PART II

Ferric Chloride Mediated Michael Addition of Dicarboxylic Acid Esters to α,β-Unsaturated Ketones

11.4 Experimental Details

This section provides all the details including experimental procedures, compound characterization and spectral data. Tools used for characterization of compounds have also received brief mentions.

Non-aqueous reactions were performed in oven (150 °C) or flame-dried glass wares, under an atmosphere of dry nitrogen at ambient temperature, unless otherwise stated.

Proton nuclear magnetic resonance (\(^1\)H nmr) spectra were recorded on Varian Unity 400 (400 MHz) and Bruker AC 300 (300 MHz) spectrometers in chloroform-d\(_4\) with residual non-deuterated solvent as internal standard.

Carbon nuclear magnetic resonance (\(^{13}\)C nmr) spectra were recorded on Varian Unity 400 (100 MHz) and Bruker AC 300 (75 MHz) spectrometers in chloroform-d\(_4\) with deuterated solvent as internal standard.

Chemical shifts for \(\delta_H\) and \(\delta_C\) are quoted in units of parts per million downfield from tetramethylsilane. Signal splitting patterns are described as singlet (s), doublet (d), triplet (t), quartet (q), unresolved multiplet (m), narrow (n), broad (br) or complex if multiple signals overlap. Coupling constants \(J\) are given in units of hertz (Hz).

Infra-red spectra were recorded on Perkin Elmer Spectrum RX I FT-IR System as evaporated films (dichloromethane) on potassium chloride plates unless otherwise stated. All absorptions shown are strong, unless indicated.
GC-MS spectra were recorded on Perkin Elmer Clarus 600 Spectrometer with Elite 5 MS column with dimension 30 m x 250 μm. The injection temperature was fixed at 290 °C. The oven temperature was initially held at 250 °C for 2 min, increased to 280 °C at 3 °C/min and held at 280 °C for 5 min. Helium was used as the carrier gas. The modes of ionization in MS were electron impact (EI).

Melting points were determined on a melting point apparatus (Scientific Device, India, Type MP-D in open capillary) and reported without further adjustment.

Refractive indexes of liquid samples were recorded on Abbe Refractometer.

Flash chromatography refers to the process of Still\textsuperscript{18} and was carried out using Merck silica gel 60H (40-60 μm, 230-300 mesh) as the stationary phase. Thin layer chromatography (tlc) was performed using manually prepared glass plates coated with Merck Silica Gel G. Detection was done in iodine chamber.

Petrol refers to the fraction of light petroleum ether which distills in the range 40-60 °C and was redistilled prior to use. Ether refers to diethyl ether. Tetrahydrofuran (THF) was dried over sodium wire and distilled under an atmosphere of nitrogen in the presence of benzophenone as an indictor and was collected once a deep blue colour was obtained. Dichloromethane was dried over calcium hydride and distilled under an atmosphere of nitrogen.\textsuperscript{19} Benzene, toluene and ether were dried over sodium wire.

Absolute ethanol and HPLC grade methanol from commercial sources were used without further treatment. Brine refers to saturated aqueous sodium chloride solution.

Olefins and esters were prepared in the laboratory as described in the preceding sections. Ferric chloride hexahydrate (Merck) was procured from commercial sources and used as such. All Michael reactions were carried out under nitrogen atmosphere.
II.4.1 Preparation of α,β-unsaturated ketones and their characterization

α,β-Unsaturated ketones, nineteen in total, used in this investigation were prepared in the laboratory using the Claisen-Schmidt methodology\textsuperscript{10} and reported procedure.\textsuperscript{11} Major chemicals procured from commercial sources are listed below.

i)  \textit{o-Methoxybenzaldehyde} (Merck Ltd.)

ii) \textit{m-Methoxybenzaldehyde} (Fluka Chemika)

iii) \textit{p-Methoxybenzaldehyde} (Merck Ltd.)

iv) \textit{o-Chlorobenzaldehyde} (Sigma Aldrich)

v) \textit{m-Chlorobenzaldehyde} (Alfa Aesar)

vi) \textit{p-Chlorobenzaldehyde} (Merck Ltd.)

vii) \textit{o-Nitrobenzaldehyde} (Alfa Aesar)

viii) \textit{m-Nitrobenzaldehyde} (Merck Ltd.)

ix) \textit{p-Nitrobenzaldehyde} (Merck Ltd.)

x) \textit{p-Methylbenzaldehyde} (Sigma Aldrich)

xi) \textit{p-Hydroxybenzaldehyde} (Fluka Chemika)

xii) \textit{Benzaldehyde} (Qualigens)

xiii) \textit{Acetone} (Merck Ltd)

xiv) \textit{Acetophenone} (Merck Ltd)

xv) \textit{Sodium hydroxide pellets} (Merck Ltd)

xvi) \textit{Malonic acid} (Loba Chemie)

xvii) \textit{Succinic acid} (Loba Chemie)

xviii) \textit{Ethanol} (Merck Ltd)

xix) \textit{Methanol} (Merck Ltd)
All the chemicals listed above were used without further treatment except benzaldehyde which was freshly distilled under reduced pressure just before use.

(i) Typical procedure for the preparation of benzylideneacetones

A mixture of the aldehyde (1 mmol) and acetone (2 mmol) was stirred at ice temperature for half an hour followed by drop wise addition of 10% sodium hydroxide solution (1 ml). Stirring was then continued at room temperature until completion of the reaction. The reaction mixture was then quenched by adding dil HCl solution, and extracted thrice with ethyl acetate. The combined organic layer was washed with brine, dried over anhydrous sodium sulfate, filtered under suction and the solvent removed under vacuum to recover the crude product. The crude product was purified by column chromatography over silica gel (60-120 mesh) using a mixture of ethyl acetate and petroleum ether as the eluent. The products were characterized by melting point, FT IR, $^1\text{H}$ NMR and mass spectra.

(ii) Typical procedure for the preparation of chalcones

A mixture of the aldehyde (1 mmol), acetophenone (2 mmol) and 10% sodium hydroxide solution (1 ml) was stirred at ice temperature for half an hour followed by stirring at room temperature until completion of the reaction. Reaction mixture was kept in refrigerator overnight. Solid product was filtered out and recrystallized from ethanol to give the chalcones. The products were characterized by melting point, FT IR, $^1\text{H}$ NMR and Mass spectra.
II.4.1.1  

*(E)-4-Phenylbut-3-en-2-one (II.1a)*

\[
\begin{align*}
\text{Formula and formula weight:} & \quad C_{10}H_{10}O, 146 \\
\text{State:} & \quad \text{yellow solid} \\
\text{m.p.:} & \quad \text{low melting solid} \\
\text{Yield (mol%):} & \quad 77 \\
\text{IR (thin film on KBr), } \nu \text{ cm}^{-1}: & \quad 487, 565, 688, 747, 860, 977, 1015, 1216, 1310, 1338, 1446, 1604, 1661, 2921, 3047. \\
\text{\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, TMS)} \delta: & \quad 2.28 \text{ (s, 3H, OMe)}, 6.63 \text{ (d, } ^3J=16.4 \text{ Hz, 1H, olefinic)}, 7.24-7.48 \text{ (m, 5H, aromatic and 1H, olefinic)}. \\
\text{MS (EI, m/z):} & \quad 18, 27, 28, 38, 39, 48, 50, 51, 58, 63, 65, 76, 77, 78, 91, 102 (100\%), 103, 115, 131, 132, 145, 146 (M^+, >90\%).
\end{align*}
\]

II.4.1.2  

*(E)-4-(\text{o-Methoxyphenyl})but-3-en-2-one (II.1b)*

\[
\begin{align*}
\text{Formula and formula weight:} & \quad C_{11}H_{12}O_2, 176 \\
\text{State:} & \quad \text{pale yellow solid} \\
\text{m.p.:} & \quad 45-48 \degree C \\
\text{Yield (mol%):} & \quad 76
\end{align*}
\]
IR (thin film on KBr), v cm$^{-1}$: 516, 736, 817, 987, 1023, 1106, 1175, 1254, 1360, 1426, 1512, 1598, 1675, 2842, 2950, 3048.

$^1$H NMR (400 MHz, CDCl$_3$, TMS) $\delta$: 2.63 (s, 3H, OMe), 3.82 (s, 3H, ArOMe), 6.62 (d, $^3J=16.4$ Hz, 1H, olefinic), 6.87-6.99 (m, 2H, aromatic), 7.31 (t, $^3J=6$ Hz, 1H, aromatic), 7.43 (d, $^3J=8.8$ Hz, 1H, aromatic), 7.92 (d, $^3J=16.8$ Hz, 1H, olefinic).

$^{13}$C NMR (75 MHz, CDCl$_3$) : 26.99, 55.34, 110.97, 120.64, 123.09, 127.54, 128.15, 131.69, 138.64, 158.07, 199.05.

MS (El) m/z : 27, 38, 39, 43, 50, 51, 55, 62, 63, 64, 74, 75, 77, 79, 80, 89, 90, 91, 102, 103, 105, 106, 115, 118, 119, 131, 133, 145, 146, 161 (100%), 162, 175, 176, (M$^+$, ~65%).

II.4.1.3 (E)-4-(m-Methoxyphenyl)but-3-en-2-one (II.1c)

![Chemical Structure]

**Formula and formula weight**: $C_{11}H_{12}O_2$, 176

**State**: yellow liquid

**Yield (mol%)**: 69

IR (thin film on KBr), v cm$^{-1}$: 516, 736, 817, 987, 1023, 1106, 1175, 1254, 1360, 1426, 1512, 1598, 1675, 2842, 2950, 3048.
Part II.4

\[ ^1H\text{ NMR (400 MHz, CDCl}_3, \text{TMS)}\delta : 2.39 \ (s, 3H, OMe), \ 3.84 \ (s, 3H, ArOMe), \ 6.70 \ (d, \ ^2J=16.0\ \text{Hz}, \ 1H, \ \text{olefinic}), \ 6.94 \ (d, \ ^3J=8.4\ \text{Hz}, \ 1H, \ \text{aromatic}), \ 7.07 \ (s, \ 1H, \ \text{aromatic}), \ 7.14 \ (d, \ ^3J=7.6\ \text{Hz}, \ 1H, \ \text{aromatic}), \ 7.32 \ (t, \ ^3J=8.0\ \text{Hz}, \ 1H, \ \text{aromatic}), \ 7.48 \ (d, \ ^3J=16.0\ \text{Hz}, \ \text{olefinic}). \]

\[ \text{MS (EI) } m/z : 28, 38, 39, 43, 50, 51, 62, 63, 64, 65, 76, 77, 79, 80, 89, 90, 92, 102, 103, 105, 115, 118, 133, 134, 145, 146, 161 \ (100\%), \ 162, 175, 176 \ (M^+) \ ~65\%. \]

II.4.1.4 \((E)-4-(\rho-\text{Methoxyphenyl})\text{but-3-en-2-one (II.1d)} \]

\[
\begin{array}{c}
\text{MeO} \\
\text{Me} \\
\end{array}
\]

Formula and formula weight : \(\text{C}_{11}\text{H}_{12}\text{O}_{2}, 176\)

State : yellow solid

m.p. : 60-62°C

Yield (mol%) : 81

\[ \text{IR (thin film on KBr), } \nu \text{ cm}^{-1} : 516, 734, 818, 851, 988, 1022, 1108, 1175, 1255, 1303, 1360, 1424, 1512, 1596, 1676, 2842, 2944, 3039. \]

\[ ^1H\text{ NMR (400 MHz, CDCl}_3, \text{TMS)}\delta : 2.35 \ (s, 3H, OMe), \ 3.82 \ (s, 3H, ArOMe), \ 6.60 \ (d, \ ^2J=16.0\ \text{Hz}, \ 1H, \ \text{olefinic}), \ 6.91 \ (d, \ ^3J=8.8\ \text{Hz}, \ 2H, \ \text{aromatic}), \ 7.44-7.50 \ (m, \ 2H, \ \text{aromatic} \ \text{and} \ 1H, \ \text{olefinic}). \]
$^{13}$C NMR (75 MHz, CDCl$_3$) : 27.31, 55.30, 114.33, 124.90, 126.92, 129.89, 143.22, 161.51, 198.41.

MS (EI) m/z : 27, 39, 43, 50, 51, 53, 62, 63, 64, 65, 76, 77, 79, 89, 90, 102, 103, 105, 118, 133, 134, 145, 161, 162, 175, 176 (M$^+$, 100%).

**II.4.1.5** *{(E)-4-(o-Chlorophenyl)but-3-en-2-one (II.1e)}*

![Chemical Structure](image)

**Formula and formula weight** : C$_{10}$H$_9$ClO, 180.5

**State** : liquid

**Yield (mol%)** : 56

IR (thin film on KBr), v cm$^{-1}$ : 450, 573, 666, 678, 770, 854, 989, 1013, 1048, 1091, 1212, 1266, 1305, 1448, 1489, 1577, 1603, 1657, 2824, 3047.

$^1$H NMR (400 MHz, CDCl$_3$, TMS) $\delta$ : 2.52 (s, 3H, OMe), 6.65 (d, $^3J$=16.4 Hz, 1H, olefinic), 6.80-6.88 (m, 2H, aromatic), 7.25 (t, $^3J$=7.6 Hz, 1H, aromatic), 7.45 (d, $^3J$=7.2 Hz, 1H, aromatic), 7.79 (d, $^3J$=16.4 Hz, 1H, olefinic).

MS (EI, m/z) : 28, 39, 43, 50, 51, 53, 62, 63, 68, 74, 75, 76, 82, 101, 102, 103, 115, 137, 139, 145 (100%), 146, 165, 167, 180, 182 (M$^+$, ~15%).
II.4.1.6  (E)-4-(m-Chlorophenyl)but-3-en-2-one (II.1f)

![Chemical Structure]

Formula and formula weight : C_{10}H_{9}ClO, 180.5

State : liquid

Yield (mol%) : 55

IR (thin film on KBr), v cm\(^{-1}\) : 517, 687, 719, 777, 822, 979, 1016, 1106, 1170, 1209, 1261, 1303, 1332, 1332, 1510, 1598, 1656, 2824.

II.4.1.7  (E)-4-(p-Chlorophenyl)but-3-en-2-one (II.1g)

![Chemical Structure]

Formula and formula weight : C_{10}H_{9}ClO, 180.5

State : yellow solid

m.p. : 58-60 °C

Yield (mol%) : 61

IR (thin film on KBr), v cm\(^{-1}\) : 450, 574, 667, 681, 770, 854, 989, 1016, 1048, 1176, 1214, 1267, 1310, 1430, 1447, 1493, 1576, 1603, 1657, 2818, 2937, 3056.
1H NMR (400 MHz, CDCl₃, TMS) δ : 2.38 (s, 3H, OMe), 6.69 (d, 3J=16 Hz, 1H, olefinic), 7.36-7.38 (m, 2H, aromatic), 7.44-7.48 (m, 2H, aromatic and 1H, olefinic).

MS (EI, m/z) : 18, 28, 39, 43, 50, 51, 58, 63, 74, 76, 101, 102, 103, 115, 136, 137, 139, 145, 146, 165 (100%), 167, 179, 180 (M⁺, ~20%).

II.4.1.8 (E)-4-(o-Nitrophenyl)but-3-en-2-one (II.1h)

![Chemical structure]

Formula and formula weight : C₁₀H₉O₃N, 191

State : yellow solid

m.p. : 53-55 °C

Yield (mol%) : 85

IR (thin film on KBr), v cm⁻¹ : 685, 738, 802, 900, 1069, 1165, 1351, 1460, 1527, 1593, 1700, 2852, 2924.

1H NMR (400 MHz, CDCl₃, TMS) δ : 2.43 (s, 3H, OMe), 6.59 (d, 3J=16 Hz, 1H, olefinic), 7.56-7.60 (m, 1H, aromatic), 7.66-7.71 (m, 2H, aromatic), 7.99 (d, 3J=16 Hz, 1H, olefinic), 8.07 (d, 3J=8.4 Hz, 1H, aromatic).
II.4.1.9  (E)-4-(m-Nitrophenyl)but-3-en-2-one (II.1i)

Formula and formula weight: C_{10}H_{9}O_{3}N, 191

State: yellow solid

m.p.: 95-98 °C

Yield (mol%): 76

IR (thin film on KBr), ν cm\(^{-1}\): 512, 650, 714, 793, 822, 977, 1024, 1111, 1171, 1258, 1317, 1365, 1451, 1514, 1582, 1601, 1626, 1697, 2921, 2960.

\(^1\)H NMR (400 MHz, CDCl\(_3\), TMS) δ: 2.42 (s, 3H, OMe), 6.84 (d, \(^3J=16.4\) Hz, 1H, olefinic), 7.53-7.62 (m, 2H, 1H aromatic & 1H, olefinic), 7.86 (d, \(^3J=7.6\) Hz, 1H, aromatic), 8.25 (d, \(^3J=8.4\) Hz, 1H, aromatic), 8.41 (s, 1H, aromatic).

II.4.1.10  (E)-4-(p-Nitrophenyl)but-3-en-2-one (II.1j)

Formula and formula weight: C_{10}H_{9}O_{3}N, 191

State: yellow solid

m.p.: 100-102 °C
Yield (mol%) : 82

IR (thin film on KBr), v cm\(^{-1}\) : 523, 822, 1018, 1092, 1165, 1353, 1381, 1494, 1594, 1700, 2852, 2931.

II.4.1.11  (E)-4-(p-Methylphenyl)but-3-en-2-one (II.1k)

Formula and formula weight : C\(_{11}\)H\(_{12}\)O, 160

State : yellow liquid

Yield (mol%) : 79

IR (thin film on KBr), v cm\(^{-1}\) : 517, 688, 774, 822, 1017, 1170, 1210, 1258, 1299, 1330, 1445, 1510, 1596, 1659, 2814, 2941.

\(^1\)H NMR (400 MHz, CDCl\(_3\), TMS) \(\delta\) : 2.58 (s, 3H, OMe), 2.60 (s, 3H, ArMe), 6.66 (d, \(J=15.2\) Hz, 1H, olefinic), 6.87-6.91 (m, 2H, aromatic), 7.20-7.24 (m, 2H, aromatic), 7.69 (d, \(J=15.2\) Hz, 1H, olefinic)

MS (EI, m/z) : 18, 27, 29, 39, 41, 43, 51, 53, 58, 63, 65, 72, 77, 89, 91, 92, 102, 115, 117, 118, 131, 144, 145 (100%), 146, 159, 160 (M\(^+\), ~35%).
II.4.1.12  (E)-4-(p-Hydroxyphenyl)but-3-en-2-one (II.11)

\[
\begin{align*}
\text{HO} & \quad \text{(E)} \quad \text{C}_10\text{H}_10\text{O}_2 \\
\text{Me} & \quad \text{brown solid} \\
\text{m.p.} & \quad 91-93^\circ C \\
\text{Yield (mol%)} & \quad 80 \\
\text{IR (thin film on KBr), v cm}^{-1} & \quad 469, 508, 546, 583, 744, 824, 969, 1007, 1170, 1207, 1262, 1362, 1448, 1514, 1599, 1626, 2813, 3009. \\
\text{H NMR (400 MHz, CDCl}_3, \text{ TMS) } \delta & \quad 2.39 \text{ (s, 3H, OMe)}, 6.61 \text{ (d, } 3^J=16.4 \text{ Hz, 1H, olefinic)}, 6.90 \text{ (d, } 3^J=8.8 \text{ Hz, 2H, aromatic)}, 7.44 \text{ (d, } 3^J=8.8 \text{ Hz, 2H, aromatic)}, 7.51 \text{ (d, } 3^J=16.4 \text{ Hz, 1H, olefinic}). \\
\text{MS (EI, m/z)} & \quad 17, 18, 26, 27, 29, 38, 39, 41, 43, 45, 50, 51, 55, 56, 60, 63, 69, 73, 77, 83, 88, 91, 101, 103, 111, 115, 121, 128, 131 (100\%), 132, 145, 146, 156, 157, 162 (M^+, ~5\%), 163.
\end{align*}
\]

II.4.1.13  (E)-1,3-Diphenylprop-2-en-1-one (II.1m)

\[
\begin{align*}
\text{Formula and formula weight} & \quad \text{C}_{15}\text{H}_{12}\text{O}, 208 \\
\text{State} & \quad \text{yellow solid}
\end{align*}
\]
Part H.4

m.p. : 55-56 °C
Yield (mol%) : 81
IR (thin film on KBr), v cm\(^{-1}\) : 454, 505, 602, 640, 707, 788, 834, 1111, 1160, 1217,
1287, 1315, 1386, 1454, 1517, 1598, 1669, 2981, 3167.

\(^1\)H NMR (400 MHz, CDCl\(_3\), TMS) \(\delta\) : 6.98-7.02 (m, 1H, aromatic), 7.18-7.35 (complex m, 9H, aromatic, & 2H, olefinic).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) : 121.92, 128.37, 128.41, 128.54, 128.87, 130.47, 132.72,
134.74, 138.07, 144.76, 190.45.
MS (EI, m/z) : 27, 28, 32, 50, 51, 63, 76, 77 (100%), 78, 89, 102, 103, 105, 130, 131,
165, 179, 207, 208 (M\(^+\), ~65%).

II.4.1.14 \((E)-3-(o\text{-Methoxyphenyl})-1\text{-phenylprop-2-en-1-one (II.1n)}\)

![Chemical Structure]

Formula and formula weight : C\(_{16}\)H\(_{14}\)O\(_2\), 238
Yield (mol%) : 86
m.p. : 46-48 °C
IR (thin film on KBr), v cm\(^{-1}\) : 414, 459, 588, 694, 753, 861, 1020, 1106, 1175, 1212,
1248, 1278, 1333, 1460, 1487, 1598, 1661, 2833, 2938,
3058.

\(^1\)H NMR (300 MHz, CDCl\(_3\), TMS) \(\delta\) : 3.93 (s, 3H, OCH\(_3\)), 6.94 – 8.04 (complex m, 10H,
aromatic 9H & olefinic 1H), 8.14 (d, 1H, \(^3\)J = 15.9 Hz, olefinic).
\[\text{II.4.1.15} \quad (E)-3-(m-\text{Methoxyphenyl})-1-\text{phenylprop-2-en-1-one (II.1o)}\]

Formula and formula weight: \(C_{16}H_{14}O_2, 238\)

State: yellow solid

m.p.: 59-60 °C

Yield (mol\%): 85

IR (thin film on KBr), \(\nu \text{ cm}^{-1}\): 415, 464, 586, 695, 752, 861, 1021, 1102, 1175, 1209, 1252, 1327, 1454, 1479, 1598, 1660, 2833, 2940, 3058

\[^1H\text{NMR (300 MHz, CDCl}_3, \text{TMS})\delta: 3.87 (s, 3H, OCH}_3), 6.97 - 7.76 \text{(complex m, 11H, aromatic 9H & olefinic 2H)}\]

\[^{13}\text{C NMR (75 MHz, CDCl}_3): 55.32, 113.37, 116.27, 121.07, 122.32, 128.48, 128.61, 129.93, 132.80, 136.19, 138.11, 144.75, 159.88, 190.55.\]

MS (EI) m/z: 28, 39, 50, 51, 63, 77 (100\%), 89, 90, 102, 105, 118, 133, 161, 165, 179, 194, 207, 208, 223, 237, 238 (M^+, \sim65\%).
II.4.1.16 (E)-3-(p-Methoxyphenyl)-1-phenylprop-2-en-1-one (II.1p)

Formula and formula weight: C₁₆H₁₆O₂, 238

State: yellow solid

m.p.: 72-74°C

Yield (mol%): 82

IR (thin film on KBr), v cm⁻¹: 418, 463, 586, 695, 752, 861, 1021, 1102, 1175, 1209, 1252, 1327, 1454, 1479, 1598, 1660, 2835, 2940, 3058.

¹H NMR (400 MHz, CDCl₃, TMS) δ: 4.00 (s, 3H, ArOMe), 6.43 (d, ³J=16 Hz, 1H, olefinic), 7.31-7.64 (complex m, 9H, aromatic), 7.98 (d, ³J=16.0 Hz, 1H, olefinic).

¹³C NMR (75 MHz, CDCl₃): 55.40, 113.92, 114.38, 119.71, 127.56, 128.12, 128.39, 128.55, 130.22, 132.55, 133.05, 136.83, 138.45, 144.70, 161.64, 190.59.

II.4.1.17  
(E)-3-(o-Chlorophenyl)-1-phenylprop-2-en-1-one (II.1q)

Formula and formula weight : C\textsubscript{15}H\textsubscript{11}ClO, 242.5

State : solid

m.p. : 48-50 °C

Yield (mol%) : 68

IR (thin film on KBr), ν cm\textsuperscript{-1} : 409, 739, 817, 900, 1023, 1091, 1214, 1266, 1322, 1405, 1489, 1602, 1660, 2930, 3058.

\textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}, TMS) δ : 7.27 – 8.04 (complex m, 11H, aromatic 9H & olefinic 2H).

\textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}) : 124.61, 126.97, 127.64, 128.01, 128.49, 128.54, 130.17, 131.08, 132.84, 133.08, 135.36, 137.75, 140.50, 190.31.

II.4.1.18  
(E)-3-(p-Chlorophenyl)-1-phenylprop-2-en-1-one (II.1r)

Formula and formula weight : C\textsubscript{15}H\textsubscript{11}ClO, 242.5

State : yellow solid

m.p. : 110-112 °C

Yield (mol%) : 71
IR (thin film on KBr), $\nu$ cm$^{-1}$: 412, 493, 532, 630, 687, 774, 823, 984, 1009, 1089, 1216, 1329, 1402, 1439, 1487, 1597, 1655, 2921, 3061.

$^1$H NMR (400 MHz, CDCl$_3$, TMS) $\delta$: 6.95 (d, $^3J$=8.4 Hz, 1H, aromatic), 7.12-7.44 (complex m, 7H, aromatic & olefinic), 8.02 (d, $^3J$=8.4 Hz, 1H, aromatic).

II.4.1.19 (E)-3-($\sigma$-Nitrophenyl)-1-phenylprop-2-en-1-one (II.1s)

![Chemical Structure](image)

Formula and formula weight: C$_{15}$H$_{11}$O$_3$N, 253

State: brown solid

m.p.: 123-125 °C

Yield (mol%): 80

IR (thin film on KBr), $\nu$ cm$^{-1}$: 561, 669, 728, 807, 978, 1091, 1204, 1260, 1352, 1430, 1524, 1616, 1669, 2920, 3077.

$^1$H NMR (300 MHz, CDCl$_3$, TMS) $\delta$: 7.33 (d, $^3J$= 15.6 Hz, 1H, olefinic), 7.51-7.77 (complex m, 6H, aromatic), 8.02 - 8.25 (complex m, 4H, aromatic).

$^{13}$C NMR (75 MHz, CDCl$_3$): 124.90, 127.25, 128.61, 128.68, 129.14, 130.22, 133.04, 133.47, 140.15, (some signals are not visible).
II.4.2 Preparation of esters and their characterization

Typical procedure for the preparation of esters

A mixture of the acid (0.1 mol), alcohol (in excess, 0.5 mol), chloroform (20 ml) and PTSA (0.5 g) was refluxed in a double neck round bottom flask connected to a reflux condenser and Dean-Stark trap. Azeotrope of chloroform and water collected in the trap was put back to the reaction mixture after separating the aqueous layer from the chloroform. This was continued until substantial degree of conversion was achieved as was monitored on TLC. The reaction was quenched by adding a solution of sodium bicarbonate and extracted with ethyl acetate. The combined organic phase was dried over anhydrous sodium sulfate, filtered and the solvent was removed under vacuum to yield the crude ester. The crude ester was purified by column chromatography over silica gel (60-120 mesh) using a mixture of ethyl acetate and petroleum ether (40-60) as the eluent. The products were characterized by refractive index, FT IR, $^1$H NMR and mass spectra.

II.4.2.1 Dimethyl malonate (II.2)

Formula and formula weight : C$_5$H$_8$O$_4$, 132

State : liquid

Yield (mol%) : 88

Refractive index : 1.413

IR (thin film on KBr), v cm$^{-1}$ : 474, 542, 697, 747, 797, 1022, 1115, 1219, 1270, 1438, 1597, 1682, 1737, 2852, 2925.

$^1$H NMR (400 MHz, CDCl$_3$, TMS) $\delta$ : 3.38 (s, 2H, COCH$_2$ CO), 3.72 (s, 6H, OCH$_3$).
II.4.2.2 Dimethyl succinate (II.3)

Formula and formula weight: C_9H_{10}O_4, 146

State: liquid

Yield (mol\%): 85

Refractive index: 1.418

IR (thin film on KBr), ν cm⁻¹: 542, 701, 761, 920, 1021, 1082, 1153, 1199, 1253, 1322, 1435, 1494, 1602, 1735, 2852, 2955, 3019.

¹H NMR (400 MHz, CDCl₃, TMS) δ: 2.54 (s, 4H, 2CH₂), 3.55 (s, 6H, 2OCH₃).

¹³C NMR (100 MHz, CDCl₃) δ: 28.74, 51.77, 172.69.

II.4.3 Ferric chloride mediated Michael addition of dimethyl malonates to α,β-unsaturated ketones

(i) Typical procedure for Michael addition at ambient temperature

To a stirred solution of dimethyl malonate (1.2 mmol, 1.2 equiv.) in dichloromethane (6 ml, 5 ml per mmol) under nitrogen atmosphere at room temperature in a dry double neck round bottom flask, ferric chloride hexahydrate (54.06 mg, 0.2 equiv.) was added, and stirring continued. After 15 min, the α,β-unsaturated carbonyl compound (1 mmol, 1 equiv.) was added to the reaction mixture, and stirring was
continued at ambient temperature for several hours until the reaction was completed or appeared to have reached equilibrium (monitored by TLC). Reaction was then quenched with water and the mixture partitioned thrice between water and ethyl acetate. The combined organic phase was washed with brine, dried over anhydrous sodium sulfate, filtered and the solvent removed under vacuum to yield the crude product. The crude product was purified by column chromatography over silica gel (60 to 120 mesh) using a mixture of ethyl acetate and petroleum ether as the eluent. Purified products were characterized by melting point, FT IR, $^1$H NMR and GC-MS.

(ii) Typical procedure for Michael addition at refluxing temperature

To a stirred solution of dimethyl malonate (1.2 mmol, 1.2 equiv.) in methanol (12 ml, 10 ml per mmol) under nitrogen atmosphere at room temperature in a dry double neck round bottom flask, ferric chloride hexahydrate (54.06 mg, 0.2 equiv.) was added, and stirring continued. After 15 min, the $\alpha,\beta$-unsaturated carbonyl compound (1 mmol, 1 equiv.) was added to the reaction mixture, and stirring was continued at refluxing temperature for several hours until the reaction was completed or appeared to have reached equilibrium (monitored by TLC). Reaction was then quenched with water and the mixture partitioned thrice between water and ethyl acetate. The combined organic phase was washed with brine, dried over anhydrous sodium sulfate, filtered and the solvent removed under vacuum to yield the crude product. The crude product was purified by column chromatography over silica gel (60 to 120 mesh) using a mixture of ethyl acetate and petrol as the eluent. Purified products were characterized by melting point, FT IR, $^1$H NMR and GC-MS.
Characterization of products

II.4.3.1 Dimethyl 2-(3-oxo-1-phenylbutyl)malonate (II.4a)

Formula & Formula weight: \( \text{C}_{15}\text{H}_{18}\text{O}_5, 278 \)

State: low melting solid

Olefin used: \((E)-4\text{-phenylbut-3-en-2-one}\)

Ester used: dimethyl malonate

Reaction conditions: 35 h at ambient temperature in dichloromethane

Yield (mol\%): 88

Reaction conditions: 50 h at ambient temperature in methanol

Yield (mol\%): 70

Reaction conditions: 30 h at refluxing temperature in methanol

Yield (mol\%): 84

IR (thin film on KBr), \( \nu \text{ cm}^{-1} \): 563, 689, 746, 863, 978, 1022, 1091, 1159, 1237, 1298, 1370, 1436, 1596, 1680, 1731, 2955, 3048.

\(^1\text{H NMR (400 MHz, CDCl}_3, \text{TMS)} \delta: 2.95 \text{ (s, 3H, -COCH}_3\), 3.50 \text{ (complex m, 5H, OCH}_3 \text{ & CH}_2\), 3.65 \text{ (s, 3H, OCH}_3\), 3.85 \text{ (d, }^3\text{J} = 9.2 \text{ Hz, 1H, COCHCO)}, 4.16-4.20 \text{ (m, 1H, PhCH)}\), 7.25 \text{ (unresolved, 2H, aromatic ortho), 7.40 (t, 2H, aromatic meta), 7.50 (t, 1H, aromatic para).}
**II.4.3.2 Dimethyl 2-(1-o-methoxyphenyl-3-oxobutyl)malonate (II.4b)**

![Chemical Structure](image)

**Formula & Formula weight**: $C_{16}H_{20}O_6$, 308

**State**: low melting solid

**Olefin used**: (E)-4-(o-methoxyphenyl)but-3-en-2-one

**Ester used**: dimethyl malonate

**Reaction conditions**: 40 h at ambient temperature in dichloromethane

**Yield (mol%)**: 75

**Reaction conditions**: 60 h at ambient temperature in methanol

**Yield (mol%)**: 52

**Reaction conditions**: 40 h at refluxing temperature in methanol

**Yield (mol%)**: 70

**IR (thin film on KBr), $\nu$ cm$^{-1}$**: 444, 503, 572, 694, 748, 801, 1021, 1092, 1259, 1357, 1443, 1489, 1592, 1685, 1720, 1749.

**$^1$H NMR (400 MHz, CDCl$_3$, TMS)** $\delta$ : 2.50 (s, 3H, -COCH$_3$), 3.46-3.55 (complex m, 2H, CH$_2$), 3.58 (s, 3H, OCH$_3$), 3.65 (s, 3H, OCH$_3$), 3.80 (s, 3H, OCH$_3$), 3.92 (d, 1H, $^3J$=9.2 Hz,
COCHCO, 4.09-4.14 (m, 1H, ArCH), 6.78-6.82 (m, 2H, aromatic), 7.10-7.16 (m, 2H, aromatic).

MS (EI) m/z: 28, 32, 43 (100%), 44, 59, 65, 69, 77, 78, 89, 91, 102, 105, 119, 131, 132, 145, 151, 161, 174, 175, 177, 178, 201, 206, 217, 219, 233, 244, 248, 277, 308, 309 (M+, ~5%).

II.4.3.3 Dimethyl 2-(1-<i>m</i>-methoxyphenyl-3-oxobutyl)malonate (II.4c)

Formula & Formula weight: C<sub>16</sub>H<sub>20</sub>O<sub>6</sub>, 308

State: thick brown liquid

Olefin used: (E)-4-<i>m</i>-methoxyphenyl)but-3-en-2-one

Ester used: dimethyl malonate

Reaction conditions: 40 h at ambient temperature in dichloromethane

Yield (mol%): 76

Reaction conditions: 60 h at ambient temperature in methanol

Yield (mol%): 51

Reaction conditions: 40 h at refluxing temperature in methanol

Yield (mol%): 71

IR (thin film on KBr), v cm<sup>-1</sup>: 503, 699, 748, 856, 1023, 1111, 1175, 1241, 1348, 1449, 1521, 1600, 1671, 1737, 2852, 2926, 2950.
**II.4.3.4 Dimethyl 2-(1-p-methoxyphenyl-3-oxobutyl)malonate (II.4d)**

![Chemical Structure]

**Formula & Formula weight**: $C_{16}H_{20}O_6$, 308

**State**: thick brown liquid

**Olefin used**: $(E)$-4-(p-methoxyphenyl)but-3-en-2-one

**Ester used**: dimethyl malonate

**Reaction conditions**: 40 h at ambient temperature in dichloromethane

**Yield (mol%)**: 80

**Reaction conditions**: 60 h at ambient temperature in methanol

**Yield (mol%)**: 56

**Reaction conditions**: 40 h at refluxing temperature in methanol

**Yield (mol%)**: 72

---

$^1$H NMR (400 MHz, CDCl$_3$, TMS) $\delta$ : 2.58 (s, 3H, -COCH$_3$), 3.62-3.80 (complex m, 5H, OCH$_3$ & CH$_2$), 3.80 (s, 6H, 2OCH$_3$), 3.86 (d, 1H, $^3$J$=9.6$ Hz, COCHCO), 4.20-4.29 (m, 1H, ArCH), 6.99-7.28 (complex m, 4H, aromatic).

MS (El) m/z : 28, 39, 43 (100%), 59, 65, 77, 78, 91, 102, 103, 104, 115, 122, 131, 132, 134, 135, 145, 147, 161, 174, 177, 187, 188, 210, 206, 217, 219, 233, 244, 245, 247, 276, 308, 309 (M$^+$, ~5%).
IR (thin film on KBr), $\nu$ cm$^{-1}$: 559, 645, 699, 802, 846, 1001, 1027, 1163, 1209, 1273, 1361, 1439, 1597, 1661, 1741, 2852, 2956, 2999.

$^1$H NMR (400 MHz, CDCl$_3$, TMS) $\delta$: 2.95 (s, 3H, -COCH$_3$), 3.4-3.6 (complex m, 5H, OCH$_3$ & CH$_2$), 3.68 (s, 6H, 2OCH$_3$), 3.86 (d, $^3J$=9.0 Hz, 1H, COCHCO), 3.94-4.2 (m, 1H, ArCH$_2$), 7.0-7.6 (complex m, 4H, aromatic).

MS (El) m/z: 28, 43, 51, 59, 77, 78, 91, 102, 103, 104, 115, 117, 121, 131 (100%), 132, 145, 146, 157, 176, 203, 216, 234, 235, 248, 277, 308, 309 (M$^+$, ~5%).

II.4.3.5 Dimethyl 2-(1-p-chlorophenyl-3-oxobutyl)malonate (II.4e)

Formula & Formula weight: C$_{15}$H$_{17}$ClO$_5$, 312.5

State: thick brown liquid

Olefin used: (E)-4-(p-chlorophenyl)but-3-en-2-one

Ester used: dimethyl malonate

Reaction conditions: 40 h at ambient temperature in dichloromethane

Yield (mol%): 80

Reaction conditions: 60 h at ambient temperature in methanol

Yield (mol%): 60
Part II.4

Reaction conditions: 35 h at refluxing temperature in methanol

Yield (mol%): 69

IR (thin film on KBr), v cm\(^{-1}\): 564, 688, 747, 763, 866, 1025, 1092, 1161, 1239, 1350, 1450, 1498, 1593, 1680, 1731, 2950, 3058.

\(^1\)H NMR (400 MHz, CDCl\(_3\), TMS) \(\delta\): 3.02 (s, 3H, -COCH\(_3\)), 3.60-3.64 (m, 5H, CH\(_2\) and OCH\(_3\)), 3.71 (s, 3H, OCH\(_3\)), 3.80 (d, 1H, \(J=9.2\) Hz, COCHCO), 4.24-4.30 (m, 1H, ArCH\(_2\)).

7.18-7.50 (m, 4H, aromatic).

MS (El) m/z: 28, 43 (100%), 59, 69, 75, 101, 102, 103, 115, 132, 137, 138, 155, 165, 179, 181, 183, 192, 205, 210, 221, 225, 235, 249, 255, 281, 312 (M\(^+\), ~7%).

II.4.3.6 Dimethyl 2-(1-o-nitrophenyl-3-oxobutyl)malonate (II.4f)

\[\text{C}_{15}\text{H}_{17}\text{O}_7\text{N}, 323\]

State: low melting solid

Olefin used: (E)-4-(o-nitrophenyl)but-3-en-2-one

Ester used: dimethyl malonate

Reaction conditions: 35 h at ambient temperature in dichloromethane

Yield (mol%): 82

Reaction conditions: 30 h at refluxing temperature in methanol
Yield (mol%) : 77

IR (thin film on KBr), v cm\(^{-1}\): 694, 748, 802, 1023, 1092, 1156, 1254, 1347, 1430, 1459, 1531, 1600, 1646, 1735, 2862, 2930.

\(^1\)H NMR (400 MHz, CDCl\(_3\), TMS) \(\delta\): 2.66 (s, 3H, -COC\(_3\)), 3.44-3.60 (m, 5H, OCH\(_3\) & CH\(_2\)), 3.82 (s, 3H, OCH\(_3\)), 4.02 (d, \(^3\)J=7.2 Hz, 1H, COCHCO), 4.39-4.47 (m, 1H, ArCH), 7.41-7.49 (m, 1H, aromatic), 7.65-7.74 (m, 1H, aromatic), 8.17 (d, \(^3\)J=3.2 Hz, 2H, aromatic).

II.4.3.7 Dimethyl 2-(1-p-nitrophenyl-3-oxobutyI)malonates (II.4g)

![Chemical Structure](image)

Formula & Formula weight : \(\text{C}_{15}\text{H}_{17}\text{O}_{7}\text{N}\), 323

State : thick liquid

Olefin used : (E)-4-(p-nitrophenyl)but-3-en-2-one

Ester used : dimethyl malonate

Reaction conditions : 35 h at ambient temperature in dichloromethane

Yield (mol%) : 85

Reaction conditions : 30 h at refluxing temperature in methanol

Yield (mol%) : 79
IR (thin film on KBr), $v \text{ cm}^{-1}$: 552, 689, 739, 808, 890, 1023, 1096, 1160, 1261, 1350, 1436, 1533, 1599, 1646, 1734, 2852, 2925, 3077.

$^1$H NMR (400 MHz, CDCl$_3$, TMS) $\delta$: 2.62 (s, 3H, -COCH$_3$), 3.28-3.44 (m, 5H, OCH$_3$ & COCH$_2$), 3.84 (s, 3H, OCH$_3$), 4.00 (d, $^3J=10$ Hz. 1H, COCHCO), 4.24-4.79 (m, 1H, CH). 8.09-8.27 (m, 4H, aromatic).

II.4.3.8 Dimethyl 2-(1-p-methylphenyl-3-oxobuty]malonate (II.4h)

![Chemical Structure](image)

Formula & Formula weight: C$_{16}$H$_{20}$O$_5$, 292

State: thick brown liquid

Olefin used: (E)-4-(p-methylphenyl)but-3-en-2-one

Ester used: dimethyl malonate

Reaction conditions: 40 h at ambient temperature in dichloromethane

Yield (mol\%): 72

Reaction conditions: 35 h at refluxing temperature in methanol

Yield (mol\%): 66

IR (thin film on KBr), $v \text{ cm}^{-1}$: 498, 517, 699, 813, 1023, 1092, 1160, 1261, 1352, 1411, 1444, 1516, 1601, 1655, 1711, 2852, 2923, 2950.
$^1$H NMR (400 MHz, CDCl$_3$, TMS) $\delta$: 3.04 (s, 3H, -COCH$_3$), 3.14 (s, 3H, ArCH$_3$), 3.42-3.50 (m, 5H, OCH$_3$ & COCH$_2$), 3.60 (s, 3H, OCH$_3$), 3.72 (d, $^3$J=8.8 Hz, 1H, COCHCO), 3.88-3.95 (m, 1H, ArCH$_3$), 7.02-7.16 (m, 4H, aromatic).

II.4.3.9 Dimethyl 2-(1-p-hydroxyphenyl-3-oxobutyl)malonate (II.4i)

![Structure](image)

**Formula & Formula weight**: C$_{15}$H$_{18}$O$_6$, 294

**State**: thick liquid

**Olefin used**: (E)-4-(p-hydroxyphenyl)but-3-en-2-one

**Ester used**: dimethyl malonate

**Reaction conditions**: 40 h at ambient temperature in dichloromethane

**Yield (mol%)**: 75

**Reaction conditions**: 30 h at refluxing temperature in methanol

**Yield (mol%)**: 68

**IR (thin film on KBr), v cm$^{-1}$**: 537, 699, 748, 857, 1077, 1106, 1165, 1350, 1521, 1600, 1663, 1703, 2852, 2920, 3448.
II.4.3.10  Dimethyl 2-(3-oxo-1,3-diphenylpropyl)malonate\textsuperscript{14} (II.4j)

\begin{center}
\includegraphics[width=0.5\textwidth]{structure.png}
\end{center}

Formula & Formula weight : C\textsubscript{20}H\textsubscript{20}O\textsubscript{5}, 340

State : white solid

m.p. : 80-82 °C

Olefin used : chalcone

Ester used : dimethyl malonate

Reaction conditions : 50 h at ambient temperature in dichloromethane

Yield (mol\%) : 80

Reaction conditions : 40 h at refluxing temperature in methanol

Yield (mol\%) : 77

IR (thin film on KBr), ν cm\textsuperscript{-1} : 542, 564, 688, 746, 763, 869, 924, 959, 978, 1024, 1093, 1160, 1239, 1309, 1368, 1450, 1489, 1595, 1680, 1731, 2842, 2901, 2954, 3048.

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}, TMS) δ : 2.05 (s, 3H, -COCH\textsubscript{3}), 2.89-2.93 (m, 2H, COCH\textsubscript{2}), 3.45-3.78 (m, 8H, 2CO\textsubscript{2}CH\textsubscript{3}, COCHCO & ArOH), 3.88-3.90 (m, 1H, PhCH), 6.66 (d, \textsuperscript{3}J=7.2 Hz, 2H, aromatic), 7.05 (d, \textsuperscript{3}J=7.2 Hz, 2H, aromatic).
$^1$H NMR (400 MHz, CDCl$_3$, TMS) $\delta$ : 3.42-3.55 (complex m, 5H, OCH$_3$ & COCH$_2$), 3.71 (s, 3H, CH$_3$), 3.84 (d, $^3$$J$=9.2 Hz, 1H, COCHCO), 4.14-4.20 (m, 1H, ArCH), 7.14-7.17 (m, 1H, aromatic), 7.20-7.24 (m, 5H, aromatic), 7.37-7.41 (m, 2H, aromatic), 7.48-7.52 (m, 1H, aromatic), 7.86-7.88 (m, 2H, aromatic).

MS (EI) m/z : 28, 39, 51, 59, 77, 78, 103, 105 (100%), 115, 131, 144, 157, 171, 189, 207, 209, 221, 231, 249, 263, 277, 309, 340 (M$^-$, ~5%).

**II.4.3.11 Dimethyl 2-(1-o-methoxyphenyl-3-oxo-3-phenylpropyl)malonate (II.4k)**

![Chemical Structure](attachment:image.png)

**Formula & Formula weight** : C$_{21}$H$_{22}$O$_6$, 370

**State** : thick brown liquid

**Olefin used** : (E)-3-(o-methoxyphenyl)-1-phenylprop-2-en-1-one

**Ester used** : dimethyl malonate

**Reaction conditions** : 50 h at ambient temperature in dichloromethane

**Yield (mol%)** : 69

**Reaction conditions** : 45 h at refluxing temperature in methanol

**Yield (mol%)** : 62
IR (thin film on KBr), $v$ cm$^{-1}$: 414, 532, 606, 742, 836, 897, 947, 1030, 1123, 1176, 1243, 1369, 1443, 1515, 1611, 1669, 1738, 2871, 2962, 3057.

$^1$H NMR (400 MHz, CDCl$_3$, TMS) $\delta$: 3.48-3.72 (complex m, 8H, 2OCH$_3$ & COCH$_2$), 3.81 (s, 3H, OCH$_3$), 4.20 (d, $^3J=9.2$ Hz, 1H, COCHCO), 4.33-5.27 (m, 1H, ArCH), 6.79-6.83 (m, 2H, aromatic), 7.14-7.17 (m, 2H, aromatic), 7.39-7.45 (d, 2H, aromatic), 7.49-7.53 (m, 1H, aromatic), 7.89-7.92 (m, 2H, aromatic).


II.4.3.12 Dimethyl 2-(1-$m$-methoxyphenyl-3-oxo-3-phenylpropyl)malonate (II.41)

![Chemical structure](image)

Formula & Formula weight: C$_{21}$H$_{22}$O$_6$, 370

State: brown solid

m.p.: 62-63°C

Olefin used: (E)-3-($m$-methoxyphenyl)-1-phenylprop-2-en-1-one

Ester used: dimethyl malonate
Reaction conditions: 50 h at ambient temperature in dichloromethane

Yield (mol%) : 72

Reaction conditions: 45 h at refluxing temperature in methanol

Yield (mol%) : 70

IR (thin film on KBr), ν cm⁻¹: 563, 650, 763, 1000, 1165, 1214, 1263, 1363, 1439, 1600, 1663, 1738, 2852, 2950, 2999.

¹H NMR (400 MHz, CDCl₃, TMS): δ: 3.40-3.80 (complex m, 12H, 3ΟCH₃, COCHCO & COCH₂), 4.06-4.17 (m, 1H, ArCH), 6.67-7.87 (complex m, 9H, aromatic).


II.4.3.13 Dimethyl 2-(1-p-methoxyphenyl-3-oxo-3-phenylpropyl)malonate (II.4m)

Formula & Formula weight: C₂₁H₂₂O₆, 370

State: brown solid

m.p.: 80-82 °C

Olefin used: (E)-3-(p-methoxyphenyl)-1-phenylprop-2-en-1-one

Ester used: dimethyl malonate
Reaction conditions : 50 h at ambient temperature in dichloromethane
Yield (mol%) : 73

Reaction conditions : 45 h at refluxing temperature in methanol
Yield (mol%) : 70

IR (thin film on KBr), v cm$^{-1}$: 434, 533, 741, 836, 897, 1030, 1123, 1176, 1243, 1369,
1443, 1515, 1611, 1669, 1738, 2871, 2962, 3057.

$^1$H NMR (400 MHz, CDCl$_3$, TMS) $\delta$: 3.47-3.55 (complex m, 5H, CO$_2$CH$_3$ & CH$_2$), 3.65
(s, 6H, OCH$_3$ & ArOCH$_3$), 3.90 (d, $^3$$J$=9.8 Hz, 1H,
COCHCO), 4.16-4.20 (m, 1H, ArCH), 7.25-7.61
(m, 9H, aromatic).

II.4.3.14 Dimethyl 2-(1-o-chlorophenyl-3-oxo-3-phenylpropyl)malonate (II.4n)

![Chemical structure](image)

Formula & Formula weight : C$_{29}$H$_{19}$O$_5$Cl, 374.5

State : thick liquid

Olefin used : (E)-3-(o-chlorophenyl)-1-phenylprop-2-en-1-one

Ester used : dimethyl malonate

Reaction conditions : 50 h at ambient temperature in dichloromethane

Yield (mol%) : 72
Part II.4

Reaction conditions : 35 h at refluxing temperature in methanol

Yield (mol%) : 67

IR (thin film on KBr), $\nu$ cm$^{-1}$ : 411, 699, 748, 856, 1028, 1106, 1175, 1242, 1348, 1444, 1520, 1600, 1665, 1736, 2852, 2926.

$^1$H NMR (400 MHz, CDCl$_3$, TMS) $\delta$ : 3.31-3.52 (complex m, 5H, OCH$_3$ & COCH$_2$).

3.71 (s, 3H, OCH$_3$), 3.80 (d, $^3$$J$=9.6 Hz, 1H, COCHCO), 4.11-4.17 (m, 1H, ArCH$_2$). 7.17-7.88 (complex m, 9H, aromatic).

MS (EI) m/z : 28, 32, 51, 59, 76, 77, 78, 101, 105 (100%), 106, 120, 137, 155, 165, 179, 207, 223, 241, 243, 255, 283, 297, 311, 317, 343, 374 (M$^+$~5%)

II.4.3.15 Dimethyl 2-(1-$p$-chlorophenyl-3-oxo-3-phenylpropyl)malonate (II.4o)

![Chemical structure](image)

Formula & Formula weight : C$_{20}$H$_{19}$O$_5$Cl, 374.5

State : white solid

m.p. : 85-87 °C

Olefin used : $(E)$-3-($p$-chlorophenyl)-1-phenylprop-2-en-1-one

Ester used : dimethyl malonate

Reaction conditions : 50 h at ambient temperature in dichloromethane

Yield (mol%) : 77
Reaction conditions: 35 h at refluxing temperature in methanol
Yield (mol%): 71

IR (thin film on KBr, ν cm⁻¹): 561, 697, 751, 1023, 1067, 1156, 1258, 1381, 1454, 1533, 1597, 1687, 1733, 2871, 2960, 3058.

¹H NMR (400 MHz, CDCl₃, TMS) δ: 3.43-3.56 (complex m, 5H, OCH₂ & COCH₂), 3.70 (s, 3H, OCH₃), 3.85 (d, ³J=9.2 Hz, 1H, COCHCO), 4.15-4.21 (m, 1H, ArCH), 7.14-7.52 (complex m, 9H, aromatic).

¹³C NMR (100 MHz, CDCl₃, TMS) δ: 40.09, 42.14, 52.67, 52.79, 57.04, 128.07, 128.65, 128.67, 129.55, 132.99, 133.28, 136.58, 138.96, 167.99, 168.53, 197.22.


II.4.3.16 Dimethyl 2-(1-o-nitrophenyl-3-oxo-3-phenylpropyl)malonate (II.4p)

Formula & Formula weight: C₂₀H₁₉O₇N, 385
State: thick liquid
Olefin used: (E)-3-(o-nitrophenyl)-1-phenylprop-2-en-1-one
Ester used: dimethyl malonate
Reaction conditions: 40 h at ambient temperature in dichloromethane

Yield (mol%): 80

Reaction conditions: 30 h at refluxing temperature in methanol

Yield (mol%): 75

IR (thin film on KBr), ν cm⁻¹: 412, 756, 802, 1023, 1150, 1248, 1351, 1438, 1489, 1597, 1665, 1733, 2852, 2952.

¹H NMR (400 MHz, CDCl₃, TMS) δ: 3.48-3.53 (complex m, 5H, OCH₃ & COCH₂), 3.72 (s, 3H, OCH₃), 3.86 (d, ³J=9.2 Hz, 1H, COCHCO), 4.19-4.20 (m, 1H, ArCH), 7.17-7.90 (complex m, 9H, aromatic).

II.4.4 Ferric chloride mediated Michael addition of dimethyl succinate to α,β-unsaturated ketones.

(i) Typical procedure for Michael addition at ambient temperature

To a stirred solution of dimethyl succinate (1.5 mmol, 1.5 equiv.) in dichloromethane (7.5 ml, 5 ml per mmol) under nitrogen atmosphere at room temperature in a dry double neck round bottom flask, ferric chloride hexahydrate (54.06 mg, 0.2 equiv.) was added, and stirring continued. After 15 min, the α,β-unsaturated carbonyl compound (1 mmol, 1 equiv.) was added to the reaction mixture, and stirring was continued at ambient temperature for several hours until the reaction was completed or appeared to have reached equilibrium (monitored by TLC). Reaction was then quenched with water and the mixture partitioned thrice between water and ethyl acetate. The combined organic phase was washed with brine, dried over anhydrous sodium sulfate, filtered and the solvent removed under vacuum to yield the crude product. The crude
product was purified by column chromatography over silica gel (60 to 120 mesh) using a mixture of ethyl acetate and petroleum ether as the eluent. Purified products were characterized by melting point, FT IR, $^1$H NMR and GC-MS.

(ii) Typical procedure for Michael addition at refluxing temperature

To a stirred solution of dimethyl malonate (1.5 mmol, 1.5 equiv.) in methanol (15 ml, 10 ml per mmol) under nitrogen atmosphere at room temperature in a dry double neck round bottom flask, ferric chloride hexahydrate (54.06 mg, 0.2 equiv.) was added, and stirring continued. After 15 min, the $\alpha,\beta$-unsaturated carbonyl compound (1 mmol, 1 equiv.) was added to the reaction mixture, and stirring was continued at refluxing temperature for several hours until the reaction was completed or appeared to have reached equilibrium (monitored by TLC). Reaction was then quenched with water and the mixture partitioned thrice between water and ethyl acetate. The combined organic phase was washed with brine, dried over anhydrous sodium sulfate, filtered and the solvent removed under vacuum to yield the crude product. The crude product was purified by column chromatography over silica gel (60 to 120 mesh) using a mixture of ethyl acetate and petrol as the eluent. Purified products were characterized by melting point, FT IR, $^1$H NMR and GC-MS.

Characterization of Products

II.4.4.1 Dimethyl 2-(3-oxo-1-phenylbutyl)succinate (II.5a)

Formula & Formula weight : $C_{16}H_{20}O_5$, 292
State: thick brown liquid

Olefin used: (E)-4-phenylbut-3-en-2-one

Ester used: dimethyl succinate

Reaction conditions: 48 h at ambient temperature in dichloromethane

Yield (mol%): 88

Reaction conditions: 40 h at refluxing temperature in methanol

Yield (mol%): 82

IR (thin film on KBr), ν cm⁻¹: 497, 518, 737, 813, 1028, 1114, 1166, 1229, 1262, 1355, 1417, 1449, 1514, 1604, 1642, 1710, 2862, 2923, 2950, 3058.

¹H NMR (400 MHz, CDCl₃, TMS) δ: 1.62 (s, 3H, CH₃CO), 2.62 (s, 3H, CO₂CH₃), 2.63-2.75 (complex m, 2H, CHHCO₂Me & CHHCOCH₃), 2.99 (dd, ²J=6 Hz, ³J=16 Hz, 1H, CHHCO₂Me or CHHCOCH₃), 3.17 (dd, ²J=10.4 Hz, ³J=16 Hz, 1H, CHHCO₂Me or CHHCOCH₃), 3.42-3.63 (complex m, 2H, CHCO₂Me & PhCH), 3.67 (s, 3H, CO₂CH₃), 7.00-7.35 (complex m, 5H, aromatic).

II.4.4.2 Dimethyl 2-(1-o-methoxyphenyl-3-oxobutyl)succinate (II.5b)

Formula & Formula weight: $C_{17}H_{22}O_6$, 322

State: thick brown liquid

Olefin: $(E)$-4-(o-methoxyphenyl)but-3-en-2-one

Ester used: dimethyl succinate

Reaction conditions: 60 h at ambient temperature in dichloromethane

Yield (mol%): 82

Reaction conditions: 50 h at refluxing temperature in methanol

Yield (mol%): 69

IR (thin film on KBr), $\nu \text{ cm}^{-1}$: 580, 699, 758, 797, 1028, 1072, 1101, 1165, 1258, 1381, 1411, 1449, 1489, 1607, 1631, 1711, 2852, 2925, 3019, 3058.

$^1$H NMR (400 MHz, CDCl$_3$, TMS) $\delta$: 1.69 (s, 3H, $CH_3$CO), 2.65-2.79 (complex m, 2H, $CH_3CO$ or $CH_2$COCH$_3$), 3.02 (dd, $^2J=6$ Hz, $^3J=16$ Hz, 1H, $CHHCO_2$Me or $CHHCOCH_3$), 3.20 (dd, $^2J=10$ Hz, $^3J=15$ Hz, 1H, $CHHCO_2$Me or $CHHCOCH_3$), 3.39 (s, 3H, ArOCH$_3$), 3.49-3.63.
II.4.4.3 Dimethyl 2-(1-m-methoxyphenyl-3-oxobutyI)succinate (II.5c)

Formula & Formula weight : C_{17}H_{22}O_{6}, 322

State : white solid
m.p. : 128-130 °C
Olefin : \((E)-4-(m\text{-methoxyphenyl})\text{but-3-en-2-one}\)
Ester used : dimethyl succinate

Reaction conditions : 60 h at ambient temperature in dichloromethane
Yield (mol%) : 84

Reaction conditions : 50 h at refluxing temperature in methanol
Yield (mol%) : 74

IR (thin film on KBr), ν cm\(^{-1}\) : 542, 601, 753, 810, 984, 1032, 1106, 1180, 1256, 1283, 1352, 1415, 1455, 1515, 1607, 1656, 1711, 2852, 2924, 3009.

\(^1\)H NMR (400 MHz, CDCl\(_3\), TMS) δ : 1.79 (s, 3H, CH\(_3\)CO), 2.81-2.90 (complex m, 2H, CH\(\text{HCO}_2\text{Me} \& \text{CH}_3\text{COCH}_3\)), 3.18 (dd, \(\text{J}=5.2\) Hz,
$^3J=16$ Hz, 1H, $CHHCO_2Me$ or $CHHCO_2CH_3$, 3.36 Hz.

(dd, $^2J=10$ Hz, $^3J=15.2$ Hz, 1H, $CHHCO_2Me$ or $CHHCO_2CH_3$), 3.47 (s, 3H, ArOCH$_3$), 3.58-3.80 Hz (complex m, 2H, $CHCO_2Me$ & PhCH$_2$), 3.85 (s, 6H, $2CO_2CH_3$), 7.38-7.70 (complex m, 4H, aromatic).

MS (EI) m/z : 28 (100%), 40, 43, 77, 89, 91, 105, 115, 121, 134, 145, 147, 159, 161, 175, 190, 175, 190, 217, 218, 231, 279, 309, 321, 322 (($M^+$, ~2%).

II.4.4.4 Dimethyl 2-(1-p-methoxyphenyl-3-oxobutyl)succinate (II.5d)

![Chemical Structure](image.png)

Formula & Formula weight : C$_{17}$H$_{22}$O$_6$, 322

State : thick brown liquid

Olefin : $(E)$-4-(p-methoxyphenyl)but-3-en-2-one

Ester used : dimethyl succinate

Reaction conditions : 60 h at ambient temperature in dichloromethane

Yield (mol%) : 85

Reaction conditions : 50 h at refluxing temperature in methanol

Yield (mol%) : 74
IR (thin film on KBr), $v \text{ cm}^{-1}$: 415, 478, 577, 685, 714, 768, 861, 935, 984, 1033, 1172, 1194, 1273, 1319, 1444, 1489, 1597, 1640, 1711, 2852, 2940, 3048.

$^1$H NMR (400 MHz, CDCl$_3$, TMS) $\delta$: 1.70 (s, 3H, $CH_3CO$), 2.47 (dd, $^2J=4.4$ Hz, $^3J=15.6$ Hz, 1H, $CHHCO_2Me$ or $CHHCOCH_3$), 2.74 (dd, $^2J=6$ Hz, $^3J=16$ Hz, 1H, $CHHCO_2Me$ or $CHHCOCH_3$), 2.94 (dd, $^2J=6.4$ Hz, $^3J=16$ Hz, 1H, $CHHCO_2Me$ or $CHHCOCH_3$), 3.27 (dd, $^2J=11.6$ Hz, $^3J=15.6$ Hz, 1H, $CHHCO_2Me$ or $CHHCOCH_3$), 3.45 (dd, $^3J=7.2$ Hz & 6.8 Hz), 3.57 (s, 3H, ArOCH$_3$), 3.65 (t, $^3J=5$ Hz), 3.76 (dt, $^3J=4.8$ Hz & 9.2 Hz), 3.84 (s, 6H, $2CO_2CH_3$), 3.85-3.90 (m), 6.75-7.24 (complex m, 4H, aromatic).

MS (EI) m/z: 27, 28, 43, 51, 55, 65, 76, 77, 89, 91, 105, 115, 121, 131, 134, 135, 145, 147, 159, 161, 175, 190, 201, 217 (100%), 218, 231, 253, 279, 309, 321, 322 ($M^+$, ~5%).

II.4.4.5 Dimethyl 2-(1-o-chlorophenyl-3-oxobutyl)succinate (II.5e)

![Chemical Structure](image)

Formula & Formula weight: $C_{16}H_{19}O_5Cl$, 326.5

State: thick brown liquid
Olefin : \((E)\)-4-(o-chlorophenyl)but-3-en-2-one

Ester used : dimethyl succinate

Reaction conditions : 50 h at ambient temperature in dichloromethane

Yield (mol%) : 77

Reaction conditions : 45 h at refluxing temperature in methanol

Yield (mol%) : 67

IR (thin film on KBr), \(\nu\) cm\(^{-1}\) : 552, 703, 759, 802, 1028, 1077, 1097, 1259, 1376, 1410, 1449, 1489, 1607, 1655, 1711, 2862, 2925, 3058.

\(^1\)H NMR (400 MHz, CDCl\(_3\), TMS) \(\delta\) : 1.63 (s, 3H, \(CH_3\)CO), 2.61-2.76 (m, 5H, \(\text{CH}_2\)CO\(_2\)Me and \(\text{CH}_2\)COCH\(_3\)), 3.02 (dd, \(^2J=5.6\) Hz, \(^3J=15.6\) Hz, 1H, \(\text{CH}_2\)CO\(_2\)Me or \(\text{CH}_2\)COCH\(_3\)).

3.19 (dd, \(^2J=10\) Hz, \(^3J=15.2\) Hz, 1H, \(\text{CH}_2\)CO\(_2\)Me or \(\text{CH}_2\)COCH\(_3\)).

3.43-3.69 (complex m, 5H, \(\text{CO}_2\)CH\(_3\), ArCH \& COCH), 7.21-7.36 (complex m, 4H, aromatic).

II.4.4.6 Dimethyl 2-(1-\(m\)-chlorophenyl-3-oxobutyl)succinate (II.5f)

[Diagram of the compound]

Formula & Formula weight : C\(_{16}\)H\(_{15}\)O\(_5\)Cl, 326.5

State : thick brown liquid

Olefin : \((E)\)-4-(\(m\)-chlorophenyl)but-3-en-2-one
Ester used: dimethyl succinate

Reaction conditions: 50 h at ambient temperature in dichloromethane

Yield (mol%): 77

Reaction conditions: 45 h at refluxing temperature in methanol

Yield (mol%): 70

IR (thin film on KBr), v cm⁻¹: 520, 748, 828, 969, 1013, 1170, 1227, 1355, 1492, 1600, 1651, 1712, 2992, 2984, 3058.

¹H NMR (400 MHz, CDCl₃, TMS) δ: 1.78 (s, 3H, CH₃CO), 2.73 (s, 3H, CO₂C₆H₃), 2.77-2.92 (m, 2H, CII/CO₂Me and CH/COCH₃), 3.17 (dd, ²J=6 Hz, ³J=16 Hz, 1H, CHHCO₂Me or CHHCOCH₃), 3.35 (dd, ²J=10 Hz, ³J=16 Hz, 1H, CHHCO₂Me or CHHCOCH₃), 3.58-3.79 (m, 2H, CHHCO₂Me & PhCH), 3.84 (s, 3H, CO₂CH₃), 7.18-7.52 (complex m, 4H, aromatic).

II.4.4.7 Dimethyl 2-(1-p-chlorophenyl-3-oxobutyl)succinate (II.5g)

Formula & Formula weight: C₁₆H₁₉O₂Cl, 326.5

State: brown solid

m.p.: 68-72°C
<table>
<thead>
<tr>
<th>Olefin</th>
<th>(E)-4-(p-chlorophenyl)but-3-en-2-one</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ester used</td>
<td>dimethyl succinate</td>
</tr>
<tr>
<td>Reaction conditions</td>
<td>48 h at ambient temperature in dichloromethane</td>
</tr>
<tr>
<td>Yield (mol%)</td>
<td>78</td>
</tr>
<tr>
<td>Reaction conditions</td>
<td>45 h at refluxing temperature in methanol</td>
</tr>
<tr>
<td>Yield (mol%)</td>
<td>69</td>
</tr>
</tbody>
</table>

IR (thin film on KBr), $v$ cm$^{-1}$: 521, 738, 827, 895, 1013, 1093, 1168, 1227, 1355, 1412, 1492, 1601, 1669, 1713, 2982, 3048.

$^1$H NMR (400 MHz, CDCl$_3$, TMS) $\delta$: 1.70 (s, 3H, CH$_3$CO), 2.61 (s, 3H, CO$_2$CH$_3$), 2.62-2.70 (m, 2H, CHHCO$_2$Me and CHHCOCH$_3$), 2.96 (dd, $^2J$=6 Hz, $^3J$=16 Hz, 1H, CHHCO$_2$Me or CHHCOCH$_3$), 3.16 (dd, $^2J$=10 Hz, $^3J$=14.8 Hz, 1H, CHHCO$_2$Me or CHHCOCH$_3$), 3.35 (t, $^3J$=6 Hz), 3.43-3.49 (m), 3.56 (dd, $^2J$=6 Hz, $^3J$=13.2 Hz), 3.64 (s, 3H, CO$_2$CH$_3$), 6.94-8.02 (complex m, 4H, aromatic).

II.4.4.8 Dimethyl 2-(1-o-nitrophenyl-3-oxobutyl)succinate (II.5h)

Formula & Formula weight: C₁₆H₁₉O₇N, 337
State: thick brown liquid
Olefin: (E)-4-(o-nitrophenyl)but-3-en-2-one
Ester used: dimethyl succinate
Reaction conditions: 50 h at ambient temperature in dichloromethane
Yield (mol%): 85
Reaction conditions: 40 h at refluxing temperature in methanol
Yield (mol%): 80
IR (thin film on KBr), v cm⁻¹: 699, 758, 1027, 1072, 1101, 1165, 1258, 1381, 1449, 1489, 1606, 1650, 1709, 2852, 2925, 3058.

¹H NMR (400 MHz, CDCl₃, TMS) δ: 1.87 (s, 3H, CH₃ CO), 2.62-2.66 (m, 3H, CO₂ CH₃ & CHHCO₂Me or CHHCOCH₃), 2.76 (dd, ²J=6.4 Hz, ³J=16 Hz, 1H, CHHCO₂Me or CHHCOCH₃), 2.98 (dd, ²J=6 Hz, ³J=16 Hz, 1H, CHHCO₂Me or CHHCOCH₃), 3.27 (dd, ²J=10 Hz, ³J=15.6 Hz, 1H, CHHCO₂Me or CHHCOCH₃), 3.45-3.74 (complex m, 5H, CHCO₂Me, ArCH, & CO₂CH₃), 7.16-8.30 (complex m, 4H, aromatic).
D.4.4.9 Dimethyl 2-(1-m-nitrophenyl-3-oxobutyl)succinate (II.5i)

Formula & Formula weight : $C_{16}H_{19}O_7N$, 337

State : thick brown liquid

Olefin : $(E)$-4-($m$-nitrophenyl)but-3-en-2-one

Ester used : dimethyl succinate

Reaction conditions : 50 h at ambient temperature in dichloromethane

Yield (mol%) : 90

Reaction conditions : 40 h at refluxing temperature in methanol

Yield (mol%) : 88

IR (thin film on KBr), $\nu$ cm$^{-1}$ : 516, 668, 701, 761, 1030, 1076, 1164, 1244, 1356, 1454, 1496, 1602, 1649, 1713, 2850, 2924, 3029, 3075.

$^1$H NMR (400 MHz, CDCl$_3$, TMS) $\delta$ : 2.12 (s, 3H, $CH_3CO$), 2.85-2.89 (complex m, 4H, $CO_2CH_2$ & $CHCO_2Me$ or $CHCOCH_3$), 2.95 (dd, $^2J=6$ Hz, $^3J=17.6$ Hz, 1H, $CHHCO_2Me$ or $CHHCOCH_3$), 3.08 (dd, $^2J=12$ Hz, $^3J=17.2$ Hz, 1H, $CHHCO_2Me$ or $CHHCOCH_3$), 3.34 (dd, $^2J=5.6$ Hz, $^3J=17.6$ Hz, 1H, $CHHCO_2Me$ or $CHHCOCH_3$), 3.42-3.71 (complex m, 2H, $CHCO_2Me$ & Ph$CH$), 3.80 (s, 3H, $CO_2CH_3$), 7.46-8.16 (complex m, 4H, aromatic).
II.4.4.10  Dimethyl 2-(1-p-nitrophenyl-3-oxobutyl)succinate (II.5j)

Formula & Formula weight: C_{16}H_{19}O_{7}N, 337

State: thick brown liquid

Olefin: (\(E\)-4-(p-nitrophenyl)but-3-en-2-one)

Ester used: dimethyl succinate

Reaction conditions: 50 h at ambient temperature in dichloromethane

Yield (mol\%): 92

Reaction conditions: 40 h at refluxing temperature in methanol

Yield (mol\%): 88

IR (thin film on KBr), \(\nu\) cm\(^{-1}\): 482, 702, 740, 1048, 1126, 1161, 1266, 1361, 1451, 1494, 1602, 1648, 1714, 2854, 2927, 2961, 3058.

\(^1\)H NMR (400 MHz, CDCl\(_3\), TMS) \(\delta\): 1.89 (s, 3H, \(CH_3\)CO), 2.62-2.66 (m, 3H, \(CO_2\)Me or \(CHHCOCH_3\)), 2.77 (dd, \(^2J=6\) Hz, \(^3J=16\) Hz, 1H, \(CHHCO_2\)Me or \(CHHCOCH_3\)), 2.98 (dd, \(^2J=6\) Hz, \(^3J=16\) Hz, 1H, \(CHHCO_2\)Me or \(CHHCOCH_3\)), 3.28 (dd, \(^2J=10\) Hz, \(^3J=15.6\) Hz, 1H, \(CHHCO_2\)Me or \(CHHCOCH_3\)), 3.43-3.74 (complex m, 5H, \(CHCO_2\)Me, \(ArCH\), & \(CO_2CH_3\)), 7.16-8.27 (complex m, 4H, aromatic).
II.4.4.11  Dimethyl 2-(3-oxo-1-p-tolylbutyl)succinate (II.5k)

Formula & Formula weight : C_{17}H_{22}O_{5}, 306

State : thick brown liquid

Olefin : (E)-4-p-tolylbut-3-en-2-one

Ester used : dimethyl succinate

Reaction conditions : 50 h at ambient temperature in dichloromethane

Yield (mol%) : 85

Reaction conditions : 45 h at refluxing temperature in methanol

Yield (mol%) : 75

IR (thin film on KBr), v cm\(^{-1}\) : 523, 738, 802, 1015, 1092, 1170, 1263, 1366, 1414, 1492, 1592, 1661, 1710, 2862, 2926, 2950, 3048.

\(^{1}\)H NMR (400 MHz, CDCl\(_3\), TMS) \(\delta\) : 1.60 (s, 3H, CH\(_3\)CO), 2.40 (s, 3H, ArCH\(_3\)), 2.60-2.65 (complex m, 2H, CHHCO\(_2\)Me & CHHCOCH\(_3\)), 2.86 (dd, \(^2\)J=6 Hz, \(^3\)J=15.6 Hz, 1H, CHHCO\(_2\)Me or CHHCOCH\(_3\)), 3.12 (dd, \(^2\)J=10 Hz, \(^3\)J=16 Hz, 1H, CHHCO\(_2\)Me or CHHCOCH\(_3\)), 3.37-3.57 (complex m, 2H, CHCO\(_2\)Me & PhCH), 3.71 (s, 6H, 2CO\(_2\)CH\(_3\)), 6.89-7.24 (complex m, 4H, aromatic).

References to Parts II.2 to II.4

12. C H Heathcock, S D Young, J P Hagen, M C Pirrung, C T White, D VanDerveer, 


   Laboratory* translated from the German by Dagmar Ringe, University Science 


