Supporting information for

Dibenzothieno and dibenzothieno[2,3-*d*]thieno [*a*]-fused BODIPYs: synthesis, unique structure and photophysical properties

Limin He,[a] Lu Li,[a] Muyao Zhao,[a] Yunxia Zhao,[a] Yanqing Li,[a] Xiangguang Li,[a,*] Yanhua Yang, [a,*] Shulin Gao, [a] Ping Lei,[b] Zhaohui Wang,[c] and Wei Jiang [c,*]

[a] Yunnan Key Laboratory of Metal-Organic Molecular Materials and Device, School of Chemistry and Chemical Engineering, Kunming University, Kunming 650214, China.

[b] Technology Center, China Tobacco Yunnan Industrial Co., Ltd., Kunming 650231, China.

[c] Key Laboratory of Organic Optoelectronics and Molecular Engineering, Department of Chemistry, Tsinghua University, Beijing 100084, China.

*Email: lixiangguang@iccas.ac.cn; yh_yangkmu@126.com; jiangwei2021@mail.tsinghua.edu.cn

Contents:

1. Experimental Details

General information. All chemicals were purchased from commercial suppliers and used without further purification unless otherwise specified. The solvent THF and toluene were distilled over sodium and benzophenone.

All reactions of air-sensitive compounds were carried out under dry argon by using Schlenk techniques. The reaction progress was monitored by thin layer chromatography (TLC) and spots were observed with a UV254 fluorescent indicator. Flash column chromatography was performed using silica gel (200-300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded in deuterated solvents using a BRUKER ASCEND^{TM}400 Spectrometer. NMR chemical shifts are reported in ppm using the residual protonated solvent as an internal standard. High resolution mass spectra (HRMS) were determined on a Thermo Scientific^{TM} Orbitrap Exploris^{TM} 120 Mass Spectrometer.

Photophysical properties measurements. Absorption spectra were measured with a Shimadzu UV3600Plus UV-VIS-NIR Spectrophotometer in a 1 cm quartz cell. Fluorescence measurements were measured with Edinburgh FS5 Spectrofluorometer at room temperature. In the fluorescence lifetime conducted using the Edinburgh FS5 Spectrofluorometer, a fluorescence decay curve was obtained by scanning the sample at its peak emission wavelength using a 450 nm TCSPC laser. The fluorescence lifetime was then determined by fitting the decay curve to a single-exponential function. For the absolute quantum yield test, the integrating sphere captures all emitted light from the sample in solution, including both diffuse and direct emission. The quantum yield is determined by comparing the peak area of the sample's emission spectrum to that of a reference solvent or standard.

Electrochemical measurements. Cyclic voltammetry (CV) was performed using a CHI620E electrochemical workstation at a scan rate of 50 mV s^{-1}, using glassy carbon discs as the working electrodes, Pt wire as the counter electrode, Ag/AgCl electrode as the reference electrode. 0.1 M tetrabutylammonium hexafuorophosphate (*n*-Bu_4NPF_6) dissolved in CH_2Cl_2 (HPLC grade) was employed as the supporting electrolyte. Ferrocene/ferrocenium was employed as an external reference, the energy

level of which is assumed to be -4.8 eV below the vacuum level.[1,2] The LUMO and HOMO levels were estimated from the onset potentials of the first reduction and oxidation waves in CV, respectively. The half-wave potential of oxidation peak of Fc was measured to be 0.48 V against Ag/AgCl.

X-ray structure analysis. Single crystals of **5a** suitable for X-ray analysis were obtained by slow diffusion of MeOH into their $CHCl_3$ solution. Single crystals of **5b** suitable for X-ray analysis was obtained by slow diffusion of hexane into their CH_2Cl_2 solution. Single crystals of **5c** suitable for X-ray analysis were obtained by slow diffusion of hexane into their CH_2Cl_2 solution. Single crystals of **8a** suitable for X-ray analysis were grown by slow diffusion of MeOH into their CH_2Cl_2 solution. Single crystals of **4b** and **4c** suitable for X-ray analysis were obtained by slow of $CHCl_3$ solution. A suitable crystal was selected and performed on a Bruker D8 VENTURE diffractometer. The crystal was kept at 193.00 K during data collection. The determination of unit cell parameters and data collections of **5a**, **5b**, **5c, 8a, 4b** and **4c** were performed with Cu Kα radiation (λ) at 1.54178 Å, Cu Kα radiation (λ) at 1.54178 Å, Cu Kα radiation (λ) at 1.54178 Å, Cu Kα radiation (λ) at 1.54178 Å, Mo Kα radiation (λ) at 0.71073 Å and Cu Kα radiation (λ) at 1.54178 Å, respectively. Using Olex2[3], the structure was solved with the olex2.solve[4] structure solution program using Charge Flipping and refined with the SHELXL[5] refinement package using Least Squares minimisation. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2. Crystal Data

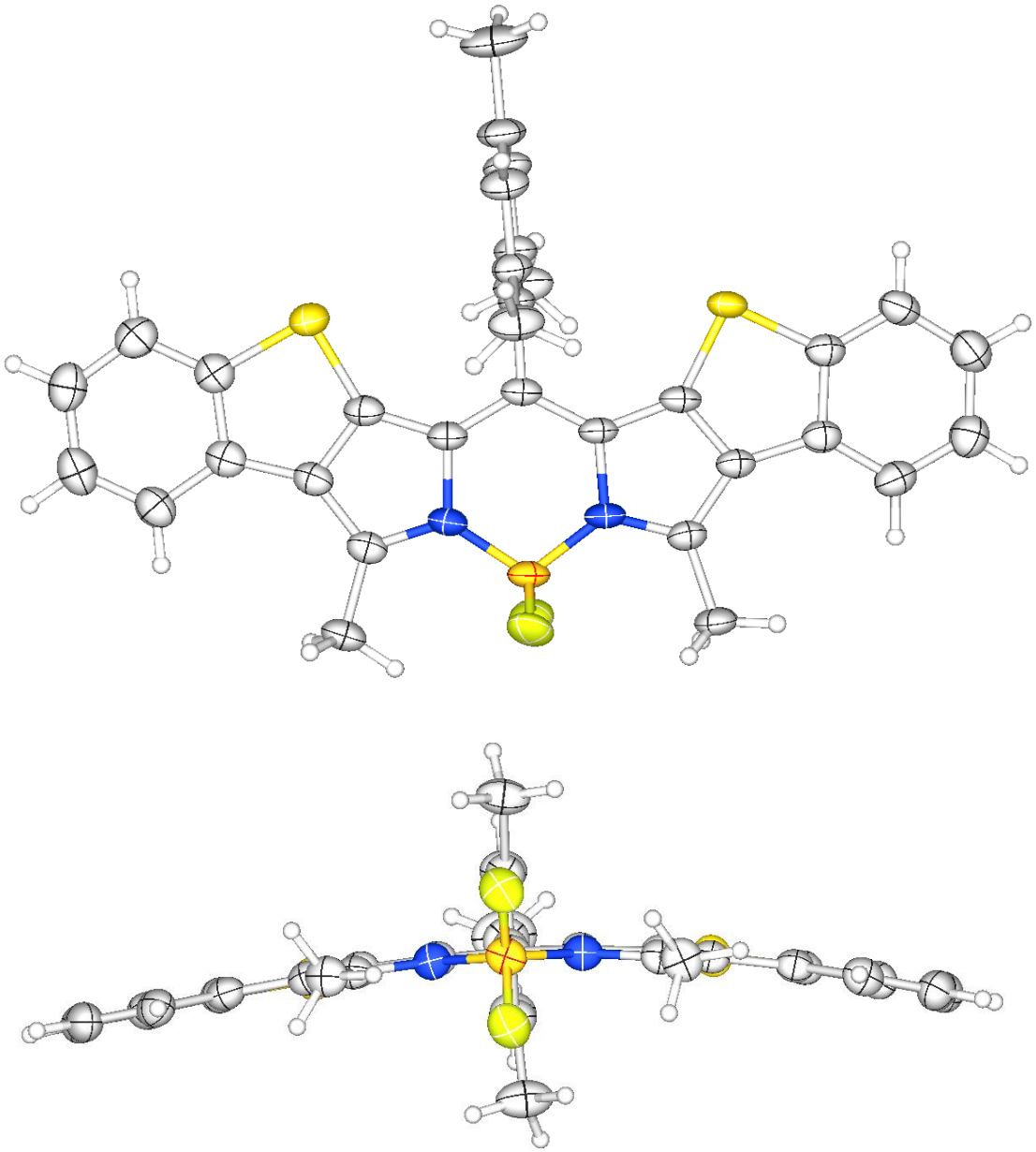


Figure S1. Single-crystal structure of **5a**, with thermal ellipsoids shown at 50% probability.

Table S1 Crystal data and structure refinement for **5a.** CCDC number= 2366236

Identification code	**5a**
Empirical formula	$C_{32}H_{25}BF_2N_2S_2$
Formula weight	550.47
Temperature/K	193.00
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	13.5779(3)
b/Å	22.7898(6)
c/Å	10.9233(3)
α/°	90
β/°	113.0340(10)
γ/°	90
Volume/Å^3	3110.59(14)
Z	4
ρ_{calc}g/cm^3	1.175
μ/mm^{-1}	1.828
F(000)	1144.0
Crystal size/mm^3	0.13 × 0.11 × 0.1
Radiation	Cu Kα (λ = 1.54178)
2Θ range for data collection/°	8.07 to 136.534
Index ranges	$-15 \leq h \leq 16$, $-25 \leq k \leq 27$, $-12 \leq l \leq 13$
Reflections collected	26246
Independent reflections	5658 [R_{int} = 0.0441, R_{sigma} = 0.0318]
Data/restraints/parameters	5658/0/357
Goodness-of-fit on F^2	1.058
Final R indexes [I>=2σ (I)]	R_1 = 0.0473, wR_2 = 0.1404
Final R indexes [all data]	R_1 = 0.0575, wR_2 = 0.1482
Largest diff. peak/hole / e Å^{-3}	0.55/-0.43

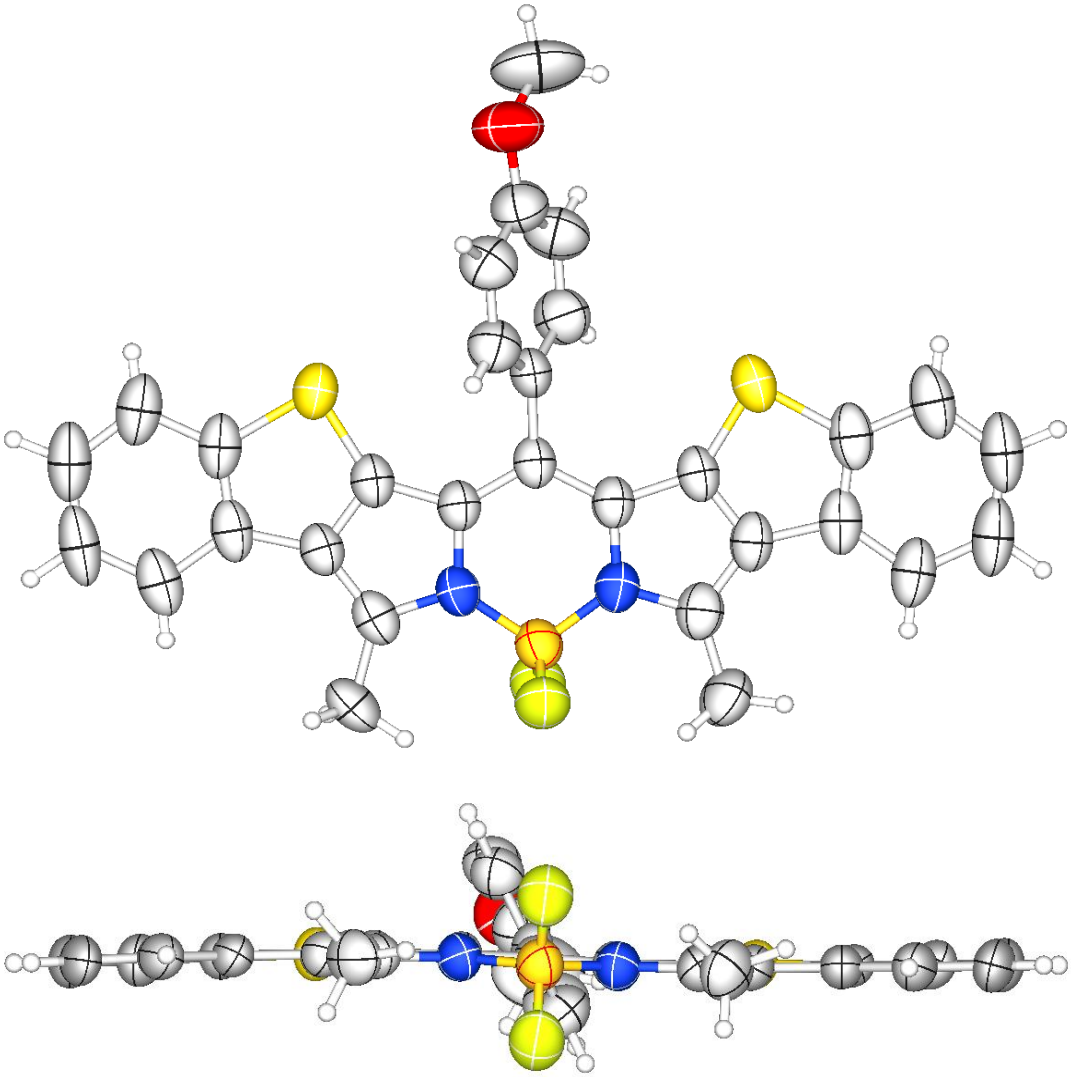


Figure S2. Single-crystal structure of **5b**, with thermal ellipsoids shown at 50% probability.

Table S2 Crystal data and structure refinement for **5b.** CCDC number= 2366239

Identification code	**5b**
Empirical formula	$C_{30}H_{21}BF_2N_2OS_2$
Formula weight	538.42
Temperature/K	193.00
Crystal system	orthorhombic
Space group	Fddd
a/Å	13.9327(4)
b/Å	36.6830(9)
c/Å	49.9694(15)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	25539.0(12)
Z	32
ρ_{calc}g/cm^3	1.120
μ/mm^{-1}	1.797
F(000)	8896.0
Crystal size/mm^3	0.15 × 0.13 × 0.1
Radiation	Cu Kα (λ = 1.54178)
2Θ range for data collection/°	7.014 to 137.298
Index ranges	-16 ≤ h ≤ 16, -44 ≤ k ≤ 34, -60 ≤ l ≤ 60
Reflections collected	34446
Independent reflections	5851 [R_{int} = 0.0916, R_{sigma} = 0.0869]
Data/restraints/parameters	5851/0/334
Goodness-of-fit on F^2	1.003
Final R indexes [I>=2σ (I)]	R_1 = 0.0732, wR_2 = 0.2095
Final R indexes [all data]	R_1 = 0.1010, wR_2 = 0.2392
Largest diff. peak/hole / e Å^{-3}	0.32/-0.42

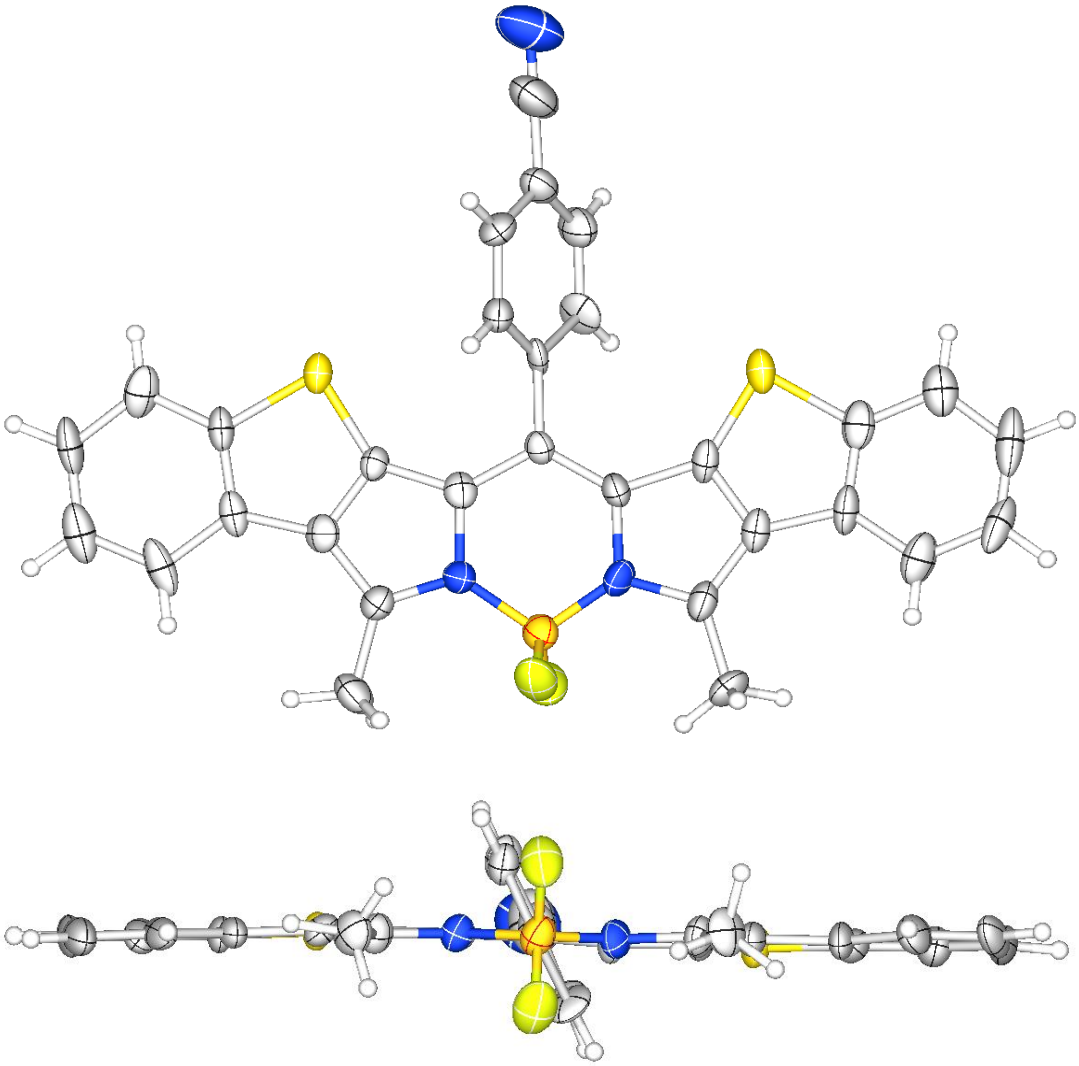


Figure S3. Single-crystal structure of **5c**, with thermal ellipsoids shown at 50% probability.

Table S3 Crystal data and structure refinement for **5c.** CCDC number= 2366259

Identification code	**5c**
Empirical formula	$C_{30}H_{18}BF_2N_3S_2$
Formula weight	533.40
Temperature/K	193.00
Crystal system	monoclinic
Space group	Pc
a/Å	9.5209(5)
b/Å	24.5517(14)
c/Å	13.7611(8)
α/°	90
β/°	105.752(3)
γ/°	90
Volume/Å^3	3095.9(3)
Z	4
ρ_{calc}g/cm^3	1.144
μ/mm^{-1}	1.835
F(000)	1096.0
Crystal size/mm^3	0.15 × 0.13 × 0.12
Radiation	Cu Kα (λ = 1.54178)
2Θ range for data collection/°	3.598 to 137.054
Index ranges	$-11 \leq h \leq 11$, $-29 \leq k \leq 25$, $-14 \leq l \leq 16$
Reflections collected	21251
Independent reflections	10033 [R_{int} = 0.0405, R_{sigma} = 0.0559]
Data/restraints/parameters	10033/245/1035
Goodness-of-fit on F^2	1.072
Final R indexes [I>=2σ (I)]	R_1 = 0.0692, wR_2 = 0.1891
Final R indexes [all data]	R_1 = 0.0818, wR_2 = 0.2055
Largest diff. peak/hole / e Å^{-3}	0.35/-0.66
Flack parameter	0.498(12)

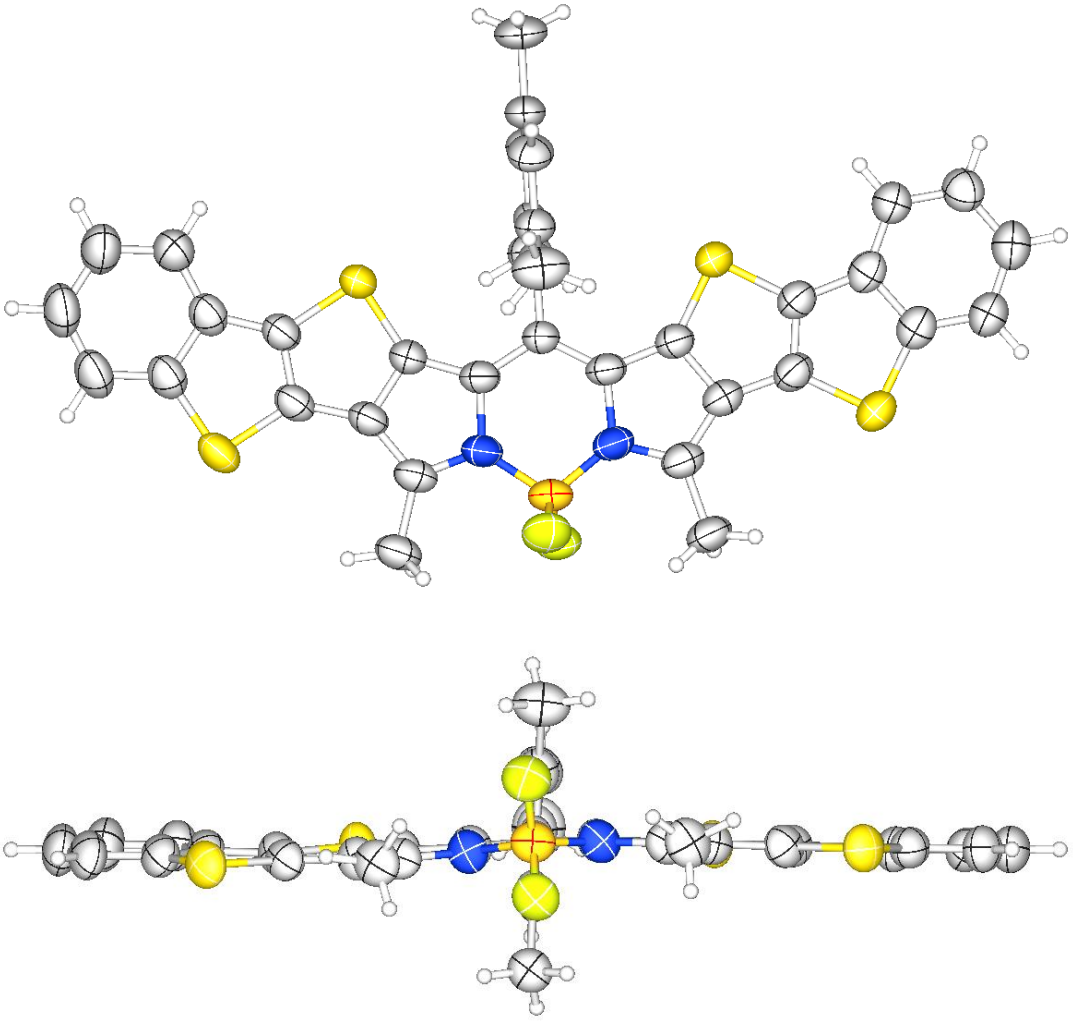


Figure S4. Single-crystal structure of **8a**, with thermal ellipsoids shown at 50% probability.

Table S4 Crystal data and structure refinement for **8a.** CCDC number= 2366238

Identification code	**8a**
Empirical formula	$C_{36}H_{25}BF_2N_2S_4$
Formula weight	662.63
Temperature/K	223.00
Crystal system	triclinic
Space group	P-1
a/Å	8.484(6)
b/Å	12.565(6)
c/Å	16.196(7)
α/°	76.79(3)
β/°	83.25(3)
γ/°	73.44(3)
Volume/Å^3	1608.5(15)
Z	2
ρ_{calc}g/cm^3	1.368
μ/mm^{-1}	3.048
F(000)	684.0
Crystal size/mm^3	0.14 × 0.13 × 0.11
Radiation	Cu Kα (λ = 1.54178)
2Θ range for data collection/°	7.5 to 147.266
Index ranges	$-10 \leq h \leq 10$, $-15 \leq k \leq 15$, $-20 \leq l \leq 19$
Reflections collected	16200
Independent reflections	6338 [R_{int} = 0.0716, R_{sigma} = 0.0658]
Data/restraints/parameters	6338/0/411
Goodness-of-fit on F^2	0.965
Final R indexes [I>=2σ (I)]	R_1 = 0.0577, wR_2 = 0.1532
Final R indexes [all data]	R_1 = 0.0940, wR_2 = 0.1749
Largest diff. peak/hole / e Å^{-3}	0.56/-0.38

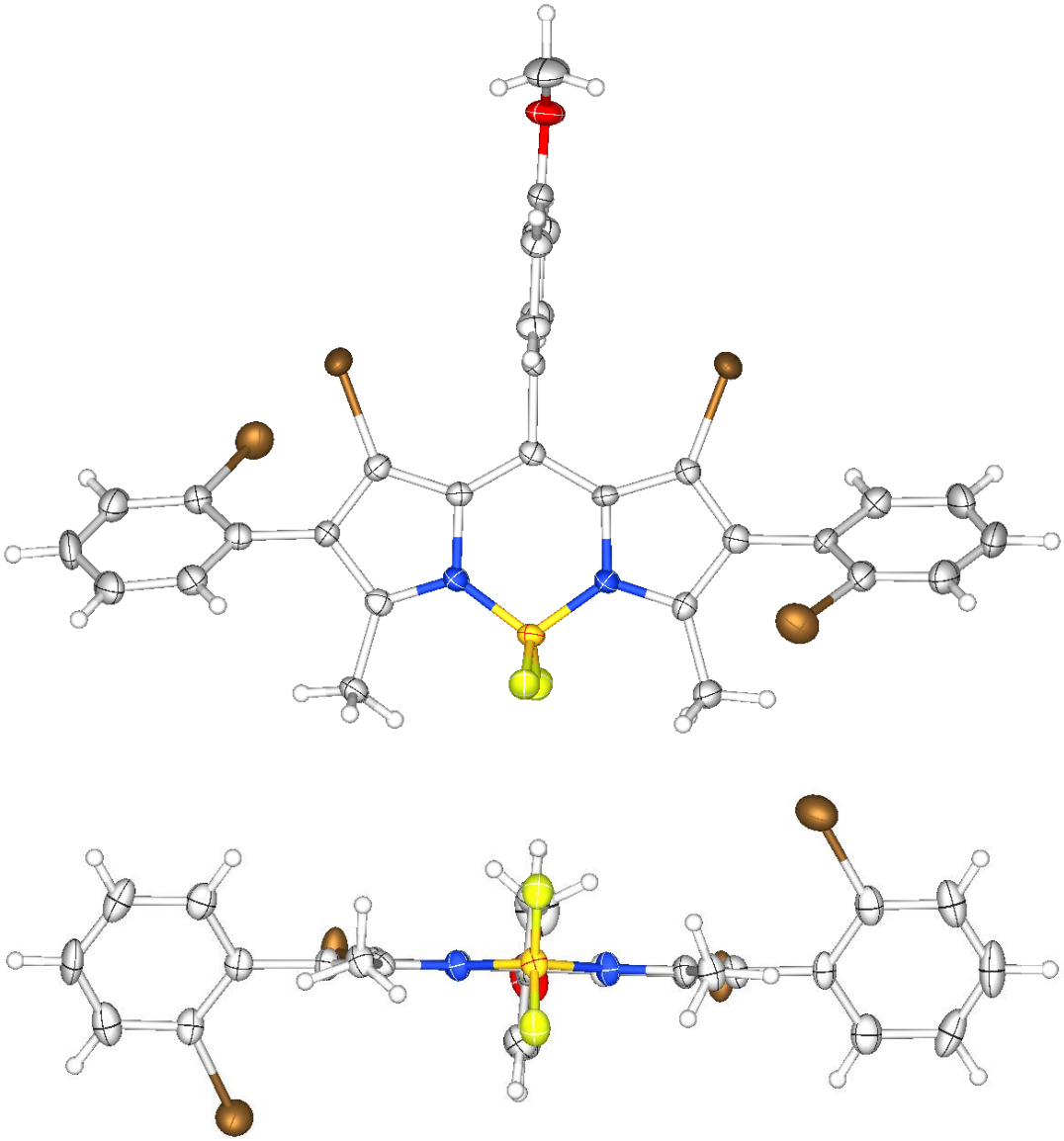


Figure S5. Single-crystal structure of **4b**, with thermal ellipsoids shown at 50% probability.

Table S5 Crystal data and structure refinement for **4b.** CCDC number= 2366240

Identification code	**4b**
Empirical formula	$C_{30}H_{21}BBr_4F_2N_2O$
Formula weight	793.94
Temperature/K	193.00
Crystal system	orthorhombic
Space group	$Pca2_1$
a/Å	13.3963(6)
b/Å	20.6772(7)
c/Å	10.5068(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2910.4(2)
Z	4
ρ_{calc}g/cm^3	1.812
μ/mm^{-1}	5.572
F(000)	1544.0
Crystal size/mm^3	0.23 × 0.16 × 0.12
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.976 to 54.948
Index ranges	$-17 \leq h \leq 15$, $-23 \leq k \leq 26$, $-12 \leq l \leq 13$
Reflections collected	32466
Independent reflections	6525 [R_{int} = 0.0742, R_{sigma} = 0.0555]
Data/restraints/parameters	6525/1/364
Goodness-of-fit on F^2	0.983
Final R indexes [I>=2σ (I)]	R_1 = 0.0354, wR_2 = 0.0768
Final R indexes [all data]	R_1 = 0.0484, wR_2 = 0.0825
Largest diff. peak/hole / e Å^{-3}	0.50/-0.42
Flack parameter	0.067(8)

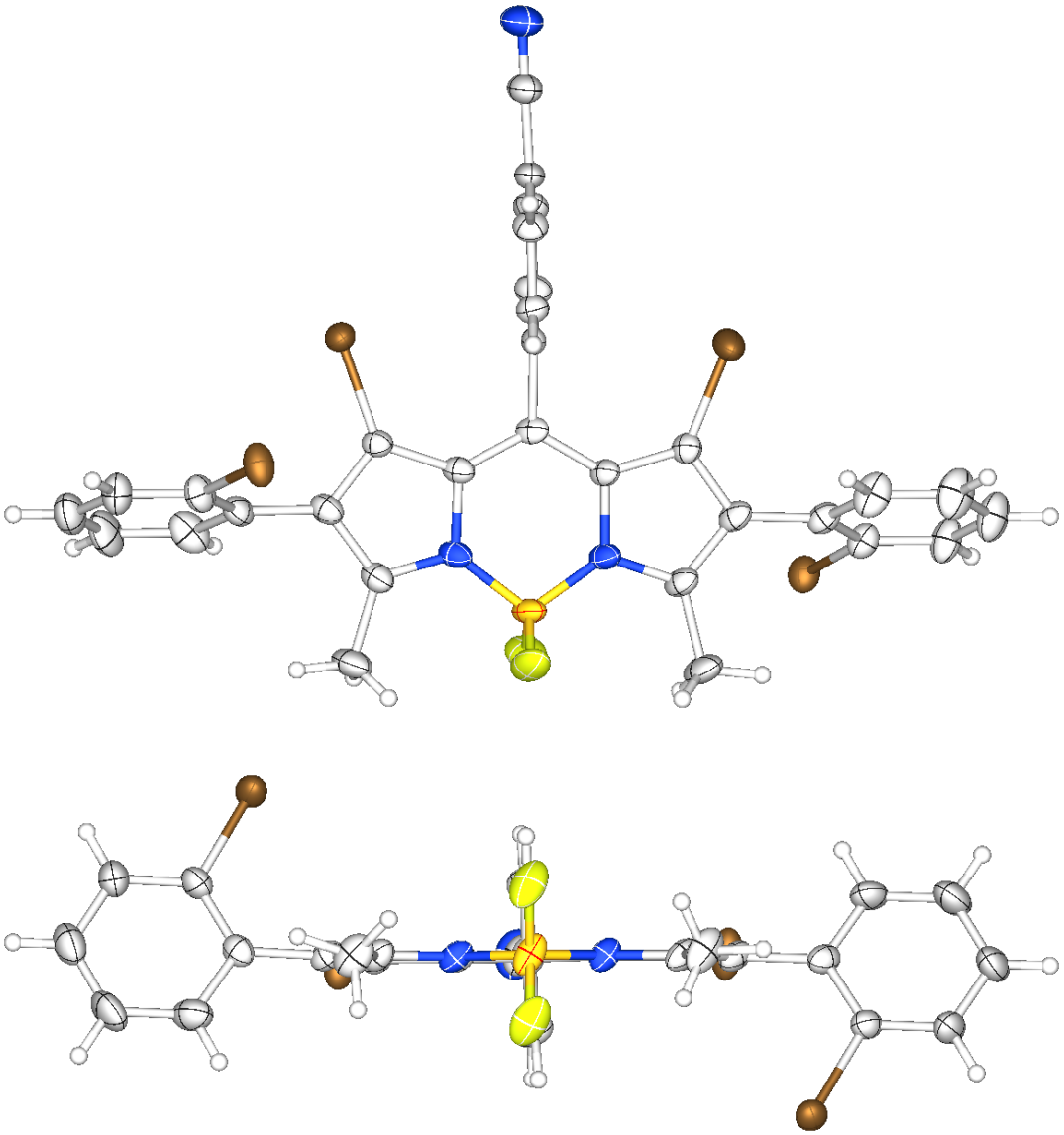
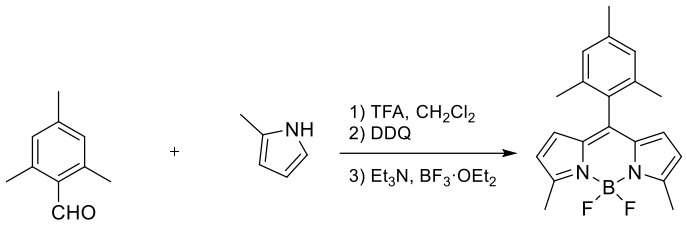


Figure S6. Single-crystal structure of **4c**, with thermal ellipsoids shown at 50% probability.

Table S6 Crystal data and structure refinement for **4c.** CCDC number= 2366260

Identification code	**4c**
Empirical formula	$C_{30}H_{18}BBr_4F_2N_3$
Formula weight	788.92
Temperature/K	193.00
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	11.1457(4)
b/Å	37.5112(13)
c/Å	7.6375(3)
α/°	90
β/°	99.698(2)
γ/°	90
Volume/Å^3	3147.5(2)
Z	4
ρ_{calc}g/cm^3	1.665
μ/mm^{-1}	6.540
F(000)	1528.0
Crystal size/mm^3	0.13 × 0.12 × 0.11
Radiation	Cu Kα (λ = 1.54178)
2Θ range for data collection/°	4.712 to 136.846
Index ranges	$-13 \leq h \leq 12$, $-45 \leq k \leq 38$, $-8 \leq l \leq 9$
Reflections collected	24312
Independent reflections	5596 [R_{int} = 0.0517, R_{sigma} = 0.0400]
Data/restraints/parameters	5596/2/382
Goodness-of-fit on F^2	1.077
Final R indexes [I>=2σ (I)]	R_1 = 0.0400, wR_2 = 0.0988
Final R indexes [all data]	R_1 = 0.0458, wR_2 = 0.1006
Largest diff. peak/hole / e Å^{-3}	0.65/-0.62

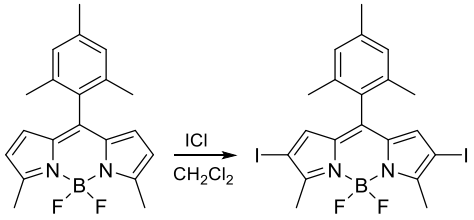
3. Synthesis and Characterization



1a

Compound **1a** was prepared by the reported procedure[6].

To a solution of 2,4,6-trimethylbenzaldehyde (1482 mg, 10 mmol) and 2-methylpyrrole (1663 mg, 20.5 mmol) in CH_2Cl_2 (250 mL), 2 drops of trifluoroacetic acid were added. After being stirred overnight at room temperature, the reaction mixture was treated with a solution of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 2270 mg, 1.0 equiv) in CH_2Cl_2 (50 mL) at room temperature for 1 h. Then, the resulting solution were treated by Et_3N (13 mL, 93.2 mol) and $BF_3{\cdot}OEt_2$ (13 mL, 102.6 mol). After being stirred for 0.5 h at room temperature, thus the mixture was washed with brine and then dried with Na_2SO_4. After removing the solvents by rotary evaporation, the residue was purified by column chromatography on silica (petroleum ether/CH_2Cl_2 =3/1, v/v) and recrystallized with methanol/dichloromethane to give 1.15 g of compound **1a** in 34% yield as orange red solids. NMR data of this compound agreed with the reported one[6]. **Mp** 216.5-217.3℃. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.92 (s, 2H), 6.46 (d, *J* = 4.1 Hz, 2H), 6.19 (d, *J* = 4.1 Hz, 2H), 2.64 (s, 6H), 2.34 (s, 3H), 2.10 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 157.77, 142.53, 138.54, 136.86, 134.97, 130.30, 129.24, 128.23, 119.59, 21.36, 20.18, 15.16.

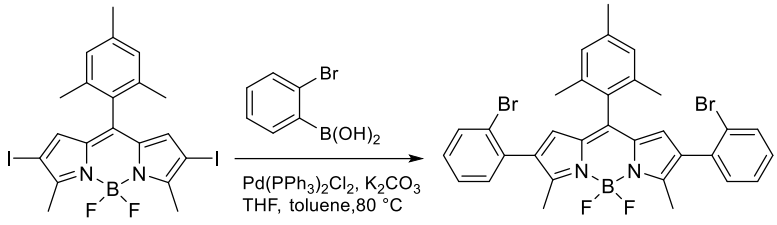


1a **2a**

Compound **2a**:

To a solution of Compound **1a** (845 mg, 2.5 mmol) in CH_2Cl_2 (100 mL), a solution of ICl (1015 mg, 6.25 mmol) in MeOH (10 mL) was added dropwise. After being stirred 15 min at room temperature, the reaction mixture was treated with a

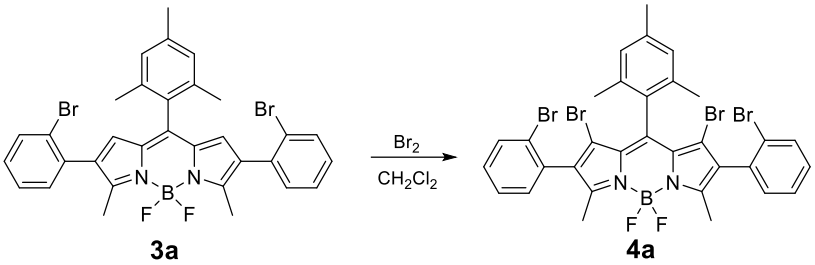
saturated solution of $Na_2S_2O_3$ (100 mL) at same temperature for 1 h. Then, the mixture was washed with brine and then dried with Na_2SO_4. After removing the solvents by rotary evaporation, the residue was purified by column chromatography on silica (petroleum ether/CH_2Cl_2 =3/1, v/v) and recrystallized with methanol/dichloromethane to give 1.34 g of compound **2a** in 91% yield as purple solids. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.93 (s, 2H), 6.70 (s, 2H), 2.65 (s, 6H), 2.35 (s, 3H), 2.09 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.00, 141.60, 139.23, 136.72, 135.65, 129.25, 128.48, 78.03, 21.36, 20.22, 15.75. **HRMS** (ESI-Orbitrap, [M-1]$^-$, 100%): calcd for $C_{20}H_{18}BF_2I_2N_2$, 588.9615; found, 588.9633.



2a **3a**

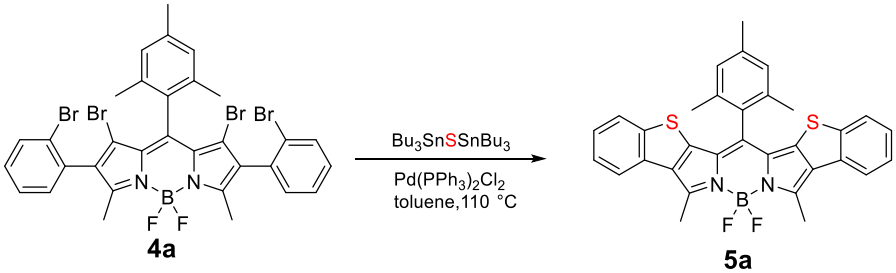
Compound **3a**:

Compound **2a** (147 mg, 0.25 mmol), 2-bromophenylboronic acid (126 mg, 0.625 mmol), $Pd(PPh_3)_2Cl_2$ (18 mg, 0.025 mmol) and K_2CO_3 (743 mg, 5.375 mmol) in THF/toluene/H_2O (15 mL/15 mL/3 mL) was stirred at 80 ºC for 1.5 h under argon atmosphere. After cooling to room temperature, the mixture was poured into water and extracted with CH2Cl2. The extractions were washed with brine and then dried with Na_2SO_4. After removing the solvents by rotary evaporation, the residue was purified by column chromatography on silica (petroleum ether/CH_2Cl_2 =2/1, v/v) to afford crude product **3a**, after recrystallization with methanol/dichloromethane to give 108 mg of compound **3a** in 67% yield as red solids. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.62 (dd, *J* = 8.0, 1.0 Hz, 2H), 7.30 (td, *J* = 7.5, 1.2 Hz, 2H), 7.23 (dd, *J* = 7.6, 1.8 Hz, 2H), 7.19-7.13 (m, 2H), 6.91 (s, 2H), 6.57 (s, 2H), 2.57 (s, 6H), 2.31 (s, 3H), 2.21 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 156.23, 142.94, 138.69, 136.95, 135.33, 133.93, 133.20, 133.11, 131.85, 130.10, 129.36, 128.95, 128.34, 127.40, 124.49, 21.32, 20.43, 13.98. **HRMS** (ESI-Orbitrap, [M-1]$^-$, 100%): calcd for $C_{32}H_{26}BBr_2F_2N_2$, 647.0498; found, 647.0514.



Compound **4a**:

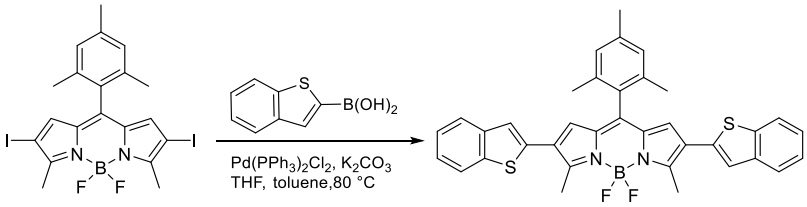
To a solution of compound **3a** (65 mg, 0.1 mmol) in dry CH_2Cl_2 (30 mL), a solution of liquid bromine (31 μL, 0.6 mmol) in dry CH_2Cl_2 (5 mL) were added dropwise. After being stirred for 0.5 h at room temperature, the reaction mixture was treated with a saturated solution of $Na_2S_2O_3$ (100 mL) at same temperature for 0.5 h. Then, the mixture was washed with brine and then dried with Na_2SO_4. After removing the solvents by rotary evaporation, the residue was purified by column chromatography on silica (petroleum ether/ethyl acetate =500/1, v/v) and recrystallized with methanol/dichloromethane to give 41 mg of compound **4a** in 51% yield as orange red solids. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.70 - 7.64 (m, 2H), 7.37 (td, *J* = 7.5, 1.1 Hz, 2H), 7.28 (d, *J* = 1.7 Hz, 2H), 7.21 (dd, *J* = 7.5, 1.6 Hz, 2H), 6.92 (s, 2H), 2.47 (s, 6H), 2.31 (s, 3H), 2.15 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 155.56, 143.89, 139.40, 136.33, 135.11, 133.94, 133.07, 132.45, 130.23, 129.10, 128.86, 127.88, 127.61, 125.31, 121.05, 21.58, 20.19, 14.15. **HRMS** (ESI-Orbitrap, $[M]^-$, 100%): calcd for $C_{32}H_{25}BBr_4F_2N_2$, 805.8766; found, 805.8768.



Compound **5a**:

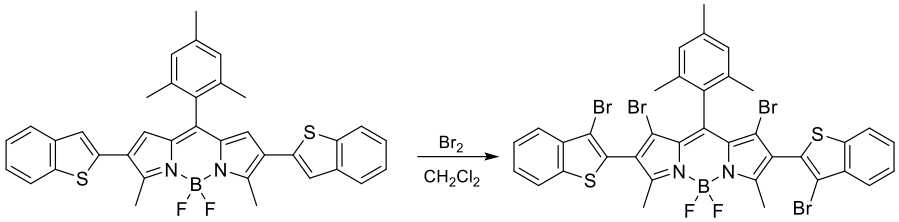
A Schlenk tube was charged with compound **4a** (24 mg, 0.03 mmol) and $Pd(PPh_3)_2Cl_2$ (2.1 mg, 0.1 eq.) under an argon atmosphere at room temperature. Then, a solution of Bis(tri-*n*-butyltin)sulfide (26.6 μL, 0.066 mmol) in dry toluene (1.0 mL) was added. The reaction mixture was stirred at 110 °C for 12 h and cooled down to

room temperature, then, the mixture was washed with brine and then dried with Na_2SO_4. After removing the solvents by rotary evaporation, the crude product was purified by column chromatography on silica (petroleum ether/CH_2Cl_2 = 2/1, v/v) and recrystallized with methanol/dichloromethane to give 12 mg of compound **5a** in 73 % yield as golden metallic luster solids. **Mp** 279.6-281.0℃. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.89 (d, *J* = 7.8 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 2H), 7.42 - 7.36 (m, 2H), 7.28 (d, *J* = 1.1 Hz, 2H), 7.18 (s, 2H), 3.06 (s, 6H), 2.51 (s, 3H), 2.15 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 149.06, 144.69, 141.16, 140.01, 136.48, 135.61, 133.25, 131.70, 130.04, 129.31, 125.59, 125.06, 125.00, 123.90, 121.36, 21.76, 19.62, 14.81. **HRMS** (ESI-Orbitrap, $[M]^+$, 100%): calcd for $C_{32}H_{25}BF_2N_2S_2$, 550.1515; found, 550.1520.



Compound **6a**:

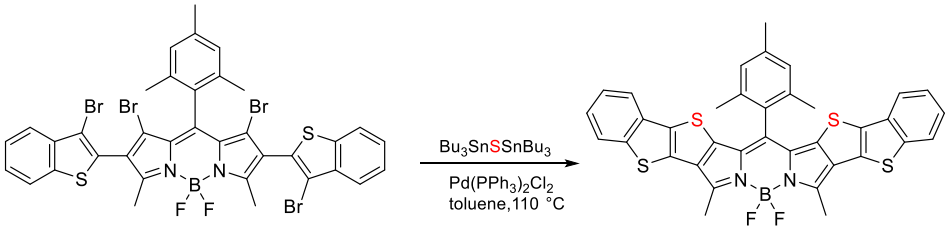
The synthesis method resembles that of compound **3a**, by the reaction of compound **2a** (147 mg, 0.25 mmol) with benzo[*b*]thiophen-2-ylboronic acid (111 mg, 0.625 mmol). The compound was purified by column chromatography on silica (petroleum ether/CH_2Cl_2 =2/1, v/v) to afford crude product **6a**, after recrystallization with methanol/dichloromethane to give 84 mg of compound **6a** in 56% yield as black solids. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 7.8 Hz, 2H), 7.76 - 7.71 (m, 2H), 7.37 - 7.28 (m, 6H), 7.00 (s, 2H), 6.69 (s, 2H), 2.94 (s, 6H), 2.40 (s, 3H), 2.19 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 156.15, 142.84, 140.56, 139.37, 139.07, 136.89, 136.41, 134.22, 129.80, 128.55, 127.44, 126.41, 124.83, 124.56, 123.61, 122.24, 121.20, 21.44, 20.38, 14.92. **HRMS** (ESI-Orbitrap, $[M]^+$, 100%): calcd for $C_{36}H_{29}BF_2N_2S_2$, 602.1828; found, 602.1838.



6a **7a**

Compound **7a**:

The synthesis method resembles that of compound **4a**, by the reaction of compound **6a** (60 mg, 0.1 mmol) with a solution of liquid bromine (154 μL, 3 mmol) in dry CH_2Cl_2 (5 mL). The compound was purified by column chromatography on silica (petroleum ether/CH_2Cl_2 =10/1, v/v) and recrystallized with methanol/dichloromethane to give 69 mg of compound **7a** in 75% yield as dark-brown solids. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.85 (dd, *J* = 11.7, 8.1 Hz, 4H), 7.53 - 7.41 (m, 4H), 6.95 (s, 2H), 2.61 (s, 6H), 2.33 (s, 3H), 2.18 (d, *J* = 3.1 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 157.03, 139.74, 139.47, 139.46, 138.26, 138.23, 136.21(t, *J* = 7.1 Hz), 129.41, 129.31, 129.26, 129.18, 127.46, 126.14, 125.47, 123.99, 122.68, 110.82, 21.61, 20.27, 14.43. **HRMS** (ESI-Orbitrap, $[M-1]^-$, 100%): calcd for $C_{36}H_{24}BBr_4F_2N_2S_2$, 916.8129; found, 916.8152.

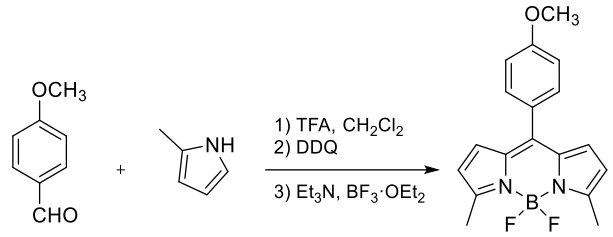


7a **8a**

Compound **8a**:

The synthesis method resembles that of compound **5a**, by the reaction of compound **7a** (37 mg, 0.04 mmol) with Bis(tri-*n*-butyltin)sulfide (35.5 μL, 0.088 mmol). The crude product was purified by column chromatography on silica (petroleum ether/CH_2Cl_2 = 2/1, v/v) and recrystallized with methanol/dichloromethane to give 10 mg of compound **8a** in 39% yield as dark-brown solids. **Mp** > 320°C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 7.8 Hz, 2H), 7.65 (d, *J* = 7.8 Hz, 2H), 7.39 - 7.30 (m, 4H), 7.22 (s, 2H), 2.98 (s, 6H),

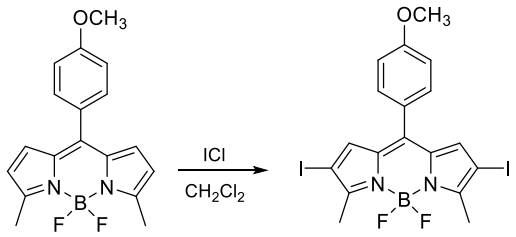
2.55 (s, 3H), 2.19 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 147.56, 142.89, 142.18, 140.15, 136.95, 135.49, 134.77, 133.10, 131.52, 130.28, 129.08, 128.77, 125.66, 125.18, 124.59, 124.25, 120.85, 21.82, 19.65, 14.72. **HRMS** (ESI-Orbitrap, $[M]^+$, 100%): calcd for $C_{36}H_{25}BF_2N_2S_4$, 662.0956; found, 662.0967.



1b

Compound **1b**:

The synthesis method resembles that of compound **1a**, by the reaction of *p*-anisaldehyde (1.36 g, 10 mmol) with 2-methylpyrrole (1663 mg, 20.5 mmol). The compound was purified by column chromatography on silica (petroleum ether/CH_2Cl_2 =3/1, v/v) and recrystallized with methanol/dichloromethane to give 1.04 g of compound **1b** in 32% yield as orange red solids. NMR data of this compound agreed with the reported one[7]. **Mp** 191.0-192.5℃. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.7 Hz, 2H), 7.00 (d, *J* = 8.7 Hz, 2H), 6.75 (d, *J* = 4.1 Hz, 2H), 6.27 (d, *J* = 4.2 Hz, 2H), 3.89 (s, 3H), 2.65 (s, 6H).

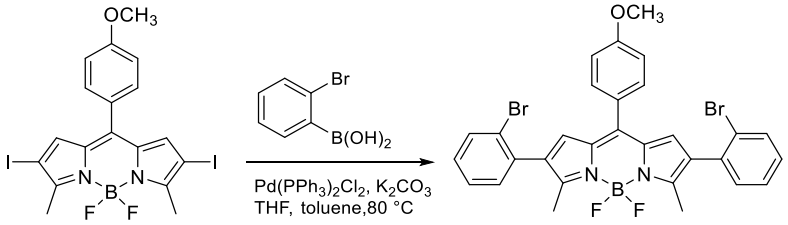


1b **2b**

Compound **2b**:

The synthesis method resembles that of compound **2a**, by the reaction of compound **1b** (815 mg, 2.5 mmol) with ICl (1015 mg, 6.25 mmol). The compound was purified by column chromatography on silica (petroleum ether/CH_2Cl_2 =3/1, v/v) and recrystallized with methanol/dichloromethane to give 1.30 g of compound **2b** in 90% yield as purple solids. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.43 (d, *J* = 8.7 Hz,

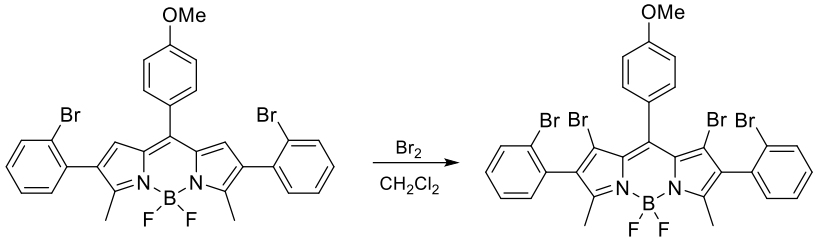
2H), 7.02 (d, *J* = 8.7 Hz, 2H), 6.98 (s, 2H), 3.90 (s, 3H), 2.65 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 162.21, 158.39, 141.90, 137.01, 135.44, 132.42, 127.44, 126.00, 114.47, 55.89, 15.79. **HRMS** (ESI-Orbitrap, $[M]^+$, 100%): calcd for $C_{18}H_{15}BF_2I_2N_2O$, 577.9329; found, 577.9337.



2b **3b**

Compound **3b**:

The synthesis method resembles that of compound **3a**, by the reaction of compound **2b** (145 mg, 0.25 mmol) with 2-bromophenylboronic acid (126 mg, 0.625 mmol). The compound was purified by column chromatography on silica (petroleum ether/CH_2Cl_2 =2/1, v/v) to afford crude product **3b**, after recrystallization with methanol/dichloromethane to give 102 mg of compound **3b** in 64% yield as red solids. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 7.9 Hz, 2H), 7.56 (d, *J* = 8.4 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 2H), 7.25 (s, 2H), 7.19 (t, *J* = 7.3 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.85 (s, 2H), 3.86 (s, 3H), 2.57 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 161.71, 155.66, 143.17, 135.55, 133.67, 133.21, 132.48, 131.97, 130.02, 129.42, 127.47, 126.68, 124.52, 114.11, 55.70, 13.97. **HRMS** (ESI-Orbitrap, $[M]^+$, 100%): calcd for $C_{30}H_{23}BBr_2F_2N_2O$, 636.0212; found, 636.0223.

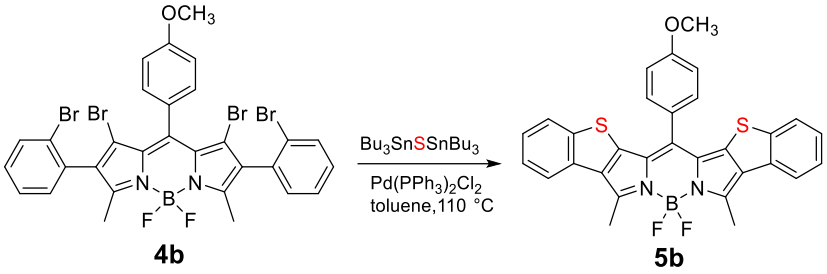


3b **4b**

Compound **4b**:

The synthesis method resembles that of compound **4a**, by the reaction of compound **3a** (64 mg, 0.1 mmol) with liquid bromine (31 μL, 0.6 mmol). The compound was purified by column chromatography on silica (petroleum ether/ethyl

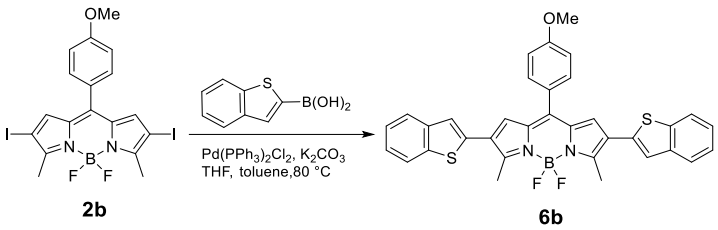
acetate =100/1, v/v) and recrystallized with methanol/dichloromethane to give 39 mg of compound **4b** in 49% yield as orange red solids. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 7.8 Hz, 2H), 7.36 (t, *J* = 7.2 Hz, 2H), 7.29-7.24 (m, 4H), 7.17 (d, *J* = 7.5 Hz, 2H), 7.01 (d, *J* = 8.6 Hz, 2H), 3.86 (s, 3H), 2.47 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 161.10, 155.83, 143.57, 135.49, 133.99, 133.07, 132.61, 130.89, 130.27, 130.08, 127.62, 125.15, 123.63, 121.55, 114.64, 55.56, 14.21. **HRMS** (ESI-Orbitrap, $[M-1]^-$, 100%): calcd for $C_{30}H_{20}BBr_4F_2N_2O$, 792.8324; found, 792.8345.



4b **5b**

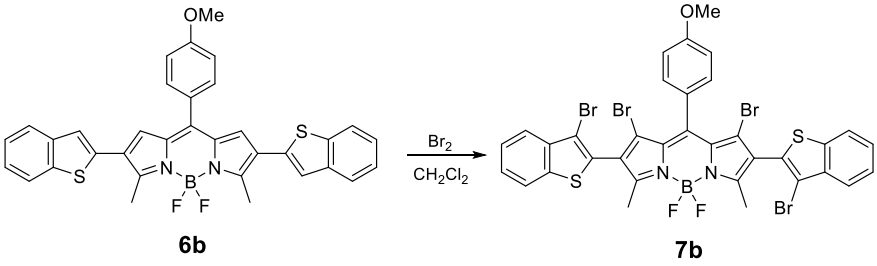
Compound **5b**:

The synthesis method resembles that of compound **5a**, by the reaction of compound **4b** (24 mg, 0.03 mmol) with bis(tri-*n*-butyltin)sulfide (26.6 μL, 0.066 mmol). The crude product was purified by column chromatography on silica (petroleum ether/CH_2Cl_2 = 2/1, v/v) and recrystallized with methanol/dichloromethane to give 11 mg of compound **5b** in 69 % yield as golden metallic luster solids. **Mp** 292.2-293.5℃. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 7.8 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.6 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.28 (d, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 8.6 Hz, 2H), 4.00 (s, 3H), 3.05 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 161.65, 148.85, 144.34, 141.87, 137.35, 133.53, 131.55, 130.03, 125.76, 125.67, 125.54, 125.07, 123.63, 121.31, 115.72, 55.73, 14.74. **HRMS** (ESI-Orbitrap, $[M]^+$, 100%): calcd for $C_{30}H_{21}BF_2N_2OS_2$, 538.1151; found, 538.1157.



Compound **6b**:

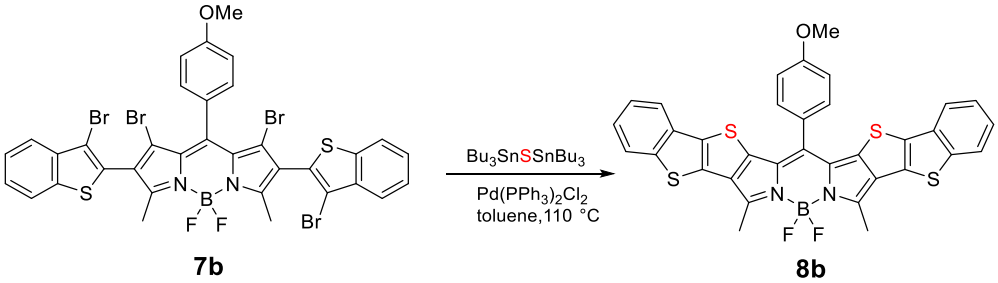
The synthesis method resembles that of compound **3a**, by the reaction of compound **2b** (145 mg, 0.25 mmol) with benzo[*b*]thiophen-2-ylboronic acid (111 mg, 0.625 mmol). The compound was purified by column chromatography on silica (petroleum ether/CH_2Cl_2 =2/1, v/v) to afford crude product **6b**, after recrystallization with methanol/dichloromethane to give 89 mg of compound **6b** in 60% yield as dark-brown solids. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82 - 7.78 (m, 2H), 7.76 (dt, *J* = 8.0, 0.9 Hz, 2H), 7.56 (d, *J* = 8.7 Hz, 2H), 7.44 - 7.28 (m, 6H), 7.09 (d, *J* = 8.8 Hz, 2H), 6.98 (s, 2H), 3.94 (s, 3H), 2.93 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 161.95, 155.44, 143.00, 140.63, 139.38, 136.57, 133.90, 132.40, 127.89, 127.18, 126.41, 124.83, 124.55, 123.62, 122.25, 121.13, 114.38, 55.78, 14.78. **HRMS** (ESI-Orbitrap, $[M]^+$, 100%): calcd for $C_{34}H_{25}BF_2N_2OS_2$, 590.1464; found, 590.1474.



Compound **7b**:

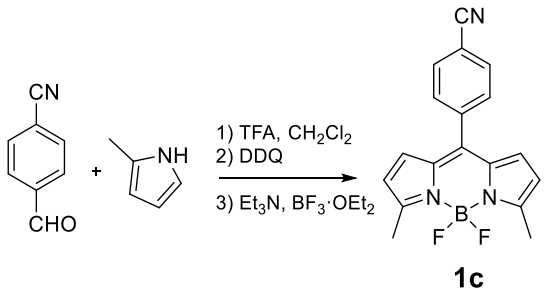
The synthesis method resembles that of compound **4a**, by the reaction of compound **6b** (59 mg, 0.1 mmol) with a solution of liquid bromine (180 μL, 3.5 mmol) in dry CH_2Cl_2 (5 mL). The compound was purified by column chromatography on silica (petroleum ether/CH_2Cl_2 =12/1, v/v) and recrystallized with methanol/dichloromethane to give 66 mg of compound **7b** in 73% yield as red solids. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 7.9 Hz, 2H), 7.83 (d, *J* = 7.9 Hz, 2H), 7.54 - 7.40 (m, 4H), 7.36 - 7.26 (m, 2H), 7.04 (d, *J* = 8.7 Hz, 2H), 3.87 (s, 3H), 2.60 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 161.31, 157.22, 144.51, 139.53,

138.23, 130.74 (t, J = 7.8 Hz), 130.55, 129.34, 127.49, 126.16, 125.47, 124.00, 123.88, 123.15, 122.69, 114.85, 110.78, 55.58, 14.42. **HRMS** (ESI-Orbitrap, $[M-1]^-$, 100%): calcd for $C_{34}H_{20}BBr_4F_2N_2OS_2$, 904.7765; found, 904.7783.



Compound **8b**:

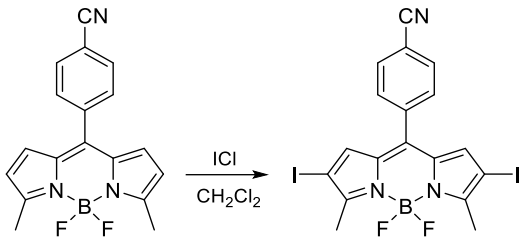
The synthesis method resembles that of compound **5a**, by the reaction of compound **7b** (36 mg, 0.04 mmol) with bis(tri-*n*-butyltin)sulfide (35.5 μL, 0.088 mmol). The crude product was purified by column chromatography on silica (petroleum ether/CH_2Cl_2 = 2/1, v/v) and recrystallized with methanol/dichloromethane to give 9.1 mg of compound **8b** in 35% yield as dark blue solids. **Mp** > 320℃. **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 7.90 (d, J = 7.9 Hz, 2H), 7.69 (d, J = 7.5 Hz, 2H), 7.62 (d, J = 8.7 Hz, 2H), 7.45 - 7.39 (m, 2H), 7.39 - 7.33 (m, 2H), 7.29 (d, J = 8.7 Hz, 2H), 4.05 (s, 3H), 2.94 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 142.21, 136.63, 135.64, 133.07, 129.93, 128.59, 126.28, 125.66, 125.26, 125.23, 124.62, 124.30, 124.25, 121.72, 120.82, 118.20, 115.94, 55.80, 14.66. HRMS (ESI-Orbitrap, $[M]^+$, 100%): calcd for $C_{34}H_{21}BF_2N_2OS_4$, 650.0592; found, 650.0605.



Compound **1c**:

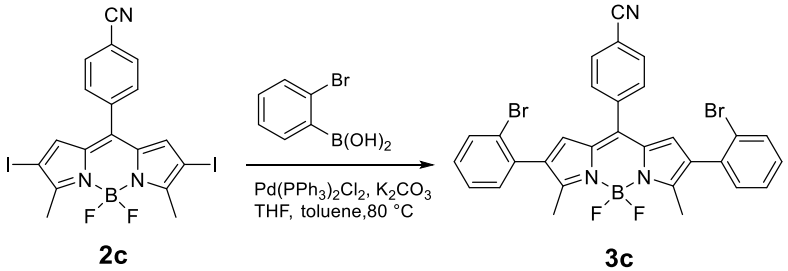
The synthesis method resembles that of compound **1a**, by the reaction of 4-cyanobenzaldehyde (1.31 g, 10 mmol) with 2-methylpyrrole (1663 mg, 20.5 mmol).

The compound was purified by column chromatography on silica (petroleum ether/CH_2Cl_2 =3/1, v/v) and recrystallized with methanol/dichloromethane to give 1.06 g of compound **1c** in 33% yield as orange red solids. NMR data of this compound agreed with the reported one[7]. **Mp** 185.7-187.0℃. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 8.3 Hz, 2H), 6.60 (d, *J* = 4.1 Hz, 2H), 6.30 (d, *J* = 4.1 Hz, 2H), 2.66 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 159.16, 139.68, 138.87, 134.25, 132.24, 131.13, 130.18, 120.38 (d, *J* = 2.9 Hz), 118.30, 114.05, 15.24.



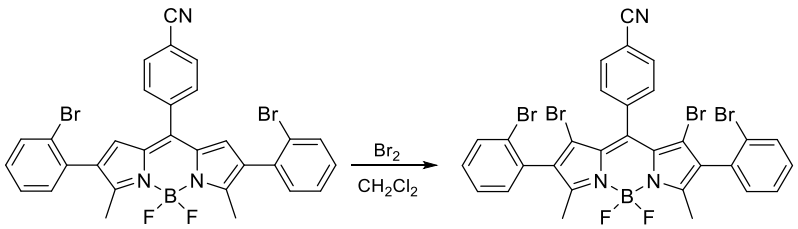
Compound **2c**:

The synthesis method resembles that of compound **2a**, by the reaction of compound **1c** (803 mg, 2.5 mmol) with ICl (1015 mg, 6.25 mmol). The compound was purified by column chromatography on silica (petroleum ether/CH_2Cl_2 =3/1, v/v) and recrystallized with methanol/dichloromethane to give 1.26 g of compound **2c** in 88% yield as purple solids. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 8.6 Hz, 2H), 6.85 (s, 2H), 2.67 (s, 6H). **^{13}C NM**R (101 MHz, Chloroform-*d*) δ 160.36, 138.31, 137.88, 136.55, 134.94, 132.55, 131.04, 118.04, 114.68, 78.88, 15.88. **HRMS** (ESI-Orbitrap, $[M]^-$, 100%): calcd for $C_{18}H_{12}BF_2I_2N_3$, 572.9176; found, 572.9188.



Compound **3c**:

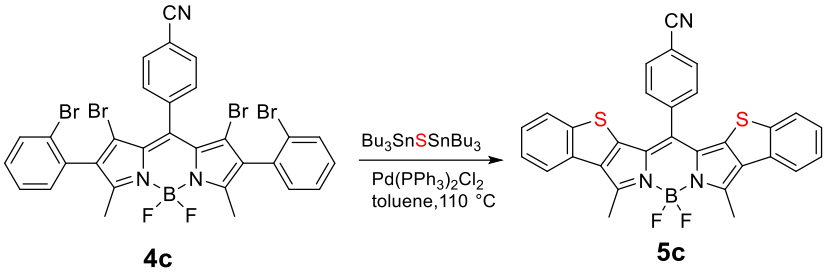
The synthesis method resembles that of compound **3a**, by the reaction of compound **2c** (143 mg, 0.25 mmol) with 2-bromophenylboronic acid (126 mg, 0.625 mmol). The compound was purified by column chromatography on silica (petroleum ether/CH_2Cl_2 =2/1, v/v) to afford crude product **3c**, after recrystallization with methanol/dichloromethane to give 93 mg of compound **3c** in 59% yield as red solids. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 8.3 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.33 (t, *J* = 7.0 Hz, 2H), 7.25 - 7.17 (m, 4H), 6.69 (s, 2H), 2.58 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 157.76, 139.90, 138.72, 134.92, 134.17, 133.29, 132.35, 131.84, 131.28, 129.74, 129.50, 127.59, 124.39, 118.26, 114.19, 14.14. **HRMS** (ESI-Orbitrap, $[M-1]^-$, 100%): calcd for $C_{30}H_{19}BBr_2F_2N_3$, 629.9981; found, 629.9999.



3c **4c**

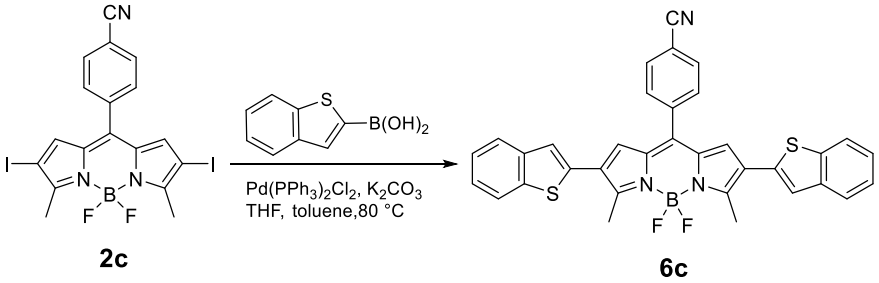
Compound **4c**:

The synthesis method resembles that of compound **4a**, by the reaction of compound **3c** (63 mg, 0.1 mmol) with liquid bromine (31 μL, 0.6 mmol). The compound was purified by column chromatography on silica (petroleum ether/ethyl acetate =100/1, v/v) and recrystallized with methanol/dichloromethane to give 32 mg of compound **4c** in 41% yield as orange red solids. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 8.7 Hz, 2H), 7.68 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 7.37 (td, *J* = 7.5, 1.3 Hz, 2H), 7.32 - 7.21 (m, 2H), 7.15 (dd, *J* = 7.5, 1.7 Hz, 2H), 2.49 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 157.10, 140.15, 136.54, 136.07, 133.41, 133.15, 132.91, 132.41, 130.87, 130.53, 128.98, 127.74, 124.97, 121.19, 118.76, 113.84, 14.33. **HRMS** (ESI-Orbitrap, $[M]^-$, 100%): calcd for $C_{30}H_{18}BBr_4F_2N_3$, 788.8249; found, 788.8249.



Compound **5c**:

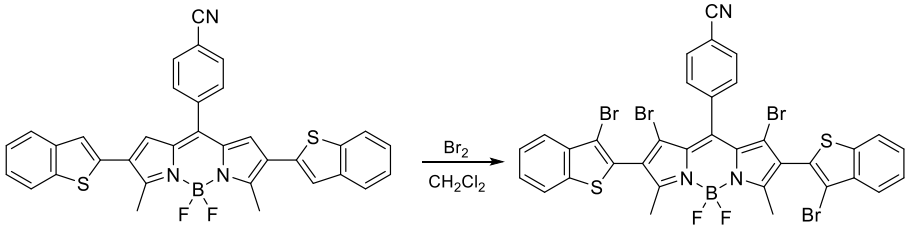
The synthesis method resembles that of compound **5a**, by the reaction of compound **4c** (24 mg, 0.03 mmol) with bis(tri-*n*-butyltin)sulfide (26.6 μL, 0.066 mmol). The crude product was purified by column chromatography on silica (petroleum ether/CH_2Cl_2 = 2/1, v/v) and recrystallized with methanol/dichloromethane to give 10.5 mg of compound **5c** in 66 % yield as golden metallic luster solids. **Mp** 298.0-299.0°C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.6 Hz, 2H), 7.88 (d, *J* = 7.5 Hz, 2H), 7.73 (d, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 7.9 Hz, 2H), 7.41 (td, *J* = 7.7, 1.1 Hz, 2H), 7.30 (ddd, *J* = 8.3, 7.3, 1.2 Hz, 2H), 3.05 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 150.21, 144.06, 141.52, 138.43, 134.26, 134.16, 134.05, 131.33, 129.66, 125.88, 125.45, 124.81, 123.75, 121.44, 118.45, 114.75, 14.82. **HRMS** (ESI-Orbitrap, $[M]^+$, 100%): calcd for $C_{30}H_{18}BF_2N_3S_2$, 533.0998; found, 533.1007.



Compound **6c**:

The synthesis method resembles that of compound **3a**, by the reaction of compound **2c** (143 mg, 0.25 mmol) with benzo[*b*]thiophen-2-ylboronic acid (111 mg, 0.625 mmol). The compound was purified by column chromatography on silica (petroleum ether/CH_2Cl_2 =2/1, v/v) to afford crude product **6c**, after recrystallization with methanol/dichloromethane to give 81 mg of compound **6c** in 55% yield as modena solids. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 8.2 Hz, 2H), 7.80

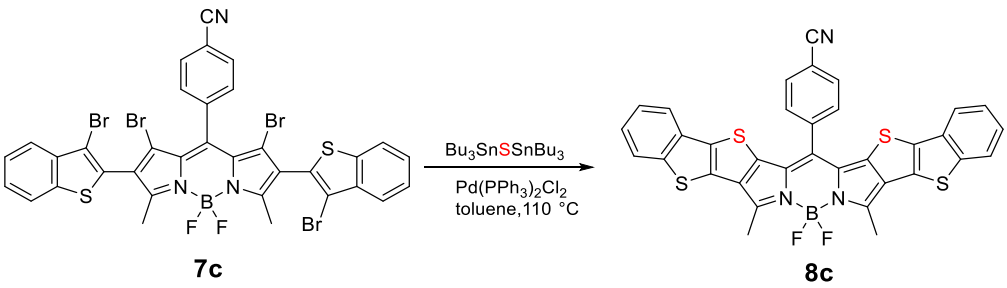
(d, *J* = 7.7 Hz, 2H), 7.76 (d, *J* = 7.5 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.40 - 7.29 (m, 6H), 6.80 (s, 2H), 2.95 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 157.46, 140.51, 139.60, 139.42, 138.43, 135.81, 133.48, 132.60, 131.18, 128.17, 127.15, 124.98, 124.84, 123.76, 122.30, 121.60, 118.22, 114.53, 14.97. **HRMS** (ESI-Orbitrap, $[M]^+$, 100%): calcd for $C_{34}H_{22}BF_2N_3S_2$, 585.1311; found, 585.1321.



6c **7c**

Compound **7c**:

The synthesis method resembles that of compound **4a**, by the reaction of compound **6c** (59 mg, 0.1 mmol) with a solution of liquid bromine (256 μL, 5 mmol) in dry CH_2Cl_2 (5 mL). The compound was purified by column chromatography on silica (petroleum ether/CH_2Cl_2 =10/1, v/v) and recrystallized with methanol/dichloromethane to give 57 mg of compound **7c** in 63% yield as red solids. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.87 (d, *J* = 7.9 Hz, 2H), 7.83 (dd, *J* = 7.8, 4.1 Hz, 4H), 7.61 (dd, *J* = 20.1, 7.6 Hz, 2H), 7.53 - 7.48 (m, 2H), 7.46 (t, *J* = 7.5 Hz, 2H), 2.62 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 158.47, 140.99, 139.48, 138.14, 136.09, 133.12 (t, *J* = 4.6 Hz), 130.72 (t, *J* = 8.6 Hz), 129.55, 128.58, 128.24, 126.36, 125.61, 124.06, 123.54, 122.71, 118.62, 114.18, 110.99, 14.55. **HRMS** (ESI-Orbitrap, $[M-1]^-$, 100%): calcd for $C_{34}H_{17}BBr_4F_2N_3S_2$, 899.7612; found, 899.7625.



7c **8c**

Compound **8c**:

The synthesis method resembles that of compound **5a**, by the reaction of compound **7c** (36 mg, 0.04 mmol) with bis(tri-*n*-butyltin)sulfide (35.5 μL, 0.088 mmol). The crude product was purified by column chromatography on silica (petroleum ether/CH_2Cl_2 = 2/1, v/v) and recrystallized with methanol/dichloromethane to give 8 mg of compound **8c** in 31% yield as bottle green solids. **Mp** > 320℃. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 8.1 Hz, 2H), 7.87 (d, *J* = 7.9 Hz, 2H), 7.79 (d, *J* = 8.1 Hz, 2H), 7.67 (d, *J* = 7.6 Hz, 2H), 7.38 (dt, *J* = 21.9, 7.1 Hz, 4H), 2.97 (s, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.51, 150.57, 148.75, 142.23, 138.48, 136.65, 134.40, 132.81, 129.57, 128.74, 125.44, 124.95, 124.30, 121.74, 120.87, 120.51, 118.43, 114.97, 14.75. **HRMS** (ESI-Orbitrap, $[M-1]^-$, 100%): calcd for $C_{34}H_{17}BF_2N_3S_4$, 644.0361; found, 644.0378.

4. **Photophysical Data**

Compound	Solvent	λ_{max} [a] [nm]	ε /10^5 [b] [$M^{-1}cm^{-1}$]	λ_{ex} [c] [nm]	λ_{em} [d] [nm]	SS [e] [cm^{-1}]	Φ_f [f] [%]	τ [g] [ns]	K_r /10^8 [h] [S^{-1}]	K_{nr} /10^8 [i] [S^{-1}]
1a	DCM	512	1.10	512	520	300	89.1	6.69	1.33	0.16
	THF	511	1.56	511	519	302	87.4	6.80	1.29	0.19
	Toluene	514	1.23	514	522	298	89.5	5.81	1.54	0.18
5a	DCM	564	1.49	563	574	309	84.2	5.17	1.63	0.31
	THF	563	1.67	563	572	279	82.3	5.21	1.58	0.34
	Toluene	567	1.93	566	575	245	82.5	5.12	1.61	0.34
8a	DCM	623	1.41	623	643	499	81.7	6.66	1.23	0.27
	THF	622	1.22	622	641	477	85.0	6.33	1.34	0.24
	Toluene	627	1.46	626	642	373	81.5	6.05	1.35	0.31
1b	DCM	510	0.65	509	520	377	25.5	2.53	1.01	2.94
	THF	509	0.82	507	519	379	28.0	2.66	1.05	2.71
	Toluene	512	0.80	511	522	374	32.2	3.50	0.92	1.94
5b	DCM	569	1.40	568	583	422	83.4	5.39	1.55	0.31
	THF	567	1.59	566	580	395	81.2	5.49	1.48	0.34
	Toluene	571	1.66	570	584	390	84.4	5.28	1.60	0.30
8b	DCM	629	1.20	629	654	608	76.7	6.76	1.13	0.34
	THF	626	0.83	627	650	590	74.4	6.27	1.19	0.41
	Toluene	631	0.92	631	652	510	83.8	6.03	1.39	0.27
1c	DCM	517	0.61	516	540	824	4.0	0.52	0.76	18.48
	THF	515	0.83	515	540	899	2.8	0.52	0.53	18.70
	Toluene	519	0.76	518	542	818	5.4	0.66	0.82	14.33
5c	DCM	575	1.10	575	611	1025	74.0	5.58	1.33	0.47
	THF	572	1.16	571	605	954	75.6	5.23	1.45	0.47
	Toluene	577	1.24	575	609	911	73.0	5.40	1.35	0.50
8c	DCM	640	0.58	639	690	1132	45.5	5.30	0.86	1.03
	THF	636	0.68	636	685	1125	43.2	5.00	0.86	1.14
	Toluene	643	0.54	642	689	1038	46.1	5.27	0.87	1.02

Table S7. [a] Absorption maxima (λ_{max}). [b] molar extinction coefficients (at λ_{max}). [c] excitation wavelength. [d] emission maxima (λ_{em}). [e] Stokes shifts. [f] fluorescence quantum yield (Φ_f). [g] lifetime (τ). [h] Radiation rate constant. [i] Non-radiation rate constant.

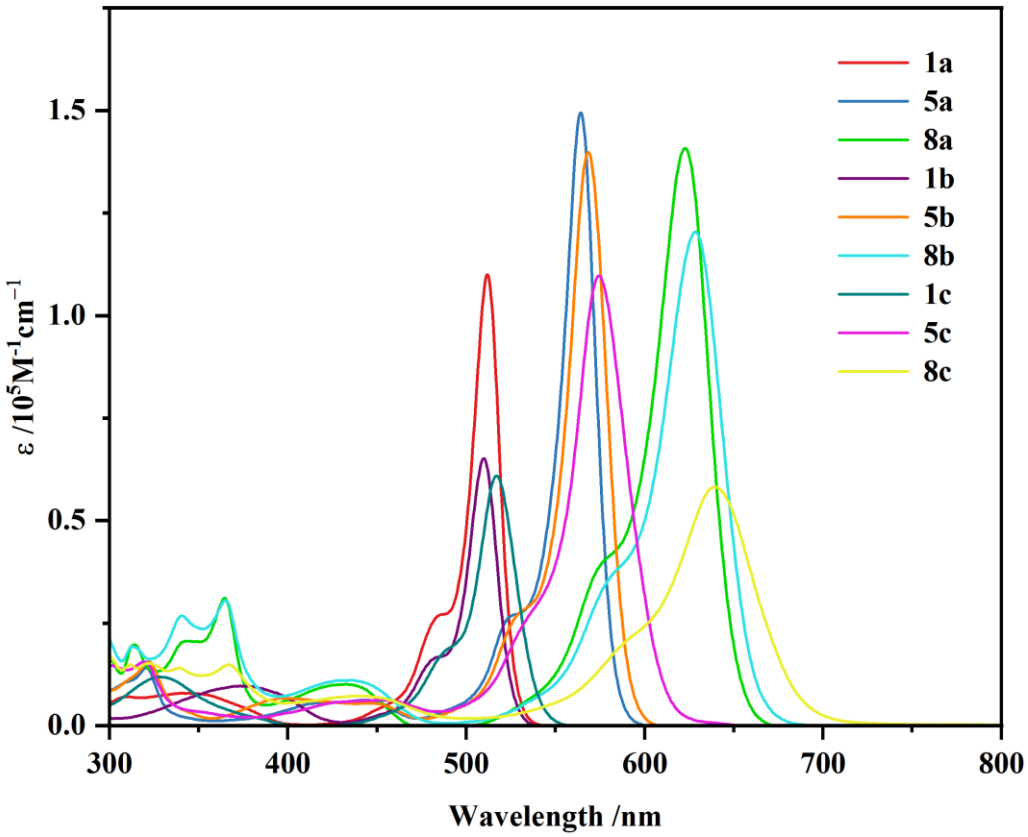


Figure S7. Absorption spectra of **1a-c**, **5a-c** and **8a-c** in dichloromethane.

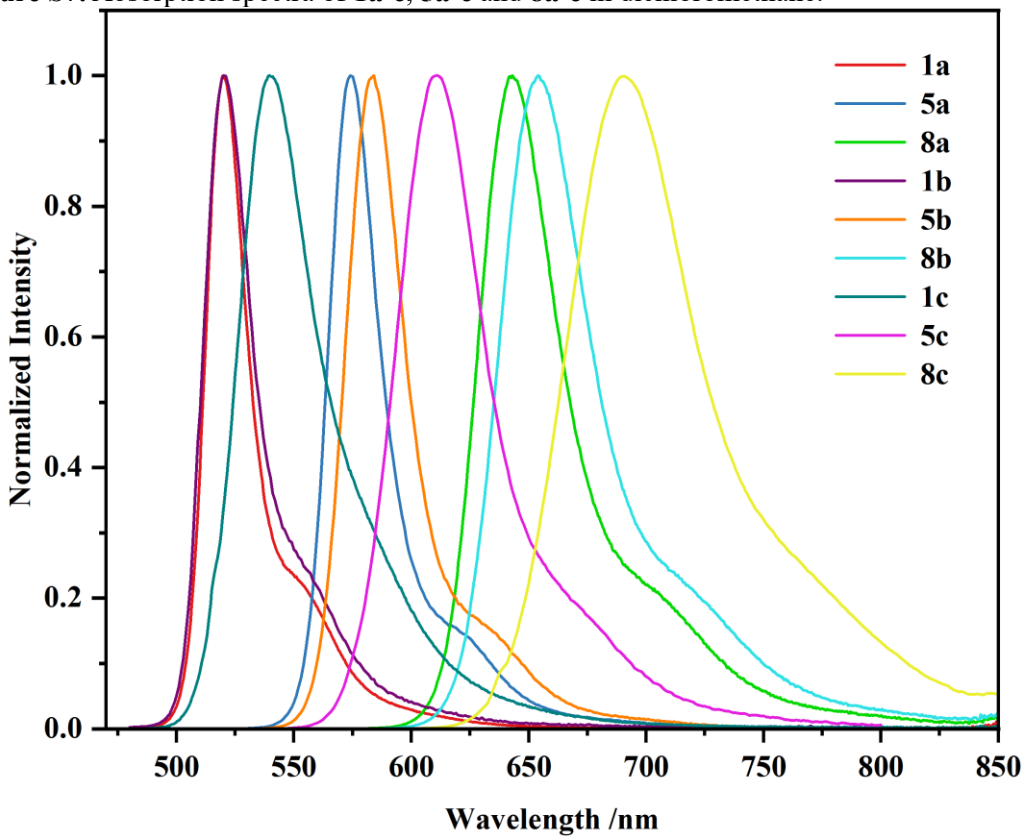


Figure S8. Normalized emission spectra of **1a-c**, **5a-c** and **8a-c** in dichloromethane.

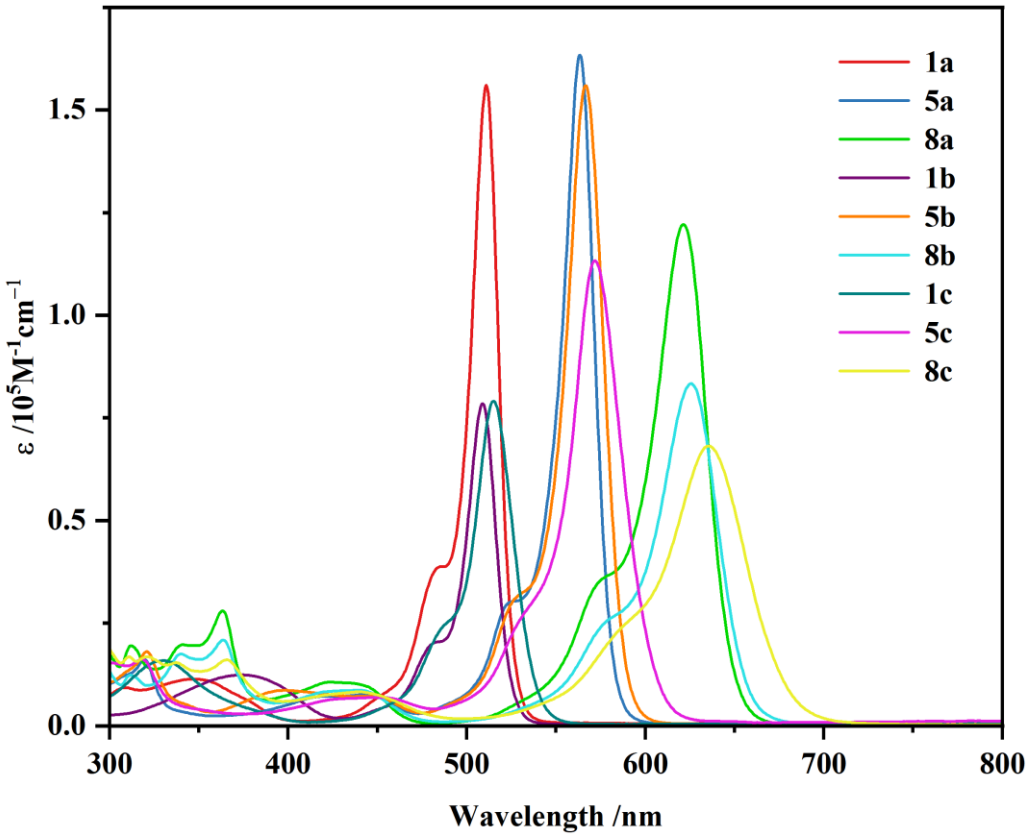


Figure S9. Absorption spectra of **1a-c**, **5a-c** and **8a-c** in tetrahydrofuran.

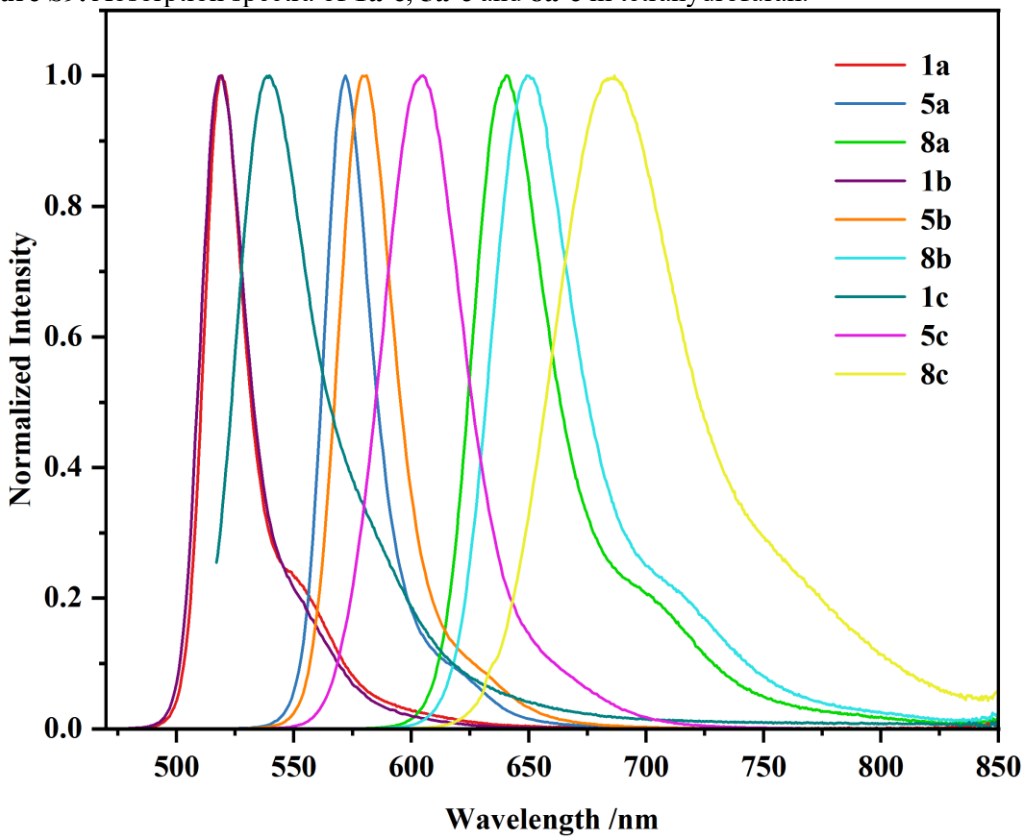


Figure S10. Normalized emission spectra of **1a-c**, **5a-c** and **8a-c** in tetrahydrofuran.

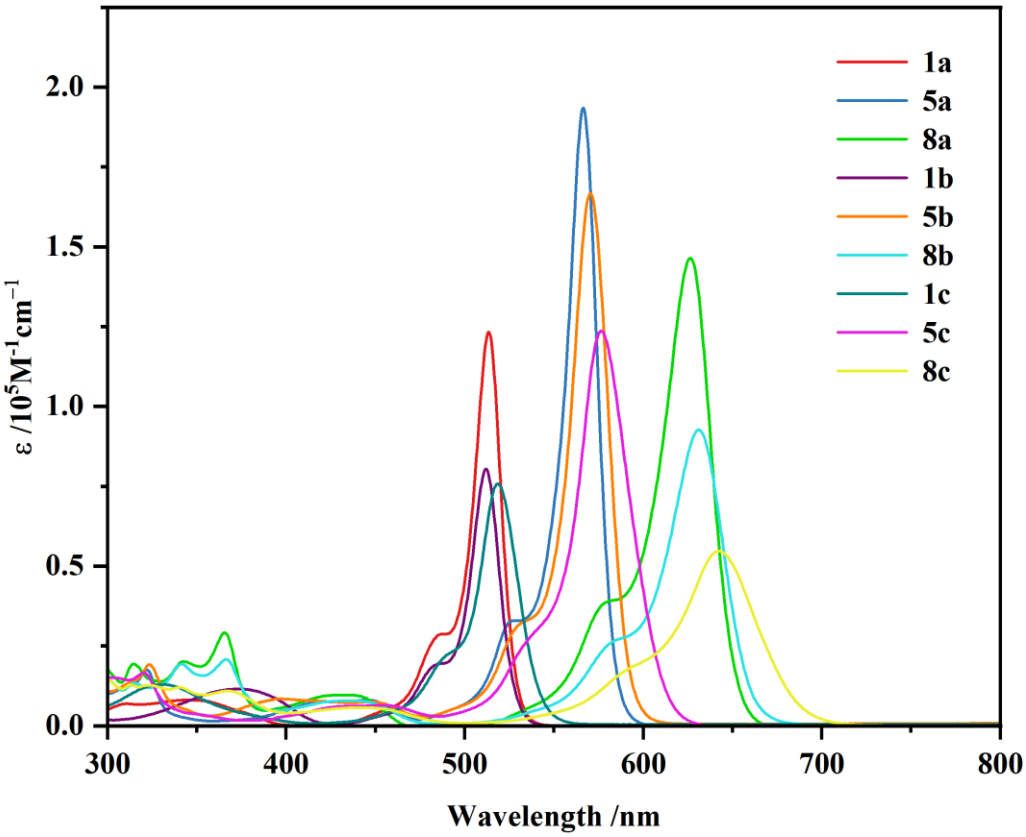


Figure S11. Absorption spectra of **1a-c**, **5a-c** and **8a-c** in toluene.

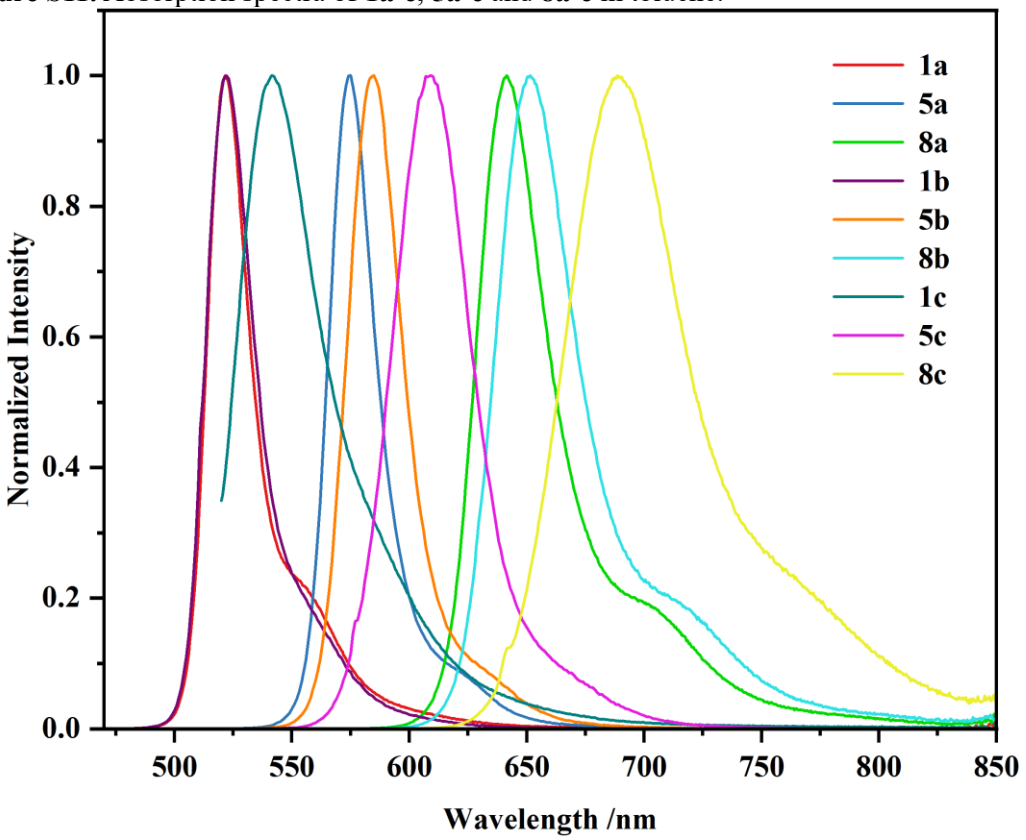


Figure S12. Normalized emission spectra of **1a-c**, **5a-c** and **8a-c** in toluene.

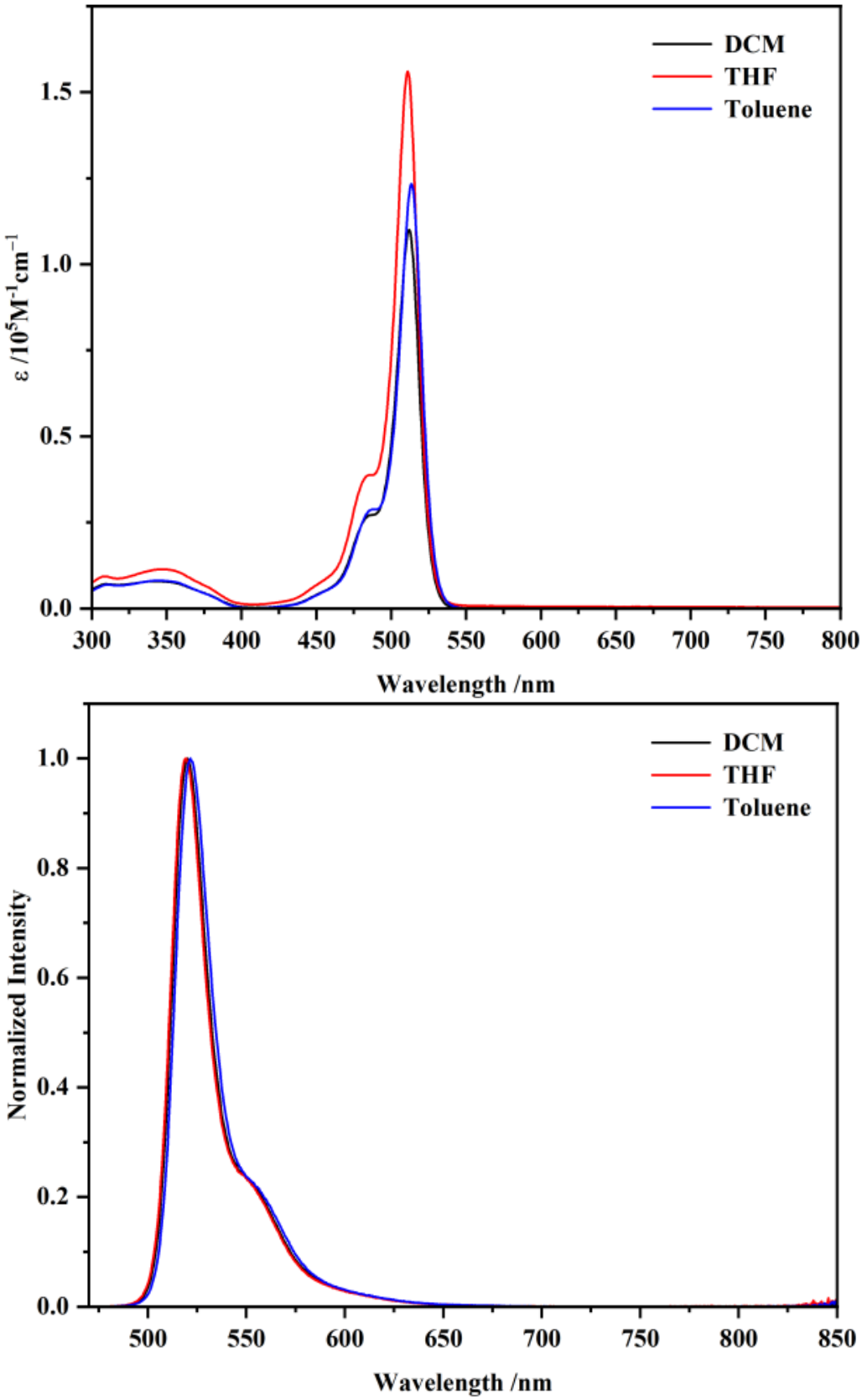


Figure S13. Absorption and Normalized emission spectra of **1a** recorded in DCM, THF and toluene at room temperature.

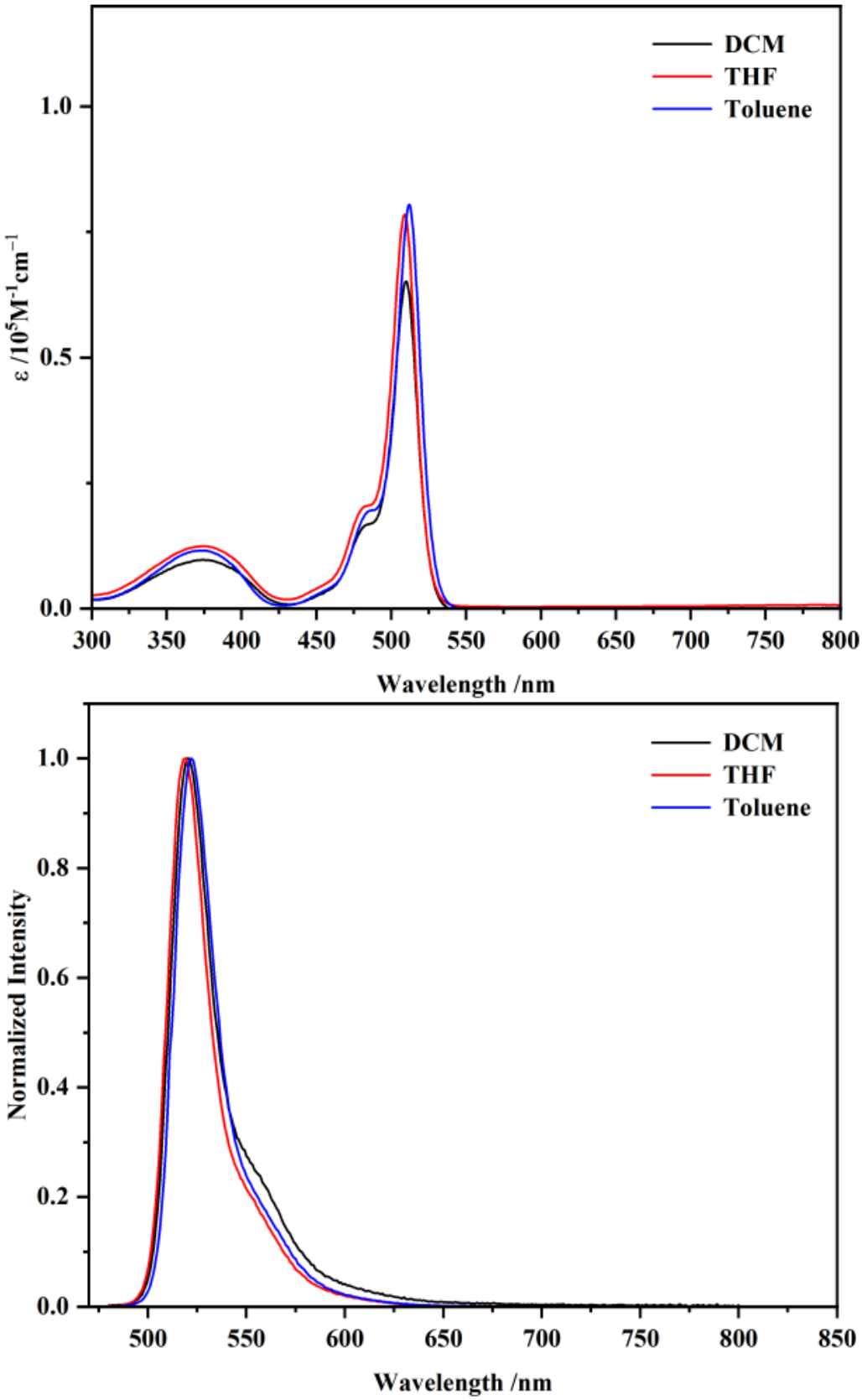


Figure S14. Absorption and Normalized emission spectra of **1b** recorded in DCM, THF and toluene at room temperature.

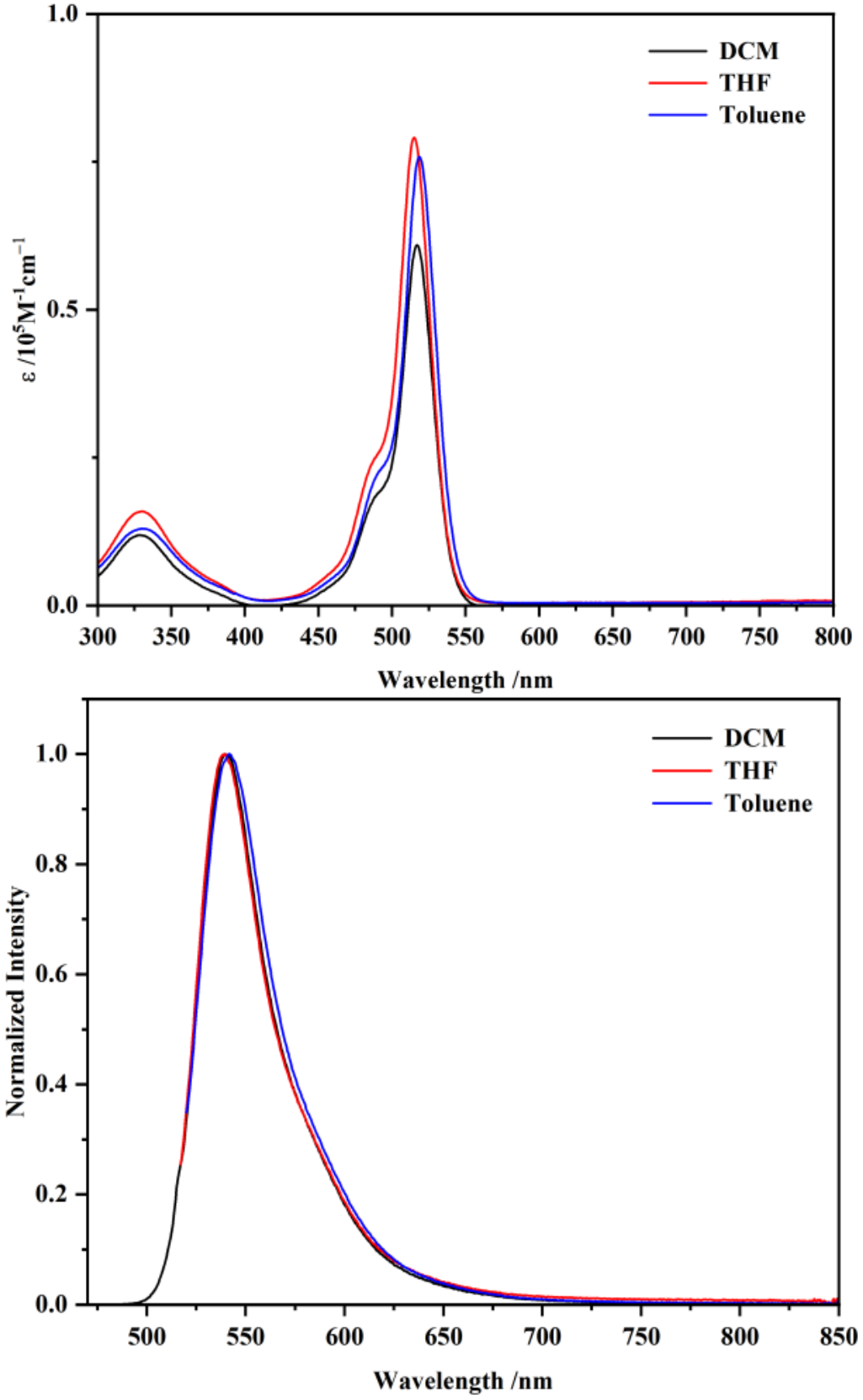


Figure S15. Absorption and Normalized emission spectra of **1c** recorded in DCM, THF and toluene at room temperature.

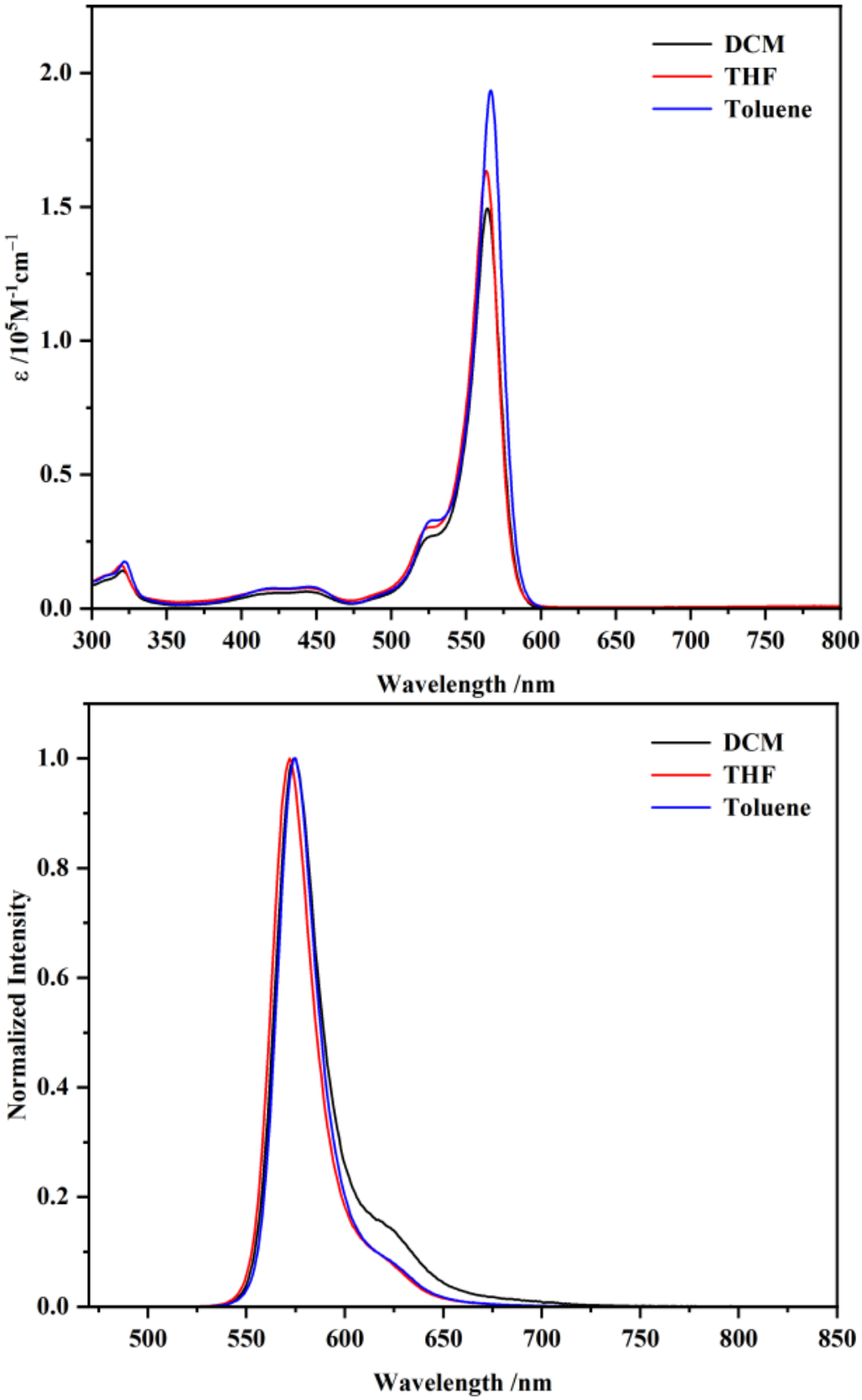


Figure S16. Absorption and Normalized emission spectra of **5a** recorded in DCM, THF and toluene at room temperature.

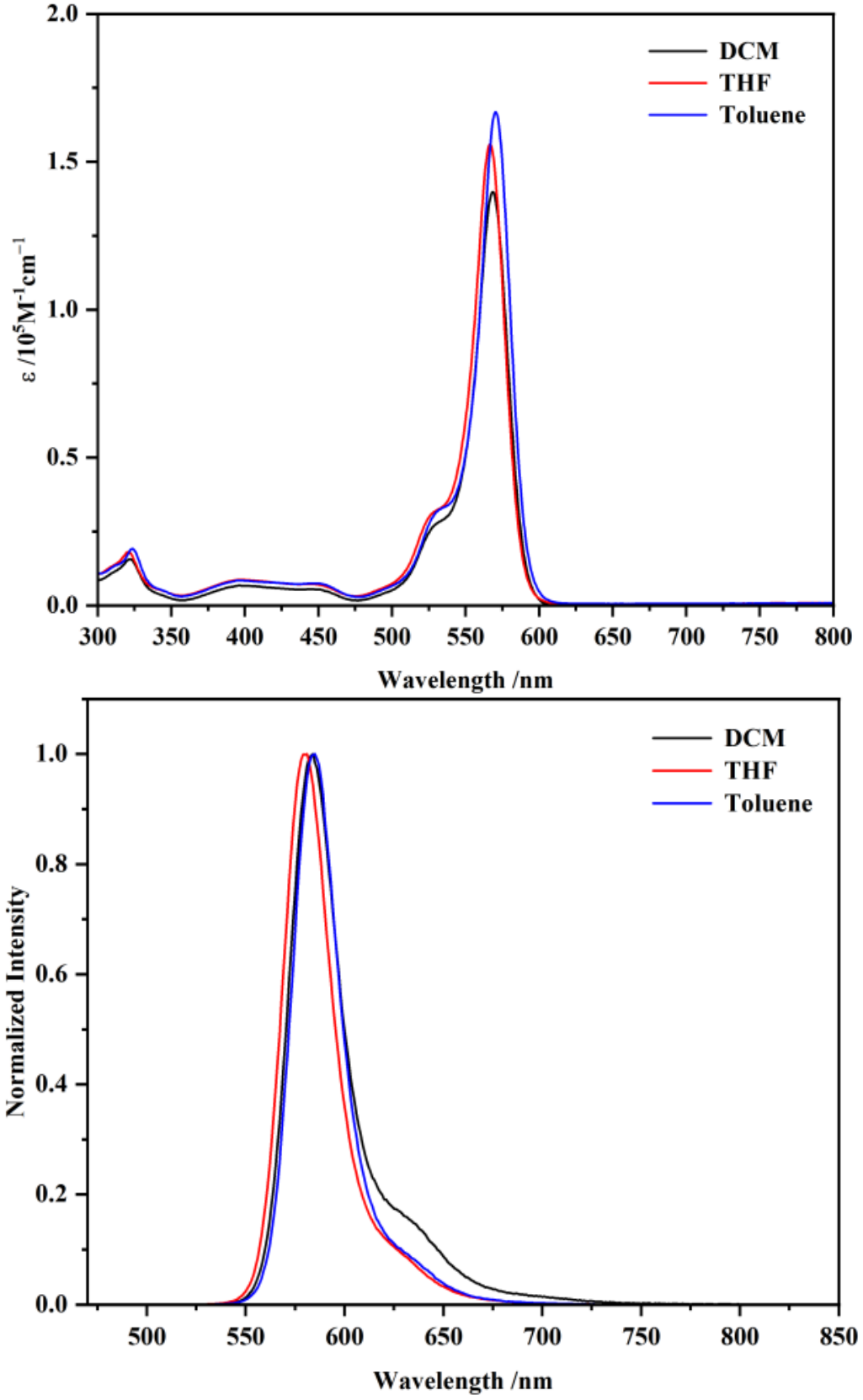


Figure S17. Absorption and Normalized emission spectra of **5b** recorded in DCM, THF and toluene at room temperature.

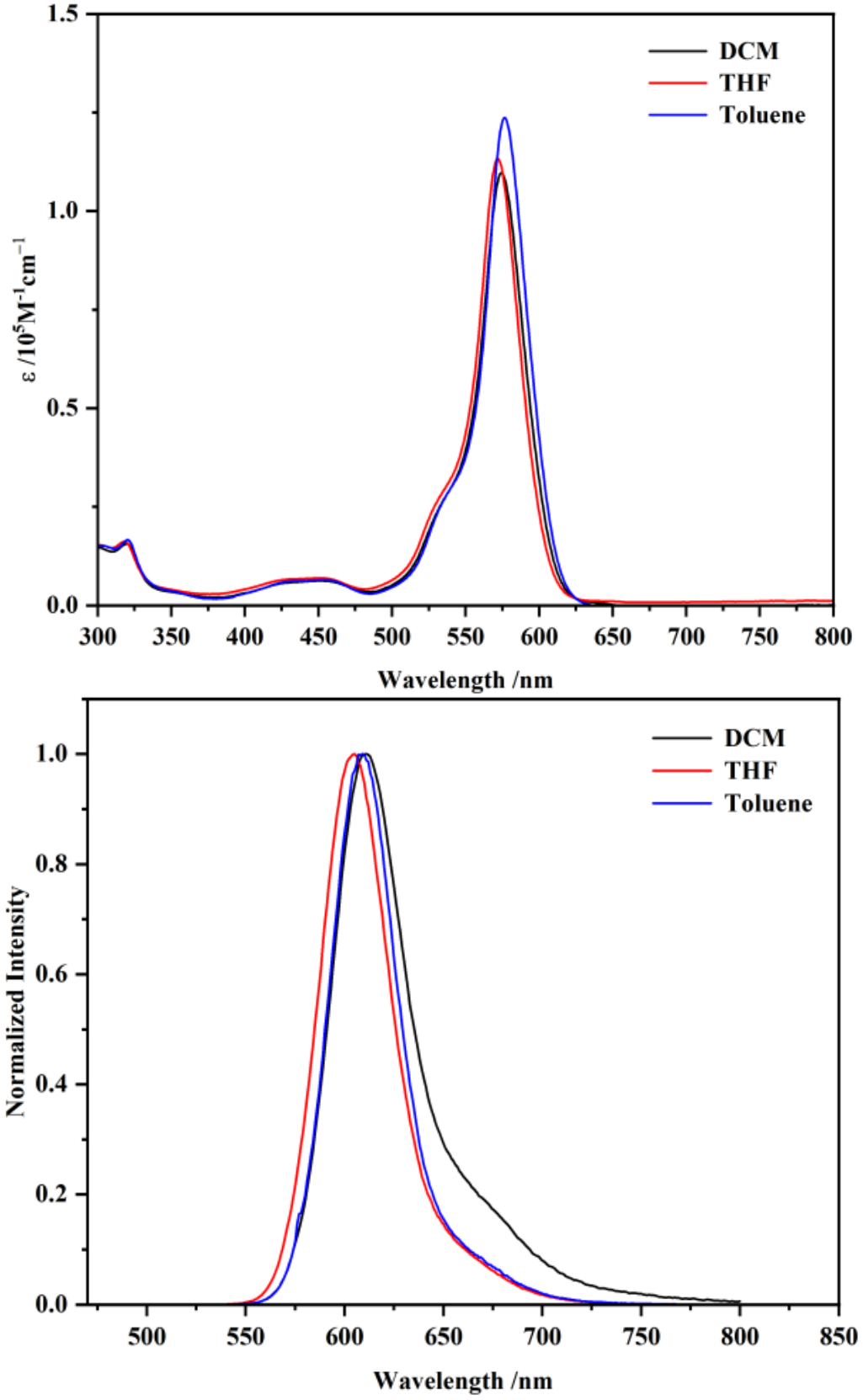


Figure S18. Absorption and Normalized emission spectra of **5c** recorded in DCM, THF and toluene at room temperature.

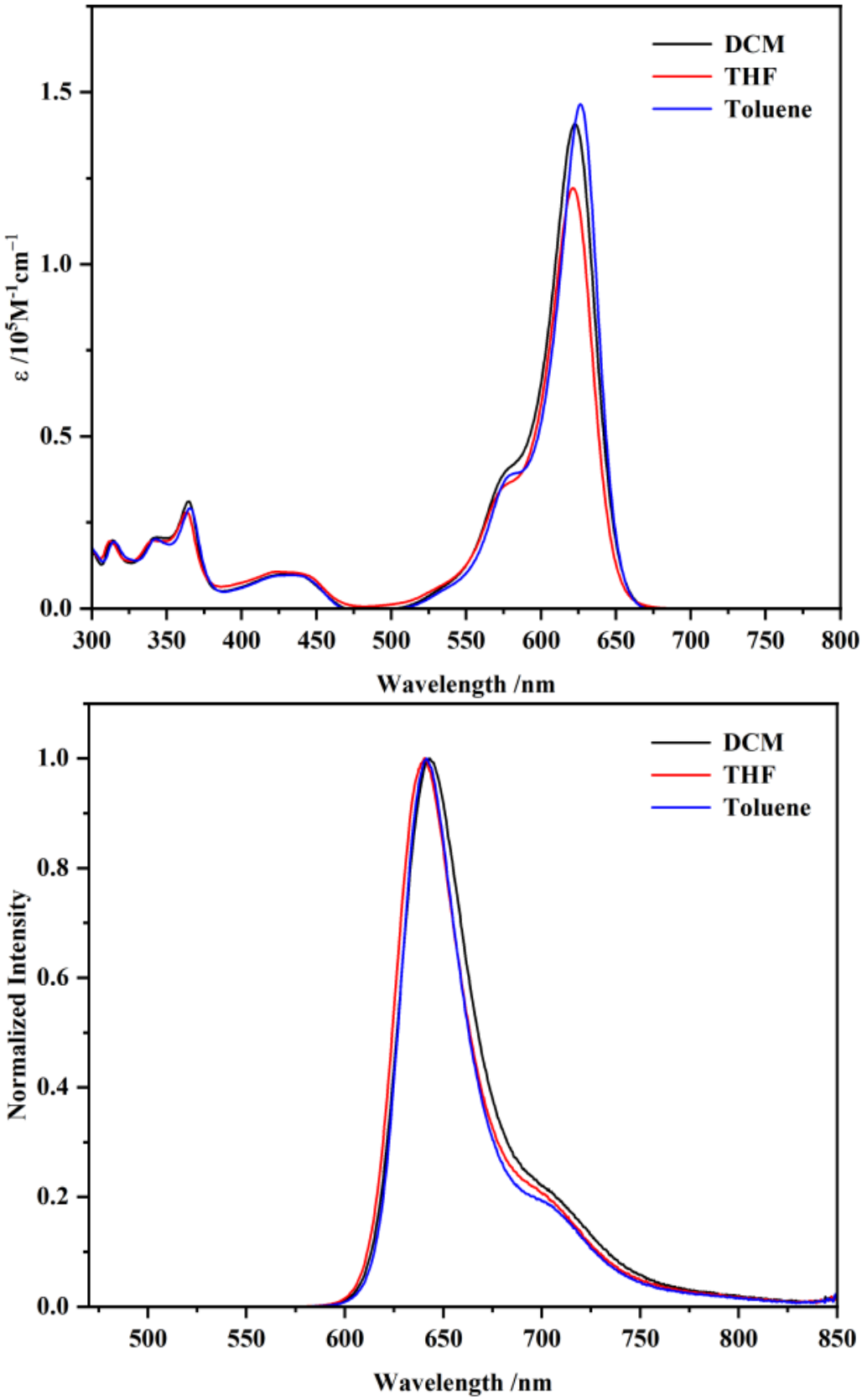


Figure S19. Absorption and Normalized emission spectra of **8a** recorded in DCM, THF and toluene at room temperature.

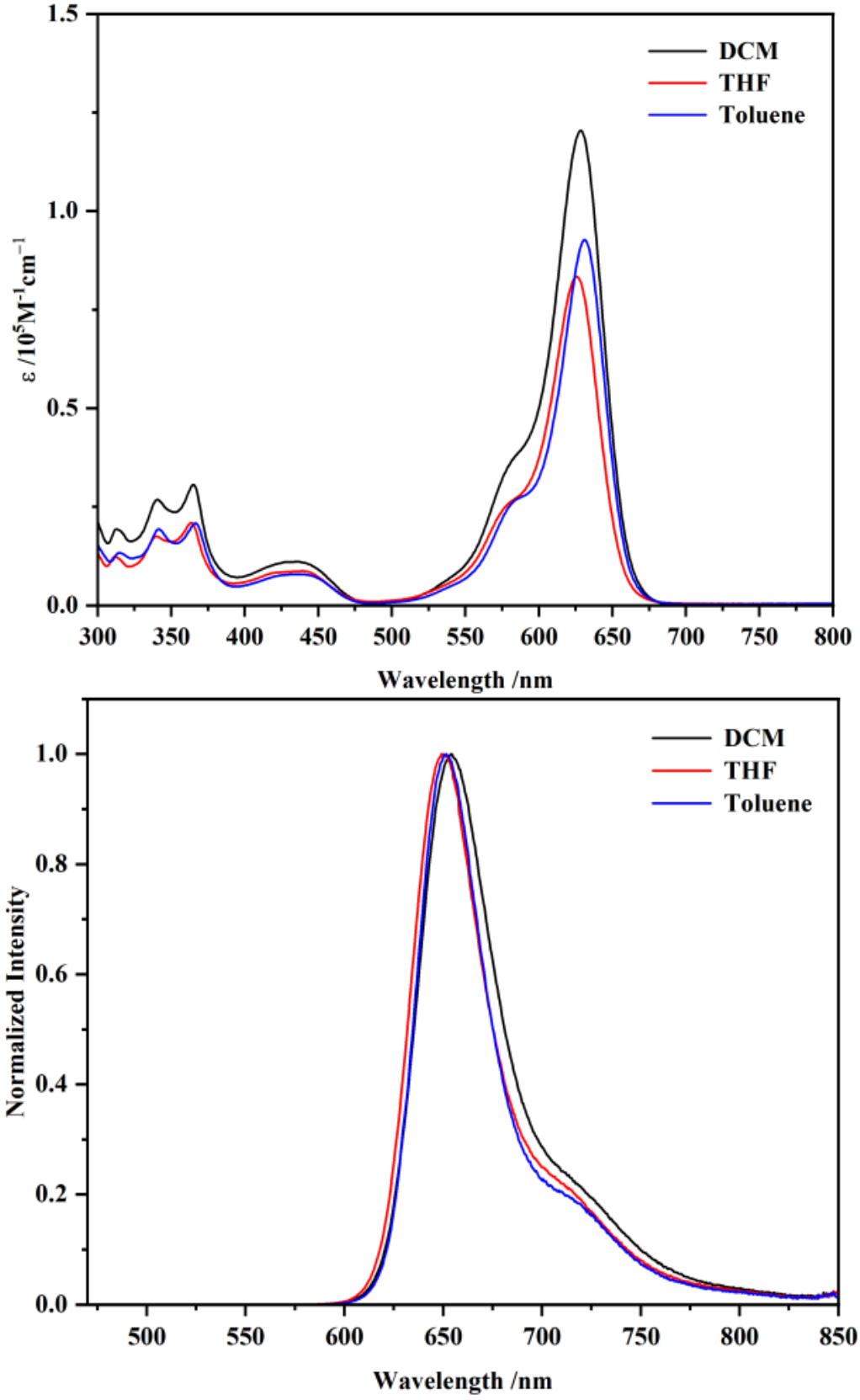


Figure S20. Absorption and Normalized emission spectra of **8b** recorded in DCM, THF and toluene at room temperature.

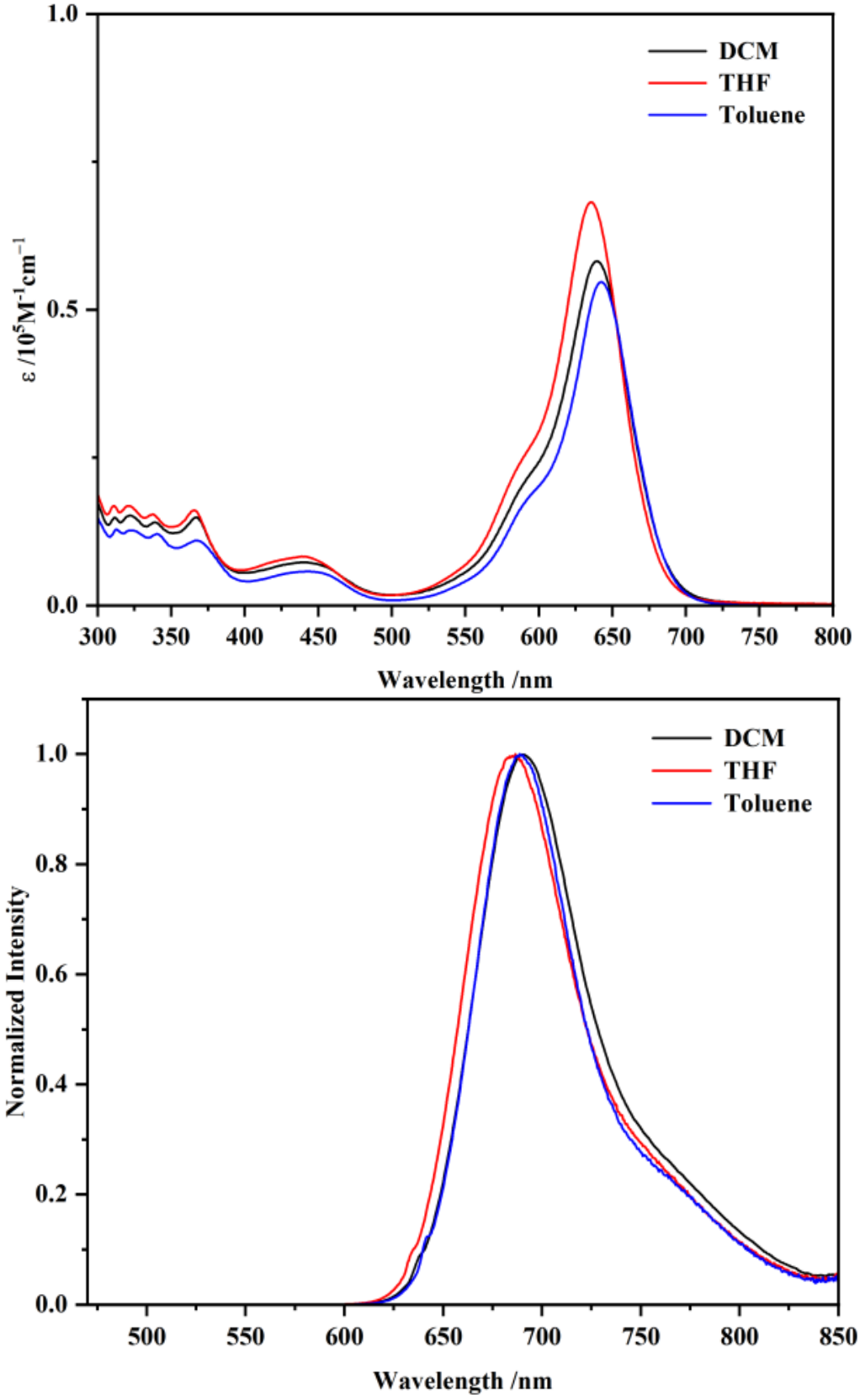


Figure S21. Absorption and Normalized emission spectra of **8c** recorded in DCM, THF and toluene at room temperature.

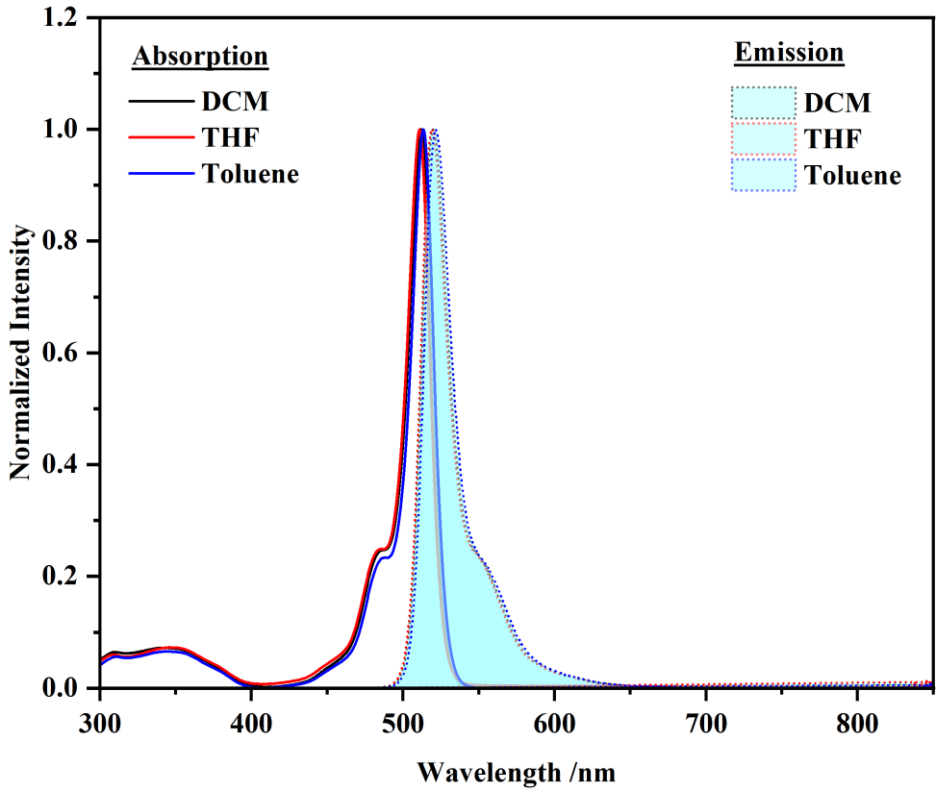


Figure S22. Normalized absorption and emission spectra of **1a** recorded in DCM, THF and toluene at room temperature.

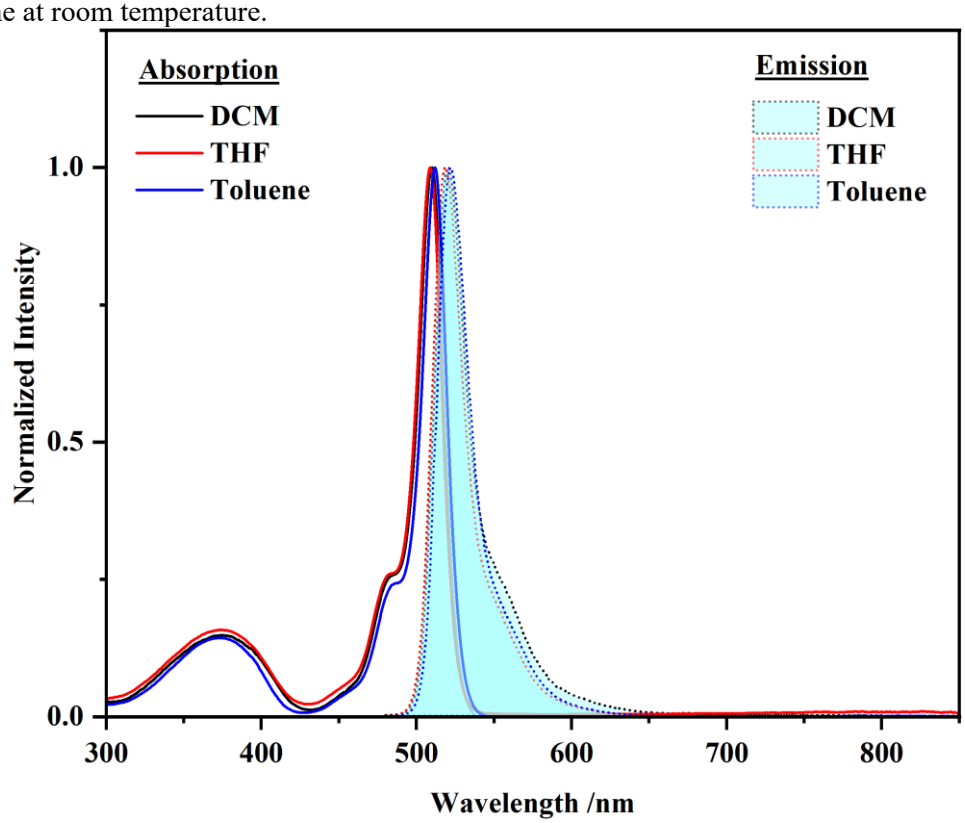


Figure S23. Normalized absorption and emission spectra of **1b** recorded in DCM, THF and toluene at room temperature.

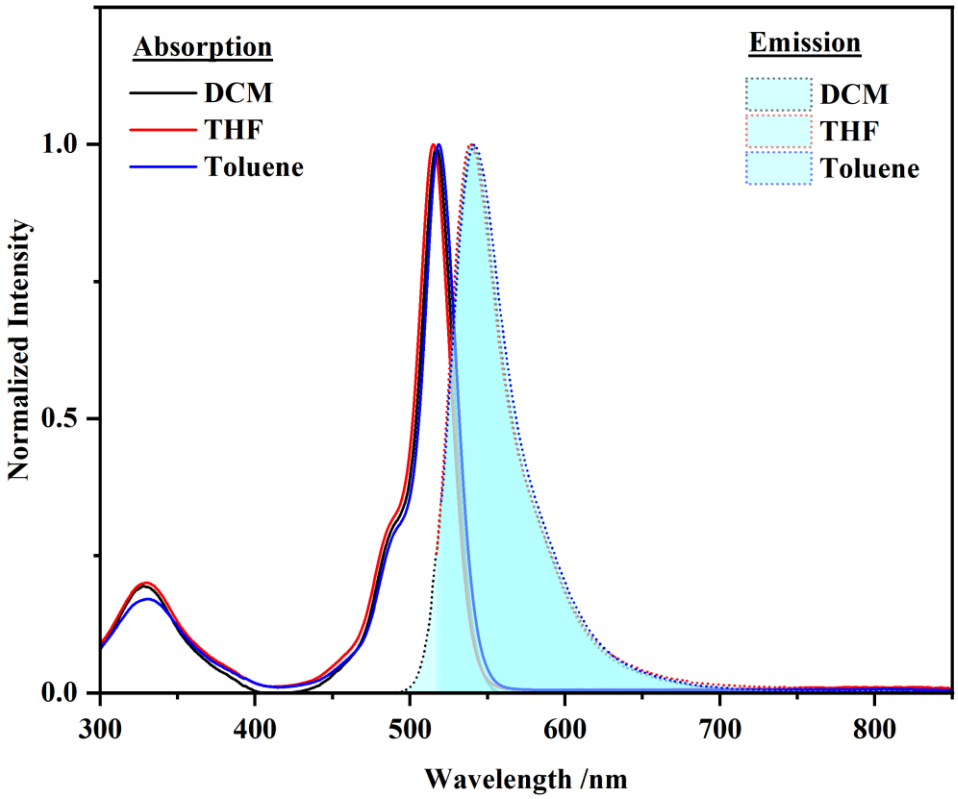


Figure S24. Normalized absorption and emission spectra of **1c** recorded in DCM, THF and toluene at room temperature.

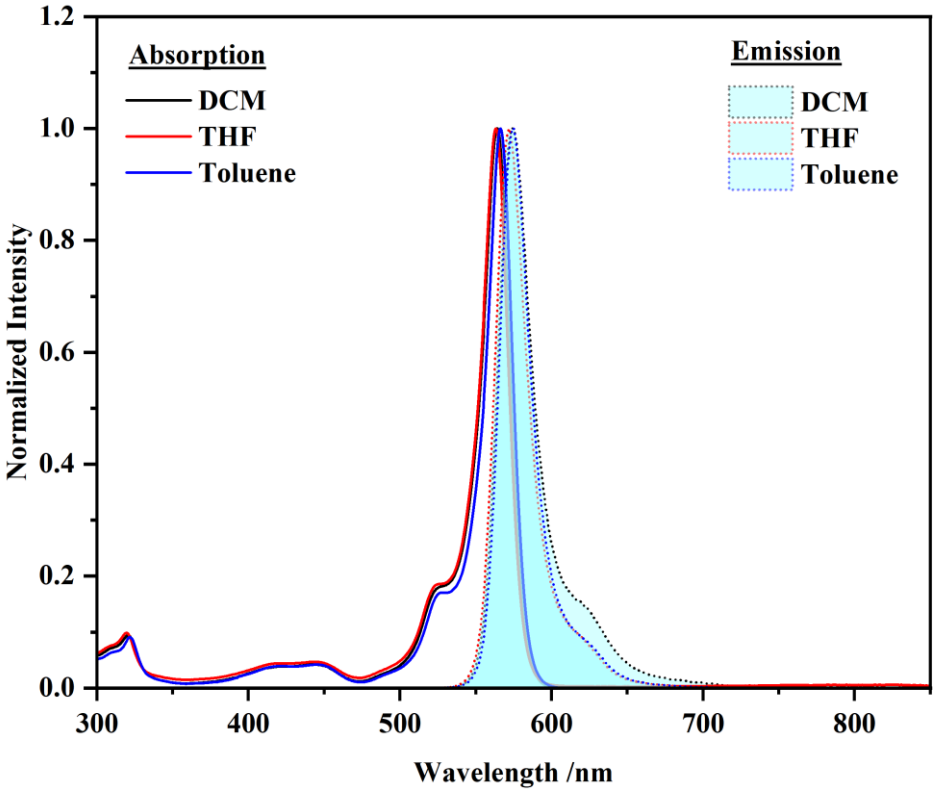


Figure S25. Normalized absorption and emission spectra of **5a** recorded in DCM, THF and toluene at room temperature.

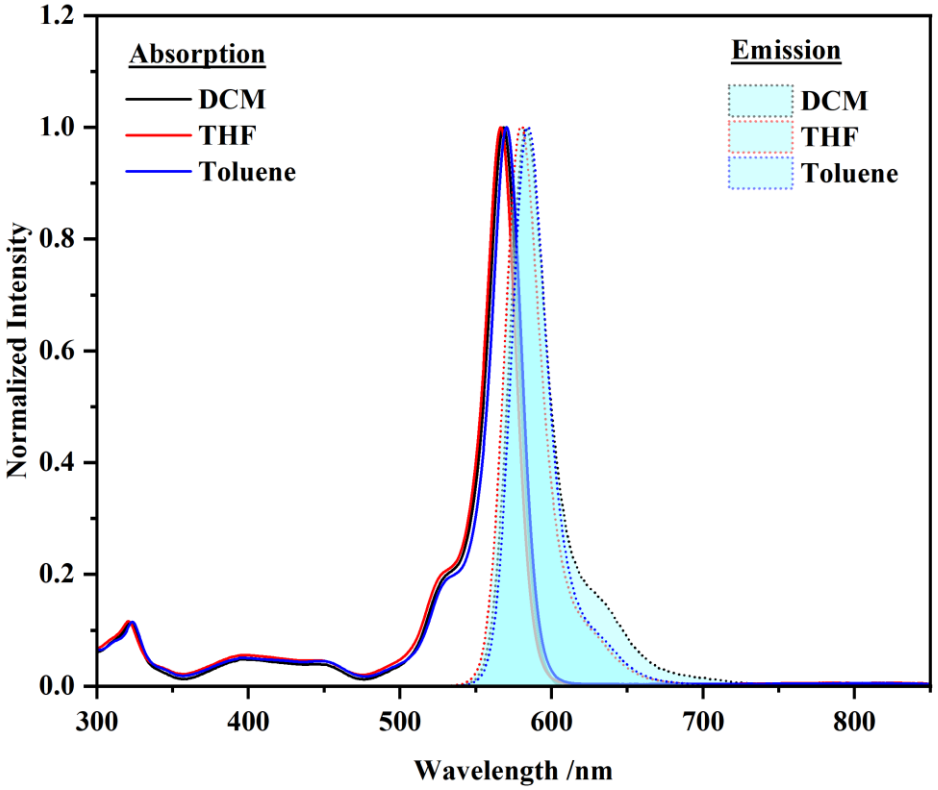


Figure S26. Normalized absorption and emission spectra of **5b** recorded in DCM, THF and toluene at room temperature.

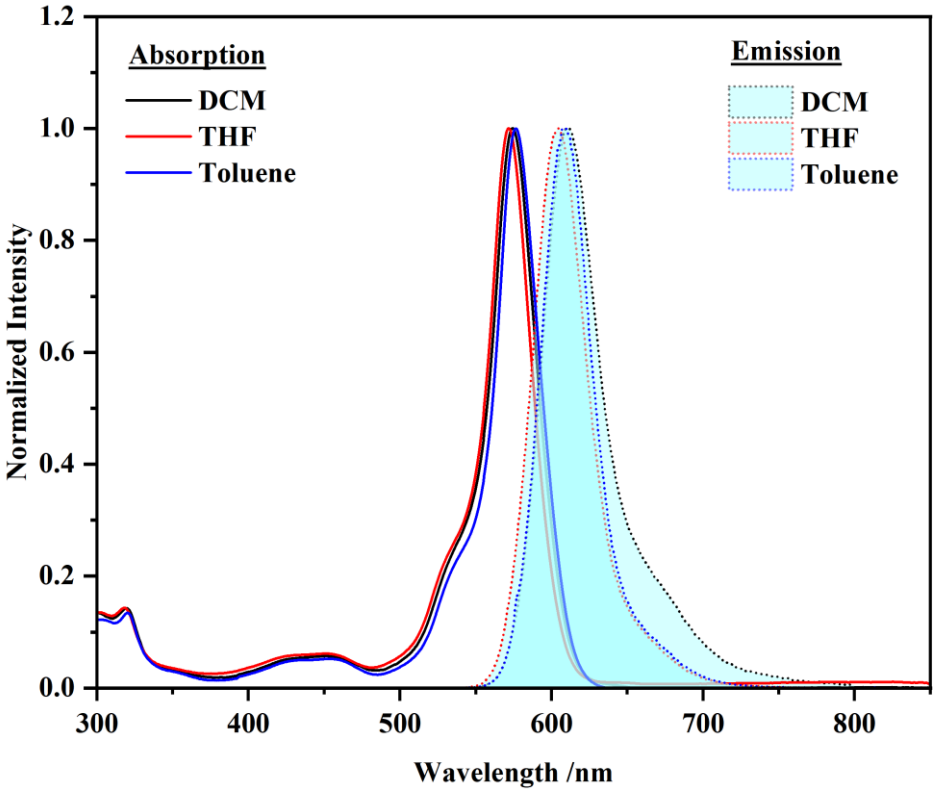


Figure S27. Normalized absorption and emission spectra of **5c** recorded in DCM, THF and toluene at room temperature.

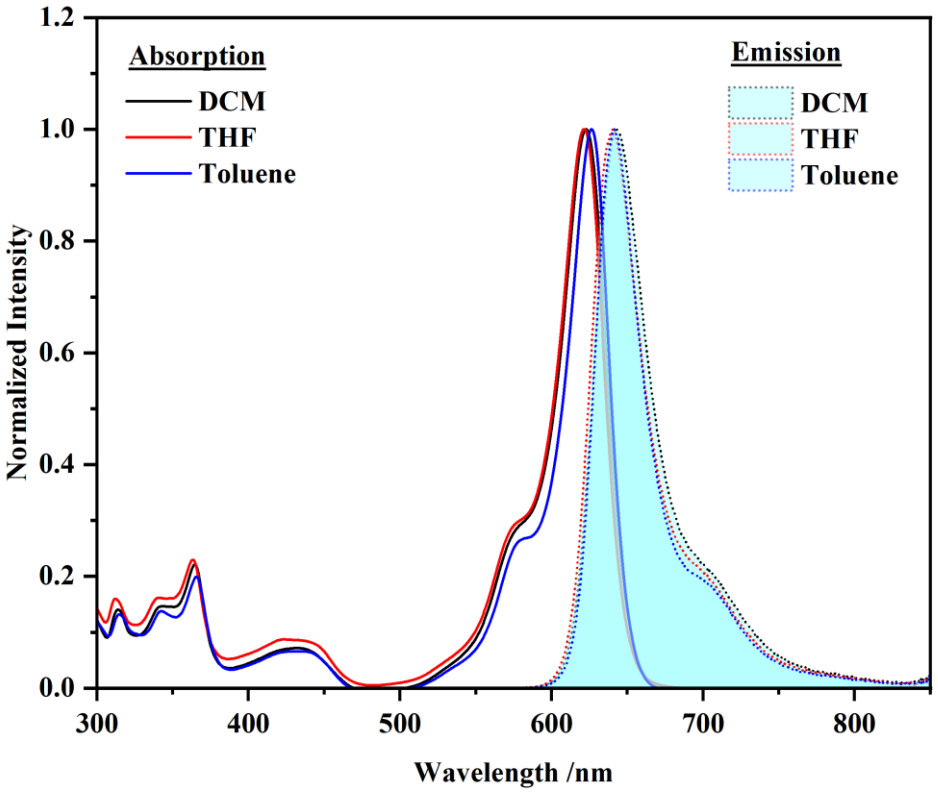


Figure S28. Normalized absorption and emission spectra of **8a** recorded in DCM, THF and toluene at room temperature.

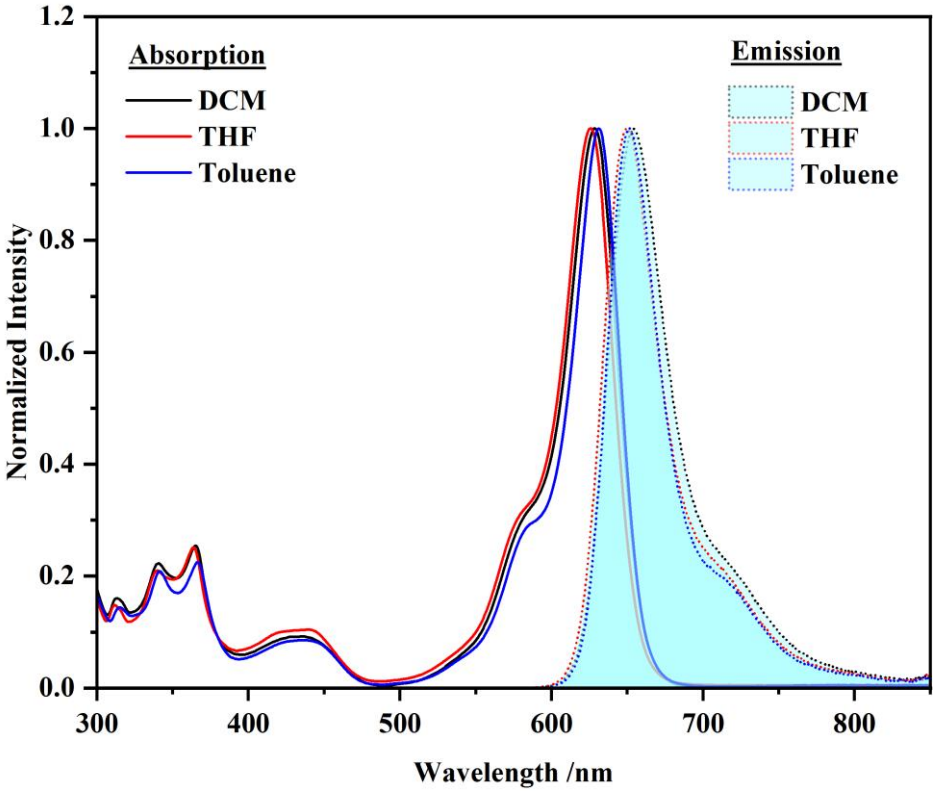


Figure S29. Normalized absorption and emission spectra of **8b** recorded in DCM, THF and toluene at room temperature.

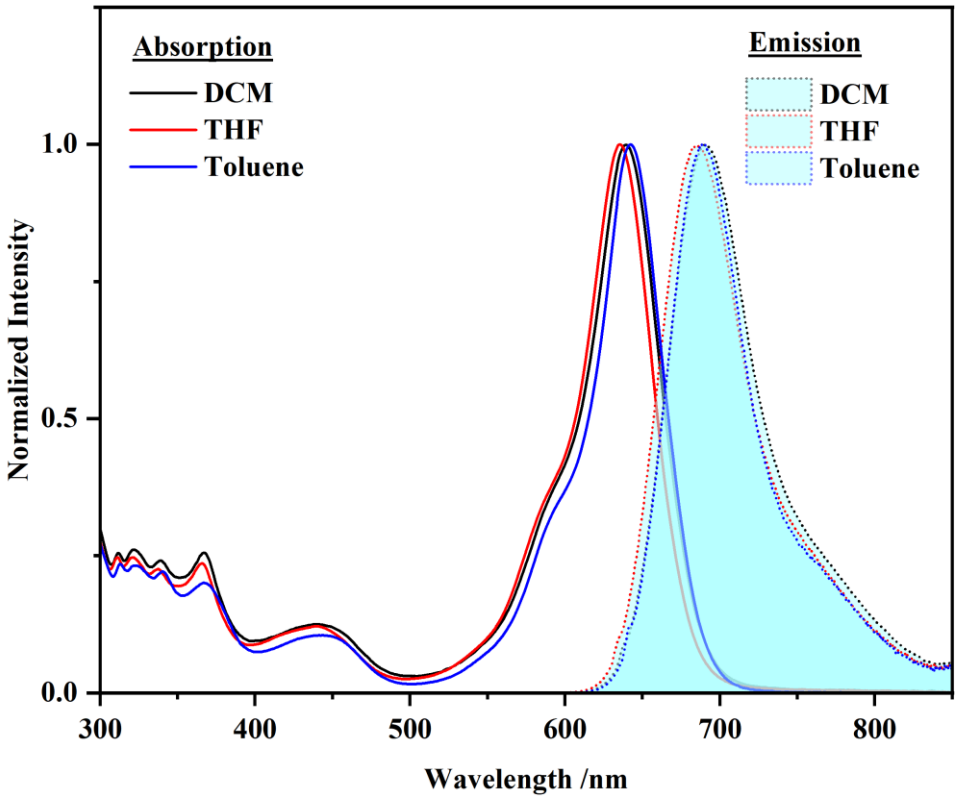


Figure S30. Normalized absorption and emission spectra of **8c** recorded in DCM, THF and toluene at room temperature.

Compound	λ_{sol}^{abs}[nm][a] (ε^{max})[b]	λ_{sol}^{em} [nm][c]	*SS* [cm^{-1}][d]	λ_{film}^{abs} [nm][e]	λ_{film}^{em} [nm][f]	*SS* [cm^{-1}][g]	λ_{film}^{abs}-λ_{sol}^{abs} [nm]	λ_{film}^{em}-λ_{film}^{abs} [nm]
5a	564(1.49)	574	309	595	611	440	31	37
5b	569(1.40)	583	422	594	626	861	25	43
5c	575(1.10)	611	1025	667	718	1065	92	107
8a	623(1.41)	643	499	661	743	1670	38	100
8b	629(1.20)	654	608	701	749	914	72	95
8c	640(0.58)	690	1132	721	770	883	81	80

Table S8. [a] Absorption maxima measured in dilute CH_2Cl_2 (1.0×10^{-5} M). [b] Molar absorption coefficients for the most intense absorption band. ($\times 10^5$, M^{-1} cm^{-1}). [c] Emission maxima measured in dilute CH_2Cl_2 solution (1.0×10^{-6} M), excited at λ_{sol}^{abs}. [d] Stokes shift in dilute CH_2Cl_2. [e] Absorption maxima measured in thin films (spin-coated on quartz substrates). [f] Emission maxima measured in thin films (spin-coated on quartz substrates), excited at λ_{film}^{abs}. [g] Stokes shift in in thin films.

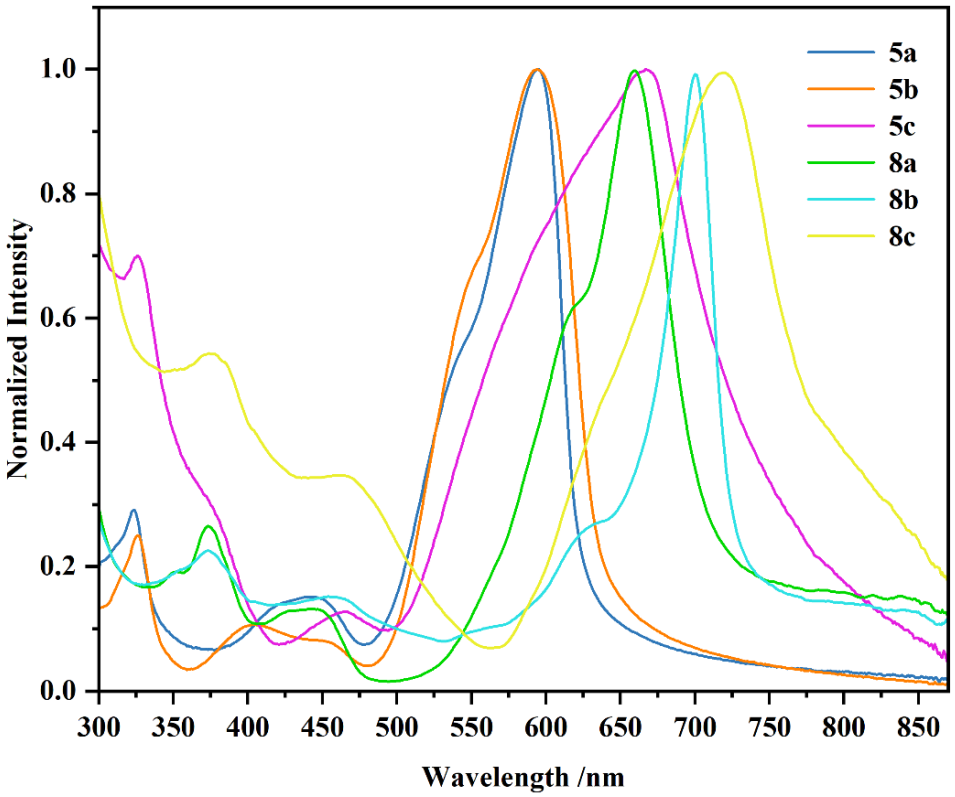


Figure S31. The solid (film) states absorption spectra of compound **5a-c** and **8a-c**.

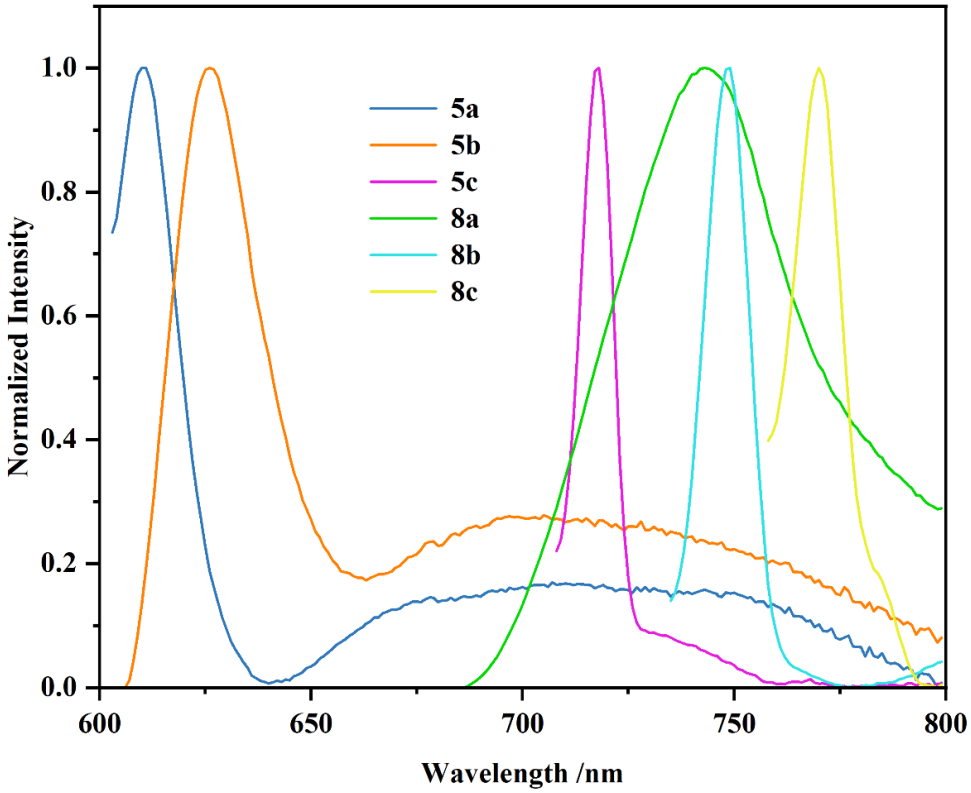


Figure S32. The solid (film) states absorption spectra of compound **5a-c** and **8a-c**.

5. Electrochemical Data

Dyes	E_{red}^{onset} (V)	E_{ox}^{onset} (V)	LUMO (eV)	HOMO (eV)	E_g^e (eV)	E_g^o (eV)
1a	-1.49	0.80	-3.31	-5.60	2.29	2.35
5a	-1.51	0.53	-3.29	-5.33	2.04	2.13
8a	-1.45	0.38	-3.35	-5.18	1.83	1.91
1b	-1.44	0.76	-3.36	-5.56	2.20	2.36
5b	-1.43	0.51	-3.37	-5.31	1.94	2.10
8b	-1.38	0.32	-3.42	-5.12	1.70	1.88
1c	-1.28	0.84	-3.52	-5.64	2.12	2.30
5c	-1.32	0.58	-3.48	-5.38	1.90	2.04
8c	-1.21	0.41	-3.59	-5.21	1.62	1.81

Table S9. E_{red}^{onset} = the onset reduction potentials; E_{ox}^{onset} = the onset oxidation potentials; LUMO = - (E_{red}^{onset}+4.8); HOMO = - (E_{ox}^{onset}+4.8); E_g^e = LUMO − HOMO; E_g^e = bandgap, obtained from the intercept of the electrochemical data; λ_{onset}= the onset of absorption in CH_2Cl_2 solution of **1a-c**, **5a-c** and **8a-c**; E_g^o =1240/λ_{onset}; E_g^o = bandgap, obtained from the intercept of the absorption spectra.

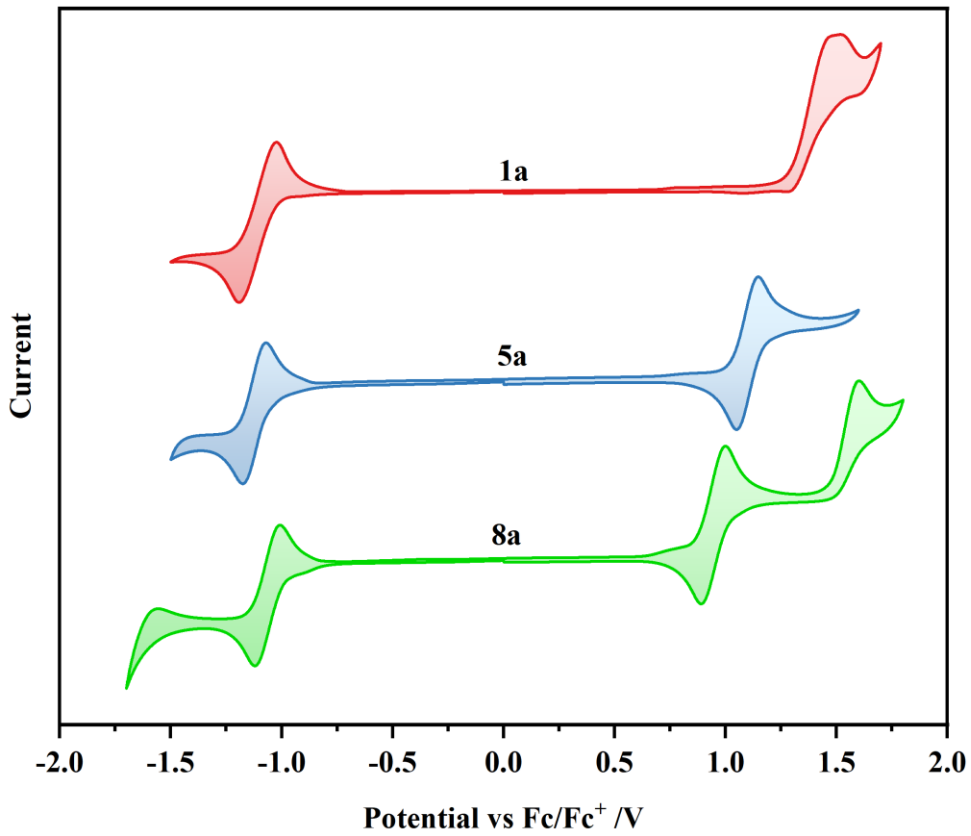


Figure S33. Cyclic voltammograms of 1 mM **1a, 5a** and **8a** in dichloromethane.

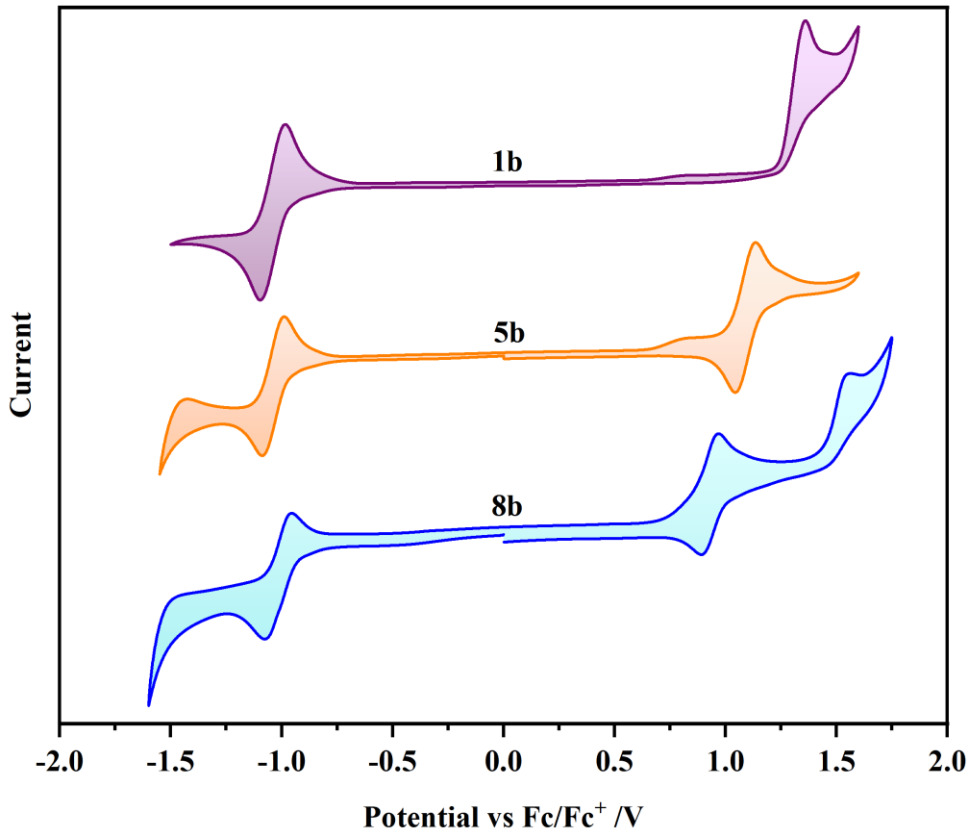


Figure S34. Cyclic voltammograms of 1 mM **1b, 5b** and **8b** in dichloromethane.

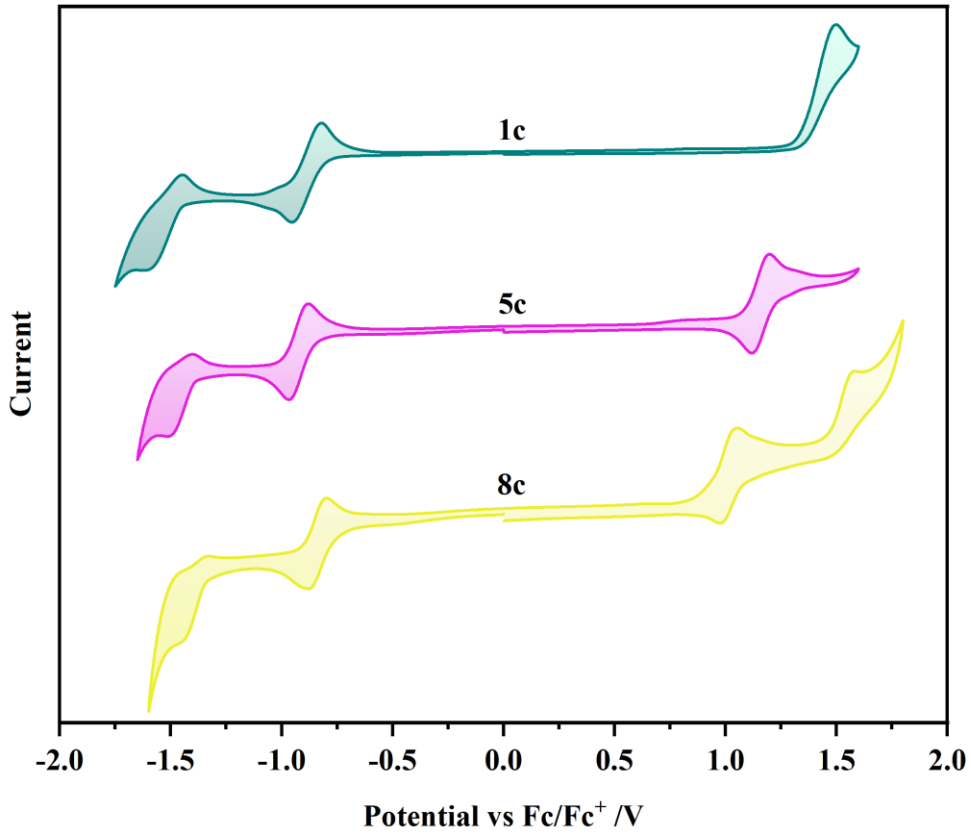


Figure S35. Cyclic voltammograms of 1 mM **1c, 5c** and **8c** in dichloromethane.

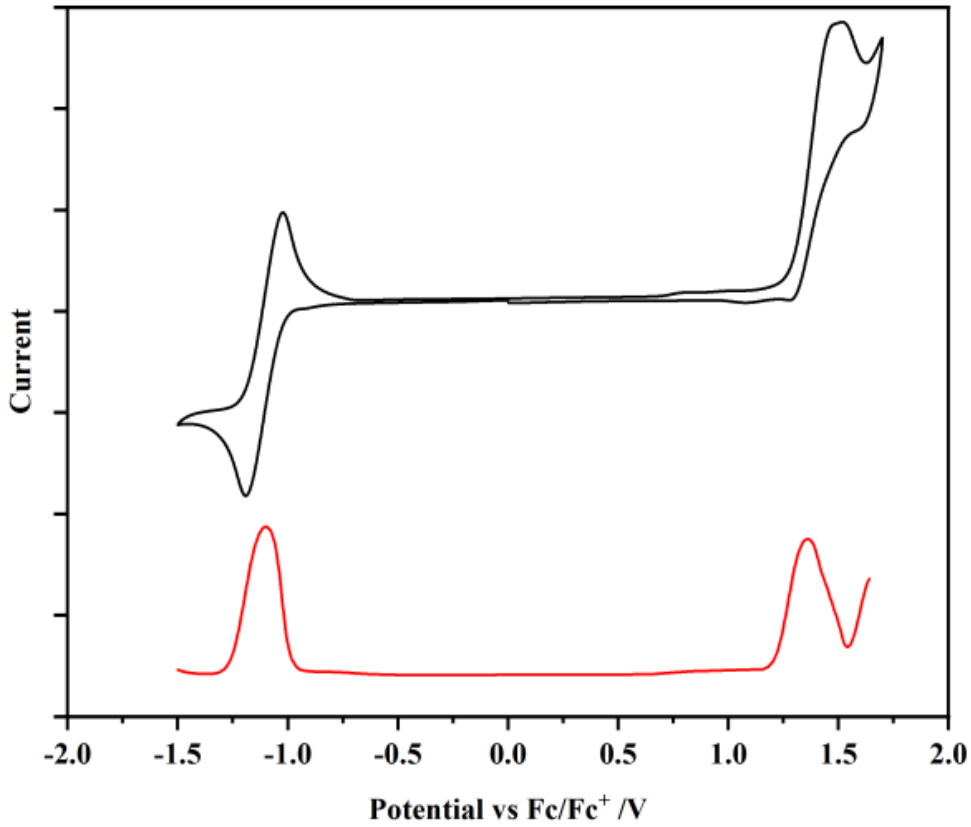


Figure S36. CV(black) and DPV(red) of 1 mM **1a** in dichloromethane.

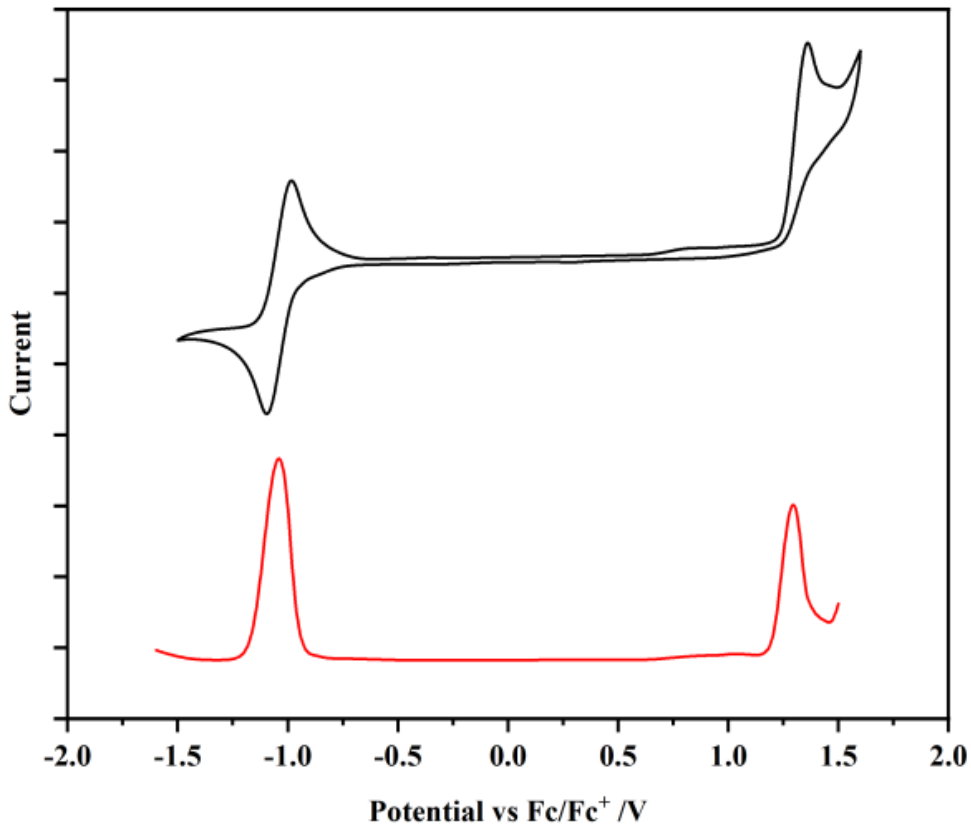


Figure S37. CV(black) and DPV(red) of 1 mM **1b** in dichloromethane.

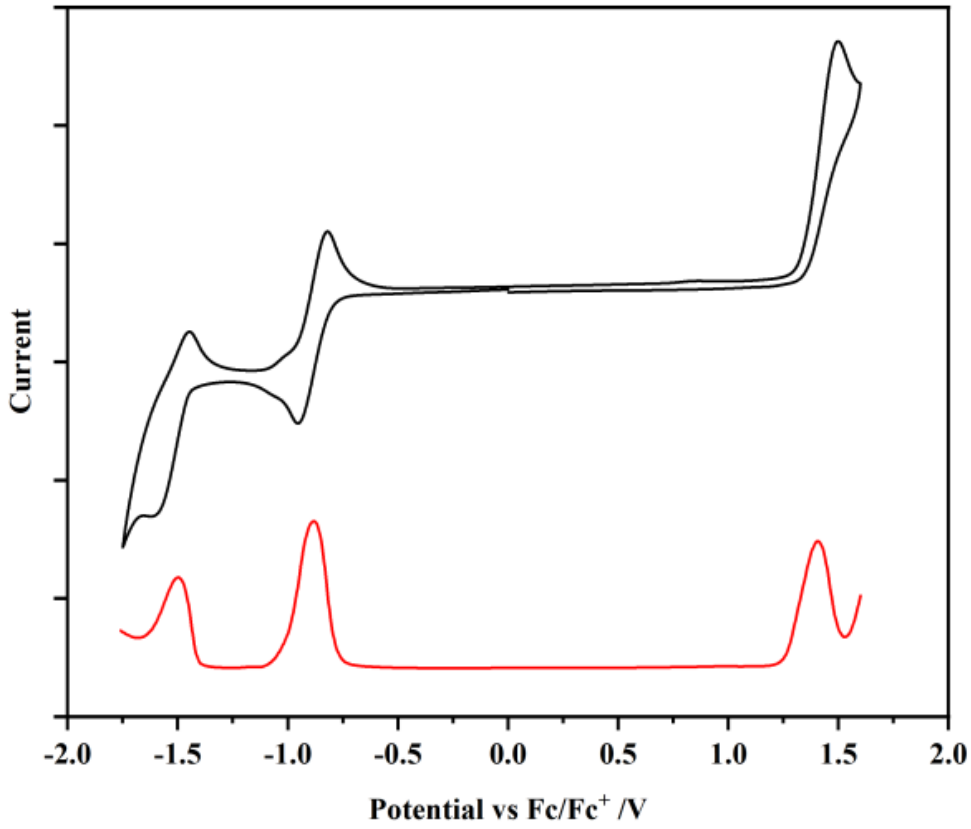


Figure S38. CV(black) and DPV(red) of 1 mM **1c** in dichloromethane.

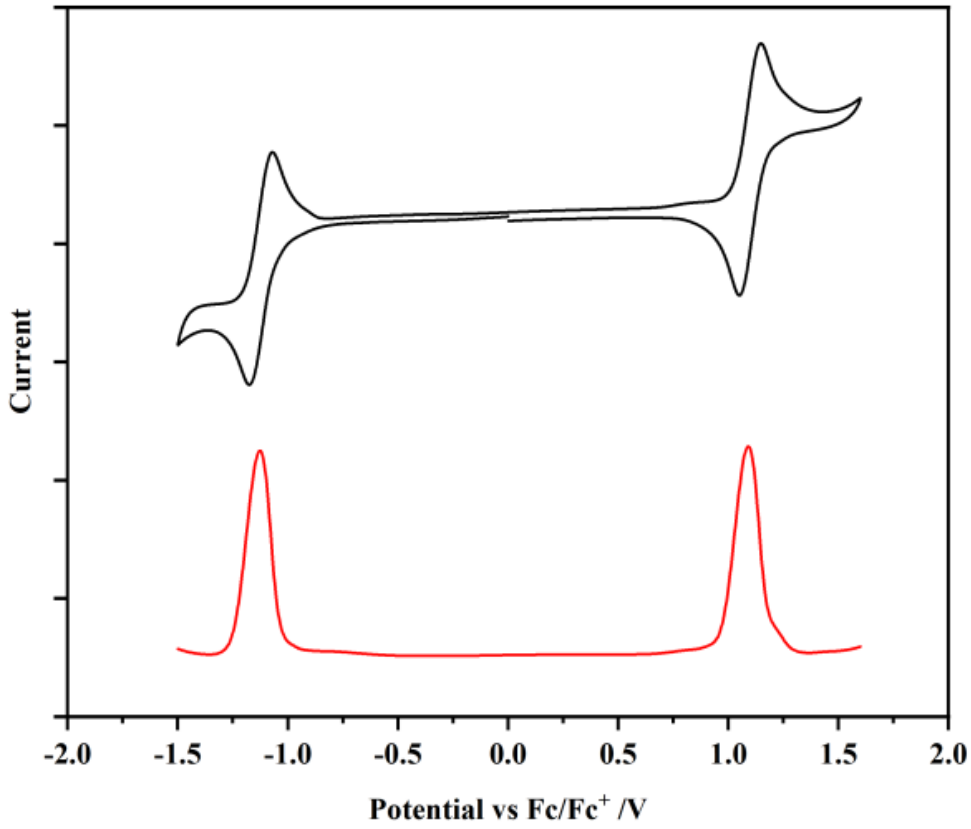


Figure S39. CV(black) and DPV(red) of 1 mM **5a** in dichloromethane.

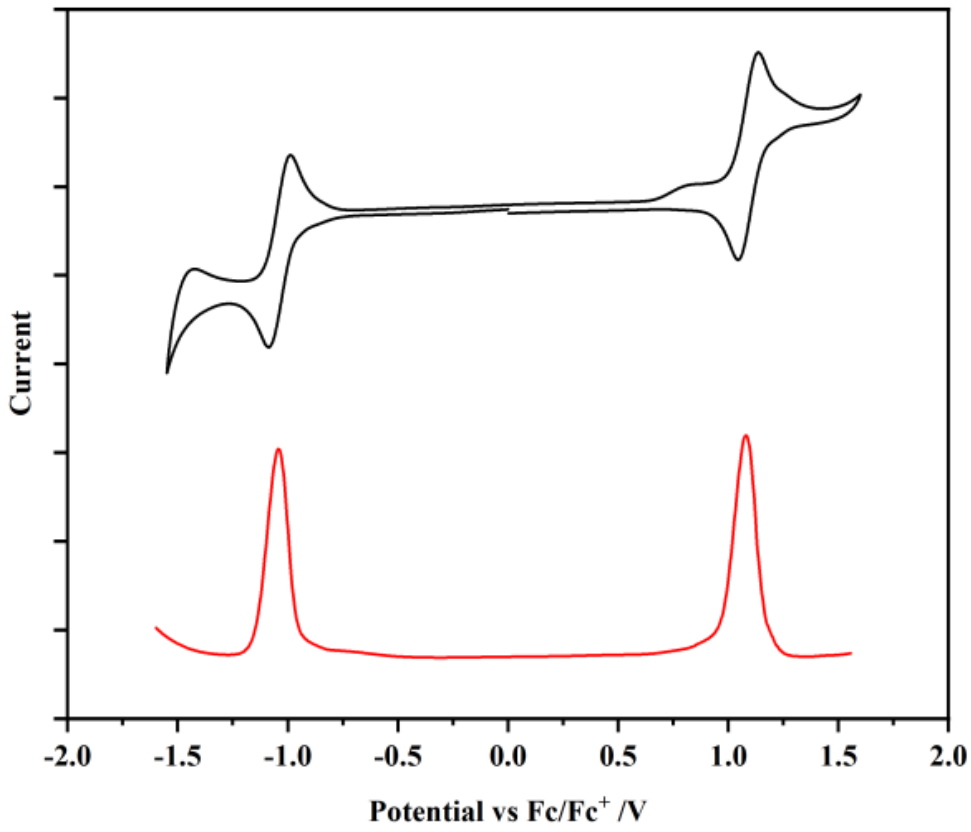


Figure S40. CV(black) and DPV(red) of 1 mM **5b** in dichloromethane.

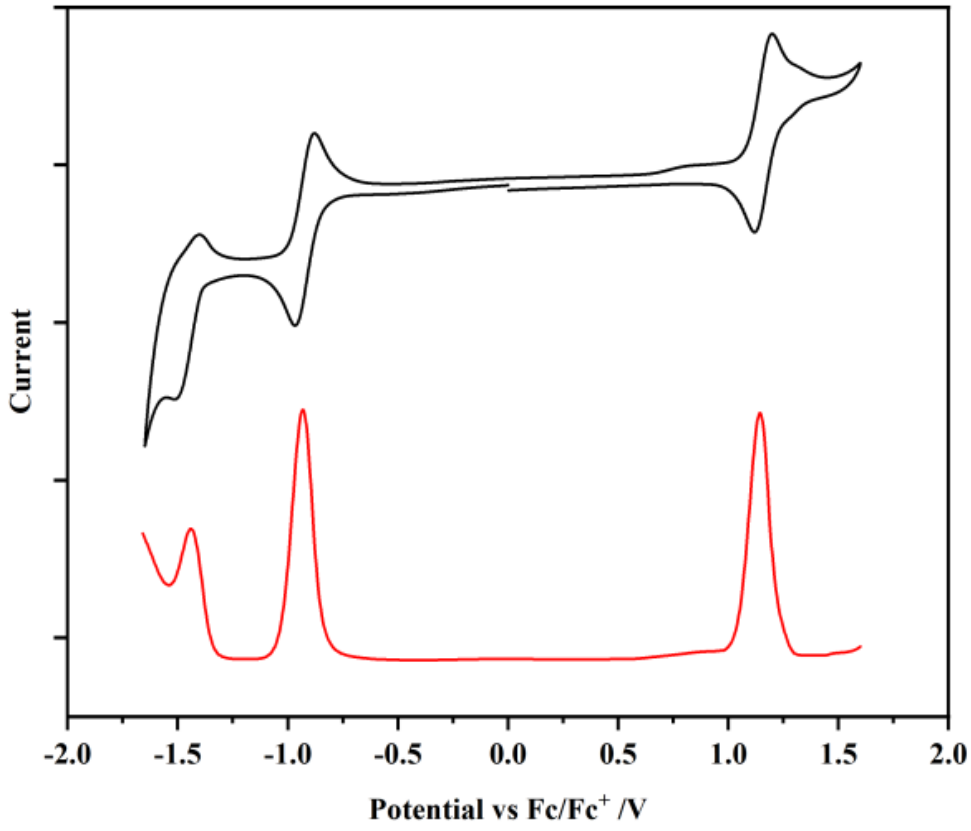


Figure S41. CV(black) and DPV(red) of 1 mM **5c** in dichloromethane.

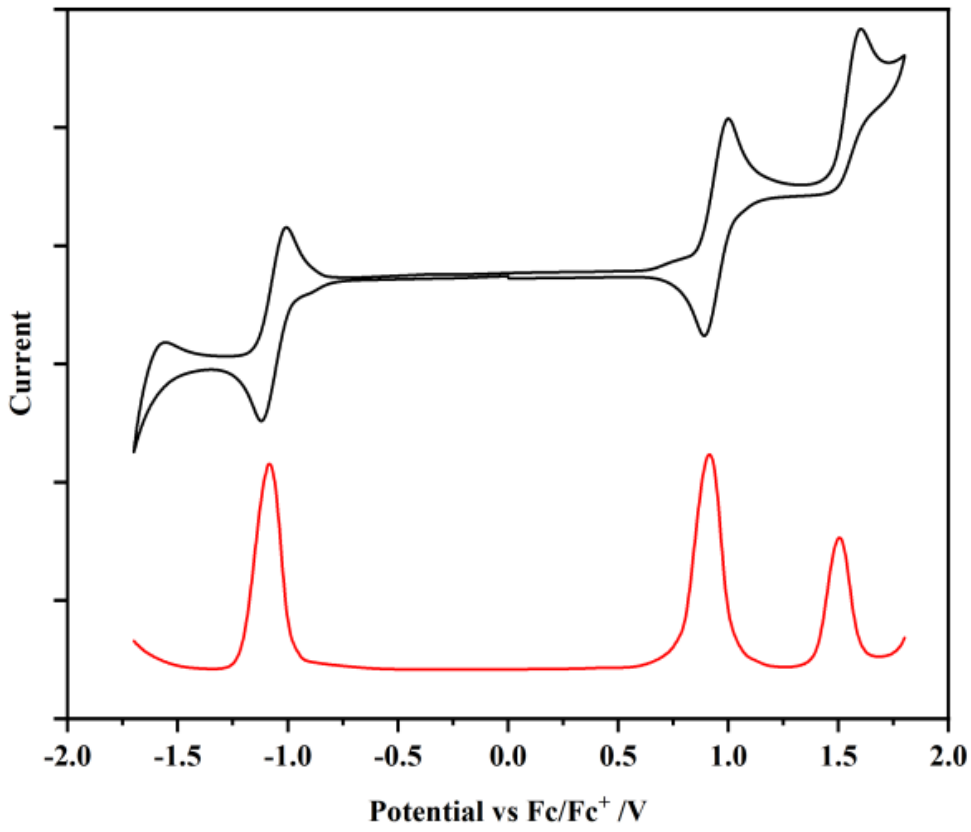


Figure S42. CV(black) and DPV(red) of 1 mM **8a** in dichloromethane.

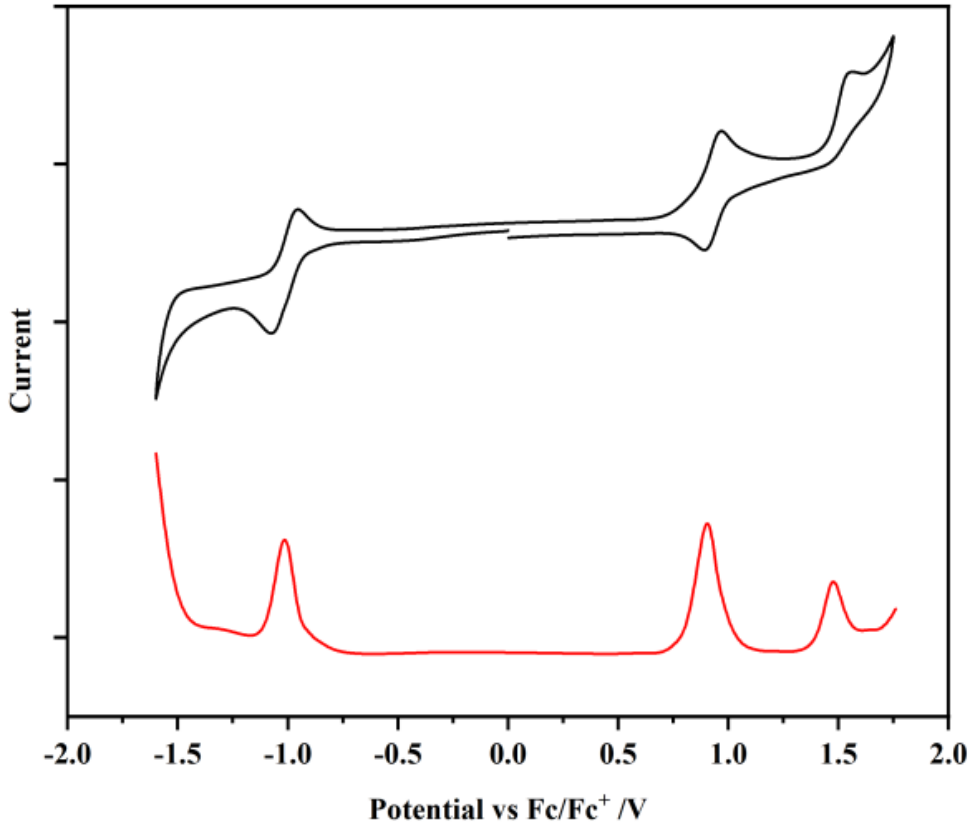


Figure S43. CV(black) and DPV(red) of 1 mM **8b** in dichloromethane.

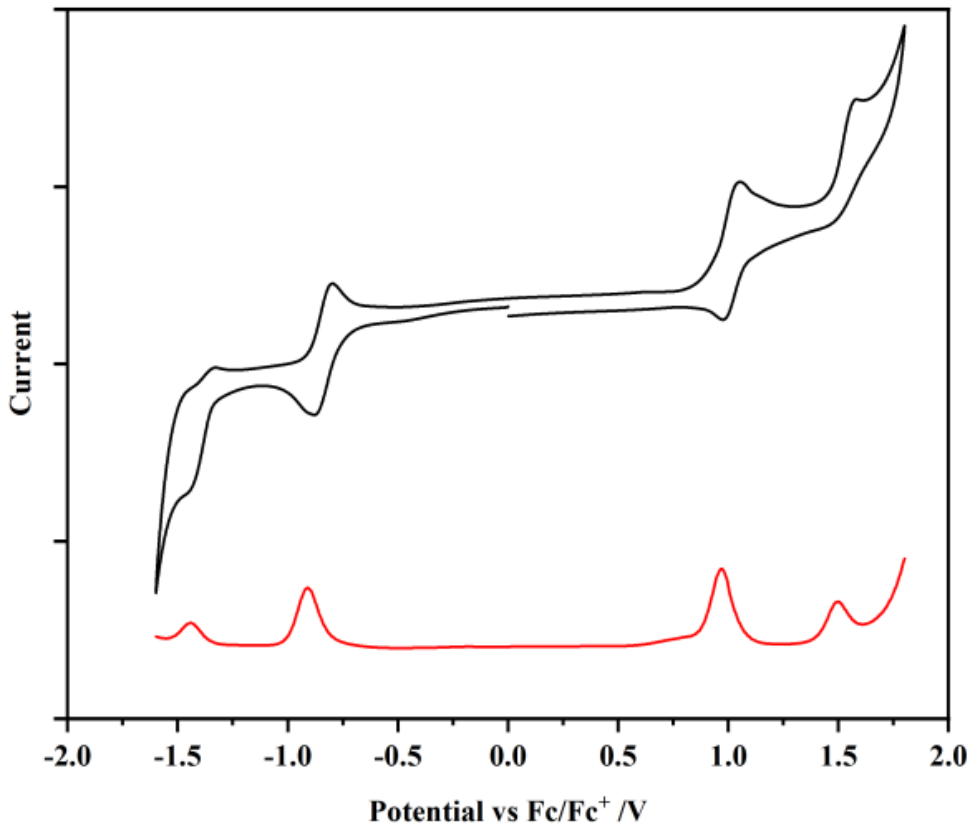


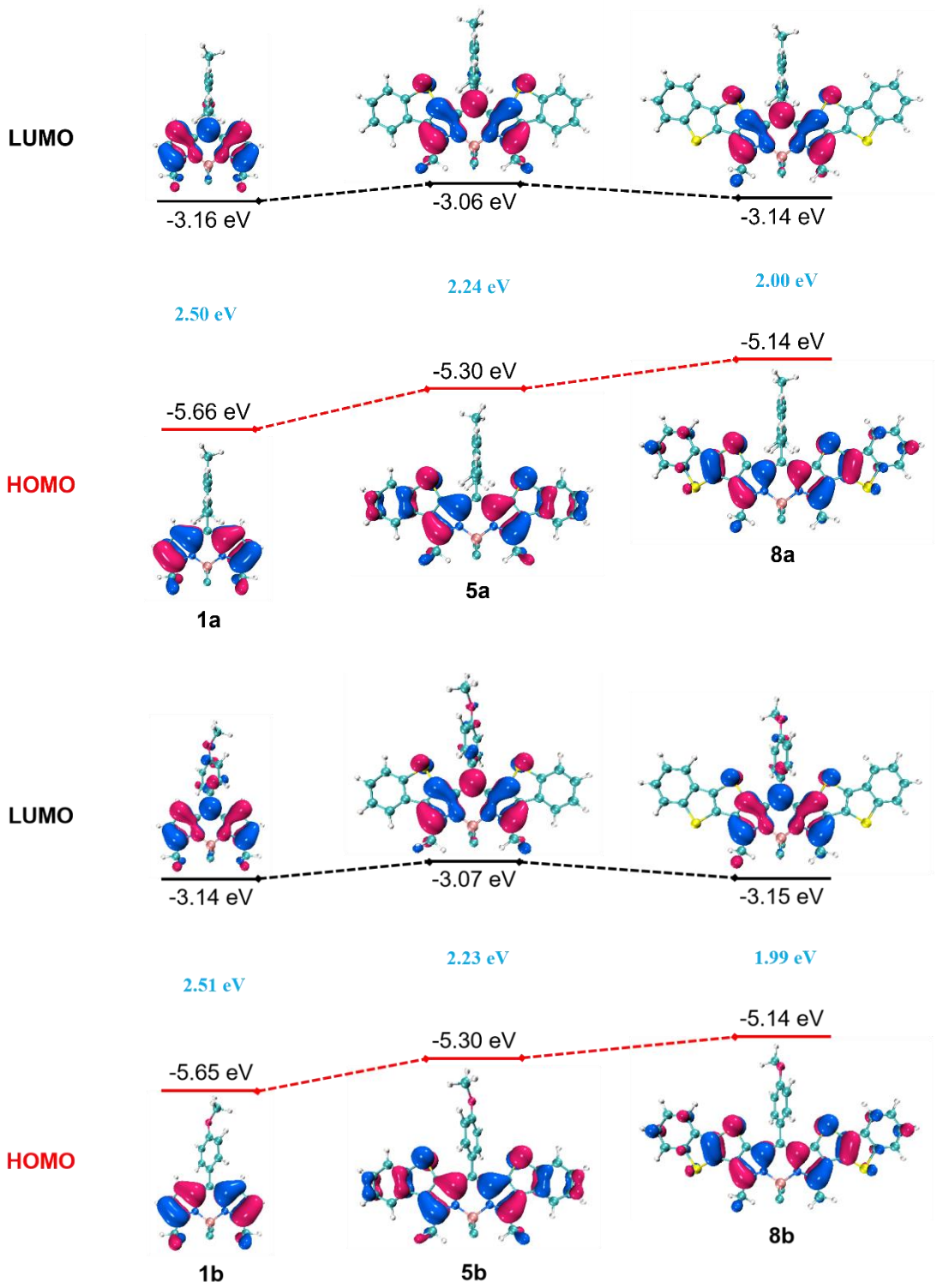
Figure S44. CV(black) and DPV(red) of 1 mM **8c** in dichloromethane.

6. DFT Calculations

Kohn-Sham density functional theory (DFT) has been employed to optimize the ground state geometries of the investigated complexes at the TPSSh[8, 9]/6-311+G(d, p) level. All the optimized geometries were tested to be local minima by frequency calculations at the same level. To get insight into the photophysical properties of the reported complexes, time-dependent density functional theory (TD-DFT) calculations using the TPSSh functional in conjunction with the 6-311+G(d, p) basis set have been performed. Several exchange correlation functionals were tested. It is found the TPSSh functional with 10% "exact" Hartree-Fock exchange component is an appropriate choice for the current calculations.

NICS(0) values were also calculated at the TPSSh/6-311+G(d, p) level. The effect of the solvent was considered in all the calculations utilizing the integral equation formalism polarized continuum model (IEF-PCM[10, 11]) with the dichloromethane as solvent. All the quantum chemical calculations were performed using the Gaussian 16 software suit[12].

According to the hole-electron analysis method, the "hole" and "electron" denote where the excited electron leaves and goes, respectively. In many cases, any excitation can be identified as a definitive distribution of hole and electron. The theory proved to be a useful and powerful method in unraveling nature of electron excitations[13]. The wavefunction analysis was calculated by means of the Multiwfn version 3.8(dev)[14, 15] code and plotted using VMD[16] software.


LUMO
-3.16 eV
-3.06 eV
-3.14 eV
2.24 eV
2.00 eV
2.50 eV
-5.14 eV
-5.30 eV
-5.66 eV
HOMO
1a
5a
8a
LUMO
-3.14 eV
-3.07 eV
-3.15 eV
2.23 eV
1.99 eV
2.51 eV
-5.14 eV
-5.30 eV
-5.65 eV
HOMO
1b
5b
8b

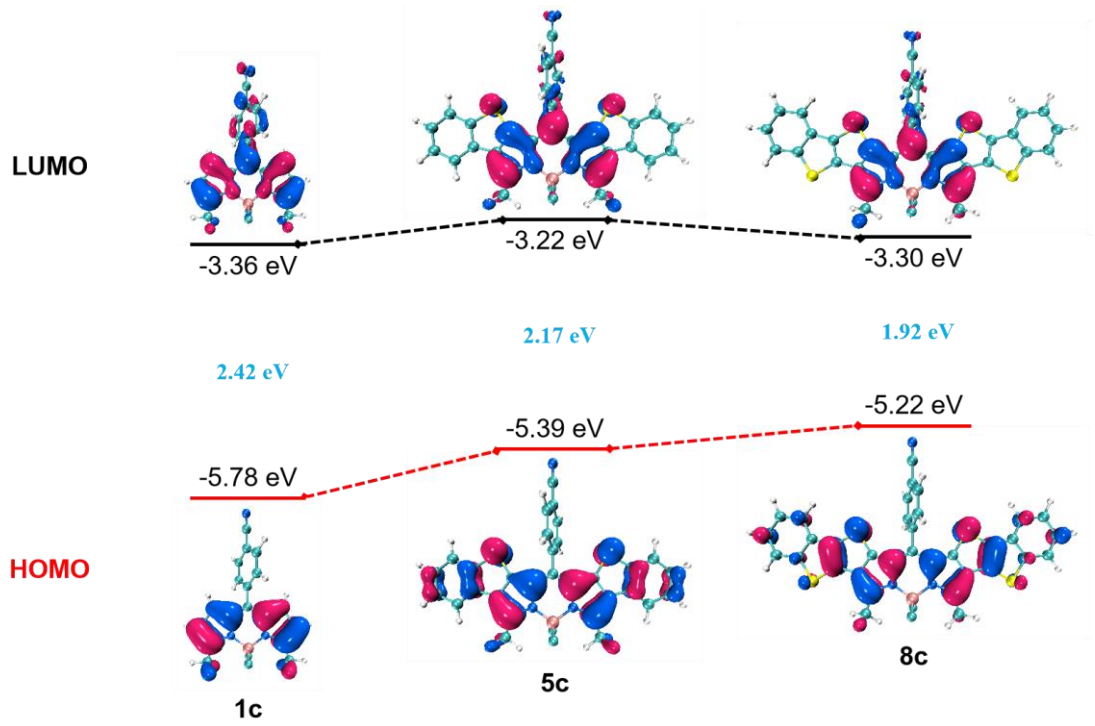
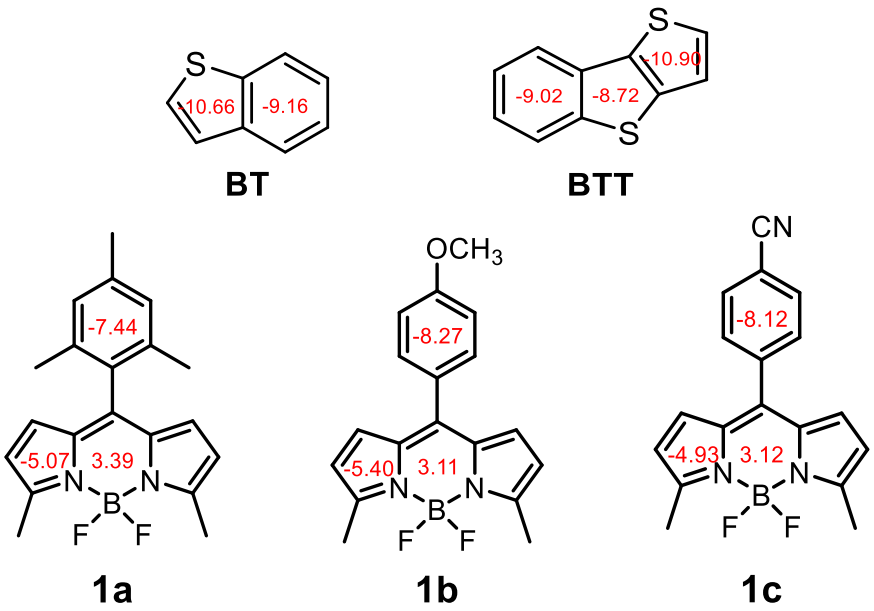


Figure S45. Pictorial presentation of LUMO, HOMO and their energy levels for **1a-c, 5a-c** and **8a-c**.



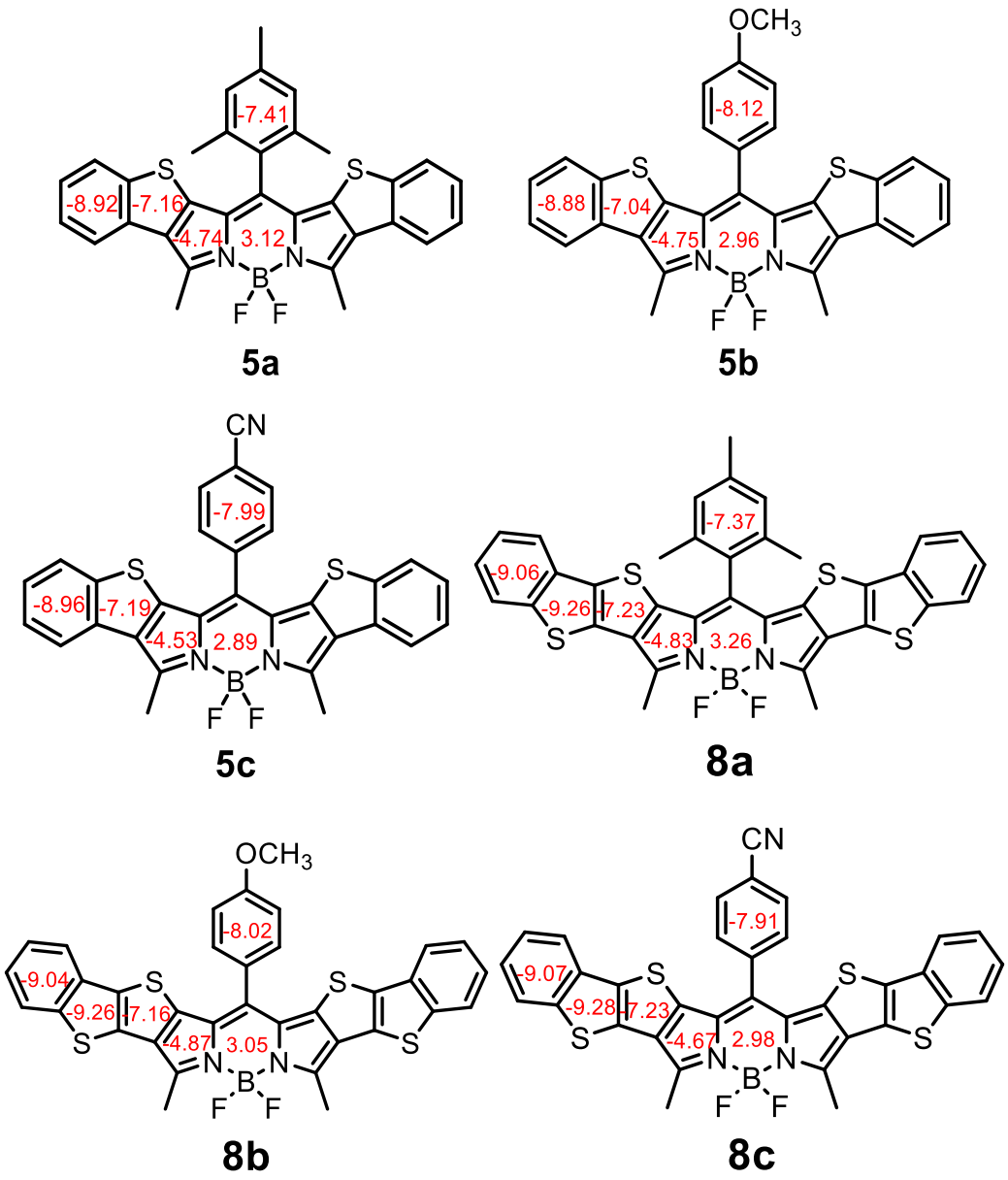
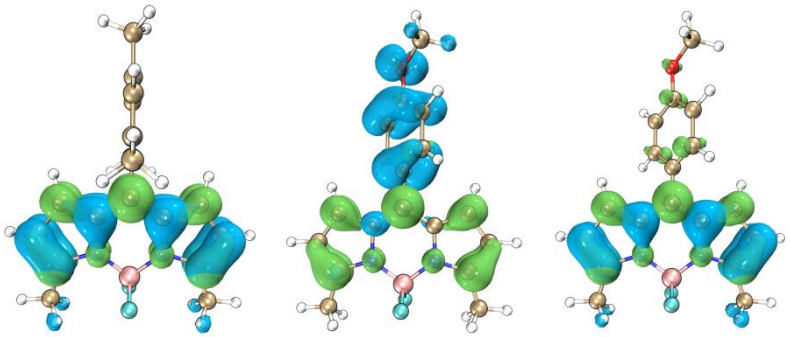
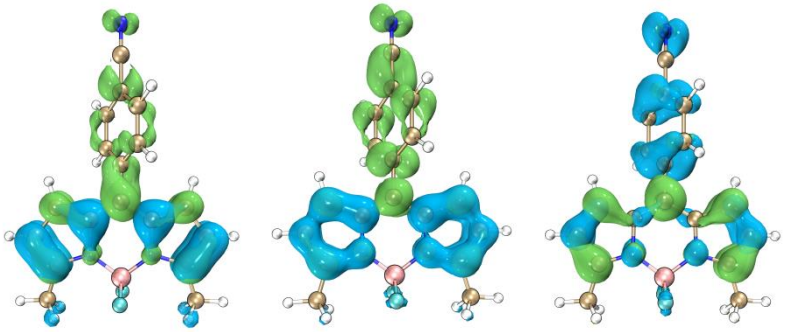


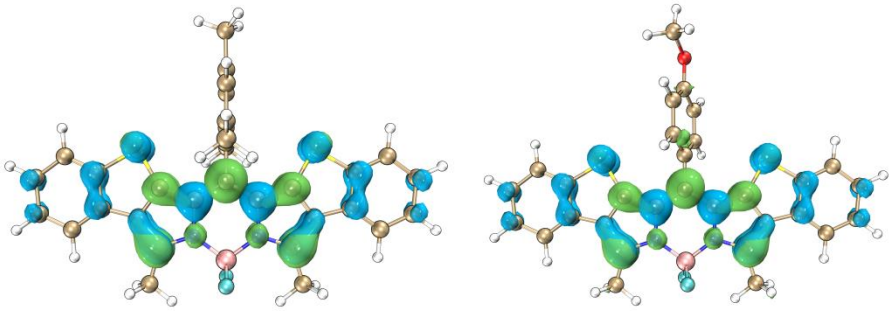
Figure S46. NICS(0) values of rings in **1a-c, 5a-c, 8a-c, BT and BTT**.



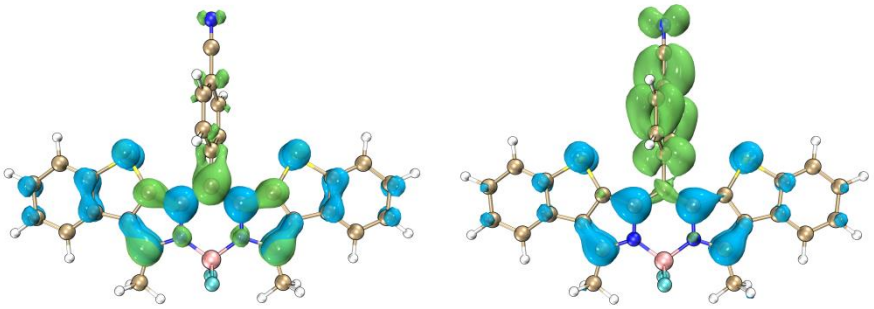
1a (S0→S1) **1b (S0→S1)** **1b (S0→S2)**



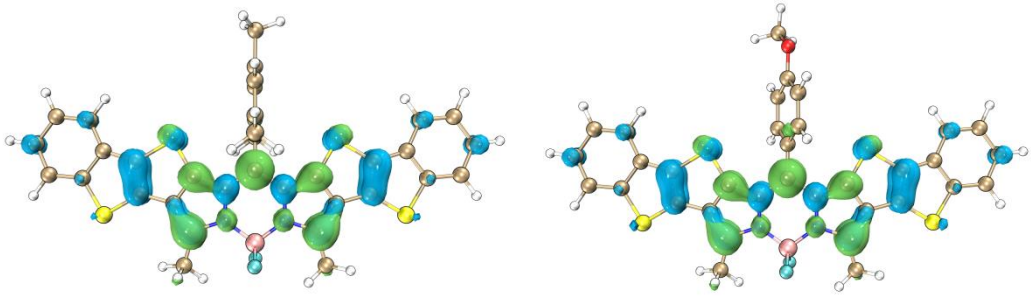
1c (S0→S1) **1c (S0→S3)** **1c (S0→S5)**



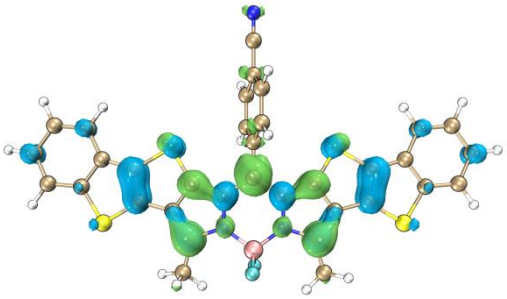
5a (S0→S1) **5b (S0→S1)**



5c (S0→S1) **5c (S0→S4)**



8a (S0→S1) **8b (S0→S1)**



8c (S0→S1)

Figure S47. Real space representation of hole and electron distributions of complexes **1a-c, 5a-c** and **8a-c** (isovalue = 0.002). Green and blue regions denote the electron and hole distributions, respectively.

Complexes	S_n	λ_{max}(nm)	E_{ex}(eV)	*f*	Major Contributions
1a	S_1	435.89	2.8444	0.52210	H → L 96.9%
5a	S_1	509.74	2.4323	0.95800	H → L 97.1%
8a	S_1	594.02	2.0872	0.73540	H → L 95.5%
1b	S_1	443.39	2.7963	0.25480	H-1 → L 97.2%
	S_2	438.31	2.8287	0.49920	H → L 95.1%
5b	S_1	516.19	2.4019	0.93750	H → L 97.5%
8b	S_1	602.27	2.0586	0.71670	H → L 95.9%
1c	S_1	454.89	2.7256	0.43590	H → L 95.0%
	S_3	359.54	3.4484	0.18660	H → L+1 55.2% H-1 → L 38.2% H → L 6.3%
	S_5	340.13	3.6452	0.27680	H-3 → L 92.1%
5c	S_1	528.78	2.3447	0.85380	H → L 95.7%
	S_4	426.03	2.9102	0.14040	H → L+1 96.9%
8c	S_1	622.72	1.9910	0.67350	H → L 95.4%

Table S10. The excited state properties of complexes **1a-c, 5a-c** and **8a-c** calculated at the IEF-PCM(dichloromethane)-TPSSh/6-311+G(d, p) level.

Cartesian coordinates：(IEF-PCM-TPSSh/6-311+G(d, p))

46

1a

C	-0.402978	-1.211017	-0.000124
N	-1.800036	-1.249411	0.000055
B	-2.720609	0.002005	-0.000045
N	-1.798418	1.252253	0.000212
C	-0.401400	1.212131	0.000030
C	0.297717	0.000108	-0.000154
C	0.074139	-2.543337	0.000033
C	-1.037793	-3.372938	-0.000227
C	-2.186683	-2.548379	-0.000066
C	-2.183446	2.551702	0.000253
C	-1.033536	3.374839	0.000167
C	0.077363	2.543855	0.000461
C	-3.616279	-2.975749	-0.000102
C	-3.612515	2.980831	0.000392
C	1.791740	-0.000847	-0.000134
C	2.489240	-0.004495	1.223995
C	3.887654	-0.009496	1.199219
C	4.606257	-0.008820	-0.000059
C	3.887676	-0.008958	-1.199278
C	2.489196	-0.003946	-1.224204
C	6.115993	0.017941	0.000151
C	1.756134	-0.006008	-2.545593
C	1.756129	-0.007167	2.545360
H	1.115994	-2.828375	0.000076
H	-1.054429	-4.453028	-0.000375
H	-1.048836	4.454948	0.000092
H	1.119572	2.827564	0.000596
H	-4.137679	-2.591048	0.880949
H	-4.137934	-2.590103	-0.880588
H	-3.678321	-4.064455	-0.000670
H	-3.673223	4.069611	-0.001488
H	-4.135126	2.594681	-0.879294
H	-4.133900	2.597904	0.882238
H	4.425825	-0.016455	2.143740
H	4.426066	-0.015509	-2.143671
H	6.520767	-0.486197	0.881487
H	6.520594	-0.464667	-0.893092
H	6.484398	1.050312	0.013099
H	2.464392	-0.009619	-3.376622
H	1.111209	-0.885379	-2.641532
H	1.115309	0.875883	-2.645919

H	1.114629	0.874227	2.645712
H	1.111854	-0.887029	2.641194
H	2.464367	-0.010327	3.376409
F	-3.540889	0.002478	1.147823
F	-3.540328	0.002595	-1.148345

41

1b

C	-0.511809	1.195796	0.084444
N	-1.904448	1.278966	0.016690
B	-2.866424	0.063488	-0.038449
N	-1.990714	-1.216598	-0.042738
C	-0.594136	-1.232240	-0.025546
C	0.152247	-0.043114	0.050408
C	-0.004107	2.509389	0.228331
C	-1.092677	3.371230	0.227245
C	-2.258416	2.586180	0.100579
C	-2.430437	-2.495564	-0.151382
C	-1.317575	-3.361410	-0.208953
C	-0.172792	-2.578776	-0.141166
C	-3.675456	3.053408	0.069098
C	-3.876220	-2.860979	-0.209589
C	1.626712	-0.095101	0.094502
C	2.401913	0.656601	-0.800163
C	3.794634	0.606274	-0.774558
C	4.439986	-0.196220	0.174772
C	3.678683	-0.947809	1.083423
C	2.294527	-0.903322	1.035515
H	1.038323	2.768757	0.332626
H	-1.078826	4.447613	0.316715
H	-1.374549	-4.436302	-0.299659
H	0.853051	-2.911897	-0.181099
H	-4.172784	2.730603	-0.849813
H	-4.241610	2.638779	0.907933
H	-3.707692	4.142087	0.125277
H	-3.982617	-3.945725	-0.246200
H	-4.411392	-2.480448	0.664686
H	-4.351517	-2.429147	-1.095072
H	4.359095	1.183648	-1.495718
H	4.191150	-1.554055	1.821830
F	-3.654857	0.117067	-1.208096
F	-3.719410	0.067458	1.086481
H	1.718241	-1.473980	1.755314
H	1.911393	1.265422	-1.551669

O	5.789825	-0.311373	0.293044
C	6.611599	0.445302	-0.606955
H	6.433032	1.517933	-0.486647
H	7.636648	0.207634	-0.330198
H	6.428049	0.147440	-1.643557

38

1c

C	-0.417775	1.215307	0.041538
N	-1.813634	1.249869	0.030890
B	-2.735601	-0.000006	0.000110
N	-1.813631	-1.249871	-0.030909
C	-0.417772	-1.215308	-0.041559
C	0.279376	0.000000	-0.000002
C	0.053110	2.548596	0.138860
C	-1.061916	3.371840	0.172700
C	-2.206510	2.545079	0.107873
C	-2.206507	-2.545076	-0.107962
C	-1.061912	-3.371834	-0.172820
C	0.053113	-2.548592	-0.138937
C	-3.637567	2.965267	0.122193
C	-3.637566	-2.965251	-0.122461
C	1.762755	0.000000	-0.000002
C	2.472105	0.681811	-1.001433
C	3.861405	0.680208	-1.009412
C	4.561238	0.000001	0.000004
C	3.861401	-0.680209	1.009416
C	2.472100	-0.681814	1.001430
H	1.090133	2.844696	0.186689
H	-1.081804	4.449441	0.242612
H	-1.081798	-4.449434	-0.242769
H	1.090137	-2.844690	-0.186771
H	-4.151225	2.627404	-0.782322
H	-4.162403	2.528308	0.976308
H	-3.704610	4.051852	0.182796
H	-3.704604	-4.051920	-0.181540
H	-4.151767	-2.626011	0.781217
H	-4.161871	-2.529561	-0.977564
H	4.404642	1.197204	-1.791108
H	4.404635	-1.197206	1.791113
F	-3.553720	0.027618	-1.147495
F	-3.553390	-0.027641	1.147967
H	1.931733	-1.194910	1.788331
H	1.931741	1.194904	-1.788339

C	5.990708	0.000002	0.000008
N	7.151601	0.000004	0.000011

64

5a

C	-1.208046	-0.522791	0.000061
N	-1.257696	-1.928853	-0.000059
B	0.000695	-2.846134	-0.000032
N	1.258593	-1.928214	0.000041
C	1.208148	-0.522187	0.000236
C	-0.000135	0.173569	0.000190
C	-2.548498	-0.076104	0.000015
C	-3.386945	-1.200301	-0.000028
C	-2.549879	-2.341438	-0.000049
C	2.551013	-2.340078	-0.000071
C	3.387434	-1.198469	0.000083
C	2.548348	-0.074746	0.000267
C	-2.957010	-3.776232	0.000012
C	2.958929	-3.774651	-0.000926
C	-0.000585	1.666364	0.000095
C	0.002466	2.363443	-1.225468
C	0.005819	3.761050	-1.200446
C	0.004237	4.478658	-0.000290
C	0.004922	3.761438	1.199879
C	0.001574	2.363630	1.225321
C	-4.788534	-0.860304	-0.000019
C	4.788817	-0.857619	0.000137
C	5.936619	-1.666540	-0.000081
C	7.196203	-1.074919	0.000069
C	7.336478	0.320679	0.000392
C	6.214796	1.147983	0.000568
C	4.953171	0.552866	0.000438
C	-4.953755	0.550075	0.000022
C	-6.215750	1.144401	0.000050
C	-7.336923	0.316400	0.000032
C	-7.195783	-1.079108	-0.000007
C	-5.935829	-1.669942	-0.000029
S	-3.408653	1.429264	0.000067
S	3.407562	1.431135	0.000590
C	-0.023787	5.988133	-0.000949
C	0.006064	1.626847	-2.544296
C	0.004160	1.627512	2.544420
H	-3.568715	-3.992479	-0.882018
H	-2.093890	-4.438259	-0.000952

H	-3.567009	-3.992880	0.883141
H	2.096185	-4.437145	0.004753
H	3.564668	-3.991718	-0.886916
H	3.575113	-3.989822	0.878209
H	0.012416	4.300031	-2.144385
H	0.010821	4.300727	2.143633
H	5.842710	-2.746660	-0.000406
H	8.081321	-1.701866	-0.000099
H	8.326203	0.764204	0.000483
H	6.322625	2.226886	0.000791
H	-6.324268	2.223236	0.000092
H	-8.326923	0.759310	0.000058
H	-8.080511	-1.706603	-0.000013
H	-5.841243	-2.750003	-0.000046
H	0.490368	6.393217	-0.876275
H	-1.056619	6.354452	-0.026488
H	0.447341	6.393139	0.898139
H	-0.874791	0.983899	-2.642214
H	0.007924	2.332466	-3.377417
H	0.887490	0.984052	-2.638009
H	0.006528	2.333431	3.377285
H	-0.877383	0.985506	2.642391
H	0.884899	0.983849	2.638581
F	0.000767	-3.664057	1.148228
F	0.001011	-3.664047	-1.148265

59

5b

C	-1.191866	-0.613891	0.034713
N	-1.220369	-2.019427	0.094444
B	0.044822	-2.923265	0.067018
N	1.289546	-1.995646	-0.026146
C	1.229952	-0.590146	-0.059764
C	0.011331	0.093976	-0.035456
C	-2.542187	-0.191095	0.005195
C	-3.360262	-1.330400	0.048394
C	-2.504715	-2.454582	0.104089
C	2.583230	-2.402022	-0.010076
C	3.413678	-1.258016	-0.031509
C	2.570615	-0.136636	-0.061312
C	-2.886087	-3.895742	0.150467
C	2.996736	-3.834255	0.038632
C	-0.005270	1.577105	-0.085118
C	0.430506	2.261855	-1.233392

C	0.409204	3.647620	-1.283643
C	-0.033780	4.385263	-0.175253
C	-0.463241	3.718412	0.978452
C	-0.453420	2.323843	1.010369
C	-4.768503	-1.023697	-0.003740
C	4.814761	-0.917568	-0.004113
C	5.961983	-1.726615	0.029947
C	7.221331	-1.134972	0.054926
C	7.361665	0.260625	0.047256
C	6.240304	1.087715	0.015270
C	4.979018	0.492164	-0.008793
C	-4.963785	0.379282	-0.092087
C	-6.237816	0.943790	-0.157244
C	-7.340607	0.091744	-0.136568
C	-7.169539	-1.297891	-0.052609
C	-5.897515	-1.858544	0.013082
S	-3.439283	1.291394	-0.100349
S	3.434747	1.369011	-0.055673
H	-3.360079	-4.190189	-0.792354
H	-2.021373	-4.533951	0.319034
H	-3.612988	-4.064697	0.950512
H	2.144141	-4.501501	-0.067128
H	3.712746	-4.044383	-0.761637
H	3.494701	-4.049893	0.990327
H	0.732145	4.177676	-2.172533
H	-0.802646	4.266058	1.848345
H	5.868090	-2.806660	0.037770
H	8.106114	-1.761851	0.081065
H	8.351163	0.704251	0.066919
H	6.348089	2.166622	0.009855
H	-6.369381	2.018062	-0.223304
H	-8.339550	0.511095	-0.187117
H	-8.040216	-1.944605	-0.039328
H	-5.779834	-2.934487	0.075685
F	0.112933	-3.699278	1.242681
F	-0.005046	-3.783271	-1.049351
H	0.771127	1.700694	-2.097074
H	-0.783192	1.813816	1.909366
O	-0.009482	5.739150	-0.315070
C	-0.451948	6.536497	0.791798
H	-1.499231	6.325791	1.028532
H	0.174468	6.361609	1.671713
H	-0.347830	7.568709	0.463646

56

5c

C	-1.212353	-0.526360	0.026822
N	-1.257447	-1.932223	0.029311
B	0.000010	-2.850076	0.000256
N	1.257457	-1.932206	-0.028900
C	1.212344	-0.526340	-0.026443
C	-0.000008	0.162883	0.000206
C	-2.557246	-0.083648	0.018674
C	-3.389066	-1.212517	0.017745
C	-2.547309	-2.349817	0.024770
C	2.547321	-2.349778	-0.024575
C	3.389061	-1.212464	-0.017778
C	2.557236	-0.083607	-0.018547
C	-2.948527	-3.785759	0.018234
C	2.948634	-3.785692	-0.018336
C	-0.000019	1.652035	0.000157
C	0.309132	2.356436	-1.172095
C	0.305860	3.746475	-1.178731
C	-0.000028	4.444690	0.000055
C	-0.305912	3.746558	1.178894
C	-0.309174	2.356521	1.172360
C	-4.793178	-0.884868	-0.003715
C	4.793171	-0.884825	0.003461
C	5.933304	-1.704450	0.010425
C	7.197696	-1.124030	0.033352
C	7.350332	0.270244	0.050067
C	6.236603	1.107906	0.044468
C	4.970339	0.523223	0.022175
C	-4.970338	0.523182	-0.022331
C	-6.236592	1.107882	-0.044798
C	-7.350329	0.270235	-0.050692
C	-7.197707	-1.124041	-0.034138
C	-5.933324	-1.704475	-0.011053
S	-3.433357	1.413774	-0.008623
S	3.433353	1.413815	0.008754
H	-3.481382	-4.021271	-0.909354
H	-2.086792	-4.444047	0.102739
H	-3.631654	-3.987009	0.849201
H	2.086648	-4.444119	-0.099066
H	3.628633	-3.987595	-0.851739
H	3.485053	-4.020360	0.907390
H	0.537848	4.290315	-2.086334
H	-0.537903	4.290465	2.086456

H	5.829860	-2.783540	-0.001605
H	8.077191	-1.758713	0.038597
H	8.343864	0.704671	0.067856
H	6.353907	2.185651	0.057660
H	-6.353879	2.185629	-0.057913
H	-8.343854	0.704674	-0.068622
H	-8.077203	-1.758719	-0.039662
H	-5.829901	-2.783567	0.000769
F	0.029081	-3.666148	1.148265
F	-0.029030	-3.666278	-1.147644
H	0.543108	1.814336	-2.081198
H	-0.543142	1.814485	2.081504
C	-0.000034	5.874730	0.000001
N	-0.000034	7.035505	-0.000045

70

8a

C	1.208807	-0.695425	0.005250
N	1.259123	-2.100867	0.010149
B	0.000051	-3.019672	0.000205
N	-1.258963	-2.100824	-0.010042
C	-1.208450	-0.695398	-0.005167
C	0.000197	0.000043	0.000045
C	2.548020	-0.246089	0.002475
C	3.386014	-1.379051	0.002693
C	2.549079	-2.519391	0.008155
C	-2.548977	-2.519171	-0.007997
C	-3.385763	-1.378711	-0.002721
C	-2.547605	-0.245877	-0.002544
C	0.000125	1.492600	0.000121
C	-0.006926	2.189817	-1.225377
C	-0.010859	3.587561	-1.199900
C	-0.006527	4.304730	0.000402
C	-0.003507	3.587287	1.200669
C	0.001136	2.189646	1.225855
C	0.020444	5.814176	0.000680
C	0.002439	1.452738	2.544515
C	-0.013473	1.453231	-2.544199
C	2.951351	-3.954732	-0.019446
C	-2.951492	-3.954438	0.019837
C	-4.761760	-0.999386	-0.003026
C	-4.937092	0.373312	-0.004556
S	-3.411566	1.259896	-0.005101
S	3.412301	1.259528	0.004836

C	4.937698	0.372666	0.004271
C	4.762083	-0.999986	0.002866
C	6.306543	0.797384	0.002225
C	7.168455	-0.331995	-0.001387
S	6.282716	-1.859612	-0.004308
S	-6.282587	-1.858681	0.004046
C	-7.167999	-0.330860	0.000960
C	-6.305843	0.798327	-0.002662
C	6.872626	2.084682	0.004119
C	8.254589	2.222254	0.002223
C	9.092622	1.094156	-0.001356
C	8.557579	-0.191251	-0.003031
C	-8.557092	-0.189800	0.002485
C	-9.091838	1.095731	0.000668
C	-8.253550	2.223641	-0.002925
C	-6.871619	2.085760	-0.004695
H	-0.020133	4.126855	-2.143598
H	-0.007447	4.126391	2.144516
H	-0.466211	6.218922	-0.890238
H	-0.478811	6.218791	0.884726
H	1.053358	6.181038	0.008270
H	-0.001643	2.158099	3.377802
H	-0.875874	0.805828	2.639117
H	0.886427	0.813892	2.641344
H	-0.896414	0.812358	-2.637067
H	-0.014741	2.158790	-3.377328
H	0.865900	0.808396	-2.643040
H	3.899980	-4.089537	0.504450
H	2.193975	-4.586917	0.442981
H	3.089734	-4.288778	-1.054079
H	-3.091258	-4.287891	1.054477
H	-3.899512	-4.089347	-0.505149
H	-2.193671	-4.586997	-0.441327
H	6.232621	2.960669	0.007241
H	8.693685	3.213973	0.003679
H	10.169422	1.222873	-0.002842
H	9.204974	-1.061000	-0.005680
H	-9.204692	-1.059398	0.005137
H	-10.168610	1.224696	0.002051
H	-8.692420	3.215461	-0.004492
H	-6.231400	2.961591	-0.007825
F	0.016546	-3.834413	-1.148074
F	-0.016440	-3.834004	1.148783

65

8b

C	1.224293	-0.749730	0.069530
N	1.274072	-2.155157	0.042971
B	0.022368	-3.075252	-0.053302
N	-1.236423	-2.160960	-0.097858
C	-1.198004	-0.755981	-0.044928
C	0.010433	-0.057272	0.033093
C	2.567341	-0.303831	0.075535
C	3.401171	-1.440517	0.052436
C	2.562267	-2.577428	0.032504
C	-2.521259	-2.593450	-0.115441
C	-3.369236	-1.463905	-0.076464
C	-2.544531	-0.321086	-0.031320
C	0.005029	1.425721	0.078856
C	-0.433972	2.173997	-1.019505
C	-0.433669	3.568600	-0.989769
C	-0.002603	4.234230	0.164172
C	0.431954	3.495145	1.275100
C	0.442706	2.109278	1.227412
C	2.961374	-4.012682	-0.029844
C	-2.907894	-4.033428	-0.129802
C	-4.750896	-1.108265	-0.041066
C	-4.947764	0.258529	0.035485
S	-3.436967	1.168247	0.056354
S	3.447450	1.195258	0.067774
C	4.965387	0.298279	0.029327
C	4.779662	-1.072274	0.029395
C	6.337194	0.712835	0.006271
C	7.190361	-0.423028	-0.015526
S	6.293279	-1.943938	-0.005225
S	-6.257708	-1.991992	-0.068737
C	-7.167104	-0.481178	0.022224
C	-6.322988	0.660511	0.072335
C	6.912992	1.995783	0.001694
C	8.295729	2.122997	-0.024329
C	9.124988	0.988651	-0.046297
C	8.580230	-0.292686	-0.041921
C	-8.558116	-0.363256	0.045826
C	-9.113291	0.911419	0.120333
C	-8.293094	2.051439	0.170439
C	-6.909223	1.936524	0.147304
H	-0.766064	4.117346	-1.861666
H	0.755934	4.024303	2.164131

H	3.901898	-4.164212	0.504212
H	2.196240	-4.655575	0.404038
H	3.114247	-4.318585	-1.071034
H	-3.029292	-4.403338	0.894584
H	-3.861082	-4.161413	-0.646761
H	-2.149446	-4.641831	-0.621779
H	6.279776	2.876521	0.018528
H	8.742260	3.111393	-0.027803
H	10.202539	1.109249	-0.066860
H	9.220805	-1.167307	-0.058768
H	-9.191610	-1.242332	0.007630
H	-10.191896	1.022314	0.140095
H	-8.747624	3.034480	0.228478
H	-6.283012	2.821531	0.186979
F	0.097488	-3.856949	-1.222651
F	-0.046456	-3.923442	1.068883
H	-0.763910	1.665128	-1.919135
H	0.775722	1.547116	2.093450
O	0.031069	5.587708	0.301970
C	-0.403550	6.387061	-0.806786
H	-0.292978	7.418784	-0.479272
H	0.223639	6.206920	-1.685050
H	-1.451737	6.183249	-1.045420

62

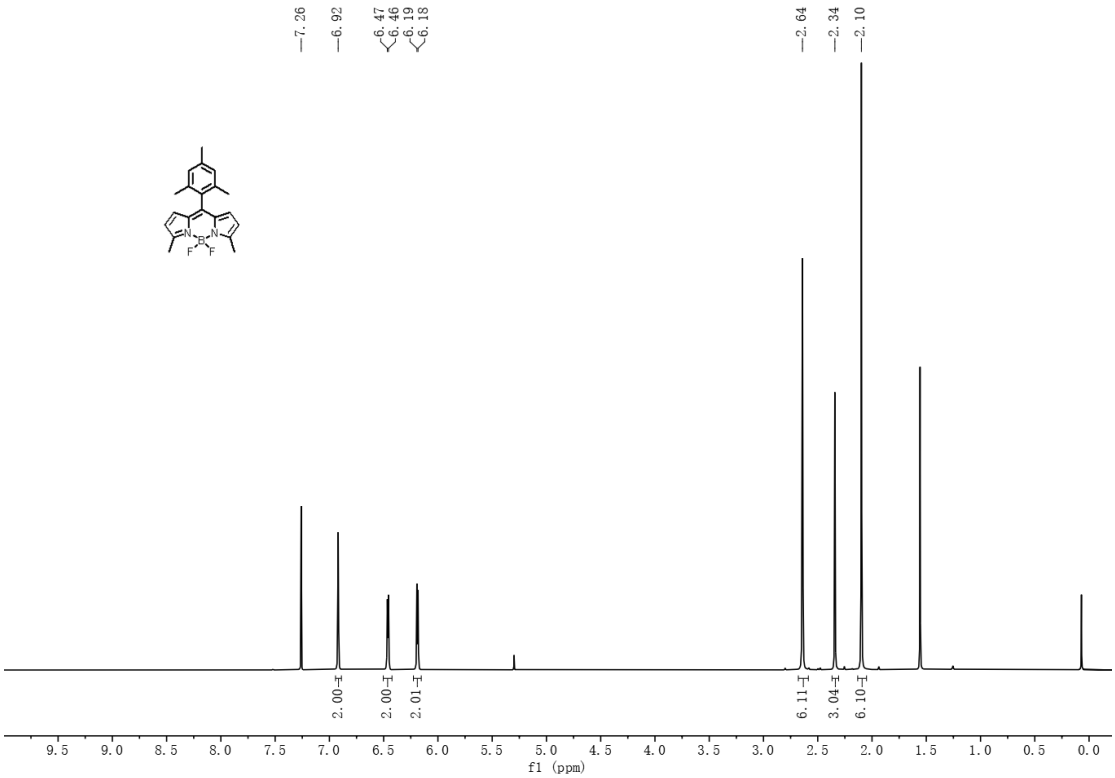
8c

C	1.212914	-0.693807	0.035459
N	1.257911	-2.099182	0.040838
B	0.000020	-3.018111	-0.000145
N	-1.257879	-2.099203	-0.040926
C	-1.212902	-0.693836	-0.035553
C	0.000002	-0.005077	-0.000070
C	2.557115	-0.249669	0.031369
C	3.387518	-1.387996	0.033321
C	2.545073	-2.523820	0.039426
C	-2.545044	-2.523863	-0.039522
C	-3.387498	-1.388052	-0.033446
C	-2.557101	-0.249711	-0.031482
C	-0.000027	1.483722	-0.000117
C	-0.319395	2.188297	-1.169751
C	-0.316280	3.578346	-1.176333
C	-0.000100	4.276538	-0.000224
C	0.316119	3.578453	1.175936
C	0.319303	2.188402	1.169463

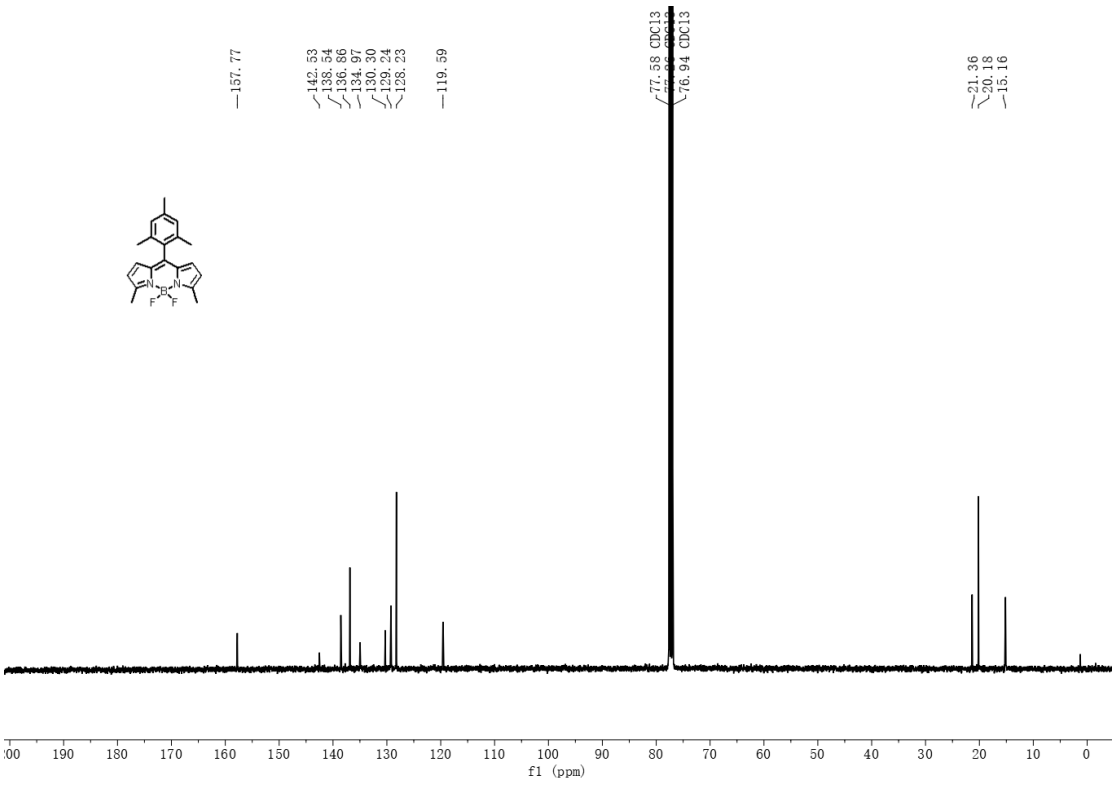
C	2.940725	-3.960568	0.011000
C	-2.940597	-3.960641	-0.011135
C	-4.766943	-1.023361	-0.016683
C	-4.955688	0.347014	0.000898
S	-3.439757	1.246760	-0.007542
S	3.439773	1.246806	0.007714
C	4.955708	0.347070	-0.000640
C	4.766960	-1.023309	0.016803
C	6.328213	0.759389	-0.016903
C	7.178702	-0.378483	-0.013589
S	6.278767	-1.897624	0.009499
S	-6.278757	-1.897668	-0.009434
C	-7.178686	-0.378526	0.013814
C	-6.328191	0.759340	0.017204
C	6.906329	2.041090	-0.034709
C	8.289421	2.164965	-0.048918
C	9.116277	1.028637	-0.045717
C	8.569071	-0.251409	-0.027880
C	-8.569054	-0.251446	0.028176
C	-9.116251	1.028602	0.046133
C	-8.289389	2.164925	0.049398
C	-6.906298	2.041042	0.035141
H	-0.555881	4.122192	-2.081951
H	0.555692	4.122380	2.081514
H	3.883365	-4.101246	0.544009
H	2.175826	-4.591257	0.462679
H	3.088591	-4.290332	-1.023667
H	-3.086832	-4.290920	1.023598
H	-3.884004	-4.101157	-0.542808
H	-2.176308	-4.591068	-0.464240
H	6.275003	2.923296	-0.037296
H	8.738163	3.152211	-0.062738
H	10.194201	1.146820	-0.057285
H	9.207929	-1.127383	-0.025411
H	-9.207917	-1.127417	0.025663
H	-10.194175	1.146790	0.057748
H	-8.738125	3.152172	0.063310
H	-6.274966	2.923244	0.037786
F	0.045087	-3.830911	-1.147896
F	-0.045015	-3.831170	1.147419
H	-0.560601	1.646272	-2.077053
H	0.560534	1.646463	2.076808
C	-0.000145	5.706598	-0.000280
N	-0.000146	6.867341	-0.000333

7. Copies of ^{1}H, ^{13}C NMR and High Resolution Mass Spectra

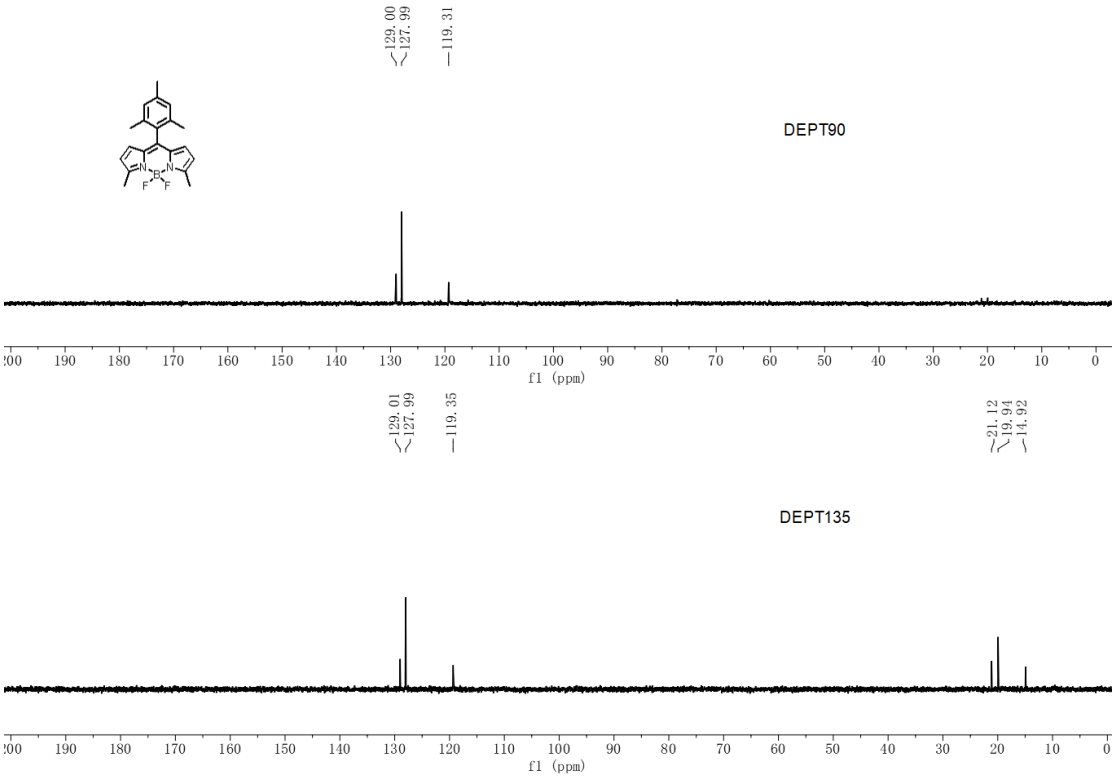
^{1}H NMR spectrum of **1a** ($CDCl_3$, 400 MHz)



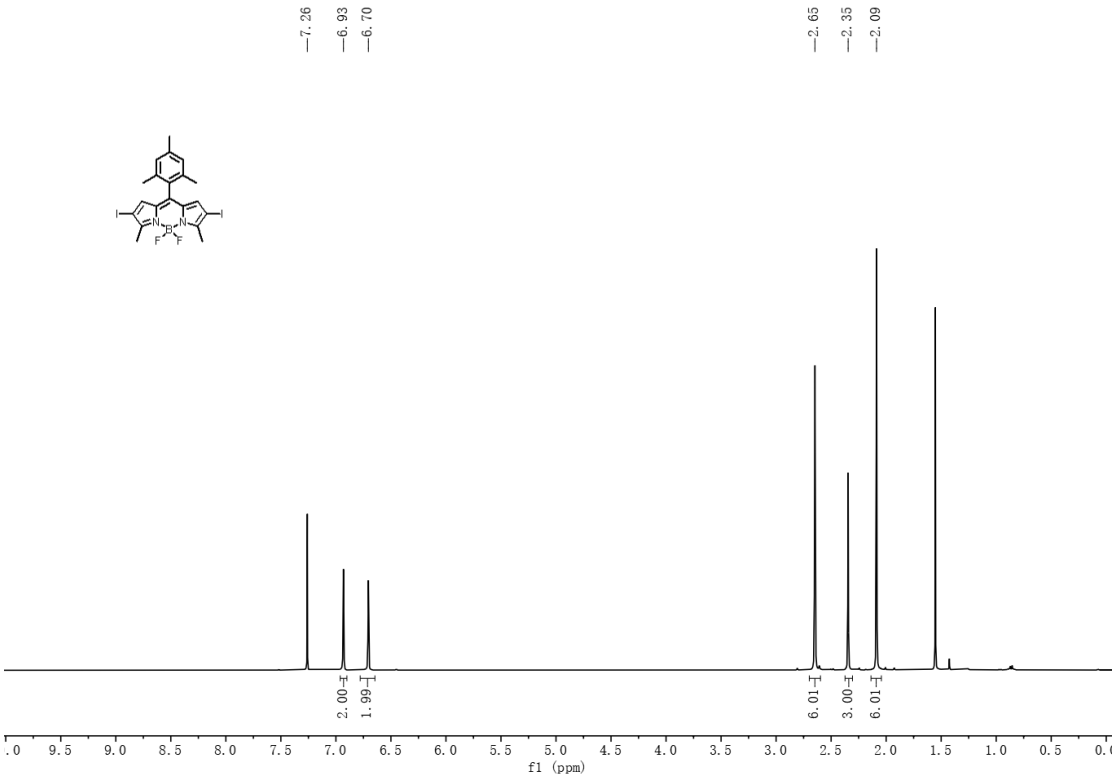
^{13}C NMR Spectrum of **1a** ($CDCl_3$, 101 MHz)



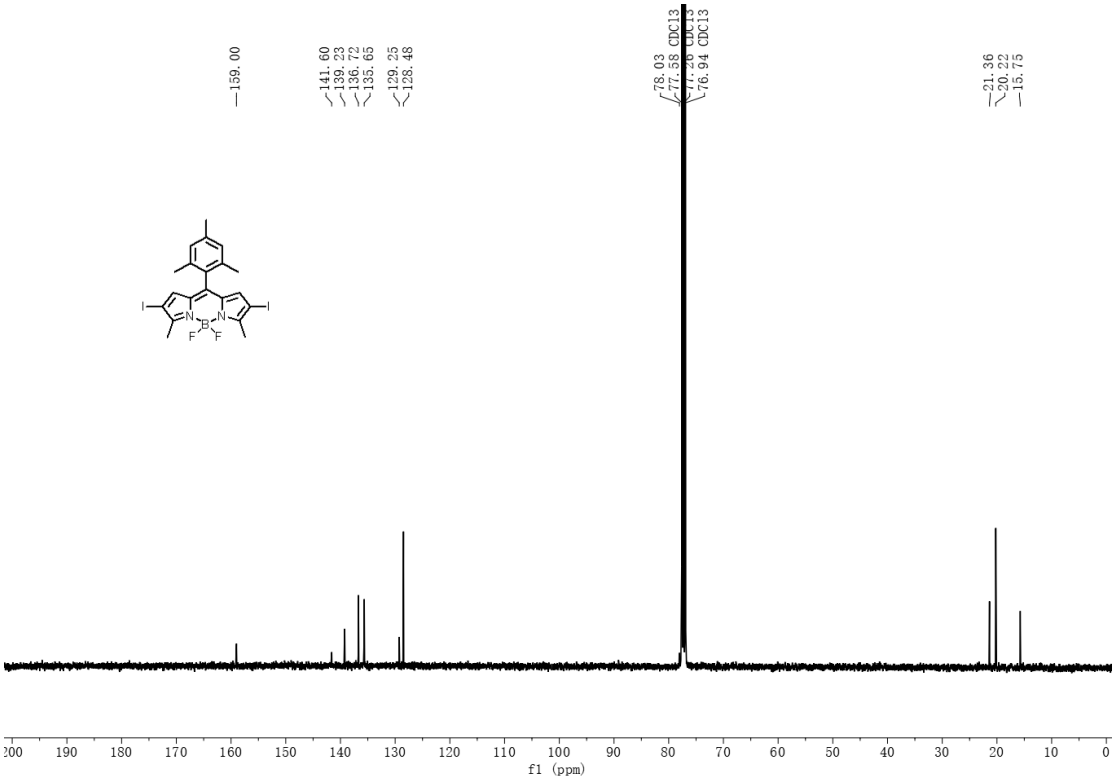
DEPT Spectrum of **1a** ($CDCl_3$, 101 MHz)



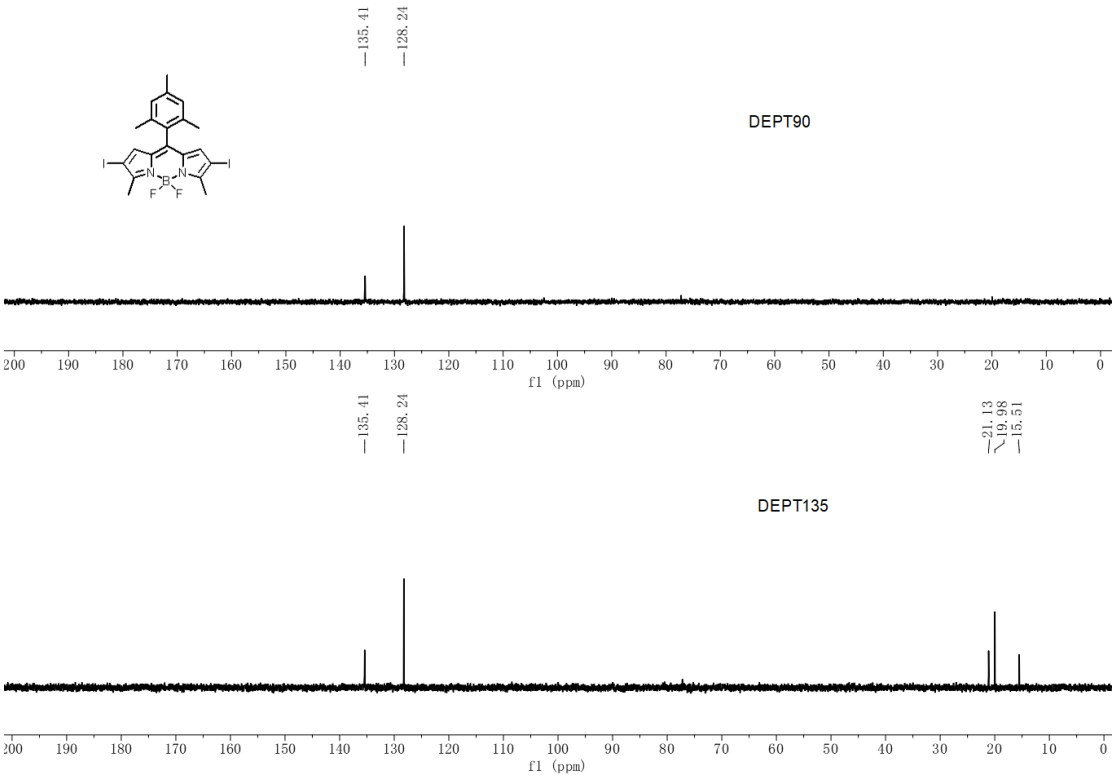
^{1}H NMR spectrum of **2a** ($CDCl_3$, 400 MHz)



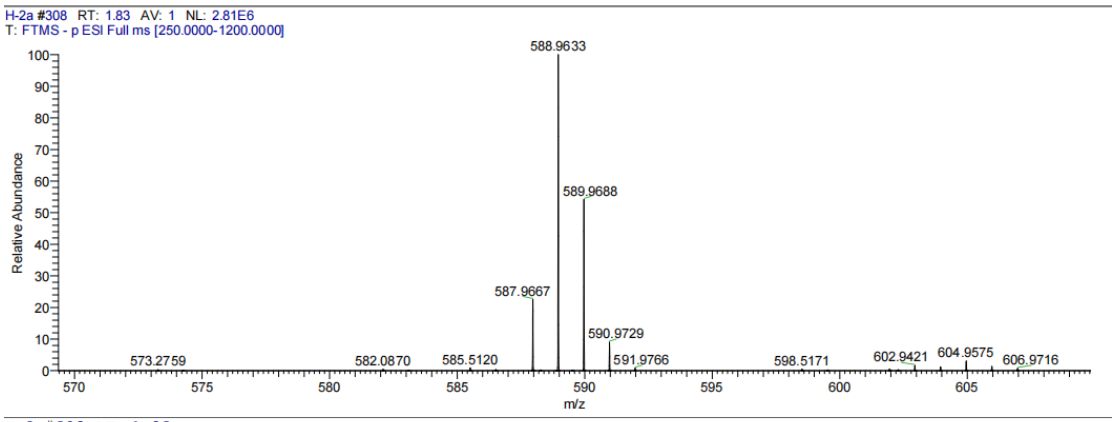
^{13}C NMR Spectrum of **2a** ($CDCl_3$, 101 MHz)



DEPT Spectrum of **2a** ($CDCl_3$, 101 MHz)



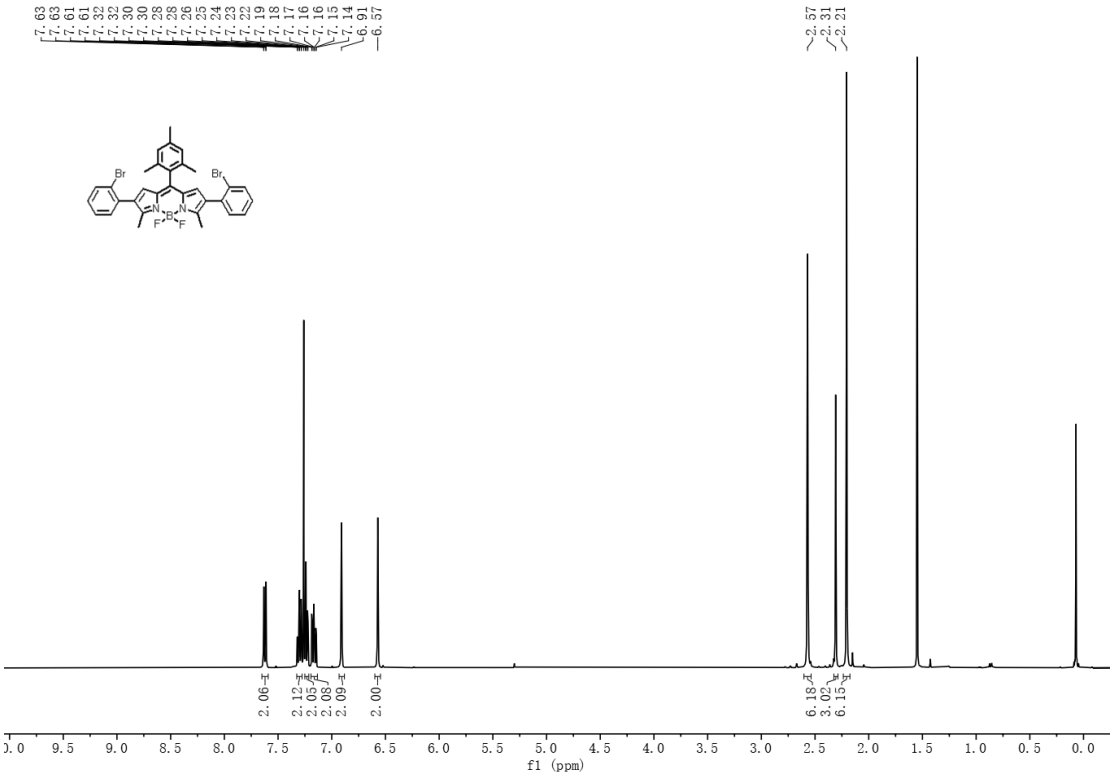
HRMS Spectrum of **2a**



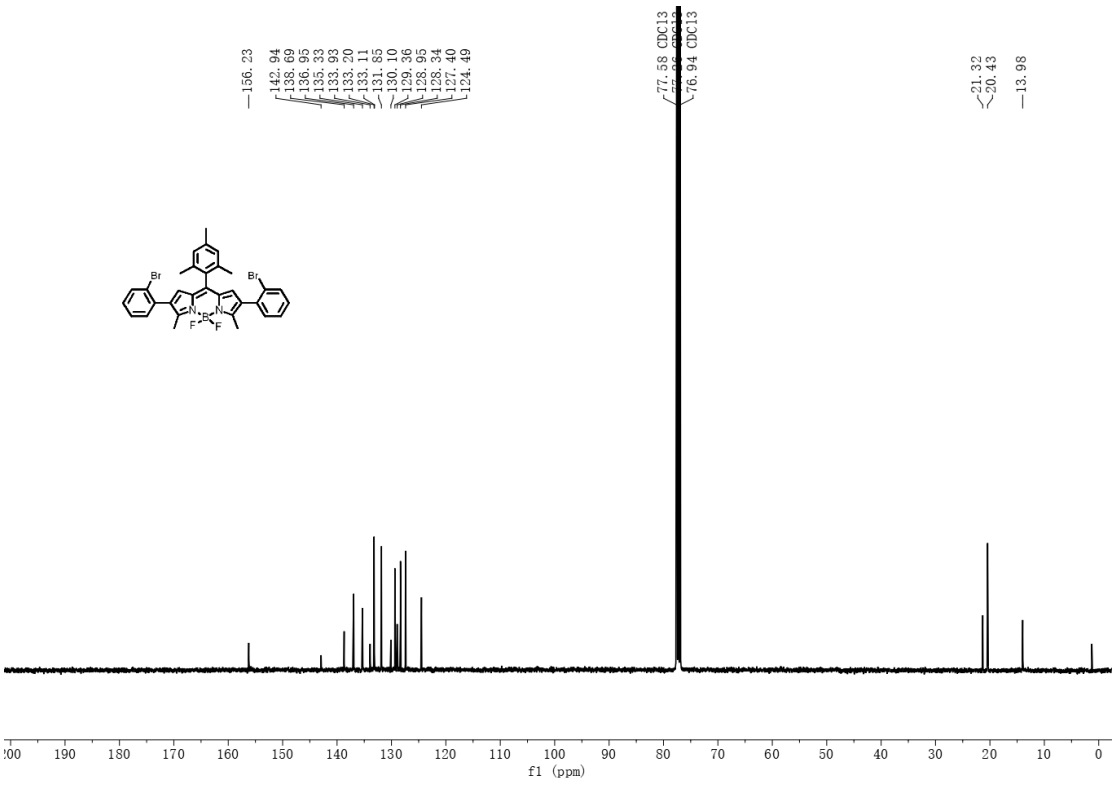
H-2a#308 RT: 1.83
T: FTMS - p ESI Full ms [250.0000-1200.0000]
m/z= 569.3644-609.8296

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
588.9633	2829804.0	100.00	588.9615	1.82	$C_{20}H_{18}N_2BF_2I_2$

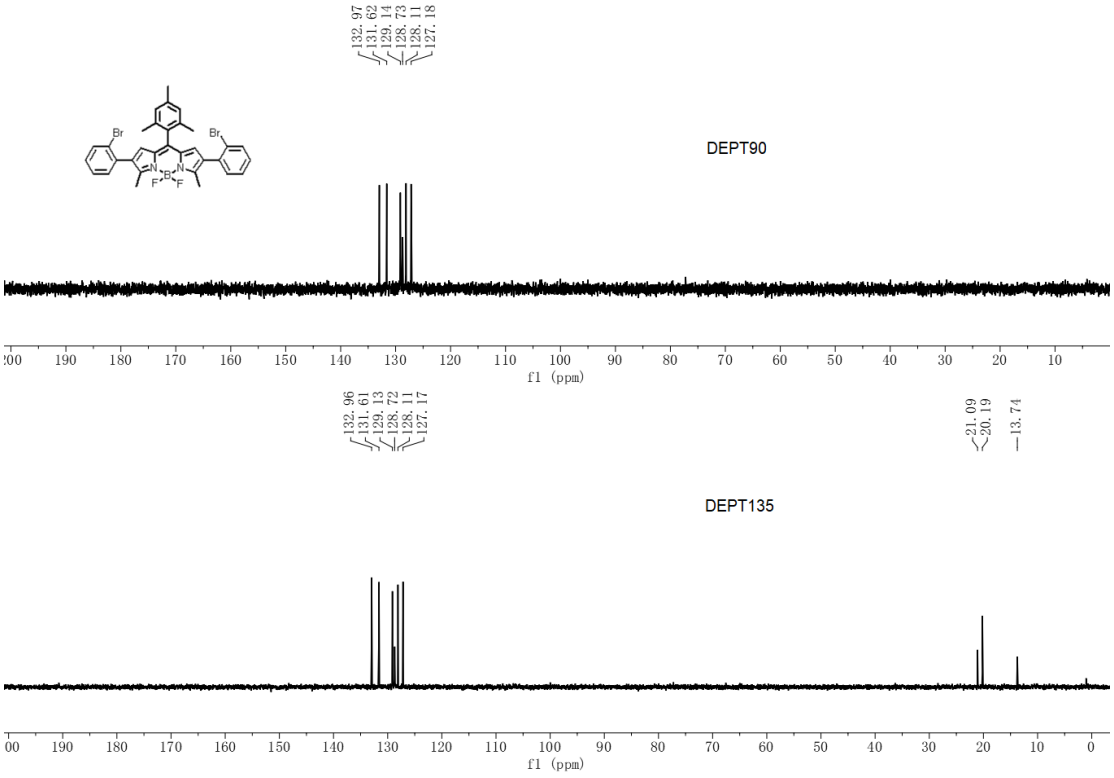
^{1}H NMR spectrum of **3a** ($CDCl_3$, 400 MHz)



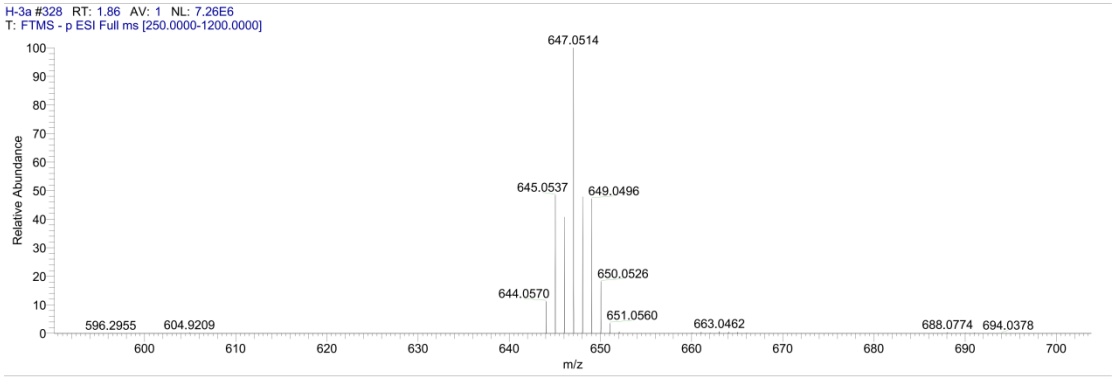
^{13}C NMR Spectrum of **3a** ($CDCl_3$, 101 MHz)



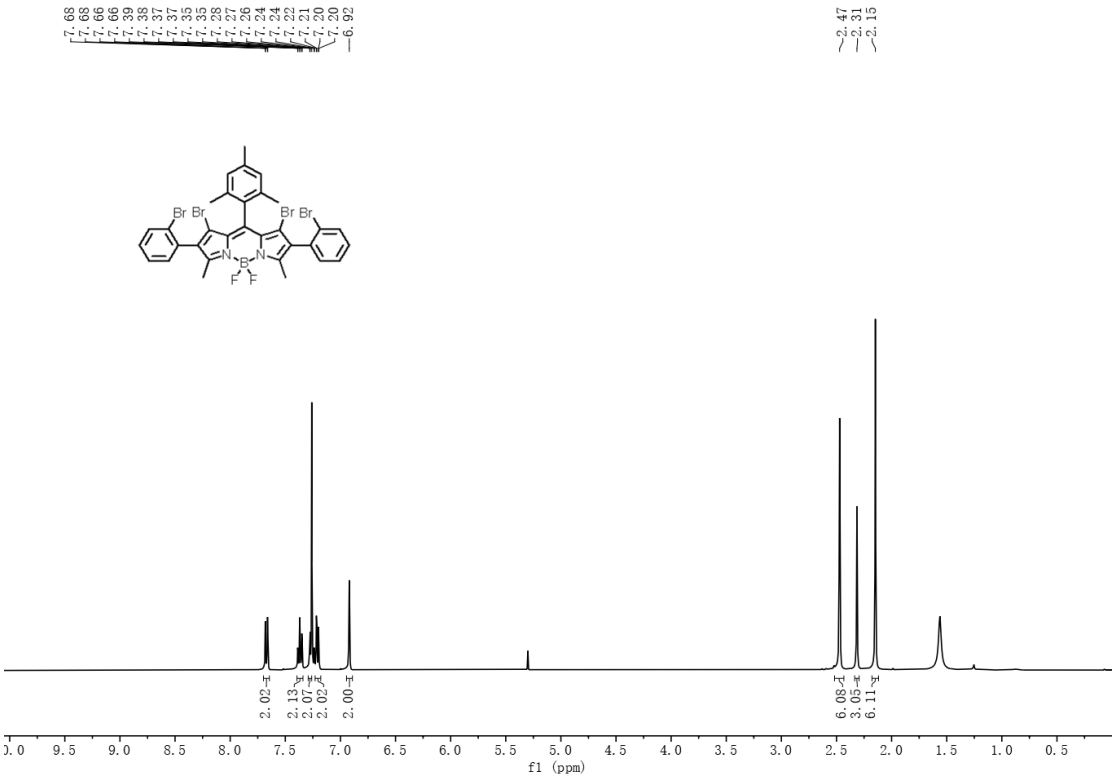
DEPT Spectrum of **3a** ($CDCl_3$, 101 MHz)



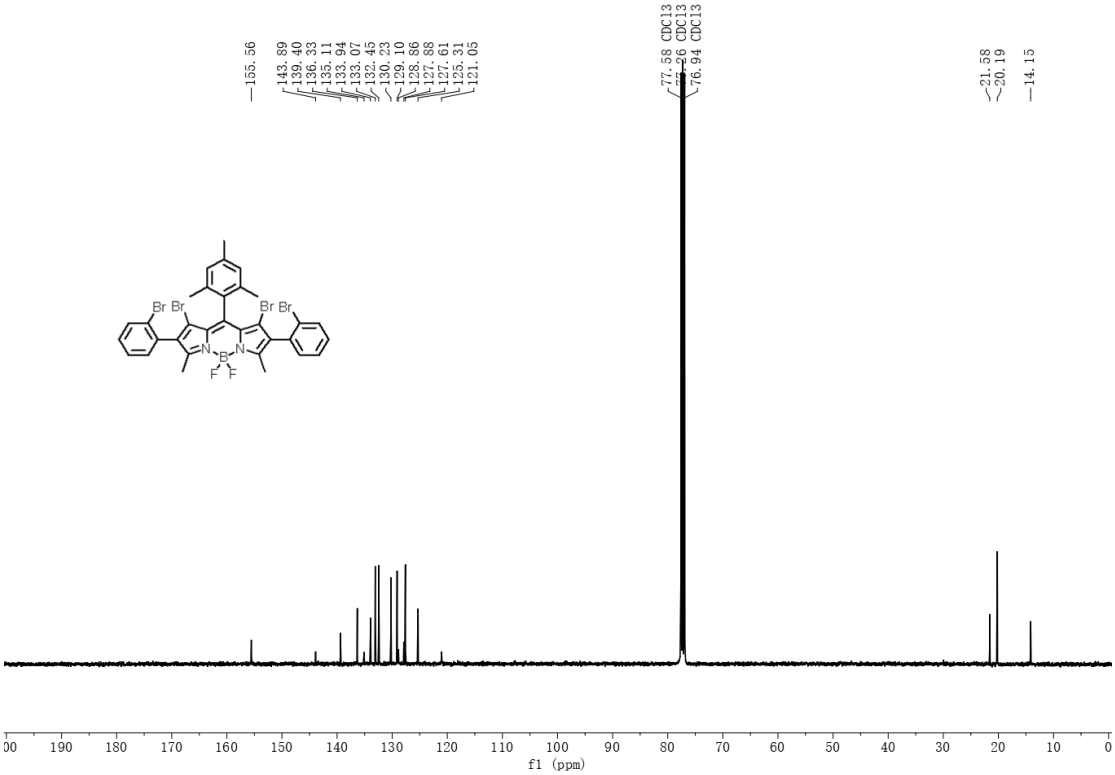
HRMS Spectrum of **3a**



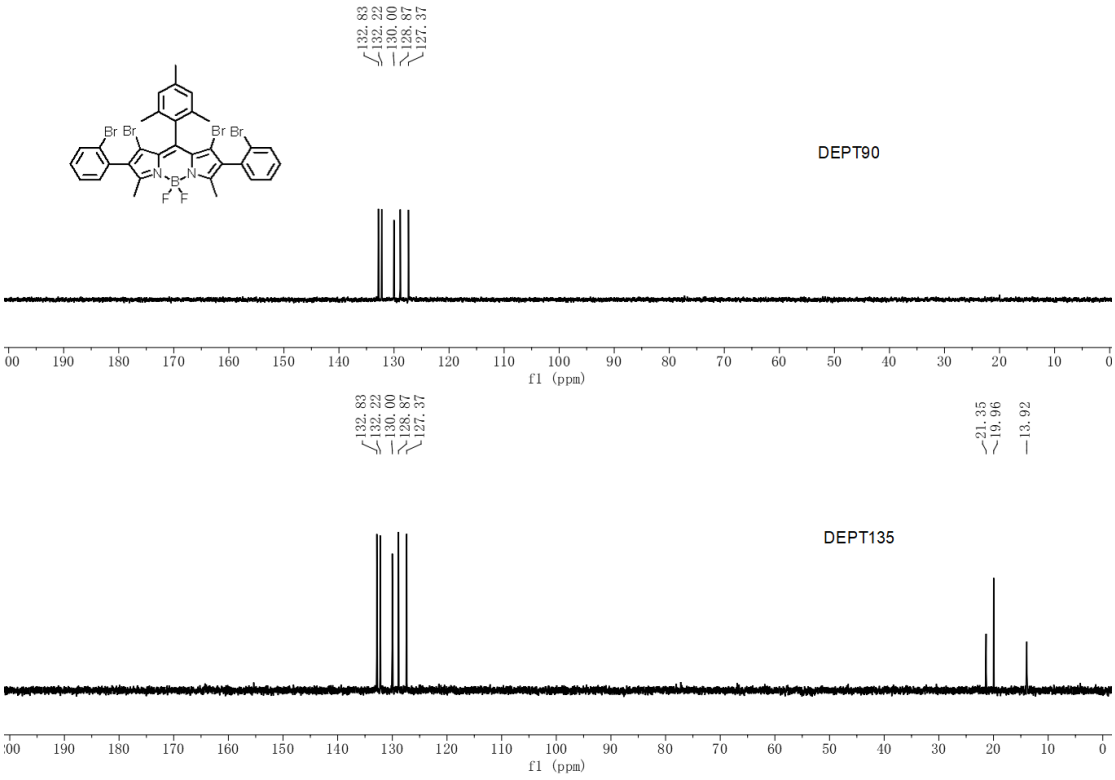
^{1}H NMR spectrum of **4a** ($CDCl_3$, 400 MHz)



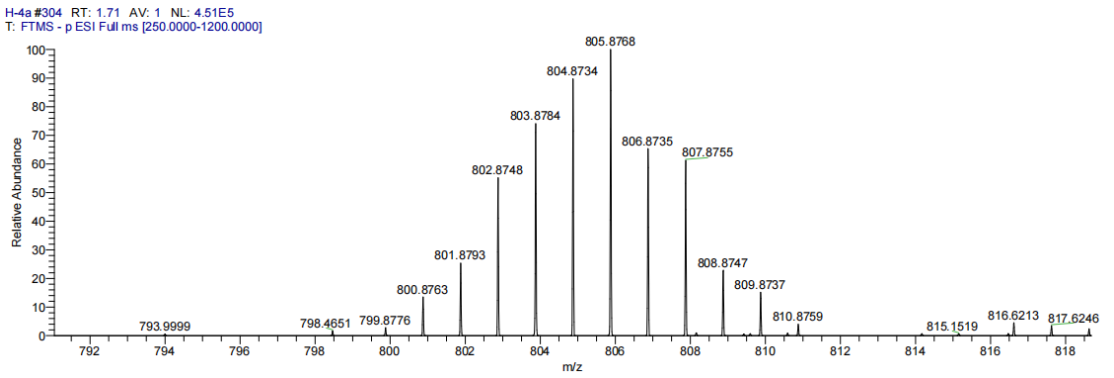
^{13}C NMR Spectrum of **4a** ($CDCl_3$, 101 MHz)



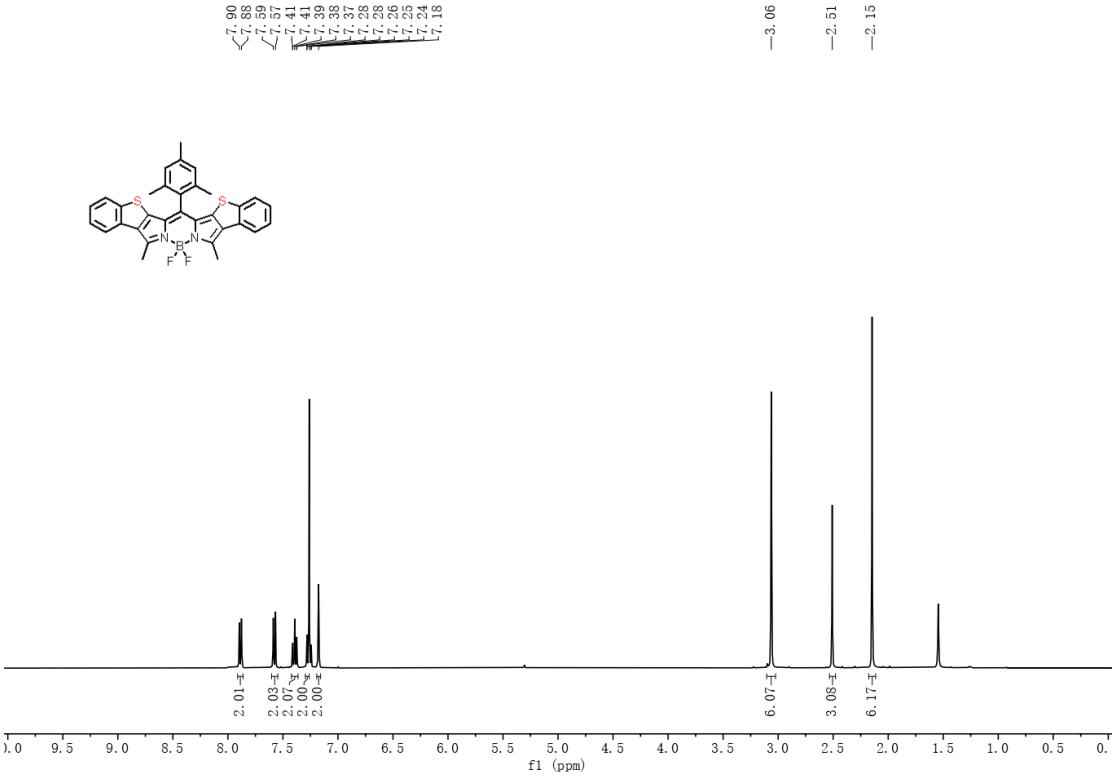
DEPT Spectrum of **4a** ($CDCl_3$, 101 MHz)



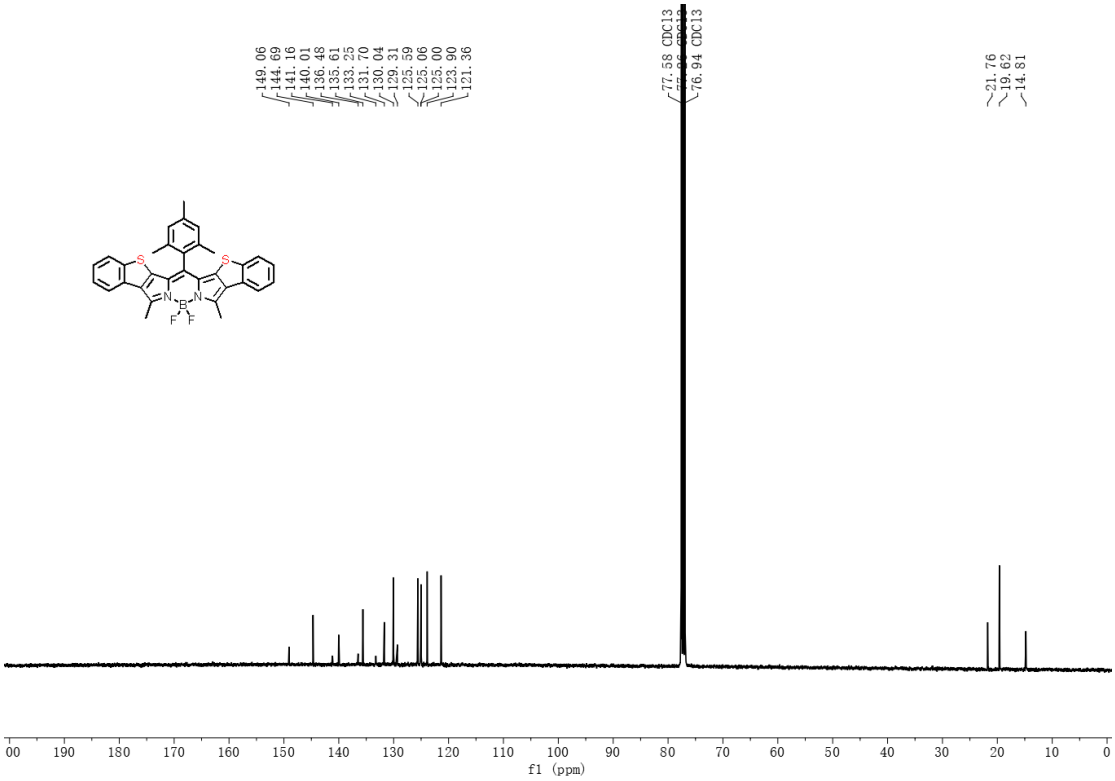
HRMS Spectrum of **4a**



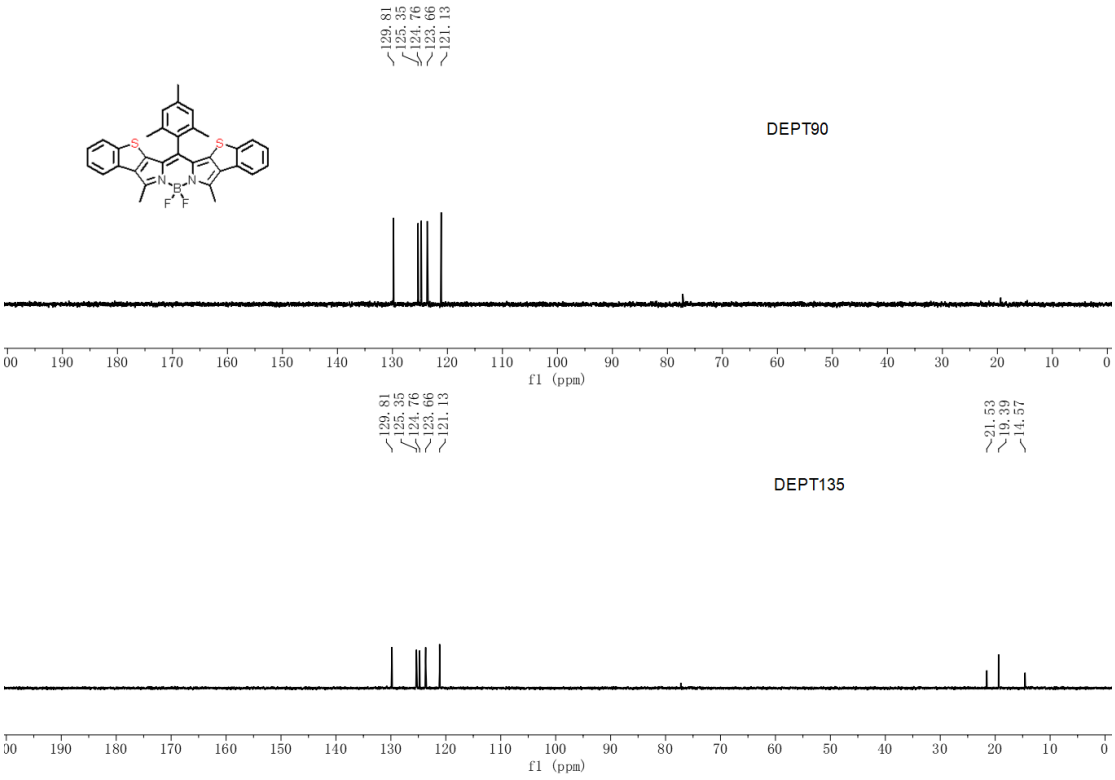
^{1}H NMR spectrum of **5a** ($CDCl_3$, 400 MHz)



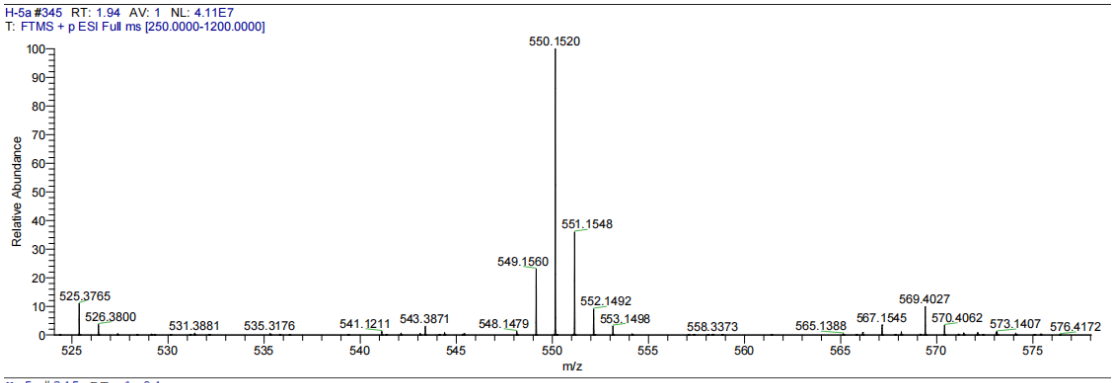
^{13}C NMR Spectrum of **5a** ($CDCl_3$, 101 MHz)



DEPT Spectrum of **5a** ($CDCl_3$, 101 MHz)



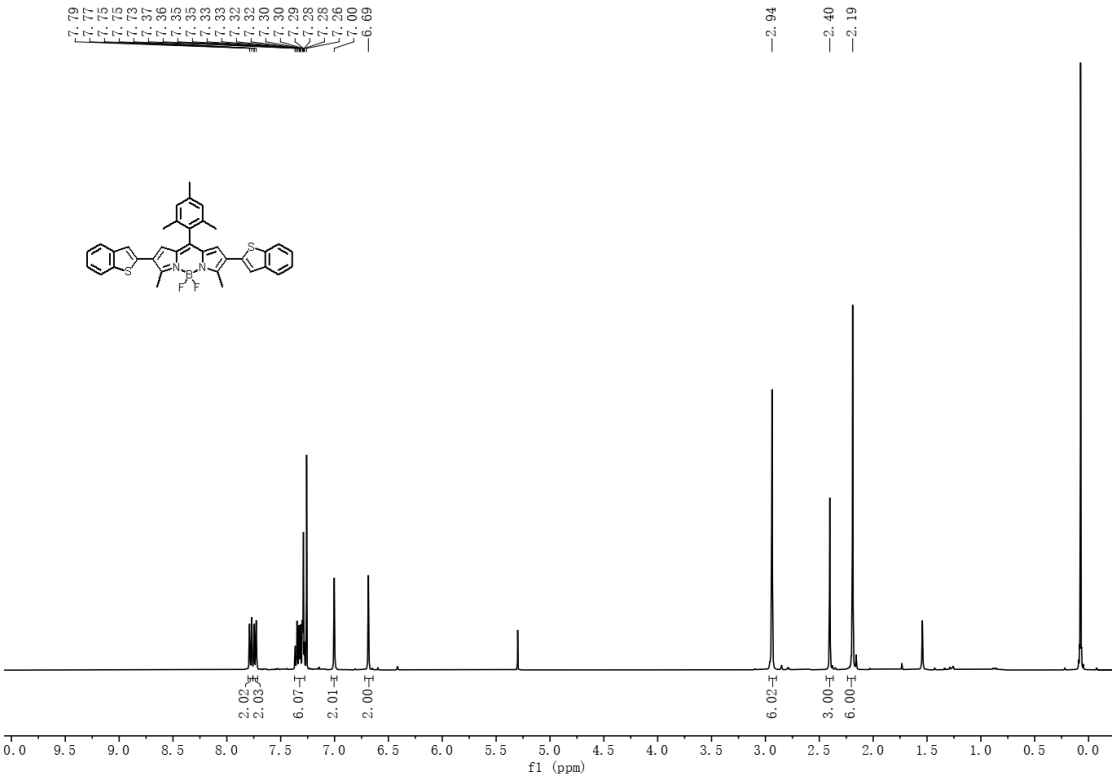
HRMS Spectrum of **5a**



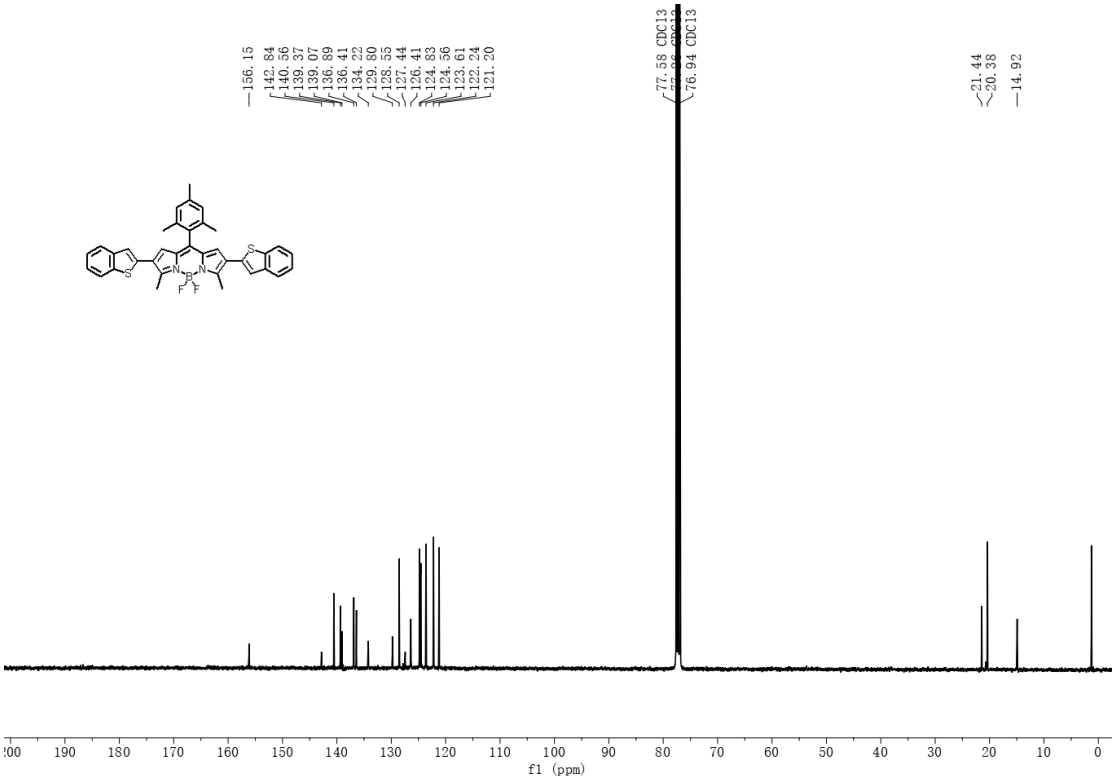
H-5a#345 RT: 1.94
T: FTMS + p ESI Full ms [250.0000-1200.0000]
m/z= 524.0801-578.0404

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
550.1520	41715632.0	100.00	550.1515	0.50	$C_{32}H_{25}N_2BF_2S_2$

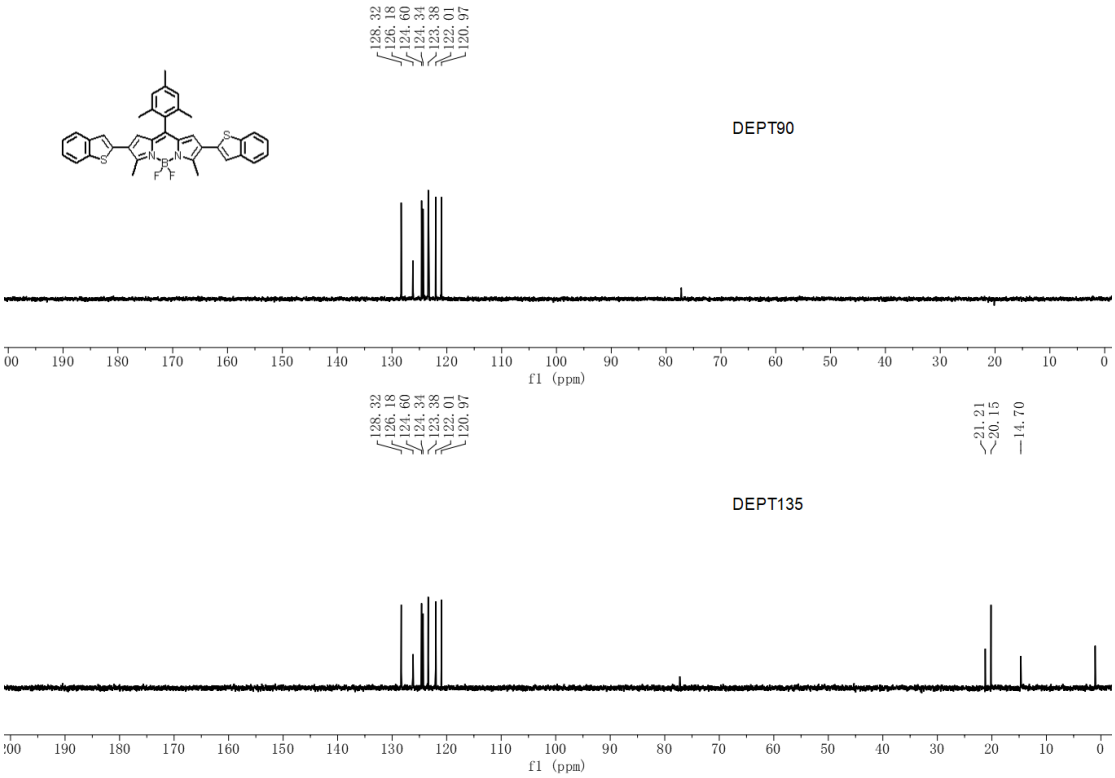
^{1}H NMR spectrum of **6a** ($CDCl_3$, 400 MHz)



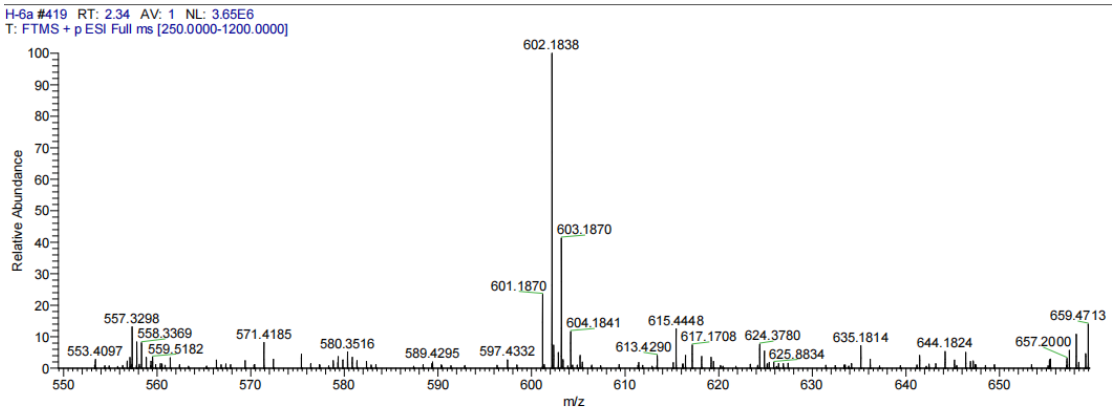
^{13}C NMR Spectrum of **6a** ($CDCl_3$, 101 MHz)



DEPT Spectrum of **6a** ($CDCl_3$, 101 MHz)



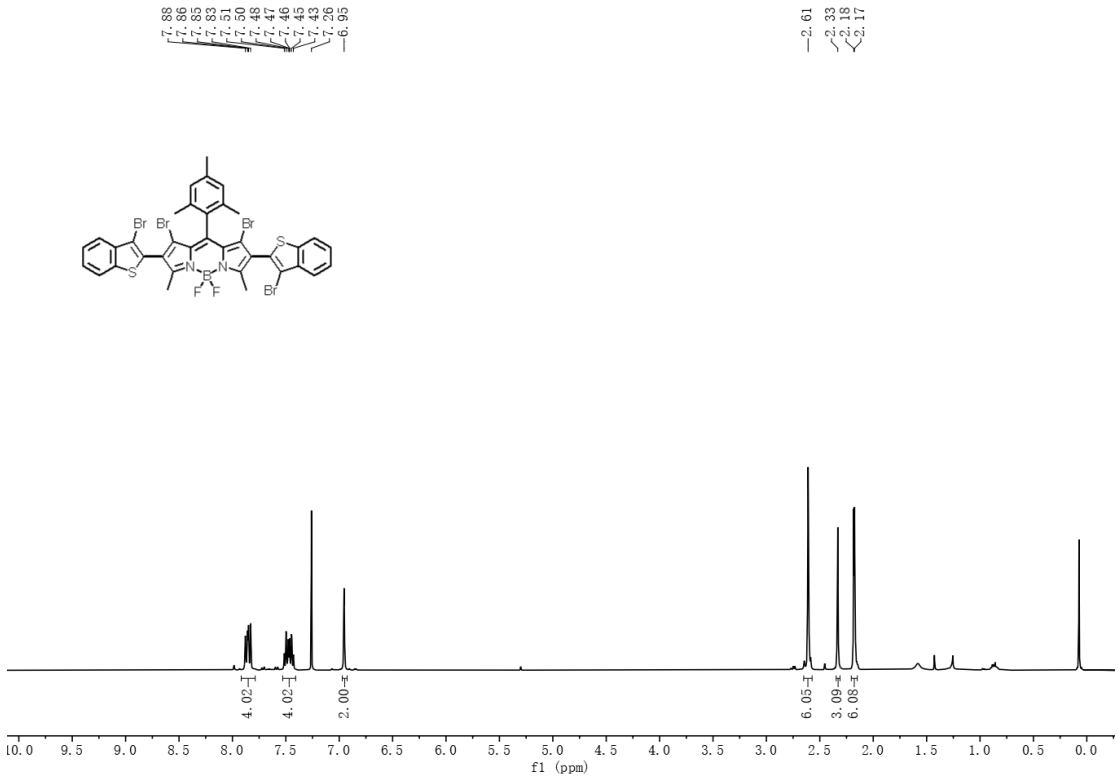
HRMS Spectrum of **6a**



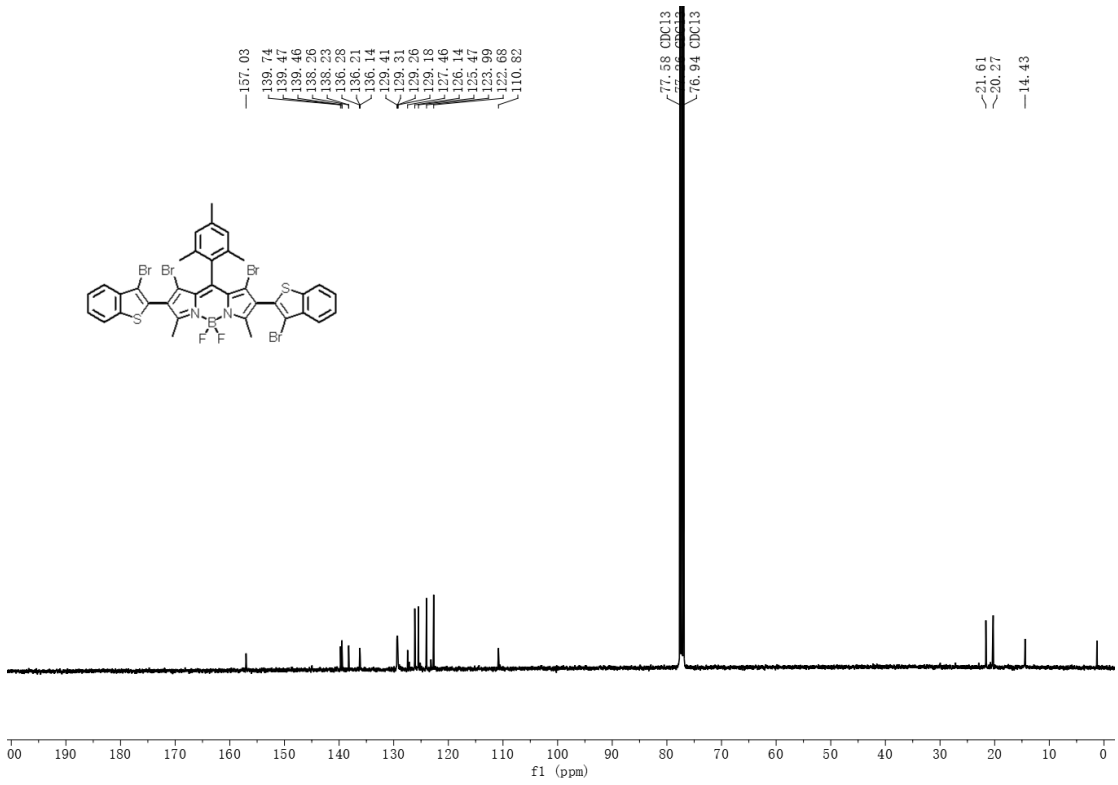
H-6a#419 RT: 2.34
T: FTMS + p ESI Full ms [250.0000-1200.0000]
m/z= 549.4430-659.6330

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
602.1838	3769975.8	100.00	602.1828	1.06	$C_{36}H_{29}N_2BF_2S_2$

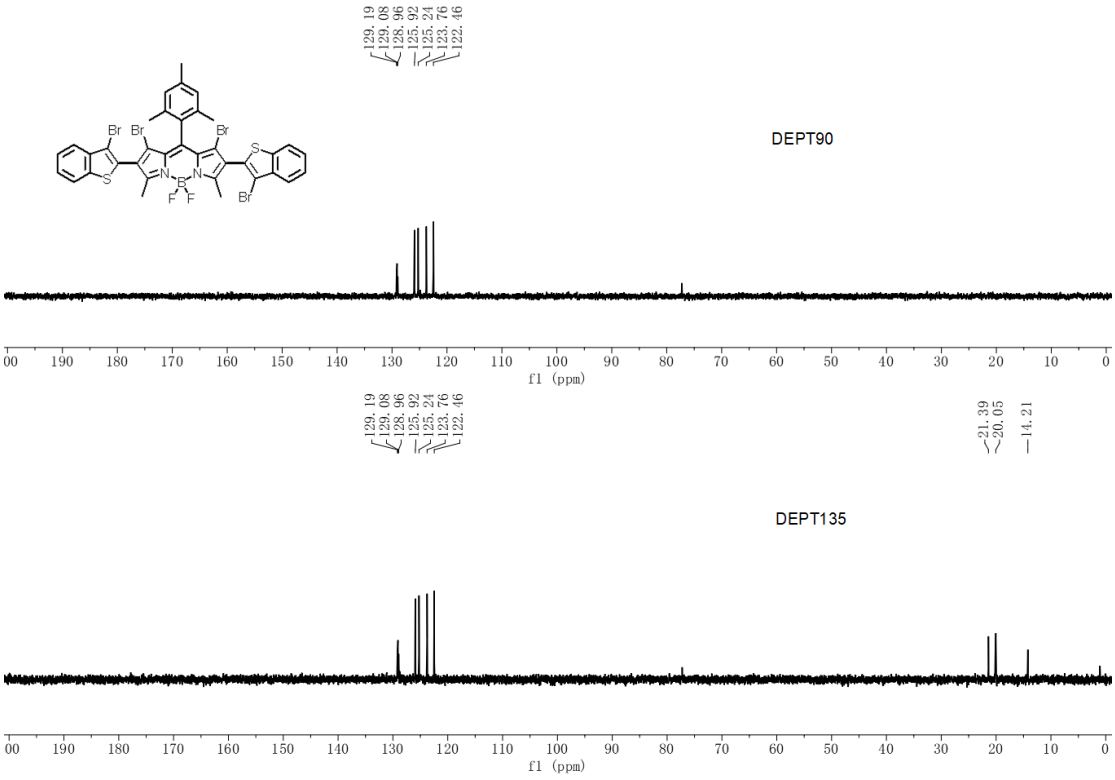
^{1}H NMR spectrum of **7a** ($CDCl_3$, 400 MHz)



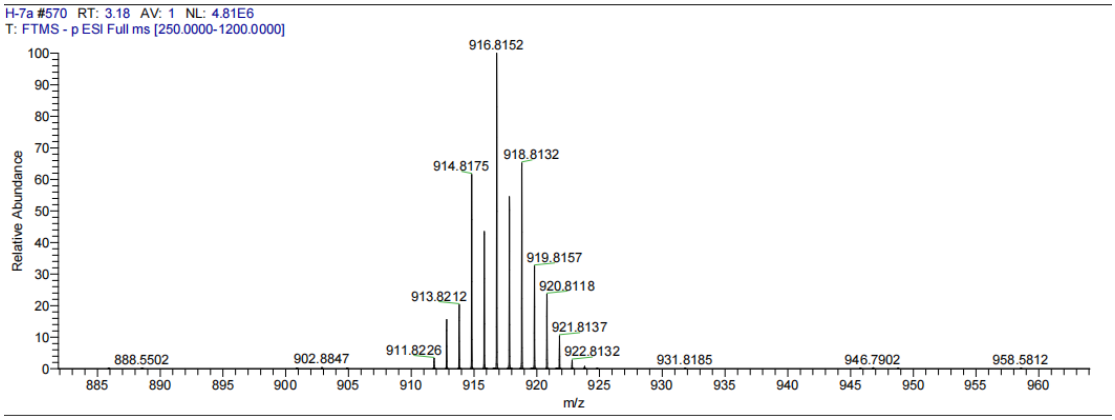
^{13}C NMR Spectrum of **7a** ($CDCl_3$, 101 MHz)



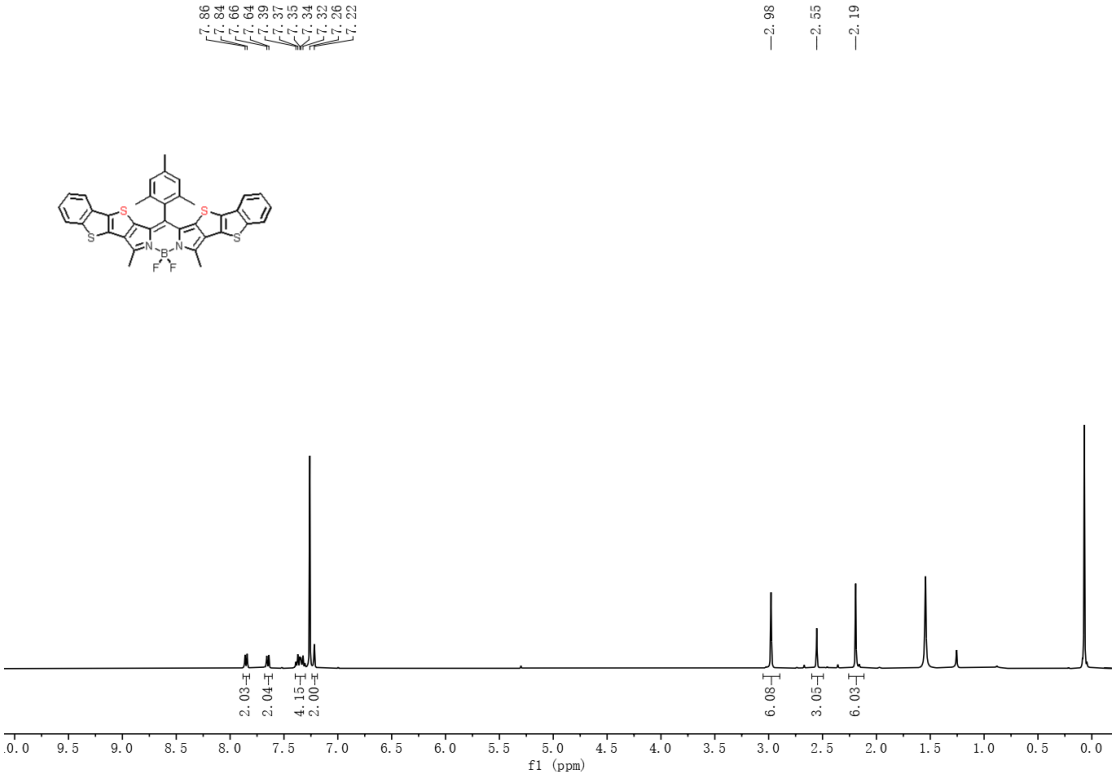
DEPT Spectrum of **7a** ($CDCl_3$, 101 MHz)



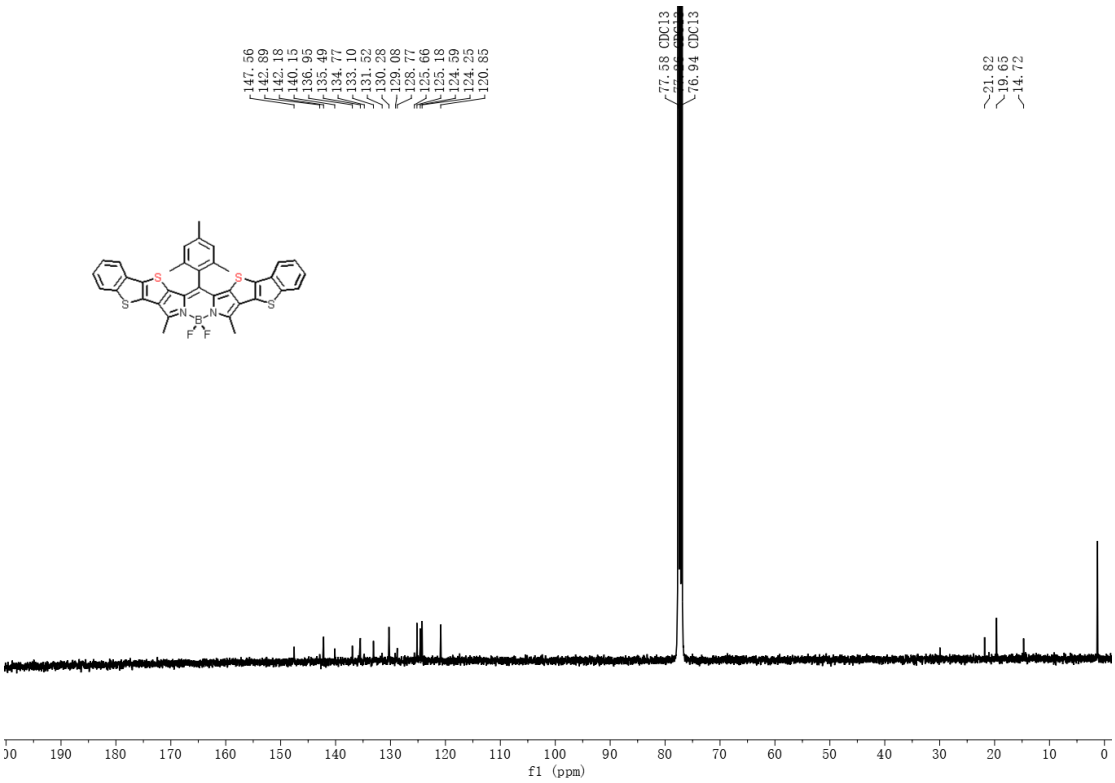
HRMS Spectrum of **7a**



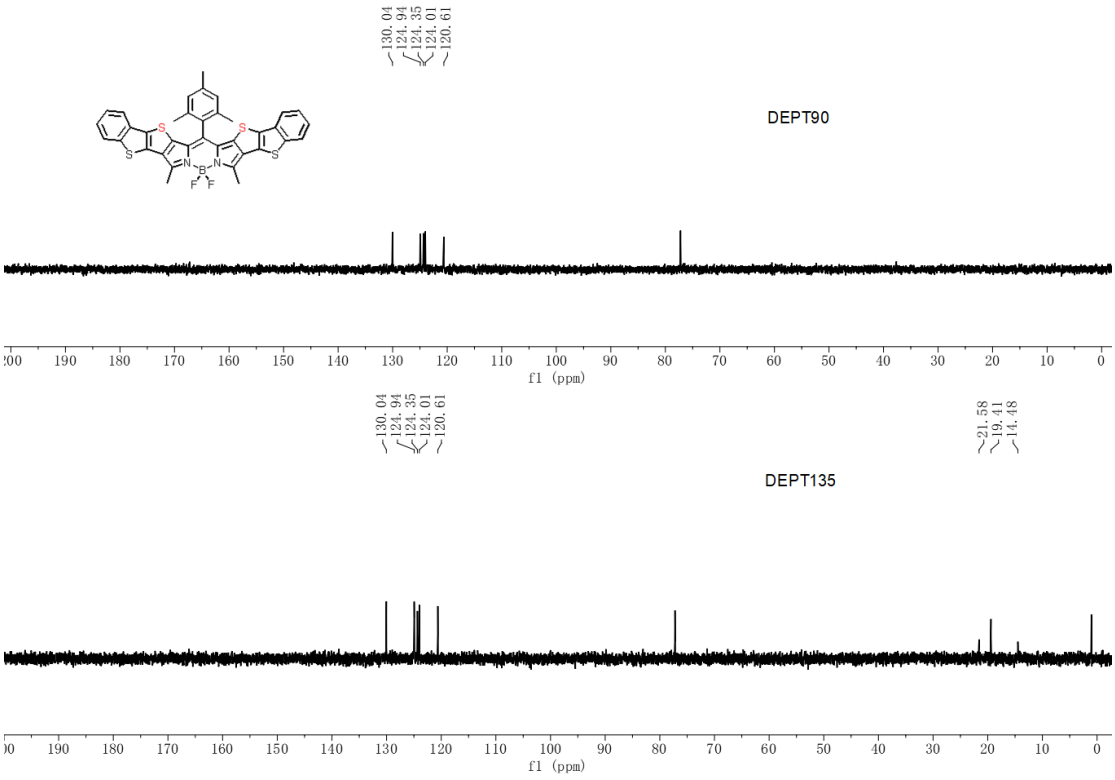
^{1}H NMR spectrum of **8a** ($CDCl_3$, 400 MHz)



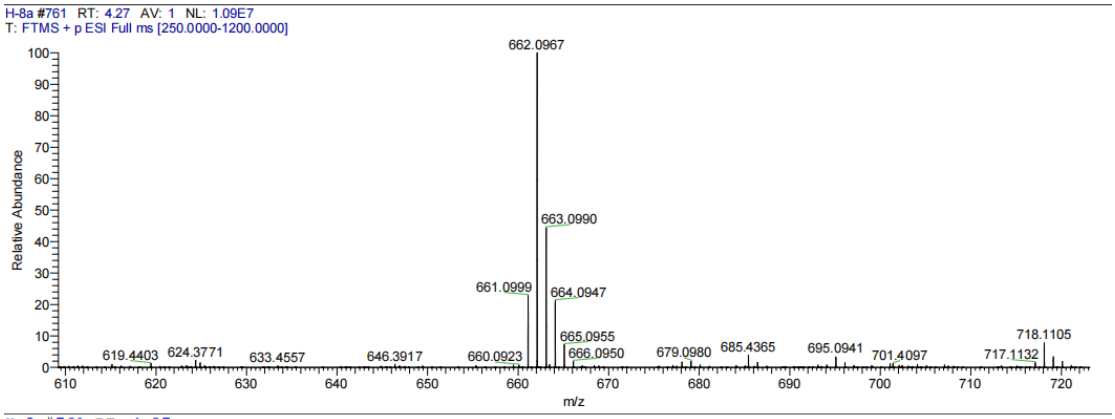
^{13}C NMR Spectrum of **8a** ($CDCl_3$, 101 MHz)



DEPT Spectrum of **8a** ($CDCl_3$, 101 MHz)



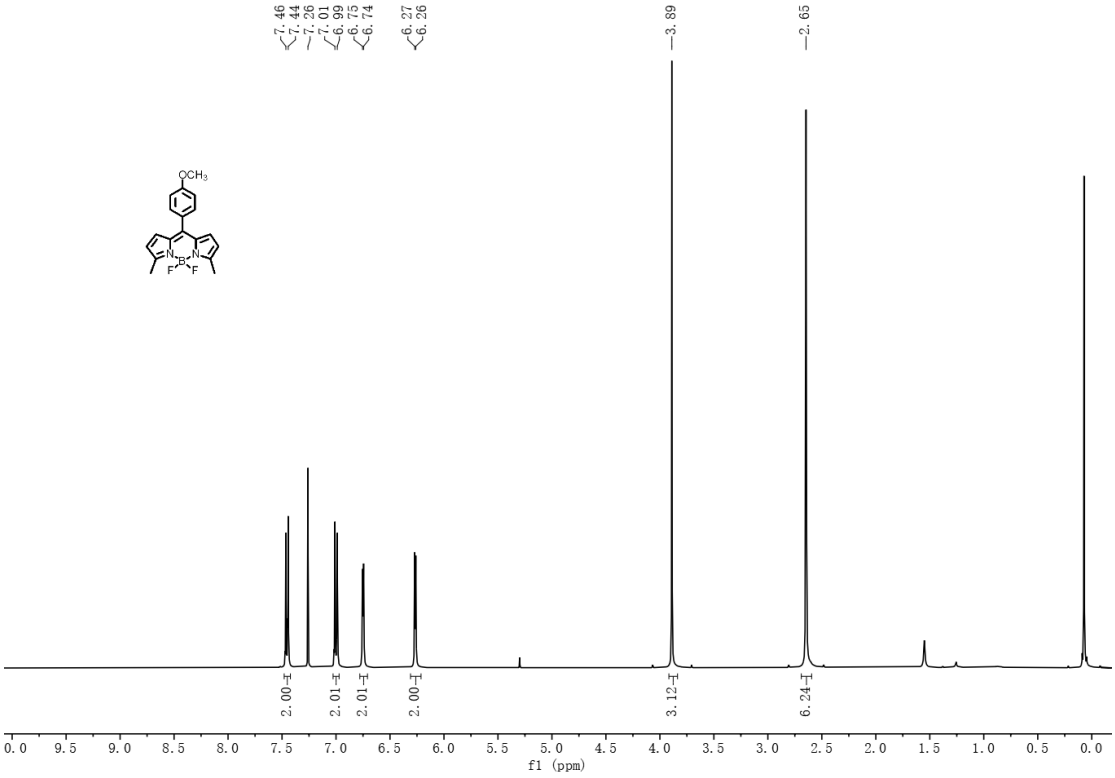
HRMS Spectrum of **8a**



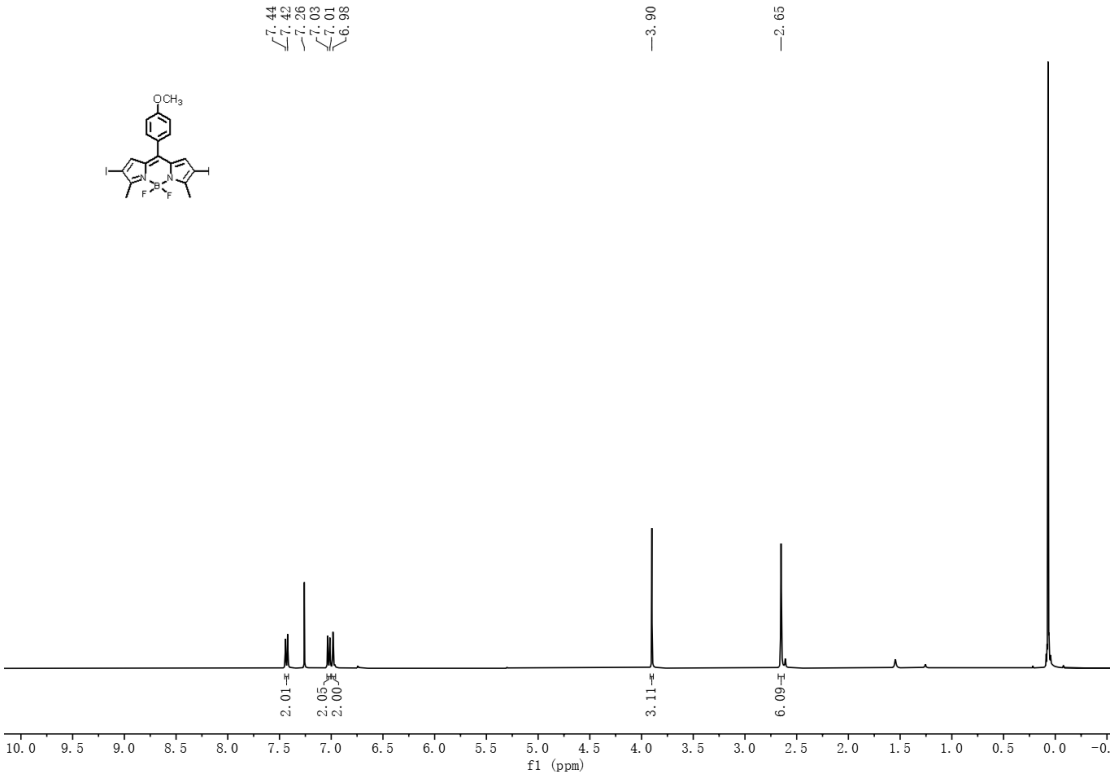
H-8a#761 RT: 4.27
T: FTMS + p ESI Full ms [250.0000-1200.0000]
m/z= 609.2071-723.1324

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
662.0967	11351029.0	100.00	662.0956	1.06	$C_{36}H_{25}N_2BF_2S_4$

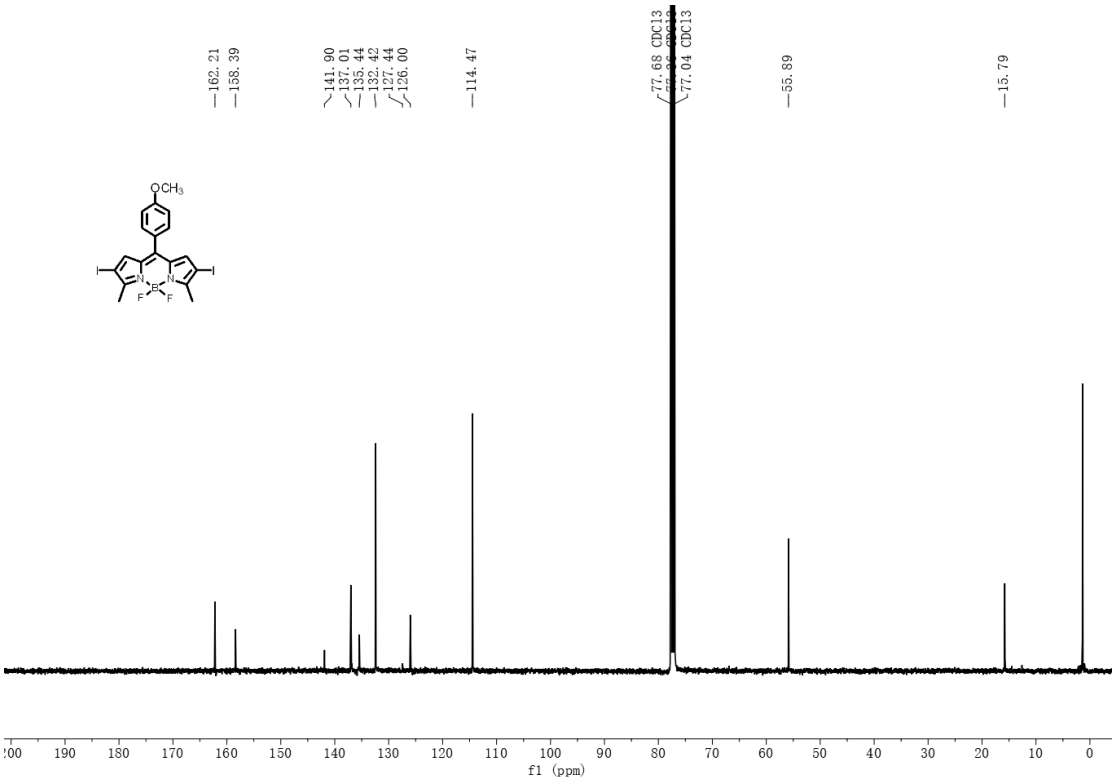
^{1}H NMR spectrum of **1b** ($CDCl_3$, 400 MHz)



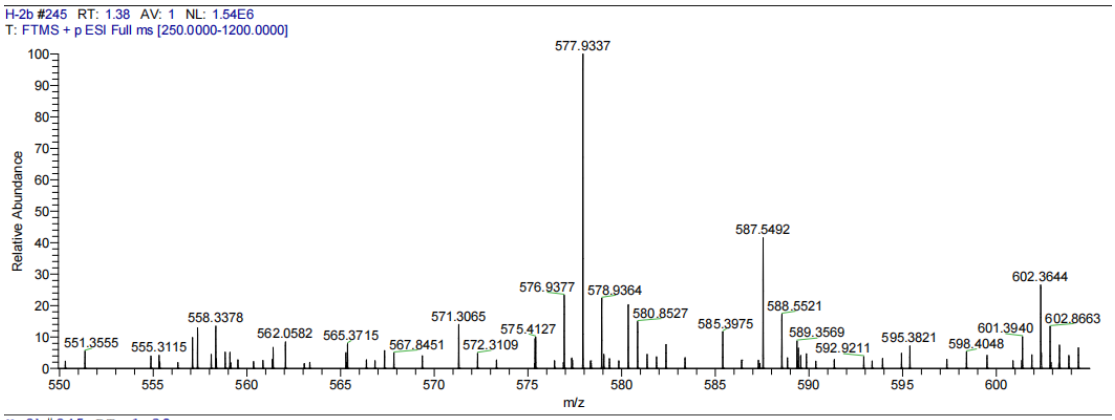
^{1}H NMR spectrum of **2b** ($CDCl_3$, 400 MHz)



^{13}C NMR Spectrum of **2b** ($CDCl_3$, 101 MHz)



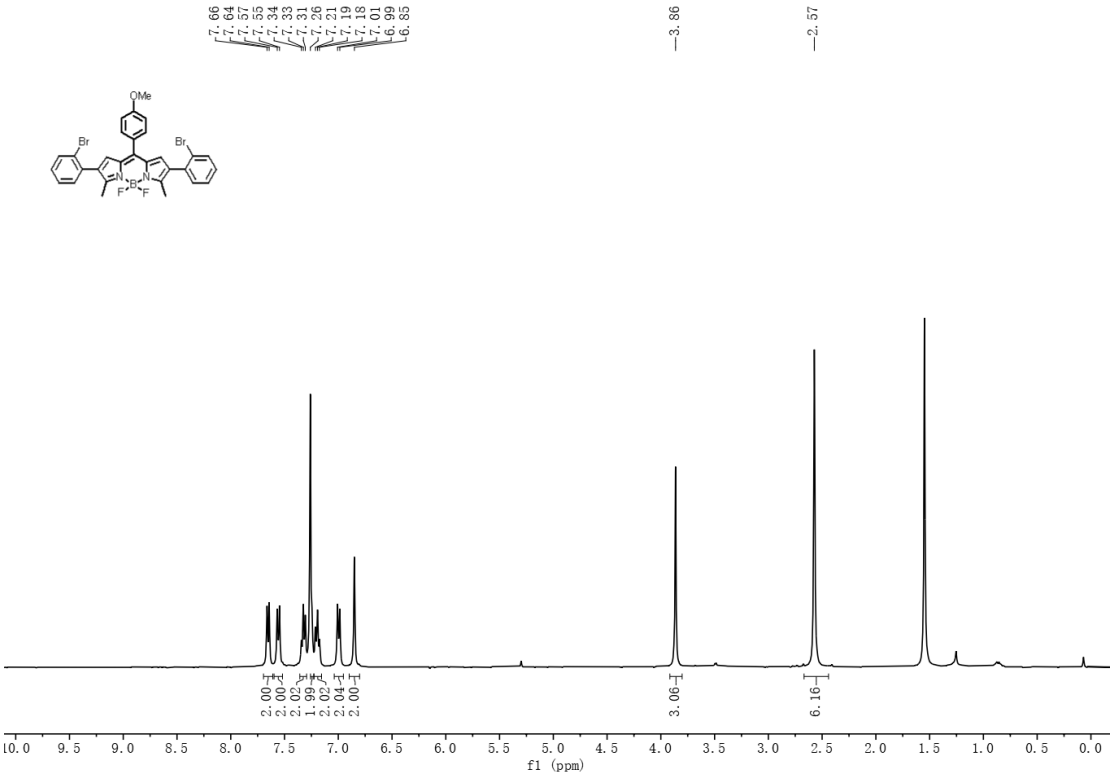
HRMS Spectrum of **2b**



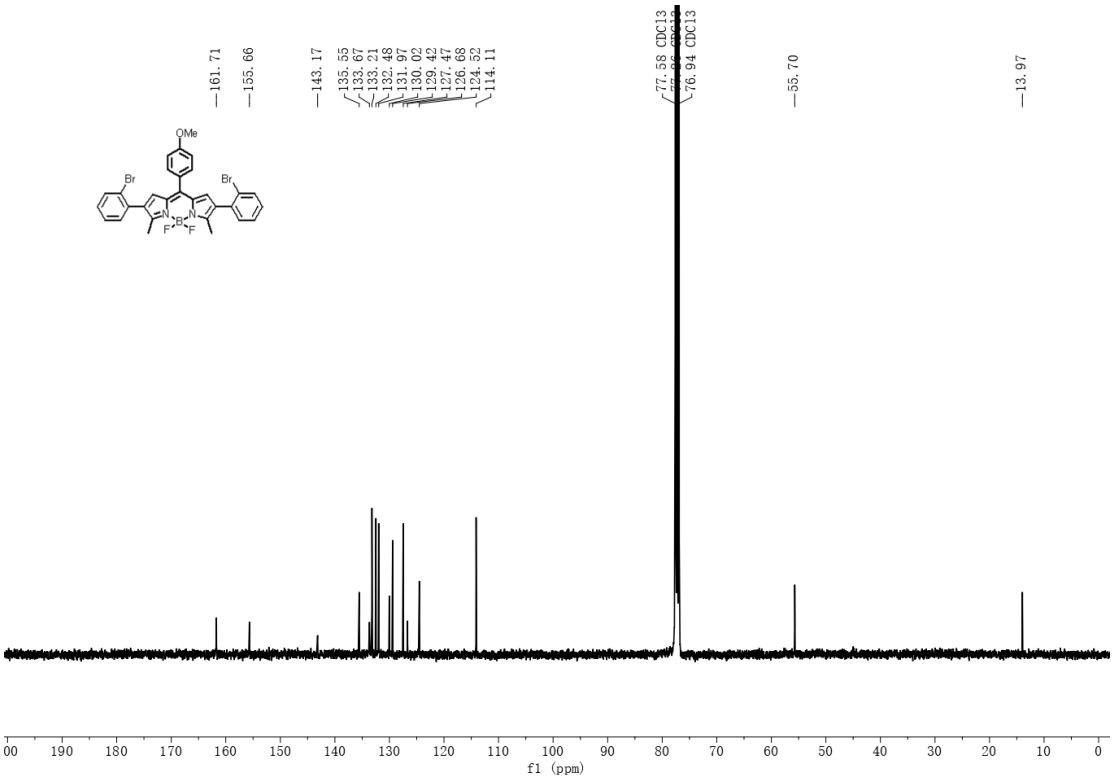
H-2b#245 RT: 1.38
T: FTMS + p ESI Full ms [250.0000-1200.0000]
m/z= 549.9321-604.9827

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
577.9337	1606000.5	100.00	577.9329	0.72	$C_{18}H_{15}ON_2BF_2I_2$

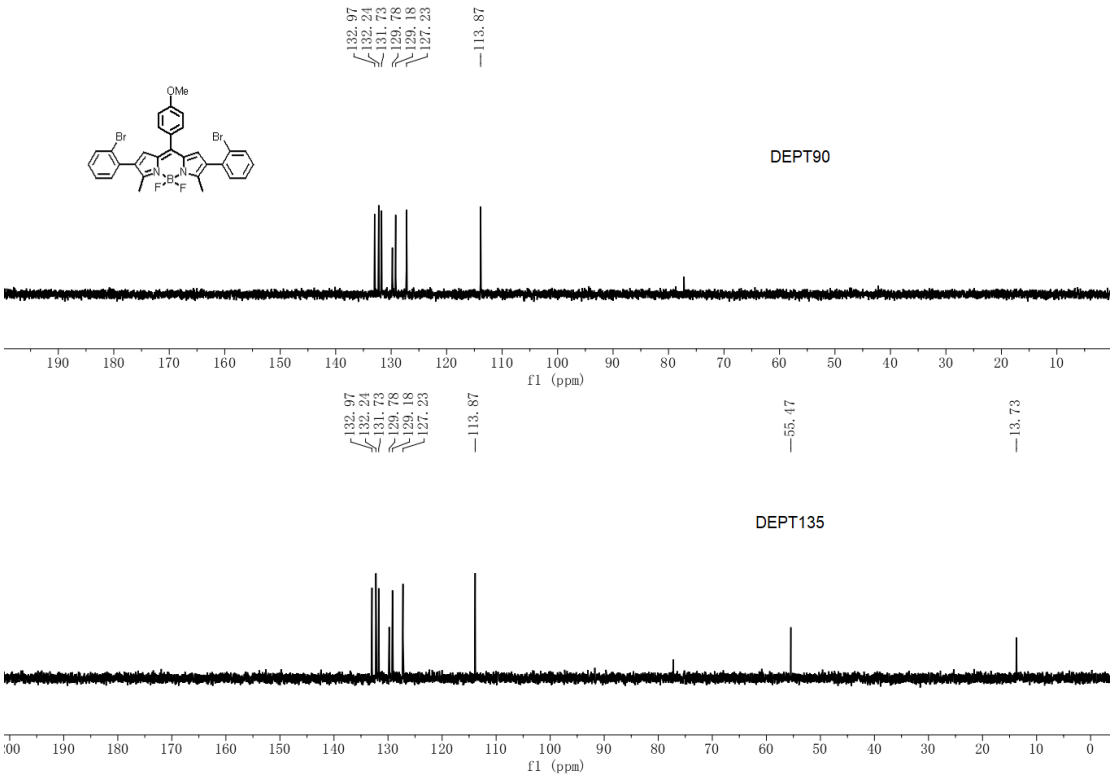
^{1}H NMR spectrum of **3b** ($CDCl_3$, 400 MHz)



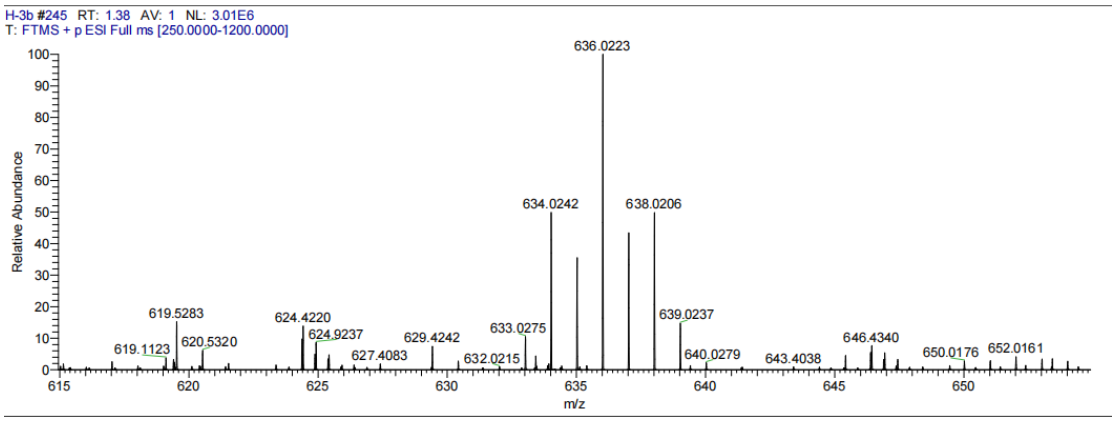
^{13}C NMR Spectrum of **3b** ($CDCl_3$, 101 MHz)



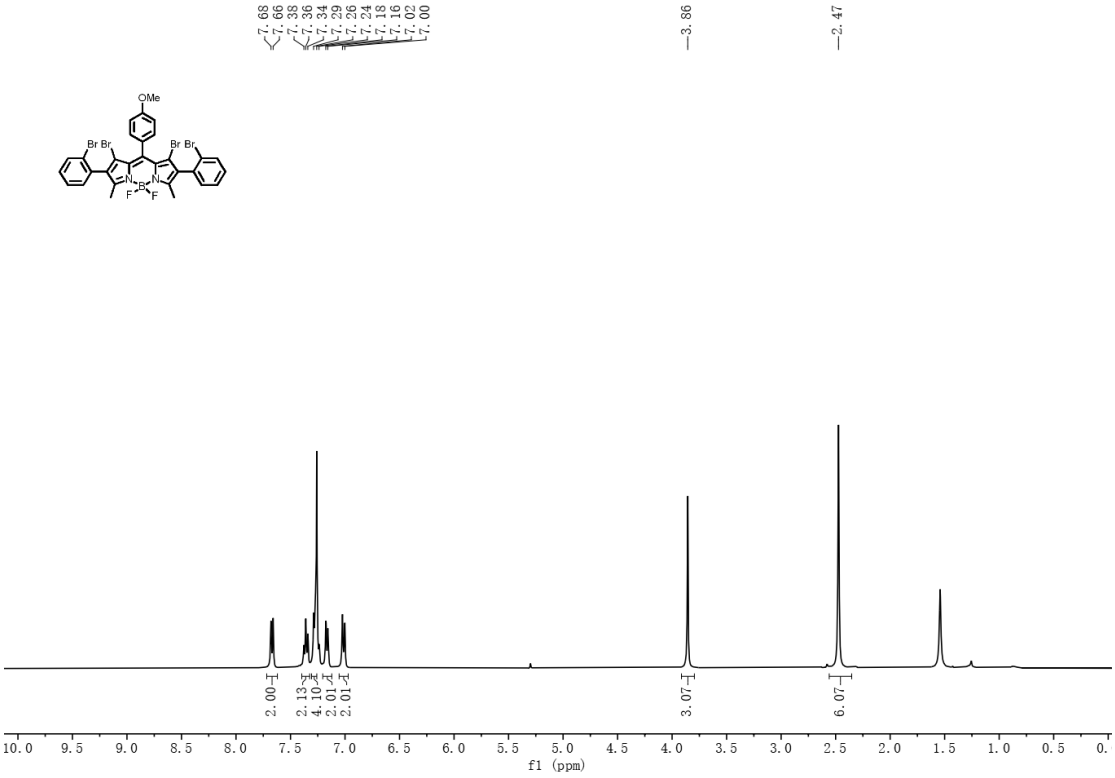
DEPT Spectrum of **3b** ($CDCl_3$, 101 MHz)



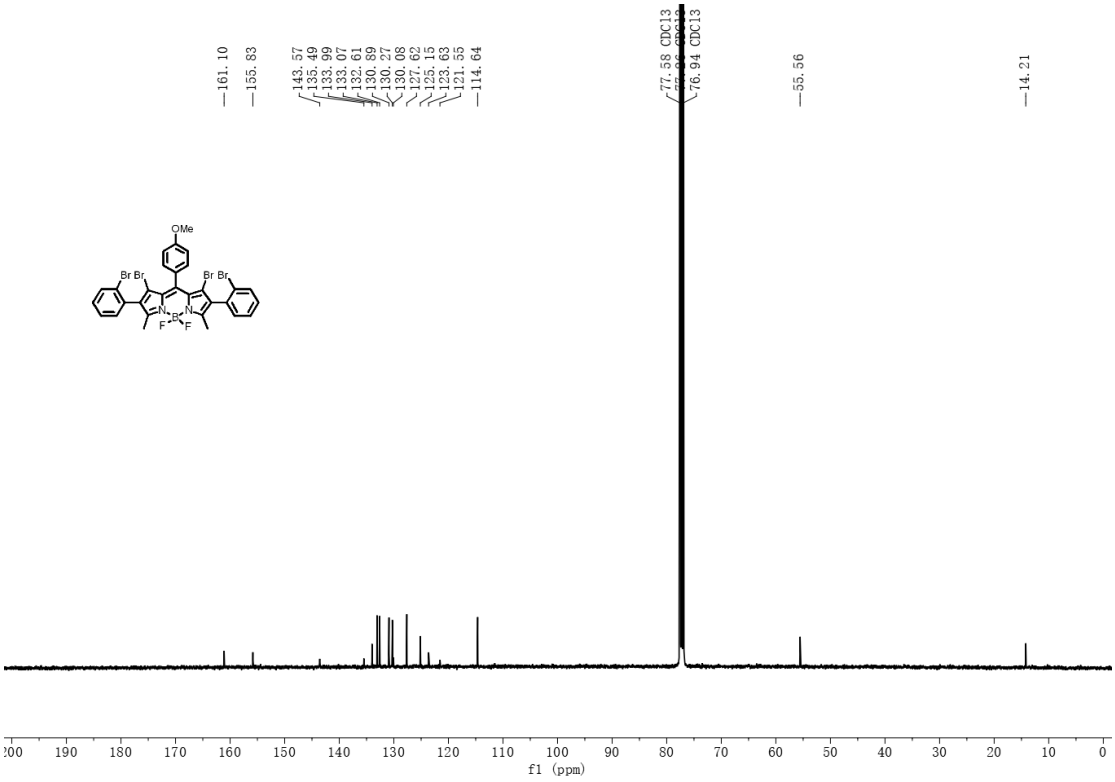
HRMS Spectrum of **3b**



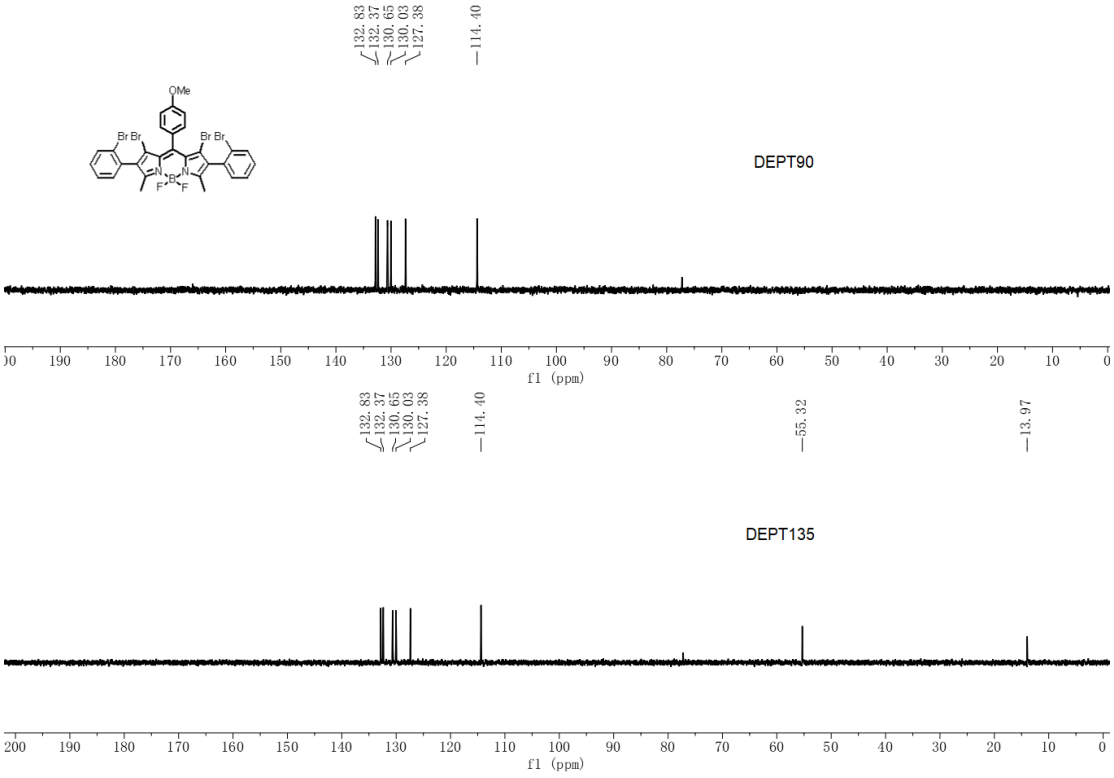
^{1}H NMR spectrum of **4b** ($CDCl_3$, 400 MHz)



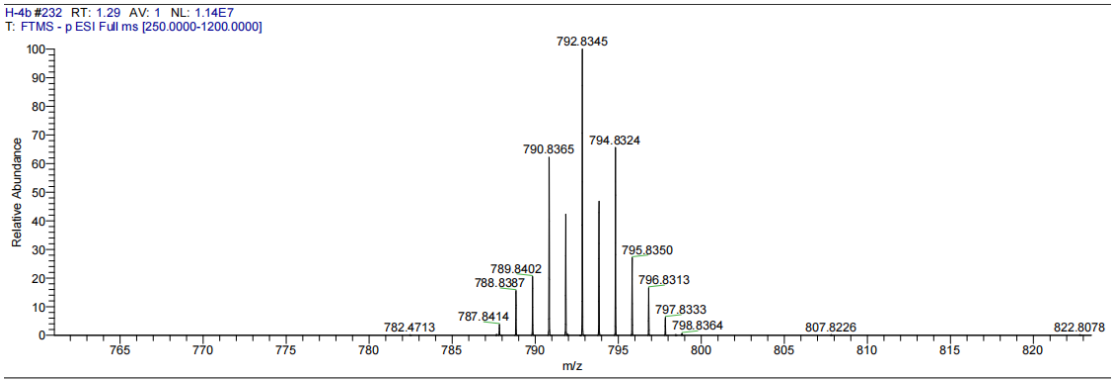
^{13}C NMR Spectrum of **4b** ($CDCl_3$, 101 MHz)



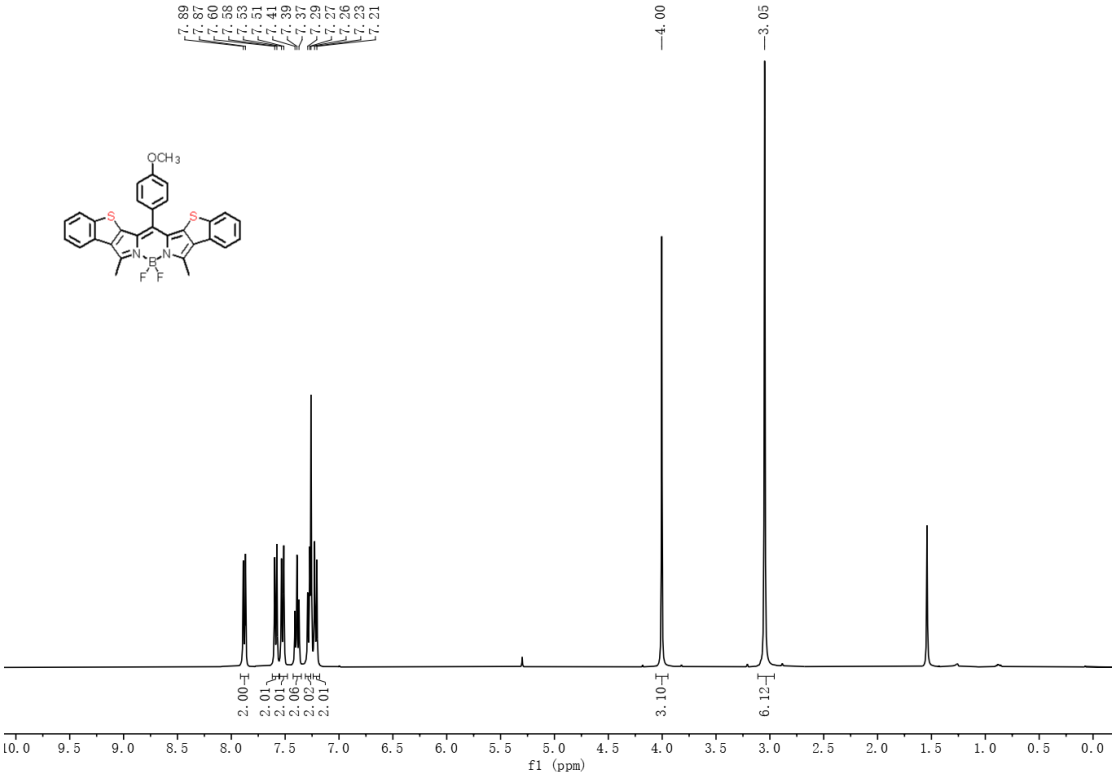
DEPT Spectrum of **4b** ($CDCl_3$, 101 MHz)



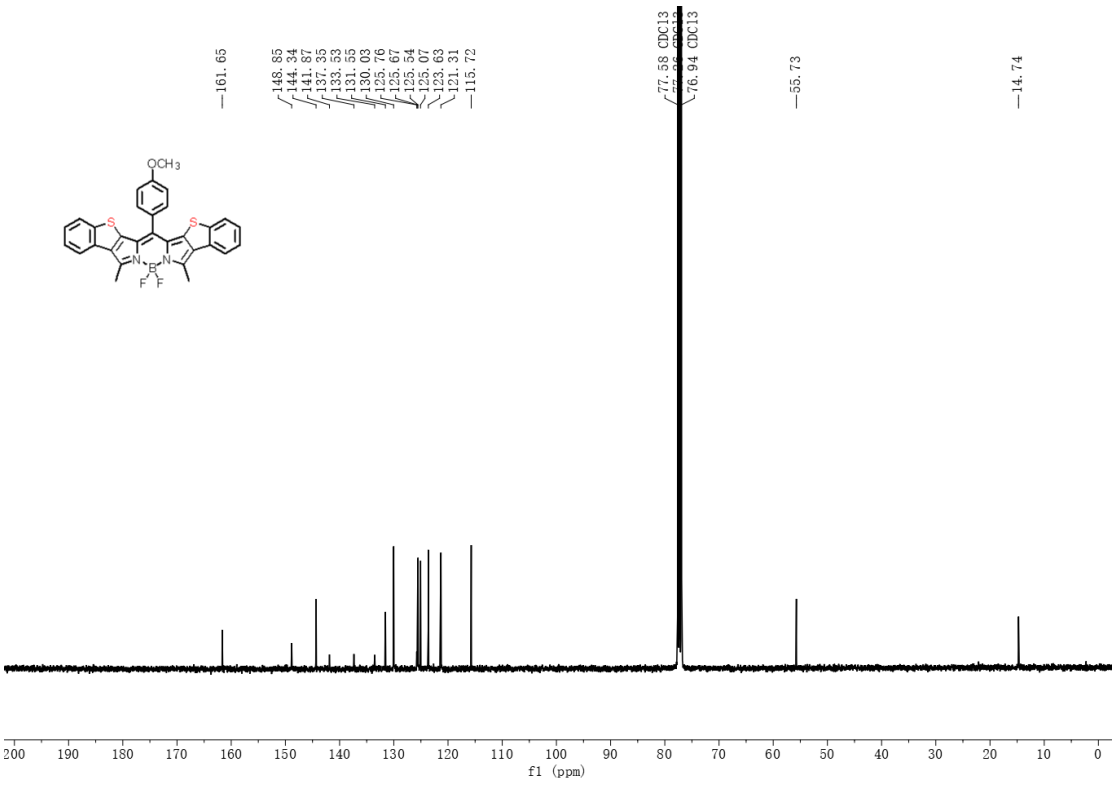
HRMS Spectrum of **4b**



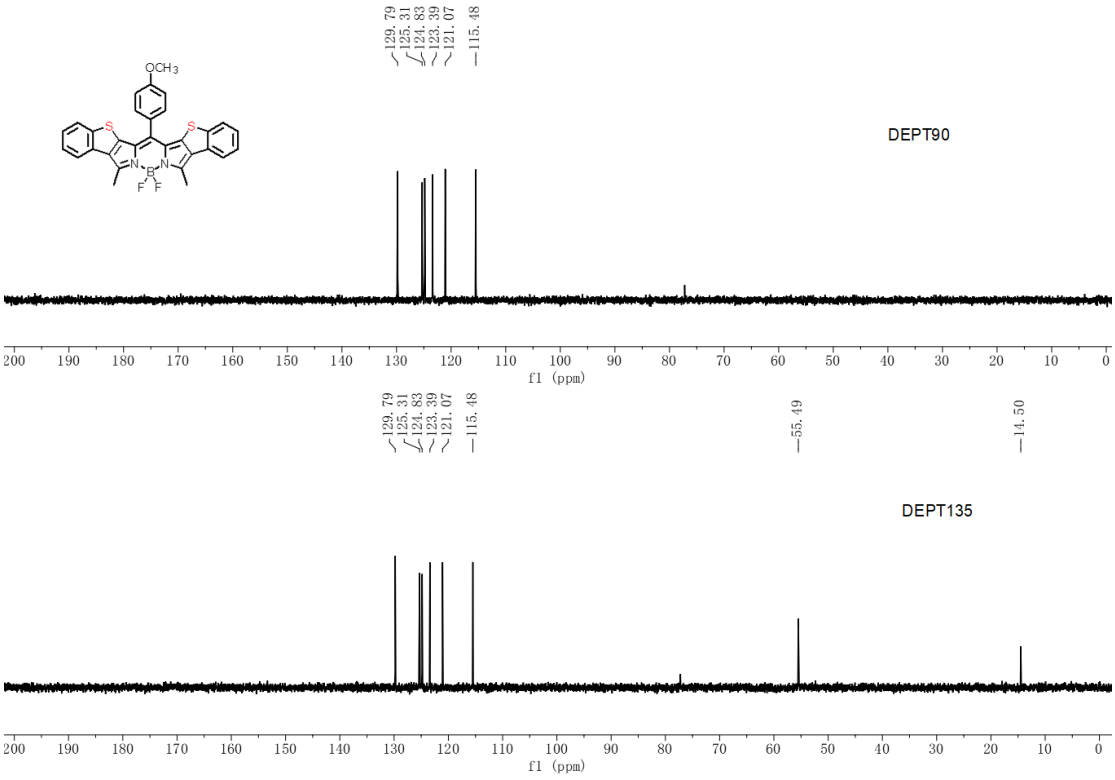
^{1}H NMR spectrum of **5b** ($CDCl_3$, 400 MHz)



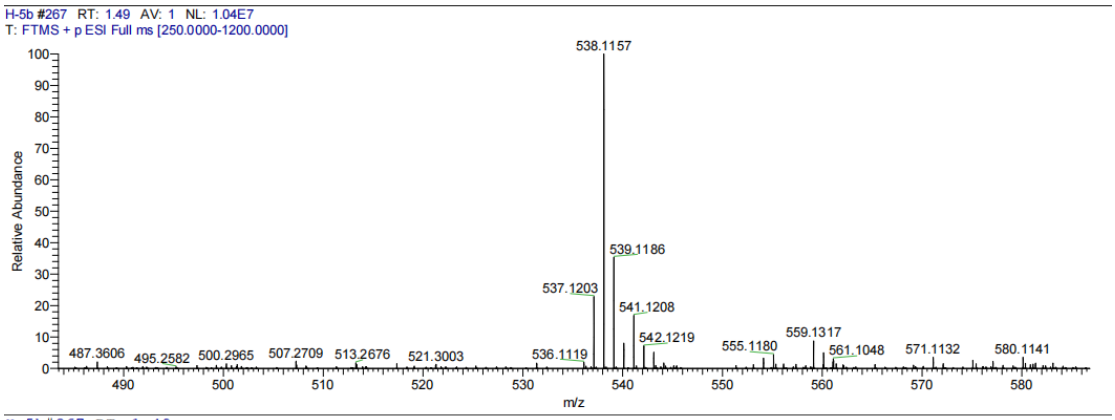
^{13}C NMR Spectrum of **5b** ($CDCl_3$, 101 MHz)



DEPT Spectrum of **5b** ($CDCl_3$, 101 MHz)



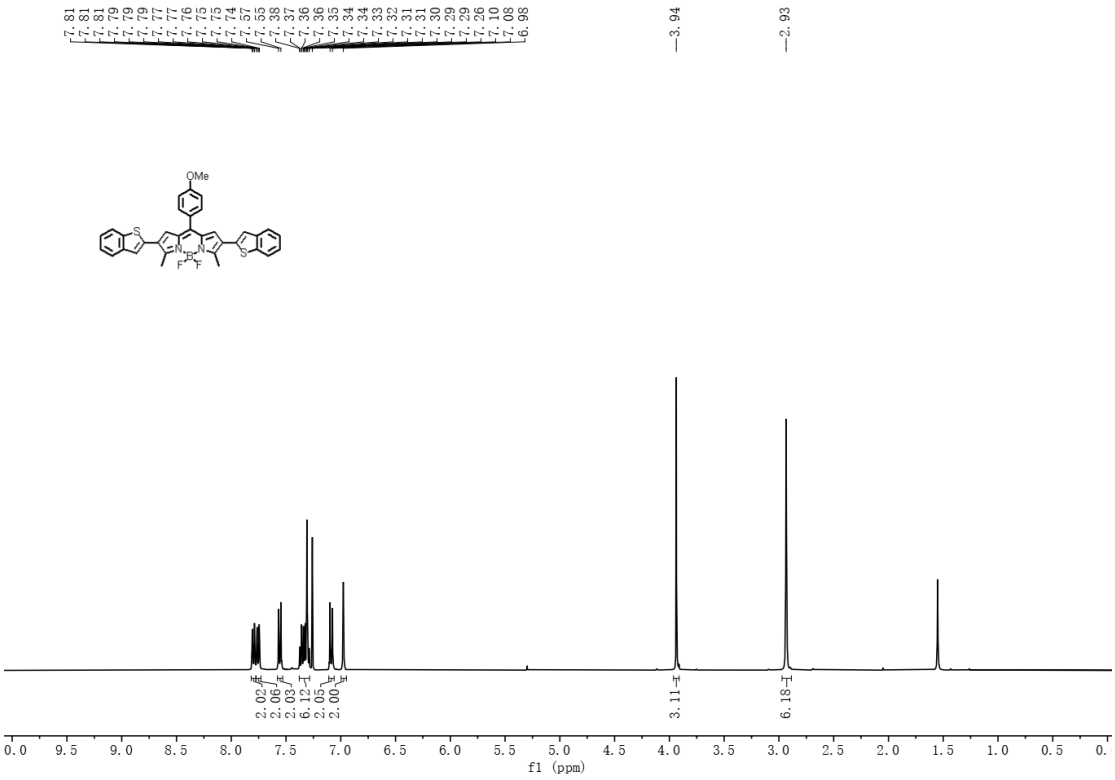
HRMS Spectrum of **5b**



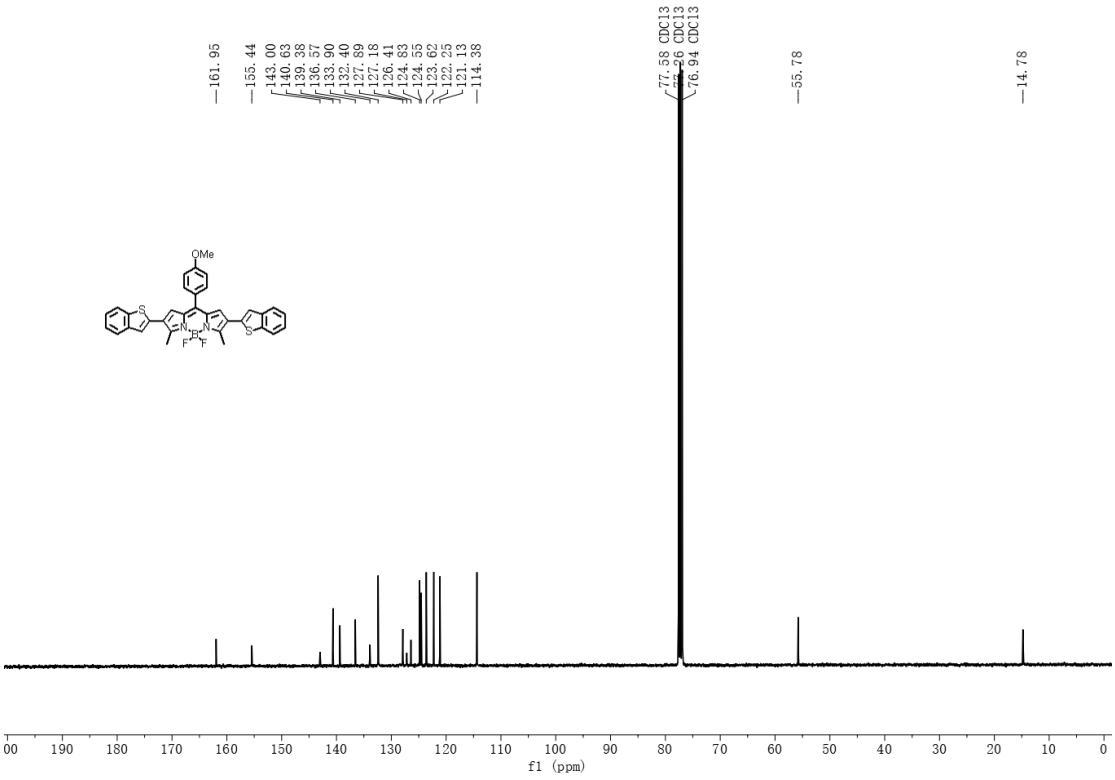
H-5b#267 RT: 1.49
T: FTMS + p ESI Full ms [250.0000-1200.0000]
m/z= 483.4535-586.7955

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
538.1157	10495452.0	100.00	538.1151	0.63	$C_{30}H_{21}ON_2BF_2S_2$

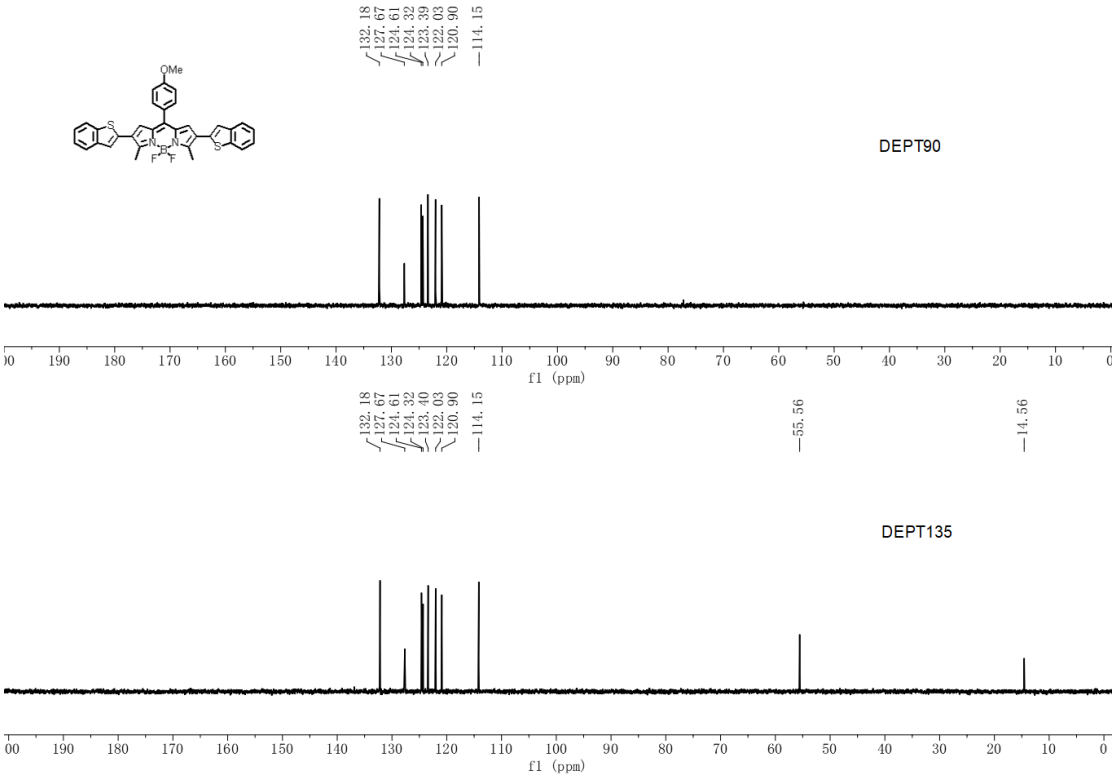
H NMR spectrum of **6b** ($CDCl_3$, 400 MHz)



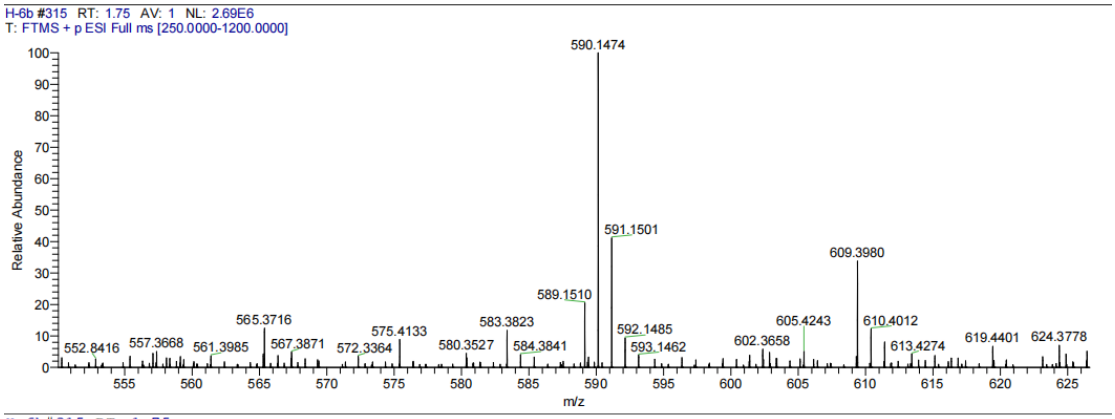
^{13}C NMR Spectrum of **6b** ($CDCl_3$, 101 MHz)



DEPT Spectrum of **6b** ($CDCl_3$, 101 MHz)



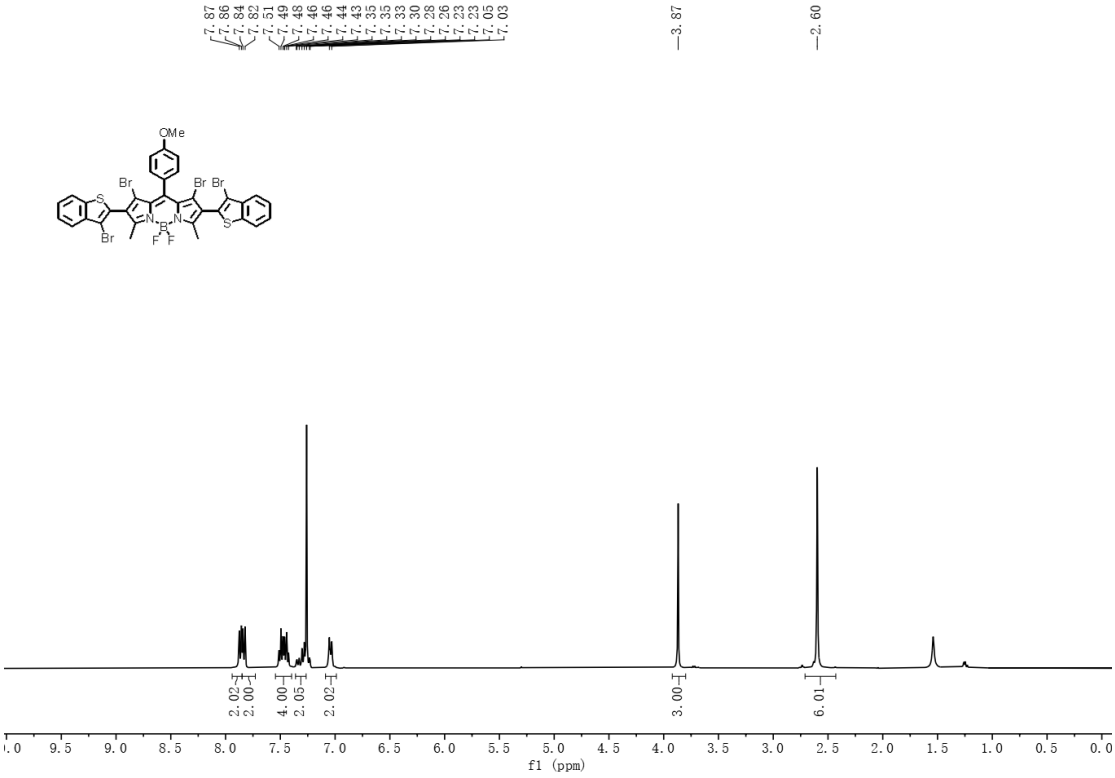
HRMS Spectrum of **6b**



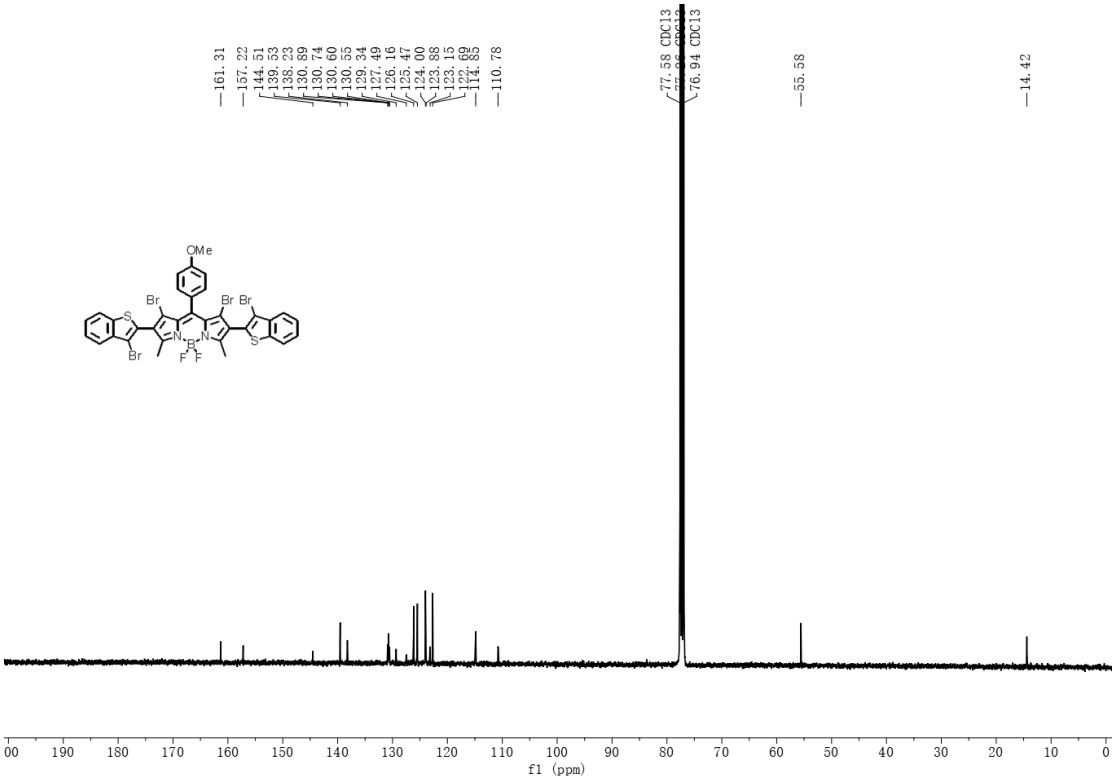
H-6b#315 RT: 1.75
T: FTMS + p ESI Full ms [250.0000-1200.0000]
m/z= 550.0655-626.6383

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
590.1474	2745336.0	100.00	590.1464	1.01	$C_{34}H_{25}ON_2BF_2S_2$

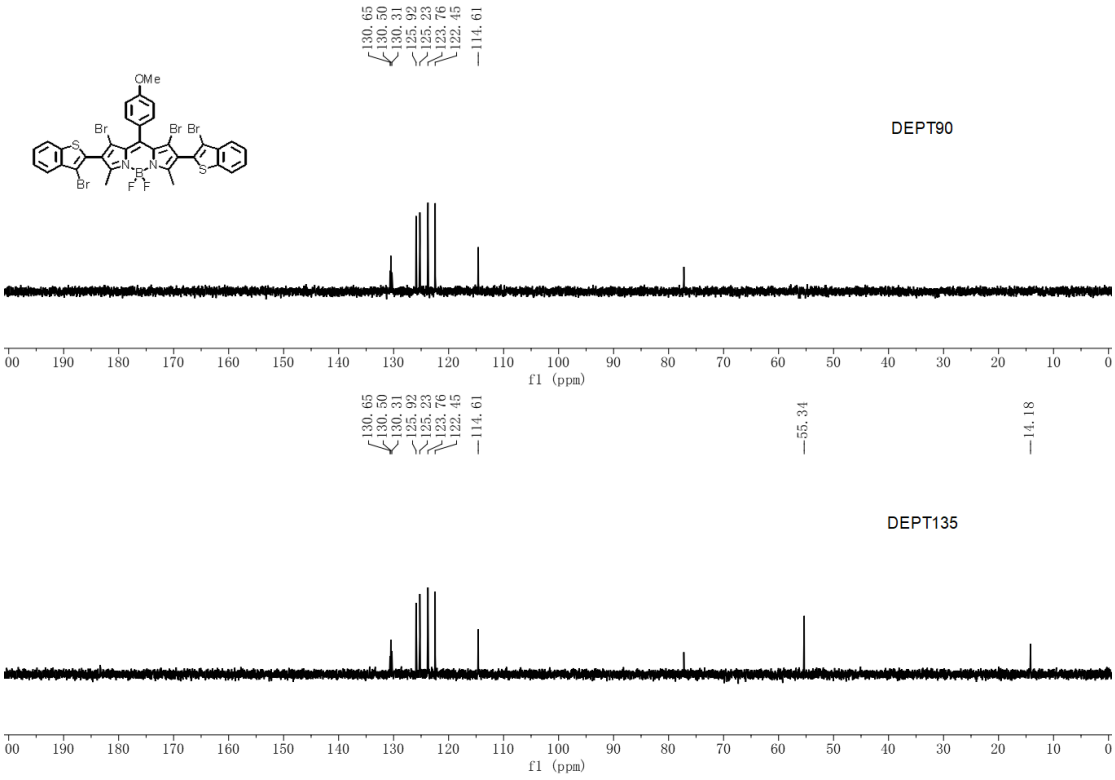
^{1}H NMR spectrum of **7b** ($CDCl_3$, 400 MHz)



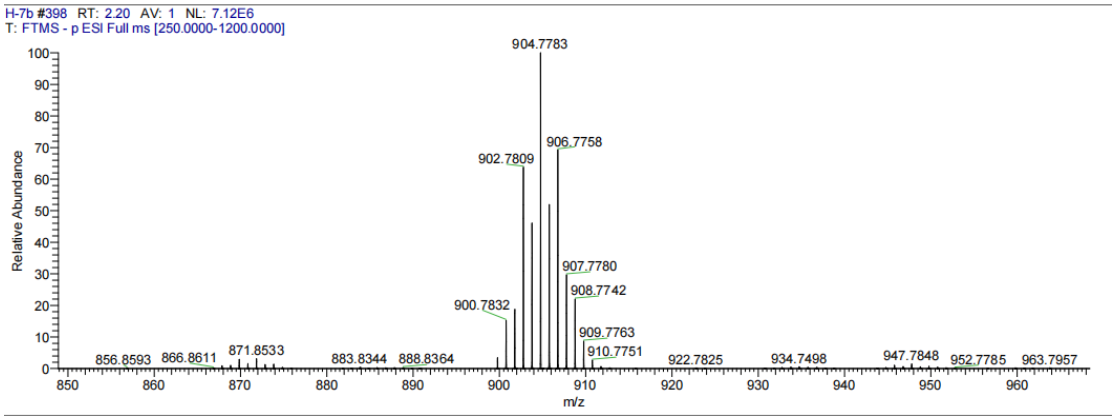
^{13}C NMR Spectrum of **7b** ($CDCl_3$, 101 MHz)



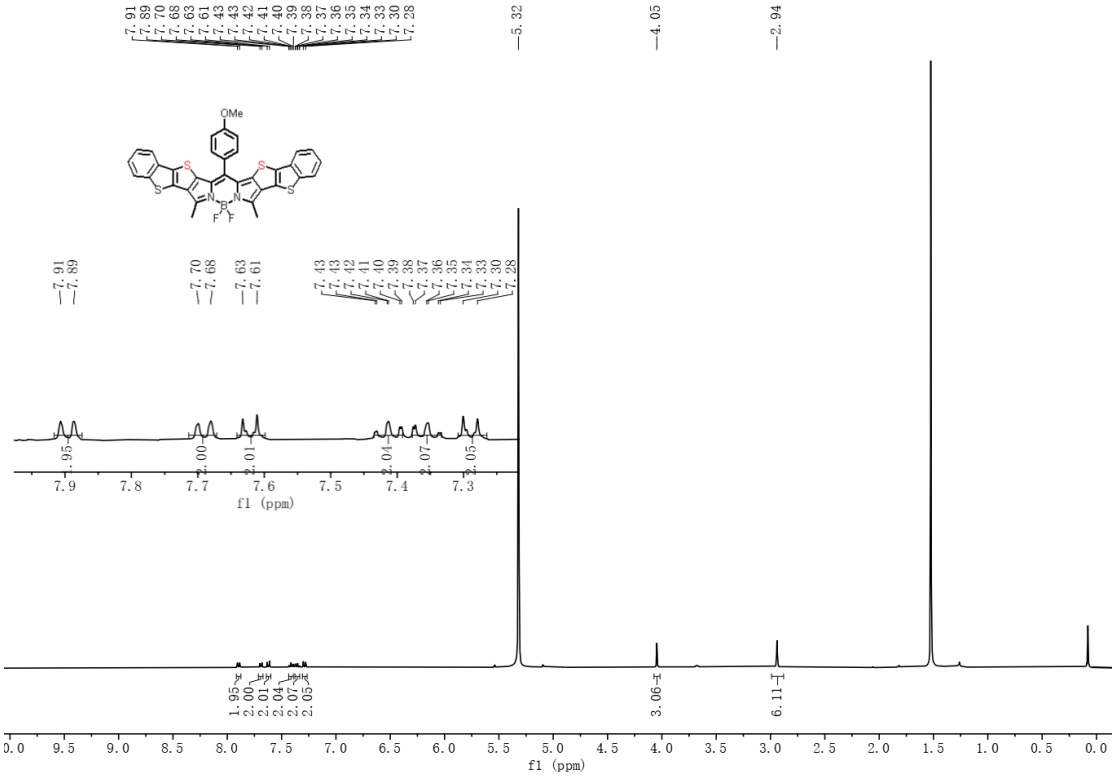
DEPT Spectrum of **7b** ($CDCl_3$, 101 MHz)



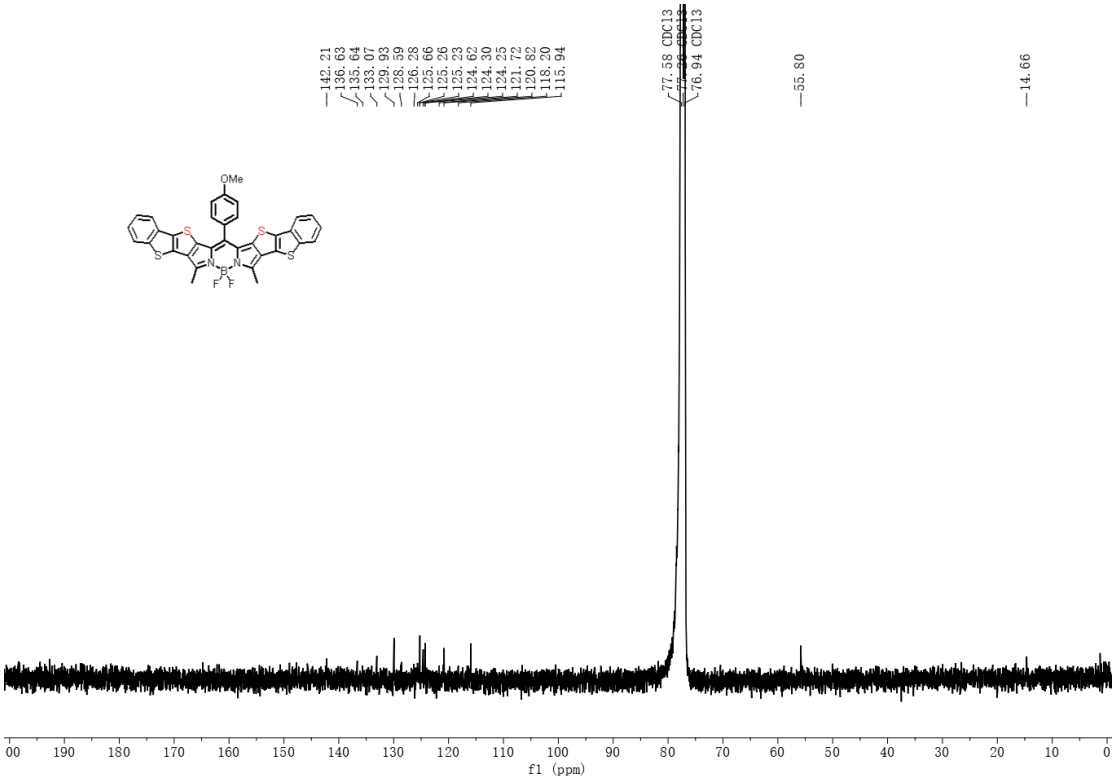
HRMS Spectrum of **7b**



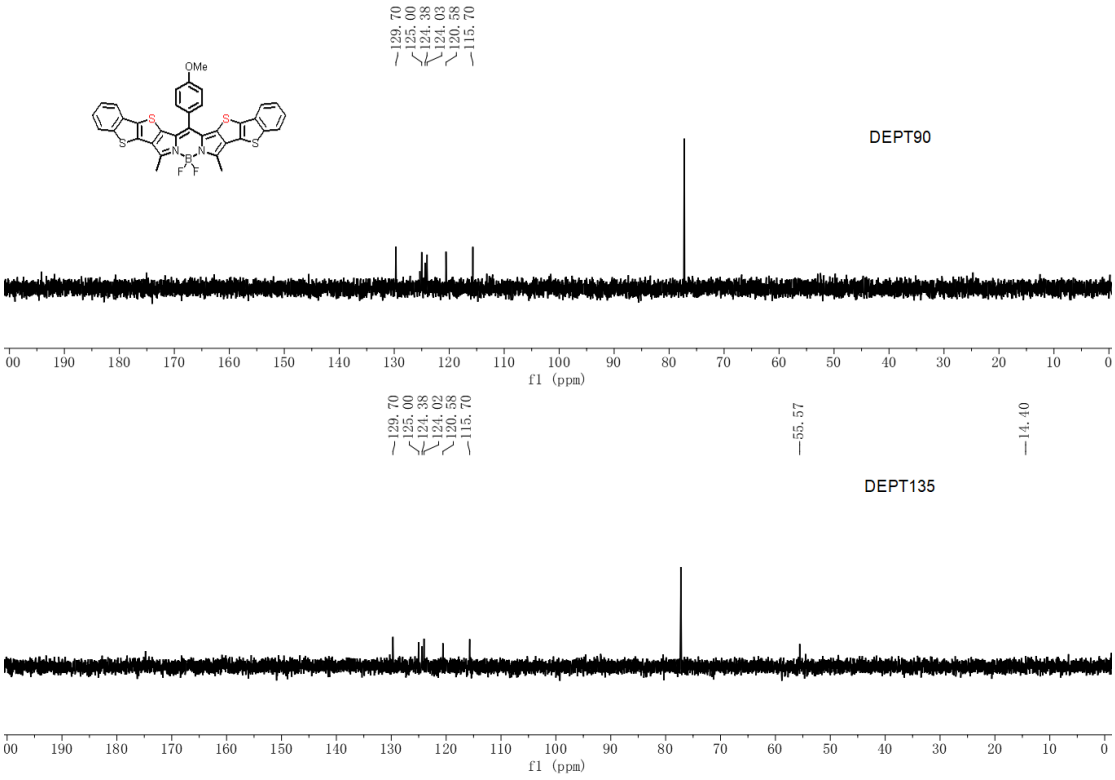
^{11}H NMR spectrum of **8b** (CD_2Cl_2, 400 MHz)



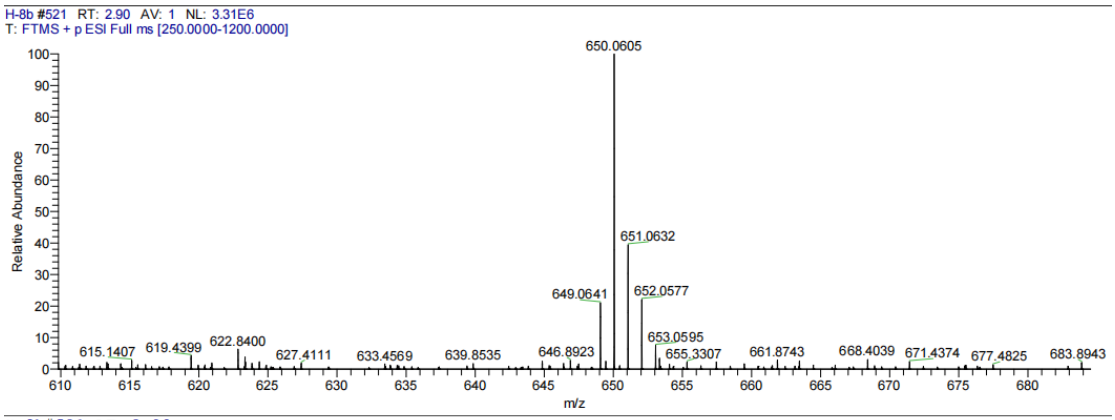
^{13}C NMR Spectrum of **8b** ($CDCl_3$, 101 MHz)



DEPT Spectrum of **8b** ($CDCl_3$, 101 MHz)



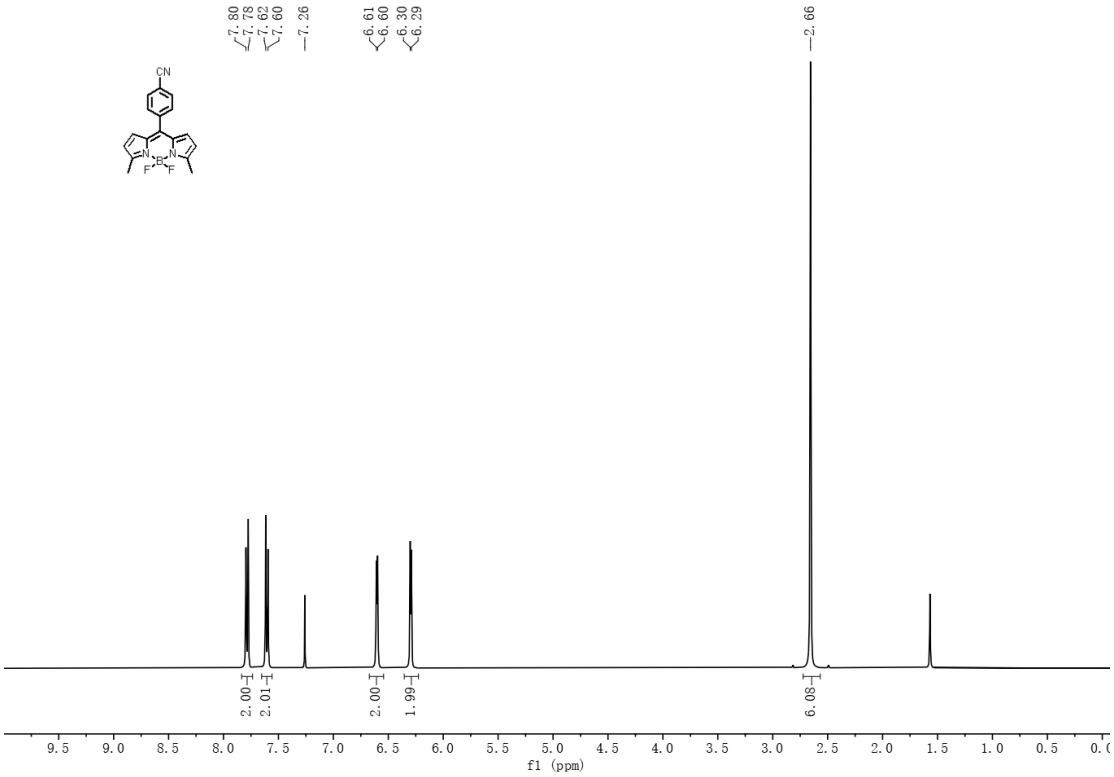
HRMS Spectrum of **8b**



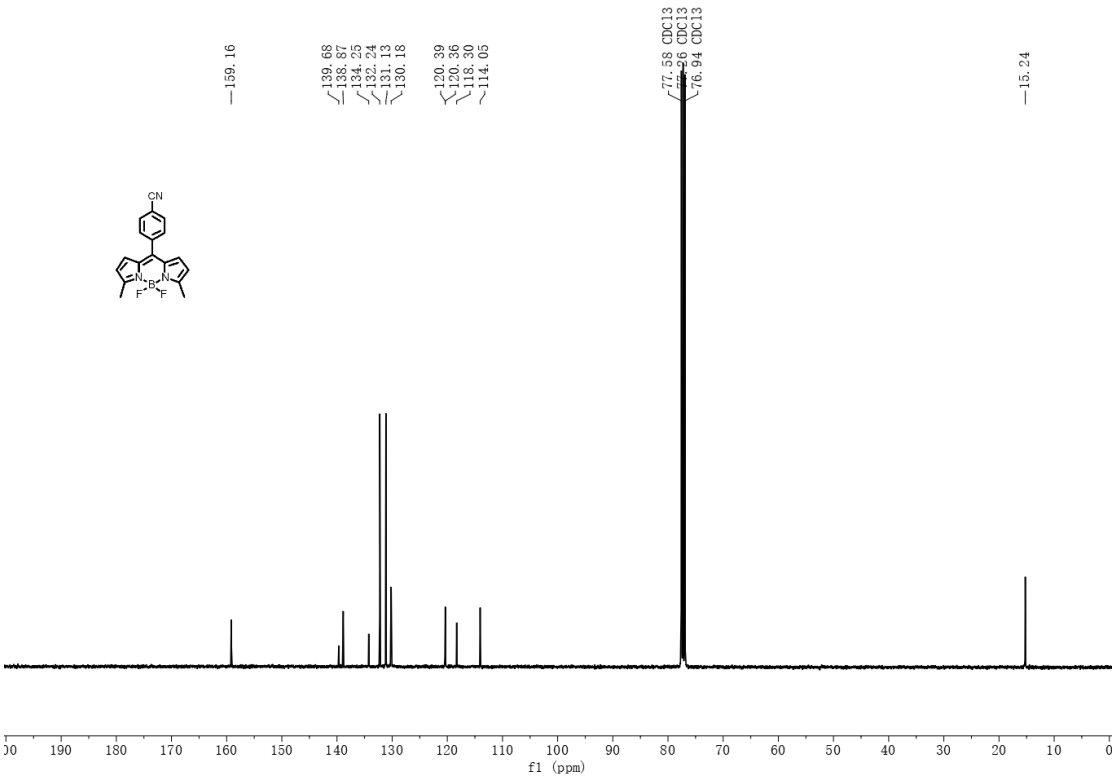
H-8b#521 RT: 2.90
T: FTMS + p ESI Full ms [250.0000-1200.0000]
m/z= 609.8296-684.5347

m/z	Intensity	Relative	Theo. Mass	Delta (mmu)	Composition
650.0605	3376788.8	100.00	650.0592	1.31	$C_{34}H_{21}ON_2BF_2S_4$

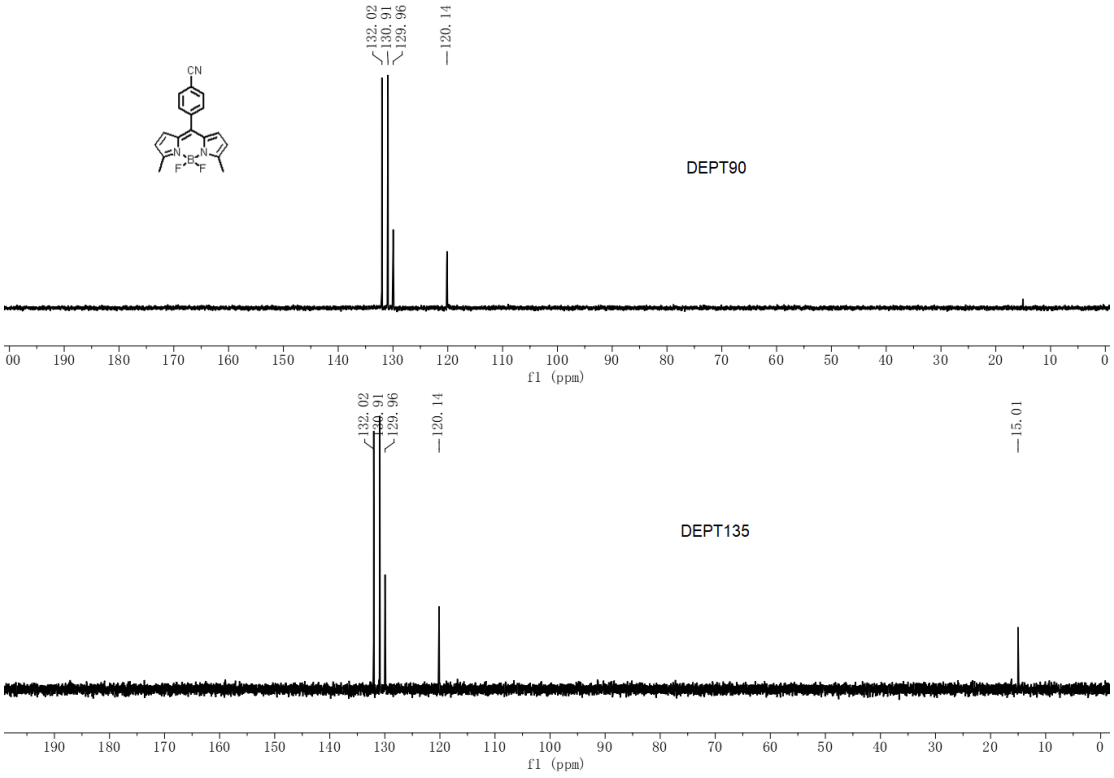
^{1}H NMR spectrum of **1c** ($CDCl_3$, 400 MHz)



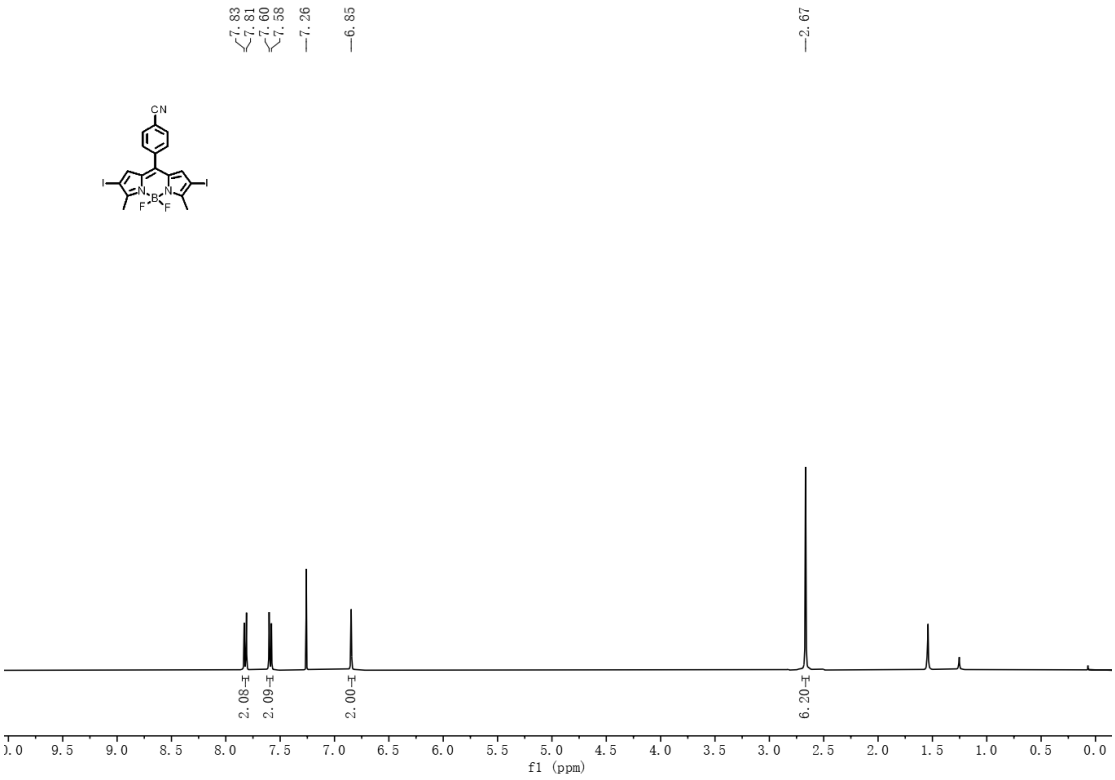
^{13}C NMR Spectrum of **1c** ($CDCl_3$, 101 MHz)



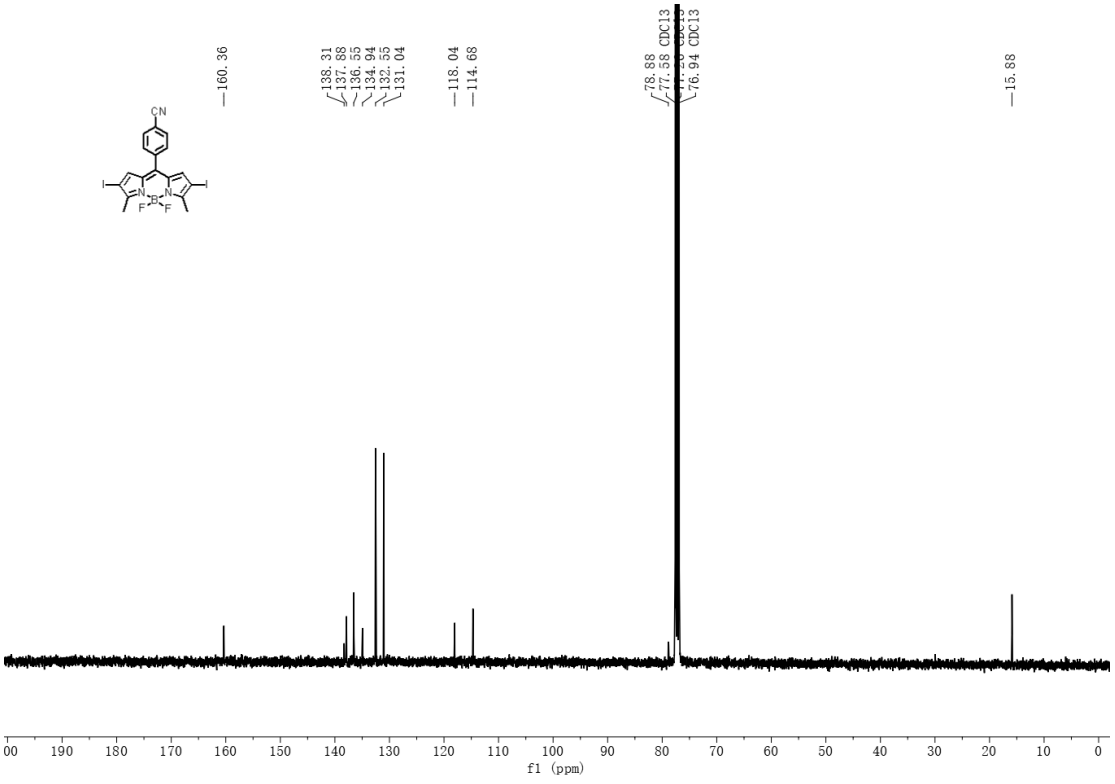
DEPT Spectrum of **1c** ($CDCl_3$, 101 MHz)



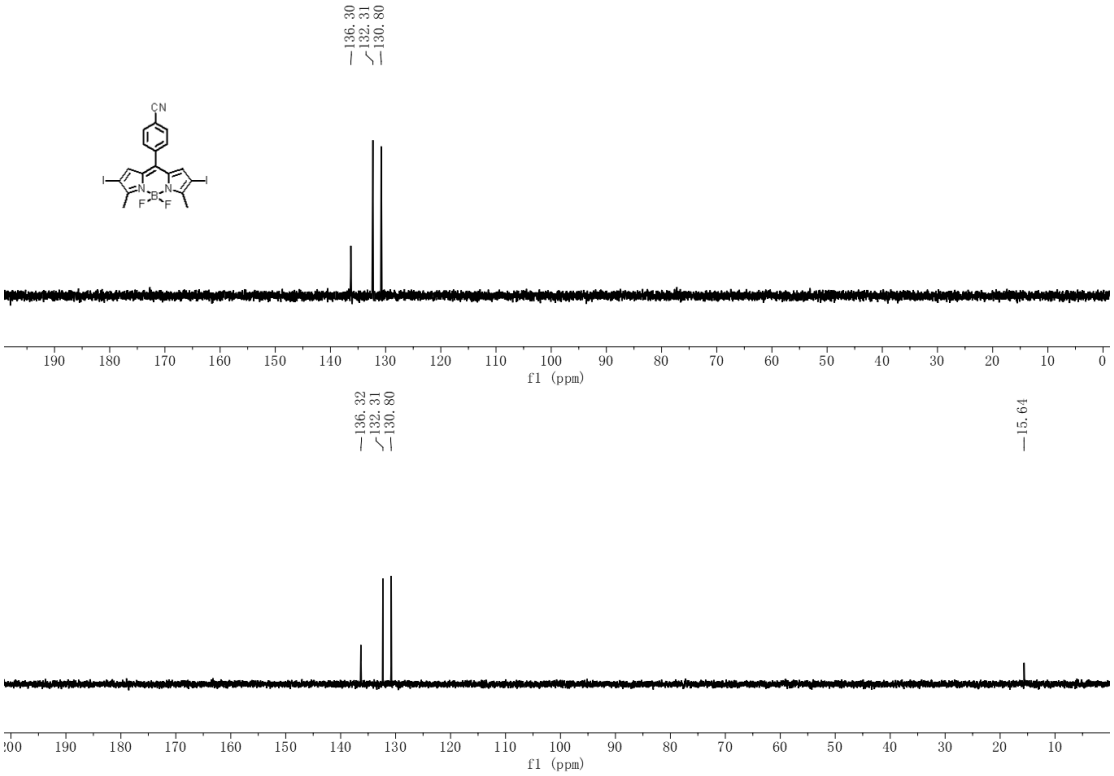
^{1}H NMR spectrum of **2c** ($CDCl_3$, 400 MHz)



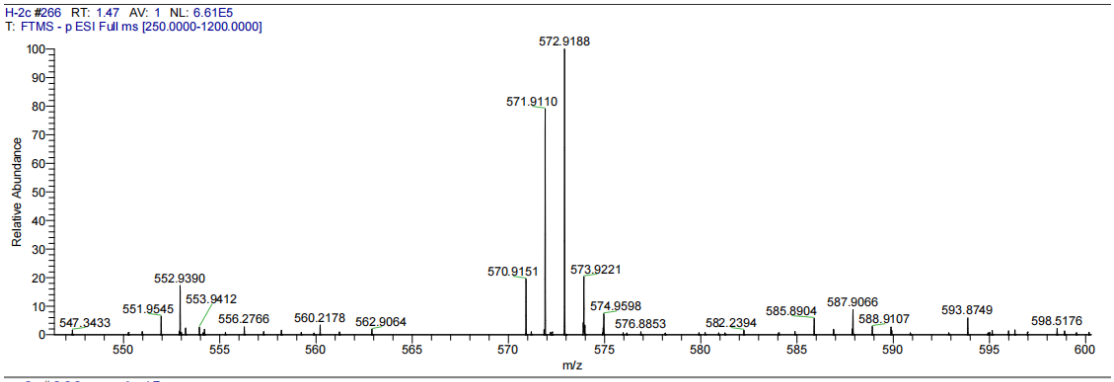
^{13}C NMR Spectrum of **2c** ($CDCl_3$, 101 MHz)



DEPT Spectrum of **2c** ($CDCl_3$, 101 MHz)



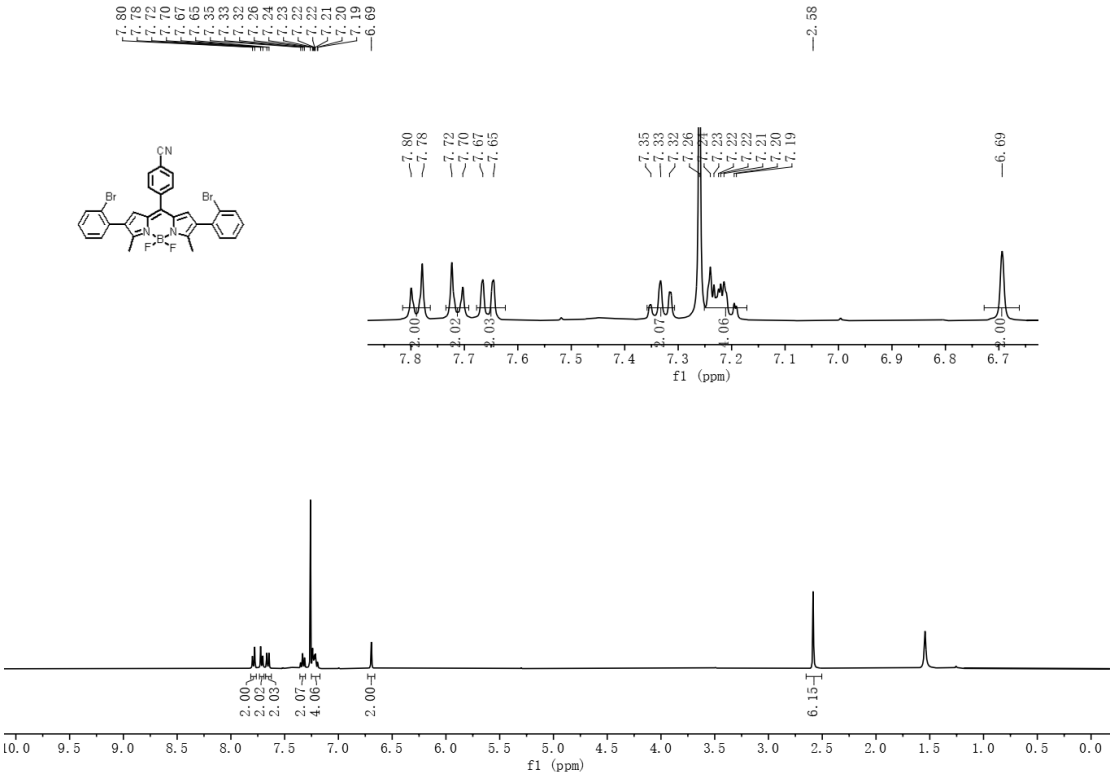
HRMS Spectrum of **2c**



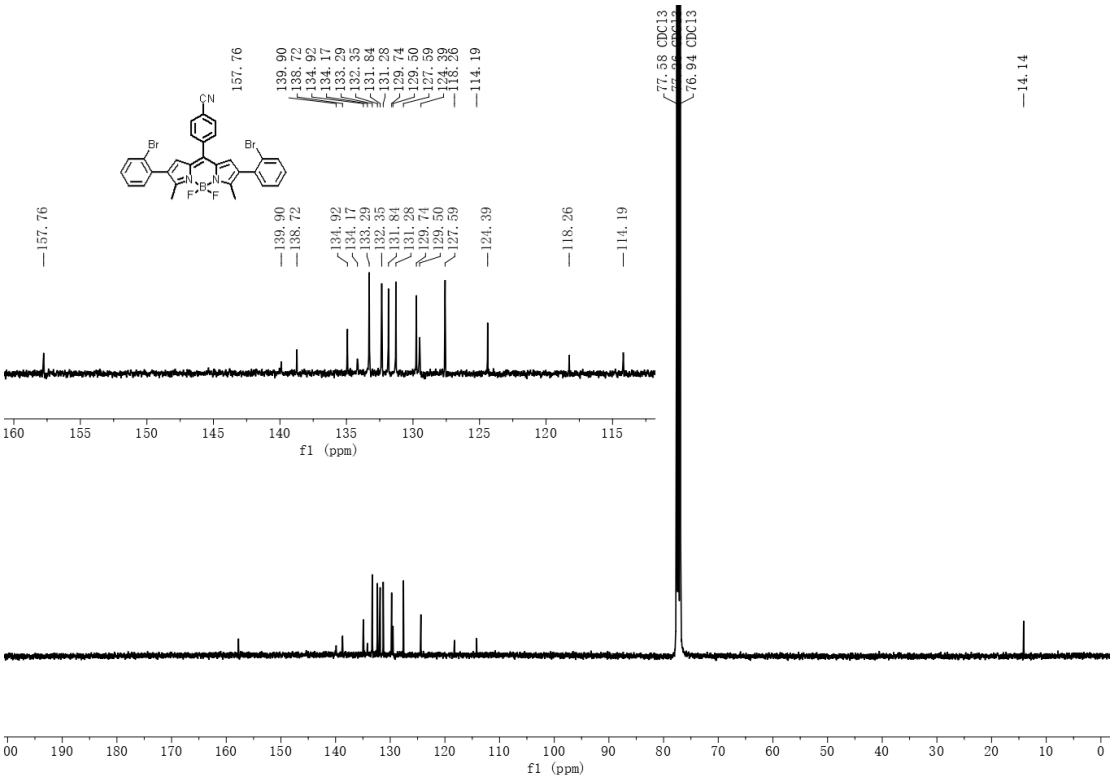
H-2c#266 RT: 1.47
T: FTMS - p ESI Full ms [250.0000-1200.0000]
m/z= 546.4000-600.2909

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
572.9188	702684.6	100.00	572.9176	1.14	$C_{18}H_{12}N_3BF_2I_2$

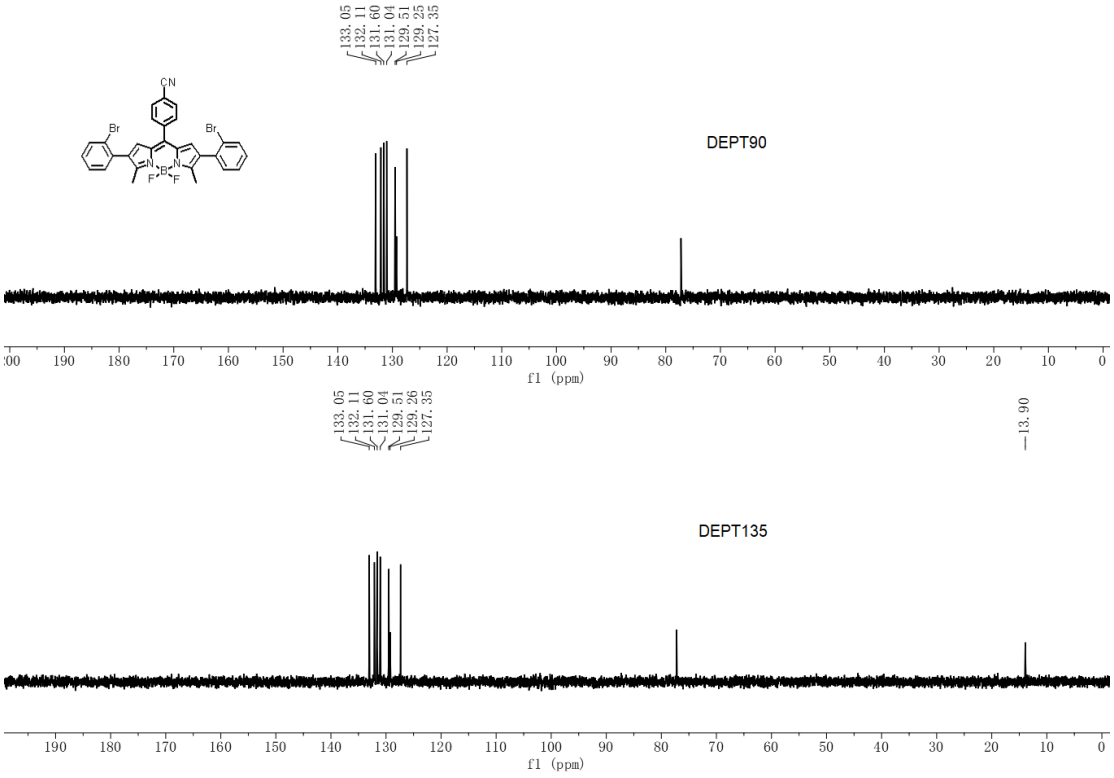
^{1}H NMR spectrum of **3c** ($CDCl_3$, 400 MHz)



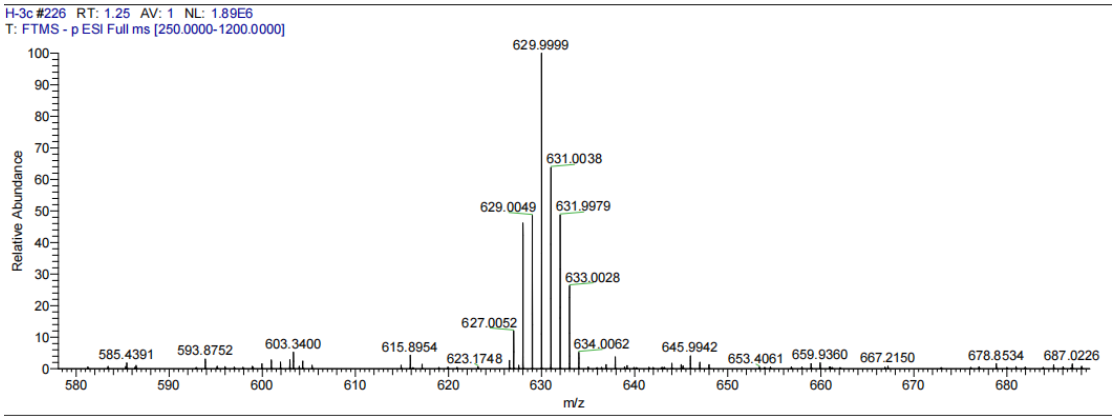
^{13}C NMR Spectrum of **3c** ($CDCl_3$, 101 MHz)



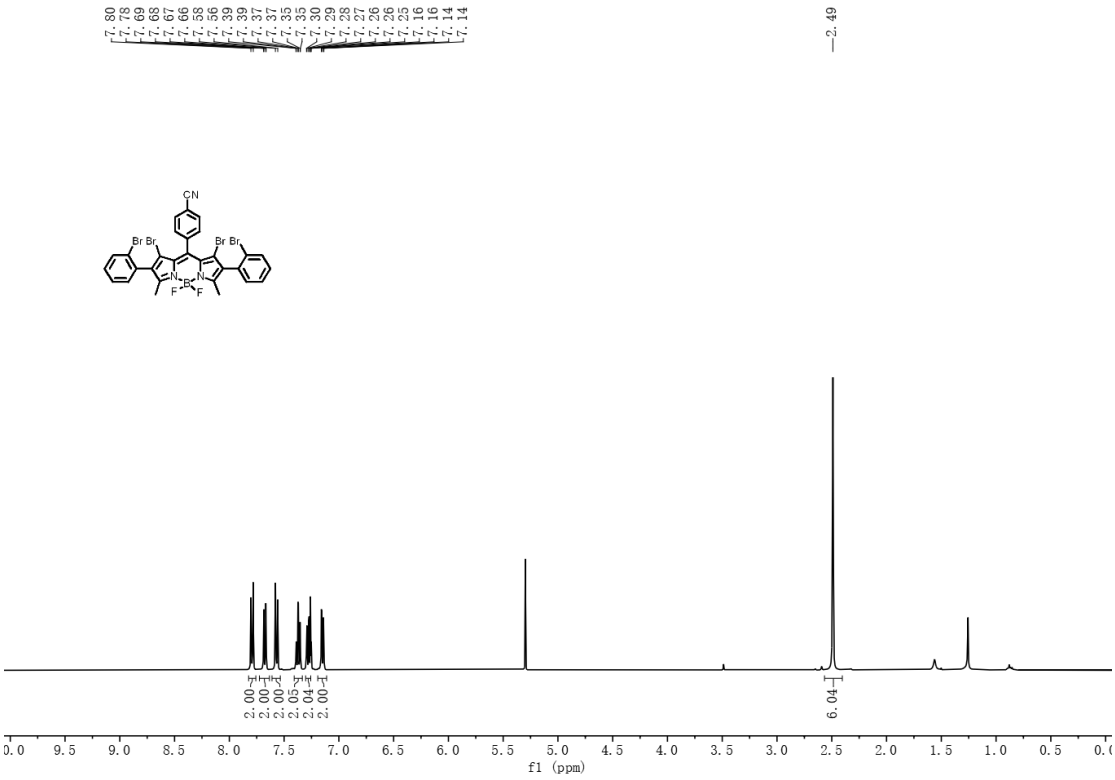
DEPT Spectrum of **3c** ($CDCl_3$, 101 MHz)



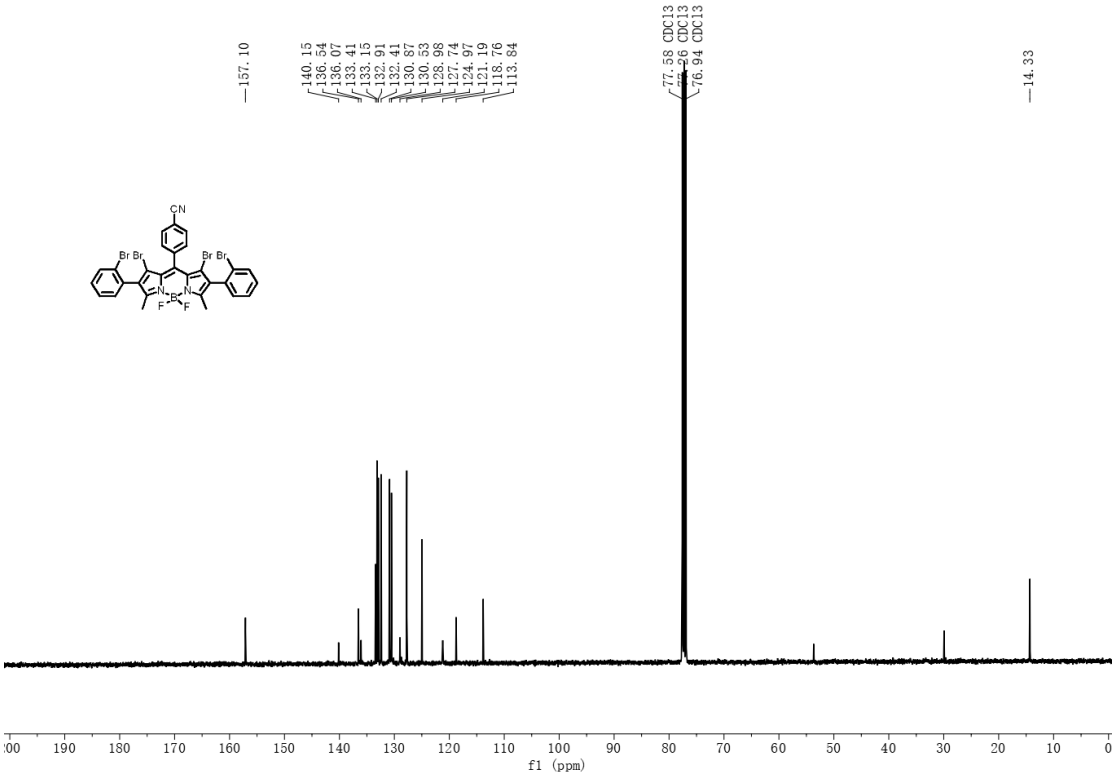
HRMS Spectrum of **3c**



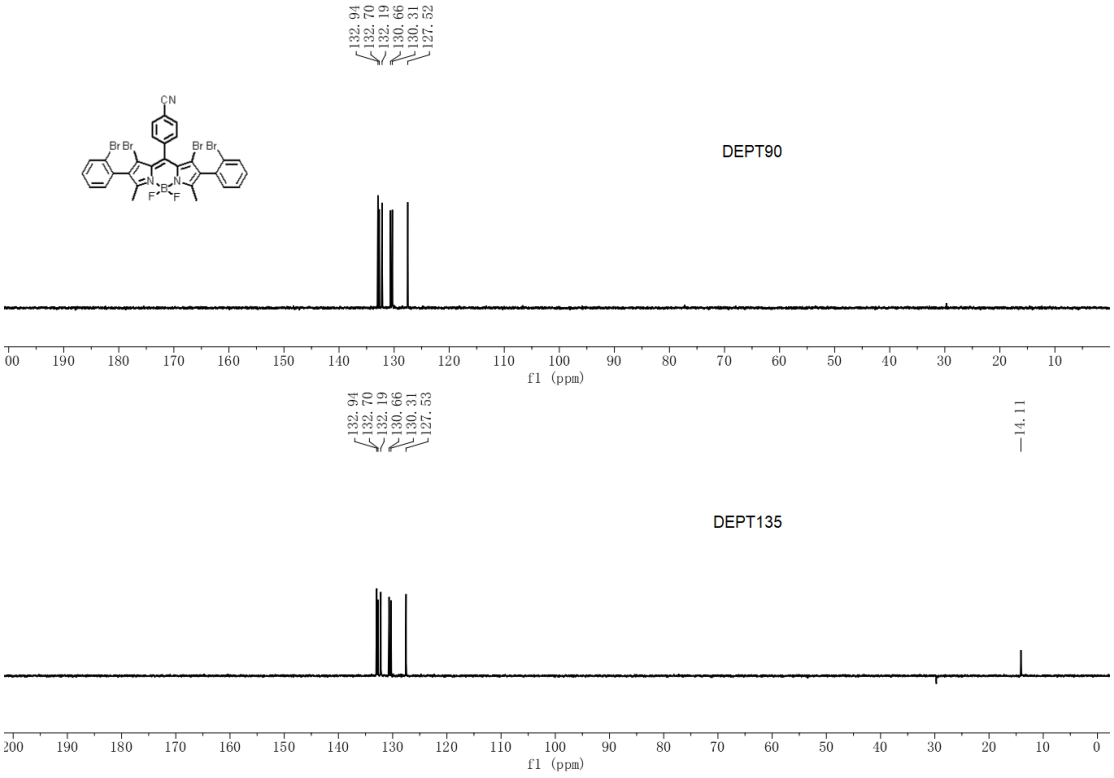
^{1}H NMR spectrum of **4c** ($CDCl_3$, 400 MHz)



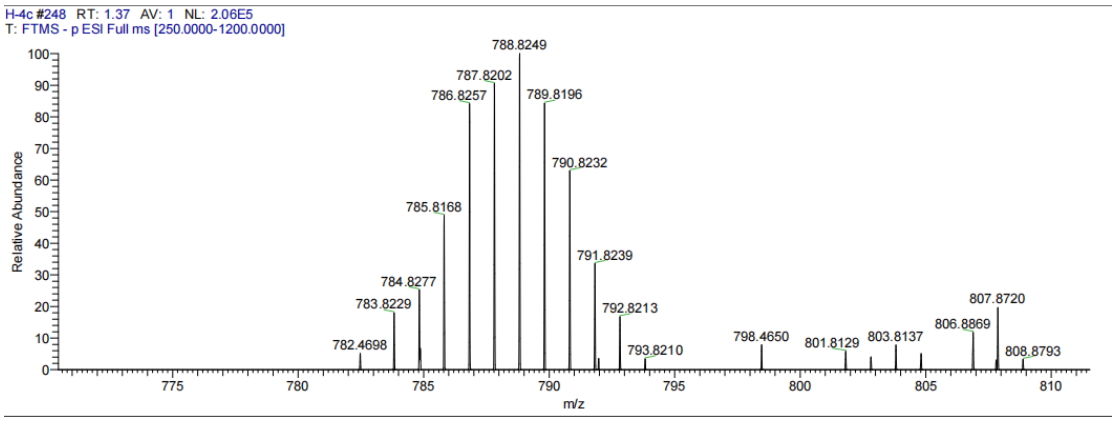
^{13}C NMR Spectrum of **4c** ($CDCl_3$, 101 MHz)



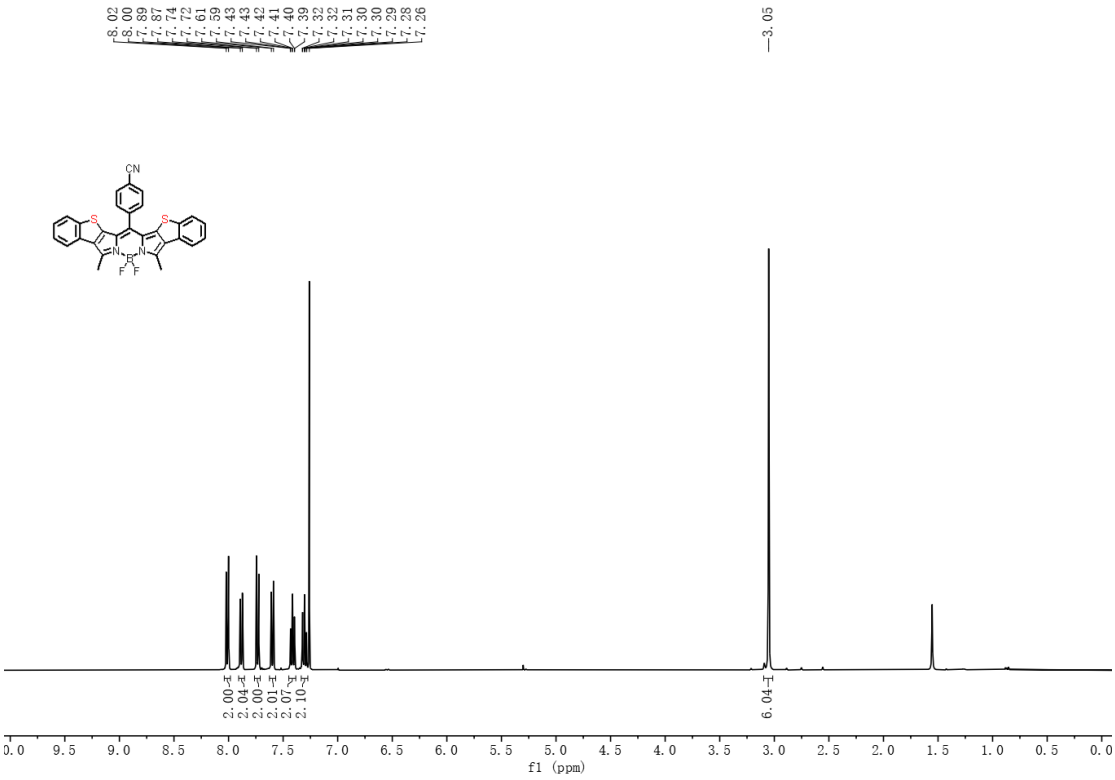
DEPT Spectrum of **4c** ($CDCl_3$, 101 MHz)



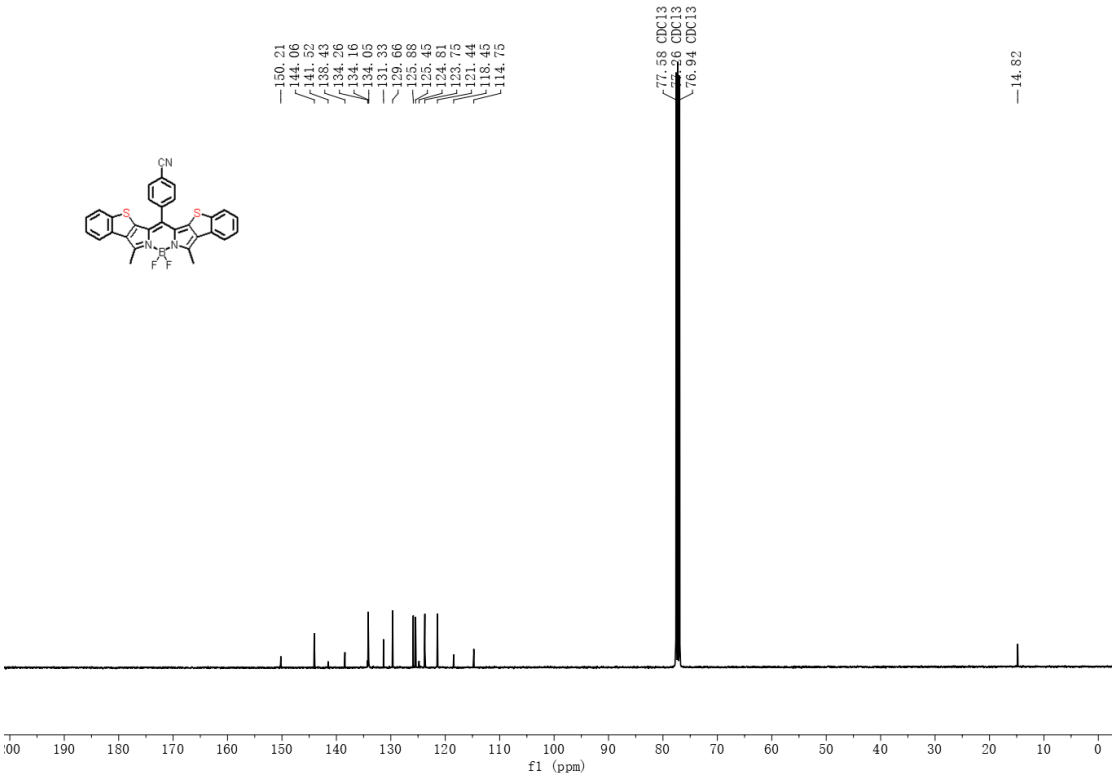
HRMS Spectrum of **4c**



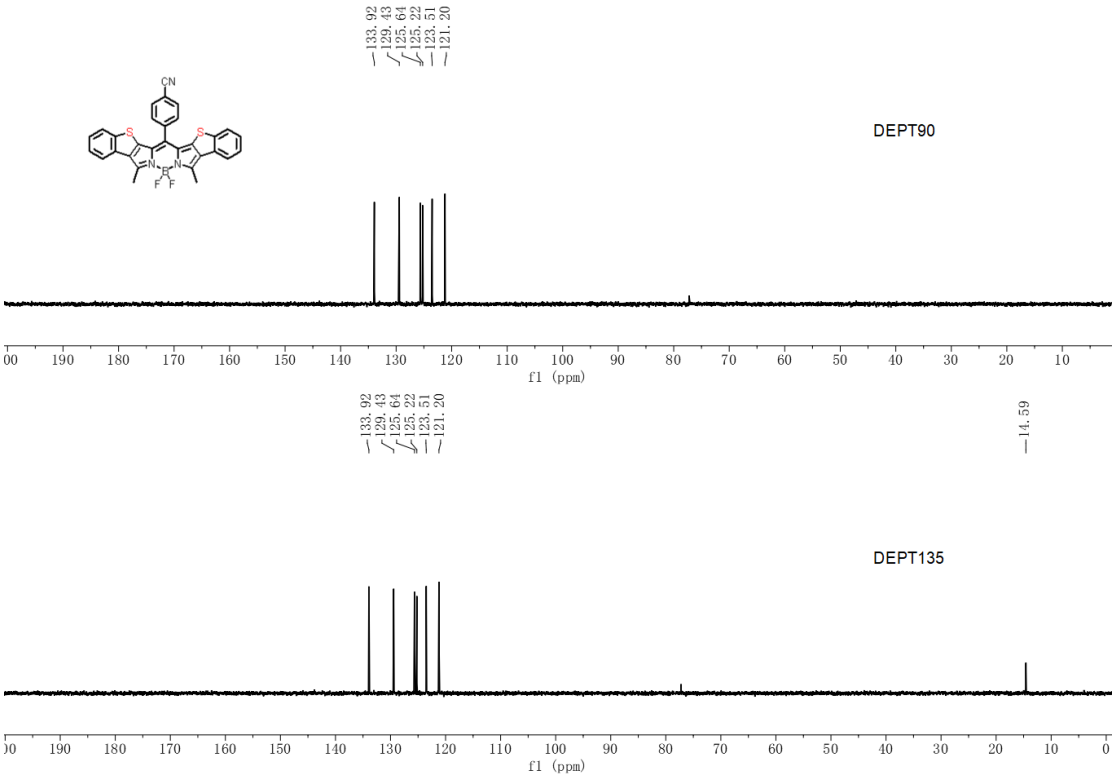
^{1}H NMR spectrum of **5c** ($CDCl_3$, 400 MHz)



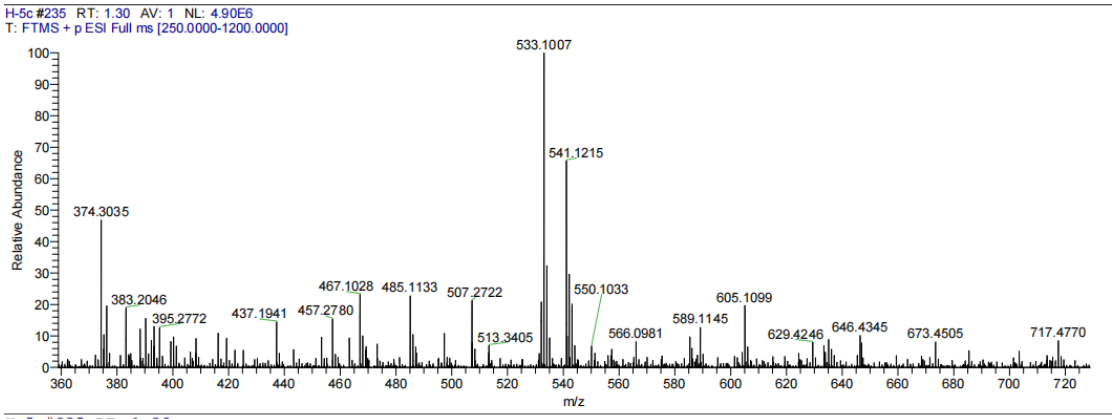
^{13}C NMR Spectrum of **5c** ($CDCl_3$, 101 MHz)



DEPT Spectrum of **5c** ($CDCl_3$, 101 MHz)



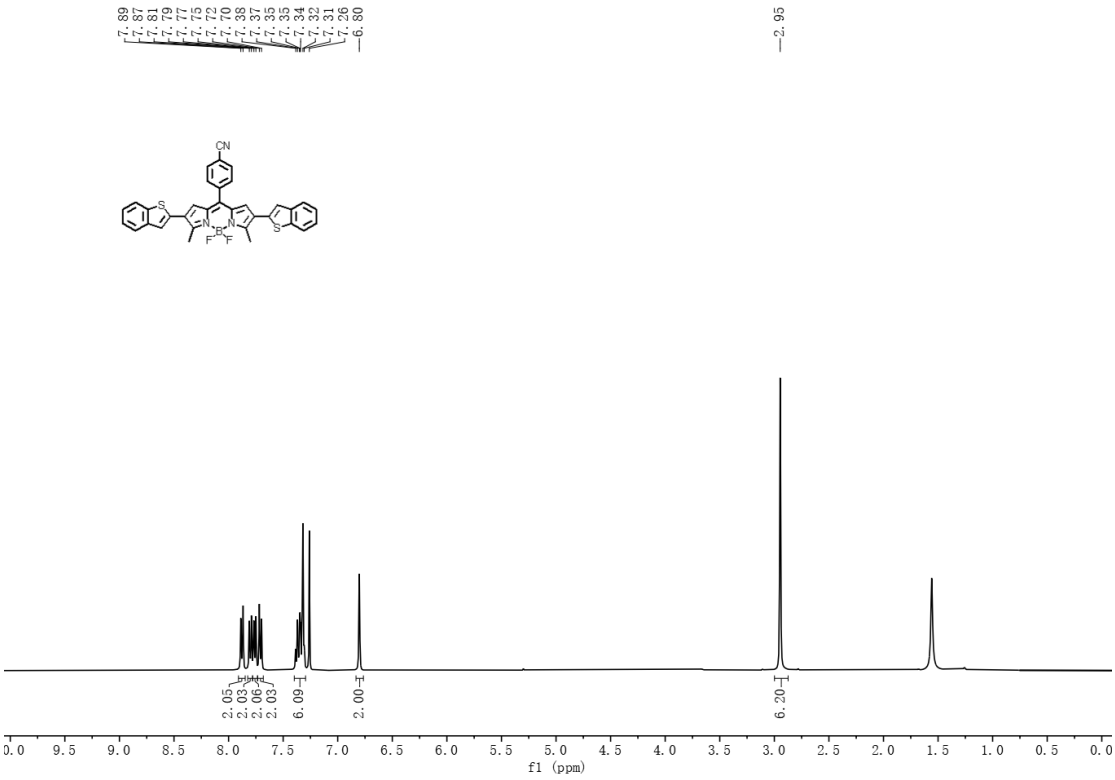
HRMS Spectrum of **5c**



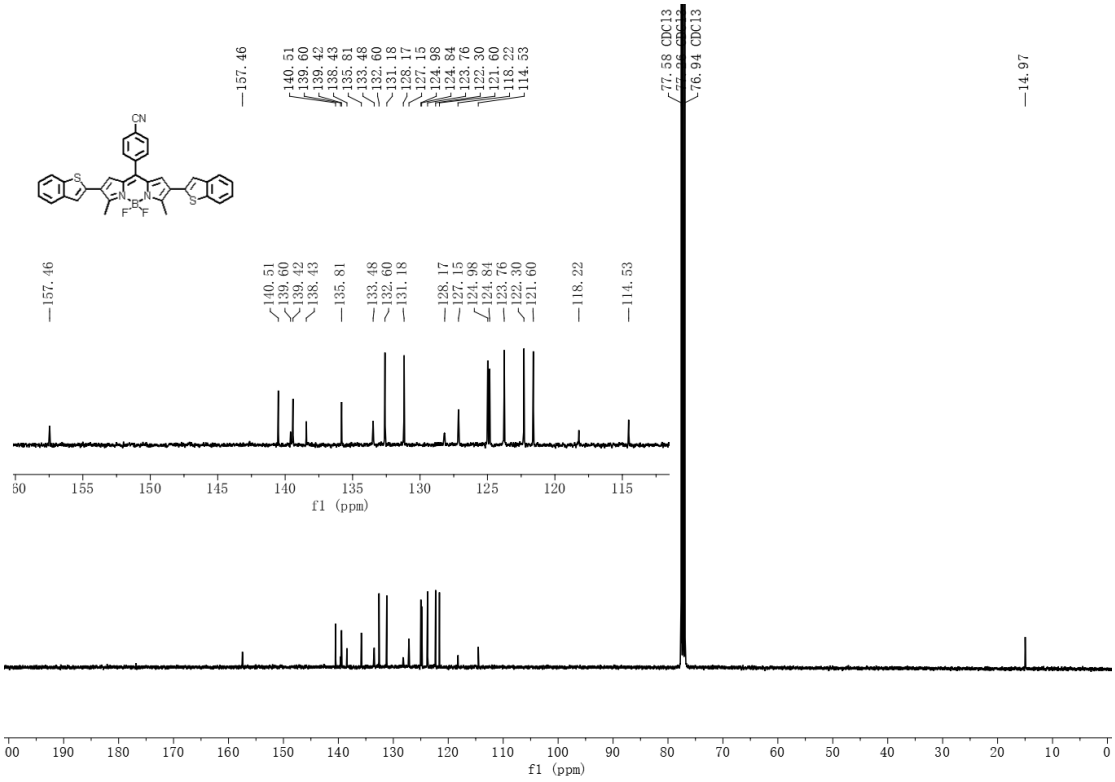
H-5c#235 RT: 1.30
T: FTMS + p ESI Full ms [250.0000-1200.0000]
m/z= 358.9450-728.7353

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
533.1007	4912553.5	100.00	533.0998	0.93	$C_{30}H_{18}N_3BF_2S_2$

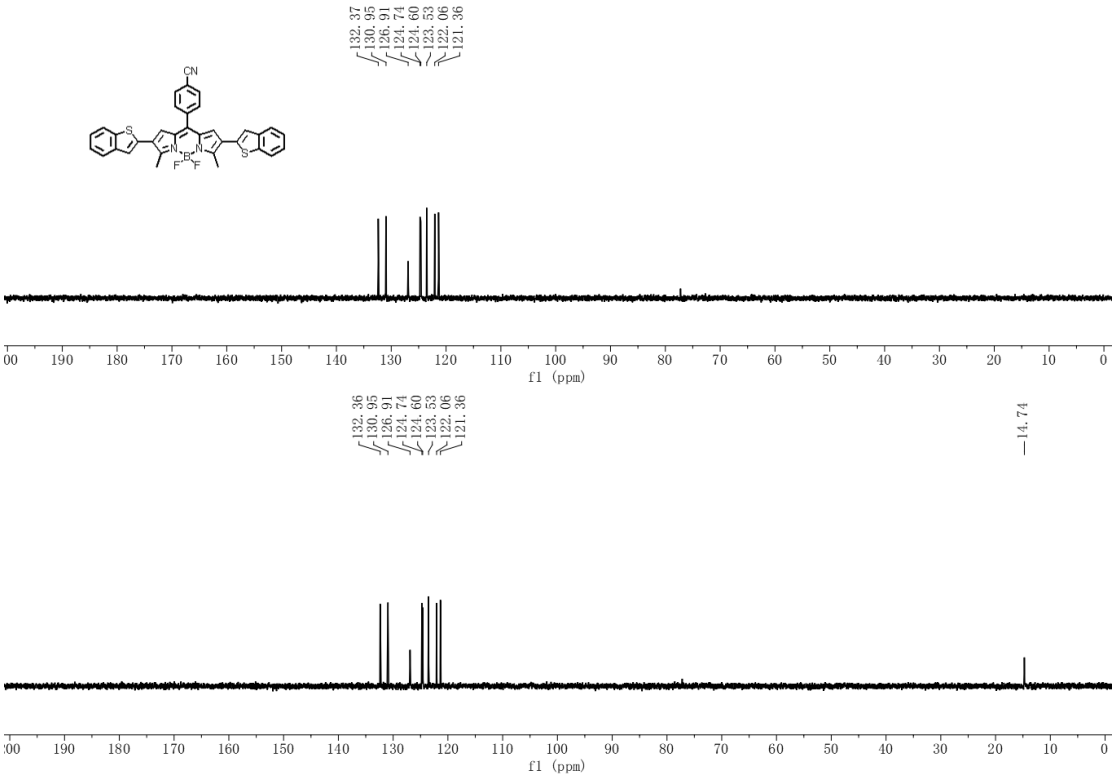
^{1}H NMR spectrum of **6c** ($CDCl_3$, 400 MHz)



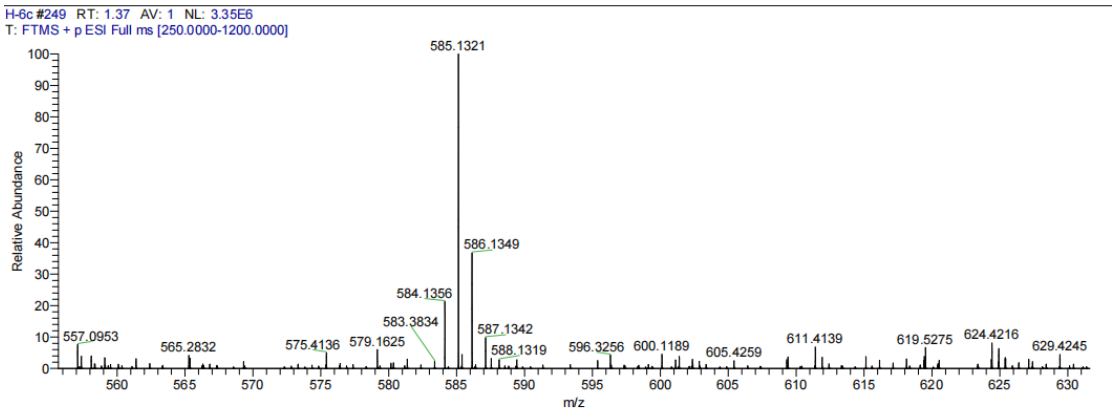
^{13}C NMR Spectrum of **6c** ($CDCl_3$, 101 MHz)



DEPT Spectrum of **6c** ($CDCl_3$, 101 MHz)



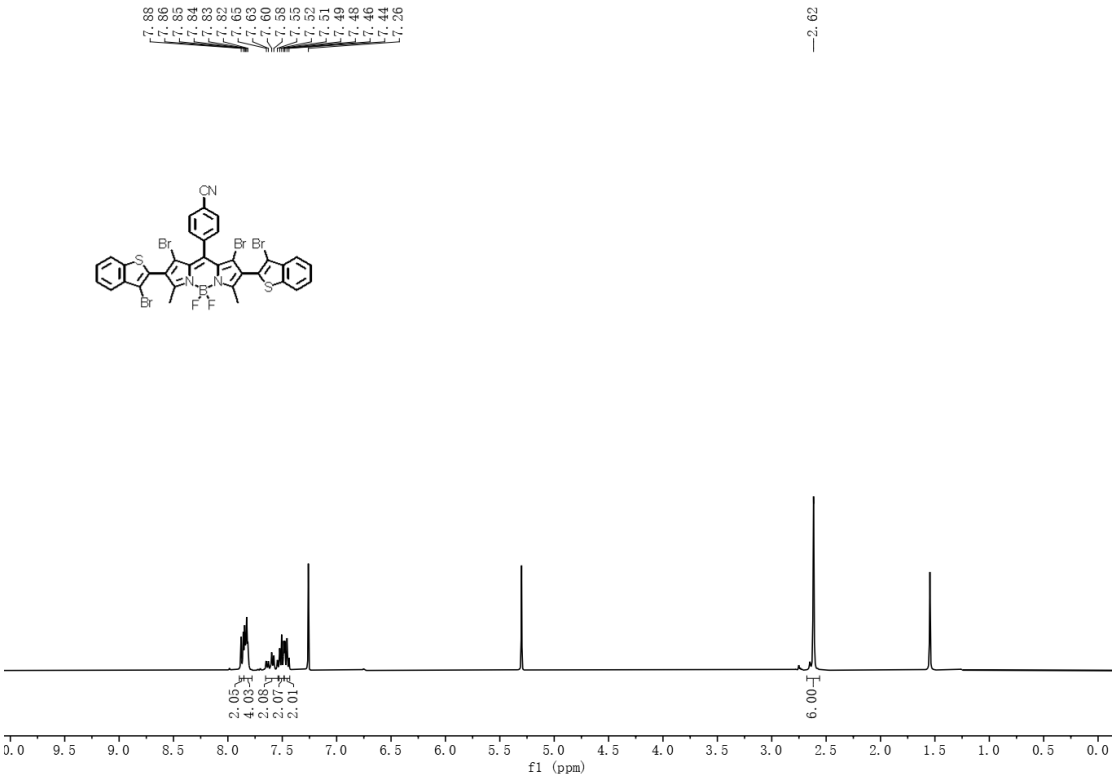
HRMS Spectrum of **6c**



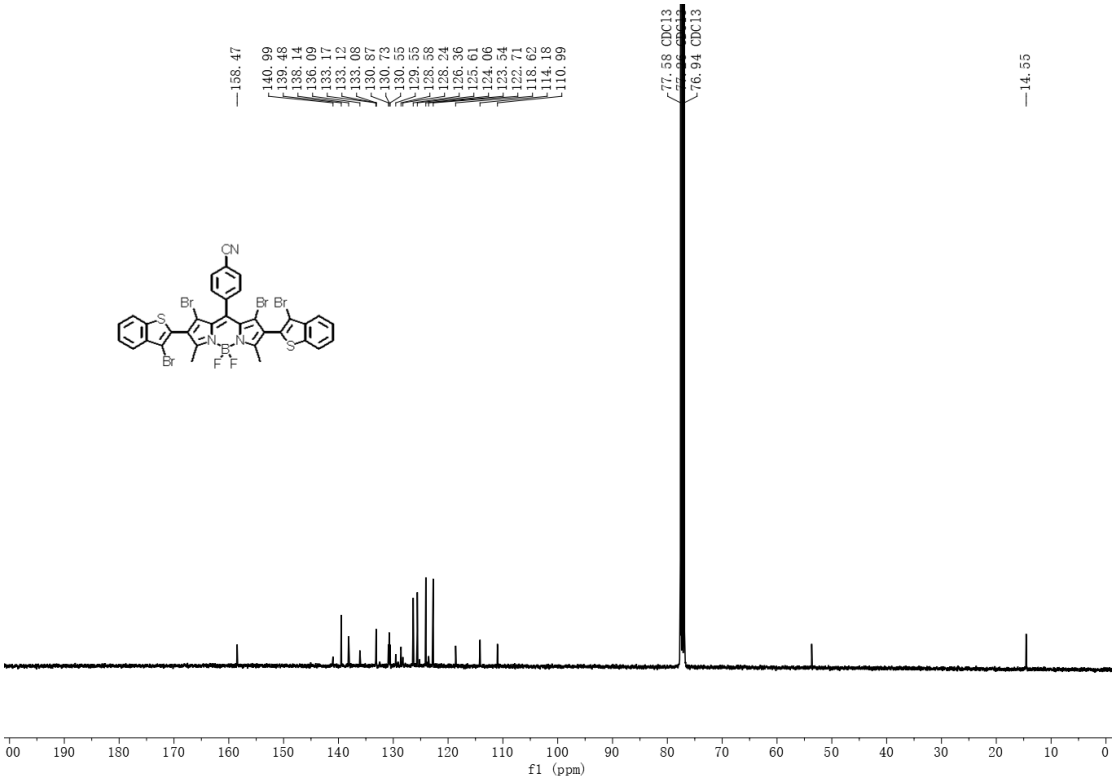
H-6c#249 RT: 1.37
T: FTMS + p ESI Full ms [250.0000-1200.0000]
m/z= 555.6684-631.6186

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
585.1321	3348374.8	100.00	585.1311	1.06	$C_{34}H_{22}N_3BF_2S_2$

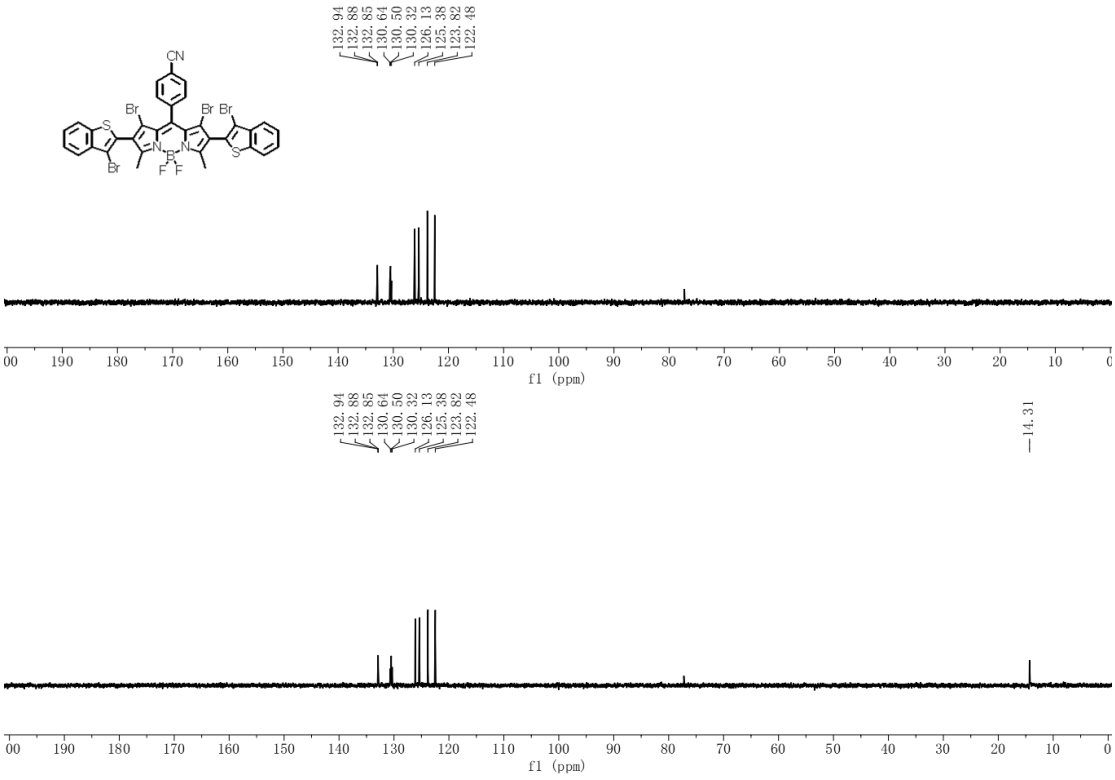
^{1}H NMR spectrum of **7c** ($CDCl_3$, 400 MHz)



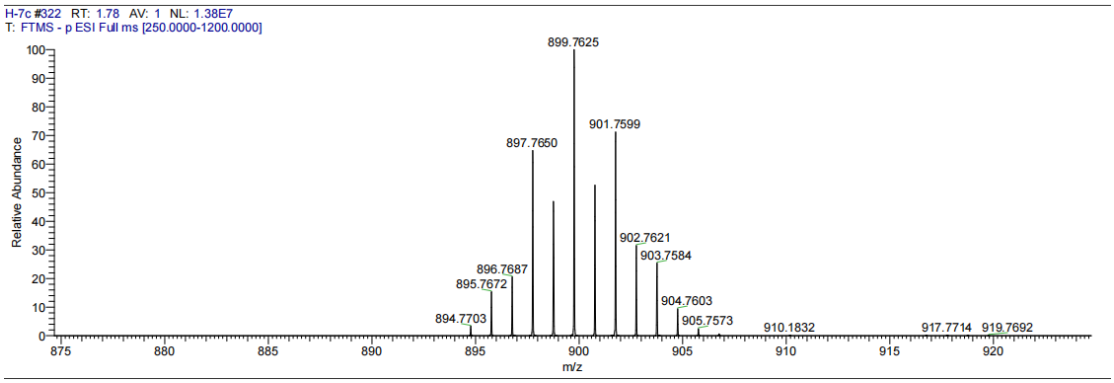
^{13}C NMR Spectrum of **7c** ($CDCl_3$, 101 MHz)



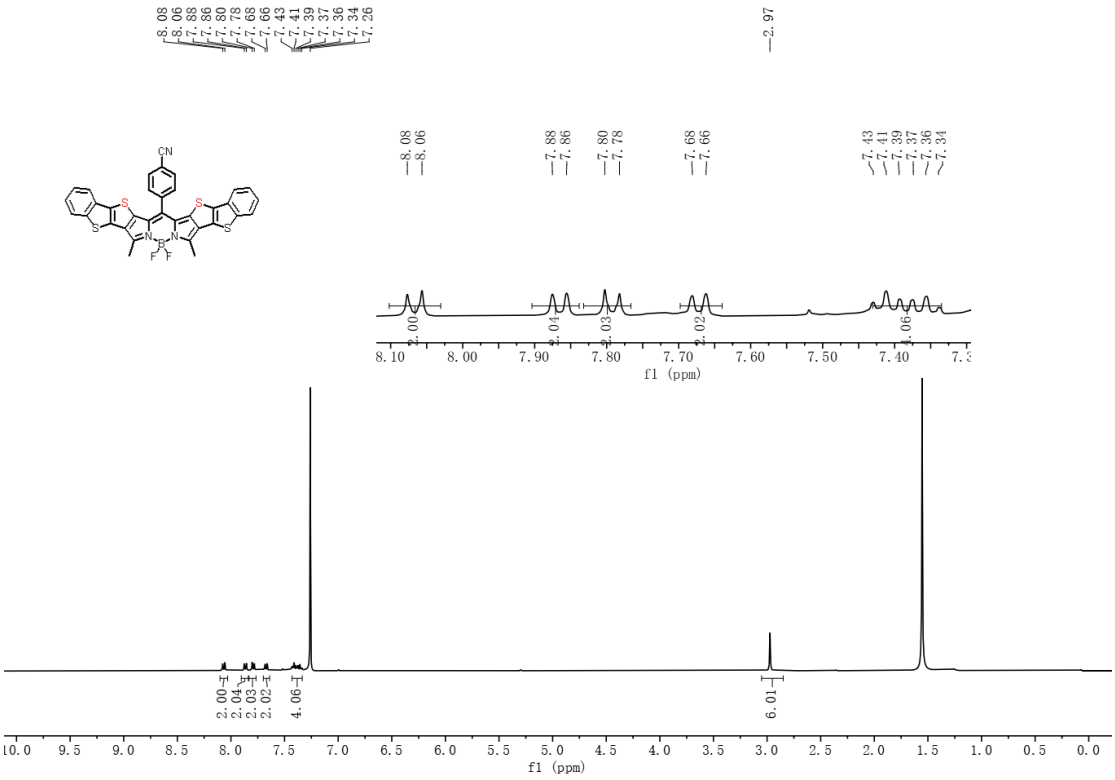
DEPT Spectrum of **7c** ($CDCl_3$, 101 MHz)



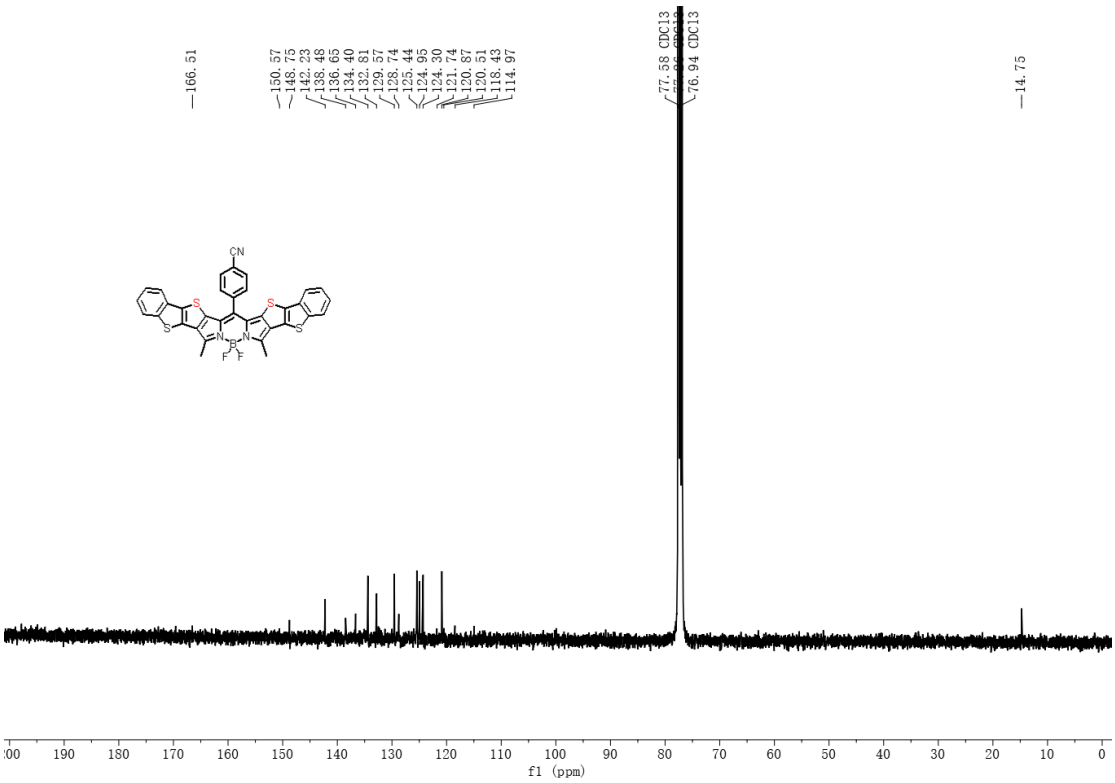
HRMS Spectrum of **7c**



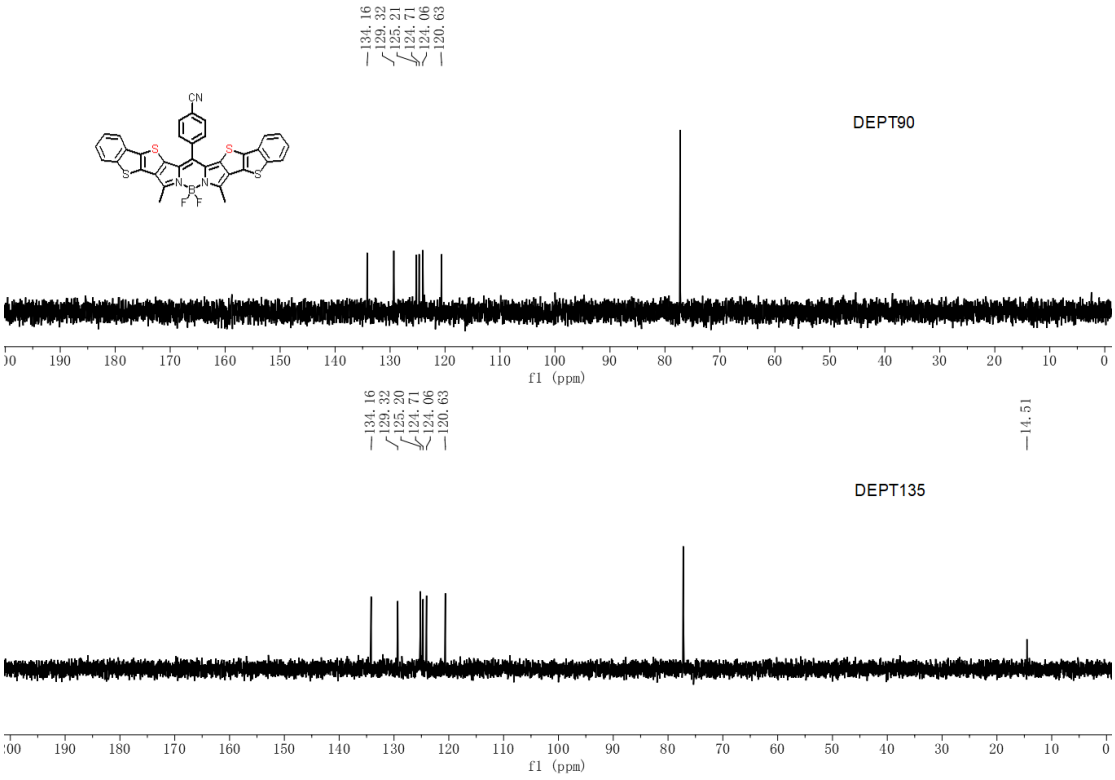
^{1}H NMR spectrum of **8c** ($CDCl_3$, 400 MHz)



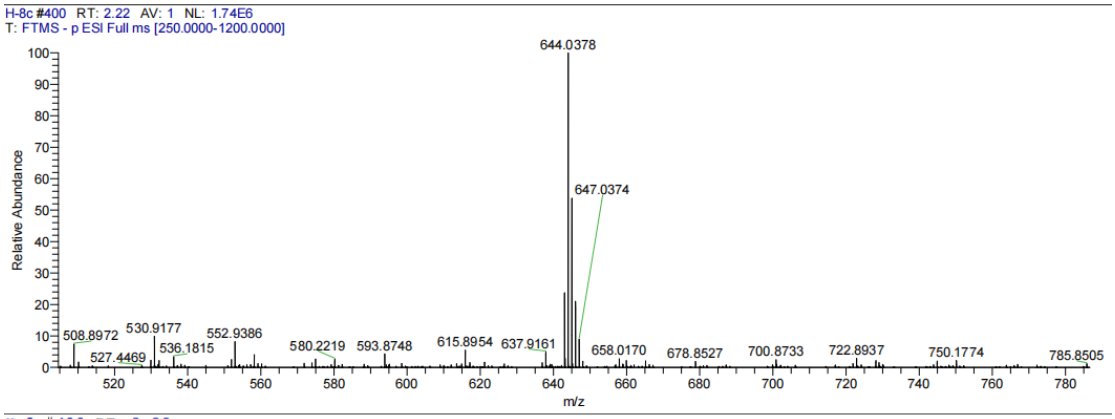
^{13}C NMR Spectrum of **8c** ($CDCl_3$, 101 MHz)



DEPT Spectrum of **8c** ($CDCl_3$, 101 MHz)



HRMS Spectrum of **8c**



H-8c#400 RT: 2.22
T: FTMS - p ESI Full ms [250.0000-1200.0000]
m/z= 504.6199-786.6317

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
644.0378	1803166.0	100.00	644.0361	1.75	$C_{34}H_{17}N_3BF_2S_4$

8. References

[1] Sun, Q.; Wang, H.; Yang, C.; Li, Y. Synthesis and electroluminescence of novel copolymers containing crown ether spacers. *J. Mater. Chem.* **2003**, *13*, 800.

[2] Cai, K.; Xie, J.; Zhao, D. NIR J-aggregates of hydroazaheptacene tetraimides. *J. Am. Chem. Soc.*, **2014**, *136*, 28.

[3] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. Olex2: A complete structure solution, refinement and analysis program, *J. Appl. Cryst*. **2009**, *42*, 339.

[4] Bourhis, L. J.; Dolomanov, O. V.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. The anatomy of a comprehensive constrained, restrained refinement program for the modern computing environment-Olex2 dissected. *Acta Cryst.* **2015**, *A71*, 59.

[5] Sheldrick, G. M. Crystal structure refinement with ShelXL, *Acta Cryst*. **2015**, *C71*, 3.

[6] Yanai H.; Hoshikawa S.; Moriiwa Y.; Shoji A.; Yanagida, A.; Matsumoto T. A fluorinated carbanionic substituent for improving water solubility and lipophilicity of fluorescent dyes. *Angew. Chem. Int. Ed*. **2021**, *60*, 5168.

[7] Miller L.; Impelmann A.; Bauer F.; Breit B. Carbonylation as a key step in new tandem reactions-a route to BODIPYs. *Chem. Eur. J.* **2024**, *30*, e202303752.

[8] Tao J.; Perdew J. P.; Staroverov V. N.; Scuseria G. E. Climbing the density functional ladder: nonempirical meta-generalized gradient approximation designed for molecules and solids. *Phys. Rev. Lett*. **2003**, *91*, 146401.

[9] Staroverov V. N.; Scuseria G. E.; Tao J.; Perdew J. P. Comparative assessment of a new nonempirical density functional: Molecules and hydrogen-bonded complexes. *J. Chem. Phys*. **2003**, *119*, 12129.

[10] Cancès E.; Mennucci B.; Tomasi J. A new integral equation formalism for the polarizable continuum model: Theoretical background and applications to isotropic and anisotropic dielectrics. *J. Chem. Phys*. **1997**, *107*, 3032.

[11] Mennucci B.; Cancès E.; Tomasi J. Evaluation of solvent effects in isotropic and anisotropic dielectrics and in ionic solutions with a unified integral equation method: theoretical bases, computational implementation, and numerical applications. *J. Phys. Chem. B* **1997**, *101*, 10506.

[12] Frisch M. J.; Trucks G; W.; Schlegel H. B.; et al. *Gaussian 16 Rev. A.03*; Wallingford, CT; Gaussian, Inc; 2016.

[13] Liu Z, Lu T, Chen Q. An sp-hybridized all-carboatomic ring, cyclo[18]carbon: Electronic

structure, electronic spectrum, and optical nonlinearity [J]. *Carbon*, **2020**, 165, 461.

[14] Zhang J.; Lu T. Efficient evaluation of electrostatic potential with computerized optimized code. *Phys. Chem. Chem. Phys.* **2021**, *23*, 20323.

[15] Lu T.; Chen F. Multiwfn: a multifunctional wavefunction analyzer. *J. Comput. Chem.* **2012**, *33*, 580.

[16] Humphrey W.; Dalke A.; Schulten K. VMD: visual molecular dynamics. *J. Mol. Graph.* **1996**, *14*, 33.