

Supporting Information

Cost effective thiophene assisted novel dopant-free hole transport materials for efficient perovskite solar cell performance

M. SasiKumar[‡], Gurulakshmi Maddala[‡], Meenakshamma Ambapuram[‡], Mahesh Subburu^Φ, Jayathirtha Rao Vaidya[‡], S. Narendra Babu^ξ, Prabhakar Chetti[¶], Raghavender Mitty^{‡,*} and Someshwar Pola^{Φ,*}

[‡]CSIR-Indian Institute of Chemical Technology, Hyderabad 500 007, T.S., India

[‡]Department of Physics, Yogi Vemana University, Kadapa 516 005, A.P., India

^ΦDepartment of Chemistry, Osmania University, Hyderabad 500 007, T.S., India

^ξDepartment of Physics, Osmania University, Hyderabad 500 007, T.S., India

[¶]Department of Chemistry, NIT, Kurukshetra 136 119, India

* Corresponding authors: somesh.pola@gmail.com; toraghavender@rediffmail.com

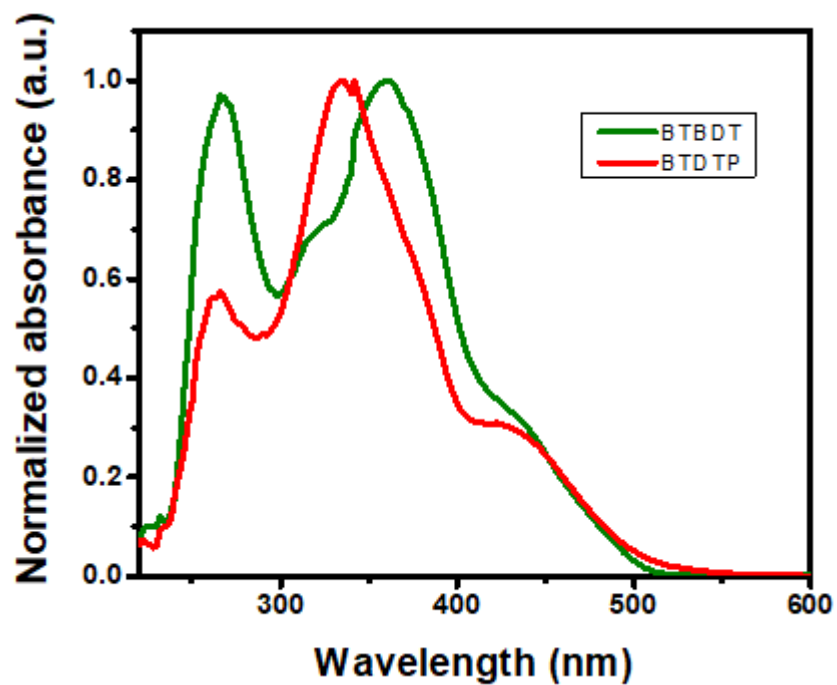


Figure S1. UV- spectra of the compounds in chloroform (1×10^{-5} M)

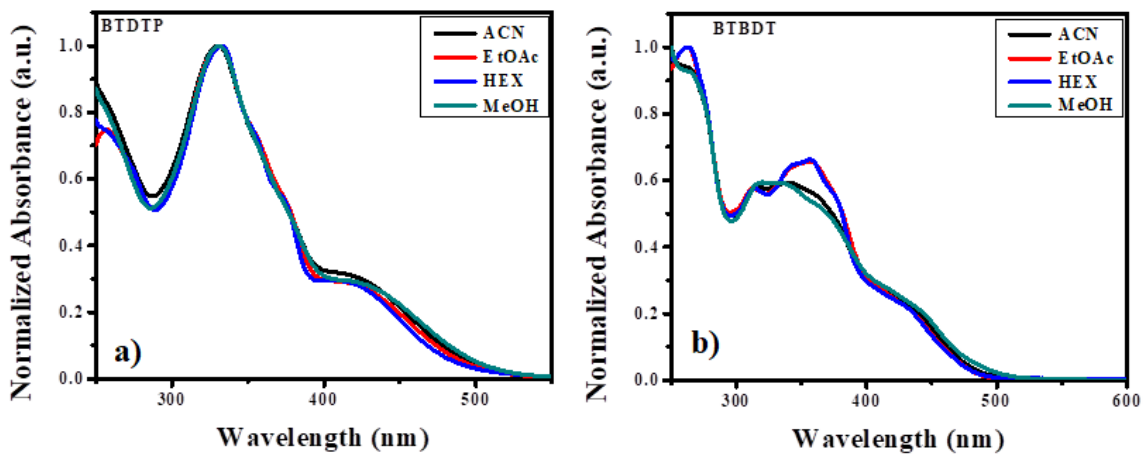


Figure S2. Normalized absorbance of compounds in diff. solvents

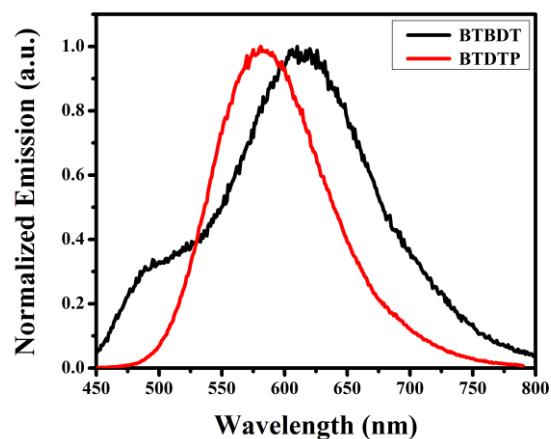


Figure S3. Normalized emission of compounds in chloroform solvent

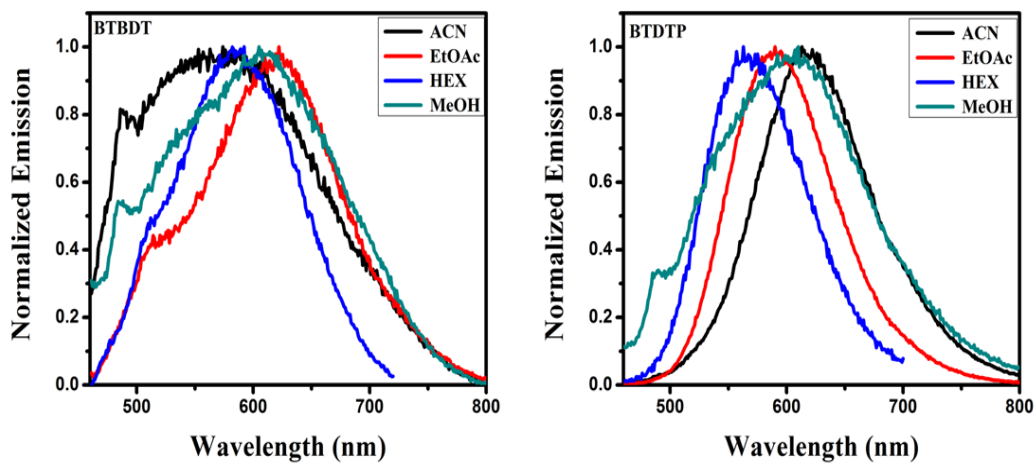


Figure S4. Normalized emission of compounds in diff. solvents

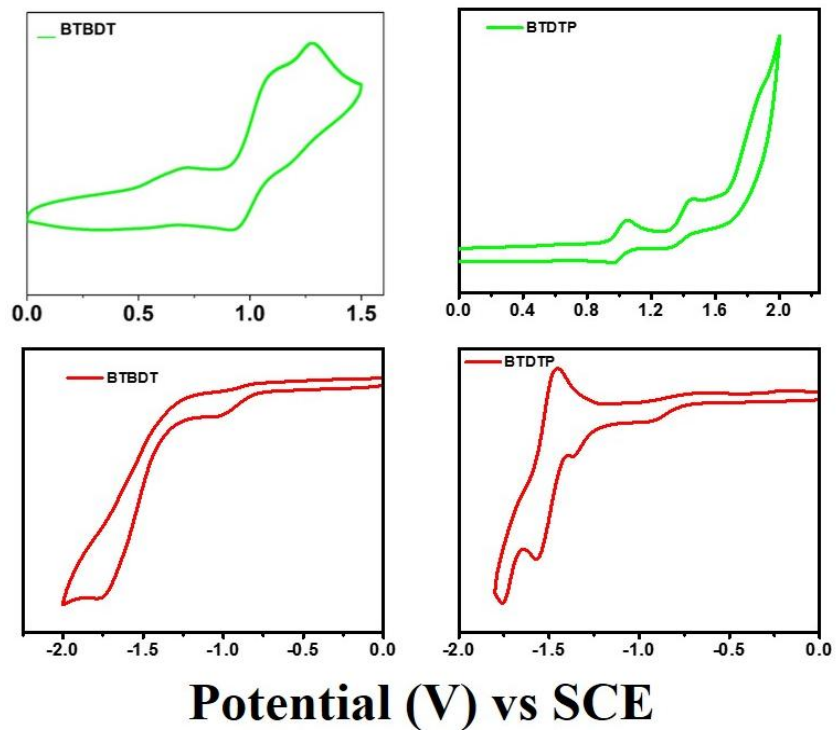


Figure S5. Cyclic-Voltammograms of compounds

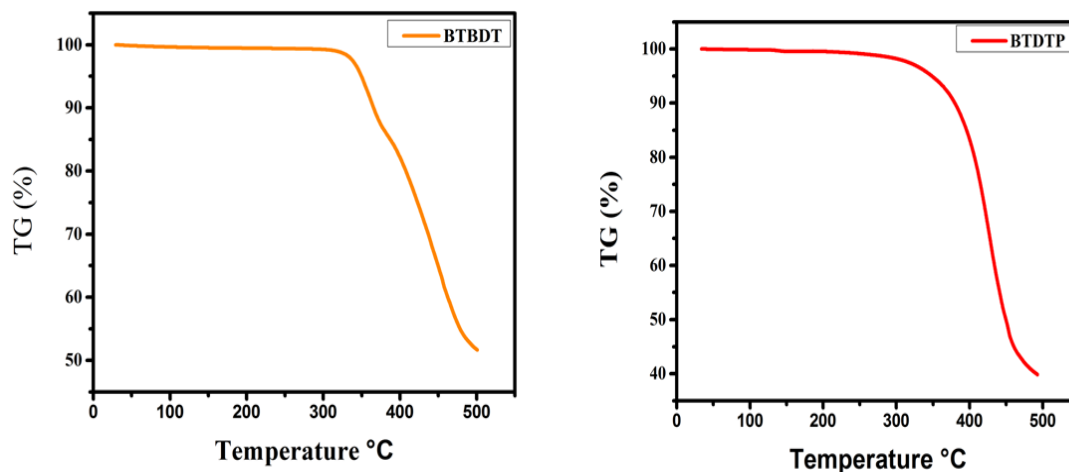


Figure S6. Thermograms of **BTBDT** and **BTDTP**

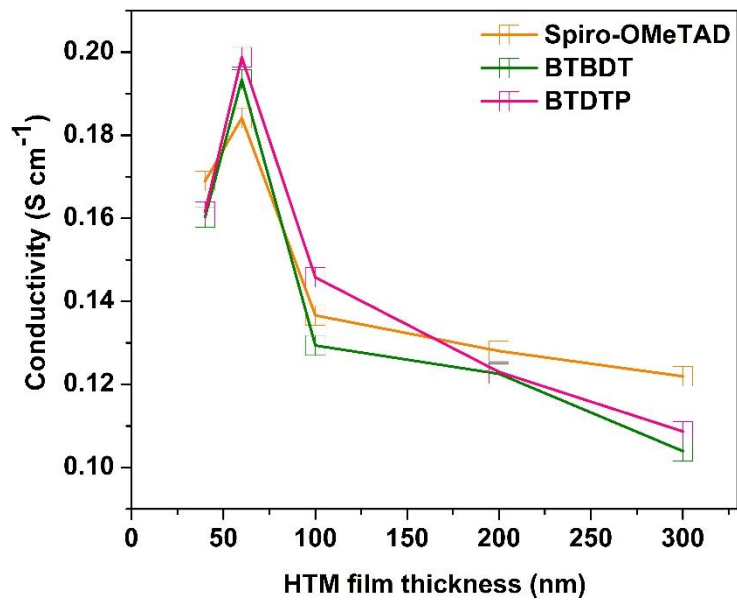


Figure S7. Conductivity variation of HTMs films thicknesses.

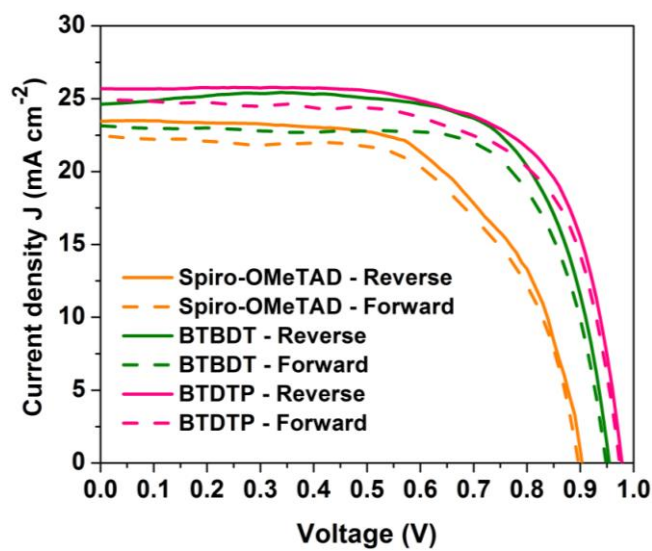


Figure S8. J-V forward and reverse scan (Hysteresis behaviour) performance of fabricated devices.

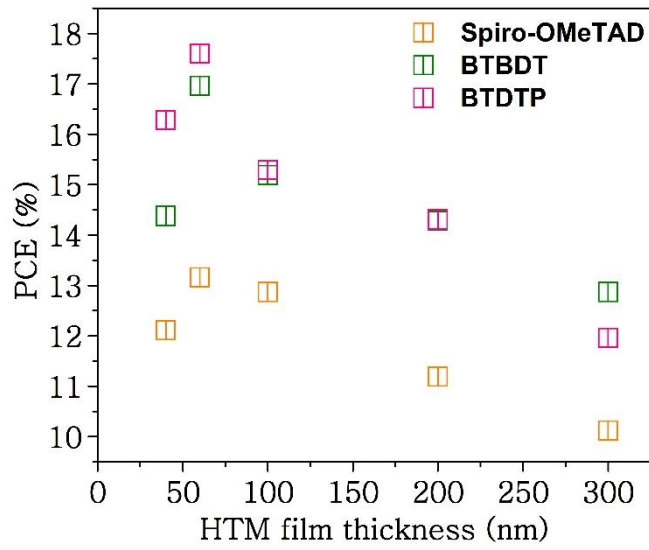


Figure S9. Comparison of power conversion efficiency performance with HTMs film thickness of fabricated devices.

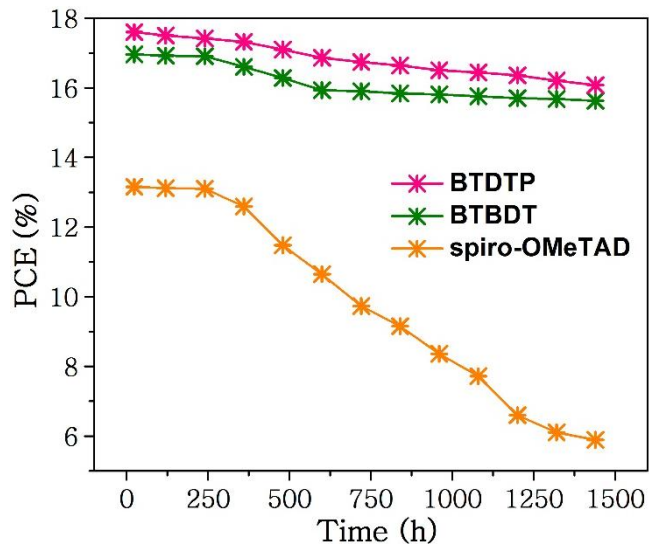


Figure S10. Long term stability of devices upto 1440 h.

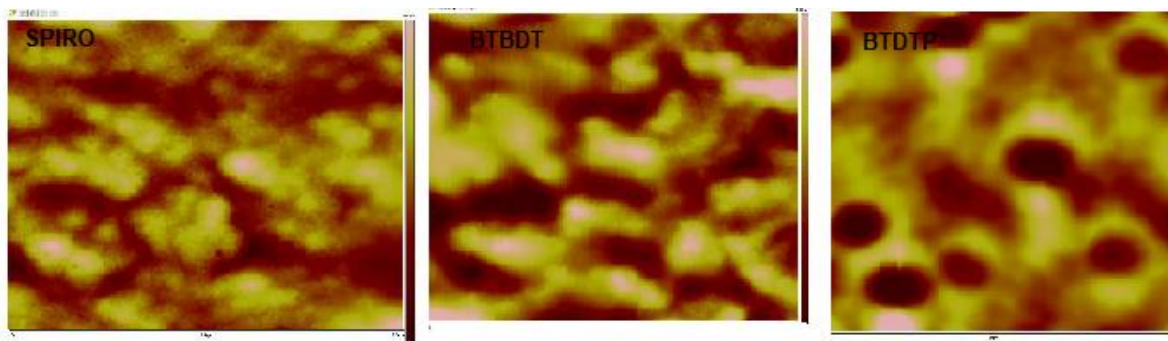


Figure S11. Atomic Force Microscopy images of TiO₂/perovskite/HTMs films over FTO plates.

Table S1. Absorption (λ_{abs} in nm), molar extinction coefficient (ϵ), and emission of **BTBDT**, and **BTDTP**

Comp.	λ_{abs} (nm)	Molar extinction coefficient (ϵ , M ⁻¹ cm ⁻¹)
BTBDT	438,360,267	13208, 44324, 42965
BTDTP	440,342,266	17611, 60614, 34515

Table S2. Absorption maximum (in nm) for the comps recorded in different solvents.

Compound	Normalized Absorption spectra in dif.Solvents (nm)			
	EtOAc	Hexane	ACN	MeOH
BTBDT	436	431	432	439
BTDTP	429	423	442	444

Table S3. Emission maximum (λ_{fluo} , nm) for the comps.in different solvents.

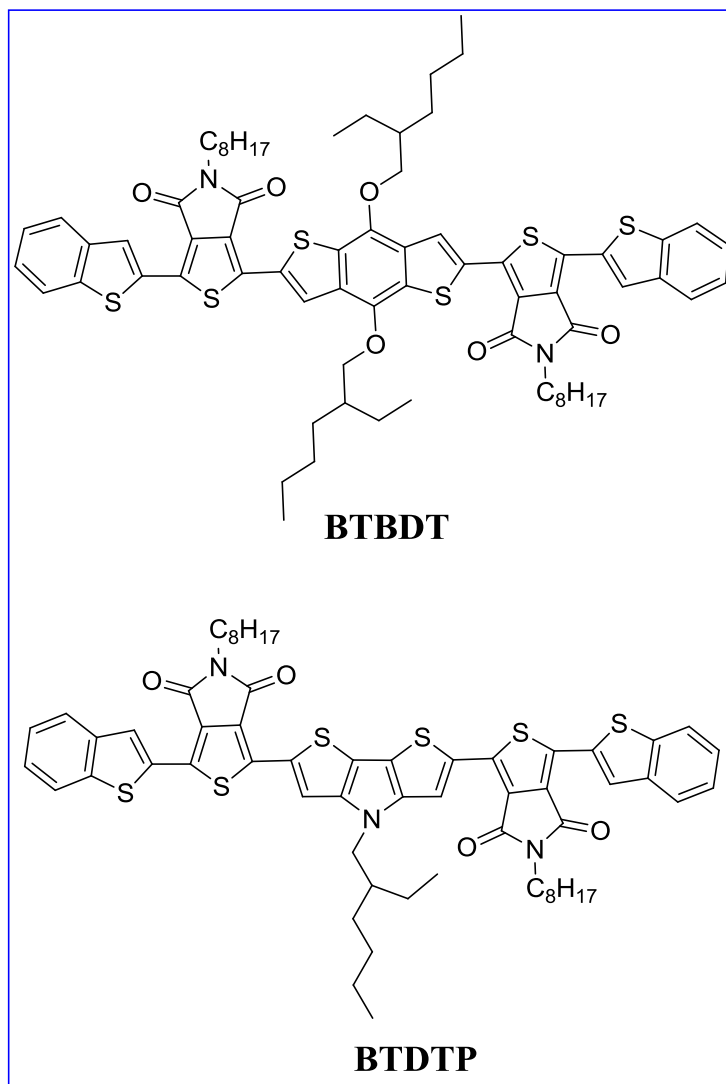
Compound	Emission spectra in dif.solvents (nm)				
	CHCl ₃	EtOAc	Hexane	ACN	MeOH
BTBDT	619	621	592	574	614
BTDTTP	585	590	563	613	609

Table S4. Oxidation potential (E_{ox}), reduction potential (E_{red}), HOMO, LUMO and electrochemical band gap (E_{g}) of the compounds.

ELECTROCHEMICAL PROPERTIES					
COMPOUND	$E_{1/2\text{ox}}(\text{V})$	$E_{1/2\text{red}}(\text{V})$	HOMO(eV)	LUMO (eV)	Bandgap(eV)
BTBDT	0.92	-1.375	5.32	3.020	2.30
BTDTTP	0.92	-1.374	5.32	3.026	2.29

Table S5. Thermal data of the compounds

compound	$T_d(^{\circ}\text{C})$
BTBDT	347
BTDTTP	343

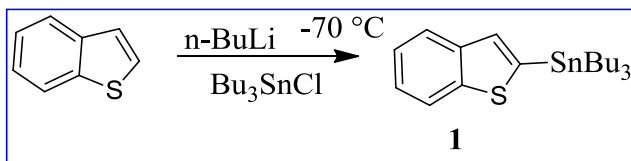


Scheme S1. Chemical structures of the target molecules

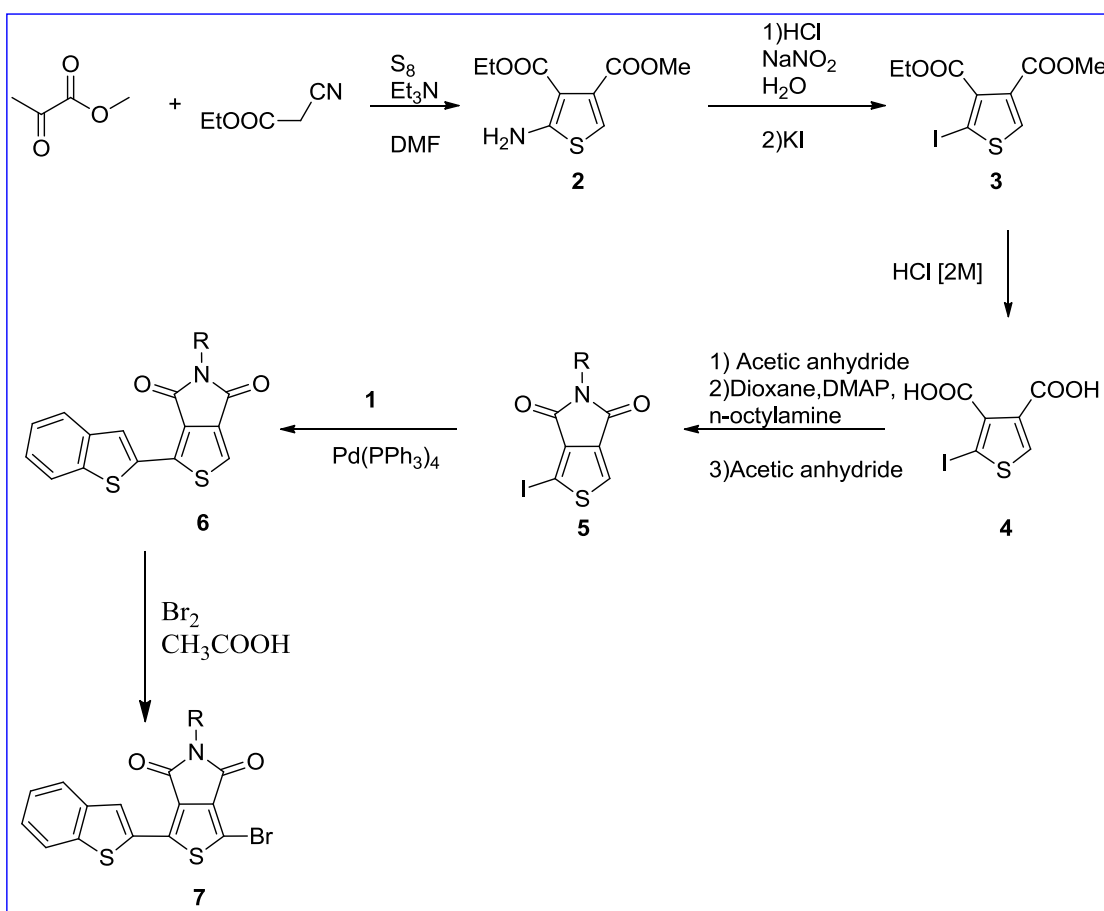
Synthesis of BTBDT and BTDTP:

Intermediate 1, the stannyl derivative of benzothiophene was synthesized using n-BuLi as base, followed by addition of Bu₃SnCl. Intermediate 7 was synthesized by sequence of steps, amine to Iodo, ester hydrolysis, lactum formation, stille coupling followed by bromination. 4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diylbis(trimethylstannane) was synthesized, starting from thiophene-3-carboxylic acid, acid to acid chloride, then to amide. Amide on treating with n-BuLi a dione is formed, which on reduction, O-alkylation followed by stannylation gives 12. 2,6-Bis(trimethylstannyl)-N-(2-ethylhexyl)-dithieno[3,2-b:2',3'-d]pyrrole was synthesized, using dibromobithiophene as starting material, which on Buchwald Hartwig

coupling using 2-ethylhexylamine to give N-alkyldithienopyrrole. Which was stannylated using n-BuLi and Me₃SnCl. The target molecules was prepared by using Stille coupling reaction.



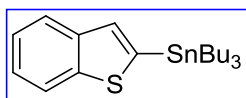
Scheme S2. Synthetic route for the preparation of compound **1**



Scheme S3. Synthetic route for the preparation of intermediate compounds **2-7**

Synthesis of benzo[b]thiophen-2-yltributylstannane (1):

Benzo[b]thiophene (5.0 g, 37.26 mmol) was taken in a dry two neck flask under a nitrogen atmosphere, dry THF 150 mL was added and cooled to $-78\text{ }^{\circ}\text{C}$. n-BuLi (16.39 mL, 40.98 mmol) was added dropwise, and the reaction was kept at $-78\text{ }^{\circ}\text{C}$ for 2h. Bu_3SnCl (12.12 mL, 44.71 mmol) was added in one portion, and the reaction was stirred at room temperature for 12 h. 100 mL water was added, and extraction was done by ether (3x 50 mL). The solvent was evaporated under reduced pressure, purified by column chromatography using hexane as eluent to obtain a colorless oil. (14.19 g, 33.53 mmol, 90% yield.)



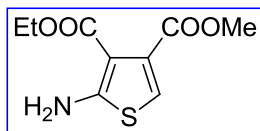
^1H NMR (CDCl_3 , 500 MHz) : δ 7.89-7.79 (m, 2H), 7.38 (s, 1H), 7.34–7.25 (m, 2H), 1.72-1.55 (m, 6H), 1.41-1.31 (m, 6H), 1.24-1.09 (m, 6H), 0.90 (t, $J = 7.33$ Hz, 9H).

^{13}C NMR (CDCl_3 , 125 MHz) : δ 144.30, 141.02, 139.66, 132.01, 123.62, 123.24, 122.66, 121.75, 28.97, 27.26, 13.65, 10.79.

Yield : 90 % (14.19 g)

Synthesis of 3-ethyl 4-methyl 2-aminothiophene-3,4-dicarboxylate (2):

In a one-neck 1L-flask methyl pyruvate (32.50g, 318.4mmol), ethyl cyanoacetate (32.75g, 289.5mmol), sulfur (11.20g, 43.66mmol) and 150 mL of N, N-dimethylformamide was taken. To this one-neck flask a solution of triethylamine (75 mL) and N, N-dimethylformamide (150 mL) was added dropwise during a period of two hours at room temperature. After the addition, the temperature was raised to $50\text{ }^{\circ}\text{C}$ overnight. The solution was cooled to room temperature, and 1L of water was added. The product crystallized after 48 hours, the flask was kept on ice for half an hour and then filtered to obtain long white needles (38.00g, 165 mmol, yield: 54%).



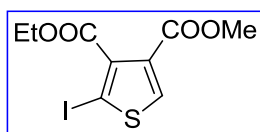
$^1\text{H NMR}$ (CDCl_3 , 500 MHz) : δ 6.60 (s, 1H), 6.02 (s, 2H), 4.25 (q, $J = 7.25\text{Hz}$, 2H), 3.82 (s, 3H), 1.29 (t, $J = 7.17\text{ Hz}$, 3H).

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) : δ 165.51, 164.54, 162.74, 132.43, 111.32, 104.95, 60.17, 52.14, 14.18.

Yield : 54 % (38.0 g)

Synthesis of 3-ethyl 4-methyl 2-iodothiophene-3,4-dicarboxylate (3):

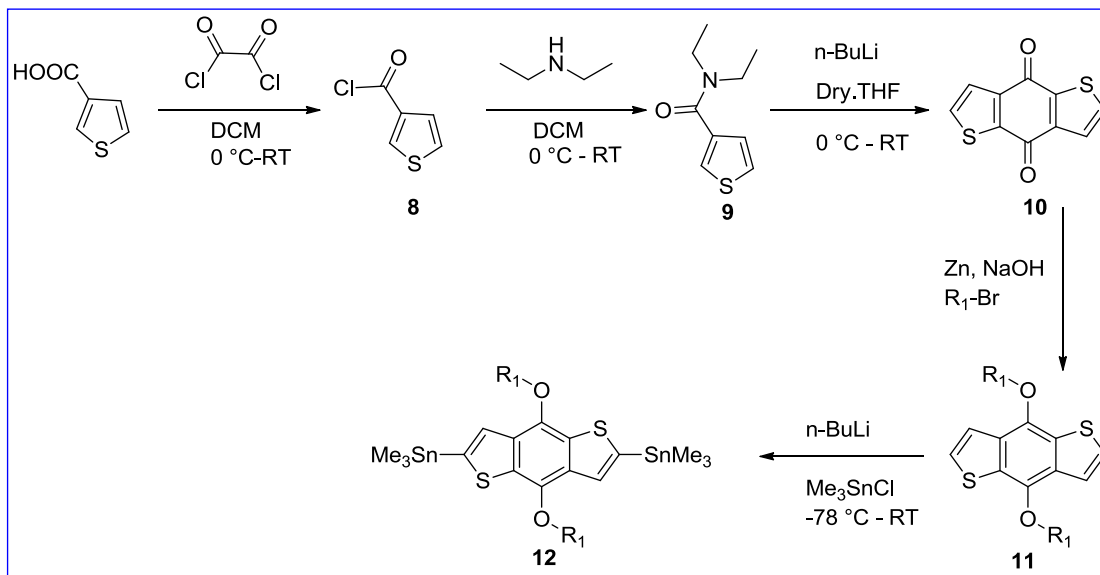
2M HCl (300 mL) was added to 3-ethyl 4-methyl 2-aminothiophene-3,4-dicarboxylate (2) (10.00 g, 43.62 mmol) taken in 1 L single neck R. B. flask at room temperature and stirred for 20 minutes. The solution was cooled to 0°C , and NaNO_2 (4.0 g, 65.44 mmol) was added to the solution. The mixture was allowed to react for 30 minutes. Then KI (18.08 g, 108.91mmol) was added in small portions. The solution was allowed to react for 50 minutes. The mixture was extracted with diethyl ether (10 x 40 mL), washed with sodium bisulfite (5 x 55 mL of saturated solution) and water (3 x 50 mL). The combined organic layer was dried over Na_2SO_4 and evaporated to dryness. The crude product was purified by column chromatography to get a yellow oil. (7.05 g, 20.0mmol, yield: 47%).



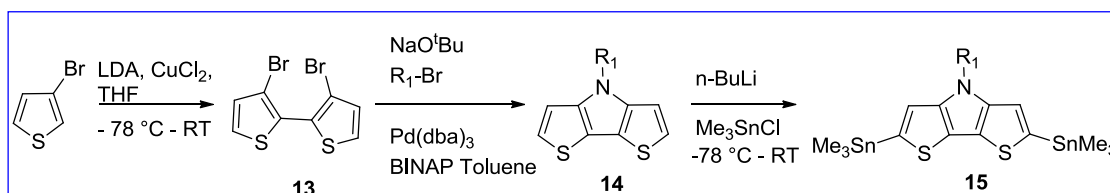
$^1\text{H NMR}$ (CDCl_3 , 500 MHz) : δ 8.09 (s, 1H), 4.42 (q, $J = 7.17\text{ Hz}$, 2H), 3.85 (s, 3H), 1.40 (t, $J = 7.17\text{ Hz}$, 3H).

$(\text{M}+\text{H})^+$: 340.933

Yield : 47 % (7.05 g)



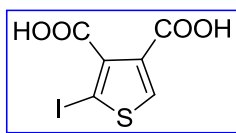
Scheme S4. Synthetic route for the preparation of **8-12**



Scheme S5. Synthetic route for the preparation of **13-15**

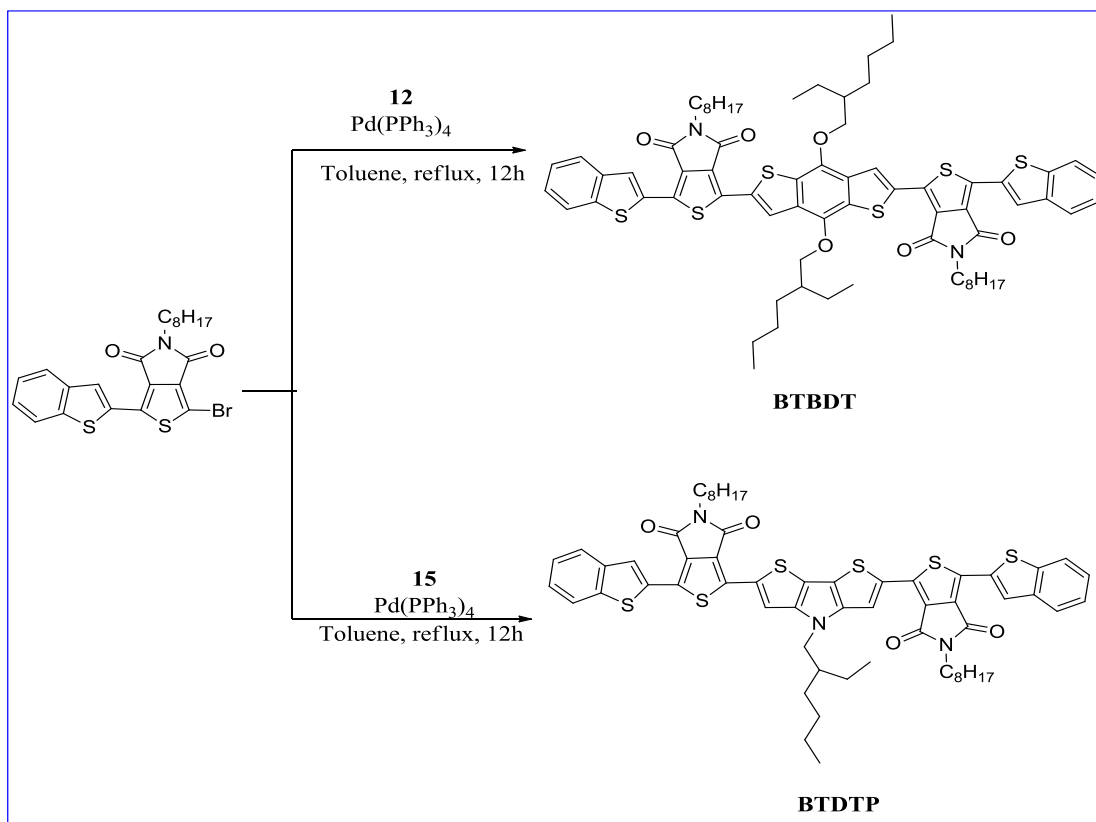
Synthesis of 2-iodothiophene-3,4-dicarboxylic acid (**4**):

3-ethyl 4-methyl 2-iodothiophene-3,4-dicarboxylate(**3**) (7 g, 20.00mmol) was taken in a one-neck flask, and 350 mL of HCl [2M] was added and stirred at reflux in for 24 hours. The solution was extracted with diethyl ether (5 x 150 mL).The combined organic layers were dried over Na₂SO₄ and evaporated to dryness to obtain a white solid (6.0 g, 20.00mmol, yield: 98%).



¹H NMR (Acetone D₆, 500MHz) : δδ 8.41 (s, 1H).

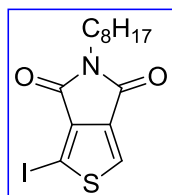
Yield : 98 % (6.0 g)



Scheme S6. Synthetic route for the target compounds (**BTBDT** and **BTDTP**)

Synthesis of 1-iodo-5-octyl-4*H*-thieno[3,4-*c*]pyrrole-4,6(5*H*)-dione(5):

A solution of 2-iodothiophene-3,4-dicarboxylic acid (4) (5.0g, 16.77mmol) in acetic anhydride (237 mL) was stirred at 75°C for 2 hours. The solvent was removed by distillation and to the crude product was added dioxane (215 mL), DMAP (5.32, 43.61mmol) and n-octylamine (5.61g, 43.61 mmol). The solution was stirred at 55 °C for 20 hours. Acetic anhydride (135 mL) was added, and the reaction mixture was stirred for 4 hours at 80°C. Then the reaction was quenched with water (500 mL) and was extracted with dichloromethane (4 X 60 mL). The combined organic layers were dried over Na₂SO₄ and evaporated to dryness to obtain a dark powder. The crude product was purified by column chromatography. White solid (3.93g, 10.04 mmol, yield: 60%).



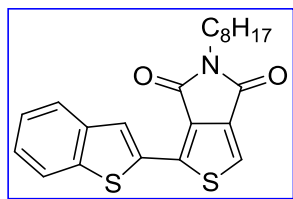
^1H NMR (CDCl_3 , 500 MHz) : δ 7.84 (s, 1H), 3.60 (t, $J = 7.34$ Hz, 2H), 1.67-1.61 (m, 2H), 1.33-1.24 (m, 10H), 0.87 (t, $J = 6.90$ Hz, 3H).

^{13}C NMR (CDCl_3 , 100 MHz) : δ 162.37, 160.76, 139.46, 137.64, 131.03, 74.28, 38.64, 31.73, 29.09, 28.33, 26.81, 22.58, 14.04.

Yield : 60 % (3.93 g)

1-(benzo[b]thiophen-2-yl)-5-octyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (6):

In a two-necked round bottom flask, 1-iodo-5-octyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (5.0g, 12.77mmol), benzo[b]thiophen-2-yltributylstannane (7.03g, 16.66 mmol) and $\text{Pd}(\text{PPh}_3)_4$ (0.27g 2 mol%) was taken under nitrogen. Dry toluene (150 mL) was added and degassed for 15 minutes. The reaction mixture was refluxed for 18 hours. Cooled to room temperature, extracted with CHCl_3 (3 X 30 mL), dried over Na_2SO_4 . The crude was recrystallized with 85% Hexane and 15% ethyl acetate to obtain pure product. (4.38g, 11.01 mmol, 85% yield).



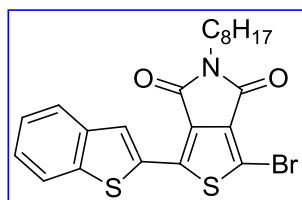
^1H NMR (CDCl_3 , 500 MHz) : δ 8.37 (s, 1H), 7.87-7.80 (m, 2H), 7.69 (s, 1H), 7.41-7.38 (m, 2H), 3.66 (t, $J = 7.44$ Hz, 2H), 1.71-1.66 (m, 2H), 1.32-1.25 (m, 10H), 0.87 (t, $J = 6.94$ Hz, 3H).

^{13}C NMR (CDCl_3 , 125 MHz) : δ 162.81, 162.30, 139.84, 132.10, 126.53, 126.07, 125.11, 124.87, 124.74, 123.67, 123.21, 122.18, 122.13, 121.35, 38.61, 31.75, 29.14, 28.48, 26.92, 22.60, 14.05.

Yield : 85 % (4.38 g)

1-(benzo[b]thiophen-2-yl)-3-bromo-5-octyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (7):

1-(benzo[b]thiophen-2-yl)-5-octyl-4H-thieno[3,4-c]pyrrole-4,6(5H)-dione (2g, 5.00 mmol) was taken in a single neck round bottom flask, to this 40 mL glacial acetic acid was added. The round bottom was kept in an ice bath and protected from light. Br₂ (0.88g, 5.53 mmol) in 5 mL acetic acid was added dropwise over 3 minutes. After the addition was completed, ice bath was removed and stirred at room temperature for 6 h. After reaction was completed, monitored by TLC, 40 mL of ice cold water was added and extracted with CHCl₃ (3 X 15 mL). The product was recrystallized (50% hexane and ethylacetate) to give pure product (2.29g, 4.80 mmol, 96% yield) as light yellow color solid.



¹H NMR (CDCl₃, 500 MHz) : δ7.91-7.87 (m, 2H), 7.83 (d, *J* = 7.17 Hz, 1H), 7.52-7.45 (m, 2H), 3.65 (t, *J* = 7.32 Hz, 2H), 1.70-1.64 (m, 2H), 1.35-1.25 (m, 10H), 0.87 (t, *J* = 6.94 Hz, 3H).

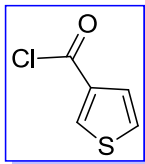
¹³C NMR (CDCl₃, 100 MHz) : δ162.80, 162.29, 140.40, 139.95, 139.83, 137.64, 132.10, 129.20, 126.53, 126.07, 125.11, 124.73, 123.21, 122.17, 38.61, 31.75, 29.14, 28.47, 26.91, 22.60, 14.05.

Yield : 96 % (2.29 g)

Synthesis of Thiophene-3-carbonyl Chloride (8):

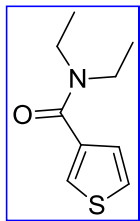
Thiophene-3-carboxylic acid (20 g, 156.07 mmol) was taken in a single neck round bottom flask and suspended in 100 mL of methylene chloride and cooled down to 0 °C. Then 39.61 g (312.58 mmol) of oxalyl chloride was added to the solution. The reaction was kept stirring overnight, the mixture becomes clear. The excess oxalyl chloride was removed under

reduced pressure; a colorless solid was obtained. And the product was subjected to the next step without further purification.



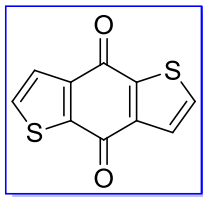
Synthesis of N, N-diethylthiophene Carboxamide (9):

Thiophene-3-carbonyl chloride (20.0g, 136.43mmol) was dissolved in 200 mL methylene chloride under ice cooling. Then diethylamine (19.95g, 272.86mmol) was added dropwise. After the addition, the ice bath was removed and kept stirring for another 6 h. Finally, the reaction was quenched with 200 mL of water and extracted with 100 mL of methylene chloride. The collected organic phase was washed several times with brine and dried with Na_2SO_4 . After removing the solvent, the crude product was purified by column chromatography to yield the colorless liquid. (20.0 g, 80% in yield).



Synthesis of benzo[1,2-b:4,5-b']dithiophene-4,8-dione (10):

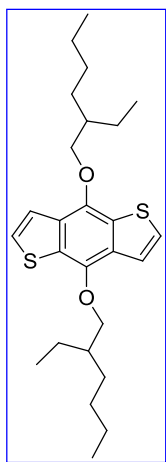
First, (10.00 g 54.57mmol) of N, N-diethylthiopheneCarboxamide was put into a dry 250 mL flask. After filling with inert gas, 45 mL of dry THF was added and then lowered the temperature to $-78\text{ }^\circ\text{C}$. 54.56 mL of n-BuLi (2.5M, 136.40 mmol) was then added dropwise. The mixture was allowed warm to room temperature and kept stirring for another 3 h. The reaction was then quenched with saturated ammonium chloride solution, and the yellow precipitate was obtained, dried under vacuum. (4.20 g, 19.06 mmol 35%).



^1H NMR (CDCl_3 , 500 MHz) : δ 7.69 (d, J = 5.03 Hz, 2H), 7.65 (d, J = 5.03 Hz, 2H).
 ^{13}C NMR ($\text{CDCl}_3+\text{DMSO}-d_6$ 125 MHz) : δ 173.62, 143.94, 141.97, 133.38, 125.70.
Yield : 35 % (4.20 g)

Synthesis of 4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene (11):

Benzo[1,2-b:4,5-b']dithiophene-4,8-dione (4.0 g, 18.16 mmol) was taken in an 250 mL flask, to this flask zinc powder (3.04 g, 46.49 mmol) and water (50 mL) were added under the protection of argon. Then NaOH (1.50 g, 37.5 mmol) was added into the mixture, and the mixture was well stirred and heated to reflux for 1 h. During the reaction, the color of the mixture changed from yellow to red and then to orange. Then 2-ethylhexyl bromide (10.80 g, 55.93 mmol) and a catalytic amount of tetrabutylammonium bromide (0.28 g, 1.08 mmol) were added into the flask. The reaction was refluxed for 2 h; the reaction mixture was poured into cold water and extracted with diethyl ether (3 X 30mL) and dried over anhydrous Na_2SO_4 . The pure compound (5.60g, 12.53 mmol, yield 70%.) was obtained as a colorless oil after subjected to silica column chromatography using hexane as eluent.



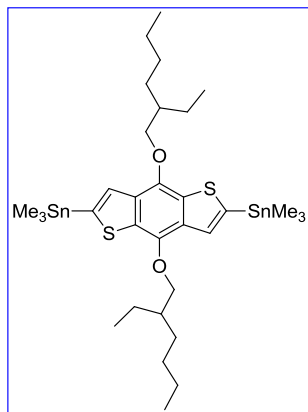
^1H NMR (CDCl_3 , 500 MHz) : δ 7.47 (d, $J = 5.49$ Hz, 2H), 7.36 (d, $J = 5.49$ Hz, 2H), 4.18 (d, $J = 5.18$ Hz, 4H), 1.85-1.77 (m, 2H), 1.74-1.65 (m, 2H), 1.61-1.53 (m, 4H), 1.52-1.35 (m, 10H), 1.01 (t, $J = 7.47$ Hz, 6H), 0.93 (t, $J = 7.01$ Hz, 6H).

^{13}C NMR (CDCl_3 , 125 MHz) : δ 144.62, 131.44, 129.89, 125.89, 120.21, 75.99, 40.63, 30.43, 29.18, 23.83, 23.09, 14.13, 11.29.

Yield : 70 % (5.60 g)

Synthesis of (4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethylstannane) (12):

4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b']dithiophene (2.00 g, 4.47 mmol) was taken in a dry two-neck flask, dry THF (40 mL) was added into a flask under an inert atmosphere. The solution was cooled down to -78 °C and n-butyllithium (5.37 mL, 2.5 M in n-hexane, 13.43 mmol) was added dropwise. After being warmed to room temperature and stirred for 3 h, the reaction mixture was cooled to -78 °C again. Then, trimethyltinchloride (2.67 g, 13.43 mmol) was added in one portion, and the reaction mixture was allowed to naturally warm to room temperature and stirred overnight. After quenched with water (100 mL), the mixture was extracted with ether (3 X 25 mL) for three times. The combined organic layer was washed with water, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was recrystallized from isopropanol to give pure compound (2.1 g, 2.79 mmol) as a white needle in a yield of 60.0 %.



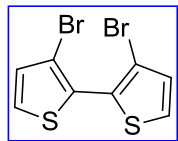
$^1\text{H NMR}$ (CDCl_3 , 500 MHz) : δ 7.51 (s, 2H), 4.19 (d, $J = 5.38$ Hz, 4H), 1.84-1.74 (m, 2H), 1.74-1.64 (m, 4H), 1.44-1.24 (m, 12H), 1.02 (t, $J = 7.45$ Hz, 6H), 0.94 (t, $J = 7.20$ Hz, 6H), 0.44 (s, 18H).

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) : δ 143.22, 140.36, 133.83, 132.86, 127.95, 75.62, 40.65, 30.52, 29.23, 23.89, 23.16, 14.17, 11.33, 8.36.

Yield : 60 % (2.1 g)

Synthesis of 3,3'-Dibromo-2,2'-bithiophene(13):

3-bromothiophene (10.0 g, 61.35 mmol) and anhydrous THF (100 ml) were taken in a 500 mL flask. The solution was cooled to -78°C and LDA (38.4 ml, 1.6 M solution) were added dropwise over 15 minutes, and the solution was stirred at the same temperature for 1 h. CuCl_2 (16.4 g, 122.70 mmol) was added in portion to the mixture then allowed to stir at -78°C for 1 h followed by at room temperature for 5 h. The reaction was quenched with 200 ml of water. The compound was extracted with dichloromethane (3 X 100 mL), washed with distilled water, dried over anhydrous Na_2SO_4 and evaporated using rotavapour to obtain a brown solid. The crude compound was passed through a short bed of silica gel column using hexane and chloroform mixture (95: 5) as eluent to yield a white solid (7.2 g, 22.21 mmol, 73 %).

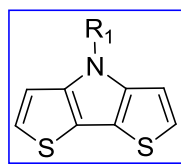


$^1\text{H NMR}$ (CDCl_3 , 500 MHz) : δ 7.69 (d, J = 5.03 Hz, 2H), 7.65 (d, J = 5.03 Hz, 2H).

Yield : 73 % (7.2 g)

Synthesis of 4-(2-ethylhexyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole (14):

In a dry two neck flask 3,3'-dibromo-2,2'-bithiophene (0.6 g, 1.85 mmol), *t*-NaOBu (0.391 g, 3.7 mmol), $\text{Pd}_2(\text{dba})_3$ (67 mg, 0.074 mmol) and BINAP (92 mg, 0.148 mmol) were taken under inert atmosphere. To this anhydrous toluene (20 ml) was added. The reaction mixture was purged in N_2 for 10 min, and a solution of alkyl amine (3.7 mmol) in toluene was added via syringe. The mixture was allowed to reflux 8h and then cooled and added to water. The organic layer was separated, and the aqueous phase was extracted with ethyl acetate. The combined organic phase was dried over anhydrous Na_2SO_4 and evaporated using rotavapour. The crude product was purified by column chromatography to obtain a colorless oil ().



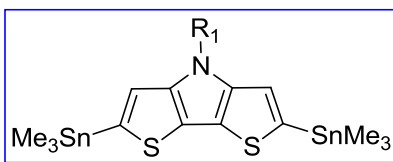
$^1\text{H NMR}$ (CDCl_3 , 400 MHz) : δ 7.12 (d, J = 5.25 Hz 2H), 6.98 (d, J = 5.25 Hz, 2H), 4.06 (t, J = 6.96 Hz, 2H), 1.98-1.90 (m, 1H), 1.36-1.26 (m, 8H), 0.91-0.85 (m, 6H).

$^{13}\text{C NMR}$ (CDCl_3 , 100 MHz) : δ 145.25, 122.64, 114.50, 111.04, 51.30, 40.43, 30.62, 28.65, 24.00, 22.94, 14.00, 10.65.

Yield : 90% (0.48 g).

2,6-Bis(trimethylstannyl)-N-(2-ethylhexyl)-dithieno[3,2-*b*:2',3'-*d*]pyrrole (15):

In a dry two neck flask, N-2-ethylhexyl-dithieno[3,2-*b*:2',3'-*d*]pyrrole (2.0 g, 6.86 mmol) was taken, and dry THF (40 mL) was added and cooled to -78 °C. 8.23 mL *n*-butyl lithium (2.5 M, 20.58 mmol) was added drop wise. The reaction mixture was stirred for 2 h at -78 °C and 1 h at 0 °C. After cooling down to -78 °C, trimethyltin chloride (4.10 g, 20.57 mmol) dissolved in 20 mL tetrahydrofuran was added, and the reaction mixture was allowed to stir for overnight at room temperature. The reaction mixture was poured into distilled water and extracted with *n*-hexane. After drying over sodium sulfate and removal of the solvents, (4.10 g, 6.60 mmol), crude product was obtained in as a slightly yellowoil, which was used without any further purification.



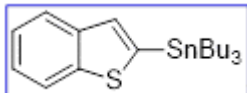
¹H NMR (CDCl₃, 500 MHz) : δ6.96 (s, 2H), 4.05 (t, *J* = 7.15 Hz, 2H), 2.01-1.95 (m, 1H), 1.34-1.27 (m, 8H), 0.94-.084 (m, 6H), 0.40 (s, 18H).

¹³C NMR (CDCl₃, 125 MHz) : δ148.24, 135.50, 120.08, 118.00, 51.25, 40.34, 30.48, 28.44, 23.98, 23.01, 14.05, 10.70, -8.14.

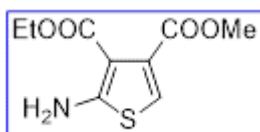
The details of synthesis of 3,3'-(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-diyl)bis(1-(benzo[*b*]thiophen-2-yl)-5-octyl-4H-thieno[3,4-*c*]pyrrole-4,6(5H)-dione) (BTBDT) is given in the main article.

Details of step-by-step cost calculation of both HTMs, BTBDT and BTDTP:

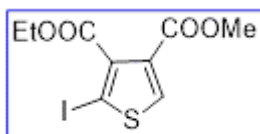
Material quantity and cost calculation:



SM for compound 1	CAS	SM[g]/Gp	SM[₹]/Gs	SM[₹]/Gp	SM[\$]/Gp
Benzothiophene	95-15-8	1.52	432.96	658.09	8.69
n-BuLi	109-72-8	0.79	491.02	387.90	5.12
Tributyltin chloride	1461-22-9	4.42	45.72	202.08	2.66
Tetrahydrofuran anhyd.	109-99-9	40.53	7.10	287.76	3.8
Total				1535.83	20.27

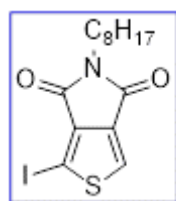
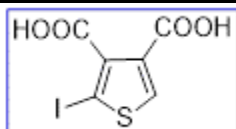


SM for compound 2	CAS	SM[g]/Gp	SM[₹]/Gs	SM[₹]/Gp	SM[\$]/Gp
Methyl pyruvate	600-22-6	5.95	57.05	339.44	4.48
Ethyl cyanoacetate	105-56-6	6.0	5.39	32.34	0.42
Octasulphur	10544-50-0	2.04	1.0	2.04	0.02
Triethylamine	121-44-8	10.07	5.43	54.68	0.72
N,N-Dimethylformamide	68-12-2	50.97	6.50	331.35	4.37
Total				759.81	10.01

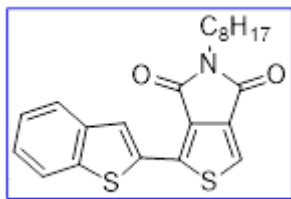


SM for compound 3	CAS	SM[g]/Gp	SM[₹]/Gs	SM[₹]/Gp	SM[\$]/Gp
Compound 2	-	6.55	116.00	759.8	10.01
Sodium nitrite	7632-00-0	2.95	7.94	23.42	0.30
Potassium iodide	7681-11-0	11.85	40.64	481.58	6.36
Hydrochloric acid	7647-01-0	14.33	32.64	467.73	6.17
Total				1732.53	22.84

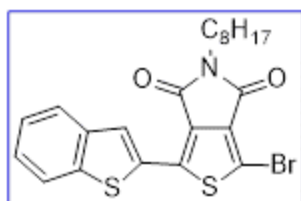
SM for compound 4	CAS	SM[g]/Gp	SM[₹]/Gs	SM[₹]/Gp	SM[\$]/Gp
Compound 3	-	4.56	379.94	1732.52	22.88
Hydrochloric acid	7647-01-0	16.63	32.64	542.80	7.17
Total				2275.32	30.05



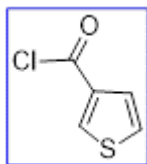
SM for compound 5	CAS	SM[g]/Gp	SM[₹]/Gs	SM[₹]/Gp	SM[\$]/Gp
Compound 4		3.91	581.92	2275.32	30.05
4-(Dimethylamino)pyridine	1122-58-3	4.16	192.20	799.55	10.56
Octylamine	111-86-4	4.40	20.14	88.61	1.17
Acetic anhydride	108-24-7	314.59	3.70	1163.98	15.37
1,4-Dioxane	123-91-1	174.37	6.06	1056.68	13.95
Total				5384.14	71.1



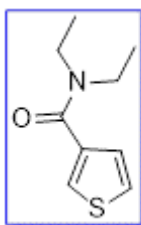
SM for compound 6	CAS	SM[g]/Gp	SM[₹]/Gs	SM[₹]/Gp	SM[\$]/Gp
Compound 5	-	3.07	1753.79	5384.14	71.12
Compound 1	-	4.31	356.34	1535.83	20.28
Pd(PPh ₃) ₄	14221-01-3	0.18	2360.8	424.94	5.61
Toluene anhyd.	108-88-3	79.85	6.079	485.40	6.41
Total				7830.31	103.42



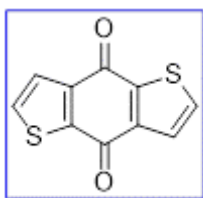
SM for compound 7	CAS	SM[g]/Gp	SM[₹]/Gs	SM[₹]/Gp	SM[\$]/Gp
Compound 6	-	2.65	2785.02	7380.31	97.49
Bromine	7726-95-6	1.17	16.73	19.57	0.25
Acetic acid	64-19-7	60.8	3.74	227.39	3.00
Total				7627.27	100.74



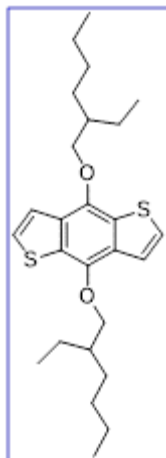
SM for compound 8	CAS	SM[g]/Gp	SM[₹]/Gs	SM[₹]/Gp	SM[\$]/Gp
3-Thiophenecarboxylic acid	88-13-1	1.26	987.9	1244.75	16.44
Oxalyl chloride	79-37-8	2.49	43.52	108.36	1.43
Dichloromethane	75-09-2	7.98	2.15	17.15	0.22
Total				1370.26	18.09



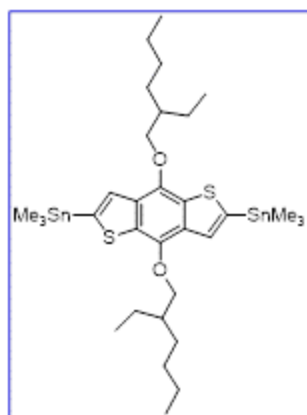
SM for compound 9	CAS	SM[g]/Gp	SM[₹]/Gs	SM[₹]/Gp	SM[\$]/Gp
Compound 8	-	1.26	1087.50	1370.26	18.10
Diethylamine	109-89-7	1.25	4.65	5.81	0.076
Dichloromethane	75-09-2	16.75	2.15	36.01	0.47
Total				1412.08	18.64



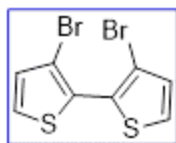
SM for compound 10	CAS	SM[g]/Gp	SM[₹]/Gs	SM[₹]/Gp	SM[\$]/Gp
Compound 9	-	1.26	1120.69	1412.08	18.65
n-Butyllithium	109-72-8	1.09	491.02	535.22	7.07
Tetrahydrofuran anhyd.	109-99-9	2.66	7.10	18.88	0.24
Total				1966.18	25.96



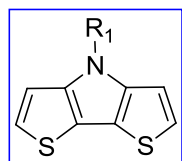
SM for compound 11	CAS	SM[g]/Gp	SM[₹]/Gs	SM[₹]/Gp	SM[\$]/Gp
Compound 10	-	0.53	3709.77	1966.18	25.97
Zinc powder	7440-66-6	0.40	10.37	4.148	0.05
Sodium hydroxide	1310-73-2	1.44	9.89	14.24	0.18
2-Ethylhexyl bromide	18908-66-2	1.42	21.75	30.88	0.40
Tertabutylammonium bromide	1643-19-2	0.038	48.61	1.84	0.02
Total				2017.28	26.62



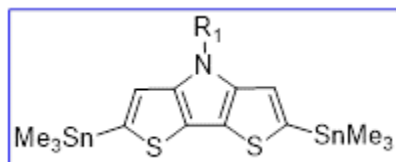
SM for compound 12	CAS	SM[g]/Gp	SM[₹]/Gs	SM[₹]/Gp	SM[\$]/Gp
Compound 11	-	0.75	2689.70	2017.28	26.64
n-Butyllithium	109-72-8	0.32	491.02	157.12	2.07
Trimethyltin chloride	1066-45-1	1.00	489.51	489.51	6.46
Tetrahydrofuran anhyd.	109-99-9	13.33	7.10	94.64	1.25
Total				2758.55	36.42



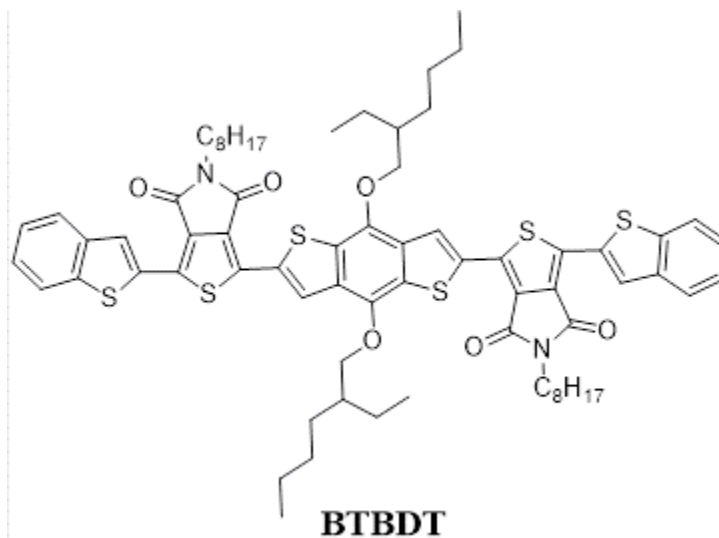
SM for compound 13	CAS	SM[g]/Gp	SM[₹]/Gs	SM[₹]/Gp	SM[\$]/Gp
3-bromothiophene	872-31-1	0.42	134.52	56.49	0.74
Lithiumdiisopropylamide	4111-54-0	0.27	282.39	76.24	1.00
Copper(II)chloride	7447-39-4	0.69	137.18	94.65	1.25
Tetrahydrofuran anhyd.	109-99-9	4.44	7.10	31.55	0.41
Total				258.93	3.4



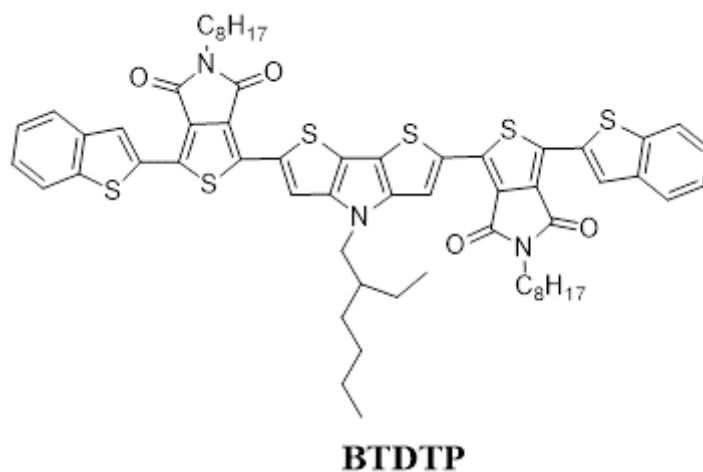
SM for compound 14	CAS	SM[g]/Gp	SM[₹]/Gs	SM[₹]/Gp	SM[\$]/Gp
Compound 13	-	0.6	431.55	258.93	3.42
Sodium tert-butoxide	865-48-5	0.391	32.30	12.62	0.16
Tris(dibenzylideneacetone) dipalladium(0)	51364-51-3	0.067	4735.26	317.26	4.19
rac-BINAP	98327-87-8	0.092	1369.19	125.96	1.66
2-Ethyl-1-hexylamine	104-75-6	0.47	110.00	51.7	0.68
Toluene anhyd.	108-24-7	19.07	3.39	64.64	0.85
Total				831.11	10.96



SM for compound 15	CAS	SM[g]/Gp	SM[₹]/Gs	SM[₹]/Gp	SM[\$]/Gp
Compound 14	-	0.47	1768.31	831.11	10.97
n-Butyllithium	109-89-7	0.309	491.02	151.72	2.00
Trimethyltin chloride	1066-45-1	0.96	489.51	469.92	6.20
Tetrahydrofuran anhyd.	109-99-9	8.89	7.10	63.11	0.83
Total				1515.86	20



SM for BTBDT	CAS	SM[g]/Gp	SM[₹]/Gs	SM[₹]/Gp	SM[\$]/Gp
Compound 12	-	0.78	3536.60	2758.55	36.44
Compound 7	-	1.19	2580.97	3071.35	40.57
Pd(PPh ₃) ₄	14221-01-3	0.057	2360.8	134.56	1.77
Toluene anhyd.	108-88-3	26.87	6.079	163.34	2.15
Total				6127.8	80.93



SM for BTDTP	CAS	SM[g]/Gp	SM[₹]/Gs	SM[₹]/Gp	SM[\$]/Gp
Compound 15	-	0.96	1579.02	1515.85	20.02
Compound 7	-	1.85	2580.97	4774.79	63.07
Pd(PPh ₃) ₄	14221-01-3	0.088	2360.8	207.75	2.74
Toluene anhyd.	108-88-3	34.68	6.079	210.81	2.78
Total				6709.2	88.61

SM: starting material; **Gs:** 1 g of starting material; **GP:** 1 g of product; **₹:** Indian National Rupee
\$: USD (US Dollar)

Compound	Cost per gram [₹]	Cost per gram [\$]
Spiro-MeOTAD	35,686.50	471.06
BTBDT	6127.8	80.93
BDTDP	6709.2	88.61

The total cost calculation of starting materials and solvents used in the respective reactions to obtain 1 gram of BTBDT and BDTDP are given in detail. The yield and compound numbers are assigned to the original information given in the synthesis part.

The CAS numbers for the products of each step, which were used as starting materials in the next step were not mentioned, even though few are available commercially. The solvents used for workup/purification methods like, column chromatography and crystallizations were not included¹.

Octasulphur (S₈) for the synthesis of compound 2 and n-Butyllithium (2.5M) price was not available in Sigma-Aldrich. So we assumed 1g of S₈ is 1.0 rupee and 2.0 M n-BuLi price was consider to calculate the cost.

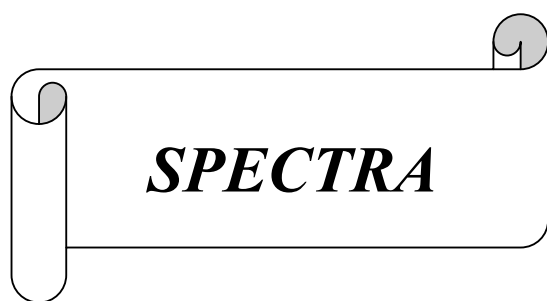
In the synthesis of Thiophene-3-carbonyl Chloride (compound 8), the % yield was assumed to be 87.5%

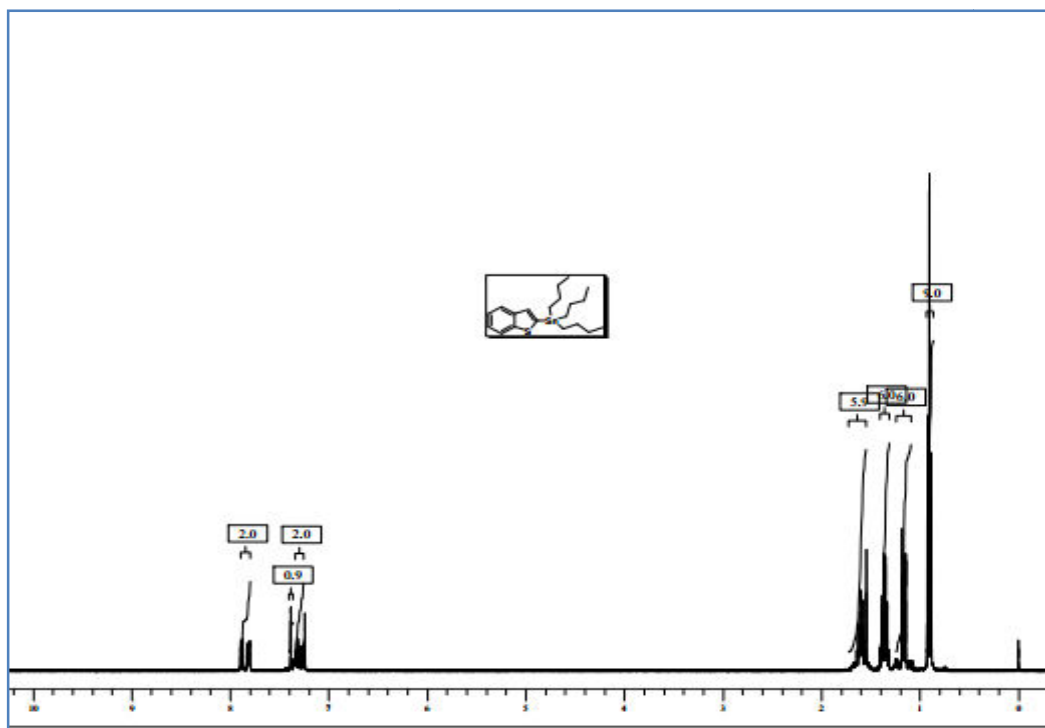
Price conversion from INR to USD was done by considering the one-month average conversion rate of
₹ 1INR = 0.0132 USD

The price of Spiro MeOTAD, reagents, solvents and chemicals were searched from <https://www.sigmaaldrich.com/india.html>

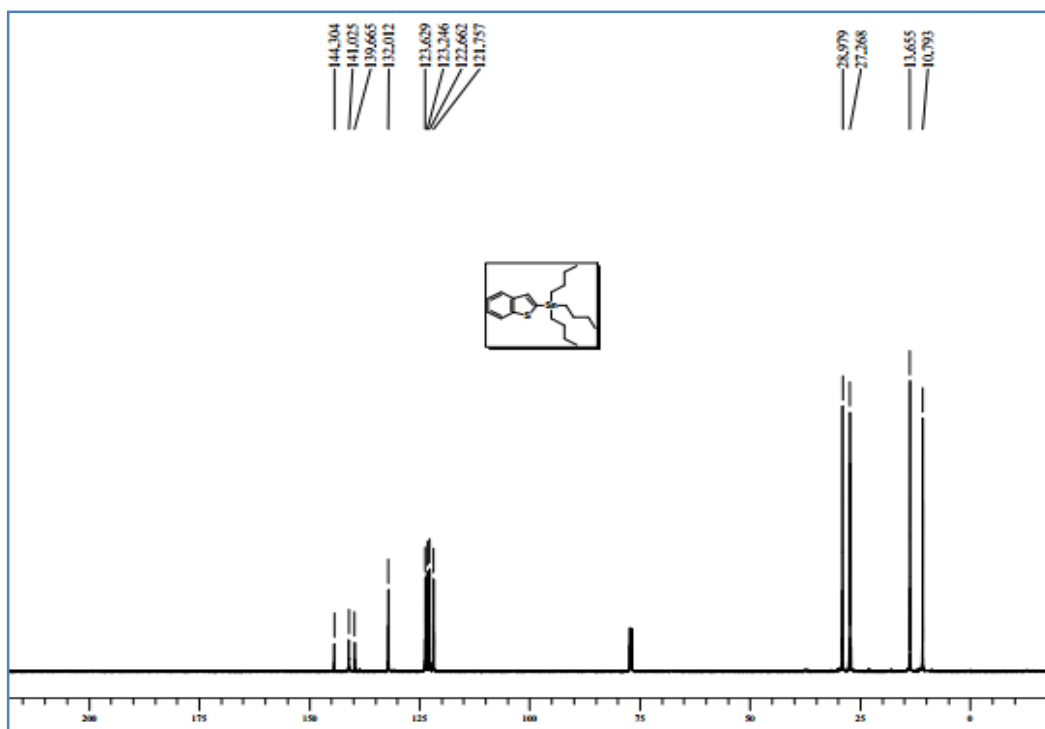
Ref:

- 1) J.Mater. Chem. C,2019, 7, 8593
- 2) J. Mater. Chem. A, 2020, 8, 1279

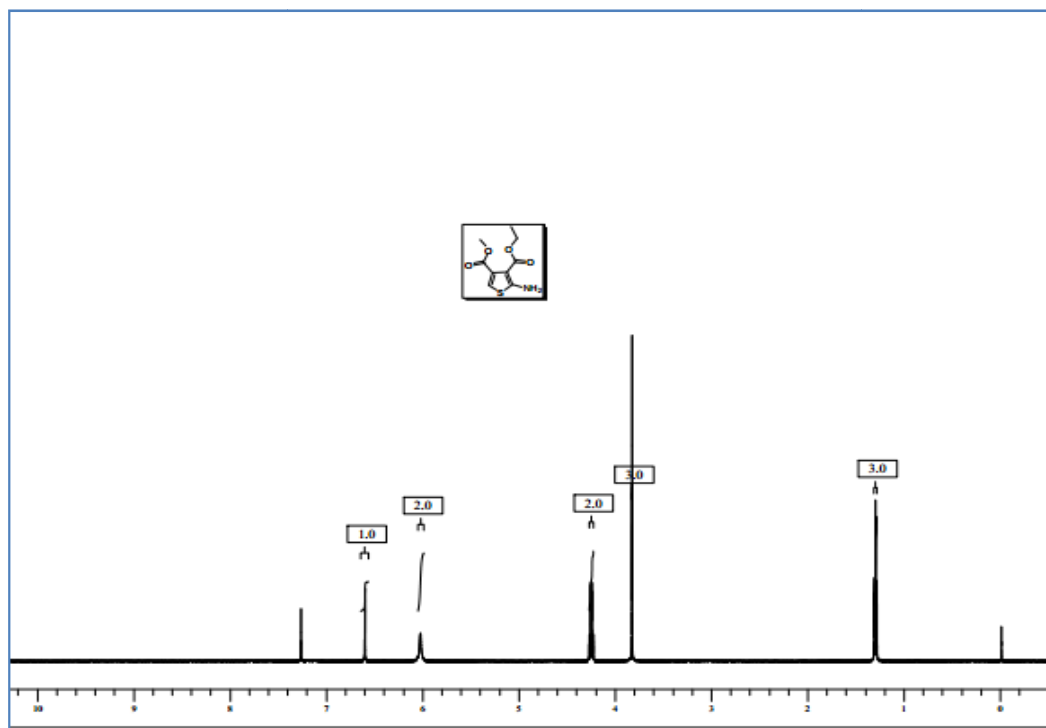




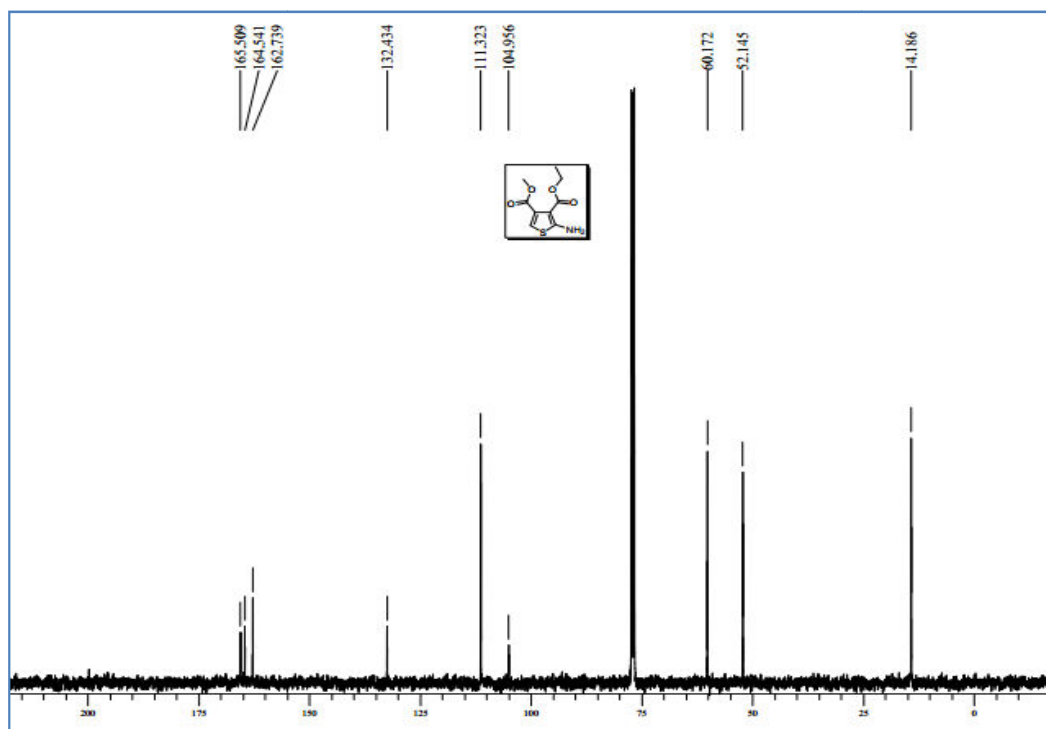
¹H NMR spectrum of compound 1



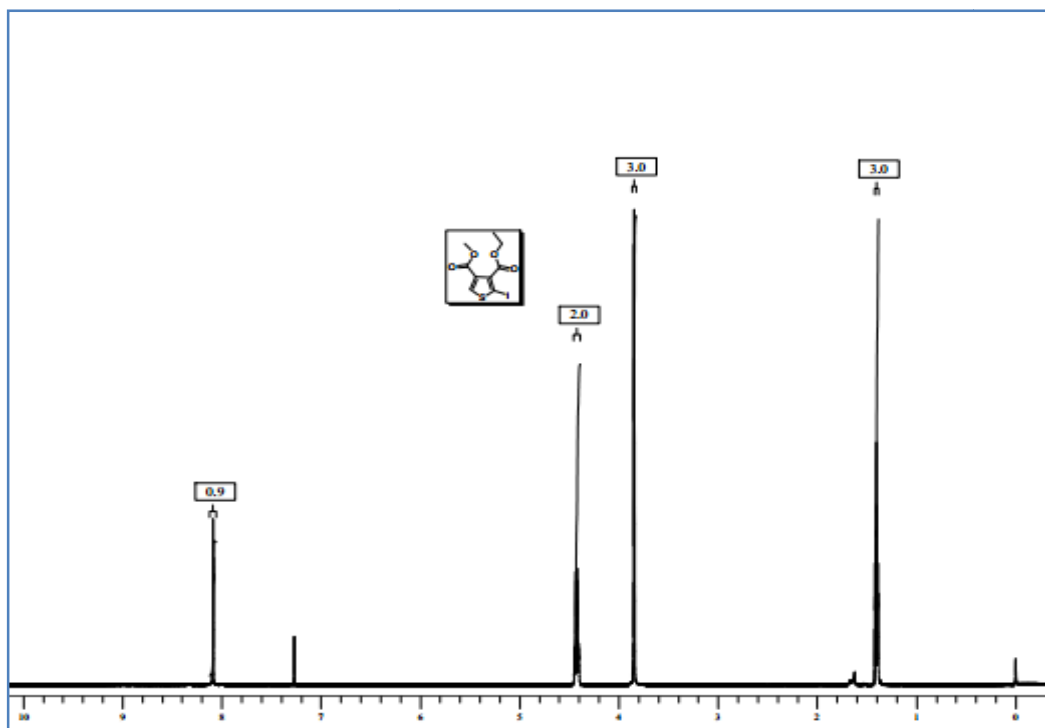
¹³C NMR spectrum of compound 1



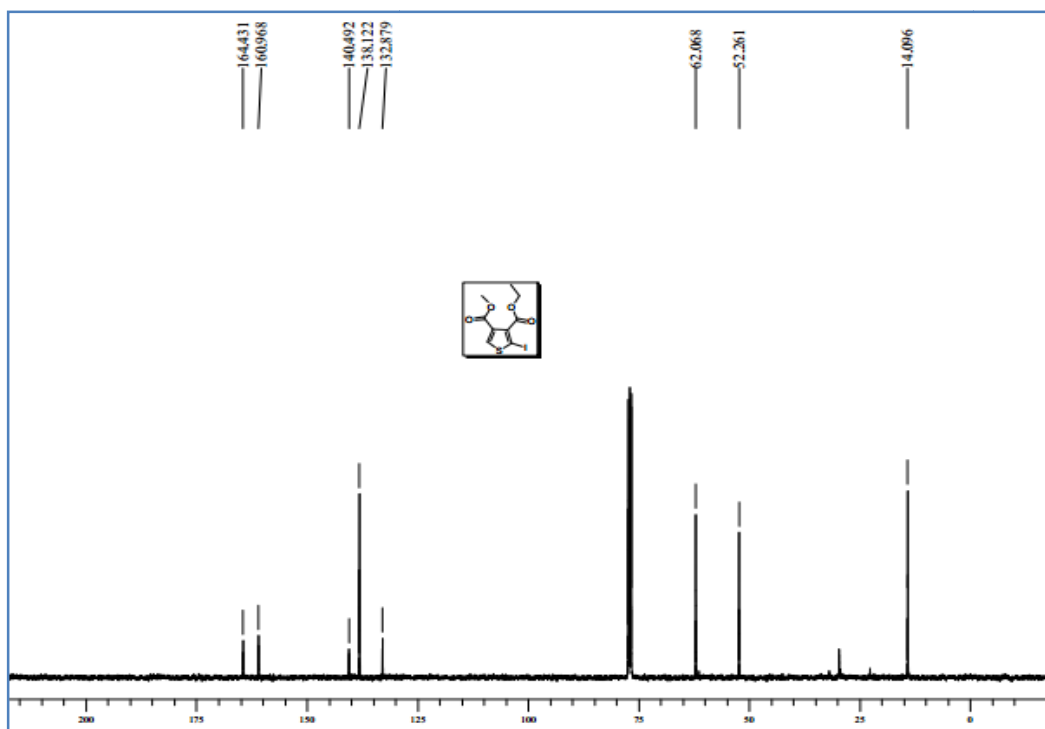
¹H NMR spectrum of compound 2



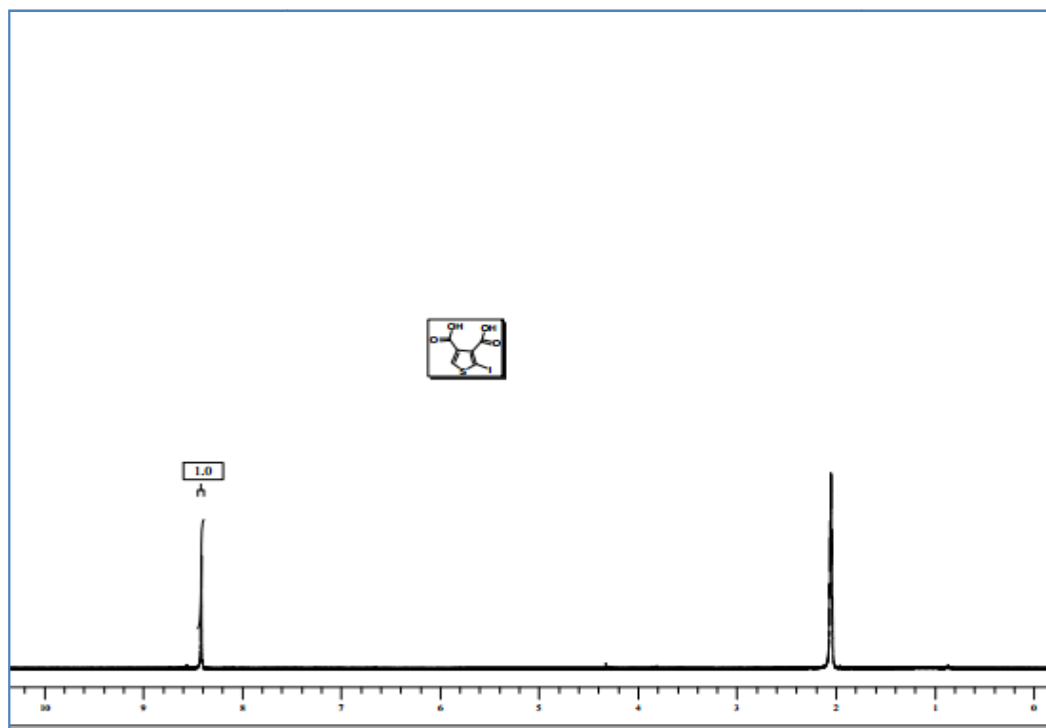
¹³C NMR spectrum of compound 2



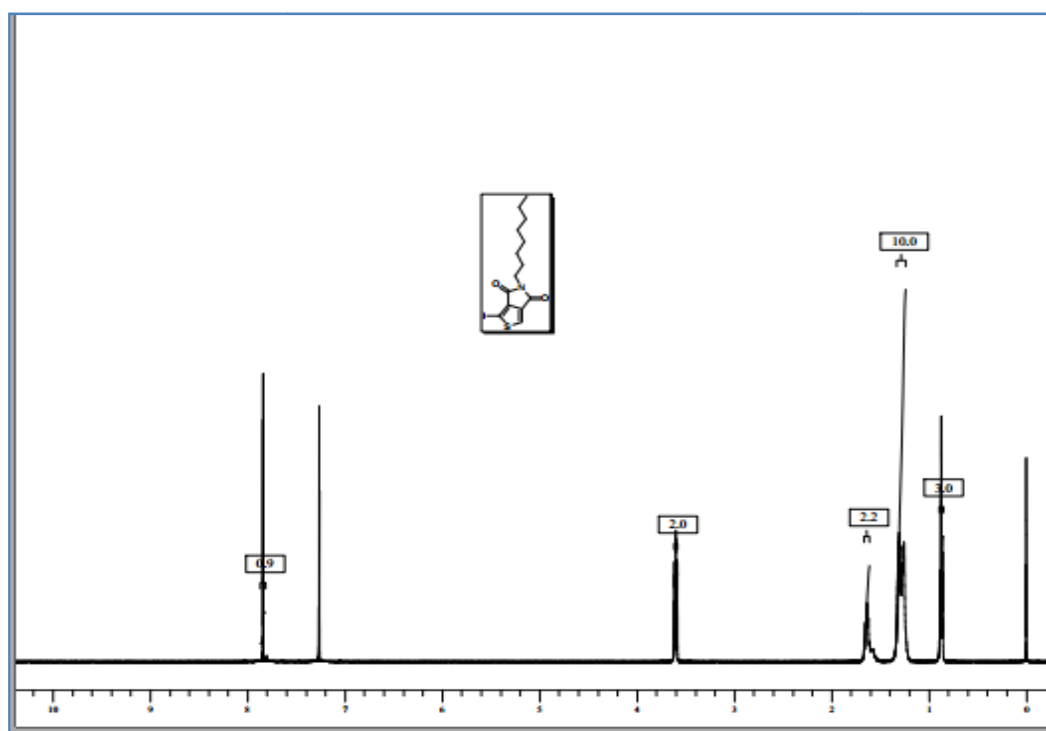
^1H NMR spectrum of compound 3



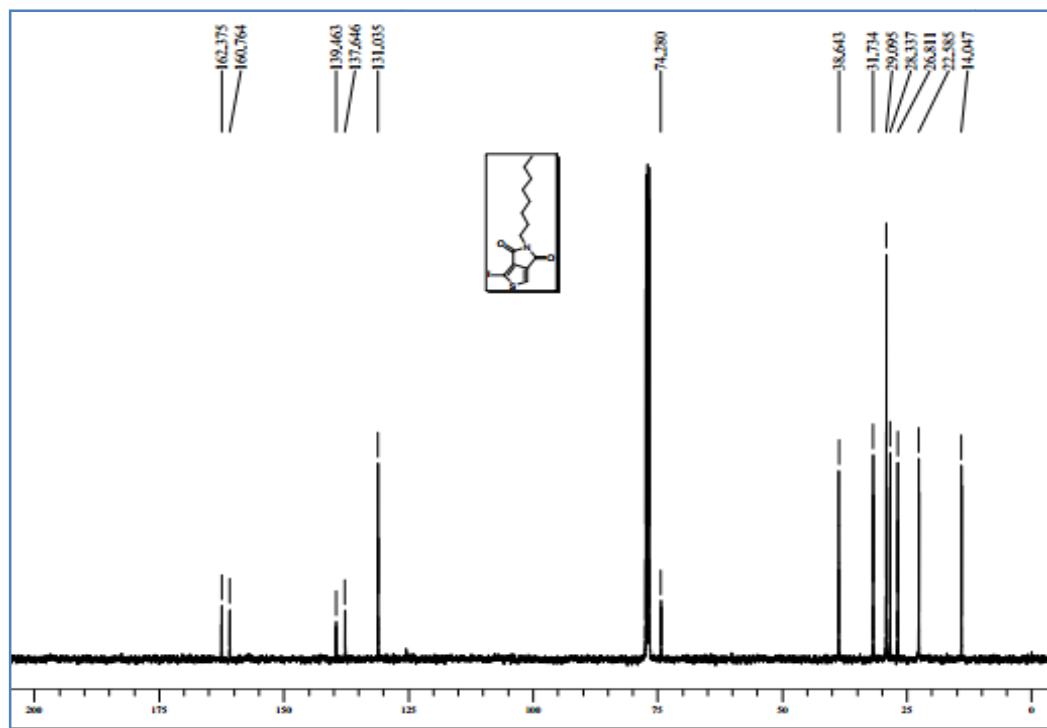
^{13}C NMR spectrum of compound 3



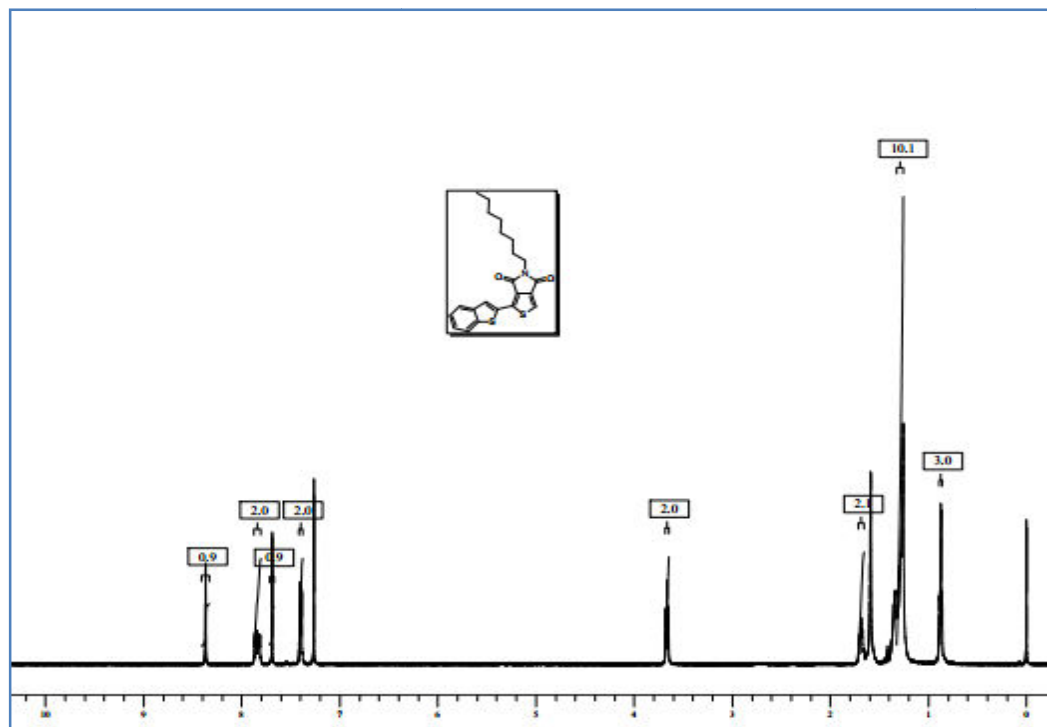
^1H NMR spectrum of compound 4



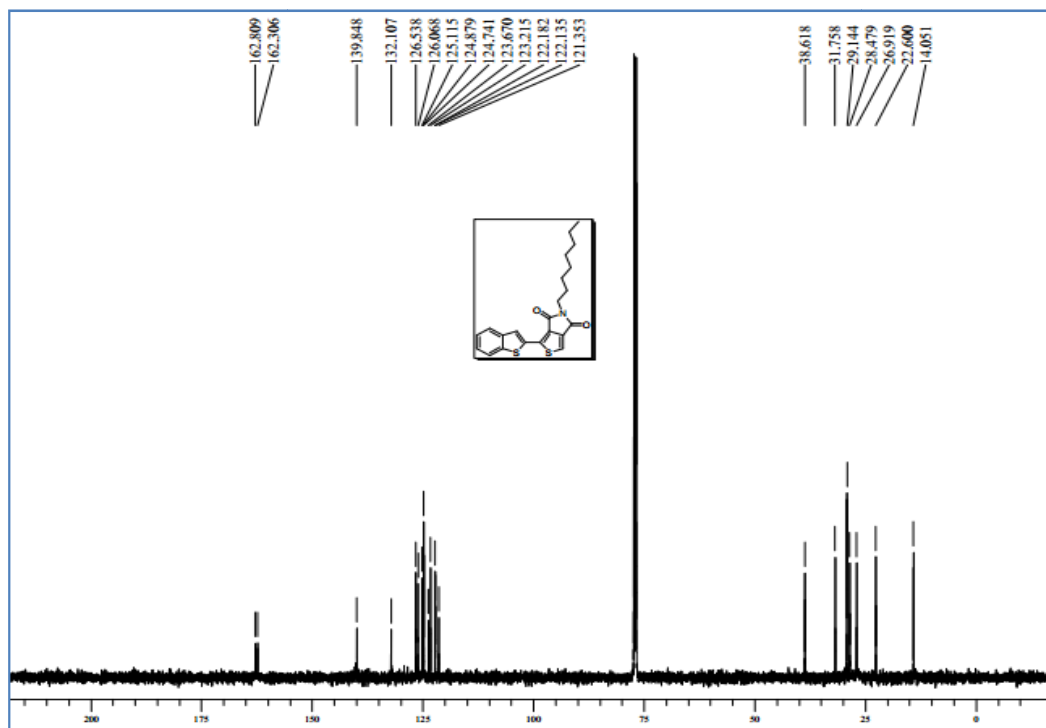
^1H NMR spectrum of compound 5



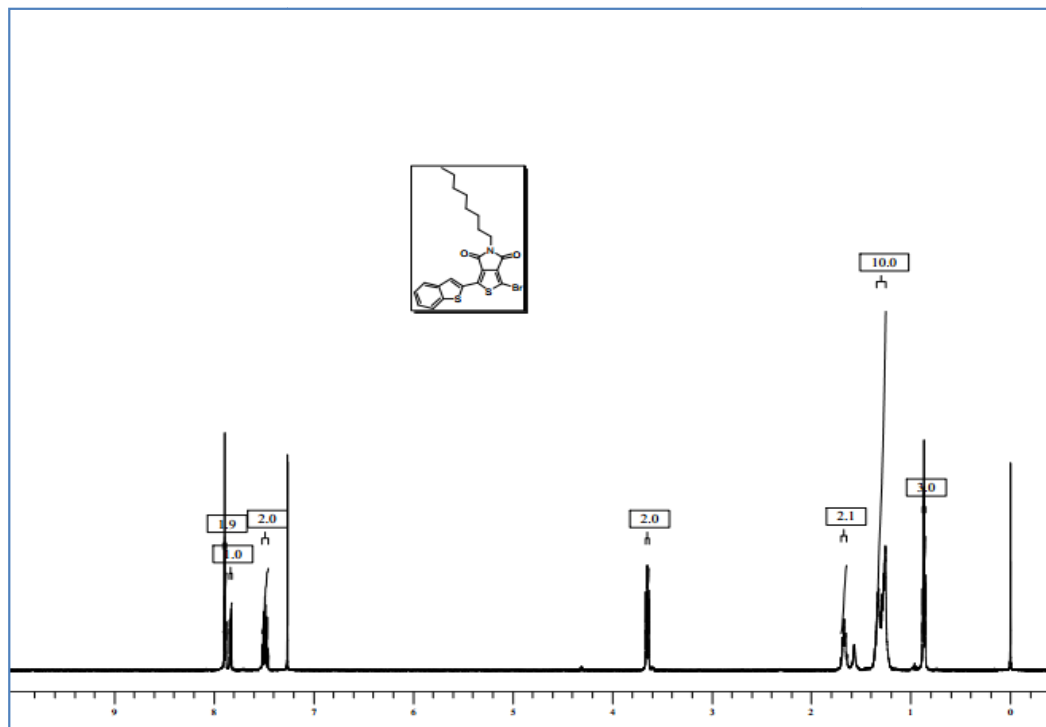
¹³C NMR spectrum of compound 5



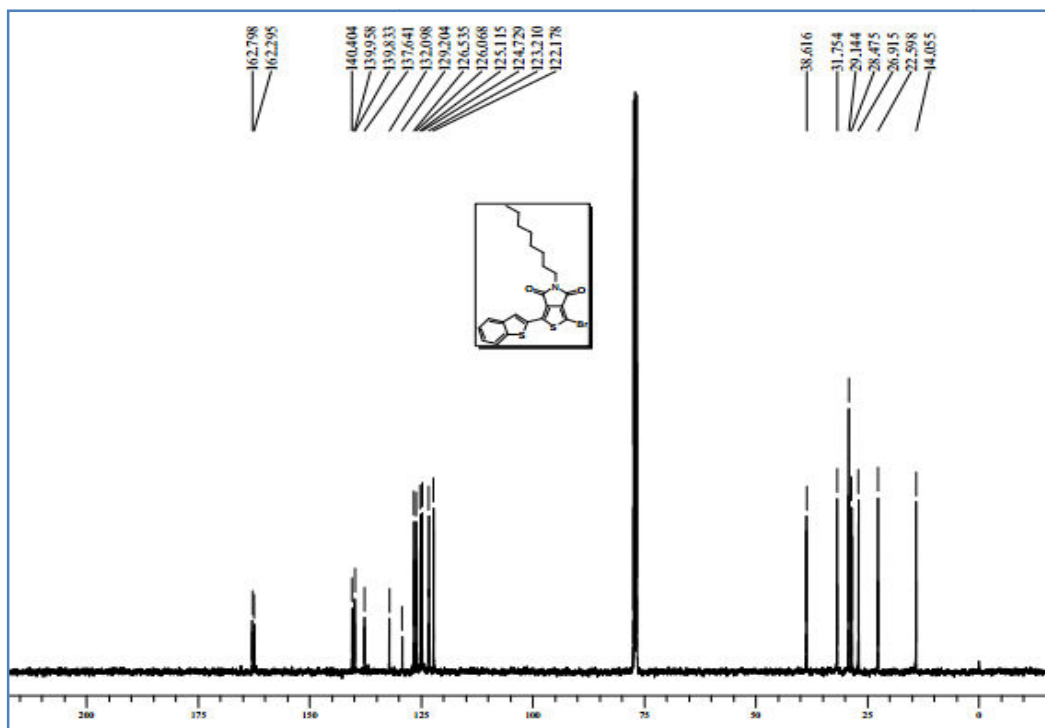
¹H NMR spectrum of compound 6



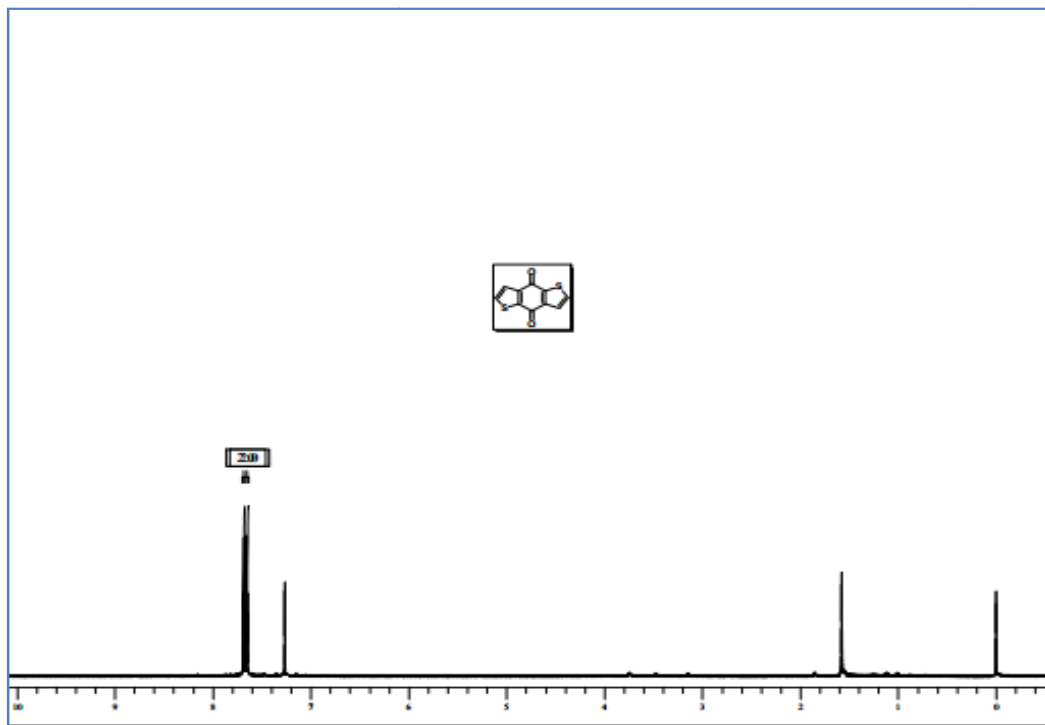
^{13}C NMR spectrum of compound 6



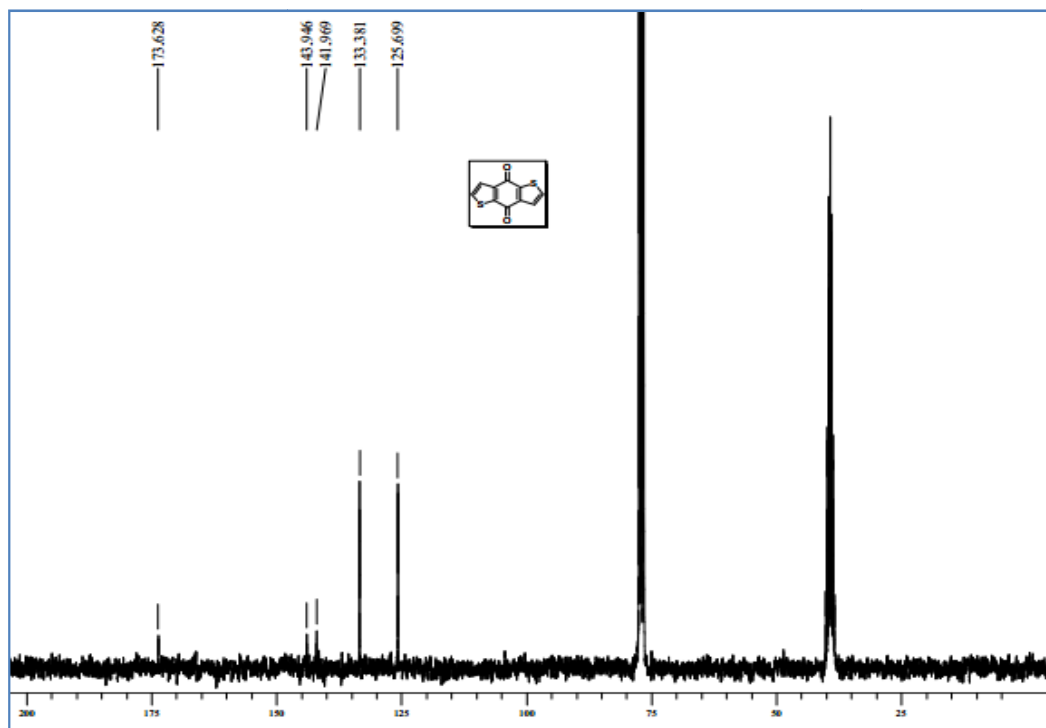
^1H NMR spectrum of compound 7



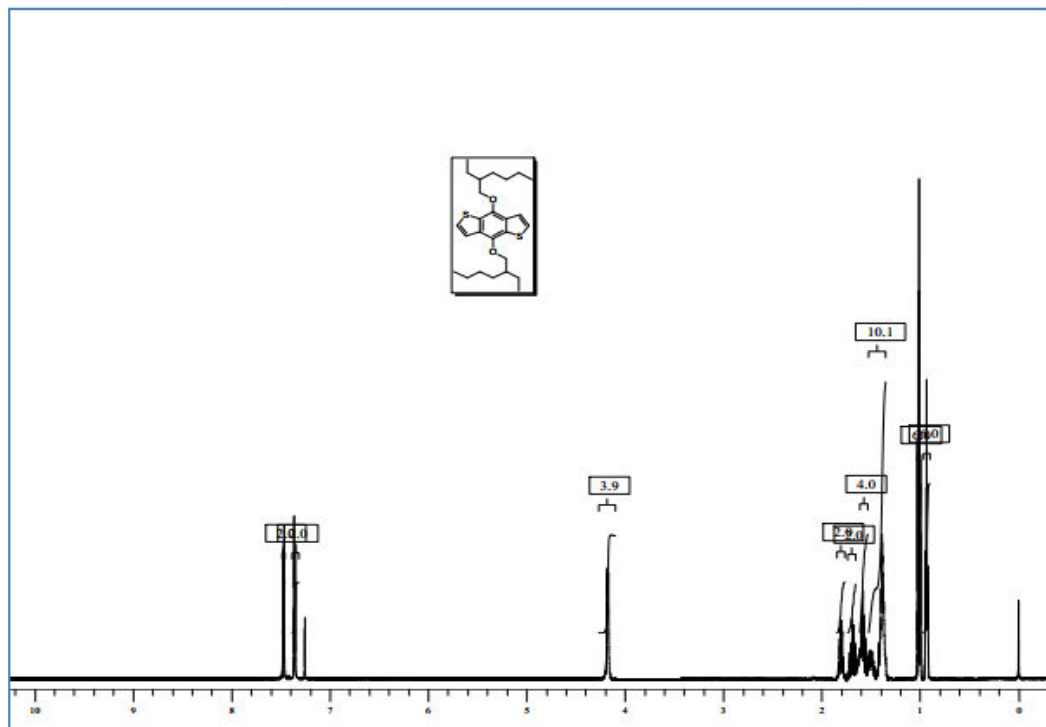
^{13}C NMR spectrum of compound 7



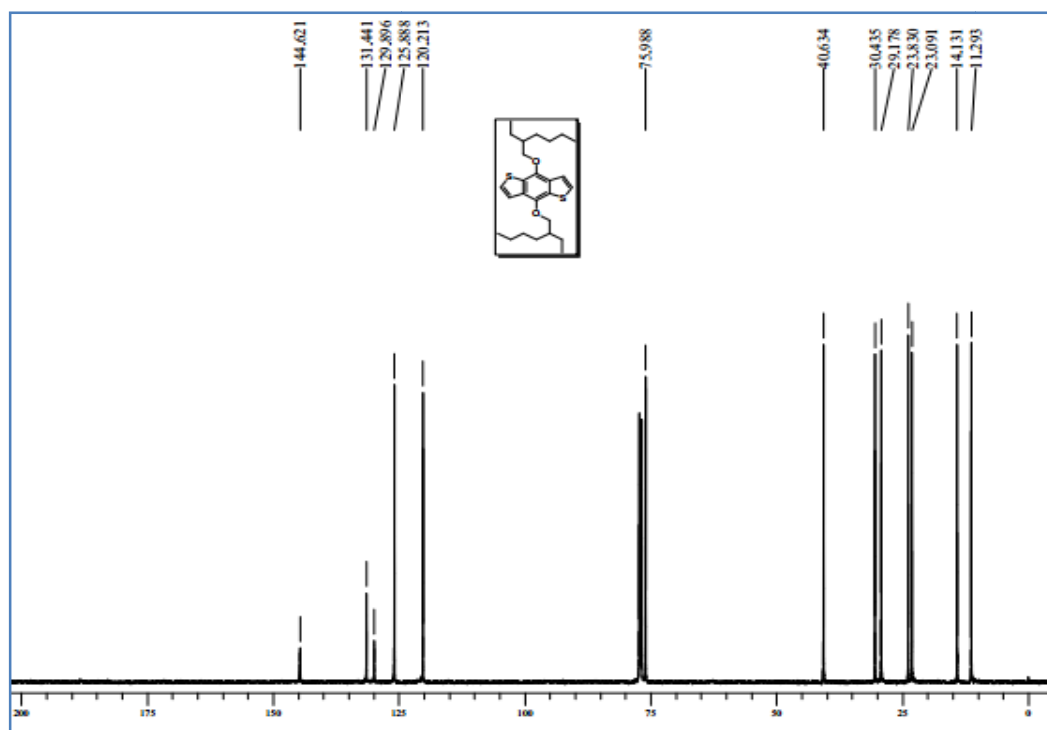
^1H NMR spectrum of compound 10



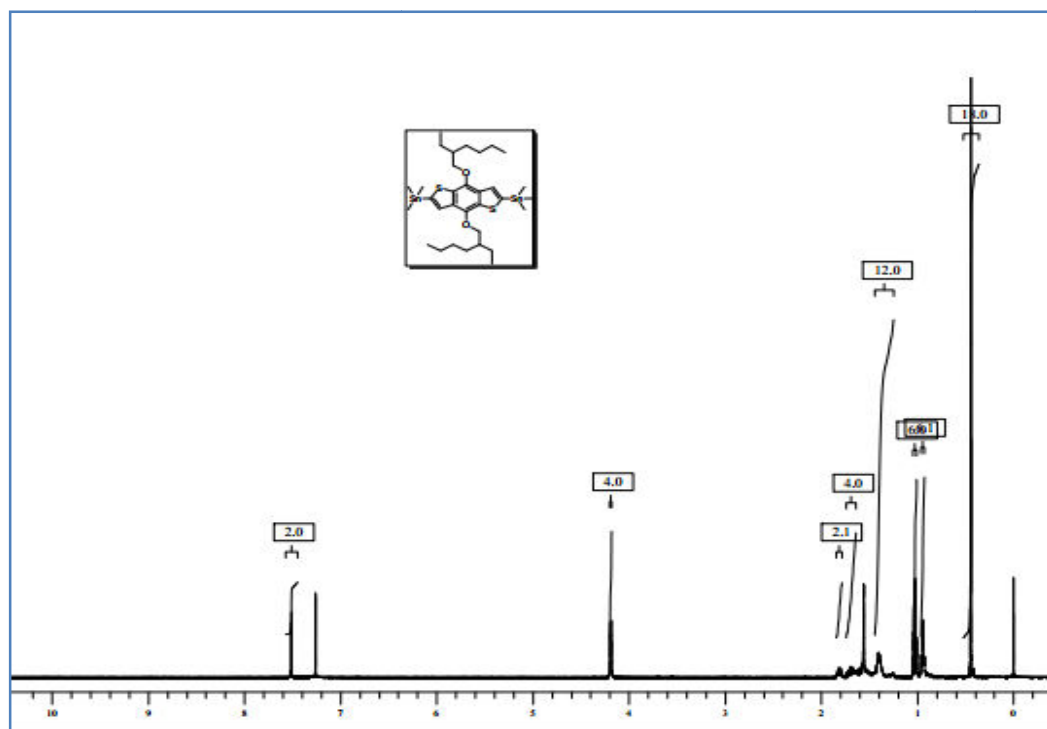
^{13}C NMR spectrum of compound 10



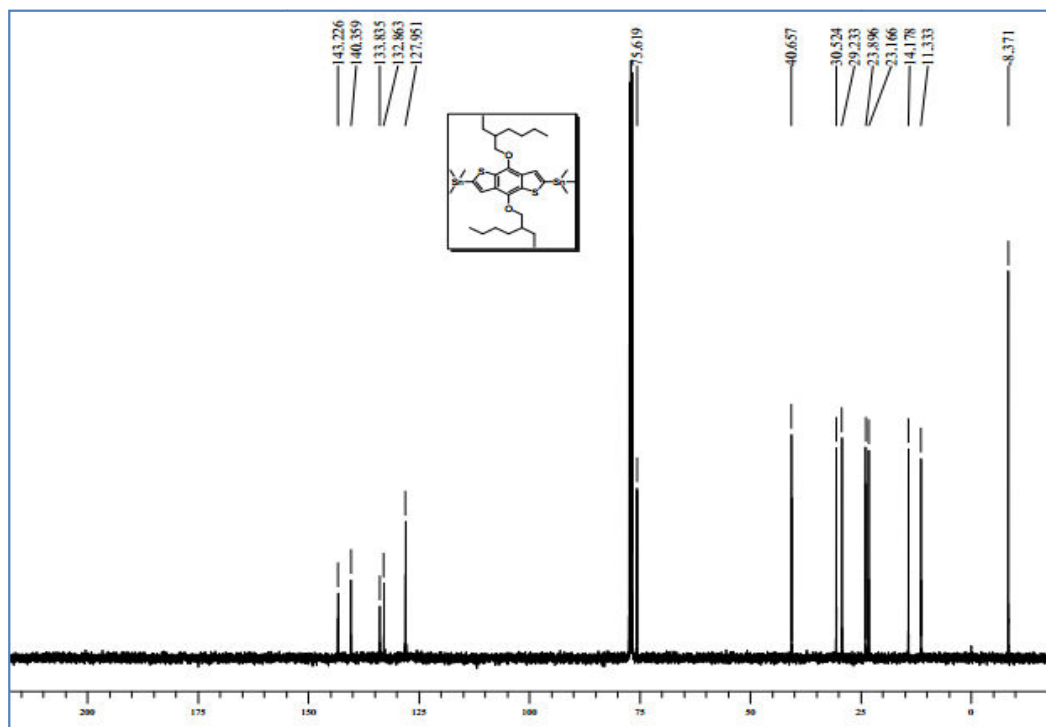
^1H NMR spectrum of compound 11



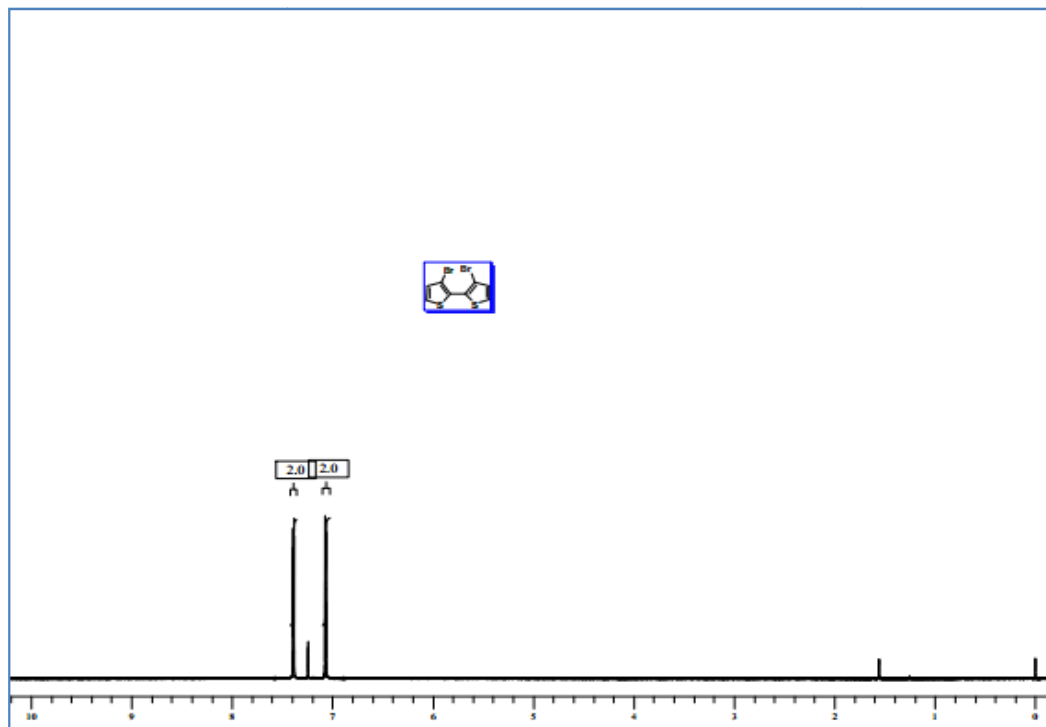
^{13}C NMR spectrum of compound **11**



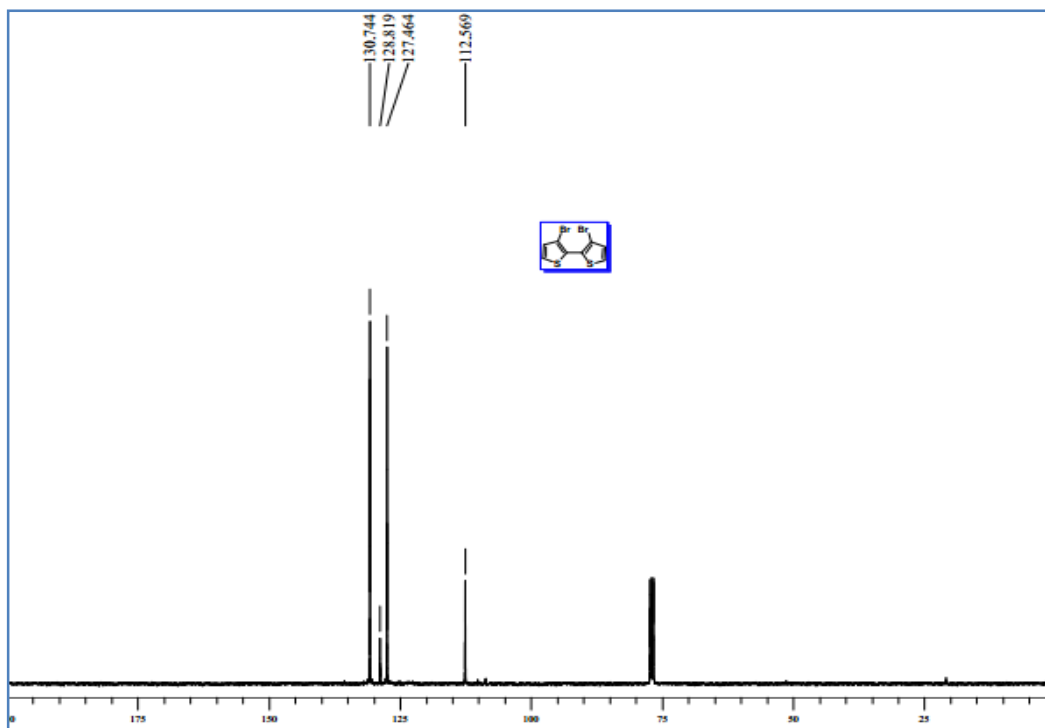
^1H NMR spectrum of compound **12**



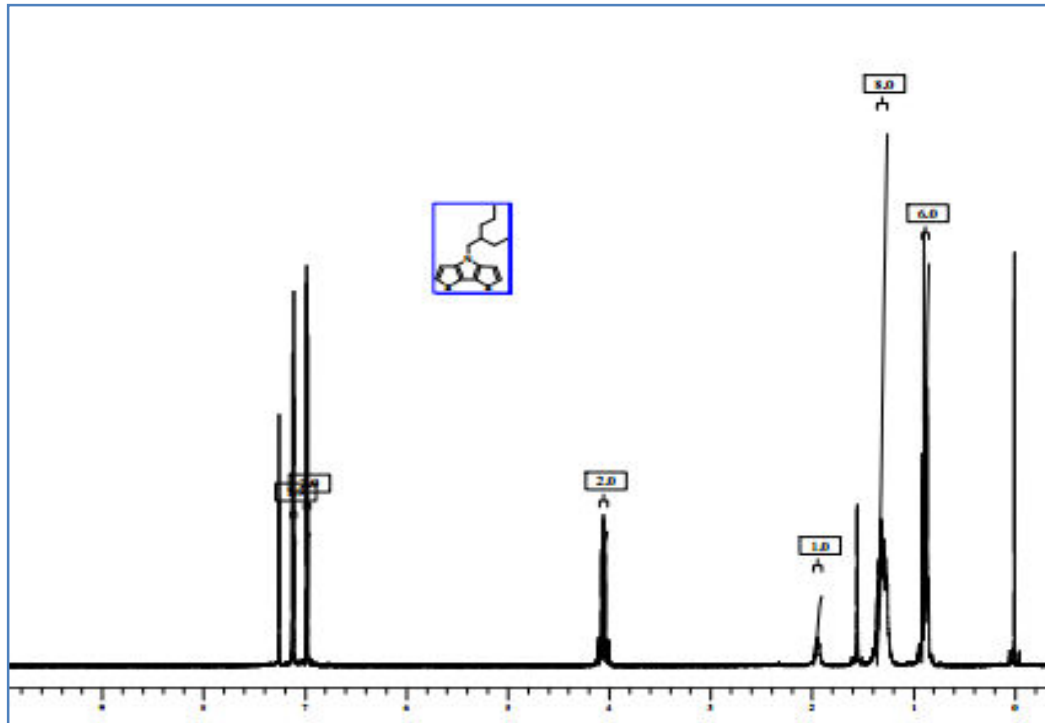
^{13}C NMR spectrum of compound 12



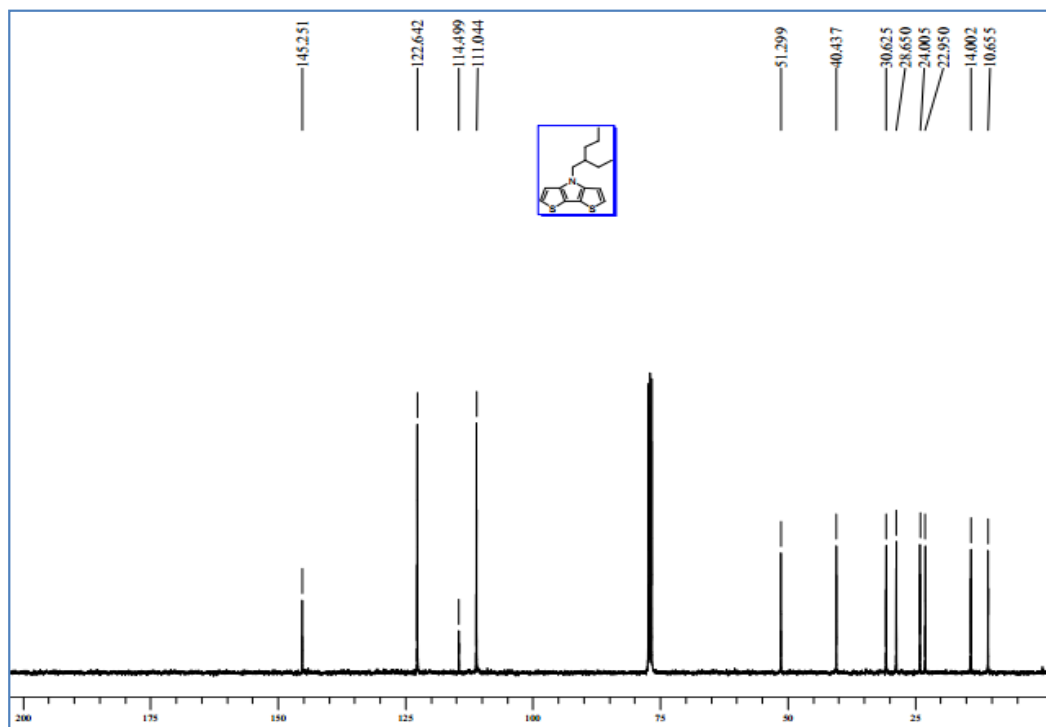
^1H NMR spectrum of compound 13



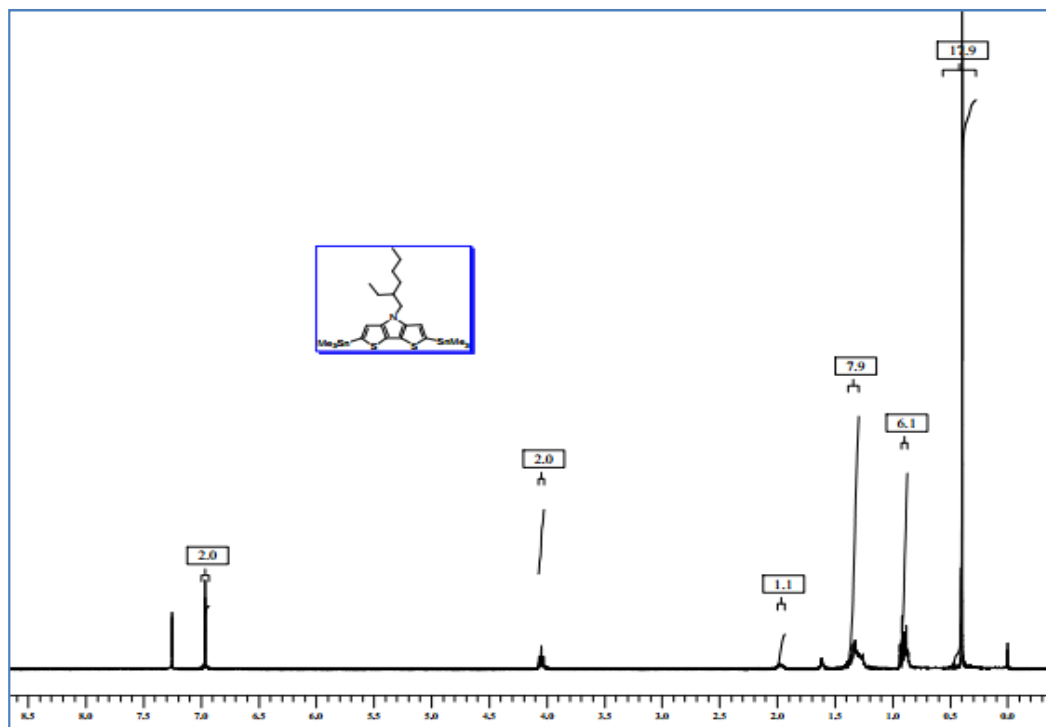
^{13}C NMR spectrum of compound 13



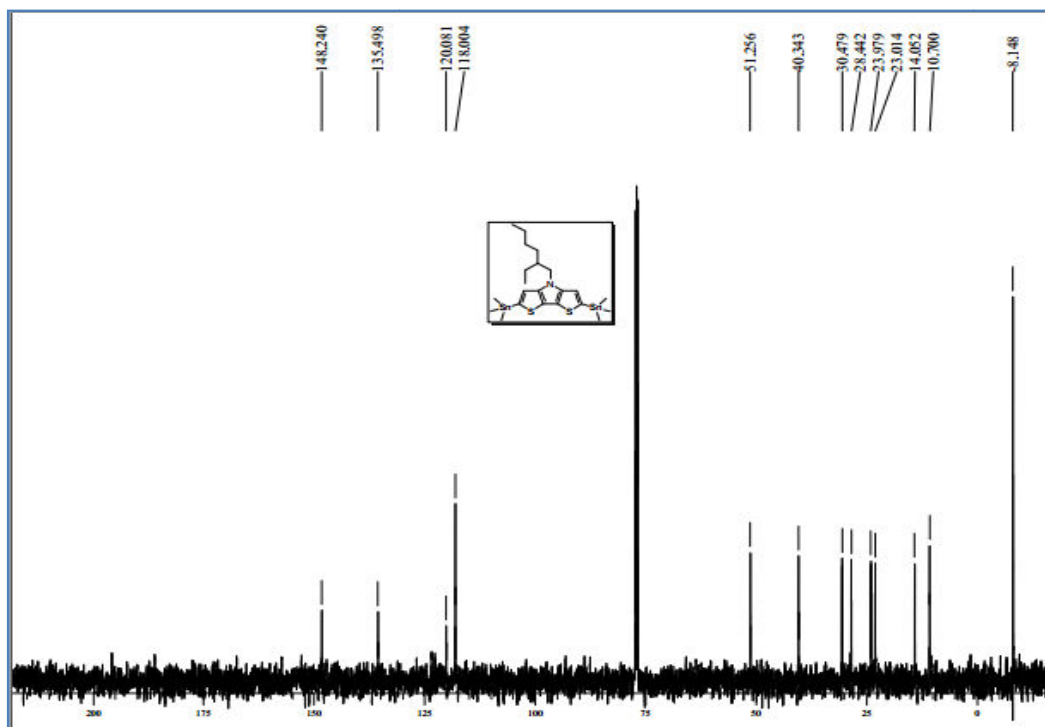
^1H NMR spectrum of compound 14



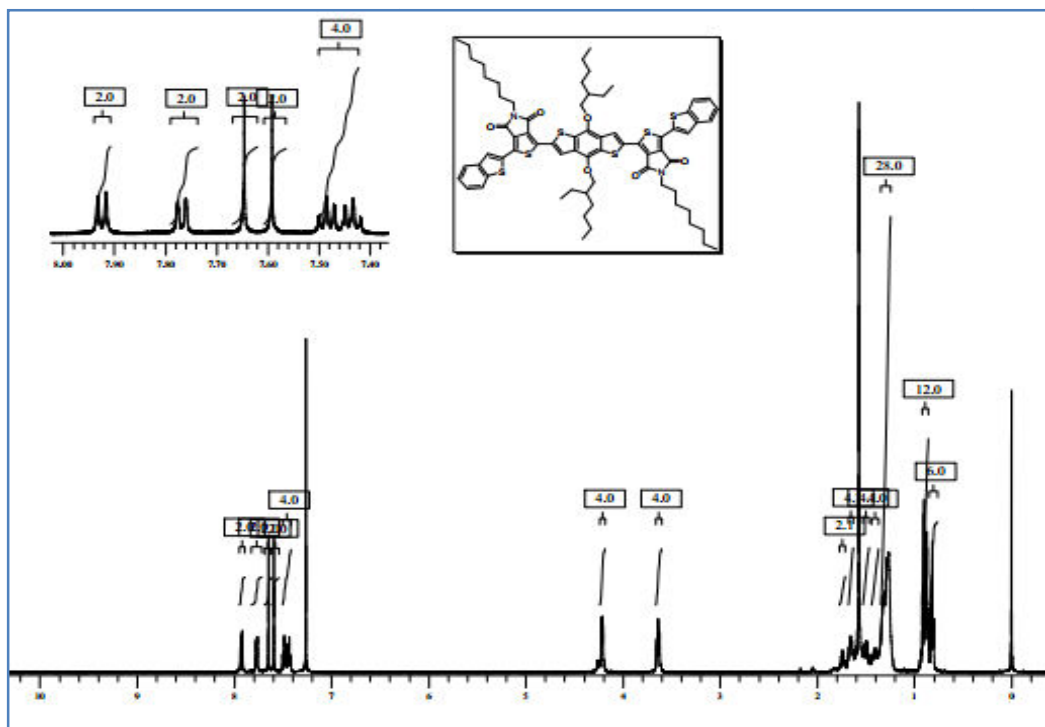
^{13}C NMR spectrum of compound **14**



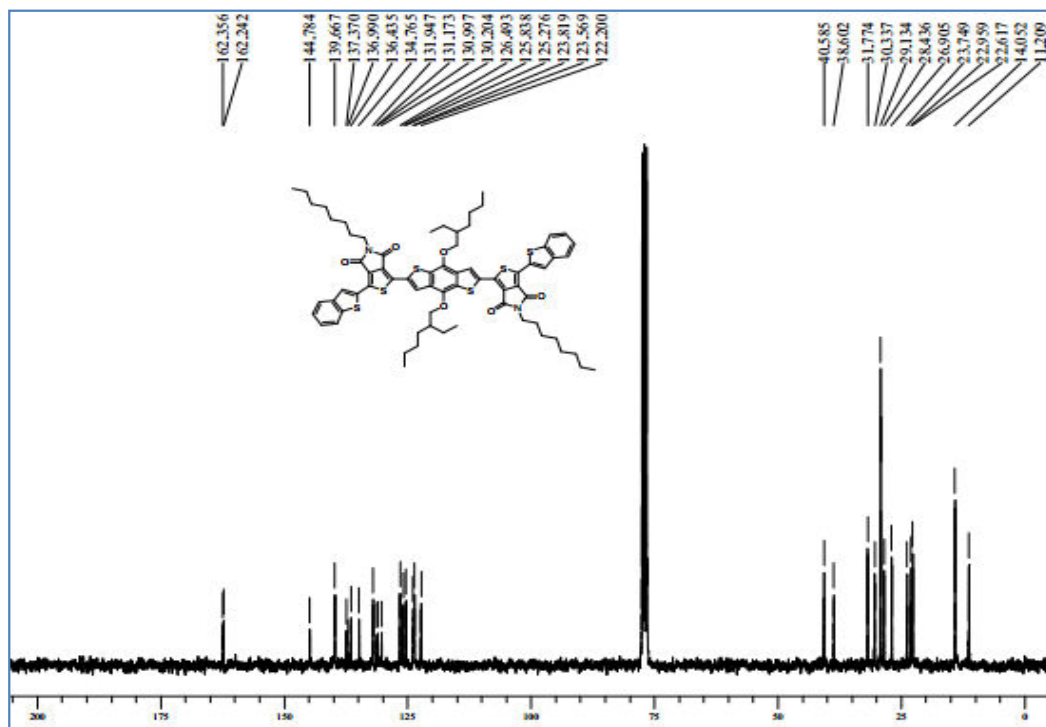
^1H NMR spectrum of compound **15**



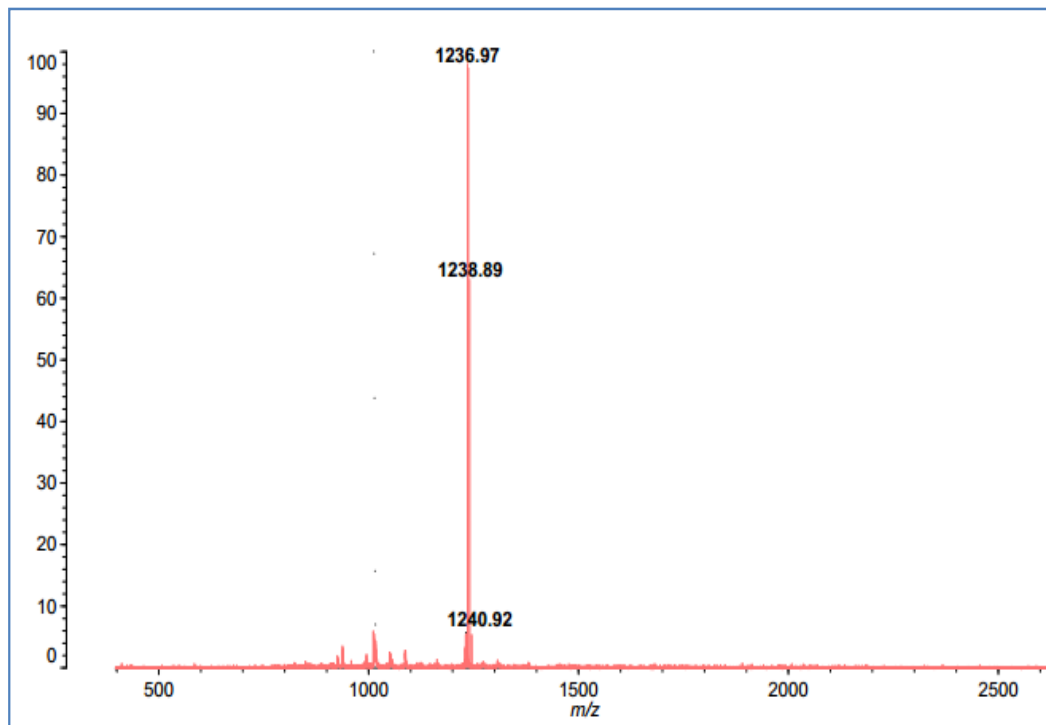
^{13}C NMR spectrum of compound **15**



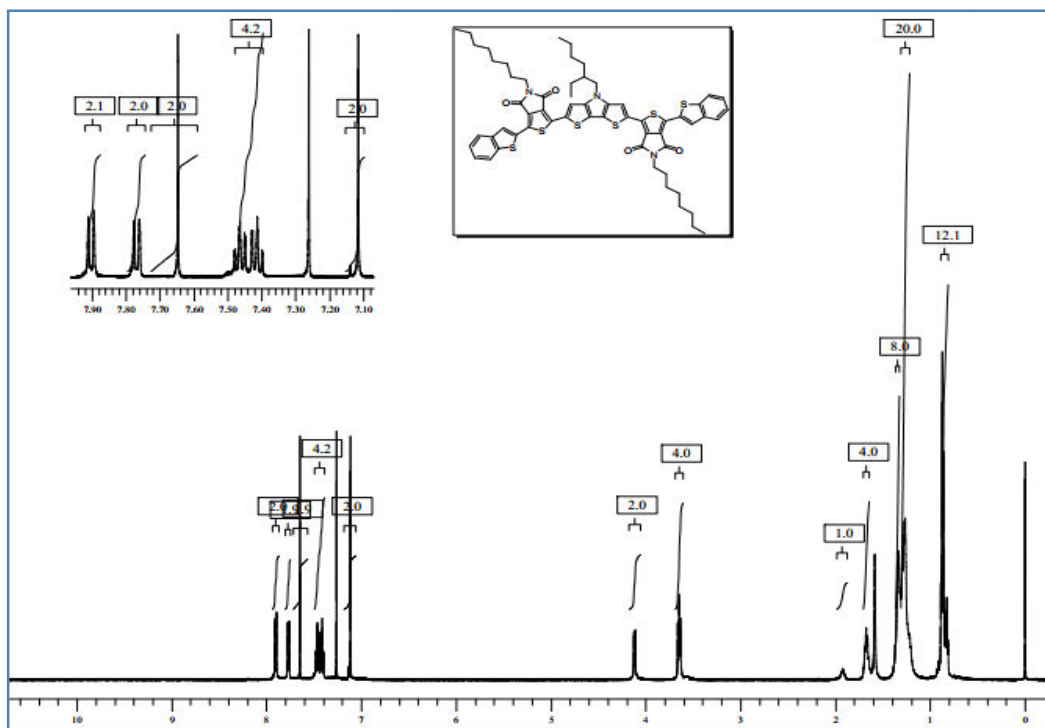
^1H NMR spectrum of compound **BTBDT**



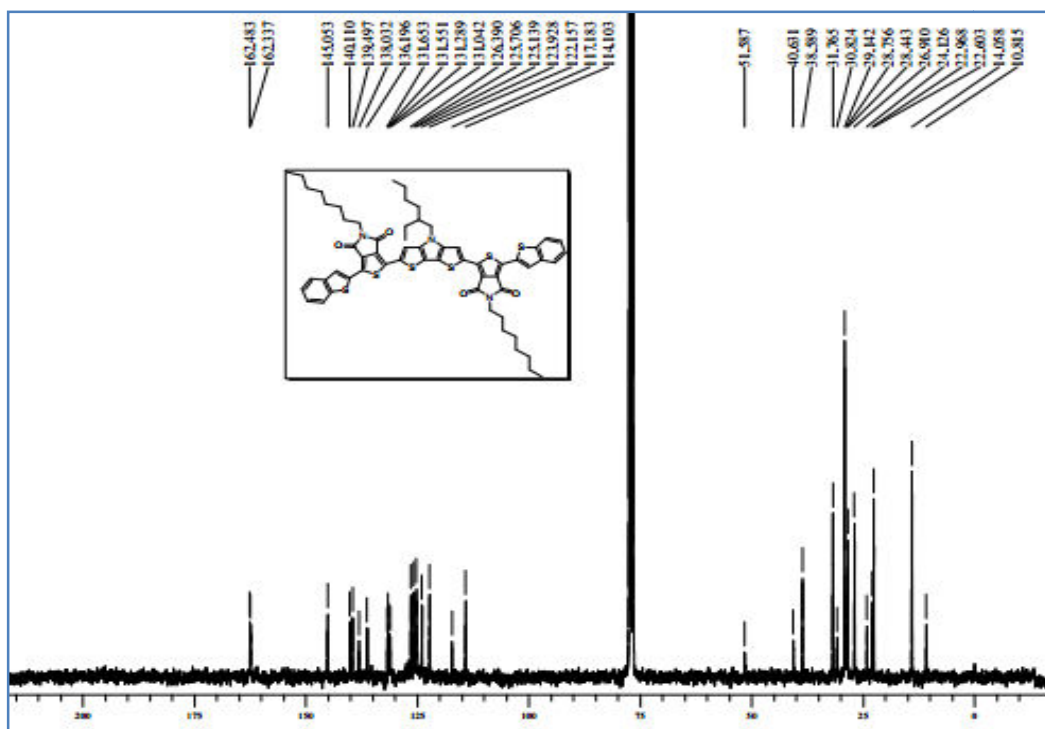
^{13}C NMR spectrum of compound **BTBDT**



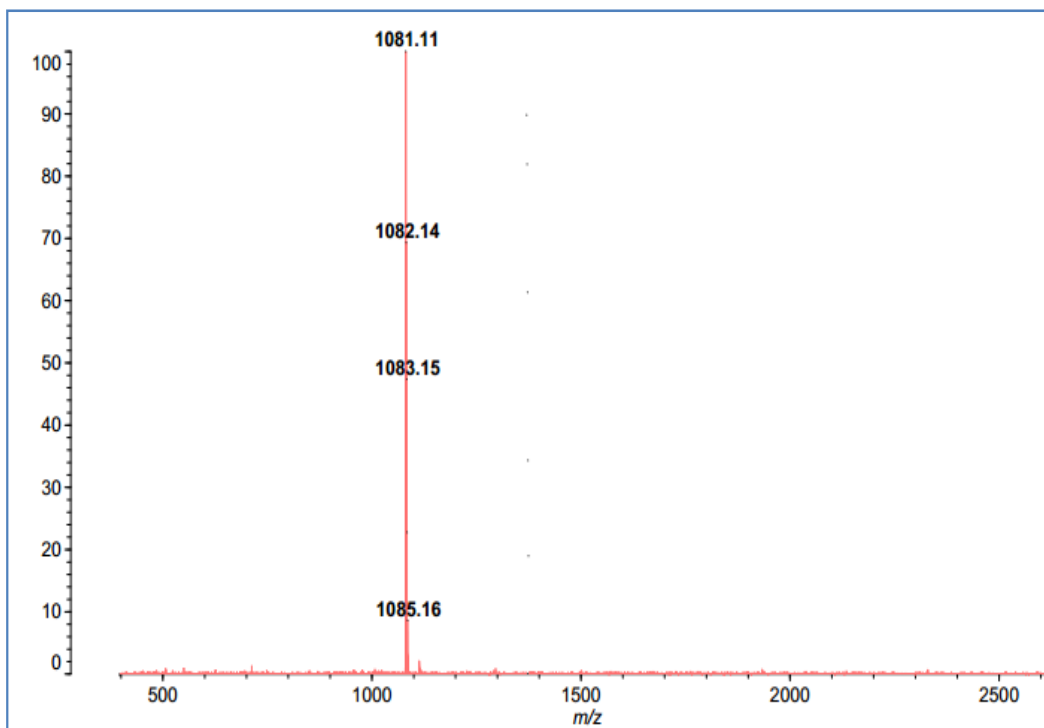
MALDI-TOF Spectrum of **BTBDT**



^1H NMR spectrum of compound **BTDTP**



^{13}C NMR spectrum of compound **BTDTP**



MALDI-TOF Spectrum of **BTDP**