Supporting information for

Pictet–Spengler Synthesis of Twist Quinoline-Fused BODIPYs as Heavy-Atom-Free Photosensitizers

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1. Experimental Details

General Information. Reagents and solvents were used as received from commercial suppliers unless noted otherwise. All reactions were performed in oven-dried or flame-dried glassware unless otherwise stated，and were monitored by TLC using 0.25 mm silica gel plates with UV indicator (60F-254) for thin-layer chromatography (TLC). Flash column chromatography was performed using silica gel (200−400 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on a 500 MHz NMR spectrometer at room temperature. Chemical shifts (δ) are given in ppm relative to internal TMS (δ = 0 ppm), $CDCl_3$ (7.26 ppm for ^{1}H NMR and 77.16 ppm for ^{13}C NMR) or d_6-DMSO (2.50 ppm for 1H NMR and 39.52 ppm for ^{13}C NMR). High-resolution mass spectra (HRMS) were obtained using APCI-TOF or ESI-TOF in positive mode.

Absorption and emission measurements. UV-visible absorption spectra and Fluorescence emission spectra were recorded on commercial spectrophotometer (Shimadzu UV-2450 and Edinburgh FS5 spectrometers, 190-900 nm scan range) at room temperature (10 mm quartz cuvette). Relative fluorescence quantum efficiencies of these BODIPY derivatives were obtained by comparing the areas under the corrected emission spectrum of the test sample in various organic solvents with Cresyl violet perchlorate (Φ = 0.54 in methanol)[1] and Rhodamine B (φ = 0.49 in ethanol)[2]. Non-degassed, spectroscopic grade solvents and a 10 mm quartz cuvette were used. Dilute solutions (0.01<A<0.05) were used to minimize the reabsorption effects. Quantum yields were determined using the following equation:

$$\Phi_x = \Phi_r \times \frac{F_x}{F_r} \times \frac{1 - 10^{-A_r(\lambda_{ex})}}{1 - 10^{-A_x(\lambda_{ex})}} \times \frac{n_x^2}{n_r^2}$$

Where the subscripts *x* and *r* respectively refer to our sample *x* and reference (standard) fluorophore *r* with known quantum yield Φ*r* in a specific solvent, *F* stands for the spectrally corrected, integrated fluorescence spectra, $A(\lambda_{ex})$ denotes the absorbance at the used excitation wavelength λ_{ex}, and *n* represents the refractive index of the solvent (in principle at the average emission wavelength).

X-ray structure analysis. Crystals of **3a** and **3c** suitable for X-ray analysis were obtained by slow evaporation of the dichloromethane solution. The vial containing this

solution was placed, loosely capped, to promote the crystallization. A suitable crystal was chosen and mounted on a glass fiber using grease. Data were collected using a Bruker APEX-II[3] CCD diffractometer operating at $T = 293(2)$ K. The determination of unit cell parameters and data collections were performed with Mo Kα radiation (λ) at 0.71073 Å. The total number of runs and images were based on the strategy calculation from the program **APEX2** (Bruker).[4] The structures were solved by the structure solution program **Olex2** (Dolomanov et al., **2009**)[5] and the model was refined with version 2014/7 of **ShelXL** (Sheldrick, **2015**)[6] using full matrix least squares on $\mathbf{F^2}$ minimisation. CCDC-2236281 (**3a**) and 2254645 (**3c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Electrochemical measurements. Cyclic voltammograms of 1 mM **3a**, **4a** and **M** were measured in dichloromethane solution, containing 0.1 M $TBAPF_6$ as the supporting electrolyte, glassy carbon electrode as a working electrode, Pt wire as a counter electrode, and saturated calomel electrode (SCE) as reference electrode at 100 mV s^{-1} of scanning rate at room temperature.

2. Crystal Data

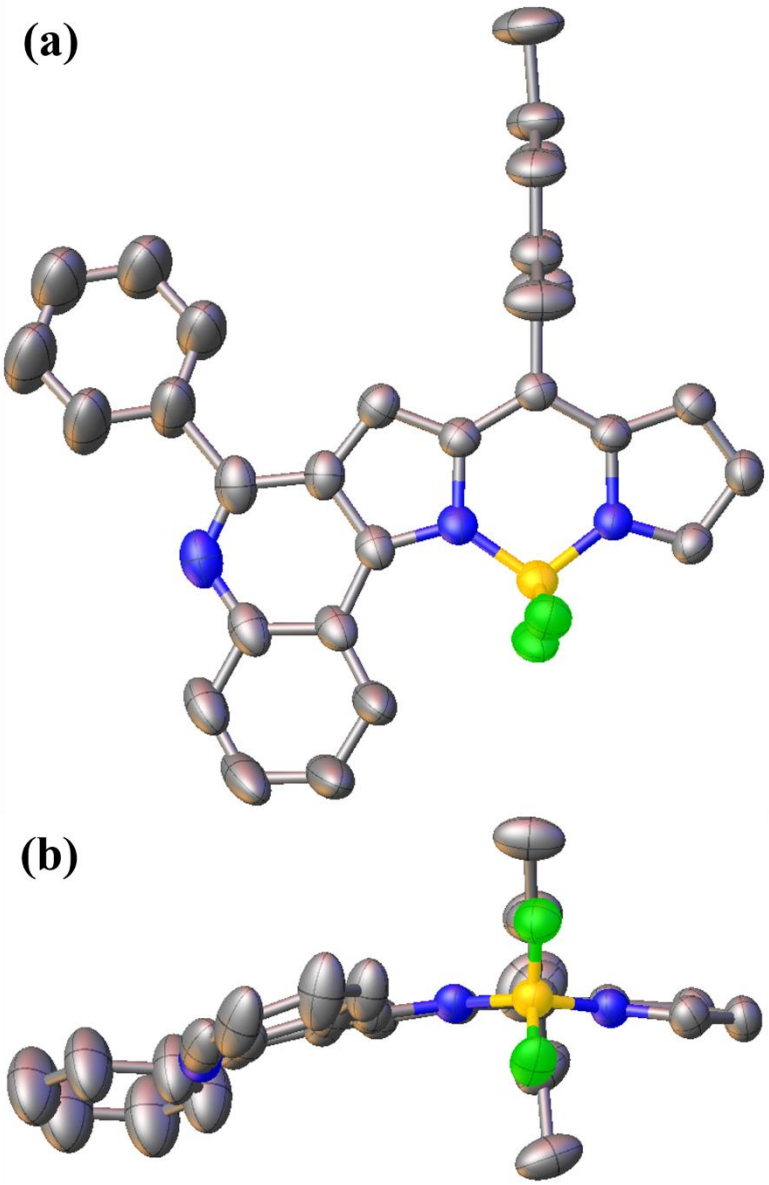


Figure S1. Single-crystal structure of **3a**, with thermal ellipsoids shown at 50% probability: (a) top view, (b) bottom view of X-ray structures of BODIPY **3a**. C, gray; N, blue; B, dark yellow; F, light green; Cl, dark green. Hydrogen atoms have removed for clarity.

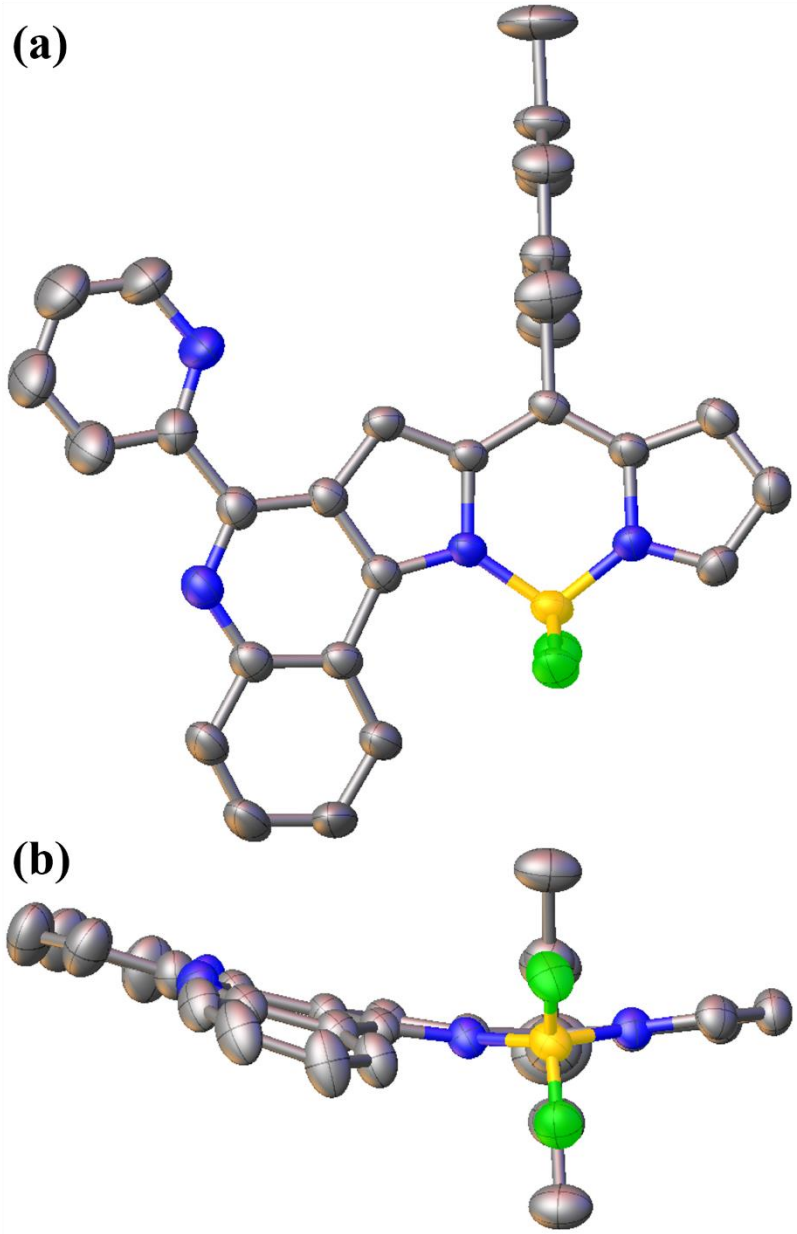
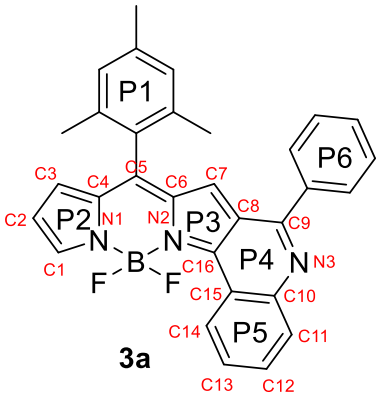
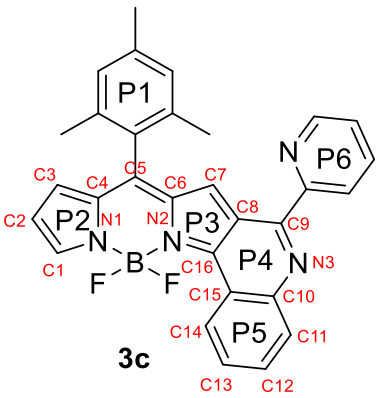


Figure S2. Single-crystal structure of **3c**, with thermal ellipsoids shown at 50% probability: (a) top view, (b) bottom view of X-ray structures of BODIPY **3c**. C, gray; N, blue; B, dark yellow; F, light green; Cl, dark green. Hydrogen atoms have removed for clarity.

Table S1. Selected Geometrical Parameters of 3a and 3c obtained from crystallography



3a



3c

Compounds	3a	3c
B-N1 bond length (Å)	1.5546(38)	1.5572(32)
B-N2 bond length (Å)	1.5477(40)	1.5486(37)
B-F bond length (Å)	1.3738(45) 1.3881(32)	1.3881(27) 1.3754(36)
C4-N1 bond length (Å)	1.3929(35)	1.3948(35)
C6-N2 bond length (Å)	1.3931(36)	1.4019(33)
C8-C9 bond length (Å)	1.4373(39)	1.4387(29)
C9-N3 bond length (Å)	1.3111(51)	1.3155(35)
C10-N3 bond length (Å)	1.3812(50)	1.3747(33)
dihedral angles between **P2** and **P3** (deg)	14.919(84)	16.159(127)
dihedral angles between **P1** and BODIPY core (deg)	82.575(340)	88.322(101)
dihedral angles between **P4** and BODIPY core (deg)	14.411(55)	15.391(70)
dihedral angles between **P5** and BODIPY core (deg)	20.032(78)	20.865(74)
dihedral angles between **P6** and BODIPY core (deg)	19.553(298)	17.705(561)
dihedral angles between **P4-P5** and BODIPY core (deg)	16.491(44)	17.746(45)

[a] BODIPY core: dipyrrin core (C_9N_2); [b] **P2** and **P3**: pyrrole rings (C_4N) in dipyrrin core (C_9N_2).

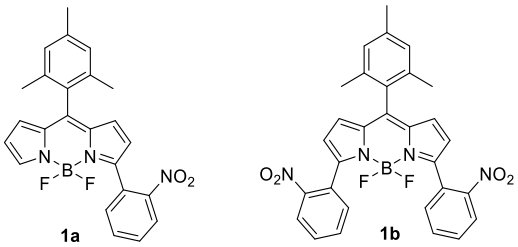
Table 1 Crystal data and structure refinement for 3a.

Identification code	3a
Empirical formula	$C_{31}H_{24}BF_2N_3$
Formula weight	487.34
Temperature/K	300.00
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.3821(12)
b/Å	18.3455(15)
c/Å	11.4591(12)
α/°	90
β/°	110.660(3)
γ/°	90
Volume/Å^3	2435.6(4)
Z	4
ρ_{calc}g/cm^3	1.329
μ/mm^{-1}	0.089
F(000)	1016.0
Crystal size/mm^3	0.13 × 0.12 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.664 to 50.312
Index ranges	$-14 \leq h \leq 14$, $-20 \leq k \leq 21$, $-13 \leq l \leq 13$
Reflections collected	65120
Independent reflections	4352 [R_{int} = 0.0693, R_{sigma} = 0.0271]
Data/restraints/parameters	4352/703/430
Goodness-of-fit on F^2	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0626, wR_2 = 0.1601
Final R indexes [all data]	R_1 = 0.0841, wR_2 = 0.1786
Largest diff. peak/hole / e Å^{-3}	0.36/-0.43

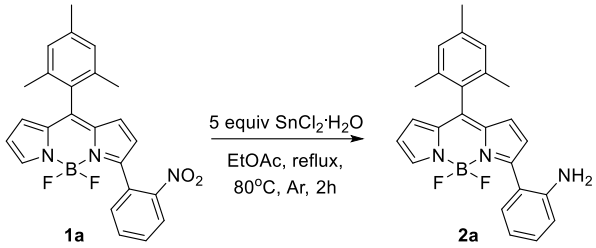
Table 1 Crystal data and structure refinement for 3c.

Identification code	3c
Empirical formula	$C_{30}H_{23}BF_2N_4$
Formula weight	488.33
Temperature/K	300.00
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.348(4)
b/Å	18.253(6)
c/Å	11.465(4)
α/°	90
β/°	110.146(9)
γ/°	90
Volume/Å^3	2425.9(14)
Z	4
ρ_{calc}g/cm^3	1.337
μ/mm^{-1}	0.090
F(000)	1016.0
Crystal size/mm^3	0.22 × 0.21 × 0.2
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.162 to 50.402
Index ranges	$-14 \leq h \leq 14$, $-21 \leq k \leq 21$, $-13 \leq l \leq 12$
Reflections collected	17303
Independent reflections	4347 [R_{int} = 0.0722, R_{sigma} = 0.0617]
Data/restraints/parameters	4347/236/383
Goodness-of-fit on F^2	1.022
Final R indexes [I>=2σ (I)]	R_1 = 0.0496, wR_2 = 0.1178
Final R indexes [all data]	R_1 = 0.0952, wR_2 = 0.1389
Largest diff. peak/hole / e Å^{-3}	0.19/-0.24

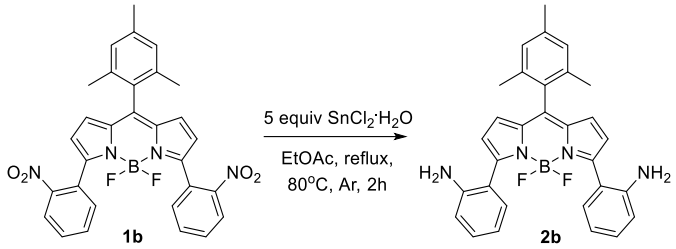
3. Synthesis and Characterization



BODIPYs **M**, **1a** and **1b** were synthesized according to the literature.[7]

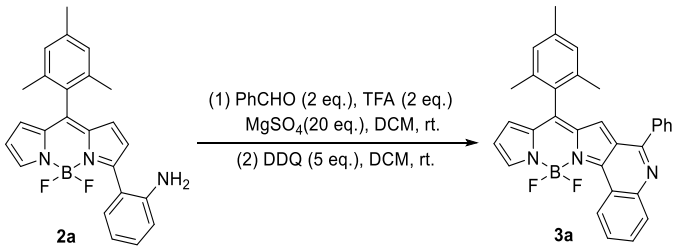


BODIPY 2a: A mixture of BODIPY **1a** (66 mg, 0.15 mmol) and $SnCl_2 \cdot 2H_2O$ (5 equiv, 169 mg, 0.75 mmol) in EtOAc (4 mL) was stirred at reflux under nitrogen for 1.5 h, and TLC was used to follow the reaction. Upon completion, the reaction mixture was cooled to room temperature, and quenched with a saturated $NaHCO_3$ aqueous solution. Then the reaction mixture was poured into water and was extracted with EtOAc (3 × 30 mL). Organic layers were combined, dried over anhydrous Na_2SO_4, and organic solvent was removed under vacuum. The crude product was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 5/1-3/1, v/v) to afford the desired BODIPY **2a** as a black solid in 66% yield (40 mg). ^{1}H NMR (500 MHz, d_6-DMSO) δ 7.83 (s, 1H), 7.52 (d, J = 7.6 Hz, 1H), 7.16 (t, J = 7.6 Hz, 1H), 7.06 (s, 2H), 6.81-6.78 (m, 2H), 6.74 (d, J = 4.3 Hz, 1H), 6.63 (t, J = 7.5 Hz, 1H), 6.55-6.50 (m, 2H), 5.26 (s, 2H), 2.34 (s, 3H), 2.09 (s, 6H); ^{13}C NMR (126 MHz, d_6-DMSO) δ 160.2, 148.2, 144.2, 142.1, 139.1, 137.2, 136.7, 134.4, 132.2, 131.7, 131.4, 130.5, 129.0, 127.8, 123.3, 118.8, 116.8, 116.4, 21.6, 20.5; HRMS (APCI) m/z: $[M - F]^+$ Calcd. for $C_{24}H_{22}BFN_3$ 382.1885; found 382.1866.

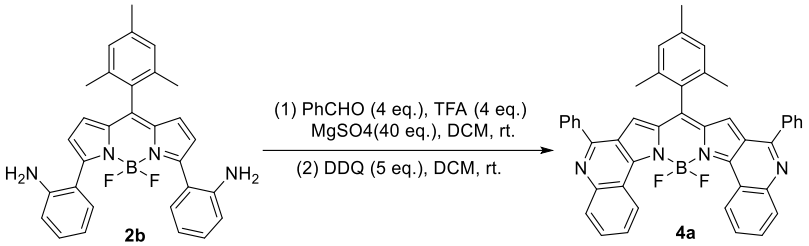


BODIPY 2b: BODIPY **2b** was obtained from BODIPY **1b** using the same procedure described for **2a**, and this reaction was completed after 2 h, providing a black solid in 25% yield (19 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (d, J = 7.6 Hz, 2H), 7.17 (t, J = 7.6 Hz, 2H), 6.99 (s, 2H), 6.80 (t, J = 5.9 Hz, 2H), 6.71 (d, J = 4.0 Hz, 4H), 6.53 (d, J = 4.0 Hz, 2H), 3.80 (s, 4H), 2.39 (s, 3H), 2.21 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.7, 145.3, 144.7, 139.1, 137.1, 136.5, 131.4, 130.8, 130.5, 130.0, 128.6, 121.5, 119.2, 118.6, 116.4, 21.6, 20.6; HRMS (APCI) m/z: $[M - F]^+$ Calcd. for $C_{30}H_{27}BFN_4$ 473.2307; Found 473.2292.

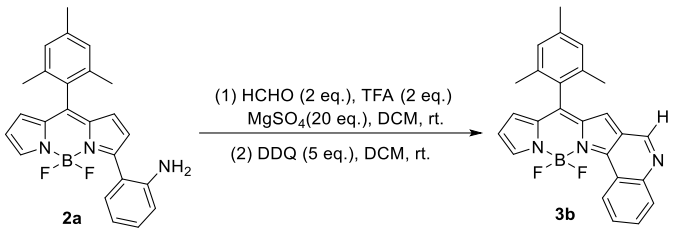
General method for the preparation of Quinoline-Fused BODIPYs 3a-c and 4a-c: To a solution of **2a** or **2b** (0.15 mmol) in dichloromethane (10 mL) was added $MgSO_4$ (20 or 40 equiv), aldehyde (2 or 4 equiv) and TFA (2 or 4 equiv). The reaction mixture was stirred under argon at room temperature for 1-3 h and monitored by TLC until no more products were generated. Then DDQ (5 equiv) was added to the reaction mixture, the resulting mixture was stirred at room temperature for an additional 20 min. Upon the completion of the reaction, the reaction mixture was quenched by a saturated $NaHCO_3$ aqueous solution. The resulting mixture was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 7/1-3/1, v/v) to afford the quinoline-fused BODIPYs **3a-c** and **4a-c**.



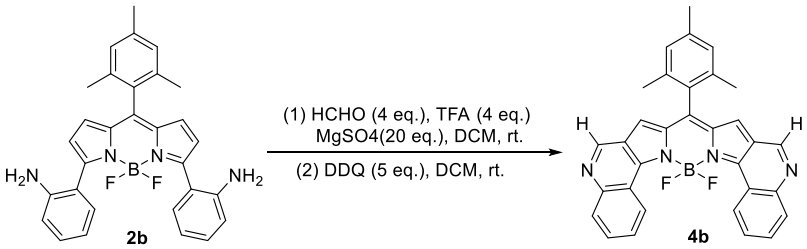
BODIPY 3a: Following the general procedure, BODIPY **2a** (60 mg, 0.15 mmol) and $MgSO_4$ (355 mg, 3 mmol), benzaldehyde (32 mg, 0.30 mmol), TFA (34.2 mg, 0.30 mmol) for 1.0 h, and then DDQ (170 mg, 0.75 mmol) for 30 min. Purification via column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1, v/v) afforded the desired BODIPY **3a** as a red solid in 40% yield (29 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.20 (d, *J* = 8.3 Hz, 1H), 8.28 (s, 1H), 8.20 (s, 1H), 7.84 (d, *J* = 7.1 Hz, 2H), 7.76 (t, *J* = 7.5 Hz, 1H), 7.68 (t, *J* = 7.6 Hz, 1H), 7.52-7.45 (m, 3H), 7.16 (s, 1H), 6.99 (s, 2H), 6.89 (d, *J* = 4.3 Hz, 1H), 6.73 (d, *J* = 4.2 Hz, 1H), 2.38 (s, 3H), 2.14 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.8, 150.5, 150.4, 150.2, 149.7, 139.8, 139.0, 138.0, 136.8, 133.1, 130.9, 130.9, 129.7, 129.4, 129.2, 128.9, 127.3, 126.9, 126.8, 126.7, 124.7, 124.2, 123.0, 118.4, 21.6, 20.6; HRMS (APCI) m/z: $[M + H]^+$ Calcd. for $C_{31}H_{25}BF_2N_3$ 488.2104; found 488.2093.



BODIPY4a: Following the general procedure, BODIPY **2b** (64 mg, 0.13 mmol) and $MgSO_4$ (612 mg, 5.2 mmol), benzaldehyde (55 mg, 0.52 mmol), TFA (60 mg, 0.52 mmol) for 2.0 h, and then DDQ (148 mg, 0.65 mmol) for 10 min. Purification via column chromatography on silica gel (petroleum ether/ethyl acetate = 4/1, v/v) afforded the desired BODIPY **4a** as a black solid in 35% yield (30 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.53-9.47 (m, 2H), 8.18 (d, *J* = 7.6 Hz, 2H), 7.86-7.79 (m, 8H), 7.55-7.49 (m, 6H), 7.29 (s, 2H), 7.02 (s, 2H), 2.40 (s, 3H), 2.18 (s, 6H)；^{13}C NMR (126 MHz, $CDCl_3$) δ 157.5, 153.5, 152.1, 148.8, 140.2, 140.2, 139.2, 137.1, 132.6, 131.4, 130.1, 129.9, 129.3, 129.3, 129.1, 128.4, 128.3, 128.2, 128.1, 128.0, 126.6, 118.4, 21.6, 20.8；HRMS (APCI) m/z: $[M + H]^+$ Calcd. for $C_{44}H_{32}BF_2N_4$ 665.2683; Found 665.2695.

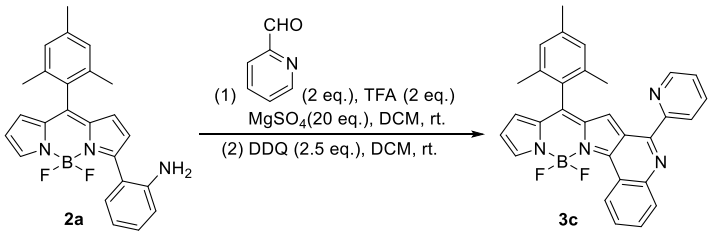


BODIPY 3b: Following the general procedure, BODIPY **2a** (59 mg, 0.15 mmol) and $MgSO_4$ (353 mg, 3 mmol), paraformaldehyde (10 mg, 0.30 mmol), TFA (34 mg, 0.30 mmol) for 2.0 h, and DDQ (85 mg, 0.38 mmol) for 20 min. Purification via column chromatography on silica gel (petroleum ether/ethyl acetate = 7/1, v/v) afforded the desired BODIPY **3b** as a red solid in 51% yield (31 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.15 (d, *J* = 8.2 Hz, 1H), 8.96 (s, 1H), 8.28 (s, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 7.76-7.73 (m, 1H), 7.71-7.67 (m, 1H), 7.10 (s, 1H), 7.02 (s, 2H), 6.94 (d, *J* = 4.3 Hz, 1H), 6.75-6.73 (m, 1H), 2.41 (s, 3H), 2.14 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.4, 149.4, 148.5, 148.0, 139.5, 138.6, 137.7, 136.5, 132.9, 130.2, 129.4, 128.4, 127.2, 126.5, 126.5, 126.4, 125.0, 123.4, 122.7, 119.0, 21.2, 20.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{25}H_{21}BF_2N_3$ 412.1791; Found 412.1779.

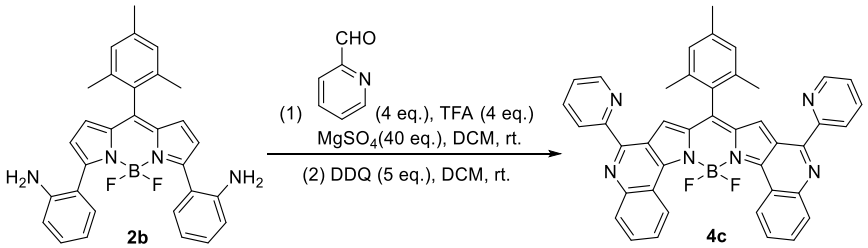


BODIPY 4b: Following the general procedure, BODIPY **2b** (64 mg, 0.13 mmol) and $MgSO_4$ (615 mg, 5.2 mmol), paraformaldehyde (16 mg, 0.52 mmol), TFA (59 mg, 0.52 mmol) for 1.5 h, and then DDQ (148 mg, 0.65 mmol) for 10 min. Purification via column chromatography on silica gel (petroleum ether/ethyl acetate = 6/1, v/v) afforded the desired BODIPY **4b** as a black solid in 45% yield (30 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.46-9.41 (m, 2H), 8.96 (s, 2H), 8.13-8.09 (m, 2H), 7.85-7.80 (m, 4H), 7.31 (s, 2H), 7.07 (s, 2H), 2.44 (s, 3H), 2.18 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.6, 152.3, 149.3, 148.4, 140.4, 140.3, 137.3, 132.5, 131.3, 130.0, 129.0, 128.4, 128.4, 127.6, 127.3, 119.3, 21.6, 20.7. HRMS (APCI) m/z: $[M + H]^+$ Calcd. for $C_{32}H_{24}BF_2N_4$

513.2057; Found 513.2083.



BODIPY 3c: Following the general procedure, BODIPY **2a** (60 mg, 0.15 mmol) and $MgSO_4$ (353 mg, 3 mmol), pyridine-2-carboxaldehyde (32 mg, 0.3 mmol), TFA (34 mg, 0.3 mmol) for 12 h, and DDQ (85 mg, 0.38 mmol) for 20 min. Purification via column chromatography on silica gel (petroleum ether/ethyl acetate = 4/1, v/v) afforded the desired BODIPY **3c** as a red solid in 32% yield (21 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.23 (d, *J* = 8.3 Hz, 1H), 8.64 (d, *J* = 4.0 Hz, 1H), 8.52 (d, *J* = 7.3 Hz, 1H), 8.23 (m, 2H), 8.08 (s, 1H), 7.86 (t, *J* = 7.5 Hz, 1H), 7.76 (t, *J* = 7.2 Hz, 1H), 7.70 (t, *J* = 7.6 Hz, 1H), 7.34-7.31 (m, 1H), 7.02 (s, 2H), 6.89 (d, *J* = 3.8 Hz, 1H), 6.71 (s, 1H), 2.42 (s, 3H), 2.16 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.0, 150.5, 149.8, 149.5, 149.4, 148.9, 139.2, 138.5, 138.0, 136.7, 136.6, 132.5, 130.6, 130.4, 129.6, 128.4, 127.7, 127.3, 126.6, 126.5, 126.5, 123.9, 123.3, 122.2, 118.7, 21.2, 20.3. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{30}H_{24}BF_2N_4$ 489.2057; Found 489.2083.



BODIPY 4c: Following the general procedure, BODIPY **2b** (50 mg, 0.1 mmol) and $MgSO_4$ (472 mg, 4 mmol), pyridine-2-carboxaldehyde (43 mg, 0.4 mmol), TFA (46 mg, 0.4 mmol) for 12 h, and then DDQ (113 mg, 0.5 mmol) for 20 min. Purification via column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1, v/v) afforded the desired BODIPY **4c** as a red solid in 15% yield (10 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.54 (d, *J* = 9.1 Hz, 2H), 8.66 (d, *J* = 4.1 Hz, 2H), 8.55 (d, *J* = 7.8 Hz, 2H), 8.30 (s, 2H), 8.20 (s, 2H), 7.89-7.82 (m, 6H), 7.37-7.34 (t, 2H), 7.08 (s, 2H), 2.47 (s, 3H), 2.22 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.1, 154.0, 153.7, 152.9, 149.4, 140.7, 139.7,

137.3, 137.2, 132.3, 131.4, 130.5, 128.9, 128.4, 125.8, 124.6, 123.7, 123.6, 119.2, 87.8, 21.8, 21.1. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{42}H_{30}BF_2N_6$ 667.2588; Found 667.2599.

4. Photophysical Data

Table S4 Photophysical properties of **2a** and **2b** in toluene at room temperature.

entry	λ_{abs}^{max} (nm)	$\varepsilon^{[a]}$	λ_{em}^{max} (nm)	$\Phi^{[b]}$	Stokes-shift (cm^{-1})
2a	516	32	565	0.01	1560
2b	530	26	648	0.01	3410

[a] Molar extinction coefficient [10^3 M^{-1} cm^{-1}]. [b] Fluorescence quantum yields of compound **2a** and **2b** were calculated using Rhodamine B (Φ = 0.49 in ethanol) as the reference.

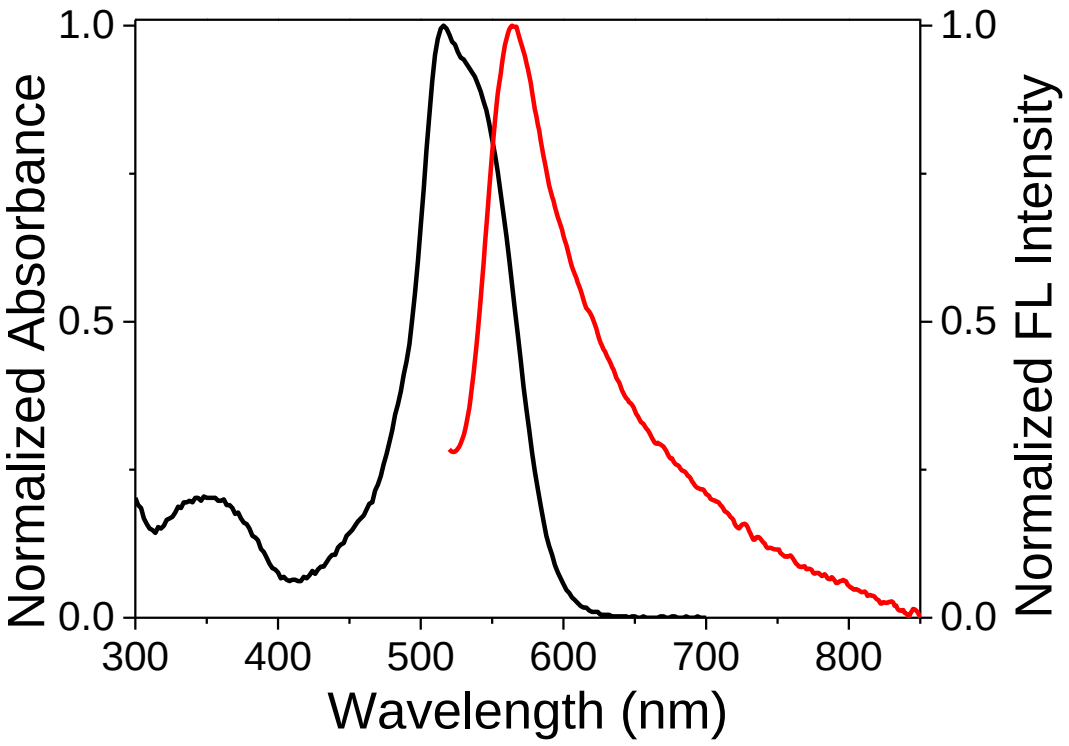


Figure S3. Normalized absorption (dark) and emission (red) spectra of BODIPY **2a** recorded in toluene, excited at 480 nm.

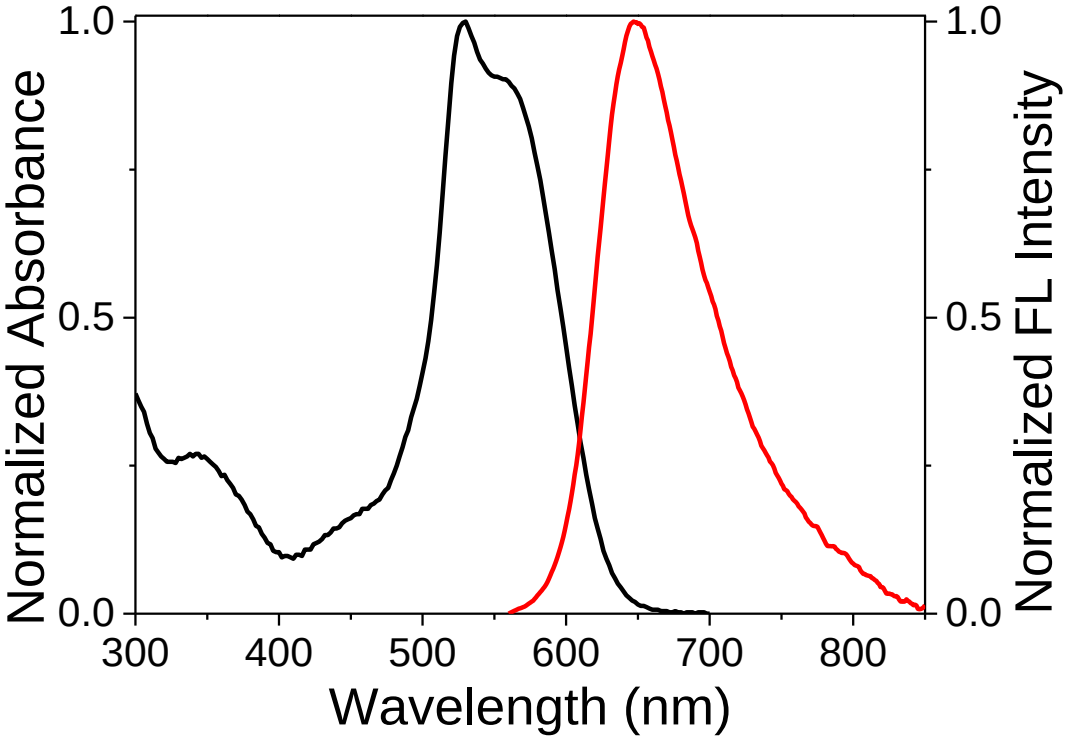


Figure S4. Normalized absorption (dark) and emission (red) spectra of BODIPY **2b** recorded in toluene, excited at 540 nm.

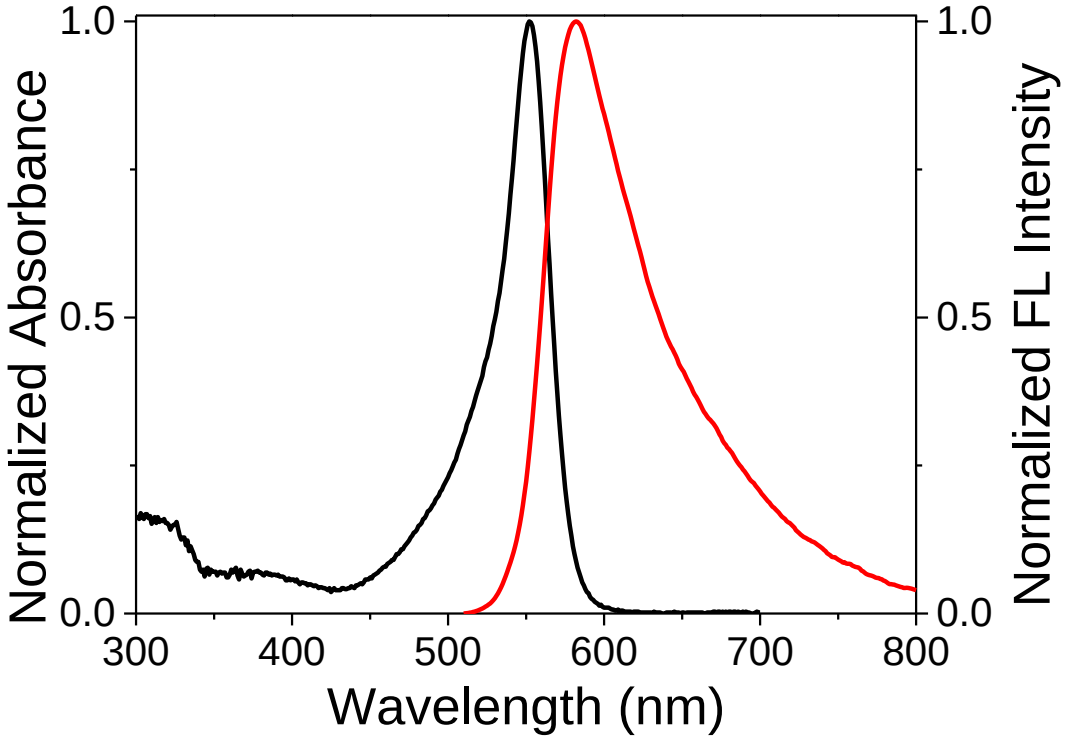


Figure S5. Normalized absorption (dark) and emission (red) spectra of BODIPY **3a** recorded in toluene, excited at 500 nm.

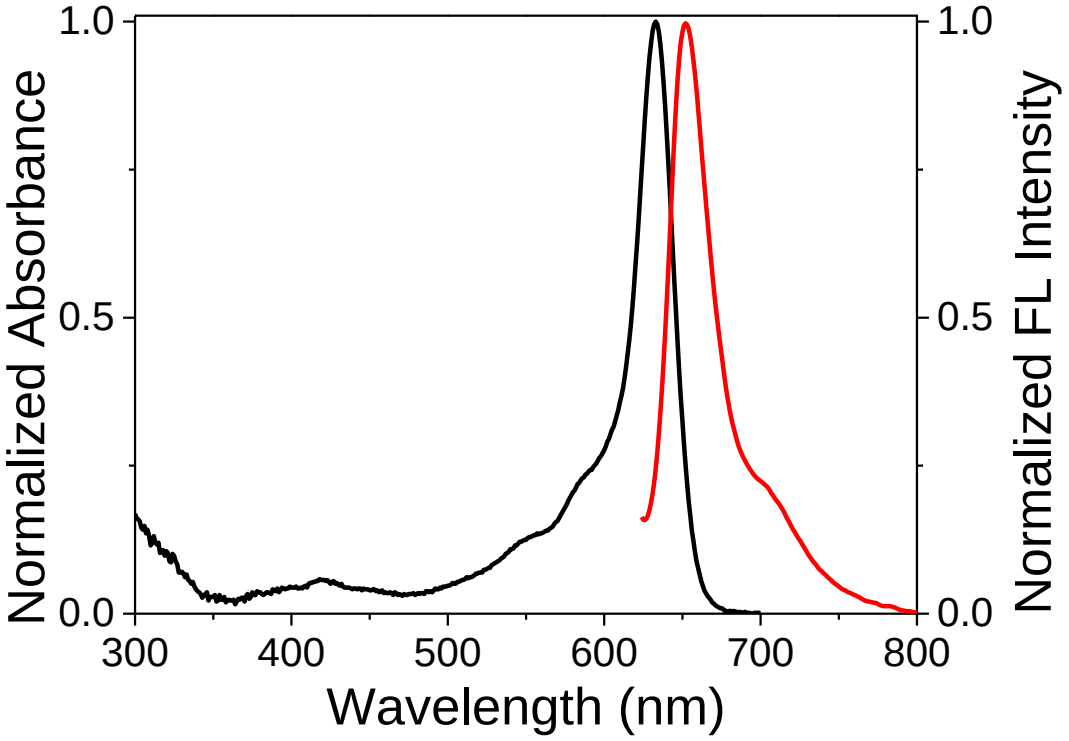


Figure S6. Normalized absorption (dark) and emission (red) spectra of quinoline-fused BODIPY **4a** recorded in toluene, excited at 590 nm.

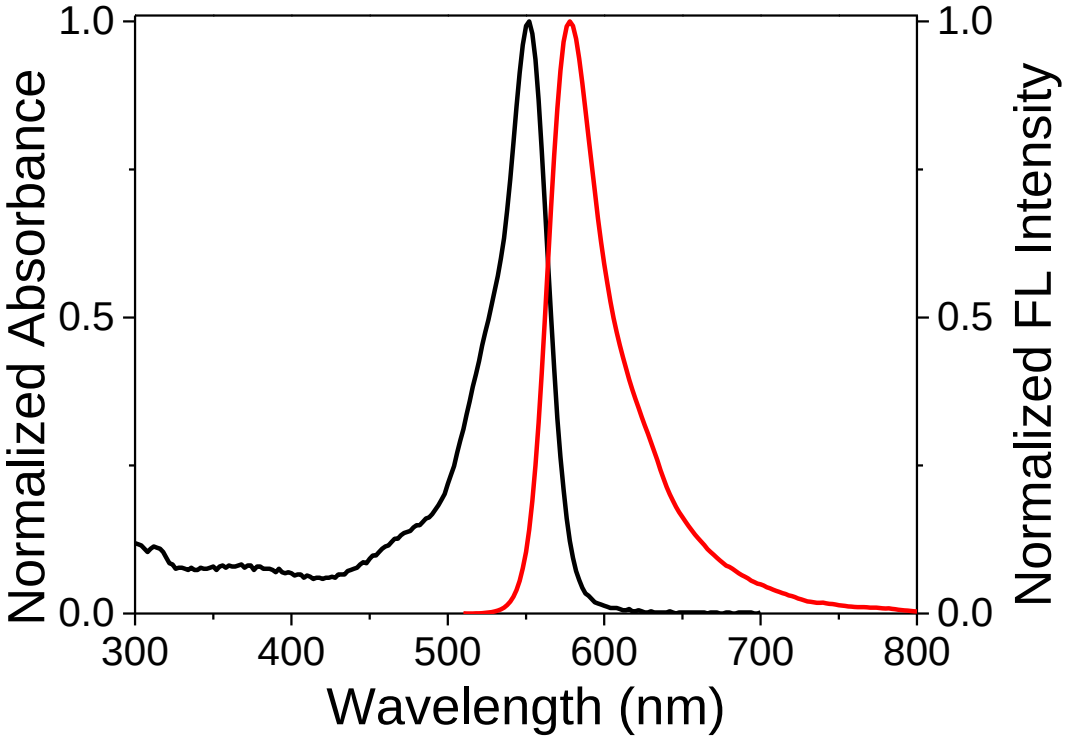


Figure S7. Normalized absorption (dark) and emission (red) spectra of quinoline-fused BODIPY **3b** recorded in different solvents, excited at 500 nm.

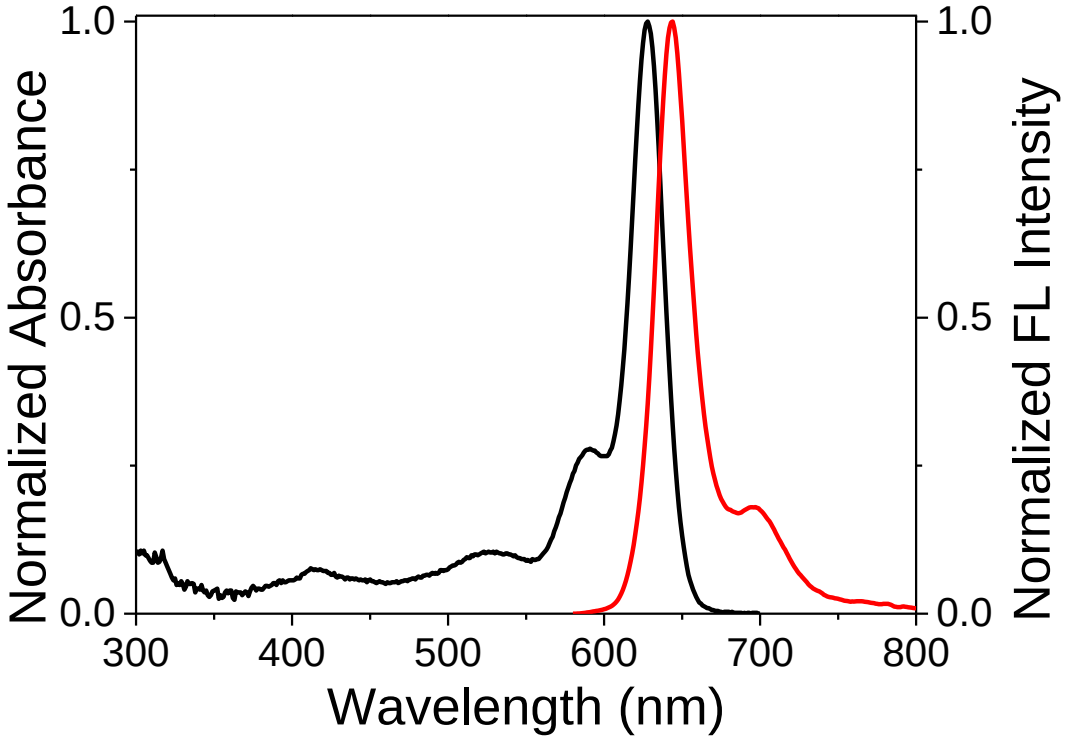


Figure S8. Normalized absorption (dark) and emission (red) spectra of quinoline-fused BODIPY **4b** recorded in different solvents, excited at 540 nm.

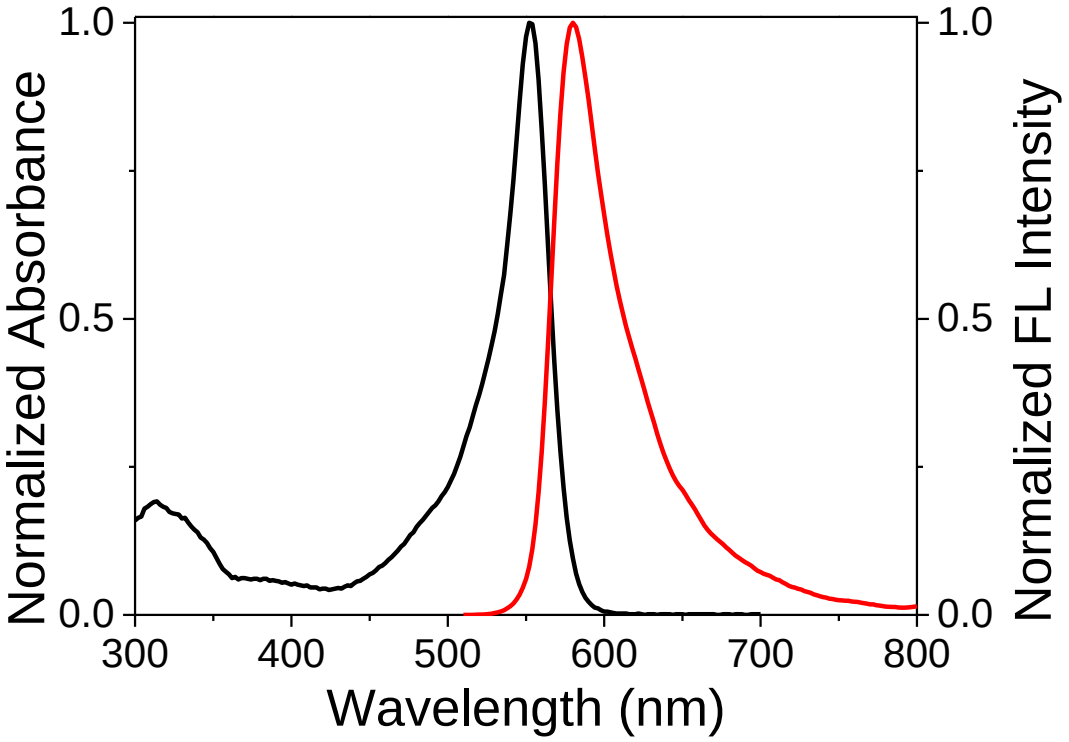


Figure S9. Normalized absorption (dark) and emission (red) spectra of quinoline-fused BODIPY **3c** recorded in different solvents, excited at 500 nm.

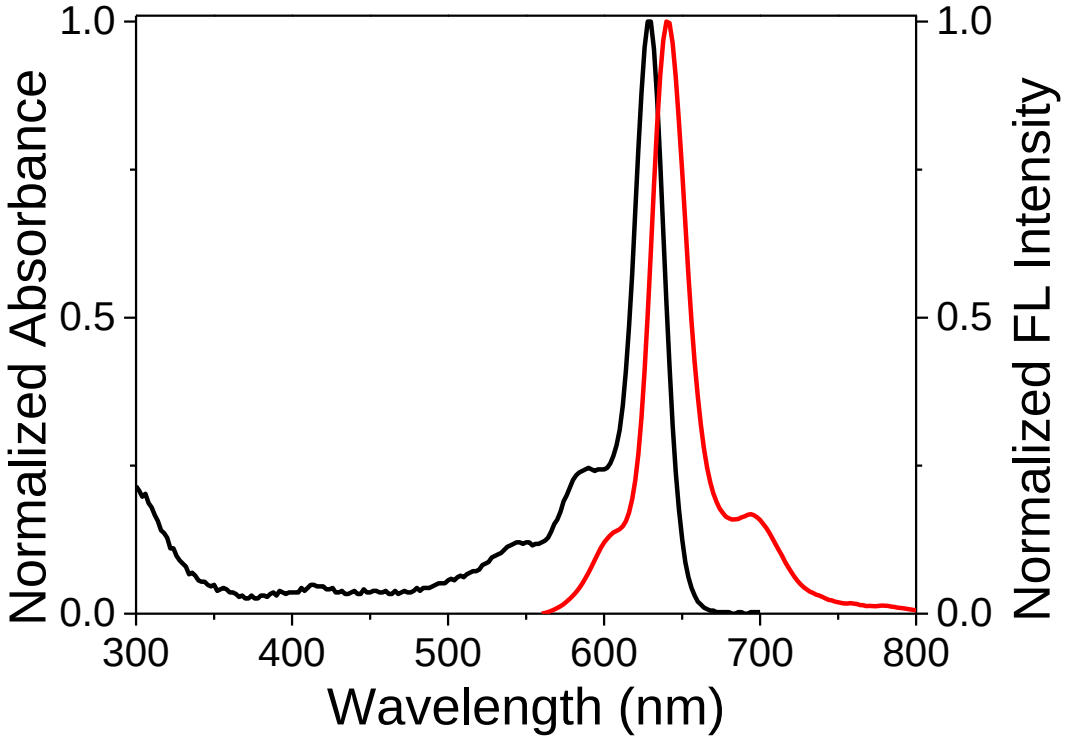


Figure S10. Normalized absorption (dark) and emission (red) spectra of quinoline-fused BODIPY **4c** recorded in different solvents, excited at 560 nm.

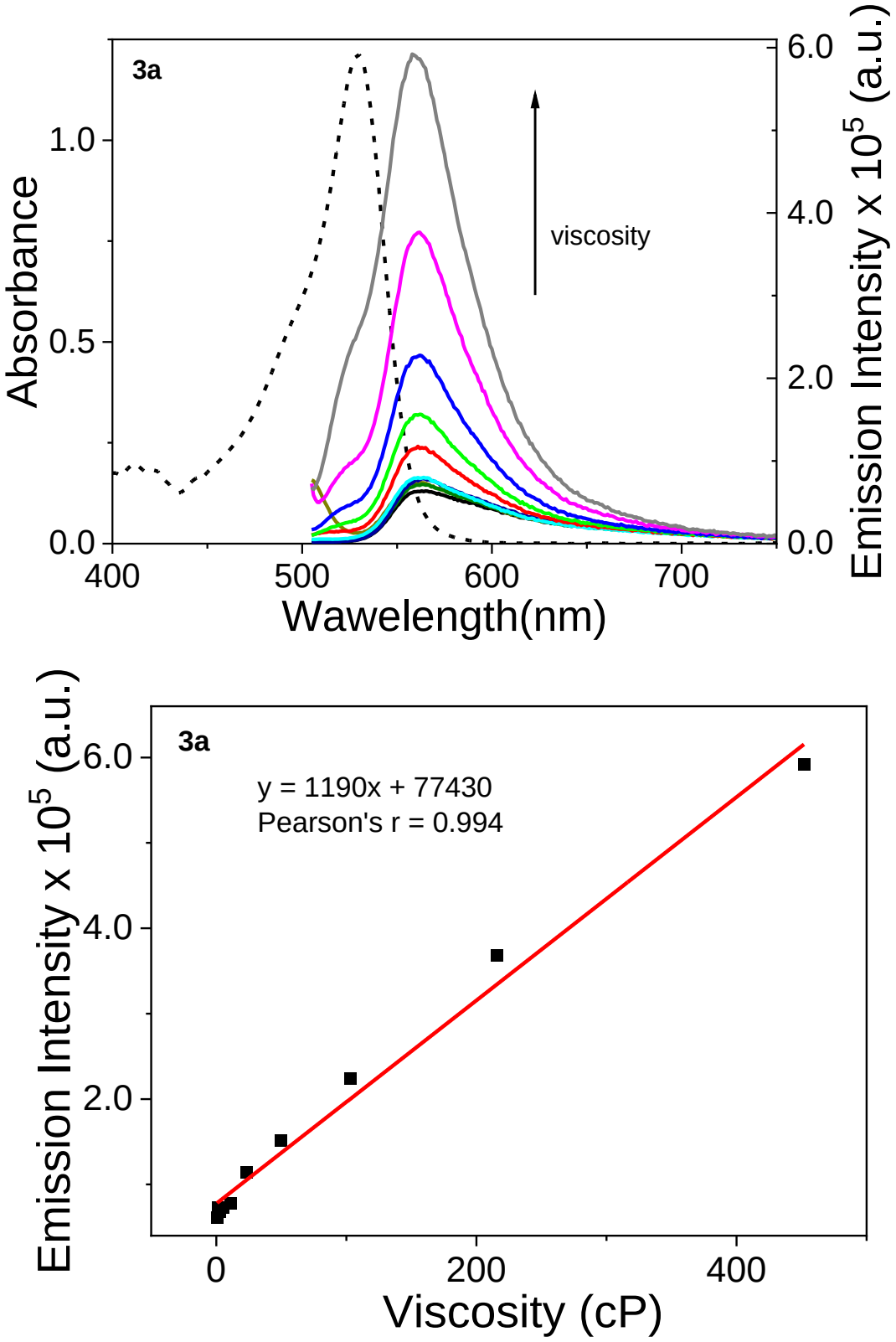


Figure S11. Fluorescence spectra of **3a** (1.0×10^{-5} M) in methanol/glycerol with different viscosities (top). Mixtures were excited at 500 nm. The linear relationship of **3a** between emission intensity and viscosity(η) (bottom).

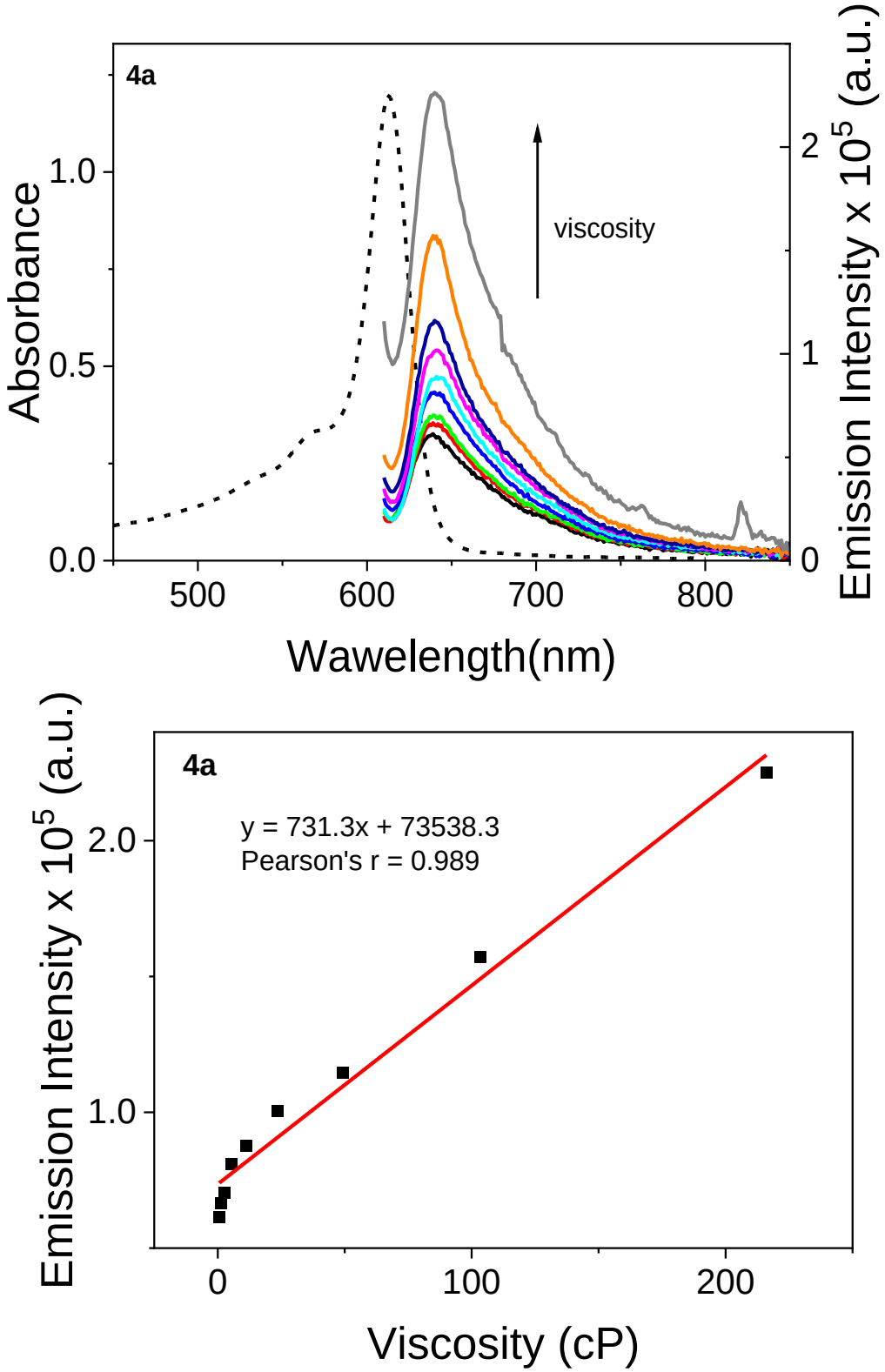


Figure S12. Fluorescence spectra of **4a** (1.0×10^{-5} M) in methanol/glycerol with different viscosities (top). Mixtures were excited at 590 nm. The linear relationship of **4a** between emission intensity and viscosity(η) (bottom).

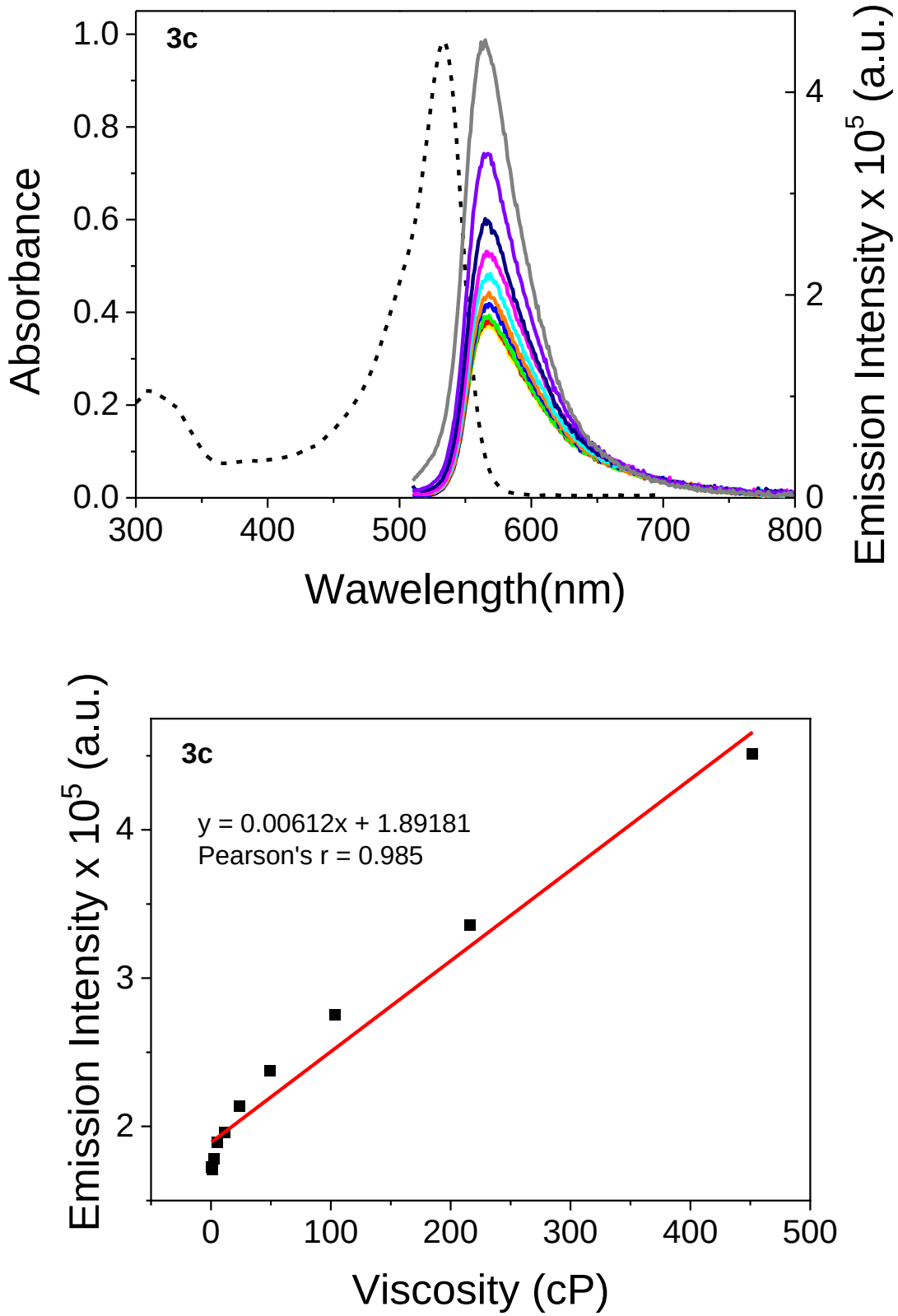


Figure S13. Fluorescence spectra of **3c** (1.0×10^{-5} M) in methanol/glycerol with different viscosities (top). Mixtures were excited at 500 nm. The linear relationship of **3c** between emission intensity and viscosity(η) (bottom).

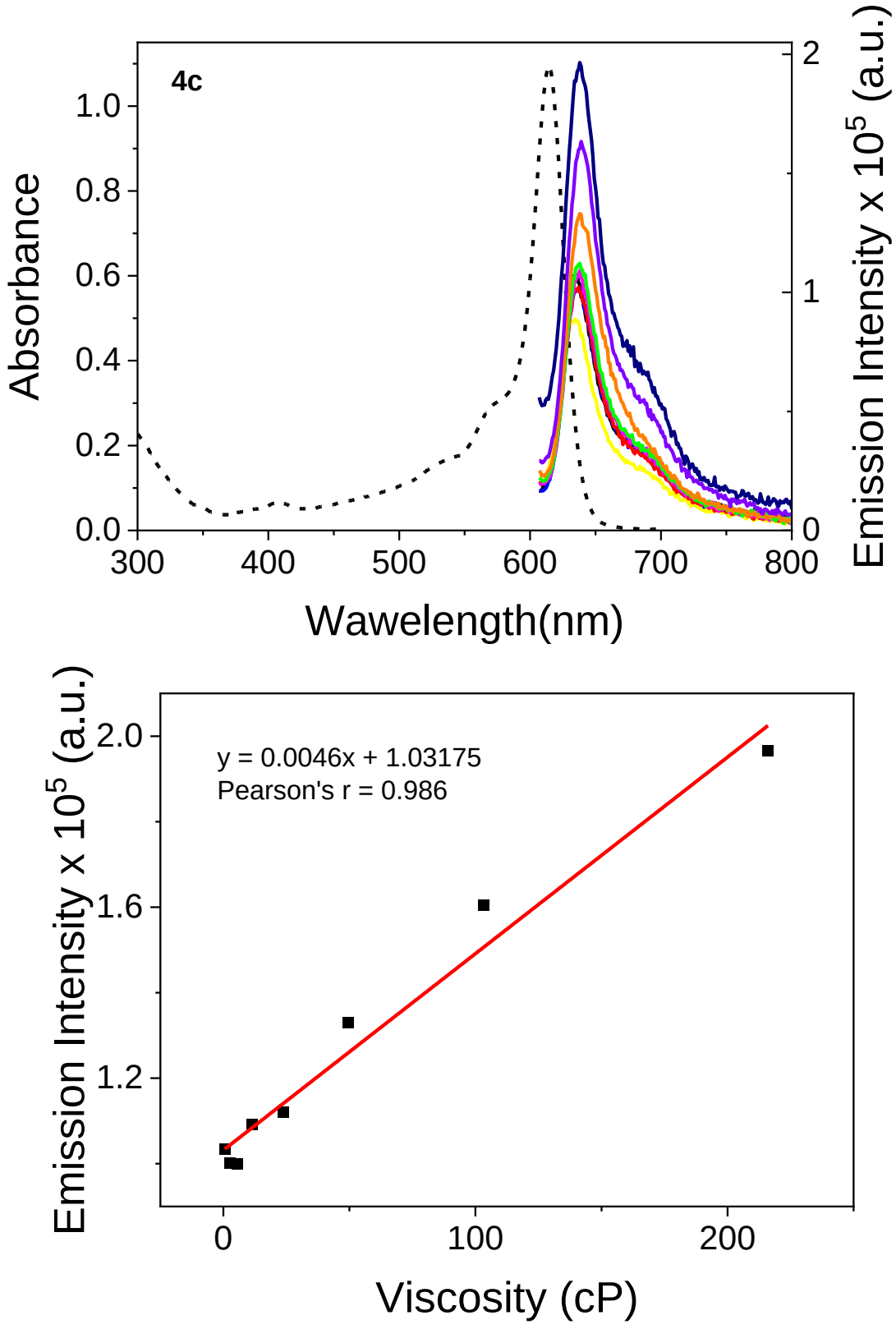


Figure S14. Fluorescence spectra of **4c** (1.0×10^{-5} M) in methanol/glycerol with different viscosities (top). Mixtures were excited at 580 nm. The linear relationship of **4c** between emission intensity and viscosity(η) (bottom).

5. Electrochemical Data

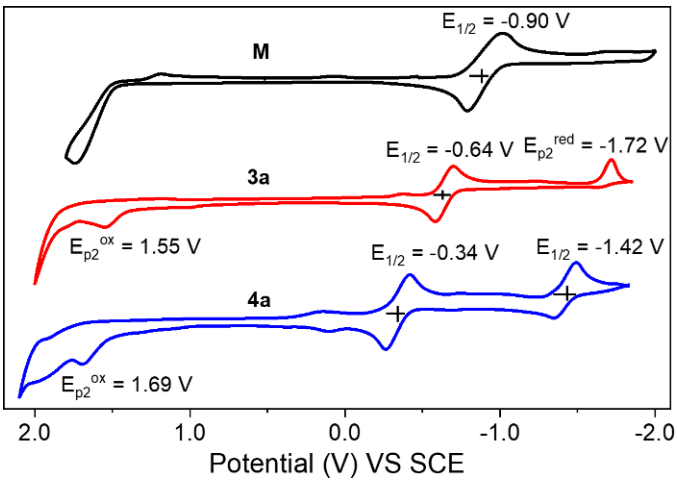
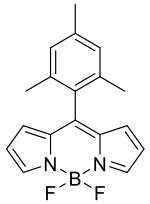
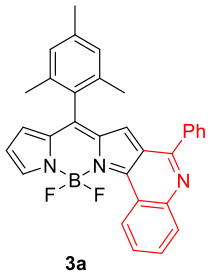


Figure S15. Cyclic voltammograms of 1 mM **M**/**3a**/**4a** in dichloromethane.

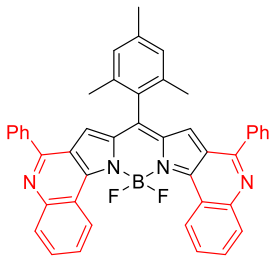
Table S5. Electrochemical data acquired at 100 mV s^{-1}, and HOMO-LUMO gaps determined from spectroscopy of dyes **M**, **3a** and **4a**.



M



3a



4a

dyes	$E^{o}_{B/B^{-\cdot}}$ (V)	E_{p2}^{red} (V)	E_{p2}^{OX} (V)	E_{red}^{onset} (V)	$E^{o}_{B^{+\cdot}/B}$ (V)	E_{ox}^{onset} (V)	LUMO (eV)	HOMO (eV)	E_g^{e} (eV)	E_g^{o} (eV)
M	-0.90	\	\	-0.80	\	1.56	-2.60	-5.96	2.36	2.38
3a	-0.64	-1.72	1.55	-0.55	\	1.41	-3.78	-5.89	1.96	2.17
4a	-0.34/ -1.42	\	1.69	-0.28	\	1.57	-4.12	-5.97	1.85	1.91

[a] E_{p2}^{red} = irreversible reduction peak potentials; E_{p2}^{OX} = irreversible oxidation peak potentials; $E^{o}_{B/B^{-\cdot}}$ = reversible reduction potential; $E^{o}_{B^{+\cdot}/B}$ = reversible oxidation potential; E_{red}^{onset} = the onset reduction potentials; E_{ox}^{onset} = the onset oxidation potentials; E_{LUMO} = -e(E_{red}^{onset} + 4.4); E_{HOMO} = -e(E_{ox}^{onset} + 4.4); E_g^{e} = bandgap, obtained from the intercept of the electrochemical data; E_g^{e} = E_{LUMO} - E_{HOMO}; E_g^{o} = bandgap, obtained from the intercept of the absorption spectra.

6. Reactive Oxygen Species (ROS) Formation

6.1 Reactive oxygen species (ROS) yields

A comparative study of the relative singlet oxygen generating efficiency of these dyes (5×10^{-6} M) was performed in air-saturated solvents under light at 532 nm irradiation (10 mW/cm^2) condition using 1,3 diphenylisobenzofuran (DPBF, 4×10^{-5} M) as a trap molecule.[8] A well-known photosensitizer against Rose Bengal (**RB**) sodium salt (1×10^{-5} M, Φ_Δ= 0.8 in methanol) was used as reference. The decrease of the absorbance band of DPBF at 415 nm was monitored. Singlet oxygen quantum yield (Φ_Δ) determinations were carried out using the chemical trapping method. The Φ_Δ value was obtained by the relative method the following equation:

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

Where $\Phi_{\Delta ref}$ and $\Phi_{\Delta sam}$ are the singlet oxygen quantum yields for the standard **RB** and the photosensitizer (**3a-c** and **4a-c**). m_{sam} and m_{ref} are the slope of the difference (ΔOD) in the change in the absorption maximum wavelength of DPBF (around 415 nm), which are plotted against the photoirradiation time, L_{ref} and L_{sam} are the light harvesting efficiency, which is given by $L = 1\text{-}10^{-A}$ ("A" is the absorbance at the photoirradiation 532 nm).

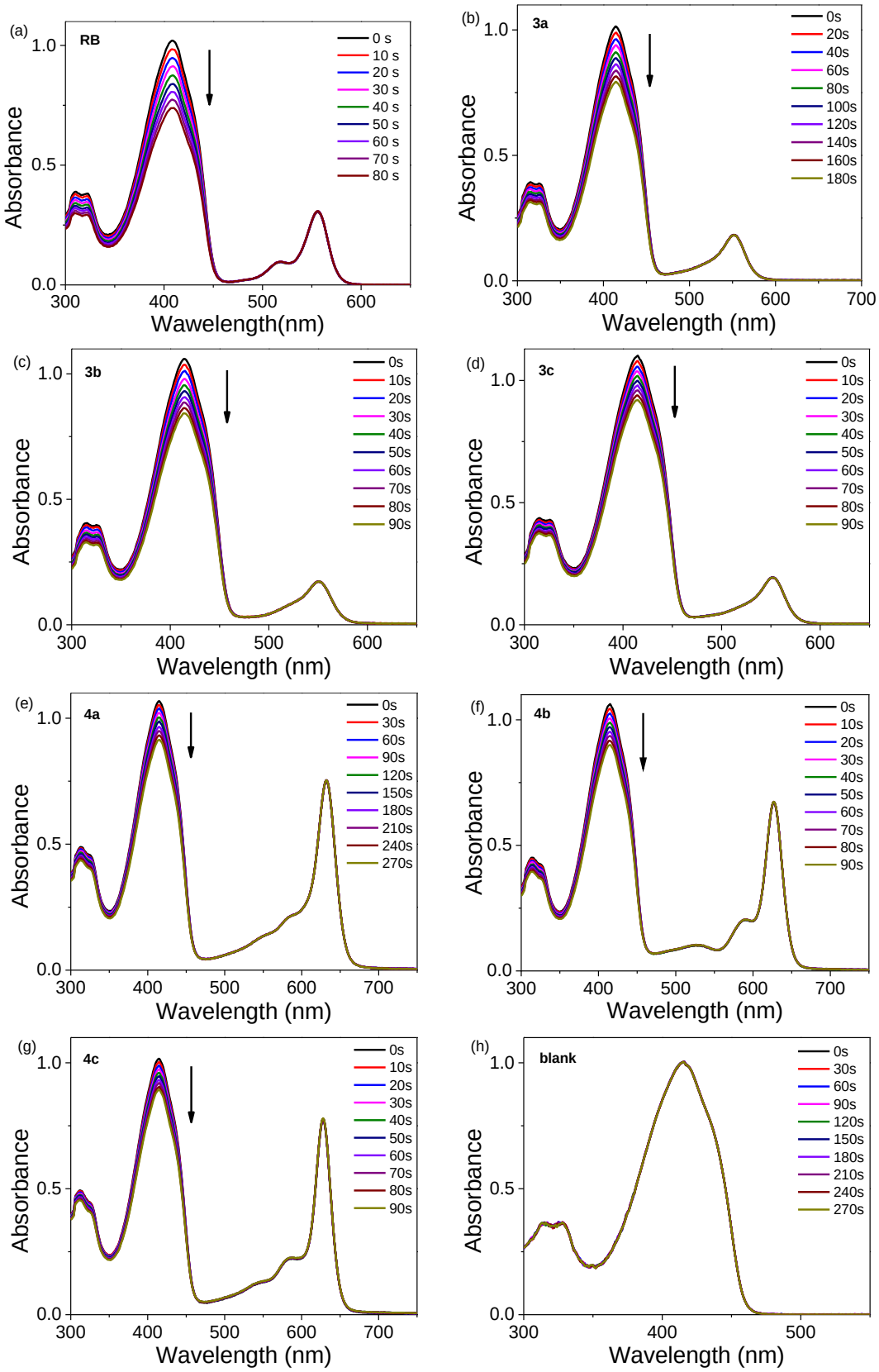


Figure S16. Absorption spectra of DPBF upon irradiation in the presence of **RB**, BODIPYs **3a-c** and **4a-c** in toluene with initial absorbance around 0.1 at 532 nm.

6.2 Reactive oxygen species trapping by EPR

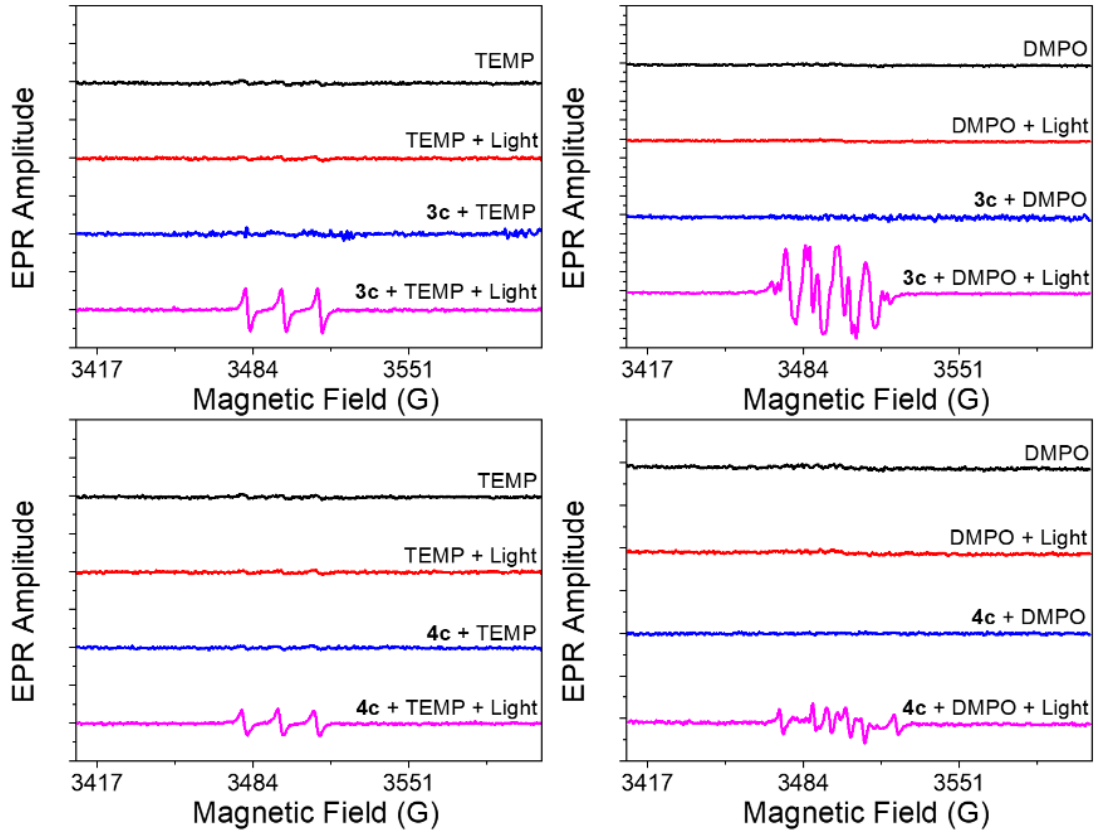


Figure S17. EPR spectra of **3c** and **4c** (0.3 mM in toluene) for $^1O_2$ characterization with 2,2,6,6-Tetramethyl-4-Piperidone (TEMP, 50 mM) or 5,5-dimethyl-1-pyrroline-N-oxide (DMPO, 200 mM) for $O_2^{\bullet-}$ characterization as the spin-trap agent in different conditions. Laser: 532 nm, irradiation time: 2 min.

7. DFT Calculations

The ground state geometry was optimized by using DFT method at B3LYP/6-31G(d) level. The same method was used for vibrational analysis to verify that the optimized structures correspond to local minima on the energy surface. TD-DFT computations were used the optimized ground state geometries under the B3LYP/6-31+G (d, p) theoretical level. The calculated molecules in dichloromethane were done using the Self-Consistent Reaction Field (SCRF) method and Polarizable Continuum Model (PCM). The geometries of the lowest singlet (S1) excited states were also optimized at the TD-B3LYP/6-31G(d) level of theory. All of the calculations were carried out by the methods implemented in Gaussian 09 package.[9a] SOCs were computed using the quadratic-response TDDFT approach,[9b] i.e. QR-TD-DFT, as implemented in the Dalton

program[9c] at their S1 optimized geometries. The SOC operator makes use of a semi-empirical effective single-electron approximation.[9d] For the latter calculations the B3LYP functional in combination to the 6-31G(d) basis set was used.

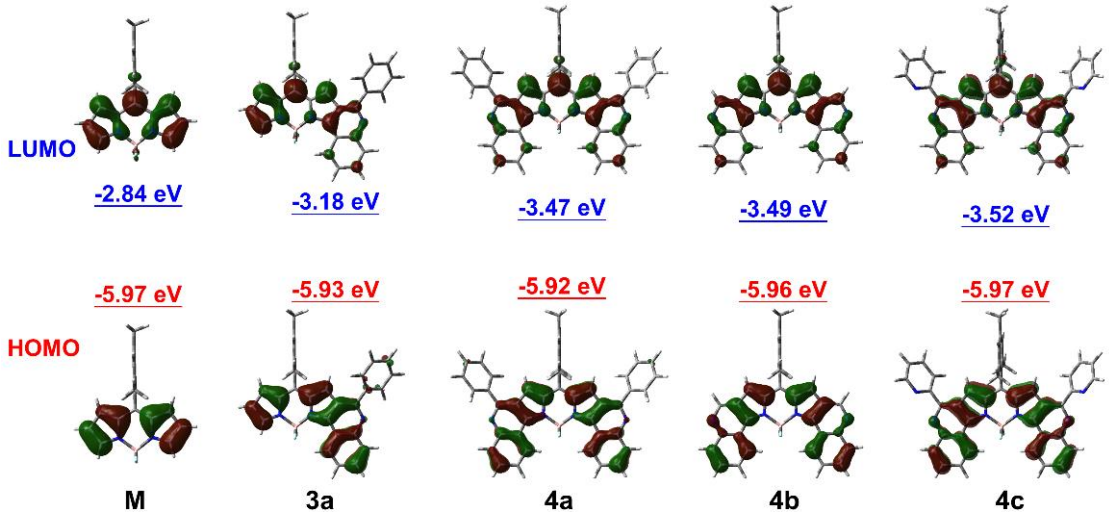


Figure S18. Pictorial presentation of LUMO, HOMO and their energy levels for **M**, **3a, 4a, 4b** and **4c** obtained from DFT calculations. (B3LYP/6-31G(d) level).

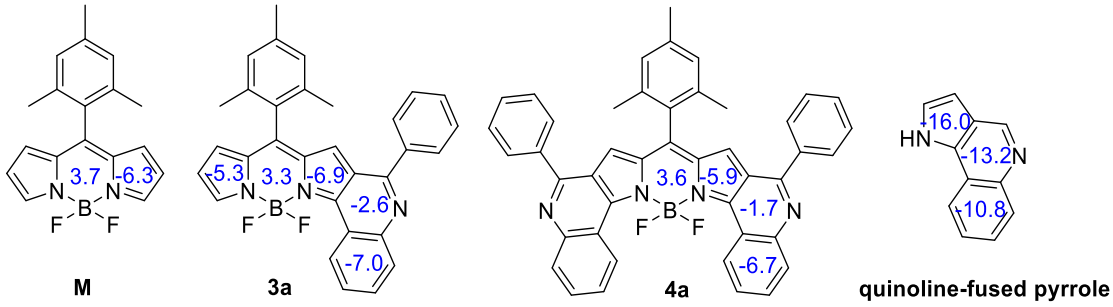


Figure S19. NICS(0) values (ppm) for BODIPY **M**, **3a**, **4a** and quinoline-fused pyrrole, calculated at the B3LYP/6-31+G(d,p)//B3LYP/6- 31G(d) level.

Table S6. Selected electronic excitation energies (eV) and oscillator strengths (*f*), configurations of the low-lying singlet excited states of **3a, 4a, 4b** and **4c** calculated by TDDFT//B3LYP/6–31+G (d, p), based on the optimized ground state geometries.

Dyes	Electronic transition	TD//B3LYP/6-31+G(d, p)			
		Energy/ eV [a]	*f* [b]	Composition [c]	CI [d]
3a	S0→S1	2.3798 eV 520.98 nm	0.0316	HOMO -1 → LUMO	0.6971
	S0→S2	2.5332 eV 489.43 nm	0.7790	HOMO → LUMO	0.6971
	S0→S3	2.6215 eV 472.95 nm	0.0003	HOMO -2 → LUMO	0.7022
4a	S0→S1	2.1452 eV 577.96 nm	0.1364	HOMO -1 → LUMO	0.6538
				HOMO → LUMO	0.2635
	S0→S2	2.1926 eV 565.48 nm	0.9514	HOMO -1 → LUMO	0.2606
				HOMO → LUMO	0.6544
	S0→S3	2.2225 eV 557.86 nm	0.0411	HOMO -2 → LUMO	0.7044
3b	S0→S1	2.5050 eV 494.95 nm	0.3917	HOMO -1 → LUMO	0.4177
				HOMO → LUMO	0.5676
	S0→S2	2.6147 eV 474.18 nm	0.0010	HOMO -2 → LUMO	0.7035
	S0→S3	2.6624 eV 465.68 nm	0.3685	HOMO -1 → LUMO	0.5615
				HOMO → LUMO	0.4195
4b	S0→S1	2.2067 eV 561.85 nm	0.6278	HOMO -1 → LUMO	0.2952
				HOMO → LUMO	0.6429
	S0→S2	2.3873 eV 519.35 nm	0.0000	HOMO -3 → LUMO	0.7049
	S0→S3	2.3930 eV 518.11 nm	0.2811	HOMO -1 → LUMO	0.6384
				HOMO → LUMO	0.2975
3c	S0→S1	2.4537 eV 505.30 nm	0.1177	HOMO -1 → LUMO	0.6270
				HOMO → LUMO	0.3170
	S0→S2	2.5609 eV 484.14 nm	0.6866	HOMO -1 → LUMO	0.3170
				HOMO → LUMO	0.6289
	S0→S3	2.6112 eV 474.81 nm	0.0004	HOMO -3 → LUMO	0.7006
4c	S0→S1	2.1753 eV 569.96 nm	0.6080	HOMO -1 → LUMO	0.3852
				HOMO → LUMO	0.5906
	S0→S2	2.2500 eV 551.04 nm	0.4526	HOMO -1 → LUMO	0.5890
				HOMO → LUMO	0.3872
	S0→S3	2.3271 eV 532.78 nm	0.0447	HOMO -2 → LUMO	0.7027

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

Table S7. Selected electronic excitation energies (eV) and oscillator strengths (*f*), configurations of the low-lying triplet excited states of **3c** and **4c** calculated by TDDFT//B3LYP/6–31+G (d, p), based on the optimized ground state geometries.

	Electronic transition	TD//B3LYP/6-31+G(d, p)			
		Energy/ eV [a]	*f* [b]	Composition [c]	CI [d]
3c	S0→T1	1.4909 eV 831.62 nm	0.0000	HOMO -1 → LUMO	0.1284
				HOMO → LUMO	0.6820
	S0→T2	2.1244 eV 583.62 nm	0.0000	HOMO -5 → LUMO	0.1352
				HOMO -1 → LUMO	0.6609
				HOMO → LUMO	0.1369
	S0→T3	2.5905 eV 478.62 nm	0.0000	HOMO -2 → LUMO	0.7000
4c	S0→T1	1.3166 eV 941.68 nm	0.0000	HOMO -1 → LUMO	0.1456
				HOMO → LUMO	0.6833
	S0→T2	1.8922 eV 655.22 nm	0.0000	HOMO -1 → LUMO	0.6654
				HOMO → LUMO	0.1615
	S0→T3	1.9764 eV 627.31 nm	0.0000	HOMO -2 → LUMO	0.6671

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

Table S8. Lowest vertical singlet and triplet electronic transition energies (in eV) and oscillator strengths (in parentheses) of **3c** and **4c** at the TD-B3LYP levels, along with vertical singlet-triplet splittings (in eV) and SOCs between the involved S1 and T1 states (in cm^{-1}).

Dyes	state/assignment[a]	TD-B3LYP	ΔE_{S1-T1}	$\langle S_1\|\hat{H}_{SO}\|T_n\rangle$[b]
3c	S_1 (H -1→L, c = 0.32; H→L, c = 0.63)	2.454 (0.1177)	-	–
	T_1(H -1→L, c = 0.13; H→L, c = 0.68)	1.491	0.963	0.36
	T_2 (H-5→L, c = 0.14; H-1→L, c = 0.66)	2.124	0.330	0.9
4c	S_1 (H -1→L, c = 0.33; H→L, c = 0.61)	2.180 (0.6104)	-	–
	T_1(H -1→L, c = 0.15; H→L, c = 0.68)	1.317	0.863	0.06
	T_2 (H -1→L, c = 0.67; H→L, c = 0.16)	1.892	0.288	0.01
	T_3 (H -2→L, c = 0.67)	1.976	0.204	1.6

[a]Only the first excited states are considered. [b]Values are shown as (x component; y component; z component) and were obtained at the QR-TD-DFT/6-31G* level of theory at the S1 optimized geometry.

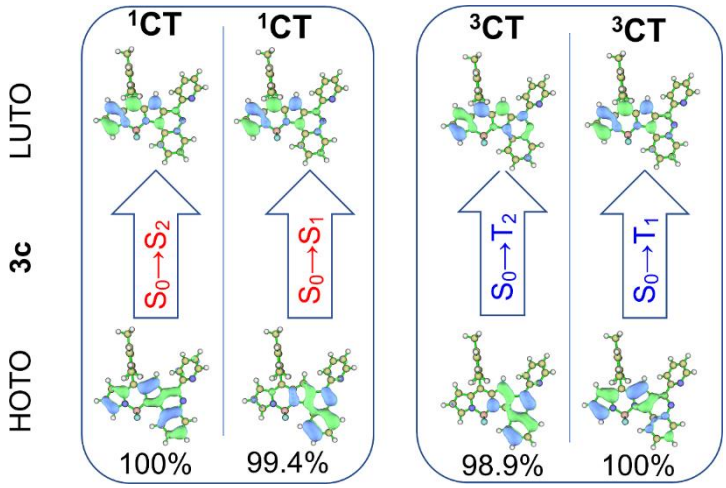


Figure S20. Calculated natural transition orbitals (NTOs) and ISC process of **3c**.

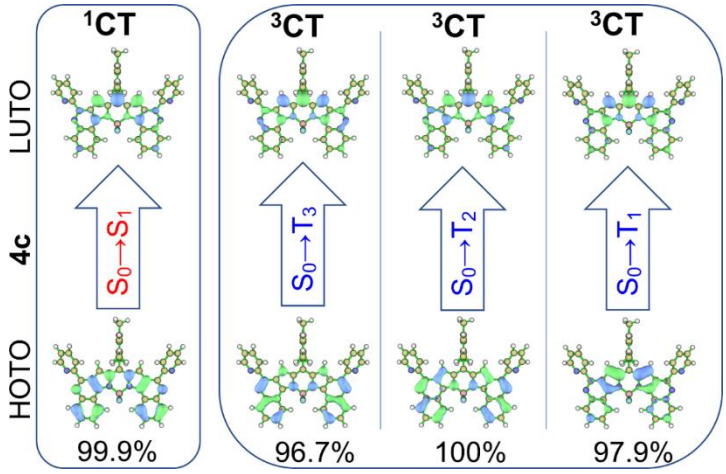


Figure S21. Calculated natural transition orbitals (NTOs) and ISC process of **4c**.

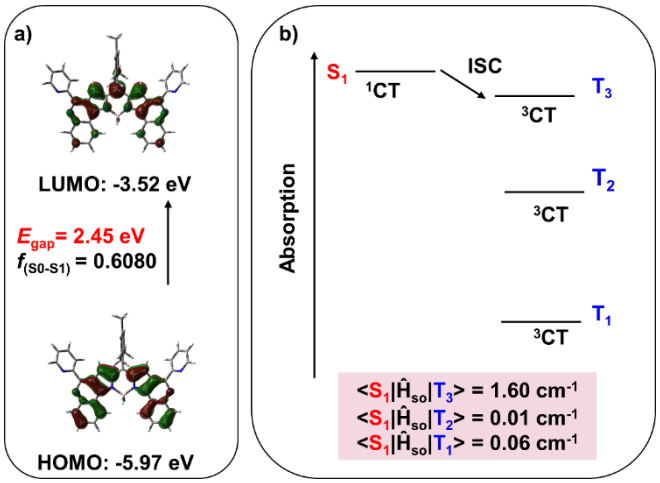


Figure S22. (a) Calculated HOMO and LUMO distributions, energy level gaps, oscillator strengths for **4c**. (b) Excited state energies and associated SOC matrix elements for **4c**.

DFT optimized coordinates for **M** optimized S_0 state Geometry by B3LYP/6-31G(d).

F	3.29520000	10.38290000	2.35720000
F	3.05010000	9.75910000	4.51200000
N	4.52070000	8.47900000	3.12680000
N	5.15710000	10.77120000	3.85890000
C	3.81980000	7.37700000	2.88440000
H	2.89460000	7.31330000	2.94960000
C	4.66880000	6.32190000	2.51620000
H	4.41320000	5.45270000	2.30660000
C	5.94020000	6.81420000	2.52480000
H	6.71480000	6.34480000	2.31170000
C	5.86330000	8.17270000	2.91660000
C	6.84370000	9.10100000	3.18390000
C	6.48330000	10.36710000	3.71310000
C	7.33260000	11.32300000	4.26270000
H	8.26170000	11.29480000	4.28090000
C	6.51460000	12.33780000	4.78550000
C	5.18170000	11.98490000	4.48600000
C	8.28420000	8.77620000	2.95740000
C	9.03740000	8.17010000	3.96970000
C	10.37680000	7.90560000	3.71850000
H	10.88070000	7.49410000	4.38340000
C	10.99450000	8.22700000	2.52260000
C	10.22010000	8.79640000	1.55010000
H	10.61610000	9.00840000	0.73590000
C	8.86270000	9.07600000	1.72080000
C	8.43200000	7.81930000	5.29750000
H	7.98710000	8.58830000	5.66000000
H	9.12400000	7.53590000	5.89990000
H	7.79780000	7.10730000	5.18210000
C	12.48240000	7.98090000	2.33160000
H	12.95230000	8.81730000	2.37520000
H	12.63200000	7.57380000	1.47590000
H	12.80180000	7.39840000	3.02450000
C	8.06100000	9.63950000	0.59040000
H	7.17900000	9.26010000	0.60350000
H	8.48820000	9.42700000	-0.24250000
H	8.00040000	10.59290000	0.68500000
B	3.94540000	9.88140000	3.47910000
H	6.83993685	13.21151932	5.31054332
H	4.32090563	12.57770595	4.71515968

SCF done: -1030.39132505 a.u.

No imaginary Frequency.

DFT optimized coordinates for **3a** optimized S_0 state Geometry by B3LYP/6-31G(d).

F	0.90697700	-3.69810400	1.06824400
F	0.87079100	-3.52263100	-1.21232800
N	-1.19725300	-3.26125200	0.00622700
N	0.57467900	-1.48684200	0.07991800
N	3.77870400	1.18336200	-0.04131300
C	-1.81348500	-4.44978800	0.01767500
H	-1.24420100	-5.36980100	0.03353600
C	-3.21812800	-4.27741200	0.00500700
H	-3.94899200	-5.07394500	0.01254300
C	-3.45253100	-2.91314500	-0.01486300
H	-4.40625500	-2.40402400	-0.02403500
C	-2.18064800	-2.27050700	-0.01226200
C	-1.83248500	-0.92397400	-0.00550200
C	-0.46835700	-0.55222900	0.03610500
C	0.06043900	0.74590100	0.03069700
H	-0.52599600	1.65041100	-0.02237400
C	1.45487600	0.61894100	0.07453600
C	1.74627300	-0.78283800	0.09467400
C	3.11450500	-1.21693200	0.08366200
C	4.08228600	-0.16289500	-0.02351100
C	5.45368500	-0.49685700	-0.09304600
H	6.16358400	0.31985300	-0.17913800
C	5.87085500	-1.81390000	-0.04294600
H	6.92946400	-2.05219900	-0.09640100
C	4.92237700	-2.84524100	0.09317100
H	5.25095800	-3.87880200	0.15399800
C	3.57113000	-2.55480000	0.15799800
H	2.86031400	-3.35637700	0.29418100
C	2.52862800	1.57717500	0.03556300
C	1.06791100	4.99688900	0.84718500
H	0.28369900	5.42306000	1.46679600
C	1.26154300	3.61472700	0.83333300
H	0.64221200	2.98325700	1.46212800
C	2.27885400	3.04301800	0.05120300
C	3.10484400	3.89185400	-0.70545400
H	3.89879000	3.45286900	-1.30060900
C	2.90489500	5.27034500	-0.69745200
H	3.54550700	5.91125300	-1.29719500
C	1.88346900	5.82836100	0.07747100
H	1.72869100	6.90380100	0.08471900
C	-2.89311900	0.13045700	-0.03843500
C	-3.36869400	0.60398500	-1.27938600
C	-4.36516000	1.58598900	-1.28334800

H	-4.73362000	1.95122500	-2.23948100
C	-4.89810300	2.10713400	-0.10080000
C	-4.41193000	1.61409800	1.11433200
H	-4.81828600	2.00041800	2.04669400
C	-3.41601500	0.63415700	1.17202100
C	-2.82797100	0.07403800	-2.58901200
H	-1.74649700	0.23230800	-2.67359500
H	-3.30711700	0.57351000	-3.43564700
H	-3.00158800	-1.00347300	-2.69235700
C	-5.95178100	3.18924900	-0.13290500
H	-5.49617100	4.18534500	-0.05583900
H	-6.65356100	3.08972300	0.70193600
H	-6.52317900	3.16377000	-1.06629200
C	-2.92920300	0.13268000	2.51365100
H	-3.10880700	-0.94222900	2.63333900
H	-3.44141800	0.65078600	3.32913600
H	-1.85170400	0.29114800	2.63855900
B	0.34751600	-3.03060400	-0.02157000

SCF done: -1584.78191625 a.u.
No imaginary Frequency.

DFT optimized coordinates for **3b** optimized S_0 state Geometry by B3LYP/6-31G(d).

F	2.01676100	2.35723900	-1.07569600
F	1.94617400	2.27052800	1.20736400
N	-0.12422100	2.54475000	-0.00174200
N	1.09858100	0.35596700	-0.02528100
N	3.44651500	-3.11089400	0.04223300
C	-0.39584000	3.85544400	-0.01554300
H	0.40124900	4.58722200	-0.01648500
C	-1.79487200	4.06991500	-0.02740200
H	-2.28237600	5.03468300	-0.04073000
C	-2.38992500	2.82025300	-0.02085300
H	-3.44578300	2.58798600	-0.02912500
C	-1.33960100	1.85692600	-0.00575600
C	-1.37181300	0.46668400	-0.00688200
C	-0.16043000	-0.26430600	-0.01194300
C	-0.00197500	-1.65781900	0.00089000
H	-0.80399000	-2.38246700	0.01280400
C	1.37566900	-1.90221500	0.00034000
C	2.03757700	-0.63684100	-0.01952500
C	3.47471000	-0.60837200	-0.02420900
C	4.11479600	-1.89457400	0.01803900
C	5.52488600	-1.95710900	0.03267200
H	5.98142800	-2.94136900	0.06770800

C	6.29239200	-0.80693900	0.00050500
H	7.37656200	-0.87491100	0.01227400
C	5.66572200	0.45166800	-0.05513500
H	6.26749200	1.35525600	-0.09144900
C	4.28566300	0.55132200	-0.06905600
H	3.82486200	1.52585100	-0.13412700
C	2.14154300	-3.10287900	0.02772000
C	-2.68046700	-0.25785700	-0.00498900
C	-3.30333900	-0.57168500	1.22174400
C	-4.53123400	-1.24109100	1.19636300
H	-5.01397100	-1.48157600	2.14119100
C	-5.15256600	-1.60636300	-0.00179600
C	-4.51409400	-1.27827500	-1.20168700
H	-4.98386800	-1.54705000	-2.14541000
C	-3.28526400	-0.61067000	-1.23014700
C	-2.67545700	-0.19853600	2.54641400
H	-1.68119200	-0.64558900	2.66268500
H	-3.29638600	-0.54078700	3.37893800
H	-2.55082800	0.88625000	2.64411700
C	-6.46371400	-2.35667600	0.00053000
H	-6.29661800	-3.44175300	0.02225000
H	-7.05212700	-2.13712200	-0.89630400
H	-7.06786100	-2.10420900	0.87806000
C	-2.63887500	-0.27742100	-2.55654600
H	-2.49025200	0.80235400	-2.67449900
H	-3.26000400	-0.62318800	-3.38745700
H	-1.65351500	-0.74774300	-2.65525300
B	1.30023600	1.90415400	0.03079600
H	1.63251000	-4.06678500	0.04287500

SCF done: -1353.72213627 a.u.
No imaginary Frequency.

DFT optimized coordinates for **3c** optimized S_0 state Geometry by B3LYP/6-31G(d).

F	0.98320400	-3.66920600	-1.06192900
F	0.94309600	-3.50211900	1.21887000
N	0.60967400	-1.46821000	-0.06722300
N	-1.12948800	-3.27474300	0.00132700
C	1.76854100	-0.74348000	-0.07832400
C	1.45103100	0.65172900	-0.05711100
C	0.05410400	0.75530000	-0.02306500
H	-0.54755400	1.65077900	0.02065200
C	-0.45022800	-0.55222100	-0.02974200
C	-1.80801800	-0.94957000	0.00613400
C	-2.13091800	-2.30174500	0.01425900

C	-3.39122800	-2.96773400	0.01448000
H	-4.35405700	-2.47600700	0.01969600
C	-3.13203600	-4.32709600	-0.00113200
C	-1.72398800	-4.47394600	-0.00891100
C	-2.88861200	0.08448600	0.03221800
C	-3.37568600	0.55448500	1.27103100
C	-4.38587100	1.52121400	1.26895300
H	-4.75824700	1.88860700	2.22286200
C	-4.92642200	2.02746300	0.08239900
C	-4.42322100	1.54471300	-1.12899900
H	-4.82555500	1.92906500	-2.06379300
C	-3.41232300	0.57874600	-1.18076200
C	-2.82668800	0.04034200	2.58347900
H	-2.98430900	-1.03908500	2.69257400
H	-3.31357200	0.53691600	3.42737700
H	-1.74772000	0.21505600	2.66737200
C	-6.03862500	3.04940900	0.11223300
H	-7.01600900	2.56475900	0.23674000
H	-6.07684600	3.62709700	-0.81675700
H	-5.91712500	3.74872400	0.94634500
C	-2.90730200	0.08838600	-2.51974800
H	-1.83138500	0.26304900	-2.63628400
H	-3.42122600	0.60045600	-3.33797700
H	-3.07012100	-0.98879300	-2.64321500
B	0.41101700	-3.01629000	0.02982700
C	3.14572800	-1.14825700	-0.07450900
C	3.62919500	-2.47667300	-0.14898900
C	4.09371600	-0.07413900	0.01831700
C	4.98705900	-2.73825100	-0.10171000
H	2.93397900	-3.29400600	-0.27145800
C	5.47258700	-0.37909700	0.06828100
C	5.91625500	-1.68731500	0.01624800
H	5.33601400	-3.76512700	-0.16221600
H	6.16584800	0.45280500	0.14328300
H	6.98009100	-1.90382400	0.05550600
C	2.50623400	1.62586600	-0.01542800
N	3.76437500	1.26683200	0.04455300
C	2.20918500	3.09122700	-0.03092200
C	1.25690800	3.62391400	-0.91229100
C	2.69120300	5.17830800	0.79997500
C	1.03401200	5.00022400	-0.91640900
H	0.72218500	2.97600500	-1.59858700
C	1.76225200	5.79964100	-0.03829500
H	3.27871500	5.77109400	1.49932300

H	0.30954000	5.43707800	-1.59765400
H	1.62204600	6.87534400	-0.00142200
N	2.92239900	3.86159400	0.81212200
H	-3.84808000	-5.13692800	-0.00863800
H	-1.13817700	-5.38356600	-0.02072500

SCF done: -1600.81703571 a.u.
No imaginary Frequency.

DFT optimized coordinates for **3c** optimized S_1 state Geometry by B3LYP/6-31G(d).

C	1.73220700	-0.76533500	-0.05108900
C	1.46494400	0.63275600	0.00060800
C	0.03687800	0.78070900	0.02732400
C	-0.49971700	-0.48997300	-0.01740800
C	-1.87991600	-0.88733900	-0.00072600
C	-2.19965900	-2.24851000	-0.02812100
C	-3.45557700	-2.91231800	-0.04500000
C	-3.19739600	-4.28660000	-0.08645200
C	-1.80757600	-4.44623500	-0.09385400
C	-2.94581400	0.15743100	0.04699200
C	-3.45229000	0.59635300	1.28959100
C	-4.44822200	1.57975400	1.31177400
C	-4.96103500	2.13942200	0.13786300
C	-4.44475100	1.69305200	-1.08299300
C	-3.44911000	0.71243100	-1.15039600
C	-2.93405800	0.02155700	2.58928900
C	-6.05896400	3.17711100	0.18452500
C	-2.93065100	0.25784100	-2.49671000
C	3.09104800	-1.22799500	-0.05095600
C	3.53901900	-2.54923900	-0.16099000
C	4.09371800	-0.17975000	0.09730000
C	4.90445300	-2.85253900	-0.09305100
C	5.48911600	-0.54263900	0.17835900
C	5.88606700	-1.85161400	0.08816700
C	2.52975600	1.54205900	0.04276400
C	2.34729500	3.00938700	-0.03508900
C	1.34803700	3.57243100	-0.84764700
C	3.06540200	5.08514700	0.63321700
C	1.22489500	4.95943700	-0.89992600
C	2.09384300	5.73662200	-0.13868500
F	0.91380400	-3.60184900	-1.13654400
F	0.87910100	-3.51089900	1.14455300
H	3.76302800	5.66487700	1.23472500
H	0.46971700	5.42017300	-1.52919600
H	2.03730000	6.82030400	-0.14513400

H	0.70648700	2.93727700	-1.44701700
H	-3.92324700	-5.08847200	-0.11156800
H	-1.21933700	-5.35283600	-0.12274900
H	-0.52986900	1.69486600	0.11205200
H	5.21080700	-3.89018100	-0.18323200
H	6.19698200	0.27017200	0.29982400
H	6.93519400	-2.12117000	0.14371600
H	2.83136100	-3.34911500	-0.31948900
H	-1.85255100	0.43296400	-2.59389400
H	-3.43421500	0.79033500	-3.30930300
H	-3.09076700	-0.81658500	-2.64424200
H	-7.04885400	2.71229900	0.08317200
H	-5.95979400	3.90340100	-0.62953300
H	-6.05293600	3.72413600	1.13306400
H	-3.12427800	-1.05614400	2.65433500
H	-3.41371700	0.50206700	3.44745500
H	-1.85051000	0.15791400	2.68604600
H	-4.82694900	2.11783300	-2.00945900
H	-4.83174300	1.91674100	2.27297500
H	-4.41765900	-2.41956000	-0.03378800
B	0.31167700	-2.99301200	-0.02386200
N	0.54839900	-1.43947400	-0.06946900
N	-1.20281300	-3.22645300	-0.05808300
N	3.82348000	1.12284500	0.15376200
N	3.20798900	3.76136900	0.68327600

SCF done: -1600.73664031 a.u.
No imaginary Frequency.

DFT optimized coordinates for **4a** optimized S_0 state Geometry by B3LYP/6-31G(d).

F	0.00144700	-2.81024600	-1.23780800
F	0.00171100	-2.80277600	1.05427000
N	1.26959500	-1.09302900	-0.10093100
N	-1.26801000	-1.09422300	-0.10076400
N	-5.41575100	-1.52711000	0.08758700
C	2.58860300	-1.44466400	-0.09321400
C	3.39276300	-0.25458500	-0.05220800
C	2.51747000	0.83083000	-0.01512700
H	2.75690100	1.88099800	0.05265000
C	1.21306900	0.30329500	-0.04924700
C	-0.00019800	1.00528900	-0.02368700
C	-1.21280700	0.30217000	-0.04970100
C	-2.51770900	0.82851200	-0.01645500
H	-2.75811900	1.87849700	0.05052500
C	-3.39197600	-0.25774200	-0.05314600

C	-2.58668900	-1.44708500	-0.09329000
C	-3.23325400	-2.72951600	-0.07461900
C	-4.66225300	-2.68477800	0.05537400
C	-5.38191800	-3.89693400	0.13352700
H	-6.46047100	-3.83237600	0.23647900
C	-4.73408000	-5.11739600	0.07130900
H	-5.30426200	-6.04005900	0.13169900
C	-3.33645600	-5.16142800	-0.08365000
H	-2.82822000	-6.11893800	-0.15049300
C	-2.59938600	-3.99243800	-0.15679700
H	-1.53115000	-4.04776200	-0.29772100
C	-4.82915400	-0.35758000	0.00632900
C	-0.00129500	2.50027800	0.03299700
C	-0.00391800	3.15362900	1.28396700
C	-0.00191500	4.55215100	1.30757000
H	-0.00044200	5.05749800	2.27090700
C	-0.00016700	5.31440200	0.13546100
C	0.00675200	4.63964400	-1.08924300
H	0.01512100	5.21388000	-2.01321400
C	0.00475800	3.24333200	-1.16701100
C	-0.00466800	2.37822000	2.58277700
H	-0.88566300	1.73136100	2.66755600
H	-0.00543600	3.05867700	3.43872900
H	0.87614800	1.73129400	2.66899200
C	-0.02995800	6.82377300	0.19037000
H	-1.06263300	7.19692100	0.19859100
H	0.46777500	7.26584600	-0.67886500
H	0.45852700	7.20092300	1.09471300
C	0.01277100	2.56410200	-2.51867400
H	0.89660700	1.92841300	-2.64771800
H	0.01243700	3.30416700	-3.32368200
H	-0.86471300	1.92095200	-2.65386600
B	0.00122200	-2.01099000	-0.09008900
C	3.23636900	-2.72649600	-0.07504600
C	2.60371900	-3.98997600	-0.15807800
C	4.66529900	-2.68048000	0.05527600
C	3.34187900	-5.15830800	-0.08539800
H	1.53557800	-4.04624000	-0.29937100
C	5.38609300	-3.89199900	0.13293100
C	4.73942400	-5.11304000	0.06991000
H	2.83456500	-6.11626100	-0.15290500
H	6.46456500	-3.82648400	0.23613800
H	5.31046800	-6.03519500	0.12991400
C	4.83002800	-0.35309700	0.00747400

N	5.41770400	-1.52212200	0.08821400
C	5.70247300	0.85027600	0.00674700
C	6.87400500	0.85175000	0.78309500
C	5.41366000	1.97685300	-0.78142200
C	7.72104300	1.95738500	0.78797700
H	7.10452000	-0.02280600	1.38252200
C	6.26863900	3.07994900	-0.78282800
H	4.53965900	1.97929700	-1.42479900
C	7.42027300	3.07709200	0.00629400
H	8.61701000	1.94711000	1.40266100
H	6.03697500	3.93809600	-1.40757900
H	8.08234300	3.93857700	0.00892100
C	-5.70272300	0.84498000	0.00490500
C	-5.41493800	1.97139300	-0.78387600
C	-6.87425700	0.84580100	0.78124900
C	-6.27094200	3.07369700	-0.78588400
H	-4.54093700	1.97428600	-1.42725500
C	-7.72230900	1.95066100	0.78554200
H	-7.10395900	-0.02864300	1.38115300
C	-7.42256900	3.07021700	0.00324700
H	-6.04009800	3.93170000	-1.41114000
H	-8.61826300	1.93989700	1.40023700
H	-8.08544100	3.93108700	0.00539900

SCF done: -2139.17028336 a.u.
No imaginary Frequency.

DFT optimized coordinates for **4b** optimized S_0 state Geometry by B3LYP/6-31G(d).

F	2.19989900	0.00809200	1.14429100
F	2.19979700	0.00303600	-1.14434500
N	0.48728300	-1.26602900	0.00203100
N	0.48097700	1.26869100	-0.00190700
N	0.87435700	5.43938100	0.00624000
C	0.84431400	-2.58298900	0.00119400
C	-0.34272600	-3.38590100	-0.00215000
C	-1.43681900	-2.52337900	-0.00236100
H	-2.48678700	-2.77992100	-0.00445000
C	-0.91302300	-1.21594200	0.00003900
C	-1.61823300	-0.00392300	0.00006500
C	-0.91907900	1.21159200	0.00009500
C	-1.44942000	2.51637600	0.00248500
H	-2.50067700	2.76759300	0.00458200
C	-0.35964900	3.38436600	0.00224000
C	0.83141000	2.58742100	-0.00109500
C	2.10486400	3.25578800	-0.00281700

C	2.04612500	4.69207500	0.00206200
C	3.24919000	5.42742600	0.00217600
H	3.17356800	6.51022000	0.00623700
C	4.47751300	4.78961100	-0.00312100
H	5.39388400	5.37288200	-0.00302700
C	4.53622800	3.38483600	-0.00936400
H	5.49913300	2.88244200	-0.01457500
C	3.37503300	2.63143700	-0.00931300
H	3.44304100	1.55455600	-0.01583500
C	-0.26522700	4.80786700	0.00567400
C	-3.11422300	-0.00762500	0.00003600
C	-3.81256800	-0.00987300	-1.22642500
C	-5.21085700	-0.01775700	-1.19926800
H	-5.75102000	-0.02342300	-2.14353700
C	-5.92985400	-0.02029400	-0.00006100
C	-5.21092700	-0.02174300	1.19917400
H	-5.75114800	-0.03045900	2.14338300
C	-3.81262300	-0.01413300	1.22643300
C	-3.08466000	-0.00827500	-2.55248000
H	-2.44343800	0.87422700	-2.66130800
H	-3.79540700	-0.00993500	-3.38346300
H	-2.43891200	-0.88745800	-2.66150700
C	-7.44033000	0.00263900	-0.00011800
H	-7.81823400	1.03361400	-0.00073200
H	-7.84803700	-0.49188700	0.88752400
H	-7.84797000	-0.49283100	-0.88727900
C	-3.08479700	-0.01698100	2.55253000
H	-2.44078300	-0.89767900	2.65957500
H	-3.79559600	-0.01919300	3.38346700
H	-2.44185200	0.86400900	2.66342300
B	1.40187300	0.00361500	0.00000400
H	-1.17532300	5.40756100	0.00842400
C	2.12108900	-3.24498200	0.00286300
C	3.38808500	-2.61426100	0.00943500
C	2.06954000	-4.68153700	-0.00214200
C	4.55305400	-3.36180900	0.00939200
H	3.45056100	-1.53704700	0.01612300
C	3.27627200	-5.41082600	-0.00235400
C	4.50138100	-4.76686400	0.00298600
H	5.51342500	-2.85459000	0.01466500
H	3.20601800	-6.49396600	-0.00652300
H	5.42066500	-5.34553400	0.00281500
C	-0.24118200	-4.80892100	-0.00568000
N	0.90154300	-5.43472600	-0.00634300

H	-1.14827500	-5.41314400	-0.00843600

SCF done: -1677.05083391 a.u.
No imaginary Frequency.

DFT optimized coordinates for **4c** optimized S_0 state Geometry by B3LYP/6-31G(d).

F	0.00096800	-2.80981600	-1.24367500
F	0.00130100	-2.80857900	1.04748500
N	1.26923500	-1.09523000	-0.10106800
N	-1.26817200	-1.09614400	-0.10081900
N	-5.42031800	-1.52248600	0.10117600
C	2.58774600	-1.44719000	-0.08220800
C	3.39067900	-0.25725400	-0.03908000
C	2.51714600	0.83002400	-0.02300200
H	2.75816000	1.88109600	0.03133300
C	1.21306500	0.30188400	-0.06253500
C	-0.00024600	1.00423300	-0.04662500
C	-1.21304600	0.30102500	-0.06282000
C	-2.51752400	0.82822500	-0.02394700
H	-2.75928800	1.87915200	0.02971600
C	-3.39025100	-0.25970700	-0.03968500
C	-2.58642400	-1.44906500	-0.08211600
C	-3.23758200	-2.72922900	-0.06678300
C	-4.66791500	-2.68209800	0.05389100
C	-5.39173000	-3.89234700	0.11371300
H	-6.47063600	-3.82522500	0.21013000
C	-4.74662200	-5.11415400	0.04612000
H	-5.31958900	-6.03577800	0.09339100
C	-3.34774700	-5.16039400	-0.09462500
H	-2.84133900	-6.11875800	-0.16291000
C	-2.60631800	-3.99309800	-0.15133800
H	-1.53660900	-4.05086800	-0.27992600
C	-4.82354000	-0.36102000	0.03535700
C	-0.00103000	2.49968700	-0.00677200
C	-0.00236300	3.16728600	1.23673200
C	0.00048200	4.56597600	1.24391500
H	0.00306600	5.08251200	2.20127600
C	0.00176400	5.31459300	0.06301500
C	0.00716900	4.62574600	-1.15382400
H	0.01509400	5.18927900	-2.08437000
C	0.00437100	3.22860800	-1.21539400
C	-0.00263500	2.40706400	2.54447100
H	-0.88374500	1.76151200	2.63737200
H	-0.00277000	3.09742700	3.39243000
H	0.87801000	1.76095100	2.63791900

C	-0.02672200	6.82451100	0.10064300
H	-1.05907100	7.19847900	0.11120000
H	0.46579900	7.25613200	-0.77675800
H	0.46764200	7.21172500	0.99750600
C	0.01101900	2.53361100	-2.55904300
H	0.89420900	1.89567100	-2.68129300
H	0.01082800	3.26425700	-3.37260600
H	-0.86703500	1.88961800	-2.68634700
B	0.00086500	-2.01373100	-0.09438800
C	3.23985900	-2.72687300	-0.06730500
C	2.60957000	-3.99118000	-0.15261400
C	4.67013500	-2.67872100	0.05366700
C	3.35187100	-5.15794200	-0.09628400
H	1.53994300	-4.04969900	-0.28157800
C	5.39485200	-3.88845200	0.11308100
C	4.75067900	-5.11071400	0.04479400
H	2.84620400	-6.11665600	-0.16516100
H	6.47369200	-3.82056700	0.20973100
H	5.32433200	-6.03192700	0.09174900
C	4.82403500	-0.35751400	0.03615000
N	5.42166200	-1.51856700	0.10156900
C	5.68395000	0.86523900	0.05259300
C	5.45310000	1.91952800	-0.84259700
C	7.49511400	1.95052900	0.95656300
C	6.30072900	3.02622200	-0.81615100
H	4.64425900	1.86073700	-1.56313600
C	7.34438400	3.04881500	0.10607800
H	8.29921700	1.93359100	1.69044800
H	6.14968800	3.85006900	-1.50764800
H	8.02847600	3.88922800	0.16781500
C	-5.68438900	0.86108400	0.05114600
C	-5.45433400	1.91508100	-0.84459200
C	-6.30285700	3.02110600	-0.81877300
H	-4.64542000	1.85653800	-1.56507200
C	-7.49642000	1.94543500	0.95451000
C	-7.34655400	3.04337100	0.10341900
H	-6.15248300	3.84468300	-1.51074100
H	-8.30051800	1.92825800	1.68839400
H	-8.03133800	3.88325700	0.16466900
N	6.69662400	0.87830100	0.93956600
N	-6.69708100	0.87383000	0.938101000

SCF done: -2171.24031994 a.u.

No imaginary Frequency.

DFT optimized coordinates for **4c** optimized S_1 state Geometry by B3LYP/6-31G(d).

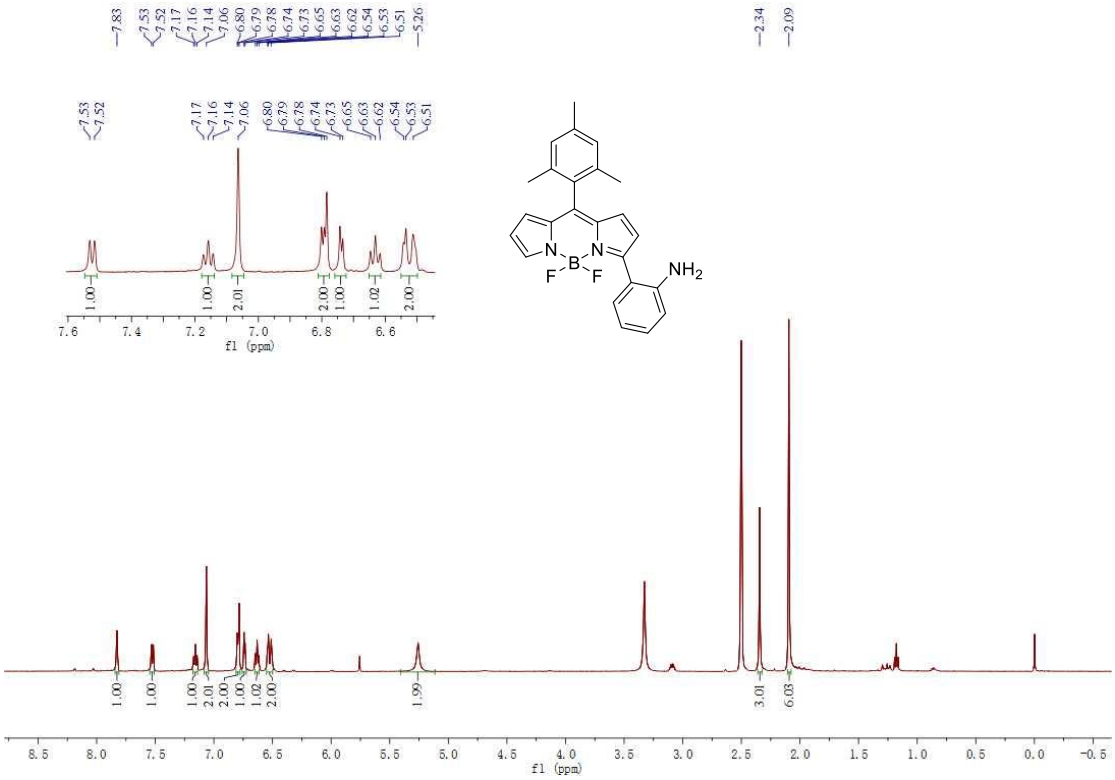
C	-2.59778100	-1.44138300	0.07166600
C	-3.40589200	-0.24767100	0.02638800
C	-2.53708000	0.83934400	-0.00965400
C	-1.21823300	0.31373000	0.02480800
C	0.00005900	1.02847400	0.00108300
C	1.21761900	0.31216600	0.02206600
C	2.53717500	0.83635600	-0.00711800
C	3.40456100	-0.25186300	0.02597500
C	2.59495700	-1.44486600	0.06293900
C	3.22629500	-2.71371600	0.05295600
C	4.66922300	-2.68409900	-0.04444300
C	5.37329700	-3.90251000	-0.10068500
C	4.70997500	-5.12005200	-0.05342100
C	3.30515600	-5.15462000	0.06390500
C	2.57759000	-3.98410700	0.11835700
C	4.84101400	-0.36690200	-0.01691100
C	0.00159300	2.52109000	-0.04502000
C	0.02637000	3.18812300	-1.28923600
C	0.02496400	4.58685400	-1.30648400
C	0.00303900	5.34165700	-0.12946000
C	-0.02565500	4.65876400	1.09064500
C	-0.02575300	3.26155100	1.15683000
C	0.04847800	2.41661200	-2.58977000
C	0.03458000	6.85164700	-0.17452300
C	-0.05818700	2.56959500	2.50146200
C	-3.23057200	-2.70951100	0.06786500
C	-2.58379400	-3.97996100	0.14889800
C	-4.67278300	-2.67891300	-0.03891100
C	-3.31214100	-5.15007600	0.09621800
C	-5.37760800	-3.89697500	-0.09361700
C	-4.71583000	-5.11482500	-0.03401200
C	-4.84229700	-0.36141800	-0.02238000
C	-5.71800700	0.84576400	-0.01845700
C	-5.43526400	1.94320200	0.80997800
C	-7.62581800	1.85992200	-0.80245500
C	-6.30578000	3.03178500	0.81312100
C	-7.42572000	2.99716000	-0.01429100
C	5.71796900	0.83934600	-0.00453100
C	5.43386800	1.93317900	0.82817500
C	6.30566500	3.02069600	0.83918500
C	7.62935200	1.85494700	-0.77785100
C	7.42813900	2.98864300	0.01510000
F	0.00300300	-2.78712700	1.21986600

F	-0.00738700	-2.79309600	-1.06904300
H	6.11231400	3.87206500	1.48533000
H	8.49531500	1.79515000	-1.43529900
H	8.13366700	3.81288000	-0.01546900
H	4.56528000	1.91803200	1.47714100
H	-8.48981700	1.79802200	-1.46229100
H	-6.11338700	3.88599600	1.45579000
H	-8.13013300	3.82209900	-0.05099900
H	-4.56873200	1.93016800	1.46172900
H	-2.79894300	-6.10481600	0.16108700
H	-6.45809600	-3.84619000	-0.18098700
H	-5.28068500	-6.04151700	-0.07815000
H	-1.51344500	-4.02445400	0.27499200
H	-0.94893500	1.93907300	2.61011200
H	-0.06335700	3.30039100	3.31538000
H	0.81158400	1.91645300	2.64092700
H	1.06726300	7.22516700	-0.17154900
H	-0.47071100	7.28905200	0.69283200
H	-0.44570300	7.23508800	-1.08077300
H	0.93380200	1.77352200	-2.66267300
H	0.05690000	3.09748800	-3.44578500
H	-0.82720900	1.76369900	-2.68707000
H	-0.04971800	5.22745600	2.01807300
H	0.04001800	5.09887900	-2.26646600
H	1.50576000	-4.02887000	0.23021300
H	2.79027100	-6.10920700	0.11644800
H	5.27426600	-6.04703100	-0.09870200
H	6.45443700	-3.85222800	-0.17984500
H	2.77798800	1.88635800	-0.07125100
H	-2.77637900	1.88921800	-0.08141900
B	-0.00184300	-1.98702700	0.06915500
N	-1.26664500	-1.07295100	0.07876900
N	1.26425400	-1.07472100	0.06962900
N	5.42962100	-1.53793800	-0.07314700
N	-6.80694000	0.80458200	-0.81179100
N	6.80926300	0.80061900	-0.79471700
N	-5.43175300	-1.53211200	-0.07743300

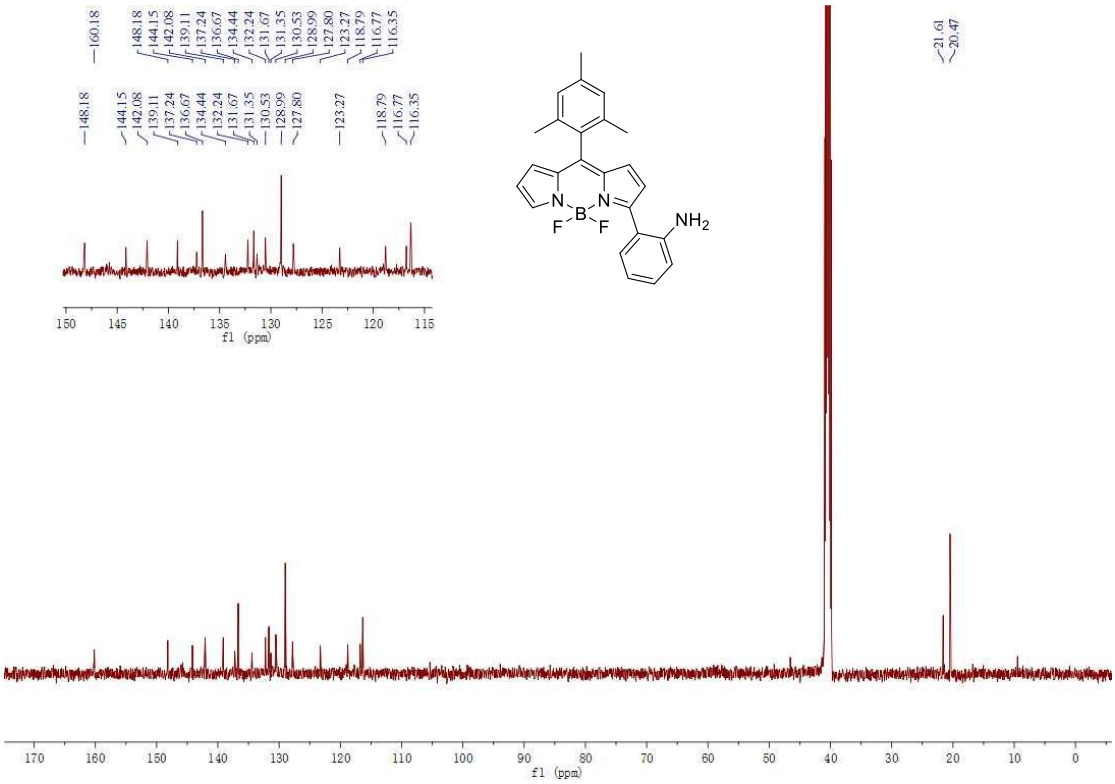
SCF done: -2171.16484905 a.u.

No imaginary Frequency.

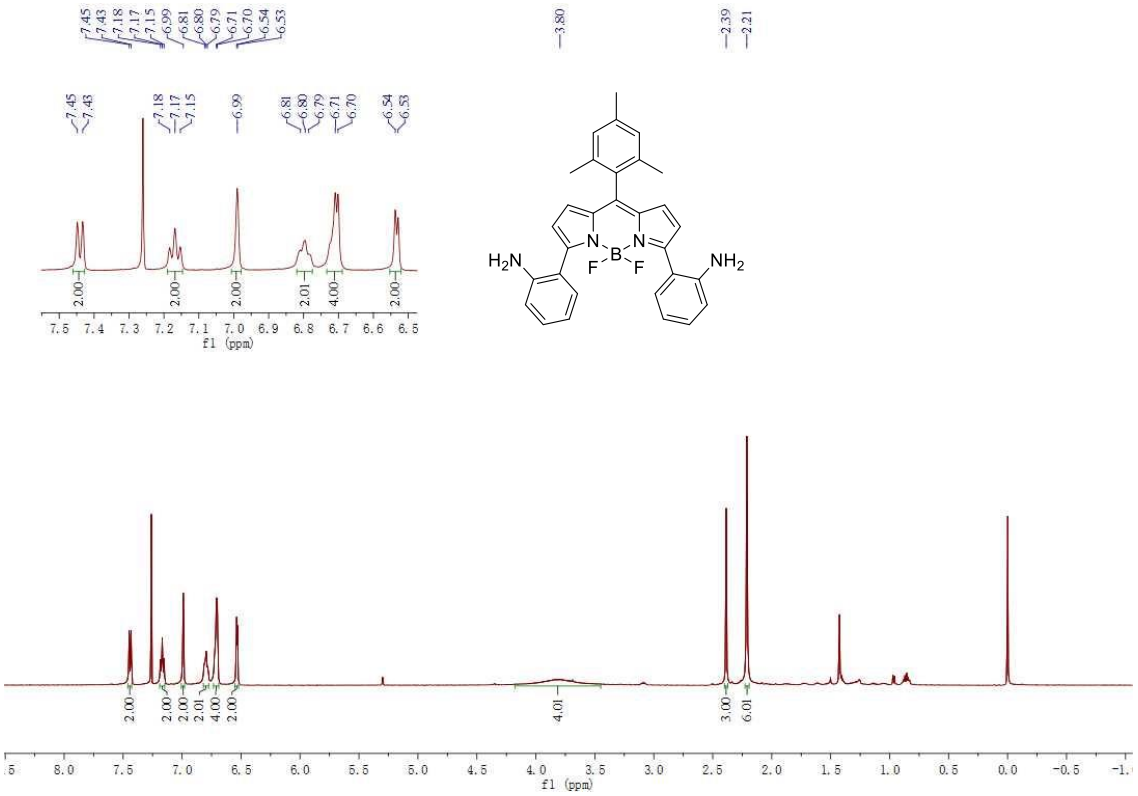
8. Copies of ^{1}H and ^{13}C NMR Spectra



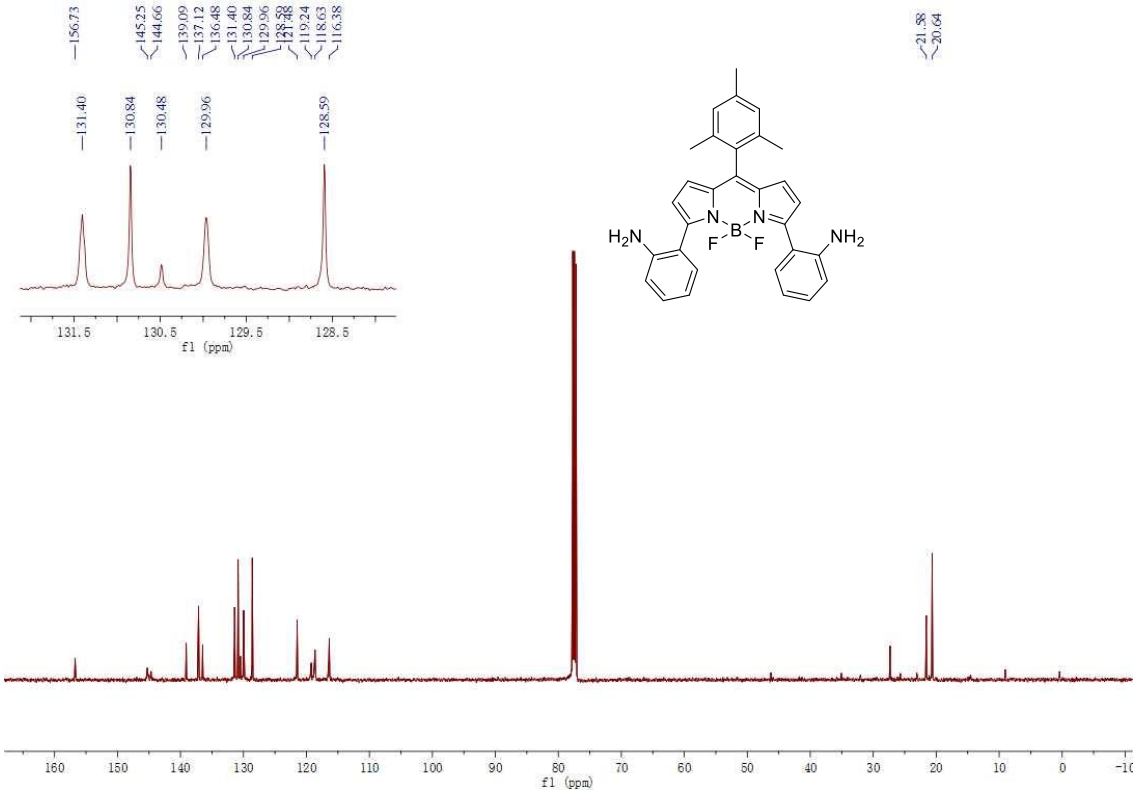
^{1}H NMR spectrum of **2a** (d_6-DMSO, 500 MHz)



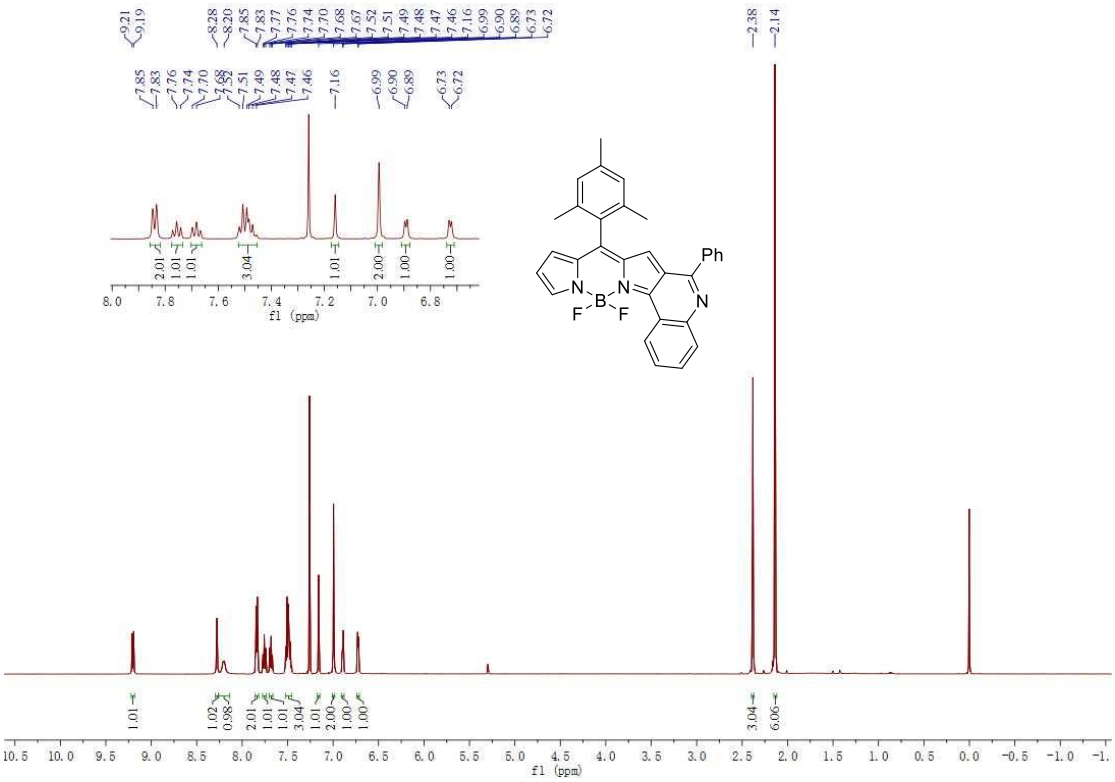
$^{13}C\{^{1}H\}$ NMR spectrum of **2a** (d_6-DMSO, 126 MHz)



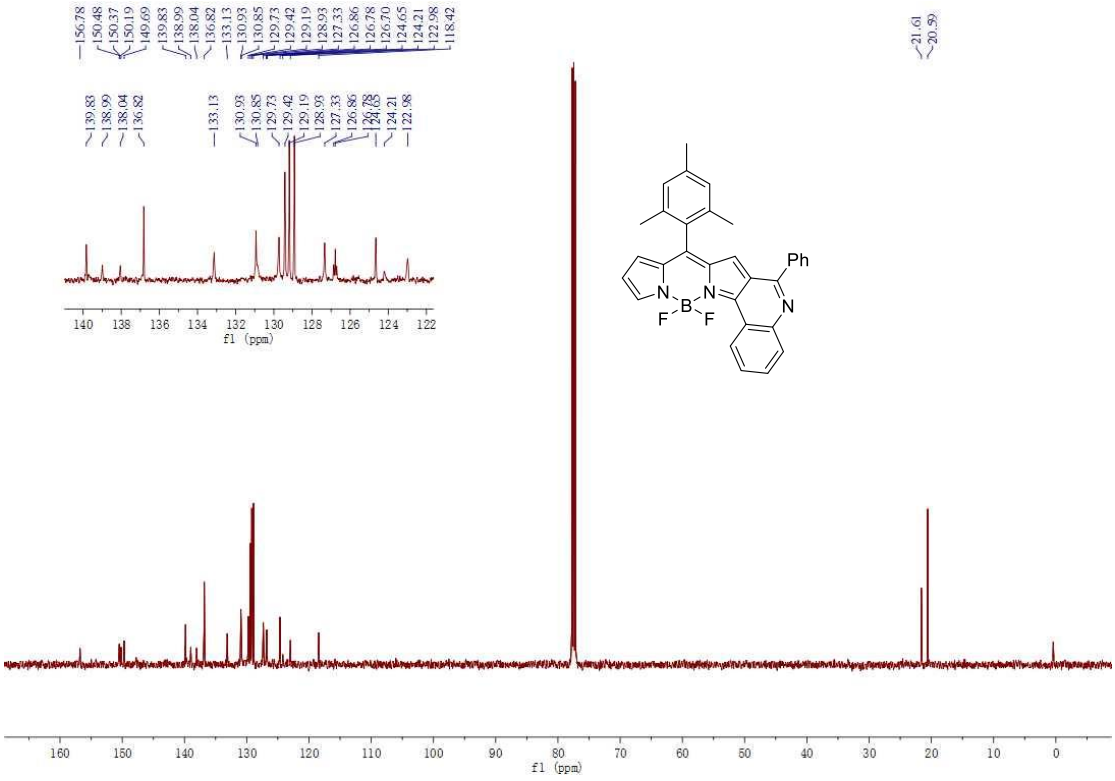
^{1}H NMR spectrum of **2b** ($CDCl_3$, 500 MHz)



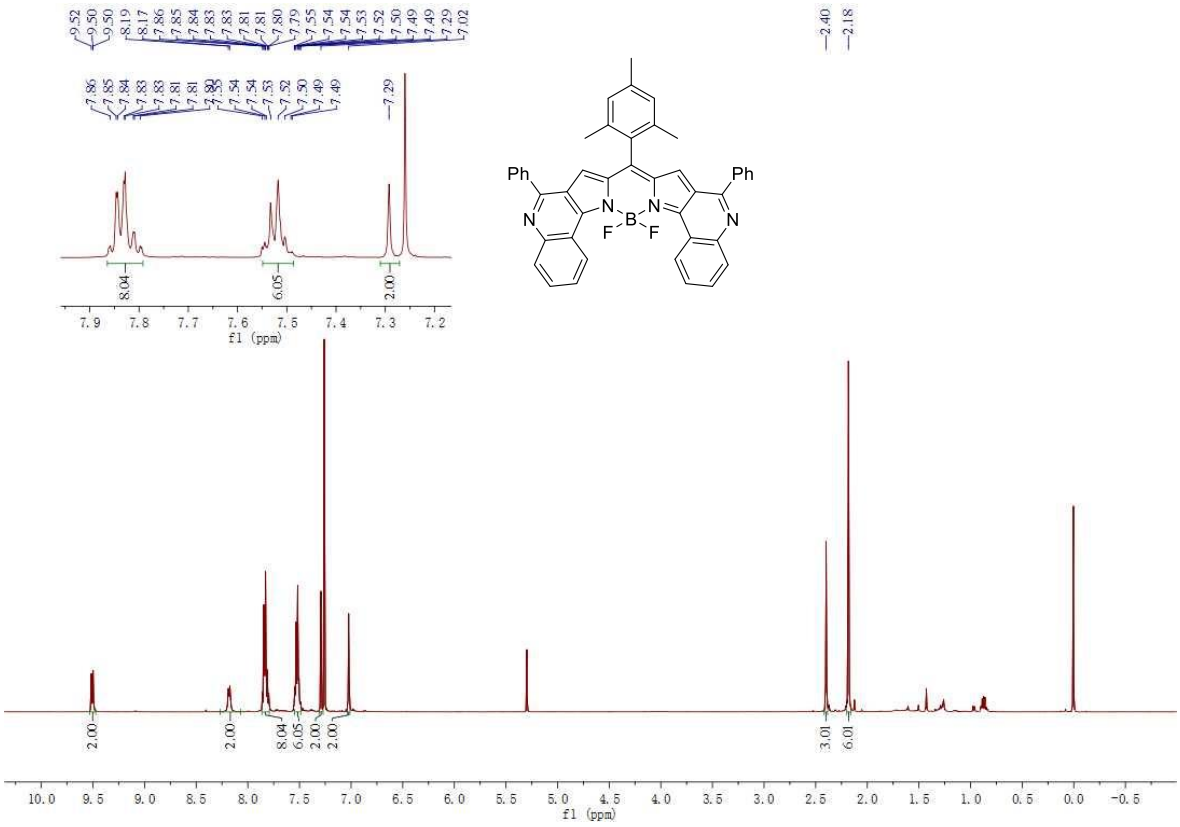
$^{13}C\{^{1}H\}$ NMR spectrum of **2b** ($CDCl_3$, 126 MHz)



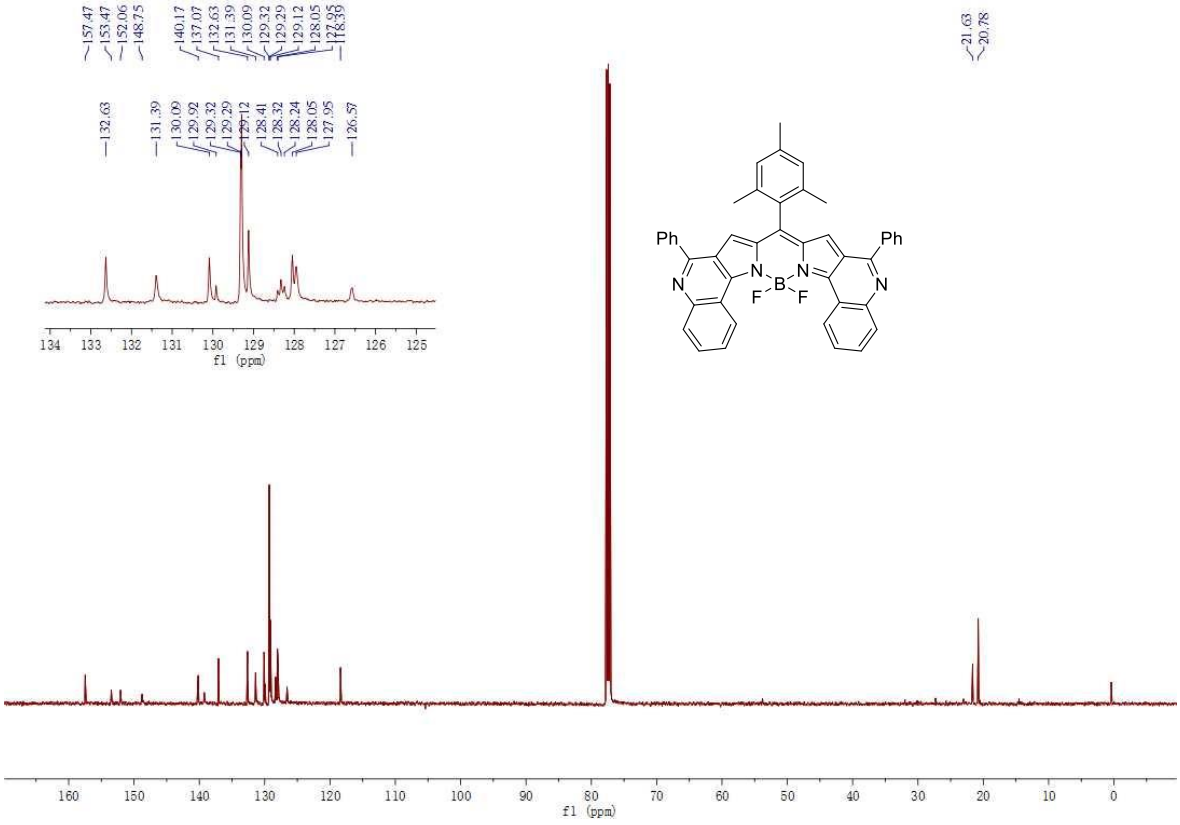
^{1}H NMR spectrum of **3a** ($CDCl_3$, 500 MHz)



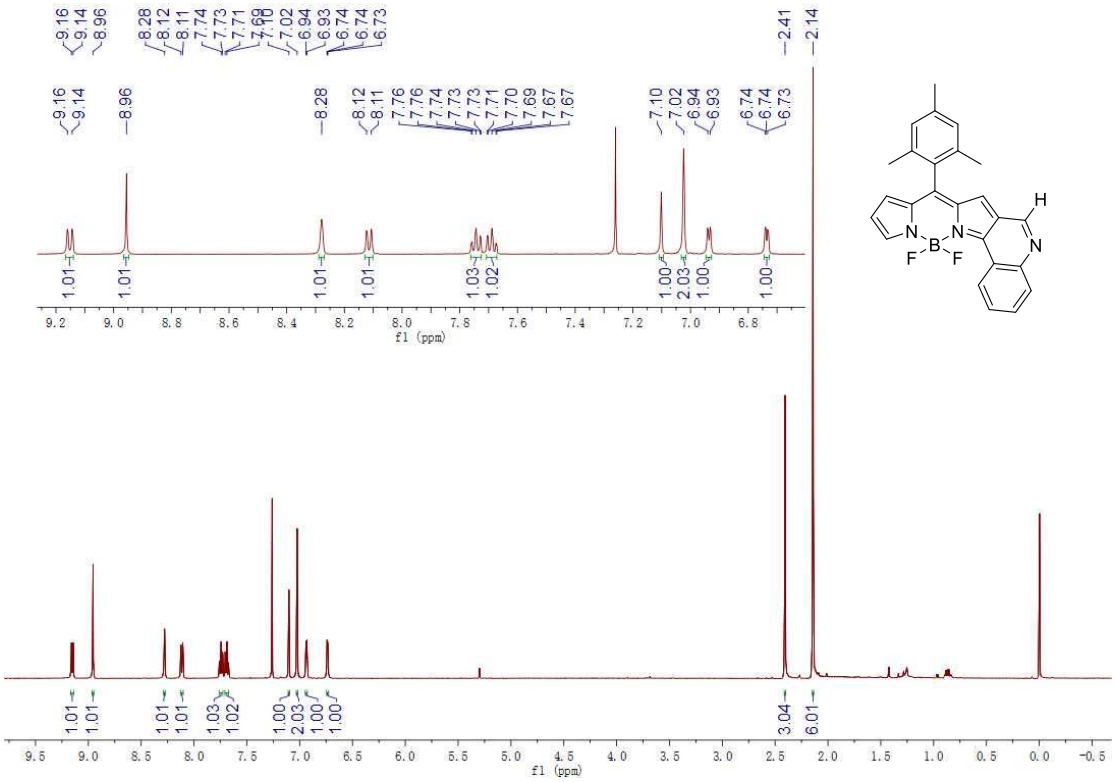
^{13}C{^{1}H} NMR spectrum of **3a** ($CDCl_3$, 126 MHz)



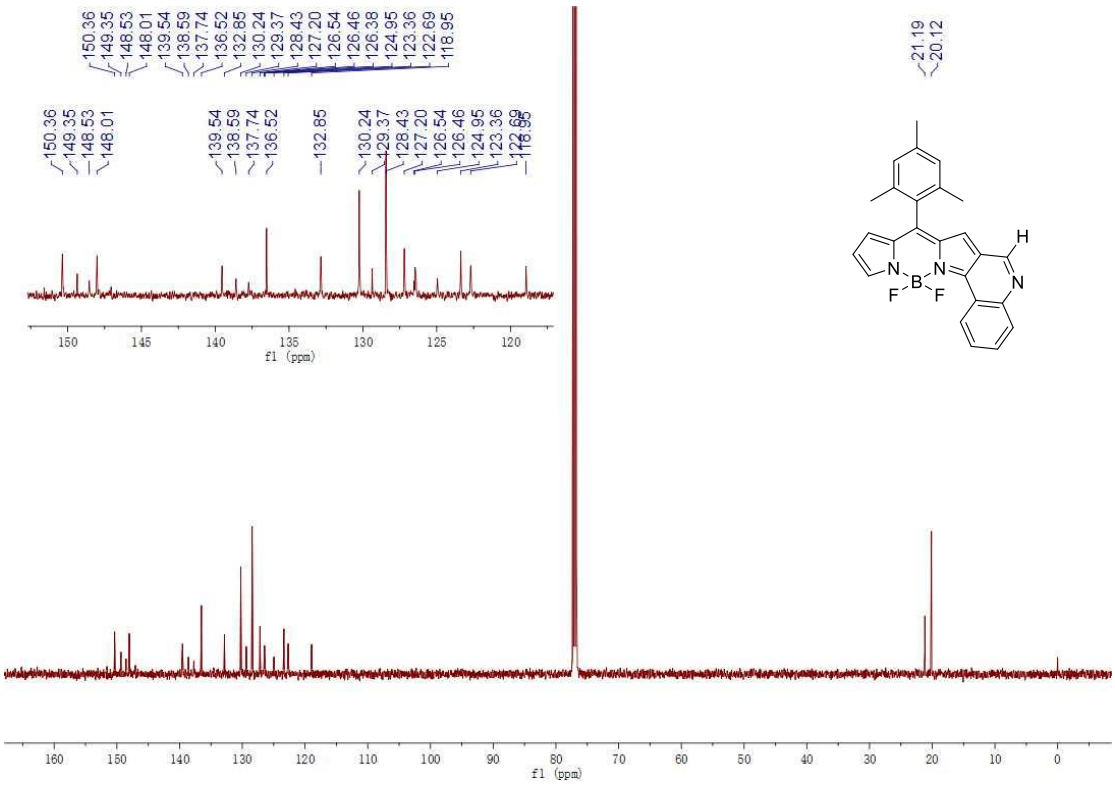
^{1}H NMR spectrum of **4a** ($CDCl_3$, 500 MHz)



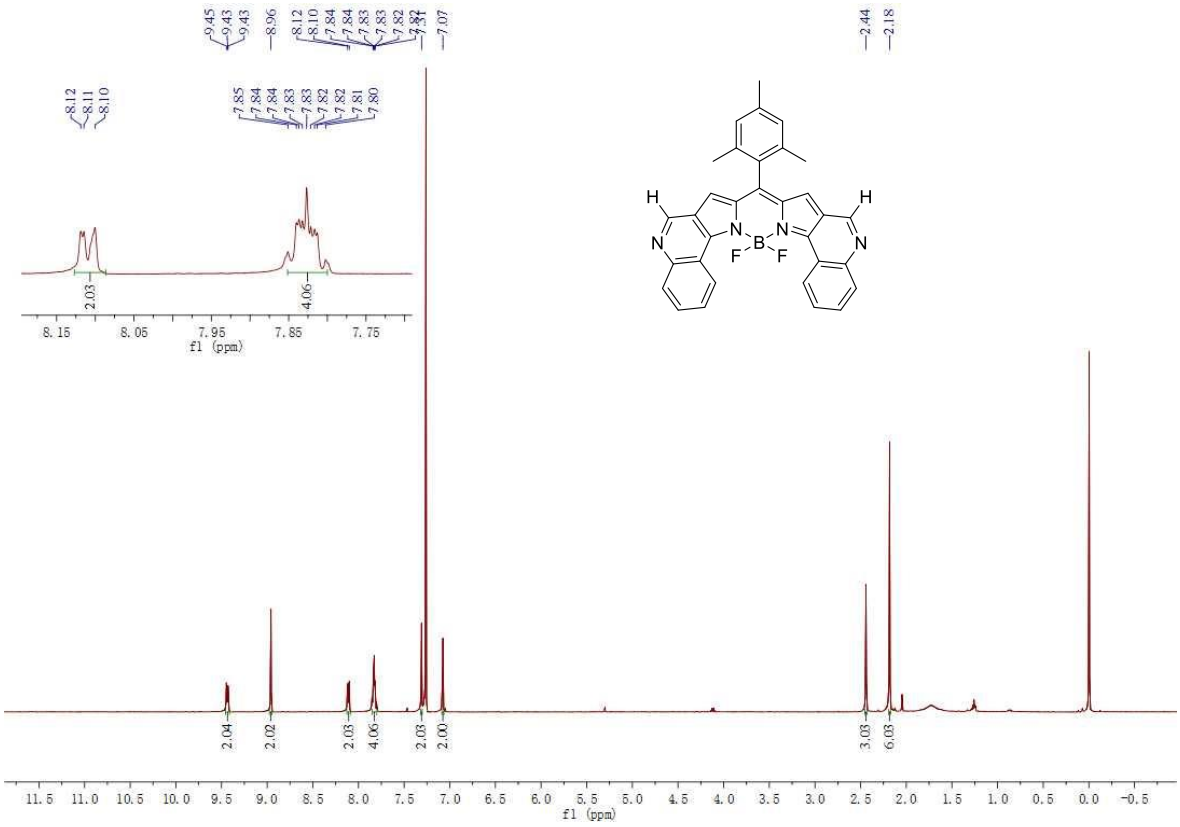
^{13}C{^{1}H} NMR spectrum of **4a** ($CDCl_3$, 126 MHz)



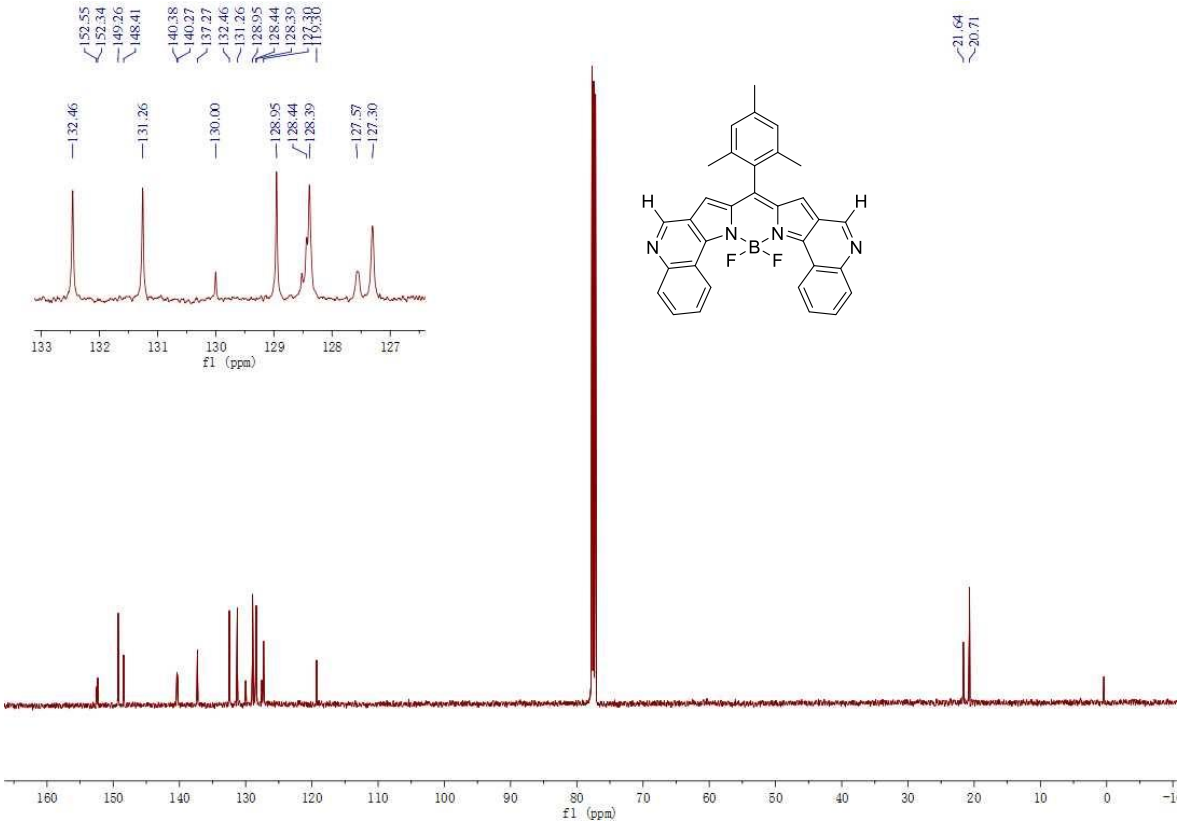
^{1}H NMR spectrum of **3b** ($CDCl_3$, 500 MHz)



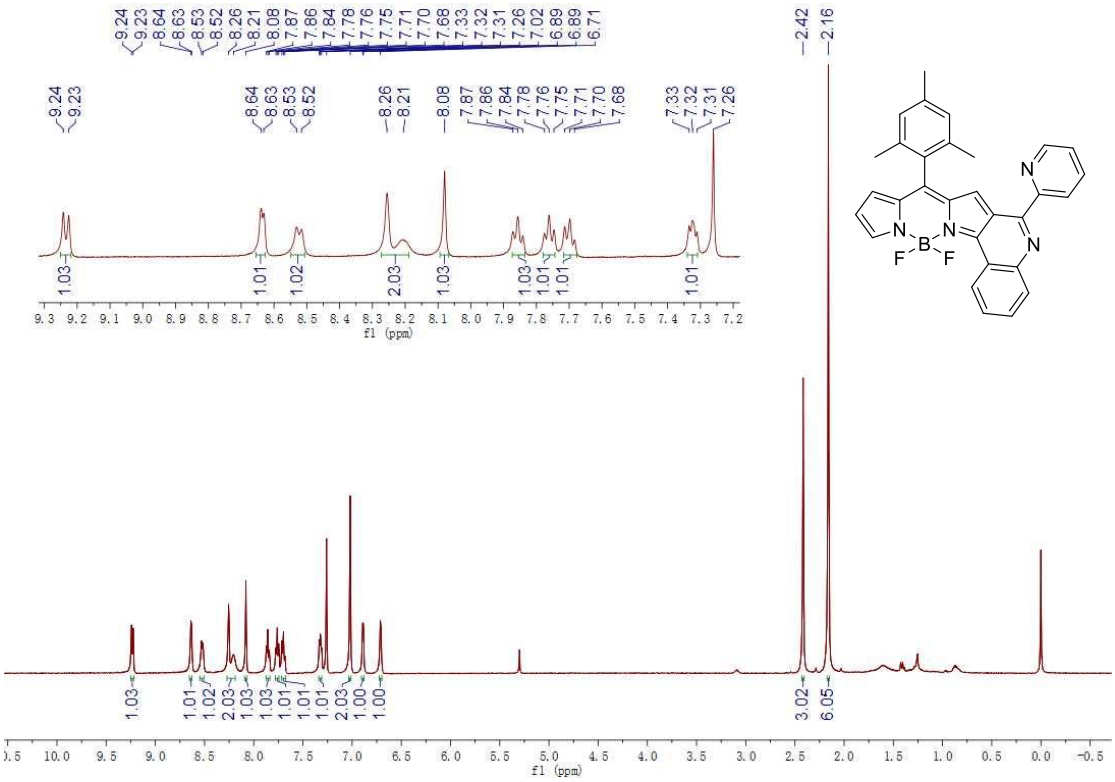
$^{13}C\{^{1}H\}$ NMR spectrum of **3b** ($CDCl_3$, 126 MHz)



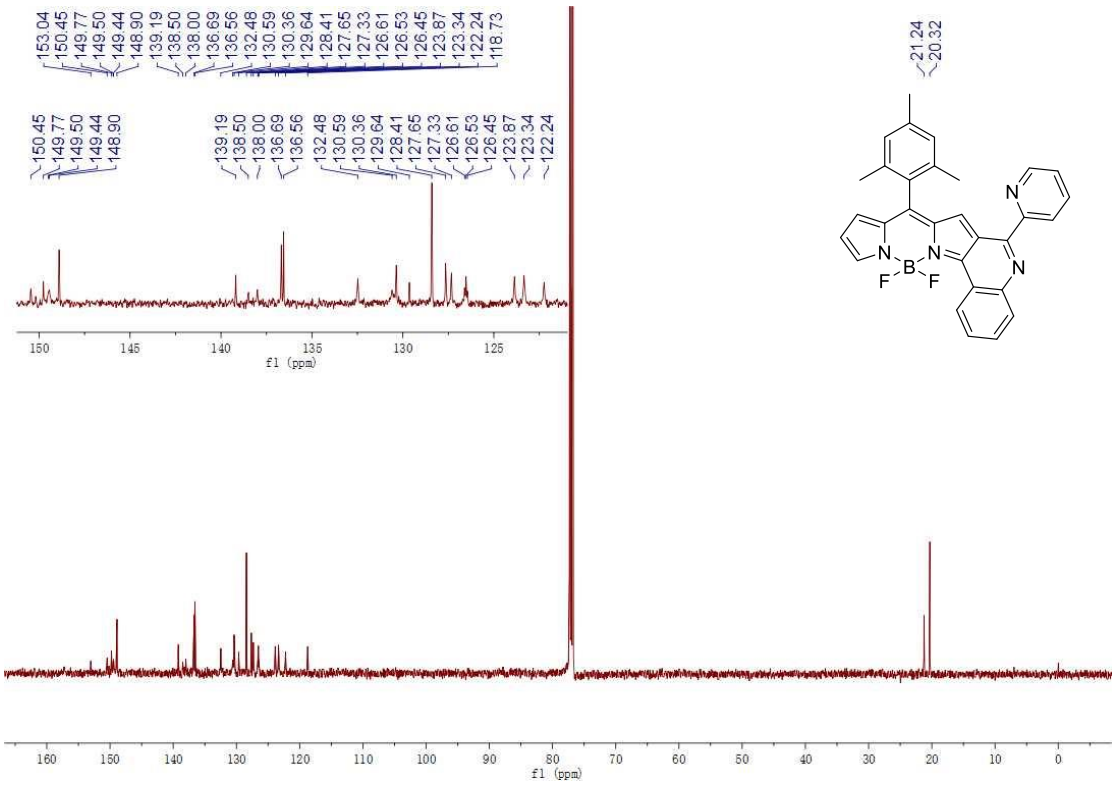
^{1}H NMR spectrum of **4b** ($CDCl_3$, 500 MHz)



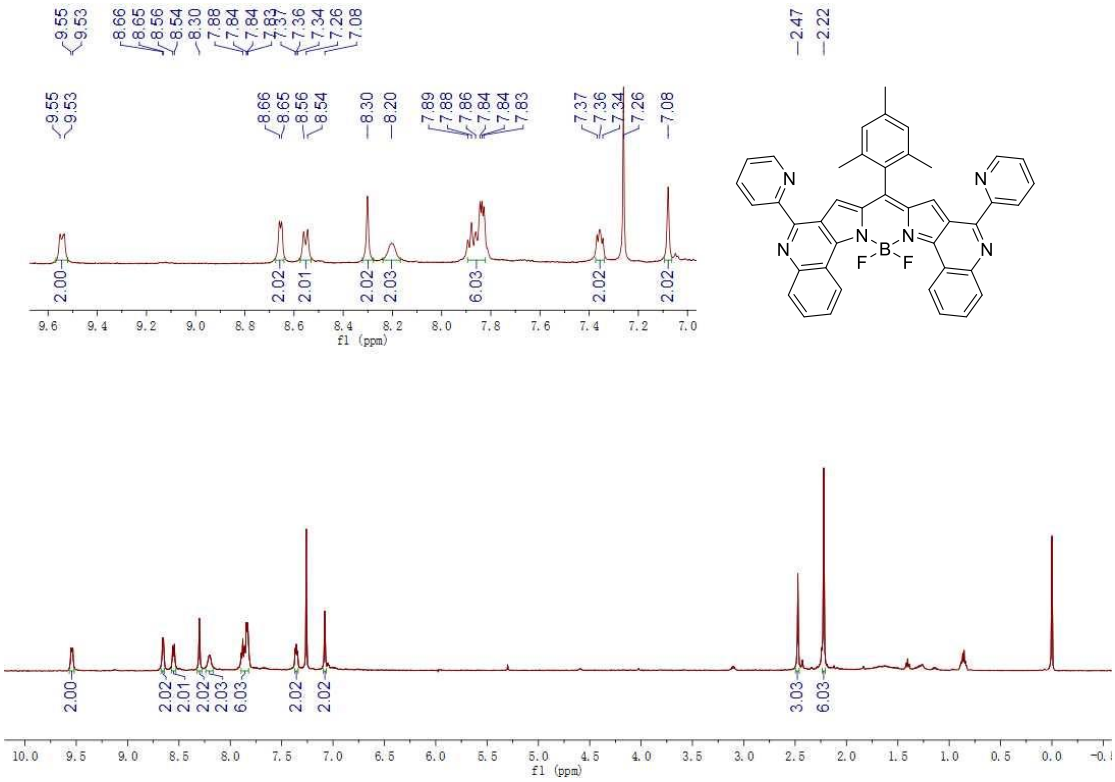
$^{13}C\{^{1}H\}$ NMR spectrum of **4b** ($CDCl_3$, 126 MHz)



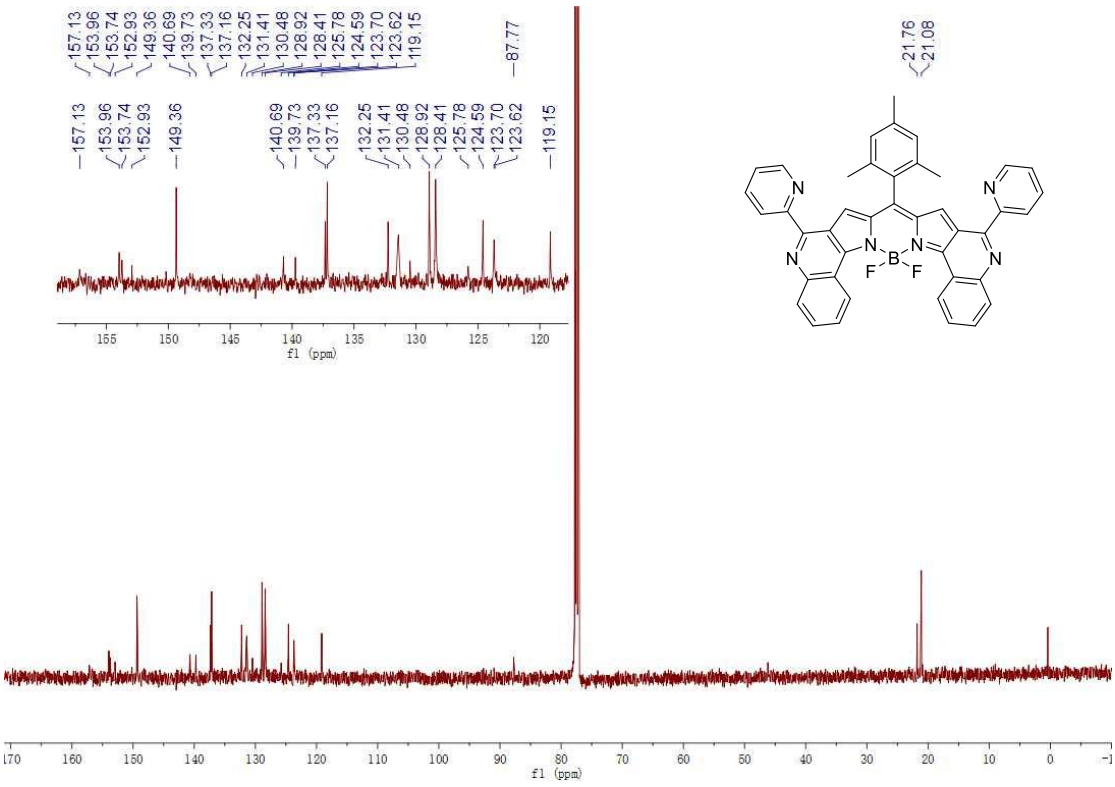
^{1}H NMR spectrum of **3c** ($CDCl_3$, 500 MHz)



$^{13}C\{^{1}H\}$ NMR spectrum of **3c** ($CDCl_3$, 126 MHz)



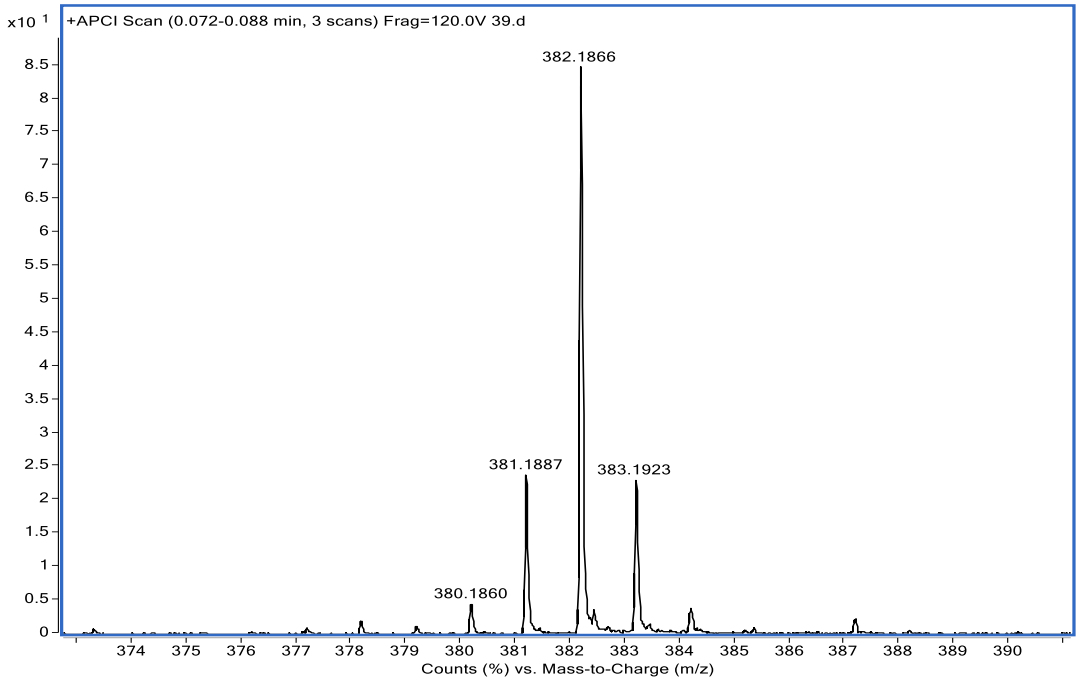
^{1}H NMR spectrum of **4c** ($CDCl_3$, 500 MHz)



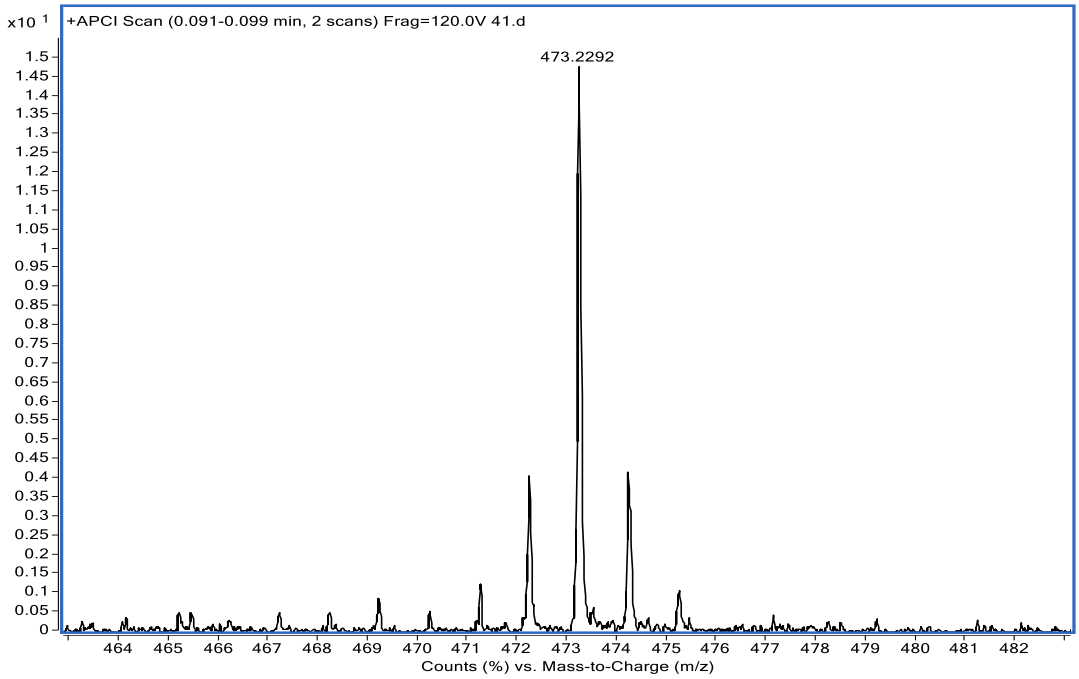
$^{13}C\{^{1}H\}$ NMR spectrum of **4c** ($CDCl_3$, 126 MHz)

9. High Resolution Mass Spectroscopes for All New Compounds

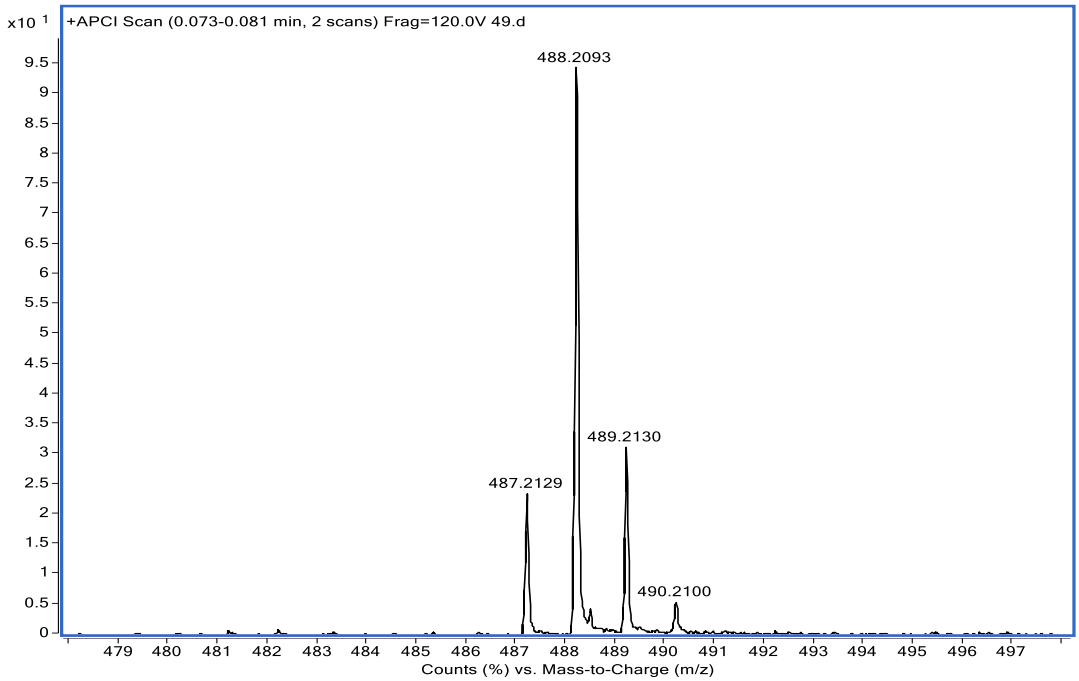
2a HRMS (APCI) m/z: $[M - F]^+$ Calcd. for $C_{24}H_{22}BFN_3$ 382.1885; Found 382.1866.



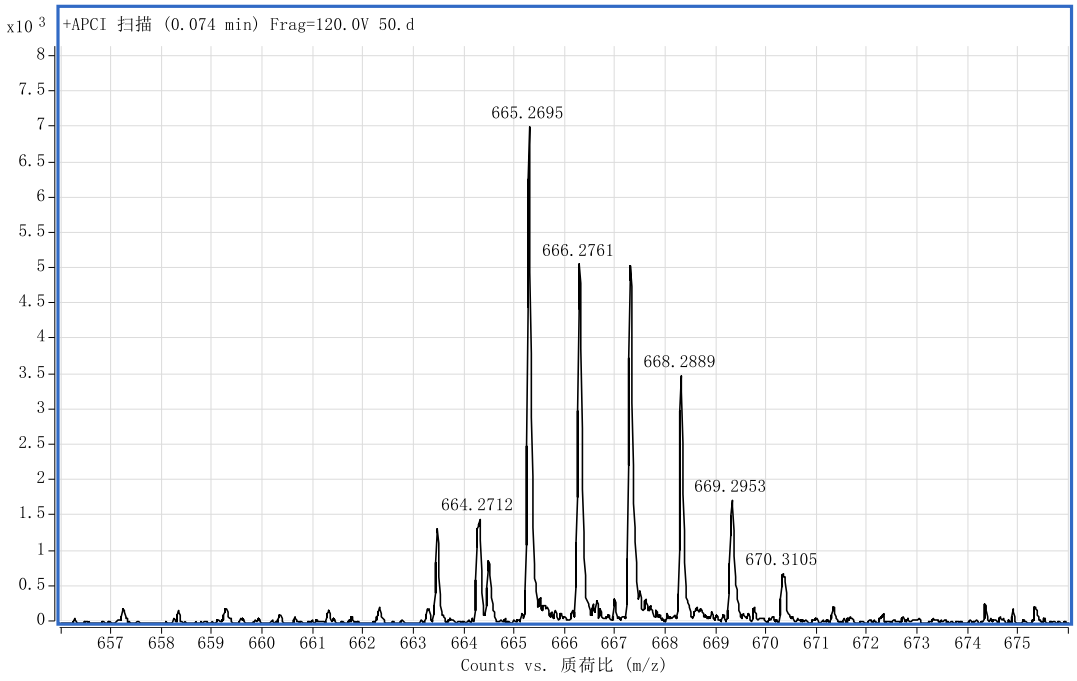
2b HRMS (APCI) m/z: $[M - F]^+$ Calcd. for $C_{30}H_{27}BFN_4$ 473.2307; Found 473.2292.



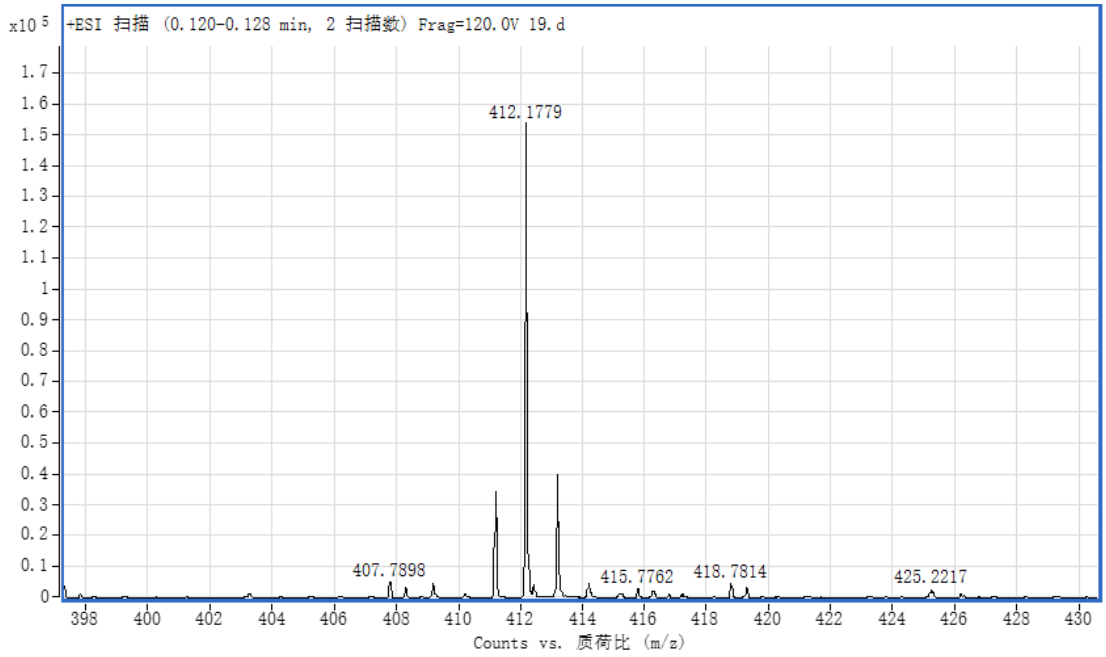
3a HRMS (APCI) m/z: $[M + H]^+$ Calcd. for $C_{31}H_{25}BF_2N_3$ 488.2104; Found 488.2093.



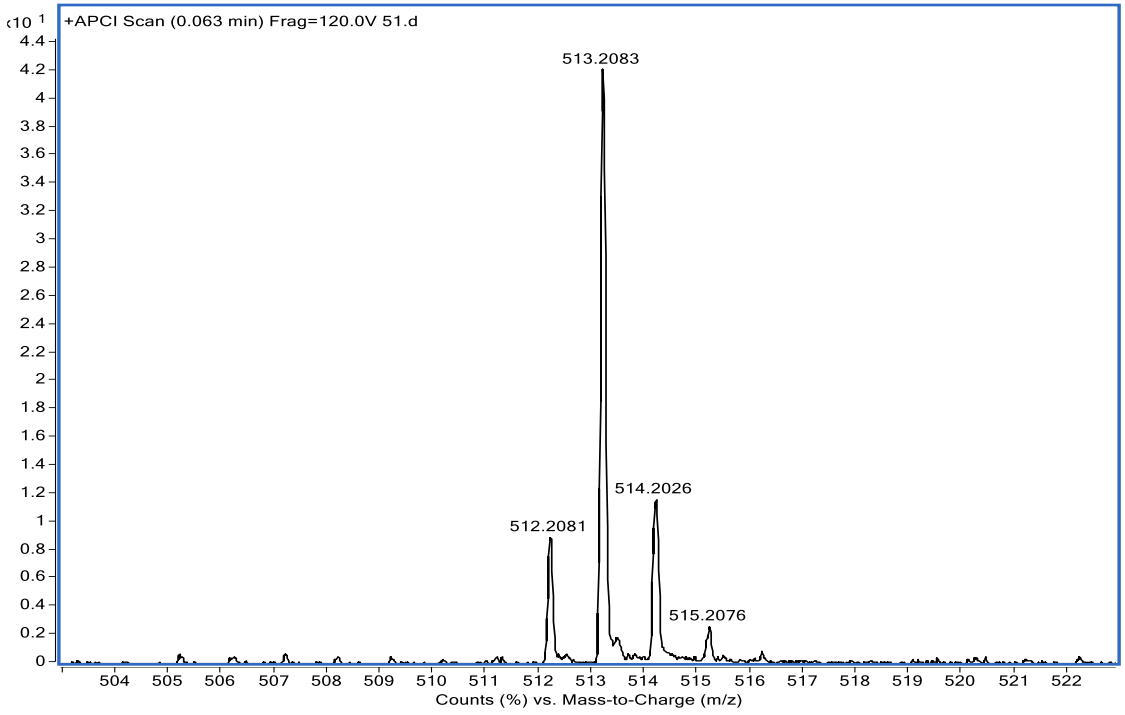
4a HRMS (APCI) m/z: $[M + H]^+$ Calcd. for $C_{44}H_{32}BF_2N_4$ 665.2683; Found 665.2695.



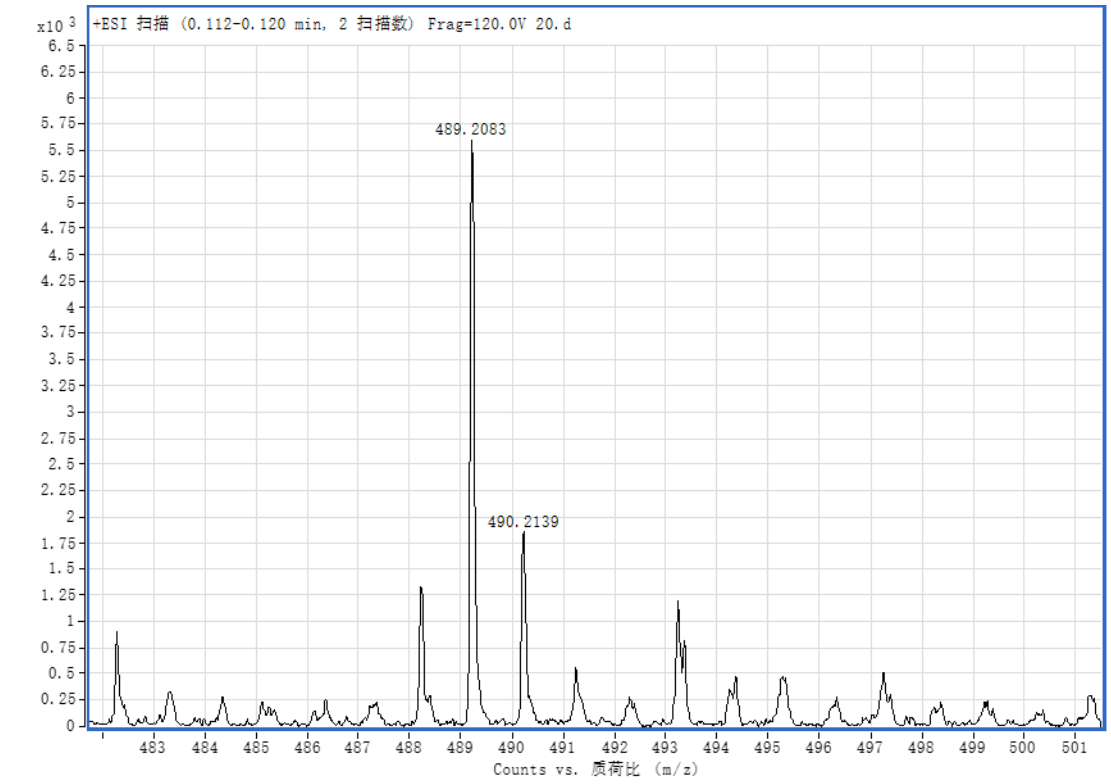
3b HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{25}H_{21}BF_2N_3$ 412.1791; Found 412.1779.



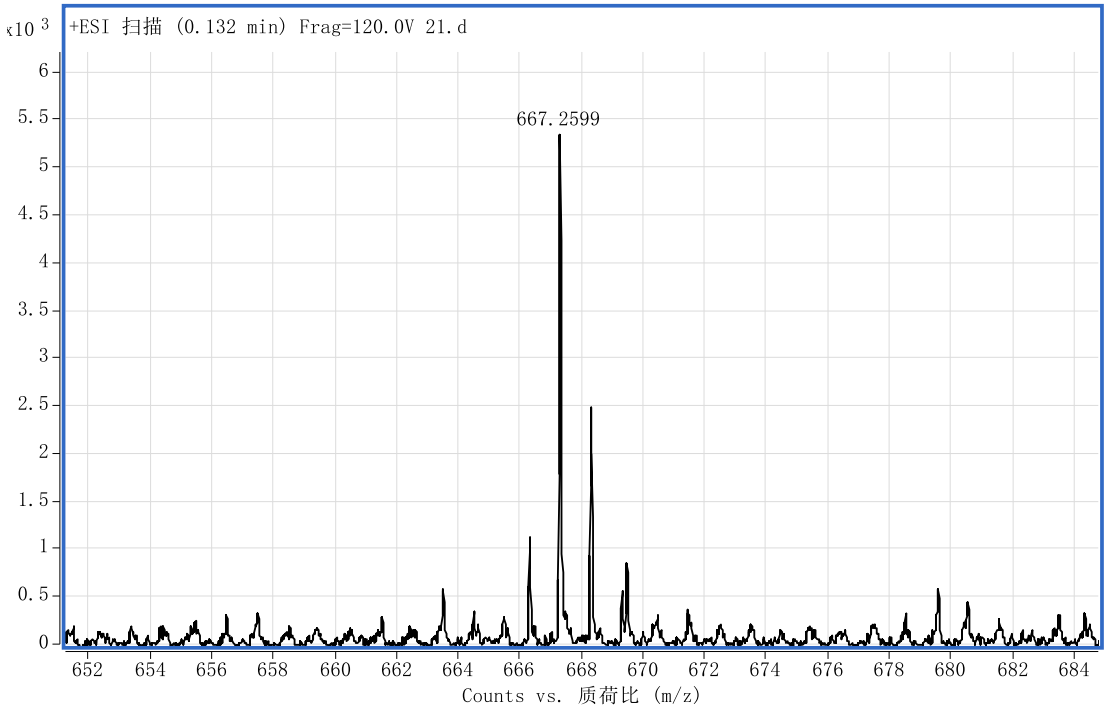
4b HRMS (APCI) m/z: $[M + H]^+$ Calcd. for $C_{32}H_{24}BF_2N_4$ 513.2057; Found 513.2083.



3c HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{30}H_{24}BF_2N_4$ 489.2057; Found 489.2083.



4c HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{42}H_{30}BF_2N_6$ 667.2588; Found 667.2599.



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