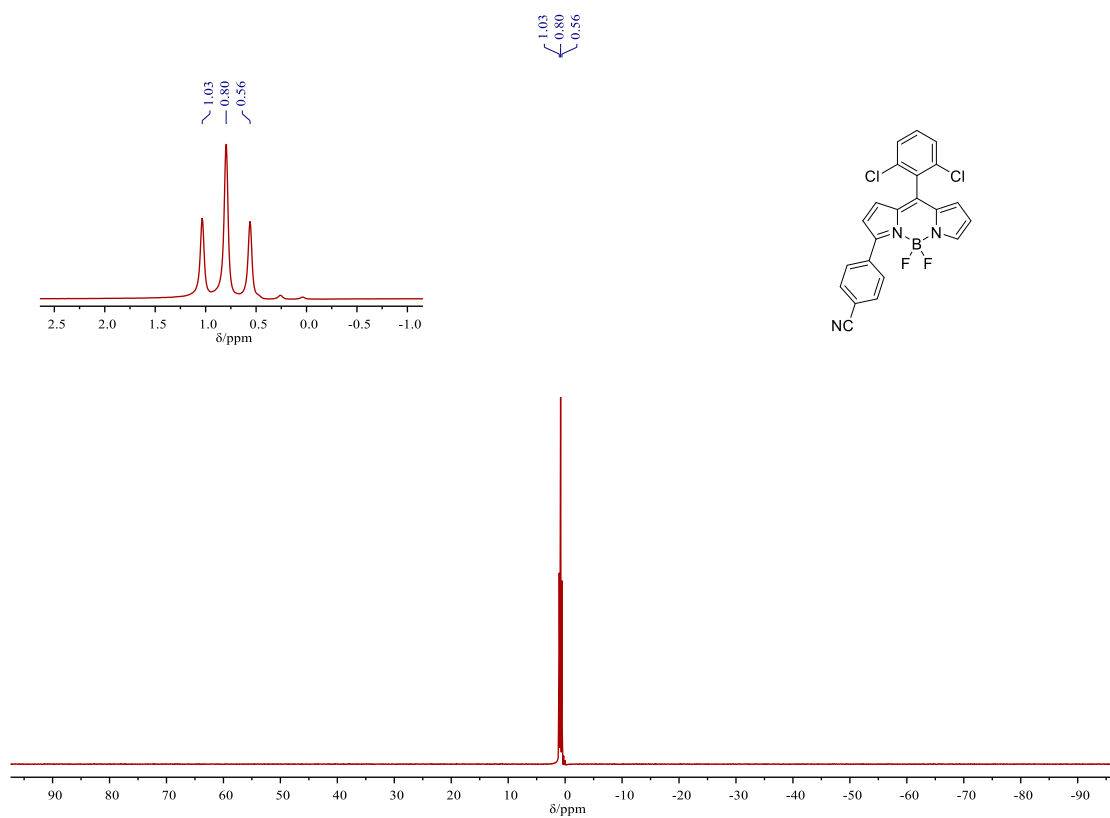
^{11}B NMR (128 MHz, CDCl_3) of compound **1b**.



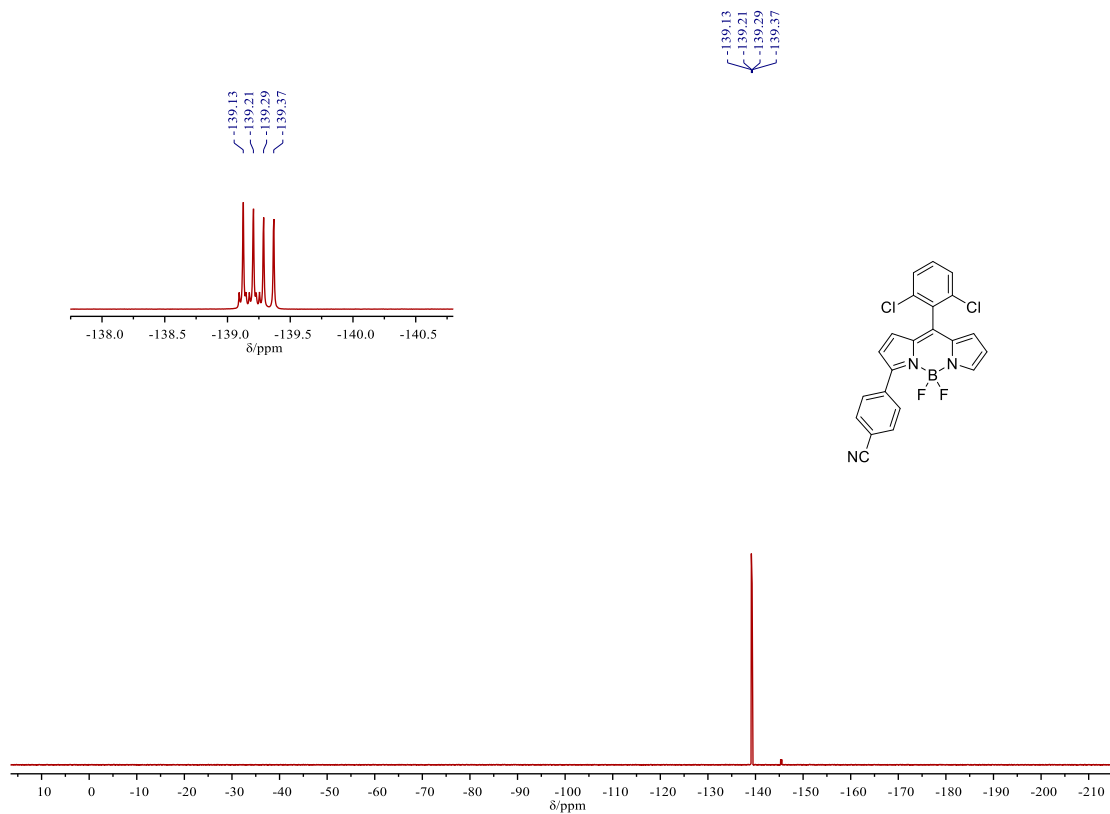
^{19}F NMR (376 MHz, CDCl_3) of compound **1b**.



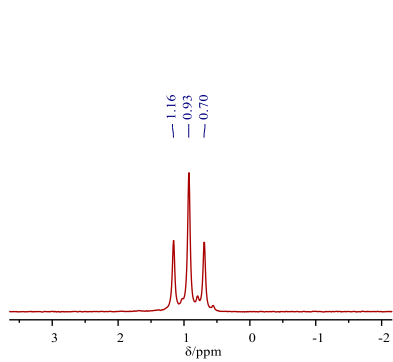
^{11}B NMR (128 MHz, CDCl_3) of compound **1bH**.



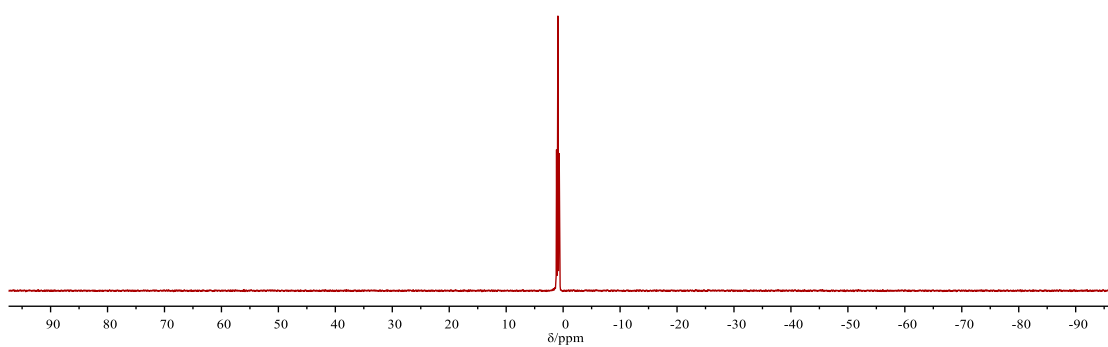
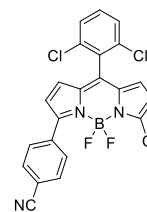
^{19}F NMR (376 MHz, CDCl_3) of compound **1bH**.



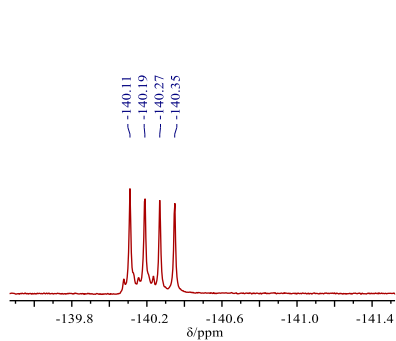
^{11}B NMR (128 MHz, CDCl_3) of compound **1bCl**.



1.16
0.93
0.70

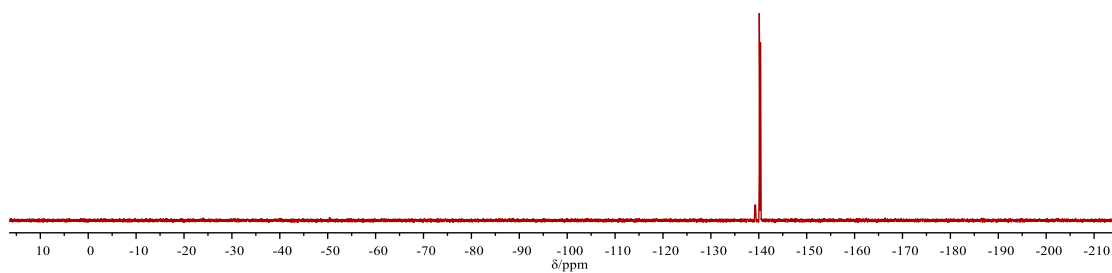
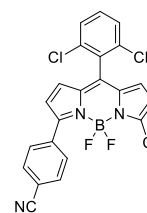


^{19}F NMR (376 MHz, CDCl_3) of compound **1bCl**.

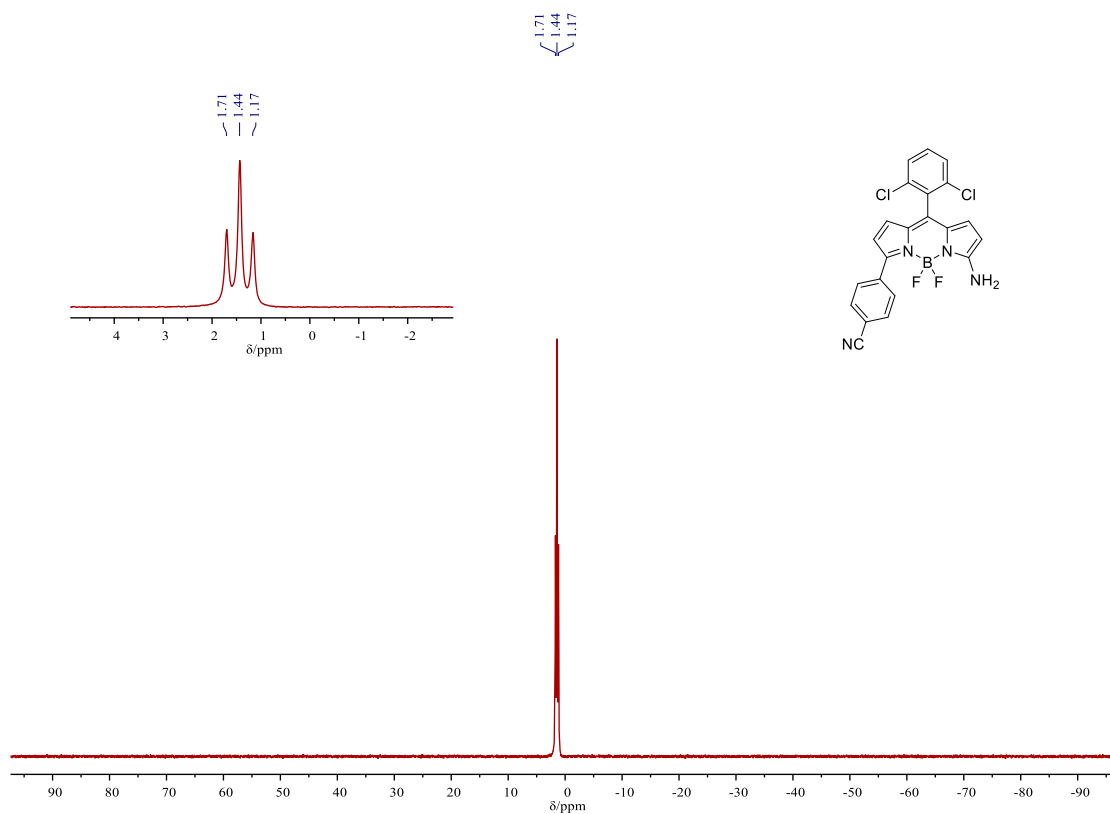


140.11
140.19
140.27
140.35

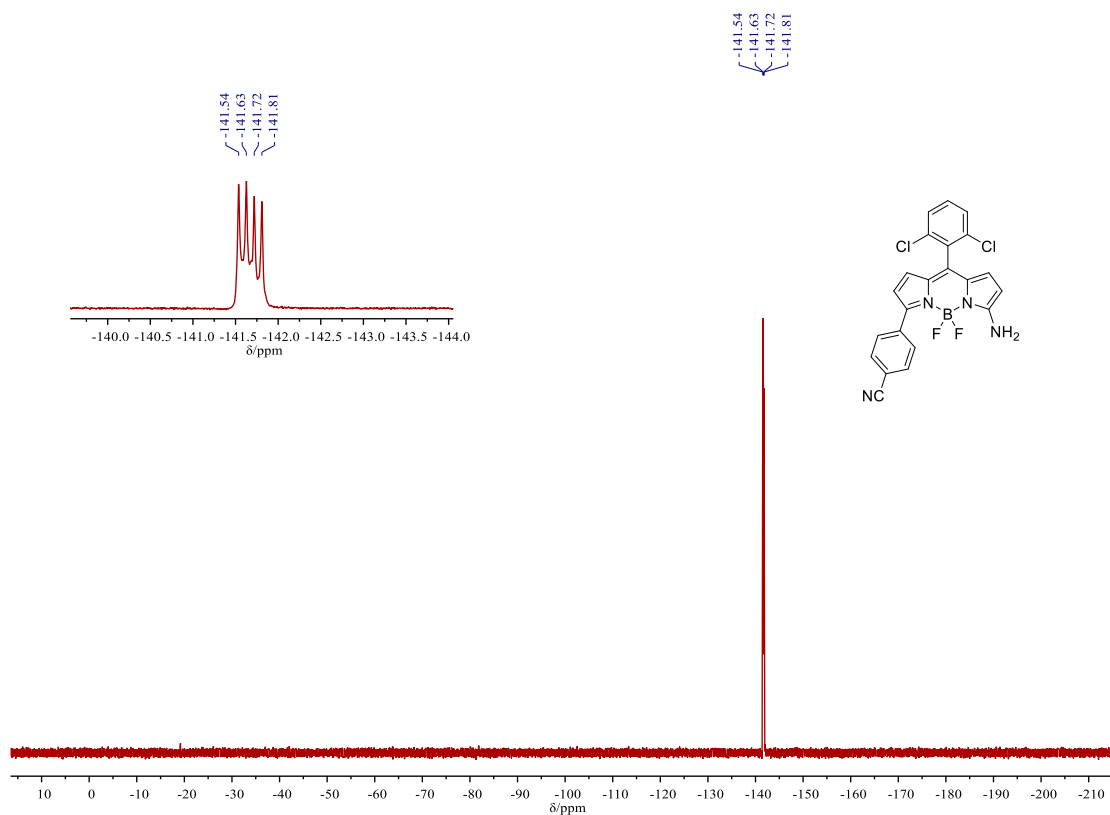
140.11
140.19
140.27
140.35



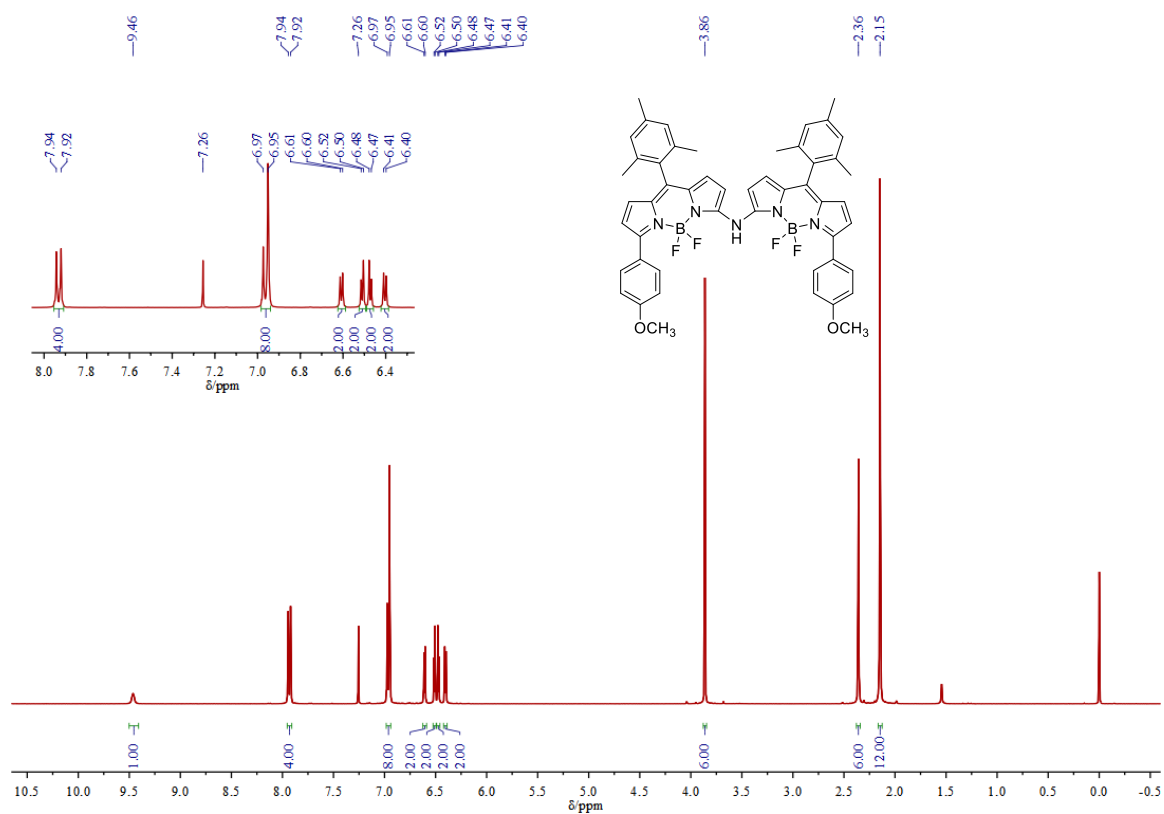
^{11}B NMR (128 MHz, CDCl_3) of compound **1bNH2**.



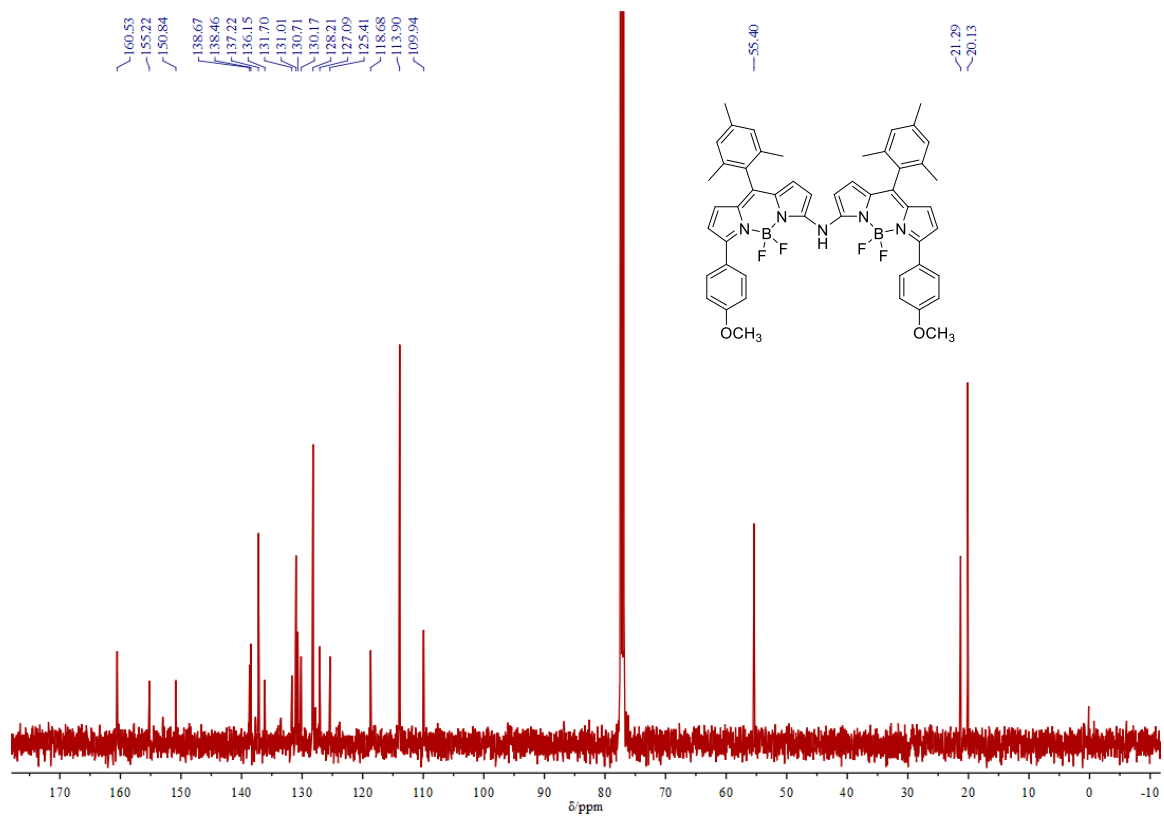
^{19}F NMR (376 MHz, CDCl_3) of compound **1bNH2**.



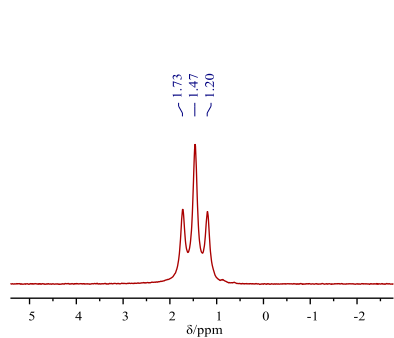
^1H NMR (400 MHz, CDCl_3) of compound **2a**.



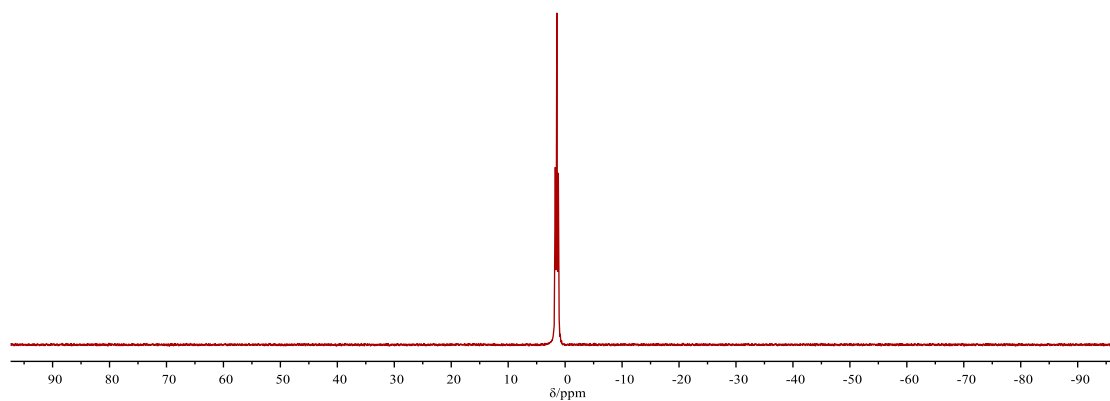
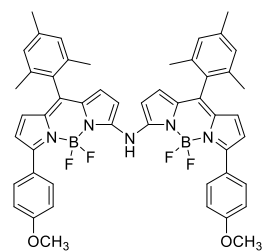
^{13}C NMR (125 M, CDCl_3) of compound **2a**.



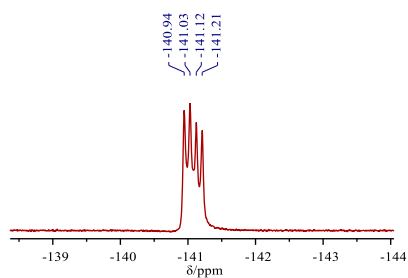
^{11}B NMR (128 MHz, CDCl_3) of compound **2a**.



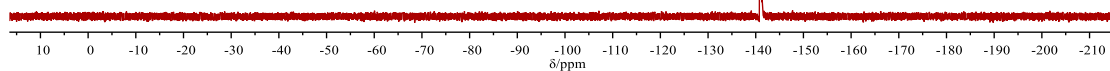
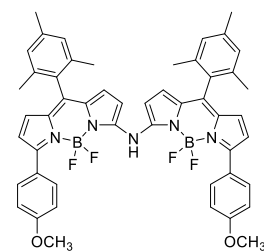
1.73
1.47
1.20



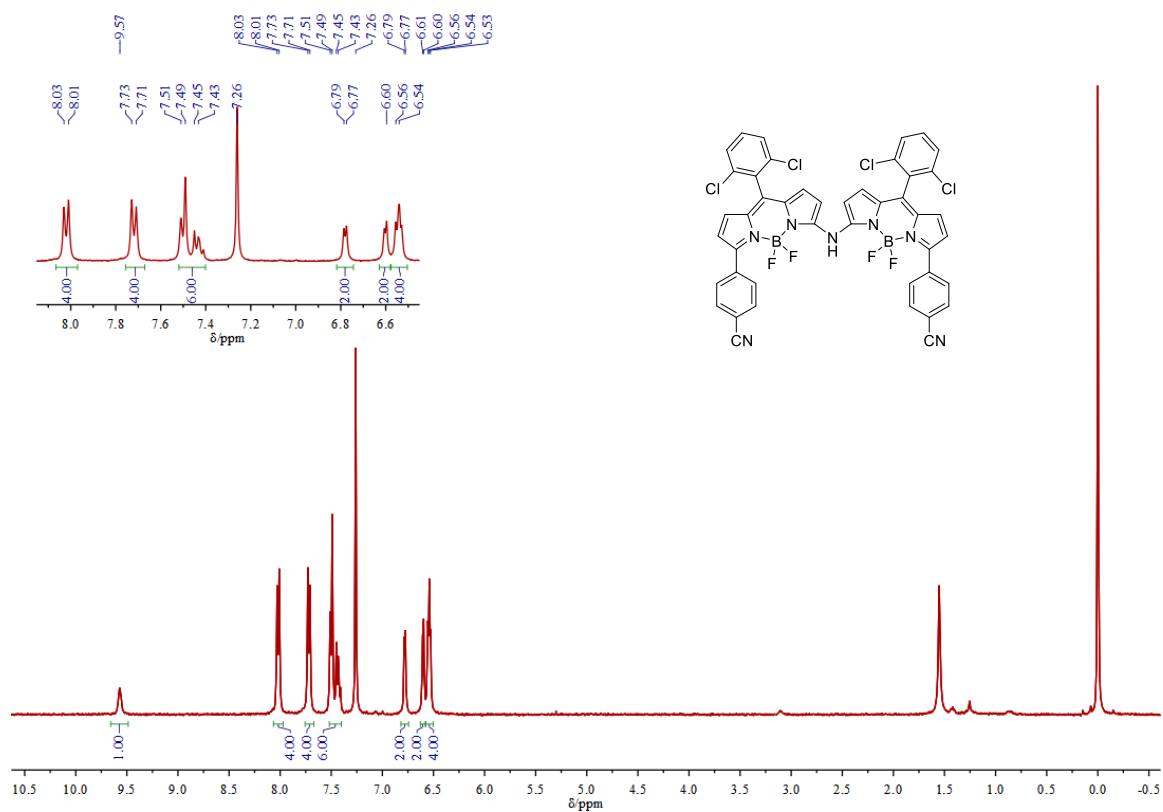
^{19}F NMR (376 MHz, CDCl_3) of compound **2a**.



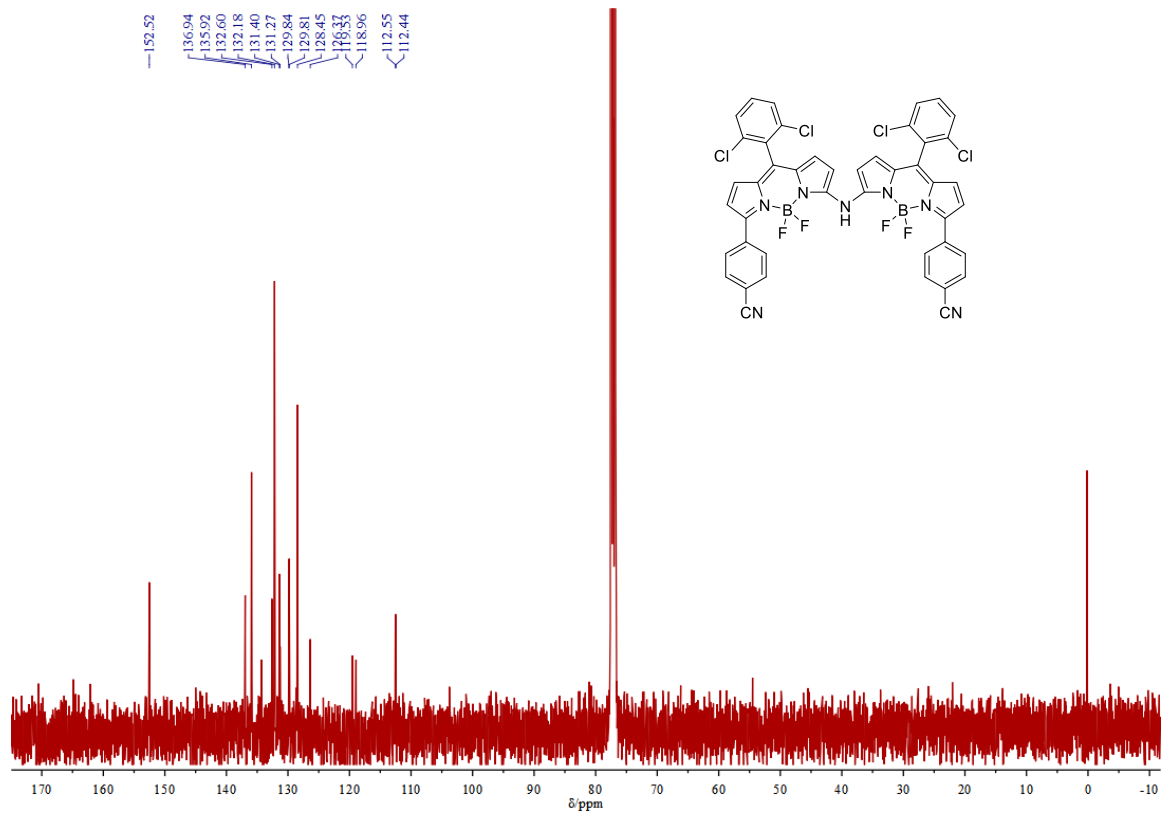
-140.94
-141.03
-141.12
-141.21



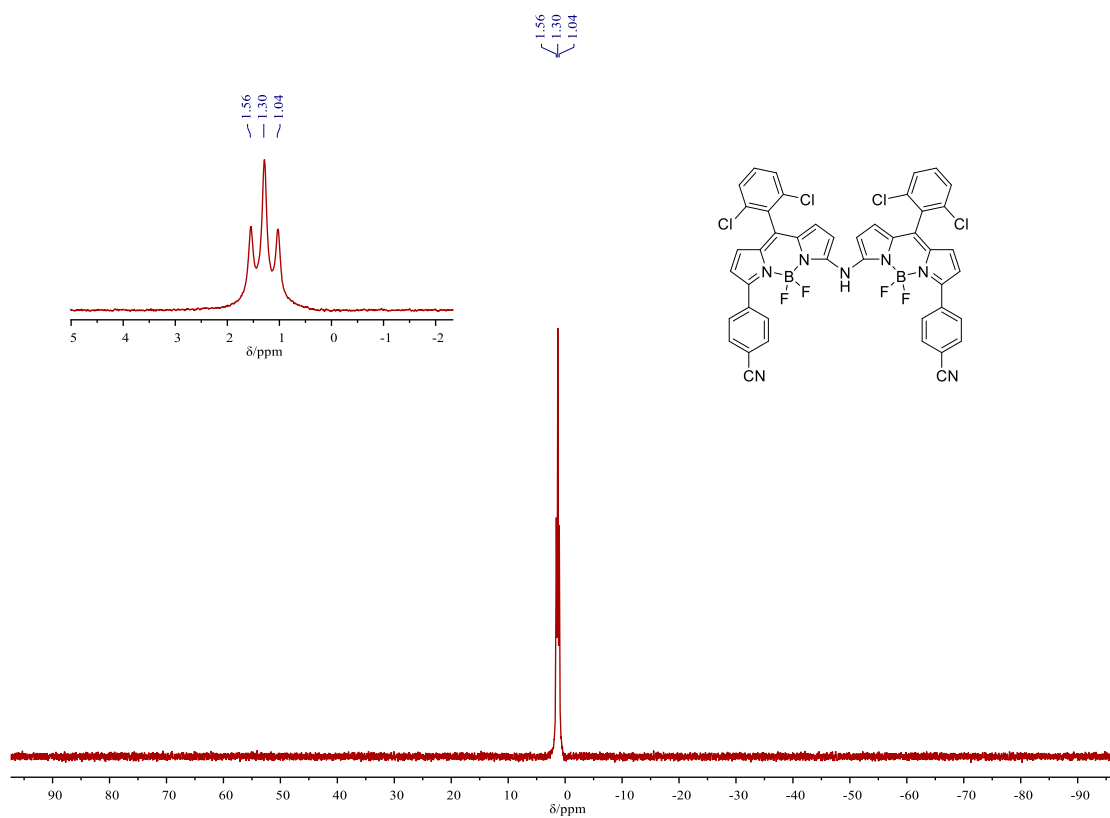
^1H NMR (400 MHz, CDCl_3) of compound **2b**.



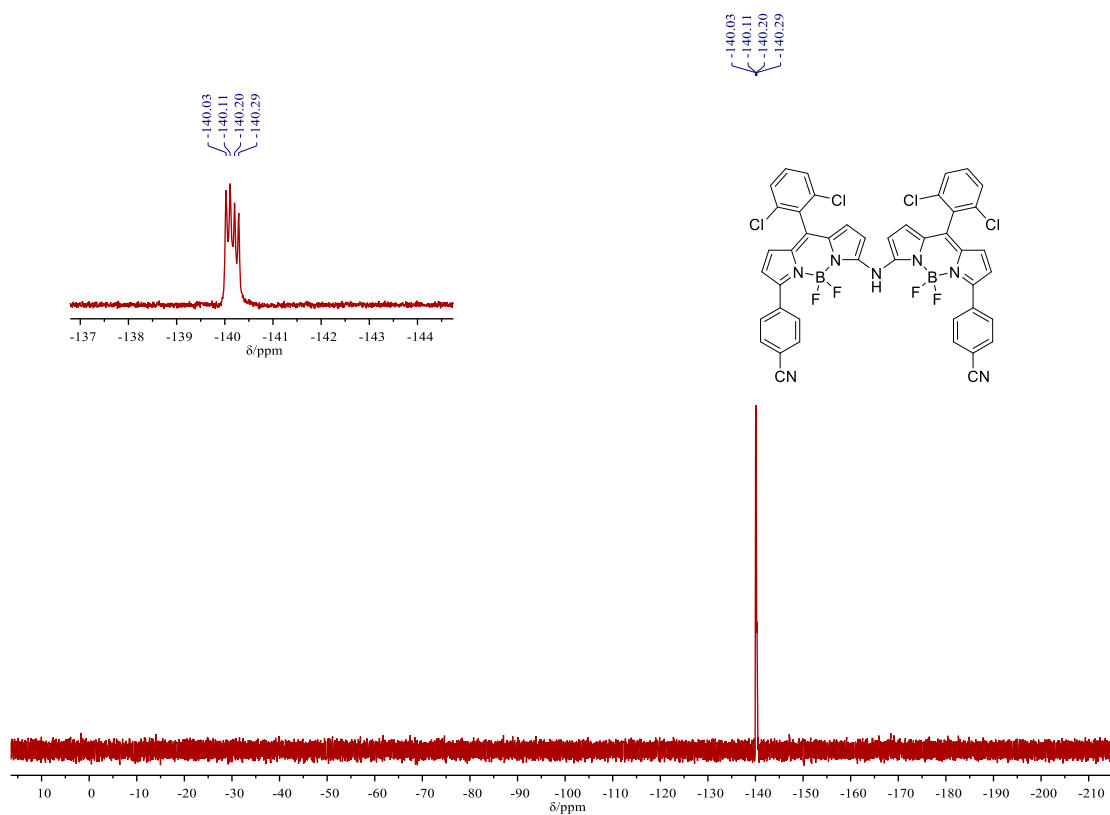
^{13}C NMR (100 M, CDCl_3) of compound **2b**.



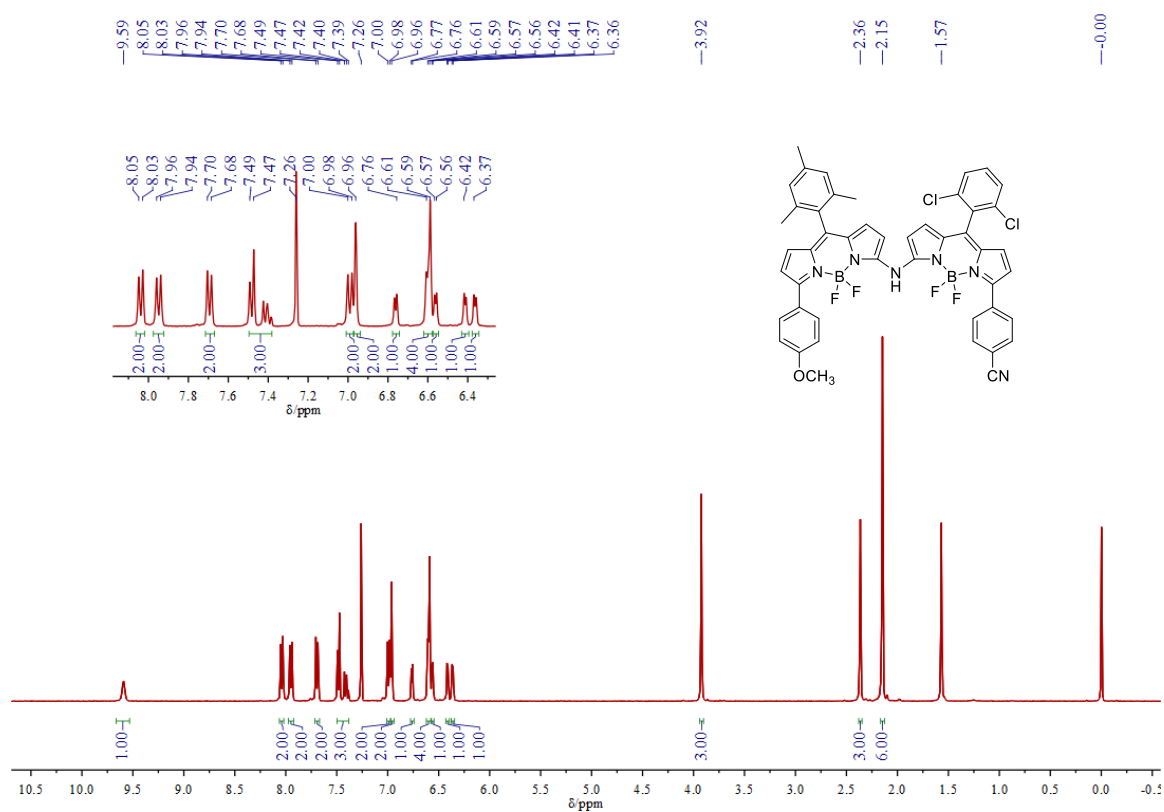
^{11}B NMR (128 MHz, CDCl_3) of compound **2b**.



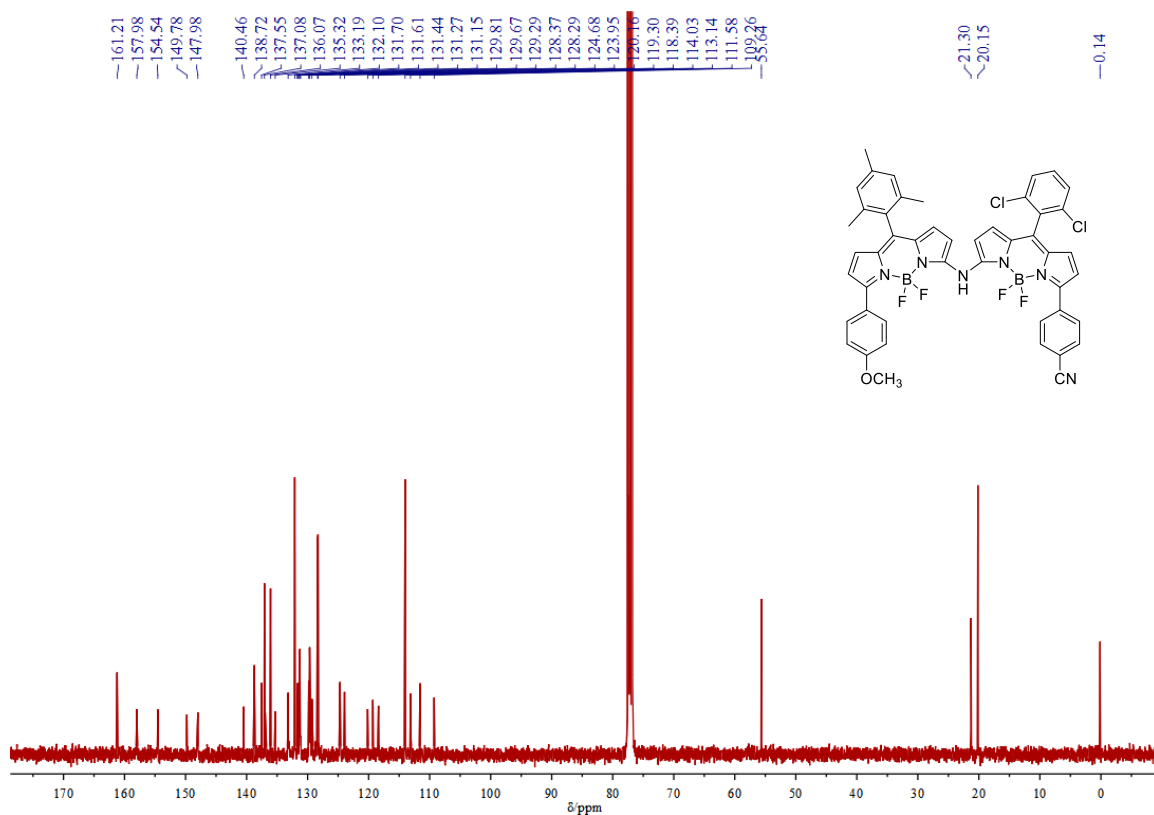
^{19}F NMR (376 MHz, CDCl_3) of compound **2b**.



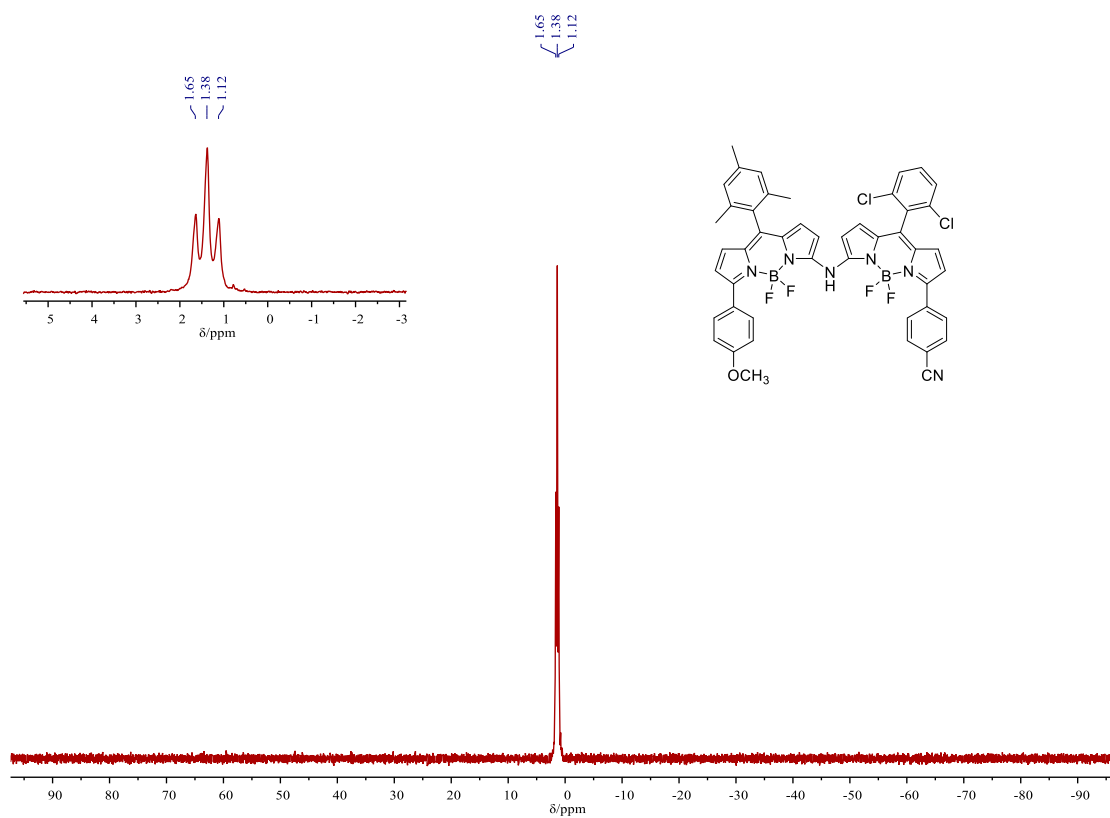
^1H NMR (400 MHz, CDCl_3) of compound **2c**.



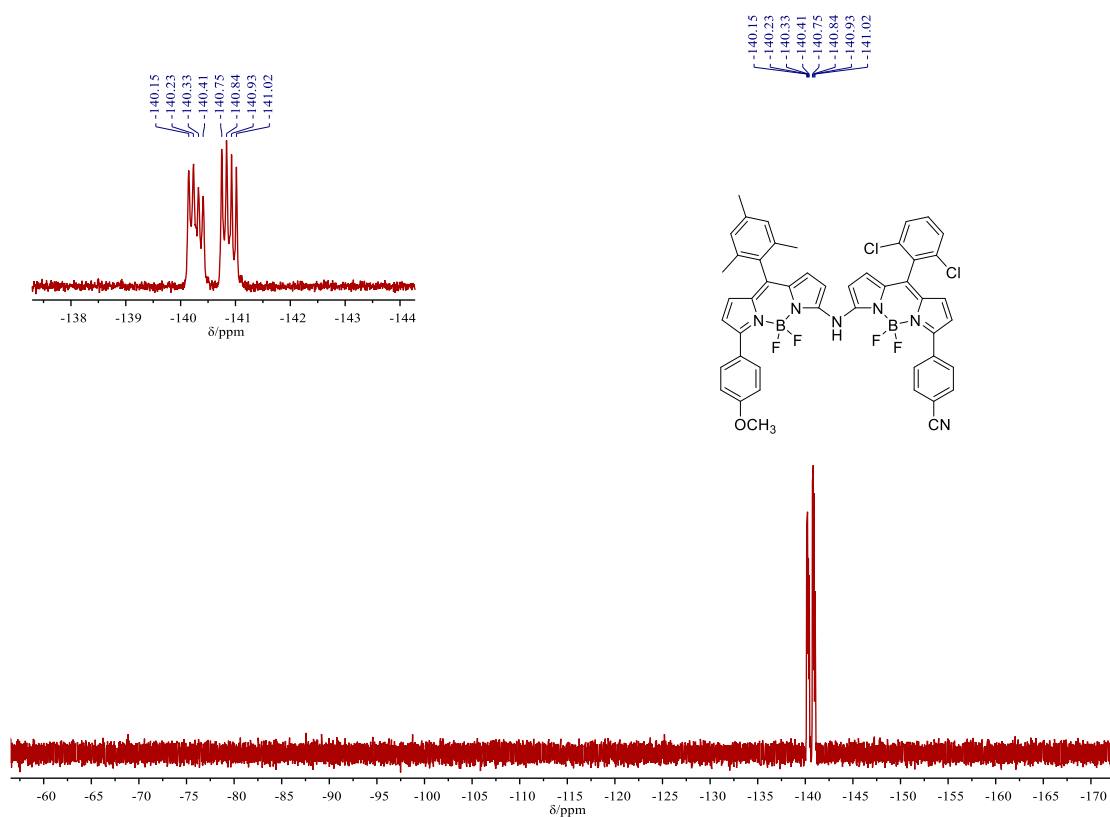
^{13}C NMR (100 M, CDCl_3) of compound **2c**.



^{11}B NMR (128 MHz, CDCl_3) of compound **2c**.

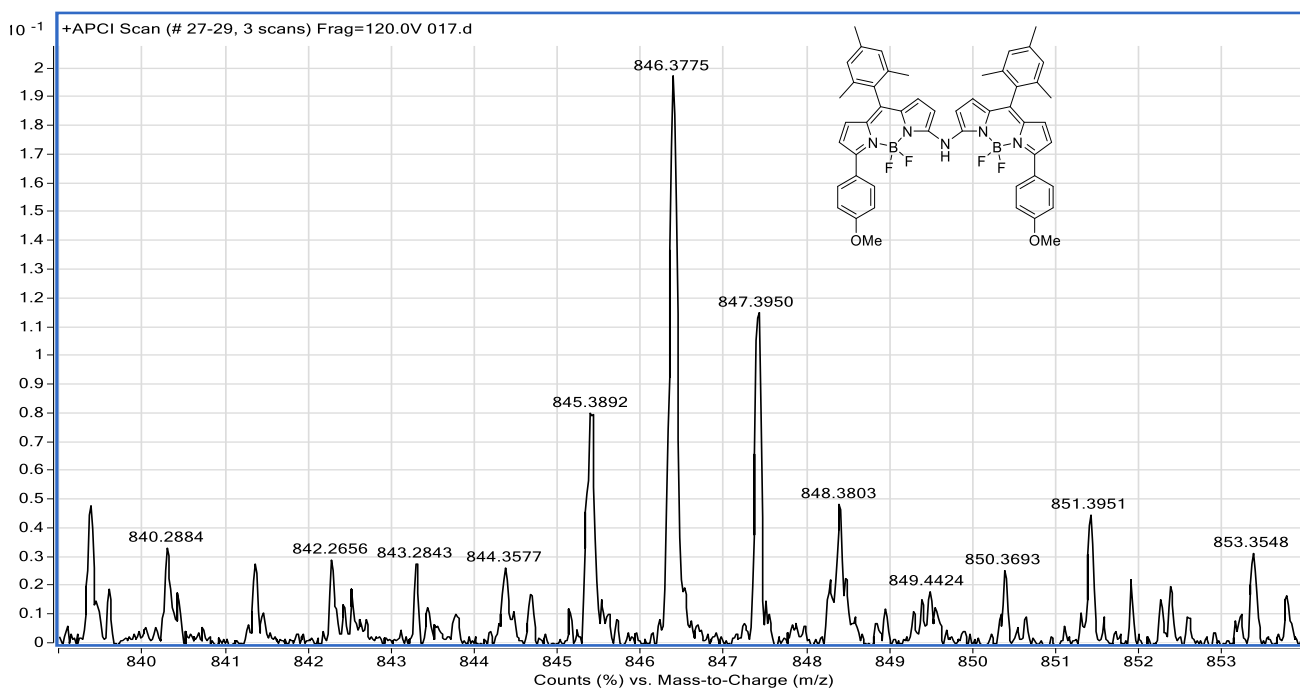


^{19}F NMR (376 MHz, CDCl_3) of compound **2c**.

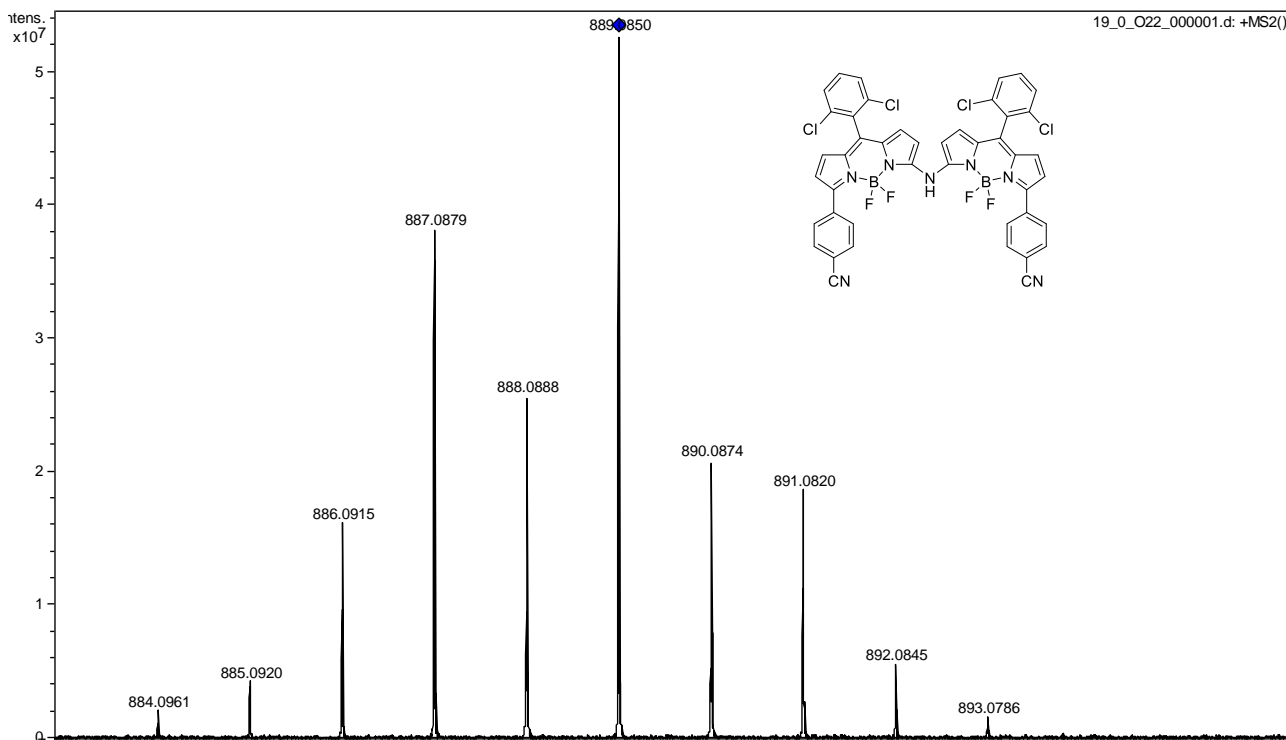


9. HRMS spectra of all new compounds.

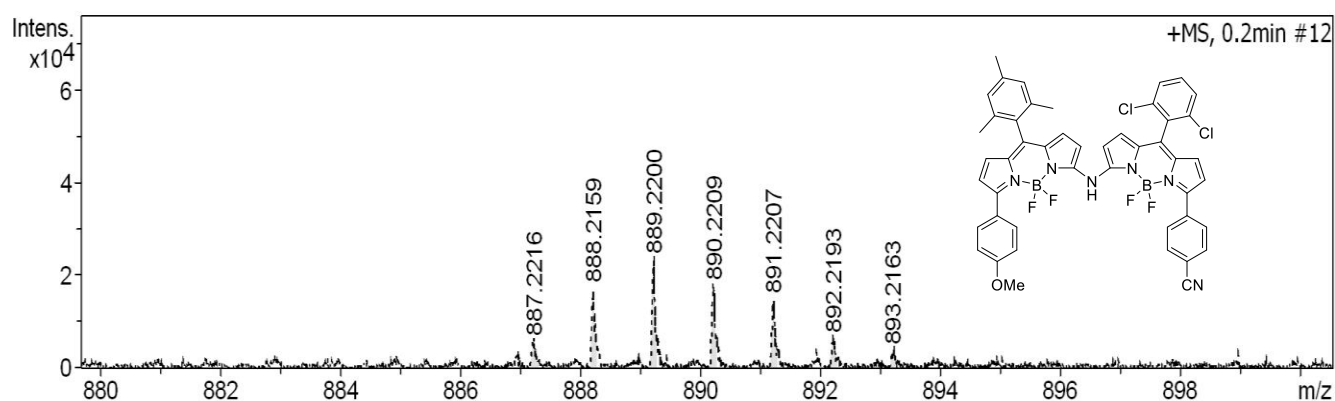
HRMS spectra of compound 2a



HRMS spectra of compound 2b



HRMS spectra of compound **2c**.



10. Author contribution statement

Long Wang: Investigation, data testing, validation, editing.

Cheng Cheng: Investigation, data testing.

Changjiang Yu: Supervision, writing, reviewing, funding acquisition.

Qinghua Wu: Carried out theoretical calculations, Writing about theoretical calculations.

Zhengxin Kang: Data testing.

Hua Wang: Supervision, reviewing.

Lijuan Jiao: Reviewing, supervision.

Erhong Hao: Funding acquisition, validation, reviewing, supervision.

11. References

1. Benson, R. C.; Kues, H. A. Fluorescence properties of indocyanine green as related to angiography. *Phys. Med. Biol.* **1978**, *23*, 159.
2. Lakowicz, J. R. Principles of Fluorescence Spectroscopy, 3rd ed.; Springer: New York, **2006**.
3. Software for the integration of CCD detector system Bruker analytical X-ray systems, Bruker axS, Madison, WI (after **2013**).
4. APEX2 suite for crystallographic software, Bruker axS, Madison, WI.
5. Dolomanov, O.; Bourhis, J.; Gildea, R.; Howard, J.; Puschmann, H. Olex2: A complete structure solution, refinement and analysis program, *J. Appl. Cryst.* **2009**, *42*, 339.
6. Sheldrick, G.M. Crystal structure refinement with ShelXL, *Acta Cryst.* **2015**, *A71*, 3.
7. (a) Feng, Z.; Feng, Y.; Yu, C.; Chen, N.; Wei, Y.; Mu, X.; Jiao, L.; Hao, E. Regioselective and stepwise syntheses of functionalized BODIPY dyes through palladium-catalyzed cross-coupling reactions and direct C–H arylations. *J. Org. Chem.* **2016**, *81*, 6281; (b) Li, W.; Li, L.; Xiao, H.; Qi, R.; Huang, Y.; Xie, Z.; Jing, X.; Zhang, H. Iodo-BODIPY: A visible-light-driven, highly efficient and photostable metal-free organic photocatalyst. *RSC Adv.* **2013**, *3*, 13417; (c) Batat, P.; Cantuel, M.; Jonusauskas, G.; Scarpantonio, L.; Palma, A.; O’Shea, D. F.; McClenaghan, N. D. BF₂-azadipyrrromethenes: Probing the excited-state dynamics of a NIR fluorophore and photodynamic

- therapy agent. *J. Phys. Chem. A*. **2011**, *115*, 14034. (d) Usui, Y. Determination of quantum yield of singlet oxygen formation by photosensitization. *Chem. Lett.* **1973**, *2*, 743.
8. Rohand, T.; Dolusic, E.; Ngo, T. H.; Maes, W.; Dehaen, W. Efficient synthesis of arylidipyrromethanes in water and their application in the synthesis of corroles and dipyrromethenes. *Arkivoc* **2007**, *10*, 307.
9. Zhou, X.; Yu, C.; Feng, Z.; Yu, Y.; Wang, J.; Hao, E.; Wei, Y.; Mu, X.; Jiao, L. Highly regioselective α -chlorination of the BODIPY chromophore with copper(II) chloride. *Org. Lett.* **2015**, *17*, 4632.
10. Wang, L.; Wu, Q.; Kang, Z.; Guo, X.; Miao, W.; Li, Z.; Zuo, H.; Wang, H.; Si, H.; Jiao, L.; Hao, E. Regioselective synthesis of directly connected BODIPY dimers through oxidative coupling of α -amino-substituted BODIPYs. *Org. Lett.* **2023**, *25*, 5055.
11. Yu, C.; Jiao, L.; Yin, H.; Zhou, J.; Pang, W.; Wu, Y.; Wang, Z.; Yang, G.; Hao, E. α -/ β -ornylated boron-dipyrin (BODIPY) dyes: Regioselective syntheses and photophysical properties. *Eur. J. Org. Chem.* **2011**, *28*, 5460.
12. Wang, D.; Cheng, C.; Wu, Q.; Wang, J.; Kang, Z.; Guo, X.; Wu, H.; Hao, E.; Jiao, L. Visible-light excitation of BODIPYs enables self-promoted radical arylation at their 3,5-positions with diazonium salts. *Org. Lett.* **2019**, *21*, 5121.
13. Zhang, D.; Wu, L.; Yang, Q.; Li, X.; Zhang, L.; Tung, C. Versatile photosensitization system for $^1\text{O}_2$ -mediated oxidation of alkenes based on nafion-supported platinum(II) terpyridyl acetylide complex. *Org. Lett.* **2003**, *5*, 3221.
14. Tian, L.; Tang, Z.; Hao, L.; Dai, T.; Zou, J.; Liu, Z. Efficient homolytic cleavage of H_2O_2 on hydroxyl-enriched spinel CuFe_2O_4 with dual lewis acid sites. *Angew. Chem., Int. Ed.* **2024**, *63*, e202401434.
15. Gaussian 09, Revision A.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P. A.; Izmaylov, F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Jr., Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2009**.