SYNTHESIS OF (i) 3'-ARYL-5-(1-METHOXYNAPHTHALEN-2-YL)-1'-PHENYL-3,4-DIHYDRO-1'H,2'H-3,4'-BIPYRAZOLES, (ii) 3'-ARYL-5-(1-ETHOXYNAPHTHALEN-2-YL)-1',2-DIPHENYL-3,4-DIHYDRO-1'H,2'H-3,4'-BIPYRAZOLES, (iii) 3'-ARYL-5-(2-METHOXYNAPHTHALEN-1-YL)-1'-PHENYL-3,4-DIHYDRO-1'H,2'H-3,4'-BIPYRAZOLES (4.23 A-F) AND (iv) 3'-ARYL-5-(2-METHOXYNAPHTHALEN-1-YL)-1',2-DIPHENYL-3,4-DIHYDRO-1'H,2'H-3,4'-BIPYRAZOLES

Introduction:

Pyrazole refers to the class of five member aromatic nitrogen heterocyclic motifs embedded in several natural products and drugs\(^1\)\(^2\). Pyrazole derivatives have been found to possess significant biological activities such as antimicrobial\(^3\), antiviral\(^4\), antitumor\(^5\), antihistaminic\(^7\), antidepressant\(^8\), insecticides\(^9\), fungicides\(^10\), 5-α-reductase inhibitor\(^11\), antiproliferative\(^12\), antiparasitic\(^13\), herbicides\(^14\), anti-inflammatory\(^15\), antiprotozoal\(^16\),\(^17\) analgesic\(^18\), antipyretic\(^19\), antiarrhythmic\(^20\), psychoanaleptic\(^21\), anticonvulsant\(^22\), mono aminoxidase inhibitor\(^23\) and antidiabetic\(^24\) activities. The pyrazole ring is present as the core in a variety of leading Non Steroidal Anti-Inflammatory Drugs (NSAIDs)\(^25\) and antihypertensive drugs\(^26\). They have also found use as bifunctional ligands\(^27\) for metal catalysis, and in various building blocks for pharmaceutical and agricultural research. In 1959, the first natural pyrazole, 1-pyrazolyl-alanine\(^28\), was isolated from seeds of watermelons. Pyrazole derivatives have a long history of application in agrochemicals and pharmaceutical industry as herbicides and active pharmaceuticals\(^29\) respectively.

The recent success of pyrazole COX-2 inhibitor\(^30\) has further highlighted the importance of these heterocyclic rings in medicinal chemistry. A systematic investigation of this class of heterocyclic lead revealed that pyrazole containing pharmacoactive agents play important role in medicinal chemistry. The prevalence of pyrazole cores in biologically active molecules has stimulated the need for elegant and efficient ways to make these heterocyclic lead. Pyrazoles have been the recent target of numerous methodologies, mostly due to their prevalence as scaffolds in drug discovery programs and synthesis in particular of bioactive compounds and reactions in different media. The pyrazole ring is present as the core in a variety of leading drugs such as Celebrex, Viagra or Rimonabant\(^31\). Many synthetic pyrazole compounds are of
importance as dyes and medicinals. Among them are: antipyrine, used as an analgesic and febrifuge; tartrazine, most commonly used as a yellow dye for food; phenylbutazone (Butazolidin), an anti-inflammatory drug used in treatment of arthritis. Moreover, considerable attention has been focused on pyrazolines and substituted pyrazolines due to their interesting biological importance such as antifungal, antidepressant, anticonvulsant, anti-inflammatory, antibacterial, antitumor, antiviral, antiparasitic and insecticidal activities. Some of these compounds have also antidiabetic and potent selective activity such as Nitric oxide synthase (NOS) inhibitor and Cannabinoid CB1 receptor antagonist activity.

In recent years, a significant portion of research in heterocyclic chemistry has been devoted to 2-pyrazolines containing different aryl groups as substituents, as evident from the literature. 2-pyrazolines seem to be the most frequently studied pyrazoline type compounds. 2-Pyrazolines display a broad spectrum of potential pharmacological activities and are present in a number of pharmacologically active molecules such as Phenazone/Amidopyrene/ Methampyrone (analgesic and antipyretic), Azolid/Tandearil (anti-inflammatory), Indoxacarb (insecticidal), Anturane (uricosuric) etc. A variety of methods have been reported for the preparation of 2-pyrazolines. A classical synthesis of these compounds involves the base-catalyzed aldol condensation reaction of aromatic ketones and aldehydes to give, α,β-unsaturated ketones (chalcones), which undergo a subsequent cyclization reaction with hydrazines affording 2-pyrazolines. Some of these methods suffer from disadvantages such as longer reaction time, uses of organic solvents, chalcone intermediate isolation and purification. Recently, K$_2$CO$_3$-mediated microwave irradiation has been shown to be an efficient method for the synthesis of pyrazolines. The recent interest in green chemistry has posed a new challenge for organic synthesis in that new reaction conditions need to be found which reduce the number of reaction steps, the emission of volatile organic solvents and the use of hazardous toxic chemicals. Ultrasound and microwave irradiation methods have increasingly been used in organic synthesis in the last few decades compared with conventional heating methods.
Previous approach:
1) Traven et al.,\textsuperscript{54} have reported the synthesis of 1,3,5-Triphenyl-4,5-dihydro-1H-pyrazole (4.4) by refluxing acetophenone (4.1), benzaldehyde (4.2) and phenylhydrazine (4.3) in ethanolic 10% NaOH.

\textbf{Scheme-4.1: Synthesis of 1,3,5-Triphenyl-4,5-dihydro-1H-pyrazole (4.4).}

![Chemical structure of 1,3,5-Triphenyl-4,5-dihydro-1H-pyrazole](image)

2) B. Movassagh \textit{et al.,}\textsuperscript{55} have reported the synthesis of 2-Pyrazoline derivatives by the reaction of a solution of $t$-BuOK in dry $t$-BuOH, aryl methyl ketones (4.5), aryl aldehydes (4.6) and phenylhydrazine (4.3).

\textbf{Scheme-4.2: Synthesis of 2-Pyrazoline derivatives (4.7)}

![Chemical structure of 2-Pyrazoline derivatives](image)

3) D. J. Pacheco \textit{et al.,}\textsuperscript{56} have synthesized 2-Pyrazoline derivatives (4.9) by the 1,4-Michael addition of acetylamino chalcones (4.8) with hydrazine hydrate in the presence of sodium acetate in acetic acid:water (2:1) under ultrasound irradiation.

\textbf{Scheme-4.3: Synthesis of 2-Pyrazoline derivatives (4.9).}

![Chemical structure of 2-Pyrazoline derivatives](image)
4) Kukharev et al.,\textsuperscript{57} have synthesized 5-Methyl-3,5-dialkyl-2-pyrazoline (4.11) by the reaction of 1,2-bis(1-alkylethylidene)hydrazine (4.10) and Iodine using stirring condition.

\textbf{Scheme-4.4: Synthesis of 5-Methyl-3,5-dialkyl-2-pyrazoline (4.11).}

\[
\begin{align*}
\text{NH}_2\text{NH}_2 & \xrightarrow{\text{Iodine, 140 }^\circ\text{C, 1 hr}} \text{N-NH} \\
\text{R} & \quad \text{N-NH} \quad \text{R}
\end{align*}
\]

5) Y. Ju and R. S. Varma\textsuperscript{58} has reported the synthesis of 1-(Alkylphenyl)-4,5-dihydro-1\textit{H}-pyrazoles (4.13) by reaction of phenyl hydrazine (4.3) and 1,3-dihalopropane (4.12) in the presence of potassium carbonate in water under microwave irradiation.

\textbf{Scheme-4.5: Synthesis of 1-(Alkylphenyl)-4,5-dihydro-1\textit{H}-pyrazoles (4.13).}

\[
\begin{align*}
\text{NH}_2\text{NH}_2 & \xrightarrow{\text{K}_2\text{CO}_3, \text{H}_2\text{O, MWI}} \text{N-N} \\
\text{X} & \quad \text{N-N} \\
\text{X} & \quad \text{X}
\end{align*}
\]

6) Rei Kinjo et al.,\textsuperscript{59} have reported the synthesis of 3-Methyl-3a,4,5,6,7,7a-hexahydro-1\textit{H}-indazole (4.15) by the reaction of ethynylcyclohexane (4.14) with anhydrous hydrazine in CDCl\textsubscript{3} or C\textsubscript{6}D\textsubscript{6} in the presence of [(CAAC)AuCl] complex and KB(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}.

\textbf{Scheme-4.6: Synthesis of 3-Methyl-3a,4,5,6,7,7a-hexahydro-1\textit{H}-indazole (4.15).}

\[
\begin{align*}
\text{H} & \xrightarrow{\text{i) NH}_2\text{NH}_2, \text{(CAAC)AuCl} & \text{KB(C}_6\text{F}_5)_4, 90 \text{ }^\circ\text{C, 14 hr} \quad \text{H}} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H}
\end{align*}
\]

7) S. N. Shelke et al.,\textsuperscript{60} have reported the synthesis of 5-(4-Alkylphenyl)-3'-(4-fluorophenyl)-1'-phenyl-3,4-dihydro-1'H,2'H-3,4'-bipyrazoles (4.17) by 1,4-Michael addition of 3-(4-fluorophenyl)-1-phenyl-1'H-pyrazole-4-carbaldehyde (4.16) with hydrazine hydrate in the presence of acetic acid in ethanol under ultrasound irradiation.
Scheme-4.7: Synthesis of 5-(4-Alkylphenyl)-3’-(4-fluorophenyl)-1’-phenyl-3,4-dihydro-1’H,2H-3,4’-bipyrazoles (4.17).

8) Shridhar Malladi et al.,$^{61}$ have reported the synthesis of 2-Pyrazoline derivatives (4.19) by the refluxing of pyrazolylchalcones (4.18) and phenylhydrazine (4.3) in glacial acetic acid.

Scheme-4.8: Synthesis of 2-Pyrazoline derivatives (4.19).

9) S. Y. Jadhav et al.,$^{62}$ have synthesized 2-Pyrazoline derivatives (4.21) by the reaction of pyrazolylchalcones (4.20) with hydrazine hydrate in PEG-400 in the presence of glacial acetic acid.

Scheme-4.9: Synthesis of 2-Pyrazoline derivatives (4.21).
Present work:

Encouraged by the biological activities of 2-pyrazoline and pyrazole moieties, we have taken up the synthesis of 3'-Aryl-5-(1-methoxynaphthalen-2-yl)-1'-phenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazoles (4.22 a-g), 3'-Aryl-5-(1-methoxynaphthalen-2-yl)-1',2-diphenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazoles (4.22 h-m), 3'-Aryl-5-(2-methoxynaphthalen-1-yl)-1'-phenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazoles (4.23 a-f) and 3'-Aryl-5-(2-methoxynaphthalen-1-yl)-1',2-diphenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazoles (4.23 g-k) with a view to test their antimicrobial activity. Non-conventional techniques have gained popularity as for rapid organic synthesis it is eco-friendly, economical and is believed to be a step towards Green chemistry. Moreover, a number of synthetic approaches for the construction of 2-pyrazoline exist in which the key step is 1,4-Michael addition to chalcone with appropriate hydrazine derivative. The most straightforward method for one-pot preparation of 2-pyrazoline is the condensation of aldehyde, ketones with hydrazine derivative. The methods which are adopted for the synthesis of 2-pyrazoline are useful for the synthesis of title compounds.
SECTION-A: SYNTHESIS OF 3'-ARYL-5-(1-METHOXYNAPHTHALEN-2-YL)-1'-PHENYL-3,4-DIHYDRO-1'H,2H-3,4'-BIPYRAZoles AND 3'-ARYL-5-(1-METHOXYNAPHTHALEN-2-YL)-1',2-DIPHENYL-3,4-DIHYDRO-1'H,2H-3,4'-BIPYRAZoles

Synthesis of 3'-Aryl-5-(1-methoxynaphthalen-2-yl)-1'-phenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazoles (4.22 a-g) and 3'-Aryl-5-(1-methoxynaphthalen-2-yl)-1',2-diphenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazoles (4.22 h-m) involve three steps

1) Synthesis of 1-(1-Methoxynaphthalen-2-yl)ethanone
2) Synthesis of 3-Aryl-1-phenyl-1'H-pyrazole-4-carbaldehydes
3) Synthesis of 3'-Aryl-5-(1-methoxynaphthalen-2-yl)-1'-phenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazoles and 3'-Aryl-5-(1-methoxynaphthalen-2-yl)-1',2-diphenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazoles

1) Synthesis of 1-(1-Methoxynaphthalen-2-yl)ethanone (4.25).

A mixture of 1-(1-Hydroxynaphthalen-2-yl)ethanone (4.24), potassium carbonate and dimethyl sulfate in DMF was stirred at room temperature for 6 hr to yield 1-(1-methoxynaphthalen-2-yl)ethanone (4.25).

Scheme-4.10: Synthesis of 1-(1-Methoxynaphthalen-2-yl)ethanone (4.25).
2) Synthesis of 3-Aryl-1-phenyl-1\textit{H}-pyrazole-4-carbaldehydes (already discussed in chapter-II, section-A)

3) Synthesis of 3’-Aryl-5-(1-methoxynaphthalen-2-yl)-1’-phenyl-3,4-dihydro-1’\textit{H},2\textit{H}-3,4’-bipyrazoles (4.22 a-g) and 3’-Aryl-5-(1-methoxynaphthalen-2-yl)-1’,2-diphenyl-3,4-dihydro-1’\textit{H},2\textit{H}-3,4’-bipyrazoles (4.22 a-g) under conventional heating, microwave irradiation and ultrasound irradiation methods

**Conventional heating method:**
A solution of KOH, 1-(1-Methoxynaphthalen-2-yl)ethanone (4.25) and 3-aryl-1-phenyl-1\textit{H}-pyrazole-4-carbaldehydes (4.26 a-f) in ethanol was refluxed until the starting materials have completely disappeared, then hydrazine hydrate / phenylhydrazine hydrochloride is added and reflux continued to afford corresponding 3’-aryl-5-(1-methoxynaphthalen-2-yl)-1’-phenyl-3,4-dihydro-1’\textit{H},2\textit{H}-3,4’-bipyrazoles (4.22 a-g) / 3’-aryl-5-(1-methoxynaphthalen-2-yl)-1’,2-diphenyl-3,4-dihydro-1’\textit{H},2\textit{H}-3,4’-bipyrazoles (4.22 h-m).

**Microwave irradiation method:**
A solution of KOH, 1-(1-Methoxynaphthalen-2-yl)ethanone (4.25) and 3-aryl-1-phenyl-1\textit{H}-pyrazole-4-carbaldehydes (4.26 a-f) in ethanol was irradiated under microwave until the starting materials have completely disappeared, then hydrazine hydrate / phenylhydrazine hydrochloride is added and irradiation continued to yield corresponding 3’-aryl-5-(1-methoxynaphthalen-2-yl)-1’-phenyl-3,4-dihydro-1’\textit{H},2\textit{H}-3,4’-bipyrazoles (4.22 a-g) / 3’-aryl-5-(1-methoxynaphthalen-2-yl)-1’,2-diphenyl-3,4-dihydro-1’\textit{H},2\textit{H}-3,4’-bipyrazoles (4.22 h-m).

**Ultrasound irradiation method:**
A solution of KOH, 1-(1-Methoxynaphthalen-2-yl)ethanone (4.25) and 3-aryl-1-phenyl-1\textit{H}-pyrazole-4-carbaldehydes (4.26 a-f) in ethanol was irradiated under ultrasound until the starting materials have completely disappeared, then hydrazine hydrate / phenylhydrazine hydrochloride is added and irradiation continued to yield corresponding 3’-aryl-5-(1-
methoxynaphthalen-2-yl)-1'-phenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazoles (4.22 a-g) / 3'-aryl-5-(1-methoxynaphthalen-2-yl)-1',2-diphenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazoles (4.22 h-m).

Scheme-4.11: Synthesis of 3'-Aryl-5-(1-methoxynaphthalen-2-yl)-1'-phenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazoles (4.22 a-g) & 3'-Aryl-5-(1-methoxynaphthalen-2-yl)-1',2-diphenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazoles (4.22 h-m).

<table>
<thead>
<tr>
<th>a &amp; h</th>
<th>b &amp; i</th>
<th>c &amp; j</th>
<th>d</th>
<th>e &amp; k</th>
<th>f &amp; l</th>
<th>g &amp; m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
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</table>
Table 1: Physical data of 3'-Aryl-5-(1-methoxynaphthalen-2-yl)-1'-phenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazoles (4.22 a-g) and 3'-Aryl-5-(1-methoxynaphthalen-2-yl)-1',2-diphenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazoles (4.22 h-m)

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Compound</th>
<th>M.P. (°C)</th>
<th>M.F. (M.Wt.)</th>
<th>Reaction time</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Conv (hr)</td>
<td>USI (hr)</td>
</tr>
<tr>
<td>1</td>
<td>5-(1-Methoxynaphthalen-2-yl)-1',3'-diphenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazole (4.22 a)</td>
<td>152</td>
<td>C\textsubscript{29}H\textsubscript{24}N\textsubscript{4}O (444)</td>
<td>4.5</td>
<td>2.5</td>
</tr>
<tr>
<td>2</td>
<td>5-(1-Methoxynaphthalen-2-yl)-1'-phenyl-3'-(p-tolyl)-3,4-dihydro-1'H,2H-3,4'-bipyrazole (4.22 b)</td>
<td>138</td>
<td>C\textsubscript{30}H\textsubscript{26}N\textsubscript{4}O (458)</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>5-(1-Methoxynaphthalen-2-yl)-3'-(4-methoxyphenyl)-1'-phenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazole (4.22 c)</td>
<td>120</td>
<td>C\textsubscript{30}H\textsubscript{26}N\textsubscript{4}O\textsubscript{2} (474)</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>3'-(4-Chlorophenyl)-5-(1-methoxynaphthalen-2-yl)-1'-phenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazole (4.22 d)</td>
<td>159</td>
<td>C\textsubscript{29}H\textsubscript{23}ClN\textsubscript{4}O (478)</td>
<td>4.5</td>
<td>3</td>
</tr>
<tr>
<td>5</td>
<td>3'- (4-Bromophenyl)-5-(1-methoxynaphthalen-2-yl)-1'-phenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazole (4.22 e)</td>
<td>148</td>
<td>C\textsubscript{29}H\textsubscript{23}BrN\textsubscript{4}O (522)</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>6</td>
<td>5-(1-Methoxynaphthalen-2-yl)-3'- (4-nitrophenyl)-1'-phenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazole (4.22 f)</td>
<td>127</td>
<td>C\textsubscript{29}H\textsubscript{23}N\textsubscript{5}O\textsubscript{3} (489)</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>7</td>
<td>5-(1-Methoxynaphthalen-2-yl)-1'-phenyl-3'- (thiophen-2-yl)-3,4-dihydro-1'H,2H-3,4'-bipyrazole (4.22 g)</td>
<td>131</td>
<td>C\textsubscript{27}H\textsubscript{22}N\textsubscript{4}OS (450)</td>
<td>4</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>Molecular Formula</td>
<td></td>
<td></td>
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<tr>
<td>8</td>
<td>5-(1-Methoxynaphthalen-2-yl)-1',2,3'-triphenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazole (4.22 h)</td>
<td>C_{35}H_{28}N_{4}O (520)</td>
<td>5</td>
<td>2.5</td>
<td>3.5</td>
</tr>
<tr>
<td>9</td>
<td>5-(1-Methoxynaphthalen-2-yl)-1',2-diphenyl-3'-(p-tolyl)-3,4-dihydro-1'H,2H-3,4'-bipyrazole (4.22 i)</td>
<td>C_{36}H_{30}N_{4}O (534)</td>
<td>4.5</td>
<td>3</td>
<td>3.5</td>
</tr>
<tr>
<td>10</td>
<td>5-(1-Methoxynaphthalen-2-yl)-3'-(4-methoxyphenyl)-1',2-diphenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazole (4.22 j)</td>
<td>C_{36}H_{30}N_{4}O_{2} (550)</td>
<td>4.5</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>11</td>
<td>3'- (4-Bromophenyl)-5 -(1-methoxynaphthalen-2-yl)-1',2-diphenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazole (4.22 k)</td>
<td>C_{35}H_{27}BrN_{4}O (598)</td>
<td>5</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>12</td>
<td>5-(1-Methoxynaphthalen-2-yl)-3'-(4-nitrophenyl)-1',2-diphenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazole (4.22 l)</td>
<td>C_{35}H_{27}N_{5}O_{3} (565)</td>
<td>5</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>13</td>
<td>5-(1-Methoxynaphthalen-2-yl)-1',2-diphenyl-3'- (thiophen-2-yl)-3,4-dihydro-1'H,2H-3,4'-bipyrazole (4.22 m)</td>
<td>C_{33}H_{26}N_{4}OS (526)</td>
<td>4.5</td>
<td>2.5</td>
<td>3.5</td>
</tr>
</tbody>
</table>
CHAPTER-IV

The IR (KBr, cm\(^{-1}\)) spectrum of (Fig-4.1) (4.22 i) showed characteristic peaks at 1596 cm\(^{-1}\) (C=N of pyrazoline), 1620 (C=C). \(^1\)H-NMR (CDCl\(_3\), 400 MHz) spectrum of (Fig-4.2) (4.22 i) showed a singlet at \(\delta\) 2.42 integrating for three protons was assigned to methyl group protons. Two doublets of doublets appeared between \(\delta\) 3.36-3.42, 5.51-5.56 integrating for two protons each was assigned to pyrazoline ABX pattern groups of CH\(_2\) \((J=6.8\) Hz, 17.2 Hz) and CH \((J=6.8\) Hz, 11.8 Hz) with coupling constants respectively other pyrazoline ABX pattern CH\(_2\) one proton couple with methoxy group which was showed at \(\delta\) 3.88 as a multiplet. A singlet at \(\delta\) 7.98 integrating for one proton was assigned to pyrazole ring proton. Remaining all aromatic protons appeared in between \(\delta\) 6.78-8.28. \(^1\)C-NMR (CDCl\(_3\), 100 MHz) spectrum of (Fig-4.3) (4.22 i) showed characteristic peaks at \(\delta\) 21.3 (CH\(_3\)), 47.1 (CH\(_2\)), 56.7 (O-CH\(_3\)), 56.4 (N-CH), 112.9, 113.8, 115.9, 118.8, 119.3, 123.0, 124.7, 126.3, 126.4, 127.3, 127.9, 128.1, 128.9, 129.2, 129.3, 129.5, 130.4, 130.8, 132.8, 138.0, 139.9, 145.4, 146.9, 150.4, 155.8. In the mass spectrum of (Fig-4.4) (4.22 i) the molecular ion peak MS: [M+H]\(^+\) peak at \(m/z\) was observed at 535 (100%).
SECTION-B: SYNTHESIS OF 3'-ARYL-5-(2-METHOXYNAPHTHALEN-1-YL)-1'-PHENYL-3,4-DIHYDRO-1'H,2H-3,4'-BIPYRAZOLES AND 3'-ARYL-5-(2-METHOXYNAPHTHALEN-1-YL)-1',2-DIPHENYL-3,4-DIHYDRO-1'H,2H-3,4'-BIPYRAZOLES

Synthesis of 3'-Aryl-5-(2-methoxynaphthalen-1-yl)-1'-phenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazoles and synthesis of 3'-Aryl-5-(2-methoxynaphthalen-1-yl)-1',2-diphenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazoles involve three steps:

1) Synthesis of 1-(2-Methoxynaphthalen-1-yl)ethanone
2) Synthesis of 3-Aryl-1-phenyl-1'H-pyrazole-4-carbaldehydes
3) Synthesis of 3'-Aryl-5-(2-methoxynaphthalen-1-yl)-1'-phenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazoles and 3'-Aryl-5-(2-methoxynaphthalen-1-yl)-1',2-diphenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazoles

1) Synthesis of 1-(2-Methoxynaphthalen-1-yl)ethanone (4.28)

A mixture of 1-(2-Hydroxynaphthalen-1-yl)ethanone (4.27), potassium carbonate and dimethylsulfate in DMF was stirred for room temperature to yield 1-(2-methoxynaphthalen-1-yl)ethanone (4.28).

Scheme-4.1: Synthesis of 1-(2-Methoxynaphthalen-1-yl)ethanone (4.28).
2) Synthesis of 3-Aryl-1-phenyl-1\(H\)-pyrazole-4-carbaldehydes (4.26) (already discussed in chapter-I, section-A)

3) Synthesis of 3'-Aryl-5-(2-methoxynaphthalen-1-yl)-1'-phenyl-3,4-dihydro-1'\(H\),2\(H\)-3,4'-bipyrazoles (4.23 a-f) and 3'-Aryl-5-(2-methoxynaphthalen-1-yl)-1',2-diphenyl-3,4-dihydro-1'\(H\),2\(H\)-3,4'-bipyrazoles (4.23 g-k) under conventional heating, microwave irradiation and ultrasound irradiation methods

**Conventional heating method:**

A solution of KOH, 1-(2-Methoxynaphthalen-1-yl)ethanone (4.28), 3-aryl-1-phenyl-1\(H\)-pyrazole-4-carbaldehydes (4.26 a-f) in ethanol was refluxed until the starting materials have completely disappeared, then hydrazine hydrate / phenylhydrazine hydrochloride is added and reflux continued to afford corresponding 3'-aryl-5-(2-methoxynaphthalen-1-yl)-1'-phenyl-3,4-dihydro-1'\(H\),2\(H\)-3,4'-bipyrazoles (4.23 a-f) / 3'-aryl-5-(2-methoxynaphthalen-1-yl)-1',2-diphenyl-3,4-dihydro-1'\(H\),2\(H\)-3,4'-bipyrazoles (4.23 g-k).

**Microwave irradiation method:**

A solution of KOH, 1-(2-Methoxynaphthalen-1-yl)ethanone (4.28), 3-aryl-1-phenyl-1\(H\)-pyrazole-4-carbaldehydes (4.26 a-f) in ethanol was irradiated under microwave until the starting materials have completely disappeared, then hydrazine hydrate / phenylhydrazine hydrochloride is added and irradiation continued to yield corresponding 3'-aryl-5-(2-methoxynaphthalen-1-yl)-1'-phenyl-3,4-dihydro-1'\(H\),2\(H\)-3,4'-bipyrazoles (4.23 a-f) / 3'-aryl-5-(2-methoxynaphthalen-1-yl)-1',2-diphenyl-3,4-dihydro-1'\(H\),2\(H\)-3,4'-bipyrazoles (4.23 g-k).

**Ultrasound irradiation method:**

A solution of KOH, 1-(2-Methoxynaphthalen-1-yl)ethanone (4.28), 3-aryl-1-phenyl-1\(H\)-pyrazole-4-carbaldehydes (4.26 a-f) in ethanol was irradiated under ultrasound until the starting materials have completely disappeared, then hydrazine hydrate / phenylhydrazine hydrochloride is added and irradiation continued to yield corresponding 3'-aryl-5-(2-methoxynaphthalen-1-yl)-1'-phenyl-3,4-dihydro-1'\(H\),2\(H\)-3,4'-bipyrazoles (4.23 a-f) / 3'-aryl-5-(2-methoxynaphthalen-1-yl)-1',2-diphenyl-3,4-dihydro-1'\(H\),2\(H\)-3,4'-bipyrazoles (4.23 g-k).
Scheme-4.1: Synthesis of 3'-Aryl-5-(2-methoxynaphthalen-1-yl)-1'-phenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazoles (4.23 a-f) & 3'-Aryl-5-(2-methoxynaphthalen-1-yl)-1',2-diphenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazoles (4.23 g-k).
Table 2: Physical data of 3'-Aryl-5-(2-methoxynaphthalen-1-yl)-1'-phenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazoles (4.23 a-f) and 3'-Aryl-5-(2-methoxynaphthalen-1-yl)-1',2-diphenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazoles (4.23 g-k)

<table>
<thead>
<tr>
<th>S.No</th>
<th>Compound</th>
<th>M.P. (°C)</th>
<th>M.F. (M.Wt.)</th>
<th>Reaction time</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Conv (hr) USI (hr) MWI (min) Conv. USI MWI</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>5-(2-Methoxynaphthalen-1-yl)-1',3'-diphenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazole (4.23 a)</td>
<td>133</td>
<td>C$<em>{29}$H$</em>{24}$N$_{4}$O (444)</td>
<td>4.5 3 4</td>
<td>60 72 84</td>
</tr>
<tr>
<td>2</td>
<td>5-(2-Methoxynaphthalen-1-yl)-1'-phenyl-3'-(p-tolyl)-3,4-dihydro-1'H,2H-3,4'-bipyrazole (4.23 b)</td>
<td>202</td>
<td>C$<em>{30}$H$</em>{26}$N$_{4}$O (458)</td>
<td>4.5 2.5 3.5</td>
<td>63 75 88</td>
</tr>
<tr>
<td>3</td>
<td>5-(2-Methoxynaphthalen-1-yl)-3'-(4-methoxyphenyl)-1'-phenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazole (4.23 c)</td>
<td>119</td>
<td>C$<em>{36}$H$</em>{26}$N$<em>{4}$O$</em>{2}$ (474)</td>
<td>4 2.5 3.5</td>
<td>64 78 90</td>
</tr>
<tr>
<td>4</td>
<td>3'-(4-Bromophenyl)-5-(2-methoxynaphthalen-1-yl)-1'-phenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazole (4.23 d)</td>
<td>170</td>
<td>C$<em>{29}$H$</em>{23}$BrN$_{4}$O (522)</td>
<td>5 3 4</td>
<td>62 74 86</td>
</tr>
<tr>
<td>5</td>
<td>5-(2-Methoxynaphthalen-1-yl)-3'-(4-nitrophenyl)-1'-phenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazole (4.23 e)</td>
<td>146</td>
<td>C$<em>{29}$H$</em>{23}$N$<em>{5}$O$</em>{3}$ (489)</td>
<td>5 3 4</td>
<td>60 72 84</td>
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<td>6</td>
<td>5-(2-Methoxynaphthalen-1-yl)-1'-phenyl-3'-(thiophen-2-yl)-3,4-</td>
<td>122</td>
<td>C$<em>{27}$H$</em>{22}$N$_{4}$OS (450)</td>
<td>4 2.5 3</td>
<td>66 76 90</td>
</tr>
<tr>
<td></td>
<td>Formula</td>
<td>Mass (Da)</td>
<td>Rf</td>
<td>Yield</td>
<td>M.p. (°C)</td>
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<tr>
<td>7</td>
<td>5-(2-Methoxynaphthalen-1-yl)-1',2,3'-triphenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazole (4.23 g)</td>
<td>126</td>
<td>C\textsubscript{35}H\textsubscript{28}N\textsubscript{4}O (520)</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>8</td>
<td>5-(2-Methoxynaphthalen-1-yl)-1',2-diphenyl-3'-3-(p-tolyl)-3,4-dihydro-1'H,2H-3,4'-bipyrazole (4.23 h)</td>
<td>140</td>
<td>C\textsubscript{36}H\textsubscript{30}N\textsubscript{4}O (534)</td>
<td>4.5</td>
<td>2.5</td>
</tr>
<tr>
<td>9</td>
<td>5-(1-Methoxynaphthalen-1-yl)-3'-3-(4-methoxyphenyl)-1',2-diphenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazole (4.23 i)</td>
<td>137</td>
<td>C\textsubscript{36}H\textsubscript{30}N\textsubscript{4}O\textsubscript{2} (550)</td>
<td>4.5</td>
<td>2.5</td>
</tr>
<tr>
<td>10</td>
<td>3'-3-(4-Bromophenyl)-5-(1-methoxynaphthalen-1-yl)-1',2-diphenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazole (4.23 j)</td>
<td>125</td>
<td>C\textsubscript{35}H\textsubscript{27}BrN\textsubscript{4}O (598)</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>11</td>
<td>5-(2-Methoxynaphthalen-1-yl)-3'-3-(4-nitrophenyl)-1',2-diphenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazole (4.23 k)</td>
<td>156</td>
<td>C\textsubscript{35}H\textsubscript{27}N\textsubscript{3}O\textsubscript{3} (565)</td>
<td>5</td>
<td>3</td>
</tr>
</tbody>
</table>
The IR (KBr, cm\(^{-1}\)) spectrum of (Fig-4.5) (4.23 a) showed characteristic peaks at 1597 cm\(^{-1}\) (C=N of pyrazoline), 1623 (C=C), 3297 (N-H). \(^1\)H-NMR (CDCl\(_3\), 400 MHz) spectrum of (Fig-4.6) (4.23 a) showed a singlet at \(\delta\) 3.97 integrating for three protons were assigned to methoxy group protons. Three doublets of doublets showed between \(\delta\) 3.25-3.31, 3.44-3.51 and 5.19-5.24 integrating for three protons each were assigned to pyrazoline ABX pattern groups with coupling constants CH\(_2\) (\(J=7.4\) Hz, 16.6 Hz), (\(J=10\) Hz, 16.8 Hz) and CH (\(J=7.2\) Hz, 9.6 Hz) respectively. A broad singlet appeared at 6.05 integrating for one proton was assigned to N-H proton. Two phenyl and naphthyl ring protons were appeared range \(\delta\) 7.30-8.15 integrating for fifteen protons respectively. A singlet at \(\delta\) 8.33 integrating for one proton was assigned to pyrazol ring proton. \(^1\)C-NMR (CDCl\(_3\), 100 MHz) spectrum (Fig-4.7) (4.23 a) showed characteristic peaks at \(\delta\) 44.4 (CH\(_2\)), 55.5 (N-CH), 56.4 (O-CH\(_3\)), 112.8, 116.4, 118.9, 123.5, 123.9, 124.7, 126.2, 126.4, 127.2, 128.0, 128.1, 128.2, 128.7, 129.2, 129.4, 130.6, 132.9, 133.1, 140.0, 151.1, 155.4. In the mass spectrum (Fig-4.8) of (4.23 a) the [M+H]\(^+\) peak observed at 445 (100%).
Mechanism:

\[
\begin{align*}
&\text{Ar} - \text{HN} - \text{NH}_2 + \text{O} \\
&\rightarrow \text{Ar} - \text{HN} - \text{N} - \text{H} \\
&\rightarrow \text{Ar} - \text{HN} - \text{N} \\
&\rightarrow \text{Ar} - \text{N} - \text{N} \\
&\text{R} = \text{H} \text{ and Ph}
\end{align*}
\]

Conclusion:

In Conclusion, we have successfully synthesized new series of 3'-Aryl-5-(1-methoxynaphthalen-2-yl)-1'-phenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazoles (4.22 a-g), 3'-Aryl-5-(1-methoxynaphthalen-2-yl)-1',2-diphenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazoles (4.22 h-m), 3'-Aryl-5-(2-methoxynaphthalen-1-yl)-1'-phenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazoles (4.23 a-f) and 3'-Aryl-5-(2-methoxynaphthalen-1-yl)-1',2-diphenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazoles (4.23 g-k) under conventional, ultrasound and microwave irradiation methods. The ultrasound and microwave irradiation procedure is more convenient, can be carried out in shorter reaction time, mild reaction conditions and higher yields.
Experimental:

Section-A: Synthesis of 3'-Aryl-5-(1-methoxynaphthalen-2-yl)-1'-phenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazoles and 3'-Aryl-5-(1-methoxynaphthalen-2-yl)-1',2-diphenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazoles.

Synthesis of 3'-Aryl-5-(1-methoxynaphthalen-2-yl)-1'-phenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazoles and 3'-Aryl-5-(1-methoxynaphthalen-2-yl)-1',2-diphenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazoles involve three steps

1) Synthesis of 1-(1-Methoxynaphthalen-2-yl)ethanone
2) Synthesis of 3-Aryl-1-phenyl-1H-pyrazole-4-carbaldehydes
3) Synthesis of 3'-Aryl-5-(1-methoxynaphthalen-2-yl)-1'-phenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazoles and synthesis of 3'-Aryl-5-(1-methoxynaphthalen-2-yl)-1',2-diphenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazoles

1) Synthesis of 1-(1-Methoxynaphthalen-2-yl)ethanone (4.25)

A mixture of 1-(1-Hydroxynaphthalen-2-yl)ethanone (0.372 gm, 2 mmol) (4.24) and dimethyl sulfate (0.252 gm, 2 mmol) in DMF (10 ml) was stirred at room temperature for 6 hr. Progress of the reaction was monitored by TLC, after completion of the reaction, the reaction mixture was poured in ice cold water. The solid separated was filtered, washed with water, dried and purified by column chromatography using silica-gel (petroleum ether:ethyl acetate, 10:1, v/v) to yield the pure 1-(1-methoxynaphthalen-2-yl)ethanone (4.25).

M.P. 48-50 °C (Lit. M.P. 49-50 °C)^63

2) Synthesis of 3-Aryl-1-phenyl-1H-pyrazole-4-carbaldehyde (4.26 a-g) (already discussed in section-A, chapter-II)

3) Synthesis of 3'-Aryl-5-(1-methoxynaphthalen-2-yl)-1'-phenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazoles (4.22 a-g) and 3'-Aryl-5-(1-methoxynaphthalen-2-yl)-1',2-diphenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazoles (4.22 h-m)
Synthesis of 5-(1-Methoxynaphthalen-2-yl)-1',2-diphenyl-3'-{(p-tolyl)-3,4-dihydro-1'H,2'H-3,4'-bipyrazole (4.22 i) under conventional heating, microwave and ultrasound irradiation method.

Conventional heating method:
A solution of KOH (0.24 gm, 6 mmol) in ethanol (15 ml) was taken in a round-bottom flask, a mixture of 1-(1-Methoxynaphthalen-2-yl)ethanone (4.25) (0.2 gm, 1 mmol) and 1-phenyl-3-(p-tolyl)-1H-pyrazole-4-carbaldehyde (4.26 b) (0.262 gm, 1 mmol) was added to the above solution, and refluxed until the starting materials have completely disappeared, then phenylhydrazine hydrochloride (0.173 gm, 1.2 mmol) is added and reflux continued for 4.5 hr. Progress of the reaction was monitored by TLC, after completion of the reaction, product was extracted with ethyl acetate (2 X 20 ml). The solvent was removed under reduced pressure and the crude solid was purified by column chromatography using silica-gel (petroleum ether:ethyl acetate, 8:2, v/v) to yield 5-(1-Methoxynaphthalen-2-yl)-1',2-diphenyl-3'-(p-tolyl)-3,4-dihydro-1'H,2'H-3,4'-bipyrazole (4.22 i).

Ultrasonic irradiation method:
A solution of KOH (0.24 gm, 6 mmol) in ethanol (15 ml) was taken in a conical flask, a mixture of 1-(1-Methoxynaphthalen-2-yl)ethanone (4.25) (0.2 gm, 1 mmol) and 1-phenyl-3-(p-tolyl)-1H-pyrazole-4-carbaldehyde (4.26 b) (0.262 gm, 1 mmol) was added to the above solution, and irradiated under ultrasound until the starting materials have completely disappeared, then phenylhydrazine hydrochloride (0.173 gm, 1.2 mmol) is added and irradiation continued for 3 hr at 60 °C. Progress of the reaction was monitored by TLC, after completion of the reaction, product was extracted with ethyl acetate (2 X 20 ml). The solvent was removed under reduced pressure and the crude solid was purified by column chromatography using silica-gel (petroleum ether:ethyl acetate, 8:2, v/v) to yield 5-(1-Methoxynaphthalen-2-yl)-1',2-diphenyl-3'-(p-tolyl)-3,4-dihydro-1'H,2'H-3,4'-bipyrazole (4.22 i).

Microwave irradiation method:
A solution of KOH (0.24 gm, 6 mmol) in ethanol (15 ml) was taken in a conical flask, a mixture of 1-(1-Methoxynaphthalen-2-yl)ethanone (4.25) (0.2 gm, 1 mmol) and 1-phenyl-3-(p-
tolyl)-1H-pyrazole-4-carbaldehyde (4.26 b) (0.262 gm, 1 mmol) was added to the above solution, and irradiated under microwave until the starting materials have completely disappeared, then phenylhydrazine hydrochloride (0.173 gm, 1.2 mmol) is added and irradiation continued for 4 min at 160 watts with 30 sec interval. Progress of the reaction was monitored by TLC, after completion of the reaction, product was extracted with ethyl acetate (2 X 20 ml). The solvent was removed under reduced pressure and the crude solid was purified by column chromatography using silica-gel (petroleum ether:ethyl acetate, 8:2, v/v) to yield 5-(1-Methoxynaphthalen-2-yl)-1',2-diphenyl-3'-(p-tolyl)-3,4-dihydro-1'H,2H-3,4'-bipyrazole (4.22 i).

a) Synthesis of 5-(1-Methoxynaphthalen-2-yl)-1',3'-diphenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazole (4.22 a)

Conventional heating method:
Yield: 63%

Ultrasound irradiation method:
Yield: 71%

Microwave irradiation method:
Yield: 84%

IR (KBr): ν 3297 (N-H), 3051 (C-H), 1623 (C=C), 1597 (C=N) cm⁻¹; ¹H-NMR (CDCl₃, 400 MHz): δ 8.33 (s, 1H, pyrazole proton), 8.13-8.15 (d, 1H, ArH), 8.02-8.04 (d, 2H, ArH), 7.88-7.90 (d, 1H, ArH), 7.77-7.81 (m, 4H, ArH), 7.30-7.49 (m, 8H, ArH), 6.05 (bs, 1H, NH), 5.19-5.24 (dd, 1H, CH₂, J=7.2 Hz, 10 Hz), 3.96 (s, 3H, O-CH₃), 3.44-3.51 (dd, 1H, CH₂, J=9.6 Hz, 16.4 Hz), 3.25-3.31 (dd, 1H, CH₂, J=7.2 Hz, 16.4 Hz); ¹³C-NMR (CDCl₃, 100 MHz): δ 155.4, 151.1, 140.0, 133.1, 132.9, 130.6, 129.4, 129.2, 128.7, 128.2, 128.1, 128.0, 127.2, 126.4, 126.2, 124.7, 123.9, 123.5, 118.9, 116.4, 112.8, 56.4 (O-CH₃), 55.5 (N-CH), 44.4; MS: m/z = 445 [M+H]+ (100%). Anal. Calcd for C₂⁹H₂₄N₄O: C, 78.36, H, 5.44, N, 12.60. Found: C, 78.42, H, 5.40, N, 12.53.
b) Synthesis of 5-(1-Methoxynaphthalen-2-yl)-1'-phenyl-3'-(p-tolyl)-3,4-dihydro-1'H,2H-3,4'-bipyrazole (4.22 b)

Conventional heating method:
Yield: 66%

Ultrasound irradiation method:
Yield: 74%

Microwave irradiation method:
Yield: 88%

IR (KBr): 3332 (N-H), 3052 (C-H), 1621 (C=C), 1598 (C=N) cm$^{-1}$; $^1$H-NMR (CDCl$_3$, 400 MHz): $\delta$ 8.31 (s, 1H, pyrazole proton), 8.12-8.14 (d, 1H, ArH), 7.88-7.91 (d, 1H, ArH), 7.76-7.81 (m, 3H, ArH), 7.65-7.67 (d, 2H, ArH), 7.44-7.49 (m, 3H, ArH), 7.27-7.39 (m, 5H, ArH), 6.05 (bs, 1H, NH), 5.49-5.53 (dd, 1H, CH$_2$, $J$=7.2 Hz, 9.6 Hz), 3.96 (s, 3H, O-CH$_3$), 3.43-3.50 (dd, 1H, CH$_2$, $J$=9.6 Hz, 16.4 Hz), 3.24-3.30 (dd, 1H, CH$_2$, $J$=7.2 Hz, 16.4 Hz), 2.45 (s, 3H, CH$_3$); $^{13}$C-NMR (CDCl$_3$, 100 MHz): $\delta$ 155.4, 151.2, 140.1, 137.9, 132.9, 130.6, 130.2, 129.4, 129.2, 128.7, 128.2, 128.1, 128.0, 127.2, 126.3, 126.1, 124.7, 123.9, 123.4, 118.9, 116.5, 112.8, 56.4 (O-CH$_3$), 55.5 (N-CH), 44.4, 21.3 (CH$_3$); MS: $m/z$ = 459 [M+H]$^+$ (100%); Anal. Calcd for C$_{30}$H$_{26}$N$_4$O: C, 78.58, H, 5.72, N, 12.22. Found: C, 78.54, H, 5.78, N, 12.28.

c) Synthesis of 5-(1-Methoxynaphthalen-2-yl)-3'-(4-methoxyphenyl)-1'-phenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazole (4.22 c)

Conventional heating method:
Yield: 65%

Ultrasound irradiation method:
Yield: 73%

Microwave irradiation method:
Yield: 90%
IR (KBr): 3332 (N-H), 3053 (C-H), 1614 (C=C), 1597 (C=N) cm\(^{-1}\); \(^1\)H-NMR (CDCl\(_3\), 400 MHz): \(\delta\) 8.26 (s, 1H, pyrazole proton), 8.08-8.10 (d, 1H, ArH), 7.87-7.90 (d, 1H, ArH), 7.78-7.82 (dd, 2H, ArH), 7.72-7.74 (d, 2H, ArH), 7.54-7.56 (d, 2H, ArH), 7.28-7.50 (m, 5H, ArH), 6.84-6.86 (d, 2H, ArH), 6.05 (bs, 1H, NH), 5.49-5.53 (dd, 1H, CH\(_2\), \(J=7.2\) Hz, 9.6 Hz), 3.96 (s, 3H, O-CH\(_3\)), 3.84 (s, 3H, O-CH\(_3\)), 3.43-3.50 (dd, 1H, CH\(_2\), \(J=9.8\) Hz, 16.8 Hz), 3.25-3.31 (dd, 1H, CH\(_2\), \(J=6.8\) Hz, 16.4 Hz); \(^1^3\)C-NMR (CDCl\(_3\), 100 MHz): \(\delta\) 156.6, 155.4, 152.3, 151.4, 139.9, 132.8, 130.6, 130.2, 129.6, 129.4, 129.1, 128.8, 128.0, 127.3, 126.5, 126.3, 124.7, 124.0, 123.9, 123.5, 122.8, 119.0, 115.9, 112.8, 56.4 (O-CH\(_3\)), 55.3 (N-CH), 44.3, 21.3 (CH\(_3\)) ; MS: \(m/z = 475\) [M+H]\(^+\) (100%); Anal. Calcd for C\(_{30}\)H\(_{26}\)N\(_4\)O\(_2\): C, 75.93, H, 5.52, N, 11.81. Found: C, 75.86, H, 5.58, N, 11.78.

d) Synthesis of 3’-(4-Chlorophenyl)-5-(1-methoxynaphthalen-2-yl)-1’-phenyl-3,4-dihydro-1’H,2H-3,4’-bipyrazole (4.22 d)

Conventional heating method:
Yield: 62%

Ultrasound irradiation method:
Yield: 70%

Microwave irradiation method:
Yield: 82%

IR (KBr): 3335 (N-H), 3054 (C-H), 1622 (C=C), 1599 (C=N) cm\(^{-1}\); \(^1\)H-NMR (CDCl\(_3\), 400 MHz): \(\delta\) 8.31 (s, 1H, pyrazole proton), 8.11-8.13 (d, 1H, ArH), 7.88-7.90 (d, 1H, ArH), 7.79-7.81 (d, 2H, ArH), 7.72-7.77 (m, 4H, ArH), 7.45-7.49 (d, 3H, ArH), 7.34-7.39 (m, 2H, ArH), 7.29-7.33 (m, 2H, ArH), 6.05 (bs, 1H, NH), 5.16-5.21 (dd, 1H, CH\(_2\), \(J=6.8\) Hz, 10.4 Hz), 3.96 (s, 3H, O-CH\(_3\)), 3.43-3.49 (dd, 1H, CH\(_2\), \(J=10\) Hz, 16.4 Hz), 3.22-3.28 (dd, 1H, CH\(_2\), \(J=6.8\) Hz, 16.2 Hz); \(^1^3\)C-NMR (CDCl\(_3\), 100 MHz): \(\delta\) 155.4, 151.2, 149.9, 139.9, 134.1, 132.9, 131.7, 130.7, 129.5, 129.4, 129.1, 128.9, 128.0, 127.3, 126.6, 126.5, 124.6, 123.9, 123.4, 118.9, 116.2, 112.8,
56.4 (O-CH₃), 55.4 (N-CH), 44.4; MS: m/z = 479 [M+H]⁺ (100%); Anal. Calcd for C₂₉H₂₃ClN₄O: C, 72.72, H, 4.84, N, 11.70. Found: C, 72.64, H, 4.91, N, 11.65.

e) **Synthesis of 3’-(4-Bromophenyl)-5-(1-methoxynaphthalen-2-yl)-1’-phenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazole (4.22 e)**

Conventional heating method:
Yield: 65%

Ultrasound irradiation method:
Yield: 72%

Microwave irradiation method:
Yield: 86%

IR (KBr): 3309 (N-H), 3049 (C-H), 1621 (C=C), 1598 (C=N) cm⁻¹; ¹H-NMR (CDCl₃, 400 MHz): δ 8.33 (s, 1H, pyrazole proton), 8.11-8.13 (d, 1H, ArH), 7.87-7.89 (d, 1H, ArH), 7.75-7.79 (m, 3H, ArH), 7.64-7.66 (d, 2H, ArH), 7.58-7.60 (d, 2H, ArH), 7.44-7.49 (m, 3H, ArH), 7.26-7.37 (m, 3H, ArH), 6.05 (bs, 1H, NH), 5.20-5.25 (dd, 1H, CH₂, J=6.8 Hz, 9.4 Hz), 3.93 (s, 3H, O-CH₃), 3.45-3.50 (dd, 1H, CH₂, J=9.6 Hz, 16.4 Hz), 3.23-3.29 (dd, 1H, CH₂, J=6.8 Hz, 16.6 Hz); ¹³C-NMR (CDCl₃, 100 MHz): δ 155.4, 151.2, 149.9, 139.9, 132.9, 132.1, 131.9, 130.7, 129.7, 129.5, 129.1, 128.9, 128.0, 127.3, 126.6, 126.5, 124.6, 123.9, 123.4, 122.3, 118.9, 116.2, 112.8, 56.4 (O-CH₃), 55.5 (N-CH), 44.4; MS: m/z = 523 [M+H]⁺ (100%); Anal. Calcd for C₂₉H₂₃BrN₄O: C, 66.54, H, 4.43, N, 10.70. Found: C, 66.48, H, 4.47, N, 10.75.

f) **Synthesis of 5-(1-Methoxynaphthalen-2-yl)-3’-(4-nitrophenyl)-1’-phenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazole (4.22 f)**

Conventional heating method:
Yield: 60%
Ultrasound irradiation method:
Yield: 70%

Microwave irradiation method:
Yield: 82%

IR (KBr): 3372 (N-H), 3049 (C-H), 1622 (C=C), 1599 (C=N) cm$^{-1}$; $^1$H-NMR (CDCl$_3$, 400 MHz): $\delta$ 8.33-8.37 (s, 3H, pyrazole proton & ArH), 8.12-8.14 (d, 1H, ArH), 8.01-8.05 (m, 2H, ArH), 7.89-7.91 (d, 1H, ArH), 7.78-7.82 (dd, 2H, ArH), 7.48-7.52 (m, 3H, ArH), 7.35-7.39 (m, 2H, ArH), 7.26-7.36 (m, 2H, ArH), 6.05 (bs, 1H, NH), 5.23-5.25 (dd, 1H, CH$_2$, $J$=8 Hz, 10 Hz), 3.96 (s, 3H, O-CH$_3$), 3.46-3.53 (dd, 1H, CH$_2$, $J$=10 Hz, 16.8 Hz), 3.22-3.28 (dd, 1H, CH$_2$, $J$=8 Hz, 16 Hz); $^{13}$C-NMR (CDCl$_3$, 100 MHz): $\delta$ 155.4, 151.4, 146.5, 140.2, 139.7, 132.9, 132.1, 130.5, 129.6, 129.6, 129.3, 129.2, 128.7, 128.1, 127.2, 126.1, 125.9, 124.7, 123.9, 118.7, 115.2, 112.8, 56.4 (O-CH$_3$), 55.5 (N-CH), 44.3; MS: $m/z$ = 490 [M+H]$^+$ (100%); Anal. Caled for C$_{29}$H$_{23}$N$_5$O$_3$: C, 71.15, H, 4.74, N, 14.31. Found: C, 71.08, H, 4.79, N, 14.28.

g) Synthesis of 5-(1-Methoxynaphthalen-2-yl)-1'-phenyl-3'-(thiophen-2-yl)-3,4-dihydro-1'H,2H-3,4'-bipyrazole (4.22 g)

Conventional heating method:
Yield: 65%

Ultrasound irradiation method:
Yield: 76%

Microwave irradiation method:
Yield: 92%

IR (KBr): $\nu$ 3319 (N-H), 3067 (C-H), 1621 (C=C), 1595 (C=N) cm$^{-1}$; $^1$H-NMR (CDCl$_3$, 400 MHz): $\delta$ 8.25 (s, 1H, pyrazole proton), 8.13-8.15 (d, 1H, ArH), 7.88-7.90 (d, 1H, ArH), 7.79-7.81 (d, 1H, ArH), 7.74-7.76 (d, 2H, ArH), 7.44-7.49 (m, 4H, ArH), 7.27-7.38 (m, 4H, ArH), 7.14-7.16 (dd, 1H, ArH), 6.05 (bs, 1H, NH), 5.49-5.53 (t, 1H, CH$_2$, $J$=7.2 Hz, 9.8 Hz), 3.94 (s, 3H, O-CH$_3$), 3.49-3.56 (dd, 1H, CH$_2$, $J$=10 Hz, 16.6 Hz), 3.24-3.30 (dd, 1H, CH$_2$, $J$=7.2 Hz, 16.6 Hz).
Hz); $^{13}$C-NMR (CDCl$_3$, 100 MHz): $\delta$ 155.5, 151.1, 145.4, 139.8, 135.3, 132.9, 130.7, 129.5, 129.2, 128.0, 127.7, 127.2, 126.6, 126.4, 125.6, 125.4, 124.7, 124.2, 123.9, 122.9, 118.9, 116.5, 112.8, 56.4 (O-CH$_3$), 55.5 (N-CH), 43.9; MS: $m/z$ = 451 [M+H]$^+$ (100%); Anal. Calcd for C$_{27}$H$_{22}$N$_4$OS: C, 71.98, H, 4.92, N, 12.44, S, 7.12. Found: C, 71.88, H, 4.96, N, 12.51, S, 7.08.

h) Synthesis of 5-(1-Methoxynaphthalen-2-yl)-1',2,3'-triphenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazole (4.22 h)

Conventional heating method:
Yield: 61%

Ultrasound irradiation method:
Yield: 72%

Microwave irradiation method:
Yield: 83%

IR (KBr): ν 3055 (C-H), 1623 (C=N), 1595 (C=C) cm$^{-1}$; $^1$H-NMR (CDCl$_3$, 400 MHz): $\delta$ 8.09-8.10 (d, 1H, ArH), 7.82-7.84 (dd, 2H, ArH), 7.82 (s, 1H, pyrazole proton), 7.72-7.73 (dd, 1H, ArH), 7.61-7.66 (m, 5H, ArH), 7.38-7.40 (m, 2H, ArH), 7.45-7.52 (m, 4H, ArH), 7.20-7.25 (m, 4H, ArH), 7.14-7.16 (d, 1H, ArH), 6.81-6.84 (t, 1H, ArH), 5.23-5.76 (dd, 1H, CH$_2$, $J$=6.8 Hz, 12 Hz), 4.06-4.14 (dd, 1H, CH$_2$, $J$=12 Hz, 17.4 Hz), 3.86 (s, 3H, OCH$_3$), 3.55-3.61 (dd, 1H, CH$_2$, $J$=6.8 Hz, 17.4 Hz); $^{13}$C-NMR (CDCl$_3$, 100 MHz): $\delta$ 154.6, 150.2, 146.2, 144.7, 139.8, 135.2, 133.2, 129.3, 129.0, 128.8, 128.4, 128.3, 128.1, 126.7, 126.5, 126.4, 126.3, 125.8, 124.7, 124.3, 123.0, 122.4, 121.9, 119.5, 118.9, 113.8, 63.0 (N-CH), 56.8 (O-CH$_3$), 45.4; MS: $m/z$ = 521 [M+H]$^+$ 100%; Anal. Calc. for C$_{35}$H$_{28}$N$_4$O: C, 80.74, H, 5.42, N, 10.76. Found: C, 80.70, H, 5.48, N, 10.71.

i) Synthesis of 5-(1-Methoxynaphthalen-2-yl)-1',2-diphenyl-3'-(p-tolyl)-3,4-dihydro-1'H,2H-3,4'-bipyrazole (4.22 i)

Conventional heating method:
Yield: 63%
Ultrasound irradiation method:
Yield: 74%

Microwave irradiation method:
Yield: 86%

IR (KBr): ν 3051 (C-H), 1620 (C=N), 1596 (C=C) cm⁻¹; ¹H-NMR (CDCl₃, 400 MHz): δ 8.24-8.26 (d, 1H, ArH), 7.98 (s, 1H, pyrazole proton), 7.78-7.91 (m, 1H, ArH), 7.68-7.75 (m, 2H, ArH), 7.43-7.51 (m, 3H, ArH), 7.38-7.40 (m, 4H, ArH), 7.28-7.37 (m, 3H, ArH), 7.16-7.22 (m, 2H, ArH), 7.12-7.18 (m, 3H, ArH), 6.78-6.82 (t, 1H, ArH), 5.51-5.56 (dd, 1H, CH, J=6.8 Hz, 11.8 Hz), 3.85-3.94 (m, 4H, OCH₃ & CH₂, J methoxy proton mixed with CH₂ proton), 3.36-3.42 (dd, 1H, CH₂, J=6.8 Hz, 17.2 Hz), 2.42 (s, 3H, CH₃); ¹³C-NMR (CDCl₃, 100 MHz): δ 155.8, 150.4, 146.9, 145.4, 139.9, 138.0, 132.8, 130.8, 130.4, 129.5, 129.3, 129.2, 128.9, 128.1, 127.9, 127.3, 126.4, 126.3, 124.7, 123.0, 119.3, 118.8, 115.9, 113.8, 112.9, 56.7 (N-CH), 56.4 (O-CH₃), 47.1, 21.3 (CH₃); MS: m/z = 535 [M+H]⁺ 100%; Anal. Calc. for C₃₆H₃₀N₄O: C, 80.87, H, 5.66, N, 10.48. Found: C, 80.82, H, 5.71, N, 10.42.

j) Synthesis of 5-(1-Methoxynaphthalen-2-yl)-3’-(4-methoxyphenyl)-1’,2-diphenyl-3,4-dihydro-1’H,2H-3,4’-bipyrazole (4.22 j)

Conventional heating method:
Yield: 64%

Ultrasound irradiation method:
Yield: 75%

Microwave irradiation method:
Yield: 86%

IR (KBr): ν 3051 (C-H), 1620 (C=N), 1595 (C=C) cm⁻¹; ¹H-NMR (CDCl₃, 400 MHz): δ 8.24-8.26 (d, 1H, ArH), 7.98 (s, 1H, pyrazole proton), 7.81-7.88 (m, 4H, ArH), 7.64-7.69 (m, 4H, ArH), 7.59-7.61 (d, 2H, ArH), 7.50-7.57 (m, 3H, ArH), 7.37-7.41 (m, 2H, ArH), 7.21-7.26 (m,
2H, ArH), 6.94-6.96 (d, 2H, ArH), 5.79-5.84 (dd, 1H, CH, \(J=6.8 \text{ Hz}, 11.8 \text{ Hz}\)), 3.88 (s, 3H, OCH\(_3\)), 3.84 (s, 3H, OCH\(_3\)), 3.74-3.82 (dd, 1H, CH, \(J=6.8 \text{ Hz}, 11.8 \text{ Hz}\)), 3.34-3.45 (dd, 1H, CH, \(J=6.8 \text{ Hz}, 17.2 \text{ Hz}\)); \(^{13}\)C-NMR (CDCl\(_3\), 100 MHz): \(\delta\) 155.6, 149.7, 147.0, 145.5, 140.2, 132.8, 132.5, 131.4, 130.5, 129.0, 127.5, 127.0, 126.6, 124.8, 124.4, 124.1, 123.5, 119.7, 119.5, 118.8, 114.2, 113.8, 112.3, 56.7 (N-CH), 56.4 (O-CH\(_3\)), 55.3; MS: \(m/z = 551 \ [M+H]^+\) 100%; Anal. Calc. for C\(_{36}\)H\(_{30}\)N\(_4\)O\(_2\): C, 78.52, H, 5.49, N, 10.17. Found: C, 78.57, H, 5.55, N, 10.14.

\(k\) Synthesis of 3'- (4-Bromophenyl)-5-(1-methoxynaphthalen-2-yl)-1',2-diphenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazole (4.22 \(k\))

Conventional heating method:
 Yield: 60%

Ultrasound irradiation method:
 Yield: 72%

Microwave irradiation method:
 Yield: 84%

IR (KBr): \(\nu\) 3052 (C-H), 1623 (C=N), 1596 (C=C) cm\(^{-1}\); \(^1\)H-NMR (CDCl\(_3\), 400 MHz): \(\delta\) 8.07-8.09 (d, 1H, ArH), 7.96-7.98 (m, 2H, pyrazole proton & ArH), 7.70-7.72 (d, 2H, ArH), 7.58-7.65 (m, 4H, ArH), 7.47-7.53 (m, 2H, ArH), 7.36-7.40 (m, 2H, ArH), 7.20-7.25 (m, 2H, ArH), 7.16-7.15 (m, 3H, ArH), 7.12-7.18 (m, 2H, ArH), 6.81-6.85 (t, 1H, ArH), 5.49-5.53 (dd, 1H, CH, \(J=6.8 \text{ Hz}, 12 \text{ Hz}\)), 4.05-4.13 (dd, 1H, CH, \(J=12 \text{ Hz}, 17 \text{ Hz}\)), 3.86 (s, 3H, O-CH\(_3\)), 3.51-3.58 (dd, 1H, CH, \(J=7.2 \text{ Hz}, 17.2 \text{ Hz}\)); \(^{13}\)C-NMR (CDCl\(_3\), 100 MHz): \(\delta\) 154.3, 148.9, 146.2, 144.6, 139.6, 135.2, 132.1, 132.1, 129.5, 129.4, 129.0, 128.4, 128.0, 127.9, 126.8, 126.7, 126.6, 126.4, 125.7, 124.3, 123.0, 122.5, 122.4, 121.7, 119.6, 118.9, 113.7, 62.9 (N-CH), 56.7 (O-CH\(_3\)), 45.3; ms: \(m/z = 599 \ [M+H]^+\) 100%; Anal. Calc. for C\(_{35}\)H\(_{27}\)BrN\(_4\)O: C, 70.12, H, 4.54, N, 9.35. Found: C, 70.17, H, 4.58, N, 9.30.

\(l\) Synthesis of 5-(1-Methoxynaphthalen-2-yl)-3'- (4-nitrophenyl)-1',2-diphenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazole (4.22 \(l\))
Conventional heating method:
Yield: 62%

Ultrasound irradiation method:
Yield: 70%

Microwave irradiation method:
Yield: 82%

IR (KBr): ν 3048 (C-H), 1623 (C=N), 1597 (C=C) cm⁻¹. ¹H-NMR (CDCl₃, 400 MHz): δ 8.35-8.38 (d, 2H, ArH), 8.02-8.10 (m, 4H, ArH), 7.86 (s, 1H, pyrazol proton), 7.83-7.85 (dd, 1H, ArH), 7.65-7.68 (dd, 2H, ArH), 7.62-7.64 (d, 1H, ArH), 7.50-7.54 (m, 2H, ArH), 7.40-7.44 (m, 2H, ArH), 7.28-7.30 (d, 1H, ArH), 7.21-7.26 (m, 2H, ArH), 7.13-7.15 (dd, 2H, ArH), 6.84-6.87 (t, 1H, ArH), 5.55-5.60 (dd, 1H, CH₂, J=6.8 Hz, 11.6 Hz), 4.12-4.19 (dd, 1H, CH₂, J=12 Hz, 17 Hz), 3.87 (s, 3H, O-CH₃), 3.53-3.59 (dd, 1H, CH₂, J=6.8 Hz, 17.2 Hz); ¹³C-NMR (CDCl₃, 100 MHz): δ 156.7, 148.2, 147.8, 142.5, 13 9.6, 138.2, 133.9, 129.9, 129.7, 129.5, 128.9, 128.3, 128.2, 128.1, 127.8, 127.2, 127.1, 126.9, 126.8, 125.9, 124.6, 124.3, 124.0, 122.9, 119.6, 119.3, 64.1 (N-CH), 56.7 (O-CH₃), 45.3; MS: m/z = 566 [M+H]⁺ 100%.


m) Synthesis of 5-(1-Methoxynaphthalen-2-yl)-1',2-diphenyl-3'-(thiophen-2-yl)-3,4-dihydro-1'H,2H-3,4'-bipyrazole (4.22 m)

Conventional heating method:
Yield: 64%

Ultrasound irradiation method:
Yield: 76%

Microwave irradiation method:
Yield: 90%
IR (KBr): v 3051 (C-H), 1623 (C=N), 1596 (C=C) cm⁻¹; ¹H-NMR (CDCl₃, 400 MHz): δ 8.29-8.31 (d, 1H, ArH), 8.19-8.22 (d, 1H, ArH), 8.09-8.11 (d, 2H, ArH), 7.88 (s, 1H, pyrazole proton), 7.84-7.86 (dd, 1H, ArH), 7.65-7.68 (dd, 2H, ArH), 7.62-7.64 (d, 1H, ArH), 7.44-7.49 (m, 2H, ArH), 7.35-7.41 (m, 2H, ArH), 7.28-7.32 (m, 2H, ArH), 7.22-7.25 (dd, 1H, ArH), 7.17-7.19 (dd, 1H, ArH), 7.14-7.17 (dd, 2H, ArH), 6.82-6.85 (t, 1H, ArH), 5.60-5.65 (dd, 1H, CH₂, J=6.8 Hz, 11.8 Hz), 4.13-4.20 (dd, 1H, CH₂, J=12 Hz, 17.4 Hz), 3.87 (s, 3H, O-CH₃), 3.55-3.61 (dd, 1H, CH₂, J=6.8 Hz, 17.6 Hz); ¹³C-NMR (CDCl₃, 100 MHz): δ 154.9, 148.9, 146.6, 144.2, 139.6, 134.3, 129.9, 129.5, 128.9, 128.1, 127.8, 127.5, 127.1, 126.9, 126.8, 126.3, 125.8, 125.3, 124.5, 124.3, 123.5, 122.8, 120.3, 119.6, 117.3, 113.2, 62.9 (N-CH), 56.7 (O-CH₃)), 45.0; MS: m/z = 527 [M+H]⁺ 100%; Anal. Calc. for C₃₃H₂₆N₄O: C, 75.26, H, 4.98, N, 10.64, S, 6.09. Found: C, 75.20, H, 4.92, N, 10.69, S, 6.12.

Section-B: Synthesis of 3'-Aryl-5-(2-methoxynaphthalen-1-yl)-1'-phenyl-3,4-dihydro-1'H,2'H-3,4'-bipyrazoles and 3'-Aryl-5-(2-methoxynaphthalen-1-yl)-1',2-diphenyl-3,4-dihydro-1'H,2'H-3,4'-bipyrazoles.

Synthesis of 3'-Aryl-5-(2-methoxynaphthalen-1-yl)-1'-phenyl-3,4-dihydro-1'H,2'H-3,4'-bipyrazoles and 3'-Aryl-5-(2-methoxynaphthalen-1-yl)-1',2-diphenyl-3,4-dihydro-1'H,2'H-3,4'-bipyrazoles involve three steps

1) Synthesis of 1-(2-Methoxynaphthalen-1-yl)ethanone
2) Synthesis of 3-Aryl-1-phenyl-1H-pyrazole-4-carbaldehydes
3) Synthesis of 3'-Aryl-5-(2-methoxynaphthalen-1-yl)-1'-phenyl-3,4-dihydro-1'H,2'H-3,4'-bipyrazoles and 3'-Aryl-5-(2-methoxynaphthalen-1-yl)-1',2-diphenyl-3,4-dihydro-1'H,2'H-3,4'-bipyrazoles

1) Synthesis of 1-(2-Methoxynaphthalen-1-yl)ethanone (4.28)

A mixture of 1-(2-Hydroxynaphthalen-1-yl)ethanone (4.27) (0.372 gm, 2 mmol) and dimethyl sulfate (0.252 gm, 2 mmol) in DMF (10 ml) was stirred at room temperature for 6 hr. Progress of the reaction was monitored by TLC, after completion of the reaction, the reaction mixture was poured in ice cold water. The solid separated was filtered, washed with water, dried...
and purified by column chromatography using silica-gel (petroleum ether:ethyl acetate, 10: 1, v/v) to yield the pure 1-(2-methoxynaphthalen-1-yl)ethanone (4.28).

M.P. 56-58 °C (Lit. M.P. 57-58 °C)\(^6^4\)

2) *Synthesis of 3-Aryl-1-phenyl-1\(H\)-pyrazole-4-carbaldehyde* (already discussed in section-A, chapter-II)

3) *Synthesis of 3'-Aryl-5-(2-methoxynaphthalen-1-yl)-1'-phenyl-3,4-dihydro-1'\(H,2H\)-3,4'-bipyrazoles and 3'-Aryl-5-(2-methoxynaphthalen-1-yl)-1',2-diphenyl-3,4-dihydro-1'\(H,2H\)-3,4'-bipyrazoles*

   *Synthesis of 5-(2-Methoxynaphthalen-1-yl)-1',3'-diphenyl-3,4-dihydro-1'\(H,2H\)-3,4'-bipyrazole (4.23 a) under conventional heating, microwave and ultrasound irradiation method.*

**Conventional heating method:**

A solution of KOH (0.24 gm, 6 mmol) in ethanol (15 ml) was taken in a round-bottom flask, a mixture of 1-(2-Methoxynaphthalen-1-yl)ethanone (4.28) (0.2 gm, 1 mmol) and 1,3-diphenyl-1\(H\)-pyrazole-4-carbaldehyde (4.26 a) (0.25 gm, 1 mmol) was added to the above solution, and refluxed until the starting materials had completely disappeared, then hydrazine hydrate (0.060 gm, 1.2 mmol) is added and reflux continued for 4.5 hr. Progress of the reaction was monitored by TLC, after completion of the reaction, product was extracted with ethyl acetate (2 X 20 ml). The solvent was removed under reduced pressure and the crude solid was purified by column chromatography using silica-gel (petroleum ether:ethyl acetate, 8:2, v/v) to yield 5-(2-Methoxynaphthalen-1-yl)-1',3'-diphenyl-3,4-dihydro-1'\(H,2H\)-3,4'-bipyrazole (4.23 a).

**Ultrasonic irradiation method:**

A solution of KOH (0.24 gm, 6 mmol) in ethanol (15 ml) was taken in a conical flask, a mixture of 1-(2-Methoxynaphthalen-1-yl)ethanone (4.28) (0.2 gm, 1 mmol) and 1,3-diphenyl-1\(H\)-pyrazole-4-carbaldehyde (4.26 a) (0.25 gm, 1 mmol) was added to the above solution, and
irradiated under ultrasound until the starting materials had completely disappeared, then hydrazine hydrate (0.060 gm, 1.2 mmol) is added and irradiation continued for 3 hr at 60 °C. Progress of the reaction was monitored by TLC, after completion of the reaction, product was extracted with ethyl acetate (2 X 20 ml). The solvent was removed under reduced pressure and the crude solid was purified by column chromatography using silica-gel (petroleum ether:ethyl acetate, 8:2, v/v) to yield 5-(2-Methoxynaphthalen-1-yl)-1',3'-diphenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazole (4.23 a).

**Microwave irradiation method:**

A solution of KOH (0.24 gm, 6 mmol) in ethanol (15 ml) was taken in a conical flask, a mixture of 1-(2-Methoxynaphthalen-1-yl)ethanone (4.28) (0.2 gm, 1 mmol) and 1,3-diphenyl-1H-pyrazole-4-carbaldehyde (4.26 a) (0.25 gm, 1 mmol) was added to the above solution, and irradiated under microwave until the starting materials had completely disappeared, then hydrazine hydrate (0.060 gm, 1.2 mmol) is added and irradiation continued for 3.5 min at 160 watts with 30 sec interval. Progress of the reaction was monitored by TLC, after completion of the reaction, product was extracted with ethyl acetate (2 X 20 ml). The solvent was removed under reduced pressure and the crude solid was purified by column chromatography using silica-gel (petroleum ether:ethyl acetate, 8:2, v/v) to yield 5-(2-Methoxynaphthalen-1-yl)-1',3'-diphenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazole (4.23 a).

**a) Synthesis of 5-(2-Methoxynaphthalen-1-yl)-1',3'-diphenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazole (4.23 a)**

**Conventional heating method:**

Yield: 60%

**Ultrasound irradiation method:**

Yield: 72%

**Microwave irradiation method:**

Yield: 84%
IR (KBr): \(\nu\) 3330 (N-H), 3055 (C-H), 1621 (C=C), 1598 (C=N) cm\(^{-1}\); \(^1\)H-NMR (CDCl\(_3\), 400 MHz): \(\delta\) 8.09-8.11 (d, 1H, ArH), 8.09 (s, 1H, pyrazole proton), 7.92-7.94 (d, 1H, ArH), 7.82-7.84 (dd, 2H, ArH), 7.72-7.79 (m, 2H, ArH), 7.60-7.62 (m, 2H, ArH), 7.37-7.54 (m, 6H, ArH), 7.29-7.33 (m, 2H, ArH), 6.05 (bs, 1H, NH), 5.14-5.20 (dd, 1H, CH\(_2\), \(J=7.2\) Hz, 9.6 Hz), 3.87 (s, 3H, O-CH\(_3\)), 3.72-3.79 (dd, 1H, CH\(_2\), \(J=10\) Hz, 16.8 Hz), 3.34-3.40 (dd, 1H, CH\(_2\), \(J=7.4\) Hz, 16.6 Hz); \(^13\)C-NMR (CDCl\(_3\), 100 MHz): \(\delta\) 155.4, 151.1, 140.0, 132.9, 133.1, 130.6, 129.4, 129.2, 128.7, 128.2, 128.1, 128.0, 127.2, 126.4, 126.2, 124.7, 123.9, 123.5, 118.9, 116.4, 112.8, 56.4 (O-CH\(_3\)), 55.5 (N-CH), 44.4; MS: m/z = 445 [M+H]\(^+\) (100%); Anal. Calcd for C\(_{29}\)H\(_{24}\)N\(_4\)O: C, 78.36, H, 5.44, N, 12.60. Found: C, 78.42, H, 5.40, N, 12.53.

b) *Synthesis of* 5-(2-Methoxynaphthalen-1-yl)-1'-phenyl-3'-(p-tolyl)-3,4-dihydro-1'H,2H-3,4'-bipyrazole *(4.23 b)*

**Conventional heating method:**

Yield: 63%

**Ultrasound irradiation method:**

Yield: 75%

**Microwave irradiation method:**

Yield: 88%

IR (KBr): \(\nu\) 3339 (N-H), 3052 (C-H), 1621 (C=C), 1596 (C=N) cm\(^{-1}\); \(^1\)H-NMR (CDCl\(_3\), 400 MHz): \(\delta\) 8.11-8.14 (d, 1H, ArH), 8.05 (s, 1H, pyrazole proton), 7.82-7.92 (m, 2H, ArH), 7.59-7.76 (m, 3H, ArH), 7.30-7.49 (m, 6H, ArH), 7.14-7.16 (d, 2H, ArH), 7.07-7.09 (d, 1H, ArH), 6.05 (bs, 1H, NH), 5.15-5.22 (dd, 1H, CH\(_2\), \(J=7.2\) Hz, 9.6 Hz), 3.80-3.87 (m, 4H, CH\(_2\) & OCH\(_3\)), 3.35-3.45 (dd, 1H, CH\(_2\), \(J=9.4\) Hz, 16.8 Hz), 2.34 (s, 3H, CH\(_3\)); \(^13\)C-NMR (CDCl\(_3\), 100 MHz): \(\delta\) 159.7, 154.4, 151.0, 139.9, 135.3, 130.0, 129.4, 128.4, 128.1, 128.0, 126.5, 126.4, 126.3, 125.8, 125.7, 124.1, 122.7, 122.4, 122.1, 118.9, 114.2, 63.0 (N-CH), 56.4 (O-CH\(_3\)), 43.2; MS: m/z: 459 [M+H]\(^+\) (100%); Anal. Calcd for C\(_{30}\)H\(_{26}\)N\(_4\)O: C, 78.58, H, 5.72, N, 12.22. Found: C, 78.54, H, 5.78, N, 12.28.
c) Synthesis of 5-(2-Methoxynaphthalen-1-yl)-3’-(4-methoxyphenyl)-1’-phenyl-3,4-dihydro-1’H,2H-3,4’-bipyrazole (4.23 c)

Conventional heating method:
Yield: 64%

Ultrasound irradiation method:
Yield: 78%

Microwave irradiation method:
Yield: 90%

IR (KBr): \(\nu\) 3330 (N-H), 3056 (C-H), 1621 (C=C), 1598 (C=N) cm\(^{-1}\); \(^1\)H-NMR (CDCl\(_3\), 400 MHz): \(\delta\) 8.11-8.13 (d, 1H, ArH), 8.07 (s, 1H, pyrazole proton), 7.91-7.93 (d, 1H, ArH), 7.82-7.84 (dd, 2H, ArH), 7.71-7.75 (dd, 2H, ArH), 7.67-7.69 (m, 2H, ArH), 7.60-7.62 (d, 2H, ArH), 7.50-7.55 (m, 1H, ArH), 7.41-7.45 (m, 1H, ArH), 7.26-7.28 (m, 1H, ArH), 7.00-7.02 (d, 2H, ArH), 6.05 (bs, 1H, NH), 5.13-5.18 (dd, 1H, CH\(_2\), \(J=7.2\) Hz, 9.6 Hz), 3.87 (s, 3H, O-CH\(_3\)), 3.86 (s, 3H, O-CH\(_3\)), 3.71-3.78 (dd, 1H, CH\(_2\), \(J=10\) Hz, 16.8 Hz), 3.34-3.40 (dd, 1H, CH\(_2\), \(J=9.4\) Hz, 16.8 Hz); \(^1^3\)C-NMR (CDCl\(_3\), 100 MHz): \(\delta\) 157.6, 149.6, 139.7, 135.2, 130.2, 129.4, 128.9, 128.2, 128.0, 126.5, 126.3, 125.8, 125.1, 124.0, 123.6, 122.7, 122.2, 119.6, 116.7, 63.0 (N-CH), 56.4 (O-CH\(_3\)), 55.3 (O-CH\(_3\)), 43.0; MS: \(m/z = 475\) [M+H]\(^+\) (100%); Anal. Calcd for C\(_{30}\)H\(_{26}\)N\(_4\)O\(_2\): C, 75.93, H, 5.52, N, 11.81. Found: C, 75.86, H, 5.58, N, 11.78.

d) Synthesis of 3’-(4-Bromophenyl)-5-(2-methoxynaphthalen-1-yl)-1’-phenyl-3,4-dihydro-1’H,2H-3,4’-bipyrazole (4.23 d)

Conventional heating method:
Yield: 62%

Ultrasound irradiation method:
Yield: 74%
Microwave irradiation method:
Yield: 86%

IR (KBr): ν 3320 (N-H), 3054 (C-H), 1622 (C=C), 1596 (C=N) cm\(^{-1}\); \(^1\)H-NMR (CDCl\(_3\), 400 MHz): δ 8.10 (s, 1H, pyrazole proton), 8.09-8.12 (d, 1H, ArH), 7.92-7.94 (m, 3H, ArH), 7.84-7.86 (m, 2H, ArH), 7.61-7.89 (m, 2H, ArH), 7.41-7.49 (d, 2H, ArH), 7.27-7.29 (m, 2H, ArH), 7.12-7.20 (m, 3H, ArH), 6.05 (bs, 1H, NH), 5.14-5.21 (dd, 1H, CH\(_2\), J=7.2 Hz, 9.6 Hz), 3.89 (s, 3H, O-CH\(_3\)), 3.78-3.84 (dd, 1H, CH\(_2\), J=10 Hz, 16.4 Hz), 3.40-3.46 (dd, 1H, CH\(_2\), J=9.6 Hz, 16.8 Hz); \(^{13}\)C-NMR (CDCl\(_3\), 100 MHz): δ 157.5, 145.2, 141.3, 139.3, 133.7, 132.4, 129.7, 129.5, 128.8, 127.2, 126.0, 125.6, 124.8, 123.9, 123.4, 122.3, 119.0, 116.7, 114.5, 63.1 (N-CH), 56.5 (O-CH\(_3\)), 45.8; MS: m/z = 523 [M+H]\(^+\) (100%); Anal. Calcd for C\(_{29}\)H\(_{23}\)BrN\(_4\)O: C, 66.54, H, 4.43, N, 10.70. Found: C, 66.50, H, 4.52, N, 10.77.

e) Synthesis of 5-(2-Bethoxynaphthalen-1-yl)-3'-(4-nitrophenyl)-1'-phenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazole (4.23 e)

Conventional heating method:
Yield: 60%

Ultrasound irradiation method:
Yield: 72%

Microwave irradiation method:
Yield: 84%

IR (KBr): ν 3330 (N-H), 3056 (C-H), 1621 (C=C), 1599 (C=N) cm\(^{-1}\); \(^1\)H-NMR (CDCl\(_3\), 400 MHz): δ 8.33-8.35 (d, 2H, ArH), 8.11-8.13 (d, 1H, ArH), 8.15 (s, 1H, pyrazole proton), 7.98-8.00 (d, 1H, ArH), 7.92-7.94 (d, 1H, ArH), 7.84-7.86 (dd, 2H, ArH), 7.74-7.76 (dd, 2H, ArH), 7.62-7.64 (d, 2H, ArH), 7.46-7.54 (m, 3H, ArH), 7.32-7.36 (m, 1H, ArH), 6.05 (bs, 1H, NH), 5.13-5.18 (dd, 1H, CH\(_2\), J=7.2 Hz, 9.6 Hz), 3.87 (s, 3H, O-CH\(_3\)), 3.77-3.83 (dd, 1H, CH\(_2\), J=10 Hz, 16.4 Hz), 3.32-3.39 (dd, 1H, CH\(_2\), J=9.6 Hz, 16.8 Hz); \(^{13}\)C-NMR (CDCl\(_3\), 100 MHz): δ 159.4, 151.4, 146.5, 140.2, 139.7, 132.9, 132.1, 130.5, 129.6, 129.6, 129.3, 129.2, 128.7, 128.1, 127.2, 126.1, 125.9, 124.7, 123.9, 118.7, 115.2, 112.8, 63.0 (N-CH), 55.5 (O-CH\(_3\)), 44.4; MS:
\[ m/z = 490 \ [M+H]^+ \ (100\%); \] Anal. Calcd for C\textsubscript{29}H\textsubscript{23}N\textsubscript{5}O\textsubscript{3}: C, 71.15, H, 4.74, N, 14.31. Found: C, 71.19, H, 4.68, N, 14.24.

f) **Synthesis of 5-(2-Methoxynaphthalen-1-yl)-1'-phenyl-3'-(thiophen-2-yl)-3,4-dihydro-1'H,2H-3,4'-bipyrazole (4.23 f)**

Conventional heating method:
Yield: 66%

Ultrasound irradiation method:
Yield: 76%

Microwave irradiation method:
Yield: 90%

IR (KBr): υ 3336 (N-H), 3066 (C-H), 1621 (C=C), 1598 (C=N) cm\(^{-1}\); \(^1\)H-NMR (CDCl\(_3\), 400 MHz): δ 8.11-8.13 (d, 1H, ArH), 8.07 (s, 1H, pyrazole proton), 7.91-7.93 (d, 1H, ArH), 7.82-7.84 (dd, 2H, ArH), 7.71-7.75 (dd, 2H, ArH), 7.26-7.69 (m, 6H, ArH), 7.00-7.02 (d, 2H, ArH), 6.05 (bs, 1H, NH), 5.25-5.30 (dd, 1H, CH\(_2\), \(J=8.6\) Hz, 9.6 Hz), 3.88 (s, 3H, O-CH\(_3\)), 3.78-3.85 (dd, 1H, CH\(_2\), \(J=10\) Hz, 16.8 Hz), 3.34-3.41 (dd, 1H, CH\(_2\), \(J=8.8\) Hz, 16.8 Hz); \(^{13}\)C-NMR (CDCl\(_3\), 100 MHz): δ 159.7, 154.4, 151.0, 139.9, 135.3, 130.0, 129.6, 129.4, 128.4, 128.1, 127.6, 127.4, 126.7, 126.5, 126.4, 126.3, 125.5, 119.0, 119.4, 118.9, 63.1 (N-CH), 55.3 (O-CH\(_3\)), 49.9; MS: \(m/z = 451 \ [M+H]^+ \ (100\%); \) Anal. Calcd for C\textsubscript{27}H\textsubscript{22}N\textsubscript{4}O\textsubscript{5}: C, 71.98, H, 4.92, N, 12.44, S, 7.12. Found: C, 71.86, H, 4.90, N, 12.49, S, 7.09.

g) **Synthesis of 5-(2-Methoxynaphthalen-1-yl)-1',2,3'-triphenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazole (4.23 g)**

Conventional heating method:
Yield: 62%
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Ultrasound irradiation method:
Yield: 70%

Microwave irradiation method:
Yield: 83%

IR (KBr): \( v = 3053 \text{ (C-H)}, 1621 \text{ (C=N)}, 1596 \text{ (C=C) cm}^{-1} \);
\(^1\)H-NMR (CDCl\(_3\), 400 MHz): \( \delta \) 8.50 (s, 1H, pyrazole proton), 8.24-8.26 (d, 1H, ArH), 7.79-7.89 (m, 2H, ArH), 7.68-7.70 (m, 4H, ArH), 7.61-7.63 (m, 4H, ArH), 7.43-7.51 (m, 3H, ArH), 7.40-7.50 (m, 2H, ArH), 7.18-7.29 (m, 2H, ArH), 7.09-7.12 (d, 2H, ArH), 6.80-6.84 (t, 1H, ArH), 5.48-5.53 (dd, 1H, CH\(_2\), \( J = 6.8 \text{ Hz, 11.8 Hz} \)), 3.87-3.91 (dd, 4H, O-CH\(_3\) & CH\(_2\), \( J = \) methoxy proton mixed with CH\(_2\) proton), 3.33-3.39 (dd, 1H, CH\(_2\), \( J = 6.8 \text{ Hz, 17.2 Hz} \)); \(^{13}\)C-NMR (CDCl\(_3\), 100 MHz): \( \delta \) 155.8, 150.4, 146.9, 145.4, 139.9, 138.0, 132.8, 130.8, 130.4, 129.5, 129.3, 129.2, 128.9, 128.1, 127.9, 127.3, 126.4, 126.3, 124.7, 123.0, 119.3, 118.8, 115.9, 113.8, 112.9, 56.7 (N-CH), 56.4 (O-CH\(_3\)), 47.1; MS: \( m/z = 521 \text{ [M+H]}^+ \) 100%; Anal. Calc. for C\(_{35}\)H\(_{28}\)N\(_4\)O: C, 80.74, H, 5.42, N, 10.76. Found: C, 80.70, H, 5.37, N, 10.71.

h) Synthesis of 5-(2-Methoxynaphthalen-1-yl)-1',2-diphenyl-3'-(p-tolyl)-3,4-dihydro-1'H,2H-3,4'-bipyrazole (4.23 h)

Conventional heating method:
Yield: 64%

Ultrasound irradiation method:
Yield: 74%

Microwave irradiation method:
Yield: 85%

IR (KBr): \( v = 3054 \text{ (C-H)}, 1622 \text{ (C=N)}, 1598 \text{ (C=C) cm}^{-1} \);
\(^1\)H-NMR (CDCl\(_3\), 400 MHz): \( \delta \) 8.49 (s, 1H, pyrazole proton), 8.26-8.28 (d, 1H, ArH), 7.69-8.00 (m, 6H, ArH), 7.12-7.46 (m, 9H, ArH), 6.95-6.98 (m, 2H, ArH), 6.76-6.80 (m, 2H, ArH), 5.51-5.56 (dd, 1H, CH\(_2\), \( J = 6.8 \text{ Hz, 11.8 Hz} \)), 3.87-3.92 (dd, 4H, O-CH\(_3\) & CH\(_2\), \( J = \) methoxy proton mixed with CH\(_2\) proton), 3.36-3.42
(dd, 1H, CH₂, J=6.8 Hz, 17.2 Hz), 2.48 (s, 3H, CH₃); ¹³C-NMR (CDCl₃, 100 MHz): δ 153.9, 150.9, 144.5, 143.1, 131.2, 130.4, 129.4, 129.3, 128.8, 128.5, 128.4, 128.1, 127.9, 127.5, 126.9, 126.7, 126.4, 124.6, 124.5, 124.2, 123.8, 123.4, 122.2, 118.9, 114.3, 113.9, 113.3, 56.7 (N-CH), 55.9 (OCH₃), 47.1, 21.3 (CH₃); MS: m/z = 535 [M+H]⁺ 100%; Anal. Calc. for C₃₆H₃₀N₄O: C, 80.87, H, 5.66, N, 10.48. Found: C, 80.92, H, 5.62, N, 10.43.

i) Synthesis of 5-(2-Methoxynaphthalen-1-yl)-3'-((4-methoxyphenyl)-1',2-diphenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazole (4.23 i)

Conventional heating method:
Yield: 64%

Ultrasound irradiation method:
Yield: 75%

Microwave irradiation method:
Yield: 88%

IR (KBr): ν 3053 (C-H), 1620 (C=O), 1596 (C=C) cm⁻¹; ¹H-NMR (CDCl₃, 400 MHz): δ 8.52-8.54 (m, 3H, pyrazole proton), 8.26-8.28 (d, 1H, ArH), 7.72-7.99 (m, 10H, ArH), 6.81-7.50 (m, 7H, ArH), 5.49-5.54 (dd, 1H, CH₂, J=6.8 Hz, 11.8 Hz), 3.36-3.42 (dd, 1H, CH₂, J=6.8 Hz, 17.2 Hz), 3.81-3.91 (dd, 7H, 2 X OCH₃ & CH₂, J= methoxy proton mixed with CH₂ proton); ¹³C-NMR (CDCl₃, 100 MHz): δ 159.6, 155.8, 150.2, 146.9, 145.4, 131.2, 130.8, 129.6, 129.3, 129.2, 129.1, 128.9, 128.1, 127.9, 127.2, 126.9, 126.7, 126.4, 126.2, 124.8, 124.7, 123.9, 123.6, 122.8, 119.9, 118.7, 114.2, 113.8, 113.3, 112.9, 112.6, 56.6 (N-CH), 56.4 (O-CH₃), 55.4 (O-CH₃), 47.0; MS: m/z = 551 [M+H]⁺ 100%; Anal. Calc. for C₃₆H₃₀N₄O₂: C, 78.52, H, 5.49, N, 10.17. Found: C, 78.49, H, 5.56, N, 10.12.

j) Synthesis of 3'-(4-Bromophenyl)-5-(2-methoxynaphthalen-1-yl)-1',2-diphenyl-3,4-dihydro-1'H,2H-3,4'-bipyrazole (4.23 j)
Conventional heating method:
Yield: 61%

Ultrasound irradiation method:
Yield: 74%

Microwave irradiation method:
Yield: 86%

IR (KBr): $v$ 3052 (C-H), 1622 (C=N), 1596 (C=C) cm$^{-1}$; $^1$H-NMR (CDCl$_3$, 400 MHz): $\delta$ 8.25-8.27 (d, 1H, ArH), 8.00 (s, 1H, pyrazole proton), 7.61-7.89 (m, 8H, ArH), 7.36-7.50 (m, 6H, ArH), 7.09-7.28 (m, 4H, ArH), 6.82-6.84 (t, 1H, ArH), 5.47-5.52 (dd, 1H, J=6.8 Hz, 11.8 Hz), 3.84-3.90 (dd, 4H, OCH$_3$ & CH$_2$, $J$= methoxy proton mixed with CH$_2$ proton ), 3.32-3.39 (dd, 1H, CH$_2$, $J$=6.8 Hz, 17.2 Hz); $^{13}$C-NMR (CDCl$_3$, 100 MHz): $\delta$ 156.8, 146.9, 145.4, 139.7, 131.9, 131.8, 131.4, 130.9, 130.4, 129.6, 129.5, 129.1, 128.1, 127.9, 127.3, 126.8, 126.6, 124.6, 124.5, 123.9, 113.9, 119.7, 119.5, 119.0, 118.8, 112.8, 56.6 (N-CH), 56.4 (O-CH$_3$), 46.9; MS: m/z = 598 [M]$^+$ 100%; Anal. Calc. for C$_{35}$H$_{27}$BrN$_4$O: C, 70.12, H, 4.54, N, 9.35. Found: C, 70.06, H, 4.50, N, 9.31.

k) Synthesis of 5-(2-Methoxynaphthalene-1-yl)-3’-(4-nitrophenyl)-1’,2-diphenyl-3,4-dihydro-1’H,2H-3,4’-bipyrazole (4.23 k)

Conventional heating method:
Yield: 60%

Ultrasound irradiation method:
Yield: 70%

Microwave irradiation method:
Yield: 84%

IR (KBr): $v$ 3055 (C-H), 1625 (C=N), 1597 (C=C) cm$^{-1}$; $^1$H-NMR (CDCl$_3$, 400 MHz): $\delta$ 8.34-8.37 (d, 2H, ArH), 8.02-8.06 (m, 3H, ArH & pyrazole proton), 7.88-7.90 (m, 1H, ArH),
7.80-7.82 (d, 2H, ArH), 7.72-7.74 (m, 2H, ArH), 7.11-7.50 (m, 10H, ArH), 6.82-6.87 (t, 1H, ArH), 5.54-5.59 (dd, 1H, CH$_2$, $J$=6.8 Hz, 11.6 Hz), 3.89-4.00 (m, 4H, OCH$_3$ & CH$_2$, $J$= methoxy proton mixed with CH$_2$ proton), 3.34-3.40 (dd, 1H, CH$_2$, $J$=6.8 Hz, 17.2 Hz); $^{13}$C-NMR (CDCl$_3$, 100 MHz): δ 155.8, 147.0, 145.5, 139.3, 131.8, 130.9, 130.8, 130.4, 129.9, 129.6, 129.0, 128.6, 128.1, 126.8, 126.6, 125.4, 124.7, 124.5, 124.1, 123.9, 123.1, 122.4, 119.1, 113.8, 112.3, 57.0 (N-CH), 55.2 (O-CH$_3$), 47.5; MS: $m/z$ = 565 [M]$^+$ 100%; Anal. Calc. for C$_{35}$H$_{27}$N$_5$O$_3$: C, 74.32, H, 4.81, N, 12.38. Found: C, 74.28, H, 4.85, N, 12.36.

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