CHAPTER - 3

section 3.1 Synthesis of the compounds of Series - 1 and Series - 2

Section 3.2 Characterization of the compounds of Series - 1 and Series - 2
Section - 3.1: Synthesis of the compounds of Series -1 and Series -2

Section - 3.1.1. Synthesis of the compounds of the Series -1:

The compounds of the Series -1 were synthesised by following the first four steps of the Scheme -1 (page no.64). The procedure applied is given below:

Step -1. Synthesis of the Ethyl -N⁴ - methyl -N¹ - piperazinylacetate, Compound LS-1:

A mixture of 25 ml (0.2 mol) N⁴ - methyl -N¹- piperazine, 28ml (0.2 mol) ethyl chloro acetate and 5.0gm anhydrous K₂CO₃ in 80 ml acetone was refluxed on a steam bath for about 8 hours. The solvent was distilled off under reduced pressure and the resulting solid was poured into ice cold water and the insoluble material was recrystallised from ethanol as light reddish coloured crystals of Compound LS-1.

![Chemical structure](image)

N-methyl piperazine

Compound LS-1

Characterization data of the Compound LS-1:

M.P. : 188 - 90°

Yield : 70 %

T.L.C. : Solvent systems

<table>
<thead>
<tr>
<th>Solvent systems</th>
<th>Rf values</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHCl₃: MeOH (9:1 v/v)</td>
<td>0.72</td>
</tr>
<tr>
<td>CHCl₃: MeOH (8:2 v/v)</td>
<td>0.80</td>
</tr>
</tbody>
</table>

Molecular formula : C₉H₁₈N₂O₂

Elemental analysis :

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>H</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Found %</td>
<td>57.90</td>
<td>9.58</td>
<td>15.01</td>
</tr>
<tr>
<td>Calculated %</td>
<td>58.06</td>
<td>9.67</td>
<td>15.05</td>
</tr>
</tbody>
</table>

IR(KBr)νmax : 1420, 1345, 1200, 1125, 1110, 1080, 1050 and 830

(piperazine nucleus); 2915 and 2850 (N-CH₃ and methyl group)
in-COO \( \text{C}_2\text{H}_4 \)); 2925,1460 and 1230 (N-CH\(_3\)); 1735,1460 and 1180 (C=O); 1440 and 720 (-CH\(_2\)).

\(^1\)H NMR (CDCl\(_3\))\(\delta\):
- 1.90 (s,3H, -N-CH\(_3\));
- 2.60 (m,8H, 2x CH\(_2\)-N-CH\(_2\));
- 3.62 (s,2H,-N-CH\(_2\));
- 1.20 (t,3H, J= 7Hz, -COOCH\(_2\)CH\(_3\));
- 4.20 (q,2H, J=7Hz, -COOCH\(_2\)CH\(_3\)).

**Step 2. Synthesis of 1- (N\(^4\)-methyl-N\(^1\)-piperazinylacetyl) - thiosemicarbazide, Compound LS-2:**

25ml (0.1 mol) ethyl N\(^4\)-methyl-N\(^1\)-piperazinylacetate, **Compound LS-1** and 9.1gm (0.1mol) thiosemicarbazide in 100ml absolute alcohol was refluxed on a water bath for about 10 hours. The excess of the solvent was removed under reduced pressure. The resulting crystals was recrystallised from ethanol to get light brown coloured crystals of **Compound LS-2**.

![Chemical structures](image)

**Compound LS-1**

**Compound LS-2**

**Characterization data of the Compound LS-2:**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>M.P.</td>
<td>160 - 62(^0)C</td>
</tr>
<tr>
<td>Yield</td>
<td>85%</td>
</tr>
<tr>
<td>T.L.C.</td>
<td>Solvent system</td>
</tr>
<tr>
<td></td>
<td>CHCl(_3); MeOH (8:2 v/v)</td>
</tr>
<tr>
<td></td>
<td>CHCl(_3); MeOH (7:3 v/v)</td>
</tr>
</tbody>
</table>
Molecular formula : \( \text{C}_8\text{H}_{17}\text{N}_5\text{O}_5\text{S} \)

Elemental analysis : \( \text{C} \quad \text{H} \quad \text{N} \)

Found % : 41.49 7.28 30.19

Calculated % : 41.55 7.35 30.30

IR (KBr) \( \nu_{\text{max}} \) : 1425, 1340, 1200, 1120, 1110, 1080, 1045 and 835 (piperazine nucleus); 2910 and 2850 (N-CH\(_2\)); 2930, 1461 and 1240 (N-CH\(_2\)); 1135 (C=S); 3340, 3300, 1610 and 1230 (-NH\(_2\)); and 3340, 3300, 1675, 1530, 1235 and 765 (>CONH).

\( ^1\text{H} \text{NMR}\) (CDCl\(_3\))\( \delta \) : 1.93 (s, 2H, N-CH\(_2\)); 2.58 (m, 8H, 2xC\(_2\) - N - CH\(_2\)), 3.60(s,2H,N-CH\(_2\)); 8.30 (m, 4H, -NHNCNSNH\(_2\)).

Step-3. Synthesis of 2- Amino - 5 - (N\(^4\)-methyl -N\(^1\)-piperazinylmethyl)-1,3,4 - thiadiazone, Compound LS-3:

11.5gm (0.05 mol) of Compound LS-2 was kept over night with 25 ml conc. H\(_2\)SO\(_4\) at room temperature and the mixture was poured into ice cold water (150 ml). The excess of acid was neutralised with liquid ammonia. The separated solid thus obtained was filtered and recrystallised from ethanol to get cream coloured crystals of Compound LS-3.

\[
\text{CH}_3\text{-N}\underset{\text{N-CH}_2\text{CONHNCSNH}_2}{\text{H}_2\text{SO}_4/\text{liq. NH}_3}\]

Compound LS-2

\[
\text{CH}_3\underset{\text{N-CH}_2\text{-C-S-C-NH}_2}{\text{N}}
\]

Compound LS-3

Characterization data of the Compound LS-3:

M.P. : 165 - 67\(^\circ\)

Yield : 80%
T.L.C.: Solvent systems 
CHCl₃: MeOH (9:1 v/v) 0.60 
CHCl₃: MeOH (8:2 v/v) 0.85

Molecular formula: C₈H₁₅N₂S
Elemental analysis: C H N
Found %: 45.00 6.90 32.70
Calculated %: 45.07 7.04 33.86

IR (KBr) \( \nu_{max} \): 1430, 1340, 1210, 1125, 1110, 1080, 1050 and 840
(piperazinenucleus); 2910, and 2855 (N- CH₃ in piperazine); 2920, 1465 and 1230 (N-CH₃); 3355, 3310, 1620 and 1235 (-NH₂); 1590, 1310, 1170 and 710 (thiadiazole nucleus).

\(^1\text{H NMR (CDCl₃}) \delta \): 1.90 (s,3H, -N-CH₃); 3.60 (s, 2H, -N-CH₂); 2.65(m, 8H, 2xCH₂-N-CH₂); 8.20 (s, 2H, C-NH₂).

Step -4. Synthesis of 2-Arylidenedylamino -5- (N₄- methyl- N¹- piperazinyl methyl)-1,3,4- thiadiazoles, Compounds LS 4-13:

5.30gm (25.0 m mol) of Compound LS-3, 25m mol of various selected carbonyl compounds(as per table 3.1) and 2ml glacial acetic acid in 50 ml methanol were refluxed on a water bath for about 4-6 hours. The solvent was distilled off under reduced pressure. The crude product was recrystallised from suitable organic solvent (s) (section 3.2).
Table - 3.1: List of the reactant carbonyls for Step -4

<table>
<thead>
<tr>
<th>Compound No. (products)</th>
<th>Selected carbonyls (Reactants)</th>
<th>Quantity (gms)</th>
<th>Reaction time (hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LS-4</td>
<td>C₆H₅CHO</td>
<td>2.65</td>
<td>5</td>
</tr>
<tr>
<td>LS-5</td>
<td>N(CH₃)₂C₆H₄CHO</td>
<td>3.7250</td>
<td>4</td>
</tr>
<tr>
<td>LS-6</td>
<td>2-NO₂ C₆H₄CHO</td>
<td>3.775</td>
<td>4</td>
</tr>
<tr>
<td>LS-7</td>
<td>2-ClC₆H₄CHO</td>
<td>3.5125</td>
<td>5</td>
</tr>
<tr>
<td>LS-8</td>
<td>4-ClC₆H₄CHO</td>
<td>3.5125</td>
<td>5</td>
</tr>
<tr>
<td>LS-9</td>
<td>4-OCH₃ C₆H₄CHO</td>
<td>3.25</td>
<td>6</td>
</tr>
<tr>
<td>LS-10</td>
<td>C₆H₅-CH=CH-CHO</td>
<td>3.30</td>
<td>5</td>
</tr>
<tr>
<td>LS-11</td>
<td>C₄H₃O CHO</td>
<td>2.40</td>
<td>6</td>
</tr>
<tr>
<td>LS-12</td>
<td>CH₃COC₆H₅</td>
<td>3.0250</td>
<td>6</td>
</tr>
<tr>
<td>LS-13</td>
<td>C₆H₅COC₆H₅</td>
<td>4.5500</td>
<td>4</td>
</tr>
</tbody>
</table>
Section -3.1.2. Synthesis of the Compounds of the Series - 2:

5 m mole of the Compounds LS<sub>4-13</sub> and 1.01ml (10 m mole) of triethyl amine were mixed with 50ml dioxane and stirred well. To this solution 1.12ml (10 m mole) of chloroacetyl chloride was added dropwise at 0-5° for 214-216 about 4 hours (table - 3.2). The precipitated amino hydrochloride was filtered off and the filtrate was concentrated under reduced pressure. The viscous mass so obtained was recrystallised from suitable organic solvent(s) to get the crystals of the Compounds LS 14-23 (section -3.2).

\[
\text{Compounds LS 4-13}
\]

\[
\text{Compounds LS 14-23}
\]

\[R_1 = R_2 = \text{selected carbonyls}\]
Table - 3.2: Quantity of the Compounds LS 4-13 taken

<table>
<thead>
<tr>
<th>Compound No. (Products)</th>
<th>Compound No. (Reactants)</th>
<th>Amount reactant taken in gms</th>
<th>Stirring time in (hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LS -14</td>
<td>4</td>
<td>1.55</td>
<td>2</td>
</tr>
<tr>
<td>LS -15</td>
<td>5</td>
<td>1.73</td>
<td>2</td>
</tr>
<tr>
<td>LS -16</td>
<td>6</td>
<td>1.68</td>
<td>1</td>
</tr>
<tr>
<td>LS -17</td>
<td>7</td>
<td>1.675</td>
<td>1</td>
</tr>
<tr>
<td>LS -18</td>
<td>8</td>
<td>1.675</td>
<td>1</td>
</tr>
<tr>
<td>LS -19</td>
<td>9</td>
<td>1.655</td>
<td>3</td>
</tr>
<tr>
<td>LS -20</td>
<td>10</td>
<td>1.635</td>
<td>2</td>
</tr>
<tr>
<td>LS -21</td>
<td>11</td>
<td>1.455</td>
<td>1</td>
</tr>
<tr>
<td>LS -22</td>
<td>12</td>
<td>1.575</td>
<td>1</td>
</tr>
<tr>
<td>LS -23</td>
<td>13</td>
<td>1.885</td>
<td>2</td>
</tr>
</tbody>
</table>

Section - 3.2. Characterization data of the Compounds of Series - 1 and Series -2.

The characterization data of the compounds of Series -1 and Series -2 (Compounds No. LS 4-23) are given below.

Series - 1

**Compound No.LS-4**

**Chemical name**: 2- Benzyldenylamino -5- (N^4^-methyl -N^1^-piperazinyl methyl) -1,3,4 - thiadiazol.

**Physical State**: Cream coloured crystals from methanol.

**M.P.**: 125 - 27°

**Yield**: 60 %

**T.L.C.**: Solvent systems  
CHCl₃ : MeOH(9:1 v/v)  
CHCl₃ : MeOH(8:2 v/v)  
Rf values  
0.72  
0.91

**Molecular formula**: C_{15}H_{19}N_{5}S
Elemental analysis: | C  | H  | N  |
---|---|---|---|
Found (%) | 59.76 | 6.25 | 23.19 |
Calculated (%) | 59.80 | 6.31 | 23.25 |

IR (KBr) $v_{max}$: 1420, 1345, 1200, 1125, 1110, 1080, 1050 and 830 (piperazine nucleus); 2915 and 2850 (N-CH$_3$ in piperazine); 2925, 1461 and 1235 (N-CH$_2$); 1610, 1308, 1163 and 695 (thiadiazole nucleus); 1595 (-N=CH); 3020, 1440, 750 and 660 (benzene nucleus), (Figure - 3.1).

$^1$H NMR (CDCl$_3$) $\delta$: 3.60 (s,2H,-N-CH$_2$); 1.92 (s,3H,-N-CH$_3$); 2.30-3.10 (m,8H, 2xCH$_2$-N-CH$_2$); 4.90 (s,1H,N=CH); and 6.60-7.90 (m,5H,ArH) (Figure-3.2).

**Compound No. LS-5**

Chemical name: 2- (4-Dimethylamino benzylidenylamino) -5-(N$^{4}$-methyl-N$^{1}$- piperazinylmethyl) -1,3,4 - thiadiazole.

Physical state: Light yellow coloured crystals from ethanol.

M.P.: 180 - 82$^0$

Yield: 75%

T.L.C.: Solvent systems | Rf values
---|---
CHCl$_3$ : MeOH(9:1 v/v) | 0.77
CHCl$_3$ : MeOH(8:2 v/v) | 0.86

Molecular formula: $C_{17}H_{24}N_{6}S$

Elemental analysis: | C  | H  | N  |
---|---|---|---|
Found (%) | 59.18 | 6.90 | 24.30 |
Calculated (%) | 59.30 | 6.97 | 24.40 |
FIG. 3.1: INFRA-RED SPECTRUM OF THE COMPOUND LS-4
Fig. 3.2: $^1$H-NMR spectrum of the compound LS-4
Compound No. LS-6

Chemical name : 2-(2 - Nitro benzylidenylamino) -5- (N^4- methyl -N^1- piperazinylmethyl)-1,3,4-thiadiazole.

Physical state : Yellow coloured crystals form ethanol.

M.P. : 187 - 89^0.

Yield : 90 %

T.L.C. : Solvent systems

Rf values
CHCl_3 : MeOH (9:1 v/v) 0.76
CHCl_3 : MeOH (9:2 v/v) 0.78

Molecular formula : C_{15} H_{18} N_{6} O_{2} S

Elemental analysis:

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>H</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Found (%)</td>
<td>51.99</td>
<td>5.09</td>
<td>24.16</td>
</tr>
<tr>
<td>Calculated (%)</td>
<td>52.00</td>
<td>5.20</td>
<td>24.27</td>
</tr>
</tbody>
</table>

IR (KBr) \nu_{max} : 1425,1340,1200,1125,1105,1085,1045 and 825 (piperazine nucleus); 2905 and 2850 (N-CH_3 in piperazine); 2920,1461 and 1230 (N-CH_2); 1610,1315,1160 and 690 (thiadiazole nucleus); 3020, 1442,755 and 665 (benzene nucleus); 1590 (N=CH);1542 and 1525 (-NO_2 group in phenyl ring).

Compound No. LS-7

Chemical name : 2-(2-Chloro benzylidenylamino) -5- (N^4- methyl -N^1- piperazinylmethyl)-1,3,4- thiadiazole.

Physical state : Cream coloured crystals from ethanol.

M.P. : 188-90^0

Yield : 75 %
T.L.C. : Solvent systems

CHCl₃ : MeOH (9:1 v/v) 0.76
CHCl₃ : MeOH (8:2 v/v) 0.88

Molecular formula : C₁₅ H₁₈ N₅ S Cl

Elemental analysis : C  H  N

Found (%) : 53.58 5.25 20.79
Calculated (%) : 53.65 5.36 20.86

**Compound No. LS-8**

Chemical name : 2-(4-Chloro benzylidinylamino)-5- (N⁴-methyl - N¹-piperazinylmethyl)-1,3,4-thiadiazole.

Physical state : Yellow coloured crystals from ethanol.

M.P. : 187-90⁰

Yield : 90 %

T.L.C. : Solvent systems

CHCl₃ : MeOH (8:2 v/v) 0.72
CHCl₃ : MeOH (7:3 v/v) 0.80

Molecular formula : C₁₅ H₁₈ N₅ S Cl

Elemental analysis : C  H  N

Found (%) : 53.57 5.28 20.74
Calculated (%) : 53.65 5.36 20.86

IR (KBr) νmax : 1415,1340,1205,1125,1105,1085,1040 and 820 (piperazine nucleus); 2910 and 2850 (N-CH₃ in piperazine); 2920, 1460 and 1230 (-N-CH₂); 1605, 1310, 1170 and 700 (thiadiazole nucleus); 1595 (-N=CH); 768 (C-Cl); 3015, 1445, 755 and 665 (benzene nucleus), (Figure- 3.3).
FIG. 3.3: INFRA-RED SPECTRUM OF THE COMPOUND LS-8
Compound No. LS-9

Chemical name : 2-(4-Methoxy benzylidenlamino)-5-(N^4-methyl-N^1-piperazinylmethyl)-1,3,4-thiadiazole.

Physical state : Cream coloured crystals from ethanol.

M.P. : 175 - 80°

Yield : 75 %

T.L.C. : Solvent systems

<table>
<thead>
<tr>
<th>Solvent systems</th>
<th>Rf values</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHCl₃: MeOH (8.2 v/v)</td>
<td>0.69</td>
</tr>
<tr>
<td>CHCl₃: MeOH (7.3 v/v)</td>
<td>0.76</td>
</tr>
</tbody>
</table>

Molecular formula : C_{16}H_{21}N_{5}O_{5}S

Elemental analysis :

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>H</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Found (%)</td>
<td>57.91</td>
<td>6.21</td>
<td>21.06</td>
</tr>
<tr>
<td>Calculated (%)</td>
<td>58.00</td>
<td>6.34</td>
<td>21.14</td>
</tr>
</tbody>
</table>

IR (KBr) ε_max :

1410,1345,1210,1135, 1110, 1090,1045, and 825
(piperazine nucleus); 2905 and 2850 (N-CH₃ in piperazine); 2920,1460and1230, (N-CH₂); 1615,1315,1175 and 710
(thiadiazole nucleus); 1590(N=CH); 3025,1445, 750 and 660
(benzene nucleus) and 2870 (-OCH₃ group in phenyl ring).

Compound No. LS-10

Chemical name : 2-Cinnamylidenlamino-5-(N^4-methyl-N^1-piperazinylmethyl)-1,3,4-thiadiazole.

Physical state : Yellow coloured crystals from ethanol.

M.P. : 110 - 12°

Yield : 75 %
T.L.C. : Solvent systems  
CHCl₃ : MeOH (9:1 v/v)  
CHCl₃ : MeOH (8:2 v/v)  

Rf Values  
0.66  
0.79  

Molecular formula : C₁₇ H₂₁ N₅ S  
Elemental analysis :  
C  
H  
N  

Found (%) : 62.25  
6.37  
21.29  

Calculated (%) : 62.38  
6.42  
21.40  

Compound No. LS-11  

Chemical name : 2-(Furfurylidynamino) -5- (N⁴-methyl- N¹-piperazinyl methyl) -1,3,4 - thiadiazole.  

Physical state : Light brown coloured crystals from ethanol.  
M.P. : 145 - 47⁰  
Yield : 85 %  

T.L.C. : Solvent systems  
CHCl₃ : MeOH (9:1 v/v)  
CHCl₃ : MeOH (8:2 v/v)  

Rf values  
0.79  
0.85  

Molecular formula : C₁₃ H₁₇ N₅ O S  
Elemental analysis :  
C  
H  
N  

Found (%) : 53.49  
5.76  
23.97  

Calculated (%) : 53.60  
5.84  
24.05  

Compound No. LS-12  

Chemical name : 2-(α - Methyl benzylidenlamino) -5- (N⁴-methyl- N¹-piperazinylmethyl) -1,3,4 - thiadiazole.  

Physical state : Cream coloured crystals from ethanol.  
M.P. : 112-15⁰  
Yield : 90 %
<table>
<thead>
<tr>
<th>T.L.C.</th>
<th>Solvent systems</th>
<th>Rf values</th>
</tr>
</thead>
<tbody>
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<td></td>
<td>CHCl₃ : MeOH (9:1 v/v)</td>
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</tr>
<tr>
<td></td>
<td>CHCl₃ : MeOH (8:2 v/v)</td>
<td>0.90</td>
</tr>
</tbody>
</table>

**Molecular formula:** \( C_{16} H_{21} N_7 S \)

**Elemental analysis:**

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>H</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Found (%)</td>
<td>60.80</td>
<td>6.55</td>
<td>22.15</td>
</tr>
<tr>
<td>Calculated (%)</td>
<td>60.95</td>
<td>6.66</td>
<td>22.22</td>
</tr>
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</table>

**IR(KBr) \( \nu_{max} \):**

1425, 1340, 1210, 1130, 1105, 1075, 1045 and 830 (piperazine nucleus); 2912 and 2850 (N-CH₃ in piperazine); 2920, 1460 and 1230 (-N-CH₂); 1615, 1310, 1170 and 695 (thiadiazole nucleus); 1585 (N=C); 3015, 1445, 755 and 665 (benzene nucleus), (Figure - 3.4).

**Compound No. LS-13**

**Chemical name:** 2-(α - Phenyl benzyldenylamino) -5- (N⁴-methyl- N¹-piperazinylmethyl) -1,3,4 - thiadiazole.

**Physical state:** Light brown coloured crystals from ethanol.

**M.P.**

152-54°

**Yield:** 75 %

<table>
<thead>
<tr>
<th>T.L.C.</th>
<th>Solvent systems</th>
<th>Rf values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CHCl₃ : MeOH (9:1 v/v)</td>
<td>0.76</td>
</tr>
<tr>
<td></td>
<td>CHCl₃ : MeOH (8:2 v/v)</td>
<td>0.82</td>
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</table>

**Molecular formula:** \( C_{21} H_{23} N_5 S \)

**Elemental analysis:**

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>H</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Found (%)</td>
<td>66.72</td>
<td>6.00</td>
<td>18.43</td>
</tr>
<tr>
<td>Calculated (%)</td>
<td>66.84</td>
<td>6.10</td>
<td>18.56</td>
</tr>
</tbody>
</table>
FIG. 3.4: INFRA-RED SPECTRUM OF THE COMPOUND LS-12
Series - 2

**Compound No. LS-14**

**Chemical name**: 1-[5'-{(N<sup>4</sup>-methyl -N<sup>1</sup>-piperazinylmethyl)-1',3',4'-thiadiazol-2'-yl} -4- phenyl -3- chloro-2-oxo-azetidine.

**Physical state**: Orange yellow coloured crystals from ethanol.

**M.P.**: 143-45°

**Yield**: 50 %

**T.L.C.**: Solvent systems

<table>
<thead>
<tr>
<th>Solvent systems</th>
<th>Rf values</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHCl&lt;sub&gt;3&lt;/sub&gt; : MeOH (9:1 v/v)</td>
<td>0.73</td>
</tr>
<tr>
<td>CHCl&lt;sub&gt;3&lt;/sub&gt; : MeOH (8:2 v/v)</td>
<td>0.79</td>
</tr>
</tbody>
</table>

**Molecular formula**: C<sub>15</sub>H<sub>20</sub>N<sub>5</sub>S O Cl

**Elemental analysis**

<table>
<thead>
<tr>
<th>Found (%)</th>
<th>Calculated (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>53.92</td>
<td>5.18</td>
</tr>
<tr>
<td>54.03</td>
<td>5.29</td>
</tr>
</tbody>
</table>

**Compound No. LS-15**

**Chemical name**: 1-[5'-(N<sup>4</sup>-methyl -N<sup>1</sup>-piperazinylmethyl)-1',3',4'- thia diazol-2'-yl} -4- (4-dimethyl amino) -3- chloro-2-oxo- azetidine.

**Physical state**: Red brown coloured crystals from ethanol.

**M.P.**: 99-100°

**Yield**: 85 %

**T.L.C.**: Solvent systems

<table>
<thead>
<tr>
<th>Solvent systems</th>
<th>Rf values</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHCl&lt;sub&gt;3&lt;/sub&gt; : MeOH (8:2 v/v)</td>
<td>0.67</td>
</tr>
<tr>
<td>CHCl&lt;sub&gt;3&lt;/sub&gt; : MeOH (7:3 v/v)</td>
<td>0.81</td>
</tr>
</tbody>
</table>

**Molecular formula**: C<sub>19</sub>H<sub>25</sub>N<sub>6</sub>S O Cl

**Elemental analysis**

<table>
<thead>
<tr>
<th>Found (%)</th>
<th>Calculated (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>54.12</td>
<td>5.82</td>
</tr>
<tr>
<td>54.22</td>
<td>5.94</td>
</tr>
</tbody>
</table>
Compound No. LS-16

Chemical name: 1-[5-(N^4-methyl -N^1-piperazinylmethyl)-1',3',4'-thiadiazole-2'-yl]-4-(2-nitro phenyl)-3-chloro-2-oxo-azetidinone.

Physical state: Yellow coloured crystals from ethanol.

M.P.: 155-58^0

Yield: 60%

T.L.C.: Solvent systems

\[ \text{CHCl}_3 : \text{MeOH} \ (8:2 \ v/v) \quad 0.77 \]

\[ \text{CHCl}_3 : \text{MeOH} \ (7:3 \ v/v) \quad 0.79 \]

Molecular formula: C_{17}H_{19}N_6S O_3 Cl

Elemental analysis:

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>H</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Found (%)</td>
<td>48.12</td>
<td>4.31</td>
<td>19.76</td>
</tr>
<tr>
<td>Calculated (%)</td>
<td>48.28</td>
<td>4.49</td>
<td>19.88</td>
</tr>
</tbody>
</table>

IR(KBr) \( \nu_{\text{max}} \):

1410,1340,1200, 1125,1105,1080,1050 and 820 (piperazine nucleus); 2905 and 2850 (N-CH\textsubscript{3} in piperazine); 2920,1465 and 1230,(N-CH\textsubscript{2}); 1615,1310,1165 and 690 (thiadiazole nucleus); 1765 (>C=0); 760 (C-Cl);3020,1445,760 and 660 (benzenenucleus);1545 and 1520 (-NO\textsubscript{2} group in phenylrings), (Figure - 3.5).

\(^1\text{H NMR (CDCl}_3\delta\):

1.90 (s,1H,-N-CH\textsubscript{3}); 3.75(s,2H,-N-CH\textsubscript{2}); 2.40 - 3.00 (m,8H,2xCH\textsubscript{2}-N-CH\textsubscript{3}); 4.10 (d,1H,J=5Hz,N-CH); 5.00 (d,1H,J=5 Hz,CHCl); 6.50-7.85 (m,5H,Ar-H), (Figure - 3.6).

Compound No. LS-17

Chemical name: 1-[5'-(N^4-methyl -N^1-piperazinylmethyl)-1',3',4'-thiadiazol - 2'-yl]- 4-(4-chloro phenyl) - 3- chloro - 2-oxo - azetidine.
FIG. 3.5: INFRA-RED SPECTRUM OF THE COMPOUND LS - 16
FIG. 3.6: $^1\text{H}-\text{NMR}$ SPECTRUM OF THE COMPOUND LS - 16
Physical state : Cream coloured crystals from ethanol.
M.P. : 168-70\(^0\)
Yield : 85 %
T.L.C. : Solvent systems  
<table>
<thead>
<tr>
<th>Solvent System</th>
<th>Rf values</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHCl(_3) : MeOH (9:1 v/v)</td>
<td>0.76</td>
</tr>
<tr>
<td>CHCl(_3) : MeOH (8:2 v/v)</td>
<td>0.78</td>
</tr>
</tbody>
</table>
Molecular formula : C\(_{17}\)H\(_{19}\)N\(_5\)S O Cl\(_2\)
Elemental analysis :
<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>H</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Found (%)</td>
<td>49.47</td>
<td>4.52</td>
<td>16.80</td>
</tr>
<tr>
<td>Calculated (%)</td>
<td>49.51</td>
<td>4.61</td>
<td>16.99</td>
</tr>
</tbody>
</table>

**Compound No. LS-18**

Chemical name : 1-[5\(^1\)-(N\(^4\)-methyl -N\(^1\)-piperazinylmethyl)-1\(^\prime\),3\(^\prime\),4\(^\prime\)-thiadiazol -2\(^\prime\)-yl] -4- (4-chloro phenyl) -3- chloro-2-oxo- azetidine.

Physical state : Orange yellow coloured crystals from ethanol.
M.P. : 164-66\(^0\)
Yield : 75 %
T.L.C. : Solvent systems  
<table>
<thead>
<tr>
<th>Solvent System</th>
<th>Rf values</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHCl(_3) : MeOH (9:1 v/v)</td>
<td>0.77</td>
</tr>
<tr>
<td>CHCl(_3) : MeOH (8:2 v/v)</td>
<td>0.79</td>
</tr>
</tbody>
</table>
Molecular formula : C\(_{17}\)H\(_{19}\)N\(_5\)S O Cl\(_2\)
Elemental analysis :
<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>H</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Found (%)</td>
<td>49.40</td>
<td>4.54</td>
<td>16.86</td>
</tr>
<tr>
<td>Calculated (%)</td>
<td>49.51</td>
<td>4.61</td>
<td>16.99</td>
</tr>
</tbody>
</table>

IR (KBr) \(\nu_{max}\) : 1420, 1345, 1205, 1125, 1110, 1080, 1045 and 820 (piperazine nucleus); 2910 and 2850 (N-CH\(_3\) in piperazine nucleus); 2925, 1465 and 1230, (N-CH\(_2\))\(_3\); 1615, 1310, 1170 and 700
(thiadiazole nucleus); 1760 (>C=0); 765 (C-Cl); 3020, 1435, 745 and 660 (benzene nucleus) and 800(-Cl in phenyl ring).

**Compound No. LS-19**

**Chemical name**: 1-[5′-(N⁴-methyl -N¹-piperazinylmethyl)-1′,3′,4′-thiadiazol-2′-yl] -4- (4-methoxy phenyl) -3- chloro-2-oxo-azetidine.

**Physical state**: Orange red coloured crystals from ethanol.

**M.P.**: 180-82⁰

**Yield**: 65 %

**T.L.C.**: Solvent systems  
- CHCl₃: MeOH (8:2 v/v)  
- CHCl₃: MeOH (7:3 v/v)

**Molecular formula**: C₁₈H₂₂N₅S O₂ Cl

**Elemental analysis**

<table>
<thead>
<tr>
<th>Element</th>
<th>Found (%)</th>
<th>Calculated (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>52.96</td>
<td>53.00</td>
</tr>
<tr>
<td>H</td>
<td>5.26</td>
<td>5.39</td>
</tr>
<tr>
<td>N</td>
<td>17.10</td>
<td>17.17</td>
</tr>
</tbody>
</table>

**Compound No. LS-20**

**Chemical name**: 1-[5′-(N⁴-methyl -N¹-piperazinylmethyl)-1′,3′,4′-thiadiazol-2′-yl] -4- (2-phenyl ethenyl) -3- chloro-2-oxo-azetidine.

**Physical state**: Red yellow coloured crystals from ethanol.

**M.P.**: 162-63⁰

**Yield**: 90 %

**T.L.C.**: Solvent systems  
- CHCl₃: MeOH (9:1 v/v)  
- CHCl₃: MeOH (8:2 v/v)
**Molecular formula**: \( C_{19}H_{22}N_5SOCl \)

**Elemental analysis**:  
- Found (%): 56.41  5.38  17.25  
- Calculated (%): 56.50  5.45  17.34  

**IR(KBr) \( \nu_{\text{max}} \)**:  
1415, 1350, 1200, 1130, 1105, 1080, 1040 and 830 (piperazine nucleus); 2905 and 2850 (N-CH\(_3\) in piperazine); 2925, 1460 and 1230, (\(-N-CH\(_3\)\); 1615, 1315, 1175 and 700 (thiadiazole nucleus); 1762 (\(>\text{C}=\text{O}\)); 755 (C-Cl); 3025, 1440, 755 and 665 (benzene nucleus) and 1670 (CH=CH), (Figure - 3.7).

**Compound No. LS-21**

**Chemical name**: 1-[5'-\((N^4\text{-methyl} -N^1\text{-piperazinylmethyl})\)-1',3',4'-thiadiazol -2'-yl] -4- (2-fural) -3- chloro-2-oxo- azetidine.

**Physical state**: Brown coloured crystals from ethanol.

**M.P.**: 127-28\(^0\)

**Yield**: 78 %

**T.L.C.**: Solvent systems  
- CHCl\(_3\): MeOH (9:1 v/v)  
- CHCl\(_3\): MeOH (8:2 v/v)  

**Molecular formula**: \( C_{15}H_{18}N_5SO_2Cl \)

**Elemental analysis**:  
- Found (%): 48.84  4.70  18.94  
- Calculated (%): 48.97  4.89  19.04  

**Compound No. LS-22**

**Chemical name**: 1-[5'-\((N^4\text{-methyl} -N^1\text{-piperazinylmethyl})\)-1',3',4'-thiadiazol -2'-yl] -4- (4-methyl -4-phenyl) -3- chloro-2-oxo-azetidine.
FIG. 3.7: INFRA-RED SPECTRUM OF THE COMPOUND LS-20
Physical state : Light cream coloured crystals from ethanol.
M.P. : 160-63°
Yield : 80 %
T.L.C. : Solvent systems

<table>
<thead>
<tr>
<th>Solvent systems</th>
<th>Rf values</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHCl₃: MeOH (9:1 v/v)</td>
<td>0.81</td>
</tr>
<tr>
<td>CHCl₃: MeOH (8:2 v/v)</td>
<td>0.85</td>
</tr>
</tbody>
</table>

Molecular formula : C₁₈H₂₂N₅S0Cl

Elemental analysis : C H N

<table>
<thead>
<tr>
<th>Found (%)</th>
<th>Calculated (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>55.00</td>
<td>55.17</td>
</tr>
<tr>
<td>5.52</td>
<td>5.61</td>
</tr>
<tr>
<td>17.76</td>
<td>17.87</td>
</tr>
</tbody>
</table>

IR(KBr) νₚₓₙ : 1430, 1350, 1205, 1125, 1105, 1080, 1060 and 840 (piperazine nucleus); 2900 and 2850 (N-CH₃ in piperazine); 2920, 1460 and 1230 (N-CH₂); 1610, 1320, 1770 and 690 (thiadiazole nucleus); 1760 (>C=O); 760 (C-Cl); 2935, 1480 and 1370 (C-CH₃); 3020, 1440, 745 and 660 (benzene nucleus).

Compound No. LS-23

Chemical name : 1-[5'-{(N⁴-methyl-N¹-piperazinylmethyl)-1',3',4'-thiadiazol-2'-yl}-4-diphenyl-3-chloro-2-oxo-azetidine.

Physical state : Light yellow coloured crystals from ethanol.
M.P. : 124-26°
Yield : 82 %
T.L.C. : Solvent systems

<table>
<thead>
<tr>
<th>Solvent systems</th>
<th>Rf values</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHCl₃: MeOH (9:1 v/v)</td>
<td>0.78</td>
</tr>
<tr>
<td>CHCl₃: MeOH (8:2 v/v)</td>
<td>0.82</td>
</tr>
</tbody>
</table>

Molecular formula : C₂₃H₂₄N₅S0Cl

Elemental analysis : C H N

<table>
<thead>
<tr>
<th>Found (%)</th>
<th>Calculated (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60.72</td>
<td>60.85</td>
</tr>
<tr>
<td>5.15</td>
<td>5.29</td>
</tr>
<tr>
<td>15.20</td>
<td>15.43</td>
</tr>
</tbody>
</table>