

Supporting Information for

Insights into Dye Design for Efficient p-type Photoelectrodes: Effect
of Oligothiophene Length between the Donor and the NiO Surface

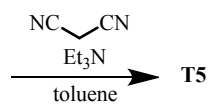
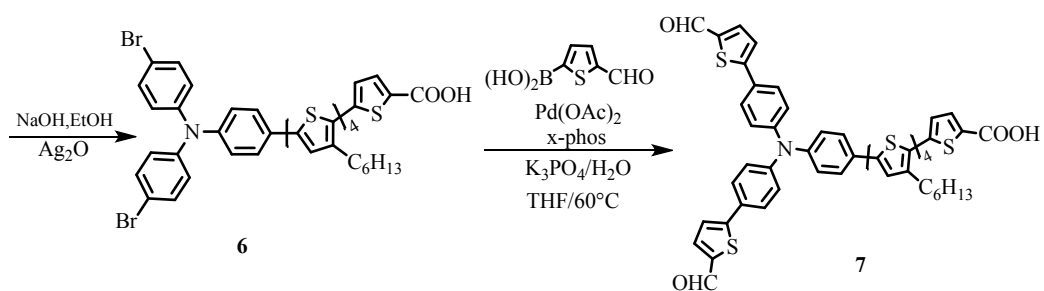
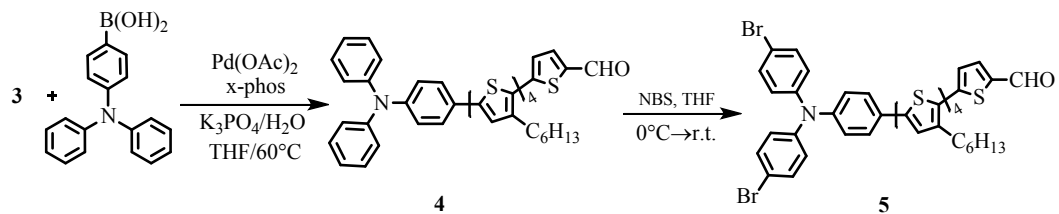
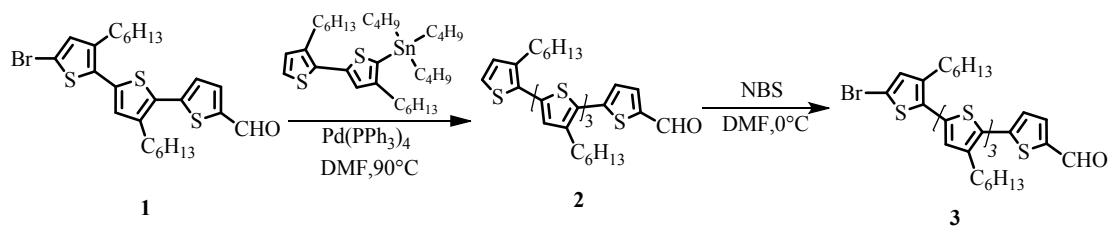
Fei Wu,^a Shangbi Zhao,^a Cheng Zhong,^b Qunliang Song,^a Linna Zhu^{*a}

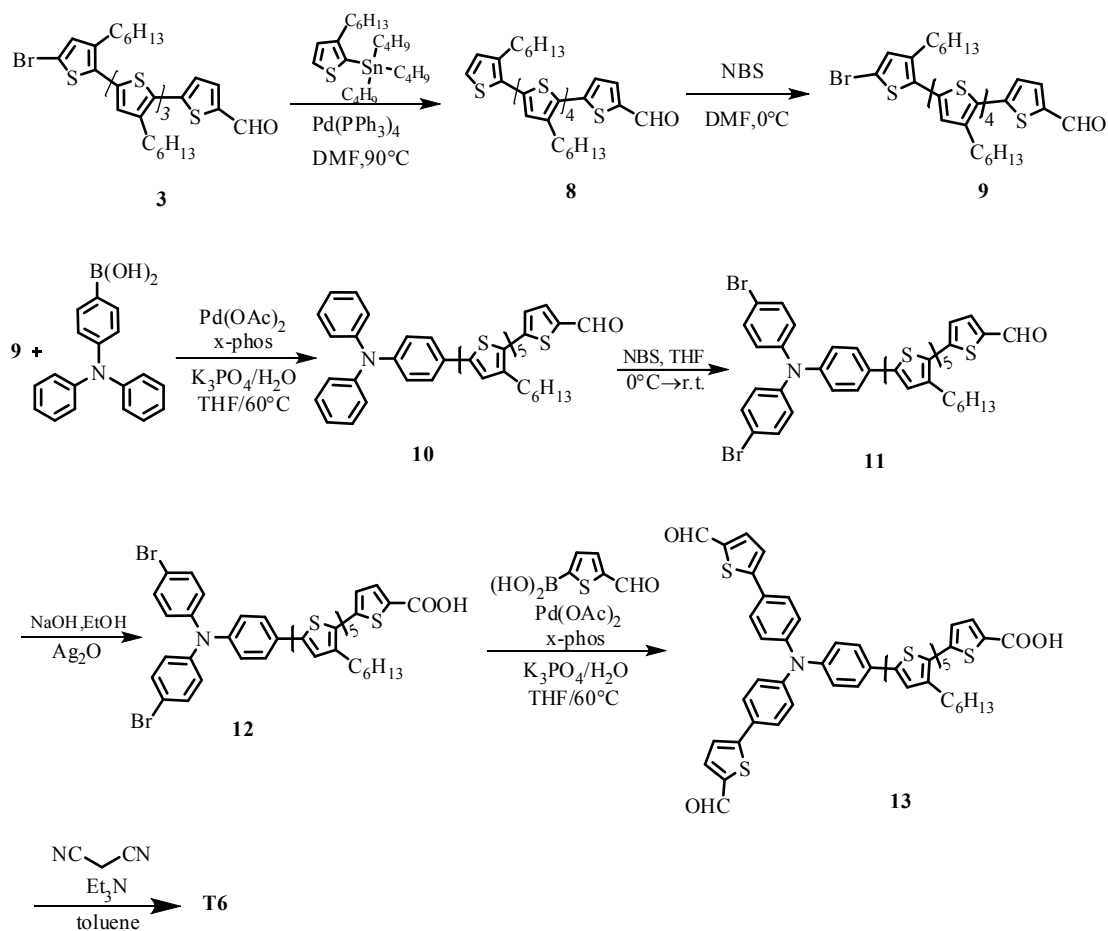
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Experimental Details

All starting materials were purchased from commercial suppliers (Sigma-Aldrich, J&K Scientific, and Energy Chemical) and used without further purification. Tetrahydrofuran (THF) for synthesis was freshly distilled over Na-K alloy under argon atmosphere prior to use. The ¹H NMR and ¹³C NMR spectra were recorded on a BRUKER AVANCE III 600 MHz NMR Instrument in CDCl₃, using tetramethylsilane as an internal reference. MALDI-TOF was performed on a Bruker Autoflex instrument, using 1,8,9-trihydroxyanthracene as a matrix. Elemental analyses of carbon, hydrogen, and nitrogen were performed on a Carlorerba-1106 microanalyzer. UV-Vis absorption spectra were recorded on a spectrophotometer (UV-2450, Shimadzu). Electrochemical experiments were performed using a CH Instruments electrochemical workstation (model 660A). The experiments were carried out in CH₂Cl₂ under Ar atmosphere in acetonitrile solution containing 0.1 mol/L tetrabutylammonium hexafluorophosphate (*n*-Bu₄NPF₆) as a supporting electrolyte at a scan rate of 50 mV s⁻¹. The potentials are quoted against the ferrocene internal standard.





Scheme S1. Synthetic routes for the new dyes T5 and T6.

Synthesis of compound 2

Compound 1 (950 mg, 1.81 mmol), tributyl(3',4'-dihexyl-2,2'-bithiophen-5-yl)stannane (1.2 g, 1.92 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (115 mg, 0.10 mmol) were dissolved in dry DMF (30 mL) in a Schlenk flask. The mixture was refluxed at 90°C for 16 h under an Ar atmosphere. Then the reaction was quenched with saturated NH_4Cl (aq). CH_2Cl_2 was used to extract the product and the organic phases are collected and dried over anhydrous sodium sulfate. After purifying by chromatography on a silica gel eluted with chloroform/ petroleum ether (1:5, v/v), red oil (compound 2) was obtained (1.158 g, 82%). ^1H NMR (600 MHz, CDCl_3): δ (ppm): 9.88 (s, 1H), 7.71 (d, $J = 3.6$ Hz, 1H), 7.27-7.23 (m, 1H), 7.16 (d, $J = 5.4$ Hz, 1H), 7.02-6.92 (m, 4H), 2.84-2.77 (m, 8H), 1.70-1.64

(m, 6H), 1.43-1.26 (m, 26H), 0.93-0.90 (m, 12H). ^{13}C NMR (150 MHz, CDCl_3): δ (ppm): 182.66, 146.29, 142.62, 142.34, 140.76, 140.16, 139.84, 136.71, 136.36, 134.71, 134.55, 130.53, 130.16, 129.76, 129.36, 129.24, 129.00, 128.90, 128.75, 125.93, 123.75, 31.74, 30.88, 30.68, 30.54, 30.45, 30.31, 29.84, 29.75, 29.61, 29.53, 29.38, 29.28, 29.15, 22.67, 14.10. Anal. calcd for $\text{C}_{45}\text{H}_{60}\text{OS}_5$ (%): C, 69.53; H, 7.78; Found: C, 69.82; H, 7.34.

Synthesis of compound 3

Compound 2 (1.13 g, 1.45 mmol) was dissolved in 25 mL of dry DMF and was cooled to 0°C. In the absence of light, a NBS solution (263 mg, 1.48 mmol dissolved in 5 mL of dry DMF) was added dropwisely, and the reaction mixture was stirred for one hour at 0 °C. The mixture was poured into water and extracted with CHCl_3 and the combined organic phases were washed with water. After the organic phase was dried over anhydrous sodium sulfate, the solvent was removed by rotary evaporation and the crude product was purified by column chromatography on silica gel using chloroform/petroleum ether (1:4, v/v) as eluent to yield a red oil (1.18 g, 95 %). ^1H NMR (600 MHz, CDCl_3): δ (ppm): 9.89 (s, 1H), 7.71 (d, $J = 4.2$ Hz, 1H), 7.24-7.22 (m, 2H), 7.00 (s, 1H), 6.96 (s, 1H), 6.89 (d, $J = 4.2$ Hz, 1H), 2.84-2.70 (m, 8H), 1.71-1.57 (m, 6H), 1.42-1.25 (m, 26H), 0.91-0.87 (m, 12H). ^{13}C NMR (150 MHz, CDCl_3): δ (ppm): 182.43, 146.20, 142.58, 142.33, 140.74, 140.36, 140.15, 136.68, 136.20, 134.33, 133.04, 132.77, 132.03, 130.74, 129.97, 129.40, 129.21, 129.01, 128.88, 126.78, 125.92, 110.46, 31.68, 31.65, 30.51, 30.48, 30.28, 29.80, 29.72, 29.65, 29.56, 29.44, 29.39, 29.25, 29.22, 29.12, 28.92, 22.63, 14.06. Anal. calcd for $\text{C}_{45}\text{H}_{59}\text{BrOS}_5$ (%): C, 63.13; H, 6.95; Found: C, 63.45; H, 6.81.

Synthesis of compound 4

In a 50 mL Schlenk tube, a mixture of compound 3 (522 mg, 0.57 mmol), (4-(diphenylamino)

phenyl) boronic acid (247 mg, 0.85 mmol), K_2CO_3 (586 mg, 4.25 mmol), $Pd(PPh_3)_4$ (49 mg, 0.043 mmol), water (3 mL), and THF (10 mL) were heated to 60 °C and refluxed overnight under an Ar atmosphere. After cooled to r.t., the mixture was washed with water and extracted with $CHCl_3$. The combined organic layer was dried over anhydrous sodium sulfate and concentrated using a rotary evaporator. The residue was purified by column chromatography on silica gel using chloroform/ petroleum ether (1:3, v/v) as eluent to yield the product as red oil (418 mg, 72%). 1H NMR (600 MHz, $CDCl_3$): δ (ppm): 9.88 (s, 1H), 7.71 (d, $J = 4.2$ Hz, 1H), 7.45 (d, $J = 8.4$ Hz, 2H), 7.28-7.22 (m, 6H), 7.15-7.11 (m, 4H), 7.06-7.00 (m, 6H), 6.97 (d, $J = 4.2$ Hz, 1H), 2.84-2.71 (m, 8H), 1.70-1.66 (m, 6H), 1.43-1.26 (m, 26H), 0.91-0.87 (m, 12H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm): 182.36, 147.48, 147.35, 146.19, 142.52, 142.21, 141.78, 140.67, 140.62, 140.11, 136.61, 136.27, 134.64, 129.80, 129.61, 129.28, 128.87, 128.58, 128.37, 128.11, 126.30, 125.81, 125.32, 124.68, 124.60, 124.54, 123.60, 123.12, 123.04, 31.64, 31.60, 30.46, 30.42, 30.20, 29.74, 29.64, 29.60, 29.50, 29.45, 29.19, 22.57, 14.06. Anal. calcd for $C_{63}H_{73}ONS_5$ (%): C, 74.14; H, 7.21; N, 1.37; Found: C, 74.55; H, 6.89; N, 1.47.

Synthesis of compound 5

Compound 4 (392 mg, 0.384 mmol) was dissolved in 15 mL THF, and the solution was cooled to 0 °C. NBS (150 mg, 0.845 mmol) was added in one portion and the mixture was stirred for 1 h at 0 °C. The mixture was allowed to warm to room temperature and stir overnight. The reaction was quenched by addition of water and extracted with $CHCl_3$. The combined organic phases were washed with water, and dried over anhydrous sodium sulfate. The crude product was purified by column chromatography on silica gel using chloroform/ petroleum ether (1:3, v/v) as eluent to obtain red oil (435 mg, 96 %). 1H NMR (600 MHz, $CDCl_3$): δ (ppm): 9.88 (s, 1H), 7.71 (d, $J = 3.6$

Hz, 1H), 7.46 (d, $J = 8.4$ Hz, 1H), 7.39-7.35(m, 4H), 7.24 (d, $J = 4.2$ Hz, 2H), 7.09-6.96 (m, 10H), 2.84-2.78 (m, 8H), 1.70-1.69 (m, 6H), 1.43-1.26 (m, 26H), 0.91-0.87 (m, 12H). ^{13}C NMR (150 MHz, CDCl_3): δ (ppm): 182.38, 146.27, 146.22, 142.54, 142.27, 141.28, 140.70, 140.16, 136.62, 136.25, 134.58, 134.39, 132.56, 132.48, 130.11, 130.05, 129.97, 129.71, 129.54, 129.47, 129.35, 129.30, 128.92, 128.66, 128.52, 126.78, 126.59, 126.12, 125.85, 125.76, 125.71, 125.50, 124.73, 124.29, 123.75, 123.10, 122.74, 115.95, 31.65, 31.63, 30.50, 30.46, 30.44, 30.24, 29.77, 29.67, 29.62, 29.53, 29.48, 29.22, 22.37, 13.95. Anal. calcd for $\text{C}_{63}\text{H}_{71}\text{Br}_2\text{NOS}_5$ (%): C, 64.21; H, 6.07; N, 1.19; Found: C, 64.67; H, 5.62; N, 1.54.

Synthesis of compound 6

Silver oxide (788 mg, 3.40 mmol) was suspended in anhydrous ethanol (40 mL) containing NaOH (748 mg, 18.7 mmol), and to this mixture was added compound 5 (405 mg, 0.34 mmol) dissolved in 10 mL toluene. The reaction was stirred at room temperature for 24 h. Then the solution was decanted and precooled hydrochloric acid was added slowly. The mixture was extracted with CHCl_3 . The organic phase was washed with water and dried with anhydrous sodium sulfate. After evaporation of the solvent, the residue was purified by column chromatography over silica gel using ethyl acetate/ petroleum ether (1:2, v/v) as the eluent to give the product as orange red oil (365 mg, 90 %). ^1H NMR (600 MHz, CDCl_3): δ (ppm): 7.83 (d, $J = 3.6$ Hz, 1H), 7.46 (d, $J = 7.8$ Hz, 1H), 7.39-7.36(m, 4H), 7.25 (s, 1H), 7.16 (d, $J = 3.6$ Hz, 1H), 7.07-6.96 (m, 10H), 2.83-2.78 (m, 8H), 1.69-1.65 (m, 6H), 1.43-1.26 (m, 26H), 0.90-0.87 (m, 12H). ^{13}C NMR (150 MHz, CDCl_3): δ (ppm): 166.67, 146.23, 144.73, 141.84, 141.24, 140.67, 140.51, 140.08, 135.66, 135.23, 134.31, 132.56, 132.48, 130.12, 129.95, 129.88, 129.76, 129.48, 129.38, 128.75, 128.63, 128.52, 126.59, 126.12, 125.91, 125.85, 125.70, 124.30, 123.74, 123.12, 115.95, 31.91, 31.67, 31.64,

31.50, 31.43, 30.50, 30.46, 30.30, 29.68, 29.62, 29.51, 29.33, 29.23, 29.19, 22.61, 14.05. Anal. calcd for C₆₃H₇₁Br₂NO₂S₅ (%): C, 63.35; H, 5.99; N, 1.19; Found: C, 63.45; H, 5.71; N, 1.34.

Synthesis of compound 7

A mixture of compound 6 (267 mg, 0.22 mmol), 5-formyl-2-thiophene-boronic acid (82.6 mg, 0.53 mmol), Pd(OAc)₂ (5.39 mg, 0.024 mmol), x-phos (14.3 mg, 0.03 mmol), and K₃PO₄ (573 mg, 2.70 mmol) in THF (10 mL) and H₂O (3 mL) were stirred at 60 °C for 24 h. After cooled to room temperature, the reaction mixture was poured into saturated NH₄Cl solution, and extracted with CHCl₃. The combined organic phases were washed with water and brine, and dried over anhydrous sodium sulfate. The crude product was purified by column chromatography on silica gel using EtOH/CHCl₃ (1:30, v/v) as eluent to give a red powder (214 mg, 77%). ¹H NMR (600 MHz, CDCl₃): δ (ppm): 9.87 (s, 2H), 7.81 (br, 1H), 7.73-7.71 (m, 2H), 7.61-7.53 (m, 5H), 7.34 (d, *J* = 4.2 Hz, 1H), 7.31 (d, *J* = 6.0 Hz, 1H), 7.25 (s, 1H), 7.20-7.09 (m, 8H), 7.04-6.98 (m, 3H), 2.83-2.78 (m, 8H), 1.71-1.69 (m, 6H), 1.43-1.26 (m, 26H), 0.91-0.87 (m, 12H). ¹³C NMR (150 MHz, CDCl₃): δ (ppm): 182.55, 153.97, 149.64, 148.00, 145.76, 145.62, 144.44, 141.97, 141.79, 140.76, 140.53, 140.48, 140.09, 137.46, 135.58, 135.04, 134.30, 134.17, 130.31, 130.10, 130.01, 129.63, 128.79, 128.70, 128.63, 127.94, 127.59, 127.47, 127.39, 126.77, 126.05, 125.94, 125.57, 125.43, 124.25, 124.13, 123.51, 123.42, 123.06, 120.35, 31.71, 31.68, 31.28, 30.84, 30.55, 30.51, 30.35, 29.71, 29.67, 29.63, 29.54, 29.51, 29.26, 29.23, 29.19, 22.61, 14.05. Anal. calcd for C₇₃H₇₇NO₄S₇ (%): C, 69.76; H, 6.18; N, 1.11; Found: C, 69.70; H, 5.76; N, 1.48.

Synthesis of compound 8

Compound 3 (624 mg, 0.73 mmol), tributyl(3-hexylthiophen-2-yl)stannane (266 mg, 0.80 mmol) and Pd(PPh₃)₄ (46.2 mg, 0.04 mmol) were dissolved in dry DMF (20 mL) in a Schlenk flask. The

mixture was refluxed at 90 °C for 16 h under an Ar atmosphere. The reaction was then quenched with saturated NH₄Cl (aq). CH₂Cl₂ was used to extract the product and dried over anhydrous sodium sulfate. After purifying by chromatography on a silica gel eluted with chloroform/petroleum ether (1:3, v/v), a red oil (compound 8) was obtained (424 mg, 62%). ¹H NMR (600 MHz, CDCl₃): δ (ppm): 9.88 (s, 1H), 7.71 (d, *J* = 4.2 Hz, 1H), 7.24-7.23 (m, 1H), 7.16 (d, *J* = 8.4 Hz, 1H), 7.01-6.92 (m, 5H), 2.84-2.76 (m, 10H), 1.70-1.58 (m, 10H), 1.43-1.25 (m, 30H), 0.90-0.87 (m, 15H). ¹³C NMR (150 MHz, CDCl₃): δ (ppm): 182.49, 146.25, 142.58, 142.21, 140.72, 140.16, 139.92, 139.70, 136.78, 136.28, 134.59, 134.27, 134.12, 132.76, 130.52, 130.30, 130.12, 129.71, 129.29, 128.92, 128.82, 128.67, 128.63, 125.85, 124.29, 123.65, 31.70, 31.67, 30.65, 30.51, 30.49, 30.47, 30.27, 29.81, 29.71, 29.65, 29.56, 29.50, 29.33, 29.26, 29.12, 28.92, 22.64, 14.09. Anal. calcd for C₅₅H₇₄OS₆ (%): C, 70.01; H, 7.90; Found: C, 70.41; H, 7.49.

Synthesis of compound 9

Compound 8 (390 mg, 0.41 mmol) was dissolved in 15 mL of dry DMF and was cooled to 0 °C. In the absence of light, a NBS solution (74.4 mg, 0.418 mmol dissolved in 5 mL of dry DMF) was added dropwisely, and the reaction mixture was stirred for another hour at 0 °C. The mixture was then poured into water and extracted with CHCl₃, and the combined organic phases were washed with water. After the organic phase was dried over anhydrous sodium sulfate, the solvent was removed by rotary evaporation and the crude product was purified by column chromatography on silica gel using chloroform/petroleum ether (1:3, v/v) as eluent to yield a red oil (377 mg, 90 %). ¹H NMR (600 MHz, CDCl₃): δ (ppm): 9.89 (s, 1H), 7.71 (d, *J* = 4.2 Hz, 1H), 7.24-7.22 (m, 2H), 7.01-6.93 (m, 3H), 6.88 (d, *J* = 4.8 Hz, 1H), 2.84-2.70 (m, 10H), 1.70-1.56 (m, 10H), 1.43-1.26 (m, 30H), 0.90-0.87 (m, 15H). ¹³C NMR (150 MHz, CDCl₃): δ (ppm): 182.78, 146.39, 142.86, 142.53,

141.00, 140.61, 140.47, 140.40, 140.23, 137.05, 136.51, 134.76, 134.56, 134.06, 133.03, 130.97, 130.68, 130.54, 130.20, 129.61, 129.46, 129.23, 129.08, 129.02, 126.16, 124.57, 110.64, 31.95, 31.92, 30.79, 30.75, 30.55, 30.08, 29.99, 29.90, 29.84, 29.76, 29.70, 29.65, 29.53, 29.39, 29.18, 22.91, 14.36. Anal. calcd for $C_{55}H_{73}BrOS_6$ (%): C, 64.61; H, 7.20; Found: C, 64.99; H, 6.83.

Synthesis of compound 10

In a 50 mL Schlenk tube, a mixture of compound 9 (240 mg, 0.23 mmol), (4-(diphenylamino)phenyl) boronic acid (99.7 mg, 0.34 mmol), K_2CO_3 (235 mg, 1.70 mmol), $Pd(PPh_3)_4$ (19.6 mg, 0.017 mmol), water (3 mL), and THF (10 mL) were heated to 60 °C and refluxed overnight under an Ar atmosphere. After cooling to r.t., the mixture was washed with water and extracted with $CHCl_3$. The combined organic layer was dried over anhydrous sodium sulfate and was concentrated using a rotary evaporator. The residue was purified by column chromatography on silica gel using chloroform/ petroleum ether (1:3, v/v) as eluent to yield the product as a red oil (235 mg, 86%). 1H NMR (600 MHz, $CDCl_3$): δ (ppm): 9.89 (s, 1H), 7.71 (d, $J = 4.2$ Hz, 1H), 7.44 (d, $J = 8.4$ Hz, 1H), 7.29-7.22 (m, 6H), 7.15-7.09 (m, 5H), 7.08-7.03 (m, 5H), 7.01-6.97 (m, 3H), 2.84-2.75 (m, 10H), 1.70-1.55 (m, 10H), 1.43-1.26 (m, 30H), 0.91-0.87 (m, 15H). ^{13}C NMR (150 MHz, $CDCl_3$): δ (ppm): 182.50, 147.52, 146.26, 142.59, 142.21, 140.72, 140.18, 139.98, 136.78, 134.61, 134.40, 130.28, 130.09, 129.34, 128.93, 128.67, 128.41, 126.34, 125.86, 125.37, 124.73, 124.57, 124.51, 124.29, 123.66, 123.15, 31.69, 31.67, 30.49, 30.36, 30.27, 29.81, 29.71, 29.66, 29.56, 29.50, 29.26, 22.61, 14.09. Anal. calcd for $C_{73}H_{87}NOS_6$ (%): C, 73.87; H, 7.39; N, 1.18; Found: C, 74.15; H, 6.88; N, 1.34.

Synthesis of compound 11

Compound 10 (210 mg, 0.18 mmol) was dissolved in 18 mL THF, and the solution was cooled to

0 °C. NBS (70 mg, 0.39 mmol) was added in one portion and the mixture was stirred for 1 h at 0 °C. The mixture was allowed to warm to room temperature and stirring overnight. The reaction was quenched by addition water and extracted with CHCl₃. The combined organic phases were washed with water, and dried over anhydrous sodium sulfate. The crude product was purified by column chromatography on silica gel using chloroform/ petroleum ether (1:4, v/v) as eluent to obtain a red oil (239 mg, 98 %). ¹H NMR (600 MHz, CDCl₃): δ (ppm): 9.89 (s, 1H), 7.71 (d, *J* = 3.6 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.39-7.36 (m, 4H), 7.25-7.22 (m, 2H), 7.08-6.96 (m, 11H), 2.85-2.77 (m, 10H), 1.70-1.55 (m, 10H), 1.43-1.26 (m, 30H), 0.90-0.87 (m, 15H). ¹³C NMR (150 MHz, CDCl₃): δ (ppm): 182.48, 163.42, 146.21, 146.10, 142.57, 142.20, 141.18, 140.71, 140.63, 140.15, 139.98, 136.76, 136.25, 135.47, 132.87, 132.56, 132.48, 132.37, 130.11, 129.69, 129.55, 128.92, 128.66, 128.51, 126.57, 126.13, 125.86, 125.71, 125.40, 124.28, 123.72, 123.11, 122.36, 116.25, 115.93, 111.10, 31.65, 31.50, 30.46, 30.25, 29.79, 29.63, 29.54, 29.48, 29.24, 29.09, 22.60, 14.05. Anal. calcd for C₇₃H₈₅Br₂NOS₆ (%): C, 65.20; H, 6.37; N, 1.04; Found: C, 65.54; H, 5.89; N, 1.31.

Synthesis of compound 12

Silver oxide (362 mg, 1.56 mmol) was suspended in anhydrous ethanol (30 mL) containing NaOH (350 mg, 8.76 mmol) and to this mixture was added compound 11 (210 mg, 0.16 mmol) dissolved in 5 mL toluene. The reaction was stirred at room temperature for 24 h. Then the solution was decanted and precooled hydrochloric acid was added slowly. The mixture was extracted with CHCl₃. The organic phase was washed with water and dried with anhydrous sodium sulfate. After evaporation of the solvent, the residue was purified by column chromatography over silica gel using ethyl acetate/ petroleum ether (1:2, v/v) as the eluent to give the product as red oil (193 mg,

88%). ^1H NMR (600 MHz, CDCl_3): δ (ppm): 7.82 (br, 1H), 7.54 (d, $J = 8.4$ Hz, 1H), 7.46 (d, $J = 2.4$ Hz, 1H), 7.39-7.36 (m, 4H), 7.15 (d, $J = 3.0$ Hz, 2H), 7.08-6.96 (m, 10H), 2.83-2.78 (m, 10H), 1.70-1.61 (m, 10H), 1.43-1.26 (m, 30H), 0.90-0.87 (m, 15H). ^{13}C NMR (150 MHz, CDCl_3): δ (ppm): 177.97, 146.21, 146.04, 145.79, 141.80, 141.78, 137.57, 135.20, 135.09, 134.28, 133.53, 132.55, 132.47, 130.05, 129.86, 129.48, 129.44, 128.67, 128.55, 126.57, 126.12, 125.90, 125.85, 125.70, 125.13, 124.29, 123.09, 116.26, 115.91, 31.92, 31.67, 30.47, 30.31, 29.69, 29.60, 29.50, 29.24, 29.20, 22.62, 14.08. Anal. calcd for $\text{C}_{73}\text{H}_{85}\text{Br}_2\text{NO}_2\text{S}_6$ (%): C, 64.44; H, 6.30; N, 1.03; Found: C, 64.67; H, 6.00; N, 1.52.

Synthesis of compound 13

A mixture of compound 12 (170 mg, 0.12 mmol), 5-formyl-2-thiophene-boronic acid (45 mg, 0.29 mmol), $\text{Pd}(\text{OAc})_2$ (3.90 mg, 0.017 mmol), x-phos (9.95 mg, 0.02 mmol), and K_3PO_4 (314 mg, 1.48 mmol) in THF (10 mL) and H_2O (3 mL) were stirred at 60 °C for 24 h. After cooling to room temperature, the reaction mixture was poured into saturated NH_4Cl solution, and then was extracted with CHCl_3 . The combined organic phases were washed with water and brine, and dried over anhydrous sodium sulfate. The crude product was purified by column chromatography on silica gel using EtOH/ CHCl_3 (1:20, v/v) as eluent to give a red powder (104 mg, 61%). ^1H NMR (600 MHz, CDCl_3): δ (ppm): 9.88 (s, 2H), 7.82 (s, 1H), 7.74-7.72 (m, 2H), 7.61-7.53 (m, 2H), 7.54 (d, $J = 5.4$ Hz, 1H), 7.37-7.32 (m, 3H), 7.21-7.09 (m, 8H), 7.08-6.96 (m, 6H), 2.83-2.78 (m, 10H), 1.71-1.59 (m, 10H), 1.43-1.26 (m, 30H), 0.90-0.85 (m, 15H). ^{13}C NMR (150 MHz, CDCl_3): δ (ppm): 182.61, 155.83, 153.96, 151.96, 149.85, 148.71, 147.95, 143.98, 141.87, 140.46, 137.55, 132.48, 132.33, 131.71, 131.31, 129.92, 129.55, 129.46, 128.72, 128.63, 128.55, 127.89, 127.85, 127.55, 127.39, 126.71, 125.90, 125.70, 125.53, 124.80, 124.51, 124.08, 123.38, 31.68, 31.65,

30.64, 30.48, 30.32, 29.69, 29.61, 29.51, 29.24, 29.21, 29.10, 28.56, 22.60, 14.05. Anal. calcd for

$C_{83}H_{91}NO_4S_8$ (%): C, 70.05; H, 6.45; N, 0.98; Found: C, 70.42; H, 6.05; N, 1.32.

1H NMR, ^{13}C NMR Spectra and the MALDI-TOF Spectra

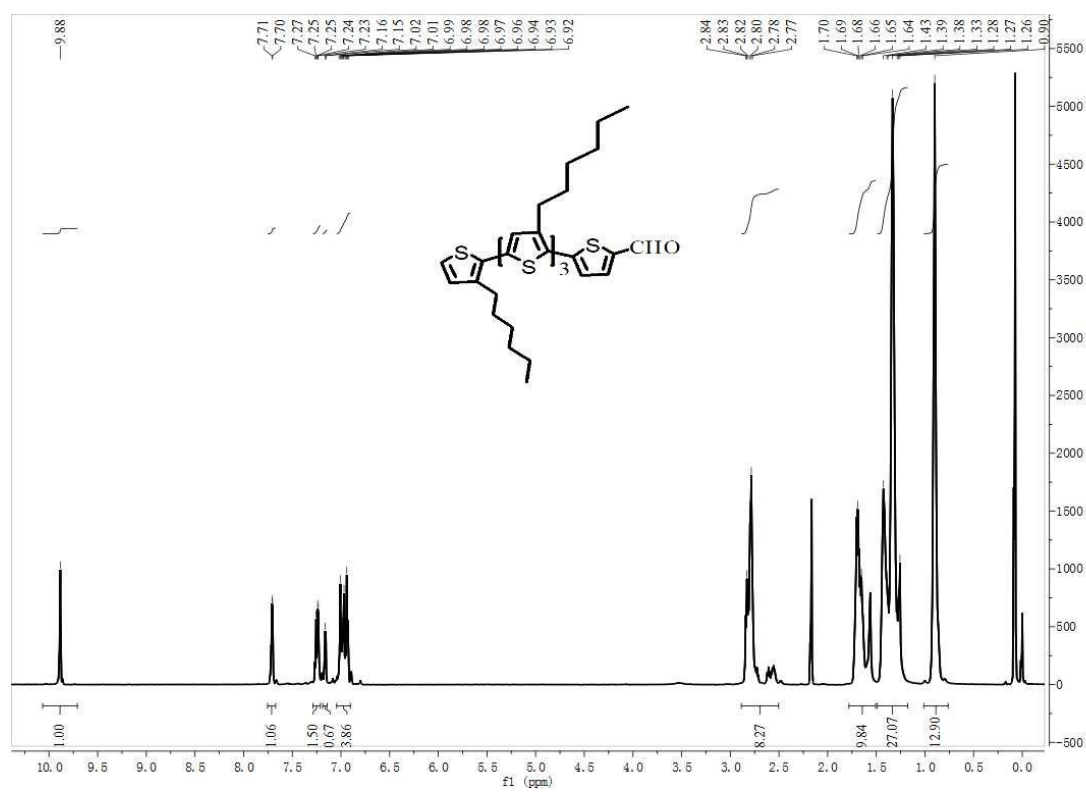


Figure S1: 1H NMR of compound 2 in $CDCl_3$

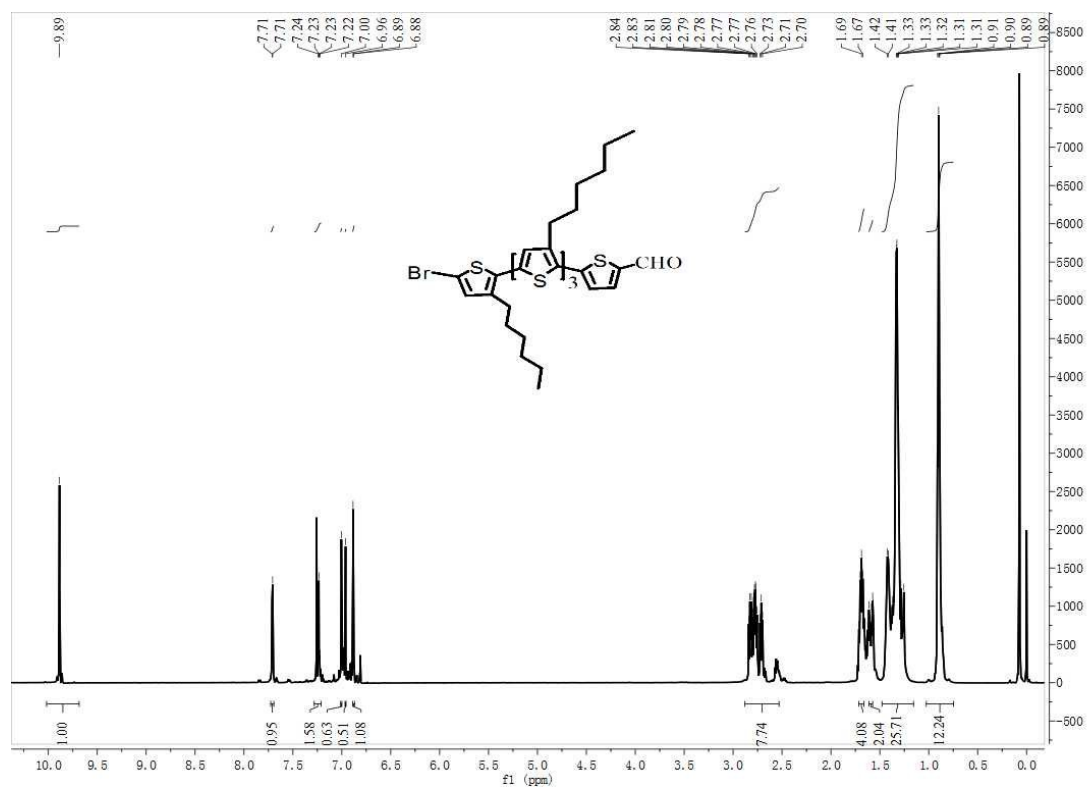


Figure S2: ^1H NMR of compound 3 in CDCl_3

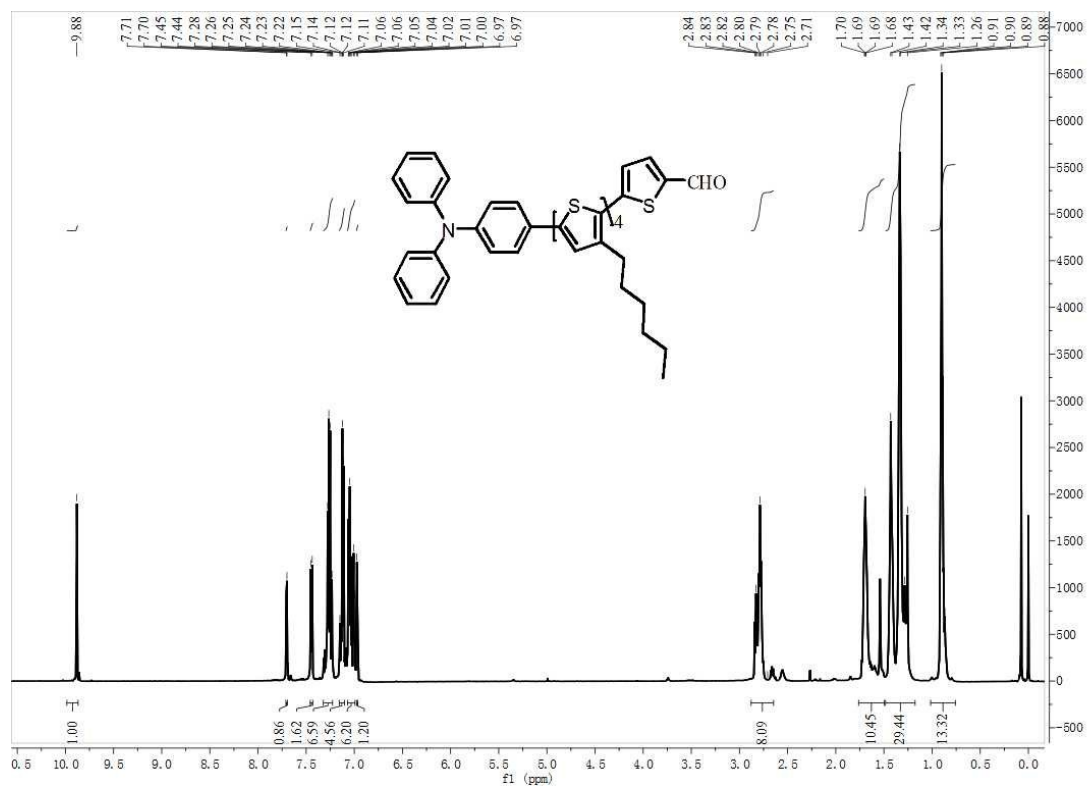


Figure S3: ^1H NMR of compound 4 in CDCl_3

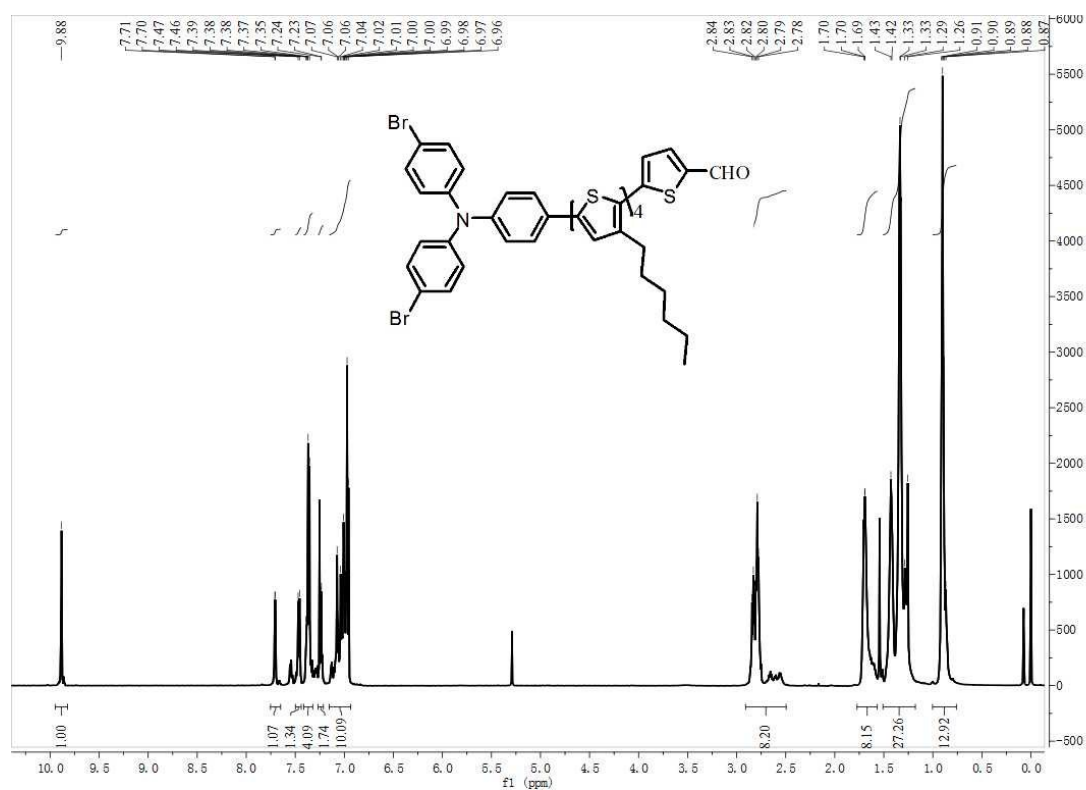


Figure S4: ^1H NMR of compound 5 in CDCl_3

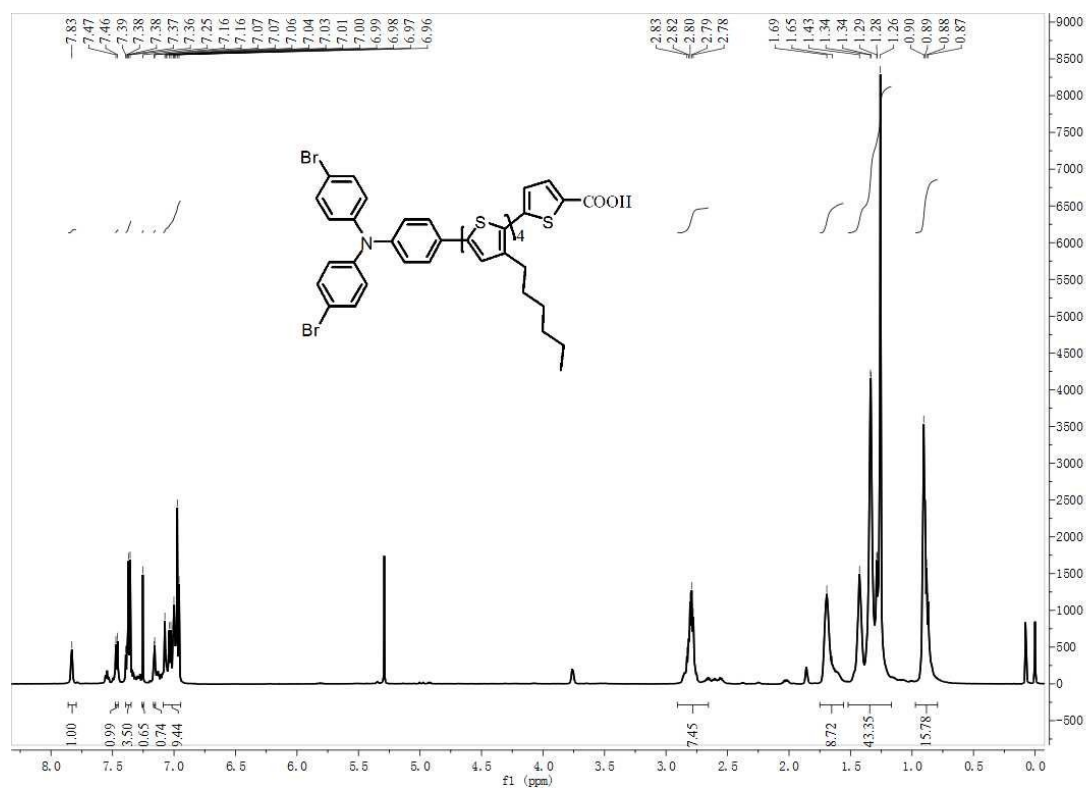


Figure S5: ^1H NMR of compound 6 in CDCl_3

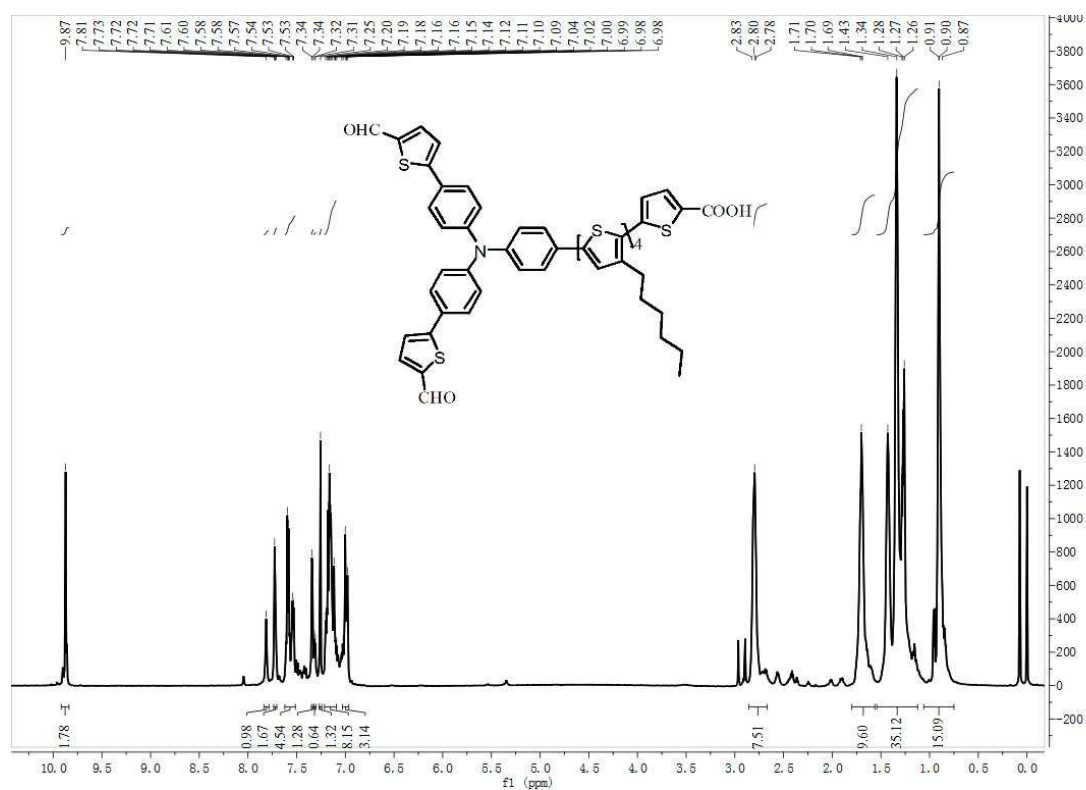


Figure S6: ^1H NMR of compound 7 in CDCl_3

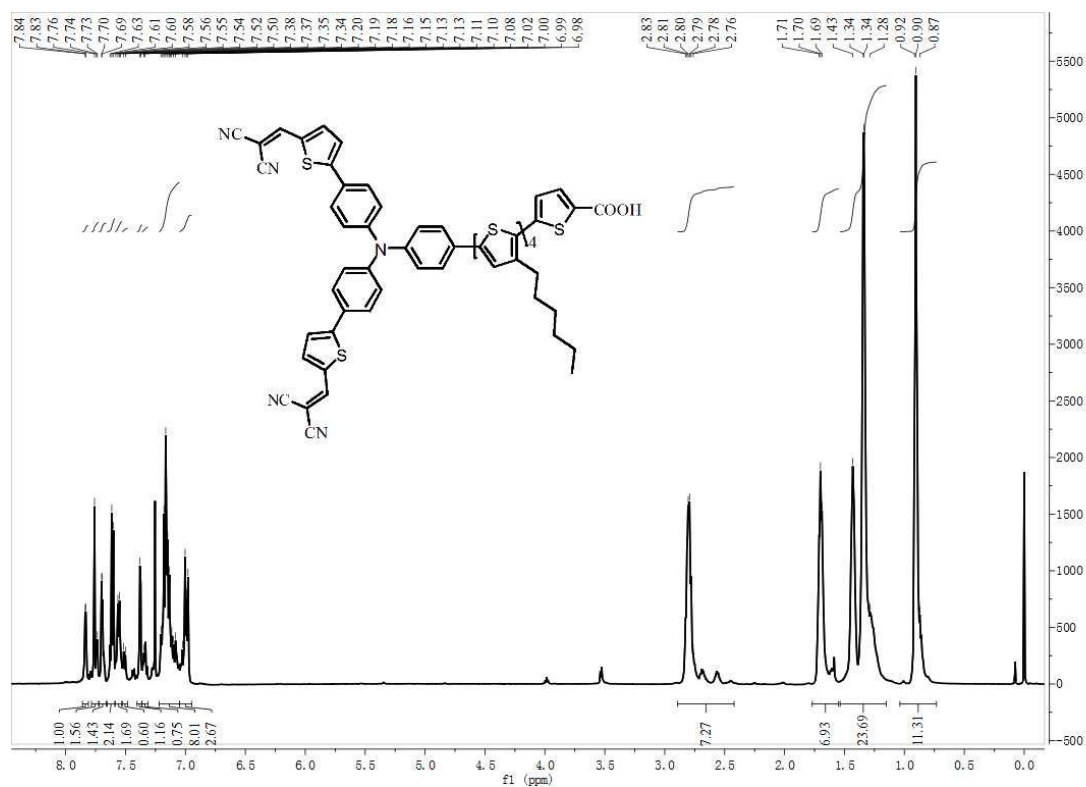


Figure S7: ^1H NMR of T5 in CDCl_3

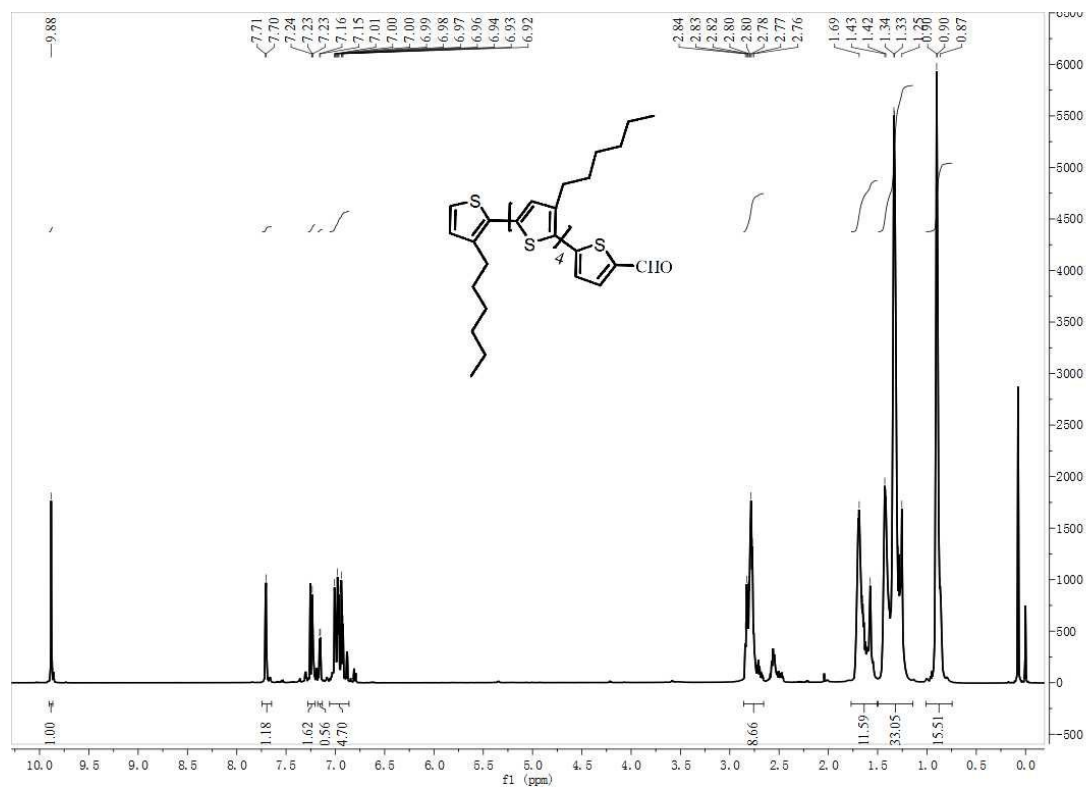


Figure S8: ^1H NMR of compound 8 in CDCl_3

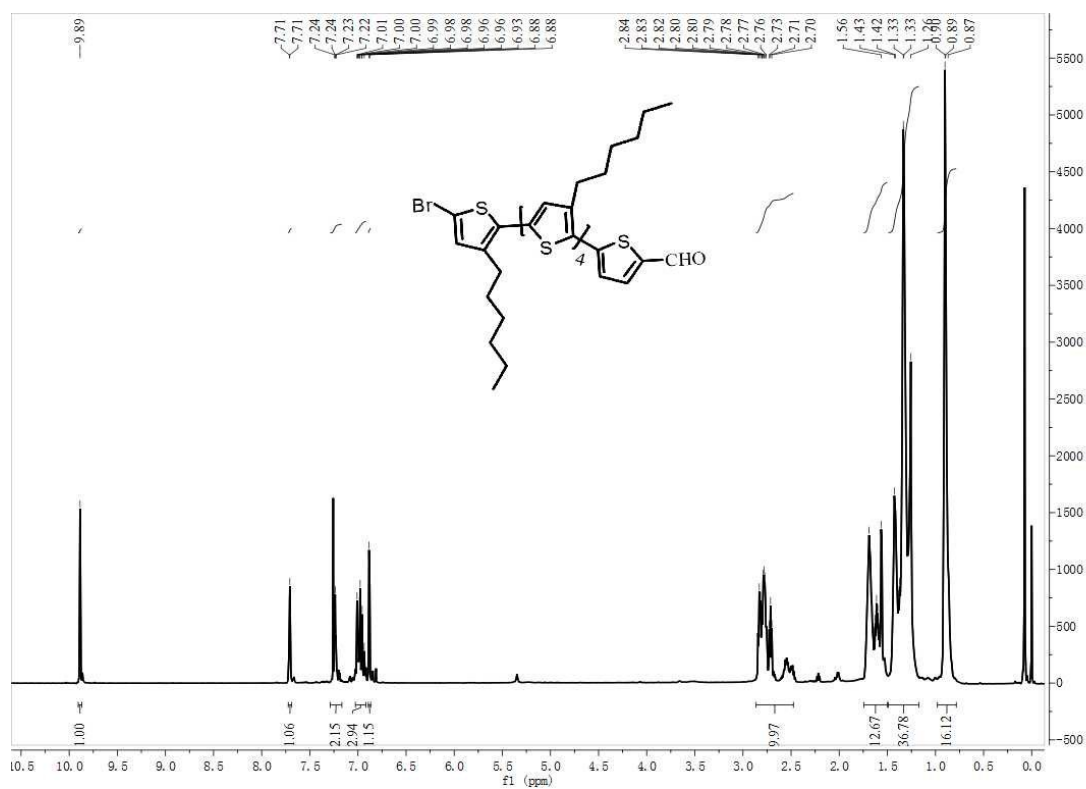


Figure S9: ^1H NMR of compound 9 in CDCl_3

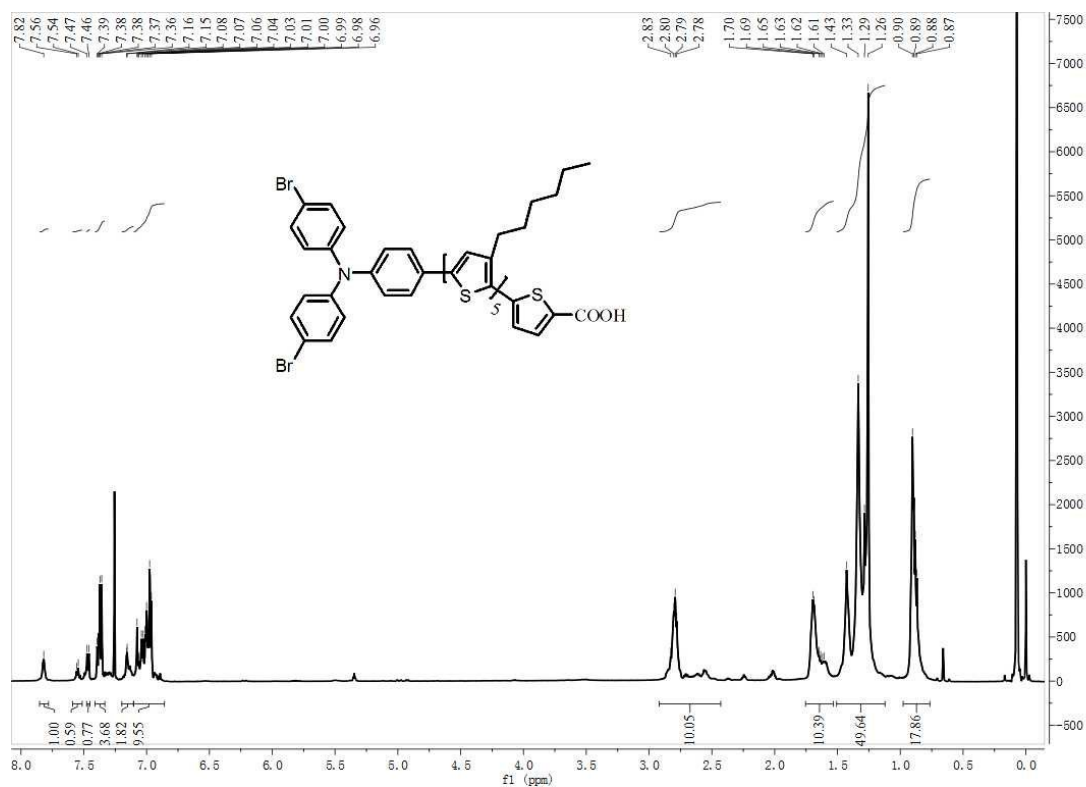


Figure S12: ¹H NMR of compound 12 in CDCl₃

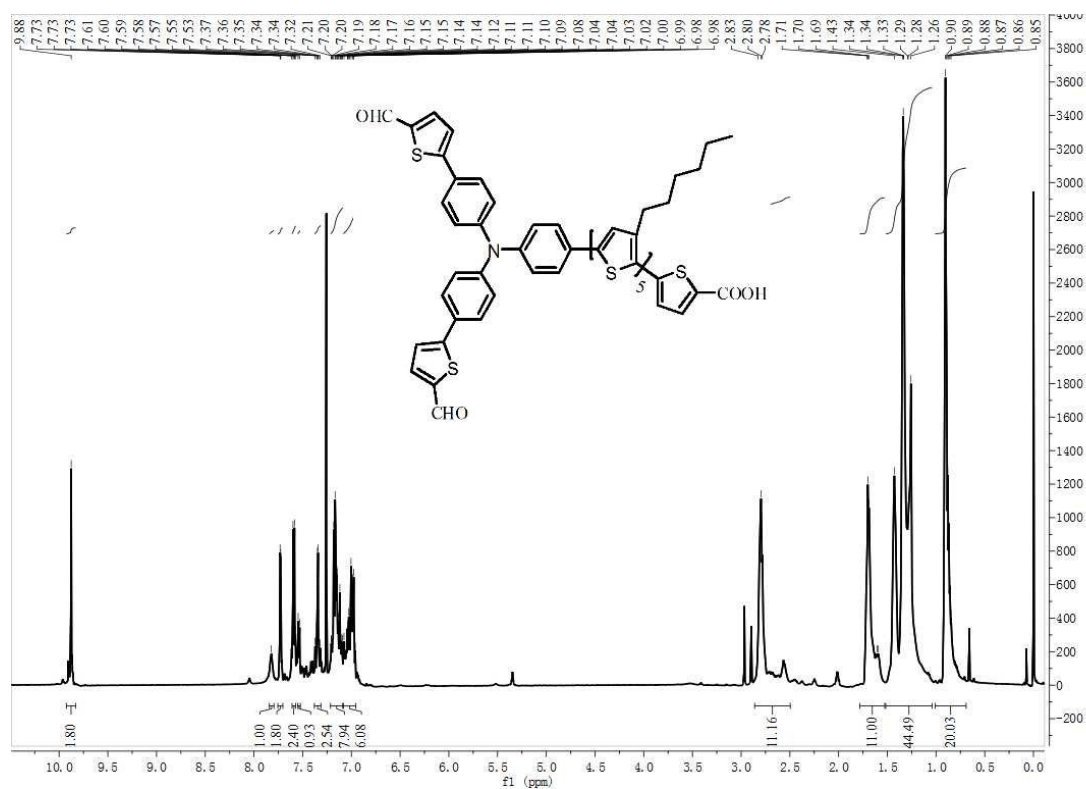


Figure S13: ¹H NMR of compound 13 in CDCl₃

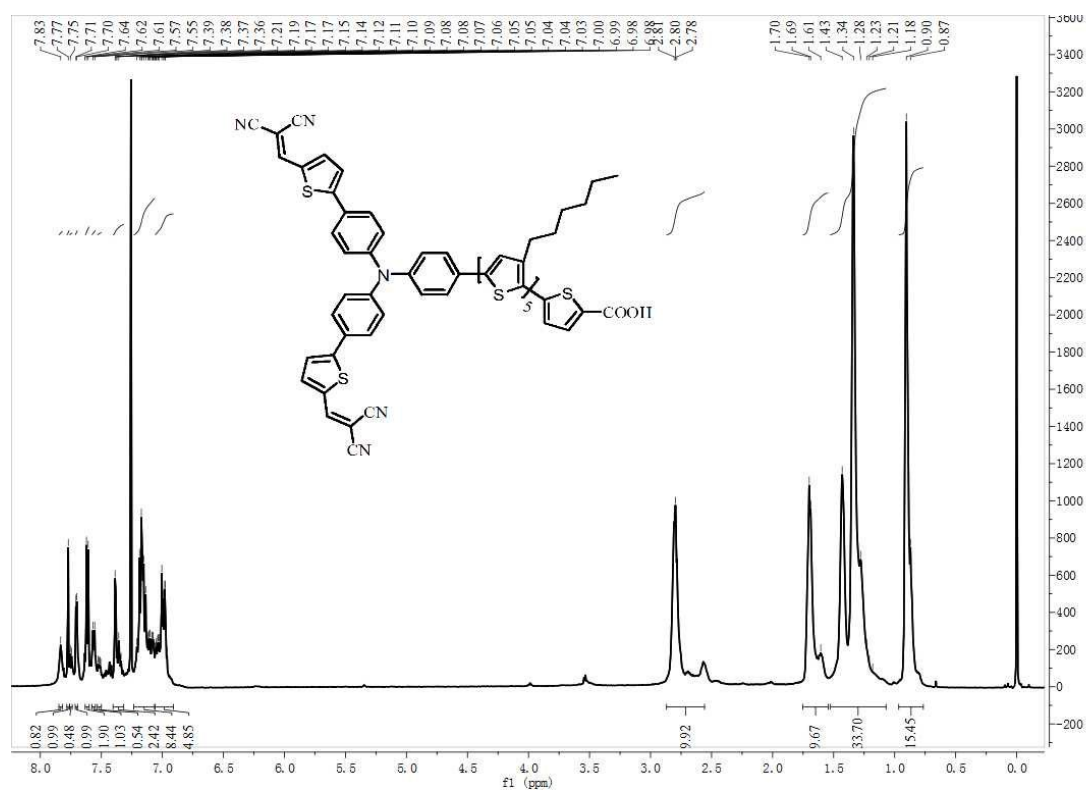


Figure S14: ¹H NMR of T6 in CDCl₃

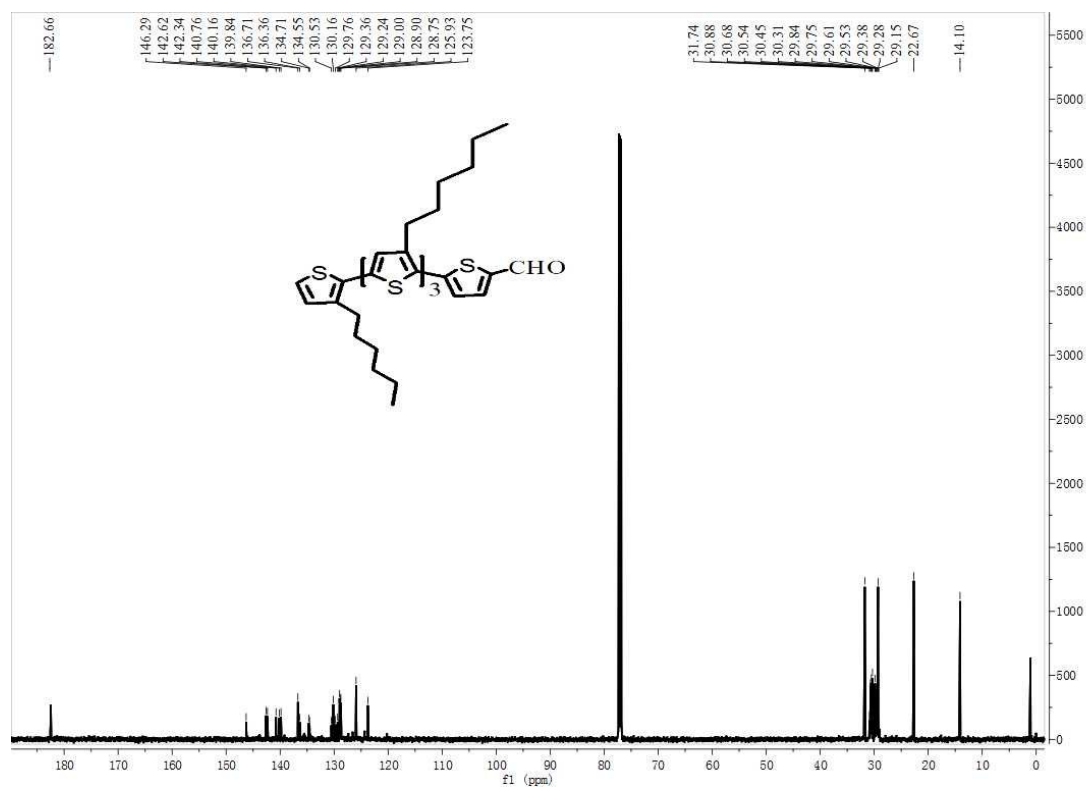


Figure S15: ¹³C NMR of compound 2 in CDCl₃

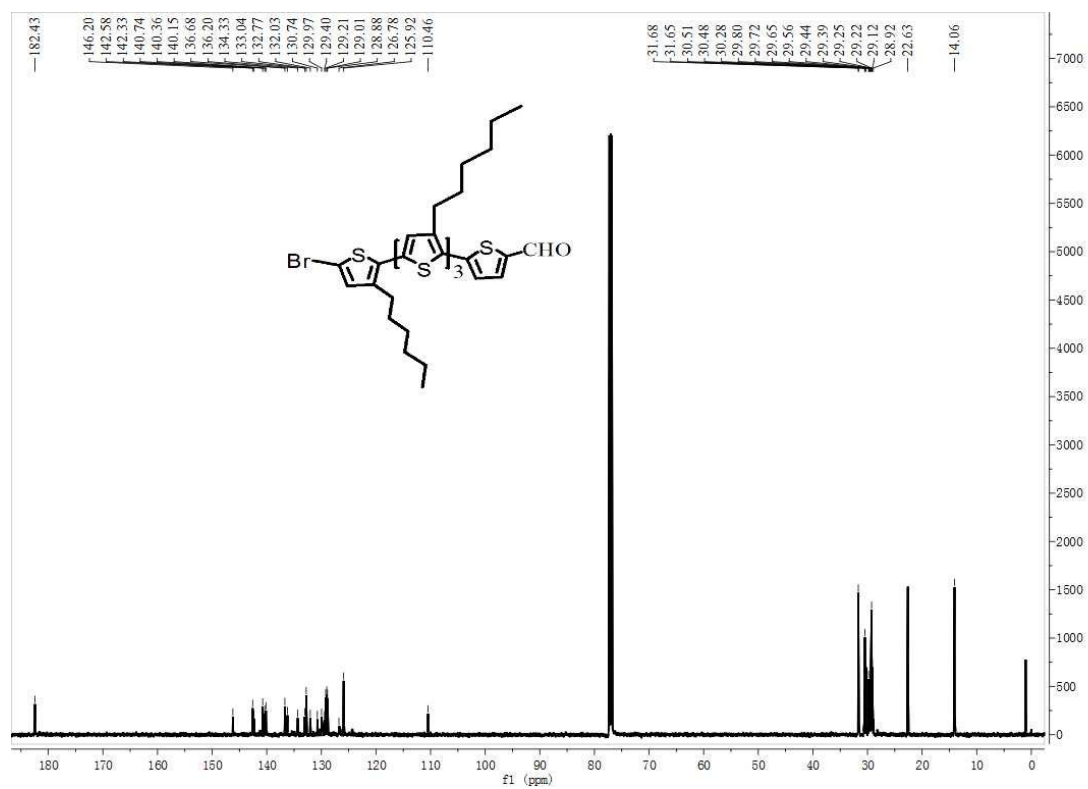


Figure S16: ¹³C NMR of compound 3 in CDCl₃

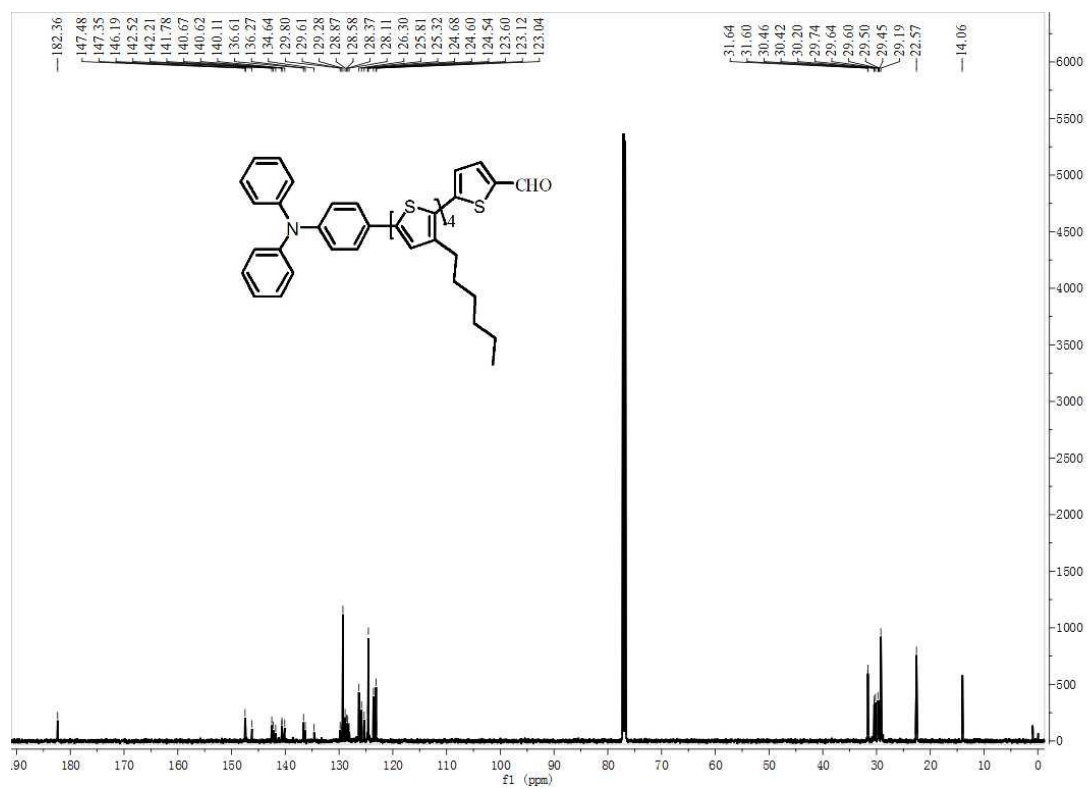


Figure S17: ¹³C NMR of compound 4 in CDCl₃

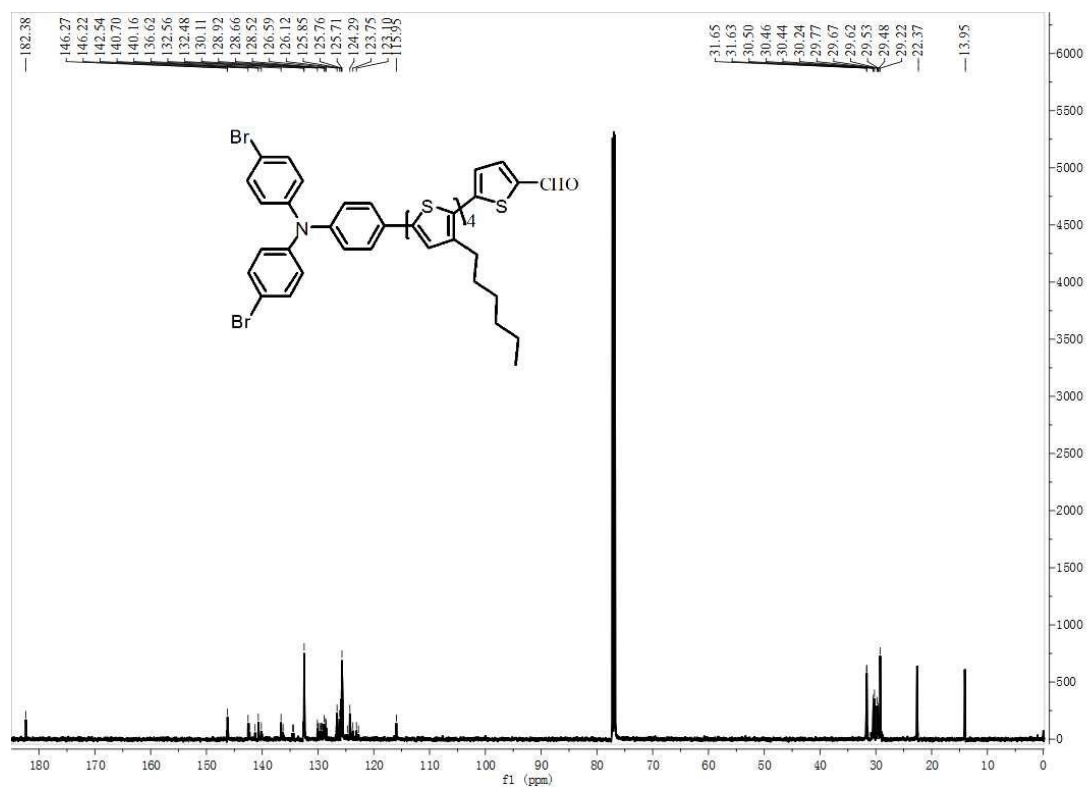


Figure S18: ¹³C NMR of compound 5 in CDCl₃

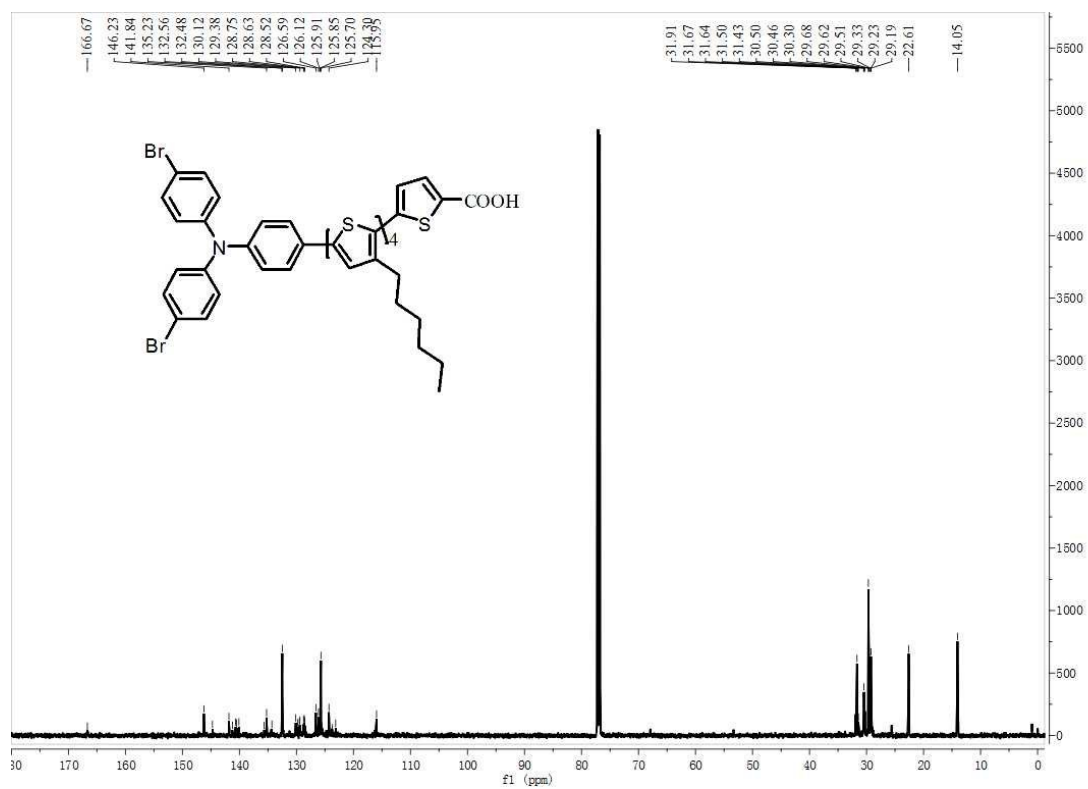


Figure S19: ¹³C NMR of compound 6 in CDCl₃

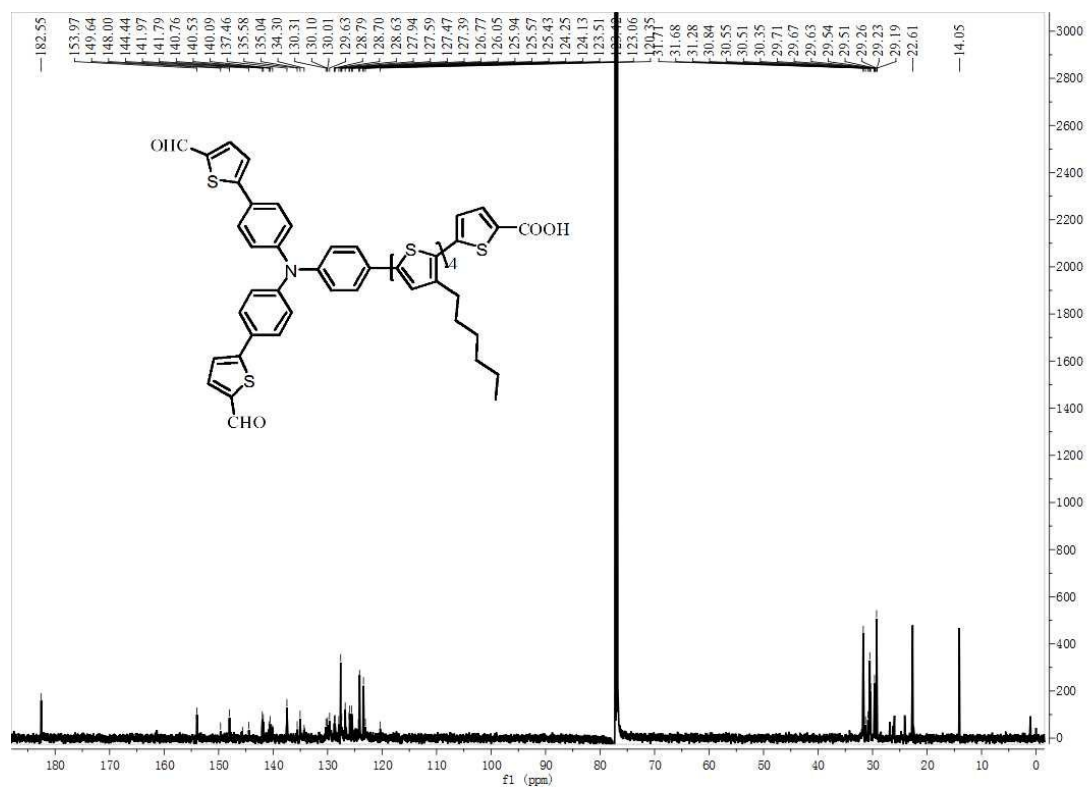


Figure S20: ^{13}C NMR of compound 7 in CDCl_3

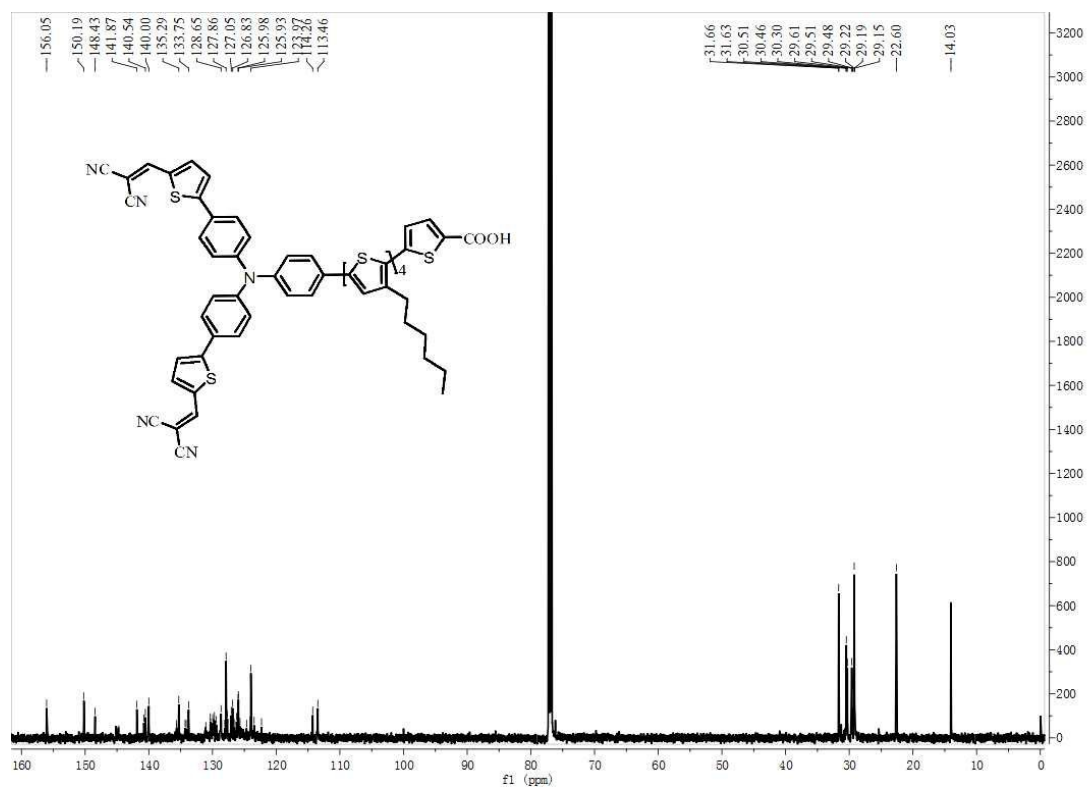


Figure S21: ^{13}C NMR of T5 in CDCl_3

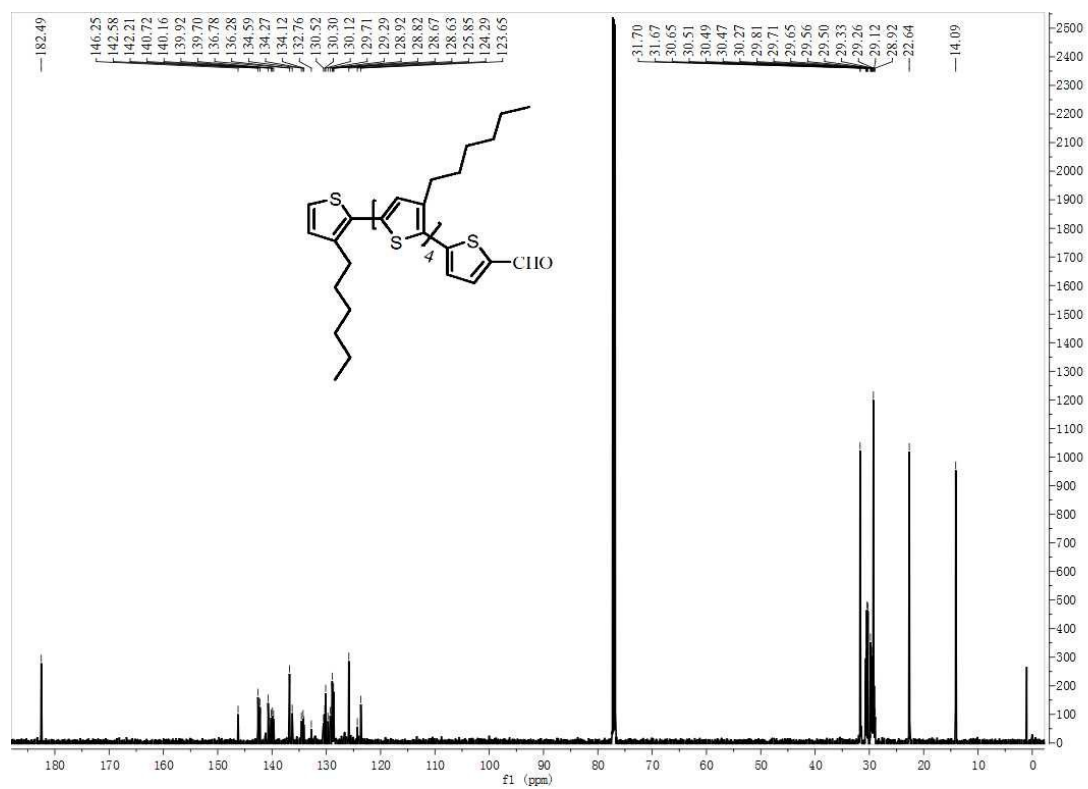


Figure S22: ¹³C NMR of compound 8 in CDCl₃

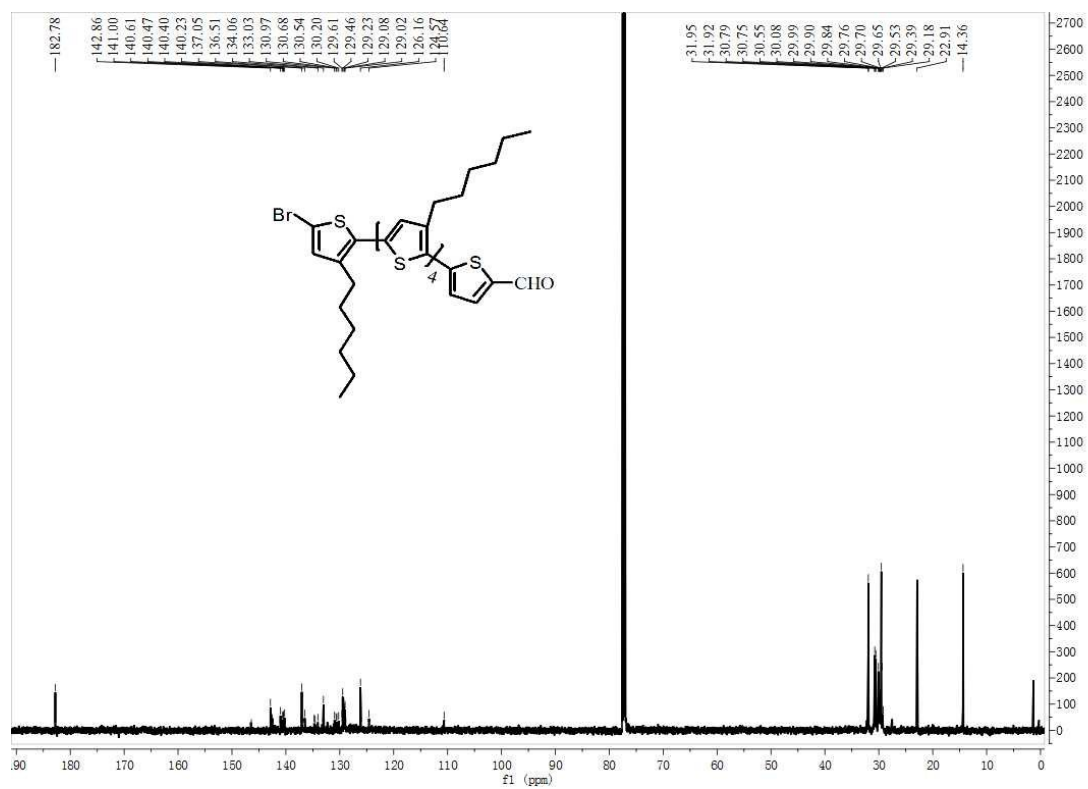
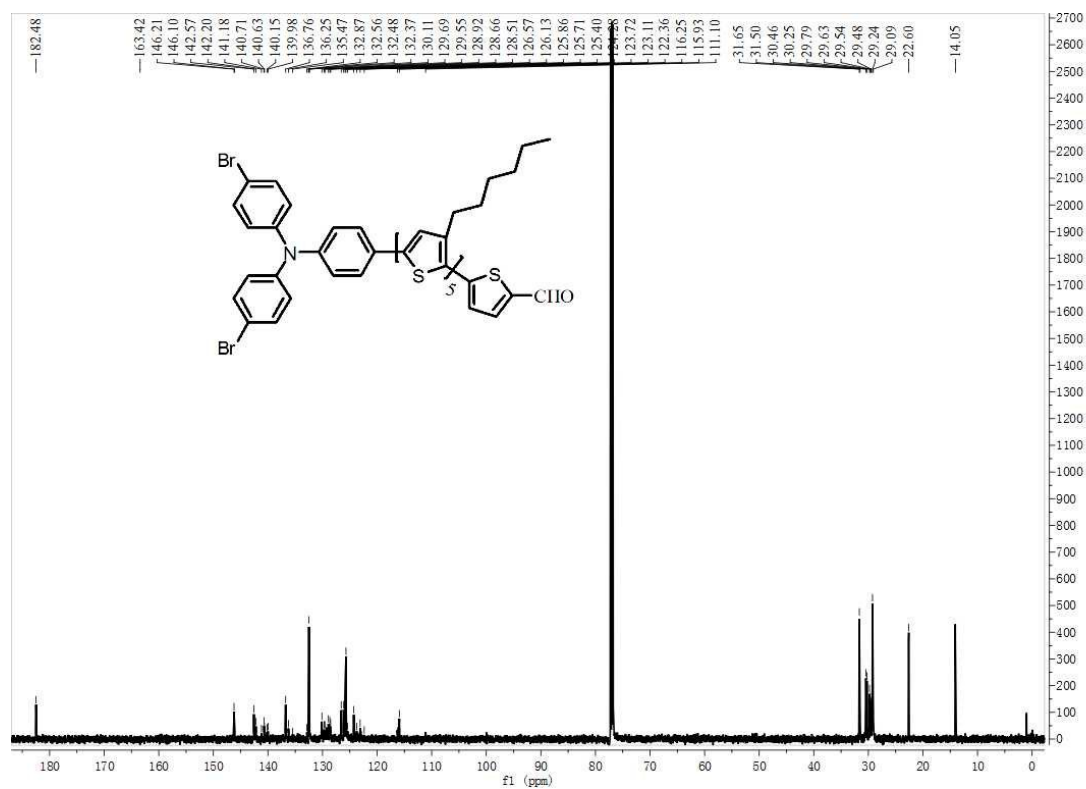
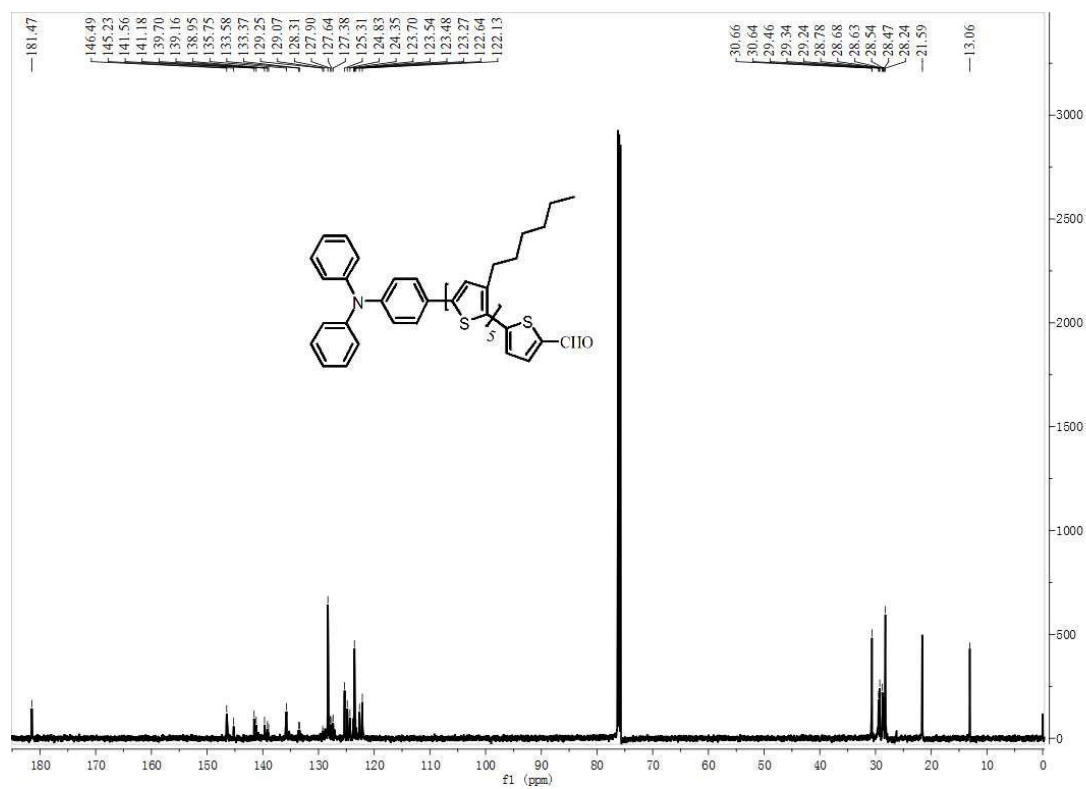


Figure S23: ¹³C NMR of compound 9 in CDCl₃



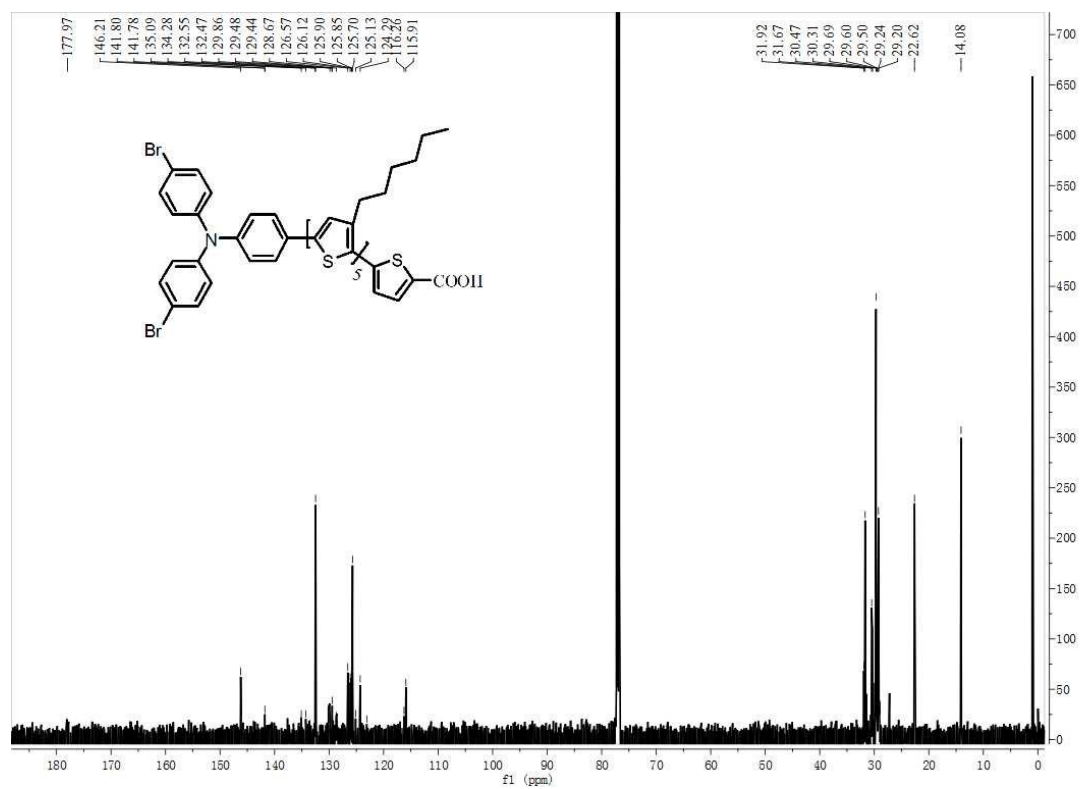


Figure S26: ¹³C NMR of compound 12 in CDCl₃

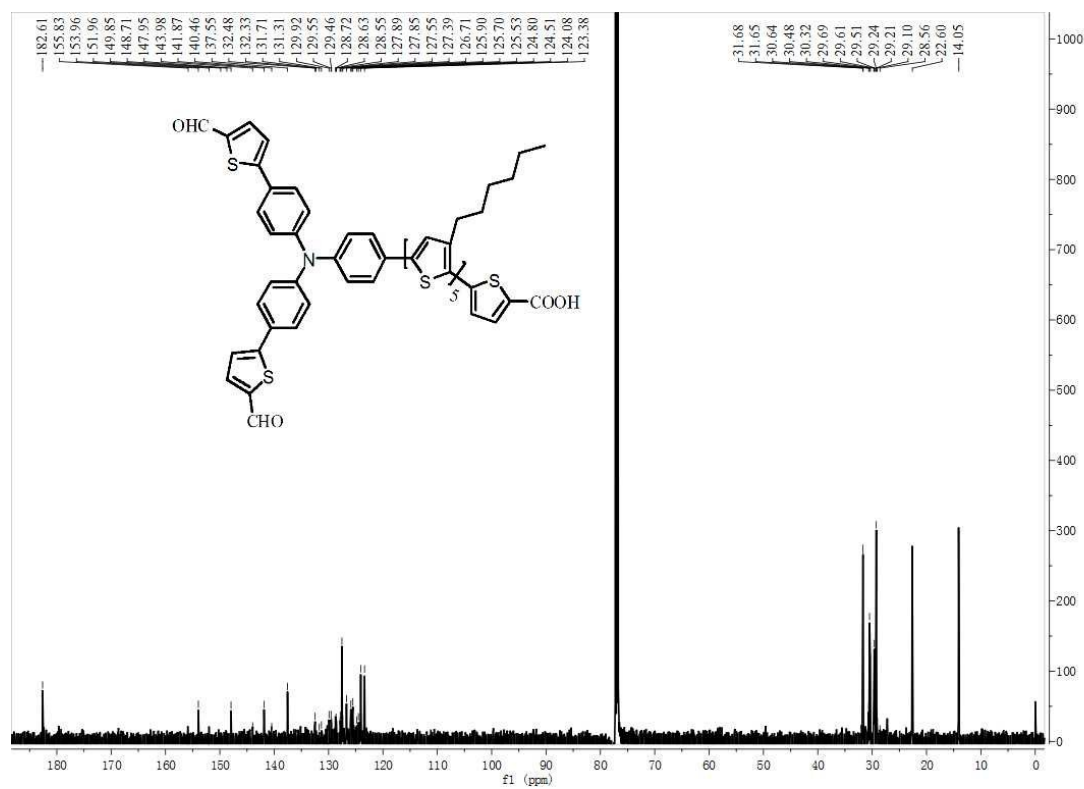


Figure S27: ¹³C NMR of compound 13 in CDCl₃

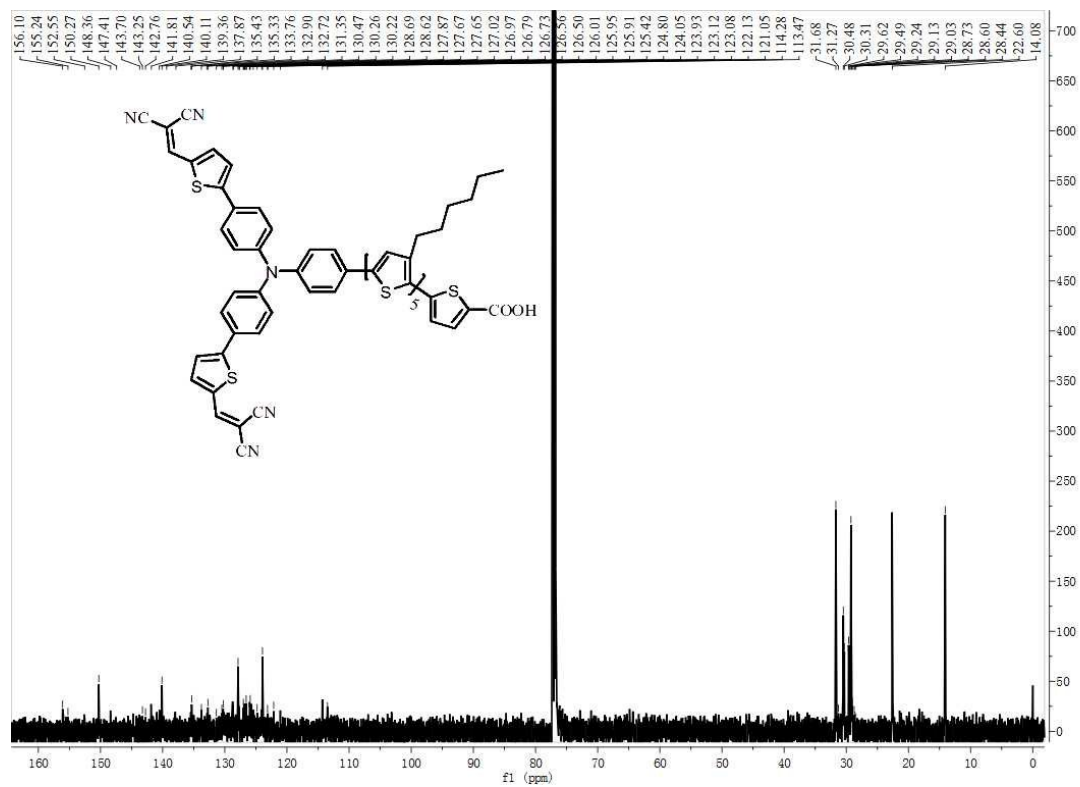


Figure S28: ^{13}C NMR of T6 in CDCl_3

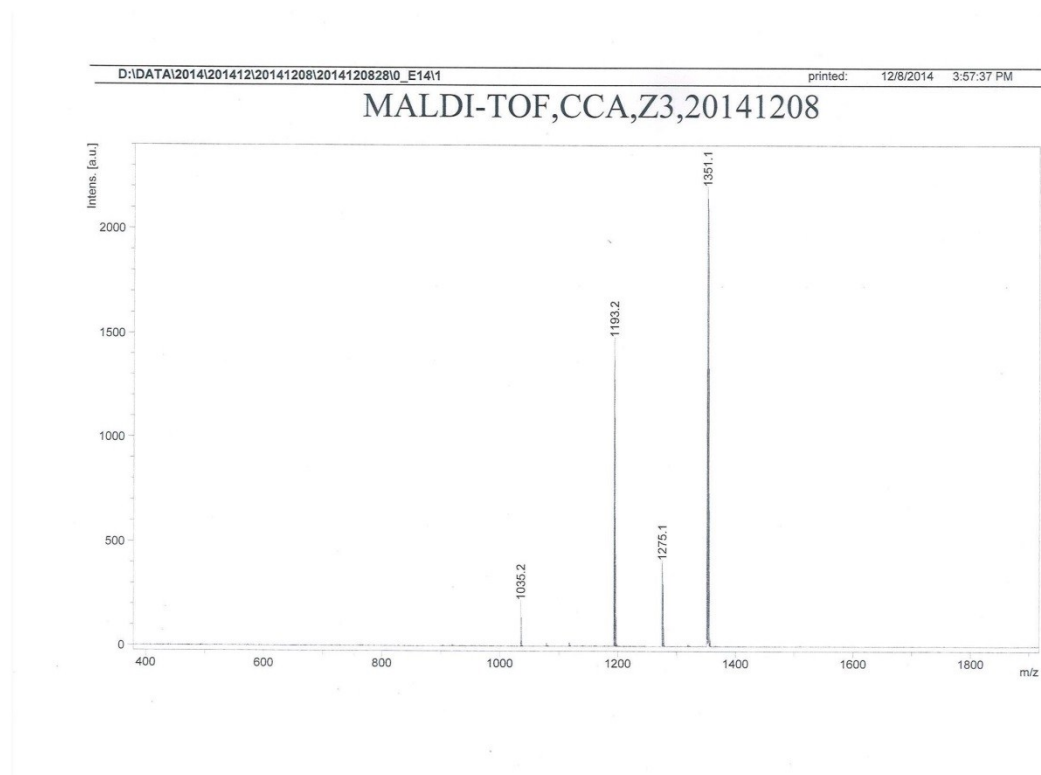


Figure S29: MALDI-TOF of T5

MALDI-TOF, CCA, Z4, 20141208

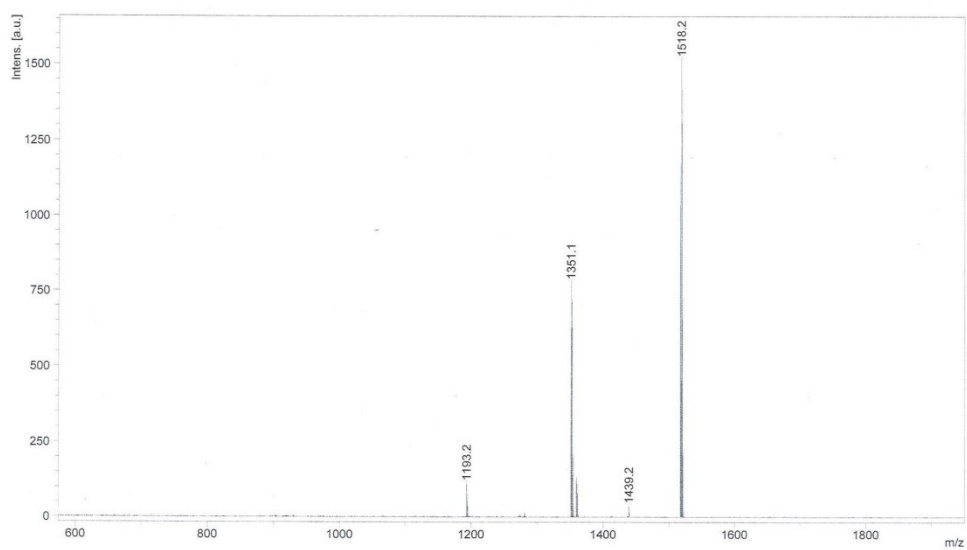


Figure S30: MALDI-TOF of T6