

## Supporting information

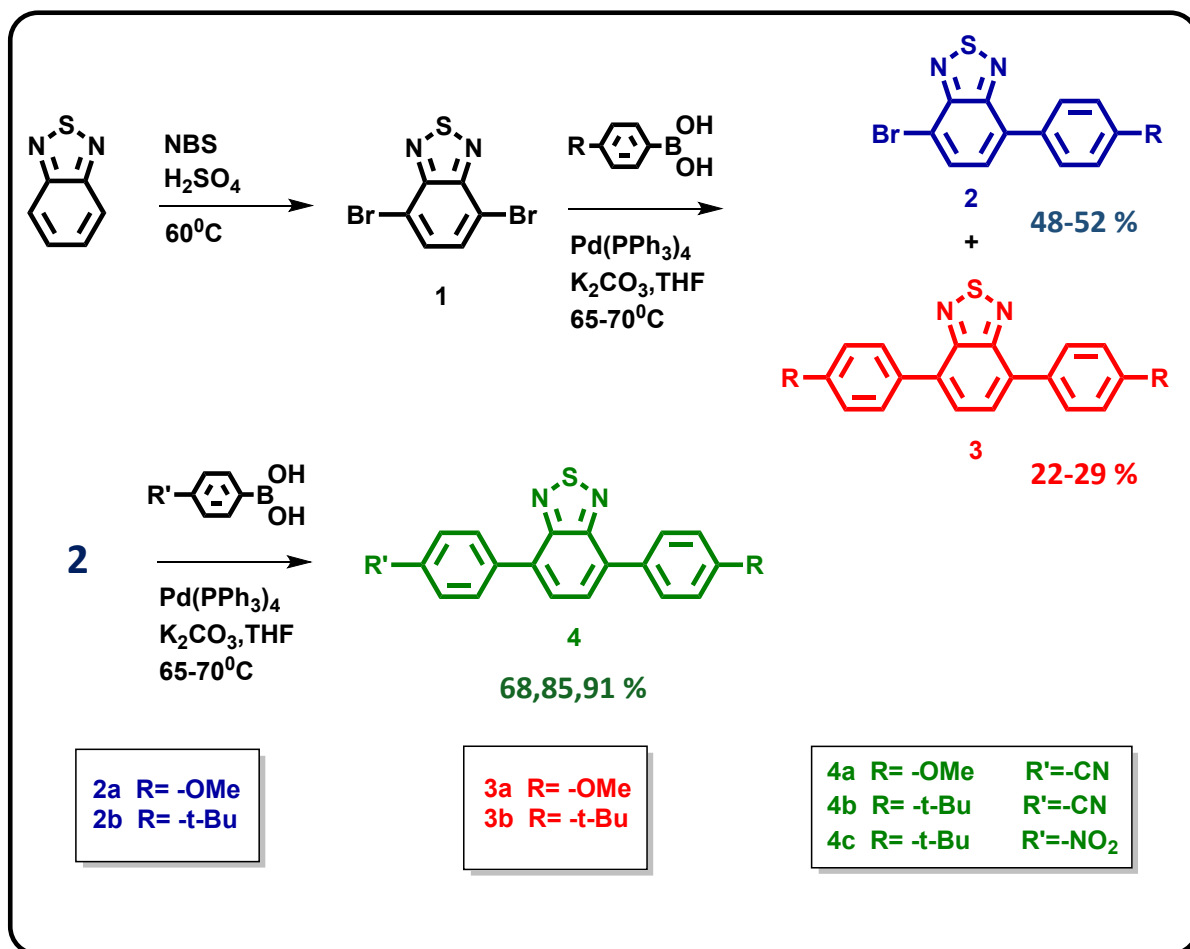
### Switching from Binary to Ternary WORM Memory Behavior of Benzothiadiazole-based D-A System

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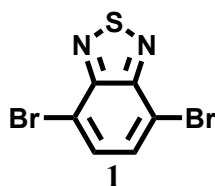
# 1. Synthetic route of the compounds 3a-b and 4a-c



Scheme S1. Synthetic route for compounds

## 2. Synthesis and analytical data of compounds 3a-b and 4a-c

### Compound 1



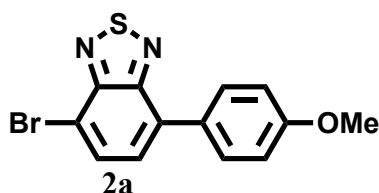
A mixture of 2,1,3-benzothiadiazole (1 g, 7.34 mmol) and NBS (2.1 equiv, 2.7 g, 15.4 mmol) was taken into a 100 mL round bottom flask. Then con. H<sub>2</sub>SO<sub>4</sub> (20 mL) was added, and the reaction mixture was stirred at 65 °C under an N<sub>2</sub> atmosphere for 3 hours. The reaction mixture was cooled at room temperature and transferred to an ice bath on completion. Distilled water was added dropwise, extracted with toluene, and dried over Na<sub>2</sub>SO<sub>4</sub> to separate the organic layer. The crude product was purified by silica gel column chromatography (using hexanes as solvent) to obtain compound **1** (90 %) as white needle crystals. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.73 (s, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 152.98, 132.39, 113.93.

### Synthesis of compounds 2a-c and 3a-b

#### General procedure

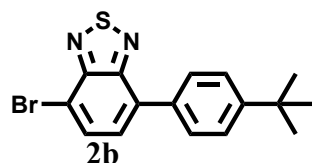
4,7-Dibromobenzothiadiazole (**1**) (500 mg, 1.7 mmol), Ar-B(OH)<sub>3</sub> (1 equiv, 1.7 mmol), Na<sub>2</sub>CO<sub>3</sub> (2 M, 5 mL), THF (20 mL) and one drop of tricaprylylmethylammonium chloride (aliquat 336) was taken in a 100 mL two neck round bottom flask. The reaction mixture was degassed with N<sub>2</sub> gas for 15 minutes, then Pd(PPh<sub>3</sub>)<sub>4</sub> (0.03 equiv, 0.051 mmol) was added to the reaction mixture. The reaction mixture was stirred at 65 °C for 10-20 hours under N<sub>2</sub> atmosphere. After completing the reaction, it was quenched with water and extracted with chloroform. The organic phase was dried and purified solvent by silica gel column chromatography.

### Compound 2a



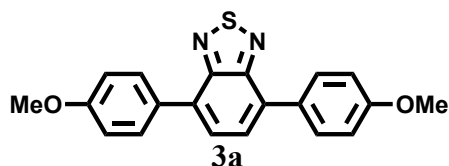
Following the general procedure, compounds **1** and 4-methoxyphenylboronic acid (1 equiv, 1.7 mmol) was allowed to react for 12 hours to yield compound **2a**. The compound was purified using column chromatography in petroleum ether/CHCl<sub>3</sub> as a greenish-yellow solid (48 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.89 (d, *J* = 7.6 Hz, 1H), 7.86 (d, *J* = 8.8 Hz, 2H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.06 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 160.11, 153.90, 153.27, 133.70, 132.35, 130.43, 129.07, 127.46, 114.22, 112.26, 55.44.

### Compound 2b



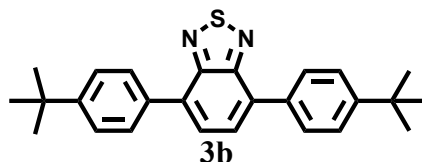
Following the general procedure, compound **1** and 4-tert-butylphenylboronic acid (1 equiv, 1.7 mmol) was reacted for 15 hours to yield compound **2b**, and the product was purified using column chromatography in petroleum ether as a yellow solid (52 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.91 (d, *J* = 7.6 Hz, 1H), 7.84 (d, *J* = 8.8 Hz, 2H), 7.56 (d, *J* = 7.6 Hz, 3H), 1.39 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 153.87, 153.28, 151.92, 134.00, 133.74, 132.35, 128.85, 128.01, 125.78, 112.72, 34.78, 31.32.

### Compound 3a



Following the general procedure, compound **1** and 4-methoxyphenylboronic acid (1 equiv, 1.7 mmol) was reacted for 12 hours to yield compound **2a**. The product was purified using column chromatography in petroleum ether/CHCl<sub>3</sub> as a fluorescent yellow solid (62 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.93 (d, *J* = 8.8 Hz, 4H), 7.72 (s, 2H), 7.08 (d, *J* = 8.4 Hz, 4H), 3.90 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 159.77, 154.23, 132.36, 130.40, 130.03, 127.44, 114.12, 55.43.

### Compound 3b



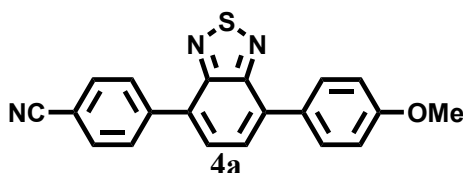
Following the general procedure, compound **1** and 4-tert-butylphenylboronic acid (1 equiv, 1.7 mmol) was reacted for 15 hours to yield compound **2b**, and the product was purified using column chromatography in petroleum ether as a fluorescent yellow solid (69 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.91 (d, *J* = 8.0 Hz, 4H), 7.76 (s, 2H), 7.58 (d, *J* = 8.4 Hz, 4H), 1.40 (s, 18H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 154.22, 151.40, 134.63, 133.01, 128.89, 127.93, 125.67, 34.75, 31.37.

### Synthesis of compound 4a-c

#### General procedure

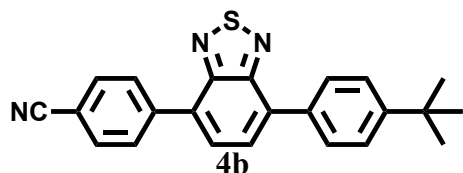
Compound **2a-c** (75 mg, 1 equiv), Ar'-B(OH)<sub>3</sub> (1.3 equiv), Na<sub>2</sub>CO<sub>3</sub> (2 M, 3 mL), THF (15 mL), and 1 drop of tricarprylmethylammonium chloride (aliquot 336) was taken in a 100 mL two-neck round bottom flask. The reaction mixture was degassed with N<sub>2</sub> gas for 15 minutes, then Pd(PPh<sub>3</sub>)<sub>4</sub> (0.1 equiv) was added to the reaction mixture. The reaction mixture was stirred at 65 °C for 24 hours. After completion of the reaction, it was quenched with water and extracted with chloroform. The organic phase was dried and purified by silica gel column chromatography.

#### Compound 4a



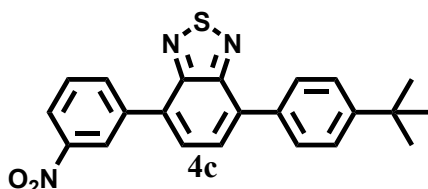
Following the general procedure, compound **2a** (75mg, 1equiv) and 4-cyanophenylboronic acid (1.3 equiv) were reacted to yield compound **4a**. The product was purified using column chromatography in hexanes: chloroform as a greenish-yellow compound (68 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.11 (d, *J* = 8.4 Hz, 2H), 7.95 (d, *J* = 8.8 Hz, 2H), 7.84 – 7.81 (m, 3H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 8.8 Hz, 2H), 3.91 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 160.15, 154.13, 141.92, 134.52, 132.37, 130.55, 130.33, 129.42, 129.04, 127.02, 118.89, 114.21, 111.66, 55.44.

#### Compound 4b



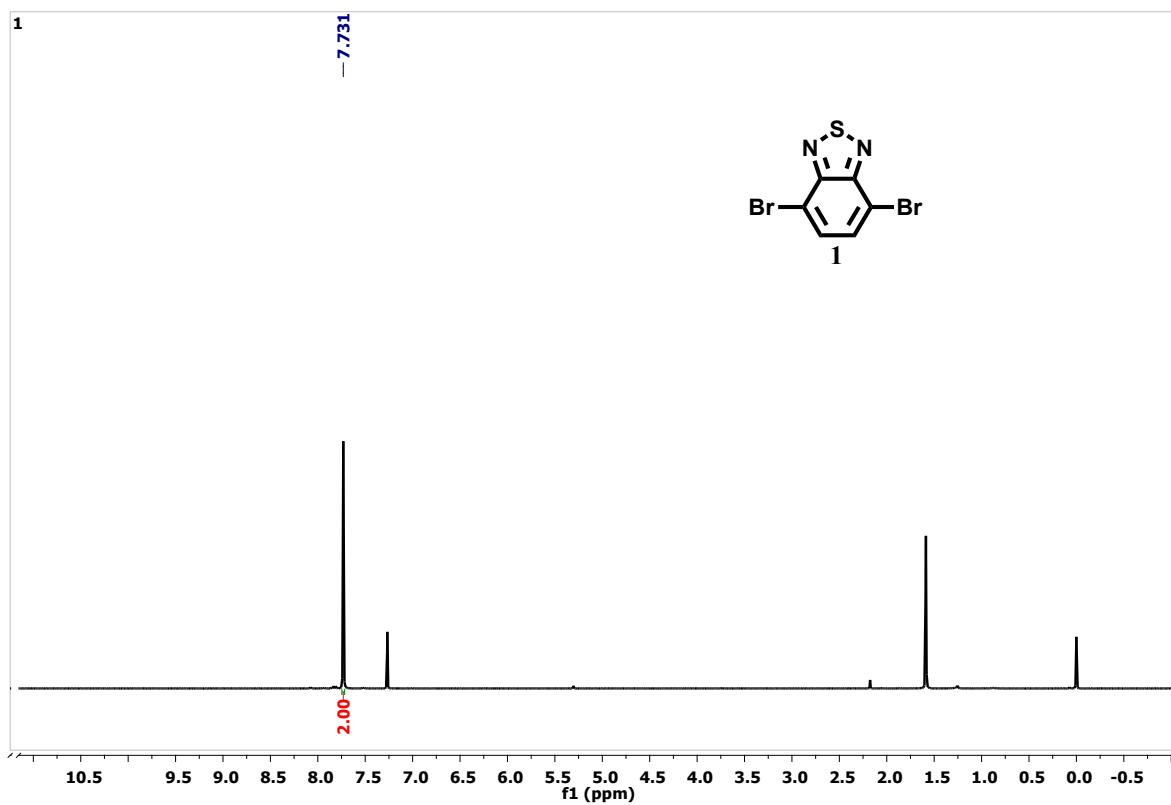
Following the general procedure, compound **2b** (75 mg, 1 equiv) and 4-cyanophenylboronic acid (1.3 equiv) were reacted to yield compound **4b** through column chromatography in hexane: EtOAc as a greenish-yellow compound (85 %).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.12 (d,  $J = 8.0$  Hz, 2H), 7.91 (d,  $J = 8.4$  Hz, 2H), 7.83 (d,  $J = 7.2$  Hz, 4H), 7.60 (d,  $J = 8.0$  Hz, 2H), 1.41 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  154.16, 153.59, 151.96, 141.90, 134.85, 134.11, 132.39, 130.71, 129.82, 128.98, 127.60, 125.77, 118.89, 111.73, 34.79, 31.33.

### Compound 4c



Following the general procedure, compound **2b** (75 mg, 1equiv) and 3-nitrophenylboronic acid (1.3 equiv) were reacted to yield compound **4c**. The product was purified using column chromatography in petroleum ether: chloroform as a greenish-yellow compound (91 %).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.87 (s, 1H), 8.36 (d,  $J = 7.6$  Hz, 1H), 8.31 (d,  $J = 9.6$  Hz, 1H), 7.92 (d,  $J = 8.0$  Hz, 2H), 7.87 (d,  $J = 7.2$  Hz, 1H), 7.82 (d,  $J = 7.2$  Hz, 1H), 7.72 (t,  $J = 8.0$  Hz, 1H), 7.60 (d,  $J = 8.4$  Hz, 2H), 1.41 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  154.15, 153.62, 151.94, 148.56, 138.98, 135.13, 134.78, 134.12, 130.13, 129.56, 128.99, 128.80, 127.61, 125.78, 124.07, 122.95, 34.80, 31.34.

### 3. $^1\text{H}$ , $^{13}\text{C}$ NMR, and HRMS Spectra of the synthesized compounds





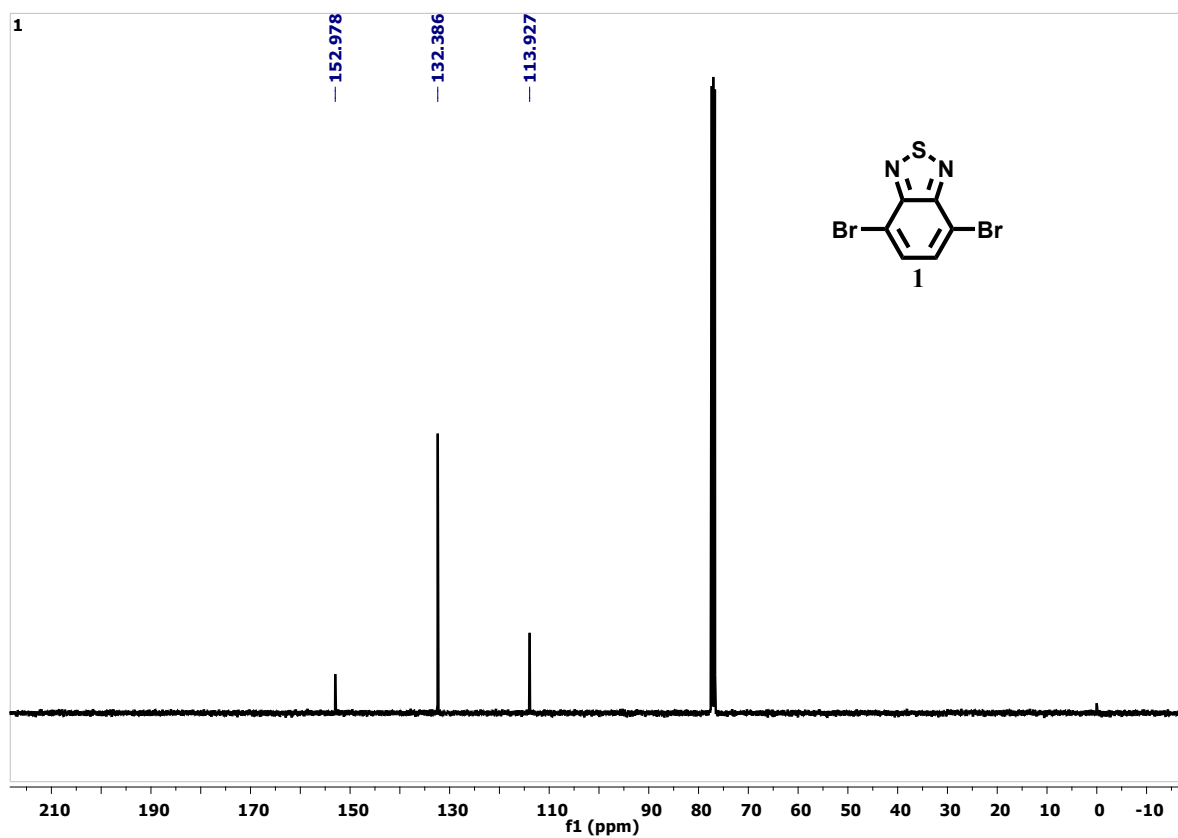


Figure S1:  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of compound 1

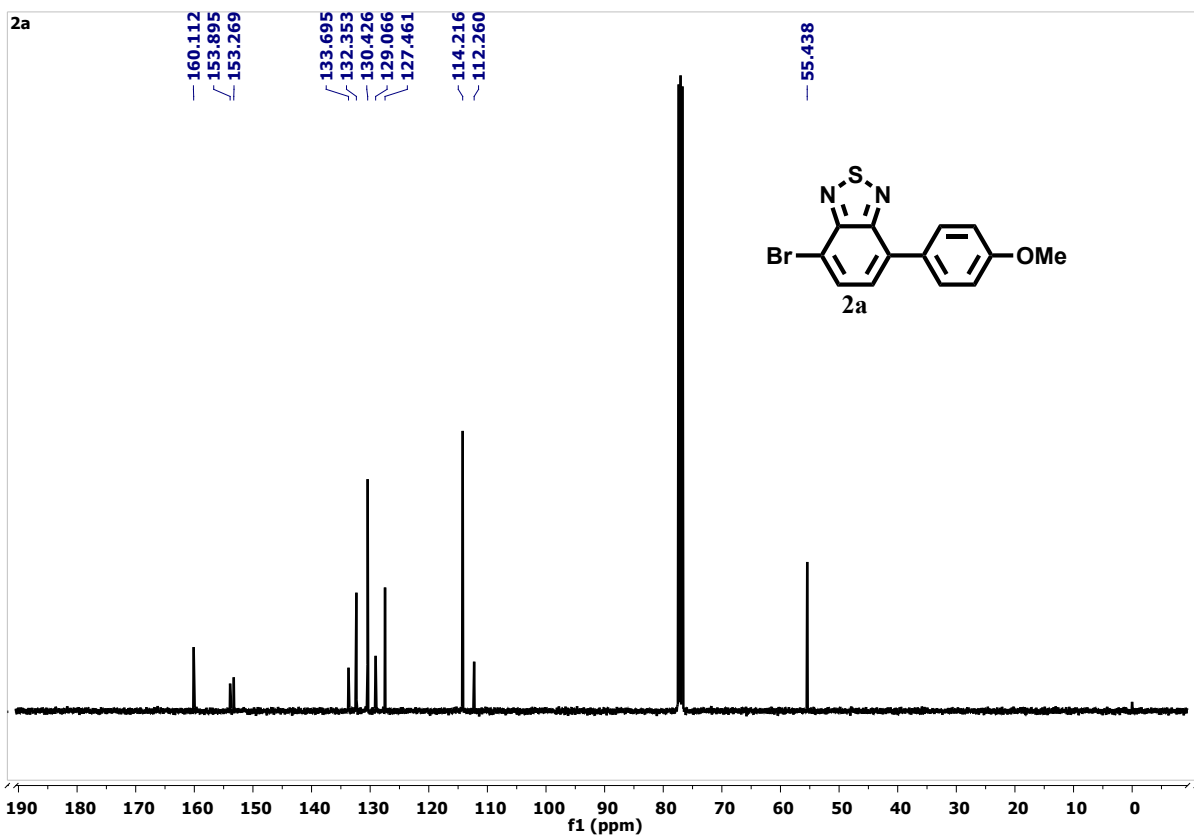
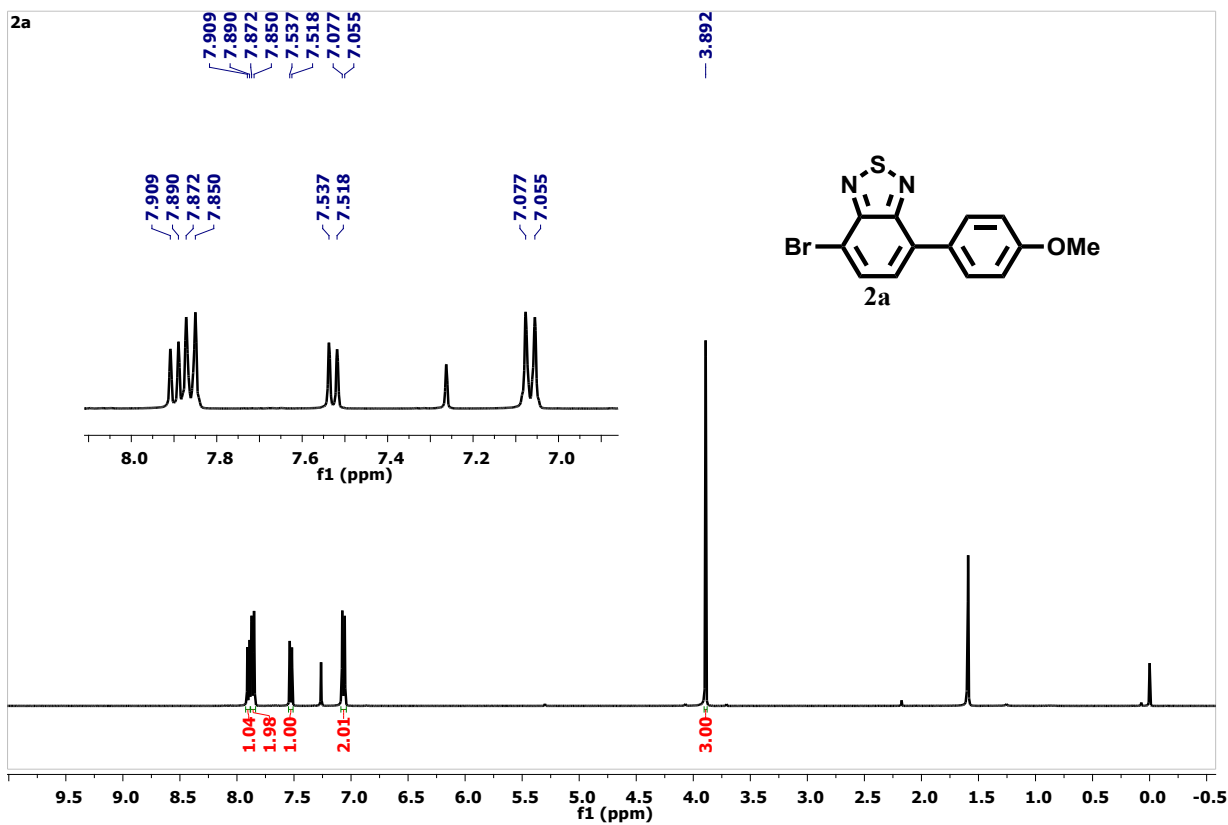


Figure S2: <sup>1</sup>H and <sup>13</sup>C NMR spectra of compound 2a

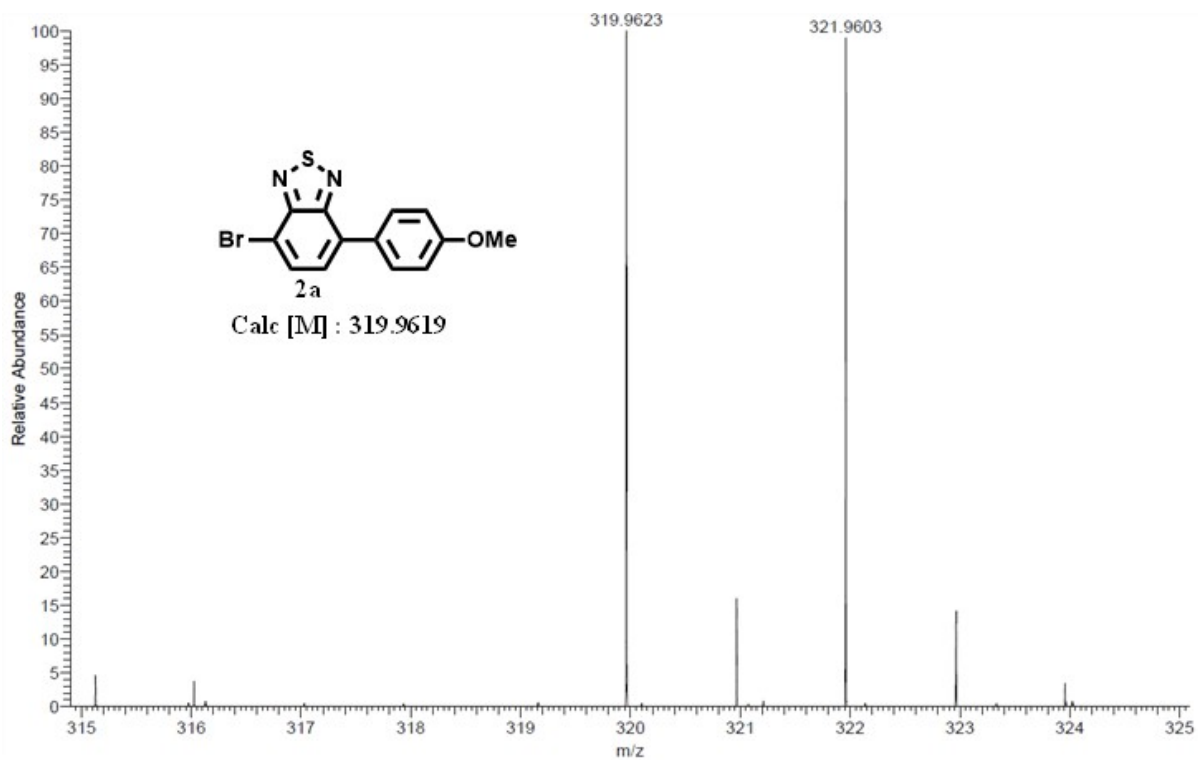
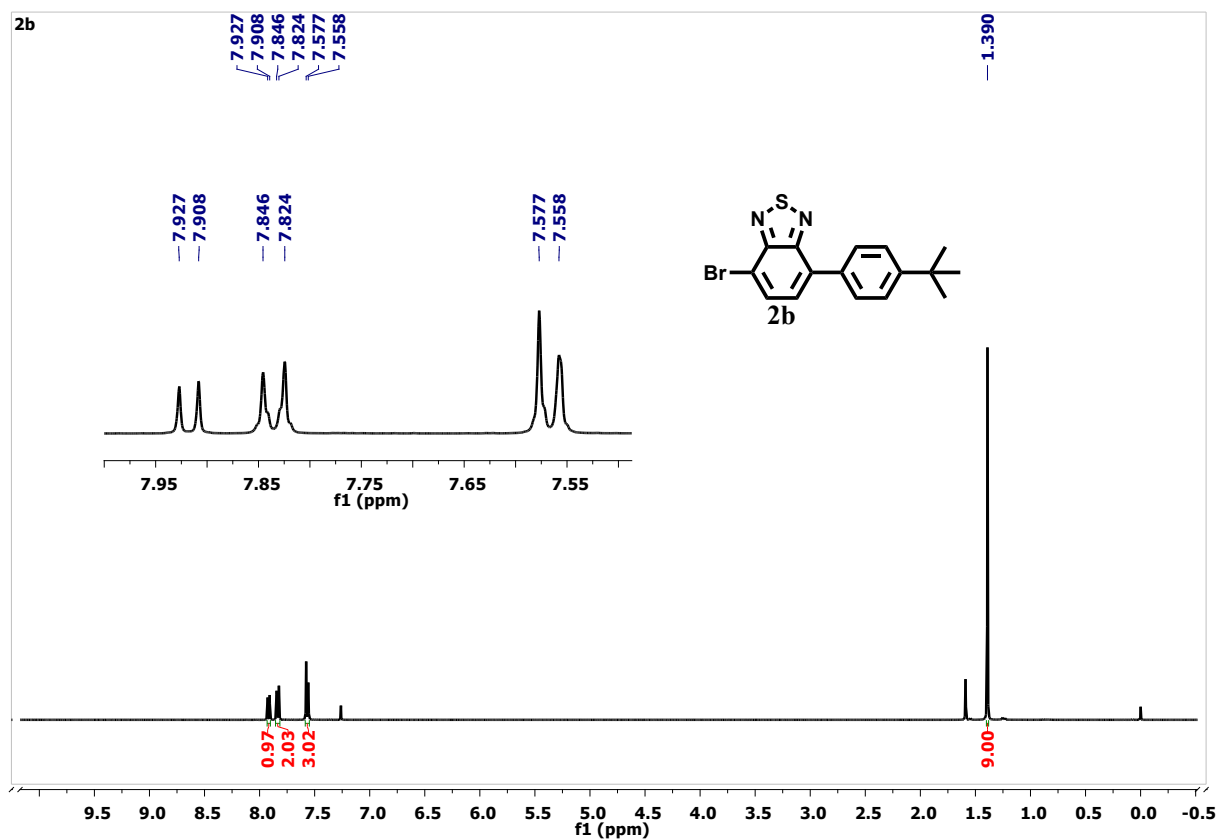
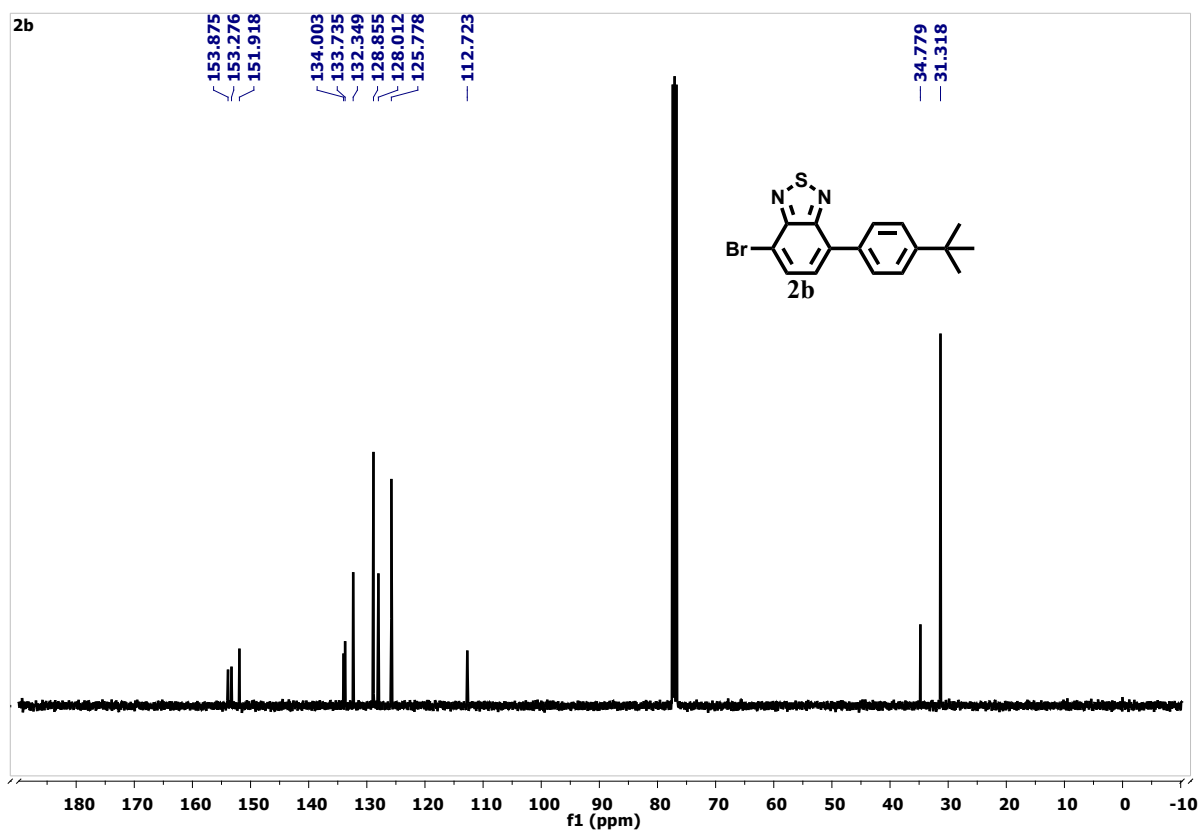
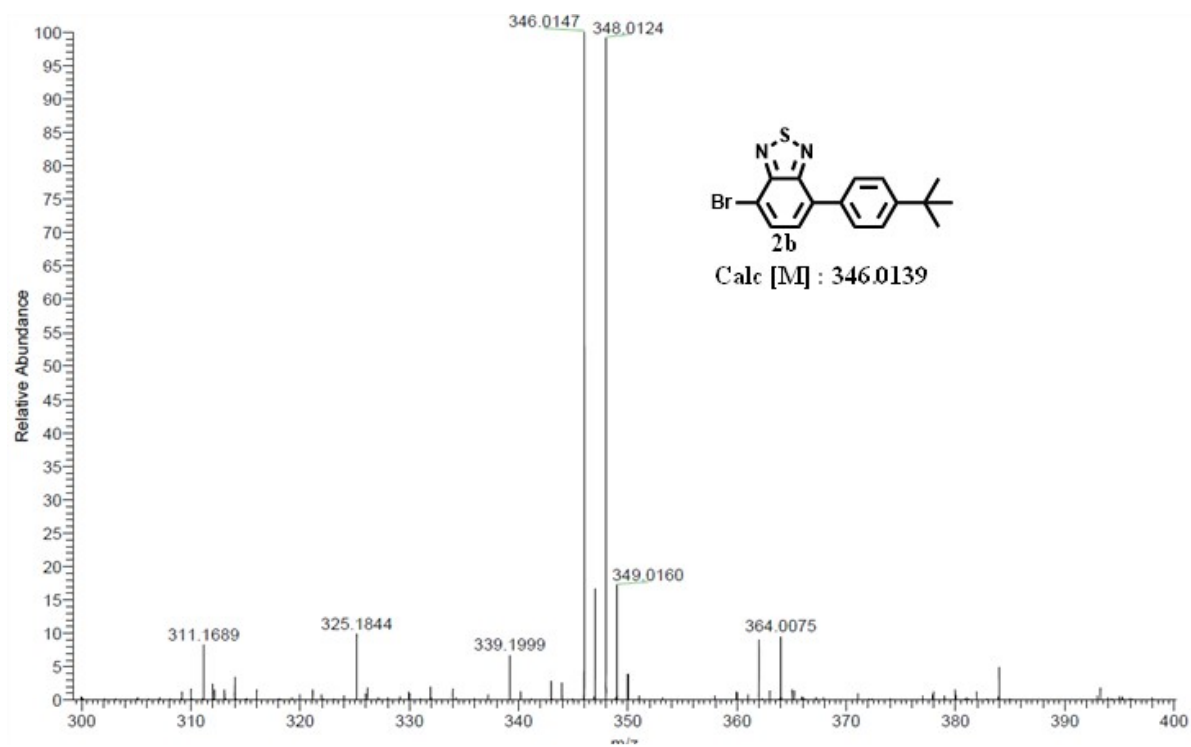


Figure S3: HRMS spectrum of compound 2a





**Figure S4:  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of compound 2b**



**Figure S5: HRMS spectrum of compound 2b**

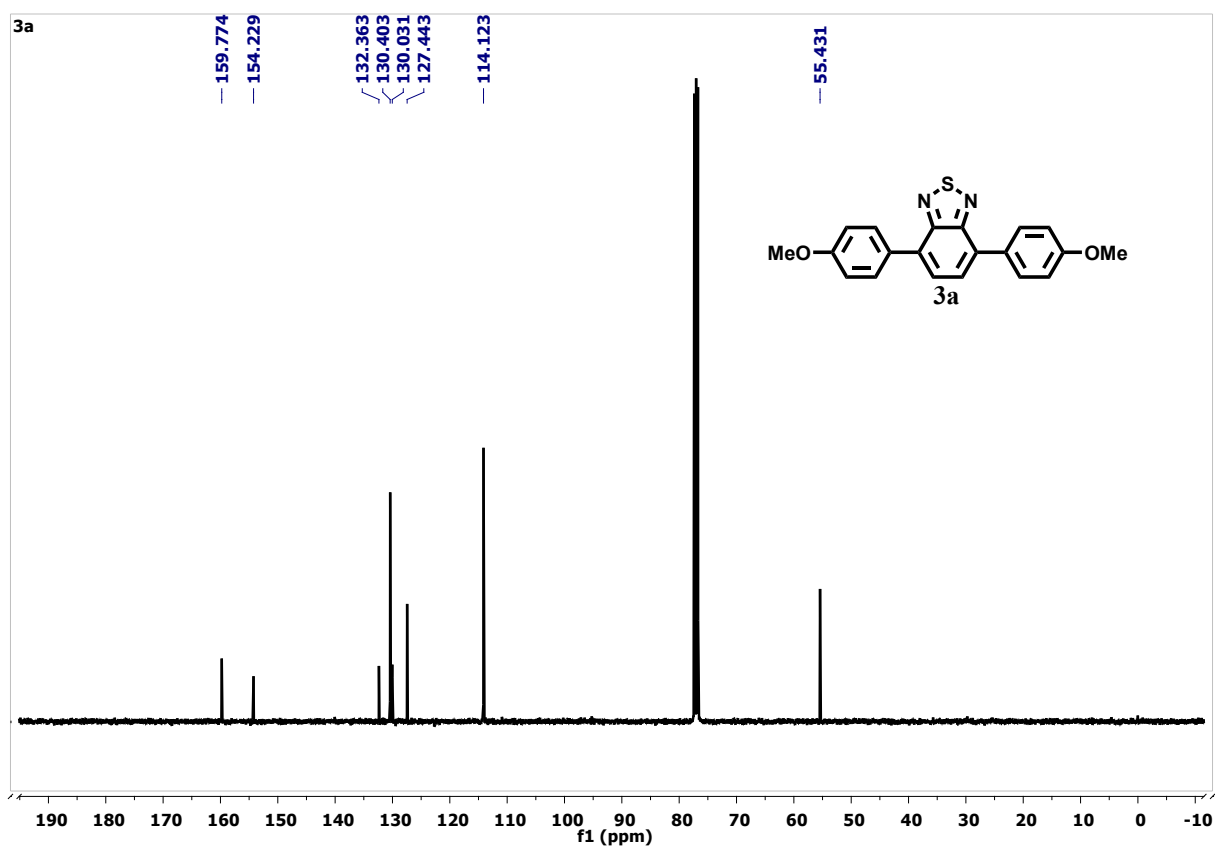
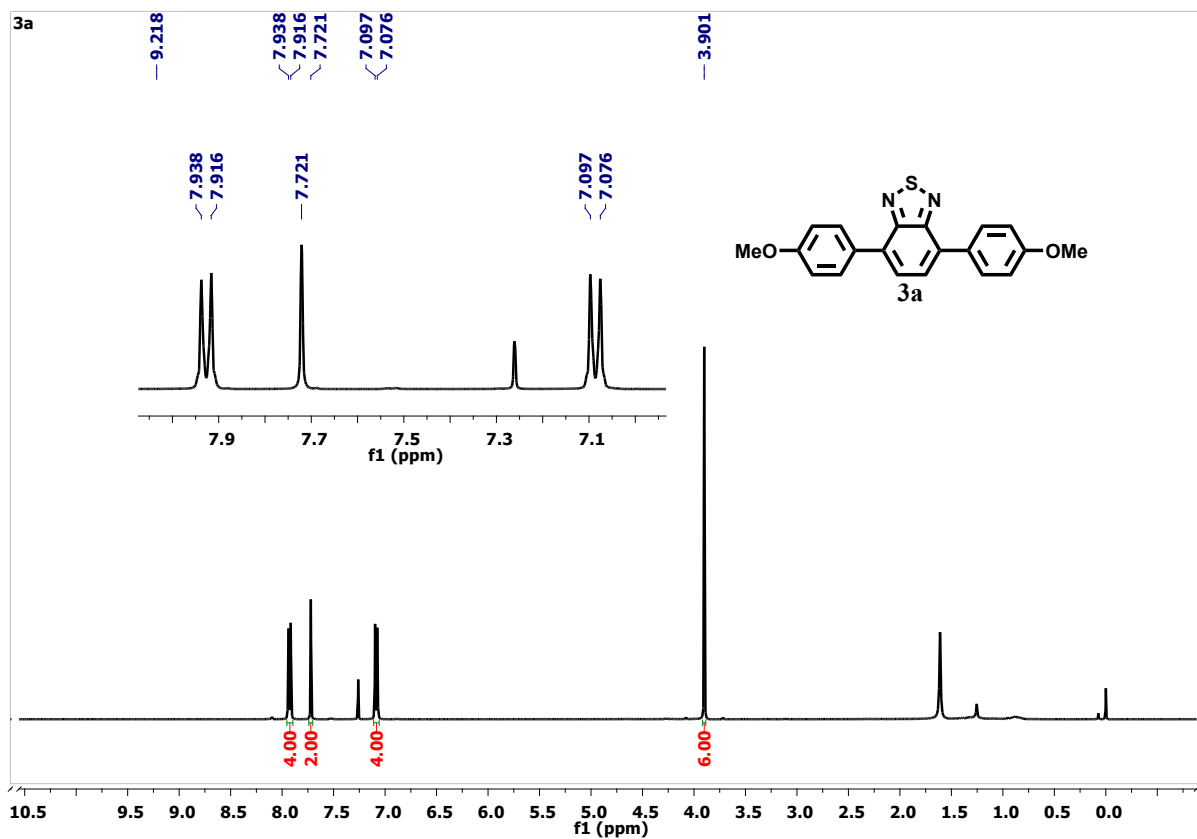


Figure S6:  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of compound 3a

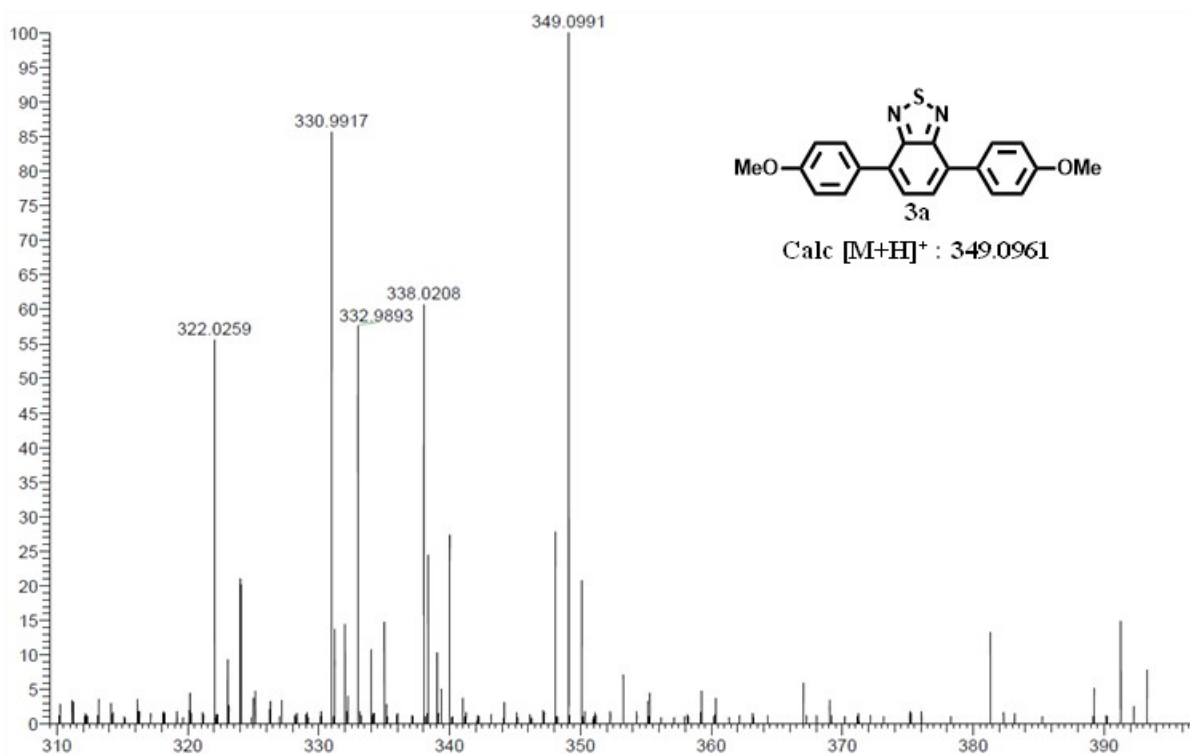
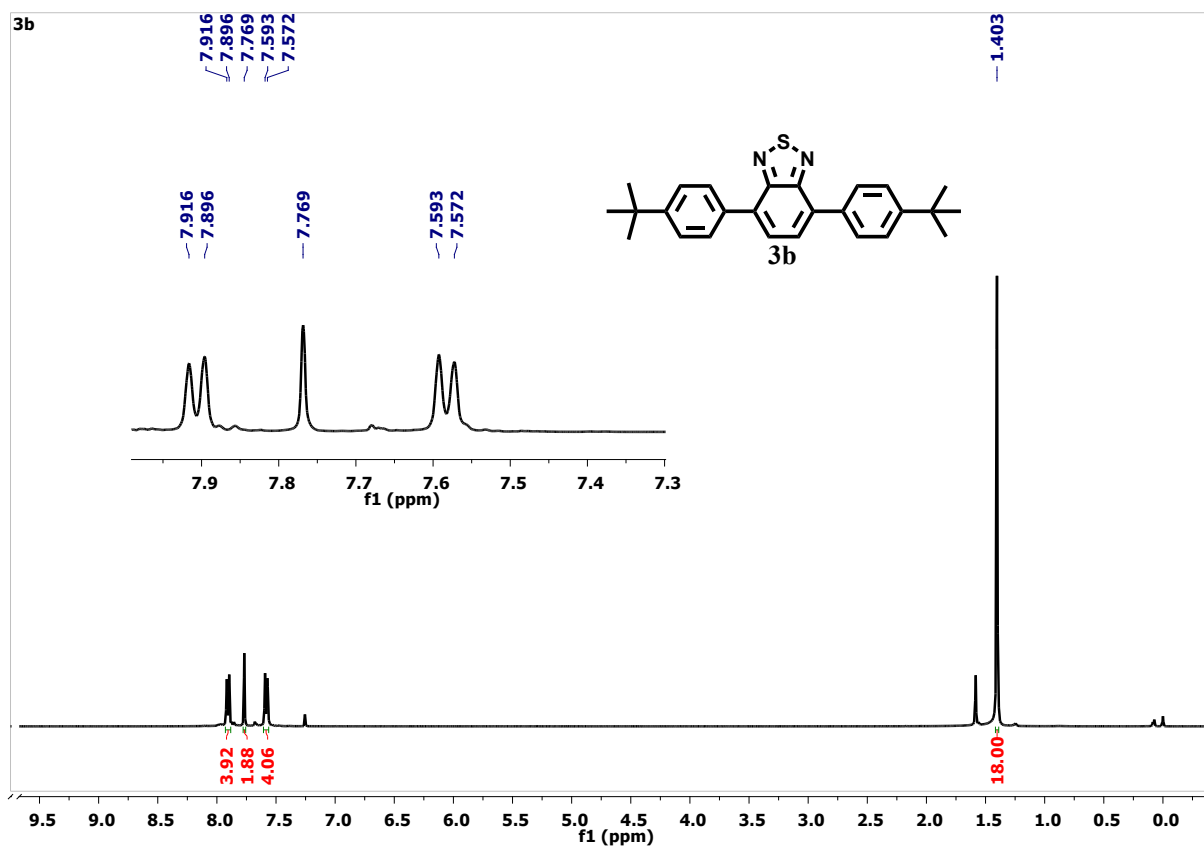
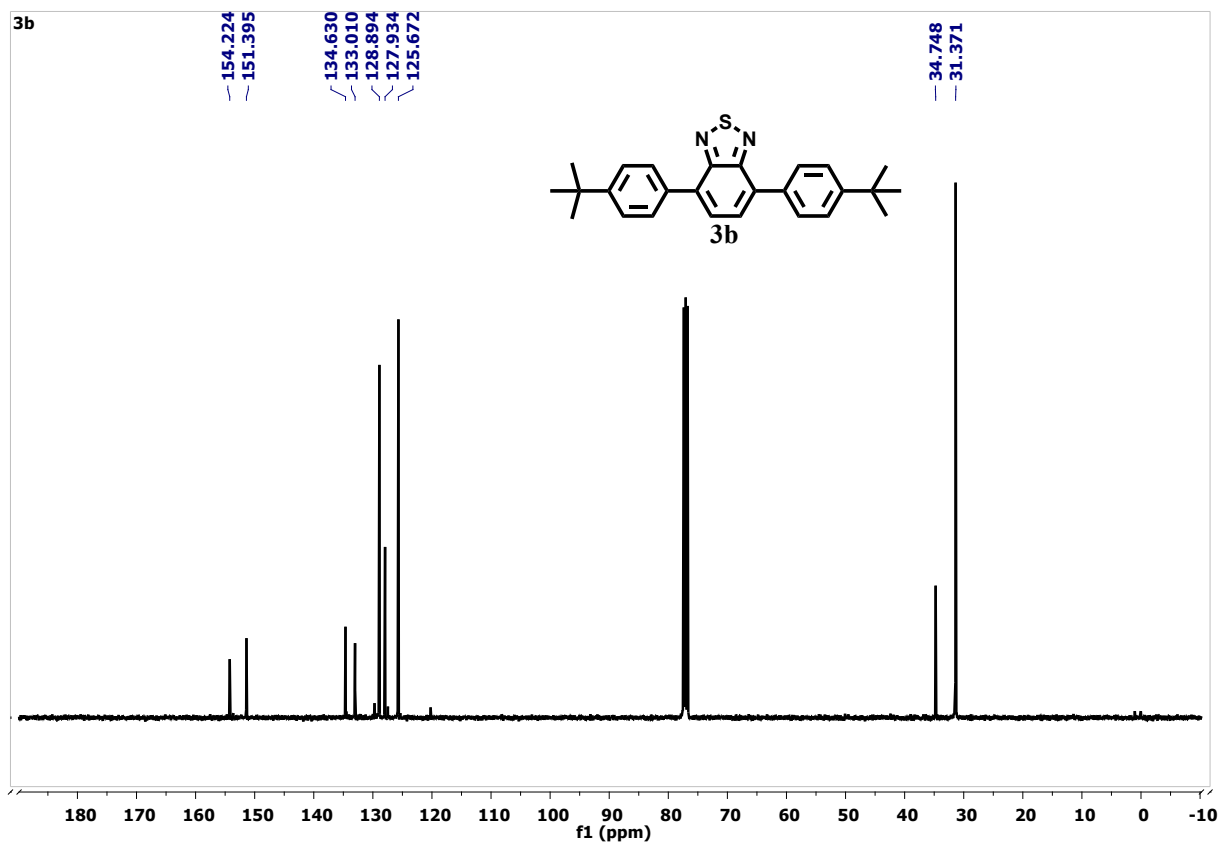
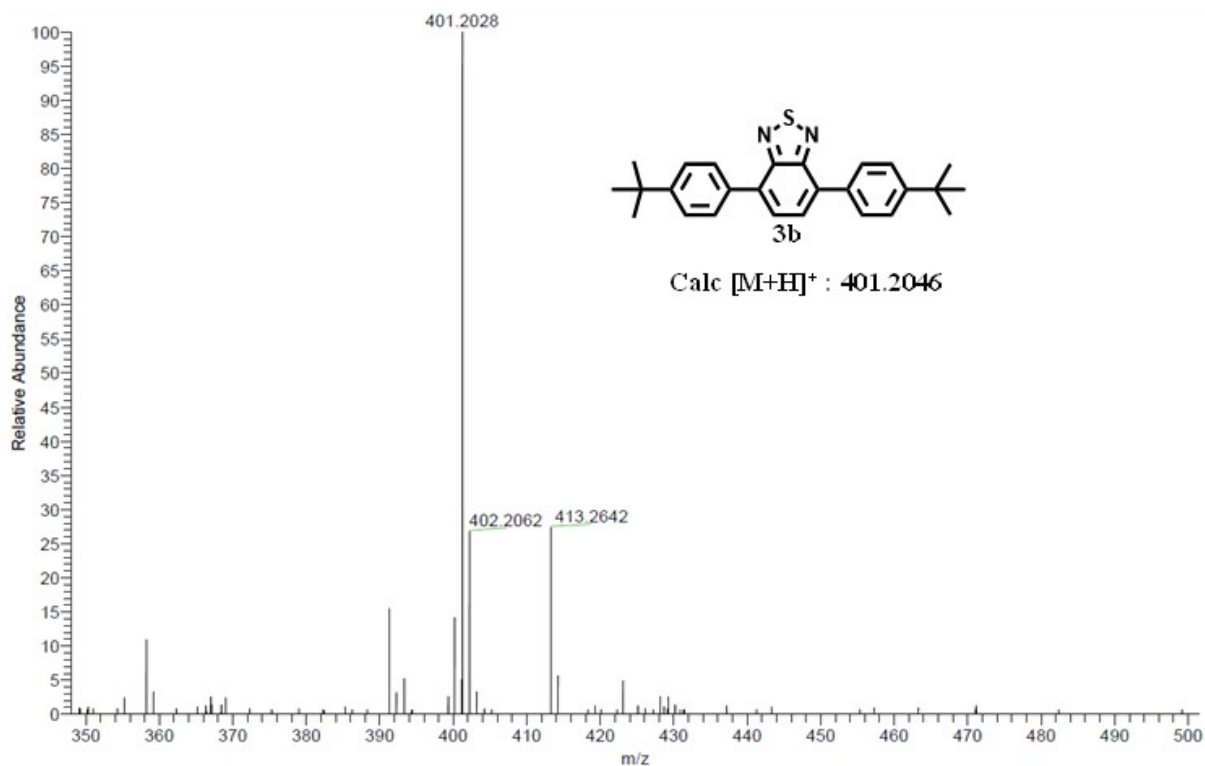


Figure S7: HRMS of spectrum compound 3a





**Figure S8:  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of compound 3b**



**Figure S9: HRMS spectrum of compound 3b**

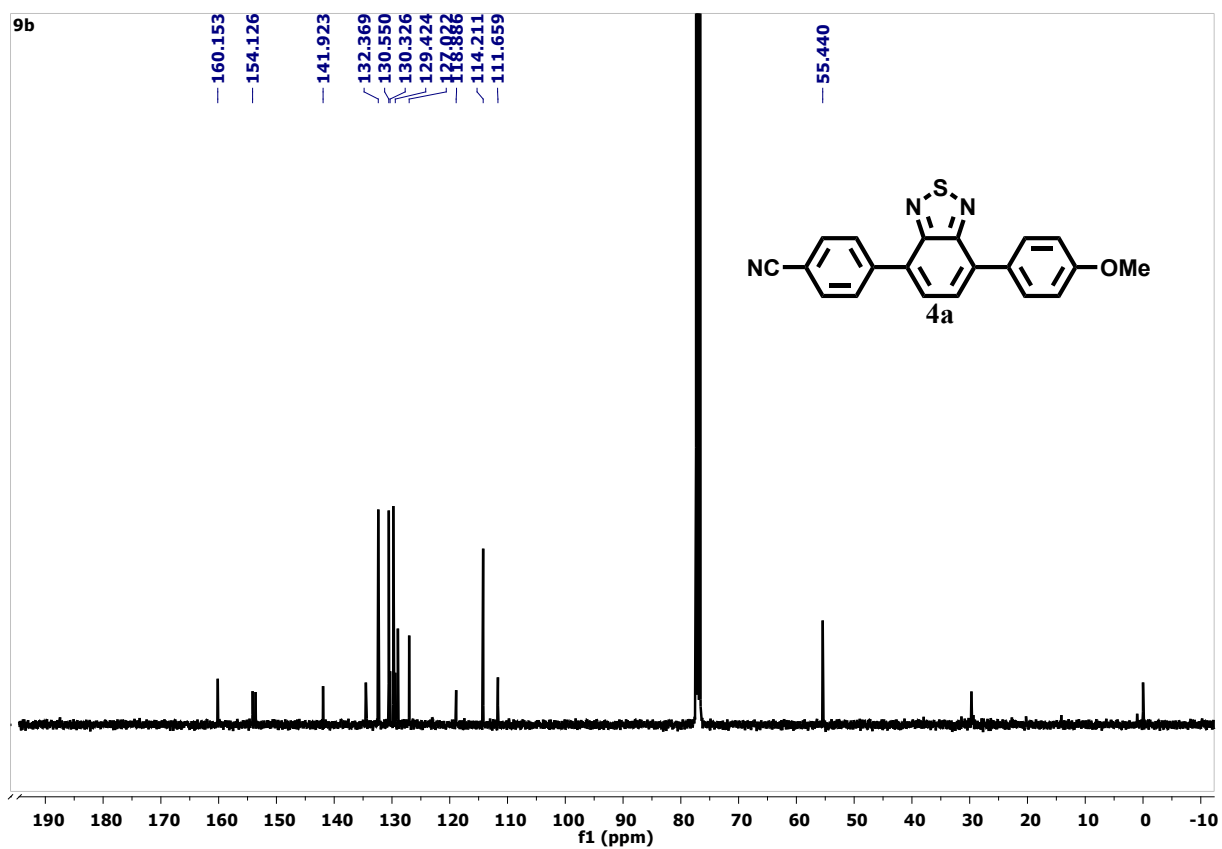
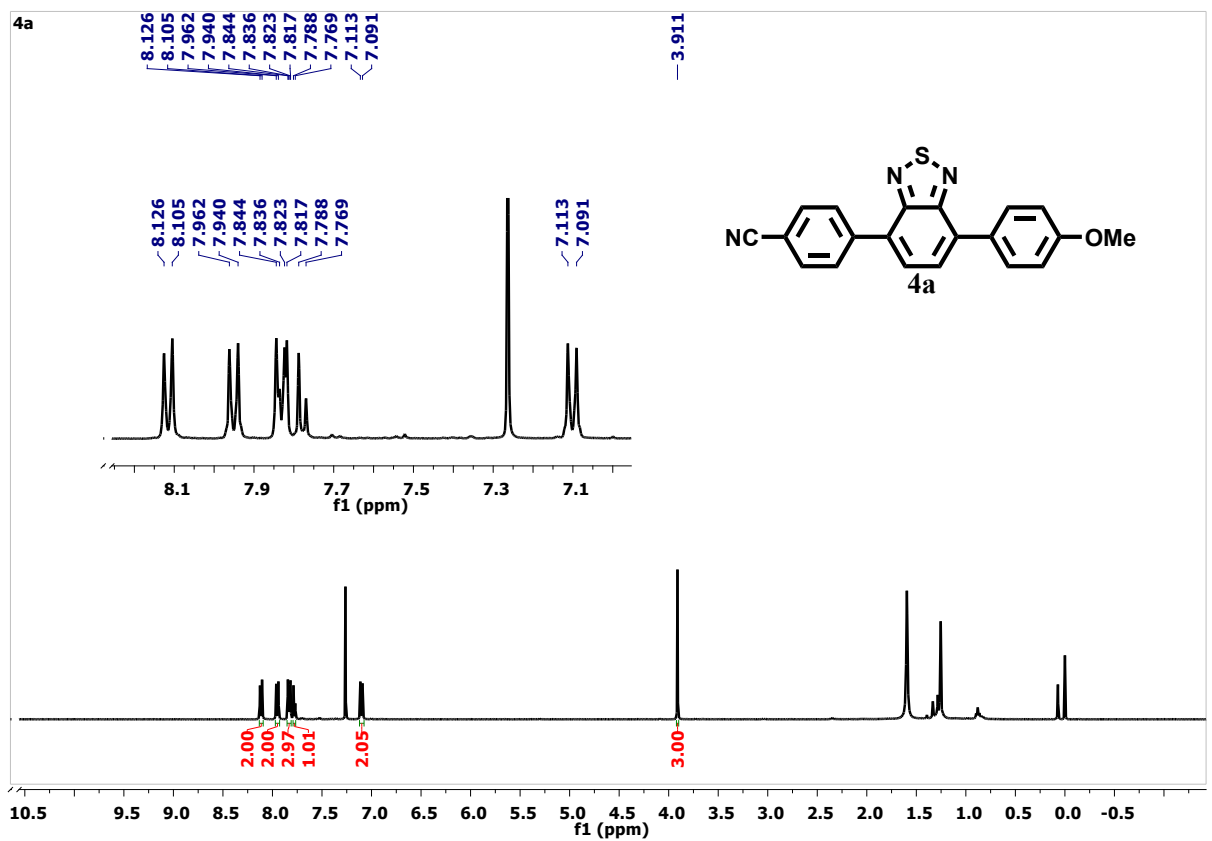


Figure S10: <sup>1</sup>H and <sup>13</sup>C NMR spectra of compound 4a



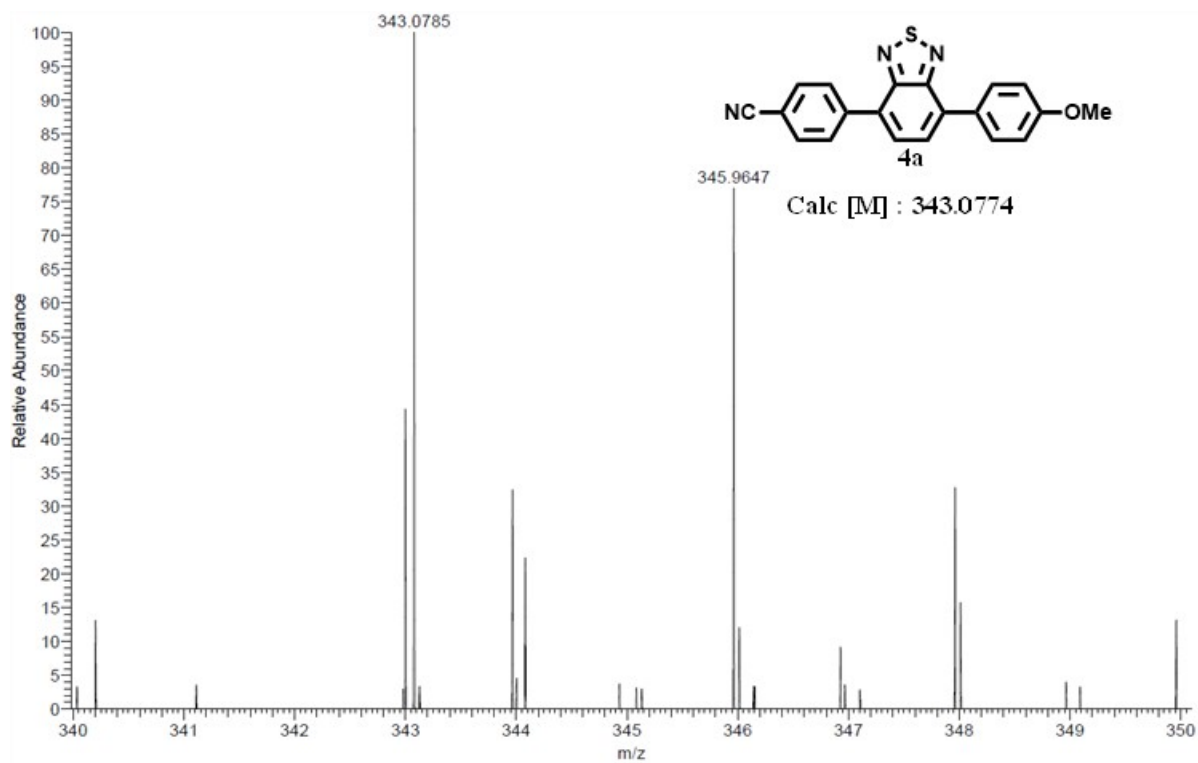
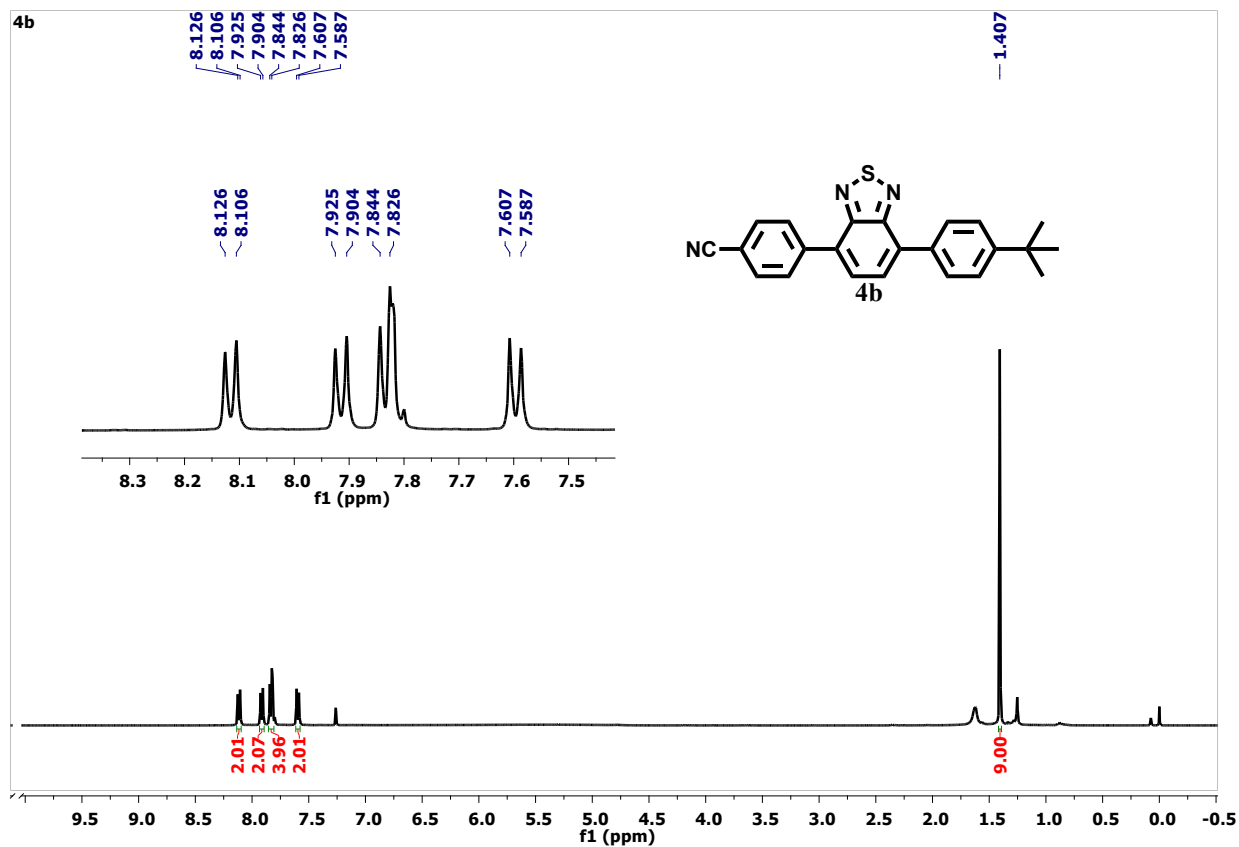


Figure S11: HRMS spectrum of compound 4a



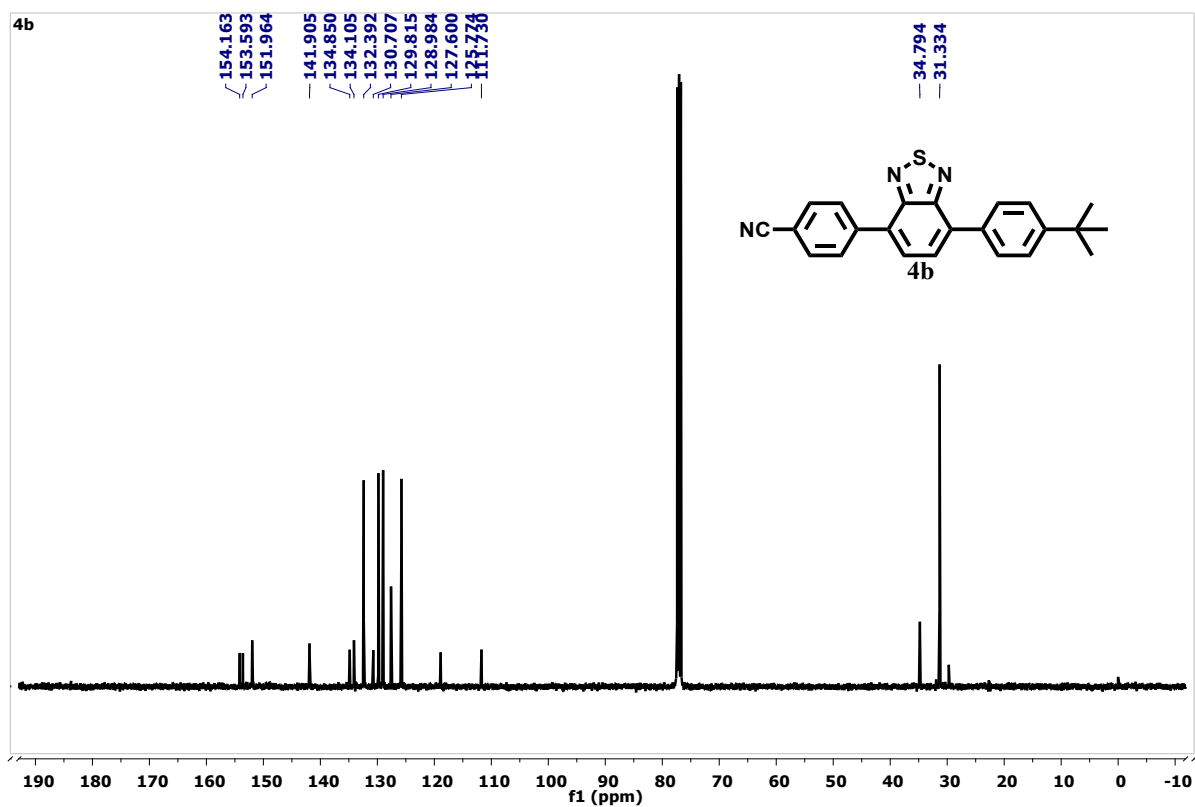


Figure S12:  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of compound 4b

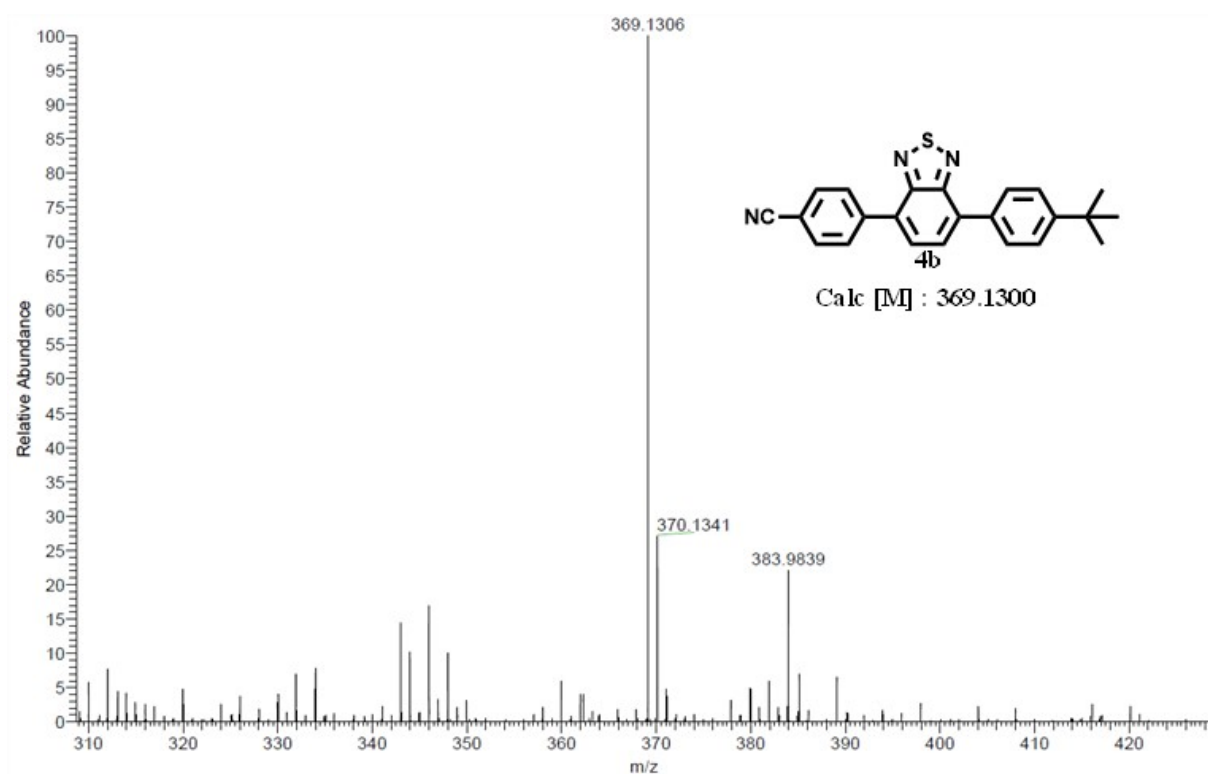


Figure S13: HRMS spectrum of compound 4b

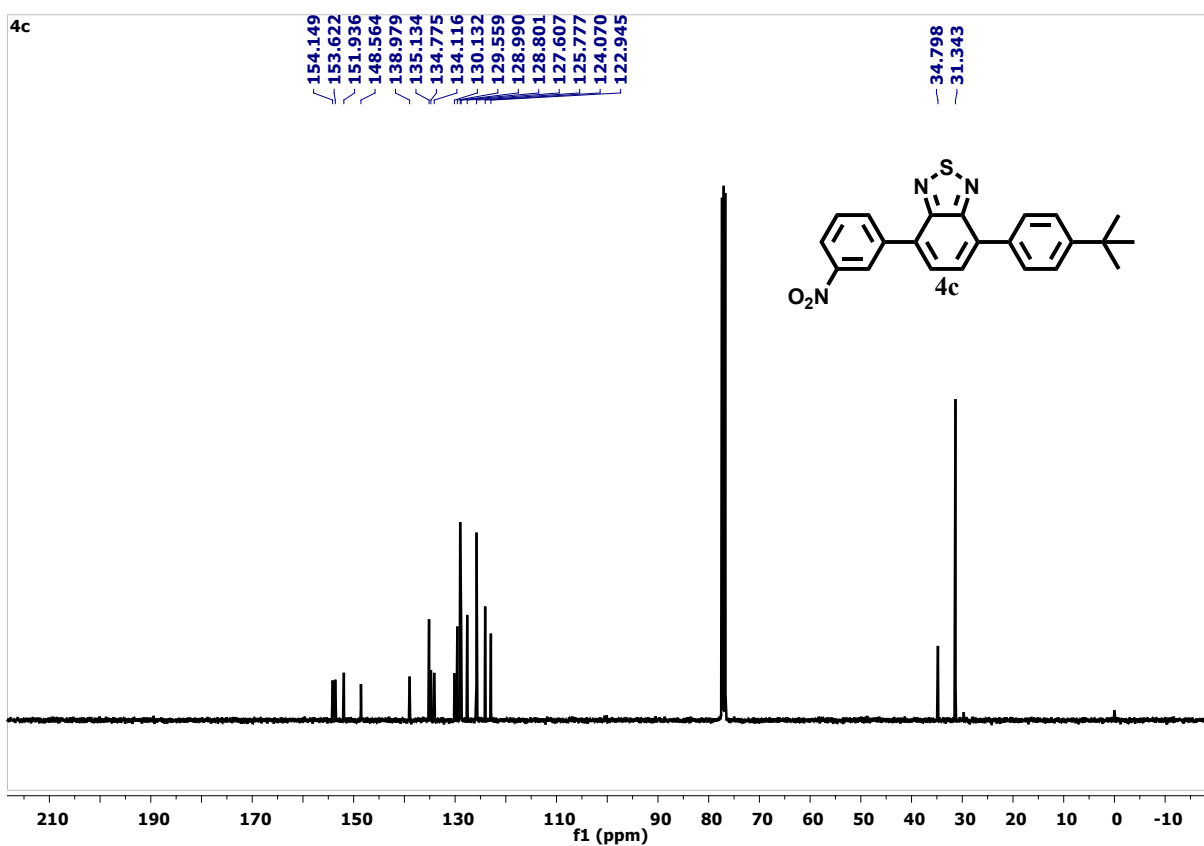
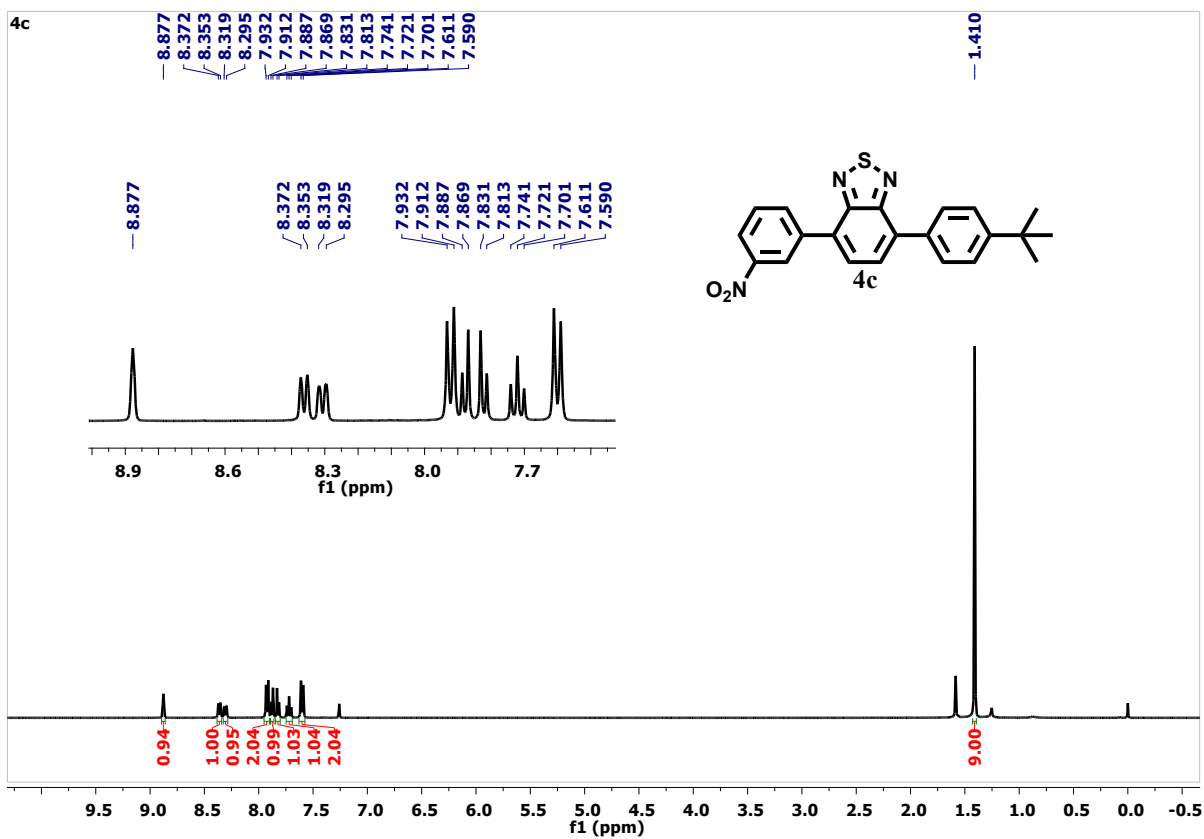
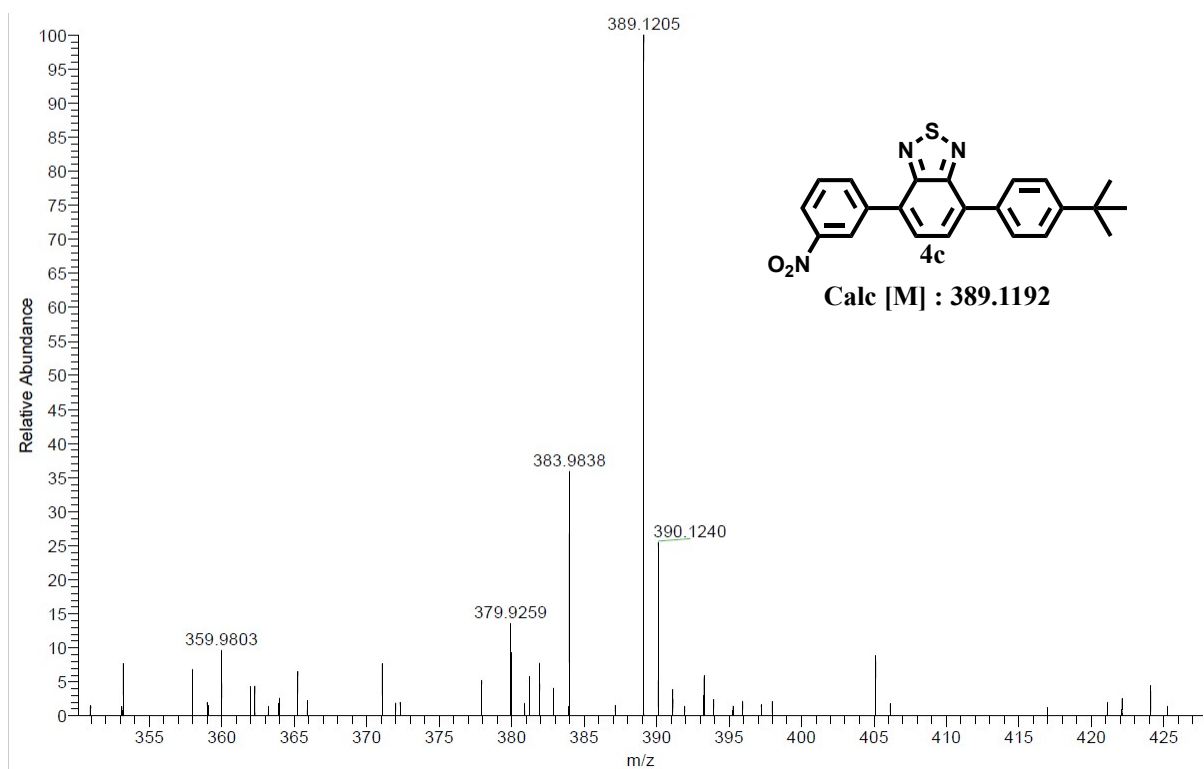
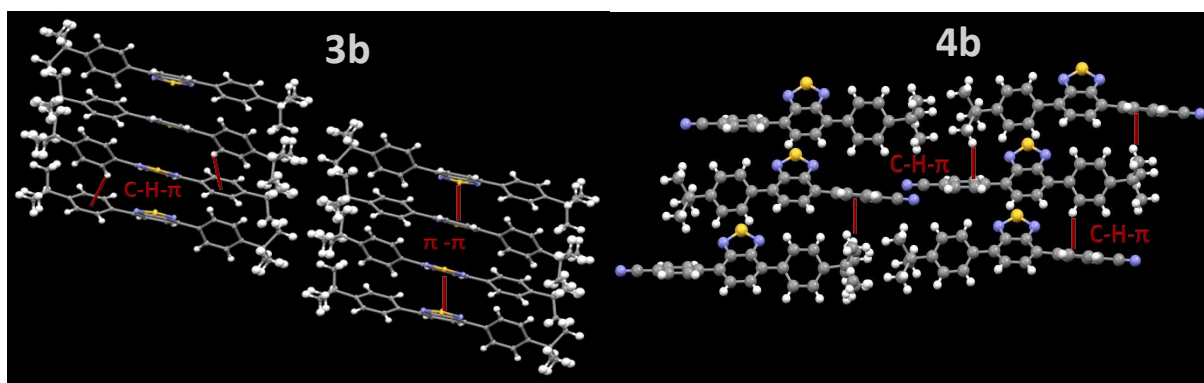


Figure S14:  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of compound 4c



**Figure S15: HRMS spectrum of compound 4c**

#### 4. Single crystal analysis data of compounds 3b and 4b



**Figure S16: C-H- $\pi$  and  $\pi$ - $\pi$  interactions of compounds 3b and 4b**

Compound	3b
CCDC	2280971
Formula	C <sub>26</sub> H <sub>28</sub> N <sub>2</sub> S
$D_{calc.}/\text{g cm}^{-3}$	1.248
$\mu/\text{mm}^{-1}$	0.167
Formula Weight	400.56
Colour	yellow
Shape	block-shaped
Size/mm <sup>3</sup>	0.35×0.27×0.14
T/K	110.00
Crystal System	triclinic
Space Group	<i>P</i> -1
$a/\text{Å}$	10.4542(5)
$b/\text{Å}$	10.5463(5)
$c/\text{Å}$	19.9888(9)
$\alpha/^\circ$	78.796(2)
$\beta/^\circ$	80.471(2)
$\gamma/^\circ$	87.250(2)
$V/\text{Å}^3$	2131.71(17)
<i>Z</i>	4
<i>Z'</i>	2
Wavelength/Å	0.71073
Radiation type	MoK $\alpha$
$\theta_{min}/^\circ$	1.976
$\theta_{max}/^\circ$	30.575
Measured Refl's.	52784
Indep't Refl's	13036
Refl's $I \geq 2 \sigma(I)$	10586
$R_{int}$	0.0568
Parameters	535
Restraints	0
Largest Peak	0.428
Deepest Hole	-0.281
GooF	1.030
$wR_2$ (all data)	0.1170
$wR_2$	0.1078
$R_1$ (all data)	0.0573
$R_1$	0.0445

Compound	4b
CCDC	2280972
Formula	C <sub>23</sub> H <sub>19</sub> N <sub>3</sub> S
$D_{calc.}/\text{g cm}^{-3}$	1.333
$\mu/\text{mm}^{-1}$	1.645
Formula Weight	369.47
Colour	yellow
Shape	plate-shaped
Size/mm <sup>3</sup>	0.53×0.33×0.03
T/K	110.00
Crystal System	triclinic
Space Group	<i>P</i> -1
$a/\text{Å}$	10.6072(8)
$b/\text{Å}$	11.1203(8)
$c/\text{Å}$	16.1456(13)
$\alpha/^\circ$	82.187(3)
$\beta/^\circ$	78.421(3)
$\gamma/^\circ$	83.462(3)
$V/\text{Å}^3$	1841.0(2)
<i>Z</i>	4
<i>Z'</i>	2
Wavelength/Å	1.54178
Radiation type	CuK $\alpha$
$\theta_{min}/^\circ$	2.813
$\theta_{max}/^\circ$	70.383
Measured Refl's.	39485
Indep't Refl's	7000
Refl's $I \geq 2 \sigma(I)$	6221
$R_{int}$	0.0511
Parameters	527
Restraints	199
Largest Peak	0.374
Deepest Hole	-0.548
GooF	1.065
$wR_2$ (all data)	0.1495
$wR_2$	0.1409
$R_1$ (all data)	0.0608
$R_1$	0.0542

#### 4. Thin film XRD

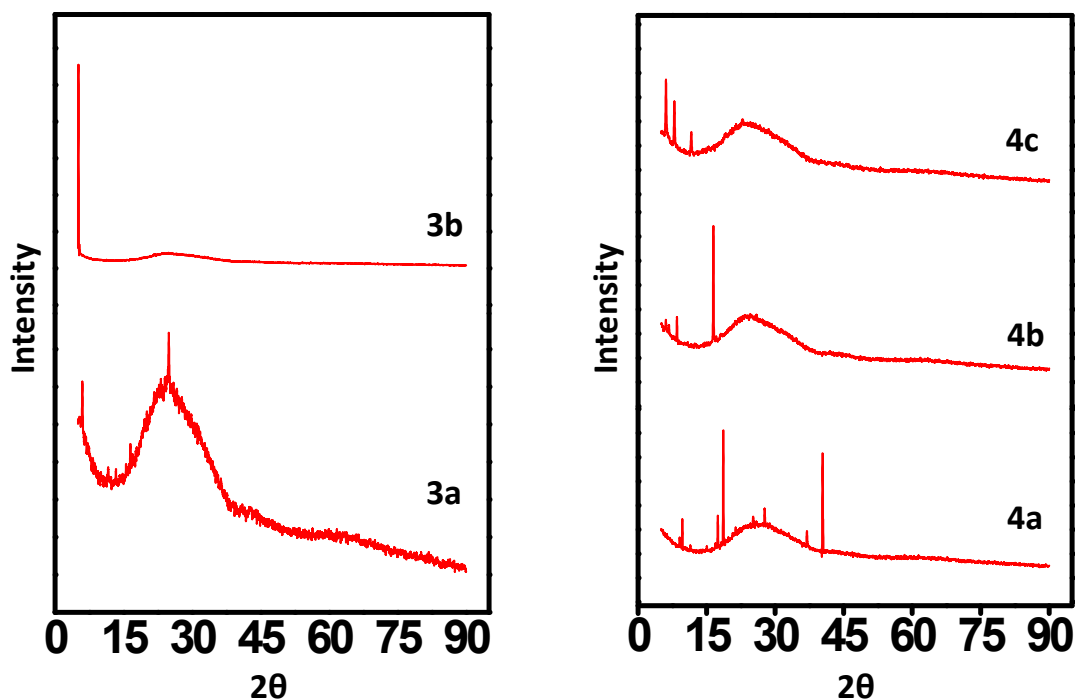
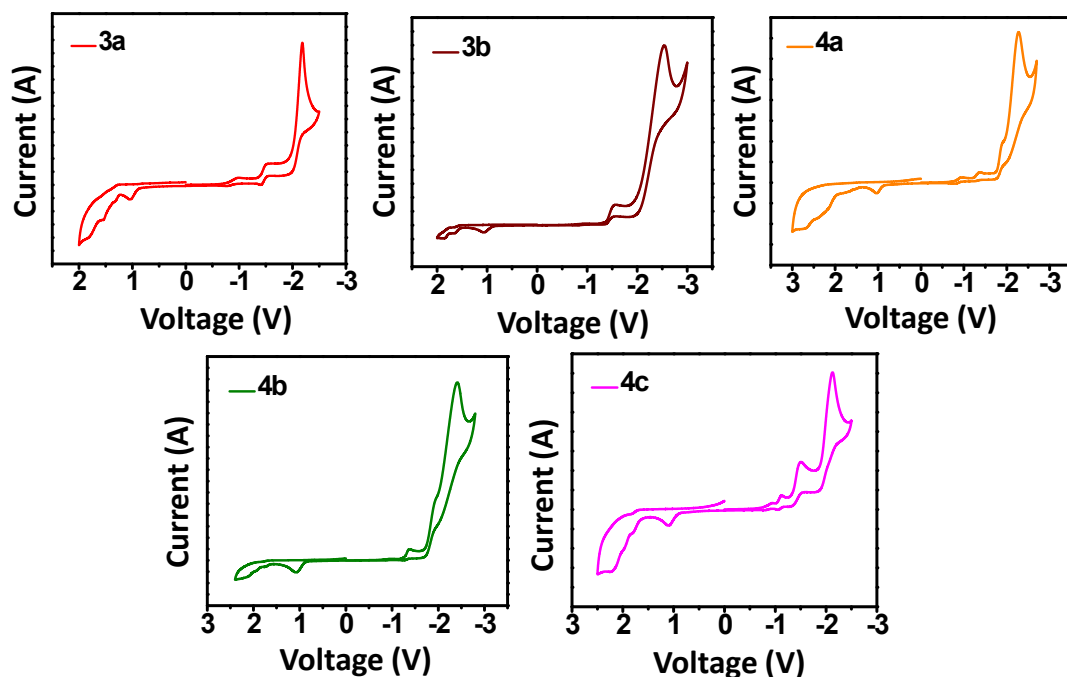


Figure S17: Thin-film XRD analysis of the compounds 3a-b and 4a-c

#### 5. Electrochemical studies of the compounds 3a-b and 4a-c

The synthesized compounds electrochemical properties were studied using cyclic voltammetry by using the conventional three-electrode cell setup in which glassy carbon acts as the working electrode, platinum wire as the counter electrode, and standard calomel as the reference electrode (**Figure S18**). The experiments were performed in anhydrous dimethylformamide solvent at room temperature with a scan rate of 100 mVs<sup>-1</sup> where tetrabutylammonium hexafluorophosphate (n-Bu<sub>4</sub>NPF<sub>6</sub>, 0.1 M) performed the role of supporting electrolyte. Experiments were conducted under a nitrogen atmosphere to neglect oxygen interference with the compounds. Ferrocene/ferrocenium ion (Fc/Fc<sup>+</sup>) redox couple was used for its calibration.



**Figure S18.** Cyclic voltammograms of the compounds **3a-b** and **4a-c**

## 6. Computational studies on the compounds **3a-b** and **4a-c**

The experimentally obtained spectral values are evaluated against the excited states of molecules calculated by the computational methods (**Table S1**). The TD-SCF (Time-Dependent SCF) theoretical calculations suggest substantial spectral details. The absorption and emission bands found through experimental methods agree with the theoretical calculations. Also, the emission spectral values are predictable. Those values with a good frequency factor and closer to the experimental ones are only taken from the values predicted by the theoretical methods. The intersystem crossing has been predicted in almost all the systems, and the values of emission spectra agree with these values. The DOS graph signifies the number of states that suggest optimum space for particle movements. The DOS gap and E-Fermi energy levels of the compounds are given in **Table S2**.

**Table S1. The predicted absorption and emission behavior of the compounds**

Compounds	Absorption wavelength (nm)	Electronic transition	Emission wavelength (nm)	Electronic transition	Dipole moment
<b>3a</b>	379.9	S <sub>-1</sub> -S <sub>1</sub>	483.6	S <sub>0</sub> -S <sub>1</sub>	1.586
	317.2	S <sub>-2</sub> -S <sub>1</sub>			
<b>3b</b>	341.7	S <sub>-1</sub> -S <sub>1</sub>	447.6	S <sub>0</sub> -S <sub>1</sub>	1.535
	331.1	S <sub>-2</sub> -S <sub>1</sub>			
<b>4a</b>	349.6	S <sub>-1</sub> -S <sub>1</sub>	471.1	S <sub>0</sub> -S <sub>1</sub>	7.327
	329.8	S <sub>0</sub> -S <sub>2</sub>			
<b>4b</b>	344.8	S <sub>1</sub> -S <sub>1</sub>	439.9	S <sub>0</sub> -S <sub>1</sub>	6.819
	332.7	S <sub>-2</sub> -S <sub>1</sub>			
<b>4c</b>	414.1	S <sub>0</sub> -S <sub>2</sub>	468.7	S <sub>0</sub> -S <sub>1</sub>	5.437
	346.3	S <sub>-1</sub> -S <sub>1</sub>			

The optimized geometry was then used as input geometry for Density of States (DOS) calculations using *VASP (MedeA reference)* software (**Figure S20**). The structures involving solvent correction parameters such as GGA-PBE (basis set) were evaluated, and the DOS graphs were subsequently obtained. The molecular packing of the compounds **3a-c** and **4a-c** are given in **Figure S21**, which offers the higher packing efficiency of the compounds.

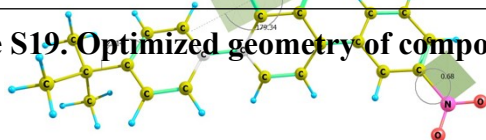
The images generated after modeling them in MedeA for solvent correction would represent their behavior in solution or gaseous phase under normal temperature and pressure, unlike the single-crystal solid-state data where the temperature is very close to absolute zero and only a single molecule is pictured (**Figure S19**). The hopping distances of the compounds are also calculated through computational methods. They could substantiate the possible charge transport happening in the molecules through the hoping of charges between the molecules (**Table S3**).

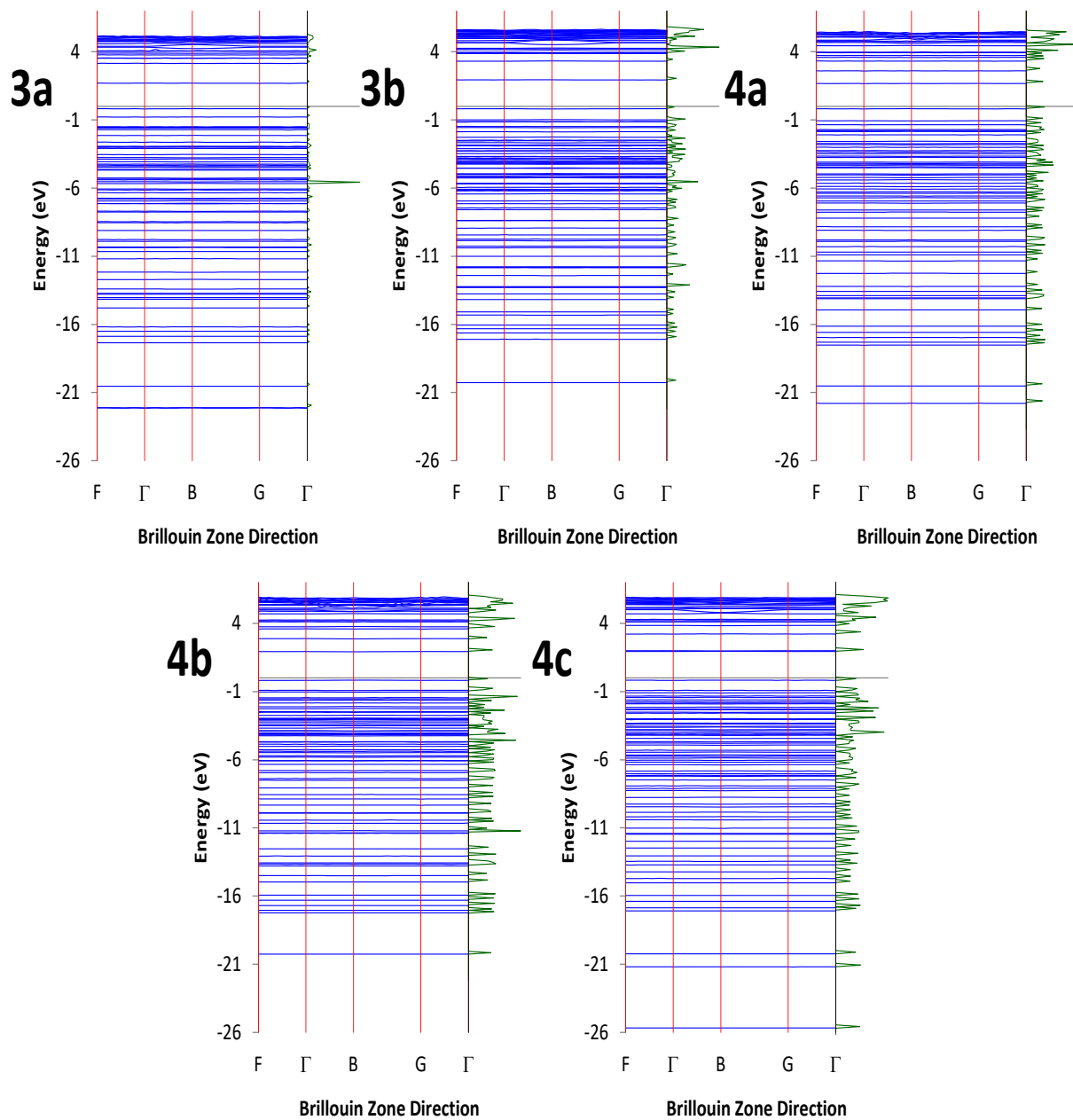


Table S2. DOS gap and E-Fermi energy of the compounds 3a-b and 4a-c

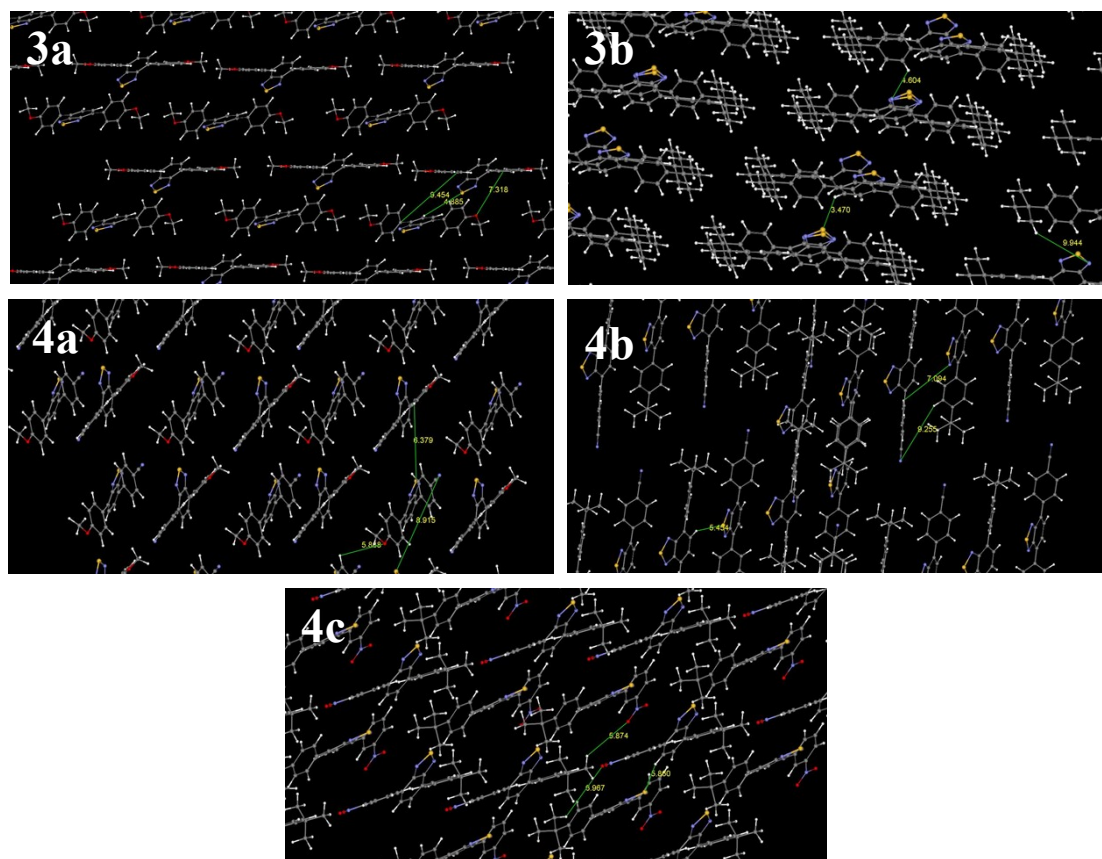
Compounds	Molecular Formula	Free Energy <b>3b</b> (eV)	Density (Mg/m <sup>3</sup> )	DOS Gap (eV)	E Fermi (eV)
<b>3a</b>	<chem>C20N2SO2H16</chem>	-271.782	0.051	3.649	-4.699
<b>3b</b>	<chem>C26N2SH28</chem>	-358.378	0.057	3.987	-5.007
<b>4a</b>	<chem>C20N3SOH13</chem>	-261.852	0.056	3.435	-5.033
<b>4b</b>	<chem>C23N3SH19</chem>	-305.126	0.059	3.720	-5.301
<b>4c</b>	<chem>C22N3SO2H19</chem>	-307.728	0.077	3.917	-5.269

Figure S19. Optimized geometry of compounds 3a-b and 4a-c





**Figure S20** Density of states graphs for compounds 3a-b and 4a-c.



**Figure S21. Molecular packing with their intermolecular interactions for the compounds 3a-b and 4a-c through computational methods**

## 7. Memory device fabrication and characterizations

The synthesized compounds (**3a-b,4a-c**) were employed as the active layer for constructing memory devices on an ITO-coated glass substrate. To prepare the substrate, the ITO-coated glass plates were meticulously cleaned through sequential sonication in a soap solution, distilled water, acetone, and ethanol, with each stage lasting for 10 minutes. The ITO layer serves as one of the electrodes in the memory device architecture. The compounds were dissolved in chloroform at a 5 mg/m concentration and coated onto the ITO-coated glass plates. The resulting thin film was then annealed at 80 °C for 25 minutes. Silver contacts, measuring 1×1 mm in dimension, were deposited onto the thin film using a sputtering method (**Figure S22**). Subsequently, the memory characteristics of the fabricated device were evaluated. Memory characterizations were performed using a Keithley 4200A semiconductor parameter analyzer under ambient conditions.

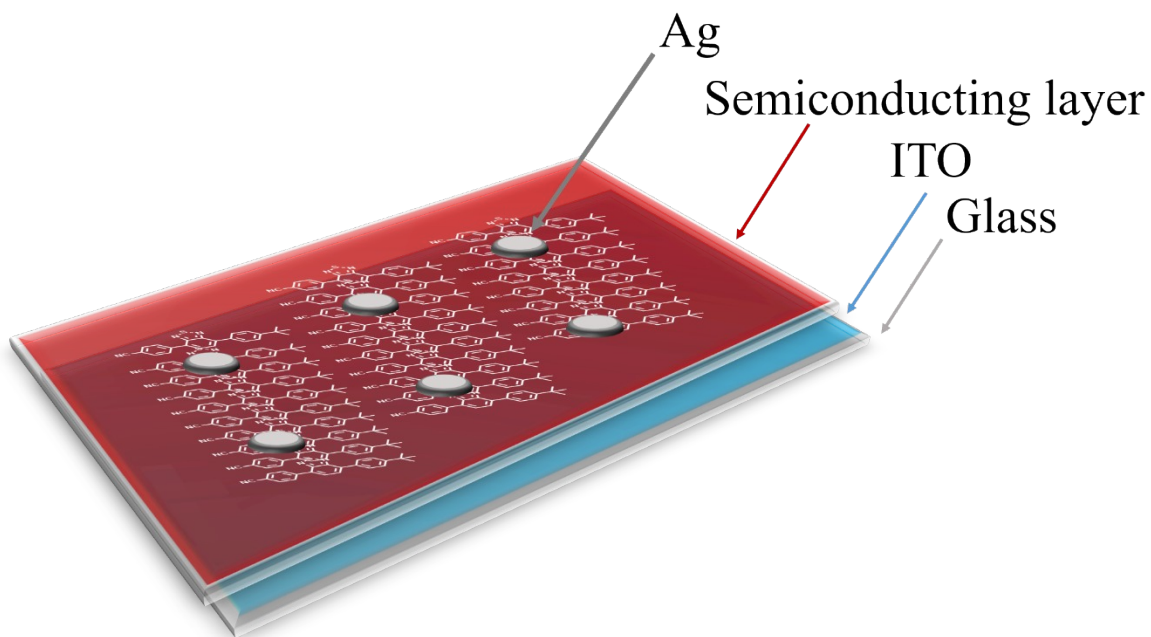


Figure S22: Device architecture

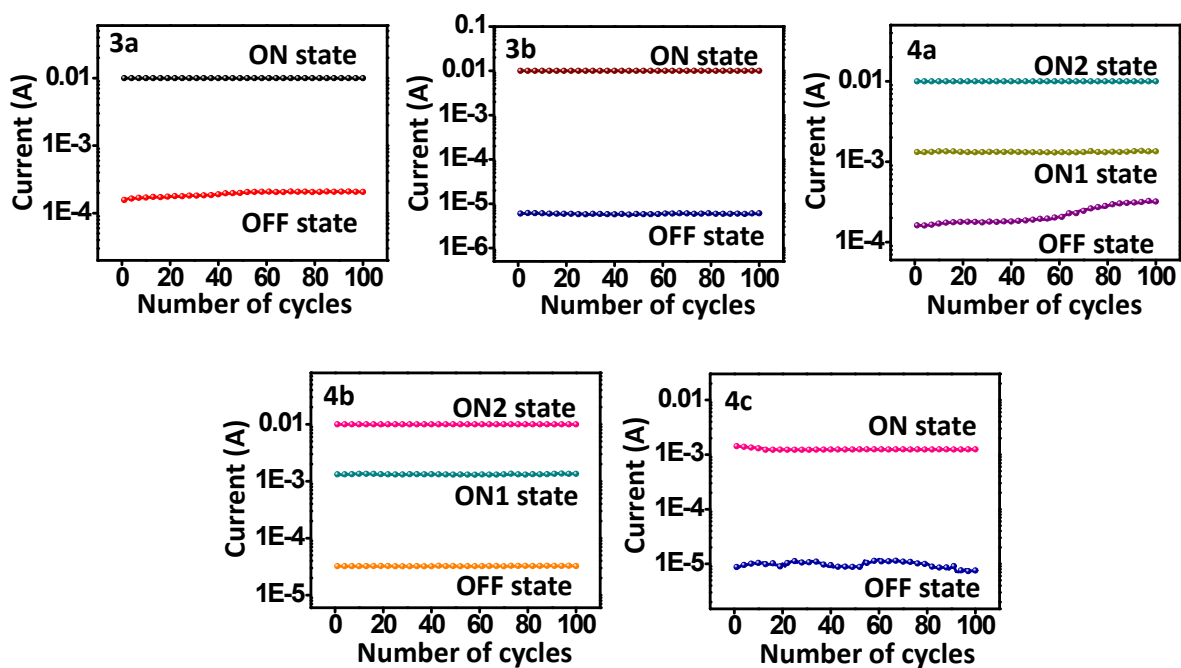


Fig S23. Endurance cycle of 100 cycles for devices 3a-b and 4a-c

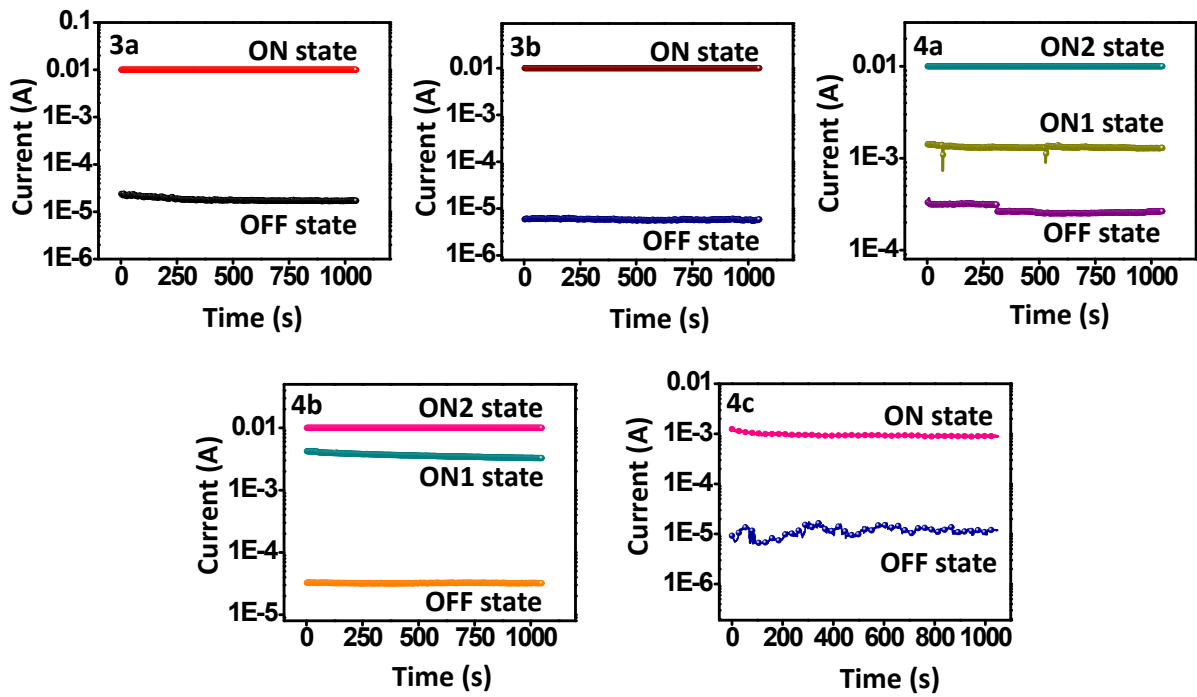


Figure S24. The retention time of the memory devices 3a-b and 4a-c