A novel regiospecific synthesis of 1-chloro-2-arylcyclohexenes and 3-chloro-2-aryl-cyclohexenones
This chapter deals with the application of 1-bromo-2-chlorocyclohexene and 2-bromo-3-chlorocyclohex-2-enone for the synthesis of 1-chloro-2-arylcylohexenes and 3-chloro-2-arylcylohex-2-enones, a new series of vinyl chlorides. This chapter is divided into two parts: **Part A** and **Part B**. Part A deals with regiospecific synthesis of 1-chloro-2-arylcylohexenes and Part B deals with regiospecific synthesis of 3-chloro-2-aryl-5,5-dimethylcylohex-2-enones.

### 3.1 Introduction

Cyclic vinyl halides and 1,2-dihalocycloalkenes serve as starting material to cyclic vinylsilanes, an important anionic synthons in organic chemistry.\textsuperscript{325} Our laboratory employs the Wurtz-Fittig coupling reaction of corresponding cyclic vinyl halide with sodium and chlorotrimethylsilane in suitable solvent to prepare the anionic synthons. Using this method, over the past four decades, we have been able to synthesize a large number of simple and substituted cyclic vinylsilanes.\textsuperscript{326, 327} Some of the novel organosilicon compounds earlier prepared in our laboratory are given in **Fig. 20**.

**1,2-Dihalocycloalkenes**

Favorskii, Wittig and several scientists have carried out enormous amount of work on cycloalkynes. They have used the 1,2-dihalocycloalkenes for the generation of cycloalkynes (Scheme 144).\textsuperscript{328}

![Scheme 144](image-url)
Figure 20

1,2-Dibromocycloalkenes undergo reaction with sodium to give the trimerization product of cycloalkyne (Scheme 145).\(^{320}\)

Scheme 145
1,2-Dibromocycloalkenes have been utilized for a facile palladium-catalyzed synthesis of acridine derivatives with tosyl hydrazone of 2-amino acetophenone is reported (Scheme 146).330

![Scheme 146](image)

Recently, 1,2-dibromocyclopentene analogues were used as potentially versatile building block to synthesize the pharmaceutically important combretastatin derivative 1,2-disubstituted aryl cyclopentene through Suzuki coupling reaction (Scheme 147).331

![Scheme 147](image)

Similarly the Heck reaction was employed for the synthesis of 1,6-disubstituted (E,Z,E)-1,3,5-hexatrienes which were prepared by vicinal two fold Heck coupling reactions from 1,2-dibromocyclopentene, 1,2-dibromocyclohexene (Scheme 148).306

![Scheme 148](image)
Woo-Jin Yoo et. al., have reported an efficient method for the synthesis of symmetrical 2,3-diarylborbornadienes by the Suzuki cross-coupling reactions between 2-bromo-3-chloro-norbornadiene and arylboronic acids (Scheme 149).\textsuperscript{332}

\textbf{Scheme 149}

Photochromic molecular switches have been synthesised by the cross coupling reaction of 1,2-dibromocyclopentene with thiophene derived boronates is reported (Scheme 150).\textsuperscript{333}
3.2 PRESENT WORK

3.2.1 Part A: Regiospecific synthesis of 1-chloro-2-arylcyclohexenes

In continuation of the synthesis of 1-bromo-2-chlorocycloalkenes, we are further interested in the synthesis of novel 1-chloro-2-arylcyclohexenes, which are not reported elsewhere in literature. These compounds would serve as important starting materials in synthetic organic chemistry. In this connection, 1-bromo-2-chloro-cyclohexene 24 was subjected to the Suzuki cross-coupling reaction with phenyl boronic acids (30-40) in the presence of various organo palladium catalysts.

Initially, the Suzuki cross-coupling reaction was performed with 24 and phenyl boronic acid (30) in the presence of palladium acetate catalyst. The reaction however yielded biphenyl as the major product (Scheme 151, Table 6), instead of the expected cross coupled product 1-chloro-2-phenylcyclohexene (42). Literature survey indicated several reports which show the use of differing palladium catalysts for the cross coupling reactions. Some of the catalysts reported are Pd(OAc)$_2$, PdCl$_2$, (PPh$_3$)$_2$PdCl$_2$, Pd(dppf)Cl$_2$ and Pd(dppf)Cl$_2$·CH$_2$Cl$_2$. We employed all the above catalysts for the Suzuki cross-coupling reaction in an effort to prepare 1-chloro-2-arylcyclohexenes 42-52 (Table 7).

![Chemical structure](image)

Scheme 151

Our investigations have shown that the best catalyst for the cross-coupling reactions to be Pd(dppf)Cl$_2$·CH$_2$Cl$_2$ (Fig. 21) under inert nitrogen atmosphere and sealed tube conditions. In a typical reaction 24 (1 mmol), phenylboronic acid 30 (1
mmol), potassium carbonate (3 mmol) and Pd(dppf)Cl₂·CH₂Cl₂ (5 mol%) in 8-10 mL 1,4-dioxane solvent was heated on pre-heated an oil bath at 80 °C in a sealed tube for 3 hours. Monitoring using TLC and GC indicated the completion of reaction. The reaction mixture was filtered and subjected to column chromatography using silica gel (60–100 mesh) and 1:10 ethyl acetate/hexane (60-80 °C fraction), to isolate 42 in 95% isolated yield (Scheme 152).

![Figure 21](image_url)

**Table 6** : Suzuki cross coupling of 24 with 30 using different palladium catalysts / solvents/bases/Ligands.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Base</th>
<th>Ligand</th>
<th>Solvent</th>
<th>% Yield of 41</th>
<th>% Yield of 42</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>Pd(OAc)₂</td>
<td>K₂CO₃</td>
<td>PPh₃</td>
<td>Ethanol</td>
<td>40</td>
<td>-</td>
</tr>
<tr>
<td>02</td>
<td>Pd(OAc)₂</td>
<td>K₂CO₃</td>
<td>P(t-Bu)₃</td>
<td>Ethanol</td>
<td>25</td>
<td>-</td>
</tr>
<tr>
<td>03</td>
<td>Pd(OAc)₂</td>
<td>TEA</td>
<td>P(o-tol)₂</td>
<td>Ethanol</td>
<td>30</td>
<td>-</td>
</tr>
<tr>
<td>04</td>
<td>(PPh₃)₂PdCl₂</td>
<td>K₂CO₃</td>
<td>PPh₃</td>
<td>Toluene</td>
<td>35</td>
<td>5</td>
</tr>
<tr>
<td>05</td>
<td>(PPh₃)₂PdCl₂</td>
<td>K₂CO₃</td>
<td>P(o-tol)₂</td>
<td>Ethanol</td>
<td>25</td>
<td>10</td>
</tr>
<tr>
<td>06</td>
<td>(PPh₃)₂PdCl₂</td>
<td>Cs₂CO₃</td>
<td>P(τ-Bu)₃</td>
<td>Toluene</td>
<td>30</td>
<td>15</td>
</tr>
<tr>
<td>07</td>
<td>Pd(PPh₃)₂Cl₂</td>
<td>TEA</td>
<td>P(o-tol)₂</td>
<td>Dioxane</td>
<td>35</td>
<td>30</td>
</tr>
<tr>
<td>08</td>
<td>Pd(PPh₃)₄</td>
<td>Cs₂CO₃</td>
<td>-</td>
<td>Dioxane</td>
<td>20</td>
<td>45</td>
</tr>
<tr>
<td>09</td>
<td>Pd(dppf)Cl₂·CH₂Cl₂</td>
<td>K₂CO₃</td>
<td>-</td>
<td>Dioxane</td>
<td>20</td>
<td>60</td>
</tr>
</tbody>
</table>

All reactions were carried both at reflux condition and in sealed tube*
Scheme 152

The reaction was extended to a wide variety of aryl boronic acids 31-40 to isolate the products 43-52. Each coupling reaction was repeated for a minimum of three trials and the optimum yields of the products are indicated in Table 2. All products 42-52 were characterised completely by IR, $^1$H-NMR, $^{13}$C-NMR, ESI/GC-MS and elemental analysis.

Table 7: Cross coupling of 1-bromo-2-chlorocyclohexene with different aryl boronic acids: Preparation of novel 1-chloro-2-arylcyclohexenes.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Aryl boronic acids (30-40)</th>
<th>Products (42-52)</th>
<th>Time (hr)</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td><img src="30.png" alt="Image" /> B(OH)$_2$</td>
<td><img src="42.png" alt="Image" /> Cl</td>
<td>3</td>
<td>95</td>
</tr>
<tr>
<td>02</td>
<td><img src="31.png" alt="Image" /> B(OH)$_2$</td>
<td><img src="43.png" alt="Image" /> Cl</td>
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<td>90</td>
</tr>
<tr>
<td>03</td>
<td><img src="32.png" alt="Image" /> B(OH)$_2$</td>
<td><img src="44.png" alt="Image" /> CHO Cl</td>
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</tr>
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<td><img src="33.png" alt="Image" /> B(OH)$_2$</td>
<td><img src="45.png" alt="Image" /> O</td>
<td>2</td>
<td>93</td>
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<tr>
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<td>34</td>
<td>46</td>
<td>2</td>
<td>90</td>
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<tr>
<td>08</td>
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<tr>
<td>09</td>
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<td>50</td>
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<tr>
<td>11</td>
<td>40</td>
<td>52</td>
<td>2.5</td>
<td>93</td>
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</tr>
</tbody>
</table>

116
Mechanism

The plausible general mechanism for the formation of the 1-chloro-2-arylcyclohexenes may be explained based on the bond dissociation energies of the carbon-bromine and carbon-chlorine which are 289 and 335 kJ mol\(^{-1}\) respectively. In the first step, due to the lower bond energy between carbon and bromine, oxidative addition of the Pd(dppe)Cl\(_2\)-CH\(_2\)Cl\(_2\) catalyst to 24 occurs to form the first intermediate A. In presence of potassium carbonate/arylboronic acid 30-40, the species eliminates KBr, CO\(_2\) and KOBH(OH) to form B. Reductive elimination of the 1-chloro-2-arylcyclohexene 42-52 restores the palladium catalyst, leading to the further cycle (Fig. 22).

![Chemical diagram](image)

**Figure 22:** Plausible mechanism for the formation of 42-52
3.2.2 Part B: Regiospecific synthesis of some novel 2-aryl-3-chloro-5,5-dimethyl cyclohex-2-enones

In continuation of the synthesis of novel 1-chloro-2-aryl-cyclohexenes, we extended the method to synthesize some novel 2-aryl-3-chloro-5,5-dimethyl cyclohex-2-enones 58-67 by the Suzuki cross coupling reaction of 2-bromo-3-chloro-5,5-dimethyl cyclohex-2-enone 53 (Fig. 23) with eleven different aryl boronic acids. All the products 58-67 synthesised being novel would serve as building block in organic synthesis.

![Figure 23](image)

Initially, the Suzuki reaction of 53 with 3-methylphenyl boronic acid 31 was carried out using Pd(dppf)Cl$_2$·CH$_2$Cl$_2$ (Figure 21) as a catalyst under inert nitrogen atmosphere. In a typical reaction 53 (1 mmol), 3-methylphenylboronic acid 31 (1 mmol), potassium carbonate (3 mmol) and Pd(dppf)Cl$_2$·CH$_2$Cl$_2$ (5 mol%) in 8-10 mL 1,4-dioxane solvent was heated on pre-heated an oil bath at 80 °C in a sealed tube for 5 hours. Monitoring using TLC and GC indicated the completion of reaction. The reaction mixture was filtered and subjected to column chromatography using silica gel (60–100 mesh) and 1:10 ethyl acetate/hexane (60–80 °C fraction), to isolate 3-Chloro-2-(3′-methylphenyl)-5,5-dimethylcyclohex-2-enone 58 in 98% isolated yield (Scheme 153).
Scheme 153

The compound 53 upon Suzuki-cross coupling reaction with ten different aryl boronic acids in the presence of Pd(dppf)Cl₂·CH₂Cl₂ in a degasified 1,4-dioxane under nitrogen atmosphere gave the compounds 58-67 in >90% yield (Table 8). All the products were characterized using IR, ES-MS, ¹H-NMR and ¹³C-NMR. The plausible mechanism for the synthesis of 58-67 is as depicted in the Figure 24.

Figure 24: The plausible mechanism for the synthesis of 2-Aryl-3-chloro-5,5-dimethylecyclohex-2-enones
Table 8: List of 2-aryl-3-chloro-5,5-dimethyl cyclohex-2-enones 58-67 and their isolated yields

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Aryl boronic acids</th>
<th>Products (58-67)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td><img src="31" alt="Structure" /></td>
<td><img src="58" alt="Structure" /></td>
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</tr>
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<td><img src="61" alt="Structure" /></td>
<td>96</td>
</tr>
<tr>
<td>05</td>
<td><img src="33" alt="Structure" /></td>
<td><img src="62" alt="Structure" /></td>
<td>90</td>
</tr>
<tr>
<td>06</td>
<td><img src="34" alt="Structure" /></td>
<td><img src="63" alt="Structure" /></td>
<td>90</td>
</tr>
<tr>
<td>07</td>
<td><img src="36" alt="Structure" /></td>
<td><img src="64" alt="Structure" /></td>
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<td><img src="image2.png" alt="Chemical Structure 65" /></td>
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<tr>
<td>09</td>
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<td><img src="image4.png" alt="Chemical Structure 66" /></td>
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<tr>
<td>10</td>
<td><img src="image5.png" alt="Chemical Structure 39" /></td>
<td><img src="image6.png" alt="Chemical Structure 67" /></td>
<td>91</td>
</tr>
</tbody>
</table>
3.3 Experimental

Materials and methods are as given in the page no. 91

3.3.1 General procedure for the synthesis of 1-chloro-2-arylcyclohexenes (42-52):

A mixture of 1-bromo-2-chlorocyclohexene 24 (1 mmol), aryl boronic acid (1 mmol), K₂CO₃ (3.0 mmol), Pd(dppf)Cl₂CH₂Cl₂ (5 mol%) in 10 mL 1,4-dioxane were heated in a sealed tube placed in an oil bath at 70-80 °C for 2-3 hr. The reaction mixture was cooled to ambient temperature, filtered, and the solvent removed in-vacuo. The crude product was then subjected to column chromatography using silica gel (60-100 mesh) and 1:10 ethyl acetate/hexane (60-80 °C fraction) to isolate 42-52 in greater than 90% yield.

3.3.2 Spectral data and characterisation

1-Chloro-2-phenylcyclohexene (42)

IR : 2929, 2858, 1440, 1004, 698 cm⁻¹; ¹H NMR (CDCl₃) δ: 1.70-1.84 (m, 4H), 2.36-2.47 (m, 2H), 2.48-2.57 (m, 2H), 7.24-7.60 (m, 5H); ¹³C NMR (CDCl₃) δ: 22.68, 23.90, 32.95, 34.09, 126.09, 127.15, 127.23, 127.80, 128.03, 128.73, 134.40, 141.56; Anal. Found: C, 74.76; H, 6.75. Calc: C, 74.80; H, 6.80.

1-Chloro-2-(3’-methylphenyl)cyclohexene (43)

IR : 2931, 2880, 1693, 1440 cm⁻¹; ¹H NMR (CDCl₃) δ: 1.69-1.84 (m, 4H), 2.35 (s, 3H), 2.36-2.58 (m, 4H), 7.04-7.59 (m, 4H); ¹³C NMR (CDCl₃) δ: 22.70, 23.34, 23.93, 33.02, 34.64, 119.56, 124.26, 125.12, 127.67, 127.94, 128.67, 137.59, 141.54; Anal. Found: C, 75.45; H, 7.27. Calc: C, 75.53; H, 7.31.

1-Chloro-2-(4’-formylphenyl)cyclohexene (44)

IR : 2933, 2860, 2837, 2731, 1701, 1602, 1209 cm⁻¹; ¹H NMR (CDCl₃) δ: 1.26-1.87 (m, 4H), 2.38-2.41 (m, 2H), 2.48-2.52 (m, 2H), 7.41-7.44 (d, 2H, J = 12 Hz) 7.85-7.88 (d, 2H, J = 12Hz), 10.00 (s, 1H); ¹³C NMR (CDCl₃) δ: 22.48, 23.74, 32.52,
34.06, 128.36, 129.23, 129.60, 130.05, 130.26, 133.52, 135.02, 147.93; GC-MS m/e (rel. int.): 221.93 (32), 219.82 (100), 184.99 (28), 154.88 (32). Anal. Found: C, 70.77; H, 5.99. Calc: C, 70.75; H, 5.94.

1-Chloro-2-(2’-methoxyphenyl)cyclohexene (45)
IR : 2931, 2856, 2837, 1596, 1490, 1249 cm⁻¹; ¹H NMR (CDCl₃) δ: 1.75-1.85 (m, 4H), 2.51 (br, 4H), 3.83 (s, 3H), 6.92-6.99 (m, 2H), 7.10-7.12 (m, 1H), 7.26-7.30 (m, 1H); ¹³C NMR (CDCl₃) δ: 22.50, 23.97, 31.65, 33.71, 55.62, 111.15, 120.41, 128.28, 128.36, 130.00, 130.57, 132.60, 156.26; Anal. Found: C, 70.15; H, 6.72; Calc: C, 70.11; H, 6.79.

1-Chloro-2-(2’-methoxy-5’-isopropylphenyl)cyclohexene (46)
¹H NMR (CDCl₃) δ: 1.23-1.25 (d, 6H, J = 6.8 Hz), 1.75-1.90 (br m, 4H), 2.10-2.35 (br, 4H), 2.10-2.60 (br, 4H), 2.82-2.92 (sep, 1H), 3.79 (s, 3H), 6.83-6.85 (d, 1H, J = 8.4 Hz), 6.96-6.97 (d, 1H, J = 2.4 Hz), 7.10-7.12 (m, 1H); ¹³C NMR (CDCl₃) δ: 22.99, 24.45, 24.59, 30.13, 32.17, 33.67, 34.23, 56.24, 111.48, 126.32, 128.56, 128.71, 130.73, 133.40, 141.18, 154.80; Anal. Found: C, 72.59; H, 7.97. Calc: C, 72.57; H, 7.99.

1-Chloro-2-(4’-ethoxyphenyl)cyclohexene (47)
IR : 2931, 2856, 2837, 1596, 1490, 1249, 1114, 1027 cm⁻¹; ¹H NMR (CDCl₃) δ: 1.40-1.43 (t, 3H, J = 7.2 Hz), 1.74-1.82 (m, 4H), 2.35-2.49 (m, 4H), 4.01-4.06 (q, 2H, J = 6.8 Hz), 6.86-6.88 (d, 2H, J = 8.4 Hz), 7.18-7.20 (d, 2H, J = 8.8 Hz); GC-MS m/e (rel. int.): 237.80 (38), 235.81 (100), 207.70 (28), 200.82 (36), 172.76 (56); Anal. Found: C, 71.09; H, 7.30. Calc: C, 71.03; H, 7.24.

1-Chloro-2-(3’,4’-dimethoxyphenyl)cyclohexene (48)
IR : 2933, 2837, 1606, 1504, 1207, 1159, 1039 cm⁻¹; ¹H NMR (CDCl₃) δ: 1.7-1.9 (broad m, 4H), 2.1-2.4 (br, 2H), 2.4-2.6 (br, 2H), 3.7 (s, 3H), 3.8 (s, 3H), 6.5 (m,
2H), 6.98-7.01 (d, 1H, J = 12 Hz); $^{13}$C NMR (CDCl$_3$) $\delta$: 22.59, 24.01, 31.89, 33.82, 55.28, 55.63, 99.00, 104.19, 106.19, 128.48, 130.39, 132.29, 157.35, 160.01; Anal. Found: C, 66.50; H, 6.72; Calc: C, 66.53; H, 6.78;

1-Chloro-2-(3'-acetylphenyl)cyclohexene (49)

IR : 2935, 2862, 1685, 1286 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$:  1.73-1.86 (m, 4H), 2.38-2.42 (m, 2H), 2.48-2.51 (m, 2H), 2.61 (s, 3H), 7.46 (s, 1H), 7.42-7.48 (m, 1H) 7.85-7.86 (m, 2H); $^{13}$C NMR (CDCl$_3$) $\delta$: 22.57, 23.81, 26.64, 32.77, 34.04, 126.91, 128.11, 128.34, 128.77, 132.98, 133.56, 137.05, 141.94, 198.04; Anal. Found: C, 71.60; H, 6.40. Calc: C, 71.64; H, 6.44.

1-Chloro-2-(3'-chlorophenyl)cyclohexene (50)

IR : 2935, 2860, 1703, 1438 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$:  1.69-1.84 (m, 4H), 2.33-2.58 (m, 4H), 7.12-7.58 (m, 4H); $^{13}$C NMR (CDCl$_3$) $\delta$: 23.34, 23.94, 34.64, 36.51, 119.56, 126.38, 127.04, 127.88, 128.30, 129.34, 130.12, 130.89; Anal. Found: C, 63.49; H, 5.38. Calc: C, 63.46; H, 5.33.

1-Chloro-2-(3',4'-dichlorophenyl)cyclohexene (51)

$^1$H NMR (CDCl$_3$) $\delta$:  1.72-1.84 (m, 4H), 2.32-2.35 (m, 2H), 2.45-2.49 (m, 2H), 7.08-7.11 (q, 1H, J = 4 Hz) 7.35-7.63 (m, 2H); $^{13}$C NMR (CDCl$_3$) $\delta$: 22.49, 23.71, 32.61, 34.04, 126.15, 127.72, 128.80, 129.33, 130.07, 130.21, 130.96, 141.34; Anal. Found: C, 55.15; H, 4.29; Calc: C, 55.10; H, 4.24.

1-Chloro-2-(2'-benzo[\beta]furan)-cyclohexene (52)

$^1$H NMR (CDCl$_3$) $\delta$:  1.82-1.84 (m, 4H), 2.61-2.73 (m, 4H), 7.23-7.32 (m, 3H), 7.47-7.49 (d, 1H, J = 7.6 Hz), 7.60-7.62 (d, 1H, J = 7.6 Hz); $^{13}$C NMR (CDCl$_3$) $\delta$: 22.39, 23.99, 28.70, 35.82, 106.85, 111.35, 121.50, 123.14, 124.62, 124.67, 129.18, 131.34, 153.97, 154.38; Anal. Found: C, 72.30; H, 5.68. Calc: C, 72.26; H, 5.63.
3.3.3 General procedure for the synthesis of 2-aryl-3-chloro-5,5-dimethyl cyclohex-2-enones (58-67):

A mixture of 2-bromo-3-chloro-5,5-dimethylcyclohex-2-enones 53 (1 mmol), aryl boronic acid (1 mmol), K$_2$CO$_3$ (3.0 mmol), Pd(dppf)Cl$_2$CH$_2$Cl$_2$ (5 mol%) in 10 mL 1,4-dioxane were heated in a sealed tube placed in an oil bath at 70-80 °C for 2-3 hr. The reaction mixture was cooled to ambient temperature, filtered, and the solvent removed in-vacuo. The crude product was then subjected to column chromatography using silica gel (60-100 mesh) and 1:10 ethyl acetate/hexane (60-80 °C fraction) to isolate 58-67 in greater than 90% yield.

3.3.4 Spectral data and characterisation

3-Chloro-2-(3′-methylphenyl)-5,5-dimethylcyclohex-2-enone (58)

IR : 2956, 2926, 2868, 1654, 1609, 1582, 1455, 1365, 1232, 1194, 1142, 788 cm$^{-1}$; $^1$H NMR (CDCl$_3$) δ: 1.14 (s, 6H), 2.24 (b, 2H), 2.35 (s, 3H), 2.51 (b, 2H), 6.81-6.83 (d, 1H, $J = 8$ Hz), 7.01-7.03 (d, 1H, $J = 8$ Hz), 7.25-7.27 (m, 2H).

3-Chloro-2-(4′-methylphenyl)-5,5-dimethylcyclohex-2-enone (59)

IR : 2956, 2926, 2868, 1654, 1609, 1365, 1232, 1194, 1156 cm$^{-1}$; $^1$H NMR (CDCl$_3$) δ: 1.14 (s, 6H), 2.23 (b, 2H), 2.35 (s, 3H), 2.54 (b, 2H), 6.91-6.93 (d, 2H, $J = 8$ Hz), 7.18-7.20 (d, 2H, $J = 8$ Hz); $^{13}$C NMR (CDCl$_3$) δ: 23.3, 26.6, 33.8, 50.7, 50.8, 123.9, 124.8, 126.9, 128.1, 128.3, 137.9, 141.9, 154.6, 189.5; ESI-MS (m/e): 248.9.

3-Chloro-2-(4′-ethylphenyl)-5,5-dimethylcyclohex-2-enone (60)

IR : 2988, 2925, 1654, 1617, 1599, 1504, 1364, 1315, 1198, 1164, 1131, 561, cm$^{-1}$; $^1$H NMR (CDCl$_3$) δ: 1.14 (s, 6H), 1.21-1.24 (t, 3H, $J = 4$ Hz), 2.23 (b, 2H), 2.50 (b, 2H), 2.61-2.65 (q, 2H, $J = 4$ Hz), 6.91-6.93 (d, 2H, $J = 8$ Hz), 7.18-7.20 (d, 2H, $J = 8$ Hz); ES-MS (m/e): 262.9.
3-Chloro-2-(4′-tert-butylphenyl)-5,5-dimethylocyclohex-2-enone (61)

IR: 2958, 2869, 1669, 1612, 1368, 1208, 1170, 1136, 832 cm⁻¹; ¹H NMR (CDCl₃)  δ: 1.14 (s, 6H), 1.29-1.32 (m, 9H), 2.24 (b, 2H), 2.52 (b, 2H), 6.75-6.78 (d, 1H, J = 12 Hz), 6.92-6.94 (d, 1H, J = 8 Hz), 7.23-7.26 (d, 1H, J = 12 Hz), 7.37-7.39 (d, 1H, J = 8 Hz); ESI-MS (m/e): 290.9.

3-Chloro-2-(3′-methoxyphenyl)-5,5-dimethylocyclohex-2-enone (62)

IR: 2995, 2935, 2835, 1676, 1605, 1494, 1463, 1295, 1252, 1206, 1157, 1034, 831 cm⁻¹; ¹H NMR (CDCl₃) δ: 1.14 (s, 6H), 2.24 (b, 2H), 2.51 (b, 2H), 3.69 (s, 3H), 6.79-6.81 (d, 1H, J = 8 Hz), 7.03-7.05 (d, 1H, J = 8 Hz), 7.23-7.27 (m, 2H); ¹³C NMR (CDCl₃) δ: 26.6, 33.8, 50.8, 50.6, 58.3, 123.9, 124.8, 128.1, 128.3, 137.9, 141.9, 153.4, 157.7 189.5; ESI-MS (m/e): 264.9.

3-Chloro-2-(2′-methoxy-5′-isopropylphenyl)-5,5-dimethylocyclohex-2-enone (63)

IR: 2926, 2869, 2856, 1676, 1604, 1496, 1458, 1276, 1244, 1181, 1142, 1028, 810 cm⁻¹; ¹H NMR (CDCl₃) δ: 1.14 (s, 6H), 1.253-1.256 (d, 6H, J = 1.2 Hz), 2.24 (b, 2H), 2.51 (b, 2H), 2.81-2.92 (sep, 1H), 3.79 (s, 3H), 6.83-6.85 (d, 1H, J = 8.4 Hz), 6.96-7.12 (m, 2H) ESI-MS (m/e): 306.6.

3-Chloro-2-(3′,4′-dimethoxyphenyl)-5,5-dimethylocyclohex-2-enone (64)

IR: 2995, 2956, 2935, 2835, 1605, 1579, 1494, 1463, 1295, 1252, 1157, 1034, 831 cm⁻¹; ¹H NMR (CDCl₃) δ: 1.14 (s, 6H), 2.23 (b, 2H), 2.54 (b, 2H), 3.78 (s, 3H), 3.81 (s, 3H), 6.49-6.53 (m, 2H), 6.98-7.01 (d, 1H, J = 12 Hz); ESI-MS (m/e): 294.9.

3-Chloro-2-(3′-chlorophenyl)-5,5-dimethylocyclohex-2-enone (66)

IR: 2958, 2929, 2862, 1656, 1500, 1461, 1363, 1267, 1112, 1002, 825 cm⁻¹; ¹H NMR (CDCl₃) δ: 1.14 (s, 6H), 2.25 (b, 2H), 2.51 (b, 2H), 7.07-7.52 (m, 4H); ESI-MS (m/e): 268.6.
3-Chloro-2-\((4'\text{-chlorophenyl})\)-5,5-dimethylcyclohex-2-enone (67)

IR: 2958, 2929, 2862, 1656, 1500, 1461, 1363, 1267, 1112, 1002, 825 cm\(^{-1}\); \(^{1}\)H NMR (CDCl\(_3\)) \(\delta\): 1.14 (s, 6H), 2.22 (b, 2H), 2.52 (b, 2H), 7.41-7.44 (d, 2H, \(J = 12\) Hz), 7.85-7.88 (d, 2H, \(J = 12\) Hz); ESI-MS (m/e): 268.6.
IR spectrum of 1-chloro-2-phenylcyclohexene (42)

$^1$H NMR spectrum of 1-chloro-2-phenylcyclohexene (42)

$^{13}$C NMR spectrum of 1-chloro-2-phenylcyclohexene (42)
IR spectrum of 1-chloro-2-(3'-methylphenyl)cyclohexene (43)

$^1$H NMR spectrum of 1-chloro-2-(3'-methylphenyl)cyclohexene (43)

$^{13}$C NMR spectrum of 1-chloro-2-(3'-methylphenyl)cyclohexene (43)
IR spectrum 1-chloro-2-(4′-formylphenyl)cyclohexene (44)

$^1$H NMR Spectrum 1-Chloro-2-(4′-formylphenyl)cyclohexene (44)

$^{13}$C NMR spectrum 1-chloro-2-(4′-formylphenyl)cyclohexene (44)
GC-MS of 1-chloro-2-(4'-formylphenyl)cyclohexene (44)
IR spectrum of 1-chloro-2-(2'-methoxyphenyl)cyclohexene (45)

$^1$H NMR of 1-chloro-2-(2'-methoxyphenyl)cyclohexene (45)

$^{13}$C-NMR of 1-chloro-2-(2'-methoxyphenyl)cyclohexene (45)
$^1$H NMR of 1-chloro-2-(2′-methoxy-5′-isopropyl phenyl)cyclohexene (46)

$^{13}$C NMR of 1-chloro-2-(2′-methoxy-5′-isopropylphenyl)cyclohexene (46)
IR of 1-chloro-2-(4′-ethoxyphenyl)cyclohexene (47)

$^1$H NMR of 1-chloro-2-(4′-ethoxyphenyl)cyclohexene (47)
IR of 1-chloro-2-(3',4'-dimethoxyphenyl)cyclohexene (48)

$^1$H NMR of 1-chloro-2-(3',4'-dimethoxyphenyl)cyclohexene (48)

$^{13}$C NMR of 1-chloro-2-(3',4'-dimethoxyphenyl)cyclohexene (48)
Chapter 3

IR of 1-chloro-2-(3'-acetylphenyl)cyclohexene (49)

$^1$H NMR of 1-chloro-2-(3'-acetylphenyl)cyclohexene (49)

$^{13}$C NMR of 1-chloro-2-(3'-acetylphenyl)cyclohexene (49)
IR of 1-chloro-2-(3′-chlorophenyl)cyclohexene (50)

$^1$H NMR of 1-chloro-2-(3′-chlorophenyl)cyclohexene (50)

$^{13}$C NMR of 1-chloro-2-(3′-chlorophenyl)cyclohexene (50)
$^1$H NMR of 1-chloro-2-(3',4'-dichlorophenyl)cyclohexene (51)

$^{13}$C NMR of 1-chloro-2-(3',4'-dichlorophenyl)cyclohexene (51)
$^1$H NMR of 1-Chloro-2-(2'-benzo[b]furano)-cyclohexene (52)

$^{13}$C NMR of 1-chloro-2-(2'-benzo[b]furano)-cyclohexene (52)
IR spectrum of 3-chloro-2-(3'-methylphenyl)-5,5-dimethylcyclohex-2-enone (58)

$^1$H NMR spectrum of 3-chloro-2-(3'-methylphenyl)-5,5-dimethylcyclohex-2-enone (58)
IR spectrum of 3-chloro-2-(4’-methylphenyl)-5,5-dimethylcyclohex-2-enone (59)

$^1$H NMR spectrum of 3-chloro-2-(4’-methylphenyl)-5,5-dimethylcyclohex-2-enone (59)
$^{13}$C NMR spectrum of 3-chloro-2-(4'-methylphenyl)-5,5-dimethylcyclohex-2-enone (59)

ESI-MS of 3-Chloro-2-(4'-methylphenyl)-5,5-dimethylcyclohex-2-enone (59)
IR spectrum of 3-chloro-2-(4′-ethylphenyl)-5,5-dimethylcyclohex-2-enone (60)

\[ \text{\textsuperscript{1}H NMR spectrum of 3-chloro-2-(4′-ethylphenyl)-5,5-dimethylcyclohexa-2-enone(60)} \]
ESI-MS of 3-chloro-2-(4'-ethylphenyl)-5,5-dimethylcyclohexa-2-enone (60)
IR spectrum of 3-chloro-2-(4′-tert-butylphenyl)-5,5-dimethylcyclohexa-2-enone (61)

$^1$H NMR spectrum of 3-chloro-2-(4′-tert-butylphenyl)-5,5-dimethylcyclohexa-2-enone (61)
ESI-MS of 3-chloro-2-(4'-tert-butylphenyl)-5,5-dimethylcyclohexa-2-enone (61)
IR spectrum of 3-chloro-2-(3′-methoxyphenyl)-5,5-dimethylcyclohex-2-enone (62)

${}^1$H NMR spectrum of 3-chloro-2-(3′-methoxyphenyl)-5,5-dimethylcyclohex-2-enone (62)
$^{13}$C NMR spectrum of 3-chloro-2-(3′-methoxyphenyl)-5,5-dimethylcyclohex-2-enone (62)

ESI-MS of 3-chloro-2-(3′-methoxyphenyl)-5,5-dimethylcyclohex-2-enone (62)
IR spectrum of 3-chloro-2-(2'-methoxy-5'-isopropylphenyl)-5,5-dimethylcyclohex-2-enone (63)

$^1$H NMR spectrum of 3-chloro-2-(2'-methoxy-5'-isopropylphenyl)-5,5-dimethyl cyclohex-2-enone (63)
ESI-MS of 3-chloro-2-(2'-methoxy-5'-isopropylphenyl)-5,5-dimethylcyclohex-2-enone (63)
IR spectrum of 3-chloro-2-(3',4'-dimethoxyphenyl)-5,5-dimethylcyclohex-2-enone (64)

\[ ^1H \text{ NMR spectrum of 3-chloro-2-(3',4'-dimethoxyphenyl)-5,5-dimethylcyclohex-2-enone (64)} \]
ESI-MS of 3-chloro-2-[(3',4'-dimethoxyphenyl)-5,5-dimethylcyclohex-2-enone (64)
IR spectrum of 3-chloro- 2-(3′-chlorophenyl)-5,5-dimethylcyclohex-2-enone (66)

\(^1\)H NMR spectrum of 3-chloro-2-(3′-chlorophenyl)-5,5-dimethylcyclohex-2-enone (66)
ESI-MS of 3-chloro-2-(3'-chlorophenyl)-5,5-dimethylcyclohex-2-enone (66)
IR spectrum of 3-chloro-2-(4′-chlorophenyl)-5,5-dimethylcyclohex-2-enone (67)

\[ \text{IR spectrum} \]

\[ \text{1H NMR spectrum of 3-chloro-2-(4′-chlorophenyl)-5,5-dimethylcyclohexa-2-enone (67)} \]
ESI-MS of 3-chloro-2-(4'-chlorophenyl)-5,5-dimethylcyclohex-2-enone (67)