Supplementary information

Synthesis, crystal structures and semiconductor properties of 2-(thiopyran-4-ylidene)-1,3-benzodithioles with an aryl substituent

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Instrumental procedures

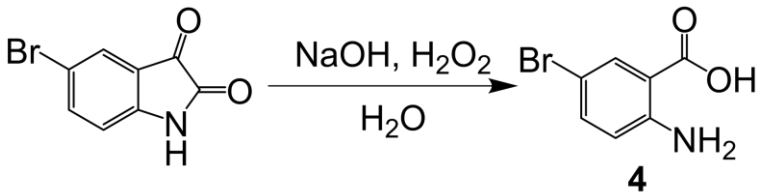
Melting points were measured using an AZ ONE melting temperature measurement device (ATM-02). NMR spectra were recorded on a JEOL JNM-ECZ-400R/S1 spectrometer. The chemical shifts (δ) were referenced to chloroform ($CHCl_3$) and tetramethylsilane (TMS). High-resolution mass spectra were recorded using a JMS-T100 GCV or LTQ Orbitrap XL spectrometer.

Synthetic experimental procedures

The synthesis of the dithiolium salt **6** was carried out in air. The other reactions were carried out under a nitrogen (N_2) atmosphere. 5-Bromoisatin, carbon disulfide (CS_2), 3-methyl-1-butanol, isoamyl nitrite, *n*-butyllithium/hexane solution (*n*-BuLi/hexane), 4-oxothiane, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), phenylboronic acid, tributyl(2-pyridyl)tin and 4-pyridylboronic acid were obtained from commercial sources and used without further purification. Lithium diisopropylamide (LDA) was prepared by the reaction of diisopropylamine with *n*-BuLi/hexane. Tetrahydrofuran (THF) was distilled over lithium aluminum hydride ($LiAlH_4$) under a N_2 atmosphere. 1,2-Dichloroethane, toluene and xylene were distilled over calcium hydride (CaH_2).

Detailed synthetic procedures

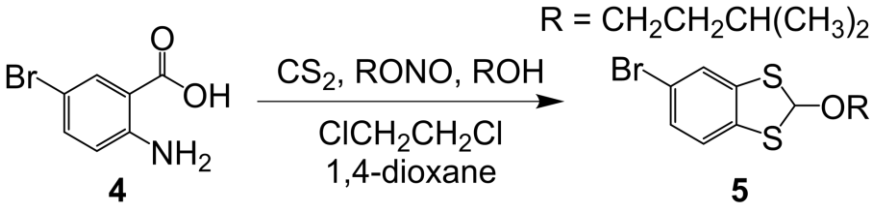
5-Bromoanthranilic acid (4)



4

5-Bromoisatin (3.39 mg, 15.0 mmol) was dissolved in 5% NaOH aq. (30 mL). 35% H_2O_2 aq. (5.3 mL) was added dropwise to the solution for 30 min at 50 °C and the solution was stirred for 1 h at 50 °C. Thereafter, the solution was cooled in an ice bath and the pH adjusted to 3–4 with concentrated HCl. The resulting precipitate was filtered and washed with water. Compound **4** (2.95 g, 13.6 mmol, 91%) was collected as a white-brown solid and dried under vacuum. Compound **4** was used in the next step without further purification.

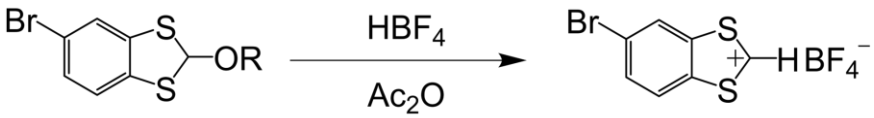
5-Bromo-2-(3-methylbutoxy)-1,3-benzodithiole (5)



4 5

A solution of **4** (2.16 g, 10.0 mmol) in 1,4-dioxane (30 mL) was added to a gently refluxing mixture of 1,2-dichloroethane (70 mL), 3-methyl-1-butanol (2.4 mL), isoamyl nitrite (2 mL) and CS_2 (27 mL) dropwise for 25 min. After the addition was complete, the mixture was refluxed for 1 h, cooled to ambient temperature, and the reaction was quenched with water (10 mL). Part of the solvent and excess reagents were removed in vacuo. The mixture was extracted with ethyl acetate (AcOEt) and the collected extracts were washed with water and brine, and dried over anhydrous Na_2SO_4. The organic layer was concentrated in vacuo and the residue was purified by silica gel column chromatography (eluent: AcOEt/hexane = 1:3) to afford **5** as a yellow oil (2.09 g, 6.55 mmol, 65% yield).

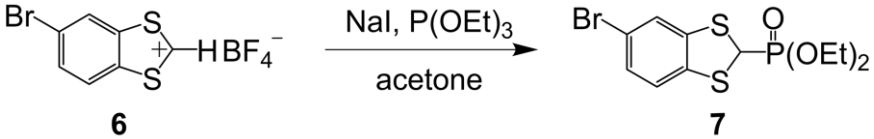
5-Bromo-1,3-benzodithiolium tetrafluoroborate (6)



5 6

5 (2.09 g. 6.55 mmol) was dissolved in acetic anhydride (Ac_2O) (20 mL) and the reaction flask was cooled to 0 °C in an ice bath. 43% HBF_4 aq (3.1 mL, 3 eq.) was slowly added to the solution at 0 °C. After the mixture was stirred for 1 h at 0 °C, Et_2O (40 mL) was added to the mixture and the resulting precipitate was collected and washed with Et_2O to afford **6** (1.86 g, 5.84 mmol, 89% yield) as a pale yellow powder. Compound **6** was used in the next step without further purification.

Diethyl 5-bromo-1,3-benzodithiol-2-yl phosphonate (7)

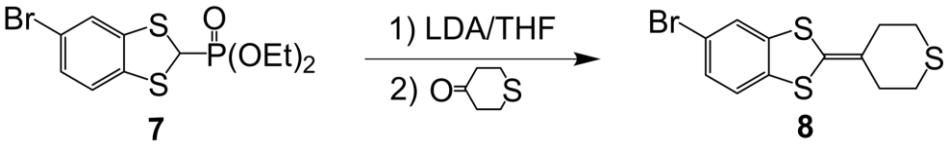


6 7

To a mixture of **6** (1.28 g, 4.00 mmol) and NaI (1.20 g, 8.00 mmol) in acetone (200 mL) was added $P(OEt)_3$ (1.45 mL, 8.40 mmol). After stirring the solution for 3 h at room temperature, the solvent was removed in vacuo. The residue was extracted with AcOEt and the collected organic layers were washed with water and brine, and dried over anhydrous Na_2SO_4. The organic extracts were concentrated in vacuo and the residue was purified by silica gel column chromatography (eluent: AcOEt/hexane = 4:1) to afford a pale-yellow oil. After recrystallization from AcOEt/hexane, compound **7** (1.07 g, 2.90 mmol, 73% yield) was obtained as an off-white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.30 (d, J = 1.6 Hz, 1H), 7.13 (dd, J = 8.4, 2.0 Hz, 1H), 7.03 (d, J = 8.4 Hz, 1H), 4.85 (d, J = 5.2 Hz, 1H), 4.08–4.26 (m, 4H), 1.25 (dt, J = 7.2 Hz, 3.6 Hz, 6H).

5-Bromo-2-(tetrahydrothiopyran-4-ylidene)-1,3-benzodithiole (8)



7 **8**

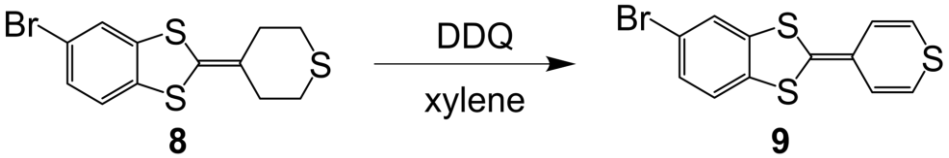
7 (738 mg, 2.00 mmol) was dissolved in THF (35 mL) and the reaction flask was cooled to −76 °C. LDA (1 M, 2.20 mmol) was added to the solution at −78 °C and the resulting mixture was stirred for 15 min at −78 °C. 4-Oxothiane (256 mg, 2.20 mmol) in THF (15 mL) was then added. The mixture was allowed to warm to room temperature and stirred overnight. Thereafter, the reaction flask was cooled in an ice bath and the reaction was quenched with NH_4Cl aq. (30 mL). The mixture was extracted with $CHCl_3$ and the collected extracts were washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by silica gel column chromatography (eluent: $CHCl_3$) to afford compound **8** as colorless crystals (622 mg, 1.89 mmol, 94% yield).

M. p. 198 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.27 (d, J = 2.4 Hz, 1H), 7.14 (dd, J = 8.0, 2.0 Hz, 1H), 7.00 (d, J = 8.0 Hz, 1H), 2.65–2.69 (m, 4H), 2.49–2.53 (m, 4H).

^{13}C NMR (400 MHz, $CDCl_3$): δ (ppm) = 138.1, 135.1, 128.4, 124.0, 123.2, 123.1, 122.4, 118.6, 35.33, 35.30, 29.04.

5-Bromo-2-(thiopyran-4-ylidene)-1,3-benzodithiole (9)



8 **9**

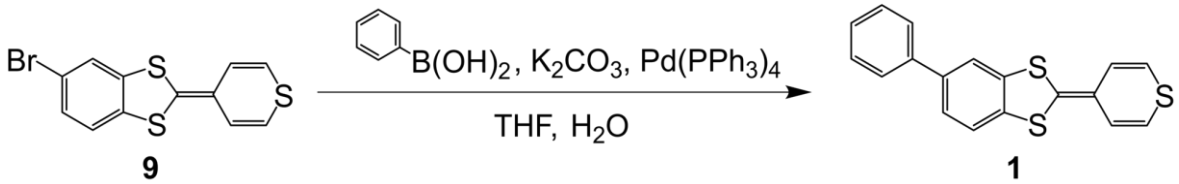
A solution of DDQ (568 mg, 2.50 mmol) in xylene (55 mL) was added to a gently refluxing solution of **8** (330 mg, 1.00 mmol) in xylene (80 mL) at 130 °C dropwise for 30 min. The reaction mixture was refluxed for 30 min (150 °C) and then cooled to ambient temperature. The precipitate was removed by filtration and washed with CS_2. The filtrate was concentrated in vacuo and the residue was purified by silica gel column chromatography (eluent: CS_2) to afford **9** as yellow crystals (238 mg, 0.730 mmol, 73% yield).

M. p. 236 °C (decomp.).

^{1}H NMR (400 MHz, $CDCl_3$, 40 °C): δ (ppm) = 7.33 (d, J = 2.0 Hz, 1H), 7.17 (dd, J = 8.4, 2.0 Hz, 1H), 7.04 (d, J = 8.4 Hz, 1H), 6.15 (d, J = 10.4 Hz, 2H), 6.07 (d, J = 10.4 Hz, 2H).

^{13}C NMR (400 MHz, $CDCl_3$, 40 °C): δ (ppm) = 138.5, 135.4, 128.6, 124.2, 123.5, 122.5, 118.9, 117.6, 117.5, 117.2.

5-Phenyl-2-(thiopyran-4-ylidene)-1,3-benzodithiole (1)



9 **1**

A mixture of **9** (130 mg, 0.400 mmol), phenylboronic acid (123 mg, 1.00 mmol), K_2CO_3 (554 mg, 4.00 mmol) and tetrakistriphenylphosphine palladium ($Pd(PPh_3)_4$) (46.2 mg, 40.0 μmol) in THF (200 mL) and water (50 mL) was stirred overnight at reflux. After cooling the reaction to room temperature, the mixture was extracted with $CHCl_3$ and the combined extracts were washed with water, brine and dried over anhydrous Na_2SO_4. The extracts were concentrated in vacuo and the residue was purified by silica gel column chromatography (eluent: toluene). Recrystallization from CS_2/EtOH afforded **1** (84.0 mg, 0.259 mmol, 65% yield) as orange-yellow crystals.

M. p. 237 °C (decomp.).

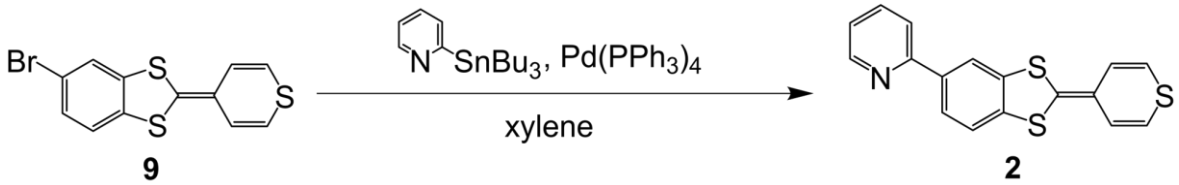
^{1}H NMR (400 MHz, $CDCl_3$, 40 °C): δ (ppm) = 7.51–7.54 (m, 2H), 7.40–7.45 (m, 3H), 7.34 (t, J = 7.2 Hz, 1H), 7.30 (dd, J = 8.4 Hz, 1.6 Hz, 1H), 7.27 (d, J = 8.4 Hz, 1H), 6.20 (d, J = 10.4 Hz, 2H), 6.05 (d, J = 10.8 Hz, 2H).

^{13}C NMR (400 MHz, $CDCl_3$, 40 °C): δ (ppm) = 140.0, 139.3, 137.0, 135.2, 128.9, 127.6, 126.9, 124.8, 123.8, 121.7, 120.1, 117.0.

MS (APCI): m/z 324 $[M]^+$, HRMS (APCI): m/z calcd for $C_{18}H_{12}S_3$: 324.0096 $[M]^+$; found: 324.0098.

Anal. Calcd for $C_{18}H_{12}S_3$: C, 66.63; H, 3.73. Found: C, 66.54; H, 3.61.

5-(2-Pyridyl)-2-(thiopyran-4-ylidene)-1,3-benzodithiole (2)



9 **2**

A mixture of **9** (228 mg, 0.700 mmol), $Pd(PPh_3)_4$ (16.2 mg, 140 μmol) and tributyl(2-pyridyl)tin (0.46 mL, 1.44 mmol) in xylene (15 mL) was stirred overnight at reflux. After cooling the reaction to room temperature, $NaHCO_3$ aq was added into the mixture. The mixture was extracted with $CHCl_3$ and the collected extracts were washed with water, brine and dried over anhydrous Na_2SO_4. The combined extracts were concentrated in vacuo and the residue was purified by silica gel column chromatography (eluent: $CHCl_3$). Recrystallization from DCM/EtOH afforded **2** (126 mg, 0.387 mmol, 55% yield) as orange-yellow crystals.

M. p. 223 °C (decomp.).

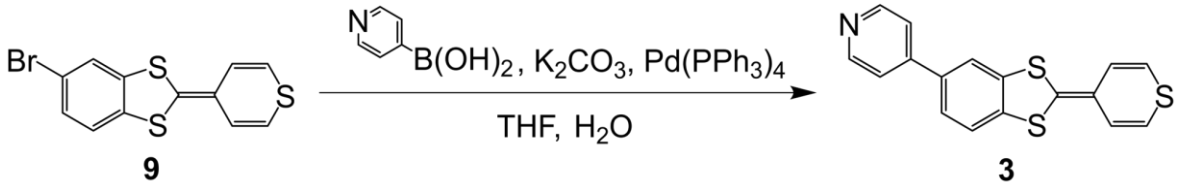
^{1}H NMR (400 MHz, $CDCl_3$, 40 °C): δ (ppm) = 8.66 (d, J = 5.2 Hz, 1H), 7.93 (d, J = 2.0 Hz, 1H), 7.65–7.76 (m, 3H), 7.30 (d, J = 8.4 Hz, 1H), 7.20–7.25 (m, 1H), 6.20 (d, J = 10.8 Hz, 2H), 6.06 (d, J = 10.8 Hz, 2H).

^{13}C NMR (400 MHz, $CDCl_3$, 40 °C): δ (ppm) = 156.0, 149.7, 137.4, 137.3, 137.2, 136.8, 124.3, 123.8, 123.7, 122.3, 121.6, 120.1, 119.9, 118.3, 117.2, 117.1.

MS (EI): m/z 325 $[M]^+$, HRMS (EI): m/z calcd for $C_{17}H_{11}NS_3$: 325.0054 $[M]^+$; found: 325.0047.

Anal. Calcd for $C_{17}H_{11}NS_3$: C, 62.74; H, 3.41; N, 4.30. Found: C, 62.73; H, 3.46; N, 4.29.

5-(4-Pyridyl)-2-(thiopyran-4-ylidene)-1,3-benzodithiole (3)



9 **3**

Following the method employed for the synthesis of **1** using 4-pyridylboronic acid instead of phenylboronic acid, compound **3** (107 mg, 0.329 mmol, 82% yield) as obtained as orange crystals. $CHCl_3$ was used as the eluent for silica gel column chromatography and recrystallization was performed from DCM/EtOH.

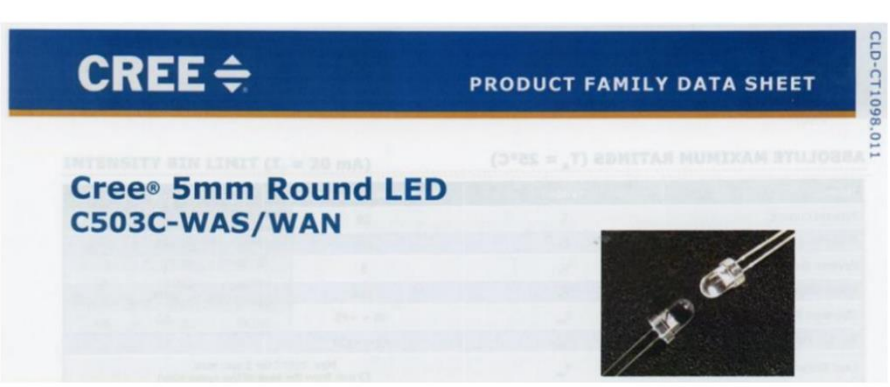
M. p. 230 °C (decomp.).

^{1}H NMR (400 MHz, $CDCl_3$, 40 °C): δ (ppm) = 8.65 (dd, J = 4.8 Hz, 1.6 Hz, 2H), 7.47 (d, J = 1.6 Hz, 1H), 7.43 (dd, J = 4.4 Hz, 2.0 Hz, 2H), 7.34 (dd, J = 8.4 Hz, 1.6 Hz, 1H), 7.30 (d, J = 8.4 Hz, 1H), 6.20 (d, J = 10.4 Hz, 2H), 6.09 (d, J = 10.4 Hz, 2H).

^{13}C NMR (400 MHz, $CDCl_3$, 40 °C): δ (ppm) = 150.4, 147.1, 137.8, 137.7, 136.1, 124.5, 123.62, 123.59, 122.0, 121.2, 119.7, 117.52, 117.49.

MS (EI): m/z 325 $[M]^+$, HRMS (EI): m/z calcd for $C_{17}H_{11}NS_3$: 325.0054 $[M]^+$; found: 325.0050.

Anal. Calcd for $C_{17}H_{11}NS_3$: C, 62.74; H, 3.41; N, 4.30. Found: C, 62.51; H, 3.40; N, 4.38.



C503C-WAN-CCADB231 provided by Cree Inc.

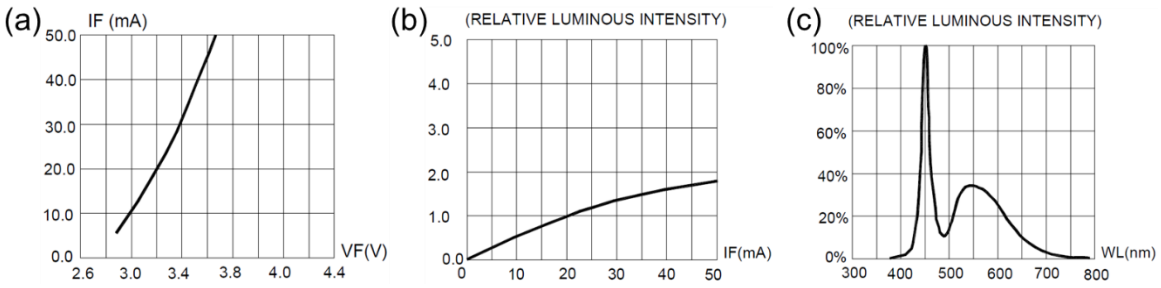


Fig. S1 LED characteristics presented by Cree, Inc. (a) Forward current vs. forward voltage. (b) Relative luminous intensity vs. forward current. (c) Relative luminous intensity vs. wavelength.

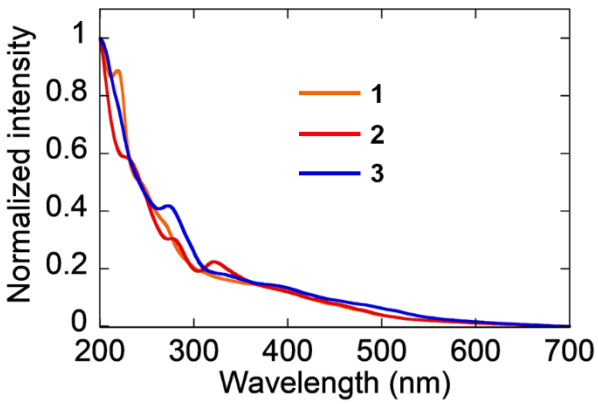


Fig. S2 UV–vis absorption spectra of **1**, **2** and **3** thin films on a quartz plate.

Table S1 Crystallographic data of **2** and **3**.

Compound	**2**	**3**
Chemical formula	$C_{17}H_{11}NS_3$	$C_{17}H_{11}NS_3$
Formula weight	325.45	325.45
Color	Orangish yellow	Orange
Shape	Plate	Plate
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$P2_12_12_1$
a (Å)	16.0602(12)	6.1579(3)
b (Å)	7.6455(9)	7.5864(4)
c (Å)	11.9152(13)	31.1475(14)
β (°)	94.692(8)	90
Volume (Å^3)	1458.1(3)	1455.10(12)
Z	4	4
D_{calc} (g/cm^3)	1.482	1.486
R_1 ($I > 2\sigma(I)$)	0.0465	0.0553
wR_2 (All reflections)	0.1120	0.1217
Reflections ($I > 2\sigma(I)$)	2758	2305
Temperature (K)	298	298
CCDC number	2234243	2234244

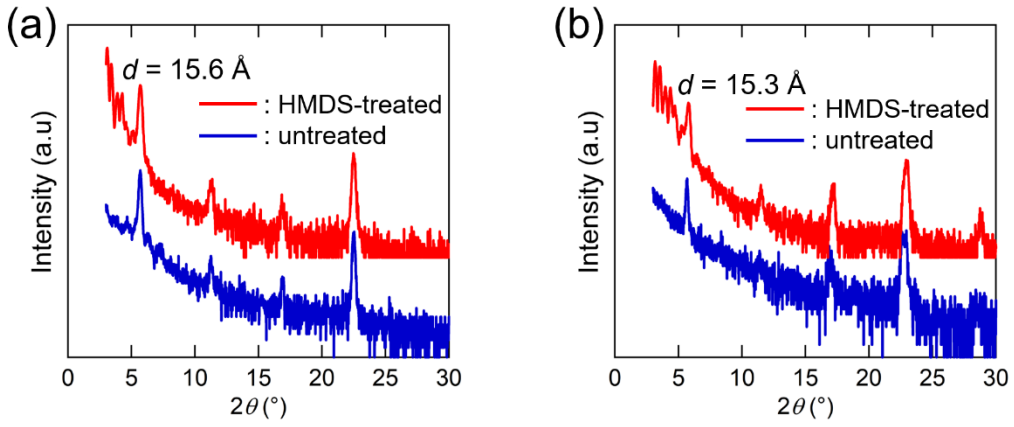


Fig. S3 XRD patterns of (a) **2** and (b) **3** films on HMDS-treated (red line) and untreated (blue line) substrates.

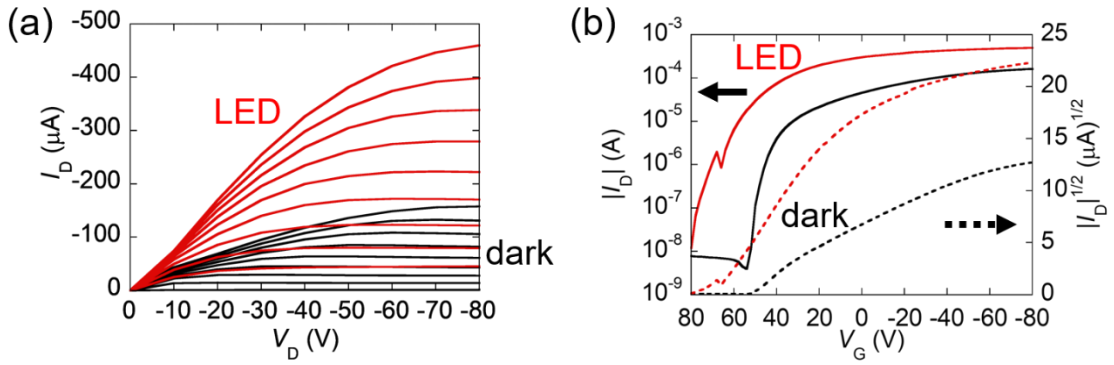


Fig. S4 (a) Output characteristics and (b) transfer characteristics ($V_D = -80$ V) of **2** (HMDS-treated substrate).

Table S2 OFET characteristics of **2**.

Substrate surface	Condition	μ (cm^2/Vs)	V_{th} (V)	ON/OFF ratio
Untreated	In dark	2.8×10^{-4}	41	3.7×10^4
Untreated	In LED	1.1×10^{-3}	66	1.1×10^5
HMDS-treated	In dark	3.2×10^{-4}	54	1.3×10^5
HMDS-treated	In LED	1.5×10^{-3}	64	4.1×10^4

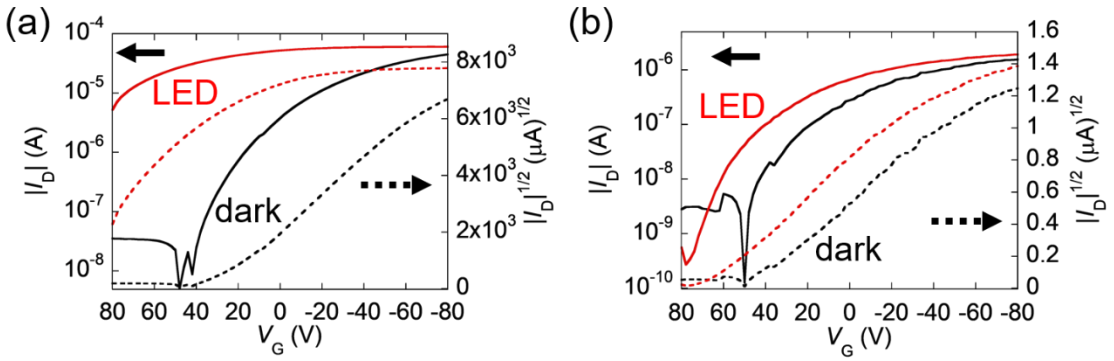
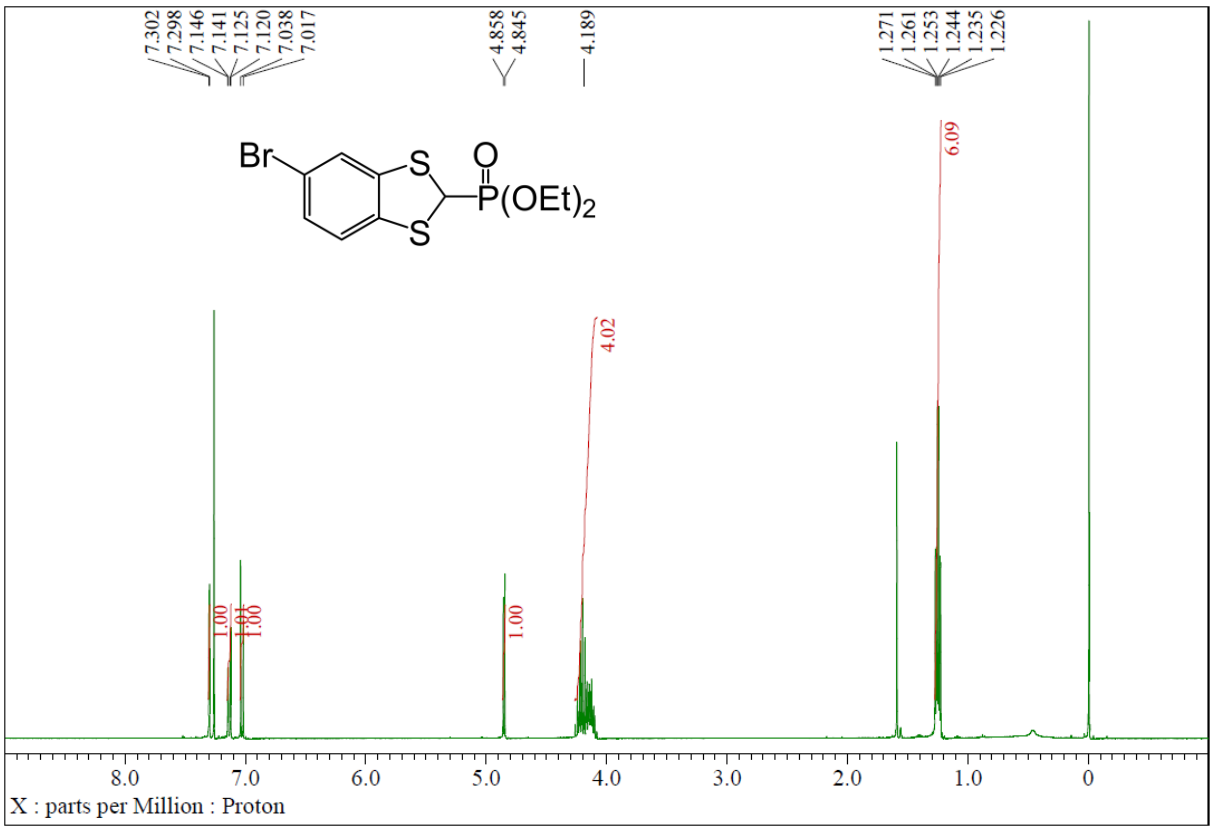
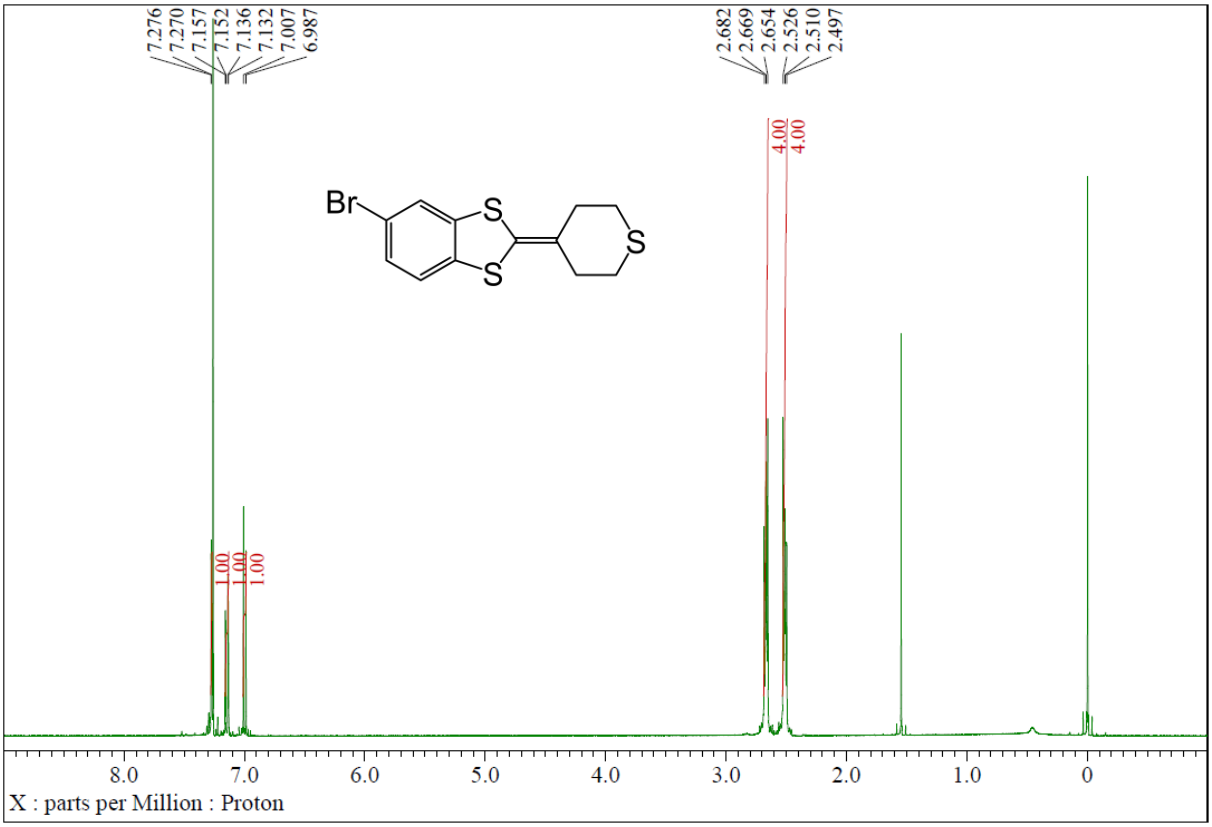


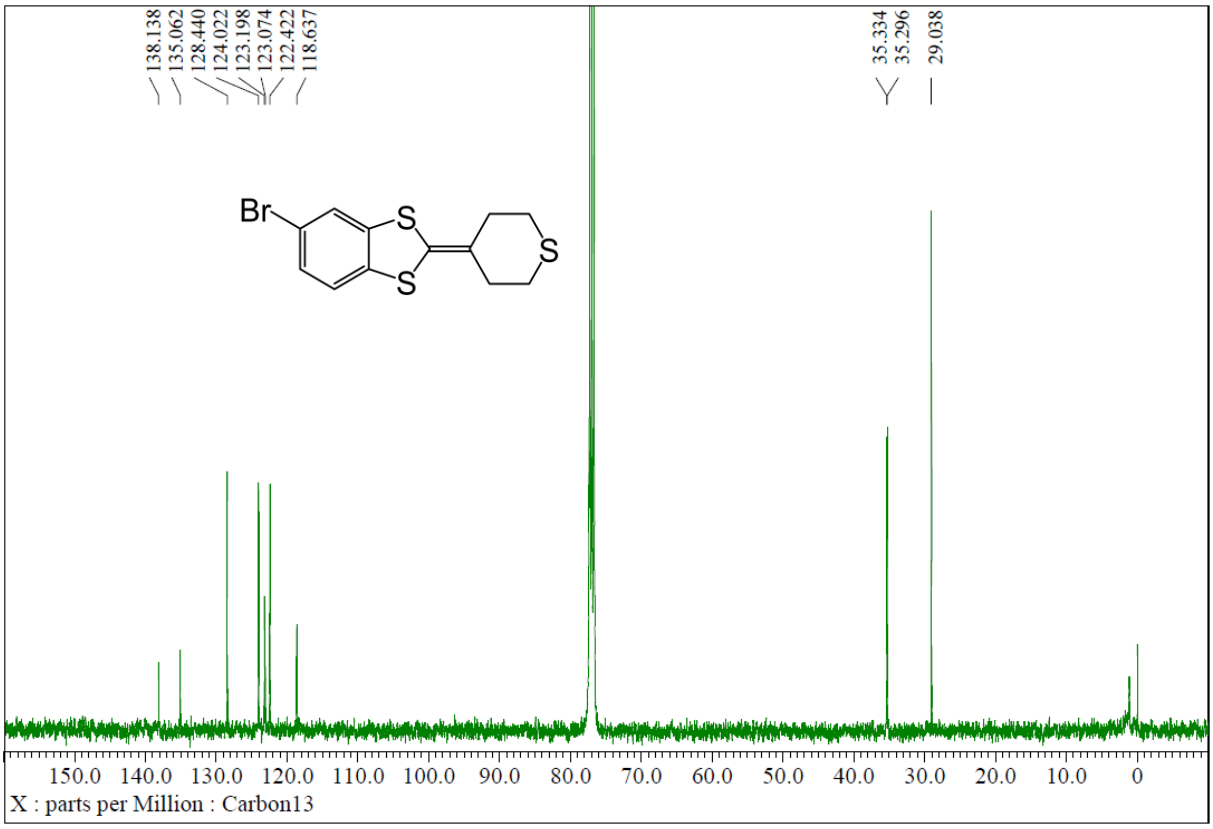
Fig. S5 Transfer characteristics ($V_D = -80$ V) of (a) **1** and (b) DBTTF (untreated substrate).



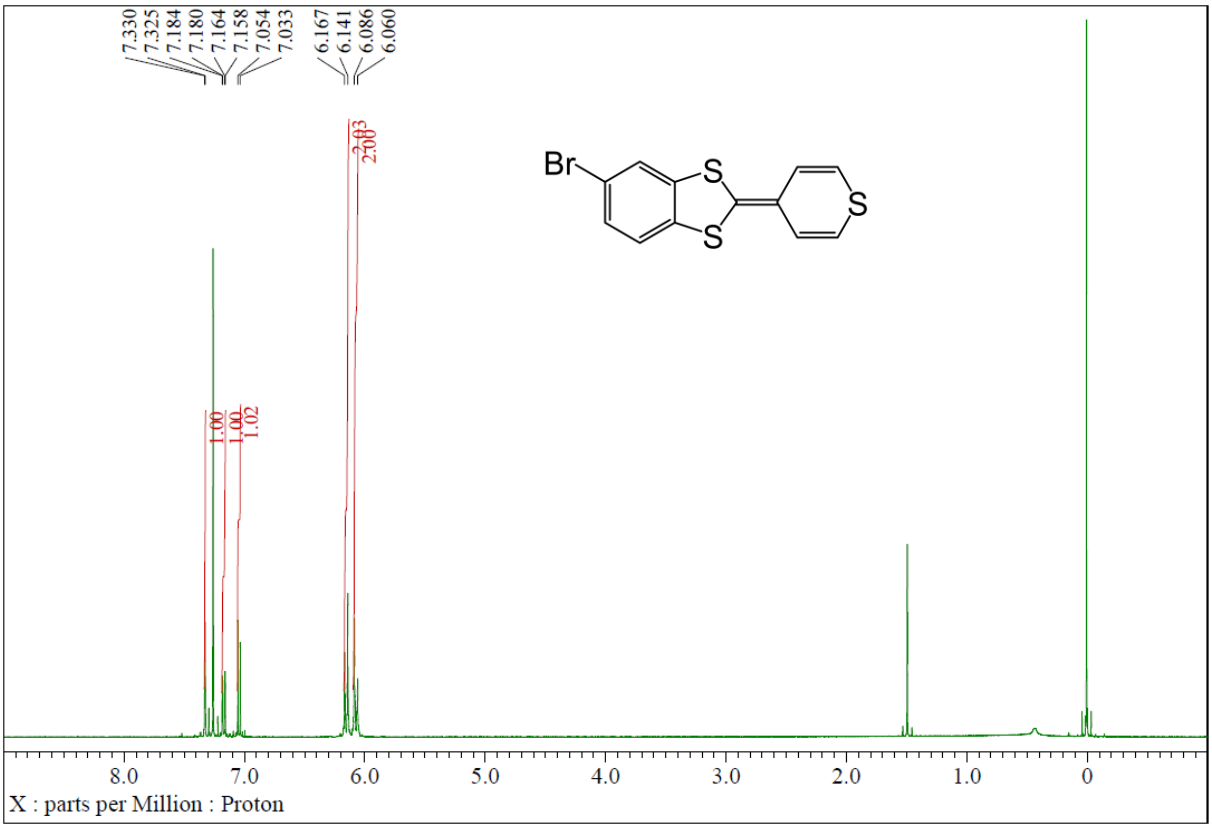
^{1}H NMR spectrum of **7**.



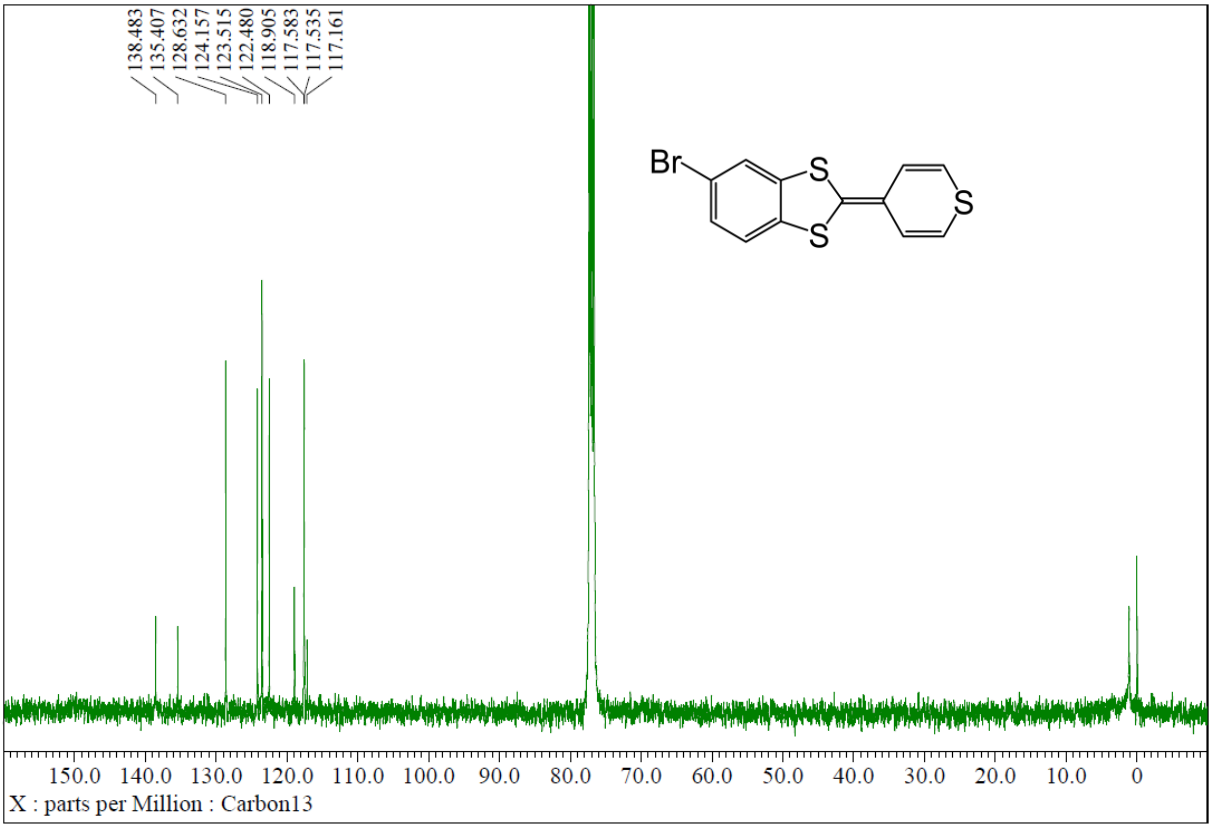
^{1}H NMR spectrum of **8**.



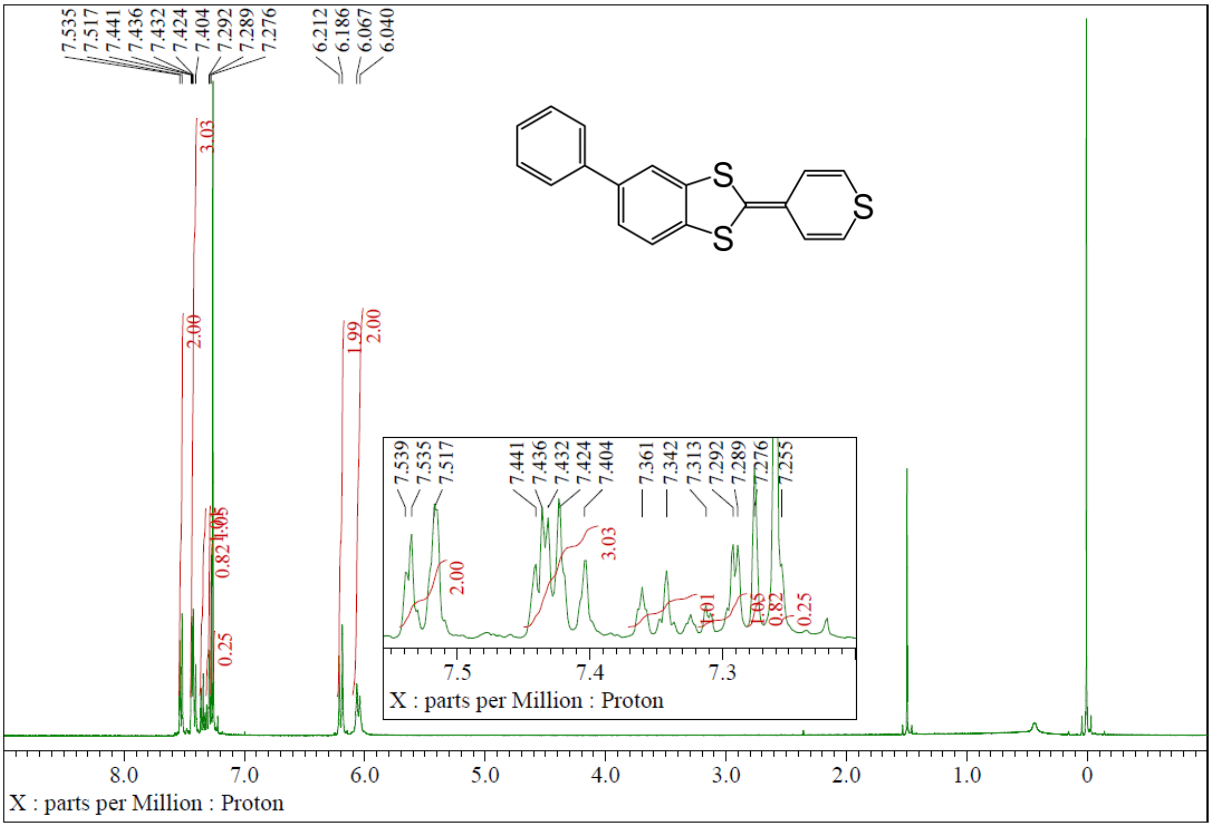
^{13}C NMR spectrum of **8**.



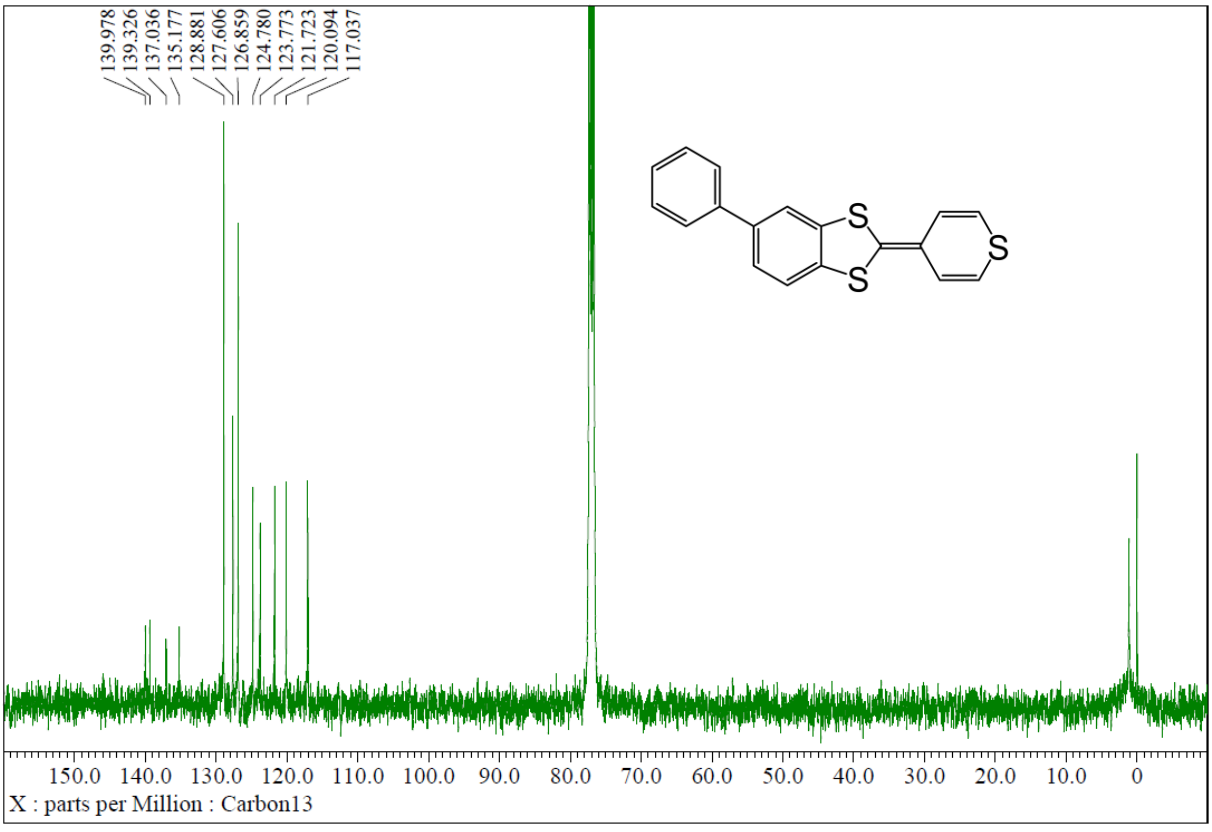
[1]H NMR spectrum of **9**.



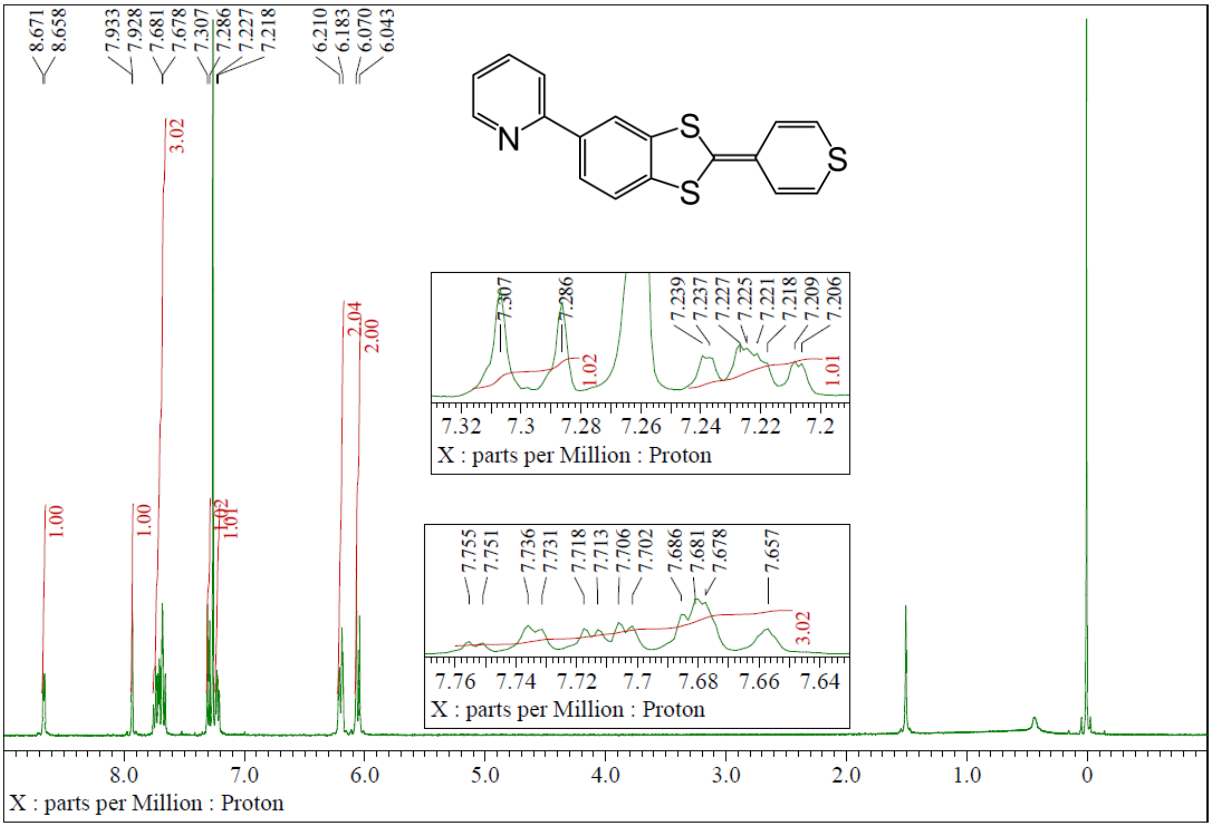
[13]C NMR spectrum of **9**.



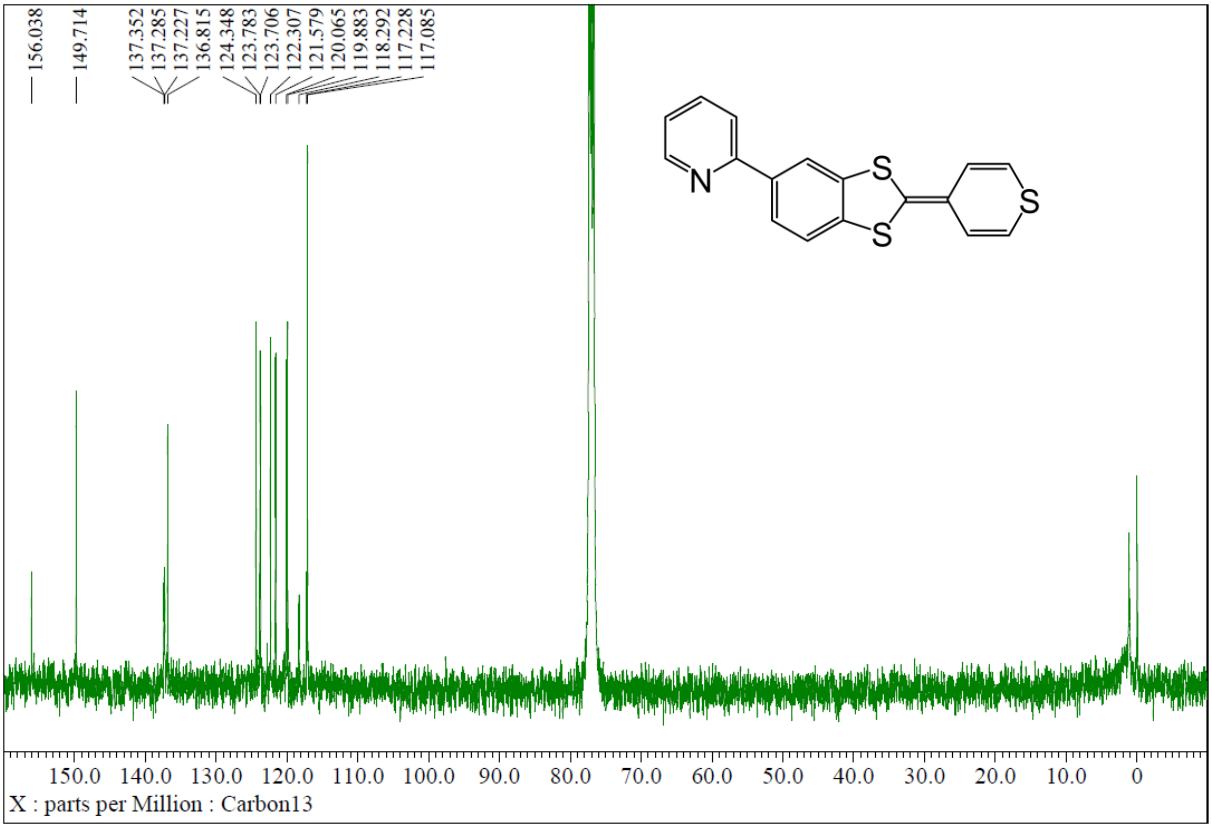
^{1}H NMR spectrum of **1**.



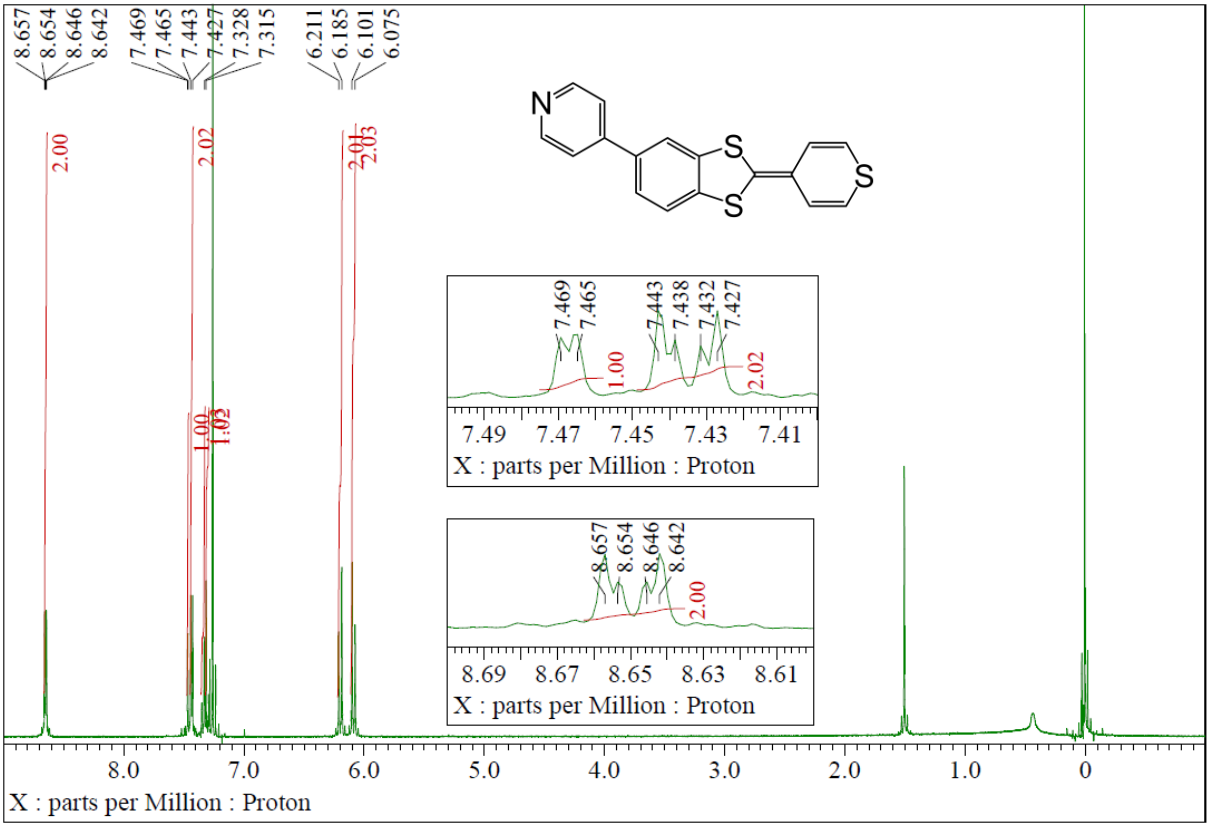
^{13}C NMR spectrum of **1**.



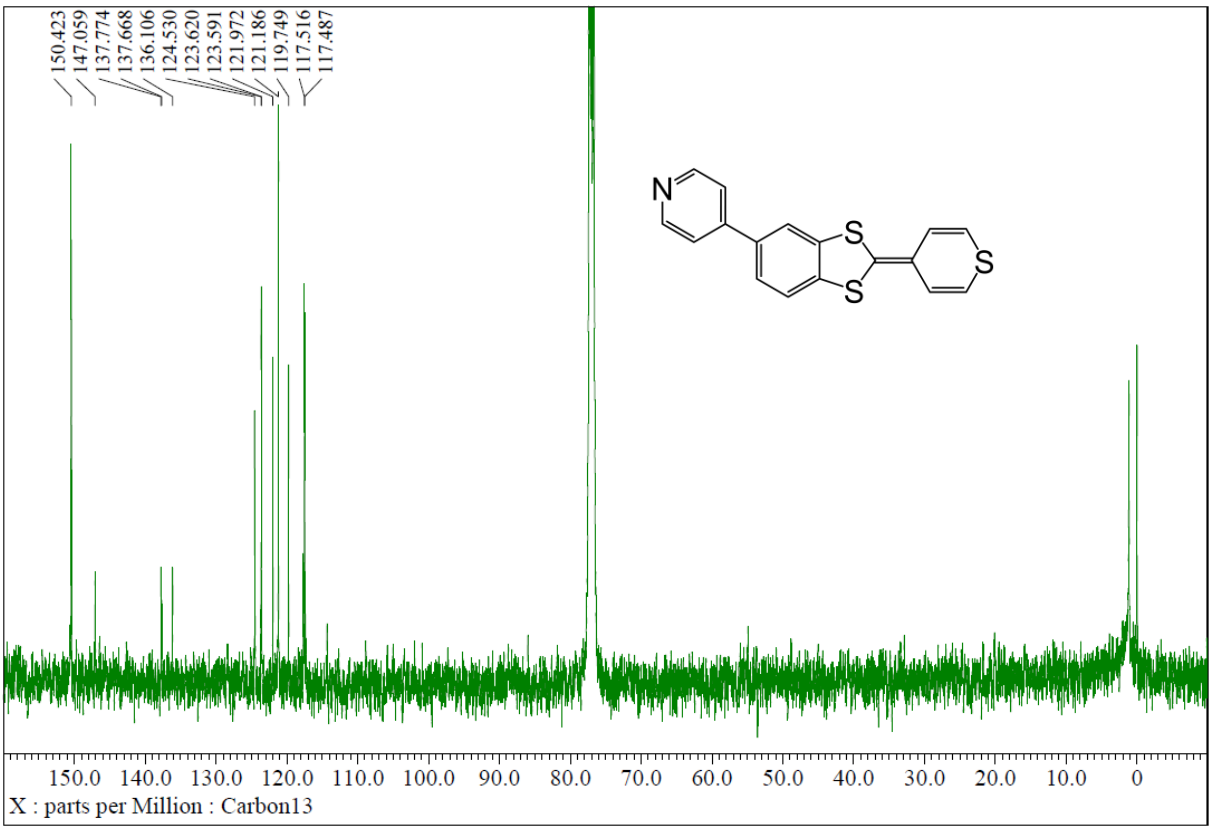
^{1}H NMR spectrum of **2**.



^{13}C NMR spectrum of **2**.



^{1}H NMR spectrum of **3**.



^{13}C NMR spectrum of **3**.