

## Supporting Information

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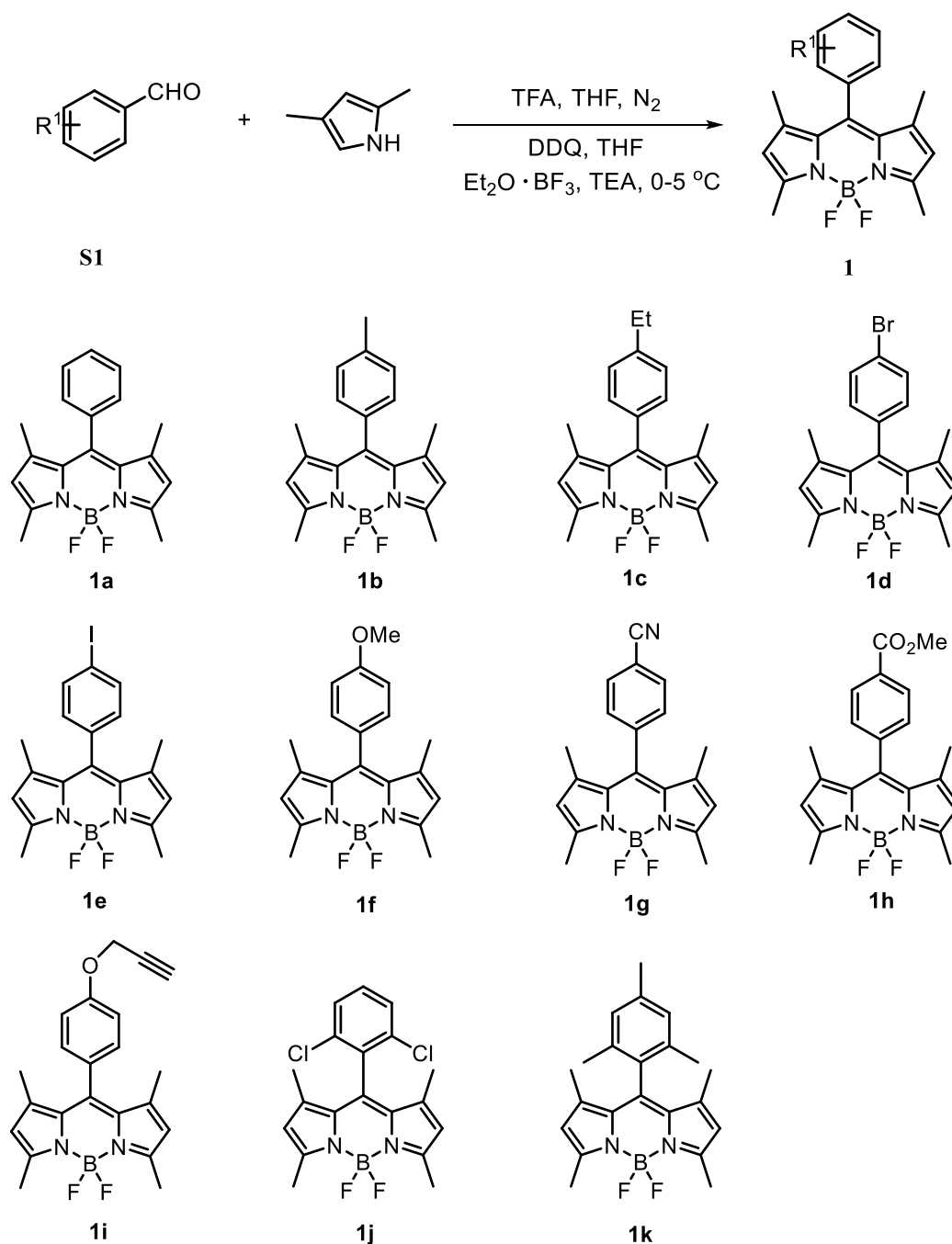
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## General methods

Unless noted, all commercial reagents and solvents were used without further purification. NMR spectra were recorded in  $\text{CDCl}_3$  or DMSO on 500 MHz spectrometers. The following abbreviations are used for multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, and m = multiplet. Mass spectra were obtained on an Ultima Global spectrometer with an ESI source. Silica gel (200–300 mesh) for column chromatography and silica GF254 for TLC were produced by Qingdao Marine Chemical Company (China). DC power supply DPS-305CF was used for all experiments.

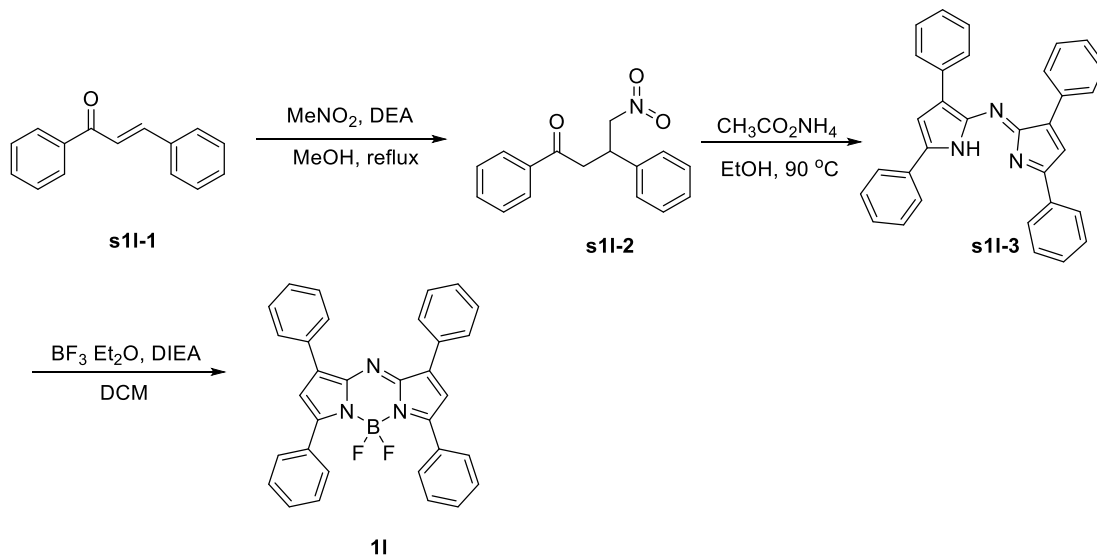
## Preparation of the starting materials

### Preparation of substrates 1<sup>1</sup>



**S1 to 1:** Under nitrogen atmosphere and in no light conditions, synthesis of **S1** (7.5 mmol) and 2,4-dimethylpyrrole 1.8 g (22.5 mmol) were dissolved in THF (30 mL), to this, TFA drop was added and stirred for 16 hours under room temperature. To the reaction mixture, 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) 1.87 g (8.3 mmol) was added, after stirring for 3 hours at room temperature. Finally, the mixture was then

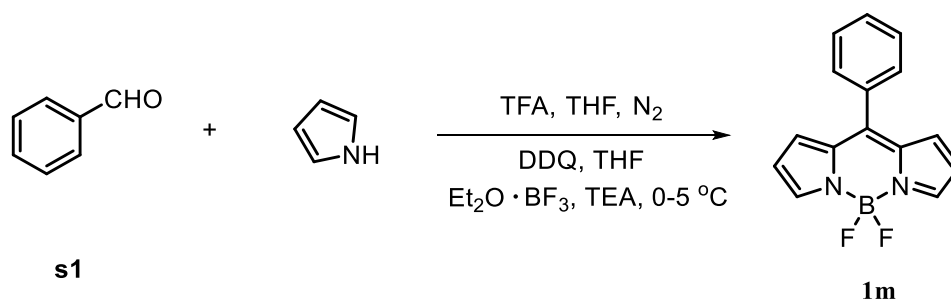
added a solution of TEA (20 mL) at 0 °C, stir for one minute and then added BF<sub>3</sub>OEt<sub>2</sub> (20 mL). The reaction was kept stirring at 0 °C for 2 h. The resulting mixture was allowed to warm to room temperature and was stirred for 12 h.



Synthesis of Aza-BODIPY **11**<sup>[2]</sup>: Prepare a solution of **s11-1** (1.0 g, 4.80 mmol) in nitromethane (10 mL). Add 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU, 146 mg, 0.96 mmol) dropwise to the above solution at room temperature. Stir the resulting solution for 2 h at room temperature, Concentrate under vacuum. Purify the residue by flash chromatography [(petroleum ether/EtOAc 9:1)] to afford **s11-2**.

A 100 mL round-bottomed flask was charged with **s11-2** (1.0 g, 3.71 mmol), ammonium acetate (10.0 g, 0.13 mol), and ethanol (40 mL) and heated under reflux for 24 h. During the course of the reaction, the product precipitated from the reaction mixture. The reaction was cooled to room temperature and filtered and the isolated solid washed with ethanol (2 × 10 mL) to yield the product **s11-3** as a blue black solid (0.30 g, 35%).

**s11-3** (0.2 g, 0.45 mmol) was dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (80 mL), treated with diisopropylethylamine (0.8 mL, 4.6 mmol) and boron trifluoride diethyl etherate (1 mL, 8.13 mmol), and stirred at room temperature under N<sub>2</sub> for 24 h. The mixture was washed with water (2 × 50 mL), and organic layer was dried over sodium sulfate and evaporated to dryness. Purification by column chromatography on silica eluting with CH<sub>2</sub>Cl<sub>2</sub>/hexane (1:1) gave the product **11** as a metallic brown solid (0.19 g, 86%).

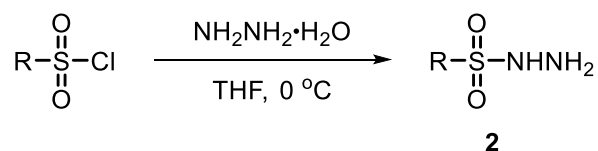


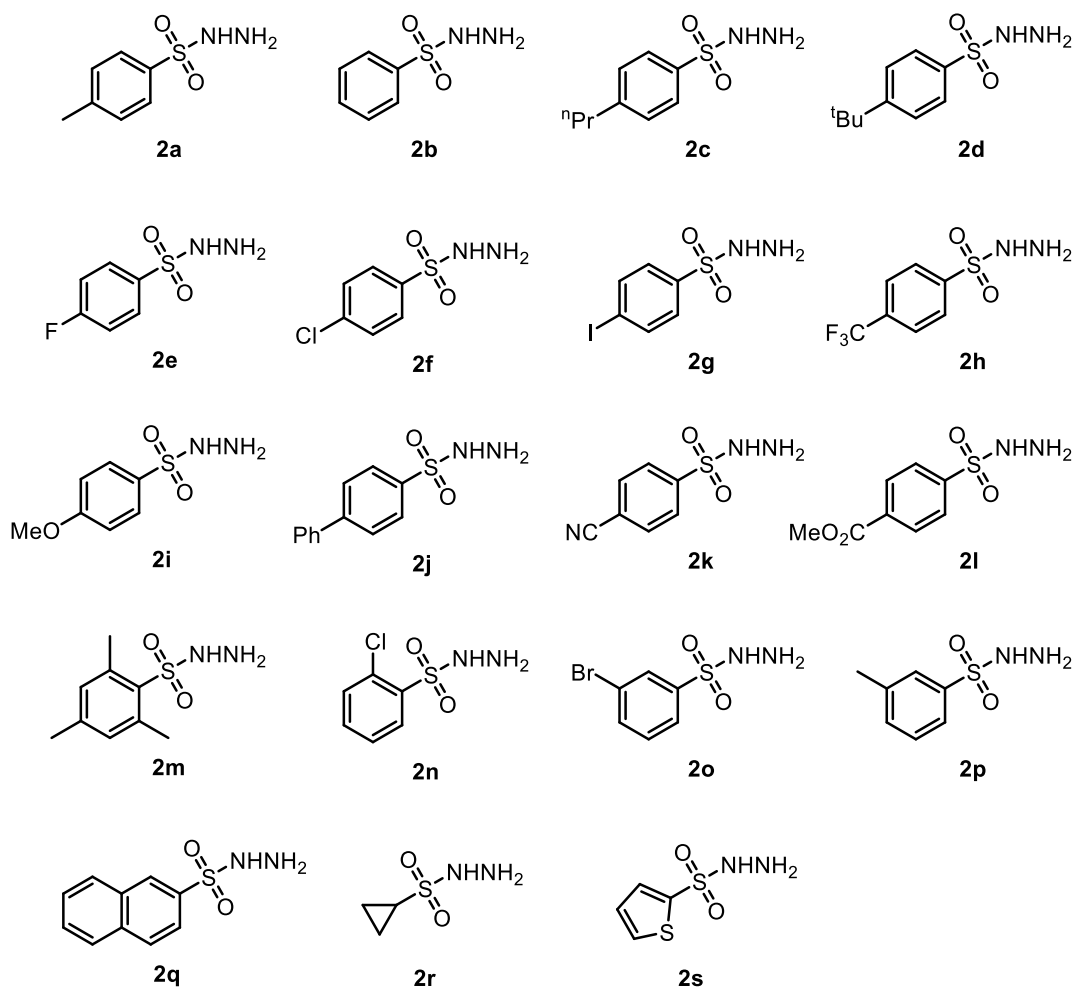
Synthesis of BODIPY **1m**<sup>[3]</sup>: To a solution of the corresponding aromatic aldehyde (1 eq.) in pyrrole (4 eq.) was added a catalytic amount of trifluoroacetic acid (TFA). The mixture was stirred at room temperature until the total consumption of the aldehyde. The crude product was washed with brine, extracted with CH<sub>2</sub>Cl<sub>2</sub>, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness under vacuum. This crude was then purified using column chromatography on silica gel using hexane/ethyl acetate.

Into the corresponding dipyrromethane dissolved in CH<sub>2</sub>Cl<sub>2</sub>, DDQ (1 eq.) was added and the solution was stirred for 1 h at room temperature. To this oxidized product, BF<sub>3</sub>Et<sub>2</sub>O (6 eq.) was added under a nitrogen atmosphere and stirred for another 15 min, then, triethylamine (3 eq.) was added dropwise and stirring was continued till the completion of the reaction which was monitored by TLC. The reaction mixture was then washed with brine and extracted with CH<sub>2</sub>Cl<sub>2</sub>, and the organic layer was combined, dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness under vacuum to give the crude product. This was further purified by silica gel column chromatography to afford the corresponding BODIPY **1m**.

### Preparation of substrates **2**<sup>3</sup>

The compound **2b** - **2r** according to previously described methods.<sup>[3]</sup>



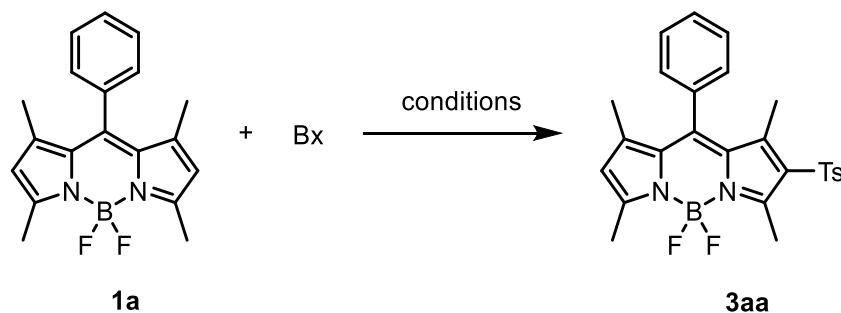


The hydrazine hydrate (80%, 30 mmol) was added dropwise into the solution of sulfonyl chloride (10 mmol) in THF (50 mL) under air at 0 °C. Subsequently, the mixture was further stirred at 0 °C for 5 minutes. After the completion of the reaction, the residue was extracted with DCM, and the combined organic layer was washed with water, and brine, and dried over MgSO<sub>4</sub>. Concentration in vacuum followed by silica gel column purification with petroleum ether/ethyl acetate eluent gave the desired products **2**.

## Conditional filter supplement

### Other sulfone-based compounds

Table S1 Screening of sulfone-based compounds

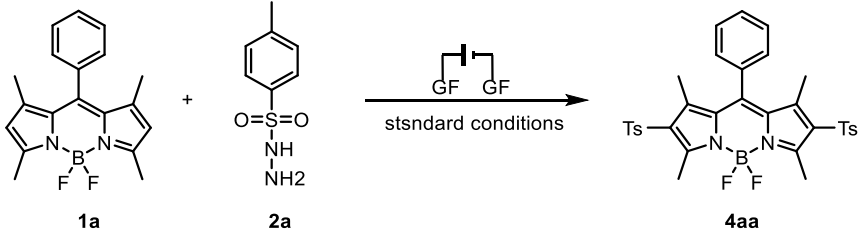


Entry	Bx	conditions	Yield
1	 H <sub>2</sub> O	HFIP (2.5 mL), CH <sub>3</sub> NO <sub>2</sub> (2.5 mL), H <sub>2</sub> O (0.2 mL), NaCl, Graphite felt electrodes, constant current = 6 mA, under N <sub>2</sub> , RT, 4h	0
2	 H <sub>2</sub> O	HFIP (2.5 mL), CH <sub>3</sub> NO <sub>2</sub> (2.5 mL), H <sub>2</sub> O (0.2 mL), NaCl, Graphite felt electrodes, constant current = 6 mA, under N <sub>2</sub> , RT, 3h	0
3	 Na <sup>+</sup>	HFIP (2.5 mL), CH <sub>3</sub> NO <sub>2</sub> (2.5 mL), H <sub>2</sub> O (0.2 mL), NaCl, Graphite felt electrodes, constant current = 6 mA, under N <sub>2</sub> , RT, 3h	0
4	 Na <sup>+</sup>	HFIP (2.5 mL), CH <sub>3</sub> NO <sub>2</sub> (2.5 mL), H <sub>2</sub> O (0.2 mL), NaCl, Graphite felt electrodes, constant current = 6 mA, under N <sub>2</sub> , RT, 3.5	10

In an undivided Schlenk flask (10 mL) equipped with a stir bar, substrate **1** (0.1 mmol, 1 equiv.), Sulfone-based compound **Bx** (0.3 mmol, 3 equiv.) and NaCl (0.15 mmol), were combined and added. The flask was equipped with a rubber stopper, a graphite felt anode (1 cm x 1 cm x 0.5 cm) and a graphite felt cathode (1 cm x 1 cm x 0.5 cm) and then flushed with nitrogen. Then HFIP (2.5 mL), CH<sub>3</sub>NO<sub>2</sub> (2.5 mL) and H<sub>2</sub>O (0.2 mL) were injected respectively into the flask via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 6.0 mA at room temperature until the end of the reaction. Only sodium p-toluenesulfonate has a corresponding product point by TLC point plate. When the reaction was finished, the residue was chromatographed through silica gel eluting with petroleum ether/ ethyl acetate eluent, and the final yield was 10%.

## Conditional screening of bissulfonylated BODIPYs

Table S2 Optimization of disulfonylation reaction conditions<sup>a</sup>

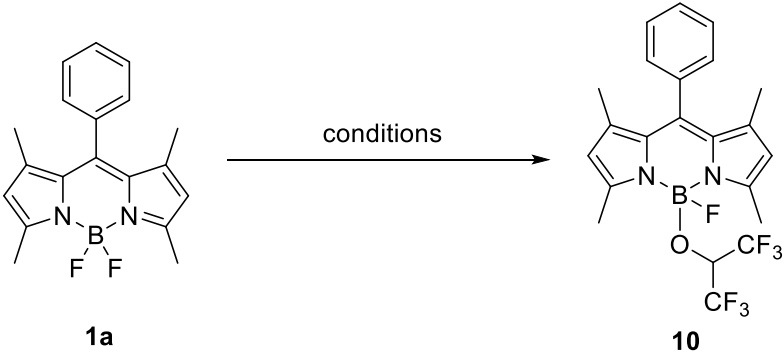


Entry	Variation from standard conditions	Yield (%) <sup>b</sup>
1	none	trace
2	5 h	11
3	7.5 h	18
4	10 h	n.p.
5	4 equiv. <b>2a</b> , 8 h	18
6	5 equiv. <b>2a</b> , 8 h	29
7	6 equiv. <b>2a</b> , 8 h	28
8	8.0 mA, 6 h	48
9	10.0 mA, 5 h	39

<sup>a</sup>Standard reaction conditions: **1a** (0.1 mmol), **2a** (0.3 mmol), NaCl (0.15 mmol), HFIP (2.5 mL), CH<sub>3</sub>NO<sub>2</sub> (2.5 mL), H<sub>2</sub>O (0.2 mL), graphite felt anode (10 mm x 10 mm x 5 mm), graphite felt cathode (10 mm x 10 mm x 5 mm), constant current = 6.0 mA, under N<sub>2</sub>, RT, 2.5 h, undivided cell. <sup>b</sup>Isolated yield. n.p. = no product.

## Side reaction

Table S3 Side reaction-related screening



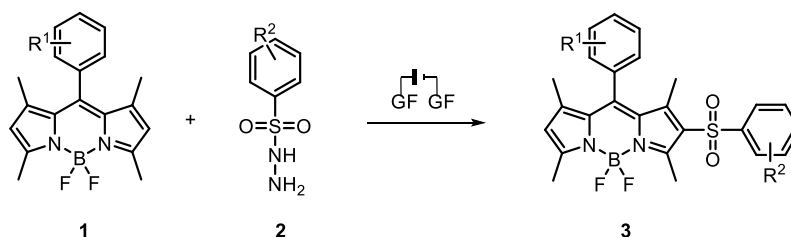
entry	conditions	Yield <sub>3aa</sub> (%)	Yield <sub>10</sub> (%)
1	<b>1a</b> , <b>2a</b> , NaCl, HFIP:MeNO <sub>2</sub> :H <sub>2</sub> O=2.5:2.5:0.2	71	trace
2	<b>1a</b> , NaCl, HFIP:MeNO <sub>2</sub> :H <sub>2</sub> O=2.5:2.5:0.2	0	trace
3	<b>1a</b> , NaCl, HFIP =5.0 ml	0	<10
4	<b>1a</b> , Et <sub>4</sub> NPF <sub>6</sub> , HFIP =5.0 ml	0	19

graphite felt anode (10 mm x 10 mm x 5 mm), graphite felt cathode (10 mm x 10 mm x 5 mm), constant current = 6.0 mA, under N<sub>2</sub>, RT, undivided cell.



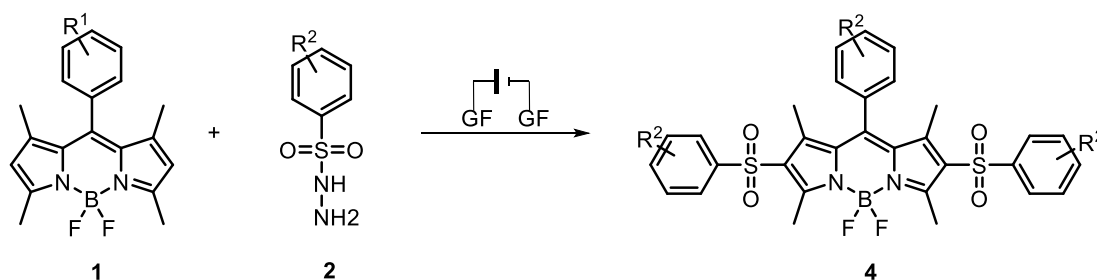
## General procedure for the synthesis of compounds **3** and **4**

### Monosulfonylated BODIPYs **3**



In an undivided Schlenk flask (10 mL) equipped with a stir bar, substrate **1** (0.1 mmol, 1 equiv.), sulfonyl hydrazide **2** (0.3 mmol, 3 equiv.) and NaCl (0.15 mmol), were combined and added. The flask was equipped with a rubber stopper, a graphite felt anode (1 cm x 1 cm x 0.5 cm) and a graphite felt cathode (1 cm x 1 cm x 0.5 cm) and then flushed with nitrogen. Then HFIP (2.5 mL), CH<sub>3</sub>NO<sub>2</sub> (2.5 mL) and H<sub>2</sub>O (0.2 mL) were injected respectively into the flask via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 6.0 mA at room temperature for 2.5 h. When the reaction was finished, the residue was chromatographed through silica gel eluting with petroleum ether/ ethyl acetate eluent to give the product **3**.

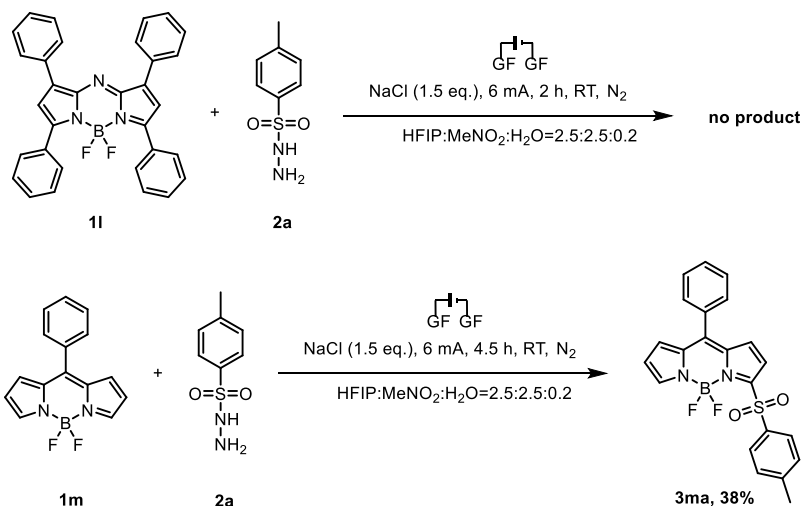
### Disulfonylated BODIPYs **3**



In an undivided Schlenk flask (10 mL) equipped with a stir bar, substrate **1** (0.1 mmol, 1 equiv.), sulfonyl hydrazide **2** (0.5 mmol, 5 equiv.) and NaCl (0.15 mmol), were combined and added. The flask was equipped with a rubber stopper, a graphite felt anode (1 cm x 1 cm x 0.5 cm) and a graphite felt cathode (1 cm x 1 cm x 0.5 cm) and then flushed with nitrogen. Then HFIP (2.5 mL), CH<sub>3</sub>NO<sub>2</sub> (2.5 mL) and H<sub>2</sub>O (0.2 mL) were injected respectively into the flask via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 8.0 mA at room temperature for 6 h. When the reaction was finished, the residue was chromatographed through silica gel eluting with

petroleum ether/ ethyl acetate eluent to give the disulfonylated product **4**.

## Electrochemical attempts at other BODIPYs

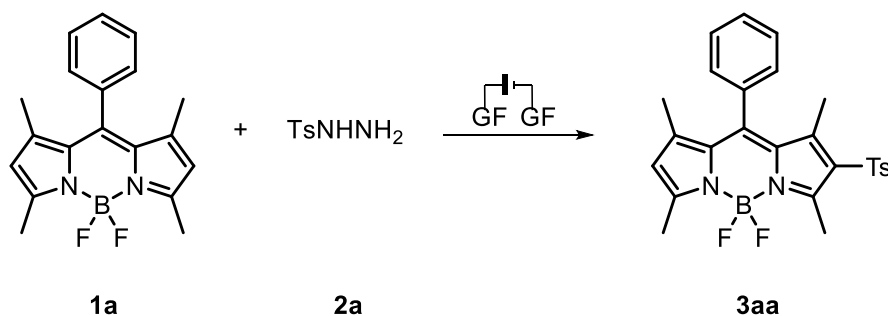


In an undivided Schlenk flask (10 mL) equipped with a stir bar, substrate **11** (0.1 mmol, 1 equiv.), sulfonyl hydrazide **2a** (0.3 mmol, 3 equiv.) and NaCl (0.15 mmol), were combined and added. The flask was equipped with a rubber stopper, a graphite felt anode (1 cm x 1 cm x 0.5 cm) and a graphite felt cathode (1 cm x 1 cm x 0.5 cm) and then flushed with nitrogen. Then HFIP (2.5 mL), CH<sub>3</sub>NO<sub>2</sub> (2.5 mL) and H<sub>2</sub>O (0.2 mL) were injected respectively into the flask via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 6.0 mA at room temperature for 2.0 h. By TLC observation, the raw materials had been completely consumed, and no product points had been observed.

In an undivided Schlenk flask (10 mL) equipped with a stir bar, substrate **1m** (0.1 mmol, 1 equiv.), sulfonyl hydrazide **2a** (0.3 mmol, 3 equiv.) and NaCl (0.15 mmol), were combined and added. The flask was equipped with a rubber stopper, a graphite felt anode (1 cm x 1 cm x 0.5 cm) and a graphite felt cathode (1 cm x 1 cm x 0.5 cm) and then flushed with nitrogen. Then HFIP (2.5 mL), CH<sub>3</sub>NO<sub>2</sub> (2.5 mL) and H<sub>2</sub>O (0.2 mL) were injected respectively into the flask via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 6.0 mA at room temperature for 4.5 h.

When the reaction was finished, the residue was chromatographed through silica gel eluting with petroleum ether/ ethyl acetate eluent to give the product **3ma**.

## Gram-scale reaction



In a round bottom three-necked flask (250 mL) equipped with a stir bar, substrate **1a** (4 mmol, 1.30 g), sulfonyl hydrazides **2a** (8 mmol, 1.49 g, 2 equiv.), and NaCl (6 mmol, 0.348 g, 1.5 equiv.) were combined and added. Then add HFIP (50 mL),  $\text{CH}_3\text{NO}_2$  (50 mL) and  $\text{H}_2\text{O}$  (4 mL) to the flask separately. The flask was equipped with a rubber stopper, a graphite felt anode (1 cm x 3 cm x 1 cm) and a graphite felt cathode (1 cm x 3 cm x 1 cm) and then flushed with nitrogen. The reaction mixture was stirred and electrolyzed at a constant current of 12 mA at room temperature for 64 h. When the reaction was finished, the residue was chromatographed through silica gel eluting with petroleum ether/ ethyl acetate eluent to give the product **3aa** (1.15 g, 60%).



**Figure S1.** Components required for gram-scale reaction

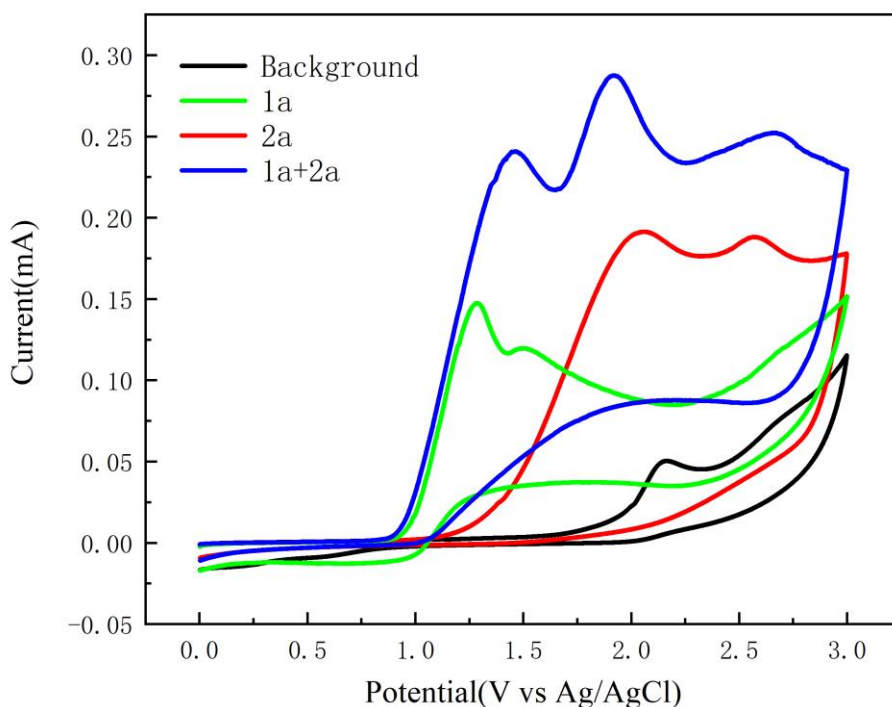
## Cyclic voltammetry study

The cyclic voltammetry experiments were carried out with a computer-controlled electrochemical analyzer for electrochemical measurements. The cyclic voltammetry experiments were measured at room temperature. The data was collected with the CS300H potentiostat (Wuhan COster Instrument Co., LTD). The experiment was performed in a three-electrode cell with HFIP (2.5 mL) and MeNO<sub>2</sub> (2.5 mL) as the solvent, Et<sub>4</sub>NPF<sub>6</sub> (0.030 M) as the supporting electrolyte, and the concentration of the **1a** was 0.020 M; the concentration of the **2a** was 0.060 M. The scan speed was 100 mV/s. The potential ranges investigated were 0 V to 3.0 V vs. SCE (saturated aqueous KCl). CV plotting convention is Origin.

**Working electrode:** The working electrode is a 3 mm diameter glassy carbon working electrode. Polished with 0.05 μm aluminum oxide and then sonicated in distilled water and ethanol before measurements.

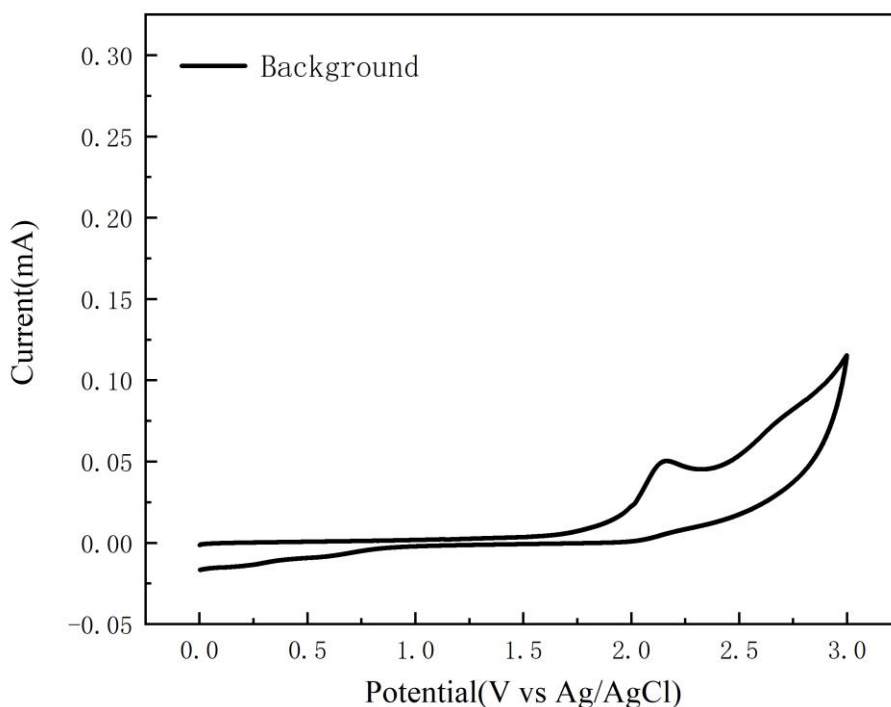
**Reference electrode:** The reference electrode is SCE (saturated aqueous KCl) that was washed with water and ethanol before measurements.

**Counter electrode:** The counter electrode is a platinum wire that was polished with 0.05 μm aluminum oxide and then sonicated in distilled water and ethanol before measurements.



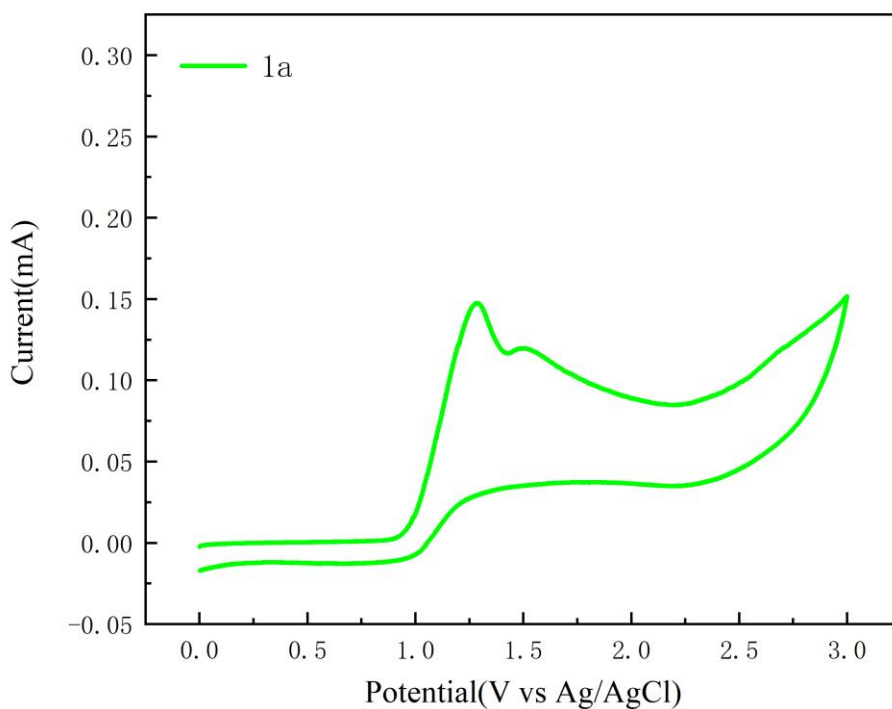
**Figure S2.** Cyclic voltammogram

**General procedure for cyclic voltammetry (CV):** Cyclic voltammograms of **1a** (0.1 mmol), **2a** (0.3 mmol), were performed in a three-electrode cell at room temperature. The working electrode was a steady glassy carbon, the counter electrode was a platinum wire, and the reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution. Mixed solvent (HFIP (2.5 mL), and CH<sub>3</sub>NO<sub>2</sub> (2.5 mL) containing Et<sub>4</sub>NPF<sub>6</sub> (0.15 mmol) were poured into the electrochemical cell in cyclic voltammetry experiments. The scan rate was 100 mV/s, ranging from 0.0 V to 3.0 V.



**Figure S3.** Cyclic voltammogram

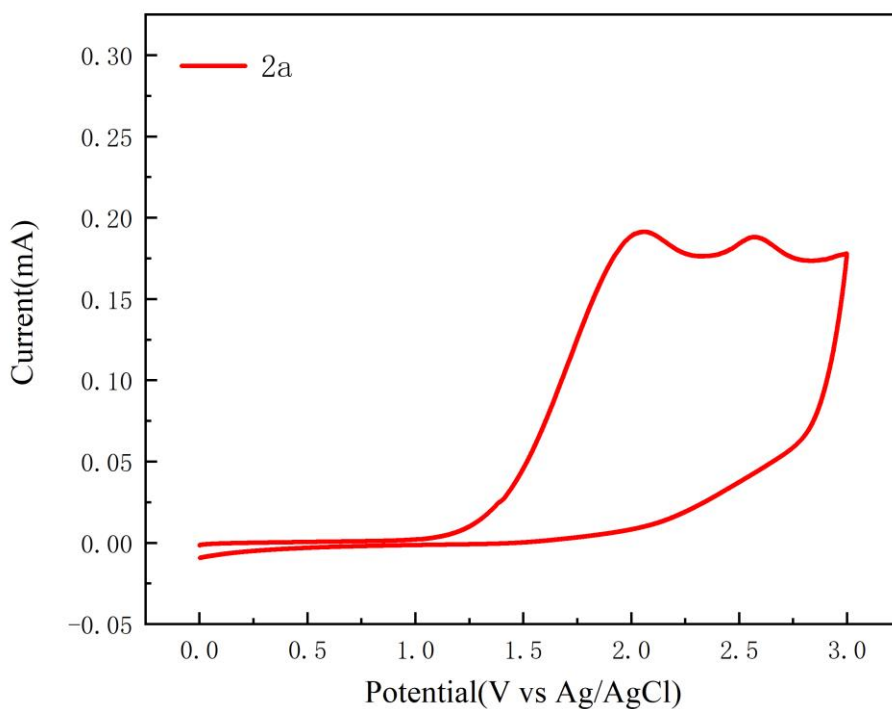
**General procedure for cyclic voltammetry (CV):** Cyclic voltammograms of background was performed in a three-electrode cell at room temperature. The working electrode was a steady glassy carbon, the counter electrode was a platinum wire, and the reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution. Mixed solvent (HFIP (2.5 mL), and  $\text{CH}_3\text{NO}_2$  (2.5 mL) containing  $\text{Et}_4\text{NPF}_6$  (0.15 mmol) were poured into the electrochemical cell in cyclic voltammetry experiments. The scan rate was 100 mV/s, ranging from 0.0 V to 3.0 V.



**Figure S4.** Cyclic voltammogram

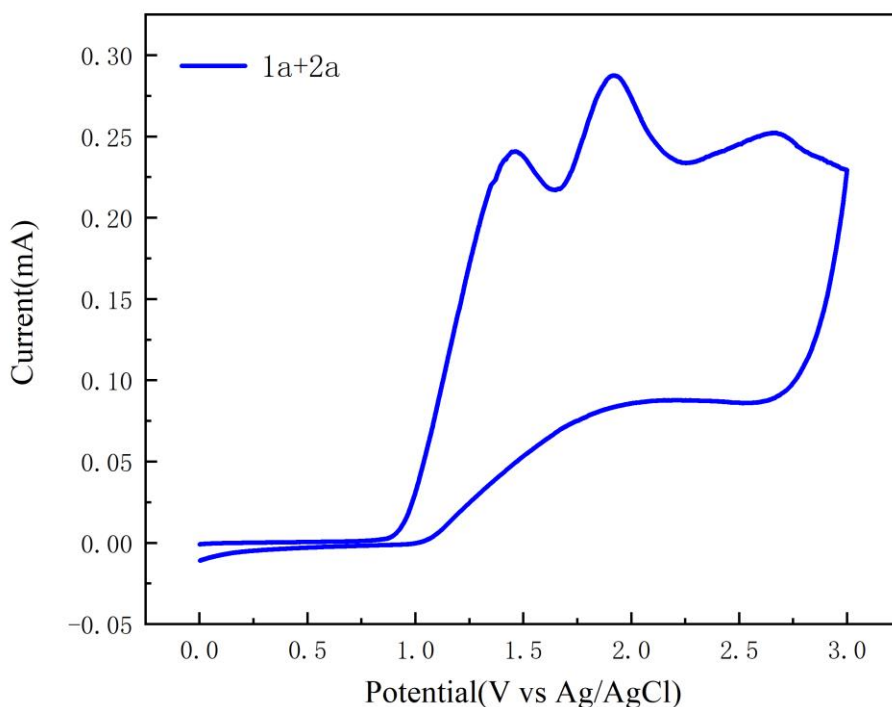
**General procedure for cyclic voltammetry (CV):** Cyclic voltammograms of **1a** (0.1 mmol) was performed in a three-electrode cell at room temperature. The working electrode was a steady glassy carbon, the counter electrode was a platinum wire, and the reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution. Mixed solvent (HFIP (2.5 mL), and CH<sub>3</sub>NO<sub>2</sub> (2.5 mL) containing Et<sub>4</sub>NPF<sub>6</sub> (0.15 mmol) were poured into the electrochemical cell in cyclic voltammetry experiments. The scan rate was 100 mV/s, ranging from 0.0 V to 3.0 V.





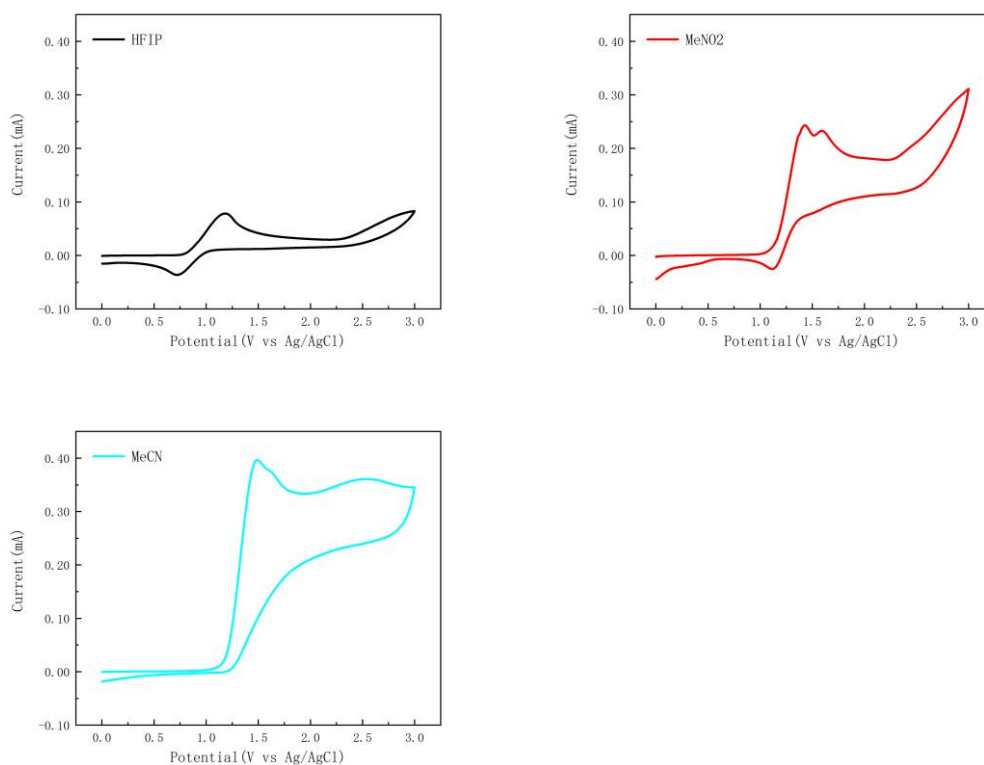
**Figure S5.** Cyclic voltammogram

**General procedure for cyclic voltammetry (CV):** Cyclic voltammograms of **2a** (0.3 mmol) was performed in a three-electrode cell at room temperature. The working electrode was a steady glassy carbon, the counter electrode was a platinum wire, and the reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution. Mixed solvent (HFIP (2.5 mL), and CH<sub>3</sub>NO<sub>2</sub> (2.5 mL) containing Et<sub>4</sub>NPF<sub>6</sub> (0.15 mmol) were poured into the electrochemical cell in cyclic voltammetry experiments. The scan rate was 100 mV/s, ranging from 0.0 V to 3.0 V.



**Figure S6.** Cyclic voltammogram

**General procedure for cyclic voltammetry (CV):** Cyclic voltammograms of **1a** (0.1 mmol) and **2a** (0.3 mmol) were performed in a three-electrode cell at room temperature. The working electrode was a steady glassy carbon, the counter electrode was a platinum wire, and the reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution. Mixed solvent (HFIP (2.5 mL), and CH<sub>3</sub>NO<sub>2</sub> (2.5 mL) containing Et<sub>4</sub>NPF<sub>6</sub> (0.15 mmol) were poured into the electrochemical cell in cyclic voltammetry experiments. The scan rate was 100 mV/s, ranging from 0.0 V to 3.0 V.



**Figure S7.** Cyclic voltammogram

**General procedure for cyclic voltammetry (CV):** Cyclic voltammograms of the single solvent was performed in a three-electrode cell at room temperature. The working electrode was a steady glassy carbon, the counter electrode was a platinum wire, and the reference was an Ag/AgCl electrode submerged in saturated aqueous KCl solution. single solvent (HFIP (5 mL), or CH<sub>3</sub>NO<sub>2</sub> (5 mL), or MeCN (5 mL) containing Et<sub>4</sub>NPF<sub>6</sub> (0.15 mmol) were poured into the electrochemical cell in cyclic voltammetry experiments. The scan rate was 100 mV/s, ranging from 0.0 V to 3.0 V.

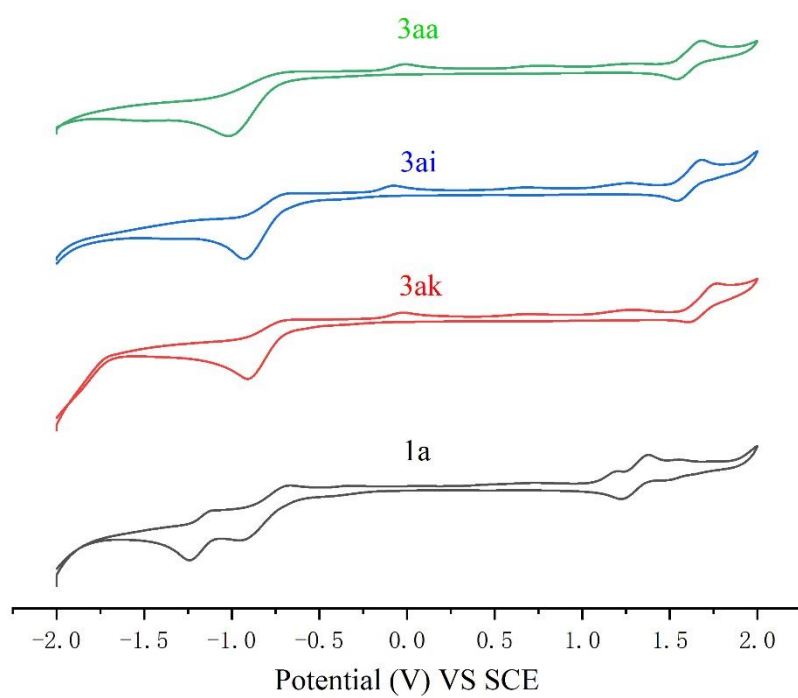


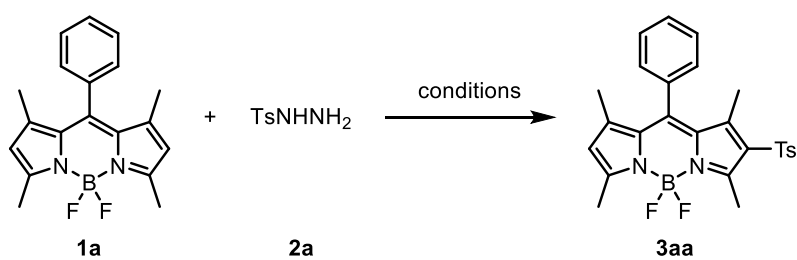
Table S4 CV study of sulfonated BODIPYs

Entry	E <sub>ox</sub> (V)	E <sub>red</sub> (V)	HOMO	LUMS
3aa	1.51	-0.70	-5.91	-3.70
3ai	1.50	-0.73	-5.90	-3.67
3ak	1.58	-0.69	-5.98	-3.71
1a	1.10	-0.64	-5.50	-3.76

$E_{\text{HOMO}} = -(E_{\text{ox}} + 4.4 \text{ eV})$ ,  $E_{\text{LUMO}} = -(E_{\text{red}} + 4.4 \text{ eV})$

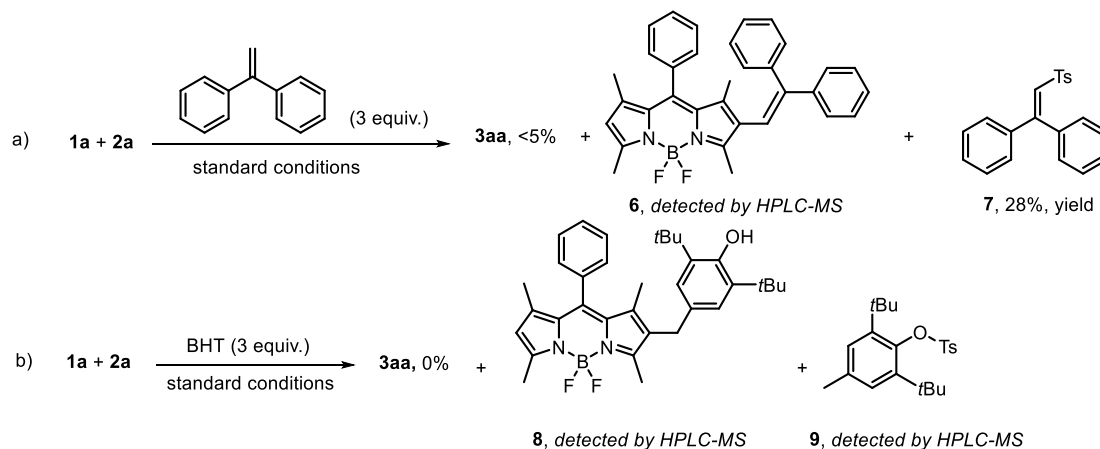
## The reaction promoted by external oxidants

Table S5 The reaction promoted by external oxidants



Entry	Conditions	Yield
1	TBAI (20 mol%), TBHP (2.0 equiv.), HFIP (2.5 mL), CH <sub>3</sub> NO <sub>2</sub> (2.5 mL), H <sub>2</sub> O, CoCl <sub>2</sub> ·6H <sub>2</sub> O (5 mol%), 80 °C	0
2	I <sub>2</sub> (50 mol%), TBHP (2.0 equiv.), HFIP (2.5 mL), CH <sub>3</sub> NO <sub>2</sub> (2.5 mL), H <sub>2</sub> O, CoCl <sub>2</sub> ·6H <sub>2</sub> O (5 mol%), 80 °C	0
3	FeCl <sub>3</sub> (10 mol%), air, HFIP (2.5 mL), CH <sub>3</sub> NO <sub>2</sub> (2.5 mL), H <sub>2</sub> O, CoCl <sub>2</sub> ·6H <sub>2</sub> O (5 mol%), 80 °C	0
4	CAN (2.0 equiv.), air, HFIP (2.5 mL), CH <sub>3</sub> NO <sub>2</sub> (2.5 mL), H <sub>2</sub> O, CoCl <sub>2</sub> ·6H <sub>2</sub> O (5 mol%), 80 °C	0
5	PCC (2.0 equiv.), air, HFIP (2.5 mL), CH <sub>3</sub> NO <sub>2</sub> (2.5 mL), H <sub>2</sub> O, CoCl <sub>2</sub> ·6H <sub>2</sub> O (5 mol%), 80 °C	0
6	KMnO <sub>4</sub> (10 mol%), air, HFIP (2.5 mL), CH <sub>3</sub> NO <sub>2</sub> (2.5 mL), H <sub>2</sub> O, CoCl <sub>2</sub> ·6H <sub>2</sub> O (5 mol%), 80 °C	0

## Control experiments



a) In a undivided Schlenk flask (10 mL) equipped with a stir bar, substrate **1a** (0.1 mmol, 32.4 mg, 1 equiv.), sulfonamide **2a** (0.3 mmol, 55.9 mg, 3 equiv.), NaCl (0.15 mmol, 8.7 mg) and 1,1-diphenylethylene (54.1 mg, 3 equiv.) were combined and added. The flask was equipped with a rubber stopper, a graphite felt anode (1 cm x 1 cm x 0.5 cm) and a graphite felt cathode (1 cm x 1 cm x 0.5 cm) and then flushed with nitrogen. Then HFIP (2.5 mL), CH<sub>3</sub>NO<sub>2</sub> (2.5 mL) and H<sub>2</sub>O (0.2 mL) were injected respectively into the flask via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 6 mA at room temperature for 2.5 h. After the reaction was completed, the reaction system was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography and eluted with petroleum ether and ethyl acetate and the white solid was obtained in **7** (28.3 mg 28%). No product **3aa** was isolated. Meanwhile, the reaction mixtures were subjected to the HPLC-MS analysis and the adducts of the reaction intermediates with the radical trap reagents were observed.

b) In an undivided Schlenk flask (10 mL) equipped with a stir bar, substrate **1a** (0.1 mmol, 32.4 mg, 1 equiv.), sulfonamide **2a** (0.3 mmol, 55.9 mg, 3 equiv.), NaCl (0.15 mmol, 8.7 mg) and BHT (66.1 mg, 3 equiv.) were combined and added. The flask was equipped with a rubber stopper, a graphite felt anode (1 cm x 1 cm x

0.5 cm) and a graphite felt cathode (1 cm x 1 cm x 0.5 cm) and then flushed with nitrogen. Then HFIP (2.5 mL), CH<sub>3</sub>NO<sub>2</sub> (2.5 mL) and H<sub>2</sub>O (0.2 mL) were injected respectively into the flask via syringes. The reaction mixture was stirred and electrolyzed at a constant current of 6 mA at room temperature for 2.5 h. After the reaction was completed, no product **3aa** was isolated. Meanwhile, the reaction mixtures were subjected to the HPLC-MS analysis and the adducts of the reaction intermediates with the radical trap reagents were observed.

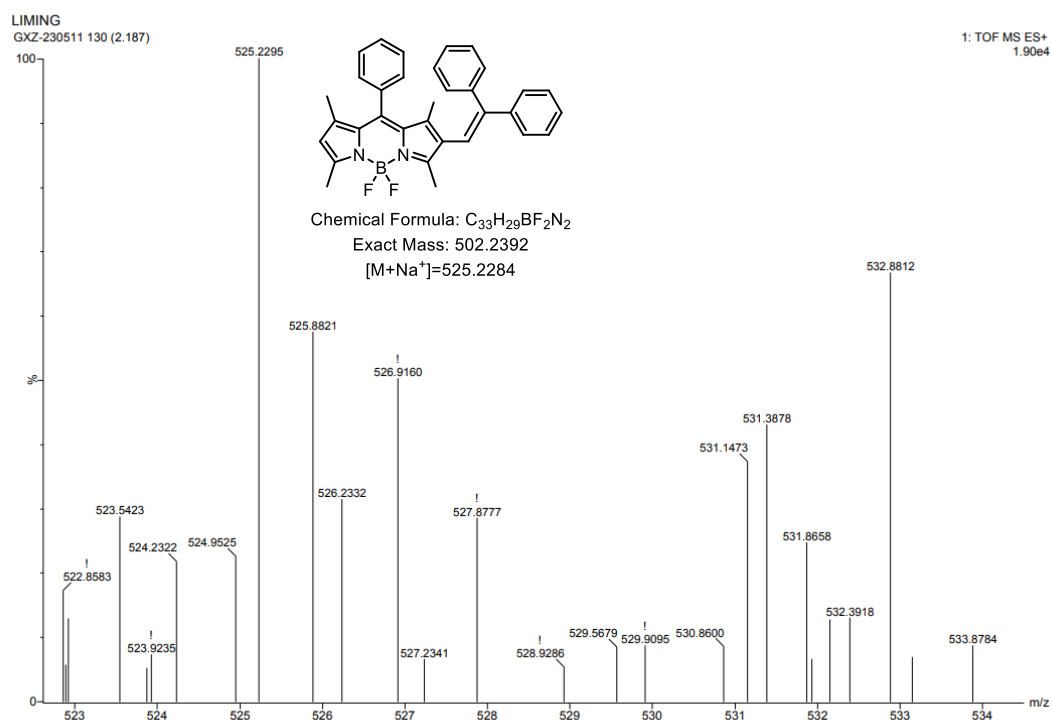


Figure S8 HPLC-MS Spectra of **6**

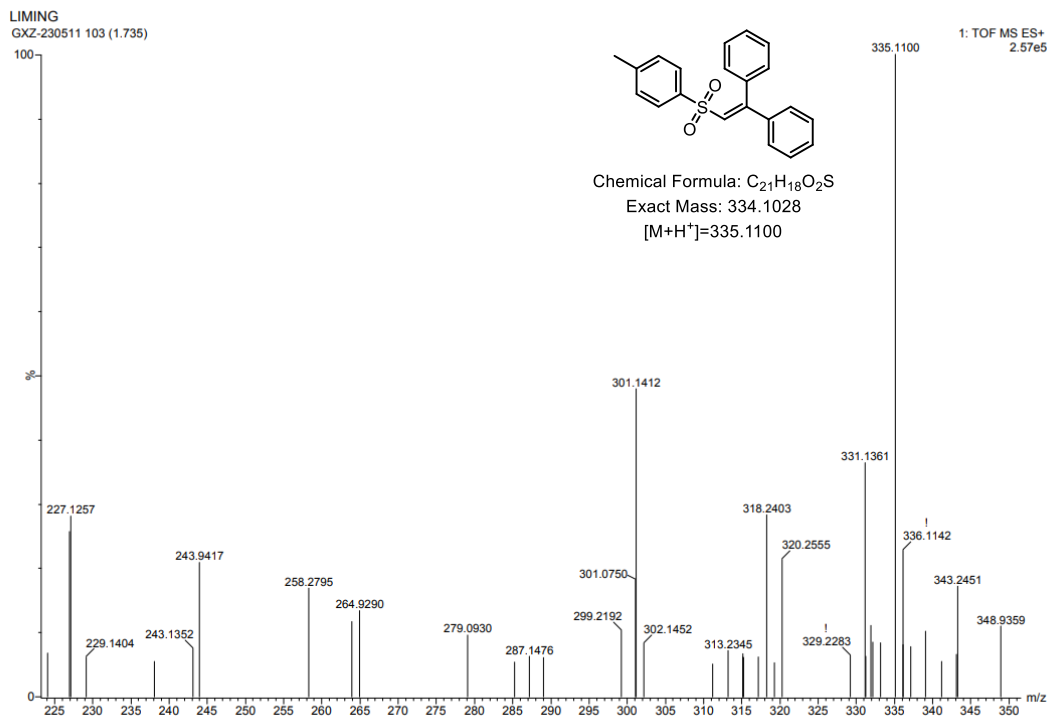


Figure S9. HPLC-MS Spectra of 7

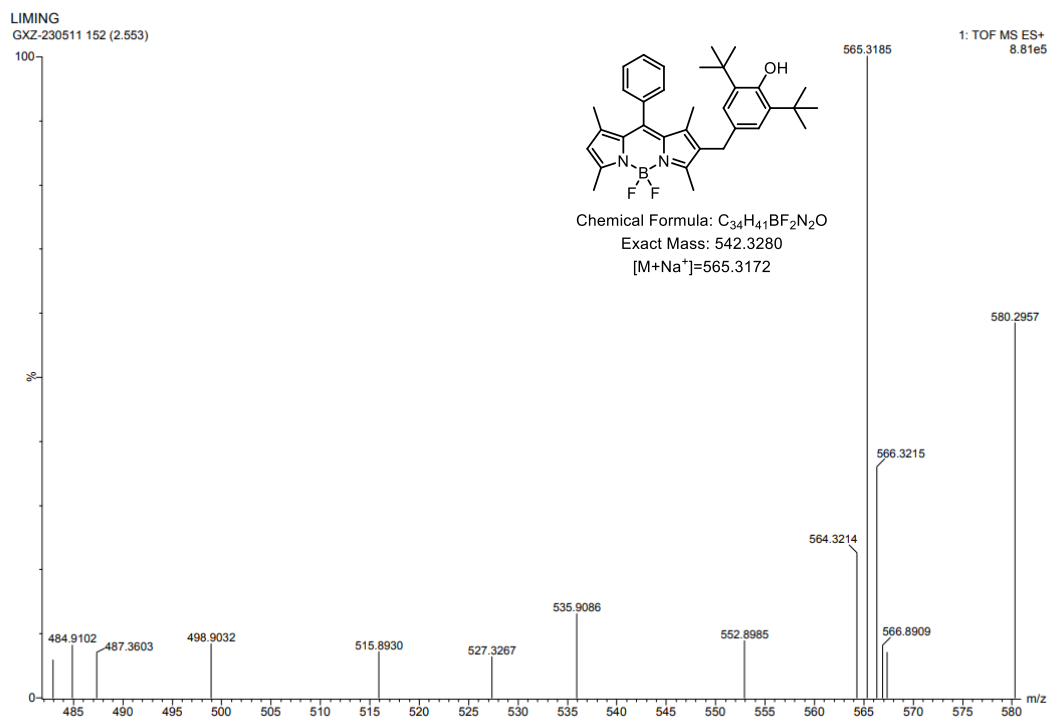


Figure S10. HPLC-MS Spectra of 8



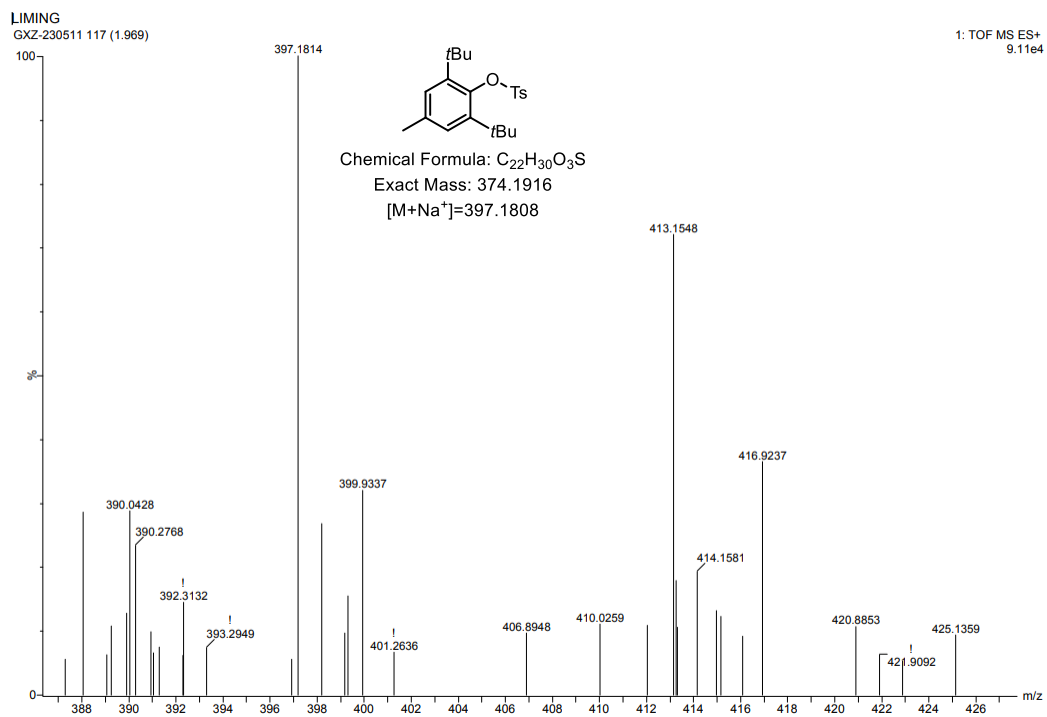
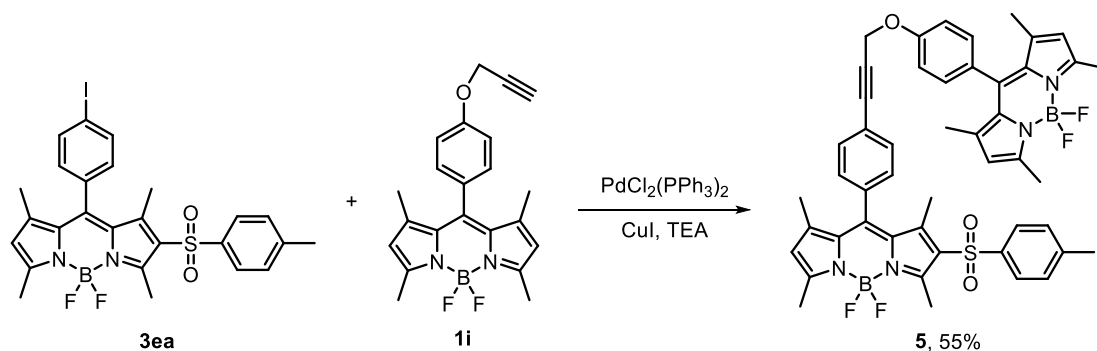


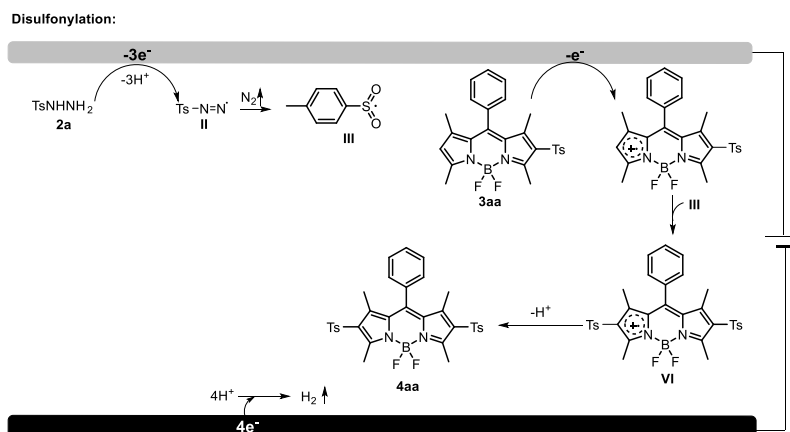
Figure S11. HPLC-MS Spectra of **9**

## Late-stage transformations



The electrochemical products **3ea** (0.3 mmol, 181.4 mg), **1i** (0.36 mmol, 113.4 mg),  $\text{PdCl}_2(\text{PPh}_3)_2$  (2 mol%, 4.2 mg),  $\text{CuI}$  (6 mol%, 3.6 mg), TEA (1.0 mL) and dry THF (2.0 mL) were charged into a thick-walled pressure pipe. And stir the reaction mixture at the room temperature for 12 h. Add saturated  $\text{NH}_4\text{Cl}$  solution and extract the mixture with ethyl acetate. The combined organic layer was dried with  $\text{Na}_2\text{SO}_4$ , and evaporated under reduced pressure. The solvent was removed under reduced pressure and the residue was purified by silica gel chromatography using petroleum ether/ ethyl acetate eluent to afford compound **5** (140.1 mg, 55%)

## Proposed Mechanism of bissulfonylation



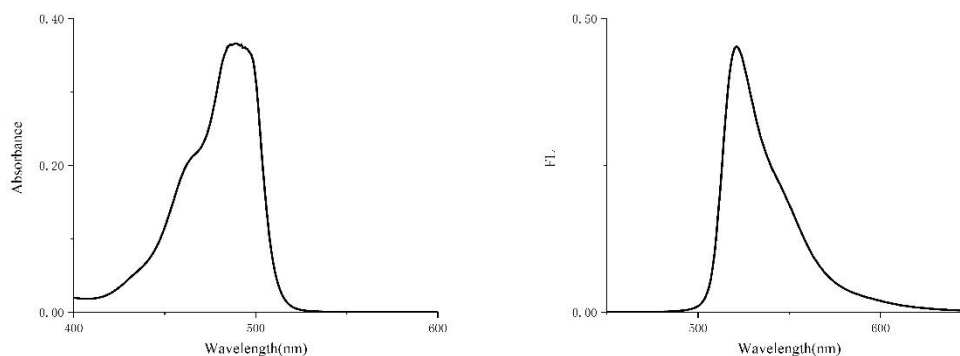
## Photophysical properties

Table S6 Absorption maxima, emission maxima, stokes shifts and relative fluorescence quantum yields ( $\Phi$ ) of products.

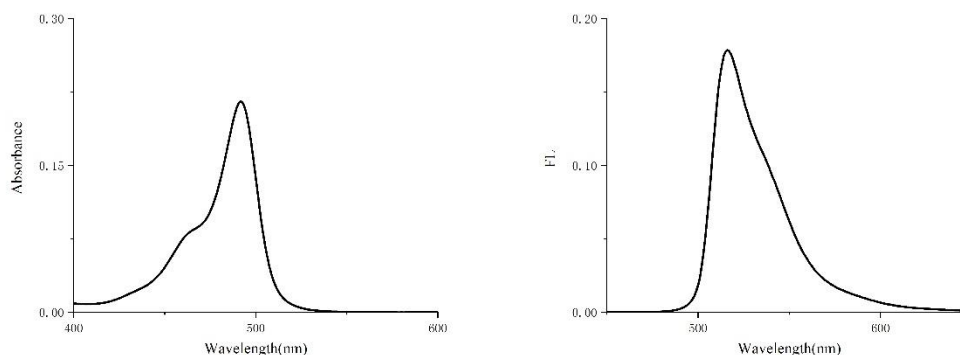
BODIPYs	$\lambda_{\text{absmax}}$ (nm)	$\lambda_{\text{emmax}}$ (nm)	Stokes Shift (nm)	$\Phi^a$
1a	488	521	33	0.26
3aa	492	517	15	0.16
3ba	490	505	15	0.27
3ca	491	508	17	0.30
3da	494	513	19	0.31
3ea	493	513	20	0.30
3fa	492	514	22	0.28
3ga	495	522	27	0.15
3ha	490	521	31	0.09
3ia	492	511	19	0.34
3ja	502	527	25	0.55
3ka	493	509	16	0.89
3ab	490	510	20	0.36
3ac	492	509	17	0.33
3ad	492	511	19	0.40
3ae	490	515	25	0.16
3af	489	508	19	0.24
3ag	491	507	16	0.28
3ah	487	508	29	0.23
3ai	492	517	25	0.14
3aj	492	512	20	0.36
3ak	486	512	26	0.18
3al	487	517	30	0.11
3am	493	512	19	0.29
3an	490	508	18	0.35
3ao	490	508	18	0.36
3ap	491	509	18	0.31
3aq	493	508	15	0.25
3ar	490	505	15	0.22
4aa	494	523	29	0.39
4ab	498	517	19	0.33
4ai	502	518	16	0.46
4ca	499	517	18	0.34
4fa	491	524	34	0.03
4ga	498	529	31	0.07
4ja	503	538	35	0.62
5	486	524	38	0.23

<sup>a</sup>Fluorescence quantum yields of these BODIPY dyes were calculated using Rhodamine 6G ( $\Phi = 0.95$  in water) as the standard.

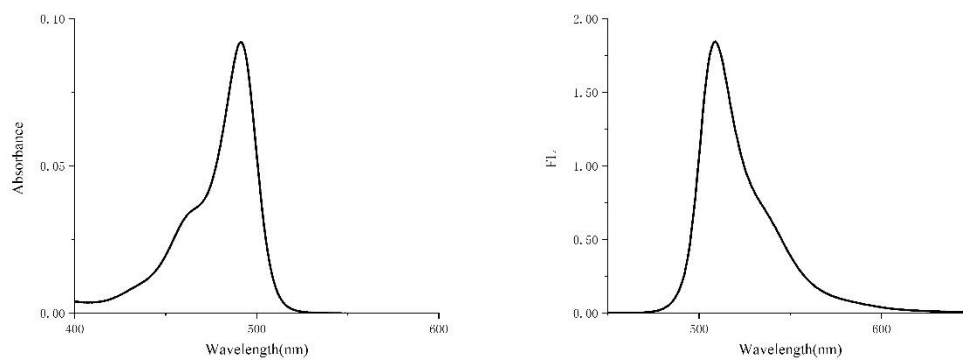
UV-visible absorption and fluorescence emission spectra were recorded on commercial spectrophotometers (Shimadzu UV-2600 and Shimadzu RF-6000 spectrometers). All measurements were made at 25 °C, using 5×10 mm cuvettes. Preliminary spectroscopic properties of these BODIPYs were investigated in dichloromethane. The concentration of the samples to be measured is  $2.5 \times 10^{-5}$  M. The following measured UV absorption absorbance intensity is 1/10 as the ordinate. The following measured fluorescence emission intensity is 1/1000000 as the ordinate. The data was as follows.



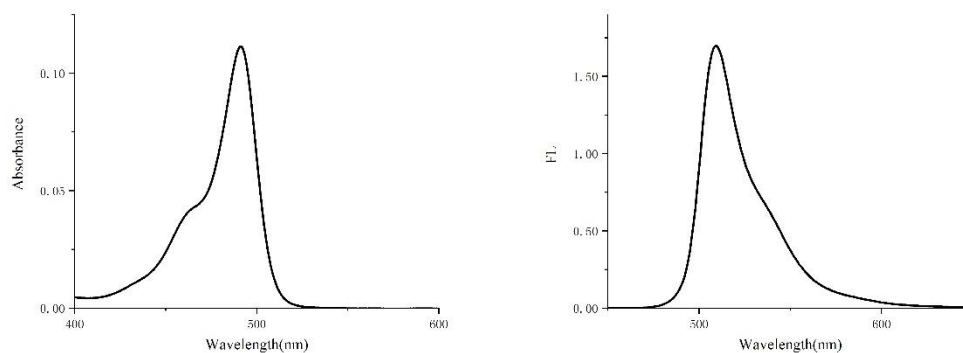
**Figure S12** Absorption (left) and emission (right) spectra of compound **1a** recorded in dichloromethane (Excited at 500 nm)



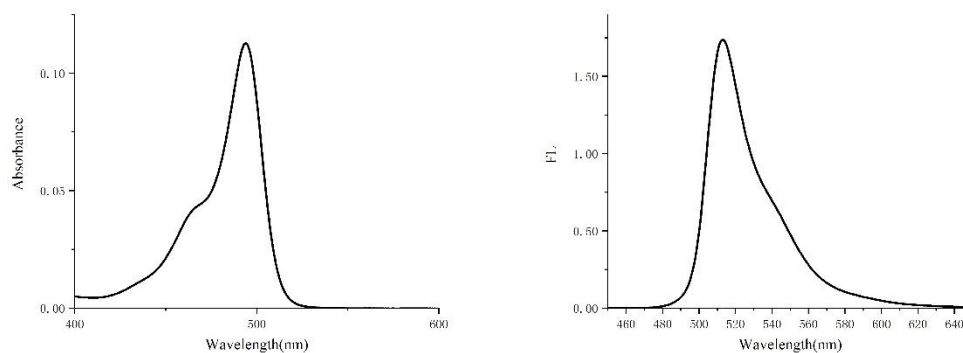
**Figure S13** Absorption (left) and emission (right) spectra of compound **3aa** recorded in dichloromethane (Excited at 490 nm)



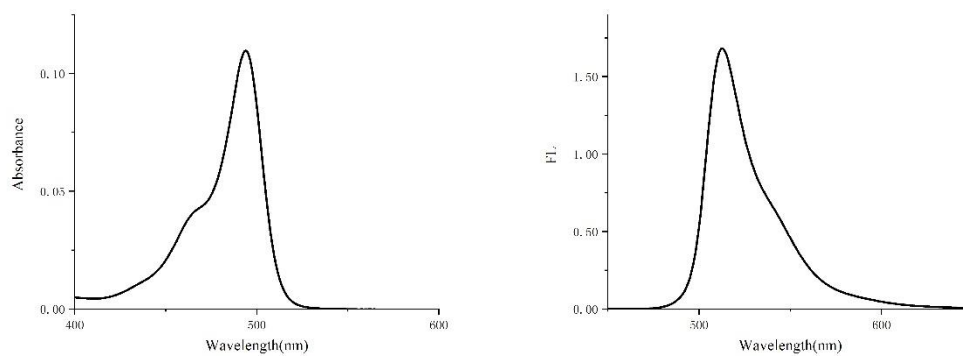
**Figure S14** Absorption (left) and emission (right) spectra of compound **3ba** recorded in dichloromethane (Excited at 490 nm)



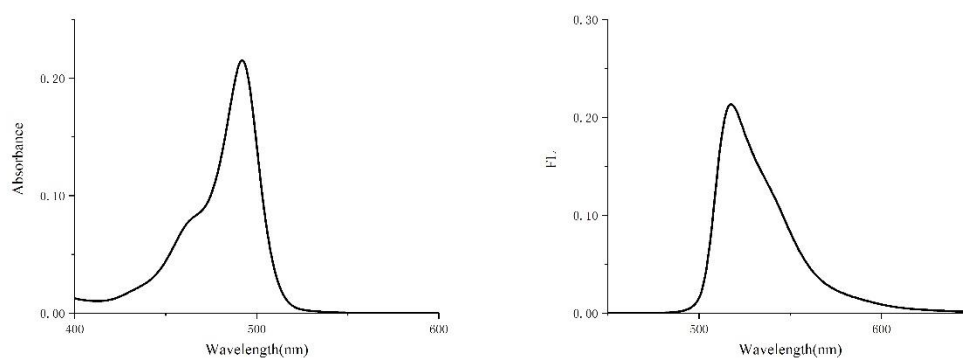
**Figure S15** Absorption (left) and emission (right) spectra of compound **3ca** recorded in dichloromethane (Excited at 490 nm)



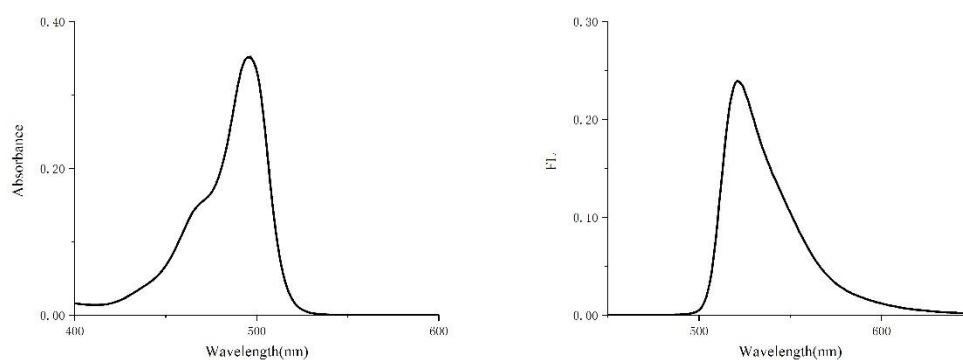
**Figure S16** Absorption (left) and emission (right) spectra of compound **3da** recorded in dichloromethane (Excited at 490 nm)



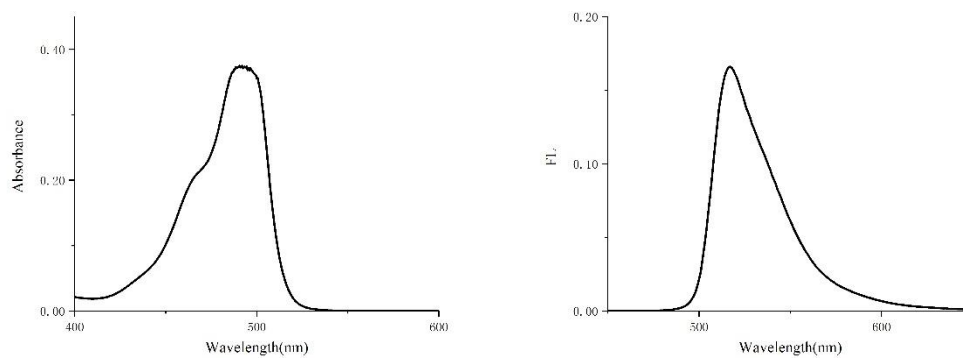
**Figure S17** Absorption (left) and emission (right) spectra of compound **3ea** recorded in dichloromethane (Excited at 490 nm)



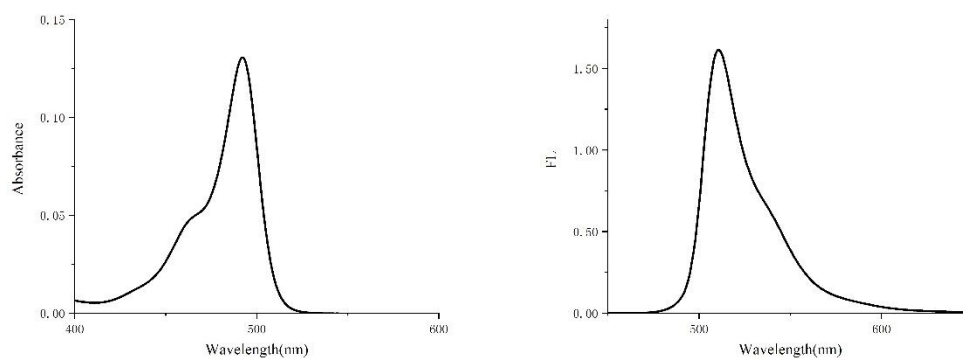
**Figure S18** Absorption (left) and emission (right) spectra of compound **3fa** recorded in dichloromethane (Excited at 490 nm)



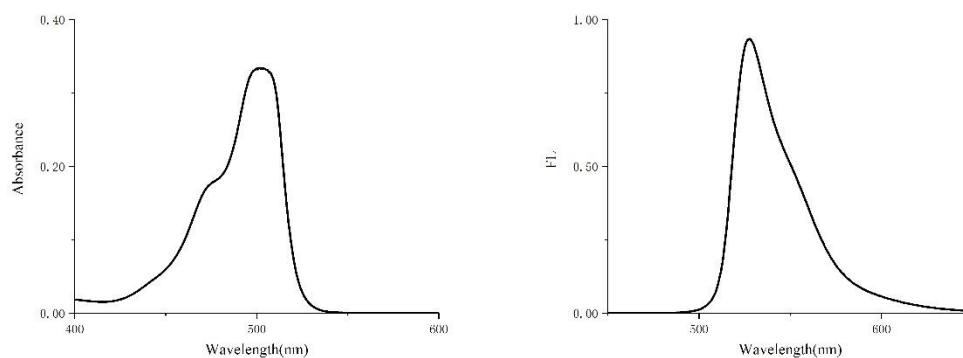
**Figure S19** Absorption (left) and emission (right) spectra of compound **3ga** recorded in dichloromethane (Excited at 490 nm)



**Figure S20** Absorption (left) and emission (right) spectra of compound **3ha** recorded in dichloromethane (Excited at 500 nm)

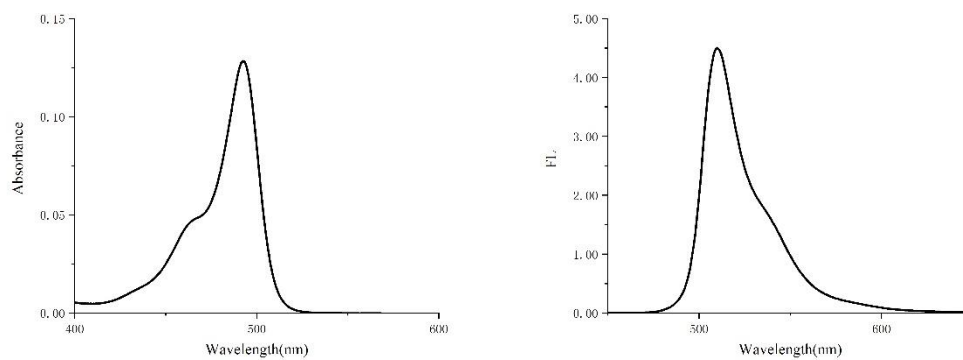


**Figure S21** Absorption (left) and emission (right) spectra of compound **3ia** recorded in dichloromethane (Excited at 490 nm)

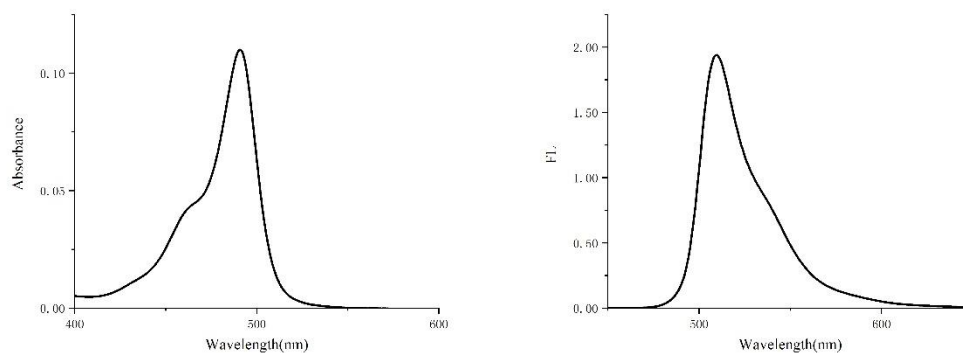


**Figure S22** Absorption (left) and emission (right) spectra of compound **3ja** recorded in dichloromethane (Excited at 500 nm)

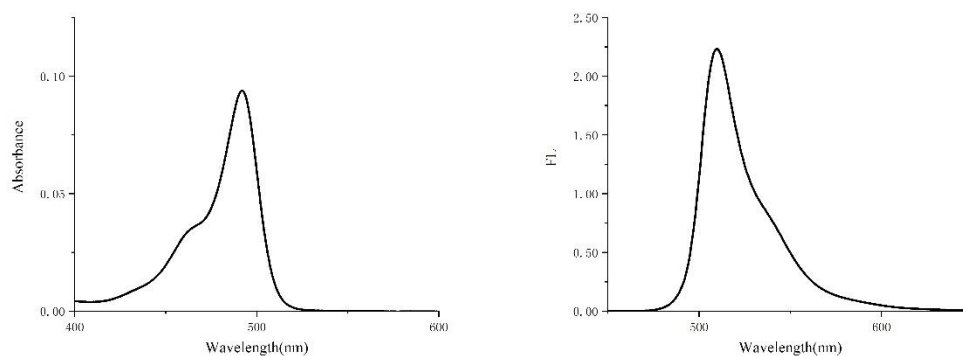




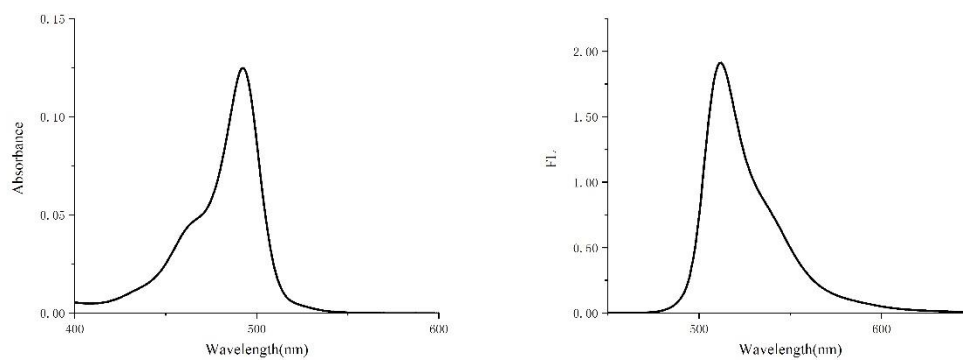
**Figure S23** Absorption (left) and emission (right) spectra of compound **3ka** recorded in dichloromethane (Excited at 490 nm)



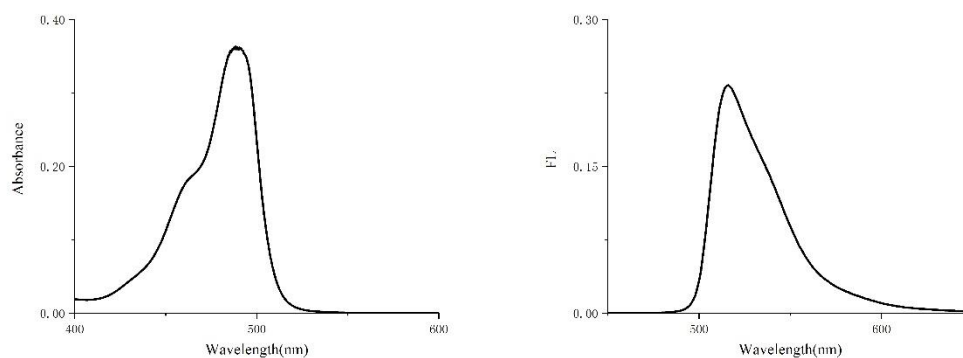
**Figure S24** Absorption (left) and emission (right) spectra of compound **3ab** recorded in dichloromethane (Excited at 490 nm)



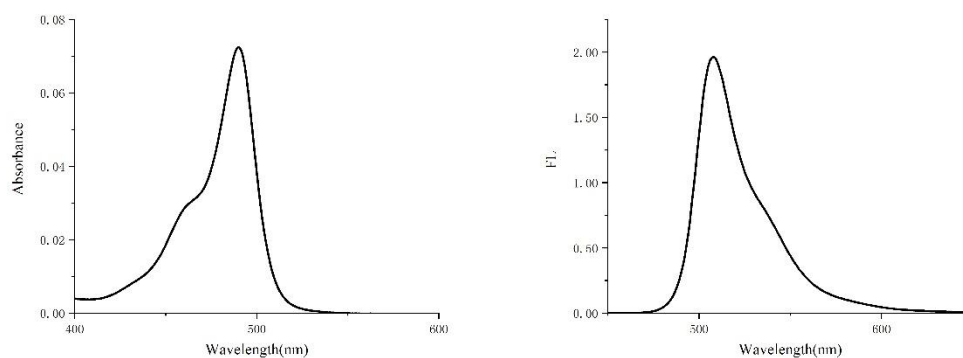
**Figure S25** Absorption (left) and emission (right) spectra of compound **3ac** recorded in dichloromethane (Excited at 490 nm)



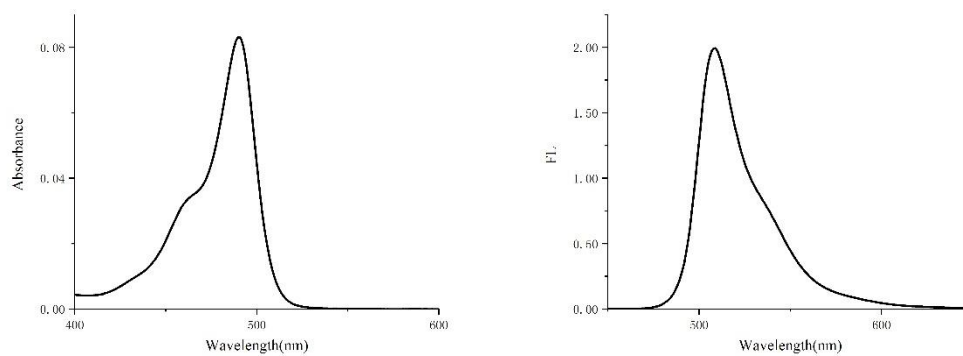
**Figure S26** Absorption (left) and emission (right) spectra of compound **3ad** recorded in dichloromethane (Excited at 490 nm)



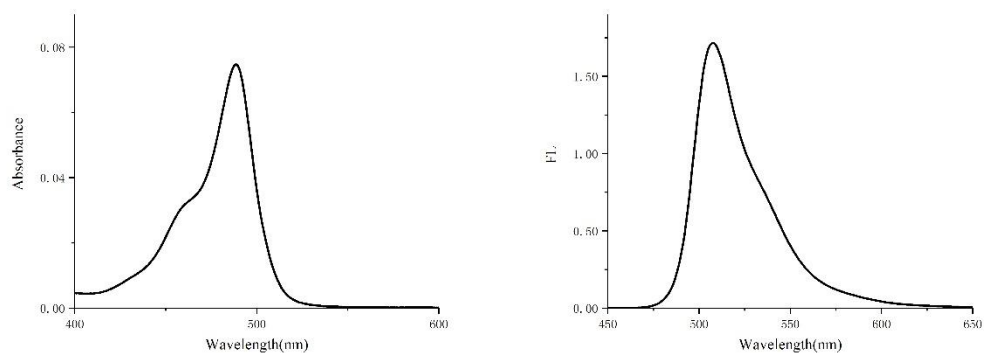
**Figure S27** Absorption (left) and emission (right) spectra of compound **3ae** recorded in dichloromethane (Excited at 490 nm)



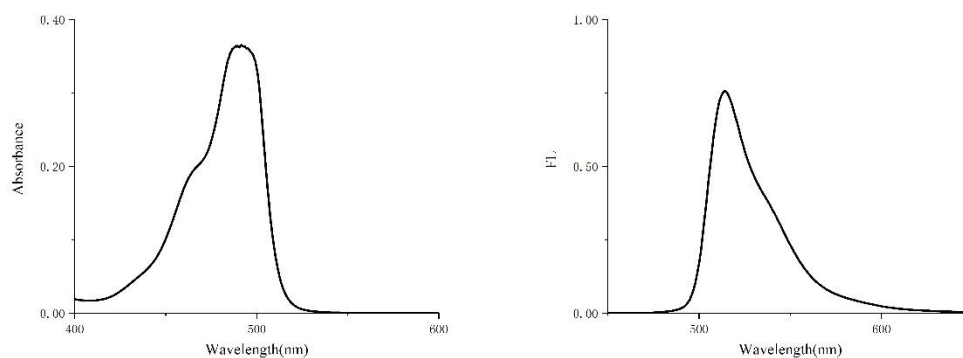
**Figure S28** Absorption (left) and emission (right) spectra of compound **3af** recorded in dichloromethane (Excited at 490 nm)



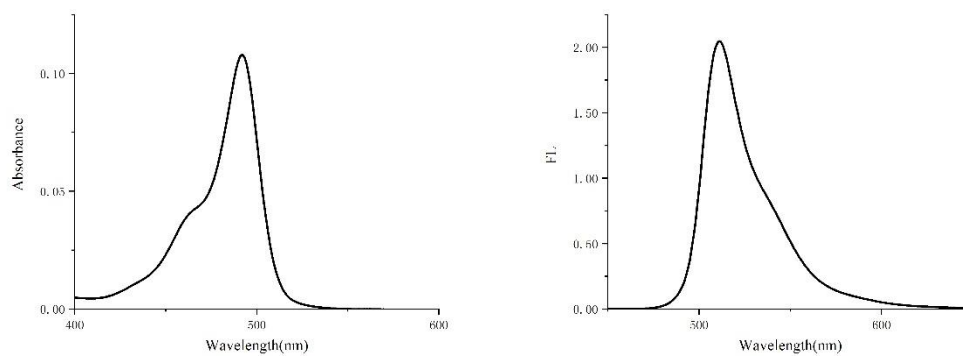
**Figure S29** Absorption (left) and emission (right) spectra of compound **3ag** recorded in dichloromethane (Excited at 490 nm)



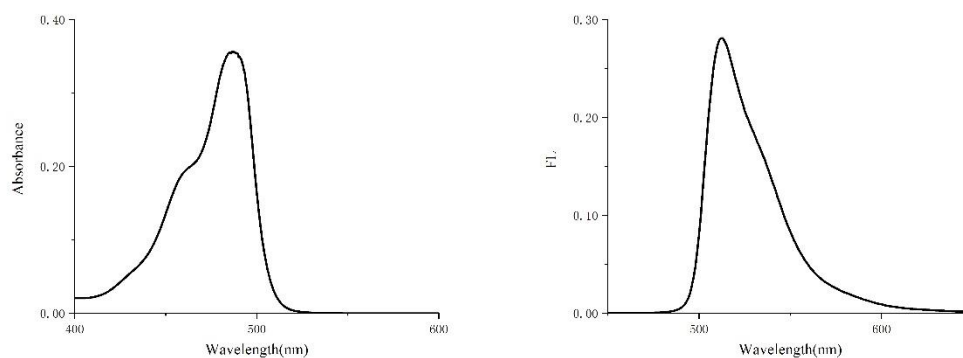
**Figure S30** Absorption (left) and emission (right) spectra of compound **3ah** recorded in dichloromethane (Excited at 490 nm)



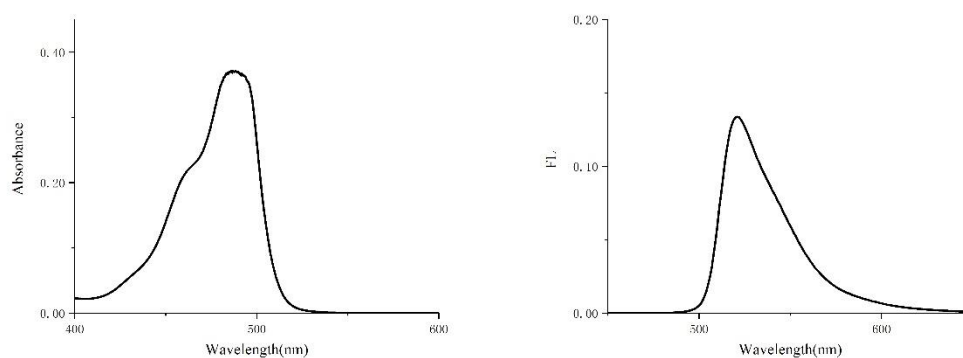
**Figure S31** Absorption (left) and emission (right) spectra of compound **3ai** recorded in dichloromethane (Excited at 490 nm)



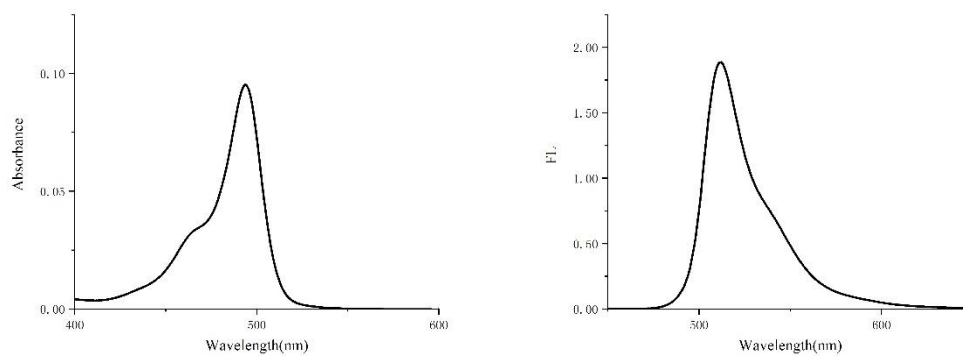
**Figure S32** Absorption (left) and emission (right) spectra of compound **3aj** recorded in dichloromethane (Excited at 490 nm)



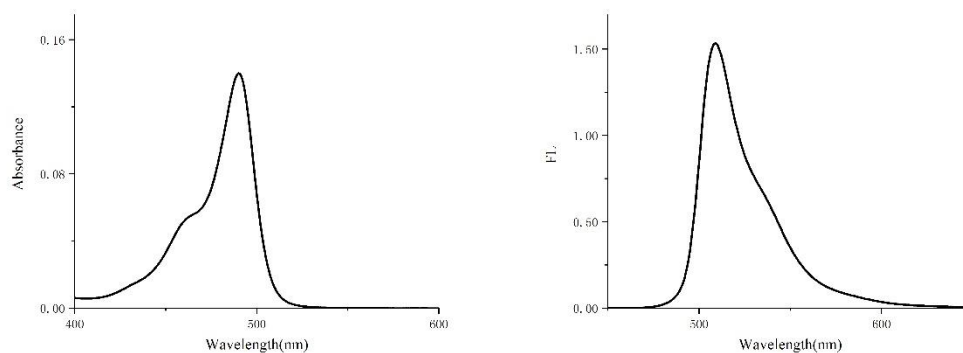
**Figure S33** Absorption (left) and emission (right) spectra of compound **3ak** recorded in dichloromethane (Excited at 490 nm)



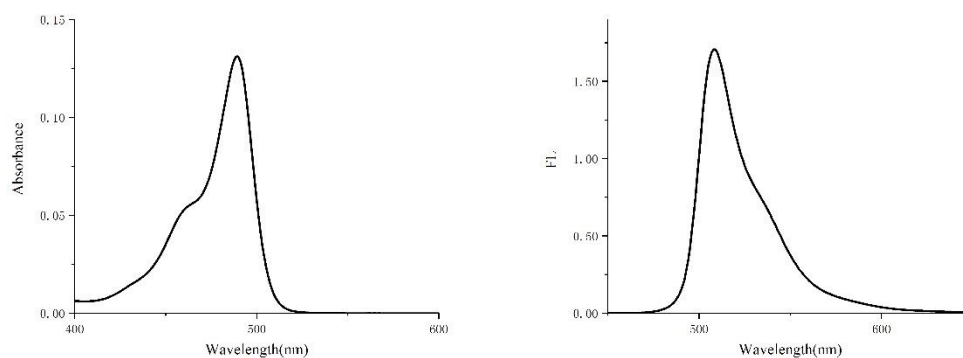
**Figure S34** Absorption (left) and emission (right) spectra of compound **3al** recorded in dichloromethane (Excited at 490 nm)



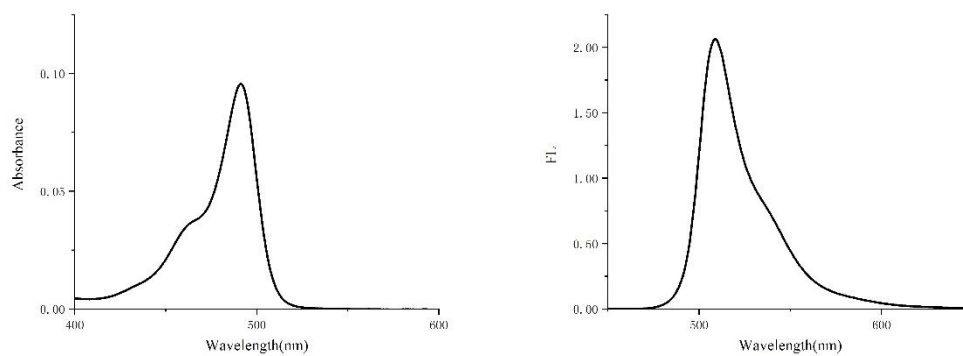
**Figure S35** Absorption (left) and emission (right) spectra of compound **3am** recorded in dichloromethane (Excited at 490 nm)



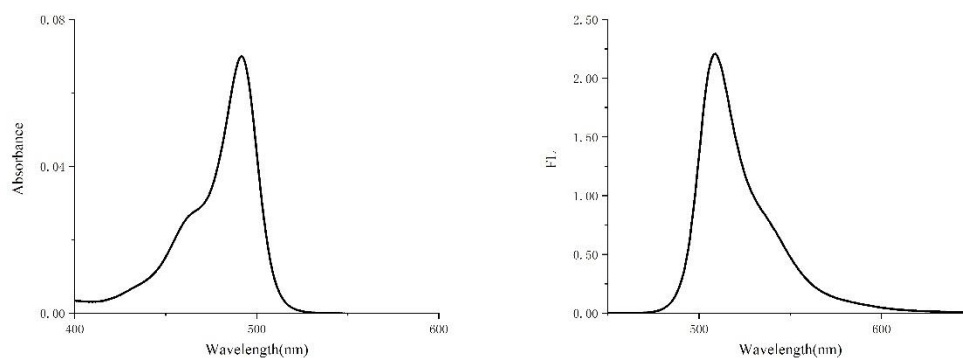
**Figure S36** Absorption (left) and emission (right) spectra of compound **3an** recorded in dichloromethane (Excited at 490 nm)



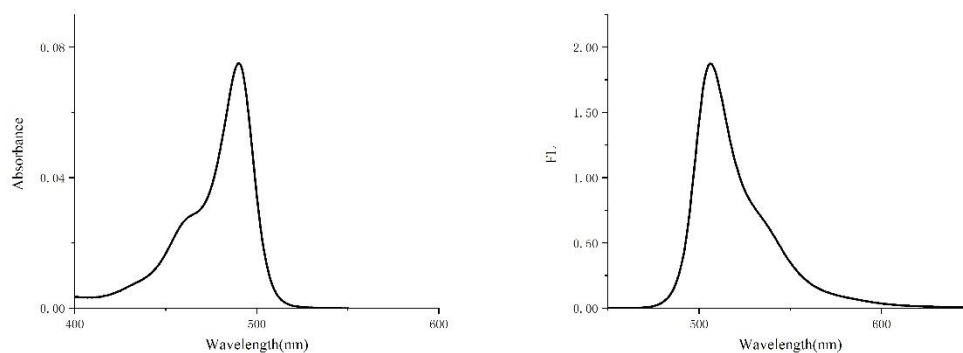
**Figure S37** Absorption (left) and emission (right) spectra of compound **3ao** recorded in dichloromethane (Excited at 490 nm)



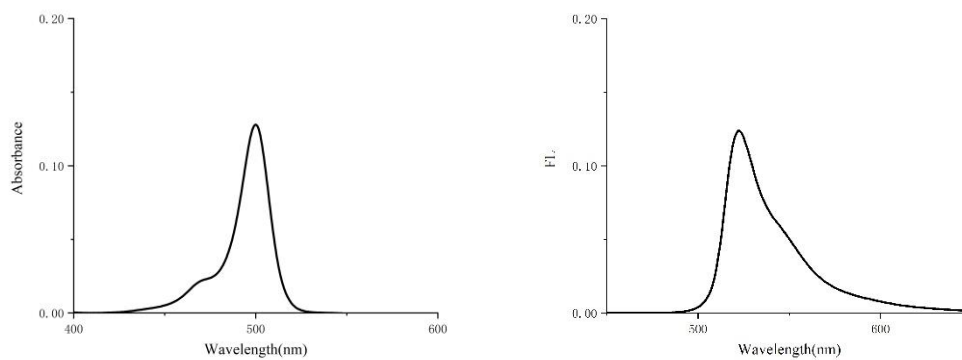
**Figure S38** Absorption (left) and emission (right) spectra of compound **3ap** recorded in dichloromethane (Excited at 490 nm)



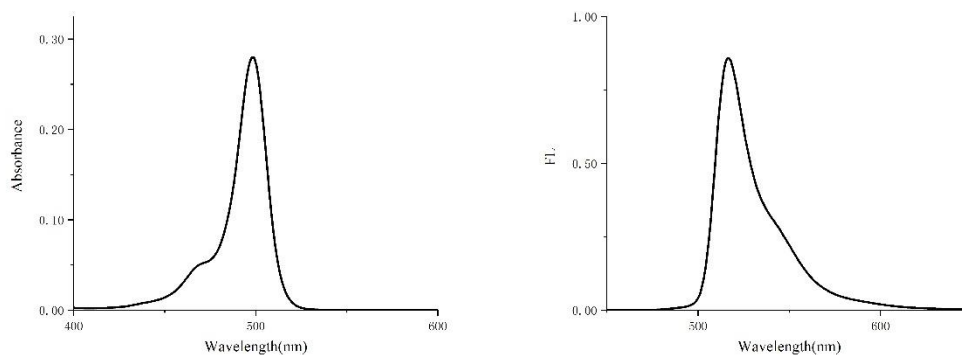
**Figure S39** Absorption (left) and emission (right) spectra of compound **3aq** recorded in dichloromethane (Excited at 490 nm)



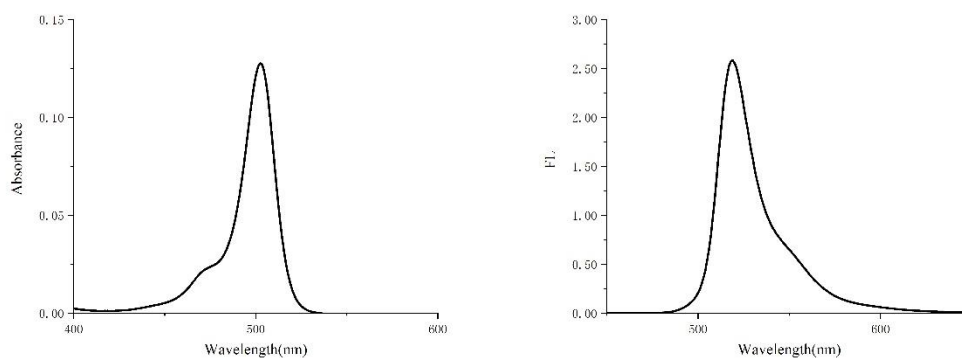
**Figure S40** Absorption (left) and emission (right) spectra of compound **3ar** recorded in dichloromethane (Excited at 490 nm)



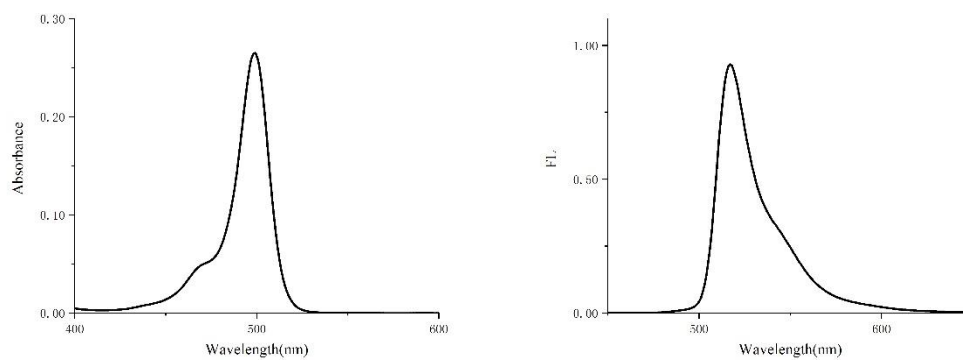
**Figure S41** Absorption (left) and emission (right) spectra of compound **4aa** recorded in dichloromethane (Excited at 500 nm)



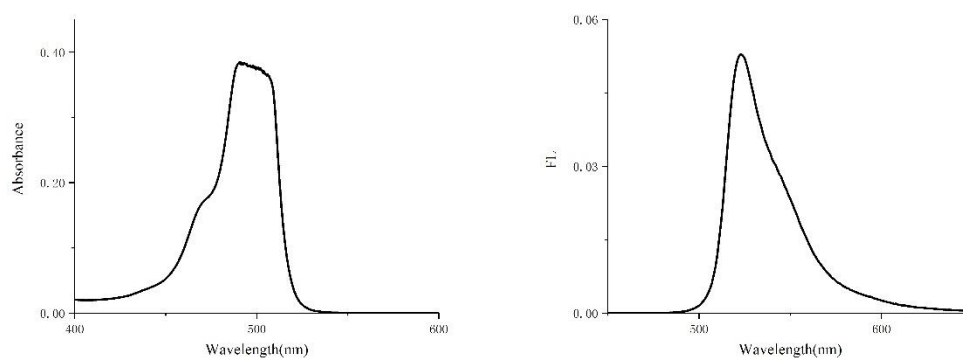
**Figure S42** Absorption (left) and emission (right) spectra of compound **4ab** recorded in dichloromethane (Excited at 500 nm)



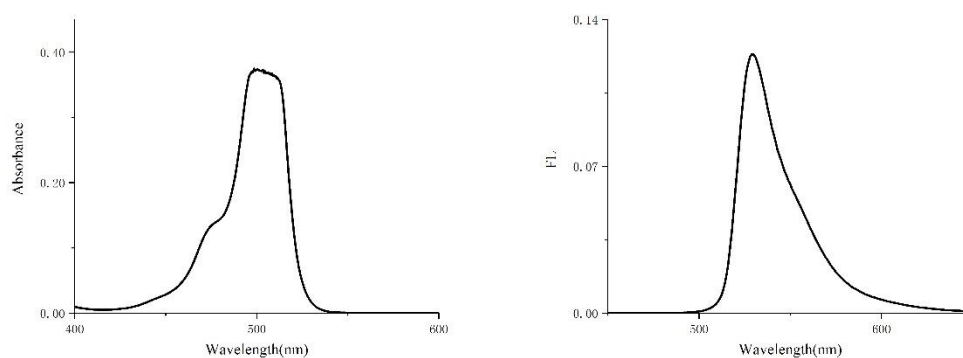
**Figure S43** Absorption (left) and emission (right) spectra of compound **4ai** recorded in dichloromethane (Excited at 500 nm)



**Figure S44** Absorption (left) and emission (right) spectra of compound **4ca** recorded in dichloromethane (Excited at 500 nm)

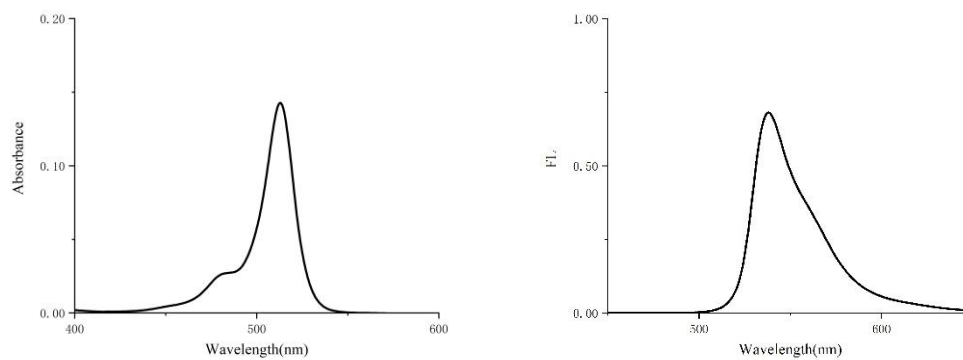


**Figure S45** Absorption (left) and emission (right) spectra of compound **4fa** recorded in dichloromethane (Excited at 500 nm)

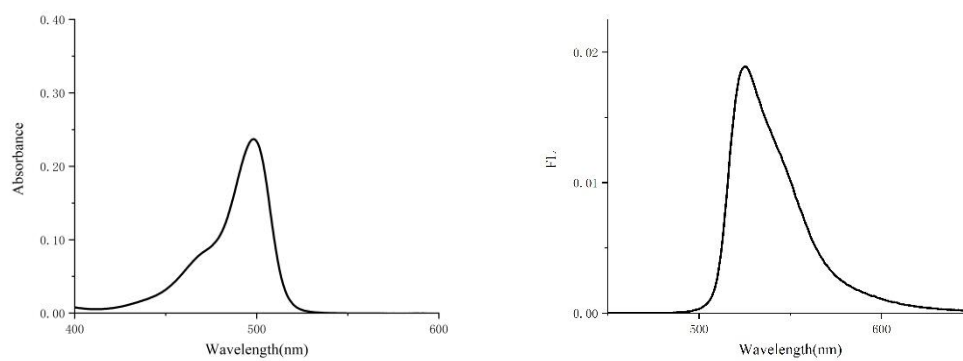


**Figure S46** Absorption (left) and emission (right) spectra of compound **4ga** recorded in dichloromethane (Excited at 500 nm)





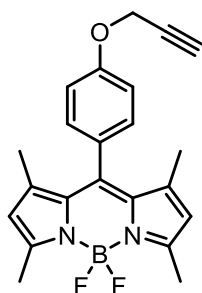
**Figure S47** Absorption (left) and emission (right) spectra of compound **4ja** recorded in dichloromethane (Excited at 510 nm)



**Figure S48** Absorption (left) and emission (right) spectra of compound **5** recorded in dichloromethane (Excited at 490 nm)

## Characterization of products

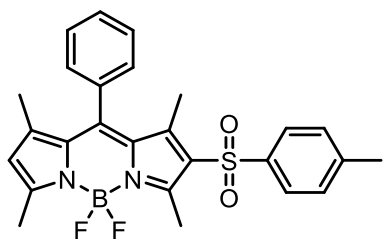
**1i**



**1i** was obtained in 38% (1.08 g) as an orange-red solid after column chromatography (eluent: petroleum ether/ethyl acetate = 30/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.20 (d, *J* = 8.6 Hz, 2H), 7.09 (d, *J* = 8.6 Hz, 2H), 5.98 (s, 2H), 4.76 (d, *J* = 2.4 Hz, 2H), 2.55 (s, 1H), 1.55 (s, 6H), 1.42 (s, 6H).

**3aa**



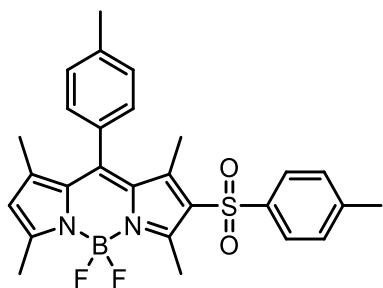
**3aa** was obtained in 71% (34.1 mg) as an orange-red solid after column chromatography (eluent: petroleum ether/ethyl acetate = 8/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.52 – 7.47 (m, 3H), 7.26 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.20 (m, 2H), 6.14 (s, 1H), 2.86 (s, 3H), 2.60 (s, 3H), 2.40 (s, 3H), 1.58 (s, 3H), 1.38 (s, 3H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 162.6, 148.1, 143.6, 143.5, 140.6, 140.2, 134.4, 134.1, 129.74, 129.68, 129.59, 129.2, 127.7, 126.6, 124.5, 21.6, 15.2, 15.0, 13.8, 12.4.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** Calcd for C<sub>25</sub>H<sub>23</sub>BF<sub>2</sub>N<sub>2</sub>O<sub>2</sub>SNa, 501.1590, Found: 501.1597.

**3ba**



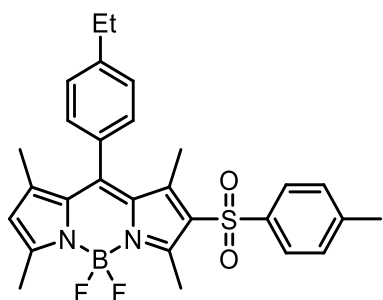
**3ba** was obtained in 56% (27.8 mg) as an orange-red solid after column chromatography (eluent: petroleum ether/ethyl acetate = 8/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 7.7 Hz, 2H), 7.25 (s, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 6.13 (s, 1H), 2.86 (s, 3H), 2.59 (s, 3H), 2.43 (s, 3H), 2.39 (s, 3H), 1.60 (s, 3H), 1.40 (s, 3H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 162.4, 152.6, 148.1, 144.0, 143.6, 140.7, 140.3, 139.8, 134.5, 131.1, 130.3, 129.8, 129.4, 127.6, 126.6, 124.3, 21.7, 21.6, 15.1, 12.5.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** Calcd for C<sub>27</sub>H<sub>27</sub>BF<sub>2</sub>N<sub>2</sub>O<sub>2</sub>SNa, 515.1747 Found: 515.1758.

### 3ca



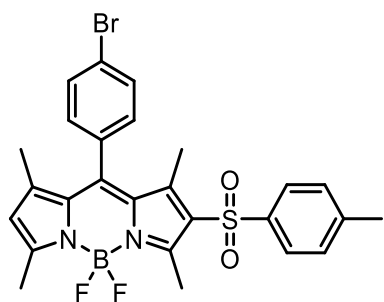
**3ca** was obtained in 54% (27.5 mg) as an orange-red solid after column chromatography (eluent: petroleum ether/ethyl acetate = 8/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 7.25 (d, *J* = 7.7 Hz, 2H), 7.11 (d, *J* = 8.1 Hz, 2H), 6.13 (s, 1H), 2.86 (s, 3H), 2.72 (q, *J* = 7.6 Hz, 2H), 2.59 (s, 3H), 2.39 (s, 3H), 1.59 (s, 3H), 1.40 (s, 3H), 1.27 (t, *J* = 7.6 Hz, 3H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 162.4, 152.5, 148.1, 146.2, 144.0, 143.6, 140.7, 140.3, 134.5, 131.3, 129.8, 129.4, 129.0, 127.6, 126.6, 124.3, 28.8, 21.6, 15.7, 15.2, 15.0, 13.8, 12.5.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** Calcd for C<sub>28</sub>H<sub>29</sub>BF<sub>2</sub>N<sub>2</sub>O<sub>2</sub>SNa, 529.1903, Found: 529.1913.

### 3da



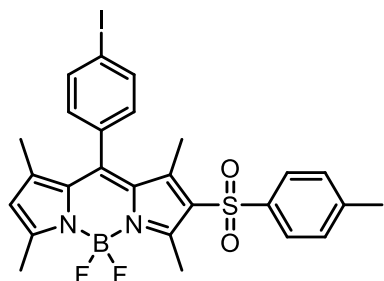
**3da** was obtained in 57% (31.3 mg) as an orange-red solid after column chromatography (eluent: petroleum ether/ethyl acetate = 8/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 8.3 Hz, 2H), 6.16 (s, 1H), 2.86 (s, 3H), 2.59 (s, 3H), 2.39 (s, 3H), 1.62 (s, 3H), 1.42 (s, 3H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 163.1, 153.1, 147.7, 143.8, 141.8, 140.6, 140.1, 134.2, 133.1, 133.0, 129.8, 129.7, 129.0, 127.0, 126.7, 124.8, 124.1, 21.7, 15.3, 13.9, 12.8.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** Calcd for C<sub>26</sub>H<sub>24</sub>BBBrF<sub>2</sub>N<sub>2</sub>O<sub>2</sub>SNa, 579.0695, Found: 579.0702.

### 3ea



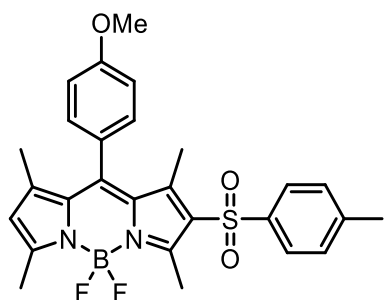
**3ea** was obtained in 58% (35.3 mg) as an orange-red solid after column chromatography (eluent: petroleum ether/ethyl acetate = 8/1 v/v).

**<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)** δ 7.93 (d, *J* = 7.7 Hz, 2H), 7.73 (d, *J* = 7.7 Hz, 2H), 7.38 (d, *J* = 7.9 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 6.48 (s, 1H), 2.73 (s, 3H), 2.54 (s, 3H), 2.35 (s, 3H), 1.55 (s, 3H), 1.39 (s, 3H).

**<sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>)** δ 164.0, 150.4, 148.2, 143.9, 142.1, 140.0, 138.4, 138.1, 133.9, 132.7, 130.1, 130.0, 128.1, 125.4, 96.5, 21.1, 14.9, 14.8, 13.3, 12.0.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** Calcd for C<sub>26</sub>H<sub>24</sub>BF<sub>2</sub>IN<sub>2</sub>O<sub>2</sub>SNa, 627.0556, Found: 627.0560.

### 3fa



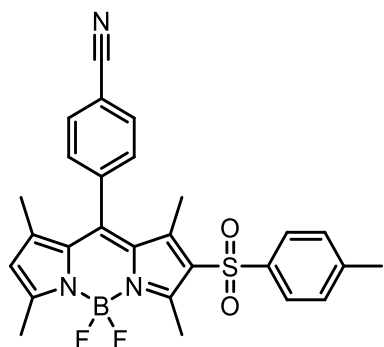
**3fa** was obtained in 60% (30.7 mg) as an orange-red solid after column chromatography (eluent: petroleum ether/ethyl acetate = 8/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8.3 Hz, 2H), 7.10 (d, *J* = 8.6 Hz, 2H), 7.00 (d, *J* = 8.6 Hz, 2H), 6.13 (s, 1H), 3.86 (s, 3H), 2.85 (s, 3H), 2.58 (s, 3H), 2.39 (s, 3H), 1.63 (s, 3H), 1.43 (s, 3H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 162.4, 160.7, 152.6, 148.1, 143.7, 143.6, 140.7, 140.3, 134.8, 129.8, 129.7, 129.1, 128.6, 126.6, 126.1, 124.4, 115.0, 55.5, 21.7, 15.3, 13.8, 12.7.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** Calcd for C<sub>27</sub>H<sub>27</sub>BF<sub>2</sub>N<sub>2</sub>O<sub>3</sub>SNa, 531.1696, Found: 531.1705.

### 3ga



**3ga** was obtained in 63% (31.9 mg) as an orange-red solid after column chromatography (eluent: petroleum ether/ethyl acetate = 4/1 v/v).

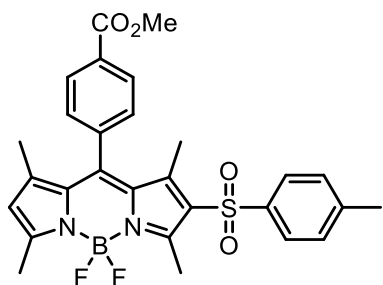
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.82 (d, *J* = 7.9 Hz, 2H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 7.9 Hz, 2H), 6.18 (s, 1H), 2.84 (s, 3H), 2.59 (s, 3H), 2.39 (s, 3H), 1.56 (s, 3H), 1.36 (s, 3H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 163.9, 153.4, 147.3, 143.9, 140.4, 139.7, 139.0, 133.8, 133.3, 129.8, 129.2, 128.4, 127.3, 126.6, 125.1, 117.8, 114.0, 21.6, 15.3, 15.2, 13.8,

12.7.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** Calcd for C<sub>27</sub>H<sub>24</sub>BF<sub>2</sub>N<sub>3</sub>O<sub>2</sub>SNa, 526.1543, Found: 526.1551.

**3ha**



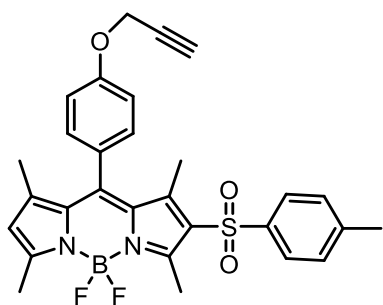
**3ha** was obtained in 68% (36.6 mg) as an orange-red solid after column chromatography (eluent: petroleum ether/ethyl acetate = 6/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.18 (d, *J* = 7.6 Hz, 2H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 7.5 Hz, 2H), 6.15 (s, 1H), 3.97 (s, 3H), 2.86 (s, 3H), 2.60 (s, 3H), 2.39 (s, 3H), 1.56 (s, 3H), 1.36 (s, 3H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 166.3, 163.2, 153.2, 147.6, 143.8, 142.0, 140.6, 140.1, 138.9, 133.9, 131.5, 130.8, 129.8, 128.7, 128.3, 127.0, 126.7, 124.8, 52.6, 21.6, 15.3, 15.2, 13.9, 12.6.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** Calcd for C<sub>28</sub>H<sub>27</sub>BF<sub>2</sub>N<sub>2</sub>O<sub>4</sub>SNa, 559.1645, Found: 559.1659.

**3ia**



**3ia** was obtained in 57% (30.4 mg) as an orange-red solid after column chromatography (eluent: petroleum ether/ethyl acetate = 8/1 v/v).

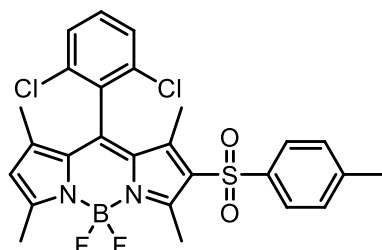
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.25 (s, 2H), 7.13 (d, *J* = 8.6 Hz, 2H), 7.09 (d, *J* = 8.7 Hz, 2H), 6.14 (s, 1H), 4.75 (d, *J* = 2.4 Hz, 2H), 2.85 (s, 3H), 2.58 (s, 3H), 2.56 (t, *J* = 2.4 Hz, 1H), 2.38 (s, 3H), 1.63 (s, 3H), 1.43 (s, 3H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 162.5, 158.6, 152.6, 148.0, 143.6, 143.5, 140.7, 140.2,

134.7, 129.8, 129.6, 129.1, 127.0, 126.6, 124.4, 116.2, 77.9, 76.21, 56.2, 21.6, 15.24, 15.21, 13.8, 12.6.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** Calcd for C<sub>29</sub>H<sub>27</sub>BF<sub>2</sub>N<sub>2</sub>O<sub>3</sub>SNa, 559.1696, Found: 555.1706.

### 3ja



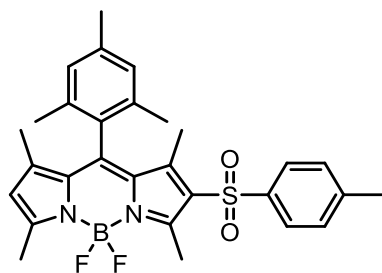
**3ja** was obtained in 70% (38.3 mg) as an orange-red solid after column chromatography (eluent: petroleum ether/ethyl acetate = 8/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 1.7 Hz, 1H), 7.46 (s, 1H), 7.41 (m, 1H), 7.27 (d, *J* = 8.1 Hz, 2H), 6.18 (s, 1H), 2.84 (s, 3H), 2.61 (s, 3H), 2.39 (s, 3H), 1.75 (s, 3H), 1.49 (s, 3H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 163.9, 153.4, 146.7, 143.7, 140.6, 139.0, 136.8, 134.6, 133.8, 132.2, 131.8, 129.8, 129.0, 127.8, 126.6, 124.8, 21.6, 15.4, 14.0, 13.9, 11.0.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** Calcd for C<sub>26</sub>H<sub>23</sub>BCl<sub>2</sub>F<sub>2</sub>N<sub>2</sub>O<sub>2</sub>SNa, 569.0811, Found: 569.0818.

### 3ka



**3ka** was obtained in 65% (34 mg) as an orange-red solid after column chromatography (eluent: petroleum ether/ethyl acetate = 8/1 v/v).

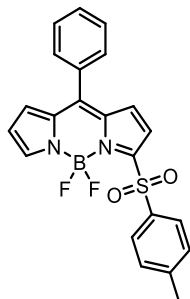
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.3 Hz, 2H), 6.95 (s, 2H), 6.13 (s, 1H), 2.84 (s, 3H), 2.60 (s, 3H), 2.40 (s, 3H), 2.33 (s, 3H), 2.02 (s, 6H), 1.64 (s, 3H), 1.38 (s, 3H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 162.2, 152.6, 147.3, 143.8, 143.6, 140.8, 139.5, 134.8, 133.7, 130.4, 129.8, 129.5, 128.3, 126.6, 126.3, 124.1, 21.7, 21.3, 19.7, 15.3, 14.1, 13.9,

11.1.

**HRMS (ESI-TOF, [M + H]<sup>+</sup>):** Calcd for C<sub>29</sub>H<sub>32</sub>BF<sub>2</sub>N<sub>2</sub>O<sub>2</sub>S, 521.2240, Found: 521.2239.

**3ma**



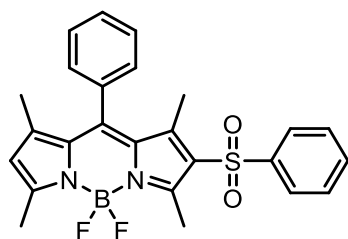
**3ma** was obtained in 38% (16.0 mg) as an orange-red solid after column chromatography (eluent: petroleum ether/ethyl acetate = 6/1 v/v).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.17 (s, 1H), 8.00 (d, J = 8.1 Hz, 2H), 7.65 – 7.58 (m, 1H), 7.54 (t, J = 7.6 Hz, 2H), 7.50 – 7.47 (m, 2H), 7.31 (d, J = 8.1 Hz, 2H), 7.17 (d, J = 4.2 Hz, 1H), 7.06 (d, J = 4.5 Hz, 1H), 6.79 (d, J = 4.2 Hz, 1H), 6.68 (d, J = 4.2 Hz, 1H), 2.40 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 151.5, 149.3, 144.6, 138.2, 137.5, 137.3, 135.5, 133.13, 131.5, 130.6, 129.6, 129.1, 128.8, 127.8, 122.6, 121.8, 21.8.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** Calcd for C<sub>22</sub>H<sub>17</sub>BF<sub>2</sub>N<sub>2</sub>O<sub>2</sub>SNa, 445.0964, Found: 445.0972.

**3ab**



**3ab** was obtained in 70% (32.7 mg) as an orange-red solid after column chromatography (eluent: petroleum ether/ethyl acetate = 8/1 v/v).

**<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)** δ 7.86 (d, J = 7.5 Hz, 2H), 7.67 (t, J = 7.0 Hz, 1H), 7.61 (d, J = 7.0 Hz, 2H), 7.59 – 7.55 (m, 3H), 7.38 (m, 2H), 6.47 (s, 1H), 2.76 (s, 3H), 2.55 (s, 3H), 1.53 (s, 3H), 1.35 (s, 3H).

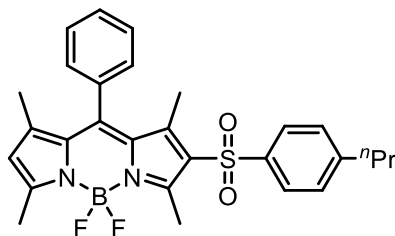
**<sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>)** δ 163.7, 150.2, 148.4, 143.3, 142.7, 138.1, 134.0, 133.3, 133.1, 129.7, 129.6, 129.5, 128.3, 127.6, 126.1, 125.6, 125.2, 14.8, 14.4, 13.2,



11.7.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** Calcd for C<sub>24</sub>H<sub>20</sub>BF<sub>2</sub>N<sub>2</sub>O<sub>2</sub>SNa, 487.1434, Found: 487.1438.

**3ac**



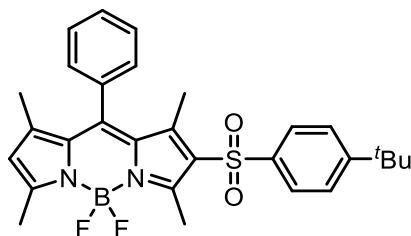
**3ac** was obtained in 68% (34.6 mg) as an orange-red solid after column chromatography (eluent: petroleum ether/ethyl acetate = 8/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.52 – 7.48 (m, 3H), 7.26 (d, *J* = 8.1 Hz, 2H), 7.22 (m, 2H), 6.14 (s, 1H), 2.86 (s, 3H), 2.65 – 2.59 (m, 2H), 2.59 (s, 3H), 1.63 (m, 2H), 1.59 (s, 3H), 1.37 (s, 3H), 0.92 (t, *J* = 7.3 Hz, 3H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 162.6, 152.7, 148.3, 143.5, 140.8, 140.3, 134.3, 134.1, 129.7, 129.6, 129.2, 127.74, 126.67, 126.6, 124.5, 38.0, 24.3, 15.2, 15.0, 13.8, 12.4.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** Calcd for C<sub>28</sub>H<sub>29</sub>BF<sub>2</sub>N<sub>2</sub>O<sub>2</sub>SNa, 529.1903, Found: 529.1913.

**3ad**



**3ad** was obtained in 67% (35.0 mg) as an orange-red solid after column chromatography (eluent: petroleum ether/ethyl acetate = 10/1 v/v).

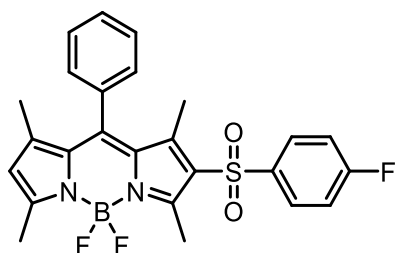
**<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)** δ 7.76 (d, *J* = 8.5 Hz, 2H), 7.62 (d, *J* = 8.5 Hz, 2H), 7.58 (m, 3H), 7.43 – 7.37 (m, 2H), 6.48 (s, 1H), 2.73 (s, 3H), 2.55 (s, 3H), 1.54 (s, 3H), 1.35 (s, 3H), 1.27 (s, 9H).

**<sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>)** δ 163.75, 156.52, 150.23, 148.45, 143.47, 140.07, 138.21, 134.12, 133.22, 129.86, 129.64, 128.41, 127.73, 126.64, 126.10, 125.30, 35.00, 30.78, 14.95, 14.57, 13.36, 11.83.

**HRMS (ESI-TOF, [M + H]<sup>+</sup>):** Calcd for C<sub>29</sub>H<sub>32</sub>BF<sub>2</sub>N<sub>2</sub>O<sub>2</sub>S, 521.2240, Found:

521.2247.

**3ae**



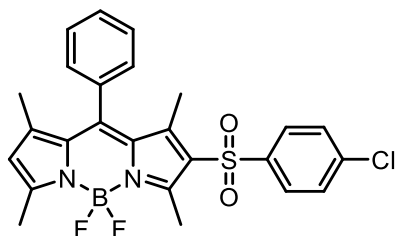
**3ae** was obtained in 64% (30.9 mg) as an orange-red solid after column chromatography (eluent: petroleum ether/ethyl acetate = 8/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.83 (m, 2H), 7.52 – 7.49 (m, 3H), 7.24 – 7.21 (m, 2H), 7.14 (t, *J* = 8.5 Hz, 2H), 6.16 (s, 1H), 2.86 (s, 3H), 2.60 (s, 3H), 1.56 (s, 3H), 1.38 (s, 3H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 166.2, 164.2, 163.2, 152.4, 148.4, 143.5, 139.9, 139.68, 139.65, 134.6, 134.0, 129.8, 129.7, 129.4, 129.3, 127.7, 126.0, 124.74, 124.71, 116.5, 116.3, 15.3, 15.1, 13.8, 12.4.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** Calcd for C<sub>25</sub>H<sub>22</sub>BF<sub>2</sub>N<sub>2</sub>O<sub>2</sub>SNa, 505.1339, Found: 505.1332.

**3af**

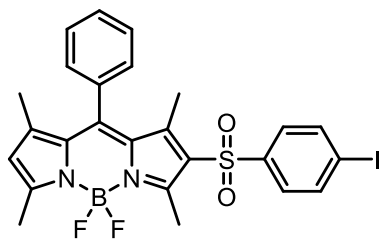


**3af** was obtained in 59% (29.5 mg) as an orange-red solid after column chromatography (eluent: petroleum ether/ethyl acetate = 8/1 v/v).

**<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)** δ 7.85 (d, *J* = 8.7 Hz, 2H), 7.66 (d, *J* = 8.6 Hz, 2H), 7.59 – 7.56 (m, 3H), 7.41 (m, 2H), 6.50 (s, 1H), 2.73 (s, 3H), 2.55 (s, 3H), 1.50 (s, 3H), 1.36 (s, 3H).

**<sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>)** δ 164.2, 150.3, 148.7, 143.4, 141.6, 138.4, 138.1, 134.3, 133.2, 129.91, 129.88, 129.6, 128.5, 128.3, 127.7, 125.5, 125.2, 15.0, 14.6, 13.3, 11.8.

**HRMS (ESI-TOF, [M + H]<sup>+</sup>):** Calcd for C<sub>25</sub>H<sub>23</sub>BF<sub>2</sub>N<sub>2</sub>O<sub>2</sub>S, 499.1224, Found: 499.1229.

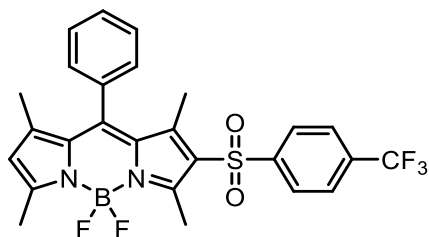
**3ag**

**3ag** was obtained in 62% (36.6 mg) as an orange-red solid after column chromatography (eluent: petroleum ether/ethyl acetate = 8/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.82 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.52 – 7.50 (m, 3H), 7.25 – 7.19 (m, 3H), 6.17 (s, 1H), 2.86 (s, 3H), 2.61 (s, 3H), 1.55 (s, 3H), 1.39 (s, 3H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 163.3, 152.5, 148.5, 143.5, 143.3, 139.9, 138.4, 134.6, 134.0, 129.8, 129.7, 129.3, 128.0, 127.8, 125.6, 124.8, 100.3, 15.3, 15.0, 13.8, 12.4.

**HRMS (ESI-TOF, [M + H]<sup>+</sup>):** Calcd for C<sub>25</sub>H<sub>23</sub>BF<sub>2</sub>IN<sub>2</sub>O<sub>2</sub>S, 591.0581, Found: 591.0583.

**3ah**

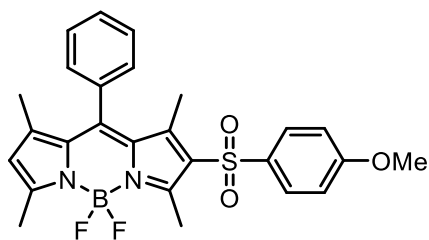
**3ah** was obtained in 43% (23.1 mg) as an orange-red solid after column chromatography (eluent: petroleum ether/ethyl acetate = 10/1 v/v).

**<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)** δ 8.06 (d, *J* = 8.3 Hz, 2H), 7.97 (d, *J* = 8.3 Hz, 2H), 7.57 (m, 3H), 7.40 (m, 2H), 6.51 (s, 1H), 2.75 (s, 3H), 2.56 (s, 3H), 1.52 (s, 3H), 1.36 (s, 3H).

**<sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>)** δ 164.5, 150.4, 148.9, 146.5, 143.4, 138.2, 134.4, 133.1, 129.9, 129.6, 128.5, 127.7, 127.3, 127.1, 127.03, 127.00, 126.97, 125.6, 124.5, 124.4, 122.3, 15.0, 14.6, 13.3, 11.8.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** Calcd for C<sub>26</sub>H<sub>22</sub>BF<sub>5</sub>N<sub>2</sub>O<sub>2</sub>SNa, 555.1307, Found: 555.1311.

**3ai**



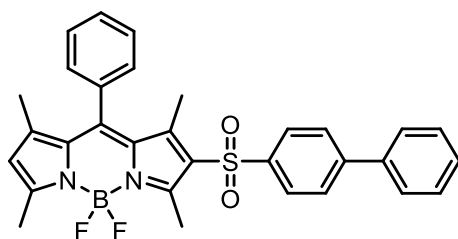
**3ai** was obtained in 65% (32.2 mg) as an orange-red solid after column chromatography (eluent: petroleum ether/ethyl acetate = 8/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.75 (d, *J* = 8.9 Hz, 2H), 7.55 – 7.43 (m, 3H), 7.25 – 7.19 (m, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 6.13 (s, 1H), 3.83 (s, 3H), 2.86 (s, 3H), 2.59 (s, 3H), 1.57 (s, 3H), 1.37 (s, 3H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 163.0, 162.5, 152.6, 148.0, 143.5, 140.1, 134.3, 134.2, 129.7, 129.6, 128.8, 127.8, 124.4, 114.3, 55.7, 15.3, 15.0, 13.8, 12.4.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** Calcd for C<sub>26</sub>H<sub>25</sub>BF<sub>2</sub>N<sub>2</sub>O<sub>3</sub>SNa, 517.1539, Found: 517.1549.

### 3aj



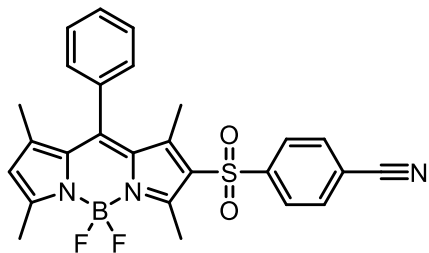
**3aj** was obtained in 66% (35.3 mg) as an orange-red solid after column chromatography (eluent: petroleum ether/ethyl acetate = 8/1 v/v).

**<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)** δ 7.92 (d, *J* = 8.5 Hz, 2H), 7.86 (d, *J* = 8.5 Hz, 2H), 7.69 (d, *J* = 7.4 Hz, 2H), 7.56 (m, 3H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.46 – 7.38 (m, 1H), 7.40 – 7.34 (m, 2H), 6.45 (s, 1H), 2.78 (s, 3H), 2.54 (s, 3H), 1.55 (s, 3H), 1.33 (s, 3H).

**<sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>)** δ 163.8, 150.3, 148.5, 144.9, 143.4, 141.5, 138.3, 138.2, 134.2, 133.2, 129.8, 129.6, 129.2, 128.7, 128.4, 127.9, 127.7, 127.2, 126.9, 125.8, 125.3, 14.9, 14.5, 13.3, 11.8.

**HRMS (ESI-TOF, [M + H]<sup>+</sup>):** Calcd for C<sub>31</sub>H<sub>28</sub>BF<sub>2</sub>N<sub>2</sub>O<sub>3</sub>S, 541.1927, Found: 541.1920.

### 3ak



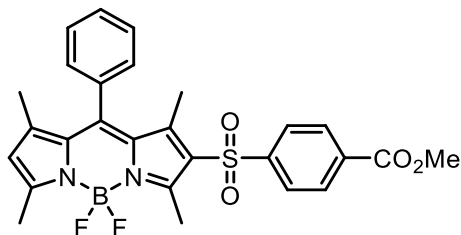
**3ak** was obtained in 54% (26.6 mg) as an orange-red solid after column chromatography (eluent: petroleum ether/ethyl acetate = 8/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.51 (m, 3H), 7.24 – 7.20 (m, 2H), 6.18 (s, 1H), 2.85 (s, 3H), 2.61 (s, 3H), 1.54 (s, 3H), 1.39 (s, 3H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 164.1, 152.4, 148.9, 147.7, 143.4, 139.5, 133.9, 133.0, 129.9, 129.7, 129.3, 127.7, 127.2, 125.1, 124.3, 117.4, 116.5, 15.4, 15.1, 13.7, 12.3.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** Calcd for C<sub>26</sub>H<sub>22</sub>BF<sub>2</sub>N<sub>3</sub>O<sub>3</sub>SNa, 512.1386, Found: 512.1390.

### 3al



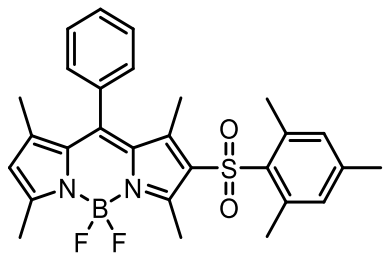
**3al** was obtained in 53% (27.8 mg) as an orange-red solid after column chromatography (eluent: petroleum ether/ethyl acetate = 8/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.11 (d, *J* = 8.0 Hz, 2H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.57 – 7.45 (m, 3H), 7.22 (m, 2H), 6.16 (s, 1H), 3.93 (s, 3H), 2.86 (s, 3H), 2.60 (s, 3H), 1.55 (s, 3H), 1.38 (s, 3H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 165.7, 163.5, 152.6, 148.5, 147.3, 143.5, 139.9, 134.7, 134.0, 133.9, 130.4, 129.8, 129.7, 129.3, 127.7, 126.6, 125.2, 124.9, 52.7, 15.3, 15.0, 13.8, 12.4.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** Calcd for C<sub>27</sub>H<sub>25</sub>BF<sub>2</sub>N<sub>2</sub>O<sub>4</sub>SNa, 545.1488, Found: 545.1497.

### 3am



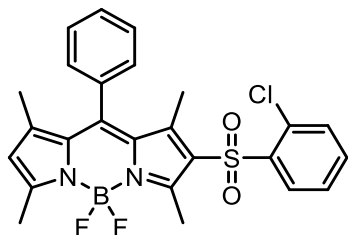
**3am** was obtained in 74% (37.6 mg) as an orange-red solid after column chromatography (eluent: petroleum ether/ethyl acetate = 10/1 v/v).

**<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)** δ 7.56 – 7.52 (m, 3H), 7.37 (m, 2H), 7.03 (s, 2H), 6.46 (s, 2H), 2.57 (s, 3H), 2.55 (s, 3H), 2.24 (s, 3H), 1.35 (s, 3H), 1.22 (s, 3H).

**<sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>)** δ 163.5, 149.8, 148.3, 143.4, 142.9, 138.3, 137.5, 135.8, 134.0, 133.2, 132.2, 129.8, 129.6, 128.1, 127.7, 125.1, 21.4, 20.5, 14.9, 14.6, 13.0, 11.1.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** Calcd for C<sub>28</sub>H<sub>29</sub>BF<sub>2</sub>N<sub>2</sub>O<sub>2</sub>SNa, 529.1903, Found: 529.1914.

### **3an**



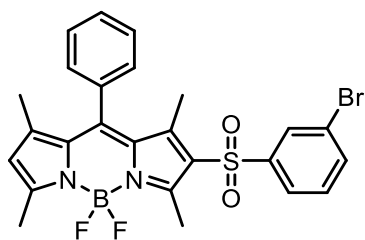
**3an** was obtained in 46% (23.1 mg) as an orange-red solid after column chromatography (eluent: petroleum ether/ethyl acetate = 8/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.20 (d, *J* = 7.8, 1H), 7.51 – 7.45 (m, 4H), 7.44 – 7.36 (m, 2H), 7.23 (m, 2H), 6.15 (s, 1H), 2.79 (s, 3H), 2.60 (s, 3H), 1.44 (s, 3H), 1.38 (s, 3H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 162.8, 153.9, 148.2, 143.5, 140.7, 139.9, 134.5, 134.1, 134.0, 133.2, 132.1, 130.5, 129.7, 129.6, 129.1, 127.8, 126.9, 124.6, 124.3, 15.3, 15.12, 14.0, 12.5.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** Calcd for C<sub>25</sub>H<sub>22</sub>BClF<sub>2</sub>N<sub>2</sub>O<sub>2</sub>SNa, 521.1044, Found: 521.1050.

### **3ao**



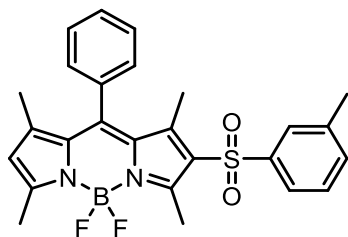
**3ao** was obtained in 59% (31.9 mg) as an orange-red solid after column chromatography (eluent: petroleum ether/ethyl acetate = 8/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.95 (s, 1H), 7.74 (d, *J* = 7.9 Hz, 1H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.52 – 7.50 (m, 3H), 7.34 (t, *J* = 7.9 Hz, 1H), 7.23 (m, 2H), 6.17 (s, 1H), 2.86 (s, 3H), 2.61 (s, 3H), 1.57 (s, 3H), 1.39 (s, 3H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 163.5, 148.5, 145.5, 143.5, 139.9, 135.9, 134.7, 134.0, 130.7, 129.8, 129.7, 129.5, 129.3, 127.8, 125.3, 125.2, 124.8, 123.1, 15.3, 15.0, 13.8, 12.4.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** Calcd for C<sub>25</sub>H<sub>22</sub>BBBrF<sub>2</sub>N<sub>2</sub>O<sub>2</sub>SNa, 565.0539, Found: 565.0549.

### **3ap**



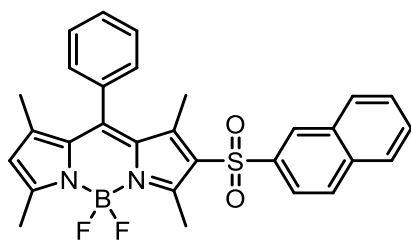
**3ap** was obtained in 61% (29.3 mg) as an orange-red solid after column chromatography (eluent: petroleum ether/ethyl acetate = 8/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.62 (m, 2H), 7.55 – 7.48 (m, 3H), 7.36 – 7.32 (m, 2H), 7.22 (m, 2H), 6.14 (s, 1H), 2.87 (s, 3H), 2.60 (s, 3H), 2.39 (s, 3H), 1.58 (s, 23), 1.38 (s, 3H).

**<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)** δ 162.6, 152.7, 148.0, 143.4, 143.2, 140.2, 139.3, 134.3, 134.0, 133.5, 129.6, 129.1, 128.9, 126.8, 126.3, 124.4, 123.7, 21.4, 15.2, 14.9, 13.7, 12.3.

**HRMS (ESI-TOF, [M + H]<sup>+</sup>):** Calcd for C<sub>25</sub>H<sub>24</sub>BF<sub>2</sub>N<sub>2</sub>O<sub>2</sub>S, 479.1171, Found: 479.1176.

### **3aq**



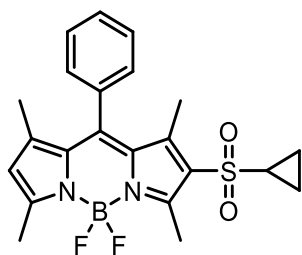
**3aq** was obtained in 53% (27.4 mg) as an orange-red solid after column chromatography (eluent: petroleum ether/ethyl acetate = 8/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.43 (s, 1H), 7.96 – 7.85 (m, 3H), 7.74 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.65 – 7.55 (m, 2H), 7.48 (dd, *J* = 4.9, 1.9 Hz, 3H), 7.20 (m, 2H), 6.14 (s, 1H), 2.94 (s, 3H), 2.60 (s, 3H), 1.60 (s, 3H), 1.37 (s, 3H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 162.9, 152.8, 148.2, 143.5, 140.3, 140.2, 135.0, 134.5, 134.1, 132.2, 129.7, 129.63, 129.60, 129.5, 129.3, 129.0, 128.0, 127.8, 127.62, 127.57, 126.2, 124.6, 122.1, 15.3, 15.0, 13.9, 12.5.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** Calcd for C<sub>29</sub>H<sub>25</sub>BF<sub>2</sub>N<sub>2</sub>O<sub>2</sub>SNa, 537.1590, Found: 537.1600.

### **3ar**



**3ar** was obtained in 38% (16.4 mg) as an orange-red solid after column chromatography (eluent: petroleum ether/ethyl acetate = 8/1 v/v).

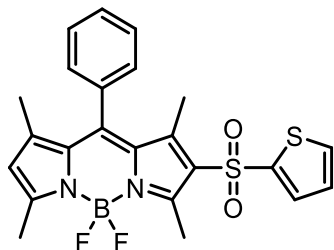
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.53 (m, 3H), 7.31 – 7.26 (m, 2H), 6.16 (s, 1H), 2.82 (s, 3H), 2.62 (s, 3H), 2.43 (m, 1H), 1.63 (s, 3H), 1.41 (s, 3H), 1.27 – 1.21 (m, 2H), 1.01 – 0.91 (m, 2H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 162.7, 152.6, 148.1, 143.6, 140.4, 134.4, 134.2, 129.78, 129.70, 129.2, 127.8, 126.4, 124.5, 34.4, 15.3, 15.0, 13.8, 12.5, 5.3.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** Calcd for C<sub>22</sub>H<sub>22</sub>BF<sub>2</sub>N<sub>2</sub>O<sub>2</sub>SNa, 451.1434, Found: 451.1439.

### **3as**





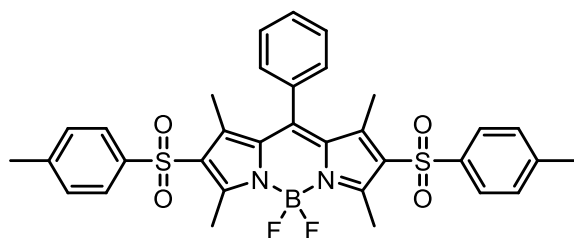
**3as** was obtained in 48% (22.6 mg) as an orange-red solid after column chromatography (eluent: petroleum ether/ethyl acetate = 8/1 v/v).

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.57 (ddd, *J* = 10.9, 4.4, 1.3 Hz, 2H), 7.54 – 7.48 (m, 3H), 7.24 (dd, *J* = 6.6, 2.9 Hz, 2H), 7.07 – 7.00 (m, 1H), 6.15 (s, 1H), 2.87 (s, 3H), 2.60 (s, 3H), 1.64 (s, 3H), 1.39 (s, 3H).

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)** δ 163.0, 152.5, 148.3, 145.7, 143.5, 140.1, 135.7, 134.7, 134.5, 134.1, 132.4, 131.4, 129.8, 129.7, 127.8, 127.6, 124.6, 15.3, 15.0, 13.9, 12.5.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** Calcd for C<sub>23</sub>H<sub>21</sub>BF<sub>2</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>Na, 493.0998, Found: 493.0997.

#### 4aa



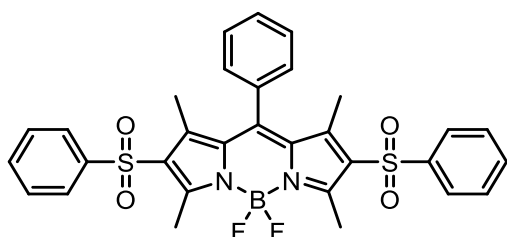
**4aa** was obtained in 48% (30.3 mg) as an orange-red solid after column chromatography (eluent: petroleum ether/ethyl acetate = 4/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.70 (d, *J* = 8.0 Hz, 4H), 7.53 (m, 3H), 7.28 (d, *J* = 8.0 Hz, 4H), 7.20 – 7.16 (m, 2H), 2.87 (s, 6H), 2.40 (s, 6H), 1.63 (s, 6H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 158.1, 147.8, 146.7, 144.4, 139.7, 133.4, 131.4, 130.4, 130.3, 130.1, 130.0, 127.3, 126.8, 21.7, 14.5, 14.0.

**HRMS (ESI-TOF, [M + H]<sup>+</sup>):** Calcd for C<sub>33</sub>H<sub>32</sub>BF<sub>2</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub>, 633.1859, Found: 633.1866.

#### 4ab



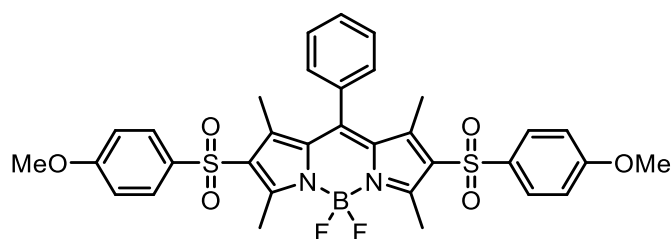
**4ab** was obtained in 50% (30.5 mg) as an orange-red solid after column chromatography (eluent: petroleum ether/ethyl acetate = 4/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.82 (d, *J* = 7.6 Hz, 4H), 7.56 (m, 5H), 7.50 (t, *J* = 7.7 Hz, 4H), 7.20 – 7.17 (dd, *J* = 7.7, 2.0 Hz, 2H), 2.88 (s, 6H), 1.65 (s, 6H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 158.3, 148.0, 147.0, 142.6, 133.4, 131.5, 130.5, 130.2, 130.0, 129.5, 129.0, 127.3, 126.8, 14.5, 13.3.

**HRMS (ESI-TOF, [M + H]<sup>+</sup>):** Calcd for C<sub>31</sub>H<sub>28</sub>BF<sub>2</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub>, 605.1546, Found: 605.1540.

#### 4ai



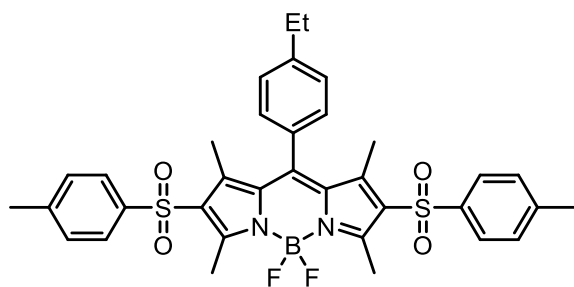
**4ai** was obtained in 46% (30.6 mg) as an orange-red solid after column chromatography (eluent: petroleum ether/ethyl acetate = 8/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.70 (d, *J* = 8.2 Hz, 4H), 7.28 (d, *J* = 8.2 Hz, 4H), 7.05 (q, *J* = 8.7 Hz, 4H), 3.87 (s, 3H), 2.87 (s, 6H), 2.40 (s, 6H), 1.70 (s, 6H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 161.2, 157.9, 148.1, 146.7, 144.4, 139.8, 131.8, 130.0, 128.8, 127.6, 126.8, 125.2, 115.5, 55.6, 21.7, 14.4, 13.5.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** Calcd for C<sub>34</sub>H<sub>33</sub>BF<sub>2</sub>N<sub>2</sub>O<sub>5</sub>S<sub>2</sub>Na, 687.1577, Found: 687.1598.

#### 4ca



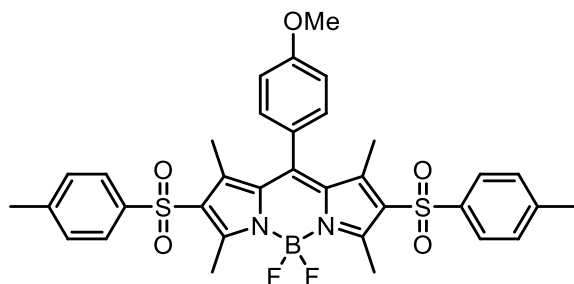
**4ca** was obtained in 42% (27.8 mg) as an orange-red solid after column chromatography (eluent: petroleum ether/ethyl acetate = 4/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.70 (d, *J* = 8.0 Hz, 4H), 7.34 (d, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 4H), 7.07 (d, *J* = 7.8 Hz, 2H), 2.87 (s, 6H), 2.73 (q, *J* = 7.7 Hz, 2H), 2.40 (s, 6H), 1.65 (s, 6H), 1.27 (t, *J* = 7.6 Hz, 3H).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  157.9, 148.3, 147.1, 146.8, 144.4, 139.8, 131.6, 130.6, 130.1, 130.0, 129.5, 127.3, 126.8, 28.8, 21.7, 15.6, 14.4, 13.3.

HRMS (ESI-TOF,  $[\text{M} + \text{Na}]^+$ ): Calcd for  $\text{C}_{35}\text{H}_{35}\text{BF}_2\text{N}_2\text{O}_4\text{S}_2\text{Na}$ , 683.1992, Found: 683.1982.

#### 4fa



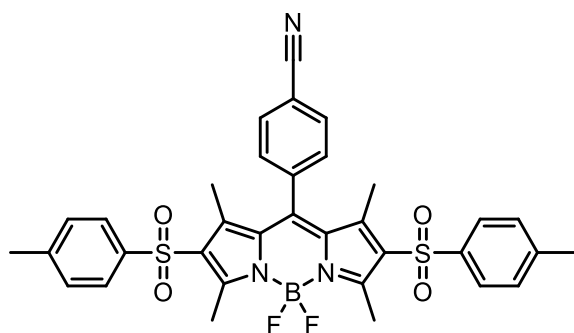
**4fa** was obtained in 50% (32.9 mg) as an orange-red solid after column chromatography (eluent: petroleum ether/ethyl acetate = 4/1 v/v).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.70 (d,  $J = 8.2$  Hz, 4H), 7.28 (d,  $J = 8.2$  Hz, 4H), 7.05 (q,  $J = 8.7$  Hz, 4H), 3.87 (s, 3H), 2.87 (s, 6H), 2.40 (s, 6H), 1.70 (s, 6H).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  161.2, 157.9, 148.1, 146.7, 144.4, 139.8, 131.8, 130.0, 128.8, 127.6, 126.8, 125.2, 115.5, 55.6, 21.7, 14.4, 13.5.

HRMS (ESI-TOF,  $[\text{M} + \text{Na}]^+$ ): Calcd for  $\text{C}_{34}\text{H}_{33}\text{BF}_2\text{N}_2\text{O}_5\text{S}_2\text{Na}$ , 685.1784, Found: 685.1785.

#### 4ga



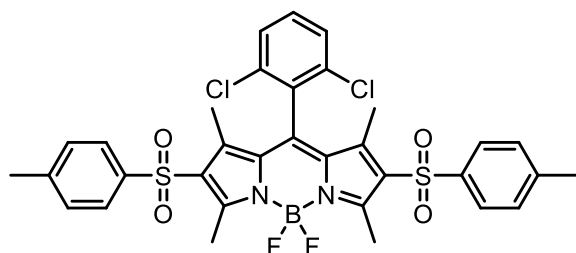
**4ga** was obtained in 45% (29.6 mg) as an orange-red solid after column chromatography (eluent: petroleum ether/ethyl acetate = 4/1 v/v).

$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (d,  $J = 8.2$  Hz, 2H), 7.69 (d,  $J = 8.3$  Hz, 4H), 7.39 (d,  $J = 8.2$  Hz, 2H), 7.30 (d,  $J = 8.3$  Hz, 4H), 2.87 (s, 6H), 2.41 (s, 6H), 1.62 (s, 6H).

$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  159.1, 146.0, 144.7, 144.5, 139.5, 138.2, 133.7, 131.0, 130.7, 130.1, 128.9, 126.8, 117.5, 114.7, 21.7, 14.6, 13.5.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** Calcd for C<sub>34</sub>H<sub>30</sub>BF<sub>2</sub>N<sub>3</sub>O<sub>4</sub>S<sub>2</sub>Na, 680.1631, Found: 680.1637.

#### 4ja



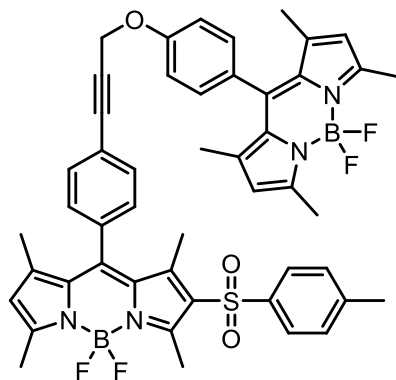
**4ja** was obtained in 50% (34.8 mg) as an orange-red solid after column chromatography (eluent: petroleum ether/ethyl acetate = 4/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.71 (d, *J* = 6.9 Hz, 4H), 7.48 (m, 3H), 7.30 (d, *J* = 7.0 Hz, 4H), 2.85 (s, 6H), 2.41 (s, 6H), 1.81 (s, 6H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 159.1, 145.4, 144.5, 141.1, 139.6, 134.2, 132.4, 131.6, 130.5, 130.4, 130.1, 129.3, 126.8, 21.7, 14.7, 11.7.

**HRMS (ESI-TOF, [M + H]<sup>+</sup>):** Calcd for C<sub>33</sub>H<sub>30</sub>BCl<sub>2</sub>F<sub>2</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub>, 701.1080, Found: 701.1089.

#### 5



**5** was obtained in 55% (140.1 mg) as an orange-red solid after column chromatography (eluent: petroleum ether/ethyl acetate = 10/1 v/v).

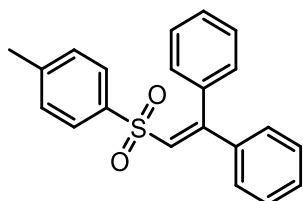
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 7.8 Hz, 2H), 7.26 (d, *J* = 7.8 Hz, 2H), 7.25 – 7.18 (m, 4H), 7.15 (d, *J* = 8.5 Hz, 2H), 6.15 (s, 1H), 5.98 (s, 2H), 5.01 (s, 2H), 2.85 (s, 3H), 2.59 (s, 3H), 2.55 (s, 6H), 2.39 (s, 3H), 1.60 (s, 3H), 1.43 (s, 6H), 1.39 (s, 3H).

**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 163.1, 158.3, 155.6, 153.1, 147.6, 143.8, 143.1, 142.3,

141.6, 140.6, 140.1, 134.7, 134.1, 132.9, 131.9, 129.8, 129.5, 128.9, 128.3, 128.2, 127.0, 126.7, 124.7, 123.8, 121.3, 115.9, 86.6, 85.5, 56.9, 21.7, 15.3, 15.2, 14.70, 14.66, 13.9, 12.7.

**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** Calcd for C<sub>48</sub>H<sub>44</sub>B<sub>2</sub>F<sub>4</sub>N<sub>4</sub>O<sub>3</sub>SNa, 877.3149, Found: 877.3154.

7

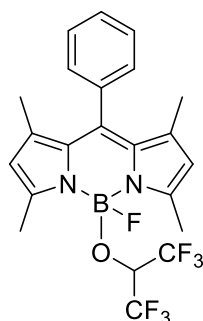


7 was obtained in 28% (28.3 mg) as a white solid after column chromatography (eluent: petroleum ether/ethyl acetate = 10/1 v/v).

**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.48 (d, J = 8.0 Hz, 2H), 7.37 (m, 2H), 7.30 (t, J = 7.6 Hz, 4H), 7.20 (d, J = 7.6 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 7.3 Hz, 2H), 6.99 (s, 1H), 2.38 (s, 3H).

**HRMS (ESI-TOF, [M + H]<sup>+</sup>):** Calcd for C<sub>21</sub>H<sub>19</sub>O<sub>2</sub>S, 335.1100, Found: 335.1100.

10

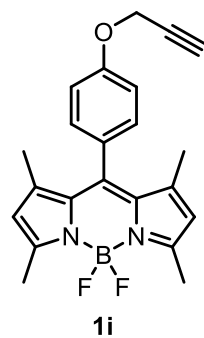


10 was obtained in 19% (9.0 mg) as an orange-red solid after column chromatography (eluent: petroleum ether/ethyl acetate = 50/1 v/v).

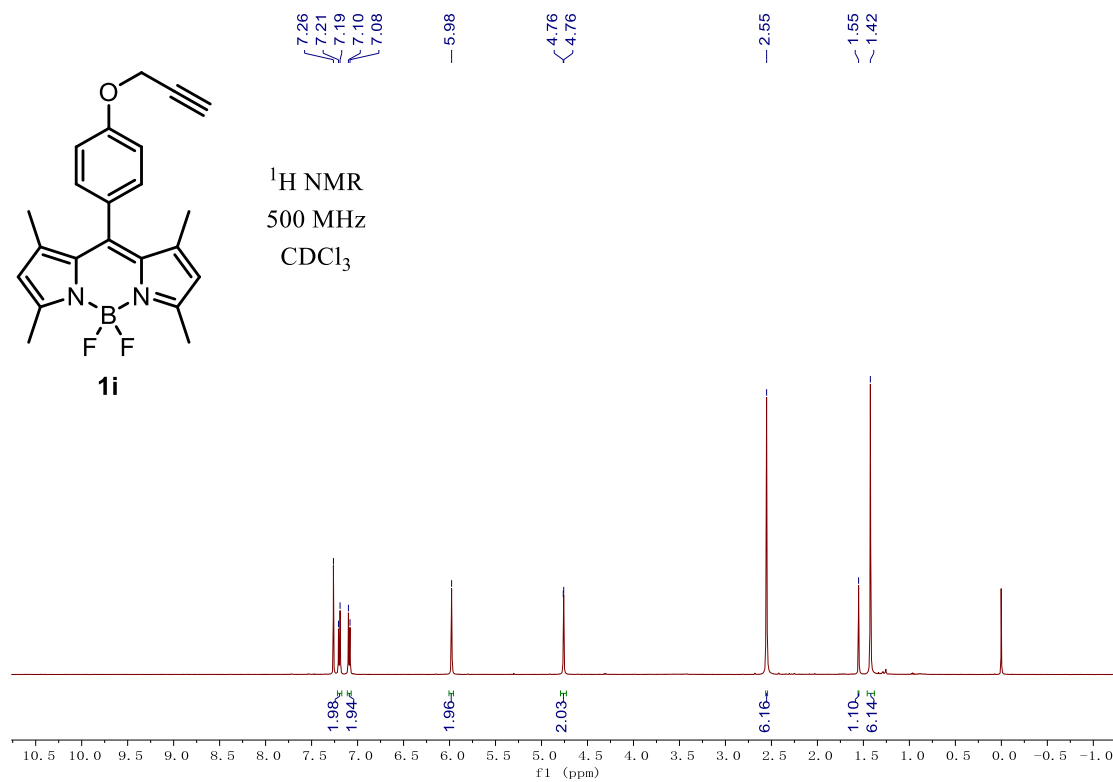
**<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.72 – 7.44 (m, 3H), 7.26 (m, 2H), 6.00 (s, 2H), 4.11 – 3.63 (m, 1H), 2.53 (s, 6H), 1.39 (s, 6H).

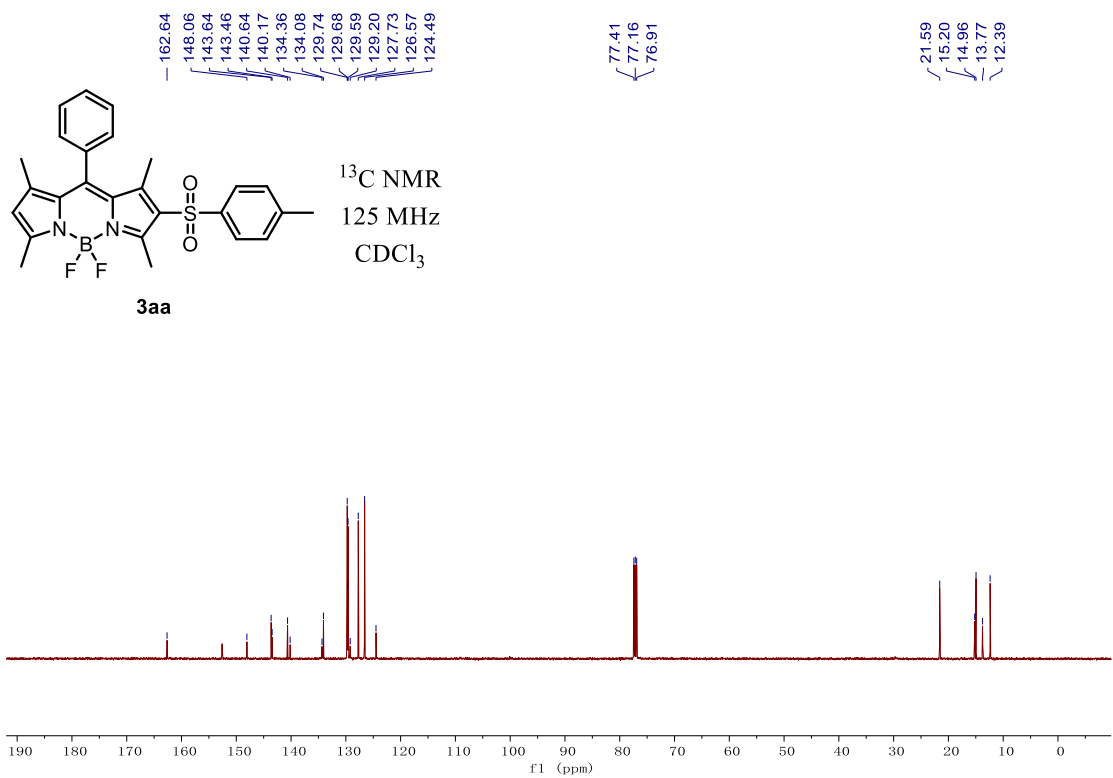
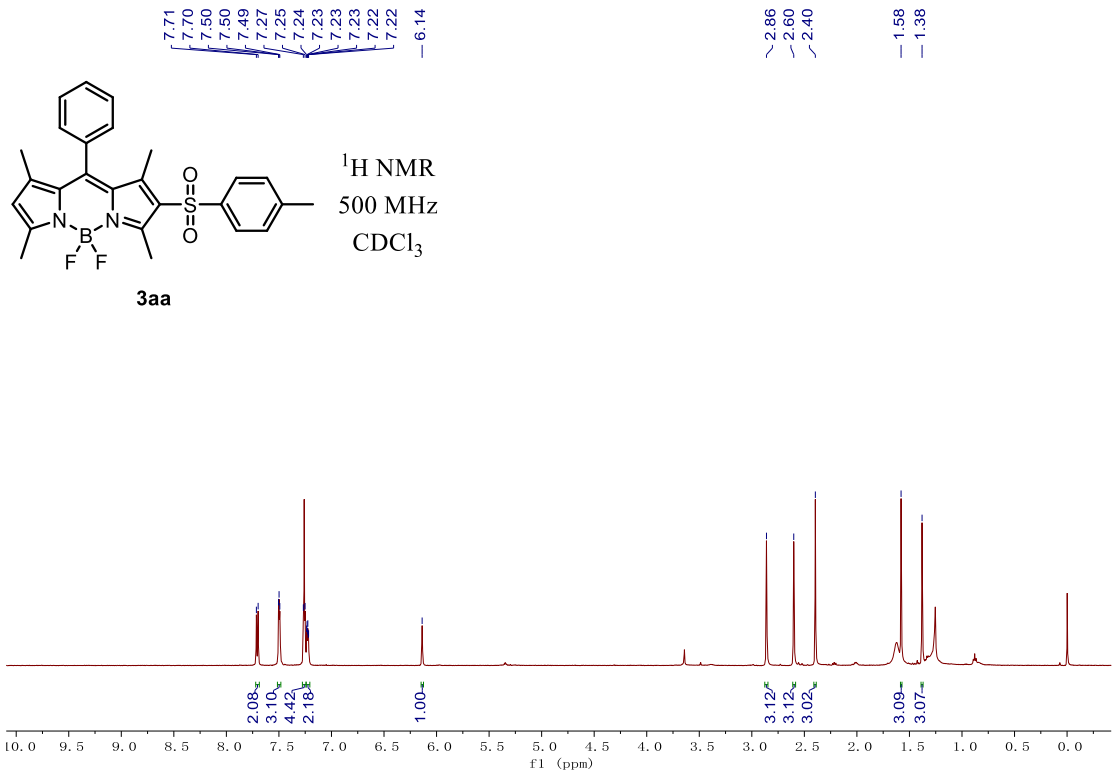
**<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 156.8, 143.6, 141.8, 134.8, 131.7, 129.4, 129.3, 128.2, 127.9, 123.5, 121.88, 121.85, 121.2, 70.89, 70.83, 70.63, 70.57, 70.38, 70.31, 70.12, 70.06, 69.86, 69.80, 14.92, 14.88, 14.6.

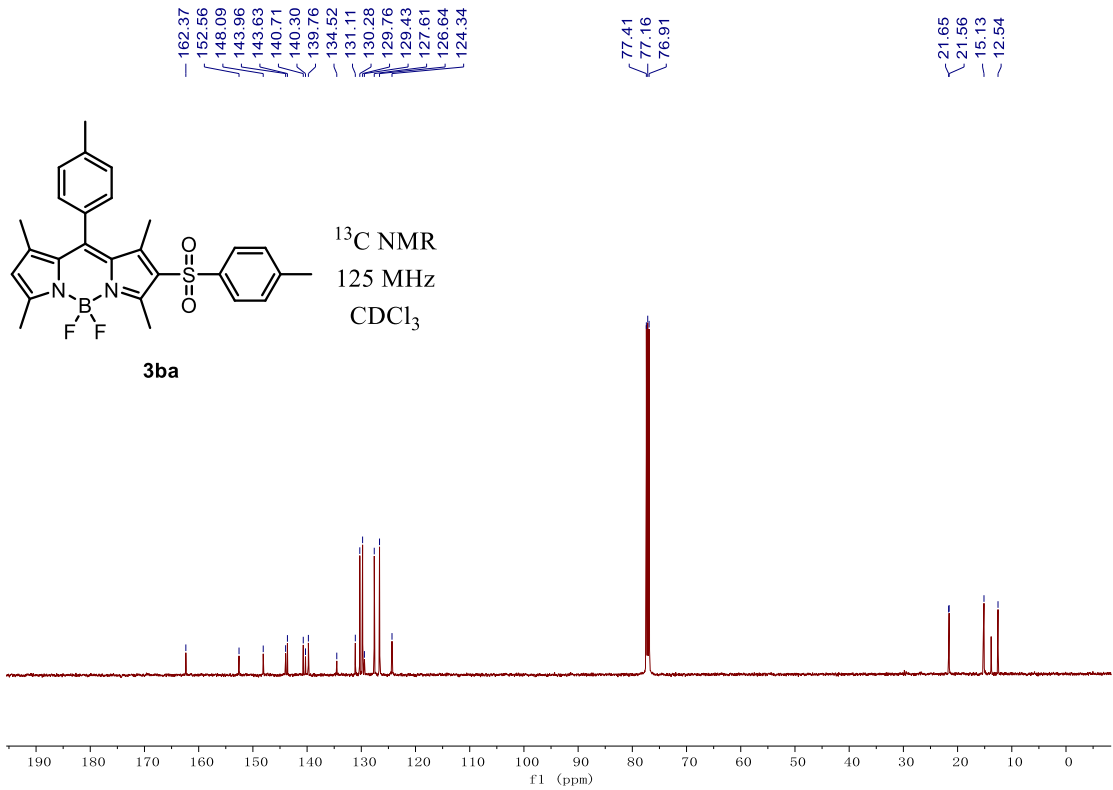
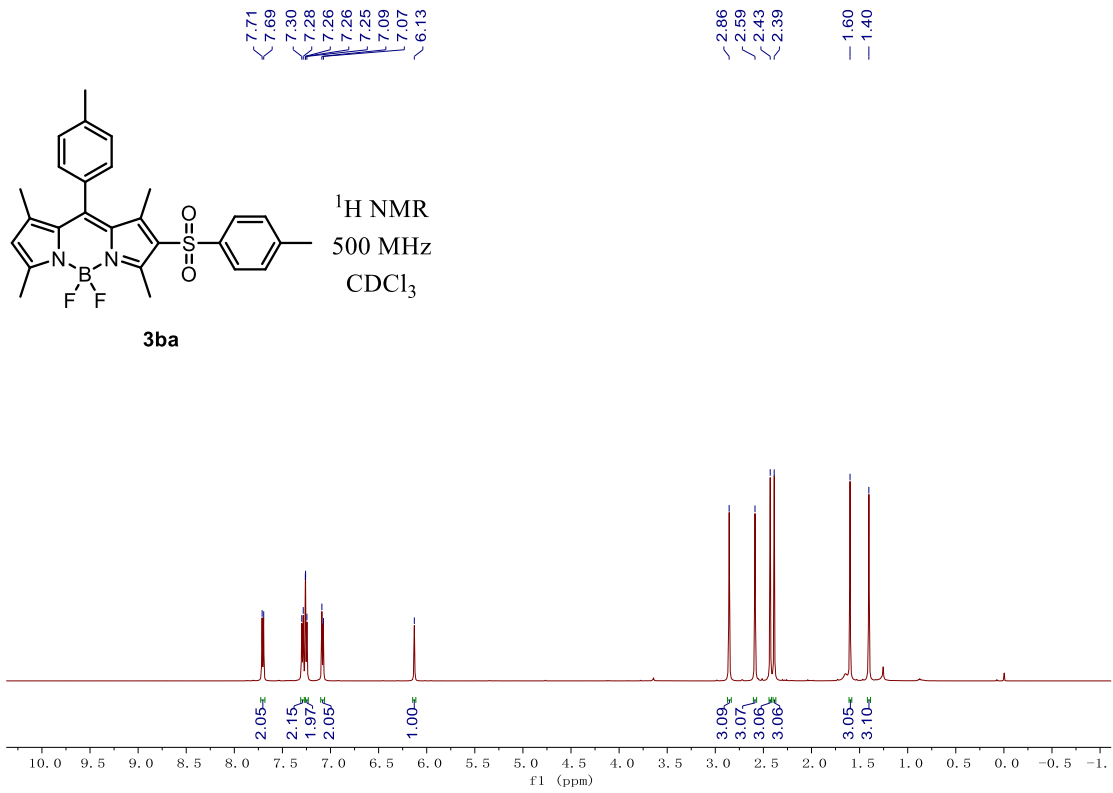
**HRMS (ESI-TOF, [M + Na]<sup>+</sup>):** Calcd for C<sub>22</sub>H<sub>20</sub>BF<sub>7</sub>N<sub>2</sub>O<sub>2</sub>Na, 495.1449, Found: 495.1456.



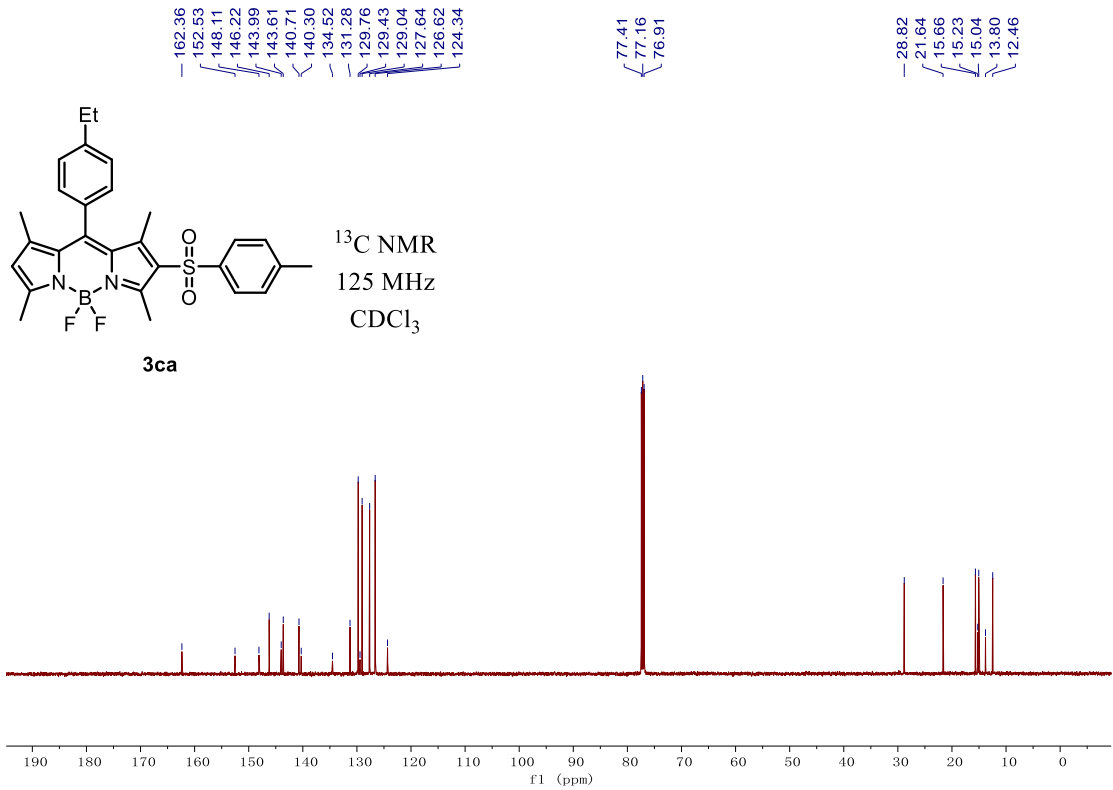
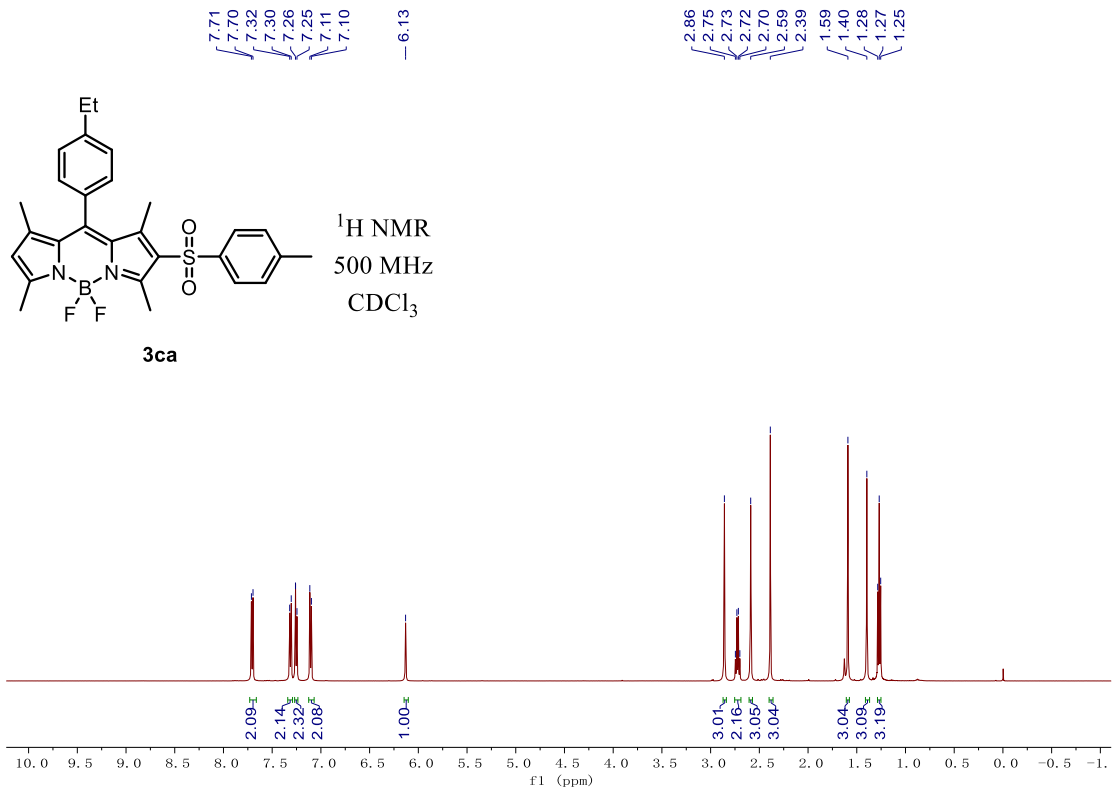
$^1\text{H}$  NMR  
500 MHz  
 $\text{CDCl}_3$

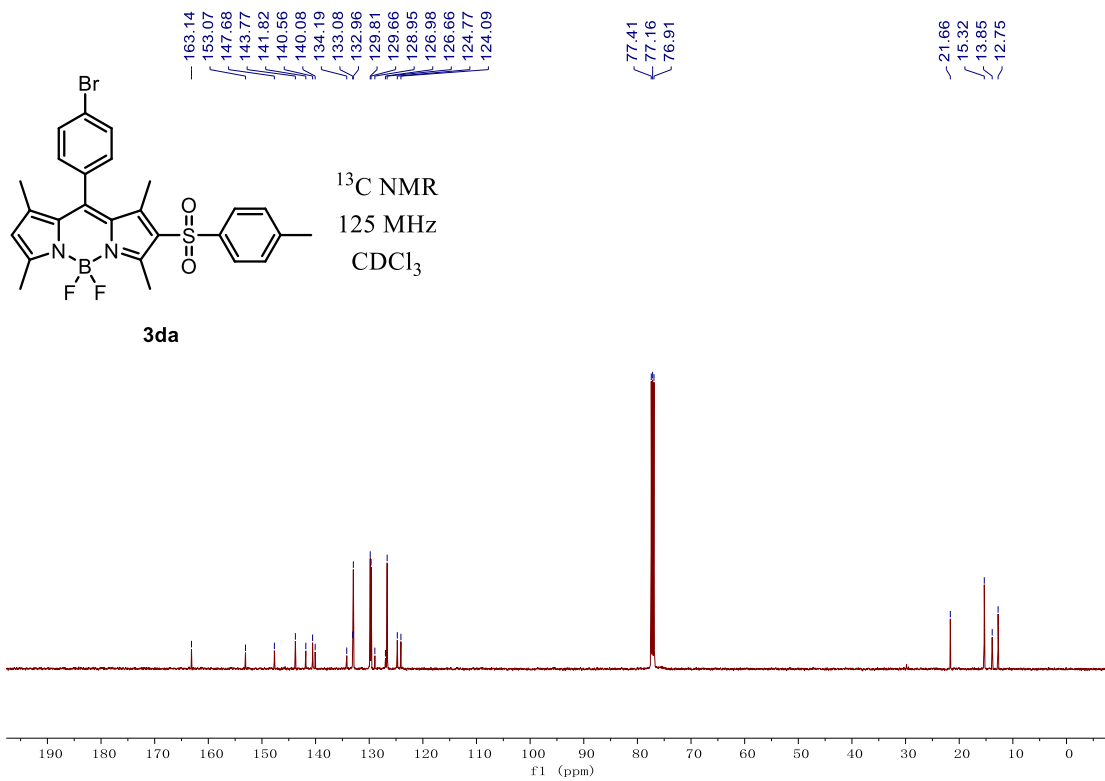
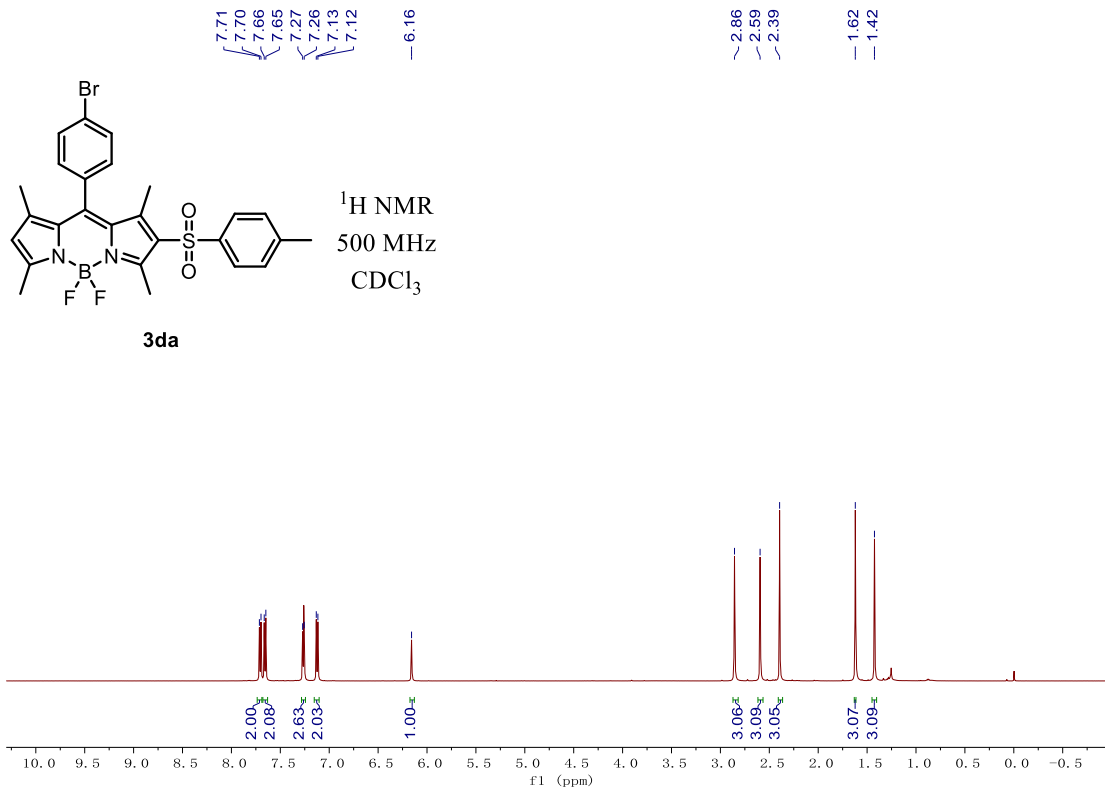


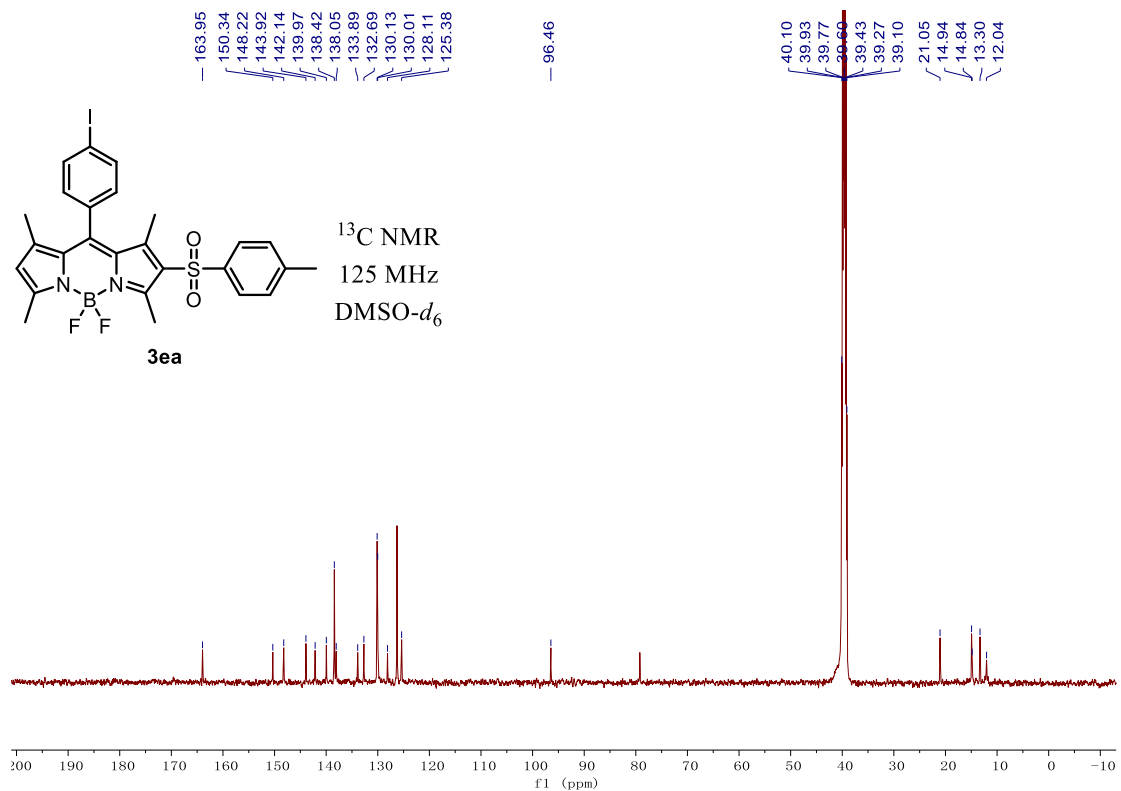
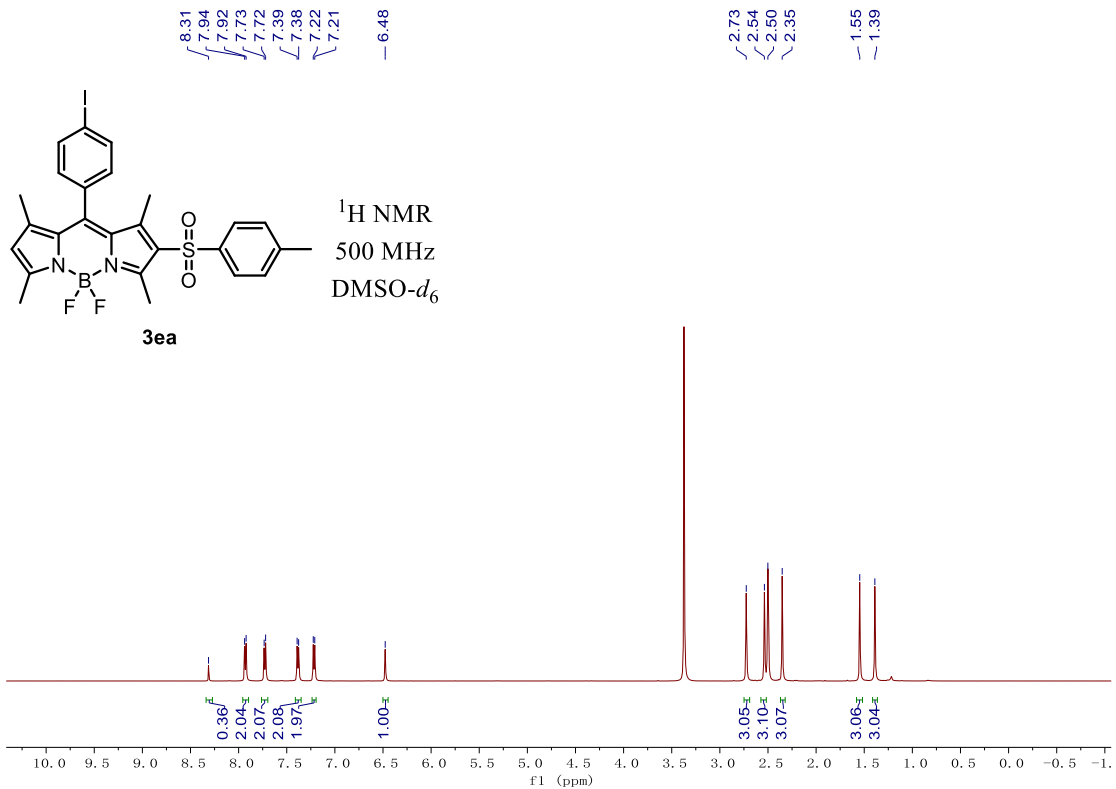


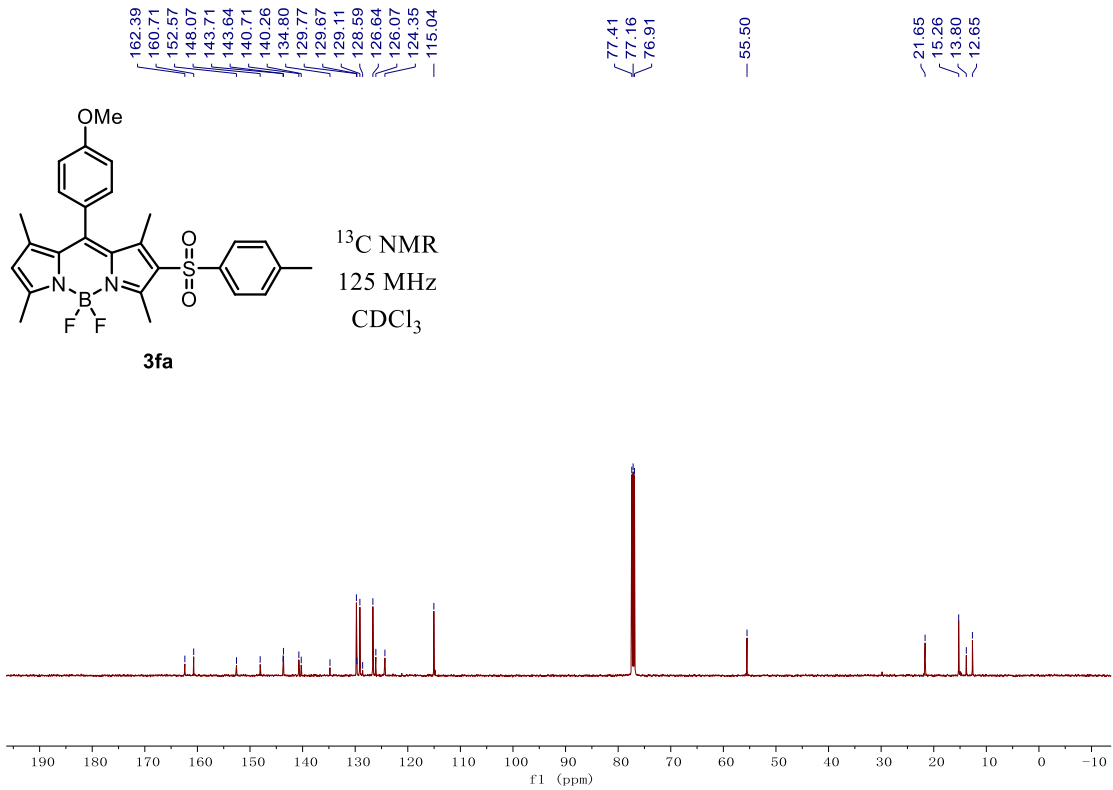
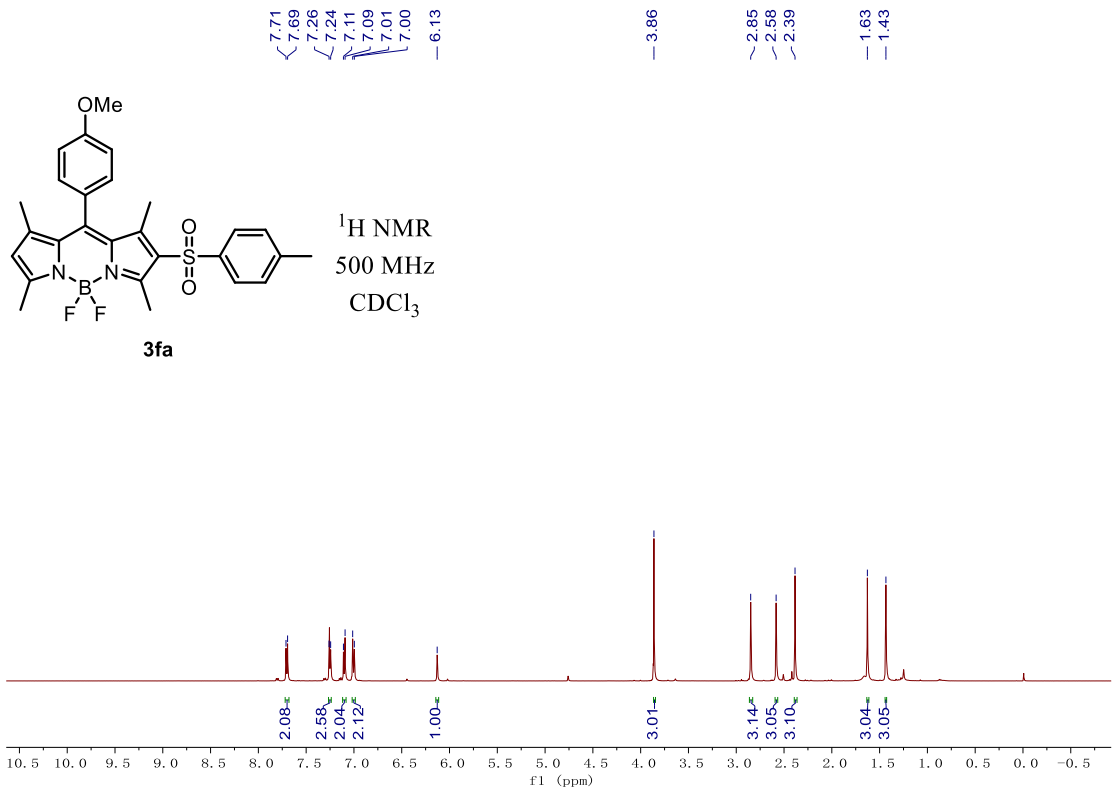


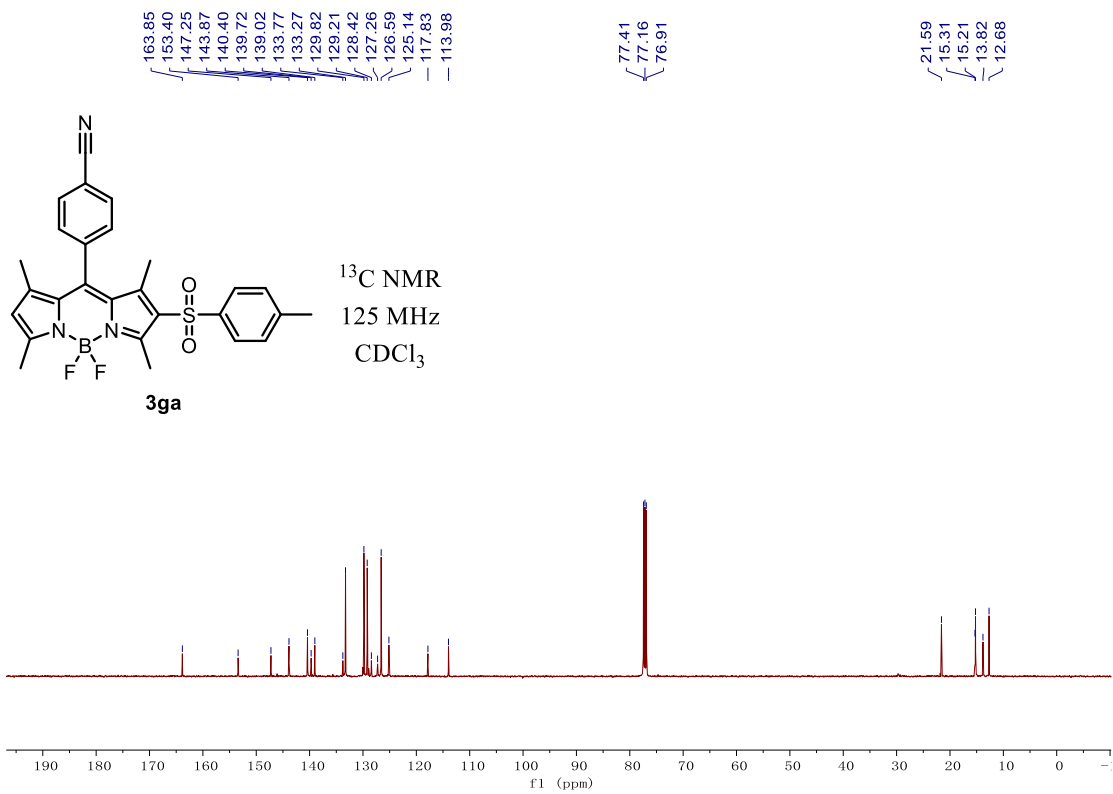
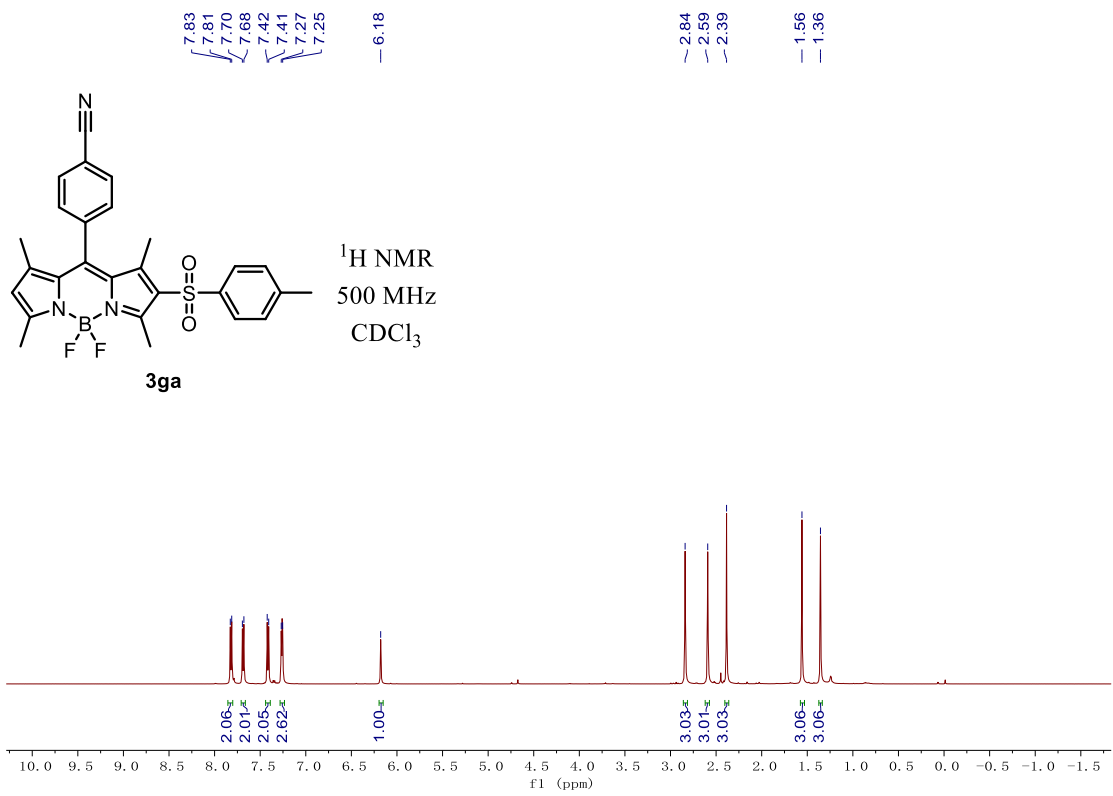


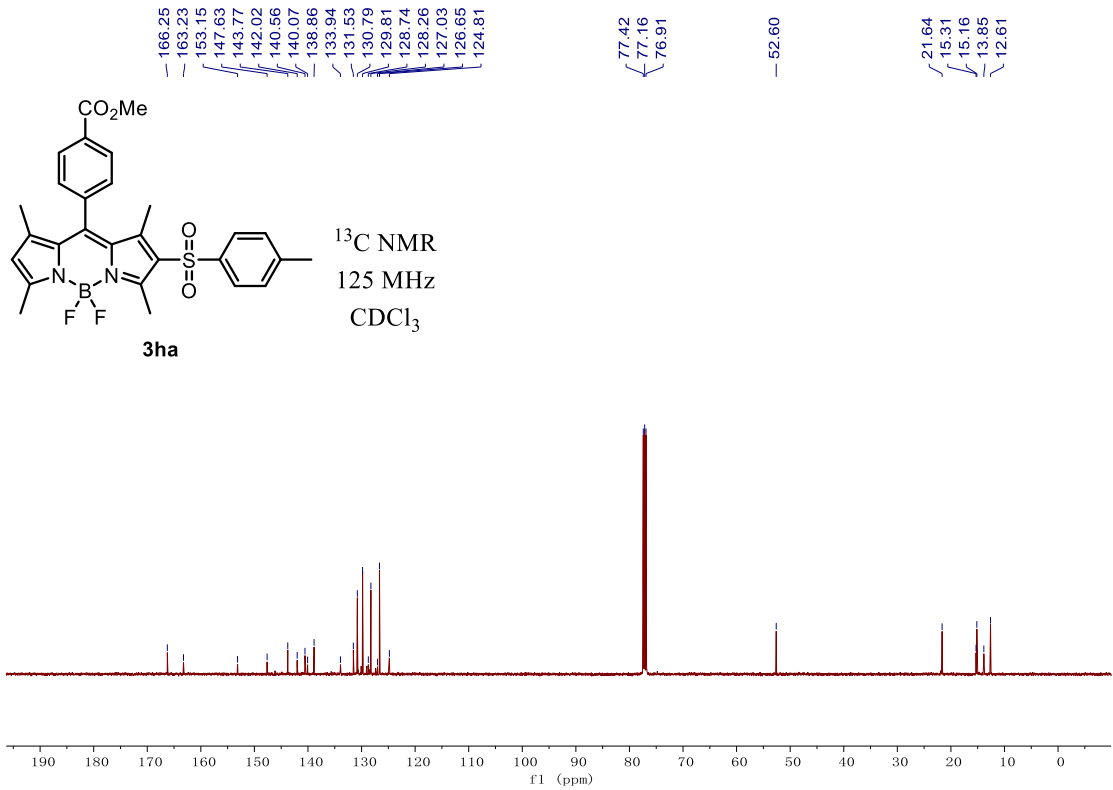
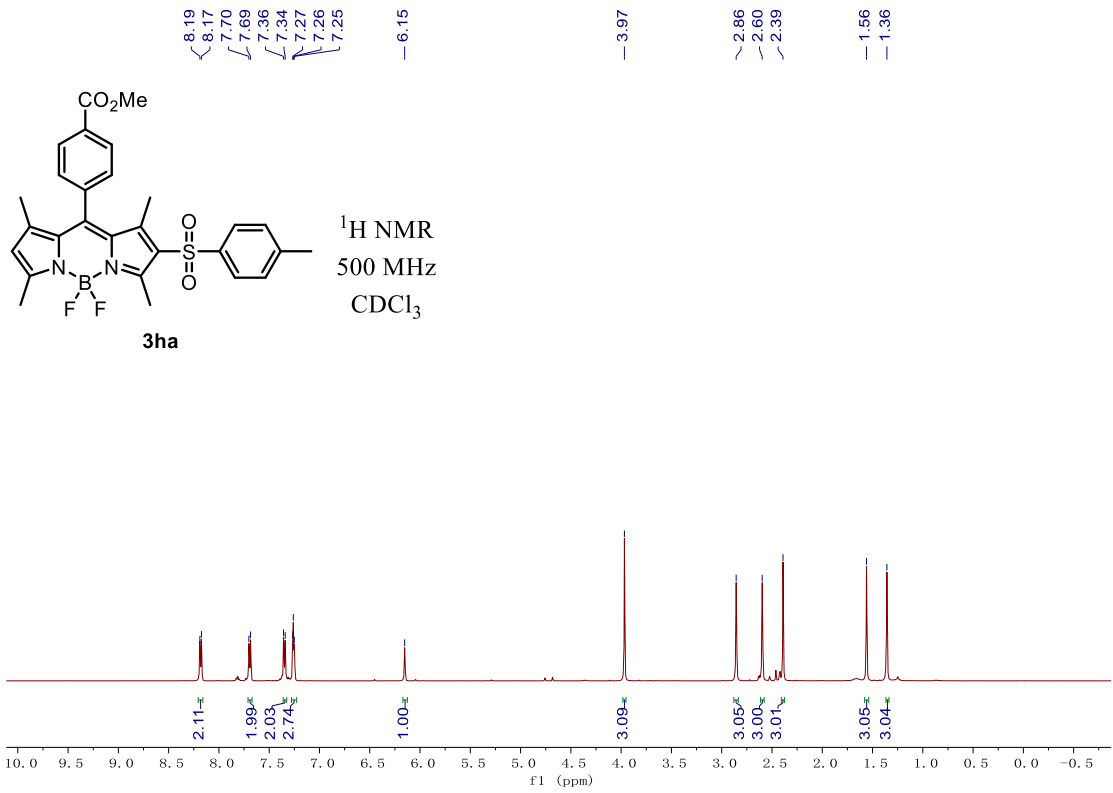


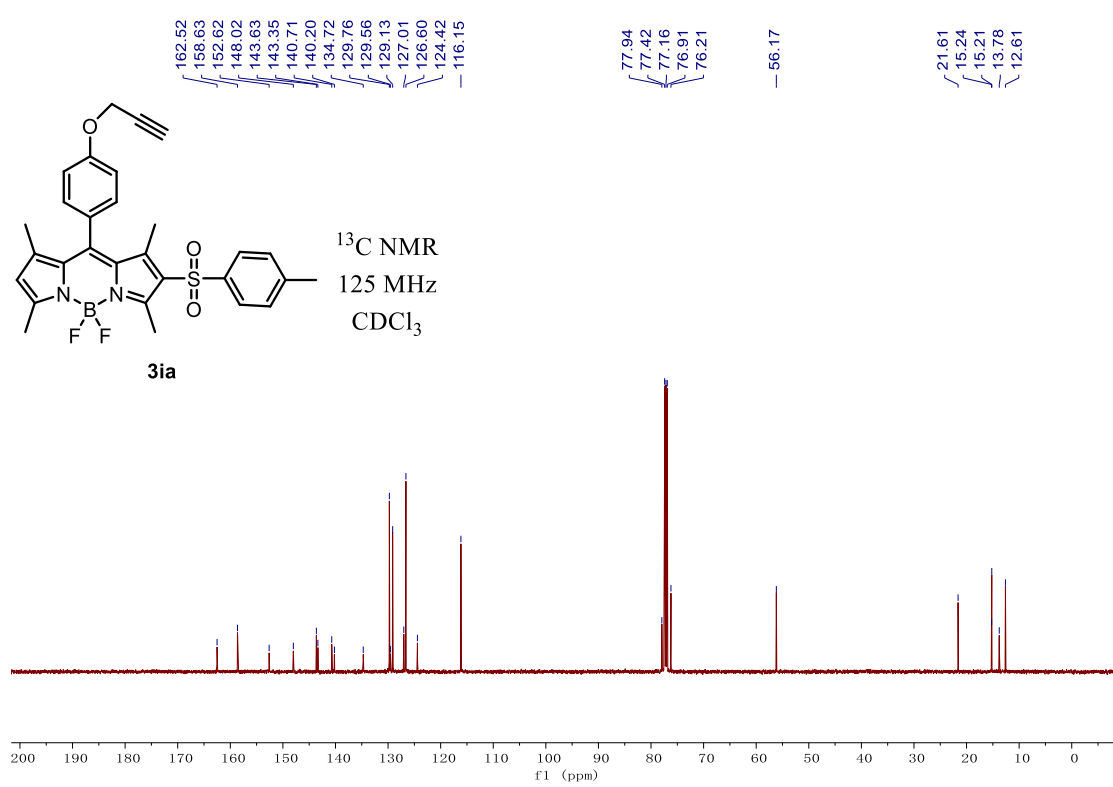
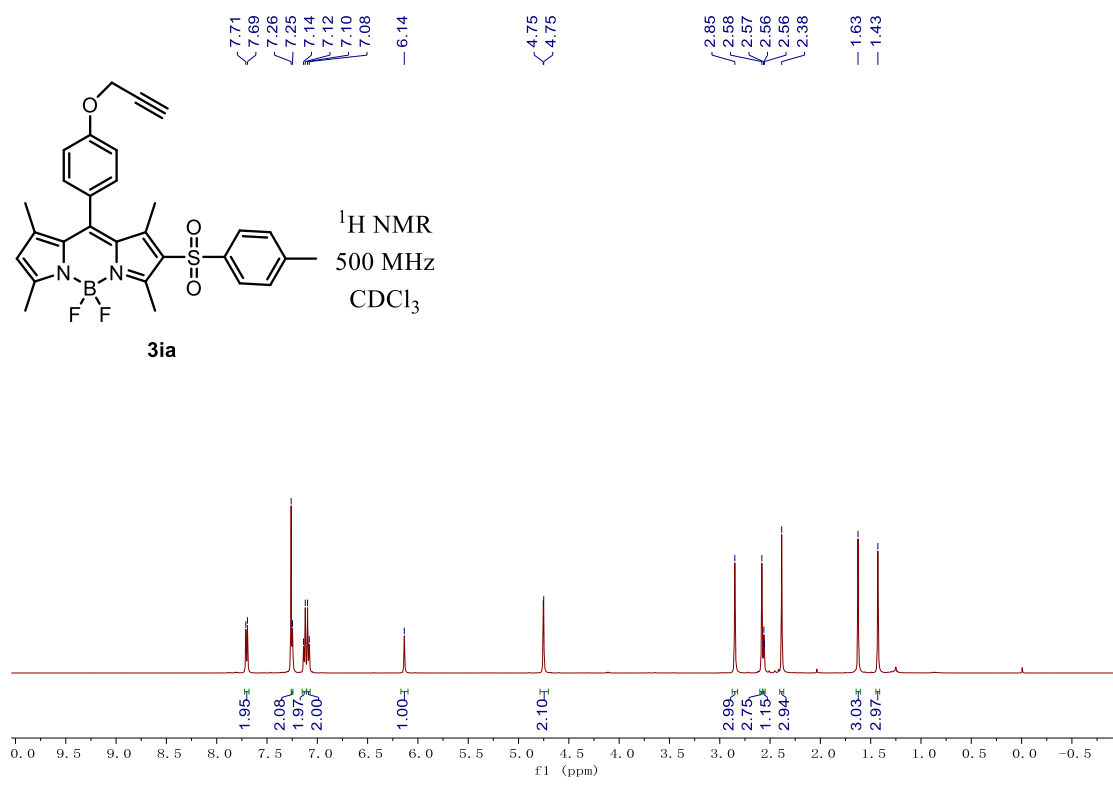


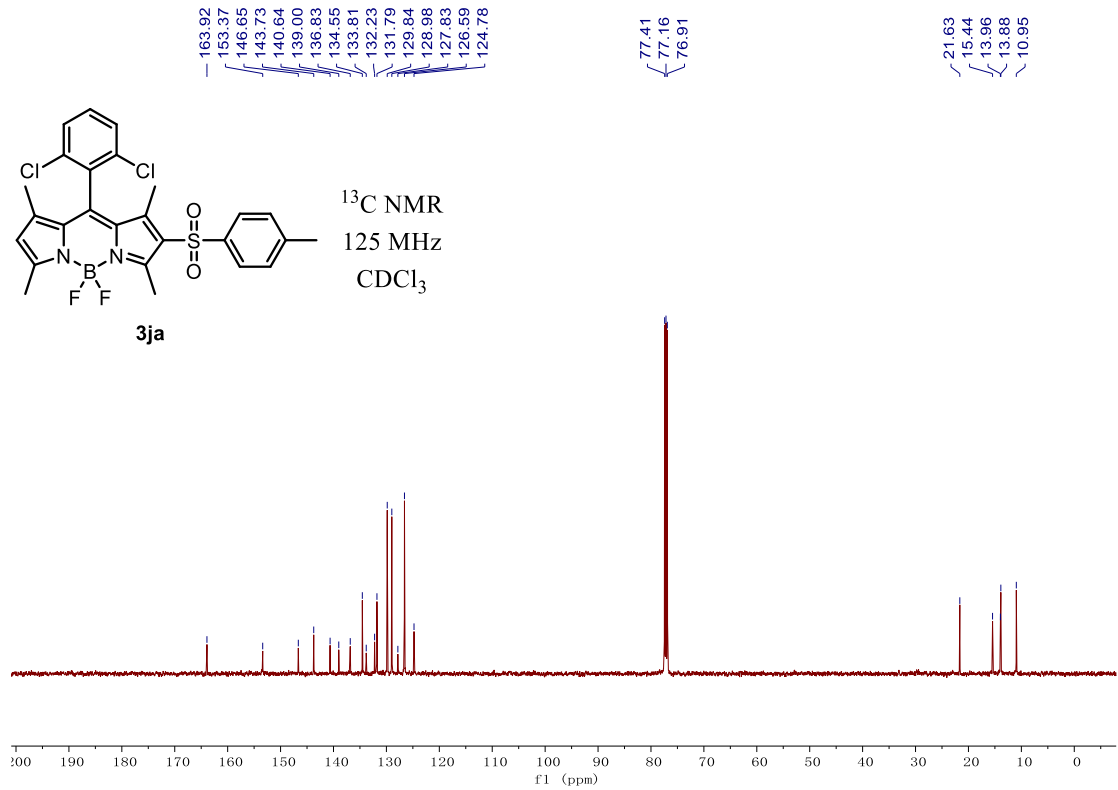
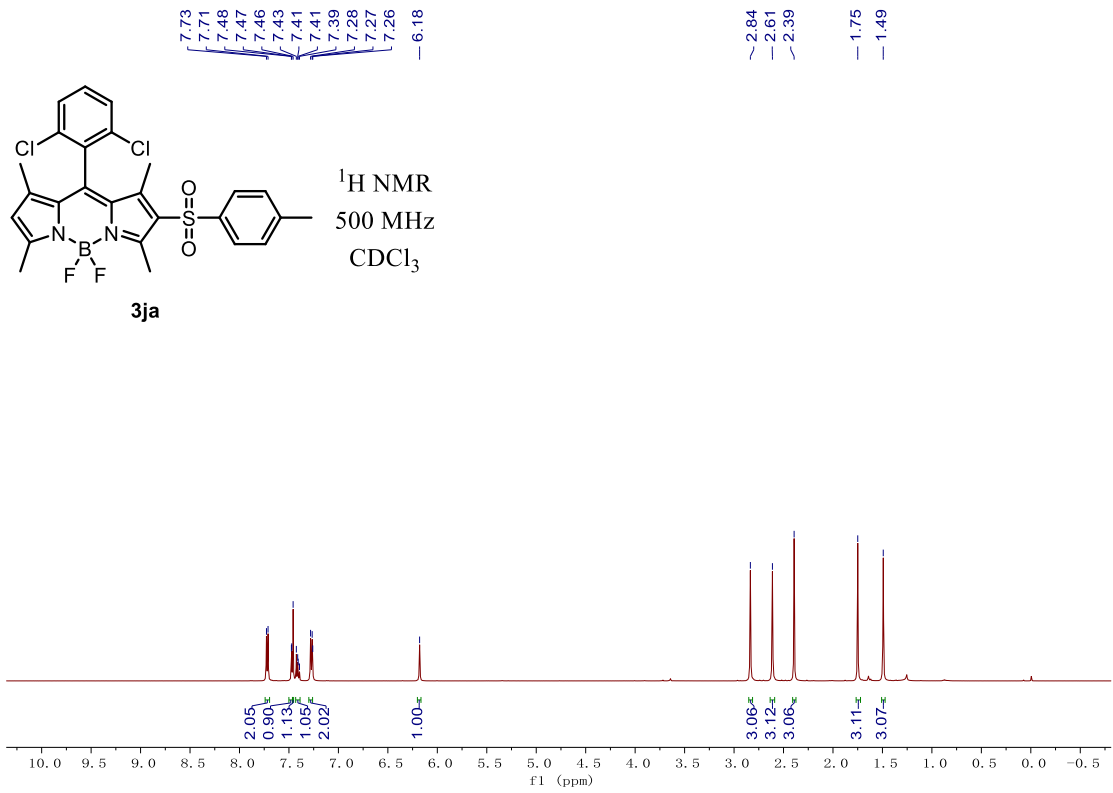




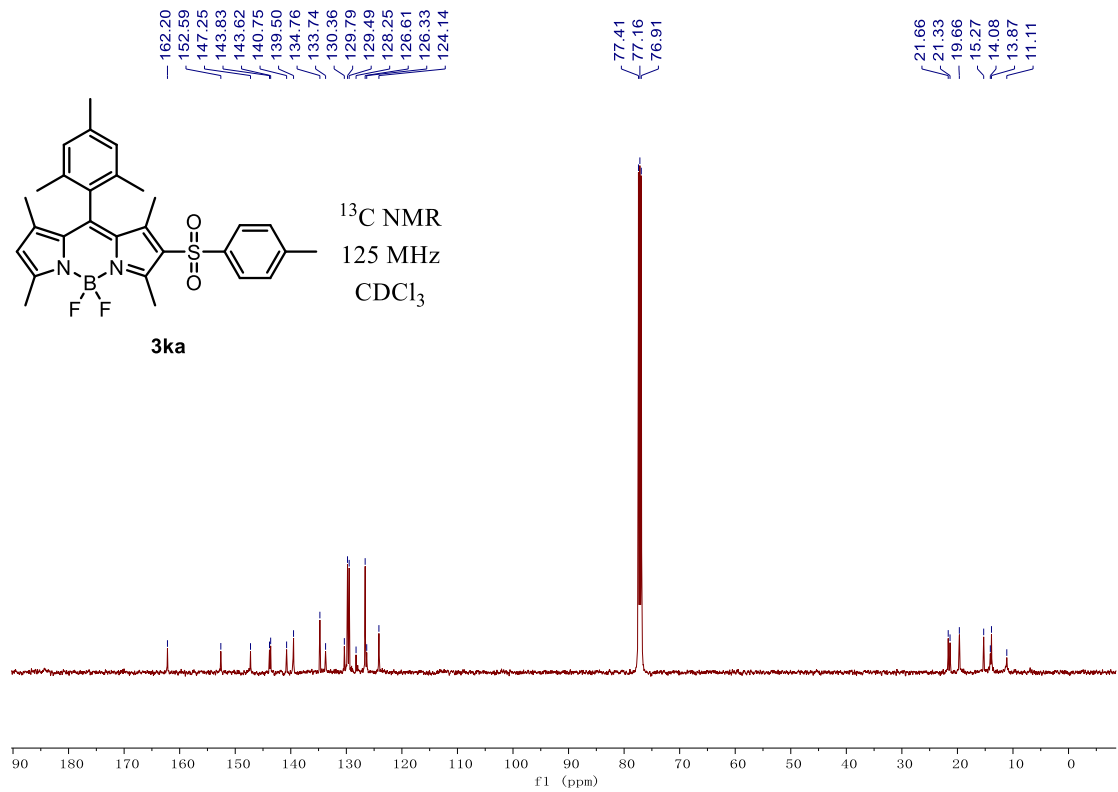
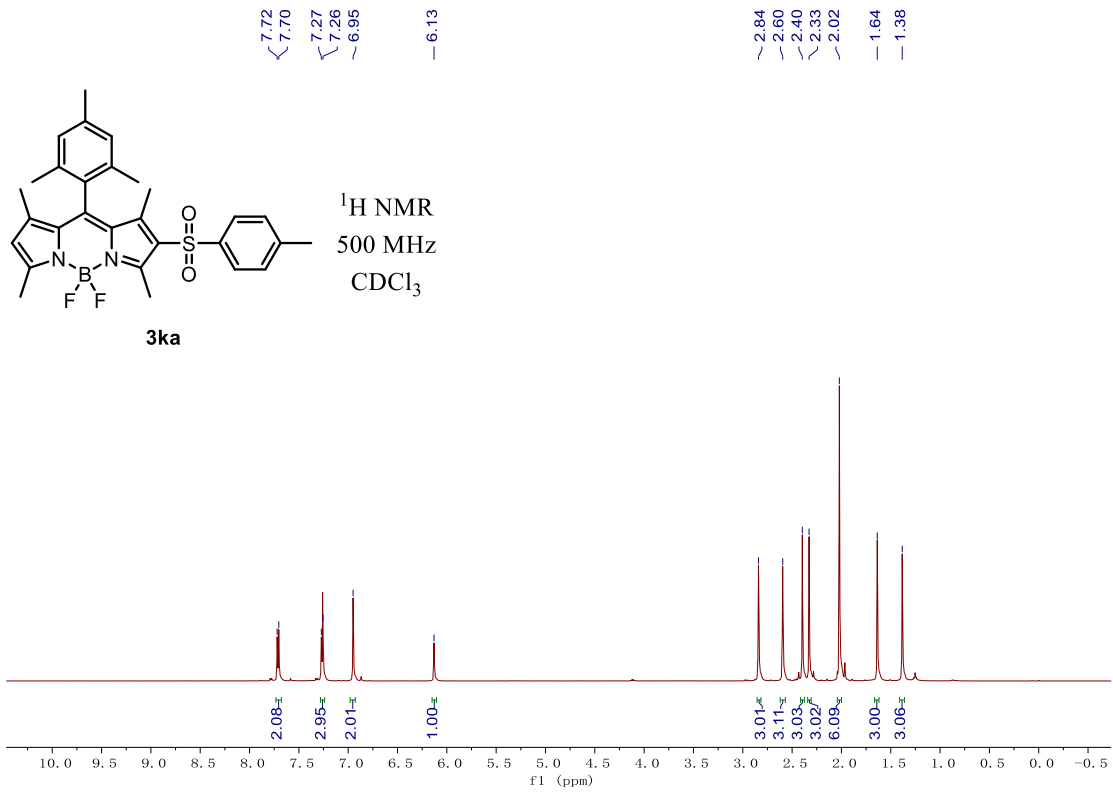


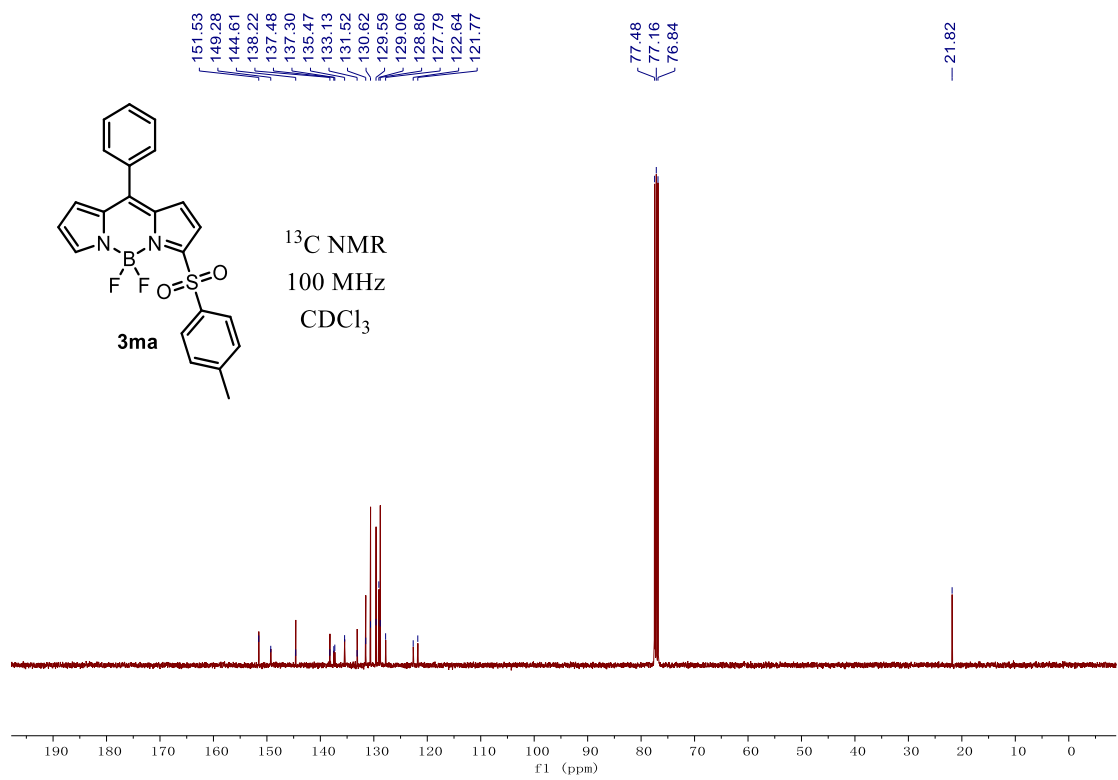
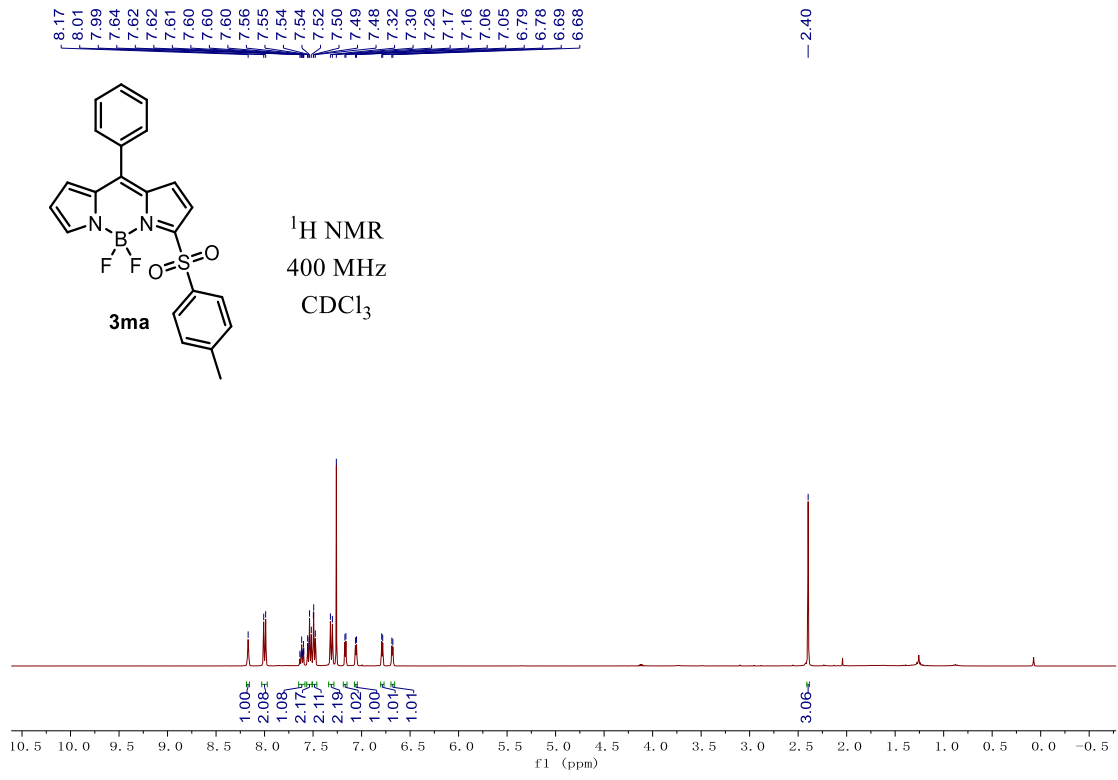


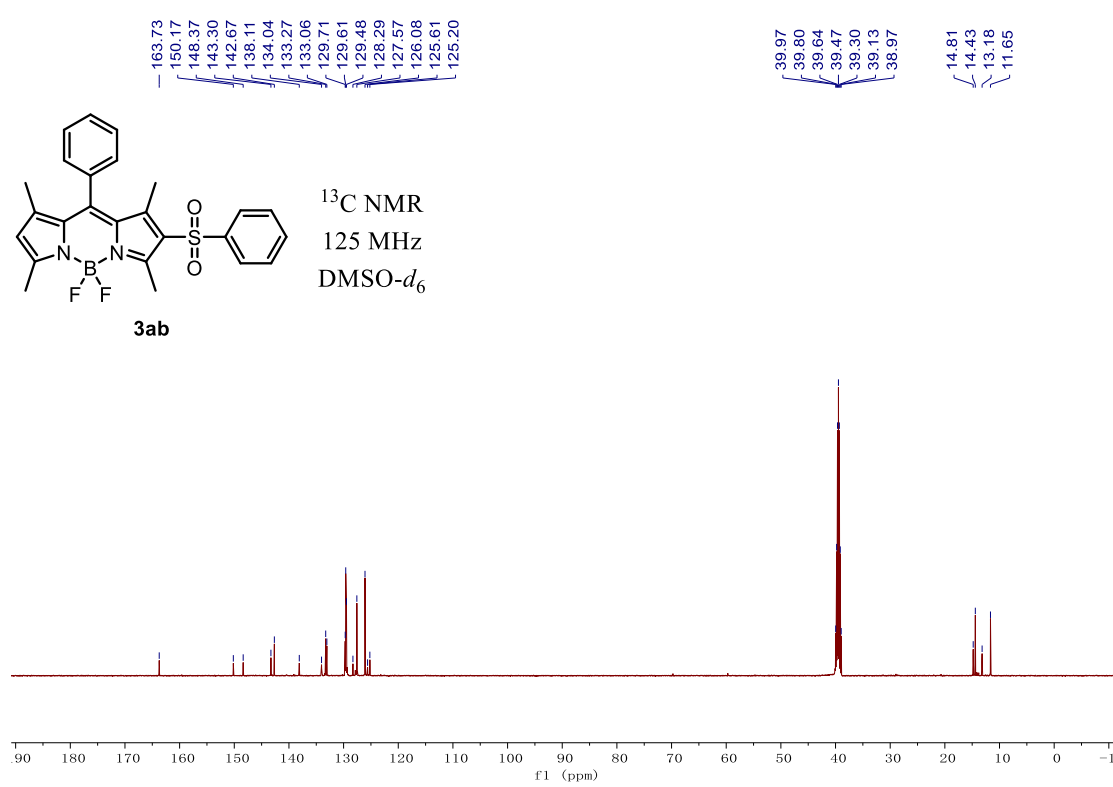
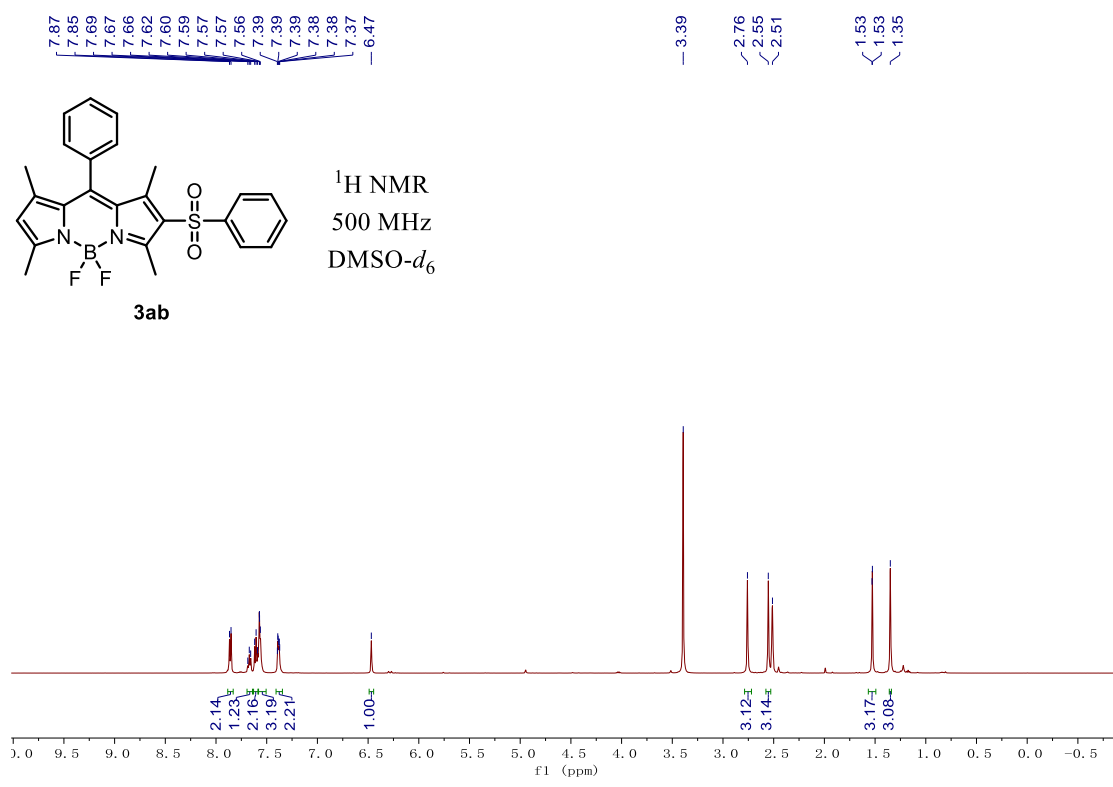


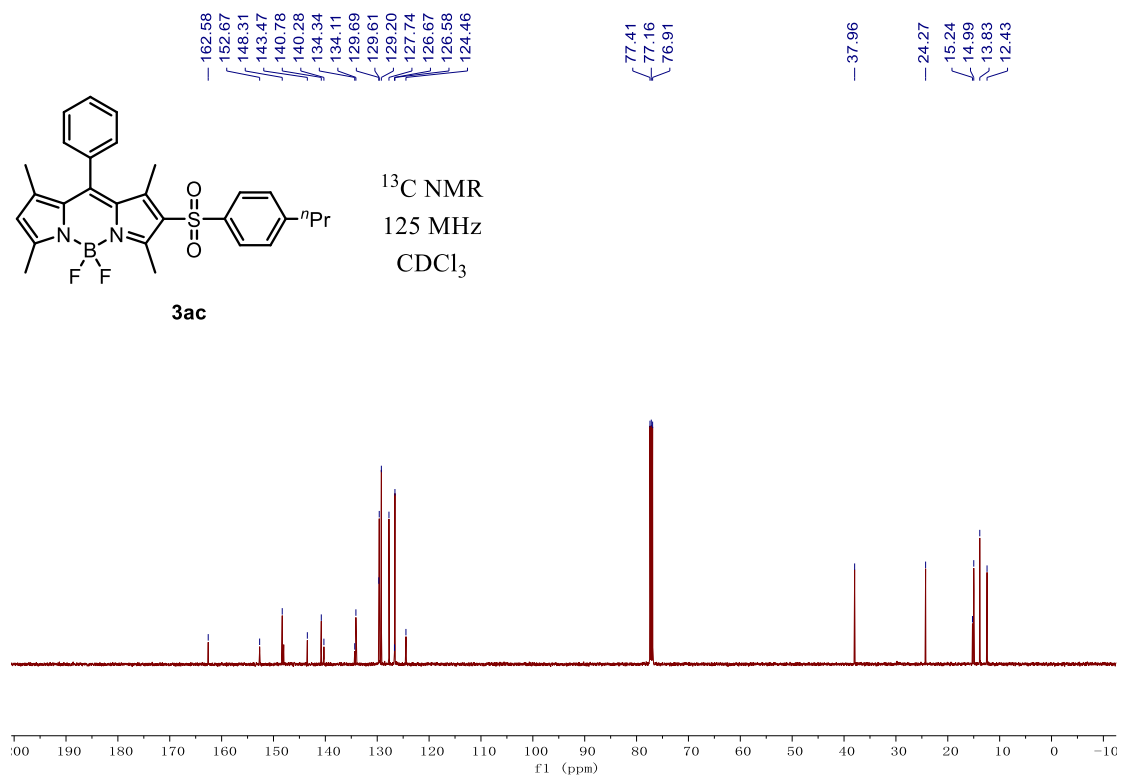
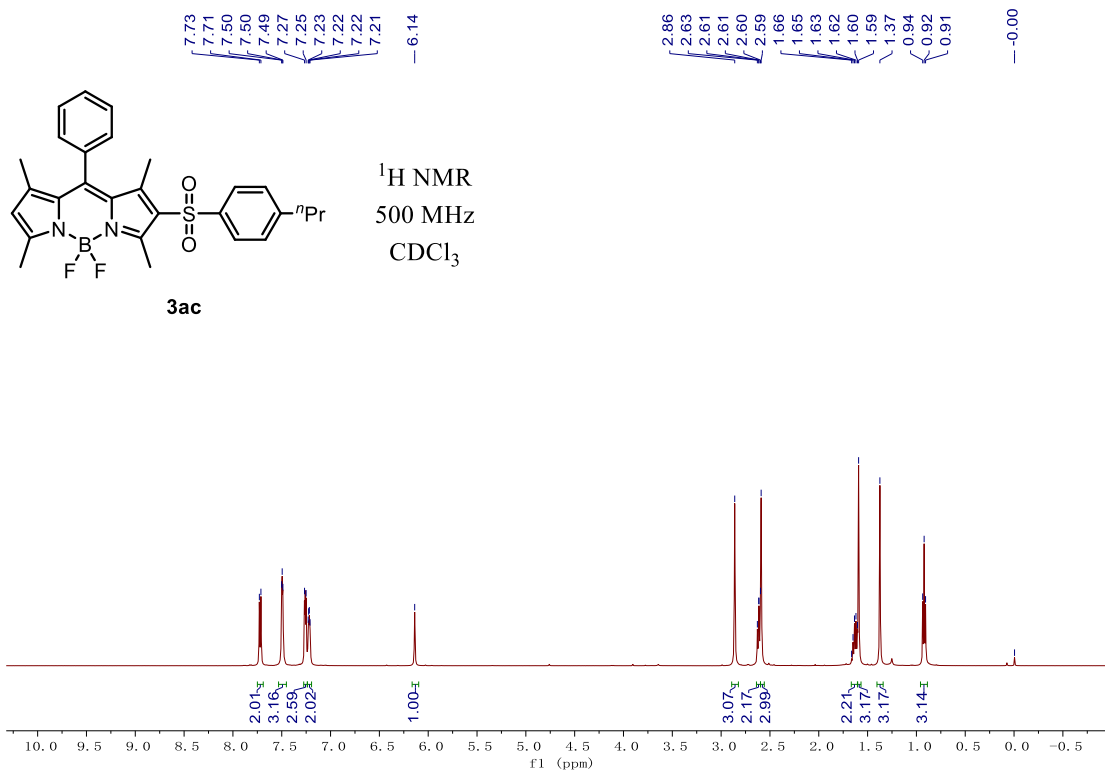


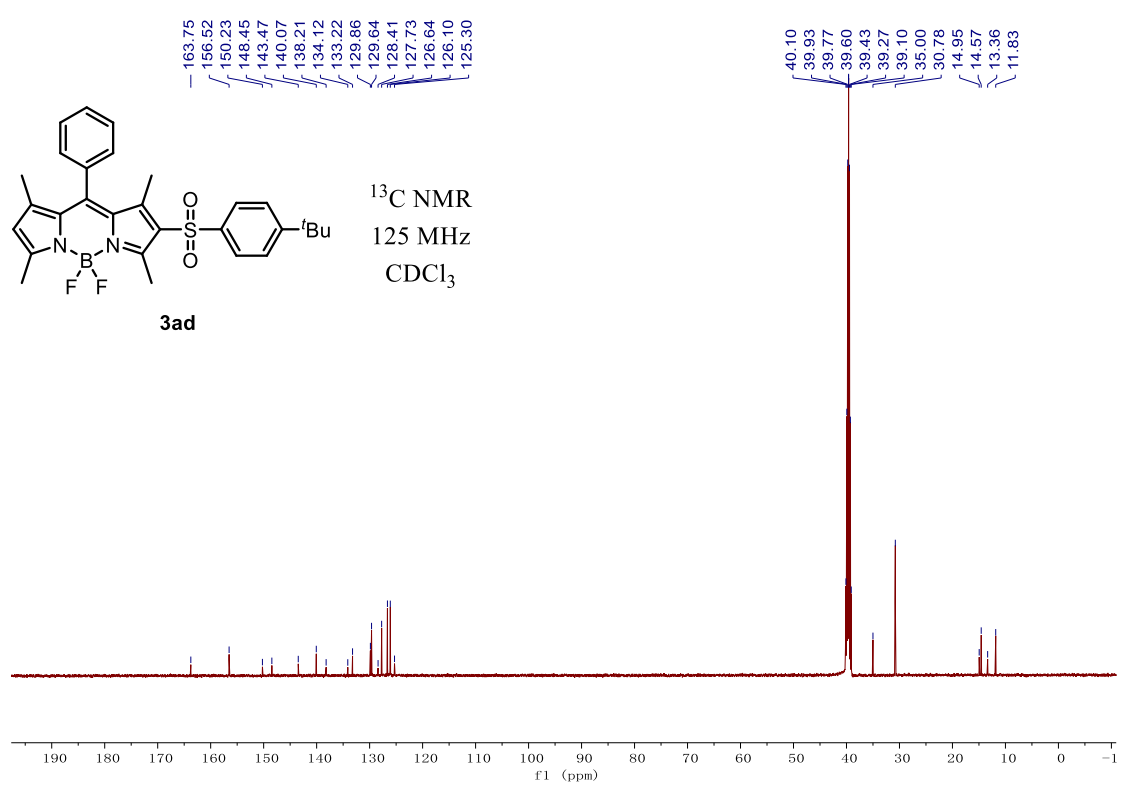
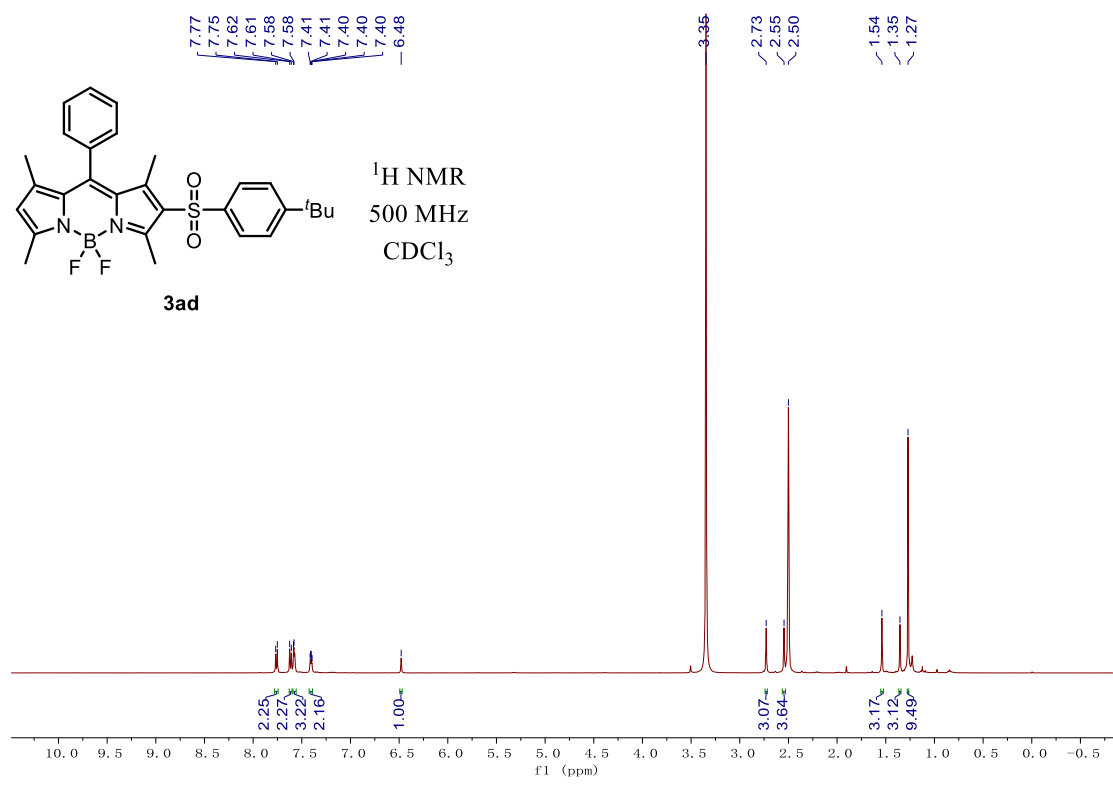


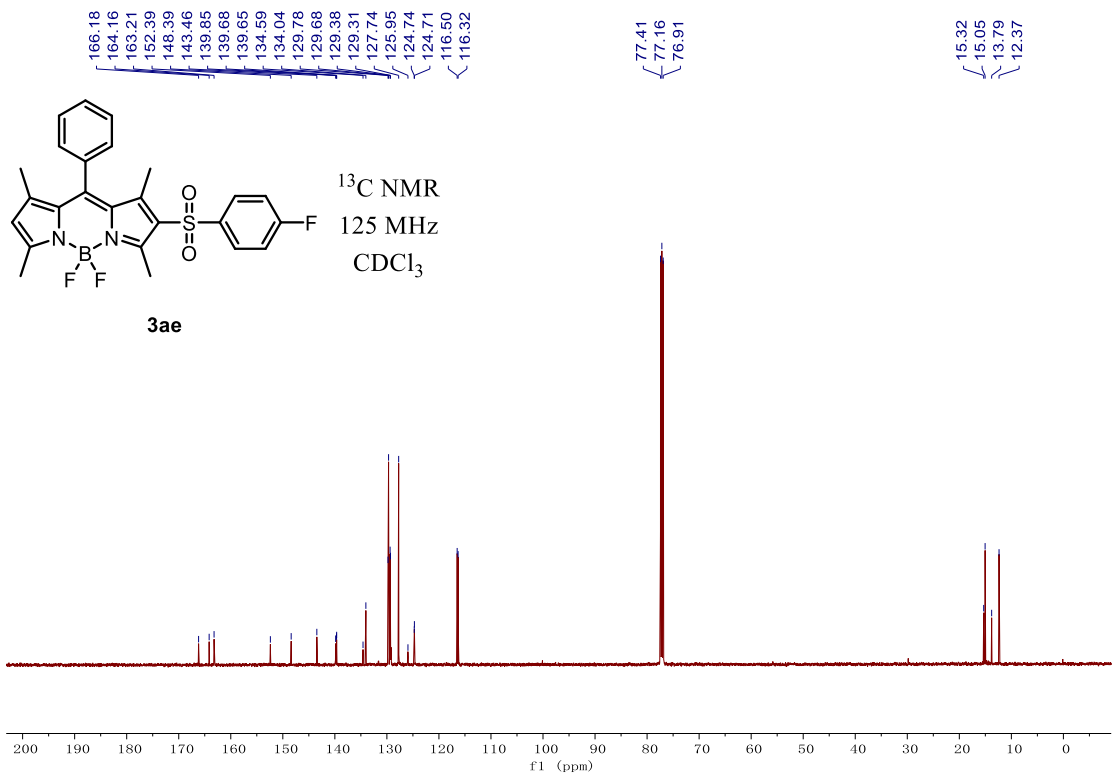
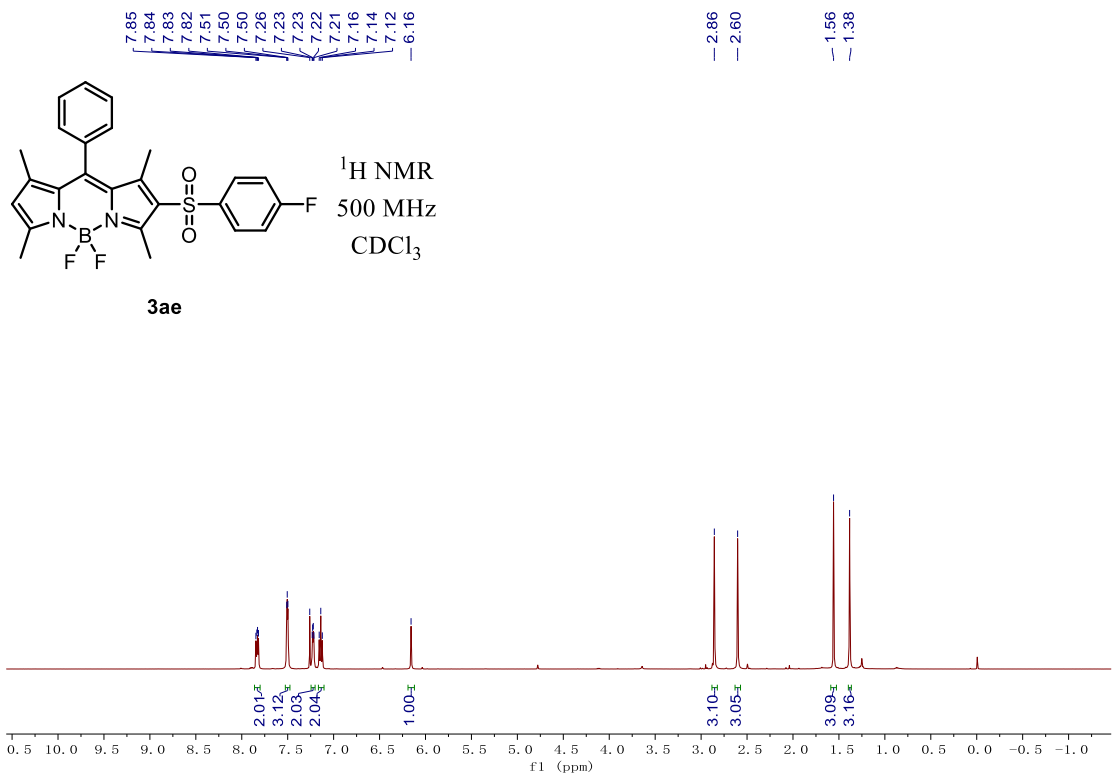


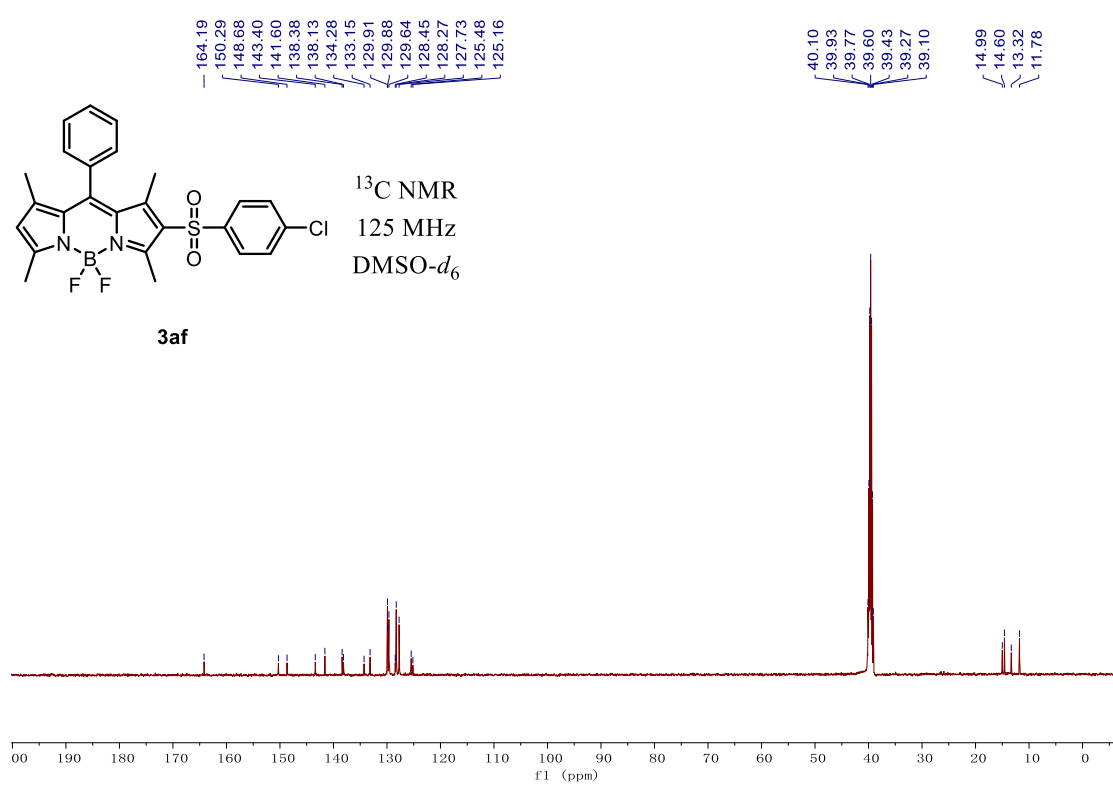
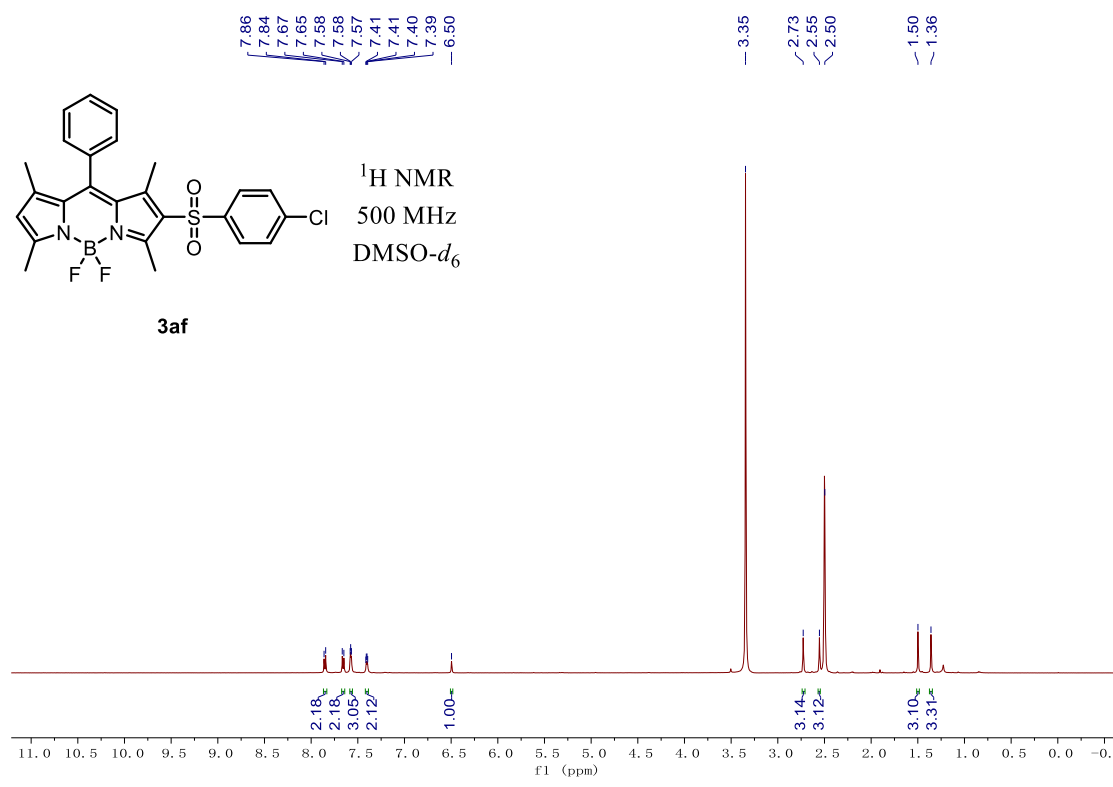


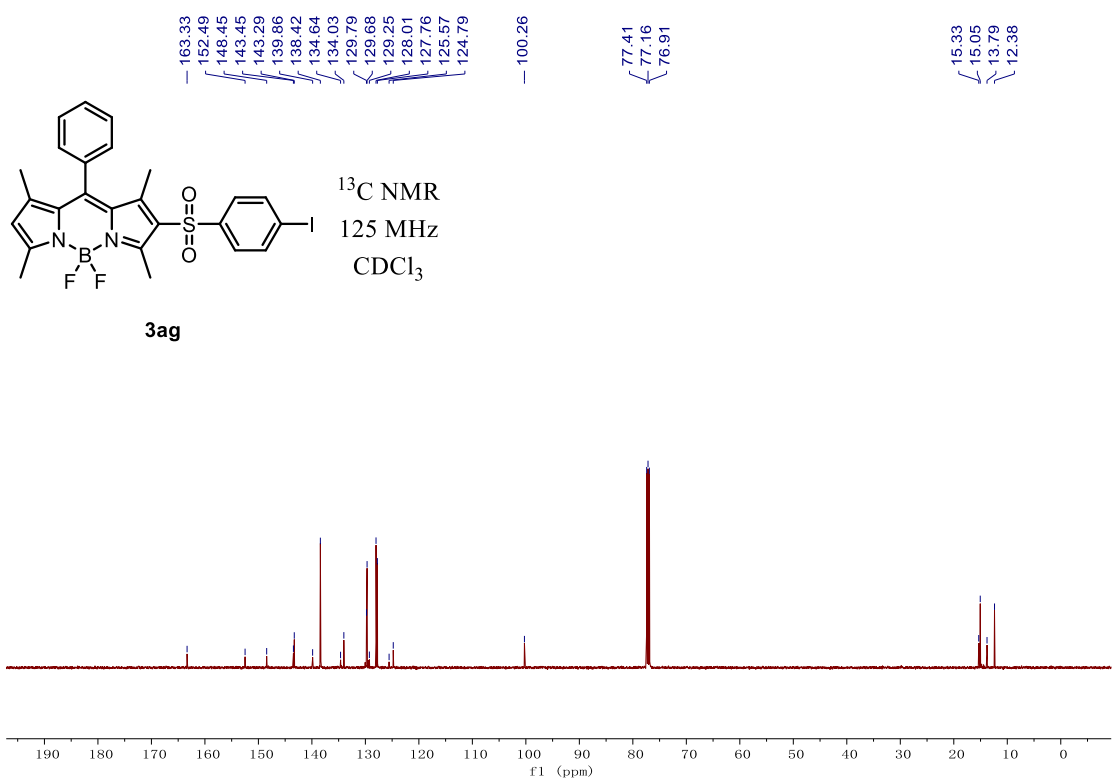
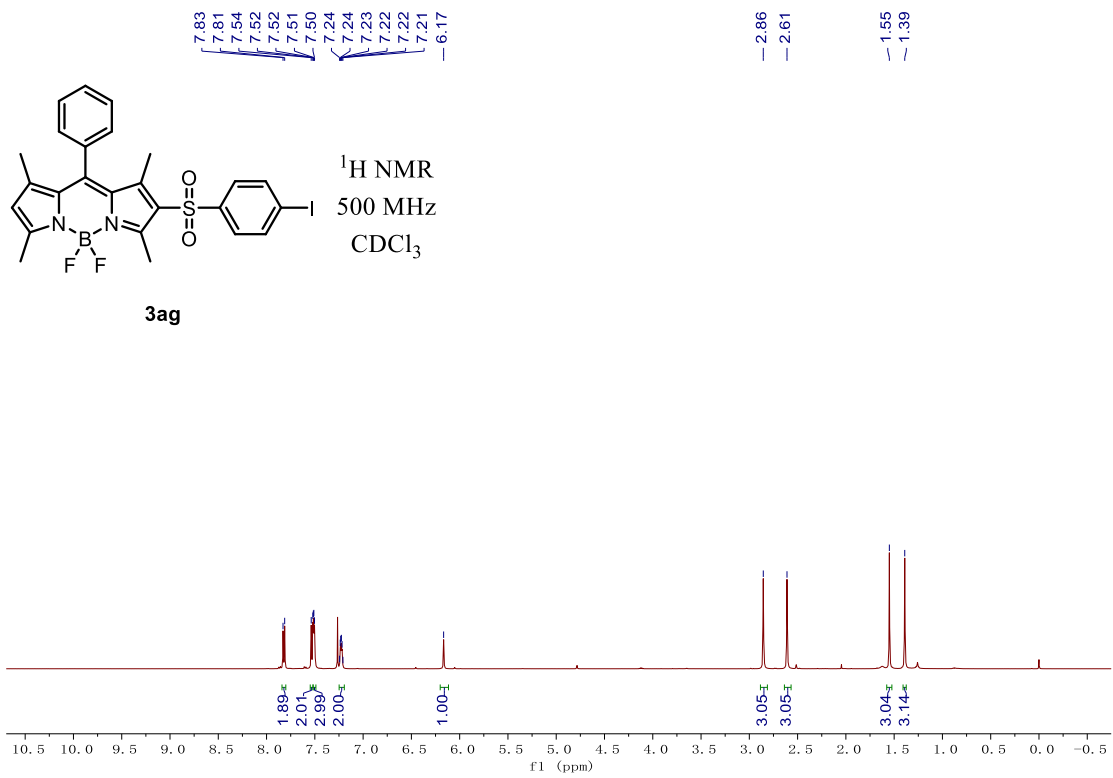




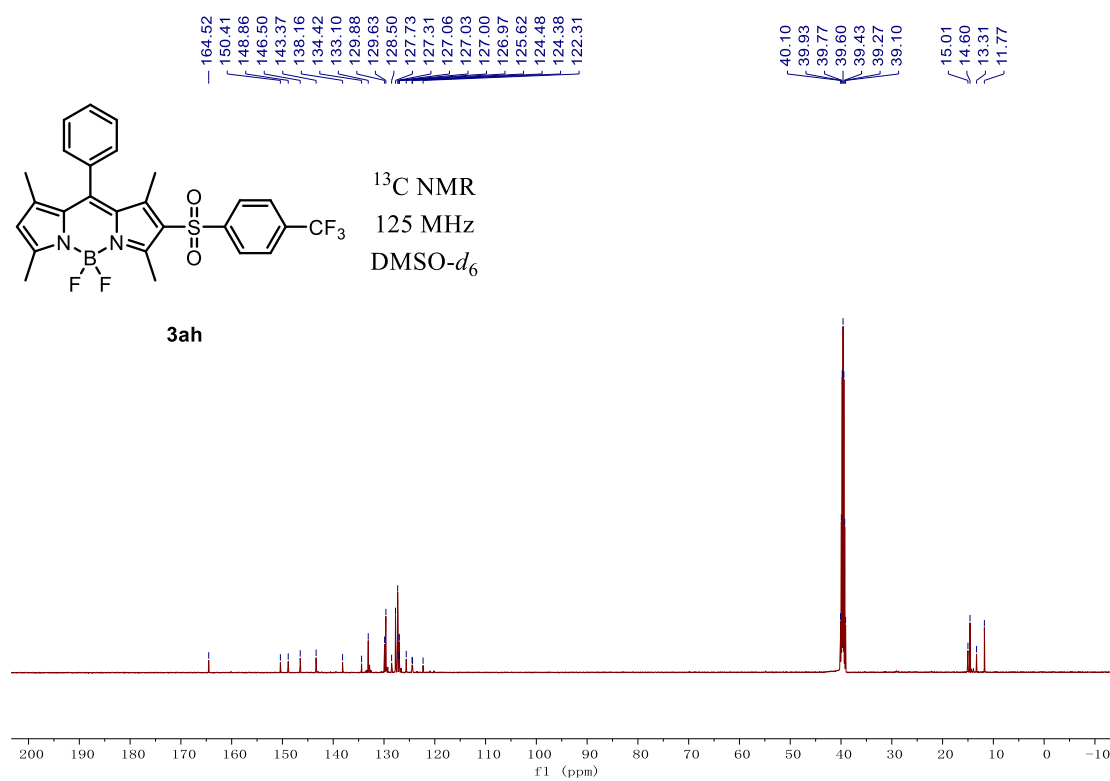
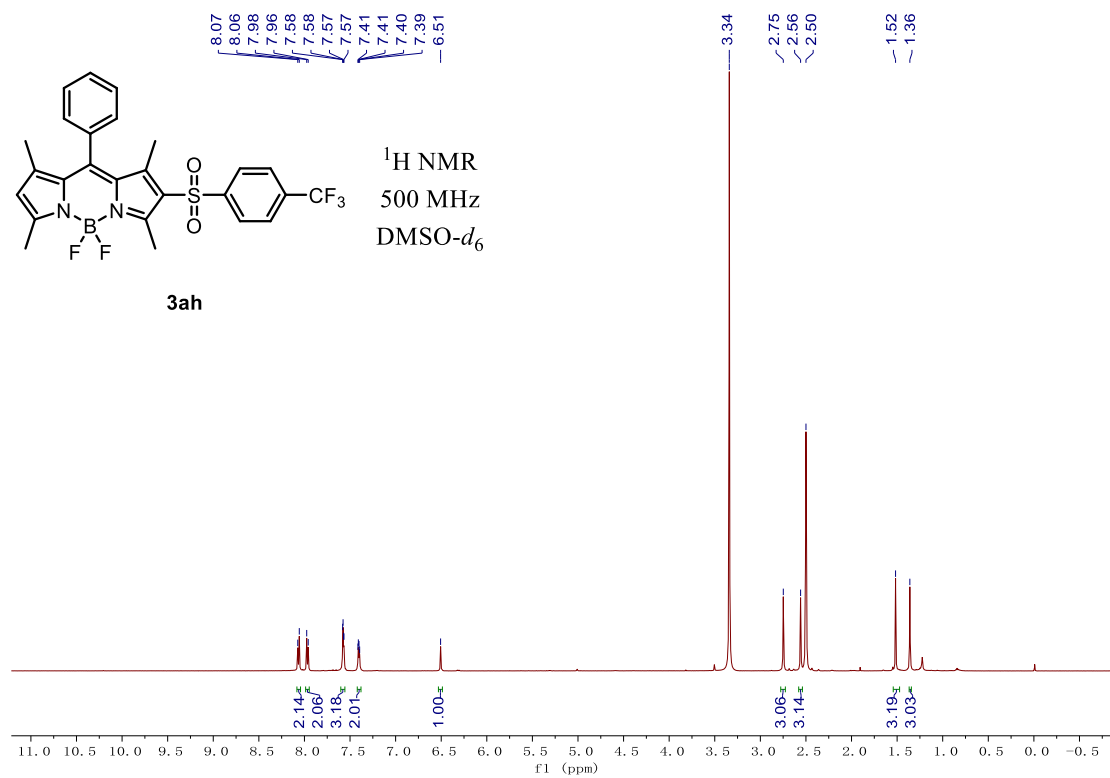


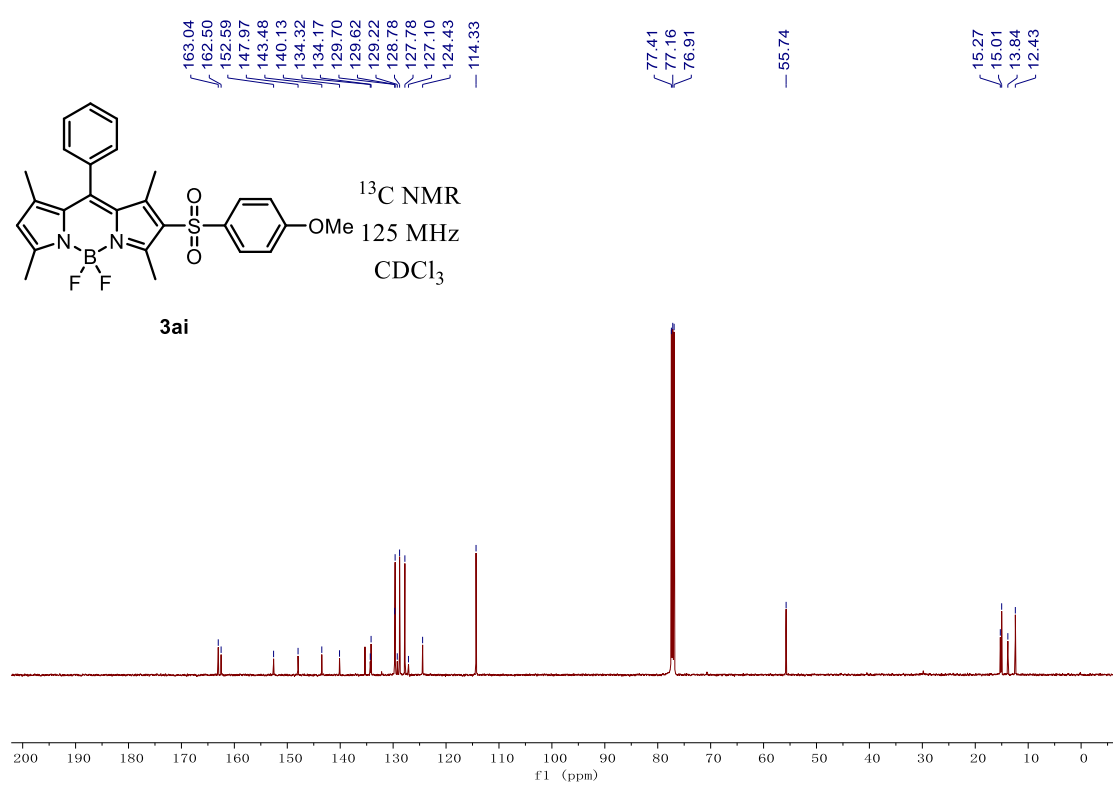
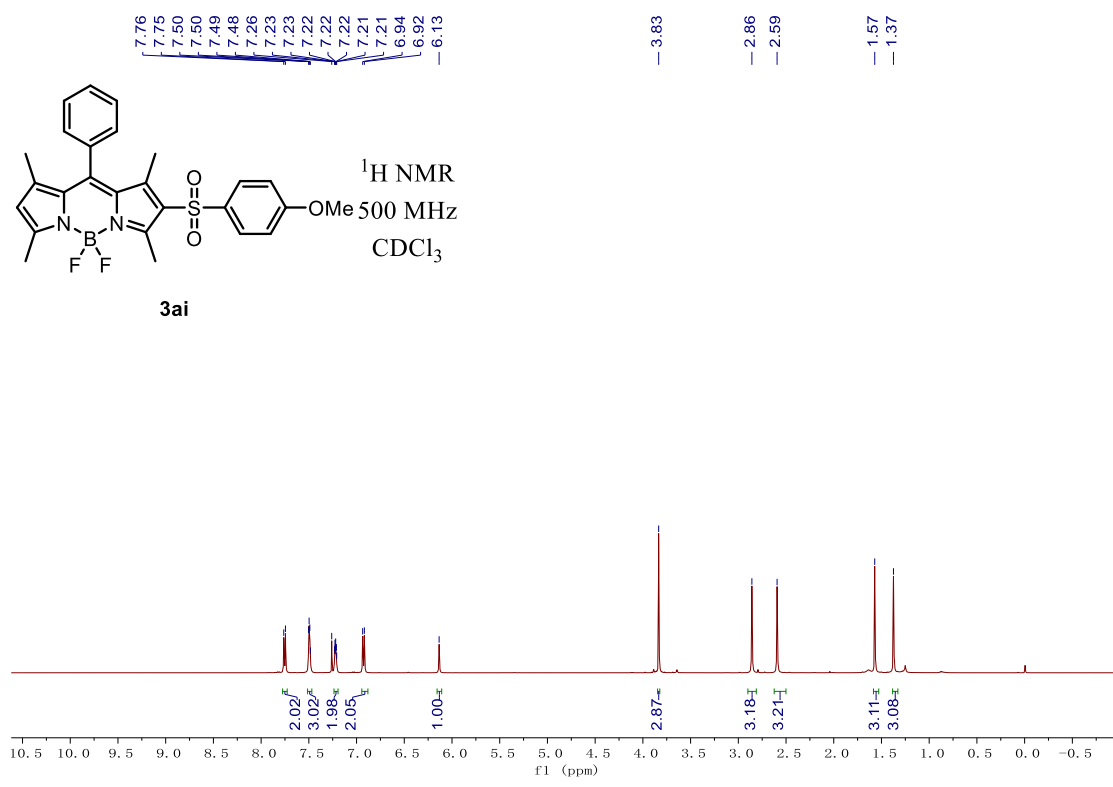


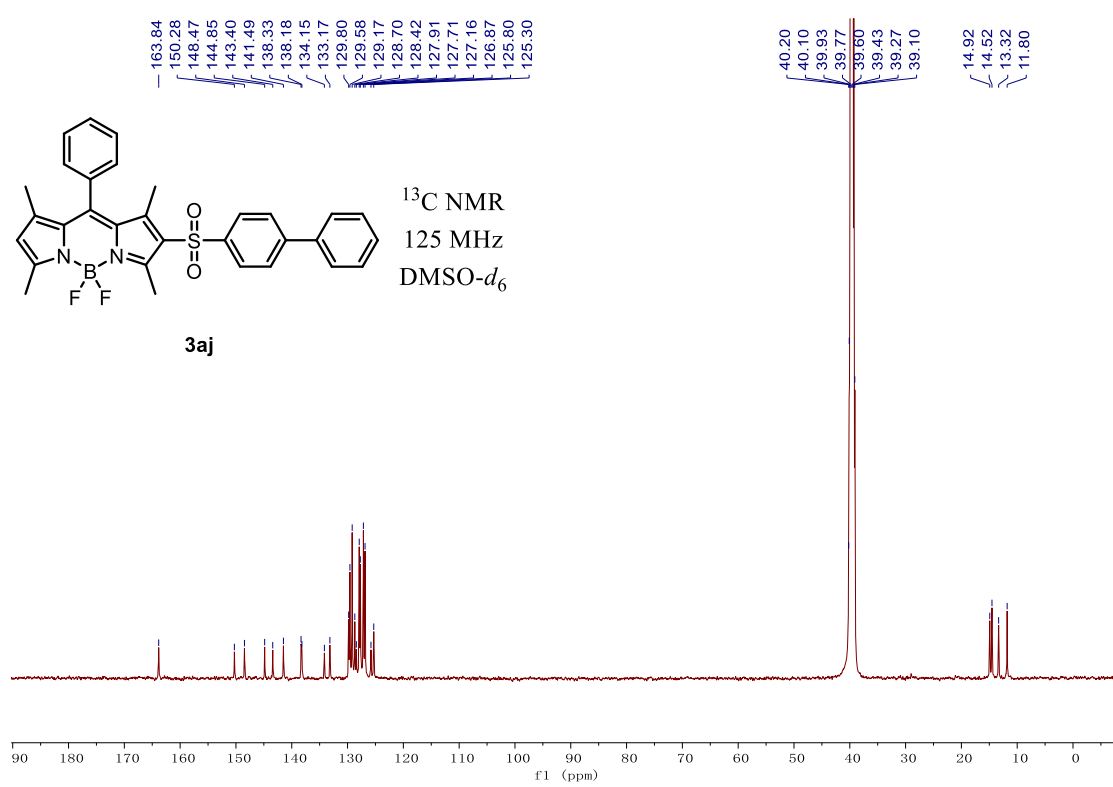
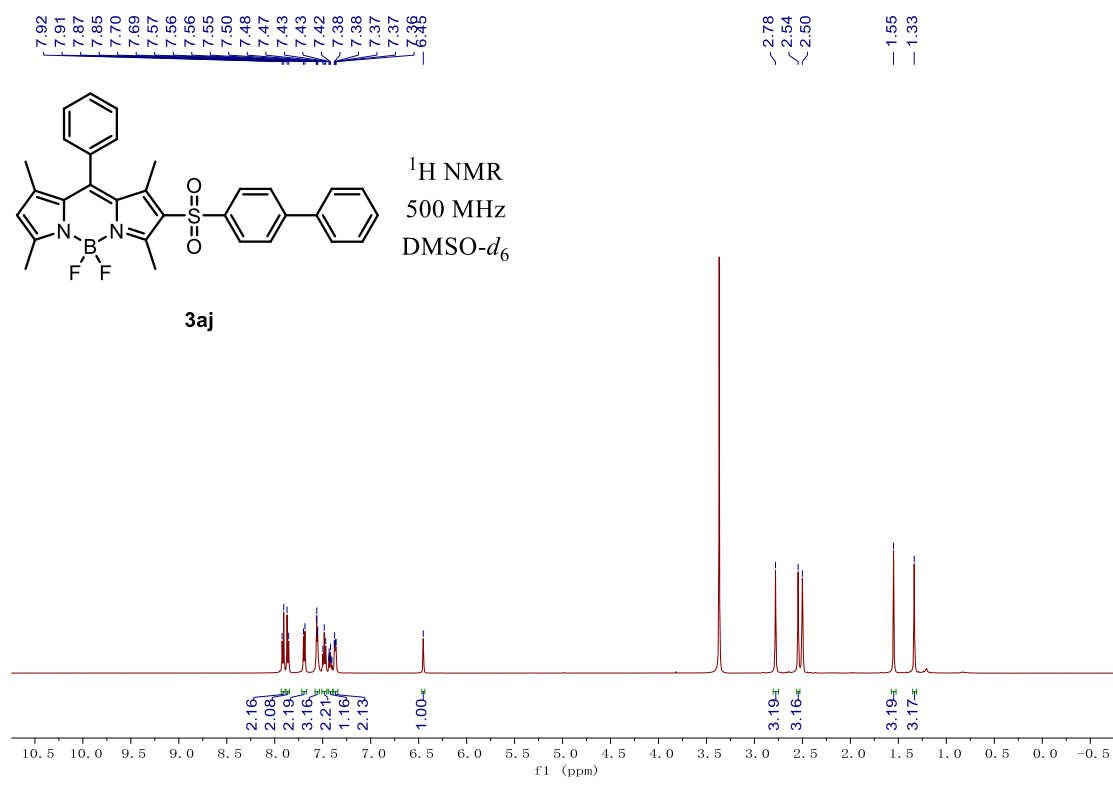


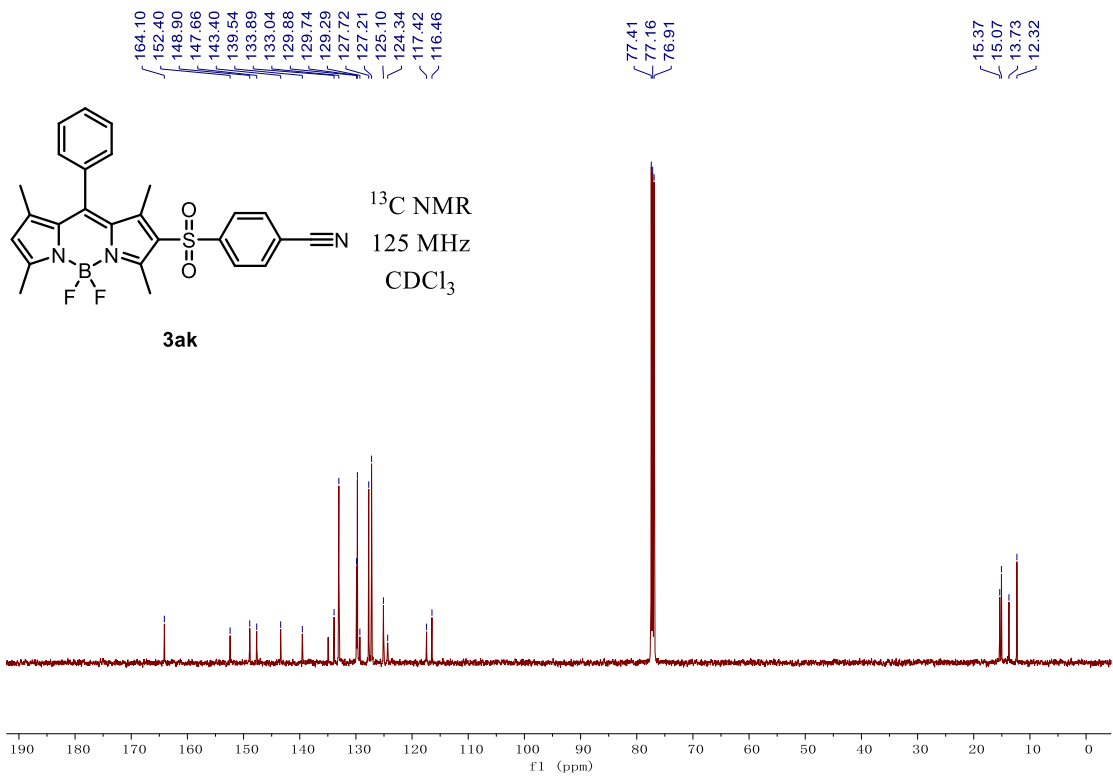
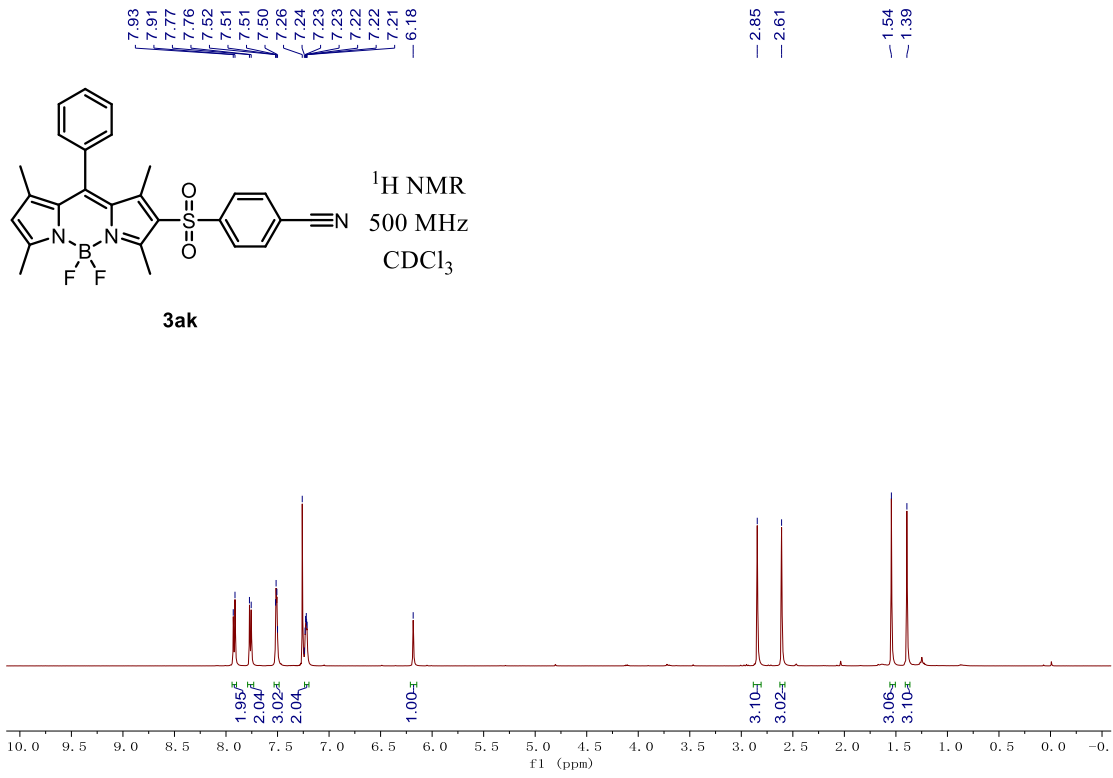


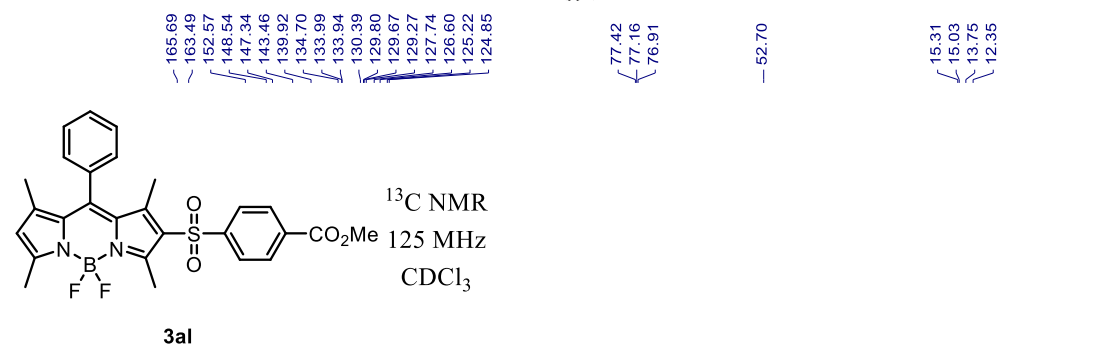
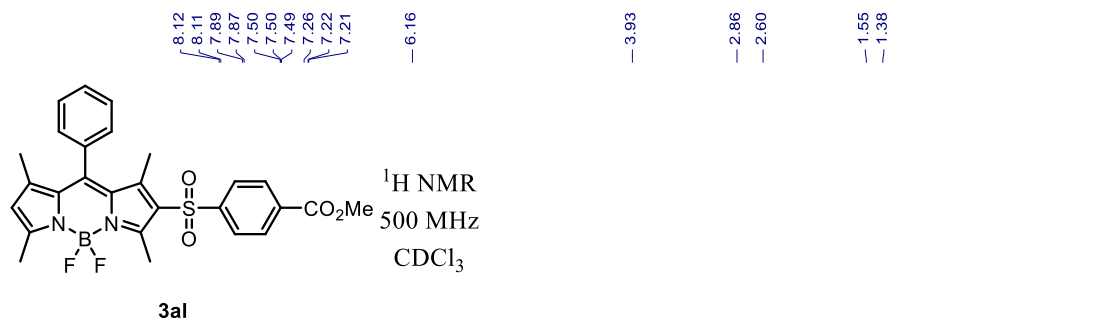


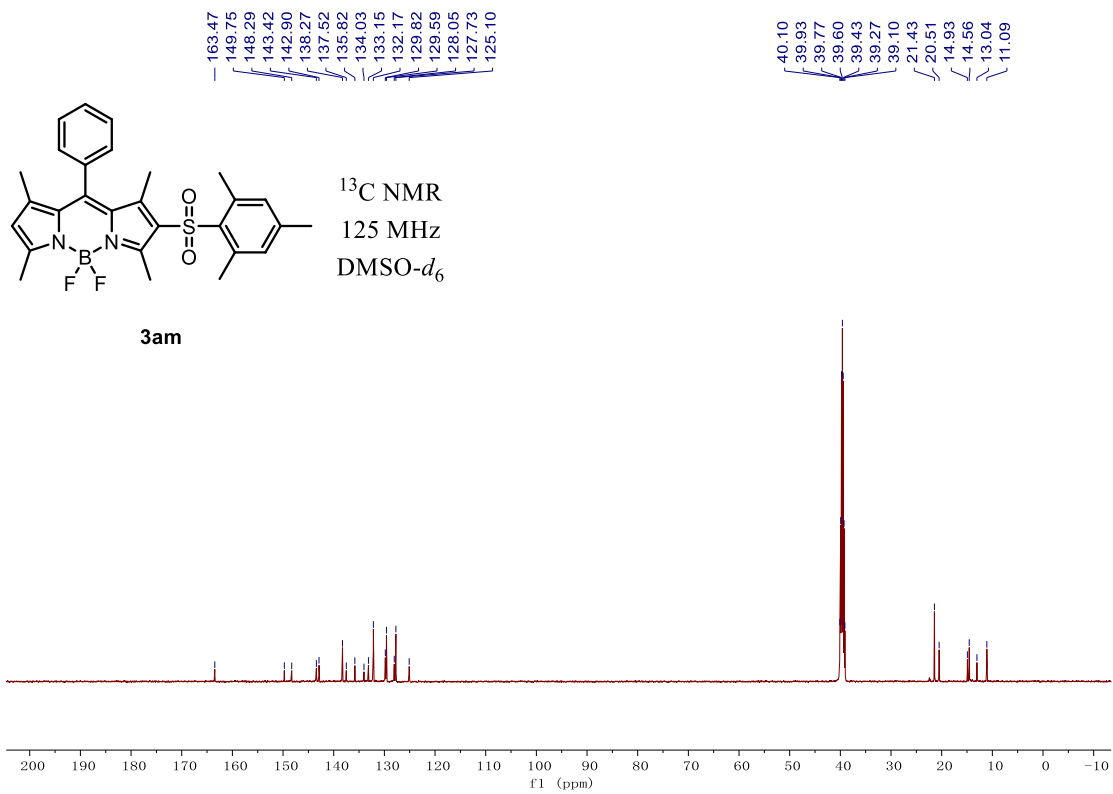
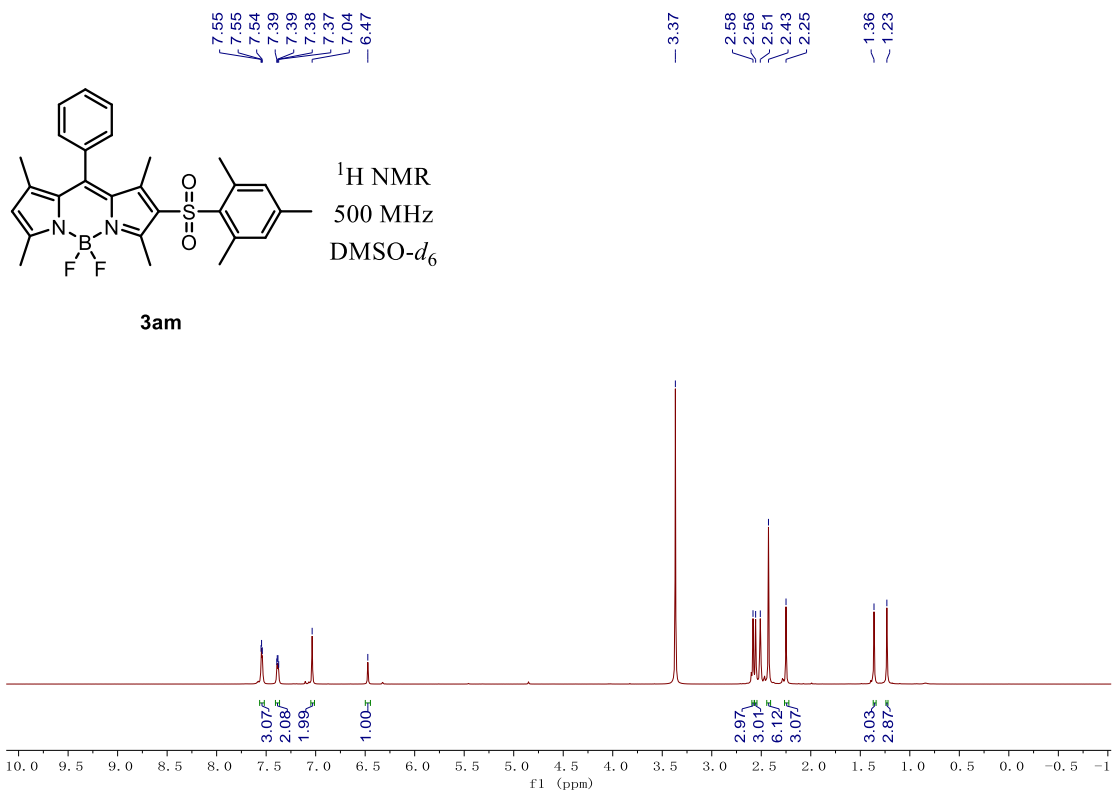


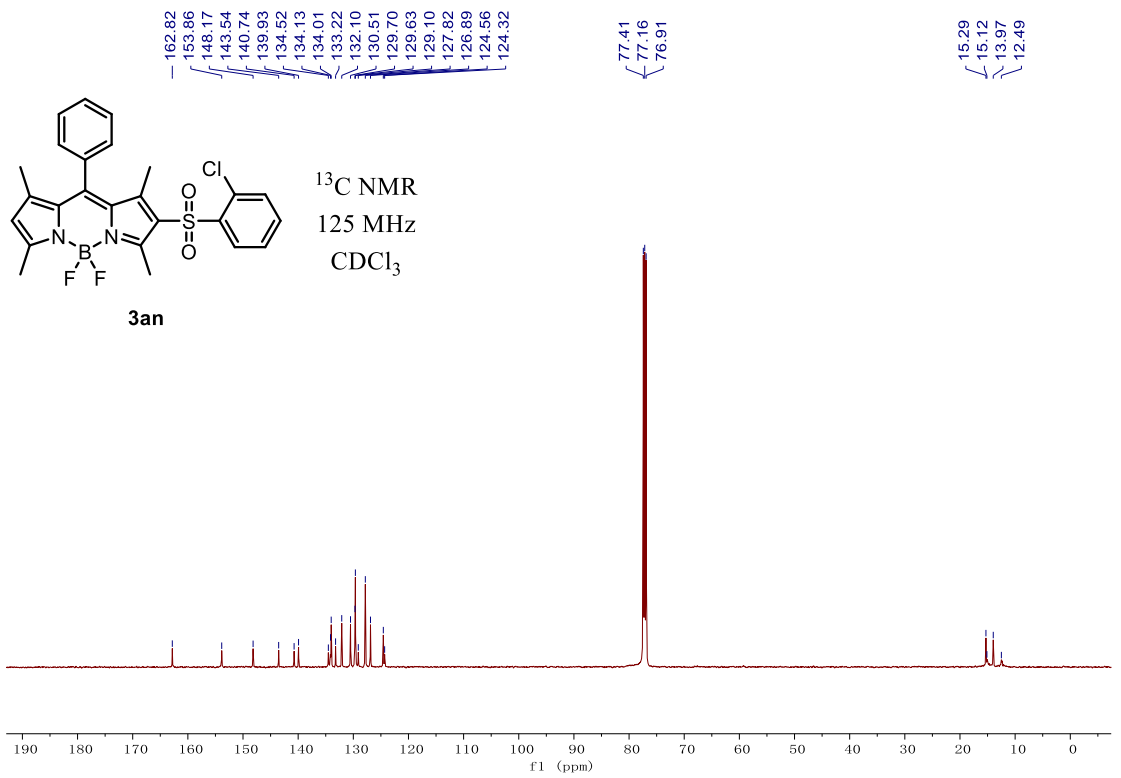
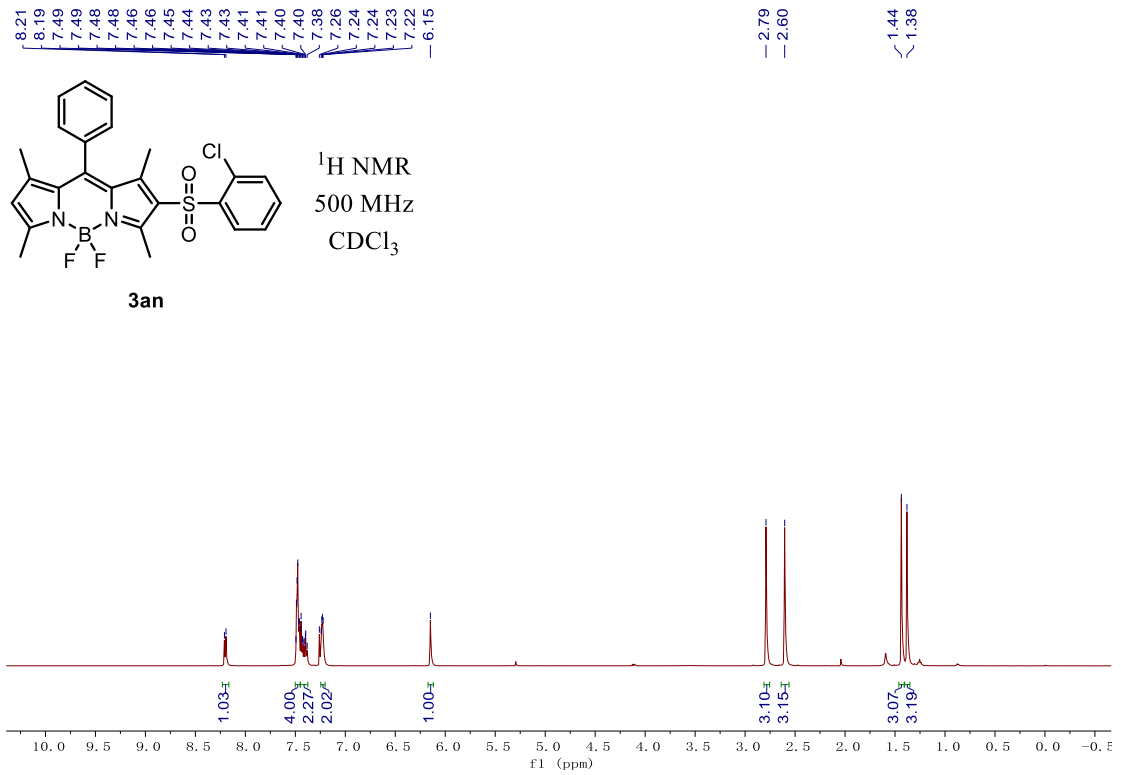


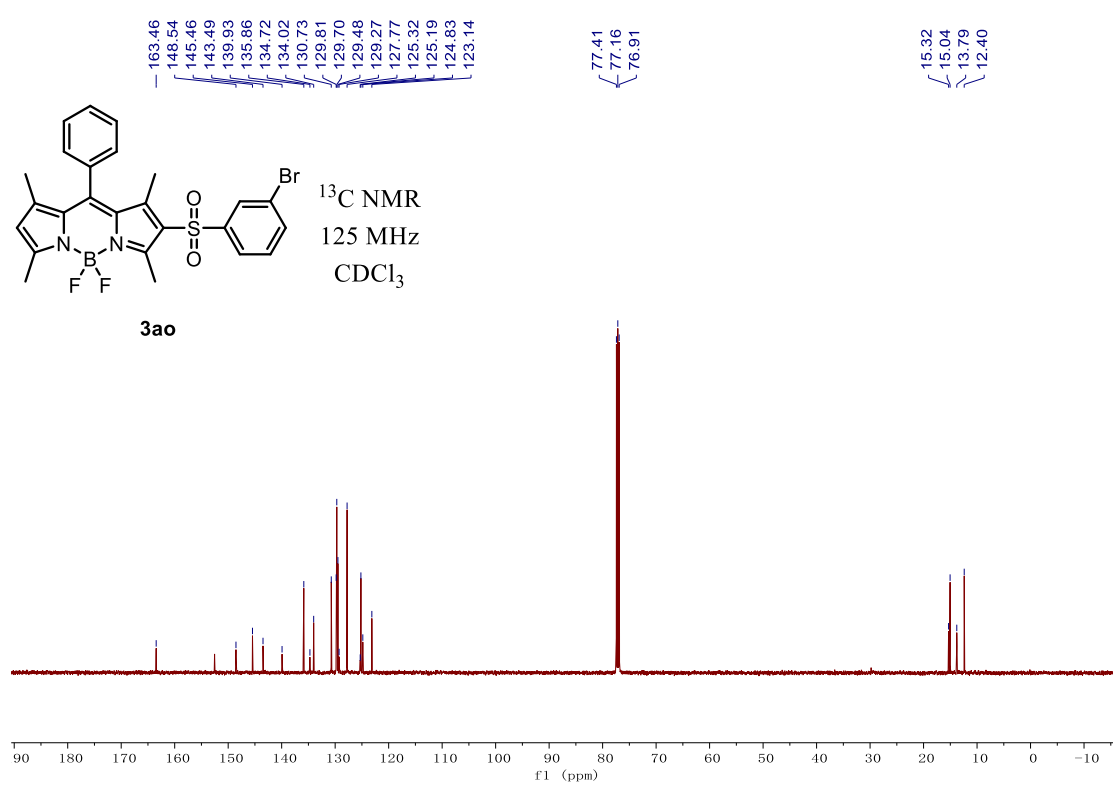
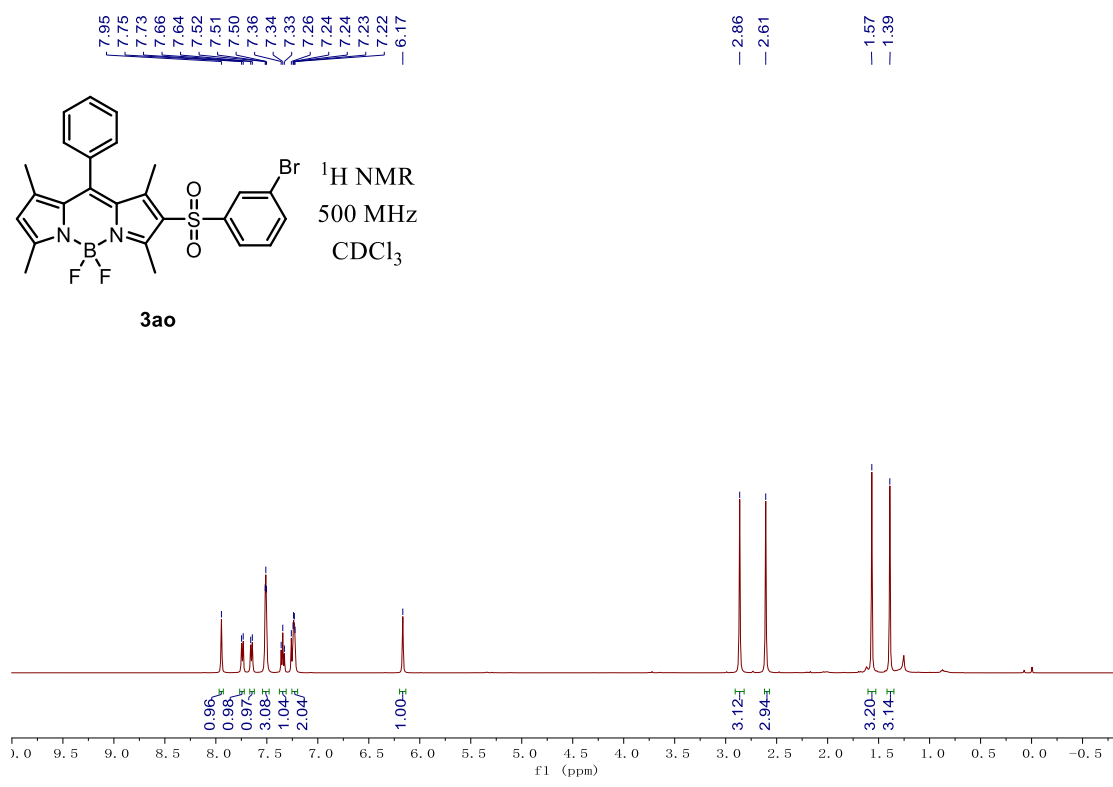




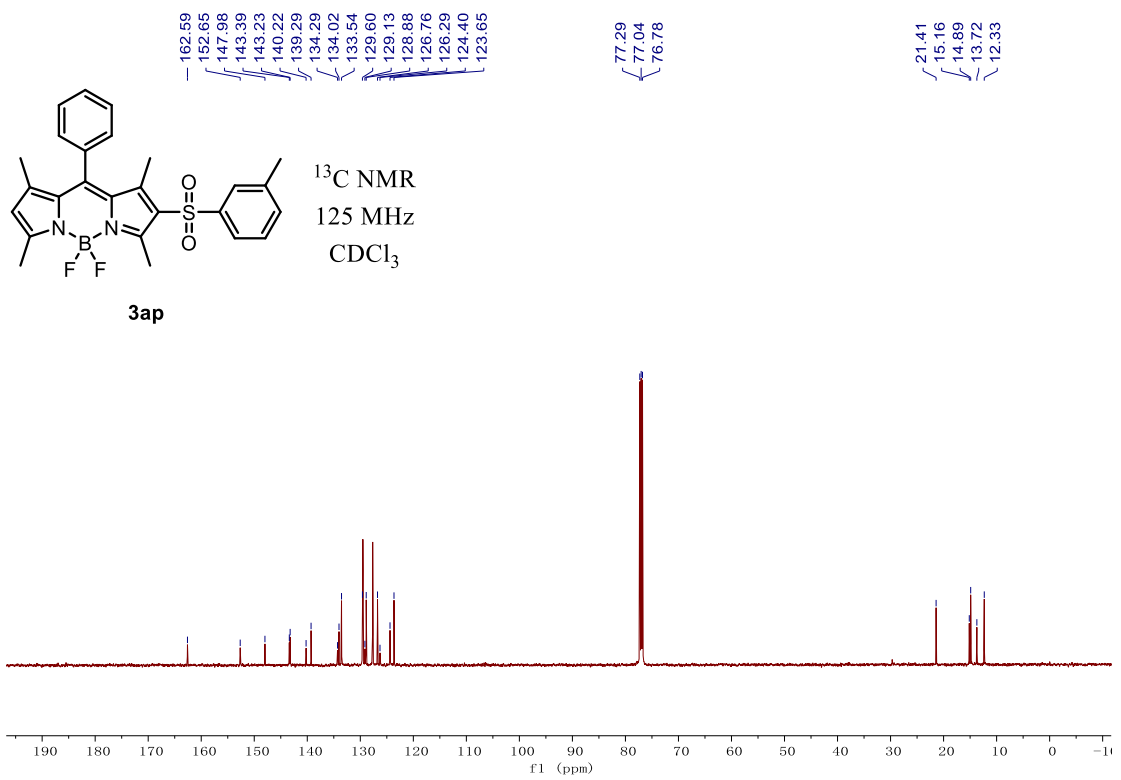
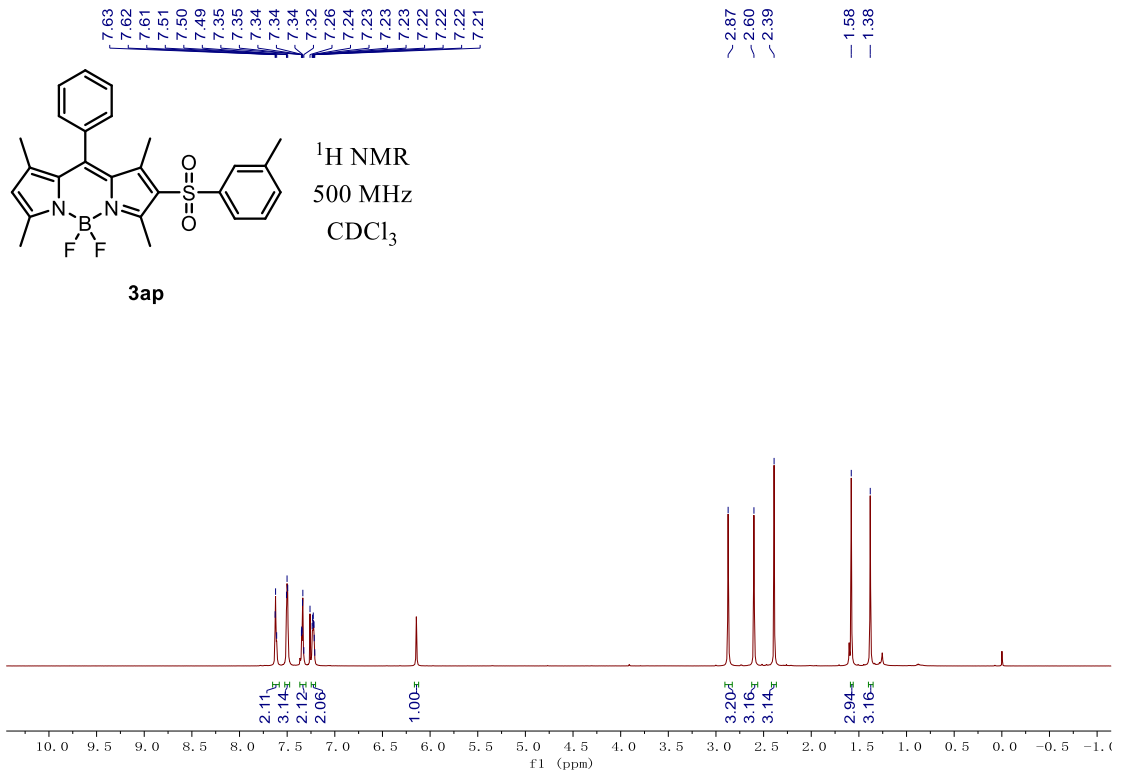


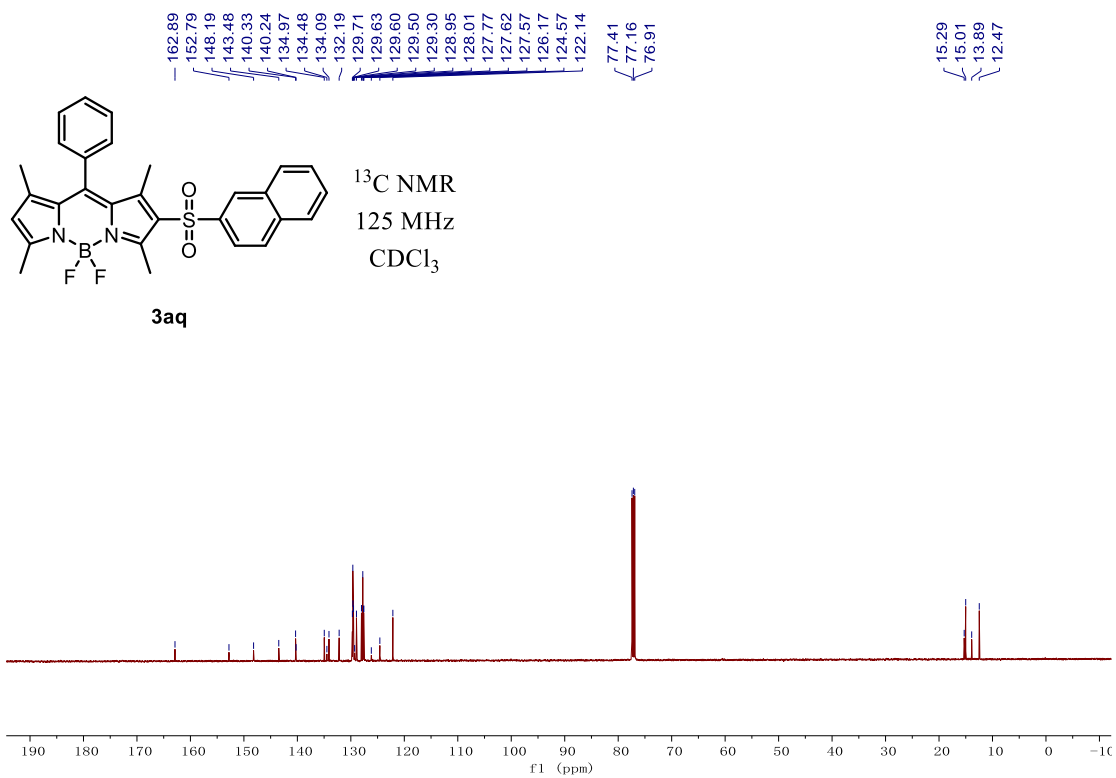
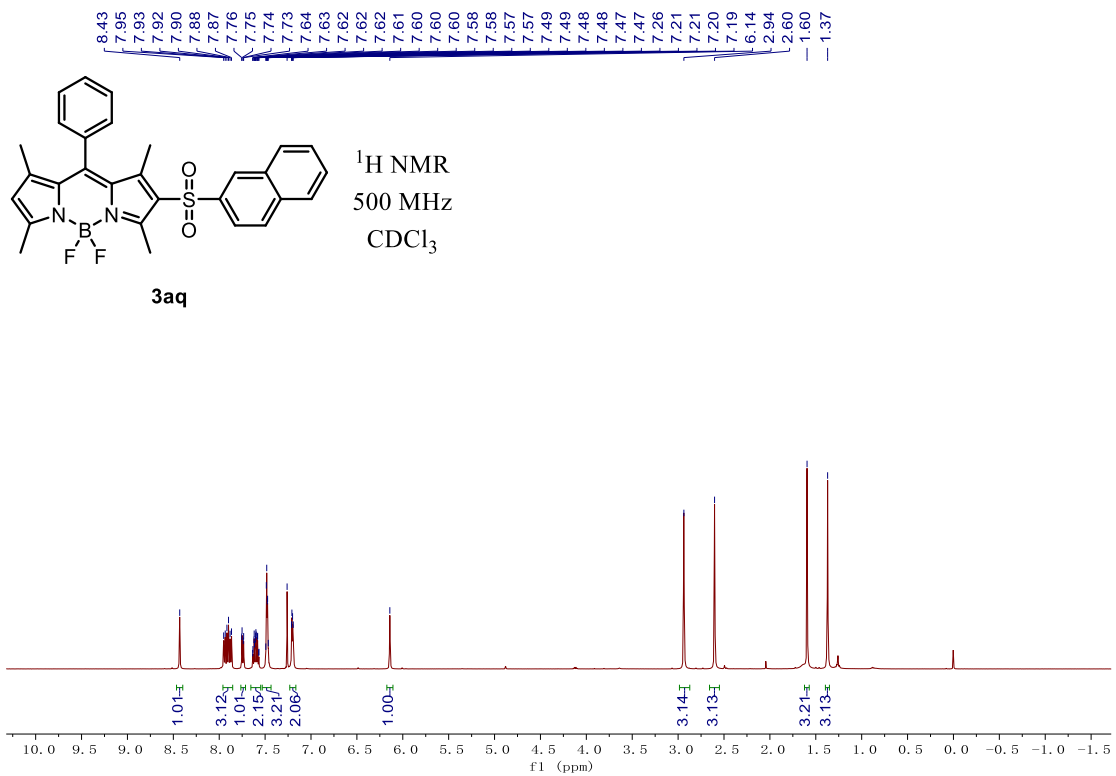


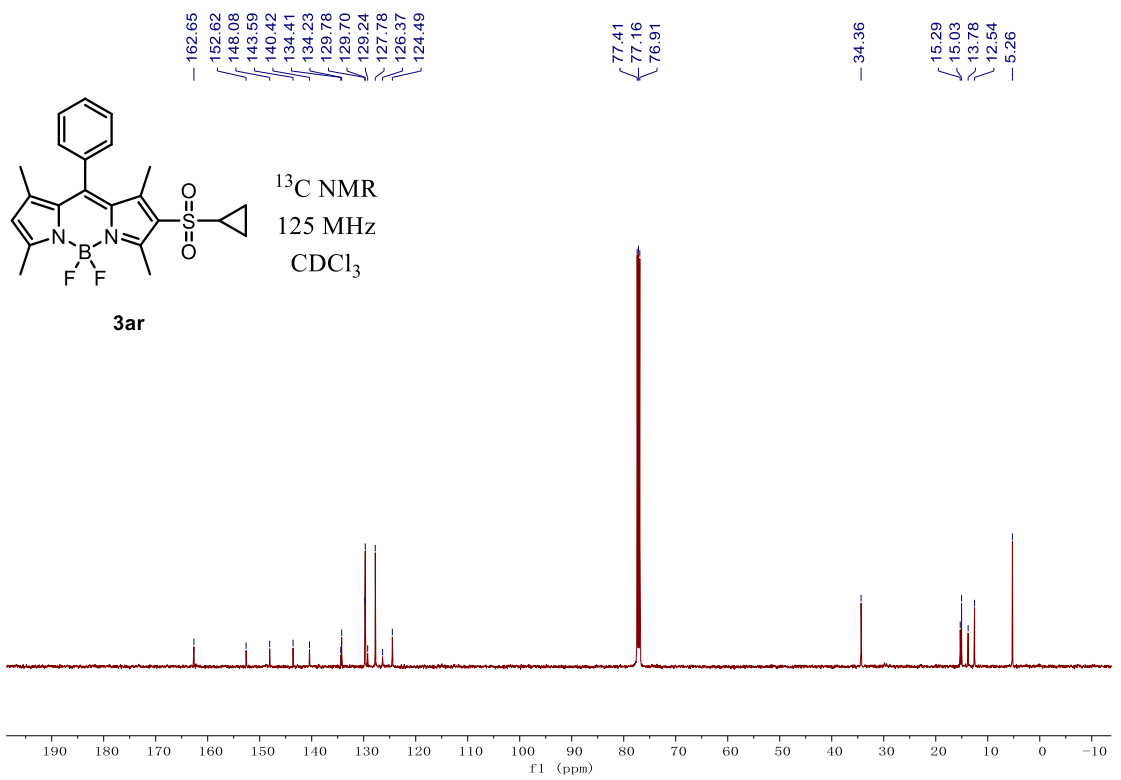
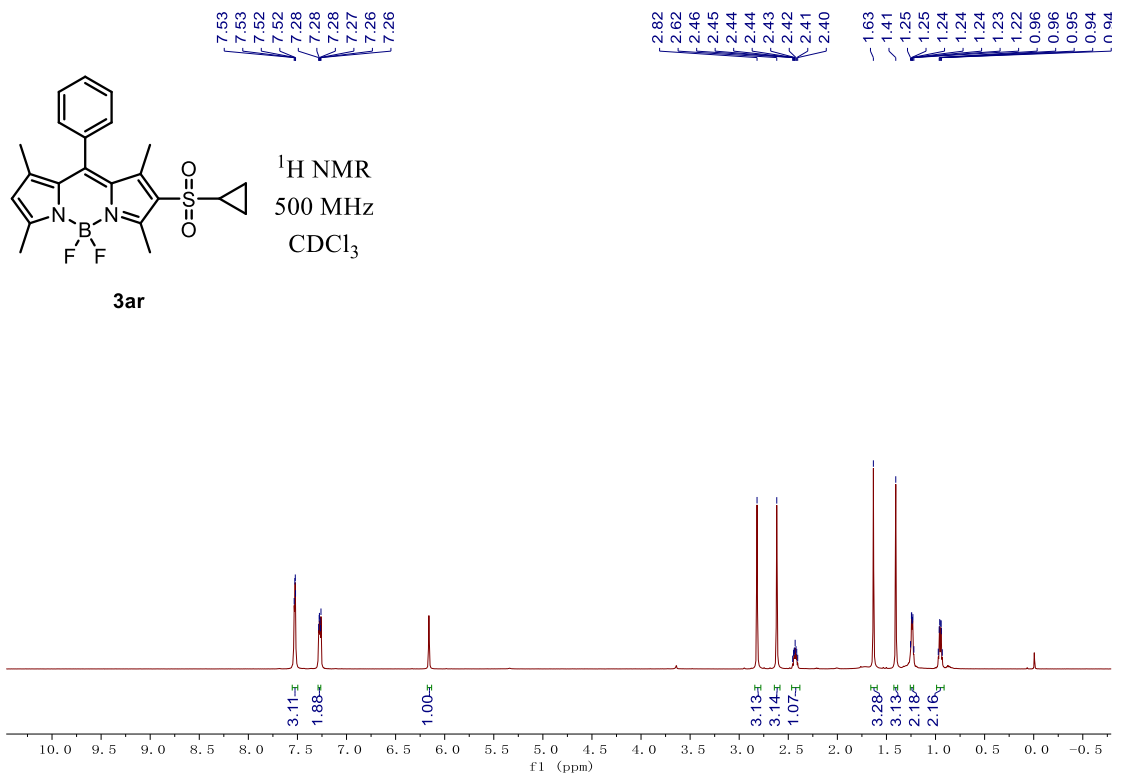


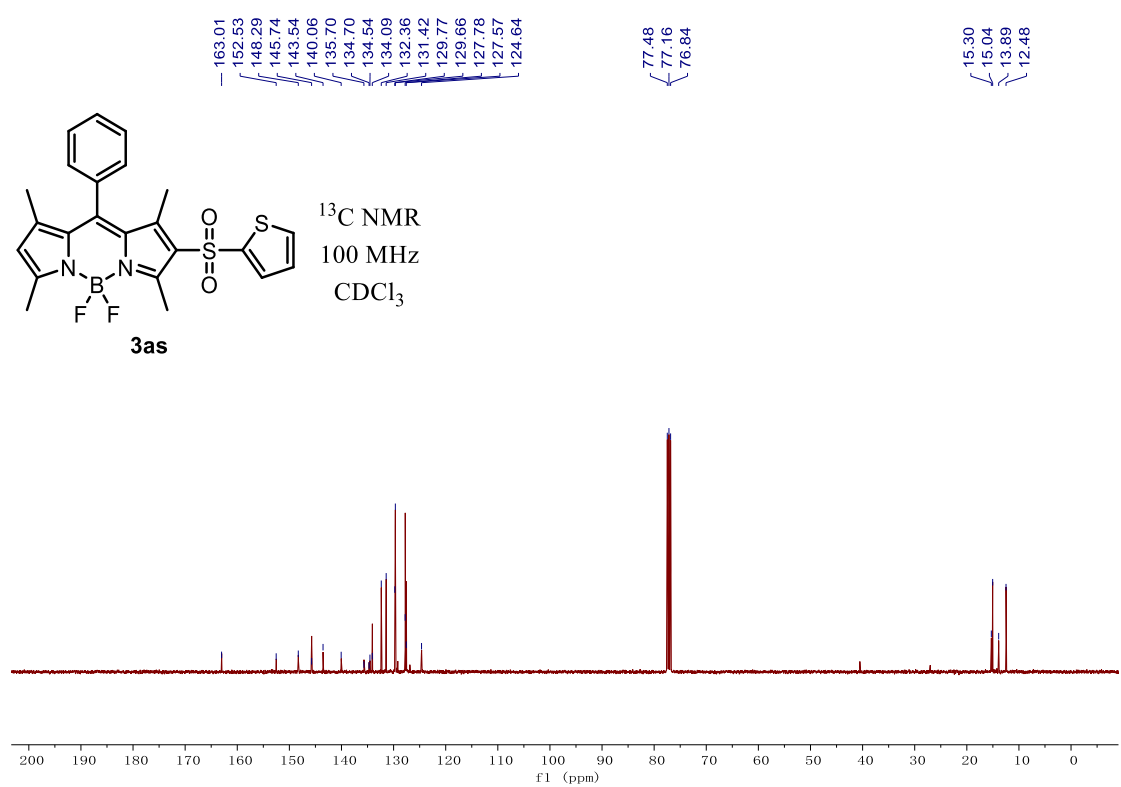
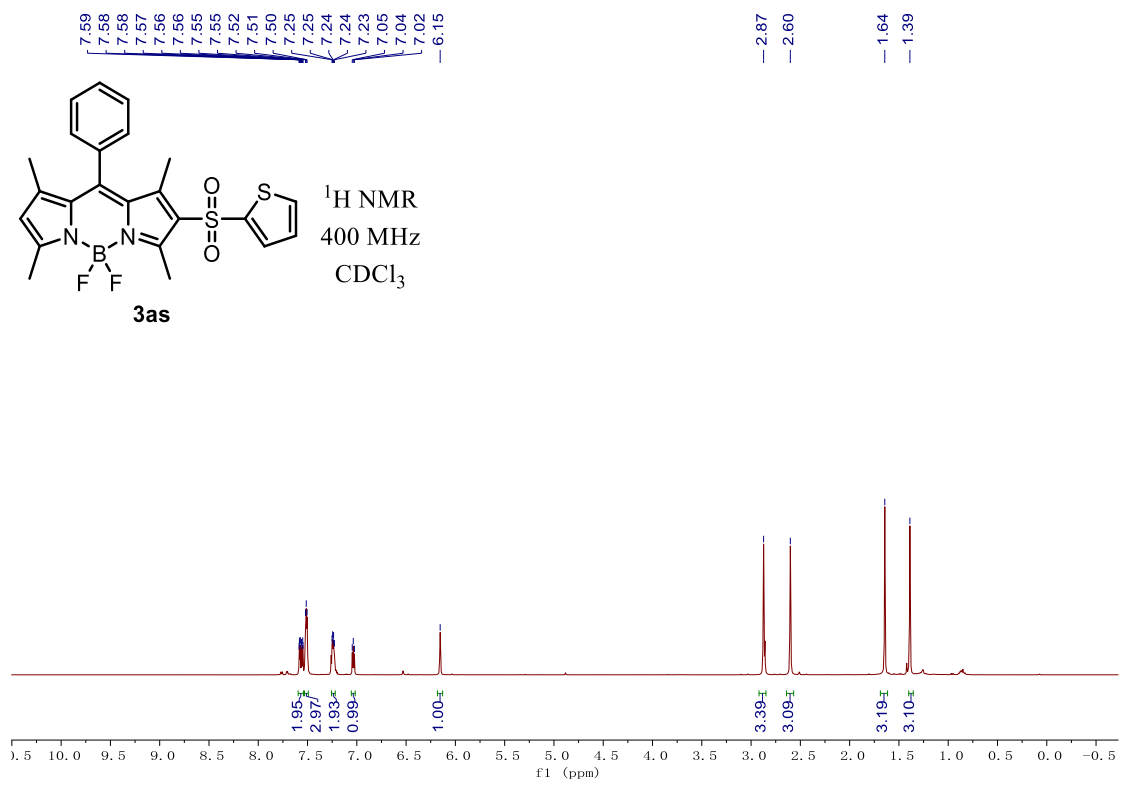


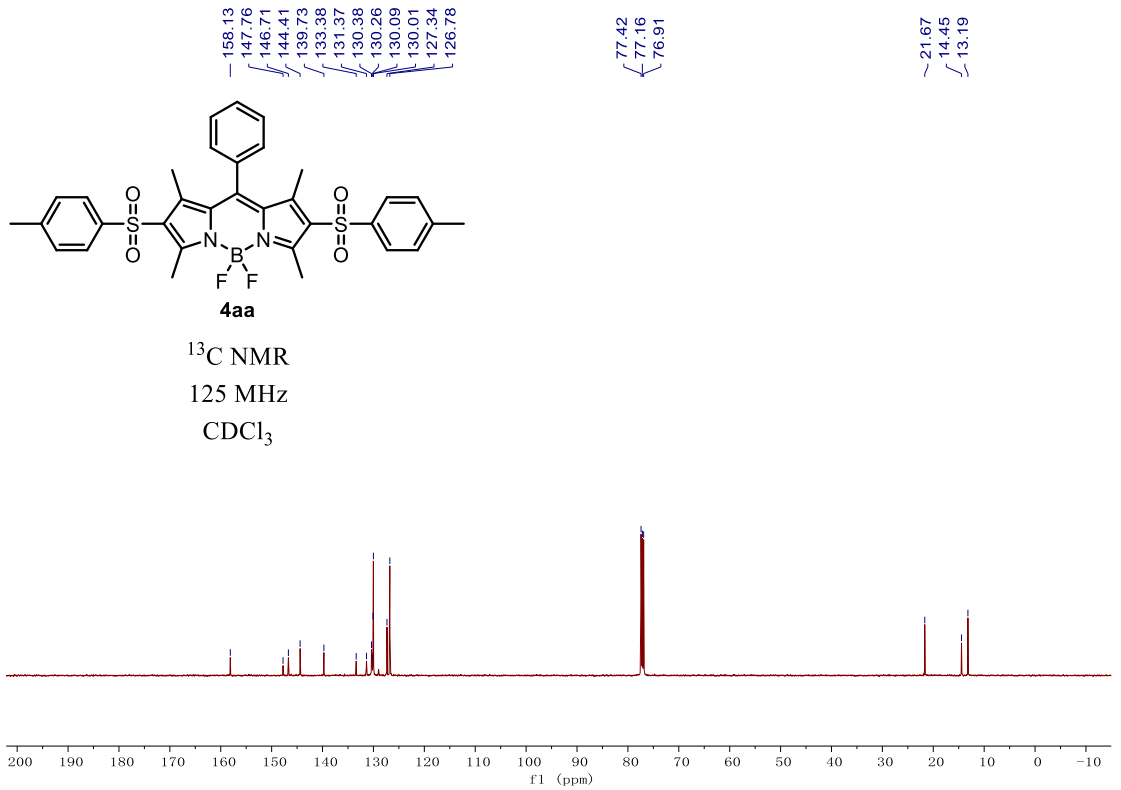
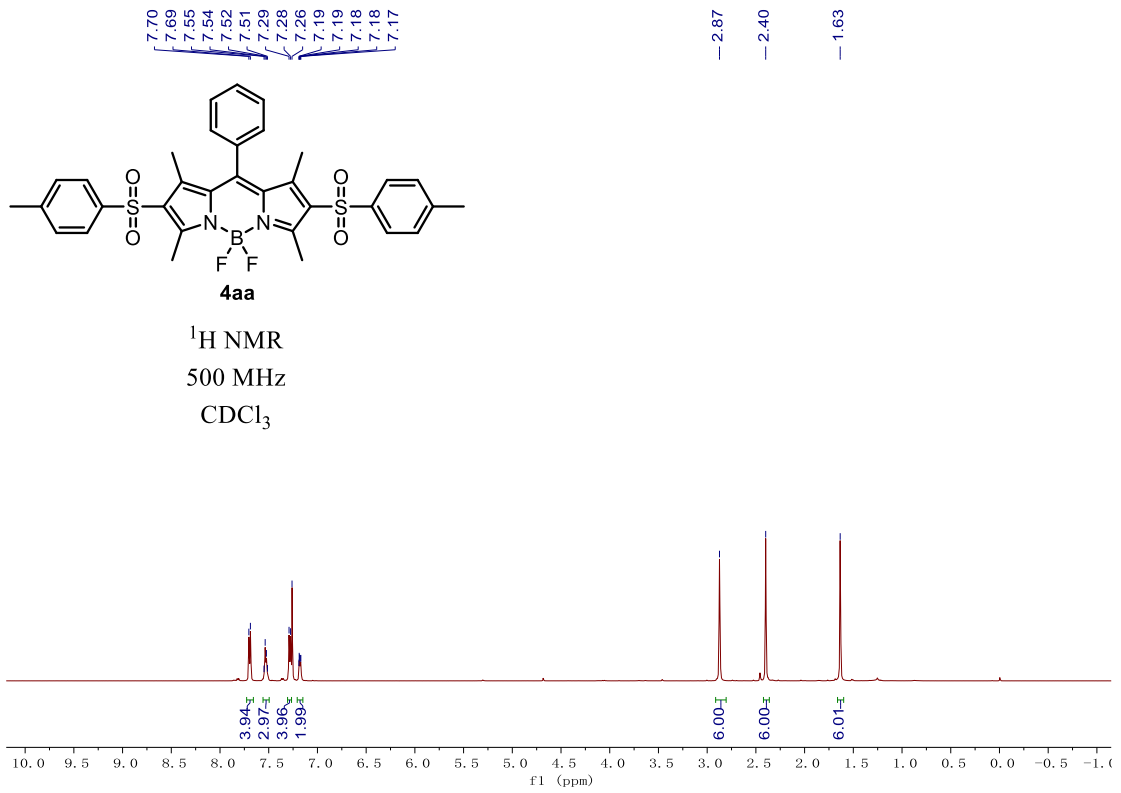


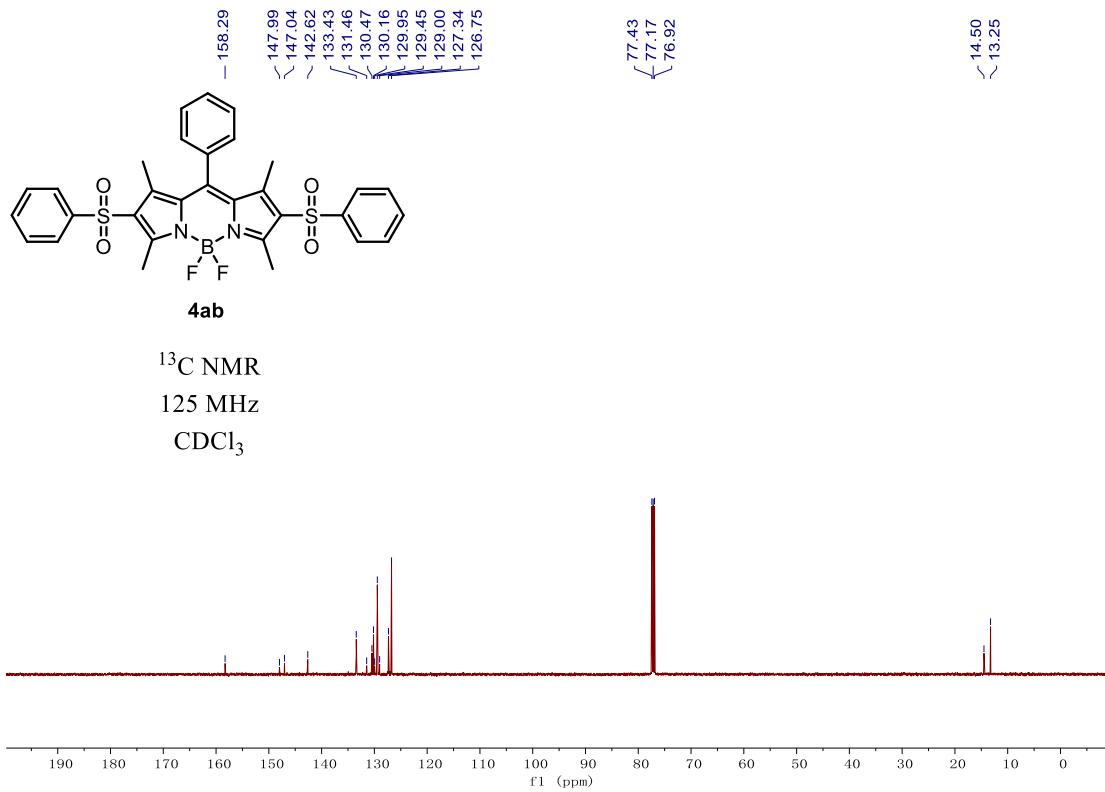
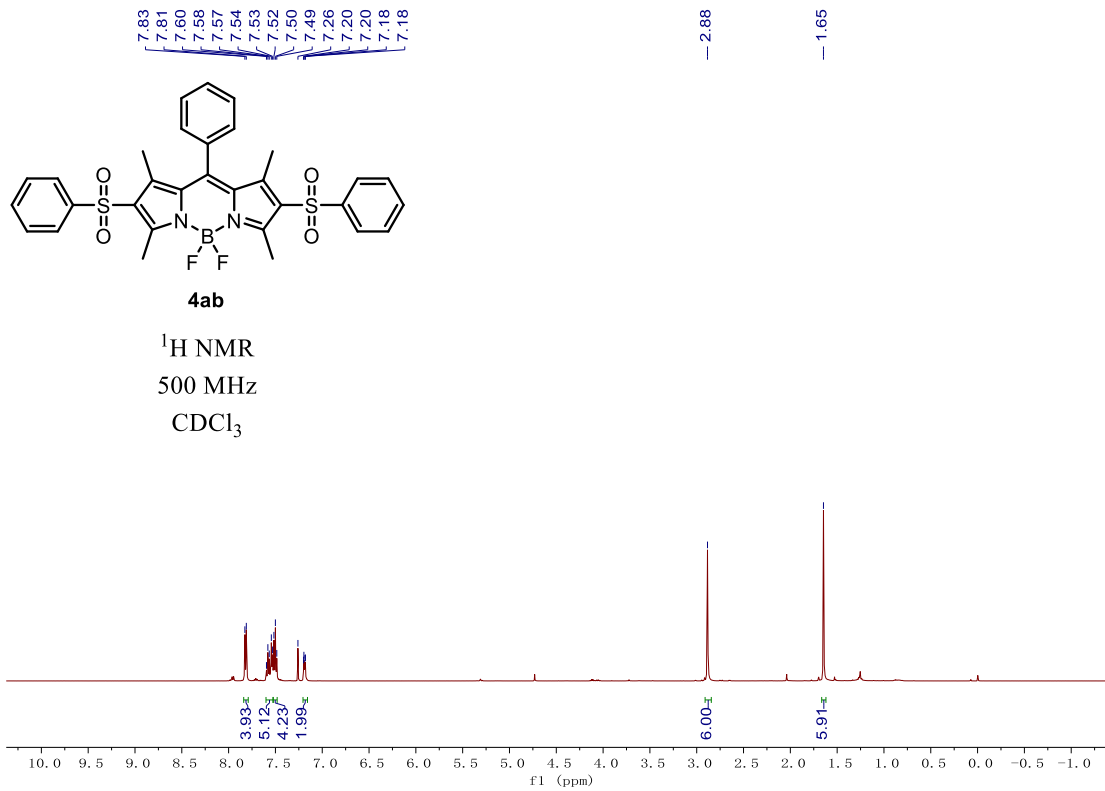


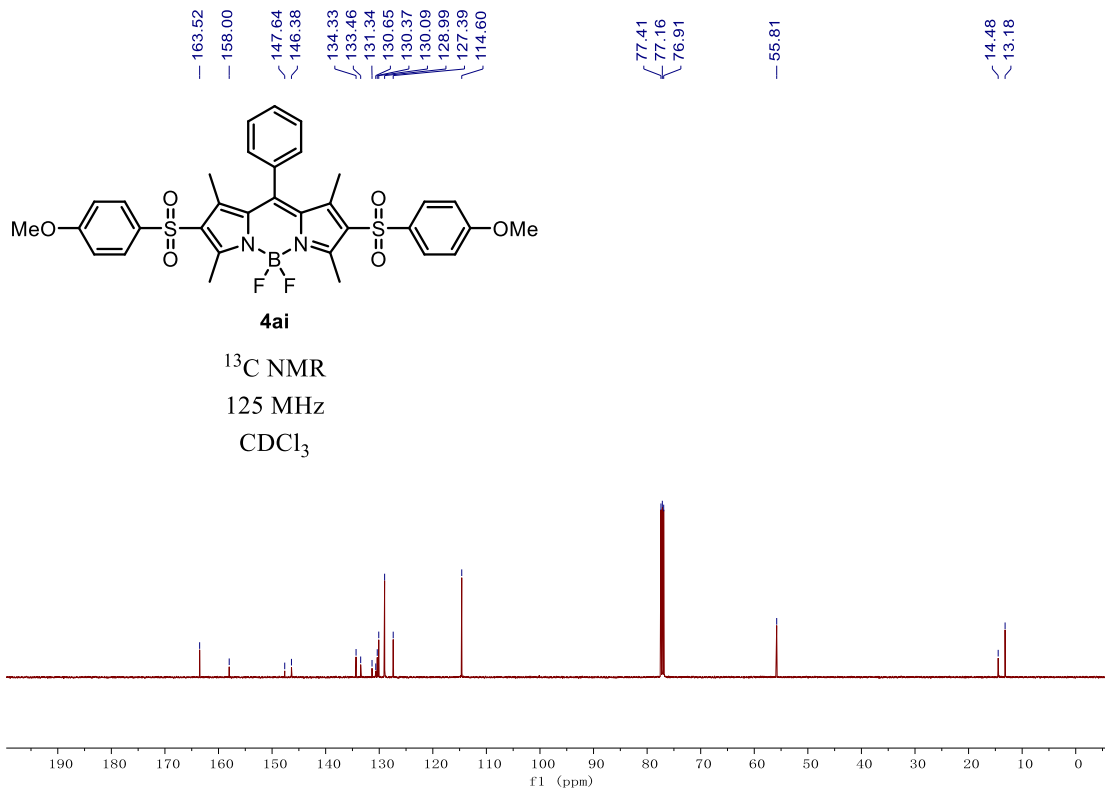
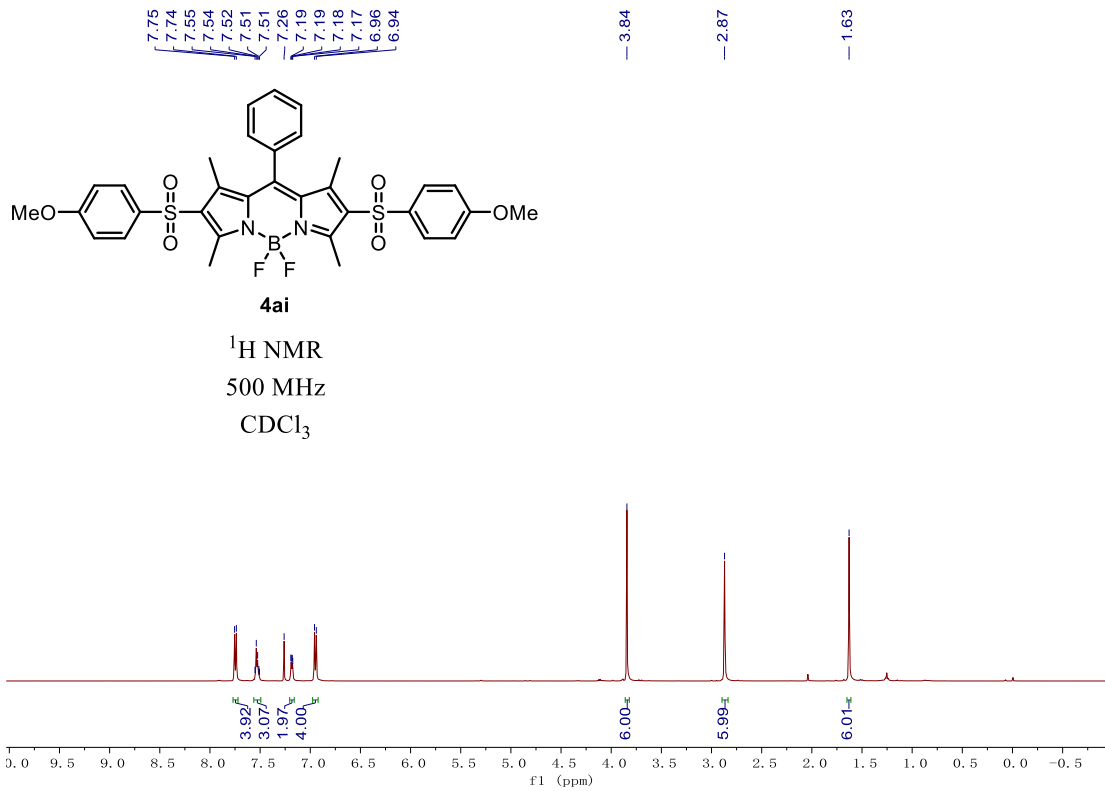


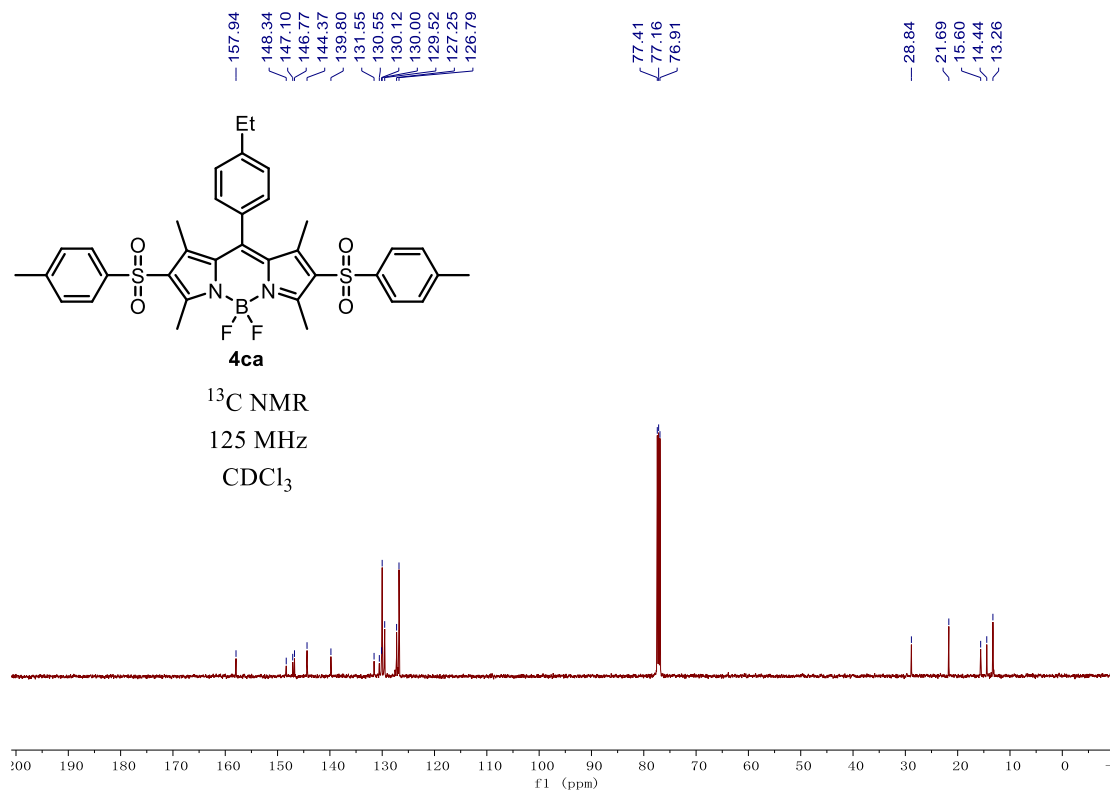
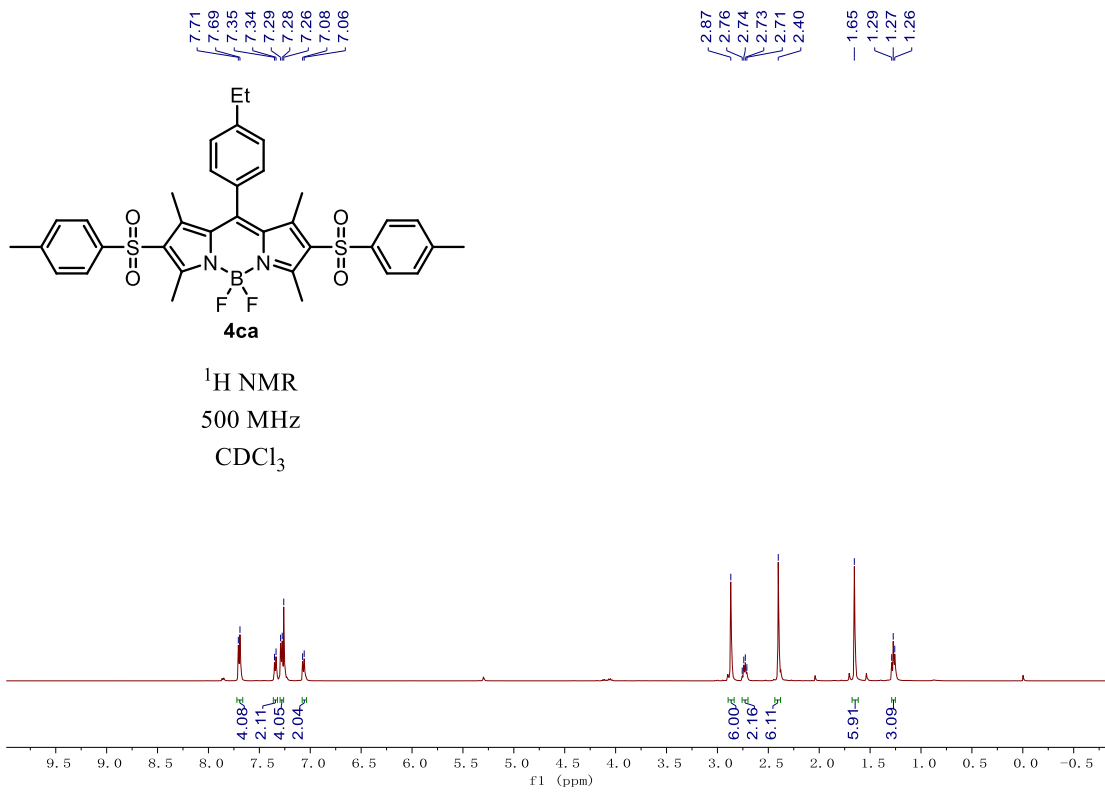




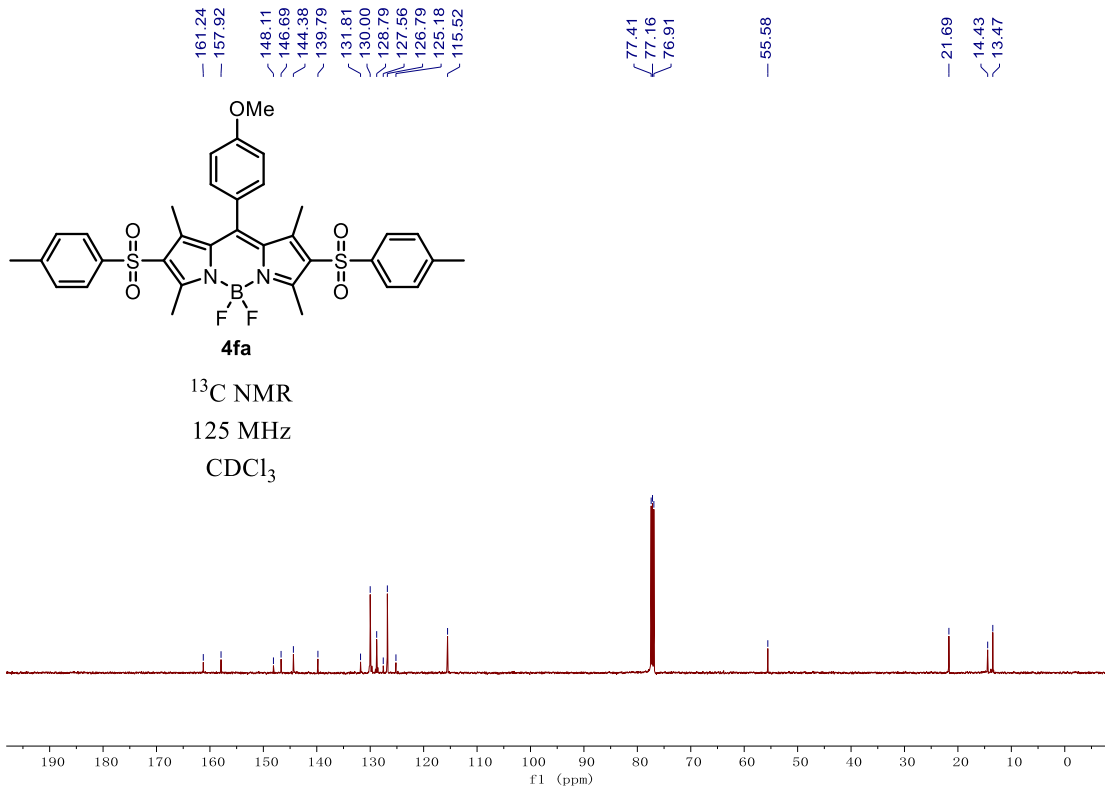
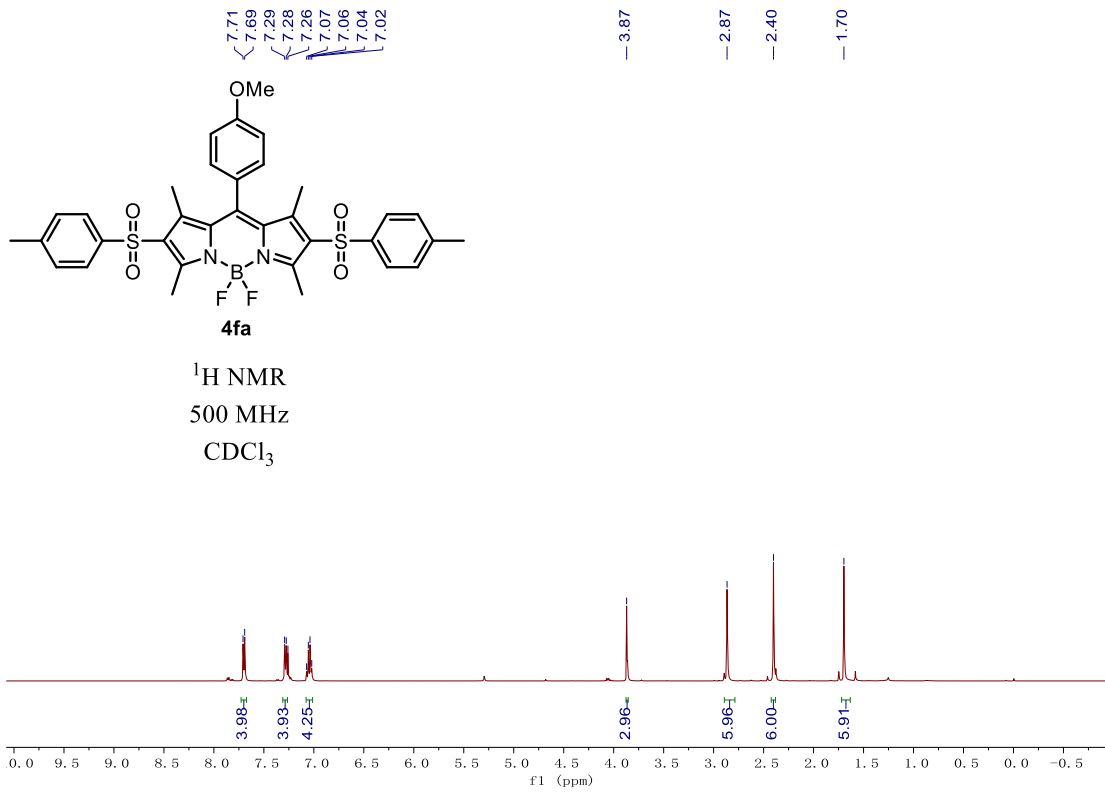


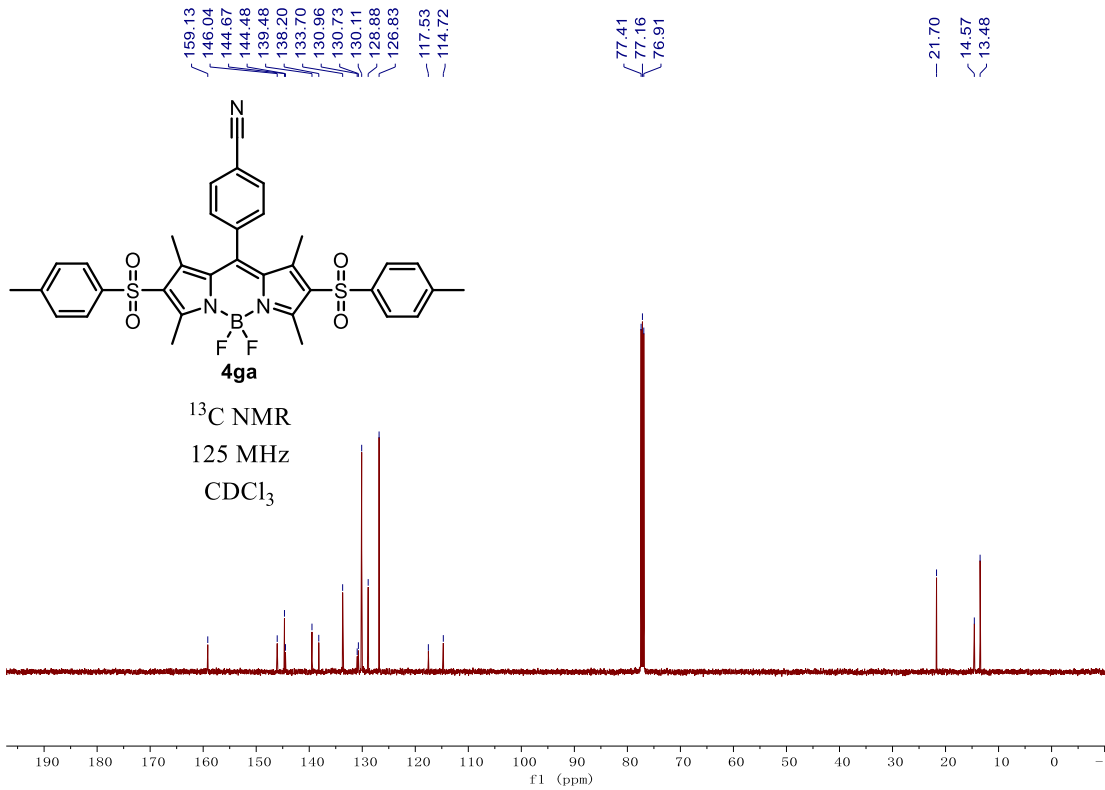
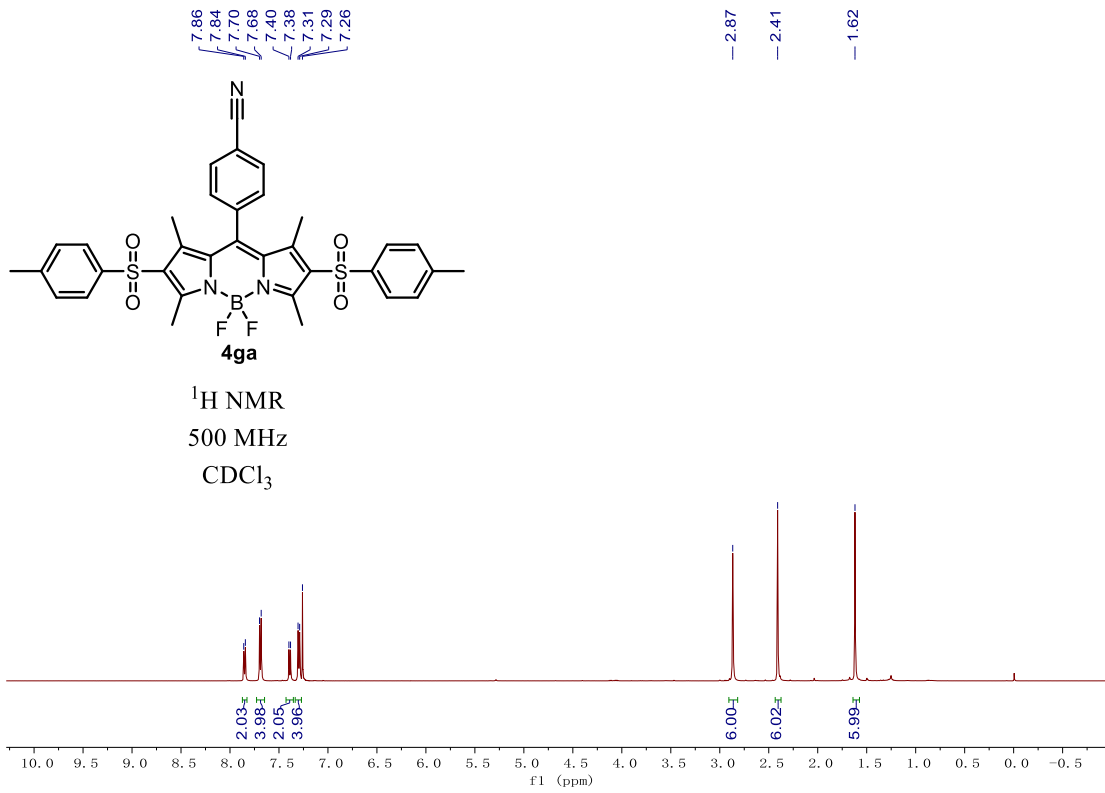


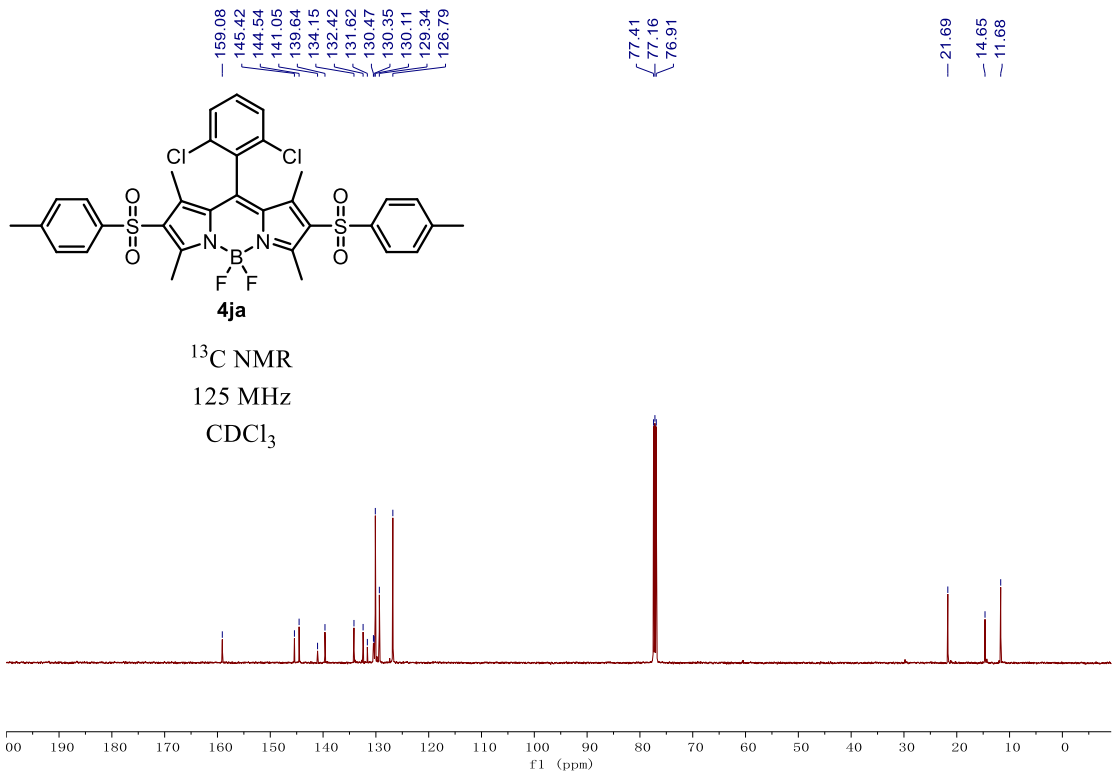
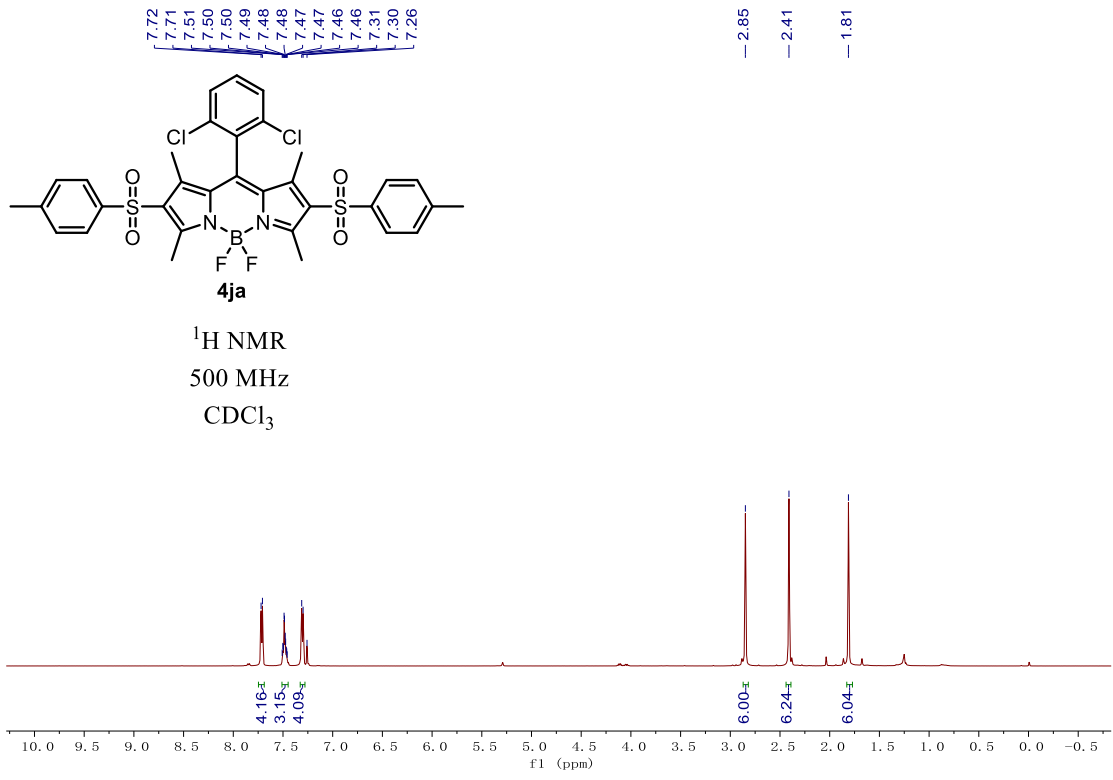


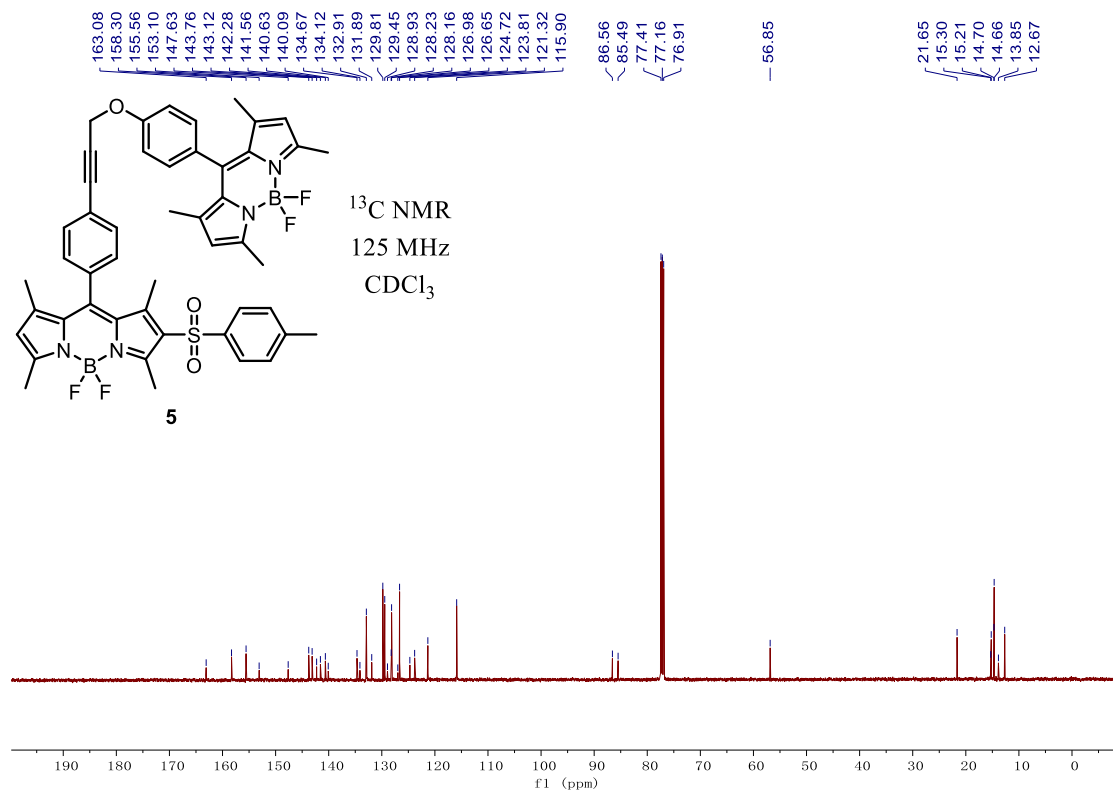
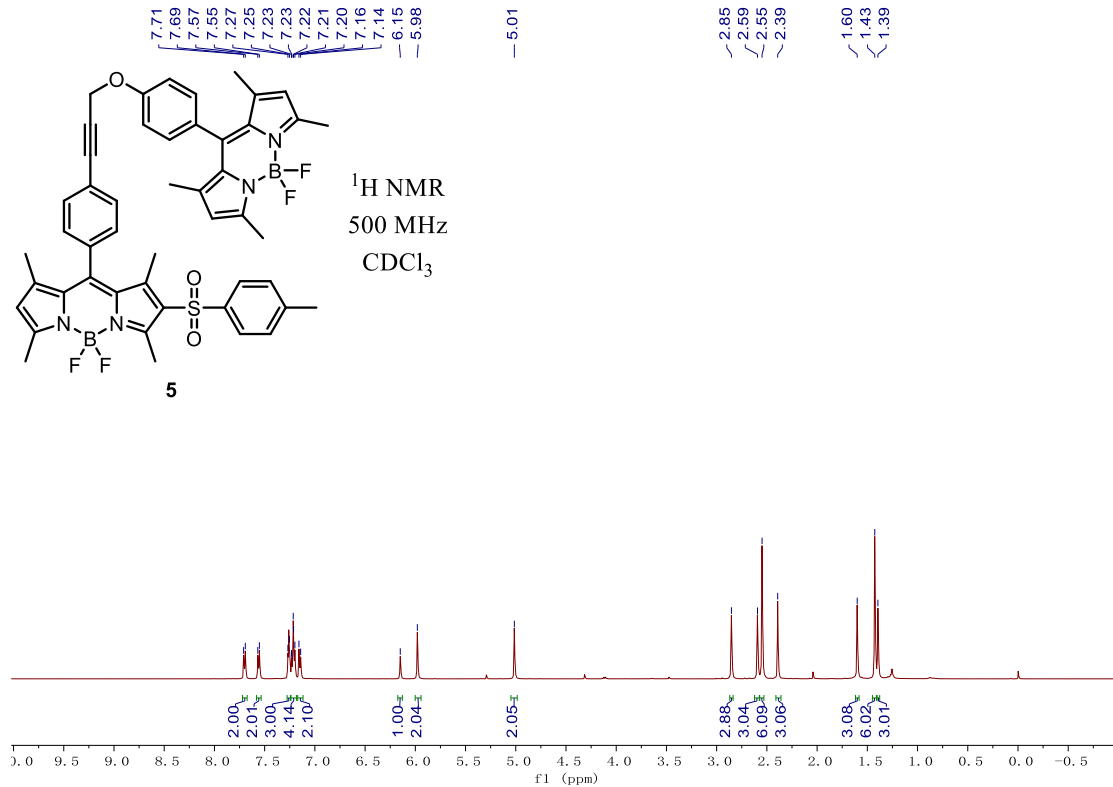


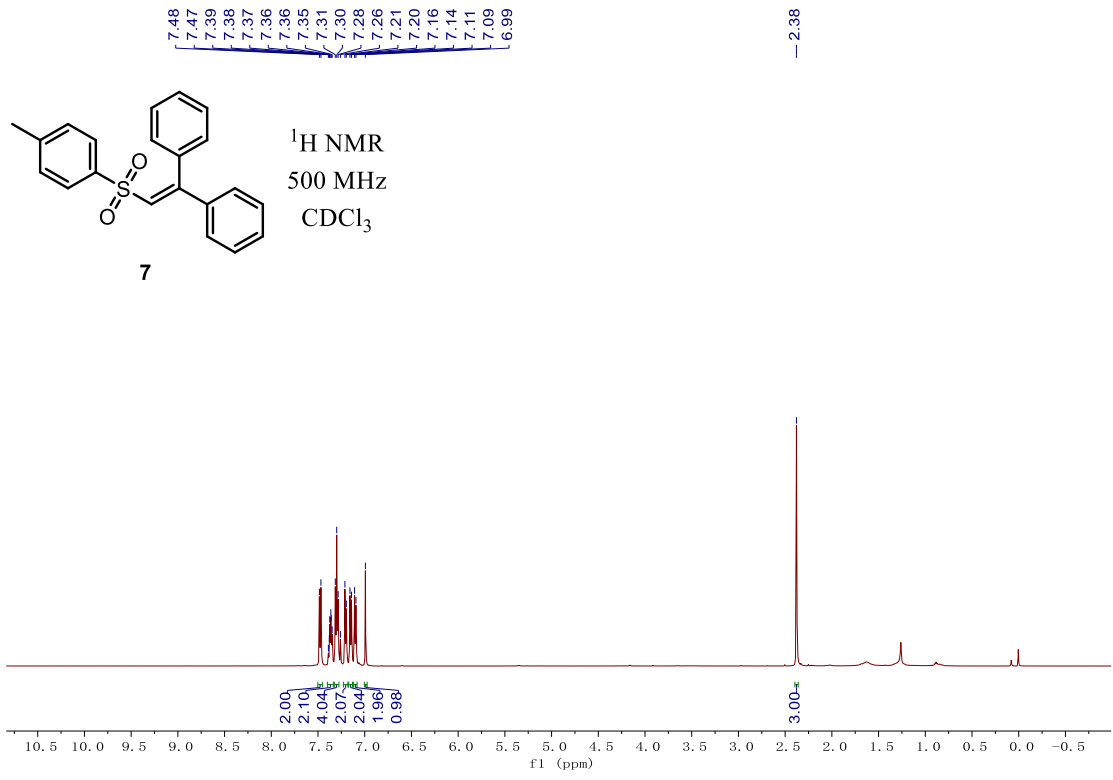


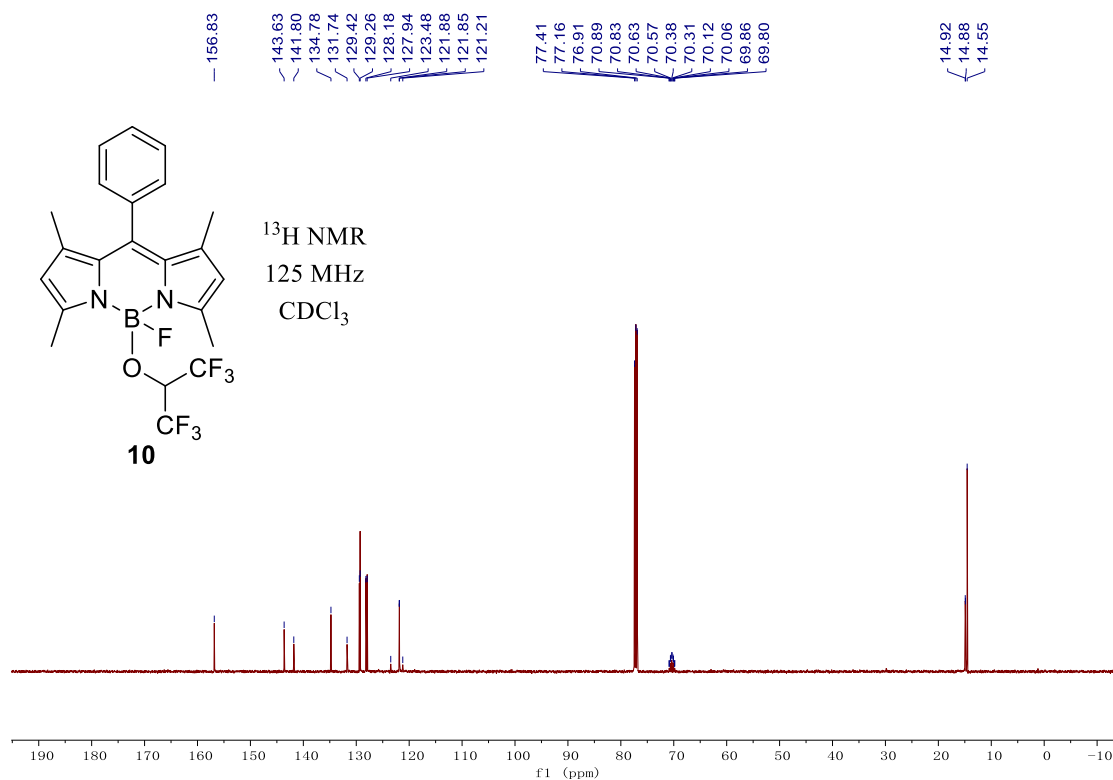
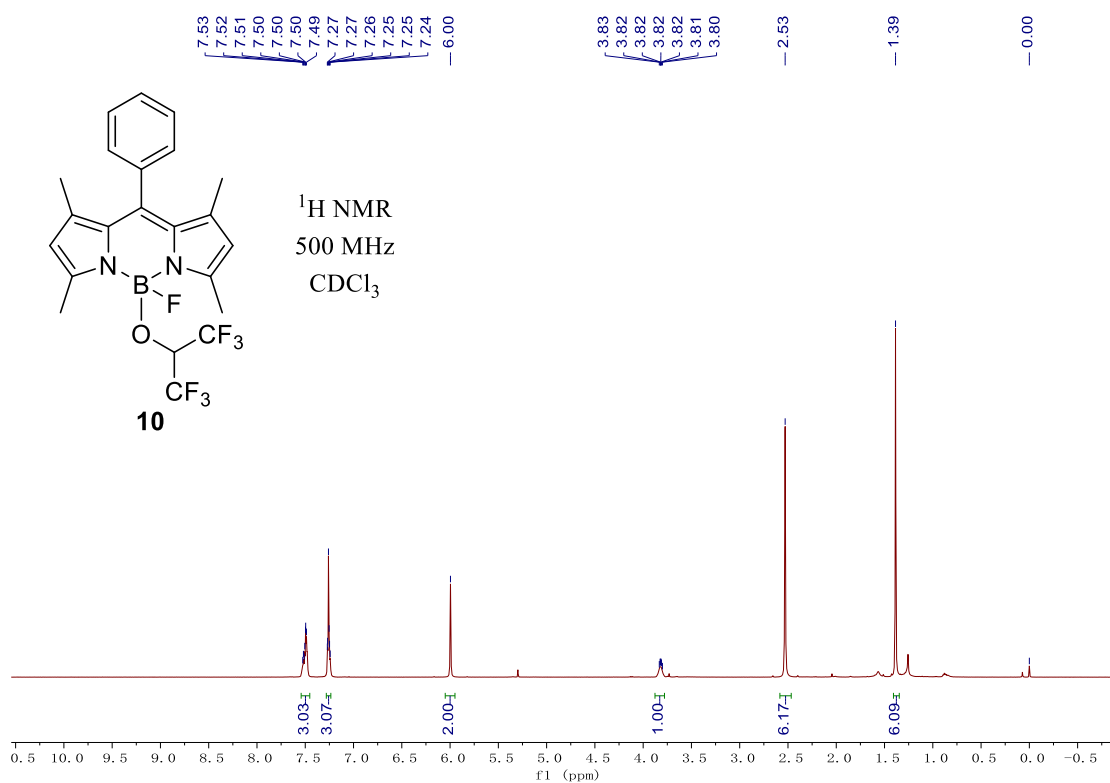












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