Reactions of Functionalized β-Oxodithioesters with α-Haloketones: Synthesis of Functionalized Thiophenes

4.1 Introduction

Functionalized dithioesters are highly reactive species, widely used in synthetic organic chemistry.\(^1\) In continuation of our studies on the application of β-oxodithiocarboxylates\(^5\) and β-oxothioamides\(^6\) as versatile multifunctional intermediates, we report here on the utility of these intermediates in the synthesis of substituted thiophene derivatives. The addition of carbanions generated from active methylene compounds to carbon disulfide followed by the alkylation of the intermediate dimetalloketene dithioacetals is one of the convenient protocols for the synthesis of substituted thiophenes and thienothiophenes.\(^7\) To circumvent the difficulties involved in the selective sequential alkylation of this method we have chosen to examine β-oxodithiocarboxylates and β-oxothioamides as useful precursors for the synthesis of substituted thiophenes. We have recently shown that the functionalized S,N-acetals derived from β-oxothioamides undergo \textit{in situ} intramolecular cyclisation leading to the formation of substituted thiophene derivatives.\(^8\) It has been found that the preferred mode of ring closure of the intermediate ketene-S,N-acetal, leading to the formation of various substituted
thiophenes largely depends on the substrate structure. The present chapter describes intramolecular aldol type condensation reaction of \( \alpha \)-oxoketene dithioacetal intermediates formed from \( \beta \)-oxodithiocarboxylates leading to the formation of functionalized thiophenes in good yields.

### 4.1.1 \( \beta \)-Oxodithioesters: Synthesis

\( \beta \)-Oxodithioesters are generally prepared by thiocarbonylation of active methylene ketones with dialkyl trithiocarbonates or chlorodithio formates.\(^{16}\) This is exemplified by the reaction of acetophenone 1 with the dimethyl trithiocarbonate 4 in benzene in the presence of a base such as sodium hydride to afford methyl benzoyl dithioacetate 3 (Scheme 1).

![Scheme 1](image)

They can also be obtained from substituted acetophenones 1 by the addition of carbodiisulfide in the presence of potassium t-butoxide as the base, followed by alkylation (Scheme 2).\(^{17, 18}\)

![Scheme 2](image)
Oliva et al. have reported the synthesis of β-oxodithioesters 7 from 2,4-pentanedione 6 by the effective methylthiocarbonylation of the active methylene group with trithiocarbonate, in the presence of sodium acetate in DMF (Scheme 3).19

\[
\begin{align*}
\text{H}_2\text{C} & \quad | \quad \text{H}_3\text{C} \quad \text{O} \\
\text{O} & \quad | \\
\text{C} & \quad \text{C} \\
\text{H}_3 & \quad \text{S} \\
\text{O} & \quad | \\
\text{C} & \quad \text{H}_3
\end{align*}
\]

\begin{align*}
\text{H}_3\text{CS} & \quad \text{S} \\
\text{S} & \quad \text{CH}_3
\end{align*}

\[
\begin{align*}
\text{H}_3\text{CS} & \quad \text{S} \\
\text{S} & \quad \text{CH}_3
\end{align*}

Scheme 3

Earlier studies from our laboratory have shown that the reaction of ethyl acetoacetate 8 with trithiocarbonate in the presence of sodium hydride in benzene leads to the formation of carboethoxy substituted dithioacetate 10 (Scheme 4).20

\[
\begin{align*}
\text{EtO} & \quad | \quad \text{H}_3\text{CS} \\
\text{O} & \quad | \\
\text{C} & \quad \text{C} \\
\text{H}_3 & \quad \text{S} \\
\text{O} & \quad | \\
\text{C} & \quad \text{H}_3
\end{align*}
\]

\begin{align*}
\text{EtO} & \quad | \quad \text{H}_3\text{CS} \\
\text{O} & \quad | \\
\text{C} & \quad \text{C} \\
\text{H}_3 & \quad \text{S} \\
\text{O} & \quad | \\
\text{C} & \quad \text{H}_3
\end{align*}

\[
\begin{align*}
\text{EtO} & \quad | \quad \text{H}_3\text{CS} \\
\text{O} & \quad | \\
\text{C} & \quad \text{C} \\
\text{H}_3 & \quad \text{S} \\
\text{O} & \quad | \\
\text{C} & \quad \text{H}_3
\end{align*}
\]

Scheme 4

We have also reported an efficient method for the transformation of α-oxoketene dithioacetals to β-oxodithioesters by the treatment with hydrogen sulfide in presence of BF₃ etherate. In this reaction hydrogen sulfide gas is bubbled through a refluxing mixture of aroyl ketene dithioacetal 11 and boron trifluoride-etherate and respective aroyl dithioesters 3 are obtained in good yields.
The ketene dithioacetals obtained from cyclic and aliphatic ketones also afforded corresponding β-oxodithioesters under the same reaction conditions.

![Scheme 5](image)

Similarly a selective demethylation reaction of dimethyl ketene dithioacetalts with dimethyl sodium resulted in the formation of β-oxodithioesters 3 in good yield (Scheme 6). Cyclic and aliphatic ketones also afforded β-oxodithioesters when treated with dimethyl sodium.

![Scheme 6](image)

The same protocol was extended to α-arylmethyldiene-1,3-dithiolanes 12 to afford vinyl benzoyl dithioacetates 13 in good yield (Scheme 7).

![Scheme 7](image)

As a continuation to these transformations α, β-unsaturated esters 15 were prepared by the sodium borohydride reduction of the ketene dithioacetals 11.
followed by treating the resulting carbinol acetals 14 with Lawesson's reagent (Scheme 8). \(^2,1\)

![Scheme 8](image)

The reaction was also extended to carbinol acetals obtained by methyl Grignard reaction on \(\alpha\)-oxoketene dithioacetals. For example the methyl Grignard reaction of 11 followed by reaction with Lawesson's reagent afforded \(\alpha,\beta\)-unsaturated ester 17 (Scheme 9). \(^23\)

![Scheme 9](image)

4.1.2 \(\beta\)-Oxodithioesters: Reactivity

\(\beta\)-Oxodithioesters are versatile intermediates in the synthesis of several heterocyclic compounds. They are useful precursors for the synthesis of thioamides and functionalized ketene dithioacetals. A few examples to demonstrate the synthetic potential of these compounds are presented here.

Clesse et al have shown that acyl dithioacetate 18 reacts with dithiolium salts 19 to afford 3-acyl substituted 2H-thiopyran 2-one derivatives 20 (Scheme 10). \(^24\)
Curphey et al have reported that $\beta$-oxodithioesters 3 on treatment with trimethyl silyl sulfide in the presence of N-chlorosuccinimide and imidazole affords substituted 1,2-dithioles 21 (Scheme 11).$^{25}$

\[ \text{Scheme 11} \]

$\beta$-Phenylamino substituted $\alpha,\beta$-unsaturated dithioester 23 obtained by the selective addition of aniline to one of the carbonyl groups of methyl dithiocarboxylate 22 undergo thermal cyclization to afford 24 (Scheme 12).$^{26}$
We have also made attempts to explore the synthetic utility of these intermediates. From our laboratory it has been reported that when methyl aryl dithioacetates 3 on treatment with two equivalents of dicyclohexyl carbodiimide (DCC) 25 in presence of DMAP in dichloromethane, 4-aryl methyldene-3-cyclohexylimino-1,3-thiazetidines 26 are obtained (Scheme 13). The reaction was aimed at the activation of the thiocarbonyl group for selective displacement with other nucleophiles. However it has been found that after the initial addition of the carbodiimide, the adduct undergoes cyclization involving intramolecular displacement of the methylthio group.

![Scheme 13](image)

When aryl dithioesters were reacted with chloromethylene-iminium salt prepared from POCl₃ and DMF β-chloro β-alkylthio-α,β-unsaturated ketones 27 were obtained in good yield (Scheme 14).

![Scheme 14](image)
In the case of aliphatic dithiocarboxylates it afforded 3,5-dichloro pentanal. For example the dithioester prepared from cyclohexanone 27 on treatment with chloromethylene iminium salt, underwent multiple iminoalkylation and afforded 2-chloro-3-(1-chloro-1-methylthio)methylene cyclohexenecarbaldehyde 28 (Scheme 15).^5

Scheme 15

When the reaction was extended to carbethoxy dithioacetate, it afforded substituted thiopyran derivative (Scheme 16).^5

Scheme 16

Recently we have found that β-oxodithioesters of substituted acetophenones on treatment with phenacyl bromide in presence of sodium hydride in benzene give oxathiole derivatives 32 in good yield (Scheme 17).^28

Scheme 17

When the reaction was extended to aliphatic dithiocarboxylates, the major product of the reaction was substituted thiophene. When bromoacetone was used
as the alkylating agent, the reaction afforded substituted thiophenes 33 as the major products (Scheme 18).

![Scheme 18](image)

In these reactions we envisaged the formation of intermediate ketene dithioacetals 34, which would cyclize to substituted oxathioles and thiophenes depending on the structure of the substrates. It was difficult to isolate the intermediate ketene dithioacetals 34 from the above reaction in pure form and hence dithiocarboxylates were treated with phenacyl bromide in the presence of potassium carbonate as the base and crude intermediates were heated with acetic acid to afford thermally cyclized thiophenes 35 (Scheme 19).

![Scheme 19](image)
The phenacylethio substituted benzoyl ketenedithioacetal 34 was treated with one equivalent of Lawesson’s reagent in benzene at room temperature. The reaction afforded 3-thiobenzoyl-4-phenacyl thiophene 38 along with 3-benzoyl thiophenes 37 and 2-phenacylidene-4-phenyl-1,3-dithiole 36 (Scheme 20).

![Scheme 20](image)

Still, the intermediate ketene dithioacetals deserve some more attention due to its high functionalization. Synthetic investigations on these valuable intermediates showed that it can be transformed into thiophene derivatives of different substitution patterns. As a continuation to this we have developed an effective method for the synthesis of 5-aryl-2-methylthio-4-phenyl thiophenes in good yields.

4.2. Results and Discussion

The β-oxodithiocarboxylates were readily available by the reaction of the respective active methylene ketones with dimethyl trithiocarbonate in the presence of a base or by the demethylation or sulphydrolysis of α-oxoketenedithioacetals. However we have developed a good yielding and convenient method for the synthesis of β-oxodithiocarboxylates by modifying the existing protocol employing trithiocarbonates. In this method the active methylene ketones were
treated with trithiocarbonate in the presence of sodium hydride as the base, in hexane/DMF solvent mixture at room temperature for 2 hrs. The reaction is good yielding, proceeds without heating and is devoid of offensive odour of the methanethiol eliminated during the reaction (Scheme 21).

![Scheme 21]

Earlier reports from our laboratory have showed that the reaction of β-oxodithioesters with α-haloketones leads to the formation of substituted oxathioles and thiophenes via an intermediate ketene dithioacetal. The mode of cyclization of the intermediate largely depends on the structure of the substrate and the alkylating agent used in the reaction. However, when 3-oxo-3-phenyl propanedithiocarboxylate was treated with phenacyl bromide using sodium hydroxide in ethanol as the base, 5-benzoyl-2-methylthio-4-phenyl thiophene was formed exclusively. The strategy was extended to other substituted dithioesters using phenacyl bromide and bromoacetone as the alkylating agent. From these reactions it was clear that this reaction is different from the earlier cases due to its selectivity, which is independent of the structure of the substrates as well as the alkylating agents used in the reaction.

4.2.1 Reaction of Functionalized β-Oxodithioesters with Phenacyl bromide

We have treated methyl-3-oxo-3-phenylpropanedithiocarboxylate in ethanol with phenacyl bromide in the presence of sodium hydroxide at room temperature. The
reaction was completed after 48 hours affording a functionalized thiophene as the single product in good yield. Earlier reports from our laboratory have well proved that the reaction of β-oxodithioesters or β-oxothioamides affords intermediate ketenedithioacetals or ketene-S,N-acetals in the first step of the reaction and this intermediate undergoes further cyclization reaction to afford a number of functionalized heterocycles depending on the reaction condition and the structure of the substrates. In the light of these results we have expected possible formation of products such as functionalized oxathioles, 5-benzoyl-2-methylthio-4-arylthiophenes and 3-aroyl-2-methylthio-4-phenylthiophene. However the splitting patterns of the aromatic peaks as well as the presence of methylthio group in the 1H NMR spectra showed that the compound is 5-benzoyl-2-methylthio-4-arylthiophene 39 (Scheme 22). The 13C NMR and mass spectral data were confirmatory to the structure. p-Chloro benzoyl dithioester also gave the corresponding substituted thiophene 39b.

![Scheme 22]

<table>
<thead>
<tr>
<th>39</th>
<th>X</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>H</td>
<td>60</td>
</tr>
<tr>
<td>b</td>
<td>Cl</td>
<td>62</td>
</tr>
</tbody>
</table>

Scheme 22
The mechanism of the reaction is explained by the formation of the enolate ion 40 in the phenacylthio moiety of the intermediate ketenedithioacetal 34 and its aldol type condensation reaction on the carbonyl carbon atom alpha to the ketenedithioacetal moiety followed by aromatization reaction (Scheme 23).

We have next examined the reaction of β-oxidithioester from α-tetralone 42 with phenacyl bromide and it afforded thiophene derivative 43 in 62% yield (Scheme 24).
The reaction was further extended to dithiocarboxylates derived from cyclohexanone 44 and it resulted in the formation of thiophene derivative 3-(methylsulfanyl)-4,5,6,7-tetrahydro-2-benzothiophene-1-yl 45 (Scheme 25). The structure of the compound was elucidated on the basis of NMR and mass spectral values and they are given in the experimental section.

![Scheme 25]

Aliphatic dithioesters like 46 also showed similar reaction resulting in the product 47 (Scheme 26).

![Scheme 26]

4.2.2 Reaction of Functionalized β-Oxodithioesters with Bromoacetone

In order to generalize the reaction, β-oxodithioesters were treated with bromoacetone in 1:1 ratio and the intermediate ketene dithioacetals formed in these reactions also preferred intramolecular aldol type condensation reaction leading to the formation of substituted thiophenes 33 (Scheme 27). The reaction
was extended to *p*-chlorobenzoyl dithiocarboxylate to get corresponding functionalized thiophene in 68% yield. These compounds were also characterized by IR, NMR and mass spectral data, which are given in the experimental section.

![Chemical structure](image)

<table>
<thead>
<tr>
<th>33</th>
<th>X</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>H</td>
<td>72</td>
</tr>
<tr>
<td>b</td>
<td>Cl</td>
<td>68</td>
</tr>
</tbody>
</table>

**Scheme 27**

The alkylation of β-oxodithioesters derived from cyclohexanone 44 with bromoacteone in the presence of sodium hydroxide also resulted in the similar reaction to afford functionalized thiophene 49 in 66% yield (Scheme 29).

![Chemical structure](image)

**Scheme 29**

Similarly the β-oxodithioester 42 gave functionalized thiophene 48 in 69% yield (Scheme 28).
4.2.3 Conclusions

The reaction of functionalized aroyl dithioacetates and aliphatic β-oxodithiocarboxylates with α-haloketones in presence of sodium hydroxide in ethanol afforded functionalized thiophenes via a selective intramolecular aldol condensation and it was found that the formation of the product highly depends on the stability of enolate ion formed from the ketenedithioacetal intermediate.

4.3 Experimental

4.3.1 Preparation of β-Oxodithioesters: General Procedure

The appropriate active methylene ketone (25 mmol) was added to a well-stirred suspension of trithiocarbonate (3.6 g, 25 mmol) and sodium hydride (200 mmol, 50% suspension) in hexane/DMF (25 mL, 4:1 ratio). The reaction mixture was stirred for further two hours at room temperature. Then the reaction mixture was poured into ice-cold water. The hexane layer was separated and the aqueous layer was acidified with dilute hydrochloric acid. The precipitated dithiocarboxylate was filtered, dried and purified by passing through a column filled with silica gel (60-120 mesh) using hexane as the eluent.
4.3.2 Reactions of Aroyldithioacetates with α-Haloketones: General Procedure

To a well-stirred and cooled suspension of sodium hydroxide (200 mg, 5 mmol) in ethanol (25 mL) β-oxodithioester (5 mmol) was added. After 15 min appropriate alkyl halide (5 mmol) was added and the mixture was stirred at room temperature for 48 hours. It was then poured over ice cold water (50 mL) and extracted with chloroform (50 mL × 3). The organic layer was dried with Na₂SO₄ and the solvent was removed under vacuum. The crude residue was column chromatographed over silica gel using a mixture of hexane-ethylacetate (20:1) as the eluent.

Phenyl-(2-methylsulphenyl)-4-phenylthiophene-5-y1 methanone 39a was obtained as yellow crystalline solid from the reaction of benzoyl dithioacetate 3a (1g, 5 mmol) with phenacyl bromide, 960 mg, 9mmol) mp: 89-90 °C, yield: 0.93 g (60%), ¹H NMR (300 MHz, CDCl₃) δ = 2.62 (s, 3H, SCH₃), 7.02 (s, 1H, thiencyl), 7.09-7.55 (m, 10H, ArH), ¹³C NMR (100.40 MHz, CDCl₃) δ = 19.6, 127.01, 128.00, 128.79, 129.20, 129.54, 130.00, 131.94, 135.94, 135.43, 136.78, 137.66, 146.17, 147.40, 188.67, IR (KBr) ν = 2918, 1620, 1563, 1264 cm⁻¹ ElMS m/z (%) = 310 (M', 90), 291 (12), 233 (40), 190 (13), 158 (24), 146(19), 114 (18), 105 (59), 77 (100).
(4-Chlorophenyl-(2-methylsulphenyl)-4-phenylthiophene-5-yl) methanone 39b was obtained as yellow crystalline solid from the reaction of 5-chloro benzoyl dithioacetate 3b (1.2 g, 5 mmol) with phenacyl bromide, 960 mg, 5 mmol) mp: 82-83 °C, yield: 1.07 g (62%), $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ = 2.62 (s, 3H, SCH$_3$), 6.96 (s, 1H, thiényl), 7.07-7.55 (m, 9H, ArH), $^{13}$C NMR (100.40 MHz, CDCl$_3$) $\delta$ = 19.6, 104.79, 127.91, 128.22, 129.49, 129.64, 130.37, 132.20, 133.86, 133.93, 136.70, 137.67, 146.09, 146.63, 188.31, IR (KBr) v = 287, 1613, 1476, 1383, 1264, 946 cm$^{-1}$, EIMS m/z (%) = 346 (M$^+$+2, 16), 344 (M$, 48), 267 (22), 232 (lo), 105 (SO), 77(100).

[3-(Methylsulphenyl)-4,5-dihydro-naptho[1,2-c]thiophen-1-yl) (phenyl) methanone 43 was obtained as yellow crystalline solid from the reaction of $\beta$-oxodithioester 42 (1.18 g, 5 mmol) with phenacyl bromide (960 mg, 5 mmol) mp: 78-79 °C, yield: 1.04 g (62%) $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ = 2.53 (s, 3H, SCH$_3$), 2.80 (t, 2H, J = 7.2 Hz, CH$_2$), 2.92 (t, 2H, J = 7.2 Hz, CH$_2$), 6.86-7.80 (m, 9H, ArH), $^{13}$C NMR (100.40 MHz, CDCl$_3$) $\delta$ = 19.96, 24.41, 30.16, 96.19 , 105.49, 127.98, 128.12, 128.22, 129.99, 137.64, 141.67, 189.23, IR (KBr) v = 2916, 1641, 1593, 1423, cm$^{-1}$, EIMS m/z (%) = 336 (M$^+$, 55), 259 (29), 216 (20), 105 (60), 77(100)

[3-(Methylsulphenyl)-4,5,6,7-tetrahydro-2-benzothiophen-1-yl) (phenyl)methanone 45 obtained as yellow crystalline solid from the reaction of $\beta$-oxodithioester 44 (940 mg, 5 mmol) with phenacyl bromide (960 mg, 5 mmol), mp: 69-70 °C, yield: 864 mg (60%) $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ = 1.7-1.85 (m, 4H, CH$_2$), 2.55 (s, 3H, SCH$_3$), 2.60 (t, 2H, J = 7Hz, CH$_2$), 3.0 (t, 2H, J = 7 Hz, CH$_2$), 7.45(t, 2H, J = 8Hz, ArH), 7.54(t, 1H, J = 8Hz, ArH), 7.77(d, 2H, J = 8Hz, ArH), $^{13}$C NMR (100.40 MHz, CDCl$_3$) $\delta$ = 18.56, 22.35, 22.67, 25.30, 28.23, 128.17, 128.49, 131.51, 132.36, 138.82, 140.66, 142.22, 148.33, 187.99, IR (KBr) v = 1620, 1565, 1505, 1435, 1380, 1320 cm$^{-1}$, EIMS m/z (%) = 288 (M$, 100), 240 (38.5), 211(7.7), 106 (50.8), 77 (46.5)
3-Methyl-5-(methylsulphanyl)-2-thienyl[(phenyl) methanone 47 was obtained as dark brown oil from the reaction β-oxodithioester 46 (740 mg, 5 mmol) with phenacyl bromide, yield: 71 g (58%). \( ^1H \) NMR (300 MHz, CDCl\(_3\)) \( \delta = \) 2.41 (s, 3H, CH\(_3\)), 2.55 (s, 3H, SCH\(_3\)), 6.83 (s, 1H, C-4), 7.46 (dd, 2H, J = 8Hz, ArH), 7.54 (dd, 1H, J = 8Hz, ArH), 7.78 (d, 2H, J = 8Hz, ArH), 13C NMR (100.40 MHz, CDCl\(_3\)) \( \delta = \) 16.83, 19.23, 128.12, 128.49, 128.70, 131.75, 134.22, 139.95, 146.64, 146.70, 188.20, GCMS m/z (%) = 248 (M\(^+\), 100), 200 (42.7), 171 (38.6), 128 (6.1), 105 (27.3), 77 (42.4).

1-{3-(4-Chlorophenyl)-5-(methylsulphanyl)-2-thienyl}-1-ethanone 33a was obtained as yellow crystalline solid from the reaction β-oxodithioester 3a (1 g, 5 mmol) with bromoacetone (680 mg, 5 mmol) mp: 86-87 °C, yield: 0.962 g (68%). \( ^1H \) NMR (300 MHz, CDCl\(_3\)) \( \delta = \) 2.36 (s, 3H, CH\(_3\)), 2.6 (s, 3H, SCH\(_3\)), 6.79 (s, 1H, 4-H), 7.31-7.37 (m, 5H, ArH), 13C NMR (75.46 MHz, CDCl\(_3\)) \( \delta = \) 19.08, 29.11, 128.70, 129.90, 130.02, 130.37, 134.59, 134.67, 138.65, 146.07, 147.72, 190.33, IR (KBr) \( \nu = \) 1630, 1540, 1480, 1360, 1260, 1080 cm\(^{-1}\), GCMS m/z (%) = 248 (M\(^+\), 80), 233 (100), 218 (5), 190 (14), 158 (20).

1-{3-(4-Chlorophenyl)-5-(methylsulphanyl)-2-thienyl}-1-ethanone 33b was obtained as yellow crystalline solid from the reaction β-oxodithioester 3b (1.2 g, 5 mmol) with bromoacetone (680 mg, 5 mmol), mp: 70-72 °C, yield: 0.892 g (72%). \( ^1H \) NMR (300 MHz, CDCl\(_3\)) \( \delta = \) 2.1 (s, 3H, CH\(_3\)), 2.6 (s, 3H, SCH\(_3\)), 6.81 (s, 1H, 4-H), 7.29 (d, 2H, J=9 Hz, ArH), 7.42 (d, 2H, J=9 Hz, ArH), 13C NMR (100.40 MHz, CDCl\(_3\)) \( \delta = \) 18.96, 29.00, 128.57, 129.74, 130.26, 134.47, 138.49, 145.95, 147.60, 190.16, IR (KBr) \( \nu = \) 1620, 1520, 1480, 1360, 1260, 1080 cm\(^{-1}\), GCMS m/z (%) = 284 (M\(^+\)+2), 269 (100), 234 (32.1), 182 (7.6), 146 (8.6).
2-Acetyl-5-methylthio-3,4-dihydronaphthothiophene 48 was obtained as yellow crystalline solid from the reaction β-oxodithioester 42 (940 mg, 5 mmol) with bromoacetone (680 mg, 5 mmol) mp: 79-80 °C Yield: 0.75g, (66%) \(^1\)HNMR (300 MHz, CDCl\(_3\)) δ = 2.54 (s, 3H, SCH\(_3\)), 2.69 (s, 3H, COCH\(_3\)), 2.72 (t, 2H, J = 7.2Hz, -CH\(_2\)CH\(_2\)), 2.85 (t, 2H, J = 7.2Hz, -CH\(_2\)CH\(_2\)), 7.25-7.82 (m, 4H, ArH) \(^1\)C NMR (100.40 MHz, CDCl\(_3\)) δ = 19.62, 24.12, 24.55, 29.26, 29.88, 30.25, 126.37, 127.97, 128.85, 129.35, 138.46, 141.28, 142.34, 190.80 IR(KBr, \(\nu_{\text{max}}\)) 3019, 2903, 1650.98, 1474.70, 1407, 1371, 1255.67, 1152, 1067.965 cm\(^{-1}\), EIMS m/z (%) 274 (M\(^+\)), 259 (80), 216 (20), 184(16), 171(21),139 (20).

\[3-(\text{Methylsulphonyl})-4,5,6,7\text{-tetrabeno}1\text{hiophen-1-yl}]1\text{-ethanone} 49 was obtained as yellow crystalline solid exclusively from the reaction β-oxodithioester 44 (1.18 g, 5 mmol) with bromoacetone (680 mg, 5 mmol), mp: 75-76 °C, yield: 0.95g (69%), \(^1\)H NMR (300 MHz, CDCl\(_3\)) δ = 1.74 (m, 4H, CH\(_3\)), 2.46 (s, 3H, CH\(_3\)), 2.55 (s, 3H, SCH\(_3\)), 2.56 (brs, 2H, CH\(_2\)), 3.00 (brs, 2H, CH\(_2\)). \(^1\)C NMR (100.40 MHz, CDCl\(_3\)) δ = 18.6, 22.35, 22.72, 25.55, 28.07, 29.43, 134.37, 139.19, 140.07, 146.43, 189.35, IR (KBr) \(\nu = 1640, 1510, 1410, 1380, 1350, 1315, 1260, 1160, 1140, 980\) cm\(^{-1}\), EIMS m/z (%) = 226 (14.1), 225 (93.6), 210 (100), 182 (14.6), 167 (11.6).

4.7 References


