Supporting Information

Mono-Substituted Dibenzofulvene-based Luminogens: Aggregation-Induced Emission Enhancement and Dual-State Emission

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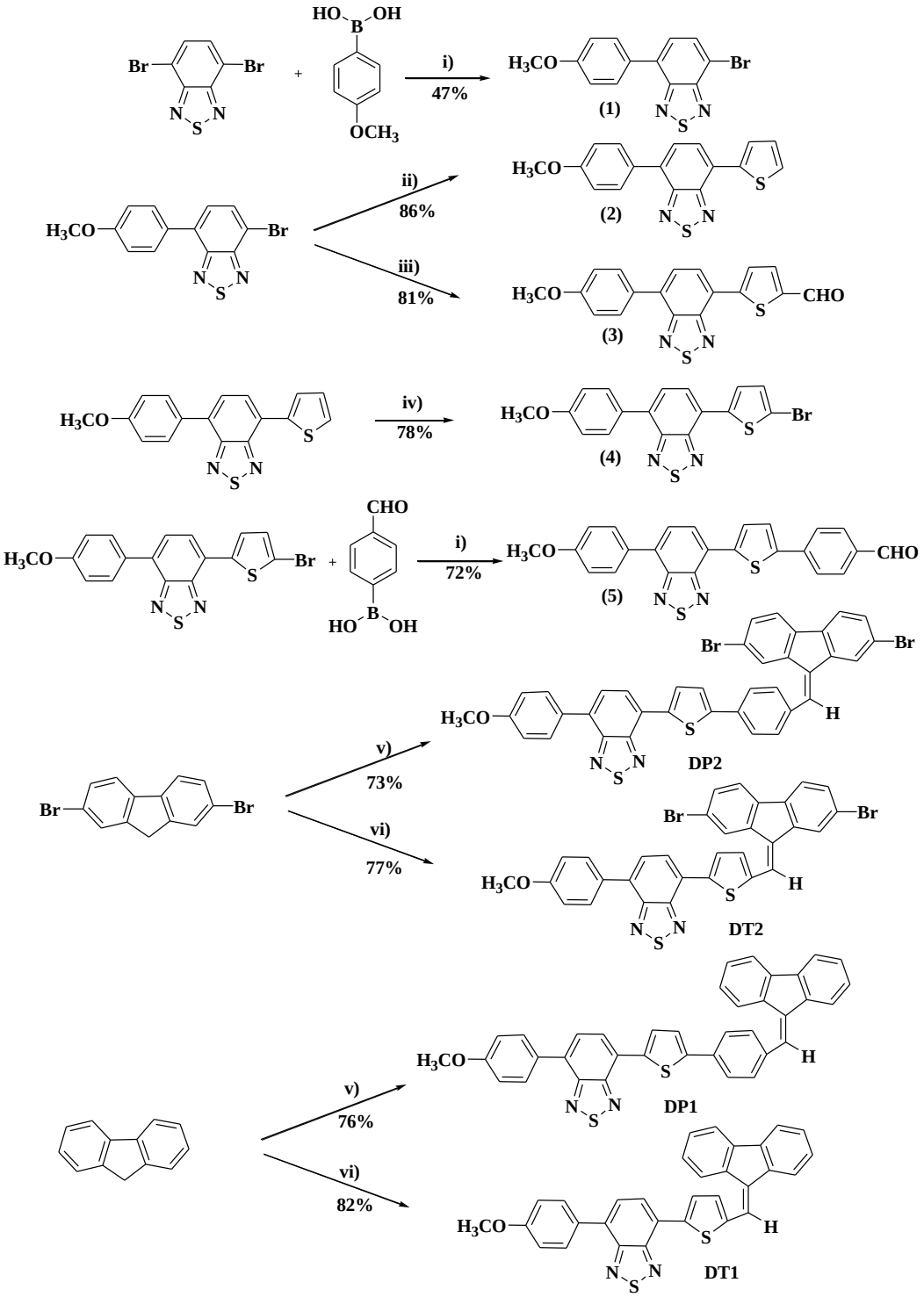

Scheme S1. Synthetic route for Monomers.

i) $Pd(PPh_3)_4$, 2M K_2CO_3, THF, 80 °C, 12 h. ii) Tributyl-thiophen-2-yl-stannane, $Pd(PPh_3)_4$, THF, 80 °C, 12 h, iii) 5-Formylthiophene-2-boronic acid, $Pd(PPh_3)_4$, 2M K_2CO_3, THF, 80 °C, 12 h. iv) NBS, THF:CH_3COOH (1:1), RT, 6 h. v) Compound (5) and EtOH, Potassium tert-butoxide, Reflux, 12 h. vi) Compound (3) and EtOH, Potassium tert-butoxide, Reflux, 12 h.

Synthetic procedure of Monomers:

Synthesis of 4-Bromo-7-(4-methoxy-phenyl)-benzo[1,2,5]thiadiazole (1);

The mixture of 4,7-dibromo-benzo[1,2,5]thiadiazole (1.eq), 4-methoxy phenyl boronic acid (0.7 eq), 12 mL THF and tetrakis(triphenyl phosphine)palladium(0) (0.015 eq) were added into a dry two neck round bottom flask. Subsequently, 4 mL 2M aqueous potassium carbonate was added to the flask. The reaction mixture was stirred at 80 °C for 12 h under argon atmosphere. The reaction mixture was then cooled to room temperature. After work up, the mixture was purified by column chromatography to give greenish yellow solid compound **1**. (yield: 47%); ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.89 (d, *J*=7.2 Hz, 1H), 7.86 (d, *J*=9 Hz, 2H), 7.52 (d, *J*=7.4 Hz, 1H), 7.05 (d, *J*=8.4 Hz, 2H), 3.89 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 160.33, 154.10, 153.49, 133.91, 132.54, 130.62, 129.28, 127.65, 114.42, 112.47, 55.63. HRMS (ESI): m/z $[M + H]^+$ Calcd: 320.9697, found 320.9690.

Synthesis of 4-(4-Methoxy-phenyl)-7-thiophen-2-yl-benzo[1,2,5]thiadiazole (2);

The mixture of 4-Bromo-7-(4-methoxy-phenyl)-benzo[1,2,5]thiadiazole (1) (1.eq), Tributyl-thiophen-2-yl-stannane (1.2 eq) 12 mL THF and tetrakis(triphenyl phosphine)palladium(0) (0.015 eq) were added into a dry round bottom flask. The reaction mixture was stirred at 80 °C for 12 h under argon atmosphere. The resulting reaction mixture was cooled to room temperature and the crude product was purified by column chromatography to give yellow solid compound **2** (yield: 86%); ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.10 (d, *J*=3.6 Hz, 1H), 7.91 (dd, *J*=8.4 Hz, 6 Hz, 2H), 7.66 (d, *J*=7.2 Hz, 1H), 7.44 (d, *J*=4.8 Hz, 1H), 7.21 (t, 1H), 7.07 (d, *J*=8.4 Hz, 2H), 3.89 (s, 3H), ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 160.05, 154.22, 153.02, 139.70, 132.74, 130.58, 129.95, 128.15, 127.91, 127.52, 127.40, 126.73, 126.21, 125.98, 114.31, 55.59. HRMS (ESI): m/z $[M + H]^+$ Calcd: 325.0469, found 325.0468.

Synthesis of 5-[7-(4-Methoxy-phenyl)-benzo[1,2,5]thiadiazol-4-yl]-thiophene-2-carbaldehyde (3):

A mixture of compound 1 (1.eq), 5-formylthiophene-2-boronic acid (1.2 eq), 12 mL THF and tetrakis(triphenyl phosphine)palladium(0) (0.015 eq) were added into a dry two neck round bottom flask. Subsequently 4 mL 2M aqueous potassium carbonate were added to the flask. The reaction mixture was stirred at 80 °C for 12 hours under argon atmosphere. The reaction mixture was then cooled to room temperature. After work up, the mixture was purified by column chromatography to give yellow solid compound **3**. (yield: 81%); ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 9.98 (s, 1H), 8.21 (d, *J*=4.2 Hz, 1H), 8.04 (d, *J*=7.2 Hz, 1H), 7.94 (d, *J*=8.4 Hz, 2H), 7.85 (d, *J*=3.6 Hz, 1H), 7.72 (d, *J*=7.2 Hz, 1H), 7.08 (d, *J*=9 Hz, 2H),

3.90 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 183.28, 160.46, 154.14, 152.83, 149.13, 143.50, 137.08, 134.95, 130.78, 129.48, 128.08, 127.83, 127.09, 124.50, 114.43, 55.65. HRMS (ESI): m/z $[M + H]^+$ Calcd: 353.0418, found 353.0416.

Synthesis of 4-(5-Bromo-thiophen-2-yl)-7-(4-methoxy-phenyl)-benzo[1,2,5]thiadiazole (4);

4-(4-Methoxy-phenyl)-7-thiophen-2-yl-benzo[1,2,5]thiadiazole (2) (1.eq), was added into 12 mL THF and glacial acetic acid (1:1). After the solid dissolved completely, *N*-bromosuccinimide (1. eq) was added in one portion and stirred at room temperature for 6 h, under argon atmosphere. The reaction mixture was washed with brine and dried over anhydrous sodium sulfate. The solvent was removed at reduced pressure and the crude product was purified by column chromatography to give the produ ct as a yellow solid compound **4** (yield: 78%); ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.915 (d, *J*=6 Hz, 2H), 7.84 (d, *J*=12 Hz, 1H), 7.795 (d, *J*=6 Hz, 1H), 7.665 (d, *J*=6 Hz, 1H), 7.155 (d, *J*=6 Hz, 1H), 7.075 (d, *J*=6 Hz, 2H), 3.90 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm):160.31, 153.84, 153.76, 133.40, 130.72, 130.57, 129.57, 127.28, 126.76, 125.59, 123.31, 114.37, 114.33, 109.27, 55.60. MALDI-TOF MS: $[M + H]^+$ Calcd. 404.53, Found: 404.08.

Synthesis of 4-{5-[7-(4-Methoxy-phenyl)-benzo[1,2,5]thiadiazol-4-yl]-thiophen-2-yl}-benzaldehyde (5);

4-(5-Bromo-thiophen-2-yl)-7-(4-methoxy-phenyl)-benzo[1,2,5]thiadiazole (3) (1.eq), 4-formyl phenyl boronic acid (1.2 eq), 12 mL of Tetrahydrofuran (THF) and tetrakis(triphenyl phosphine)palladium(0) (0.015 eq) were added into a dry two neck round bottom flask. Subsequently 4 mL 2M aqueous potassium carbonate were added to the flask. The reaction mixture was stirred at 80 °C for 12 h under argon atmosphere. The reaction mixture was then cooled to room temperature. The reaction mixture was washed with brine and dried over anhydrous sodium sulfate. The solvent was removed at a reduced pressure and the mixture purified by column chromatography to give light orange compound **5**. (yield: 72%); ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 9.96 (s, 1H), 7.92 (m, 3H), 7.85 (d, *J*=7.8 Hz, 2H), 7.77 (d, *J*=7.8 Hz, 2H), 7.54 (d, *J*=7.8 Hz, 1H), 7.49 (d, *J*=3.6 Hz, 2H), 7.05 (d, *J*=8.4 Hz, 2H), 3.88 (s, 3H).^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 191.53, 160.31, 154.03, 153.88, 143.42, 142.83, 140.85, 139.49, 136.37, 135.70, 135.21, 134.22, 131.03, 130.72, 130.44, 130.20, 129.47, 126.15, 114.34, 55.57. HRMS (ESI): m/z $[M + H]^+$ Calcd: 429.0731, found 429.0737.

Synthesis of 4-{5-[4-(2,7-Dibromo-fluoren-9-ylidenemethyl)-phenyl]-thiophen-2-yl}-7-(4-methoxy-phenyl)-benzo[1,2,5]thiadiazole (6) (DP2);

A mixture of potassium tert-butoxide (1.2 eq) and 2,7-Dibromo-9H-fluorene (1.2 eq) was dissolved in 15 mL absolute ethanol. The resulting solution was refluxed for 1 h and compound 5 (1 eq) was added into reaction mixture and again refluxed for 18 h. The solvent was concentrated, and the residue was extracted with CH_2Cl_2 and evaporated. The residue was purified by column chromatography to give the product as a orange solid compound **DP2**. (yield: 73%); ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.14, (d, *J*=3.6 Hz, 1H), 7.97, (d, *J*=7.2 Hz, 1H), 7.95, (d, *J*=7.2 Hz, 2H), 7.90, (m, 3H), 7.84, (s, 1H), 7.82, (d, *J*=7.8 Hz, 2H), 7.70, (d, *J*=7.8 Hz, 2H), 7.67, (s, 1H), 7.64, (d, *J*=7.8 Hz, 1H), 7.54, (m, 2H), 7.50, (m, 2H), 7.46, (d, *J*=1.2 Hz, 1H), 7.08, (d, *J*=9 Hz, 2H), 3.90, (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 160.19, 154.38, 154.00, 147.28, 144.57, 141.49, 141.35, 141.28, 139.49, 139.35, 138.12, 137.51, 137.11, 136.28, 135.35, 134.73, 134.10, 131.40, 130.99, 130.68, 130.36, 129.84, 129.75, 129.55, 129.36, 127.49, 126.62, 126.10, 124.67, 123.89, 121.16, 119.29, 114.34, 114.27, 55.61. MALDI-TOF MS: $[M + H]^+$ Calcd.734.95, Found: 734.10.

Synthesis of 4-[5-(2,7-Dibromo-fluoren-9-ylidenemethyl)-thiophen-2-yl]-7-(4-methoxy-phenyl)-benzo[1,2,5]thiadiazole (7) (DT2):

A mixture of potassium tert-butoxide (1.2 eq) and 2,7-Dibromo-9H-fluorene (1.2 eq) was dissolved in 15 mL absolute ethanol. The resulting solution was refluxed for 1 h and compound 3 (1 eq) was added into reaction mixture and again refluxed for 18 h. The solvent was cncentrated, and the residue was extracted with CH_2Cl_2 and evaporated. The residue was purified by column chromatography to give the product as a red solid compound **DT2**. (yield: 77%); ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.62, (s, 1H), 8.17, (d, *J*=6 Hz, 1H), 8.0, (d, *J*=7.2 Hz, 1H), 7.95, (d, *J*=8.4 Hz, 2H), 7.86, (s, 1H), 7.72, (d, *J*=7.2 Hz, 1H), 7.65, (s, 1H), 7.60, (d, *J*=3.6 Hz, 1H), 7.57, (d, *J*=7.8 Hz, 1H), 7.52, (d, *J*=8.4 Hz, 1H), 7.50, (d, *J*=7.8 Hz, 1H), 7.47, (d, *J*=6.6 Hz, 1H), 7.08, (d, *J*=9 Hz, 2H), 3.90, (s, 3H), ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 160.22, 154.19, 152.88, 142.99, 141.70, 139.44, 139.22, 137.77, 136.75, 133.50, 132.26, 131.78, 131.22, 130.67, 129.78, 127.98, 127.67, 127.34, 126.39, 123.66, 121.42, 121.30, 121.26, 121.18, 114.38, 55.64. MALDI-TOF MS: $[M + H]^+$ Calcd. 658.92, Found: 658.06.

Synthesis of 4-[5-(4-Fluoren-9-ylidenemethyl-phenyl)-thiophen-2-yl]-7-(4-methoxy-phenyl)-benzo[1,2,5]thiadiazole (8) (DP1):

A mixture of potassium tert-butoxide (1.2 eq) and 9H-fluorene (1.2 eq) was dissolved in 15 mL absolute ethanol. The resulting solution was refluxed for 1 h and compound 5 (1 eq) was added into the reaction mixture and again refluxed for 18 h. The solvent was concentrated and the residue was extracted with CH_2Cl_2 and evaporated. The residue was purified by

column chromatography to give the product as a orange solid compound **DP1**. (yield: 76%); ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 7.94, (d, *J*=8.4 Hz, 1H), 7.84, (d, *J*=8.4 Hz, 1H), 7.80, (d, *J*=8.4 Hz, 1H), 7.73, (d, *J*=7.8 Hz, 2H), 7.69, (m, 2H), 7.65, (s, 1H), 7.62, (d, *J*=7.8 Hz, 1H), 7.57, (d, *J*=7.8 Hz, 1H), 7.52, (m, 2H), 7.46, (d, *J*=7.8 Hz, 1H), 7.36, (m, 4H), 7.12, (t, 1H), 7.07, (d, *J*=8.4 Hz, 2H), 7.03, (t, 1H), 3.89, (s, 3H), ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 160.19, 154.34, 154.03, 144.71, 141.54, 139.38, 139.30, 136.95, 136.83, 136.63, 133.83, 133.64, 130.90, 130.67, 130.35, 129.85, 129.01, 128.89, 128.82, 128.49, 127.23, 127.04, 126.96, 126.82, 126.35, 125.96, 125.87, 124.65, 124.46, 120.48, 120.41, 119.98, 119.82, 119.79, 114.35, 55.61. MALDI-TOF MS: $[M]^+$ calcd.576.13 Found: 576.29

Synthesis of 4-(5-Fluoren-9-ylidenemethyl-thiophen-2-yl)-7-(4-methoxy-phenyl)-benzo[1,2,5]thiadiazole (9) (DT1):

A mixture of potassium tert-butoxide (1.2 eq) and 9H-fluorene (1.2 eq) was dissolved in 15 mL absolute ethanol. The resulting solution was refluxed for 1 h and compound 7 (1 eq.) was added into the reaction mixture and refluxed further for 18 h. The solvent was concentrated, and the residue was extracted with CH_2Cl_2 and evaporated. The residue was purified by column chromatography to give the product as a orange solid compound **DT1**. (yield: 82%); ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm): 8.35 (d, *J*=7.8 Hz, 1H), 8.19 (d, *J*=3.6 Hz, 1H), 7.97 (d, *J*=7.2 Hz, 1H), 7.94 (d, *J*=8.4 Hz, 2H), 7.75 (dd, *J*=7.2 Hz, 7.8 Hz, 2H), 7.71 (dd, *J*=3 Hz, 3 Hz, 2H), 7.76 (s, 1H), 7.59 (d, *J*=3.6 Hz, 1H), 7.37 (t, 2H), 7.33 (t, 1H), 7.24 (t, 1H), 7.08 (d, *J*=7.8 Hz, 2H), 3.90 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm): 160.17, 154.30, 152.95, 141.68, 141.52, 139.87, 139.13, 136.73, 136.33, 133.15, 131.03, 130.65, 129.89, 129.03, 128.51, 128.15, 127.41, 127.25, 127.15, 126.23, 124.77, 120.41, 120.07, 119.86, 118.98, 114.38, 55.63. MALDI-TOF MS: $[M + H]^+$ Calcd. 501.10, Found: 501.26.

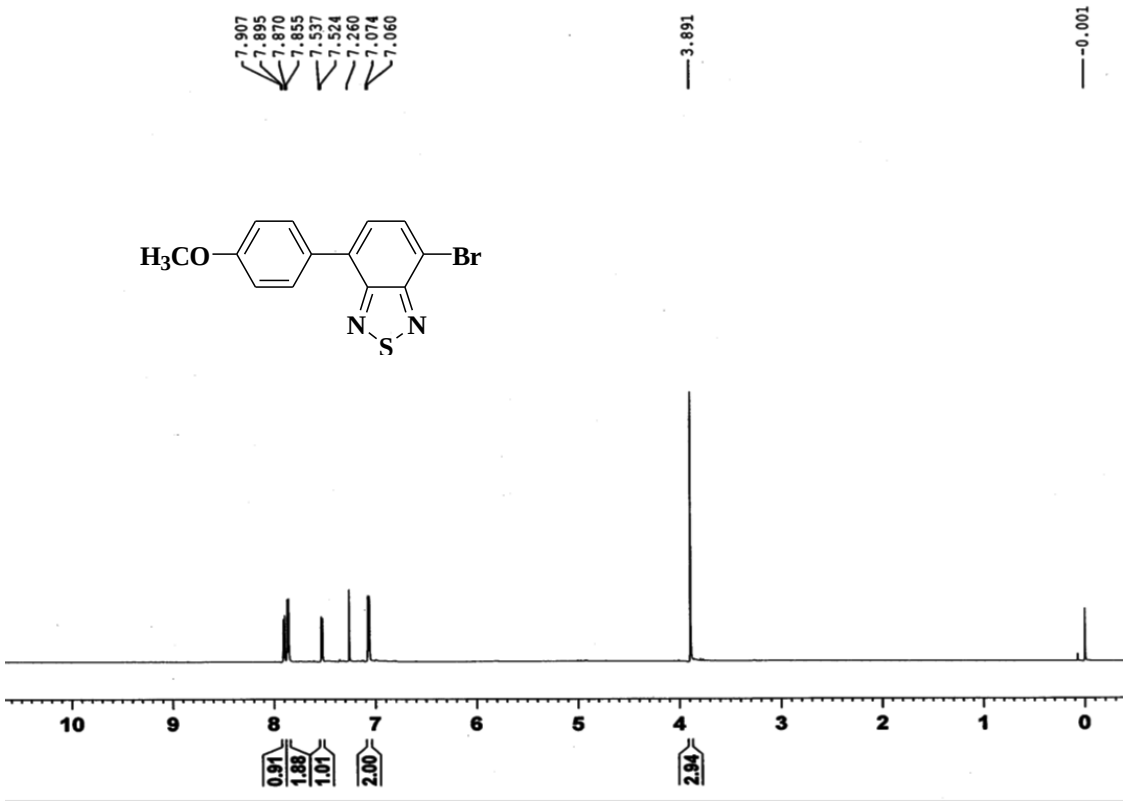

Figure S1. The ^{1}H NMR of the **Compound-1** in $CDCl_3$.

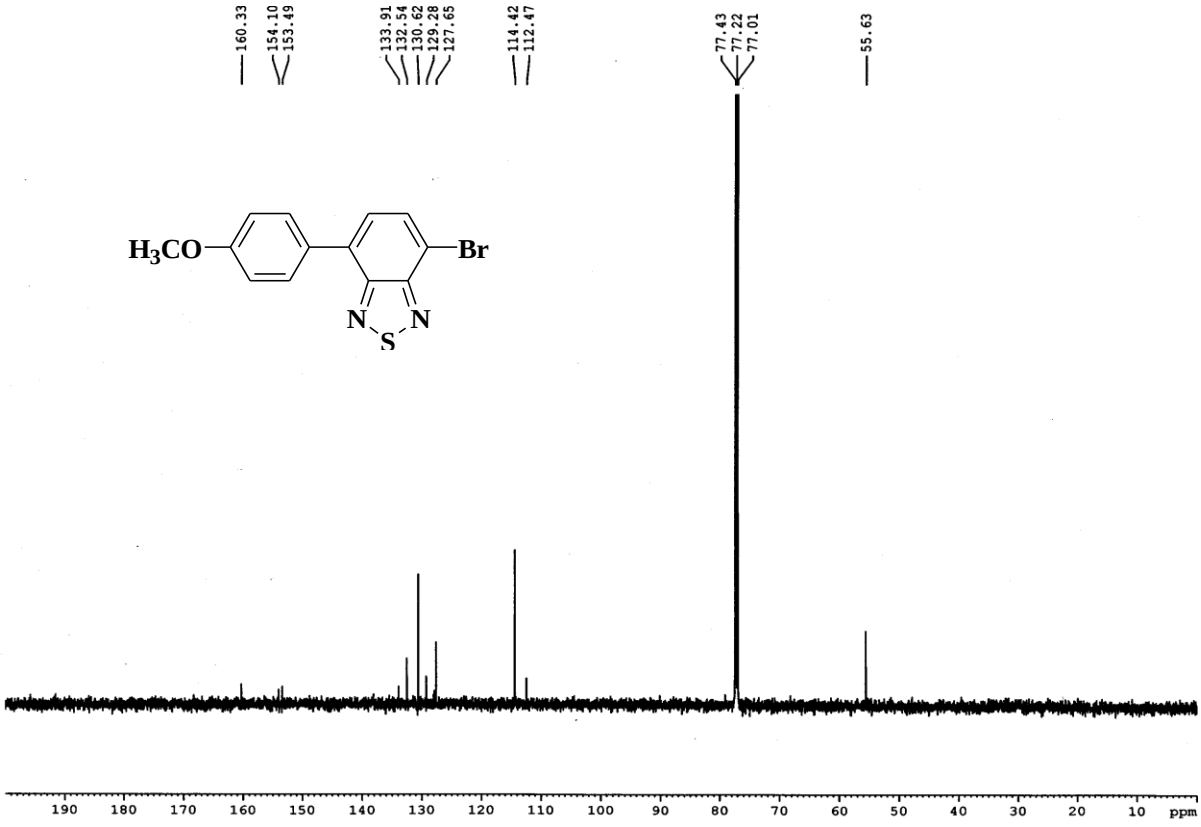

Figure S2. The ^{13}C NMR of the **Compound-1** in $CDCl_3$.

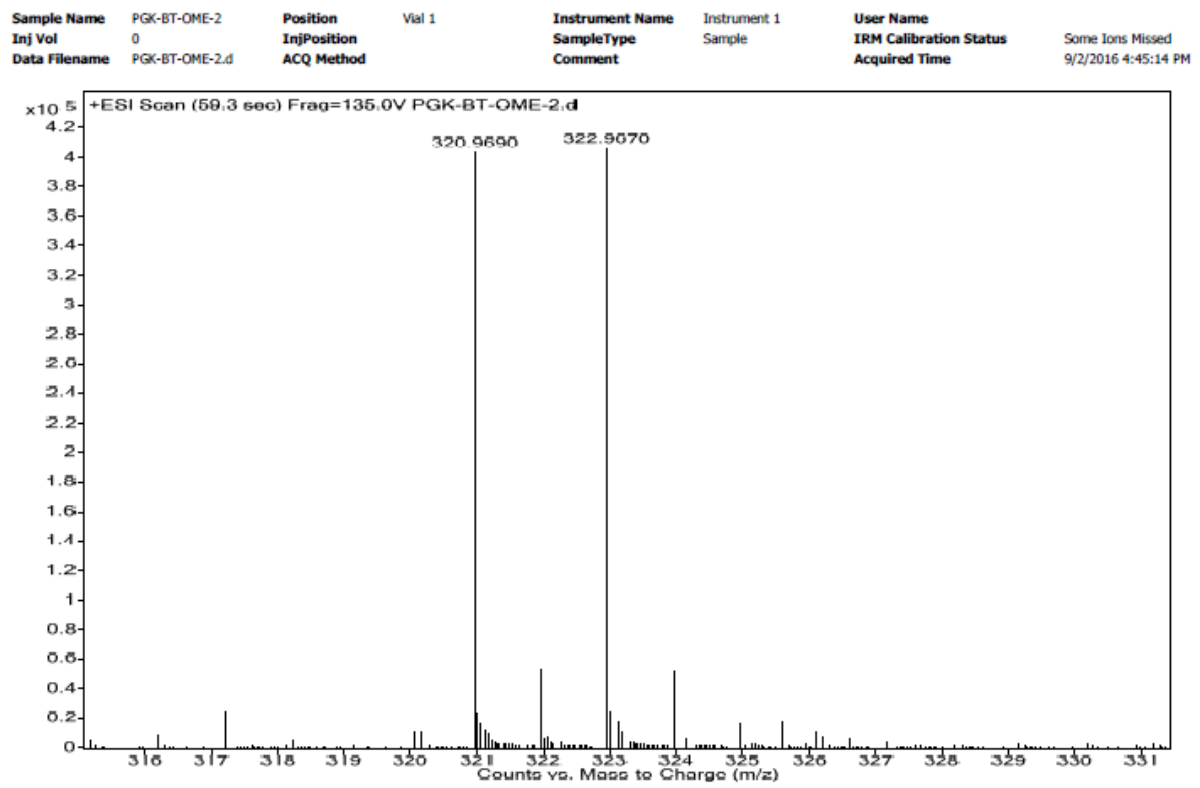

Figure S3. HRMS of the **Compound-1**.

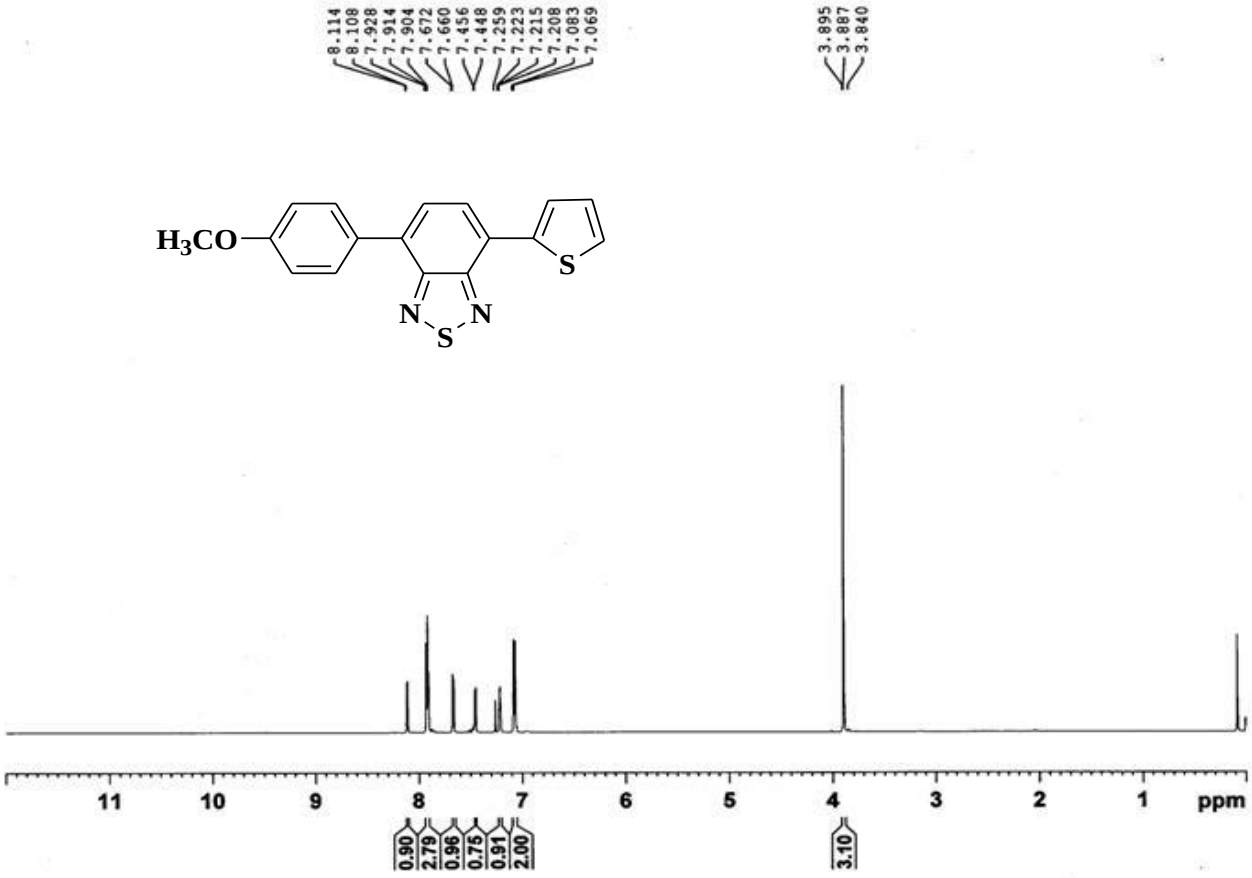

Figure S4. The ^{1}H NMR of the **Compound-2** in $CDCl_3$.

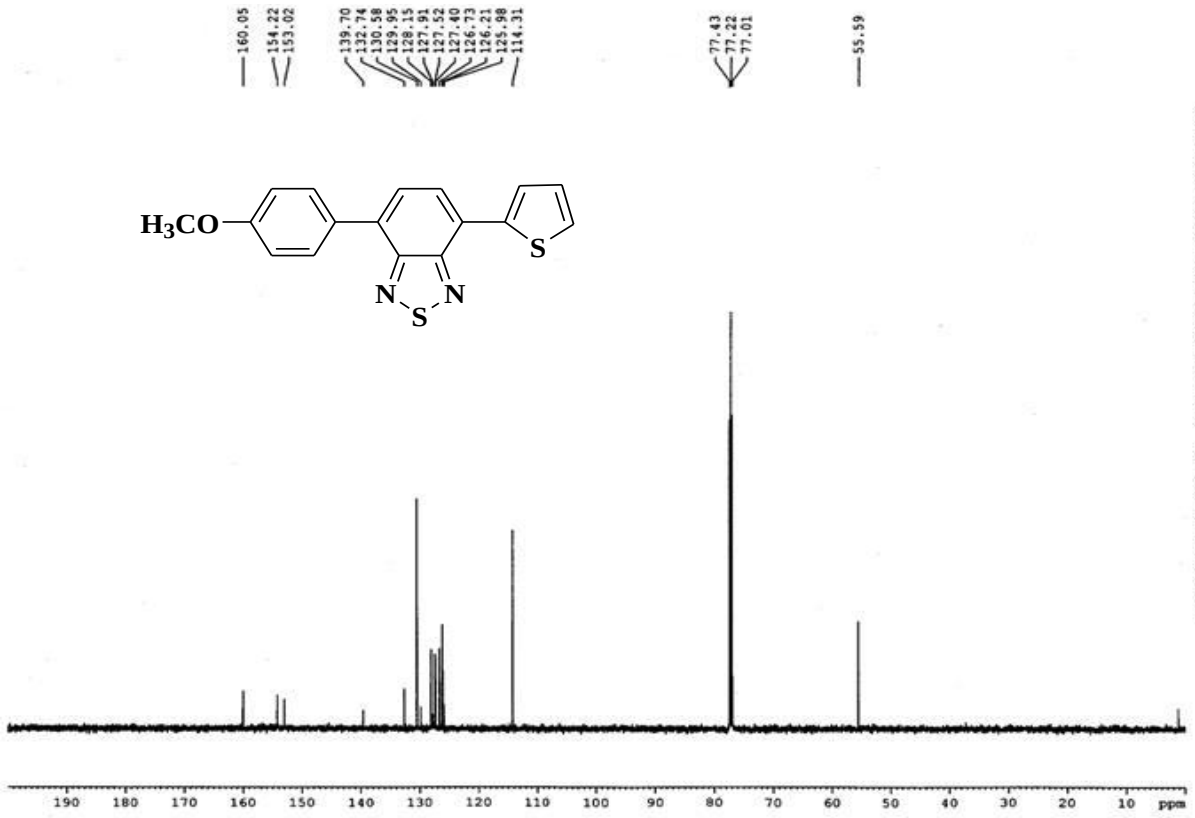

Figure S5. The ^{13}C NMR of the **Compound-2** in $CDCl_3$.

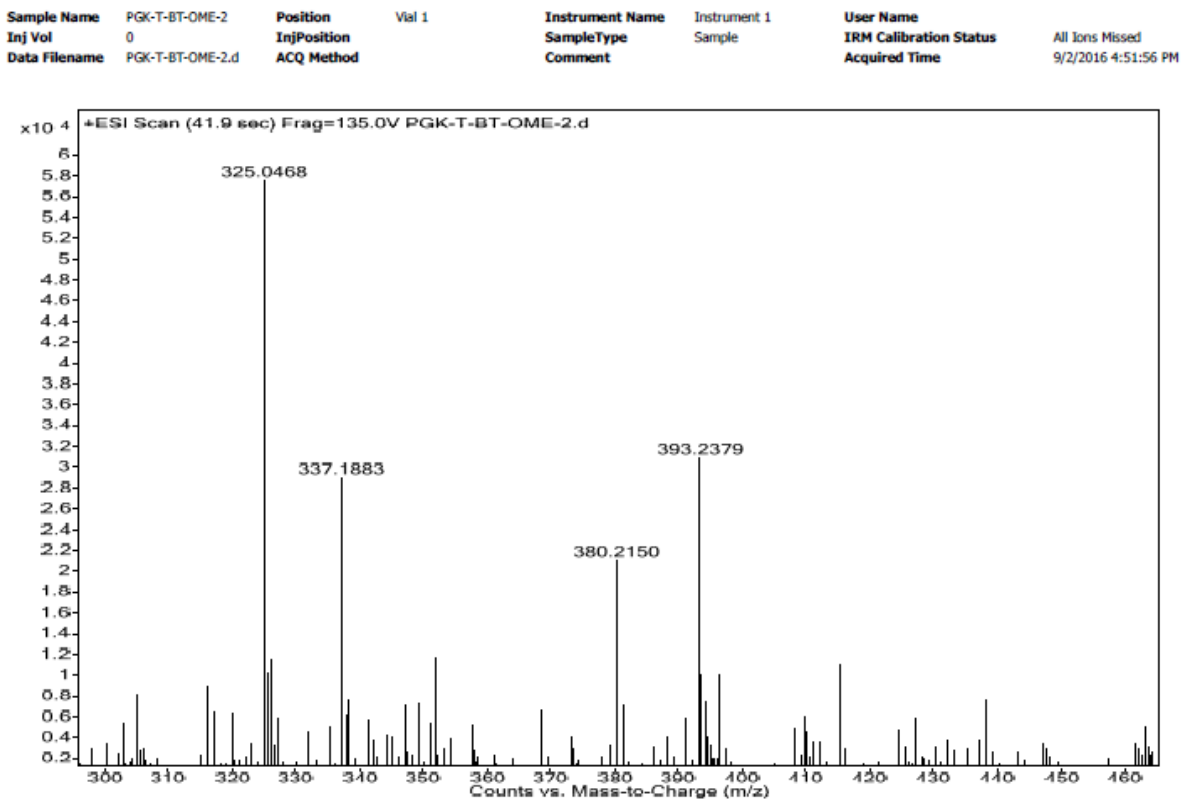

Figure S6. HRMS of the **Compound-2**.

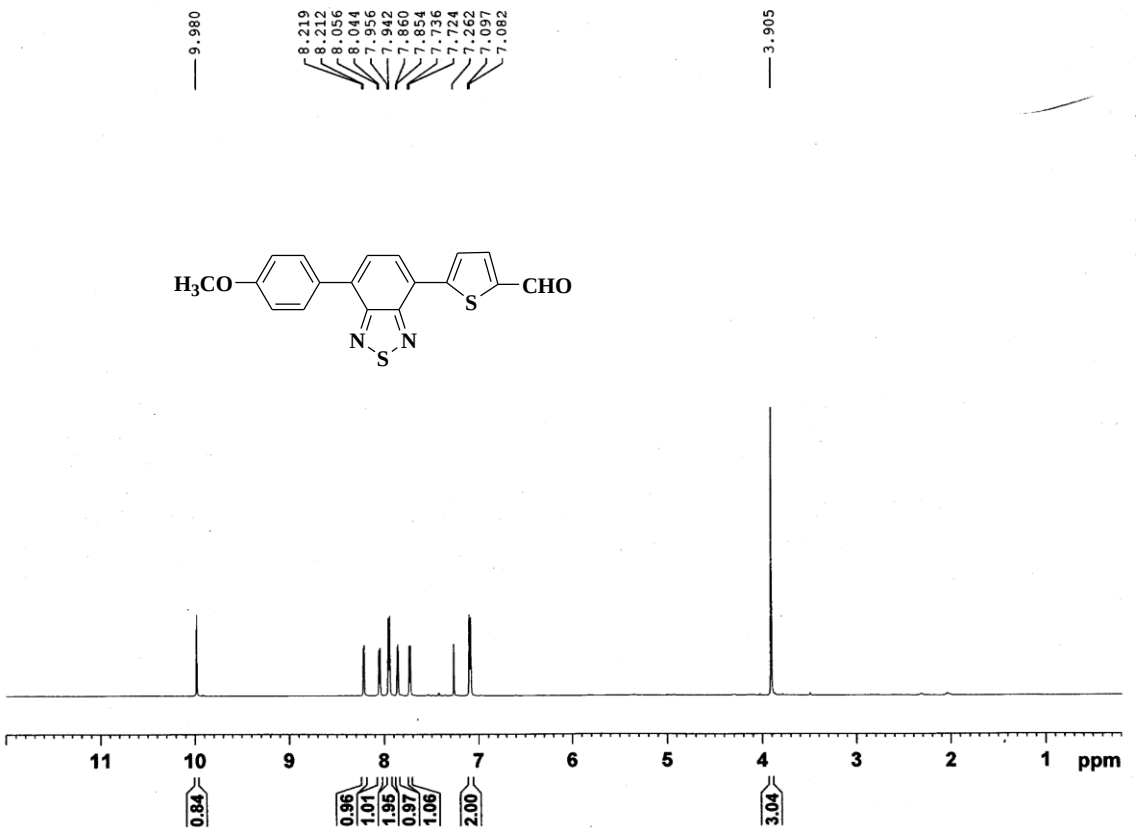

Figure S7. The ^{1}H NMR of the **Compound-3** in $CDCl_3$.

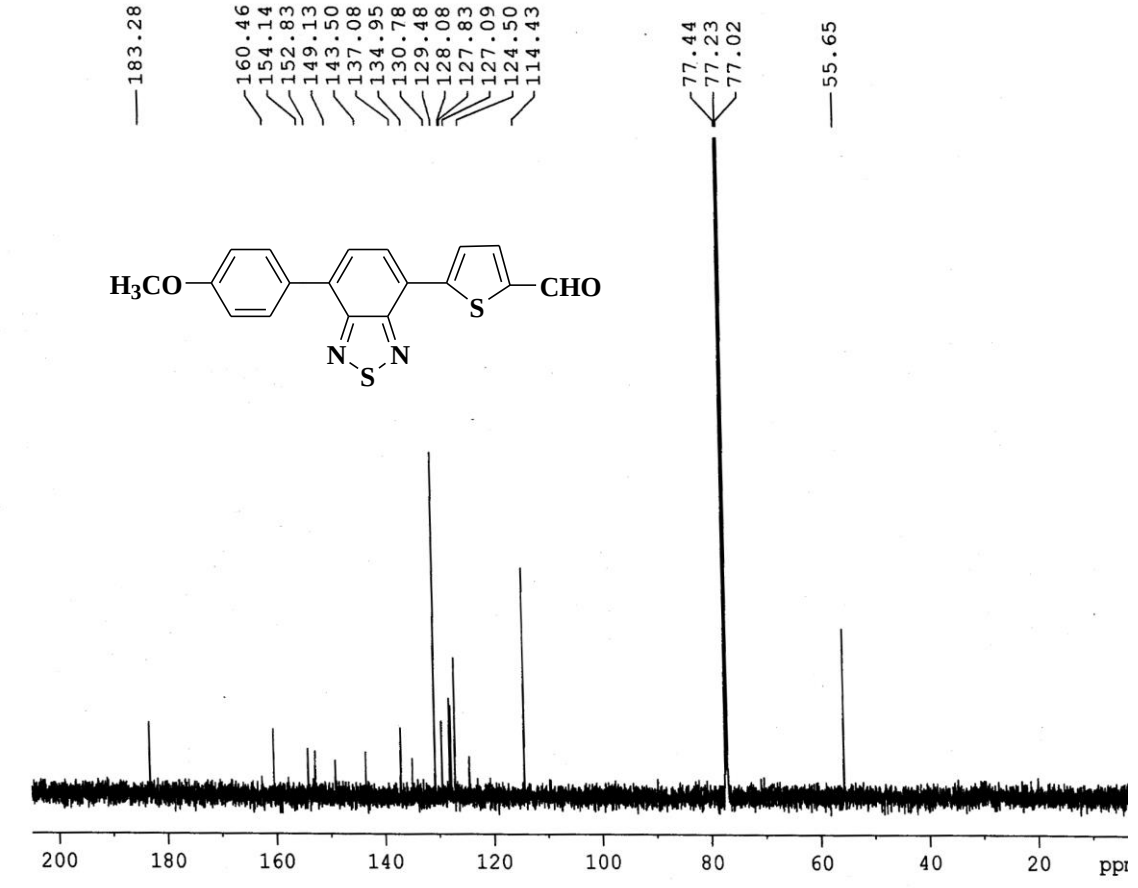

Figure S8. The ^{13}C NMR of the **Compound-3** in $CDCl_3$.

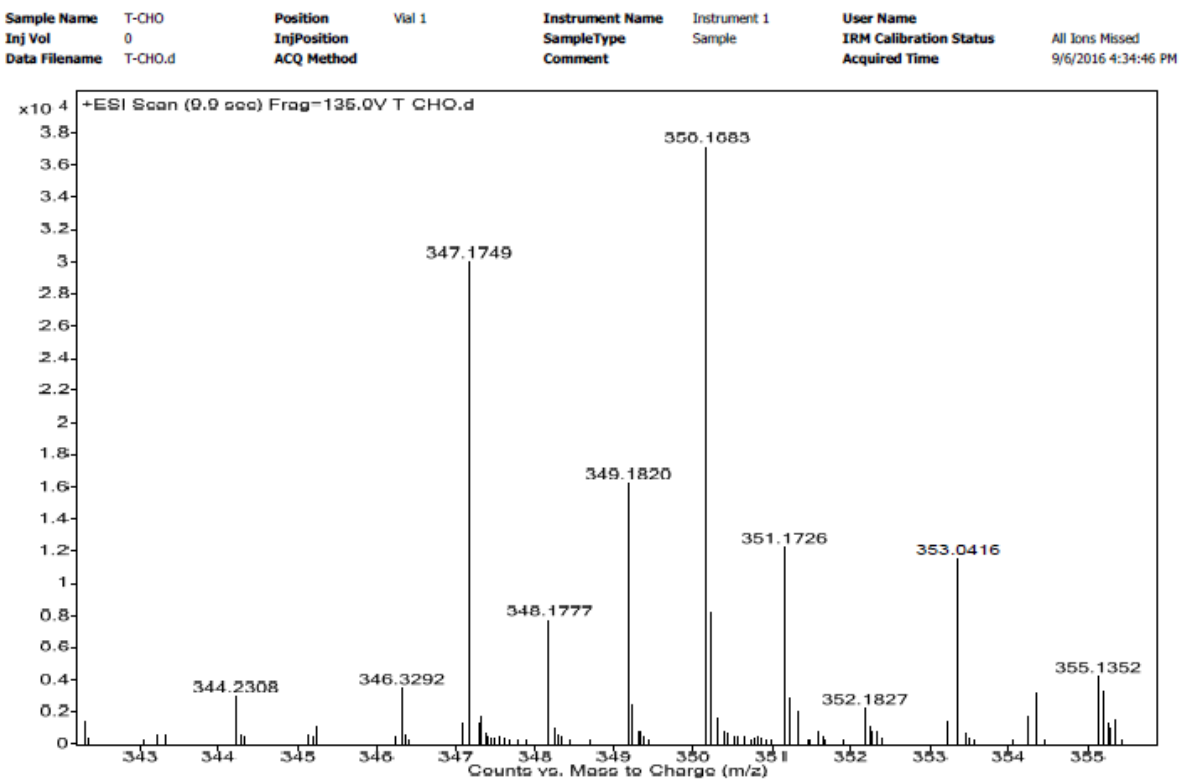

Figure S9. HRMS of the **Compound-3**.

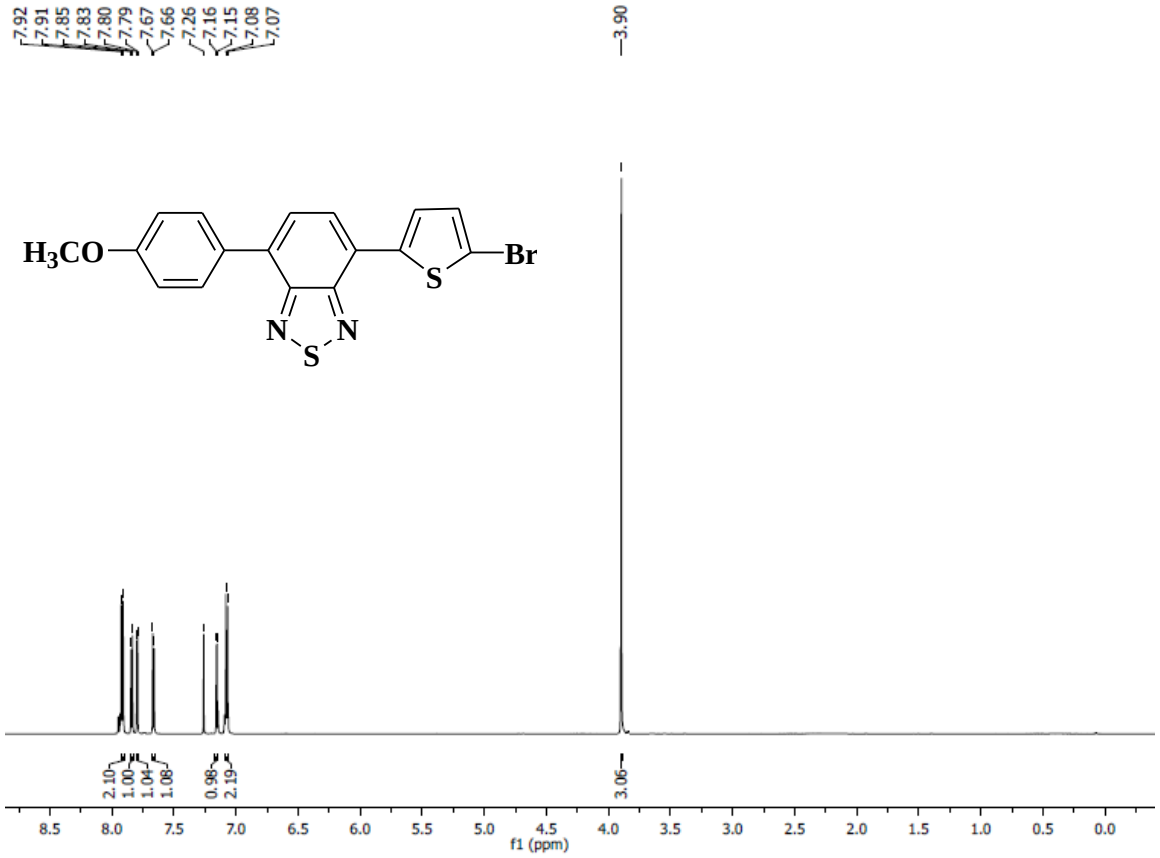

Figure S10. The ^{1}H NMR of the **Compound-4** in $CDCl_3$.

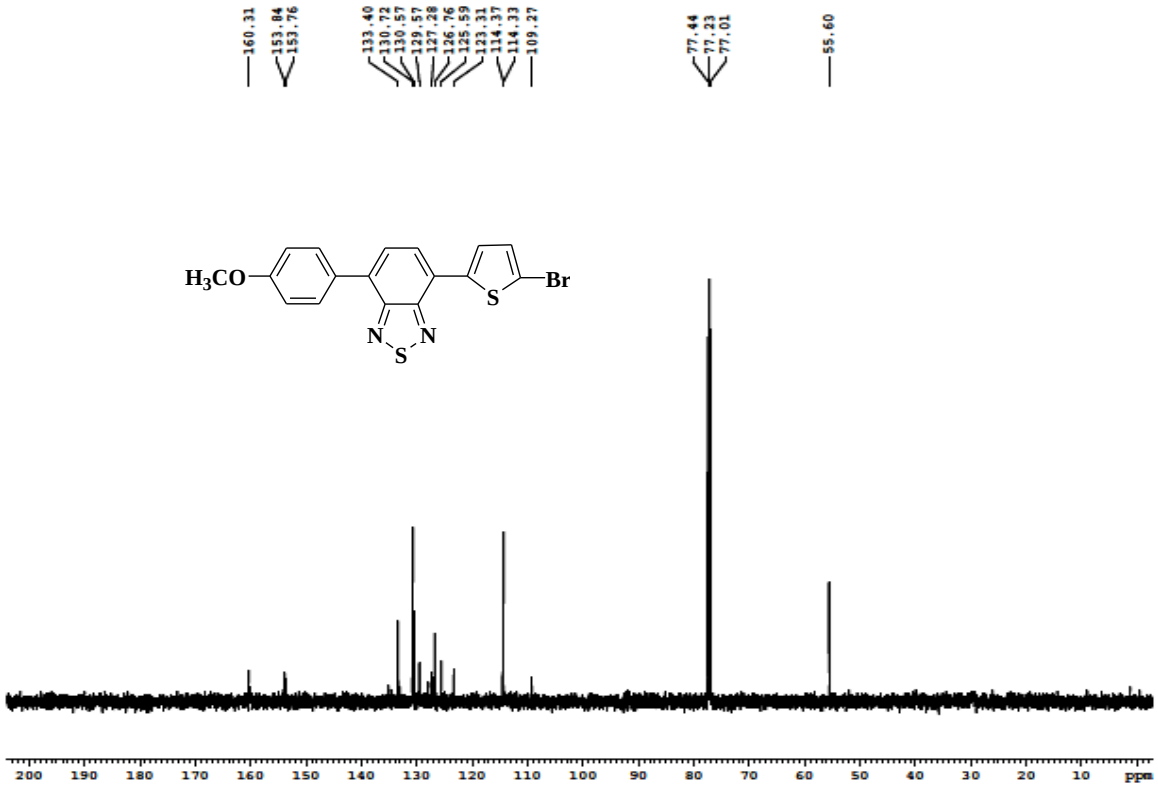

Figure S11. The ^{13}C NMR of the **Compound-4** in $CDCl_3$.

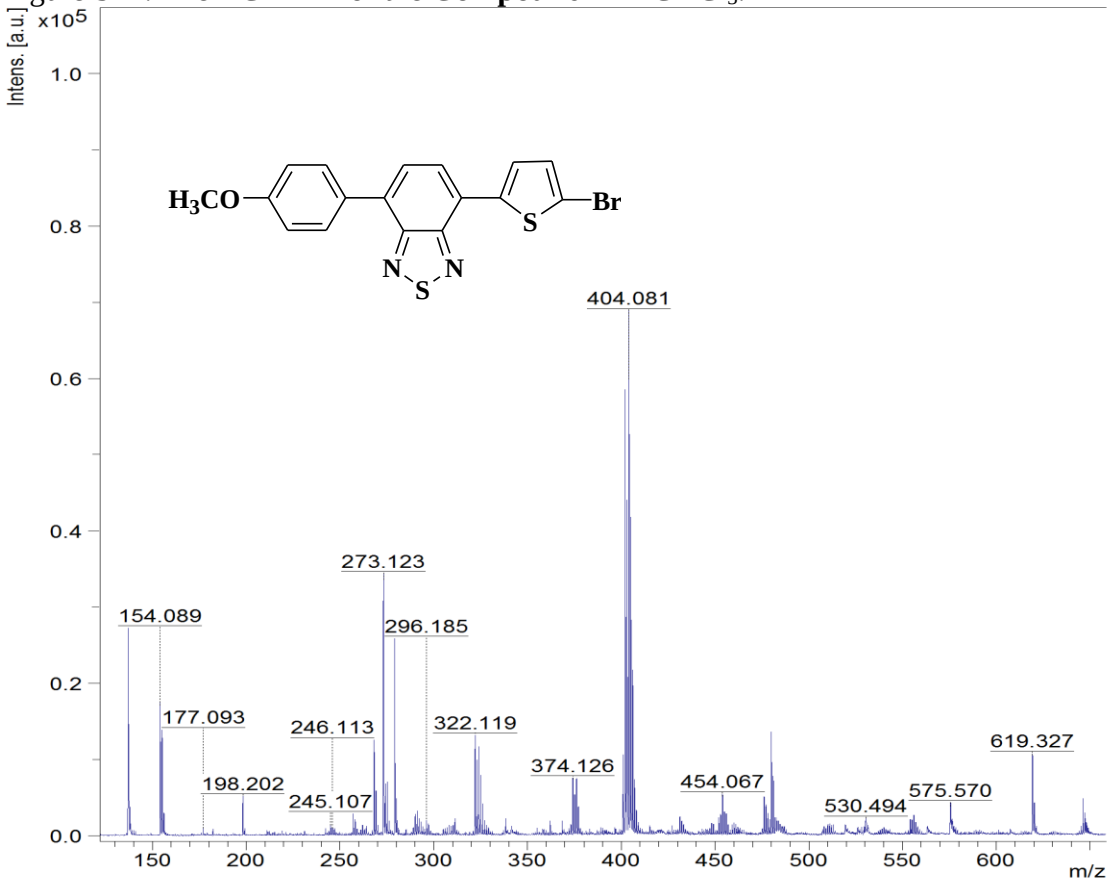

Figure S12. The time-of-flight mass spectrum of the **Compound-4**.

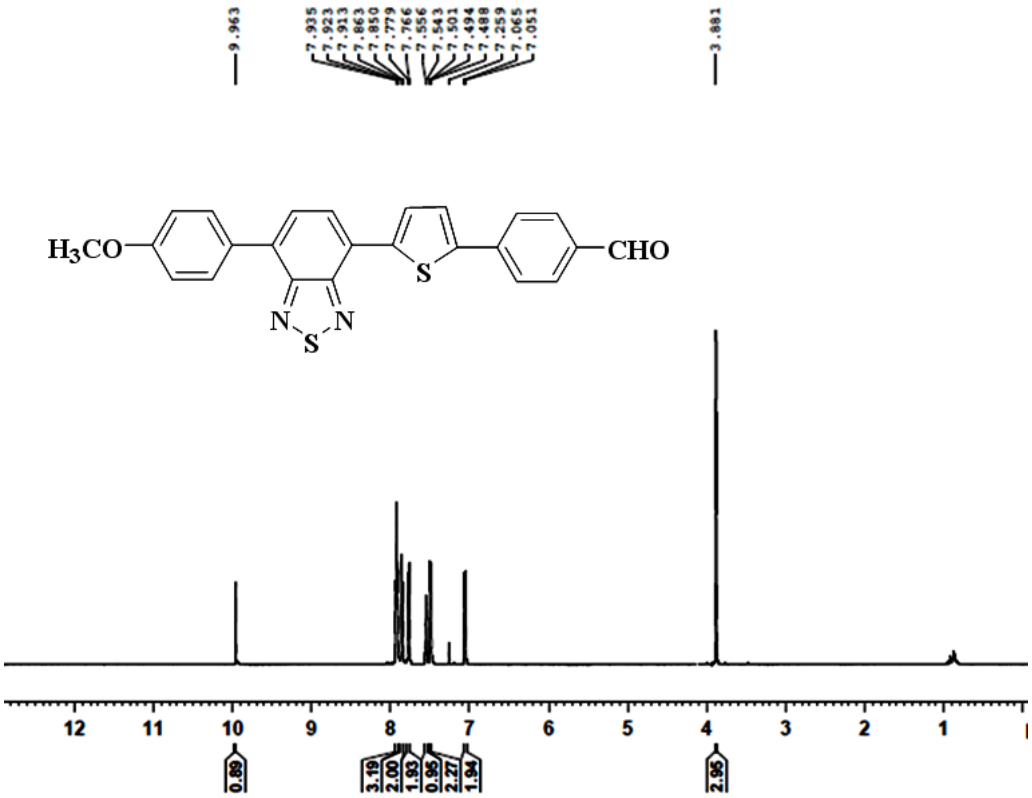

Figure S13. The ^{1}H NMR of the **Compound-5** in $CDCl_3$.

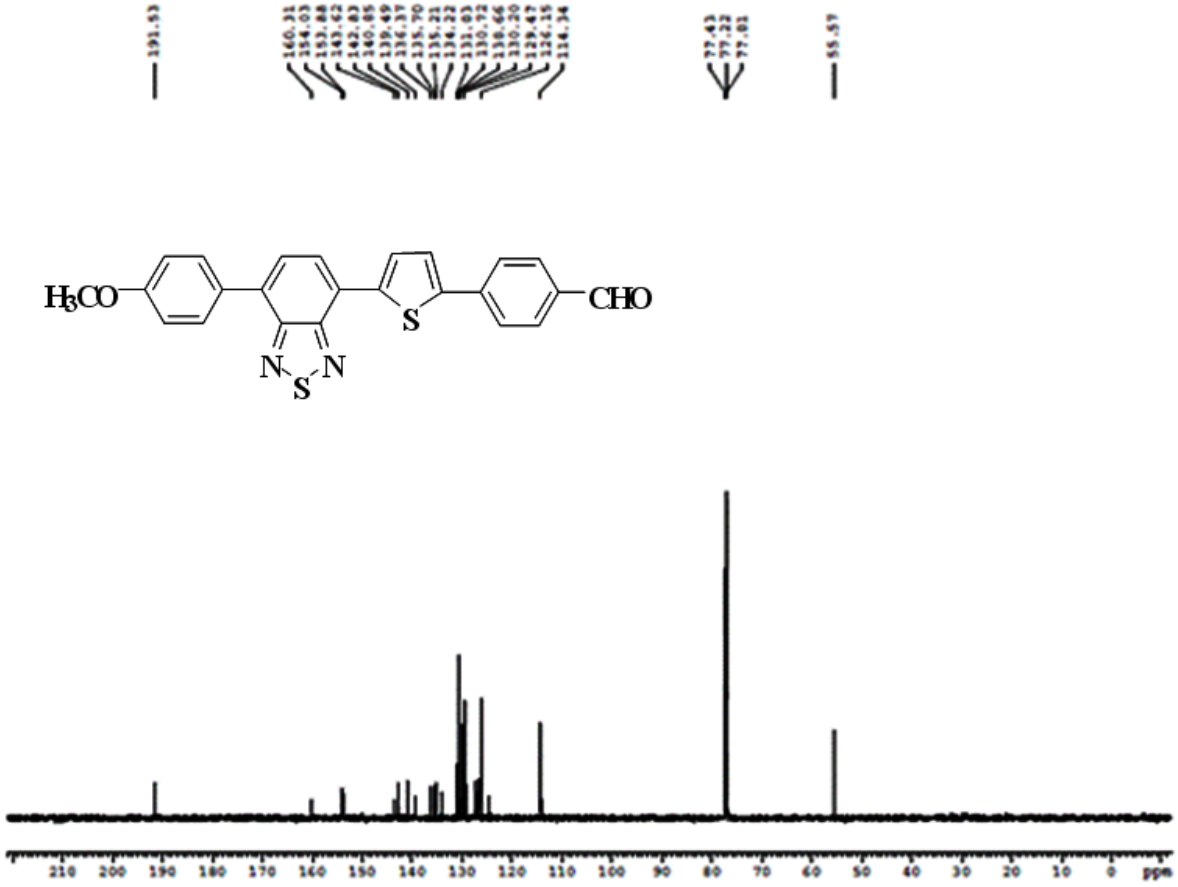

Figure S14. The ^{13}C NMR of the **Compound-5** in $CDCl_3$.

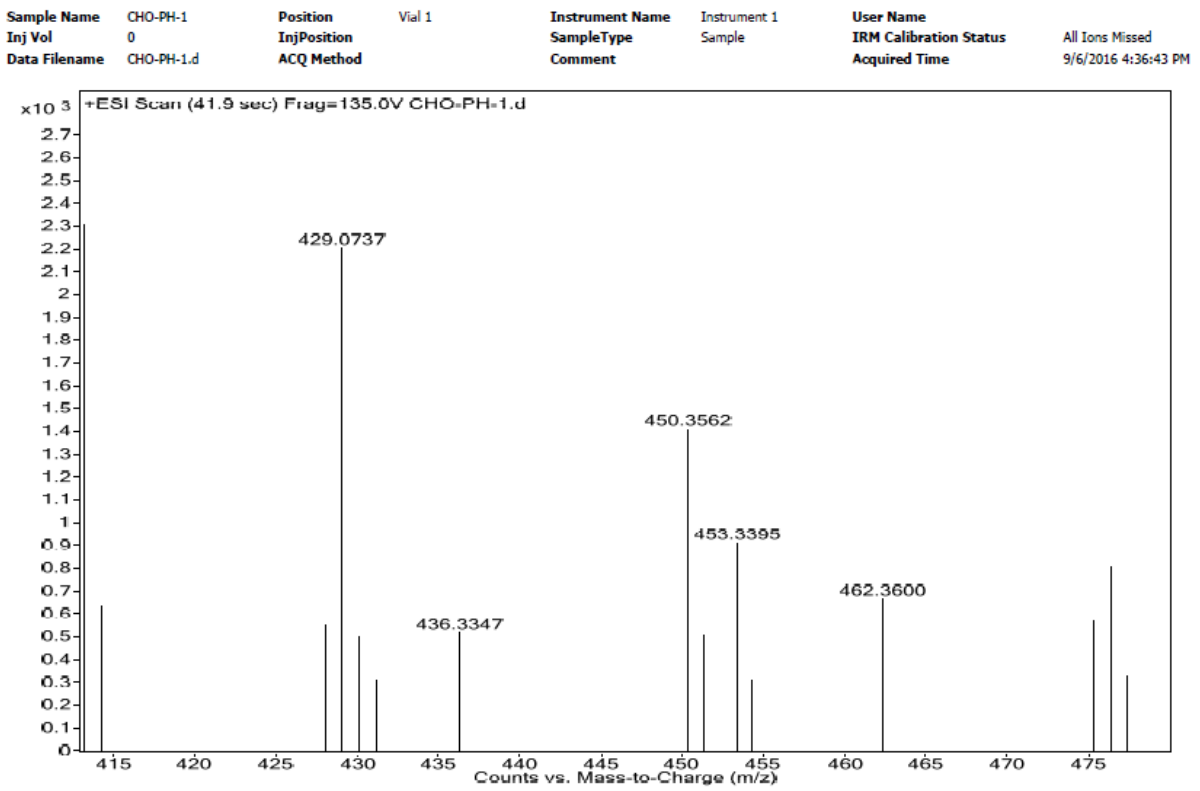

Figure S15. HRMS of the **Compound-5**.

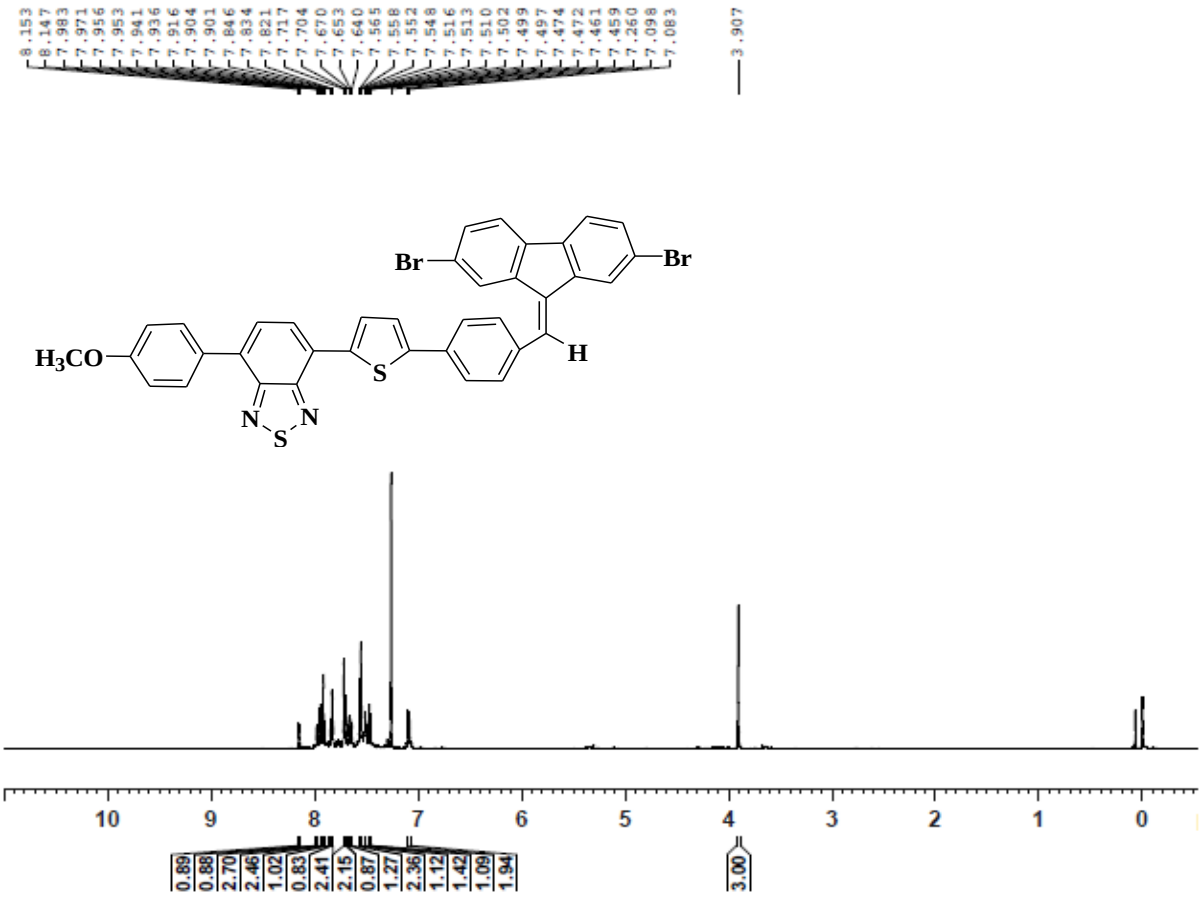

Figure S16. The ^{1}H NMR of the **DP2** in $CDCl_3$.

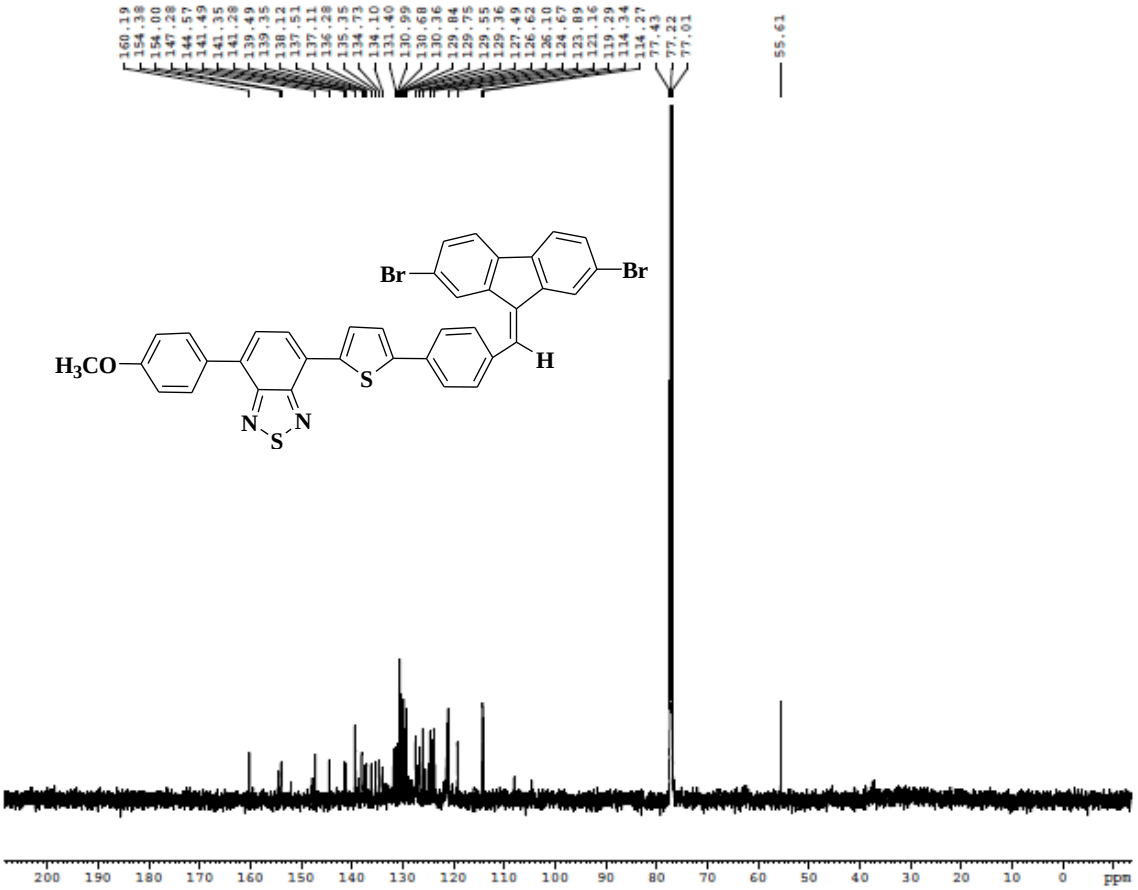

Figure S17. The ^{13}C NMR of the **DP2** in $CDCl_3$.

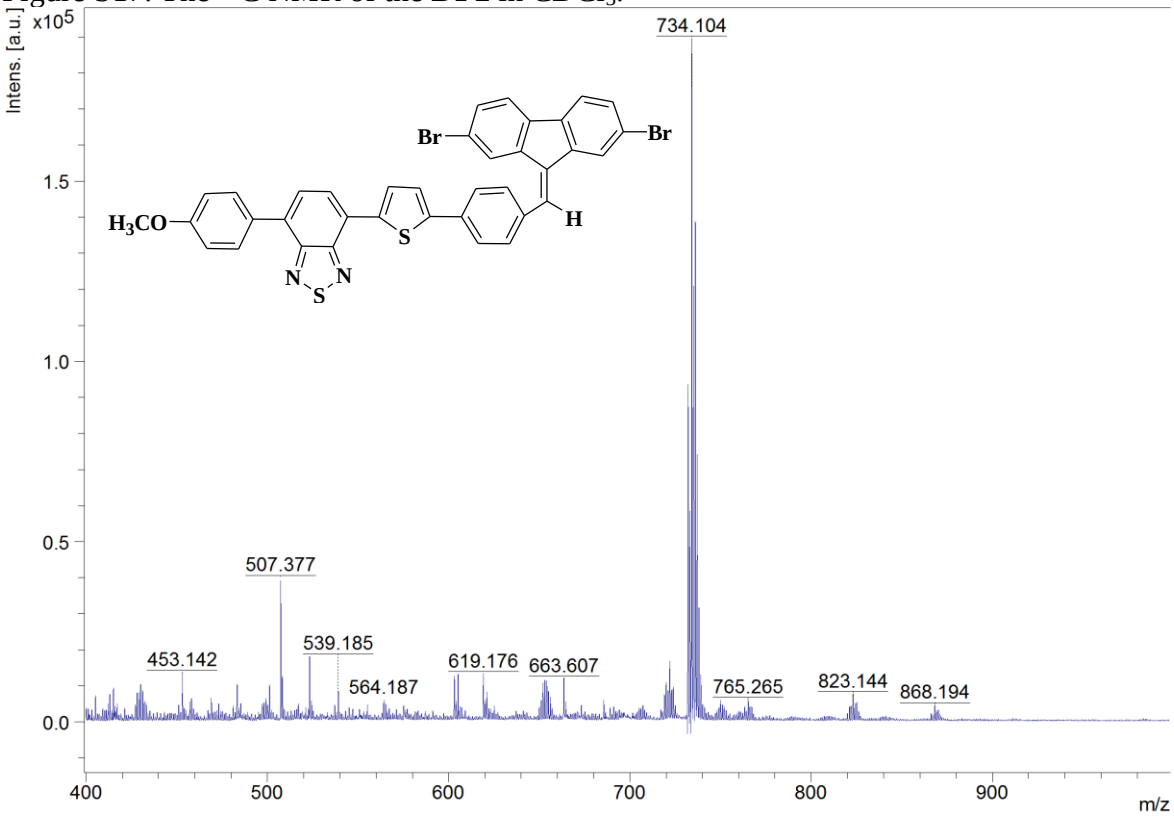

Figure S18. The time-of-flight mass spectrum of the **DP2**.

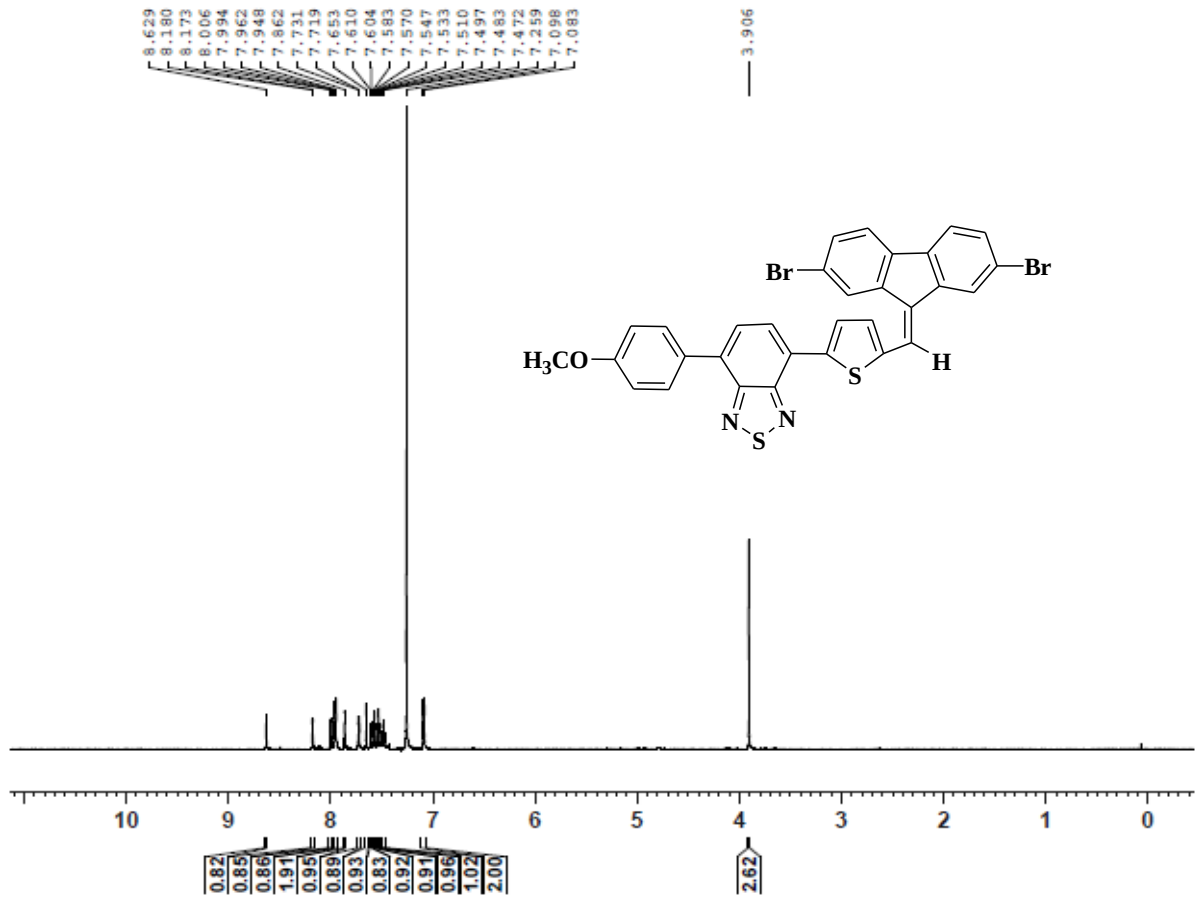

Figure S19. The ^{1}H NMR of the **DT2** in $CDCl_3$.

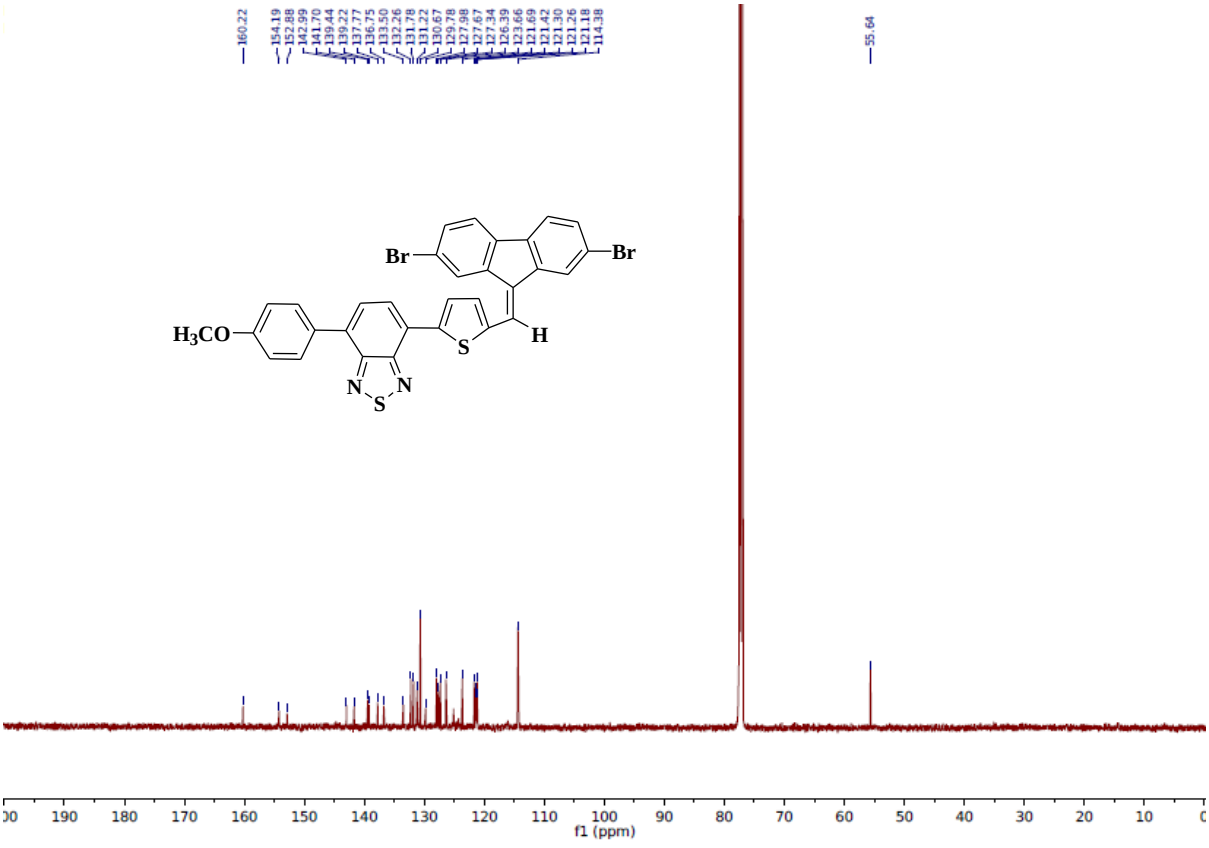

Figure S20. The ^{13} NMR of the **DT2** in $CDCl_3$.

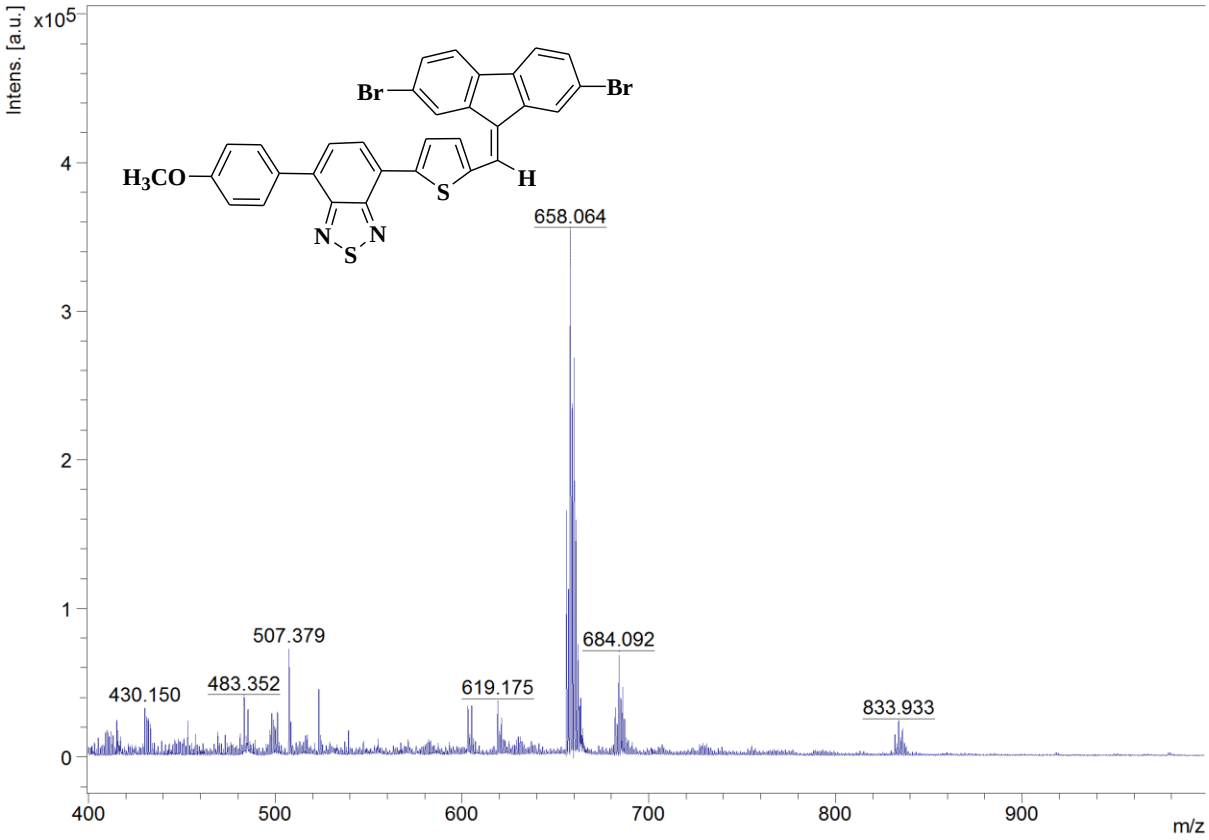

Figure S21. The time-of-flight mass spectrum of the **DT2**.

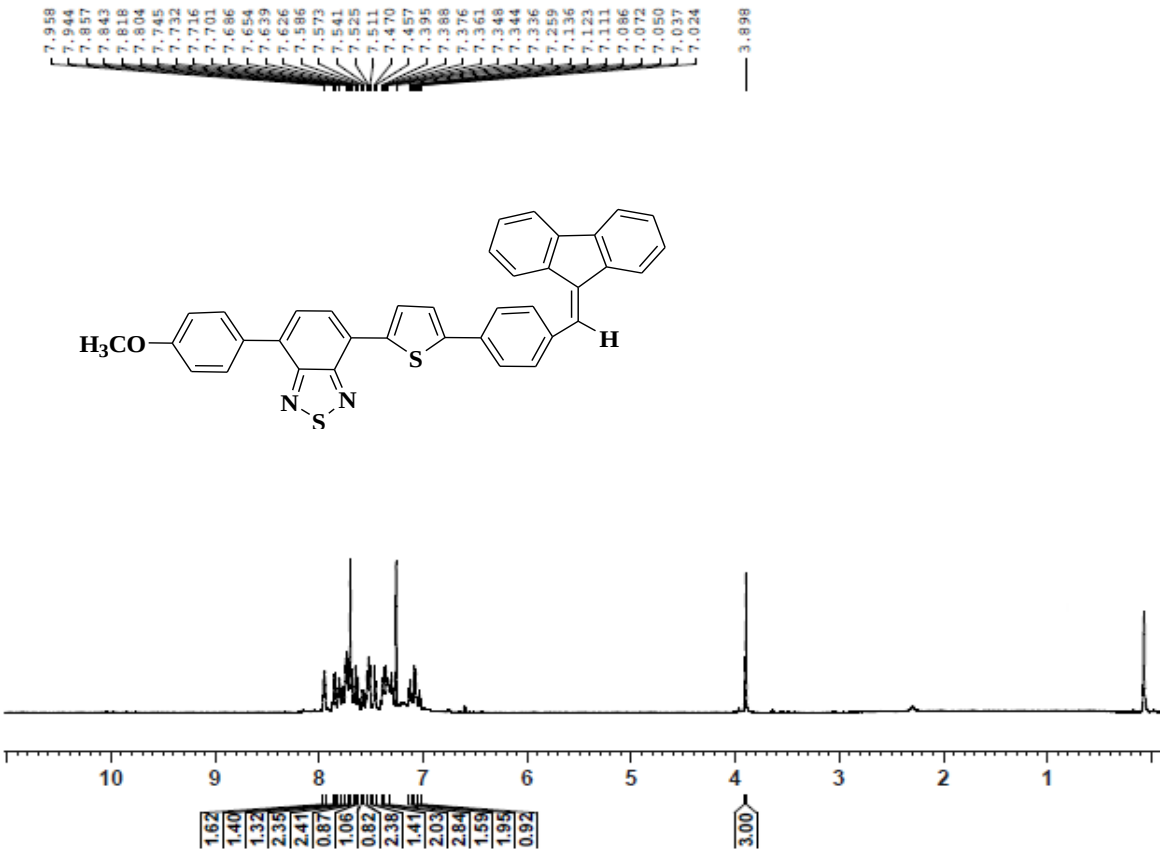

Figure S22. The ^{1}H NMR of the **DP1** in $CDCl_3$.

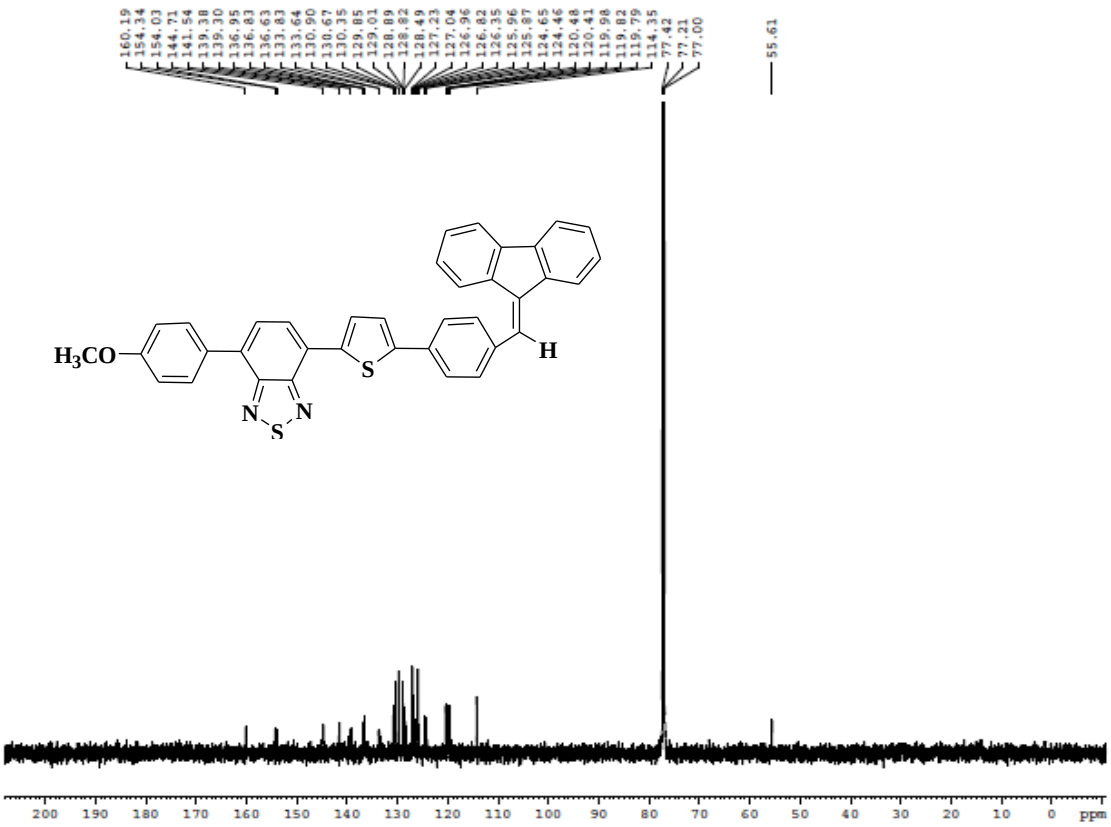

Figure S23. The ^{13}C NMR of the **DP1** in $CDCl_3$.

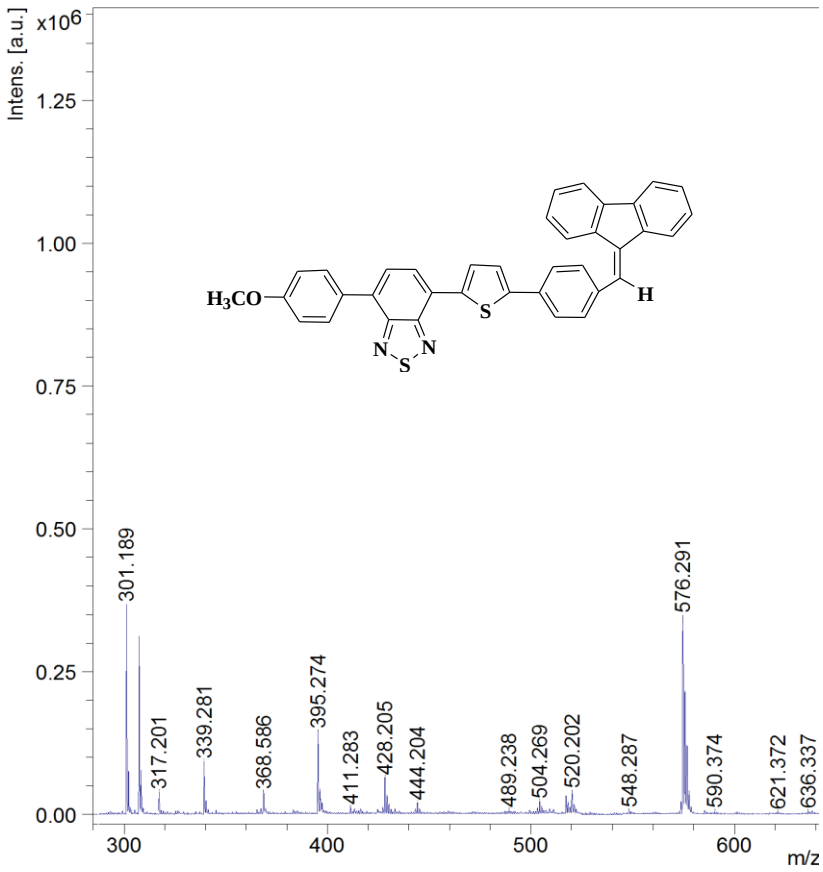

Figure S24. The time-of-flight mass spectrum of the **DT2**.

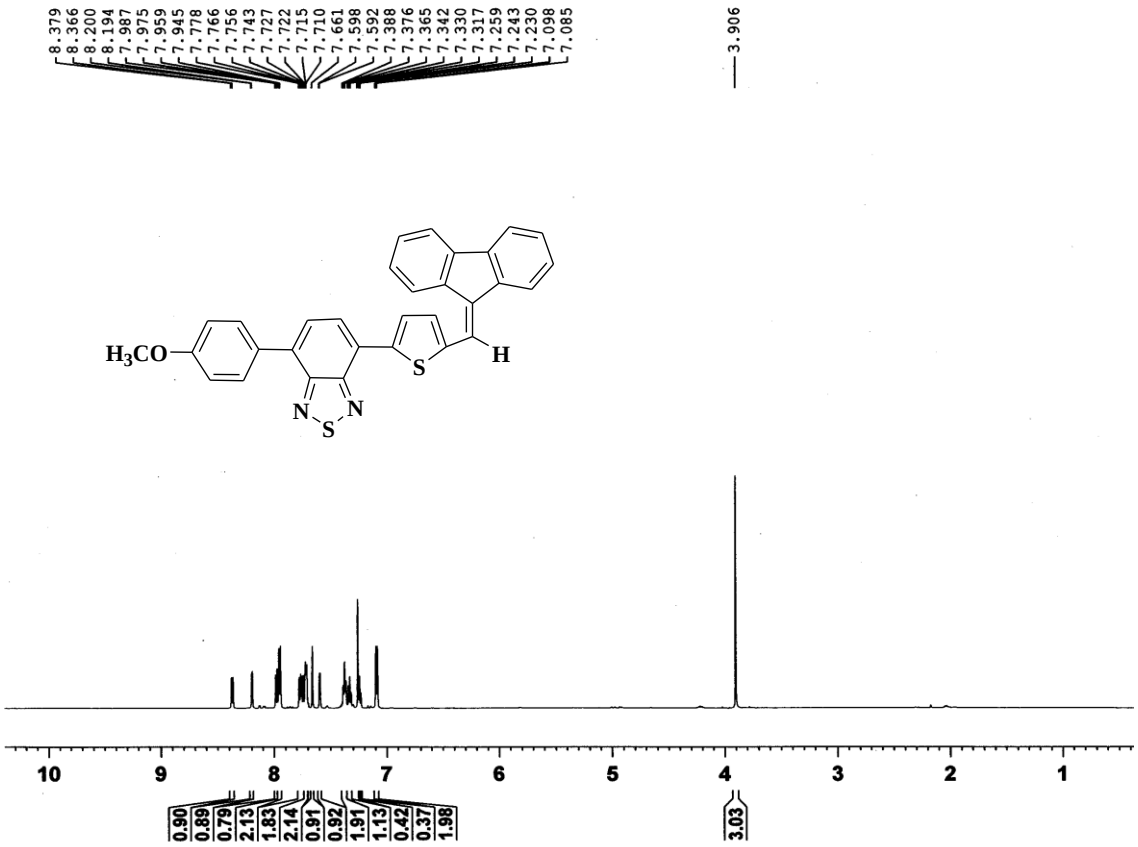

Figure S25. The ^{1}H NMR of the **DT1** in $CDCl_3$.

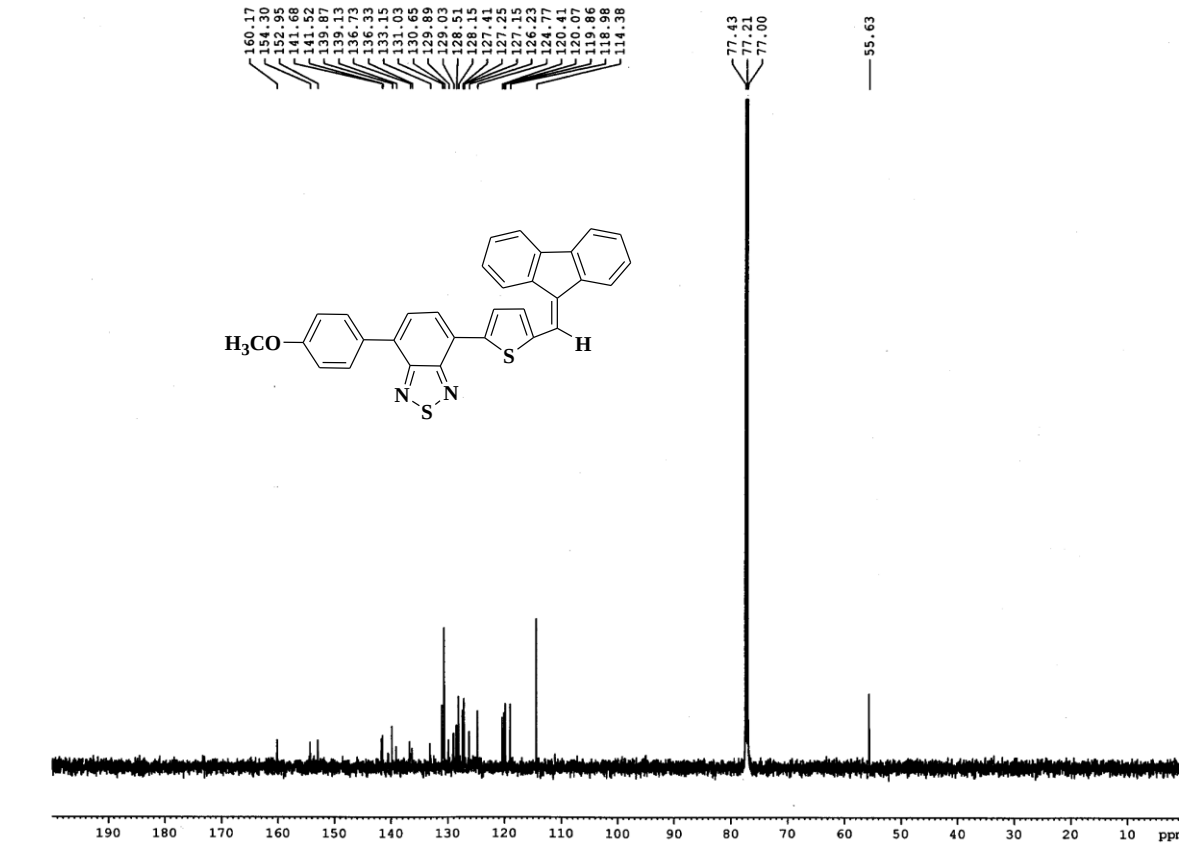

Figure S26. The ^{13}C NMR of the **DT1** in $CDCl_3$.

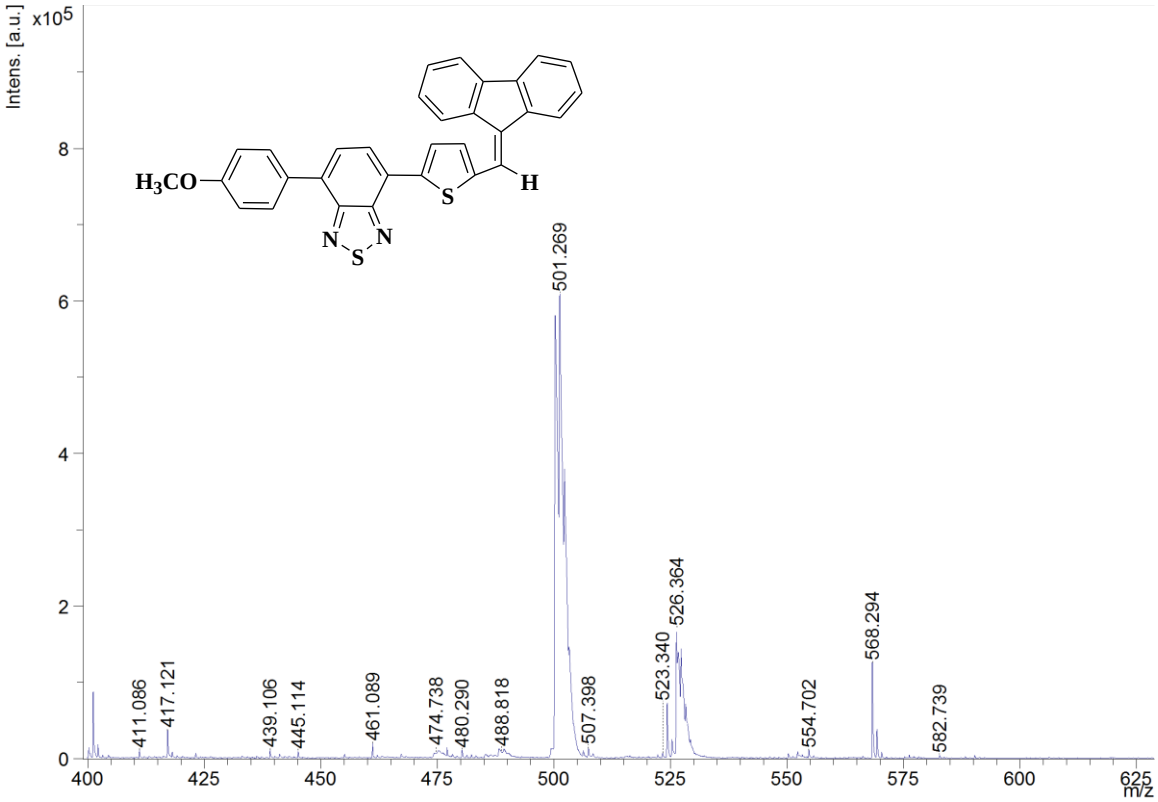

Figure S27. The time-of-flight mass spectrum of the **DT1**.

Crystal Data:

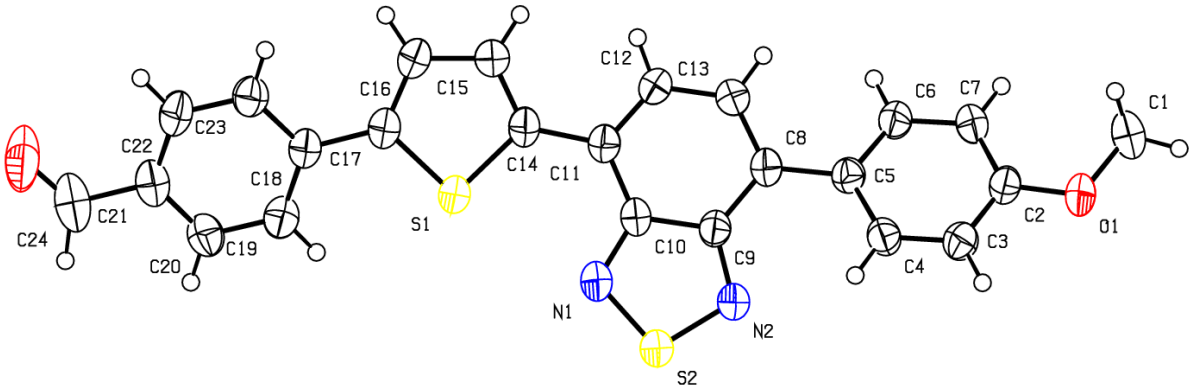

Figure S28. ORTEP diagram of **Compound-5**.

Table S1. Structure determination summary of **DT1** and **Compound-5.**

Compound	**DT1**	**Compound-5**
Empirical formula	$C_{31}H_{20}N_2Os_2$	$C_{24}H_{16}N_2O_2S_2$
CCDC NO	1445372	1446140
Formula weight	500.61	428.51
Temperature/K	296 (2)	296 (2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$
a/Å	10.1603(3)	9.4561(3)

b/Å	18.4764(5)	17.9251(6)
c/Å	12.9632(3)	12.1203(4)
α/°	90.00	90.00
β/°	92.126(2)	108.290(2)
γ/°	90.00	90.00
Volume/$Å^3$	2431.85(11)	1950.62(11)
Z	4	4
$\rho_{calc}mg/mm^3$	1.367	1.459
m/mm^{-1}	0.247	0.298
F(000)	1040.0	888.0
Crystal size/mm^3	0.32 × 0.24 × 0.12	0.28 × 0.24 × 0.21
2Θ range for data collection	3.84 to 50.5°	4.2 to 50.5°
Index ranges	$-11 \leq h \leq 12$, $-21 \leq k \leq 21$, $-15 \leq l \leq 14$	$-11 \leq h \leq 11$, $-21 \leq k \leq 21$, $-14 \leq l \leq 14$
Reflections collected	31332	17891
Independent reflections	4339[R(int) = 0.0369]	3492[R(int) = 0.0368]
Data/restraints/parameters	4339/0/326	3492/0/276
Goodness-of-fit on F^2	1.067	0.915
Final R indexes [$I>=2\sigma(I)$]	R_1 = 0.0401, wR_2 = 0.1158	R_1 = 0.0435, wR_2 = 0.1247
Final R indexes [all data]	R_1 = 0.0565, wR_2 = 0.1268	R_1 = 0.0714, wR_2 = 0.1431

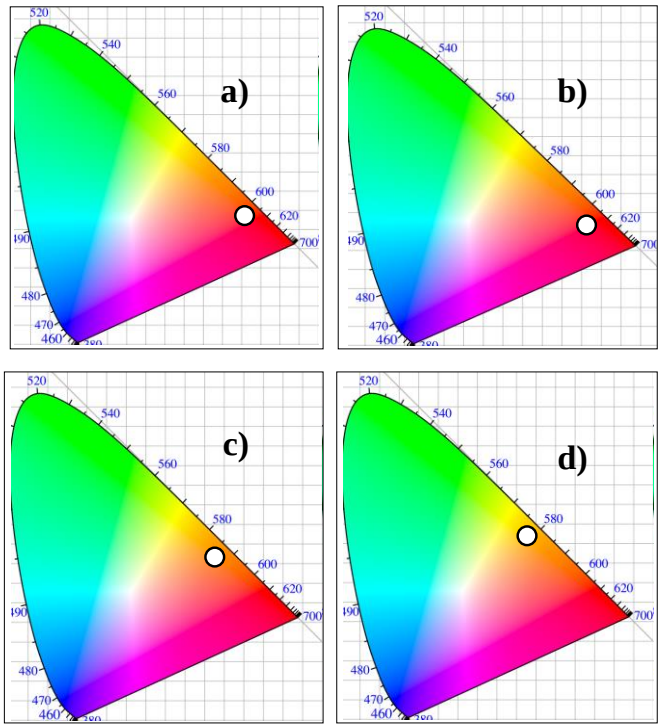

Figure S29. Chromaticity diagram representing the CIE coordinates of **a) DT1**, (0.65, 0.34), **b) DT2**, (0.66, 0.32), **c) DP1** (0.57, 0.42), and **d) DP2, (**0.51, 0.47).

Table S2. TD-DFT calculations of the luminogens.

Monomers	**TD-DFT**		
	λ_{theory} (nm)	**f**	**Composition**
DT1	370 ($S_0 \rightarrow S_8$) 500 ($S_0 \rightarrow S_3$)	0.47, 0.89	H→ L+1 (64.6%) = π−π* H-2→ L (26.0%) = π−π*, H→ L (91.2%) = π−π* (ICT)),
DT2	368, ($S_0 \rightarrow S_8$) 512 ($S_0 \rightarrow S_3$)	0.45, 0.96	H→ L+1 (73.2%) = π−π* H-2→ L(17.0%) = π−π*, H→ L (92.8%) = π−π* (ICT)
DP1	352 ($S_0 \rightarrow S_8$) 495 ($S_0 \rightarrow S_4$)	0.89 0.87	H→ L+1 (49.7%) = π−π* H-1→ L (27.3%) = π−π* H→ L (92.8%) = π−π* (ICT)
DP2	370 ($S_0 \rightarrow S_8$) 499 ($S_0 \rightarrow S_4$)	0.97 0.91	H→ L+1 (59.4%) = π−π* H-1→ L (16.8%) = π−π* H→ L (91.0%) = π−π* (ICT)

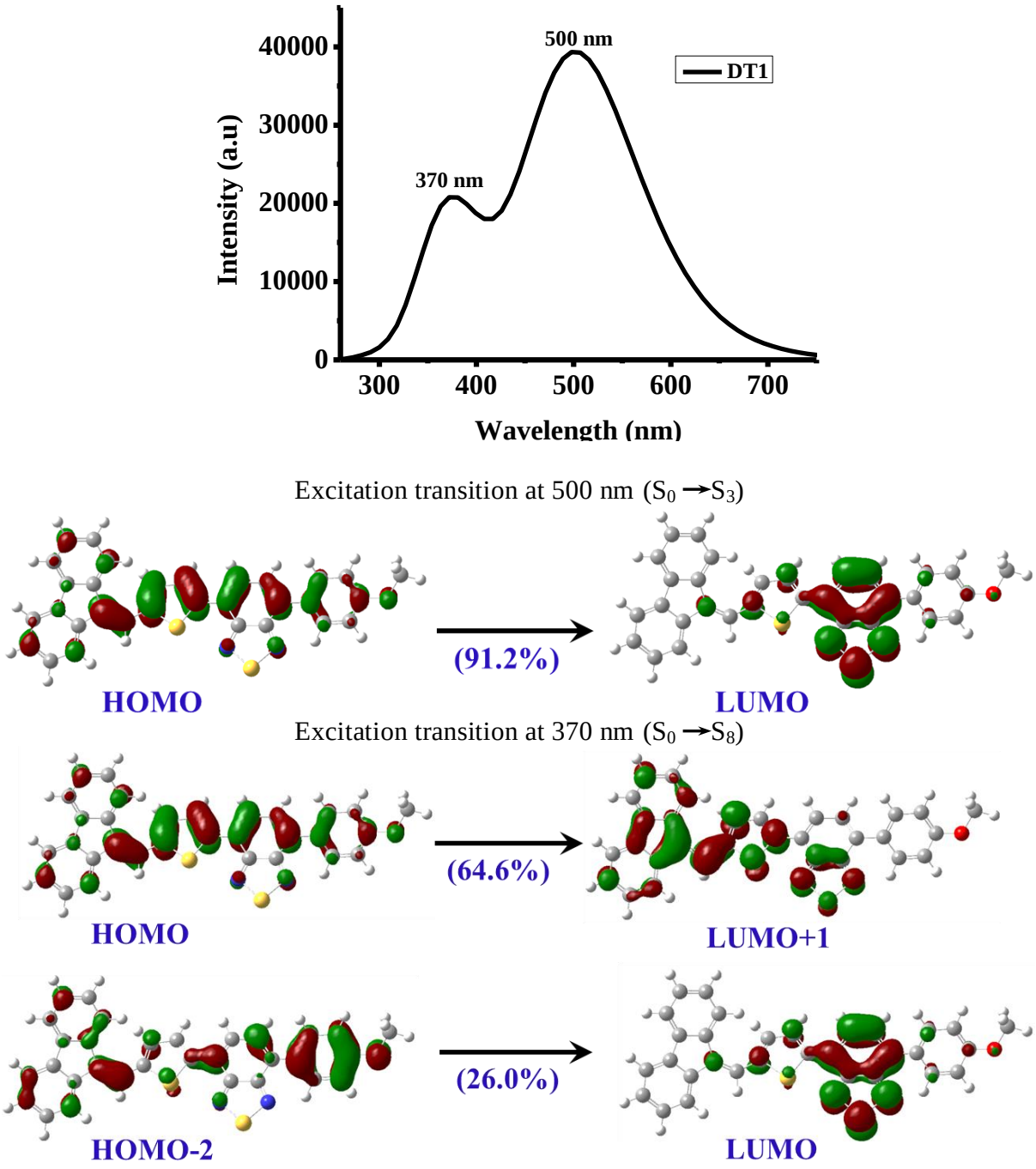

Figure S30. TD-DFT simulated absorption spectra and contributing orbitals at each excitation of **DT1** luminogen (isovalue = 0.03).

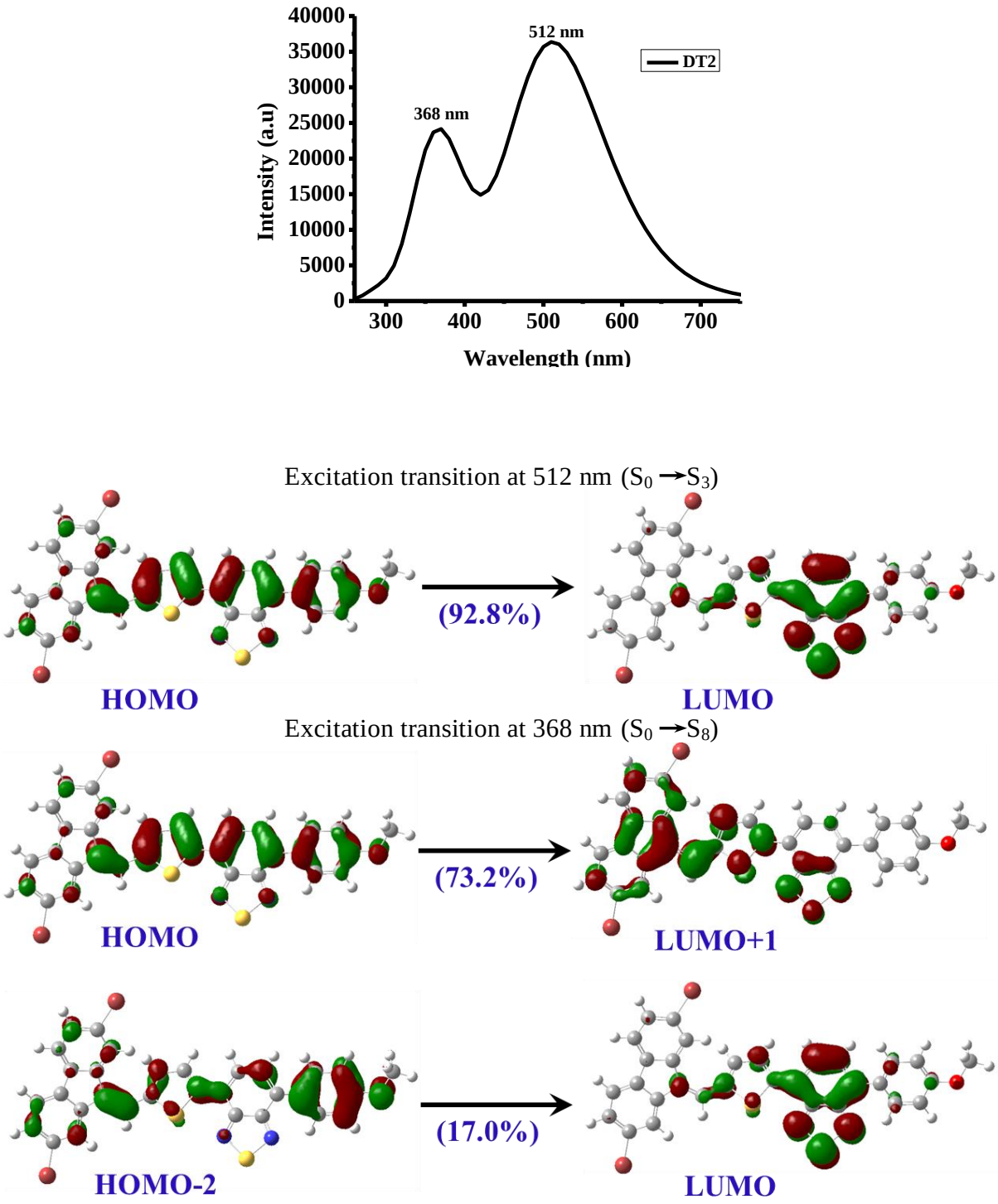

Figure S31. TD-DFT simulated absorption spectra and contributing orbitals at each excitation of **DT2** luminogen (isovalue = 0.03).

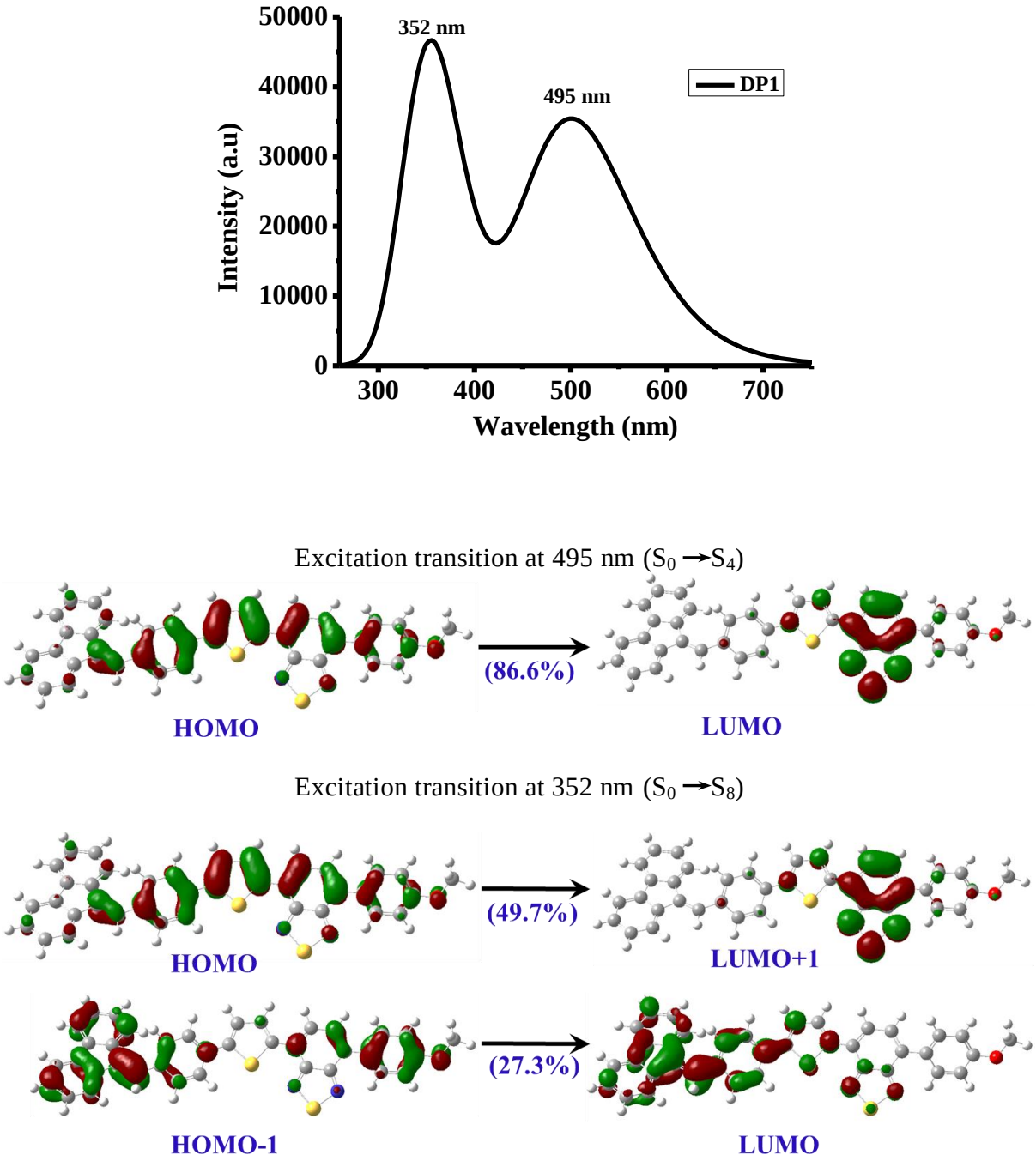

Figure S32. TD-DFT simulated absorption spectra and contributing orbitals at each excitation of **DP1** luminogen (isovalue = 0.03).

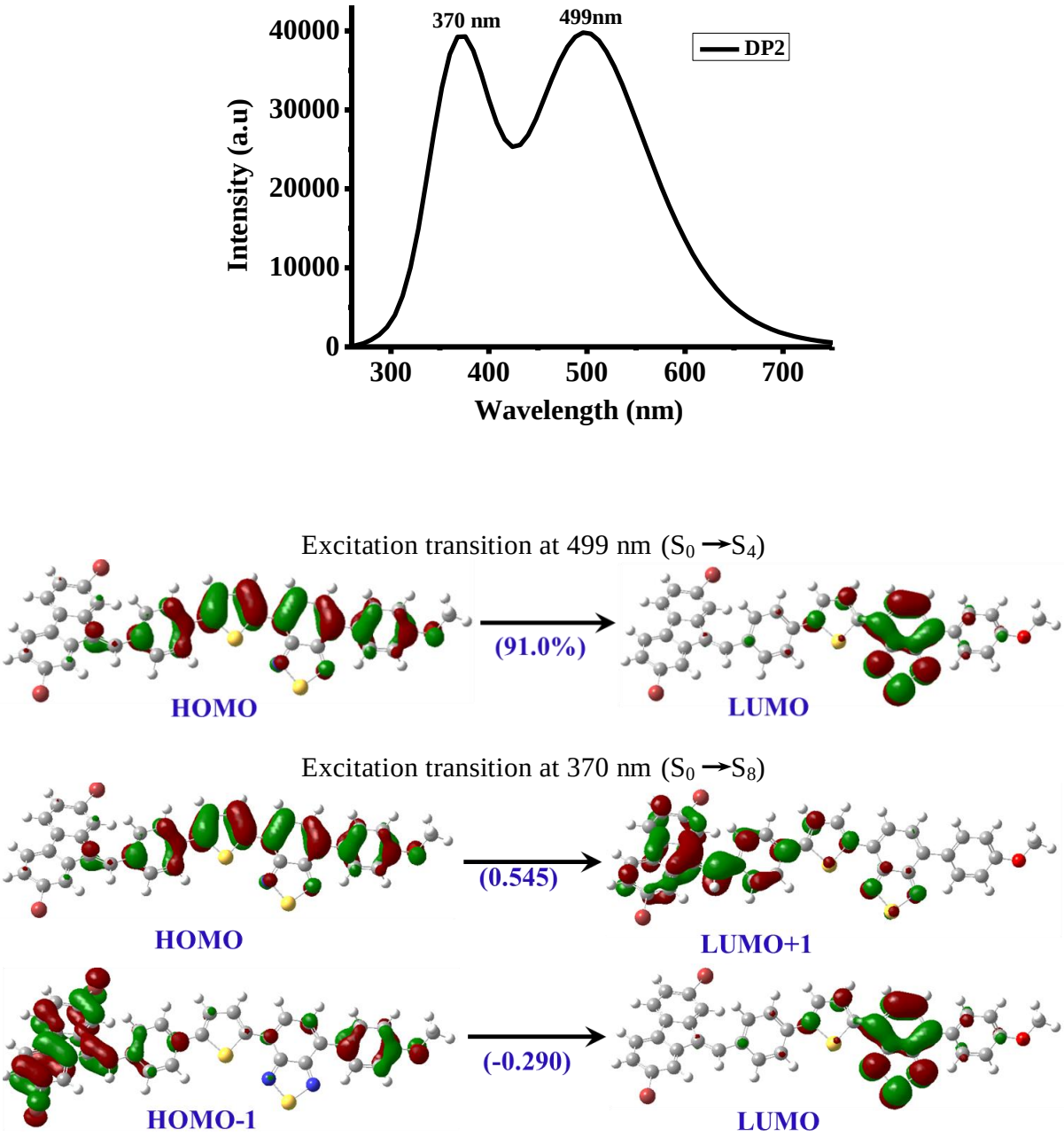

Figure S33. TD-DFT simulated absorption spectra and contributing orbitals at each excitation of **DP2** luminogen (isovalue = 0.03).

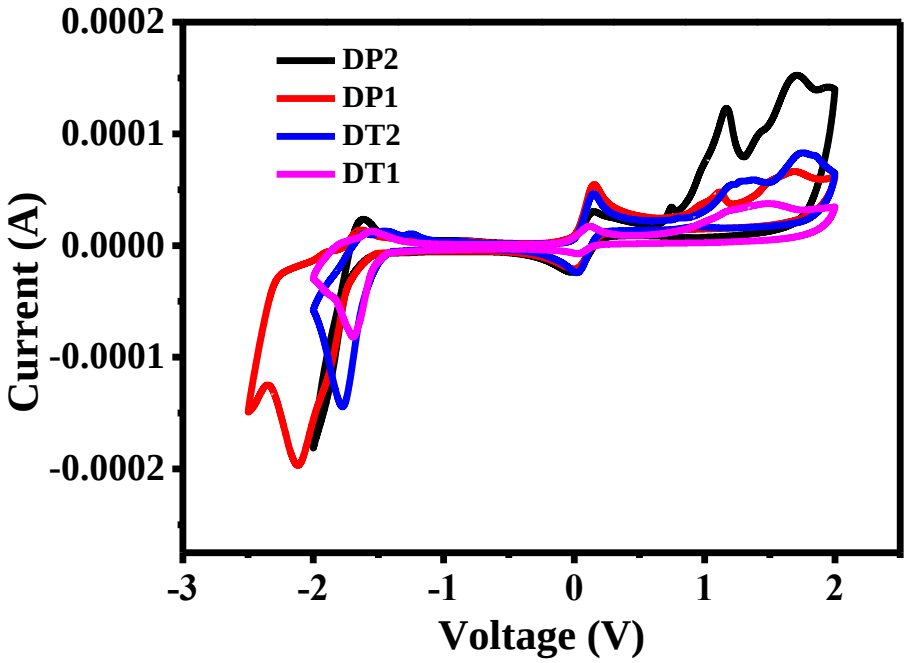

Figure S34. Cyclic voltammograms of Luminogens.