Electronic supplementary information (ESI) for

Optimizing the vectorial component of first hyperpolarizabilities of push-pull chromophores to boost the electro-optic activities of poled polymers over broad telecom wavelength bands

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Experimental section

Materials and instruments

All chemicals were purchased from Energy Chemical or Dieckmann, and used as received unless otherwise mentioned. The ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker 300MHz "AVANCE III HD" Nuclear Magnetic Resonance System (NMR-300), Bruker 400MHz "AVANCE III" Nuclear Magnetic Resonance System (NMR-400) and Bruker 600MHz "AVANCE III HD" Nuclear Magnetic Resonance System (NMR-600). High resolution mass spectrometry (HRMS) was taken at Thermo Scientific Q Exactive mass spectrometer. For the formulation of EO polymers, the solvent dibromomethane (DBM) and 1,1,2-trichloroethane (TCE) were distilled prior to use. The cyclic voltammetric data were measured by Electrochemical Analyzer (CHI 750) using Ag/AgCl as the reference electrode, the platinum wire as working electrode, platinum gauze (5*5*0.3 mm) as counter electrode and 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF) as the electrolyte in dichloromethane. Thermogravimetric analysis (TGA) were carried out on aPerkinElmer Simultaneous Thermal Analyzer STA 6000 at the heating rate of 10 °C min^{-1}. Films used in absorption spectra and EO measurements were spin-coated on glass or ITO glass substrates with SPIN-PROCESS CONTROLLER. The UV-*vis*-NIR spectra of chromophores were recorded with Ultra-Violet Visible Scanning Spectrophotometer (Shimadzu 1700) and Ultra-Violet Visible Near Infra-red Spectrophotometer with Integrating Sphere (PE Lamda 750). DFT calculations using Gaussian 09 package were carried out at the level

of B3LYP/6-31G(d,p) for ground-state geometry optimization and CAM-B3LYP/6-31G(d,p) for static hyperpolarizability calculation.[1]

Poling and measurement of r_{33} values and refractive indices

For studying the EO property derived from the chromophores, guest-host polymers were formulated by mixing chromophores at a given loading density into the host polymer Poly(styrene-*co*-methyl methacrylate) (P(S-*co*-MMA)) in the solvent DBM or TCE. The resulting solutions were filtered through a 0.22 μm PTFE filter and spin-coated onto indium tin oxide (ITO) glass substrates. After the soft baking, films of doped polymers were baked in a vacuum oven overnight at 60-70 °C to ensure the removal of the residual solvent. Thicknesses of films were measured by DektakXT Stylus Profiler and confirmed on the subsequent optical measurement for refractive indices at the wavelengths of 1304 nm and 1541 nm by a commercial prism-coupler system (Metricon 2010/M). Then using the Desk V HP Cold Sputter Unit (Denton Vacuum LLC), a thin layer (~20 nm) of semi-transparent gold was sputtered onto the films as a top electrode for contact poling and subsequent EO modulation measurement. The electric field poling of films was conducted at central processor-controlled Mettler FP82 hot stage. The poling field was set at 100 V μm^{-1} with the assist of monitoring the LTC by Keithley 2657A Source-Meter Unit. The optical poling temperature were around 100-110 °C. After the poling, the refractive indices and r_{33} values of poled films were measured using the attenuated total reflectance (ATR) method in slab waveguide geometry on Metricon 2010/M, in which modulation voltages were provided for EO coefficient measurement.

Preparation of N-2

To a solution of compound **N-1** (5.0 g, 24.3 mmol) in 20 mL of DMF was cooled in ice-bath for 15 min. A solution of NBS (4.55 g, 25.6 mmol) in DMF (10 mL) was added slowly and the mixture was stirred for 12 h. The reaction mixture was dropped into water and extracted with hexane. The organic layer was dried with anhydrous Na_2SO_4 and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography (silica gel, hexane) to give **N-2** as a colorless liquid (6.57 g, 95%).

^{1}H NMR ($CDCl_3$, 400MHz, ppm): δ 7.25 (d, J= 9.2Hz, 2H), 6.50 (d, J= 8.4 Hz, 2H), 3.22 (t, J= 7.7 Hz, 4H), 1.58-1.52 (m, 4H), 1.37-1.31 (m, 4H), 0.95 (t, J= 7.4 Hz, 6H).

HR-MS calcd for $C_{14}H_{23}BrN$ $[M+H]^+$ m/z 284.10084, found m/z 284.10110.

Preparation of N-3

$Pd_2(dba)_3$ (0.25 g, 0.3 mmol) and tri-*o*-tolylphosphine (0.34g, 1.1 mmol) were added to a solution of **N-2** (4.0 g, 14.1 mmol) and 2-tributylstannyl thiophene (5.8 g, 15.5 mmol) in toluene. The mixture was stirred and refluxed under nitrogen for 24 h. After completion of the reaction, the solvent was evaporated under vacuum and the residue was purified by column chromatography on silica gel with dichloromethane/hexane as eluent, which gave the product as a yellow oil (quantitative).

^{1}H NMR ($CDCl_3$, 400MHz, ppm): δ 7.45 (d, J= 8.8Hz, 2H), 7.13-7.11 (m, 2H), 7.02 (dd, J= 3.6 Hz, 5.0 Hz, 1H), 6.63 (d, J= 8.9Hz, 2H), 3.28 (t, J= 7.9Hz, 3H), 1.66-1.59 (m, 4H), 1.39-1.31 (m, 4H), 0.96 (t, J= 7.3 Hz, 6H).

HR-MS calcd for $C_{18}H_{26}NS$ $[M+H]^+$ m/z 288.17805, found m/z 288.17807.

Preparation of N-4

Phosphorus oxychloride (1.43 ml, 15.3 mmol) was added dropwise to a solution of DMF (20 ml) containing **N-3** (4.0 g, 13.9 mmol) at 0 °C. The solution was reacted at 70 °C for 5 h and cooled to ambient temperature. DI Water (100 ml) was added to the solution and the mixture was neutralized with sodium bicarbonate. The mixture was extracted with CH_2Cl_2 and washed with brine. After the solvent was removed by evaporator, the residue was purified by chromatography (silica gel, dichloromethane/hexane) to give **N-4** as a deep yellow solid (2.48 g, 56 %).

^{1}H NMR ($CDCl_3$, 400MHz, ppm): δ 9.80 (s, 1H), 7.67 (d, J= 4.0 Hz, 1H), 7.53 (d, J= 8.9 Hz, 2H), 7.21 (d, J= 4.0Hz, 1H), 6.64 (d, J= 9.0 Hz, 2H), 3.31 (t, J= 7.7Hz, 4H), 1.63-1.55 (m, 4H), 1.40-1.34 (m, 4H), 0.97 (t, J= 7.3 Hz, 6H).

^{13}C NMR ($CDCl_3$, 100MHz, ppm): δ 182.42, 156.39, 149.05, 139.68, 138.28, 127.70, 121.11, 119.70, 111.51, 50.79, 29.40, 20.33, 14.02.

HR-MS calcd for $C_{19}H_{26}NOS$ $[M+H]^+$ m/z 316.17296, found m/z 316.17242.

Preparation of N-5

4-methoxybenzeneacetonitrile (0.28 g, 1.9 mmol) and *t*-BuOK (0.27 g, 2.4 mmol) were successively added to anhydrous EtOH (5 mL) in a round bottomed flask, which was stirred at room temperature for 10 min. Then **N-4** (0.5 g, 1.6 mmol) was added to the

solution, and the mixture was further stirred at room temperature for 24h. Then the solid was filtered off, washed with 10 mL EtOH and dried under vacuum to give **N-5** as an orange solid (0.61 g, 87 %).

^{1}H NMR ($CDCl_3$, 600MHz, ppm): δ 7.56 (d, J= 8.9Hz, 2H), 7.52 (d, J= 8.9 Hz, 2H), 7.48 (d, J= 3.4 Hz, 2H), 7.14 (d, J= 4.1Hz, 1H), 6.94 (d, J= 8.8 Hz, 2H), 6.64 (d, J= 8.9Hz, 2H), 3.85 (s, 3H), 3.31 (t, J= 7.7Hz, 4H), 1.62-1.57 (m, 4H), 1.40-1.34 (m, 4H), 0.97 (t, J= 7.4 Hz, 6H).

^{13}C NMR ($CDCl_3$, 100MHz, ppm): δ 159.89, 150.20, 148.41, 134.82, 133.95, 132.83, 127.34, 127.00, 126.79, 120.70, 120.36, 118.90, 114.45, 111.59, 105.04, 55.44, 50.78, 29.45, 20.36, 14.04.

HR-MS calcd for $C_{28}H_{33}N_2OS$ $[M+H]^+$ m/z 445.23081, found m/z 445.23059.

Preparation of N-6

The procedure for compound **N-5** was followed to prepare **N-6** from **N-4** and 4-(dimethylamino)benzeneacetonitrile as an orange solid (0.39 g, 81 %).

^{1}H NMR ($CDCl_3$, 600MHz, ppm): δ 7.53-7.50 (m, 4H), 7.45 (d, J= 3.8 Hz, 1H), 7.41 (s, 1H), 7.12 (d, J= 4.0Hz, 1H), 6.72 (d, J= 9.0 Hz, 2H), 6.63 (d, J= 8.9Hz, 2H), 3.30 (t, J= 7.7Hz, 4H), 3.01 (s, 6H), 1.62-1.57 (m, 4H), 1.40-1.34 (m, 4H), 0.97 (t, J= 7.4 Hz, 6H).

^{13}C NMR ($CDCl_3$, 100MHz, ppm): δ 150.42, 149.10, 148.26, 135.43, 133.00, 130.29, 127.25, 126.47, 122.07, 120.66, 120.59, 119.14, 112.30, 111.61, 105.87, 50.80, 40.31, 29.49, 20.40, 14.11.

HR-MS calcd for $C_{29}H_{36}N_3S$ $[M+H]^+$ m/z 458.26245, found m/z 458.26208.

Preparation of N-7

The solution of **N-5** (0.25 g, 0.56 mmol) in dry toluene was cooled to -78 °C, and the solution of diisobutyl aluminum hydride (DIBAL-H) in hexane (1.0 M, 1.68 mL, 1.68 mmol) was added dropwise using a syringe. The solution was warmed on an ice bath and stirred for 3 h. Wet silica gel was added to quench the reaction and the mixture was stirred at 0 °C for 1 h. The product mixture was evaporated and purified by chromatography to give the product as a dark red oil (0.18 g, 72 %). The ratio of the Z : E isomers is 12% : 88% calculated by the integration of respective protons.

^{1}H NMR ($CDCl_3$, 300MHz, ppm): δ 10.60 (s, 0.12H, CHO), 9.66 (s, 0.88H, CHO), 7.61 (s, 0.12H), 7.51 (s, 0.87H), 7.38 (d, J=8.7Hz,0.27H), 7.32 (d, J=8.9Hz,1.75H), 7.24-7.14

(m, 3H), 7.05-6.92 (m, 3H), 6.65 (d, J= 8.8 Hz, 0.29H), 6.57 (d, J= 8.7 Hz, 1.75H), 3.88 (s, 3H), 3.27 (t, J= 7.6 Hz, 4H), 1.59-1.51 (m, 4H), 1.41-1.29 (m, 4H), 0.96 (t, J= 7.2 Hz, 6H).

^{13}C NMR ($CDCl_3$, 75MHz, ppm): δ 193.04, 159.97, 152.78, 148.43, 143.14, 137.13, 136.28, 134.85, 131.15, 127.29, 125.15, 120.53, 120.26, 114.62, 111.46, 55.35, 50.78, 29.40, 20.33, 14.02.

HR-MS calcd for $C_{28}H_{34}NO_2S$ $[M+H]^+$ m/z 448.23048, found m/z 448.23041.

Preparation of N-8

The procedure for compound **N-7** was followed to prepare **N-8** from **N-6** as a dark red solid (0.16 g, 80 %).

^{1}H NMR ($CDCl_3$, 600MHz, ppm): δ 9.66 (s, 1H, CHO), 7.46 (s, 1H), 7.33 (d, J= 8.8Hz, 2H), 7.23 (d, J= 4.0Hz, 1H),7.13 (d, J= 8.6Hz, 2H), 7.03 (d, J= 3.9Hz, 1H), 6.82 (d, J= 8.5Hz, 2H), 6.57 (d, J= 8.8 Hz, 2H), 3.27 (t, J= 7.7 Hz, 4H), 3.02 (s, 6H), 1.58-1.53 (m, 4H), 1.38-1.31 (m, 4H), 0.95 (t, J= 7.4 Hz, 6H).

^{13}C NMR ($CDCl_3$, 100MHz, ppm): δ 193.51, 152.08, 150.81, 148.34, 142.40, 137.68, 135.78, 135.35, 130.63, 127.32, 120.61, 120.53, 120.30, 112.87, 111.48, 50.78, 40.57, 29.44, 20.35, 14.05.

HR-MS calcd for $C_{29}H_{37}N_2OS$ $[M+H]^+$ m/z 461.26211, found m/z 461.26205.

Preparation of N-9

To a solution of **N-3** (0.5 g, 1.7 mmol) in THF was added 1.2 mL of *n*-BuLi (1.6 M, 1.9 mmol) in hexanes dropwise at 0 °C, under nitrogen for 1 h. The solution was warmed up to room temperature and stirred for 1 h, and then cooled to 0 °C. A solution of 3-(dimethylamino)acrolein (0.20 g, 2.0 mmol) in THF was added dropwise, and the resulting mixture was stirred for 6 h at room temperature. The reaction was then quenched with 10 mL water, and the mixture was extracted with CH_2Cl_2. The combined organic layer was washed with water and dried over Na_2SO_4. After the solvent was evaporated, the residue was purified by chromatography to give the product as a dark red solid (0.31 g, 52 %).

^{1}H NMR ($CDCl_3$, 300MHz, ppm): δ 9.57 (d, J= 7.8Hz, 1H), 7.53-7.46 (m, 3H), 7.25 (d, J= 3.8Hz, 1H), 7.11 (d, J= 3.9Hz, 1H), 6.62 (d, J= 8.9Hz, 2H), 6.41 (dd, J= 7.8Hz,

15.4Hz, 1H), 3.30 (t, J= 7.6 Hz, 4H), 1.63-1.53 (m, 4H), 1.43-1.30 (m, 4H), 0.97 (t, J= 7.3 Hz, 6H).

^{13}C NMR ($CDCl_3$, 75MHz, ppm): δ 192.91, 151.63, 148.61, 145.12, 135.65, 134.45, 127.34, 125.38, 121.47, 120.06, 111.55, 50.79, 29.42, 20.35, 14.04.

HR-MS calcd for $C_{21}H_{28}NOS$ $[M+H]^+$ m/z 342.18861, found m/z 342.18857.

Preparation of APTBD-1

N-7 (0.11 g, 0.25 mmol) and the CF_3-TCF acceptor (68 mg, 0.27 mmol) were added in anhydrous ethanol (3 mL). The reaction mixture was allowed to stir at 65 °C for 2 h and monitored by TLC. After the removal of the solvents, the residue was purified by column chromatography eluting with hexane/ethyl acetate to give the chromophore product as a dark solid (110 mg, 65 %).

^{1}H NMR ($CDCl_3$, 300MHz, ppm): δ 8.31 (d, J= 14.9Hz, 1H), 7.51 (s, 1H), 7.32-7.27 (m, 3H), 7.13-7.06 (m, 5H), 6.56 (d, J= 8.9Hz, 2H), 5.71 (d, J= 14.9Hz, 1H), 3.94 (s, 3H), 3.29 (t, J= 7.6 Hz, 4H), 1.70 (s, 3H), 1.62-1.51 (m, 4H), 1.41-1.29 (m, 4H), 0.96 (t, J= 7.3 Hz, 6H).

^{13}C NMR ($CDCl_3$, 100MHz, ppm): δ 175.81, 162.05, 160.43, 157.42, 154.48, 149.17, 142.61, 139.39, 137.10, 131.00, 127.68, 125.74, 121.76, 115.42, 112.89, 111.64, 111.54, 111.45, 110.86, 94.15, 93.35, 57.25, 55.44, 50.83, 29.43, 20.30, 18.95, 13.98.

HR-MS calcd for $C_{39}H_{38}F_3N_4O_2S$ $[M+H]^+$ m/z 683.26621, found m/z 683.26428.

Preparation of APTBD-2

N-7 (0.12 g, 0.27 mmol) and the TCF acceptor (58.8 mg, 0.30 mmol) were added in anhydrous ethanol. The reaction mixture was allowed to stir at 65 °C for 12 h and monitored by TLC. After the removal of the solvents, the residue was purified by column chromatography eluting with hexane/ethyl acetate to give the chromophore product as a dark solid (118 mg, 70 %).

^{1}H NMR ($CDCl_3$, 300MHz, ppm): δ 7.94 (d, J= 15.2Hz, 1H), 7.39 (s, 1H), 7.29 (d, J= 8.9Hz, 2H), 7.17 (d, J= 4.1Hz, 1H), 7.13-7.05 (m, 5H), 6.56 (d, J= 9.0 Hz, 2H), 5.75 (d, J= 15.2Hz, 1H), 3.94 (s, 3H), 3.28 (t, J= 7.6 Hz, 4H), 1.63-1.51 (m, 10H), 1.41-1.28 (m, 4H), 0.95 (t, J= 7.3 Hz, 6H).

^{13}C NMR ($CDCl_3$, 100MHz, ppm): δ 176.31, 173.26, 160.36, 155.01, 152.74, 148.77, 140.08, 137.46, 136.70, 136.47, 130.98, 127.40, 126.03, 121.20, 120.12, 115.46,

113.89, 112.59, 111.74, 111.49, 111.44, 97.03, 94.47, 55.43, 50.80, 29.42, 26.33, 20.31, 14.01.

HR-MS calcd for $C_{39}H_{41}N_4O_2S$ $[M+H]^+$ m/z 629.29447, found m/z 629.29285.

Preparation of APTBD-3

The procedure for compound **APTBD-1** was followed to prepare **APTBD-3** from **N-8** as a dark solid (145 mg, 60 %).

^1H NMR ($CDCl_3$, 300MHz, ppm): δ 8.31 (d, J= 14.8Hz, 1H), 7.49 (s, 1H), 7.33 (d, J= 8.8Hz, 2H), 7.27-7.25 (m, 1H), 7.11(d, J= 4.1Hz, 1H), 7.00 (d, J= 8.7Hz, 2H), 6.85 (d, J= 8.8 Hz, 2H), 6.56 (d, J= 8.4 Hz, 2H), 5.81 (d, J= 14.9 Hz, 1H), 3.29 (t, J= 7.7 Hz, 4H), 3.08 (s, 6H), 1.61-1.51 (m, 4H), 1.41-1.29 (m, 4H), 0.95 (t, J= 7.3 Hz, 6H).

^{13}C NMR ($CDCl_3$, 100MHz, ppm): δ 175.94, 162.16, 157.03, 155.23, 151.06, 149.06, 142.77, 138.99, 138.24, 137.46, 130.35, 127.68, 121.86, 120.44, 120.15, 113.28, 113.08, 111.74, 111.58, 111.51, 110.98, 93.65, 93.33, 56.92, 50.81, 40.48, 29.44, 20.31, 19.00, 13.99.

HR-MS calcd for $C_{40}H_{41}F_3N_5OS$ $[M+H]^+$ m/z 696.29784, found m/z 696.29639.

Preparation of APTBD-4

The procedure for compound **APTBD-2** was followed to prepare **APTBD-4** from **N-8** as a dark solid (180 g, 72 %).

^1H NMR ($CDCl_3$, 300MHz, ppm): δ 7.94 (d, J= 15.1Hz, 1H), 7.37 (s, 1H), 7.31 (d, J= 8.9Hz, 2H), 7.18-7.15 (m, 1H), 7.06 (d, J= 3.9Hz, 1H), 7.01 (d, J= 8.7Hz, 2H), 6.85 (d, J= 8.9 Hz, 2H), 6.56 (d, J= 9.0Hz, 2H), 5.84 (d, J= 15.2Hz, 1H), 3.28 (t, J= 7.5 Hz, 4H), 3.08 (s, 6H), 1.60 (s, 6H), 1.58-1.51 (m, 4H), 1.41-1.28 (m, 4H), 0.95 (t, J= 7.3 Hz, 6H).

^{13}C NMR ($CDCl_3$, 100MHz, ppm): δ 176.44, 173.47, 154.59, 153.51, 151.01, 148.67, 140.11, 137.53, 137.16, 137.03, 130.34, 130.01, 127.42, 121.32, 120.78, 120.36, 113.96, 113.35, 112.71, 112.27, 111.84, 111.54, 111.47, 97.04, 94.11, 54.91, 50.78, 40.48, 29.43, 26.35, 20.32, 14.01.

HR-MS calcd for $C_{40}H_{44}N_5OS$ $[M+H]^+$ m/z 642.32611, found m/z 642.32459.

Preparation of APTBD-5

The procedure for compound **APTBD-1** was followed to prepare **APTBD-5** from **N-9** as a dark solid (176 mg, 65 %).

^{1}H NMR ($CDCl_3$, 300MHz, ppm): δ 7.97 (dd, J= 11.4Hz, 14.8Hz, 1H), 7.51 (d, J= 8.9Hz, 2H), 7.39 (d, J= 14.4Hz, 1H), 7.32 (d, J= 4.1Hz, 1H), 7.21 (d, J= 4.1Hz, 1H), 6.73 (dd, J= 11.4 Hz, 14.4Hz, 1H), 6.64 (d, J=9.0Hz, 2H), 6.32 (d, J= 14.9Hz, 1H), 3.33 (t, J= 7.7 Hz, 4H), 1.86 (s, 3H), 1.65-1.55 (m, 4H), 1.44-1.32 (m, 4H), 0.97 (t, J= 7.3 Hz, 6H).

^{13}C NMR ($CDCl_3$, 100MHz, ppm): δ 175.44, 162.03, 154.95, 150.81, 149.32, 142.19, 137.92, 136.81, 127.78, 125.51, 123.49, 122.75, 120.65, 119.78, 114.71, 111.68, 111.35, 111.28, 110.72, 95.54, 93.75, 93.43, 57.79, 50.86, 29.45, 20.32, 19.14, 14.00.

HR-MS calcd for $C_{32}H_{32}F_3N_4OS$ $[M+H]^+$ m/z 577.22434, found m/z 577.22308.

Preparation of APTBD-6

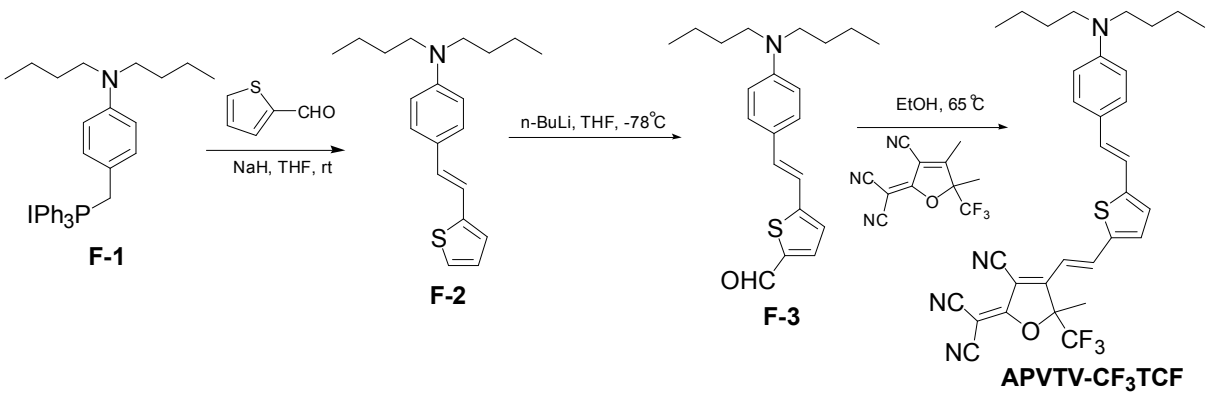
The procedure for compound **APTBD-2** was followed to prepare **APTBD-6** from **N-9** as a dark solid (120 mg, 71 %). The ratio of the Z : E isomers is 13% : 87% calculated by the integration of respective protons.

^{1}H NMR ($CDCl_3$, 300MHz, ppm): δ 7.78 (d, J= 15.5Hz, 0.14H), 7.60-7.42 (m, 3.11H), 7.30 (s, 0.39H), 7.25-7.23 (m, 1.39H), 7.16-6.93 (m, 1.14H), 6.74-6.61 (m, 2.93H), 6.53 (d, J= 15.6Hz, 0.15H), 6.38 (d, J= 15.2Hz, 0.87H), 3.32 (t, J= 7.5 Hz, 4H), 1.69 (s, 6H), 1.64-1.54 (m, 4H), 1.43-1.33 (m, 4H), 0.97 (t, J= 7.3 Hz, 6H).

^{13}C NMR ($CDCl_3$, 100MHz, ppm): δ 176.00, 173.22, 173.16, 156.58, 152.61, 149.60, 148.93, 148.43, 139.93, 139.76, 138.60, 138.41, 137.70, 136.55, 134.94, 127.95, 127.49, 127.21, 125.09, 122.65, 122.16, 119.95, 119.39, 115.88, 112.43, 111.68, 111.65, 111.62, 111.31, 111.27, 110.76, 97.04, 96.91, 95.63, 55.65, 50.82, 29.72, 29.44, 26.62, 26.45, 20.33, 20.31, 14.02.

HR-MS calcd for $C_{32}H_{35}N_4OS$ $[M+H]^+$ m/z 523.25261, found m/z 523.25203.

Synthesis of chromophore APVTV-CF_3TCF



Scheme 1 Synthesis of chromophore **APVTV-CF_3TCF**

Chromophore **APVTV-CF_3TCF** was synthesized in three steps starting from 4-(N,N-dibutylaminobenzyl)triphenylphosphonium iodide (**F-1**).[2] As shown in Scheme 1, **F-1** was condensed with 2-thenaldehyde by Wittig condensation to obtain **F-2**. After the introduction of the thiophene-based bridge, the treatment of compound **F-2** with *n*-BuLi and DMF gave aldehyde **F-3**. The target chromophore **APVTV-CF_3TCF** was obtained via the Knoevenagel condensation reaction of aldehyde **F-3** with **CF_3-TCF** acceptor.

Preparation of F-2

To a mixture of 2-thenaldehyde (0.16 g, 1.43 mmol) and 4-(N,N-dibutylaminobenzyl)triphenylphosphonium iodide (0.75 g, 1.23 mmol) in dry THF (10 mL) at room temperature, NaH (56 mg, 1.4 mmol, 60% dispersion in mineral oil) was added. The mixture turned yellow and was stirred at room temperature for 24h. Saturated NH_4Cl was added and the resulting mixture was extracted with EtOAc. The combined extracts were washed with water and dried over Na_2SO_4. After the filtration and removal of the solvent under vacuum, the residue was purified by column chromatography on silica gel (hexane/DCM) to obtain product as a yellow oil (0.28 g, 72 %).

^{1}H NMR ($CDCl_3$, 300MHz, ppm): δ 7.39-7.29 (m, 2H), 7.16-7.13 (m, 1H), 7.10-6.88 (m, 3.22H), 6.68-6.48 (m, 2.80H), 3.36-3.29 (m, 4H), 1.68-1.58 (m, 4H), 1.47-1.35 (m, 4H), 1.04-0.99 (m, 6H).

^{13}C NMR ($CDCl_3$, 75MHz, ppm): δ 147.84, 147.67, 144.23, 140.88, 130.12, 130.09, 128.91, 127.67, 127.52, 127.11, 126.60, 124.55, 124.36, 124.07, 123.53, 122.83, 119.79, 116.97, 111.67, 111.20, 50.85, 50.80, 29.55, 29.51, 20.44, 14.13.

HR-MS calcd for $C_{20}H_{28}NS$ $[M+H]^+$ m/z 314.19370, found m/z 314.19302.

Preparation of F-3

To a solution of compound **F-2** (0.25 g, 0.80 mmol) in dry THF (5mL) a 1.6 M solution of *n*-BuLi in hexane (l mL, 1.60 mmol) was added dropwise at -78 °C under N_2. After the mixture was stirred at this temperature for 1 h, dry DMF (0.14 g, 1.92 mmol) was introduced. The resulting solution was stirred for another 1 h at -78 °C and then allowed to warm up to room temperature. The reaction was quenched by water. The mixture was extracted using CH_2Cl_2. The organic layer was dried by Na_2SO_4 and concentrated in

vacuo. The residue was purified by column chromatography on silica gel (hexane/DCM) to obtain the product as a thick oil (0.20 g, 74 %).

^{1}H NMR ($CDCl_3$, 300MHz, ppm): δ 9.80 (s, 1H), 7.63-7.57 (m, 1H), 7.37-7.23 (m, 2H), 7.13-6.93 (m, 2.83H), 6.67-6.41 (m, 2.57H), 3.33-3.26 (m, 4H), 1.61-1.53 (m, 4H), 1.43-1.30 (m, 4H), 0.97 (t, J= 7.3 Hz, 6H).

^{13}C NMR ($CDCl_3$, 75MHz, ppm): δ 182.38, 154.62, 148.70, 139.93, 137.76, 134.70, 133.76, 130.20, 128.60, 128.13, 124.82, 122.73, 115.45, 111.52, 111.12, 50.77, 29.45, 20.35, 14.04.

HR-MS calcd for $C_{21}H_{28}NOS$ $[M+H]^+$ m/z 342.18861, found m/z 342.18851.

Preparation of APVTV-CF_3TCF

The procedure for compound **APTBD-1** was followed to prepare **APVTV-CF_3TCF** from **F-3** as a dark solid (0.18 g, 67 %).

^{1}H NMR ($CDCl_3$, 300MHz, ppm): δ 8.15 (d, J= 15.2Hz, 1H), 7.46 (d, J= 4.2Hz, 1H), 7.39 (d, J= 8.9Hz, 2H), 7.18-6.97 (m, 3H), 6.63 (d, J= 9.0Hz, 2H), 6.46 (d, J= 15.2 Hz, 1H), 3.33 (t, J= 7.6 Hz, 4H), 1.91 (s, 3H), 1.65-1.55 (m, 4H), 1.44-1.31 (m, 4H), 0.97 (t, J= 7.3 Hz, 6H).

^{13}C NMR ($CDCl_3$, 100MHz, ppm): δ 175.34, 161.90, 157.65, 149.59, 141.20, 140.03, 137.92, 136.69, 129.56, 127.58, 123.51, 122.52, 120.67, 115.20, 111.75, 111.26, 111.24, 110.73, 110.30, 95.47, 93.76, 93.44, 93.11, 57.73, 50.86, 29.49, 20.32, 19.24, 14.00.

HR-MS calcd for $C_{32}H_{32}F_3N_4OS$ $[M+H]^+$ m/z 577.22434, found m/z 577.22430.

Table S1. Optical birefringence and properties of unpoled and poled films.

Chromophore /P(S-*co*-MMA)	N 10^{20} cm^{-3}	λ_{max} nm	n_{TE}/n_{TM} at 1304 nm (unpoled)	n_{TE}/n_{TM} at 1541 nm (unpoled)	n_{TE}/n_{TM} at 1304 nm (pole films)	r_{33} at 1304 nm (pm/V)
APTBD-1	1.94	725	1.6004/1.5994	1.5881/1.5912	1.5854/1.6291	53.8
APTBD-3	1.90	737	1.5895/1.5893	1.5794/1.5755	1.5783/1.6107	53.4
APTBD-5	2.30	716	1.6213/1.6202	1.6061/1.6063	1.6034/1.6632	78.9
APTBD-5	2.87	719	1.6381/1.6384	1.6219/1.6203	1.6149/1.7092	106.1
APVTV-CF_3TCF	2.30	722	1.5962/1.6419	1.5962/1.6419	1.5962/1.6419	60.8
APTBD-2	2.11	648	1.5841/1.5836	1.5772/1.5777	1.5790/1.5937	26.5
APTBD-4	2.06	654	1.5872/1.5863	1.5800/1.5808	1.5767/1.6079	28.3
APTBD-6	1.27	639	1.5531/1.5543	1.5480/1.5490	1.5494/1.5632	18.1

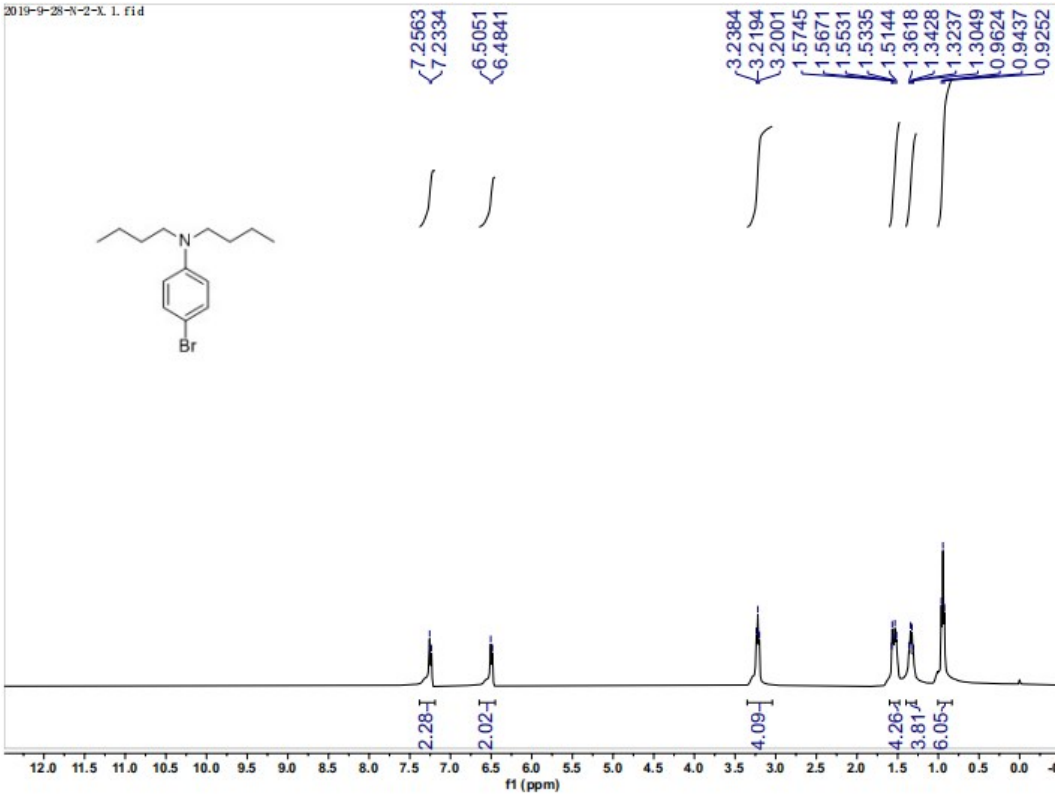


Fig. S1 ^{1}H NMR spectrum of compound **N-2**

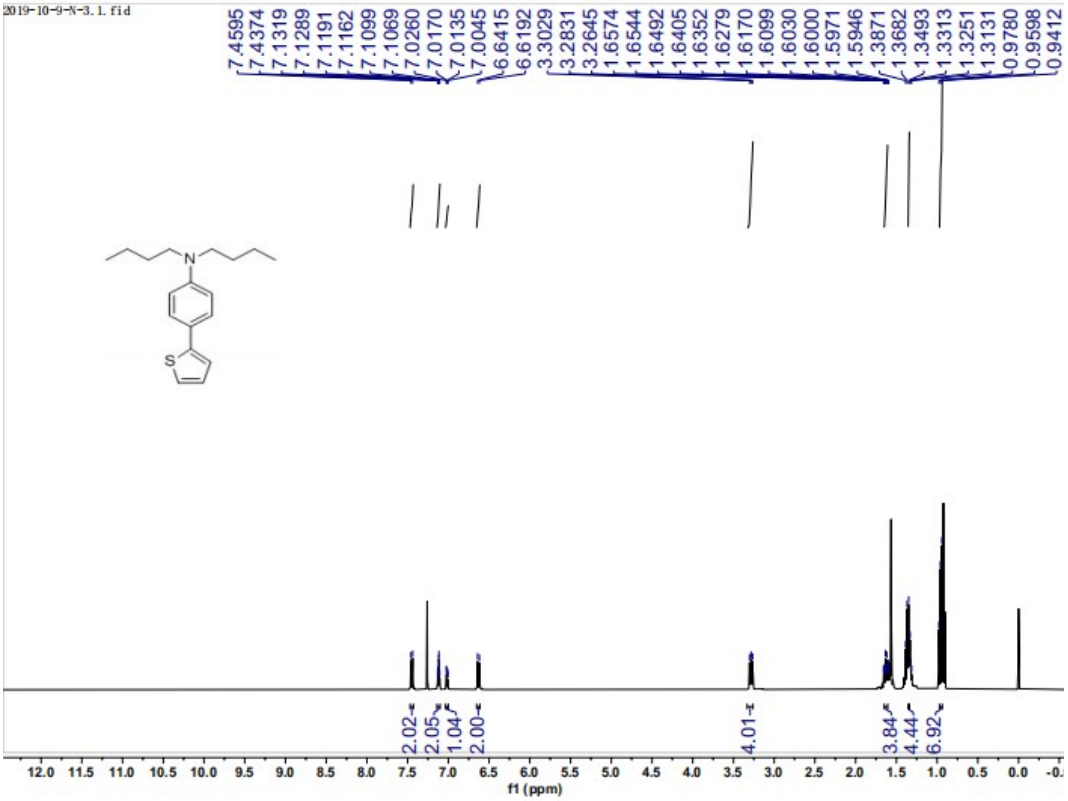


Fig. S2 ^{1}H NMR spectrum of compound **N-3**

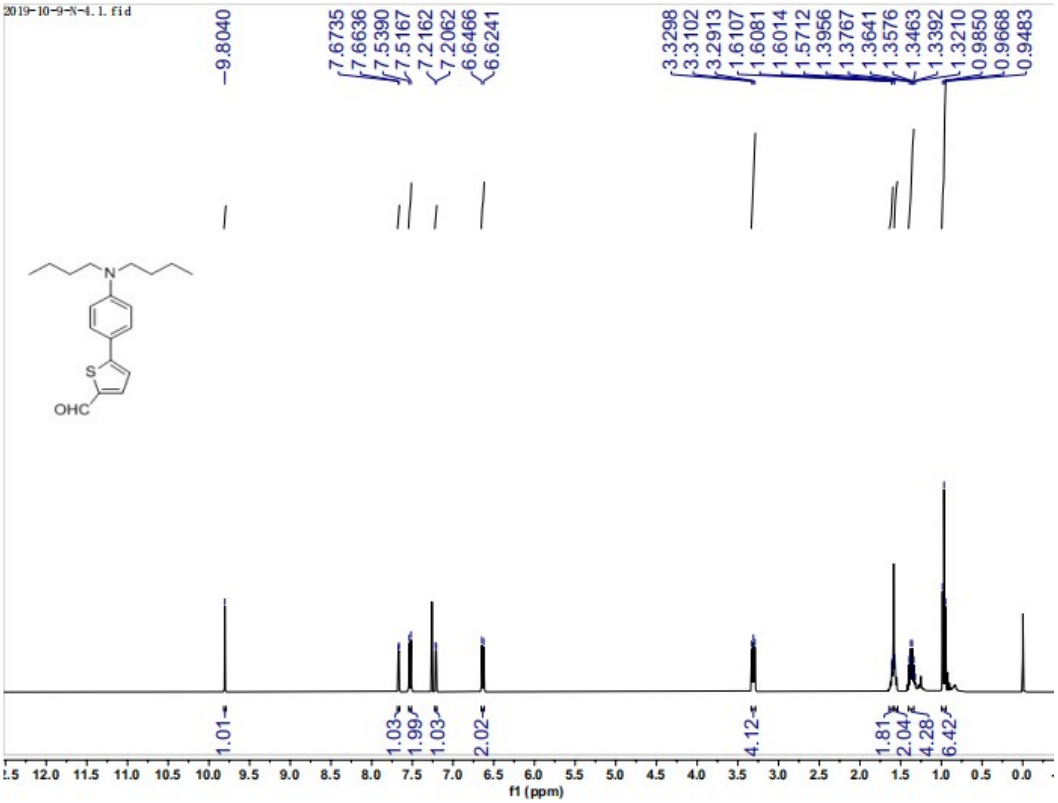


Fig. S3 ^{1}H NMR spectrum of compound **N-4**

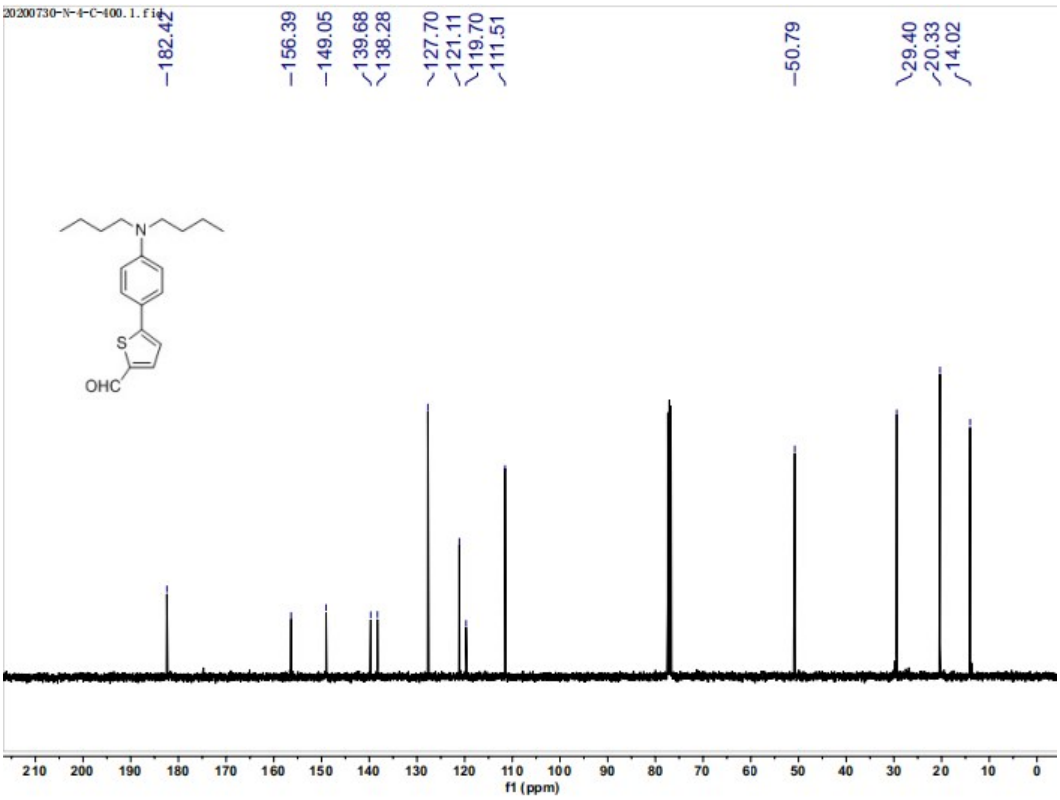


Fig. S4 ^{13}C NMR spectrum of compound **N-4**

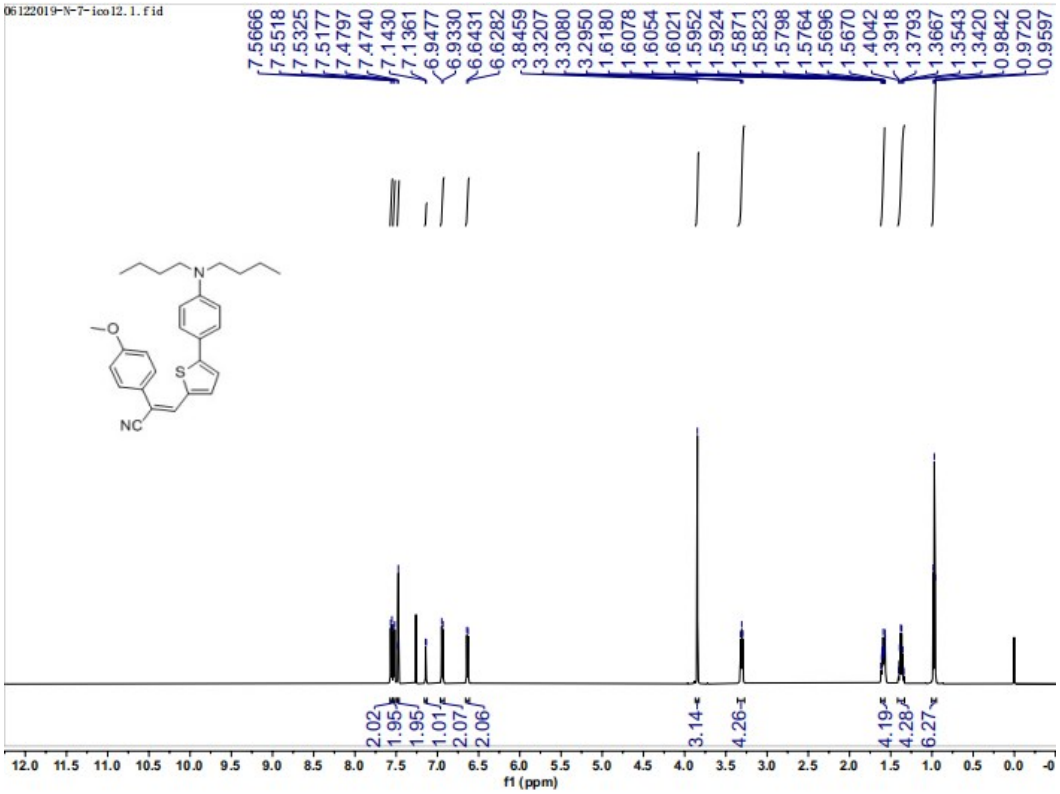


Fig. S5 ^{1}H NMR spectrum of compound **N-5**

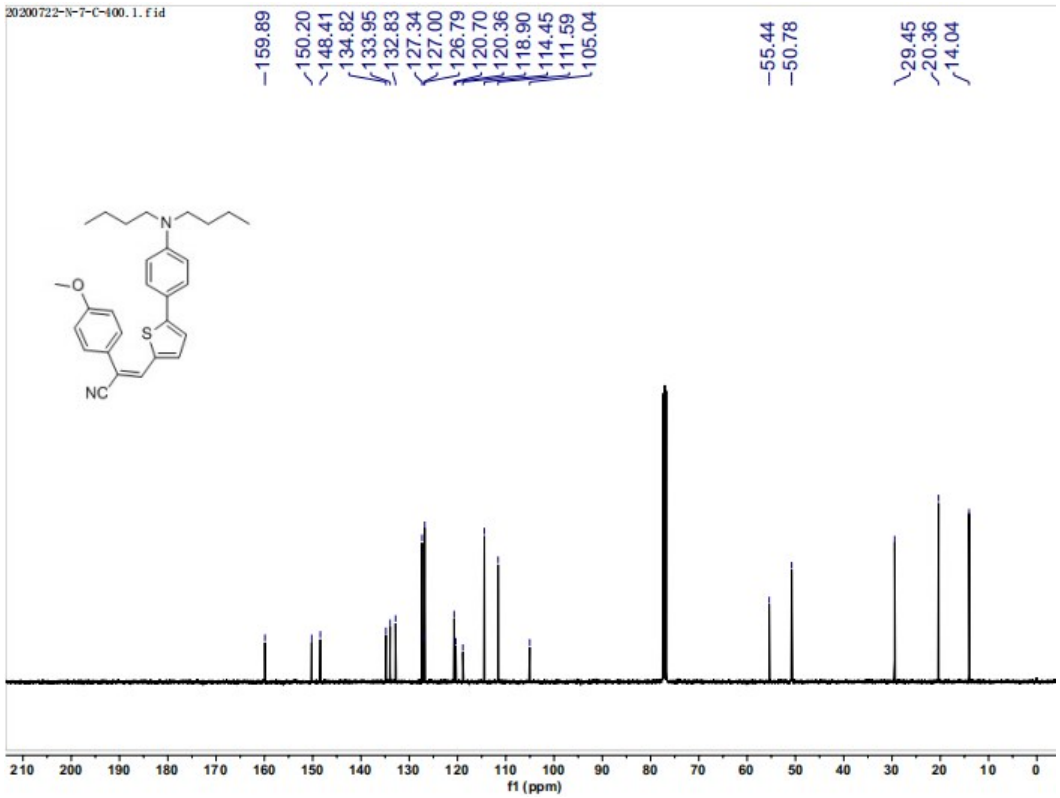


Fig. S6 ^{13}C NMR spectrum of compound **N-5**

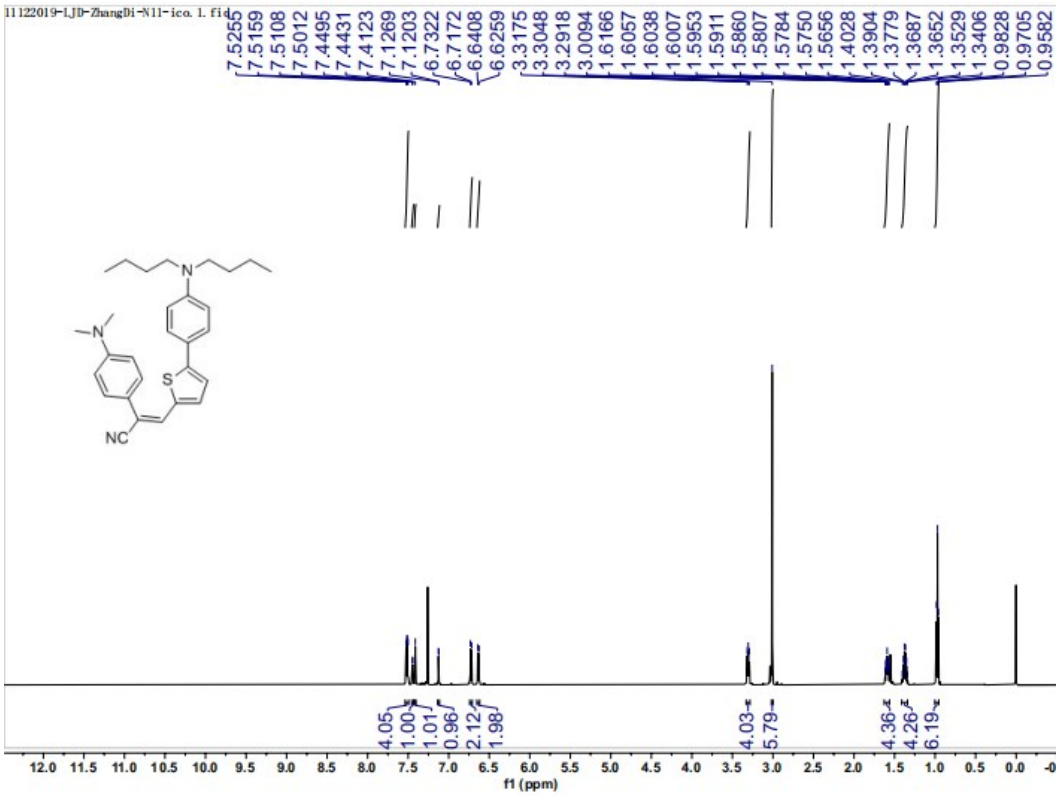


Fig. S7 ^{1}H NMR spectrum of compound **N-6**

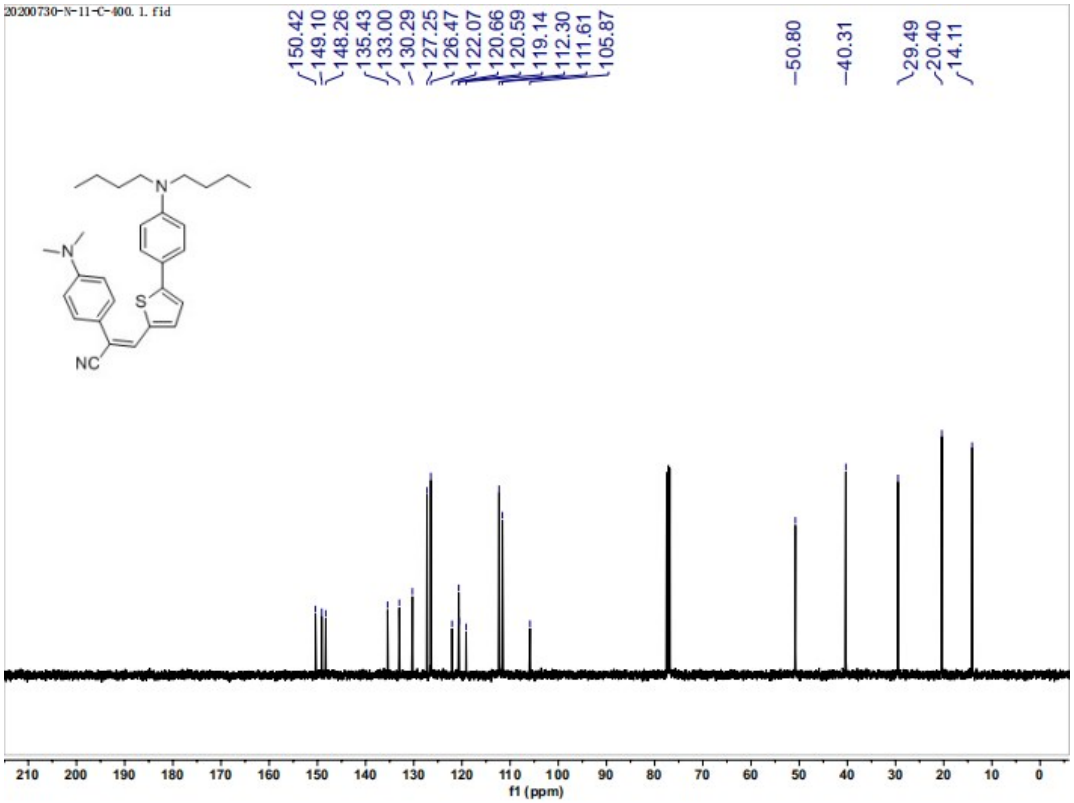


Fig. S8 ^{13}C NMR spectrum of compound **N-6**

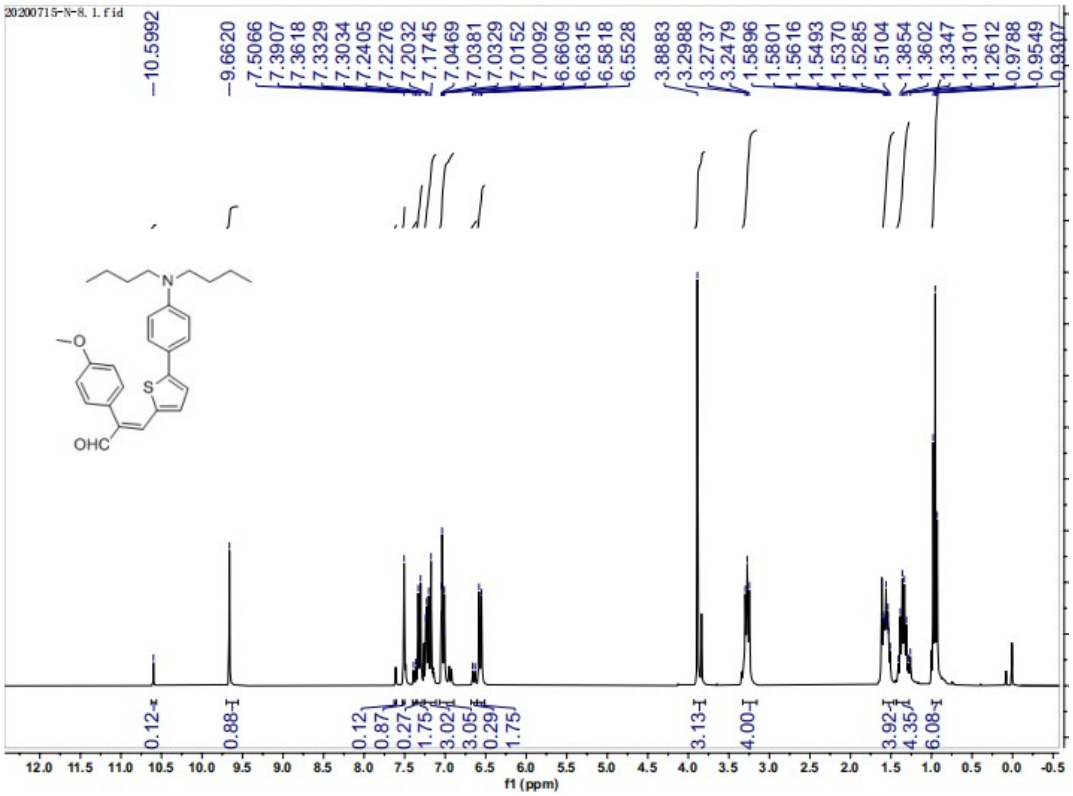


Fig. S9 ^{1}H NMR spectrum of compound **N-7**

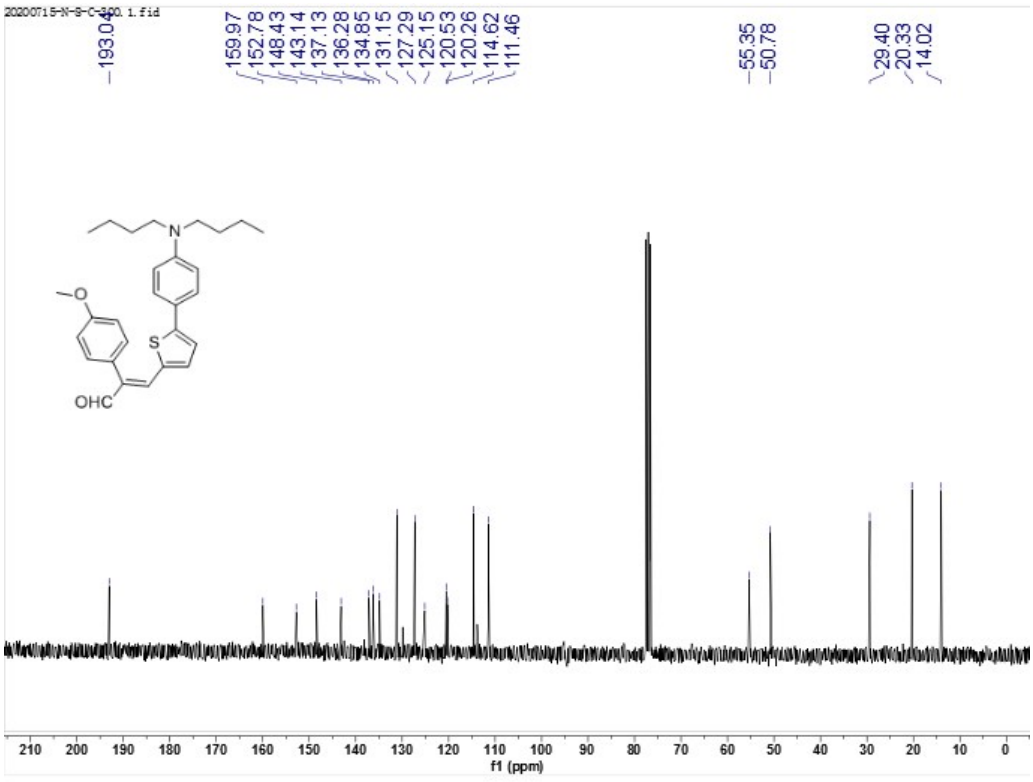


Fig. S10 ^{13}C NMR spectrum of compound **N-7**

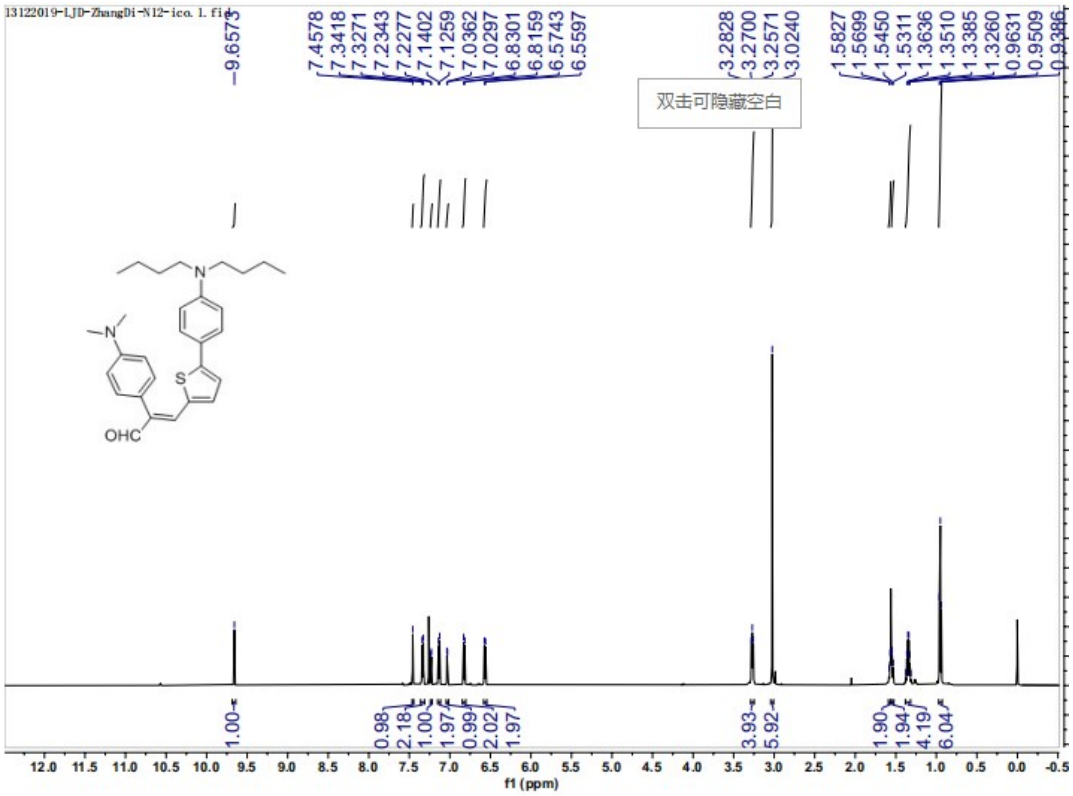


Fig. S11 ^{1}H NMR spectrum of compound **N-8**

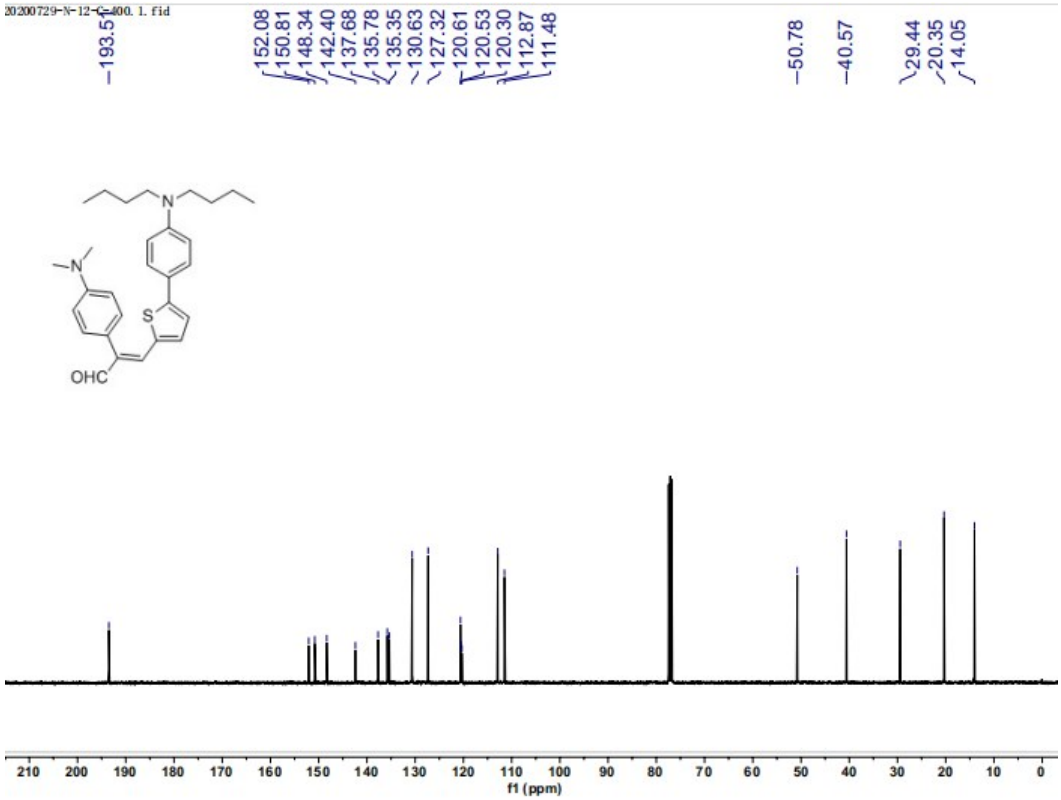


Fig. S12 ^{13}C NMR spectrum of compound **N-8**

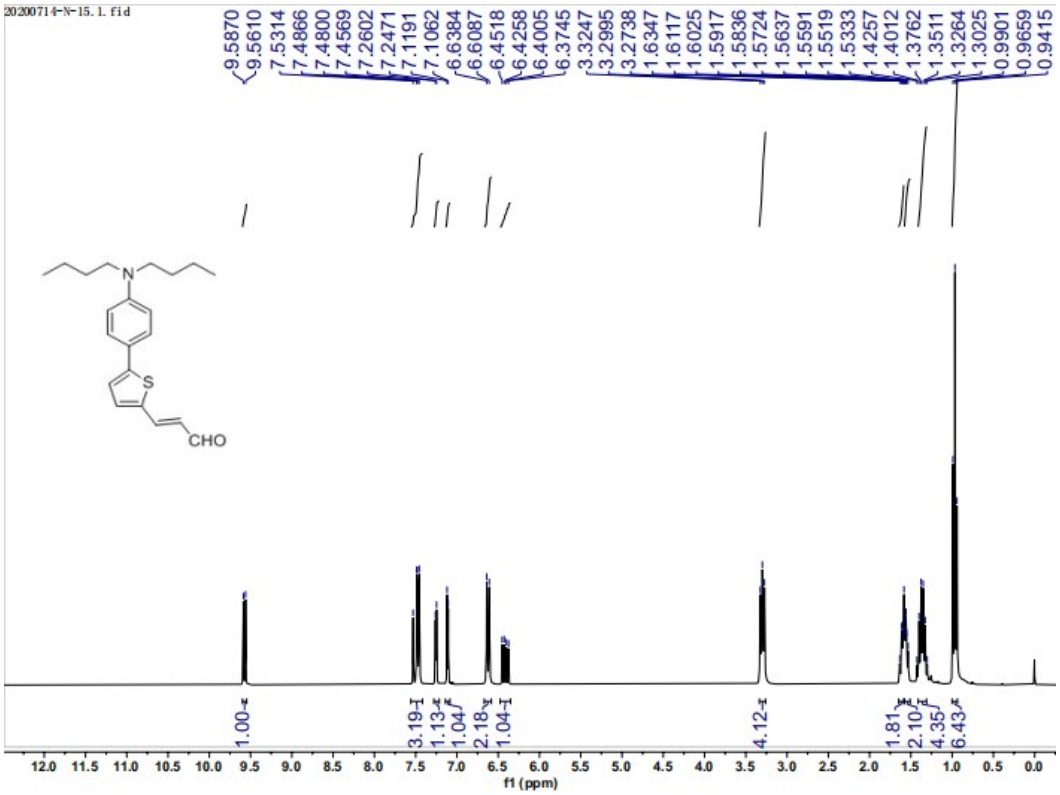


Fig. S13 ^{1}H NMR spectrum of compound **N-9**

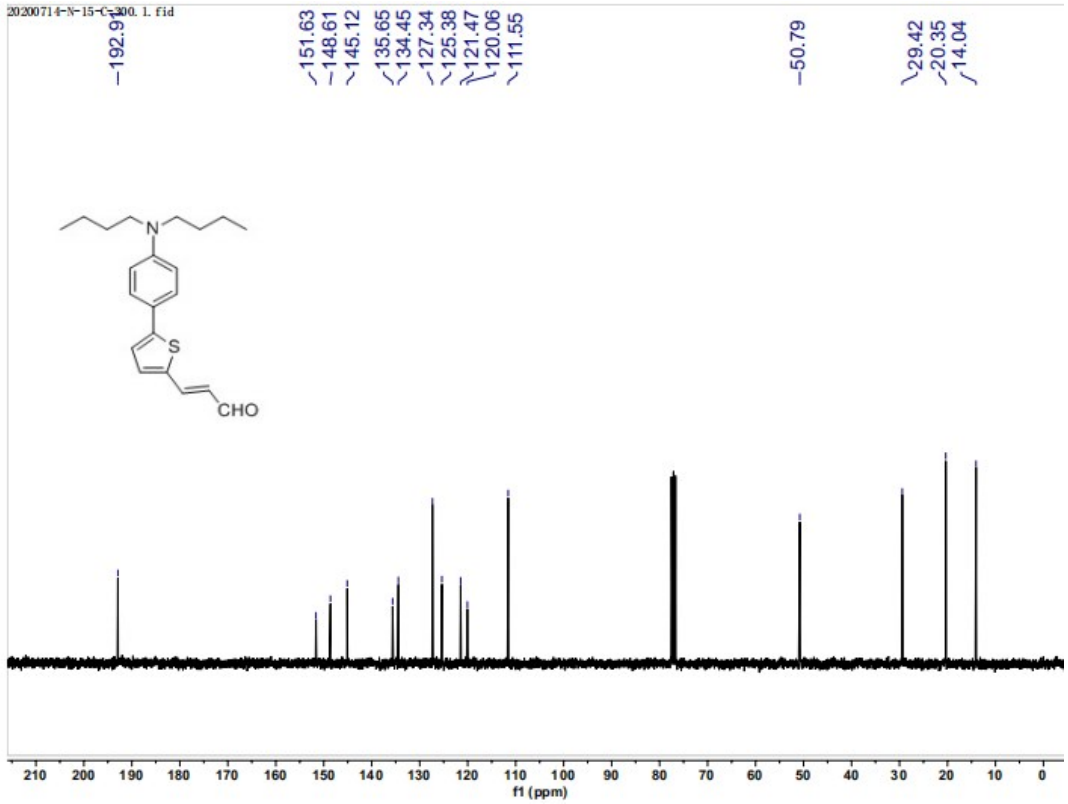


Fig. S14 ^{13}C NMR spectrum of compound **N-9**

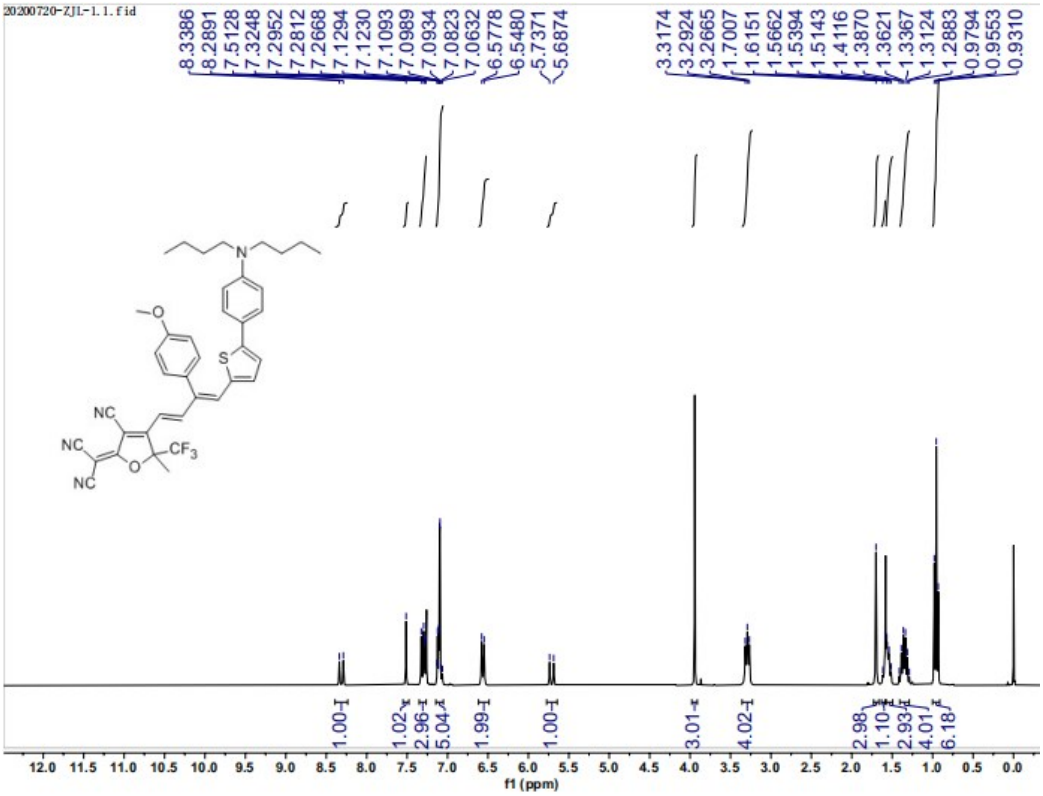


Fig. S15 ^{1}H NMR spectrum of compound **APTBD-1**

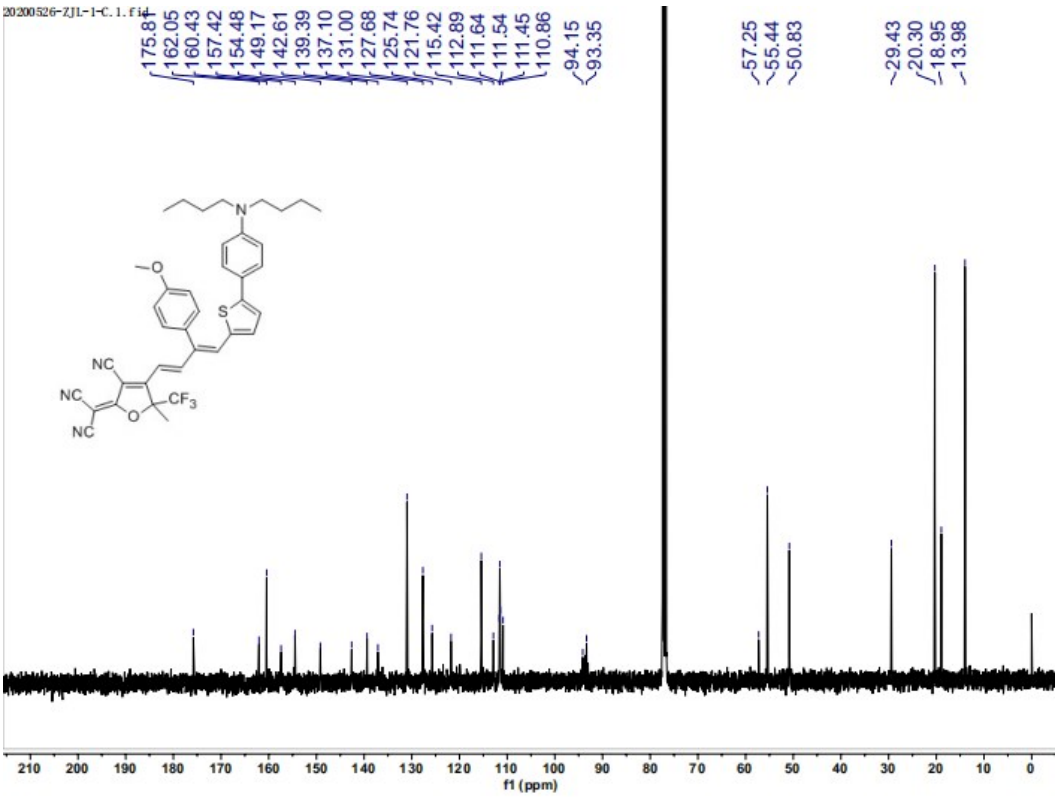


Fig. S16 ^{13}C NMR spectrum of compound **APTBD-1**

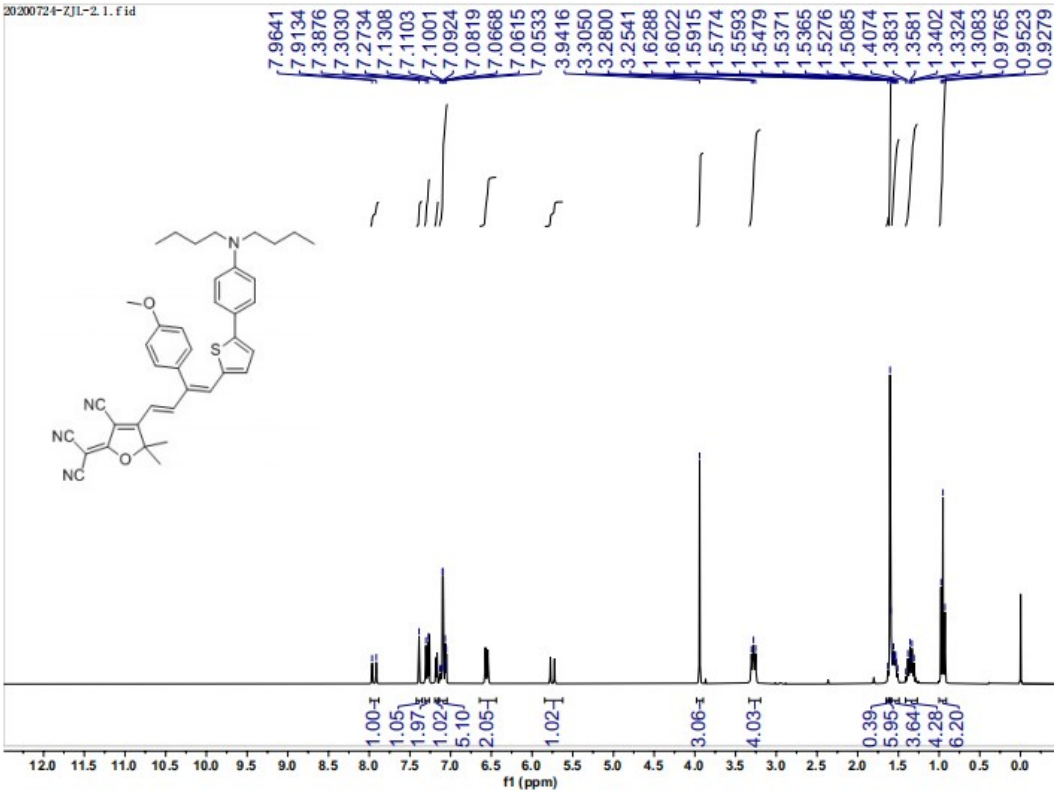


Fig. S17 ^{1}H NMR spectrum of compound **APTBD-2**

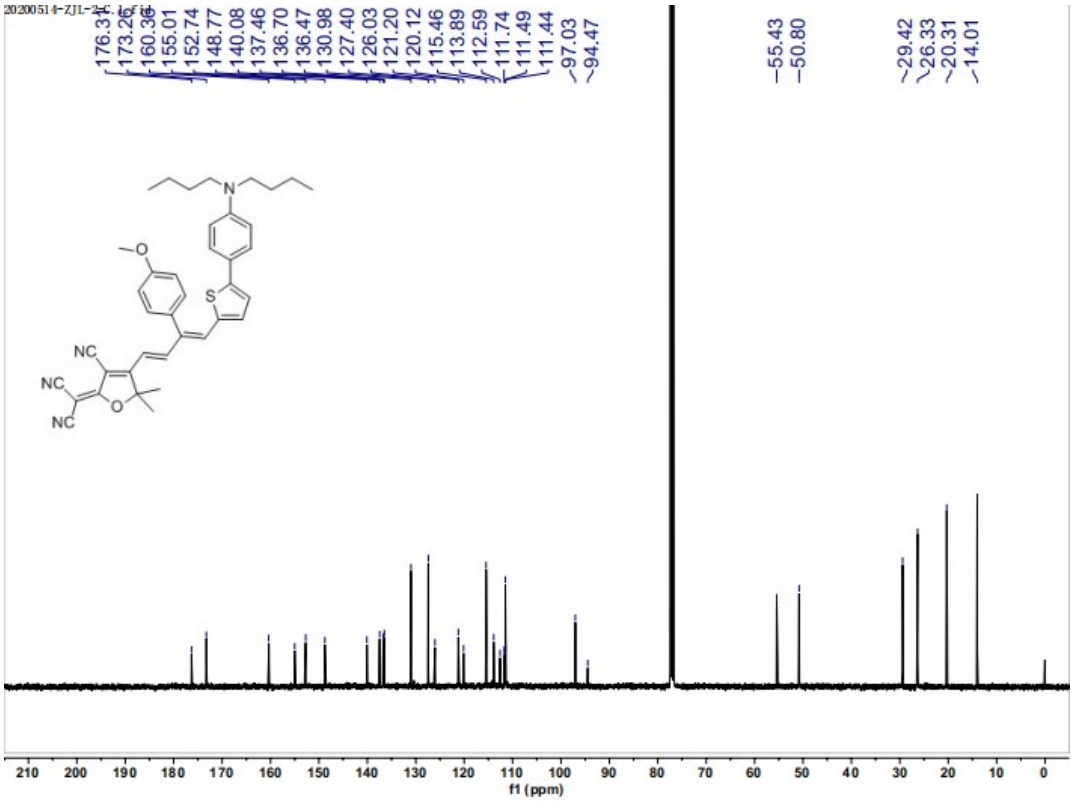


Fig. S18 ^{13}C NMR spectrum of compound **APTBD-2**

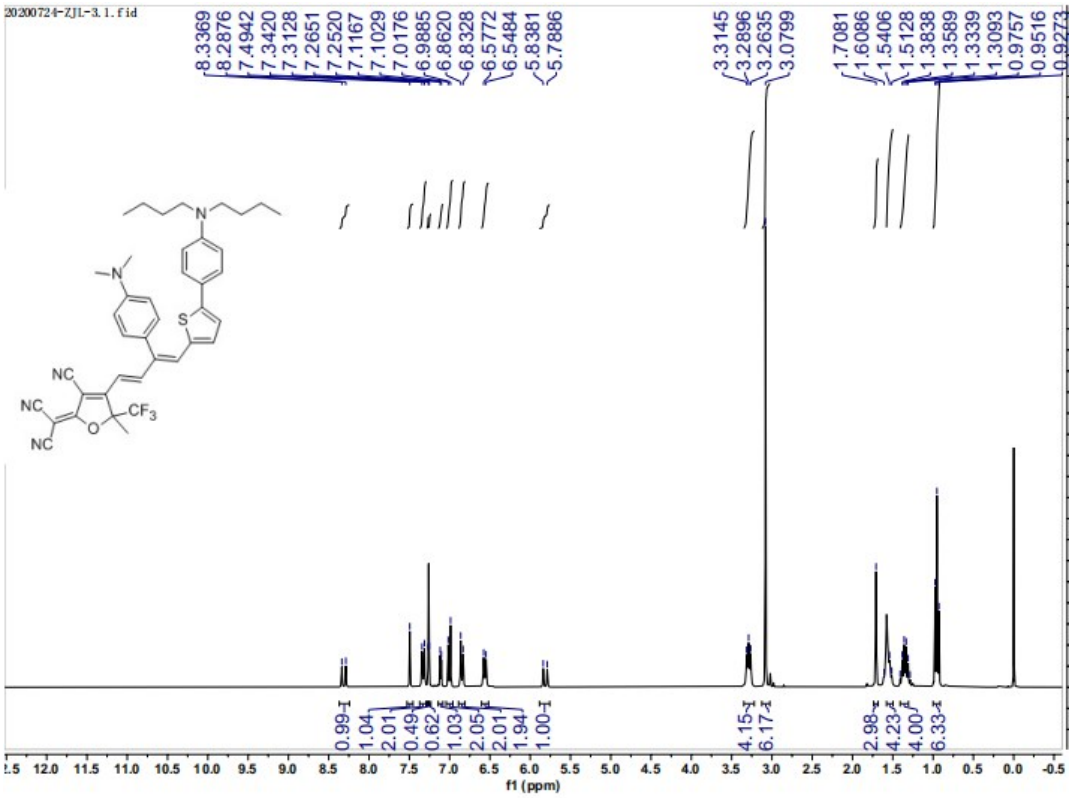


Fig. S19 ^{1}H NMR spectrum of compound **APTBD-3**

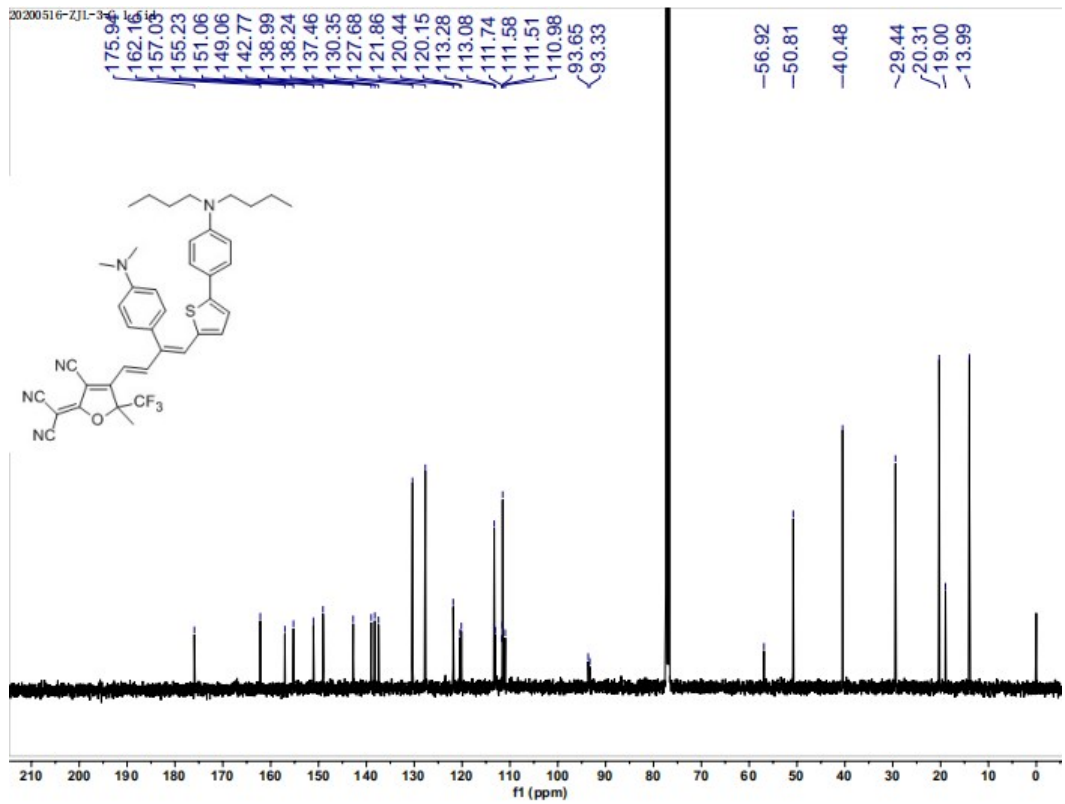


Fig. S20 ^{13}C NMR spectrum of compound **APTBD-3**

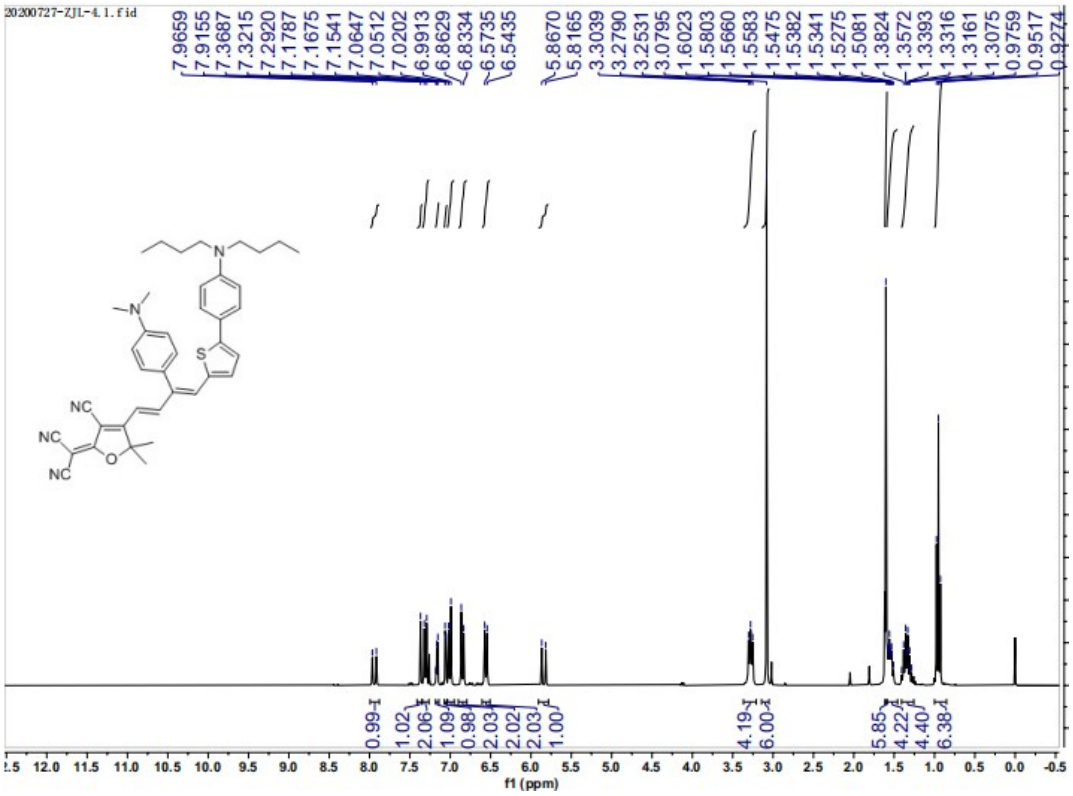


Fig. S21 ^{1}H NMR spectrum of compound **APTBD-4**

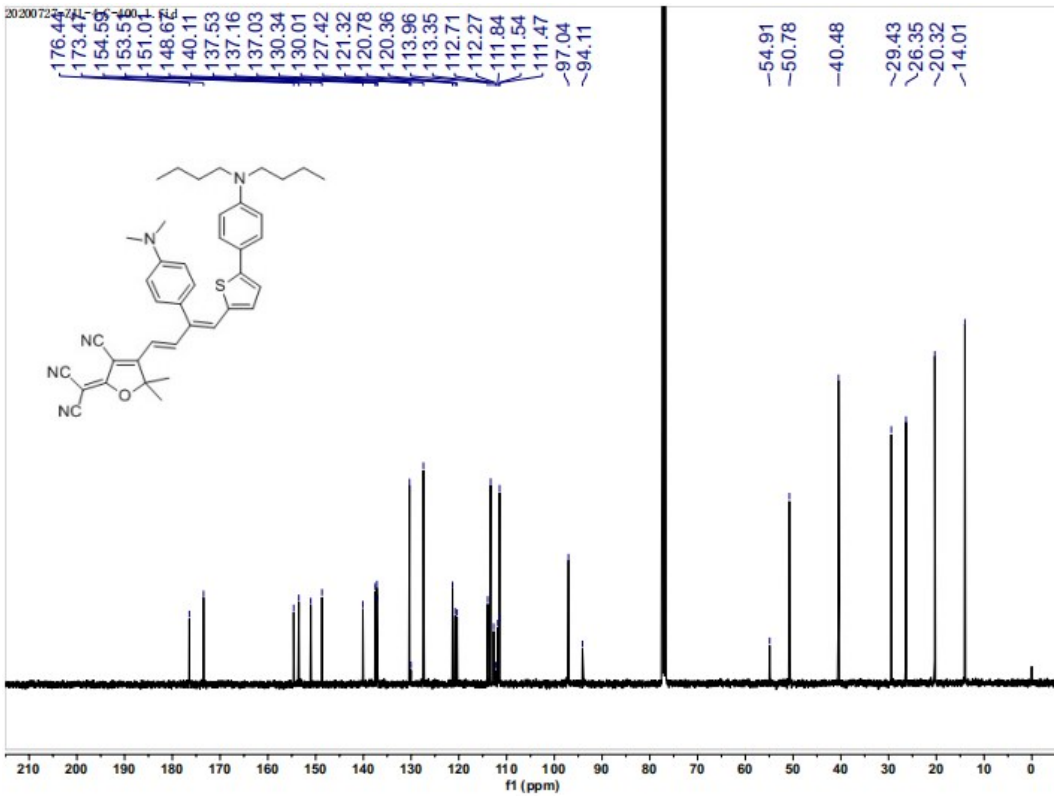


Fig. S22 ^{13}C NMR spectrum of compound **APTBD-4**

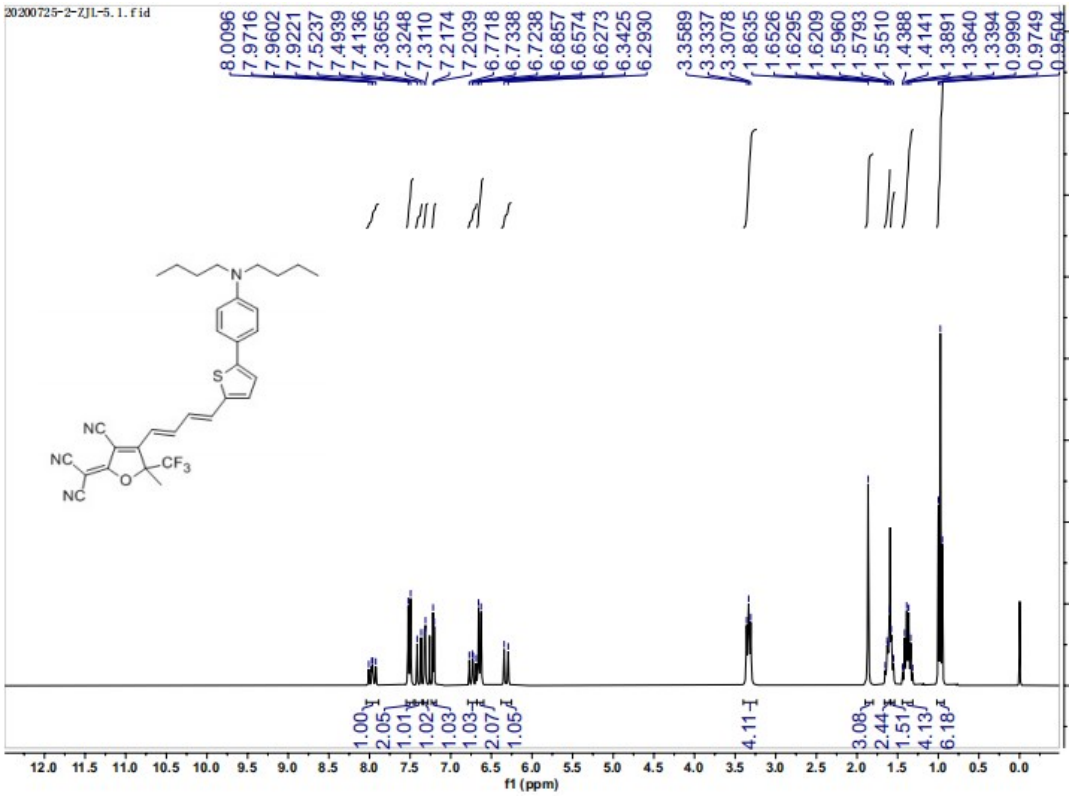


Fig. S23 ^{1}H NMR spectrum of compound **APTBD-5**

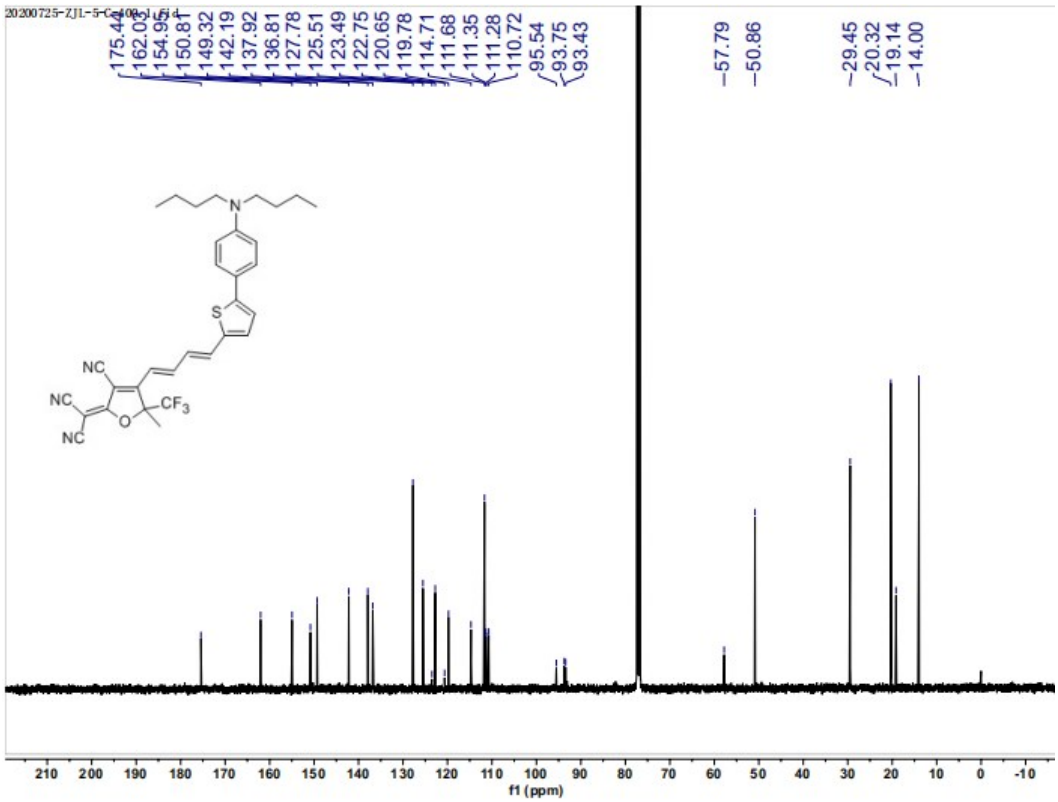


Fig. S24 ^{13}C NMR spectrum of compound **APTBD-5**

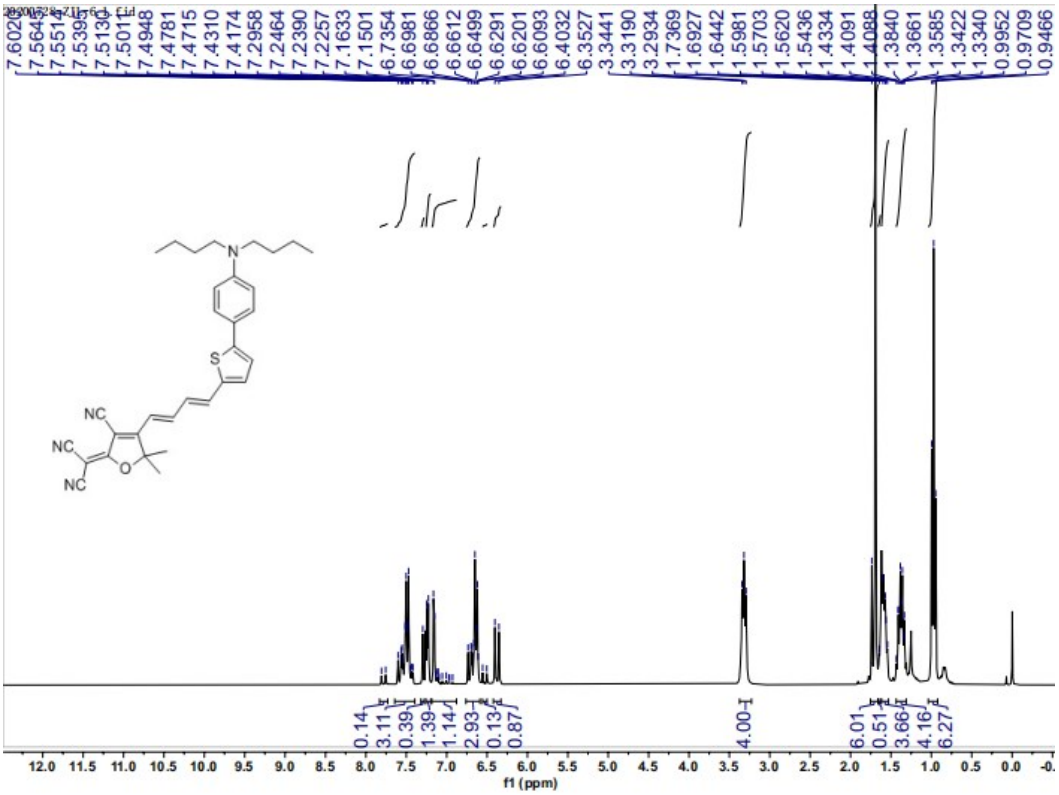


Fig. S25 ^{1}H NMR spectrum of compound **APTBD-6**

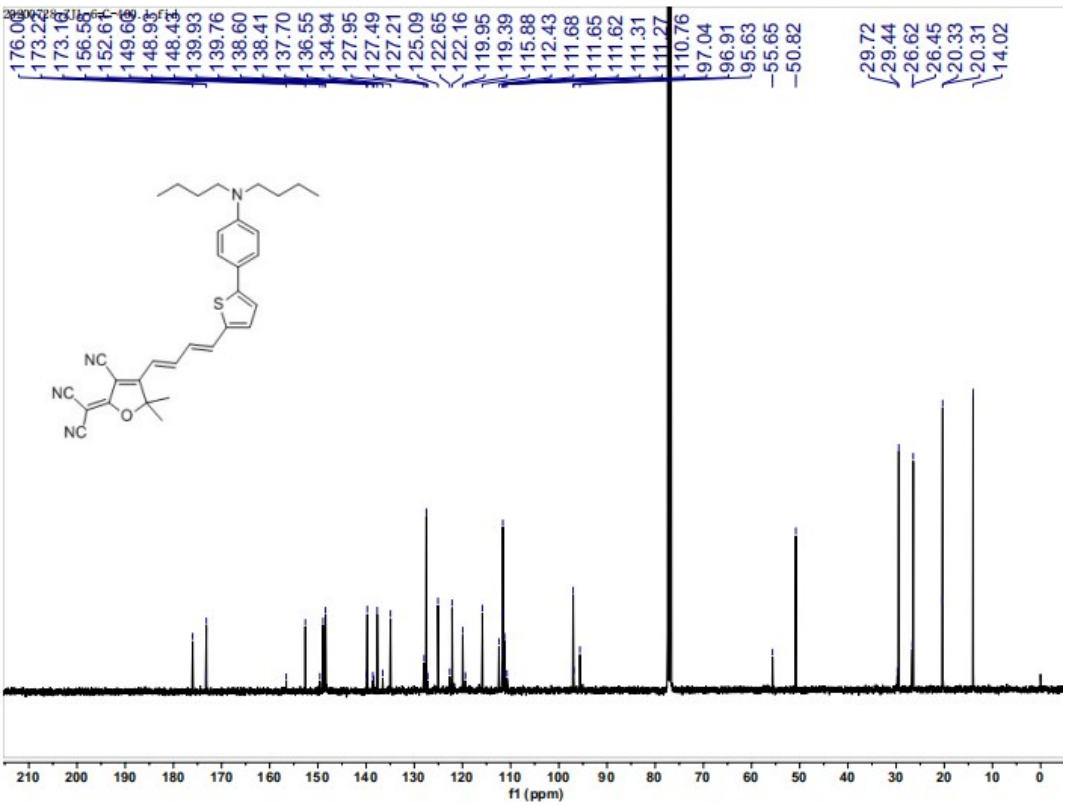


Fig. S26 ^{13}C NMR spectrum of compound **APTBD-6**

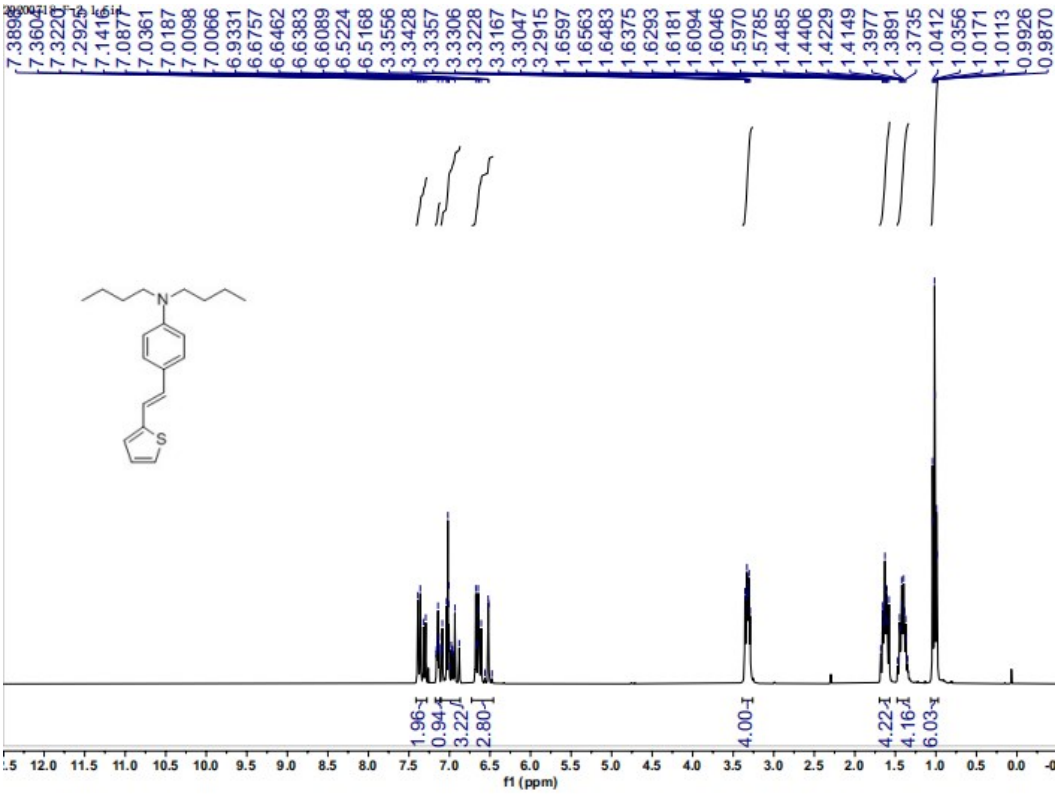


Fig. S27 ^{1}H NMR spectrum of compound **F-2**

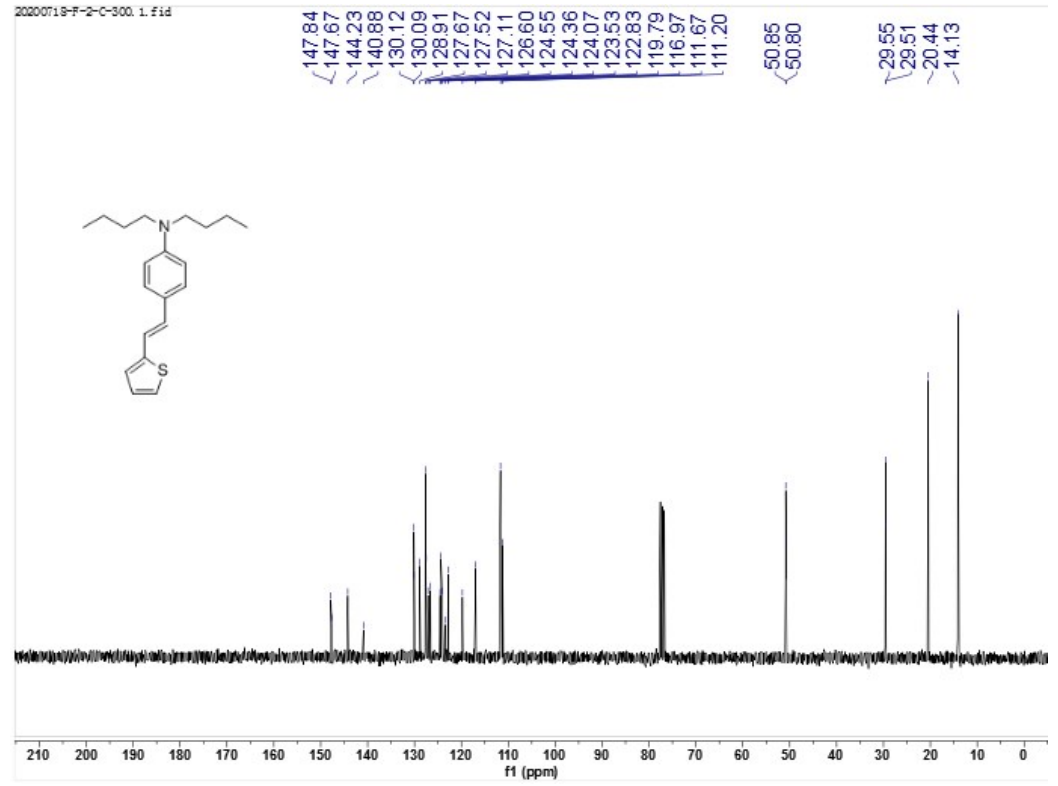


Fig. S28 ^{13}C NMR spectrum of compound **F-2**

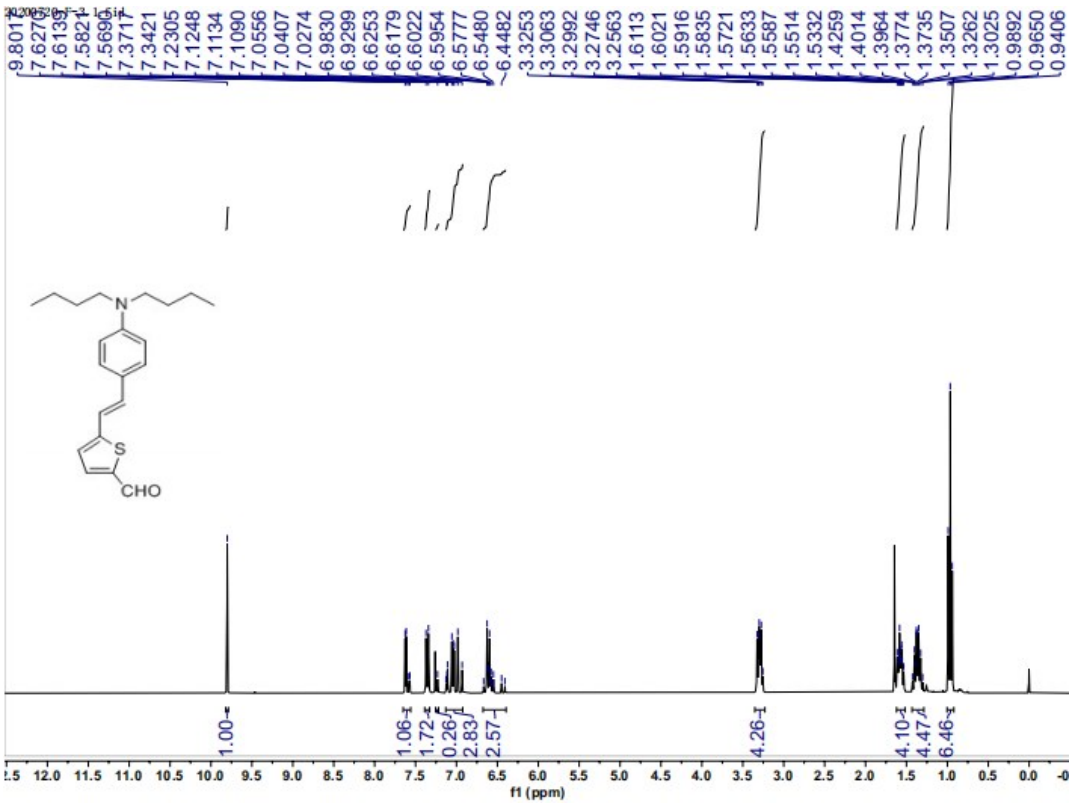


Fig. S29 ^{1}H NMR spectrum of compound **F-3**

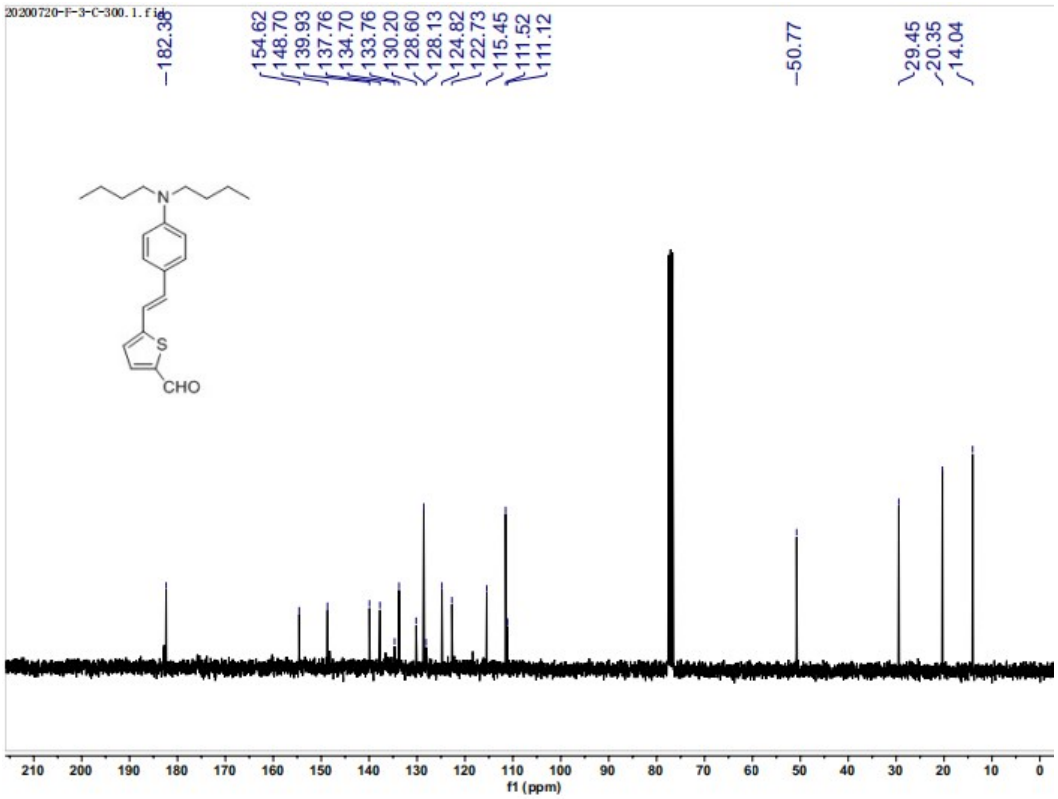


Fig. S30 ^{13}C NMR spectrum of compound **F-3**

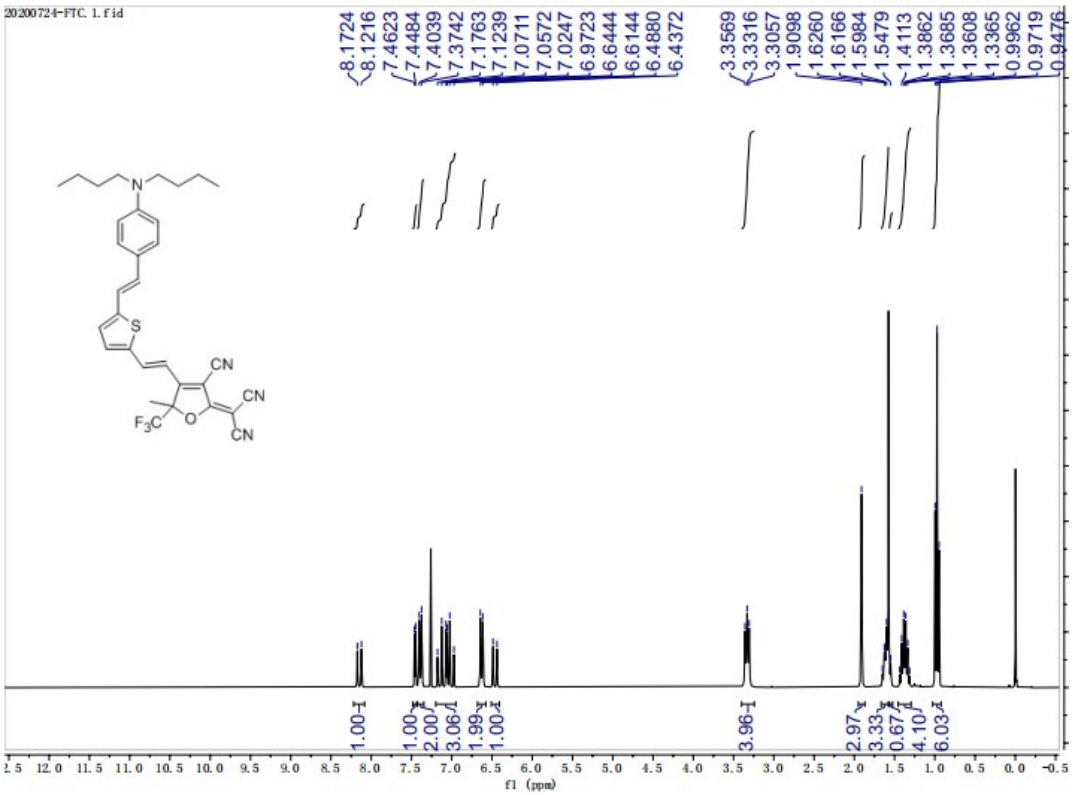


Fig. S31 ^{1}H NMR spectrum of compound **APVTV-CF$_3$TCF**

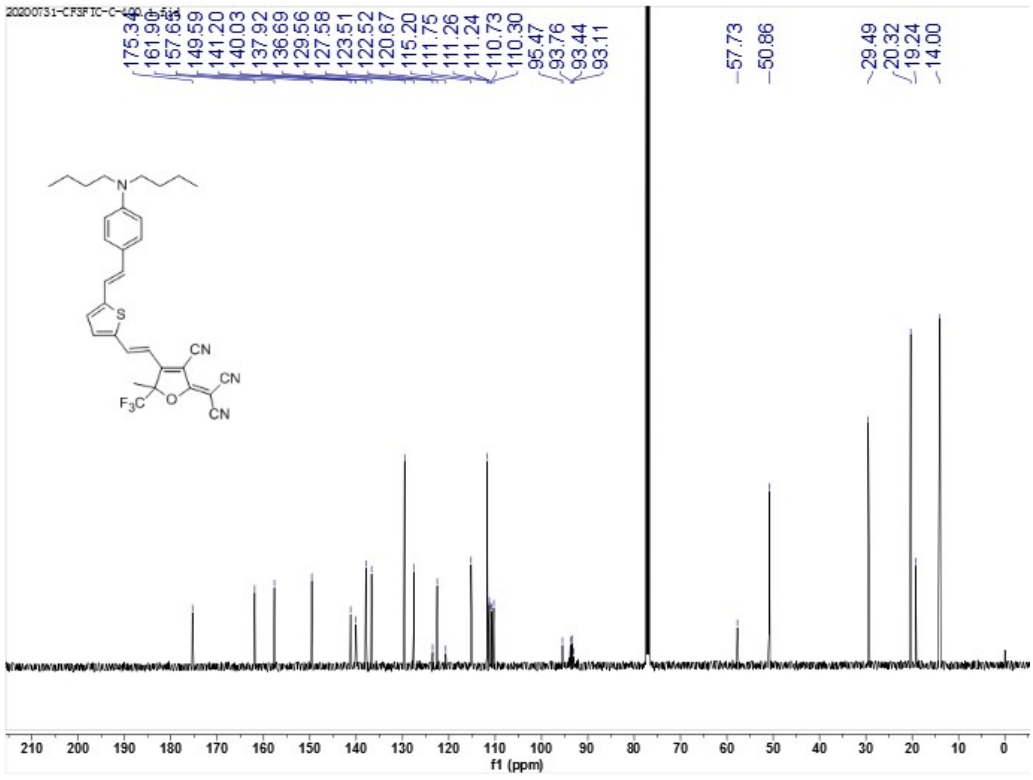


Fig. S32 ^{13}C NMR spectrum of compound **APVTV-CF$_3$TCF**

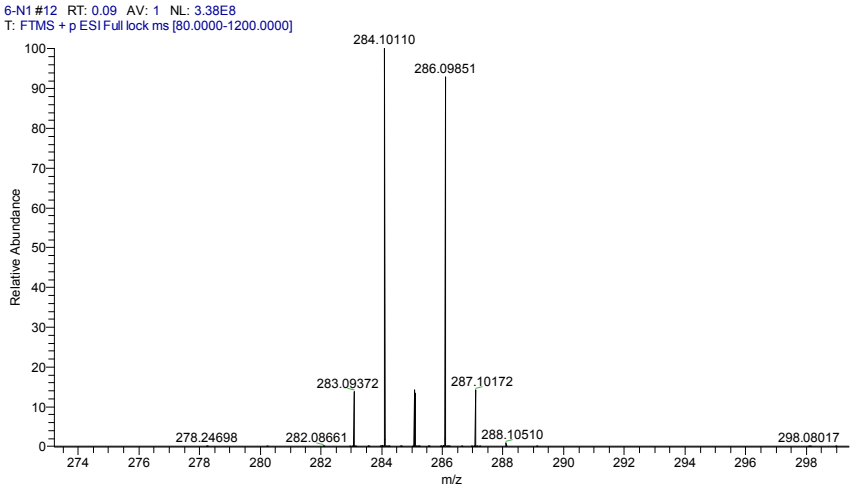


Fig. S33 HRMS spectrum of compound **N-2**

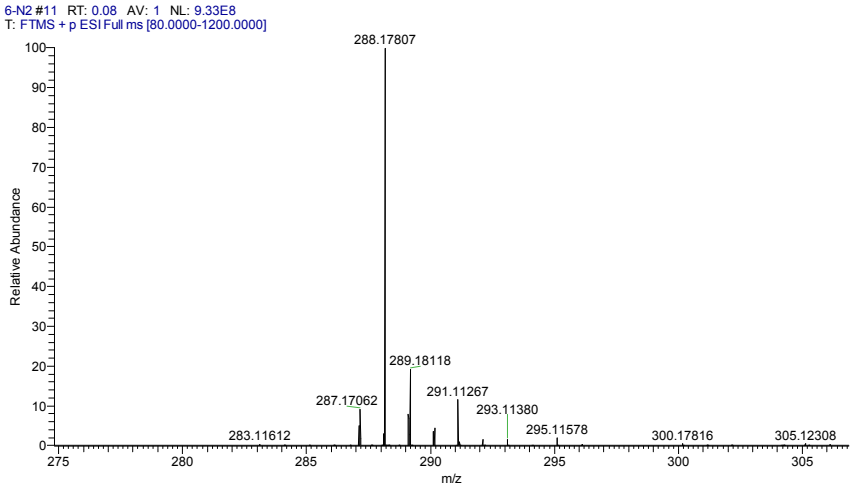


Fig. S34 HRMS spectrum of compound **N-3**

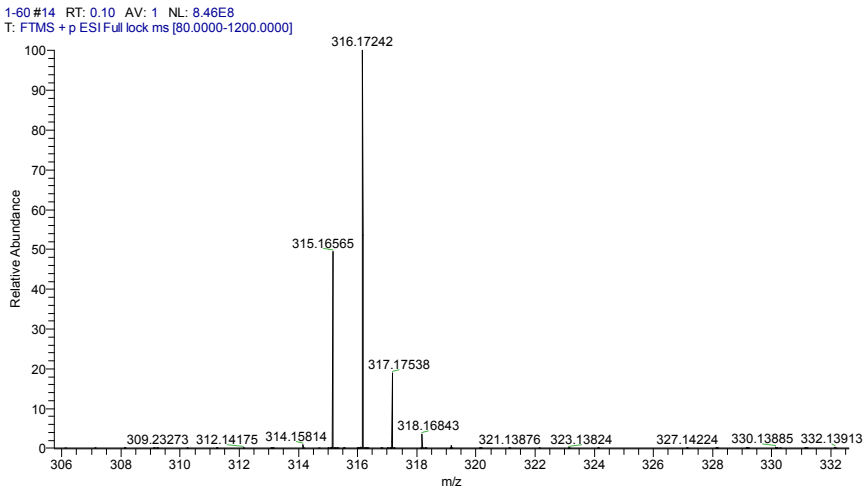


Fig. S35 HRMS spectrum of compound **N-4**

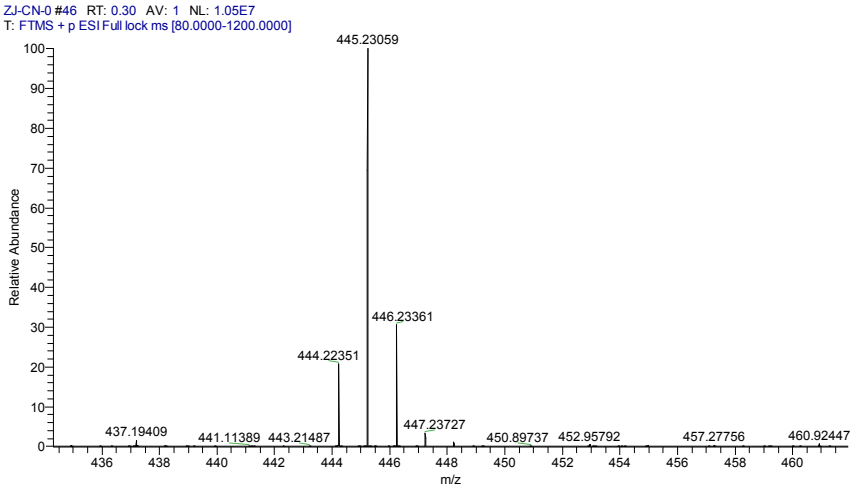


Fig. S36 HRMS spectrum of compound **N-5**

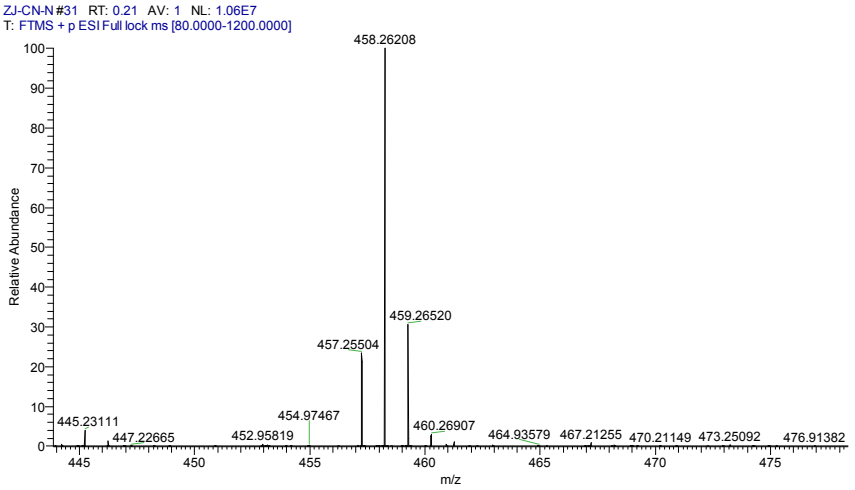


Fig. S37 HRMS spectrum of compound **N-6**

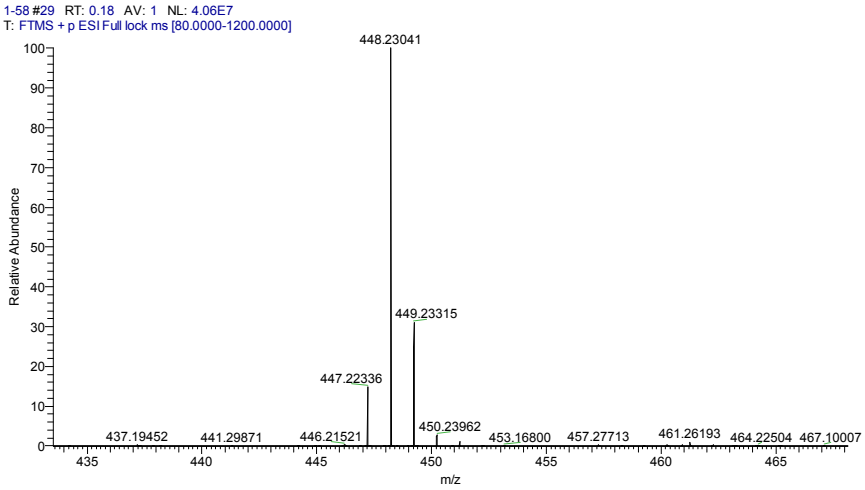


Fig. S38 HRMS spectrum of compound **N-7**

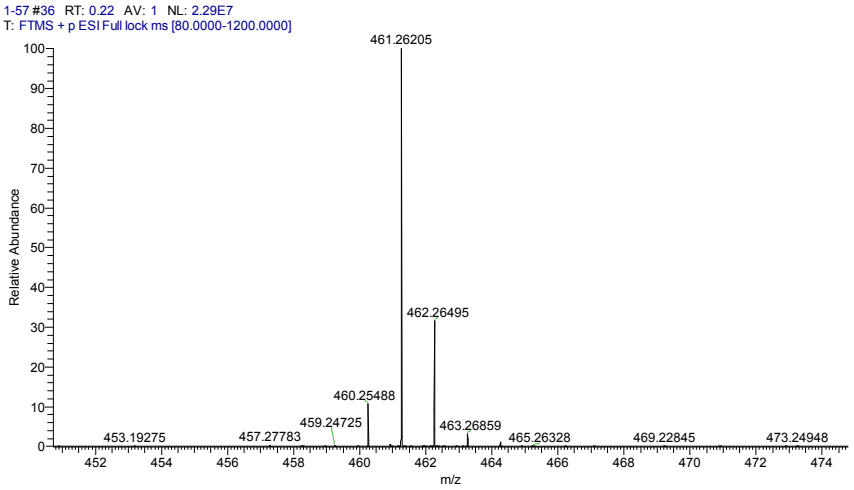


Fig. S39 HRMS spectrum of compound **N-8**

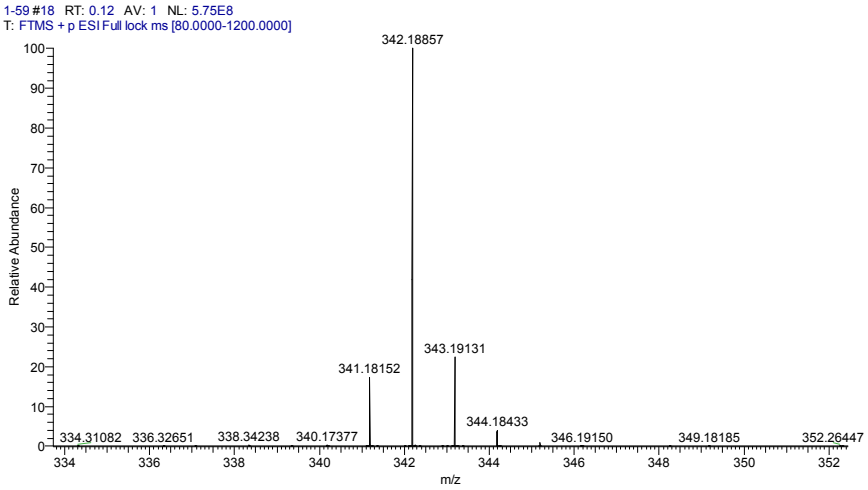


Fig. S40 HRMS spectrum of compound **N-9**

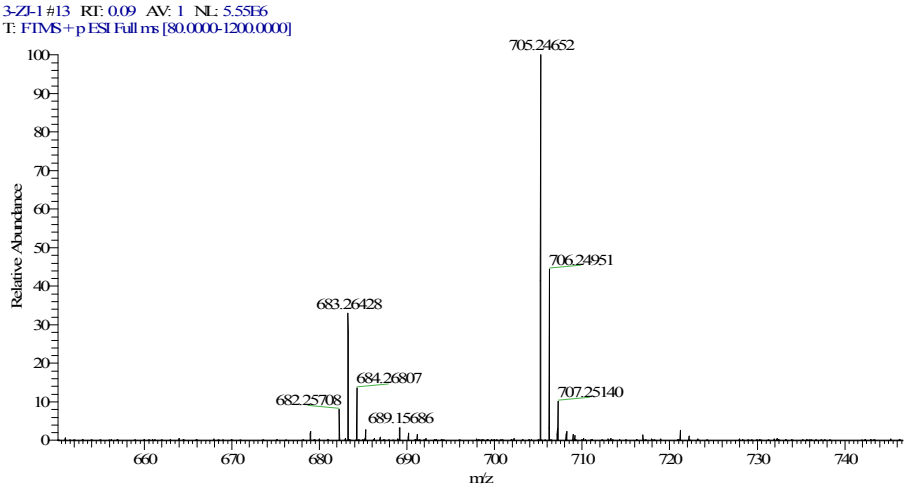


Fig. S41 HRMS spectrum of compound **APTBD-1**

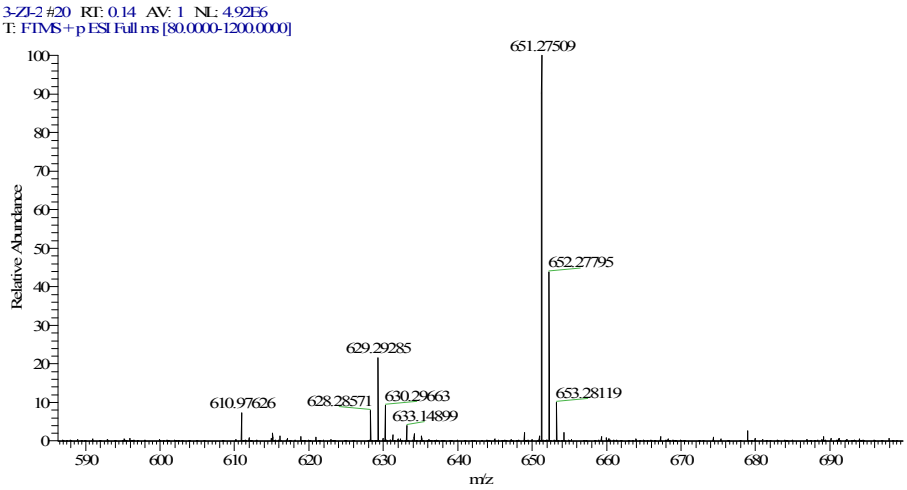


Fig. S42 HRMS spectrum of compound **APTBD-2**

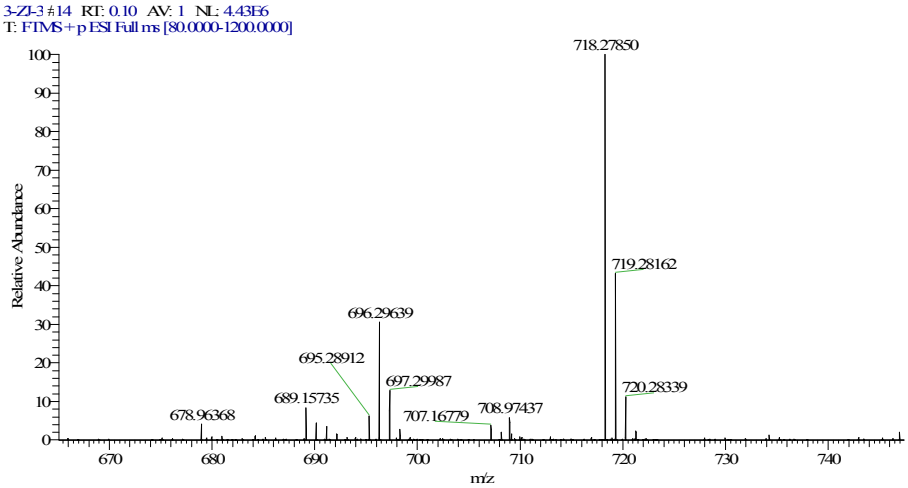


Fig. S43 HRMS spectrum of compound **APTBD-3**

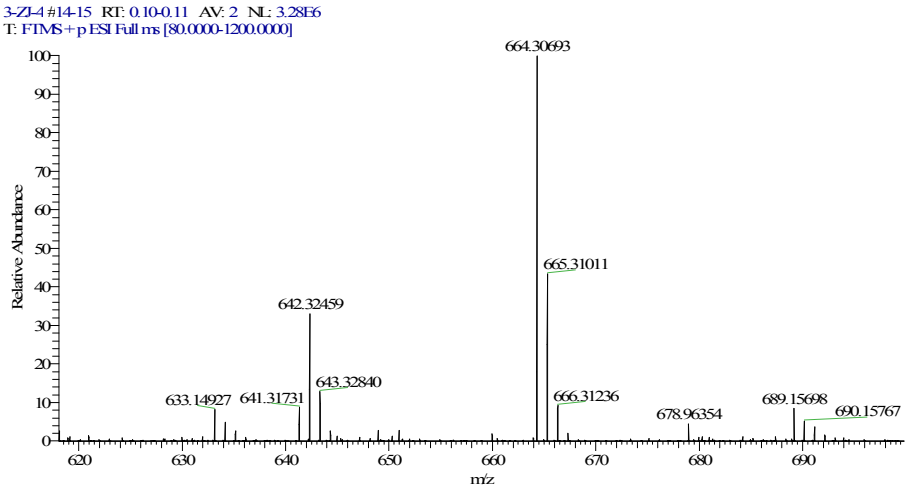


Fig. S44 HRMS spectrum of compound **APTBD-4**

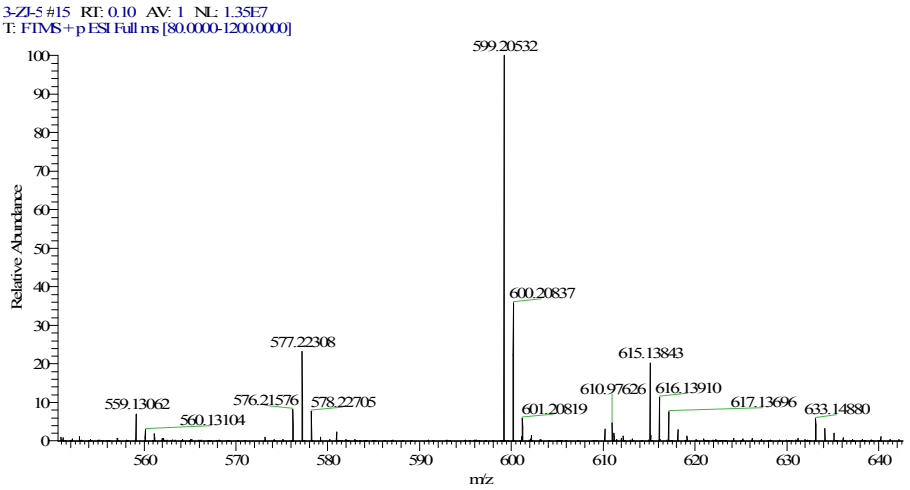


Fig. S45 HRMS spectrum of compound **APTBD-5**

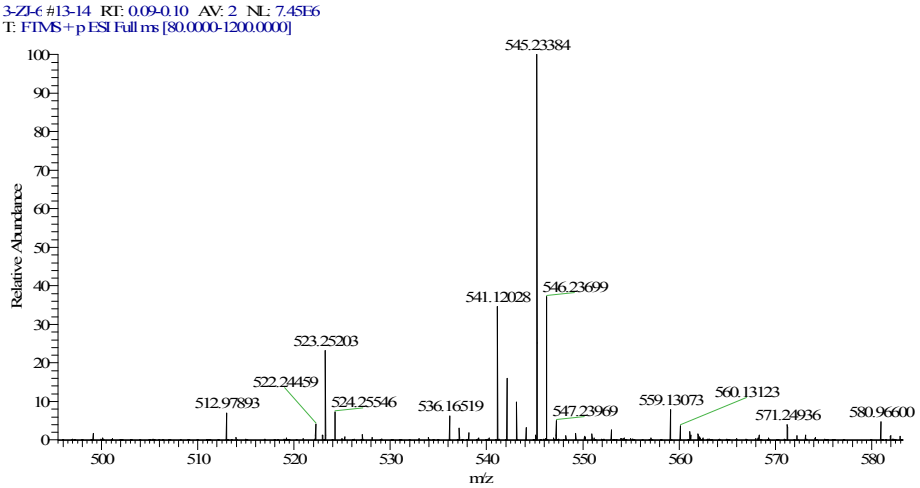


Fig. S46 HRMS spectrum of compound **APTBD-6**

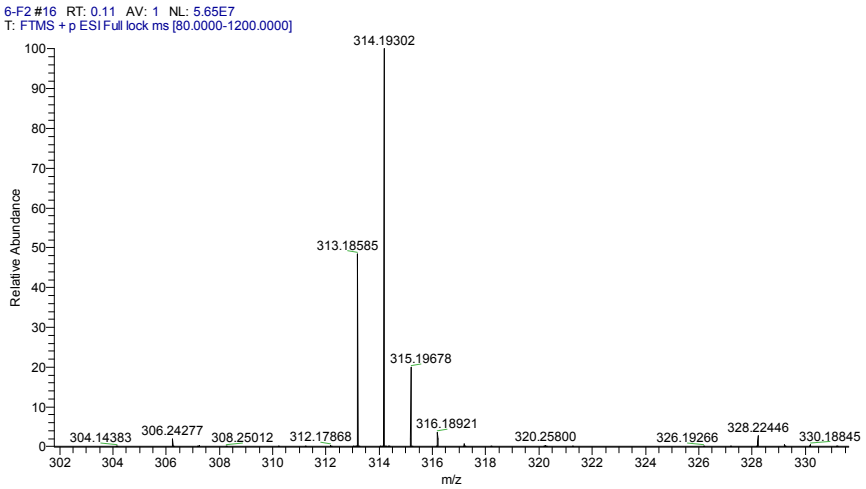


Fig. S47 HRMS spectrum of compound **F-2**

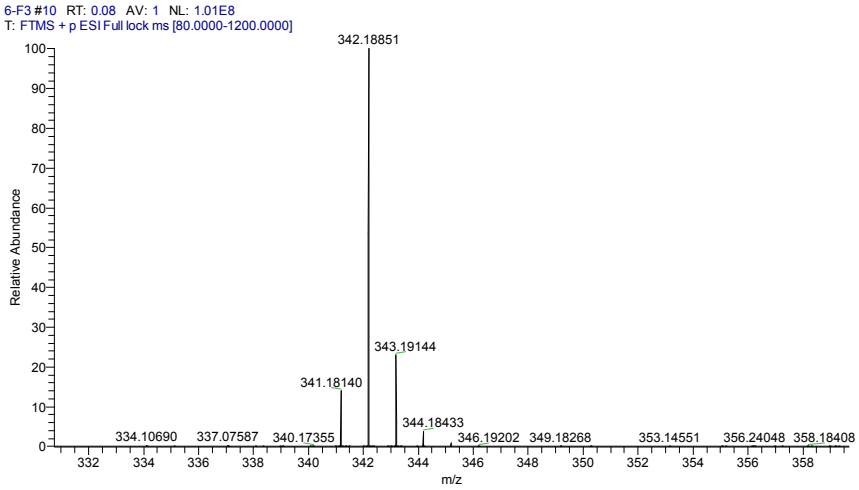


Fig. S48 HRMS spectrum of compound **F-3**

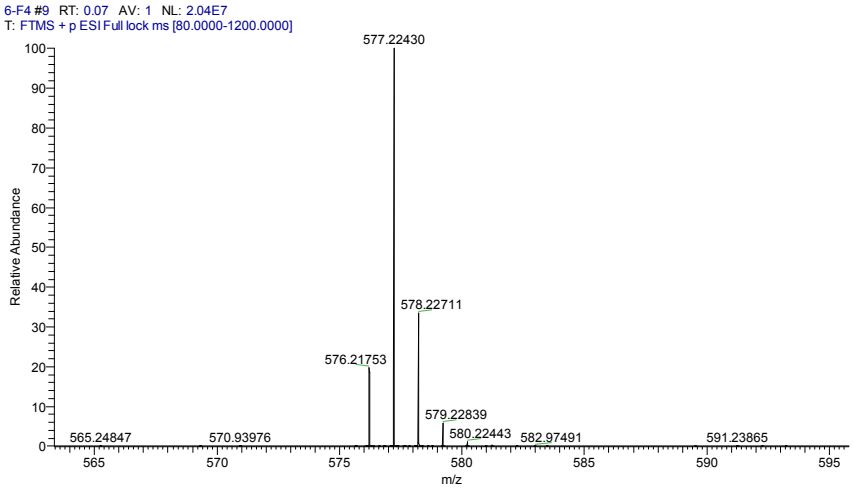


Fig. S49 HRMS spectrum of compound **APVTV-CF3TCF**

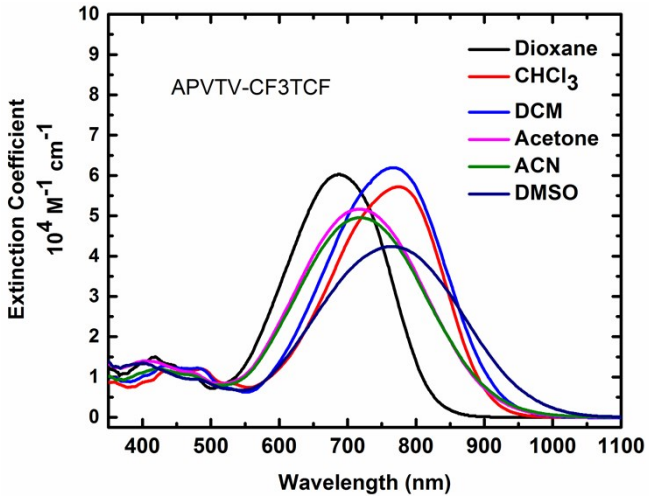


Fig. S50 UV-vis-NIR absorption spectra of **APVTV-CF_3TCF** in different solvents.

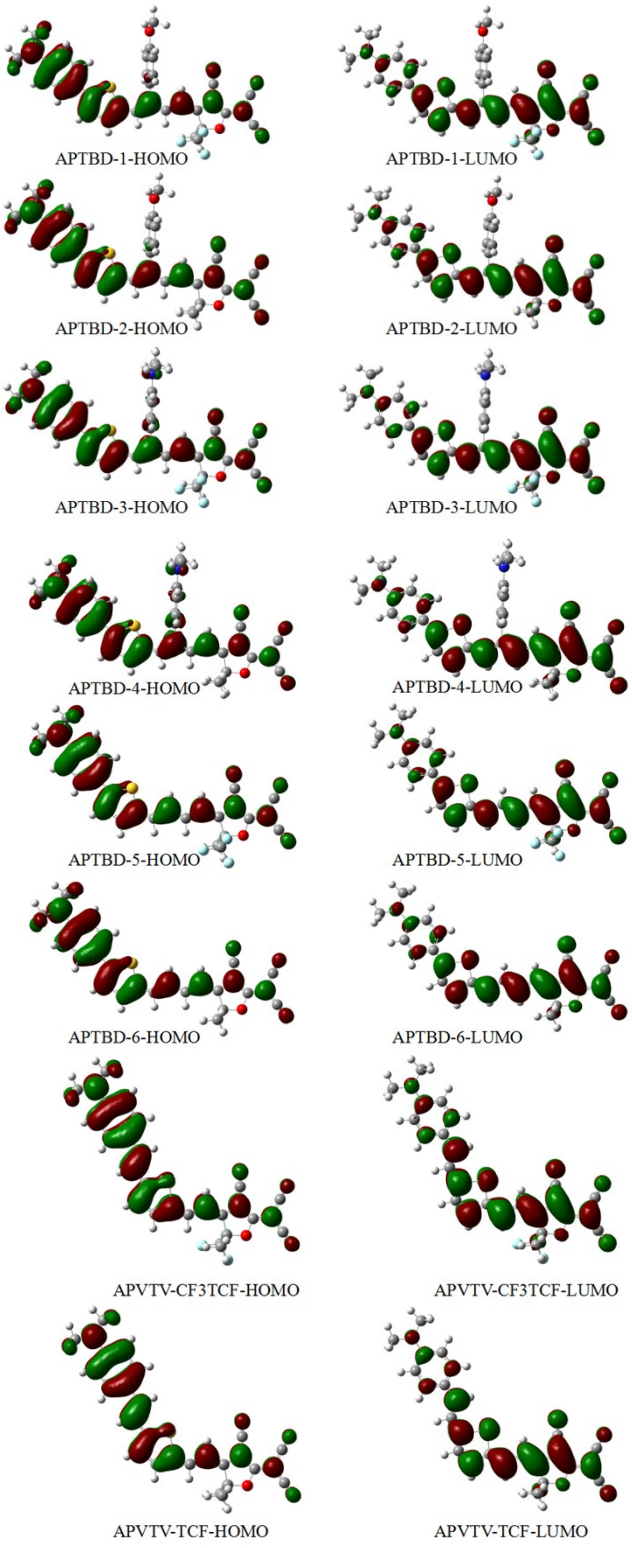


Fig. S51 HOMO and LUMO energy levels in vaccum of the chromophores.

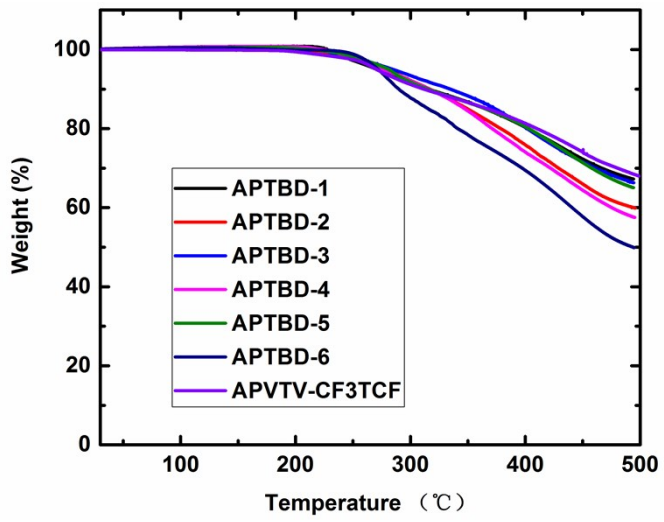


Fig. S52 TGA curves of chromophores with a heating rate of 10 °C min^{-1} under nitrogen.

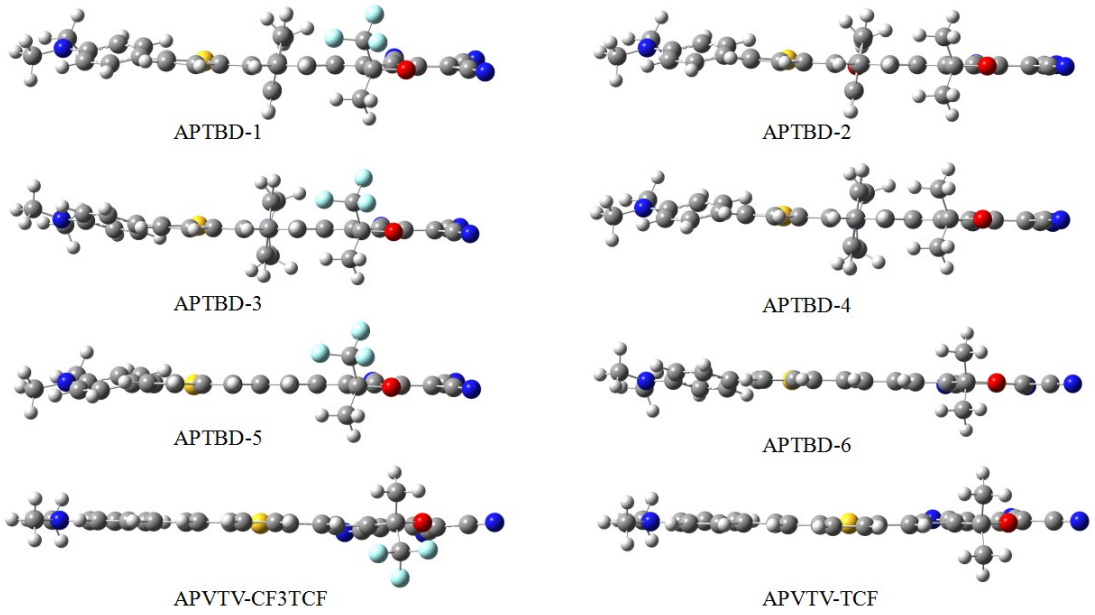


Fig. S53 The optimized structures of the chromophores

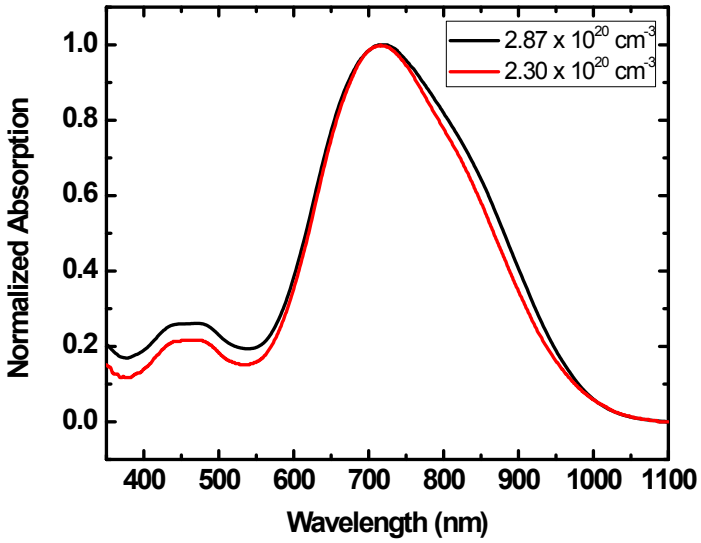


Fig. S54 Thin film absorption spectra of **APTBD-5** in P(S-*co*-MMA) at the loading density of 2.87×10^{20} cm^{-3} and 2.30×10^{20} cm^{-3}, respectively.

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