Supporting Information for

# Narrow Bandgap Nonfullerene Acceptor Based on Thiophene-fused Benzothiadiazole Unit with High Short-circuit Current Density over 20 mA $cm^{-2}$

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## Instruments and measurements

$^{1}$H-NMR and $^{13}$C-NMR were measured on a Bruker AVANCE III HD 400MHz. ESI-MS analysis was determined on a Finnigan-LCQ advantage mass spectrometer. MALDI-TOF analysis was performed on an Applied Biosystems 4700 proteomics Analyzer 155 mass spectrometer. The thermo-gravimetric analysis (TGA) was performed on NETZSCH STA449C thermal analyzer. Elemental analyses were carried out on a 73 CARLOERBA-1106 microelemental analyzer. The electrochemical Cyclic Voltammetry(CV) was conducted on a CHI voltammetric analyzer with glassy carbon disk, Pt wire and Ag/Ag+ electrode as working electrode, counter electrode and reference electrode respectively in a 0.1mol/L tetrabutylammonium hexafluorophosphate ($Bu_4NPF_6$) acetonitrile solution. The UV-vis absorption spectra of the polymers were measured by a Varian Cary 5000 UV-vis-NIR spectrophotometer. The film morphology was measured using an atomic force microscope (Cypher ES, Asylum Research) using the tapping mode and TEM measure by JEM-2010HT.

## Device fabrication

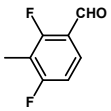
Bulk heterojunction solar cells were fabricated with a architecture of ITO/ZnO/PTB7-Th:A1 or A2/$MoO_3$/Ag. The patterned indium tin oxide (ITO) glass (sheet resistance= 10 Ω $sq^{-1}$) was pre-cleaned in an ultrasonic bath of deionized water, acetone and isopropanol. ZnO layer (ca. 30 nm) was spin-coated onto the ITO glass at 4000 rpm and baked subsequently at 200$^{o}$C for 30 min. The mixture of PTB7-Th: A1 or A2 in *o*-dichlorobenzene solvent (20 mg $mL^{-1}$ in total) with or without additive was spin-coated on a ZnO layer to form an active layer. $MoO_3$ (ca. 3 nm) and Ag (ca. 100 nm) layers were deposited onto the active layer in a vacuum at a pressure of ca. 5.0×10-5 Pa to form the positive electrode. The active area of the device was 4

mm$^2$. The current density−voltage (*J-V*) characteristics were measured on a computer–controlled B2912A Precision Source/Measure Unit (Agilent Technologies). A XES-70S1 (SAN-EI Electric Co., Ltd) solar simulator (AAA grade, 70×70 mm$^2$ photobeam size) coupled with AM 1.5 G solar spectrum filters was used as the light source, and the optical power at the sample was 100 mW/cm$^2$. A 2×2 cm$^2$ monocrystalline silicon reference cell (SRC-1000-TC-QZ) was purchased from VLSI Standards Inc. A Solar Cell Spectral Measurement System QE-R3011 (Enlitech Co., Ltd) was used for the EQE spectrum measurement. The light intensity at each wavelength was calibrated using a standard single crystal Si photovoltaic cell. The hole mobility and electron mobility were measured using the structure: ITO/PEDOT:PSS/ PTB7-Th: A1 or A2 /Au and ITO/ZnO/ PTB7-Th: A1 or A2/Al respectively. And the mobility was extracted by fitting the current *J–V* curves using the Mott–Gurney relationship (space charge limited current).

## Materials and Synthesis

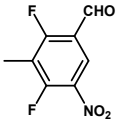
All the chemicals were used as commercially purchased without further purification except specified stated. Compound 11 and Compound12 were prepared according to the procedure described in the literature[1-2].

**2,4-Difluoro-3-methylbenzaldehyde (1)**




A solution of 1-bromo-2,4-difluoro-3-methylbenzene (1.76 g, 8.48 mmol) in anhydrous THF (20 mL) at -78°C was placed in a 100 mL argon purged flask under argon atmosphere. Then n-butyllithium (4.2 ml, 10.18 mmol) was added dropwise. The reaction mixture was then stirred for 30mins at -78°C. Subsequently, anhydrous DMF (1.31 ml, 16.96mmol) was added and the mixture was stirred for an additional 4h at ambient temperature. Then the mixture was extracted by chloroform and the combined organic phase was concentrated to obtain crude product. Further purification by column chromatography on silica gel with petroleum ether/ dichloromethane (3:1) as eluent was performed 1 (968 mg, 73.1%) was finally obtained as a colorless oil. $^1$H-NMR (400 MHz, $CDCl_3$ δ ppm): 10.29(s, 1H), 7.72(m, 1H), 6.97(m, 1H), 2.26(s, 3H).

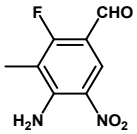
**2,4-Difluoro-3-methyl-5-nitrobenzaldehyde (2)**




To a solution of compound 1 (1.31 g, 8.4mmol) at -10$^o$C was slowly added 20mL concentrated $H_2SO_4$ ,and -10$^o$C was slowly added concentrated 0.4 mL $HNO_3$,and the solution

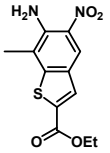
was stirred for 3 hours at -10°C. After reaction, the mixture was poured into a mass of ice water and extracted with chloroform. The organic layer was washed with water for three times, then dried over $Na_2SO_4$. Combined organic phase was concentrated to obtain crude product. Further purification by column chromatography on silica gel with petroleum ether/ chloroform (1:1) as eluent was performed 2 (1.27g, 75.0%) was finally obtained as a colorless oil. $^1$H-NMR (400 MHz, $CDCl_3$, δ ppm): 10.31(s, 1H), 8.50(m, 1H), 2.38(s, 3H). $^{13}$C-NMR (100MHz, $CDCl_3$, δ ppm): 184.17, 184.16, 184.12, 184.10, 166.72, 166.63, 164.07, 163.98, 159.46, 159.35, 156.75, 156.65, 134.83, 124.04, 123.99, 120.26, 120.22, 120.15, 120.11, 118.33, 118.12, 117.91, 7.59, 7.55, 7.51. EI-MS: Calcd. for $[C_8H_5F_2NO_3+H^+]^+$:202.13; Found:202.11.

**4-Amino-2-fluoro-3-methyl-5-nitrobenzaldehyde (3)**



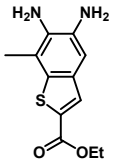

To a solution of compound 2(3.9g, 19.4mol) in THF (100mL) at 0°C was slowly added $NH_3{\cdot}H_2O$ (10mL). After addition, the mixture was kept at room temperature for 30min.A little too much concentrated hydrochloric acid was added dropwise. The mixture was extracted with ethyl acetate twice. After drying over $MgSO_4$,the solvent was removed under vacuum to give 3(3.54g, 92.1%) as a yellow solid. $^1$H-NMR (400 MHz, DMSO, δ ppm): 9.90(s, 1H), 8.49 (d, *J* = 8.0 Hz 1H), 8.05 (br, 2H), 2.12(d, *J*=2.4 Hz 3H). $^{13}$C-NMR (100MHz, DMSO, δ ppm):186.11, 186.09, 164.39, 161.81, 150.29, 150.18, 128.85, 128.78, 128.36, 113.74, 113.60, 112.05, 111.86, 9.37, 9.31. EI-MS: Calcd. for $[C_8H_7FN_2O_3]^+$:198.04;Found:198.00.

**Ethyl 6-amino-7-methyl-5-nitrobenzo[b]thiophene-2-carboxylate (4)**



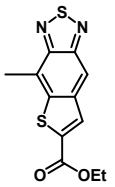

Compound 3(2.34g, 11.8mmol), ethyl 2-mercaptoacetate (1.71g, 14.16mmol) and $K_2CO_3$(2.49g, 17.7mmol) were dissolved in DMSO(10mL). The mixture was reacted in a microwave reactor for 1.5h at 80°C. After reaction, the mixture was poured into ice water and the crude product was filtered, washed with methanol and then dried to give 4(2.94g, 88.9%) as a red solid. $^1$ H-NMR (400 MHz, $CDCl_3$, δ ppm): 8.62(s, 1H), 7.94(s, 1H), 6.11(s, 2H), 4.40(m, 2H), 2.41(s, 3H), 1.43(t, *J*=6.8 Hz, 3H). $^{13}$C-NMR (100MHz, $CDCl_3$, δ ppm): 162.31, 149.92, 140.00, 132.35, 131.66, 128.61, 121.94, 116.07 , 61.79, 15.9, 14.35. EI-MS: Calcd. for $[C_{12}H_{12}N_2O_4S]^+$:280.05;Found:280.02.

**Ethyl 5,6-diamino-7-methylbenzo[b]thiophene-2-carboxylate (5)**



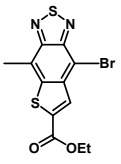
Compound 4(1.65g, 5.88mmol) and $SnCl_2{\cdot}2H_2O$ (5.30g, 23.5mmol) were dissolved in THF (100 mL) and then stirred at refluxing temperature overnight. After reaction, the mixture was poured into excessive sodium bicarbonate solution. Then, the mixture was extracted with ethyl acetate for several times. The organic layer was dried over $Na_2SO_4$.The solvent was removed under vacuum. A yellow solid was obtain is 4(1.21g, 91.7%). $^1$H-NMR (400 MHz, $CDCl_3$, δ ppm): 7.86(s, 1H), 7.10(s, 1H), 4.38(m, 2H), 3.78 (br, 4H), 2.37(s, 3H), 1.40(t, *J*=8.0 Hz, 3H). $^{13}$C-NMR(100MHz, $CDCl_3$, δ ppm):163.36, 137.73, 135.42, 133.74, 130.99, 130.80, 129.10, 114.20, 109.71, 61.14, 15.36, 14.43. EI-MS: Calcd. for $[C_{12}H_{14}N_2O_2S]^+$:250.08;Found:250.01.

**Ethyl 4-methylthieno[2,3-f]-2,1,3-benzothiadiazole-6-carboxylate (6)**



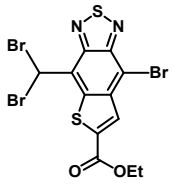
Compound 5(2.29g, 10.22mmol) and triethylamine (4.27mL) were dissolved in $CH_2Cl_2$ (60 mL). Then thionyl chloride 4.47 mL, 4.47 mmol) was added with vigorous stirring in a ice-water bath. After the dropwise addition, the solution was refluxed for 6 h. Evaporation of the solvent and purification by column chromatography on silica gel with petroleum ether/$CHCl_3$ (1:4) as eluent was performed. 6 (1.57 g, 73.6%) was finally obtained as a orange solid. $^1$H-NMR (400 MHz, $CDCl_3$, δ ppm): 8.40(s, 1H), 8.10(s, 1H), 4.45(m, 2H), 2.98(s, 3H), 1.46(t, *J*=6.8 Hz, 3H). $^{13}$C-NMR(100MHz, $CDCl_3$, δ ppm): 162.10, 152.99, 141.81, 141.41, 137.42, 130.63, 123.98, 114.30, 62.14, 16.59, 14.33. EI-MS: Calcd. for $[C_{12}H_{10}N_2O_2S_2]^+$:278.02;Found:277.95.

**Ethyl 8-bromo-4-methylthieno[2,3-f]-2,1,3-benzothiadiazole-6-carboxylate (7)**



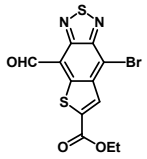
The yellow solid compound 6 (1.23 g, 4.63 mmol) was dissolved in $CHCl_3$ (30 mL), then $Br_2$ (1.48 g, 9.26 mmol) was added dropwise. The solution was refluxed for 8 h and the solvent was removed under vacuum to get a light yellow solid 7 (1.45 g, 87.2%). The unstable brominated product was used without further purification.$^1$H-NMR (400 MHz, $CDCl_3$, δ ppm): 8.26(s, 1H), 4.47(m, 2H), 2.94(s, 3H), 1.47(t, *J*=6.8 Hz, 3H). EI-MS: Calcd. for $[C_{12}H_9BrN_2O_2S_2]^+$:355.93;Found:357.85.

**Ethyl 8-bromo-4-(dibromomethyl)thieno[2,3-f]-2,1,3-benzothiadiazole-6-carboxylate (8)**



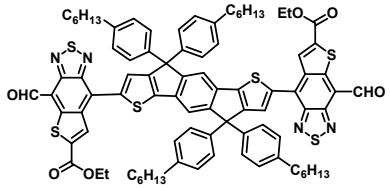
Compound 7(1.62 g, 4.53 mmol) NBS (2.42 g, 13.59 mmol) and BPO (219 mg, 0.916mmol) were dissolved in chlorobenzene (50 mL) and then stirred at 80oC for 24 hours. Evaporation of the solvent and purification by column chromatography on silica gel with petroleum ether/$CHCl_3$ (1:2) as eluent was performed 8. (2.07 g, 89.2%) was finally obtained as a yellow solid. $^1$H-NMR (400 MHz, $CDCl_3$, δ ppm): 8.37(s, 1H), 8.00(s, 1H), 4.50(m, 2H), 1.49(t, J=6.8 Hz, 3H). $^{13}$C-NMR(100MHz, $CDCl_3$, δ ppm): 161.50, 150.92, 147.80, 143.12, 139.64, 129.55, 124.30, 111.54, 62.65, 31.51, 14.36. EI-MS: Calcd. for $[C_{12}H_7Br_3N_2O_2S_2]$+:515.04;Found:515.77.

**Ethyl 8-bromo-4-formylthieno[2,3-f]-2,1,3-benzothiadiazole-6-carboxylate (9)**



Compound 8 (1.48 g, 2.89 mmol) was disolved in formic acid (50 mL), then the solution was refluxed at 110oC for 12 hours and the solvent was removed under vacuum to get a light yellow solid 7(1.02 g, 95.3%).$^1$H-NMR (400 MHz, $CDCl_3$, δ ppm): 11.21(s, 1H), 8.38(s, 1H), 4.49(m, 2H), 1.48(t, J=6.8 Hz, 3H). $^{13}$C-NMR(100MHz, $CDCl_3$, δ ppm): 187.65, 161.69, 152.64, 152.08, 144.19, 142.77, 142.36, 128.61, 118.36, 117.79, 62.54, 14.31. EI-MS: Calcd. for $[C_{12}H_7BrN_2O_3S_2]$+:371.23;Found:371.82.

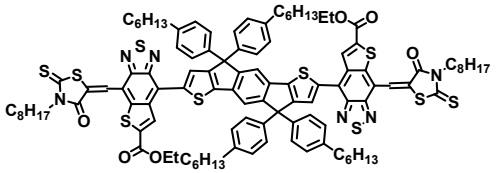
**Synthesis of compound (10)**



Compound 9 (180 mg, 0.486 mmol), (4,4,9,9-tetrakis(4-hexylphenyl)-4,9-dihydro-s-indaceno[1,2-b:5,6-b']dithiophene-2,7-diyl)bis(trimethylstannane) (200 mg, 0.162mmol) and $Pd(PPh_3)_4$ (10 mg, 0.008 mmol) were dissolved in anhydrous toluene (15 mL) under argon atmosphere. The mixture was stirred at 110°C for 48 h. After cooling to room temperature, the solvent was removed under vacuum, and the crude product was purified by column chromatography on silica gel with petroleum ether/$CHCl_3$ (1:2) as eluent to give compound 10 as a blue solid(513 mg, 71.1%).$^1$H-NMR (400 MHz, $CDCl_3$, δ ppm): 11.18(s, 2H), 8.67(s, 2H), 8.04(s, 2H), 7.68(s, 2H), 7.31(d, J=8.0 Hz 8H), 7.15(d, J=8.0 Hz 8H), 4.47(m, 4H),

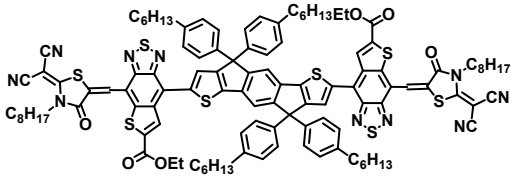
2.59(m, 8H), 1.60(m, 8H), 1.46(t, J=8.0 Hz, 6H), 1.38-1.25(m, 24H), 0.88-0.84(m, 12H). $^{13}$C-NMR(100MHz, $CDCl_3$, δ ppm): 187.29, 162.04, 157.54, 154.38, 154.05, 151.35, 147.98, 146.10, 142.05, 141.23, 140.49, 139.06, 137.97, 135.86, 130.44, 129.24, 129.02, 128.68, 127.90, 118.78, 116.64, 63.33, 62.17, 35.64, 31.76, 31.42, 29.20, 22.63, 14.40, 14.16. . MS (MALDI-TOF): calculated for $C_{88}H_{86}N_4O_6S_6$, 1486.49; found: 1486.11.

**Synthesis of compound A1**



To a three-necked round-bottomed flask were added compound 10 (132 mg, 0.089 mmol), 3-n-octylrhodanine (436 mg, 1.77 mmol), chloroform (30 mL), and triethylamine (1 mL). The mixture was deoxygenated with nitrogen for 15 min and then refluxed for 12 h. After cooling to room temperature, the mixture was poured into methanol (200 mL) and filtered. The residue was purified by column chromatography on silica gel using petroleum ether/$CHCl_3$ (1 : 1) as an eluent yielding a dark green solid (164 mg, 94.9%).$^1$H-NMR (400 MHz, CDCl3, δ ppm): 8.62(s, 2H), 8.20(s, 2H), 7.93(s, 2H), 7.64(s, 2H), 7.29(d, J=8.0 Hz 8H), 7.14(d, J=8.0 Hz 8H), 4.46(m, 4H), 4.17(t, J=8.0 Hz, 4H), 2.58(t, J=8.0 Hz, 8H), 1.78-1.74(m, 4H), 1.63-1.60(m, 6H), 1.48(t, J=8.0 Hz, 6H), 1.37-1.28(m, 48H), 0.91-0.84(m, 16H). $^{13}$C-NMR(100MHz, $CDCl_3$, δ ppm): 195.04, 168.11, 161.53, 157.29, 154.17, 151.63, 150.56, 148.66, 146.91, 141.95, 141.34, 139.29, 137.51, 136.75, 135.78, 130.60, 128.62, 128.33, 128.10, 127.90, 126.79, 125.36, 118.55, 117.63, 63.26, 62.37, 44.93, 35.63, 31.83, 31.75, 31.42, 29.74, 29.20, 27.10, 26.86, 22.68, 22.63, 14.38, 14.15. MS (MALDI-TOF): calculated for $C_{110}H_{120}N_6O_6S_{10}$, 1940.65; found: 1940.21. Anal. calcd for $C_{110}H_{120}N_6O_6S_{10}$ (%): C, 68.00; H, 6.23; N, 4.33. Found (%): C, 67.55; H, 6.29; N, 4.30.

**Synthesis of compound A2**



To a three-necked round-bottomed flask were added compound 10 (143 mg, 0.096 mmol), 2-(3-octyl-4-oxothiazolidin-2-ylidene)malononitrile (503 mg, 1.92 mmol), chloroform (30 mL), and triethylamine (1 mL). The mixture was deoxygenated with nitrogen for 15 min and then refluxed for 12 h. After cooling to room temperature, the mixture was poured into methanol (200 mL) and filtered. The residue was purified by column chromatography on silica gel using petroleum ether/$CHCl_3$ (1 : 1) as an eluent yielding a dark green solid (156 mg, 81.1%).$^1$H-NMR (400 MHz, $CDCl_3$, δ ppm): 8.63(s, 2H), 8.35(s, 2H), 7.98(s, 2H), 7.66(s,

2H), 7.30(d, *J*=8.0 Hz 8H), 7.15(d, *J*=8.0 Hz 8H), 4.47(m, 4H), 4.27(t, *J*=8.0 Hz, 4H), 2.59(t, *J*=8.0 Hz, 8H), 1.82-1.78(m, 4H), 1.62-1.56(m, 6H), 1.46(t, *J*=8.0 Hz, 6H), 1.42-1.25(m, 48H), 0.91-0.84(m, 16H). $^{13}$C-NMR(100MHz, $CDCl_3$, δ ppm): 166.86, 166.81, 161.37, 157.49, 154.28, 151.46, 150.63, 149.76, 147.52, 142.01, 141.18, 139.16, 137.26, 136.60, 135.80, 130.65, 128.61, 128.49, 127.84, 127.74, 121.36, 118.64, 116.29, 113.21, 112.49, 63.23, 62.45, 55.55, 45.44, 35.59, 31.72, 31.40, 29.71, 29.16, 29.11, 29.07, 28.81, 25.99, 22.63, 22.60, 14.34, 14.12. MS (MALDI-TOF): calculated for $C_{116}H_{120}N_{10}O_6S_8$, 2004.71; found: 2005.08. Anal. calcd for $C_{116}H_{120}N_{10}O_6S_8$ (%): C, 69.43; H, 6.03; N, 6.98. Found (%): C, 69.65; H, 6.05; N, 6.95.

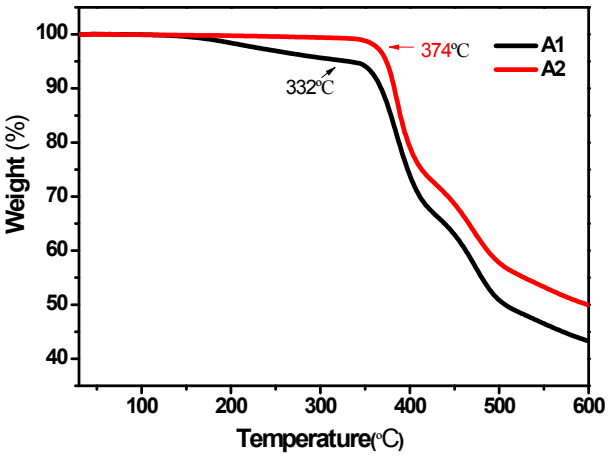



**Figure S1**. The TGA curves of A1 and A2.

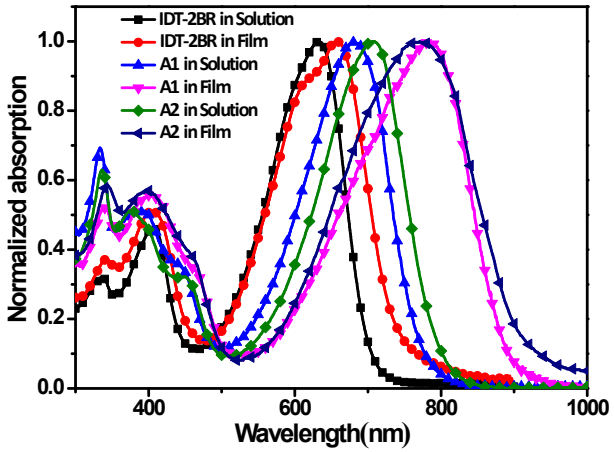



**Figure S2.** The normalized UV-vis absorption spectra of IDT-2BR, A1 and A2 in solution and in thin film.

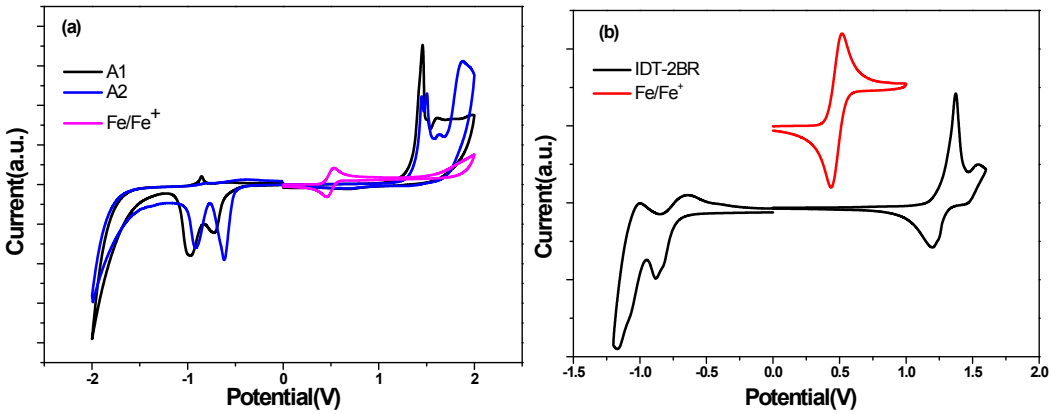



**Figure S3.** Cyclic voltammogram of A1 and A2 (a) and IDT-2BR (b) in $CH_3CN$/0.1 M $Bu_4NPF_6$ at 100 mV $s^{-1}$.

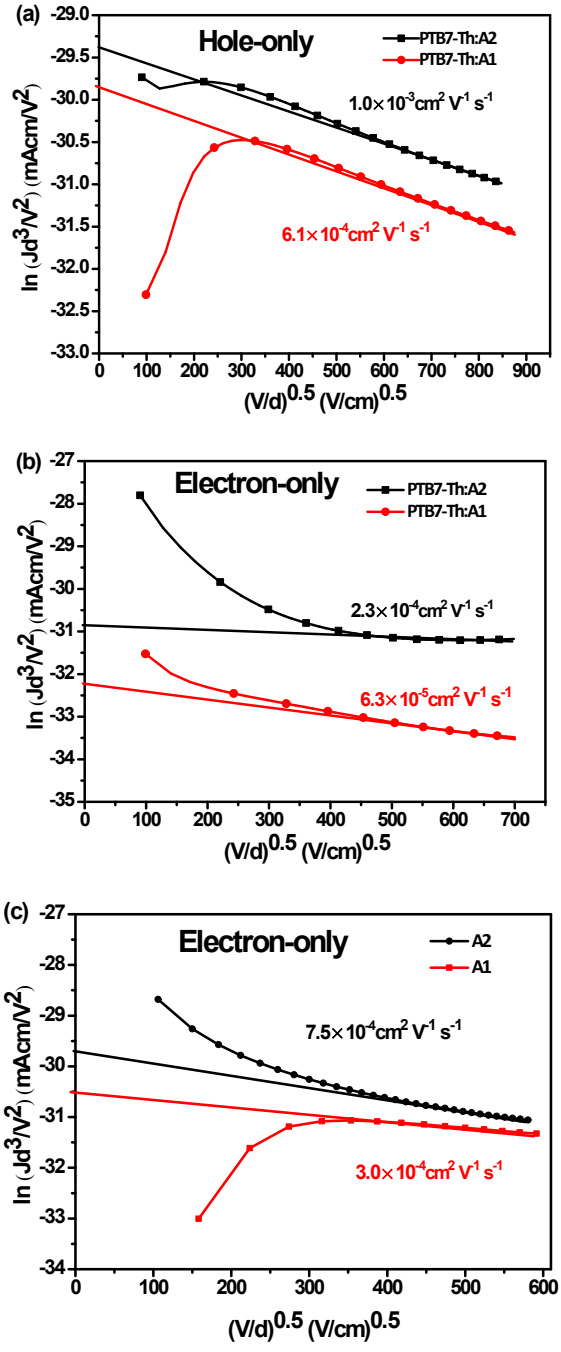



**Figure S4.** Ln($JL^3/V^2$) vs (V/L)0.5 plots of the A1/A2:PTB7-Thwith 1% additive of hole mobility (a), electron mobility (b) and neat A1/A2 film of electron mobility (c) by the SCLC method.

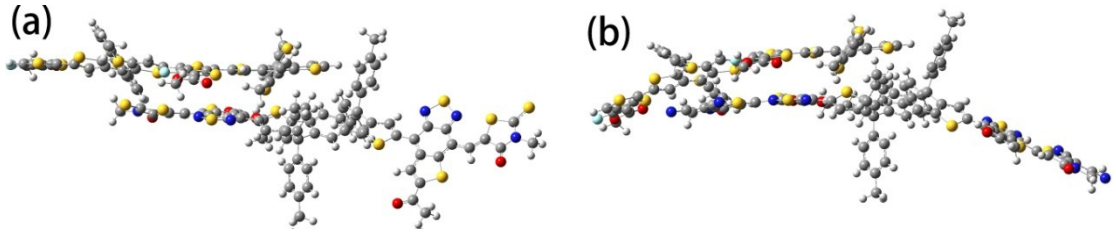



**Figure S5.** The optimized configurations of (a) (TB7-Th)-A1 and (b) (TB7-Th)-A2 is as the model oligomers of PTB7-Th. The optimizations were done with ORCA 4.0 software at BLYP/def2-SVP level with the resolution of identity approximation. BSSE correction was considered by Grimme's gCP method. The dispersion forces were corrected by Grimme's D3 version with BJ damping function.

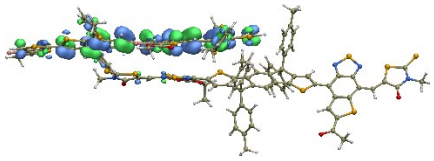
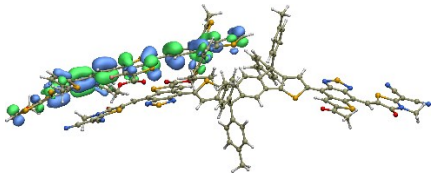
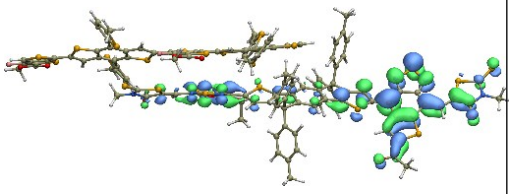
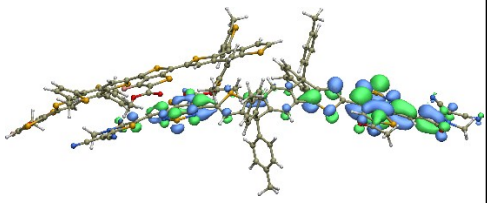
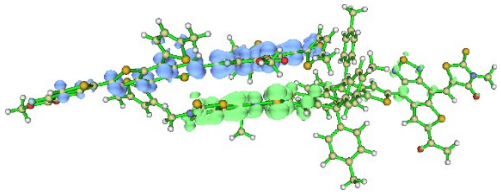
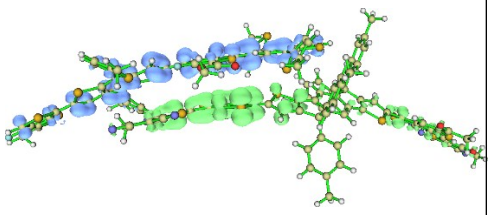
| | (TB7-Th)-A1 | (TB7-Th)-A2 |
|---|---|---|
| HOMO |  |  |
| LUMO |  |  |
| Hole-electron |  |  |

**Figure S6.** HOMO, LUMO, and S1 hole-electron distribution of (TB7-Th)-A1 and (TB7-Th)-A2. Calculated at PBE0/def2-SVP and TD-PBE0/def2-SVP level using Gaussian 09 software. The S1 hole-electron distribution was obtained using Multiwfn software.

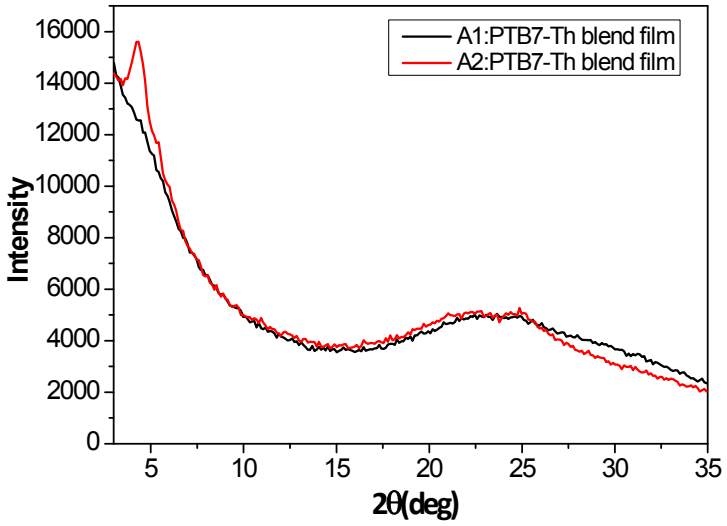



**Figure S7.** X-ray diffraction (XRD) patterns of A1:PTB7-Th blend film and A2:PTB7-Th blend film.

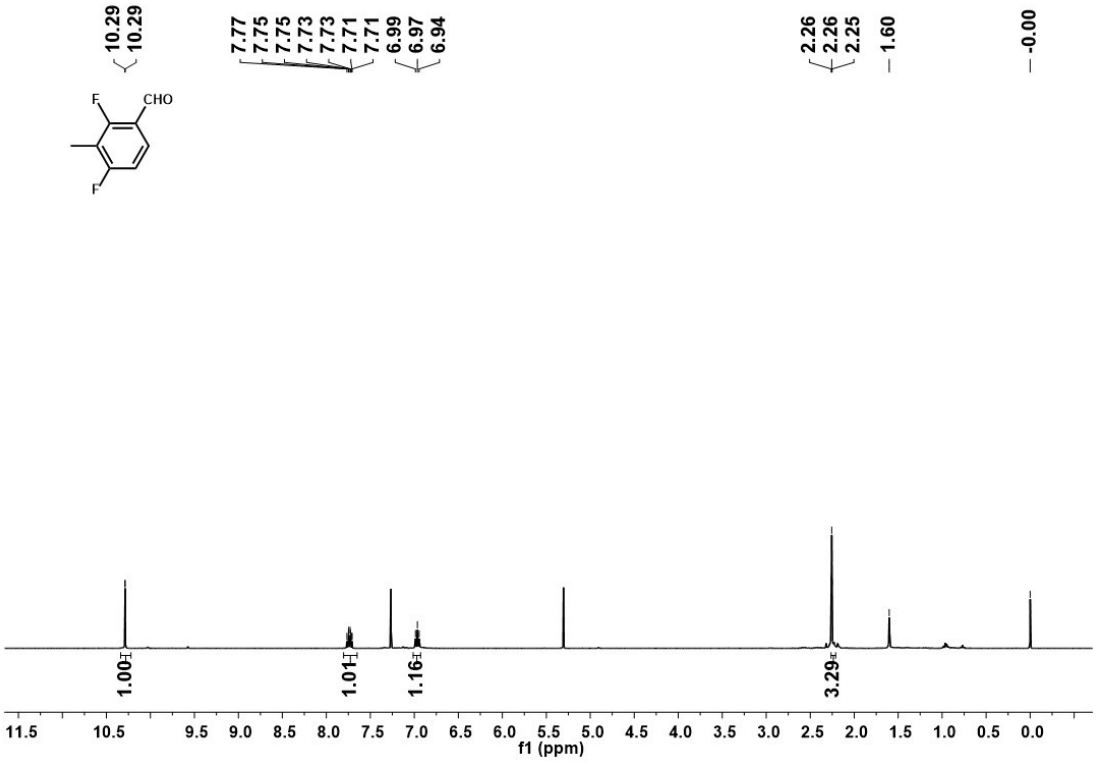



**Figure S8.** $^{1}H$ NMR of compound 1 in $CDCl_3$.

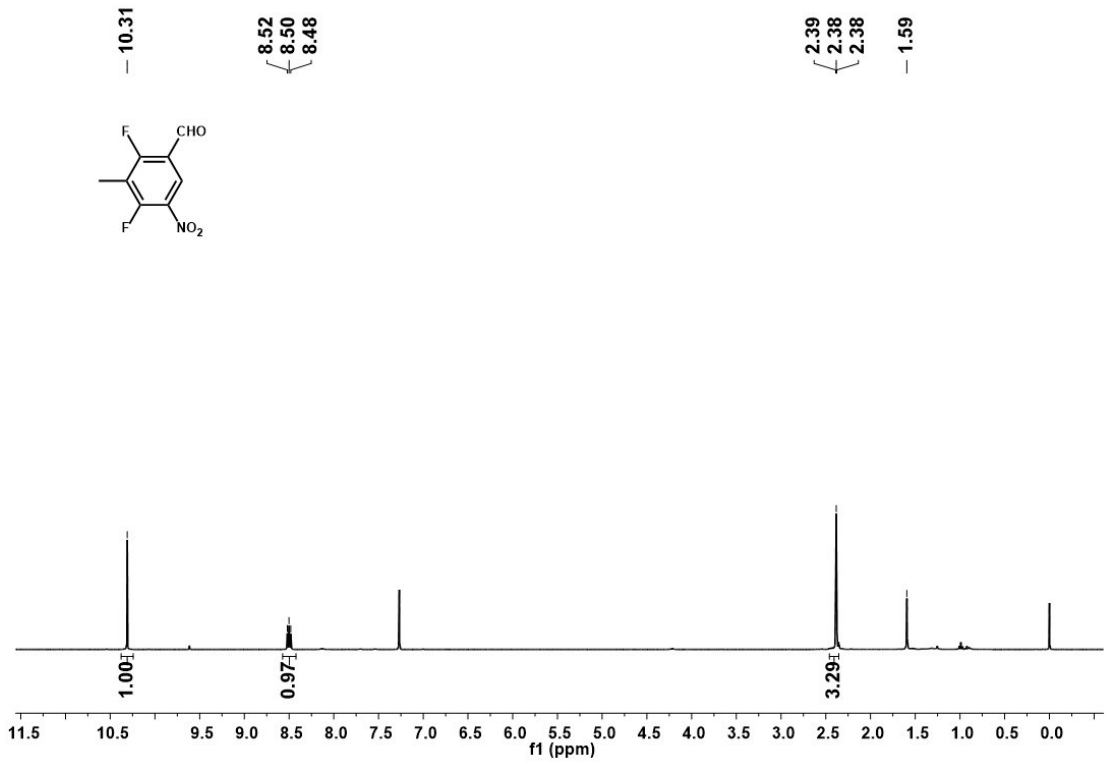



**Figure S9.** $^{1}H$ NMR of compound 2 in $CDCl_3$.

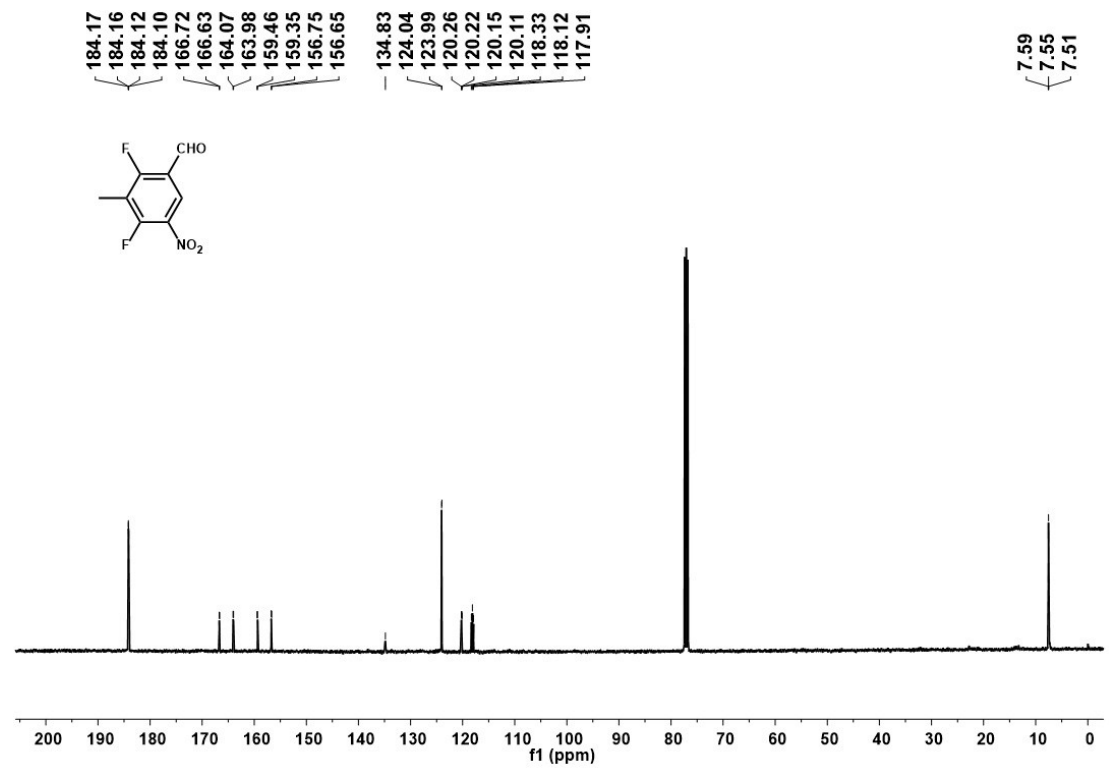



**Figure S10.** $^{13}C$ NMR of compound 2 in $CDCl_3$.

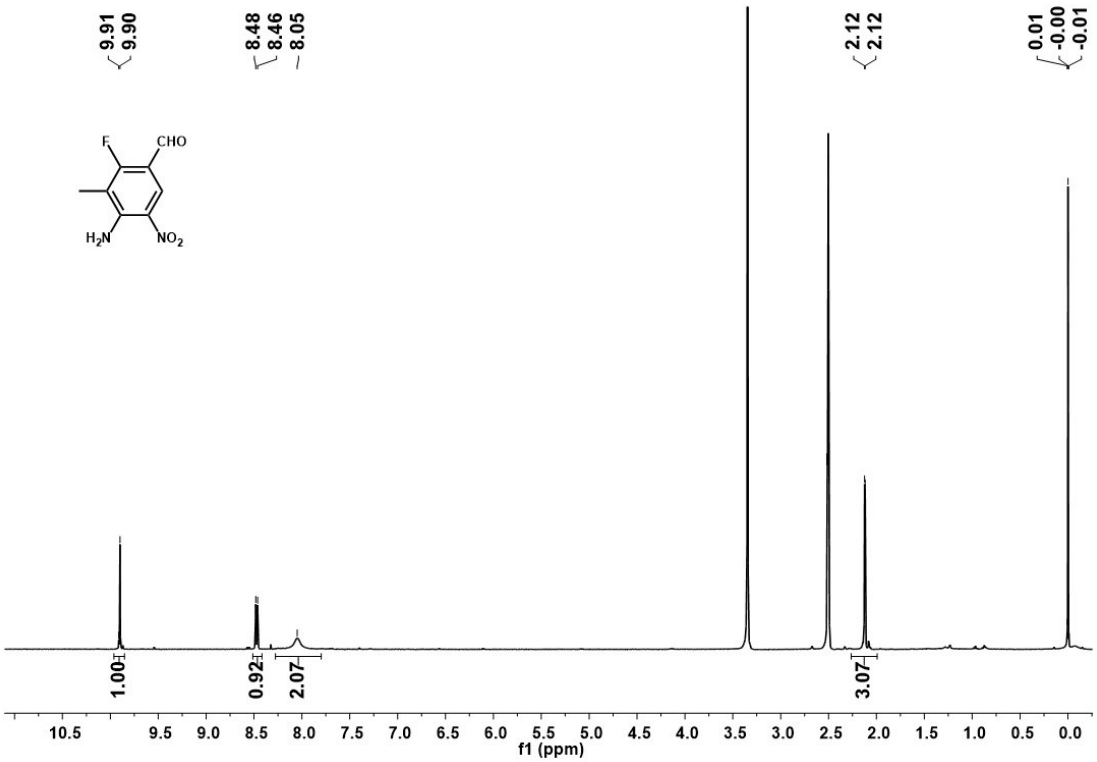



**Figure S11.** [1]H NMR of compound 3 in DMSO.

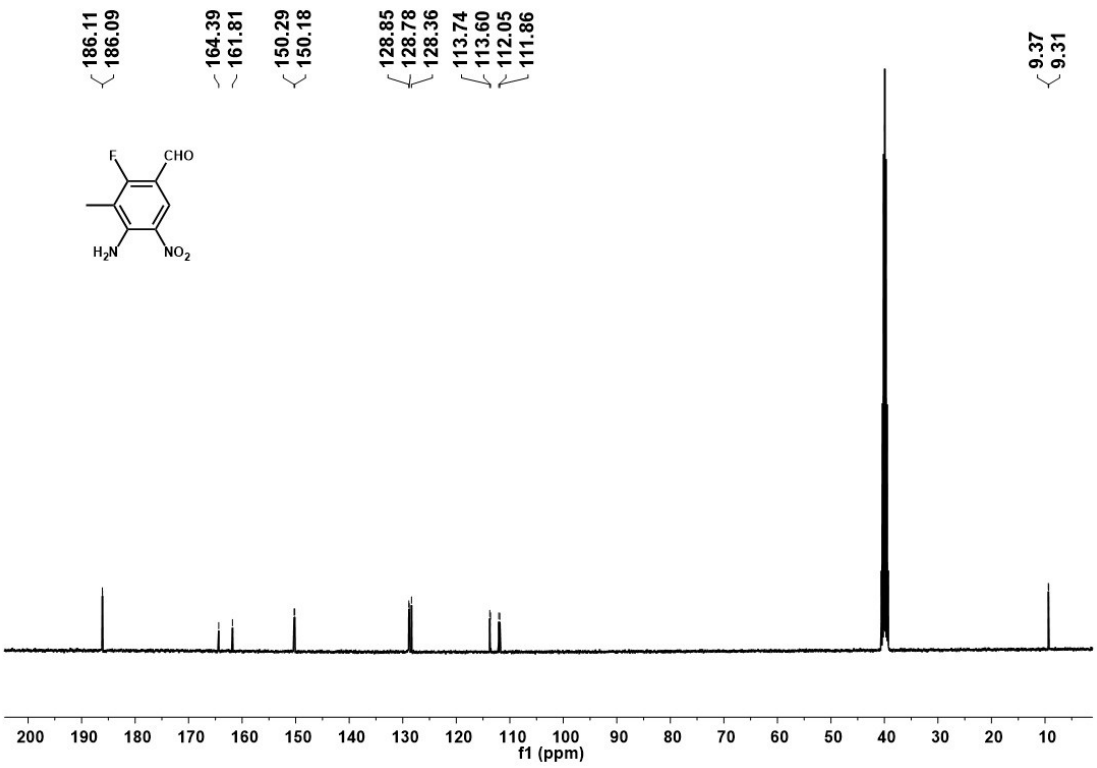



**Figure S12.** [13]C NMR of compound 3 in DMSO.

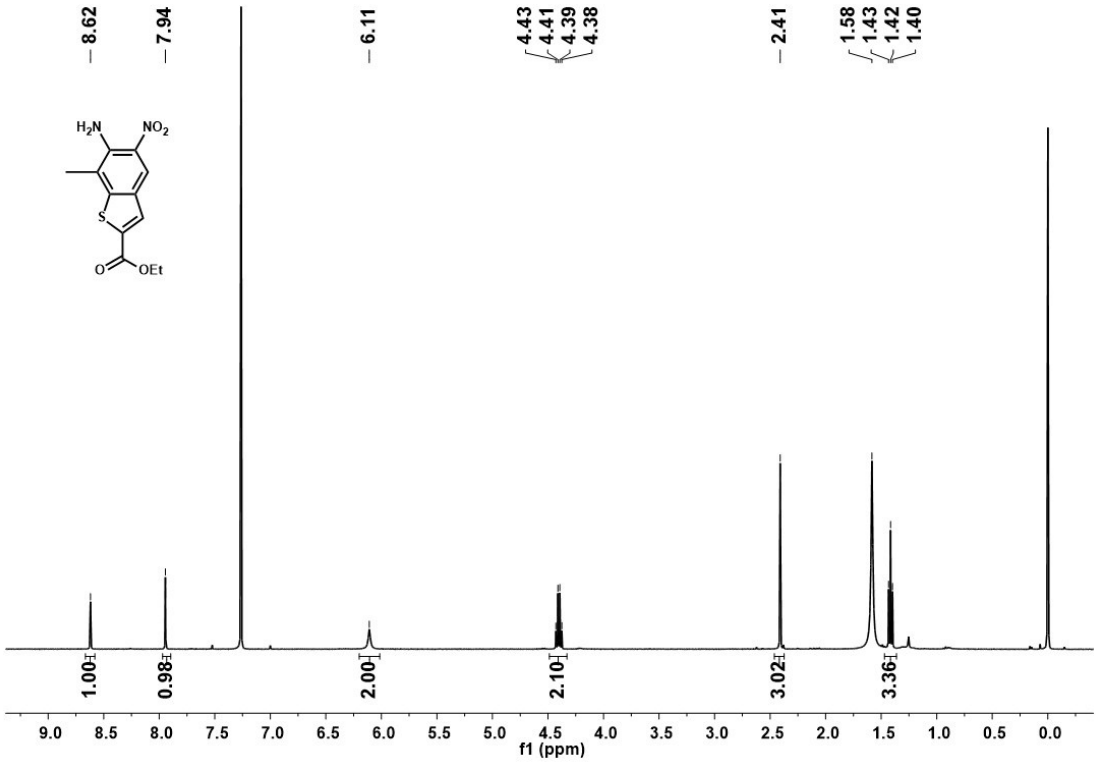



**Figure S13.** $^{1}H$ NMR of compound 4 in $CDCl_3$.

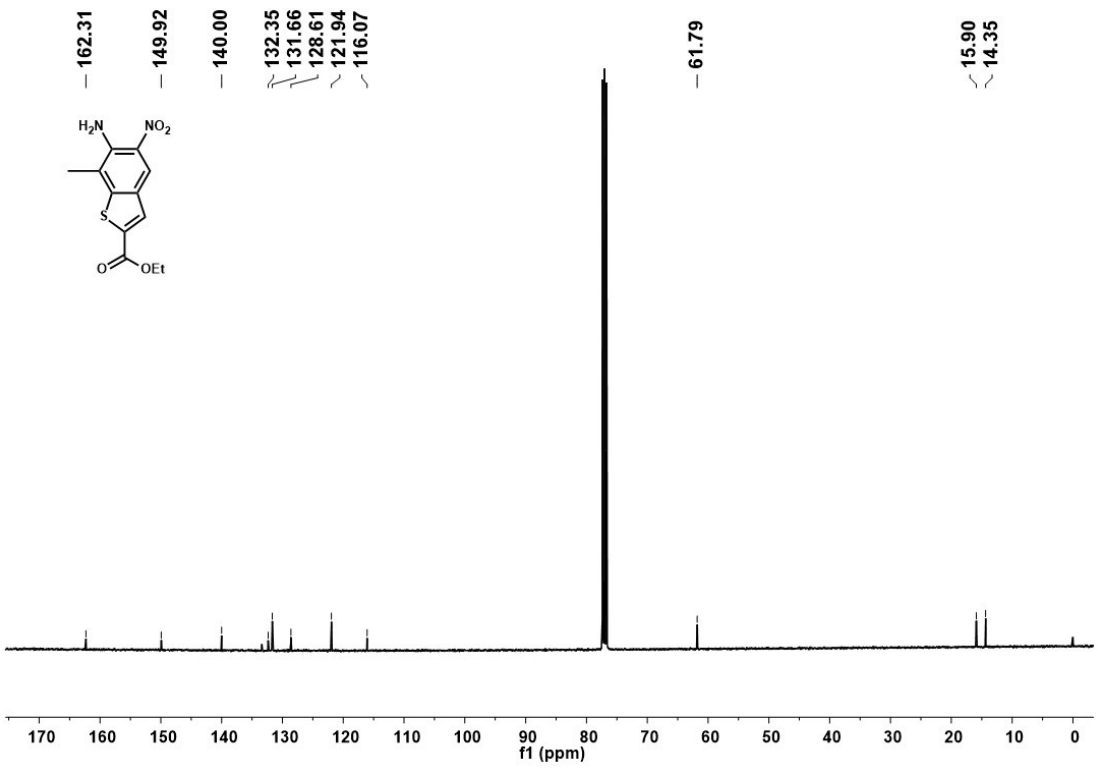



**Figure S14.** $^{13}C$ NMR of compound 4 in $CDCl_3$.

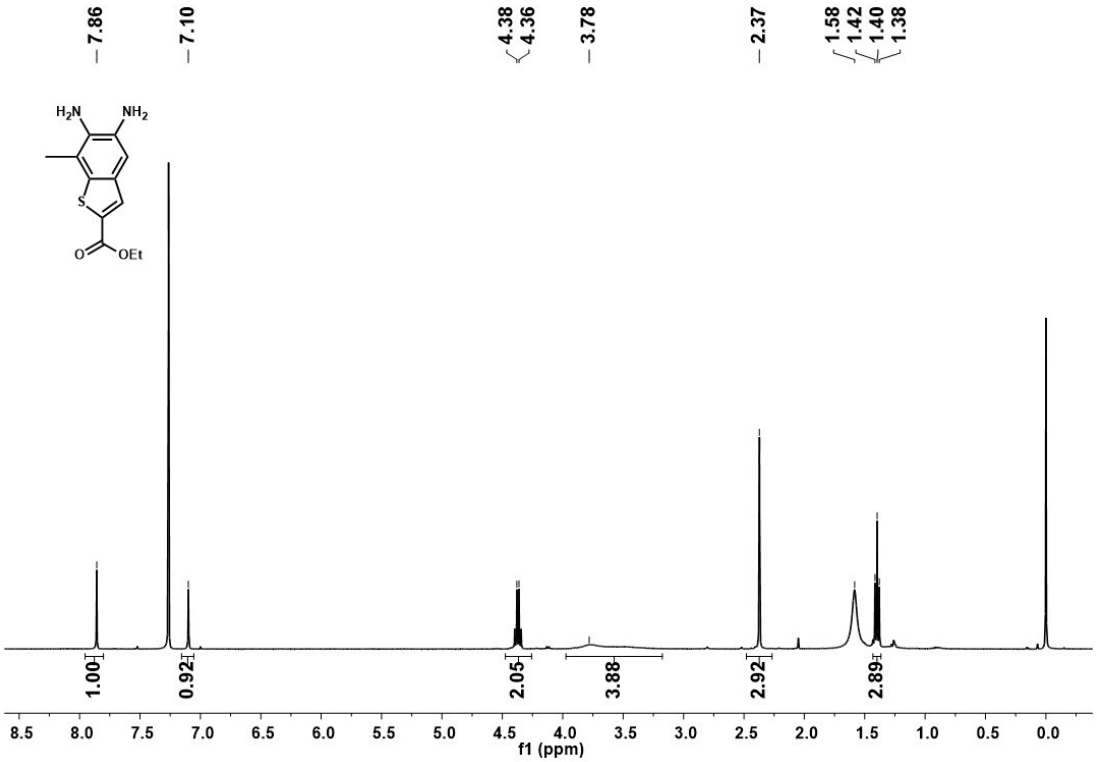



**Figure S15.** $^{1}H$ NMR of compound 5 in $CDCl_3$.

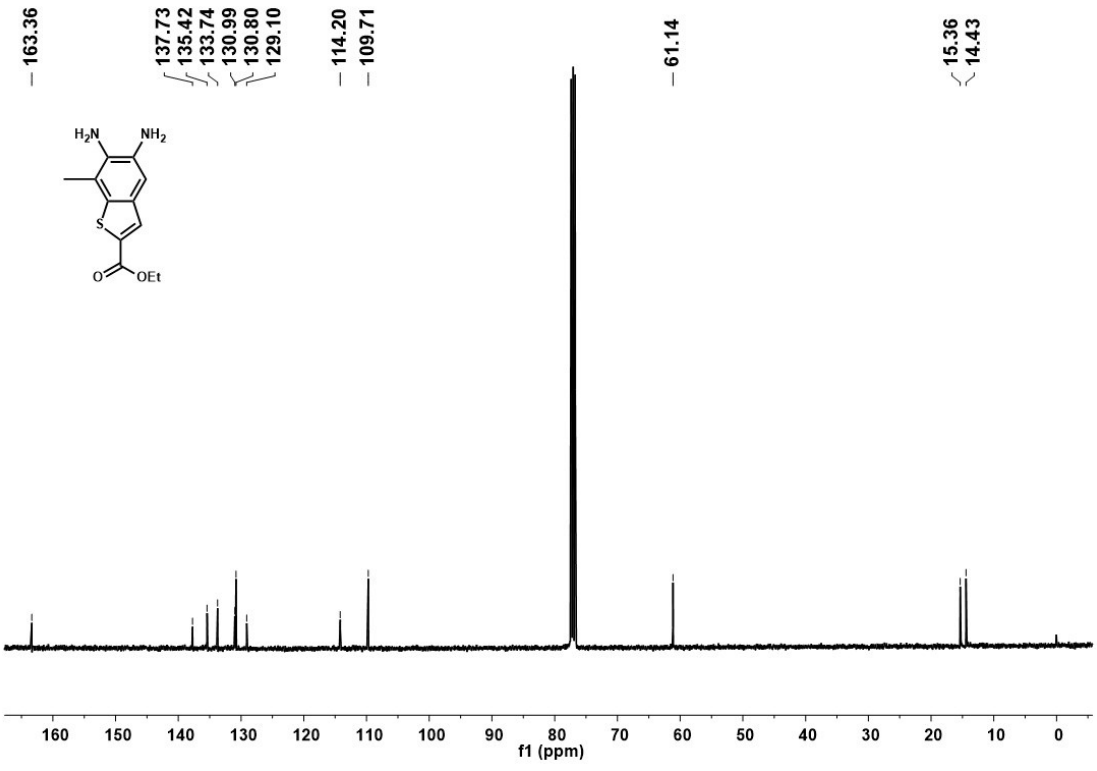



**Figure S16.** $^{13}C$ NMR of compound 5 in $CDCl_3$.

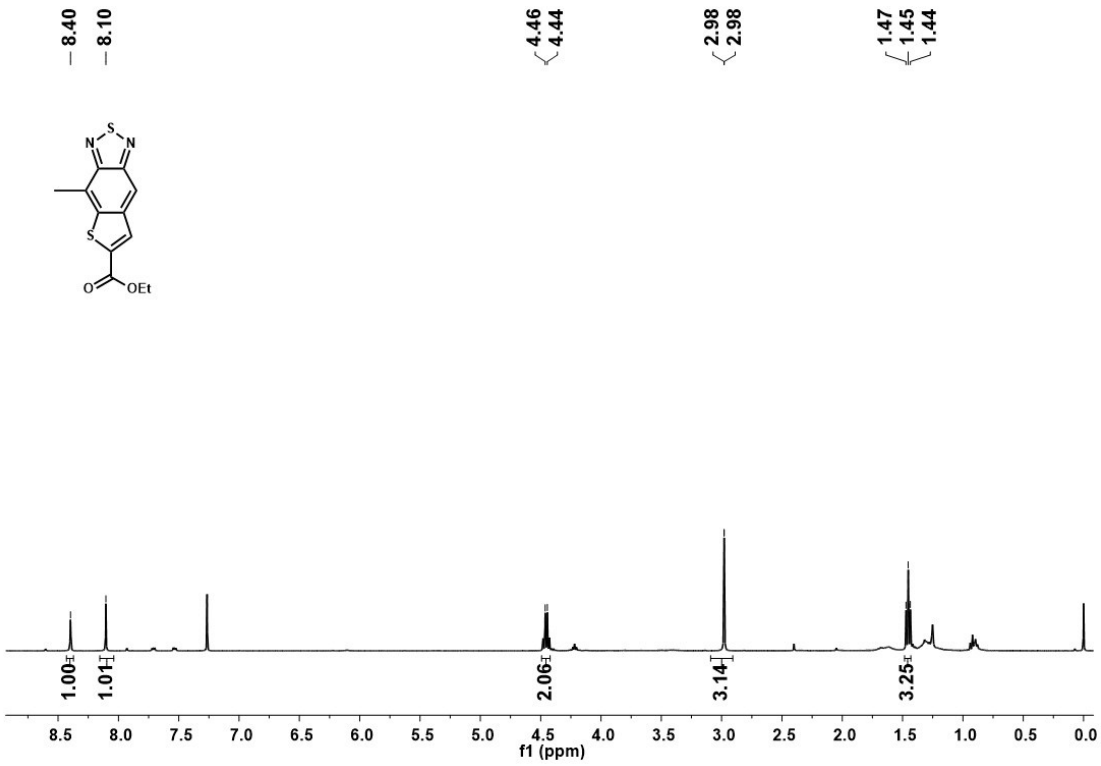



**Figure S17.** $^{1}H$ NMR of compound 6 in $CDCl_3$.

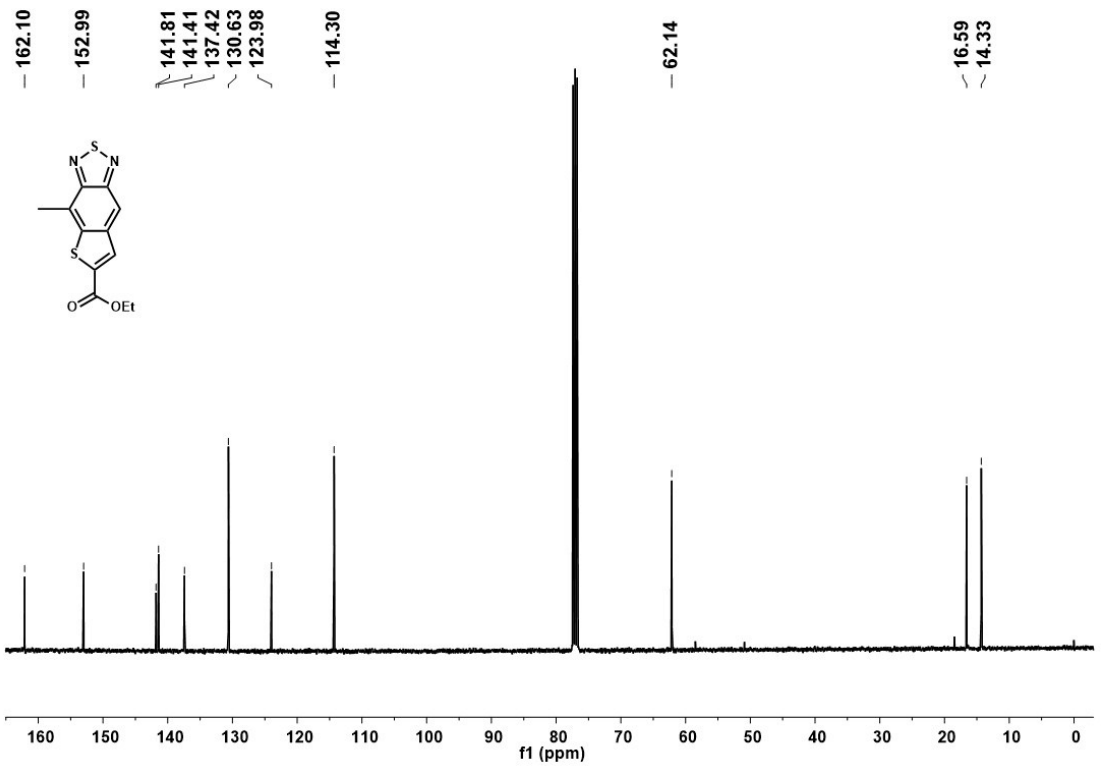



**Figure S18.** $^{13}C$ NMR of compound 6 in $CDCl_3$.

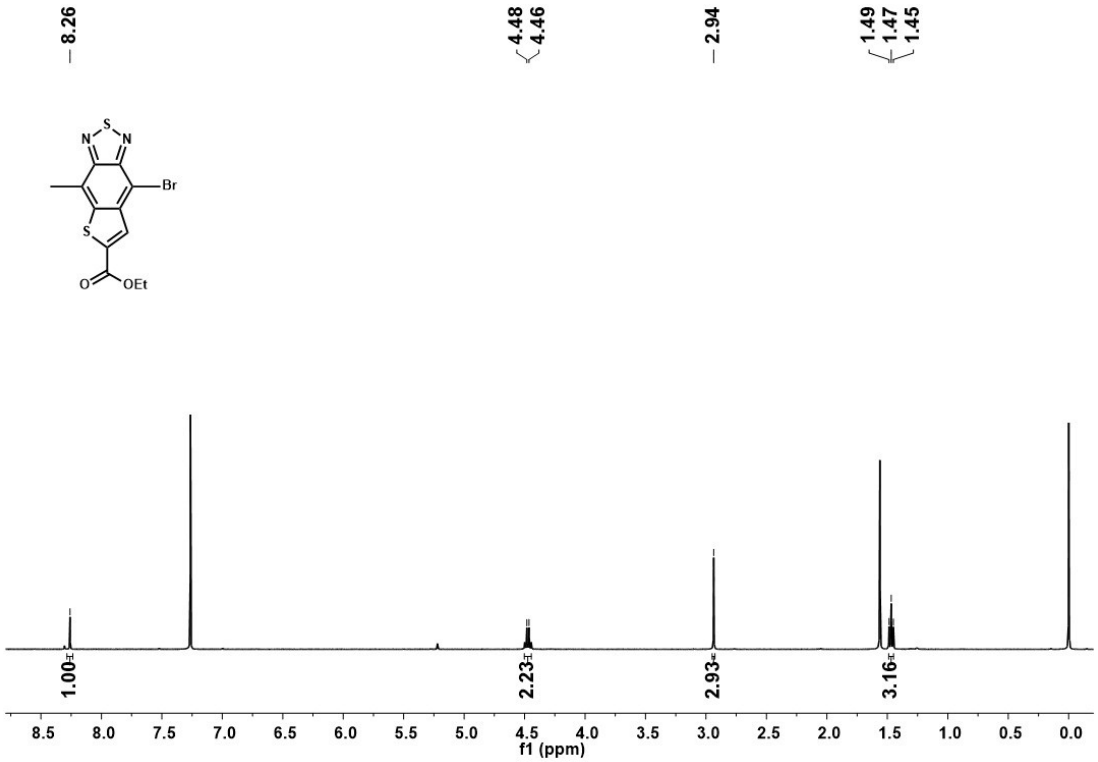



**Figure S19.** $^{1}H$ NMR of compound 7 in $CDCl_3$.

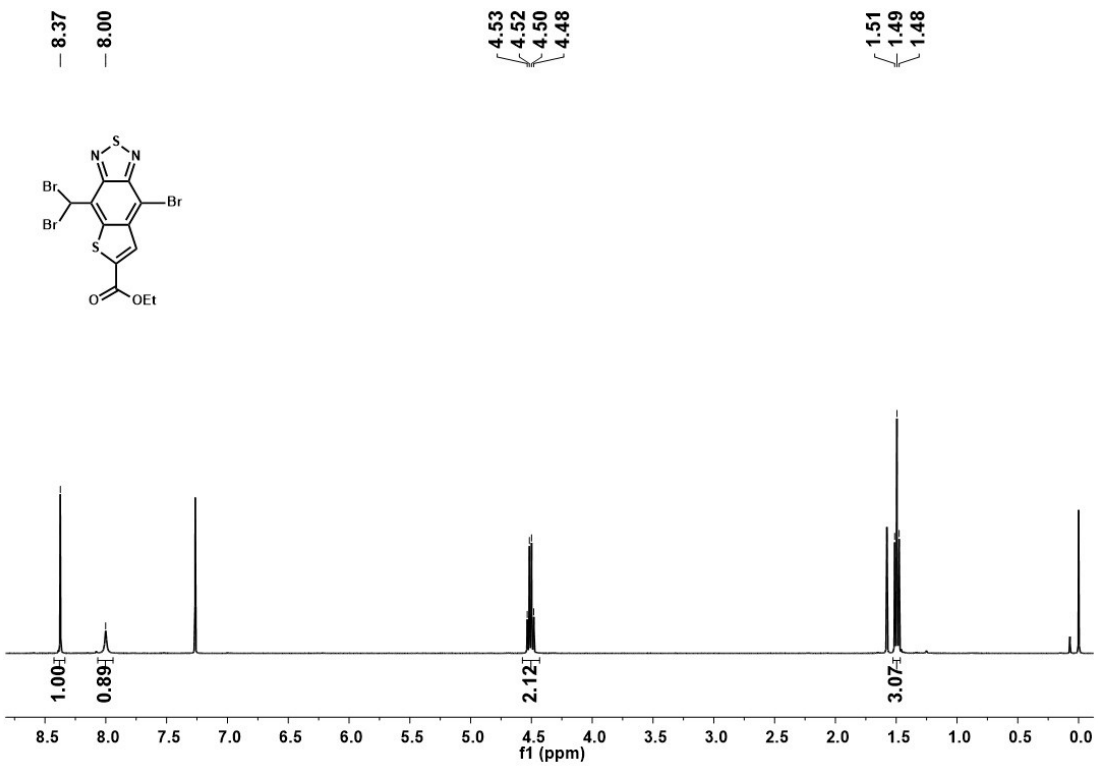



**Figure S20.** $^{1}H$ NMR of compound 8 in $CDCl_3$.

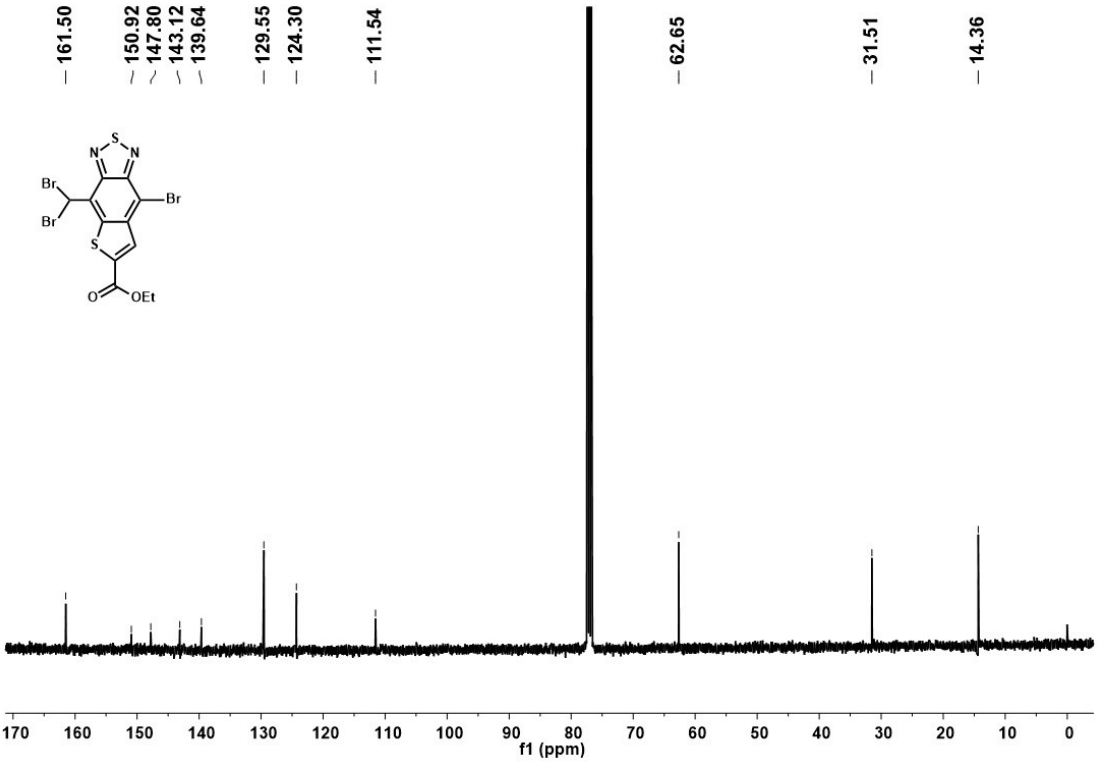



**Figure S21.** $^{13}C$ NMR of compound 8 in $CDCl_3$.

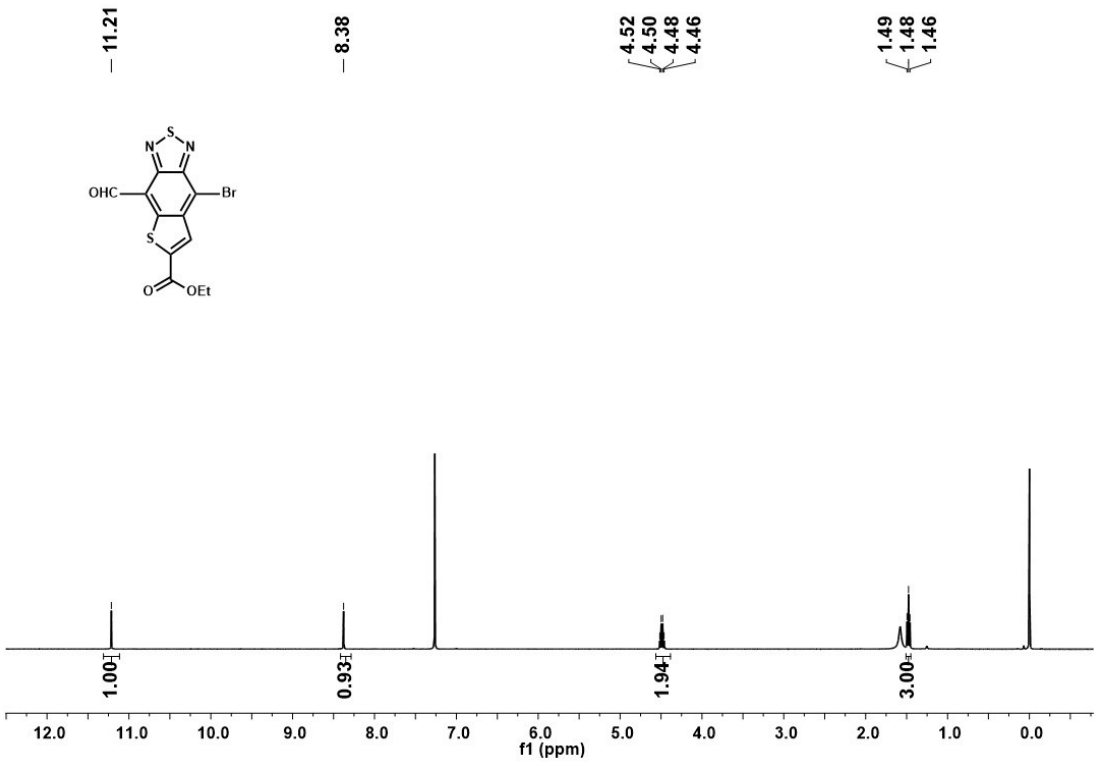



**Figure S22.** $^{1}H$ NMR of compound 9 in $CDCl_3$.

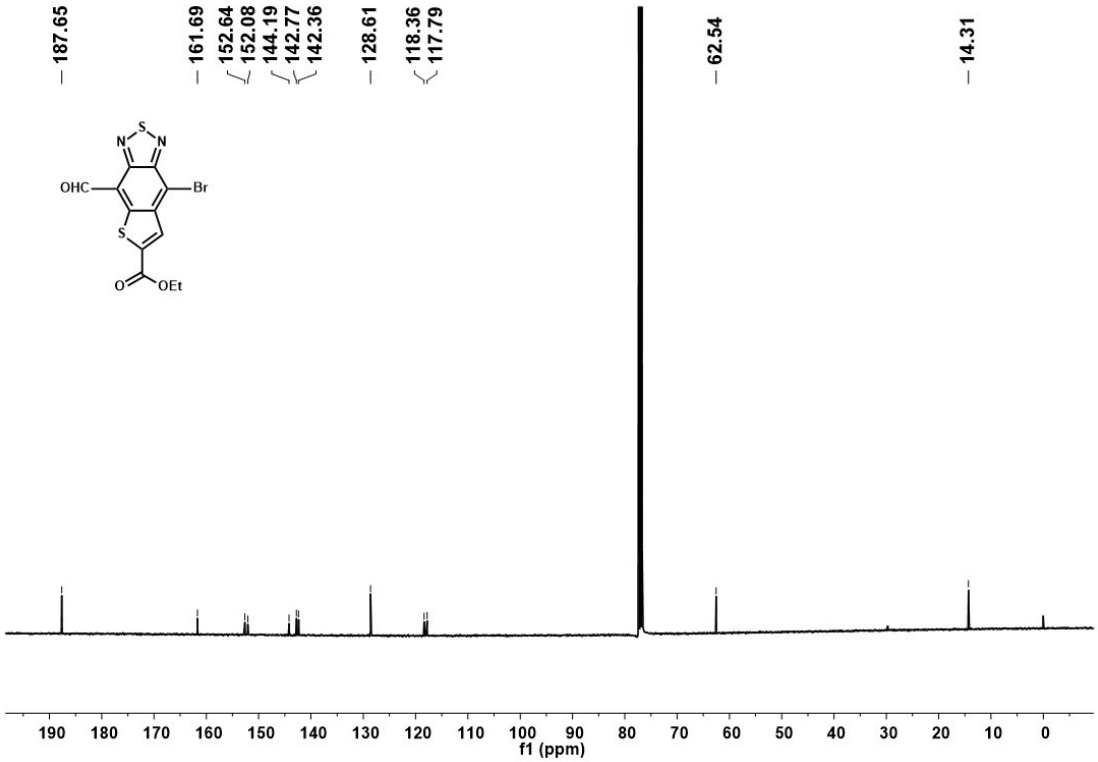



**Figure S23.** $^{13}C$ NMR of compound 9 in $CDCl_3$.

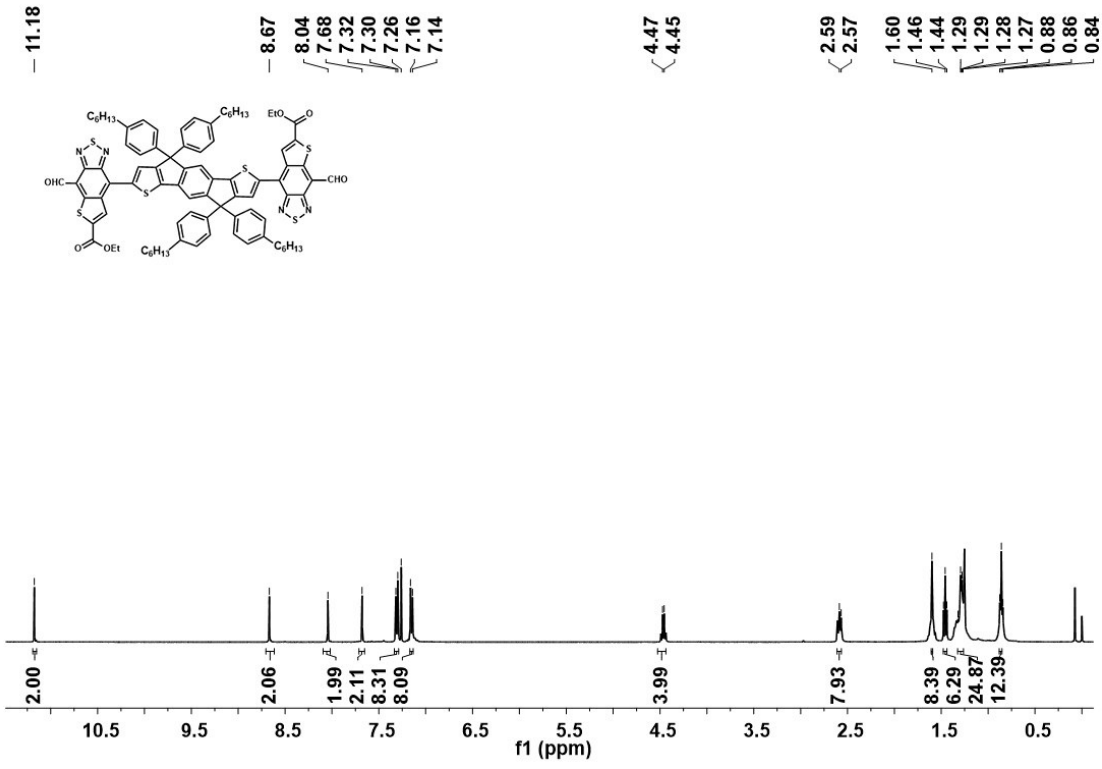



**Figure S24.** $^{1}H$ NMR of compound 10 in $CDCl_3$.

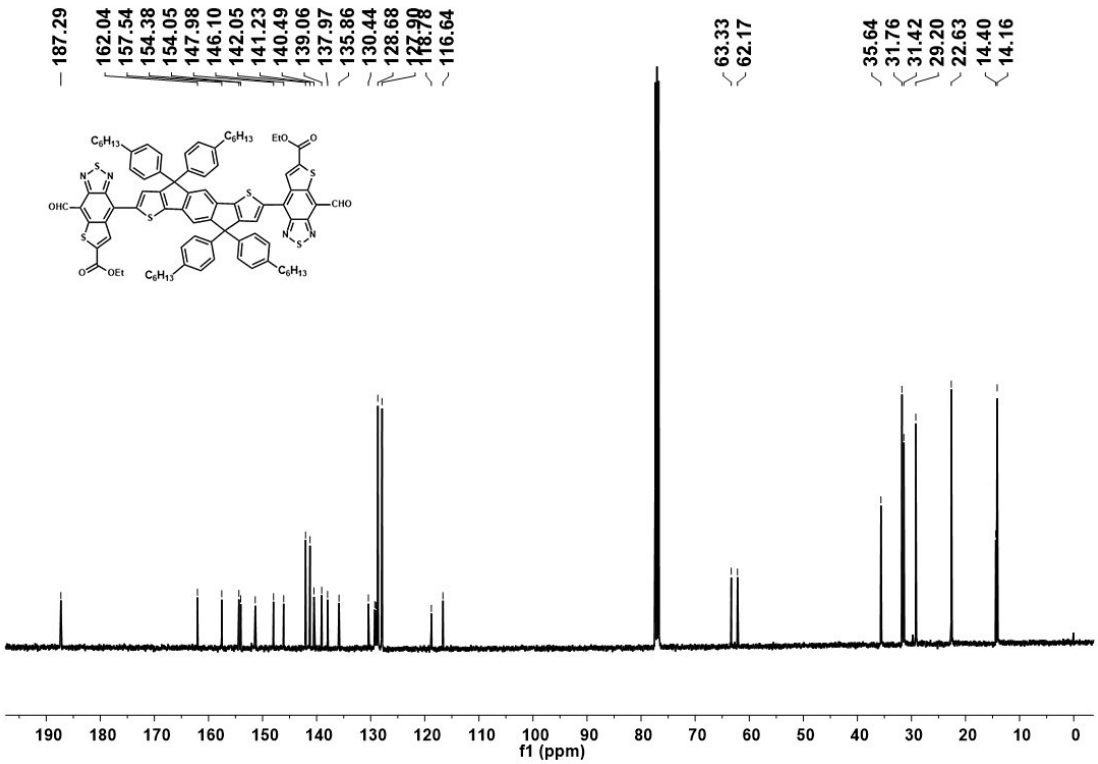



**Figure S25.** $^{13}C$ NMR of compound 10 in $CDCl_3$.

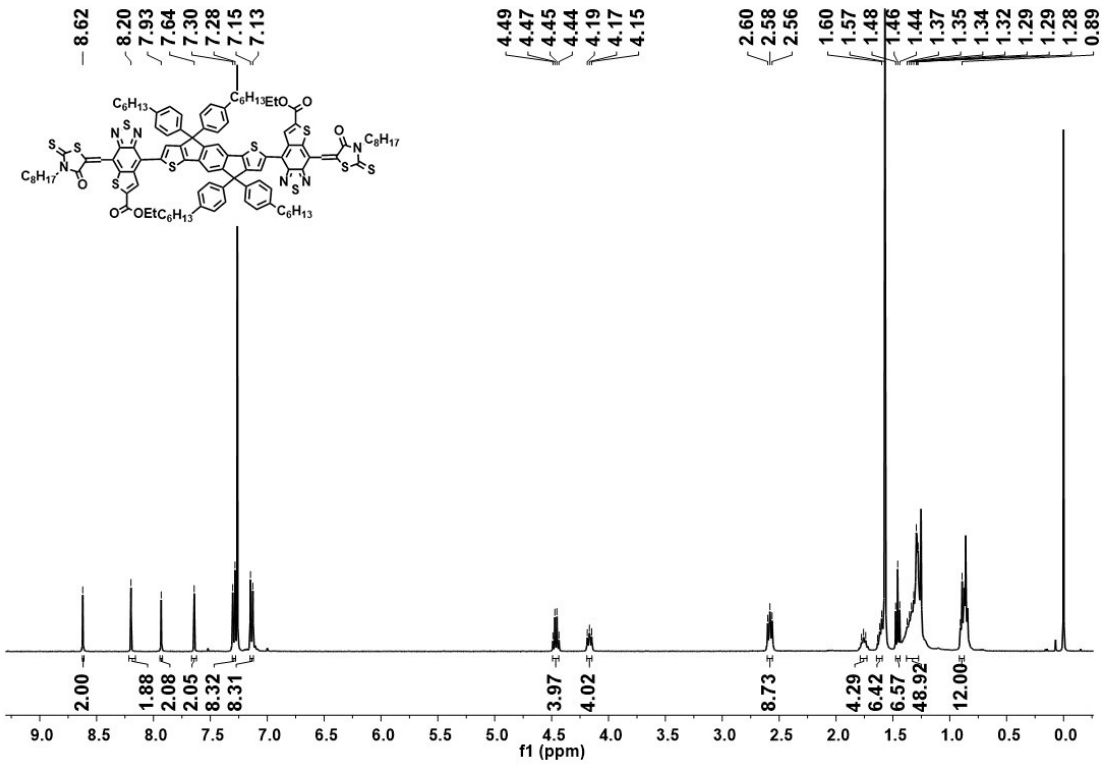



**Figure S26.** $^{1}H$ NMR of compound A1 in $CDCl_3$.

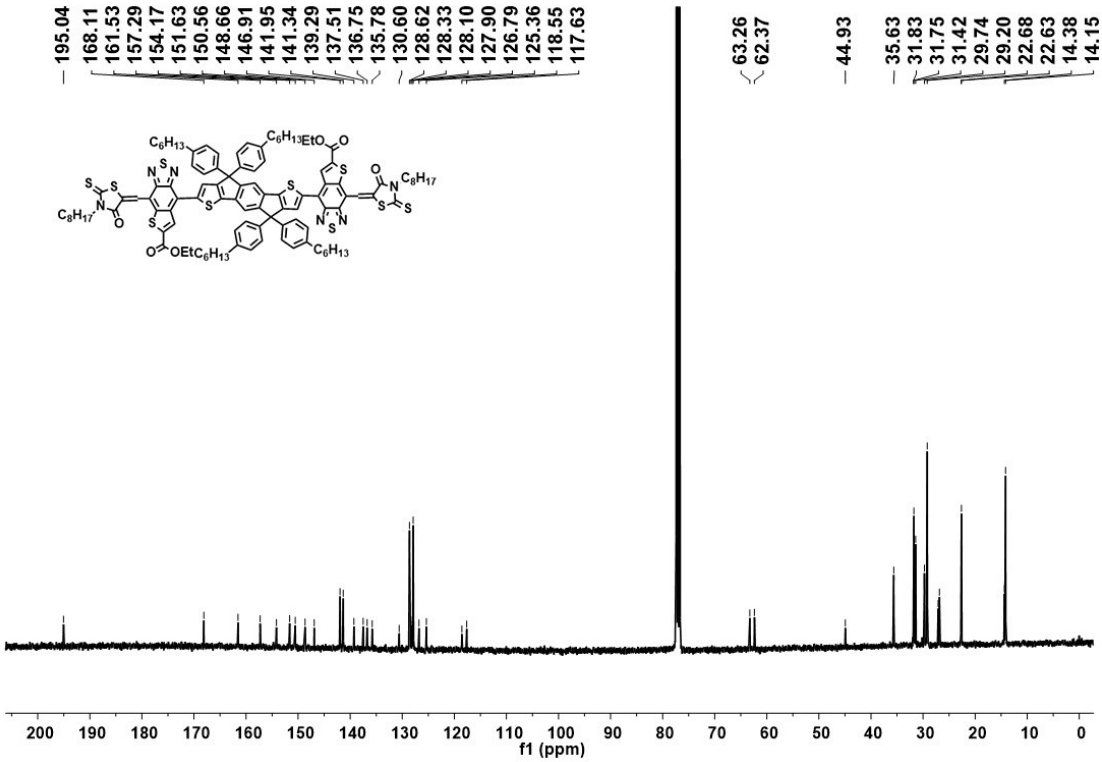



**Figure S27.** $^{13}C$ NMR of compound 10 in $CDCl_3$.

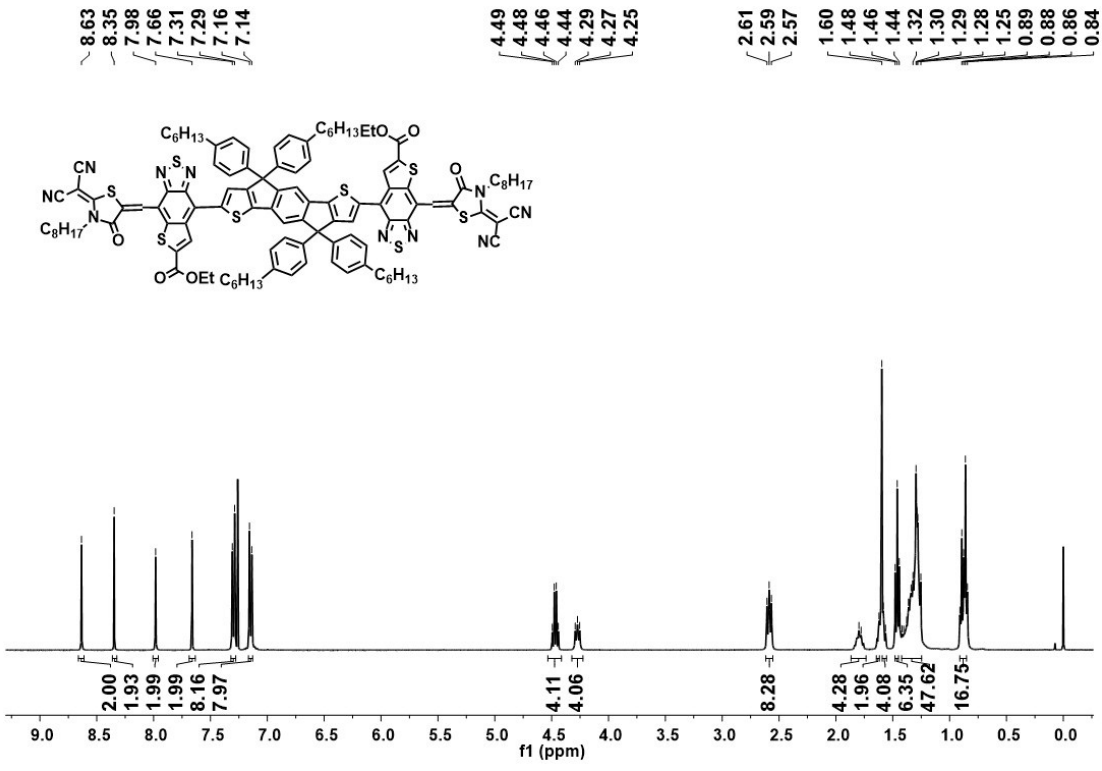



**Figure S28.** $^{1}H$ NMR of compound A2 in $CDCl_3$.

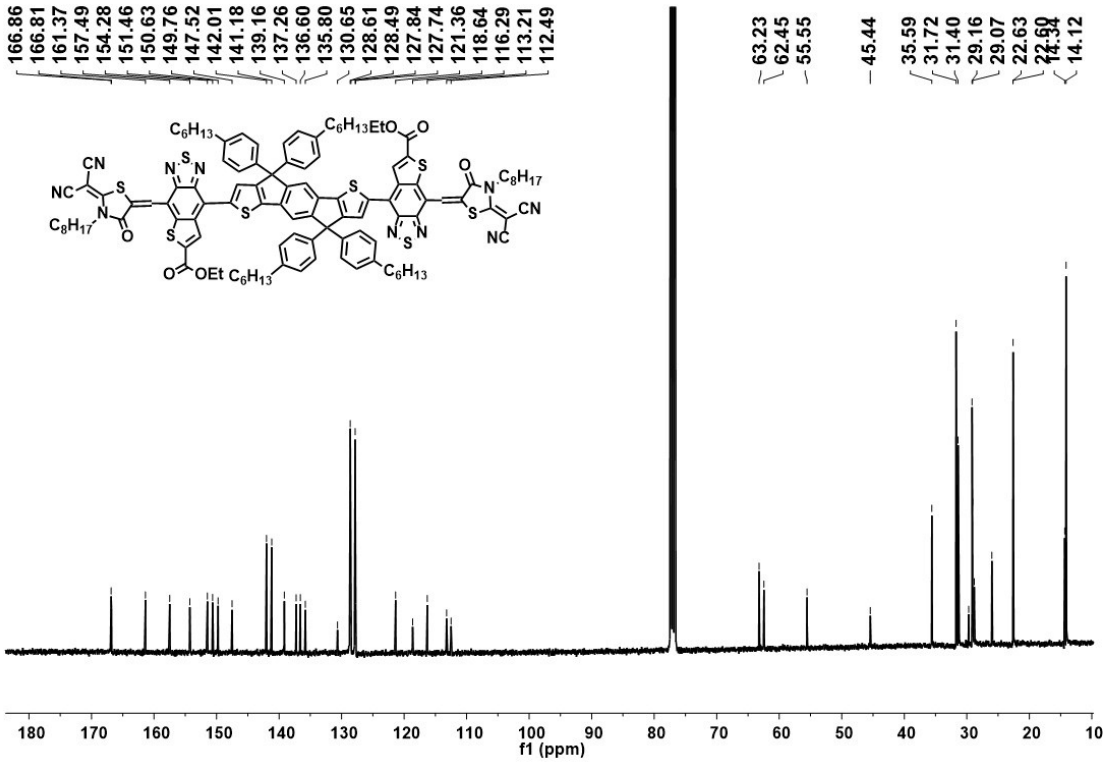



**Figure S29.** $^{13}C$ NMR of compound A2 in $CDCl_3$.

**Table S1**. Device parameters for A1/A2:PTB7-Th based OSCs with different D/A ratio and different amounts of additive.

| Acceptor | D/A ratio(w/w) | Addtive | $V_{oc}$ (V) | $J_{sc}$ (mA cm$^{-2}$) | FF (%) | PCE (%) |
|---|---|---|---|---|---|---|
| A1 | 1 : 1 | 0 | 0.86 | 5.63 | 42.65 | 2.05 |
| A1 | 1.5 : 1 | 0 | 0.90 | 7.86 | 46.78 | 3.32 |
| A1 | 2 : 1 | 0 | 0.84 | 5.77 | 38.88 | 1.89 |
| A1 | 1.5 : 1 | 0.5%[a] | 0.88 | 11.13 | 48.99 | 4.77 |
| A1 | 1.5 : 1 | 1%[a] | 0.89 | 12.54 | 51.75 | 5.79 |
| A1 | 1.5 : 1 | 1.5%[a] | 0.88 | 9.89 | 50.96 | 4.43 |
| A2 | 1 : 1 | 0 | 0.69 | 18.50 | 47.53 | 6.08 |
| A2 | 1 : 2 | 0 | 0.71 | 17.57 | 57.65 | 7.20 |
| A2 | 1 : 2.5 | 0 | 0.71 | 16.85 | 54.66 | 6.53 |
| A2 | 1 : 2 | 0.5%[b] | 0.70 | 18.59 | 61.74 | 8.08 |
| A2 | 1 : 2 | 1%[b] | 0.71 | 20.33 | 62.80 | 9.07 |
| A2 | 1 : 2 | 1.5%[b] | 0.70 | 16.93 | 57.18 | 7.80 |

[a]CN is added. [b]DIO is added.

**Table S2.** Exciton binding energy, excited state energy, IP, and EA of (TB7-Th)-A1 and (TB7-Th)-A2.

| | EA (Ha) | IP (Ha) | $E_{S1}$ (eV) | $E_b$ (eV) |
|---|---|---|---|---|
| **(TB7-Th)-A1** | 0.132 | 0.190 | 1.187 | 0.406 |
| **(TB7-Th)-A2** | 0.136 | 0.193 | 1.162 | 0.385 |

**Table S3**. First three excited state information for (TB7-Th)-A1 and (TB7-Th)-A2.

| | No. | E (eV) | λ (nm) | f | Orb. Composition (%) |
|---|---|---|---|---|---|
| **(TB7-Th)-A1** | 1 | 1.1865 | 1044.95 | 0.0177 | HOMO->LUMO:63.6; HOMO->L+1:33.3 |
| | 2 | 1.3714 | 904.05 | 2.2116 | H-1->LUMO:93.3 |
| | 3 | 1.4824 | 836.4 | 0.0097 | HOMO->L+1:62.7; HOMO->LUMO:33.3 |
| **(TB7-Th)-A2** | 1 | 1.1624 | 1066.66 | 0.0707 | HOMO->LUMO:66.8; HOMO->L+1:29.7 |
| | 2 | 1.3404 | 925 | 2.196 | H-1->LUMO:93.6 |
| | 3 | 1.4535 | 853.02 | 0.0053 | HOMO->L+1:66.2; HOMO->LUMO:30.2 |

## REFERENCES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2. Higashijima. S, Miura. H, Fujita. T, Kubota. Y, Funabiki. K, Yoshida. T, Matsui. M, *Tetrahedron*., 2011, 67, 6289-6293.