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Supporting Information

Thienoquinolinone as a New Building Block for Wide Bandgap Semiconducting Polymer Donors for Organic Solar Cells

*Jong-Woon Ha,[a] Hee Su Kim,[a] Chang Eon Song,[b] Hea Jung Park,[a] and Do-Hoon Hwang[a,]**

[a] *Department of Chemistry, and Chemistry Institute for Functional Materials, Pusan National University, Busan 46241, Korea.*

[b] *Energy Materials Research Center, Korea Research Institute of Chemical Technology (KRICT), Daejeon 34114, Republic of Korea.*

*Corresponding author. Tel.: +82-51-510-2232, Fax: +82-51-516-7421, E-mail address:

dohoonhwang@pusan.ac.kr (D.-H. Hwang)

Experimental Section

Materials. All starting materials and reagents were purchased from Sigma Aldrich, TCI, and Alfa Aesar and used without further purification. Tetrakis(triphenylphosphine)palladium(0) was purchased from Strem Chemicals. BDT, ITIC, IT-4F, and $PC_{71}BM$ were purchased from 1-Materials and OSM. Ethyl 2-bromothiophene-3-carboxylate and 2-hexyldecanal were synthesized according to the reported procedures.[1,2]

Measurements. ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were measured on a Varian Mercury Plus 300 MHz spectrometer. High-resolution mass spectra were acquired by liquid chromatography/tandem mass spectrometry (Agilent 6410 QQQ LC/MS). The UV-Vis absorption spectra were recorded on a UV-1800 UV-Vis spectrophotometer. Gel permeation chromatography (GPC) was used to check the molecular weight and confirm the polydispersity indices (PDIs), using a Shimadzu LC solution at a flow rate of 1.0 mL min^{-1} with chlorobenzene as an eluent at 40 °C. Cyclic voltammetry experiments were performed with a CH Instruments electrochemical analyzer in acetonitrile solutions containing 0.1 M tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) as the supporting electrolyte. $Ag/AgNO_3$ was used as the reference electrode, and a platinum wire as the counter electrode and also the working electrode. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) measurements were performed on a TA Instruments Q600, under a nitrogen atmosphere at a heating rate of 10 °C/min.

2D-GIXD experiments were performed at the 3C beamlines of the Pohang Accelerator Laboratory (PAL), Korea. X-rays with a wavelength of 1.2301 Å (10.0791 keV) were used. The incidence angle of -0.10° was chosen to allow complete X-ray penetration into the polymer film.

The surface morphologies of the polymer thin films were characterized by AFM (SPM System) operating in the tapping mode. The organic photovoltaic (OPV) performances were confirmed by using a McScience K201 LAB50 Solar Simulator. The current density-voltage (J-V) data of the devices were measured under AM 1.5G condition, and the light intensity was calibrated using a Si standard reference device (PV Measurements Inc., calibrated at the National Renewable Energy Laboratory). The external quantum efficiency (EQE) data were measured by a McScience K3100 EQX system. The EQE values were obtained as a function of wavelength in the range from 300 to 900 nm using a Xenon Short Arc Lamp as the light source, and the calibration was performed using a Si photodiode.

Theoretical Calculations. Density functional theory (DFT) calculations were performed using the Gaussian 09W package with the Becke three-parameter Lee-Yang-Parr (B3LYP) functional and the 6-31G(d) basis set to elucidate the HOMO and LUMO energy levels and backbone planarity.

Fabrication of Inverted Photovoltaic Devices. Inverted OSC devices were fabricated with the structure of indium tin oxide (ITO)/ZnO/polymer donor:fullerene or non-fullerene acceptor/MoO_3/Ag. The active layer solutions were dissolved in chlorobenzene (1.0:2.0 and 1.0:0.7, w/w, for fullerene and non-fullerene OSC devices, respectively; total concentration = 30 mg mL^{-1}) and stirred overnight at 80 °C. The effective area of the device was 9 mm^2. A ZnO sol-gel solution was prepared according to a previous report.[3] ITO substrates were prepared by conventional cleaning and treatment with UV-ozone plasma for 20 min. Then, the ZnO layer as the electron transfer layer was deposited on the ITO at 2,000 rpm for 30 s by spin coating, before baking at 200 °C for 60 min. The active layer was fabricated by spin coating at various rpm values for 30 s in the glove box filled with argon. After drying the active layer, a pre-annealing process was carried out at 160 °C for 10 min, except for the fullerene OSC. Then, the MoO_3 (8 nm) and Ag (100 nm) layers were formed by thermal evaporation under a base pressure of 10^{-7} torr.

Syntheses of Monomers and Copolymers.

*Synthesis of 4-bromo-1-iodo-2-nitrobenzene (**1**).* A mixture of 4-bromo-1-iodo-2-nitrobenzene (15.00 g, 45.7 mmol) and bis(triphenylphosphine)palladium(II) ($Pd(PPh_3)_2Cl_2$) (0.96 g, 1.4 mmol) was dissolved in anhydrous toluene. Subsequently, 2-tributylstannylthiophene (17.07 g, 45.7 mmol) was added into the mixture, heated to 120 °C, and kept overnight. The mixture was concentrated and purified by silica column chromatography with dichloromethane/hexane (1/6, v/v) to obtain a yellow compound (yield: 75%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 7.89 (d, *J*=1.8 Hz, 1H), 7.71 (dd, *J*=8.1, 2.4 Hz, 1H), 7.44 (m, 2H), 7.09 (d, *J*=3.0 Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) 135.94, 134.99, 133.42, 127.99, 127.64, 127.47, 127.30, 126.83, 122.17, 121.74. MS (LC/MS): m/z founded 283.26 $[M]^+$, calcd. 282.93.

*Synthesis of 5-bromo-2-(thiophen-2-yl)aniline (**2**).* Fe (7.66 g, 137.3 mmol) was slowly added to a solution of **1** (13.00 g, 45.8 mmol) in acetic acid (200 mL), and then heated to 60 °C and kept overnight. The reaction mixture was quenched by adding NaOH aqueous solution and extracted with ethyl acetate and brine several times. The organic layer was dried over anhydrous $MgSO_4$ and concentrated. The crude product was purified by silica column chromatography using dichloromethane/hexane (1/2, v/v) as eluent to obtain an orange oil (yield: 70%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 7.37 (d, *J*=1.2 Hz, 1H), 7.19 (d, *J*=1.2 ,1H), 7.14 (m, 2H), 6.92 (m, 2H), 4.06 (br, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) 145.38, 139.83, 132.21, 127.75, 126.06, 125.64, 122.68, 121.38, 118.80, 118.30. MS (LC/MS) m/z: founded 254.0 $[M+H]^+$, calcd. 252.96.

*Synthesis of 5-bromo-N-(2-hexyldecyl)-2-(thiophen-2-yl)aniline (**3**).* A mixture of **3** (5.00 g, 19.7 mmol) and 2-hexyldecanal (4.73 g, 19.7 mmol) was dissolved in dichloroethane (100 mL) and acetic acid (5 mL), and stirred at room temperature for 30 min. Sodium triacetoxyborohydride (6.25 g, 29.5 mmol) was added in small portions. After stirring overnight at 50 °C, the reaction mixture was quenched by sodium bicarbonate aqueous solution and extracted with dichloromethane three times. The collected organic layer was dried over anhydrous $MgSO_4$, then the residue was purified by silica column chromatography using hexane as eluent to give the desired colorless liquid (yield: 75%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 7.37 (t, *J*=3.0 Hz, 1H), 7.12 (d, *J*=3.0, 2H), 7.08 (d, *J*=7.8, 1H), 6.92 (m, 2H), 4.39 (br, 1H), 2.98 (m, 2H), 1.59 (br, 1H), 1.26 (m, 24H), 0.91 (m, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) 147.08, 139.90, 131.95, 127.60, 126.09, 125.67, 123.57, 118.96, 118.30, 113.04, 47.13, 37.26, 32.22, 31.92, 31.83, 30.00, 29.67, 29.57, 29.34, 26.65, 26.60, 22.70, 14.16. MS (LC/MS) m/z: founded 478.2 $[M+H]^+$, calcd. 477.21.

*Synthesis of 7-bromo-5-(2-hexldecyl)thieno[3,2-c]quinolin-4(5H)-one (**5**).* A solution of trichloromethyl chloroformate (5.51 g, 27.9 mmol) in dichloroethane (20 mL) was added dropwise at 0 °C to **3** (8.90 g, 18.6 mmol) in dichloroethane (160 mL) and pyridine (20 mL). After stirring at 50 °C for 4 h, the reaction mixture was extracted with dichloromethane several times. The combined organic layer was washed with 1 M HCl and brine and then dried over anhydrous $MgSO_4$. The crude product (**4**) was used in the following reaction without further purification. A mixture of **4** and indium chloride (III) (4.11 g, 18.6 mmol) in tetrachloroethane (100 mL) was refluxed overnight. After cooling to room temperature, the reaction mixture was filtered through Celite and then concentrated under vacuum. The crude product was purified by silica gel chromatography using dichloromethane/hexane (2/1, v/v) as eluent. The product was recrystallized from hexane to give a white solid (yield: 55%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 7.69 (d, *J*=5.4 Hz, 1H), 7.62 (d, *J*=8.1, 1H), 7.53 (s, 1H), 7.35 (m, 2H), 4.25 (br, 2H), 1.94 (br, 1H), 1.35 (m, 24H), 0.84 (m, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) 158.80, 144.57, 137.86, 130.78, 126.80, 125.45, 125.19, 125.05, 122.85, 118.70, 117.06, 46.07, 36.33, 31.87, 31.80, 31.52, 29.94, 29.64, 29.53, 29.27, 26.57, 22.67, 22.62, 14.13. MS (LC/MS): m/z founded 504.2 $[M+H]^+$, calcd. 503.19.

Synthesis of 2,7-dibromo-5-(2-hexyldecyl)thieno[3,2-c]quinolin-4(5H)-one (TQO). Bromine (0.35 g, 2.2 mmol) was slowly added to a mixture of **5** (1.13 g, 2.2 mmol) and a given amount of iron(III) chloride in dichloromethane. After stirring at room temperature overnight, the mixture was extracted by dichloromethane and dried over anhydrous $MgSO_4$. The crude product was purified by recrystallization from hexane to obtain a white solid (yield: 80%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 7.57 (s, 1H), 7.48 (s, 2H), 7.40 (d, *J*=8.1 Hz, 1H), 7.28 (d, *J*=9.0 Hz, 1H), 4.18 (m, 2H), 1.89 (br, 1H), 1.33 (m, 24H), 0.84 (m, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) 157.33, 145.59, 137.77, 131.03, 129.17, 125.37, 125.07, 123.28, 118.74, 116.09, 113.37, 46.13, 36.30, 31.86, 31.78, 31.52, 31.47, 29.93, 29.62, 29.50, 29.25, 26.53, 22.65, 22.60, 14.10, 14.07. Elem Anal.

Calcd. for $C_{27}H_{37}Br_2NOS$: C, 55.58; H, 6.39; N, 2.40; O, 2.74; S, 5.50. Found: C, 55.72; H, 6.05; N, 2.43; O, 2.63; S, 5.46. MS (LC/MS) m/z: founded 582.1 $[M+H]^+$, calcd. 581.10.

*Synthesis of ethyl 2-(4-bromophenyl)thiophene-3-carboxylate (**6**)*. A mixture of ethyl 2-bromothiophene-3-carboxylate (13.30 g, 56.6 mmol), (4-bromophenyl)boronic acid (11.36 g, 56.6 mmol), and $Pd(PPh_3)_4$ (1.96 g, 1.7 mmol) was dissolved in toluene (100 mL) and 2 M potassium carbonate (100 mL), and then heated to 80 °C and kept overnight. Afterwards, the reaction mixture was extracted by ethyl acetate and brine several times and dried over anhydrous $MgSO_4$. The crude product was purified by silica column chromatography using dichloromethane/hexane (1/1, v/v) to obtain a white solid (yield: 62%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 7.58 (m, 3H), 7.37 (d, *J*=9.0 Hz, 2H), 7.25 (d, *J*=5.4, 1H), 4.24 (qt, *J*=6.9 Hz, 2H), 1.27 (t, *J*=6.9 Hz, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) 163.07, 149.35, 132.30, 131.95, 131.46, 131.07, 130.43, 130.11, 128.51, 124.36, 122.92, 60.62, 14.10. MS (LC/MS): m/z founded 311.0 $[M+H]^+$, calcd. 309.97.

Synthesis of 2-(4-bromophenyl)thiophene-3-carboxylic acid (7). Compound **6** (17.60 g, 56.6 mmol) was dissolved in tetrahydrofuran and sodium hydroxide aqueous solution, and heated to 80 °C. After overnight heating, the reaction mixture was concentrated and acidified by HCl aqueous solution. The white solid was collected via reduced pressure filtration (yield: 92%). ^{1}H-NMR (300 MHz, DMSO-d_6): δ (ppm) 12.71 (s, 1H), 7.60 (m, 3H), 7.42 (m, 3H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) 169.12, 152.95, 137.58, 136.79, 136.19, 135.41, 134.52, 130.94, 127.14. MS (LC/MS): m/z 282.92 $[M+H]^+$, calcd 281.94.

*Synthesis of tert-butyl (2-(4-bromophenyl)thiophen-3-yl)carbamate (**8**)*. Triethylamine (7.53 g, 74.5 mmol) and diphenylphosphoryl azide (12.29 g, 44.7 mmol) were added to a solution of **7** (10.50 g, 37.2 mmol) in toluene. After stirring at 80 °C for 2 h, *tert*-butylalcohol (8.28 g, 111.7 mmol) was injected into the reaction mixture and further stirred overnight. The reaction mixture was concentrated and purified by silica column chromatography using ethyl acetate/hexane (1/7, v/v) to obtain a white solid (yield: 60%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 7.58 (d, *J*=8.7 Hz, 2H), 7.33 (d, *J*=8.4 Hz, 2H), 7.25 (d, *J*=5.4 Hz, 2H), 6.51 (d, *J*=5.4 Hz, 1H), 1.48 (s, 9H) ^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) 152.81, 132.39, 132.18, 131.79, 130.23, 123.87, 123.41, 121.84, 28.29. MS (LC/MS): m/z founded 354.1 $[M+H]^+$, calcd 353.01.

*Synthesis of 2-(4-bromophenyl)-N-(2-hexyldecyl)thiophen-3-amine (**10**)*. Compound **8** (5.83 g, 16.5 mmol) was dissolved in chloroform/trifluoroacetic acid (1/2, v/v, total volume 150 mL) and stirred at room temperature overnight. After terminating the reaction, the mixture was extracted with dichloromethane and brine several times and dried over anhydrous $MgSO_4$. The crude product **9** obtained by concentrating the organic layer was used in the following reaction without further purification. A mixture of **9** and 2-hexyldecanal (3.96 g, 16.5 mmol) was dissolved in dichloroethane (100 mL) and acetic acid (5 mL), and stirred at room temperature for 30 min. Sodium triacetoxyborohydride (5.25 g, 29.5 mmol) was added in small portions. After stirring overnight at 50 °C, the reaction mixture was quenched by sodium bicarbonate aqueous solution and extracted with dichloromethane three times. The collected organic layer was dried over anhydrous $MgSO_4$, then the residue was purified by silica column chromatography using dichloromethane/hexane (1/5, v/v) as eluent to give the desired colorless liquid (yield: 52%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 7.52 (d, *J*=8.1 Hz, 2H), 7.38 (d, *J*=8.4 Hz, 2H), 7.19 (d, *J*=5.4, 1H), 6.77 (d, *J*=5.4 Hz 1H), 3.91 (s, 1H), 3.05 (d, *J*=4.8 Hz), 1.54 (s, 1H), 1.26 (m, 24H), 0.89 (m, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ(ppm) 144.68, 133.80, 132.10, 129.23, 123.97, 119.80, 119.16, 113.18, 50.64, 38.15, 34.06, 32.07, 31.90, 31.83, 30.02, 29.68, 29.57, 29.47, 29.33, 26.73, 26.69, 22.67, 14.12. MS (LC/MS): m/z founded 478.2 $[M+H]^+$, calcd. 477.21.

*Synthesis of 7-bromo-4-(2-hexyldecyl)thieno[3,2-c]isoquinolin-5(4H)-one (**12**).* A solution of trichloromethyl chloroformate (2.21 g, 4.62 mmol) in dichloroethane (5 mL) was added dropwise at 0 °C to **10** (1.37 g, 6.93 mmol) in dichloroethane (40 mL) and pyridine (5 mL). After stirring at 50 °C for 4 h, the reaction mixture was extracted by dichloromethane several times. The organic layer was washed with 1 M HCl and brine and then dried over anhydrous $MgSO_4$. The crude product **9** was obtained by concentrating the organic layer and used in the following reaction without further purification. A mixture of **9** and indium chloride (III) (1.02 g, 4.62 mmol) in tetrachloroethane (40 mL) was refluxed overnight. Subsequently, the reaction mixture was allowed to cool to room temperature and filtered through Celite, then concentrated under vacuum. The crude product was purified by silica gel chromatography using dichloromethane/hexane (2/1, v/v) as eluent, followed by recrystallization from hexane (yield: 65%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 8.58 (d, *J*=1.8 Hz, 1H), 7.71 (dd, *J*=8.7, 2.4 Hz, 1H), 7.52 (d, *J*=8.1, 1H), 7.45 (d, *J*=5.4 Hz, 1H), 7.04 (d, *J*=5.1 Hz, 1H), 4.17 (d, *J*=7.2 Hz, 2H), 1.96 (br, 1H), 1.32 (m, 24H), 0.86 (m, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) 160.85, 139.93, 135.45v 132.04, 131.12, 126.05, 125.10, 123.64, 120.03, 117.79, 116.69, 49.53, 37.03, 31.84, 31.75, 31.57, 31.52, 29.91, 29.62, 29.47, 29.24, 26.57, 22.62, 22.59, 14.09, 14.04. MS (LC/MS): m/z 504.2 $[M+H]^+$, calcd. 503.19.

Synthesis of 2,7-dibromo-5-(2-hexyldecyl)thieno[3,2-c]quinolin-4(5H)-one (TIQO). Bromine (0.53 g, 1.05 mmol) was slowly added to a mixture of **5** (0.42 g, 2.63 mmol) and a given amount of iron(III) chloride in dichloromethane. After stirring at room temperature overnight, the mixture was extracted by dichloromethane and dried over anhydrous $MgSO_4$. The crude product was purified by recrystallization from hexane to obtain a white solid (yield: 80%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm) 8.59 (s 1H), 7.60 (dd, *J*=8.7, 1.8 Hz, 1H), 7.45 (d, *J*=8.1, 1H), 7.05 (s, 1H), 4.12 (d, *J*=7.2 Hz, 2H), 1.94 (br, 1H), 1.29 (m, 24H), 0.85 (m, 6H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ (ppm) 160.39, 139.18, 135.64, 132.04, 130.29, 125.01, 123.23, 120.89, 120.35, 117.62, 114.91, 49.53, 36.93, 31.84, 31.76, 31.43, 31.38, 29.91, 29.62, 29.48, 29.25, 26.45, 22.64, 22.60, 14.10, 14.06. Elem Anal. Calcd. for $C_{27}H_{37}Br_2NOS$: C, 55.58; H, 6.39; N, 2.40; O, 2.74; S, 5.50. Found: C, 55.65; H, 6.19; N, 2.39; O, 2.65; S, 5.39. MS (LC/MS): m/z founded 582.1 $[M+H]^+$, calcd. 581.10.

Polymerization Procedure. The two copolymers were synthesized via Stille coupling polymerization. Generally, a mixture of ditinated monomer (0.3 mmol), dibrominated monomer (0.3 mmol), and $Pd(PPh_3)_4$ (8.9 μmol) was dissolved in anhydrous toluene (5 mL) and DMF (1 mL) and then stirred at 110 °C for 1 day. Subsequently, excess 2-bromothiophene and tributyl(thiophen-2-yl)stannane as end capper were added to the reaction mixture followed by further stirring. After 2 h, the reaction mixture was poured into methanol (200 mL), and the crude polymer was collected by filtration and purified by Soxhlet extraction using methanol, acetone, and hexane, respectively. The polymers were obtained by reprecipitation from the chloroform solution in methanol (200 mL).

Synthesis of PBDT-TQO. BDT (269.0 mg, 0.3 mmol), TQO (150.0 mg, 0.3 mmol), and $Pd(PPh_3)_4$ (10.3 mg, 8.9 μmol) were dissolved anhydrous toluene (5 mL) and DMF (1 mL). PBDT-TQO was then synthesized using the general polymerization procedure as an orange solid (yield: 68%). M_n = 19,100 g/mol, PDI = 5.49, T_d = 396.0 °C.

Synthesis of PBDT-TIQO. BDT (269.0 mg, 0.3 mmol), TIQO (150.0 mg, 0.3 mmol), and $Pd(PPh_3)_4$ (10.3 mg, 8.9 μmol) were dissolved anhydrous toluene (5 mL) and DMF (1 mL). PBDT-TQO was then synthesized using the general polymerization procedure as a red solid (yield: 75%). M_n = 23,100 g/mol, PDI = 4.04, T_d = 372.8 °C.

References

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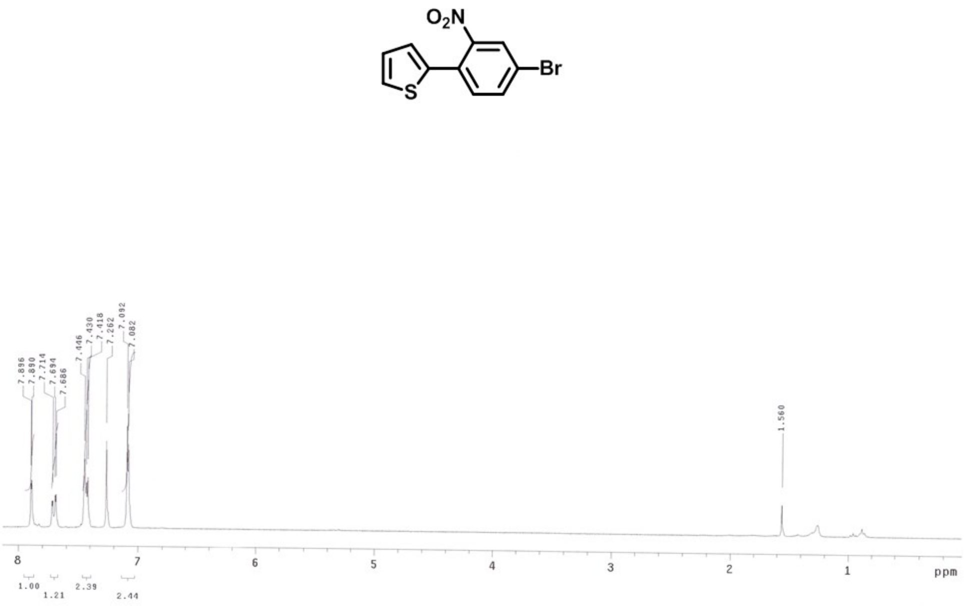


Fig. S1. ^{1}H NMR spectrum of **1** in CDCl$_3$.

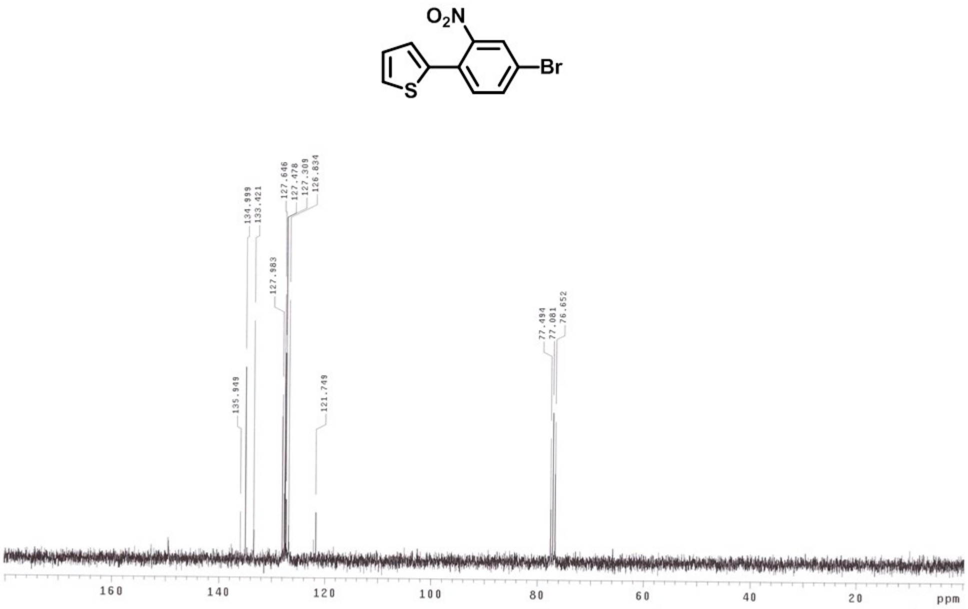


Fig. S2. ^{13}C NMR spectrum of **1** in CDCl$_3$.

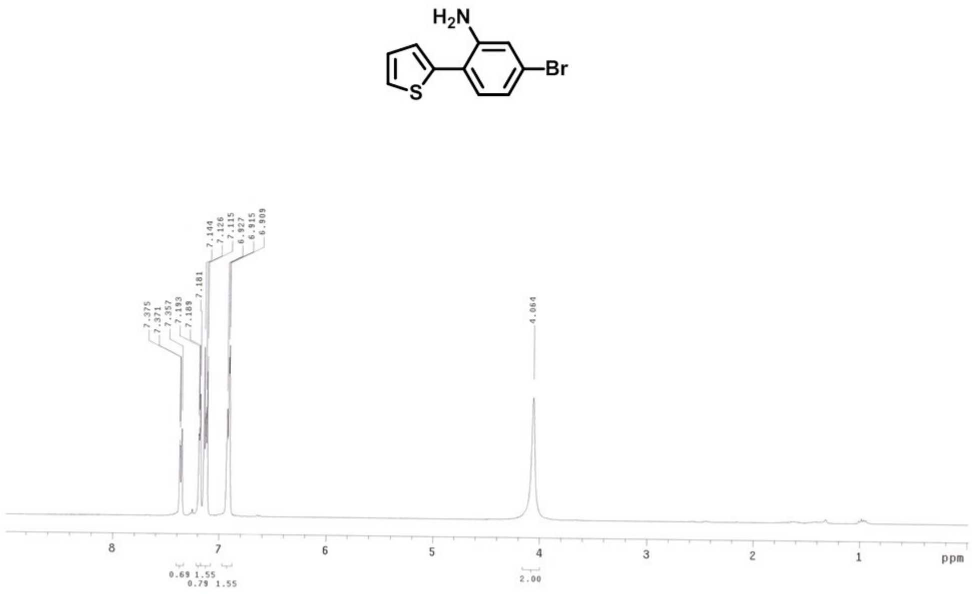


Fig. S3. ^{1}H NMR spectrum of **2** in CDCl$_3$.

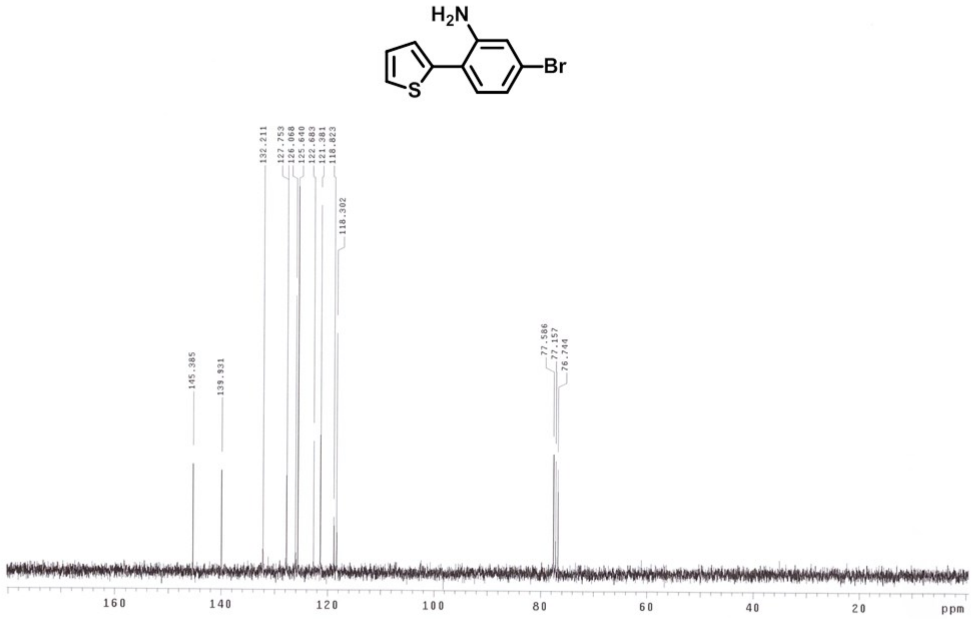


Fig. S4. ^{13}C NMR spectrum of **2** in CDCl$_3$.

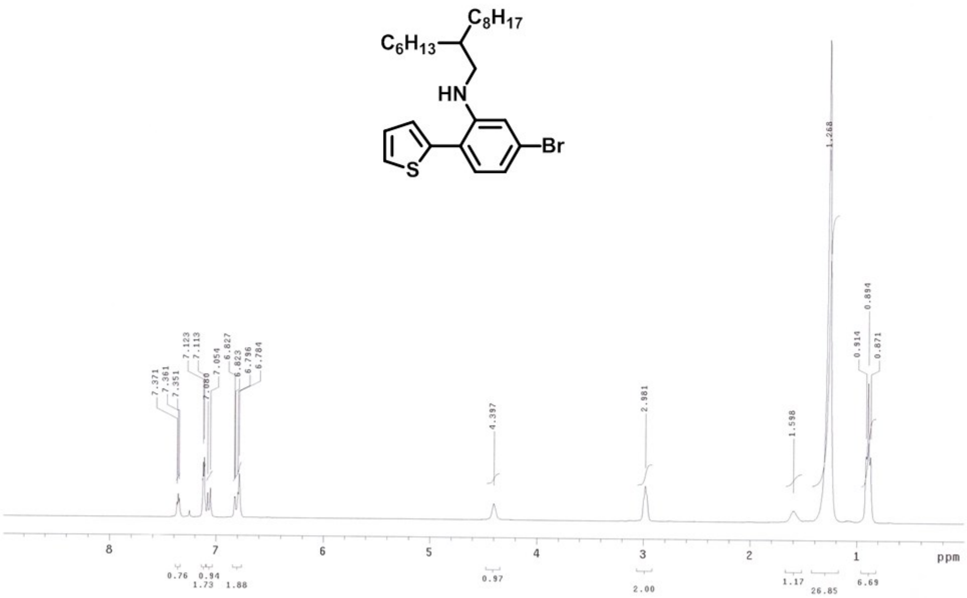


Fig. S5. ^{1}H NMR spectrum of **3** in $CDCl_3$.

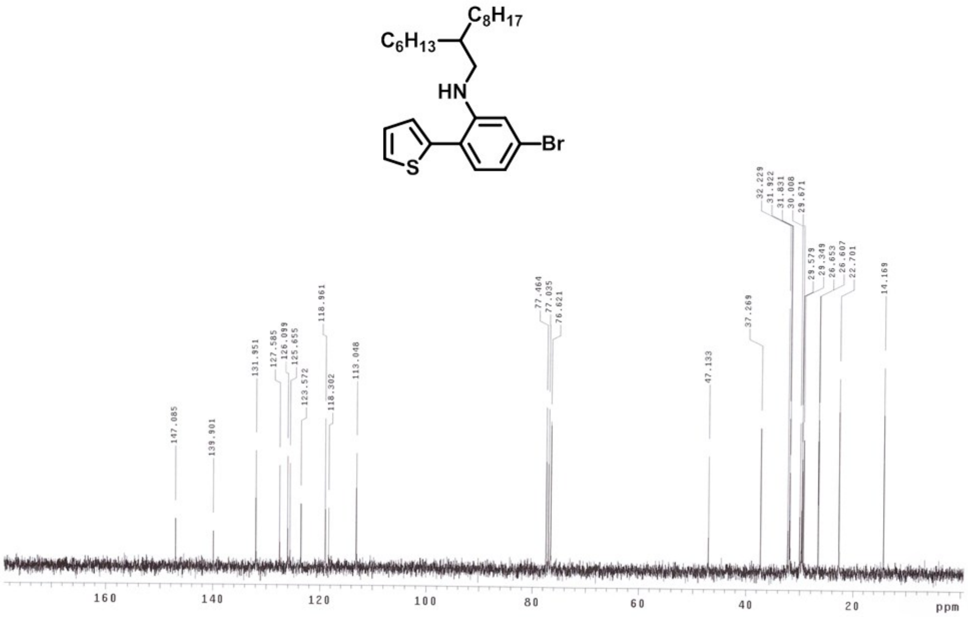


Fig. S6. ^{13}C NMR spectrum of **3** in $CDCl_3$.

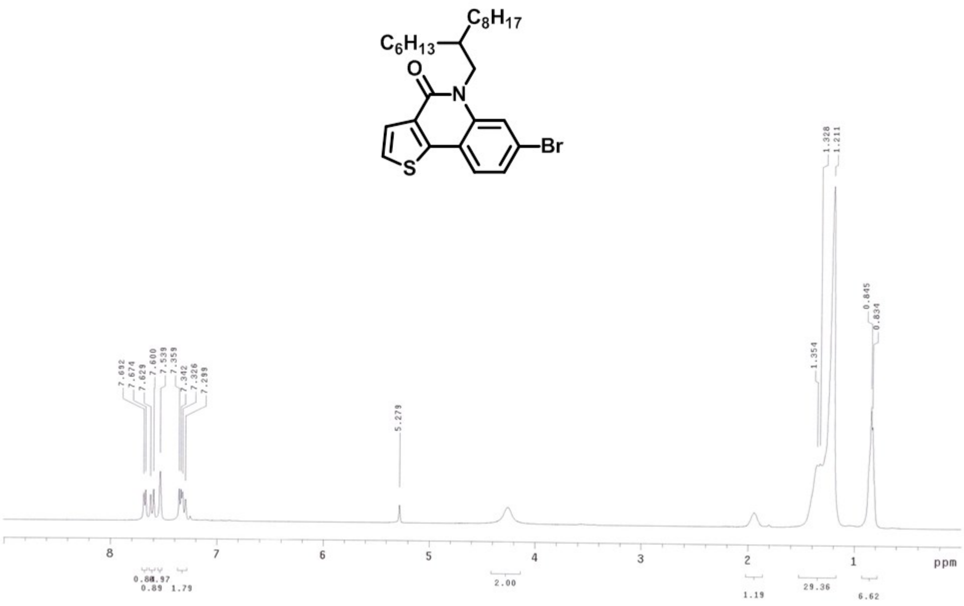


Fig. S7. ^{1}H NMR spectrum of **5** in CDCl$_3$.

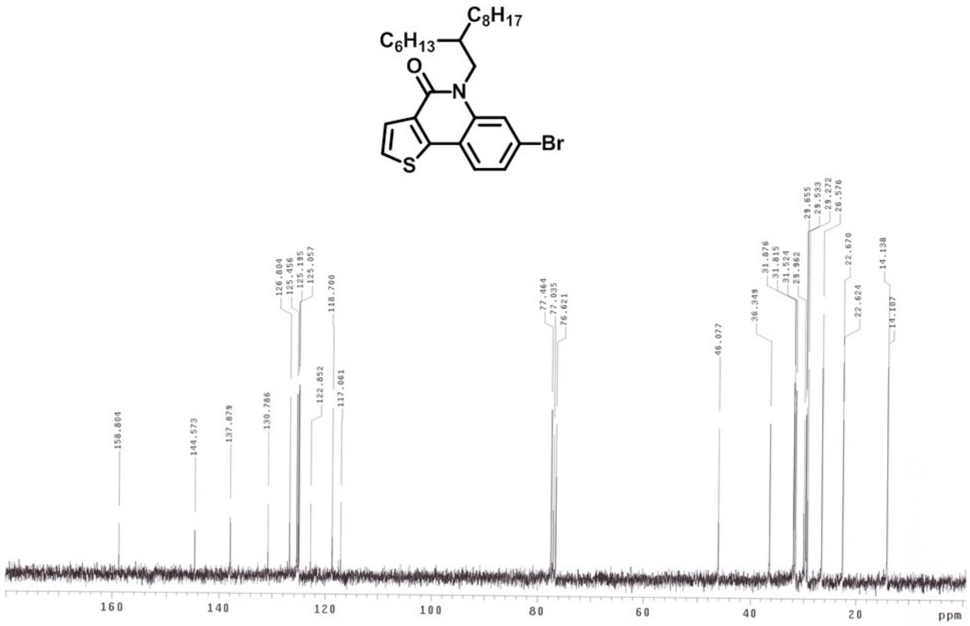


Fig. S8. ^{13}C NMR spectrum of **5** in CDCl$_3$.

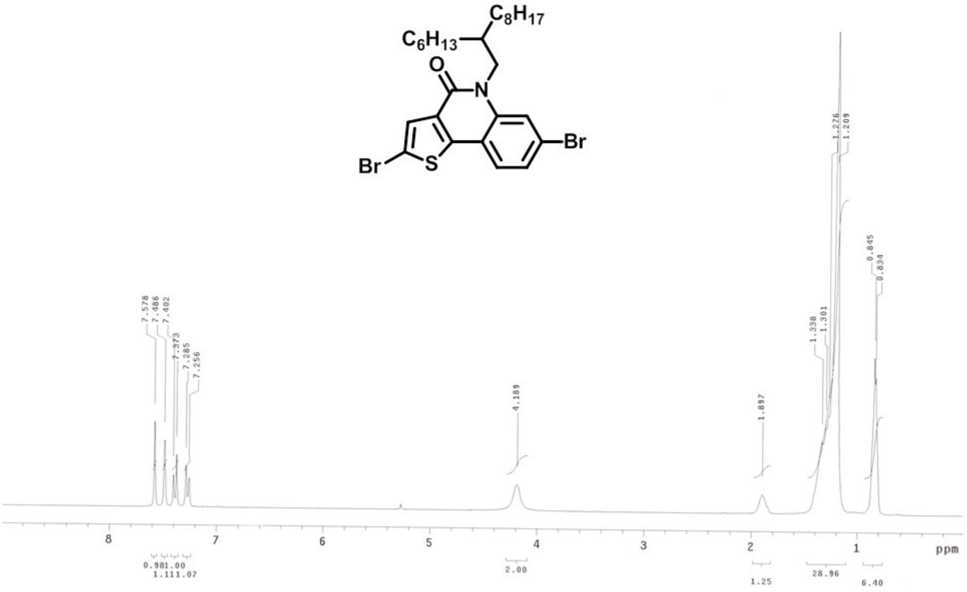


Fig. S9. ^{1}H NMR spectrum of TQO in $CDCl_3$.

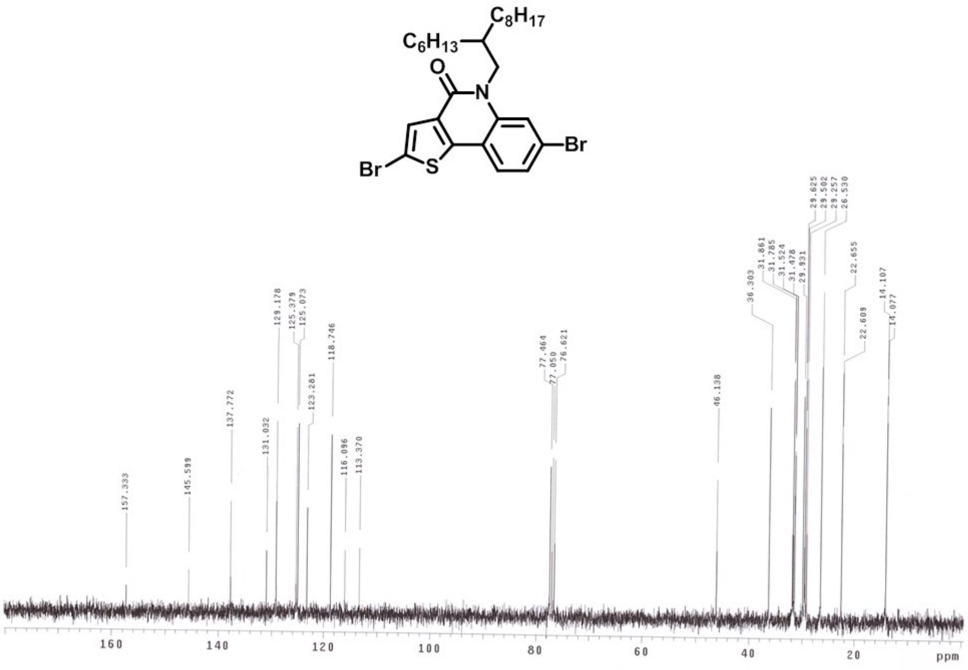


Fig. S10. ^{13}C NMR spectrum of TQO in $CDCl_3$.

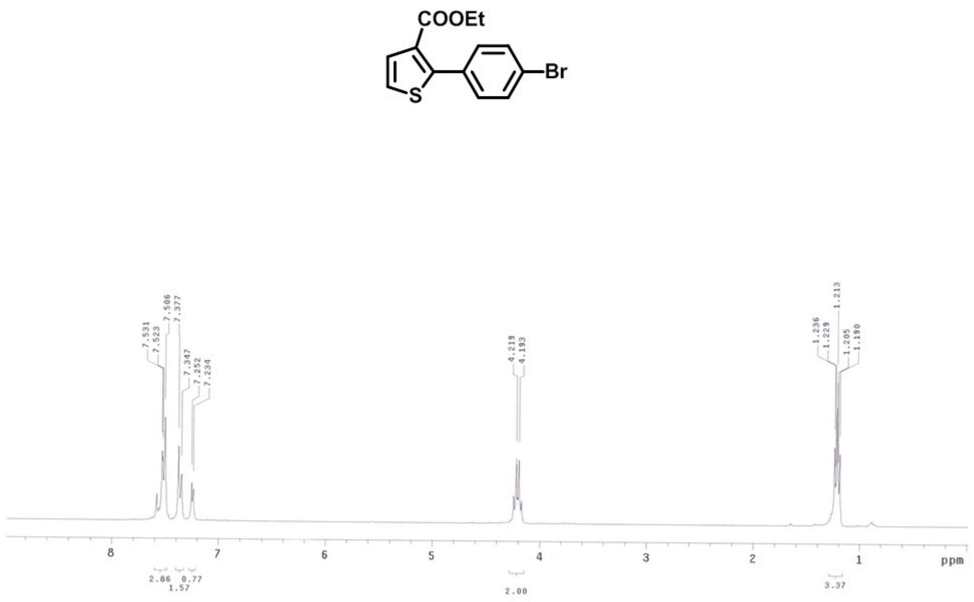


Fig. S11. ^{1}H NMR spectrum of **6** in CDCl$_3$.

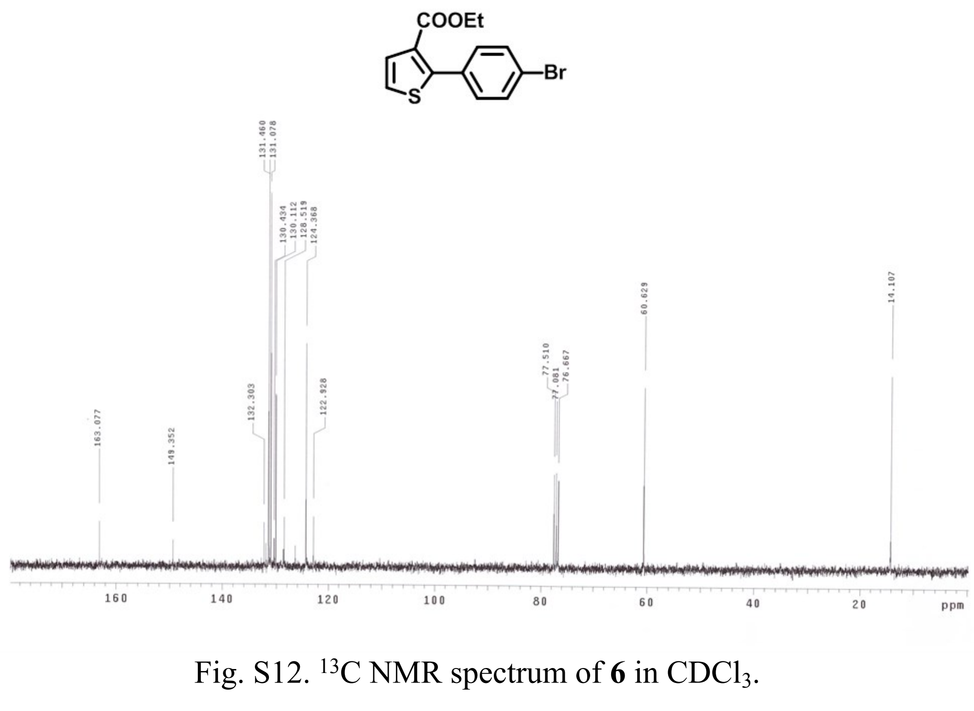


Fig. S12. ^{13}C NMR spectrum of **6** in CDCl$_3$.

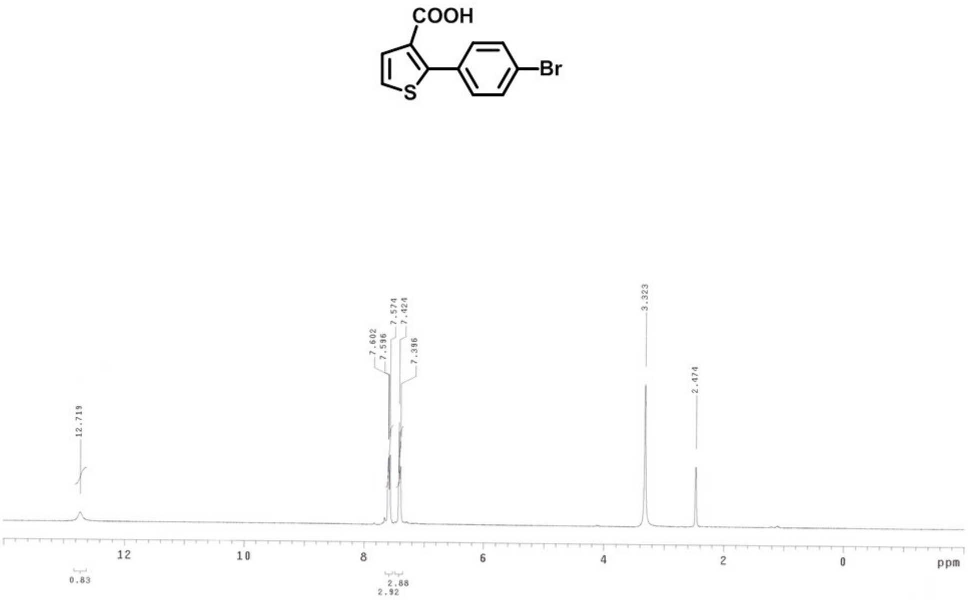


Fig. S13. ^{1}H NMR spectrum of **7** in DMSO-d$_6$.

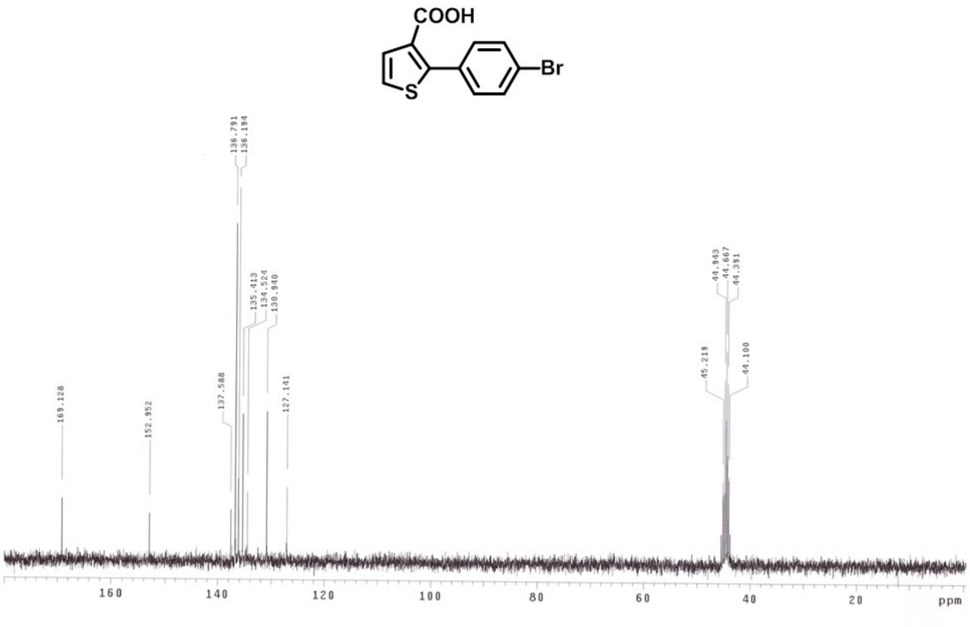


Fig. S14. ^{13}C NMR spectrum of **7** in DMSO-d$_6$.

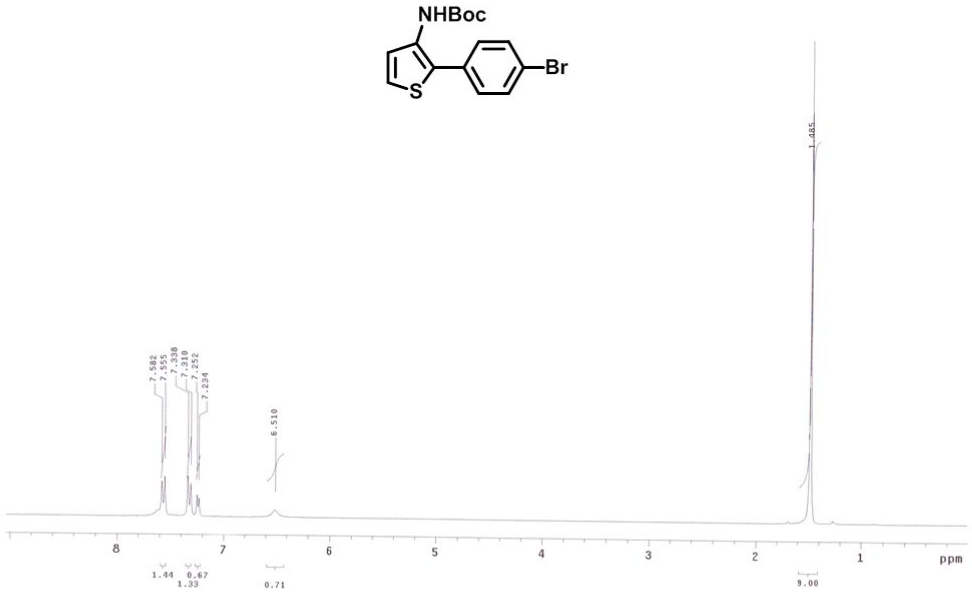


Fig. S15. ^{1}H NMR spectrum of **8** in $CDCl_3$.

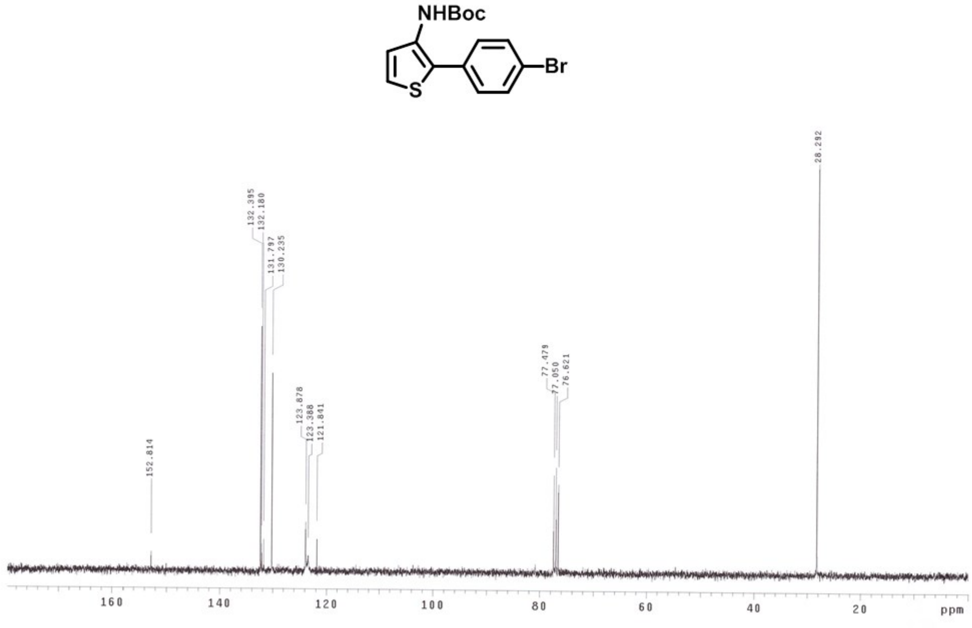


Fig. S16. ^{13}C NMR spectrum of **8** in $CDCl_3$.

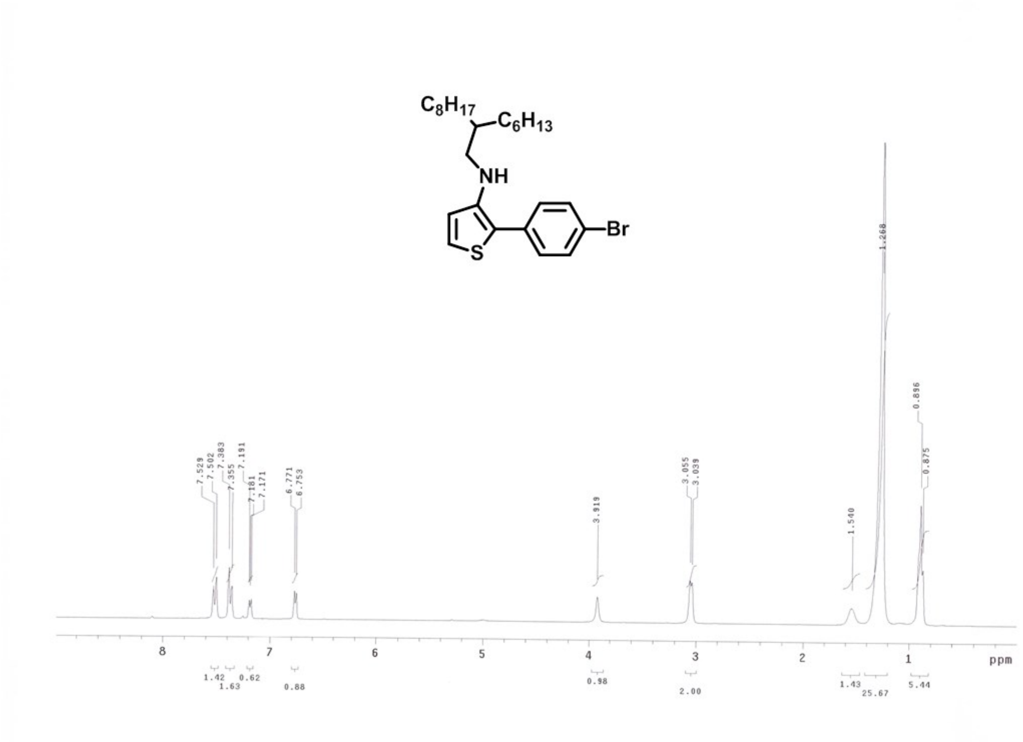


Fig. S17. ^{1}H NMR spectrum of **10** in CDCl$_3$.

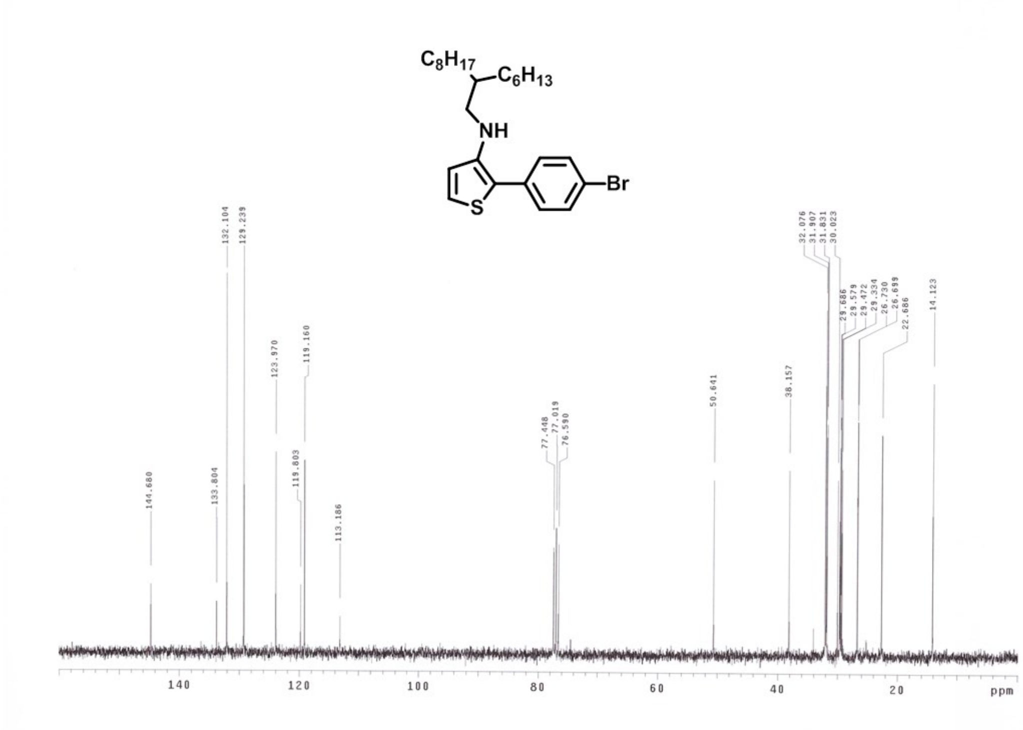


Fig. S18. ^{13}C NMR spectrum of **10** in CDCl$_3$.

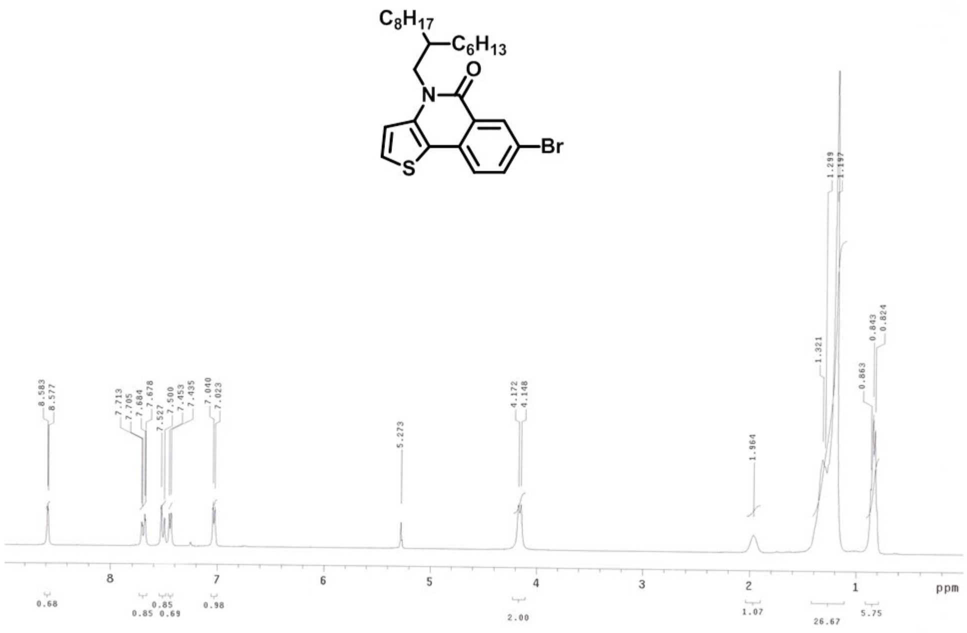


Fig. S19. ^{1}H NMR spectrum of **11** in $CDCl_3$.

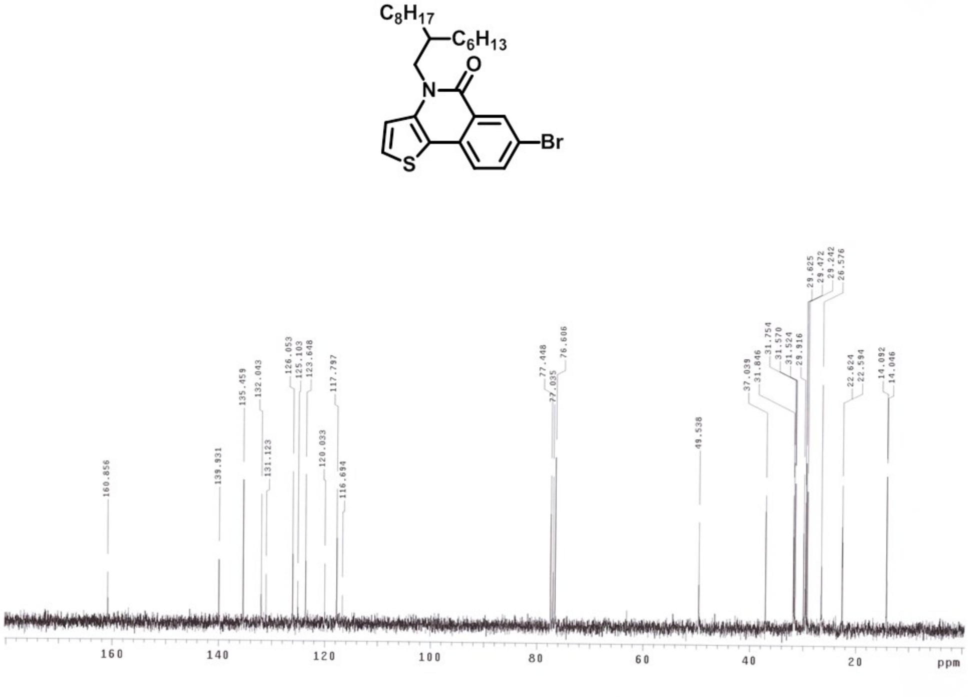


Fig. S20. ^{13}C NMR spectrum of **11** in $CDCl_3$.

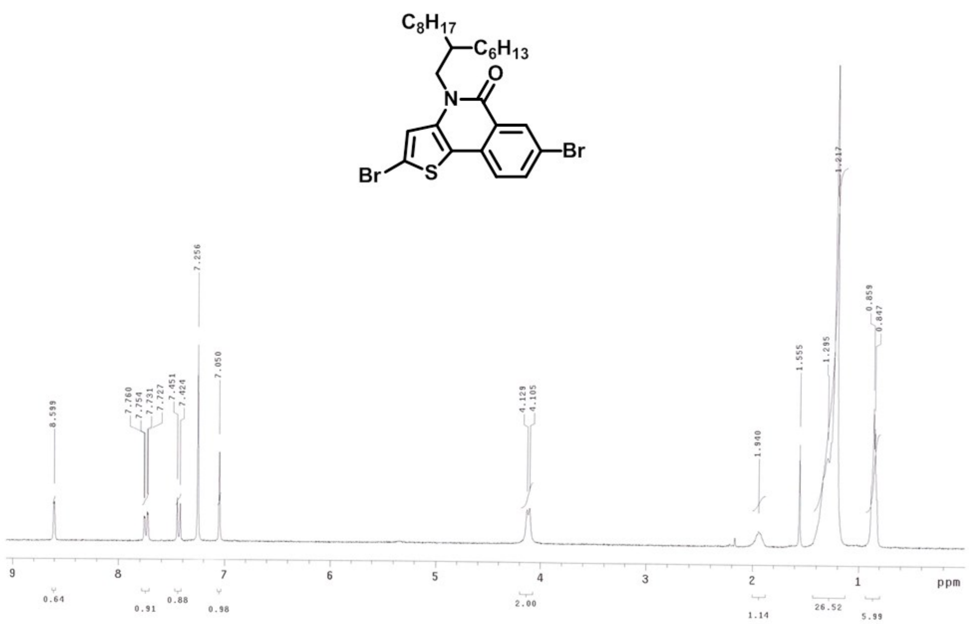


Fig. S21. ^{1}H NMR spectrum of TIQO in $CDCl_3$.

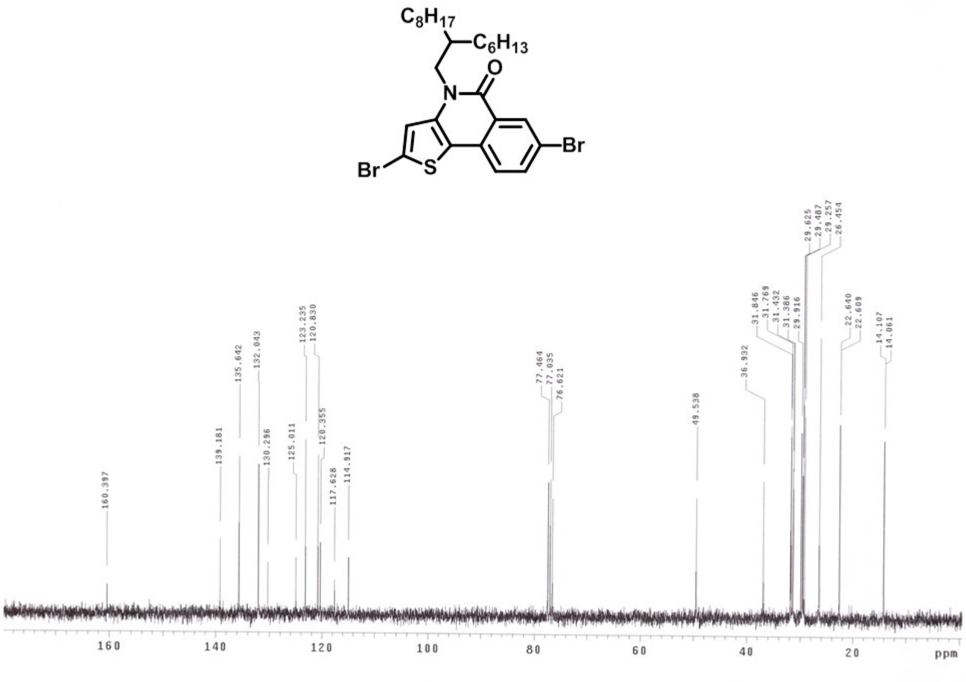
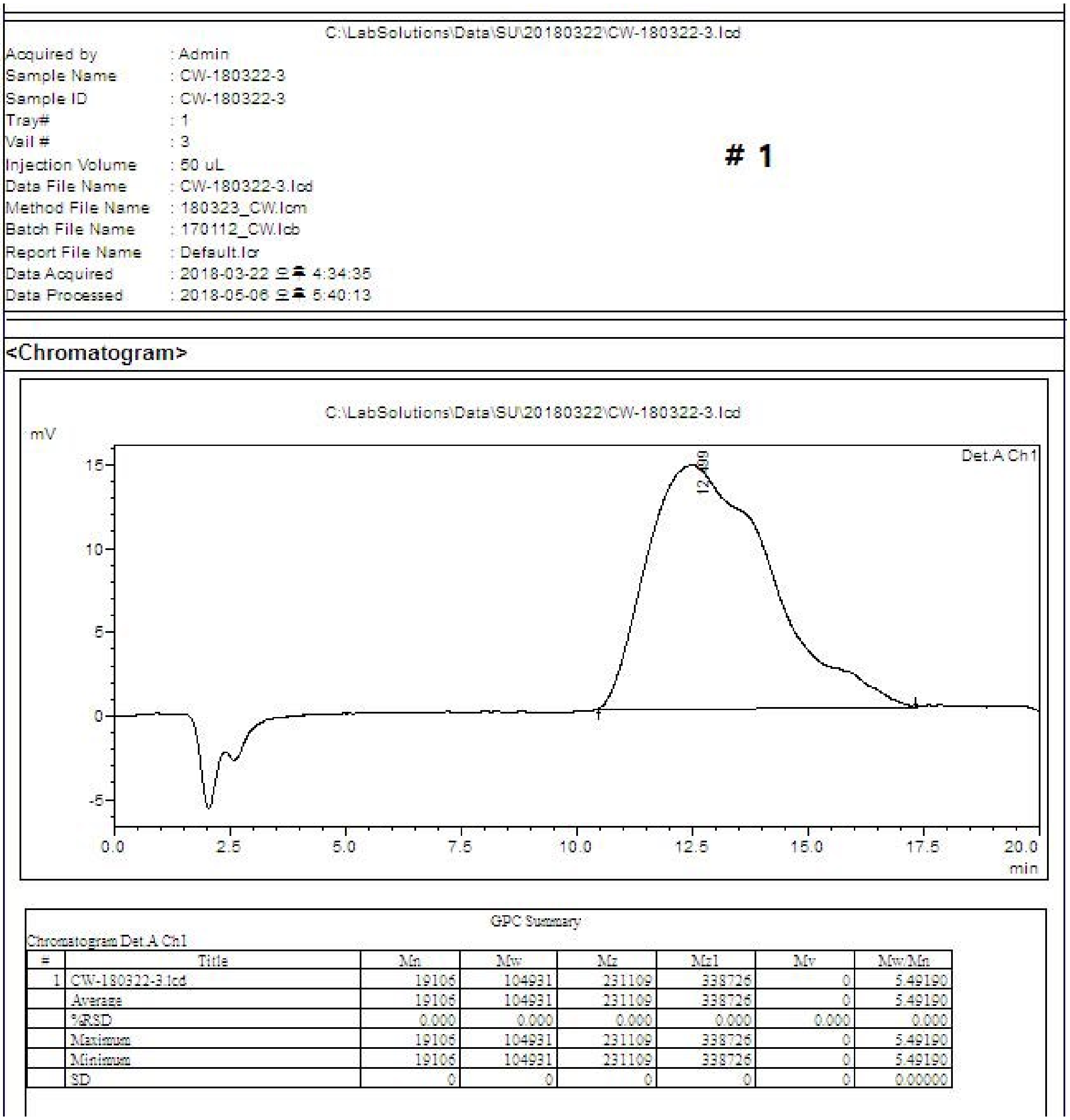


Fig. S22. ^{13}C NMR spectrum of TIQO in $CDCl_3$.



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 # 1

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GPC Summary

Chromatogram Det.A Ch1

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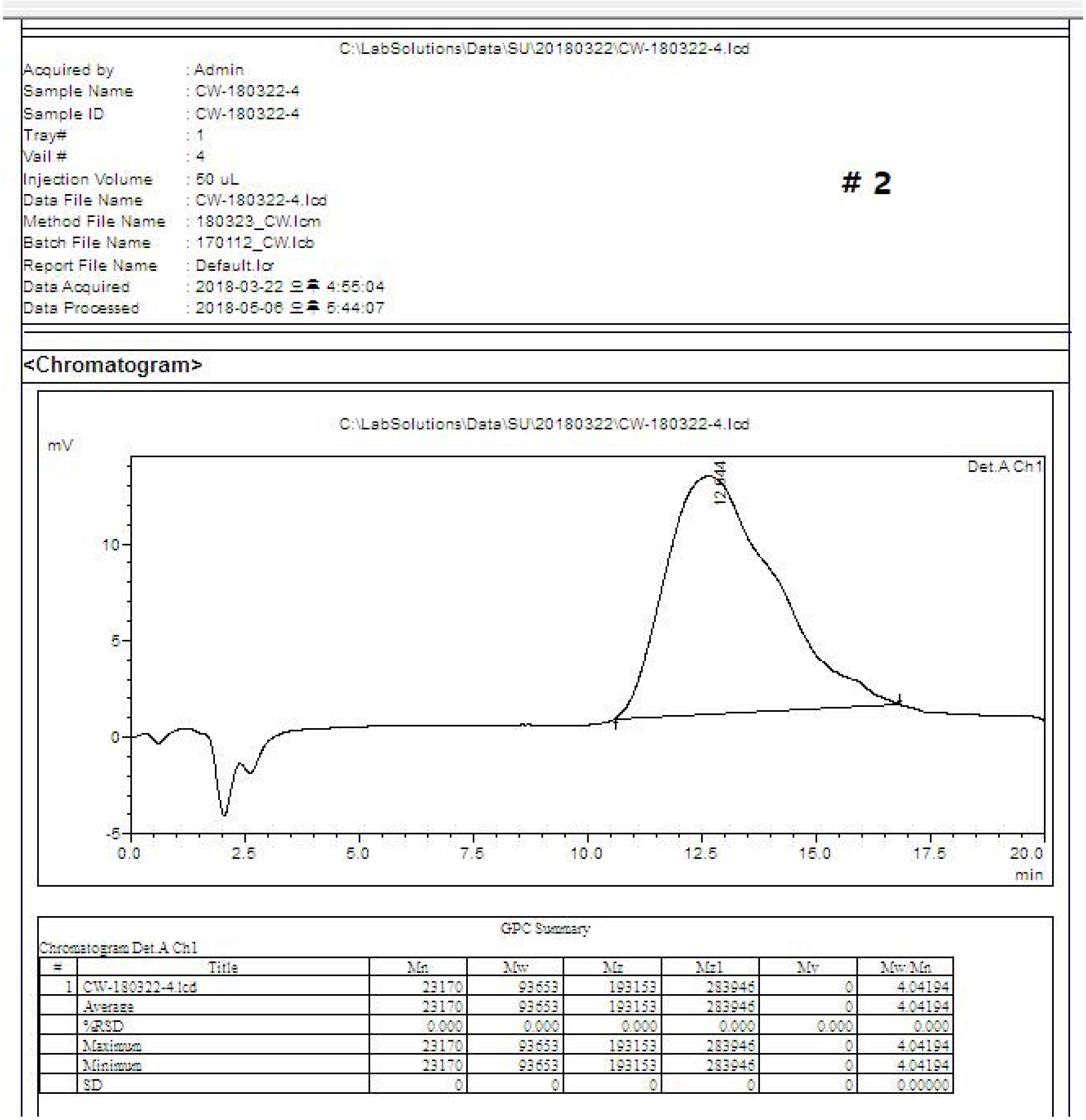
	Average	19106	104931	231109	338726	0	5.49190
	%RSD	0.000	0.000	0.000	0.000	0.000	0.000
	Maximum	19106	104931	231109	338726	0	5.49190
	Minimum	19106	104931	231109	338726	0	5.49190
	SD	0	0	0	0	0	0.00000

Fig. S23. The gel permeation chromatography result of PBDT-TQO.



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<Chromatogram>

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Chromatogram Det.A Ch1

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	Average	23170	93653	193153	283946	0	4.04194
	%RSD	0.000	0.000	0.000	0.000	0.000	0.000
	Maximum	23170	93653	193153	283946	0	4.04194
	Minimum	23170	93653	193153	283946	0	4.04194
	SD	0	0	0	0	0	0.00000

Fig. S24. The gel permeation chromatography result of PBDT-TIQO.

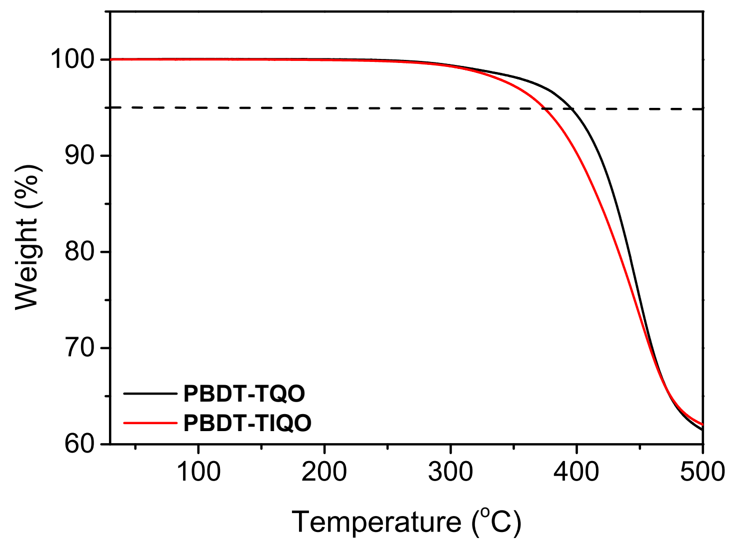

Fig. S25. The TGA curves of PDBT-TQO and PBDT-TIQO.

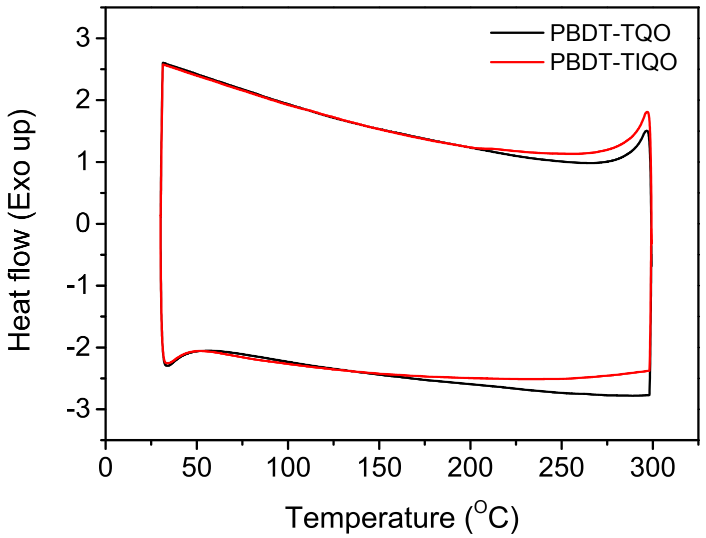

Fig. S26. The DSC curves of PBDT-TQO and PBDT-TIQO.

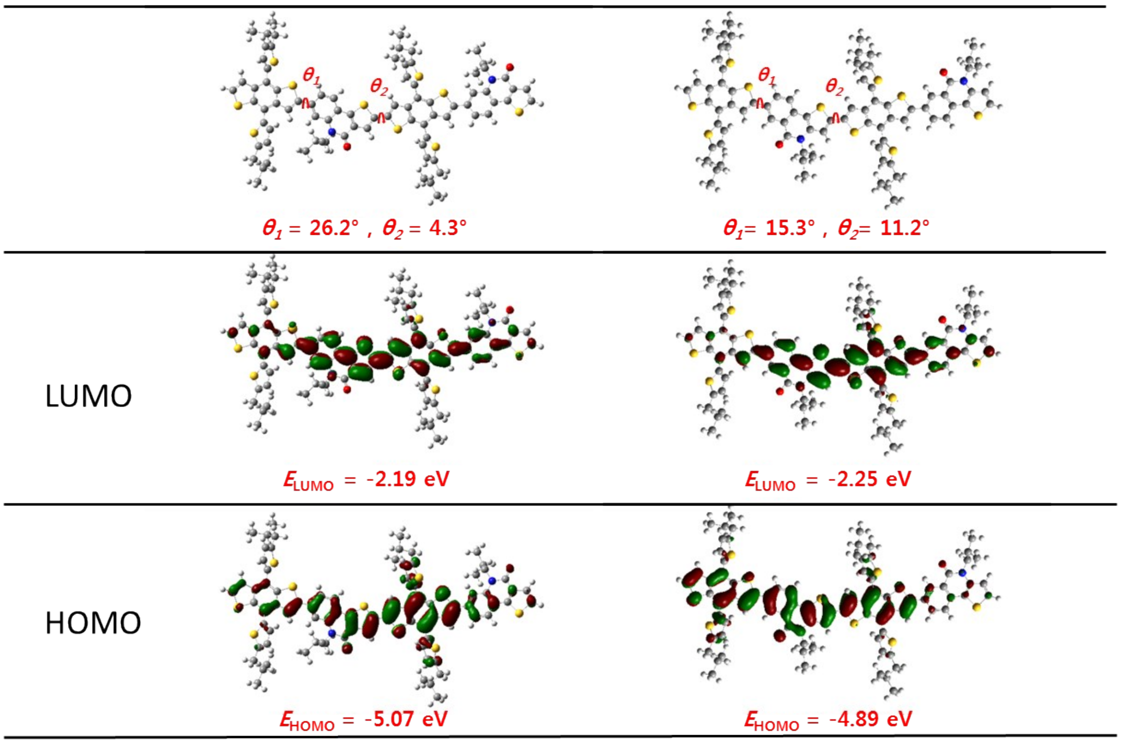

Fig. S27. Energy-minimized structures (B3LYP/6-31G(d)) of the HOMO and LUMO of the model compounds.

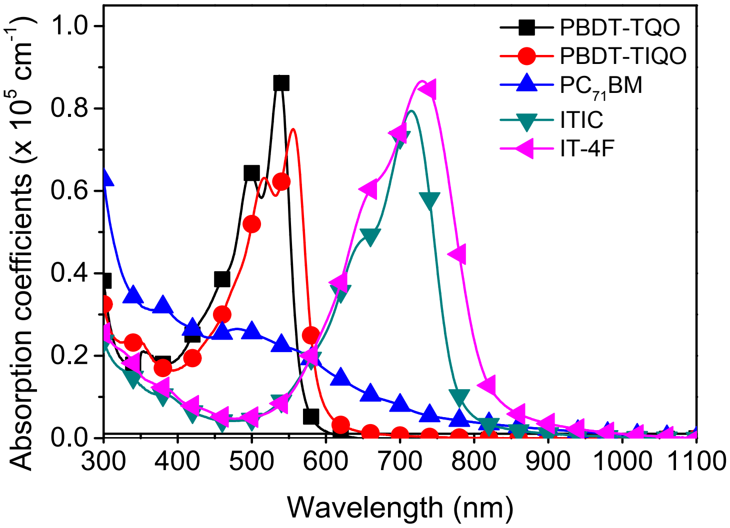

Fig. S28. Absorption coefficients of the polymers and acceptors.

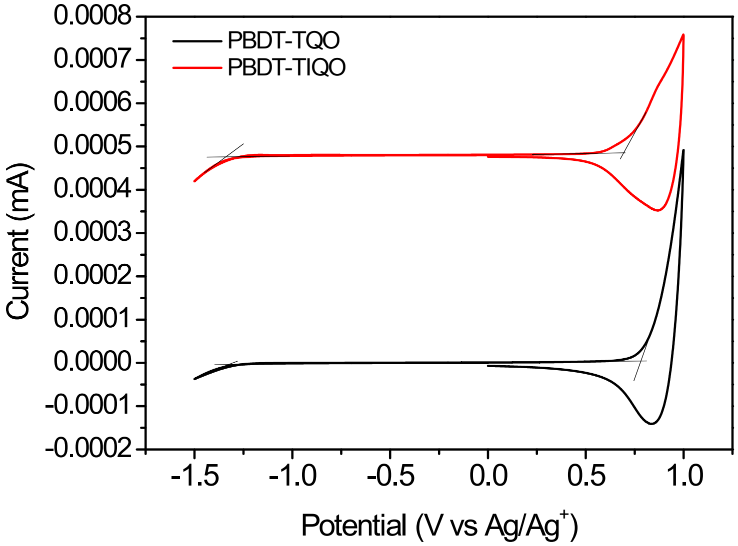

Fig. S29. Cyclic voltammograms for the polymers.

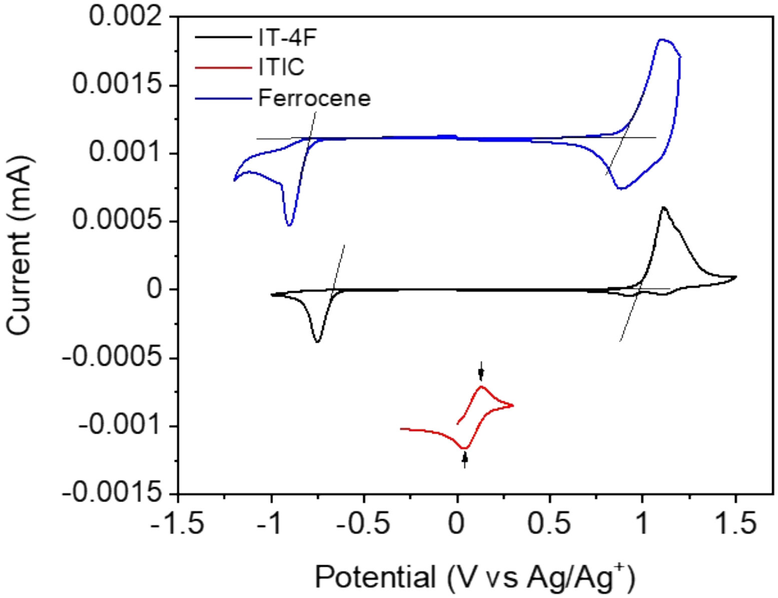

Fig. S30. Cyclic voltammograms for the non-fullerene acceptors.

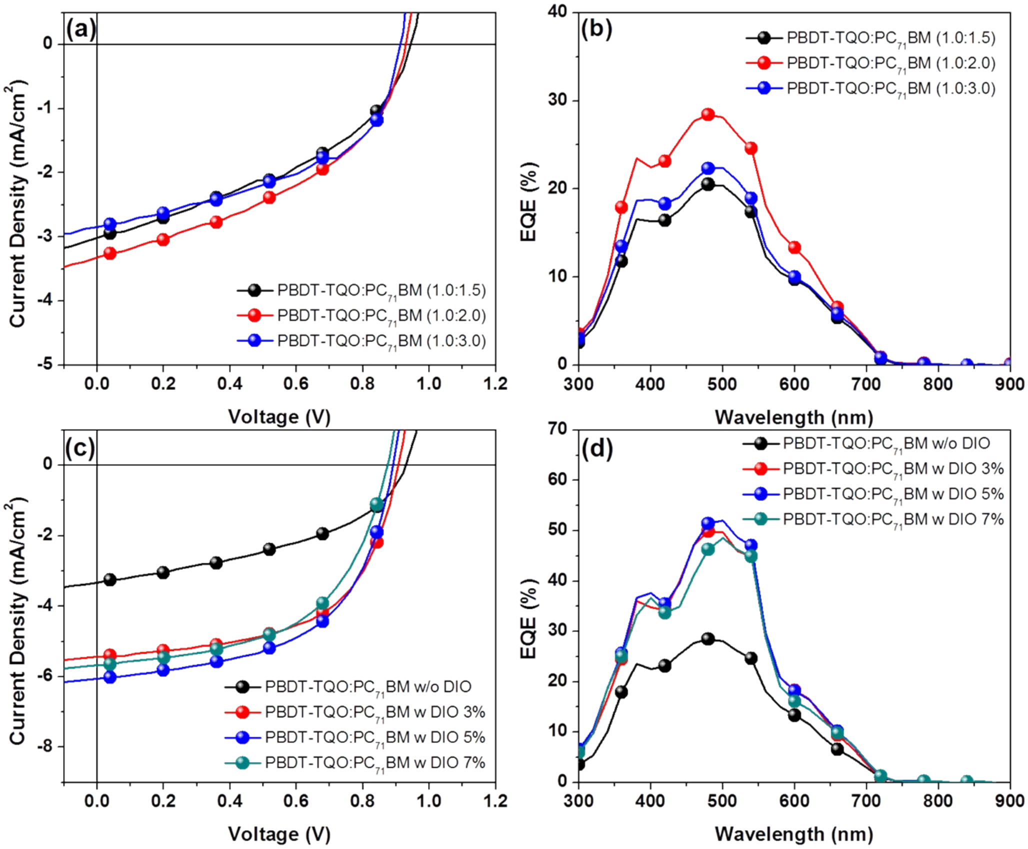

Fig. S31. (a) and (c) J-V characteristics, (b) and (d) EQE curves for BHJ OSCs based on PBDT-TQO:PC$_{71}$BM under illumination of AM 1.5G, 100 mW cm^{-2}.

Table S1. Device performance parameters of conventional PSCs with the structure of ITO/ZnO/PBDT-TQO:$PC_{71}BM/MoO_3$/Ag.

	Ratio	Addtive	V_{oc} (V)	J_{sc} (mA/cm^2)	$J_{calc.}$ (mA/cm^2)	*FF* (%)	*PCE* (%)
PBDT-TQO :$PC_{71}BM$	1.0:1.5	w/o	0.91 ± 0.04 (0.94)	0.91 ± 0.04 (0.94)	2.61	33.94 ± 8.71 (40.10)	0.92 ± 0.32 (1.14)
	1.0:2.0	w/o	0.87 ± 0.06 (0.93)	3.28 ± 0.09 (3.32)	3.60	37.89 ± 4.59 (43.84)	1.09 ± 0.20 (1.35)
		DIO 3 %	0.90 ± 0.01 (0.91)	5.44 ± 0.20 (5.58)	5.79	55.89 ± 3.35 (58.26)	2.79 ± 0.11 (2.87)
		DIO 5 %	0.89 ± 0.00 (0.89)	6.01 ± 0.11 (6.06)	5.98	56.27 ± 1.03 (55.98)	3.01 ± 0.02 (3.02)
		DIO 7 %	0.87 ± 0.00 (0.87)	5.68 ± 0.00 (5.68)	5.55	54.54 ± 0.00 (54.54)	2.71 ± 0.00 (2.71)
	1.0:3.0	w/o	0.86 ± 0.05 (0.91)	2.79 ± 0.05 (2.84)	2.84	43.21 ± 5.73 (49.43)	1.04 ± 0.21 (1.28)

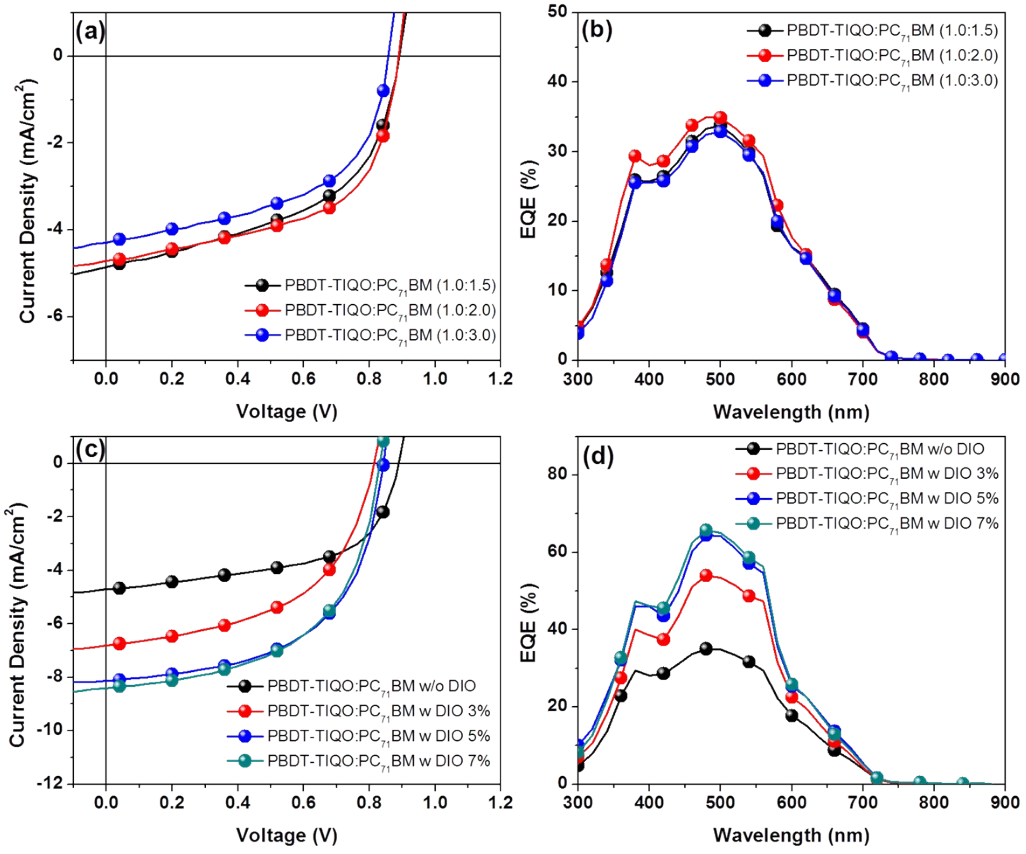

Fig. S32. (a) and (c) J-V characteristics, (b) and (d) EQE curves for BHJ OSCs based on PBDT-TIQO:PC$_{71}$BM under illumination of AM 1.5G, 100 mW cm^{-2}.

Table S2. Device performance parameters of conventional PSCs with the structure of ITO/ZnO/PBDT-TIQO:$PC_{71}BM/MoO_3$/Ag.

	Ratio	Addtive	V_{oc} (V)	J_{sc} (mA/cm^2)	$J_{calc.}$ (mA/cm^2)	FF (%)	PCE (%)
PBDT-TIQO :$PC_{71}BM$	1.0:1.5	w/o	0.83 ± 0.06 (0.89)	4.74 ± 0.14 (4.85)	4.45	41.66 ± 7.59 (50.68)	1.65 ± 0.45 (2.19)
	1.0:2.0	w/o	0.89 ± 0.00 (0.89)	4.71 ± 0.00 (4.71)	4.71	55.88 ± 2.34 (55.88)	2.34 ± 0.00 (2.34)
		DIO 3%	0.83 ± 0.02 (0.81)	6.86 ± 0.06 (6.82)	6.77	50.62 ± 2.92 (52.90)	2.87 ± 0.20 (2.94)
		DIO 5%	0.84 ± 0.01 (0.84)	8.17 ± 0.15 (8.14)	7.96	56.23 ± 1.21 (57.10)	3.84 ± 0.06 (3.92)
		DIO 7%	0.84 ± 0.01 (0.83)	8.29 ± 0.17 (8.41)	8.11	55.74 ± 0.52 (55.37)	3.86 ± 0.02 (3.87)
	1.0:3.0	w/o	0.86 ± 0.00 (0.86)	4.24 ± 0.07 (4.29)	4.38	51.75 ± 2.26 (55.35)	1.89 ± 0.11 (1.96)

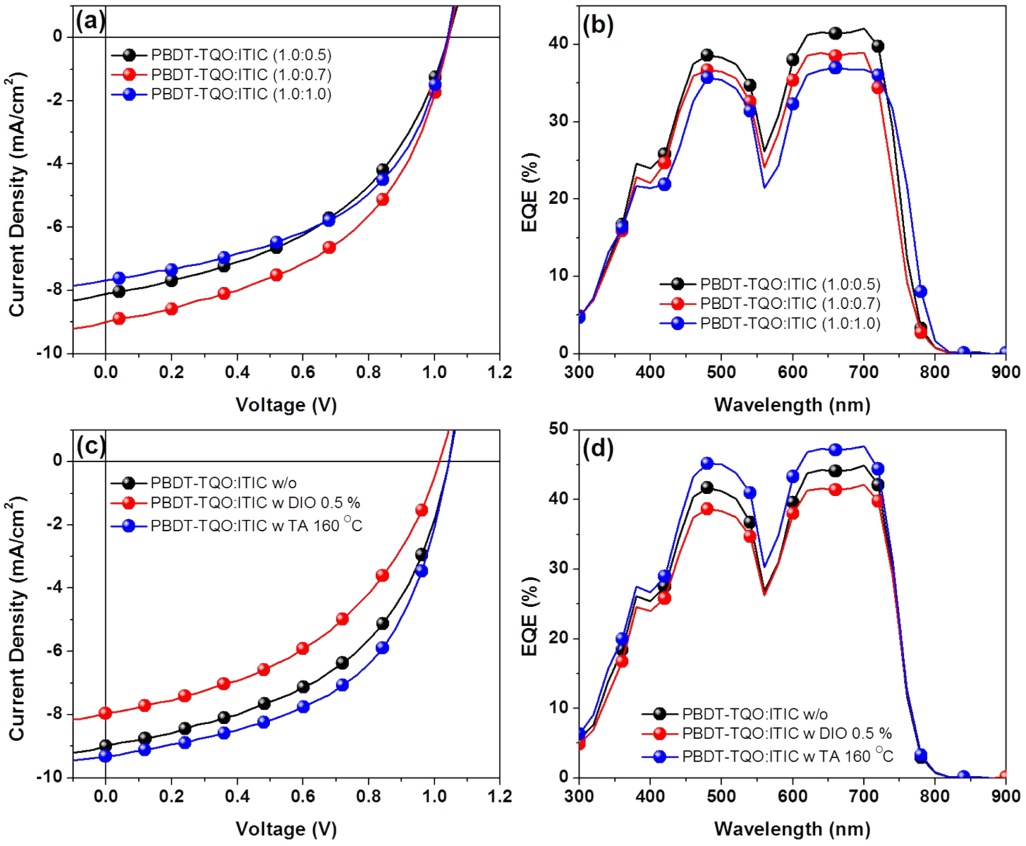

Fig. S33. (a) and (c) J-V characteristics, (b) and (d) EQE curves for BHJ OSCs based on PBDT-TQO:non-fullerene acceptor under illumination of AM 1.5G, 100 mW cm^{-2}.

Table S3. Device performance parameters of conventional PSCs with the structure of ITO/ZnO/PBDT-TQO:ITIC/MoO_3/Ag.

	Ratio	Addtive	TA	V_{oc} (V)	J_{sc} (mA/cm^2)	$J_{calc.}$ (mA/cm^2)	*FF* (%)	*PCE* (%)
PBDT-TQO :ITIC	1.0:0.5	w/o	w/o	1.03 ± 0.02 (1.04)	7.68 ± 0.37 (8.10)	8.69	44.54 ± 2.23 (46.42)	3.52 ± 0.40 (3.92)
	1.0:0.7	w/o	w/o	1.04 ± 0.01 (1.04)	8.77 ± 0.21 (9.00)	9.34	48.40 ± 1.27 (48.55)	4.42 ± 0.14 (4.56)
		w/o	160 °C	1.04 ± 0.01 (1.04)	9.29 ± 0.23 (9.32)	9.91	52.47 ± 1.30 (53.04)	5.08 ± 0.10 (5.16)
		DIO 0.5%	w/o	1.02 ± 0.01 (1.01)	7.23 ± 0.67 (7.96)	8.69	44.81 ± 0.44 (44.83)	3.32 ± 0.30 (3.68)
	1.0:1.0	w/o	w/o	1.04 ± 0.01 (1.04)	7.57 ± 0.10 (7.69)	7.84	48.89 ± 1.01 (49.71)	3.85 ± 0.15 (3.98)

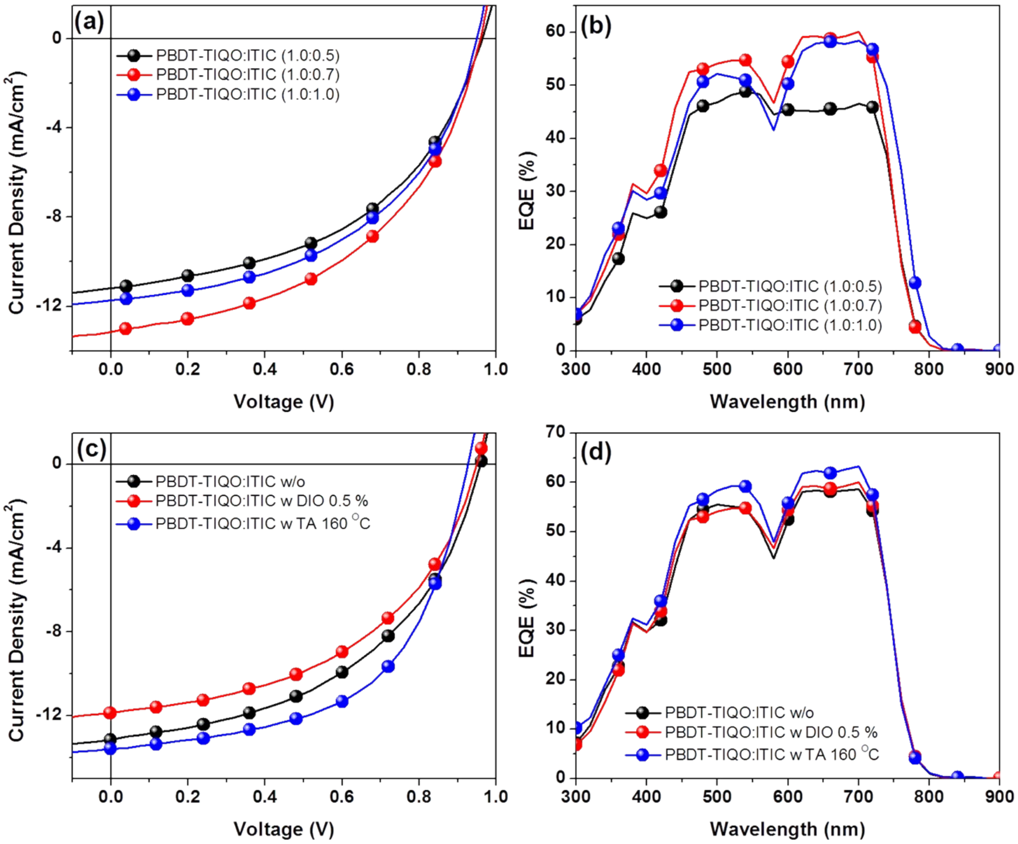

Fig. S34. (a) and (c) J-V characteristics, (b) and (d) EQE curves for BHJ OSCs based on PBDT-TQO:non-fullerene acceptor under illumination of AM 1.5G, 100 mW cm^{-2}.

Table S4. Device performance parameters of conventional PSCs with the structure of ITO/ZnO/PBDT-TQO:ITIC/MoO_3/Ag.

	Ratio	Addtive	TA	V_{oc} (V)	J_{sc} (mA/cm^2)	$J_{calc.}$ (mA/cm^2)	*FF* (%)	*PCE* (%)
PBDT-TIQO :ITIC	1.0:0.5	w/o	w/o	0.96 ± 0.01 (0.96)	11.05 ± 0.24 (11.18)	11.72	47.18 ± 0.97 (48.35)	5.01 ± 0.23 (5.21)
	1.0:0.7	w/o	w/o	0.96 ± 0.01 (0.96)	12.96 ± 0.27 (13.16)	13.20	48.75 ± 0.31 (48.45)	6.07 ± 0.08 (6.11)
		w/o	160 °C	0.95 ± 0.00 (0.95)	13.09 ± 0.31 (13.33)	13.17	51.83 ± 0.46 (51.67)	6.45 ± 0.09 (6.56)
		DIO 0.5%	w/o	0.95 ± 0.01 (0.95)	11.42 ± 0.24 (11.67)	12.51	47.15 ± 0.85 (48.02)	5.11 ± 0.19 (5.21)
	1.0:1.0	w/o	w/o	0.94 ± 0.01 (0.95)	11.47 ± 0.25 (11.74)	11.89	47.94 ± 1.19 (49.27)	5.17 ± 0.31 (5.49)

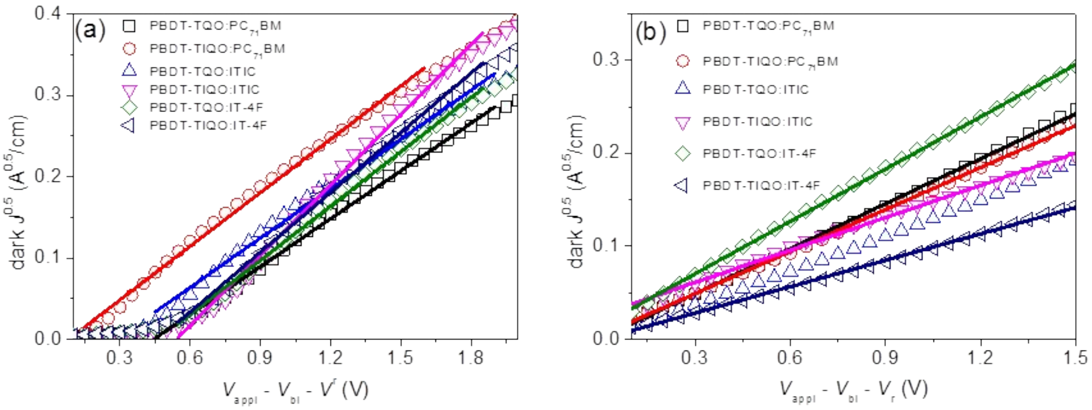

Fig. S35. *J*–*V* characteristics of (a) hole-only and (b) electron-only devices based on BHJ films.

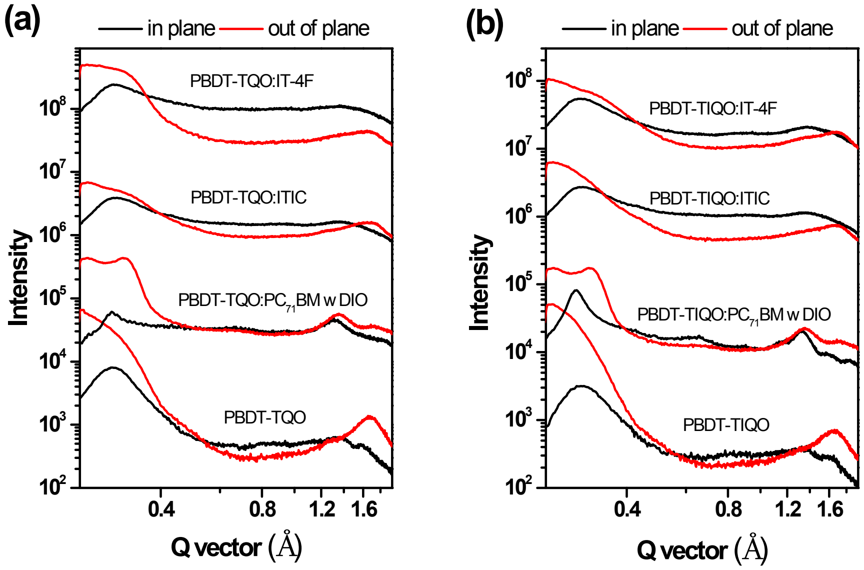

Fig. S36. The in-plane and out-of-plane line cut profiles in the 2D-GIWAXS data for: (a) neat and blended films of PBDT-TQO and (b) neat and blended films of PBDT-TIQO.