CHAPTER-IV
STANNOUS CHLORIDE PROMOTED SYNTHESIS OF DITHIOCARBAMATES

IV. A. INTRODUCTION

Organic dithiocarbamates are valuable synthetic intermediates, which are ubiquitously found in a variety of biologically active compounds. Functionalization of the carbamate moiety offers an attractive method for the generation of derivatives, which may constitute interesting medicinal and biological properties. Due to the ability of dithiocarbamates to chelate with different metal ions many of the dithiocarbamates have found applications in inorganic analysis. A number of these dithiocarbamates have been used in the rubber industry as vulcanization accelerators. Their applications in the field of agriculture are also unlimited. Pyrrolidine dithiocarbamates have been reported to have antiviral activity against influenza virus. Pyrrolidine dithiocarbamate (PDTC) is also considered an antioxidant and is frequently used to study the role of free radical reactions in various biological processes and against free radical-induced cellular injuries. Reports in the literature demonstrate that the dithiocarbamate containing molecules show
antibacterial, antihelmintic, anti-cancer, fungicidal and growth depressant properties.\textsuperscript{8,9}

The utility of dithiocarbamate group as linkers in solid phase organic synthesis\textsuperscript{10} and in certain photochemical applications\textsuperscript{11} is also well documented. They have been used extensively as intermediates in organic synthesis,\textsuperscript{12} for the protection of amino groups in peptide synthesis,\textsuperscript{13} as linkers in solid phase organic synthesis,\textsuperscript{14} as radical precursors\textsuperscript{15} and recently in the synthesis of ionic liquids.\textsuperscript{16} They have also been widely used in the synthesis of trifluoromethylamines,\textsuperscript{17} thioureas,\textsuperscript{18} aminobenzimidazoles,\textsuperscript{19} isothiocyanates,\textsuperscript{20} alkoxyamines,\textsuperscript{21} 2-imino-1,3-dithiolane,\textsuperscript{22} and total synthesis of (-)-aphanorphine.\textsuperscript{23} For these reasons, the synthesis of dithiocarbamate derivatives with different substitution patterns at the thiol chain has become a field of increasing interest in synthetic organic chemistry during the past few years.

**IV. B. SYNTHETIC METHODS OF DITHIOCARBAMATES**

In fact, few methods for the synthesis of dithiocarbamate derivatives have been reported in the literature, and among them, condensation of primary and secondary amines with costly and toxic reagents, such as thiophosgene and isothiocyanate constitute the most widely used general methods for the synthesis of this class of compounds.\textsuperscript{24} The method involves simple alkylation of sodium salt of \textit{N,N}-dimethyl dithiocarbamate 2 by methyl
iodide in ethanol to yield the corresponding methyl N,N-dimethyl dithiocarbamate 3 in good yields. The sodium dithiocarbamate 2 was prepared by reacting dimethyl amine in carbon disulphide in the presence of NaOH (scheme-1).

\[ \text{N–H} \xrightarrow{\text{NaOH, CS}_2} \text{N} \xrightarrow{\text{CH}_3/\text{EtOH}} \text{N} \]

**Scheme-1**

Subsequently, Grunwell\(^{25}\) reported the reaction of primary, secondary and tertiary alkyl, alkenyl and aryl Grignard reagents 4 with tetramethyl thiuram disulphide (TMTD) 5 to form the corresponding dithiocarbamate 6 (scheme-2).

\[ \text{R-MgX + } \text{N(CH}_3)_2 \xrightarrow{\text{1. Et}_2\text{O, rt}} \text{N} \xrightarrow{\text{2. NH}_4\text{Cl, H}_2\text{O}} \]

**Scheme-2**
Later on Barret and co-workers\textsuperscript{26} developed a novel method for synthesis of dithiocarbamates \textbf{13} through aminolysis of tertiary alkyl xanthates \textbf{11}. The xanthates were prepared from tertiary alcohols and showed that the amines react with these xanthates to afford the corresponding thioureas \textbf{12} in good yields. The steric hinderance of these tertiary alkyl group facilitates the elimination of alcohol during this reaction gives rise to dithiocarbamates \textbf{13}. In this way, dithiocarbamate \textbf{10} can also be prepared from hindered xanthates by reactions with L-\textit{\alpha}-amino acid (scheme-3).

\textbf{Scheme-3}

The reaction of aniline \textbf{14} with aqueous 20M sodium hydroxide and carbon disulphide in DMSO as solvent yielded initially the corresponding sodium
N-aryl dithiocarbamates\textsuperscript{27} 15 which are converted in situ to the corresponding methyl N-aryl dithiocarbamates 16 by alkylation with methyl iodide (scheme-4).

![Scheme-4](image)

Salvatore and co-workers\textsuperscript{28} reported cesium carbonate and tetrabutylammonium iodide (TBAI) facilitated efficient thiocarbamation of amines, using carbon disulfide with alkyl halides (scheme-5). This protocol was mild, chemoselective, and efficient, compared to the existing methods.

![Scheme-5](image)

Saidi and co-workers\textsuperscript{29} performed an efficient one-pot Michael addition of dithiocarbamate anion to $\alpha,\beta$-unsaturated olefins mediated by lithium
perchlorate (scheme-6). The reaction of substituted dithiocarbamates with electrophilic alkenes in the presence of LiClO$_4$ was investigated in an attempt to prepare numerous ethyl dithiocarbamates bearing β-electron withdrawing group substituents 23. The reaction conditions are mild, neutral, with extremely simple work-up procedures, and offer high yield.

\[
\begin{align*}
&\text{R'N} + \text{CS}_2 + \text{R''EWG} \xrightarrow{\text{Solid LiClO}_4, \text{DMF, r.t.}} \text{R'N} \text{R''} S S \text{EWG} \\
&\text{R''}=\text{H or Me}
\end{align*}
\]

Scheme-6

Saidi \textit{et al.} also reported one pot synthesis of dithiocarbamates accelerated in water.\textsuperscript{30} The organic reactions in aqueous media have attracted much attention in synthetic organic chemistry, not only because water is one of the most abundant, cheapest, and environmentally friendly solvents but also because water exhibits unique reactivity and selectivity, which is different from those in conventional organic solvents. Highly efficient one-pot reactions of primary and secondary amines 24 and carbon disulphide with α,β -unsaturated compounds 25 were carried out in water under a mild and green procedure to give dithiocarbamate 26 in good yield (scheme-7). This protocol avoids the use of basic and highly toxic organic solvents, such as
DMF or DMSO, and catalysts by playing the dual role of water as a solvent and a promoter.

\[ RR'NH + CS_2 + \text{r.t., 5-18h} \rightarrow \text{R'RN}_2\text{S}_2\text{O}_2 \]

\(X= \text{CN, COOMe, COR, CONH}_2\)

**Scheme-7**

Recently, highly efficient, one-pot and three component reactions of amines and carbon disulfide with alkyl vinyl ethers 27 via Markovnikov addition reaction were carried out in water under a mild and green procedure to afford dithiocarbamate 28 with excellent yield and complete regiospecificity\(^{31}\) (scheme-8).

\[ RR'NH + CS_2 + \text{r.t.,} \rightarrow \text{R'RN}_2\text{S}_2\text{O}_2 \]

**Scheme-8**

The advantageous of this procedure including excellent yields, clean reaction conditions, catalyst-free, and simple experimental procedures make it a useful and attractive strategy in MCRs in combinational chemistry.
Behalo and co-workers\textsuperscript{32} also reported a facile one-pot three component synthesis of dithiocarbamate derivatives \textsuperscript{31} from the reaction of chalcones \textsuperscript{29}, amine, and carbon disulfide (scheme-9).

![Scheme-9](image)

**Scheme-9**

**IV. C. SYNTHETIC APPLICATION OF STANNOUS CHLORIDE**

Stannous chloride dihydrate, which is cheap and commercially available, is known to be an efficient Lewis acid type precatalyst for carbon-carbon bond forming reactions and allylic addition of functionalized compounds to aldehydes and ketones. To name a few, SnCl\textsubscript{2}.2H\textsubscript{2}O has been found to be useful and highly efficient for the preparation of $\beta$-acetamido ketones and $\beta$-acetamido ketoesters \textsuperscript{33} by a one-pot reaction of aryl aldehydes, \textsuperscript{32} enolisable ketones, \textsuperscript{33} acetyl chloride and acetonitrile in a solvent-free media at room temperature (scheme-10). This method offers several advantages such as excellent yields, simple procedure, short reaction times (1–2.5h) and milder conditions.
Scheme-10

Sujit Roy et al.\textsuperscript{34} reported SnCl\textsubscript{2} mediated efficient \(N,N\)-dialkylation of azides \textsuperscript{36} to tertiary-amine \textsuperscript{38} via potential stannaimine intermediate (scheme-11). This new carbon–nitrogen bond formation strategy adds to the repertoire of tin (II) chemistry.

Scheme-11

Liu and co-workers\textsuperscript{35} performed systematic studies on SnCl\textsubscript{2}-mediated carbonyl allylation reaction between aldehydes \textsuperscript{39} and allyl halides \textsuperscript{40} in fully aqueous media (scheme-12). Totally three valuable reaction systems were discovered, which were SnCl\textsubscript{2}/CuCl\textsubscript{2}, SnCl\textsubscript{2}/TiCl\textsubscript{3}, and SnCl\textsubscript{2}/PdCl\textsubscript{2}. They all provided good to excellent yields in the allylation of aliphatic and aromatic aldehydes under very mild and convenient conditions. SnCl\textsubscript{2}, by itself, was also found to be effective for the allylation reaction when allyl...
bromide was employed. However, the SnCl$_2$-only reaction could only tolerate very small amount of water as the solvent.

![Chemical structure]

\[ R\text{H}XR\xrightarrow{\text{MCl}_n/\text{SnCl}_2, H_2O} R\text{OH} \]

\[ X = \text{Br, Cl} \]

\[ \text{MCl}_n = \text{CuCl}_2, \text{TiCl}_3, \text{PdCl}_2 \]

**Scheme-12**

Yasuda *et al.*$^{36}$ reported highly stereoselective synthesis of vicinal diols (scheme-13) by stannous chloride mediated addition of hydroxyallylic stannanes to aldehydes. A new protocol for the synthesis of vicinal diols was accomplished by the reaction of unprotected $\alpha$-hydroxymethylmetals, 42 as hydroxymethyl anion equivalents, with aldehydes 39. The treatment of hydroxyallylic stannanes, which were prepared from $\alpha,\beta$-unsaturated aldehydes and Bu$_3$SnLi in situ, with various aldehydes gave but-3-en-1,2-diols 43 in the presence of SnCl$_2$. The stereochemistry of the diol and olefin moieties demonstrated syn- and $E$-selectivities, respectively.

![Chemical structure]

**Scheme-13**
Li and co-workers\textsuperscript{37} also reported SnCl\textsubscript{2}-mediated carbonyl allylation of aldehydes and ketones \textbf{44} in ionic liquid. In ionic liquid [bmim]BF\textsubscript{4}, SnCl\textsubscript{2}.2H\textsubscript{2}O acts as an inexpensive and efficient metal salt for carbonyl allylation. By applying ionic liquid, some previously reported serious operational problems associated with the SnCl\textsubscript{2}-mediated allylation reaction are avoided. Furthermore, ketones, which are less reactive than aldehydes, can also be allylated in high yields with this system (\textbf{scheme-14}).

\begin{center}
\begin{tikzpicture}
    \node at (0,0) {\textbf{scheme-14}};
    \node at (-1.5,0) \begin{tabular}{c}
    \textbf{44} \quad \textbf{40} \quad \textbf{45}
    \end{tabular};
    \node at (-2.5,0) \begin{tabular}{c}
    \textbf{R} \quad \textbf{H(Me)} \quad \textbf{Br} \quad \textbf{SnCl}_2.2\text{H}_2\text{O} \quad [\text{bmim}]\text{BF}_4 \\
    \textbf{O} \quad \textbf{SnCl}_2.2\text{H}_2\text{O} \quad [\text{bmim}]\text{BF}_4 \\
    \textbf{H(Me)} \quad \textbf{OH} \quad \textbf{R} \quad \textbf{Br}
    \end{tabular};
    \node at (-4.5,0) \begin{tabular}{c}
    \textbf{R} \quad \textbf{H(Me)} \quad \textbf{OH}
    \end{tabular};
\end{tikzpicture}
\end{center}

Scheme-14

Rai \textit{et al.} reported the reduction of nitroarenes, \textbf{46} to the corresponding aromatic amines, \textbf{47} using stannous chloride in ionic liquid medium under sonication.\textsuperscript{38}

\begin{center}
\begin{tikzpicture}
    \node at (0,0) {\textbf{scheme-15}};
    \node at (-1.5,0) \begin{tabular}{c}
    \textbf{46} \quad \textbf{47}
    \end{tabular};
    \node at (-2.5,0) \begin{tabular}{c}
    \textbf{NO}_2 \quad \textbf{NH}_2 \\
    \textbf{R} \quad \textbf{R}
    \end{tabular};
    \node at (-4.5,0) \begin{tabular}{c}
    \textbf{SnCl}_2.2\text{H}_2\text{O}, \text{Ionic liquid, sonication} \\
    \textbf{rt, 10-15 min.}
    \end{tabular};
\end{tikzpicture}
\end{center}

Scheme-15
IV. D. PRESENT WORK, RESULTS AND DISCUSSION

With the increasing interest in developing environmentally benign reactions, the atom-economic catalytic processes or solventless reactions are ideal processes in organic chemistry. As a continuation of our research devoted to the development of green chemistry by performing organic transformations under solvent-free conditions, herein we report an efficient, novel and entirely green procedure for the synthesis of S-allyl-N-aryl-dithiocarbamate under solvent free condition at room temperature.

Initially, we examined the three-component one pot reaction using aniline (6 mmol), CS$_2$ (6 mmol), allylbromide (3 mmol) with SnCl$_2$.2H$_2$O (0.01 mmol) as catalyst under solvent-free conditions to afford the S-allylated-N-aryl dithiocarbamate 49a, in 93% yield (scheme-16).

Scheme-16. One pot three component synthesis of S-allyl-N-aryl-dithiocarbamate 49a.

Next, we evaluated the scope of this catalytic system by employing a wide range of metal salts. The reaction between aniline, CS$_2$ and allylbromide was carried out as a template using different metal salts as catalysts. The yields of
products under different catalysts are summarized in table-1. The best yield was obtained by using SnCl₂·2H₂O and duration of completion of the reaction was only 20min, whereas in the other catalytic systems the duration for completion was at the range of 3-6h to get the maximum yield.

**Table-1.** Synthesis of S-allyl-N-phenyl dithiocarbamate using different catalyst.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Time</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SnCl₂</td>
<td>10 min</td>
<td>93</td>
</tr>
<tr>
<td>2</td>
<td>CuCl₂</td>
<td>3 h</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td>FeCl₃</td>
<td>4 h</td>
<td>81</td>
</tr>
<tr>
<td>4</td>
<td>ZnCl₂</td>
<td>6 h</td>
<td>70</td>
</tr>
<tr>
<td>5</td>
<td>AlCl₃</td>
<td>5 h</td>
<td>75</td>
</tr>
</tbody>
</table>

*Reaction conditions: solvent-free, aniline (6 mmol), CS₂ (6 mmol), allyl bromide (3 mmol), catalyst (0.01 mmol).

Thus, we optimized the reaction using SnCl₂·2H₂O (0.01 mmol) as the catalyst and stirring the reaction mixture at room temperature for 20 min only. The generality of the present method was extended to different substituted aromatic amines and substituted allyl bromide.
Table 2. Stannous Chloride promoted allylated dithiocarbamates

\[
\begin{align*}
\text{R}_4 = \text{H, CH}_3
\end{align*}
\]

<table>
<thead>
<tr>
<th>Entry</th>
<th>R₁</th>
<th>R₂</th>
<th>R₃</th>
<th>R₄</th>
<th>Product</th>
<th>(^c\text{Yield (%)})</th>
<th>Mp.(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>49a</td>
<td>90</td>
<td>185</td>
</tr>
<tr>
<td>2</td>
<td>CH₃</td>
<td>H</td>
<td>CH₃</td>
<td>H</td>
<td>49b</td>
<td>92</td>
<td>157</td>
</tr>
<tr>
<td>3</td>
<td>C₂H₅</td>
<td>H</td>
<td>C₂H₅</td>
<td>H</td>
<td>49c</td>
<td>95</td>
<td>145</td>
</tr>
<tr>
<td>4</td>
<td>Cl</td>
<td>H</td>
<td>CH₃</td>
<td>H</td>
<td>49d</td>
<td>89</td>
<td>163</td>
</tr>
<tr>
<td>5</td>
<td>Cl</td>
<td>CH₃</td>
<td>H</td>
<td>H</td>
<td>49e</td>
<td>91</td>
<td>201</td>
</tr>
<tr>
<td>6</td>
<td>C₂H₅</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>49f</td>
<td>94</td>
<td>115</td>
</tr>
<tr>
<td>7</td>
<td>Cl</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>49g</td>
<td>95</td>
<td>215</td>
</tr>
<tr>
<td>8</td>
<td>CH₃</td>
<td>H</td>
<td>CH₃</td>
<td>CH₃</td>
<td>49h</td>
<td>93</td>
<td>135</td>
</tr>
<tr>
<td>9</td>
<td>C₂H₅</td>
<td>H</td>
<td>C₂H₅</td>
<td>CH₃</td>
<td>49i</td>
<td>91</td>
<td>115</td>
</tr>
</tbody>
</table>

\(^b\)Reaction conditions: solvent-free, aniline (6 mmol), CS₂ (6 mmol), allyl/crotyl bromide (3 mmol), SnCl₂·2H₂O (0.01 mmol). \(^c\)Isolated yields.

As can be seen from Table 2, various substituted anilines, CS₂ and allyl/crotyl bromide were treated under the solvent-free, multicomponent reactions to yield the corresponding S-allyl-N-aryl dithiocarbamates 49a-i in good to excellent yields. The present method is experimentally simple and generates no byproducts.
IV. E. CONCLUSION

In summary, we have described a novel, highly efficient and entirely green protocol for one pot preparation of S-allyl-N-aryl dithiocarbamates catalyzed by stannous chloride under solvent-free conditions. The shorter reaction time and good to excellent yield of the desired products is the speciality of this synthetic protocol.

IV. F. EXPERIMENTAL SECTION

General: Reagents were commercially purchased from Aldrich and used without further purification. Commercial solvents were used after distillation. Melting points were determined on a “Veego MP-I” capillary melting point apparatus and are uncorrected. The IR spectra were recorded on a Perkin Elmer 983 and Shimadzu IR-408 spectrometers. Infrared spectra were recorded as thin films on KBr plates with ν max in cm⁻¹. ¹H NMR spectra were taken in commercial DMSO-d₆ or CDCl₃ on a multinuclear spectrometer (300MHz) with all chemical shifts being reported in parts per million δ relative to internal tetramethylsilane (TMS, δ 0.0). Data are reported as follows: chemical shift (multiplicity [singlet (s), doublet (d), triplet (t), quartet (q), broad (brs), and multiplet (m)], coupling constants [Hz], integration). ¹³C NMR spectra were taken on a multinuclear spectrometer (75.5 MHz), using diluted solutions of each compound in DMSO-d₆ or CDCl₃ as the solvent, and the chemical shifts are reported in ppm (δ unit) downfield from tetramethylsilane as the internal standard. Mass
measurements were carried out with Jeol JMSD-300 spectrometer. Elemental analyses were performed on a Heracus CHN-O-Rapid Analyzer. Column chromatography was performed on Merck Silica Gel 60 (230-400 mesh) using analytical reagent grade hexane and ethyl acetate as eluents.

**General experimental procedure for the preparation of compound (49a-i):** To a mixture of CS$_2$ (6 mmol) and allyl/crotyl bromide (3 mmol) was added an aromatic amine (6 mmol) in presence of catalytic amount of SnCl$_2$.2H$_2$O (0.01 mmol). The reaction mixture was stirred at room temperature under vigorous magnetic stirring for 10-30 min. Then the organic materials were extracted with chloroform or ethyl acetate (2×10 mL). The combined organic phases were washed with water and dried over anhydrous sodium sulphate. The solvent was evaporated & white crystals of allylated dithiocarbamates were found at the bottom of the flask. Analytically pure products could be obtained by simple crystallisation using either diethyl ether or ethylacetate and thus column chromatography was not required.

**S-Allyl-N-phenyl dithiocarbamate (49a):** Colourless solid, m.p.185°C; IR (KBr) (v max): 1235, 1600, 3137 cm$^{-1}$, $^1$H NMR (DMSO-d$_6$, 300 MHz) δ 3.91-3.93 (d, $J = 6.2$Hz, 2H), 5.03 5.12 (m, 2H), 5.96-6.01 (m, 1H), 6.79-7.01 (m, 5H); $^{13}$CNMR (DMSO-d$_6$, 75.5 MHz) 51.7, 124.3, 126.1, 128.3, 129.1, 133.1, 139.3, 199.9; MS: m/z = 209 (M$^+$). Anal. Calcd for C$_{10}$H$_{11}$NS$_2$: C, 57.38; H, 5.30; N, 6.69; Found: C, 57.37; H, 5.33; N, 6.67.
**S- Allyl-N-(2,6-dimethylphenyl)dithiocarbamate** (49b): Colourless solid, m.p. 157°C; IR (KBr) (v max): 1237, 1569, 3137 cm⁻¹; ¹HNMR (CDCl₃, 300 MHz) δ 2.63 (s, 6H), 4.14-4.15 (d, J =6Hz, 2H), 5.31-5.33 (m, 2H), 6.05-6.15 (m, 1H), 7.08-7.10 (d, J = 5.4Hz, 2H), 7.18-7.22 (m, 1H); ¹³C NMR (CDCl₃, 75.5 MHz) 19.4, 51.9, 124.5, 126.2, 128.6, 129.3, 131.2, 132.1, 199.5; MS: m/z = 237 (M⁺). Anal. Calcd for C₁₂H₁₅NS₂: C, 60.72; H, 6.37; N, 5.90; Found: C, 60.71; H, 6.39, N, 5.89.

**S- Allyl-N-(2,6-diethylphenyl)dithiocarbamate** (49c): Colourless solid, m.p.145°C; IR (KBr) ( v max): 1276, 1573, 3145 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 1.31-1.35 (t, J = 9Hz, 6H), 3.01-3.03 (d, J = 6Hz, 4H), 4.14-4.16 (d, J = 5.4 Hz, 2H), 5.27-5.29 (d, J = 5.4 Hz, 2H), 6.04-6.13 (m, 1H), 7.18-7.20 (d, J = 5.4 Hz, 2H), 7.31-7.35 (m, 1H), 10.38 (s, br, 1NH); ¹³C NMR (CDCl₃, 75.5 MHz) 15.5, 24.8, 53.9, 125.17, 126.75, 127.77, 129.6, 130.0, 138.5, 199.7; MS: m/z=265 (M⁺). Anal. Calcd for C₁₄H₁₉NS₂: C, 63.35; H, 7.21; N, 5.28; Found: C, 63.51; H, 7.19, N, 5.29.

**S- Allyl-N-(2-chloro-6-methylphenyl)dithiocarbamate** (49d): Colourless solid, m.p. 163°C; IR (KBr) (v max): 1275, 1579, 3147 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 2.61 (s, 3H), 4.11-4.15 (d, J = 5.4Hz, 2H), 5.33-5.35 (m, 2H), 6.01-6.13 (m, 1H), 7.29-7.39 (m, 3H); ¹³CNMR (CDCl₃, 75.5 MHz) 19.1, 51.5, 124.1, 126.5, 128.9, 129.1, 131.7, 132.3, 140.7, 199.9; MS: m/z = 257 (M⁺). Anal. Calcd for C₁₁H₁₂NS₂Cl: C, 51.25; H, 4.69; N, 5.43; Found: C, 51.51; H, 4.19, N, 5.45.
S-Allyl-N-(2-chloro-3-methylphenyl)dithiocarbamate (49e): Colourless solid, m.p. 201°C; IR (KBr) (ν max): 1273, 1587, 3149 cm\(^{-1}\); \(^1\)HNMR (DMSO-d\(_6\), 300 MHz) δ 2.63 (s, 3H), 4.10-4.23 (d, J = 5.4 Hz, 2H), 5.29-5.33 (m, 2H), 6.09-6.15 (m, 1H), 7.19-7.27 (m, 3H); \(^13\)CNMR (DMSO-d\(_6\), 75.5 MHz) 19.7, 51.3, 124.5, 126.7, 128.3, 129.1, 131.9, 133.1, 140.9, 199.7; MS: m/z = 257 (M\(^+\)). Anal. Calcd for C\(_{11}\)H\(_{12}\)NS\(_2\)Cl: C, 51.25; H, 4.69; N, 5.43; Found: C, 51.33; H, 4.59, N, 5.47.

S-Allyl-N-(2-ethylphenyl)dithiocarbamate (49f): Colourless solid, m.p. 115°C; IR (KBr) (ν max): 1275,1589, 3149 cm\(^{-1}\); \(^1\)HNMR (CDCl\(_3\), 300MHz) δ 1.31-1.33 (t, J = 9Hz, 3H), 3.03-3.05 (q, 2H), 4.11-4.14 (d, J = 5.4Hz, 2H), 5.59-6.13 (m, 2H), 6.07- 6.11 (m, 1H), 7.29-7.37 (m, 4H); \(^13\)CNMR (CDCl\(_3\), 75.5 MHz) 15.5, 24.9, 51.5, 125.17, 126.75, 127.77, 129.6, 130.0, 133.1, 136.1 138.5, 199.7; MS: m/z = 237 (M\(^+\)). Anal. Calcd for C\(_{12}\)H\(_{15}\)NS\(_2\): C, 60.72; H, 6.37; N, 5.90; Found: C, 60.51; H, 6.19, N, 5.99.

S-Allyl-N-(2-chlorophenyl)dithiocarbamate (49g): Colourless solid, m.p. 215°C; IR (KBr) ( ν max): 1279, 1587, 3147 cm\(^{-1}\); \(^1\)HNMR (DMSO-d\(_6\), 300 MHz) δ 4.14-4.16 (d, J = 5.4 Hz, 2H), 5.27-5.29 (d, J =5.4 Hz, 2H), 6.04-6.13 (m, 1H), 7.18-7.25 (m, 4H), 10.38 (s, br, 1NH); \(^13\)CNMR (DMSO-d\(_6\), 75.5 MHz) 53.9, 125.1, 126.7, 127.2, 127.9 129.6, 130.0, 136.3, 138.5, 199.9; MS: m/z = 243 (M\(^+\)). Anal. Calcd for C\(_{19}\)H\(_{10}\)NS\(_2\)Cl: C, 49.27; H, 4.13; N, 5.75; Found: C, 49.31; H, 4.19, N, 5.79.
But-3-en-2-yl(2,6-dimethylphenyl)dithiocarbamate (49h): Colourless solid, m.p. 135°C; IR (KBr) (ν max): 1275, 1589, 3145 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 1.62-1.63 (d, J = 4.2 Hz, 3H), 2.64-2.68 (s, 6H), 4.07-4.09 (d, J = 5.1 Hz, 2H), 5.03-5.12 (m, 1H), 5.65-5.80 (m, 1H), 7.07-7.09 (d, J = 5.7 Hz, 2H), 7.17-7.27 (m, 1H); ¹³C NMR (CDCl₃, 75.5 MHz) 17.8, 19.8, 52.1, 119.5, 129.2, 129.9, 131.8, 132.9, 137.5, 199.7; MS: m/z = 251 (M⁺). Anal. Calcd for C₁₃H₁₇NS₂: C, 62.1; H, 6.82; N, 5.57; Found: C, 62.51; H, 6.79, N, 5.59.

But-3-en-2-yl (2,6-diethylphenyl)dithiocarbamate (49i): Colourless solid, m.p. 115°C; IR (KBr) (ν max): 1269, 1591, 3153 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 1.31-1.35 (t, J = 7.5 Hz, 6H), 1.61-1.63 (d, J = 4.2 Hz, 3H), 3.01-3.03 (d, J = 6 Hz, 4H), 4.14-4.16 (m, 1H), 5.27-5.29 (m, 2H), 6.04-6.13 (m, 1H), 7.18-7.20 (d, J = 5.4 Hz, 2H), 7.31-7.35 (m, 1H), 10.38 (s, br, NH); ¹³C NMR (CDCl₃, 75.5 MHz) 17.5, 19.3, 24.8, 53.9, 119.5, 129.5, 129.9, 131.7, 132.9, 137.9, 199.7; MS: m/z = 279 (M⁺). Anal. Calcd for C₁₅H₂₁NS₂: C, 64.47; H, 7.57; N, 5.01; Found: C, 64.51; H, 7.59, N, 5.09.

REFERENCES

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