CHAPTER - 1

SYNTHESIS OF QUINAZOLINE-2(1H)-THIONES AND THEIR ALKYL/ARALKYL DERIVATIVES

EXPERIMENTAL

Melting points are uncorrected and were taken on a capillary melting point apparatus. Infra red spectra were recorded on Perkin-Elmer RX IFT-IR system. Proton magnetic resonance spectra were recorded on Bruker Advance II 400 NMR spectrometer with tetra methyl silane as internal standard. Mass spectra were recorded by the National Institute of Pharmaceutical Research (NIPER), Mohali.

For all the reactions, chemicals of Sigma Aldrich standard were used. All solvents were distilled before use.

SYNTHESIS OF 4-SUBSTITUTED PHENYL-3,4,5,6-
TETRAHYDROBENZO[h]QUINAZOLINE-2(1H)-THIONES

General Procedure

A mixture of α-tetralone (0.01 mole), thiourea (0.01mole) and substituted aromatic aldehydes (0.01 mole) were irradiated in unmodified
domestic microwave (at 30% microwave power) using acetonitrile (5 ml) as an energy transfer medium and conc. HCl (3-4 drops) as a catalyst. The reaction was monitored by thin layer chromatography (TLC) using silica gel-G plates. Ethyl acetate and n-hexane mixture was used as eluting solvent taken in ratio of 1:1. After drying of plates in air, spots were marked and exposed to iodine chamber. The reaction mixture on standing for a few hours afforded product which was filtered under reduced pressure and recrystallised out of alcohol.

A typical procedure is given below:

(Ia) 4-(4-methoxyphenyl)-3,4,5,6-tetrahydrobenzo[h]quinazoline-2(1H)-thione

A mixture of α-tetralone (0.01 mole, 1.46 g), 4-methoxy benzaldehyde (0.01 mole, 1.36 ml), thiourea (0.01 mole, 0.76 g) and concentrated HCl (3-4 drops) was dissolved in acetonitrile (5 ml) taken in borosil beaker (100 ml) and was irradiated in unmodified domestic microwave at 30% microwave power for 5.00 min. The reaction was monitored by thin layer chromatography (TLC) using silica gel-G plates. Ethyl acetate and n-hexane mixture was used as eluting solvent (1:1). After drying the plates, spots were exposed to iodine chamber. The reaction mixture on standing for a few hours afforded product
which was filtered under reduced pressure and recrystallized out of alcohol for 2-3 times to give pure product.

M.P. = 219-220°C.

Yield = 40 %.

PMR (CDCl₃ + DMSO) δ:

7.82 (s, 1H, NH), 7.28-6.85 (m, 9H, Ar-H & NH), 5.04 (s, 1H, 4-CH), 3.77 (s, 3H, OCH₃), 2.77-2.67 (m, 2H, C₆CH₂), 2.09-1.93 (m, 2H, C₅CH₂).

IR (KBr) cm⁻¹:

3195.2 (N-H str.), 2934.4 (C-H str.), 1611.6 (C=C str.), 1485.8 (C=C), 1359.3 (C-N), 1273.2 (C=S)

Mass fragments (m/z):


Other compounds (I b –I g) were also synthesized similarly and are listed in Table -1 along with their characterization data.
\[
\begin{align*}
\text{C} & \quad \text{CHO} \\
\text{H} & \quad \text{N} \\
\text{N} & \quad \text{S} \\
\text{H} & \quad \text{O} \\
\text{CHO} & \quad \text{+} \\
\text{C} & \quad \text{S} \\
\text{H} & \quad \text{N} \\
\text{N} & \quad \text{H} \\
\text{2} & \quad \text{R} \\
\text{R} & \quad 30 \% \mu \text{w} \\
\text{Conc. HCl} & \quad \text{acetonitrile}
\end{align*}
\]

**TABLE – 1**

**CHARACTERIZATION DATA OF PRODUCTS (Ia–Ig):**

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Compounds</th>
<th>R</th>
<th>Time (min)</th>
<th>M.P. (°C)</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Ia</td>
<td>4-OCH₃</td>
<td>5.00</td>
<td>219-220</td>
<td>40</td>
</tr>
<tr>
<td>2.</td>
<td>Ib</td>
<td>3-NO₂</td>
<td>6.30</td>
<td>246-247</td>
<td>53</td>
</tr>
<tr>
<td>3.</td>
<td>Ic</td>
<td>2-CH₃</td>
<td>6.00</td>
<td>228-229</td>
<td>45</td>
</tr>
<tr>
<td>4.</td>
<td>Id</td>
<td>2,4-(Cl)</td>
<td>4.00</td>
<td>218-219</td>
<td>36</td>
</tr>
<tr>
<td>5.</td>
<td>Ie</td>
<td>2,3-(O-CH₂-O)</td>
<td>3.30</td>
<td>224-225</td>
<td>47</td>
</tr>
<tr>
<td>6.</td>
<td>If</td>
<td>4-OH,3-OCH₃</td>
<td>3.30</td>
<td>212-213</td>
<td>35</td>
</tr>
<tr>
<td>7.</td>
<td>Ig</td>
<td>H</td>
<td>5.30</td>
<td>256-257</td>
<td>46</td>
</tr>
</tbody>
</table>
Note: All the above compounds were recrystallized from ethanol.

Spectral data of compounds (Ib-Ig) are listed below:

(Ib) PMR (CDCl$_3$ + DMSO) $\delta$:

9.11 (s, 1H, NH), 8.96 (s, 1H, NH), 8.27-7.30 (m, 8H, Ar-H), 5.19 (s, 1H, 4-CH), 2.80-2.62 (m, 2H, C$_6$CH$_2$), 2.28-1.91 (m, 2H, C$_5$CH$_2$).

IR (KBr) cm$^{-1}$:

3171.1 (N-H str.), 2987.7 (C-H str.), 1581.3 (C=C str.), 1567 & 1498 (NO$_2$), 1515.8 (C═C), 1348.7 (C-N)

(Ic) PMR (CDCl$_3$ + DMSO) $\delta$:

8.93 (s, 1H, NH), 7.88 (s, 1H, NH), 7.67-7.30 (m, 8H, Ar-H), 5.11 (s, 1H, 4-CH), 2.94-2.62 (m, 2H, C$_6$CH$_2$), 2.29-1.96 (m, 2H, C$_5$CH$_2$).

IR (KBr) cm$^{-1}$:

3210.1 (N-H str.), 2830 (C-H str.), 1564.8 (C═C str.), 1480.9 (C═C), 1345 (C-N)

(Id) PMR (CDCl$_3$ + DMSO) $\delta$:
7.84 (s, 1H, NH), 6.88 (s, 1H, NH), 7.43-7.19 (m, 7H, Ar-H), 5.62-5.63 (s, 1H, 4-CH), 2.84-2.75 (m, 2H, C₆CH₂), 2.22-1.97 (m, 2H, C₅CH₂).

IR (KBr) cm⁻¹:

3190.8 (N-H str.), 2890 (C-H str.), 1557.8 (C=C str.), 1485 (C≡C), 1385.6 (C-N)

(Ie) PMR (CDCl₃ + DMSO) δ:

8.36 (s, 1H, NH), 8.18 (s, 1H, NH), 7.45-6.74 (m, 7H, Ar-H), 5.95-5.94 (s, 2H, O-CH₂-O), 4.95 (s, 1H, 4-CH), 2.78-2.65 (m, 2H, C₆CH₂), 2.11-1.97 (m, 2H, C₅CH₂).

IR (KBr) cm⁻¹:

3201.6 (N-H str.), 2924.3 (C-H str.), 1575 (C≡C str.), 1487.8 (C≡C), 1303.9 (C-N)

(If) PMR (CDCl₃ + DMSO) δ:

9.11 (s, 1H, OH), 8.45 (s, 1H, NH), 8.12 (s, 1H, NH), 7.47-6.65 (m, 7H, Ar-H), 5.05 (s, 1H, 4-CH), 3.13 (s, 3H, OCH₃), 2.67-2.55 (m, 2H, C₆CH₂), 2.08-1.98 (m, 2H, C₅CH₂).
IR (KBr) cm⁻¹:

3346.9 (O-H str.), 3176.9 ( N-H str.), 2992 (C-H str.), 1577.3 (C=C str.), 1514 (C=C), 1355.9 (C-N).

(Ig) PMR (CDCl₃ + DMSO) δ:

8.68 (s, 1H, NH), 8.56 (s, 1H, NH), 7.59-7.12 (m, 9H, Ar-H), 5.01 (s, 1H, 4-CH), 2.83-2.61 (m, 2H, C₆CH₂), 2.19-1.89 (m, 2H, C₅CH₂).

IR (KBr) cm⁻¹:

3192.0 (N-H str.), 2892 (C-H str.), 1560.1 (C=C str.), 1495 (C=C), 1352.8 (C-N).

SYNTHESIS OF 2-(METHYLTHIO)-4-SUBSTITUTEDPHENYL-1,4,5,6-TETRAHYDROBENZO[h]QUINAZOLINES

General Procedure

Quinazoline-2-thione (0.004 mole) was dissolved in 25 ml ethanol. To it, added NaOH solution, which was prepared by dissolving NaOH (0.004 mole, 0.160 g) in water (2 ml). The reaction mixture was cooled. To this cold mixture, dimethyl sulphate (0.5 ml, 0.004 mole) was added dropwise while stirring the mixture continuously. The reaction mixture was refluxed for 3
hours. The reaction was monitored by thin layer chromatography (TLC) using silica gel-G plates. Ethyl acetate and n-hexane mixture was used as eluting solvents and spots were exposed to iodine chamber. The mixture was cooled and poured over crushed ice. Solid separated was filtered under reduced pressure, washed with ethanol and dried. It was recrystallised from ethanol to provide a pure sample of the product.

A typical procedure is given below:

(IIa) 4-(4-methoxyphenyl)-2-(methylthio)-1,4,5,6-tetrahydrobenzo[h]quinazoline

4-(4-methoxyphenyl)-3,4,5,6-tetrahydrobenzo[h]quinazoline-2(1H)-thione Ia (0.004 mole, 1.288g) was dissolved in 25 ml ethanol. To it, added NaOH solution, which was prepared by dissolving NaOH (0.004 mole, 0.160 g) in water (2 ml). The mixture was cooled. To this mixture, dimethyl sulphate (0.5 ml, 0.004 mole) was added dropwise while stirring the mixture continuously. The reaction mixture was refluxed for 3 hours. The reaction was monitored by thin layer chromatography (TLC) using silica gel-G plates. Ethyl acetate and n-hexane mixture was used as eluting solvents (1:1) and after drying, the plates were exposed to iodine chamber. The mixture was
cooled and poured over crushed ice. Solid separated was filtered under reduced pressure, washed with ethanol and dried. It was recrystallised from ethanol to provide a pure sample of the product.

M.P. = 180-181°C.

Yield = 38%.

PMR (CDCl$_3$ + DMSO) $\delta$:

7.82 (s, 1H, NH), 7.30-6.86 (m, 8H, Ar-H), 5.04 (s, 1H, 4-CH), 3.77 (s, 3H, OCH$_3$), 2.81-2.63 (m, 2H, C$_6$CH$_2$), 2.11-1.93 (m, 2H, C$_5$CH$_2$), 1.25 (s, 3H, S-CH$_3$).

IR (KBr) cm$^{-1}$:

3165 (N-H str.), 2830 (C-H str.), 1677 (C=N), 1612.6 (C=C str.), 1557.7 (C$\equiv$C).

Mass fragments (m/z):

336 M$^+$, 322, 289, 263.

(IIb) PMR (CDCl$_3$ + DMSO) $\delta$:
9.11 (s, 1H, NH), 8.27-7.30 (m, 8H, Ar-H), 5.24 (s, 1H, 4-CH), 2.83-2.68 (m, 2H, C₆H₅CH₂), 1.89-2.17 (m, 2H, C₅H₅CH₂), 1.22-1.26 (s, 3H, S-CH₃).

IR (KBr) cm⁻¹:

3173.2 (N-H str.), 2938 (C-H str.), 1676.7 (C=N), 1565 (C=C str.), 1529.1 (C=C), 1348.2 (C-N).

(IIC) PMR (CDCl₃ + DMSO) δ:

7.92 (s, 1H, NH), 7.28-6.65 (m, 8H, Ar-H), 5.03 (s, 1H, 4-CH), 2.82-2.65 (m, 2H, C₆H₅CH₂), 2.12-1.94 (m, 2H, C₅H₅CH₂), 1.25 (s, 3H, S-CH₃), 1.09 (s, 1H, CH₃).

IR (KBr) cm⁻¹:

3173.4 (N-H str.), 2932 (C-H str.), 1673.7 (C=N), 1568.3 (C=C str.), 1486.9 (C=C), 1337.9 (C-N).

(IID) PMR (CDCl₃ + DMSO) δ:

7.84 (s, 1H, NH), 7.50-7.19 (m, 7H, Ar-H), 5.62 (s, 1H, 4-CH), 2.84-2.75 (m, 2H, C₆H₅CH₂), 2.20-1.97 (m, 2H, C₅H₅CH₂), 1.25 (s, 3H, S-CH₃).

IR (KBr) cm⁻¹:
3177.7 (N-H str.), 2928 (C-H str.), 1674 (C=N), 1557.6 (C=C str.), 1440 (C=C).

(IIe) PMR (CDCl₃ + DMSO) δ:

8.82 (s, 1H, NH), 7.65-6.74 (m, 7H, Ar-H), 5.95-5.94 (s, 2H, O-CH₂-O), 4.91 (s, 1H, 4-CH), 2.77-2.67 (m, 2H, C₆CH₂), 2.12-1.96 (m, 2H, C₅CH₂), 3.13 (s, 3H, S-CH₃).

IR (KBr) cm⁻¹:

3201.7 (N-H str.), 2978.5 (C-H str.), 1672.6 (C=N), 1575.2 (C=C str.), 1487.8 (C=C), 1339.1 (C-N).

Mass fragments (m/z):

350 M⁺, 303, 276, 215, 128, 76.

(IIf) PMR (CDCl₃ + DMSO) δ:

8.92 (s, 1H, OH), 8.65 (s, 1H, NH), 7.65-6.80 (m, 7H, Ar-H), 5.10 (s, 1H, 4-CH), 3.68 (s, 3H, OCH₃), 2.78-2.72 (m, 2H, C₆CH₂), 2.09-1.92 (m, 2H, C₅CH₂), 3.03 (s, 3H, S-CH₃).

IR (KBr) cm⁻¹:
3290 (O-H str.), 3182 (N-H str.), 2931.8 (C-H str.), 1670 (C=N),
1602.5 (C=C str.), 1579.2 (C=CC), 1363.8 (C-N).

SYNTHESIS OF 2-(ETHYLTHIO)-4-(4-SUBSTITUTEDPHENYL) -
1,4,5,6-TETRAHYDROBENZO[h]QUINAZOLINES

General Procedure

Quinazoline-2-thione (0.004 mole) was dissolved in ethanol. To it, added NaOH solution, which was prepared by dissolving NaOH (0.004 mole, 0.16 g) in water (2 ml). The mixture was cooled. To this mixture, diethyl sulphate (0.4 ml, 0.004 mole) was added dropwise while stirring the mixture continuously. The reaction mixture was refluxed for 3 hours. The reaction was monitored by thin layer chromatography (TLC) using silica gel-G plates. Ethyl acetate and n-hexane mixture was used as eluting solvents (1:1) and after drying, the plates were exposed to iodine chamber. The reaction mixture was cooled and poured over crushed ice. Solid separated was filtered under reduced pressure, washed with ethanol and dried. It was recrystallised from ethanol to provide a pure sample of the product.

A typical procedure is given below:
(IIh) 2-(ethylthio)-4-(4-methoxyphenyl)-1,4,5,6-tetrahydrobenzo[h]quinazoline

4-(4-methoxyphenyl)-3,4,5,6-tetrahydrobenzo[h]quinazoline-2(1H)-thione (0.004 mole, 1.288g) was dissolved in ethanol. To it, added NaOH solution, which was prepared by dissolving NaOH (0.004 mole, 0.16 g) in water (2 ml). The mixture was cooled. To this mixture, diethyl sulphate (0.4 ml, 0.004 mole) was added dropwise while stirring the mixture continuously. The reaction mixture was refluxed for 3 hours. The reaction was monitored by thin layer chromatography (TLC) using silica gel-G plates. Ethyl acetate and n-hexane mixture was used as eluting solvents (1:1) and after drying, the plates were exposed to iodine chamber. The mixture was cooled and poured over crushed ice. Solid separated was filtered under reduced pressure, washed with ethanol and dried. It was recrystallised from ethanol to provide a pure sample of the product.

M.P. = 177-178°C.

Yield = 40%.

PMR (CDCl₃ + DMSO) δ:
7.82 (s, 1H, NH), 7.28-6.85 (m, 8H, Ar-H), 5.04 (s, 1H, 4-CH), 3.77 (s, 3H, OCH₃), 3.30-3.24 (q, 2H, S-CH₂-CH₃), 3.07-2.98 (t, 3H, S-CH₂-CH₃), 2.77-2.65 (m, 2H, C₆CH₂), 2.09-1.90 (m, 2H, C₅CH₂).

IR (KBr) cm⁻¹:

3194.5 (N-H str.), 2930 (C-H str.), 1677.2 (C=N), 1609.6 (C=C str.), 1511.5 (C=C), 1253.2 (C-N).

(IIi) IR (KBr) cm⁻¹:

3170.3 (N-H str.), 2927.7 (C-H str.), 1672.2 (C=N), 1570 (C=C str.), 1525.2 (C=C), 1347.4 (C-N).

(IIj) IR (KBr) cm⁻¹:

3174.7 (N-H str.), 2915 (C-H str.), 1673.8 (C=N), 1568.3 (C=C str.), 1487.1 (C=C), 1337.9 (C-N).

(IIk) IR (KBr) cm⁻¹:

3191.5 (N-H str.), 2923.8 (C-H str.), 1674.2 (C=N), 1567.3 (C=C str.), 1485.6 (C=C), 1376.5 (C-N).

(III) PMR (CDCl₃ + DMSO) δ:
8.67 (s, 1H, NH), 7.47-6.74 (m, 7H, Ar-H), 5.95-5.94 ( s, 2H, O-CH₂-O), 4.93-4.92 (s, 1H, 4-CH), 3.54-3.62 ( q, 2H, S-CH₂-CH₃), 3.19-3.25 ( t, 3H, S-CH₂-CH₃), 2.77-2.68 (m, 2H, C₆CH₂), 2.16-1.92 (m, 2H, C₅CH₂).

IR (KBr) cm⁻¹:

3200.7 ( N-H str.), 2890.3 (C-H str.), 1672.5 (C=N), 1575.2 (C=C str.), 1487.7 (C=Ĉ), 1339 (C-N).

(IIm) IR (KBr) cm⁻¹:

3180.4 (N-H str.), 2932.3 (C-H str.), 1673.9 (C=N), 1513 (C=C str.), 1477.9 (C=Ĉ), 1367.3 (C-N).

SYNTHESIS OF 2-(BENZYLTHIO)-4-(4-SUBSTITUTEDPHENYL)-1,4,5,6-TETRAHYDROBENZO[h] QUINAZOLINES

General Procedure

Quinazoline-2-thione (0.004 mole) was dissolved in alcohol (2-3 ml). The solution was diluted with water (2 ml). To it, benzyl chloride (0.8 ml, 0.004 mole) was added and the mixture was refluxed for 5 hours. The reaction was monitored by thin layer chromatography (TLC) using silica gel-G plates.
Ethyl acetate and n-hexane mixture was used as eluting solvents (1:1) and after drying, the plates were exposed to iodine chamber. The reaction mixture was cooled and poured over crushed ice. Solid separated was filtered under reduced pressure, washed with ethanol and dried. It was recrystallised from ethanol to provide a pure sample of the product.

A typical procedure is given below:

\[(\text{IIo}) \] 2-(benzylthio)-4-(4-methoxyphenyl)-1,4,5,6-tetrahydrobenzo[\(h\)]

quinazoline

4-(4-methoxyphenyl)-3,4,5,6-tetrahydrobenzo[\(h\)]quinazoline-2(1\(H\))-thione (0.004 mole, 1.288g) was dissolved in alcohol (2-3 ml). The solution was diluted with water (2 ml). To it, benzyl chloride (0.506 ml, 0.004 mole) was added and the mixture was refluxed for 5 hours. The reaction was monitored by thin layer chromatography (TLC) using silica gel-G plates. Ethyl acetate and n-hexane mixture was used as eluting solvents (1:1) and after drying, the plates were exposed to iodine chamber. The reaction mixture was cooled and poured over crushed ice. Solid separated was filtered under reduced pressure, washed with ethanol and dried. It was recrystallised from ethanol to provide a pure sample of the product.
M.P. = 202-203\(^0\)C.

Yield = 60%.

PMR (CDCl\(_3\) + DMSO) \(\delta\):

11.65 (s, 1H, NH), 7.71-6.82 (m, 13H, Ar-H), 5.36 (s, 1H, 4-CH), 4.96-4.92 (d, 1H of S-CH\(_2\)), 4.46-4.42 (d, 1H of S-CH\(_2\)), 3.81 (s, 3H, OCH\(_3\)), 2.78-2.73 (m, 2H, C\(_6\)CH\(_2\)), 2.23-2.02 (m, 2H, C\(_5\)CH\(_2\)).

IR (KBr) cm\(^{-1}\):

3120 (N-H str.), 2969.1 (C-H str.), 1670.3 (C=N), 1580 (C=C str.), 1534.7 (C\(=\)C), 1174.4 (C-N).

\((\text{IIp})\) PMR (CDCl\(_3\) + DMSO) \(\delta\):

11.90 (s, 1H, NH), 8.21-7.02 (m, 13H, Ar-H), 5.61 (s, 1H, 4-CH), 5.04-5.00 (d, 1H of S-CH\(_2\)), 4.43-4.39 (d, 1H of S-CH\(_2\)), 2.89-2.68 (m, 2H, C\(_6\)CH\(_2\)), 2.35-1.90 (m, 2H, C\(_5\)CH\(_2\)).

IR (KBr) cm\(^{-1}\):

3103 (N-H str.), 2834.2 (C-H str.), 1673.4 (C=N), 1585 (C=C str.), 1538.4 (C\(=\)C), 1347.9 (C-N).
(IIq) PMR (CDCl₃ + DMSO) δ:

10.68 (s, 1H, NH), 7.68-7.10 (m, 12H, Ar-H), 5.48 (s, 1H, 4-CH), 4.99-4.97 (d, 1H of S-CH₂), 4.55-4.49 (d, 1H of S-CH₂), 2.88-2.82 (m, 2H, C₆H₂), 2.24-2.11 (m, 2H, C₅H₂).

IR (KBr) cm⁻¹:

3058.5 (N-H str.), 2774.1 (C-H str.), 1693.5 (C=N), 1663.1 (C=C str.), 1538.5 (C=C), 1321.5 (C-N).

(IIr) PMR (CDCl₃ + DMSO) δ:

10.72 (s, 1H, NH), 7.70-7.15 (m, 12H, Ar-H), 5.95-5.94 (s, 2H, O-CH₂-O), 5.36 (s, 1H, 4-CH), 5.01-4.98 (d, 1H of S-CH₂), 4.58-4.50 (d, 1H of S-CH₂), 2.83-2.76 (m, 2H, C₆H₂), 2.28-2.15 (m, 2H, C₅H₂).

IR (KBr) cm⁻¹:

3028.7 (N-H str.), 2826.5 (C-H str.), 1672.8 (C=N), 1598 (C=C str.), 1542.7 (C=C), 1306.7 (C-N).

(IIś) PMR (CDCl₃ + DMSO) δ:
11.48 (s, 1H, NH), 7.64-7.08 (m, 14H, Ar-H), 5.47-5.46 (s, 1H, 4-CH), 5.03-5.00 (d, 1H of S-CH), 4.53-4.47 (d, 1H of S-CH), 2.78-2.76 (m, 2H, C₆CH₂), 2.25-2.10 (m, 2H, C₅CH₂).

IR (KBr) cm⁻¹:

3043 (N-H str.), 2930 (C-H str.), 1677.8 (C=N), 1605.7 (C=C str.), 1583.6 (C≡C), 1303.9 (C-N).

**SYNTHESIS OF 2-(BUTYLTHIO)-4-(4-SUBSTITUTEDPHENYL)-1,4,5,6-TETRAHYDROBENZO[h]QUINAZOLINE**

**General Procedure**

A mixture of powdered quinazoline-2-thione (0.004 mole), butyl bromide (0.004 mole) and absolute alcohol (2ml) was taken in round bottom flask (100 ml) and was refluxed for 5 hours. The reaction was monitored by thin layer chromatography (TLC) using silica gel-G plates. Ethyl acetate and n-hexane mixture was used as eluting solvents (1:1) and after drying, the plates were exposed to iodine chamber. After refluxing, the reaction mixture was transferred to 100 ml beaker. It was allowed to stand at room temperature for 36 hours. The product separated after continuous scratching with the glass.
rod. It was filtered under reduced pressure and washed with alcohol and dried. The product was recrystallised from ethanol.

A typical procedure is given below:

\[
\text{(IIx) } 2\text{-}(\text{butylthio})\text{-}4\text{-}(2,3\text{-Methylenedioxyphenyl})\text{-}1,4,5,6\text{-tetrahydro benzo}[h]\text{quinazoline}
\]

A mixture of powdered 4-(2,3-Methylenedioxyphenyl)-3,4,5,6-tetrahydrobenzo[h]quinazoline-2(1H)-thione (0.004 mole, 1.704g), butyl bromide (0.004 mole, 0.506 ml) and absolute alcohol (2ml) was taken in round bottom flask (100 ml) and was refluxed for 5 hours. The reaction was monitored by thin layer chromatography (TLC) using silica gel-G plates. Ethyl acetate and n-hexane mixture was used as eluting solvents (1:1) and after drying, the plates were exposed to iodine chamber. After refluxing the reaction mixture was transferred to 100 ml beaker. It was allowed to stand at room temperature for 36 hours. The product separated after continuous scratching with the glass rod. It was filtered under reduced pressure and washed with alcohol and dried. Then, the product was recrystallised from ethanol.

M.P. = 200-201°C.
Yield = 80%.

PMR (CDCl$_3$ + DMSO) $\delta$:

11.46 (s, 1H, NH), 7.71-6.79 (m, 7H, Ar-H), 5.98-5.97 (s, 2H, O-CH$_2$-O),
5.41-5.40 (s, 1H, 4-CH), 3.63-3.56 (m, 1H of S-CH$_2$), 3.25-3.18 (m, 1H of S-CH$_2$), 2.83-2.79 (m, 2H, C$_6$CH$_2$), 2.31-2.27 (m, 1H of C$_5$CH$_2$), 2.15-2.09 (m, 1H of C$_5$CH$_2$), 1.55-1.34 (m, S-CH$_2$-CH$_2$-CH$_2$-CH$_3$), 0.85-0.81 (t, 3H, S-CH$_2$-CH$_2$-CH$_2$-CH$_3$).

IR (KBr) cm$^{-1}$:

3095.8 (N-H str.), 2933.1 (C-H str.), 1675.3 (C=N), 1595.1 (C=C str.), 1546 (C=C), 1339.2 (C-N).

(II) PMR (CDCl$_3$ & DMSO) $\delta$:

10.98 (s, 1H, NH), 7.85-6.92 (m, 8H, Ar-H), 5.39 (s, 1H, 4-CH), 3.77 (s, 3H, OCH$_3$), 3.60-3.58 (m, 1H of S-CH$_2$), 3.30-3.23 (m, 1H of S-CH$_2$), 2.92-2.84 (m, 2H, C$_6$CH$_2$), 2.36-2.31 (m, 1H of C$_5$CH$_2$), 2.15-2.09 (m, 1H of C$_5$CH$_2$), 1.60-1.38 (m, S-CH$_2$-CH$_2$-CH$_2$-CH$_3$), 0.92-0.89 (t, 3H, S-CH$_2$-CH$_2$-CH$_2$-CH$_3$).

IR (KBr) cm$^{-1}$:
3092 (N-H str.), 2928.8 (C-H str.), 1672 (C≡N), 1604.3 (C=C str.),
1534.6 (C≡C), 1374.4 (C-N).

(IIu) PMR (CDCl₃ & DMSO) δ:

11.01 (s, 1H, NH), 7.93-6.96 (m, 8H, Ar-H), 5.23 (s, 1H, 4-CH), 3.62-
3.58 (m, 1H of S-CH₂), 3.26-3.18 (m, 1H of S-CH₂), 2.85-2.76 (m,
2H, C₆H₂), 2.21-1.98 (m, 2H, C₅H₂), 1.45-1.30 (m, S-CH₂-CH₂-
CH₂-CH₃), 0.97-0.94 (t, 3H, S-CH₂-CH₂-CH₂-CH₃).

IR (KBr) cm⁻¹:

3169 (N-H str.), 2950 (C-H str.), 1678 (C≡N), 1582 (C≡C str.), 1532 (C≡C), 1510 (NO₂), 1348.5 (C-N).

(IIv) PMR (CDCl₃ & DMSO) δ:

10.99 (s, 1H, NH), 8.26-7.23 (m, 8H, Ar-H), 5.19 (s, 1H, 4-CH), 3.55-
3.43 (m, 1H of S-CH₂), 3.23-3.15 (m, 1H of S-CH₂), 2.86-2.78 (m,
2H, C₆H₂), 2.25-1.99 (m, 2H, C₅H₂), 1.49-1.32 (m, S-CH₂-CH₂-
CH₂-CH₃), 1.12-1.09 (t, 3H, S-CH₂-CH₂-CH₂-CH₃), 0.99 (s, 3H, CH₃).

IR (KBr) cm⁻¹:

3110.7 (N-H str.) 1675.9 (C≡N), 1591.7 (C≡C str.).
(IIw) PMR (CDCl₃ & DMSO) δ:

10.85 (s, 1H, NH), 8.11-7.45 (m, 7H, Ar-H), 5.32 (s, 1H, 4-CH), 3.63-3.58 (m, 1H of S-CH₂), 3.44-3.28 (m, 1H of S-CH₂), 2.93-2.85 (m, 2H, C₆H₂), 2.32-2.12 (m, 2H, C₅H₂), 1.51-1.36 (m, S-CH₂-CH₂-CH₂-CH₃), 0.95-0.89 (t, 3H, S-CH₂-CH₂-CH₂-CH₃).

IR (KBr) cm⁻¹:

3083.3 (N-H str.), 2952 (C-H str.), 1672.3 (C=N), 1585.6 (C=C str.).

(IIy) PMR (CDCl₃ & DMSO) δ:

10.25 (s, 1H, OH), 9.77 (s, 1H, NH), 8.12-7.36 (m, 7H, Ar-H), 5.25 (s, 1H, 4-CH), 3.77 (s, 3H, OCH₃), 3.56-3.42 (m, 1H of S-CH₂), 3.25-3.13 (m, 1H of S-CH₂), 2.91-2.82 (m, 2H, C₆H₂), 2.22-1.92 (m, 2H, C₅H₂), 1.52-1.40 (m, S-CH₂-CH₂-CH₂-CH₃), 0.92-0.87 (t, 3H, S-CH₂-CH₂-CH₂-CH₃).

IR (KBr) cm⁻¹:

3290 (O-H), 3097.7 (N-H str.), 2926.5 (C-H str.), 1596.3 (C=N), 1551.1 (C=C str.), 1526 (C=C), 1355.8 (C-N).

(IIz) PMR (CDCl₃ & DMSO) δ:
9.85 (s, 1H, NH), 8.12-6.93 (m, 9H, Ar-H), 5.32 (s, 1H, 4-CH), 3.56-3.43 (m, 1H of S-CH2), 3.29-3.12 (m, 1H of S-CH2), 2.92-2.83 (m, 2H, C6CH2), 2.25-1.99 (m, 2H, C5CH2), 1.43-1.35 (m, S-CH2-CH2-CH2-CH3), 0.96-0.84 (t, 3H, S-CH2-CH2-CH2-CH3).

IR (KBr) cm⁻¹:

3088 (N-H str.), 2928.4 (C-H str.), 1675.2 (C=N), 1585 (C=C str.), 1540.7 (C=C).

Ia-g

IIa-z
## TABLE – 2

CHARACTERIZATION DATA OF PRODUCTS (IIa-IIz):

<table>
<thead>
<tr>
<th>S.No</th>
<th>Product</th>
<th>R</th>
<th>X</th>
<th>Reagent</th>
<th>Time (hrs.)</th>
<th>M.P. (°C)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>IIa</td>
<td>4-OCH₃</td>
<td>-CH₃</td>
<td>Dimethyl Sulphate</td>
<td>3.0</td>
<td>180-181</td>
<td>38</td>
</tr>
<tr>
<td>2.</td>
<td>IIb</td>
<td>3-NO₂</td>
<td>-CH₃</td>
<td>Dimethyl Sulphate</td>
<td>3.0</td>
<td>211-213</td>
<td>30</td>
</tr>
<tr>
<td>3.</td>
<td>IIc</td>
<td>2-CH₃</td>
<td>-CH₃</td>
<td>Dimethyl Sulphate</td>
<td>3.0</td>
<td>189-190</td>
<td>40</td>
</tr>
<tr>
<td>4.</td>
<td>IIId</td>
<td>2,4-(Cl)</td>
<td>-CH₃</td>
<td>Dimethyl Sulphate</td>
<td>3.0</td>
<td>170-172</td>
<td>31</td>
</tr>
<tr>
<td>5.</td>
<td>IIe</td>
<td>2,3-(O-CH₂-O)</td>
<td>-CH₃</td>
<td>Dimethyl Sulphate</td>
<td>3.0</td>
<td>186-187</td>
<td>73</td>
</tr>
<tr>
<td>6.</td>
<td>IIif</td>
<td>4-OH,3-OCH₃</td>
<td>-CH₃</td>
<td>Dimethyl Sulphate</td>
<td>3.0</td>
<td>150-152</td>
<td>20</td>
</tr>
<tr>
<td>7.</td>
<td>IIg</td>
<td>H</td>
<td>-CH₃</td>
<td>Dimethyl Sulphate</td>
<td>3.0</td>
<td>198-200</td>
<td>45</td>
</tr>
<tr>
<td>8.</td>
<td>IIh</td>
<td>4-OCH₃</td>
<td>-C₂H₅</td>
<td>Diethyl Sulphate</td>
<td>3.0</td>
<td>177-178</td>
<td>40</td>
</tr>
<tr>
<td>9.</td>
<td>IIi</td>
<td>3-NO₂</td>
<td>-C₂H₅</td>
<td>Diethyl Sulphate</td>
<td>3.0</td>
<td>79-81</td>
<td>20</td>
</tr>
<tr>
<td>10.</td>
<td>IIj</td>
<td>2-CH₃</td>
<td>-C₂H₅</td>
<td>Diethyl Sulphate</td>
<td>3.0</td>
<td>195-197</td>
<td>22</td>
</tr>
<tr>
<td>No.</td>
<td>Compound</td>
<td>R Group</td>
<td>Functional Group</td>
<td>Compound</td>
<td>R Group</td>
<td>Functional Group</td>
<td>Boiling Point</td>
</tr>
<tr>
<td>-----</td>
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</tr>
<tr>
<td>11.</td>
<td>IIk</td>
<td>2,4-(Cl)</td>
<td>-C₂H₅</td>
<td>Diethyl Sulphate</td>
<td>3.0</td>
<td>181-183</td>
<td>10</td>
</tr>
<tr>
<td>12.</td>
<td>III</td>
<td>2,3-(O-CH₂-O)</td>
<td>-C₂H₅</td>
<td>Diethyl Sulphate</td>
<td>3.0</td>
<td>173-175</td>
<td>38</td>
</tr>
<tr>
<td>13.</td>
<td>IIIm</td>
<td>4-OH,3-OCH₃</td>
<td>-C₂H₅</td>
<td>Diethyl Sulphate</td>
<td>3.0</td>
<td>98-100</td>
<td>78</td>
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<tr>
<td>14.</td>
<td>IIIn</td>
<td>H</td>
<td>-C₂H₅</td>
<td>Diethyl Sulphate</td>
<td>3.0</td>
<td>208-210</td>
<td>16</td>
</tr>
<tr>
<td>15.</td>
<td>IIo</td>
<td>4-OCH₃</td>
<td>-CH₂</td>
<td>Benzyl Chloride</td>
<td>5.0</td>
<td>202-203</td>
<td>60</td>
</tr>
<tr>
<td>16.</td>
<td>IIp</td>
<td>3-NO₂</td>
<td>-CH₂</td>
<td>Benzyl Chloride</td>
<td>5.0</td>
<td>214-216</td>
<td>65</td>
</tr>
<tr>
<td>17.</td>
<td>IIq</td>
<td>2,4-(Cl)</td>
<td>-CH₂</td>
<td>Benzyl Chloride</td>
<td>5.0</td>
<td>204-205</td>
<td>51</td>
</tr>
<tr>
<td>18.</td>
<td>IIr</td>
<td>2,3-(O-CH₂-O)</td>
<td>-CH₂</td>
<td>Benzyl Chloride</td>
<td>5.0</td>
<td>179-181</td>
<td>53</td>
</tr>
<tr>
<td>19.</td>
<td>IIIs</td>
<td>H</td>
<td>-CH₂</td>
<td>Benzyl Chloride</td>
<td>5.0</td>
<td>218-219</td>
<td>65</td>
</tr>
<tr>
<td>20.</td>
<td>IIt</td>
<td>4-OCH₃</td>
<td>-C₄H₉</td>
<td>Butyl bromide</td>
<td>5.0</td>
<td>89-91</td>
<td>60</td>
</tr>
<tr>
<td>21.</td>
<td>IIu</td>
<td>3-NO₂</td>
<td>-C₄H₉</td>
<td>Butyl bromide</td>
<td>5.0</td>
<td>220-223</td>
<td>20</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>22.</td>
<td>IIv</td>
<td>2-CH₃</td>
<td>-C₄H₉</td>
<td>Butyl bromide</td>
<td>5.0</td>
<td>202-204</td>
<td>85</td>
</tr>
<tr>
<td>23.</td>
<td>IIw</td>
<td>2,4-(Cl)</td>
<td>-C₄H₉</td>
<td>Butyl bromide</td>
<td>5.0</td>
<td>177-179</td>
<td>69</td>
</tr>
<tr>
<td>24.</td>
<td>IIx</td>
<td>2,3-(O-CH₂-O)</td>
<td>-C₄H₉</td>
<td>Butyl bromide</td>
<td>5.0</td>
<td>200-201</td>
<td>80</td>
</tr>
<tr>
<td>25.</td>
<td>Ily</td>
<td>4-OH,3-OCH₃</td>
<td>-C₄H₉</td>
<td>Butyl bromide</td>
<td>5.0</td>
<td>83-85</td>
<td>70</td>
</tr>
<tr>
<td>26.</td>
<td>IIz</td>
<td>H</td>
<td>-C₄H₉</td>
<td>Butyl bromide</td>
<td>5.0</td>
<td>219-221</td>
<td>56</td>
</tr>
</tbody>
</table>

Note: All the above compounds were recrystallized from ethanol.
RESULTS AND DISCUSSIONS

Quinazolines and their ring-fused derivatives display a broad spectrum of biological activities. Among a wide variety of heterocycles that have been explored for developing pharmaceutically important molecules, quinazolines also have played an important role in medicinal chemistry. As our research plan aimed to synthesize heterocyclic compounds of biological importance, Quinazoline-2-thiones and their alkyl/aralkyl derivatives were synthesized, in line with this. Biological activity of this class of compounds was found to be because of the following factors:

1. The stereochemistry between the aryl group and dihydropyrimidine ring.

2. Chiral centre at position 4.

3. The ring distortions are found to be influenced to a great extent by the position of substituent in the 4-phenyl ring and the inter-ring bond\(^4\). These derivatives have been synthesized through one-pot multicomponent Biginelli’s reaction, which have received considerable attention as the two or more steps in the synthetic sequence. Now, these can be carried out in one step without the isolation of intermediates. This leads to reduction in time, money and energy. The MORE technique has become an
established tool in organic synthesis because of rate enhancement and higher yields with respect to conventional reaction conditions. Thus, the synthesis of quinazoline-2-thiones were carried out through one-pot multicomponent condensation reactions under microwave irradiations. For the reactions, the equimolar mixture of α-tetralone, thiourea and substituted aldehydes were irradiated in microwave for 2-8 minutes using 3-4 drops of conc. HCl and acetonitrile as solvent.

The details about this method are given under experimental section. In most of the cases the product separated out on keeping the reaction mixture at room temperature for 24-36 hours.

The following compounds were synthesized, as detailed in Table 1.
### TABLE – 1

**CHARACTERIZATION DATA OF PRODUCTS (Ia –Ig)**

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Compound</th>
<th>R</th>
<th>Time (min)</th>
<th>M.P. (°C)</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ia</td>
<td>4-OCH₃</td>
<td>5.00</td>
<td>219-220</td>
<td>40</td>
</tr>
<tr>
<td>2</td>
<td>Ib</td>
<td>3-NO₂</td>
<td>6.30</td>
<td>246-247</td>
<td>53</td>
</tr>
<tr>
<td>3</td>
<td>Ic</td>
<td>2-CH₃</td>
<td>6.00</td>
<td>228-229</td>
<td>45</td>
</tr>
<tr>
<td>4</td>
<td>Id</td>
<td>2,4-(Cl)</td>
<td>4.00</td>
<td>218-219</td>
<td>36</td>
</tr>
<tr>
<td>5</td>
<td>Ie</td>
<td>2,3-(O-CH₂-O)</td>
<td>3.30</td>
<td>224-225</td>
<td>47</td>
</tr>
<tr>
<td>6</td>
<td>If</td>
<td>4-OH,3-OCH₃</td>
<td>3.30</td>
<td>212-213</td>
<td>35</td>
</tr>
<tr>
<td>7</td>
<td>Ig</td>
<td>H</td>
<td>5.30</td>
<td>256-257</td>
<td>46</td>
</tr>
</tbody>
</table>

As a case in illustration compound Ia was synthesized by taking α-tetralone, 4-methoxy benzaldehyde and thiourea dissolved in acetonitrile to which catalytic amount of concentrated hydrochloric acid was added in open borosil glass beaker. The reaction mixture was zapped inside the domestic microwave oven at 30% microwave power for 5.00 minutes. The reaction mixture was allowed to stand overnight at room temperature. The product
separated was filtered, washed with alcohol and recrystallized out of ethanol. The product had melting point at 219-220°C. The PMR spectrum of compound Ia (Plate 1) showed a characteristic singlet at δ 7.82, was assigned to one of the NH proton. A multiplet at δ 6.85-7.28 was assigned to aromatic protons and second NH proton. A three proton singlet was assigned at δ 3.77 due to 4- OCH₃. Also, two proton multiplet were observed at δ 2.77-2.67 and δ 2.09-1.93 for 6-CH₂ and 5-CH₂ respectively. A very fine doublet J = 0.8 Hz at 5.04 due to 4-CH proton. The splitting of this signal may be occurring due to some long range coupling. Similarly, the PMR spectrum of compound Ig (Plate 2) showed a characteristic singlet at δ 5.01 due to 4-CH proton. Two singlets at δ 8.56 and δ 8.68 were assigned to 1-NH and 3-NH protons. A multiplet at δ 7.59-7.12 was assigned to aromatic protons. Also, two multiplets were observed at δ 2.83-2.61 and δ 2.19-1.89 due to 6-CH₂ and 5-CH₂ respectively.

The IR spectra of compound Ia (Plate 3) exhibit absorption band for secondary amino group at 3195.2 cm⁻¹, for aromatic C-H stretching at 2934.4 cm⁻¹, C = C stretching vibration at 1611.6 cm⁻¹, C≡C skeletal vibration of ring at 1485.2 cm⁻¹, C-N stretching at 1359.3 cm⁻¹ and C=S stretching at
1273.2 cm$^{-1}$. Mass spectra of compound Ia (Plate 4) showed M$^+$ at m/z 322 and other peaks at m/z 321, 289, 262, 215, 154, 151, 127, 59, 108, 107, 77 etc.

Thus all the spectral data support the assigned structure Ia.

The fragmentation pattern of compound Ia (Plate 4), is given on the next page:
m/z = 322 (63.32%)

m/z = 321 (37.42%)

m/z = 59 (2.29%)

m/z = 262 (15.97%)

m/z = 155 (1.92%)

m/z = 107

m/z = 128 (18.08%)

m/z = 108 (13.44%)

m/z = 77 (21.45%)

m/z = 215 (100%)

m/z = 107

m/z = 262 (15.97%)

m/z = 155 (1.92%)

m/z = 107

m/z = 59 (2.29%)

m/z = 215 (100%)
Using same procedure, other compounds Ib to Ig were obtained by making use of 3-nitro benzaldehyde, 2-methyl benzaldehyde, 2,4-dichloro benzaldehyde, 2,3-methylenedioxy benzaldehyde, 4-hydroxy-3-methoxy benzaldehyde and benzaldehyde respectively.

The second aspect of these derivatives was to convert the pyrimidine ring into dihydropyrimidine system. The thiones were converted to their thioethers.

Where X was –CH₃, -C₂H₅, -CH₂C₆H₅ and –CH₂(CH₂)₂CH₃. In these cases, thiones were treated with dimethyl sulphate, diethyl sulphate, benzyl chloride and butyl bromide respectively and were refluxed using ethanol as solvent (as explained in experimental section).
TABLE – 2

CHARACTERIZATION DATA OF PRODUCTS (IIa –IIz):

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Product</th>
<th>R</th>
<th>X</th>
<th>Reagent</th>
<th>Time (hrs.)</th>
<th>M.P. (°C)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>IIa</td>
<td>4-OCH₃</td>
<td>-CH₃</td>
<td>Dimethyl Sulphate</td>
<td>3.0</td>
<td>180-181</td>
<td>38</td>
</tr>
<tr>
<td>2.</td>
<td>IIb</td>
<td>3-NO₂</td>
<td>-CH₃</td>
<td>Dimethyl Sulphate</td>
<td>3.0</td>
<td>211-213</td>
<td>30</td>
</tr>
<tr>
<td>3.</td>
<td>IIc</td>
<td>2-CH₃</td>
<td>-CH₃</td>
<td>Dimethyl Sulphate</td>
<td>3.0</td>
<td>189-190</td>
<td>40</td>
</tr>
<tr>
<td>4.</td>
<td>IId</td>
<td>2,4-(Cl)</td>
<td>-CH₃</td>
<td>Dimethyl Sulphate</td>
<td>3.0</td>
<td>170-172</td>
<td>31</td>
</tr>
<tr>
<td>5.</td>
<td>IIe</td>
<td>2,3-(O-CH₂-O)</td>
<td>-CH₃</td>
<td>Dimethyl Sulphate</td>
<td>3.0</td>
<td>186-187</td>
<td>73</td>
</tr>
<tr>
<td>6.</td>
<td>IIf</td>
<td>4-OH,3-OCH₃</td>
<td>-CH₃</td>
<td>Dimethyl Sulphate</td>
<td>3.0</td>
<td>150-152</td>
<td>20</td>
</tr>
<tr>
<td>7.</td>
<td>IIg</td>
<td>H</td>
<td>-CH₃</td>
<td>Dimethyl Sulphate</td>
<td>3.0</td>
<td>198-200</td>
<td>45</td>
</tr>
<tr>
<td>No.</td>
<td>Subscript</td>
<td>R-Substitution</td>
<td>R-Substitution</td>
<td>Name of Compound</td>
<td>Concentration</td>
<td>M.p.</td>
<td>Literature</td>
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</tr>
<tr>
<td>8.</td>
<td>Iih</td>
<td>4-OCH$_3$</td>
<td>-C$_2$H$_5$</td>
<td>Diethyl Sulphate</td>
<td>3.0</td>
<td>177-178</td>
<td>40</td>
</tr>
<tr>
<td>9.</td>
<td>IIi</td>
<td>3-NO$_2$</td>
<td>-C$_2$H$_5$</td>
<td>Diethyl Sulphate</td>
<td>3.0</td>
<td>79-81</td>
<td>20</td>
</tr>
<tr>
<td>10.</td>
<td>IIj</td>
<td>2-CH$_3$</td>
<td>-C$_2$H$_5$</td>
<td>Diethyl Sulphate</td>
<td>3.0</td>
<td>195-197</td>
<td>22</td>
</tr>
<tr>
<td>11.</td>
<td>IIk</td>
<td>2,4-(Cl)</td>
<td>-C$_2$H$_5$</td>
<td>Diethyl Sulphate</td>
<td>3.0</td>
<td>181-183</td>
<td>10</td>
</tr>
<tr>
<td>12.</td>
<td>III</td>
<td>2,3-(O-CH$_2$-O)</td>
<td>-C$_2$H$_5$</td>
<td>Diethyl Sulphate</td>
<td>3.0</td>
<td>173-175</td>
<td>38</td>
</tr>
<tr>
<td>13.</td>
<td>IIIm</td>
<td>4-OH,3-OCH$_3$</td>
<td>-C$_2$H$_5$</td>
<td>Diethyl Sulphate</td>
<td>3.0</td>
<td>98-100</td>
<td>78</td>
</tr>
<tr>
<td>14.</td>
<td>IIIn</td>
<td>H</td>
<td>-C$_2$H$_5$</td>
<td>Diethyl Sulphate</td>
<td>3.0</td>
<td>208-210</td>
<td>16</td>
</tr>
<tr>
<td>15.</td>
<td>IIo</td>
<td>4-OCH$_3$</td>
<td>-CH$_2$C$_6$H$_5$</td>
<td>Benzyl Chloride</td>
<td>5.0</td>
<td>202-203</td>
<td>60</td>
</tr>
<tr>
<td>16.</td>
<td>IIp</td>
<td>3-NO$_2$</td>
<td>-CH$_2$C$_6$H$_5$</td>
<td>Benzyl Chloride</td>
<td>5.0</td>
<td>214-216</td>
<td>65</td>
</tr>
<tr>
<td>17.</td>
<td>IIq</td>
<td>2,4-(Cl)</td>
<td>-CH$_2$C$_6$H$_5$</td>
<td>Benzyl</td>
<td>5.0</td>
<td>204-205</td>
<td>51</td>
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<tr>
<td>18.</td>
<td>IIr</td>
<td>2,3-(O-CH₂-O)</td>
<td>C₆H₅</td>
<td>Benzyl Chloride</td>
<td>5.0</td>
<td>179-181</td>
<td>53</td>
</tr>
<tr>
<td>19.</td>
<td>IIi</td>
<td>H</td>
<td>-CH₂</td>
<td>C₆H₅</td>
<td>Benzyl Chloride</td>
<td>5.0</td>
<td>218-219</td>
</tr>
<tr>
<td>20.</td>
<td>IIt</td>
<td>4-OCH₃</td>
<td>-C₄H₉</td>
<td>Butyl bromide</td>
<td>5.0</td>
<td>89-91</td>
<td>60</td>
</tr>
<tr>
<td>21.</td>
<td>IIu</td>
<td>3-NO₂</td>
<td>-C₄H₉</td>
<td>Butyl bromide</td>
<td>5.0</td>
<td>220-223</td>
<td>20</td>
</tr>
<tr>
<td>22.</td>
<td>IIV</td>
<td>2-CH₃</td>
<td>-C₄H₉</td>
<td>Butyl bromide</td>
<td>5.0</td>
<td>202-204</td>
<td>85</td>
</tr>
<tr>
<td>23.</td>
<td>IIw</td>
<td>2,4-(Cl)</td>
<td>-C₄H₉</td>
<td>Butyl bromide</td>
<td>5.0</td>
<td>177-179</td>
<td>69</td>
</tr>
<tr>
<td>24.</td>
<td>IIx</td>
<td>2,3-(O-CH₂-O)</td>
<td>-C₄H₉</td>
<td>Butyl bromide</td>
<td>5.0</td>
<td>200-201</td>
<td>80</td>
</tr>
<tr>
<td>25.</td>
<td>IIy</td>
<td>4-OH,3-OCH₃</td>
<td>-C₄H₉</td>
<td>Butyl bromide</td>
<td>5.0</td>
<td>83-85</td>
<td>70</td>
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<tr>
<td>26.</td>
<td>IIz</td>
<td>H</td>
<td>-C₄H₉</td>
<td>Butyl bromide</td>
<td>5.0</td>
<td>219-221</td>
<td>56</td>
</tr>
</tbody>
</table>
Note: All the above compounds were recrystallized from ethanol.

The ultraviolet spectra of Ie show $\lambda_{\text{max}}$ at 275.8 nm where as its S-methyl (IIe) derivative show $\lambda_{\text{max}}$ at 276.2 nm. This shows that S-methyl did not show any bathochromic shift, which would have been possible if the two double bonds in pyrimidine ring got conjugated in the preparation of S-methyl. Thus, structure IIa-z for two non-conjugated double bonds is suggested. Further conformation of the total structure was done through IR, PMR and mass spectra. The IR spectra of compound IIe (plate 5)exhibit absorption band for secondary amino group at 3201.7 cm$^{-1}$, for alkyl group C-H stretching at 2978.5 cm$^{-1}$, C=N band at 1672.6 cm$^{-1}$, C = C stretching vibration at 1575.2 cm$^{-1}$, C=C skeletal vibration of ring at 1487.8 cm$^{-1}$ and C-N stretching at 1339.1 cm$^{-1}$. The mass spectra are completely in line with the fragmentation of S-derivatives. In the case of S-methyl derivative (compound IIe, Plate 6), the mass spectrum showed M$^+$ peak at m/z 350 and base peak at m/z 215 and other important peaks at m/z 303, 276, 128, 76 etc.

A possible fragmentation pattern of the compound IIe (Plate 6) is given on the next page:
A possible fragmentation pattern of compound IIp (Plate 7) is given below:
A possible fragmentation pattern of compound IIx (Plate 8) is given below:
The PMR spectra of IIs (Plate 9) showed a characteristic difference when compared with PMR spectra of Ig (Plate 2). The obvious and expected difference in PMR spectra was due to S-benzyl group. The non-equivalence of two protons attached to carbon which in turn were attached to sulphur, were clearly seen as doublets at $\delta$ 4.89-4.84 and at $\delta$ 4.47- 4.43. Also, a singlet is obtained at $\delta$ 11.79 due to 1-NH proton in IIs, which got exchanged with D$_2$O.