CHAPTER II

Silver (I) Catalyzed Synthesis of Tetrasubstituted 2-Imidazolones
3.1. Introduction

3.1.1. Transition Metal Catalyzed Coupling Reactions

Heterocyclic compounds have always been of great attention due to their biological and pharmaceutical properties. There are numerous drugs available today which are heterocyclic in nature. Organic chemists are making extensive efforts to produce these heterocyclic compounds by developing new, simple and efficient synthetic methodology. Transition metal catalyzed reactions are one of the most attractive methodologies known for synthesizing heterocyclic compounds. A transition metal catalyzed reactions can directly construct complicated molecules from readily accessible starting materials under mild conditions and these catalysts have been widely used in the synthesis of many new drugs and drugs based on natural products.¹

A coupling reaction in organic chemistry is a comprehensive term for a variety of reactions where two hydrocarbon fragments are coupled with the support of a metal catalyst. In addition to the C−C bonds, C−X (X = heteroatom) bonds are the basis of many organic structures. Contributions to coupling reactions by Ei-ichi Negishi and Akira Suzuki were recognized with the 2010 Nobel Prize in Chemistry, which was shared with Richard F. Heck.² Coupling reactions are important methods to form molecules through specific bond formation. Many efforts have been made in the development of new and versatile methods for various bond constructions. From the variation of the coupling partners, coupling reactions can be classified into three types: traditional coupling, oxidative coupling and reductive coupling (Figure 1).

![Figure 1](image-url)

Figures
Along with the rapid development of organometallic chemistry in the last several decades, many kinds of metal catalysts and ligands were discovered and applied in coupling reactions, making the metal-catalyzed C-C coupling reactions the hottest research spot in chemical synthesis. Cross-coupling reactions have made the use of carbon-based nucleophiles such as aryl and vinyl derivatives of:

- magnesium (Kumada-Corriu coupling)
- boron (Suzuki-Miyaura coupling)
- tin (Stille-Migita coupling)
- zinc (Negishi coupling)
- silicon (Hiyama coupling)

In most cases the catalysts are palladium-based, although various nickel-based (Kumada and Negishi coupling) and iron-based catalysts (Kochi coupling) have been reported.

The widely accepted mechanism of metal catalyzed cross coupling reactions contains three main parts as shown in Figure 2:

1. Oxidative addition of the C–X bond of electrophiles R\textsubscript{1}–X to the metal center of the catalyst to form the intermediate R\textsubscript{1}–M–X;
2. Transmetalation of nucleophiles R\textsubscript{2}–M\textsubscript{1} with the metal–X bond to form the intermediate R\textsubscript{1}–M–R\textsubscript{2};
3. Reductive elimination of intermediate R\textsubscript{1}–M–R\textsubscript{2} to release the coupling product R\textsubscript{1}–R\textsubscript{2} and regenerate the low valent transition-metal species.

The metal centers are normally late transition metals, such as Pd, Ni, etc., and the electrophile in the oxidative addition step is usually an organic halide or pseudohalide. So far this classic model has been extensively studied and widely applied in cross-coupling reactions.
3.1.2. Role of Silver Catalysis in Organic Synthesis

From the last few years, catalysis by coinage metals (including copper, silver and gold) has emerged as a powerful tool for various C-C and C-X bond formation reactions, often with interesting mechanistic pathways. Although silver chemistry has a long history in organic chemistry, it has typically been used in stoichiometric amounts and is developed mostly for anion metathesis (anion exchange, halogen scavengers) and oxidation reactions. Silver (I) complexes have long been believed to have low catalytic efficiency, and most commonly, they are used as either co-catalysts or Lewis acids. Silver catalyzed reactions emerged as important synthetic methods for a variety of organic transformations viz. cycloadditions, cycloisomerizations, allylations, aldol reactions and even C—H bond activation of terminal alkynes. Ag(I) is known to interact with multiple bonds, such as alkenes, alkynes and allenes. In addition, the use of Ag(I) compounds is economic relative with respect to other expensive transition metals.

3.1.3. Imidazolones

3.1.3.1. Natural Occurrence and Bioactivities of Imidazolones

Imidazolones are heterocyclic organic compounds that contain imidazole nucleus and a carbonyl group. Imidazolones can be classified into two types, i.e. 2H-imidazolones and 4H-imidazolones (Figure 3).
Imidazolones have become an attractive target for many organic and medicinal chemists over last few years, due to their interesting biological properties such as anti-inflammatory,\textsuperscript{19} anticancer,\textsuperscript{20} cardio active agents,\textsuperscript{21} angiotensin II receptor antagonists\textsuperscript{22} and others.\textsuperscript{23,24} These motif appear in many natural products, for example Leucetta\textsuperscript{25} (1-2) and bis(indole) alkaloids rhopaladins (3a-d) were isolated from the Okinawan marine tunicate Rhopalaea sp. These compounds exhibited antibacterial activity against Sarcina lutea and Corynebacterium xerosis and, inhibitory activity against cyclin-dependent kinase 4 and c-erbB-2 kinase.\textsuperscript{26} Also, imidazolones are important synthetic intermediates in the synthesis of natural products such as biotin,\textsuperscript{27} slagenins,\textsuperscript{28} axinoxydantoins\textsuperscript{29} and oroidin-derived alkaloids.\textsuperscript{30}

2-Alkylthio imidazolones shows interesting biological properties. For example, the S-glucosylated 5-arylidene imidazolones (6) have been recognised as antiviral agents for the herpes simplex virus\textsuperscript{31} (HSV) and the human immunodeficiency virus (HIV).\textsuperscript{32} The isatinylidene derivative 4 exhibits immunosuppressive activity,\textsuperscript{33} and the 5-
alkylimidene imidazolone (5) substituted with a (biphenyl)tetrazole (BPT) group at the C-2 position shows activities as angiotensine II receptor antagonists.\textsuperscript{34}

Novel bromopyrrole alkaloids, Dispacamide (7) and its monobromo derivative 8, containing an aminimidazolone moiety were reported by Cafieri \textit{et al.}\textsuperscript{35} has reported Dispacamide (7) and its monobromo derivative 8, are novel bromopyrrole alkaloids containing an aminimidazolone moiety. It was isolated from four Caribbean \textit{Agelas} sponges (\textit{A. conifera}, \textit{A. longissima}, \textit{A. clathrodes}, \textit{A. dispar}), and its monobromo derivative, are novel bromopyrrole alkaloids and exhibit remarkably selective antihistamine activity, tested on the guinea pig ileum. Grunwald \textit{et al.}\textsuperscript{36} reported the synthesis of new imidazolones (9) (R = aryl) as modulators of GABA\textsubscript{A} receptors.

\begin{equation}
\begin{array}{c}
\text{\begin{tabular}{c}
\includegraphics[width=1.5cm]{image1.png} \\
7: R = \text{Br} \\
8: R = \text{H}
\end{tabular}} \\
\begin{tabular}{c}
\includegraphics[width=1.5cm]{image2.png} \\
9
\end{tabular} \\
\begin{tabular}{c}
\includegraphics[width=1.5cm]{image3.png} \\
10
\end{tabular}
\end{array}
\end{equation}

4-Aroyl-1,3-dihydro-2\textit{H}-imidazol-2-ones by acylation of the appropriate 2\textit{H}-imidazol-2-ones and evaluated as a new class of cardiotonic agents.\textsuperscript{37} Amongst the synthesized compounds, the most important compound was 4-methyl-5-[4-(methylthio)benzoyl]-1\textit{H}-imidazol-2(3\textit{H})-one (Perfan or Enoximone) (10). This compound exhibited significant inotropic and vasodilating properties and could be useful in the postoperative management of infants and children having cardiac surgery.\textsuperscript{38}

\textbf{3.1.3.2. General Methods for the Synthesis of Imidazolones}

Due to its increasing interest among the chemists, several synthetic approaches of these compounds have been investigated via solution\textsuperscript{39} or solid-phase\textsuperscript{40} synthesis. Few examples are discussed in this section.

Recently, Lima \textit{et al.}\textsuperscript{41} reported the synthesis of 2-imidazolones (14) from 2-thio-substituted imidazoles 11 via hydrolysis of the corresponding imidazolium salt (12) presumably via intermediate 13 (Scheme 1).
A variety of imidazolinone derivatives 17 were synthesised by Zhao et al., via α-amination process of aryl ketones (15) under mild conditions using CuCl as a catalyst and di-tert-butylidiaziridinone (16) as the source of nitrogen (Scheme 2).

Recently, Gong et al. also reported a simple and efficient copper-catalyzed synthesis of 4-arylidene-2-alkyl-4,5-dihydro-1H-imidazol-5-ones (2,4-disubstituted imidazolones) (18) without addition of any ligand or additive under mild conditions (Scheme 3).

The solid-phase synthesis of analogues of 2-imidazolones type 23 has been reported by Cheng et al. In their synthetic method, the polymer-bound glycerol resin (19) was first reacted with bromoacetaldehyde diethyl acetal to give the cyclic acetal bromide (20) on the solid support. Further, amination of the resin-bound acetal bromide (20) was achieved to afford compound 21, which was further treated with isocyanates to afford the resin-bound urea acetics (22). Upon treatment of 21 with...
TFA, aldehyde urea intermediate was released from the resin, which immediately cyclized to ensure the desired 2-imidazolones (23) as shown in Scheme 4.

Scheme 4

The synthesis of imidazolones has been reported via one-pot multicomponent reaction by Siamaki and his co-workers. They reported palladium-catalyzed coupling of imines (24), chloroformates (25), organotin reagents (26) and carbon monoxide which leads to the formation of highly substituted 2-imidazolones (27) as shown in Scheme 5.

Scheme 5
AlNashef et al.\textsuperscript{46} has described a simple and efficient method for the synthesis of highly pure 2-imidazolones in good yield by the reaction of a superoxide ion and the cations of imidazolium-based ionic liquids (Scheme 6).

![Scheme 6](image)

Verniest et al.\textsuperscript{47} has reported gold catalysed cycloisomerisation of substituted $N$-propargylamides and results in corresponding dihydroimidazolone followed by 5-\textit{exo}-dig cyclisation (Scheme 7).

![Scheme 7](image)
3.2. Present Work

For the last few decades, transition metal catalyzed reactions have become the most attractive methodologies, since these reactions can directly construct complicated molecules from readily accessible starting materials under mild conditions.\textsuperscript{48} A rapid and diversity-oriented Ag(I)-mediated synthesis of 2-iminoimidazolines via guanylation of secondary propargylamines followed by 5-exo-dig cyclization has been recently reported by our group.\textsuperscript{49} 2-Iminoimidazolines have a strong structural resemblance to 2-imidazolones which is important from both synthetic and biological point of view. In our present study, we have synthesized 2-imidazolones from secondary propargylamines and isocyanates \textit{via} a one-pot multicomponent reaction, Ag(I) catalyzed cycloisomerisation methodology.

3.2.1. Synthesis of 2-Imidazolone

For the synthesis of 2-imidazolone, we started our study with the optimization of reaction between the substrates methylpropargylamine (34a) and phenyl isocyanate (35a) as shown in Scheme 8. The acylation of methylpropargylamine (34a) with phenyl isocyanate (35a) appeared to be very fast in acetonitrile at low temperature (0-5 °C), resulting in the formation of propargylic urea (36a) in 81 % yield in 5 minutes whereas no desired product 37a was obtained even after 2 h of reaction at room temperature. Also, reaction attempted with Ag(I) catalyst (AgOTf) at room temperature did not result in any conversion of urea intermediate 36a into 2-imidazolone (37a). However, at elevated temperature (80 °C) with 10 mol % of AgOTf catalyst, the reaction proceeded smoothly and the desired 2-imidazolone (37a) was obtained in high yield (94 %). Further, various silver and copper catalysts were investigated for the optimization of reaction and the results are shown in Table 1.

Among all the silver catalyst studied, AgOTf was found to be the best catalyst though the use of Cu(OTf)\textsubscript{2} (10 mol%) led to the desired 2-imidazolones (37a) but the yield was very low and the unreacted urea (36a) was recovered in 85 % yield (Table 1).
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Table 1. Reaction optimization for the synthesis of 2-imidazolone (37a) starting from methylpropargylamine (34a)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Temperature (°C)</th>
<th>Yield (%) (^{\text{a}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>RT</td>
<td>- (81) (^{\text{b}})</td>
</tr>
<tr>
<td>2</td>
<td>10 mol % AgOTf</td>
<td>RT</td>
<td>- (82) (^{\text{b}})</td>
</tr>
<tr>
<td>3</td>
<td>10 mol % AgOTf</td>
<td>80</td>
<td>94</td>
</tr>
<tr>
<td>4</td>
<td>10 mol % AgOOCF(_3)</td>
<td>80</td>
<td>86</td>
</tr>
<tr>
<td>5</td>
<td>10 mol % AgSbF(_6)</td>
<td>80</td>
<td>89</td>
</tr>
<tr>
<td>6</td>
<td>10 mol % AgNO(_3)</td>
<td>80</td>
<td>76</td>
</tr>
<tr>
<td>7</td>
<td>10 mol % Cu(OTf)(_2)</td>
<td>80</td>
<td>8 (85) (^{\text{b}})</td>
</tr>
</tbody>
</table>

\(^{\text{a}}\) Isolated yields; \(^{\text{b}}\) Isolated yield for the propargylic urea (36a) is given in parentheses

Scheme 8

Scheme 9
After successfully optimizing reaction conditions, we evaluated the scope of our procedure for the synthesis of substituted 2-imidazolones using different aromatic and aliphatic isocyanates (35) as shown in Scheme 9. With aromatic isocyanates (35a-e) the corresponding 2-imidazolones (37a-e) were obtained in high yields ranging from 82 to 94 % whereas, with the meta-chlorophenyl isocyanate (35e), the use of higher temperature of 110 °C was required to reach the full conversion of propargylic urea (36e) into final compound 2-imidazolone (37e) in 91 % yield. While, the use of aliphatic hexyl and benzyl isocyanates (35f, 35g) resulted in low conversion of ureas (36f, 36g) and in the formation of the corresponding 2-imidazolones (37f, 37g) in low yield as shown in Scheme 9. We attempted to improve the yield of (37f) by increasing the reaction temperature but no improvement was observed. On the other hand, the reaction of methyl propargylamine (34a) with tosyl isocyanate (35h) resulted in a formation of 2-imidazolone (37h) in a moderate yield of 66 % (Scheme 9).

### 3.2.2. Synthesis of Tetrasubstituted Imidazolones

After evaluation of isocyanate substrate scope, we decided to adapt our protocol for the synthesis of tetrasubstituted 2-imidazolones and the reaction conditions were optimized using substrate N-benzyl-1-phenylhex-1-yn-3-amine (34b) and phenyl isocyanate (35a) as shown in Scheme 10. Using the optimized protocol, we did not observe the formation of propargyl urea from the condensation of substituted propargylamines (34b) with phenyl isocyanate (35a) even at room temperature, but running the same reaction for longer time and at higher temperature (80 °C) we observed the formation propargyl urea (37i). On further heating the reaction for 2h at 80 °C with the addition of silver triflate, the desired 2-imidazolones (37i) was obtained in traces. The increase in reaction temperature from 80 °C to 110 °C resulted in the isolation of 2-imidazolones (37i) in low yield (18 %). In order to optimize the reaction conditions we tried different solvents and an improved yield of 35 % was observed with DCE, whereas yield of 72 % was obtained in toluene. Further attempt to improve the yield through increasing of reaction time met with failure and the results are summarized in Table 2.
Scheme 10

Table 2. Optimization of the one-pot synthesis of tetrasubstituted 2-imidazolones (371) from N-benzyl-1-phenylhex-1-yn-3-amine (34b)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvents</th>
<th>Temperature</th>
<th>Time</th>
<th>Yielda</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MeCN</td>
<td>80 °C</td>
<td>2 h</td>
<td>Traces, (81)b</td>
</tr>
<tr>
<td>2</td>
<td>MeCN</td>
<td>110 °C</td>
<td>2 h</td>
<td>18</td>
</tr>
<tr>
<td>3</td>
<td>DCE</td>
<td>110 °C</td>
<td>2 h</td>
<td>35</td>
</tr>
<tr>
<td>4</td>
<td>Toluene</td>
<td>110 °C</td>
<td>2 h</td>
<td>72</td>
</tr>
<tr>
<td>5</td>
<td>Toluene</td>
<td>110 °C</td>
<td>4 h</td>
<td>57</td>
</tr>
</tbody>
</table>

*Isolated yieldb

Isolated yield for the propargylic urea (36i) is given in parentheses.

Scheme 11

The scope and limitations of the optimized protocol was evaluated applying various propargylamines (34b-f) and aromatic isocyanates (35a-d), for the generation of a small
library of tetrasubstituted 2-imidazolones (37i-t). With the propargylamines (34b, 34c and 34f) bearing both unbranched aliphatic R₂-substituents and aromatic R₃-substituents, the corresponding 2-imidazolones (37i-m, 37r-t) was obtained in 50-72% yields (Scheme 11). There was significant drop in yield when propargylamine (34d) was used; the corresponding 2-imidazolones (37n, 37o) were obtained only in low yields of 33 and 32%, respectively. This decrease in yield might be attributed to relative bulkiness of branched R₂-substituents. Similarly, with propargylamine (34e) low yields of 25% and 21% was observed for corresponding 2-imidazolones (37p and 37q) which might be ascribed to less electrophilicity of the triple bond bearing aliphatic R₃-substituents (Scheme 11).

3.2.3. Proposed Mechanism for the Formation of 2-Imidazolones

A possible mechanism for the one-pot formation of the 2-imidazolones (37) is shown in Scheme 12. Propargylic urea (36), derived from the corresponding propargylamine (34) and isocyanate (35), undergoes 5-exo-dig cyclization through transition state A. Subsequent proton transfer in intermediate B provides the 2-imidazolone (37′) bearing an exocyclic double bond. Finally, double-bond migration results in the formation of the 2-imidazolone (37). We presume that this migration process occurs very fast as the formation of the intermediate 2-imidazolones (37′) could not be observed under the applied reaction conditions.
However, when reaction with methyl propargylamine (34a) and tosyl isocyanate (35h) was performed in wet acetonitrile, both 37'\textsuperscript{h} and 37\textsuperscript{h} have been isolated in 52 \% and 20 \% yields, respectively (Scheme 13). In order to verify the role of the Ag(I) catalyst in the double-bond migration process, we set up two experiments (Scheme 13). Heating a mixture of 37\textsuperscript{h} with 10 mol\% of AgOTf in dry acetonitrile for 4 h at 80 °C resulted in full conversion into 37h. Running the same reaction in the absence of AgOTf resulted in 90 \% conversion, as determined by \textsuperscript{1}H NMR spectrum. This indicates that the Ag(I) catalyst might participate in the double-bond migration process.

\begin{center}
\begin{tikzpicture}
\begin{scope}[scale=0.8]
\node at (0,0) {34a} edge[->,thick, bend left] node {\textsuperscript{N}N\textsuperscript{O}SO\textsuperscript{O}N} (1,1) edge[<-,thick, bend left] node {\textsuperscript{O}SO\textsuperscript{O}N} (1,-1) edge[<-,thick, bend left] node {\textsuperscript{N}N\textsuperscript{O}SO\textsuperscript{O}N} (-1,1) edge[->,thick, bend left] node {\textsuperscript{O}SO\textsuperscript{O}N} (-1,-1);
\node at (1,1) {(35h)} edge[<-,thick, bend left] node {O\textsuperscript{N}=C=N\textsuperscript{O}} (0,0) edge[<-,thick, bend left] node {NH} (0,0) edge[<-,thick, bend left] node {O\textsuperscript{N}=C=N\textsuperscript{O}} (0,-1) edge[->,thick, bend left] node {O\textsuperscript{N}=C=N\textsuperscript{O}} (0,1);
\node at (1,-1) {\textsuperscript{37}'\textsuperscript{h}} edge[<-,thick, bend left] node {37\textsuperscript{h}} (1,-1) edge[<-,thick, bend left] node {37\textsuperscript{h}} (1,1) edge[<-,thick, bend left] node {37\textsuperscript{h}} (1,1) edge[<-,thick, bend left] node {37\textsuperscript{h}} (1,-1) edge[<-,thick, bend left] node {37\textsuperscript{h}} (1,-1);
\node at (-1,1) {37\textsuperscript{h}} edge[<-,thick, bend left] node {\textsuperscript{N}N\textsuperscript{O}SO\textsuperscript{O}N} (-1,1) edge[<-,thick, bend left] node {\textsuperscript{O}SO\textsuperscript{O}N} (-1,-1) edge[<-,thick, bend left] node {\textsuperscript{N}N\textsuperscript{O}SO\textsuperscript{O}N} (1,1) edge[<-,thick, bend left] node {\textsuperscript{O}SO\textsuperscript{O}N} (1,-1) edge[<-,thick, bend left] node {\textsuperscript{N}N\textsuperscript{O}SO\textsuperscript{O}N} (-1,1) edge[<-,thick, bend left] node {\textsuperscript{O}SO\textsuperscript{O}N} (-1,-1);
\node at (1,1) {\textsuperscript{37}'\textsuperscript{h}} edge[<-,thick, bend left] node {37\textsuperscript{h}} (1,-1) edge[<-,thick, bend left] node {37\textsuperscript{h}} (1,1) edge[<-,thick, bend left] node {37\textsuperscript{h}} (1,-1) edge[<-,thick, bend left] node {37\textsuperscript{h}} (1,-1);
\end{scope}
\end{tikzpicture}
\end{center}

\textbf{Scheme 13.} (a) Yield was determined by \textsuperscript{1}H NMR spectroscopy due to contamination by tosylamide, which was formed in wet acetonitrile as a byproduct (b) Isolated yield (c) Determined by \textsuperscript{1}H NMR spectrum
3.3. Results and Discussion

Compounds 37a-t are new and being reported for the first time. The structure of all the compounds 37a-t were unambiguously established on the basis of spectral data (\(^1\)H NMR, \(^{13}\)C NMR and HRMS). The structural characterization of a few representative examples is discussed in this section.

3.3.1. 3-Benzyl-1-methyl-1-(prop-2''-yn-1''-yl)urea (36g)

![Chemical Structure of 36g]

Compound 36g was obtained as colourless solid. Its mass spectrum showed [M+H]\(^+\) peak at \(m/z\) 203, which confirmed its molecular formula to be C\(_{12}\)H\(_{14}\)O\(_2\) (calcd. 202). In the \(^1\)H NMR spectrum (CDCl\(_3\)), the characteristic peak for acetylenic proton appeared as a broad singlet at \(\delta\) 5.09. The methyl protons appeared as a singlet at \(\delta\) 2.92 and the benzylic protons appeared at \(\delta\) 4.40 (d, \(J = 5.6\) Hz). Two peaks were observed for NH proton in the ratio 9:1 because of the rotamers, one is observed as a broad singlet at \(\delta\) 2.15 (0.1H) while the other is appeared as a triplet at \(\delta\) 2.24 (0.9H, \(J = 2.4\) Hz) as shown in Figure 4. Similarly, in its \(^{13}\)C NMR spectrum (CDCl\(_3\)), the characteristic peak for carbonyl carbon appeared at \(\delta\) 157.74; the peak for acetylenic carbons, \(i.e.\) C-1'' and C-2'' appeared at \(\delta\) 72.05 and 79.35, respectively and peak for benzylic carbon appeared at \(\delta\) 139.47 as shown in Figure 4.

The peaks of all other protons and carbons of the molecule were present in \(^1\)H and \(^{13}\)C NMR spectra of the molecule. Based on the above spectral data analysis, the structure of the compound 36g was unambiguously established as 3-benzyl-1-methyl-1-(prop-2''-yn-1''-yl)urea.

On the similar basis, we have characterized 1-methyl-3-phenyl-1-(prop-2''-yn-1''-yl)urea (36a) and 1-benzyl-3-phenyl-1-(1''-phenylhex-1''-yn-3''-yl)urea (36i).
Figure 4. $^1$H and $^{13}$C NMR spectra of compound 36g (300, 75 MHz, CDCl$_3$)
3.3.2. 3-(4'-methoxyphenyl)-1,4-dimethyl-1H-imidazol-2(3H)-one (37c)

Compound 37c was obtained as colourless solid in 91 % yield. Its HRMS showed peak at \( m/z \) 218.1073, which is in close agreement with the molecular formula C_{12}H_{14}O_{2}N_{2} (calcd. 218.1055). In the \(^1\)H NMR spectrum, the characteristic peak of proton at C-5 appeared as a doublet at \( \delta \) 6.02 (\( ^1J = 1.1 \) Hz) due to the coupling with methyl protons at C-4, and confirms the cycloisomerisation of propargylurea, while its corresponding carbon appeared at \( \delta \) 108.23. Similarly, the methyl protons at C-4 appeared as a doublet at \( \delta \) 1.87 (\( ^1J = 1.1 \) Hz) due to the coupling with proton at C-5, while its corresponding carbon appeared at \( \delta \) 10.83 in its \(^{13}\)C NMR (Figure 5). N-CH\(_3\) and O-CH\(_3\) protons appeared as a singlet at \( \delta \) 3.24 and 3.80, respectively; while their corresponding carbons appeared at \( \delta \) 30.09 (N-CH\(_3\)) and 55.38 (O-CH\(_3\)). Two doublets were observed for protons at \( \delta \) 7.19 (C-2'H & C-6'H) and 6.95 (C-3'H & C-5'H) with coupling constant 9.1 Hz each, confirming the ortho coupling of protons. In its \(^{13}\)C NMR spectrum, the characteristic peak of olefinic carbon C-4 appeared at \( \delta \) 118.88 and carbonyl carbon, i.e. C-2 appeared at \( \delta \) 153.30. Carbon bearing methoxy group, i.e. C-4' appeared at \( \delta \) 158.87.

The peaks of all other protons and carbons of the molecule were present in \(^1\)H and \(^{13}\)C NMR spectra of the molecule. Based on the above spectral data analysis, the structure of the compound 37c was unambiguously established as 3-(4'-methoxyphenyl)-1,4-dimethyl-1H-imidazol-2(3H)-one.
Figure 5. $^1$H and $^{13}$C Spectra of compound 37c (300, 75 MHz, CDCl$_3$)
3.3.3. 1,4-Dimethyl-3-tosyl-1H-imidazol-2(3H)-one (37h)

Compound 37h was obtained as a colourless solid in 66 % yield. Its HRMS showed peak at \textit{m/z} 266.0728, which is in close agreement with the molecular formula C_{12}H_{14}O_3N_2S (calcd. 266.0725). In the \textit{\textsuperscript{1}}H NMR spectrum, the characteristic peak of proton at C-5 appeared as a doublet at \(\delta 5.90\) \((J = 1.1\text{ Hz})\) due to the coupling with methyl protons at C-4, and confirms the cycloisomerisation of propargylurea, the corresponding carbon appeared at \(\delta 111.80\). Similarly the methyl protons at C-4 appeared as a doublet at \(\delta 2.28\) \((J = 1.1\text{ Hz})\) due to the coupling with proton at C-5, while its corresponding carbon appeared at \(\delta 13.14\) in \textit{\textsuperscript{13}}C NMR spectrum (Figure 6). N-CH\(_3\) and Ph-CH\(_3\) protons appeared as a singlet at \(\delta 3.05\) and 2.41, respectively; while their corresponding carbons appeared at \(\delta 29.92\) (N-CH\(_3\)) and 21.69 (Ph-CH\(_3\)). Two doublets were observed for protons at \(\delta 7.95\) (C-2'H & C-6'H) and \(7.32\) (C-3'H & C-5'H) with coupling constant 8.2 Hz each, confirming the ortho coupling of protons. In its \textit{\textsuperscript{13}}C NMR spectrum, the characteristic peak of olefinic carbon \textit{i.e.} C-4 appeared at \(\delta 118.39\) and carbonyl carbon, \textit{i.e.} C-2 appeared at \(\delta 150.97\); carbon bearing methyl group, \textit{i.e.} C-4' appeared at \(\delta 135.48\) and carbon C-1' attached to sulphur appeared downfield at \(\delta 145.33\).

The peaks of all other protons and carbons of the molecule were present in \textit{\textsuperscript{1}}H and \textit{\textsuperscript{13}}C NMR spectra of the molecule. Based on the above spectral data analysis, the structure of the compound 37h was unambiguously established as 1,4-dimethyl-3-tosyl-1H-imidazol-2(3H)-one.

On the same basis 1,4-dimethyl-3-phenyl-1H-imidazol-2(3H)-one (37a), 1,4-dimethyl-3-p-tolyl-1H-imidazol-2(3H)-one (37b), 3-(4'-fluorophenyl)-1,4-dimethyl-1H-imidazol-2(3H)-one (37d), 3-(3'-chlorophenyl)-1,4-dimethyl-1H-imidazol-2(3H)-one (37e), 3-hexyl-1,4-dimethyl-1H-imidazol-2(3H)-one (37f) and 3-benzyl-1,4-dimethyl-1H-imidazol-2(3H)-one (37g) have been characterized.
Figure 6. $^1$H and $^{13}$C NMR spectra of compound 37h (300, 75 MHz, CDCl$_3$)
3.3.3.1. 4-Ethyl-1-(4'-fluorophenyl)-3-(4''-methoxybenzyl)-5-(thiophen-3'''-ylmethyl)-1H-imidazol-2(3H)-one (37m)

Compound 37m was obtained as a colourless solid in 58% yield. Its HRMS showed peak at \( m/z \) 422.1468, which is in close agreement with the molecular formula \( C_{26}H_{25}O_{2}N_{2}F_{2}S \) (calcd. 422.1464). In the \(^1\)H NMR spectrum, the characteristic peak of methylene proton at C-5 appeared as a singlet at \( \delta \) 3.61 while its corresponding carbon appeared at \( \delta \) 24.34; N-CH\(_2\) and O-CH\(_3\) protons appeared as a singlet at \( \delta \) 4.87 and 3.79, respectively while their corresponding carbons appeared at \( \delta \) 44.26 (N-CH\(_2\)) and 55.30 (O-CH\(_3\)) in its \(^{13}\)C NMR spectrum. Similarly protons for CH\(_2\)CH\(_3\) and CH\(_2\)CH\(_3\) appeared at 2.41 (q, \( J = 7.6 \) Hz) and 1.03 (t, \( J = 7.4 \) Hz), respectively (Figure 7). In its \(^{13}\)C NMR spectrum, the characteristic peak of olefinic carbon, C-4 and C-5 appeared at \( \delta \) 121.54 and 116.32 and carbonyl carbon, \( i.e. \) C-2 appeared at \( \delta \) 153.46; carbon bearing methoxy group, \( i.e. \) C-4'' appeared at \( \delta \) 158.97 and a doublet was observed for carbon bearing flourine, \( i.e. \) C-4' at \( \delta \) 161.75 (\( ^1\)J\(_{CF} = 245.7 \) Hz).

The peaks of all other protons and carbons of the molecule were present in \(^1\)H and \(^{13}\)C NMR spectra of the molecule. Based on the spectral data analysis, the structure of the compound 37m was unambiguously established as 4-ethyl-1-(4'-fluorophenyl)-3-(4''-methoxybenzyl)-5-(thiophen-3'''-ylmethyl)-1H-imidazol-2(3H)-one.
Figure 7. $^1$H and $^{13}$C NMR spectra of compound 37m (300, 75 MHz, CDCl$_3$)
3.3.4. 1,4-Dibenzyl-5-(dec-9''''-enyl)-3-phenyl-1H-imidazol-2(3H)-one (37r)

Compound 37r was obtained as a colourless solid in 52 % yield. Its HRMS showed peak at \( m/z \) 478.2981, which is in close accordance with the molecular formula \( \text{C}_{33}\text{H}_{38}\text{ON}_2 \) (calcd. 478.2984). In the \(^1\text{H}\) NMR spectrum, the characteristic peak of vinylic protons, \textit{i.e.} C-9'''' appeared as a double doublet of triplet at \( \delta \) 5.80 (ddt, \( J = 6.7, 10.2, 17.1 \) Hz) and C-10'''' appeared as a multiplet in the range of 4.92-5.02 while their corresponding carbons appeared at \( \delta \) 139.16 and 114.22 respectively. The methylene protons at C-4 and nitrogen appeared as a singlet at \( \delta \) 3.71 (CH\textsubscript{2}-Ph) and 4.95 (N-CH\textsubscript{2}) while their corresponding carbons appeared at \( \delta \) 33.81 and 44.24 respectively in its \(^{13}\text{C}\) NMR spectrum (\textbf{Figure 8}). In its \(^{13}\text{C}\) NMR spectrum, the characteristic peak of olefinic carbons, C-4 and C-5 appeared at \( \delta \) 120.80 and 116.84 respectively; carbonyl carbon, \textit{i.e.} C-2 appeared at \( \delta \) 153.55.

The peaks of all other protons and carbons of the molecule were present in \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectra of the molecule. Based on the spectral data analysis, the structure of the compound 37r was unambiguously established as 1,4-dibenzyl-5-(dec-9''''-enyl)-3-phenyl-1H-imidazol-2(3H)-one.
Figure 8. $^1$H and $^{13}$C NMR spectra of compound 37r (400, 75 MHz, CDCl$_3$)
On the similar basis, we have characterized the 1,4-dibenzyl-3-phenyl-5-propyl-1\textsubscript{H}-imidazol-2(3\textsubscript{H})-one (37\textit{i}), 1,4-dibenzyl-3-(4'-methoxyphenyl)-5-propyl-1\textsubscript{H}-imidazol-2(3\textsubscript{H})-one (37\textit{j}), 1,4-dibenzyl-3-(4'-fluorophenyl)-5-propyl-1\textsubscript{H}-imidazol-2(3\textsubscript{H})-one (37\textit{k}), 4-ethyl-3-(4''-methoxybenzyl)-1-phenyl-5-(thiophen-3''-ylmethyl)-1\textsubscript{H}-imidazol-2(3\textsubscript{H})-one (37\textit{l}), 1,4-dibenzyl-5-(dec-9'''-enyl)-3-(4'-fluorophenyl)-1\textsubscript{H}-imidazol-2(3\textsubscript{H})-one (37\textit{s}) and 1,4-dibenzyl-5-(dec-9'''-enyl)-3-(4'-methoxyphenyl)-1\textsubscript{H}-imidazol-2(3\textsubscript{H})-one (37\textit{t}).
3.4. Conclusions

- An efficient one-pot methodology was developed for the synthesis of tetrasubstituted 2-imidazolone \(37a-t\) from readily available secondary propargylamines via Ag(I)-catalyzed cycloisomerization of an \textit{in situ} formed propargylic urea.
- The compounds \(37a-t\) are novel and have not been reported in literature, earlier.
- The structure of all the compounds \(37a-t\) were unambiguously established on the basis of spectral data (\(^1\)H NMR, \(^{13}\)C NMR spectra and HRMS).
3.5. Experimental

3.5.1. General
Analytical TLCs were performed on Merck silica gel 60 \( \text{F}_{254} \) plates. All flash chromatographic separations were performed on 100-200 mesh silica gel and using solvent as eluent. The \( ^1 \text{H} \) NMR and \( ^{13} \text{C} \) NMR spectra (in \( \text{CDCl}_3 \), DMSO-\( \text{d}_6 \) and CD\( \text{OD} \)) were recorded on Bruker Avance 300 (300 and 75 MHz) or a Bruker AMX-400 (400 and 100 MHz) spectrometers at Karholieke Universiteit Leuven, Belgium. TMS was used as an internal standard. The chemical shifts values were quoted on \( \delta \) scale \( i.e. \) in ppm and the coupling constant \( (J) \) were quoted in Hertz (Hz). Low-resolution mass spectra were recorded on a HEWLETT-PACKARD instrument (CI or EI) and LCQ Advantage instrument (ESI). High-resolution mass spectra (EI) were recorded on a KRATOS MS50TC instrument. Melting Points were determined using Reichert-Jung Thermovar apparatus and are uncorrected.

3.5.2. Microwave Irradiation Experiments
Microwave irradiation experiments were carried out in a dedicated CEM-Discover mono-mode microwave apparatus or Milestone MicroSYNTH multi-mode microwave reactor (Laboratory Microwave Systems). Microwave system were used in the standard configuration as delivered, operating at a frequency 2.45 GHz with continuous irradiation power from 0 to 400 W. The reactions were carried out in 10, 20, 30 and 50 mL glass tubes, sealed with Teflon septum and placed in the microwave cavity. The temperature was measured with an IR sensor on the outer surface of the process vials or fibre optic sensor inside the process vial. After the irradiation period, the reaction vessel was cooled rapidly (2-5 min) to ambient temperature by air jet cooling.

3.5.3. Materials
Chemicals were obtained from commercial suppliers and were used without further purification unless otherwise noted. Solvents, \( i.e. \) dichloromethane, heptane, tetrahydrofuran, methanol, \( N, N \)-dimethyl formamide, ethyl acetate and acetone were distilled prior to use.
3.5.4. Procedure for the synthesis of propargylamines 34c and 34e

*p*-Methoxybenzylamine (2.0 mmol), aldehyde (propanaldehyde/*n*-butanaldehyde) (2.0 mmol), acetylene (3-ethynylthiophene/1-pentyne) (4.0 mmol), copper bromide (0.4 mmol) and toluene (2.0 mL) were loaded to a glass tube with a screw cap. The mixture was degassed and flushed with argon. The reaction vessel was conventionally heated with stirring for 4 h at 100 °C. The resulting reaction mixture was cooled to mixture was degassed and flushed with argon. The reaction vessel was conventionally heated with stirring for 4 h at 100 °C. The resulting reaction mixture was cooled to ambient temperature and subjected to the column chromatography with EtOAc/heptane (1:4) to afford the product 34c and 34e.

Propargylamines 34b and 34d were synthesized, following known procedure.50

3.5.4.1. *N*-(4'-*Methoxybenzyl)-1-(thiophen-3''-yl)pent-1-yn-3-amine (34c)

It was obtained in 30 % yield.

**1H NMR (300 MHz, CDCl3):** δ 1.06 (3H, t, *J* = 7.4 Hz, C-5H), 1.49 (1H, s, NH), 1.66-1.76 (2H, m, C-4H), 3.49 (1H, ddd, *J* = 7.4, 5.8 and 1.3 Hz, C-3H), 3.78-4.02 (5H, m, OCH3, H4 and H5), 6.86 (2H, d, *J* = 8.6 Hz, C-3'H and C-5'H), 7.16-7.03 (1H, m, C-4'H), 7.34-7.18 (3H, m, C-2'H and C-6'H & C-2''H), 7.46-7.35 (1H, m, C-5'H).

**13C NMR (75 MHz, CDCl3):** δ 10.64 (C-5), 29.18 (C-4), 50.98 and 51.37 (C-3 and CH2-Ph), 55.29 (OCH3), 79.00 (C-1), 90.51 (C-2), 113.81 (C-3' and C-5'), 122.45 (C-3''), 125.18 (C-4'') and 128.16 (C-2''), 129.62 (C-2' and C-6'), 130.10 (C-5''), 132.23 (C-1'), 158.69 (C-4').

**HRMS (EI) m/z:** C17H19ONS calcd. 285.1187, found 285.1172.
3.5.4.2. N-(4'-Methoxybenzyl)non-5-yn-4-amine (34e)

It was obtained in 24 % yield.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 0.91 (3H, t, $J = 7.2$ Hz, C-1H), 1.01 (3H, t, $J = 7.3$ Hz, C-9H), 1.35 (1H, s, NH), 1.41-1.61 (6H, m, C-2H, C-3H and C-8H), 2.18-2.24 (2H, m, C-7H), 3.33 (1H, ddd, $J = 7.4$, 5.3, and 2.5 Hz, C-4H), 3.73 (1H, d, $J = 12.6$ Hz, H$_a$), 3.79 (3H, s, OCH$_3$), 3.94 (1H, d, $J = 12.7$ Hz, H$_b$), 6.85 (2H, d, $J = 8.4$ Hz, C-3'H and C-5'H), 7.27 (2H, d, $J = 8.4$ Hz, C-2'H and C-6'H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 13.54 and 13.94 (C-1 and C-9), 19.38, 20.78 and 22.51 (C-2, C-7 and C-8), 38.59, (C-3), 49.30 (C-4), 50.82 (CH$_2$-Ph), 55.25 (OCH$_3$), 81.70 (C-6), 83.73 (C-5), 113.73 (C-3' and C-5'), 129.56 (C-2' and C-6'), 132.48 (C-1'), 158.59 (C-4').

MS (ESI$^+$) $m/z$: C$_{17}$H$_{25}$ON calcd. 259.2, found [M+H]$^+$ 260.7.

3.5.5. Procedure for the synthesis of propargylamine (34f)

Benzylamine (214 mg, 2.0 mmol), undec-10-enal (2.0 mmol), phenyl acetylene (4.0 mmol), copper bromide (0.4 mmol) and toluene (2.0 mL) were loaded to a microwave vial equipped with a magnetic stirring bar. The mixture was degassed and flushed with argon. The reaction vessel was sealed and irradiated in the cavity of a CEM-Discover microwave reactor for 25 min at a ceiling temperature of 100 °C and a maximum power of 80 W. The resulting reaction mixture was cooled to ambient temperature and subjected to the column chromatography with EtOAc/heptane (1:4) to afford propargylamine 34f (51 %).
3.5.5.1. *N*-Benzyl-1-phenyltridec-12-en-1-yn-3-amine (34f)

It was obtained in 51 % yield.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 1.29-1.38 (12H, m, C-5H, C-6H, C-7H, C-8H, C-9H and C-10H), 1.52 (1H, s, NH), 1.67-1.75 (2H, m, C-4H), 1.99-2.06 (2H, m, C-11H), 3.55-3.60 (1H, m, C-3H), 3.88 and 4.08 (2H, 2 x d, $J$ = 12.8 Hz each, H$_a$ and H$_b$), 4.90-5.01 (2H, m, C-13H), 5.75-5.85 (1H, m, C-12H), 7.21-7.46 (10H, m, Ar-H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 26.20, 29.00, 29.19, 29.49 and 29.57 (Aliphatic Carbons), 33.89 (C-11), 36.23 (C-4), 50.12 (C-3), 51.61 (CH$_2$-Ph), 84.01 (C-1), 91.24 (C-2), 114.20 (C-13), 123.54 (C-1"), 127.04, 127.95, 128.31, 128.46 and 131.75 (Ar-C), 139.25 (C-12), 140.22 (C-1').

HRMS (EI) $m$/z: C$_{26}$H$_{33}$N calcd. 359.2613, found 359.2602.

3.5.6. General procedure for the synthesis of the imidazol-2-ones (37a-h) via one-pot acylation, Ag (I)-catalyzed cycloisomerization

To a solution of methylpropargylamine (34a, 1 mmol) in dry MeCN (2.5 mL), the appropriate isocyanate (35a-h, 1.1 mmol) was added at 0-5 °C. The glass tube with reaction mixture was degassed and flushed with argon. Intermediate propargyl urea (36a-h) was formed in situ after stirring the reaction mixture for 5 min at RT, further silver triflate (0.1 mmol) was added and the reaction mixture was sealed and stirred for 2h at 80 °C. Upon completion of reaction, MeCN was removed under reduced pressure. The crude product was loaded onto a silica gel column for chromatography. The impurities were removed by elution with EtOAc/heptane (1:1) followed by elution with DCM/MeOH (9:1) providing the target imidazol-2-one (37a-h).
From all the intermediates of the series of desired 2-imidazolones (37a-h) only intermediate 36a and 36g was isolated.

3.5.6.1. 1-Methyl-3-phenyl-1-(prop-2″-yn-1″-yl)urea (36a)

Mixture of rotamers was obtained in the ratio 9:1.

\( ^1H \text{ NMR (300 MHz, CDCl}_3 \): \( \delta \) 2.03 (0.1H, brs, NH), 2.29 (0.9H, t, \( J = 2.1 \) Hz, NH), 3.02 (3H, s, N-CH\(_3\)), 4.14 (2H, d, \( J = 2.1 \) Hz, N-CH\(_2\)), 6.74 (1H, brs, C-3″H), 7.07-6.96 (1H, m, C-4″H), 7.19-7.30 (2H, m, C-3″H & C-5″H), 7.31-7.42 (2H, m, C-2″H & C-6″H).

\( ^13C \text{ NMR (75 MHz, CDCl}_3 \): \( \delta \) 34.15 (CH), 37.92 (N-CH\(_2\)), 72.45 (C-3″), 78.99 (C-2″), 120.26 (C-2″ & C-6″), 123.20 (C-4″), 128.76 (C-3″ & C-5″), 138.88 (C-1″), 155.35 (C-2).

\( \text{MS (Cl) m/z: } C_{11}H_{12}ON_2 \text{ calcd. 188, found } [M + H]^+ : 189. \)

3.5.6.2. 3-Benzyl-1-methyl-1-(prop-2″-yn-1″-yl)urea (36g)

Mixture of rotamers was obtained in the ratio 9:1.

\( ^1H \text{ NMR (300 MHz, CDCl}_3 \): \( \delta \) 2.15 (0.1H, bs, NH), 2.24 (0.9H, t, \( J = 2.4 \) Hz, NH), 2.92 (3H, s, N-CH\(_3\)), 4.10 (2H, d, \( J = 2.4 \) Hz, N-CH\(_2\)), 4.40 (d, \( J = 5.6 \) Hz, 2H, CH\(_2\)-Ph), 5.09 (1H, brs, C-3″H), 7.17-7.37 (m, 5H, Ar-H).

\( ^13C \text{ NMR (75 MHz, CDCl}_3 \): \( \delta \) 33.74 (CH\(_3\)), 37.83 (N-CH\(_2\)), 44.92 (CH\(_2\)-Ph), 72.05 (C-3″), 79.35 (C-2″), 127.16 (C-4″), 127.57 (C-2″ & C-6″), 128.51 (C-3″ & C-5″), 139.47 (C-1″), 157.74 (C-2).

\( \text{MS (Cl): } C_{12}H_{14}ON_2 \text{ calcd. 202, found } [M + H]^+ : 203. \)
3.5.6.3. 1,4-Dimethyl-3-phenyl-1H-imidazol-2(3H)-one (37a)

It was obtained in 94 % yield.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 1.90 (3H, d, $J = 1.2$ Hz, CH$_3$), 3.25 (3H, s, N-CH$_3$), 5.98-6.06 (1H, m, C-5H), 7.24-7.37 (3H, m, Ar-H), 7.38-7.48 (2H, m, Ar-H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 11.02 (CH$_3$), 30.13 (N-CH$_3$), 108.68 (C-5), 118.59 (C-4), 127.40 and 127.59 (C-2' & C-6' and C-4'), 129.11 (C-3' & C-5'), 135.21 (C-1'), 153.11 (C-2).

HRMS (EI) $m/z$: C$_{11}$H$_{12}$O$_2$ calcd. 188.0950, found 188.0957.

3.5.6.4. 1,4-Dimethyl-3-p-tolyl-1H-imidazol-2(3H)-one (37b)

It was obtained in 93 % yield.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 1.82-1.94 (3H, m, CH$_3$), 2.37 (3H, s, Ph-CH$_3$), 3.26 (3H, s, N-CH$_3$), 5.94-6.04 (1H, m, C-5H), 7.16 (2H, d, $J = 8.2$ Hz, C-3'H & C-5'H), 7.24 (2H, d, $J = 8.2$ Hz, C-2'H & C-6'H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 10.99 (Ph-CH$_3$), 21.12 (CH$_3$), 30.16 (N-CH$_3$), 108.35 (C-5), 118.77 (C-4), 127.30 (C-2' & C-6'), 129.79 (C-3' & C-5'), 132.59 (C-1'), 137.54 (C-4'), 153.26 (C-2).

HRMS (EI) $m/z$: C$_{12}$H$_{14}$O$_2$ calcd. 202.1106, found 202.1103.
3.5.6.5. 3-(4'-Methoxyphenyl)-1,4-dimethyl-(1H)-imidazol-2(3H)-one (37c)

It was obtained in 91 % yield.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 1.87 (3H, d, $J = 1.1$ Hz, CH$_3$), 3.24 (3H, s, N-CH$_3$), 3.80 (3H, s, O-CH$_3$), 6.02 (1H, d, $J = 1.1$ Hz, C-5H), 6.95 (2H, d, $J = 9.1$ Hz, C-3'H & C-5'H), 7.19 (2H, d, $J = 9.1$ Hz, C-2'H & C-6'H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 10.85 (CH), 30.11 (N-CH$_3$), 30.18 (N-CH$_3$), 55.40 (O-CH$_3$), 108.24 (C-5), 114.36 (C-3' & C-5'), 118.55 (C-4), 127.88 (C-1'), 128.71 (C-2' & C-6'), 153.30 (C-2), 158.87 (C-4').

HRMS (EI) $m/z$: C$_{12}$H$_{14}$O$_2$N$_2$ calcd. 218.1055, found 218.1073.

3.5.6.6. 3-(4'-Fluorophenyl)-1,4-dimethyl-1H-imidazol-2(3H)-one (37d)

It was obtained in 82 % yield.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 1.88-1.92 (3H, m, CH$_3$), 3.26 (3H, s, N-CH$_3$), 5.97-6.05 (1H, m, C-5H), 7.05-7.19 (2H, m, C-3'H & C-5'H), 7.20-7.32 (2H, m, C-2'H & C-6'H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 10.93 (CH), 30.18 (N-CH$_3$), 108.69 (C-5), 116.11 (d, $^2$$J_{CF} = 22.64$ Hz, C-3' & C-5'), 118.55 (C-4), 129.23 (d, $^3$$J_{CF} = 8.73$ Hz, C-2' & C-6'), 131.19 (d, $^4$$J_{CF} = 3.0$ Hz, C-1'), 153.17 (C-2), 161.80 (d, $^1$$J_{CF} = 245.73$ Hz, C-4').

HRMS (EI) $m/z$: C$_{11}$H$_{11}$FON$_2$ calcd. 206.0855, found 206.0869.
3.5.6.7. 3-(3’-Chlorophenyl)-1,4-dimethyl-(1H)-imidazol-2(3H)-one (37e)

It was obtained in 91 % yield.

\[ ^1H \text{ NMR (300 MHz, CDCl}_3\] : \( \delta \) 1.93 (3H, d, \( J = 1.2 \text{ Hz, CH}_3 \)), 3.26 (3H, s, N-CH\(_3\)), 5.99-6.09 (1H, m, C-5H), 7.15-7.25 (1H, m, Ar-H), 7.27-7.45 (3H, m, Ar-H).

\[ ^13C \text{ NMR (75 MHz, CDCl}_3\] : \( \delta \) 11.05 (CH\(_3\)), 30.16 (N-CH\(_3\)), 109.15 (C-5), 118.25 (C-4), 125.55 (C-6’), 127.59 and 127.78 (C-4’ and C-5’), 130.08 (C-2’), 134.57 (C-1’), 136.37 (C-3’), 152.89 (C-2).

HRMS (EI) \( m/\text{z} \): \( C_{11}H_{11}ClON \) calcd. 222.0560, found 222.0558.

3.5.6.8. 3-Hexyl-1,4-dimethyl-1H-imidazol-2(3H)-one (37f)

It was obtained in 34 % yield.

\[ ^1H \text{ NMR (300 MHz, CDCl}_3\] : \( \delta \) 0.88 (3H, t, \( J = 6.6 \text{ Hz, C-6’H} \)), 1.22-1.36 (6H, m, C-5’H, C-4’H and C-3’H), 1.52-1.68 (2H, m, C-2’H), 2.00-2.06 (3H, m, CH\(_3\)), 3.20 (3H, s, N-CH\(_3\)), 3.57 (2H, t, \( J = 7.5 \text{ Hz, C-1’H} \)), 5.84-5.90 (1H, m, C-5H).

\[ ^13C \text{ NMR (75 MHz, CDCl}_3\] : \( \delta \) 10.16 (CH\(_3\)), 13.95 (C-6’), 22.46 (C-5’), 26.37 (C-3’), 29.64 and 29.88 (N-CH\(_3\) and C-2’), 31.43 (C-4’), 41.14 (C-1’), 107.27 (C-4), 118.21 (C-5), 153.40 (C-2).

HRMS (EI) \( m/\text{z} \): \( C_{11}H_{20}ON \) calcd. 196.1576, found 196.1569.
3.5.6.9. 3-Benzyl-1,4-dimethyl-(1H)-imidazol-2(3H)-one (37g)

It was obtained in 32 % yield.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 1.85-1.94 (3H, m, CH$_3$), 3.25 (3H, s, N-CH$_3$), 4.83 (2H, s, CH$_2$), 5.84- 5.95 (1H, m, C-5H), 7.10-7.40 (m, 5H, Ar-H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 10.38 (CH$_3$), 30.16 (N-CH$_3$), 44.54 (CH$_2$), 107.66 (C-5), 118.56 (C-4), 126.99 and 127.31 (C-2' & C-6' and C-4'), 128.62 (C-3' & C-5'), 137.68 (C-1'), 153.83 (C-2).

HRMS (EI) $m/z$: calcd. for C$_{12}$H$_{14}$ON$_2$ 202.1106; found 202.1107.

3.5.6.10. 1,4-Dimethyl-3-tosyl-1H-imidazol-2(3H)-one (37h)

It was obtained in 66 % yield.

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 2.28 (3H, d, $J$ = 1.1 Hz, CH$_3$), 2.41 (3H, s, Ph-CH$_3$), 3.05 (3H, s, N-CH$_3$), 5.90 (1H, d, $J$ = 1.1 Hz, C-5H), 7.32 (2H, d, $J$ = 8.2 Hz, C-3'H & C-5'H), 7.95 (2H, d, $J$ = 8.2 Hz, C-2'H & C-6'H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 13.14 (CH$_3$), 21.69 (Ph-CH$_3$), 29.92 (N-CH$_3$), 111.80 (C-5), 118.39 (C-4), 128.03 (C-2' & C-6'), 129.69 (C-3' & C-5'), 135.48 (C-4'), 145.33 (C-1'), 150.97 (C-2).

HRMS (EI) $m/z$: C$_{12}$H$_{14}$O$_3$N$_2$S calcd. 266.0725, found 266.0728.
3.5.6.11. 1-Methyl-4-methylene-3-tosylimidazolidin-2-one (37'h)

\[
\begin{align*}
\begin{array}{c}
\text{O} \\
\text{S} \\
\text{N} \\
\text{O} \\
\end{array}
\end{align*}
\]

\(\text{H NMR (300 MHz, CDCl}_3\): \delta 2.42 (3H, s, Ph-CH}_3\), 2.79 (3H, s, N-CH}_3\), 3.96 (2H, s, C-5H), 4.49 (1H, d, \text{J} = 2.07 \text{ Hz, C-4H}_b\), 5.50 (1H, d, \text{J} = 2.25 \text{ Hz, C-6H})

\(\text{C NMR (75 MHz, CDCl}_3\): \delta 21.70 (\text{Ph-CH}_3\), 29.98 (N-CH}_3\), 49.85 (C-5), 91.46 (CH}_2\), 127.82 (C-2' & C-6'), 129.66 (C-3' & C-5'), 134.39 (C-1'), 135.44 (C-4'), 145.21 (C-4), 152.96 (C-2).

3.5.7. General procedure for the synthesis of the tetrasubstituted imidazol-2-ones (37i-t) via one-pot, Ag (I)-catalyzed cycloisomerization

To a solution of propargylamine (34b-f, 0.33 mmol) in dry toluene (2.5 mL), the appropriate isocyanate (35a-d, 0.4 mmol) was added. The glass tube with reaction mixture was degassed and flushed with argon. Intermediate propargyl urea (37i-t) was formed in situ after heating the reaction mixture for 1h at 110 °C, further silver triflate (0.07 mmol) was added and the reaction mixture was sealed and stirred for 2h at 110 °C. The resulting reaction mixture was cooled to ambient temperature and subjected to the column chromatography with EtOAc/heptane (1:1) as eluent to afford imidazol-2-one (37i-t).

From all the intermediates of the series of desired tetrasubstituted 2-imidazolones (37i-t) only intermediate 36i was isolated.
3.5.7.1. 1-Benzyl-3-phenyl-1-(1''-phenylhex-1''-yn-3''-yl)urea (36i)

\[ \text{H NMR (300 MHz, CDCl}_3\text{): } \delta \text{ 1.00 (3H, t, } J = 7.3 \text{ Hz, C-6''H), 1.42-1.72 (2H, m, C-5''H), 1.75-1.95 (2H, m, C-4''H), 4.54 (1H, d, } J = 17.1 \text{ Hz, H}_a, 4.85 (d, } J = 17.1 \text{ Hz, 1H, H}_b, 5.50 (t, } J = 7.7 \text{ Hz, 1H, C-3''H), 6.45 (brs, 1H, NH), 6.90-7.05 (m, 1H, Ar-H), 7.06-7.61 (m, 14H, Ar-H).} \\
\text{13C NMR (75 MHz, CDCl}_3\text{): } \delta \text{ 13.71 (C-6''), 19.62 (C-5''), 36.90 (C-4''), 48.25 and 48.67 (C-3'' and CH}_2\text{-Ph), 85.17 (C-2''), 87.95 (C-1''), 119.68 (C-2' and C-6''), 122.55, 123.00, 126.93, 127.97, 128.26, 128.31, 128.73, 129.15 and 131.54 (Ar-C), 137.62 (C-1''), 138.87 (C-1''), 155.20 (C-2).} \\
\text{MS (CI) } m/z: \text{ C}_{26}\text{H}_{26}\text{ON}_2 \text{ calcd. 382, found [M + H]}^+: 383.} \\

3.5.7.2. 1,4-Dibenzyl-3-phenyl-5-propyl-1H-imidazol-2(3H)-one (37i)

\[ \text{It was obtained in 72% yield.} \\
\text{H NMR (CDCl}_3\text{, 300 MHz): } \delta \text{ 0.85 (3H, t, } J = 7.3 \text{ Hz, CH}_2\text{CH}_2\text{CH}_3), 1.29-1.46 (2H, m, CH}_2\text{CH}_2\text{CH}_3), 2.31 (2H, t, } J = 7.8 \text{ Hz, CH}_2\text{CH}_2\text{CH}_3), 3.67 (2H, s, CH}_2\text{-Ph), 4.95 (2H, s, N-CH}_2\text{), 6.78-6.90 (2H, m, Ar-H), 7.05-7.18 (5H, m, Ar-H), 7.20-7.40 (8H, m, Ar-H).} \]
13C NMR (CDCl3, 75 MHz): δ 13.93 (CH2CH2CH3), 23.10 (CH2CH2CH3), 25.63 (CH2CH2CH3), 29.41 (CH2-Ph), 44.83 (N-CH2), 117.01 (C-5), 120.61 (C-4), 126.27, 127.02, 127.39, 127.56, 127.88, 128.02, 128.30, 128.70 and 128.90 (Ar-C), 135.33 (C-1'), 138.0 and 138.33 (C-1'' and C-1''), 153.55 (C-2).

HRMS (EI) m/z: C24H26ON2 calcd. 382.2045, found 382.2049.

3.5.7.3. 1,4-Dibenzyl-3-(4'-methoxyphenyl)-5-propyl-1H-imidazol-2(3H)-one (37j)

It was obtained in 53 % yield.

1H NMR (300 MHz, CDCl3): δ 0.86 (3H, t, J = 7.4 Hz, CH2CH2CH3), 1.30-1.47 (2H, m, CH2CH2CH3), 2.31 (2H, t, J = 7.9 Hz, CH2CH2CH3), 3.65 (2H, s, CH2-Ph), 3.78 (3H, s, O-CH3), 4.96 (2H, s, N-CH2), 6.80 (2H, d, J = 8.9 Hz, C-3'H & C-5'H), 6.84-6.91 (2H, m, Ar-H), 7.00 (2H, d, J = 8.9 Hz, C-2'H & C-6'H), 7.11-7.21 (3H, m, Ar-H), 7.24-7.39 (5H, m, Ar-H).

13C NMR (75 MHz, CDCl3): δ 13.89 (CH2CH2CH3), 23.10 (CH2CH2CH3), 25.63 (CH2CH2CH3), 29.37 (CH2-Ph), 44.82 (N-CH2), 55.46 (O-CH3), 114.19 (C-2' and C-6'), 117.37 (C-5), 120.22 (C-4), 126.25, 127.98, 127.34, 127.89, 128.05, 128.29, 128.66, 129.33 (Ar-C), 138.06 and 138.44 (C-1'' and C-1''), 153.80 (C-2), 158.92 (C-4').

HRMS (EI) m/z: C27H28O2N2 calcd. 412.2151, found 412.2157.
3.5.7.4. 1,4-Dibenzyl-3-(4'-fluorophenyl)-5-propyl-1H-imidazol-2(3H)-one (37k)

It was obtained in 71% yield.

$^1$H NMR (CDCl$_3$, 300 MHz): $\delta$ 0.87 (3H, t, $J = 7.3$ Hz, CH$_2$CH$_3$CH$_3$), 1.31-1.48 (2H, m, CH$_2$CH$_2$CH$_3$), 2.32 (2H, t, $J = 7.8$ Hz, CH$_2$CH$_2$CH$_3$), 3.65 (2H, s, CH$_2$-Ph), 4.95 (2H, s, N-CH$_2$), 6.80 (2H, d, $J = 8.9$ Hz, Ar-H), 6.79-6.88 (2H, m, Ar-H), 6.89-7.07 (4H, m, Ar-H), 7.08-7.20 (3H, m, Ar-H), 7.22-7.40 (5H, m, Ar-H).

$^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta$ 13.92 (CH$_2$CH$_2$CH$_3$), 23.15 (CH$_2$CH$_2$CH$_3$), 25.57 (CH$_2$CH$_2$CH$_3$), 29.39 (CH$_2$-Ph), 44.85 (N-CH$_2$), 115.85 (d, $^2J_{CF} = 22.63$ Hz, C-3' & C-5'), 117.0 (C-5), 120.74 (C-4), 126.42, 126.94, 127.46, 127.83, 128.38 and 128.73 (Ar-C), 129.85 (d, $^3J_{CF} = 8.73$ Hz, C-2' & C-6'), 131.24 (d, $^4J_{CF} = 3.0$ Hz, C-1'), 137.82 and 138.03 (C-1" and C-1"), 153.58 (C-2), 161.80 (d, $^1J_{CF} = 245.73$ Hz, C-4').

HRMS (EI) m/z: C$_{26}$H$_{25}$ON$_2$F calcd. 400.1951, found 400.1953.

3.5.7.5. 4-Ethyl-3-(4''-methoxybenzyl)-1-phenyl-5-(thiophen-3''-ylmethyl)-1H-imidazol-2(3H)-one (37l)

It was obtained in 50% yield.
Chapter II
Silver (I) Catalyzed Synthesis of Tetrasubstituted 2-Imidazolones

**1H NMR (400 MHz, CDCl₃):** δ 1.05 (3H, t, J = 7.5 Hz, CH₂CH₃), 2.43 (2H, q, J = 7.5 Hz, CH₂CH₃), 3.67 (2H, s, C5-CH₂), 3.82 (3H, s, O-CH₃), 4.91 (2H, s, N-CH₂), 6.57-6.61 (1H, m, Ar-H), 6.64-6.68 (1H, m, Ar-H), 6.90 (2H, d, J = 8.6 Hz, C-3''H & C-5''H), 7.13-7.19 (3H, m, Ar-H), 7.24-7.39 (5H, m, Ar-H).

**13C NMR (75 MHz, CDCl₃):** δ 14.48 (CH₂CH₃), 16.82 (N-CH₂), 24.33 (C5-CH₂), 44.21 (N-CH₂), 55.28 (O-CH₃), 114.04, 116.37, 121.09, 121.42, 125.60, 127.51, 127.55, 128.45, 128.94 and 130.10 (Ar-C), 135.31, 138.95, 153.40 (C-2), 158.93 (C-4').

**HRMS (EI) m/z:** C₂₄H₂₄O₂N₂S calcd. 404.1558, found 404.1574.

3.5.7.6. 4-Ethyl-1-(4'-fluorophenyl)-3-(4''-methoxybenzyl)-5-(thiophen-3'''-ylmethyl)-1H-imidazol-2(3H)-one (37m)

![37m](image)

It was obtained in 58% yield.

**1H NMR (300 MHz, CDCl₃):** δ 1.03 (3H, t, J = 7.4 Hz, CH₂CH₃), 2.41 (2H, q, J = 7.6 Hz, CH₂CH₃), 3.61 (2H, s, C5-CH₂), 3.79 (3H, s, O-CH₃), 4.88 (2H, s, N-CH₂), 6.58-6.64 (2H, m, Ar-H), 6.87 (2H, d, J = 8.7 Hz, Ar-H), 6.97-7.17 (5H, m, Ar-H), 7.24 (2H, d, J = 8.7 Hz, Ar-H).

**13C NMR (75 MHz, CDCl₃):** δ 14.56 (CH₂CH₃), 16.82 (N-CH₂), 24.34 (C5-CH₂), 44.26 (N-CH₂), 55.30 (O-CH₃), 114.08 (C-3'' and C-5''), 115.84 (d, ²JCF = 22.70 Hz, C-3' and C-5''), 116.32 (C-5), 121.15 and 121.54 (C-2'' and C-4), 125.82 (C-5''), 127.44 (C-4''), 128.44 (C-2'' and C-6''), 129.66 (d, ³JCF = 8.76 Hz, C-2' and C-6'), 129.97 (C-1'), 131.28 (d, ⁴JCF = 3.2 Hz, C-1'), 138.78 (C-3''''), 153.46 (C-2), 158.97 (C-4''), 161.75 (d, ¹JCF = 247.8 Hz, C-4').

**HRMS (EI) m/z:** C₂₄H₂₃O₂N₂S calcd. 422.1464, found 422.1468.
3.5.7.7. 4-Benzyl-5-isobutyl-3-phenyl-1-propyl-1H-imidazol-2(3H)-one (37n)

It was obtained in 33 % yield.

$^1$H NMR (300 MHz, CDCl$_3$): δ 0.98-1.02 (9H, m, 2 x C-3'''H and C-3''''H), 1.74-1.93 (3H, m, C-2'''H and C-2''''H), 2.37 (2H, d, $J = 7.5$ Hz, C-1''''H), 3.66 (2H, t, $J = 7.6$ Hz, C-1'''H), 3.71 (2H, s, CH$_2$-Ph), 6.82-6.90 (2H, m, Ar-H), 7.04-7.10 (2H, m, Ar-H), 7.11-7.19 (3H, m, Ar-H), 7.23-7.31 (3H, m, Ar-H).

$^{13}$C NMR (75 MHz, CDCl$_3$): δ 11.36 (C-3''''), 22.38 and 22.77 (2 x C-3'''' and C-2''''') 28.83 and 29.47 (C-2''' and C-1'''''), 32.54 (CH$_2$-Ph), 43.21 (C-1''''), 117.14 (C-5), 119.58 (C-4), 126.19 (C-4''), 127.39, 127.81, 127.98, 128.23 and 128.78 (Ar-C), 135.36 (C-1'''), 138.34 (C-1'''), 153.13 (C-2).

HRMS (EI) m/z: C$_{23}$H$_{28}$O$_{2}$ calcd. 348.2202, found 348.2195.

3.5.7.8. 4-Benzyl-3-(4'-fluorophenyl)-5-isobutyl-1-propyl-1H-imidazol-2(3H)-one (37o)

It was obtained in 32 % yield.

$^1$H NMR (300 MHz, CDCl$_3$): δ 0.94-1.05 (9H, m, 2 x C-3'''H and C-3''''H), 1.73-1.94 (3H, m, C-2'''H and C-2''''H), 2.38 (2H, d, $J = 7.4$ Hz, C-1''''H), 3.60-3.71 (4H, m, C-
1''''H and CH₂-Ph), 6.82-6.89 (2H, m, Ar-H), 6.91-7.04 (4H, m, Ar-H), 7.11-7.20 (3H, m, Ar-H).

$^{13}$C NMR (75 MHz, CDCl₃): δ 11.34 (C-3'''''), 22.38 and 22.76 (2 x C-3'''' and C-2'''''), 28.85 and 29.47 (C-2''' and C-1'''), 32.50 (CH₂-Ph), 43.23 (C-1'''''), 115.68 (d, $^2J_{CF} = 22.5$ Hz, C-3' and C-5'), 117.13 (C-5), 119.69 (C-4), 126.33 (C-4'''), 127.77 (C-3'' and C-5''), 128.31 (C-2'' and C-6''), 129.78 (d, $^3J_{CF} = 9$ Hz, C-2' and C-6'), 131.31 (d, $^4J_{CF} = 3$ Hz, C-1''), 138.10 (C-1'''), 153.18 (C-2), 161.69 (d, $^1J_{CF} = 245.25$ Hz, C-1').

HRMS (EI) m/z: C$_{25}$H$_{27}$ON$_2$F calcd. 366.2107, found 366.2101.

3.5.7.9. 4-Butyl-1-(4''-methoxybenzyl)-5-propyl-3-p-tolyl-1H-imidazol-2(3H)-one (37p)

It was obtained in 25 % yield.

$^1$H NMR (300 MHz, CDCl₃): δ 0.75 (3H, t, $J = 7.0$ Hz, C-4''''H), 0.92 (3H, t, $J = 7.3$ Hz, C-3''''''H), 1.08-1.18 (4H, m, C-2''''H and C-3''''H), 1.36-1.47 (2H, m, C-2''''''H), 2.25-2.35 (4H, m, C-1''''H and C-1''''''H), 2.40 (3H, s, Ph-CH₃), 3.81 (3H, s, O-CH₃), 4.85 (2H, s, N-CH₂), 6.87 (2H, d, $J = 8.6$ Hz, Ar-H), 7.18-7.28 (6H, m, Ar-H).

$^{13}$C NMR (75 MHz, CDCl₃): δ 13.61 and 13.86 (C-3'''' and C-3''''''), 21.15 (Ph-CH₃), 22.07 (C-2'''''), 23.02 and 23.19 (C-2''' and C-3''''), 25.49 (C-1'''''), 31.11 (C-1'''''), 44.17 (N-CH₂), 55.27 (O-CH₃), 113.96 (C-3'' and C-5''), 118.63 and 118.85 (C-5 and C-4), 127.55 (C-2' and C-6'), 128.41 (C-3'' and C-5''), 129.70 (C-2'' and C-6''), 130.41 (C-1'''), 133.23 (C-1'), 137.30 (C-4'), 153.61 (C-2), 158.84 (C-4'').

HRMS (EI) m/z: C$_{25}$H$_{32}$O$_2$N$_2$ calcd. 392.2464, found 392.2449.
3.5.7.10. 4-Butyl-3-(4'-fluorophenyl)-1-(4''-methoxybenzyl)-5-propyl-1H-imidazol-2(3H)-one (37q)

It was obtained in 21 % yield.

**1H NMR (300 MHz, CDCl₃):** δ 0.75 (3H, t, J = 6.9 Hz, C-4''''H), 0.93 (3H, t, J = 7.3 Hz, C-3''''H), 1.07-1.18 (4H, m, C-2''''H and C-3''''H), 1.36-1.48 (2H, m, C-2''''''H), 2.25-2.36 (4H, m, C-1''''H and C-1''''''H), 3.81 (3H, s, O-CH₃), 4.83 (2H, s, N-CH₂), 6.87 (2H, d, J = 8.6 Hz, C-3'' and C-5''), 7.12-7.18 (2H, m, C-3' and C-5''), 7.22 (2H, d, J = 8.6 Hz, C-2'' and C-6''), 7.29-7.34 (2H, m, C-2' and C-6').

**13C NMR (75 MHz, CDCl₃):** δ 13.60 and 13.88 (C-3'''' and C-3'''''''), 22.07 (C-2'''''''), 22.97 and 23.17 (C-2'''' and C-3'''''), 25.43 (C-1'''''), 31.10 (C-1'''''''), 44.21 (N-CH₂), 55.27 (O-CH₃), 114.0 (C-3'' and C-5''), 116.06 (d, ²JC_F = 23.25 Hz, C-3' and C-5''), 118.66 and 119.03 (C-5 and C-4), 128.38 (C-2'' and C-6''), 129.46 (d, ³JC_F = 9.0 Hz, C-2' and C-6''), 130.07 (C-1'''), 131.78 (d, ⁴JC_F = 3.0 Hz, C-1''), 153.49 (C-2), 158.89 (C-4''), 161.76 (d, ¹JC_F = 246.0 Hz, C-4').

**HRMS (EI) m/z:** C₂₄H₂₉O₂N₂F calcd. 396.2213, found 396.2217.

3.5.7.11. 1,4-Dibenzyl-5-(dec-9'''-enyl)-3-phenyl-1H-imidazol-2(3H)-one (37r)

It was obtained in 52 % yield.
$^1$H NMR (400 MHz, CDCl$_3$): δ 1.18-1.39 (12H, m, C-2'''H, C-3'''H, C-4'''H, C-5'''H, C-6'''H and C-7'''H), 2.03 (2H, dd, J = 6.8, 14.4 Hz, C-8'''H), 2.31 (2H, t, J = 7.8 Hz, C-1'''H), 3.66 (2H, s, CH$_2$-Ph), 4.92-5.02 (4H, m, C-10'''H and N-CH$_2$), 5.80 (1H, ddt, J = 6.7, 10.2, 17.1 Hz, C-9'''H), 6.84-6.86 (2H, m, Ar-H), 7.10-7.16 (5H, m, Ar-H), 7.22-7.35 (8H, m, Ar-H).

$^{13}$C NMR (75 MHz, CDCl$_3$): δ 23.62 (C-2''''), 28.86, 29.04, 29.16, 29.31, 29.39 and 29.82 (C-1'''', C-3'''', C-4'''', C-5'''', C-6'''', C-7''''), 33.78 (C-8'''' and CH$_2$), 44.85 (N-CH$_2$), 114.22 (C-10'''''), 115.80 (d, J = 7.8 Hz, C-1''''), 115.80 (d, J = 7.8 Hz, C-1''''), 115.80 (d, J = 7.8 Hz, C-1''''), 115.80 (d, J = 7.8 Hz, C-1''''), 115.80 (d, J = 7.8 Hz, C-1''''), 115.80 (d, J = 7.8 Hz, C-1''''), 115.80 (d, J = 7.8 Hz, C-1''''), 115.80 (d, J = 7.8 Hz, C-1'''').

HRMS (EI) m/z: C$_{33}$H$_{38}$ON$_2$ calcd. 478.2984, found 478.2981.

3.5.7.12. 1,4-Dibenzyl-5-(dec-9''''-eny)-3-(4'-fluorophenyl)-1H-imidazol-2(3H)-one (37s)

It was obtained in 54 % yield.

$^1$H NMR (400 MHz, CDCl$_3$): δ 1.17-1.44 (12H, m, C-2'''H, C-3'''H, C-4'''H, C-5'''H, C-6'''H and C-7'''H), 2.01-2.14 (2H, m, C-8'''H), 2.36 (2H, t, J = 7.8 Hz, C-1'''H), 3.67 (2H, s, CH$_2$-Ph), 4.90-5.12 (4H, m, C-10'''H and N-CH$_2$), 5.84 (1H, ddt, J = 6.7, 10.3, 17.0 Hz, C-9'''H), 6.84-6.94 (2H, m, Ar-H), 6.95-7.10 (4H, m, Ar-H), 7.14-7.24 (3H, m, Ar-H), 7.29-7.43 (5H, m, Ar-H).

$^{13}$C NMR (75 MHz, CDCl$_3$): δ 23.62 (C-2''''), 28.86, 29.04, 29.16, 29.31, 29.39 and 29.82 (C-1'''', C-3'''', C-4'''', C-5'''', C-6'''', C-7''''), 33.78 (C-8'''' and CH$_2$-Ph), 44.86 (N-CH$_2$), 114.22 (C-10'''''), 115.80 (d, $^2$J$_{CF} = 22.5$ Hz, C-3' and C-5'), 116.79 (C-5'), 120.91, 126.41, 126.99, 127.46, 127.84, 128.38 and 128.72 (Ar-C’s), 129.82 (d, $^3$J$_{CF}$
= 9.0 Hz, C-2' and C-6'), 131.26 (d, \(^1J\text{CF} = 3.0\) Hz, C-1'), 137.86, 138.09 (C-1''' and C-1''), 139.14 (C-9''''), 153.59 (C-2), 161.78 (d, \(^1J\text{CF} = 246.0\) Hz, C-4').

**HRMS (EI) m/z:** \(C_{33}H_{37}ON_2F\) calcd. 496.2890, found 496.2876.

3.5.7.13. 1,4-Dibenzyl-5-(dec-9''''-enyl)-3-(4'-methoxyphenyl)-1\(H\)-imidazol-2(3\(H\))-one (37t)

It was obtained in 52 % yield.

**\(^1H\text{ NMR (400 MHz, CDCl}_3\):}** \(\delta 1.43-1.17\) (12H, m, C-2''''H, C-3''''H, C-4''''H, C-5''''H, C-6''''H and C-7''''H), 2.01-2.14 (2H, m, C-8''''H), 2.34 (2H, t, \(J = 7.8\) Hz, C-1''''H), 3.66 (2H, s, CH-Ph), 3.80 (3H, s, O-CH), 4.92-5.08 (4H, m, C-10''''H and N-CH), 5.84 (1H, ddt, \(J = 6.6, 10.3, 17.0\) Hz, C-9''''H), 6.83 (2H, d, \(J = 8.8\) Hz, C-3' and C-5'), 6.88-6.95 (2H, m, Ar-H), 7.03 (2H, d, \(J = 8.8\) Hz, C-2' and C-6'), 7.13-7.24 (3H, m, Ar-H), 7.29-7.42 (5H, m, Ar-H).

**\(^{13}C\text{ NMR (75 MHz, CDCl}_3\):}** \(\delta 23.7\) (C-2''''), 28.9, 29.0, 29.2, 29.3, 29.4 and 29.8 (C-1''''H), 33.8 (C-8'''' and CH-Ph), 44.8 (N-CH), 55.5 (O-CH), 114.2 (C-10''''), 117.2 (C-5), 120.4 (C-4), 126.3, 127.0, 127.4, 127.9, 128.1, 128.3, 128.7 and 129.3 (Ar-C), 138.1 and 138.5 (C-1'''' and C-1''), 139.1 (C-9''''), 153.8 (C-2), 158.9 (C-4').

**HRMS (EI) m/z:** \(C_{34}H_{40}O_2N_2\) calcd. 508.3090, found 508.3091.
3.6. References


Chapter II  
Silver (I) Catalyzed Synthesis of Tetrasubstituted 2-Imidazolones


