Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

$FeCl_3$-Promoted Regioselective Synthesis of BODIPY Dimers through Oxidative Aromatic Homocoupling Reactions

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Contents

1. Experimental details

General information. Reagents and solvents were used as received from commercial suppliers (Energy Chemicals, Shanghai, China) unless noted otherwise. All reactions were performed in oven-dried or flame-dried glassware unless stated otherwise and were monitored by TLC using 0.25 mm silica gel plates with UV indicator (60F-254). ^{1}H and ^{13}Cspectra were recorded on a 300 or 400 or 500 MHz NMR spectrometer at room temperature. Chemical shifts (δ) are given in ppm relative to $CDCl_3$ (7.26 ppm for ^{1}H and 77 ppm for ^{13}C) or to internal TMS. High-resolution mass spectra (HRMS) were obtained using APCI-TOF or ESI-TOF in positive mode.

Absorption and emission measurements. UV-visible absorption and fluorescence emission spectra were recorded on commercial spectrophotometers (Shimadzu UV-2450 and Edinburgh FS5 spectrometers). All measurements were made at 25 ^{o}C, using 5 × 10 mm cuvettes. Relative fluorescence quantum efficiencies of BODIPY derivatives were obtained by comparing the areas under the corrected emission spectrum of the test sample in various solvents with 1,7-diphenyl-3,5-di(4-methoxyphenyl)-azadipyrromethene (Φ = 0.36 in chloroform)[1] and Indocyanine Green (Φ = 0.12 in DMSO).[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[2]:

$$\Phi_X = \Phi_S (I_X/I_S) (A_S/A_X) (n_X/n_S)^{2,3} \quad \ldots\ldots(1)$$

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

X-ray structure analysis. Crystals of compounds **2c** and **2e** suitable for X-ray analysis were obtained *via* the slow diffusion of petroleum ether into their dichloromethane solutions. 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 diffractometer equipped with a graphite crystal monochromator situated in the incident beam for data collection at room temperature. Cell parameters were retrieved using SMART[4] software and refined using SAINT on all observed reflections. The determination of unit cell parameters and data collections were performed with Mo *Kα* radiation (λ) at 0.71073 Å. Data reduction was performed using the SAINT software,[5] which corrects for Lp and decay. The structure was solved by the direct method using the

SHELXS-97[4] program and refined by least squares method on F^2, SHELXL-2018/3,[6] incorporated in SHELXTL V5.10.[7] CCDC-2053912 (**2c**) and CCDC-2095140 (**2e**) containing the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Electrochemical measurements. Cyclic voltammograms of 1 mM **M**, **1a** and **2a** 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.

Cell culture. HeLa cells (human cervical cancer cells) were cultured in culture media (RPMI-1640, supplemented with 10% FBS and 1% penicillin/streptomycin solution) at 37 °C in an atmosphere of 5% CO_2 and 95% humidified atmosphere for 24 h.

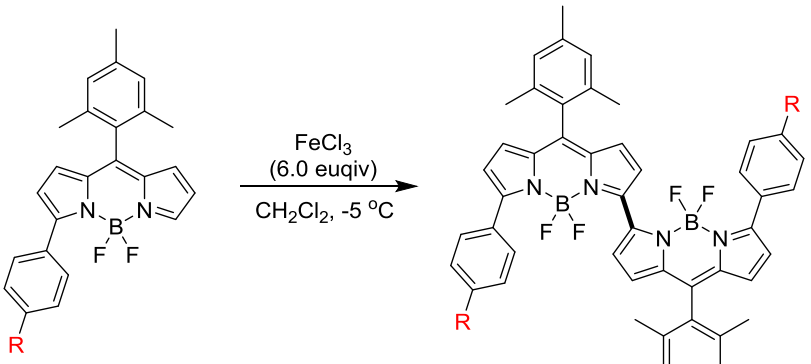
Cell incubation and colocalization imaging. A total of 30000 HeLa cells were seeded into a glass bottom dish and were cultured in culture media (RPMI-1640, supplemented with 10% FBS and 1% penicillin and streptomycin) at 37 ºC in an atmosphere of 5% CO_2 and 95% humidified atmosphere for 24 h. HeLa cells were first stained with **2g** micelles (3 μM) and LysoTracker™ Green DND-26 (1 μM) at 37 ºC in an atmosphere of 5% CO_2 for 2 h. After washing the plates two times with PBS, the cells were fixed by 4% formaldehyde for 20 min. The organelle tracer 4,6-diamidino-2-phenylindole (DAPI, 0.08 μg/mL) was added subsequently and was incubated for 30 min to stain the nucleus. Finally, the plates were washed again with PBS and the morphologies of the HeLa cells were observed using a confocal fluorescence microscope (Leica Microsystems SP8 MP).

Cytotoxicity determined by the CCK-8 method. The cytotoxicity of the **2g** was evaluated on Hela cells. These cells were seeded into 96-well plates with a density of 5000 cells per well and cultured overnight. Then, solutions of **2g** with a serious of different concentrations were added and incubated with cells for 24 h. Every experiment was performed for at least six times. The working solutions were then removed, and the cells were washed with PBS buffer for one times. A total of 10 μL of CCK-8 (Cell Counting Kit-8, BIOMIKY) was added into each well, and the cells were further incubated at 37 ºC for 40 min. Then the plate was shaken for 5 min (protect from light), and the absorbance at 450 nm was measured with a microplate reader (Multiskan Sky).

2. Synthesis and characterization

BODIPYs **1a-d** and **1e** were synthesized according to our previously reported literature.[8,9]

Synthesis of dimers 2a-d.



Syntheses of BODIPY **2a**: To **1a** (77 mg, 0.2 mmol) in 10 mL of freah dried dichloromethane was drop wisely added $FeCl_3$ (194 mg, 1.2 mmol, 6.0 eq) in 1 mL of CH_3NO_2. The reaction mixture was stirred at -5 °C for 30 minute, and was quenched by adding saturated aqueous solution of $NaHCO_3$. The reaction mixture was diluted with dichloromethane, washed twice with water, dried over anhydrous Na_2SO_4, and evaporated under vacuum. The residue was purified by column chromatography on silica gel with CH_2Cl_2/petroleum ether as eluent to give the desired **2a** in 63% isolated yield (49 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 – 7.88 (m, 4H), 7.42 (d, *J* = 3.9 Hz, 8H), 6.97 (s, 4H), 6.68 (d, *J* = 4.2 Hz, 2H), 6.58 (d, *J* = 3.6 Hz, 4H), 2.37 (s, 6H), 2.19 (s, 12H).^{13}C NMR (125 MHz, $CDCl_3$) δ 160.2, 147.3, 143.7, 138.6, 137.8, 137.4, 136.9, 132.4, 130.3, 130.2, 129.8, 129.6, 128.2, 128.1, 128.0, 124.5, 121.7, 21.7, 20.3. HRMS (APCI) m/z: Calcd for $C_{48}H_{41}N_4B_2F_4^+$ $[M+H]^+$ 771.3448, Found 771.3449.

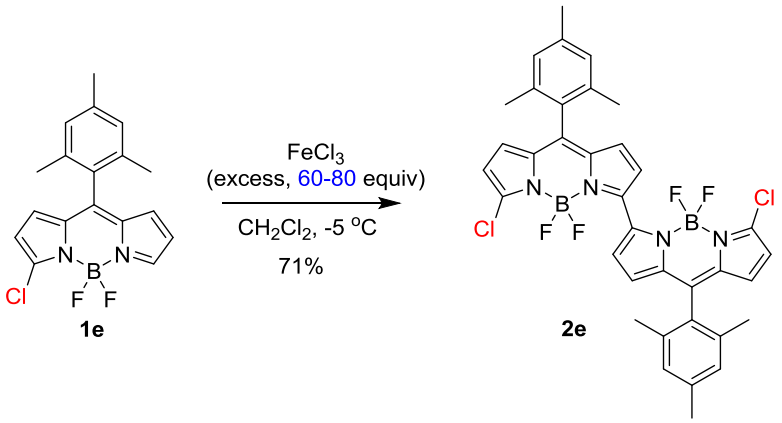
Syntheses of BODIPY **2b**: BODIPY **2b** was prepared in 72% yield (64 mg) from BODIPY **1b** (83 mg, 0.2 mmol) using the same procedure described for **2a**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.5 Hz, 4H), 7.44 (d, *J* = 8.5 Hz, 4H), 7.40 (d, *J* = 4.5 Hz, 2H), 6.97 (s, 4H), 6.67 (d, *J* = 4.5 Hz, 2H), 6.59 (d, *J* = 4.5 Hz, 2H), 6.58 (d, *J* = 4.5 Hz, 2H), 2.37 (s, 6H), 2.20 (s, 12H), 1.33 (s, 18H).^{13}C NMR (125 MHz, $CDCl_3$) δ 160.5, 153.1, 147.0, 142.9, 138.5, 137.9, 137.2, 136.9, 130.4, 130.2, 129.4, 128.2, 128.1, 127.5, 125.3, 124.3, 121.9, 34.8, 31.1, 21.2, 20.4. HRMS (APCI) m/z: Calcd for

$C_{56}H_{57}B_2F_4N_4^+$ $[M+H]^+$ 883.4700, Found 883.4711.

Syntheses of BODIPY **2c**: BODIPY **2c** was prepared in 67% yield (56 mg) from BODIPY **1c** (88 mg, 0.2 mmol) using the same procedure described for **2a**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.5 Hz, 4H), 7.38 (d, *J* = 4.0 Hz, 2H), 6.97 (s, 4H), 6.94 (d, *J* = 9.0 Hz, 4H), 6.66 (d, *J* = 4.5 Hz, 2H), 6.58 (d, *J* = 4.5 Hz, 2H), 6.55 (d, *J* = 4.5 Hz, 2H), 3.84 (s, 6H), 2.37 (s, 6H), 2.19 (s, 12H).^{13}C NMR (125 MHz, $CDCl_3$) δ 161.7, 161.1, 144.7, 141.4, 138.9, 138.1, 137.0, 134.4, 131.9, 131.7, 130.6, 128.5, 127.6, 124.8, 121.4, 117.9, 114.3, 55.7, 21.5, 20.4. HRMS (APCI) m/z: Calcd for $C_{50}H_{45}O_2N_4B_2F_4^+$ $[M+H]^+$ 831.3659, Found 831.3648.

Syntheses of BODIPY **2d**: BODIPY **2d** was prepared in 68% yield (57 mg) from BODIPY **1d** (84 mg, 0.2 mmol) using the same procedure described for **2a**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.5 Hz, 4H), 7.39 (d, *J* = 8.5 Hz, 4H), 7.37 (d, *J* = 4.5 Hz, 2H), 6.98 (s, 4H), 6.69 (d, *J* = 4.3 Hz, 2H), 6.62 (d, *J* = 4.5 Hz, 2H), 6.56 (d, *J* = 4.3 Hz, 2H), 2.38 (s, 6H), 2.19 (s, 12H).^{13}C NMR (125 MHz, $CDCl_3$) δ 158.9, 148.0, 144.5, 139.2, 138.2, 137.9, 137.2, 136.4, 131.3, 131.2, 130.6, 130.5, 128.9, 128.8, 128.6, 125.1, 121.8, 21.6, 20.7. HRMS (APCI) m/z: Calcd for $C_{48}H_{39}N4B_2Cl_2F_4^+$ $[M+H]^+$ 839.2674, Found 839.2673

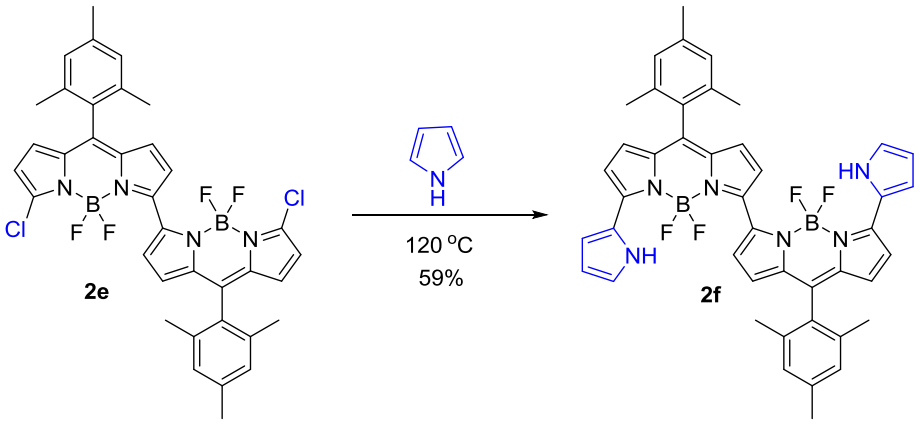
Syntheses of dimer 2e.



Syntheses of BODIPY **2e**: A solution of BODIPY **1e** (52 mg, 0.15 mmol) was dissolved in fresh and dried CH_2Cl_2 (10 mL) and stirred at -5 °C, then the excess $FeCl_3$ (1.46-1.94 g, 9-12 mmol) was added into the mixture and continued to stir at -5 °C for 25-30 min, and was quenched by adding saturated aqueous solution of $NaHCO_3$. The reaction mixture was diluted with dichloromethane, washed twice with water, dried over anhydrous Na_2SO_4, and evaporated under vacuum. The residue

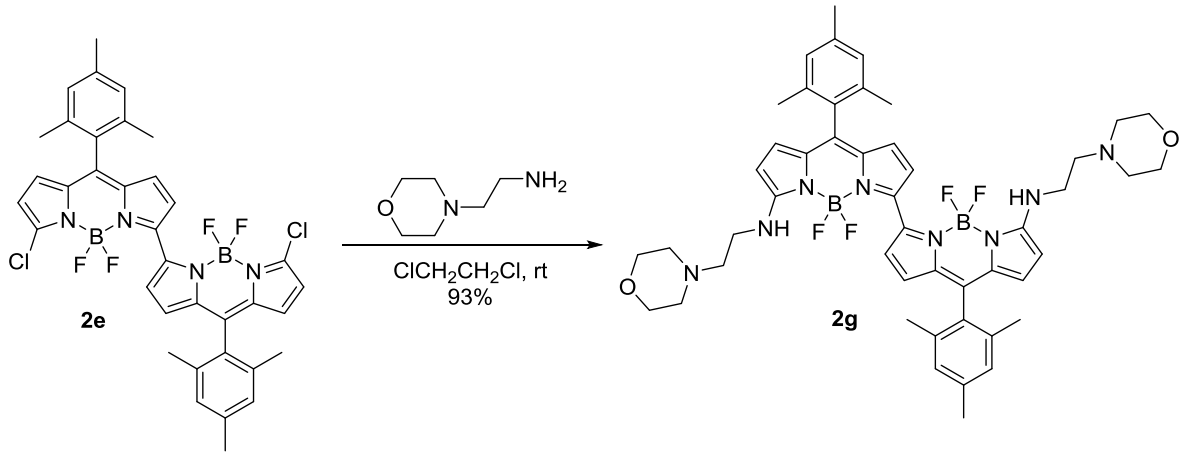
was purified by column chromatography on silica gel with CH_2Cl_2/petroleum ether (1/2, v/v) as eluent to give the desired **2e** in 71% isolated yield (37 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 4.5 Hz, 2H), 6.97 (s, 4H), 6.70 (d, *J* = 4.5 Hz, 2H), 6.63 (d, *J* = 4.0 Hz, 2H), 6.37 (d, *J* = 4.5 Hz, 2H), 2.37 (s, 6H), 2.15 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.2, 144.8, 144.4, 139.1, 137.9, 136.67, 134.8, 129.9, 129.7, 129.1, 128.2, 124.6, 119.3, 21.1, 20.1. HRMS (APCI) m/z: Calcd for $C_{36}H_{30}B_2Cl_2F_3N_4^+$ $[M-F]^+$ 667.1986, Found 667.2034.

Syntheses of dimer 2f.



Syntheses of BODIPY **2f**: BODIPY **2e** (137 mg, 0.2 mmol) was dissolved in pyrrole (2.0 mL) and stirred under argon at 120 ºC for 12 hours. After cooling down to room temperature, the excess pyrrole was removed under reduced pressure. The residue was purified through column chromatography on silica using CH_2Cl_2/petroleum (1:2, v/v) as eluent, from which the desired product **2f** was obtained in 59% yield (88 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.51 (brs, 2H), 7.34 (d, *J* = 4.0 Hz, 2H), 7.13 (s, 2H), 6.98 (s, 6H), 6.85 (d, *J* = 4.4 Hz, 2H), 6.64 (d, *J* = 4.8 Hz, 2H), 6.49 (d, *J* = 4.4 Hz, 2H), 6.34 (s, 2H), 2.38 (s, 6H), 2.20 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 143.8, 138.3, 138.0, 137.3, 137.1, 136.3, 130.6, 130.4, 128.1, 126.1, 124.5, 123.9, 122.5, 121.4, 118.1, 111.4, 21.2, 20.3. HRMS (ESI) m/z calcd for $C_{44}H_{39}B_2F_4N_6^+$ $[M+H]^+$ 749.3353, found 749.3356.

Synthesis of dimer 2g.



Syntheses of 2g: In a 10 mL flask, a solution of **2e** (69 mg, 0.1 mmol) was dissolved in 1,2-dichloroethane (3.0 mL) and 4-(2-aminoethyl)morpholine (78 μL, 0.6 mmol) was added to the mixture and stirred at room temperature for 2.5 hours. The solvent was concentrated under reduced pressure and the residue was purified by silica-gel column chromatography (eluent: ethyl acetate/n-hexane = 1/3). Recrystallization from CH_2Cl_2/ petroleum afforded pure dye **2g** as dark green powder (81 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, *J* = 4.0 Hz, 2H), 6.93 (s, 4H), 6.78 (s, 2H), 6.60 (d, *J* = 4.8 Hz, 2H), 6.24 (d, *J* = 4.0 Hz, 2H), 6.04 (d, *J* = 4.8 Hz, 2H), 3.71 – 3.67 (m, 8H), 3.41 (d, *J* = 5.6 Hz, 4H), 2.61 (t, *J* = 6.2 Hz, 4H), 2.49 (s, 8H), 2.35 (s, 6H), 2.16 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 139.9, 137.7, 137.5, 134.6, 133.2, 131.2, 130.7, 127.9, 120.4, 118.7, 109.4, 66.8, 57.0, 53.3, 41.1, 21.1, 20.1. HRMS (ESI) m/z calcd for $C_{48}H_{57}B_2F_4N_8O_2^+$ $[M+H]^+$ 875.4721, found 875.4727.

3. Crystal data

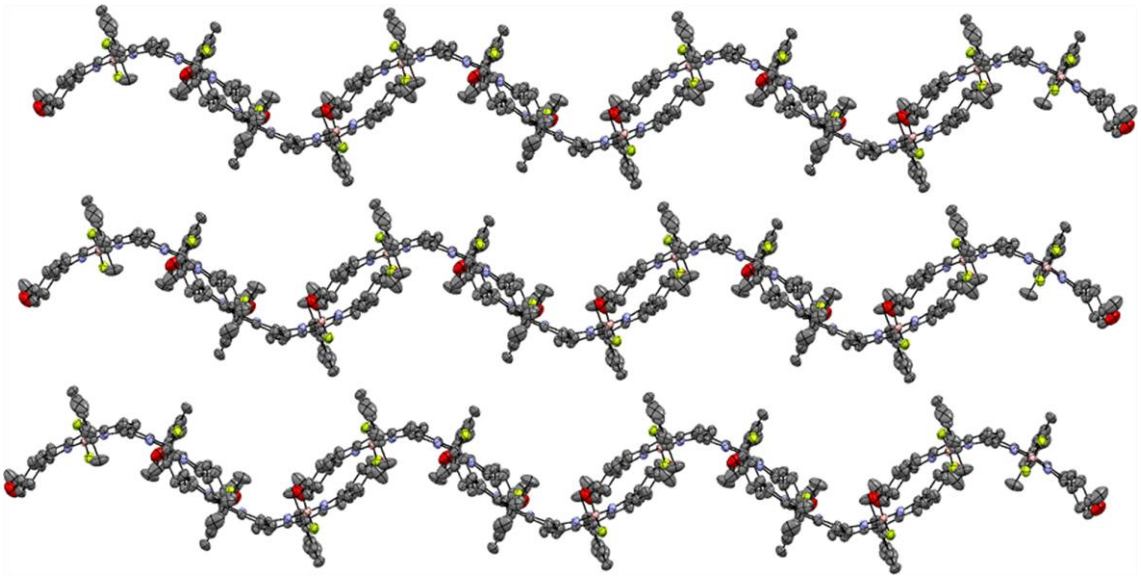


Figure S1. The packing of dimer **2c:** C, gray; N, purple; B, pink; F, yellow; O, red. Hydrogen atoms were removed for clarity. Thermal ellipsoids are shown at the 50% probability level.

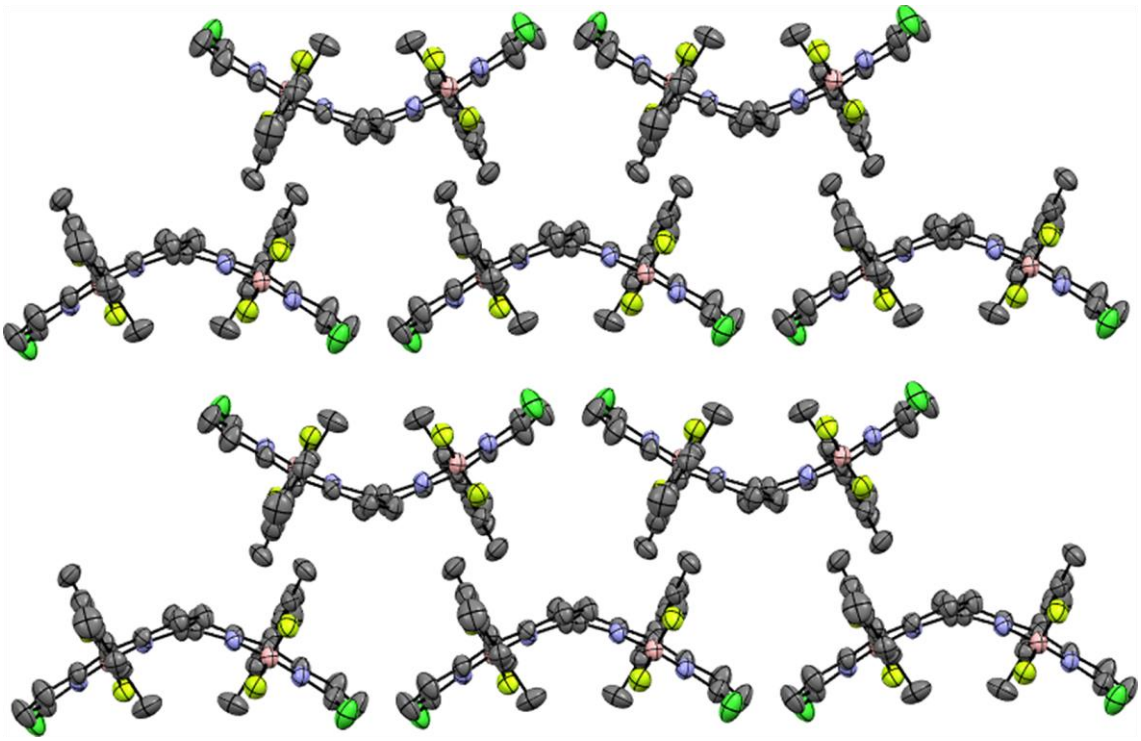
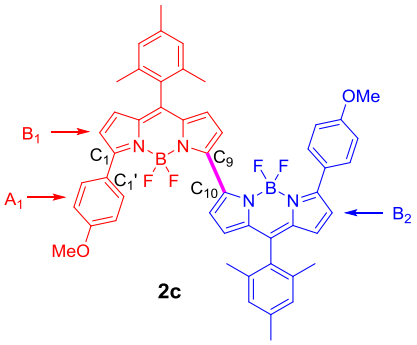
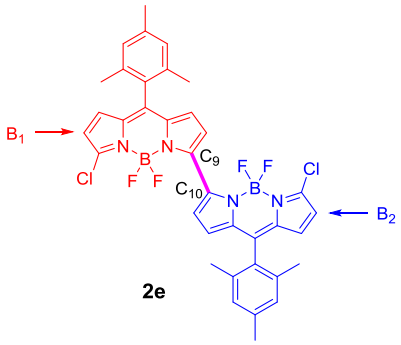


Figure S2. The packing of dimer **2e**: C, gray; N, purple; B, pink; F, yellow; Cl, green. Hydrogen atoms were removed for clarity. Thermal ellipsoids are shown at the 50% probability level.

Table S1. Selected geometrical parameters of compound **2c** and **2e** obtained from crystallography



2c



2e

	2c	**2e**
the C_1-C_1' bond length (Å)	1.46(4)	/
the C_9-C_{10} bond length (Å)	1.4(5)	1.45(8)
the C-O bond length (Å)	1.36(6) 1.36(6)	/
the C-Cl bond length (Å)	/	1.69(8), 1.69(8)
the B-N bond length (Å)	1.58(5), 1.56(9) 1.56(9), 1.58(5)	1.56(9), 1.56(2) 1.56(9), 1.56(2)
the B-F bond length (Å)	1.39(1), 1.37(4) 1.39(1), 137(4)	1.37(9), 1.36(9) 1.37(9), 1.36(9)
dihedral angles between *meso*-aryl and dipyrrin core in B_1 (deg)	89.53	89.00
dihedral angles between *meso*-aryl and dipyrrin core in B_2 (deg)	89.53	89.00
dihedral angles of two dipyrrin cores in B_1 and B_2 (deg)	52.67	57.21
dihedral angles between α-benzene ring and dipyrrin core in B_1 (deg)	43.00	/

Table S2. Crystal data and structure refinement for **2c** and **2e**.

Crystal data	**2c**	**2e**
CCDC number	2053912	2095140
Empirical formula	$C_{50}H_{44}B_2F_4N_4O_2$	$C_{36}H_{30}B_2Cl_2F_4N_4$
Formula weight	830.51	687.16
Temperature/K	298	298
Crystal system	orthorhombic	orthorhombic
Space group	Pbcn	Pbcn
a (Å)	15.4942(8)	15.1048(5)
b (Å)	12.4379(8)	12.2629(4)
c (Å)	25.9022(17)	18.3629(6)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
Volume ($Å^{3)}$	4991.8(5)	3401.34(2)
Z	4	4
ρ_{calc} g/cm^3	1.105	1.342
μ ($mm^{-1)}$	0.077	0.245
F(000)	1736.0	1416.0
Crystal size ($mm^{3)}$	0.21 × 0.22 × 0.19	0.18 × 0.20 × 0.21
Radiation	MoKα, (λ = 0.71073)	MoKα, (λ = 0.71073)
2θ range for data collection/°	3.144 to 55.096	6.164 to 55.07
Index ranges	-17 ≤ h ≤ 19, -16 ≤ k ≤ 16, -33 ≤ l ≤ 33	-19 ≤ h ≤ 18, -15 ≤ k ≤ 15, -23 ≤ l ≤ 23
Reflections collected	131551	39671
Independent reflections	5589 [R_{int} = 0.1002, R_{sigma} = 0.0271]	3874 [R_{int} = 0.1094, R_{sigma} = 0.0394]
Data/restraints/parameters	5589/0/284	3874/0/220
Goodness-of-fit on F^2	1.103	1.110
Final R indexes [I>=2σ (I)]	R_1 = 0.0846 wR_2 = 0.2539	R_1 = 0.0713 wR_2 = 0.1365
Final R indexes [all data]	R_1 = 0.1135 wR_2 = 0.2974	R_1 = 0.0892 wR_2 = 0.1492
Largest diff. peak/hole / e $Å^{-3}$	0.60/-0.49	0.32/-0.35

4. Photophysical properties

Table S3. Spectroscopic and photophysical properties of BODIPYs in different solvents.

dyes	solvent	λ_{abs}^{max} (nm)	ε^{a}	λ_{em}^{max} (nm)	Φ^{b}	Stokes shift (cm^{-1})
1a	Toluene	531	62000	552	0.85	720
	CH_2Cl_2	527	66300	549	0.87	760
2a	Cyclohexane	723	56600	752	0.30	530
	Toluene	718	57100	776	0.33	1040
	THF	717	59700	773	0.30	1010
	$CHCl_3$	717	51400	768	0.37	930
	CH_3CN	693	49100	772	0.31	1480
2b	Cyclohexane	735	59500	789	0.13	930
	Toluene	726	60000	784	0.21	1020
	THF	729	64600	780	0.15	900
	$CHCl_3$	726	51200	789	0.16	1100
	CH_3CN	699	53300	767	0.13	1270
2c	Cyclohexane	739	58400	797	0.21	990
	Toluene	736	57300	799	0.19	1070
	THF	738	62800	797	0.14	1000
	$CHCl_3$	736	46600	797	0.19	1040
	CH_3CN	715	50300	782	0.15	1200
2d	Cyclohexane	726	46500	777	0.23	900
	Toluene	723	47100	777	0.25	960
	THF	722	49800	778	0.25	1000
	$CHCl_3$	719	40200	780	0.24	1090
	CH_3CN	698	41000	785	0.20	1590
2e	Cyclohexane	687	78900	729	0.45	840
	Toluene	688	74900	732	0.51	870
	THF	680	76700	725	0.42	910
	$CHCl_3$	685	68300	729	0.54	880
	CH_3CN	663	63600	713	0.30	1060
2f	Cyclohexane	796	58700	834	0.02	570
	Toluene	773	55000	827	0.03	850
	THF	785	70600	829	0.01	680
	$CHCl_3$	784	51800	829	0.02	700
	CH_3CN	760	55800	821	0.02	980

	Cyclohexane	667	51900	740	0.17	1480
	Toluene	673	51200	736	0.21	1270
2g	THF	649	52300	724	0.18	1600
	$CHCl_3$	656	45500	734	0.20	1620
	CH_3CN	615	46800	710	0.17	2180

[a]Data corresponding to the strongest absorption maximum, the unit for ε is M^{-1} cm^{-1}. [b]Fluorescence quantum yields of **2a-e** and **2g** were calculated using 1,7-diphenyl-3,5-di(4-methoxyphenyl)-azadipyrromethene (Φ = 0.36 in chloroform) as the reference. Fluorescence quantum yields of **2f** was calculated using Indocyanine Green (Φ = 0.12 in DMSO) as the reference. The standard errors are less than 5% from three independent measurements.

Absorption and emission spectra of BODIPY 1a and all BODIPY dimers at different solvents

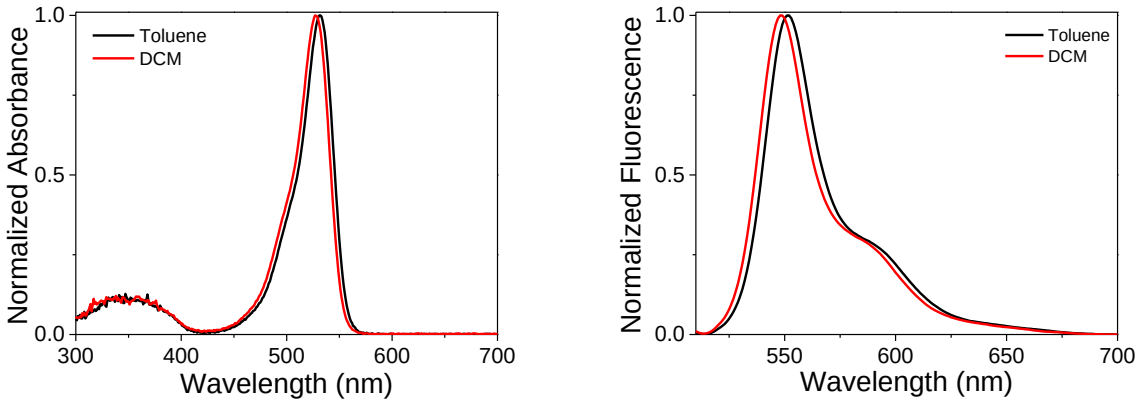


Figure S3. Absorption (left) and emission (right) spectra of compound **1a** recorded in different solvents. Excited at 500 nm.

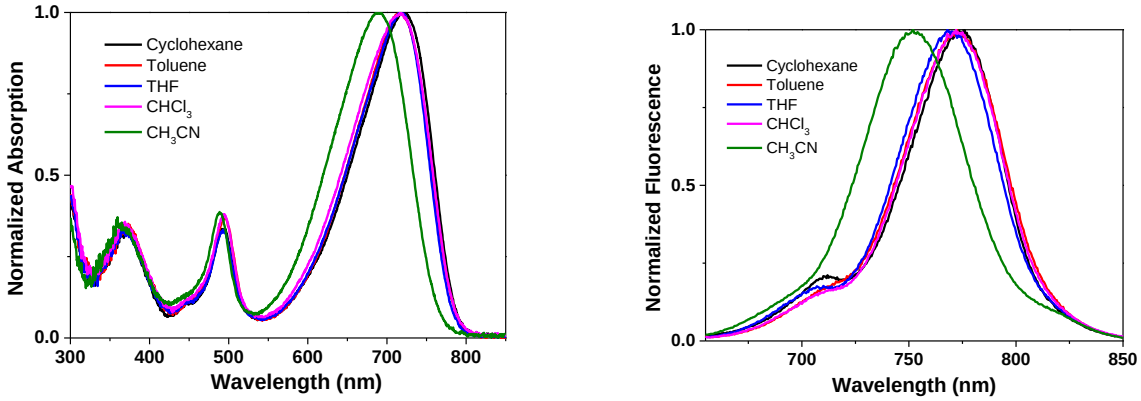


Figure S4. Absorption (left) and emission (right) spectra of compound **2a** recorded in different solvents. Excited at 655 nm.

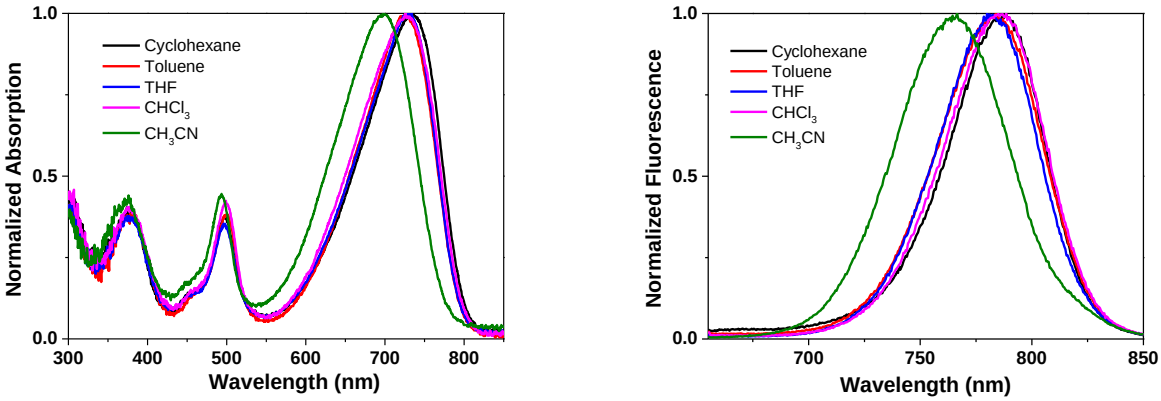


Figure S5. Absorption (left) and emission (right) spectra of compound **2b** recorded in different solvents. Excited at 655 nm.

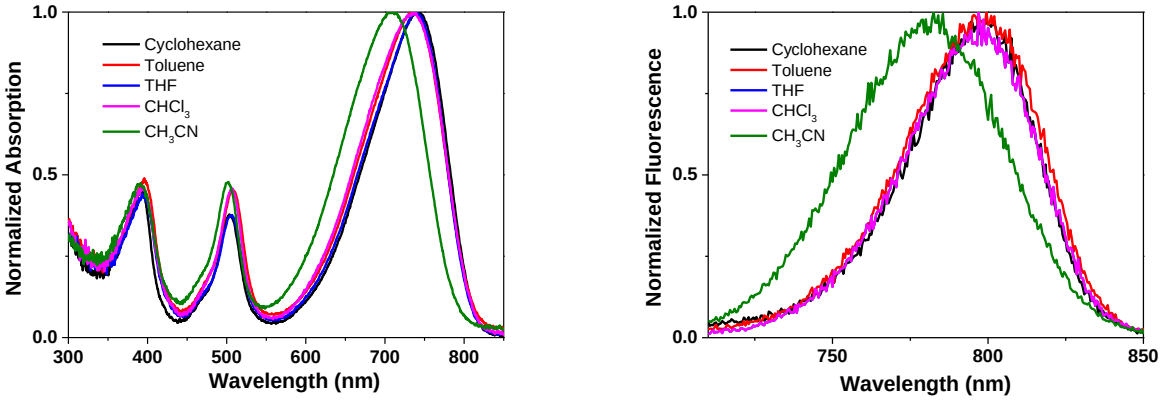


Figure S6. Absorption (left) and emission (right) spectra of compound **2c** recorded in different solvents. Excited at 655 nm.

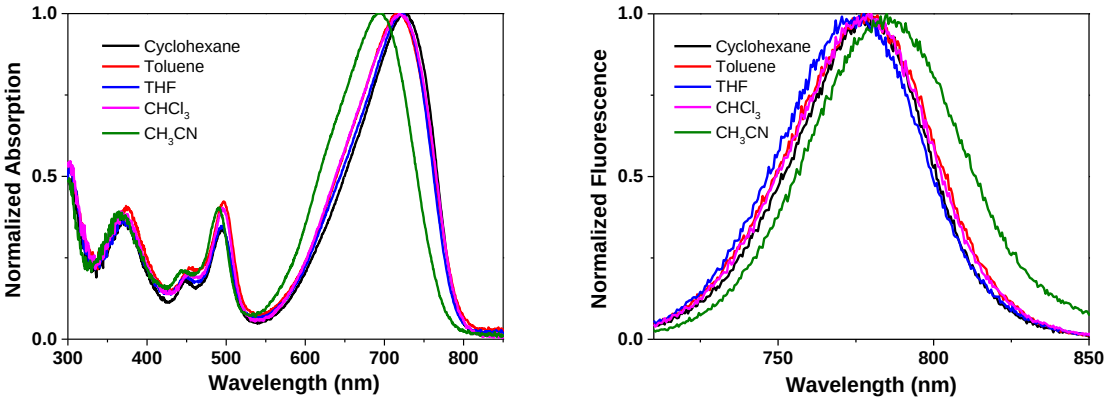


Figure S7. Absorption (left) and emission (right) spectra of compound **2d** recorded in different solvents. Excited at 655 nm.

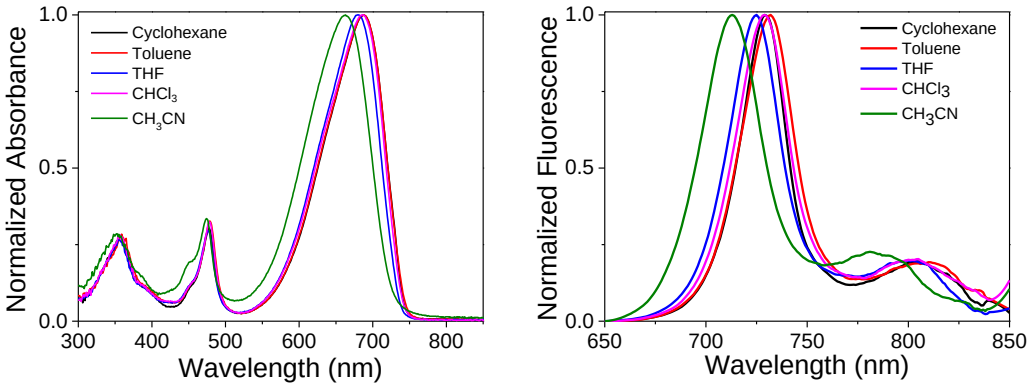


Figure S8. Absorption (left) and emission (right) spectra of compound **2e** recorded in different solvents. Excited at 640 nm.

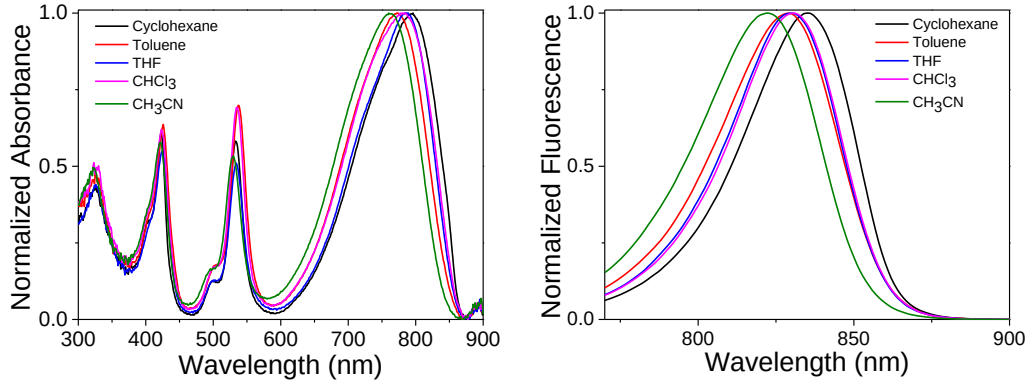


Figure S9. Absorption (left) and emission (right) spectra of compound **2f** recorded in different solvents, excited at 760 nm.

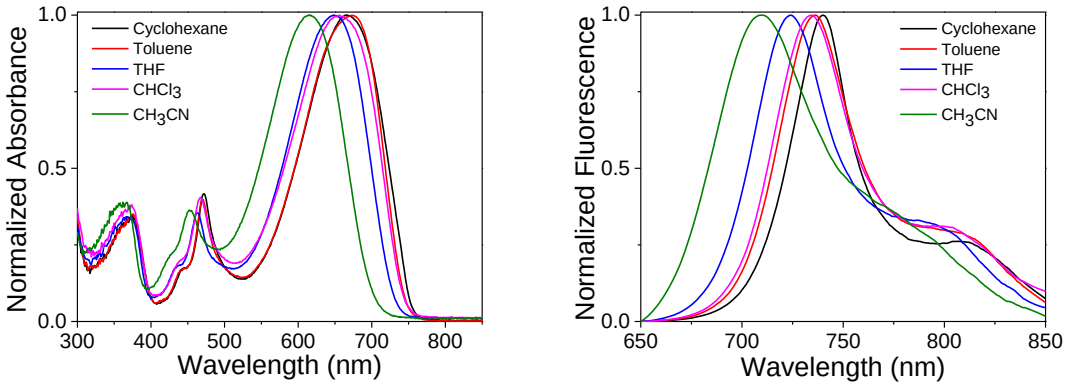


Figure S10. Absorption (left) and emission (right) spectra of compound **2g** recorded in different solvents. Excited at 640 nm.

5. Electrochemical spectra

Table S4. Electrochemical data acquired at 100 mV/s, and HOMO-LUMO Gaps determined from spectroscopy of dyes M, 1a and 2a[a]

dyes	$E_{1/2}^{red}$ (V)	E_{red}^{onest} (V)	E_p^{ox} (V)	E_{ox}^{onest} (V)	LUMO (eV)	HOMO (eV)	E_g^e (eV)	E_g^o (eV)
M	-0.93	-0.86	1.71	1.46	-3.94	-6.26	2.32	2.38
1a	-0.93	-0.74	1.51	1.31	-4.06	-6.11	2.05	2.23
2a	-0.59; -1.08	-0.51	1.09	1.05	-4.29	-5.85	1.56	1.55

[a] $E_{1/2}^{red}$ = reversible reduction peak potentials; E_p^{ox} = oxidation peak potentials; E_{red}^{onset} = the onset reduction potentials; E_{ox}^{onset} = the onset oxidation potentials; E_{LUMO} = -e(E_{red}^{onset} + 4.8); E_{HOMO} = -e(E_{ox}^{onset} + 4.8); 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. DFT calculation

The ground state geometry was optimized by using DFT method at B3LYP/6-31G(d, p) 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/6-31G (d, p) theoretical level. The calculated molecules in dichloromethane were done using the Self-Consistent Reaction Field (SCRF) method and Polarizable Continuum Model (PCM). All of the calculations were carried out by the methods implemented in Gaussian 09 package[10].

The Mulliken spin density calculations and the natural population analysis were performed at the B3LYP/6-311G(d, p) level on the basis of the optimized structures.[11] The natural population analysis values cation radical **M** and **1a** are presented in Figure S11.

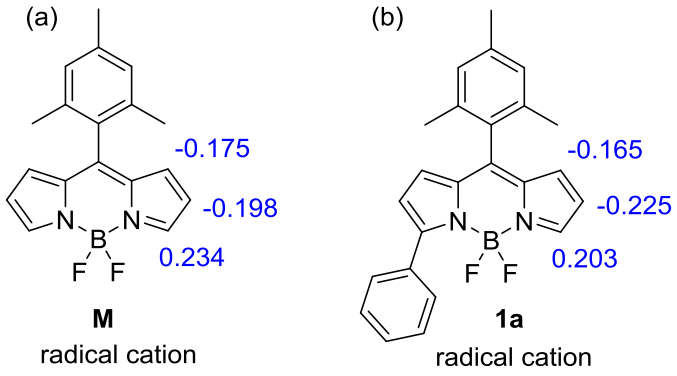


Figure S11. The natural population analysis values (charge density distributions) for cation radicals of **M** and **1a**.

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

	Electronic transition	TD//B3LYP/6-31G(d, p)			
		Energy/ eV [a]	*f* [b]	Composition [c]	CI [d]
M	S0→S1	2.9248 eV 423.90 nm	0.0000	HOMO → LUMO +1	0.7050
	S0→S2	3.0107 eV 411.81 nm	0.4328	HOMO → LUMO	0.6710
				HOMO ← LUMO	0.1013
	S0→S3	3.0719 eV 403.61 nm	0.0206	HOMO → LUMO	0.1300
				HOMO -2 → LUMO	0.6935
1a	S0→S1	2.7165 eV 456.41 nm	0.6870	HOMO → LUMO	0.7023
	S0→S2	2.9416 eV 421.49 nm	0.0017	HOMO -1 → LUMO	0.7046
	S0→S3	3.0824 eV 402.24 nm	0.0007	HOMO -2 → LUMO	0.7064
2a	S0→S1	1.8995 eV 652.72 nm	1.0060	HOMO → LUMO	0.7078
	S0→S2	2.4164 eV 513.09 nm	0.0001	HOMO -1 → LUMO	0.4812
				HOMO → LUMO +1	0.5154
	S0→S3	2.7480 eV 451.19 nm	0.0005	HOMO -2 → LUMO	0.6765
				HOMO -3 → LUMO +1	0.1943

[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.

Optimized Geometries of the Compounds

M, optimized S_0 state Geometry.

B	-14.90043263	9.54503278	8.96819373
C	-12.38363263	8.78123278	9.38569373
C	-11.31223263	8.37723278	8.57089373
C	-11.76183263	8.36403278	7.27739373
C	-13.09453263	8.79003278	7.28749373
C	-13.93833263	9.01853278	6.19809373
C	-15.20683263	9.53733278	6.38869373
C	-16.24083263	9.85193278	5.48189373
C	-17.30593263	10.29893278	6.22349373
C	-16.91523263	10.24823278	7.57609373
C	-13.47733263	8.65543278	4.82039373
C	-13.83513263	7.40703278	4.29449373
C	-13.35433263	7.06923278	3.02979373
C	-12.55663263	7.92143278	2.29739373
C	-12.27263263	9.16753278	2.81599373
C	-12.69673263	9.55503278	4.08979373
C	-14.67243263	6.41583278	5.05579373
C	-11.96703263	7.46663278	0.97959373
C	-12.27323263	10.88513278	4.64939373
F	-15.60783263	8.51413278	9.61579373
F	-14.89513263	10.58043278	9.75829373
N	-13.47153263	9.03623278	8.60639373
N	-15.66123263	9.81113278	7.67209373

H	-10.45473263	8.15983278	8.85749373
H	-11.27003263	8.11453278	6.52829373
H	-16.20733263	9.77243278	4.55689373
H	-18.12843263	10.58153278	5.89589373
H	-17.45433263	10.48443278	8.29639373
H	-13.57893263	6.24253278	2.66889373
H	-11.78383263	9.76913278	2.30189373
H	-14.92673263	5.69723278	4.47199373
H	-15.46033263	6.85183278	5.38789373
H	-14.16503263	6.06593278	5.79129373
H	-12.01633263	8.18193278	0.34269373
H	-12.46093263	6.71163278	0.65199373
H	-11.04943263	7.21603278	1.10849373
H	-13.01703263	11.29683278	5.09369373
H	-11.97423263	11.45133278	3.93359373
H	-11.55763263	10.75593278	5.27569373
H	-12.35014323	8.87400022	10.45113855

SCF done: -1030.41688463 Hartree
No imaginary Frequency.

1a, optimized S_0 state Geometry.

B	-1.63866900	1.52017400	-0.12607000
C	-0.14387100	3.59890200	0.23405800
C	1.24610500	3.95841800	0.27631300
C	1.95865400	2.79366400	0.16240100
C	0.99975000	1.72292000	0.06296000
C	1.18156400	0.34812700	-0.01151800
C	0.03624900	-0.49206500	-0.02638300
C	0.02085500	-1.92288800	0.08686100
C	-1.28664100	-2.29782800	0.16238500
C	-2.10131200	-1.09968600	0.04965800
C	2.54907900	-0.25061000	-0.02745500
C	3.25885600	-0.41503600	1.18300700
C	4.53262800	-0.98747900	1.13040200
C	5.12150000	-1.38603200	-0.07412200
C	4.39181800	-1.21020300	-1.25454100
C	3.11162300	-0.65108200	-1.26023600
C	2.67205600	-0.01029100	2.51840100
C	6.51356100	-1.96817500	-0.10151200
C	2.37195400	-0.47149500	-2.56802100
F	-2.52558000	1.84546800	0.86412100
F	-2.09116300	1.84066600	-1.39173500
N	-0.28165700	2.28378700	0.10845000
N	-1.26768200	-0.02243200	-0.06068100
H	1.62644400	4.96521900	0.37873200
H	3.03146800	2.66136700	0.15532300
H	0.90214700	-2.54747600	0.11616200
H	-1.67382600	-3.30359400	0.23530800
H	5.07848000	-1.12911400	2.06015900
H	4.83077300	-1.51651800	-2.20104800
H	3.31929700	-0.33483800	3.33708400
H	1.68211100	-0.45163600	2.68577800
H	2.55663700	1.07707800	2.60616000
H	6.64227300	-2.66247700	-0.93755100
H	6.74387000	-2.50156400	0.82589600
H	7.26457000	-1.17595200	-0.21708800
H	1.43660700	-1.04438700	-2.59668900

H	2.98537900	-0.80690700	-3.40801800
H	2.10993200	0.57807500	-2.74945900
H	-1.01026800	4.24701100	0.28302100
C	-3.54039900	-1.10044000	0.02949400
C	-4.31394500	-0.08661700	-0.59663500
C	-4.21576400	-2.19438700	0.64160400
C	-5.69695600	-0.16673600	-0.59206600
H	-3.82382300	0.72339600	-1.11847900
C	-5.59830700	-2.24950900	0.65909300
H	-3.64727100	-2.97047700	1.14180600
C	-6.34484300	-1.23696100	0.03955600
H	-6.27929100	0.60292200	-1.08832600
H	-6.10169300	-3.07557300	1.15089700
H	-7.42970300	-1.28717100	0.04261000

SCF done: -1261.48392383 Hartree
No imaginary Frequency.

2a, optimized S_0 state Geometry.

B	1.98130200	-1.84158100	0.18692000
C	0.66094800	0.30354700	1.00823900
C	0.99315900	1.61721900	1.43215000
C	2.36664100	1.74017200	1.36072700
C	2.87226900	0.51013300	0.87187400
C	4.18615200	0.17417200	0.50702100
C	4.45011100	-1.05105700	-0.11052000
C	5.65772800	-1.52150000	-0.68846200
C	5.37281200	-2.73080500	-1.28794500
C	3.99759600	-3.01650800	-1.05862200
C	5.29437300	1.15518800	0.73212400
C	6.01271100	1.12418400	1.94656900
C	7.04346600	2.04865500	2.14119600
C	7.37835300	2.99975100	1.17208400
C	6.65347100	3.00524500	-0.02292200
C	5.61329900	2.10088400	-0.26483200
C	5.69054600	0.11500500	3.02543200
C	8.47553800	4.00703500	1.42171700
C	4.86195000	2.15169400	-1.57607600
F	1.82000400	-2.69865500	1.29402600
F	1.06793000	-2.13062600	-0.81001300
N	1.80784100	-0.36299600	0.67527200
N	3.44711100	-1.99516200	-0.34690000
B	-1.98130100	1.84157900	0.18692300
C	-0.66095100	-0.30355000	1.00824200
C	-0.99316400	-1.61721700	1.43216500
C	-2.36664600	-1.74017000	1.36073900
C	-2.87227200	-0.51013300	0.87187900
C	-4.18615400	-0.17417100	0.50702100
C	-4.45011000	1.05105600	-0.11052300
C	-5.65772500	1.52149900	-0.68846900
C	-5.37280600	2.73080400	-1.28795200
C	-3.99759000	3.01650400	-1.05862900
C	-5.29437800	-1.15518500	0.73212500
C	-6.01272200	-1.12417200	1.94656400
C	-7.04348200	-2.04864000	2.14118900
C	-7.37836600	-2.99973900	1.17208100
C	-6.65347600	-3.00524100	-0.02292200
C	-5.61330000	-2.10088600	-0.26482900

C	-5.69056200	-0.11498900	3.02542400
C	-8.47554800	-4.00702700	1.42170800
C	-4.86194600	-2.15170200	-1.57606900
F	-1.82000600	2.69865500	1.29402700
F	-1.06792500	2.13062000	-0.81000700
N	-1.80784300	0.36299400	0.67527800
N	-3.44710900	1.99515900	-0.34690300
H	0.27479800	2.35268300	1.75532300
H	2.96673600	2.60321600	1.61023000
H	6.60406400	-1.00117600	-0.65722300
H	6.05741700	-3.38133000	-1.81236000
H	7.59905100	2.02241000	3.07573700
H	6.90173600	3.73256500	-0.79219500
H	6.34706500	0.24734100	3.88854500
H	5.81016800	-0.91204900	2.66420900
H	4.65559200	0.21170600	3.37056100
H	8.89266900	4.38426000	0.48387900
H	9.28997000	3.57343900	2.00976800
H	8.09667100	4.87073800	1.98197000
H	4.95084200	1.20995800	-2.12790000
H	5.24742400	2.95189400	-2.21210300
H	3.79266000	2.32985500	-1.42089100
H	-0.27480600	-2.35268000	1.75534400
H	-2.96674300	-2.60321200	1.61024500
H	-6.60406200	1.00117600	-0.65723100
H	-6.05741000	3.38133000	-1.81236800
H	-7.59907400	-2.02238700	3.07572600
H	-6.90173900	-3.73256300	-0.79219400
H	-6.34708600	-0.24732000	3.88853300
H	-5.81018000	0.91206400	2.66419600
H	-4.65561100	-0.21169000	3.37056000
H	-8.89294600	-4.38395700	0.48386800
H	-9.28979900	-3.57355400	2.01009700
H	-8.09658600	-4.87092100	1.98160300
H	-4.95083800	-1.20997000	-2.12790000
H	-5.24741300	-2.95190700	-2.21209300
H	-3.79265500	-2.32985800	-1.42087800
C	3.31722500	-4.23320700	-1.52598500
C	2.35924100	-4.92291400	-0.76021000
C	3.69440600	-4.76691900	-2.77427600
C	1.79367900	-6.10280700	-1.23883400
H	2.07506900	-4.54112800	0.21143600
C	3.12023900	-5.94308000	-3.24980200
H	4.42354200	-4.24124900	-3.38233600
C	2.16702100	-6.61680400	-2.48275300
H	1.06084800	-6.62683900	-0.63255700
H	3.41505100	-6.33114000	-4.22004500
H	1.72044900	-7.53569100	-2.85055600
C	-3.31721700	4.23320200	-1.52599200
C	-2.35923700	4.92291200	-0.76021400
C	-3.69438900	4.76691000	-2.77428700
C	-1.79367200	6.10280300	-1.23883800
H	-2.07507100	4.54113000	0.21143600
C	-3.12021800	5.94306800	-3.24981400
H	-4.42352100	4.24123700	-3.38235000
C	-2.16700500	6.61679500	-2.48276200
H	-1.06084400	6.62683700	-0.63255900
H	-3.41502500	6.33112400	-4.22006100

H	-1.72043100	7.53568000	-2.85056600

SCF done: -2521.77515860 Hartree
No imaginary Frequency.

M$^{+\cdot}$

B	-3.16168800	0.00258500	0.14080900
C	-2.55903400	2.51517500	-0.14497300
C	-1.39851900	3.37709600	-0.19809700
C	-0.30212800	2.56344400	-0.13539400
C	-0.78939400	1.20742500	-0.05322500
C	-0.07161500	0.00024400	-0.02705600
C	-0.79103100	-1.20611300	-0.04888700
C	-0.30553900	-2.56312000	-0.12556500
C	-1.40301200	-3.37552700	-0.18530100
C	-2.56239100	-2.51185600	-0.13570500
C	1.42110600	-0.00065600	0.00136100
C	2.08562500	0.00151800	1.24782700
C	3.48267000	-0.00388500	1.24860200
C	4.22908100	-0.00838700	0.06506000
C	3.53798900	-0.01397700	-1.15146300
C	2.14240600	-0.00883700	-1.21328700
C	1.32668700	0.00517300	2.55678900
C	5.73733000	0.01594300	0.09998600
C	1.44242200	-0.01555100	-2.55438700
F	-3.64389300	0.00507000	1.41797400
F	-4.12065000	0.00160500	-0.82723100
N	-2.19273000	1.24529500	-0.05685600
N	-2.19440400	-1.24211400	-0.05256400
H	-1.42837000	4.45507200	-0.27771600
H	0.74247200	2.84044100	-0.15632800
H	0.73869100	-2.84167500	-0.14500600
H	-1.43428200	-4.45377400	-0.26060100
H	-3.61002900	-2.78859100	-0.15686600
H	4.00237700	-0.00595200	2.20364400
H	4.10054300	-0.02389200	-2.08185100
H	2.01730100	0.00685000	3.40349900
H	0.68161000	-0.87608000	2.66310900
H	0.68299800	0.88795100	2.65859000
H	6.16724900	-0.47929900	-0.77592100
H	6.12571700	-0.47514600	0.99737000
H	6.10912700	1.04870700	0.10634900
H	0.80269400	-0.89809600	-2.68253200
H	2.16912600	-0.01919600	-3.37032500
H	0.80242900	0.86555800	-2.69065800
H	-3.60630300	2.79321100	-0.16724300

SCF done: -1030.36192126 Hartree
No imaginary Frequency.

1a$^{+\cdot}$

B	1.63866900	1.52017400	0.12607000
C	0.14387100	3.59890200	-0.23405800
C	-1.24610500	3.95841800	-0.27631300
C	-1.95865400	2.79366400	-0.16240100
C	-0.99975000	1.72292000	-0.06296000
C	-1.18156400	0.34812700	0.01151800
C	-0.03624900	-0.49206500	0.02638300
C	-0.02085500	-1.92288800	-0.08686100

C	1.28664100	-2.29782800	-0.16238500
C	2.10131200	-1.09968600	-0.04965800
C	-2.54907900	-0.25061000	0.02745500
C	-3.25885600	-0.41503600	-1.18300700
C	-4.53262800	-0.98747900	-1.13040200
C	-5.12150000	-1.38603200	0.07412200
C	-4.39181800	-1.21020300	1.25454100
C	-3.11162300	-0.65108200	1.26023600
C	-2.67205600	-0.01029100	-2.51840100
C	-6.51356100	-1.96817500	0.10151200
C	-2.37195400	-0.47149500	2.56802100
F	2.52558000	1.84546800	-0.86412100
F	2.09116300	1.84066600	1.39173500
N	0.28165700	2.28378700	-0.10845000
N	1.26768200	-0.02243200	0.06068100
H	-1.62644400	4.96521900	-0.37873200
H	-3.03146800	2.66136700	-0.15532300
H	-0.90214700	-2.54747600	-0.11616200
H	1.67382600	-3.30359400	-0.23530800
H	-5.07848000	-1.12911400	-2.06015900
H	-4.83077300	-1.51651800	2.20104800
H	-3.31929700	-0.33483800	-3.33708400
H	-1.68211100	-0.45163600	-2.68577800
H	-2.55663700	1.07707800	-2.60616000
H	-6.64227300	-2.66247700	0.93755100
H	-6.74387000	-2.50156400	-0.82589600
H	-7.26457000	-1.17595200	0.21708800
H	-1.43660700	-1.04438700	2.59668900
H	-2.98537900	-0.80690700	3.40801800
H	-2.10993200	0.57807500	2.74945900
H	1.01026800	4.24701100	-0.28302100
C	3.54039900	-1.10044000	-0.02949400
C	4.31394500	-0.08661700	0.59663500
C	4.21576400	-2.19438700	-0.64160400
C	5.69695600	-0.16673600	0.59206600
H	3.82382300	0.72339600	1.11847900
C	5.59830700	-2.24950900	-0.65909300
H	3.64727100	-2.97047700	-1.14180600
C	6.34484300	-1.23696100	-0.03955600
H	6.27929100	0.60292200	1.08832600
H	6.10169300	-3.07557300	-1.15089700
H	7.42970300	-1.28717100	-0.04261000

SCF done: -1261.49370053 Hartree

No imaginary Frequency.

7. Cellular study

Darkcytotoxicity of 2g

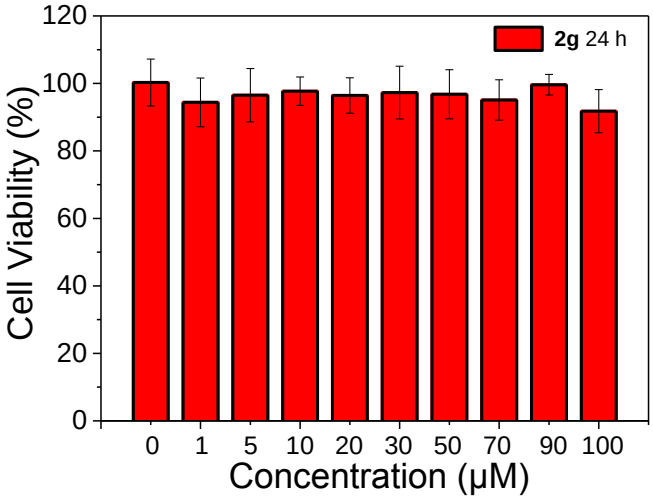
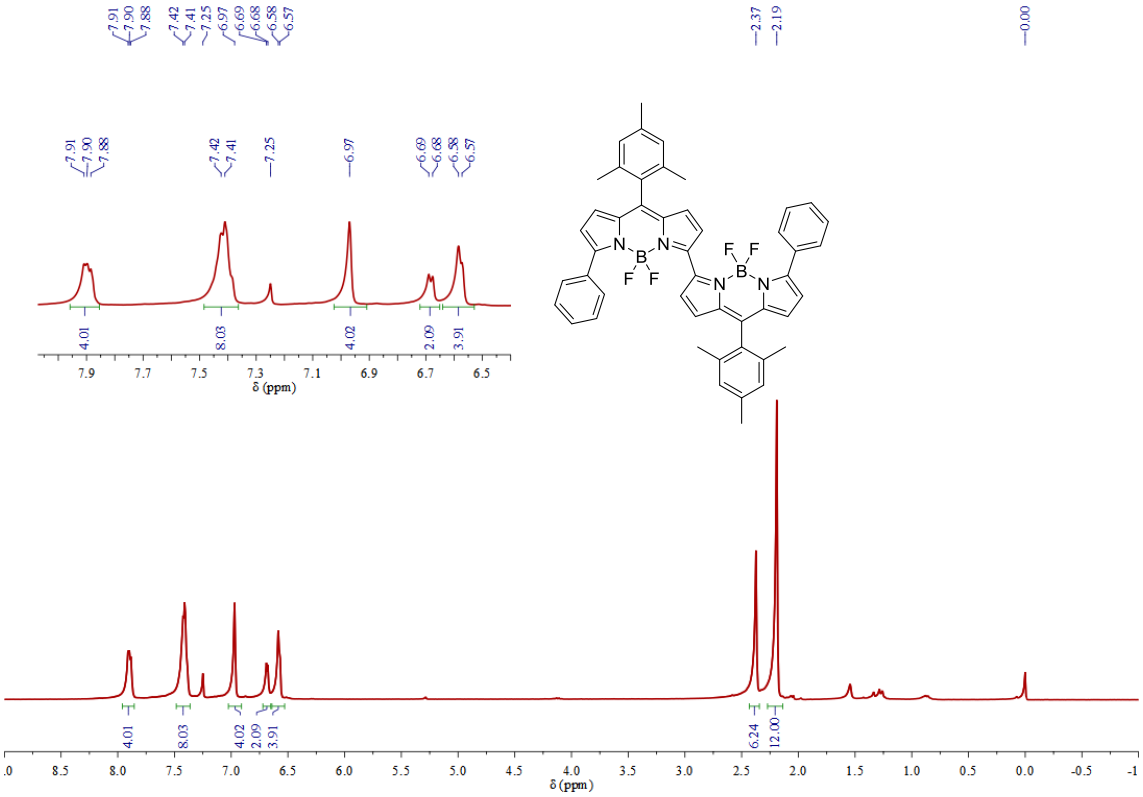


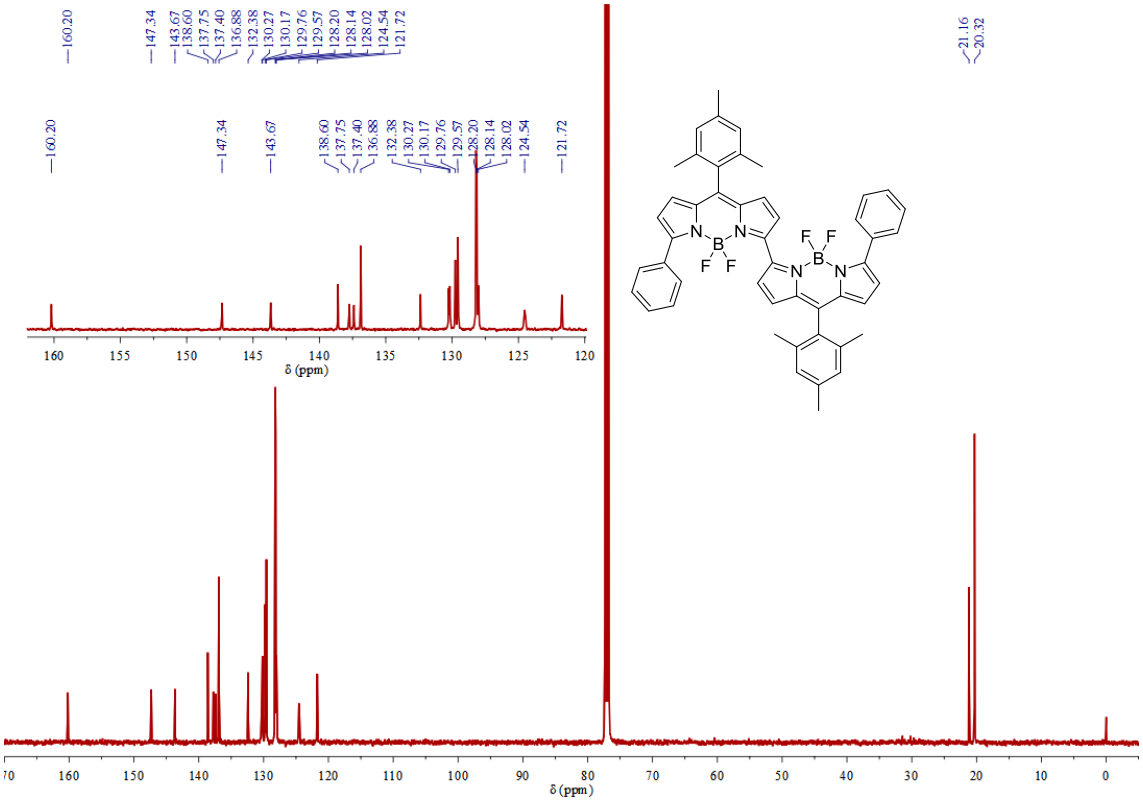
Figure S12. Cytotoxicity of HeLa cells treated with different concentrations of **2g** for 24 h as demonstrated by CCK-8 assay.

8. ^{1}H and ^{13}C NMR spectra for all new compounds

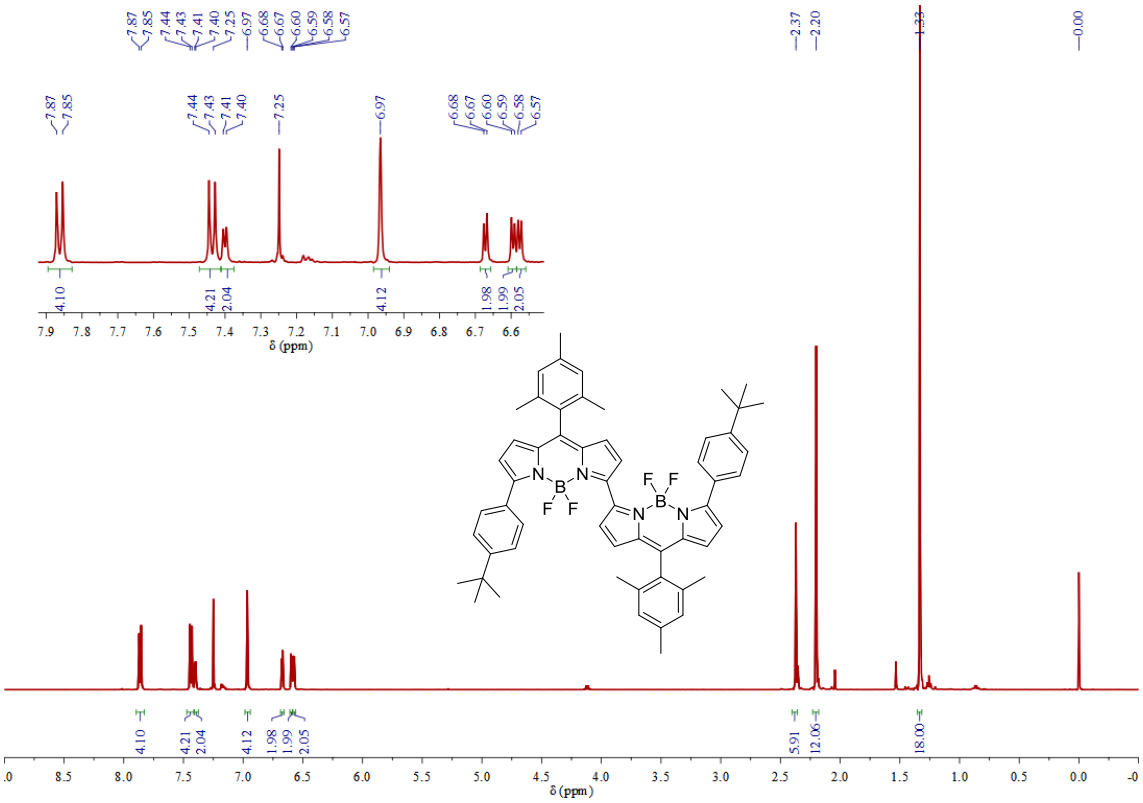
^{1}H NMR (300 MHz) spectrum of **2a** in $CDCl_3$



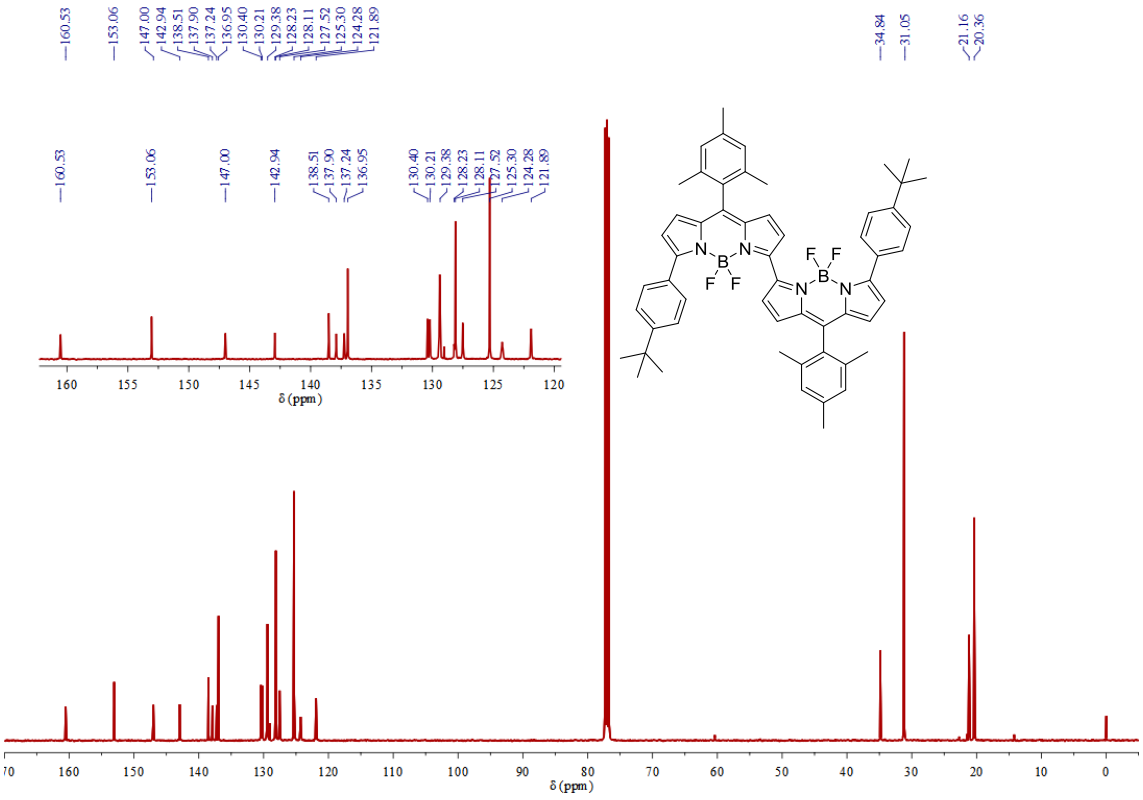
^{13}C NMR (125 MHz) spectrum of **2a** in $CDCl_3$



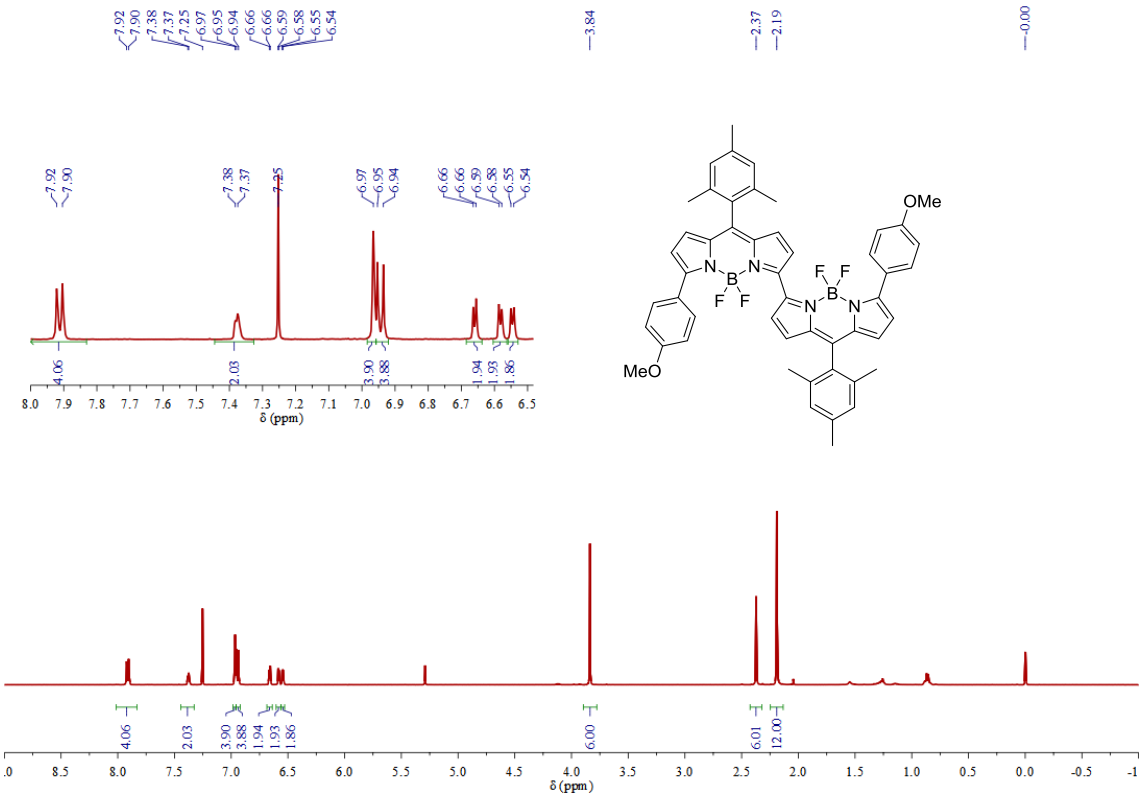
^{1}H NMR (500 MHz) spectrum of **2b** in $CDCl_3$



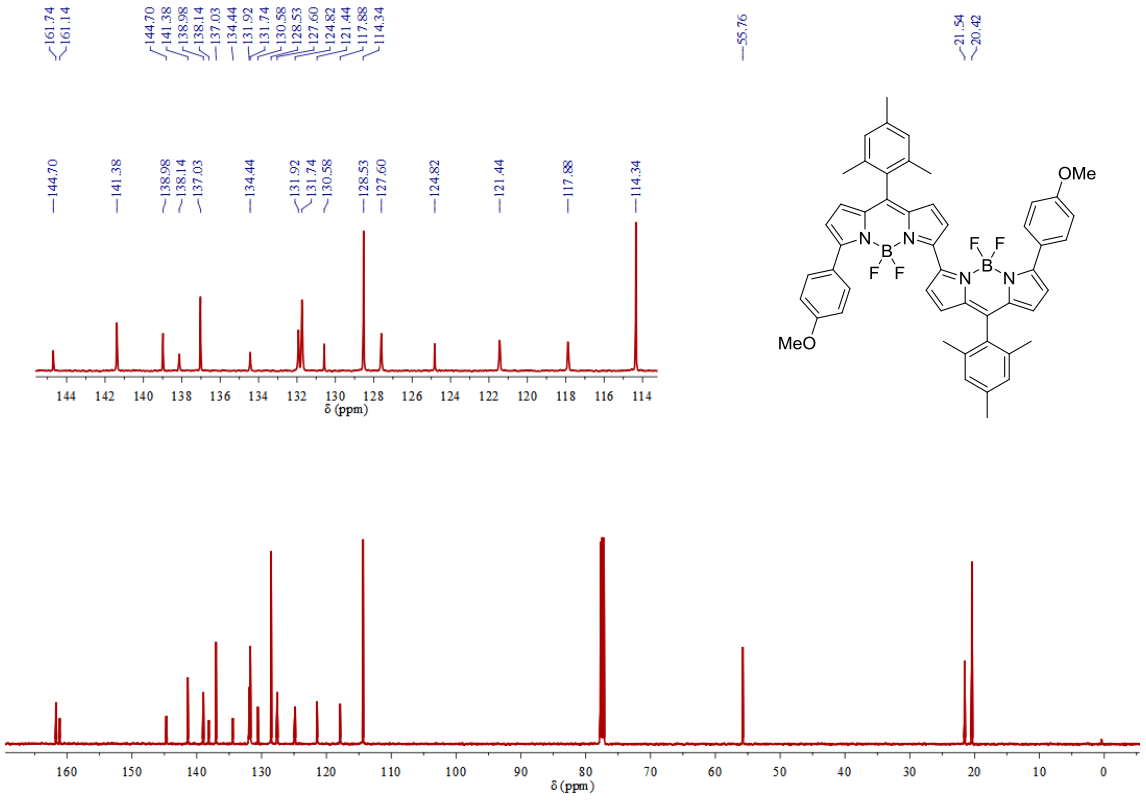
^{13}C NMR (125 MHz) spectrum of **2b** in $CDCl_3$



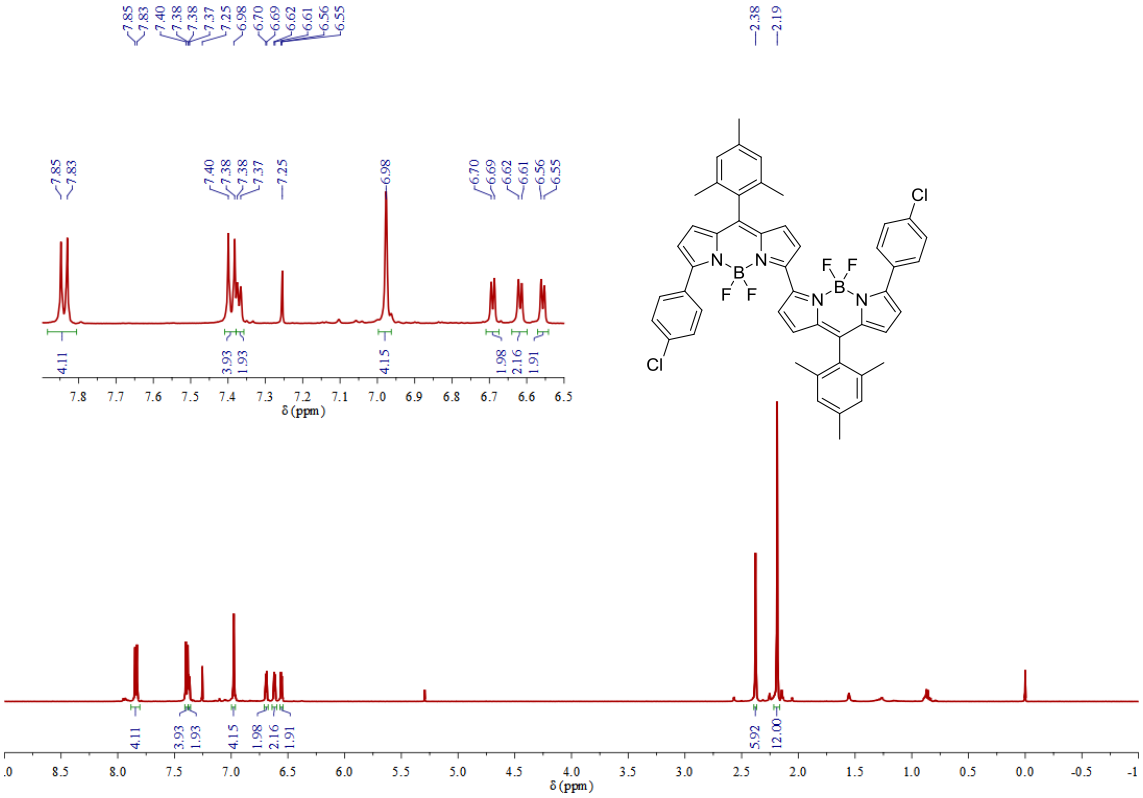
^{1}H NMR (500 MHz) spectrum of **2c** in $CDCl_3$



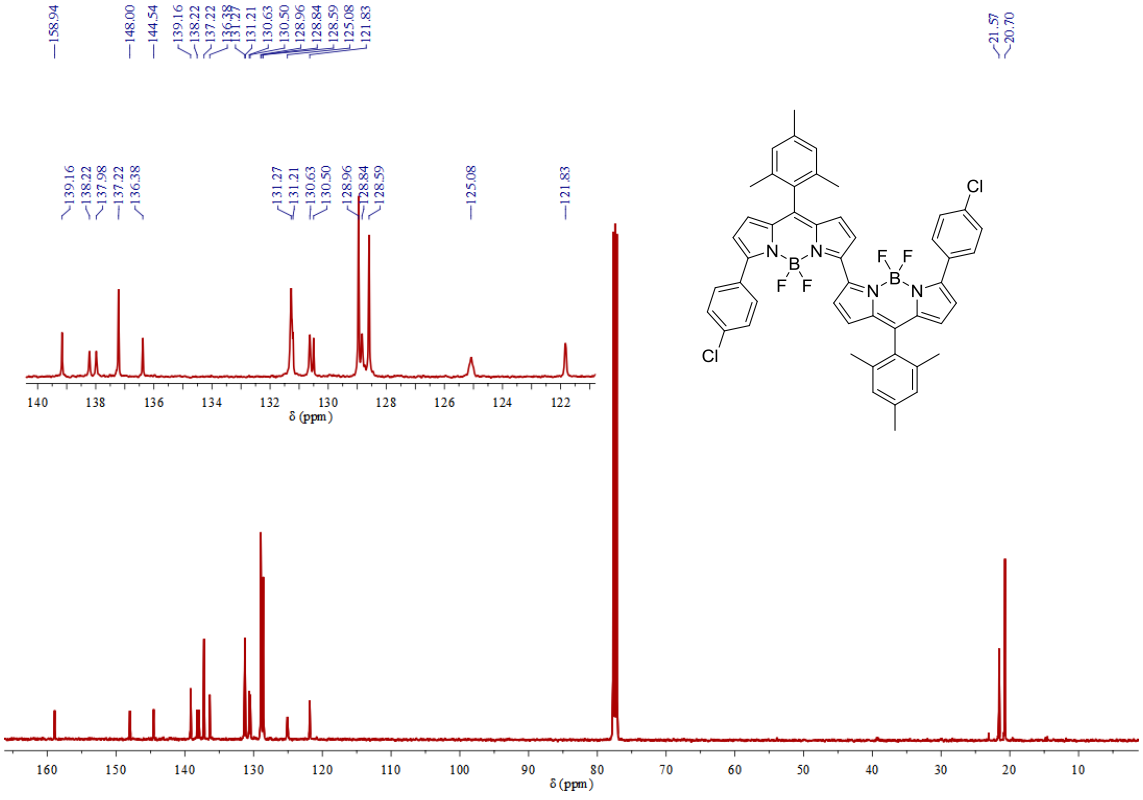
^{13}C NMR (125 MHz) spectrum of **2c** in $CDCl_3$



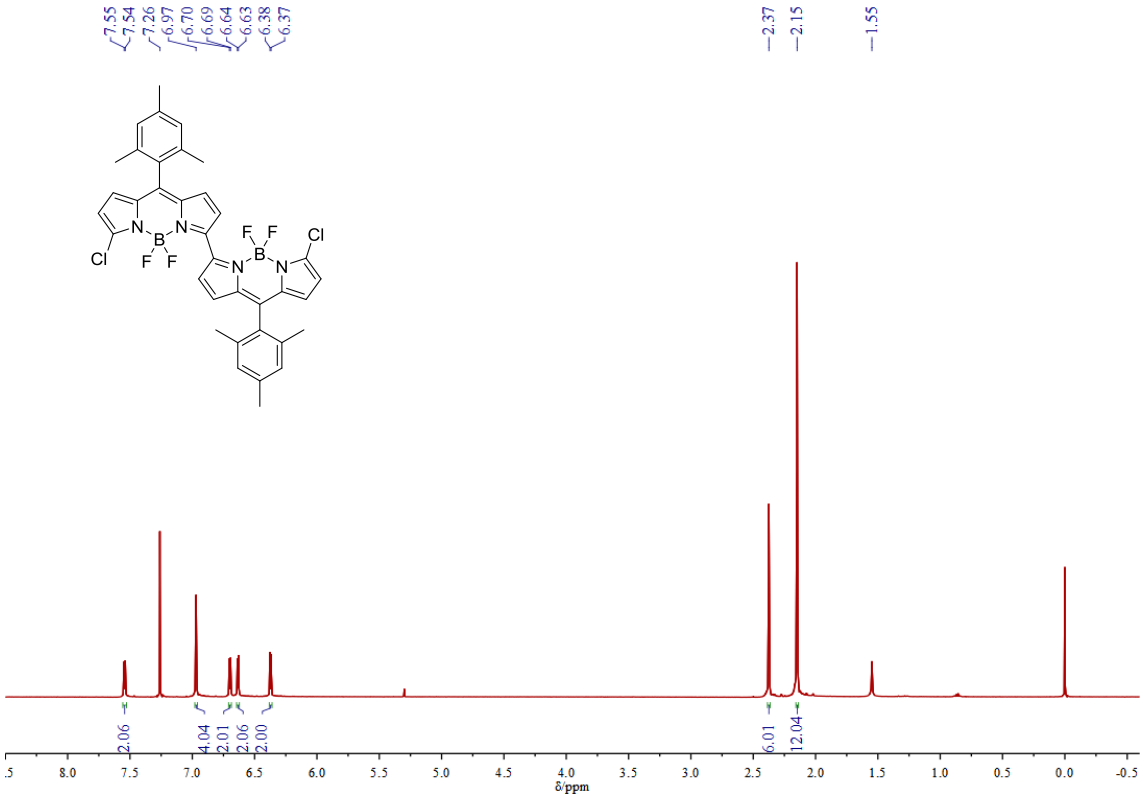
^{1}H NMR (500 MHz) spectrum of **2d** in $CDCl_3$



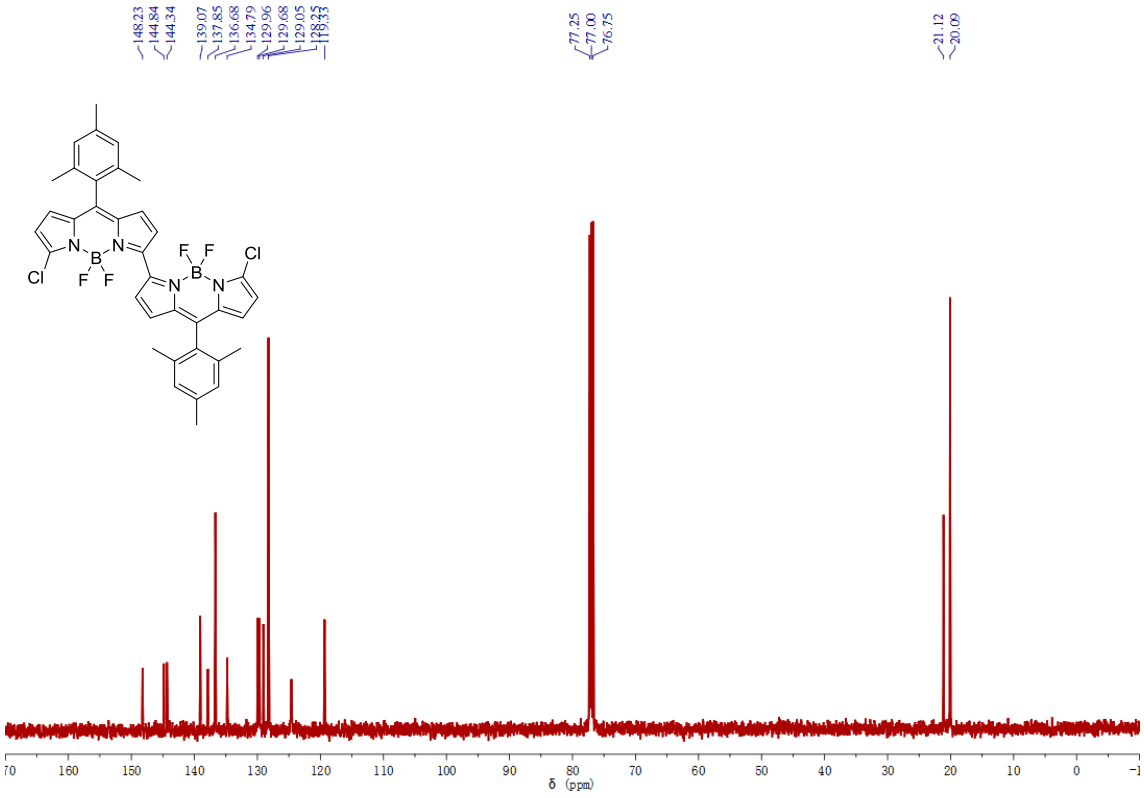
^{13}C NMR (125 MHz) spectrum of **2d** in $CDCl_3$



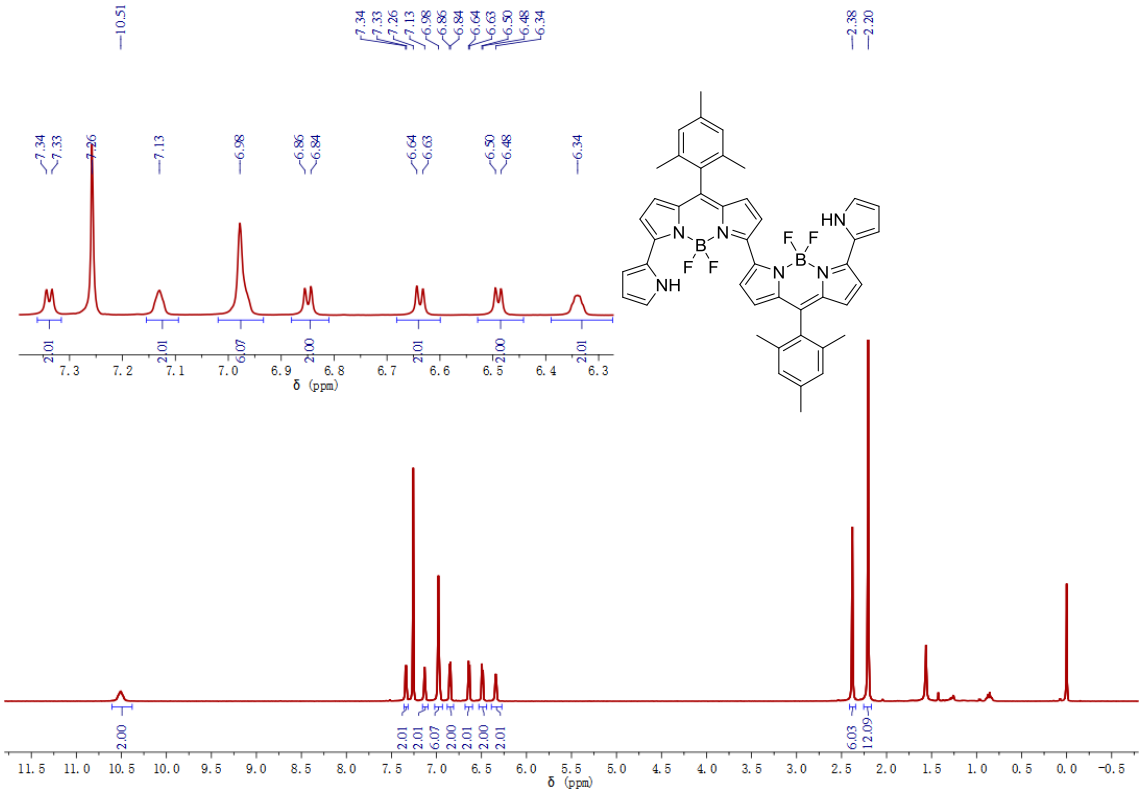
^{1}H NMR (500 MHz) spectrum of **2e** in $CDCl_3$



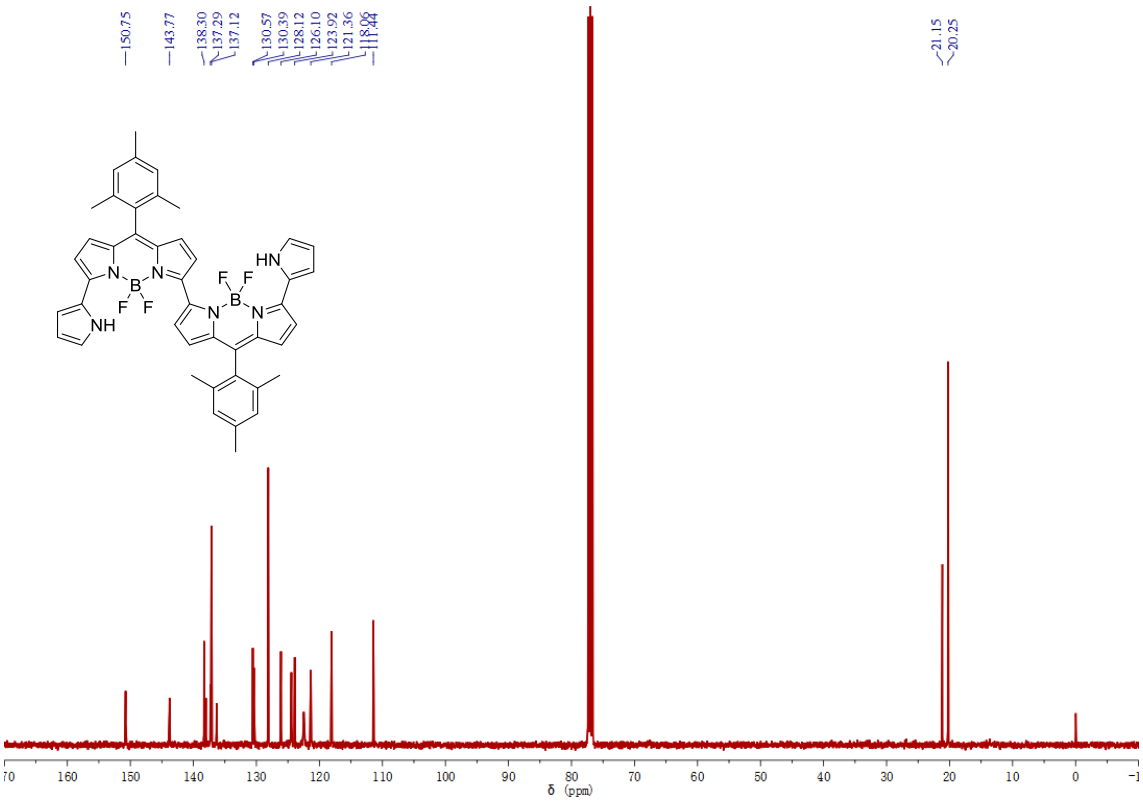
^{13}C NMR (125 MHz) spectrum of **2e** in $CDCl_3$



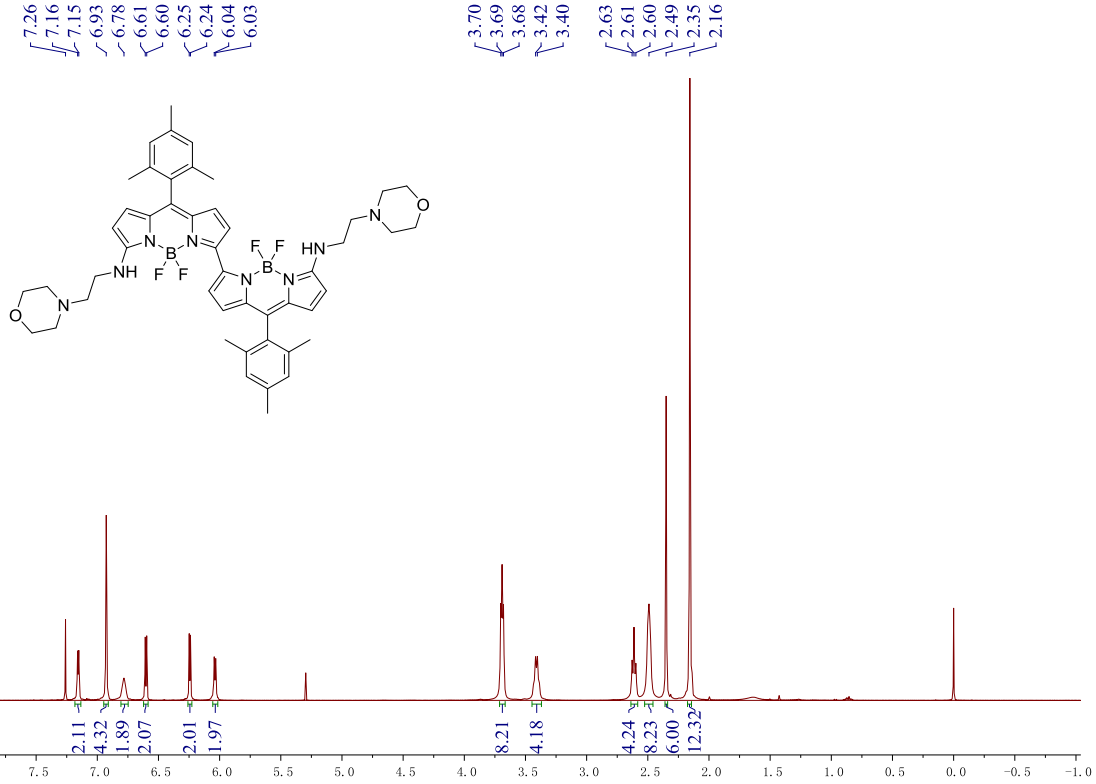
^{1}H NMR (400 MHz) spectrum of **2f** in $CDCl_3$



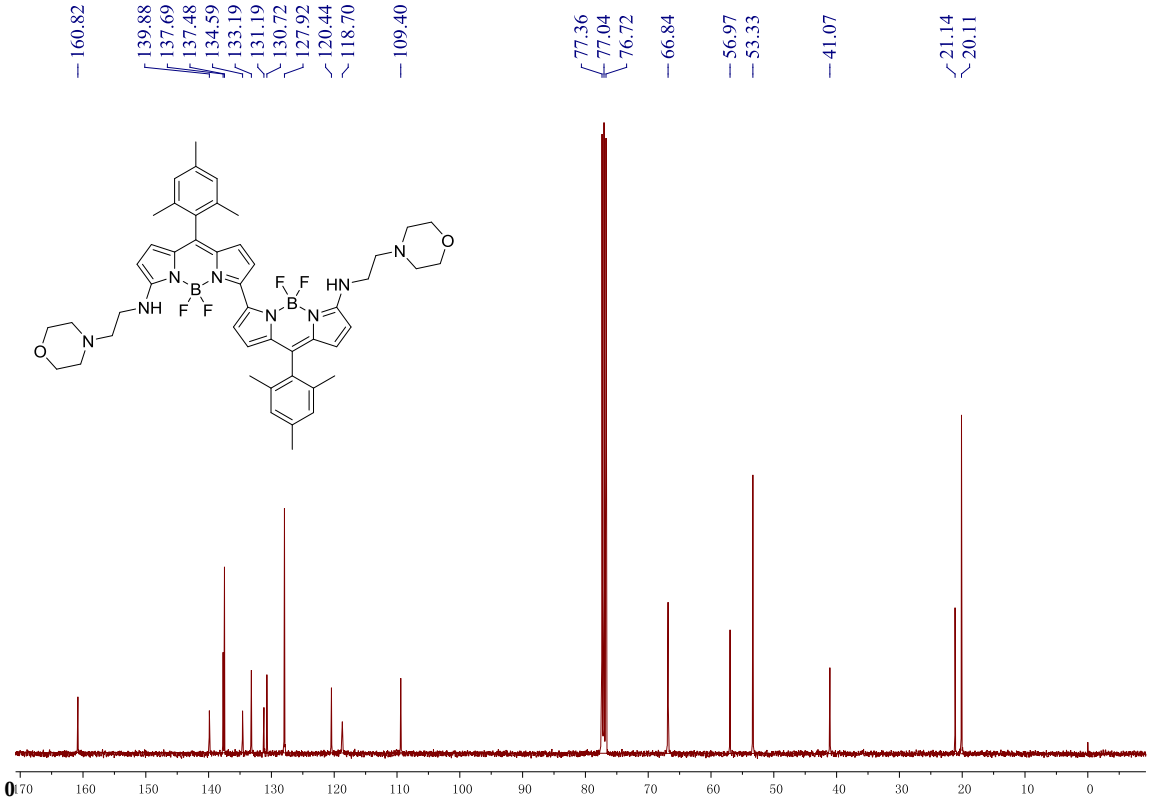
^{13}C NMR (100 MHz) spectrum of **2f** in $CDCl_3$



^{1}H NMR (400 MHz) spectrum of **2g** in $CDCl_3$

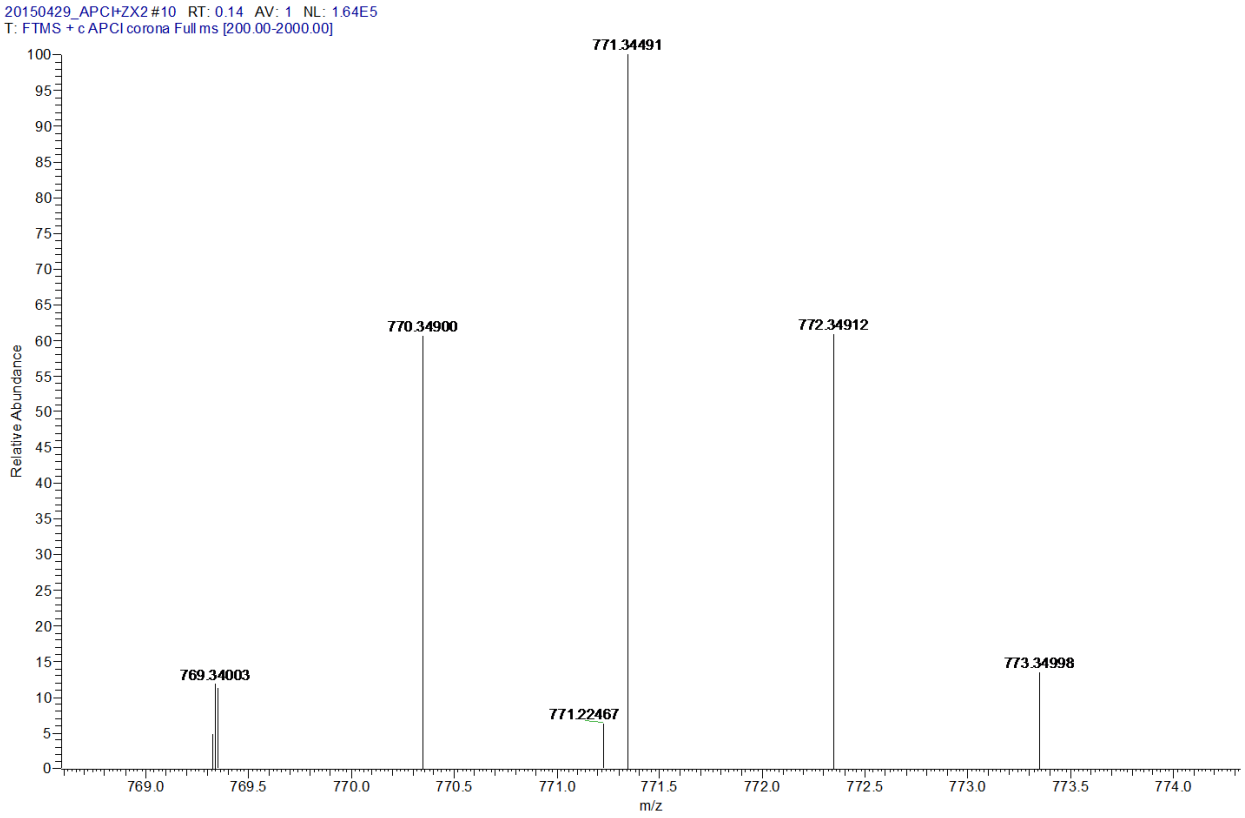


^{13}C NMR (100 MHz) spectrum of **2g** in $CDCl_3$



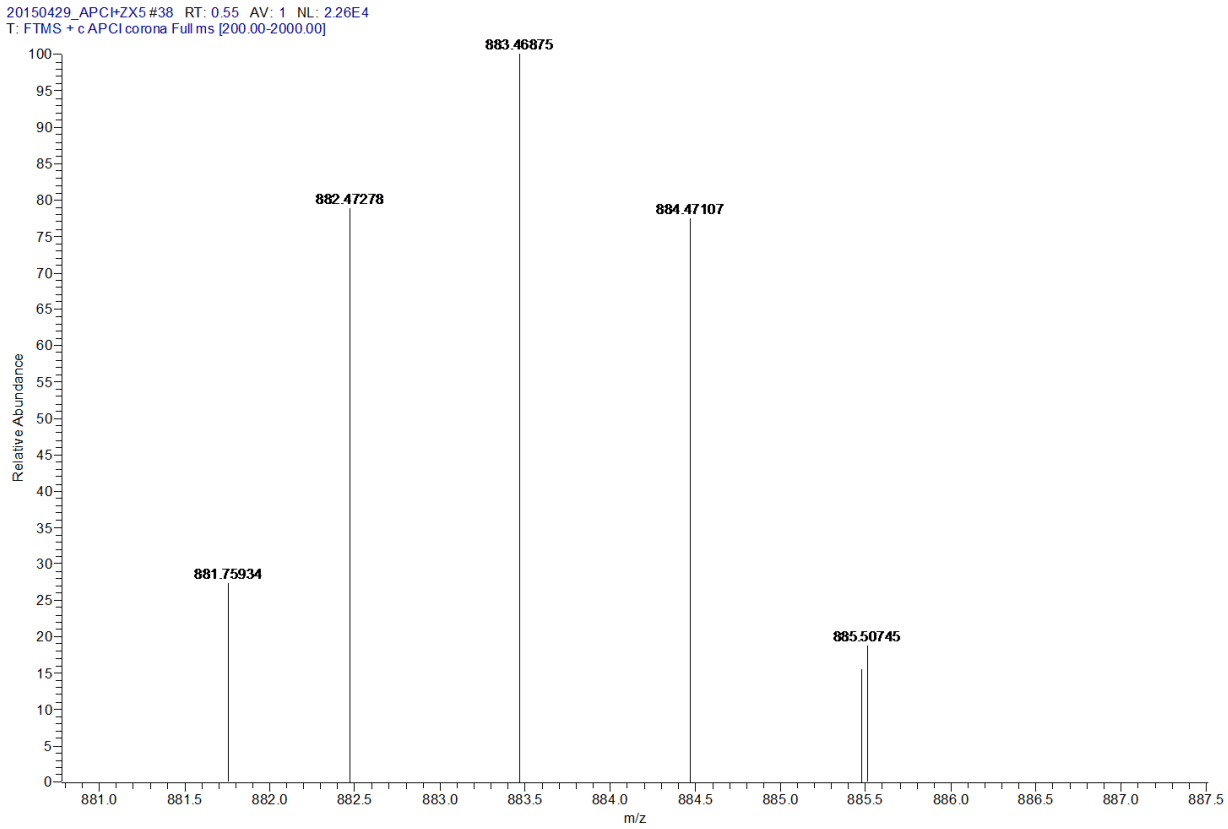
9. HRMS spectra for all new compounds

HRMS for **2a**



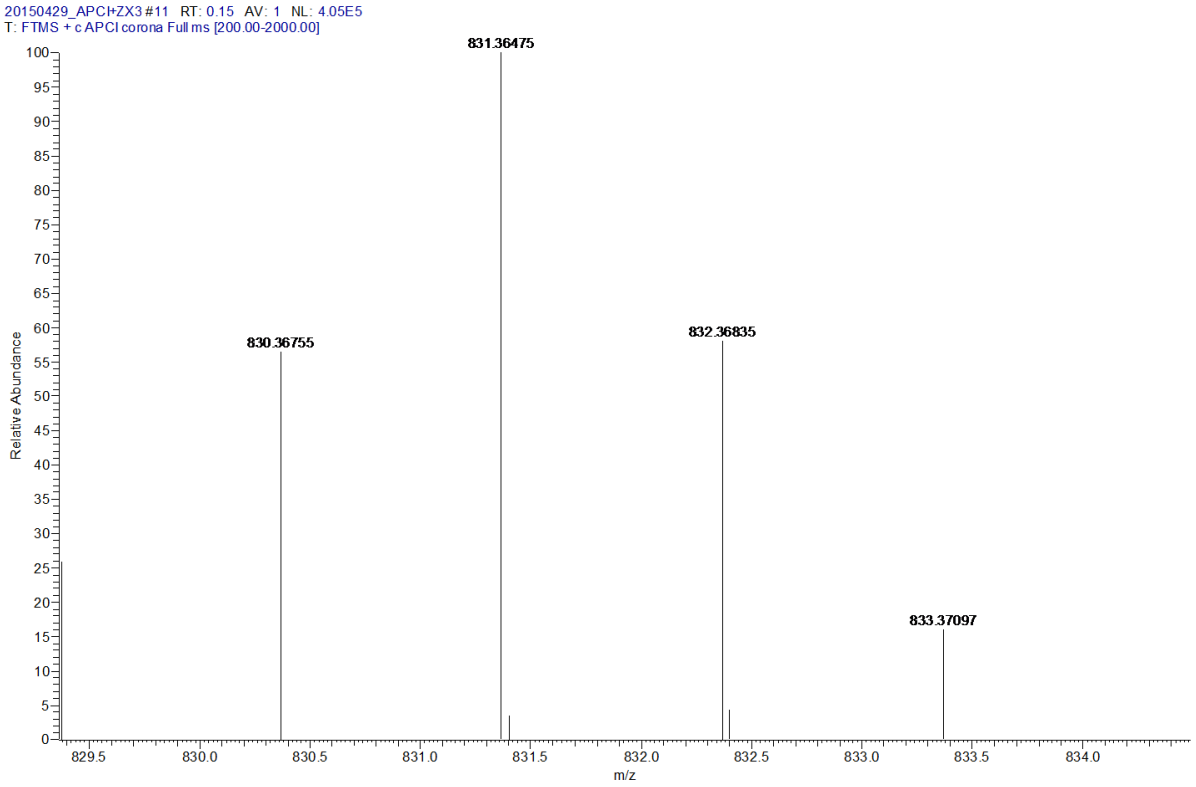
m/z	Intensity	Relative	Theo. Mass	Delta (mmu)	RDB equiv.	Composition
771.34491	163652.3	100	771.3448	0.11	28.5	$C_{48}H_{41}N_4B_2F_4$

HRMS for **2b**



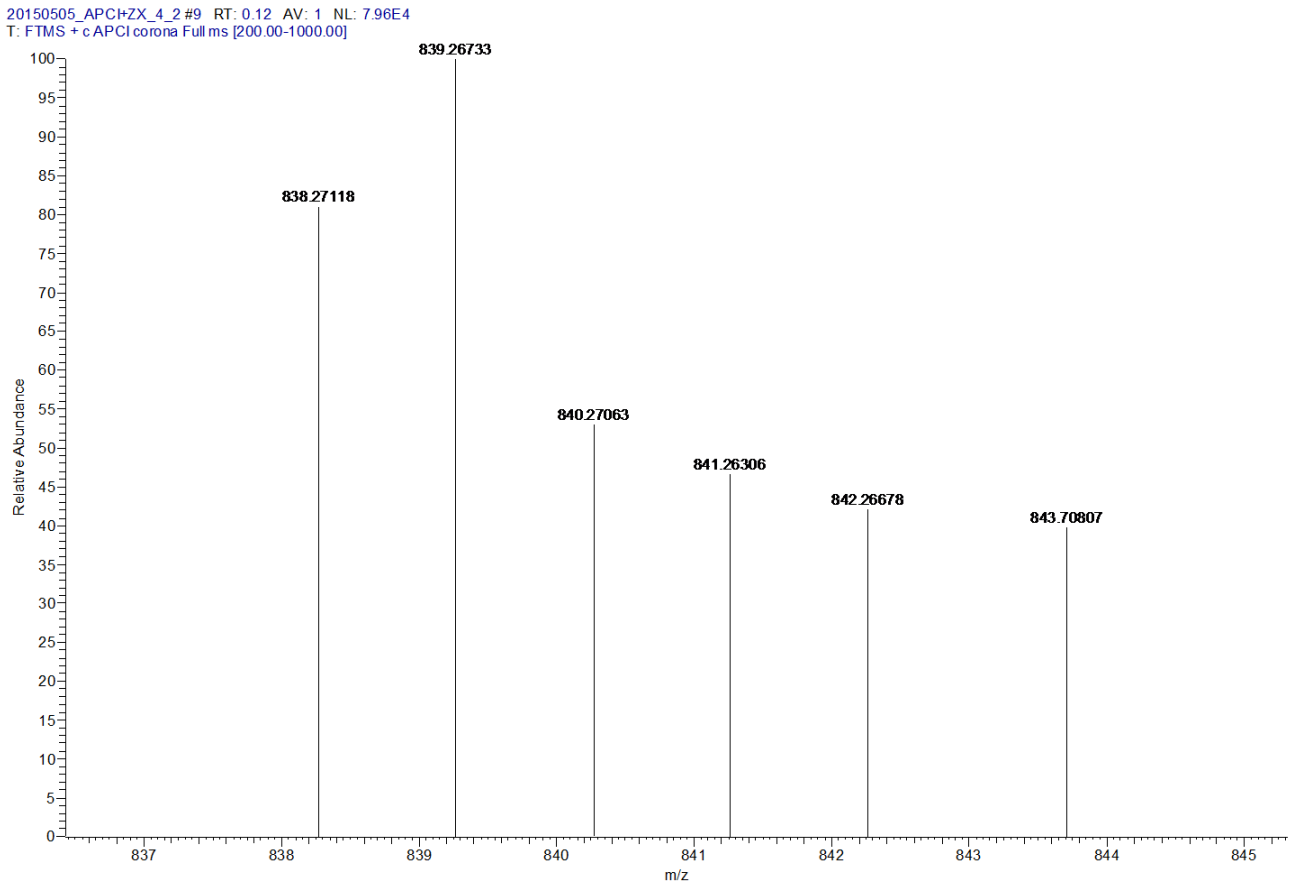
m/z	Intensity	Relative	Theo. Mass	Delta (mmu)	RDB equiv.	Composition
883.47107	252870.8	100	883.4700	-1.25	28.5	$C_{56}H_{57}N_4B_2F_4$

HRMS for **2c**



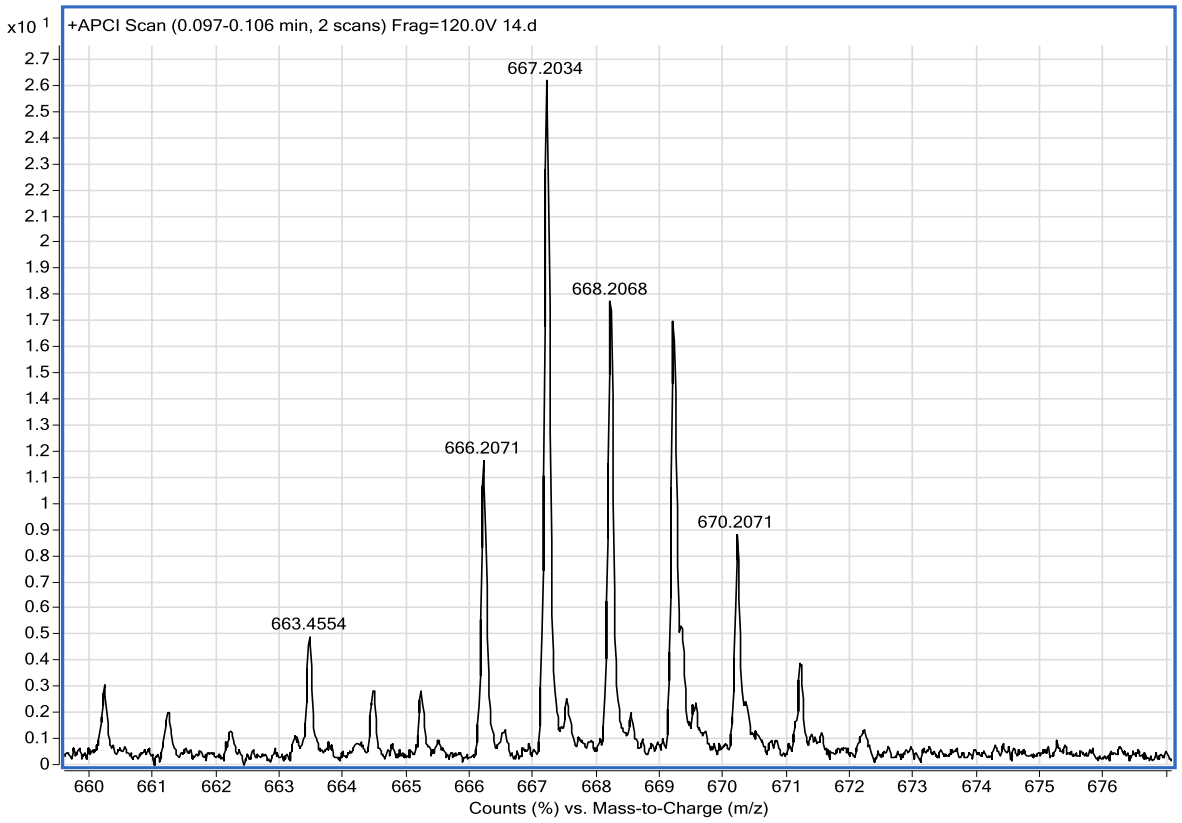
m/z	Intensity	Relative	Theo. Mass	Delta (mmu)	RDB equiv.	Composition
831.36475	404509.6	100	831.36593	-1.18	28.5	$C_{50}H_{45}O_2N_4B_2F_4$

HRMS for **2d**

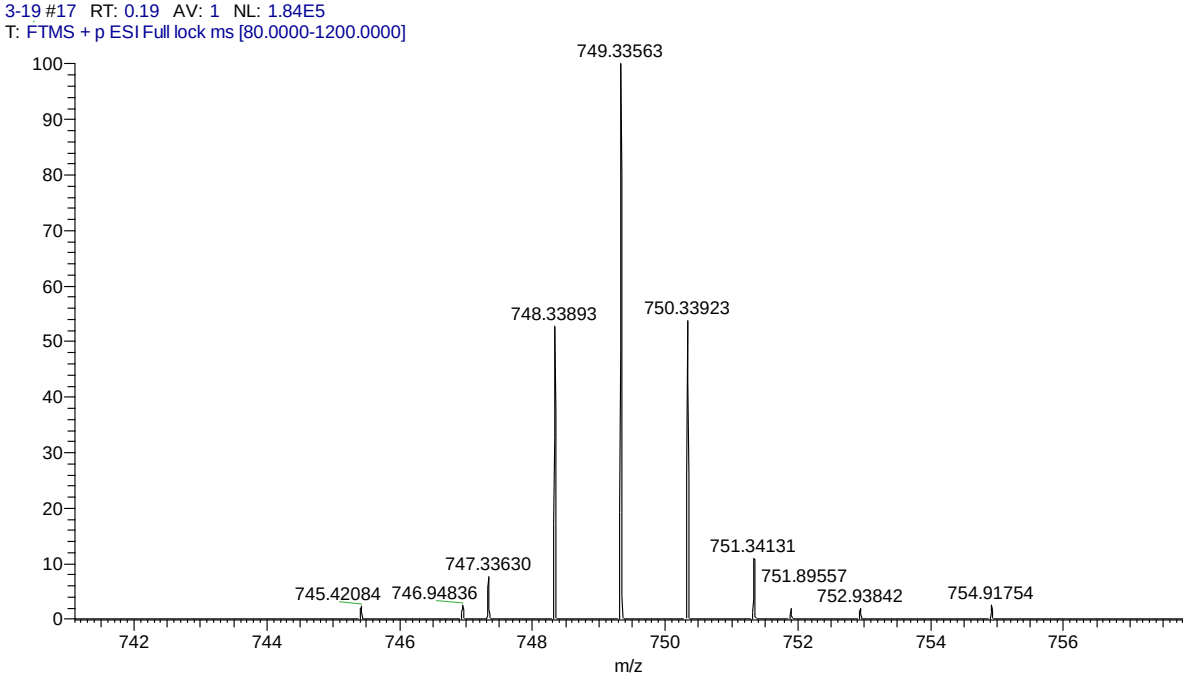


m/z	Intensity	Relative	Theo. Mass	Delta (mmu)	Composition
839.26733	79633.2	100	839.26685	0.48	$C_{48}H_{39}N4B_2Cl_2F_4$

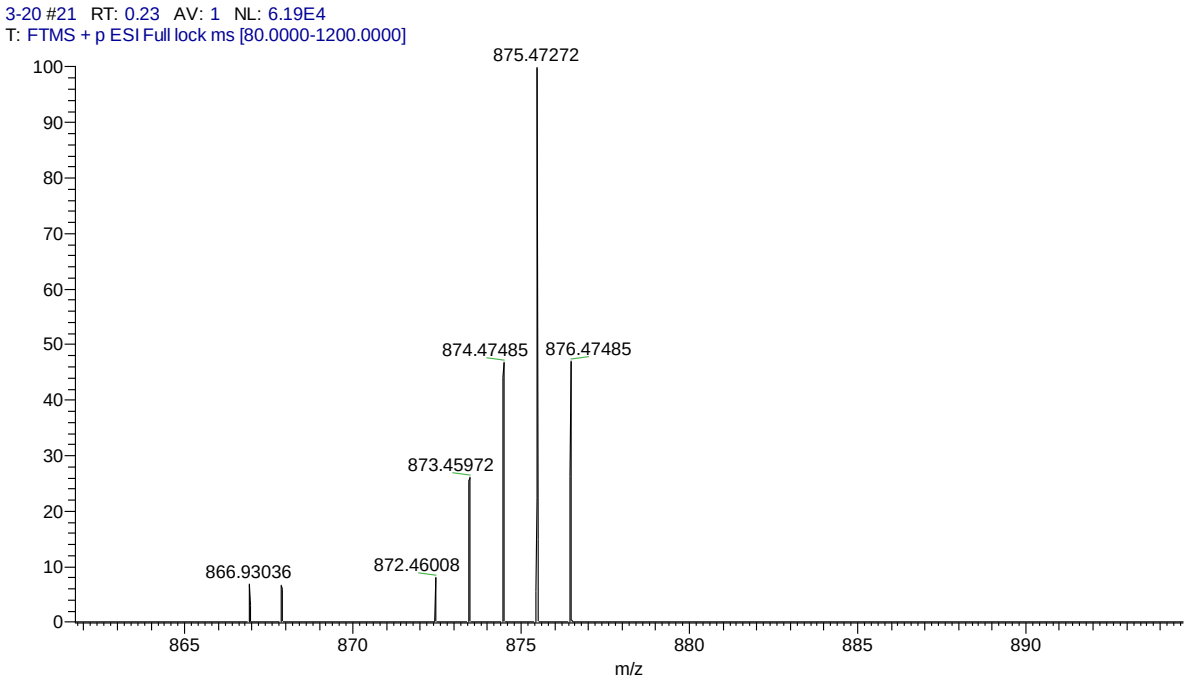
HRMS for **2e**


x10 1
+APCI Scan (0.097-0.106 min, 2 scans) Frag=120.0V 14.d
667.2034
668.2068
666.2071
670.2071
663.4554
Counts (%) vs. Mass-to-Charge (m/z)

HRMS for **2f**


3-19 #17 RT: 0.19 AV: 1 NL: 1.84E5
T: FTMS + p ESI Full lock ms [80.0000-1200.0000]
749.33563
748.33893
750.33923
747.33630
751.34131
751.89557
745.42084
746.94836
752.93842
754.91754
m/z

HRMS of **2g**


3-20 #21 RT: 0.23 AV: 1 NL: 6.19E4
T: FTMS + p ESI Full lock ms [80.0000-1200.0000]
875.47272
874.47485
876.47485
873.45972
872.46008
866.93036
100
90
80
70
60
50
40
30
20
10
0
865
870
875
880
885
890
m/z

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