Chapter II

1. Stereoselective Synthesis of E-Trisubstituted Alkenes

1.1. Introduction

The trisubstituted olefinic moiety\textsuperscript{1-5} is a core constituent of many naturally occurring biologically active compounds found in terpenoids, pheromones, macrolide antibiotics, etc. For example, Kijanolide, Tetronolide and Chlorothricolide, the Aglycons of the spirotetronate antibiotics Kijanimicin, Tetrocarcin A and Chlorothricin respectively, have trisubstituted olefinic units as core structures.\textsuperscript{6} Halichomycin\textsuperscript{7} is a new class of potent cytotoxy macrolide which constitutes three tri substituted alkene units in the structure (Fig. 1).

![Figure 1](image1.png)

Figure 1

Milnamide A, Hemiasterlin, Criamide A are members of a small family of tri- and tetra- peptides containing two highly modified amino acids possesses a trisubstituted olefin as core unit whose structure is shown in Fig.2. These naturally occurring substances, which have been isolated from marine sponges, show potent \textit{in vitro} cytotoxicity against marine leukemia P388 and human breast, ovarian, colon, and lung cancer cell lines.\textsuperscript{8}

![Figure 2](image2.png)

Figure 2
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Phenoxan and its structurally related compounds Spectinabilin and Aureothin possess potent inhibitory activity against HIV-1 infection. These compounds contain aromatic ring as one of the substitution in the trisubstituted olefin moiety (Fig. 3).

![Figure 3](image)

Since the wide spread occurrence and importance of the trisubstituted alkenes and difficult in construction of E-trisubstituted alkenes many synthetic methods have been developed for its construction. Some of the literature methods especially from Baylis-Hillman adducts for the synthesis of trisubstituted alkenes are described in the following sections.

1.2. Synthesis of Trisubstituted Alkenes from Baylis-Hillman Adducts

The Baylis-Hillman adducts namely α-methylene-β-hydroxyalkanoates, in particular, were shown to be a versatile precursors for trisubstituted alkene synthesis. Drewes and Emslie reported the first serious of application of Baylis-Hillman reaction involved ethyl acrylate and acetaldehyde with subsequent transformation to integerrinecic acid, a C_{10} necic acid. The C_{10} necic acid constitute the acidic portion of pyrrolizidine alkaloids which are widespread in nature and frequently occur as macrocyclic dilactones (Scheme 1).

![Scheme 1](image)
Later in 1987, Mihara et al.\textsuperscript{11} described the isolation and identification of four hydroxy nitriles (2-5, Fig.4) in nature. They isolated these compounds from Blackcurrant, \textit{(Ribes Nigrum L.)} an important raw material for the food industry in Central and Northern Europe. The Blackcurrant buds absolute, which have a very characteristic and powerful odour, serve as a flavour enhancer and, have been used as a major ingredient in some luxury fragrances. As shown compounds 2 and 3 are diastereomer and those can be prepared from the Baylis-Hillman adduct 1 by hydrogenation. Compounds 4 and 5 are isomerized product of the adduct 1.

\textbf{Figure 4}

Elliot et al.\textsuperscript{12} reported an improved synthesis of 7-substituted pyrrolo [3, 2,-d] pyrimidines. For example, 7-phenyl (methyl) pyrrolo [3, 2,-d] pyrimidine, a potent inhibitor of the enzyme purine nucleoside phosphorylase (PNP) which is an important to the T-cell mediated part of the immune system as such, is an important therapeutic target. The authors have synthesized this pyrimidine 6 from trisubstituted alkene 7 which can in turn be obtained from the Baylis-Hillman adduct 1. (Scheme 2, Fig.5).

\textbf{Scheme : 2 Synthesis of Pyrimidines}
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1.3. Literature on Isomerisation of Baylis-Hillman Adducts

With this brief introduction, it is very clear that simple isomerisation of Baylis-Hillman adducts gives valuable synthons for organic synthesis. During the last five years there has been number of reports on the subject of isomerisation of Baylis-Hillman adducts and its synthetic use in organic synthesis. The following sections delineate a brief overview on isomerization of Baylis-Hillman adducts with various reaction conditions.

1.3.1. Isomerization of Adducts Using Conventional Acids

The $\alpha$-methylene-\(\beta\)-hydroxyalkanenitriles (secondary allylic alcohols) have been conveniently isomerized into 3-aryl-2-(hydroxymethyl)prop-2-enenitriles (primary alcohols) by Basavaiah and co-workers via treatment with aqueous sulfuric acid (20%). These primary alcohols were further converted into the corresponding cinnamaldehydes, which are important synthons in organic synthesis (Scheme 4).

The acetates of Baylis-Hillman adducts viz. methyl-3-acetoxy-3-aryl-2-methylene propanoates and 3-acetoxy-3-aryl-2-methylene propanenitriles were stereoselectively converted under the influence of TMSOTf into methyl (2E)-2-(acetoxy)methyl)-3-arylprop-2-enoates and (2E)-2-(acetoxy)methyl)-3-arylprop-2-enenitriles, respectively (Scheme 5). The remarkable reversal in stereochemistry from ester to nitrile in these reactions has been discussed in result and discussion section.
Kim et al.\textsuperscript{16} have reported an interesting facile one-pot stereoselective synthesis of (E)-cinnamyl alcohols \textit{via} the treatment of ethyl-3-aryl-3-hydroxy-2-methylene propanoates with TFA. However, a similar reaction of 3-aryl-3-hydroxy-2-methylene propanenitriles with TFA provided the (E)-allyl alcohols in low yields (Scheme 6).

Later, Basavaiah \textit{et al.}\textsuperscript{17} developed an alternative, simple, and one-pot stereoselective synthesis of methyl (2E)-3-aryl-2-(hydroxymethyl)-prop-2-enoates \textit{via} sequential treatment of methyl 3-aryl-3-hydroxy-2-methylene propanoates with Ac\textsubscript{2}O/TMSOTf and K\textsubscript{2}CO\textsubscript{3} in methanol (Scheme 7).

### 1.4. Definition of the Problem

Literature search revealed that most of the transformations of the densely functionalized Baylis-Hillman adducts occur mainly through isomerization of allylic double bond. The literature survey also revealed that all the isomerization reactions of Baylis-
Hillman adduct are made use of either conventional acids as catalyst or harmful, irritant and environment polluting reagents. Further, these reactions were performed successfully on an organic solvent medium and obviously, it needs a lengthy rigorous work-up procedure. To avoid the use of environmental polluting reagents, conventional acids, and organic solvents and lengthy work-up procedure for the isomerization of Baylis-Hillman adducts and its derivatives, we envisaged an alternative and efficient method which will address the problems associated with reaction. In order to address these problems, we chose a clay-microwave system as an alternative, environmentally friendly, non-polluting effective catalyst system for this transformation. A complete study of the isomerization reactions under this catalyst system is the subject matter of this chapter. The chapter also describes how the clay-microwave catalyst system is useful in the synthesis of functionalized propargyl ethers, potential precursors for lignin core structures in this first part and indenes and 1-aryl indenes in part 2.

1.5. Results and Discussion

The results obtained during the studies on isomerization of Baylis-Hillman adduct using Montmorillonite K10 clay catalyst and microwave system have been discussed in the following sections.

1.5.1. Montmorillonite-K10 Clay Catalyzed Isomerization

The study was initiated with the preparation of literature known simple acetate of Baylis-Hillman adduct 9. The simple adduct 8 and its acetate 9 were prepared according to standard procedure (Scheme 8).
The preliminary studies of isomerization reaction of the adduct 9 was attempted by the treatment of acetate of adduct 9 with 50% w/w commercial, pre-activated Montmorillonite K-10 clay in dichloromethane. The mixture was stirred at room temperature for 48 h and monitored by TLC. Even after prolonged stirring (62 h), the reaction furnished only the starting material. Repeating the experiment in dichloromethane with activated 50% w/w Montmorillonite K-10 clay at reflux for 24 h furnished the starting material quantitatively.

However, when slurry made of the acetate 9 with 50% w/w montmorillonite K-10 clay under solvent free condition was irradiated in a microwave oven for 6 min., a clean isomerised product 10 was obtained in 60% yield after column purification (Scheme 9). The compound 10 was isolated by diluting with dichloromethane and filtration through a celite pad. Among the several variations tested (Irradiation time and Power Level) to optimize the condition, the following conditions involving acetate 9 with 30% w/w of montmorillonite K-10 clay, 70% microwave power level (PL) and 13 min. irradiation time was found to be the best and yielded a clean isomerised product 10 (9:1, E:Z isomer ratio) in 74% after purification by silica gel column chromatography. The ratio of the E:Z isomers were confirmed by proton NMR spectroscopy.

\[
\begin{align*}
\text{OAc} & \quad \text{CO}_2\text{Et} \\
\text{OAc} & \quad \text{CO}_2\text{Et}
\end{align*}
\]

\[
\begin{align*}
\text{9} & \quad \text{30% w/w Mont. K10, mw, 13 min. (70% PL)} \\
\text{Neat, 74%} & \quad \text{10}
\end{align*}
\]

Scheme 9

The experiment with microwave irradiation of the acetate 9 under optimized conditions without any montmorillonite K10 clay furnished the starting material quantitatively confirming the necessity of clay catalyst for this transformation. The isomerization of simple adducts 8 (without acetate protection of the alcohol) under similar conditions furnished only 20% of the isomerised product 10 with remaining dimerised product. Hence, acetate protection of the Baylis-Hillman adduct is necessary for good yields. The results of the preliminary studies are summarized in Table 1.
Table 1

<table>
<thead>
<tr>
<th>Entry</th>
<th>Condition</th>
<th>Product, Yield</th>
<th>E/Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50% w/w mont. K10 CH₂Cl₂, RT, 48 h</td>
<td>No reaction, 9 recovered</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>50% w/w mont. K10, CH₂Cl₂, 40 °C, 24 h</td>
<td>&quot;</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>MW, 6 min. (without clay)</td>
<td>&quot;</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>50% w/w mont. K10, MW, 6 min</td>
<td>10, 60%</td>
<td>9:1</td>
</tr>
<tr>
<td>5</td>
<td>30% w/w mont. K10, MW, 13min (70% PL)</td>
<td>10, 74%</td>
<td>9:1</td>
</tr>
</tbody>
</table>

In order to exemplify the general nature and applicability of this reaction, a number of acetylated Baylis-Hillman adducts described below were subjected to isomerization reaction under optimized reaction condition. All the acetylated adducts underwent isomerization reaction smoothly to give clean trisubstituted alkenes (Scheme 10). As shown in Scheme 10 and Table 2, it should be noted that the yields of adducts with nitrile and carbonyl groups were lower compared to the ester functional group at the activated alkene and it needed longer irradiation time with higher power level. The results are summarized in Table 2.

Scheme 10

The isomer ratio (E: Z) of the products was estimated by ¹H NMR (by integrating the alkene proton peaks at δ 7.9 and δ 7.1 respectively). A remarkable observation was noted that the ratio of isomers obtained from adducts with CN substituted is more compared to the CO₂Et substituted adducts. The remarkable reversal in stereochemistry from ester (or ketone) to nitrile in these reactions is consistent with literature reports.
Table 2 Isomerisation of Acetates of Baylis-Hillman adduct with Mont.K10/µw catalyst system

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Ar</th>
<th>Z</th>
<th>µw irradiation (PL), Time</th>
<th>Product, (E/Z)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9</td>
<td>Ph</td>
<td>CO₂Et</td>
<td>13 min.</td>
<td>10, 9:1</td>
<td>74</td>
</tr>
<tr>
<td>2</td>
<td>11</td>
<td>4-Cl-Ph</td>
<td>CO₂Et</td>
<td>13 min.</td>
<td>15, 9.3:0.7</td>
<td>60</td>
</tr>
<tr>
<td>3</td>
<td>12</td>
<td>4-Me-Ph</td>
<td>CO₂Et</td>
<td>13 min.</td>
<td>16, 9:1</td>
<td>71</td>
</tr>
<tr>
<td>4</td>
<td>13</td>
<td>2,4-Cl₂-Ph</td>
<td>CO₂Et</td>
<td>13 min.</td>
<td>17, 9.2:0.8</td>
<td>72</td>
</tr>
<tr>
<td>5</td>
<td>14</td>
<td>Naphth-2-yl</td>
<td>CO₂Et</td>
<td>13 min.</td>
<td>18, 9.1:0.9</td>
<td>68</td>
</tr>
<tr>
<td>6</td>
<td>19</td>
<td>Ph</td>
<td>COCH₃</td>
<td>13 min.</td>
<td>21, 9.6:0.4</td>
<td>59</td>
</tr>
<tr>
<td>7</td>
<td>20</td>
<td>4-Me-Ph</td>
<td>COCH₃</td>
<td>13 min.</td>
<td>22, 9.1:0.9</td>
<td>65</td>
</tr>
<tr>
<td>8</td>
<td>23</td>
<td>Ph</td>
<td>CN</td>
<td>15 min.</td>
<td>29, 9.5:0.5</td>
<td>68</td>
</tr>
<tr>
<td>9</td>
<td>24</td>
<td>4-Cl-Ph</td>
<td>CN</td>
<td>(80%PL), 16 min.</td>
<td>30, 9.5:0.5</td>
<td>57</td>
</tr>
<tr>
<td>10</td>
<td>25</td>
<td>4-Me-Ph</td>
<td>CN</td>
<td>(80%PL), 16 min.</td>
<td>31, 8:2</td>
<td>66</td>
</tr>
<tr>
<td>11</td>
<td>26</td>
<td>2,4-Cl₂-Ph</td>
<td>CN</td>
<td>(80%PL), 16 min.</td>
<td>32, 8.7:1.3</td>
<td>70</td>
</tr>
<tr>
<td>12</td>
<td>27</td>
<td>4-MeO-Ph</td>
<td>CN</td>
<td>(80%PL), 16 min.</td>
<td>33, 9.2:0.8</td>
<td>76</td>
</tr>
<tr>
<td>13</td>
<td>28</td>
<td>Naphth-2-yl</td>
<td>CN</td>
<td>(80%PL), 16 min.</td>
<td>34, 9.5:0.5</td>
<td>62</td>
</tr>
</tbody>
</table>

The reversal in the stereochemistry between ester and nitrile as reported earlier can be explained by conformational and steric hindrance studies. When the electron withdrawing group is ester or ketone, the (E)-trisubstituted alkene in which the aryl group is trans to the ester group is the major product (Figure 6).

When the electron withdrawing group is nitrile, the (E)-trisubstituted alkene in which the aryl group is cis to the nitrile group is the major product (Figure 7).
From the literature, it is clear that all the transformation on Baylis-Hillman adducts is based on the double bond migration, i.e., 1,3-sigmatropic shift. Nucleophilic substitution reaction of Baylis-Hillman adducts undergo via $S_N2'$ pathway resulting in the formation of stereoselective E-trisubstituted alkene.

The efficiency of commercial montmorillonite K10 (2:1 layer type, available from Aldrich Co.,) clay was compared with $Fe^{3+}$-montmorillonite K10 (an ion exchanged clay) as well as acid treated regional natural Kaolinite clay. The use of $Fe^{3+}$-montmorillonite K10 was found to be as good as montmorillonite K10 clay while with acid treated regional natural Kaolinite (1:1 layer type) clay, the reaction was unsuccessful and starting material was recovered quantitatively. The reason for this observation with natural Kaolinite clay may be that the interlayer distance is $< 7 \text{ Å}$ when compared to montmorillonite K10 clay whose interlayer gap is 10 Å where the clay reactions actually taken place. Due to the small interlayer distance in the acid treated regional natural Kaolinite clay, the reacting molecules are presumably unable to enter the interlayer space and hence the reaction failed. The results are summarized in Table 3. The clay recovered from the reaction mixture by filtration can be recycled three times without losing its activity by activating the clay at 100 °C for 3 hours.

<table>
<thead>
<tr>
<th>Clay</th>
<th>Condition</th>
<th>Product E/Z</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Montmorillonite K10</td>
<td>30% w/w clay, MW, 13 min</td>
<td>10, 9:1</td>
<td>74</td>
</tr>
<tr>
<td>$Fe^{3+}$-montmorillonite K10</td>
<td>30% w/w clay, MW, 6 min</td>
<td>10, 9:1</td>
<td>72</td>
</tr>
<tr>
<td>Natural Kaolinite clay</td>
<td>30% w/w clay, MW, 8 min</td>
<td>-</td>
<td>no reaction</td>
</tr>
</tbody>
</table>
1.5.2. Protection of Baylis-Hillman Adduct with Trimethyl Orthoformate

Encouraged by the preliminary results obtained in the previous section, we were interested to use the isomerization methodology for the protection of Baylis-Hillman adducts as methyl ether instead of conventional acylation, which is known for using pyridine base (health hazard!) and irritant acetyl chloride as reagents. Hence the choice of the reagent is trimethyl orthoformate, which could be used for the protection of alcohols (secondary alcohol present in Baylis-Hillman adduct) in presence of clay-microwave catalyst system.

To achieve the reaction, treatment of adduct 8 with slight excess of trimethyl orthoformate in the presence of 100% w/w montmorillonite-K10 clay on microwave irradiation for 7 min. furnished the simple methyl protected adduct 35 along with its isomerised product 36 in 6:4 ratio in 80% combined yield after column purification. The structures and the product ratio were established by IR, proton NMR, $^{13}$C NMR spectroscopy and analytical methods. We observed similar results with other adducts shown in Table 4.

![Scheme 11]

1.5.3. Isomerisation of Adduct with Trimethyl Orthoformate

As a logical extension of the results obtained in the previous section, we explored the one-pot protection followed by isomerization of Baylis-Hillman adducts. The advantages of this method are: i) the reaction is solvent free ii) direct isomerization product formation without acetate protection of adducts thereby avoiding pyridine as base and iii) eco-friendly catalyst clay mediated efficient method.

To show the methodology, the reaction of simple adduct 8 as shown in Scheme 11, under optimized conditions but the irradiation time was increased up to 20 min afforded only the methyl protected isomerised ether 36 as sole product in 76% yield after column purification (Scheme 12). Similarly other adducts 37-44 under conditions mentioned in Table 4 afforded the corresponding isomerised product 45-53 in 52-77% yield. All the
compounds obtained are characterized by spectral and analytical means (see experimental). The result obtained from various adducts and yields are summarized in Table 4.

![Scheme 12](image)

Table 4 Isomerisation of Baylis-Hillman Adduct with Trimethyl Orthoformate

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reactant</th>
<th>R</th>
<th>Z</th>
<th>Condition</th>
<th>Product</th>
<th>Yield, (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8</td>
<td>Ph</td>
<td>CO₂Et</td>
<td>Clay, MW, 20 min.</td>
<td>36</td>
<td>76</td>
</tr>
<tr>
<td>2</td>
<td>37</td>
<td>Ph</td>
<td>CN</td>
<td>Clay, MW, 22 min.</td>
<td>45</td>
<td>70</td>
</tr>
<tr>
<td>3</td>
<td>38</td>
<td>4-Cl-Ph</td>
<td>CO₂Et</td>
<td>Clay, MW, 19 min.</td>
<td>47</td>
<td>62</td>
</tr>
<tr>
<td>4</td>
<td>39</td>
<td>4-Cl-Ph</td>
<td>CN</td>
<td>Clay, MW, 20 min.</td>
<td>48</td>
<td>52</td>
</tr>
<tr>
<td>5</td>
<td>40</td>
<td>4-Me-Ph</td>
<td>CO₂Et</td>
<td>Clay, MW, 18 min.</td>
<td>49</td>
<td>70</td>
</tr>
<tr>
<td>6</td>
<td>41</td>
<td>4-Me-Ph</td>
<td>CN</td>
<td>Clay, MW 21 min.</td>
<td>50</td>
<td>64</td>
</tr>
<tr>
<td>7</td>
<td>42</td>
<td>4-MeO-Ph</td>
<td>CN</td>
<td>Clay, MW 21 min.</td>
<td>51</td>
<td>77</td>
</tr>
<tr>
<td>8</td>
<td>43</td>
<td>Naphth-2-yl</td>
<td>CO₂Et</td>
<td>Clay, MW, 21 min.</td>
<td>52</td>
<td>69</td>
</tr>
<tr>
<td>9</td>
<td>44</td>
<td>Naphth-2-yl</td>
<td>CN</td>
<td>Clay, MW 22 min</td>
<td>53</td>
<td>63</td>
</tr>
</tbody>
</table>

The following section explains structural assignment for some of typical compounds obtained above.

![Figure 8](image)

Figure 8 ¹H NMR Spectrum of Compound 36

Besides typical IR spectrum of the compound 36, the ¹H NMR spectrum (Fig.8) showed the ester methyl and methylene protons as triplet centered at δ 1.36 and quartet
centered at δ 4.28 respectively (J = 7.1Hz). The methoxy protons were apparent as a singlet at δ 3.43. A singlet at δ 4.22 revealed the presence of allylic methylene protons. A singlet at δ 7.9 was discernible for the vinylic proton. The $^{13}$C NMR and analytical data were consistent with assigned structure (see experimental).

The $S_N2$ substitution product, the simple methyl protected product 46 was isolated when the irradiation of Baylis-Hillman adduct 38 with trimethyl orthoformate under clay-microwave catalyst was stopped after 7 min. Its $^1$H NMR spectrum (Fig. 9) showed the ester methyl and methylene protons as a triplet centered at δ 1.24 and a quartet centered at δ 4.14 (J = 7.1Hz). The methoxy protons appeared as a singlet at δ 3.3. The allylic proton was apparent as a singlet at δ 5.06. The two singlets at δ 5.91 and 6.31 were discernible for the olefinic protons. The aromatic protons appeared as singlet at δ 7.28. The $^{13}$C NMR and analytical data were consistent with assigned structure and presented in the experimental section.
The $^1$H NMR Spectrum (Fig. 10) of compound 48 showed the methoxy protons as a singlet at $\delta$ 3.44. The allylic protons were discernible at $\delta$ 4.15 as a singlet. The vinylic proton which is trans to nitrile group was apparent at $\delta$ 7.10. The aromatic protons showed two doublets centered at $\delta$ 7.5 and 7.8 ($J = 8.4$Hz). The $^{13}$C NMR and analytical data were consistent with assigned structure.

1.5.4. Isomerisation with Various Alcohols: Synthesis of Enyne Ethers

The above results showed that mechanistically, the methoxide anion generated from trimethyl orthoformate in presence of clay undergoes both S$_{N}$2 and S$_{N}$2' nucleophilic substitution reaction with Baylis-Hillman adducts giving rise to the methyl protected simple and isomerised ethers respectively. It lends further exploration on the alcohol substitution reactions of Baylis-Hillman adducts using alkoxide oxygen as nucleophile derived from various saturated and unsaturated alcohols. The earlier studies$^{19}$ on nucleophilic substitution reactions of Baylis-Hillman adducts are known only with amines as nucleophiles and the alcohols as nucleophile is unknown. Since the main aim of present study is looking forward the synthetic use of Baylis-Hillman adducts, we explored the nucleophilic substitution reaction with alcohols that would lead to various functionalized enyne-ethers which could be used as starting material for the stereoselective synthesis various cyclic ethers (oxacycles such as tetrahydrofuran, tetrahydropyran and oxepanes) by radical cyclization pathways.

Hence the initial study was carried out with simple and protected Baylis-Hillman adducts with propargyl alcohol as shown in Scheme 13. The simple Baylis-Hillman adduct 54 and propargyl alcohol in presence of 30% w/w Mont. K10 clay without any solvent was heated at 75 °C and the reaction was followed by TLC. After 6 hrs of heating, the reaction was found to be completed and diluting the slurry with dichloromethane and isolation of the products by filtration, column purification showed the formation of two products. The products were identified as two possible enyne-ethers 56 and 57 in 2:3 ratio in 90% combined yield. It is evident that the ethers 56 and 57 are formed by S$_{N}$2 and S$_{N}$2' substitution reaction of adducts with propargyl alcohol. The formations of products were conformed by spectral and analytical analysis. The known product 56 is compared with
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literature reported data\textsuperscript{19a}. The spectral analysis of the isomerized product 57 is discussed below.

In order to compare the reactivity of simple unprotected adduct with acetylated adduct towards the nucleophilic substitution, the acetyl protected adduct 55 was treated with propargyl alcohol under similar reaction condition used for the simple adduct 54. Surprisingly, the reaction afforded the ethers 56 and 57 in same yield and product ratio. From the results, it is clear that both simple and protected adducts 54 and 55 respectively have same reactivity pattern towards nucleophilic substitution with alcohols as they furnished identical $S_N2$ and $S_N2'$ products 56 and 57 (Scheme 13).

\begin{center}
\begin{tikzpicture}
\node at (0,0) {\includegraphics[width=\textwidth]{scheme13}};
\end{tikzpicture}
\end{center}

Our preliminary results revealed the isomerization of acetylated adduct 9 in presence of clay catalyst to give the clean isomerised product 10 (section 1.4.1). Since, simple and protected adduct have same reactivity pattern towards nucleophilic substation with alcohols, we also intended to study the nucleophilic substitution reaction of isomerised adduct 58 and isomerised acetate adduct 59. Thus, the isomerised adducts 58 and 59 were subjected to the reaction with propargyl alcohol separately under similar reaction conditions. To our surprise, the reaction yielded compounds 56 and 57 in almost same yields and product ratio (Scheme 14) as obtained for adducts 54 and 55.

\begin{center}
\begin{tikzpicture}
\node at (0,0) {\includegraphics[width=\textwidth]{scheme14}};
\end{tikzpicture}
\end{center}

These experiments clearly indicate that the simple adduct, acetylated adduct and isomerised adducts towards nucleophilic substitution reaction with propargyl alcohol are
identical since all of them afforded same products with identical product ratio irrespective of nature of starting material. The results also revealed that the reaction of alcohol with simple unisomerized adduct itself provides the required products in excellent yield and no protected/isomerised starting materials are necessary to effect this transformation.

To obtain the isomerised enyne-ether 57 as only product, the reaction mixture was allowed for the longer time and it furnished the enyne-ether having \( E \)-trisubstituted alkene 57 as sole product. Complete conversion of simple protected Enyne-ether into isomerised product was observed at the reaction time 24 h and was purified by passing through a silica gel column chromatography (Scheme 15). The distribution of products with respect to reaction time is summarized in Table 5.

![Scheme 15](image)

Table 5

<table>
<thead>
<tr>
<th>time (h)</th>
<th>56 (%)</th>
<th>57 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>42</td>
<td>58</td>
</tr>
<tr>
<td>15</td>
<td>25</td>
<td>75</td>
</tr>
<tr>
<td>22</td>
<td>&lt;5</td>
<td>&gt;95</td>
</tr>
<tr>
<td>24</td>
<td>&lt;1</td>
<td>&gt;99</td>
</tr>
</tbody>
</table>

All the products obtained are characterized by IR, \(^1\)H NMR, \(^13\)C NMR and analytical methods. Typical characterizations of some of the compounds are described as following.

![Figure 11 \(^1\)H NMR Spectrum of Compound 57](image)
The $^1$H NMR spectrum (Fig. 11) of compound 57 showed a triplet for the terminal alkyne proton at $\delta$ 2.42 ($J=2.6$ Hz). The propargyl methylene proton displayed a characteristic doublet centered at $\delta$ 4.26 with coupling constant 2.34 Hz. The allylic methylene protons were apparent as a singlet at $\delta$ 4.39. The vinylic proton showed a singlet at $\delta$ 7.92. A noticeable singlet at $\delta$ 3.84 reveals the presence of ester methyl.

![Figure 12 $^{13}$C NMR Spectrum of Compound 57](image)

Its $^{13}$C NMR spectrum (Fig.12) showed the resonance of terminal alkyne carbon at $\delta$ 74.70. The representative signals at $\delta$ 58.08 and 64.25 were corresponding to the two methylene carbons. The quaternary alkyne carbon resonance was observed at $\delta$ 79.63. The vinylic carbon at the benzylic position was perceptible at $\delta$ 145.27. The characteristic signal for ester methyl carbon appeared at $\delta$ 52.26. A signal at $\delta$ 134.51 was attributed to the resonance of quaternary alkene carbon. The typical carbonyl signal was found at $\delta$ 167.98. The compound also provided satisfactory micro analytical data.

To show generality of this method for the preparation of protected isomerised products through various alcohols as nucleophiles, the simple adducts 8, 37, 54 were treated with various alkyl alcohols (allyl, isopropyl, $n$-octyl) under optimized condition to yield corresponding alkyl protected isomerised adducts 58-62 in excellent yield. The reaction is represented in Scheme 16 and the results are summarized in table 6.
Like in the case of methyl protection of Baylis-Hillman adduct (section 1.4.2), the isopropyl protected compound 63 was isolated when heating Baylis-Hillman adduct with isopropyl alcohol for 6 h under optimized condition. The $^1$H NMR spectrum (Fig. 13) showed the presence of six methyl protons and one methine proton of isopropyl group as two doublets centered at $\delta$ 1.15 and 1.24 and one septet centered at $\delta$ 3.64 respectively with coupling constant 6.1 Hz. The allylic proton was apparent as singlet at $\delta$ 4.93. The two singlets at $\delta$ 5.92 and 5.96 were discernible for the presence of olefinic protons. The aromatic protons showed a singlet at $\delta$ 7.3.

After the detailed study on nucleophilic substitution of alcohols with Baylis-Hillman adducts, under optimized condition, a number of potential enyne-ethers were synthesized by the reaction of propargyl alcohol with various Baylis-Hillman adducts having different substitutions on aromatic ring and electron withdrawing groups at activated alkene (Scheme 17). The results are summarized in table 7. These highly functionalized enyne ethers are
Chapter II

Synthesis of E-trisubstituted alkenes

successfully used for the synthesis of oxacycles by vinyl radical cyclization and it will be discussed in detail in chapter IV.

![Scheme 17]

Table 7

<table>
<thead>
<tr>
<th>Entry</th>
<th>Reactant</th>
<th>Ar</th>
<th>Z</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8</td>
<td>C₆H₅</td>
<td>CO₂Et</td>
<td>66</td>
<td>92</td>
</tr>
<tr>
<td>2</td>
<td>37</td>
<td>&quot;</td>
<td>CN</td>
<td>67</td>
<td>90</td>
</tr>
<tr>
<td>3</td>
<td>38</td>
<td>4-Cl-C₆H₄</td>
<td>CO₂Et</td>
<td>68</td>
<td>91</td>
</tr>
<tr>
<td>4</td>
<td>39</td>
<td>&quot;</td>
<td>CN</td>
<td>69</td>
<td>89</td>
</tr>
<tr>
<td>5</td>
<td>41</td>
<td>4-Me-C₆H₄</td>
<td>&quot;</td>
<td>70</td>
<td>86</td>
</tr>
<tr>
<td>6</td>
<td>42</td>
<td>4-MeO-C₆H₄</td>
<td>&quot;</td>
<td>71</td>
<td>52</td>
</tr>
<tr>
<td>7</td>
<td>54</td>
<td>C₆H₅</td>
<td>CO₂Me</td>
<td>57</td>
<td>95</td>
</tr>
<tr>
<td>8</td>
<td>64</td>
<td>4-Cl-C₆H₄</td>
<td>&quot;</td>
<td>72</td>
<td>90</td>
</tr>
<tr>
<td>9</td>
<td>65</td>
<td>4-Me-C₆H₄</td>
<td>&quot;</td>
<td>73</td>
<td>85</td>
</tr>
</tbody>
</table>

![Figure 14]

Figure 14 ¹H NMR Spectrum of Compound 71

The ¹H NMR spectrum (Fig. 14) of compound 71 showed the presence of terminal alkyne proton as a singlet at δ 2.48. The methoxy protons were apparent as a singlet at δ 3.83. The two set of methylene protons displayed characteristic two singlets at δ 4.25 and δ 4.32. The vinylic proton showed a singlet at δ 7.92. The aromatic protons displayed two doublets centered at δ 6.94 and 7.75 (f = 8.7 Hz).
Chapter II

Synthesis of E-trisubstituted alkenes

Figure 15: $^{13}$C NMR Spectrum of Compound 71

Its $^{13}$C NMR spectrum (Fig. 15) showed the terminal alkyne carbon resonance at δ 75.66. The representative signals at δ 57.45 and 70.35 were corresponding to the two methylene carbons. The quaternary alkyne carbon was apparent at δ 79.15. The vinylic carbon at the benzylic position was perceptible at δ 145.20. The characteristic signal for nitrile carbon appeared at δ 105.01. A signal at δ 118.12 was corresponds to the resonance of quaternary alkene carbon. The typical methoxy carbon signal was noticeable at δ 55.34. The compound also provided satisfactory micro analytical data. For complete spectral details of the new compounds, refer experimental section placed at the end of this Chapter.

1.6. Conclusion

The acetates of Baylis-Hillman adducts have been isomerised to trisubstituted alkene using Montmorillonite K10 clay under microwave irradiation with E selectivity and good yields. The efficiency of Montmorillonite K10 clay was compared with Fe$^{3+}$-ion exchanged Montmorillonite and Kaolinite clay. A one pot protection and isomerization of Baylis-Hillman adduct with trimethyl orthoformate using Montmorillonite K10 clay under microwave irradiation resulted in the formation of trisubstituted alkene was highly E-selective. The results showed that under microwave irradiation with the trimethyl orthoformate in presence of Montmorillonite K10 clay generates methoxide anion which then undergoes $S_N2$ and $S_N2'$ substitution reaction with Baylis-Hillman adducts. A variety of alcohols also undergoes $S_N2$ and $S_N2'$ substitution reaction with Baylis-Hillman adducts and on longer reaction time the $S_N2$ products undergo isomerization under Montmorillonite K10 clay giving E trisubstituted alkenes. Using the method various enyne ethers were prepared from the Baylis-Hillman adducts and propargyl alcohol.
2. Synthesis of 1H-Indenes and 1-Aryl Indenes

2.1. Definition of the Problem

The prime aim for the synthesis of enyne ethers (Section 1.4.4) was to utilize them in the construction of substituted tetrahydrofuran ring systems (and other oxacycles like tetrahydropyran and oxepanes), which are core structure of lignan natural products via vinyl radical cyclization methodology (Discussed in Chapter IV). If one looks at the structural features of the Natural Lignans, it is clear that most of them consist of highly electron rich substituted aromatic moieties. Hence, the nucleophilic substitution reaction with propargyl alcohol was aimed at Baylis-Hillman adducts having highly electron rich substitutions in the aromatic ring in order to synthesis corresponding enyne ethers for the synthesis of lignan core structures.

To achieve the conception, the preliminary experiment on the nucleophilic substitution of Baylis-Hillman adduct with highly electron rich aryl ring such as compound 74 with propargyl alcohol was attempted under previously optimized clay catalytic condition (Scheme 18). Surprisingly, we did not get the expected product but it yielded indene 75 as a single product. This unexpected product formation led us to explore the effect of Electron Withdrawing Groups at the olefin and Electron Releasing Groups at aryl part of Baylis-Hillman adducts and mechanistic aspects in detail. The investigations are also aimed at the importance of β-phenyl substituted, protected adducts for indene synthesis.

2.2. Result and Discussion

The results obtained during the studies on role of electron withdrawing and electron donating groups which are present in Baylis-Hillman adduct have been discussed in the following section.
2.2.1. Synthesis of 5,6-dialkoxy-1H-indene-2-carboxylic acid methyl ester

A systematic investigation on the reactivity of highly electron rich Baylis-Hillman adduct with propargyl alcohols was initiated with the adduct 74 under clay catalyst conditions. Thus, treatment of adduct 74 with propargyl alcohol in presence of montmorillonite K10 clay on heating in an oil bath at 80 °C for 12 h furnished only the indene 75 in 55% yield after column purification. The reaction did not yield the expected enyne ether 75a (Scheme 18) and a rationalization and discussion have been made on this observation later in this chapter. The formation of indene 75 from the adduct 74 under optimized clay catalytic condition could be explained based on literature known electrocyclic ring closure reaction.\(^\text{20}\)

![Scheme 18](image)

It should be noted that Basavaiah et al.\(^\text{20}\) have reported a similar transformations of Baylis-Hillman adducts into indenes using P₂O₅ as catalyst limited to substrates having ester substitution at activated alkene position. Since, our preliminary experiments showed that the electrocyclic ring closure undergone successfully in presence of clay catalyst without any solvent, we envisaged that this eco-friend method would be better replacement for the reported conventional procedure in the synthesis of indenes from Baylis-Hillman adducts (Scheme 19). Therefore heating the adduct 74 at 80 °C for 3 h furnished the indene 75 in 54% yield after purification. The formation of the indene 75 was established by comparing with literature report and it’s IR, NMR and HRMS analysis.

![Scheme 19](image)
Thus, the $^1$H NMR spectrum of compound 75 (Fig. 16) showed a singlet for the presence of methylene protons at $\delta$ 3.62. The vinylic proton was apparent at $\delta$ 7.64 as a singlet. The ester methyl protons appeared as a singlet at $\delta$ 3.82 and the aromatic methyl protons appeared as two singlets at $\delta$ 3.90 and 3.92.

As shown in Scheme 19, thermal heating at 80 °C for 3 h of the adduct 74 with the clay was essential in order to obtain the desired indene. To achieve a simple and faster reaction, without affecting the yield, we envisaged that a microwave irradiation of the mixture could be a simple and speedy method without affecting the yields of the products. Hence, as outlined in scheme 20, the microwave irradiation of the adduct 74 in the presence of clay without any solvent for 8 minutes afforded the desired indene 75 in 52% yield after column purification. To show the generality of the method, the other adducts 76 and 77 furnished the corresponding indenes 78 and 79 in good yield and the results are summarized in table 8.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Adduct</th>
<th>R</th>
<th>Indene</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>74</td>
<td>Methyl</td>
<td>75</td>
<td>52</td>
</tr>
<tr>
<td>2.</td>
<td>76</td>
<td>Ethyl</td>
<td>78</td>
<td>50</td>
</tr>
<tr>
<td>3.</td>
<td>77</td>
<td>-CH$_2$-</td>
<td>79</td>
<td>49</td>
</tr>
</tbody>
</table>
Basavaiah et al.\textsuperscript{20}, proposed a mechanism explaining that the reaction might proceed through a electrocyclic ring closure facilitated by alkoxy group at 3-position of aryl ring leading to the formation of indene derivative (Fig. 17). It should be noted that the role of 4-alkoxy substitution is not revealed by this mechanism. Hence, we arrived with an alternate mechanism where the role of 4-alkoxy substitution is incorporated and discussed later in this chapter. The substitution at activated alkene (ester Vs nitrile) also playing an important role in the product formation and was supported by the following experiments.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure17.png}
\caption{Electro cyclic ring closure mechanism for the formation of indene}
\end{figure}

\textbf{2.2.2. Synthesis of 5-Methoxy-1H-Indene-2-Carboxylic Acid Methyl Ester}

The cyclization of the 3-methoxy substituted adduct 80 under the condition described for compound 76, furnished only 12\% of the indene derivative 81 as shown in Scheme 20.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{scheme20.png}
\caption{Scheme 20}
\end{figure}

The structure of the compound was determined by spectral studies. The proton NMR of compound 81 (Fig. 18) showed the benzylic methylene protons appeared as a singlet at $\delta$ 3.6. The methoxy proton and ester methyl protons are appeared at $\delta$ 3.82. The vinylic proton was apparent at $\delta$ 7.64.
Its $^{13}\text{C}$ NMR spectrum (Fig. 19) showed the benzylic methylene carbon at $\delta$ 37.51. The ester methyl carbon and methoxy methyl carbon showed peaks at $\delta$ 51.35 and 55.18 respectively. The vinylic carbon at benzylic position was observed at $\delta$ 140.98. A typical carbonyl resonance was observed at $\delta$ 164.90. The methoxy attached quaternary aromatic carbon showed a signal at $\delta$ 158.99.

Hence, it is clear from the low yield of the reaction that there is a significant role of 4-alkoxy substitution in the aryl group during cyclization in addition to the electron release group at the 3\textsuperscript{rd} position.

2.2.3. Reactivity of Nitrile substituted Adduct

To compare and examine the difference in the reactivity of the Baylis-Hillman adduct bearing the nitrile substitution, we attempted an experiment with adduct 82 and propargyl alcohol. Surprisingly, in contrary with the result obtained from adduct 74; we obtained only the eneyne ether 83 in 70\% as represented in Scheme 21 and it should be noted that the reaction did not yield any indenes as product.
Similarly, the other adducts bearing nitrile group 84 and 85 furnished only the corresponding enyne ethers 86 and 87 in good yield (Table 9).

Table 9

<table>
<thead>
<tr>
<th>Entry</th>
<th>Adduct</th>
<th>R</th>
<th>Indene</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>82</td>
<td>Methyl</td>
<td>83</td>
<td>70</td>
</tr>
<tr>
<td>2.</td>
<td>84</td>
<td>Ethyl</td>
<td>86</td>
<td>69</td>
</tr>
<tr>
<td>3.</td>
<td>85</td>
<td>-CH₂⁻</td>
<td>87</td>
<td>65</td>
</tr>
</tbody>
</table>

The 

The experiments described above revealed the following points to be considered for a revised mechanism.

1. The necessity of electron releasing group at 4th position of the benzene ring to facilitate the ring closure and furnish the indene in good yield.
2. The difference in reactivity between CO₂CH₃ and CN substituted adducts is probably due to the difference in carbocation stabilization with respect to the aryl group (Fig. 21).

Hence, we propose a revised mechanism to explain the role of 4-methoxy group in the electrocyclic ring closure as detailed in Fig. 21. Further explanation on the stability of carbocation is discussed as follows.

![Figure 21: The revised mechanism for electrocyclic ring closure](image)

### 2.3. Significance of β-Phenyl Substituted Adducts

Literature reports showed that the Baylis-Hillman adducts which are not having electron releasing groups at 3<sup>rd</sup> and 4<sup>th</sup> position of the aromatic ring (i.e. unsubstituted adducts) will not undergo intramolecular Friedel-Craft reaction to afford the corresponding Indenes. The failure of intramolecular Friedel-Craft reaction is attributed due to destabilization of the allylic carbocation (88) in the case of presence of an electron withdrawing group. On the other hand, the electron release groups at the 3<sup>rd</sup> and 4<sup>th</sup> position of aryl ring could stabilize the carbocation (89) more to facilitate the electrocyclic ring closure. For details see Fig. 17, 21 and 22.

![Figure 22](image)
The Baylis-Hillman adducts which are not having electron releasing groups at the phenyl ring are not giving the corresponding indenes. To overcome this problem, we intended to study the reactivity of diaryl allylic carbocation (90) (Fig. 23) as intermediate in the facile synthesis of Indenes. As a result, by the use of intermediate (90), indenes can be synthesized even from the simple Baylis-Hillman adducts which not necessarily have electron releasing groups at phenyl ring via intramolecular Friedel-Crafts reactions. The intermediate 90 can be generated from the Baylis-Hillman adduct in presence of an acid, if the adduct is substituted with a phenyl group at β- position of the double bond. Thus, the suitable precursor for the construction of indenes would be the β-phenyl substituted Baylis-Hillman adducts (91) irrespective of any substitution at aryl ring. This can be visualized in Fig. 23.

\begin{figure}[h]
\centering
\includegraphics[width=0.7\textwidth]{figure23.png}
\caption{1-arylindene}$\rightleftharpoons$ 90
\end{figure}

\textbf{Figure 23}

\section{2.3.1. Synthesis of β-Phenyl Substituted Protected Adduct}

In order to generate the novel diaryl stabilized carbocation 90, following the literature known Heck coupling procedure\textsuperscript{21} for the preparation of β-phenyl substituted Baylis-Hillman adduct 93 was attempted from the acetate of adduct 92. The reaction failed to afford 93 instead it afforded compound 94.

The spectral analysis showed that the reported peak at δ 4.9 is not corresponding to the methine proton of the compound 93, rather corresponds to methylene protons of isomerized product 94 (compared with the reported value). The δ value for the methine proton of compound 93 would be more than 4.9 since the methine proton for the simple acylated adduct 92 appears at δ 6.6. Thus the reaction failed to afford 93 instead it afforded its isomerized product 94 as evidenced by the spectral studies (Scheme 22).
Hence, we developed a procedure for the preparation of the required β-phenyl substituted protected Baylis-Hillman adduct 95 by a three step reaction sequence viz.

1. Intermolecular Friedel-Crafts reactions of Baylis-Hillman adduct 54 with benzene catalyzed by Mont. K10 clay;
2. Allylic bromination followed by
3. Substitution reaction by the use of an alkoxide (methanol)

Thus, compound 95 was prepared in 65% overall yield as detailed in Scheme 23.

The key compound 95 was characterized by spectral and analytical means. Thus, the $^1$H NMR (Fig. 24) showed signal at δ 3.29 for the methoxy proton which is at the benzylic carbon. The ester methyl peak was noticed at δ 3.52. The representative signal of vinylic proton which is *trans* to the ester group was perceptible at δ 6.64. The benzylic methine proton showed a singlet at δ 5.06.
Its $^{13}$C NMR spectrum (Fig. 25) showed the methoxy attached benzylic carbon resonance at $\delta$ 83.73. The signals at $\delta$ 51.51 and 57.14 were corresponding to the ester methyl and methoxy methyl carbons respectively. The resonance of benzylic vinyl carbon was observed at $\delta$ 133.29. A typical carbonyl peak was visible at $\delta$ 168.76.

![Figure 25 $^{13}$C NMR Spectrum of Compound 95](image)

As shown, the procedure described above furnished only the Z-β-phenyl substituted protected adduct as a sole product as evidenced by the $^1$H NMR. We were also interested to study the effect of alkoxide substitution at allylic position with various alcohols (viz. ethanol, propargyl alcohol, homopropargyl alcohol, phenol and p-cresol). All of them selectively furnished the corresponding functionalized Z-β-phenyl products in good yield (Schemes 23 and 24). The results are summarized in Table 10.

<table>
<thead>
<tr>
<th>Entry</th>
<th>ROH</th>
<th>Product</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Methanol</td>
<td>95</td>
<td>82</td>
</tr>
<tr>
<td>2</td>
<td>Propargyl alcohol</td>
<td>97</td>
<td>80</td>
</tr>
<tr>
<td>3</td>
<td>Homo propargyl</td>
<td>98</td>
<td>76</td>
</tr>
<tr>
<td>4</td>
<td>Phenol</td>
<td>99 &amp; 100</td>
<td>74</td>
</tr>
<tr>
<td>5</td>
<td>p-cresol</td>
<td>101</td>
<td>65</td>
</tr>
</tbody>
</table>

The intermediate bromide derivative was isolated and characterized by spectral means. In the $^1$H NMR of compound 96 (Fig. 26), the benzylic proton at bromine attached carbon showed a singlet at $\delta$ 5.6 and the vinylic proton which is trans to the ester group signal was apparent at $\delta$ 6.92. A singlet at $\delta$ 3.53 showed the presence of ester methyl group.
The reaction of compound 94 with p-cresol and phenol is depicted in Scheme 24. The reaction with p-cresol afforded compound 101 and with phenol, it afforded an inseparable O- and C- substituted products 99 and 100 in good yield.

In the $^1$H NMR spectrum of compound 99 (Fig. 27), the ester methyl protons showed a singlet at $\delta$ 3.61. The benzylic methine proton appeared as a singlet at $\delta$ 6.15. The vinylic proton which is trans to the ester group was apparent as a singlet at $\delta$ 6.82. All other peaks were consistent with the assigned structure.

Its $^{13}$C NMR Spectrum (Fig. 28) showed the ester methyl carbon resonance at $\delta$ 51.35. The $sp^3$ benzylic tertiary carbon showed a characteristic signal at $\delta$ 79.88. The signal
at δ 134.44 was corresponds to the resonance of $sp^2$ benzyllic carbon and the carbonyl signal was visible at δ 168.03. All other peaks are in agreement with the assigned structure.

2.3.2. Synthesis of 1-Aryl Indenes

From the discussion made on the novel diaryl stabilized carbocation 90 (page 61), it is understood that irrespective of substitution on aryl ring of the Baylis-Hillman adduct for the synthesis of indene; a suitable precursor 95 was synthesized as detailed above. Thus, the reaction of β-phenyl substituted protected adduct 95 in the presence of Mont.K10 clay-microwave combination furnished the functionalized 1-aryl indene 102 in 90% yield after silica gel column purification. The reaction is shown in Scheme 25.

Figure 28 $^{13}$C NMR Spectrum of Compound 99

Figure 29 $^1$H NMR Spectrum of Compound 102
The structure of the product was assigned based on spectral studies. In the $^1$H NMR spectrum of the compound 102, the ester methyl protons appeared as a singlet at $\delta$ 3.69. In the indene ring, the proton at benzylic tertiary methine signal was perceptible as a singlet at $\delta$ 4.85. The vinylic proton was apparent at $\delta$ 7.79 (Fig. 29).

In $^{13}$C NMR spectrum, the quaternary benzylic carbon resonance was observed at $\delta$ 55.79. The benzylic vinylic carbon showed a signal at $\delta$ 141.43. The ester methyl carbon showed a representative signal at $\delta$ 51.43. The typical ester carbonyl was apparent at $\delta$ 164.44 (Fig. 30).

![Figure 30 $^{13}$C NMR Spectrum of Compound 102](image)

The precursor 94 was prepared by the reaction of Baylis-Hillman adduct 54 with excess of benzene in presence of Montmorillonite K10 clay at reflux for 6h. We found that the reaction also afforded a minor amount of dimerised product 103 along with the major desired product 94 as shown in Scheme 26.

![Scheme 26](image)

We have found that the side dimerised product 103 is readily convertible to compound 102 upon longer heating time (18 h) under Mont. K10 clay catalytic condition.
Similarly, as shown in Scheme 27, the compounds 54, 64, 65, 81 were converted to key compounds 94, 104, 105, 106 respectively under the optimized conditions.

![Scheme 27]

The results of this study are summarized in Table 11.

**Table 11**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ar</th>
<th>Product</th>
<th>Yield (%)</th>
<th>E/Z ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ph</td>
<td>94</td>
<td>70</td>
<td>95:5</td>
</tr>
<tr>
<td>2</td>
<td>4-Cl-Ph</td>
<td>104</td>
<td>72</td>
<td>95:5</td>
</tr>
<tr>
<td>3</td>
<td>4-Me-Ph</td>
<td>105</td>
<td>68</td>
<td>96:4</td>
</tr>
<tr>
<td>4</td>
<td>3-OMe-Ph</td>
<td>106</td>
<td>65</td>
<td>85:15</td>
</tr>
</tbody>
</table>

In this light, we successfully synthesized 1-aryl indenes 102 and 107 from adducts 54 and 64 respectively in one-pot without isolation and purification of intermediates as shown in Scheme 28. Accordingly, treatment of the adducts with benzene and Mont.K10 clay at reflux for 12hr, then after removal of benzene, treatment with NBS in CCl₄ reflux for 4 hr followed by treatment of methanol and continued the reflux for 2 hr. Finally after evaporating the solvents, microwave irradiation of the crude mixture in presence of the clay catalyst afforded the 1-aryl indenes in good yield.

![Scheme 28]

a) (i) Benzene, Mont.k10, reflux, 12h; (ii) 2 equi. NBS, CCl₄,4h,reflux; (iii) Methanol, reflux,2h; (iv) Mont.K10, microwave, 4min.
2.3.3. Recent Related Literature Reports on Cyclization

During 2004, a considerable work has been reported on intermolecular and followed by intramolecular bond formation on Baylis-Hillman adduct to form various interesting benzofused rings. In this line, Basavaiah and Satyanarayana\(^\text{22}\) have described a novel reaction involving tandem construction of C-N and C-C bonds via the simultaneous Ritter and Houben-Hoesch reactions on Baylis-Hillman adducts leading to a convenient, one-pot synthesis of 2-benzazepine derivatives. They also suggested that there would be a nitrilium ion as intermediate in this transformation as shown below and a representative example is given in Scheme 29.

![Nitrilium ion intermediate](image)

Subsequently, Basavaiah \textit{et al.}\(^\text{23}\) described a facile one-pot synthesis of 2-benzoxepines, from Baylis-Hillman adducts by the treatment with HCHO in the presence of concentrated H\(_2\)SO\(_4\), involving tandem construction of C-O and C-C bonds. They envisaged that the C-O bond could be constructed through a Prins-type reaction on Baylis-Hillman adducts and the C-C bond could be constructed simultaneously through a Friedel-Crafts reaction via a carbocation (oxonium ion), intermediate. An example is given in Scheme 30.

![Scheme 29](image)

![Scheme 30](image)
Kim and co-workers\textsuperscript{24} developed a facile synthetic method for 9-phenyl-7H-benzocycloheptene derivatives from the Baylis-Hillman adduct. A representative example is given in Scheme 31. They showed the reaction mechanism involved the selective formation of vinyl cation at the benzylic site following intramolecular Friedel-Crafts alkenylation.

![Scheme 31](image)

Later Kim et al.\textsuperscript{25} have reported a facile synthesis of dihydronaphthalenes from methyl 2-isobutenylcinnamate which were derived from the acetates of Baylis-Hillman adducts.

![Scheme 32](image)

Very recently Kim et al.\textsuperscript{26} have showed that the Baylis-Hillman derivative, prepared from its acetates and aniline, in acidic medium followed by a 1, 3-\textit{H} transfer could be protonated to generate the corresponding iminium ion, which then undergoes intramolecular Friedel-Crafts reaction to give 1-amino indenes. The proposed mechanism is given in Scheme 33.

![Scheme 33](image)
2.3.4. Scope of 1-Aryl Indene Frame works

The 1-aryl indene systems hold importance because it is found as core structure of many biologically active compounds. For example, the Endothelin receptor antagonists SB-209670 and SB-217242\(^2\) discovered by SmithKline Beecham, which possess three contiguous stereocenters upon an indan ring framework. The double bond functionality at our 1-ary-indene 102 could be used to introduce the aryl group at the 3\(^{rd}\) position, to show its potential applicability.

![Chemical structure of SB-209670 and SB-217242](attachment:image)

Molecules having 1-aryl indan frame work have been used as drug in neuronal network related disease. Indatraline is a potent psychoactive compound with high binding and inhibitory affinity for neuronal monoamine reuptake sites including the dopamine (DA) transporter and the serotonin (5HT) transporter.\(^2\) Some of the important molecules\(^2\) consist of 1-aryl indan frame work as core structures are listed in Fig. 31.

![Figure 31](attachment:image)

2.4. Conclusion

The Baylis-Hillman adduct having electron releasing group at 3\(^{rd}\) and 4\(^{th}\) position of aryl ring and ester group at the alkene undergoes electro cyclic ring closure under Montmorillonite K10 and microwave combination. Adduct with methoxy substitution at 3\(^{rd}\)
position also undergoes the electro cyclic ring closure. Adduct having nitrile substitution undergoes nucleophilic substitution with propargyl alcohol giving the desired enyne ethers. A revised mechanism for the formation of indenes has been discussed.

The Baylis-Hillman adducts having β-phenyl substitution and various alcohol protection were prepared through montmorillonite K10 clay mediated arylation, bromination followed by alkoxide substitution with Z selectivity.

The β-phenyl substituted adduct undergoes intramolecular Friedel-Crafts reaction under montmorillonite K10 and microwave combination giving 1-aryl-indenes in very good yield.
3. Experimental details

3.1. General Considerations

Melting points were recorded on a Buchi melting point apparatus and are uncorrected. NMR spectra were recorded at 300 ($^1$H) and 75($^{13}$C) MHz respectively on a Bruker Avance DPX-300 MHz NMR spectrometer. NMR spectra were obtained using chloroform-$d_2$ or a 7:3 mixture of CDCl$_3$ and CCl$_4$ as solvent unless otherwise mentioned. Chemical shifts are given in $\delta$-scale with tetramethyl silane as internal standard. Coupling constants ($J$) are reported in hertz (Hz). Mass spectra were recorded under EI/HRMS (at 5000) resolution using Auto Spec. mass spectrometer. IR spectra were taken on Nicolet (Impact 400D FT-IR) spectrophotometer or Bomem MB-series FT-IR spectrophotometer. Elemental analyses were performed on a Perkin Elmer-2400 Elemental Analyzer. Abbreviations used in $^1$H NMR are: s-singlet, d-doublet, dd-doublet of a doublet, brs-broad singlet, q-quartet and m-multiplet.

Analytical thin layer chromatography (TLC) was performed on glass plates coated with silica gel (Merck) containing 13% calcium sulphate as binder. Column chromatography was done using 100-200 mesh silica gel and appropriate mixture of petroleum ether (60-80 °C) and ethyl acetate for elution unless otherwise specified. The solvents were removed (under reduced pressure where necessary) using Heidolph or Buchi rotary evaporator. All solvents were distilled prior to use and reactions requiring dry conditions were carried out using dry solvents which were dried according to the literature procedure.

Extraction of the reaction mixtures were done with the appropriate organic solvents, the extraction was repeated with fresh solvent at least three times before the organic layers were combined. Washing of the combined organic layer was also repeated three times in each case (distilled water, 2 N hydrochloric acid, saturated sodium bicarbonate solution, brine, etc. as required by the procedure).

3.2. General Experimental Procedure for Isomerisation of Acetates of Baylis-Hillman adducts

A mixture of the acetates of Baylis-Hillman adduct (200 mg) and Montmorillonite K-10 (60 mg, 30% w/w of the adduct) was taken in a stoppered 25 ml conical flask and irradiated in the microwave oven (70% power mode) for 13 minutes. The mixture was cooled to room
temperature and treated with CH₂Cl₂ (10 mL). Montmorillonite K-10 clay was recovered by 
filtration and washed with CH₂Cl₂ (2 X 5 mL). The solvent was removed in vacuo and the 
crude mixture was purified by silica gel column chromatography using petroleum ether-
ethyl acetate (92:8) to give pure colourless isomerised products in 9:1 (E:Z) isomers as 
estimated by ¹H NMR (300 MHz) and ¹³C NMR (75 MHz).

All the compounds synthesized in this section are known in the literature. We compared 
the spectral data and found consistent with literature data(¹5). Typical data for selected 
compounds are given below.

Ethyl (2E)-2-Acetoxymethyl-3-phenylprop-2-enoate ¹⁰

Colourless oil; Yield: 74%; IR (neat) νmax: 2982, 1744, 1726, 1633 cm⁻¹.

```
  CO₂Et
 OAc

  H NMR: δ 1.35 (t, 3H, J= 7.1 Hz), 2.10(s, 3H), 4.31 (q, 2H, J= 7.1 Hz), 4.95 (s, 2H), 7.39 (s, 5H), 7.98 (s, 1H);
  ¹³C NMR: δ 14.25, 20.86, 59.22, 61.03, 126.77, 128.64, 129.37, 129.47, 134.23, 144.98, 166.57, 170.37.
```

Mass spectra m/z: 248 (M⁺); Elemental analysis: Calc for C₁₄H₁₆O₄: C, 67.73 %, H, 6.50 %.
Found: C, 67.60 %, H, 6.42 %.

(2E)-2-Acetoxymethyl-3-phenyl prop-2-enenitrile ²⁹(¹⁵)

Colourless oil; Yield: 68%; IR (neat) νmax: 3033, 2213, 1748, 1620 cm⁻¹.

```
  CN
 OAc

  H NMR: δ 2.16 (s, 3H), 4.82 (s, 2H), 7.23 (s, 1H), 7.45 (m, 3H), 7.79 (m, 2H).
  ¹³C NMR: δ 20.51, 65.02, 105.88, 117.04, 128.58, 128.86, 130.75, 132.16, 146.90, 169.76.
```

Mass spectra m/z: 201 (M⁺); Elemental analysis: Calc for C₁₂H₁₁NO₂: C, 71.63 %, H, 5.51 %.
Found: C, 71.60 %, H, 5.44 %

33. General Experimental Procedure for One-Pot Protection-Isomerisation Reaction

A mixture of the Baylis-Hillman adducts (200 mg) and Montmorillonite K-10 (60 mg, 
30% w/w of the adduct) and trimethyl orthoformate (125 mg, 1.15 mole) was taken in a
stopped 25 ml conical flask and irradiated in the microwave oven (100% power mode) for 20 minutes. The mixture was cooled to room temperature and treated with CH$_2$Cl$_2$ (10 ml). Montmorillonite K-10 clay was recovered by filtration and washed with CH$_2$Cl$_2$ (2 X 5 ml). The solvent was removed in vacuum and the crude mixture was purified by silica gel column chromatography using petroleum ether-ethyl acetate (99.8:0.2) to give pure colourless isomerised products in 99.1:0.9 (E: Z) isomers as estimated by $^1$H NMR (300 MHz) and $^{13}$C NMR (75 MHz). By reducing irradiation time (7 min. 100% PL) the -OMe protected compounds are obtained.

**Ethyl (2E)-2-methoxymethyl-3-phenyl prop-2-enoate 36**

Colourless oil; Yield: 74%; IR (neat) $v_{max}$: 3010, 1718, 1635 cm$^{-1}$.

$^1$H NMR: $\delta$ 1.36 (t, 3H, $J$= 7.1 Hz), 3.43 (s, 3H), 4.22 (s, 2H), 4.28 (q, 2H, $J$= 7.1 Hz), 7.35-7.52 (m, 5H), 7.9 (s, 1H).

$^{13}$C NMR: $\delta$ 14.36, 58.27, 60.94, 66.50, 128.51, 129.07, 129.29, 129.85, 134.87, 144.33, 167.45.

Mass spectra $m/z$: 220 (M$^+$); Elemental analysis: C$_{13}$H$_{16}$O$_3$: Cacl. C, 70.89 %, H, 7.32 %; Found: C, 70.85%, H, 7.30%

**(2E)-2-methoxymethyl-3-phenyl prop-2-enenitrile 45**

Colourless oil; Yield: 70%; IR (neat) $v_{max}$: 3022, 2208, 1626 cm$^{-1}$.

$^1$H NMR: 3.43 (s, 3H), 4.16 (s, 2H), 7.14 (s, 1H), 7.14-7.42 (m, 3H), 7.75 -7.78 (m, 2H).

$^{13}$C NMR: $\delta$ 58.25, 73.46, 108.04, 117.41, 128.83, 128.93, 130.53, 132.95, 144.45.

Mass spectra $m/z$: 173 (M$^+$); Elemental analysis: C$_{11}$H$_{11}$NO: Cacl. C, 76.28 %, H, 6.40 %, N, 8.09%; Found: C, 76.23%, H, 6.33 %, N, 8.05%

**Ethyl (2E)-2-methoxymethyl-3-(4-chlorophenyl) prop-2-enoate 47**

Colourless oil; Yield: 62%; IR (neat) $v_{max}$: 3012, 1715, 1638 cm$^{-1}$.
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**1H NMR:** δ 1.35 (t, 3H, J=7.1 Hz), 3.42 (s, 3H), 4.18 (s, 2H), 4.29 (q, 2H, J=7.1Hz), 7.37 (d, 5H, J=8.5 Hz), 7.47 (d, 2H, J=8.5 Hz), 7.9 (s, 1H).

**13C NMR:** δ 14.21, 58.29, 61.17, 66.30, 128.50, 129.42, 131.12, 133.17, 135.41, 143.05, 167.32.

**Mass spectra m/z:** 254 (M⁺); **HRMS:** Cacld for C₁₃H₁₅ClO₃: 254.0710; Found: 254.0701.

(2E)-2-methoxymethyl-3-(4-chlorophenyl) prop-2-enenitrile 48

Colourless oil; **Yield:** 52%; **IR (neat)** νmax: 3021, 2210, 1634 cm⁻¹.

**1H NMR:** δ 3.44 (s, 3H), 4.15 (s, 2H), 7.10 (s, 1H), 7.50 (d, 2H, J=8.4 Hz), 7.80 (d, 2H, J=8.4 Hz).

**13C NMR:** δ 58.31, 73.16, 108.52, 117.15, 128.98, 130.00, 131.22, 136.36, 142.96.

**Mass spectra m/z:** 208 (M⁺); **HRMS:** Cacld for C₁₁H₁₀ClNO: 207.0451; Found: 207.0444.

Ethyl (2E)-2-methoxymethyl-3-(4-methylphenyl) prop-2-enoate 49

Colourless oil; **Yield:** 70%; **IR (neat)** νmax: 3010, 1720, 1638 cm⁻¹.

**1H NMR:** δ 1.35 (t, 3H, J=7.1 Hz), 2.39 (s, 3H), 3.43 (s, 3H), 4.21 (s, 2H), 4.32 (q, 2H, J=7.1 Hz), 7.20 (d, 5H, J=8.0 Hz), 7.30 (d, 2H, J=8.0 Hz), 7.9 (s, 1H);

**13C NMR:** δ 14.36, 21.22, 58.27, 60.95, 66.56, 125.74, 129.37, 129.52, 131.34, 139.87, 144.37, 167.45.

**Mass spectra m/z:** 234 (M⁺); **Elemental analysis:** C₁₄H₁₈O₃: Cacld. C, 71.77 %, H, 7.74 %; Found: C, 71.72%, H, 7.70 %

(2E)-2-methoxymethyl-3-(4-methylphenyl) prop-2-enenitrile 50

Colourless oil; **Yield:** 64%; **IR (neat)** νmax: 3021, 2212, 1624 cm⁻¹.

**1H NMR:** δ 43 (s, 3H), 1.16 (s, 2H), 7.10 (s, 1H), 7.24 (d, 2H, J=8.2 Hz), 7.69 (d, 2H, J=8.2 Hz).
$^{13}$C NMR: $\delta$ 8.24, 73.45, 104.04, 117.41, 129.22, 129.64, 129.92, 141.76, 146.35, 170.20.

Mass spectra $m/z$: 187 (M+); Elemental analysis: C$_{12}$H$_{13}$NO: Cacl. C, 76.98 %, H, 7.00 %, N, 7.48%; Found: C, 76.90%, H, 6.92 %, N, 7.41%

(2E)-2-methoxymethyl-3-(4-methoxyphenyl) prop-2-enenitrile 51

Colourless oil; Yield: 77%; IR (neat) $\nu_{max}$ 3015, 2214, 1622 cm$^{-1}$.

$^1$H NMR: 3.43 (s, 3H), 3.8 (s, 2H), 6.95 (d, 2H $J=8.8$ Hz), 7.06 (s, 1H), 7.75 (d, 2H, $J=8.8$ Hz).

$^{13}$C NMR: $\delta$ 55.34, 58.23, 73.86, 104.95, 114.34, 118.14, 125.82, 130.93, 144.48, 161.51.

Mass spectra $m/z$: 203 (M+); Elemental analysis: C$_{12}$H$_{13}$NO$_2$: Cacl. C, 70.92%, H, 6.45 %, N, 6.89%; Found: C, 70.90%, H, 6.40 %, N, 6.80%

Ethyl (2E)-2-methoxymethyl-3-naphth-2-yl prop-2-enoate 52

Colourless oil; Yield: 69%; IR (neat) $\nu_{max}$ 3005, 1726, 1630 cm$^{-1}$.

$^1$H NMR: 1.35 (t, 3H $J=7.1$ Hz), 3.43 (s, 3H), 3.8 (s, 3H), 4.32 (q, 2H $J=7.1$ Hz), 7.41-7.56 (m, 4H), 7.81-7.84 (m, 3H), 8.2 (s, 1H).

$^{13}$C NMR: $\delta$ 14.36, 58.20, 60.72, 73.45, 124.14, 124.92, 126.06, 126.38, 126.96, 128.29, 128.96, 129.31, 131.01, 131.23, 133.05, 143.12, 166.16.

Mass spectra $m/z$: 270 (M+); Elemental analysis: C$_{17}$H$_{18}$O$_3$: Cacld. C, 75.53 %, H, 6.71 % Found: C, 75.50%, H, 6.68%

(2E)-2-methoxymethyl-3-naphth-2-yl prop-2-enenitrile 53

Colourless oil; Yield: 63%; IR (neat) $\nu_{max}$: 3018, 2212, 1620 cm$^{-1}$.

$^1$H NMR: 3.43 (s, 2H), 4.16 (s, 2H), 7.52-7.6 (m, 4H), 7.81-7.92 (m, 4H).

$^{13}$C NMR: $\delta$ 58.24, 73.43, 105.85, 117.80, 124.52, 125.01,
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126.43, 126.93, 128.50, 129.05, 129.85, 131.31, 131.62, 133.21, 146.15.

Mass spectra $m/z$: 223 (M$^+$); Elemental analysis: C$_{15}$H$_{13}$NO: Cacl'd. C, 80.69 %, H, 5.87 %, N, 6.27%; Found: C, 80.65%, H, 5.82%, N, 6.21 %

3.4. General Procedure for the Reaction of Baylis-Hillman Adducts with Various Alcohols

A slurry made of the adduct (150 mg), propargyl alcohol (2.5 equiv.) and Montmorillonite K10 clay (60% w/w) was taken in a 50ml RB flask and was tightly closed and kept in an oil bath (85 °C) for 24h. Then the flask was cooled to room temperature and 20mL of CH$_2$Cl$_2$ was added and filtered through a celite pad. The clay was repeatedly washed with (3 x 10mL) CH$_2$Cl$_2$ and the combined solvent was removed under vacuum. The crude mixture was purified through a column of silica gel using 98:2 mixture of hexane: ethyl acetate afforded isomerised compound with high $E$-selectivity.

Methyl (2E)-3-phenyl-2-[(prop-2-ynyloxy) methyl] acrylate 57

Colourless oil; Yield: 95%; IR (neat) $\nu_{max}$: 3300, 2100, 1715, 1620cm$^{-1}$.

$^1$H NMR: δ 2.42 (t, 1H, $J$= 2.34 Hz), 3.84 (s, 3H), 4.26 (d, 2H, $J$= 2.34 Hz), 4.39 (s, 2H), 7.32 (m, 3H), 7.53 (m, 2H), 7.92 (s, 1H); $^{13}$C NMR: δ 52.26, 58.08, 64.25, 74.70, 79.63, 128.51, 18.54, 129.55, 129.99, 134.51, 145.27, 167.98.

Mass Spectra $m/z$: 230(M$^+$); Elemental Analysis: C$_{14}$H$_{14}$O$_3$: Cacl'd. C, 73.03 %, H, 6.13 %; Found: C, 73.00%, H, 6.12%.

Ethyl (2E)-2-[(allyloxy) methyl]-3-phenylacrylate 58

Colourless oil; Yield: 94%; IR (neat) $\nu_{max}$: 1712, 1617cm$^{-1}$.

$^1$H NMR: δ 1.36 (t, 3H, $J$ = 7.11 Hz), 4.15 (d, 2H, $J$ = 5.67 Hz), 4.27 (s, 2H), 4.30 (q, 2H, $J$ = 7.11 Hz), 5.2 (dd, 2H, $J$ = 17.19 and 10.23 Hz), 5.98 (m, 1H), 7.33 (m, 3H), 7.52 (m, 2H), 7.89 (s, 1H); $^{13}$C NMR: δ 14.29, 61.09, 64.07, 71.60, 117.11, 128.36, 128.77, 129.18, 129.76, 134.67, 134.71, 144.4, 167.72.
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Mass spectra m/z: 246 (M⁺); Elemental analysis: C₁₅H₁₈O₃: Cacld. C, 73.15 %, H, 7.37 %; Found: C, 73.10 %, H, 7.32 %.

Methyl (2E)-2-[(allyloxy) methyl]-3-phenylacrylate 59

Colourless oil; Yield: 95%; IR (neat) νₘₐₓ: 2990, 1710, 1615 cm⁻¹.

\[ \text{H NMR: } \delta \ 3.83 \ (s, \ 3H), \ 4.09 \ (d, \ 2H, \ J = 5.67 \text{ Hz}), \ 4.27 \ (s, \ 2H), \ 5.16 \ (d, \ 1H, \ J = 10.41 \text{ Hz}), \ 5.28 \ (\text{ABq, } 1H, \ J = 1.55 \text{ and } 17.19 \text{ Hz}), \ 5.97 \ (m, \ 1H), \ 7.38 \ (m, \ 3H), \ 7.53 \ (m, \ 2H), \ 7.89 \ (s, \ 1H). \]

\[ \text{¹⁳C NMR: } \delta \ 51.94, \ 64.07, \ 71.60, \ 117.11, \ 128.36, \ 128.77, \ 129.18, \ 129.76, \ 134.67, \ 134.71, \ 144.44, \ 167.72. \]

Mass spectra m/z: 232 (M⁺); Elemental analysis: C₁₄H₁₆O₃: Cacld. C, 72.39 %, H, 6.94 %; Found: C, 72.35 %, H, 6.98 %.

Methyl (2E)-2-[(octyloxy) methyl]-3-phenylacrylate 60

Colourless oil; Yield: 97%; IR (neat) νₘₐₓ: 2991, 1718, 1622 cm⁻¹.

\[ \text{H NMR: } \delta \ 0.88 \ (t, \ 3H, \ J = 6.93 \text{ Hz}), \ 1.25 \ (m, \ 10H), \ 1.63 \ (m, \ 2H), \ 3.54 \ (t, \ 2H, \ J = 6.54 \text{ Hz}), \ 3.83 \ (s, \ 3H), \ 4.26 \ (s, \ 2H), \ 7.39 \ (m, \ 3H), \ 7.53 \ (m, \ 2H), \ 7.9 \ (s, \ 1H). \]

\[ \text{¹³C NMR: } \delta \ 14.14, \ 26.33, \ 27.71, \ 29.17, \ 29.35, \ 29.47, \ 29.77, \ 51.90, \ 64.81, \ 70.91, \ 128.29, \ 128.52, \ 129.36, \ 129.96, \ 134.88, \ 144.58, \ 167.42. \]

Mass spectra m/z: 304 (M⁺).

Methyl (2E)-2-(isopropoxymethyl)-3-phenylacrylate 61

Colourless oil; Yield: 95%; IR (neat) νₘₐₓ: 2985, 1716, 1620 cm⁻¹.

\[ \text{H NMR: } \delta \ 1.24 \ (d, \ 6H, \ J = 6.12 \text{ Hz}), \ 3.72 \ (\text{sextet, } 1H, \ J = 6.12 \text{ Hz}), \ 3.83 \ (s, \ 3H), \ 4.27 \ (s, \ 2H), \ 7.38 \ (m, \ 3H), \ 7.58 \ (m, \ 2H), \ 7.9 \ (s, \ 1H); \text{¹³C NMR: } \delta \ 21.04, \ 21.51, \ 51.08, \ 61.42, \ 70.81, \ 127.41, \ 128.13, \ 128.25, \ 128.86, \ 133.87, \ 143.28, \ 167.23. \]

Mass spectra m/z: 234 (M⁺); Elemental analysis: C₁₄H₁₈O₃: Cacld. C, 71.77 %, H, 7.74 %; Found: C, 71.85 %, H, 7.70 %.
(2E)-2-[(octyloxy) methyl]-3-phenylacrylonitrile 62

Colourless oil; **Yield:** 98%; **IR** (neat) $v_{\text{max}}$: 2982, 2214, 1622 cm$^{-1}$

$^1$H NMR: $\delta$ 0.98 (t, 3H, $J = 6.9$ Hz), 1.3 (m, 10H), 1.7 (m, 2H), 3.62 (t, 2H, $J = 6.52$ Hz), 4.3 (s, 2H), 7.24 (s, 1H), 7.47 (m, 3H), 7.85 (m, 2H).

$^{13}$C NMR: $\delta$ 14.09, 22.62, 26.10, 29.21, 29.36, 29.58, 31.78, 71.03, 71.73, 106.03, 126.89, 128.65, 128.78, 128.91, 130.38, 143.83.

Ethyl (2E)-3-phenyl-2-[(prop-2-ynyloxy) methyl] acrylate 66

Colourless oil; **Yield:** 92%; **IR** (neat) $v_{\text{max}}$: 3300, 2124, 1720, 1622 cm$^{-1}$

$^1$H NMR: $\delta$ 1.36 (t, 3H, $J = 7.11$ Hz), 2.4 (t, 1H, $J = 2.34$ Hz), 4.26 (d, 2H, $J = 2.34$ Hz), 4.30 (q, 2H, $J = 7.11$ Hz), 4.37 (s, 2H), 7.38 (m, 3H), 7.55 (m, 2H), 7.89 (s, 1H).

$^{13}$C NMR: $\delta$ 14.29, 58.05, 61.09, 64.21, 74.64, 79.69, 128.30, 128.50, 129.44, 129.95, 134.58, 144.90, 167.45.

Mass spectra $m/z$: 244 (M$^+$); **Elemental analysis:** C$_{13}$H$_{16}$O$_3$: Cacl. C, 73.75 %, H, 6.60 %; Found: C, 73.80%, H, 6.63%.

(2E)-3-phenyl-2-[(prop-2-ynyloxy) methyl] acrylonitrile 67

Colourless oil; **Yield:** 90%; **IR** (neat) $v_{\text{max}}$: 3300, 2200, 2112, 1620 cm$^{-1}$

$^1$H NMR: $\delta$ 2.48 (s, 1H), 4.25 (s, 2H), 4.32 (s, 2H), 7.18 (s, 1H), 7.41 (m, 3H), 4.77 (m, 2H).

$^{13}$C NMR: $\delta$ 57.47, 70.35, 75.67, 79.10, 108.17, 117.01, 128.93, 129.10, 130.53, 132.95, 144.45.

Mass spectra $m/z$: 197 (M$^+$); **Elemental analysis:** C$_{13}$H$_{11}$NO: Cacl. C, 79.16 %, H, 5.62, N, 7.10 %; Found: C, 79.15%, H, 5.60% N, 7.13 %.

Ethyl (2E)-3-(4-chlorophenyl)-2- [(prop-2-ynyloxy) methyl] acrylate 68

Colourless oil; **Yield:** 91%; **IR** (neat) $v_{\text{max}}$: 3305, 2150, 1712, 1622 cm$^{-1}$.
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1H NMR: δ 1.36 (t, 3H, J = 7.11 Hz), 2.4 (t, 1H, J = 2.34 Hz), 4.25 – 4.32 (m, 4H), 4.35 (s, 2H), 7.35 (d, 2H, J = 8.4 Hz), 7.5 (d, 2H, J = 8.4 Hz), 7.83 (s, 1H).

13C NMR: δ 14.29, 58.10, 61.12, 64.25, 74.61, 79.64, 128.77, 128.40, 130.98, 13.20, 135.45, 143.12, 167.42.

Mass spectra m/z: 278 (M+); HRMS: Cacld for C15H15ClO3: 278.0710; Found: 278.0701.

(2E)-3-(4-chlorophenyl)-2-[(prop-2-ynyloxy) methyl] acrylonitrile 69

Colourless oil; Yield: 89%; IR (neat) νmax: 3302, 2210, 2140 cm⁻¹.

1H NMR: δ 2.47 (t, 1H, J = 2.34 Hz), 4.28 (s, 2H), 4.30 (s, 2H), 7.19 (s, 1H), 7.38 (d, 2H, J = 8.4 Hz), 7.5 (d, 2H, J = 8.4 Hz);

13C NMR: δ 57.45, 70.32, 75.66, 79.10, 108.52, 117.12, 128.98, 130.02, 131.23, 136.36, 143.06.

Mass spectra m/z: 231 (M+); HRMS: Cacld for C13H10ClO3: 231.0451; Found: 231.0450.

(2E)-3-(4-Methylphenyl)-2-[(prop-2-ynyloxy) methyl] acrylonitrile 70

Colourless oil; Yield: 86%; IR (neat) νmax: 3300, 2208, 2145 cm⁻¹.

1H NMR: δ 2.34 (s, 3H), 2.42 (t, 1H, J = 2.3 Hz), 4.25 (s, 2H), 4.32 (s, 2H), 7.18 (s, 1H), 7.12 (d, 2H, J = 7.8 Hz), 7.22 (d, 2H, J = 7.8 Hz);

13C NMR: δ 42.10, 57.45, 70.40, 75.62, 79.10, 108.18, 117.04, 127.58, 129.00, 135.12, 138.00, 144.19.

Mass spectra m/z: 211 (M+).

(2E)-3-(4-Methoxyphenyl)-2-[(prop-2-ynyloxy) methyl] acrylonitrile 71

Colourless oil; Yield: 72%; IR (neat) νmax: 3300, 2210, 2100, 1600 cm⁻¹.

1H NMR: δ 2.48 (s, 1H), 3.83 (s, 3H), 4.25 (s, 2H), 4.32 (s, 2H), 7.00 (d, 2H, J = 8.8 Hz), 7.09 (s, 1H), 7.74 (d, 2H, J = 8.8 Hz).

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\(^{13}\text{C NMR}\): δ 55.34, 57.45, 70.35, 75.66, 79.15, 105.01, 114.34, 118.12, 125.82, 130.94, 144.50, 161.52.

**Mass Spectra m/z**: 227(M\(^+\))

Methyl (2E)-3-(4-chlorophenyl)-2-[(prop-2-ynyloxy) methyl] acrylate 72

Colourless oil; **Yield**: 90%; **IR** (neat) \(v_{\text{max}}\): 3300, 2100, 1710, 1620 cm\(^{-1}\).

1\(^{H}\) NMR: δ 2.42 (t, 1H, \(J = 2.3\) Hz), 3.85 (s, 3H), 4.28 (d, 2H, \(J = 2.34\) Hz), 4.4 (s, 2H), 7.35 (d, 2H, \(J = 8.4\) Hz), 7.5 (d, 2H, \(J = 8.4\) Hz), 7.84 (s, 1H).

1\(^{3}\text{C NMR}\): δ 52.08, 58.10, 64.20, 74.68, 79.64, 128.75, 129.42, 131.12, 133.17, 135.41, 143.03, 167.96.

**Mass Spectra m/z**: 264 (M\(^+\)); **HRMS**: Calcd for C\(_{14}\)H\(_{13}\)ClO\(_3\): 264.0553; Found: 264.0550.

Methyl (2E)-3-(4-Methylphenyl)-2-[(prop-2-ynyloxy) methyl] acrylate 73

Colourless oil; **Yield**: 85%; **IR** (neat) \(v_{\text{max}}\): 3300, 2100, 1710, 1620 cm\(^{-1}\).

1\(^{H}\) NMR: δ 2.32 (s, 3H), 2.42 (t, 1H, \(J = 2.3\) Hz), 3.83 (s, 3H), 4.25 (d, 2H, \(J = 2.3\) Hz), 4.39 (s, 2H), 7.14 (d, 2H, \(J = 7.8\) Hz), 7.26 (d, 2H, \(J = 7.8\) Hz), 7.9 (s, 1H).

1\(^{3}\text{C NMR}\): δ 42.08, 52.24, 58.10, 64.26, 74.68, 79.60, 127.80, 129.04, 134.54, 135.20, 138.10, 145.22, 167.89.

**Mass Spectra m/z**: 244 (M\(^+\)); **Elemental Analysis**: C\(_{15}\)H\(_{16}\)O\(_3\): Calcd. C, 73.75 %; H, 6.60 %; Found: C, 73.70%, H, 6.57%.

3-(3,4-Dimethoxy-phenyl)-2-prop-2-ynyloxy methyl-acrylonitrile 83

White Solid; **M.P**: 70-72 °C; **Yield**: 70%; **IR** (neat) \(v_{\text{max}}\): 3295, 2215, 2111 cm\(^{-1}\).

1\(^{H}\) NMR: δ 2.49 (t, 1H, \(J = 2.25\) Hz), 3.92 (s, 6H), 4.25 (d, 2H, \(J = 2.25\) Hz), 4.31 (s, 2H), 6.87 (d, 1H, \(J = 8.35\) Hz), 7.09 (s, 1H), 7.22 (d, 1H, \(J = 8.35\) Hz), 7.60 (s, 1H).

1\(^{3}\text{C NMR}\): δ 55.86, 55.89, 57.24, 70.58, 75.51, 78.74, 104.12, 110.59, 110.83, 118.11, 124.17, 125.90, 145.51, 151.41.

**Mass Spectra m/z**: 257 (M\(^+\)); **HRMS**: Calcd for C\(_{15}\)H\(_{15}\)NO\(_3\): 257.1052; Found: 257.1048.
3-(3,4-Diethoxy-phenyl)-2-prop-2-ynyloxy methyl-acrylonitrile 86

White Solid; M.P: 62-64 °C; Yield: 69%; IR (neat) ν<sub>max</sub>: 3298, 2215, 2110 cm<sup>-1</sup>.

![3-(3,4-Diethoxy-phenyl)-2-prop-2-ynyloxy methyl-acrylonitrile 86](image)

<sup>1</sup>H NMR: δ 1.49 (m, 6H), 2.48 (t, 1H, J = 2.2 Hz), 4.12 (m, 4H), 4.25 (d, 2H, J = 2.2 Hz), 4.30 (s, 2H), 6.88 (d, 1H, J = 8.3 Hz), 7.09 (s, 1H), 7.22 (d, 1H, J = 8.3 Hz), 7.60 (s, 1H).

<sup>13</sup>C NMR: δ 14.70, 57.25, 64.52, 10.56, 75.51, 78.74, 104.14, 110.57, 110.84, 118.11, 124.18, 125.92, 145.51, 151.42.

3-Benzol [1,3]dioxo-5-yl-2-prop-2-ynyloxymethyl-acrylonitrile 87

White Solid; M.P: 84-86 °C; Yield: 65%; IR (neat) ν<sub>max</sub>: 3295, 2215 cm<sup>-1</sup>.

![3-Benzol [1,3]dioxo-5-yl-2-prop-2-ynyloxymethyl-acrylonitrile 87](image)

<sup>1</sup>H NMR: δ 2.48 (t, 1H, J = 2.2 Hz), 4.25 (d, 2H, J = 2.2 Hz), 4.31 (s, 2H), 5.99 (s, 2H), 6.86 (d, 1H, J = 8.3 Hz), 7.08 (s, 1H), 7.2 (d, 1H, J = 8.3 Hz), 7.57 (s, 1H).

<sup>13</sup>C NMR: δ 57.25, 70.56, 5.50, 78.72, 101.39, 104.10, 110.54, 110.70, 118.11, 124.14, 125.88, 145.50, 151.42.

Mass Spectra m/z: 241 (M<sup>+</sup>); HRMS: Cacld for C<sub>14</sub>H<sub>11</sub>N<sub>2</sub>O<sub>2</sub>: 241.0739; Found: 241.0748.

3.5. General Experimental Procedure for Synthesis of Indenes

A mixture of adduct (150mg) and Montmorillonite K-10 (45mg, 30% w/w of the adduct) was taken in a 25ml conical flask and irradiated in microwave oven for 8min. The surface of clay became green in colour. The mixture was cooled to room temperature and treated with 5ml of CH<sub>2</sub>Cl<sub>2</sub>. The solvent was removed using vacuo and the crude mixture was purified through silicagel column, using petroleum ether and Ethyl acetate (95:5) to give the indene as colourless solid.

*All the compounds synthesized in this section are known in the literature. We compared the spectral data and found consistent with literature data*<sup>(29)</sup>. Typical data for selected compounds are given below.

5,6-Dimethoxy-1H-indene-2-carboxylic acid methyl ester 75<sup>(29)</sup>

White Solid; M.P: 106-107 °C; Yield: 52%; IR (neat) ν<sub>max</sub>: 1700, 1610 cm<sup>-1</sup>.
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**1H NMR:** δ 3.62 (d, 2H, J = 1.5 Hz), 3.82 (s, 3H), 3.90 (s, 3H), 3.92 (s, 3H), 7.02 (s, 1H), 7.06 (s, 1H), 7.64 (s, 1H).

**13C NMR:** δ 38.39, 51.42, 56.16, 106.20, 107.75, 135.42, 138.37, 141.42, 148.85, 149.92, 165.00.

**Mass Spectra m/z:** 234 (M⁺); **HRMS:** Cacl for C₁₃H₁₄O₄: 234.0892; Found: 234.0898.

**5-Methoxy-1H-indene-2-carboxylic acid methyl ester 81**

White Solid; **M.P:** 86-88 °C; Yield: 12%; **IR** (neat) ν_max: 1721 cm⁻¹.

**1H NMR:** δ 3.6 (s, 2H), 3.82 (s, 6H), 6.86(1H, dd, J= 8.26 and 2.35 Hz), 7.0 (d, 1H, J= 2.35 Hz), 7.36 (d, 1H, J= 8.26 Hz), 7.64 (s, 1H).

**13C NMR:** δ 37.51, 51.35, 55.18, 107.86, 114.24, 124.57, 136.76, 138.07, 140.98, 143.79, 158.99, 164.90.

**Mass Spectra m/z:** 204 (M⁺); **HRMS:** Cacl for C₁₂H₁₂O₃: 204.0786; Found: 204.0794.

**3.6. General Procedure for Synthesis of 2-Benzyl-3-aryl acrylic acid methyl esters**

A mixture of Baylis-Hillman adduct (200 mg) and Montmorillonite K10 (100mg) in 5 ml of benzene was taken in 25 mL round bottom flask. The mixture was refluxed at 80 °C for 18 hr. The mixture was cooled to room temperature and clay was filtered out using cindered crucible. The solvent was removed under reduced pressure and the crude mixture was purified through silica gel column, using petroleum ether and Ethyl acetate (95:5) to give the phenylated product as colourless liquid.

**2-Benzyl-3-phenyl-acrylic acid methyl ester 94**

Yield: 70%; **IR** (neat) ν_max: 1712, 1632 cm⁻¹.

**1H NMR:** δ 3.6 (s, 2H), 3.82 (s, 6H), 6.86(1H, dd, J= 8.26 and 2.35 Hz), 7.0 (d, 1H, J= 2.35 Hz), 7.36 (d, 1H, J= 8.26 Hz), 7.64 (s, 1H).

**13C NMR:** δ 37.51, 51.35, 55.18, 107.86, 114.24, 124.57, 136.76, 138.07, 140.98, 143.79, 158.99, 164.90.

**Mass Spectra m/z:** 266 (M⁺).
3.7. General Procedure for Synthesis of 2-(Alkoxy-phenyl-methyl)-3-phenyl acrylic acid methyl esters

A mixture of 2-Benzyl-3-phenyl-acrylic acid methyl ester 94 (200 mg), NBS (2 equi.) and 10 mg of AIBN in 6 ml of carbon tetrachloride was taken in 25 ml round bottom flask. The mixture was refluxed at 80 °C for 4 hr. The corresponding alcohol (4 equi.) was added into the reaction mixture and the reflux was continued until complete disappearance of the brominated compound (TLC). The solvent was removed under reduced pressure and the crude mixture was purified through silica gel column, using petroleum ether and Ethyl acetate to give the protected phenylated adduct as colourless liquid.

2-(Methoxy-phenyl-methyl)-3-phenyl-acrylic acid methyl ester 95

Yield: 82%; IR (neat) $\nu_{\text{max}}$: 1722 cm$^{-1}$.

$^1$H NMR: $\delta$ 3.29 (s, 3H), 3.52 (s, 3H), 5.06 (s, 1H), 6.64 (s, 1H), 7.15-7.32 (m, 10H).

$^{13}$C NMR: $\delta$ 51.51, 57.14, 83.73, 127.36, 128.03, 128.14, 128.31, 133.29, 134.96, 135.23, 138.64, 168.76.

Mass Spectra $m/z$: 282 (M$^+$); HRMS: Cacl for C$_{18}$H$_{18}$ClO$_3$: 282.1256; Found: 282.1259.

3-Phenyl-2-(phenyl-prop-2-ylnloxy-methyl)-acrylic acid methyl ester 97

Yield: 80%; IR (neat) $\nu_{\text{max}}$: 3298, 1722 cm$^{-1}$.

$^1$H NMR: $\delta$ 2.43 (t, 1H, $J$= 2.2 Hz), 3.56 (s, 3H), 4.10 and 4.24 (d AB, 2H, $J$= 15.7 and 2.2 Hz), 5.52 (s, 1H), 6.86 (s, 1H), 7.24-7.42 (m, 10H).

$^{13}$C NMR: $\delta$ 51.56, 56.03, 74.92, 79.38, 80.40, 127.87, 128.17, 128.23, 128.34, 128.42, 128.51, 134.05, 134.57, 135.42, 138.14, 168.32.

Mass Spectra $m/z$: 306 (M$^+$); HRMS: Cacl for C$_{20}$H$_{18}$O$_3$: 306.1256; Found: 306.1262.

2-(But-3-ynloxy-phenyl-methyl)-3-phenyl-acrylic acid methyl ester 98

Yield: 76%; IR (neat) $\nu_{\text{max}}$: 3300, 1722 cm$^{-1}$. 
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*1H NMR:* \( \delta 1.85 \) (t, 1H, \( J= 2.5 \) Hz), 2.43 (m, 2H), 3.5 (s, 3H), 3.6 (m, 2H), 5.2 (s, 1H), 6.66 (s, 1H), 7.26 (m, 10H)

*13C NMR:* \( \delta 20.63, 52.18, 68.22, 70.30, 81.80, 82.91, 128.28, 128.82, 128.86, 129.06, 129.14, 134.18, 135.92, 136.18, 139.58, 169.27. \)

**Mass Spectra** \( m/z: 320 (M^+); \) HRMS: Cacld for \( \text{C}_{14}\text{H}_{13}\text{ClO}_3: 320.1412; \) Found: 320.1407.

2-(Phenoxy-phenyl-methyl)-3-phenyl-acrylic acid methyl ester 99

White Solid; **M.P:** 86-88 °C; **Yield:** 25%; **IR** (neat) \( \nu_{max}: 1722, 1631 \text{ cm}^{-1}. \)

*1H NMR:* \( \delta 3.61 \) (s, 3H), 6.15 (s, 1H), 6.82 (s, 1H), 6.90-7.01 (m, 3H), 7.21-7.509 (m, 12H).

*13C NMR:* \( \delta 51.35, 79.88, 115.84, 121.13, 127.21, 127.79, 127.95, 128.03, 128.11, 128.34, 129.11, 133.76, 134.44, 135.06, 138.04, 157.50, 168.03. \)

**Mass Spectra** \( m/z: 344 (M^+); \) HRMS: Cacld for \( \text{C}_{23}\text{H}_{20}\text{O}_3: 344.1412; \) Found: 344.1414.

2-[(2-Hydroxy-5-methyl-phenyl)-phenyl-methyl]-3-phenyl-acrylic acid methyl ester 101

Yield: 50%; **IR** (neat) \( \nu_{max}: 3295, 1728, 1628 \text{ cm}^{-1}. \)

*1H NMR:* \( \delta 2.24 \) (s, 3H), 3.49 (s, 3H), 558 (s, 1H), 5.75 (s, 1H), 6.34 (s, 1H), 6.6 (s, 1H), 6.62 (d, 1H, \( J= 8.2 \) Hz), 6.84 (d, 1H, \( J= 7.7 \) Hz), 7.14-7.5 (m, 10H).

*13C NMR:* \( \delta 21.12, 48.69, 51.84, 116.99, 121.26, 124. 86, 126.93, 127.87, 128.08, 128.15, 128.55, 129.45, 129.88, 136.15, 136.29, 136.55, 138.16, 140.21, 153.65, 170.80. \)

3.8. One-Pot Synthesis of Indenes

A mixture of adduct (250mg) and dry benzene (3mL) in presence of Montmorillonite K-10 (125mg, 50% w/w of adduct) was refluxed for 4 hours. The clay was filtered out and 125mg of fresh clay was added into the reaction mixture and the reflux was continued for another 6 hours. The clay was filtered out and solvent was removed under vacum. N-bromosuccinimide (231mg, 2eq), 5mL of carbon tetrachloride and 50mg of AIBN were added.
into the reaction mixture and refluxed for 4h. Then 3 equivalent of methanol was added into that and the reflux was continued for 2 hours. The solvents were removed under vacuum. The crude mixture was treated with Montmorillonite K-10 clay (75mg, 30% w/w) and irradiated in microwave oven for 4 minutes. Finally, the mixture was cooled to room temperature and diluted with 5ml of CH$_2$Cl$_2$. The solvent were removed under vacuum and the crude mixture was purified through silicagel column using petrol ether and ethyl acetate (95:5) to give highly functionalized indenes.

1-Phenyl-1H-indene-2-carboxylic acid methyl ester 102
Colourless Solid; M.P: 126-128 °C; Yield: 61%; IR (neat) $\nu_{\max}$: 1702, 1610 cm$^{-1}$.

$^1$H NMR: $\delta$ 3.69 (s, 3H), 4.85 (s, 1H), 7.06-7.33 (m, 8H), 7.50 (d, 1H, $J=7.23$ Hz), 7.79 (s, 1H).

$^{13}$C NMR: $\delta$ 51.50, 55.64, 123.42, 124.48, 126.87, 127.29, 127.83, 128.31, 128.52, 128.61, 138.31, 141.13, 141.56, 150.41, 164.72.

Mass Spectra $m/z$: 250 (M$^+$); HRMS: Cacl for C$_{14}$H$_{16}$O$_2$: 250.0994; Found: 250.0992.

6-Chloro-1-phenyl-1H-indene-2-carboxylic acid methyl ester 107
Solid M.P 118-120 °C; Yield: 54%; IR (neat) $\nu_{\max}$: 1700, 1612 cm$^{-1}$.

$^1$H NMR: $\delta$ 3.70 (s, 3H), 4.78 (s, 1H), 6.9-7.5 (m, 8H), 7.75 (s, 1H).

$^{13}$C NMR: $\delta$ 51.33, 54.80, 123.39, 124.33, 127.41, 127.65, 128.31, 128.60, 129.14, 132.58, 136.72, 141.03, 141.43, 149.77, 164.06.

Mass Spectra $m/z$: 284 (M$^+$); HRMS: Cacl for C$_{14}$H$_{16}$O$_2$: 284.0604; Found: 284.0610.

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