Supplementary Information (SI) for New Journal of Chemistry.

Supporting information for

Sulfur-bridged annulated BODIPYs: synthesis, structure and photophysical properties

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1. Materials and General Methods

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 or a Waters GCT Premier TOF 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.

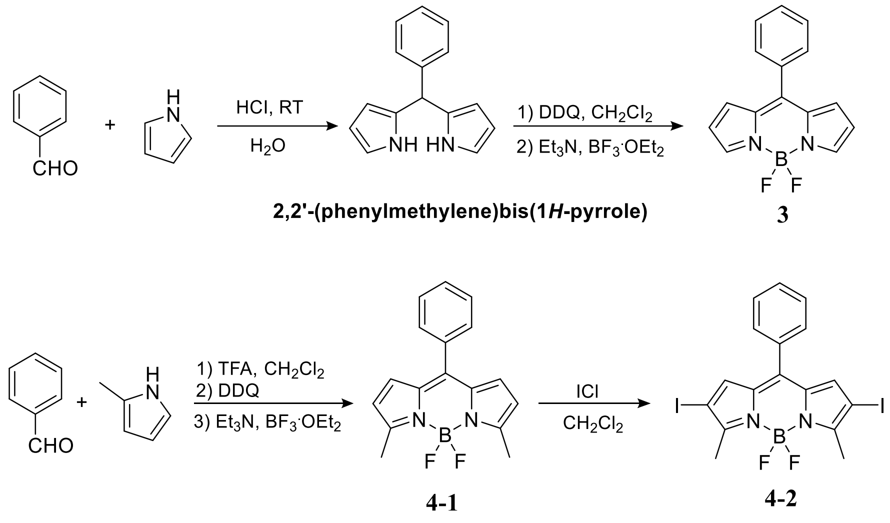
Electrochemical measurements. Cyclic voltammetry (CV) was performed using a CHI620E electrochemical workstation at a scan rate of 50 mV s^{-1}, using glassy carbon discs as the working electrodes, Pt wire as the counter electrode, Ag/AgCl electrode as the reference electrode. 0.1 M tetrabutylammonium hexafuorophosphate (n-Bu$_4$NPF$_6$) dissolved in CH$_2$Cl$_2$ (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 stucture analysis. Single crystals of **2a** suitable for X-ray analysis were obtained by slow diffusion of MeOH into their toluene solution. A suitable crystal was selected and performed on a Bruker D8 VENTURE diffractometer. The crystal was kept at 198.00 K during data collection. The determination of unit cell parameters and data collections of **2a** was performed with Cu Kα radiation (λ) at 1.54178 Å in the scan range 6.736° ≤ 2θ ≤ 137.628°. 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.

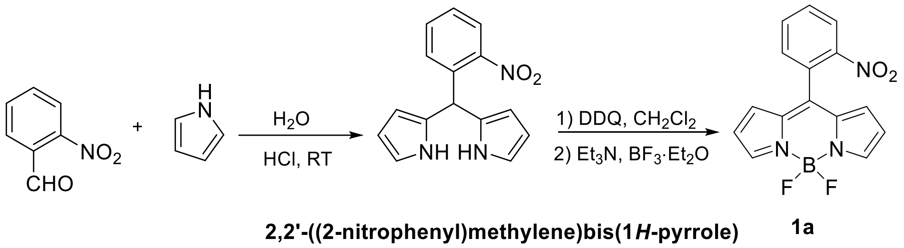
Single crystals of **2b** suitable for X-ray analysis were grown by slow diffusion of MeOH into their CH_2Cl_2 solution. A suitable crystal was selected and performed on a Bruker D8 VENTURE diffractometer. The crystal was kept at 193.00 K during data collection. The determination of unit cell parameters and data collections of **2b** was performed with Cu Kα radiation (λ) at 1.54178 Å in the scan range 8.896° ≤ 2θ ≤ 135.838°. 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. Synthesis and Characterization

Compounds **3**, **4-2** were synthesized according to literatures[6,7].



Scheme S1 Synthesis procedure of BODIPYs **3**, **4-2**



Syntheses of 1a:

In a 250 mL clean beaker, pyrrole (2.80 mL, 40.5 mmol) was dissolved in 100 mL of 0.18 M hydrochloric acid solution. Then, 2-nitrobenzaldehyde (2.04 g, 13.5 mmol) was added to media and the composition was stirred at room temperature for 1.5 h. The reaction was monitored by TLC until completion. Afterward, the reaction mixture was filtered with suction, the filter cake was washed successively with 200 mL of water and 100 mL of petroleum ether, and then dry it. Subsequently, the crude product was subject to rough purification via silica gel column chromatography using a gradient eluent (PE/EA = 5/1 to 2/1, v/v). The resulting compound **2,2'-((2-nitrophenyl)methylene)bis(1H-pyrrole)** obtained from this purification can be directly used in the next reaction.

To a solution of compound **2,2'-((2-nitrophenyl)methylene)bis(1H-pyrrole)** (2.2 g, 8.23 mmol) in CH_2Cl_2 (200 mL), a solution of 2,3-dichloro-5,6-dicyano-1,4-

benzoquinone (DDQ, 1.87 g, 8.23 mmol) in CH_2Cl_2 (50 mL) was added at room temperature for 1 h. Then, the resulting solution were treated by Et_3N (7.0 mL, 50 mmol) and $BF_3 \cdot OEt_2$ (9.5 mL, 77 mmol). After being stirred for 2 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 =8/1, v/v) and recrystallized with methanol/dichloromethane to give 902 mg of compound **1a** in 35 % yield as red solids. NMR data of this compound agreed with the reported one.[8] ^1H NMR (400 MHz, Chloroform-*d*) δ 8.22 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.95 (s, 2H), 7.77 (2td, *J* = 7.5, 1.5 Hz, 2H), 7.58 (dd, *J* = 7.1, 1.9 Hz, 1H), 6.67 (d, *J* = 4.2 Hz, 2H), 6.51 (d, *J* = 4.1 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 149.36, 145.56, 142.87, 134.87, 133.38, 132.57, 131.48, 129.99, 128.70, 125.39, 119.47. HRMS (EI, $[M]^+$, 100%): calcd for $C_{15}H_{10}BF_2N_3O_2$, 313.0834; found, 313.0839.

3. Crystal Data

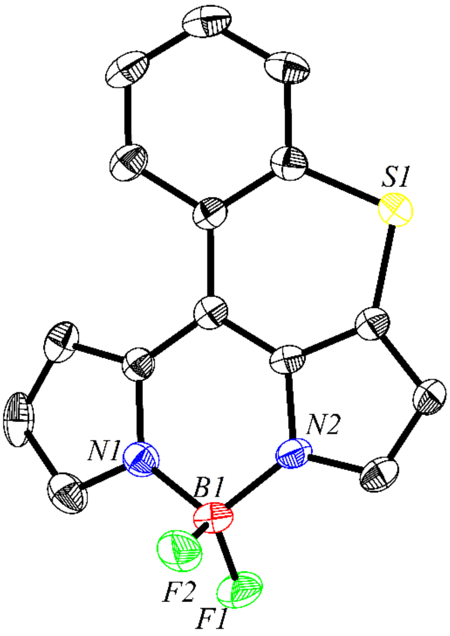


Figure S1. Single-crystal structure of **2a**, with thermal ellipsoids shown at 50% probability. (Hydrogen atoms and solvent molecules are omitted for clarity.)

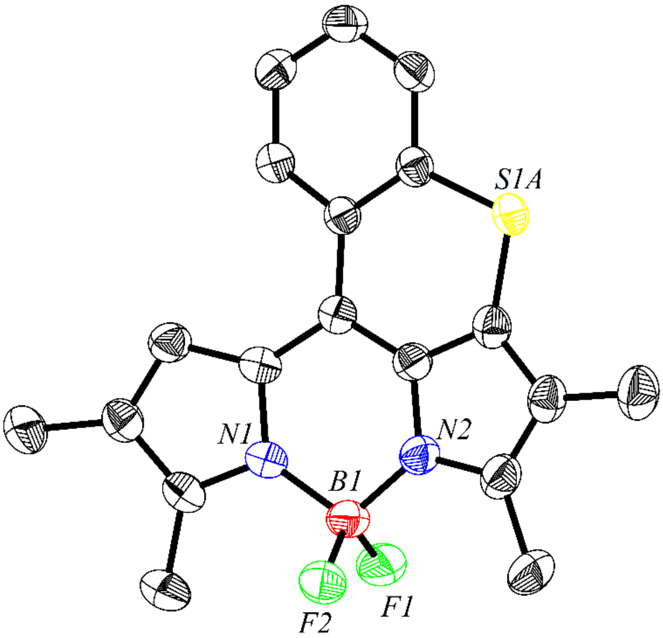


Figure S2. Single-crystal structure of **2b**, with thermal ellipsoids shown at 50% probability. (Hydrogen atoms and solvent molecules are omitted for clarity.)

Table S1. Crystal data and structure refinement for **2a**. CCDC number = 2381648

Identification code	**2a**
Empirical formula	$C_{15}H_9BF_2N_2S$
Formula weight	298.11
Temperature/K	198.00
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	7.24650(10)
b/Å	20.7755(4)
c/Å	16.9252(3)
α/°	90
β/°	90.1620(10)
γ/°	90
Volume/Å^3	2548.07(8)
Z	8
ρ_{calc}g/cm^3	1.554
μ/mm^{-1}	2.420
F(000)	1216.0
Crystal size/mm^3	0.18 × 0.13 × 0.12
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.736 to 137.628
Index ranges	$-8 \leq h \leq 8$, $-18 \leq k \leq 25$, $-20 \leq l \leq 20$
Reflections collected	17855
Independent reflections	4700 [R_{int} = 0.0546, R_{sigma} = 0.0515]
Data/restraints/parameters	4700/3/379
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0653, wR_2 = 0.1754
Final R indexes [all data]	R_1 = 0.0797, wR_2 = 0.1890
Largest diff. peak/hole / e Å^{-3}	0.90/-0.45

Table S2. Crystal data and structure refinement for **2b**. CCDC number = 2381649

Identification code	**2b**
Empirical formula	$C_{19}H_{17}BF_2N_2S$
Formula weight	354.21
Temperature/K	193.00
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	7.1383(2)
b/Å	11.5671(3)
c/Å	19.5512(5)
α/°	90
β/°	96.209(2)
γ/°	90
Volume/Å^3	1604.86(7)
Z	4
ρ_{calc}g/cm^3	1.466
μ/mm^{-1}	2.012
F(000)	736.0
Crystal size/mm^3	0.15 × 0.13 × 0.12
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	8.896 to 135.838
Index ranges	$-8 \leq h \leq 7$, $-13 \leq k \leq 12$, $-23 \leq l \leq 23$
Reflections collected	13426
Independent reflections	2908 [R_{int} = 0.0431, R_{sigma} = 0.0319]
Data/restraints/parameters	2908/0/240
Goodness-of-fit on F^2	1.071
Final R indexes [I>=2σ (I)]	R_1 = 0.0367, wR_2 = 0.0981
Final R indexes [all data]	R_1 = 0.0449, wR_2 = 0.1034
Largest diff. peak/hole / e Å^{-3}	0.24/-0.20

4. Photophysical Properties

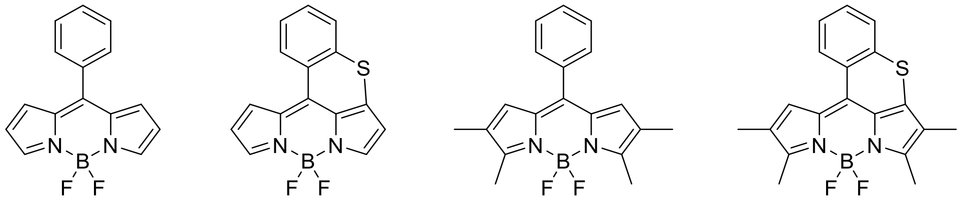

3 **2a** **4** **2b**

Figure S3 Structure of BODIPYs **3**, **2a**, **4**, **2b**

Table S3. Spectroscopic and photophysical properties of **3**, **2a**, **4**, **2b** in different solvents.

Compound	Solvent	$\lambda_{max}{}^{a}$ [nm]	ε / $10^{5\,b}$ [$M^{-1}cm^{-1}$]	$\lambda_{em}{}^{c}$ [nm]	SS ^{d} [cm^{-1}]	$\Phi_f{}^{e}$ [%]	T ^{f} [ns]	$K_r{}^{g}$ [10^8 S^{-1}]	$K_{nr}{}^{h}$ [10^8 S^{-1}]
3	DCM	501	0.718554	518	655	1.40	0.53	0.26	18.6
	THF	501	0.601767	517	618	1.00	0.45	0.22	22.0
	TOL	504	0.612743	521	647	2.80	0.67	0.42	14.5
2a	DCM	507	0.631483	521	530	23.2	3.25	0.71	2.36
	THF	508	0.514545	521	491	23.5	3.15	0.75	2.43
	TOL	512	0.702364	528	592	31.0	3.68	0.84	1.88
4	DCM	538	1.042260	554	537	47.5	4.17	1.14	1.26
	THF	536	1.217043	553	574	44.2	3.82	1.16	1.46
	TOL	539	1.045912	556	567	58.8	4.62	1.27	0.89
2b	DCM	538	0.714180	560	730	53.7	5.28	1.02	0.88
	THF	538	1.048462	560	730	50.5	5.30	0.95	0.93
	TOL	543	0.842006	560	559	54.5	5.12	1.06	0.89

[a] Absorption maxima (λmax). [b] Molar extinction coefficients (at λmax). [c] Emission maxima (λem). [d] Stokes shifts. [e] Fluorescence quantum yield (Φ_f). [f] Lifetime (τ). [g] Radiation rate constant. [h] Non-radiation rate constant. of **3**, **2a**, **4**, **2b** in different solvents.

UV-Vis absorption and fluorescence emission spectra of the same compound in different solvents at room temperature.

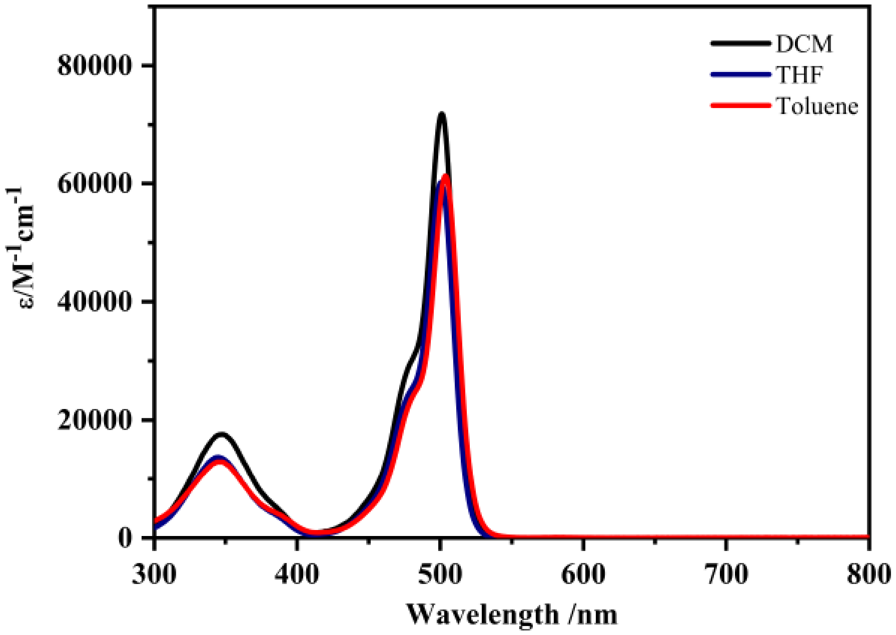


Figure S4. Room-temperature absorption spectra of compound **3** recorded in different solvents (1×10^{-5} mol/L).

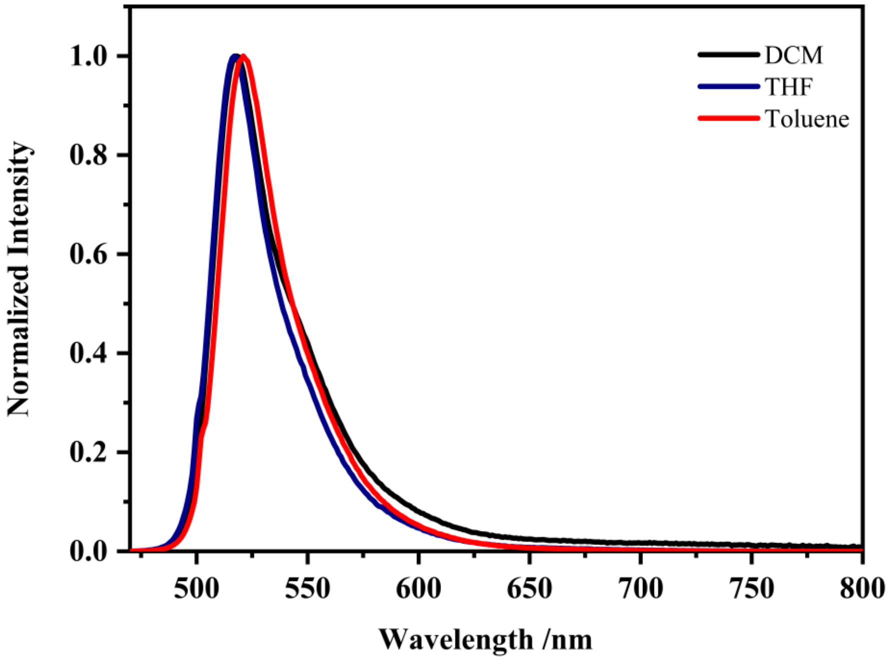


Figure S5. Room-temperature emission spectra of compound **3** recorded in different solvents (1×10^{-6} mol/L).

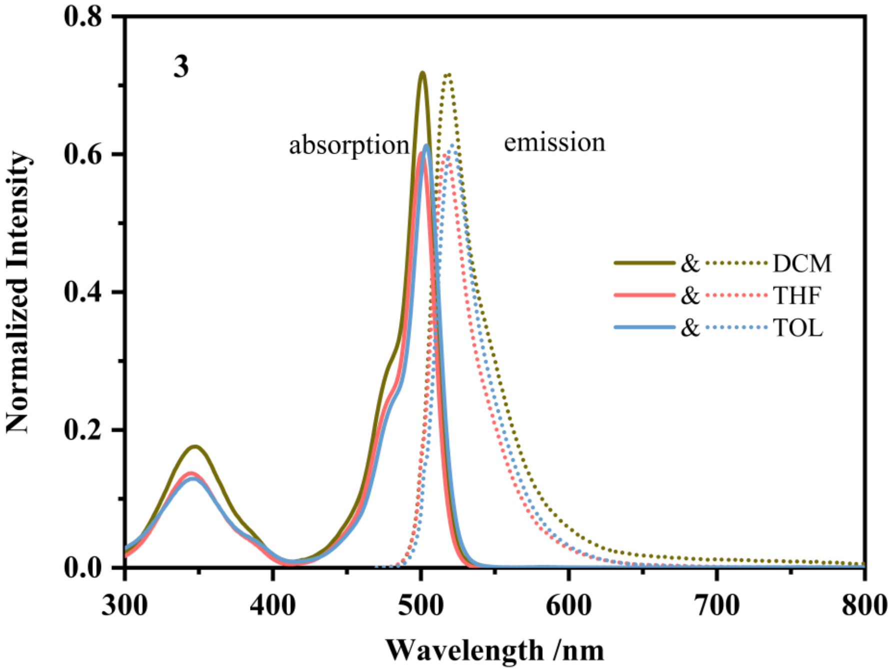


Figure S6. Room-temperature normalized absorption and emission spectra of compound **3** recorded in different solvents.

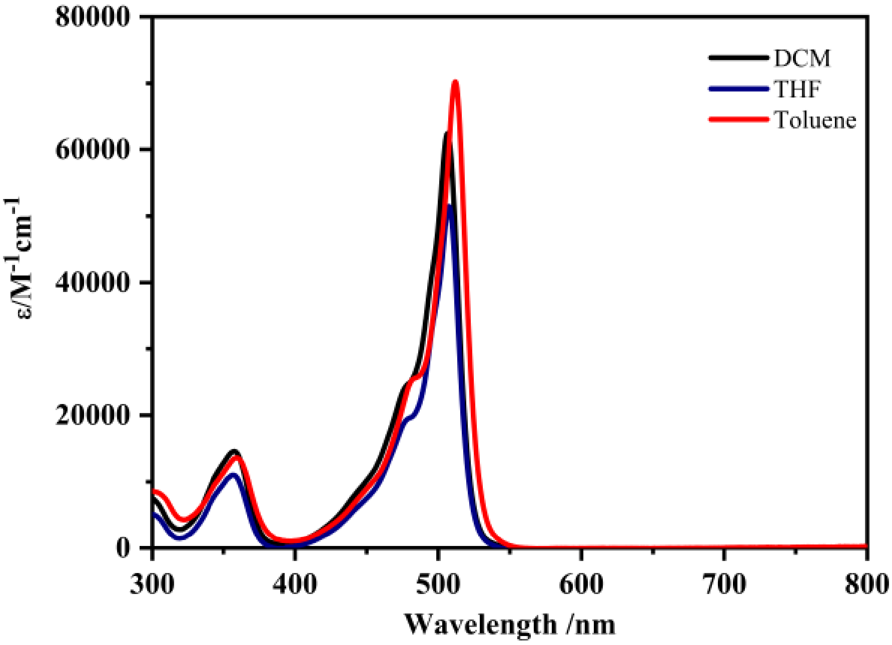


Figure S7. Room-temperature absorption spectra of compound **2a** recorded in different solvents (1×10^{-5} mol/L).

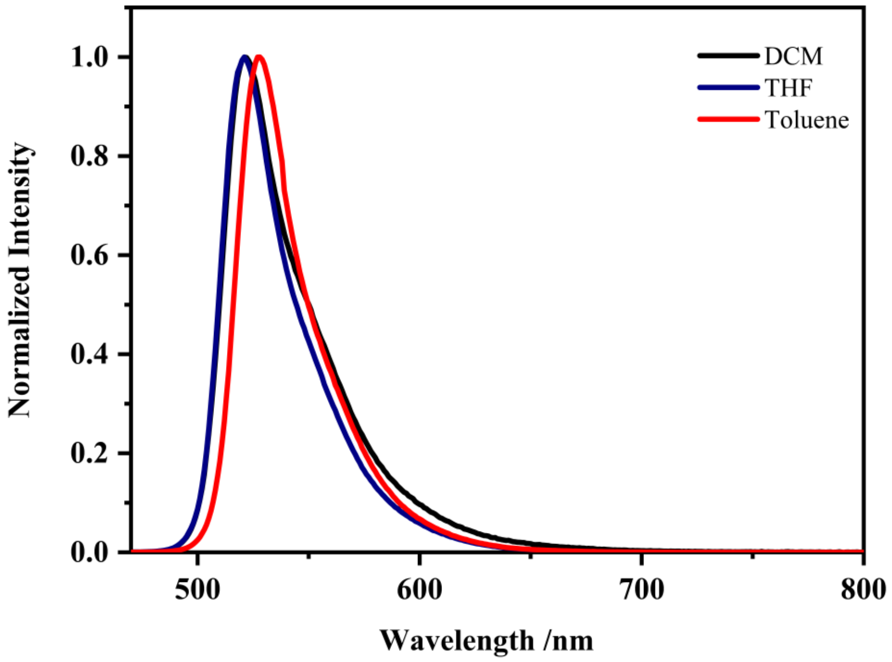


Figure S8. Room-temperature emission spectra of compound **2a** recorded in different solvents (1×10^{-6} mol/L).

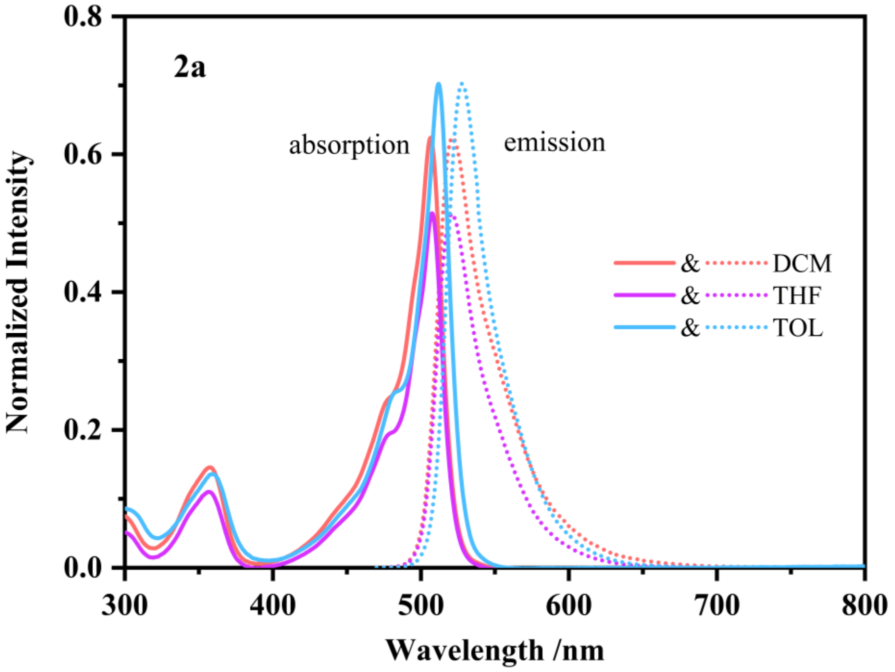


Figure S9. Room-temperature normalized absorption and emission spectra of compound **2a** recorded in different solvents.

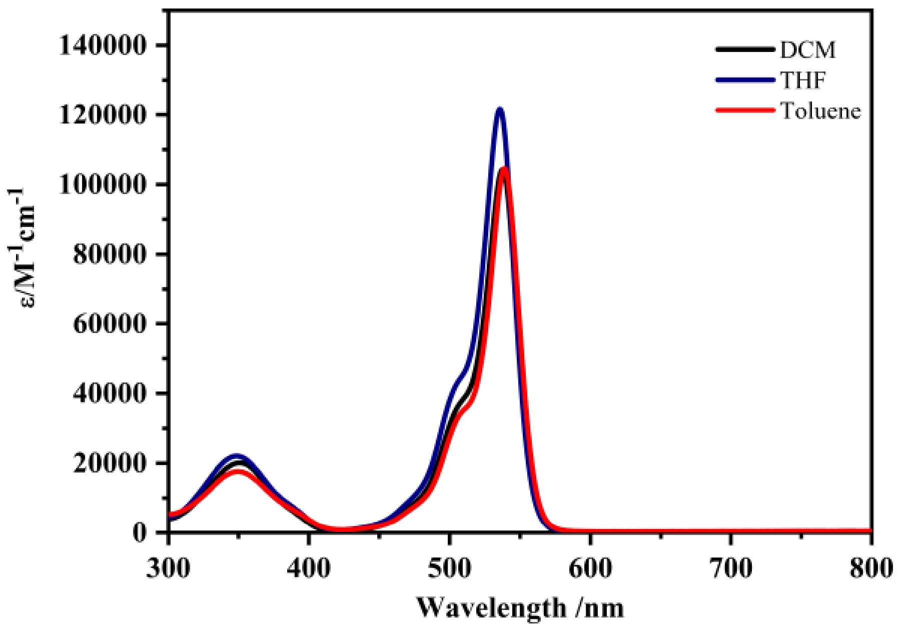


Figure S10. Room-temperature absorption spectra of compound **4** recorded in different solvents (1×10^{-5} mol/L).

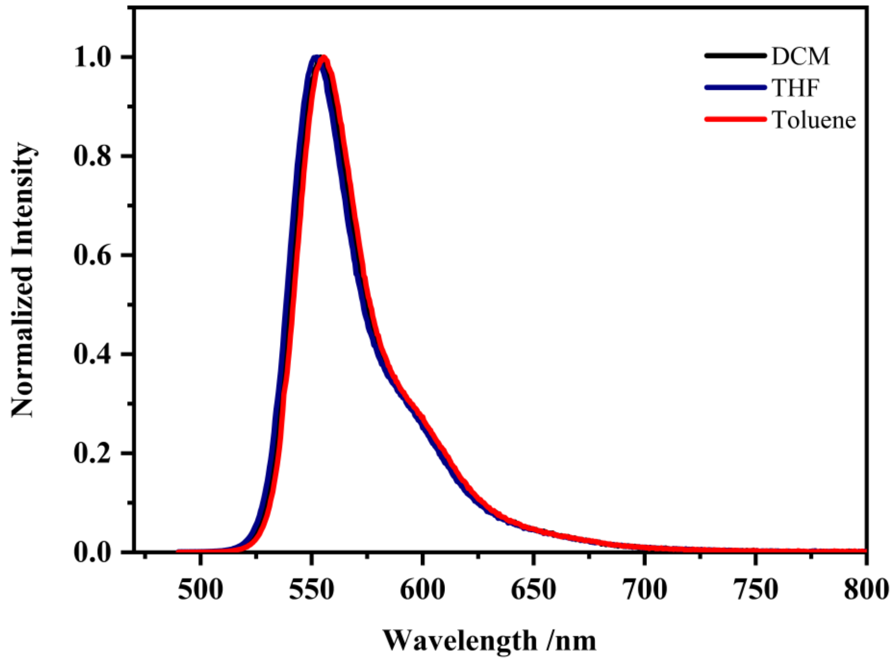


Figure S11. Room-temperature emission spectra of compound **4** recorded in different solvents (1×10^{-6} mol/L).

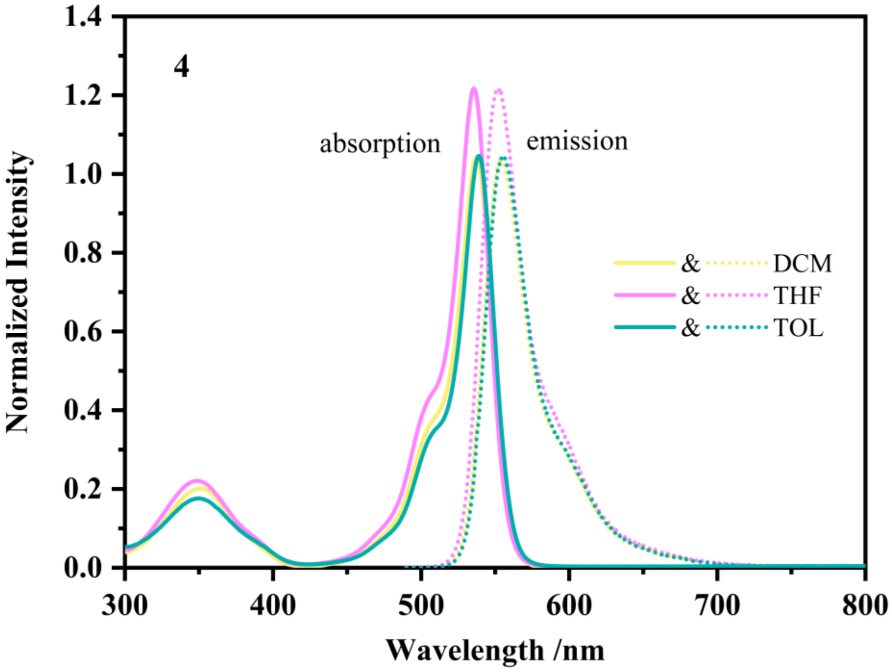


Figure S12. Room-temperature normalized absorption and emission spectra of compound **4** recorded in different solvents.

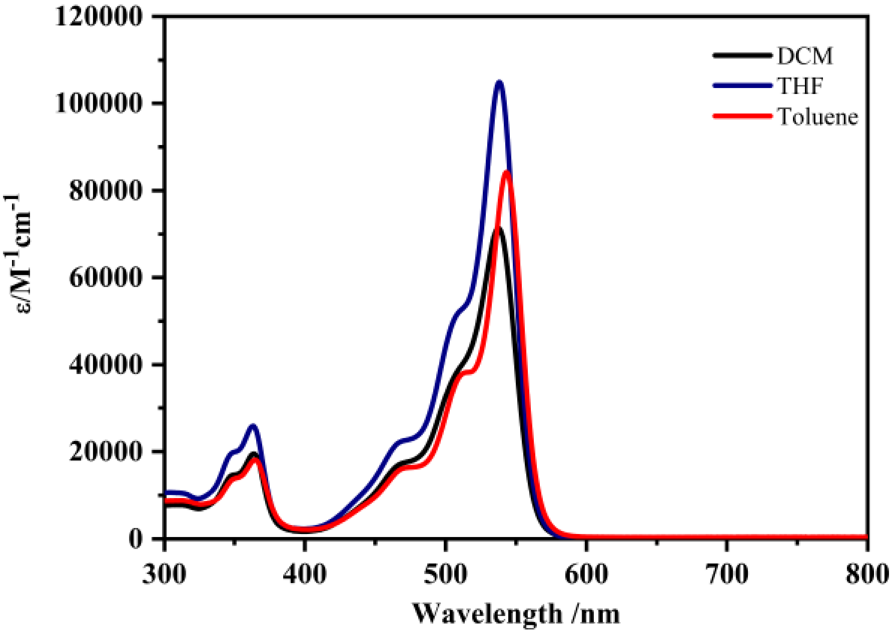


Figure S13. Room-temperature absorption spectra of compound **2b** recorded in different solvents (1×10^{-5} mol/L).

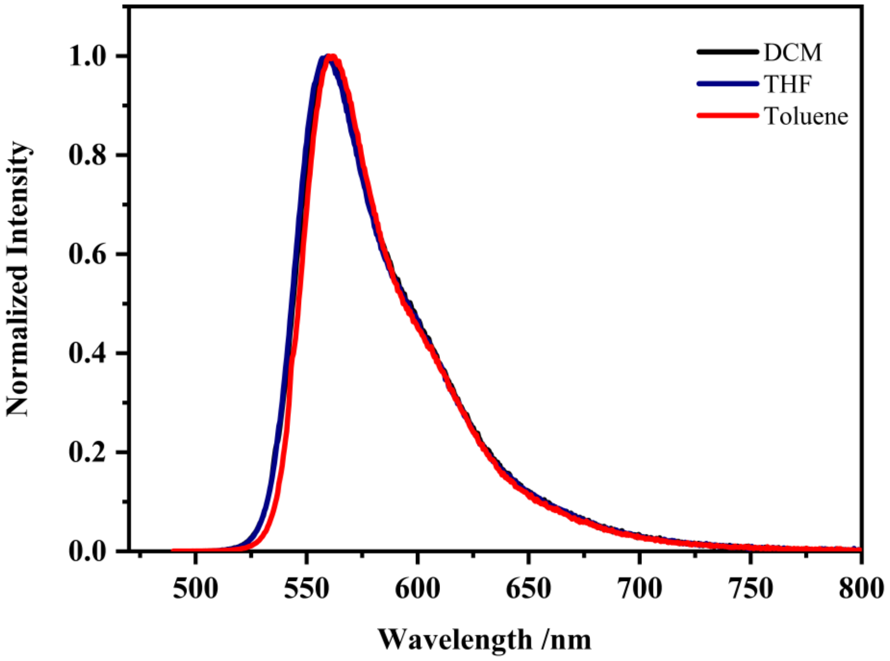


Figure S14. Room-temperature emission spectra of compound **2b** recorded in different solvents (1×10^{-6} mol/L).

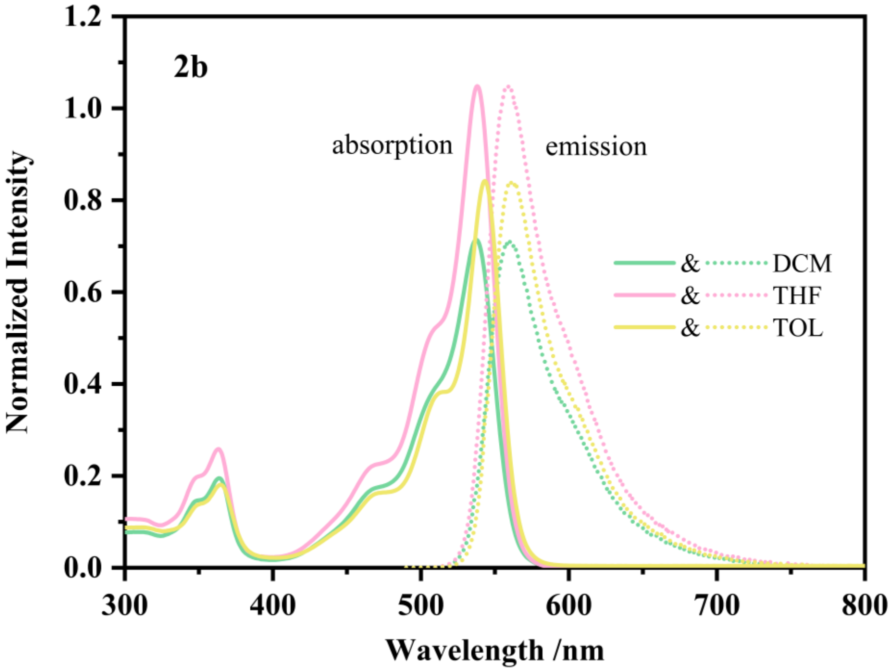


Figure S15. Room-temperature normalized absorption and emission spectra of compound **2b** recorded in different solvents.

UV-Vis absorption and fluorescence emission spectra of different compounds in same solvents at room temperature.

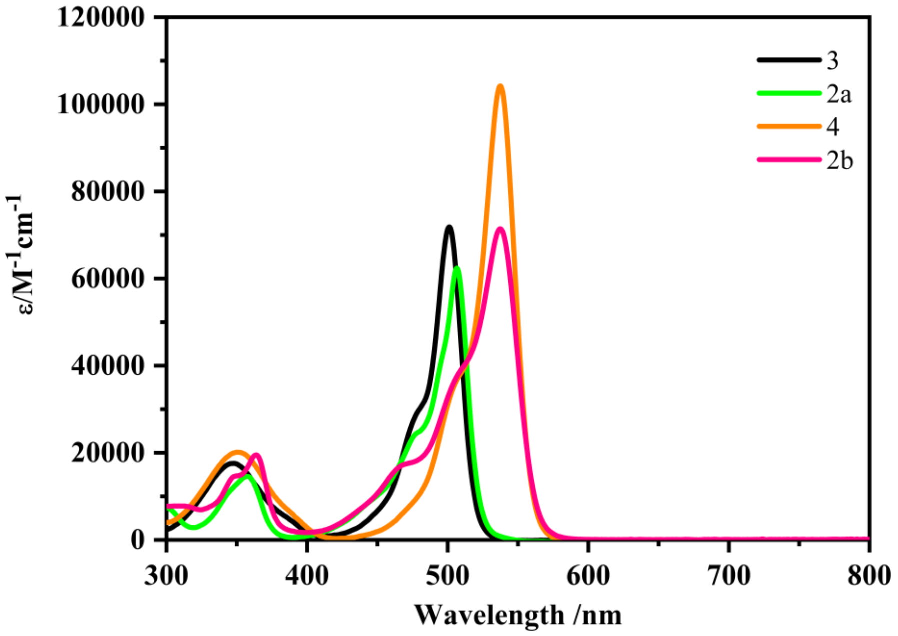


Figure S16. Room-temperature absorption spectra of compounds **3**, **2a**, **4**, **2b** recorded in dichloromethane (1×10^{-5} mol/L).

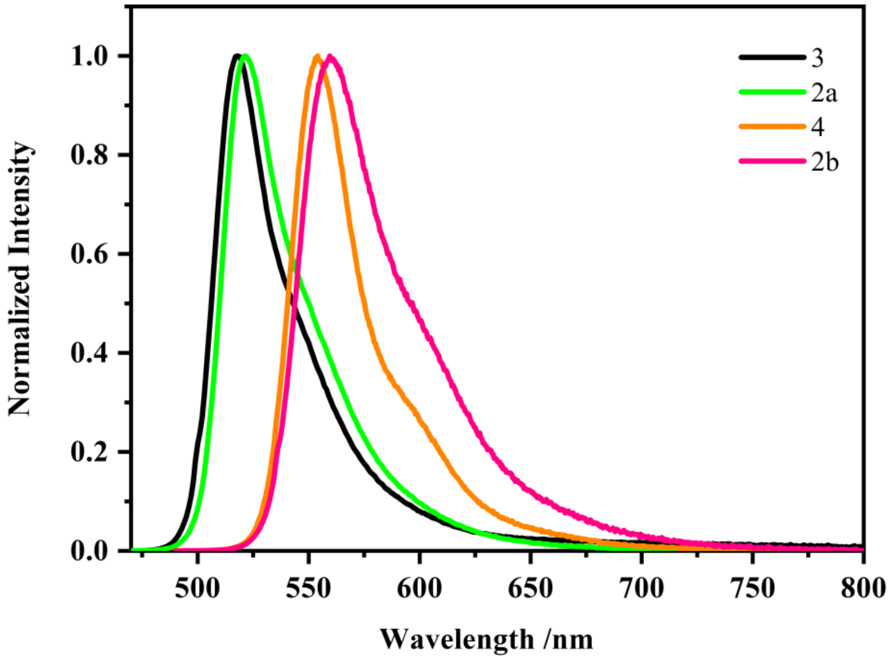


Figure S17. Room-temperature emission spectra of compounds **3**, **2a**, **4**, **2b** recorded in dichloromethane (1×10^{-6} mol/L).

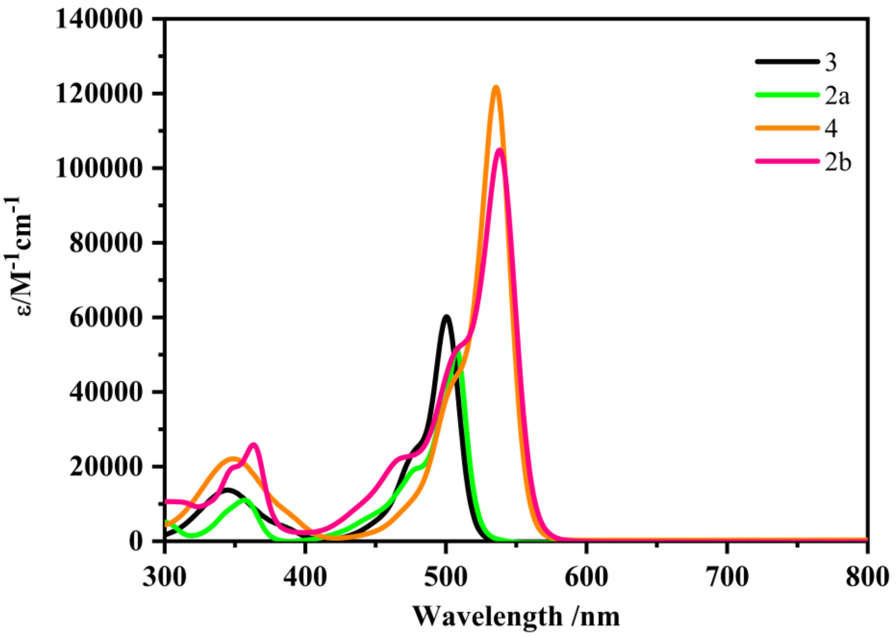


Figure S18. Room-temperature absorption spectra of compounds **3**, **2a**, **4**, **2b** recorded in tetrahydrofuran (1×10^{-5} mol/L).

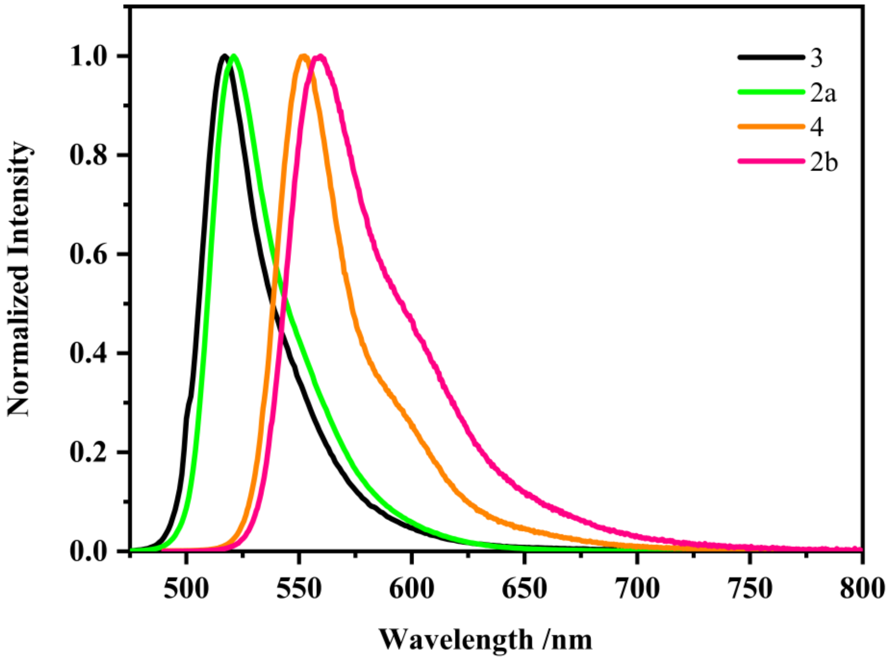


Figure S19. Room-temperature emission spectra of compounds **3**, **2a**, **4**, **2b** recorded in tetrahydrofuran (1×10^{-6} mol/L).

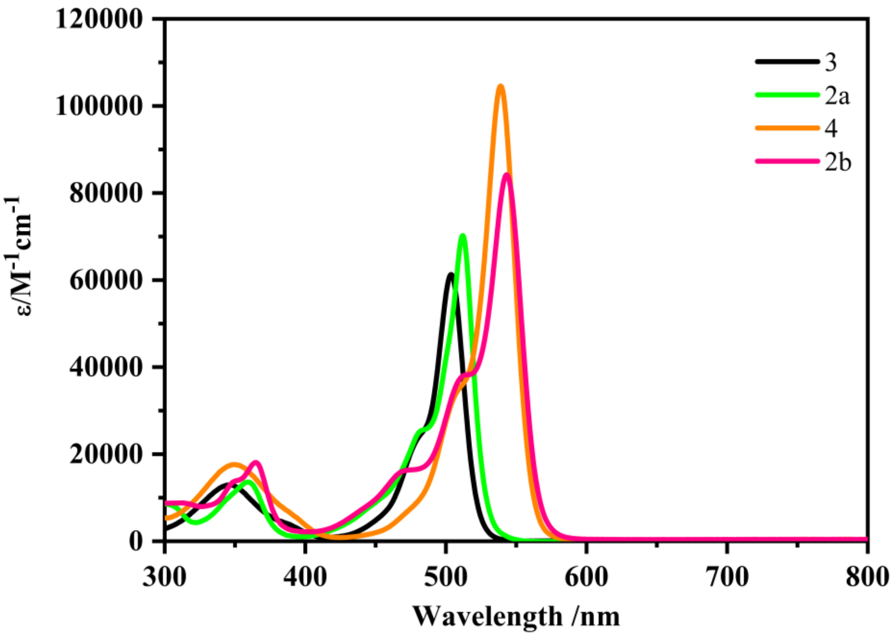


Figure S20. Room-temperature absorption spectra of compounds **3**, **2a**, **4**, **2b** recorded in toluene (1×10^{-5} mol/L).

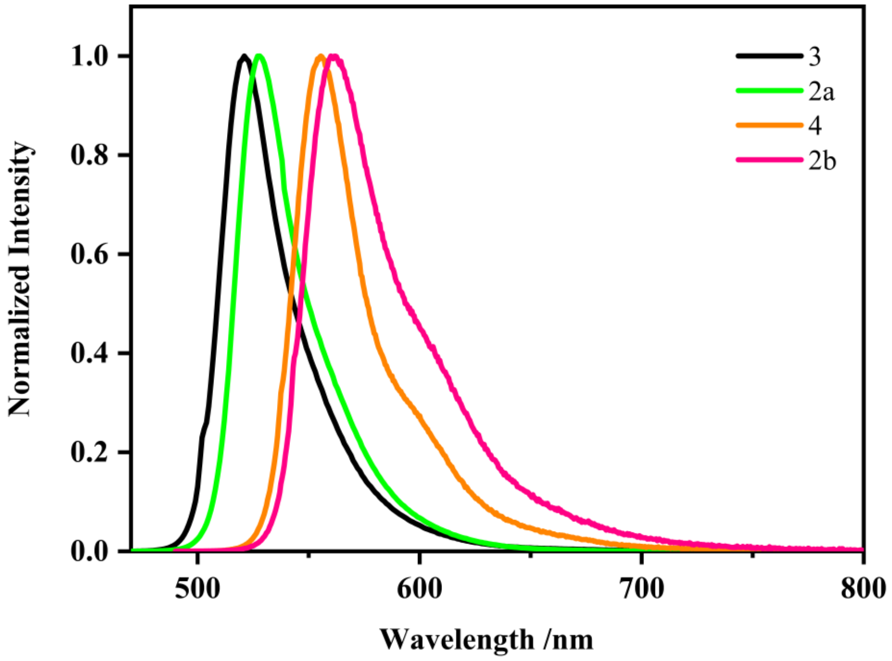


Figure S21. Room-temperature emission spectra of compounds **3**, **2a**, **4**, **2b** recorded in toluene (1×10^{-6} mol/L).

5. Electrochemical Data

Table S4. Electrochemical properties of **3**, **2a**, **4**, **2b** in dichloromethane at rt.

Compound	E_{red}^{onset} (V)	E_{ox}^{onset} (V)	LUMO (eV)	HOMO (eV)	E_g^e (eV)	E_g^o (eV)
3	-1.24	0.97	-3.56	-5.77	2.21	2.38
2a	-1.23	0.90	-3.57	-5.70	2.13	2.37
4	-1.50	0.58	-3.30	-5.38	2.08	2.22
2b	-1.47	0.58	-3.33	-5.38	2.05	2.20

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 theintercept of the electrochemical data; λ_{onset} = the onset of absorption in CH_2Cl_2 soluntion of **3**, **2a**, **4**, **2b**; E_g^o=1240/λ_{onset}; E_g^o= bandgap, obtained from the intercept of the absorption spectra.

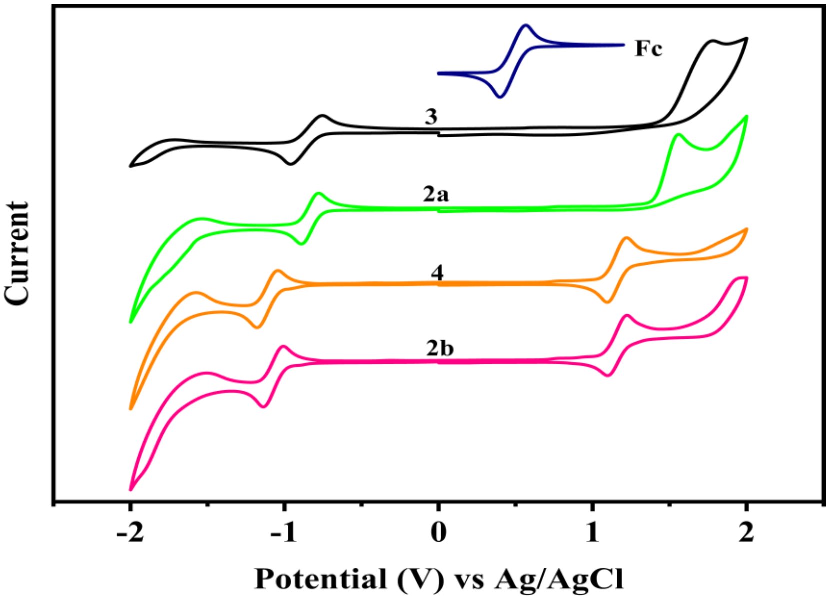


Figure S22. Cyclic voltammograms of **Fc**, **3**, **2a**, **4** and **2b** in dichloromethane with 0.1 M *n*-Bu_4PF_6 as supporting electrolyte (scan rate: 50 mV s^{-1}).

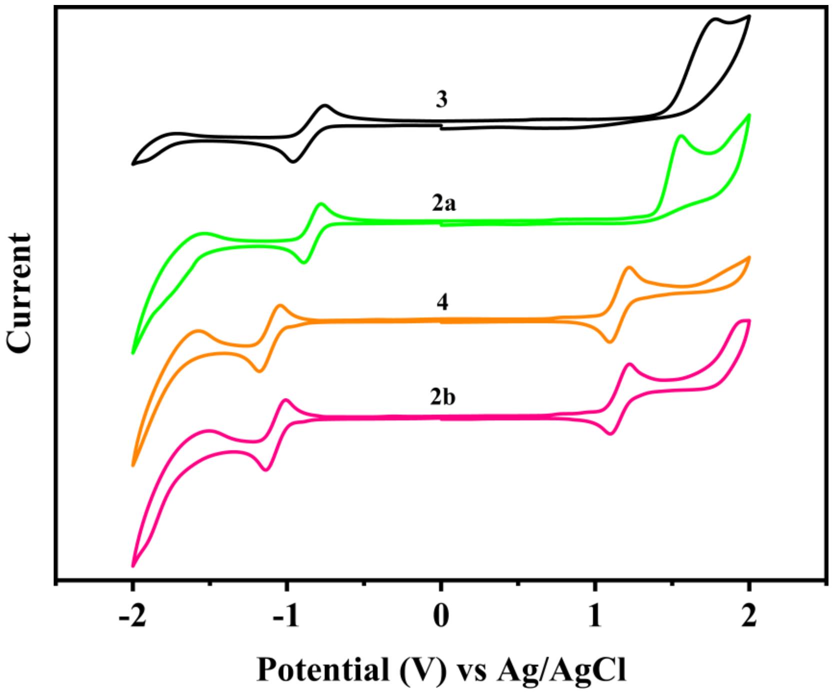


Figure S23. Cyclic voltammograms of **3**, **2a**, **4** and **2b** in dichloromethane with 0.1 M *n*-Bu_4PF_6 as supporting electrolyte (scan rate: 50 mV s^{-1}).

3

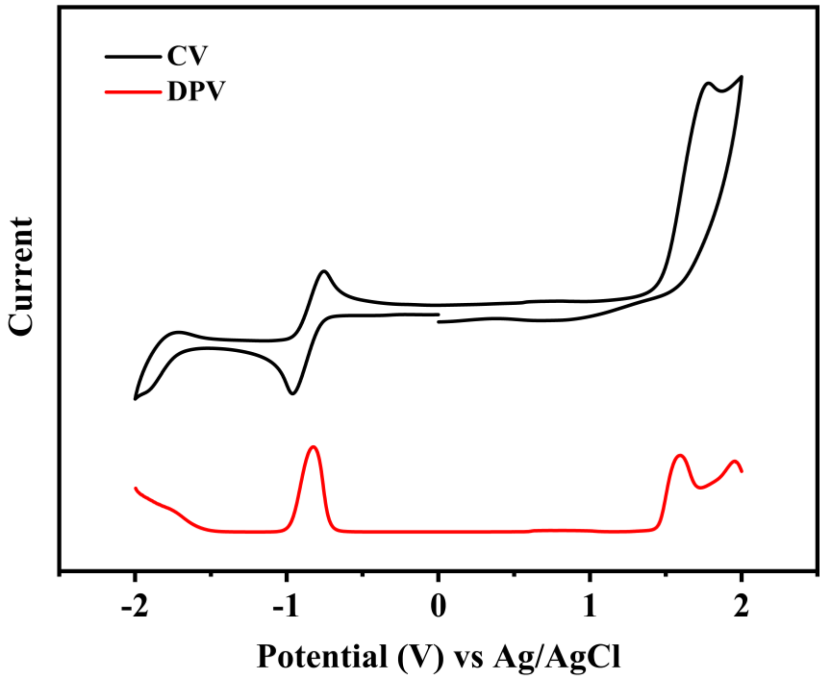


Figure S24. Cyclic voltammograms (CV) and Differential Pulse Voltammetry (DPV) of **3** in dichloromethane with 0.1 M n-Bu_4PF_6 as supporting electrolyte (scan rate: 50 mV s^{-1}).

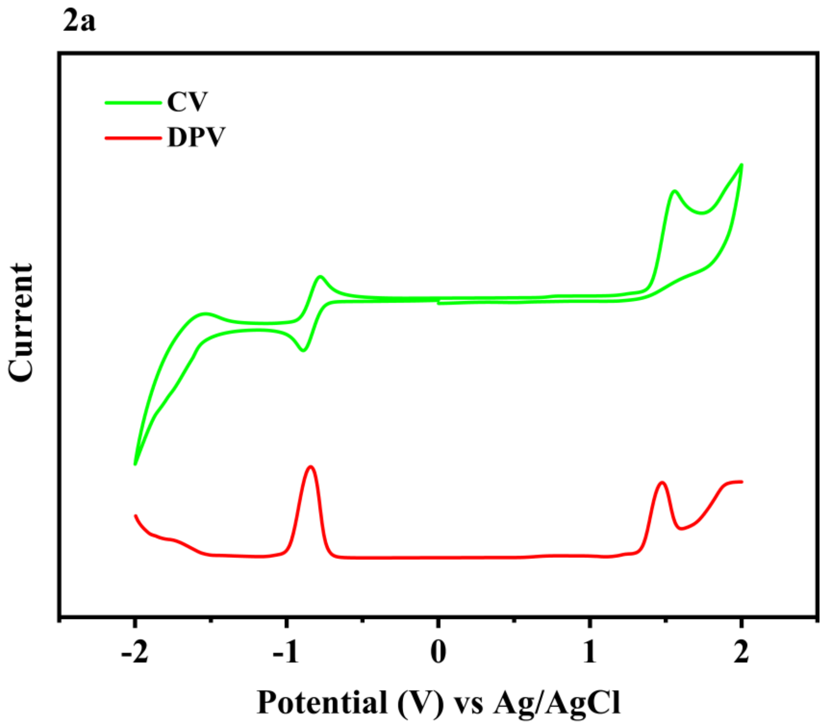


Figure S25. Cyclic voltammograms (CV) and Differential Pulse Voltammetry (DPV) of **2a** in dichloromethane with 0.1 M n-Bu_4PF_6 as supporting electrolyte (scan rate: 50 mV s^{-1}).

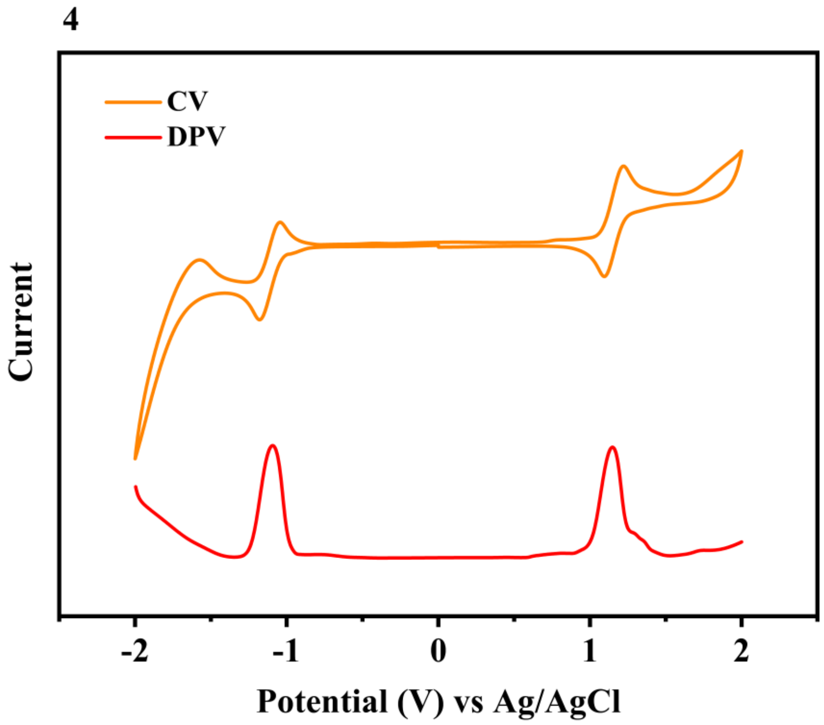


Figure S26. Cyclic voltammograms (CV) and Differential Pulse Voltammetry (DPV) of **4** in dichloromethane with 0.1 M n-Bu_4PF_6 as supporting electrolyte (scan rate: 50 mV s^{-1}).

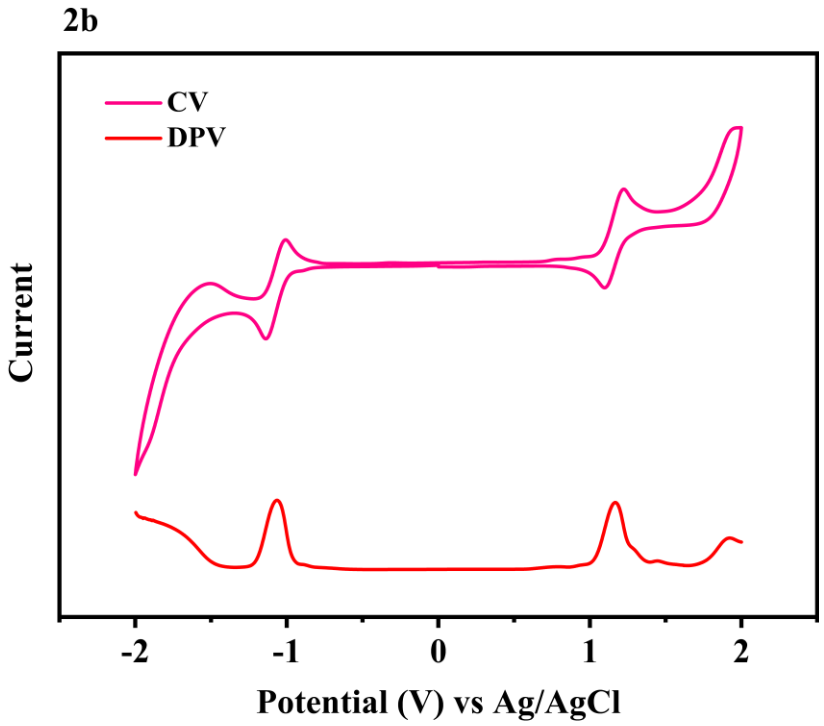


Figure S27. Cyclic voltammograms (CV) and Differential Pulse Voltammetry (DPV) of **2b** in dichloromethane with 0.1 M n-Bu_4PF_6 as supporting electrolyte (scan rate: 50 mV s^{-1}).

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[9,10]/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, where ring centers are located as ring critical points (RCPs) by topology analysis[11]. The effect of the solvent was considered in all the calculations utilizing the integral equation formalism polarized continuum model (IEF-PCM[12,13]) with the dichloromethane as solvent. All the quantum chemical calculations were performed using the Gaussian 16 software suit[14]. The wavefunction analysis was calculated by means of the Multiwfn version 3.8(dev)[15,16] code and plotted using VMD[17] software.

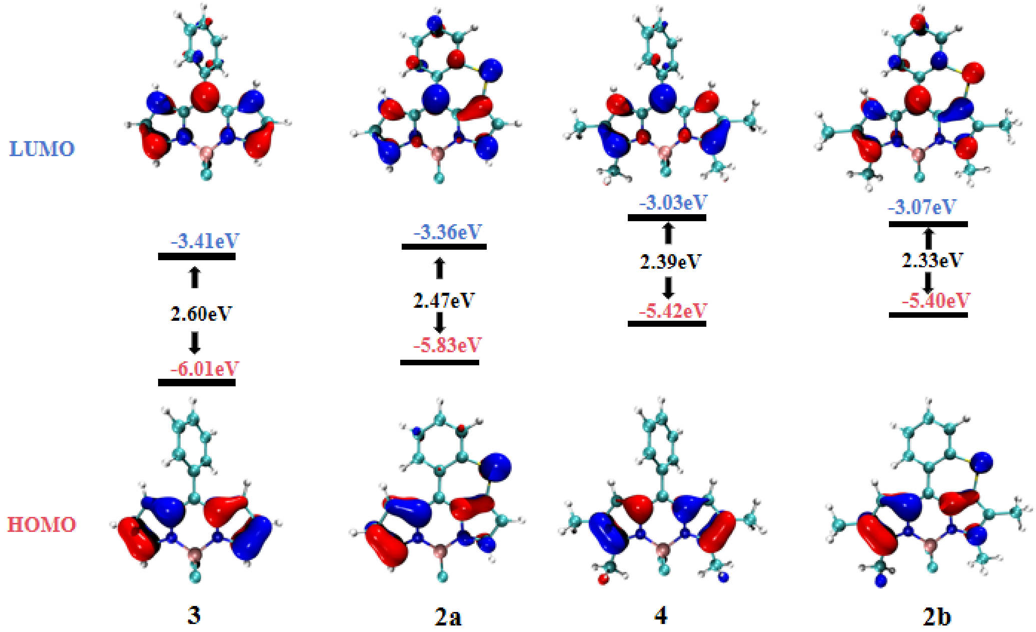
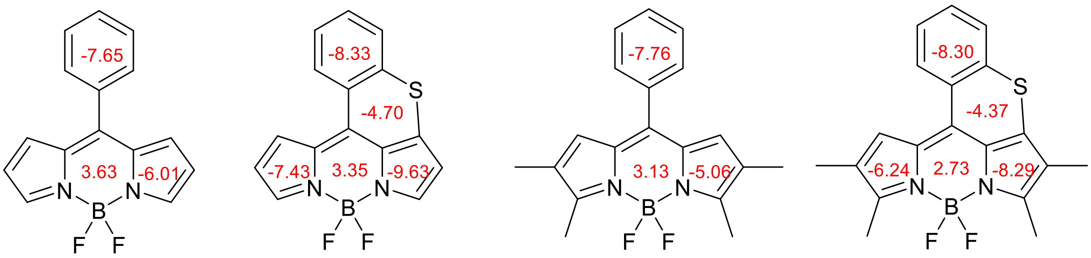


Figure S28. Pictorial presentation of LUMO, HOMO and their energy levels for **3**, **2a**, **4**, **2b**.



3 **2a** **4** **2b**

Figure S29. NICS(0) values of rings in **3**, **2a**, **4**, **2b**.

Table S5. The excited state properties of complexes **3**, **4**, **2a**, **2b** calculated at the IEF-PCM(dichloromethane)-TPSSh/6-311+G(d, p) level.

Complexes	**S_n**	**λ_{max}(nm)**	**E_{ex}(eV)**	***f***	**Major Contributions**
3	S1	424.94	2.9177	0.43090	H → L 91.9% H-2 → L 7.5%
	S3	371.38	3.3385	0.18150	H-1 → L 98.2%
	S4	357.66	3.4665	0.10120	H-3 → L 71.6% H-2 → L 21.8% H → L 6.1%
2a	S1	462.59	2.6802	0.31410	H → L 79.8% H-1 → L 19.4%
	S2	434.00	2.8568	0.17080	H-1 → L 77.8% H → L 19.0%
	S4	348.76	3.5550	0.25040	H-3 → L 90.2%
4	S1	460.53	2.6922	0.51780	H → L 96.0% H-1 → L 5.1%
	S2	363.92	3.4069	0.14270	H-1 → L 93.1% H → L 5.0%
	S3	351.83	3.5240	0.24880	H-2 → L 84.5% H-3 → L 11.5%
2b	S1	479.69	2.5847	0.49850	H → L 96.3%
	S4	349.35	3.5490	0.24700	H-3 → L 82.2% H-2 → L 9.3%

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

31

3

C	-4.011456	0.750826	-0.946578
C	-2.618107	0.759491	-0.943805
C	-1.906750	0.000028	0.000010
C	-2.618102	-0.759464	0.943807
C	-4.011449	-0.750792	0.946594
C	-4.711160	0.000023	0.000014
C	-0.427365	0.000018	0.000013
C	0.277294	-1.214839	-0.059390
N	1.672141	-1.241441	-0.043251
B	2.602144	-0.000027	0.000005
N	1.672177	1.241417	0.043235
C	0.277329	1.214859	0.059404

C	-0.181624	-2.550059	-0.190135
C	0.940980	-3.368719	-0.237285
C	2.062822	-2.526192	-0.148776
C	2.062902	2.526149	0.148812
C	0.941090	3.368725	0.237223
C	-0.181542	2.550103	0.190089
H	-4.549813	1.328283	-1.690340
H	-2.076257	1.329642	-1.690279
H	-2.076244	-1.329636	1.690261
H	-4.549801	-1.328260	1.690351
H	-5.795880	0.000018	0.000014
H	-1.215811	-2.851996	-0.253435
H	0.967283	-4.443543	-0.333220
H	3.111567	-2.785084	-0.165021
H	3.111656	2.785003	0.165101
H	0.967428	4.443552	0.333120
H	-1.215717	2.852081	0.253367
F	3.418436	0.036184	-1.145479
F	3.418395	-0.036261	1.145501

43

4

C	4.442498	-0.692650	-0.996041
C	3.048414	-0.694982	-0.993939
C	2.338474	-0.009109	0.004592
C	3.053266	0.672936	1.002318
C	4.447315	0.662023	1.003622
C	5.145426	-0.017583	0.003652
C	0.855424	-0.003898	0.006260
C	0.160964	1.214761	-0.008993
N	-1.234054	1.254881	0.010393
B	-2.157858	0.008932	0.034224
N	-1.244912	-1.244939	0.002533
C	0.150561	-1.216896	0.016651
C	0.630379	2.548683	-0.089838
C	-0.475719	3.389460	-0.107518
C	-1.621485	2.552362	-0.046254
C	-1.642969	-2.540367	0.037378
C	-0.504098	-3.387667	0.078290
C	0.609004	-2.555627	0.073343
H	4.978805	-1.215545	-1.780829

H	2.504260	-1.208070	-1.779427
H	2.512603	1.189988	1.787634
H	4.987288	1.181966	1.787854
H	6.230268	-0.020927	0.003308
H	1.668828	2.842240	-0.138704
H	1.644965	-2.858861	0.114632
F	-3.017337	0.017306	-1.084387
F	-2.942143	0.008165	1.211576
C	-3.050826	2.979157	-0.071351
H	-3.399119	3.091436	-1.104965
H	-3.693389	2.251250	0.423536
H	-3.161415	3.948777	0.420006
C	-0.491882	4.887280	-0.187264
H	-1.009286	5.236279	-1.087364
H	-1.004484	5.329473	0.674055
H	0.526457	5.280574	-0.210383
C	-3.075443	-2.956253	0.008367
H	-3.718616	-2.204331	0.465361
H	-3.409474	-3.103773	-1.025623
H	-3.202207	-3.905312	0.534173
C	-0.530537	-4.886963	0.119796
H	-1.109630	-5.255230	0.973494
H	-0.983679	-5.306026	-0.785228
H	0.482611	-5.285417	0.203743

30

2a

C	-3.453625	2.178510	0.519340
C	-2.102259	1.903595	0.440662
C	-1.612514	0.620533	0.090025
C	-2.582123	-0.407494	-0.086424
C	-3.956729	-0.113743	-0.027134
C	-4.391056	1.168598	0.255346
C	-0.180958	0.374745	-0.025432
C	0.804773	1.395117	-0.166533
N	2.157339	1.059188	-0.066610
B	2.728934	-0.327082	0.324753
N	1.589171	-1.330931	0.030731
C	0.261960	-0.955790	-0.019364
C	0.735993	2.753426	-0.554965
C	2.044361	3.225869	-0.666516

C	2.890404	2.157665	-0.351185
C	1.642897	-2.685212	-0.057370
C	0.366870	-3.225529	-0.194587
C	-0.515906	-2.132464	-0.158060
S	-2.223038	-2.102902	-0.366567
H	-3.785544	3.170677	0.802766
H	-1.391072	2.676167	0.696379
H	-4.675256	-0.911444	-0.183747
H	-5.453661	1.377371	0.306204
H	-0.158832	3.306026	-0.791885
H	2.356454	4.217016	-0.959292
H	3.969145	2.119546	-0.321881
H	2.591153	-3.200041	-0.012597
H	0.119519	-4.269219	-0.307503
F	3.865121	-0.625934	-0.441438
F	3.069761	-0.357290	1.694458

42

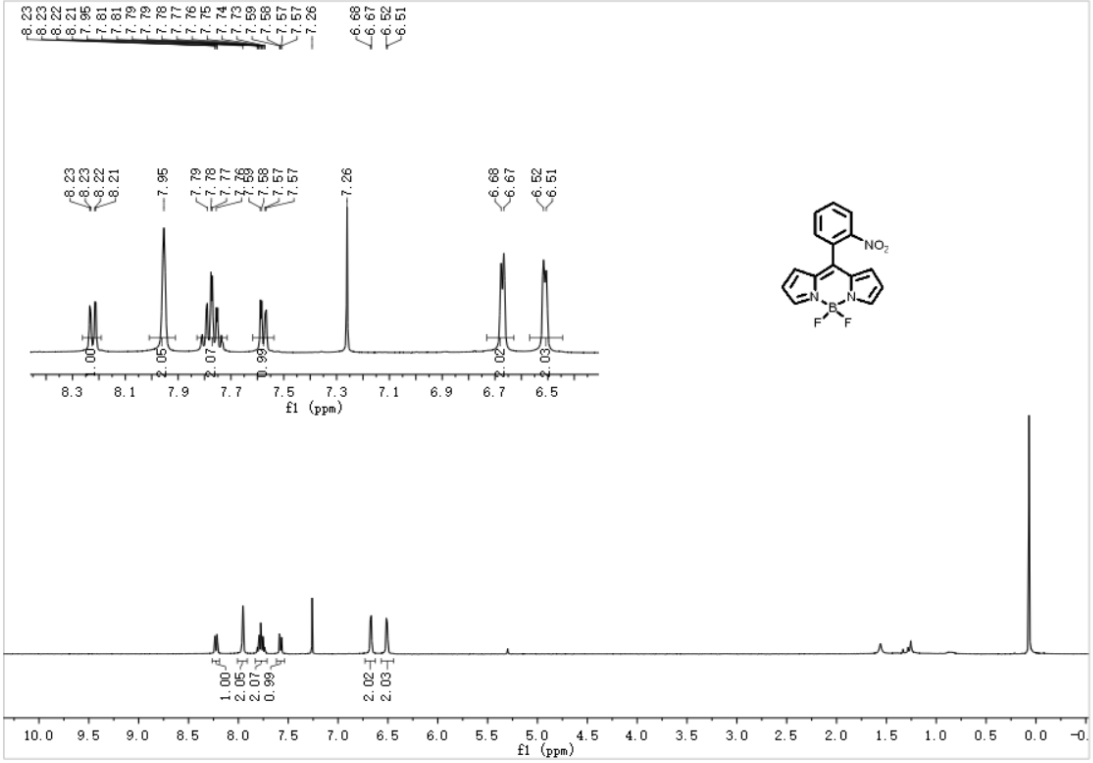
2b

C	2.555307	-3.695844	0.579668
C	1.456452	-2.858891	0.515595
C	1.559737	-1.500843	0.126548
C	2.874597	-1.004469	-0.094625
C	3.985668	-1.865847	-0.050682
C	3.829557	-3.204271	0.264038
C	0.369039	-0.656167	0.024699
C	-0.960170	-1.149906	-0.058915
N	-2.039539	-0.267969	0.071890
B	-1.946539	1.260778	0.320806
N	-0.470752	1.654962	0.090205
C	0.552229	0.733195	0.012010
C	-1.496632	-2.424140	-0.356383
C	-2.885646	-2.317531	-0.379338
C	-3.192238	-0.968374	-0.094702
C	0.075178	2.908855	0.013206
C	1.467926	2.822808	-0.153854
C	1.761916	1.447945	-0.141599
S	3.282087	0.677962	-0.403447
H	2.428701	-4.726187	0.892077
H	0.489465	-3.238880	0.812192
H	4.974444	-1.462202	-0.242905

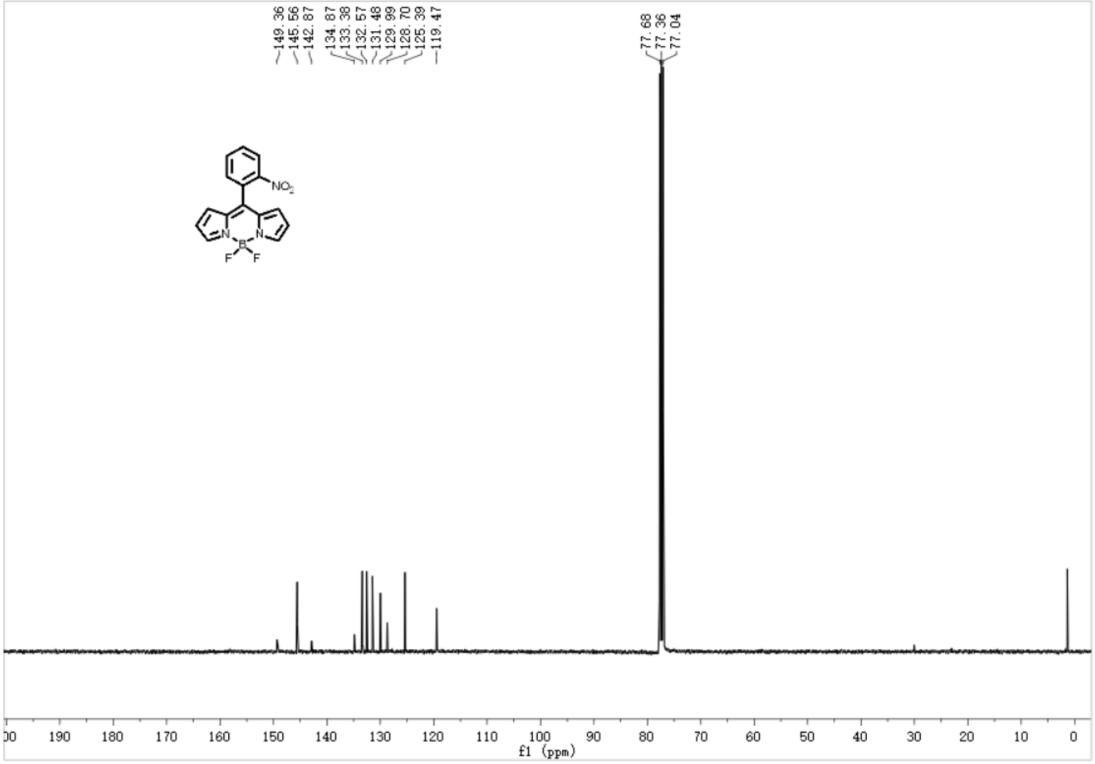
H	4.696837	-3.853763	0.302165
H	-0.935584	-3.315733	-0.588354
F	-2.777484	1.951091	-0.584817
F	-2.349553	1.578378	1.640373
C	-4.548468	-0.351565	0.007868
H	-4.581925	0.408670	0.790171
H	-4.833561	0.130079	-0.933838
H	-5.289809	-1.121901	0.230211
C	-3.877134	-3.407445	-0.664409
H	-4.568816	-3.550417	0.173123
H	-4.481083	-3.182984	-1.550069
H	-3.363979	-4.355554	-0.839416
C	-0.765521	4.138965	0.100861
H	-1.300997	4.310497	-0.838515
H	-1.512246	4.043761	0.892080
H	-0.144379	5.012005	0.304605
C	2.445027	3.945782	-0.327560
H	3.324199	3.803388	0.309060
H	2.796282	4.014134	-1.363475
H	1.996174	4.906094	-0.067211

7. ^{1}H, ^{13}C, ^{19}F NMR and HRMS spectra for all new compounds

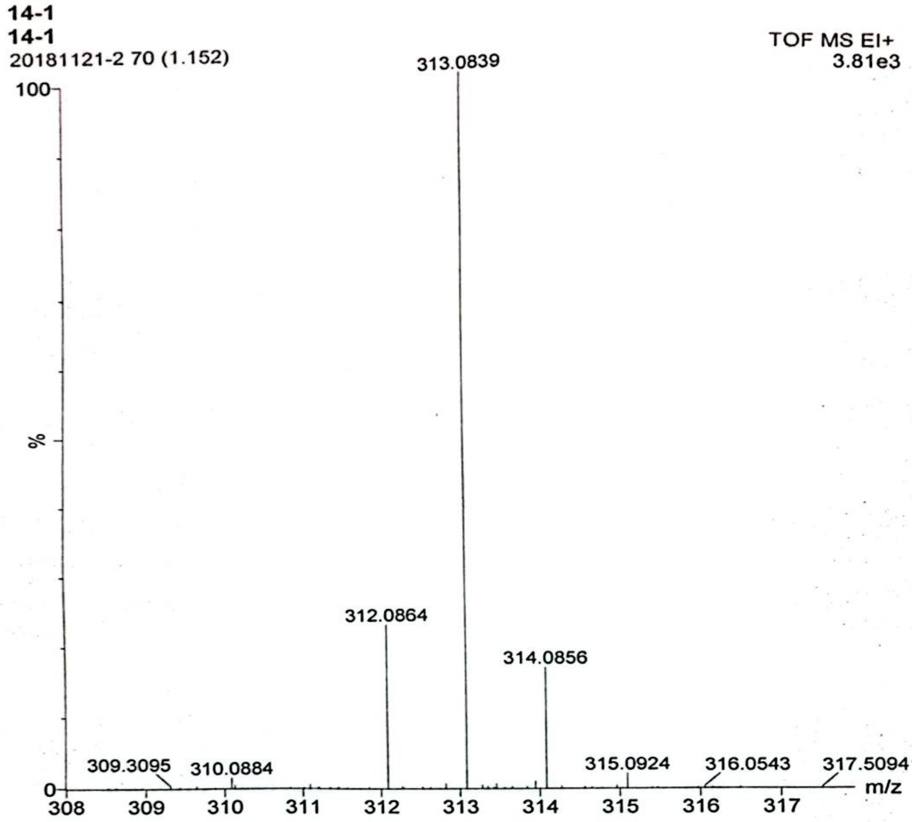
^{1}H NMR specta of compound **1a** in $CDCl_3$ (400 MHz)



^{13}C NMR Spectra of compound **1a** in $CDCl_3$ (101 MHz)



HRMS Spectrum of **1a**



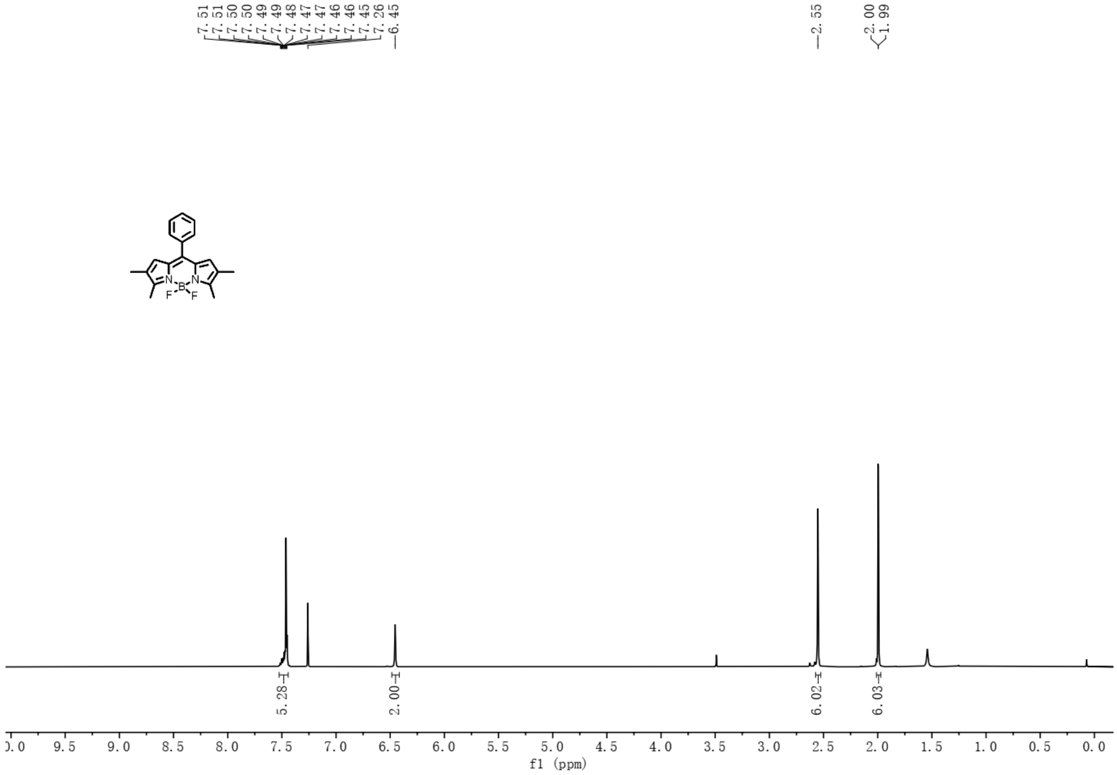
Elemental Composition Report

Tolerance = 100.0 PPM / DBE: min = -1.5, max = 50.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

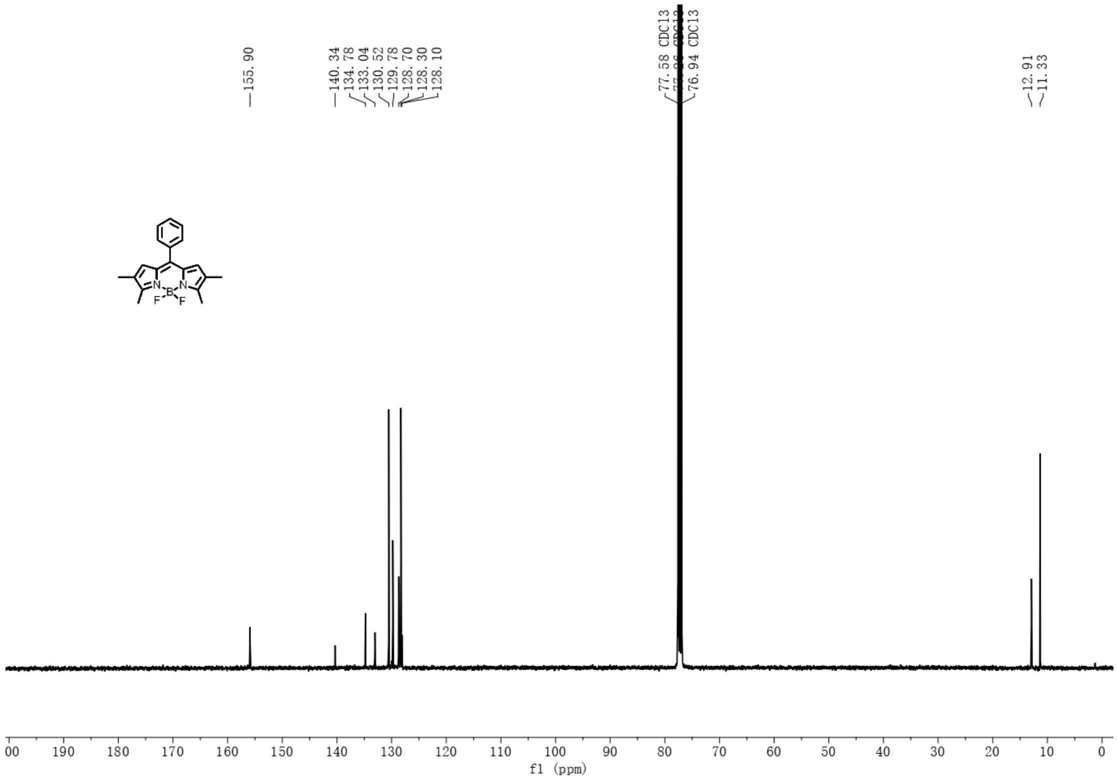
Monoisotopic Mass, Odd and Even Electron Ions
60 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Minimum:	30.00				-1.5		
Maximum:	100.00		200.0	100.0	50.0		
Mass	RA	Calc. Mass	mDa	PPM	DBE	Score	Formula
313.0839	100.00	313.0834	0.5	1.6	12.0	1	C15 H10 B N3 O2 F2

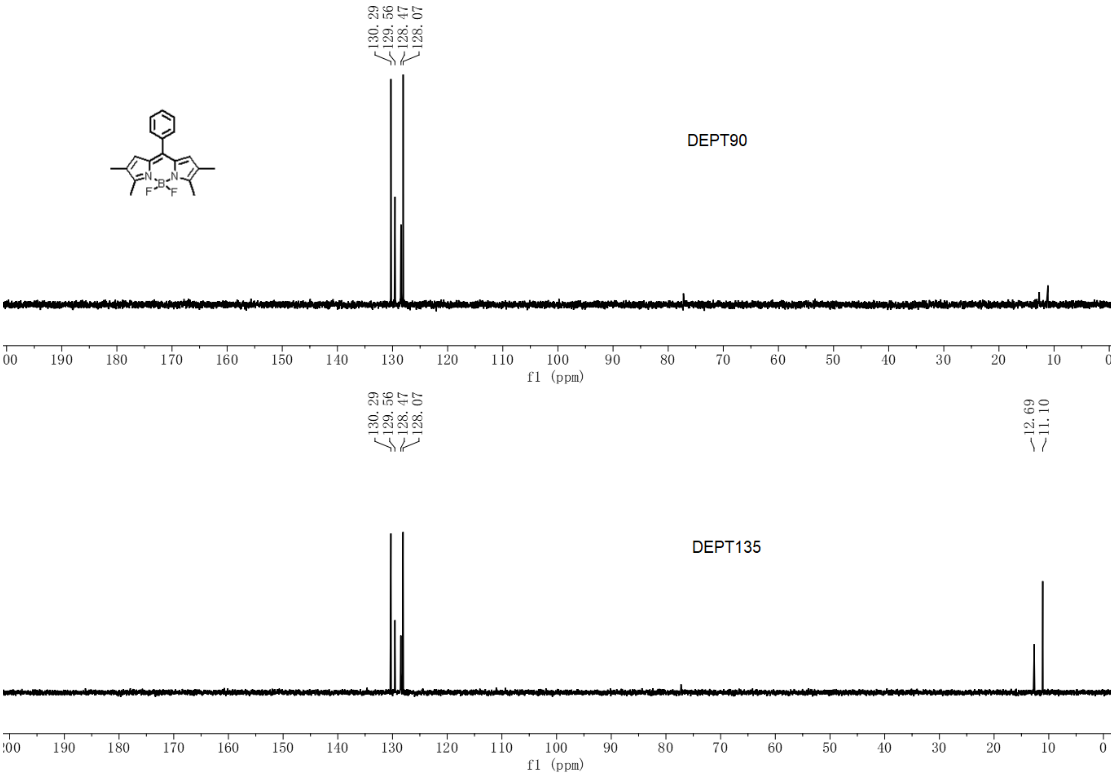
^{1}H NMR specta of compound **4** in $CDCl_3$ (400 MHz)



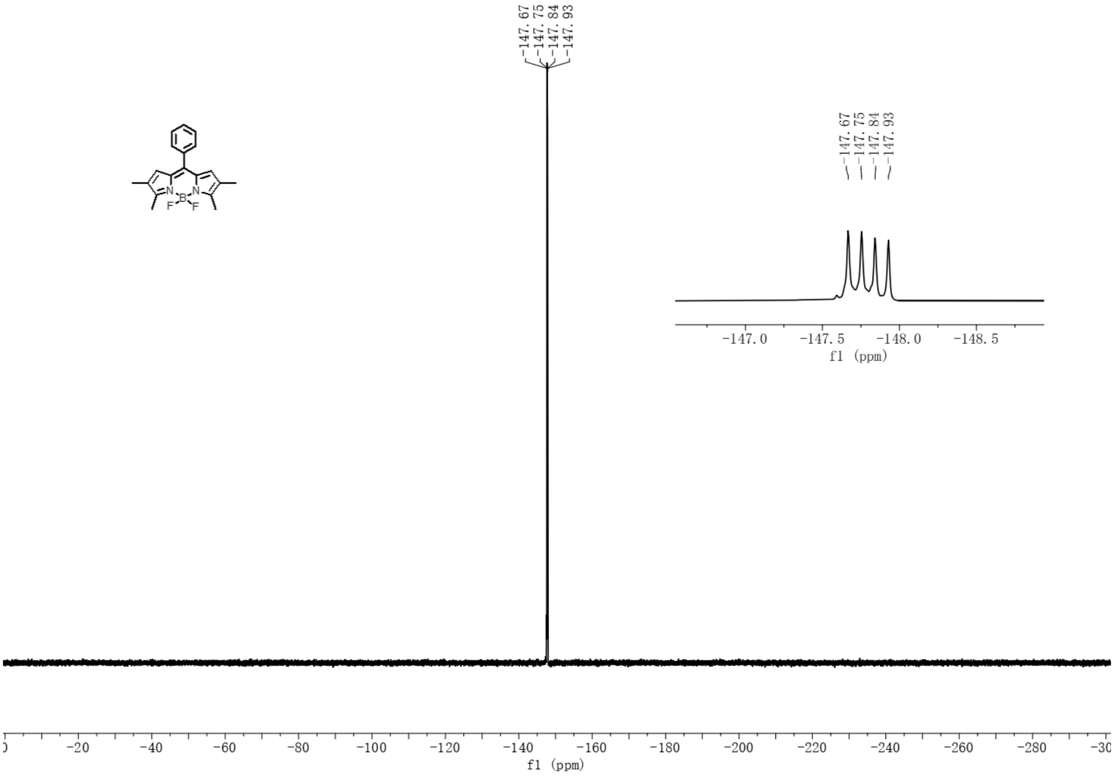
^{13}C NMR Spectra of compound **4** in $CDCl_3$ (101 MHz)



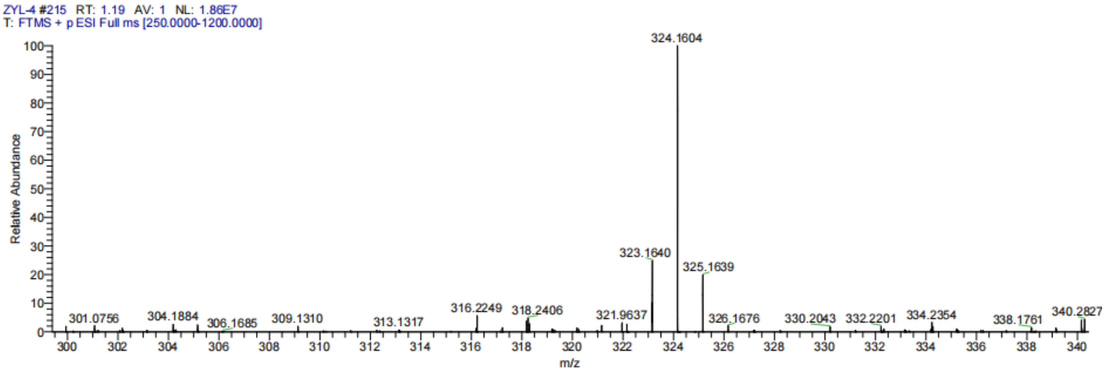
DEPT Spectra of compound **4** in $CDCl_3$ (101 MHz)



^{19}F NMR Spectra of compound **4** in $CDCl_3$ (376 MHz)



Observed HRMS Spectra of compound **4**



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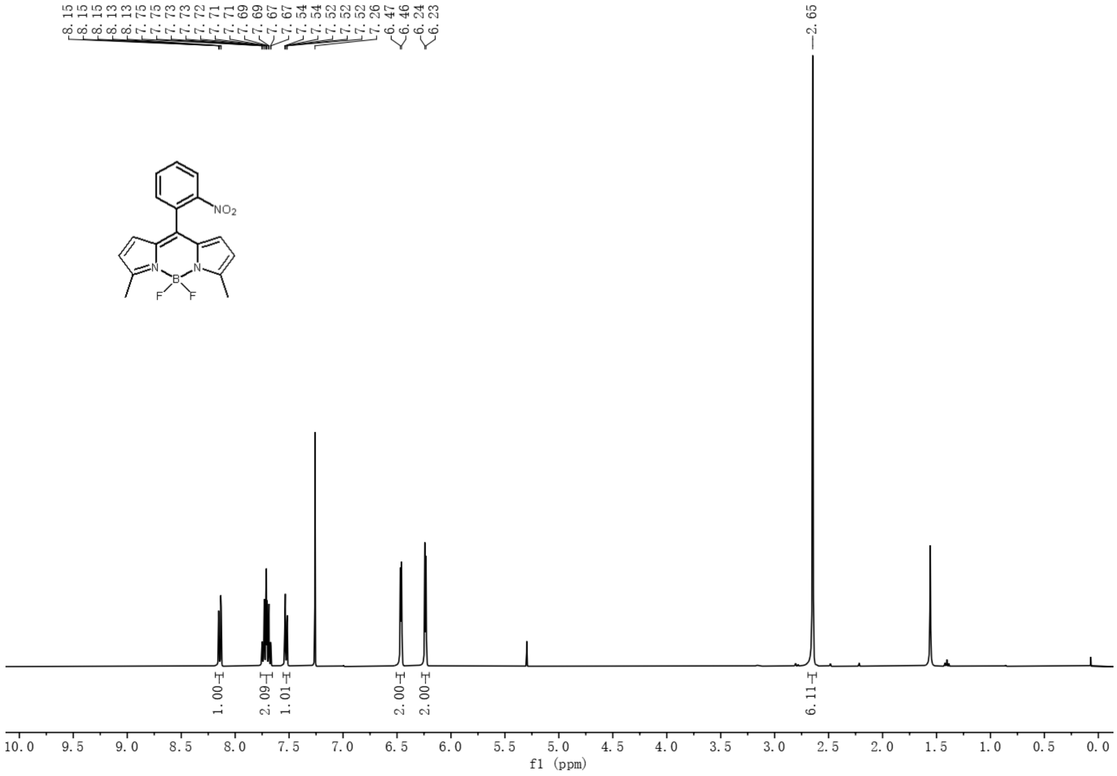
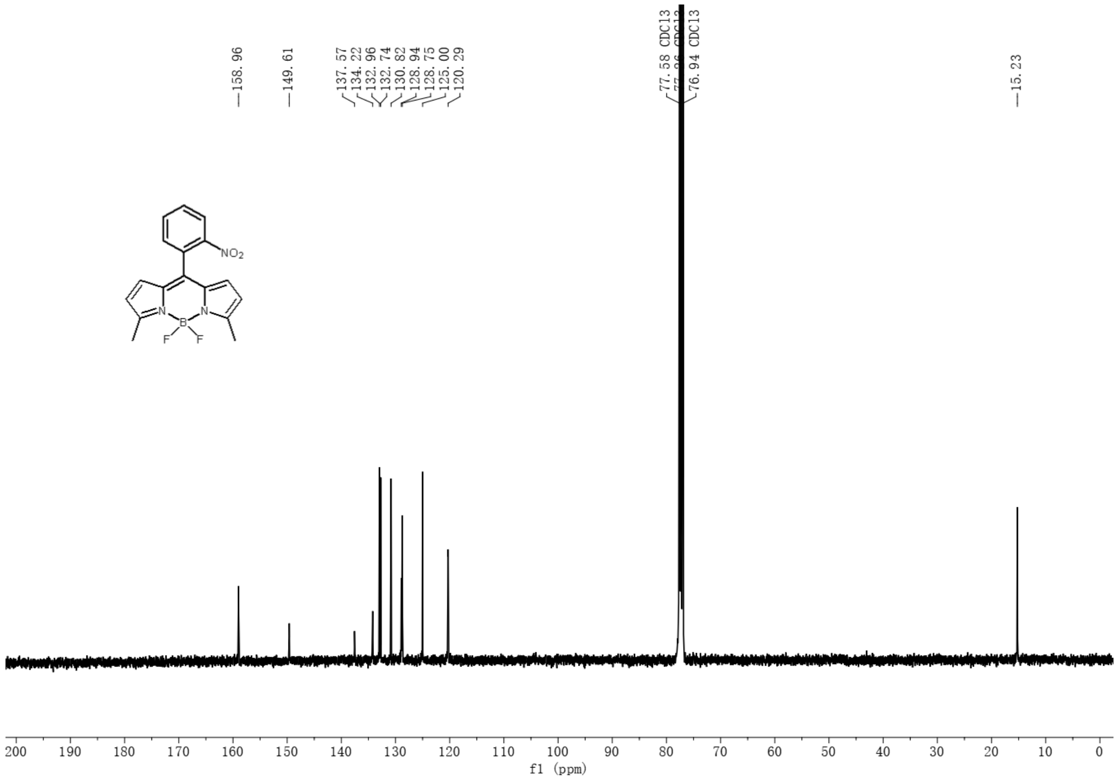
T: FTMS + p ESI Full ms [250.0000-1200.0000]
m/z= 299.3982-340.4334
     m/z     Intensity  Relative Theo. Mass  Delta     Composition
                                             (ppm)
  324.1604  18621030.0   100.00   324.1604   -0.02 C19 H19 N2 B F2
```

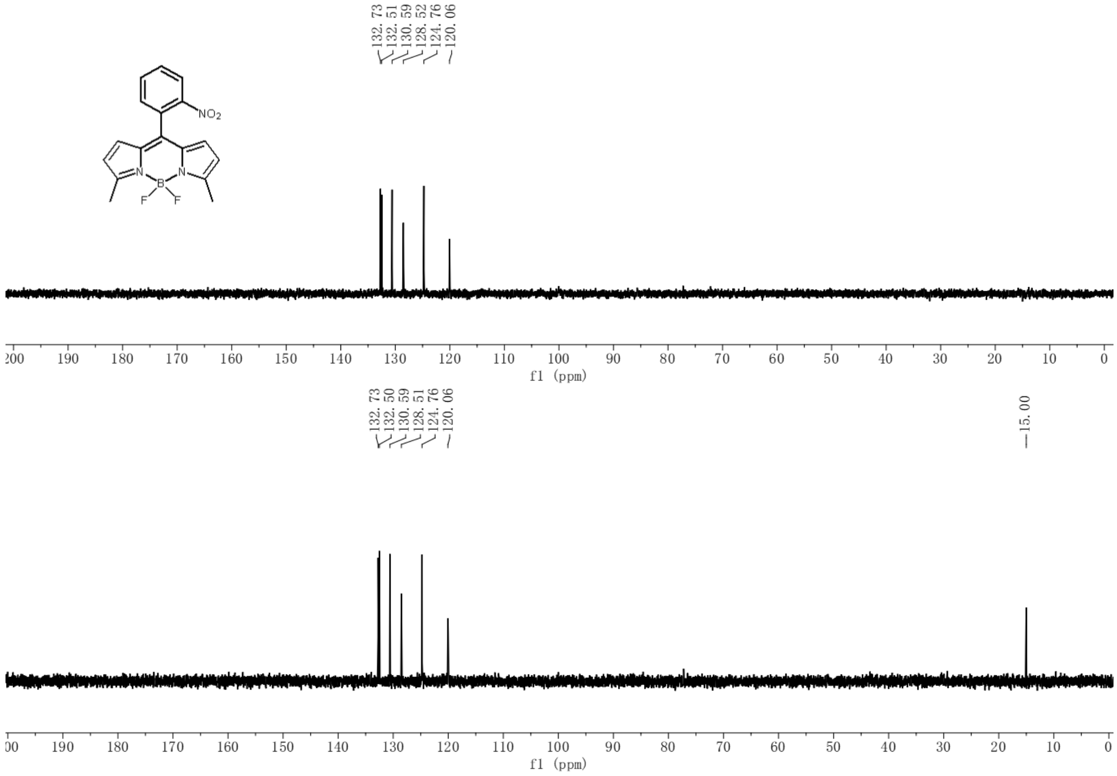
^{1}H NMR specta of compound **1-1b** in $CDCl_3$ (400 MHz)



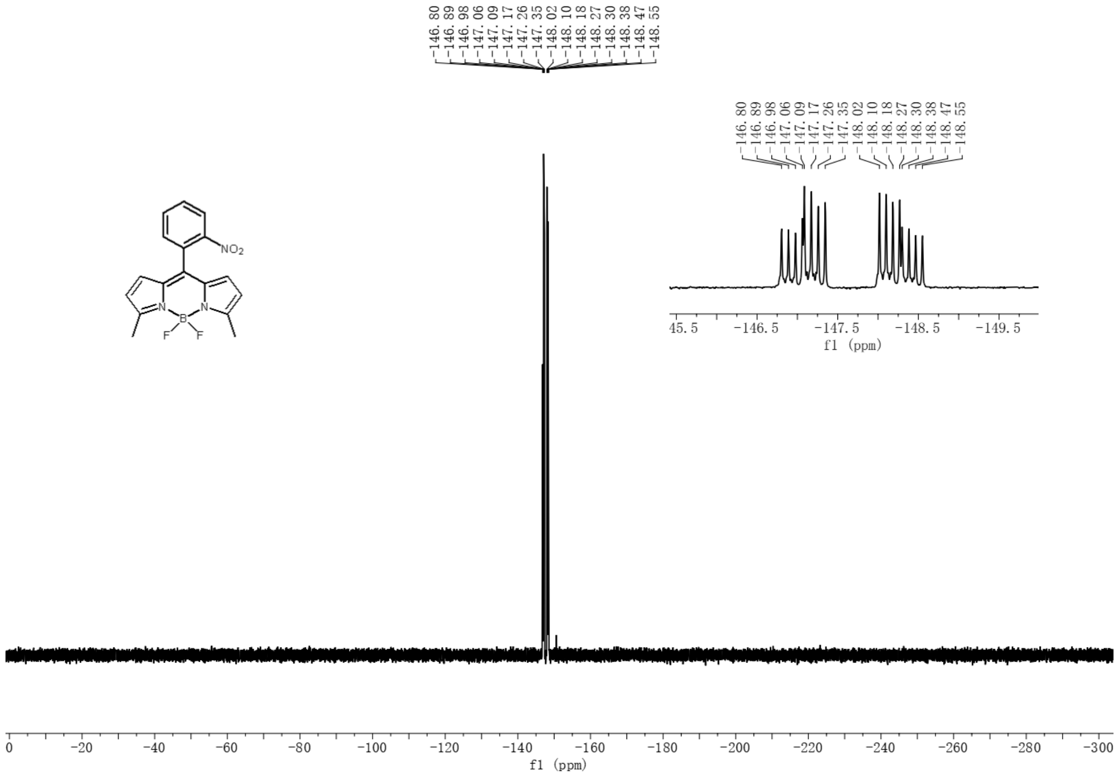
^{13}C NMR Spectra of compound **1-1b** in $CDCl_3$ (101 MHz)



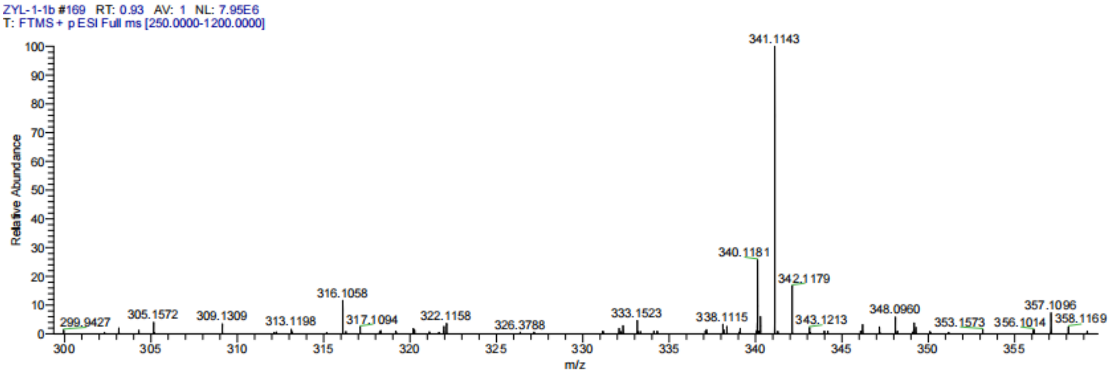
DEPT Spectra of compound **1-1b** in $CDCl_3$ (101 MHz)

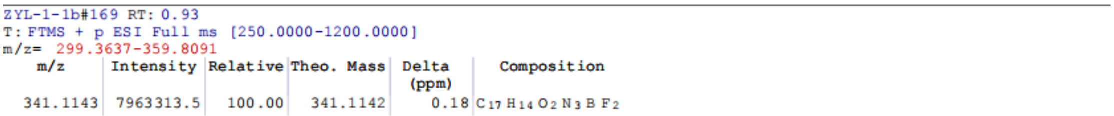


^{19}F NMR Spectra of compound **1-1b** in $CDCl_3$ (376 MHz)



Observed HRMS Spectra of compound **1-1b**





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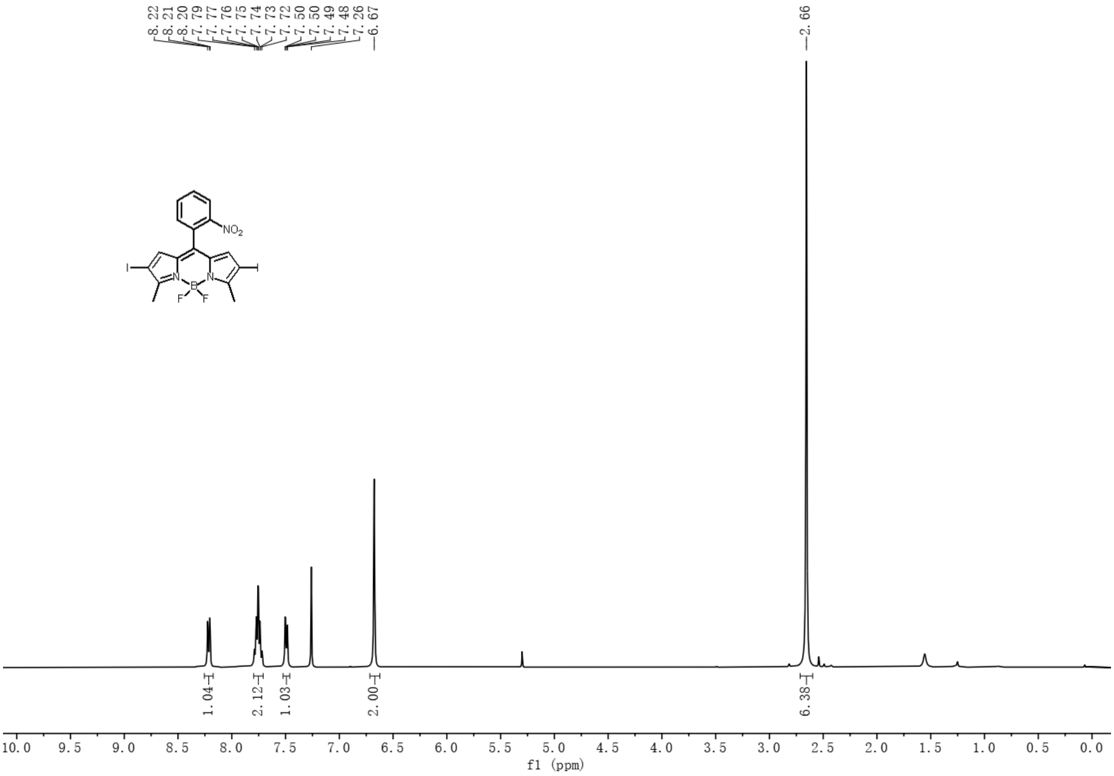
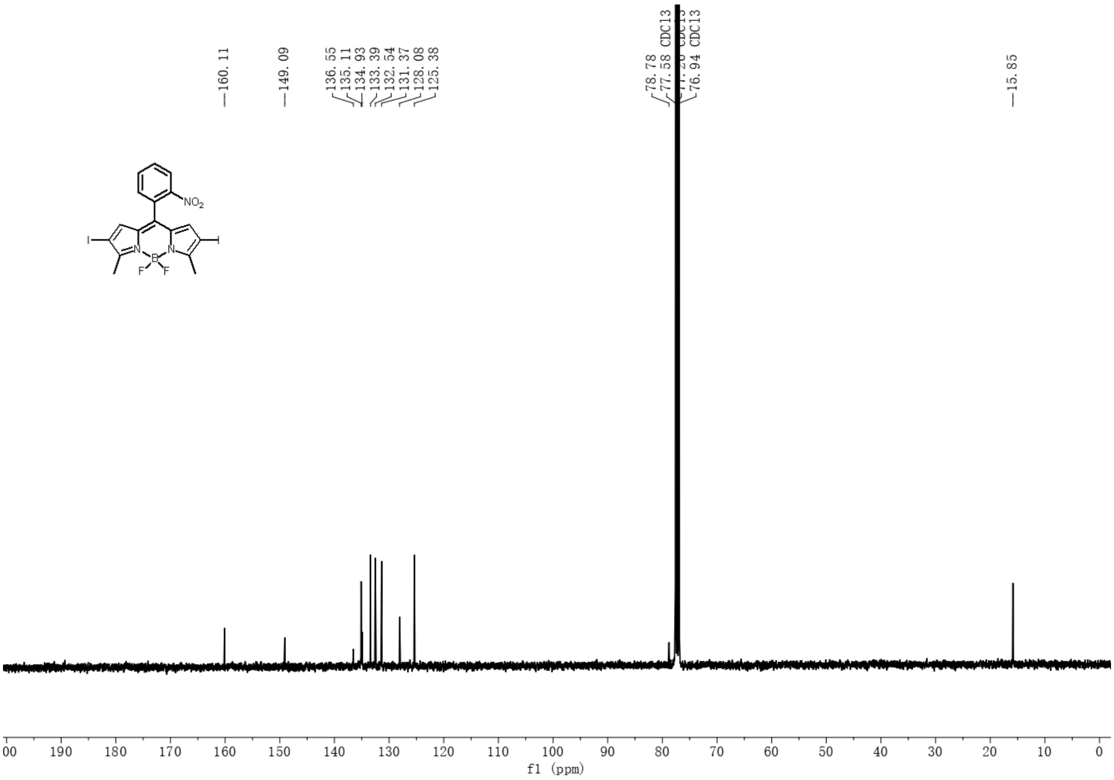
m/z= 299.3637-359.8091
     m/z   | Intensity |Relative|Theo. Mass| Delta  |    Composition
           |           |        |          | (ppm)  |
  341.1143 | 7963313.5 | 100.00 | 341.1142 |   0.18 |C17 H14 O2 N3 B F2
```

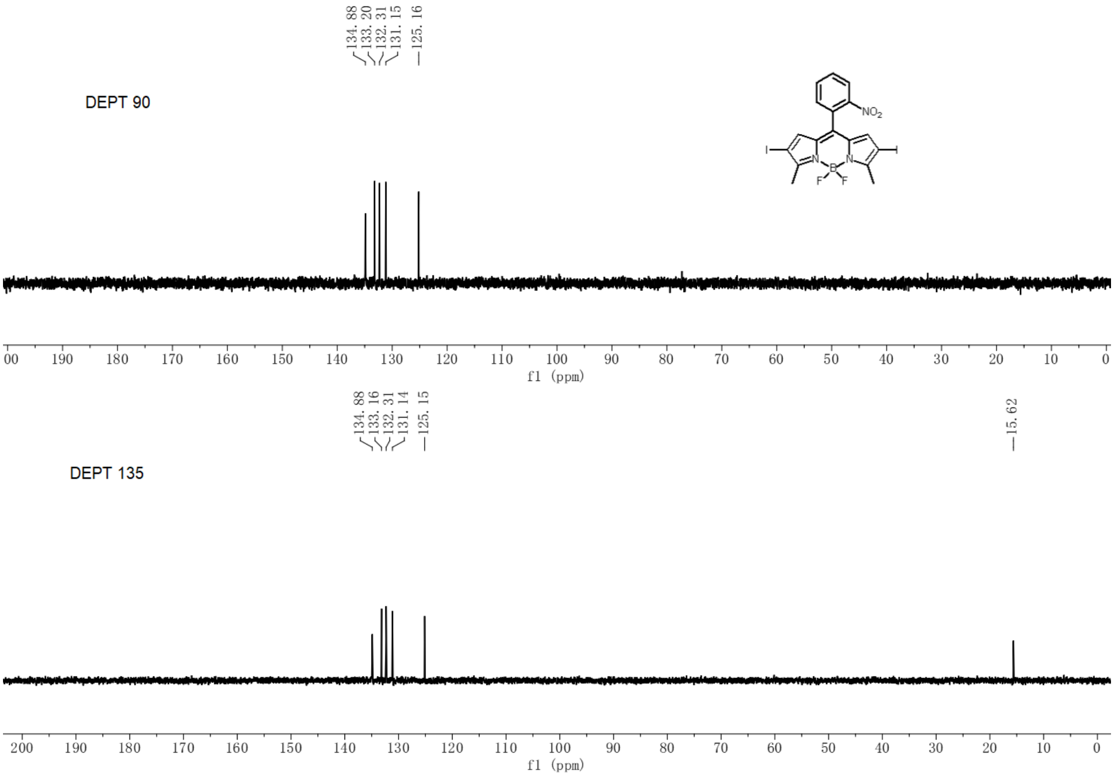
^{1}H NMR specta of compound **1-2b** in $CDCl_3$ (400 MHz)



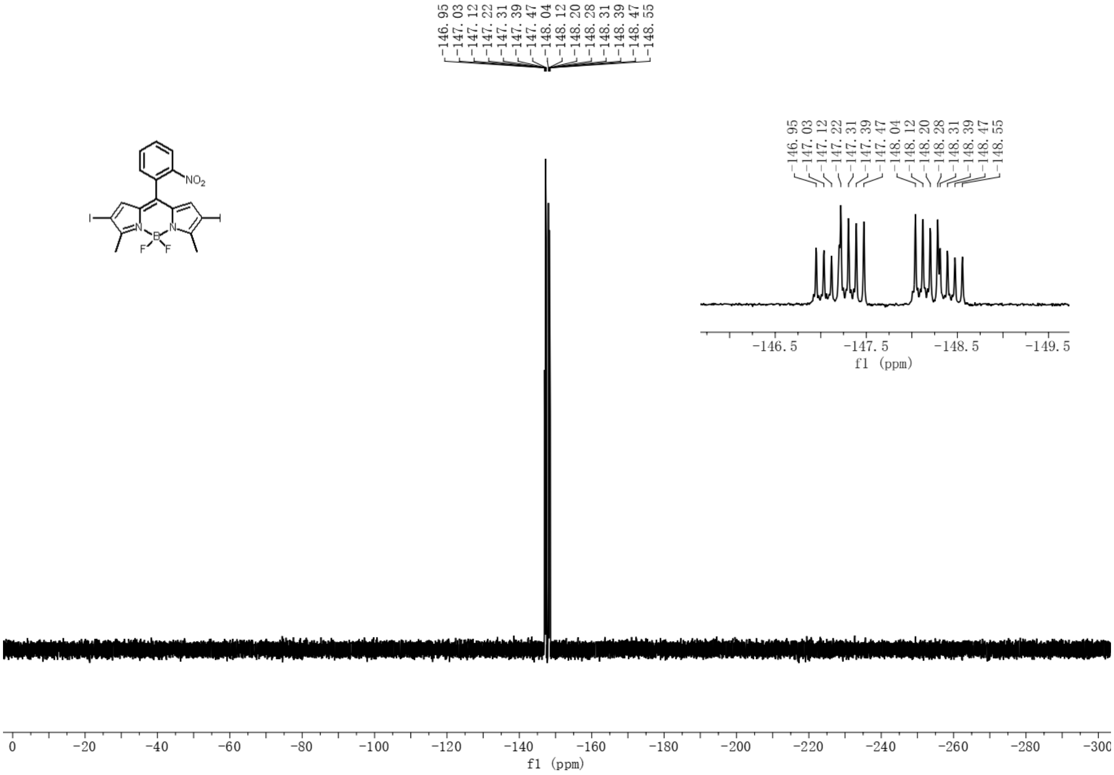
^{13}C NMR Spectra of compound **1-2b** in $CDCl_3$ (101 MHz)



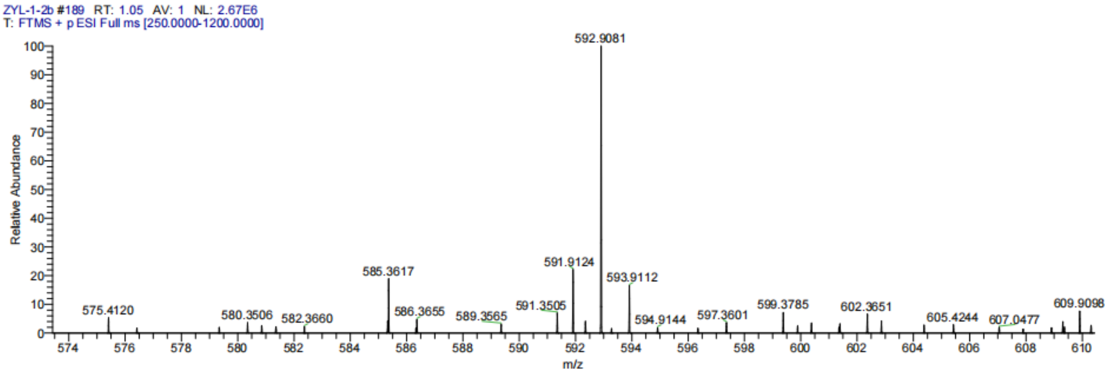
DEPT Spectra of compound **1-2b** in $CDCl_3$ (101 MHz)



^{19}F NMR Spectra of compound **1-2b** in $CDCl_3$ (376 MHz)



Observed HRMS Spectra of compound **1-2b**



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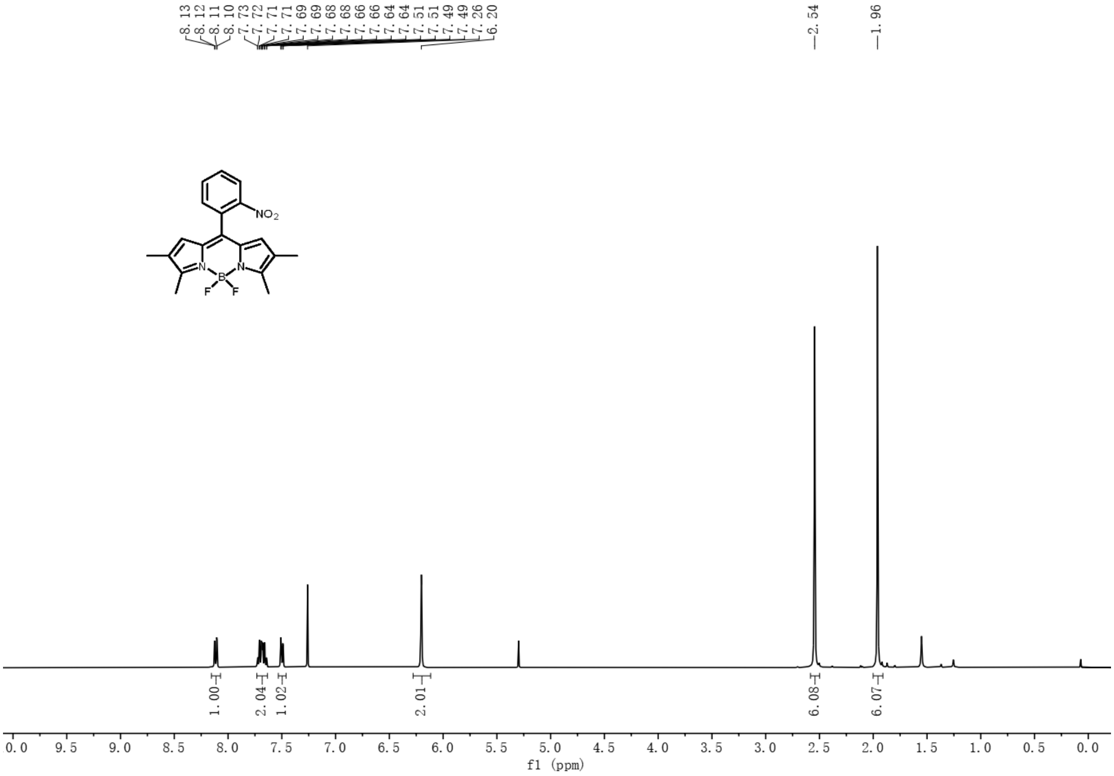
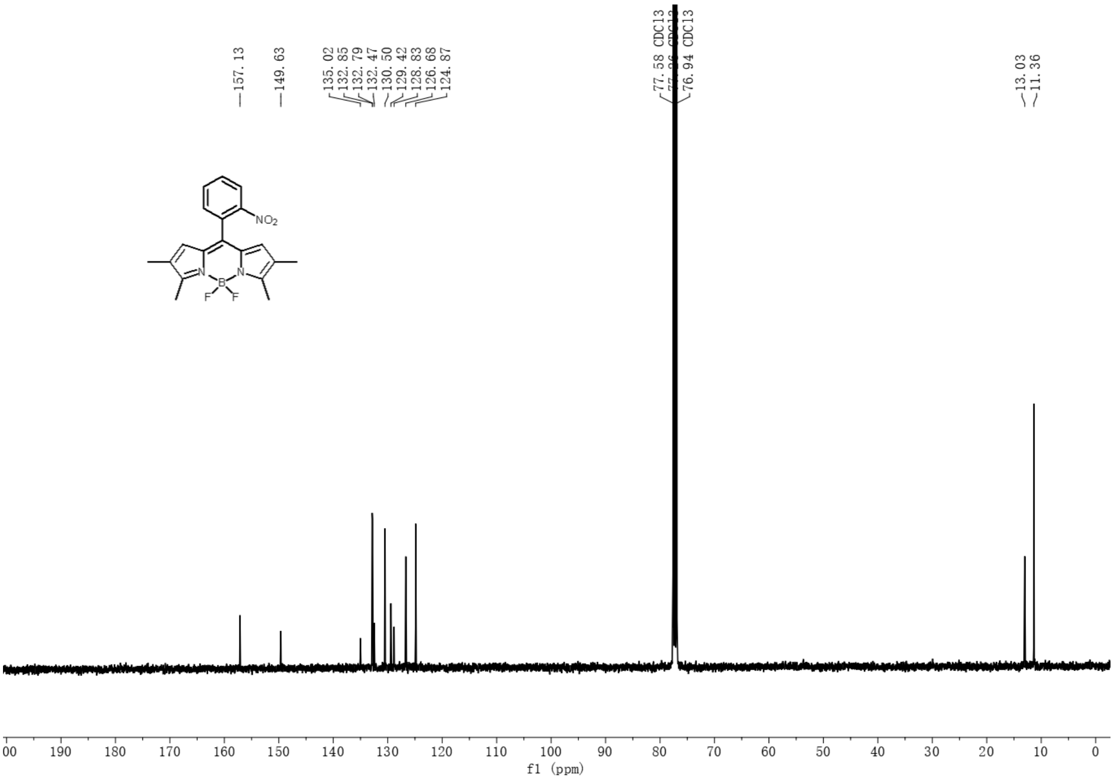
ZYL-1-2b#189 RT: 1.05
T: FTMS + p ESI Full ms [250.0000-1200.0000]
m/z= 573.4218-610.4330
     m/z    Intensity Relative Theo. Mass  Delta      Composition
                                           (ppm)
  592.9081  2836550.0   100.00   592.9075    0.63 C17 H12 O2 N3 B F2 I2
```

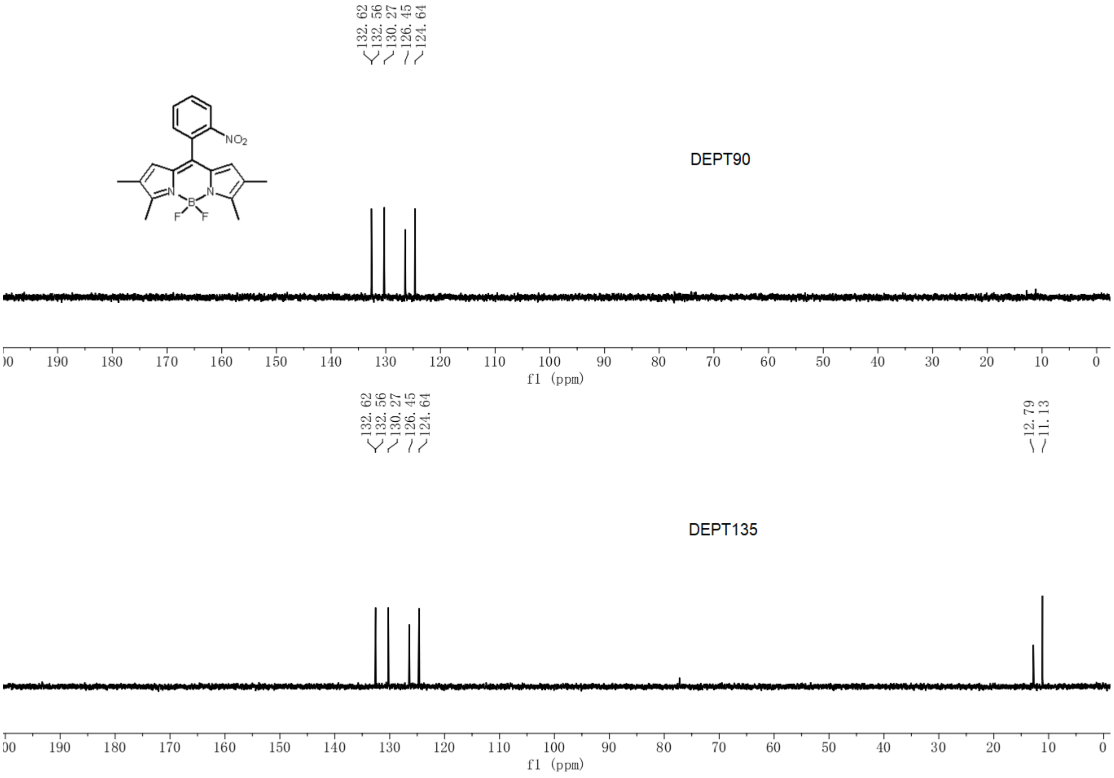
^{1}H NMR specta of compound **1b** in CDCl$_3$ (400 MHz)



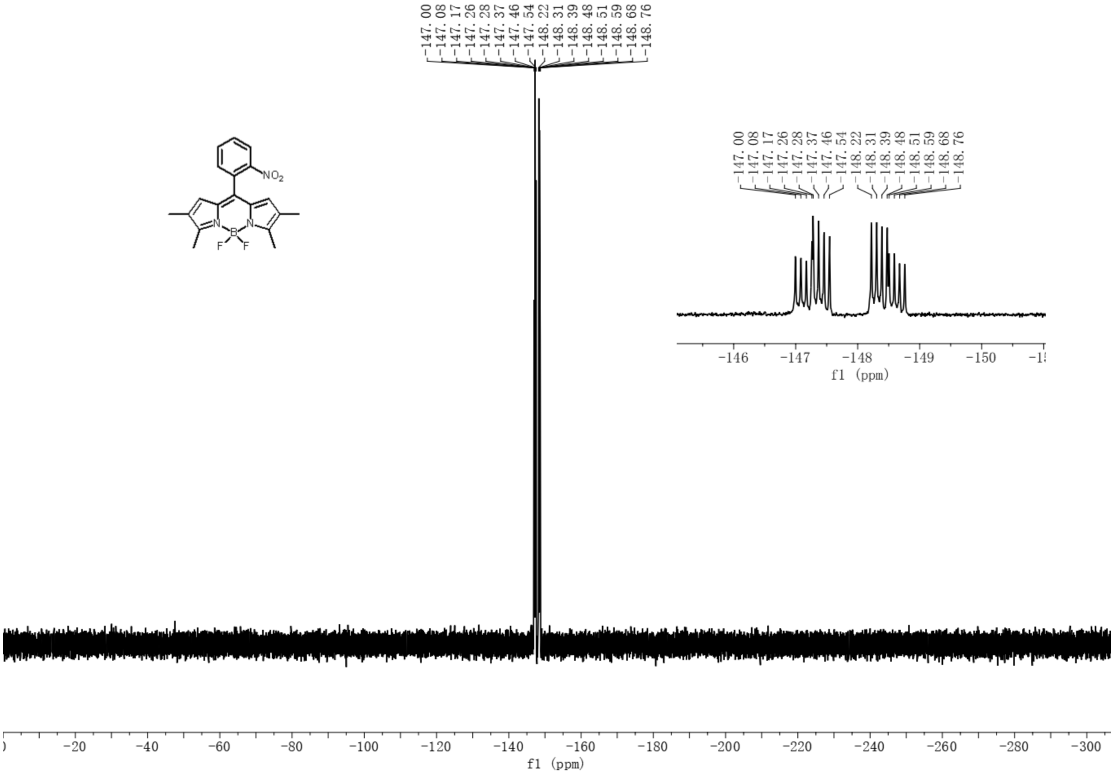
^{13}C NMR Spectra of compound **1b** in $CDCl_3$ (101 MHz)



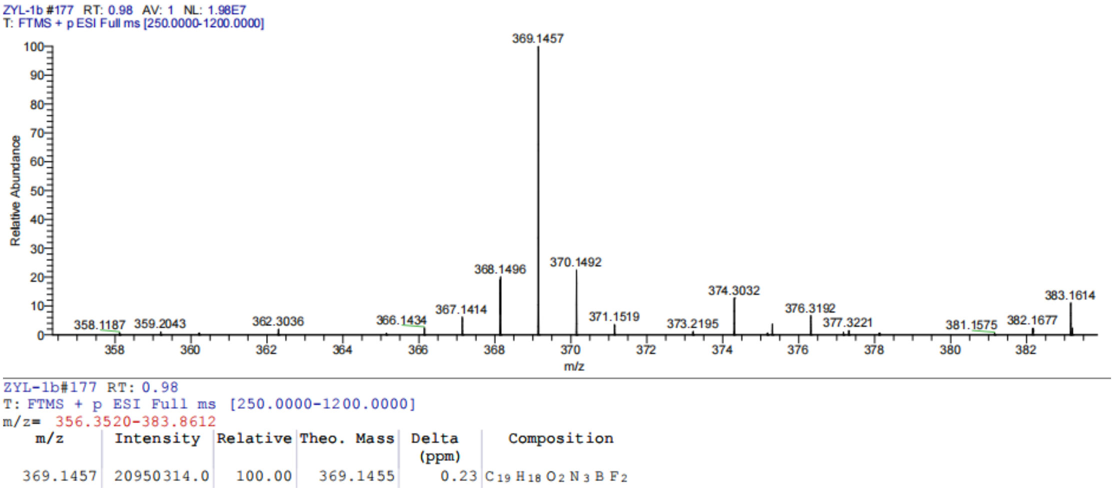
DEPT Spectra of compound **1b** in $CDCl_3$ (101 MHz)



^{19}F NMR Spectra of compound **1b** in $CDCl_3$ (376 MHz)



Observed HRMS Spectra of compound **1b**



```
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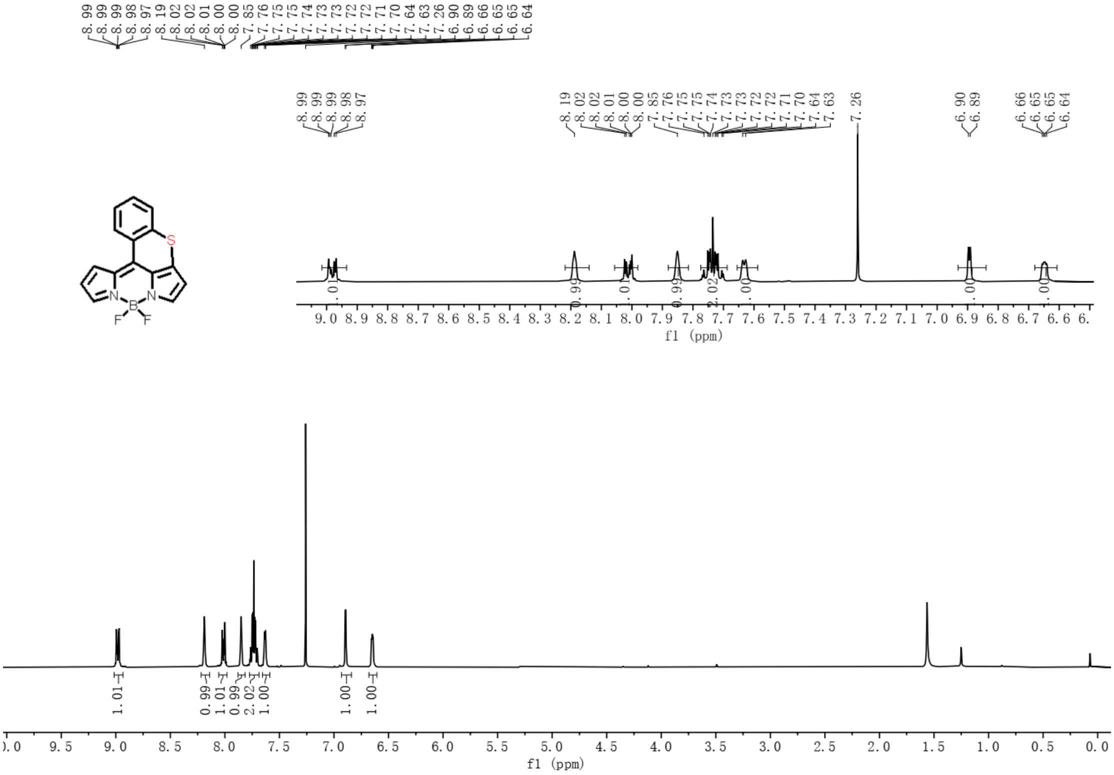
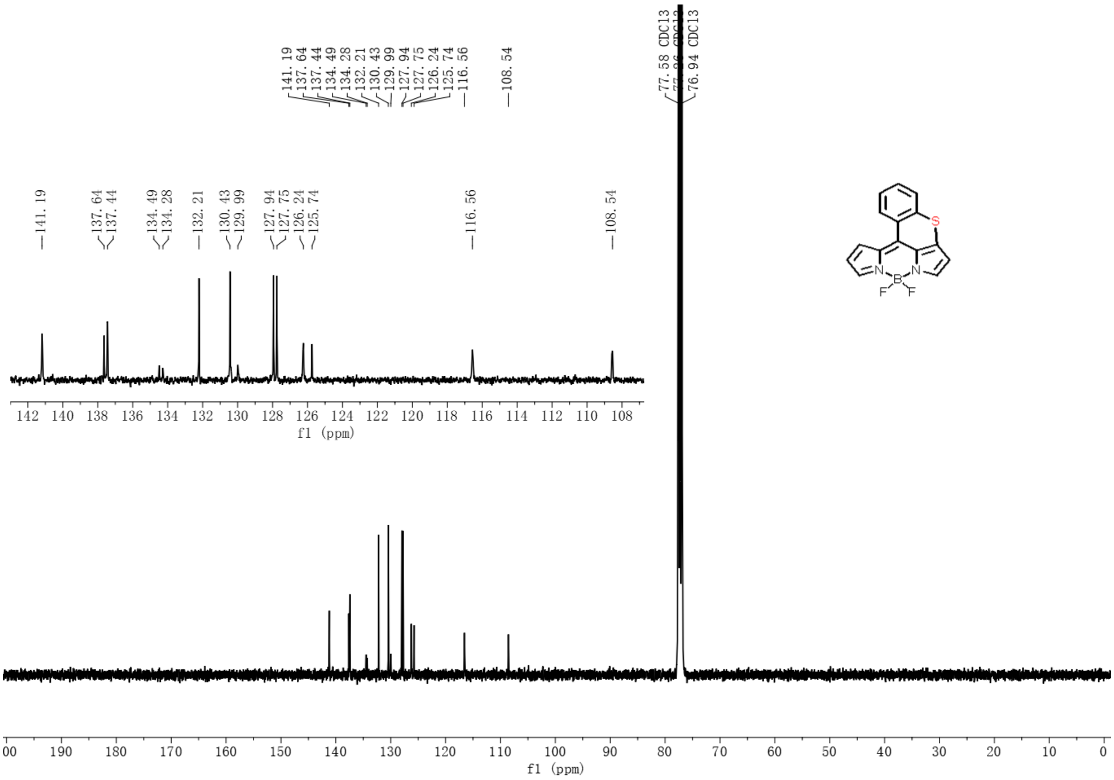
T: FTMS + p ESI Full ms [250.0000-1200.0000]
m/z= 356.3520-383.8612
   m/z     Intensity   Relative  Theo. Mass   Delta      Composition
                                               (ppm)
 369.1457  20950314.0   100.00    369.1455      0.23  C19 H18 O2 N3 B F2
```

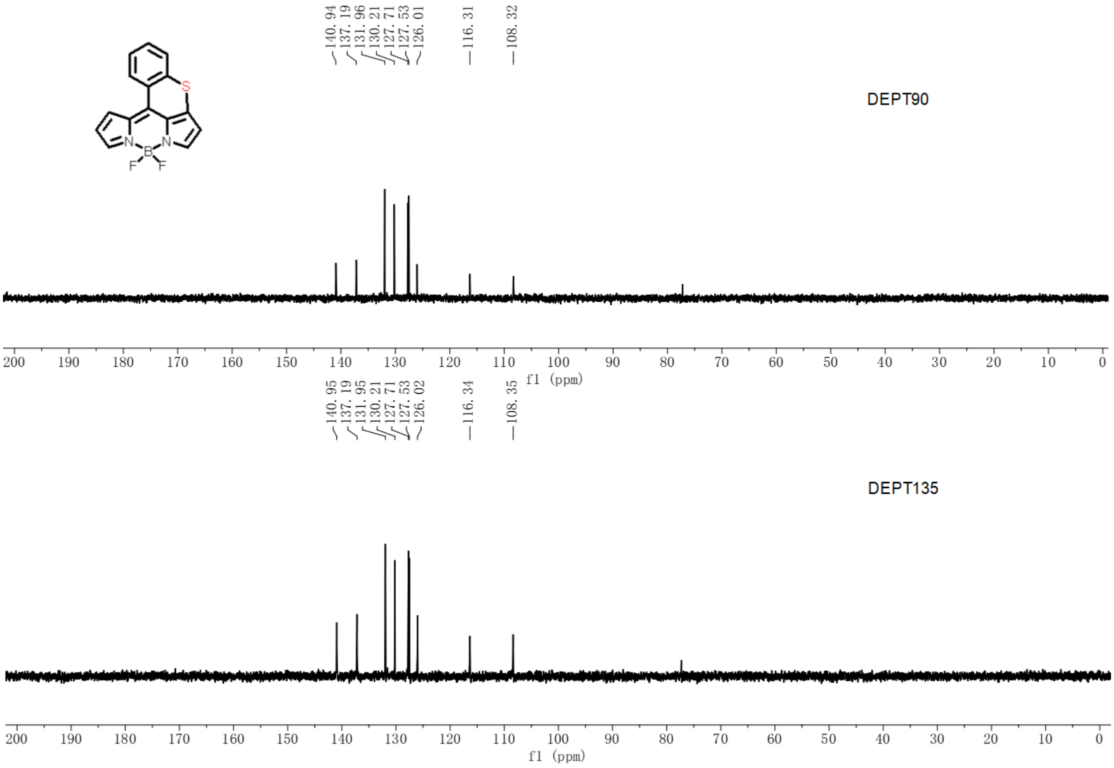
^{1}H NMR specta of compound **2a** in $CDCl_3$ (400 MHz)



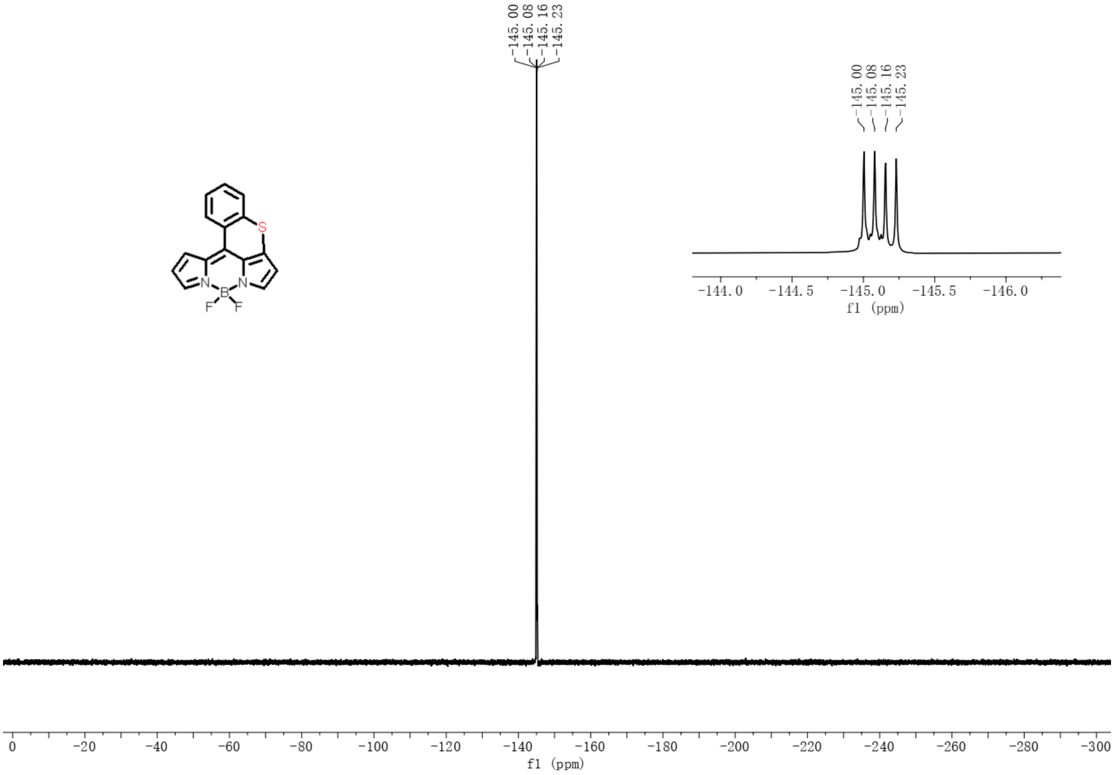
^{13}C NMR Spectra of compound **2a** in $CDCl_3$ (101 MHz)



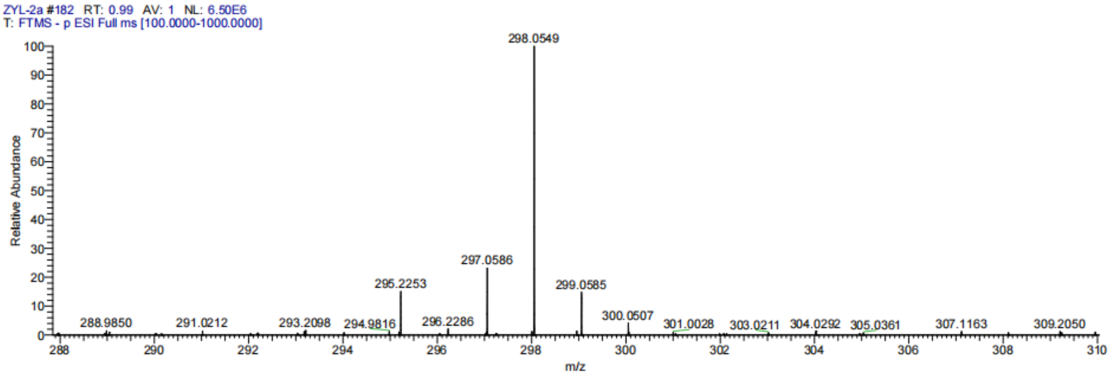
DEPT Spectra of compound **2a** in CDCl₃ (101 MHz)



^{19}F NMR Spectra of compound **2a** in CDCl₃ (376 MHz)

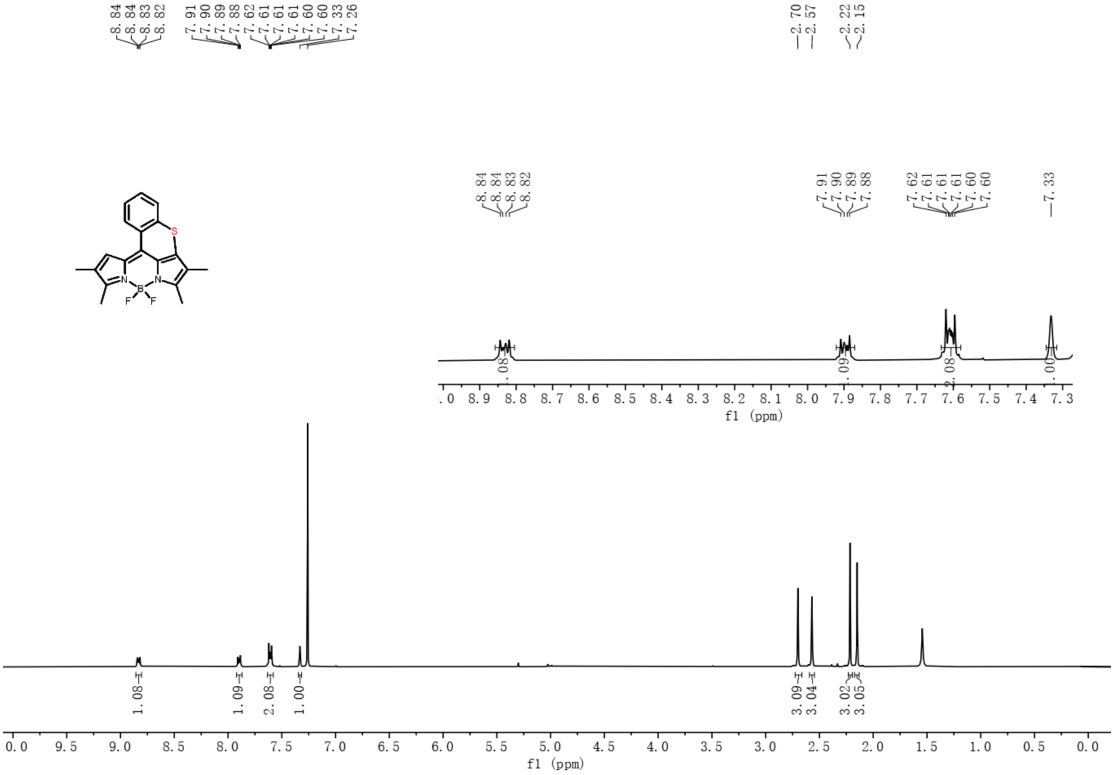


Observed HRMS Spectra of compound **2a**

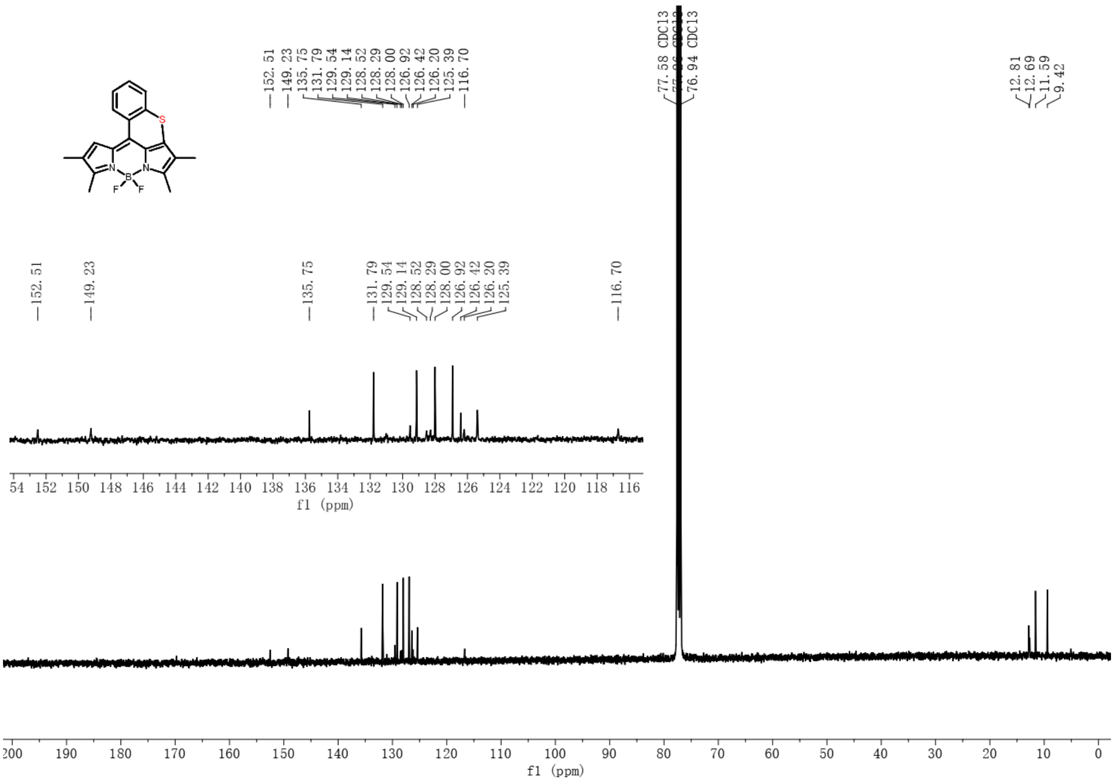


```
ZYL-2a#182 RT: 0.99
T: FTMS - p ESI Full ms [100.0000-1000.0000]
m/z= 287.8444-310.0352
    m/z     Intensity  Relative Theo. Mass  Delta      Composition
                                            (ppm)
  298.0549  6627151.0   100.00   298.0542    0.69  C15 H9 N2 B F2 S
```

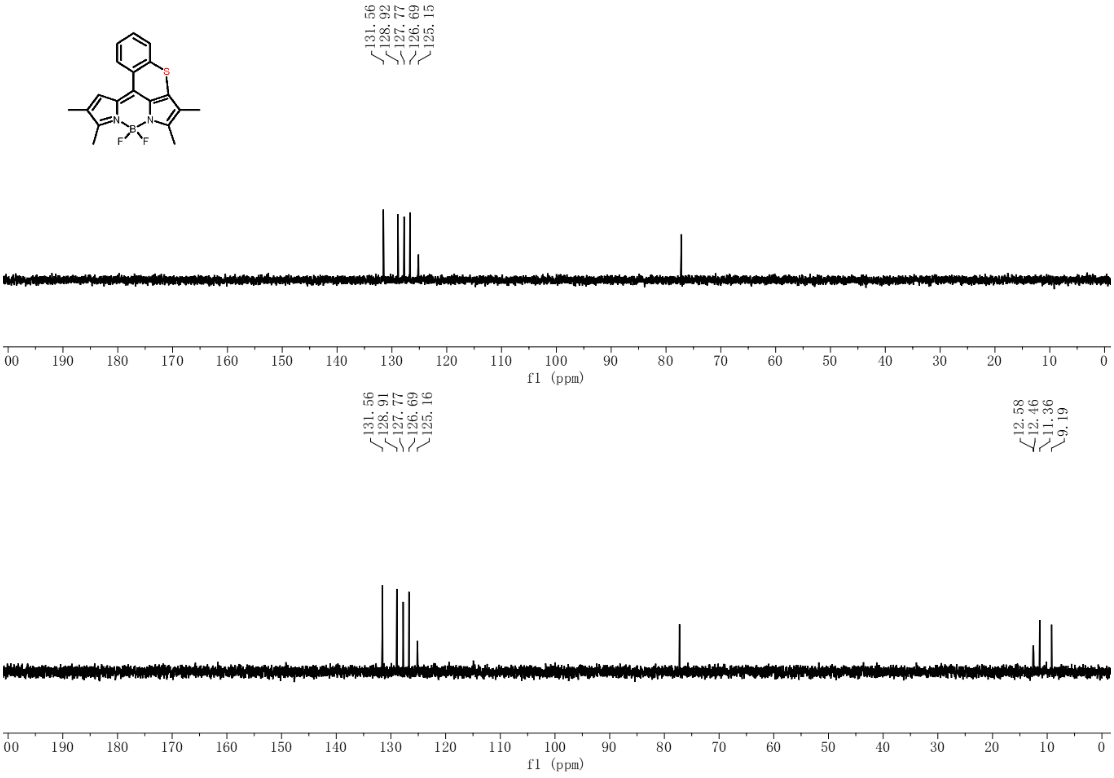
^{1}H NMR specta of compound **2b** in $CDCl_3$ (400 MHz)



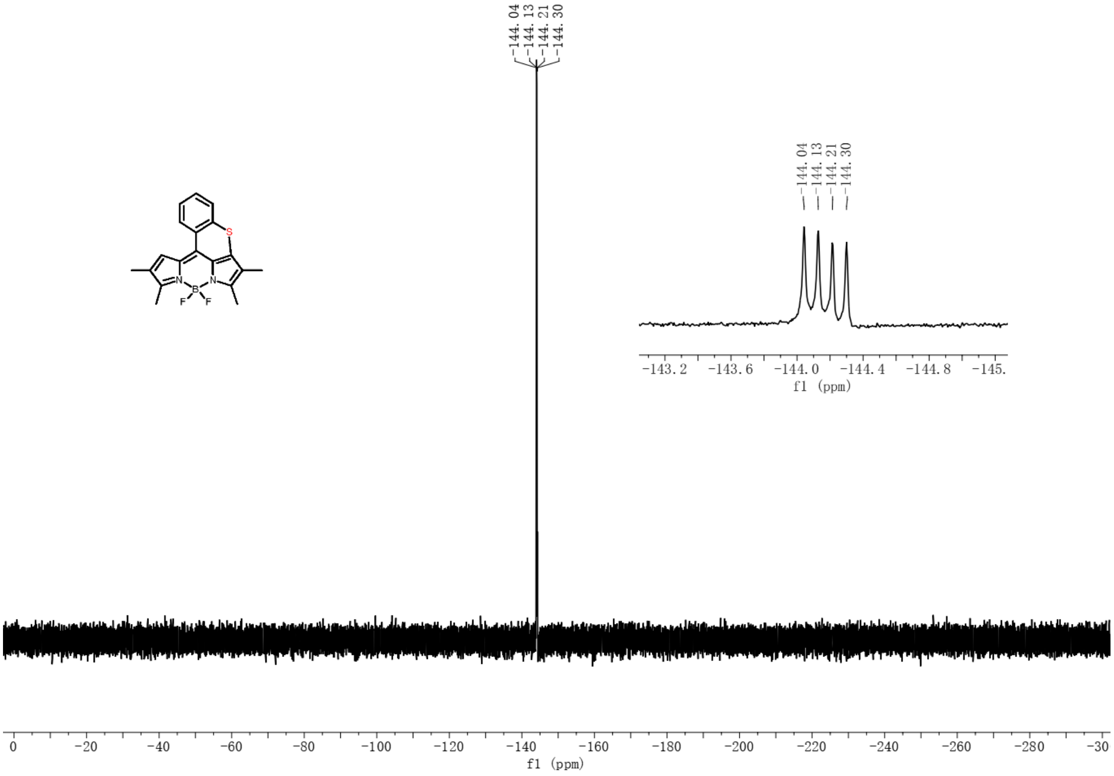
^{13}C NMR Spectra of compound **2b** in $CDCl_3$ (101 MHz)



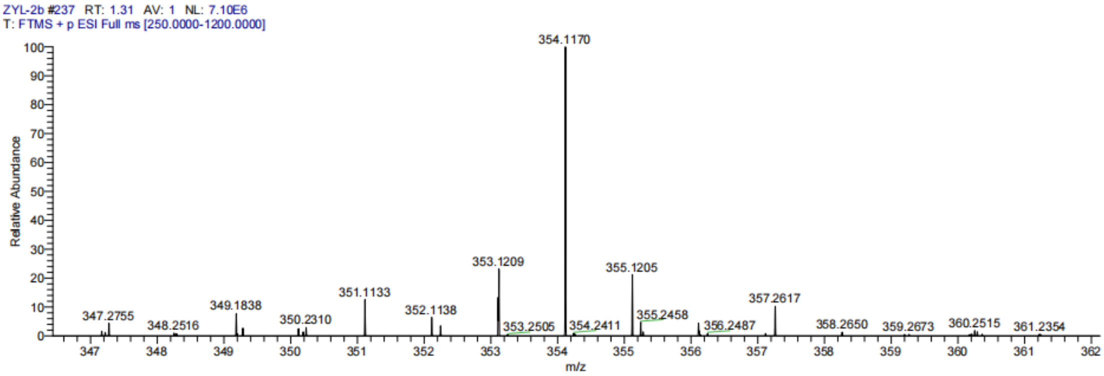
DEPT Spectra of compound **2b** in $CDCl_3$ (101 MHz)



^{19}F NMR Spectra of compound **2b** in $CDCl_3$ (376 MHz)



Observed HRMS Spectra of compound **2b**



```
ZYL-2b#237 RT: 1.31
T: FTMS + p ESI Full ms [250.0000-1200.0000]
m/z= 346.4344-362.1261
```

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
354.1170	7337967.0	100.00	354.1168	0.23	$C_{19}H_{17}N_2BF_2S$

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