

*Supporting Information for*

**An Air-Stable Organoboron Compound,**

**Dithienooxadiborepine: Preparation and Functionalization**

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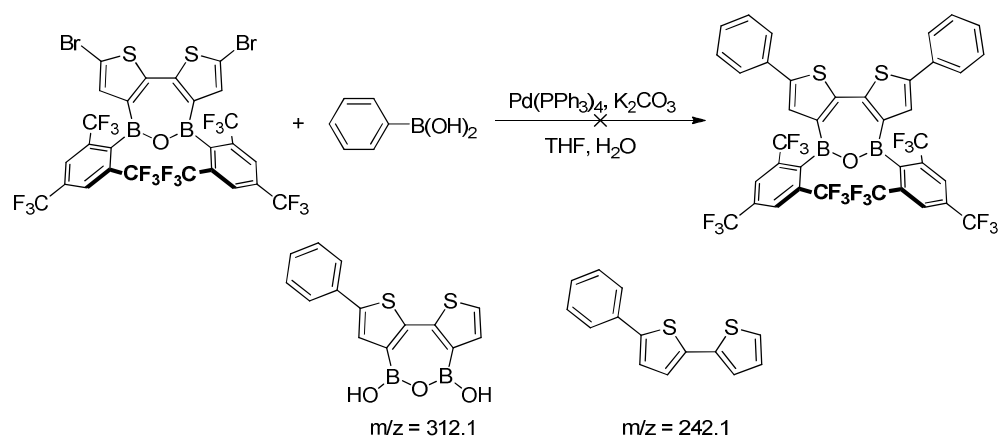
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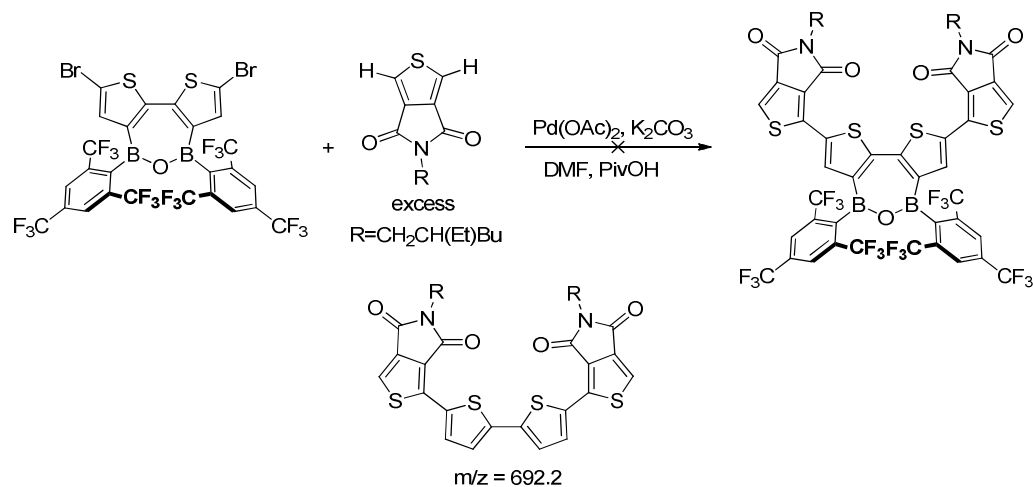
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## I. Synthetic Trials



**Trial of Suzuki reaction.** No desired product was found in the reaction mixture. In the mass spectrum of crude reaction mixture, peaks at  $m/z = 312.1$  and  $242.1$  were observed. Fragmented structures with such  $m/z$  values were proposed.



**Trial of C-H arylation.** No desired product was found in the reaction mixture. In the mass spectrum of crude reaction mixture, a peak at  $m/z = 692.2$  was observed. Fragmented structure with such  $m/z$  values was proposed.

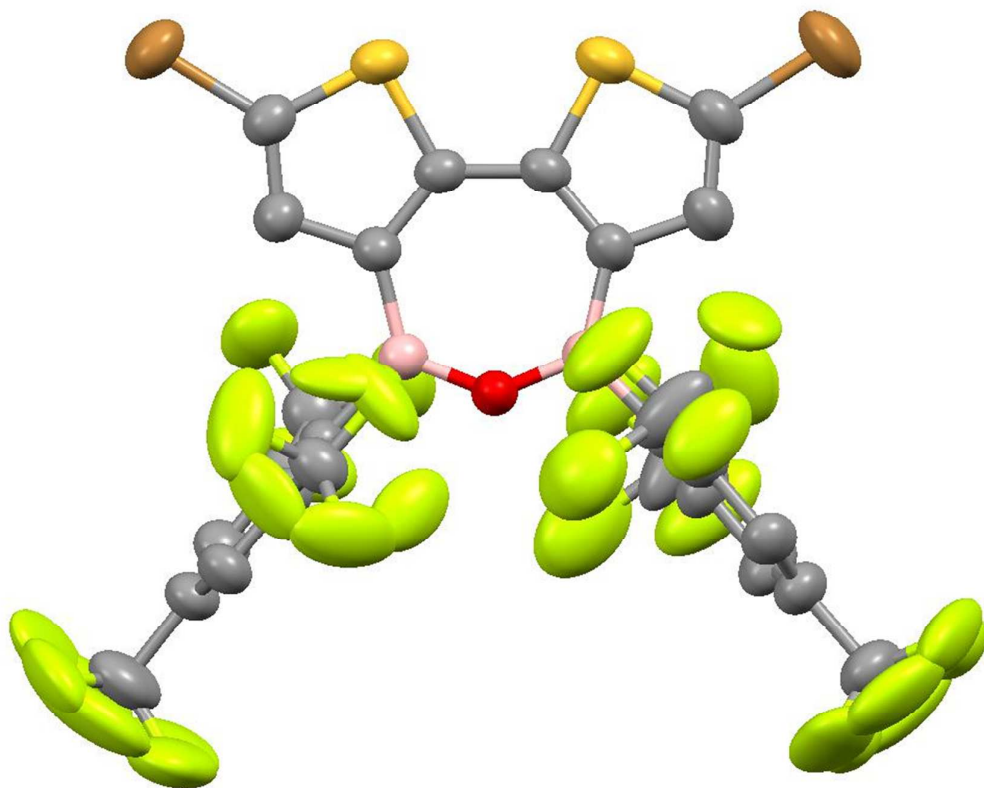
## II. X-Ray Crystallography

Single crystals of **4**, **5A** and **5B** suitable for X-ray crystal analysis were obtained by slowly evaporation of their solution in ethyl acetate, petroleum ether, and DCM/heptane, respectively. Diffraction data of **4**, **5A** and **5B** were collected at 296 K, 173 K, and 173 K, respectively, on a Bruker SMART APEX single crystal CDD X-ray diffractometer with Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The crystal data for these compounds are summarized in Table S1. The structures were solved with the SHELX-97 program and refined by the full-matrix least-squares on  $F^2$ . Crystallographic data for the structures of **4**, **5A**, and **5B** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication CCDC1826019, 1826020, and 1826021, respectively.

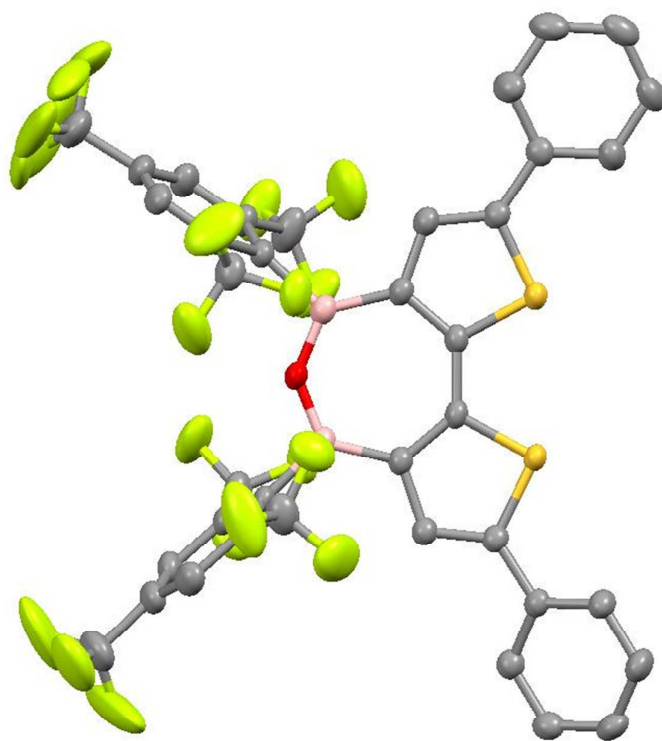
**Table S1.** Crystal structure and refinement data for **4**, **5A**, and **5B**.

Compound	<b>4</b>	<b>5A</b>	<b>5B</b>
Formula	C <sub>26</sub> H <sub>6</sub> B <sub>2</sub> Br <sub>2</sub> F <sub>18</sub> OS <sub>2</sub>	C <sub>38</sub> H <sub>16</sub> B <sub>2</sub> F <sub>18</sub> OS <sub>2</sub>	C <sub>34</sub> H <sub>12</sub> B <sub>2</sub> F <sub>18</sub> OS <sub>4</sub>
Formula weight ( <i>M<sub>w</sub></i> )	921.87	916.25	928.30
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	P 21/c	P b c a	P 21/c
a[Å]	11.7222(5)	9.2316(3)	15.4128(8)
b[Å]	15.8690(6)	24.6720(8)	15.3848(8)
c[Å]	17.8469(7)	32.5936(10)	16.3220(8)
$\alpha$ [°]	90	90	90
$\beta$ [°]	107.1070(10)	90	111.557(2)
$\gamma$ [°]	90	90	90
V[Å <sup>3</sup> ]	3173.0(2)	7423.6(4)	3599.6(3)
Z	4	8	4
$d_{\text{calcd}}$ [g cm <sup>-3</sup> ]	1.930	1.640	1.713
Reflections:	67844/5896	39510/7272	78388/7039

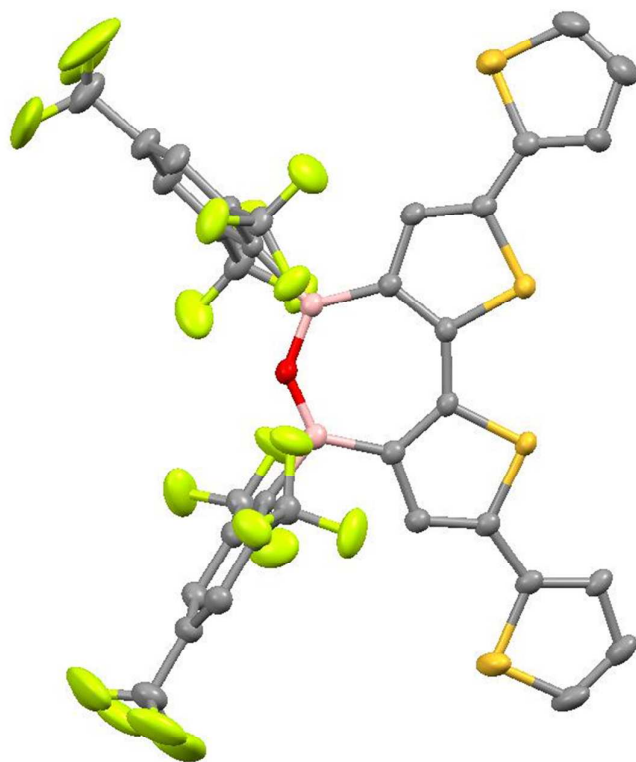
total/independent			
R <sub>int</sub>	0.0501	0.0329	0.0528
Final R1 and wR2	0.0480, 0.1150	0.0526, 0.1409	0.0427, 0.1137
Temperature [K]	296	173	173
Crystal size [mm <sup>3</sup> ]	0.200 x 0.170 x 0.130	0.200 x 0.170 x 0.130	0.200 x 0.170 x 0.130
θ range for data collection [°]	1.818 to 25.496	2.500 to 25.999	1.942 to 26.000



**Figure S1.** Single crystal structure of **4** (displacement ellipsoid set at 50% probability level, hydrogens omitted)



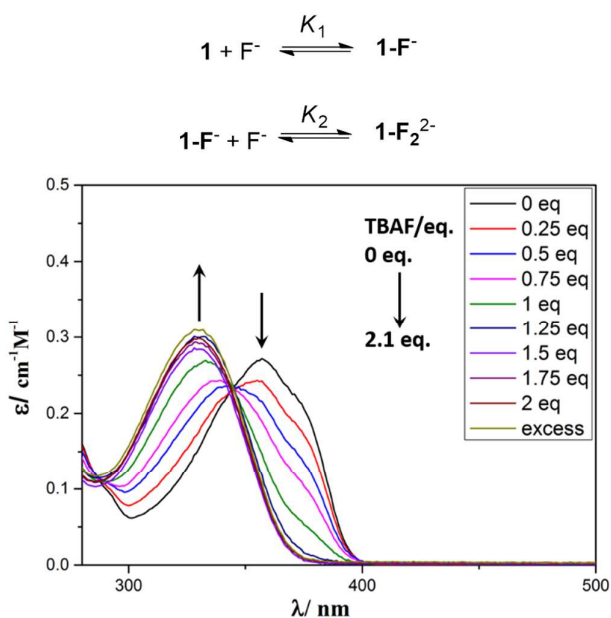
**Figure S2.** Single crystal structure of **5A** (displacement ellipsoid set at 50% probability level, hydrogens omitted)



**Figure S3.** Single crystal structure of **5B** (displacement ellipsoid set at 50% probability level, hydrogens omitted)

### III. Photophysical and Electrochemical Measurements

Tetrahydrofuran (THF) and toluene were distilled over sodium and benzophenone prior to use. UV-Vis absorption spectra were recorded on a Varian Cary 500 spectrophotometer using the absorption mode in a 1-cm quartz cell. Fluorescence emission spectra were recorded in 1-cm quartz cuvette on a Horiba Jobin Yvon FluoroMax-4 spectrofluorometer. Fluorescence quantum yield was determined using absolute method by a calibrated integrating sphere system on a Horiba Jobin Yvon FluoroMax-4 spectrofluorometer.



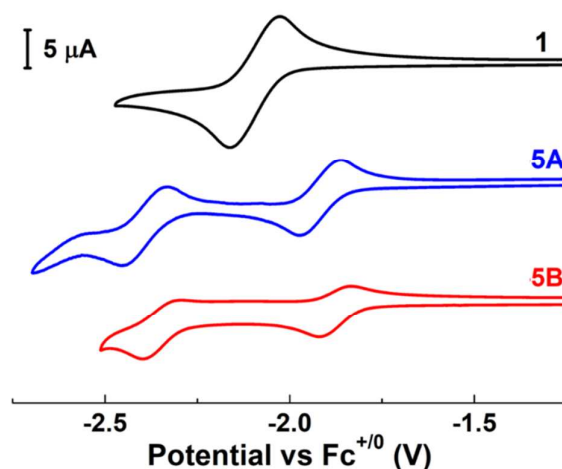
**Figure S4.** UV-vis absorption titration of TABF (tetrabutylammonium fluoride) to compound **1** (20  $\mu\text{M}$ ) in THF (arrows indicated change of direction upon adding TABF)

We examined fluoride ion ( $\text{F}^-$ ) binding properties of compound **1** by carrying out TABF (tetrabutylammonium fluoride) titration experiment (Figure S4). Upon adding TABF, the original absorption peak at 359 nm of **1** decreased accompanied by the rise of a new absorption band around 330 nm, evidencing coordination of  $\text{F}^-$  to the boron centers. The spectral change occurred with a *quasi*-isobestic point at 344 nm and became saturated after ca. 1.5 eq. of  $\text{F}^-$ . As there are two boron centers in **1**, two  $\text{F}^-$



binding ability had been expected. However, Job plot results were inconclusive to determine a dominant binding species ( $\mathbf{1}\text{-F}^-$  or  $\mathbf{1}\text{-F}_2^{2-}$ ). Such results implied that two boron centers in **1** can coordinate to  $\text{F}^-$ , sequentially, but with attenuated association constant ( $K_2 < K_1$ ). We think after the first  $\text{F}^-$  coordination, the oxadiborepine moiety became twisted and negative charged, so affinity to the second  $\text{F}^-$  was weakened.

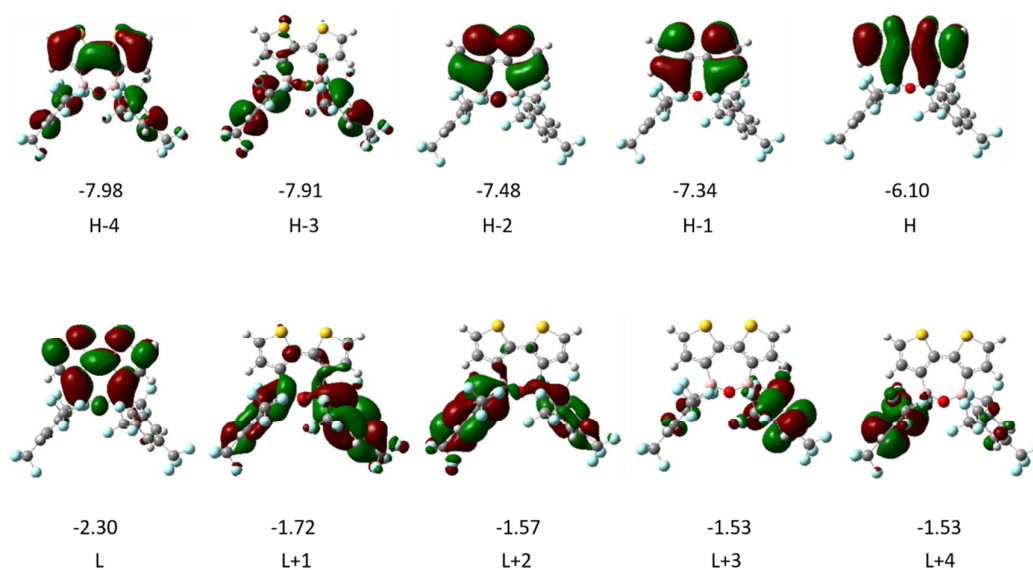
Differential pulse voltammetry (DPV) and cyclic voltammetry (CV) was performed on a CHI610E electrochemical workstation with three electrodes configuration, using Ag/AgCl as the reference electrode, a Pt plate as the counter electrode, and a glassy carbon as the working electrode. Samples were dissolved in THF with 0.1 M  $\text{Bu}_4\text{NPF}_6$  as the supporting electrolyte. Half-wave potentials were determined by DPV.



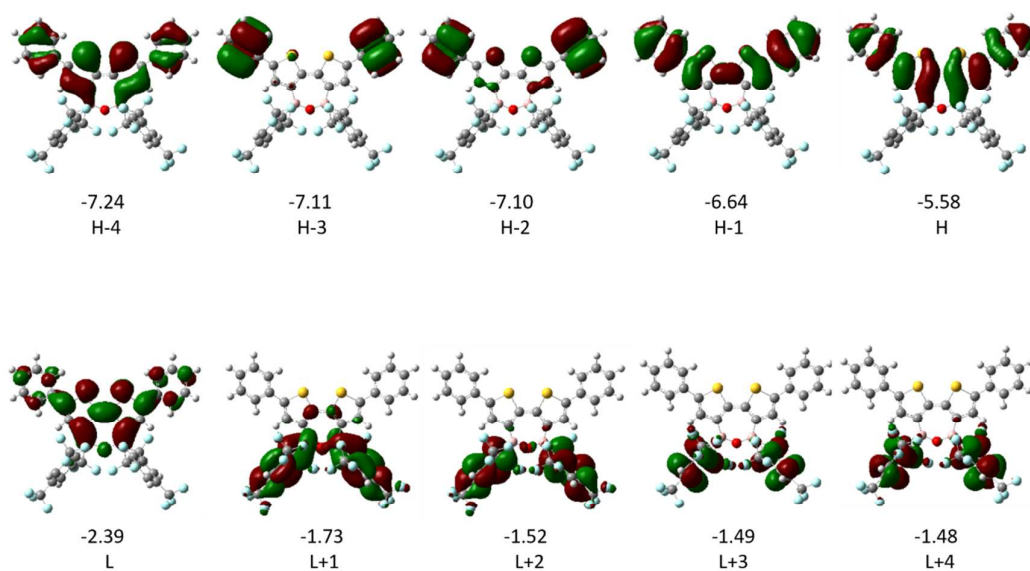
**Figure S5.** Cyclic voltammograms of **1**, **5A**, and **5B** in THF

#### IV. DFT Calculations

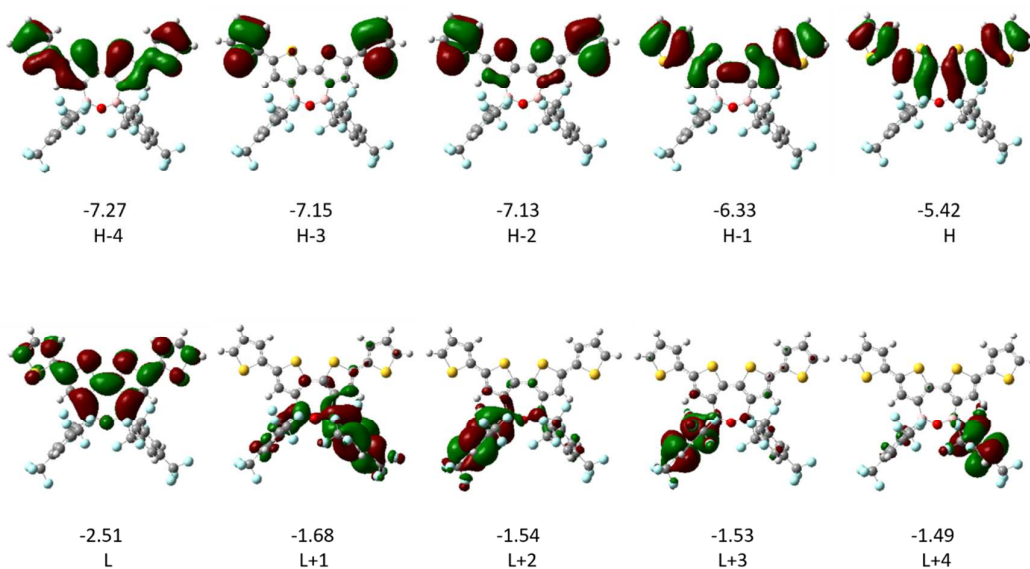
DFT calculations were carried out on compounds **1**, **5A**, and **5B** at theory level of B3LYP/6-31G(d,p) for geometry and frontier molecular orbital (FMO) energy level, and B3LYP/6-311G+(d,p) for nuclear independent chemical shift (NICS) and TD-DFT calculations. Quantum-chemical calculation was performed with the Gaussian09<sup>S1</sup> package and the orbital pictures were prepared using Gaussview.<sup>S2</sup>



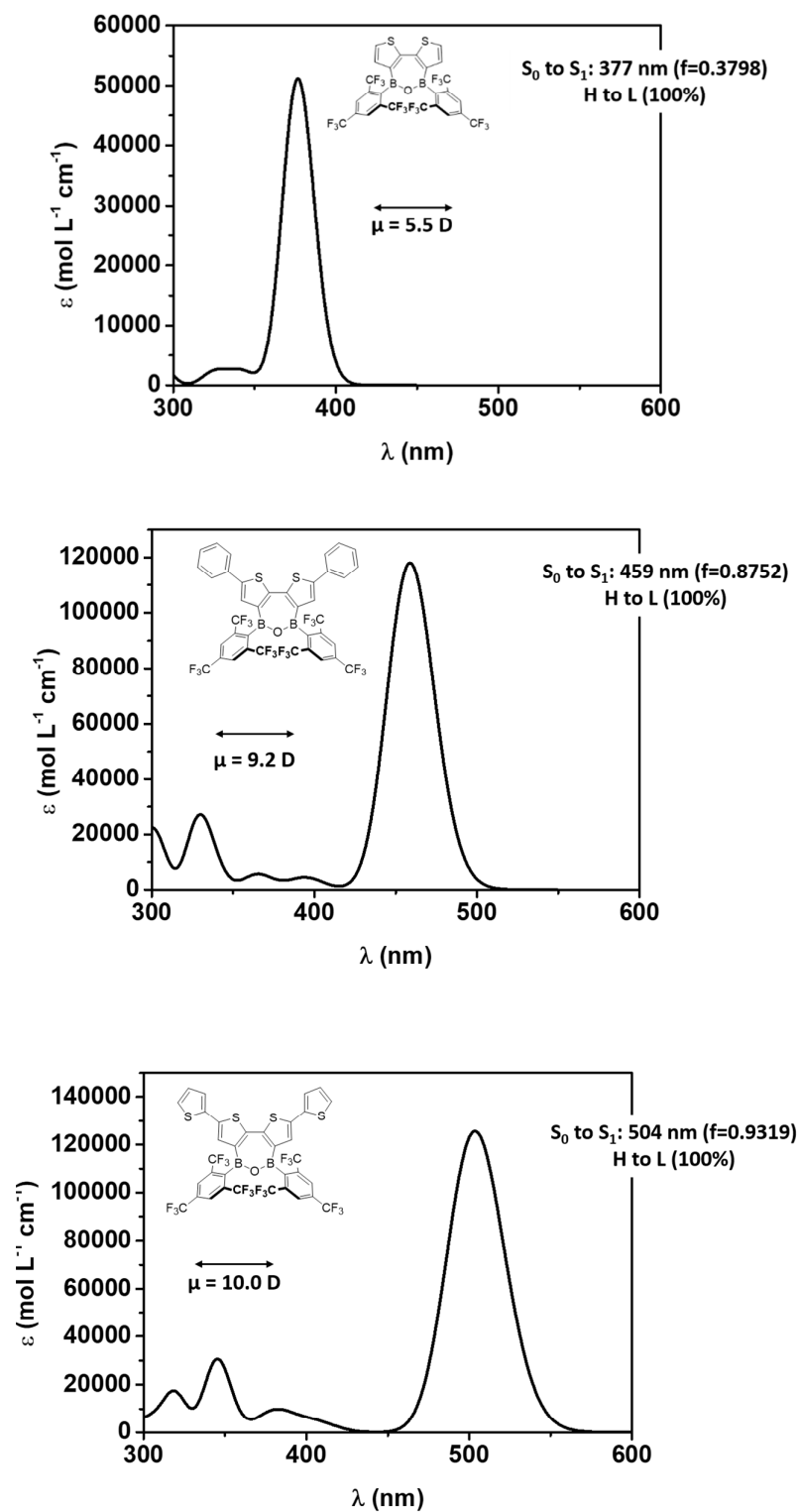
**Figure S6.** DFT calculated FMO distributions of **1** (Isovalue set as 0.02; H: HOMO; L: LUMO; energy levels in eV)



**Figure S7.** DFT calculated FMO distributions of **5A** (Isovalue set as 0.02; H: HOMO; L: LUMO; energy levels in eV)



**Figure S8.** DFT calculated FMO distributions of **5B** (Isovalue set as 0.02; H: HOMO; L: LUMO; energy levels in eV)



**Figure S9.** TD-DFT calculated UV-visible absorption spectra of **1**, **5A**, and **5B**

Table S2. Cartesian coordinates of optimized structure of **1** (Sum of electronic and zero-point Energies of **1** is -3713.902233 Hartree)

C	0.767248	3.483475	0.363283
C	-0.66416	3.516193	0.160424
C	-1.57068	2.459204	-0.00291
B	-1.24309	0.955712	-0.01383
O	0.016924	0.428343	0.027155
B	1.28728	0.91288	0.136136
C	1.650975	2.39547	0.35006
S	-1.49622	5.060897	0.115028
C	-3.034	4.29803	-0.11277
C	-2.91544	2.942639	-0.15384
C	3.00212	2.819371	0.592654
C	3.146954	4.159257	0.784376
S	1.627609	4.981713	0.676145
C	-2.40733	-0.14609	-0.10578
C	2.415928	-0.22613	0.064031
C	-2.8776	-0.62996	-1.34402
C	-3.82086	-1.65335	-1.4299
C	-4.32834	-2.2281	-0.26752
C	-3.90541	-1.76159	0.972946
C	-2.9618	-0.73553	1.045986
C	2.637191	-1.10658	1.142357
C	3.592191	-2.12094	1.085163
C	4.35209	-2.29406	-0.06898
C	4.147594	-1.45752	-1.1621
C	3.19432	-0.44096	-1.08937
C	-2.43605	0.021704	-2.63435
C	-2.63372	-0.2114	2.424995
C	-5.2923	-3.38324	-0.3517
C	3.035263	0.456452	-2.29517
C	1.788707	-1.01336	2.391225
C	5.424418	-3.35189	-0.11309
F	-3.54004	0.714806	2.81445
F	-1.42021	0.383595	2.478532
F	-2.64518	-1.19024	3.351422
F	2.415071	-1.53995	3.464365
F	1.484723	0.271171	2.696182
F	-2.58556	-0.7967	-3.69502
F	-1.13786	0.401564	-2.59781
F	-6.14799	-3.39254	0.692482
F	-6.02471	-3.33812	-1.48476

F	-3.16197	1.136846	-2.88621
F	-4.64347	-4.5685	-0.34405
F	3.40052	-0.1635	-3.43535
F	1.752048	0.863146	-2.45099
F	6.60209	-2.87768	0.351868
F	5.100314	-4.41979	0.64597
F	3.792416	1.572194	-2.19124
F	5.641154	-3.78934	-1.37115
F	0.619821	-1.67377	2.249315
H	-3.92582	4.901806	-0.20636
H	-3.76349	2.284702	-0.29794
H	3.838438	2.131901	0.620353
H	4.049838	4.719559	0.983248
H	-4.15767	-1.99997	-2.3991
H	-4.30674	-2.19345	1.882169
H	3.737092	-2.77716	1.934639
H	4.715361	-1.60435	-2.07277

Table S3. Cartesian coordinates of optimized structure of **5A** (Sum of electronic and zero-point Energies of **5A** is -4175.873407 Hartree)

C	0.718272	2.513281	0.033025
C	-0.72166	2.515201	-0.03097
C	-1.6276	1.44251	-0.0344
B	-1.27511	-0.05602	-0.00189
O	-0.00556	-0.55734	-0.00832
B	1.265424	-0.05908	-0.00781
C	1.621648	1.438358	0.032146
S	-1.57435	4.046145	-0.12558
C	-3.14164	3.264929	-0.14935
C	-2.97984	1.903713	-0.10141
C	2.974992	1.896002	0.101882
C	3.140052	3.25662	0.155721
S	1.574589	4.041664	0.134789
C	-2.40425	-1.195	-0.01592
C	2.391538	-1.20095	0.006454
C	-2.68085	-1.92836	-1.18778
C	-3.64054	-2.93929	-1.21719
C	-4.34706	-3.2592	-0.06015
C	-4.08398	-2.57332	1.12155
C	-3.12598	-1.55856	1.136318
C	2.655166	-1.94429	1.17476
C	3.607742	-2.96228	1.203977
C	4.320346	-3.27837	0.049937
C	4.068599	-2.58361	-1.12935
C	3.117965	-1.5623	-1.14382
C	-1.89108	-1.67217	-2.45267
C	-2.90306	-0.82554	2.439235
C	-5.3466	-4.38676	-0.07644
C	2.900424	-0.82625	-2.44603
C	1.851681	-1.69994	2.433296
C	5.39244	-4.33639	0.089328
F	-3.66348	0.290255	2.521496
F	-1.6135	-0.43626	2.580765
F	-3.21088	-1.59136	3.505214
F	2.516468	-2.09896	3.538042
F	1.557493	-0.38712	2.595625
F	-2.5627	-2.07086	-3.55326
F	-0.71205	-2.32895	-2.44558
F	-6.30201	-4.21854	0.862137
F	-5.95997	-4.48699	-1.27512

F	-1.608	-0.35644	-2.61124
F	-4.75425	-5.57675	0.166806
F	3.210584	-1.59014	-3.51265
F	1.612095	-0.43429	-2.59122
F	6.593932	-3.80726	0.413769
F	5.118845	-5.28911	1.005221
F	3.66304	0.288437	-2.52299
F	5.536679	-4.94354	-1.10728
F	0.677877	-2.36577	2.412763
C	4.383584	4.030729	0.231339
C	5.539875	3.455694	0.791085
C	6.731379	4.172423	0.853613
C	6.793439	5.481933	0.372003
C	5.651563	6.067414	-0.17679
C	4.460138	5.349889	-0.25031
C	-4.38345	4.042154	-0.22128
C	-4.4574	5.358853	0.267446
C	-5.6473	6.079255	0.197455
C	-6.79024	5.499149	-0.35484
C	-6.73074	4.192158	-0.84356
C	-5.54075	3.472614	-0.78454
H	-3.82558	1.22803	-0.07897
H	3.819065	1.218342	0.076913
H	-3.84198	-3.46862	-2.1405
H	-4.61978	-2.82652	2.028173
H	3.787051	-3.51065	2.120647
H	4.596468	-2.8462	-2.03798
H	5.494505	2.450502	1.197677
H	7.611613	3.710849	1.291224
H	7.722425	6.041156	0.426809
H	5.689181	7.083629	-0.55768
H	3.586461	5.808234	-0.70451
H	-3.58288	5.812873	0.724369
H	-5.68292	7.093471	0.583818
H	-7.71803	6.060602	-0.40692
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H	-5.49722	2.469598	-1.19668

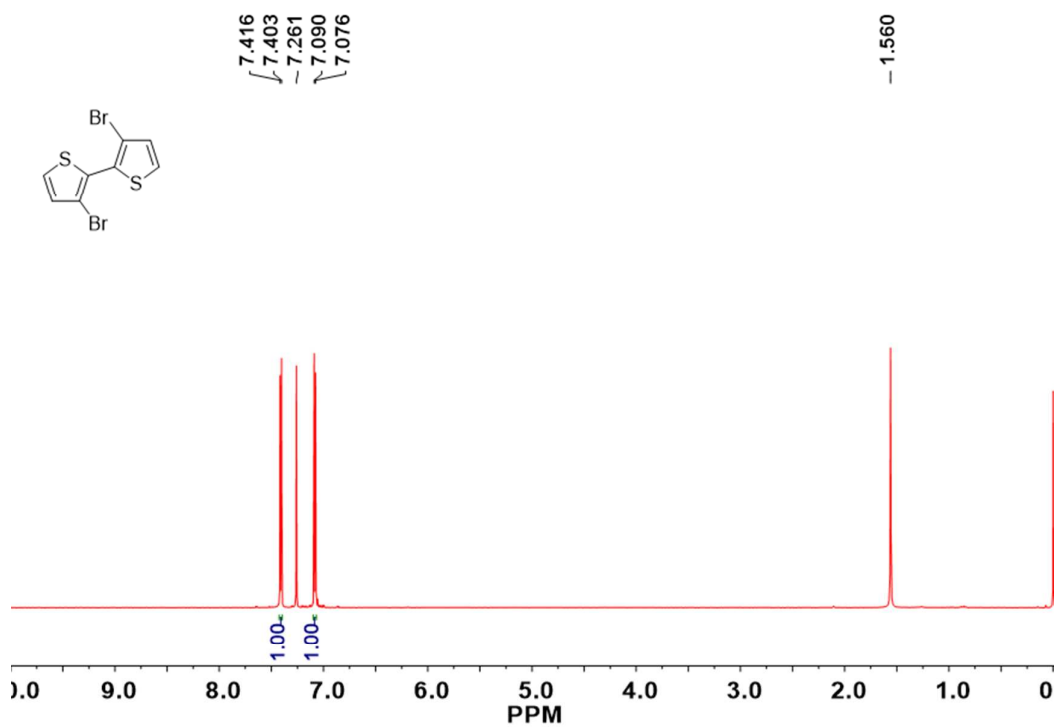
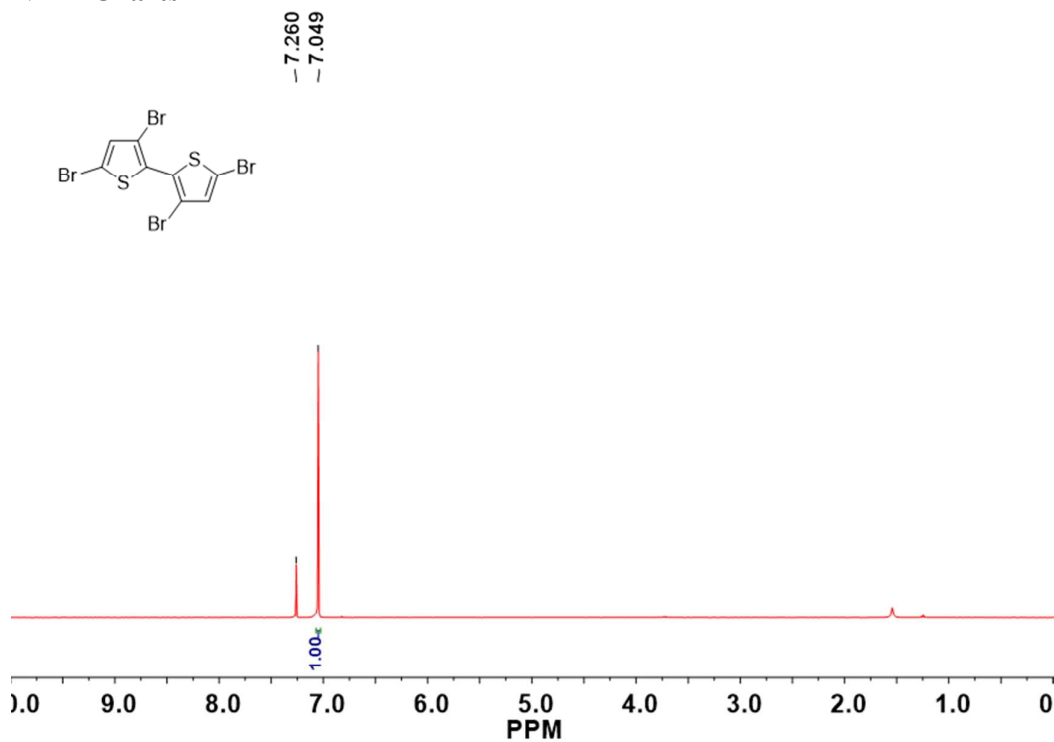


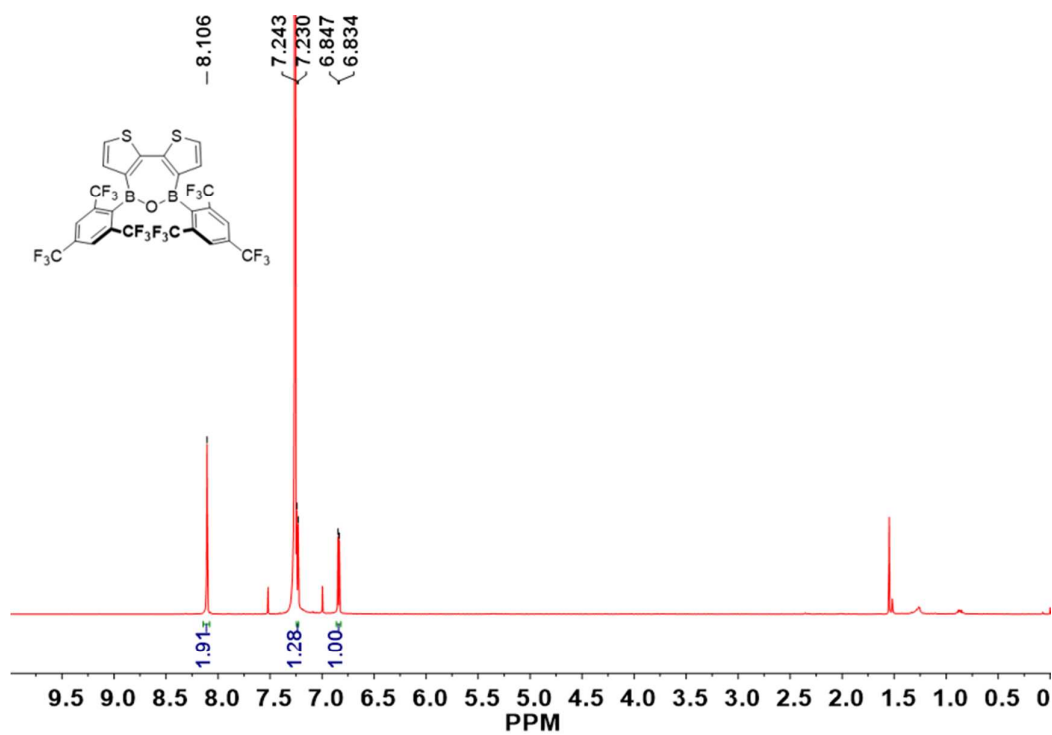
Table S4. Cartesian coordinates of optimized structure of **5B** (Sum of electronic and zero-point Energies of **5B** is -4817.444896 Hartree)

C	0.751022	2.510971	0.133318
C	-0.68376	2.528341	0.031125
C	-1.5968	1.462411	-0.0118
B	-1.25847	-0.04094	0.030665
O	0.006509	-0.55695	-0.00829
B	1.277835	-0.06302	-0.03566
C	1.644763	1.428776	0.093543
S	-1.52363	4.070628	-0.03544
C	-3.09573	3.297298	-0.08699
C	-2.94452	1.93177	-0.07255
C	2.99957	1.866854	0.206066
C	3.174536	3.223416	0.33522
S	1.616971	4.027217	0.332207
C	4.398653	3.982555	0.471407
C	-4.30745	4.085558	-0.14918
C	-2.41712	-1.15085	0.084056
C	2.406542	-1.19506	-0.17374
C	-3.04117	-1.62976	-1.08862
C	-4.00169	-2.63852	-1.0582
C	-4.37364	-3.20757	0.158535
C	-3.78691	-2.75711	1.334601
C	-2.82392	-1.74534	1.291158
C	2.732351	-2.0382	0.907157
C	3.688677	-3.0475	0.796964
C	4.342542	-3.25328	-0.41454
C	4.032718	-2.45369	-1.51121
C	3.081233	-1.44122	-1.38555
C	-2.73695	-1.0016	-2.4296
C	-2.27509	-1.30903	2.629854
C	-5.36723	-4.34013	0.186847
C	2.806386	-0.5848	-2.60055
C	1.99652	-1.91309	2.222677
C	5.414396	-4.30622	-0.53028
F	-3.25033	-0.77928	3.40206
F	-1.30539	-0.37258	2.517446
F	-1.75691	-2.34882	3.314354
F	2.724137	-2.39291	3.252723
F	1.697435	-0.62341	2.510206
F	-2.98531	-1.84586	-3.45109
F	-1.44262	-0.61782	-2.52978

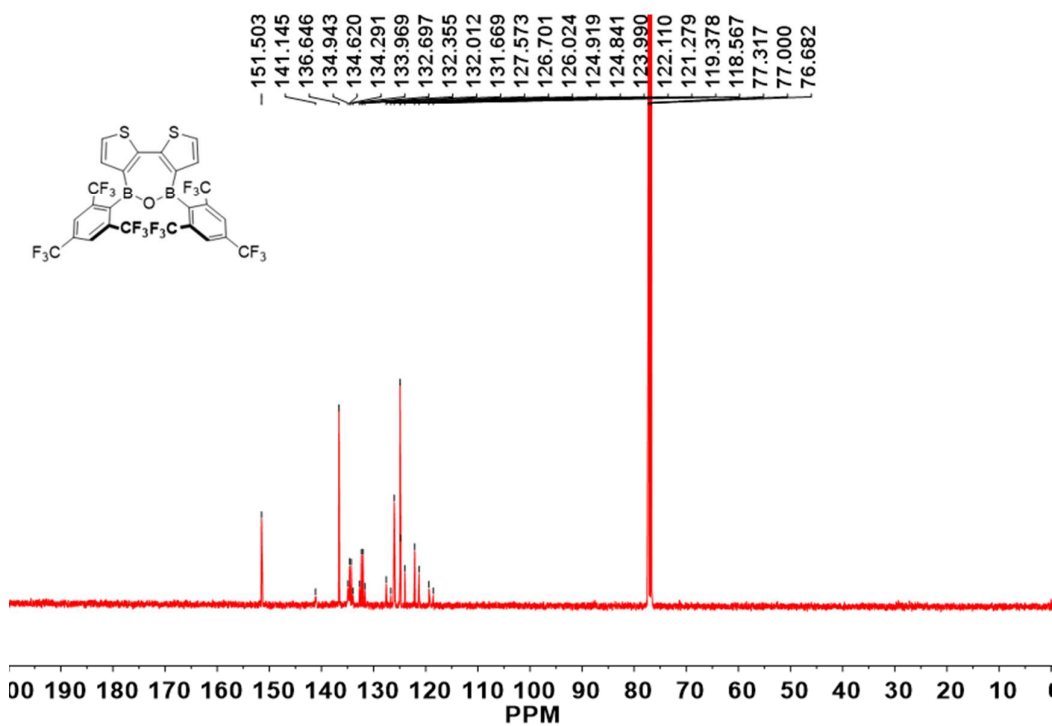
F	-6.01726	-4.40273	1.367746
F	-6.29329	-4.21008	-0.78711
F	-3.49069	0.103352	-2.63644
F	-4.76112	-5.53345	0.000842
F	3.083882	-1.23665	-3.74784
F	1.507838	-0.20143	-2.65997
F	5.233282	-5.30245	0.361615
F	5.438295	-4.85528	-1.76321
F	3.550739	0.543579	-2.59594
F	6.641915	-3.7867	-0.30404
F	0.831478	-2.5951	2.206671
C	-4.48783	5.422546	0.138492
C	-5.82971	5.862772	-0.02971
C	-6.66806	4.863949	-0.44381
S	-5.82732	3.362187	-0.6493
S	5.908902	3.190296	0.88985
C	6.771593	4.692878	0.835013
C	5.947423	5.740194	0.525823
C	4.598787	5.338764	0.318699
H	-3.79506	1.261252	-0.09703
H	3.838288	1.181782	0.172182
H	-4.45854	-2.97916	-1.97942
H	-4.07853	-3.18755	2.285929
H	3.916387	-3.67416	1.650371
H	4.517162	-2.62696	-2.46452
H	-3.68317	6.064217	0.479622
H	-6.15828	6.878485	0.156426
H	-7.72895	4.916747	-0.64424
H	7.833507	4.709407	1.036175
H	6.29065	6.764584	0.441636
H	3.803212	6.023566	0.047309

## NMR Charts

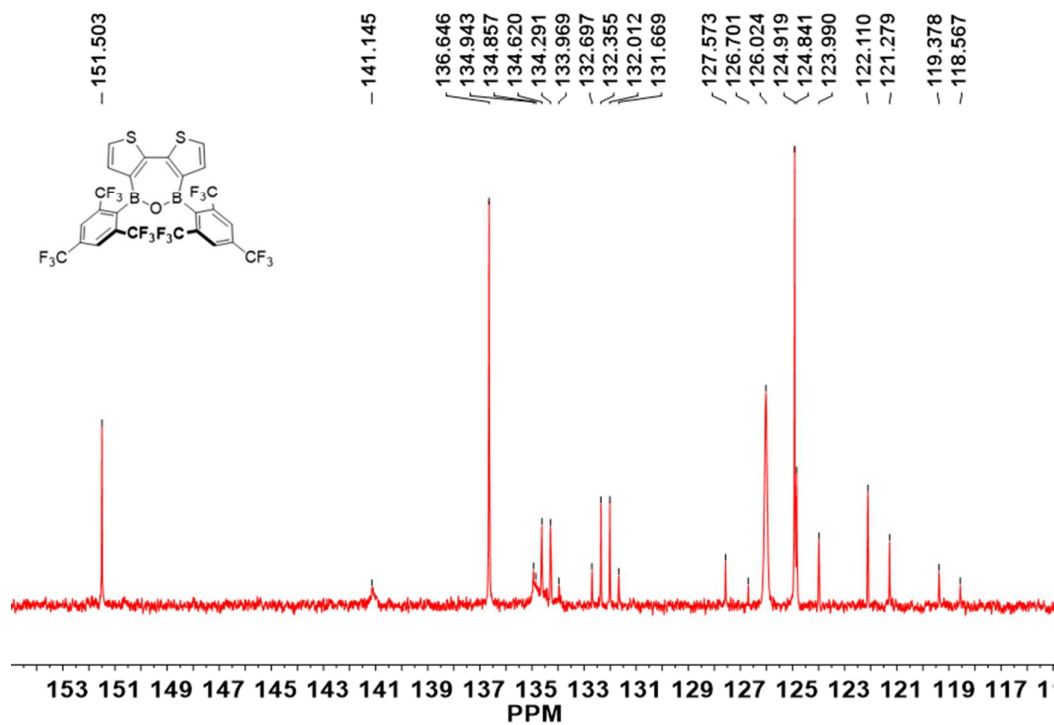




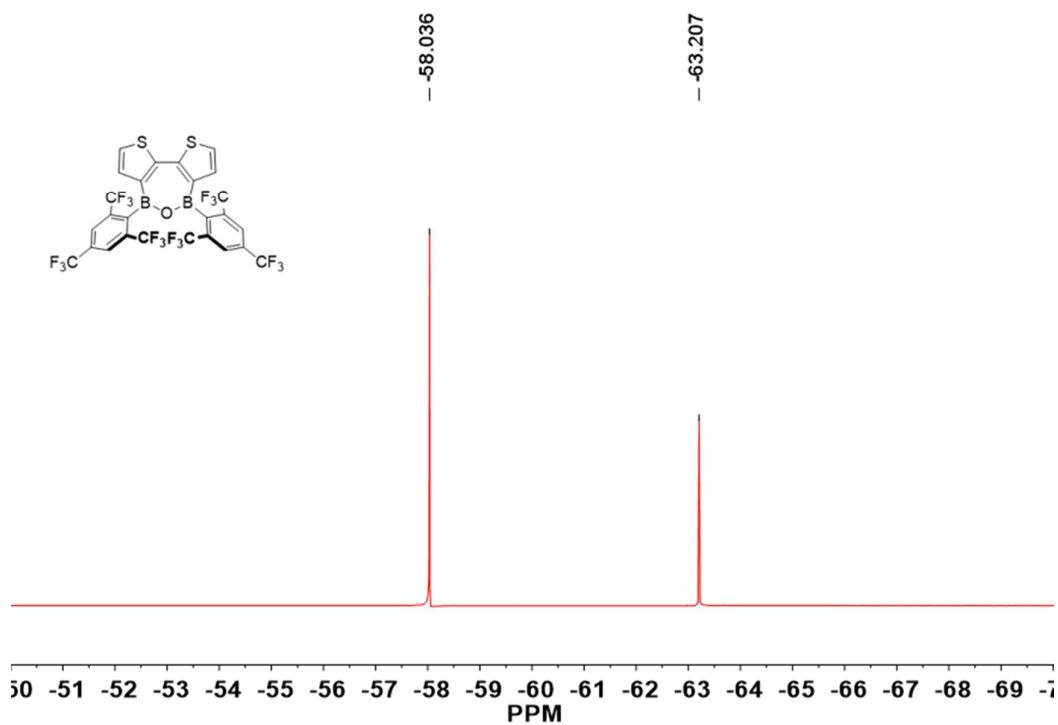
<sup>1</sup>H NMR spectrum of **1**



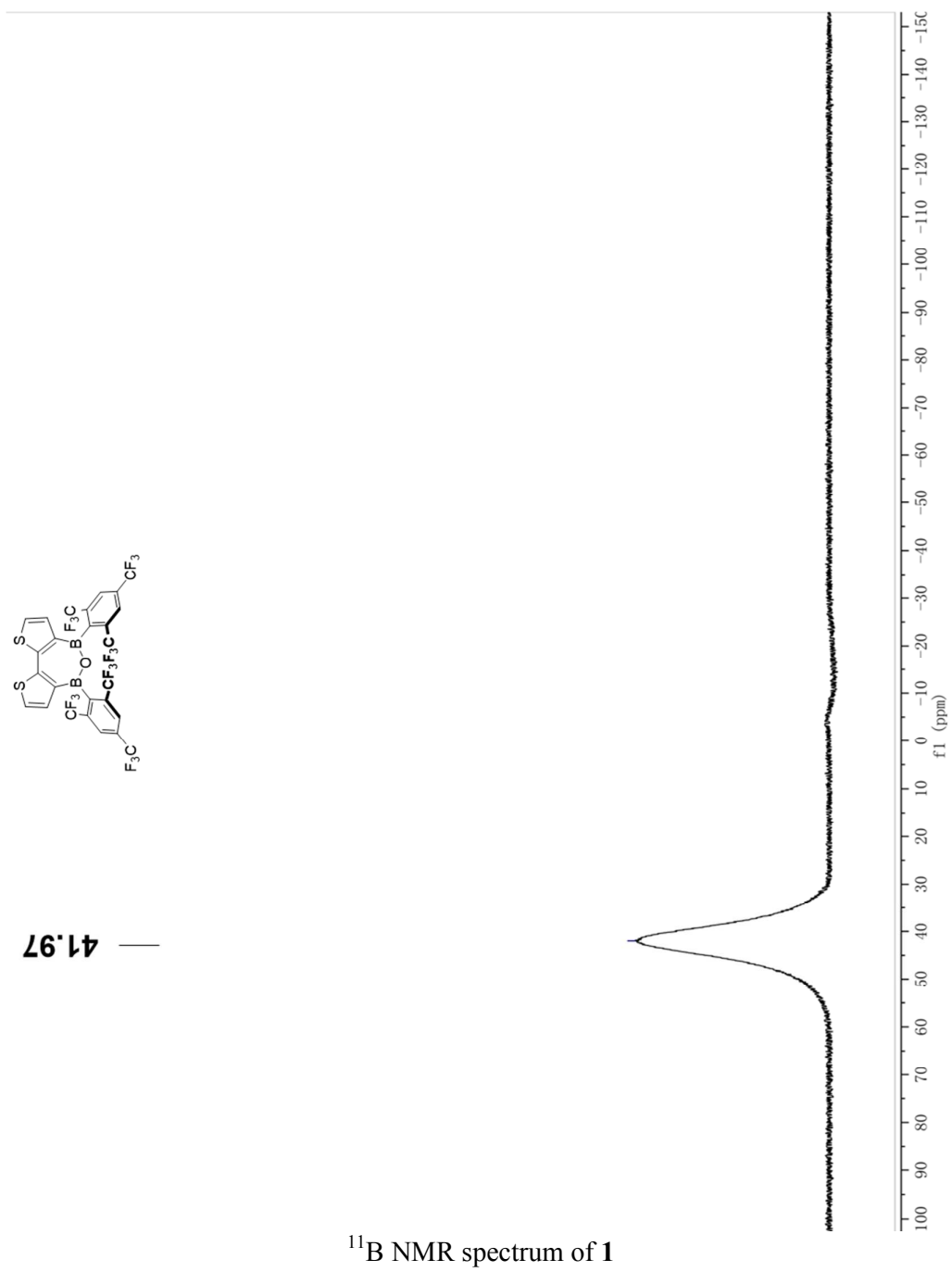
<sup>13</sup>C NMR spectrum of **1**

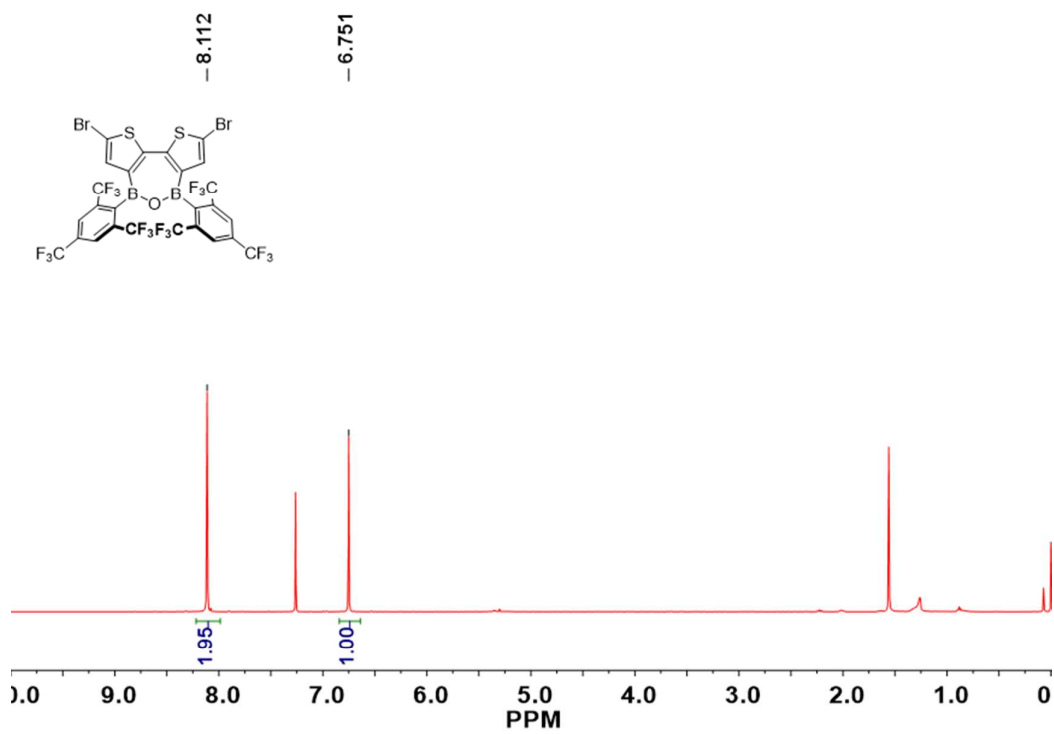


<sup>13</sup>C NMR spectrum of **1** (aromatic region)

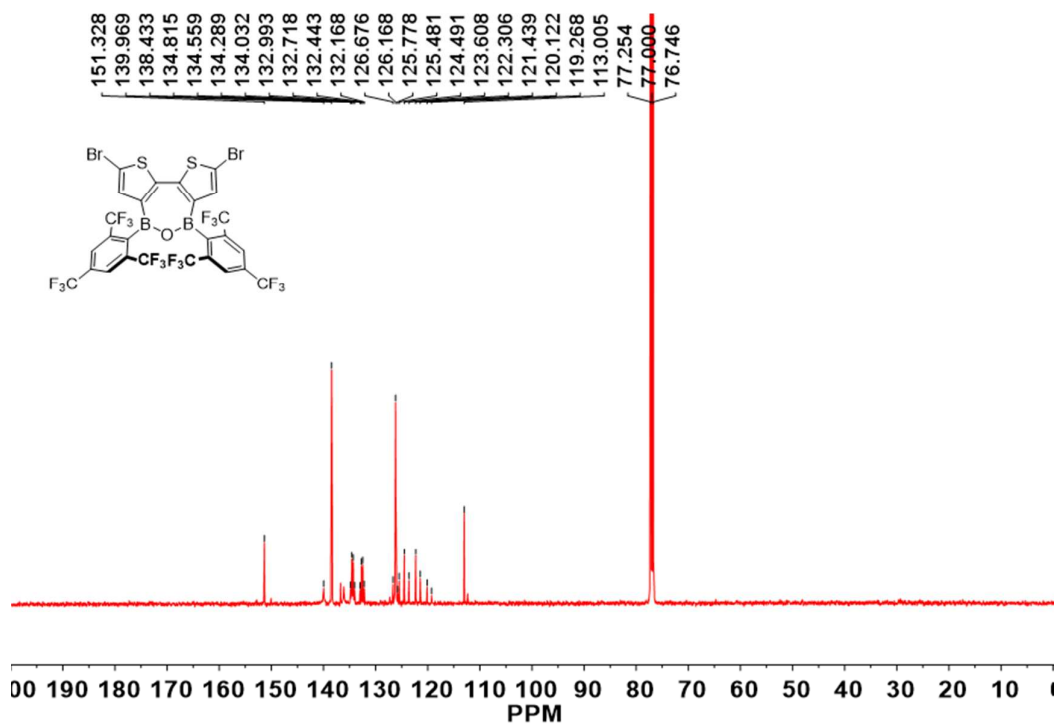


<sup>19</sup>F NMR spectrum of **1**

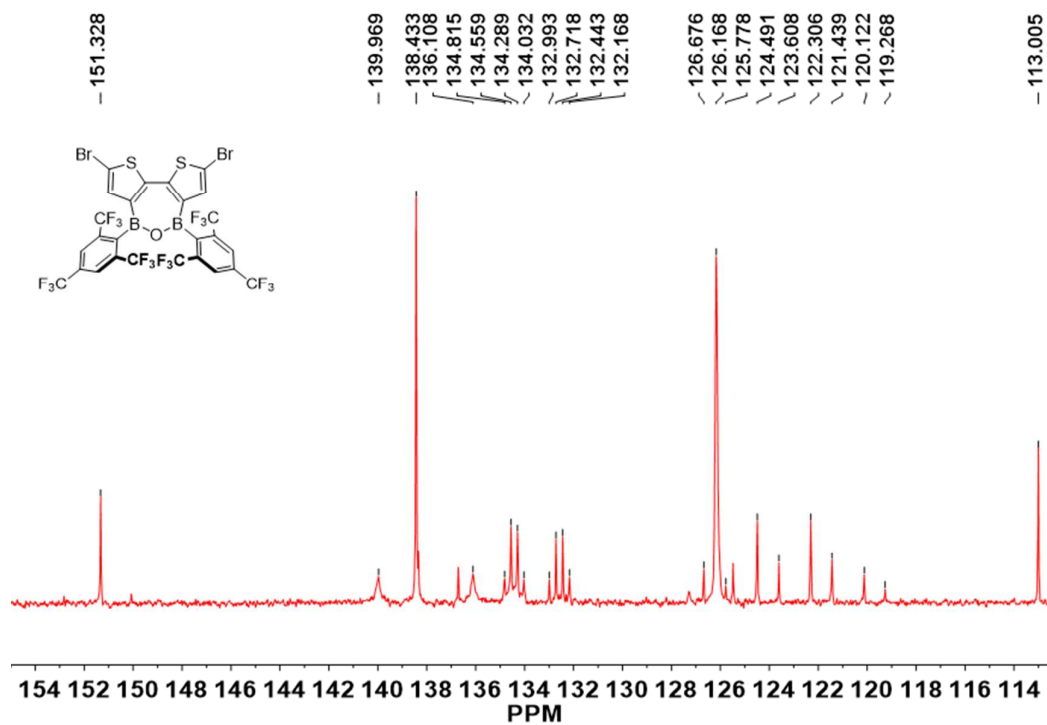




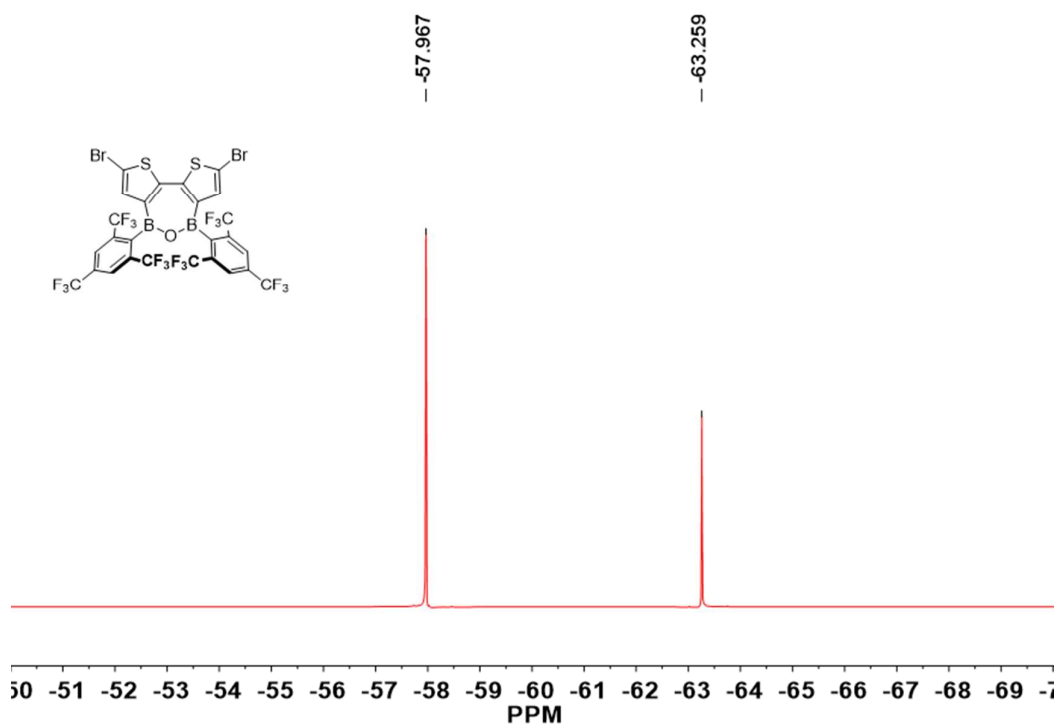
$^1\text{H}$  NMR spectrum of **4**



$^{13}\text{C}$  NMR spectrum of **4**



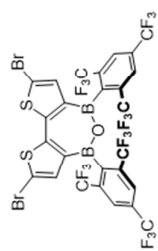
<sup>13</sup>C NMR spectrum of **4** (aromatic region)



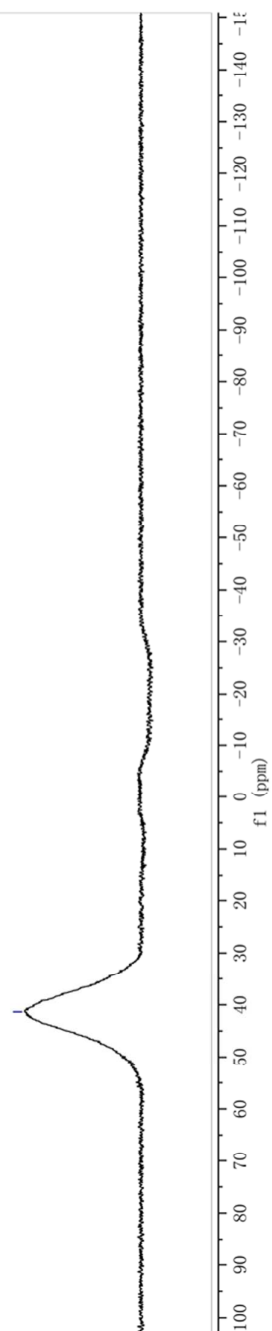
<sup>19</sup>F NMR spectrum of **4**

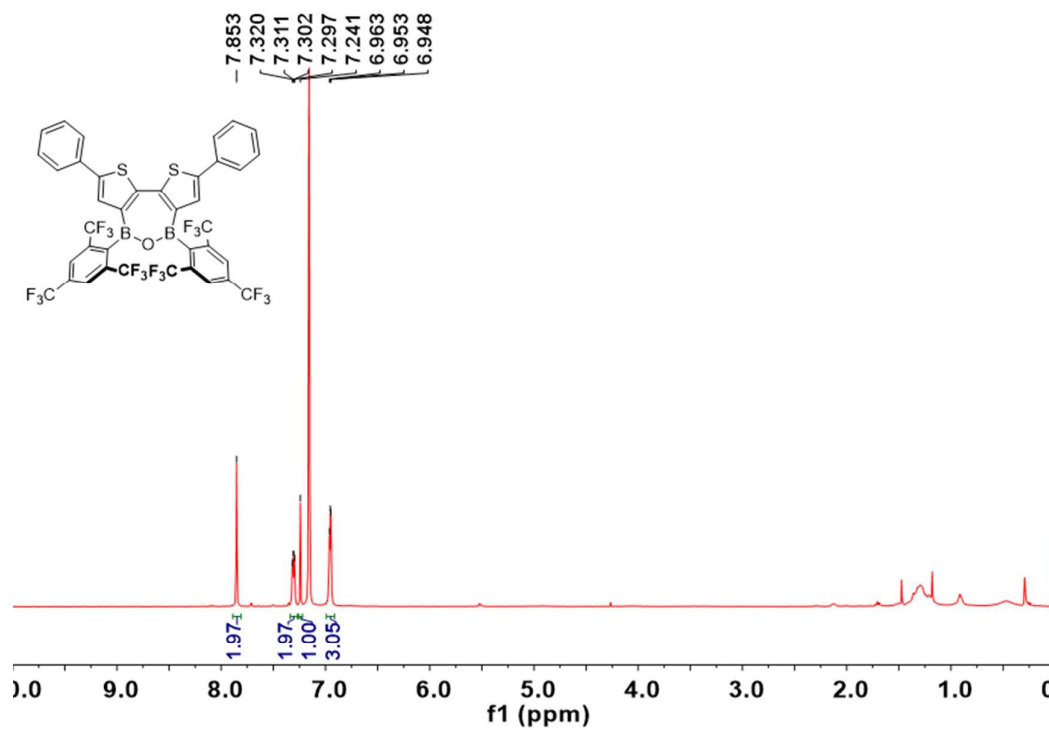


$^{11}\text{B}$  NMR spectrum of **4**

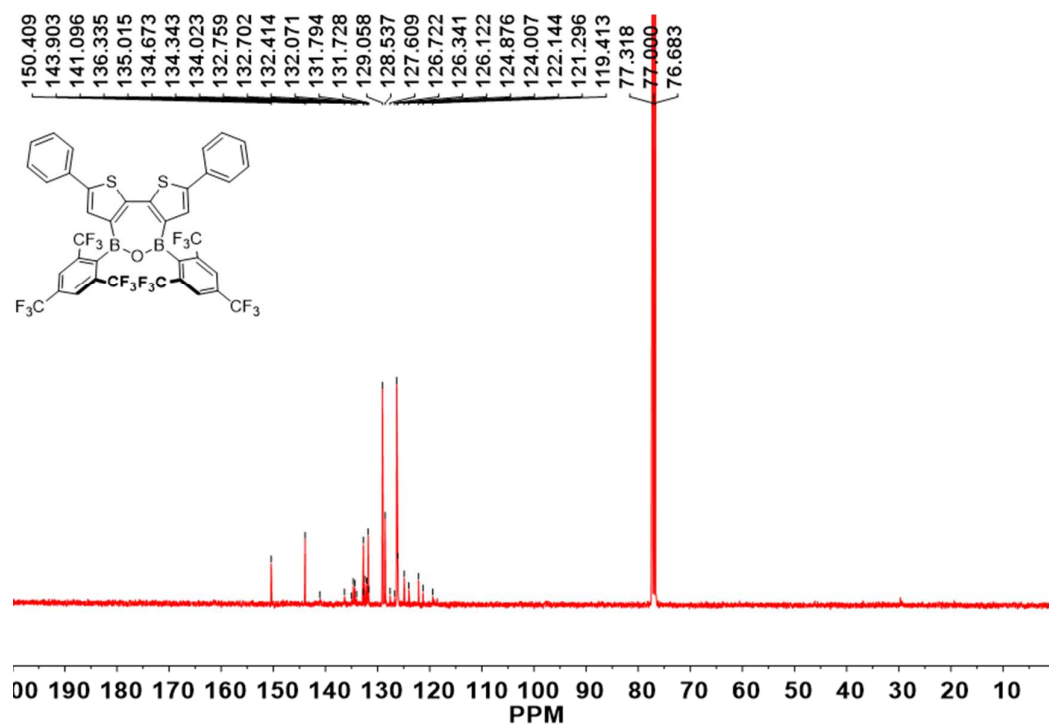


41.35

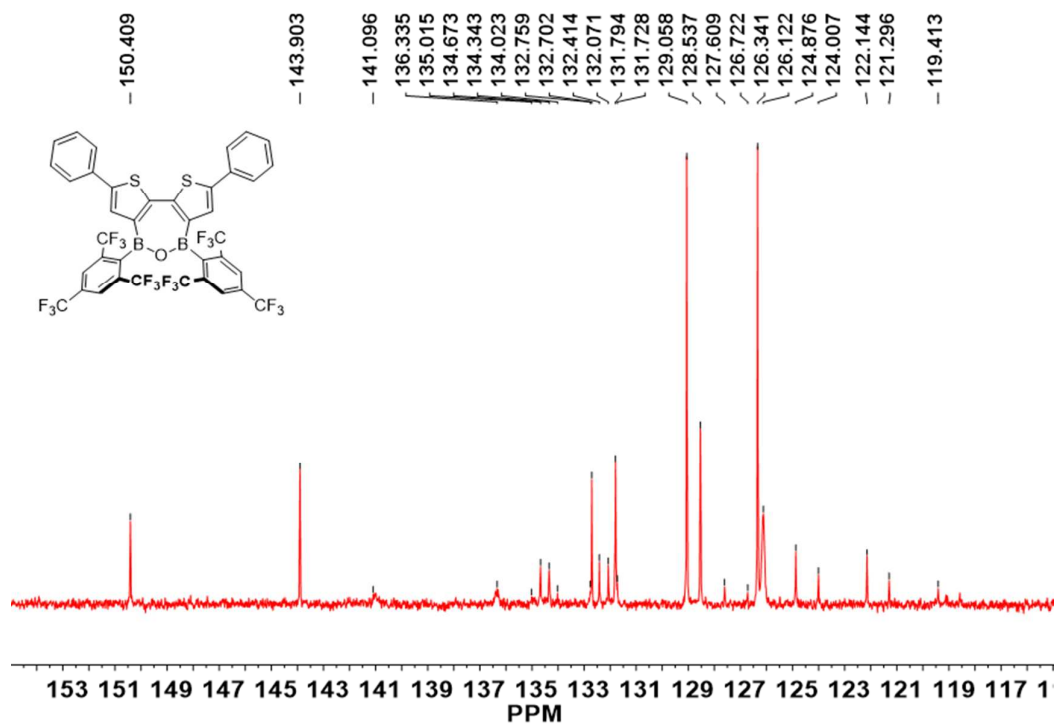




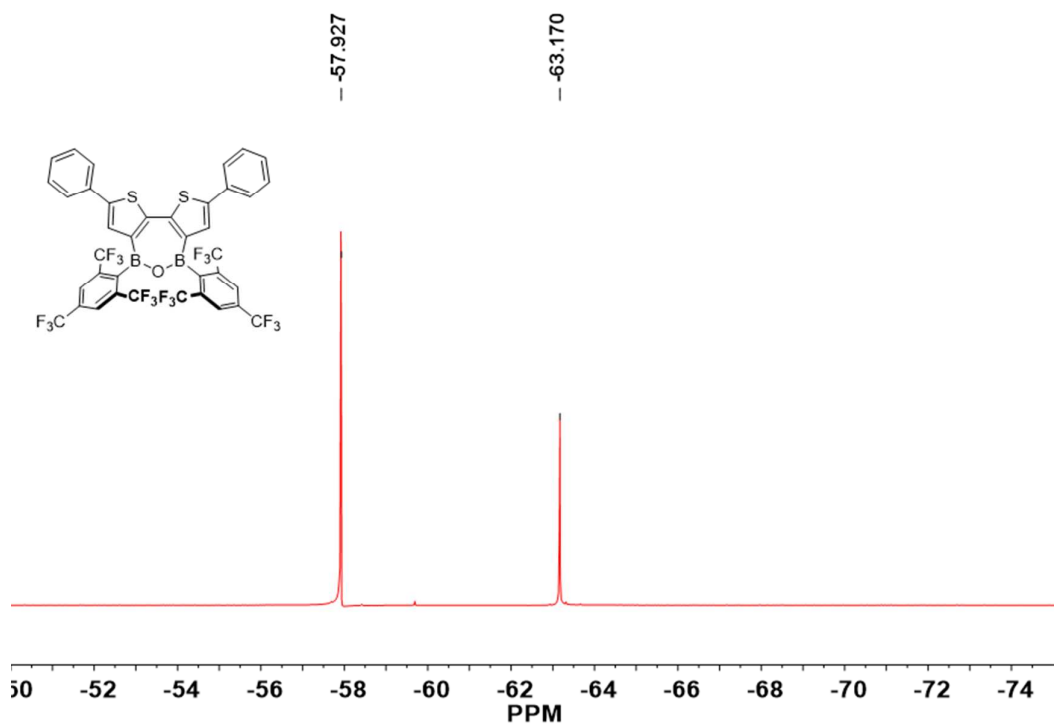
<sup>1</sup>H NMR spectrum of **5A**



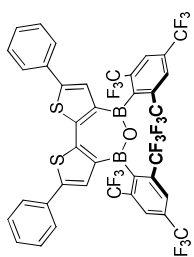
<sup>13</sup>C NMR spectrum of **5A**



<sup>13</sup>C NMR spectrum of **5A** (aromatic region)

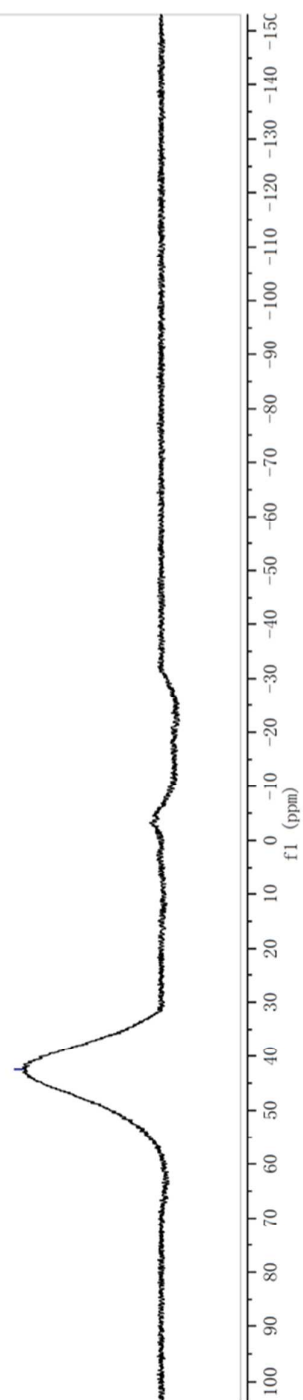


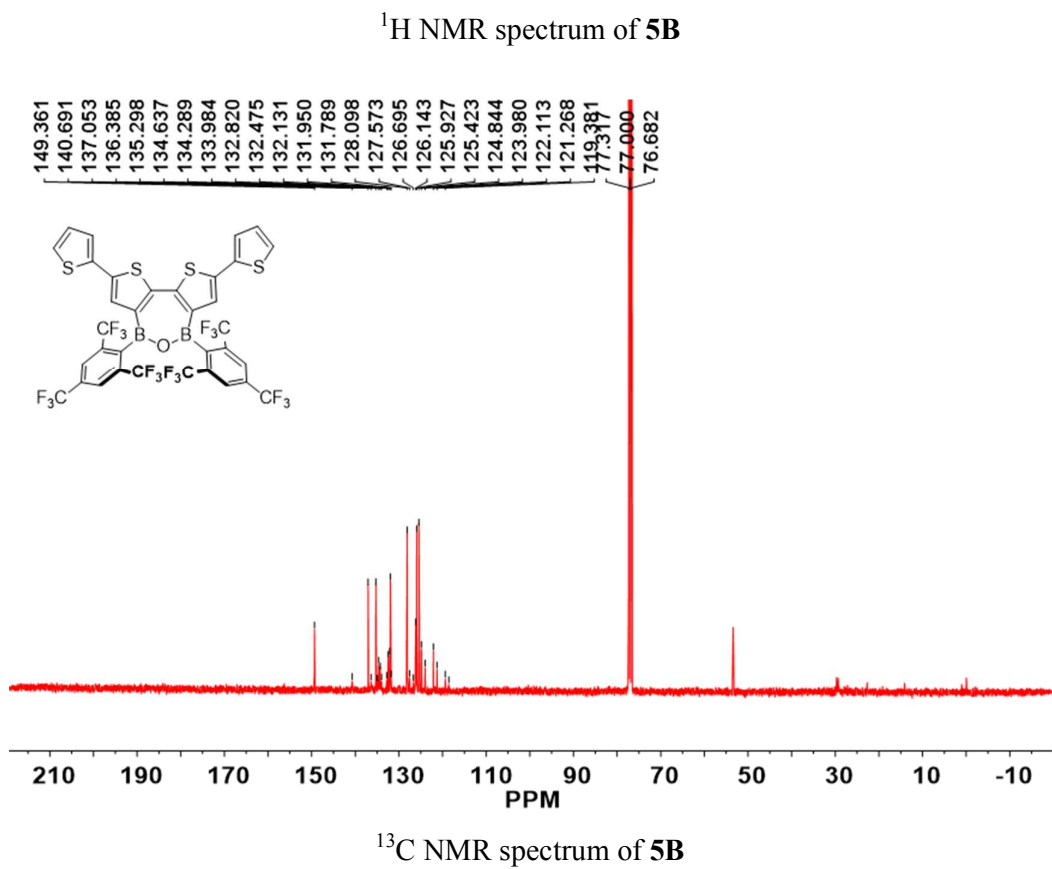
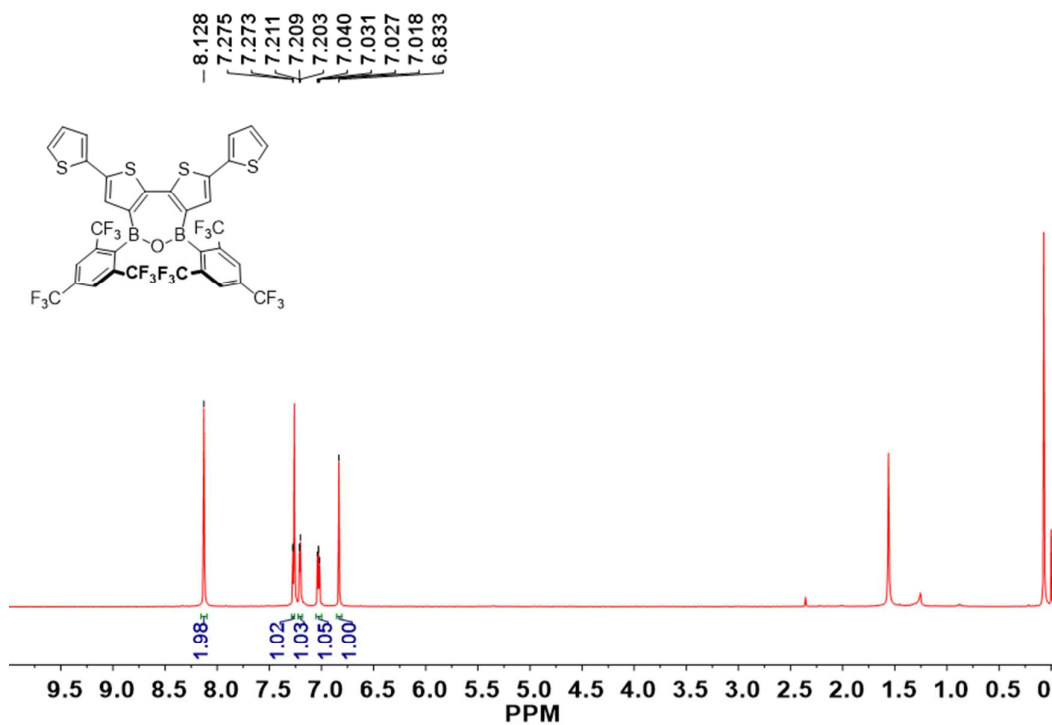
<sup>19</sup>F NMR spectrum of **5A**

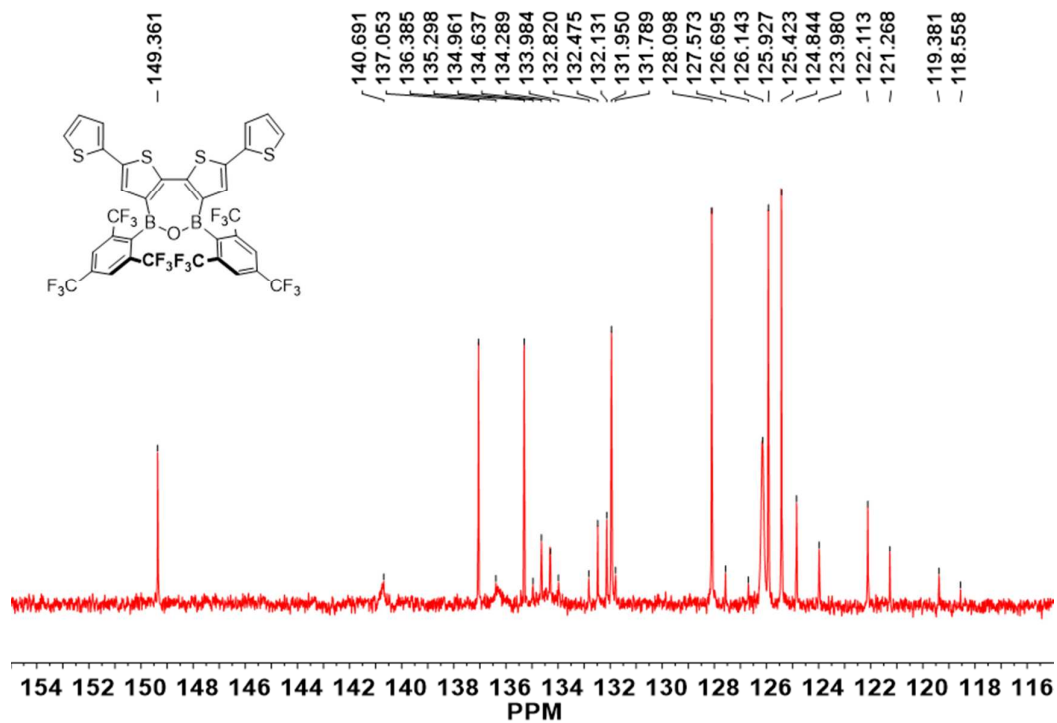


42.49

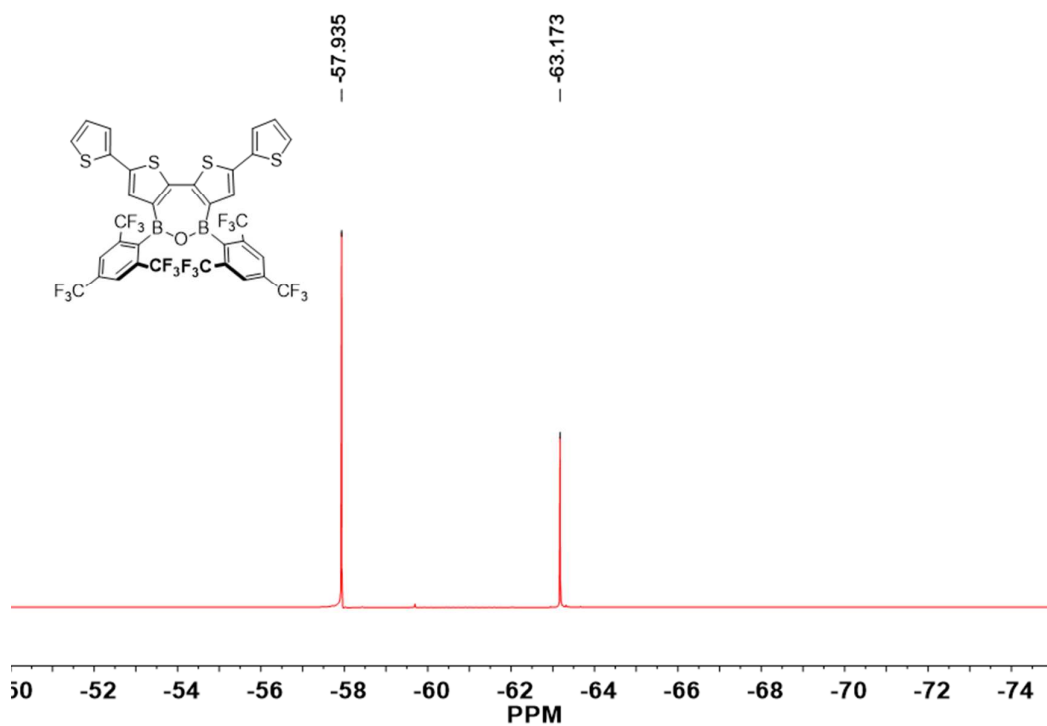
$^{11}\text{B}$  NMR spectrum of **5A**



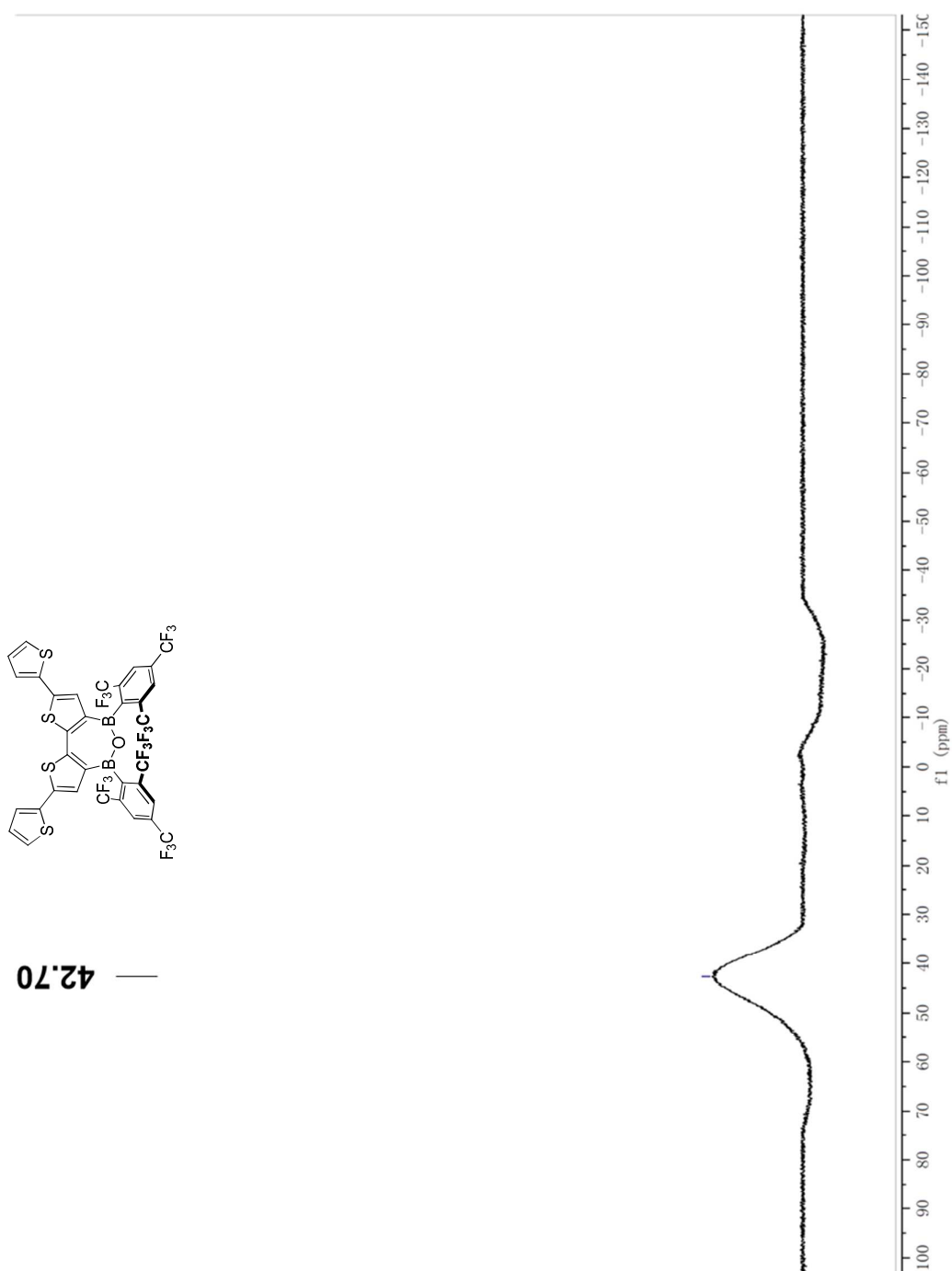




<sup>13</sup>C NMR spectrum of **5B** (aromatic region)



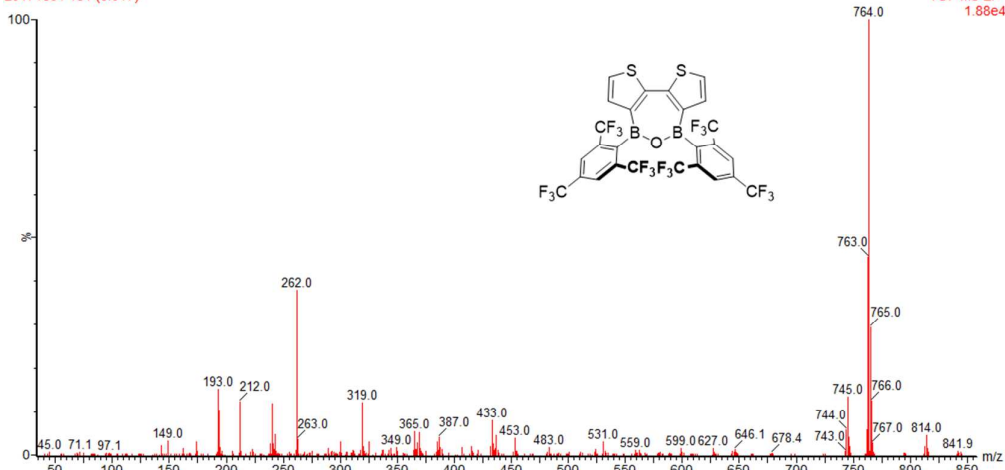
<sup>19</sup>F NMR spectrum of **5B**



<sup>11</sup>B NMR spectrum of **5B**

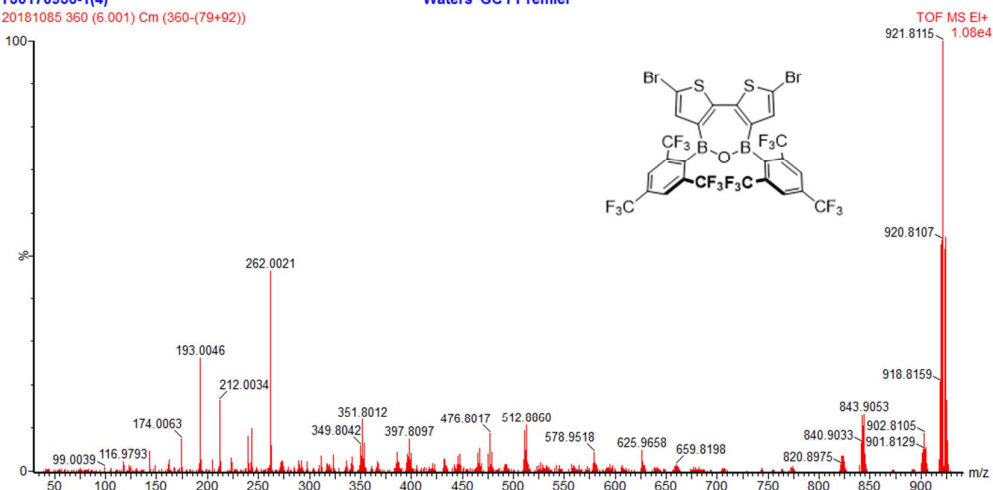
Y30151137-8  
20171631 181 (3.017)

TOF MS EI+  
1.88e4



Y30170956-1(4)  
20181085 360 (6.001) Cm (360-(79+92))

Waters GCT Premier



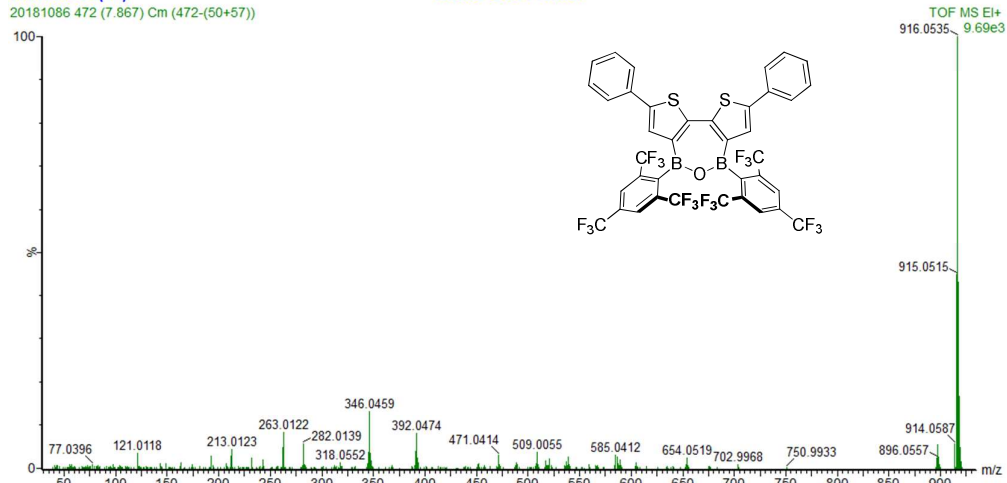
S32



Y30170956-2(5A)

20181086 472 (7.867) Cm (472-(50+57))

Waters GCT Premier

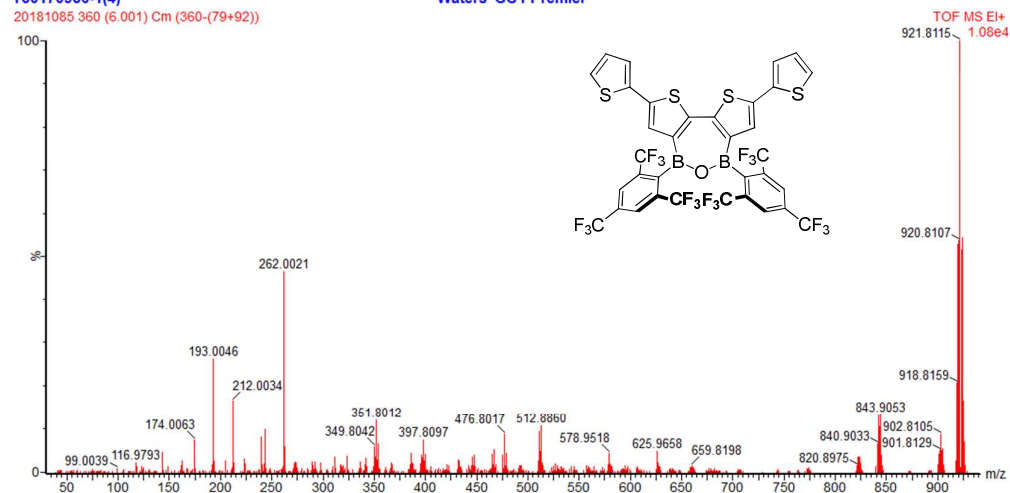


MS of 5A

Y30170956-1(4)

20181085 360 (6.001) Cm (360-(79+92))

Waters GCT Premier



HR-MS of 5B

**References:**

- S1. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., *Gaussian 09, Revision D.01*, Wallingford CT, 2013.
- S2. Dennington, R. II ; Keith, T.; Millam, J.; Eppinnett, K.; Hovell, W. L.; Gilliland, R. *GaussView*, Version 3.09; Semichem, Inc.: Shawnee Mission, KS, 2003.