Chapter 2

Synthesis of donor and acceptor units of the low band gap polymers from single precursor–Dimethyl thiophene dicarboxylate

2.1 Introduction

Conjugated polymers have acquired much interest because of its direct applications in development of various electronic devices like photovoltaic devices, light emitting diodes (LEDs), field effect transistors (FETs) and sensors [1]. Amongst them organic photovoltaic devices are often seen as inexpensive, greener and renewable alternate energy sources to that of the conventional ones [2]. The light weight, flexibility and ability to cast it over large area are described as their advantages [3].

The donor-acceptor concept has been greatly exploited in the conjugated polymers. Quinoid character is one of the essential factors in achieving the low band gap properties for conjugated polymer [4, 5]. To impart the delocalization in the polymer back bone which provides quinoid character, donor-acceptor alternating co-monomer strategy is often used. The electron donating and electron withdrawing properties of alternating monomer efficiently increases the intramolecular charge transfer setting up the push-pull effect which narrows the band gap of the conjugated polymer [6, 7].

The fused-thiophene ring system in the conjugated polymer backbone possesses several advantages. Such fused-thiophene systems exhibits extended π-conjugation along with structural rigidity in the conjugated polymer. These factors improve the intermolecular interaction in the solid films as well as lower the band gap of the polymer. The flat π–systems improve charge transport properties as well as they increase quinoidal character of the systems which leds lowering of the bandgap. Among fused-thiophene systems most explored units are thieno[*3,4-c*]pyrrole-4,6-dione (TPD) and benzo[*1,2-b:4,5-b*']dithiophene (BDT) as a acceptor unit and donor unit, respectively.

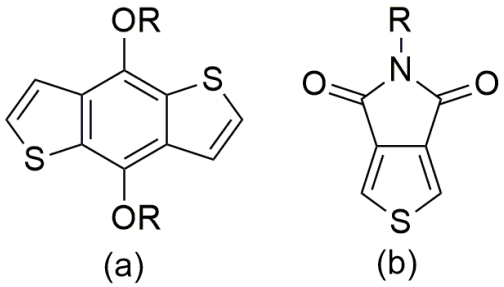


Figure 2.1 Structures of (a) benzo[*1,2-b:4,5-b'*]dithiophene (BDT) and (b) thieno[*3,4-*c]pyrrole-4,6-dione (TPD) [35]

TPD has been considered as an excellent unit in the synthesis of low band gap polymers [8]. TPD have distinct benefit of lower energy band resulted from stabilization energy acquired from the formation of a quinoidal thiophene-maleimide species in their excited state. Substitution of alkyl groups increases in solubility while the rigidity enhances the favorable solid state arrangement [9]. Similarly, BDT based materials have emerged as leading candidates for a number of organic electronic applications [10]. Initially, these building blocks were used as an active materials in organic field effect transistors (OFETs), including devices with small molecules [11] or polymers [12]. In recent years, BDTs have emerged as prominent building blocks in small molecules [13] and polymers [14] for use as donor materials in organic photovoltaic (OPV) devices. Of particular note is the fact that power conversion efficiencies have excluded 8% when BDT-based materials have been used in the active layer of bulk heterojunction solar cells for both small molecules [15] and polymeric donors [16]. The symmetric and large planar character of BDT imparts convenient charge transportation as well as rigidity. The symmetric and large planar character of BDT imparts convenient charge transportation as well as rigidity. Increased charge mobility accounted by the facial π-π stacking of planar conjugated structure of BDT. The salient features of these units are the alkoxy groups at 4 and 8 positions which improve the solubility of polymer and avoid the steric hindrance for adjacent units. Recently, two dimensional conjugations on BDT units have been reported where the BDT has been functionalized through two perpendicular directions [17].

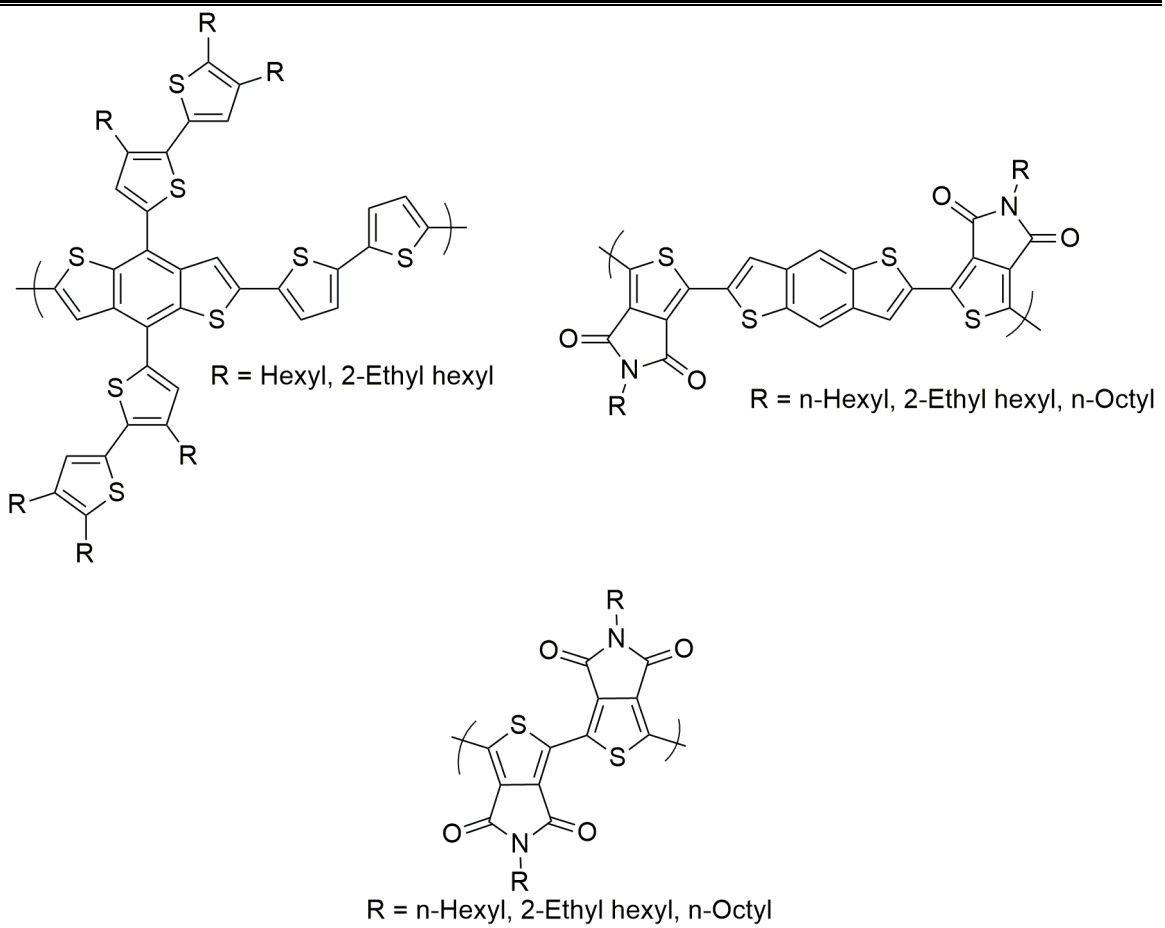
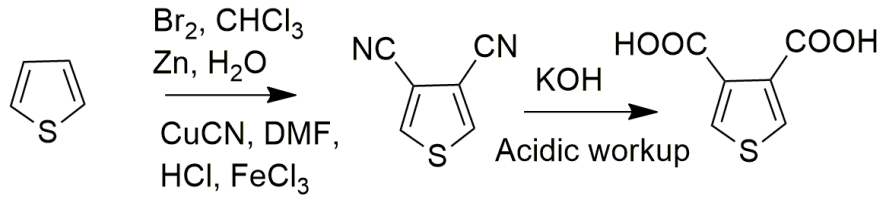


Figure 2.2 Some reported BDT and TPD units based conjugated polymers [8, 16, 17].

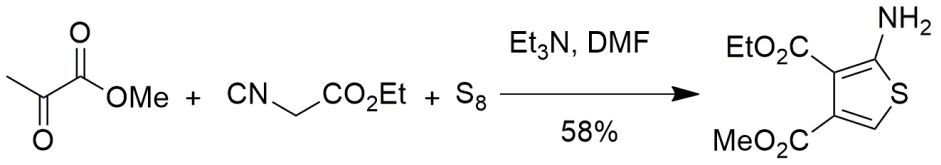
The benefit of organic solar cells (OSCs) over the conventional inorganic solar cells involves the low cost of production [18]. The low cost of production can be easily achievable if price of precursor are sufficiently low and easy availability. The most common precursor used in the synthesis of OSCs are the 3,4 disubstituted derivatives of thiophene molecule. Although, thiophene chemistry has been reported since long back, the cost of some precursors such as 3,4-dicyanothiophene as well 3,4-thiophene dicarboxylic acid are quite expensive. The synthesis of 3,4 disubstituted thiophene from thiophene involves lengthy and non selective procedures which end up yielding the 3,4-disubstituted thiophene in mixture or in low yield.

The traditional route for synthesis of 3,4-disubstituted thiophene uses Rosenmund-von Braun reaction [19]. This overall four steps reaction mainly involves reaction of 3,4-dibromo thiophene with cuprous cyanide affording expected compound in moderate yields (Scheme 2.1).



Scheme 2.1 Synthesis of 3, 4-disubstituted thiophene involving Rosenmund-von Braun reaction [19]

One of the common synthetic routes through which 3,4-disubstituted thiophene can be obtained was Gewald reaction (Scheme 2.2) [20]. This procedure has been regarded as a cheap and efficient method to synthesis amino functionalized 3,4-disubstituted thiophene in decent yield. To obtain 3,4-disubstituted thiophene from this precursor commonly standard Sandmeyer reaction was used [21]. Recently, Leclerc and coworkers have synthesized 3,4-thiophene dicarboxylate using the Gewald reaction followed by the Sandmeyer reaction to extrude the amino group [21].



Scheme 2.2 Synthesis of amino functionalized 3,4-disubstituted thiophene using Gewald reaction [20]

Kazuo Achiwa *et al* in 1986 used sila-Pummerer type rearrangement involving exclusion of disiloxane from bis(trimethylsilylmethyl) sulfoxide to yield dimethyl 2,5-dihydrothiophene-3,4-dicarboxylate as product [22]. However, it involves use of other expensive and non-easy accessible compounds.

We have developed a new methodology in which cheap and easily available maleic acid has been used as starting material. 3,4-Dimethyl thiophene dicarboxylate was used as a precursor for the synthesis of TPD (acceptor units) and BDT (donor units).

With suitable selection of electron withdrawing and electron releasing groups, the polymer can be modified yielding a significant change in the physical properties that are depended on the nature of the π-conjugation [23]. The ring-fused thiophene units in the conducting polymers contribute few advantages over the conventional thiophene units. The fused thiophene units provides an extended conjugation with more rigidity imparting increased intermolecular interactions in solid state and overall causes lowering of the band gap of the polymer. To maintain regioregularity of polythiophenes, symmetrical substitution at 3 and 4 positions of thiophene units are required [24]. The alkyl or aryl substituent at 3 and 4 positions create steric hindrance resulting in the twisting of polymer chains. To minimize these steric hindrances at 3 and 4 position substitutions in the form of fused ring (5-6 membered ring system) are introduced. Five-membered ring cyclopentyl system offers more planar conformation and thus creates least steric repulsion. Cyclopentane ring yields many advantages over other substituents. Substituents at 3 and 4 position avoid *β-β'* and *α-β'* coupling during electropolymerization [25]. Various research groups have reported methods on synthesis of cyclopenta thiophene (CPT) derivatives. Pioneer work on CPT molecule was reported from Mac Dowell *et al* in 1966 [26]. Y. Aso *et al* (2006) reported various CPT derivatives which were another significant contribution in the field of CPT [27].

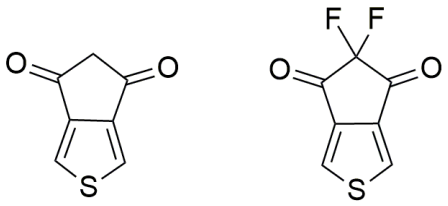
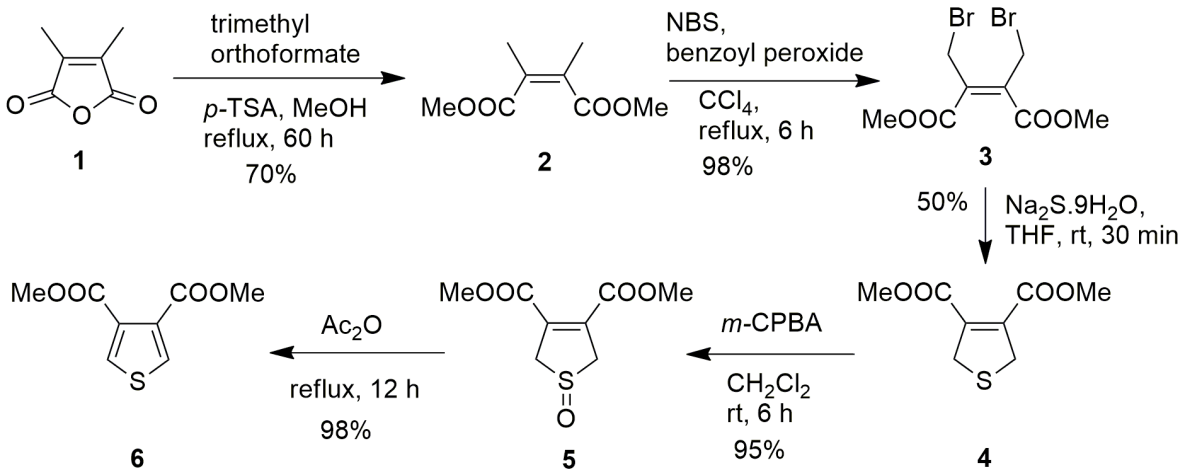


Figure 2.3 CPT derivatives reported by Y.Aso *et al* [28]

In present work, we report the synthesis of BDT (donor unit) and TPD (acceptor unit), two important building blocks for the conjugated polymers, from a single precursor, dimethyl thiophene-3,4-dicarboxylate **(6)**. This compound **6**, in turn, was synthesized from maleic anhydride. Along with that we developed method for synthesis of cyclopenta [*c*]thiophene-5, 5(*6H*)-dicarbonitrile **(20)** from dimethyl thiophene dicarboxylate without involving any transition metal mediated catalyst reaction step. This methodology involves economic, environmental benign conditions for synthesis of compound **20**.

2.2 Results and discussion

2.2.1 Experimental

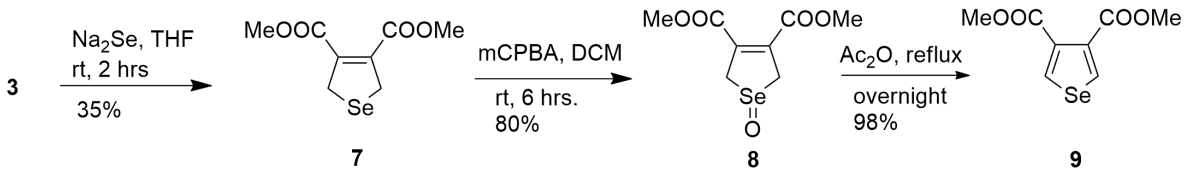


Scheme 2.3 Synthesis of 3,4 dimethyl thiophene dicarboxylate (**6**) from 2,3 dimethyl maleic anhydride (**1**) [28]

Synthesis of compound **6** was accomplished in six steps from maleic anhydride as shown in scheme 2.3. The maleic anhydride was converted in to 2,3-dimethyl maleic anhydride **(1)** following the reported procedure [29]. Compound **1** was further converted into 2,3-dimethyl dimethyl maleate **(2)** [30]. The bromination of compound **2** was carried out by NBS and benzoyl peroxide as an initiator [31]. Dibromo compound **3** was cyclized to dimethyl 2,5-dihydrothiophene-3,4-dicarboxylate **(4)** using sodium sulfide in THF as solvent at room temperature. Aromatization of compound **4** was accomplished by oxidation and followed by dehydration. Compound **4** was oxidized using *m*-CPBA to afford sulfoxide **(5)** and further dehydrated using acetic anhydride to afford compound **6**. This synthetic pathway to synthesize compound **6** is simple with overall yield of 32%.

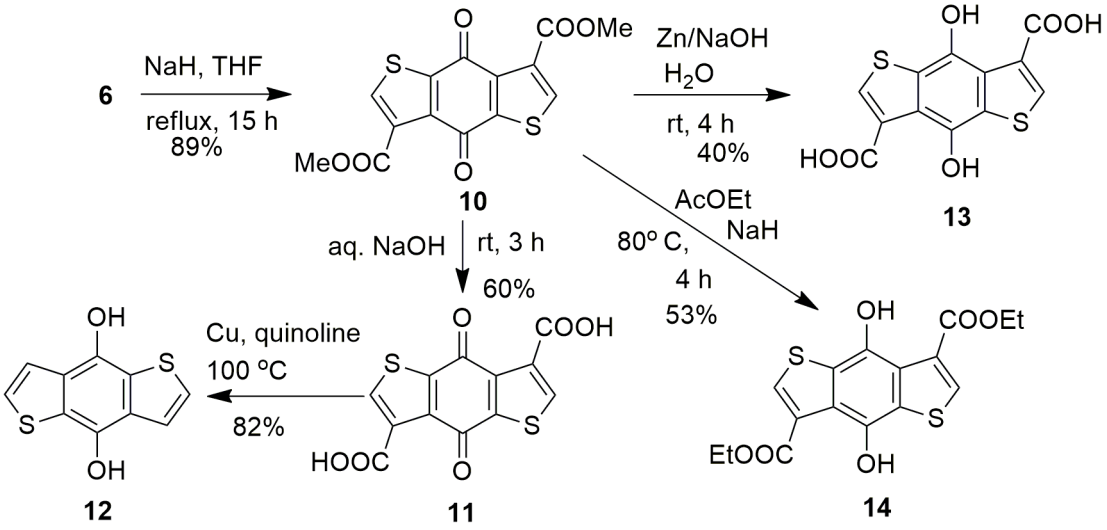
Oligo-selenophene and polyselenophene are often more rigid compared to its thiophene counterparts. Also, the substituent of the selenophene causes lesser twisting in the polymers preserving the planarity. Very few routes are available in the literature for the synthesis of substituted selenophene. We have synthesized dimethyl selenophene dicarboxylate by similar methodology (Scheme 2.4). Dibromo compound **3** was cyclized to

give compound **7** using Na_2Se in dry THF at room temperature stirring with yield of 35%. Compound **7** was later oxidized to using *m*-CPBA in DCM at room temperature stirring for 6 hours to yield compound **8** with 80% yield. Compound **8** was finally aromatized by treating with acetic anhydride under refluxing conditions for 12 hours, giving a colorless oil, 3, 4-dimethyl selenophene dicarboxylate **(9)** with 98% yield.



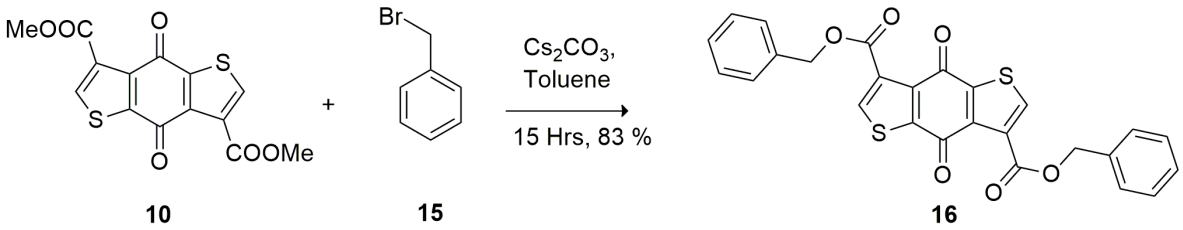
Scheme 2.4 Synthesis of 3, 4-dimethyl selenophene dicarboxylate (**9)**

Synthesis of 3,7-dimethyl-4,8-dihydrobenzo[*1,2-b:4,5-b'*]dithiophen-4,8-dione-dicarboxylate **(10)**, a precursor to dihydroxy benzodithiophene **12**, was accomplished by new and unconventional approach. Compound **10** was obtained by treating compound **6** with an excess of sodium hydride under refluxing condition in dry THF for 15 hours in 89% yield. The plausible mechanism of the formation of compound **10** may include the abstraction of α-H of compound **6** to form carbanion which reacts with carboxylate group of another molecule of compound **6** to cyclize into the *p*-benzoquinone moiety. Most common route to synthesize *p*-benzoquinonedithiophene comprises 3-thiophene carboxylic acid as starting material [32]. After functionalization of thiophene carboxylic acid into amide, *p*-benzoquinonedithiophene was obtained by treating resulting amide with *n*-BuLi at low temperature. In the synthesis of compound **10**, NaH effectively works as base due to presence of two electron-withdrawing carboxylate groups in compound **6**, which, in turn, increase the acidity of α-H of compound **6**. Compound **10** can be used as precursor to obtain many benzodithiophene derivatives. Additionally, the carboxylate groups may play an important role in controlling conformation by nonbonding interactions in the resulting conjugated systems [33]. The electron-withdrawing carboxylate substituent as the side chains are known to lower the HOMO level of the conjugated systems with minor effect on the optical bandgaps [34].



Scheme 2.5 Synthesis of various derivatives of compound **10** [28]

The diester **10** was hydrolyzed with aqueous NaOH to afford dicarboxylic acid **11**, which subsequently aromatize and decarboxylated by heating with Cu/quinolone to afford dihydroxy benzodithiophene **12**. When compound **10** was treated with aqueous NaOH solution in presence of Zn powder, it afforded dihydroxy benzodithiophene dicarboxylic acid **13**. Interestingly, when compound **10** was stirred with excess of NaH in ethyl acetate, aromatization with *trans*-esterification occurred to afford dicarboxylate **14** (Scheme 2.5).

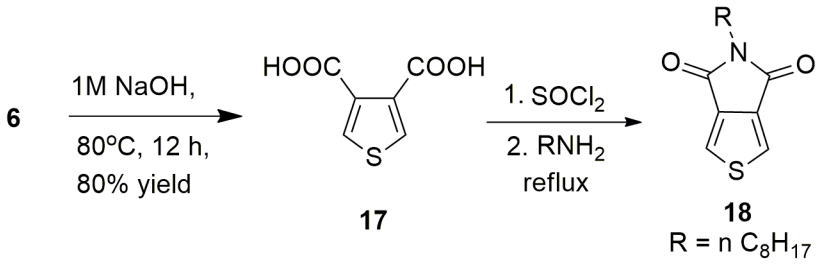


Scheme 2.6 Synthesis of dibenzyl 4,8-dioxo-4,8-dihydrobenzo[*1,2-b:4,5-b'*]dithiophene-3,7-dicarboxylate **(16)**

Dibenzyl diester derivative of BDT, dibenzyl 4,8-dioxo-4,8-dihydrobenzo[*1,2-b:4,5-b'*]dithiophene-3,7-dicarboxylate **(16)** was synthesized by treating compound **10** with benzyl bromide in presence of 1.2 equivalents of Cs_2CO_3 in dry toluene under refluxing conditions for 15 hours (Scheme 2.6). Compound **16** was isolated and purified by column chromatography to yield light yellow colored solid with yield of 83%. Compound **16**

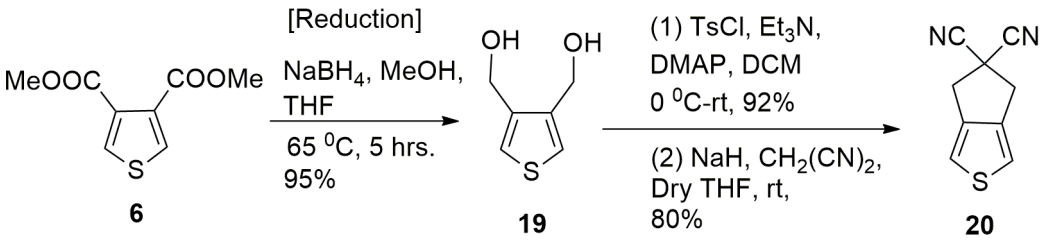
showed good solubility in organic solvents. Single crystal of compound **16** was obtained by slow evaporation from petroleum ether: ethyl acetate solvent system.

n-Octylthieno[*3,4-c*]pyrrole-4-6-dione (OTPD) **(18)** was synthesized from compound **6** in three steps, which mainly includes hydrolysis of compound **6** in aqueous NaOH solution followed by its reaction with thionyl chloride to form diacid dichloride and its subsequent reaction with alkyl amine in one-pot method (Scheme 2.7). The reported method for the synthesis of **18** involve condensation of 3,4-thiophene dicarboxylic acid (**17**) with appropriate amine [35].



Scheme 2.7 Synthesis of n-octylthenio[*3,4-c*]pyrrole-4-6-dione (OTPD) **(18)** [38]

Cyclopenta rings yields lesser steric hindrance and maintains more planarity in conjugated polymers. In present work, cyclopenta-thiophene derivatives are synthesized from compound **6**.



Scheme 2.8 Synthesis of cyclopenta[*c*]thiophene-5, 5(*6H*)-dicarbonitrile **(20)**

The synthesis of cyclopenta[*c*]thiophene-5, 5(*6H*)-dicarbonitrile **(20)** was carried out from dimethyl thiophene dicarboxylate which was synthesized from maleic anhydride by multiple steps

Synthesis of compound **20** was carried out from compound **6** in overall three steps (Scheme 2.8). Compound **6** was reduced using sodium borohydride/methanol system in

THF following the reported procedure [36] which affords compound **19** in good yield of 95%. The obtained *cis*-diol compound **19** was converted to *cis*-ditosylates intermediate using *p*-toulene sulfonyl chloride (*p*-TsCl) in dichloromethane (DCM) with dimethyl aminopyridine (DMAP)/triethylamine (TEA) conditions. Finally intermediate was reacted with malononitrile in presence of sodium hydride as base in dry tetrahydrofuran (THF) to yield solid compound **20** with yield of 80%. Compound **20** was purified by column chromatography and characterized by ^{1}H and ^{13}C NMR spectroscopy. Crystals were developed by slow evaporation and suitable crystals were diffracted confirming the structure by SCXRD experiment.

2.2.2. Photophysical properties

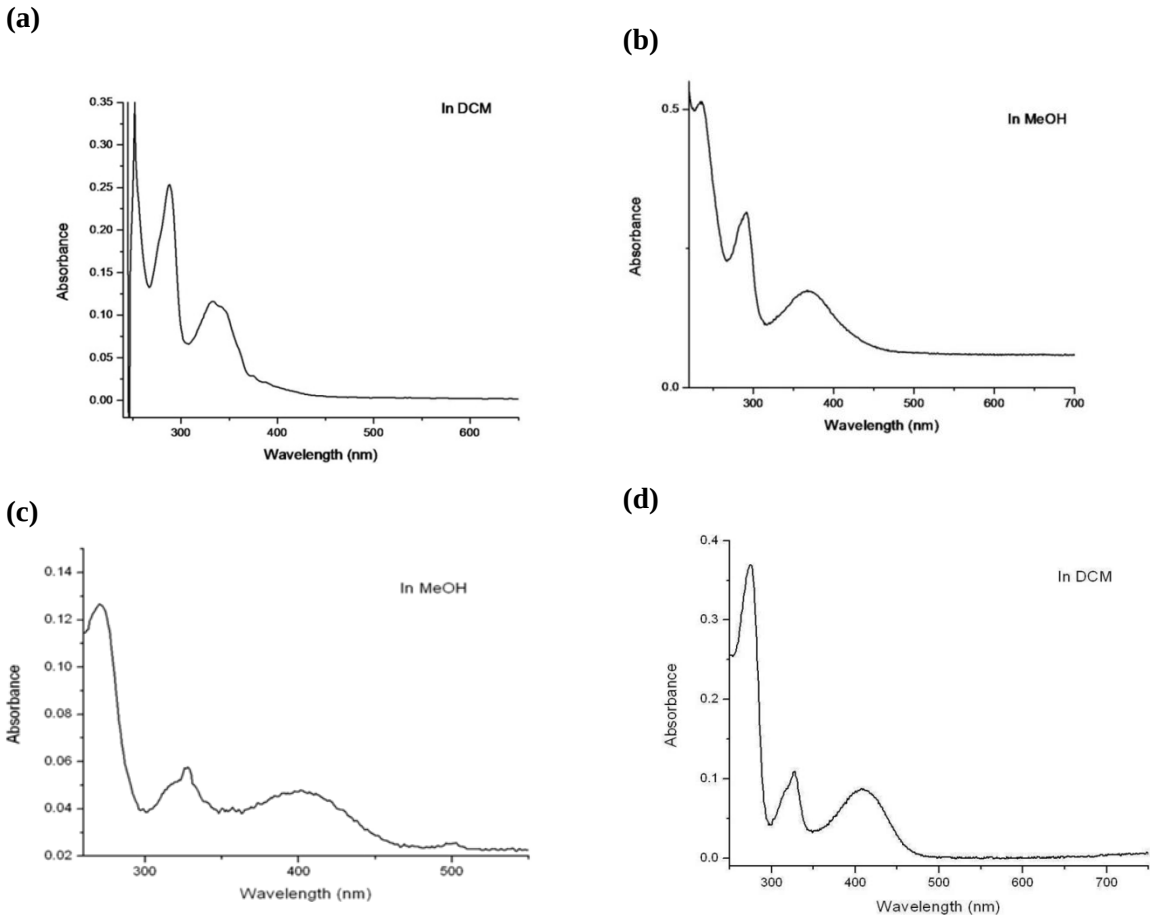


Figure 2.4 UV-visible absorption spectra of compound (a) compound **10** in DCM (b) compound **11** in MeOH (c) compound **13** in MeOH and (d) compound **14** in DCM

Compound **10**, **11** and **13** were green colored solid while compound **14** was yellow in color. Compounds **10** and **14** were soluble in non-polar solvent while **11** and **13** were soluble in methanol. Most of these compounds were showing three distinct absorption peaks. Compound **10**, **11**, **13** and **14** showed π-π* absorption peaks at 332, 407, 403, 368 nm respectively (Figure 2.4)

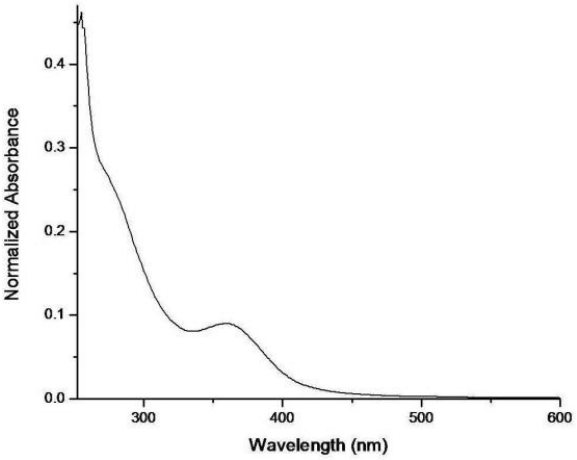


Figure 2.5 UV-visible absorption spectrum of compound **20**

The UV-visible spectrum of the compound **20** was obtained from the solution of compound in chloroform at concentration of 10^{-5} M (Figure 2.5). The absorption spectrum of compound **20** shows absorption maxima at 255 nm. A distinguishable hump was observed at 360 nm. This peak may be resulted from π -π* transitions [37]. The onset of the absorption has been observed around 418 nm.

2.2.3. Electrochemical properties

Cyclic voltammetry (CV) is a dynamic electrochemical method where current-potential curves are recorded at well-defined scan rates. This makes CV as very useful tool to determine the electrochemical properties and behavior of conjugated polymer/molecules. Often cyclic voltammetry is used with combination of UV/visible spectroscopy to estimate the band structure of the conjugated polymers and conjugated molecules. The measured oxidation potential of an electroactive substance correlates directly with ionization potential (Ip) and reduction potential to that of electron affinity.

(a) (b)

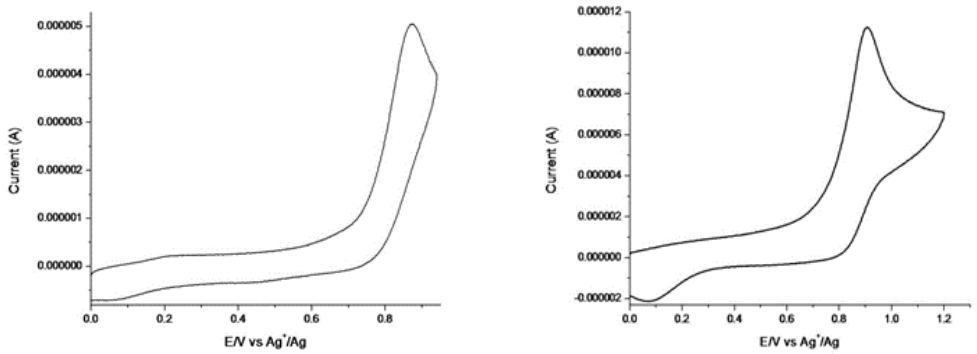


Figure 2.6 (a) CV of compound **11** and (b) CV of compound **14.** Curves were obtained in CH_3CN/DCM solution of $[Bu_4N]ClO_4$ at 50 mVs^{-1}

The CV experiment which was employed to determine the oxidation potential of compound **11** and **14** was consists of a three-electrode cell having Pt-disk working electrode, Pt-wire counter electrode and an Ag/Ag^+reference electrode using 0.1 M tetrabutylammonium perchlorate ($[Bu_4N]ClO_4$) as the supporting electrolyte in acetonitrile/DCM solution under nitrogen atmosphere.

The CV curves of compound **11** and **14** have reversible peak in oxidation region. The oxidation potential of compound **11** was obtained at 0.8 V, whereas for compound **14**, oxidation potential was obtained at 0.9 V versus Ag^+/Ag (Figure 2.6).

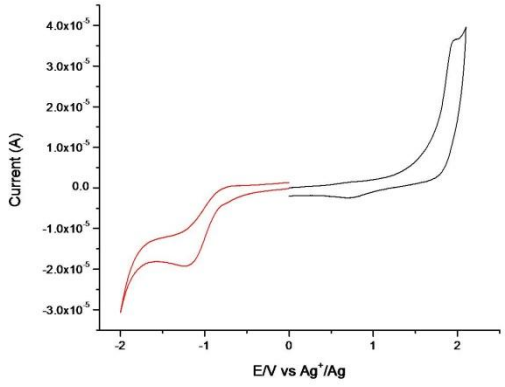


Figure 2.7 CV curves of compound **20.** CV curves were obtained in ACN solution having ($TBAPF_6$) (0.1 M) as electrolyte at a scan rate of 100 mV s^{-1}

Electrochemical analysis of compound **20** was carried out by cyclic voltammetry. The CV curve of compound **20** reveals one reversible oxidation peak and two reversible reduction peaks. The oxidation potential of compound **20** was obtained at 1.95 V. The reduction potential of compound **20** was obtained at -1.17 V. The onset of oxidation potential was found to be 1.42 V while onset for reduction potential was obtained as -0.92 V (Figure 2.7). The HOMO-LUMO values were calculated from these CV data which were obtained as HOMO energy levels -3.01 eV and LUMO energy levels at -5.32 eV. [(HOMO= - (E_{ox} + 4.40)eV) (LUMO= - (E_{red} + 4.40)eV)] [38].

2.2.4. Single crystal X-ray diffraction (SCXRD) study

Crystals of compound **10** and **14** suitable for single crystal X-ray diffraction were obtained by slow evaporation of saturated solution in hexane. The compound **10** was crystallizing with triclinic crystal packing system with space group *P-1*. Molecular structure of compound **10** possess centre of symmetry. The unit cell of compound **10** contains two non symmetric equivalent molecules (Figure 2.8). These two molecules differ in the dihedral angle between the plane of benzodithiophene and carboxylate group. Compound **10** shows π-stacking (C4…C10, 3.346 (3) Å) and intermolecular CH…O interaction (H4…O5, 2.479; H4…O6, 2.610 Å). These interactions result in the formation of 1-Dimensional molecular sheets along *a*-axis.

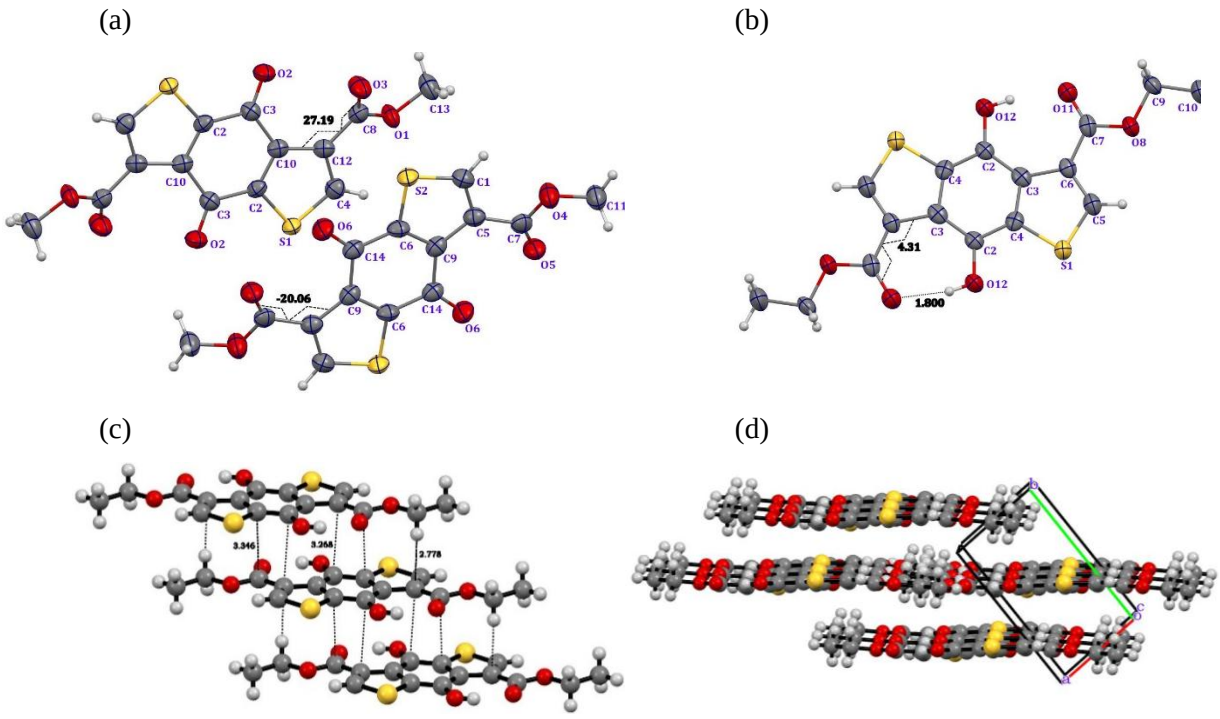


Figure 2.8 ORTEP diagram of compound (a) **10** and (b) **14** (ellipsoids are drawn at the 50% probability level). Packing diagram of **14** (c) showing π-stacking and CH…π interactions and (d) formation of parallel 1-D molecular sheets

Compound **14** crystallizes in *P-1* space group. In the structure of compound **14**, molecules possess centre of symmetry (Figure 2.8 (b)). Because of intramolecular hydrogen bonding between phenolic OH and C=O of carboxylate group (O11-H12, 1.80 Å; O12-H12…O11, 166.4°) compound **14** adopts nearly planar geometry (except H of COOEt groups). Compound **14** exhibit strong π-stacking (C2-C6′, 3.268 (3) Å; C4-C7′, 3.346 (3) Å), CH…π (H9B…C6, 2.778 Å) and intermolecular CH…O (H9A…O12, 2.642 Å) interactions to form π-stacked molecular chain along *a*-axis (Figure 2.8(c)). Molecules form one dimensional sheet along *c*-axis with interlayer distance of 3.326 Å.

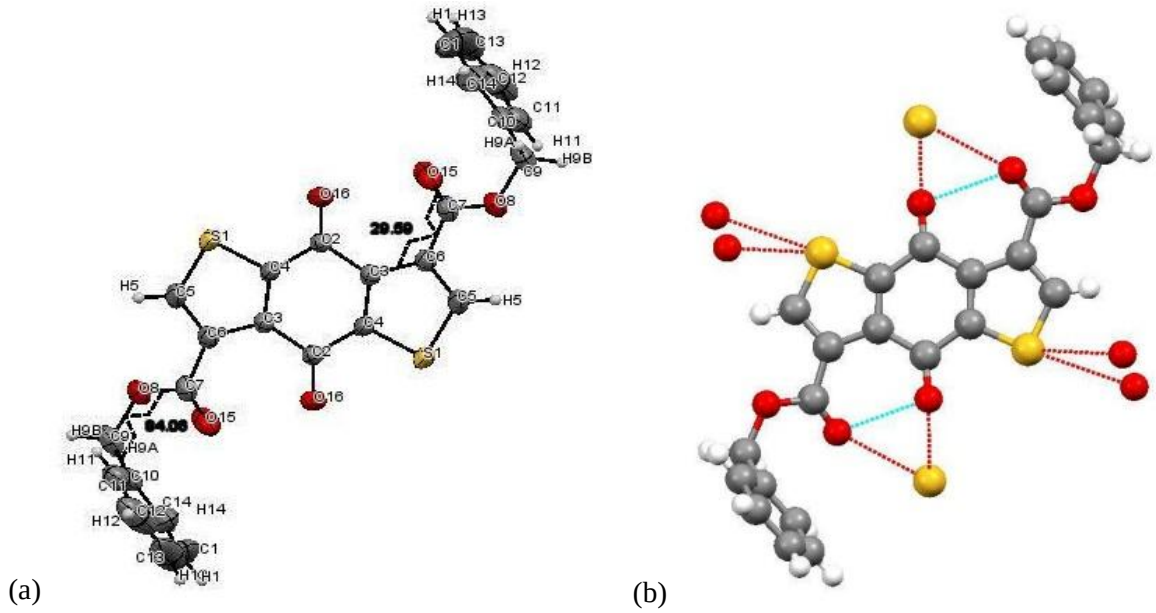


Figure 2.9 (a) ORTEP diagram of compound **16** (ellipsoids are drawn at the 50% probability level). (b) S-O intermolecular interactions and O-O intramolecular interactions

Compound **16** shows two phenyl rings oriented in opposite to each other. The phenyl rings are twisted at about 84^{o} with respect to the QDT ring, resulting in non-planer molecule. This twisting disrupts 1D/2D molecular sheet packing observed in the methyl and diethyl derivatives. Compound **16** shows two types of S-O intermolecular interactions (Figure 2.9). The S atom of benzodithiophene and O atom of carbonyl of ester (3.087 A) and another one is with O atom of quinone ring and with S atom of benzodithiophene (3.268 A).

(a) (b)

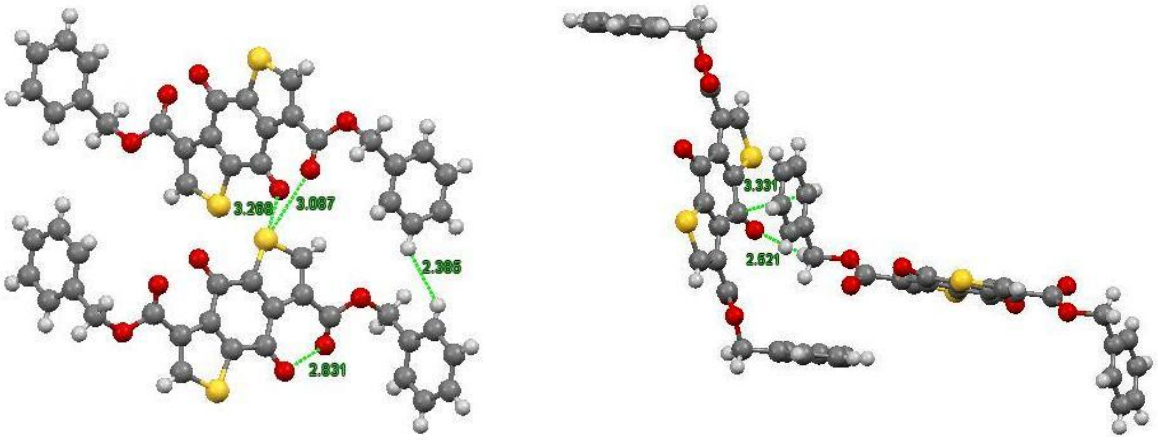
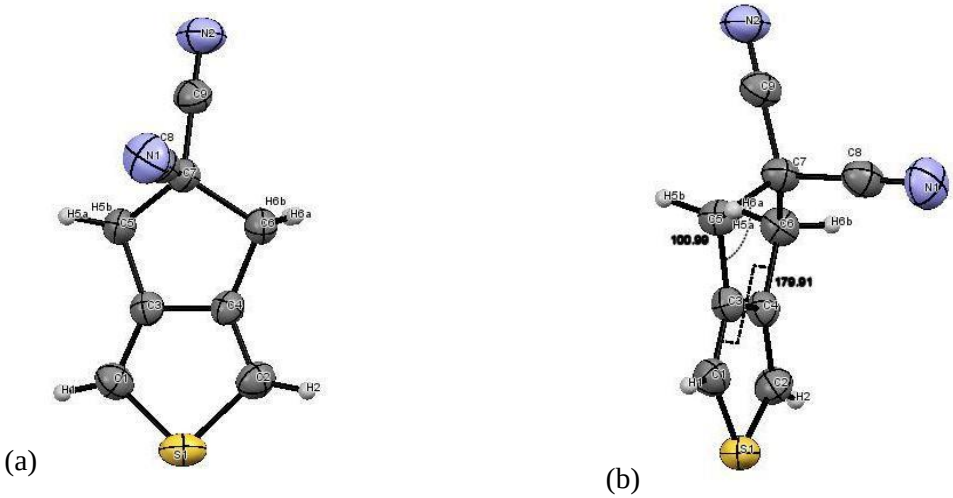


Figure 2.10 (a) S-O intermolecular interactions (b) packing diagram of molecule showing π-π stacking and C-H..π interactions observed in compound **16**

Alongwith S-O interaction, π-π stacking has been observed between phenyl ring and benzodithiophene rings (3.488 A). C-H..π interaction has been observed between CH_2 and benzodithiophene ring (2.521 A) (Figure 2.10).



(a) (b)

Figure 2.11 (a) ORTEP diagram of compound (ellipsoids are drawn at the 50% probability level). (b) Bond angles and dihedral angle of the compound **20**

Compound **20** crystallizes with orthorhombic crystal system and space group *Pbca* (Figure 2.11). The fusion of both rings has been almost planar with dihedral angle of 0.1^{o}

between thiophene and cyclopentyl ring. The carbon atom (C7) having dicyano groups bears bent of 34^{o} with respect to thiophene ring. The cyano groups are separated from each other by an angle of 108^{o}. Cyano groups of ring system involves in two types of strong intermolecular H-bonding. Nitrogen (N1 and N2) atoms of cyano group forms two different types of conventional H-boding with H6a and H5b atoms of two different molecules. N1 atom of cyano group showed H-bonding interaction with H5b of $–CH_2$ group (N1…H5b, 2.688Å) of cyclopentyl ring while other nitrogen atom (N2) possesses-bonding interaction with H6a of $–CH_2$ group (N2…H6a, 2.703 Å). The H-bonding interaction arose from N2…H6a reciprocates between two molecules. Along with this S-H intermolecular H-bonding interaction has been also observed in the crystal structure. S-atom of thiophene ring shows S-CH_2 interaction with H5a atom of neighboring cyclopentyl ring (S…H5a, 2.952 Å).

2.2.5. Computational data

Theoretical calculations were done using density functional theory (DFT) which were carried out with the Gaussian 09 [39] series of programs. Becke's three-parameter exchange functional combine with the LYP correlation functional (B3LYP) was used. The geometric optimization was carried out for synthesized benzodithiophene derivatives. The calculated data was used to develop the understanding of FMO and electronic distribution in the benzodithiophene derivatives. These data will be helpful to seek its applications in organic-electronic devices.

The crystal structures of compound **10** and **14** were used as input data and it was observed that calculated data after geometric optimizations were in good agreement with the experimental data. Similarly, for compound **11** and **13** data was calculated by geometric optimizations (Figure 2.12).

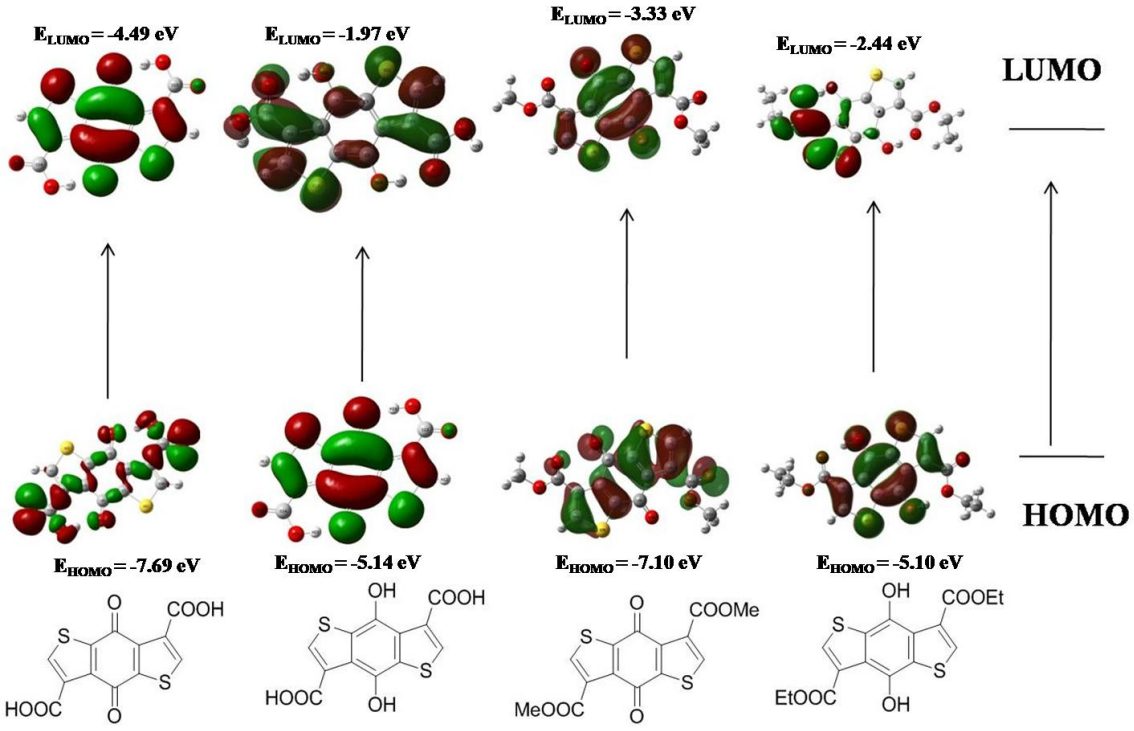


Figure 2.12 Representations of HOMO-LUMO and its values for compound **10, 11, 13** and **14**

Calculated data provided geometric parameters for compound **10** which was having *C1* symmetry point group. The dipole moment was calculated to be 2.8256 Debye and the global energy minimum was -1786.023 a.u. Similarly, for compound **11** symmetry point group was found to be *C1* and dipole moment was calculated 0.0044 Debye. The global energy minimum was -1707.424.

Computational data of compound **13** revealed its symmetry point group as *C1* and dipole moment as 2.853 Debye with global energy minimum to be -1708.641. For compound **14**, *C1* symmetry point group was calculated with dipole moment of 3.406 Debye and global energy minimum was -1865.897.

Theoretical Highest Occupied Molecular Orbital (HOMO) energy levels and theoretical Lowest Occupied Molecular Orbital (LUMO) energy levels were calculated from the DFT calculations. The HOMO energy levels of compound **10** and **11** were calculated as -7.10 eV and -7.69 eV, while LUMO energy levels were found to be -3.33 eV and -4.49 eV respectively. The band gap calculated for compound **10** was 3.7 eV and for

compound **11** was 3.20 eV. For compound **13** and **14**, HOMO energy levels were calculated -5.14 eV and -5.10 eV while LUMO energy levels were obtained as -1.97 eV and -2.44 eV. The band gaps were calculated for compound **13** was 3.17 eV and for compound **14** was 2.65 eV (Table 2.1).

Table 2.1 Calculated HOMO-LUMO energies of compounds

Compound	**Compound 11**	**Compound 13**	**Compound 10**	**Compound 14**
HOMO	-7.69 eV	-5.14 eV	-7.10 eV	-5.10 eV
LUMO	-4.49 eV	-1.97 eV.	-3.33 eV	-2.44 eV
Band gap	3.20 eV	3.17 eV	3.7 eV	2.65 eV

The calculated data shows band gap of compound **13** and **14** to be low when compared to compound **10** and **11**. The possible reason suggested that since compound **13** and compound **14** possesses aromatic core, which results in more planar structure, thus conjugation among the core benzene and peripheral thiophene rings enhances lowering the overall band-gap.

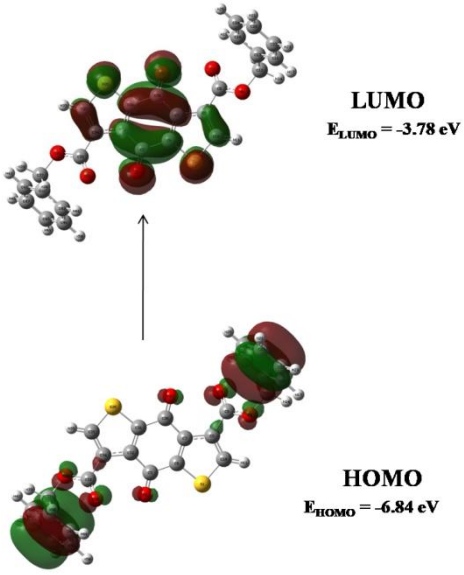


Figure 2.13 HOMO-LUMO representations of compound **16**

Computational studies of dibenzyl 4,8-dioxo-4,8-dihydrobenzo[*1,2-b:4,5-b'*]dithiophene-3,7-dicarboxylate **(16)** were performed using DFT. Crystal data was used as input file on which geometric optimization was done. The FMO analysis showed that HOMO energy level of compound was localized in the outer phenyl rings and valued -6.84 eV, whereas, LUMO was uniformly distributed over the BDT ring system with value of -3.78 eV (Figure 2.13). The calculated energy band gap of the molecule was 3.06 eV.

Quantum chemical data of compound **20** were obtained by DFT calculation carried on Gaussian 09 software. Obtained theoretical data was used to develop the understanding regarding the FMO and structural properties (Figure 2.14).

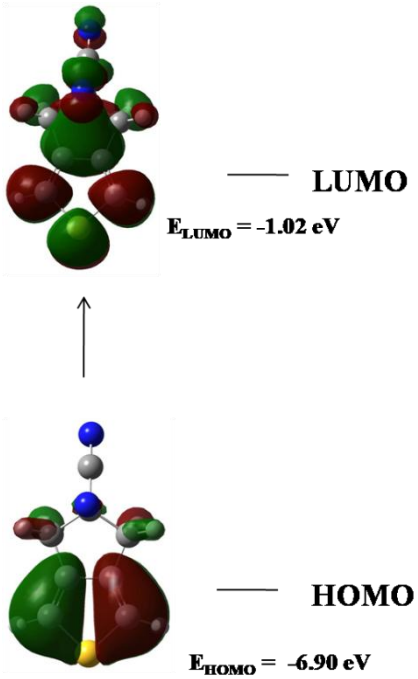


Figure 2.14 HOMO-LUMO representations of compound **20**

The calculations were performed for geometric optimization for which structural data from SCXRD experiments were used. The optimized structure showed a good agreement with the SCXRD data. The global energy minimum calculated for the optimized structure was -854.200 and the structure have *C1* symmetry point group. The calculated dipole moment of optimized structure was 4.268 Debye. The fusion of thiophene and cyclopenta ring was almost planar (with torsion angle of 0.52^{o}). The optimized structure showed interplanar angle of 29.8^{o} (in crystal structure it was obtained as 34.0^{o}).

The frequency calculations of molecule were done to obtain theoretical IR spectra. These calculated frequencies values were correlated with experimental values and this data was further used to predict the nature of experimental frequencies. The predicated vibrational spectra had no imaginary frequency. The cyano group (C≡N) stretching experimentally observed at 2248 cm^{-1} which was obtained at 2371 cm^{-1} in theoretical spectrum. The skeletal vibration of thiophene ring (C=C) was obtained at 1636 and 1430 cm^{-1}(experimental) comparable to the theoretical values of 1633 and 1428 cm^{-1}. The C-H in plane and outplane bending vibrations were found at 1381 and 1164 cm^{-1}corresponding to 1331 and 1109 cm^{-1}values of theoretical one.

TD-DFT data for compound 20

To predict the UV-visible spectra of the compound TD-DFT/PCM method was used with basis set 6-31G at B3LYP level. (Figure 2.15) The dichloromethane solvent was used under PCM condition. The calculated UV-visible spectra of compound **20** showed broad absorption range from 230 nm to 370 nm. Electronic transition at 312 nm arises from *HOMO→ LUMO* transition with contribution of 70%. The electronic transitions at 283 nm and 277 nm were obtained due to *HOMO-1→ LUMO* (64%, 28%) and *HOMO→ LUMO+1* (28%, 64%) transitions respectively. These data show that the lowest singlet excitation was resulted from *HOMO→ LUMO* transitions involving π-π* type transitions.

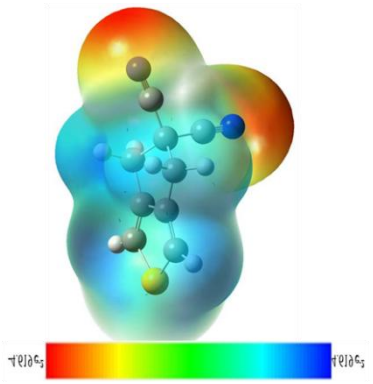


Figure 2.15 B3LYP/6-31G(d) calculated electrostatic potential of compound **20**

The *HOMO-LUMO* distribution of compound revealed that the *HOMO* energy levels concentrate to the thiophene ring whereas the *LUMO* levels reside with the electron withdrawing groups CN (Figure 2.15). The electrostatic potential map of the molecule shows the CN groups part of molecule was more negatively charged compared to the thiophene rings.

2.3 Conclusion

In summary, dimethyl thiophene dicarboxylate, a precursor for conjugated polymers, was synthesized from maleic anhydride in simple six-step synthetic pathway involving mild reagents and in moderate yield. Similarly, dimethyl selenophenedicarboxylate was synthesized. Dimethyl thiophene dicarboxylate diester

obtained was successfully converted into TPD and BDT derivatives which were useful building blocks for π-conjugated polymer. TPD, BDT and CPT derivative were synthesized, characterized by NMR and SCXRD.

Single crystal data revealed that benzodithiophene dicarboxylate derivative forms 1D- molecular sheet type structures in solid state. Along with these theoretical studies showed that conversion of quinone derivative to benzoquinone derivative decreases the bandgap of the molecules. Crystal data of compound **20** showed that ring system is planar and the cyano groups facilitate intermolecular H-bonding. Theoretical data suggest cyano exerts electron withdrawing effect on this CPT ring system.

2.4 Experimental section

2.4.1 General

All chemicals were reagent grade and were used as purchased. Moisture sensitive reactions were performed under an inert atmosphere of dry nitrogen with dried solvent. THF was dried over sodium/benzophenone and was distilled prior to use. Reactions were monitored by TLC analysis using Merck silica gel 60 F-254 thin-layer plates. Column chromatography was done on Silica Gel (60-140 mesh). NMR spectra were recorded on Jeol-ECS/ Bruker AV-III 400 MHz spectrometer using $CDCl_3$/DMSO-d_6 as solvent and chemical shifts are reported in parts per million (δ scale) relative to tetramethylsilane (TMS) as the internal standard.

Fine crystals of compound **16** and **20** were collected on a SuperNova, Dual, Cu/Mo at zero, Eos diffractometer. Using Olex2 [40] the structure was solved with the Superflip [41] structure solution programme applying Charge Flipping and refined with the ShelXL [42] refinement package applying Least Squares Minimization.

2.4.2 Synthesis

2.4.2.1 Dimethyl 2,3-dimethylmaleate (2) [30]

Dimethyl maleic anhydride 5.30g (42 mmol) in 50 mL methanol was taken in round-bottom flask. To this solution 5.885g (55.52 mmol) of trimethyl orthoformate and 1.050g (5.530 mmol) of *p*-toluene sulfonic acid (*p*TSA) was added. The reaction mixture was refluxed for 60 hours under nitrogen atmosphere. The excess of methanol was removed under reduced pressure and the crude product was purified by column chromatography (SiO_2, hexane: ethyl acetate, 9:1) to give pale yellow liquid (yield 5.06g, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.76 (s, 6H), 1.94 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.2, 51.8, 133.1, 168.9. IR (KBr) (cm^{-1}): v 2999, 2953, 1741, 1725, 1647, 1436, 1298, 1270, 1198, 1165, 1100.

2.4.2.2 Dimethyl 2,3-bis(bromomethyl)maleate (3) [31]

Dimethyl 2,3-dimethylmaleate 10.0g (0.058 mol) was taken in the round-bottom flask containing 80 mL of CCl_4. To this mixture 23.0g (0.129 mol) *N*-bromosuccinimide (NBS) was added in one portion and 2.131g (0.0088 mol) of benzoyl peroxide was added alongwith it. The reaction mixture was refluxed for 6 hours under nitrogen atmosphere. The reaction mixture was cooled to room temperature and was filtered. The filtrate was concentrated under low pressure to obtain product as pale yellow oil (yield 19.06g, 98%). Two isomers obtained in 1:1 ratio. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.50 (s, 4H), 4.27 (s, 4H), 3.93 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.2, 26.9, 52.9, 53.0, 53.3, 128.4, 130.2, 133.7, 137, 165.5, 166.0.

2.4.2.3. Dimethyl thiophene-3,4-dicarboxylate (6)

Dimethyl 2,3-bis(bromomethyl)maleate (**3**) (11.39g, 34.5 mmol) was dissolved in 60 mL of THF taken in dry round bottom flask and stirred at room temperature. To this solution $Na_2S.9H_2O$ (9.94g, 41.4 mmol) was added portion wise. After complete addition the solution was stirred for 1 hour during which color of reaction mixture turn black. The reaction mixture was filtered off and the filtrate was concentrated to get crude product which was purified by column chromatography (SiO_2, hexane: ethyl acetate, 8:2). Compound **4** was obtained as a pale yellow liquid (yield, 3.50g, 50%) and used for the next reaction. Compound **4** (3.46g, 17.1 mmol) was dissolved in 50 mL chloroform and cooled to 0^o C. The solution of *meta*-chloroperbenzoic acid (*m*-CPBA) (2.95g, 17.1 mmol) in 15 mL of chloroform was added drop-wise to the reaction mixture. After addition was over the reaction mixture was stirred at room temperature for more 5 hours. Work-up involves water washing and extraction of the compound in dichloromethane. Organic layer was dried over sodium sulfate and concentrated to afford compound **5** as yellow viscous oil (yield 3.54g, 95%) which was used for the next reaction without any further purification. Compound **5** (3.25g, 14.9 mmol) and 50 mL acetic anhydride was taken in round bottom flask. The reaction mixture was refluxed under nitrogen for overnight. The acetic anhydride was removed under reduced pressure to obtain dimethyl thiophene-3,4-dicarboxylate as colorless oil (yield 2.92g, 98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (s, 2H), 3.88 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 52.3, 131.9, 133.1, 163.4. IR (KBr) (cm^{-1}): ν 3109, 3000, 2953, 1747, 1579, 1520, 1455, 1283, 1122, 1049.

2.4.2.4 3,4-dimethyl selenophene dicarboxylate (9)

Dimethyl 2,3-bis(bromomethyl)maleate **(3)** (7.32g, 22.1 mmol) was dissolved in 40 mL of dry THF taken in dry round bottom flask and stirred at room temperature. To this solution freshly prepared Na_2Se in dry THF (3.04g, 24.3 mmol) was added portion wise at 0^o C. After complete addition the solution was stirred for 1 hour during which color of reaction mixture turn black. The resulting solution was filtered off and the filtrate was concentrated to get crude product which was purified by column chromatography (SiO_2, hexane: ethyl acetate, 8:2). Compound **7** was obtained as pale yellow oil (yield, 1.93g, 32%) and used for the next reaction. Compound **7** (1.8g, 10.0 mmol) was dissolved in 20 mL DCM and cooled to 0^o C. The solution of *meta*-chloroperbenzoic acid (*m*-CPBA) (1.73g, 10.0 mmol) in 5 mL of DCM was added drop-wise to the reaction mixture. After addition was over the reaction mixture was stirred at room temperature for more 5 hours. Work-up involves water washing and extraction of the compound in dichloromethane. Organic layer was dried over sodium sulfate and concentrated to afford compound **8** as dark yellow viscous oil (yield 1.54g, 80%) which was used for the next reaction without any further purification. Compound **8** (1.5g, 10 mmol) and 20 mL acetic anhydride was taken in roundbottom flask. The reaction mixture was refluxed under nitrogen atmosphere for overnight. The acetic anhydride was removed under reduced pressure to obtain 3, 4-dimethyl selenophene dicarboxylate as yellow viscous oil (yield 1.61g, 98%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57 (s, 2H), 3.88 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 52.3, 133.9, 137.1, 164.4.

2.4.2.4 3,7-dimethyl-4,8-dihydrobenzo[*1,2-b:4,5-b'*]dithiophen-4,8-dione-dicarboxylate (10)

Dimethyl thiophene-3,4-dicarboxylate 0.4g (0.002 mol) was dissolved in 60 mL dry THF under nitrogen atmosphere. To this solution 0.96g (0.04 mol) of NaH (60% suspension in mineral oil) was added portion wise and reaction mixture was refluxed for 15 hours. After completion of reaction the solvent was evaporated under reduced pressure. The

product was extracted with ethyl acetate, dried over sodium sulfate and concentrated to obtain crude product which was further purified by column chromatography (SiO_2, hexane:EA, 7:3) to afford light green solid, (yield 0.30g, 89%). M.P 194 ^oC (dec). ^1H NMR (400 MHz, $CDCl_3$): δ 8.07 (s, 2H), 3.97 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 52.9, 133.7, 143.2, 162.9, 172.9. Elemental Analysis for $C_{14}H_8O_6S_2$: %C: 49.80 (49.99); %H:2.59 (2.40); %S:19.27 (19.07). Values in parentheses are calculated values.

2.4.2.5 4,8-dioxo-4,8-dihydrobenzo[*1,2-b:4,5-b'*]dithiophene-3,7-dicarboxylic acid (11)

3, 7-dimethyl-4,8-dihydrobenzo[*1,2-b:4,5-b'*]dithiophen-4,8-dione-dicarboxylate 0.12g (0.357 mmol) was taken in round bottom flask. 10% aqueous NaOH solution was added to it and the reaction mixture was allowed to stir at room temperature for 3 hours. After completion of reaction the reaction mixture was acidified by dilute HCl till pH 3-4. The green colored product was precipitate out, filtered and dried (yield 66 mg, 60%). M.P 280 ^oC (dec). ^1H NMR (400 MHz, DMSO-d_6): δ 8.14 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 133.1, 137.7, 142.3, 147.2, 163.6, 173.2. IR (KBr) (cm^{-1}): *v* 3107 (sh), 2951, 1741, 1694, 1657, 1560, 1523, 1464, 1281. Elemental Analysis for $C_{12}H_4O_6S_2$: %C, 46.35 (46.75); %H 1.22 (1.31); %S 20.98 (20.80). Values in parentheses are calculated values.

2.4.2.6 Diethyl 4,8-dihydroxybenzo[*1,2-b:4,5-b'*]dithiophen-3,7-dicarboxylate (14)

3,7-Dimethyl-4,8-dihydrobenzo[*1,2-b:4,5-b'*]dithiophen-4,8-dione-dicarboxylate 0.200g (0.6 mmol) was dissolved in 30 mL ethyl acetate. To this solution, NaH 0.043g (1.8 mmol) was added and solution was stir at room temperature for 4 hours. Crude product was isolated by aqueous workup, and compound was purified by column chromatography (SiO_2, Hexane:EA, 9:1) as a yellow solid (yield 0.115g, 53%). M.P 222 ^oC (dec); UV-visible in DCM: λ_{max} (nm) = 407. ^1H NMR (400 MHz, $CDCl_3$): δ 11.61 (s, 1H), 8.44 (s, 2H), 4.49-4.45 (q, 4H, J= 7 Hz), 1.47-1.44 (t, 6H, J= 7 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.2, 62.5, 120.8, 125.6, 126.2, 139.6, 139.9, 166.1. IR (KBr) (cm^{-1}): *v* 3118, 3053, 2978, 1725,

1660, 1465, 1447, 1278, 1229, 1080. Elemental Analysis for $C_{16}H_{14}O_6S_2$: % C: 52.40 (52.45); % H: 3.90 (3.85); %S: 17.62(17.50). Values in parentheses are calculated values.

2.4.2.7 4,8-dihydroxybenzo[*1,2-b:4,5-b'*]dithiophene-3,7-dicarboxylic acid (13)

3,7-Dimethyl-4,8-dihydrobenzo[*1,2-b:4,5-b'*]dithiophen-4,8-dione-dicarboxylate 0.155g (0.4613 mmol) was taken in round-bottom flask. To this solution Zn powder 75 mg (1.153 mmol) and NaOH 2.76g (0.069 mol) in water:ethanol (10:1) system was added. This reaction mixture was refluxed for 3 hours. After completion of reaction dark purple coloration were observed. The reaction was acidified by using dilute HCl till pH 3. The crude product was precipitates, filtered and dried (yield 62 mg, 40%). M.P 310 ^oC (dec). ^1H NMR (400 MHz, DMSO-d_6): δ 11.62 (s, 1H), 8.21 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 129.3, 133.1, 137.8, 138.0, 147.2, 163.6, 164.3. IR (KBr) (cm^{-1}): v 3450 (br), 3113, 1710, 1658, 1489, 1465, 1265. Elemental Analysis for $C_{12}H_6O_6S_2$: % C: 46.30 (46.45); % H: 1.92 (1.95); % S: 20.79 (20.67). Values in parentheses are calculated values.

2.4.2.8 Benzo[*1,2-b:4,5-b'*]dithiophene-4,8-diol (12)

3,7-Dimethyl-4,8-dihydrobenzo[*1,2-b:4,5-b'*]dithiophen-4,8-dione-dicarboxylate 90 mg (0.29 mmol) was taken in round-bottom flask. To this reaction mixture 46 mg (0.732 mmol) of Cu powder and 10 mL of quinoline was added. The reaction mixture was heated at 100 ^oC for 1 hour. After completion of the reaction 1M HCl was added. The product was extracted with DCM and dried over sodium sulfate, concentrated to afford the product. Crude product was further purified on column chromatography (SiO_2, Hexane:EA, 4:1). The colorless solid was obtained (yield 53 mg, 82%). M.P 240 ^oC (dec). ^1H NMR (400 MHz, $CDCl_3$): δ 7.19 (d, 2H), 7.17 (d, 2H), 4.62 (b, 2H). Elemental Analysis for $C_{10}H_6O_2S_2$: % C: 54.33 (54.03); % H: 2.95 (2.72); % S: 28.62 (28.85). Values in parentheses are calculated values.

2.4.2.9 Dibenzyl 4,8-dioxo-4,8-dihydrobenzo[*1,2-b:4,5-b'*]dithiophene-3,7-dicarboxylate (16)

In dry three neck round bottom flask 3,7-dimethyl-4,8-dihydrobenzo[*1,2-b:4,5-b'*]dithiophen-4,8-dione-dicarboxylate (45 mg) (0.145 mmol) was taken. To this dry toluene (10 ml) and 1.1 equivalents of benzyl bromide (0.247 mmol) was added and stirred at room temperature kept under nitrogen atmosphere. 1.2 equivalents of Cs_2CO_3 was added and reaction mixture was heated to reflux for 15 hours. The completion of reaction was confirmed by consumption of starting material monitored by TLC. On completion of the reaction the ethyl acetate was added and then water was added. The organic layer was separated, dried over sodium sulphate, concentrated under reduced pressure to yield crude product. The product was further purified by column chromatography using SiO_2 and (30:70 EA:PE) solvent system to yield yellow solid compound. (yield 83%). M.P 330 ^oC (dec) ^1H NMR (400 MHz, $CDCl_3$): δ 5.14 (s, 2H) 7.37-7.43 (m, 3H), 7.47-7.50 (m, 1H), 8.10 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 67.9, 128.5, 128.6, 133.6, 135.1, 137.1, 137.9, 148.1, 162.2, 172.6.

2.4.2.10 3,4-Bis(hydroxymethyl)thiophene (19)

12 equivalents of sodium borohydride was suspended in the dry THF. The suspension was heated at 65 ^oC for 15 minutes stirring under nitrogen atmosphere. The solution of dimethyl thiophene-3,4-dicarboxylate in THF was added dropwise to this solution. After complete addition 10 mL of methanol was added dropwise over period of 1 hour during addition effervescence being observed. The reaction was heated with stirring at 65^oC for 5 hours. The reaction mixture was cooled to room temperature and the residual solvent was evaporated and washed with aqueous ammonium chloride solution and extracted with DCM, dried over sodium sulfate and concentrated to yield 3,4-bis(hydroxymethyl)thiophene as product.

^1H NMR (400 MHz, $CDCl_3$, ppm): δ 3.15 (s, OH), 4.67 (s, 4H), 7.24 (s, 2H)

2.4.2.10 4*H*-Cyclopenta[*c*]thiophene-5,5 (*6H*)-dicarbonitrile(CPTDC) (20)

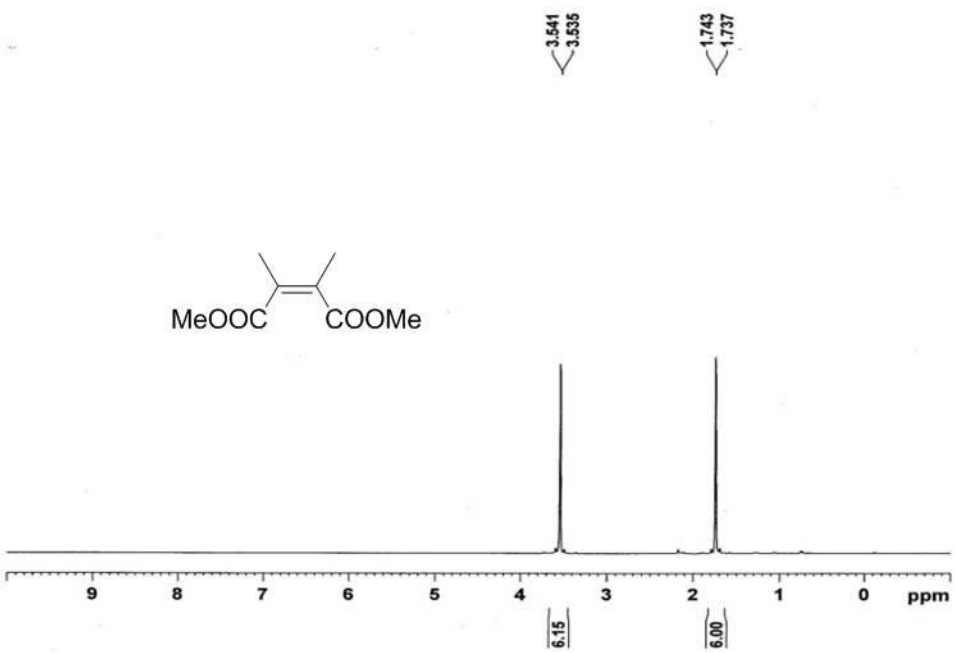
1.2g (0.008 mol) 1 equivalent of 3,4-Bis(hydroxymethyl)thiophene was taken in dry DCM (10 mL) under nitrogen atmosphere. To this solution (2.4g, 0.024 mol) 3 equivalents of TEA was added alongwith catalytic amount of DMAP (0.39g, 0.0032 mol) (0.4 equivalents) at 0 ^{0}C temperature. *p*-TsCl (3.64 g, 0.0192 mol) 2.4 equivalents was added to this solution at 0 ^{0}C. The reaction mixture was allowed to reach to room temperature and stirred for overnight. Excess of solvent was evaporated and crude product was repeatedly washed with water. The crude product was extracted with DCM and dried over sodium sulfate. The extract was concentrated under low pressure to yield colourless oil. The product was directly used for next step without further purification.

To this crude product 15 mL of dry THF was taken and the solution was cooled down to 0 ^{0}C. To this solution of sodium hydride (0.57g, 0.024 mol) 3 equivalents was added portion wise under nitrogen atmosphere with constant stirring. 1.2 equivalents of malononitrile (0.63g, 0.0096 mol) was added dropwise to this mixture solution having 1 equivalent of the product in 10 mL dry THF. The reaction mixture was stirred under nitrogen atmosphere at room temp for 8 hours. Excess of solvent was evaporated under low pressure, washed with water and extracted in ethyl acetate. The resulting extract was concentrated to yield crude product which was further purified by column chromatography on silica (7:3 hexane-ethyl acetate) to afford pale yellow solid compound. Yield = 1.16g (80%).

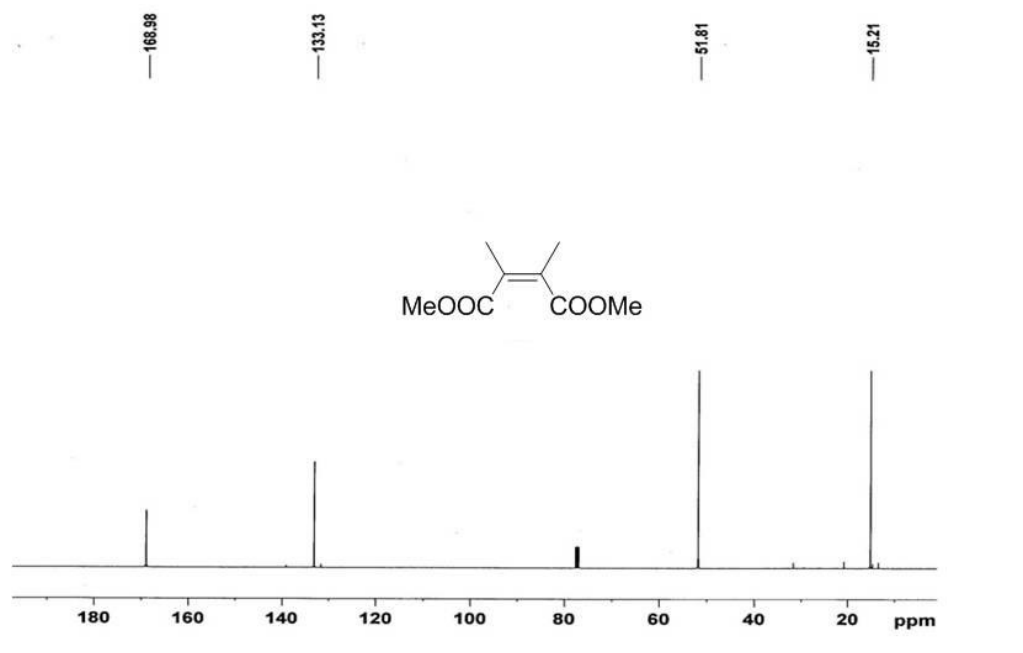
IR (KBr) (cms^{-1}): ν 3133, 2248, 1636, 1430, 1381, 1164, 1077, 719. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 3.52 (s, 4H), 7.05 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 29.6, 39.7, 115.8, 118.2, 139.5. Elemental Analysis for $C_9H_6N_2S$: C, 62.09 (62.05); H, 3.44 (3.47); N, 16.05 (16.08); S, 18.42 (18.40). The values in parenthesis were calculated values.

2.5 Spectra data

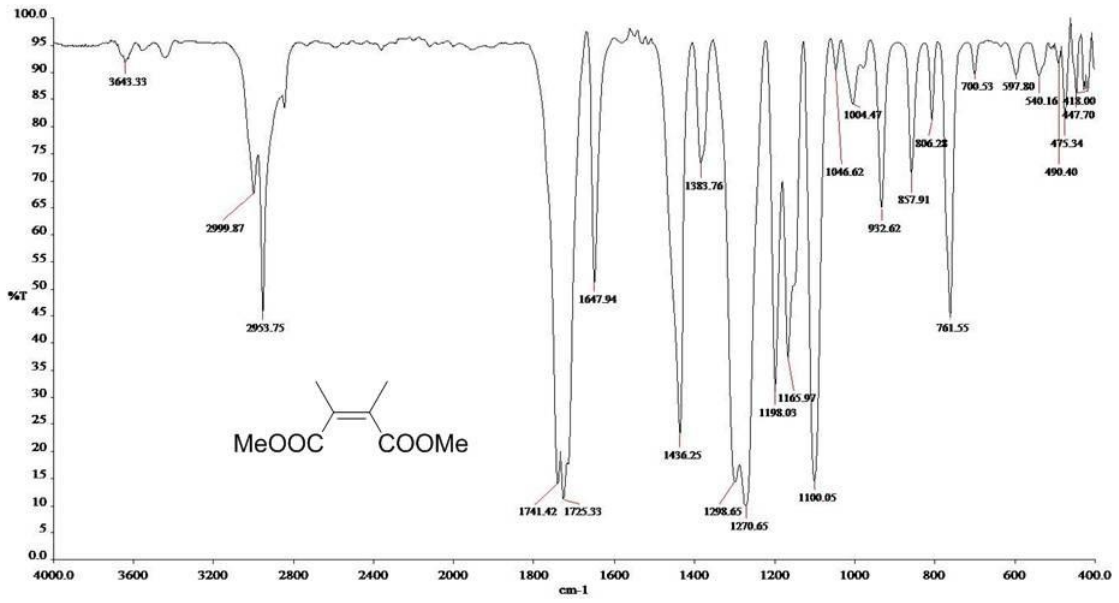
2.5.1 Dimethyl 2,3-dimethylmaleate (2)



^{1}H NMR spectrum

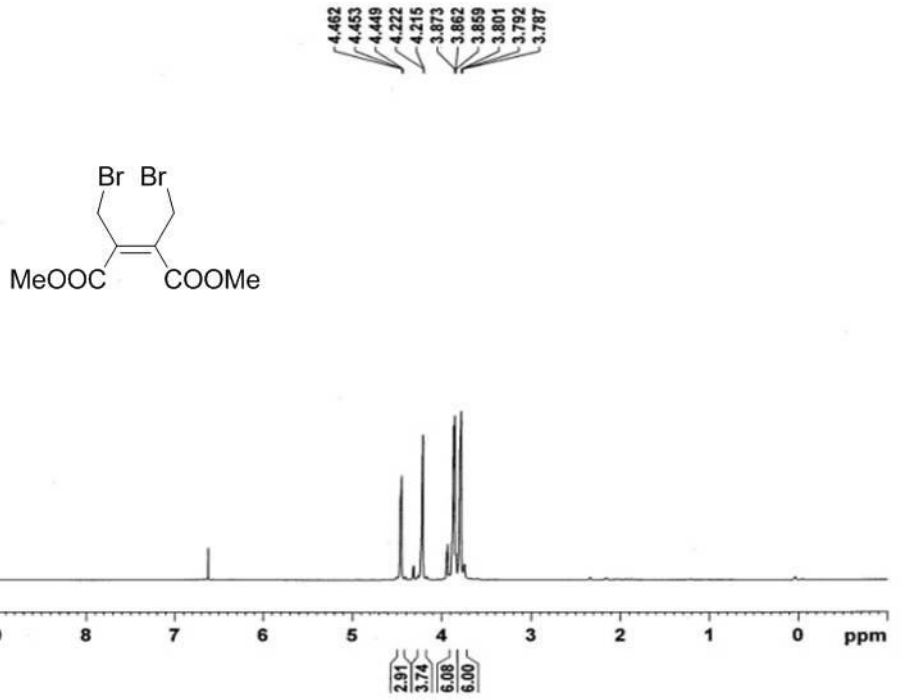


^{13}C NMR spectrum

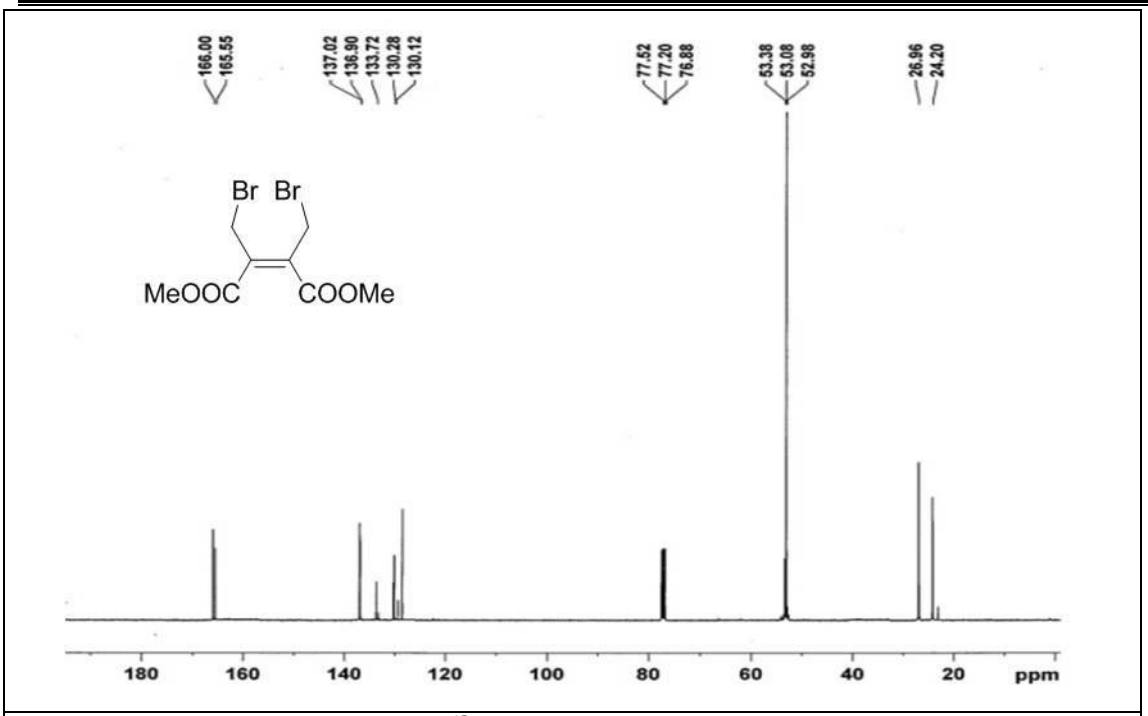


IR spectrum

2.5.2 Dimethyl 2,3-bis(bromomethyl)maleate (3)

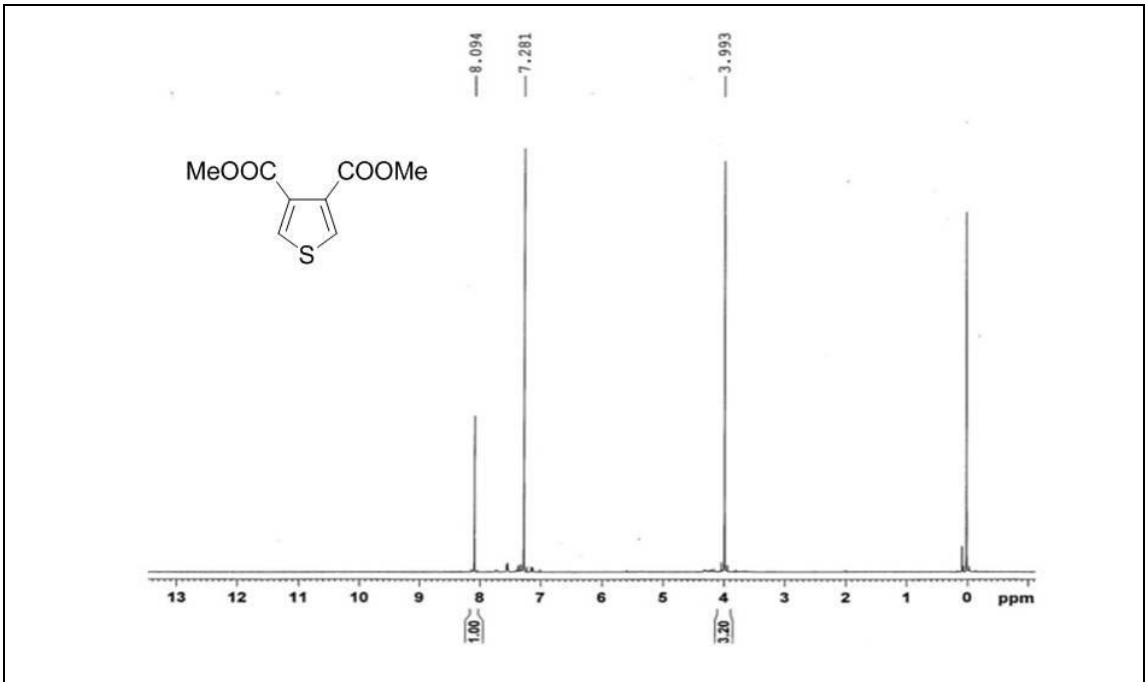


^{1}H NMR spectrum

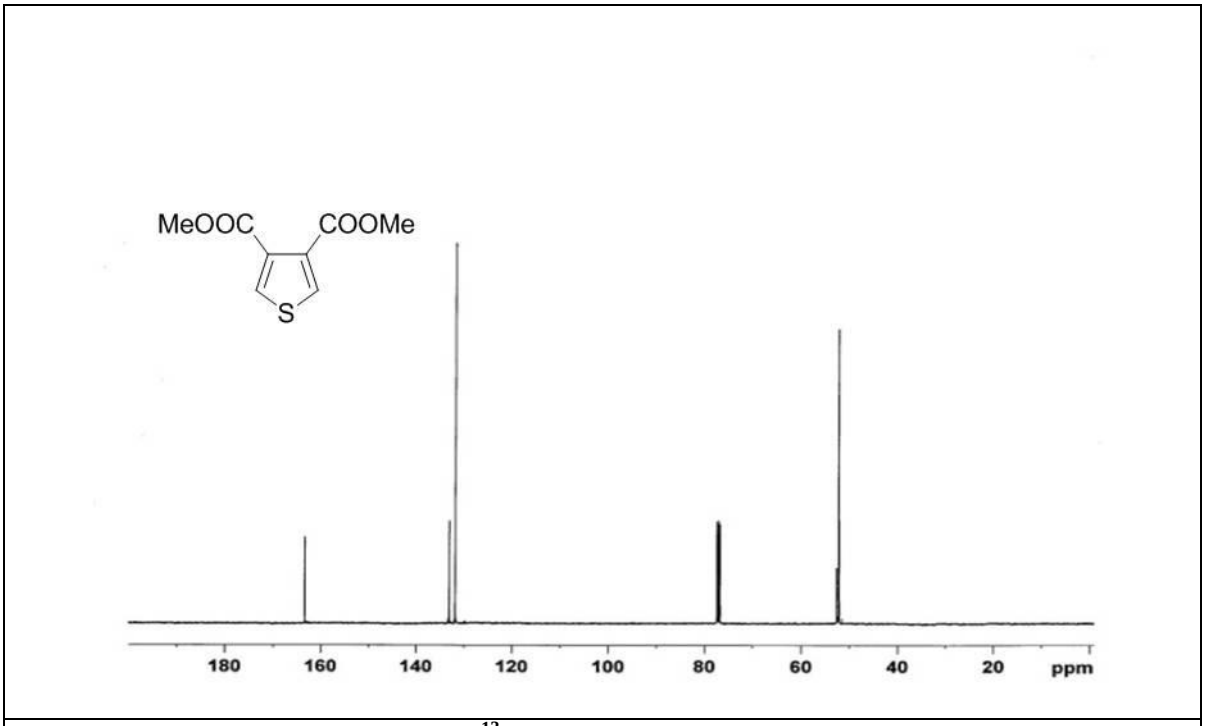


^{13}C NMR spectrum

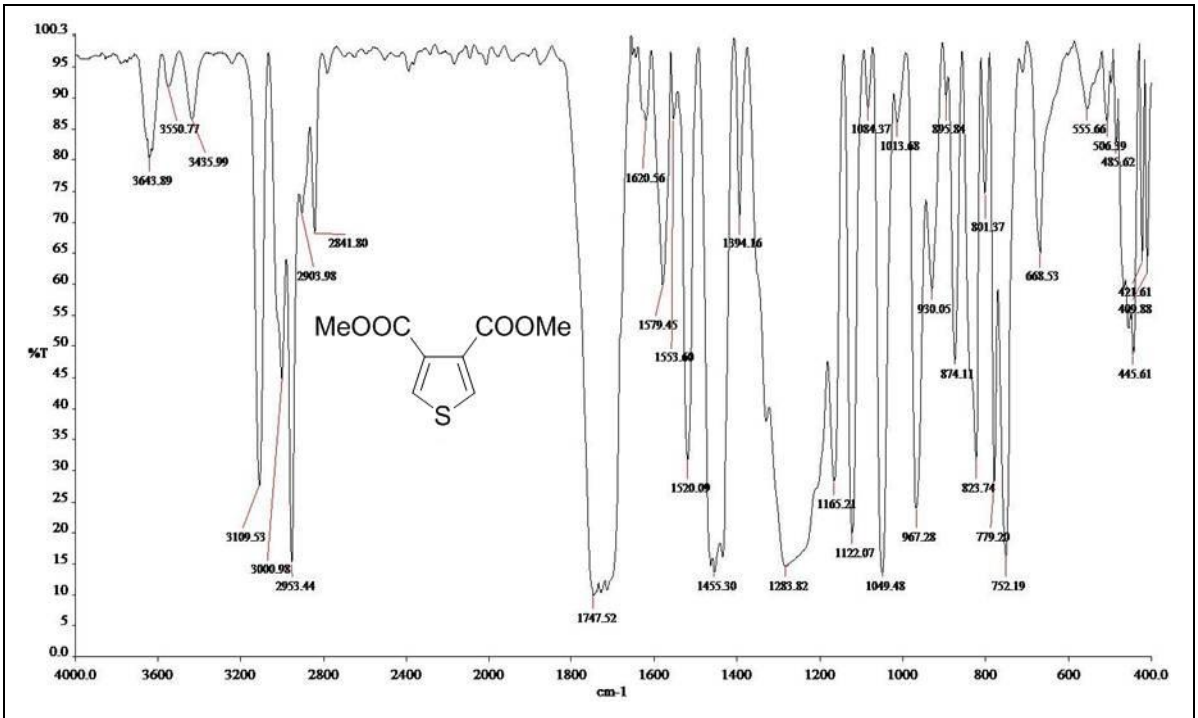
2.5.3 Dimethyl thiophene-3,4-dicarboxylate (6)



^{1}H NMR spectrum

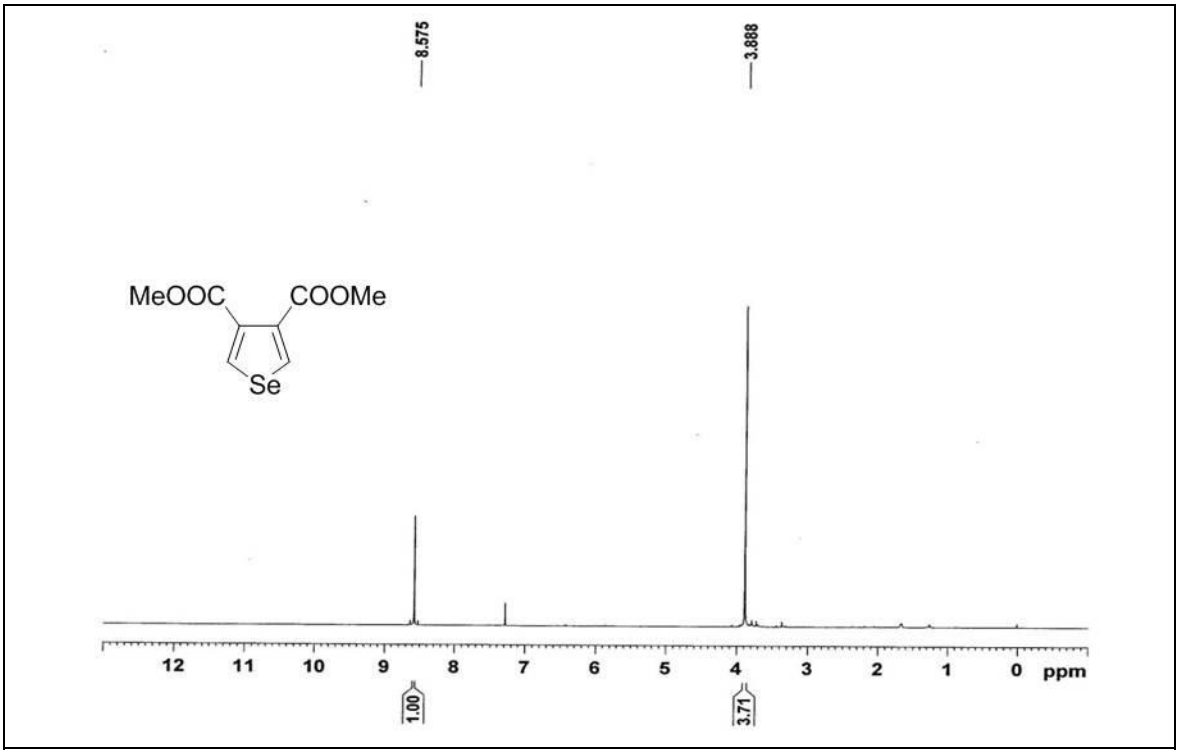


^{13}C NMR spectrum

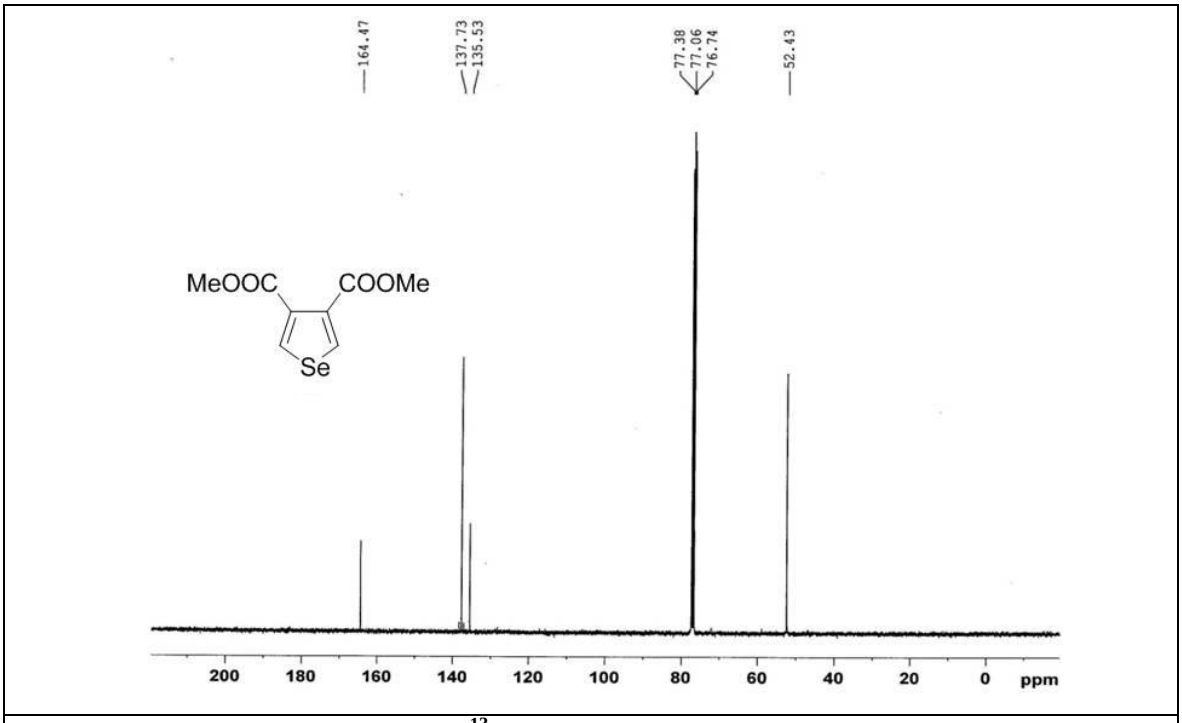


IR spectrum

2.5.4 Dimethyl selenophene dicarboxylate (9)

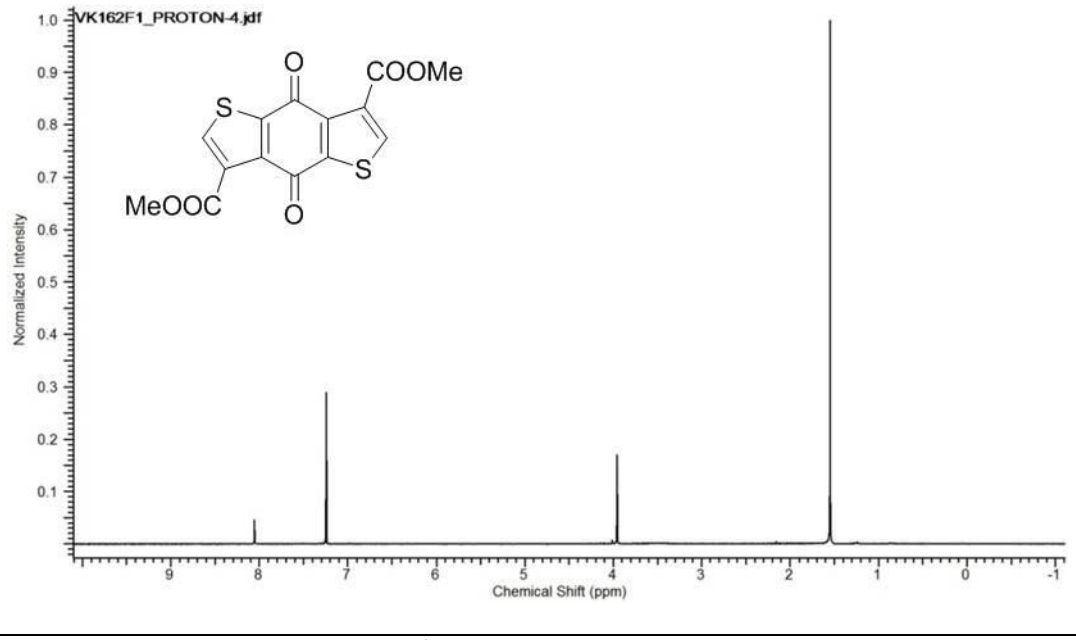


^{1}H NMR spectrum

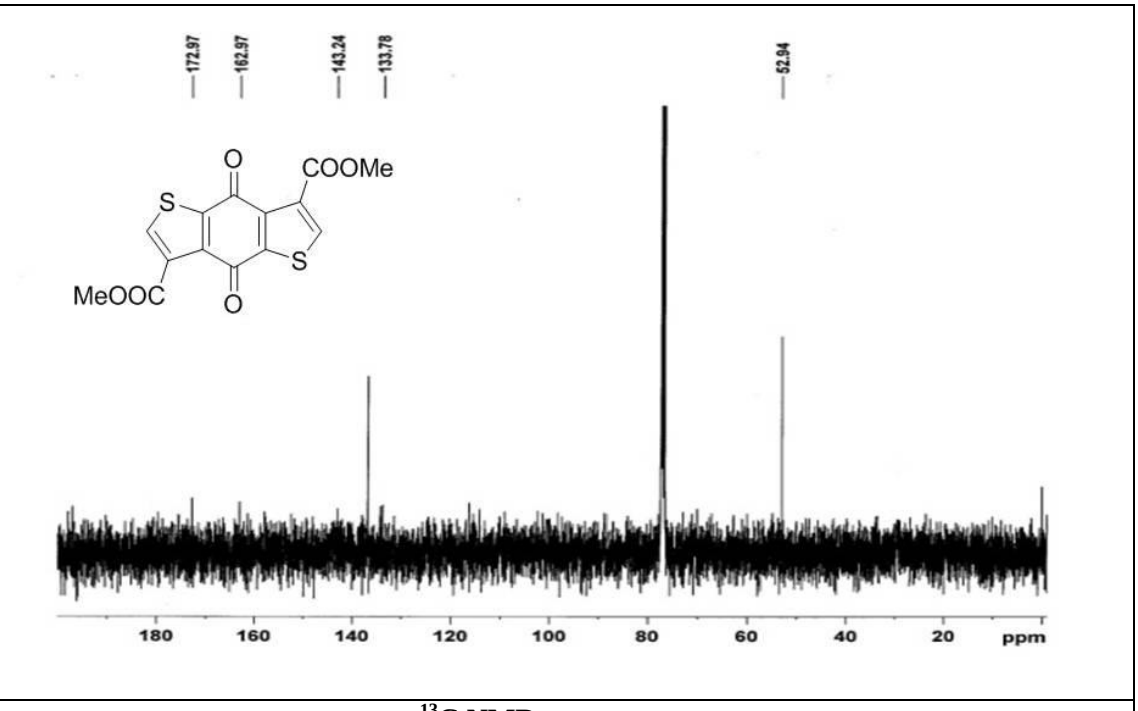


^{13}C NMR spectrum

2.5.4 3,7-dimethyl-4,8-dihydrobenzo[*1,2-b:4,5-b'*]dithiophen-4,8-dione-dicarboxylate (10)

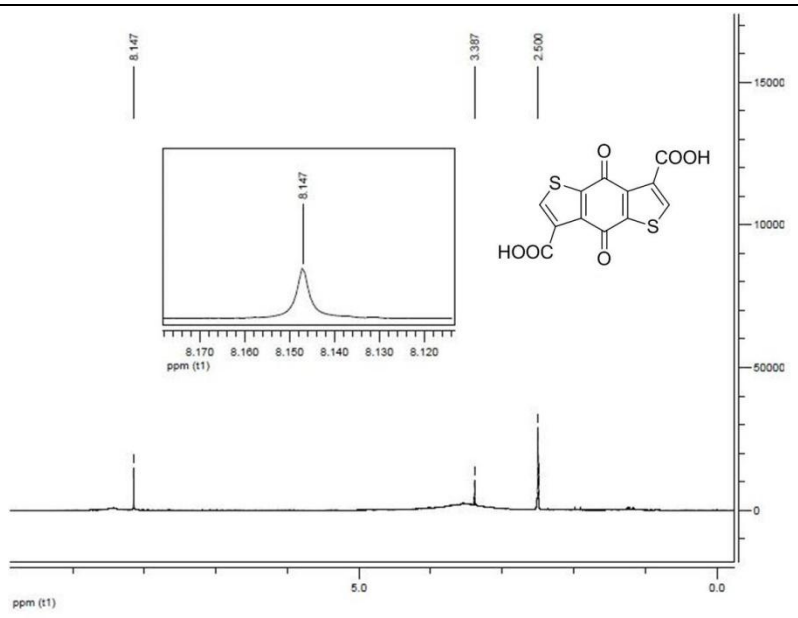


^{1}H NMR spectrum

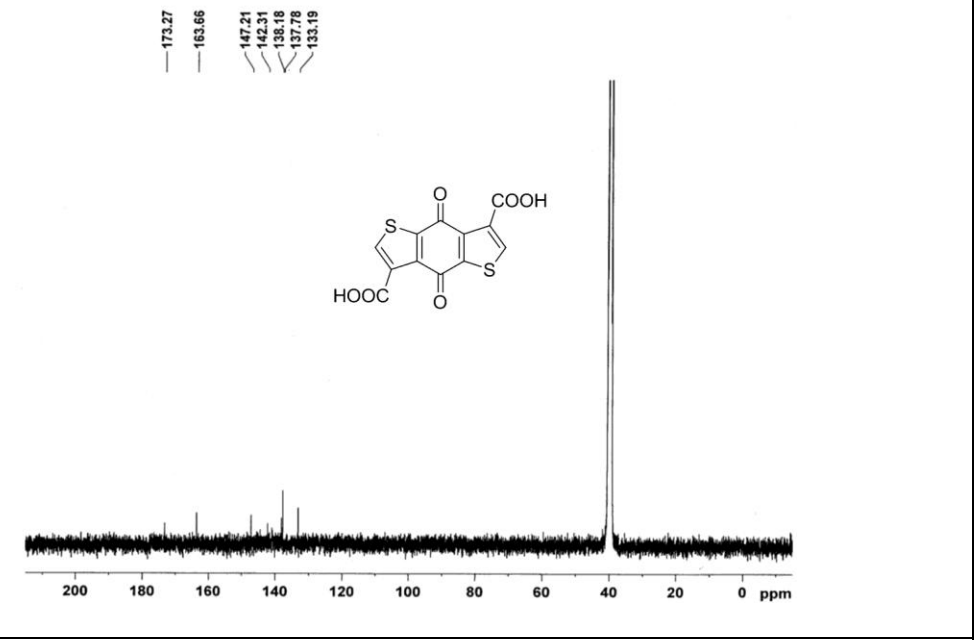


^{13}C NMR spectrum

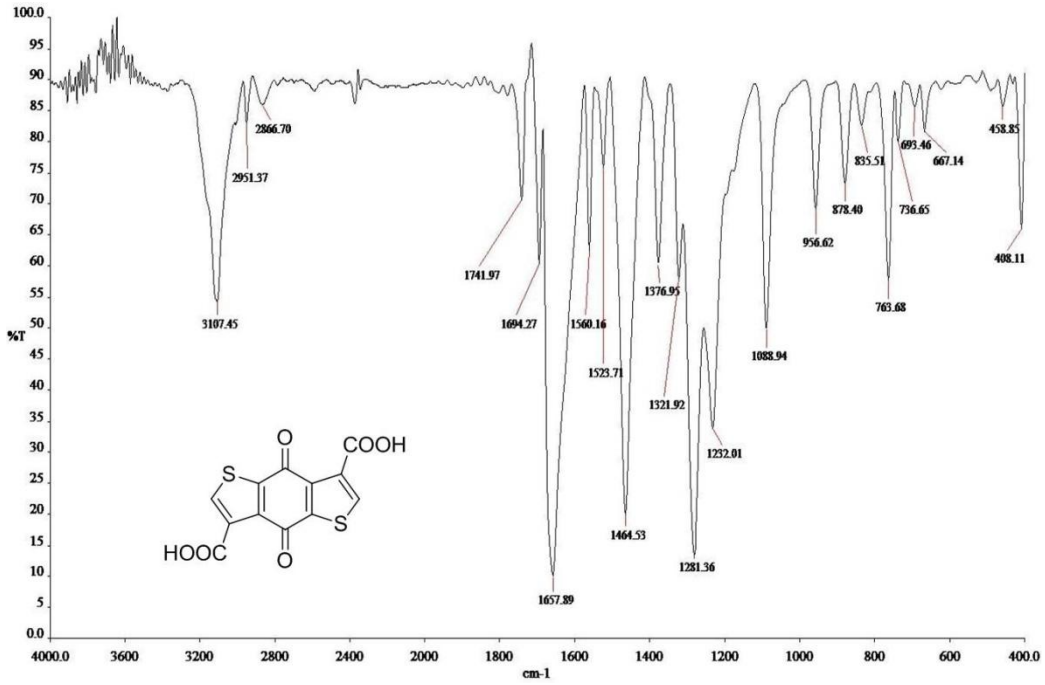
2.5.5 4,8-dioxo-4,8-dihydrobenzo[*1,2-b:4,5-b'*]dithiophene-3,7-dicarboxylic acid (11)



^{1}H NMR spectrum

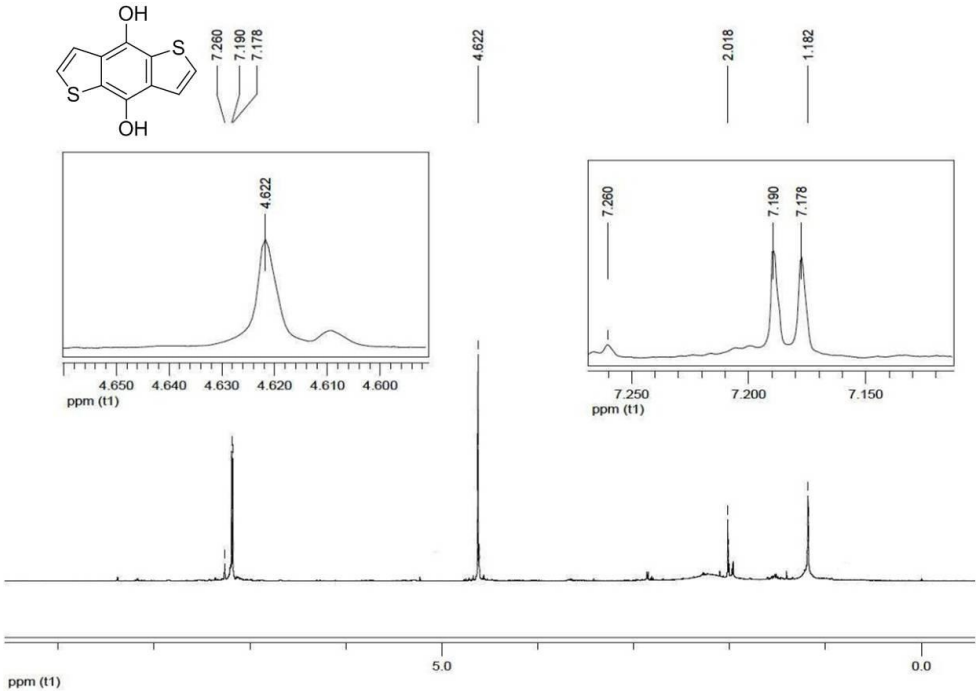


^{13}C NMR spectrum



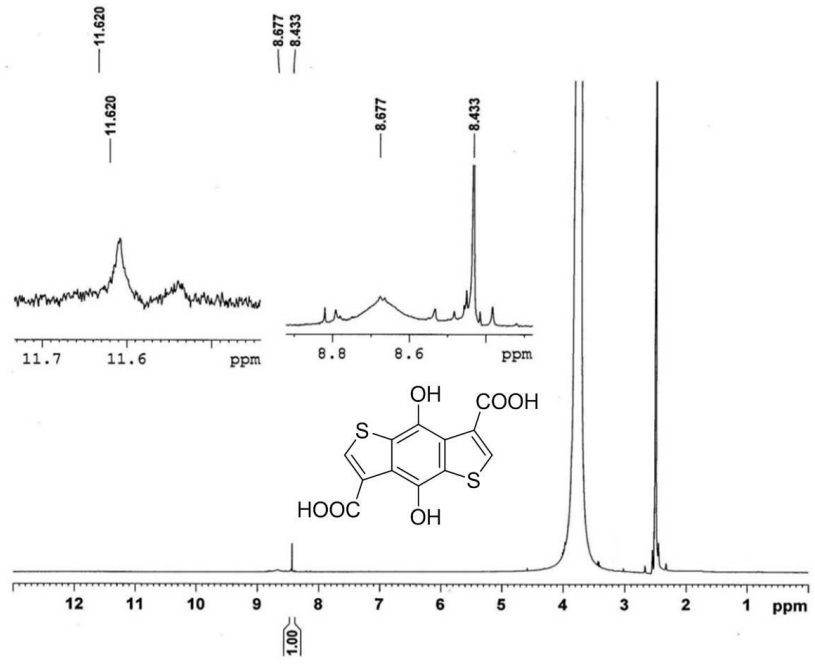
IR spectrum

2.5.6 Benzo[*1,2-b:4,5-b'*]dithiophene-4,8-diol (12)

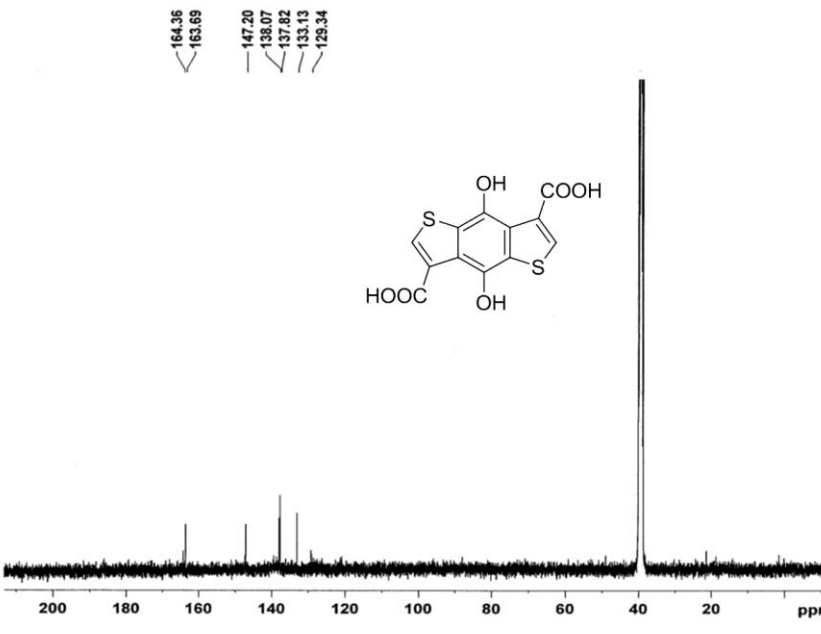


^{1}H NMR spectrum

2.5.7 4,8-dihydroxybenzo[*1,2-b:4,5-b'*]dithiophene-3,7-dicarboxylic acid (13)

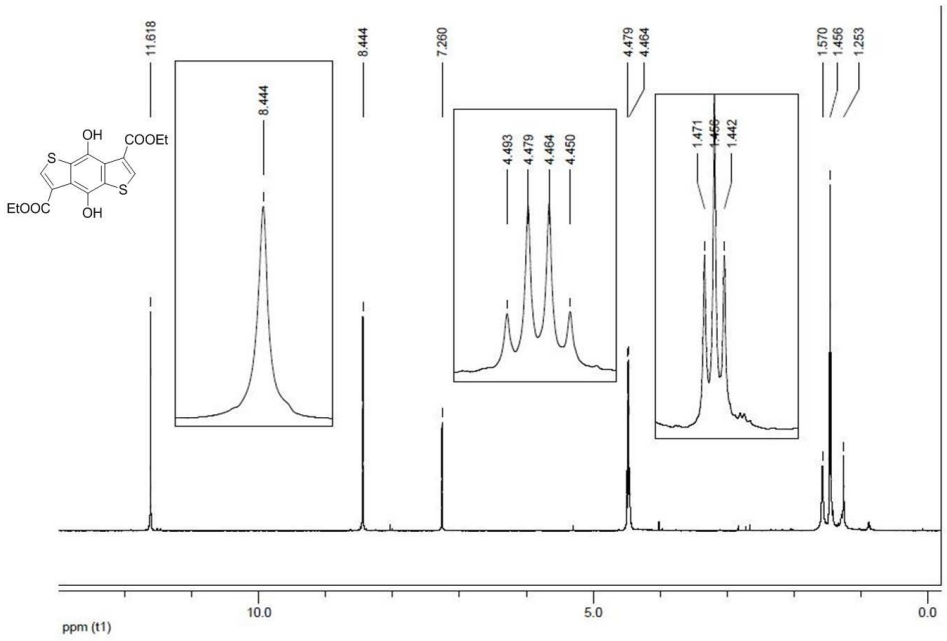


^{1}H NMR spectrum

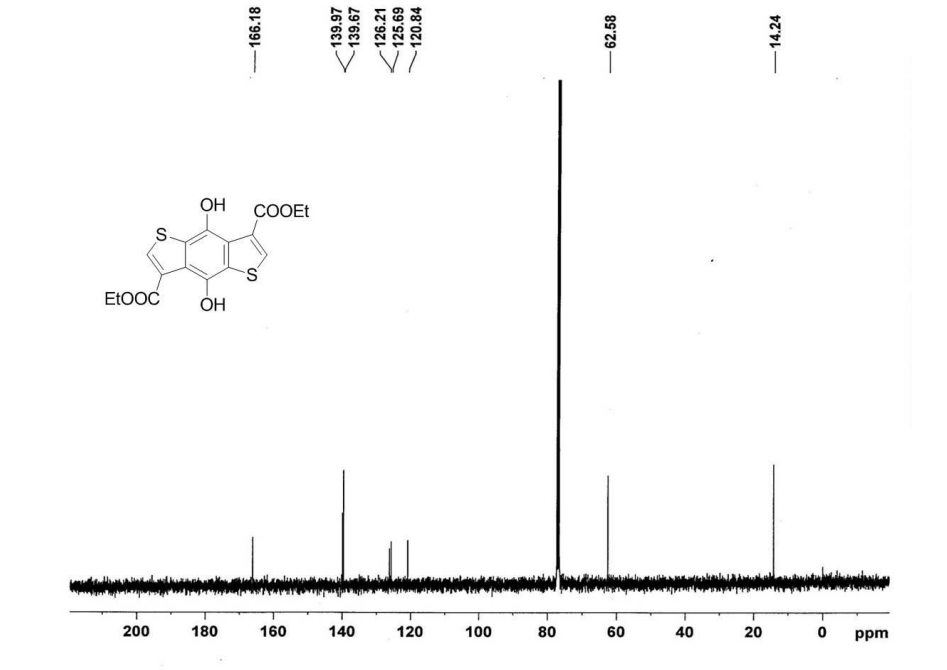


^{13}C NMR spectrum

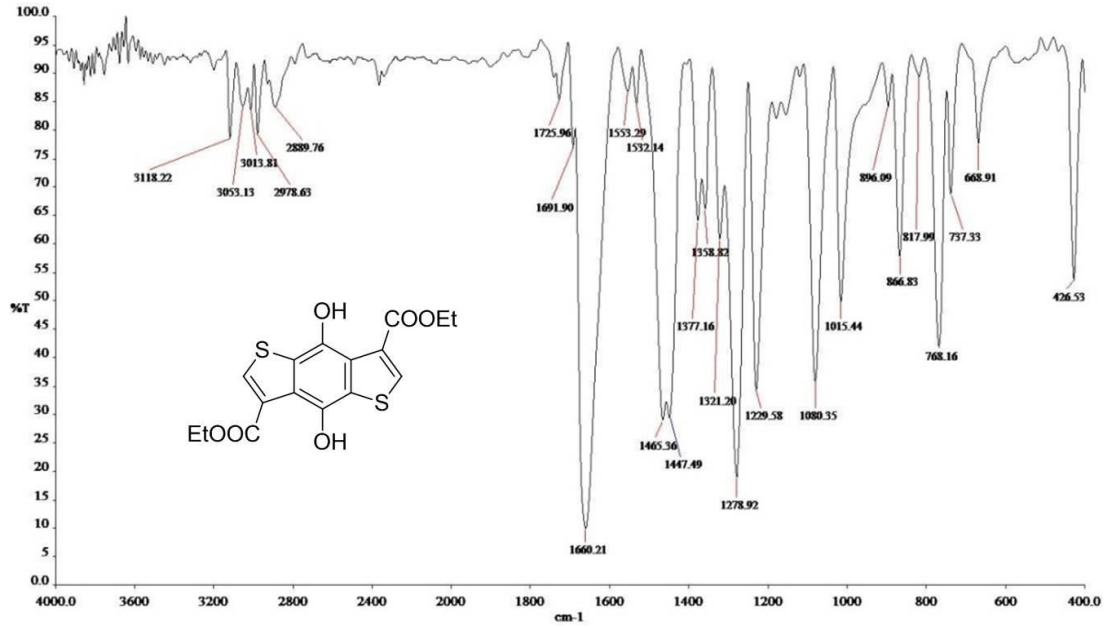
2.5.8 Diethyl 4,8-dihydroxybenzo[*1,2-b:4,5-b'*]dithiophene-3,7-dicarboxylate (14)



^{1}H NMR spectrum

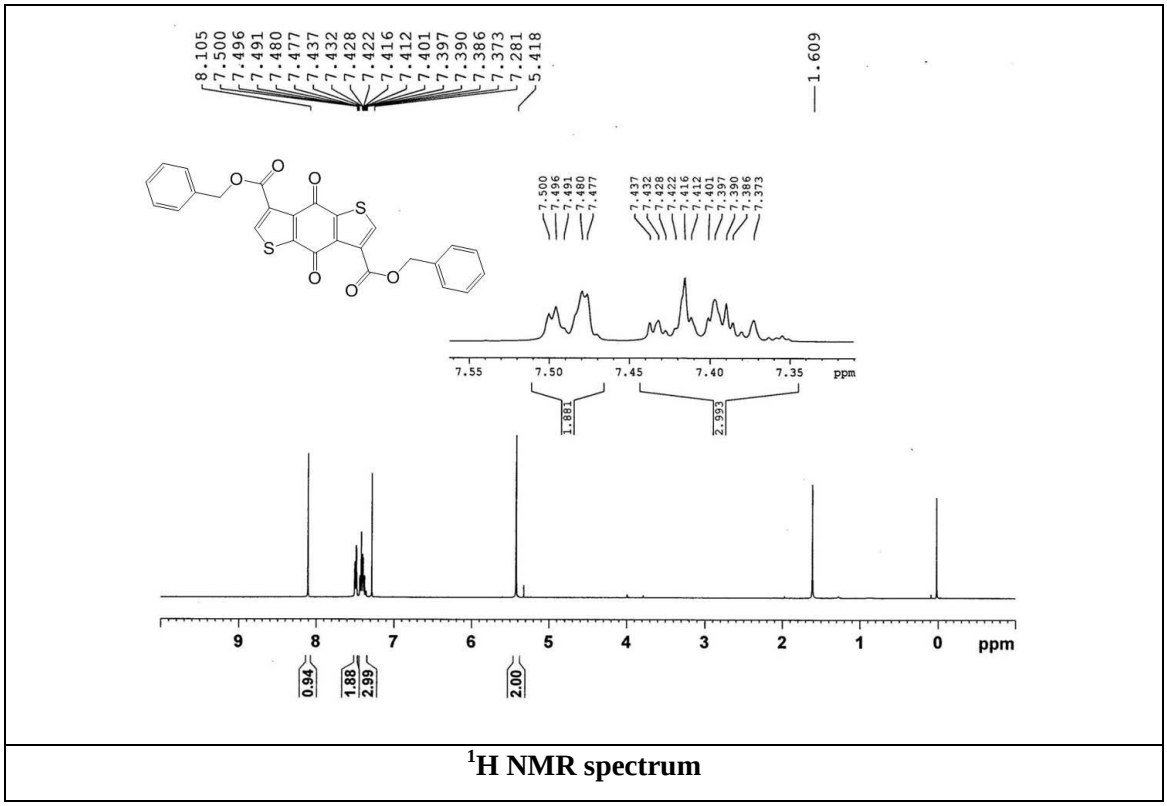


^{13}C NMR spectrum

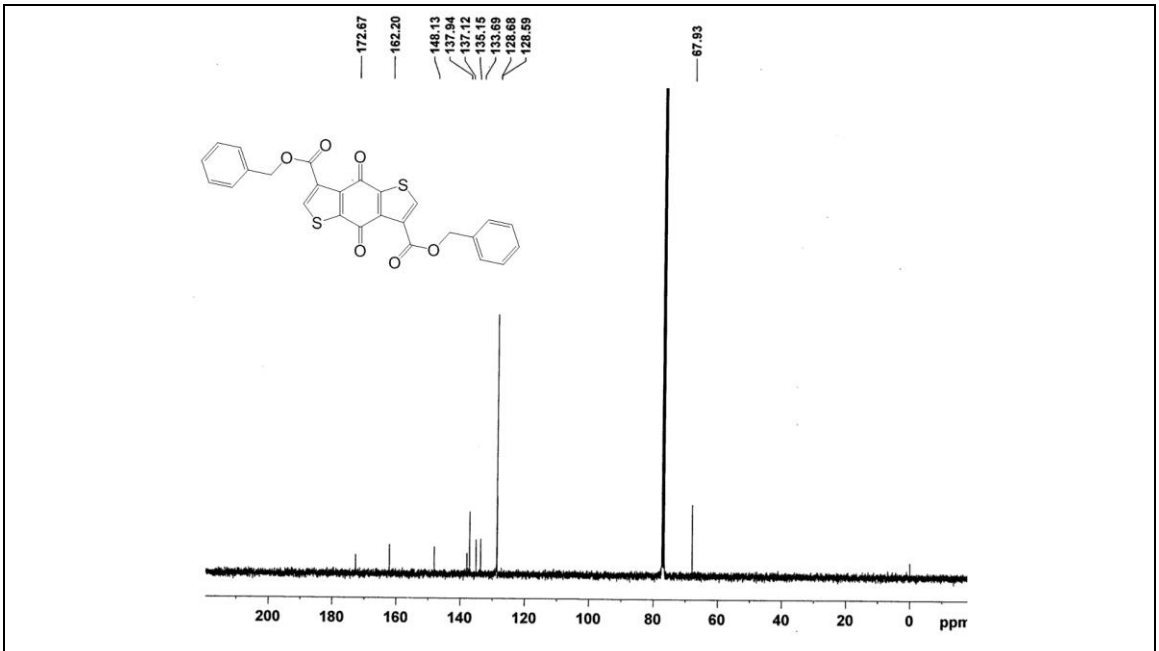

100.0
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0.0
%T
4000.0
3600
3200
2800
2400
2000
1800
1600
1400
1200
1000
800
600
400.0
cm-1
3118.22
3053.13
3013.81
2978.63
2889.76
1725.96
1691.90
1660.21
1553.29
1532.14
1465.36
1447.49
1377.16
1358.82
1321.20
1278.92
1229.58
1080.35
1015.44
896.09
866.83
817.99
768.16
737.33
668.91
426.53
OH
COOEt
S
S
EtOOC
OH

IR spectrum

2.5.9 Dibenzyl 4,8-dioxo-4,8-dihydrobenzo[*1,2-b:4,5-b'*]dithiophene-3,7-dicarboxylate (16)

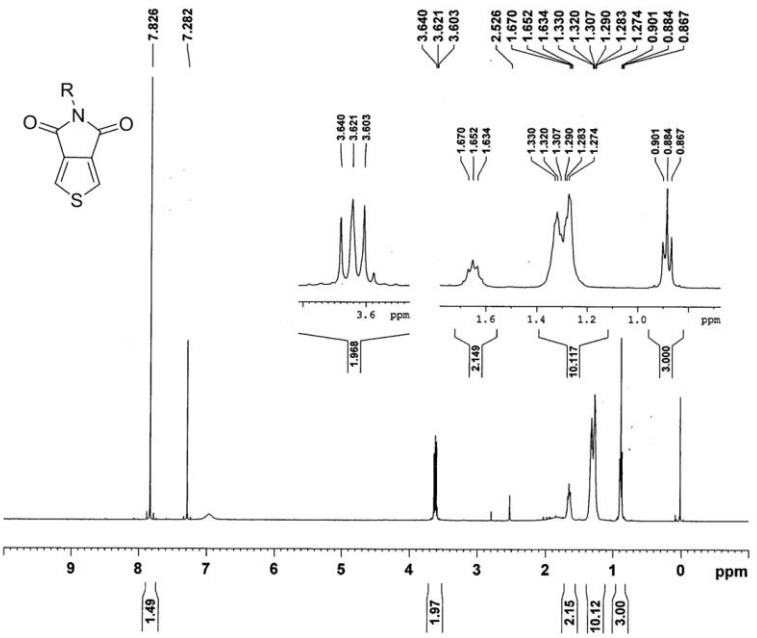


^{1}H NMR spectrum



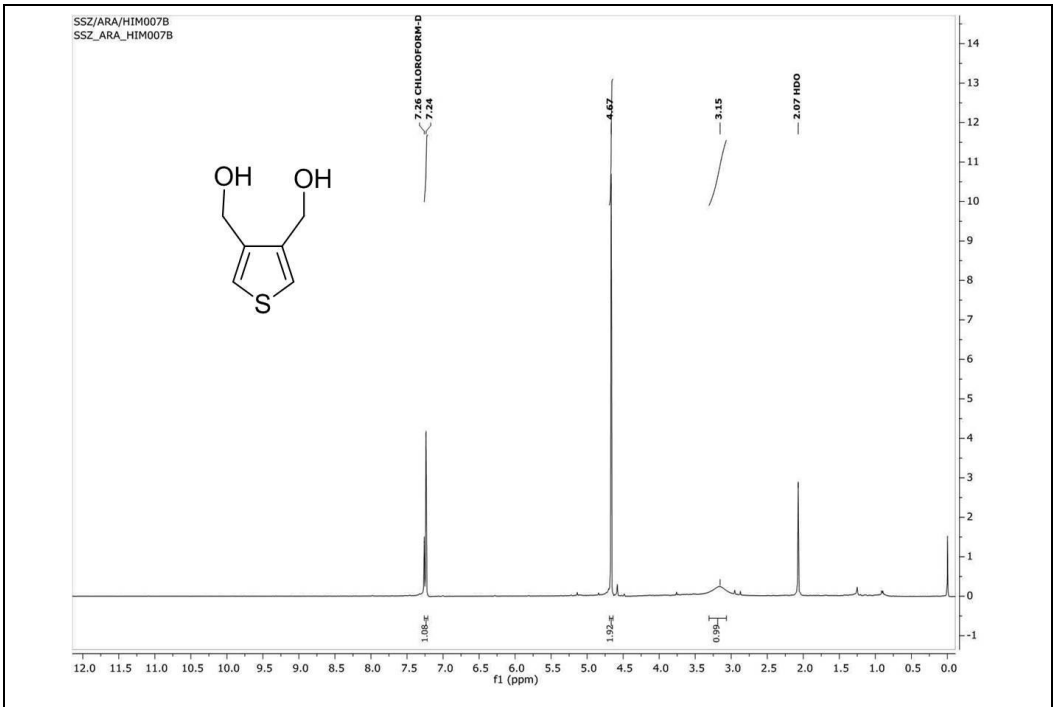
^{13}C NMR spectrum

2.5.10 n-Octylthenio[*3,4-c*]pyrrole-4-6-dione (18)



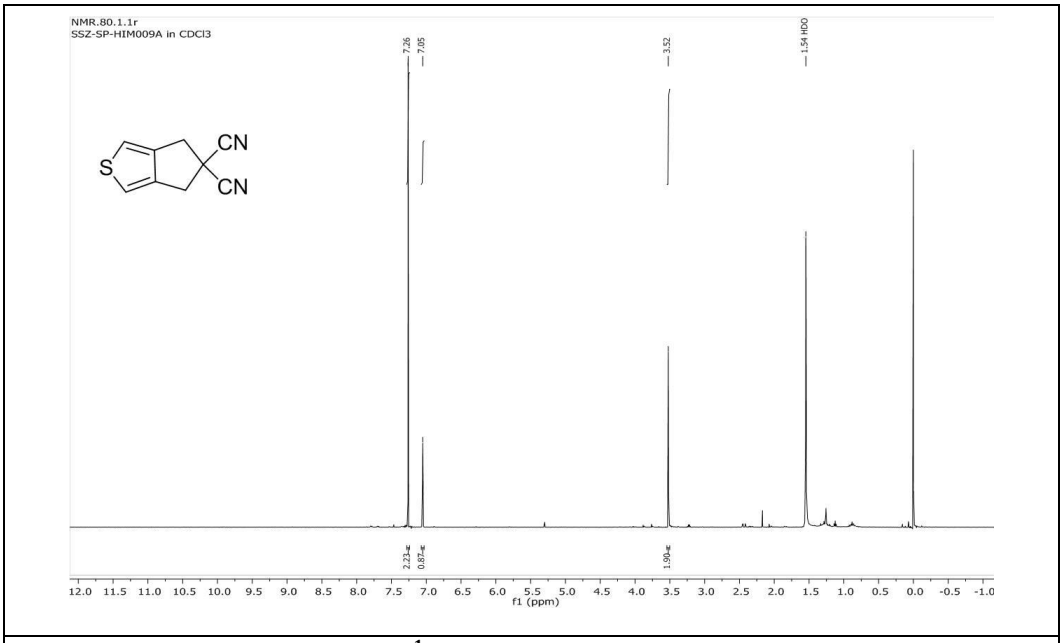
^{1}H NMR spectrum

2.5.11 3,4-Bis(hydroxymethyl)thiophene (19)

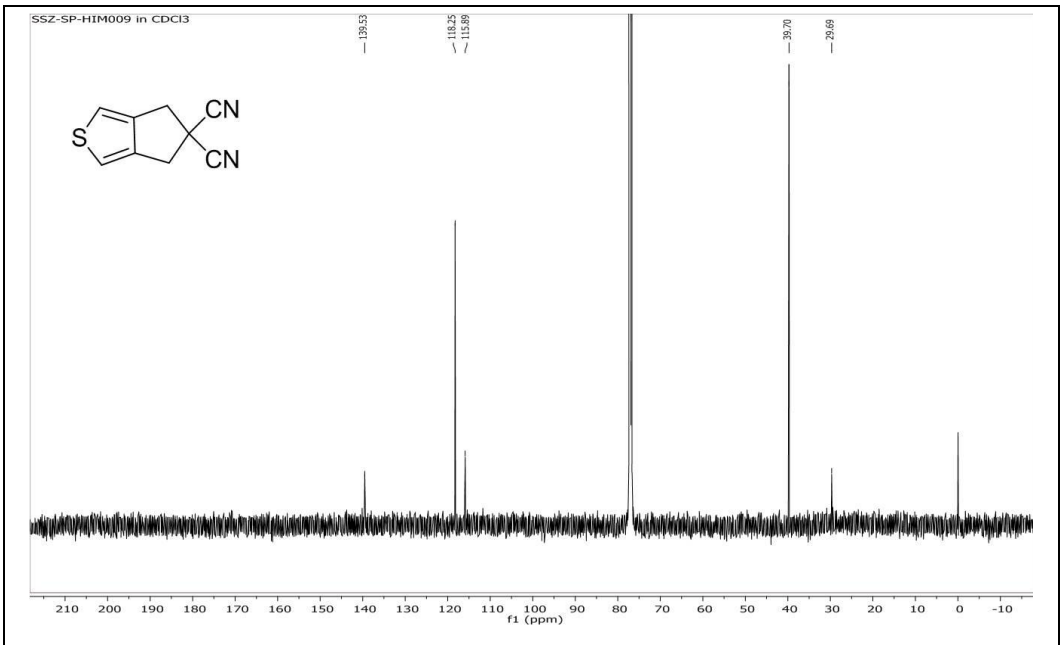


^{1}H NMR spectrum

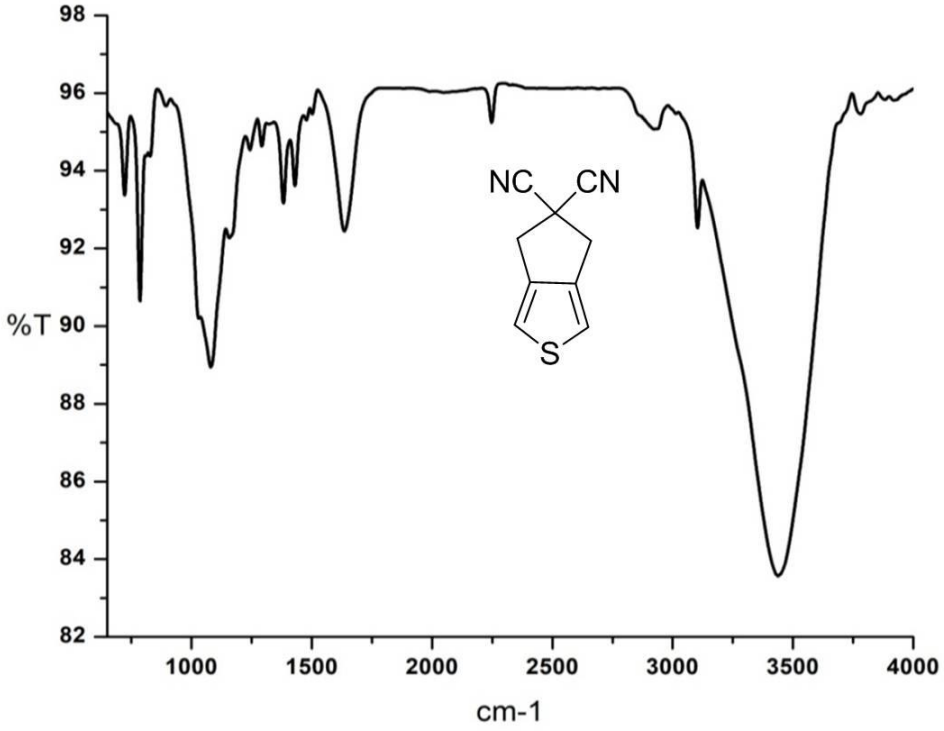
2.5.12 4H-cyclopenta[c]thiophene-5,5(6H)-dicarbonitrile (20)



^{1}H NMR spectrum



^{13}C NMR spectrum



IR spectrum

2.5.13 Crystal data and structure refinement for Compound 10 and Compound 14

	Compound **10**	Compound **14**
Empirical formula	$C_{14}H_8O_6S_2$	$C_{16}H_{14}O_6S_2$
Formula weight	336.35	366.39
Temperature/K	100.00(10)	293(2)
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a/Å	5.8732(4)	5.0114(4)
b/Å	11.1406(9)	8.6784(7)
c/Å	11.4042(7)	8.8841(9)
α/°	62.951(7)	95.275(7)
β/°	80.698(5)	100.345(7)
γ/°	86.114(6)	91.731(6)

Volume/Å^3	655.81(9)	378.06(6)
Z	2	1
ρ_{calc}g/cm^3	1.7032	1.609
μ/mm^{-1}	0.435	0.384
F(000)	344.7	190.0
Crystal size/mm^3	N/A × N/A × N/A	0.5 × 0.3 × 0.1
Radiation	Mo Kα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.06 to 52.74	4.68 to 55.8
Index ranges	-7 ≤ h ≤ 6, -13 ≤ k ≤ 13, -14 ≤ l ≤ 13	-6 ≤ h ≤ 6, -10 ≤ k ≤ 11, -11 ≤ l ≤ 8
Reflections collected	4231	2418
Independent reflections	2678 [R_{int} = 0.0288, R_{sigma} = 0.0506]	1807 [R_{int} = 0.0248, R_{sigma} = N/A]
Data/restraints/parameters	2678/0/90	1807/0/111
Goodness-of-fit on F^2	1.439	1.088
Final R indexes [I>=2σ (I)]	R_1 = 0.0663, wR_2 = N/A	R_1 = 0.0432, wR_2 = 0.0896
Final R indexes [all data]	R_1 = 0.0735, wR_2 = 0.2056	R_1 = 0.0503, wR_2 = 0.0940
Largest diff. peak/hole / e Å^{-3}	1.56/-1.51	0.49/-0.26
CCDC deposit no.	1021176	1417655

2.5.14 Crystal data and structure refinement for compound 16 and compound 20

	Compound **16**	Compound **20**
Empirical formula	$C_{26}H_{16}O_6S_2$	$C_9H_6N_2S$
Formula weight	488.51	174.22
Temperature/K	293(2)	290.80(10)
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	Pbca
a/Å	10.6289(10)	11.2900(8)

b/Å	8.8723(9)	7.1210(5)
c/Å	12.7436(12)	21.3850(15)
α/°	90.00	90
β/°	111.535(11)	90
γ/°	90.00	90
Volume/$Å^3$	1117.9(19)	1719.3(2)
Z	2	8
$\rho_{calc}g/cm^3$	1.451	1.3461
μ/mm^{-1}	0.281	0.316
F(000)	504.0	720.0
Radiation	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	6.28 to 57.44°	3.8 to 56.64
Index ranges	$-14 \leq h \leq 7$, $-9 \leq k \leq 11$, $-15 \leq l \leq 17$	$-14 \leq h \leq 15$, $-9 \leq k \leq 9$, $-24 \leq l \leq 28$
Reflections collected	5346	11014
Independent reflections	2884[R(int) = 0.0237]	2149 [R_{int} = 0.0447, R_{sigma} = 0.0343]
Data/restraints/parameters	2884/0/157	2149/0/109
Goodness-of-fit on F^2	0.861	1.038
Final R indexes [I>=2σ (I)]	R_1 = 0.0570, wR_2 = 0.1935	R_1 = 0.0471, wR_2 = 0.1081
Final R indexes [all data]	R_1 = 0.0758, wR_2 = 0.2218	R_1 = 0.0557, wR_2 = 0.1141
Largest diff. peak/hole / e $Å^{-3}$	0.39/-0.35	0.26/-0.38
CCDC	1934661	1882100

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