

Supporting Information

Large Disc-like Donor-Acceptor Polymers for Photodetectors with High Detectivity and Photoresponsivity from 300 nm to 1600 nm

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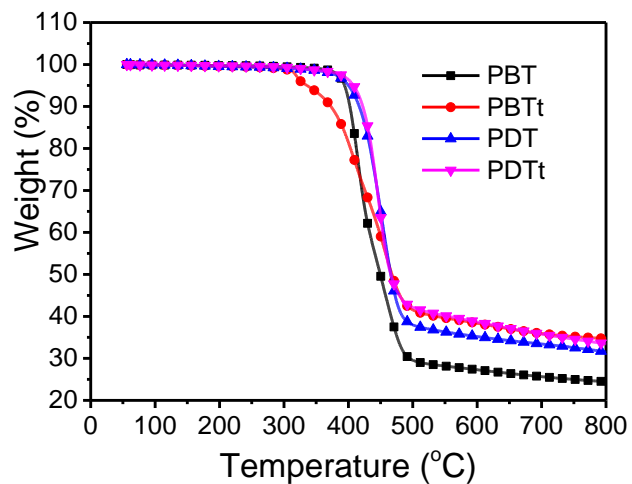


Figure S1. TGA thermograms of polymers under nitrogen flow.

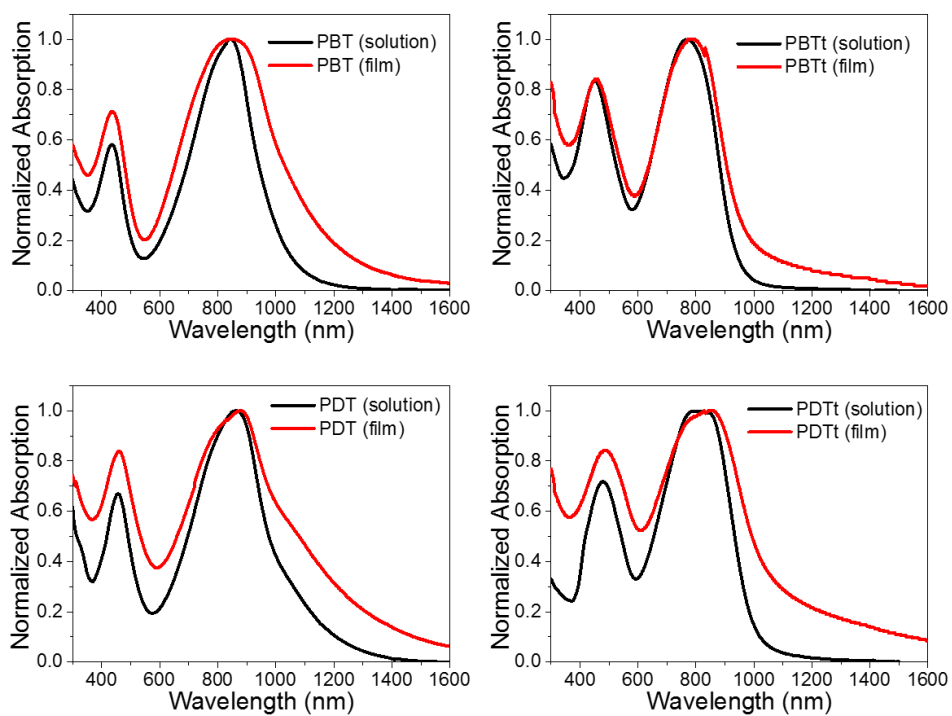


Figure S2. Normalized absorption spectra of polymers in solution of chlorobenzene and as film.

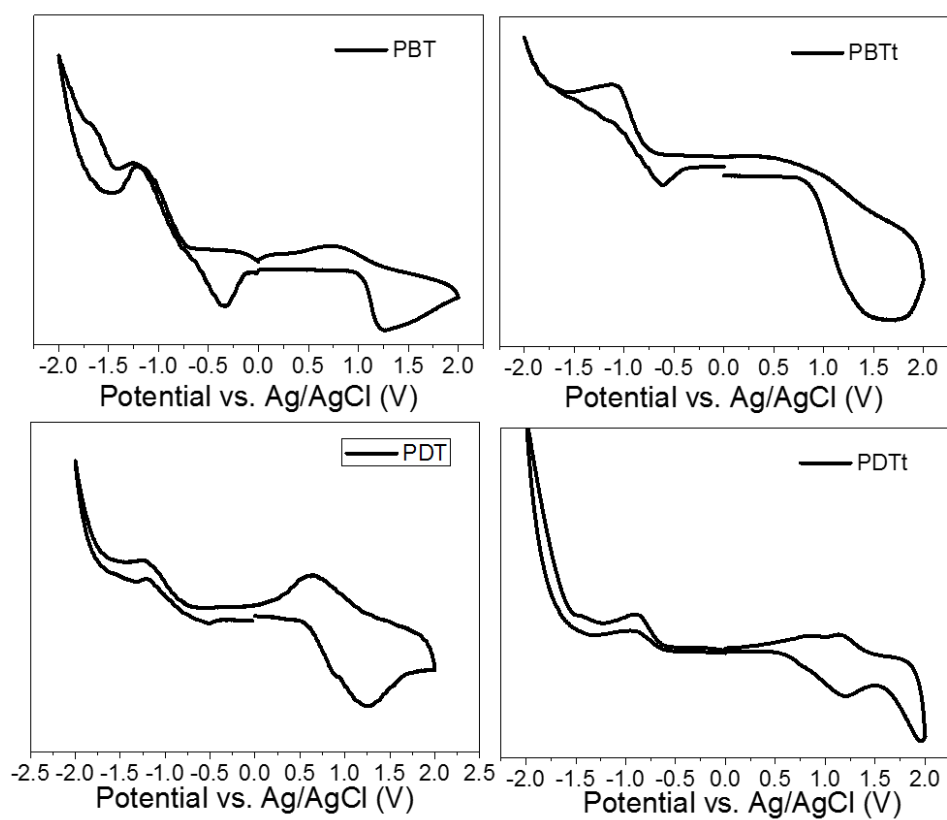


Figure S3. Cyclic voltammograms of polymer films on Pt electrode in 0.1 M $n\text{-Bu}_4\text{NPF}_6$ solution in dry acetonitrile with a scan rate of 50 mV/s.

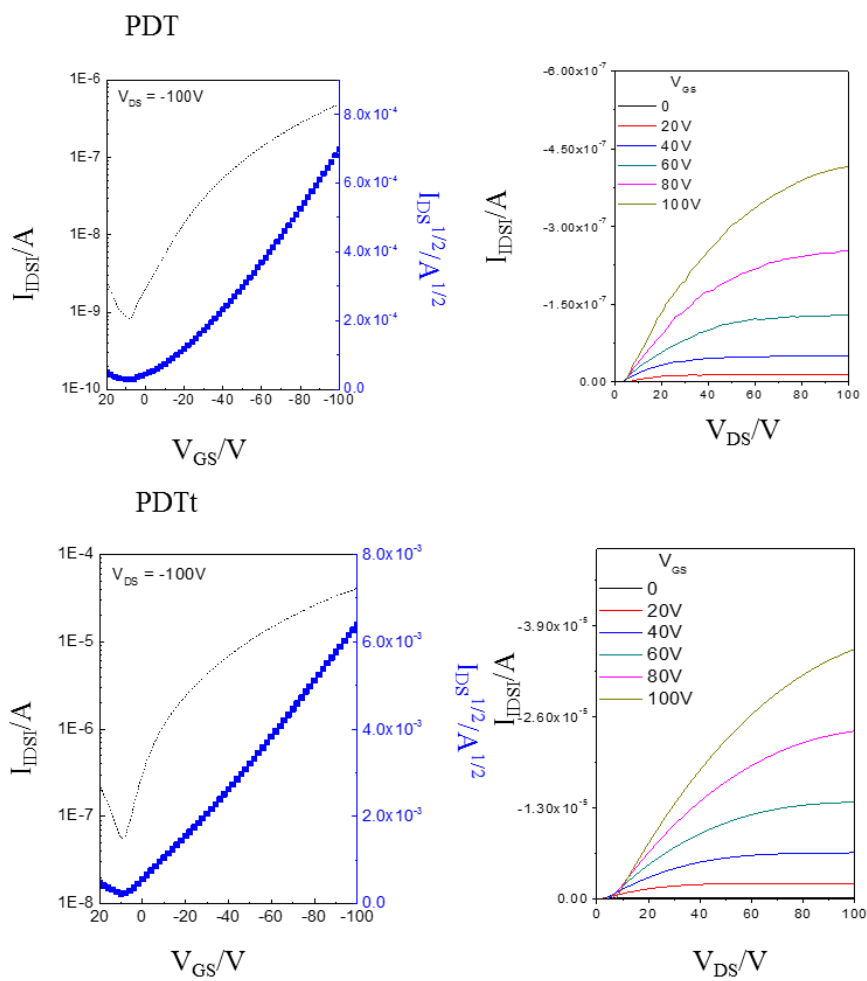


Figure S4. Typical output and transfer characteristics of OTFT devices of PDT and PDTt.

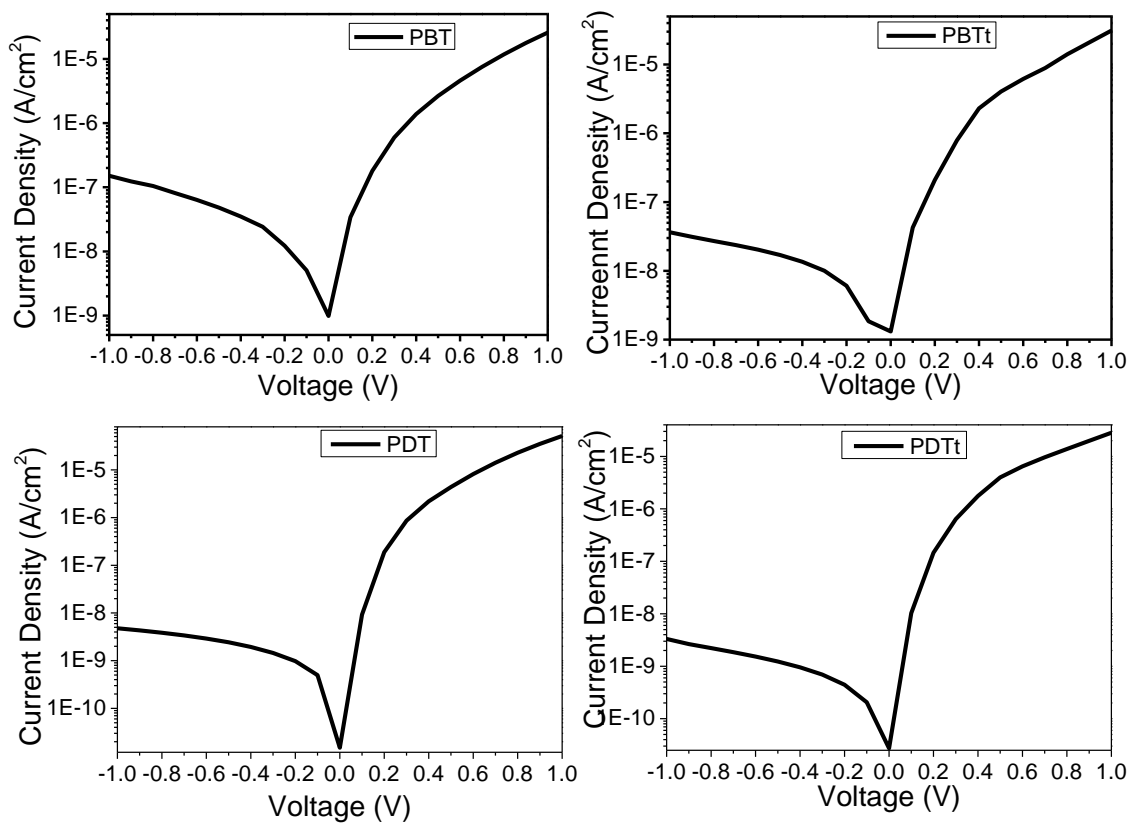


Figure S5. The J - V curves of polymer photodetectors.

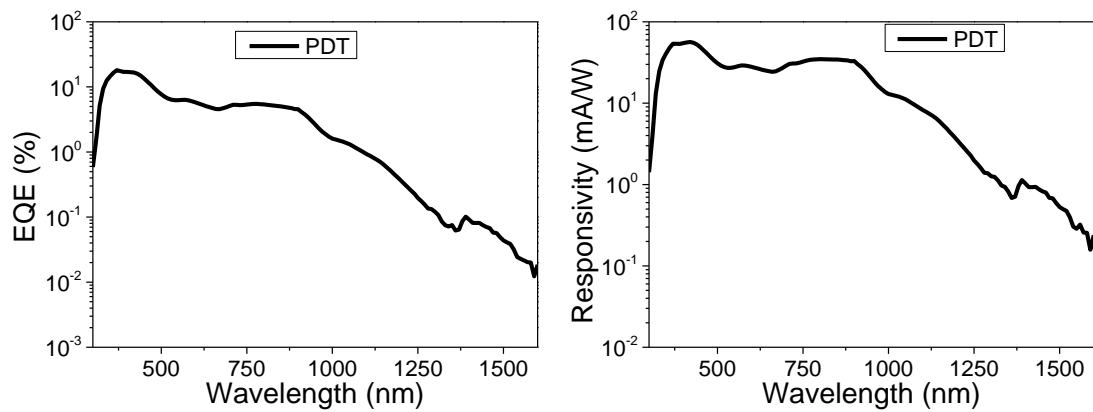


Figure S6. EQE and responsivity of PDT-based photodetector under $-0.1V$.

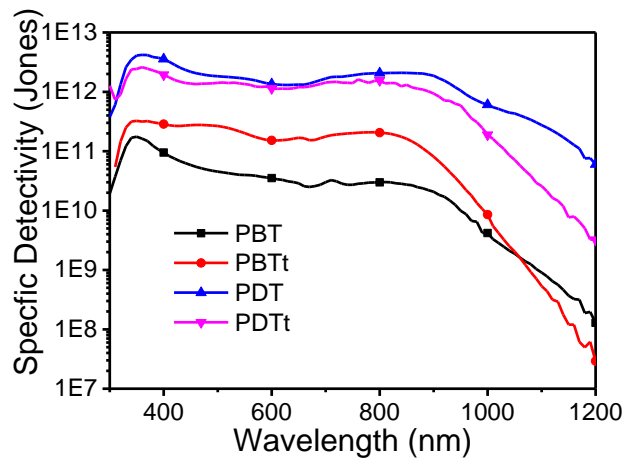


Figure S7. The detectivity of devices based on four polymers under -1 V.

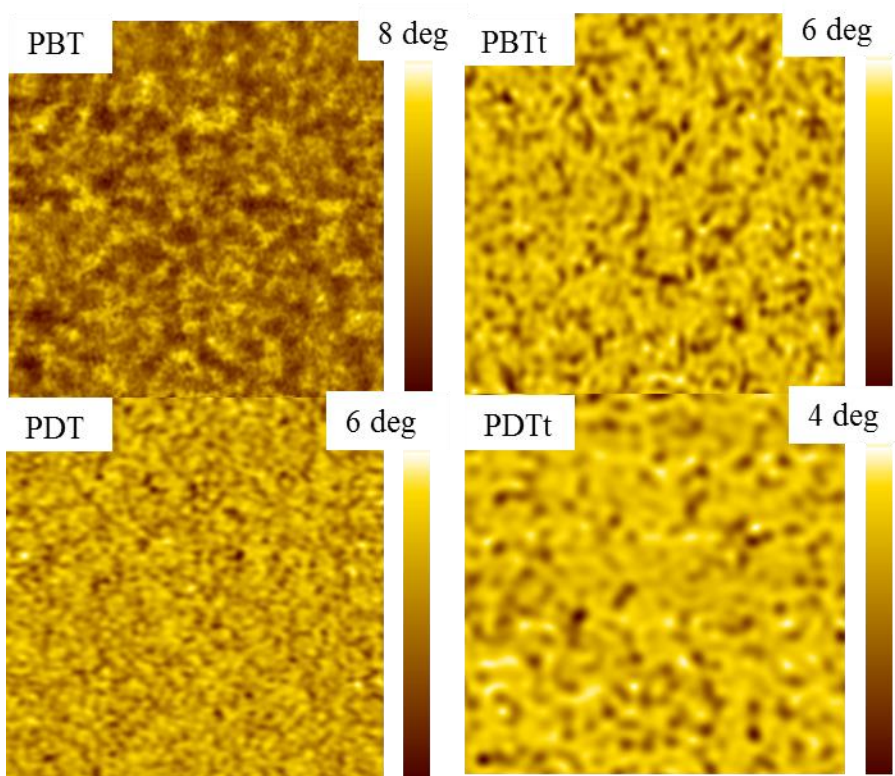


Figure S8. The AFM phase diagrams (3 μm x 3 μm) of the blends of polymer/ PC_{61}BM .

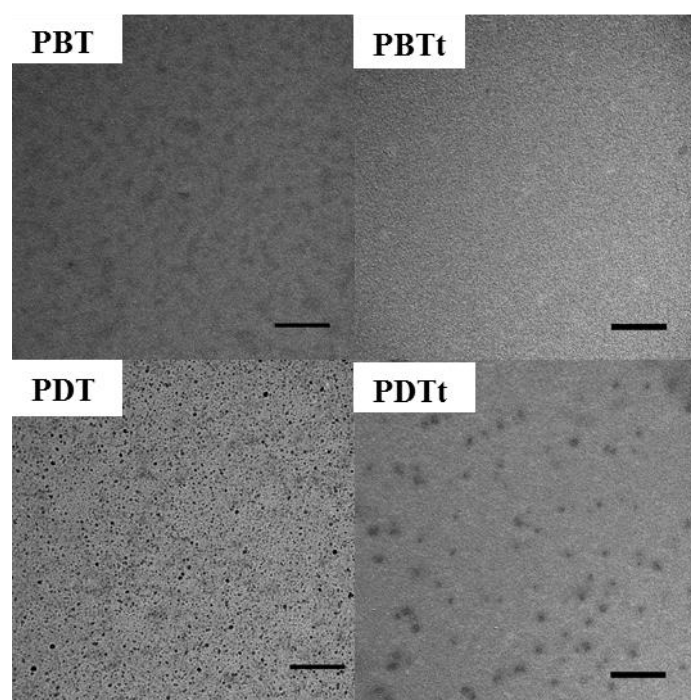
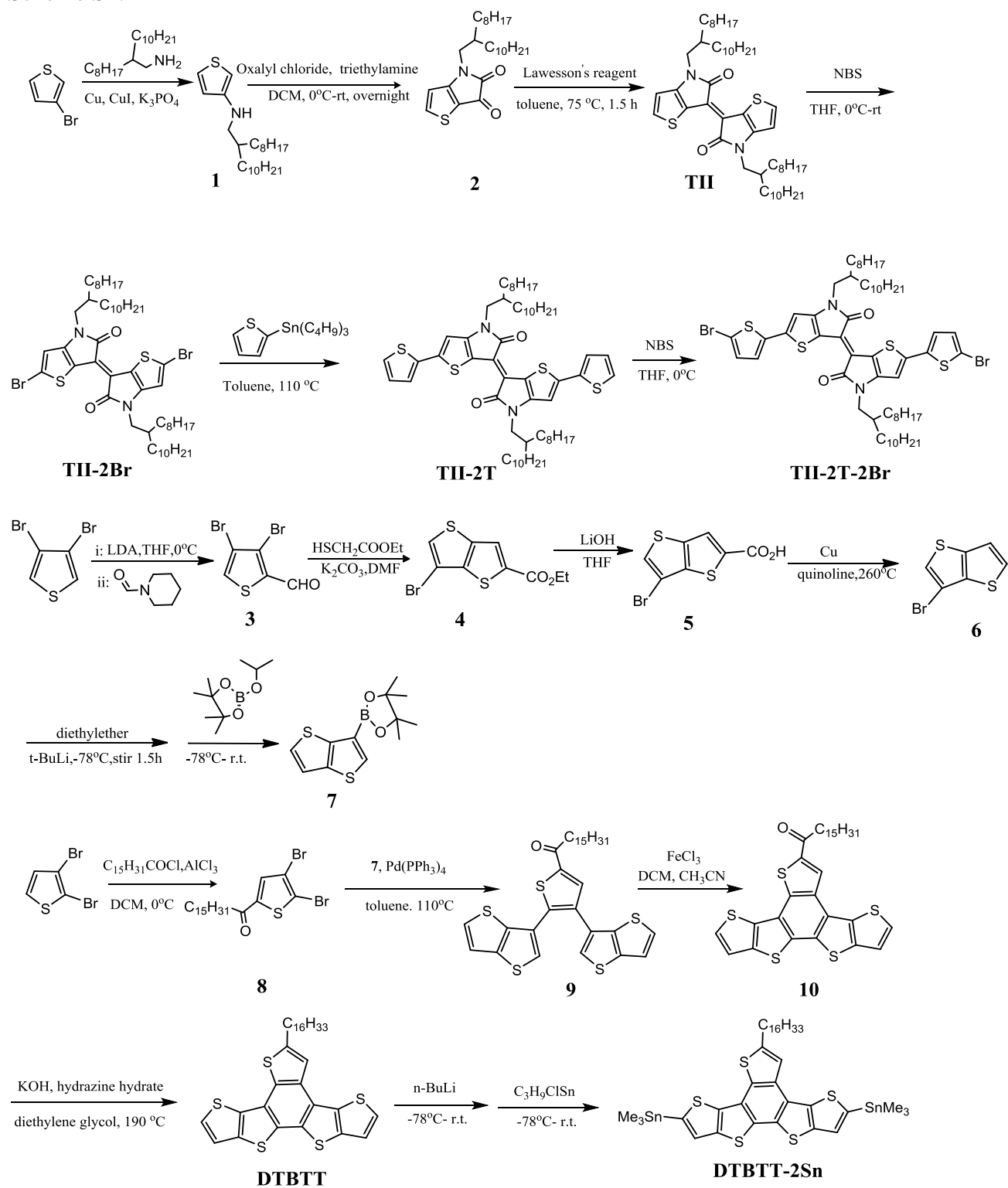
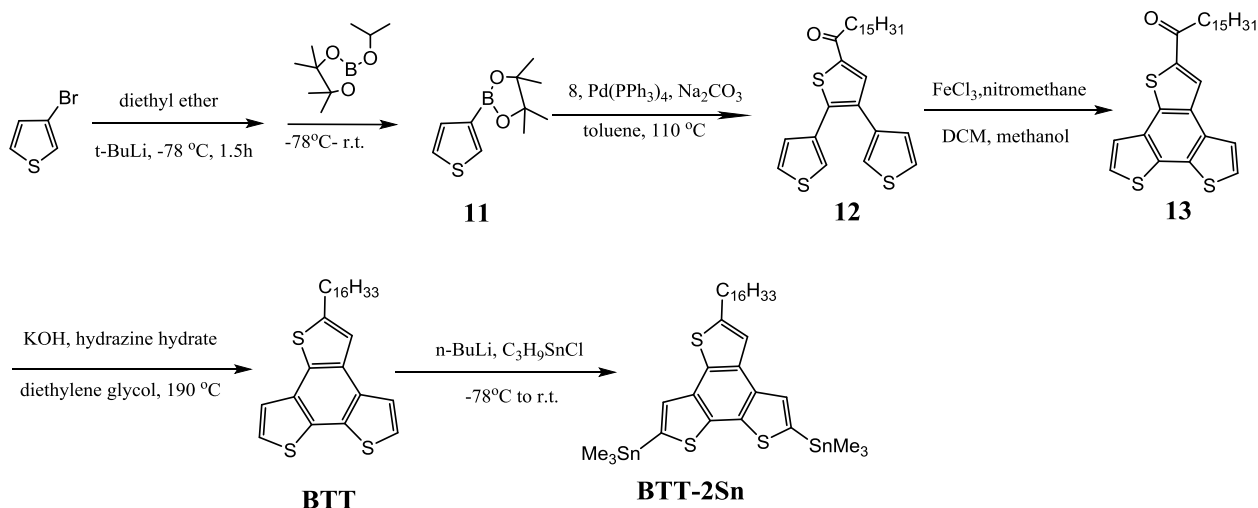


Figure S9. The TEM images of polymer:PC₆₁BM blends. The scale bar is 200 nm.

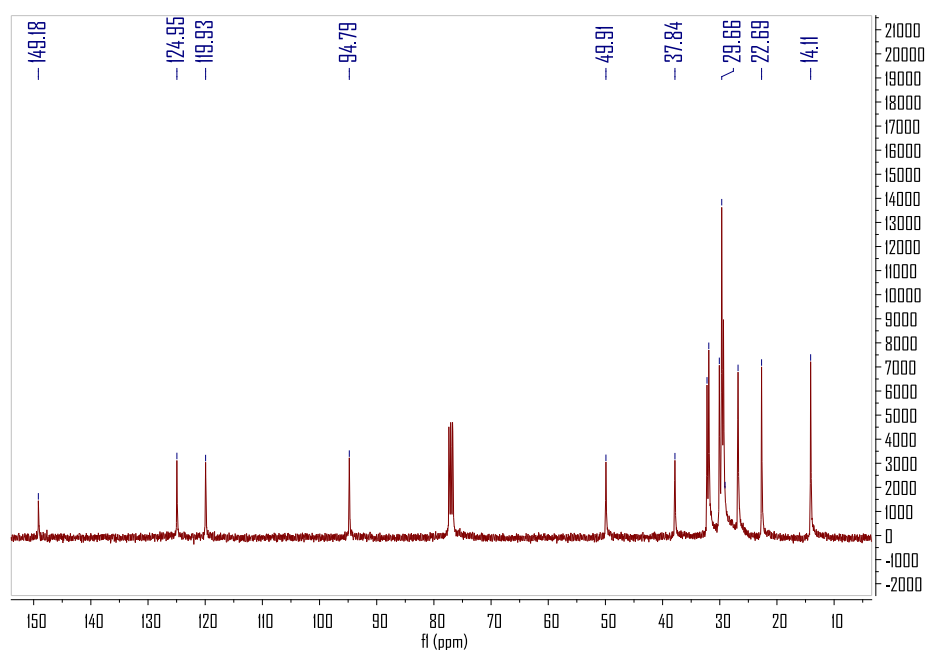
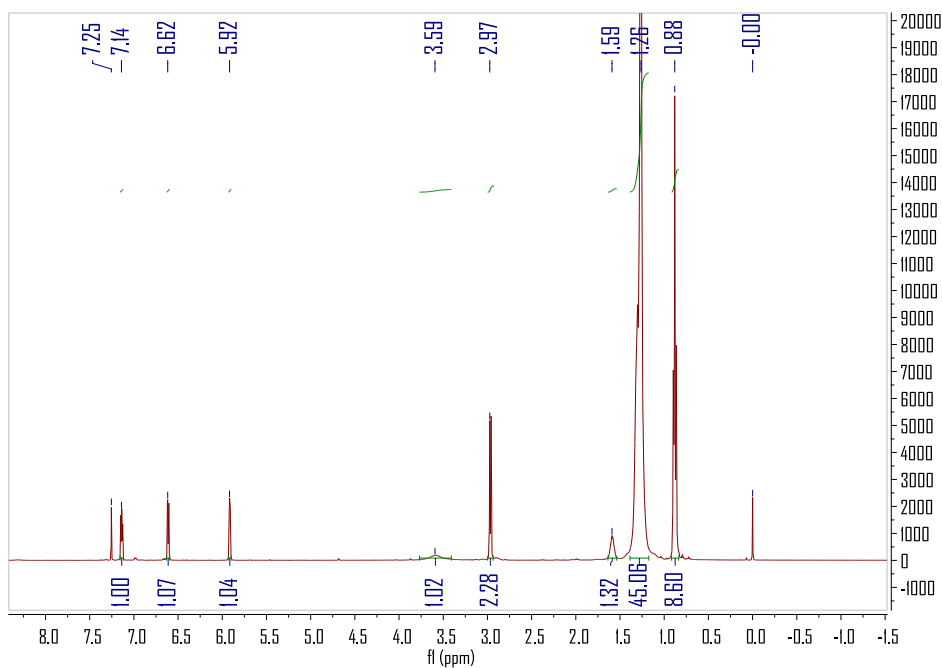
Scheme S1:





Compound 1:

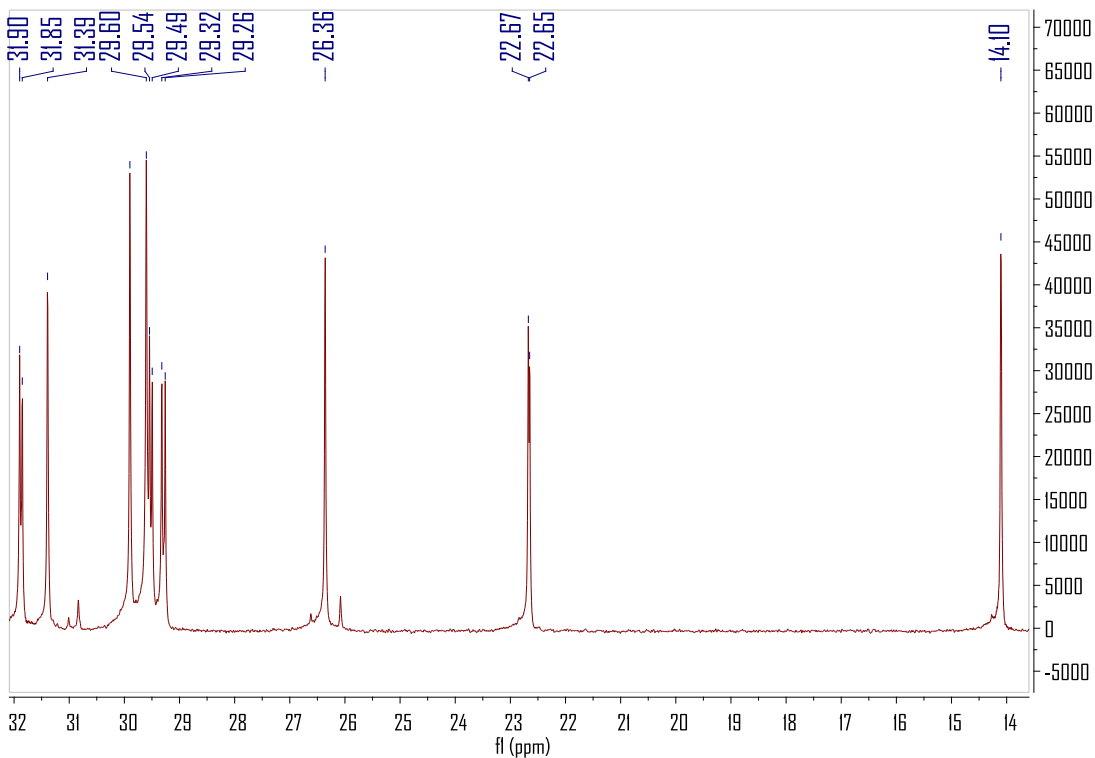
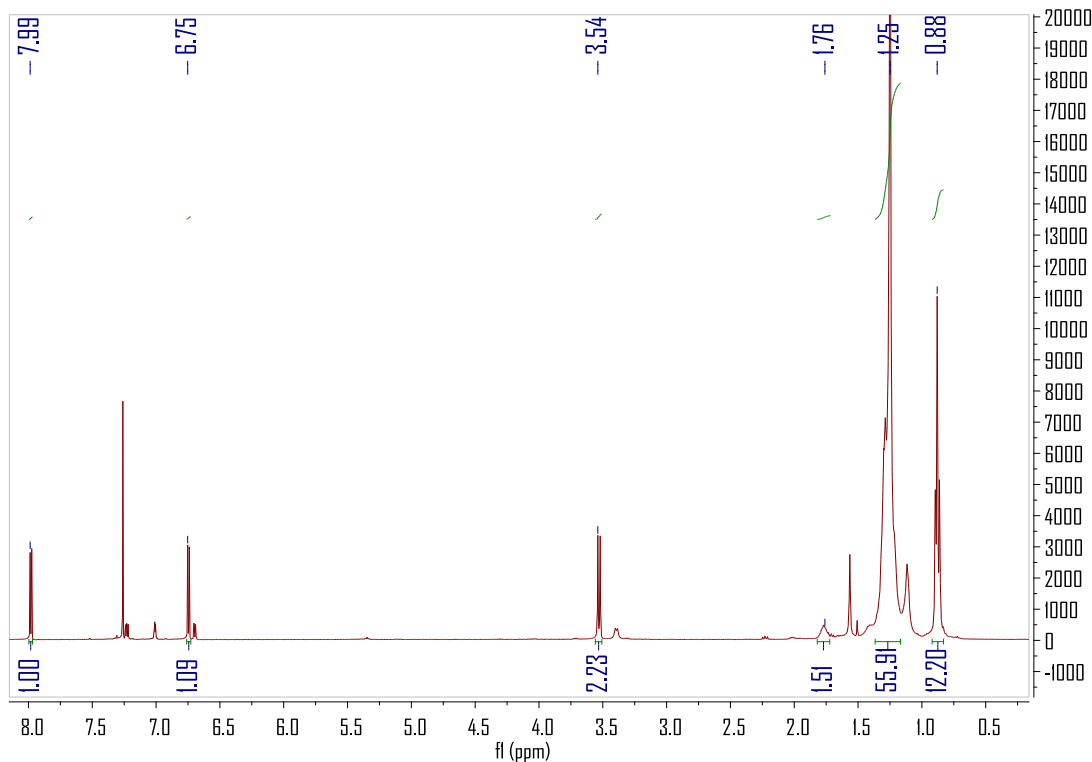
3-Bromothiophene (5.64 mL, 60.0 mmol), 2-octyldodecan-1-amine (28.200 g, 90.0 mmol), copper (0.200 g, 3.00 mmol), copper(I) iodide (0.572 g, 3.00 mmol) and potassium phosphate tribasic (25.92 g, 120.0 mmol) were stirred in 100 mL of dimethyl aminoethanol at 80 -90 °C for 40 h. The mixture is filtered and solvent removed by reduced pressure distillation. The crude product was then purified by chromatography over silica gel (2.5% EtOAc/hexanes). Compound **1** was obtained as brawn yellow oil (9.48 g, 43.2% yield). ^1H NMR (CDCl_3 , 400 MHz): δ /ppm: 7.14 (dd, 1H), 6.62 (dd, 1H), 5.92 (m, 1H), 3.59 (s, 1H), 2.97 (d, 2H), 1.59 (m, 1H), 1.26-1.30 (bm, 32H), 0.88 (m, 6H). ^{13}C NMR (CDCl_3 , 100 MHz): δ /ppm: 149.18, 124.95, 119.93, 94.79, 49.91, 37.84, 32.23, 31.92, 30.08, 29.66, 29.08, 26.80, 22.69, 14.11.

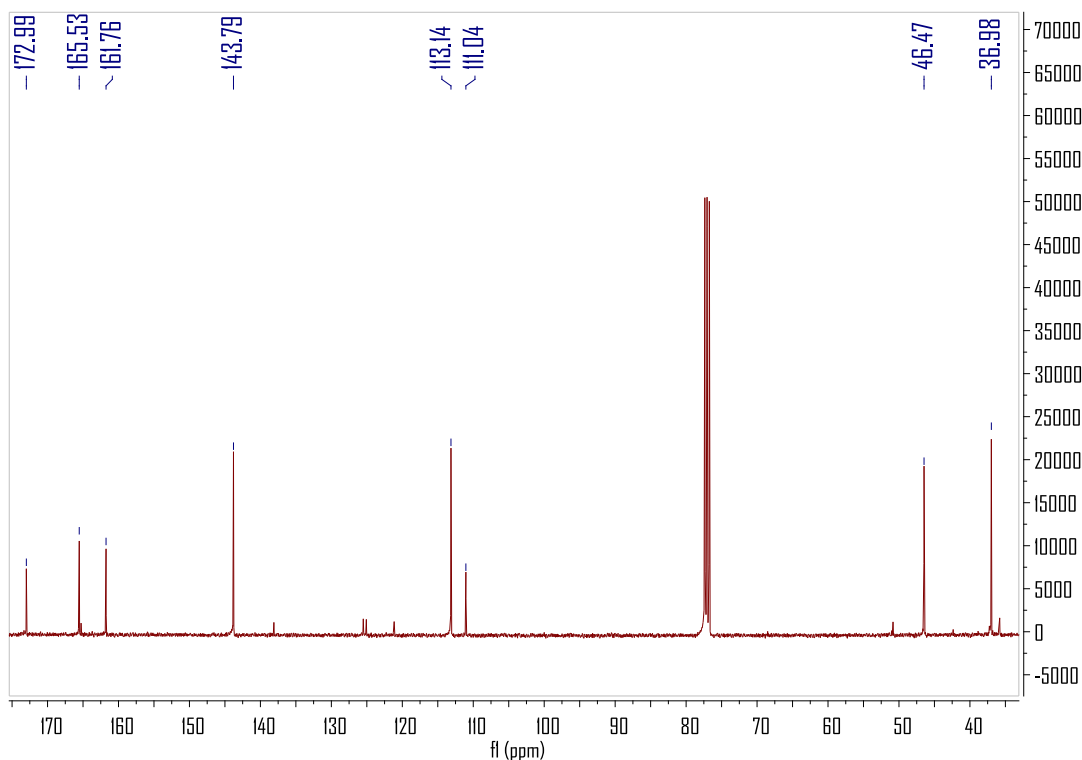


Compound 2:

Compound **1** (18.00 g, 49.23 mmol) in 60 mL of DCM was added dropwise to oxalyl dichloride (5.50 mL, 64.00 mmol) in 150 mL of DCM at 0 °C. After 1 h, triethylamine (31.4 mL, 226.5 mmol) in 50 mL of DCM was added dropwise and stirred 24 h at room temperature. Solvents were removed under vacuum and crude product was obtained as black solid. The crude product was purified by silica gel column chromatography with hexane/ethyl acetate (4.5:1 v/v) as eluent. Compound **2** was

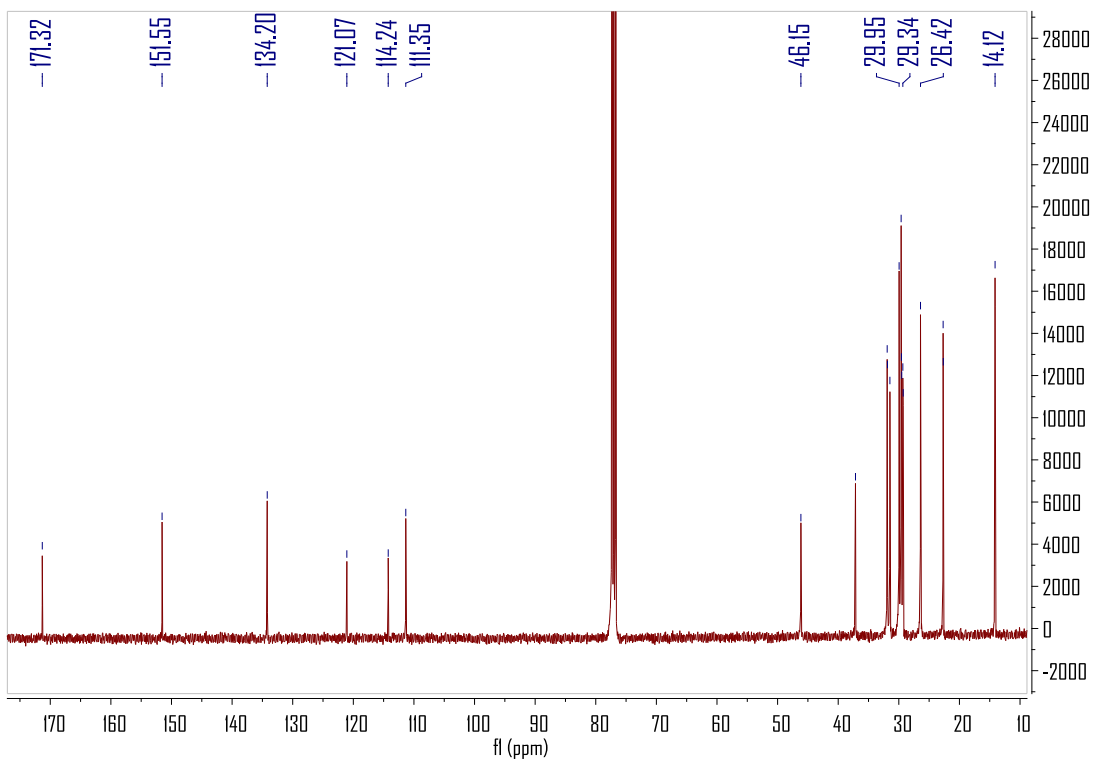
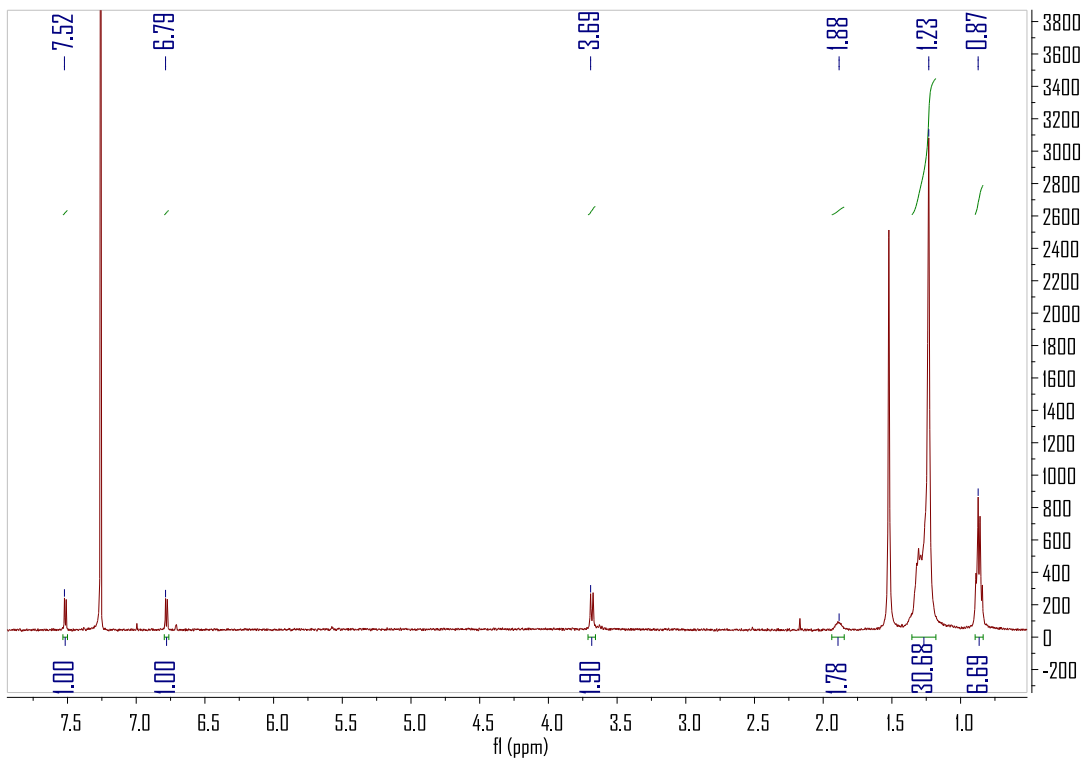
obtained as brawn-red oil (14.0 g, 65.5% yield). ^1H NMR (CDCl_3 , 400 MHz): δ /ppm: 7.99 (d, 1H), 6.75 (d, 1H), 3.54 (d, 2H), 1.76 (m, 1H), 1.2-1.3 (bm, 32H), 0.88 (m, 6H). ^{13}C NMR (CDCl_3 , 100 MHz): δ /ppm: 172.99, 165.53, 161.76, 143.79, 113.14, 111.04, 46.47, 36.98, 31.90, 31.85, 31.39, 29.90, 29.60, 29.54, 29.49, 29.32, 29.26, 26.36, 22.67, 22.65, 14.10.





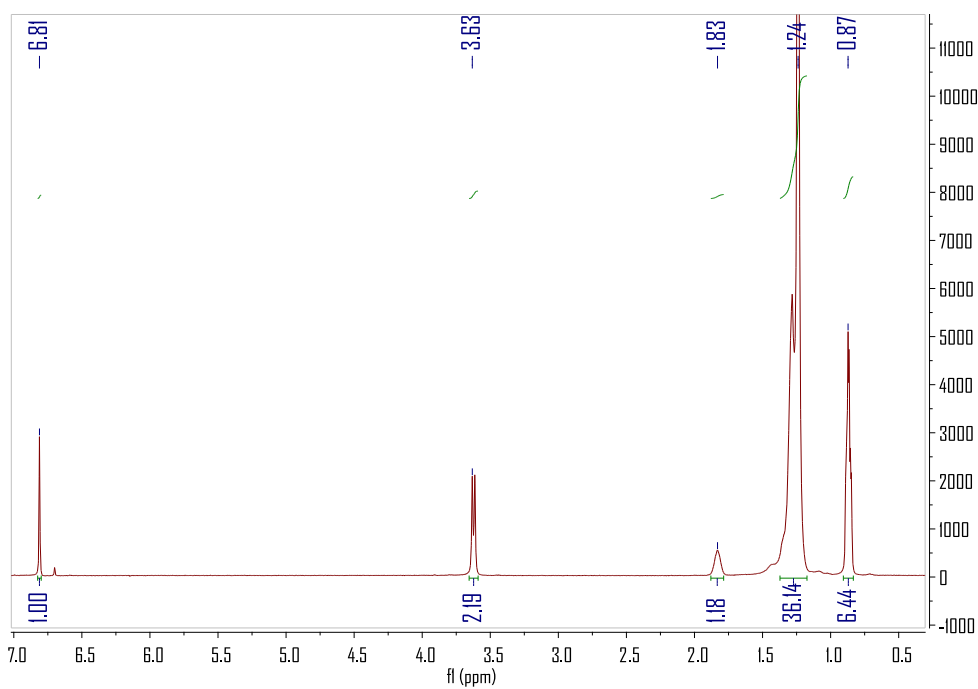
II:

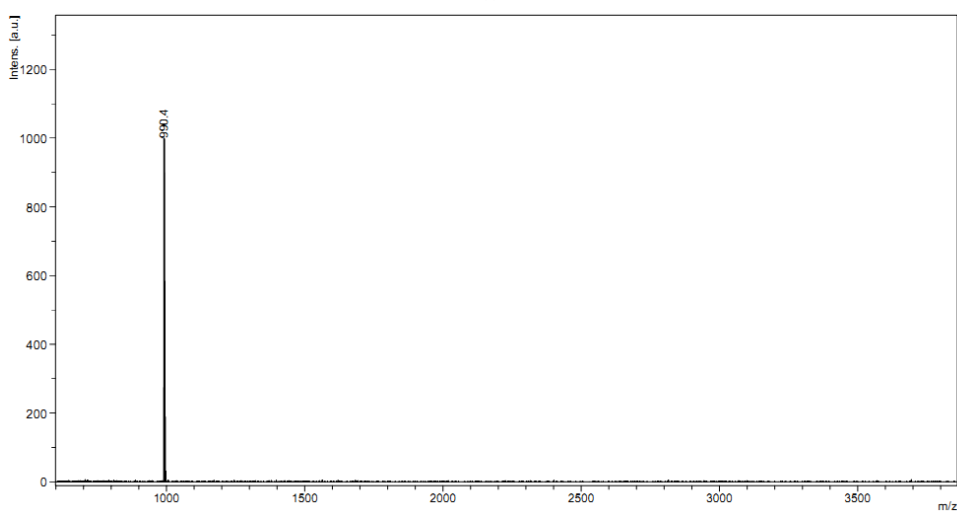
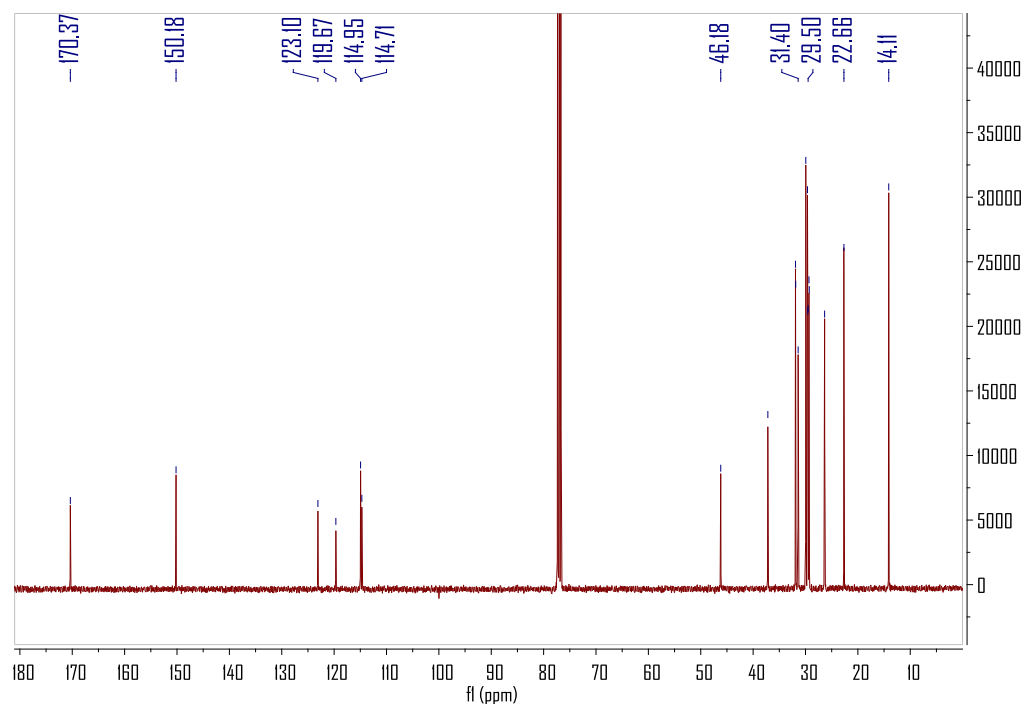
N,N,N',N',N'',N''-Hexaethylphosphinetriamine (1.93 mL, 7.00 mmol) was added to the stirred solution of compound **2** (3.00 g, 7.00 mmol) and dichloromethane (30 mL) at -60 °C for 20 min. The crude product was obtained after the solvent was removed and it was purified by silica gel column chromatography with dichloromethane as eluent. **II** was obtained as claret-red oil (1.81 g, 62% yield). ¹H NMR (CDCl₃, 400 MHz): δ/ppm: 7.52 (d, 2H), 7.69 (d, 2H), 3.69 (d, 4H), 1.78 (m, 2H), 1.2-1.3 (bm, 64H), 0.87 (m, 12H). ¹³C NMR (CDCl₃, 100 MHz): δ/ppm: 171.32, 151.56, 134.19, 121.07, 114.25, 111.34, 46.16, 37.15, 31.87, 31.48, 29.95, 29.61, 29.56, 29.51, 29.33, 29.27, 26.42, 22.68, 22.66, 14.10.



TII-2Br:

N-Bromosuccinimide (0.68 g, 3.80 mmol) in anhydrous tetrahydrofuran (THF) (10 mL) was dropped to a stirred solution of compound **TII** (0.94 g, 1.13 mmol) and THF (70 mL), then the mixture was stirred at 0 °C for 1 h, 40 mL of water was added. The mixture was diluted with DCM, and the separated organic layer was washed with distilled water. Then the organic solvent was dried by anhydrous sodium sulfate and then removed by rotary evaporateion. Purification was done by silica gel column chromatography with petroleum ether/DCM (4:1 v/v) as eluent. **TII-2Br** was obtained as blue solid (0.90 g, 80% yield). ¹H NMR (CDCl₃, 400 MHz): δ/ppm: 6.81 (s, 2H), 3.63 (d, 4H), 1.83 (m, 2H), 1.2-1.3 (bm, 64H), 0.87 (m, 12H). ¹³C NMR (CDCl₃, 100 MHz): δ/ppm: 170.37, 150.18, 123.10, 119.67, 114.95, 114.71, 46.18, 37.19, 31.91, 31.87, 31.40, 29.94, 29.62, 29.56, 29.50, 29.34, 29.28, 26.35, 22.66, 14.11. MALDI-TOF-MS: m/z 990.4 [M]⁺.

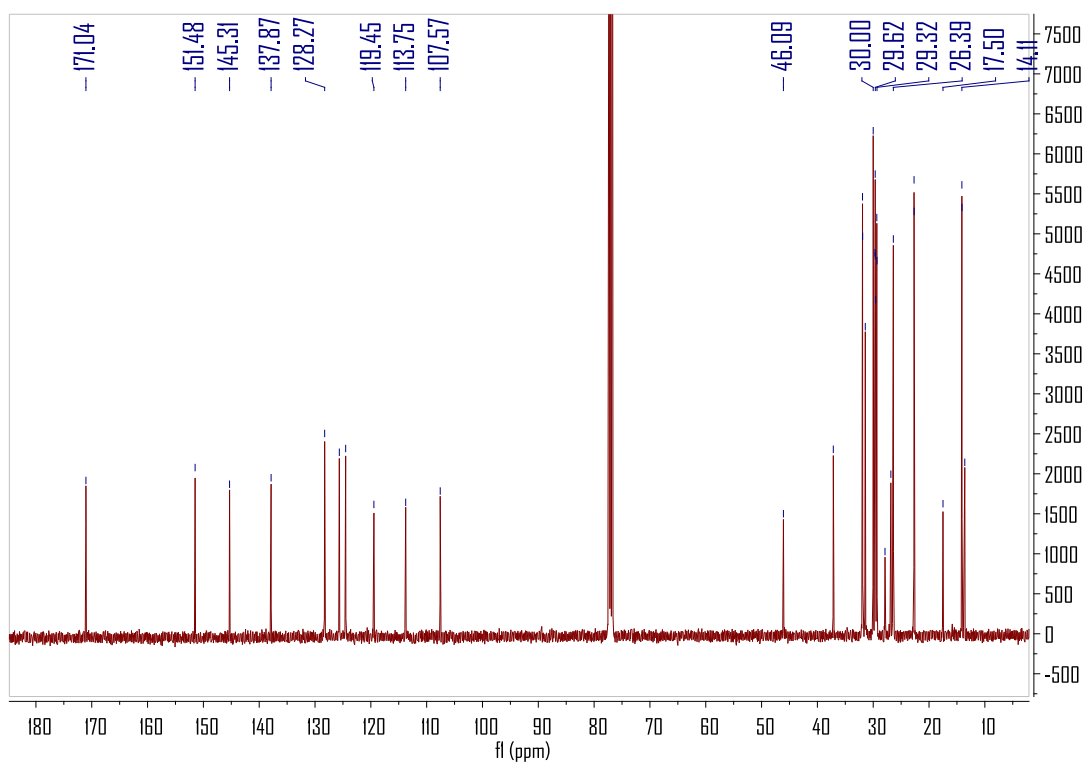
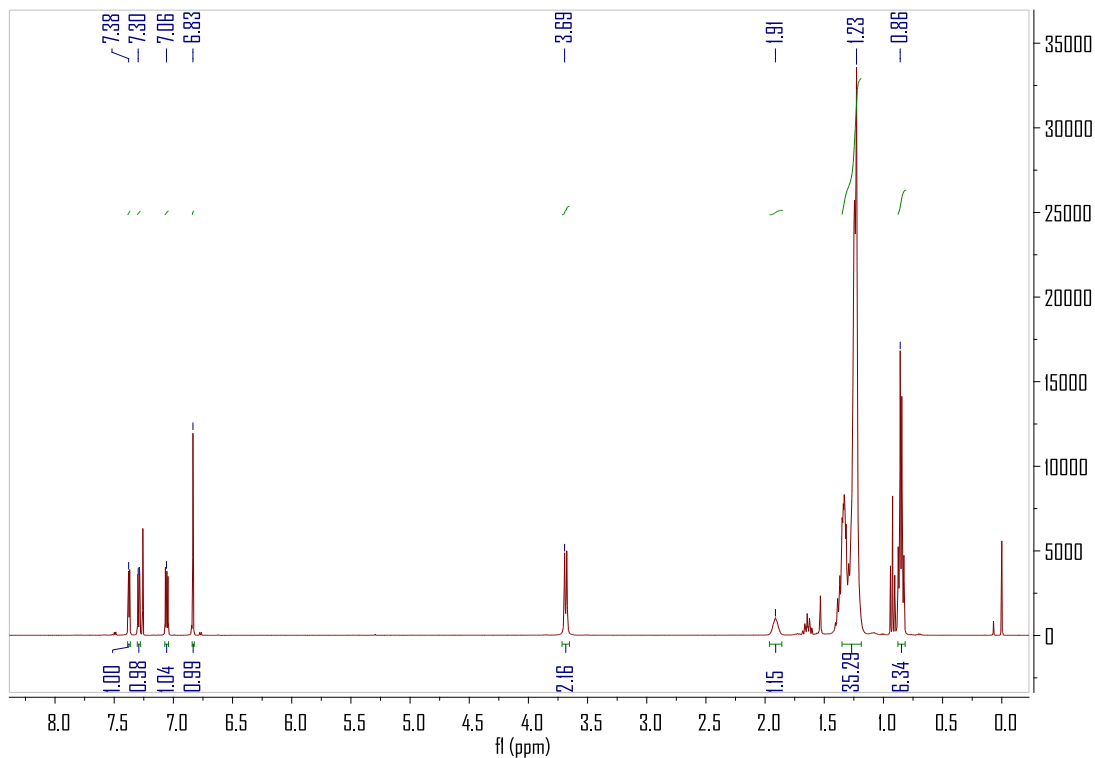




TII-2T:

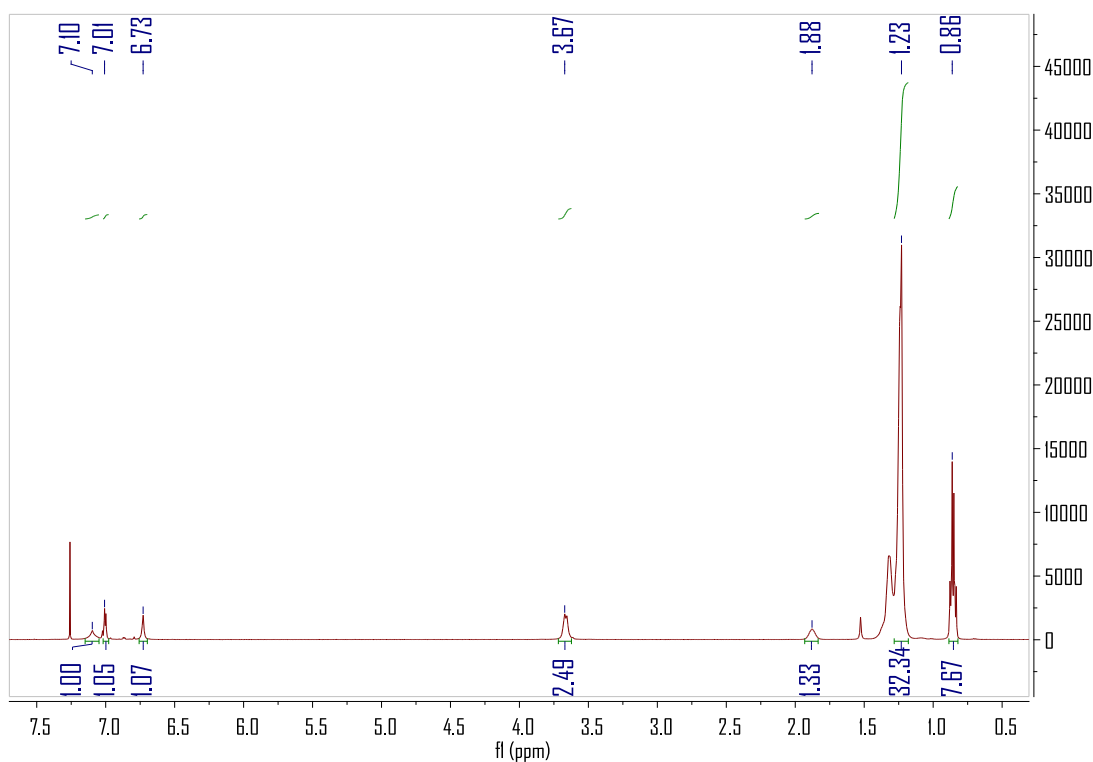
The mixture of **TII-2Br** (1.20 g, 1.23 mmol), tributyl(thiophen-2-yl)stannane (6.00 g), PdCl₂(PPh₃)₂ (100 mg), triphenylphosphine (100 mg) and toluene (50 mL) was stirred at 110 °C for 24 h. Then 50 mL of water was added and solvent in organic phase was removed. The crude product was purified by silica gel column chromatography with petroleum ether/ DCM (3:1 v/v) as eluent. The product was obtained as blue solid (1.03 g, 83.8% yield). ¹H NMR (CDCl₃, 400 MHz): δ 7.38 (dd, 2H), 7.30 (dd, 2H), 7.06 (m, 2H), 6.83(s, 2H), 3.69(d, 4H), 1.91 (m, 2H), 1.23 (m, 64H), 0.86 (t, 12H); ¹³C NMR (CDCl₃, 100 MHz): δ/ppm: 171.04, 151.48, 145.31, 137.87, 128.27, 125.65, 124.51, 119.45,

113.75, 107.57, 46.09, 37.15, 31.92, 31.89, 31.42, 30.00, 29.68, 29.64, 29.62, 29.57, 29.35, 29.32, 26.39, 22.68, 22.67, 17.50, 14.11, 14.10, 13.59.



III-2T-2Br:

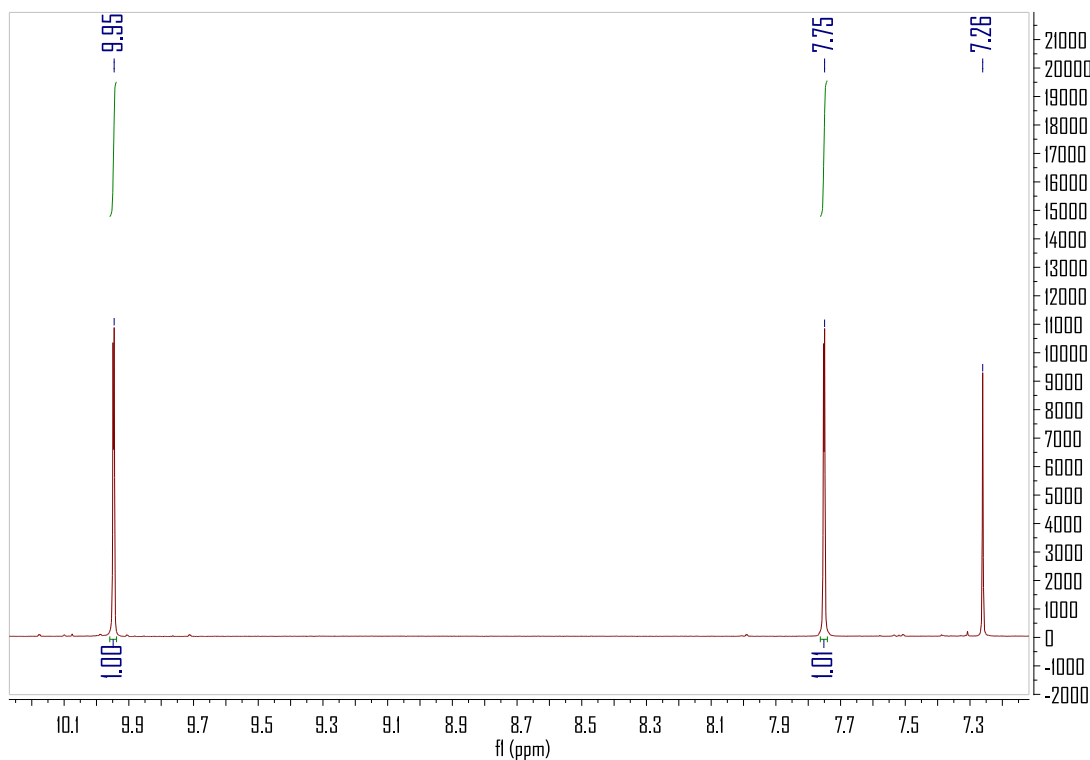
N-Bromosuccinimide (230 mg, 1.32 mmol) was added to a stirred solution of **III-2T** (0.66 g, 0.66 mmol) and anhydrous THF (30 mL) at 0 °C, then the mixture was warmed to r.t slowly and stirred for 1 h, then 40 mL of water was added. The mixture was diluted with DCM and the separated organic layer was washed with distilled water. Then the organic solvent was removed. Purification by silica gel column chromatography with petroleum ether/DCM (3.2:1 v/v) as eluent gave **III-2T-2Br** as blue solid (0.62 g, 81% yield). $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 7.10 (bs, 2H), 7.01 (d, 2H), 6.73 (s, 2H), 3.67(d, 4H), 1.88 (m, 2H), 1.23 (m, 64H), 0.86 (t, 12H); MALDI-TOF-MS: m/z 1154.4 $[\text{M}]^+$.

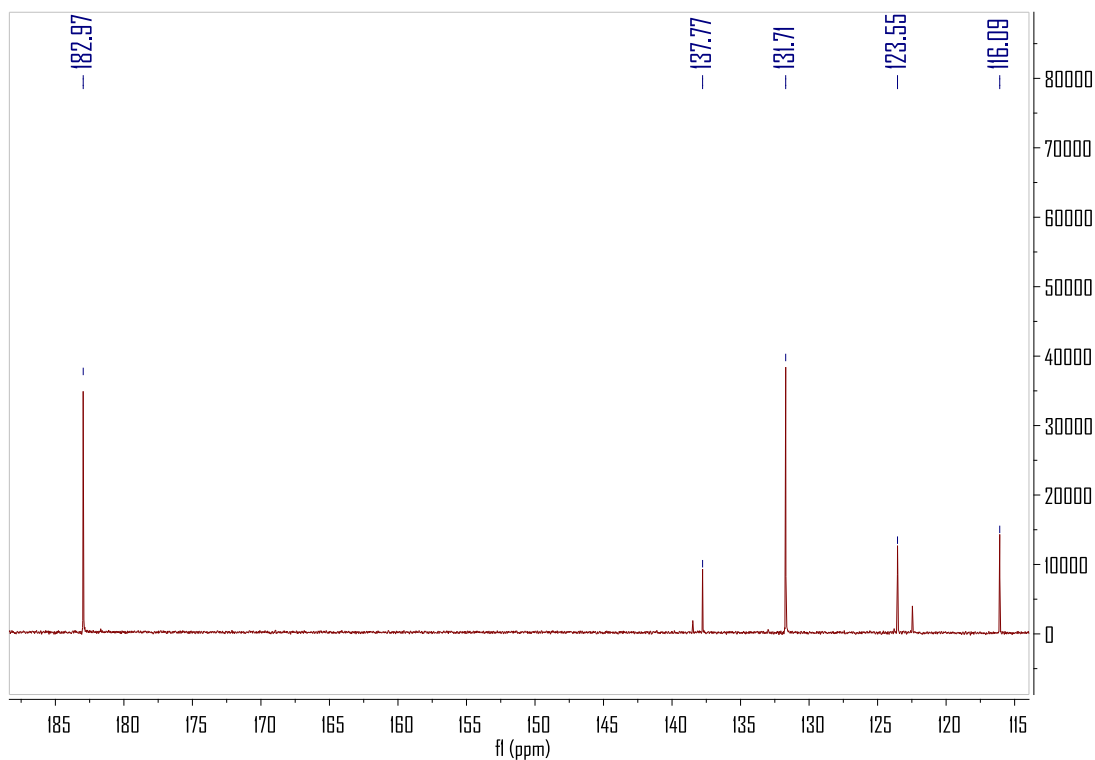


Compound 3:

3,4-Dibromothiophene (24.20 g, 100.0 mmol) was added dropwise to a stirred solution of lithium diisopropylamide, prepared by addition of *n*-BuLi (2.5 M in hexane; 40.80 mL, 102.0 mmol) to diisopropylamine (14.38 mL, 10.33 g, 102.0 mmol) in tetrahydrofuran (280 mL) at 0 °C, and the

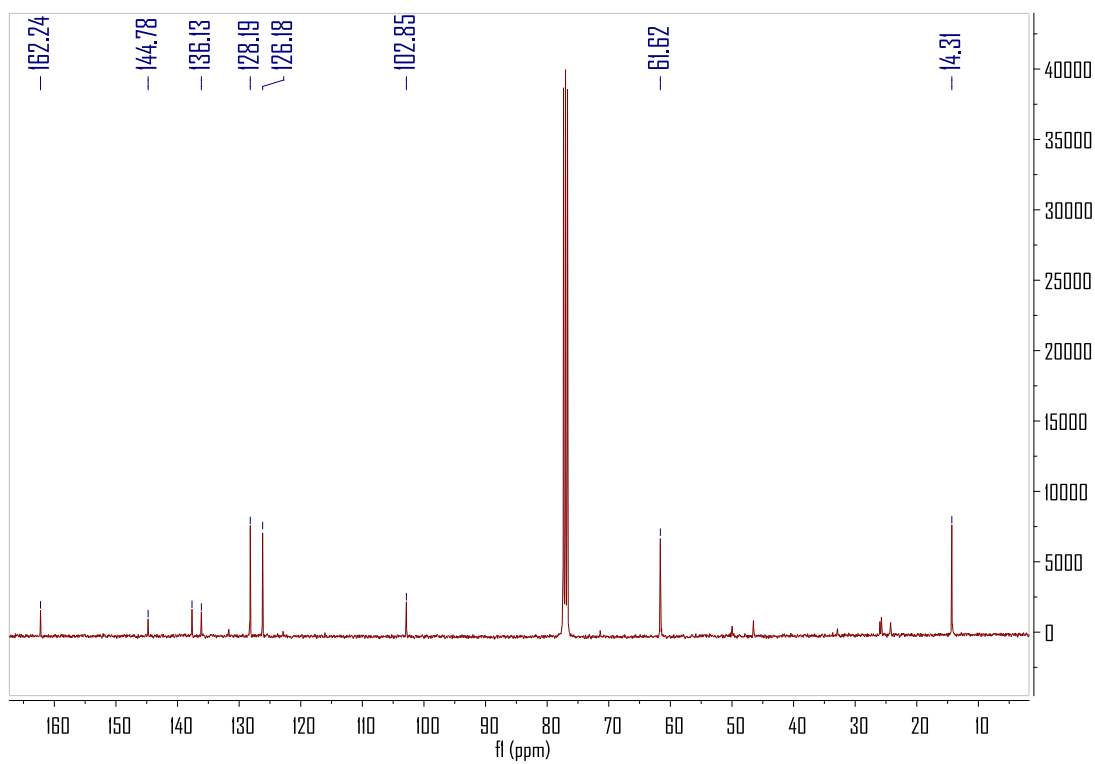
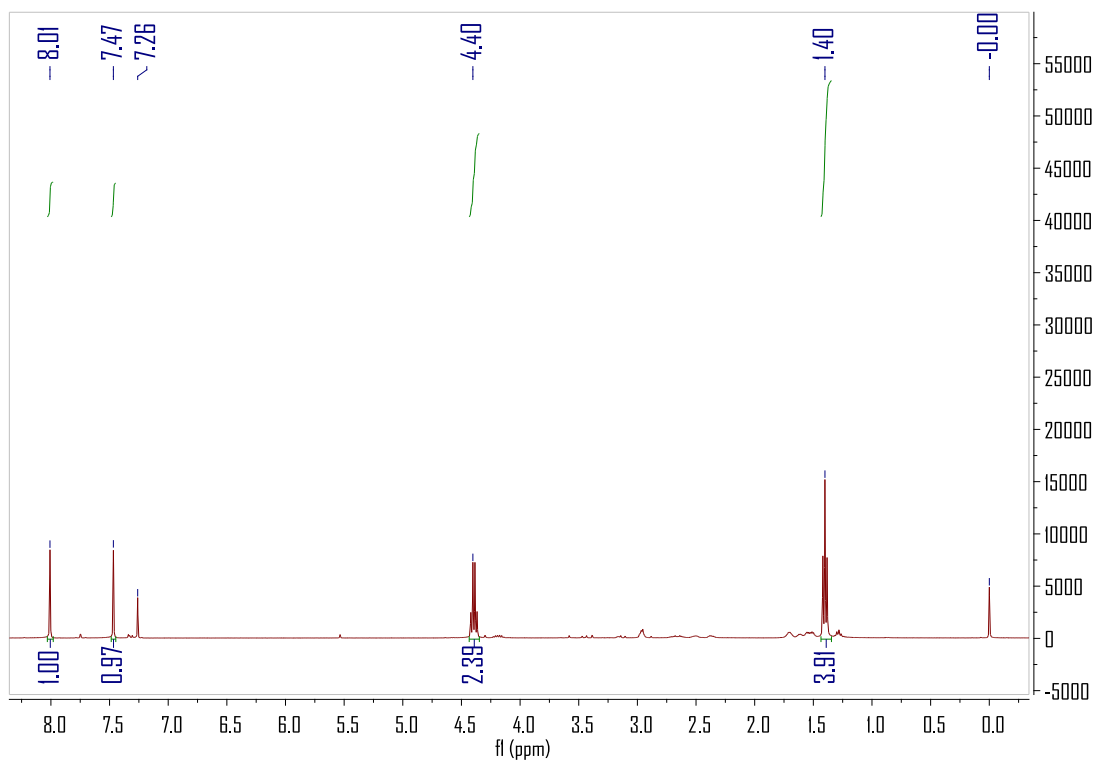
resulting mixture was stirred for 1 h prior to addition of N-formylpiperidine (12.2 mL, 12.45 g, 110.0 mmol). After 24 h at room temperature, an excess of 20% aqueous ammonium chloride was added and stirred for 1 h. The mixture was then filtered to collect the product as light yellow solid (16.15 g, 95% yield). ^1H NMR (CDCl_3 , 400 MHz): δ /ppm: 9.95 (d, 1H), 7.75 (d, 1H); ^{13}C NMR (CDCl_3 , 100 MHz): δ /ppm: 182.97, 137.77, 131.71, 136.13, 123.55, 116.09.





Compound 4:

Compound **3** (34.00 g, 126.0 mmol) was added to the stirred mixture of ethyl 2-thioacetate (19 mL, 172.6 mmol), potassium carbonate (34.20 g, 246.6 mmol), anhydrous DMF (400 mL) at room temperature and the resulting mixture was stirred for further 72 h. The mixture was then poured into water (1.5 L) and the product was collected by filtration, washed with water and dried. The product was obtained as white solid (26.7 g, 73.0% yield). ¹H NMR (CDCl₃, 400 MHz): δ/ppm: 8.01 (s, 1H), 7.47 (s, 1H), 4.40 (m, 2H), 1.40 (t, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ/ppm: 162.24, 144.78, 137.65, 136.13, 128.19, 126.18, 102.85, 61.62, 14.31.

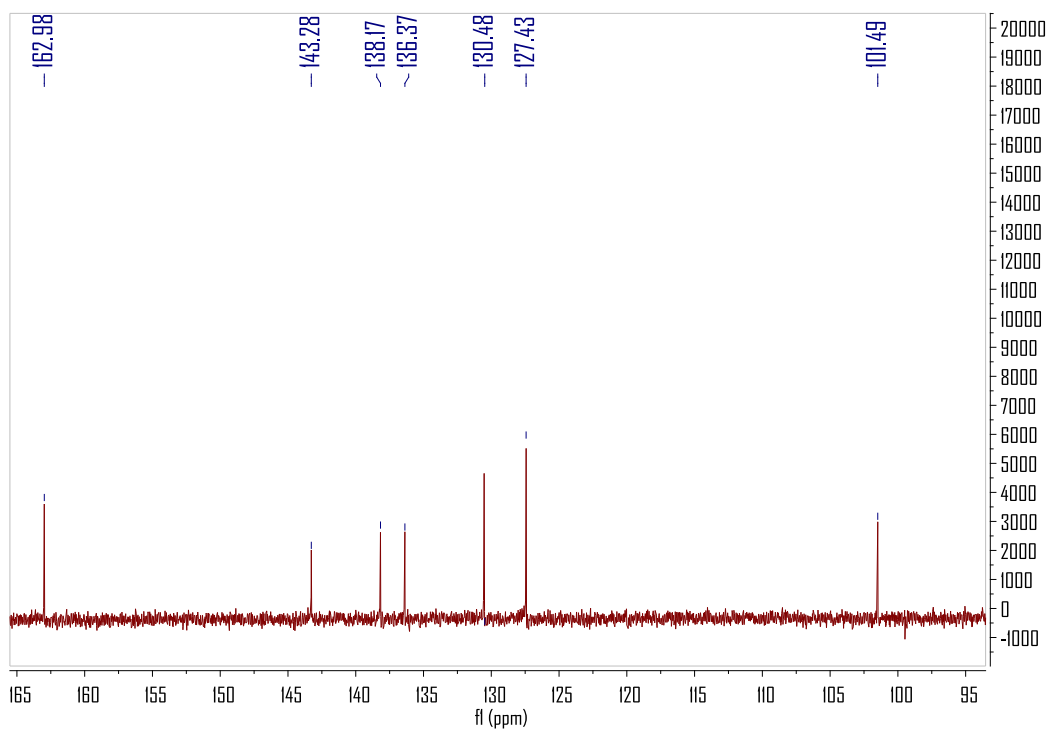
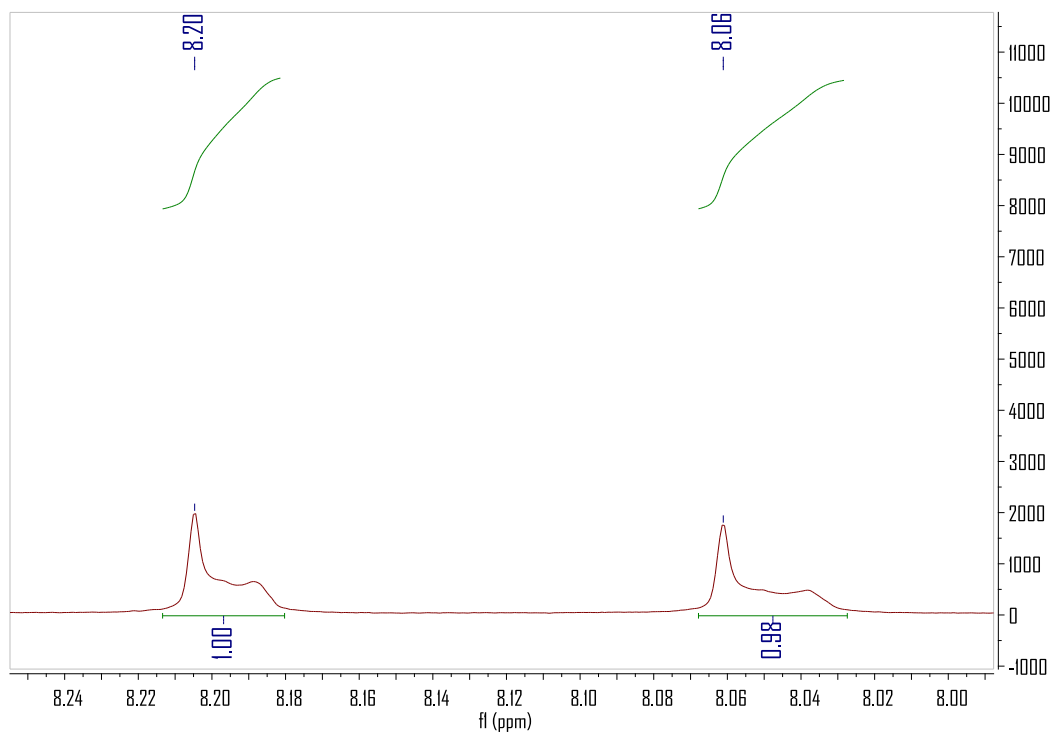


Compound 5:

A stirred mixture of compound **4** (20.00 g, 68.8 mmol), LiOH (4.00 g, 164.8 mmol), water (170 mL) and THF (170 mL) was heated under reflux for 12 h. Then, hydrochloric acid (1 M, 500 mL) was

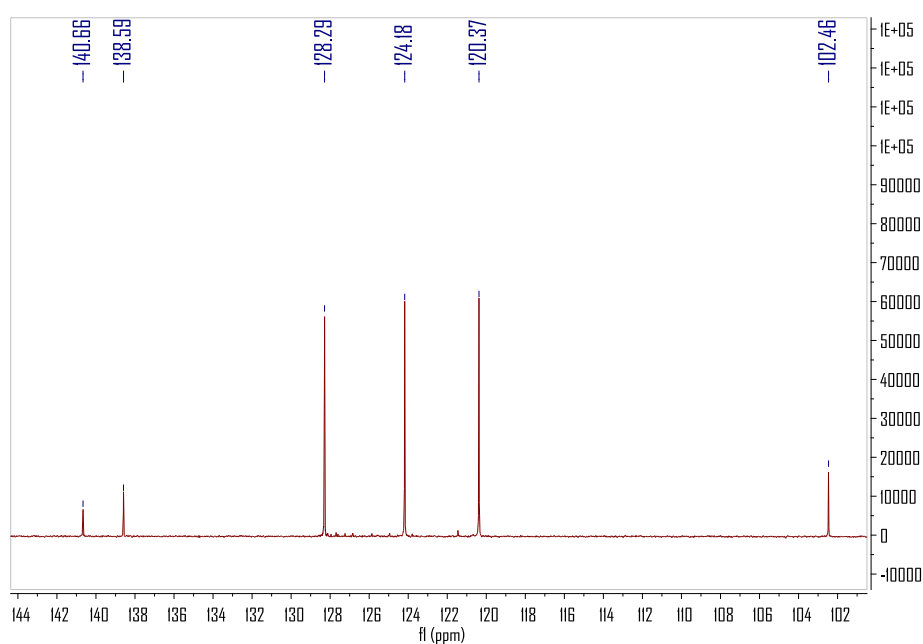
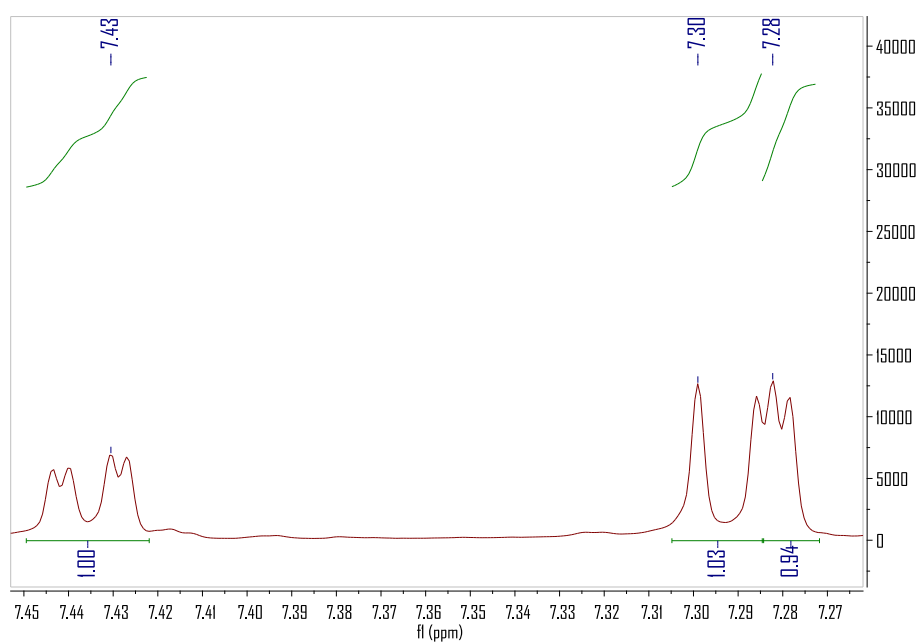
added and the reaction continued for 1 h. Compound **5** as precipitate was filtered off, washed with water and dried in a vacuum desiccator (16.6 g, 91.7% yield). ^1H NMR (DMSO- d_6 , 400 MHz):

δ /ppm: 8.20 (s, 1H), 8.06(s, 1H); ^{13}C NMR (DMSO- d_6 , 100 MHz): δ /ppm: 162.98, 143.28, 138.17, 136.37, 130.48, 127.43, 101.49.



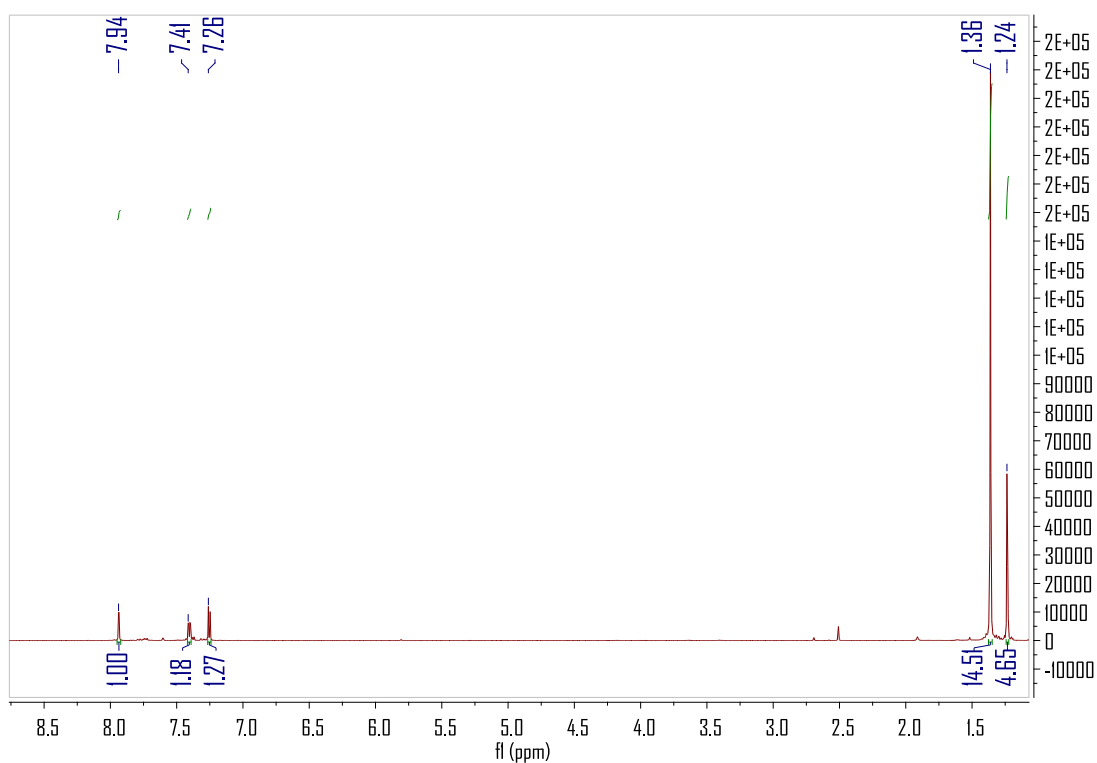
Compound 6:

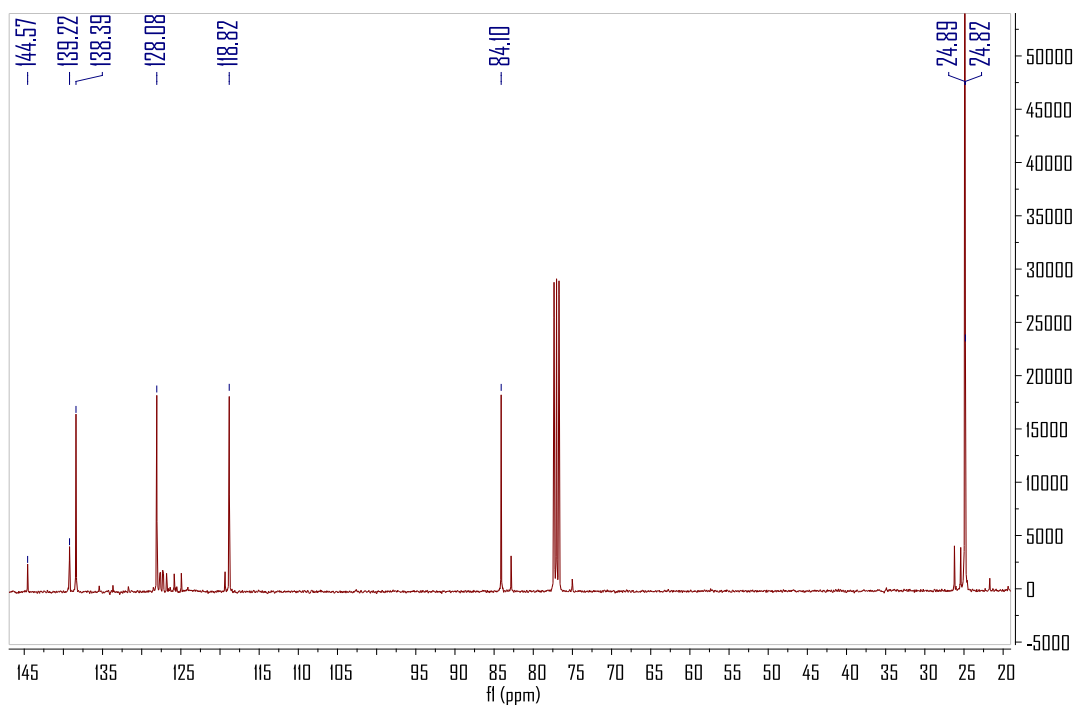
A solution of compound **5** (15.20 g, 57.80 mmol), copper powder (2.20 g) and quinolone (100 mL) was heated at 260 °C for 2 h. Ether (60 mL) was added, followed by addition of hydrochloric acid (1 M, 500 mL). The organic phase was dispensed and washed with dilute hydrochloric acid. After removal of solvent, compound **6** was obtained and used in the next step without further purification (10.80 g, 85.3% yield). ^1H NMR (CDCl_3 , 400 MHz): δ /ppm: 7.43 (dd, 1H), 7.30 (d, 1H), 7.28 (d, 1H); ^{13}C NMR (CDCl_3 , 100 MHz): δ /ppm: 140.66, 138.59, 128.29, 124.18, 120.37, 102.46.



Compound 7:

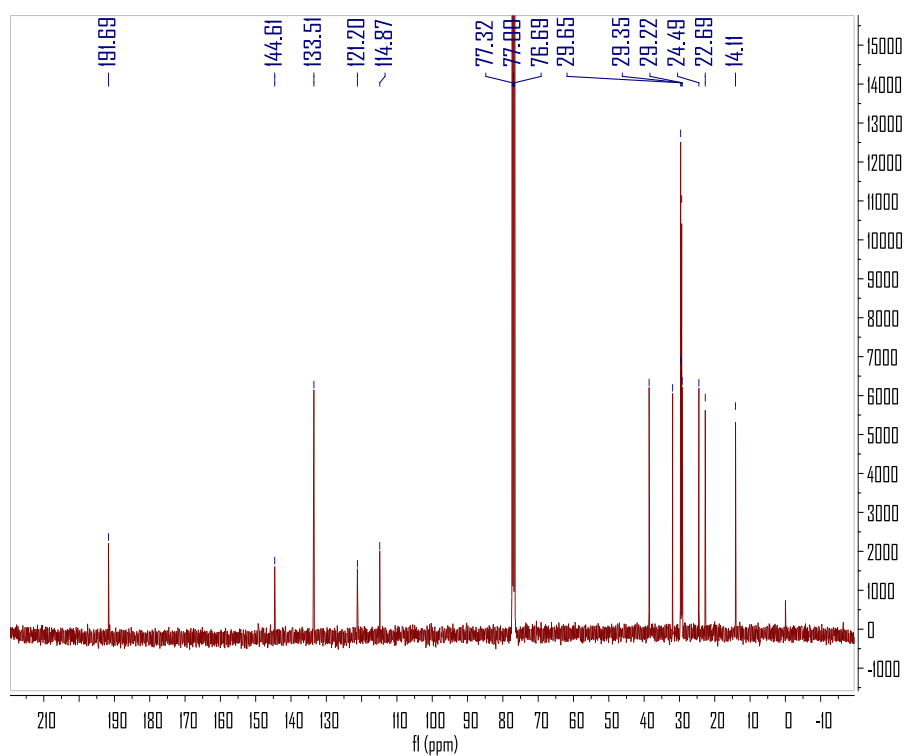
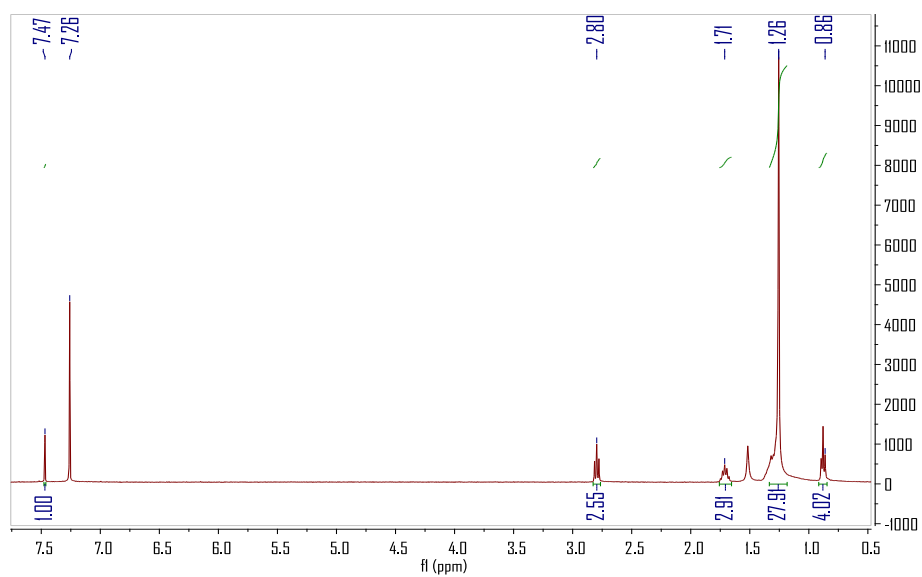
n-BuLi (82.20 mmol, 2.50 M in hexane, 33 mL) was introduced dropwise into a solution of Compound 6 (15.00 g, 68.50 mmol) in anhydrous diethyl ether (280 mL) at -78 °C. After 1.5 h, 2-iso-propoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (137.00 mmol, 28.00 ml) was added and the resulting solution was stirred for 1 h at -78 °C and then at 25 °C overnight. Deionized water (200 mL) was added and the organic phase was separated and dried with Na₂SO₄. After removal of solvent, crude product was obtained as a pink solid (22.4 g, 88% yield) and used in the next reaction without further purification. ¹H NMR (CDCl₃, 400 MHz): δ/ppm: 7.94 (s, 1H), 7.41 (d, 1H), 7.26 (d, 1H); ¹³C NMR (CDCl₃, 100 MHz): δ/ppm: 140.66, 138.59, 128.29, 124.18, 120.37, 102.46.





Compound 8:

To an ice-cooled solution of 2,3-dibromothiophene (36.30 g, 150.00 mmol) and palmitoyl chloride (47.42 g, 172.50 mmol) in dichloromethane (260 mL) was added aluminium chloride (26.00 g, 195.00 mmol) in portions over 20 min. The reaction mixture was stirred for 4 h and then quenched with ice-cold hydrochloric acid (2 M, 500 mL). The quenched reaction mixture was extracted with diethyl ether and dried over anhydrous Na₂SO₄; Solvent was removed and crude product was obtained as pale yellow solid (70 g, 97% yield) and used in next step without further purification. ¹H NMR (CDCl₃, 400 MHz): δ/ppm: 7.47 (s, 1H), 2.80 (t, 2H), 1.71 (m, 2H), 1.21 (m, 24H), 0.86 (t, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ/ppm: 140.66, 138.59, 128.29, 124.18, 120.37, 102.46.

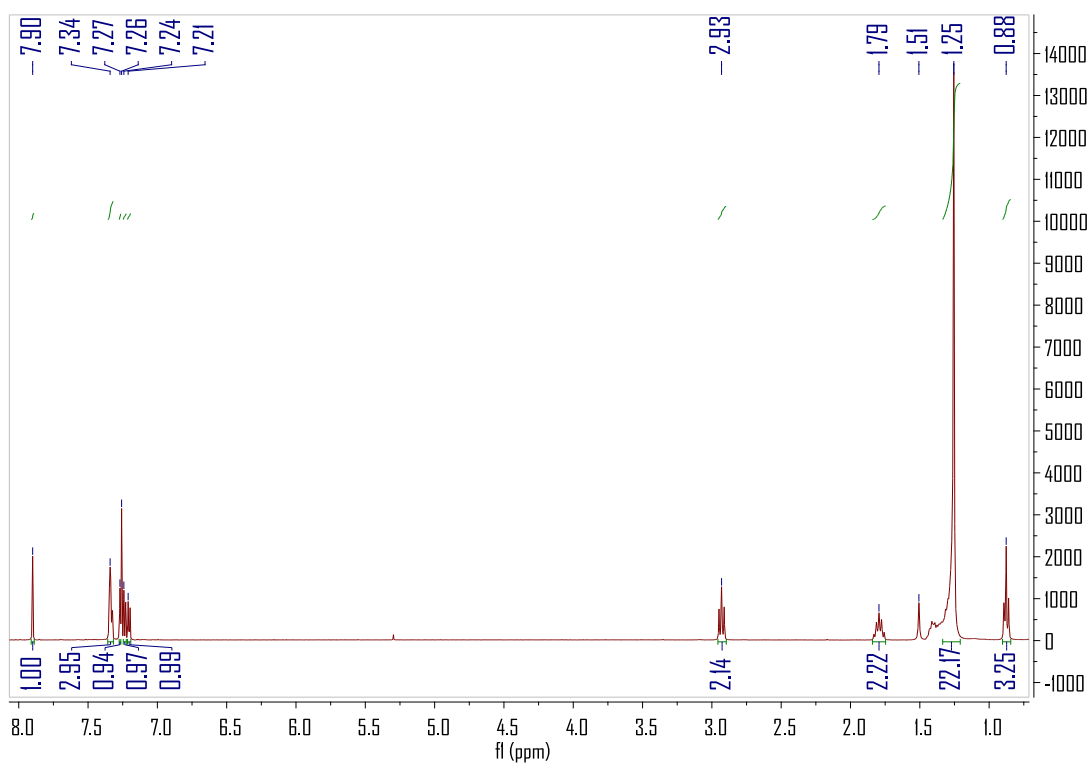


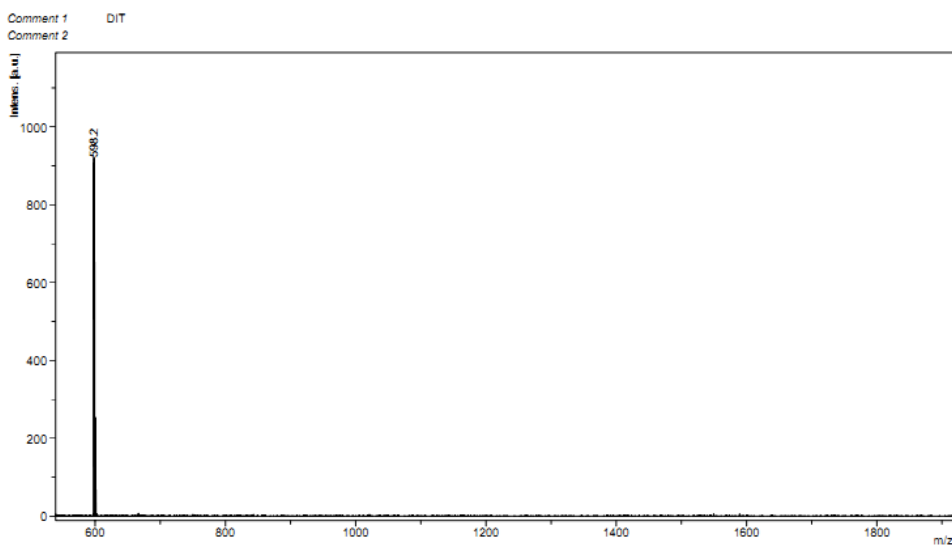
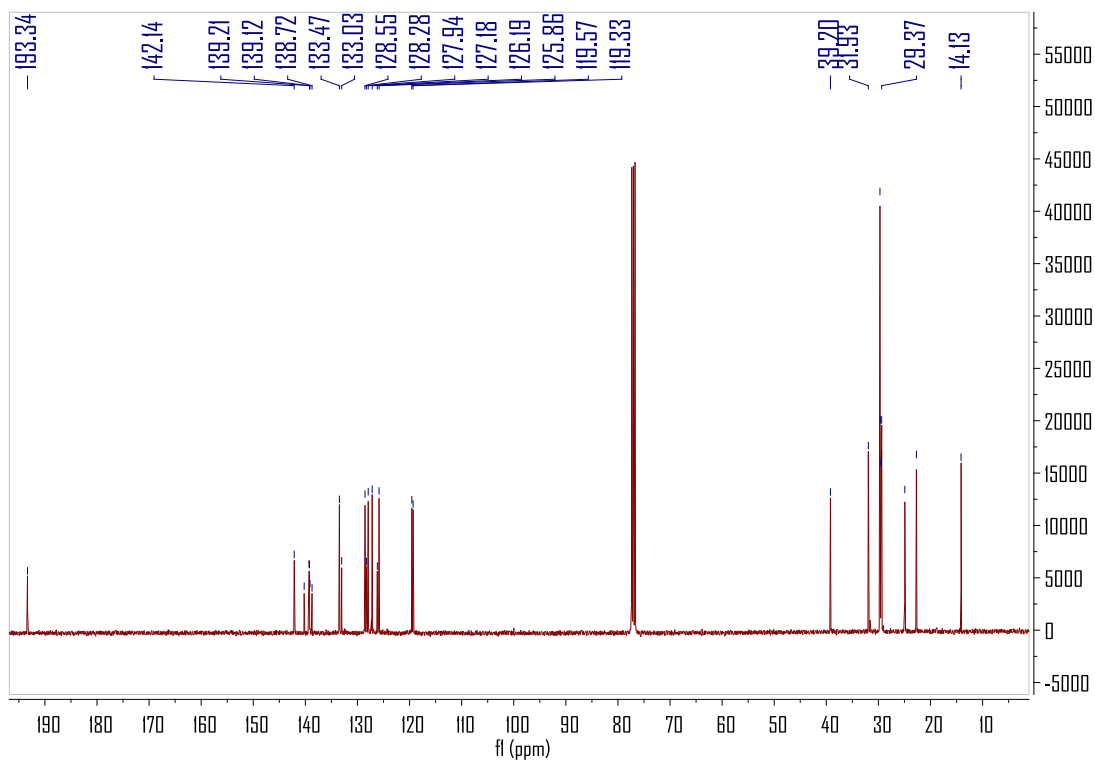
Compound 9:

Compound **7** (16.50 g, 62.00 mmol), compound **8** (12.80 g, 26.65 mmol), Pd(PPh₃)₄ (1.20 g), tetrabutylammonium hydroxide (20% in water) and toluene (200 mL) were put into a 500 mL flask. The mixture was well stirred and heated to reflux overnight under argon atmosphere. Then, the mixture was cooled down to room temperature, and 200 mL distilled water was added. The resulted

mixture was extracted with diethyl ether for three times, and the combined organic phase was dried over anhydrous Na₂SO₄. After the solvent was removed under vacuum, purification was carried out via silica gel column chromatography with light petroleum/chloroform (4:1 v/v) as eluent.

Compound **9** (14.0 g, 90 % yiled) was obtained as green-yellow solid. ¹H NMR (CDCl₃, 400 MHz): δ/ppm: 7.90 (s, 1H), 7.32-7.34 (m, 3H), 7.27 (d, 1H), 7.24 (d, 1H), 7.21 (d, 1H), 2.93 (t, 2H), 1.79 (m, 2H), 1.25 (m, 24H), 0.88 (t, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ/ppm: 193.34, 142.14, 140.23, 139.31, 139.21, 139.12, 138.72, 133.47, 133.03, 128.55, 128.28, 127.94, 126.19, 125.86, 119.57, 119.33, 39.20, 31.93, 29.70, 29.64, 29.51, 29.45, 29.40, 29.37, 24.93, 22.70, 14.13; MALDI-TOF-MS: m/z 598.2 [M]⁺.

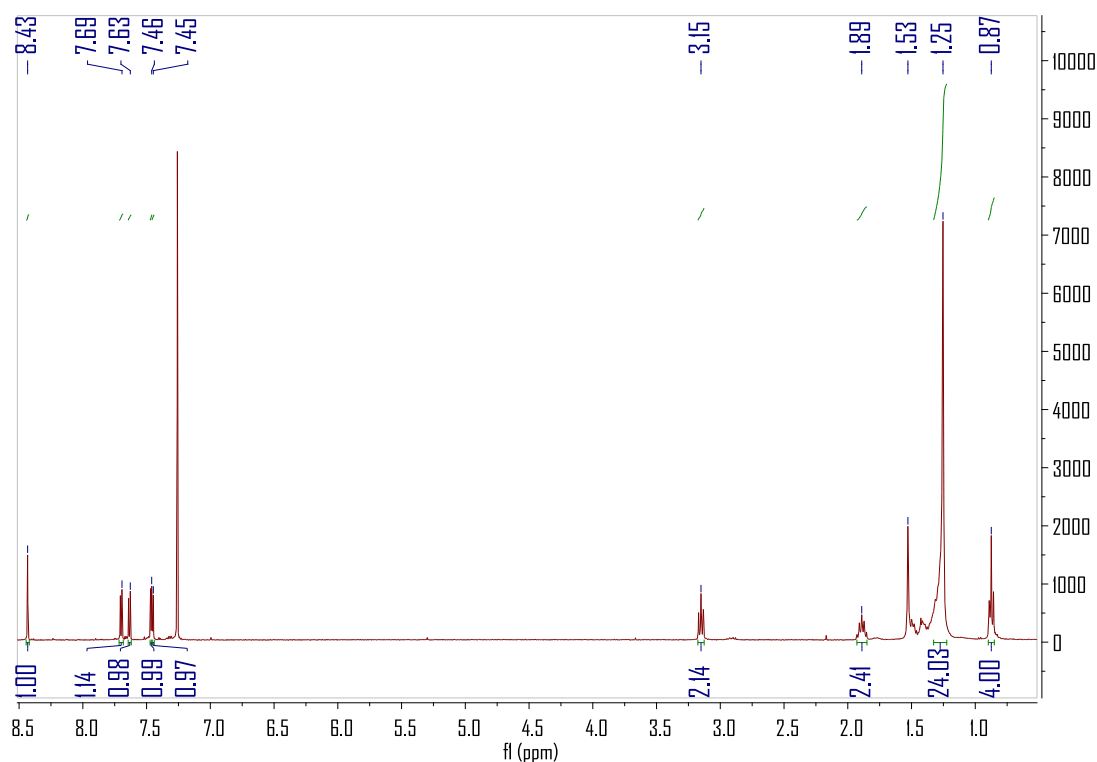


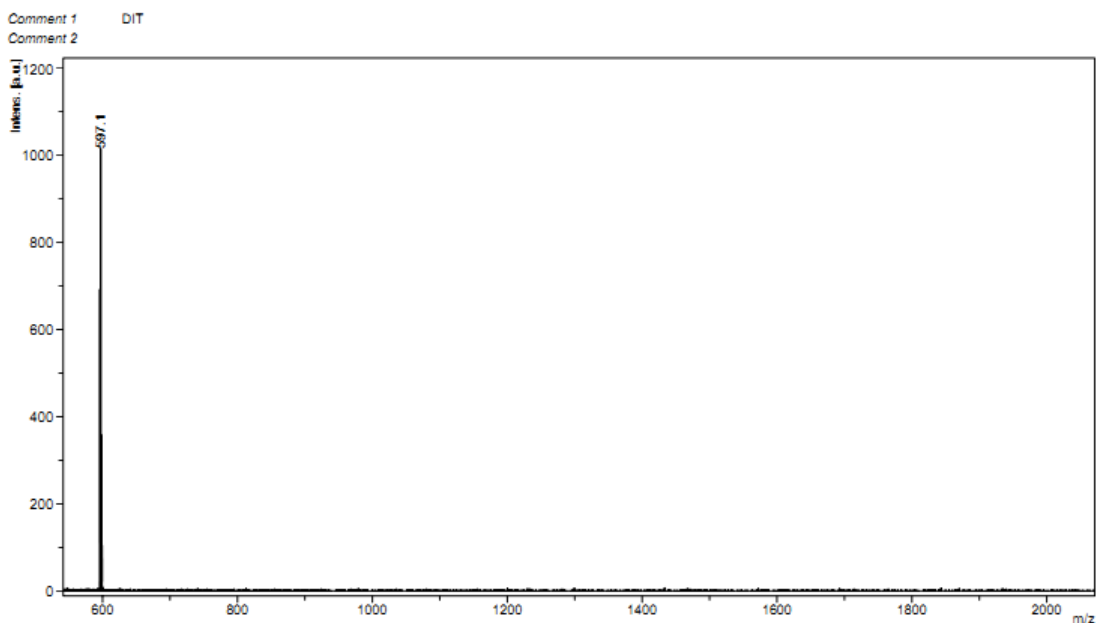


Compound 10:

A solution of iron chloride (1.24 g, 7.60 mmol) in nitromethane (24 mL) was added dropwise to a stirred solution of compound **9** (1.40 g, 2.34 mmol) in dichloromethane (200 mL) under argon. After the mixture was stirred for 50 min at 30-35 °C, anhydrous methanol (20 mL) was added and the mixture was stirred for another 1 h, followed by addition of 220 mL of methanol. The resulting

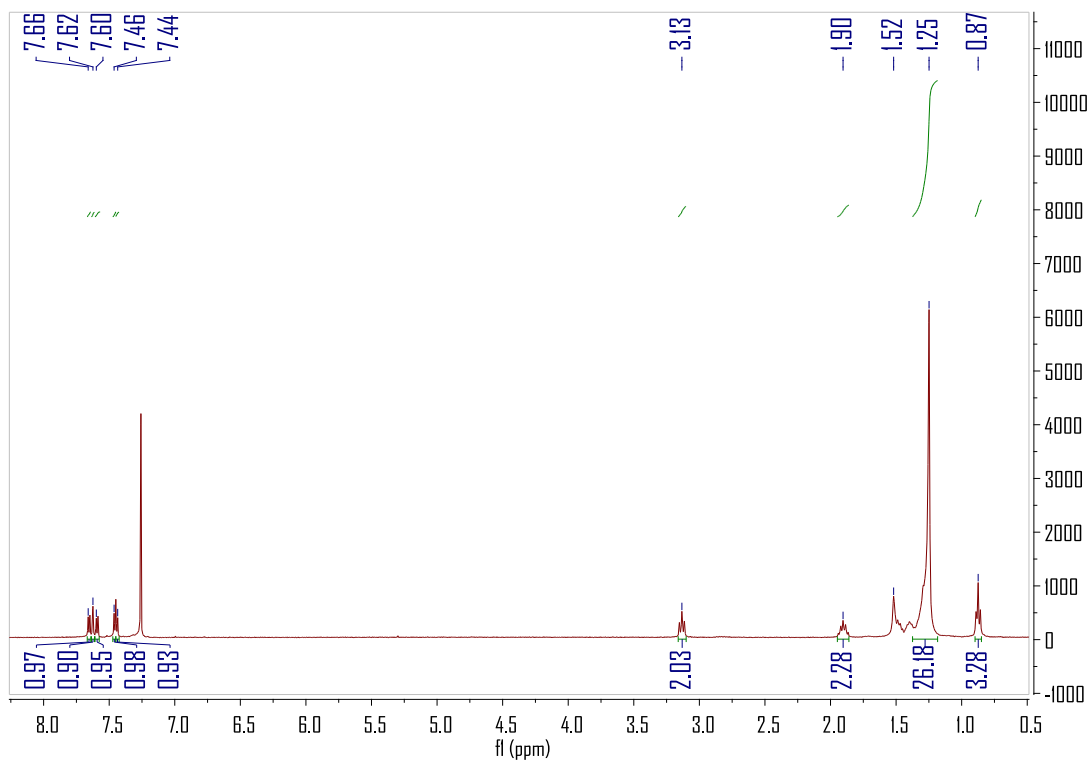
precipitates were filtered and washed with methanol to afford 1.13 g of the product as a green-yellow solid. The organic filtrate was diluted with dichloromethane and stirred with NH_4OH . The organic layer was further washed with aqueous NH_4OH and NH_4Cl and dried. After removal of solvent, the residue was purified by silica gel column chromatography with light petroleum/chloroform (4:1 v/v) as eluent to give compound **10** (1.02 g, 73 % yield) was obtained as yellow solid. ^1H NMR (CDCl_3 , 400 MHz): δ /ppm: 8.43 (s, 1H), 7.69 (d, 1H), 7.63 (d, 1H), 7.46 (d, 1H), 7.45 (d, 1H), 3.15 (t, 2H), 1.89 (m, 2H), 1.25 (m, 24H), 0.87 (t, 3H); MALDI-TOF-MS: m/z 597.1 $[\text{M}]^+$.



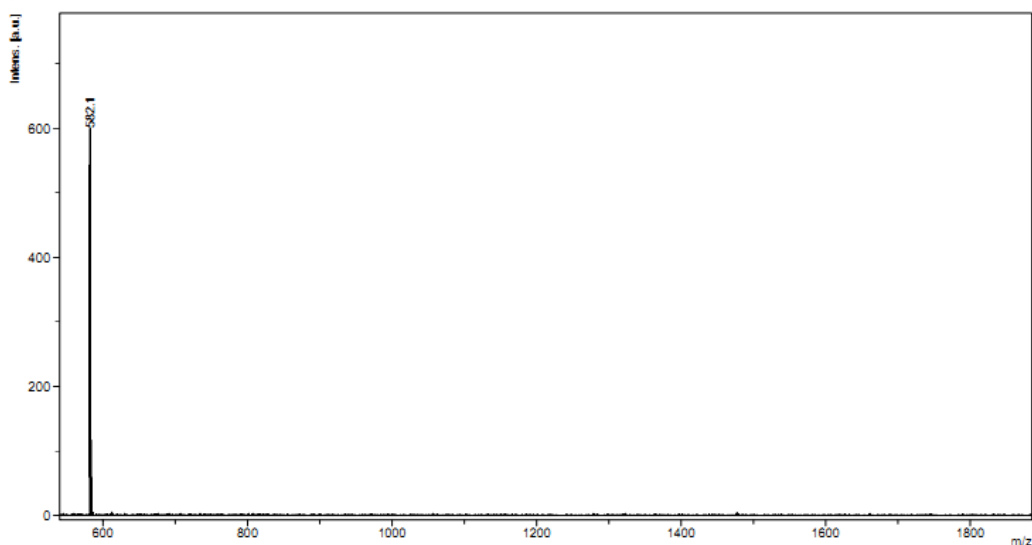


DTBTT:

To a suspension of **10** (3.30 g, 5.53 mmol) in diethylene glycol (300 mL) were added hydrazine monohydrate (14.00 mL, 277.00 mmol) and potassium hydroxide (8.10 g, 143.78 mmol). The reaction mixture was stirred at 190 °C overnight. After cooling to room temperature, water (200 mL) was poured into the reaction mixture and the crude product was obtained by filtration. Purification was done by silica gel column chromatography with petroleum ether/ chloroform (3:1 v/v) as eluent to give **DTBTT** as pale yellow solid (1.60 g, 50% yield). ¹H NMR (CDCl₃, 400 MHz): δ/ppm: 7.66 (d, 1H), 7.62 (s, 1H), 7.60 (d, 1H), 7.46(d, 1H), 7.44 (d, 1H), 3.13 (t, 2H), 1.90 (m, 2H), 1.25 (m, 26H), 0.87 (t, 3H); MALDI-TOF-MS: m/z 582.1 [M]⁺.



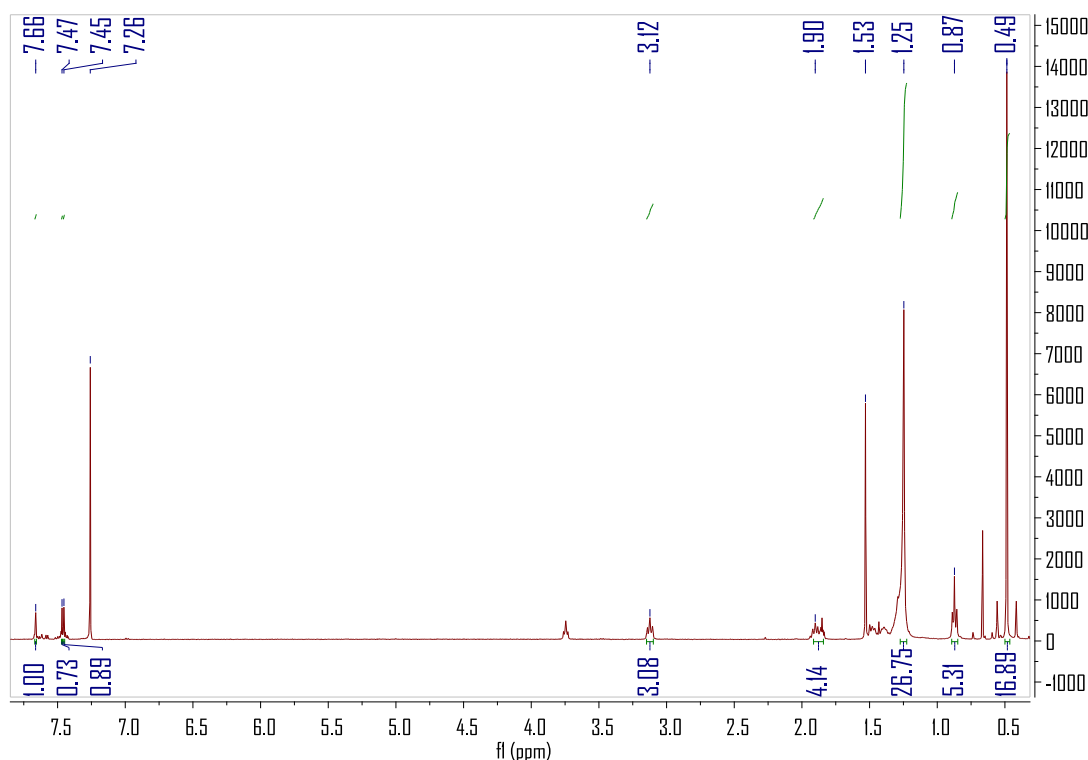
Comment 1 DIT
 Comment 2



DTBTT-2Sn:

A solution of n-BuLi in hexanes (2.50 M, 1.50 mL, 3.90 mmol) was injected slowly via syringe into a solution of **DTBTT** (0.45 g, 2.68 mmol) in anhydrous THF (70 mL) at $-78\text{ }^{\circ}\text{C}$. After stirring for 1 h at low temperature, the mixture was stirred at room temperature for 2.5 h. The mixture was cooled once again to $-78\text{ }^{\circ}\text{C}$ and then a solution of trimethyltin chloride (1 M, 3.60 mL, 3.60 mmol) in THF was added; the mixture was then warmed slowly to room temperature and stirred overnight. The

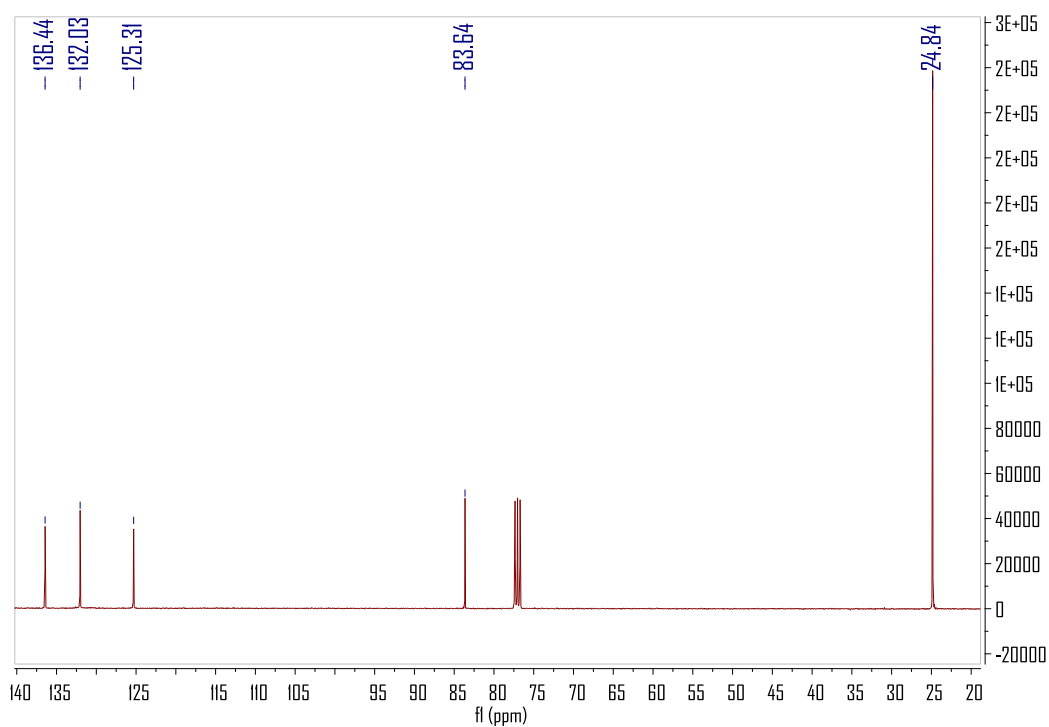
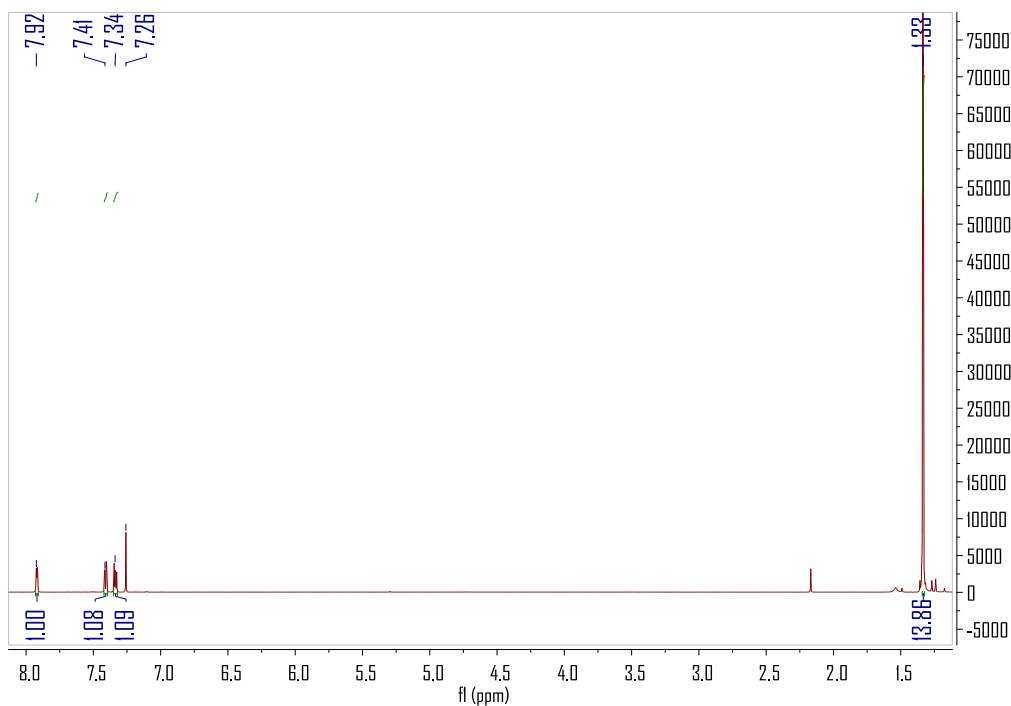
reaction was quenched through the addition of water and the aqueous phase extracted with diethyl ether. The combined organic extracts were dried with Na_2SO_4 and concentrated to afford a yellow solid (0.58 g, 83% yield). ^1H NMR (CDCl_3 , 400 MHz): δ /ppm: 7.66 (s, 1H), 7.47 (s, 1H), 7.45 (s, 1H), 3.08 (t, 2H), 1.90 (m, 2H), 1.25 (m, 26H), 0.87 (t, 3H), 0.43 (s, 18H).



Compound **11**:

To a solution of 3-bromothiophene (6.52 g, 40.00 mmol) in anhydrous diethyl ether (80 mL) in a flame-dried 250 mL flask, n-butyllithium (2.5 M in hexane, 17.3 mL) was dropped at $-78\text{ }^\circ\text{C}$ under argon atmosphere in 30 min. After the reaction was stirred at $-78\text{ }^\circ\text{C}$ for another 1.5 h, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (14.88 g, 80.00 mmol) was added in one portion. And the solution was stirred for another hour at $-78\text{ }^\circ\text{C}$. Then the resulted mixture was warmed to room temperature naturally and stirred overnight. After the reaction was quenched with distilled water, 100 mL water was poured into the mixture, the organic phase was separated in separating funnel, then the solvent was removed under reduced pressure, the products were obtained as colorless and clear

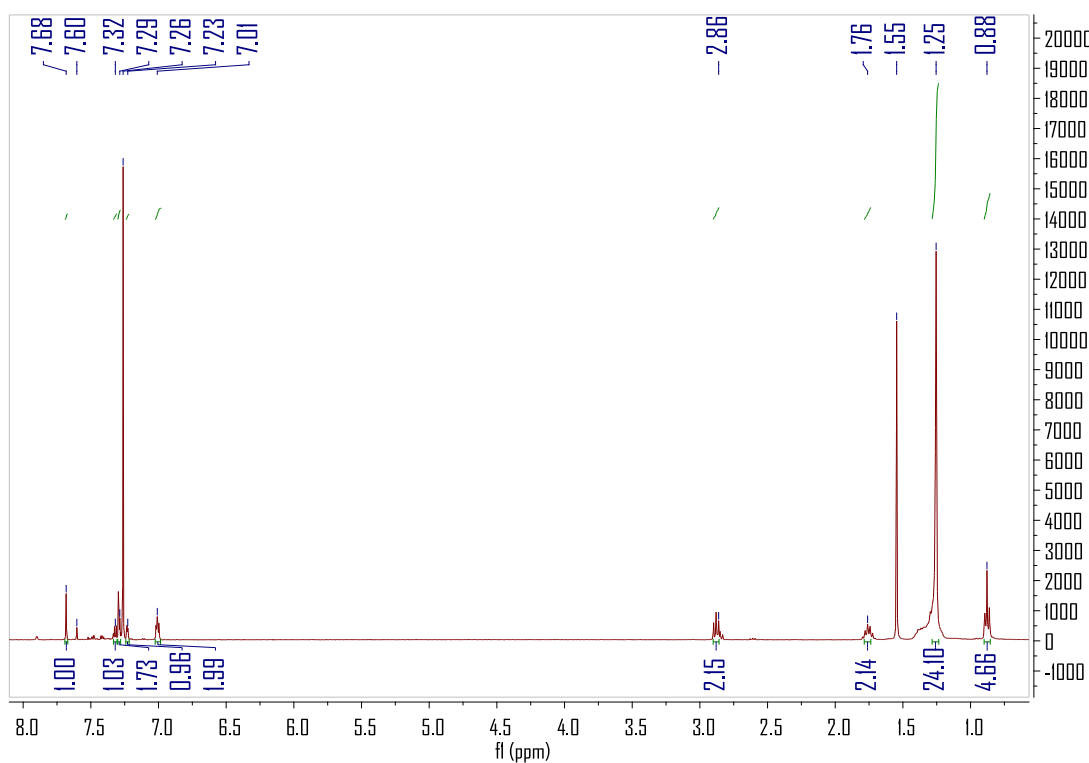
crystals (7.56 g, 90% yield). ^1H NMR (CDCl_3 , 400 MHz): δ /ppm: 7.92 (dd, 1H), 7.41 (dd, 1H), 7.34 (m, 1H), 1.33 (m, 12H); ^{13}C NMR (CDCl_3 , 100 MHz): δ /ppm: 136.44, 132.03, 125.31, 83.64, 24.84.

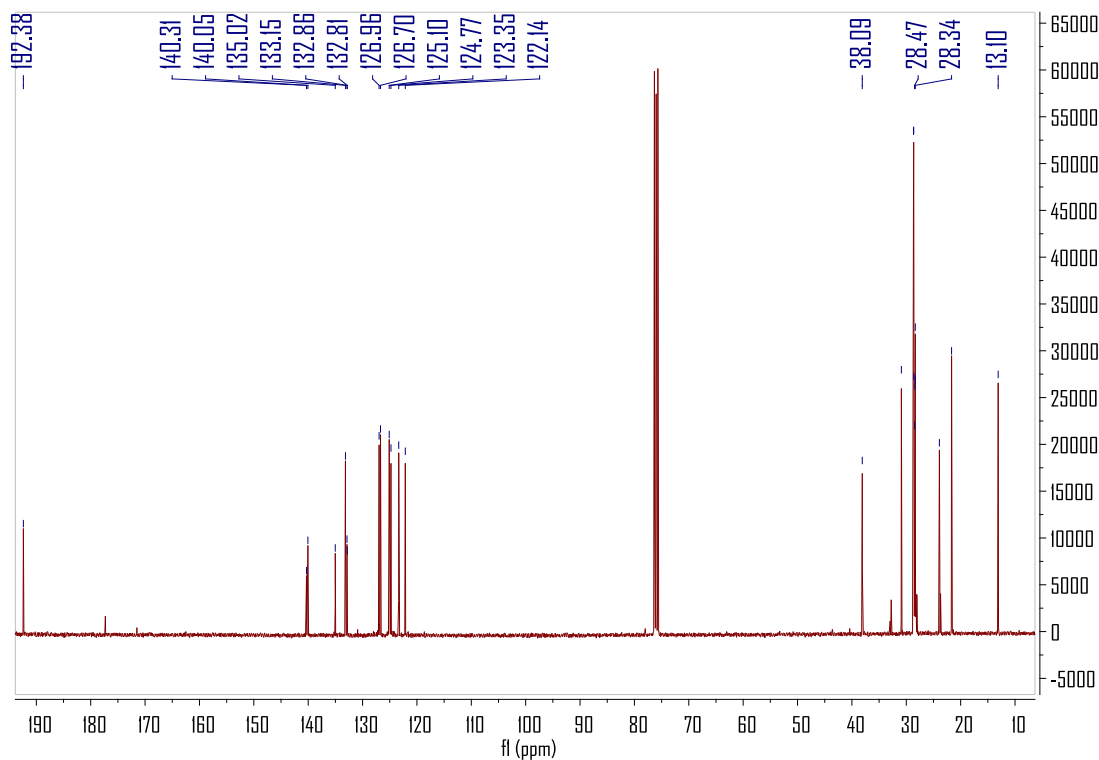


Compound 12:

Compound **11** (4.20 g, 20.00 mmol), compound **8** (4.37 g, 9.10 mmol), $\text{Pd}(\text{PPh}_3)_4$ (300 mg), tetrabutylammonium hydroxide (3.5 g, 10% in water) and toluene (50 mL) were put into a 250 mL

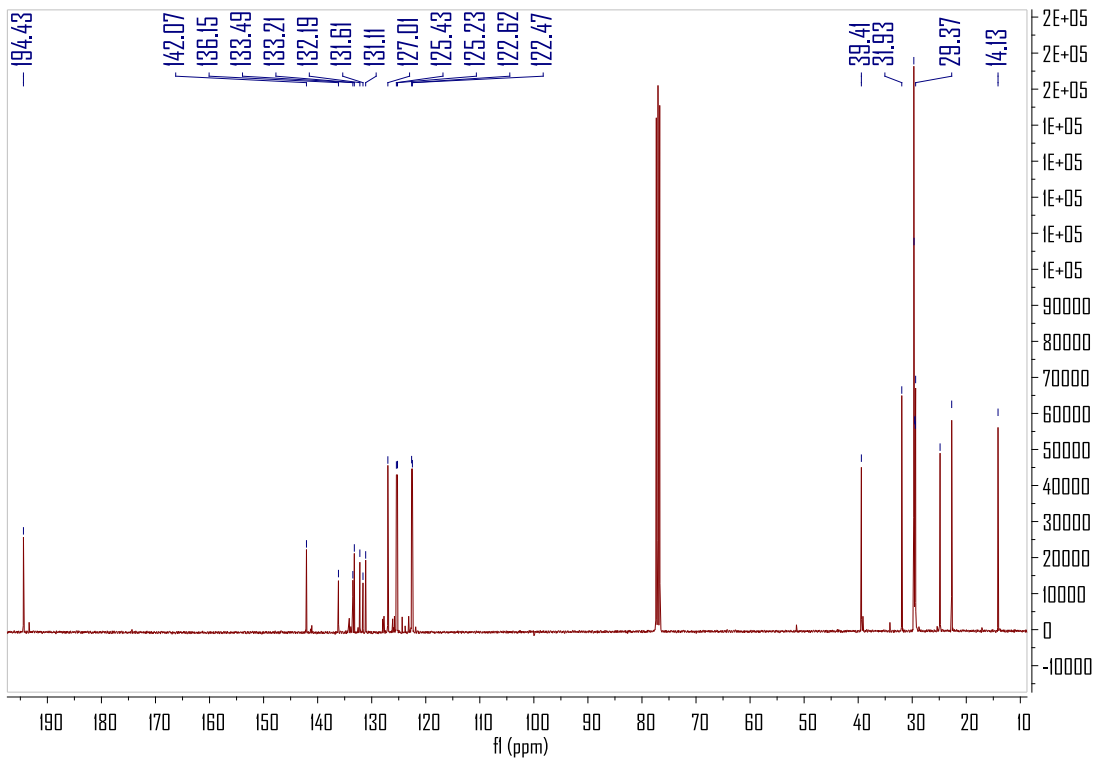
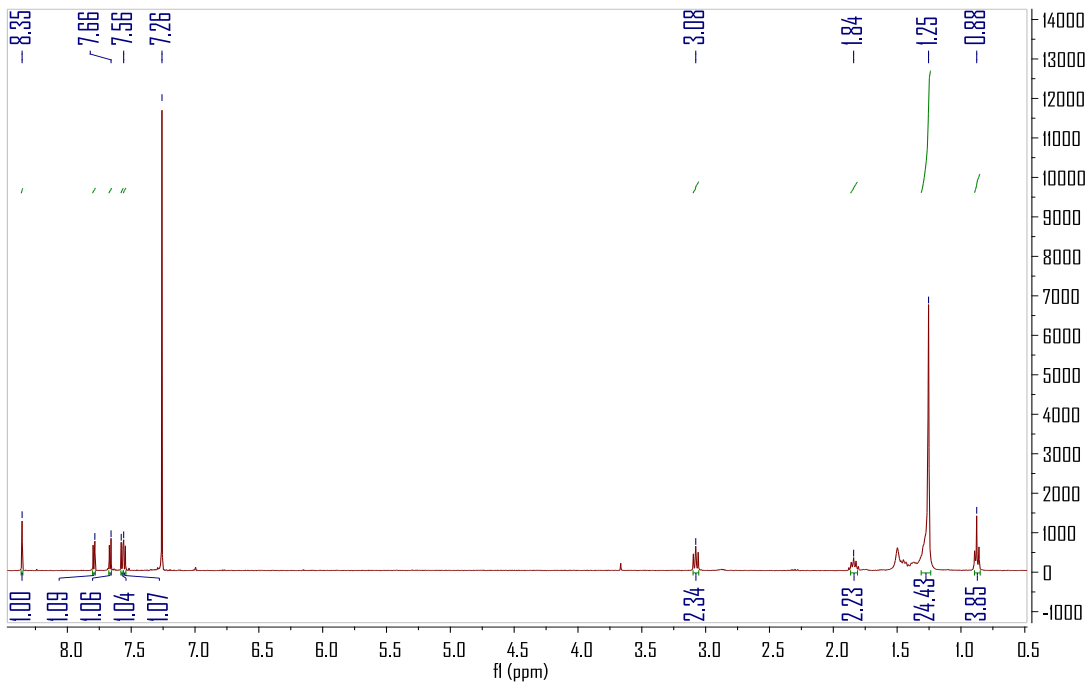
flask. The mixture was well stirred and heated to reflux overnight under argon atmosphere. Then, the mixture was cooled down to room temperature, and 200 mL distilled water was added. The resulted mixture was extracted with DCM for three times, then the combined organic phase was dried over anhydrous Na_2SO_4 , then solvent was removed. Purification was done by silica gel column chromatography with petroleum ether/ DCM (4:1 v/v) as eluent to give the product (3.54 g, 80% yield). ^1H NMR (400 MHz, CDCl_3): δ /ppm: 7.68 (s, 1H), 7.32 (dd, 1H), 7.29 (m, 2H), 7.23 (m, 1H), 7.01 (m, 2H), 2.86 (t, 2H), 1.74 (m, 2H), 1.25 (m, 24H), 0.88 (t, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ /ppm: 192.38, 140.31, 140.05, 135.02, 133.15, 132.86, 132.81, 126.96, 126.70, 125.10, 124.77, 123.35, 122.14, 38.09, 30.90, 28.66, 28.64, 28.60, 28.47, 28.41, 28.35, 28.34, 23.91, 21.67.

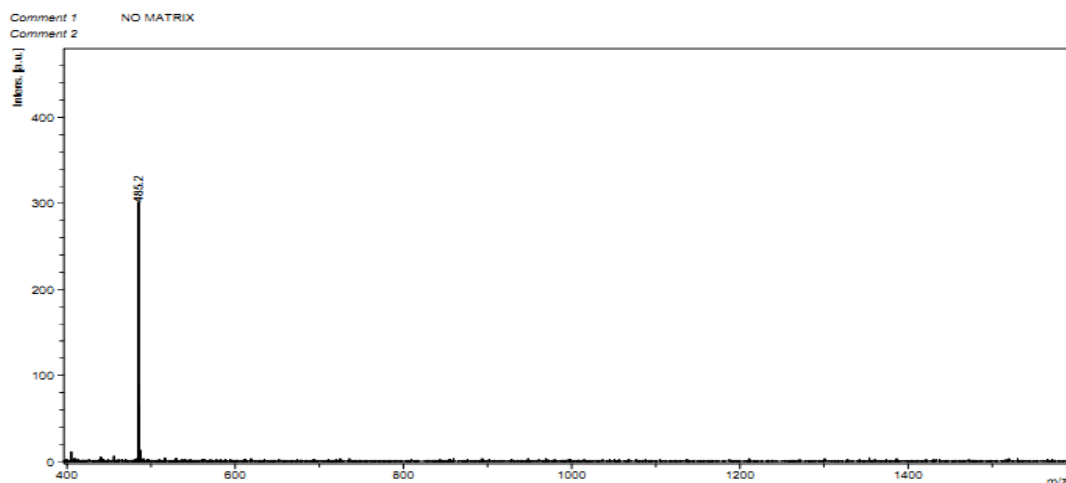




Compound **13**:

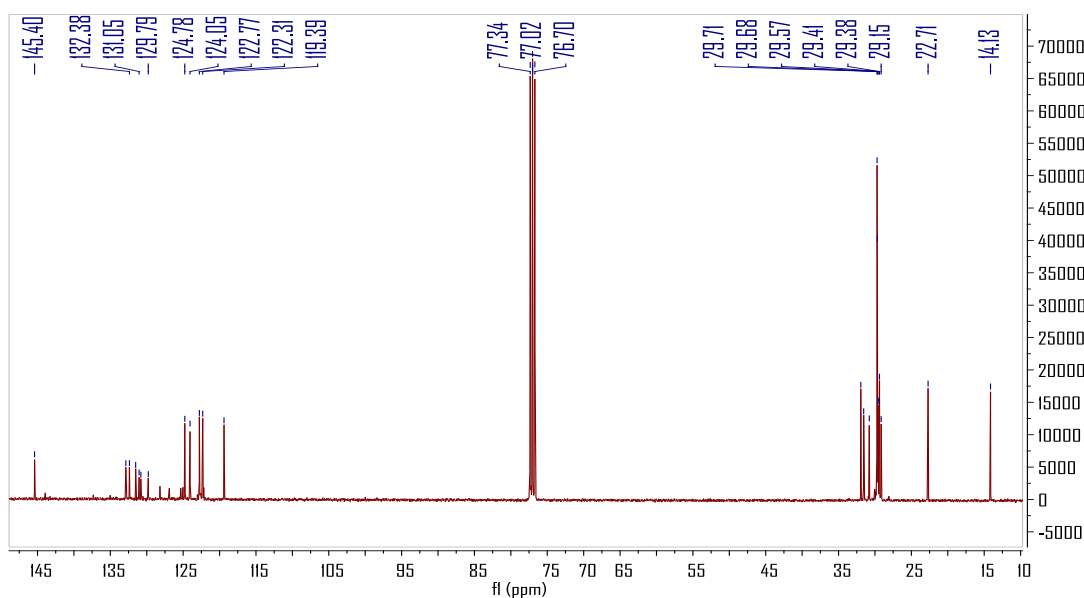
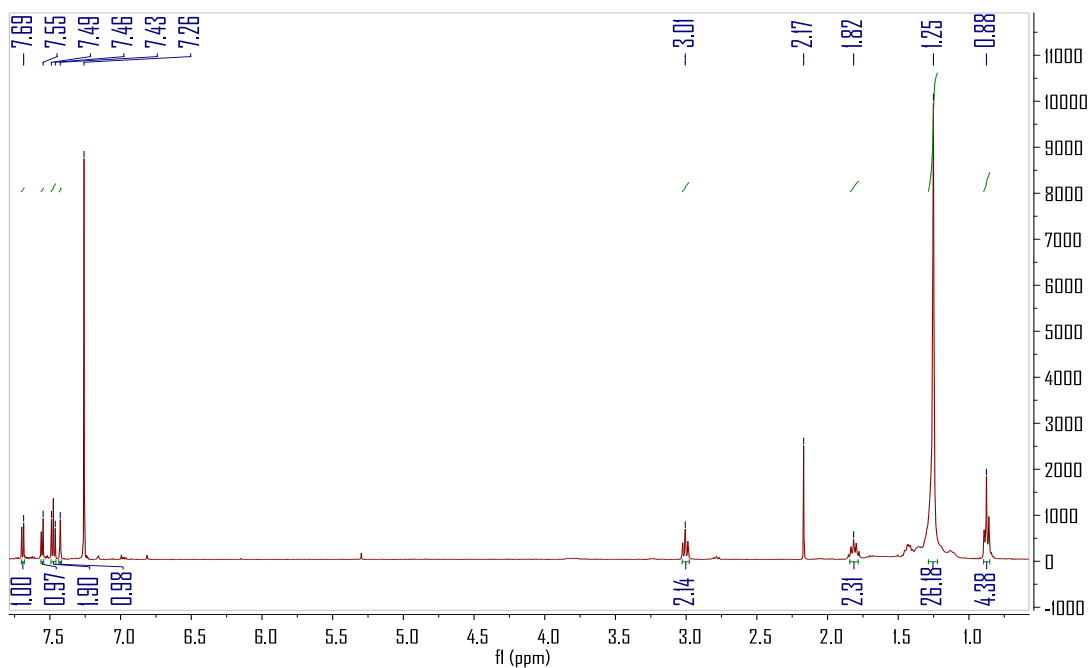
A solution of iron chloride (2.00 g, 12.33 mmol) in nitromethane (25 mL) was added dropwise to a stirred solution of compound **12** (2.00 g, 4.10 mmol) in dichloromethane (40 mL) under argon. After the mixture was stirred for 30 min, anhydrous methanol (15 mL) was added in 3 minutes and the mixture was stirred for another 30 min. Then the solvent was removed by reduced pressure distillation and the resulted solid was purified by silica gel column chromatography with petroleum ether/dichloromethane (4:1 v/v) as eluent to give compound **13** as green solids (0.38 g, 20% yield). ¹H NMR (400 MHz, CDCl₃): δ/ppm: 8.35 (s, 1H), 7.78 (d, 1H), 7.66 (d, 1H), 7.58 (d, 1H), 7.56 (d, 1H), 3.08 (t, 2H), 1.84 (m, 2H), 1.25 (m, 24H), 0.88 (t, 3H); ¹³C NMR (100 MHz, CDCl₃): δ/ppm: 194.43, 142.07, 136.15, 133.49, 133.21, 132.19, 131.61, 131.11, 127.01, 125.43, 125.23, 122.62, 122.47, 39.41, 31.93, 29.70, 29.67, 29.54, 29.50, 29.42, 29.37, 24.85, 22.70, 14.13; MALDI-TOF-MS: m/z 485.2 [M]⁺.





BTT:

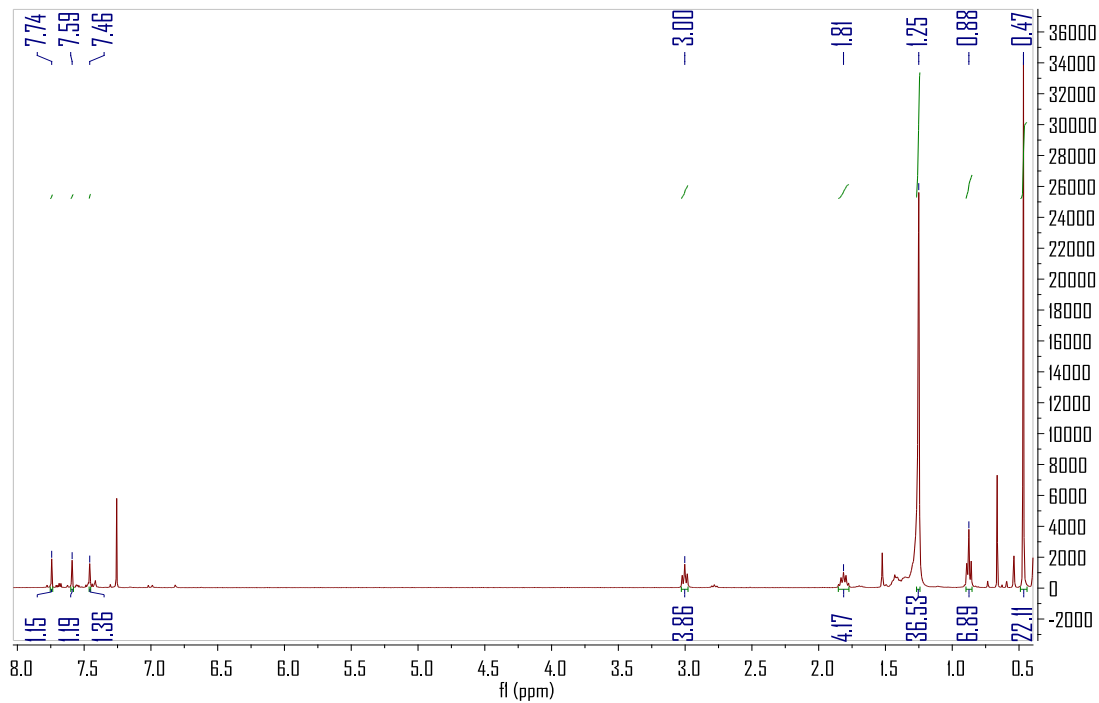
To a suspension of compound **13** (1.11 g, 2.30 mmol) in diethylene glycol (100 mL) was added hydrazine monohydrate (860 mL, 0.10 mol) and potassium hydroxide (3.50 g, 60.0 mmol) and the reaction mixture was stirred at 190 °C overnight. The cooled reaction mixture was poured into water, extracted with dichloromethane, dried over anhydrous sodium sulphate and concentrated to afford the crude product. Purification was done by silica gel column chromatography with petroleum ether/DCM (4:1 v/v) as eluent to give **BTT** as green-yellow solid (1.00 g, 90% yield). ¹H NMR (CDCl₃, 400 MHz): δ/ppm: 7.69 (d, 1H), 7.55 (d, 1H), 7.49 (d, 1H), 7.46 (d, 1H), 7.43 (s, 1H), 3.01 (t, 2H), 1.82 (m, 2H), 1.25 (m, 26H), 0.88 (t, 3H); ¹³C NMR (CDCl₃, 100 MHz): δ/ppm: 145.40, 132.87, 132.38, 131.52, 131.05, 130.81, 129.79, 124.78, 124.05, 122.77, 122.31, 119.39, 31.94, 31.55, 30.78, 29.71, 29.69, 29.57, 29.38, 29.15, 22.71, 14.13.



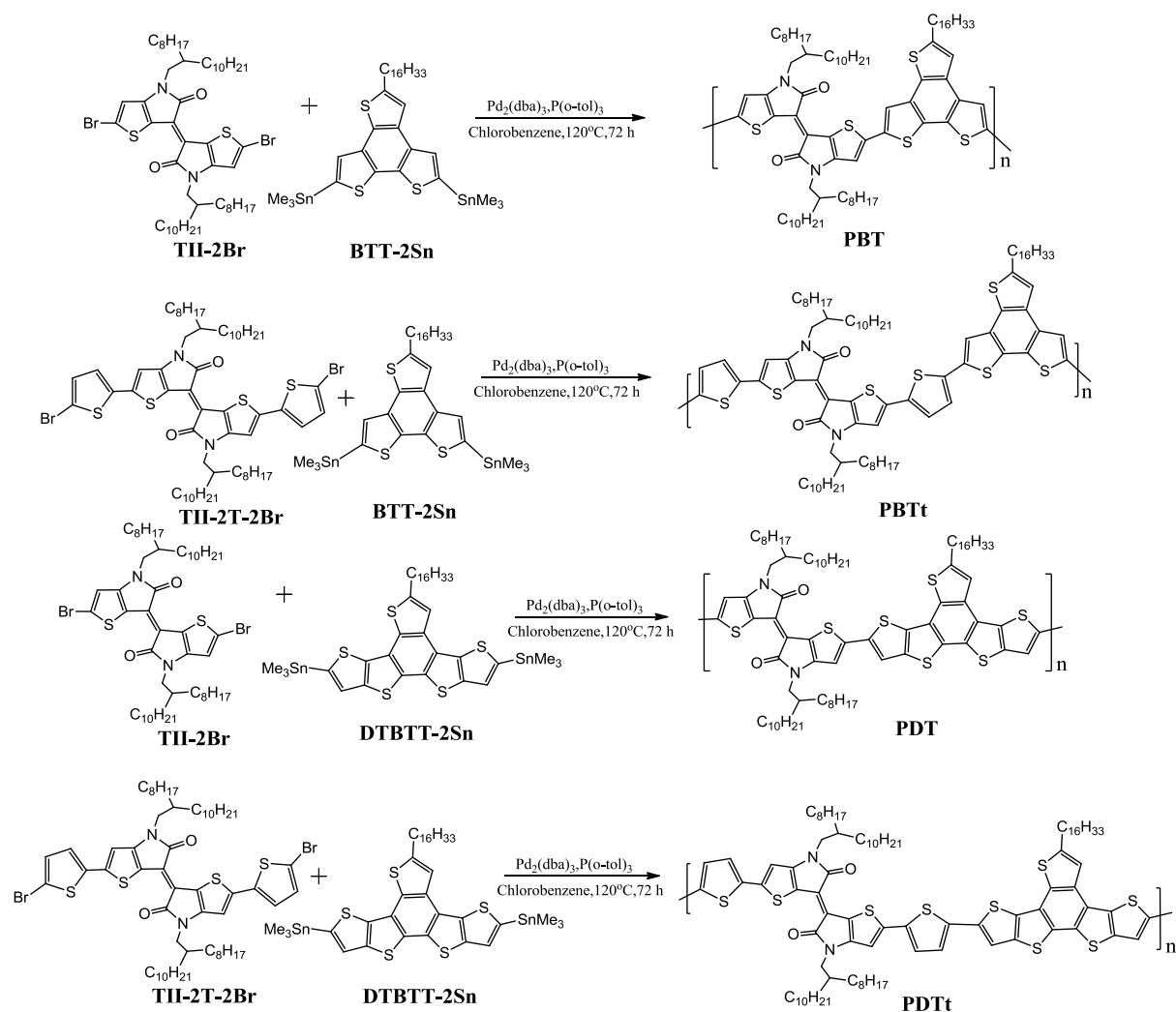
BTT-2Sn:

BTT (568 mg, 1.21 mmol) was dissolved in 35 mL of anhydrous THF and cooled to -78 °C. n-BuLi in hexane (2.5 M, 1.11 mL, 2.78 mmol) was added slowly to the reaction mixture. After 2 hours of stirring at this temperature, trimethyltin chloride in hexane solution (1 M, 3.00 mL, 3.00 mmol) was added in one portion and the reaction mixture was allowed to warm to room temperature and reacted for 18 h. The mixture was poured into water and extracted with diethyl ether (3×50 mL). The organic

phase was dried with NaSO₄. After removal of solvent, **BTT-2Sn** was obtained as orange oil (0.90 g, 90% yiled). ¹H NMR (CDCl₃, 400 MHz): δ/ppm: 7.74 (s, 1H), 7.59 (s, 1H), 7.46 (s, 1H), 3.00 (t, 2H), 1.81 (m, 2H), 1.25 (m, 26H), 0.88 (t, 3H), 0.47 (m, 18H).



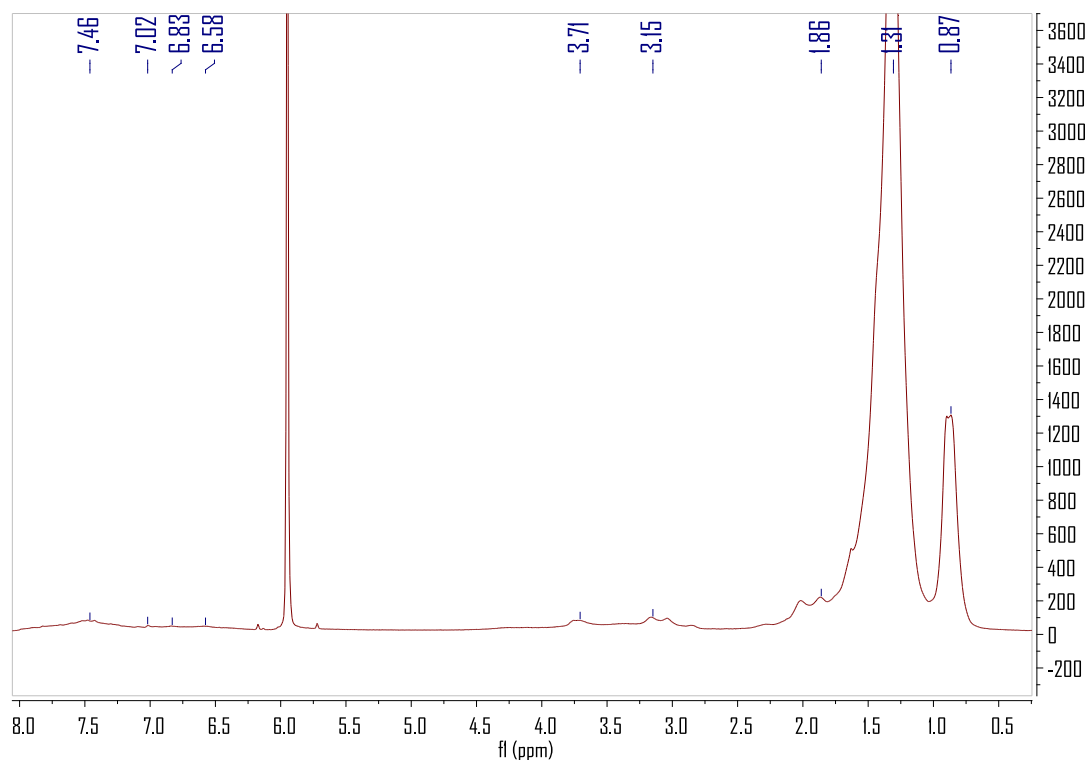
Polymer Synthesis



Polymer PBT:

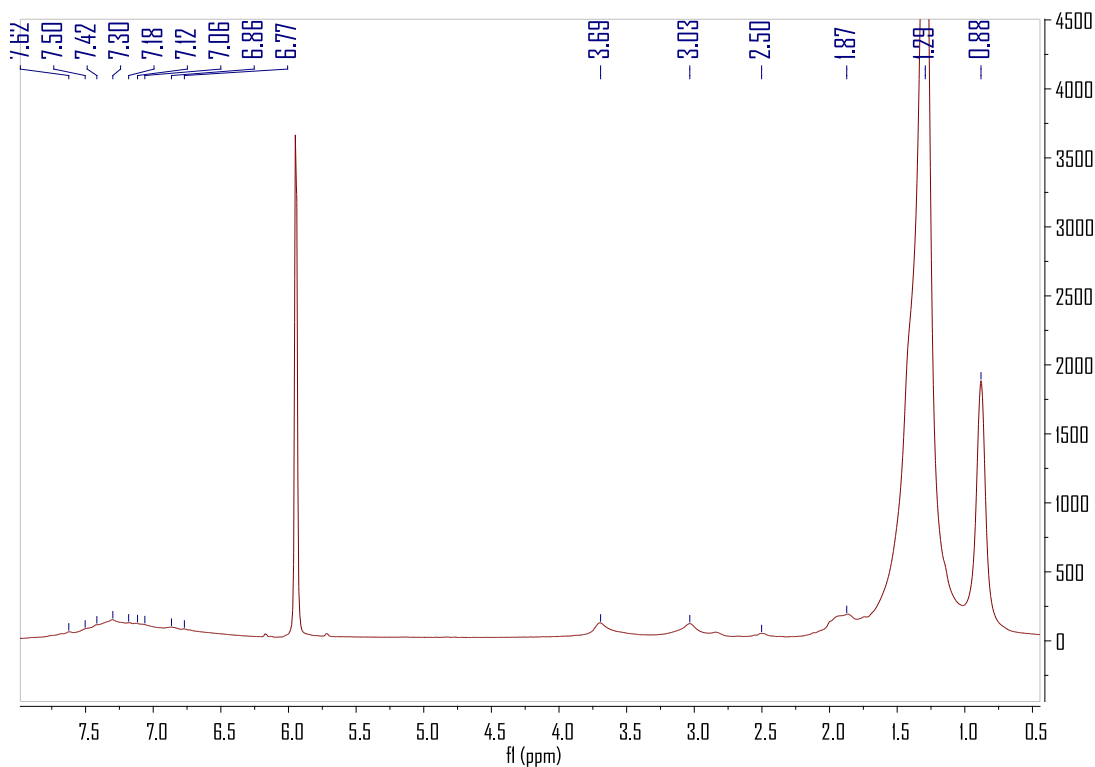
Compound **BTT-2Sn** (240 mg, 0.30 mmol), compound **TII-2Br** (300 mg, 0.30 mmol) and anhydrous chlorobenzene (15 mL) were added to a dried 50-mL Schlenk tube. The mixture was purged by argon for 15 min, then $\text{Pd}_2(\text{dba})_3$ (12 mg) and $\text{P}(\text{o-Tolyl})_3$ (36 mg) were added. The reaction medium was then stirred for 72 h at 120°C under argon. Then 0.2 mL of 2-bromothiophene was added to it after which reacted for further 12 h. After cooling to room temperature, the polymer was precipitated into methanol (300 mL) and filtered, then dried in vacuum drying oven. The polymer was washed in Soxhlet extractor with acetone and hexane overnight. The final product was

dried under reduced pressure at room temperature to obtain a black solid (324 mg, 83% yield). GPC (chloroform): Mn = 11 kDa, Mw = 22 kDa, PDI = 2.2. ^1H NMR (400 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 130 $^\circ\text{C}$).



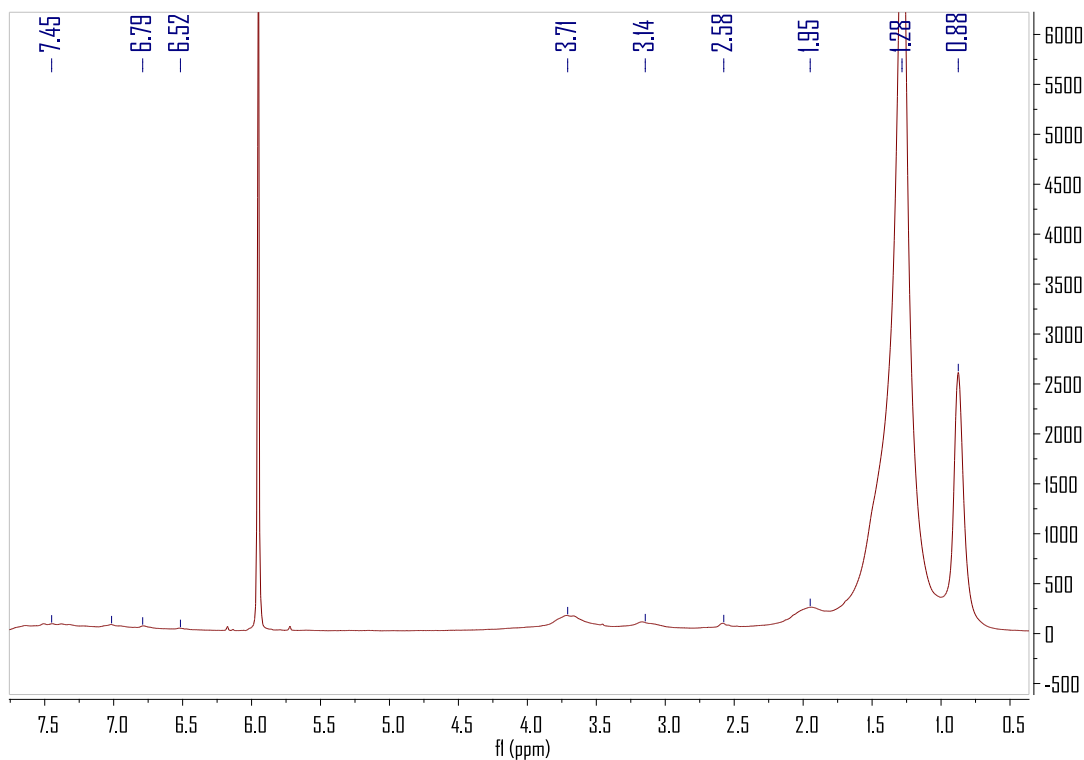
Polymer PBTt:

Compound **BTT-2Sn** (200 mg, 0.25 mmol), compound **TH-2T-2Br** (289 mg, 0.25 mmol) and chlorobenzene (12 mL) were added to a dried 50-mL Schlenk tube. The mixture was flushed by argon for 15 min and $\text{Pd}_2(\text{dba})_3$ (10 mg) and $\text{P}(\text{o-Tolyl})_3$ (30 mg) were then added. The reaction medium was stirred for 72 h at 120 $^\circ\text{C}$ under argon. Then 0.2 mL of 2-bromothiophene was added and the reaction continued for further 12 h. After cooling to room temperature, the polymer was precipitated into methanol (300 mL), filtered and dried in vacuum oven. The polymer was washed in Soxhlet extractor with acetone and hexane overnight and was dried under the reduced pressure at room temperature (304 mg, 83% yield). GPC (chloroform): Mn = 11.3 kDa, Mw = 23.8 kDa, PDI = 1.9. ^1H NMR (400 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 130 $^\circ\text{C}$).



Polymer PDT:

Compound **DTBTT-2Sn** (227 mg, 0.25 mmol), compound **TH-2Br** (250 mg, 0.25 mmol) and chlorobenzene (12 mL) were added to a dried 50-mL Schlenk tube. The mixture was purged by argon for 15 min, then Pd₂(dba)₃ (10 mg) and P(o-Tolyl)₃ (30 mg) were added. The reaction medium was then stirred for 72 h at 120 °C under argon. Then 0.2 mL of 2-bromothiophene was added to it after which reacted for further 12 h. After cooling to room temperature, the polymer was precipitated into methanol (300 mL) and filtered, then dried in vacuum drying oven. The polymer was washed in Soxhlet extractor with acetone and hexane overnight. The final product was dried under reduced pressure at room temperature to obtain a black solid (318 mg, 90% yield). GPC (chloroform): Mn = 73.4 kDa, Mw = 132 kDa, PDI = 1.8. ¹H NMR (400 MHz, C₂D₂Cl₄, 130 °C).



Polymer PDTt:

Compound **DTBTT-2Sn** (227 mg, 0.25 mmol), compound **III-2T-2Br** (289 mg, 0.25 mmol) and anhydrous chlorobenzene (12 mL) were added to a dried 50- mL Schlenk tube. The mixture was purged by argon for 15 min, then Pd₂(dba)₃ (10 mg) and P(o-Tolyl)₃ (30 mg) were added. The reaction medium was then stirred for 72 h at 120 °C under argon. Then 0.2 mL of 2-bromothiophene was added to it after which reacted for further 12 h. After cooling to room temperature, the polymer was precipitated into methanol (300 mL) and filtered, then dried in vacuum drying oven. The polymer was washed in Soxhlet extractor with acetone, hexane and chlorobenzene overnight, then chlorobenzene was removed and about 20 mL of o-dichlorobenzene was added, the solution was precipitated into methanol (300 mL) and filtered. The final product was dried under reduced pressure at room temperature to obtain a black solid (118 mg, 30% yield). GPC (chloroform): Mn = 35.8 kDa, Mw = 71.3 kDa, PDI = 2. ¹H NMR (400 MHz, C₂D₂Cl₄, 130 °C).

