Supporting Information

Base Promoted Michael Reaction Concomitant with Alkylation of Cyclic-1,3-diones: An Efficient Approach to Access 2-Substituted Vinylogous Esters

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Materials and Methods

Unless otherwise stated, reactions were performed in oven-dried glassware fitted with rubber septa under a nitrogen atmosphere and were stirred with Teflon-coated magnetic stirring bars. Liquid reagents and solvents were transferred via syringe using standard Schlenk techniques. Tetrahydrofuran (THF) was distilled over sodium/benzophenone ketyl. Acetonitrile was distilled over potassium carbonate. All other solvents such as DMSO, DMF, and reagents such as alkyl halides, cyclohexane 1,3-dione, cyclopenatne 1,3-dione, KO'Bu, Cs$_2$CO$_3$, K$_2$CO$_3$ were used as received, unless otherwise noted.

Thin layer chromatography was performed using Merck Silicagel 60 F-254 precoated plates (0.25 mm) and visualized by UV irradiation, anisaldehyde stain and other stains. Silicagel from Merck (particle size 100-200 mesh) was used for flash chromatography. Melting points were recorded on a digital melting point apparatus from Jyoti Scientific (AN ISO 9001:2000) and are uncorrected. $^1$H and $^{13}$C NMR spectra were recorded on Bruker 400, 500 MHz spectrometers with $^{13}$C operating frequencies of 100, 125 MHz, respectively. Chemical shifts (δ) are reported in ppm relative to the residual solvent signal (δ = 7.26 for $^1$H NMR and δ = 77.0 for $^{13}$C NMR). Data for $^1$H NMR spectra are reported as follows: chemical shift (multiplicity, coupling constants, number of hydrogens). Abbreviations are as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). IR spectra were recorded on a FT-IR system (Spectrum BX) from PerkinElmer spectrometer and are reported in frequency of absorption (cm$^{-1}$). High resolution mass spectral data were obtained from the Central Instrumentation Facility (CIF) at the Indian Institute of Science Education and Research (IISER) Bhopal.
Figure 1. Important 2-alkyl-2-cyclohexenones intermediates.

Table 1: Optimization of 2-substituted vinylogous ester synthesis.

<table>
<thead>
<tr>
<th>entry</th>
<th>basea</th>
<th>solvent</th>
<th>temp</th>
<th>timeb</th>
<th>yieldcd</th>
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<tr>
<td>1.</td>
<td>NaH</td>
<td>THF</td>
<td>25 ºC</td>
<td>12h/4h</td>
<td>traces</td>
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<tr>
<td>2.</td>
<td>NaH</td>
<td>DMF</td>
<td>25 ºC</td>
<td>12h/4h</td>
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<td>3.</td>
<td>NaH</td>
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<td>60 ºC</td>
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<tr>
<td>4.</td>
<td>NaH</td>
<td>DMF</td>
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<td>90%</td>
</tr>
<tr>
<td>5.</td>
<td>NaH</td>
<td>MeCN</td>
<td>50 ºC</td>
<td>3h/1.5h</td>
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</tr>
<tr>
<td>6.</td>
<td>NaH</td>
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<td>3h/1h</td>
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</tr>
<tr>
<td>7.</td>
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<td>THF</td>
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<td>5h/5h</td>
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<tr>
<td>8.</td>
<td>K₂CO₃</td>
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<td>80 ºC</td>
<td>4h/1h</td>
<td>82%</td>
</tr>
<tr>
<td>9.</td>
<td>K₂CO₃</td>
<td>MeCN</td>
<td>50 ºC</td>
<td>6h/3h</td>
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<tr>
<td>10.</td>
<td>K₂CO₃</td>
<td>DMSO</td>
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<tr>
<td>11.</td>
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<td>DMF</td>
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<td>4h/1h</td>
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<tr>
<td>12.</td>
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<td>13.</td>
<td>Cs₂CO₃</td>
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<td>decomp.</td>
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<tr>
<td>14.</td>
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<td>15.</td>
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<td>16.</td>
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<tr>
<td>17.</td>
<td>KOʻBu</td>
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<td>4h/1h</td>
<td>decomp.</td>
</tr>
<tr>
<td>18.</td>
<td>KOʻBu</td>
<td>MeCN</td>
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<td>DMSO</td>
<td>80 ºC</td>
<td>4h/1h</td>
<td>decomp.</td>
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<tr>
<td>20.</td>
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<td>DMF</td>
<td>80 ºC</td>
<td>4h/1h</td>
<td>21%</td>
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</table>

*a1.5 equiv. of base was used under inert atmosphere. bTime refers are for first Michael step followed by alkylation. cReactions were carried out on a 0.5 mmol of 6a with 0.75 mmol of ethyl acrylate in 2 mL of solvent. dIsolated yields. eDecomposition of remaining materials.
General experimental procedure for 2-Substituted Vinylogous Esters:

A flame-dried round-bottom flask was charged with cyclic 1,3-dione [1.0 mmol (1.0 equiv.)] in anhydrous DMSO (4 mL) and the round bottom flask was placed at 0 ºC. To this reaction mixture was added NaH [1.2 mmol (1.2 equiv.)] (condition A) or Cs₂CO₃ [1.2 mmol (1.2 equiv.)] (condition B) and stirring was continued for 5 mins. Ethylacrylate [1.2 mmol (1.2 equiv.)] was added to the reaction mixture and it was placed on a oil-bath pre-heated at 80 ºC and stirred for indicated time (see, Figure 2). Upon completion of the Michael reaction (TLC showed complete consumption of starting cyclic 1,3-dione), it was brought to room temperature and alkyl halide [1.2 mmol (1.2 equiv.)] was added to the reaction mixture, followed by heating continued for indicated time (for O-alkylations). Upon completion of the alkylation (judged by running TLC), water (10 mL) was added to the reaction mixture and it was extracted with ethylacetate (10 mL X 2). The organic layer was separated and dried with anhydrous MgSO₄ and finally evaporated under reduced pressure. The crude vinylogous ester was purified by a silica-gel column chromatography (ethyl acetate and petroleum ether as eluents).
Figure 2: Substrates scopes for vinylogous esters synthesis.

Ethyl 3-(2-((2-bromoallyl)oxy)-6-oxocyclohex-1-en-1-yl)propanoate (5a): R_f = 0.54 (50% EtOAc in hexane), ^1H NMR (400 MHz, CDCl_3) δ 5.95 (m, 1H), 5.69 (m, 1H), 4.63 (t, J = 1.44 Hz, 2H), 4.10 (q, J = 7.12 Hz, 2H), 2.65 (m, 2H), 2.55 (t, J = 6.2 Hz, 2H), 2.34-2.38 (m, 4H), 1.99 (m, 2H), 1.24 (t, J = 7.16 Hz, 3H); ^13C NMR (100 MHz, CDCl_3) δ 197.9, 173.4, 170.2, 126.5, 119.0, 117.9, 70.4, 60.1, 36.3, 33.0, 25.1, 20.9, 18.0, 14.2; IR (film) 2939, 1728, 1589, 1446, 1385, 1354, 1277, 1169, 1072, 1041, 856 cm^-1; HRMS (ESI) m/z 353.0342 [(M + Na)+; calculated for [C_{14}H_{19}BrO_4 + Na]^+: 353.0359].

Figure 3: Substrates scopes for vinylogous esters synthesis.

Ethyl 3-(2-(allyloxy)-6-oxocyclohex-1-en-1-yl)propanoate (5b): R_f = 0.59 (50% EtOAc in hexane), ^1H NMR (400 MHz, CDCl_3) δ 5.88-5.98 (m, 1H), 5.31-5.36 (m, 1H), 5.24-5.28 (m, 1H), 4.55 (m, 2H), 4.08 (q, J = 7.12 Hz, 2H), 2.59-2.64 (m, 2H), 2.55 (t, J = 6.24 Hz, 2H),
2.33 (m, 4H), 1.95 (m, 2H), 1.22 (t, J = 7.16 Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 198.0, 173.6, 171.8, 132.8, 118.2, 117.5, 68.1, 60.1, 36.3, 33.1, 25.3, 20.9, 17.9, 14.2; IR (film) \(\nu_{\text{max}}\) 2931, 1724, 1597, 1438, 1385, 1265, 1184, 1076, 1030, 930, 860 cm\(^{-1}\); LRMS (ESI) m/z 313.1273 [(M+H)+; calculated for [C\(_{19}\)H\(_{21}\)O\(_4\) + Na]+: 313.1434].

**Ethyl 3-(2-methoxy-6-oxocyclohex-1-en-1-yl)propanoate (5c):** \(R_f = 0.54\) (75% EtOAc in hexane), \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 4.09 (q, J = 7.16 Hz, 2H), 3.81 (s, 3H), 2.57 (m, 4H), 2.29-2.35 (m, 4H), 1.95-2.01 (m, 2H), 1.21-1.26 (m, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 197.9, 173.7, 172.6, 117.8, 60.1, 55.2, 36.2, 33.1, 24.8, 20.7, 17.8, 14.2; IR (film) \(\nu_{\text{max}}\) 2927, 1728, 1608, 1446, 1373, 1246, 1165, 1088, 1049, 864 cm\(^{-1}\); HRMS (ESI) m/z 249.1098 [(M + Na)+; calculated for [C\(_{12}\)H\(_{18}\)O\(_4\) + Na]+: 249.1097].

**Ethyl 3-(2-(benzyloxy)-6-oxocyclohex-1-en-1-yl)propanoate (5d):** \(R_f = 0.68\) (50% EtOAc in hexane), \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.33-4.41 (m, 5H), 5.13 (s, 2H), 4.08 (q, J = 7.15 Hz, 2H), 2.68 (t, J = 7.6 Hz, 2H), 2.59 (t, J = 6.2 Hz, 2H), 2.31-2.38 (m, 4H), 1.96 (m, 2H), 1.22 (t, J = 7.16 Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 197.9, 173.6, 171.8, 136.4, 128.8, 128.3, 126.7, 118.6, 69.4, 60.1, 36.3, 33.2, 25.6, 20.9, 18.1, 14.2; IR (film) \(\nu_{\text{max}}\) 2966, 1732, 1647, 1616, 1454, 1377, 1315, 1180, 1080, 1034, 744 cm\(^{-1}\); HRMS (ESI) m/z 325.1421 [(M + Na)+; calculated for [C\(_{18}\)H\(_{22}\)O\(_4\) + Na]+: 325.1410].

**Ethyl 3-(6-oxo-2-(prop-2-yn-1-yloxy)cyclohex-1-en-1-yl)propanoate (5e):** \(R_f = 0.61\) (50% EtOAc in hexane), \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 4.68 (d, J = 2.4 Hz, 2H), 4.10 (q, J = 7.16 Hz, 2H), 3.81 (s, 3H), 2.57 (m, 4H), 2.29-2.35 (m, 4H), 1.95-2.01 (m, 2H), 1.21-1.26 (m, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 197.9, 173.7, 172.6, 117.8, 60.1, 55.2, 36.2, 33.1, 24.8, 20.7, 17.8, 14.2; IR (film) \(\nu_{\text{max}}\) 2927, 1728, 1608, 1446, 1373, 1246, 1165, 1088, 1049, 864 cm\(^{-1}\); HRMS (ESI) m/z 313.1273 [(M+H)+; calculated for [C\(_{19}\)H\(_{21}\)O\(_4\) + Na]+: 313.1434].
Hz, 2H), 2.67 (t, J = 6.2 Hz, 2H), 2.57-2.63 (m, 2H), 2.31-2.37 (m, 4H), 2.01 (m, 2H), 1.21-1.29 (m, 4H); \(^{13}\text{C NMR}\) (100 MHz, CDCl₃) \(\delta 198.0, 173.5, 170.5, 119.8, 77.9, 76.3, 60.1, 55.3, 36.4, 33.1, 25.0, 20.8, 17.9, 14.2; \text{IR (film) } \nu_{\text{max}} 3263, 2939, 1728, 1616, 1377, 1269, 1176, 1080, 1045, 929, 852 \ \text{cm}^{-1}; \ \text{HRMS (ESI) } m/z \ 273.1105 [(\text{M + Na})^+] ; \text{calculated for } [\text{C}_{14}\text{H}_{18}\text{O}_4 + \text{Na}]^+ : 273.1097].

![Ethyl 3-(2-(allyloxy)-5-oxocyclopent-1-en-1-yl)propanoate (5f): 52% yield, R_f = 0.54 (50% EtOAc in hexane), \(^1\text{H NMR}\) (400 MHz, CDCl₃) \(\delta 5.92-6.01 (m, 1H), 5.34-5.39 (m, 1H), 5.28-5.31 (m, 1H), 4.68 (m, 2H), 4.09 (q, J = 7.12 Hz, 2H), 2.66 (m, 2H), 2.41-2.45 (m, 6H), 1.22 (t, J = 7.16 Hz, 3H); \(^{13}\text{C NMR}\) (100 MHz, CDCl₃) \(\delta 204.5, 184.4, 173.2, 132.2, 119.0, 118.2, 69.7, 60.2, 33.5, 32.0, 24.7, 17.0, 14.2; \text{IR (film) } \nu_{\text{max}} 2924, 2855, 1732, 1620, 1450, 1389, 1269, 1165, 1096, 987, 934 \ \text{cm}^{-1}; \ \text{HRMS (ESI) } m/z \ 261.1099 [(\text{M + Na})^+] ; \text{calculated for } [\text{C}_{13}\text{H}_{18}\text{O}_4 + \text{Na}]^+ : 261.1097].

![Ethyl 3-(2-((2-bromoallyl)oxy)-5-oxocyclopent-1-en-1-yl)propanoate (5g): \ R_f = 0.51 (50% EtOAc in hexane), \(^1\text{H NMR}\) (500 MHz, CDCl₃) \(\delta 5.99 (m, 1H), 5.72 (m, 1H), 4.76 (t, J = 1.4 Hz, 2H), 4.11 (q, J = 7.15 Hz, 2H), 2.67 (m, 2H), 2.48 (m, 6H), 1.24 (t, J = 7.15 Hz, 3H); \(^{13}\text{C NMR}\) (125 MHz, CDCl₃) \(\delta 204.3, 182.9, 173.1, 125.9, 119.9, 118.4, 71.8, 60.3, 33.6, 31.9, 24.5, 17.0, 14.2; \text{IR (film) } \nu_{\text{max}} 2986, 2924, 1732, 1628, 1447, 1385, 1269, 1169, 1092, 1007, 910 \ \text{cm}^{-1}; \ \text{HRMS (ESI) } m/z \ 339.0204 [(\text{M + Na})^+] ; \text{calculated for } [\text{C}_{13}\text{H}_{17}\text{BrO}_4 + \text{Na}]^+ : 339.0202].
Ethyl 3-(2-methoxy-5-oxocyclopent-1-en-1-yl)propanoate (5h): \( R_f = 0.39 \) (50% EtOAc in hexane). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 4.11 (q, \( J = 7.16 \) Hz, 2H), 3.95 (s, 3H), 2.67 (m, 2H), 2.43-2.46 (m, 6H), 1.25 (t, \( J = 7.52 \) Hz, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 204.4, 185.1, 173.2, 118.8, 60.2, 56.4, 33.4, 32.1, 24.5, 17.0, 14.2; IR (film) \( \nu_{\max} \) 2924, 1732, 1624, 1462, 1369, 1261, 1177, 1095, 999, 760 cm\(^{-1}\); HRMS (ESI) m/z 235.0951 [(M + Na)\(^+\); calculated for [C\(_{11}\)H\(_{16}\)O\(_4\) + Na\(^+\): 235.0941].

Ethyl 3-(2-(benzyloxy)-5-oxocyclopent-1-en-1-yl)propanoate (5i): \( R_f = 0.59 \) (75% EtOAc in hexane). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.35-7.43 (m, 5H), 5.23 (s, 2H), 4.08 (q, \( J = 7.16 \) Hz, 2H), 2.69 (m, 2H), 2.46-2.53 (m, 4H), 2.43 (m, 2H), 1.22 (t, \( J = 7.16 \) Hz, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 204.5, 184.3, 173.2, 135.8, 128.9, 128.6, 127.0, 119.4, 70.9, 60.2, 33.6, 32.1, 25.1, 17.1, 14.2; IR (film) \( \nu_{\max} \) 2928, 1728, 1686, 1628, 1354, 1261, 1173, 1088, 995, 906 cm\(^{-1}\); HRMS (ESI) m/z 311.1240 [(M + Na)\(^+\); calculated for [C\(_{17}\)H\(_{20}\)O\(_4\) + Na\(^+\): 311.1254].

Ethyl 3-(5-oxo-2-(prop-2-yn-1-yloxy)cyclopent-1-en-1-yl)propanoate (5j): \( R_f = 0.50 \) (50% EtOAc in hexane). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 4.78 (d, \( J = 2.36 \) Hz, 2H), 4.09 (q, \( J = 7.08 \) Hz, 2H), 2.78 (t, \( J = 4.72 \) Hz, 2H), 2.63 (t, \( J = 2.4 \) Hz, 1H), 2.46 (m, 6H), 1.23 (t, \( J = 7.08 \) Hz, 3H); \(^13\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 204.4, 183.1, 173.1, 120.3, 77.4, 76.9, 60.2, 56.7, 33.6, 32.0, 24.5, 17.0, 14.2; IR (film) \( \nu_{\max} \) 3252, 2928, 1732, 1632, 1447, 1393, 1334, 1269, 1088, 995, 898 cm\(^{-1}\); LRMS (ESI) m/z 259.2902 [(M + Na)\(^+\); calculated for [C\(_{13}\)H\(_{16}\)O\(_4\) + Na\(^+\): 259.0941].
Ethyl 3-(2-(allyloxy)-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)propanoate (5k): \( R_f = 0.63 \) (50% EtOAc in hexane), \(^1\text{H NMR} (400 \text{ MHz, CDCl}_3) \delta 5.89-5.98 \) (m, 1H), 5.32-5.37 (m, 1H), 5.26-5.29 (m, 1H), 4.55 (m, 2H), 4.09 (q, \( J = 7.12 \text{ Hz} \)), 2.64 (t, \( J = 7.6 \text{ Hz} \)), 2.41 (s, 2H), 2.35 (m, 2H), 2.22 (s, 2H), 1.24 (t, \( J = 7.2 \text{ Hz} \)), 1.07 (s, 6H); \(^{13}\text{C NMR} (100 \text{ MHz, CDCl}_3) \delta 197.8, 173.6, 169.9, 132.9, 117.4, 117.1, 68.0, 60.1, 50.2, 39.1, 33.1, 32.1, 29.7, 28.4, 17.9, 14.2; \( \text{IR (film)} \nu_{\text{max}} 2931, 1728, 1616, 1373, 1296, 1169, 1072, 925 \text{ cm}^{-1} \); \( \text{HRMS (ESI)} m/z \) 281.1737 [(M+H)\(^+\); calculated for \([\text{C}_{16}\text{H}_{25}\text{O}_4]^+\): 281.1747].

Ethyl 3-(2-((2-bromoallyl)oxy)-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)propanoate (o): \( R_f = 0.58 \) (50% EtOAc in hexane), \(^1\text{H NMR} (400 \text{ MHz, CDCl}_3) \delta 5.92 \) (m, 1H), 5.66 (m, 1H), 4.59 (t, \( J = 1.49 \text{ Hz} \)), 4.06 (q, \( J = 7.12 \text{ Hz} \)), 2.63 (m, 2H), 2.37 (s, 2H), 2.34 (m, 2H), 2.20 (s, 2H), 1.21 (t, \( J = 7.16 \text{ Hz} \)), 1.05 (s, 6H); \(^{13}\text{C NMR} (100 \text{ MHz, CDCl}_3) \delta 197.7, 173.4, 168.5, 126.6, 117.8, 117.7, 70.3, 60.1, 50.1, 38.8, 33.0, 32.2, 29.6, 28.3, 17.9, 14.2; \( \text{IR (film)} \nu_{\text{max}} 2963, 1728, 1616, 1373, 1296, 1169, 1072, 925 \text{ cm}^{-1} \); \( \text{HRMS (ESI)} m/z \) 381.0677 [(M + Na)\(^+\); calculated for \([\text{C}_{16}\text{H}_{23}\text{BrO}_4 + \text{Na}]^+\): 381.0672].

Ethyl 3-(2-methoxy-4,4-dimethyl-6-oxocyclohex-1-en-1-yl)propanoate (5m): \( R_f = 0.57 \) (50% EtOAc in hexane), \(^1\text{H NMR} (400 \text{ MHz, CDCl}_3) \delta 4.08 \) (q, \( J = 7.16 \text{ Hz} \)), 3.78 (s, 3H), 2.56 (m, 2H), 2.40 (s, 2H), 2.32 (m, 2H), 2.21 (s, 2H), 1.23 (m, 3H), 1.07 (s, 6H); \(^{13}\text{C NMR} (100 \text{ MHz, CDCl}_3) \delta 197.7, 173.6, 170.8, 116.5, 60.1, 55.1, 50.1, 38.7, 33.2, 32.0, 29.7, 28.4, 17.9, 14.2; \( \text{IR (film)} \nu_{\text{max}} 2963, 1728, 1616, 1373, 1296, 1169, 1072, 925 \text{ cm}^{-1} \); \( \text{HRMS (ESI)} m/z \) 381.0677 [(M + Na)\(^+\); calculated for \([\text{C}_{16}\text{H}_{23}\text{BrO}_4 + \text{Na}]^+\): 381.0672].
29.6, 28.5, 17.7, 14.2; IR (film) \( \nu_{\text{max}} \) 2963, 1732, 1616, 1458, 1373, 1238, 1184, 1088, 1030 cm\(^{-1}\); HRMS (ESI) m/z 255.1597 [(M+H\(^+\)]; calculated for [C\(_{14}H_{23}O_4\)]\(^+\): 255.1591.

**Ethyl 3-(4,4-dimethyl-6-oxo-2-phenoxy-cyclohex-1-en-1-yl)propanoate (5n):** 
\( \text{R}_f = 0.70 \) (50% EtOAc in hexane), \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.33-7.42 (m, 5H), 51.2 (s, 2H), 4.08 (q, \( J = 7.16 \) Hz, 2H), 2.69 (m, 2H), 2.45 (s, 2H), 2.38 (t, \( J = 8.06 \) Hz, 2H), 2.22 (s, 2H), 1.27 (s, 3H), 1.23 (t, \( J = 7.16 \) Hz, 3H), 1.04 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 198.8, 173.5, 169.9, 136.5, 128.8, 128.2, 126.7, 117.5, 69.4, 60.1, 50.2, 39.5, 33.2, 32.2, 29.7, 28.4, 18.0, 14.2; IR (film) \( \nu_{\text{max}} \) 2956, 2855, 1732, 1612, 1458, 1373, 1300, 1165, 1076, 1026, 856, 741, 698 cm\(^{-1}\); HRMS (ESI) m/z 353.1729 [(M + Na\(^+\)]; calculated for [C\(_{20}H_{26}O_4 + Na\)]\(^+\): 353.1723.

**Ethyl 3-(4,4-dimethyl-6-oxo-2-(prop-2-yn-1-yloxy)cyclohex-1-en-1-yl)propanoate (m):** 
\( \text{R}_f = 0.64 \) (50% EtOAc in hexane), \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 4.67 (d, \( J = 2.36 \) Hz, 2H), 4.10 (m, 2H), 2.62 (m, 2H), 2.57 (t, \( J = 2.36 \) Hz, 1H), 2.52 (s, 2H), 2.35 (m, 2H), 2.24 (s, 2H), 1.25 (m, 3H), 1.1 (s, 6H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 197.9, 173.5, 168.7, 118.7, 78.1, 76.3, 60.1, 55.2, 50.3, 38.7, 33.2, 32.3, 29.7, 28.4, 17.8, 14.2; IR (film) \( \nu_{\text{max}} \) 3275, 2963, 1732, 1624, 1458, 1377, 1261, 1177, 1080, 1022, 802 cm\(^{-1}\); HRMS (ESI) m/z 301.1409 [(M + Na\(^+\)]; calculated for [C\(_{16}H_{22}O_4 + Na\)]\(^+\): 301.1410.
Ethyl 3-(2-(allyloxy)-4-methyl-6-oxocyclohex-1-en-1-yl)propanoate (5p): $R_f = 0.65$ (50\% EtOAc in hexane), $^1\text{H NMR}$ (400 MHz, CDCl$_3$) $\delta$ 5.90-5.99 (m, 1H), 5.33-5.38 (m, 1H), 5.26-5.30 (m, 1H), 4.52-4.63 (m, 2H), 4.10 (q, $J = 7.12$ Hz, 2H), 2.61-2.67 (m, 2H), 2.43 (m, 1H), 2.34 (m, 2H), 2.00-2.08 (m, 1H), 1.80 (br, s, 2H), 1.25 (m, 4H), 1.09 (d, $J = 6.2$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl$_3$) $\delta$ 197.9, 173.6, 171.1, 132.8, 117.9, 117.5, 68.1, 60.1, 44.6, 33.5, 33.1, 28.6, 21.1, 17.9, 14.2; IR (film) $\nu_{\text{max}}$ 2982, 2932, 1732, 1609, 1454, 1381, 1180, 1076, 926, 860 cm$^{-1}$; HRMS (ESI) m/z 289.1413 [(M + Na)$^+$; calculated for [C$_{15}$H$_{22}$O$_4$ + Na]$^+$: 289.1410].

![Image](5p)

Ethyl 3-(2-((2-bromoallyl)oxy)-4-methyl-6-oxocyclohex-1-en-1-yl)propanoate (5q): $R_f = 0.60$ (50\% EtOAc in hexane), $^1\text{H NMR}$ (400 MHz, CDCl$_3$) $\delta$: 5.95 (m, 1H), 5.72 (m, 1H), 4.63 (m, 2H), 4.09 (q, $J = 7.14$ Hz, 2H), 2.67 (m, 2H), 2.46 (m, 1H), 2.40 (m, 3H), 2.24 (m, 2H), 2.10 (m, 1H), 1.25 (t, $J = 7.15$ Hz, 3H), 1.09 (d, $J = 6.2$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl$_3$) $\delta$: 198.6, 175.0, 171.5, 129.2, 119.6, 118.2, 70.2, 60.8, 45.3, 33.8, 33.6, 30.0, 22.1, 18.1, 14.2; IR (film) $\nu_{\text{max}}$ 2970, 2862, 1728, 1728, 1616, 1450, 1377, 1172, 1080, 1010, 907 cm$^{-1}$; HRMS (ESI) m/z 367.0517 [(M + Na)$^+$; calculated for [C$_{15}$H$_{21}$BrO$_4$ + Na]$^+$: 367.0515].

![Image](5q)

Ethyl 3-(2-methoxy-4-methyl-6-oxocyclohex-1-en-1-yl)propanoate (5r): $R_f = 0.55$ (50\% EtOAc in hexane), $^1\text{H NMR}$ (400 MHz, CDCl$_3$) $\delta$ 4.10 (q, $J = 7.16$ Hz, 2H), 3.81 (s, 3H), 2.58 (m, 1H), 2.42 (m, 1H), 2.32 (m, 2H), 2.13-2.24 (m, 2H), 1.79 (br, s, 2H), 1.30 (m, 4H), 1.1 (d, $J = 6.04$ Hz, 3H); $^{13}\text{C NMR}$ (100 MHz, CDCl$_3$) $\delta$ 197.8, 173.6, 171.9, 117.3, 64.5, 55.2, 44.6, 33.2, 33.0, 28.4, 21.2, 17.8, 14.2; IR (film) $\nu_{\text{max}}$ 2925, 2872, 1728, 1616, 1377, 1238, 1165, 1088, 1026, 856 cm$^{-1}$; LRMS (ESI) m/z 263.1286 [(M + Na)$^+$; calculated for [C$_{13}$H$_{20}$O$_4$ + Na]$^+$: 263.1254].

![Image](5r)
Ethyl 3-(2-(benzyl oxy)-4-methyl-6-oxocyclohex-1-en-1-yl)propanoate (5s): \( R_f = 0.69 \) (50% EtOAc in hexane), \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.31-7.40 (m, 5H), 5.10 (m, 2H), 4.05 (q, \( J = 7.16 \) Hz, 2H), 2.65 (m, 2H), 2.38-2.43 (m, 1H), 2.33 (m, 2H), 2.02 (m, 1H), 1.82 (br, s, 2H), 1.18-1.24 (m, 4H), 1.04 (d, \( J = 6.2 \) Hz, 3H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 197.9, 173.5, 171.1, 136.4, 128.8, 128.3, 126.7, 118.2, 69.4, 60.1, 44.6, 33.7, 33.2, 28.5, 21.1, 18.1, 14.2; IR (film) \( \nu_{\text{max}} \) 2966, 1732, 1647, 1616, 1454, 1377, 1315, 1180, 1080, 1034, 745 cm\(^{-1}\); HRMS (ESI) m/z 339.1568 [(M + Na)\(^+\); calculated for [C\(_{19}\)H\(_{24}\)O\(_4\) + Na]\(^+\): 339.1567].

Ethyl 3-(4-methyl-6-oxo-2-(prop-2-yn-1-yl)oxy)cyclohex-1-en-1-yl)propanoate (r): \( R_f = 0.62 \) (50% EtOAc in hexane), \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 4.68 (d, \( J = 2.4 \) Hz, 2H), 4.10 (q, \( J = 7.16 \) Hz, 2H), 2.74 (dd, \( J = 16.36, 3.8 \) Hz, 1H), 2.58 (m, 1H), 2.35 (s, 1H), 2.32 (m, 2H), 2.02-2.09 (m, 2H), 1.84 (br, s, 2H), 1.23-1.29 (m, 4H), 1.11 (d, \( J = 6.32 \) Hz, 3H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 198.0, 173.5, 169.9, 119.4, 78.0, 76.3, 60.1, 55.3, 44.7, 33.1, 33.09, 28.5, 21.1, 17.9, 14.2; IR (film) \( \nu_{\text{max}} \) 3279, 2967, 1728, 1624, 1450, 1377, 1184, 1080, 1030, 860 cm\(^{-1}\); HRMS (ESI) m/z 287.1258 [(M + Na)\(^+\); calculated for [C\(_{15}\)H\(_{20}\)O\(_4\) + Na]\(^+\): 287.1254].
Spectral data

$^1$H NMR (400 MHz, CDCl$_3$) of compound (5a)
$^{13}$C NMR (100 MHz, CDCl$_3$) of compound (5a)
\(^1\)H NMR (400 MHz, CDCl\textsubscript{3}) of compound (5b)
$^{13}$C NMR (100 MHz, CDCl$_3$) of compound (5b)
$^1$H NMR (400 MHz, CDCl$_3$) of compound (5c)
\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) of compound (5c)
$^1$H NMR (400 MHz, CDCl$_3$) of compound (5d)
$^{13}$C NMR (100 MHz, CDCl$_3$) of compound (5d)
$^1$H NMR (400 MHz, CDCl$_3$) of compound (5e)
$^{13}$C NMR (100 MHz, CDCl$_3$) of compound (5e)
$^1$H NMR (400 MHz, CDCl$_3$) of compound (5f)
$^{13}$C NMR (100 MHz, CDCl$_3$) of compound (5f)
$^{1}$H NMR (500 MHz, CDCl$_3$) of compound (5g)
\[ 1^3\text{C NMR (125 MHz, CDCl}_3\text{) of compound (5g)} \]
$^1$H NMR (400 MHz, CDCl$_3$) of compound (5h)
$^{13}$C NMR (100 MHz, CDCl$_3$) of compound (5h)
Display Report

Acquisition Parameter
Source Type: ESI
Focus: Active
Scan Begin: 50 m/z
Scan End: 3000 m/z
Ion Polarity: Positive
Set Collar:
Set Capillary: 4500 V
Set End Plate Offset: -500 V
Set Collision Cell RF: 130.0 Vpp
Set Nebulizer: 0.4 Bar
Set Dry Heater: 180 °C
Set Dry Gas: 4.0 l/min
Set Divert Valve: Waste

--- TIC + All MS ---

--- MS, 0.2-1 min #12-1 ---

--- MS, 0.2-0.3 min #12-1 ---

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$^1$H NMR (400 MHz, CDCl$_3$) of compound (5i)
$^{13}$C NMR (100 MHz, CDCl$_3$) of compound (5i)
$^1$H NMR (400 MHz, CDCl$_3$) of compound (5j)
$^{13}$C NMR (100 MHz, CDCl$_3$) of compound (5j)
$^1$H NMR (400 MHz, CDCl$_3$) of compound (5k)
$^{13}$C NMR (100 MHz, CDCl$_3$) of compound (5k)
Display Report

Analysis Info
Analysis Name: D:\Data\user data\ AUG 5\Alkesh Biaasi-AB-SD-1-294.d
Method: tune_low.m
Sample Name: AB-SD-1-294
Comment

Acquisition Date: 8/5/2011 11:57:31 AM
Operator: MEENA SHARMA
Instrument: micrOTOF-Q II 10330

Acquisition Parameter
Source Type: ESI
Ion Polarity: Positive
Set Nebulizer: 0.4 Bar
Focus: Active
Set Capillary: 4500 V
Set Dry Heater: 180 °C
Scan Begin: 50 m/z
Set End Plate Offset: -500 V
Set Dry Gas: 4.0 l/min
Scan End: 1500 m/z
Set Collision Cell RF: 130.0 Vpp
Set Diver Valve: Waste

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$^{13}$C NMR (100 MHz, CDCl$_3$) of compound (5l)
$^1$H NMR (400 MHz, CDCl$_3$) of compound (5m)
$^1$H NMR (400 MHz, CDCl$_3$) of compound (5n)
$^{13}$C NMR (100 MHz, CDCl$_3$) of compound (5n)
$^1$H NMR (400 MHz, CDCl$_3$) of compound (5o)
$^{13}$C NMR (100 MHz, CDCl$_3$) of compound (5o)
$^1$H NMR (400 MHz, CDCl$_3$) of compound (5p)
$^{13}$C NMR (100 MHz, CDCl$_3$) of compound (5p)
\(^1\)H NMR (400 MHz, CDCl\(_3\)) of compound (5q)
$^{13}$C NMR (100 MHz, CDCl$_3$) of compound (5q)
$^1$H NMR (400 MHz, CDCl$_3$) of compound (5r)
\[ ^{13}C \text{NMR (100 MHz, CDCl}_3\text{)} \text{ of compound (5r)} \]
$^1$H NMR (400 MHz, CDCl$_3$) of compound (5s)
$^{13}$C NMR (100 MHz, CDCl$_3$) of compound (5s)
$^1$H NMR (400 MHz, CDCl$_3$) of compound (5t)
$\text{\textsuperscript{13}C NMR (100 MHz, CDCl}_3\text{) of compound (5t)}$